
Supplementary information

Selective methylene oxidation in α,β -unsaturated carbonyl natural products

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Supplementary Information

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I. General Information

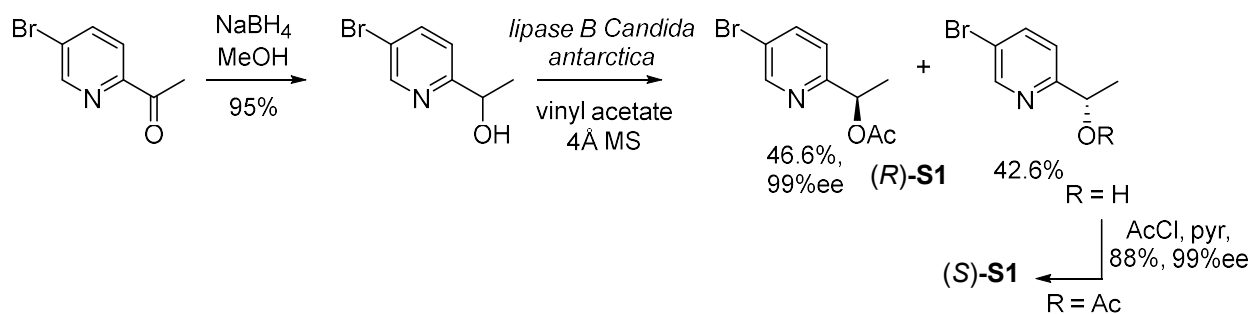
Mn(CF₃-PDP) **1** (commercial as the chloride precursor, Strem chemicals, 254160) was prepared according to the reported procedure¹. AgSbF₆ was purchased from Strem Chemicals and stored in a glove box prior to use. All PDP-catalyzed oxidations were conducted in ambient air using clear glass vials, Restek Norm-Ject Plastic Syringes, an InfusionONE Single Channel Syringe Pump, and a Hamilton 1 mL Gastight Syringe (Model 1001 RN, 22 gauge, 2 in.). All other reactions were carried out using flame-dried glassware under dry nitrogen or argon atmosphere. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was obtained from Oakwood Chemical. Solvents, including THF, diethyl ether, DCM, benzene, pentane, toluene, and DMF, were dried using an activated alumina-based JC Meyer Solvent Drying System (SDS). All other commercially available reagents were obtained from suppliers such as Sigma-Aldrich, TCI America, Strem Chemicals, Oakwood Chemicals, Alfa Aesar, etc., and were used as received.

Thin-layer chromatography (TLC) was performed on Merck Silica Gel 60 F254 precoated plates (0.25 mm) and visualized with UV light or staining reagents, including potassium permanganate, ceric ammonium molybdate, or polymolybdic acid. Flash column chromatography was conducted using EM reagent silica gel 60 (230-400 mesh).

¹H NMR/ ¹³C NMR (proton-decoupled)/ ¹⁹F NMR/ COSY (Correlated Spectroscopy)/ HSQC (Heteronuclear Single Quantum Coherence)/ HMBC (Heteronuclear Multiple Bond Correlation)/ 1D & 2D NOESY (Nuclear Overhauser Effect Spectroscopy) and ROESY (Rotating-Frame Overhauser Enhancement Spectroscopy) data were obtained using B600 Bruker NEO NMR Spectrometer (600 MHz), Carver B500 Bruker Avance III HD NMR Spectrometer (500MHz), Varian Unity-500 Spectrometer (500MHz), Varian Unity Inova-500 Spectrometer (500MHz),

using deuterated solvents as internal standards. Abbreviations for multiplicities are: s=singlet, d=doublet, t=triplet, q=quartet, quint = quintet, sext=sextet, m=multiplet, br=broad, app=apparent; coupling constants are reported in Hz. High-resolution mass spectrometry (HRMS) was conducted with a Waters Q-TOF Ultima spectrometer or a Waters GCT Premier EI spectrometer. High-performance liquid chromatography (HPLC) spectra were acquired using an Agilent 1260 Infinity II HPLC System, and gas chromatography (GC) data were collected with an Agilent 6890N Network Gas Chromatograph system equipped with an HP-5MS GC column.

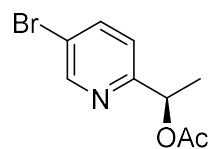
II. Synthesis and Characterization of Mn(MeCF₃-PDP)



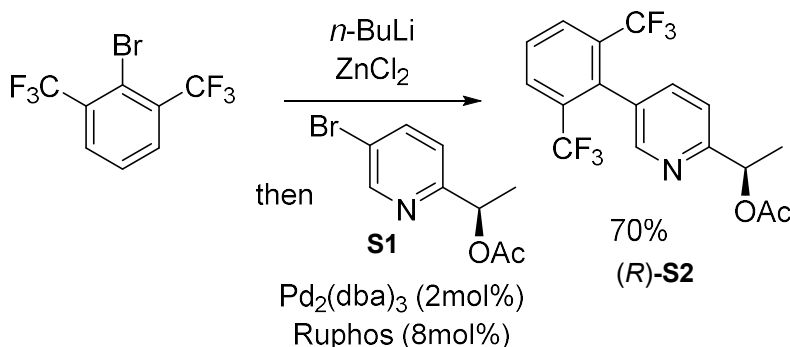
Ketone reduction. 1-(5-bromopyridin-2-yl)ethan-1-one was prepared according to the reported literature². To a stirred solution of 1-(5-bromopyridin-2-yl)ethan-1-one (1.5 g, 7.5 mmol, 1.0 equiv.) in THF (15 mL, 0.5M) was added NaBH₄ (369 mg, 9.75 mmol, 1.3equiv.) and MeOH (5mL, × 1/3 of THF by volume) at 0°C. The reaction mixture was stirred for 1.5 hours, with completion confirmed by TLC (silica, EA: hexane = 2: 1). Upon completion, the reaction was quenched with brine, extracted with EA, dried over MgSO₄ and concentrated *in vacuo*. Subsequent chromatographic separation (EA: hexane = 2: 1) yielded 1-(5-bromopyridin-2-yl)ethan-1-ol as a pale-yellow oil (1.43 g, 7.1 mmol, 95% yield).

Enzymatic resolution of 1-(5-bromopyridin-2-yl)ethan-1-ol. This enzymatic acetylation is a modification of a reported procedure³. A 1 L round-bottom flask was charged with 4 Å molecular sieves (36 g, × 3 by weight of 1-(5-bromopyridin-2-yl)ethan-1-ol), and thoroughly flame-dried and cooled to room temperature. Isopropyl ether (800 mL, 1.0 equiv., 0.07 M) and 1-(5-bromopyridin-2-yl)ethan-1-ol (12 g, 59 mmol, 1.0 equiv.) were added. To the stirred heterogeneous mixture, vinyl acetate (22 mL, 238 mmol, 4.0 equiv.) and lipase B *Candida antarctica* (4.0 g, × 1/3 by weight of 1-(5-bromopyridin-2-yl)ethan-1-ol, purchased from Sigma-Aldrich, immobilized on Immobead 150, >2000 U/g,) were introduced. The mixture was stirred for 140 minutes, with completion confirmed by TLC (silica, EA: hexane = 1: 1). Upon completion, the reaction was filtered through a Celite pad with EA and concentrated in vacuo. The resulting crude product was purified by column chromatography (silica, EA: hexane = 1: 2), furnishing (*R*)-**S1** (7 g, 28.7 mmol, 49% yield, 99%ee) and (*S*)- 1-(5-bromopyridin-2-yl)ethan-1-ol (5.7 g, 28.3 mmol, 48% yield). (*S*)- 1-(5-bromopyridin-2-yl)ethan-1-ol (5.7 g, 28.3 mmol, 1.0 equiv.) was dissolved in pyridine (28 mL, 1 M), and acetyl chloride (3 mL, 42 mmol, 1.5 equiv.) was added dropwise at 0°C. The reaction mixture was stirred for 30 minutes, with completion confirmed by TLC (silica, EA: hexane = 1: 1). Upon completion, the reaction was quenched with water, and the organic layer was extracted with EA, combined, and concentrated. Residual pyridine was removed by azeotropic evaporation with n-heptane. The crude product was purified by column chromatography (silica, EA: hexane = 1: 2 → EA) furnishing (*S*)-**S1** (6.1 g, 25 mmol, 88% yield, 99%ee). The enantiomeric excess of (*R*)-**S1** and (*S*)-**S1** was confirmed by HPLC (Column specification: Chiralcel® OJ-H (particle size 5µm, 4.6mm*150mm), flow rate: 1ml/min, hexane: IPA = 98: 2, retention time of (*R*)-**S1** 3: 4.02min, retention time of (*S*)-**S1** 3: 4.23min).

(R)-1-(5-bromopyridin-2-yl)ethyl acetate [(R)-S1]. ¹H NMR (600 MHz, CDCl₃) δ 8.60 (d, *J* = 2.1 Hz, 1H), 7.77 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 5.82 (q, *J* = 6.7 Hz, 1H), 2.09 (s, 3H), 1.54 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 170.05, 158.84, 150.30, 139.23, 121.77, 119.49, 72.39, 21.13, 20.52. [α]_D²² = 98.34 (c=1.0, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₉H₁₁NO₂Br [M+H]⁺: 243.9973, found 243.9976.



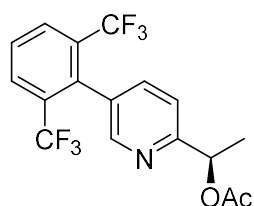
(S)-1-(5-bromopyridin-2-yl)ethyl acetate [(S)-S1]: [α]_D²² = -100.82 (c=1.0, CHCl₃).



Negishi coupling. 2-bromo-1,3-bis(trifluoromethyl)benzene (3.4 g, 11.6 mmol, 1.5 equiv.) was transferred to a round-bottom flask and backfilled with nitrogen three times. THF (15 mL, 0.77 M) was then introduced, and the mixture was cooled to -78°C (*Note: on a larger scale, a THF: toluene = 2: 1 mixture should be used for the lithiation step*). To the stirred mixture was 1.6 M nBuLi (8 mL, 12.8 mmol, 1.65 equiv.) slowly added along the flask wall for cooling. The reaction mixture turned yellow and gradually to pale brown. The mixture was stirred for 20min at -78°C under nitrogen atmosphere. ZnCl₂ (1.9 g, 1.4 mmol, 1.8 equiv.) was transferred into a 1-dram vial. The septum on the reaction flask was removed, and ZnCl₂ was quickly added to the reaction mixture at -78°C. The mixture was immediately sealed with a septum and returned to a nitrogen

atmosphere. The reaction mixture was allowed to warm gradually to room temperature over 6 hours, during which the white-yellow suspension turned into a yellow/pale brown solution. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (142 mg, 0.14 mmol, 1.8 mol%) and Ruphos (289 mg, 0.62 mmol, 8mol%) was transferred into a 1-dram vial. Aryl bromide **S1** (1.9 g, 7.78 mmol, 1.0 equiv.) was added directly to the organozinc solution via syringe at room temperature and rinsed with ~2 mL of THF, followed by the quick addition of the $\text{Pd}_2(\text{dba})_3$ and Ruphos mixture. The reaction mixture was sealed with a septum and placed under a nitrogen atmosphere. The dark brown mixture was heated to 70°C and stirred for 38 hours under reflux. Completion of 2-bromo-1,3-bis(trifluoromethyl)benzene consumption was confirmed by TLC analysis (silica, EA: hexane = 1: 9, developed twice). Upon completion, the mixture was cooled to room temperature, and EA containing ~5% triethylamine (by volume) was added. The organic layer was extracted with EA three times after the addition of brine. The combined organic extracts were dried over MgSO_4 and concentrated in vacuo. The resulting red-brown oil was purified via flash column chromatography (hexane only → 1% EA in hexane → 2% EA in hexane → 5% EA in hexane → 10% EA in hexane) or via MPLC (Teledyne Combiflash® system, hexane only → EA: hexane=1: 10) to furnish the biaryl acetate (*R*)-**S2** as a pale-yellow oil (2.1 g, 5.5 mmol, 71% yield).

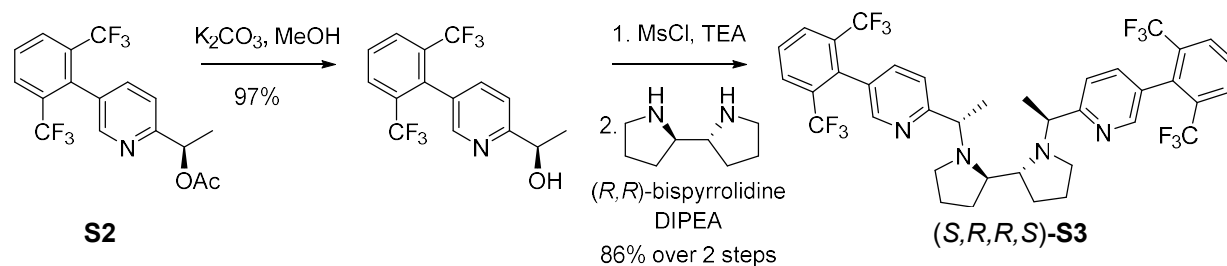
(*R*)-1-(5-(2,6-bis(trifluoromethyl)phenyl)pyridin-2-yl)ethyl acetate [(*R*)-S2**]** ^1H NMR (600



MHz, CDCl_3) δ 8.45 (s, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.68 (t, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 6.02 (q, J = 6.6 Hz, 1H), 2.16 (s, 3H), 1.65 (d, J = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.24, 160.28, 149.31, 138.01, 136.36, 131.77 (q, J = 29.7 Hz), 131.75 (q, J = 29.9 Hz), 129.38 (q, J = 5.5 Hz), 128.96, 128.79, 123.03 (q, J = 274.6 Hz), 123.02 (q, J = 274.4 Hz), 118.76, 72.70,

21.32, 20.63. ^{19}F NMR (565 MHz, CDCl_3) δ -57.44, -57.45. $[\alpha]_{\text{D}}^{22} = 59.26$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{17}\text{H}_{14}\text{NO}_2\text{F}_6$ $[\text{M}+\text{H}]^+$: 378.0929, found 378.0934.

(S)-1-(5-(2,6-bis(trifluoromethyl)phenyl)pyridin-2-yl)ethyl acetate [(S)-S2]: $[\alpha]_{\text{D}}^{23} = -63.36$ ($c=1.0$, CHCl_3).



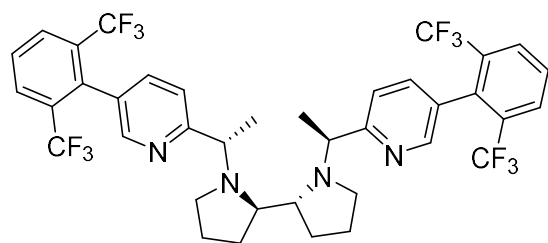
Alcohol deprotection. To a stirred solution of acetate **S2** (2.3 g, 6 mmol, 1.0 equiv.) in MeOH (30 mL, 0.2M) was added oven-dried K_2CO_3 (1.25 g, 9.1 mmol, 1.5equiv.). The mixture was stirred for 4 hours, with completion confirmed by TLC (silica, DCM: MeOH = 30: 1). Upon completion, the reaction was quenched with saturated NH_4Cl solution. The organic layer was extracted with EA, dried over MgSO_4 and concentrated *in vacuo*. The resulting crude product was purified by column chromatography (silica, DCM: MeOH = 30: 1) to furnish 1-(5-(2,6-bis(trifluoromethyl)phenyl)pyridin-2-yl)ethan-1-ol as a pale yellow oil (97% yield).

N-alkylation. (*R,R*) and (*S,S*)-bispyrrolidine were prepared following a reported procedure⁴. (*R*)-1-(5-(2,6-bis(trifluoromethyl)phenyl)pyridin-2-yl)ethan-1-ol (787 mg, 2.4 mmol, 1.0 equiv.) was dissolved in DCM (4 mL, 0.6M) and cooled to 0°C . To the stirred solution, MsCl (0.2 mL, 2.6 mmol, 1.1 equiv.) was added, followed by the addition of TEA (1.0 mL, 7.1 mmol, 3.0 equiv.).

The mixture was stirred for 10 minutes at 0°C with progress confirmed by TLC (silica, DCM: MeOH = 30: 1). Upon completion, the reaction mixture was filtered through a silica pad with a mixture of EA: hexane = 1: 1 to remove solid byproducts. The filtrate was concentrated in vacuo, yielding (*R*)-1-(5-(2,6-bis(trifluoromethyl)phenyl)pyridin-2-yl)ethyl methanesulfonate (911 mg, 2.2 mmol, 94% yield) as a yellow oil. (*R*)-1-(5-(2,6-bis(trifluoromethyl)phenyl)pyridin-2-yl)ethyl methanesulfonate (911 mg, 2.2 mmol, 1.0 equiv.) was dissolved in MeCN (10mL, 0.22 M) and the flask was purged with argon. To the stirred solution was added (*R,R*)-bispyrrolidine (164 mg, 1.17 mmol, 0.53equiv.) directly via syringe, immediately followed by the addition of DIPEA (1.15 mL, 6.6 mmol, 3.0 equiv.) The reaction was stirred overnight at 80°C under an argon atmosphere, and completion was confirmed by TLC (alumina, acetone: hexane = 1: 4). Upon completion, the reaction was quenched with saturated NaHCO₃, and the organic layer was extracted with EA (*Note: Further basification with 1 N NaOH was effective in cases of sluggish phase separation*). The organic layer was dried over Na₂SO₄ and purified by column chromatography (alumina, EA: hexane = 1: 8) to furnish ligand (*S,R,R,S*)-**S3** (767 mg, 1.0 mmol, 91% yield, 86% yield over 2 steps) as a white foamy solid. The obtained ligand was used for metal complexation immediately after the residual solvents were removed under vacuum. (*R,S,S,R*)-**S3** was prepared using the same procedure starting from the material with the corresponding chirality.

(2*R*,2'*R*)-1,1'-bis((*S*)-1-(5-(2,6-bis(trifluoromethyl)phenyl)pyridin-2-yl)ethyl)-2,2'-

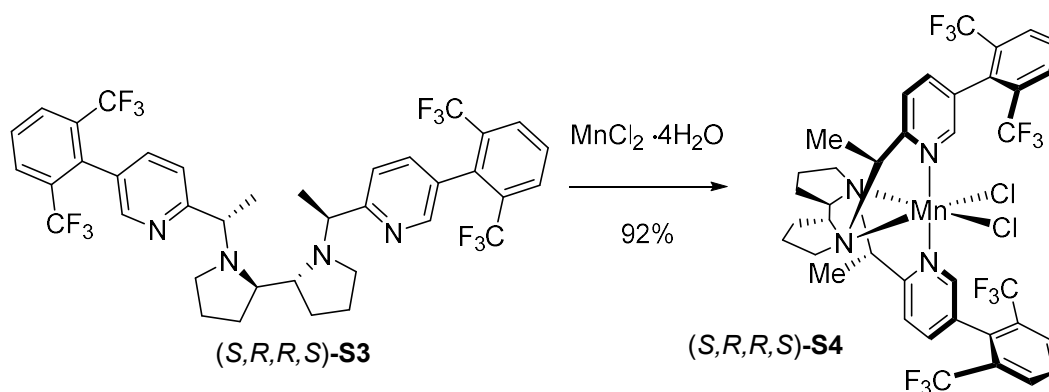
bipyrrolidine [(*S,R,R,S*)-S3**].** ¹H NMR (500 MHz, CDCl₃) δ 8.41 (s, 2H), 7.98 (d, *J* = 8.0 Hz,



4H), 7.66 (t, *J* = 8.0 Hz, 2H), 7.56 – 7.49 (m, 4H), 3.92 (q, *J* = 6.7 Hz, 2H), 2.87 – 2.78 (m, 2H), 2.70 – 2.61 (m, 2H), 2.45 (q, *J* = 8.3 Hz, 2H), 1.82 – 1.72

(m, 2H, contains a broad H₂O signal), 1.69 – 1.57 (m, 6H), 1.38 (d, $J = 6.7$ Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 165.73, 148.60, 137.52, 137.27, 131.98 (q, $J = 29.7$ Hz), 129.45 (q, $J = 5.7$ Hz), 128.62, 127.92, 123.27 (q, $J = 274.7$ Hz), 121.01, 63.51, 61.49, 49.45, 26.07, 24.01, 15.25. ¹⁹F NMR (471 MHz, CDCl₃) δ -57.24, -57.29. $[\alpha]_D^{23} = -14.8$ (c=0.5, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₃₈H₃₅F₁₂N₄ [M+H]⁺: 775.2670, found 775.2682.

(2*S*,2'*S*)-1,1'-bis((*R*)-1-(5-(2,6-bis(trifluoromethyl)phenyl)pyridin-2-yl)ethyl)-2,2'-bipyrrolidine [(*R,S,S,R*)-S3]. $[\alpha]_D^{23} = 21.96$ (c=1.0, CHCl₃).



Metal complexation. To a stirred solution of (*S,R,R,S*)-S3 (767 mg, 1.0 mmol, 1.0 equiv.) in acetonitrile (5.0 mL, 0.2 M) under an argon atmosphere was added pulverized MnCl₂·4H₂O (187 mg, 0.945 mmol, 0.95 equiv.). The reaction mixture was stirred for 17 hours under an argon atmosphere. The supernatant was removed from the resulting suspension by decanting, and the remaining solid was rinsed with distilled diethyl ether until the supernatant became completely colorless (approximately 6-8 times). The white solid was then dried under a stream of N₂ for 1 hour, furnishing (*S,R,R,S*)-Mn(MeCF₃-PDP)-Cl₂ S4 as a white powder (828 mg, 0.92 mmol, 92% yield). (*R,S,S,R*)-Mn(MeCF₃-PDP)-Cl₂ S4 was prepared in the same manner, and its structure was

confirmed by X-ray crystallography. MS (TOF MALDI-DCTB+) m/z calculated for $C_{38}H_{34}ClF_{12}MnN_4$ $[M-Cl]^+$: 864.1655, found 864.076.

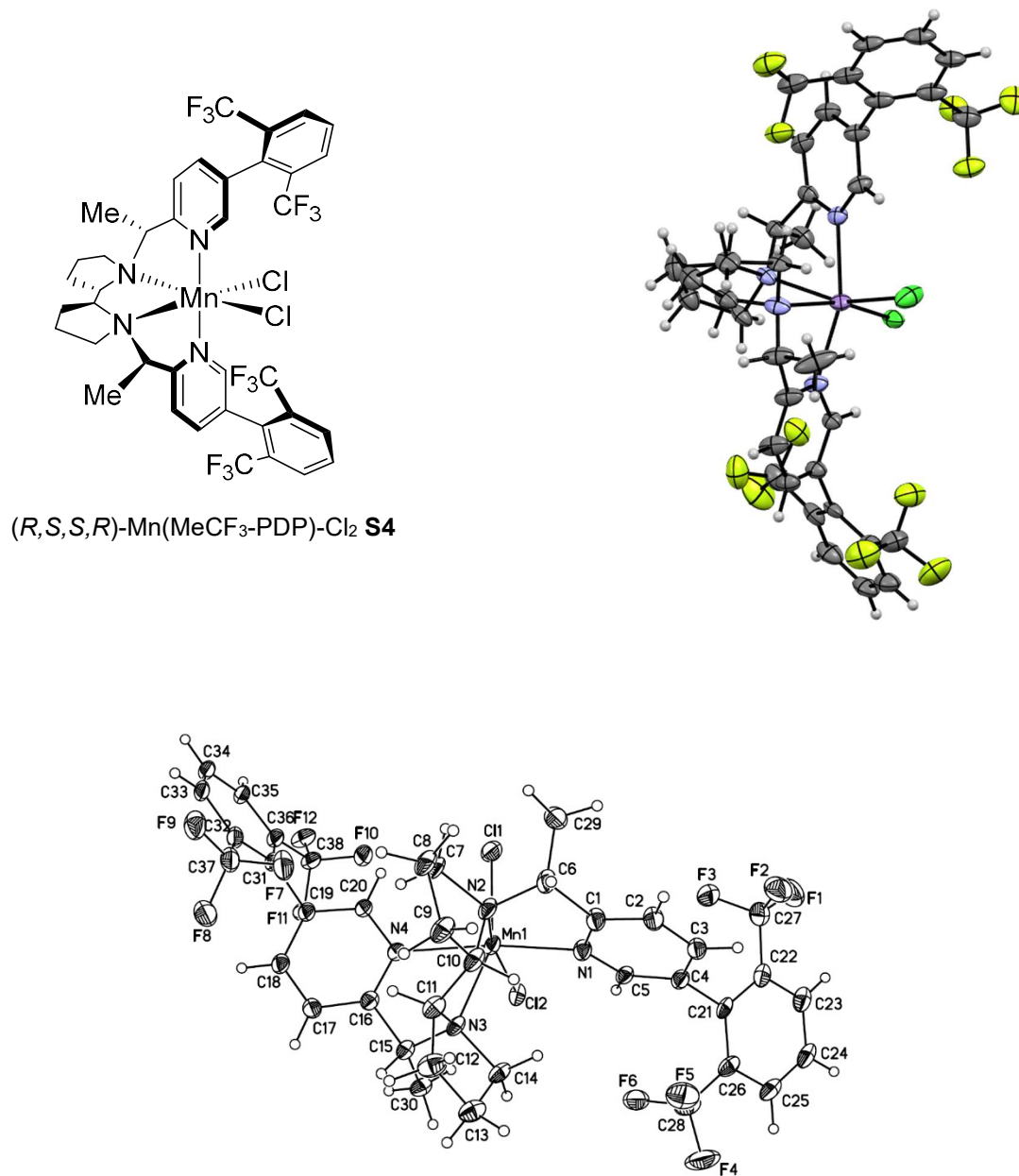
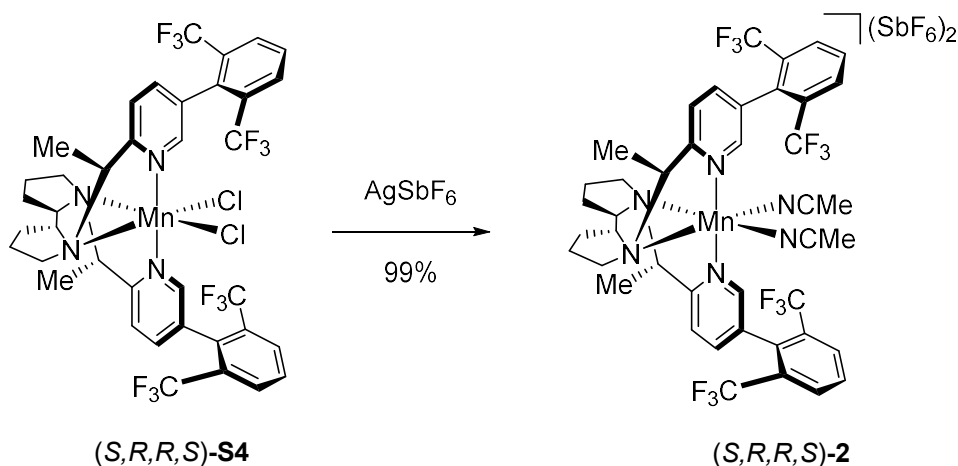


Figure S1. X-ray Crystal Data of $(R,S,S,R)\text{-S4}$.

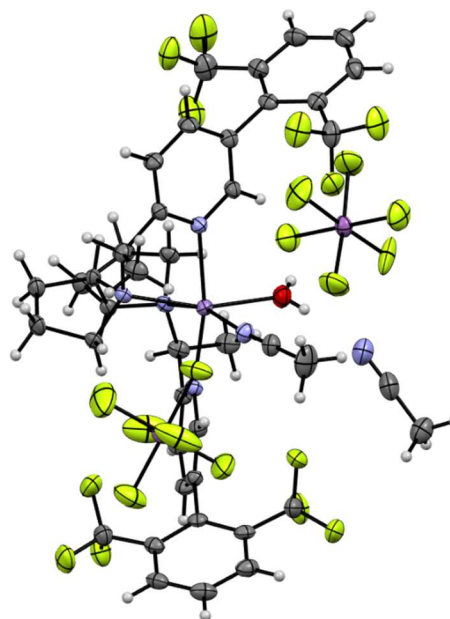
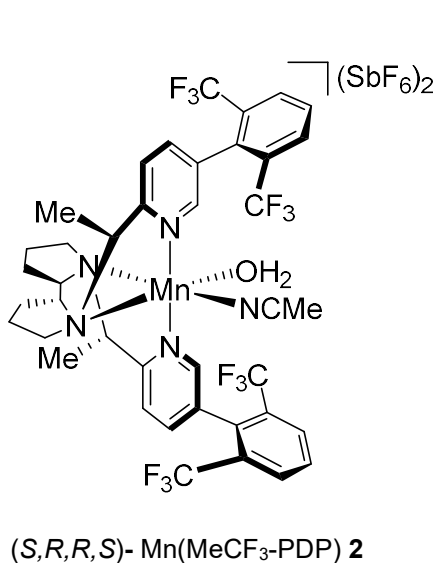
Empirical formula	C ₃₈ H ₃₄ Cl ₂ F ₁₂ Mn N ₄ O _{0.38}	
Formula weight	906.67	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	P6 ₁	
Unit cell dimensions	a = 9.3988(3) Å	a = 90°.
	b = 9.3988(3) Å	b = 90°.
	c = 75.920(2) Å	g = 120°.
Volume	5808.0(4) Å ³	
Z	6	
Density (calculated)	1.555 Mg/m ³	
Absorption coefficient	4.887 mm ⁻¹	
F(000)	2760	
Crystal size	0.205 x 0.120 x 0.074 mm ³	
Theta range for data collection	2.328 to 68.257°.	
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -91 ≤ l ≤ 91	
Reflections collected	67985	
Independent reflections	7102 [R(int) = 0.0646]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5723	
Refinement method	Full-matrix least-squares on F ²	

Data / restraints / parameters	7102 / 3030 / 1025
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0322$, $wR2 = 0.0866$
R indices (all data)	$R1 = 0.0327$, $wR2 = 0.0873$
Absolute structure parameter	0.003(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.205 and -0.194 e.Å ⁻³



Ligand metathesis. A round-bottom flask covered with aluminum foil was charged with $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})\text{-Cl}_2$ **S4** (828 mg, 0.92 mmol, 1.0 equiv.), followed by the addition of MeCN (46 mL, 0.02 M). To a stirred suspension of $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})\text{-Cl}_2$ **S4** in acetonitrile was added AgSbF_6 (98% purity, 654 mg, 1.87 mmol, 2.03 equiv.). The reaction mixture was stirred under an argon atmosphere for 15 hours. The resulting white suspension was filtered through a syringe filter (Fisherbrand, PVDF membrane, pore size 0.22 μm) with acetonitrile. The filtrate was concentrated nearly to dryness and filtered again through a syringe filter. This filtration-concentration process was repeated three times. The resulting filtrate was dried under a

stream of nitrogen for 10 hours to furnish (*S,R,R,S*)-Mn(MeCF₃-PDP) **2** as a white solid (1.26 g, 0.91 mmol, 99% yield). The structure of (*S,R,R,S*)-Mn(MeCF₃-PDP) **2** was confirmed by X-ray crystallography (*Note: in the crystal structure, one acetonitrile molecule coordinated to the Mn center was replaced by an H₂O molecule*). MS (TOF MALDI-CHCA+) *m/z* calculated for C₃₈H₃₄F₁₈MnN₄Sb [M-SbF₆-2(MeCN)]⁺: 1064.09, found 1064.002. (*R,S,S,R*)-Mn(MeCF₃-PDP) **2**. was also prepared following the same procedure.



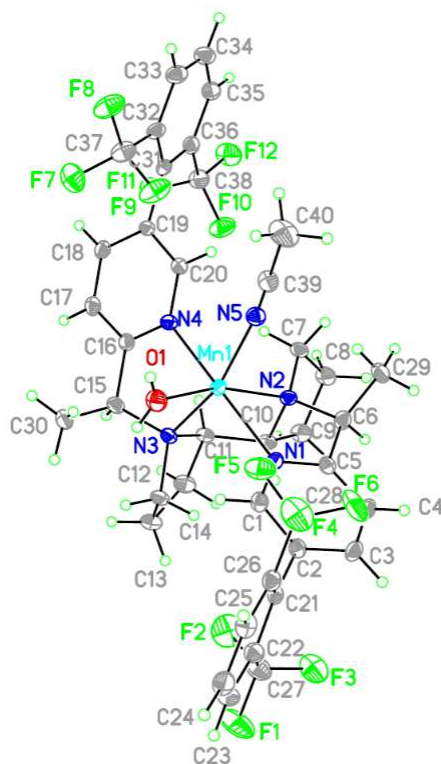
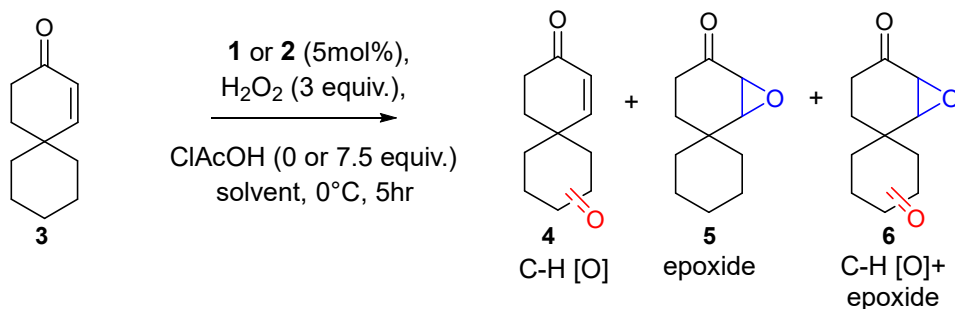


Figure S2. X-ray Crystal Data of (*S,R,R,S*)-**2**.

Identification code	ed29n1s	
Empirical formula	C ₃₈ H ₄₅ F ₂₄ Mn N ₇ O Sb ₂	
Formula weight	1442.31	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 16.1332(6) Å	a = 90°.
	b = 16.9942(7) Å	b = 90°.
	c = 19.9401(7) Å	g = 90°.

Volume	5467.0(4) Å ³
Z	4
Density (calculated)	1.752 Mg/m ³
Absorption coefficient	1.332 mm ⁻¹
F(000)	2836
Crystal size	0.179 x 0.116 x 0.086 mm ³
Theta range for data collection	2.018 to 26.759°.
Index ranges	-20 ≤ h ≤ 20, -21 ≤ k ≤ 21, -25 ≤ l ≤ 24
Reflections collected	62126
Independent reflections	11631 [R(int) = 0.0560]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6787
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11631 / 340 / 817
Goodness-of-fit on F ²	1.044
Final R indices [I > 2σ(I)]	R1 = 0.0294, wR2 = 0.0561
R indices (all data)	R1 = 0.0353, wR2 = 0.0591
Absolute structure parameter	-0.022(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.757 and -0.485 e.Å ⁻³

III. Reaction Optimization



entry	catalyst	H_2O_2 equiv.	additives	solvent	rsm	C-H [O] yield	epoxide yield	C-H [O] + epoxide	$\frac{\text{C-H [O]}}{\text{epoxide}}$
1	1	5 equiv.	Cl-AcOH	MeCN	-	7% ^a	5%	55%	1.0
2	2	5 equiv.	Cl-AcOH	MeCN	10%	16% ^b	32%	24%	0.7
3	1	5 equiv.	-	MeCN	45%	21% ^c	8%	2%	2.3
4	2	5 equiv.	-	MeCN	92%	<1% ^d	-	-	-
5*	1	3 equiv.	Cl-AcOH	HFIP:MeCN = 10:1	-	49% ^e	-	26%	3.0
6*	2	3 equiv.	Cl-AcOH	HFIP:MeCN = 10:1	-	64% ^f	-	10%	7.4
7*	1	3 equiv.	-	HFIP:MeCN = 10:1	-	75% ^g	-	5%	16
8*	2	3 equiv.	-	HFIP:MeCN = 10:1	7%	70% ^h	1%	4%	14.8
9	1	5 equiv.	AcOH	MeCN	14%	21% ⁱ	25%	16%	0.9
10	1	5 equiv.	tBuOH	MeCN	69%	13% ^j	3%	0.4%	3.9
11	1	5 equiv.	HFIP	MeCN	20%	22% ^k	20%	10%	1.1
12	1	5 equiv.	TFE	MeCN	27%	23% ^l	16%	9%	1.3
13*	1	3 equiv.	-	TFE:MeCN = 10:1	22%	22% ^m	7%	3%	2.5

* 5hr addition, double slow addition. Alcohol:ketone ratio = ^a1:14. ^b1:1.7. ^c1:4.4. ^dnot determined due to low yield. ^e1.1:1. ^f2.6:1. ^g1:1.7. ^h2.3:1. ⁱ1.8:1. ^j1:2.3. ^k1:1.3. ^l1:>20. ^m1:1.9.

Table S1. Optimization of Chemoselective Remote C-H Oxidation in the Presence of Enone

General Procedure of Yield & Product Ratio Determination

Oxidation of spiro[5.5]undec-1-en-3-one can lead to multiple products (**Figure S3**).

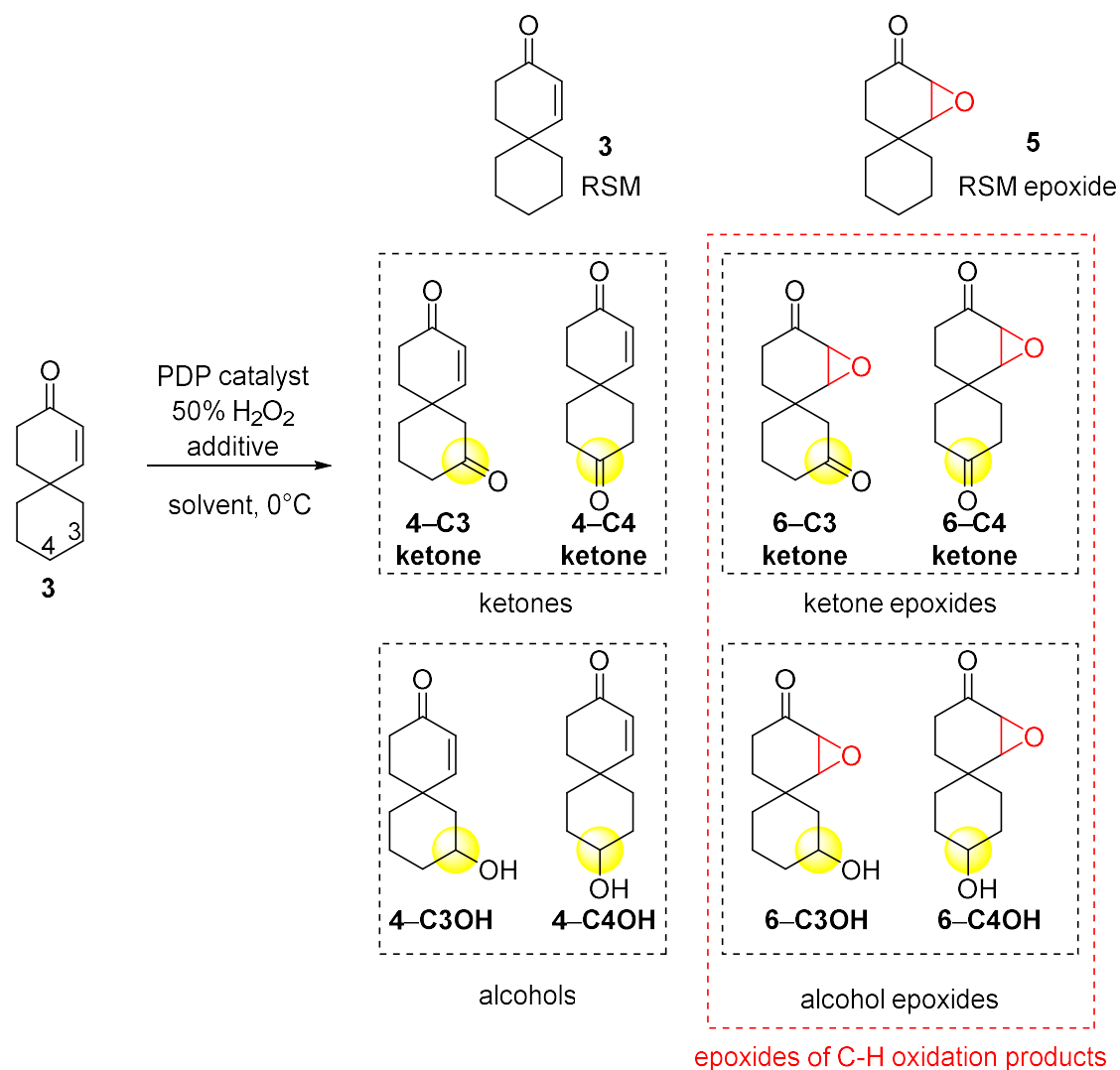


Figure S3. Oxidation Product Profile of **3**

The oxidation reaction mixture was purified by flash column chromatography (acetone: hexane = 1: 10 $\rightarrow$ 1: 4), resulting in the separation of three groups of compounds:

1. First group: recovered starting material (RSM) and RSM epoxide.

2. Second group: Ketones and ketone epoxides.

3. Third group: Alcohols and alcohol epoxides.

Each group was tared and subjected to quantitative ^1H NMR analysis (relaxation delay (d1) = 10 seconds). For each NMR spectrum, the integration of the $\text{Csp}^2\text{-H}$ proton of the enone and the C-H protons α to the epoxide were calculated. Using the total mass of each separated mixture, molecular weight and NMR ratios, the yield for RSM, ketones, alcohols and their epoxides was determined.

1) C-H oxidation yield: Calculated by the summation of the ketone and alcohol product yields.

2) Epoxide: Defined as the sum of the yields of RSM epoxide, ketone epoxides, and alcohol epoxides.

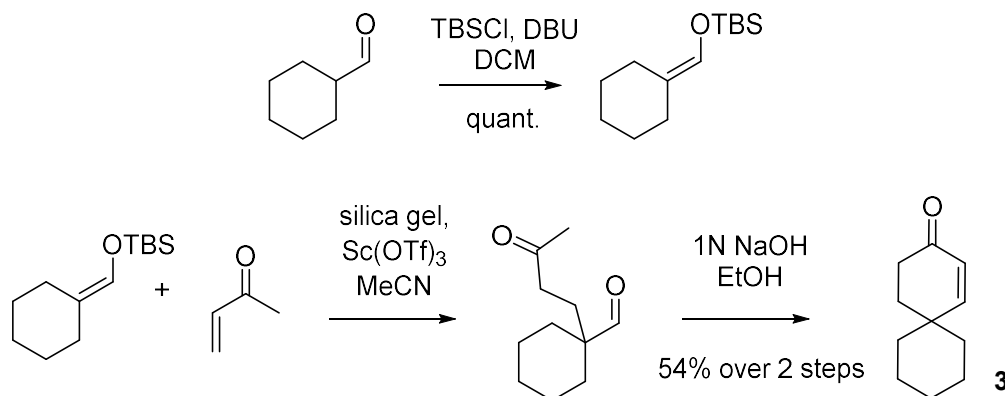
3) Alcohol to ketone ratio: Calculated as the ratio of alcohols to ketones. Alcohol & ketones of epoxides were not included in the calculation.

4) C4: C3 ratio: Calculated as the ratio of 4-ketones + 4-alcohols to (3-ketones + 3-alcohols)/2 (statistically corrected). Alcohol & ketones of epoxides were not included in the calculation.

The summation of C3 oxidation products was divided by 2 to account for the presence of two C3 oxidation sites, compared to a single C4 oxidation site.

Authentic samples of ketones, alcohols, and their corresponding epoxides were prepared to determine the NMR ratio. Ketones and alcohols were obtained under the Standard Condition (entry 7, **Table S1**). Epoxides were synthesized by epoxidation of the authentic ketone and alcohol samples (*vide infra*).

Preparation and Characterization of Oxidation Starting Material



Synthesis of spiro[5.5]undec-1-en-3-one [3]. To a stirred solution of cyclohexanecarbaldehyde (2.4 mL, 20 mmol, 1.0 equiv.) in DCM (40 mL, 0.5 M) were added TBSCl (3.3 g, 22 mmol, 1.1 equiv.) and DBU (3.6 mL, 24 mmol, 1.2 equiv.) at 0°C. The mixture was gradually warmed to room temperature over 15 hours, and the reaction was monitored by TLC (silica gel, EA: hexane = 1: 8). Upon completion, the reaction mixture was concentrated. To the resulting yellow solid was added hexane, and the suspension was filtered through a pad of silica with a solvent mixture of EA: hexane = 1: 1. The organic filtrate was collected and concentrated in vacuo to afford silyl enol ether (tert-butyl(cyclohexylidenemethoxy)dimethylsilane, 4.5 g, 20 mmol, quantitative yield) as a colorless oil. Spectroscopic data matched the published literature⁵. To a stirred solution of silyl enol ether (15 g, 66.2 mmol, 1.0 equiv.) in MeCN (330 mL, 0.2 M), silica gel (60 g, 4× w/w) and freshly distilled methyl vinyl ketone (7.7 mL, 92.7 mmol, 1.4 equiv.) were added at 0°C under a nitrogen atmosphere. Sc(OTf)₃ (652 mg, 1.32 mmol, 2 mol%) was then added at 0°C. The mixture was gradually warmed to room temperature over 24 hours, and the reaction was monitored by TLC (silica gel, EA: hexane = 1: 3). Upon completion, the mixture was concentrated and directly purified by flash column chromatography (ether: pentane = 1: 3), yielding aldehyde as a yellow oil (1-(3-oxobutyl)cyclohexane-1-carbaldehyde, quantitative). The aldehyde was dissolved in

ethanol (327 mL, 0.2 M), and 1N NaOH solution (98 mL, 1.5 equiv.) was added at room temperature. The mixture was stirred for 15 hours, with progress monitored by TLC (silica, EA: hexane = 1: 3). After completion, the reaction mixture was concentrated to reduce the volume to approximately 20% of the original. The reaction was quenched with sat. NaHCO₃ aqueous solution, and the organic layer was extracted with EA/hexane mixture (1: 9) and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (ether:pentane = 1: 5) to afford spiroenone **3** (5.9 g, 36 mmol, 54% yield over two steps) as a colorless oil. Spectroscopic data matched the published literature⁶.

General Oxidation Procedures for Table S1

Entry 1 (PDP/carboxylic acid condition in MeCN). The reaction was carried out following the reported conditions for methylene oxidation using Mn(CF₃-PDP), with a modification to the reaction concentration¹. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), Cl-AcOH (283.5 mg, 3 mmol, 7.5 equiv.), (*R,R*)-Mn(CF₃-PDP) **1** (27.1 mg, 0.02 mmol, 5mol%) and a stir bar. MeCN (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (152.4 mg, 2.24mmol) in MeCN (2.8 mL, 0.8M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.5 mL (2.0 mmol) could be precisely dispensed while accounting for dead volume in the syringe. The syringe was installed into a syringe pump with an outlet needle inserted through the septum, and room temperature solution of oxidant was added dropwise over 3 hours (0.83 mL/hr) to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the H₂O₂ addition was complete, the reaction was quenched with saturated

NaHCO₃ solution, extracted with DCM, and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** C-H oxidation yield: 6% yield, RSM epoxide: 3% yield, C-H oxidation product epoxides yield: 54% yield, alcohol: ketone = 1: 10, C4: C3 = 1: 1.8. **Run 2:** C-H oxidation yield: 7% yield, RSM epoxide: 6% yield, C-H oxidation product epoxides yield: 56% yield, alcohol: ketone = 1: 20, C4: C3 = 1: 2.8. **Average:** C-H oxidation yield: 7% ± 0.5%, RSM epoxide: 5% ± 1.6%, C-H oxidation product epoxides yield: 55% ± 0.8%, alcohol: ketone = 1: 14, C4: C3 = 1: 2.3.

Entry 2. The reaction was carried out following the reported conditions for methylene oxidation using Mn(CF₃-PDP), with a modification to the reaction concentration¹. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), Cl-AcOH(283.5 mg, 3 mmol, 7.5 equiv.), (*R,S,S,R*)-Mn(MeCF₃-PDP) **2** (27.7 mg, 0.02 mmol, 5mol%) and a stir bar. MeCN (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (152.4 mg, 2.24mmol) in MeCN (2.8 mL, 0.8M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.5 mL (2.0 mmol) could be precisely dispensed while accounting for dead volume in the syringe. The syringe was installed into a syringe pump with an outlet needle inserted through the septum, and room temperature solution of oxidant was added dropwise over 3 hours (0.83 mL/hr) to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the H₂O₂

addition was complete, the reaction was quenched with saturated NaHCO₃ solution, extracted with DCM, and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** 10% RSM, C-H oxidation yield: 17% yield, RSM epoxide: 33% yield, C-H oxidation product epoxides yield: 22% yield, alcohol: ketone = 1: 1.4, C4: C3 = 1: 1.8. **Run 2:** 10% RSM, C-H oxidation yield: 14% yield, RSM epoxide: 31% yield, C-H oxidation product epoxides yield: 24% yield, alcohol: ketone = 1: 1.9, C4: C3 = 1: 1.4. **Average:** 10% RSM, C-H oxidation yield: 16% ± 1.5%, RSM epoxide: 32% ± 1.2%, C-H oxidation product epoxides yield: 24% ± 1.3%, alcohol: ketone = 1: 1.7, C4: C3 = 1: 1.6.

Entry 3. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), (*R,R*)-Mn(CF₃-PDP) **1** (27.1 mg, 0.02 mmol, 5mol%) and a stir bar. MeCN (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (152.4 mg, 2.24mmol) in MeCN (2.8 mL, 0.8M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.5 mL (2.0 mmol) could be precisely dispensed while accounting for dead volume in the syringe. The syringe was installed into a syringe pump with an outlet needle inserted through the septum, and room temperature solution of oxidant was added dropwise over 3 hours (0.83 mL/hr) to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the H₂O₂ addition was complete, the reaction was quenched with saturated NaHCO₃ solution, extracted with DCM, and dried over

Na₂SO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** 43% RSM, C-H oxidation yield: 20% yield, RSM epoxide: 9% yield, C-H oxidation product epoxide: 3% yield, alcohol: ketone = 1: 4.7, C4: C3 = 1: 1.3. **Run 2:** 47% RSM, C-H oxidation yield: 21% yield, RSM epoxide: 7% yield, C-H oxidation product epoxides yield: 2% yield, alcohol: ketone = 1: 4.1, C4: C3 = 1: 1.4. **Average:** 45% RSM ± 2%, C-H oxidation yield: 21% ± 0.5%, RSM epoxide: 8% ± 0.7%, C-H oxidation product epoxides yield: 2% ± 0.4%, alcohol: ketone = 1: 4.4, C4: C3 = 1: 1.4.

Entry 4. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), (*R,S,S,R*)-Mn(MeCF₃-PDP) **2** (27.7 mg, 0.02 mmol, 5mol%) and a stir bar. MeCN (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (152.4 mg, 2.24mmol) in MeCN (2.8 mL, 0.8M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.5 mL (2.0 mmol) could be precisely dispensed while accounting for dead volume in the syringe. The syringe was installed into a syringe pump with an outlet needle inserted through the septum, and room temperature solution of oxidant was added dropwise over 3 hours (0.83 mL/hr) to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the H₂O₂ addition was complete, the reaction was quenched with saturated NaHCO₃ solution, extracted with DCM, and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by flash

column chromatography (acetone: hexane = 1: 10 $\rightarrow$ 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** C-H oxidation yield: <1% (trace alcohol only), epoxides yield: 0% yield, 90% RSM. **Run 2:** C-H oxidation yield: <1% (trace alcohol only), epoxides yield: 0%, 93% RSM. **Average:** C-H oxidation yield: <1% (trace alcohol only), epoxides yield: 0%, 92% RSM $\pm$ 1.5%.

Entry 5 (PDP/carboxylic acid condition in HFIP). A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), Cl-AcOH(283.5 mg, 3 mmol, 7.5 equiv.) and a stir bar. HFIP (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (88.4 mg, 1.3 mmol) in HFIP (2.6 mL, 0.5M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.4 mL (1.2 mmol) could be precisely dispensed while accounting for dead volume in the syringe. In another 1-dram vial, a solution of (*R,R*)-Mn(CF₃PDP) **1** (27.1 mg, 0.02 mmol, 5 mol%) in MeCN (0.32 mL) was swirled to homogeneity. A 1 mL microsyringe (Gastight Syringe Model 1001 RN, Large Removable Needle, 22 gauge, 2 in., point style 2, catalogue number 81330) was charged with 0.32 mL of the catalyst solution. The dead volume of this microsyringe is negligible, eliminating the need for excess catalyst solution. Both the catalyst-loaded syringe and the H₂O₂-loaded syringe were installed into a syringe pump, with an outlet needle inserted through the septum (see **Figure S5**). Room temperature solutions of the catalyst (0.064 mL/hr) and H₂O₂ (0.48 mL/hr) were added dropwise over 5 hours to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the H₂O₂ addition was complete, the

reaction was quenched with saturated NaHCO₃ solution, extracted with DCM, and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** C-H oxidation yield: 46% yield, C-H oxidation product epoxides yield: 25% yield, alcohol: ketone = 1.5: 1, C4: C3 = 1: 1. **Run 2:** C-H oxidation yield: 51% yield, C-H oxidation product epoxides yield: 27% yield, alcohol: ketone = 1.1: 1, C4: C3 = 1: 1. **Average:** C-H oxidation yield: 49% ± 2.5%, C-H oxidation product epoxides yield: 26% ± 1.0%, alcohol: ketone = 1.1: 1, C4: C3 = 1: 1.

Entry 6. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), Cl-AcOH(283.5 mg, 3 mmol, 7.5 equiv.) and a stir bar. HFIP (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (88.4 mg, 1.3 mmol) in HFIP (2.6 mL, 0.5M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.4 mL (1.2 mmol) could be precisely dispensed while accounting for dead volume in the syringe. In another 1-dram vial, a solution of a solution of (*S,R,R,S*)-Mn(MeCF₃PDP) **2** (27.7 mg, 0.02 mmol, 5 mol%) in MeCN (0.32 mL) was swirled to homogeneity. A 1 mL microsyringe (Gastight Syringe Model 1001 RN, Large Removable Needle, 22 gauge, 2 in., point style 2, catalogue number 81330) was charged with 0.32 mL of the catalyst solution. The dead volume of this microsyringe is negligible, eliminating the need for excess catalyst solution. Both the catalyst-loaded syringe and the H₂O₂-loaded syringe were installed into a syringe pump, with an outlet needle inserted through the septum (see **Figure S5**). Room temperature solutions of the catalyst

(0.064 mL/hr) and H₂O₂ (0.48 mL/hr) were added dropwise over 5 hours to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the H₂O₂ addition was complete, the reaction was quenched with saturated NaHCO₃ solution, extracted with DCM, and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** C-H oxidation yield: 65% yield, C-H oxidation product epoxides yield: 11% yield, alcohol: ketone = 3.6: 1, C4: C3 = 1.1: 1. **Run 2:** C-H oxidation yield: 63% yield, C-H oxidation product epoxides yield: 9% yield, alcohol: ketone = 1.9: 1, C4: C3 = 1.1: 1. **Average:** C-H oxidation yield: 64% ± 1.0%, C-H oxidation product epoxides yield: 10% ± 1.0%, alcohol: ketone = 2.6: 1, C4: C3 = 1.1: 1.

Entry 7 (Standard condition). A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.) and a stir bar. HFIP (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (88.4 mg, 1.3 mmol) in HFIP (2.6 mL, 0.5M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.4 mL (1.2 mmol) could be precisely dispensed while accounting for dead volume in the syringe. In another 1-dram vial, a solution of (*R,R*)-Mn(CF₃PDP) **1** (27.1 mg, 0.02 mmol, 5 mol%) in MeCN (0.32 mL) was swirled to homogeneity. A 1 mL microsyringe (Gastight Syringe Model 1001 RN, Large Removable Needle, 22 gauge, 2 in., point style 2, catalogue number 81330) was charged with 0.32 mL of the catalyst solution. The dead volume of this microsyringe is negligible,

eliminating the need for excess catalyst solution. Both the catalyst-loaded syringe and the H₂O₂-loaded syringe were installed into a syringe pump, with an outlet needle inserted through the septum (see **Figure S5**). Room temperature solutions of the catalyst (0.064 mL/hr) and H₂O₂ (0.48 mL/hr) were added dropwise over 5 hours to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the addition of H₂O₂ was complete, the reaction mixture was concentrated to the minimal amount of HFIP under a stream of nitrogen. The resulting crude product was purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4), yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Isolated yields are reported. Enone: epoxide ratio was determined by ¹H NMR (*vide supra*). **Run 1:** C-H oxidation yield: 75% yield, C-H oxidation product epoxides yield: 6% yield, alcohol: ketone = 1: 2.1, C4: C3 = 1.1: 1. **Run 2:** C-H oxidation yield: 75% yield, C-H oxidation product epoxides yield: 6% yield, alcohol: ketone = 1: 1.8, C4: C3 = 1.1: 1. **Run 3:** C-H oxidation yield: 76% yield, C-H oxidation product epoxides yield: 4% yield, alcohol: ketone = 1: 1.4, C4: C3 = 1.1: 1. **Average:** C-H oxidation yield: 75% ± 0.5%, C-H oxidation product epoxides yield: 5% ± 0.9%, alcohol: ketone = 1: 1.7, C4: C3 = 1.1: 1.

Entry 8. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.) and a stir bar. HFIP (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (88.4 mg, 1.3 mmol) in HFIP (2.6 mL, 0.5M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.4 mL (1.2 mmol) could be precisely dispensed while accounting for dead volume in the syringe. In another 1-dram vial, a

solution of a solution of (*S,R,R,S*)-Mn(MeCF₃PDP) **2** (27.7 mg, 0.02 mmol, 5 mol%) in MeCN (0.32 mL) was swirled to homogeneity. A 1 mL microsyringe (Gastight Syringe Model 1001 RN, Large Removable Needle, 22 gauge, 2 in., point style 2, catalogue number 81330) was charged with 0.32 mL of the catalyst solution. The dead volume of this microsyringe is negligible, eliminating the need for excess catalyst solution. Both the catalyst-loaded syringe and the H₂O₂-loaded syringe were installed into a syringe pump, with an outlet needle inserted through the septum (see **Figure S5**). Room temperature solutions of the catalyst (0.064 mL/hr) and H₂O₂ (0.48 mL/hr) were added dropwise over 5 hours to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the addition of H₂O₂ was complete, the reaction mixture was concentrated under a stream of nitrogen. The resulting crude product was purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** 6% RSM, C-H oxidation yield: 67% yield, RSM epoxide: 1.2%, C-H oxidation product epoxides yield: 4.3%, alcohol: ketone = 2.7: 1, C4: C3 = 1.1: 1. **Run 2:** 7% RSM, C-H oxidation yield: 72% yield, RSM epoxide: 1% yield, C-H oxidation product epoxides yield: 3.5%, alcohol: ketone = 2: 1, C4: C3 = 1.2: 1. **Average:** 7% RSM ± 0.5%, C-H oxidation yield: 70% ± 2.5%, RSM epoxide: 1% ± 0.1%, C-H oxidation product epoxides yield: 4% ± 0.4%, alcohol: ketone = 2.3: 1, C4: C3 = 1.2: 1.

Entry 9. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), AcOH (0.17 ml, 3 mmol, 7.5 equiv.), (*R,R*)-Mn(CF₃-PDP) **1** (27.1 mg, 0.02 mmol, 5mol%) and a stir bar. MeCN (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed

with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (152.4 mg, 2.24mmol) in MeCN (2.8 mL, 0.8M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.5 mL (2.0 mmol) could be precisely dispensed while accounting for dead volume in the syringe. The syringe was installed into a syringe pump with an outlet needle inserted through the septum, and room temperature solution of oxidant was added dropwise over 3 hours (0.83 mL/hr) to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the H₂O₂ addition was complete, the reaction was quenched with saturated NaHCO₃ solution, extracted with DCM, and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** 16% RSM, C-H oxidation yield: 21% yield, RSM epoxide: 26% yield, C-H oxidation product epoxides yield: 16% yield, alcohol: ketone = 1: 1.8, C4: C3 = 1: 1.1. **Run 2:** 12% RSM, C-H oxidation yield: 20% yield, RSM epoxide: 24% yield, C-H oxidation product epoxides yield: 16% yield, alcohol: ketone = 1: 1.7, C4: C3 = 1: 1.1. **Average:** 14% RSM ± 2%, C-H oxidation yield: 21% ± 0.5%, RSM epoxide: 25% ± 1.2%, C-H oxidation product epoxides yield: 16% ± 0.3%, alcohol: ketone = 1: 1.8, C4: C3 = 1: 1.1.

Entry 10. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), tBuOH (0.28 ml, 3 mmol, 7.5 equiv.), (*R,R*)-Mn(CF₃-PDP) **1** (27.1 mg, 0.02 mmol, 5mol%) and a stir bar. MeCN (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50%

H₂O₂ (152.4 mg, 2.24mmol) in MeCN (2.8 mL, 0.8M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.5 mL (2.0 mmol) could be precisely dispensed while accounting for dead volume in the syringe. The syringe was installed into a syringe pump with an outlet needle inserted through the septum, and room temperature solution of oxidant was added dropwise over 3 hours (0.83 mL/hr) to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the addition of H₂O₂ was complete, the reaction mixture was concentrated under a stream of nitrogen. The resulting crude product was purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** 69% RSM, C-H oxidation yield: 12% yield, RSM epoxide: 3% yield, C-H oxidation product epoxides yield: 0.4%, alcohol: ketone = 1: 2.5, C4: C3 = 1: 1.5. **Run 2:** 68% RSM, C-H oxidation yield: 13% yield, RSM epoxide: 3% yield, C-H oxidation product epoxides yield: 0.5%, alcohol: ketone = 1: 2.2, C4: C3 = 1: 1.3. **Average:** 69% RSM ± 0.5%, C-H oxidation yield: 13% ± 0.5%, RSM epoxide: 3% ± 0.05%, C-H oxidation product epoxides yield: 0.4% ± 0.06%, alcohol: ketone = 1: 2.3, C4: C3 = 1: 1.4.

Entry 11. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), HFIP (0.32 ml, 3 mmol, 7.5 equiv.), (*R,R*)-Mn(CF₃-PDP) **1** (27.1 mg, 0.02 mmol, 5mol%) and a stir bar. MeCN (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (152.4 mg, 2.24mmol) in MeCN (2.8 mL, 0.8M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.5 mL (2.0 mmol) could be

precisely dispensed while accounting for dead volume in the syringe. The syringe was installed into a syringe pump with an outlet needle inserted through the septum, and room temperature solution of oxidant was added dropwise over 3 hours (0.83 mL/hr) to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the H₂O₂ addition was complete, the reaction was quenched with saturated NaHCO₃ solution, extracted with DCM, and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** 22% RSM, C-H oxidation yield: 21% yield, RSM epoxide: 21% yield, C-H oxidation product epoxides yield: 9% yield, alcohol: ketone = 1: 1.4, C4: C3 = 1: 1.3. **Run 2:** 17% RSM, C-H oxidation yield: 23% yield, RSM epoxide: 19% yield, C-H oxidation product epoxides yield: 11% yield, alcohol: ketone = 1: 1.3, C4: C3 = 1: 1.2. **Average:** 20% RSM ± 2.5%, C-H oxidation yield: 22% ± 1.0%, RSM epoxide: 20% ± 1.2%, C-H oxidation product epoxides yield: 10% ± 1.1%, alcohol: ketone = 1: 1.3, C4: C3 = 1: 1.2.

Entry 12. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.), TFE (0.22 ml, 3 mmol, 7.5 equiv.), (*R,R*)-Mn(CF₃-PDP) **1** (27.1mg, 0.02mmol, 5mol%) and a stir bar. MeCN (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (152.4 mg, 2.24mmol) in MeCN (2.8 mL, 0.8M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.5 mL (2.0 mmol) could be precisely dispensed while accounting for dead volume in the syringe. The syringe was installed

into a syringe pump with an outlet needle inserted through the septum, and room temperature solution of oxidant was added dropwise over 3 hours (0.83 mL/hr) to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the addition of H₂O₂ was complete, the reaction mixture was concentrated under a stream of nitrogen. The resulting crude product was purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** 26% RSM, C-H oxidation yield: 24% yield, RSM epoxide: 16% yield, C-H oxidation product epoxides yield: 9% yield, alcohol: ketone = 1:>20, C4: C3 = 1: 1.1. **Run 2:** 28% RSM, C-H oxidation yield: 22% yield, RSM epoxide: 16% yield, C-H oxidation product epoxides yield: 8% yield, alcohol: ketone = 1:>20, C4: C3 = 1: 1.1. **Average:** 27% RSM ± 1.0%, C-H oxidation yield: 23% ± 1.0%, RSM epoxide: 16% ± 0.2%, C-H oxidation product epoxides yield: 9% ± 0.4%, alcohol: ketone = 1:>20, C4: C3 = 1: 1.1.

Entry 13. A 15 ml vial was charged with spiroenone **3** (66 mg, 0.4 mmol, 1 equiv.) and a stir bar. TFE (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (88.4 mg, 1.3 mmol) in TFE (2.6 mL, 0.5M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.4 mL (1.2 mmol) could be precisely dispensed while accounting for dead volume in the syringe. In another 1-dram vial, a solution of (*R,R*)-Mn(CF₃PDP) **1** (27.1 mg, 0.02 mmol, 5 mol%) in MeCN (0.32 mL) was swirled to homogeneity. A 1 mL microsyringe (Gastight Syringe Model 1001 RN, Large Removable Needle, 22 gauge, 2 in., point style 2, catalogue number 81330) was charged with 0.32 mL of the

catalyst solution. The dead volume of this microsyringe is negligible, eliminating the need for excess catalyst solution. Both the catalyst-loaded syringe and the H₂O₂-loaded syringe were installed into a syringe pump, with an outlet needle inserted through the septum (see **Figure S5**). Room temperature solutions of the catalyst (0.064 mL/hr) and H₂O₂ (0.48 mL/hr) were added dropwise over 5 hours to a solution of substrate that has been cooled to 0°C. The reaction progress was monitored by TLC (silica, acetone: hexane=1: 3). After the addition of H₂O₂ was complete, the reaction mixture was concentrated under a stream of nitrogen. The resulting crude product was purified by flash column chromatography (acetone: hexane = 1: 10 → 1: 4, yielding three compound mixtures (starting material (RSM) and its epoxide/ ketones and their epoxides/ alcohols and their epoxides, *vide supra*). Individual yields were determined by NMR spectroscopy (*vide supra*). **Run 1:** 23% RSM, C-H oxidation yield: 21% yield, RSM epoxide: 8% yield, C-H oxidation product epoxides yield: 2% yield, alcohol: ketone = 1: 1.5, C4: C3 = 1: 1. **Run 2:** 21% RSM, C-H oxidation yield: 22% yield, RSM epoxide: 7% yield, C-H oxidation product epoxides yield: 3% yield, alcohol: ketone = 1: 2.4, C4: C3 = 1: 1.1. **Average:** 22% RSM% ± 1.0%, C-H oxidation yield: 22% ± 0.5%, RSM epoxide: 7% ± 0.3%, C-H oxidation product epoxides yield: 3% ± 0.4%, alcohol: ketone = 1: 1.9, C4: C3 = 1: 1.

Guidelines for Determining Catalyst and Oxidant Loading

Standard oxidation conditions (25 out of 45 substrates): commercial catalyst Mn(CF₃PDP) **1** at 5 mol%, 50 wt% H₂O₂ (3 equiv.) in HFIP:CH₃CN (10:1 final solvent volume ratio). Both the catalyst **1** [0.06 M in CH₃CN] and H₂O₂ (0.5 M in HFIP) are added separately via syringe pump to a 0°C solution of the substrate (0.4 mmol) in HFIP (0.5M) over 5 hours. At a given reaction scale reagent solution volumes remained constant when adjusting the catalyst and oxidant loadings. The standard conditions were found to be generally effective and were used for >50% of the substrates in this manuscript. Typically, the catalyst/oxidant ratio is kept 1 mol% catalyst per 0.6 equiv. of oxidant, with a maximum oxidant loading of 4.5 equiv. due to solubility limitations in HFIP (0.75M).

Low conversion with standard conditions: If standard conditions give low conversion (ca. < 50%), **1** (10 mol%, 0.125 M in CH₃CN) and H₂O₂ (4.5 equiv., 0.75M in HFIP) are used and the reaction is monitored for disappearance of starting material [thin layer chromatography (TLC) or quantitatively by gas chromatography (GC) or high performance liquid chromatography (HPLC)]. The amount of catalyst needed to reach high conversion is calculated first. Oxidant loading is then determined based on this catalyst loading, maintaining the standard catalyst/oxidant ratio (1 mol% catalyst per 0.6 equiv. of oxidant) with a maximum oxidant loading of 4.5 equiv. The calculated catalyst and oxidant loadings are used in the subsequent reaction. For example, if full conversion is achieved at 3.75 hours, the reaction is repeated at 7.5 mol% catalyst **1** (0.09M in CH₃CN) and 4.5 equiv. H₂O₂ (0.75M in HFIP) over a 5-hour addition time.

High conversion and over-oxidized byproducts with standard conditions: If standard conditions give full conversion of starting material with observation of over-oxidized products, the reaction is monitored and the amount of catalyst and oxidant needed for full consumption of starting

material is calculated and used in the subsequent reaction. For example, if full conversion is achieved at 2.5 hours, the reaction is repeated at 2.5mol% catalyst **1** (0.03M in CH₃CN) and 1.5 equiv. H₂O₂ (0.25M in HFIP) over a 5 hr addition time.

Using Catalyst Mn(MeCF₃PDP) **2**: In cases where catalyst **1** does not provide preparative yields of mono-oxidized products, catalyst Mn(MeCF₃PDP) **2** was used under the standard conditions described above for catalyst **1**. The same procedures described for reaction optimization under conditions of low and high conversions were applied. Improved yields with catalyst **2** were observed when 5 mol% or less of catalyst **1** resulted in low mass balance due to poor chemoselectivity (**47**, **48**, **49**, **51**, **53**, **63**, **67**) or when 10 mol% catalyst **1** shows low conversion (**55**, **59**, **77**). If catalyst **2** shows low conversion, Cl-AcOH (7.5 equiv.) can improve conversion and yield, as demonstrated for **59**. Addition of Cl-AcOH to catalyst **1** leads to epoxidation.

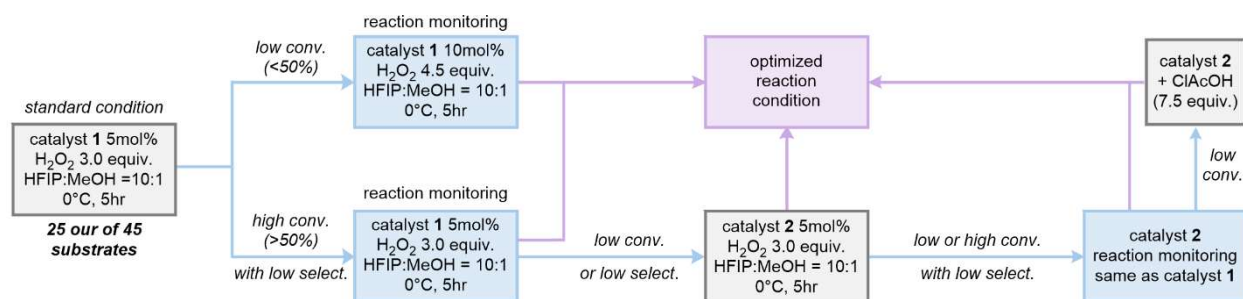


Figure S4. Flowchart for Reaction Condition Optimization

Detailed Procedure for Standard Conditions

A 15 ml vial was charged with substrate (0.4 mmol, 1 equiv.) and a stir bar. HFIP (0.8 mL, 0.5 M) was added, ensuring no residue remained on the vial walls. The vial was sealed with a silicon septum cap, stirred, and cooled to 0°C. In a separate 1-dram vial, a solution of 50% H₂O₂ (88.4 mg, 1.3 mmol, 3.25 equiv.) in HFIP (2.6 mL, 0.5M) was swirled to achieve homogeneity. A 5 mL syringe (22 gauge) was charged with the H₂O₂ solution so that 2.4 mL (1.2 mmol, 3.0 equiv.) could be precisely dispensed while accounting for dead volume in the syringe. In another 1-dram vial, a solution of Mn(CF₃PDP) **1** (27.1 mg, 0.02 mmol, 5 mol%) or Mn(MeCF₃PDP) **2** (27.7 mg, 0.02 mmol, 5 mol%) in MeCN (0.32 mL, 0.06M) was swirled to homogeneity. A 1 mL microsyringe (Gastight Syringe Model 1001 RN, Large Removable Needle, 22 gauge, 2 in., point style 2, catalogue number 81330) was charged with 0.32 mL of the catalyst solution. The dead volume of this microsyringe is negligible, eliminating the need for excess catalyst solution. When increasing the reaction scale (for example 0.4 mmol to 0.8 mmol substrate), the initial concentration of substrate (0.5M) in HFIP was held constant and the solvent volumes and reagent amounts were scaled accordingly. At a given reaction scale, reagent solution volumes remained constant

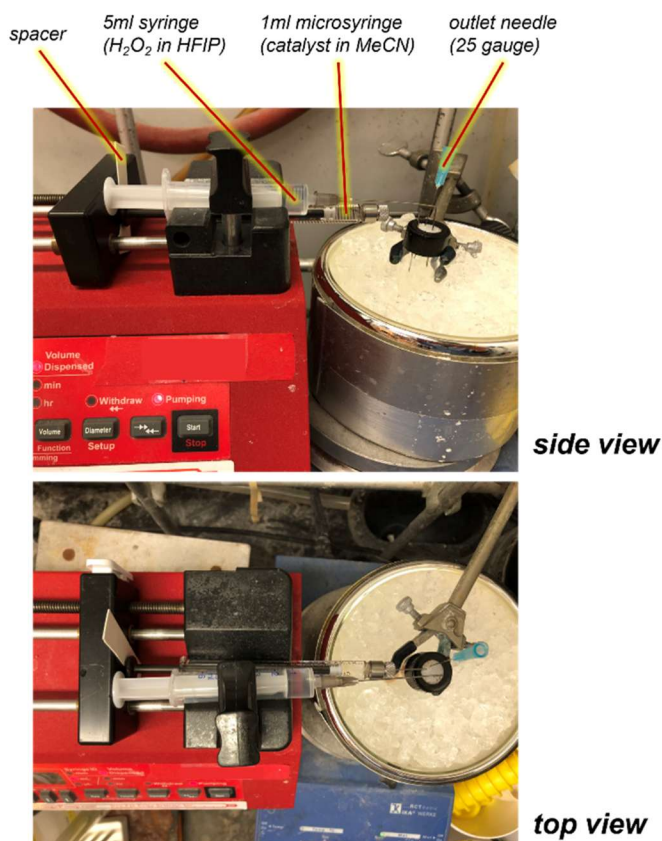
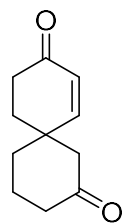


Figure S5. Experimental Setup for the Standard conditions

when adjusting catalyst and oxidant loadings. Both the catalyst-loaded syringe and the H₂O₂-loaded syringe were installed into a syringe pump, with an outlet needle inserted through the septum (see **Figure S5**). Room temperature solutions of the catalyst (0.064 mL/hour) and H₂O₂ (0.48 mL/hour) were added dropwise over 5 hours to a solution of substrate that has been cooled to 0°C. Reaction progress can be monitored by TLC, GC, or HPLC. (*Note: Optimal catalyst and oxidant loadings were determined based on TLC analysis during the reaction. For instance, if the substrate was fully consumed after 2.5 hours of addition, optimal conditions were identified as 2.5 mol% catalyst and 1.5 equiv. oxidant.*). After the addition of H₂O₂ was complete, the reaction mixture was concentrated to the minimal amount of HFIP under a stream of nitrogen. The mixture filtered through a pad of silica with EtOAc and concentrated. The resulting crude product was purified by flash column chromatography. Isolated yields are reported. On a multigram scale, an aqueous saturated NaHCO₃ workup followed by water washes are recommended to remove unreacted H₂O₂.

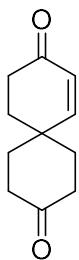
Characterization of Oxidation Products

spiro[5.5]undec-7-ene-2,9-dione [4-C3ketone]. ^1H NMR (500 MHz, CDCl_3) δ 6.66 (d, $J = 10.2$



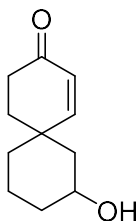
Hz, 1H), 5.93 (d, $J = 10.1$ Hz, 1H), 2.46 (t, $J = 6.8$ Hz, 2H), 2.43 – 2.38 (m, 4H), 2.05 – 1.86 (m, 5H), 1.84 – 1.77 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.27, 198.54, 154.98, 128.54, 50.54, 41.02, 40.57, 35.28, 33.66, 32.64, 22.22. HRMS (TOF ESI+) m/z calculated for $\text{C}_{11}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 179.1072, found 179.1075.

spiro[5.5]undec-1-ene-3,9-dione [4-C4ketone]. ^1H NMR (500 MHz, CDCl_3) δ 6.86 (dt, $J = 10.2$,

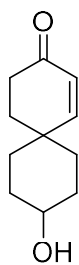


0.9 Hz, 1H), 6.01 (d, $J = 10.2$ Hz, 1H), 2.52 (dd, $J = 7.4$, 6.2 Hz, 2H), 2.45 (t, $J = 7.0$ Hz, 4H), 2.11 (td, $J = 6.8$, 0.9 Hz, 2H), 1.95 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.90, 198.91, 155.58, 129.09, 37.36, 35.53, 34.90, 34.01, 31.71. HRMS (TOF ESI+) m/z calculated for $\text{C}_{11}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 179.1072, found 179.1079.

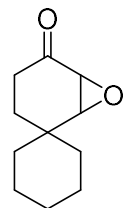
8-hydroxyspiro[5.5]undec-1-en-3-one [4-C3OH]. diastereomeric mixture (11.5: 1). ^1H NMR



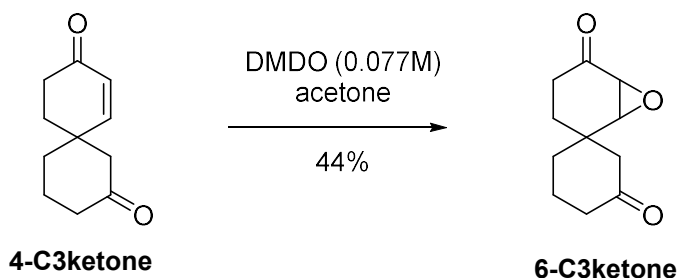
(500 MHz, CDCl_3) δ 6.97 (d, $J = 10.4$ Hz, 0.92H), 6.67 (d, $J = 10.2$ Hz, 0.08H), 5.92 (d, $J = 10.3$ Hz, 0.92H), 5.88 (d, $J = 10.2$ Hz, 0.08H), 3.86 (tt, $J = 10.5$, 4.2 Hz, 1H), 2.57 – 2.39 (m, 2H), 2.11 – 2.01 (m, 1.8H), 1.94 – 1.86 (m, 0.2H), 1.90 (t, $J = 1.9$ Hz, 2H), 1.82 – 1.75 (m, 1H), 1.70 – 1.64 (m, 1H), 1.61 – 1.51 (m, 1H), 1.40 – 1.27 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.79 (199.49), 159.38 (155.68), 128.33 (127.46), 67.19 (66.81), 45.50 (43.90), 37.52 (37.30), 37.17, 36.31 (35.15), 35.50 (34.37), 34.10 (33.80), 20.04. HRMS (TOF ESI+) m/z calculated for $\text{C}_{11}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 181.1229, found 181.1233.

4'-hydroxy-7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexan]-5-one**[4-C4OH].**

Diastereomeric mixture (1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.00 (d, $J = 10.2$ Hz, 0.5H), 6.63 (d, $J = 10.2$ Hz, 0.5H), 5.91 (d, $J = 10.3$ Hz, 0.5H), 5.88 (d, $J = 10.1$ Hz, 0.5H), 3.79 (tt, $J = 8.5, 3.4$ Hz, 0.5H), 3.71 (tt, $J = 9.0, 4.1$ Hz, 0.5H), 2.44 (t, $J = 6.6$ Hz, 1H), 2.40 (t, $J = 6.6$ Hz, 1H), 1.96 (t, $J = 6.8$ Hz, 1H), 1.88 – 1.79 (m, 5H), 1.70 (m, 1H), 1.61 – 1.36 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 200.07 (199.82), 159.21 (156.97), 127.99 (127.97), 69.38 (68.84), 35.06 (34.77), 34.54 (30.51), 34.13 (33.79), 33.19 (32.90), 30.38 (30.28). HRMS (TOF ESI+) m/z calculated for $\text{C}_9\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 181.1229, found 181.1229.

7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexan]-5-one [5].

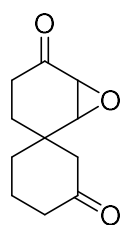
^1H NMR (500 MHz, CDCl_3) δ 3.35 (dd, $J = 4.0, 1.3$ Hz, 1H), 3.23 (d, $J = 4.0$ Hz, 1H), 2.40 (ddd, $J = 18.7, 6.4, 3.7$ Hz, 1H), 2.16 (ddd, $J = 18.5, 11.2, 7.0$ Hz, 1H), 1.77 (ddd, $J = 13.9, 11.2, 6.4$ Hz, 1H), 1.72 – 1.44 (m, 10H), 1.42 – 1.35 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 206.81, 63.47, 56.01, 36.02, 33.38, 32.69, 31.85, 27.25, 26.21, 21.75, 21.64. HRMS (TOF ESI+) m/z calculated for $\text{C}_{11}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 181.1229, found 181.1235.

**Preparation of 7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexane]-3',5-dione [6-C3ketone].**

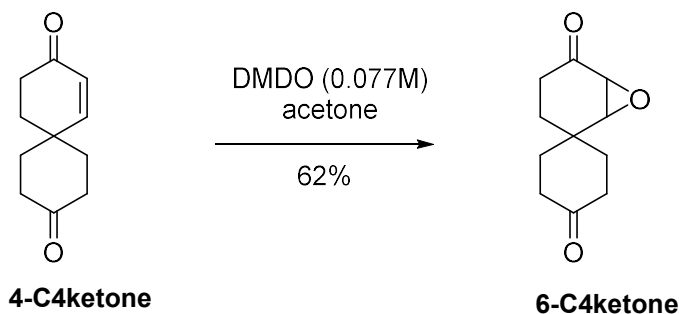
An authentic sample of epoxide **6-C3ketone** was synthesized from the oxidation product **4-**

C3ketone. To a solution of spiro[5.5]undec-7-ene-2,9-dione **6-C3ketone** (21 mg, 0.118 mmol, 1.0 equiv.) was added DMDO (0.077M in acetone, 2.3ml, 1.5 equiv.). The mixture was stirred at room temperature overnight. Completion of the reaction was confirmed by TLC (silica, ether: pentane = 3: 1). After removal of the solvent, the crude material was purified by flash column chromatography (silica, ether: pentane = 3: 1) to furnish 7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexane]-3',5-dione (10mg, 0.051mmol, 44%).

7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexane]-3',5-dione [6-C3ketone]. diastereomeric



mixture (1.3: 1). ^1H NMR (500 MHz, CDCl_3) δ 3.33 – 3.25 (m, 2H), 2.61 – 1.69 (m, 11H), 1.52 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.10 (209.03), 204.94 (204.55), 62.73 (61.81), 55.92 (55.53), 50.94 (47.16), 41.20 (41.00), 39.08 (38.85), 34.73 (32.46), 32.32 (30.43), 27.44 (26.55), 22.03 (21.80). HRMS (TOF ESI+) m/z calculated for $\text{C}_{11}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 195.1021, found 195.1023.

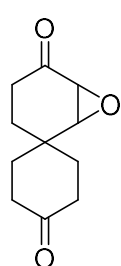


Preparation of 7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexane]-4',5-dione [6-C4ketone].

An authentic sample of epoxide **6-C4ketone** was synthesized from the oxidation product **4-C4ketone**. To a solution of spiro[5.5]undec-1-ene-3,9-dione **6-C4ketone** (18.3 mg, 0.1 mmol, 1.0 equiv.) was added DMDO (0.077M in acetone, 2.1 ml, 1.5 equiv.). The mixture was stirred at room temperature overnight. Completion of the reaction was confirmed by TLC (silica, ether:

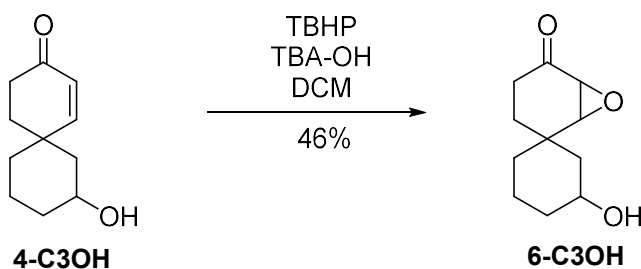
pentane = 3: 1). After solvent was removed, the crude was purified by flash column chromatography (silica, ether: pentane = 3: 1) to furnish 7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexane]-4',5-dione **6-C4ketone** (12 mg, 0.062 mmol, 62%).

7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexane]-4',5-dione [6-C4ketone]. ^1H NMR (500



MHz, CDCl_3) δ 3.41 (dd, $J = 4.0, 1.2$ Hz, 1H), 3.33 (d, $J = 3.9$ Hz, 1H), 2.58 – 2.38 (m, 5H), 2.23 (ddd, $J = 18.6, 11.1, 6.7$ Hz, 1H), 2.16 – 2.10 (m, 1H), 2.04 – 1.76 (m, 5H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.94, 205.17, 62.29, 55.85, 37.20, 36.98, 35.20, 33.06, 32.76, 31.10, 26.37. HRMS (TOF ESI+) m/z calculated for $\text{C}_{11}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$:

195.1021, found 195.1025.

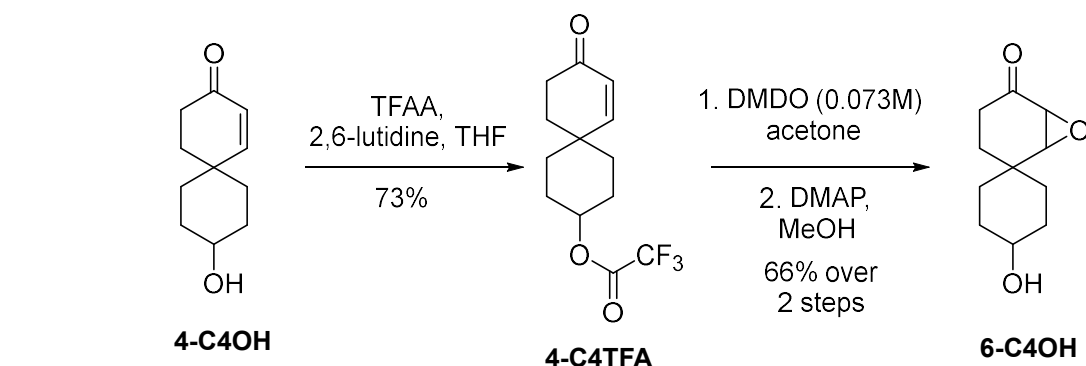


Preparation of 3'-hydroxy-7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexan]-5-one [6-C3OH]. An authentic sample of epoxide **6-C3OH** was synthesized from the oxidation product **4-C3OH**. To a solution of 8-hydroxyspiro[5.5]undec-1-en-3-one **6-C3OH** (10 mg, 0.055 mmol) in DCM (0.5 ml, 0.1 M) was added TBHP (5.5 M, 0.03 ml, 0.17 mmol, 3.0 equiv.) and TBA–OH (44 mg, 0.17 mmol, 3.0 equiv.) at rt. The mixture was stirred at room temperature for 2 hours. Completion of the reaction was confirmed by TLC (silica, EA only). After removal of solvent, the crude was directly loaded on silica column and the subsequent flash column chromatography (EA

only) to furnish 3'-hydroxy-7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexan]-5-one **6-C3OH** as a diastereomeric mixture (major: minors = 0.6: 0.4, 5mg, 0.025mmol, 46%).

3'-hydroxy-7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexan]-5-one [6-C3OH]. mixture of

four diastereomers. ¹H NMR (500 MHz, CDCl₃) δ 4.02 (tt, *J* = 10.3, 4.2 Hz, 0.6H), 3.95 – 3.79 (m, 0.4H), 3.43 – 3.36 (m, 0.81H), 3.34 – 3.16 (m, 1.17H), 2.50 – 2.37 (m, 1H), 2.30 – 1.76 (m, 5H), 1.69 – 1.40 (m, 4H), 1.37 – 1.23 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 206.27 (206.10, 206.00), 67.07 (67.03, 66.78), 61.35 (64.52, 60.65), 56.14 (56.20, 55.95), 44.14 (44.68, 42.30), 35.23 (35.47, 35.37), 34.99, 35.14 (34.74, 33.07), 32.91 (32.85), 32.59 (32.56, 31.36, 29.67), 20.15 (19.92, 19.47). HRMS (TOF ESI+) *m/z* calculated for C₁₁H₁₇O₃ [M+H]⁺: 197.1178, found 197.1179.

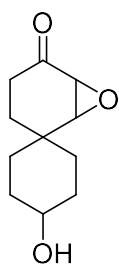


Preparation of 7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexane]-3',5-dione [6-C4OH]. An authentic sample of epoxide **6-C4OH** was synthesized from the oxidation product **4-C4OH**. To a stirred solution of 4'-hydroxy-7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexan]-5-one **4-C4OH** (101 mg, 0.56 mmol, 1.0 equiv.) and 2,6-lutidine (0.12 ml, 1.01 mmol, 1.8 equiv.) in THF (5.6 ml, 0.1 M) were added trifluoroacetic anhydride (TFAA, 0.09 ml, 0.67 mmol, 1.2 equiv.) at -78°C under a nitrogen atmosphere. The mixture was gradually warmed to room temperature over

2 hours, and and directly purified by flash column chromatography (EA: hexane = 1: 2.5), yielding **4-C4TFA** as a clear oil (113 mg, 0.41 mmol, 73%).

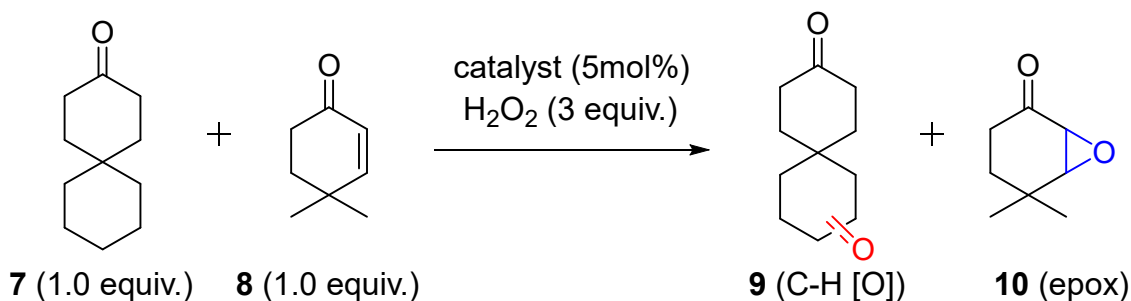
To a solution of TFA ester **4-C4TFA** (30 mg, 0.109 mmol, 1.0 equiv.) was added DMDO (0.073M in acetone, 2.7 ml, 1.8 equiv.). The mixture was stirred at room temperature for 2 hours. The reaction was monitored by TLC (silica gel, ether: pentane = 1: 2). Upon completion, the mixture was concentrated. The resulting mixture was dissolved in methanol (0.7 ml, 0.16 M), and DMAP (4.4 mg, 0.036 mmol, 0.33 equiv.). The mixture was stirred at room temperature for 2 hours. The reaction was monitored by TLC (silica, EA only). Upon completion, the mixture was concentrated in vacuo and purified by flash column chromatography (silica, EA only) to afford hydroxy epoxide **6-C4OH** as a diastereomeric mixture (major: minors = 1: 1, 14 mg, 0.07 mmol, 66% yield over two steps).

7-oxaspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexane]-3',5-dione [6-C4OH]. diastereomeric



mixture (1: 1). ^1H NMR (500 MHz, CDCl_3) δ 3.81 (tt, J = 8.2, 3.8 Hz, 0.5H), 3.73 (ddt, J = 13.4, 9.1, 4.1 Hz, 0.5H), 3.50 (d, J = 4.0, 0.5H), 3.26 (d, J = 4.1 Hz, 0.5H), 3.23 (d, J = 4.0 Hz, 0.5H), 3.17 (d, J = 3.9 Hz, 0.5H), 2.47– 2.39 (m, 1H), 2.21 – 2.10 (m, 1H), 2.03 – 1.73 (m, 5H), 1.70 – 1.31 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 206.38 (206.26), 69.63 (68.92), 63.98 (61.78), 56.08 (55.82), 33.28 (32.35), 33.00 (32.65), 32.92 (32.59), 30.33, 30.16 (30.06), 29.41 (29.03), 28.23 (24.92). HRMS (TOF ESI+) m/z calculated for $\text{C}_{11}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$: 197.1178, found 197.1169.

IV. Competitive Kinetic Experiments



entry	catalyst	solvent	additive	$k_{9(\text{C-H[O]})}/k_{10(\text{epox})}$	chemoselectivity ([9]/[10] ^a)
1	1	MeCN	ClAcOH	1.6	1.6
2	1	MeCN	-	1.8	1.5
3	1	HFIP/MeCN ^b	-	38.5	39.3
4	1	HFIP/MeCN ^b	ClAcOH	9.6	9.4
5	2	MeCN	ClAcOH	1.1	1.5
6	2	MeCN	-	3.3	5.4
7	2	HFIP/MeCN ^b	-	59.1	59.0
8	2	HFIP/MeCN ^b	ClAcOH	30.0	41.6

Table S2. Observed rates, relative rates ($k_{\text{rel}} = \text{C—H oxidation rate/ epoxidation rate}$) and GC yield ratio. ^ameasured at the end of the initial rate measurements ($t=1440$ seconds). ^bfinal solvent volume ratio HFIP: MeCN = 5: 1.

The competitive kinetic experiment was designed based on the proposed mechanism for the formation of the active oxidant in PDP catalysis^{7–10}, where formation of active oxidant species does not involve substrate binding. Competitive reactions of aliphatic substrate **7** and enone substrate **8** were performed in the same reaction vial and relative rates of formation of C—H oxidation product **9** and epoxide **10** were measured. Identical lag times for catalyst **2** were observed for epoxidation and C—H oxidation supporting that both processes in the competing reaction are

mediated by the same active oxidant¹¹. Significantly, the relative rate ratio trends are consistent with the product ratios (chemoselectivity, [9]/[10]) measured at the end of the initial rate measurements (1440 seconds) as well as the product distributions of C—H oxidization to epoxidation products in reactions where both functional groups are present in the same molecule (see fig. 1c).

Procedure of Competitive Kinetic Study

Preparation of starting materials. Spiroketone **7** was prepared from spiroenone **3** according to the reported procedure¹². Enone **8** was purchased from Combi-blocks (4,4-Dimethylcyclohex-2-enone, 5g, catalogue number OT-0020) and used as received.

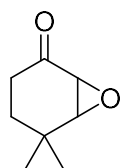
Preparation of Gas Chromatography (GC) samples. The reaction vial was fitted with a punctured silicon septum, allowing sampling during the run without removing the cap. Samples were taken at required time points using a 9-inch Pasteur pipette and diluted directly with ca. 0.4 mL of a 1: 1.5 ether mixture. The resulting mixture was kept at room temperature for 2-5 minutes and filtered through glass wool packed in a 5 ¼-inch Pasteur pipette. The filtrate was collected into a 1 mL GC vial, capped, and submitted for GC analysis.

Procedure of reaction setup and monitoring. A 15 ml vial was first charged with nitrobenzene 15-20 mg (ca. 0.4 equiv.) and the exact amount was recorded. A mixture of spiroketone **7** and

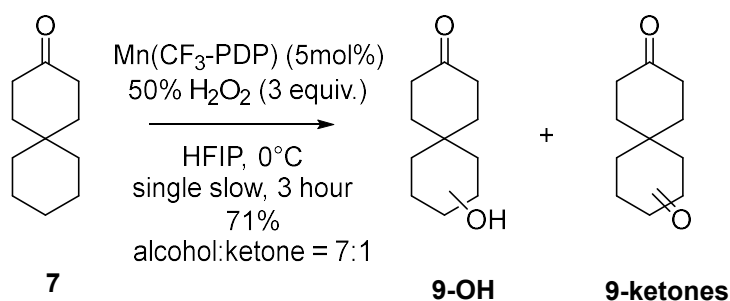
enone **8** (1: 1 molar ratio, 87.2 mg, 0.3 mmol each) and a stir bar were added (*Note: Separate substrate transfer was more error-prone due to the volatility of enone 8*). The vial was sealed with a puncturable silicon septum. Solvent (1.0 mL of MeCN or 1.0 mL of HFIP + 0.05 mL of MeCN) was added through the septum, ensuring no residue remained on the walls. If Cl-AcOH was required, 1 mL of 2.25 M Cl-AcOH stock solution (7.5 equiv.) in the required solvent was used instead. The catalyst (20.3 mg for catalyst **1** or 20.7 mg for catalyst **2**, 0.015 mmol, 5 mol%) was then added as a solid at room temperature. The mixture was stirred and cooled to 0°C. A 1 mL syringe with a 23-gauge needle was charged with the appropriate H₂O₂ stock solution (0.2 mL of 4.5M in MeCN when the main solvent is MeCN, 0.15 mL of 6M in MeCN when the main solvent is HFIP) and installed in a syringe pump. The t₀ sample was taken prior to initiating the oxidant addition, and time measurement started with the introduction of the first drop of the oxidant. Samples for GC analysis were taken at 1.5, 3, 4.5, 6, 9, 12, 15, 18, 21, 24, 27, 30, 45, and 60 minutes. The concentration of the remaining starting material was determined based on the GC integration ratio between the starting material and the internal standard, compared to the t₀ sample. Product concentrations were calculated from calibration curves.

Preparation of Authentic Oxidation Product Standards

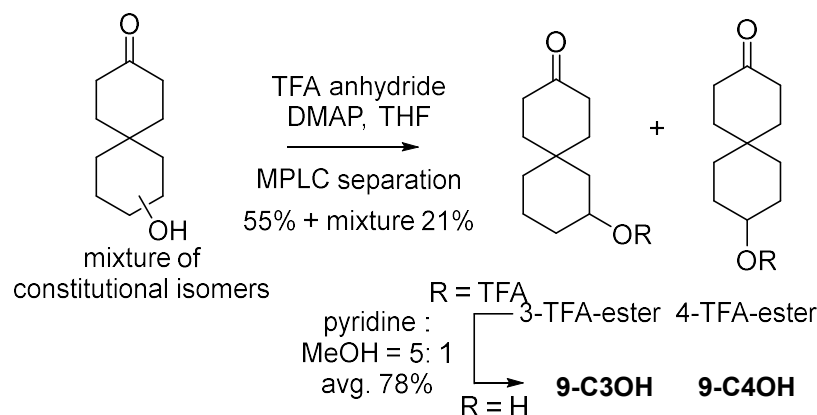
Preparation of 5,5-dimethyl-7-oxabicyclo[4.1.0]heptan-2-one [10]. Epoxide **10** was prepared



according to the reported procedure¹³.



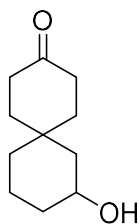
Preparation of alcohol authentic samples. A 15 mL vial was charged with ketone **7** (50 mg, 0.3 mmol, 1.0 equiv.), (*R,R*)-Mn(CF₃-PDP) (20.3 mg, 0.015 mmol, 5 mol%). HFIP (4.0 mL) was introduced, and the mixture was cooled to 0°C. A 1 mL syringe was charged with a solution of H₂O₂ (61.2 mg, 0.9 mmol, 3.0 equiv.) in 0.4 mL MeCN, and slowly added to the mixture over 3 hours at 0°C using syringe pump. Upon addition, the reaction mixture was concentrated using nitrogen flow. The resulting mixture was purified by column chromatography (silica, acetone: hexane = 1: 10 → 1: 4) to furnish alcohols **9-OH** (34 mg 0.19 mmol) and the corresponding ketones **9-ketones** (4.8 mg, 0.026 mmol, 71% total yield, alcohol: ketone = 7: 1).



Separation of alcohol mixture. To a stirred mixture of alcohol mixture **9-OH** (31 mg, 0.17 mmol, 1.0 equiv.) in THF (1 mL, 0.17 M) was added DMAP (31 mg, 0.26 mmol, 1.5 equiv.) and TFA anhydride (0.05 mL, 0.35 mmol, 2.0 equiv.) at 0°C. The reaction was completed in 10min at 0°C (confirmed by TLC analysis, EA: hexane = 1: 1). Upon completion, the resulting mixture concentrated in vacuo and purified by MPLC (Teledyne Combiflash® system, pentane only → ether: pentane = 1: 3), separating 3-TFA ester (16 mg, 0.058 mmol, 34% yield), 4-TFA ester (10 mg, 0.036 mmol, 21% yield) and mixed portion (10 mg, 0.036 mmol, 21% yield).

Each TFA ester was transferred into a separate vial, and a mixture of pyridine: MeOH = 1: 5 (0.1 M) was added. The mixture was stirred for 3 hours at room temperature. Each reaction mixture was concentrated in vacuo and purified by column chromatography (acetone: hexane = 1: 4), resulting in the completed separated 3-alcohol (8.6 mg, 0.047 mmol, 81% yield) as a clear oil and 4-alcohol (5 mg, 0.027 mmol, 75% yield) as a white solid.

8-hydroxyspiro[5.5]undecan-3-one [9-C3OH]. ^1H NMR (600 MHz, CDCl_3) δ 3.79 (tt, $J = 10.3$,

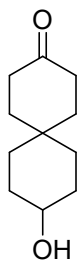


4.3 Hz, 1H), 2.37 (t, $J = 7.0$ Hz, 2H), 2.36 – 2.25 (m, 2H), 2.07 – 1.94 (m, 2H), 1.86 – 1.62 (m, 7H), 1.46 (qt, $J = 12.9$, 3.4 Hz, 1H), 1.27 – 1.14 (m, 3H). ^{13}C NMR (151

MHz, CDCl_3) δ 212.36, 67.41, 44.72, 40.61, 37.57, 37.19, 36.19, 34.74, 34.22, 32.74,

20.35. HRMS (TOF ESI+) m/z calculated for $\text{C}_{11}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 183.1385, found 183.1389.

9-hydroxyspiro[5.5]undecan-3-one [9-C4OH]. ^1H NMR (600 MHz, CDCl_3) δ 3.73 (tt, $J = 9.0$,



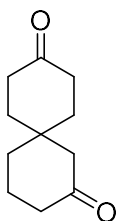
4.1 Hz, 1H), 2.33 (app dt, $J = 13.0$, 6.9 Hz, 4H), 1.86 – 1.73 (m, 6H), 1.66 (t, $J = 6.9$ Hz, 2H), 1.53 – 1.44 (m, 3H), 1.36 – 1.30 (m, 2H). ^{13}C NMR (151 MHz, CD_3CN) δ 212.63,

70.20, 38.15, 37.68, 37.23, 33.36, 32.83, 31.62, 30.71. HRMS (TOF ESI+) m/z calculated

for $\text{C}_{11}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 183.1385, found 183.1389.

Preparation of ketone authentic samples. The 4-ketone and 3-ketone isomers were prepared by Dess-Martin Periodinane (DMP) oxidation (DMP 1.5 equiv. in DCM (0.1M)) of the obtained alcohol products.

spiro[5.5]undecane-2,9-dione [9-C3ketone]. ^1H NMR (600 MHz, CDCl_3) δ 2.43 – 2.28 (m, 8H),

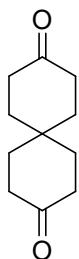


1.93 (p, $J = 6.5$ Hz, 2H), 1.82 (dd, $J = 7.7$, 4.6 Hz, 2H), 1.74 (t, $J = 6.8$ Hz, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 210.93, 210.81, 51.40, 41.28, 38.03, 37.07, 36.07, 34.42,

22.06. HRMS (TOF EI+) m/z calculated for $\text{C}_{11}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 180.1150, found

180.1145.

spiro[5.5]undecane-3,9-dione [9-C4ketone]. ^1H NMR (600 MHz, CDCl_3) δ 2.39 (t, J = 6.9 Hz,

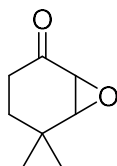


8H), 1.88 (t, J = 6.9 Hz, 8H). ^{13}C NMR (151 MHz, CDCl_3) δ 211.31, 37.44, 35.07, 31.78.

HRMS (TOF EI+) m/z calculated for $\text{C}_{11}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 180.1150, found 180.1145.

Calibration Curves

Epoxide 10. Samples were prepared through serial dilution of the epoxide **10** solution in ether and



mixing it with an internal standard (IS, nitrobenzene) solution at a constant concentration.

amount (mg)		amount (mmol)		peak area (%)		compound/IS peak area ratio	compound/IS mol ratio
IS	10	IS	10	IS	10	0	0
0.5	0.01	0.0040614	0.0000713	89.89667	1.97424	0.021961214	0.017564309
0.5	0.02	0.0040614	0.0001427	88.44471	4.15586	0.046988226	0.035128619
0.5	0.04	0.0040614	0.0002853	83.73182	7.45288	0.089008934	0.070257237
0.5	0.08	0.0040614	0.0005707	78.29738	13.00741	0.166128292	0.140514474
0.5	0.16	0.0040614	0.0011414	70.90603	22.87715	0.322640402	0.281028948
0.5	0.32	0.0040614	0.0022827	58.205	36.66345	0.62990207	0.562057896
0.5	0.64	0.0040614	0.0045655	46.30789	53.69211	1.15945922	1.124115792
0.5	1.28	0.0040614	0.0091310	28.60368	71.39632	2.496053655	2.248231585

Table S3. Gas Chromatography Calibration Data for Compound **10**

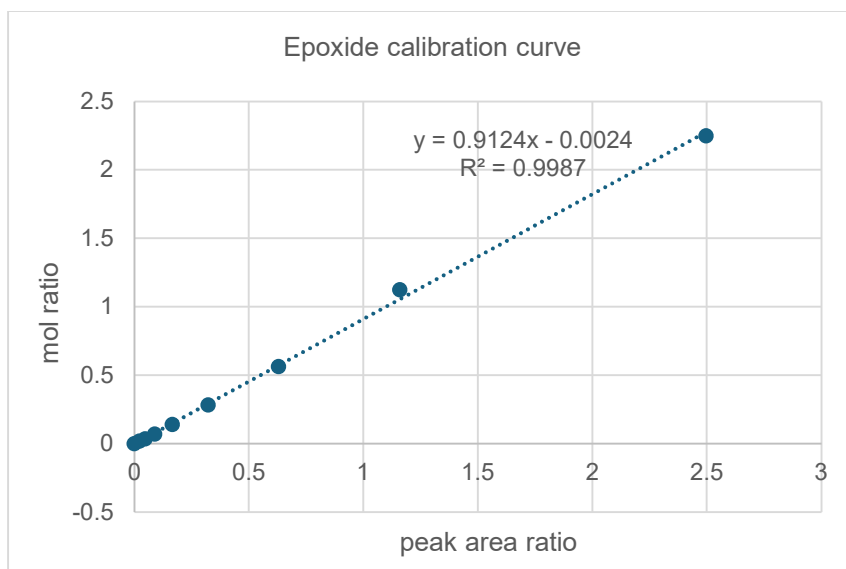
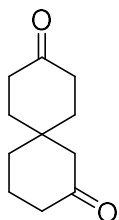


Figure S6. Calibration Curve for Compound **10**

3-ketone [9-C3ketone]. Samples were prepared through serial dilution of the 3-ketone **9-C3ketone** solution in ether and mixing it with an internal standard (IS, nitrobenzene) solution at a constant concentration.



amount (mg)		amount (mmol)		peak area(%)		compound/IS peak area ratio	compound/IS mol ratio
IS	9-C3ketone	IS	9-C3ketone	IS	9-C3ketone	0	0
0.5	0.01	0.0040614	0.0000555	97.71153	2.28847	0.023420675	0.01366
0.5	0.02	0.0040614	0.0001110	95.69359	4.30641	0.045002074	0.02732
0.5	0.04	0.0040614	0.0002219	92.15039	7.84961	0.085182602	0.054641
0.5	0.08	0.0040614	0.0004438	85.37136	14.62864	0.171353016	0.109281
0.5	0.16	0.0040614	0.0008877	75.56188	24.43812	0.323418634	0.218562
0.5	0.32	0.0040614	0.0017753	62.27006	37.72994	0.605908201	0.437125
0.5	0.64	0.0040614	0.0035507	44.28948	55.71052	1.257872524	0.874249
0.5	1.28	0.0040614	0.0071014	27.30807	72.69193	2.661921183	1.748498

Table S4. Gas Chromatography Calibration Data for Compound **9-C3ketone**

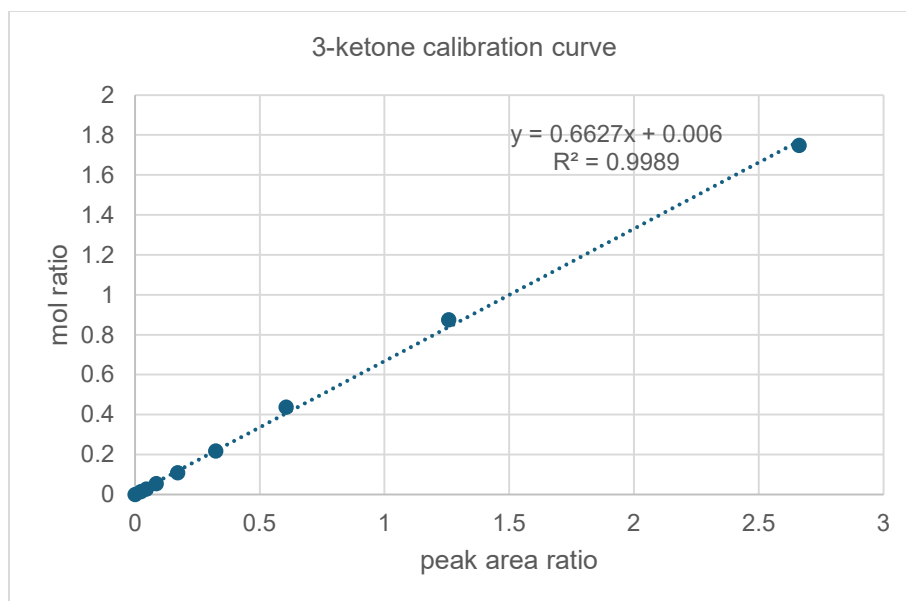
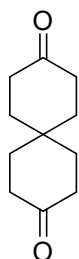


Figure S7. Calibration Curve for Compound **9-C3ketone**

4-ketone [9-C4ketone]. Samples were prepared through serial dilution of the 4-ketone **9-**



C4ketone solution in ether and mixing it with an internal standard (IS, nitrobenzene) solution at a constant concentration.

amount(mg)		amount(mmol)		peak area(%)		compound/IS peak area ratio	compound/IS mol ratio
IS	9-C4ketone	IS	9-C4ketone	IS	9-C4ketone	0	0
0.5	0.01	0.0040614	0.0000555	97.77903	2.22097	0.02271418	0.01366014
0.5	0.02	0.0040614	0.0001110	95.56949	4.43051	0.04635904	0.02732029
0.5	0.04	0.0040614	0.0002219	91.79844	8.20156	0.08934313	0.05464058
0.5	0.08	0.0040614	0.0004438	85.41464	14.58536	0.17075949	0.10928115
0.5	0.16	0.0040614	0.0008877	74.26839	25.73161	0.34646786	0.21856231
0.5	0.32	0.0040614	0.0017753	59.47425	40.52575	0.68139993	0.43712461
0.5	0.64	0.0040614	0.0035507	44.20818	55.79182	1.26202481	0.87424922
0.5	1.28	0.0040614	0.0071014	27.04159	72.95841	2.6980074	1.74849845

Table S5. Gas Chromatography Calibration Data for Compound **9-C4ketone**

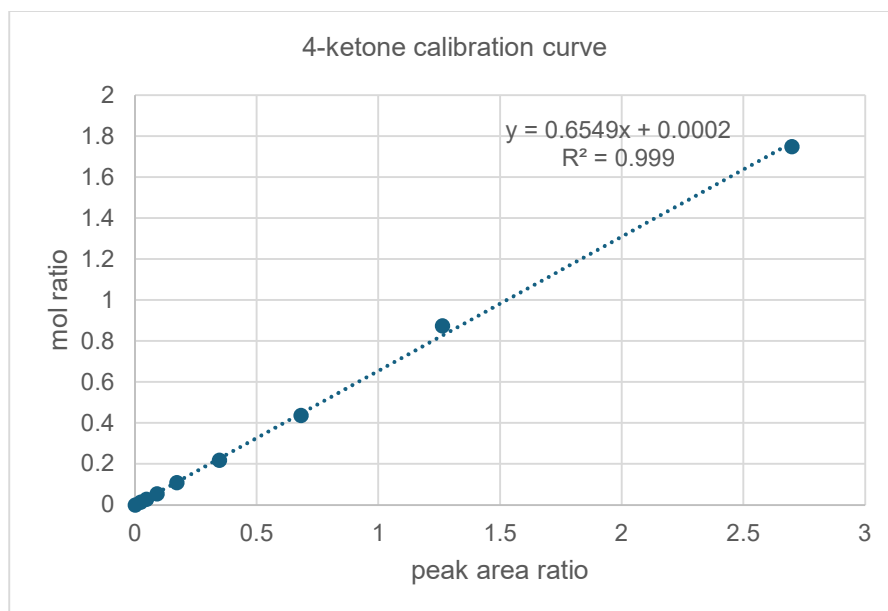
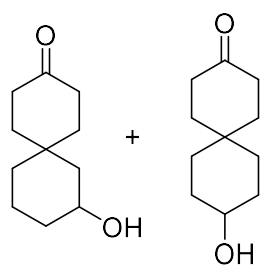


Figure S8. Calibration Curve for Compound **9-C4ketone**

3- and 4-alcohol [9-OH]. Samples were prepared through serial dilution of the 3- and 4-alcohol



9-OH solution in ether and mixing it with an internal standard (IS, nitrobenzene) solution at a constant concentration. Due to incomplete separation in GC, the alcohol isomers were not analyzed separately, unlike the ketone isomers. Separate calculations indicated that the response factors

for each alcohol were very similar (0.6294 for 3-alcohol and 0.6368 for 4-alcohol), allowing combined analysis without affecting the calculation outcome.

amount (mg)		amount (mmol)		3-alcohol peak area (%)		4-alcohol peak area (%)		compound/IS peak area ratio	compound/IS mol ratio
IS	9-OH	IS	9-OH	IS	9-OH	IS	9-OH	0	0
0.5	0.01	0.0040614	0.0000549	99.08498	0.91502	99.33494	0.66506	0.00796491	0.01350905
0.5	0.02	0.0040614	0.0001097	97.18282	2.81718	98.04068	1.95932	0.02448661	0.0270181
0.5	0.04	0.0040614	0.0002195	93.8402	6.1598	94.10805	5.89195	0.06412487	0.0540362
0.5	0.08	0.0040614	0.0004389	86.7704	13.2296	88.63449	11.36551	0.14034786	0.108072401
0.5	0.16	0.0040614	0.0008779	75.12895	24.87105	77.66071	22.33929	0.30934861	0.216144802
0.5	0.32	0.0040614	0.0017557	59.2897	40.7103	63.00978	36.99022	0.63684441	0.432289603
0.5	0.64	0.0040614	0.0035114	42.52289	57.47711	45.84391	54.15609	1.2664947	0.864579207
0.5	1.28	0.0040614	0.0070228	26.75674	73.24326	26.75069	73.24931	2.7377987	1.729158414

Table S6. Gas Chromatography Calibration Data for Compound **9-OH**

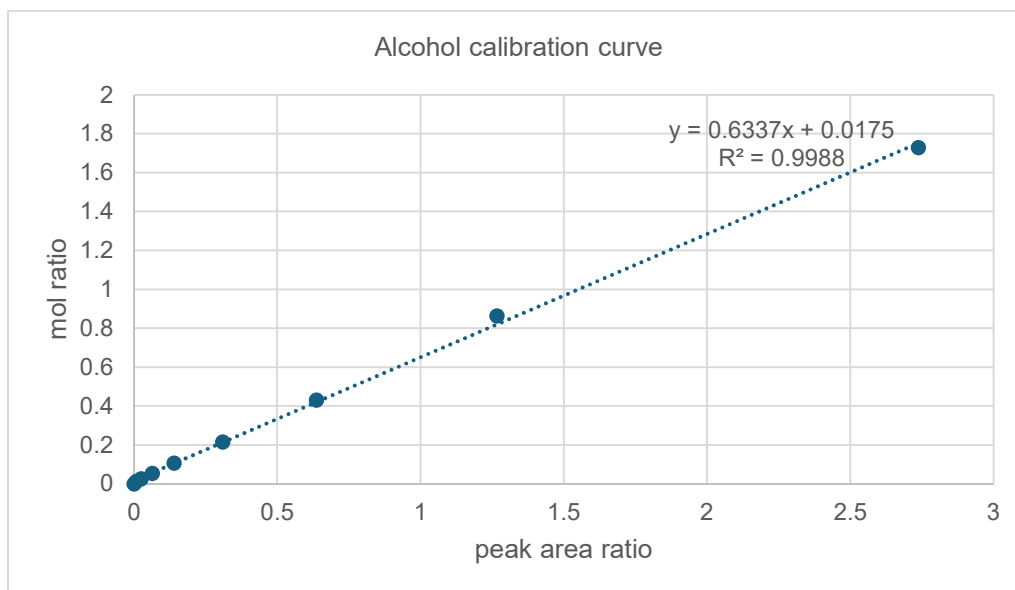


Figure S9. Calibration Curve for Compound **9-OH**

Concentration-Time Plots and Observed Rates

The initial point t_0 was defined as the time at which the first drop of oxidant solution was added to the reaction mixture. Each experiment was carried out in triplicate, and concentrations of **9** (C—H oxidation products) and **10** (epoxidation products) were determined using GC at each time point based on standard curve measurements and were averaged before plotting. Observed rates were determined from the slopes of the early phase ($t_0 - t_{1440}$) concentration-time plots for C—H oxidation and epoxidation, respectively. For catalyst **2**, a non-linear kinetic profile was observed during the initial phase. In this case, the observed rate was determined based on the subsequent linear region, ensuring that the same time frame was used for both C—H oxidation and epoxidation.

1) Catalyst **1** in MeCN with Cl-AcOH (Table S2, entry 1)

time (sec)	1st run				2nd run				3rd run			
	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)
0	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000
90	0.2925	0.2836	0.0040	0.0065	0.2894	0.2838	0.0037	0.0088	0.2935	0.2859	0.0040	0.0133
180	0.2887	0.2740	0.0068	0.0116	0.2832	0.2732	0.0068	0.0140	0.2887	0.2774	0.0069	0.0182
270	0.2820	0.2640	0.0098	0.0159	0.2783	0.2631	0.0097	0.0167	0.2832	0.2668	0.0097	0.0253
360	0.2781	0.2523	0.0131	0.0228	0.2732	0.2535	0.0125	0.0249	0.2753	0.2523	0.0145	0.0314
540	0.2651	0.2322	0.0195	0.0337	0.2612	0.2307	0.0200	0.0397	0.2653	0.2347	0.0203	0.0424
720	0.2559	0.2144	0.0254	0.0432	0.2502	0.2131	0.0260	0.0496	0.2556	0.2162	0.0263	0.0468
900	0.2460	0.1974	0.0313	0.0520	0.2411	0.1970	0.0316	0.0556	0.2414	0.1936	0.0346	0.0610
1080	0.2346	0.1820	0.0368	0.0609	0.2284	0.1780	0.0392	0.0639	0.2324	0.1761	0.0407	0.0705
1260	0.2216	0.1618	0.0447	0.0707	0.2187	0.1618	0.0450	0.0725	0.2220	0.1632	0.0466	0.0797
1440	0.2114	0.1464	0.0506	0.0788	0.2070	0.1459	0.0519	0.0820	0.2077	0.1426	0.0546	0.0836
1620	0.2017	0.1331	0.0563	0.0833	0.1975	0.1312	0.0583	0.0883	0.1984	0.1279	0.0606	0.0917
1800	0.1922	0.1205	0.0620	0.0899	0.1880	0.1193	0.0631	0.0925	0.1873	0.1155	0.0660	0.0967
2700	0.1440	0.0662	0.0888	0.1126	0.1406	0.0653	0.0913	0.1161	0.1375	0.0605	0.0960	0.1227
3600	0.1099	0.0369	0.1082	0.1180	0.1013	0.0323	0.1139	0.1233	0.0985	0.0296	0.1171	0.1290

Table S7. Concentration-time Data for Catalyst **1**/MeCN/Cl-AcOH Condition

time (sec)	epxRSM_avg (M)	epxRSM_std (M)	C_H[O]RSM_avg (M)	C_H[O]RSM_std (M)	epoxide_avg (M)	epoxide_std (M)	C_H[O]_avg (M)	C_H[O]_std (M)
0	0.3000	0.0000	0.3000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.2918	0.0017	0.2844	0.0010	0.0039	0.0001	0.0095	0.0028
180	0.2868	0.0026	0.2749	0.0018	0.0068	0.0000	0.0146	0.0028
270	0.2812	0.0021	0.2646	0.0016	0.0097	0.0000	0.0193	0.0042
360	0.2755	0.0020	0.2527	0.0006	0.0133	0.0008	0.0263	0.0037
540	0.2639	0.0019	0.2325	0.0016	0.0199	0.0004	0.0386	0.0037
720	0.2539	0.0026	0.2146	0.0013	0.0259	0.0004	0.0465	0.0026
900	0.2429	0.0022	0.1960	0.0017	0.0325	0.0015	0.0562	0.0037
1080	0.2318	0.0025	0.1787	0.0025	0.0389	0.0016	0.0651	0.0040
1260	0.2208	0.0015	0.1623	0.0007	0.0454	0.0008	0.0743	0.0039
1440	0.2087	0.0019	0.1450	0.0017	0.0524	0.0017	0.0814	0.0020
1620	0.1992	0.0018	0.1307	0.0021	0.0584	0.0017	0.0878	0.0035
1800	0.1892	0.0022	0.1184	0.0021	0.0637	0.0017	0.0931	0.0028
2700	0.1407	0.0027	0.0640	0.0025	0.0921	0.0030	0.1171	0.0042
3600	0.1032	0.0049	0.0329	0.0030	0.1131	0.0037	0.1234	0.0045

Table S8. Averaged Concentration-time Data for Catalyst **1**/MeCN/Cl-AcOH Condition

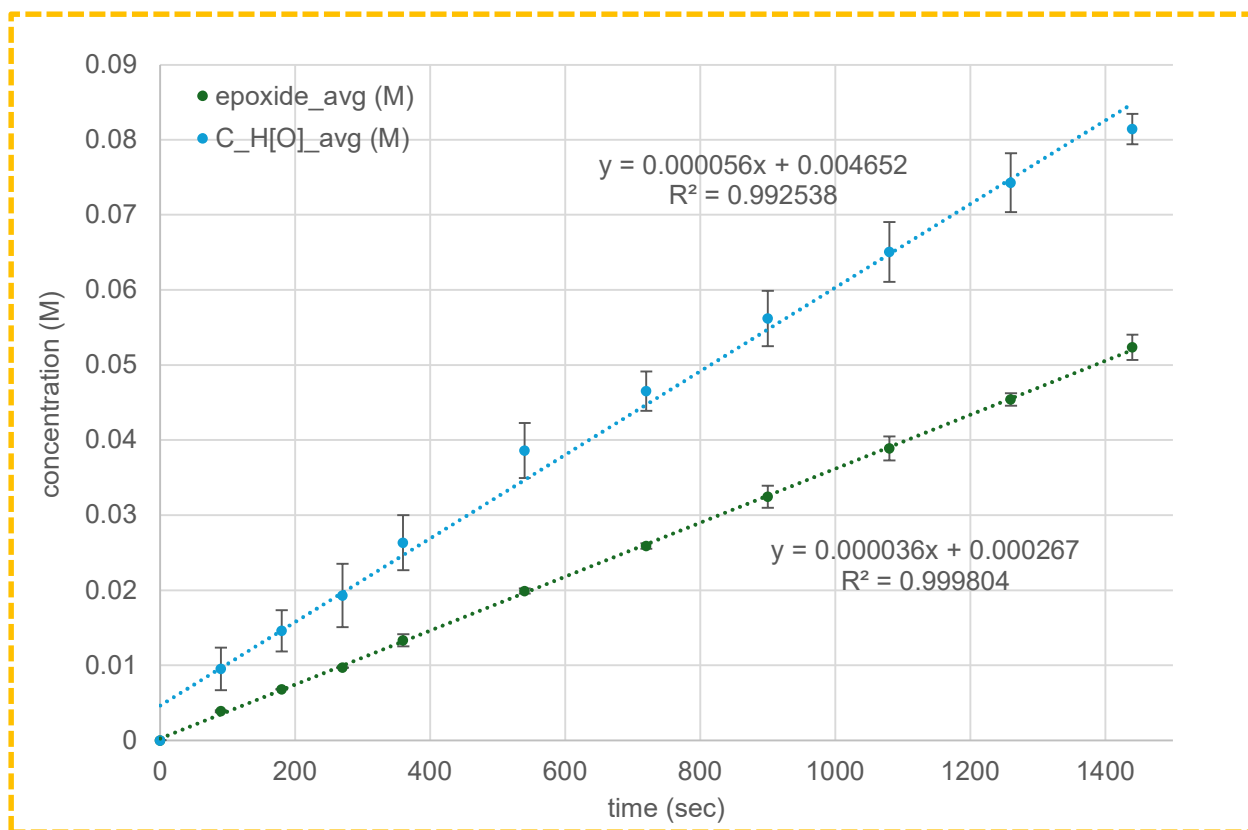
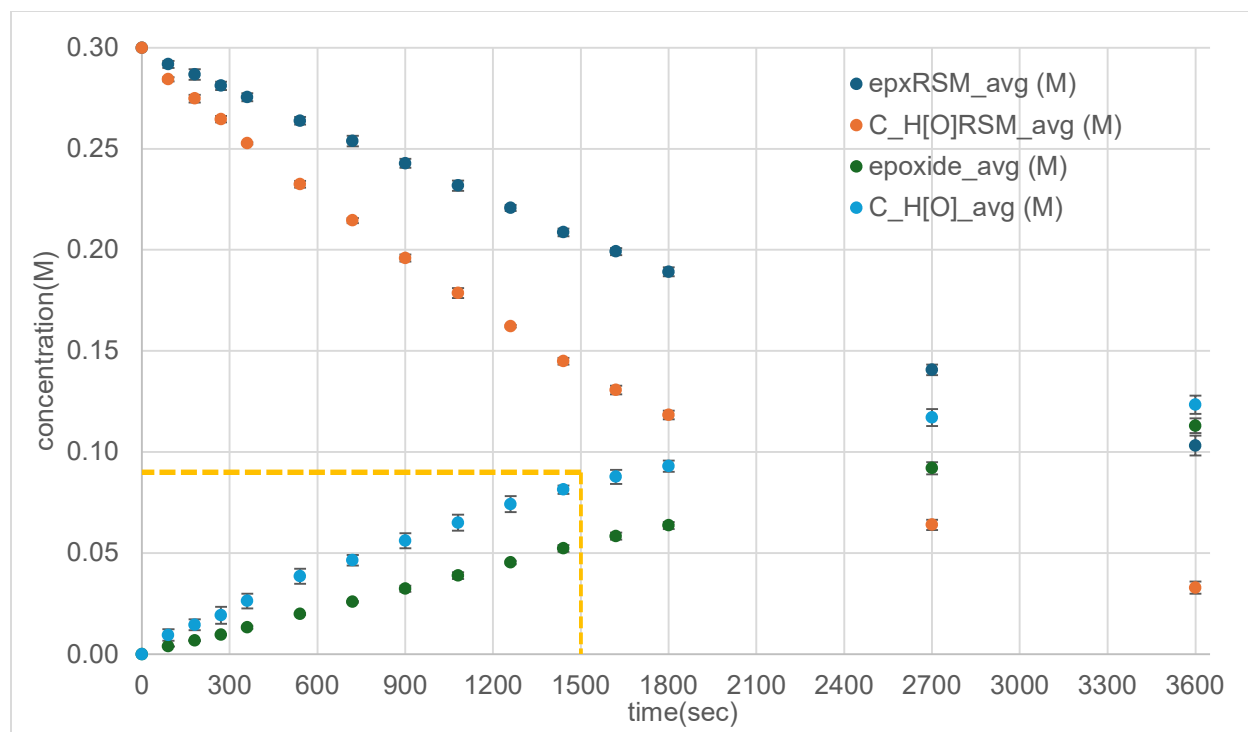


Figure S10. Concentration-time Plot for Catalyst 1/MeCN/Cl-AcOH Condition.

2) Catalyst **1** in MeCN without acid (**Table S2**, entry 2)

time (sec)	1st run				2nd run				3rd run			
	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)
0	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000
90	0.2968	0.2918	0.0010	0.0043	0.2913	0.2874	0.0020	0.0023	0.2957	0.2930	0.0015	0.0037
180	0.2943	0.2873	0.0018	0.0060	0.2874	0.2811	0.0029	0.0045	0.2931	0.2874	0.0023	0.0044
270	0.2917	0.2826	0.0026	0.0070	0.2836	0.2753	0.0036	0.0063	0.2910	0.2828	0.0031	0.0052
360	0.2889	0.2784	0.0034	0.0076	0.2806	0.2692	0.0045	0.0066	0.2887	0.2784	0.0038	0.0065
540	0.2835	0.2677	0.0053	0.0113	0.2748	0.2559	0.0068	0.0089	0.2830	0.2669	0.0056	0.0094
720	0.2788	0.2613	0.0064	0.0128	0.2697	0.2465	0.0082	0.0145	0.2781	0.2597	0.0067	0.0122
900	0.2736	0.2501	0.0083	0.0159	0.2634	0.2374	0.0103	0.0148	0.2741	0.2513	0.0081	0.0148
1080	0.2690	0.2442	0.0096	0.0193	0.2579	0.2292	0.0118	0.0182	0.2682	0.2414	0.0098	0.0170
1260	0.2638	0.2337	0.0111	0.0208	0.2529	0.2191	0.0134	0.0243	0.2632	0.2323	0.0112	0.0197
1440	0.2586	0.2243	0.0124	0.0237	0.2484	0.2109	0.0149	0.0262	0.2581	0.2236	0.0124	0.0230
1620	0.2540	0.2171	0.0136	0.0271	0.2441	0.2046	0.0159	0.0284	0.2534	0.2162	0.0137	0.0253
1800	0.2500	0.2098	0.0149	0.0303	0.2398	0.1984	0.0168	0.0324	0.2494	0.2091	0.0143	0.0286
2700	0.2337	0.1791	0.0170	0.0445	0.2241	0.1688	0.0190	0.0467	0.2330	0.1793	0.0165	0.0426
3600	0.2218	0.1628	0.0170	0.0495	0.2131	0.1546	0.0187	0.0476	0.2213	0.1611	0.0168	0.0472

Table S9. Concentration-time Data for Catalyst **1**/MeCN/no acid Condition

time (sec)	epxRSM_avg (M)	epxRSM_std (M)	C_H[O]RSM_avg (M)	C_H[O]RSM_std (M)	epoxide_avg (M)	epoxide_std (M)	C_H[O]_avg (M)	C_H[O]_std (M)
0	0.3000	0.0000	0.3000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.2946	0.0024	0.2907	0.0024	0.0015	0.0004	0.0035	0.0008
180	0.2916	0.0030	0.2853	0.0029	0.0023	0.0004	0.0050	0.0007
270	0.2888	0.0037	0.2802	0.0035	0.0031	0.0004	0.0062	0.0007
360	0.2861	0.0039	0.2753	0.0043	0.0039	0.0005	0.0069	0.0005
540	0.2804	0.0040	0.2635	0.0054	0.0059	0.0006	0.0099	0.0010
720	0.2755	0.0042	0.2559	0.0066	0.0071	0.0008	0.0132	0.0009
900	0.2704	0.0049	0.2463	0.0063	0.0089	0.0010	0.0152	0.0005
1080	0.2650	0.0050	0.2383	0.0065	0.0104	0.0010	0.0182	0.0010
1260	0.2600	0.0050	0.2284	0.0066	0.0119	0.0010	0.0216	0.0020
1440	0.2550	0.0047	0.2196	0.0061	0.0133	0.0012	0.0243	0.0014
1620	0.2505	0.0045	0.2126	0.0057	0.0144	0.0010	0.0270	0.0013
1800	0.2464	0.0047	0.2058	0.0052	0.0154	0.0011	0.0304	0.0015
2700	0.2302	0.0044	0.1757	0.0049	0.0175	0.0011	0.0446	0.0017
3600	0.2187	0.0040	0.1595	0.0035	0.0175	0.0009	0.0481	0.0010

Table S10. Averaged Concentration-time Data for Catalyst **1**/MeCN/no acid Condition

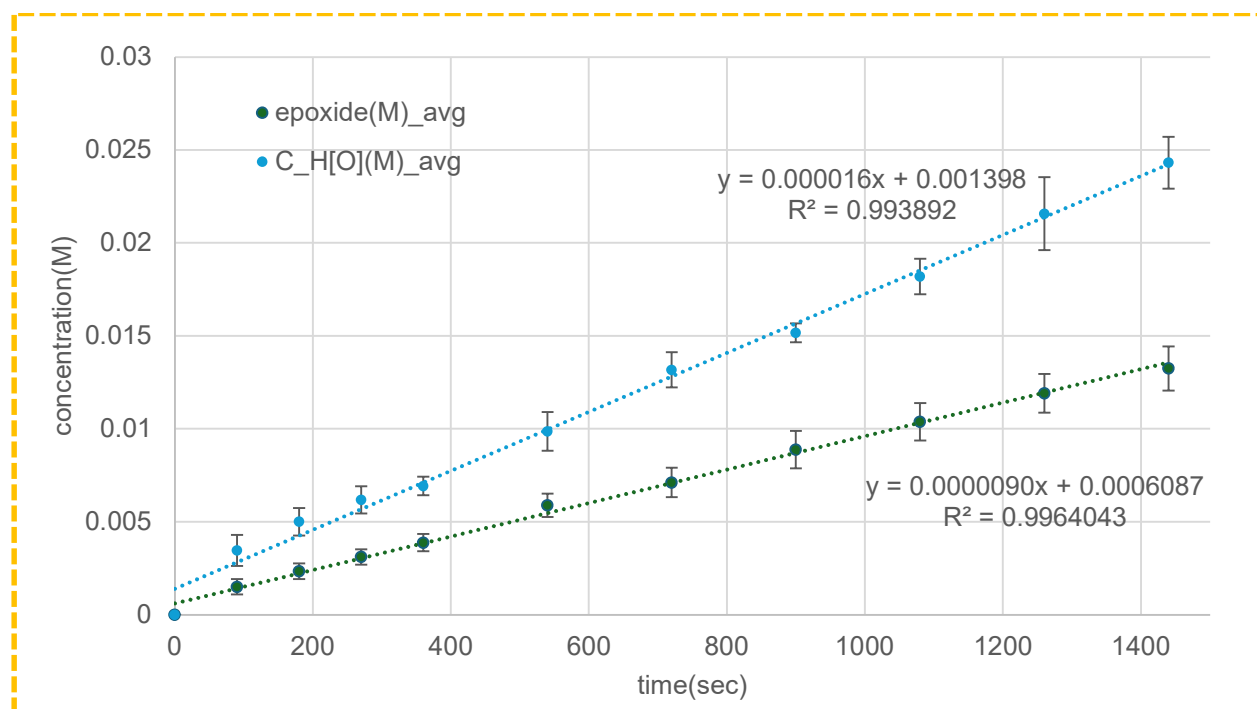
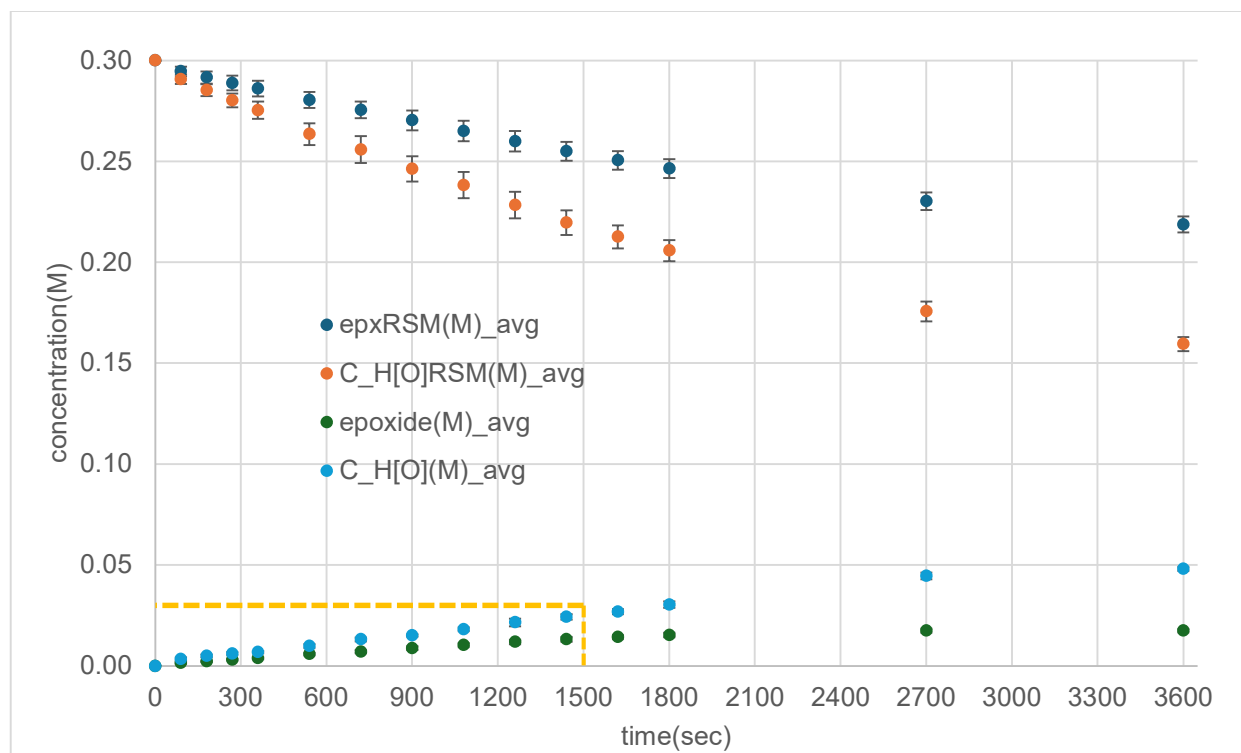


Figure S11. Concentration-time Plot for Catalyst 1/MeCN/no acid Condition

3) Catalyst **1** in HFIP without acid (Table S2, entry 3)

time (sec)	1st run				2nd run				3rd run			
	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)
0	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000
90	0.2975	0.2920	0.0001	0.0064	0.2983	0.2950	0.0001	0.0079	0.2980	0.2935	0.0001	0.0054
180	0.2957	0.2781	0.0002	0.0135	0.2964	0.2820	0.0001	0.0128	0.2964	0.2765	0.0002	0.0130
270	0.2944	0.2633	0.0002	0.0237	0.2950	0.2673	0.0001	0.0188	0.2955	0.2635	0.0002	0.0227
360	0.2928	0.2439	0.0005	0.0328	0.2938	0.2486	0.0003	0.0292	0.2933	0.2423	0.0004	0.0344
540	0.2891	0.2075	0.0011	0.0537	0.2902	0.2089	0.0008	0.0570	0.2899	0.2059	0.0010	0.0583
720	0.2851	0.1764	0.0018	0.0725	0.2862	0.1718	0.0016	0.0780	0.2856	0.1685	0.0018	0.0789
900	0.2816	0.1483	0.0024	0.0892	0.2822	0.1454	0.0021	0.0941	0.2826	0.1413	0.0023	0.0984
1080	0.2783	0.1182	0.0029	0.1099	0.2792	0.1186	0.0026	0.1119	0.2794	0.1134	0.0027	0.1161
1260	0.2752	0.0943	0.0033	0.1245	0.2759	0.0920	0.0030	0.1256	0.2762	0.0883	0.0031	0.1324
1440	0.2718	0.0739	0.0038	0.1298	0.2727	0.0696	0.0034	0.1447	0.2726	0.0682	0.0036	0.1495
1620	0.2678	0.0555	0.0042	0.1447	0.2695	0.0505	0.0040	0.1509	0.2696	0.0477	0.0043	0.1596
1800	0.2647	0.0382	0.0050	0.1556	0.2659	0.0355	0.0045	0.1578	0.2662	0.0327	0.0048	0.1678
2700	0.2460	0.0037	0.0099	0.1600	0.2473	0.0032	0.0095	0.1693	0.2461	0.0030	0.0103	0.1717
3600	0.2258	0.0003	0.0165	0.1485	0.2273	0.0002	0.0160	0.1552	0.2260	0.0002	0.0171	0.1571

Table S11. Concentration-time Data for Catalyst **1**/HFIP/no acid Condition

time (sec)	epxRSM_avg (M)	epxRSM_std (M)	C_H[O]RSM_avg (M)	C_H[O]RSM_std (M)	epoxide_avg (M)	epoxide_std (M)	C_H[O]_avg (M)	C_H[O]_std (M)
0	0.3000	0.0000	0.3000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.2980	0.0003	0.2935	0.0012	0.0001	0.0000	0.0065	0.0010
180	0.2962	0.0003	0.2789	0.0023	0.0001	0.0000	0.0131	0.0003
270	0.2949	0.0004	0.2647	0.0018	0.0002	0.0000	0.0217	0.0021
360	0.2933	0.0004	0.2449	0.0027	0.0004	0.0001	0.0321	0.0022
540	0.2897	0.0005	0.2074	0.0012	0.0010	0.0001	0.0563	0.0019
720	0.2856	0.0005	0.1722	0.0033	0.0017	0.0001	0.0764	0.0028
900	0.2821	0.0004	0.1450	0.0029	0.0023	0.0001	0.0939	0.0038
1080	0.2790	0.0005	0.1167	0.0024	0.0027	0.0001	0.1126	0.0026
1260	0.2758	0.0004	0.0915	0.0025	0.0031	0.0001	0.1275	0.0035
1440	0.2724	0.0004	0.0706	0.0024	0.0036	0.0002	0.1414	0.0084
1620	0.2690	0.0009	0.0512	0.0032	0.0041	0.0001	0.1517	0.0061
1800	0.2656	0.0006	0.0355	0.0023	0.0048	0.0002	0.1604	0.0053
2700	0.2465	0.0006	0.0033	0.0003	0.0099	0.0003	0.1670	0.0050
3600	0.2264	0.0006	0.0002	0.0000	0.0165	0.0004	0.1536	0.0037

Table S12. Averaged Concentration-time Data for Catalyst **1**/HFIP/no acid Condition

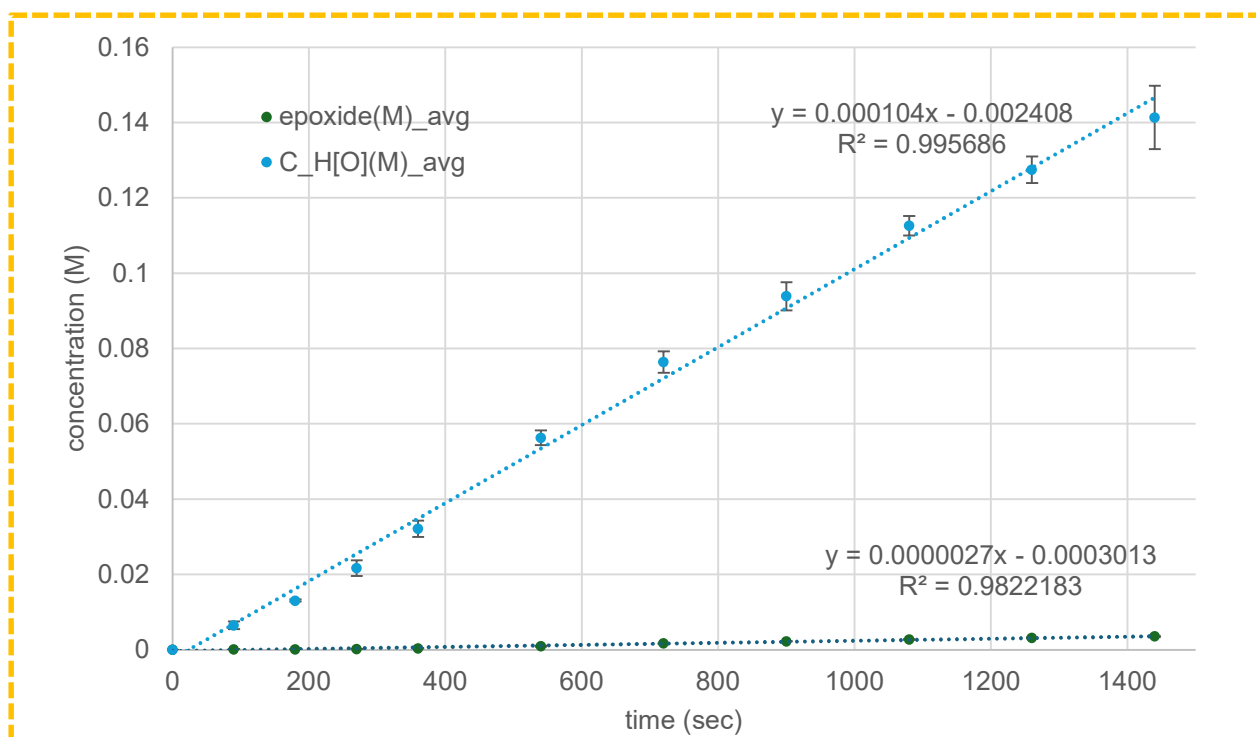
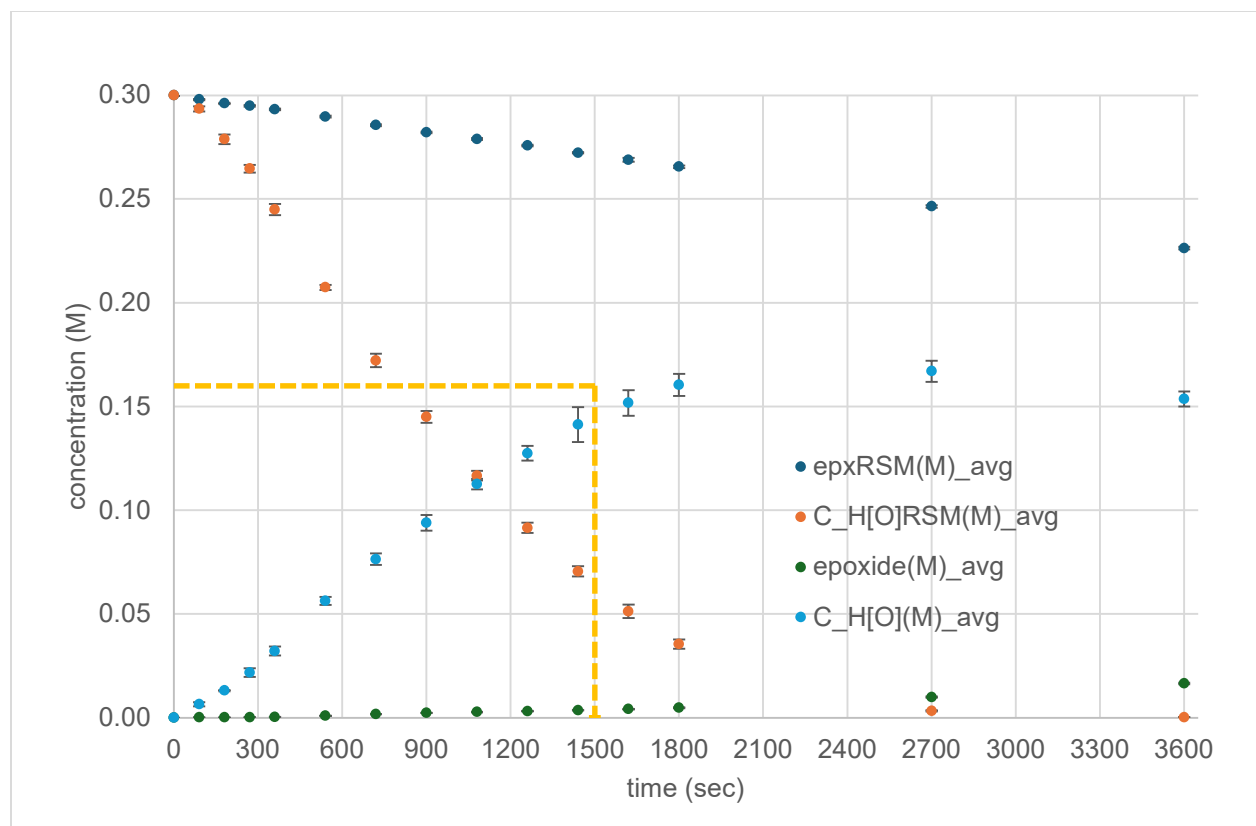


Figure S12. Concentration-time Plot for Catalyst 1/HFIP/no acid Condition

4) Catalyst **1** in HFIP with Cl-AcOH (Table S2, entry 4)

time (sec)	1st run				2nd run				3rd run			
	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)
0	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000
90	0.2959	0.2852	0.0002	0.0059	0.2978	0.2764	0.0006	0.0106	0.2994	0.2885	0.0001	0.0101
180	0.2932	0.2686	0.0006	0.0121	0.2958	0.2647	0.0010	0.0183	0.2962	0.2739	0.0005	0.0180
270	0.2911	0.2519	0.0012	0.0198	0.2940	0.2510	0.0016	0.0244	0.2952	0.2560	0.0011	0.0281
360	0.2885	0.2345	0.0020	0.0286	0.2918	0.2363	0.0022	0.0323	0.2921	0.2411	0.0017	0.0323
540	0.2842	0.2006	0.0036	0.0532	0.2861	0.2020	0.0038	0.0499	0.2872	0.2089	0.0031	0.0586
720	0.2789	0.1747	0.0049	0.0657	0.2813	0.1690	0.0057	0.0683	0.2827	0.1780	0.0047	0.0744
900	0.2733	0.1469	0.0068	0.0836	0.2755	0.1431	0.0074	0.0901	0.2774	0.1506	0.0065	0.0936
1080	0.2689	0.1199	0.0091	0.1020	0.2697	0.1096	0.0103	0.1115	0.2729	0.1262	0.0085	0.1117
1260	0.2624	0.0922	0.0121	0.1174	0.2652	0.0924	0.0124	0.1138	0.2674	0.1025	0.0108	0.1250
1440	0.2565	0.0725	0.0146	0.1315	0.2581	0.0726	0.0149	0.1334	0.2622	0.0827	0.0132	0.1379
1620	0.2491	0.0545	0.0177	0.1396	0.2525	0.0576	0.0176	0.1522	0.2558	0.0667	0.0158	0.1479
1800	0.2443	0.0414	0.0211	0.1402	0.2451	0.0416	0.0214	0.1532	0.2511	0.0507	0.0182	0.1536
2700	0.2143	0.0106	0.0361	0.1493	0.2091	0.0076	0.0408	0.1654	0.2220	0.0141	0.0326	0.1596
3600	0.1877	0.0032	0.0482	0.1389	0.1793	0.0017	0.0557	0.1450	0.1945	0.0038	0.0461	0.1418

Table S13. Concentration-time Data for Catalyst **1**/HFIP/Cl-AcOH Condition

time (sec)	epxRSM_avg (M)	epxRSM_std (M)	C_H[O]RSM_avg (M)	C_H[O]RSM_std (M)	epoxide_avg (M)	epoxide_std (M)	C_H[O]_avg (M)	C_H[O]_std (M)
0	0.3000	0.0000	0.3000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.2977	0.0014	0.2834	0.0051	0.0003	0.0002	0.0088	0.0021
180	0.2951	0.0014	0.2691	0.0038	0.0007	0.0002	0.0162	0.0029
270	0.2934	0.0017	0.2530	0.0022	0.0013	0.0002	0.0241	0.0034
360	0.2908	0.0016	0.2373	0.0028	0.0020	0.0002	0.0311	0.0018
540	0.2858	0.0013	0.2038	0.0036	0.0035	0.0003	0.0539	0.0036
720	0.2810	0.0016	0.1739	0.0037	0.0051	0.0004	0.0695	0.0037
900	0.2754	0.0017	0.1469	0.0031	0.0069	0.0004	0.0891	0.0042
1080	0.2705	0.0017	0.1186	0.0069	0.0093	0.0007	0.1084	0.0045
1260	0.2650	0.0021	0.0957	0.0048	0.0118	0.0007	0.1187	0.0047
1440	0.2589	0.0024	0.0759	0.0048	0.0142	0.0008	0.1343	0.0027
1620	0.2525	0.0028	0.0596	0.0052	0.0170	0.0009	0.1466	0.0052
1800	0.2468	0.0030	0.0446	0.0044	0.0202	0.0014	0.1490	0.0063
2700	0.2152	0.0053	0.0108	0.0026	0.0365	0.0033	0.1581	0.0067
3600	0.1871	0.0062	0.0029	0.0009	0.0500	0.0041	0.1419	0.0025

Table S14. Averaged Concentration-time Data for Catalyst **1**/HFIP/Cl-AcOH Condition

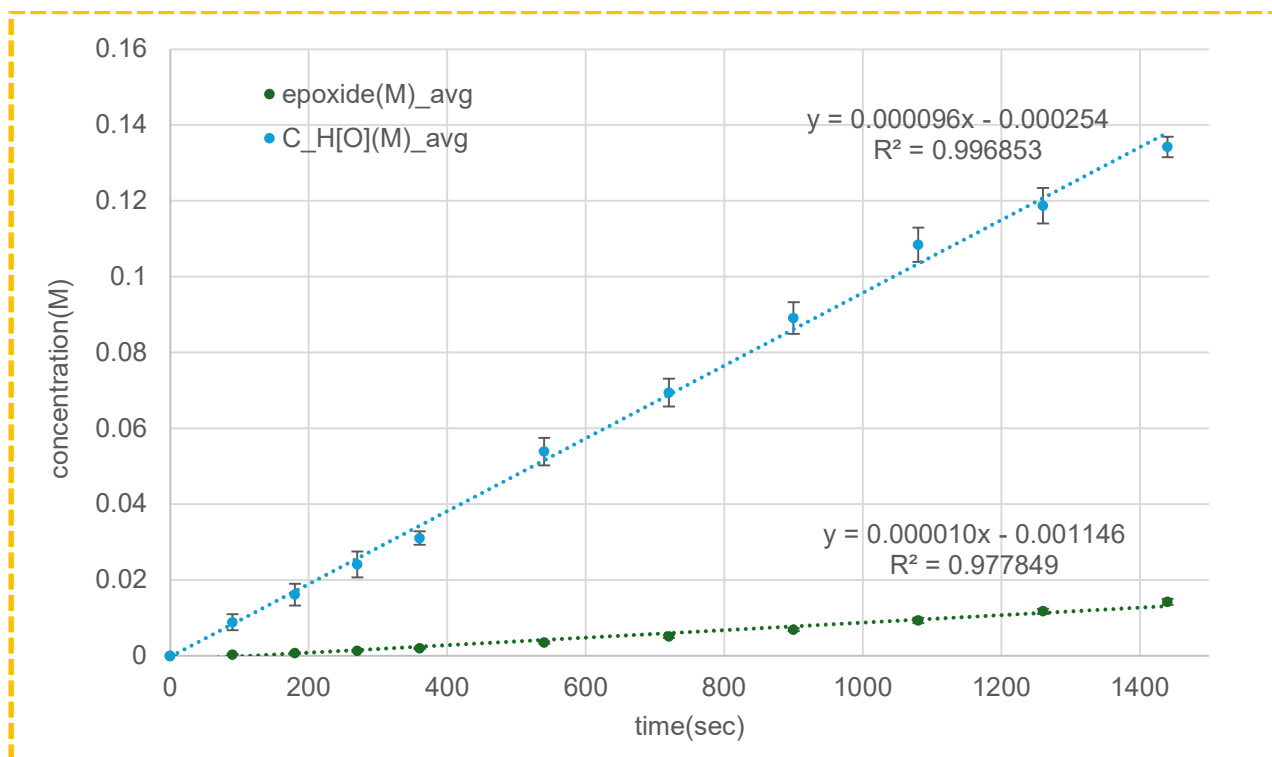
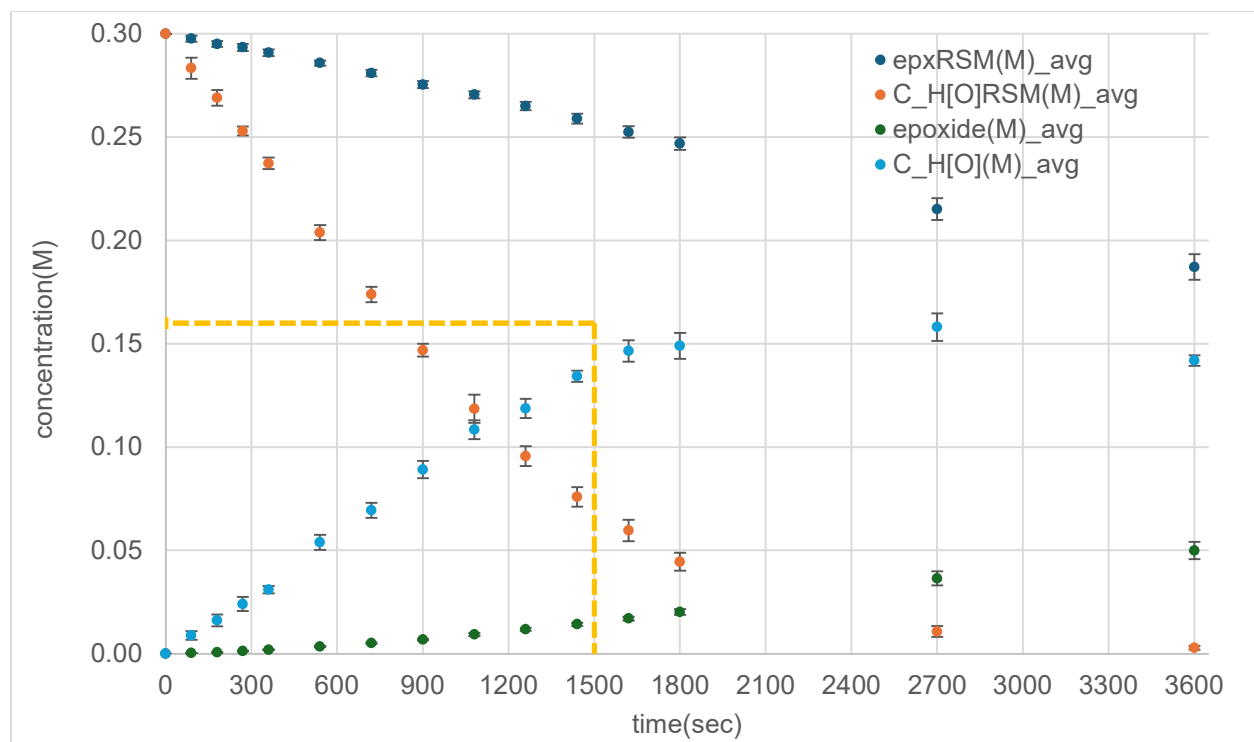


Figure S13. Concentration-time Plot for Catalyst 1/HFIP/Cl-AcOH Condition

5) Catalyst **2** in MeCN with Cl-AcOH (Table S2, entry 5)

time (sec)	1st run				2nd run				3rd run			
	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)
0	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000
90	0.2994	0.2999	0.0000	0.0055	0.2879	0.2967	0.0005	0.0101	0.3028	0.3042	0.0000	0.0074
180	0.2990	0.2977	0.0000	0.0062	0.2997	0.2974	0.0006	0.0094	0.2983	0.2946	0.0000	0.0067
270	0.2951	0.2856	0.0006	0.0064	0.2934	0.2883	0.0005	0.0079	0.2979	0.2869	0.0000	0.0078
360	0.2909	0.2681	0.0016	0.0094	0.2929	0.2815	0.0009	0.0108	0.2961	0.2705	0.0010	0.0122
540	0.2836	0.2497	0.0035	0.0150	0.2872	0.2660	0.0014	0.0134	0.2875	0.2546	0.0019	0.0156
720	0.2751	0.2333	0.0069	0.0204	0.2795	0.2457	0.0028	0.0188	0.2709	0.2265	0.0061	0.0238
900	0.2647	0.2144	0.0121	0.0259	0.2704	0.2264	0.0068	0.0241	0.2602	0.2081	0.0119	0.0303
1080	0.2527	0.1987	0.0182	0.0324	0.2614	0.1942	0.0119	0.0265	0.2488	0.1929	0.0186	0.0384
1260	0.2417	0.1854	0.0243	0.0350	0.2482	0.1909	0.0192	0.0407	0.2356	0.1770	0.0265	0.0460
1440	0.2282	0.1724	0.0313	0.0385	0.2326	0.1770	0.0264	0.0493	0.2225	0.1639	0.0343	0.0496
1620	0.2179	0.1620	0.0381	0.0422	0.2194	0.1630	0.0344	0.0547	0.2089	0.1527	0.0418	0.0564
1800	0.2060	0.1512	0.0450	0.0452	0.2070	0.1506	0.0410	0.0574	0.1973	0.1417	0.0487	0.0603
2700	0.1599	0.1160	0.0715	0.0558	0.1533	0.1072	0.0724	0.0760	0.1498	0.1047	0.0783	0.0779
3600	0.1384	0.0980	0.0802	0.0646	0.1270	0.0874	0.0792	0.0395	0.1265	0.0863	0.0861	0.0838

Table S15. Concentration-time Data for Catalyst **2**/MeCN/Cl-AcOH Condition

time (sec)	epxRSM_avg (M)	epxRSM_std (M)	C_H[O]RSM_avg (M)	C_H[O]RSM_std (M)	epoxide_avg (M)	epoxide_std (M)	C_H[O]_avg (M)	C_H[O]_std (M)
0	0.3000	0.0000	0.3000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.2967	0.0063	0.3003	0.0031	0.0002	0.0002	0.0077	0.0019
180	0.2990	0.0006	0.2966	0.0014	0.0002	0.0003	0.0074	0.0014
270	0.2955	0.0019	0.2869	0.0011	0.0004	0.0003	0.0074	0.0007
360	0.2933	0.0021	0.2734	0.0058	0.0011	0.0003	0.0108	0.0012
540	0.2861	0.0017	0.2568	0.0068	0.0022	0.0009	0.0147	0.0009
720	0.2752	0.0035	0.2352	0.0079	0.0053	0.0017	0.0210	0.0021
900	0.2651	0.0041	0.2163	0.0076	0.0103	0.0024	0.0268	0.0026
1080	0.2543	0.0053	0.1953	0.0025	0.0163	0.0031	0.0324	0.0048
1260	0.2418	0.0051	0.1844	0.0057	0.0234	0.0031	0.0406	0.0045
1440	0.2278	0.0041	0.1711	0.0054	0.0307	0.0032	0.0458	0.0052
1620	0.2154	0.0047	0.1592	0.0046	0.0381	0.0030	0.0511	0.0063
1800	0.2034	0.0044	0.1478	0.0044	0.0449	0.0031	0.0543	0.0065
2700	0.1543	0.0042	0.1093	0.0048	0.0741	0.0030	0.0699	0.0100
3600	0.1306	0.0055	0.0906	0.0052	0.0818	0.0031	0.0626	0.0182

Table S16. Averaged Concentration-time Data for Catalyst **2**/MeCN/Cl-AcOH Condition

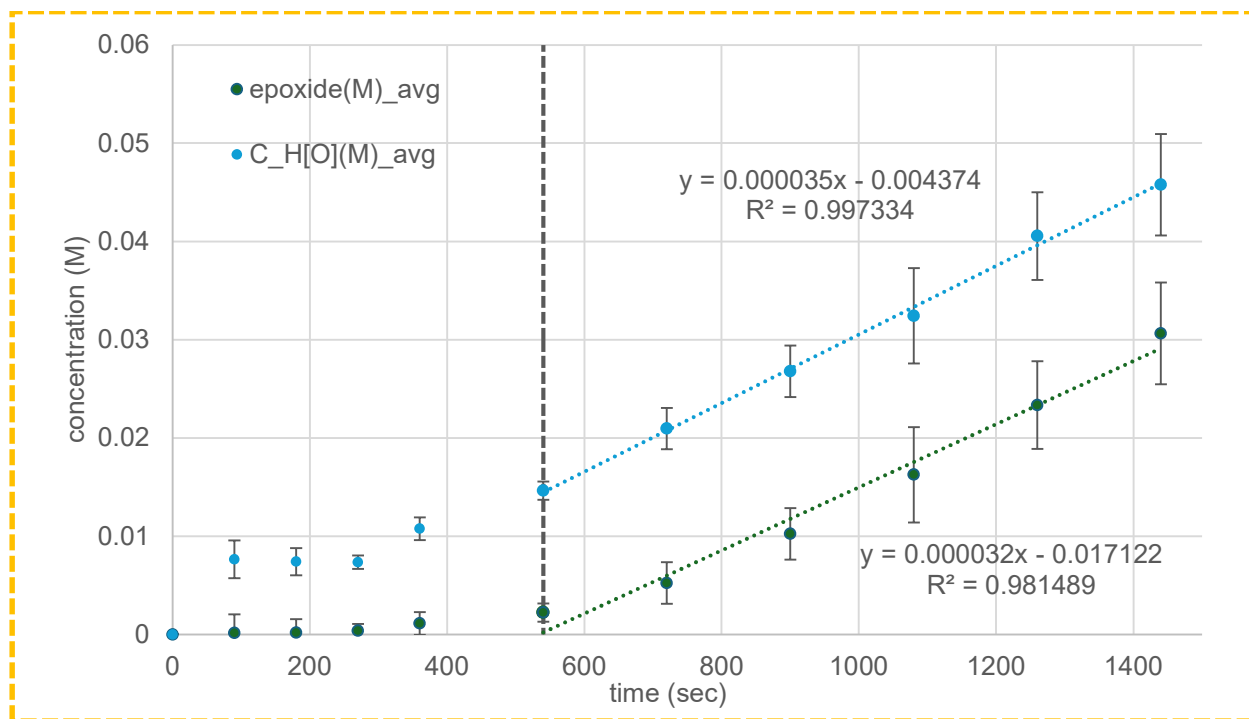
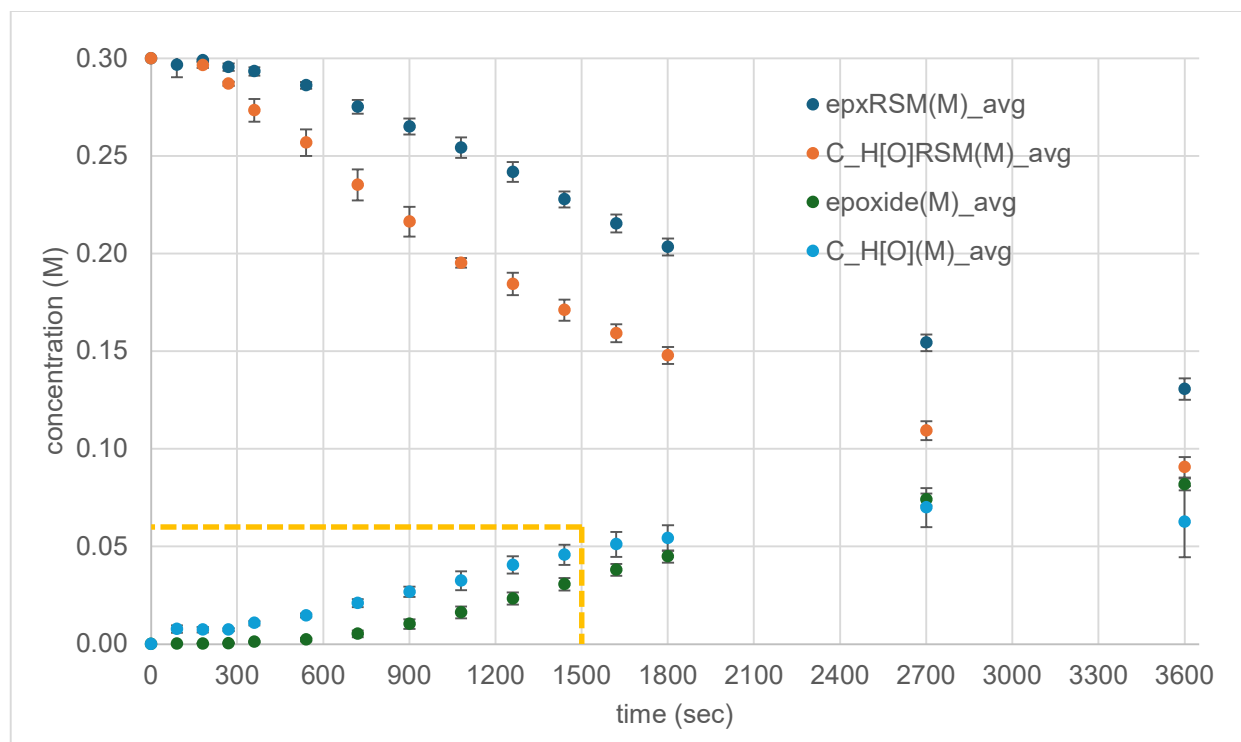


Figure S14. Concentration-time Plot for Catalyst 2/MeCN/Cl-AcOH Condition

6) Catalyst **2** in MeCN without acid (Table S2, entry 6)

time (sec)	1st run				2nd run				3rd run			
	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)
0	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000
90	0.2981	0.2991	0.0000	0.0079	0.3012	0.2967	0.0005	0.0013	0.2991	0.2972	0.0004	0.0022
180	0.2964	0.2994	0.0000	0.0077	0.3001	0.2935	0.0006	0.0028	0.2961	0.2914	0.0005	0.0038
270	0.2952	0.2980	0.0000	0.0077	0.2977	0.2883	0.0007	0.0043	0.2942	0.2873	0.0007	0.0051
360	0.2944	0.2957	0.0005	0.0082	0.2963	0.2844	0.0008	0.0046	0.2923	0.2826	0.0008	0.0056
540	0.2906	0.2878	0.0005	0.0095	0.2915	0.2792	0.0010	0.0049	0.2887	0.2767	0.0011	0.0063
720	0.2870	0.2815	0.0007	0.0105	0.2881	0.2743	0.0011	0.0058	0.2847	0.2715	0.0014	0.0069
900	0.2835	0.2769	0.0008	0.0113	0.2858	0.2702	0.0012	0.0060	0.2817	0.2663	0.0018	0.0079
1080	0.2805	0.2731	0.0010	0.0122	0.2813	0.2657	0.0014	0.0065	0.2774	0.2622	0.0021	0.0086
1260	0.2771	0.2687	0.0011	0.0123	0.2785	0.2627	0.0015	0.0071	0.2741	0.2571	0.0023	0.0091
1440	0.2741	0.2644	0.0012	0.0126	0.2759	0.2589	0.0016	0.0073	0.2714	0.2532	0.0027	0.0101
1620	0.2717	0.2621	0.0013	0.0133	0.2732	0.2564	0.0017	0.0079	0.2680	0.2494	0.0027	0.0104
1800	0.2683	0.2590	0.0013	0.0134	0.2701	0.2527	0.0016	0.0075	0.2646	0.2453	0.0028	0.0104
2700	0.2553	0.2447	0.0016	0.0141	0.2553	0.2380	0.0016	0.0076	0.2524	0.2314	0.0031	0.0128
3600	0.2439	0.2320	0.0016	0.0145	0.2421	0.2254	0.0016	0.0078	-	-	-	-

Table S17. Concentration-time Data for Catalyst **2**/MeCN/no acid Condition

time (sec)	epxRSM_avg (M)	epxRSM_std (M)	C_H[O]RSM_avg (M)	C_H[O]RSM_std (M)	epoxide_avg (M)	epoxide_std (M)	C_H[O]_avg (M)	C_H[O]_std (M)
0	0.3000	0.0000	0.3000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.2994	0.0013	0.2977	0.0010	0.0003	0.0002	0.0038	0.0029
180	0.2975	0.0018	0.2947	0.0034	0.0004	0.0003	0.0047	0.0021
270	0.2957	0.0015	0.2912	0.0048	0.0005	0.0003	0.0057	0.0014
360	0.2943	0.0017	0.2876	0.0058	0.0007	0.0002	0.0061	0.0015
540	0.2903	0.0012	0.2812	0.0048	0.0009	0.0003	0.0069	0.0019
720	0.2866	0.0014	0.2758	0.0042	0.0011	0.0003	0.0077	0.0020
900	0.2837	0.0017	0.2712	0.0044	0.0013	0.0004	0.0084	0.0022
1080	0.2797	0.0017	0.2670	0.0046	0.0015	0.0004	0.0091	0.0024
1260	0.2766	0.0018	0.2628	0.0047	0.0016	0.0005	0.0095	0.0021
1440	0.2738	0.0019	0.2588	0.0046	0.0019	0.0006	0.0100	0.0021
1620	0.2710	0.0022	0.2560	0.0052	0.0019	0.0006	0.0105	0.0022
1800	0.2677	0.0023	0.2523	0.0056	0.0019	0.0006	0.0105	0.0024
2700	0.2543	0.0014	0.2380	0.0054	0.0021	0.0007	0.0115	0.0028
3600	0.2430	0.0009	0.2287	0.0033	0.0016	0.0000	0.0112	0.0033

Table S18. Averaged Concentration-time Data for Catalyst **2**/MeCN/no acid Condition

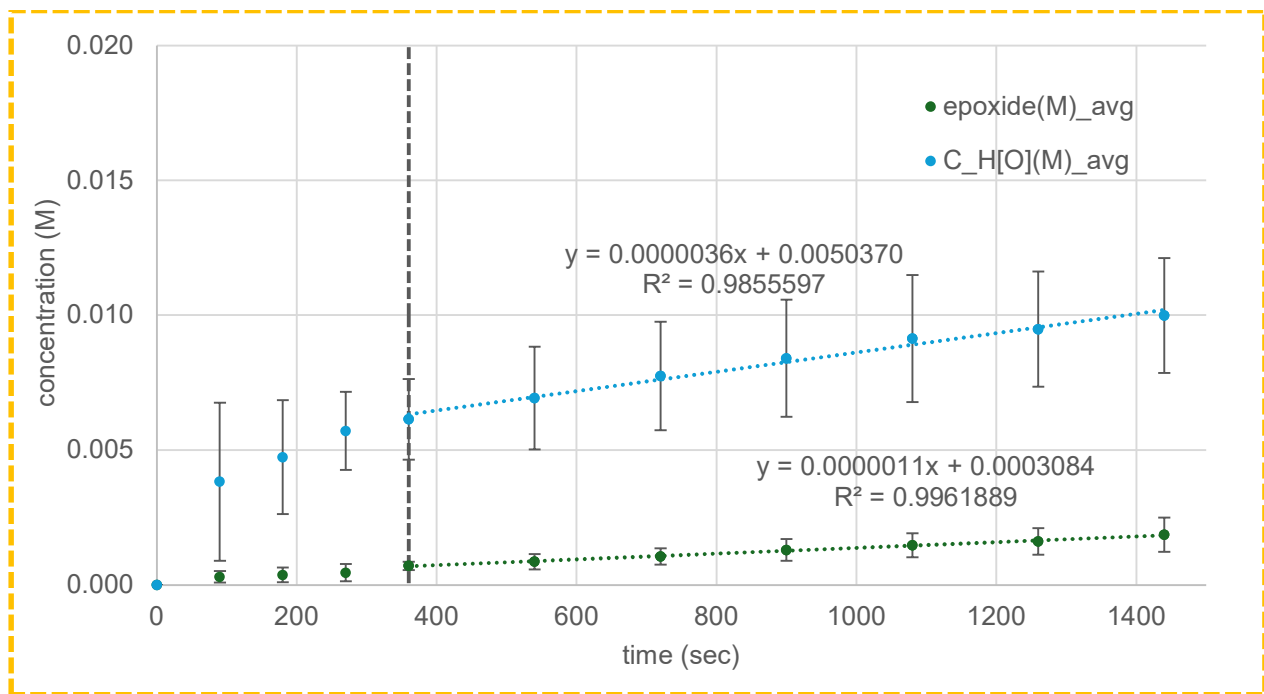
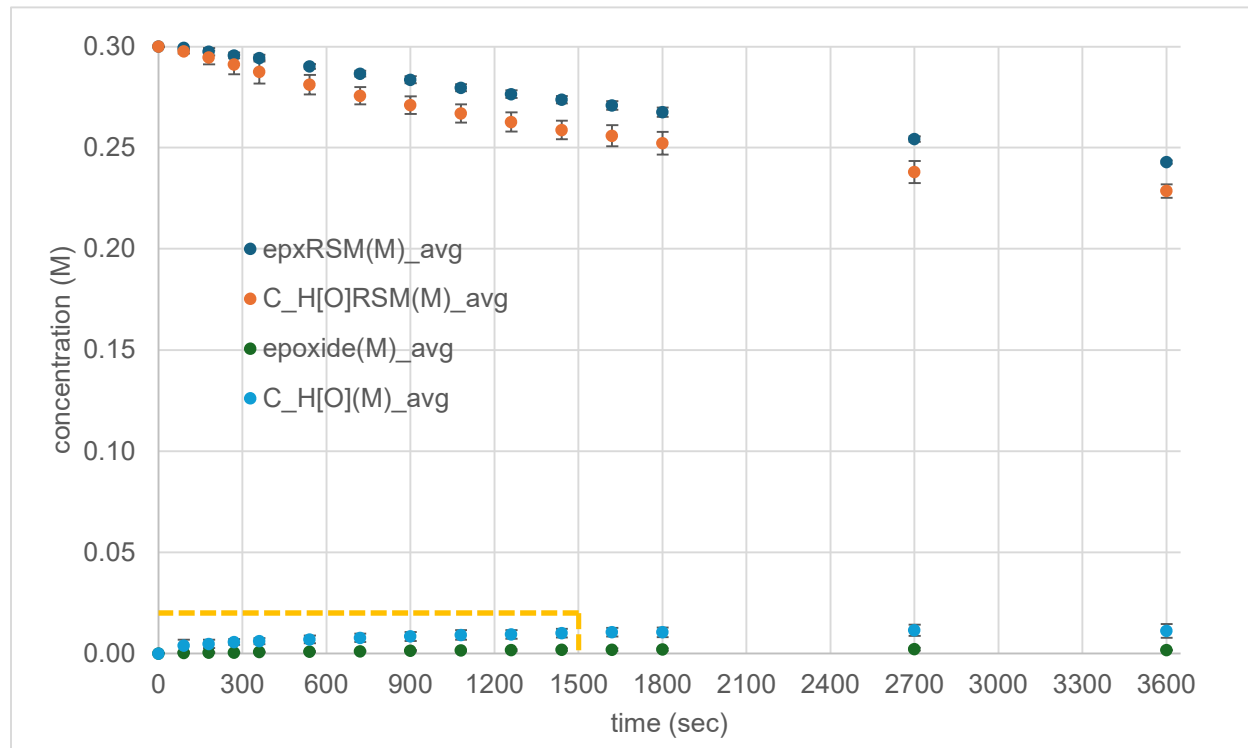


Figure S15. Concentration-time Plot for Catalyst 2/MeCN/no acid Condition

7) Catalyst **2** in HFIP without acid (Table S2, entry 7)

time (sec)	1st run				2nd run				3rd run			
	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)
0	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000
90	0.2971	0.2939	0.0002	0.0038	0.2972	0.2911	0.0001	0.0027	0.2982	0.2959	0.0000	0.0034
180	0.2959	0.2880	0.0001	0.0063	0.2951	0.2822	0.0001	0.0042	0.2964	0.2904	0.0001	0.0066
270	0.2946	0.2820	0.0002	0.0055	0.2932	0.2715	0.0001	0.0045	0.2948	0.2808	0.0001	0.0042
360	0.2922	0.2712	0.0003	0.0066	0.2921	0.2617	0.0002	0.0076	0.2931	0.2733	0.0000	0.0060
540	0.2892	0.2534	0.0003	0.0110	0.2892	0.2433	0.0002	0.0136	0.2905	0.2482	0.0001	0.0088
720	0.2861	0.2317	0.0003	0.0181	0.2861	0.2232	0.0003	0.0242	0.2878	0.2285	0.0001	0.0187
900	0.2836	0.2104	0.0004	0.0283	0.2833	0.2025	0.0004	0.0347	0.2847	0.2094	0.0003	0.0274
1080	0.2806	0.1902	0.0006	0.0366	0.2805	0.1844	0.0006	0.0441	0.2815	0.1898	0.0004	0.0369
1260	0.2773	0.1706	0.0008	0.0461	0.2770	0.1629	0.0008	0.0548	0.2786	0.1693	0.0006	0.0483
1440	0.2740	0.1494	0.0011	0.0578	0.2741	0.1417	0.0011	0.0673	0.2755	0.1485	0.0009	0.0595
1620	0.2705	0.1282	0.0015	0.0700	0.2707	0.1210	0.0015	0.0810	0.2721	0.1277	0.0012	0.0719
1800	0.2670	0.1089	0.0018	0.0783	0.2667	0.1013	0.0019	0.0953	0.2683	0.1076	0.0016	0.0840
2700	0.2508	0.0434	0.0035	0.1051	0.2503	0.0389	0.0037	0.1225	0.2521	0.0421	0.0032	0.1131
3600	0.2384	0.0237	0.0049	0.1055	0.2370	0.0034	0.0052	0.1192	0.2390	0.0224	0.0048	0.1138

Table S19. Concentration-time Data for Catalyst **2**/HFIP/no acid Condition

time (sec)	epxRSM_avg (M)	epxRSM_std (M)	C_H[O]RSM_avg (M)	C_H[O]RSM_std (M)	epoxide_avg (M)	epoxide_std (M)	C_H[O]_avg (M)	C_H[O]_std (M)
0	0.3000	0.0000	0.3000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.2975	0.0005	0.2936	0.0020	0.0001	0.0001	0.0033	0.0005
180	0.2958	0.0005	0.2869	0.0035	0.0001	0.0000	0.0057	0.0011
270	0.2942	0.0007	0.2781	0.0047	0.0001	0.0001	0.0047	0.0005
360	0.2925	0.0004	0.2687	0.0050	0.0002	0.0001	0.0068	0.0007
540	0.2896	0.0006	0.2483	0.0041	0.0002	0.0001	0.0111	0.0020
720	0.2867	0.0008	0.2278	0.0035	0.0003	0.0001	0.0203	0.0027
900	0.2839	0.0006	0.2075	0.0035	0.0004	0.0001	0.0301	0.0032
1080	0.2809	0.0005	0.1881	0.0026	0.0005	0.0001	0.0392	0.0034
1260	0.2776	0.0007	0.1676	0.0033	0.0008	0.0001	0.0497	0.0037
1440	0.2745	0.0007	0.1465	0.0034	0.0010	0.0001	0.0615	0.0042
1620	0.2711	0.0007	0.1256	0.0033	0.0014	0.0001	0.0743	0.0048
1800	0.2673	0.0007	0.1059	0.0033	0.0017	0.0001	0.0859	0.0071
2700	0.2511	0.0008	0.0414	0.0019	0.0035	0.0002	0.1135	0.0071
3600	0.2381	0.0008	0.0165	0.0093	0.0050	0.0002	0.1128	0.0056

Table S20. Averaged Concentration-time Data for Catalyst **2**/HFIP/no acid Condition

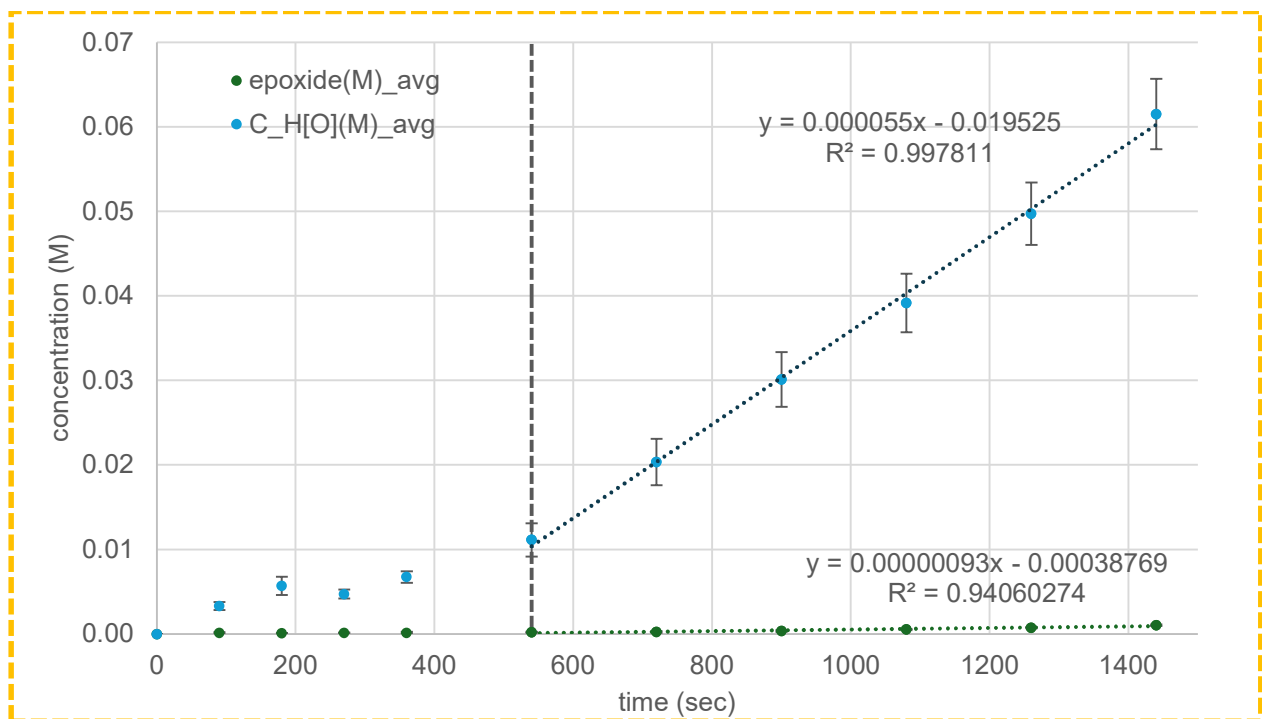
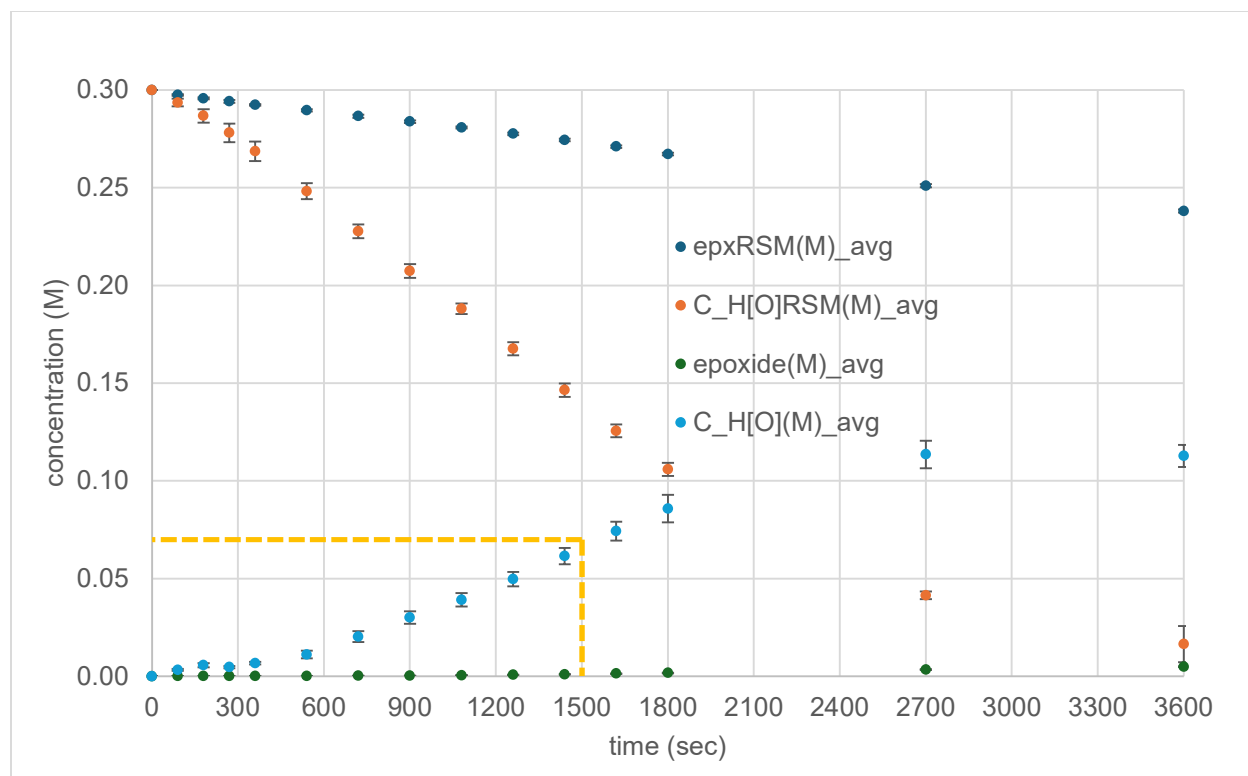


Figure S16. Concentration-time Plot for Catalyst 2/HFIP/no acid Condition

8) Catalyst **2** in HFIP with Cl-AcOH (Table S2, entry 8)

time (sec)	1st run				2nd run				3rd run			
	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)	epxRSM (M)	C_H[O]RSM (M)	Epoxide (M)	C_H[O] (M)
0	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000	0.3000	0.3000	0.0000	0.0000
90	0.2986	0.2880	0.0001	0.0087	0.2982	0.2831	0.0000	0.0067	0.3000	0.2889	0.0000	0.0080
180	0.2954	0.2773	0.0001	0.0090	0.2962	0.2715	0.0000	0.0067	0.2972	0.2789	0.0000	0.0104
270	0.2950	0.2669	0.0001	0.0115	0.2947	0.2611	0.0000	0.0082	0.2957	0.2691	0.0000	0.0160
360	0.2918	0.2523	0.0001	0.0206	0.2933	0.2489	0.0000	0.0131	0.2943	0.2531	0.0000	0.0195
540	0.2891	0.2317	0.0002	0.0347	0.2901	0.2254	0.0001	0.0221	0.2914	0.2321	0.0000	0.0329
720	0.2862	0.2063	0.0003	0.0460	0.2871	0.2021	0.0002	0.0361	0.2880	0.2059	0.0002	0.0500
900	0.2833	0.1823	0.0006	0.0602	0.2839	0.1772	0.0004	0.0464	0.2857	0.1802	0.0005	0.0613
1080	0.2790	0.1583	0.0010	0.0737	0.2795	0.1529	0.0008	0.0637	0.2818	0.1579	0.0009	0.0720
1260	0.2759	0.1370	0.0016	0.0854	0.2756	0.1290	0.0013	0.0741	0.2771	0.1368	0.0015	0.0841
1440	0.2721	0.1181	0.0024	0.0962	0.2720	0.1101	0.0020	0.0854	0.2740	0.1174	0.0022	0.0922
1620	0.2687	0.1006	0.0033	0.1057	0.2692	0.0912	0.0030	0.0942	0.2703	0.1006	0.0031	0.1008
1800	0.2645	0.0856	0.0045	0.1121	0.2638	0.0755	0.0042	0.1007	0.2666	0.0864	0.0041	0.1103
2700	0.2452	0.0325	0.0118	0.1218	0.2390	0.0243	0.0141	0.1118	0.2484	0.0354	0.0100	0.1186
3600	0.2248	0.0116	0.0197	0.1109	0.2144	0.0088	0.0246	0.1034	0.2279	0.0137	0.0156	0.1032

Table S21. Concentration-time Data for Catalyst **2**/HFIP/Cl-AcOH Condition

time (sec)	epxRSM_avg (M)	epxRSM_std (M)	C_H[O]RSM_avg (M)	C_H[O]RSM_std (M)	epoxide_avg (M)	epoxide_std (M)	C_H[O]_avg (M)	C_H[O]_std (M)
0	0.3000	0.0000	0.3000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.2990	0.0008	0.2867	0.0025	<0.0001	0.0000	0.0078	0.0008
180	0.2963	0.0007	0.2759	0.0032	<0.0001	0.0000	0.0087	0.0015
270	0.2952	0.0004	0.2657	0.0034	<0.0001	0.0000	0.0119	0.0032
360	0.2931	0.0010	0.2514	0.0018	<0.0001	0.0000	0.0177	0.0033
540	0.2902	0.0009	0.2297	0.0031	0.0001	0.0001	0.0299	0.0056
720	0.2871	0.0007	0.2047	0.0019	0.0002	0.0001	0.0441	0.0058
900	0.2843	0.0010	0.1799	0.0021	0.0005	0.0001	0.0560	0.0068
1080	0.2801	0.0012	0.1564	0.0025	0.0009	0.0001	0.0698	0.0044
1260	0.2762	0.0007	0.1342	0.0037	0.0015	0.0001	0.0812	0.0051
1440	0.2727	0.0009	0.1152	0.0036	0.0022	0.0002	0.0913	0.0044
1620	0.2694	0.0007	0.0975	0.0044	0.0031	0.0001	0.1002	0.0047
1800	0.2650	0.0012	0.0825	0.0050	0.0043	0.0002	0.1077	0.0050
2700	0.2442	0.0039	0.0307	0.0047	0.0119	0.0017	0.1174	0.0042
3600	0.2224	0.0058	0.0114	0.0020	0.0200	0.0037	0.1058	0.0036

Table S22. Averaged Concentration-time Data for Catalyst **2**/HFIP/Cl-AcOH Condition

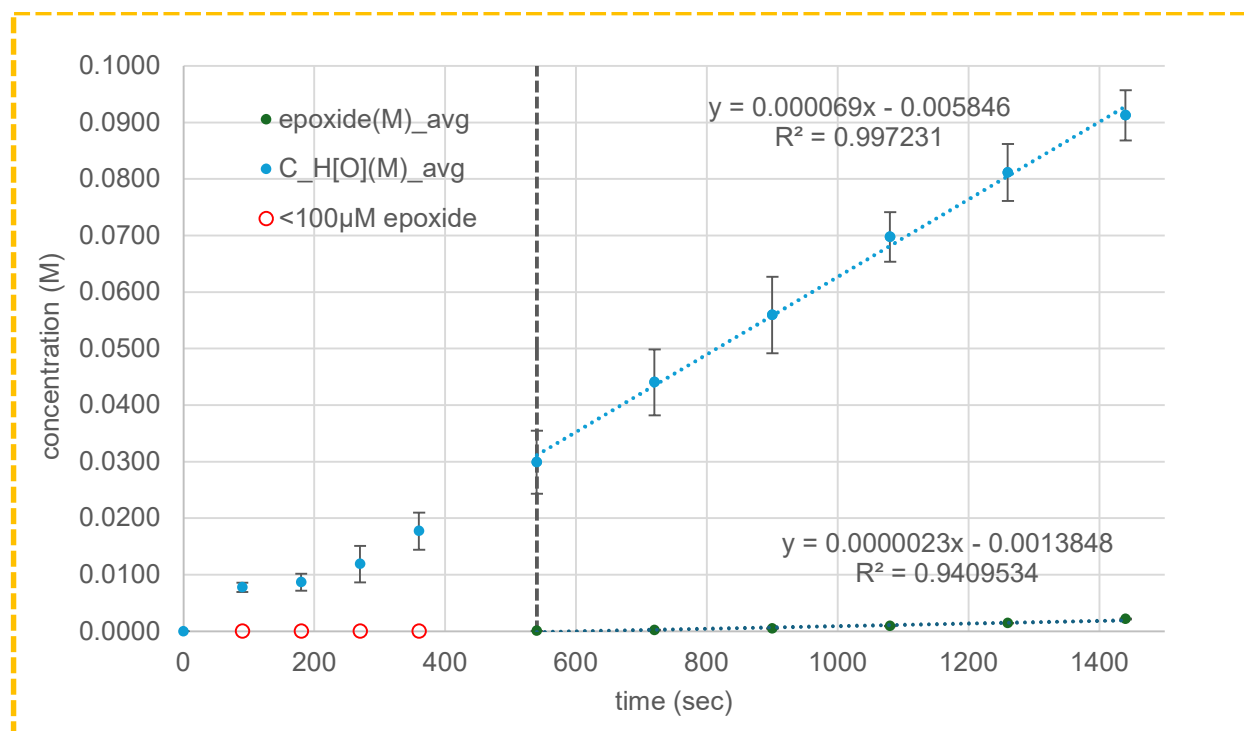
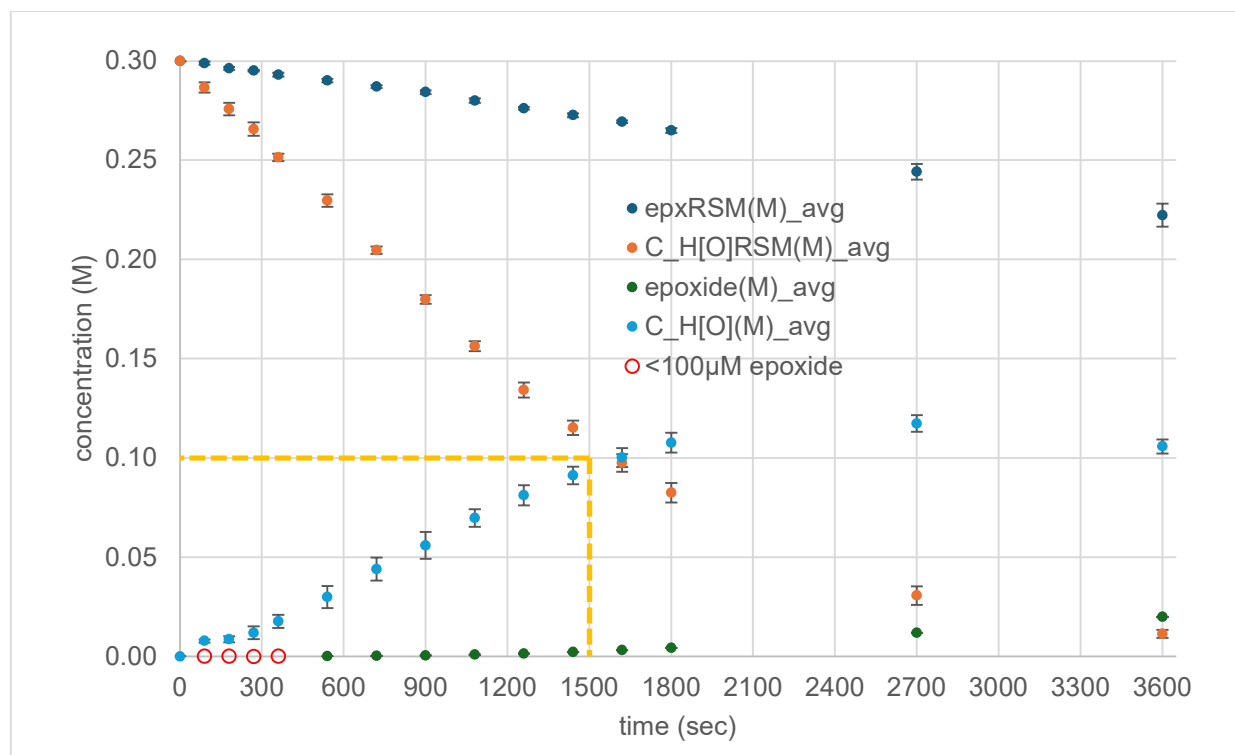


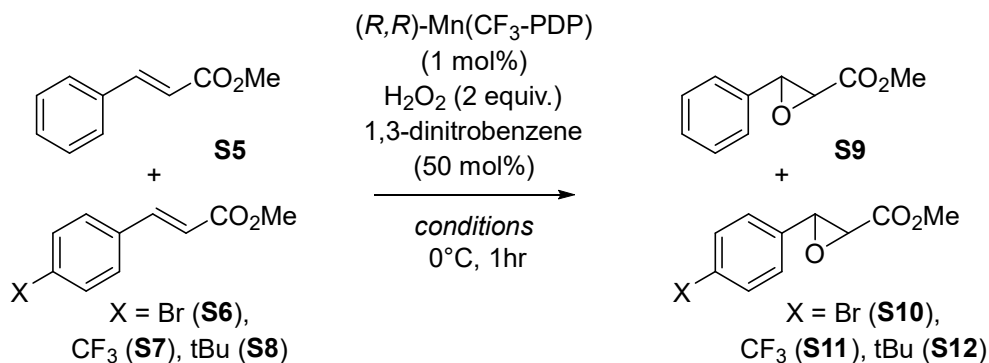
Figure S17. Concentration-time Plot for Catalyst 2/HFIP/Cl-AcOH Condition

entry	condition	C—H oxidation (M/s)	epoxidation (M/s)	$k_{9(C-H[O])}/$ $k_{10(epx)}$	$[9(C-H[O])]/$ $[10(epx)]^*$
1	catalyst 1 , MeCN + Cl-AcOH	5.6×10^{-5}	3.6×10^{-5}	1.6	1.6
2	catalyst 1 , MeCN	1.6×10^{-5}	9.0×10^{-6}	1.8	1.8
3	catalyst 1 , HFIP	1.0×10^{-4}	2.7×10^{-6}	38.5	39.3
4	catalyst 1 , HFIP + Cl-AcOH	9.6×10^{-5}	1.0×10^{-5}	9.6	9.5
5	catalyst 2 , MeCN + Cl-AcOH	3.5×10^{-5}	3.2×10^{-5}	1.1	1.5
6	catalyst 2 , MeCN	3.6×10^{-6}	1.1×10^{-6}	3.3	5.3
7	catalyst 2 , HFIP	5.5×10^{-5}	9.3×10^{-7}	59.1	61.5
8	catalyst 2 , HFIP + Cl-AcOH	6.9×10^{-5}	2.3×10^{-6}	30.0	41.5

*GC yield ratio after initial phase (t=1440 sec)

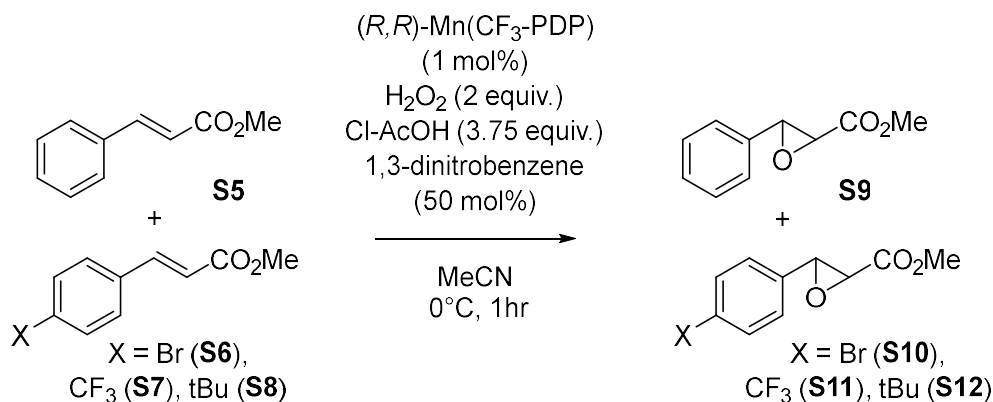
Table S23. Observed rates, relative rates (C—H oxidation rate/ epoxidation rate) and GC yield ratio at t=1440 seconds.

V. Hammett Analysis



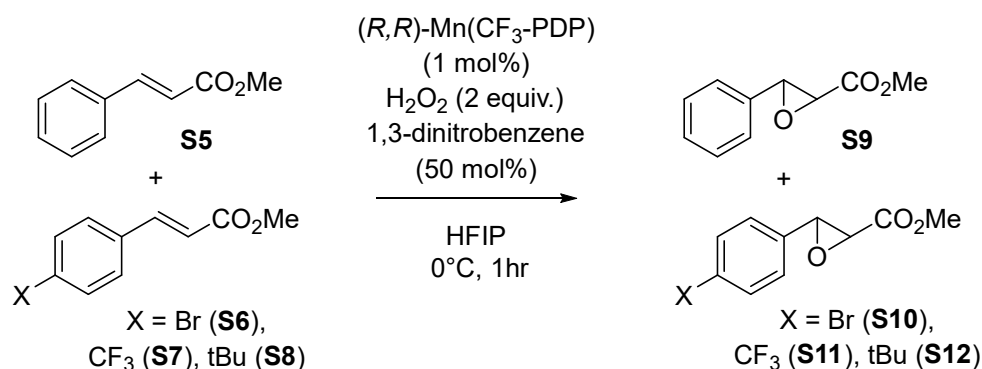
conditions	ρ
MeCN, ClAcOH	-1.9
HFIP, acid-free	-3.1

General procedures for Hammett analysis



Acetonitrile/chloroacetic acid conditions. A 30 mL vial equipped with a stir bar was charged with methyl cinnamate (48.7 mg, 0.3 mmol, 1 equiv.), substituted cinnamate ester (0.3 mmol, 1 equiv.), chloroacetic acid (106.3 mg, 1.125 mmol, 3.75 equiv.), (*R,R*)-MnCF₃-PDP **1** (4.1 mg, 0.003 mmol, 1 mol%), 1,3-dinitrobenzene (25.2 mg, 0.15 mmol, 0.5 equiv.), and acetonitrile (1 mL). In a 1-dram vial, a 3M solution of hydrogen peroxide (50% w/w) in acetonitrile was prepared

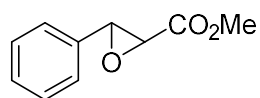
and 0.2 mL were drawn into a 1 mL syringe. This oxidant solution (2.0 equiv.) was added dropwise over 1 hour by syringe pump with aliquots collected for HPLC analysis every 1.5 minutes for the first 6 minutes (4 samples), every 3 minutes until the half hour point (8 samples), and then every 15 minutes (2 samples) until the end of the addition. The observed formation rate ratio (k_X/k_H) was measured under each substituted cinnamate ester.



HFIP/acid-free conditions. A 30 mL vial equipped with a stir bar was charged with methyl cinnamate (48.7 mg, 0.3 mmol, 1 equiv.), substituted cinnamate ester (0.3 mmol, 1 equiv.), (*R,R*)- $\text{MnCF}_3\text{-PDP}$ **1** (4.1 mg, 0.003 mmol, 1 mol%), 1,3-dinitrobenzene (25.2 mg, 0.15 mmol, 0.5 equiv.), and HFIP (1 mL). In a 1-dram vial, a 3M solution of hydrogen peroxide (50% w/w) in acetonitrile was prepared and 0.2 mL were drawn into a 1 mL syringe. This oxidant solution (2.0 equiv.) was added dropwise over 1 hour by syringe pump with aliquots collected for HPLC analysis every 1.5 minutes for the first 6 minutes (4 samples), every 3 minutes until the half hour point (8 samples), and then every 15 minutes (2 samples) until the end of the addition. The observed formation rate ratio (k_X/k_H) was measured under each substituted cinnamate ester.

Calibration Curves

Epoxide S9. Samples were prepared through serial dilution of the epoxide **S9** solution in ether



and mixing it with an internal standard (IS, 1,3-dinitrobenzene) solution at a constant concentration.

amount (mg)		amount (mmol)		peak area (%)		compound/IS peak area ratio	compound/IS mol ratio
IS	15	IS	15	IS	15		
0.025	0.066821	0.0015	0.000375	93.98	6.02	0.064074729	0.25
0.025	0.133643	0.0015	0.00075	88.49	11.51	0.130043118	0.5
0.025	0.267285	0.0015	0.0015	78.78	21.22	0.269337898	1
0.025	0.400928	0.0015	0.00225	72.34	27.66	0.382300623	1.5
0.025	0.53457	0.0015	0.003	66.34	33.66	0.507296014	2

Table S24. HPLC Calibration Data for Compound **S9**

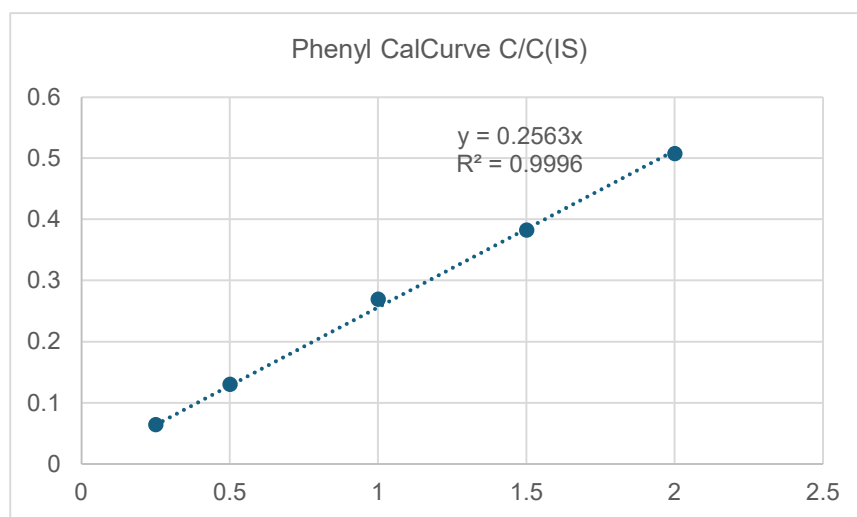
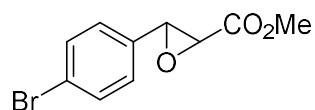


Figure S18. Calibration Curve for Compound **S9**

Epoxide S10. Samples were prepared through serial dilution of the epoxide **S10** solution in ether



and mixing it with an internal standard (IS, 1,3-dinitrobenzene) solution at a constant concentration.

amount (mg)		amount (mmol)		peak area (%)		compound/IS peak area ratio	compound/IS mol ratio
IS	16	IS	16	IS	16		
0.025	0.066584	0.0015	0.000259	88.10	11.90	0.135119301	0.172666667
0.025	0.133167	0.0015	0.000518	78.84	21.16	0.268335949	0.345333333
0.025	0.266335	0.0015	0.001036	65.00	35.00	0.538528152	0.690666667
0.025	0.399502	0.0015	0.001554	54.09	45.91	0.848679974	1.036
0.025	0.53267	0.0015	0.002072	46.93	53.07	1.130999824	1.381333333

Table S25. HPLC Calibration Data for Compound **S10**

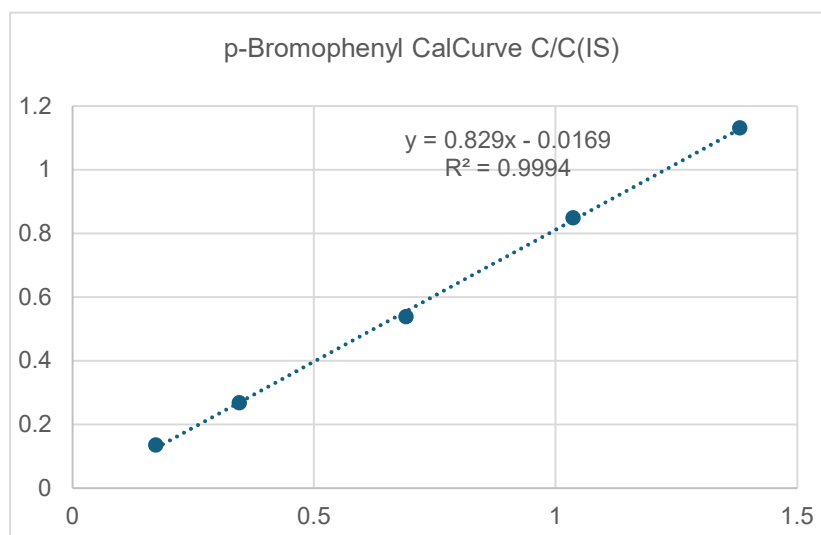
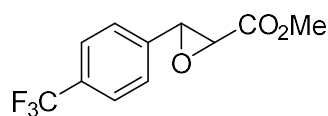


Figure S19. Calibration Curve for Compound **S10**

Epoxide S11. Samples were prepared through serial dilution of the epoxide **S11** solution in ether



and mixing it with an internal standard (IS, 1,3-dinitrobenzene)

solution at a constant concentration.

amount (mg)		amount (mmol)		peak area (%)		compound/IS peak area ratio	compound/IS mol ratio
IS	17	IS	17	IS	17		
0.025	0.046161	0.0015	0.000188	95.23	4.77	0.050035211	0.125
0.025	0.092321	0.0015	0.000375	91.58	8.42	0.091993354	0.25
0.025	0.184643	0.0015	0.00075	84.61	15.39	0.181839658	0.5
0.025	0.276964	0.0015	0.001125	78.56	21.44	0.272966777	0.75
0.025	0.369285	0.0015	0.0015	73.54	26.46	0.359891074	1

Table S26. HPLC Calibration Data for Compound **S11**

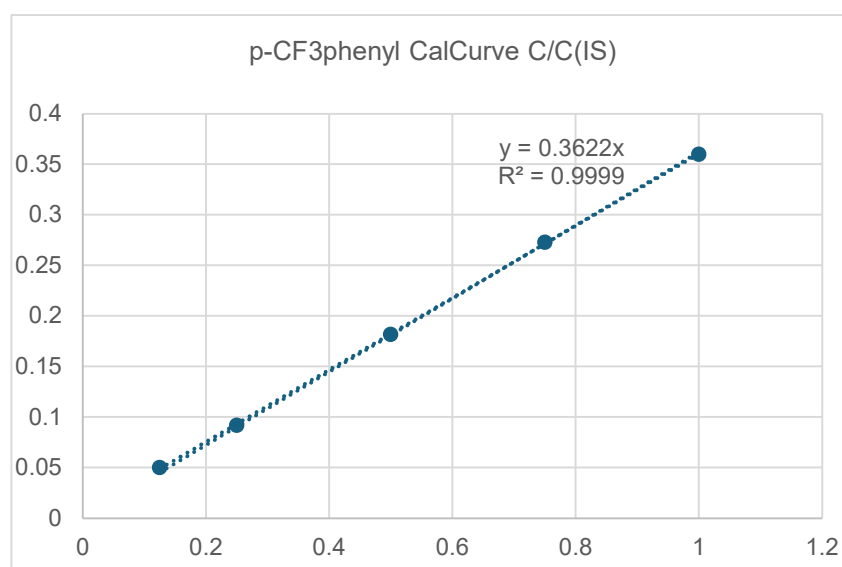
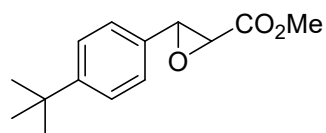


Figure S20. Calibration Curve for Compound **S11**

Epoxide S12. Samples were prepared through serial dilution of the epoxide **S12** solution in ether



and mixing it with an internal standard (IS, 1,3-dinitrobenzene) solution at a constant concentration.

amount (mg)		amount (mmol)		peak area (%)		compound/IS peak area ratio	compound/IS mol ratio
IS	18	IS	18	IS	18		
0.025	0.087863	0.0015	0.000375	89.43	10.57	0.118205853	0.25
0.025	0.175725	0.0015	0.00075	80.20	19.80	0.246829548	0.5
0.025	0.35145	0.0015	0.0015	67.11	32.89	0.490080018	1
0.025	0.527175	0.0015	0.00225	57.70	42.30	0.733201651	1.5
0.025	0.7029	0.0015	0.003	51.30	48.70	0.949169318	2

Table S27. HPLC Calibration Data for Compound **S12**

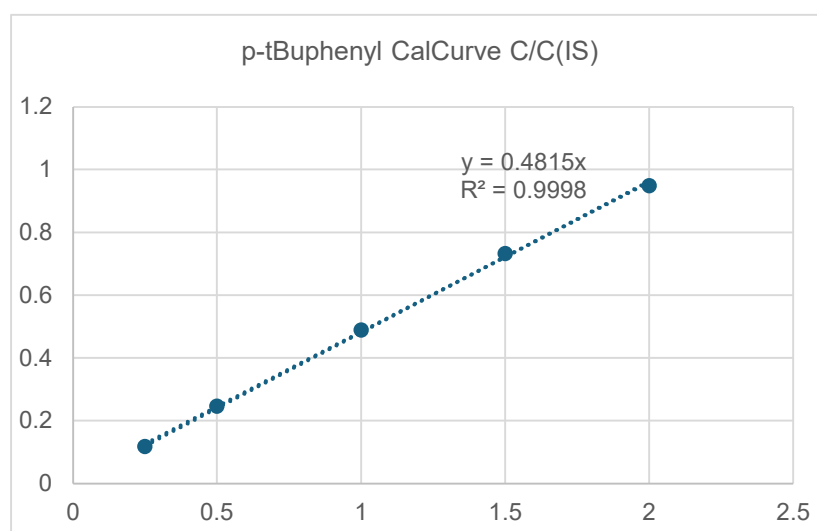


Figure S21. Calibration Curve for Compound **S12**

Concentration-Time Plots and Observed Rate: The significantly lower loading and initial concentration of catalyst **1** (1 mol%, 0.003M) compared to the competitive kinetic study (5 mol%, 0.015M) likely resulted in the observed initial lag time (0–400 seconds, Figures S22–S27). Lower catalyst loadings can prolong lag phases when pre-formation of the active catalytic species is required¹⁴.

1) Phenyl & *p*-bromophenyl in MeCN with Cl-AcOH

time (sec)	1st run		2nd run		3rd run	
	phenyl epoxide (M)	Br-phenyl epoxide (M)	phenyl epoxide (M)	Br-phenyl epoxide (M)	phenyl epoxide (M)	Br-phenyl epoxide (M)
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.0010	0.0006	0.0000	0.0000	0.0000	0.0000
180	0.0012	0.0007	0.0000	0.0000	0.0000	0.0000
270	0.0072	0.0040	0.0009	0.0003	0.0004	0.0001
360	0.0104	0.0059	0.0028	0.0013	0.0008	0.0005
540	0.0221	0.0126	0.0150	0.0081	0.0146	0.0080
720	0.0284	0.0168	0.0247	0.0139	0.0262	0.0145
900	0.0368	0.0228	0.0313	0.0182	0.0338	0.0193
1080	0.0420	0.0256	0.0373	0.0218	0.0398	0.0233
1260	0.0473	0.0287	0.0422	0.0250	0.0450	0.0267
1440	0.0520	0.0319	0.0472	0.0283	0.0502	0.0302
1620	0.0557	0.0346	0.0519	0.0315	0.0548	0.0337
1800	0.0623	0.0389	0.0555	0.0342	0.0577	0.0364
2700	0.0797	0.0527	0.0720	0.0471	0.0769	0.0510
3600	0.0901	0.0634	0.0830	0.0571	0.0885	0.0623

Table S28. Concentration-time Data for Phenyl & *p*-bromophenyl in MeCN/Cl-AcOH

time (sec)	phenyl epoxide avg. (M)	phenyl epoxide std. dev. (M)	Br-phenyl epoxide avg. (M)	Br-phenyl epoxide std. dev. (M)
0	0	0	0	0
90	0.000325098	0.000459757	0.000190865	0.000269924
180	0.000387928	0.000548613	0.000225114	0.00031836
270	0.002856843	0.003086335	0.001486369	0.001811662
360	0.004706737	0.004135223	0.002573782	0.002393791
540	0.017227751	0.003438893	0.009588227	0.002137999
720	0.026460298	0.001510191	0.015083392	0.001249426
900	0.03397271	0.00227523	0.020092312	0.001965737
1080	0.039691288	0.001930201	0.023579667	0.001571927
1260	0.044848511	0.002081997	0.026808051	0.001514686
1440	0.049791263	0.001946428	0.03013711	0.001482478
1620	0.054128733	0.001628068	0.033281366	0.001299952
1800	0.058511779	0.002801675	0.036522545	0.001926297
2700	0.07618459	0.003199353	0.050266242	0.002342825
3600	0.087216117	0.003049229	0.060923197	0.002749129

Table S29. Averaged Concentration-time Data for Phenyl & *p*-bromophenyl in MeCN/Cl-AcOH

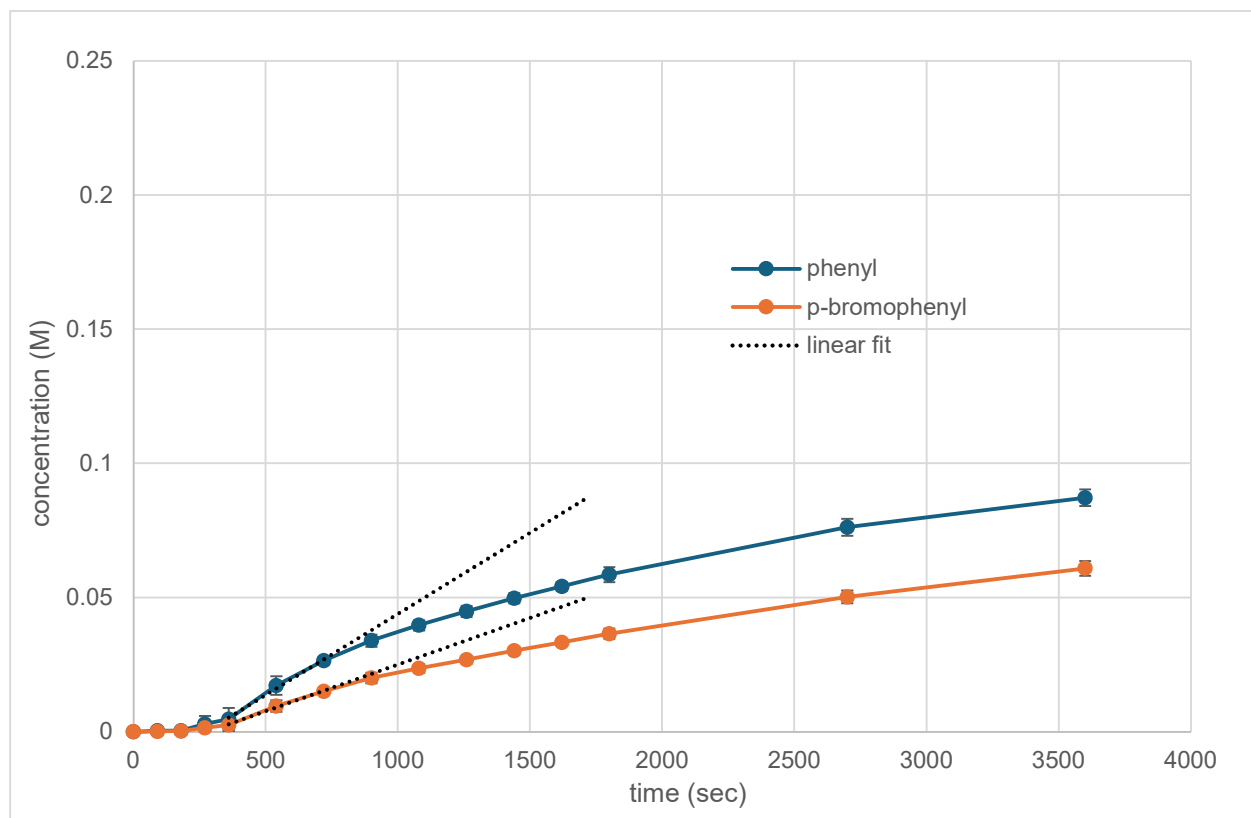


Figure S22. Concentration-time Plot for Phenyl & *p*-bromophenyl in MeCN with Cl-AcOH

phenyl + p-bromophenyl in MeCN w/ Cl-AcOH						
	k_{Br}	R^2	k_H	R^2	k_{Br}/k_H	$\log(k_{Br}/k_H)$
run 1	3.345E-05	9.911E-01	5.952E-05	9.943E-01	5.620E-01	-0.2502322
run 2	3.503E-05	9.974E-01	6.084E-05	9.960E-01	5.758E-01	-0.2397264
run 3	3.899E-05	9.984E-01	7.048E-05	9.976E-01	5.533E-01	-0.257078
average	3.583E-05	9.956E-01	6.361E-05	9.960E-01	5.637E-01	-2.490E-01
std. dev.	2.330E-06	3.249E-03	4.885E-06	1.327E-03	9.281E-03	7.136E-03

Table S30. Observed Rates for Phenyl & *p*-bromophenyl in MeCN/Cl-AcOH

2) Phenyl & *p*-bromophenyl in HFIP

time (sec)	1st run		2nd run		3rd run	
	phenyl epoxide (M)	Br-phenyl epoxide (M)	phenyl epoxide (M)	Br-phenyl epoxide (M)	phenyl epoxide (M)	Br-phenyl epoxide (M)
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.0017	0.0005	0.0009	0.0002	0.0019	0.0007
180	0.0015	0.0004	0.0042	0.0012	0.0035	0.0010
270	0.0059	0.0016	0.0105	0.0024	0.0082	0.0022
360	0.0211	0.0054	0.0170	0.0041	0.0140	0.0037
540	0.0336	0.0081	0.0298	0.0073	0.0254	0.0062
720	0.0407	0.0103	0.0390	0.0097	0.0332	0.0083
900	0.0494	0.0128	0.0472	0.0121	0.0396	0.0100
1080	0.0600	0.0153	0.0541	0.0143	0.0440	0.0113
1260	0.0649	0.0173	0.0588	0.0158	0.0504	0.0131
1440	0.0693	0.0187	0.0642	0.0176	0.0554	0.0148
1620	0.0757	0.0210	0.0711	0.0195	0.0600	0.0163
1800	0.0813	0.0231	0.0760	0.0214	0.0648	0.0178
2700	0.0995	0.0309	0.0992	0.0320	0.0875	0.0267
3600	0.1108	0.0374	0.1155	0.0423	0.1054	0.0361

Table S31. Concentration-time Data for Phenyl & *p*-bromophenyl in HFIP

time (sec)	phenyl epoxide avg. (M)	phenyl epoxide std. dev. (M)	Br-phenyl epoxide avg. (M)	Br-phenyl epoxide std. dev. (M)
0	0	0	0	0
90	0.001520399	0.000450331	0.000461564	0.000188579
180	0.003067061	0.001135814	0.000852856	0.000347574
270	0.008204518	0.001889182	0.002042324	0.000351915
360	0.017351061	0.002908635	0.00438732	0.00072316
540	0.02956277	0.003355067	0.007208602	0.00078502
720	0.037629062	0.00321439	0.009430122	0.000832208
900	0.045412681	0.004179796	0.011613376	0.001202409
1080	0.052694046	0.006602841	0.013621813	0.001700864
1260	0.05804602	0.005984313	0.015425907	0.001734392
1440	0.062963784	0.00574293	0.017030741	0.00165938
1620	0.068933644	0.006574798	0.018917354	0.001971172
1800	0.074022459	0.006875227	0.02074759	0.002219381
2700	0.095433595	0.005585092	0.029869338	0.002277618
3600	0.110579838	0.004144081	0.038605204	0.002679028

Table S32. Averaged Concentration-time Data for Phenyl & *p*-bromophenyl in HFIP

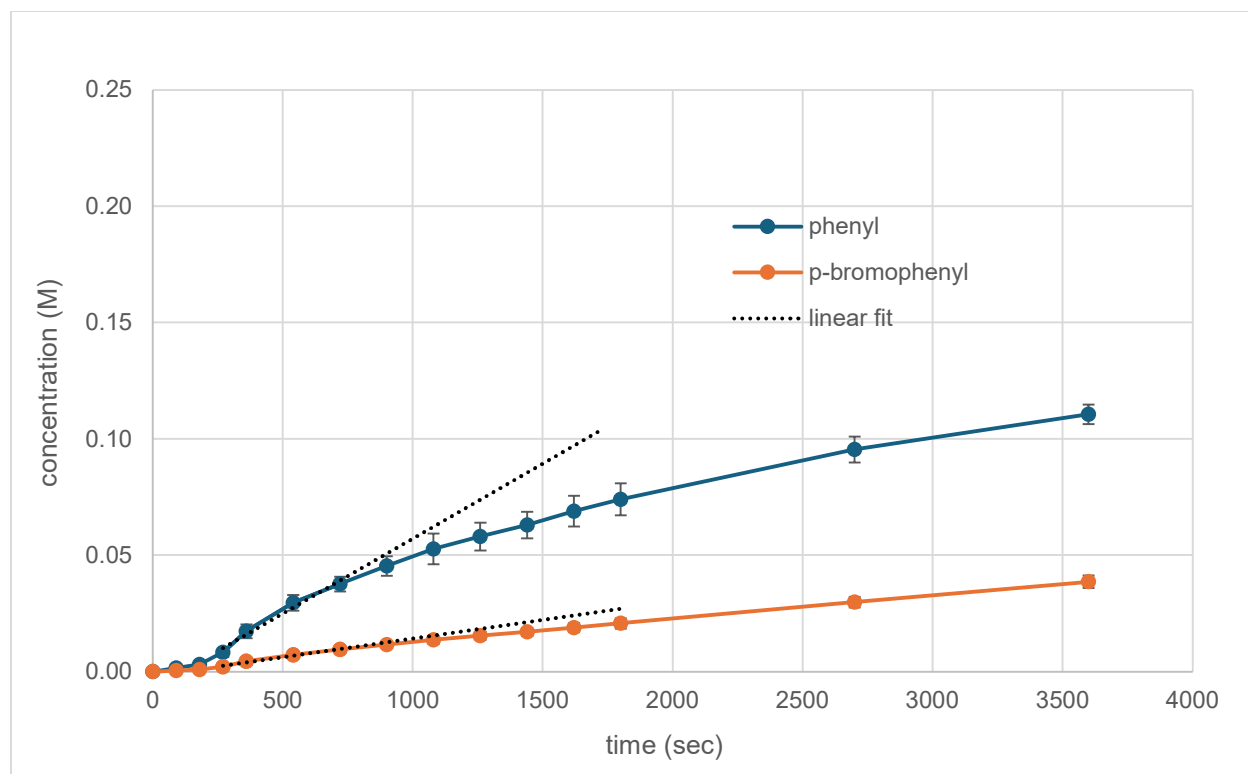


Figure S23. Concentration-time Plot for Phenyl & *p*-bromophenyl in HFIP

phenyl + p-bromophenyl in HFIP						
	k_{Br}	R^2	k_H	R^2	k_{Br}/k_H	$\log(k_{Br}/k_H)$
run 1	1.372E-05	9.953E-01	5.451E-05	9.756E-01	2.518E-01	-0.5990049
run 2	1.717E-05	9.965E-01	7.113E-05	1.000E+00	2.414E-01	-0.6173453
run 3	1.165E-05	9.905E-01	4.714E-05	9.827E-01	2.472E-01	-0.6069639
average	1.418E-05	9.941E-01	5.760E-05	9.861E-01	2.468E-01	-6.078E-01
std. dev.	2.274E-06	2.579E-03	1.003E-05	1.026E-02	4.261E-03	7.509E-03

Table S33. Observed Rates for Phenyl & *p*-bromophenyl in HFIP

3) Phenyl & *p*-CF₃phenyl in MeCN with Cl-AcOH

time (sec)	1st run		2nd run		3rd run	
	phenyl epoxide (M)	CF ₃ -phenyl epoxide (M)	phenyl epoxide (M)	CF ₃ -phenyl epoxide (M)	phenyl epoxide (M)	CF ₃ -phenyl epoxide (M)
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
180	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
270	0.0009	0.0000	0.0000	0.0000	0.0000	0.0000
360	0.0045	0.0000	0.0000	0.0000	0.0008	0.0000
540	0.0206	0.0014	0.0029	0.0003	0.0166	0.0011
720	0.0301	0.0025	0.0189	0.0013	0.0300	0.0021
900	0.0383	0.0028	0.0312	0.0022	0.0382	0.0028
1080	0.0477	0.0033	0.0408	0.0030	0.0451	0.0034
1260	0.0492	0.0041	0.0485	0.0036	0.0514	0.0039
1440	0.0558	0.0041	0.0548	0.0042	0.0574	0.0045
1620	0.0599	0.0044	0.0608	0.0048	0.0623	0.0050
1800	0.0642	0.0059	0.0658	0.0053	0.0674	0.0055
2700	0.0817	0.0087	0.0863	0.0076	-	-
3600	0.0937	0.0100	0.0983	0.0096	0.0995	0.0101

Table S34. Concentration-time Data for Phenyl & *p*-CF₃phenyl in MeCN/Cl-AcOH

time (sec)	phenyl epoxide avg. (M)	phenyl epoxide std. dev. (M)	CF ₃ -phenyl epoxide avg. (M)	CF ₃ -phenyl epoxide std. dev. (M)
0	0	0	0	0
90	0	0	0	0
180	0	0	0	0
270	0.000297872	0.000421254	0	0
360	0.001777475	0.001945582	0	0
540	0.013338624	0.007571685	0.00095181	0.00047111
720	0.026310372	0.005261677	0.001976116	0.000493214
900	0.035894699	0.003347887	0.002590035	0.00025471
1080	0.044533592	0.002860849	0.003225106	0.000170529
1260	0.049677485	0.001258363	0.003867744	0.000180594
1440	0.056015137	0.001074474	0.004239302	0.000165382
1620	0.06099903	0.000994275	0.004732617	0.00022315
1800	0.065794441	0.001281767	0.00554849	0.000246939
2700	0.083989098	0.002269204	0.008170119	0.000524887
3600	0.09717216	0.002513581	0.00987468	0.000198726

Table S35. Averaged Concentration-time Data for Phenyl & *p*-CF₃phenyl in MeCN/Cl-AcOH

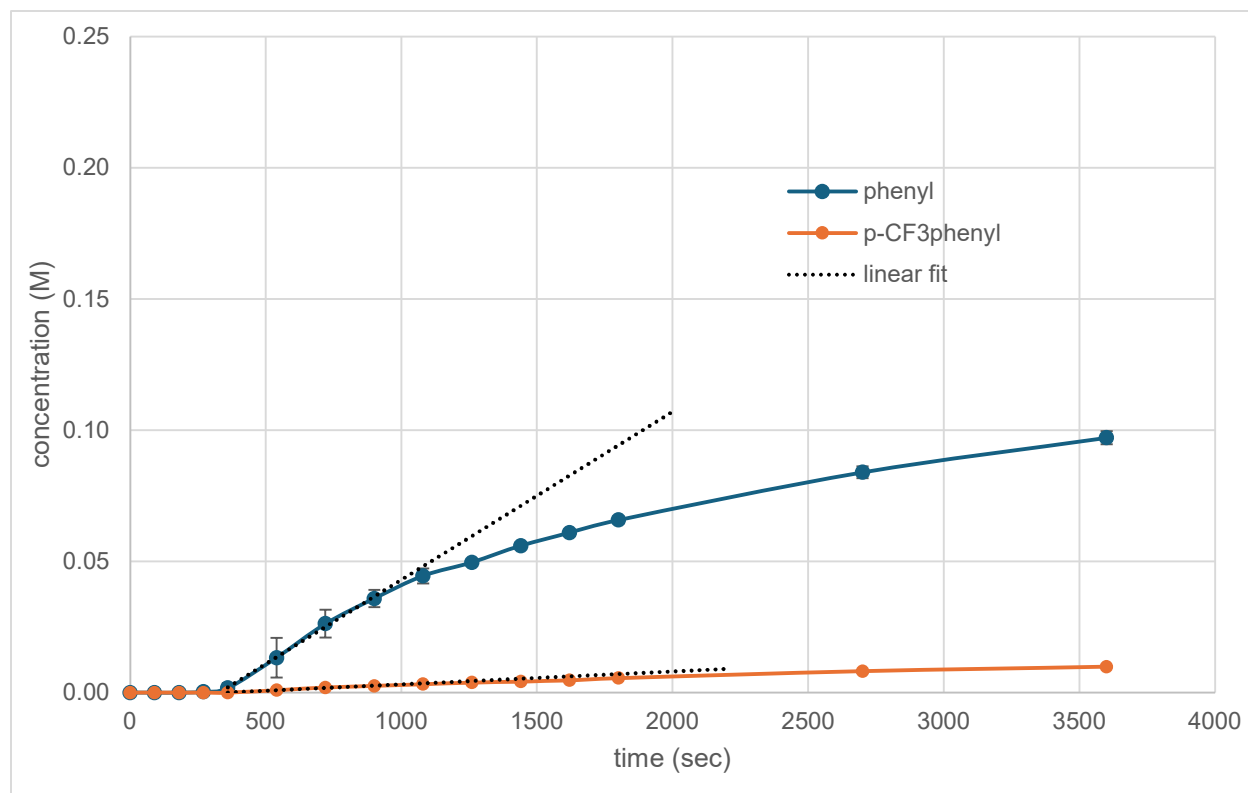


Figure S24. Concentration-time Plot for Phenyl & *p*-CF₃phenyl in MeCN/Cl-AcOH

phenyl + <i>p</i> -CF ₃ phenyl in MeCN w/ Cl-AcOH						
	k_{CF_3}	R ²	k_H	R ²	k_{CF_3}/k_H	log(k_{CF_3}/k_H)
run 1	5.195E-06	9.264E-01	6.168E-05	9.736E-01	8.422E-02	-1.0746063
run 2	4.277E-06	9.596E-01	6.082E-05	9.429E-01	7.033E-02	-1.1528604
run 3	5.186E-06	9.874E-01	6.971E-05	9.819E-01	7.439E-02	-1.1284833
average	4.886E-06	9.578E-01	6.407E-05	9.661E-01	7.631E-02	-1.119E+00
std. dev.	4.303E-07	2.491E-02	4.003E-06	1.674E-02	5.830E-03	3.270E-02

Table S36. Observed Rates for Phenyl & *p*-CF₃phenyl in MeCN/Cl-AcOH

4) Phenyl & *p*-CF₃phenyl in HFIP

time (sec)	1st run		2nd run		3rd run	
	phenyl epoxide (M)	CF ₃ -phenyl epoxide (M)	phenyl epoxide (M)	CF ₃ -phenyl epoxide (M)	phenyl epoxide (M)	CF ₃ -phenyl epoxide (M)
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.0003	0.0000	0	0.0000	0.0000	0.0000
180	0.0006	0.0000	0.0000	0.0000	0.0005	0.0000
270	0.0021	0.0000	0.0000	0.0000	0.0015	0.0000
360	0.0045	0.0000	0.0025	0.0000	0.0062	0.0000
540	0.0172	0.0002	0.0198	0.0000	0.0240	0.0004
720	0.0286	0.0002	0.0379	0.0003	0.0393	0.0007
900	0.0421	0.0004	0.0540	0.0004	0.0537	0.0010
1080	0.0517	0.0005	0.0685	0.0006	0.0596	0.0011
1260	0.0625	0.0006	0.0800	0.0007	0.0674	0.0014
1440	0.0693	0.0007	0.0875	0.0008	0.0753	0.0015
1620	0.0770	0.0008	0.0970	0.0009	0.0835	0.0017
1800	0.0861	0.0010	0.1040	0.0010	0.0907	0.0019
2700	0.1193	0.0017	0.1367	0.0016	0.1230	0.0021
3600	0.1430	0.0024	0.1616	0.0028	0.1425	0.0026

Table S37. Concentration-time Data for Phenyl & *p*-CF₃phenyl in HFIP

time (sec)	phenyl epoxide avg. (M)	phenyl epoxide std. dev. (M)	CF ₃ -phenyl epoxide avg. (M)	CF ₃ -phenyl epoxide std. dev. (M)
0	0	0	0	0
90	9.68928E-05	0.000137027	0	0
180	0.000365237	0.000258741	0	0
270	0.001193083	0.000872018	0	0
360	0.004391267	0.001529916	0	0
540	0.020338228	0.00277937	0.000185385	0.00016368
720	0.035246487	0.004768207	0.000419821	0.000226138
900	0.049974404	0.005544204	0.000583587	0.000274381
1080	0.059916725	0.006842942	0.000711729	0.000265844
1260	0.069962411	0.007399597	0.000896087	0.000380264
1440	0.077390595	0.007589867	0.001010094	0.000362901
1620	0.085840903	0.008352841	0.001116116	0.000391418
1800	0.093613341	0.007602039	0.001314196	0.000415822
2700	0.126340286	0.007495976	0.001816611	0.000199421
3600	0.149018877	0.008875339	0.002590042	0.000183258

Table S38. Averaged Concentration-time Data for Phenyl & *p*-CF₃phenyl in HFIP

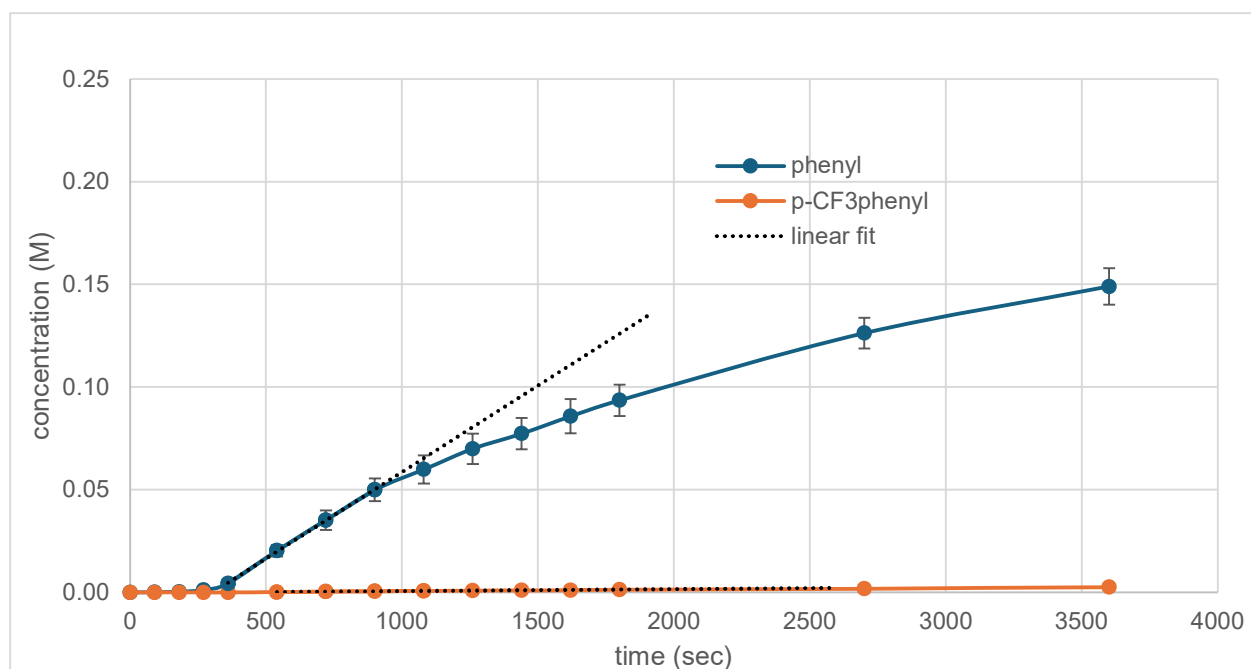


Figure S25. Concentration-time Plot for Phenyl & *p*-CF₃phenyl in HFIP

phenyl + p-CF ₃ phenyl in HFIP						
	k_{CF_3}	R^2	k_H	R^2	k_{CF_3}/k_H	$\log(k_{CF_3}/k_H)$
run 1	6.902E-07	9.849E-01	6.905E-05	9.989E-01	9.997E-03	-2.000132
run 2	8.544E-07	9.693E-01	9.597E-05	9.995E-01	8.903E-03	-2.0504604
run 3	1.030E-06	9.753E-01	9.191E-05	9.982E-01	1.120E-02	-1.9506501
average	8.581E-07	9.765E-01	8.564E-05	9.989E-01	1.003E-02	-2.000E+00
std. dev.	1.386E-07	6.431E-03	1.185E-05	5.330E-04	9.395E-04	4.075E-02

Table S39. Observed Rates for Phenyl & *p*-CF₃phenyl in HFIP

5) Phenyl & *p*-tBuphenyl in MeCN with Cl-AcOH

time (sec)	1st run		2nd run		3rd run	
	phenyl epoxide (M)	tBu-phenyl epoxide (M)	phenyl epoxide (M)	tBu-phenyl epoxide (M)	phenyl epoxide (M)	tBu-phenyl epoxide (M)
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
180	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
270	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
360	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
540	0.0033	0.0115	0.0019	0.0066	0.0013	0.0049
720	0.0122	0.0434	0.0113	0.0400	0.0114	0.0403
900	0.0175	0.0602	0.0160	0.0554	0.0181	0.0623
1080	0.0218	0.0736	0.0200	0.0667	0.0227	0.0764
1260	0.0254	0.0849	0.0233	0.0776	0.0270	0.0895
1440	0.0290	0.0961	0.0266	0.0874	0.0308	0.1006
1620	0.0318	0.1035	0.0295	0.0962	0.0341	0.1103
1800	0.0358	0.1135	0.0322	0.1031	0.0377	0.1208
2700	0.0493	0.1483	0.0453	0.1353	0.0532	0.1598
3600	0.0602	0.1724	0.0548	0.1560	0.0656	0.1856

Table S40. Concentration-time Data for Phenyl & *p*-tBuphenyl in MeCN/Cl-AcOH

time (sec)	phenyl epoxide avg. (M)	phenyl epoxide std. dev. (M)	tBu-phenyl epoxide avg. (M)	tBu-phenyl epoxide std. dev. (M)
0	0	0	0	0
90	0	0	0	0
180	0	0	0	0
270	0	0	0	0
360	0	0	0	0
540	0.002128444	0.000995336	0.00817004	0.00330413
720	0.011629449	0.000372528	0.041235107	0.001563045
900	0.017204685	0.000874074	0.059258926	0.002882945
1080	0.021476099	0.001124887	0.072237147	0.004044782
1260	0.025230592	0.001501654	0.084014948	0.004879654
1440	0.02882106	0.001700414	0.09471578	0.005455747
1620	0.031794224	0.001868477	0.103322035	0.005744709
1800	0.035245667	0.002316756	0.112447752	0.007251383
2700	0.049262969	0.001922531	0.154067576	0.010006924
3600	0.060187059	0.002699081	0.178985796	0.012112837

Table S41. Averaged Concentration-time Data for Phenyl & *p*-tBuphenyl in MeCN/Cl-AcOH

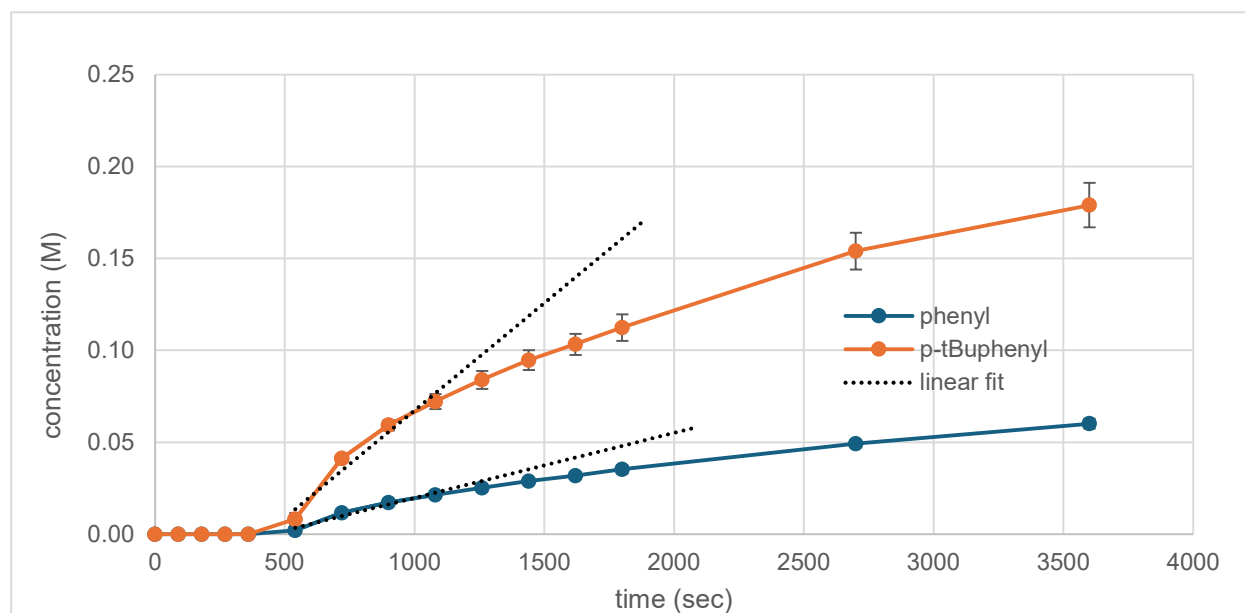


Figure S26. Concentration-time Plot for Phenyl & *p*-tBuphenyl in MeCN/Cl-AcOH

phenyl +tBuphenyl in MeCN w/ Cl-AcOH						
	k_{IBu}	R^2	k_H	R^2	k_{IBu}/k_H	$\log(k_{IBu}/k_H)$
run 1	1.102E-04	9.355E-01	3.057E-05	9.168E-01	3.606E+00	0.55703433
run 2	8.206E-05	9.985E-01	2.286E-05	9.645E-01	3.590E+00	0.55512446
run 3	1.234E-04	9.356E-01	3.579E-05	9.327E-01	3.448E+00	0.53760012
average	1.052E-04	9.566E-01	2.974E-05	9.380E-01	3.548E+00	5.499E-01
std. dev.	1.725E-05	2.969E-02	5.314E-06	1.982E-02	7.096E-02	8.746E-03

Table S42. Observed Rates for Phenyl & *p*-tBuphenyl in MeCN/Cl-AcOH

6) Phenyl & *p*-tBuphenyl in HFIP

time (sec)	1st run		2nd run		3rd run	
	phenyl epoxide (M)	tBu-phenyl epoxide (M)	phenyl epoxide (M)	tBu-phenyl epoxide (M)	phenyl epoxide (M)	tBu-phenyl epoxide (M)
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
90	0.0000	0.0015	0.0000	0.0010	0.0000	0.0000
180	0.0000	0.0025	0.0007	0.0020	0.0011	0.0028
270	0.0022	0.0104	0.0017	0.0062	0.0019	0.0054
360	0.0034	0.0164	0.0030	0.0136	0.0027	0.0120
540	0.0103	0.0475	0.0097	0.0437	0.0088	0.0389
720	0.0135	0.0615	0.0153	0.0683	0.0135	0.0582
900	0.0170	0.0769	0.0190	0.0839	0.0174	0.0740
1080	0.0210	0.0926	0.0237	0.1026	0.0207	0.0872
1260	0.0243	0.1062	0.0262	0.1126	0.0240	0.0999
1440	0.0274	0.1184	0.0297	0.1256	0.0272	0.1118
1620	0.0303	0.1302	0.0330	0.1378	0.0301	0.1222
1800	0.0337	0.1416	0.0363	0.1492	0.0332	0.1328
2700	0.0497	0.1922	0.0540	0.2016	0.0495	0.1802
3600	0.0687	0.2181	0.0668	0.2277	0.0665	0.2149

Table S43. Concentration-time Data for Phenyl & *p*-tBuphenyl in HFIP

time (sec)	phenyl epoxide avg. (M)	phenyl epoxide std. dev. (M)	tBu-phenyl epoxide avg. (M)	tBu-phenyl epoxide std. dev. (M)
0	0	0	0	0
90	0	0	0.000842535	0.000632695
180	0.000601997	0.000446331	0.002420454	0.000311603
270	0.001923432	0.000189516	0.007305971	0.002183071
360	0.003043107	0.000247589	0.013970524	0.00181215
540	0.009599811	0.000604352	0.043361845	0.003544006
720	0.014086314	0.000865976	0.062661059	0.004181966
900	0.017817743	0.000866863	0.078262936	0.004190333
1080	0.021794155	0.001349104	0.094124421	0.006353624
1260	0.024841883	0.000984437	0.106231083	0.005195856
1440	0.028103364	0.001104375	0.118602365	0.005640184
1620	0.03114924	0.001343811	0.130089451	0.00634393
1800	0.034383892	0.001338156	0.141199998	0.006686025
2700	0.051048645	0.002060474	0.191313213	0.008781542
3600	0.067342698	0.000970859	0.220272085	0.005429663

Table S44. Averaged Concentration-time Data for Phenyl & *p*-tBuphenyl in HFIP

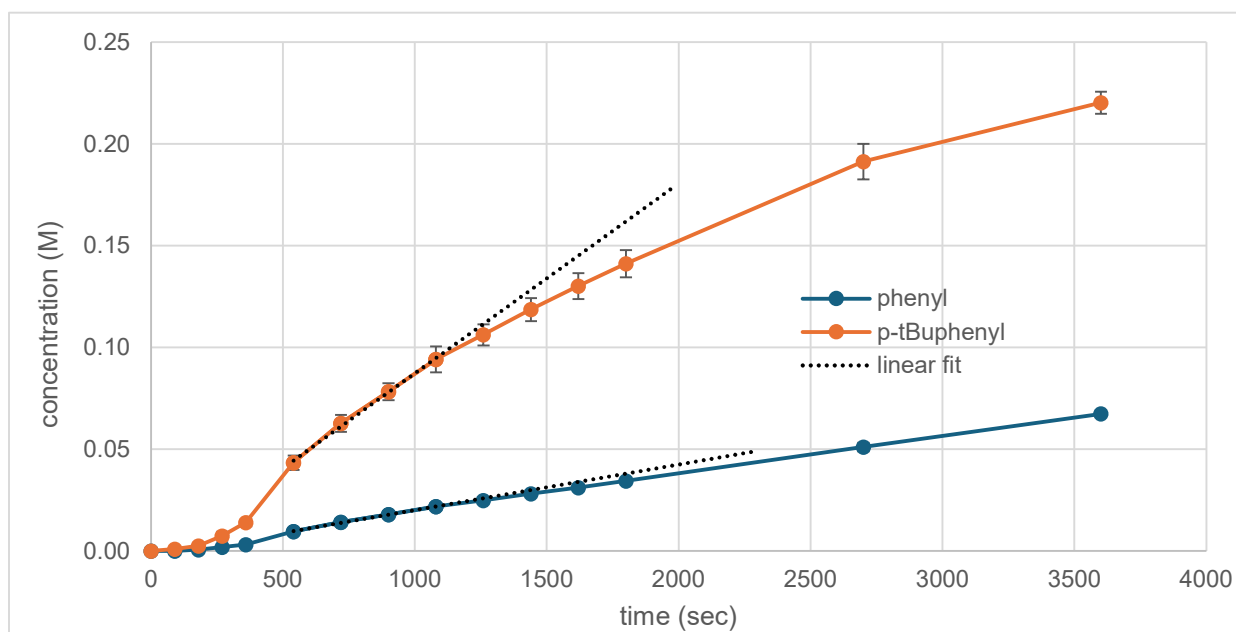


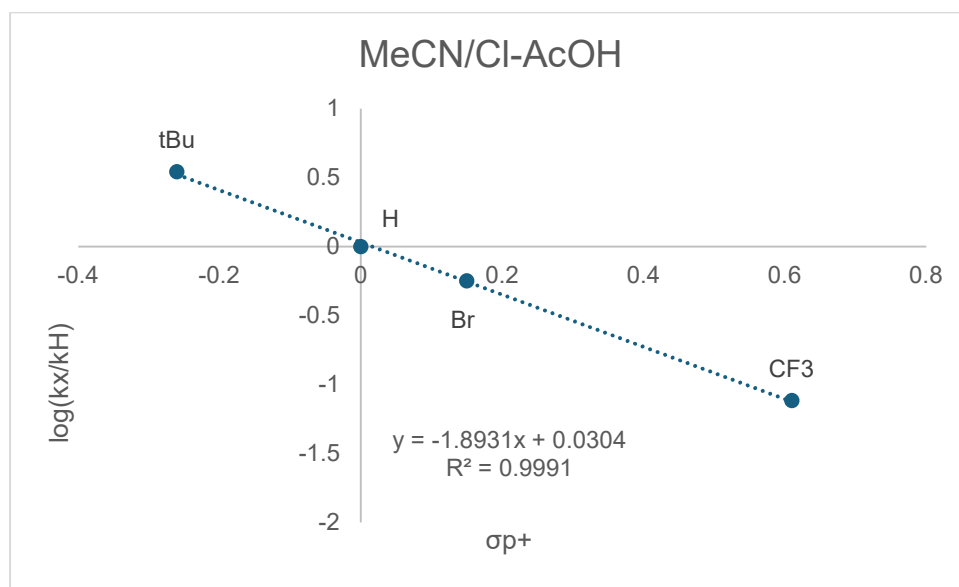
Figure S27. Concentration-time Plot for Phenyl & *p*-tBuphenyl in HFIP

phenyl + tBuphenyl in HFIP						
	k_{tBu}	R^2	k_H	R^2	k_{tBu}/k_H	$\log(k_{tBu}/k_H)$
run 1	1.086E-04	9.599E-01	2.459E-05	9.638E-01	4.418E+00	0.64520726
run 2	1.519E-04	9.967E-01	3.410E-05	9.976E-01	4.454E+00	0.64876919
run 3	1.284E-04	9.911E-01	2.985E-05	9.944E-01	4.302E+00	0.6336671
average	1.297E-04	9.826E-01	2.951E-05	9.853E-01	4.391E+00	6.425E-01
std. dev.	1.767E-05	1.619E-02	3.888E-06	1.525E-02	6.491E-02	6.446E-03

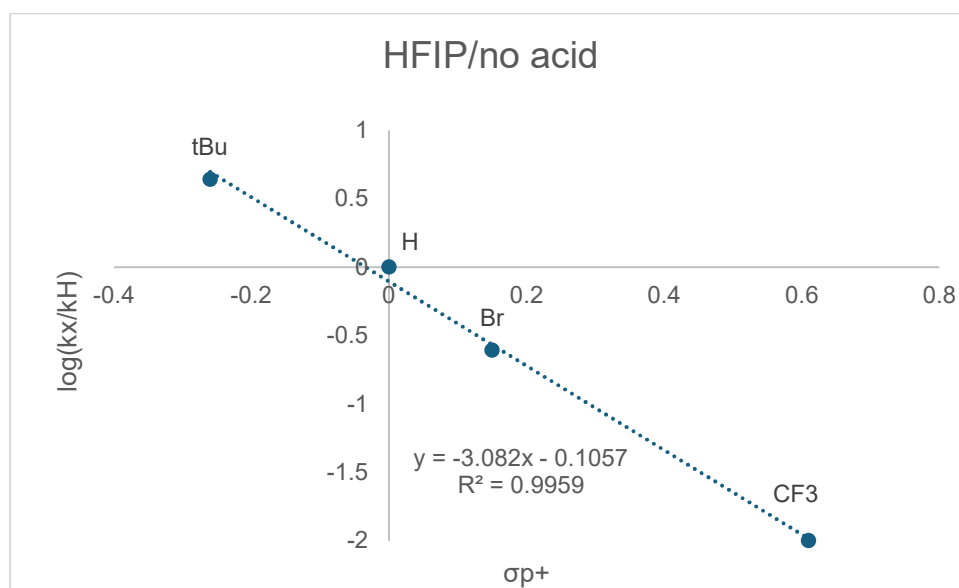
Table S45. Observed Rates for Phenyl & *p*-tBuphenyl in HFIP

Hammett Plots

σ^+ values were reported in the literature¹⁵.



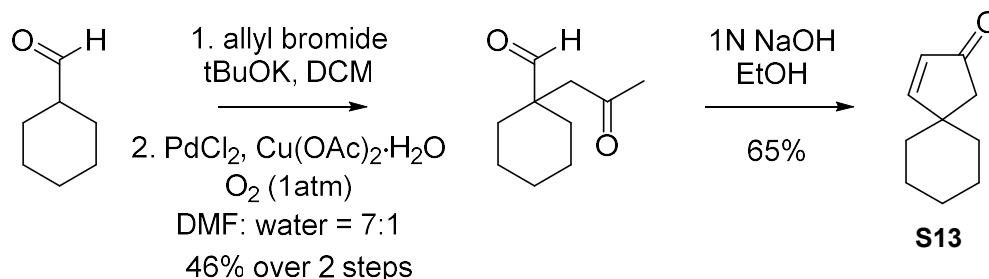
$$\rho = -1.89$$



$$\rho = -3.08$$

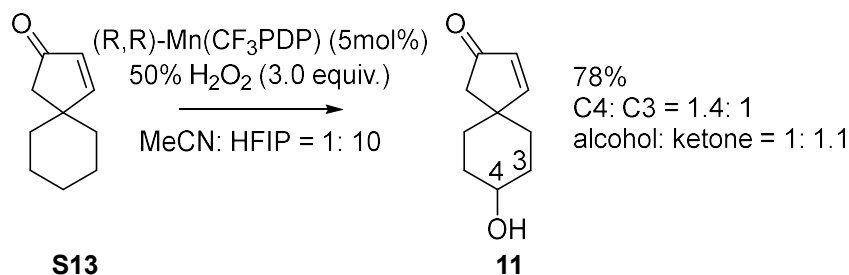
Figure S28. Hammett Plots: MeCN/Cl-AcOH vs. HFIP/no acid

VI. Experimental Procedures and Compound Characterization for Figure 2



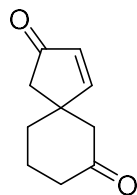
Preparation of spiro[4.5]dec-3-en-2-one [S13]. To a stirred solution of cyclohexylcarbaldehyde (95% purity, 5 g, 42 mmol, 1.0 equiv.) and allyl bromide (11 ml, 127 mmol, 3.0 equiv.) in DCM (84 ml, 0.5 M) was added tBuOK (8.4 g, 75 mmol, 1.8 equiv.) at 0°C under open air. Once the effervescence ceased, the reaction mixture was sealed with a septum. The mixture gradually warmed to room temperature over 4 hours, and the reaction was monitored by TLC (silica gel, EA: hexane = 1: 9). Upon completion, the reaction was quenched with saturated KH₂PO₄ solution, extracted with DCM, and dried over Na₂SO₄. The crude product was concentrated and used directly without further purification. To a stirred solution of the resulting crude (*ca.* 40mmol) in dimethyl acetamide: H₂O = 7: 1 (57 ml, 0.7 M) was added PdCl₂ (709 mg, 4 mmol, 0.1 equiv.) and Cu(OAc)₂·H₂O (1.6 g, 8 mmol, 0.2 equiv.). The mixture was stirred for 15 hours at 60°C under an oxygen atmosphere (1 atm, balloon). Upon completion, brine was added, and the organic layer was extracted with hexane and dried over MgSO₄. The mixture was concentrated in vacuo and purified by flash column chromatography (silica gel, EA: hexane = 1: 2) to afford 1-(2-oxopropyl)cyclohexane-1-carbaldehyde as a yellow oil (3.3 g, 19.3 mmol, 46% over 2 steps). Spectroscopic data matched the published literature¹⁶.

To a stirred solution of 1-(2-oxopropyl)cyclohexane-1-carbaldehyde (3.1 g, 18.4 mmol, 1.0 equiv.) in ethanol (184 ml, 0.1 M) was added 1N NaOH (27.6 ml, 27.6 mmol, 1.5 equiv.) at room temperature. The mixture was stirred for 5 hours, and the reaction was monitored by TLC (silica gel, EA: hexane = 1: 3). Upon completion, the reaction mixture was concentrated, reducing the volume to approximately 10% of the original, removing most of the ethanol. The reaction was then quenched with saturated NH₄Cl aqueous solution, and the organic layer was extracted with hexane and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by vacuum distillation (Welch DuoSeal vacuum pump, ultimate pressure: 1×10^{-4} Torr, head temperature: 150-160°C) to afford spiroenone **S13** as a clear oil (1.8 g, 11.9 mmol, 65%). Spectroscopic data matched the published literature¹⁷.



Oxidation of spiro[4.5]dec-3-en-2-one [S13]. spiro[4.5]dec-3-en-2-one in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) and 3.0 equiv. of H₂O₂. The resulting mixture was purified with column chromatography (EA: hexane = 1: 2 → EA: hexane = 2: 1 → EA: hexane: MeOH = 200: 100: 20). **Run 1:** 77% yield, alcohol: ketone = 1: 1.1, C4: C3 = 1.4: 1. **Run 2:** 79% yield, alcohol: ketone = 1: 1.1, C4: C3 = 1.4: 1. **Run 3:** 79% yield, alcohol: ketone = 1: 1.1, C4: C3 = 1.4: 1. **Average:** 78% ± 0.8% yield, alcohol: ketone = 1: 1.1, C4: C3 = 1.4: 1.

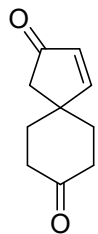
spiro[4.5]dec-3-ene-2,7-dione [11-C3ketone]. ^1H NMR (500 MHz, CDCl_3) δ 7.48 (d, $J = 5.6$ Hz,



1H), 6.12 (d, $J = 5.6$ Hz, 1H), 2.50 (d, $J = 13.3$ Hz, 1H), 2.47 – 2.35 (m, 2H), 2.26 (dt, $J = 13.5, 1.7$ Hz, 1H), 2.23 (s, 2H), 2.15 – 2.07 (m, 1H), 1.95 – 1.83 (m, 2H), 1.77 – 1.71 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.81, 207.48, 168.90, 132.86, 51.66,

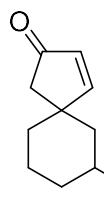
49.68, 46.33, 40.83, 35.58, 23.85. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 165.0916, found 165.0919.

spiro[4.5]dec-3-ene-2,8-dione [11-C4ketone]. ^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, $J = 5.6$ Hz,



1H), 6.18 (d, $J = 5.6$ Hz, 1H), 2.47 (s, 2H), 2.55 – 2.39 (m, 4H), 2.06 – 1.97 (m, 2H), 1.91 – 1.84 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.49, 207.88, 170.20, 133.04, 45.85, 45.10, 38.82, 36.75. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 165.0916, found 165.0915.

7-hydroxyspiro[4.5]dec-3-en-2-one [11-C3OH]. Only one diastereomer was observed. ^1H NMR

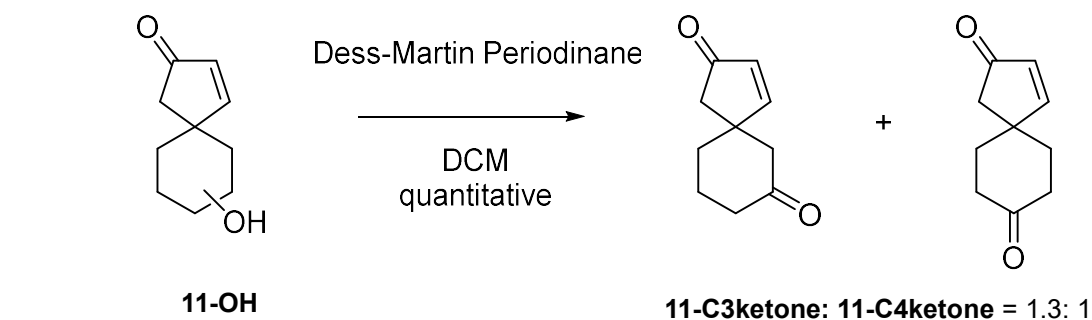


(500 MHz, CDCl_3) δ 7.47 (d, $J = 5.6$ Hz, 1H), 6.06 (d, $J = 5.6$ Hz, 1H), 3.70 (tt, $J = 10.5, 4.2$ Hz, 1H), 2.22 (d, $J = 18.5$ Hz, 1H), 2.17 (d, $J = 18.5$ Hz, 1H), 2.03 – 1.97 (m, 1H), 1.86 – 1.80 (m, 1H), 1.76 (br s, 1H), 1.72 (ddt, $J = 12.5, 4.1, 2.0$ Hz, 1H),

1.49 – 1.33 (m, 4H), 1.29 – 1.21 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.33, 172.99, 131.76, 68.46, 46.82, 46.81, 45.05, 35.75, 34.69, 21.79. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 167.1072, found 167.1078.

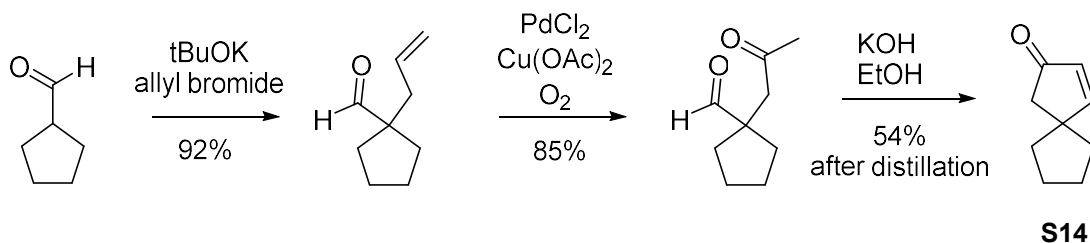
8-hydroxyspiro[4.5]dec-3-en-2-one [11-C4OH]. Only one diastereomer was observed. ^1H NMR

(500 MHz, CDCl_3) δ 7.43 (d, $J = 5.6$ Hz, 1H), 6.06 (d, $J = 5.5$ Hz, 1H), 3.67 (tt, $J = 10.4$, 4.2 Hz, 1H), 2.25 (s, 2H), 2.04 – 1.93 (m, 2H), 1.65 (br s, 1H), 1.62 – 1.48 (m, 4H), 1.43 – 1.34 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.37, 172.97, 132.11, 69.62, 46.51, 45.45, 34.68, 32.62. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 167.1072, found 167.1068.



Regioisomeric ratio determination of alcohols 11-OH. To a stirred solution of **11-OH** (3.7mg, 0.022mmol) in DCM (0.4ml, 0.05M) was added DMP (12.3mg, 0.029mmol, 1.3equiv.) at rt. The mixture was stirred for 1.5hrs, and the completion of the reaction was confirmed by TLC analysis (EA: hexane = 2: 1, silica TLC). The resulting mixture was concentrated, and hexane was added to the mixture. After white solid byproduct was precipitated, the organic portion was collected and concentrated. Flash column chromatography on silica (EA: hexane = 2: 1) furnished the mixture of **11-C3ketone** and **11-C4ketone**. The resulting mixture was further purified with short alumina (basic, Brockmann grade II) pad filtration (EA: hexane = 2: 1), furnishing 3.4mg of the mixture of **11-C3ketone** and **11-C4ketone** (0.022mmol, quantitative), The regioisomeric ratio was

determined to be **11-C3ketone: 11-C4ketone** = 1.34: 1 by quantitative ^1H NMR (relaxation delay (d1) = 10s).

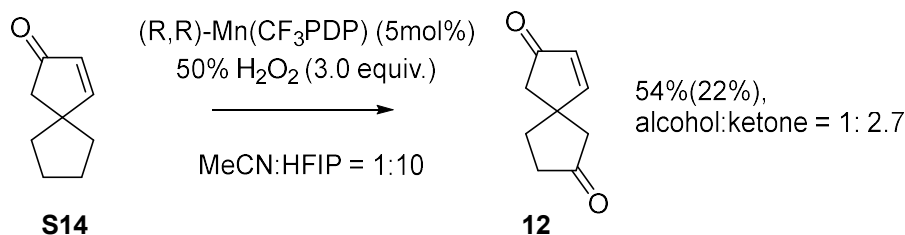


Synthesis of spiro[4.4]non-3-en-2-one [S14]. To a stirred solution of cyclopentylcarbaldehyde (3.1 ml, 30 mmol, 1.0 equiv.) and allyl bromide (7.8 ml, 90 mmol, 3.0 equiv.) in DCM (60 ml, 0.5 M) was added tBuOK (6.1 g, 54 mmol, 1.8 equiv.) at 0°C under open air. Once effervescence ceased, the reaction mixture was sealed with a septum. The mixture gradually warmed to room temperature over 15 hours, and the reaction was monitored by TLC (silica gel, EA: hexane = 1: 8). Upon completion, the reaction was quenched with saturated KH_2PO_4 solution, extracted with hexane, and dried over Na_2SO_4 . The crude product was concentrated in vacuo and purified by vacuum distillation (Welch DuoSeal vacuum pump, ultimate pressure: 1×10^{-4} Torr, head temperature: 130-140°C) to afford 1-allylcyclopentane-1-carbaldehyde as a clear oil (3.8 g, 27.5 mmol, 92%).

To a stirred solution of 1-allylcyclopentane-1-carbaldehyde (730 mg, 5.3 mmol, 1.0 equiv.) in DMF: H_2O = 7: 1 (10.6 ml, 0.5 M) was added PdCl_2 (95 mg, 0.53 mmol, 0.1 equiv.) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (211.6 g, 1.06 mmol, 0.2 equiv.). The mixture was stirred for 1 day at 60°C under an oxygen atmosphere (1 atm, balloon). The reaction was monitored by TLC (silica gel, EA: hexane = 1: 3). Upon completion, brine was added, and the organic layer was extracted with hexane and dried over MgSO_4 . The mixture was concentrated in vacuo and purified by flash column

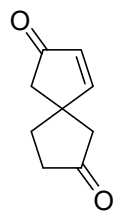
chromatography (silica gel, ether: pentane = 1: 2) to afford 1-(2-oxopropyl)cyclopentane-1-carbaldehyde as a colorless oil (690 mg, 4.5 mmol, 85%).

To a stirred solution of 1-(2-oxopropyl)cyclopentane-1-carbaldehyde (830 mg, 5.4 mmol, 1.0 equiv.) in ethanol (100 ml, 0.05 M) was added 1N NaOH (6.4 ml, 6.4 mmol, 1.2 equiv.) at room temperature. The mixture was stirred for 15 hours, and the reaction was monitored by TLC (silica gel, EA: hexane = 1: 3). Upon completion, the reaction mixture was concentrated, reducing the volume to approximately 10% of the original, removing most of the ethanol. The reaction was then diluted with water, and the organic layer was extracted with hexane and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by vacuum distillation (Welch DuoSeal vacuum pump, ultimate pressure: 1×10^{-4} Torr, head temperature: 150-160°C) to afford spiroenone **S14** as a clear oil (393 g, 2.89 mmol, 54%). Spectroscopic data matched the published literature¹⁸.



Oxidation of spiro[4.4]non-3-en-2-one [S14]. spiro[4.4]non-3-en-2-one **S14** was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) and 3.0 equiv. of H₂O₂. The resulting mixture was purified with column chromatography (EA: hexane = 1: 2 → EA: hexane = 3: 1 → EA only). **Run 1:** 7% RSM, 80% yield, alcohol: ketone = 1: 1.6. **Run 2:** 20% RSM, 53% yield, alcohol: ketone = 1: 2.5. **Run 3:** 22% RSM, 56% yield, alcohol: ketone = 1: 2.5. **Average:** 22% RSM ± 1.2%, 54% ± 2.1% yield, alcohol: ketone = 1: 2.7.

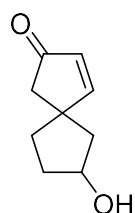
spiro[4.4]non-3-ene-2,7-dione [12-ketone]. ^1H NMR (500 MHz, CDCl_3) δ 7.52 (d, J = 5.5 Hz,



1H), 6.16 (d, J = 5.5 Hz, 1H), 2.48 – 2.25 (m, 6H), 2.15 (dt, J = 12.9, 9.3 Hz, 1H), 2.01 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 215.82, 207.69, 168.62, 133.51, 50.18, 49.29, 47.84, 37.49, 35.54. HRMS (TOF ESI+) m/z calculated for $\text{C}_9\text{H}_{11}\text{O}_2$ $[\text{M}+\text{H}]^+$: 151.0759,

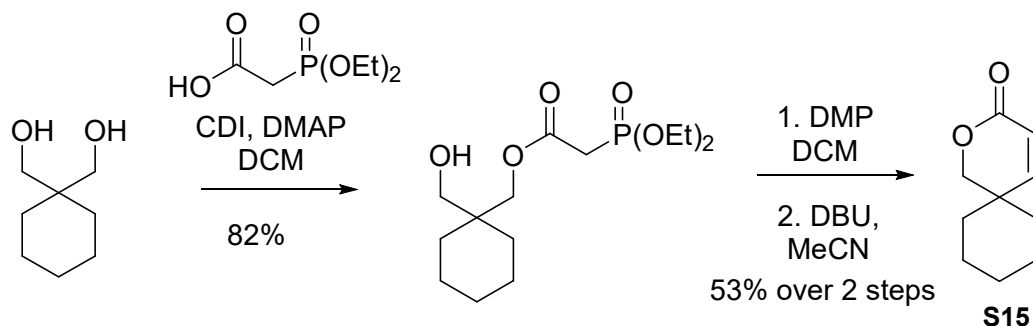
found 151.0764.

7-hydroxyspiro[4.4]non-3-en-2-one [12-OH]. Diastereomeric mixture (d.r. = 1: 1). ^1H NMR



(500 MHz, CDCl_3) δ 7.64 (d, J = 5.6 Hz, 0.5H), 7.41 (d, J = 5.6 Hz, 0.5H), 6.04 (d, J = 5.5 Hz, 0.5H), 6.02 (d, J = 5.5 Hz, 0.5H), 4.55 – 4.48 (m, 1H), 2.60 (d, J = 18.8 Hz, 0.5H), 2.42 (d, J = 18.8 Hz, 0.5H), 2.32 (d, J = 18.5 Hz, 0.5H), 2.26 (d, J = 18.4

Hz, 0.5H), 2.22 – 2.13 (m, 0.5H), 2.11 – 1.90 (m, 2H), 1.90 – 1.58 (m, 4.5H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.27 (209.75), 172.46 (171.45), 131.98 (131.47), 73.60 (73.56), 51.49 (51.37), 50.40 (49.85), 48.46 (48.31), 37.97 (37.17), 35.82 (35.56). HRMS (TOF ESI+) m/z calculated for $\text{C}_9\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 153.0916, found 153.0917.



Preparation of 2-oxaspiro[5.5]undec-4-en-3-one [S15]. Cyclohexane-1,1-diyldimethanol was prepared according to the reported literature¹⁹. To a stirred solution of 2-(diethoxyphosphinyl)acetic acid (96% purity, 2.1g, 10.2 mmol, 0.8 equiv.) in THF (1 ml, 10 M) was added CDI (1.7 g, 10.2 mmol, 0.8 equiv.) at room temperature under open air. Once

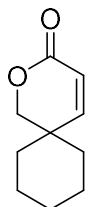
effervescence ceased, the reaction mixture was sealed with a septum and stirred for 30 minutes under nitrogen atmosphere. Cyclohexane-1,1-diylidimethanol (1.8 g, 12.7 mmol, 1.0 equiv.) was introduced to the activated acid and rinsed with ca. 2ml of THF, followed by the addition of DMAP (465 mg, 3.8 mmol, 0.3 equiv.). The resulting mixture was stirred for 15 hours at room temperature, and the reaction was monitored by TLC (silica gel, EA: DCM = 1: 1). Upon completion, the reaction was concentrated in vacuo and purified by flash column chromatography (silica gel, EA: DCM = 1: 1 → EA: DCM: MeOH = 10: 10: 1) to afford (1-(hydroxymethyl)cyclohexyl)methyl 2-(diethoxyphosphoryl)acetate (2.7g, 8.4 mmol, 82% yield) as a yellow oil.

To a stirred solution of (1-(hydroxymethyl)cyclohexyl)methyl 2-(diethoxyphosphoryl)acetate (2.7g, 8.4 mmol, 1.0 equiv.) in DCM (17 ml, 0.5 M) was added Dess-Martin Periodinane (4.6 g, 10.9 mmol, 1.3 equiv.) at room temperature. The reaction mixture was sealed with a septum and stirred for 30 minutes under nitrogen atmosphere, with progress monitored by TLC (silica gel, EA: DCM: MeOH = 10: 10: 1). Upon completion, the reaction was concentrated in vacuo and filtered through a celite pad with ether. The organic filtrate was collected, concentrated in vacuo and purified by flash column chromatography (silica gel, EA: DCM = 1: 1) to afford (1-formylcyclohexyl)methyl 2-(diethoxyphosphoryl)acetate (2.1 g, 6.7 mmol, 80% yield) as a yellow oil.

To a stirred solution of (1-formylcyclohexyl)methyl 2-(diethoxyphosphoryl)acetate (1 g, 3.2 mmol, 1.0 equiv.) in MeCN (5 ml, 0.64 M) was added DBU (1.2 ml, 8.3 mmol, 2.6 equiv.) at room temperature. The reaction mixture was sealed with a septum and stirred for 3 hours under nitrogen atmosphere, with progress monitored by TLC (silica gel, EA: DCM = 1: 1). Upon completion, the reaction was quenched with saturated NH_4Cl aqueous solution, and the organic layer was extracted with DCM, and dried over Na_2SO_4 . The crude product was concentrated in vacuo and purified by

flash column chromatography (ether:pentane = 1: 1.5) to afford lactone **S15** (350 mg, 2.1 mmol, 66% yield) as a white solid.

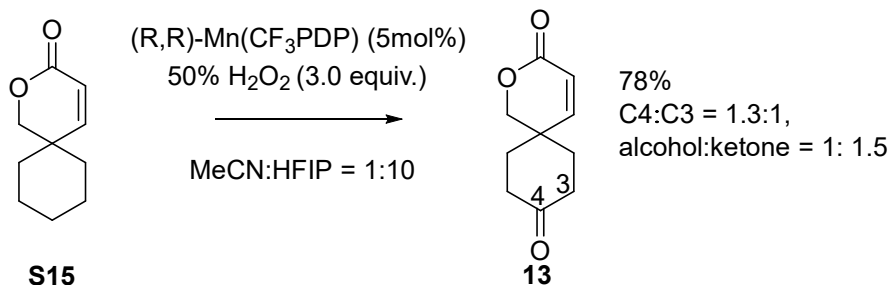
2-oxaspiro[5.5]undec-4-en-3-one [S15]. ^1H NMR (500 MHz, CDCl_3) δ 6.85 (d, J = 9.8 Hz, 1H),



5.91 (d, J = 9.9 Hz, 1H), 4.16 (d, J = 1.0 Hz, 2H), 1.59 – 1.43 (m, 10H). ^{13}C NMR (126

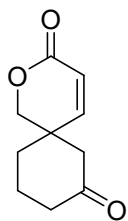
MHz, CDCl_3) δ 164.24, 155.06, 119.19, 75.22, 35.15, 33.05, 25.73, 21.50. HRMS (TOF

ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 167.1072, found 167.1077.



Oxidation of 2-oxaspiro[5.5]undec-4-en-3-one [S15]. 2-oxaspiro[5.5]undec-4-en-3-one **S15** in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)- $\text{Mn}(\text{CF}_3\text{-PDP})$ and 3.0 equiv. of H_2O_2 . The resulting mixture was purified with column chromatography (EA: hexane = 2: 1 $\rightarrow$ EA: hexane: MeOH = 200: 100: 20). **Run 1:** 80% yield, alcohol: ketone = 1: 1.6, C4: C3 = 1.3: 1. **Run 2:** 79% yield, alcohol: ketone = 1: 1.5, C4: C3 = 1.3: 1. **Run 3:** 75% yield, alcohol: ketone = 1: 1.4, C4: C3 = 1.2: 1. **Average:** 78% $\pm$ 2.1%, alcohol: ketone = 1: 1.5, C4: C3 = 1.3: 1.

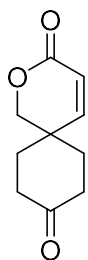
2-oxaspiro[5.5]undec-4-ene-3,8-dione [13-C3ketone]. ^1H NMR (500 MHz, CDCl_3) δ 6.71 (d, J



= 9.9 Hz, 1H), 5.97 (d, J = 9.8 Hz, 1H), 4.19 (dd, J = 11.3, 1.3 Hz, 1H), 4.12 (d, J = 11.3 Hz, 1H), 2.45 – 2.40 (m, 2H), 2.36 (s, 2H), 2.01 – 1.93 (m, 3H), 1.89 – 1.82 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 207.68, 162.83, 151.51, 120.42, 74.16, 47.34,

40.95, 39.69, 32.28, 21.87. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{13}\text{O}_3$ $[\text{M}+\text{H}]^+$: 181.0865, found 181.0863.

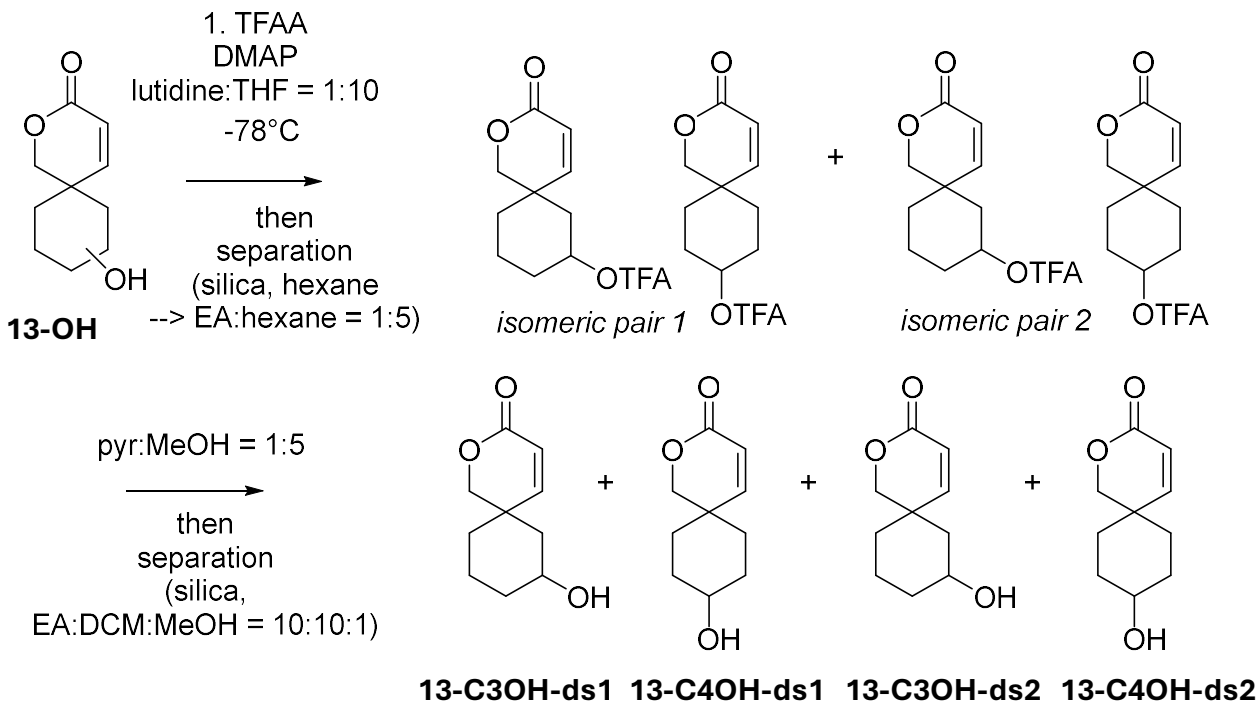
2-oxaspiro[5.5]undec-4-ene-3,9-dione [13-C4ketone]. ^1H NMR (500 MHz, CDCl_3) δ 6.95 (dt, J



= 10.0, 1.1 Hz, 1H), 6.07 (d, J = 9.8 Hz, 1H), 4.33 (d, J = 1.1 Hz, 2H), 2.51 – 2.39 (m, 4H), 2.03 – 1.88 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.58, 163.27, 151.76, 120.94,

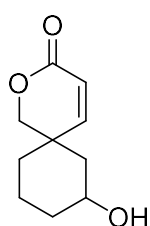
73.85, 36.84, 34.41, 32.32. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{13}\text{O}_3$ $[\text{M}+\text{H}]^+$:

181.0865, found 181.0864.



Separation and Identification of alcohol mixture 13-OH. To a stirred solution of the mixture of alcohols (8 mg, 0.044 mmol, 1.0 equiv.) in a 2,6-lutidine = 1: 10 mixture (0.3 mL, 0.15 M) were added DMAP (2.7 mg, 0.022 mmol, 0.5 equiv.) and trifluoroacetic anhydride (TFAA, 0.012 mL, 0.088 mmol, 2 equiv.) at -78°C under a nitrogen atmosphere. The mixture was stirred at -78°C for 10 minutes, then concentrated in vacuo. The resulting mixture was separated by MPLC (Teledyne Combiflash® system, hexane only → EA: hexane = 1: 5) to afford TFA ester isomeric pair 1 (3.3 mg, 0.012 mmol, 27% yield) and TFA ester isomeric pair 2 (4.1 mg, 0.015 mmol, 34% yield, 60% total yield for the TFA protection step). Each isomeric pair was dissolved in a pyridine: MeOH = 1: 5 mixture (0.05M) and stirred for 30 minutes at room temperature. The full consumption of the TFA ester was monitored by TLC (silica gel, EA: hexane = 1: 3). Upon completion, each reaction mixture was concentrated and purified separately by MPLC (Teledyne Combiflash® system, EA: DCM = 1: 1 → EA: DCM: MeOH = 10: 10: 1), yielding all four diastereomers of the alcohol product, with TFA deprotection yields ranging from 60% to 80%.

8-hydroxy-2-oxaspiro[5.5]undec-4-en-3-one. [13-C3OH-ds1]. ¹H NMR (600 MHz, CDCl₃) δ



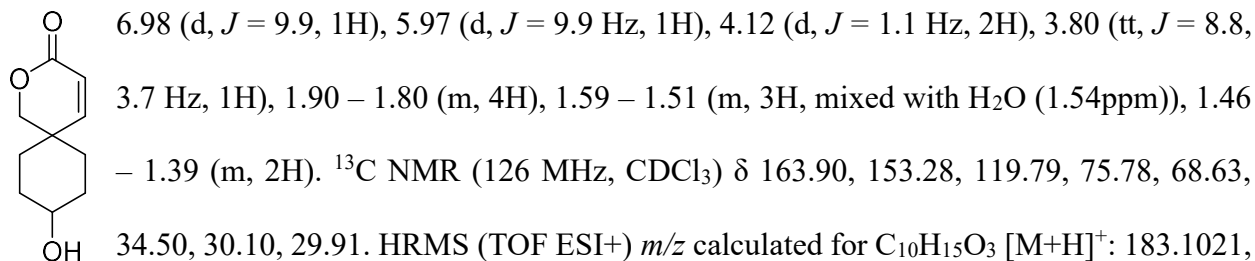
6.84 (d, *J* = 9.8 Hz, 1H), 5.90 (d, *J* = 9.8 Hz, 1H), 4.19 (dd, *J* = 11.3, 0.7 Hz, 1H), 4.17 (app d, *J* = 11.2 Hz, 1H), 3.92 – 3.86 (m, 1H), 1.92 – 1.87 (m, 1H), 1.87 – 1.81 (m, 2H), 1.60 – 1.55 (m, 1H), 1.52 – 1.46 (m, 2H), 1.46 – 1.37 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 163.96, 155.63, 118.90, 73.89, 66.35, 40.97, 36.35, 34.30,

31.52, 19.05. HRMS (TOF ESI+) *m/z* calculated for C₁₀H₁₅O₃ [M+H]⁺: 183.1021, found 183.1019.

[13-C3OH-ds2]. ¹H NMR (500 MHz, CDCl₃) δ 6.85 (dd, *J* = 9.8, 1.2 Hz, 1H), 5.95 (d, *J* = 9.9 Hz, 1H), 4.25 (d, *J* = 11.0 Hz, 1H), 4.18 (d, *J* = 11.0 Hz, 1H), 3.91 (tt, *J* = 8.6, 3.9 Hz, 1H), 2.01 – 1.87 (m, 2H), 1.87 – 1.78 (m, 1H), 1.62 – 1.48 (m, 3H, mixed with H₂O (1.54ppm)), 1.46 – 1.37

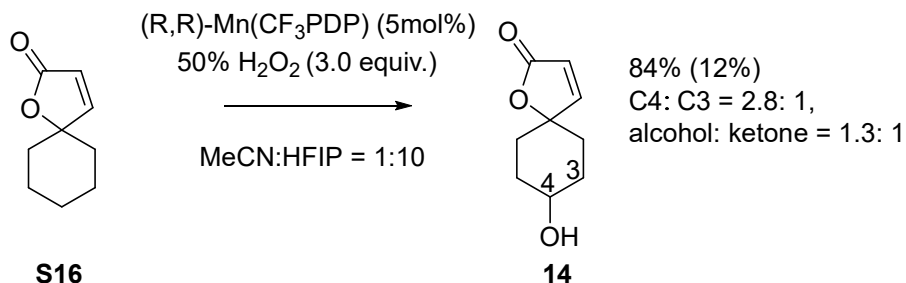
(m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.81, 153.26, 119.94, 76.55, 66.39, 41.65, 36.37, 34.58, 32.10, 18.77. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 183.1021, found 183.1023.

9-hydroxy-2-oxaspiro[5.5]undec-4-en-3-one [13-C4OH-ds1]. ^1H NMR (500 MHz, CDCl_3) δ



[13-C4OH-ds2]. ^1H NMR (500 MHz, CDCl_3) δ 6.71 (d, $J = 9.9$, 1H), 5.93 (d, $J = 9.8$ Hz, 1H), 4.25 (d, $J = 1.0$ Hz, 2H), 3.85 – 3.75 (m, 1H), 1.90 – 1.77 (m, 4H), 1.57 – 1.45 (m, 5H, mixed with H_2O (1.54ppm)). ^{13}C NMR (126 MHz, CDCl_3) δ 164.02, 154.76, 119.84, 73.65, 68.44, 34.55, 30.02, 29.64. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 183.1021, found 183.1028.

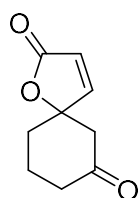
Preparation of 1-oxaspiro[4.5]dec-3-en-2-one [S16]. S16 was prepared according to the reported literature²⁰. Spectroscopic data matched the published literature²¹.



Oxidation of 1-oxaspiro[4.5]dec-3-en-2-one [S16]. 1-oxaspiro[4.5]dec-3-en-2-one (60.9mg, 0.4mmol) in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-

PDP) and 3.0 equiv. of H₂O₂. The resulting mixture was purified with column chromatography (EA: DCM: MeOH = 20: 30: 1). **Run 1:** 10% RSM, 82% yield, alcohol: ketone = 1.2: 1, C4: C3 = 2.7: 1. **Run 2:** 11% RSM, 85% yield, alcohol: ketone = 1.4: 1, C4: C3 = 2.8: 1. **Run 3:** 14% RSM, 84% yield, alcohol: ketone = 1.3: 1, C4: C3 = 2.9: 1. **Average:** 12% RSM $\pm$ 1.7%, 84% $\pm$ 1.2% yield, alcohol: ketone = 1.3: 1, C4: C3 = 2.8: 1.

1-oxaspiro[4.5]dec-3-ene-2,7-dione [14-C3ketone]. ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* =

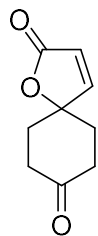


5.6 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 2.64 (dt, *J* = 15.0, 0.9 Hz, 1H), 2.57 – 2.45 (m, 2H), 2.38 (dddd, *J* = 14.7, 11.2, 5.9, 1.0 Hz, 1H), 2.28 – 2.16 (m, 1H), 2.11 – 1.98 (m, 2H), 1.97 – 1.89 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 205.40, 171.18, 157.59,

121.57, 89.71, 49.02, 40.06, 33.57, 21.39. HRMS (TOF ESI+) *m/z* calculated for C₉H₁₁O₃ [M+H]⁺:

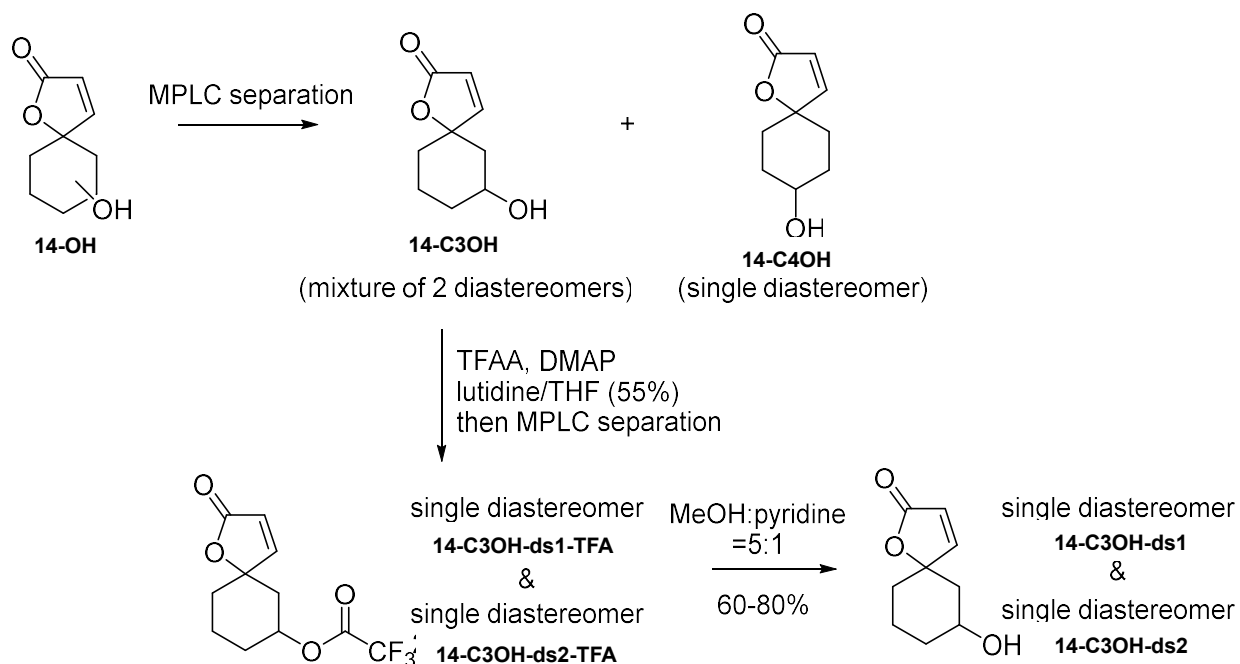
167.0708, found 167.0715.

1-oxaspiro[4.5]dec-3-ene-2,8-dione [14-C4ketone]. ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, *J* =



5.7 Hz, 1H), 6.14 (d, *J* = 5.6 Hz, 1H), 2.85 (td, *J* = 14.3, 6.3 Hz, 2H), 2.46 (ddt, *J* = 15.1, 4.6, 2.0 Hz, 2H), 2.19 (td, *J* = 13.8, 5.1 Hz, 2H), 2.02 (ddt, *J* = 14.8, 6.1, 3.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 208.52, 171.78, 159.05, 121.43, 86.13, 37.56, 34.61.

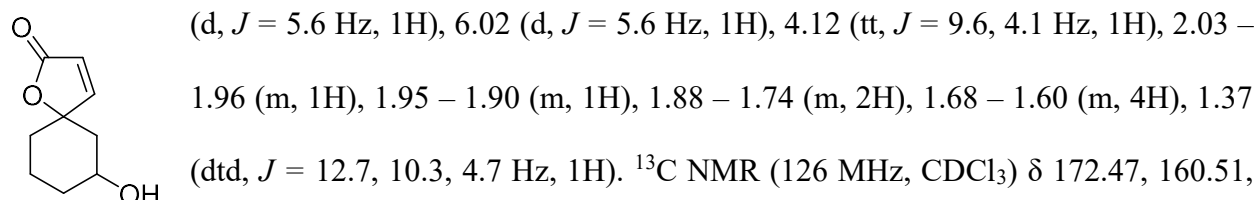
HRMS (TOF ESI+) *m/z* calculated for C₉H₁₁O₃ [M+H]⁺: 167.0708, found 167.0716.



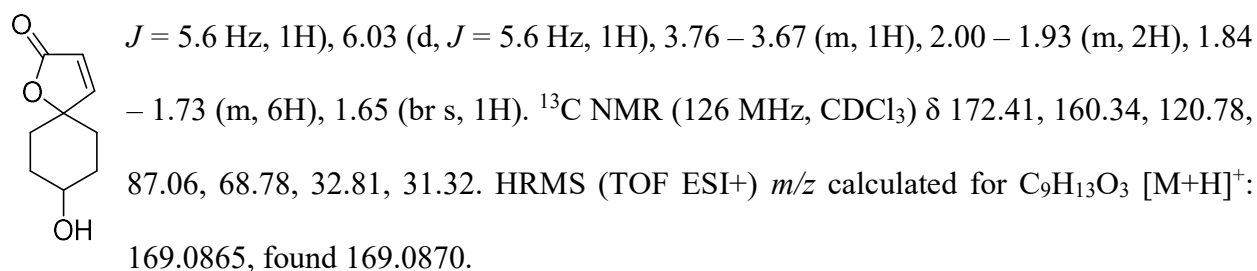
Separation and Identification of alcohol mixture 14-OH. Alcohol mixture **14-OH** was subject to MPLC (Teledyne Combiflash® system, EA: DCM: MeOH = 100: 100: 4) furnishing **14-C3OH** (mixture of 2 diastereomers) and **14-C4OH** (single diastereomer). To a stirred mixture of **14-C3OH** (7.0 mg, 0.042 mmol, 1.0 equiv.) in 2,6-lutidine/THF = 1: 10 mixture (0.4 ml, 0.1 M) was added DMAP (2.6 mg, 0.021 mmol, 0.5equiv.) and TFAA (0.01 ml, 0.063 mmol, 1.5 equiv.) at -78°C. The mixture was stirred for 5 min at -78°C. The completion of the reaction was confirmed by TLC analysis (silica, ether: MeOH = 10: 1). Upon completion, the reaction mixture was concentrated and directly purified with flash column chromatography (silica, ether: pentane=1: 1) to yield **14-C3OH-ds1-TFA** and **14-C3OH-ds2-TFA** (6.1 mg in total, 0.023 mmol, 55% total yield). Each TFA ester was separately dissolved in a pyridine: MeOH = 1: 5 mixture (0.05M) and stirred for 30 minutes at room temperature. The full consumption of the TFA ester was monitored by TLC analysis (silica, ether: MeOH = 10: 1). Upon completion, each reaction mixture was concentrated and purified separately by flash column chromatography (silica, ether: MeOH = 10:

1), yielding two diastereomers of the γ - alcohols **14-C3OH-ds1** and **14-C3OH-ds2**, with TFA deprotection yields ranging from 60% to 80%.

7-hydroxy-1-oxaspiro[4.5]dec-3-en-2-one [14-C3OH-ds1]. ^1H NMR (500 MHz, CDCl_3) δ 7.48



8-hydroxy-1-oxaspiro[4.5]dec-3-en-2-one [14-C4OH]. ^1H NMR (500 MHz, CDCl_3) δ 7.37 (d,



Confirmation of diastereomer. X-ray crystallography analysis of the 4-chlorobenzoyl ester of **14-C4OH** confirmed that O1 of lactone is axial, 1,4-anti to 8-hydroxy group.

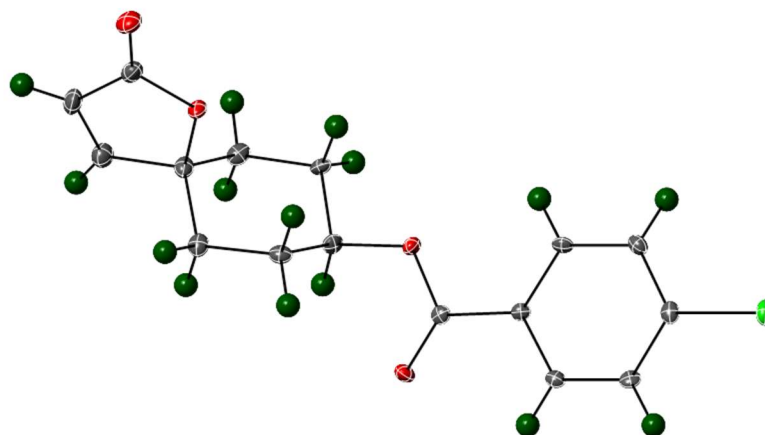
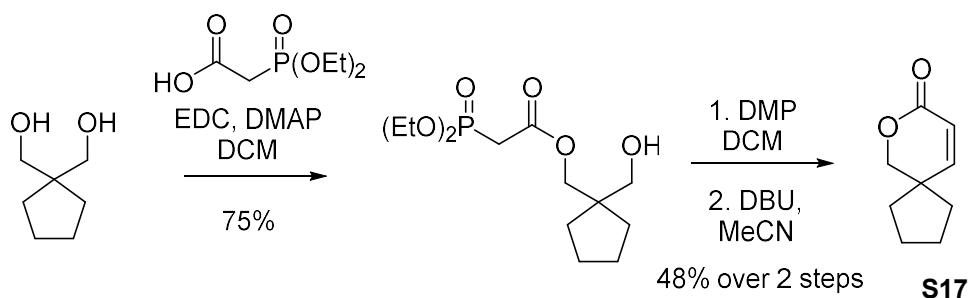


Figure S29. X-ray Crystal Data of **14-C4OH** 4-chlorobenzoyl ester.

Identification code	twin5	
Empirical formula	C _{17.75} H _{16.75} Cl O ₄	
Formula weight	329.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.3646(6) Å	a = 76.175(3)°.
	b = 10.9179(8) Å	b = 84.014(3)°.
	c = 20.3627(17) Å	g = 89.635(3)°.
Volume	1580.9(2) Å ³	

Z	4
Density (calculated)	1.384 Mg/m ³
Absorption coefficient	0.259 mm ⁻¹
F(000)	689
Crystal size	0.186 x 0.183 x 0.039 mm ³
Theta range for data collection	1.921 to 25.424°.
Index ranges	-8<=h<=8, -13<=k<=13, -24<=l<=24
Reflections collected	36926
Independent reflections	36925 [R(int) = ?]
Completeness to theta = 25.242°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745210 and 0.615480
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	36925 / 0 / 417
Goodness-of-fit on F ²	1.115
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1226
R indices (all data)	R1 = 0.0709, wR2 = 0.1272
Extinction coefficient	n/a
Largest diff. peak and hole	0.491 and -0.564 e.Å ⁻³



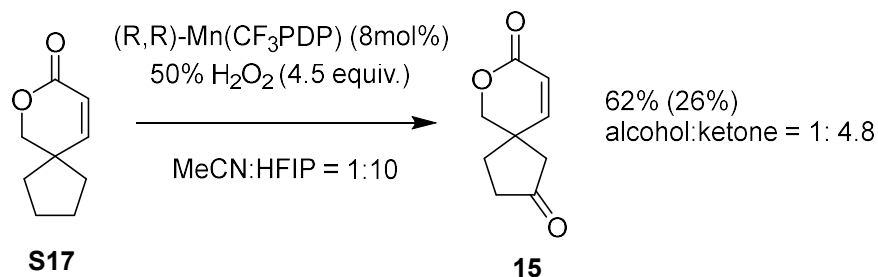
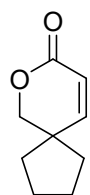
Synthesis of 7-oxaspiro[4.5]dec-9-en-8-one [S17]. Cyclopentane-1,1-diylmethanol was prepared according to the reported literature²². To a stirred solution of 2-(diethoxyphosphoryl)acetic acid (96% purity, 250 mg, 1.2 mmol, 0.5 equiv.) in DCM (12 ml, 0.2 M) was added EDC (236 mg, 1.2 mmol, 0.5 equiv.) and DMAP (30 mg, 0.25 mmol, 0.1 equiv.) at room temperature. After the reaction was stirred for 1 hr at room temperature, cyclopentane-1,1-diylmethanol (319 mg, 2.45 mmol, 1.0 equiv.) was added to the mixture. The resulting mixture was stirred for 30 hours at room temperature, and the reaction was monitored by TLC (silica gel, DCM: MeOH = 20: 1). Upon completion, the reaction was quenched with saturated NH_4Cl aqueous solution, and the organic layer was extracted with DCM and dried over MgSO_4 . The crude product was concentrated in vacuo and purified by reverse phase MPLC (Teledyne CombiFlash system on RediSep® Rf Reversed-phase C18 column, MeCN: water = 5: 95 $\rightarrow$ 40: 60) to afford (1-(hydroxymethyl)cyclopentyl)methyl 2-(diethoxyphosphoryl)acetate (284 mg, 0.92 mmol, 75% yield) as a colorless oil.

To a stirred solution of (1-(hydroxymethyl)cyclopentyl)methyl 2-(diethoxyphosphoryl)acetate (231 mg, 0.75 mmol, 1.0 equiv.) in DCM (7.5 ml, 0.1 M) was added Dess-Martin Periodinane (573 mg, 1.35 mmol, 1.8 equiv.) at room temperature. The reaction mixture was sealed with a septum and stirred for 12 hours under nitrogen atmosphere, with progress monitored by TLC (silica gel, EA: DCM: MeOH = 8: 8: 1). Upon completion, the reaction was diluted with hexane to precipitate oxidant-related byproduct. The resulting biphasic mixture

was filtered through celite with EA. The filtrate was collected, concentrated in vacuo and purified by flash column chromatography (silica gel, EA: DCM: MeOH = 10: 10: 1) to afford (1-formylcyclopentyl)methyl 2-(diethoxyphosphoryl)acetate (172 mg, 0.56 mmol, 75% yield) as a colorless oil.

To a stirred solution of (1-formylcyclopentyl)methyl 2-(diethoxyphosphoryl)acetate (439 mg, 1.4 mmol, 1.0 equiv.) in MeCN (143 ml, 0.01 M) was added DBU (0.4 ml, 2.9 mmol, 2.0 equiv.) at room temperature. The reaction mixture was sealed with a septum and stirred for 5 hours under argon atmosphere at 50°C, with progress monitored by TLC (silica gel, EA: hexane = 2: 1). Upon completion, the reaction was concentrated in vacuo and directly purified by flash column chromatography (EA: hexane = 1: 3) to afford lactone **S17** (141 mg, 0.9 mmol, 65% yield) as a clear oil.

7-oxaspiro[4.5]dec-9-en-8-one [S17]. ¹H NMR (500 MHz, CDCl₃) δ 6.74 (d, *J* = 9.6 Hz, 1H), 5.85 (d, *J* = 9.7 Hz, 1H), 4.11 (d, *J* = 1.0 Hz, 2H), 2.01 – 1.40 (m, 8H). ¹³C NMR (126 MHz, CDCl₃) δ 164.33, 156.07, 118.38, 74.43, 43.05, 35.04, 24.89. HRMS (TOF ESI+) *m/z* calculated for C₉H₁₃O₂ [M+H]⁺: 153.0916, found 153.0919.

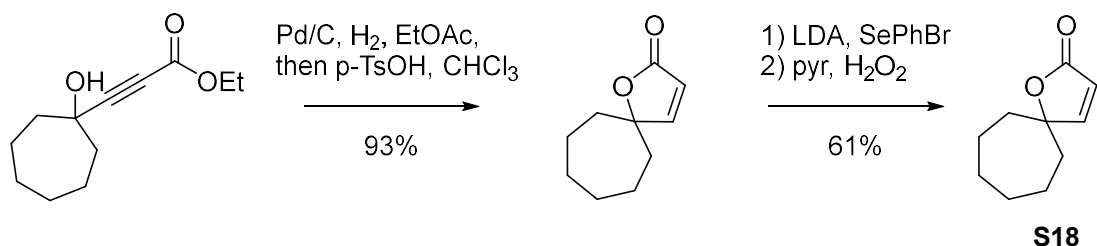


Oxidation of 7-oxaspiro[4.5]dec-9-en-8-one [S17]. 7-oxaspiro[4.5]dec-9-en-8-one (46 mg, 0.3 mmol) in HFIP was oxidized according to the Standard conditions with 8 mol% (*R,R*)-Mn(CF₃-

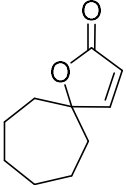
PDP) and 4.5 equiv. of H₂O₂. The resulting mixture was purified with two sequential column chromatography (First column purification - acetone: hexane = 1: 6 (RSM) → acetone: hexane = 1: 2 (product mixture). Second column purification with product mixture - EA: DCM = 1: 1 (ketone product) → acetone: hexane = 1: 2 (alcohol product)). **Run 1:** 28% RSM, 58% yield, alcohol: ketone = 1: 3.8. **Run 2:** 29% RSM, 62% yield, alcohol: ketone = 1: 5.9. **Run 3:** 22% RSM, 66% yield, alcohol: ketone = 1: 5. **Average:** 26% RSM ± 3.1%, 62% yield ± 3.3%, alcohol: ketone = 1: 4.8.

7-oxaspiro[4.5]dec-9-ene-2,8-dione [15-ketone]. ¹H NMR (500 MHz, CDCl₃) δ 6.81 (d, *J* = 9.6 Hz, 1H), 6.02 (d, *J* = 9.7 Hz, 1H), 4.28 (dd, *J* = 11.3, 1.2 Hz, 1H), 4.22 (d, *J* = 11.3 Hz, 1H), 2.49 – 2.38 (m, 2H), 2.38 – 2.33 (m, 2H), 2.22 (m, 1H), 2.04 (dt, *J* = 13.5, 9.1 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 214.35, 163.04, 152.41, 120.73, 73.38, 46.61, 40.36, 35.98, 30.24. HRMS (TOF ESI+) *m/z* calculated for C₉H₁₁O₃ [M+H]⁺: 167.0708, found 167.0714.

2-hydroxy-7-oxaspiro[4.5]dec-9-en-8-one [15-OH]. ¹H NMR (500 MHz, CDCl₃) δ 6.96 (d, *J* = 9.7 Hz, 0.5H), 6.70 (d, *J* = 9.7 Hz, 0.5H), 5.86 (dd, *J* = 9.7, 7.1 Hz, 1H), 4.48 (m, 1H), 4.36 (d, *J* = 11.0 Hz, 0.5H), 4.32 (d, *J* = 11.0 Hz, 0.5H), 4.11 (d, *J* = 0.9 Hz, 1H), 2.05 – 1.56 (m, 8H). ¹³C NMR (126 MHz, CDCl₃) δ 164.29, 164.14, 156.82, 155.63, 118.68, 117.97, 75.45, 74.83, 73.48, 73.41, 44.55, 44.04, 42.31, 42.23, 34.79, 34.70, 32.83, 32.39. HRMS (TOF ESI+) *m/z* calculated for C₉H₁₁O₃ [M+H]⁺: 169.0865, found 169.0871.



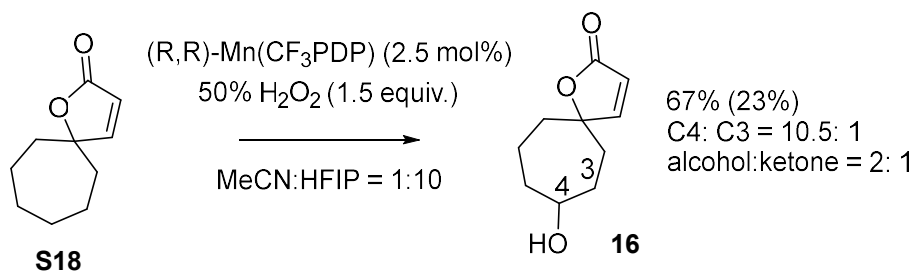
Preparation of 1-oxaspiro[4.6]undec-3-en-2-one [S18]. Ethyl 3-(1-



hydroxycycloheptyl)propiolate (1.g, 8.46 mmol, 1.0 equiv.) and 30% w/w palladium on carbon (75 mg, 0.21 mmol, 2.5 mol%) were added to a 100 mL round bottom flask equipped with a stir bar. The reaction vessel was evacuated & backfilled with argon, then 42 mL of ethyl acetate were added. The reaction vessel was evacuated & backfilled with hydrogen gas (balloon), and stirred under positive pressure of hydrogen for 4h until completion was confirmed by TLC analysis (silica, EA: hexane = 1: 2). The reaction was filtered through celite, and concentrated under reduced pressure. The crude reaction mixture was added to a 250 mL round bottom flask along with chloroform (80 mL) and p-toluenesulfonic acid (80 mg). The solution was stirred for 1h before completion was confirmed by TLC analysis (silica, EA: hexane = 1: 2). The reaction was quenched with aqueous sodium bicarbonate & extracted 3 times with dichloromethane. Combined organics were dried over sodium sulfate, filtered, and concentrated under reduced pressure to yield a crude mixture which was purified by flash column chromatography on silica (EA: hexane = 1: 6) to furnish 1-oxaspiro[4.6]undecan-2-one (1.327 g, 7.89 mmol, 93%).

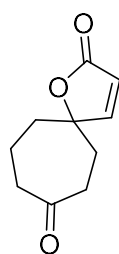
A solution of 2,2,6,6-tetramethylpiperidine (1.0 mL, 5.88 mmol, 1.1 equiv.) in THF (7.5 mL) was cooled to 0 °C, and n-BuLi (3.68 mL, 5.88 mmol, 1.1 equiv.) was added dropwise. After the solution was stirred for 30 minutes, it was cooled to -78 °C and a solution of 1-oxaspiro[4.6]undecan-2-one (900 mg, 5.35 mmol, 1.0 equiv.) in THF (3.75 mL) was added

dropwise. The reaction was stirred for 1 hour before the addition of cycloheptanone (2.4 mL, 20.0 mmol, 2.0 equiv.) The reaction was warmed slowly to 0 °C, stirred for an additional 30 minutes, then cooled again to -78 °C. A solution of phenylselenium bromide (1.64 g, 6.96 mmol, 1.3 equiv.) in THF (3.75 mL) was added dropwise and the reaction was stirred for 30 min until completion was confirmed by TLC analysis (silica, EA: hexane = 1: 9). The reaction was quenched with saturated aqueous ammonium chloride & extracted 3 times with dichloromethane. Combined organics were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude mixture was subjected to flash column chromatography on silica (EA: hexane = 1: 9), furnishing 3-(phenylselanyl)-1-oxaspiro[4.6]undecan-2-one (1.385 g, 4.28 mmol, 80% yield) as a clear oil. 3-(phenylselanyl)-1-oxaspiro[4.6]undecan-2-one (1.385 g, 4.28 mmol, 1.0 equiv.) was dissolved in dichloromethane (43 mL) in a 100 mL round bottom flask and pyridine (2.59 mL, 32.1 mmol, 7.5 equiv.) was added to the solution. A 50% w/w aqueous solution of hydrogen peroxide (0.9 mL, 15.9 mmol, 3.7 equiv.) was added dropwise to the reaction, which was then stirred for 1 hour until completion was confirmed by TLC analysis (silica, EA: hexane = 1: 4). Solvent was removed under reduced pressure, and the crude reaction mixture was directly loaded onto a silica flash column for purification (ethyl acetate: hexane = 1: 4), furnishing 1-oxaspiro[4.6]undec-3-en-2-one **S18** as a colorless oil (543 mg, 3.27 mmol, 76% yield). The spectroscopic data of **S18** matched those reported in the literature²³.

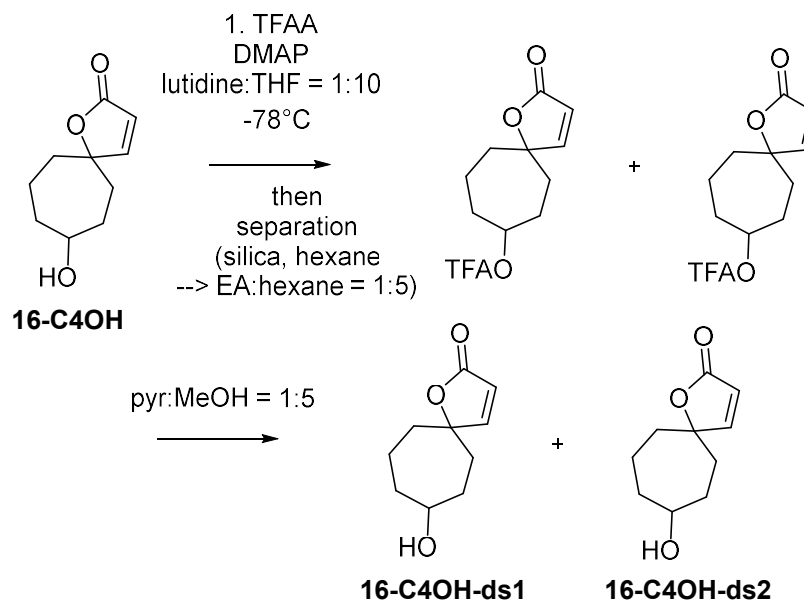


Oxidation of 1-oxaspiro[4.6]undec-3-en-2-one [S18]. 1-oxaspiro[4.6]undec-3-en-2-one in HFIP was oxidized according to the Standard conditions with 2.5 mol% (*R,R*)-Mn(CF₃-PDP) and 1.5 equiv. of H₂O₂. The resulting mixture was purified with column chromatography (ethyl acetate: hexane = 1: 2 → 2: 1 → 3: 1). **Run 1:** 21% RSM, 66% yield, alcohol: ketone = 2.3: 1, C3: C4 = 1: 10.5. **Run 2:** 23% RSM, 68% yield, alcohol: ketone = 1.7: 1, C3: C4 = 1: 10.5. **Run 3:** 25% RSM, 66% yield, alcohol: ketone = 1.9: 1, C3: C4 = 1: 10.5. **Average:** 23% RSM ± 1.6%, 67% yield ± 0.9%, alcohol: ketone = 2.0: 1, C3: C4 = 1: 10.5.

1-oxaspiro[4.6]undec-3-ene-2,8-dione [16-C4-ketone]. Product isolated with minor

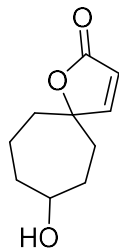


constitutional isomer present as impurity. ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 5.6 Hz, 1H), 6.02 (app dt, *J* = 5.6, 2.1 Hz, 1H), 3.07 (app ddq, *J* = 14.7, 11.8, 2.8 Hz, 1H), 2.68 – 2.60 (m, 1H), 2.51 – 2.39 (m, 2H), 2.25 – 2.14 (m, 1H), 2.01 – 1.78 (m, 5H). ¹³C NMR (126 MHz, CDCl₃) δ 212.56, 171.93, 160.34, 120.27, 89.21, 43.39, 38.55, 38.17, 32.73, 18.85. HRMS (TOF ES+) *m/z* calculated for C₁₀H₁₂O₃Na [M+Na]⁺ 203.0684, found 203.0688.

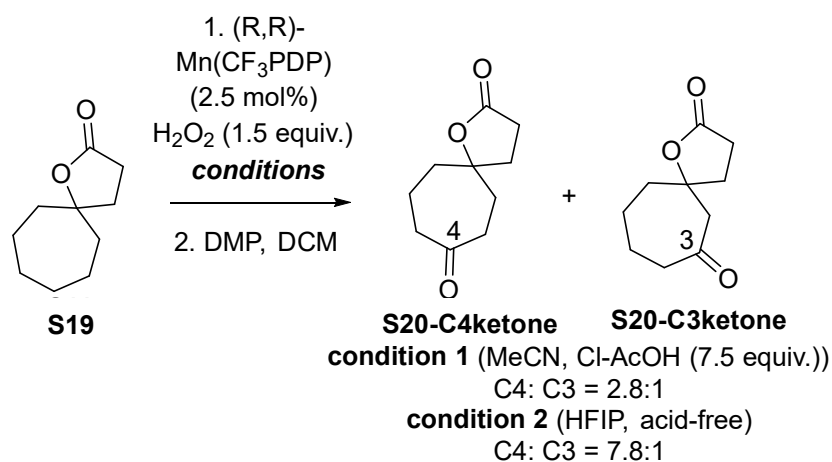


Separation and Identification of alcohol mixture 16-OH. To a stirred solution of a mixture of alcohols (32 mg, 0.176 mmol, 1.0 equiv.) in dichloromethane (1.8 mL, 0.1 M) were added DMAP (11 mg, 0.088 mmol, 0.5 equiv.) and trifluoroacetic anhydride (TFAA, 0.05 mL, 0.351 mmol, 2.0 equiv.) at -78°C under a nitrogen atmosphere. The mixture was stirred at -78°C for 10 minutes, then concentrated in vacuo. The resulting mixture was separated by flash column chromatography (silica gel, hexane only → EA: hexane = 1: 5) to afford each diastereomer of the corresponding TFA ester (major diastereomer: 23.4 mg, 48% yield; minor diastereomer: 10.0 mg, 20% yield). Each diastereomer was dissolved in a pyridine: MeOH = 1: 5 mixture (0.05M) and stirred for 30 minutes at room temperature. The full consumption of the TFA ester was monitored by TLC (silica gel, EA: hexane = 1: 3). Upon completion, each reaction mixture was concentrated and purified separately by flash column chromatography (silica gel, EA: hexanes = 2: 1), yielding both diastereomers of the alcohol product in quantitative yield.

8-hydroxy-1-oxaspiro[4.6]undec-3-en-2-one [16-C4OH]. Product isolated as a 2: 1 mixture of



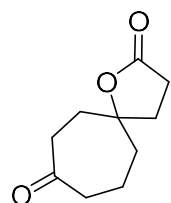
diastereomers, which were separated by flash column chromatography after trifluoroacetylation. The trifluoroacetates were converted back to alcohols following separation. Major diastereomer [**16-C4OH-ds1**]: ^1H NMR (500 MHz, CDCl_3) δ 7.42 (d, $J = 5.6$ Hz, 1H), 5.95 (d, $J = 5.5$ Hz, 1H), 3.95 – 3.87 (m, 1H), 2.05 – 1.83 (m, 6H), 1.83 – 1.64 (m, 4H), 1.52 – 1.41 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.58, 161.16, 119.54, 91.34, 71.68, 38.25, 37.41, 31.56, 31.29, 18.52. HRMS (TOF EI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 183.1021, found 183.1030. Minor diastereomer [**16-C4OH-ds2**]: ^1H NMR (500 MHz, CDCl_3) δ 7.47 (d, $J = 5.6$ Hz, 1H), 5.96 (d, $J = 5.6$ Hz, 1H), 4.10 – 4.02 (m, 1H), 2.18 – 2.02 (m, 3H), 1.89 – 1.82 (m, 2H), 1.79 – 1.65 (m, 4H), 1.62 – 1.46 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.64, 161.44, 119.43, 91.36, 70.66, 38.32, 38.07, 30.98, 30.15, 18.85. HRMS (TOF EI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 183.1021, found 183.1018.



Change in site-selectivity depending on oxidation conditions. 1-Oxaspiro[4.6]undecan-2-one [**S19**] was prepared according to the reported procedure²⁴. 1-Oxaspiro[4.6]undecan-2-one was

oxidized using either the Standard conditions or PDP/carboxylic acid condition in MeCN outlined in Table S1 with 2.5 mol% of catalyst **1** and 1.5 equivalents of H₂O₂. The resulting mixture was purified with column chromatography (ethyl acetate: hexane = 2: 1 → 3: 1). The purified mixtures, containing both alcohol and ketone oxidation products, were subsequently subjected to Dess-Martin Periodinane (DMP) oxidation to convert the alcohols into ketones. The site-selectivity ratios were confirmed by quantitative NMR analysis of the ketone mixtures. **In MeCN:** 20% RSM, 72% yield, alcohol: ketone = 1: 3.7, **C3: C4 = 1: 2.8**. **In HFIP:** 18% RSM, 74% yield, alcohol: ketone = 1.8: 1, **C3: C4 = 1: 7.8**.

1-oxaspiro[4.6]undecane-2,8-dione [S20-C4ketone]. ¹H NMR (500 MHz, CDCl₃) δ 2.93 (ddd,

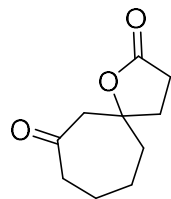


$J = 15.2, 11.7, 2.3$ Hz, 1H), 2.67 – 2.56 (m, 3H), 2.51 – 2.33 (m, 2H), 2.17 – 2.01 (m, 5H), 1.91 – 1.83 (m, 1H), 1.79 – 1.67 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ

213.09, 176.14, 87.05, 43.45, 41.06, 37.61, 35.22, 34.10, 28.57, 18.49. HRMS

(TOF ESI+) m/z calculated for C₁₀H₁₅O₃ [M+H]⁺: 183.1021, found: 183.1018.

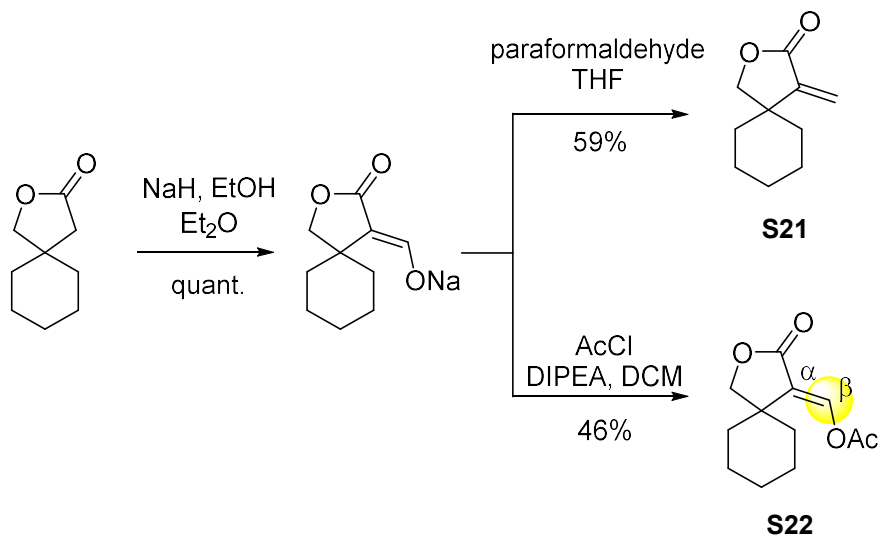
1-oxaspiro[4.6]undecane-2,7-dione [S20-C3ketone]. ¹H NMR (500 MHz, CDCl₃) δ 2.99 (d, J



= 14.2 Hz, 1H), 2.81 (d, $J = 14.1$ Hz, 1H), 2.69 – 2.54 (m, 3H), 2.48 (ddd, $J = 17.1, 7.8, 3.5$ Hz, 1H), 2.21 – 1.97 (m, 3H), 1.98 – 1.80 (m, 3H), 1.80 – 1.63 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 208.97, 175.78, 84.59, 54.33, 43.95, 41.69, 34.01,

28.22, 24.31, 23.59. HRMS (TOF ESI+) m/z calculated for C₁₀H₁₅NaO₃ [M+Na]⁺: 205.0841, found: 205.0840.



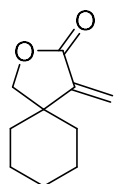
Synthesis of 4-methylene-2-oxaspiro[4.5]decan-3-one [S21] & (E)-(3-oxo-2-oxaspiro[4.5]decan-4-ylidene)methyl acetate [S22]. 2-oxaspiro[4.5]decan-3-one was prepared according to the reported literature²⁵. sodium (E)-(3-oxo-2-oxaspiro[4.5]decan-4-ylidene)methanolate was prepared according to the reported literature²⁶. 60% NaH (676mg, 16.9 mmol, 1.3 equiv.) was rinsed with hexane three times and dried under vacuum. To a stirred suspension of NaH in ether (12 mL, 1.1 M) was added EtOH (anhydrous, 0.1 mL, 1.56 mmol, 0.12 equiv.) at 0°C. Butyrolactone (2 g, 13 mmol, 1.0 equiv.) and ethyl formate (1.4 mL, 16.9 mmol, 1.3 equiv.) was introduced to the suspension at 0°C. Mild bubbling was observed. The reaction mixture was gradually warmed to room temperature over 30 minutes, then heated to reflux condition (70°C) and stirred for additional 2 hours. The mixture was filtered with ether, and the resulting solid was rinsed with ether three times furnishing sodium salt (2.6g, 13 mmol, quantitative).

To a stirred suspension of sodium salt (1.3 g, 6.5 mmol, 1.0 equiv.) in THF (33 mL, 0.2 M) was added paraformaldehyde (585 mg, 19.5 mmol, 3.0 equiv.). The mixture was stirred at 0°C for

9 hours, with progress monitored by TLC (silica gel, EA: hexane = 1: 1). Upon completion, the reaction was quenched with saturated NH_4Cl aqueous solution, and the organic layer was extracted with an EA/hexane mixture (1: 9) and dried over MgSO_4 . The crude product was concentrated in vacuo and purified by vacuum distillation (Welch DuoSeal vacuum pump, ultimate pressure: 1×10^{-4} Torr, head temperature: 200°C) to afford butanolide **S21** (634 mg, 3.8 mmol, 59% yield) as a clear oil.

To a stirred suspension of sodium salt (1.3 g, 6.5 mmol, 1.0 equiv.) in DCM (65 mL, 0.1 M) was added acetyl chloride (0.7 mL, 9.8 mmol, 1.5 equiv.) and DIPEA (2.2 mL, 13 mmol, 2.0 equiv.). The mixture was stirred at room temperature for 6 hours, with progress monitored by TLC (silica gel, EA: hexane = 1: 1). Upon completion, the reaction was quenched with saturated NH_4Cl aqueous solution, and the organic layer was extracted with DCM and dried over MgSO_4 . The crude product was concentrated in vacuo and purified by flash column chromatography (hexane only $\rightarrow$ EA: hexane = 1: 2) to afford a yellow solid. The yellow solid was dissolved in a minimal volume of ether and triturated by the addition of pentane. The resulting solid was filtered and rinsed with hexane three times, yielding AcO-butenolide **S22** (678 mg, 3.0 mmol, 47% yield) as a white solid. The identification was done by analogy to the reported compound 3-(hydroxymethylene)dihydro-2(3H)-furanone²⁷. The reported signal at the β - C & H NMR signal (structure highlighted) of E isomer was 8.25 (H), 140.29 (C) ppm, and Z isomer 7.62 (H), 137.28 (C) ppm. The corresponding H & C NMR signal of **S22** was analogous to the reported E isomer.

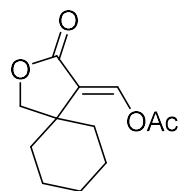
4-methylene-2-oxaspiro[4.5]decan-3-one [S21]. ^1H NMR (500 MHz, CDCl_3) δ 6.21 (s, 1H), 5.52



(s, 1H), 4.14 (s, 2H), 1.76 – 1.63 (m, 5H), 1.49 – 1.39 (m, 2H), 1.34 – 1.22 (m, 3H). ^{13}C

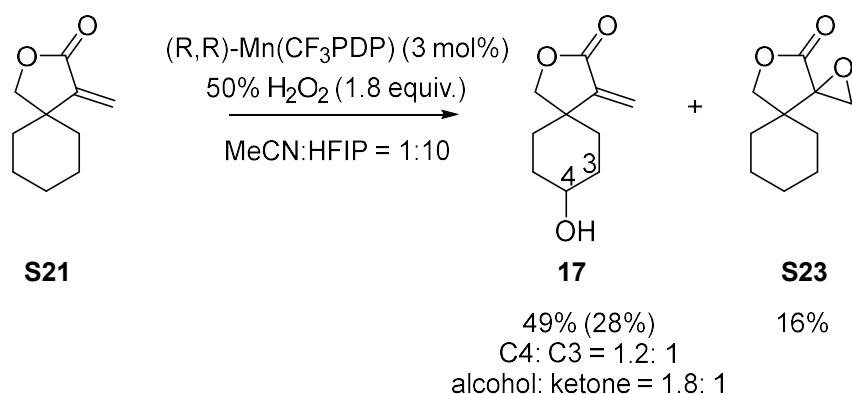
NMR (126 MHz, CDCl₃) δ 171.37, 144.52, 120.82, 75.37, 42.50, 36.34, 25.15, 22.66. HRMS (TOF ESI+) m/z calculated for C₁₀H₁₅O₂ [M+H]⁺: 167.1072, found 167.1075.

(E)-(3-oxo-2-oxaspiro[4.5]decan-4-ylidene)methyl acetate [S22]. ¹H NMR (500 MHz, CDCl₃)



δ 8.22 (s, 1H), 4.17 (s, 2H), 2.27 (s, 3H), 1.94 (td, J = 13.0, 3.3 Hz, 2H), 1.79 – 1.70 (m, 3H), 1.70 – 1.64 (m, 2H), 1.30 – 1.19 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 171.83, 166.15, 143.09, 118.95, 75.10, 42.79, 33.60, 25.15, 22.70, 20.69.

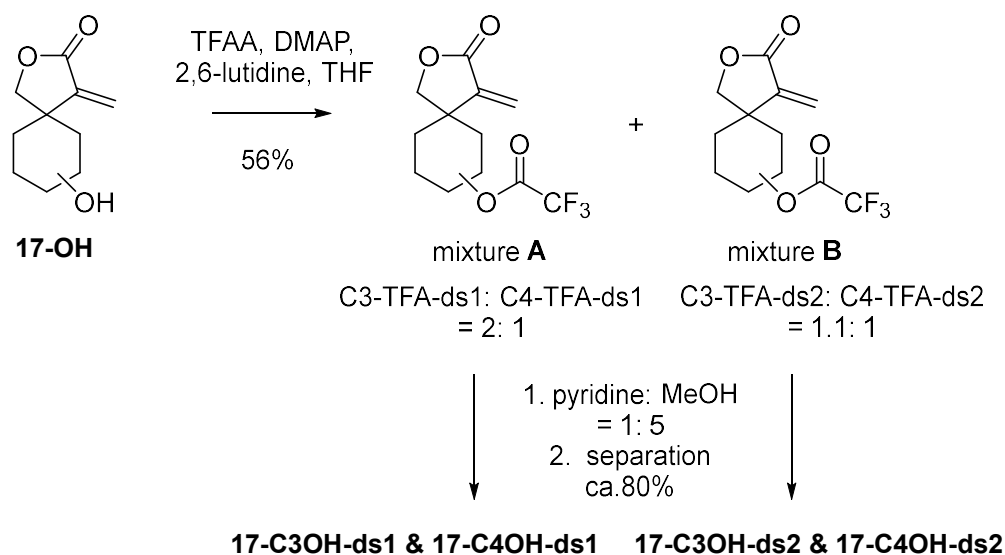
HRMS (TOF ESI+) m/z calculated for C₁₂H₁₇O₄ [M+H]⁺: 225.1127, found 225.1126.



Oxidation of 4-methylene-2-oxaspiro[4.5]decan-3-one [S21]. 4-methylene-2-oxaspiro[4.5]decan-3-one (**13**) in HFIP was oxidized according to the Standard conditions with 3mol% (*R,R*)-Mn(CF₃-PDP) and 1.8 equiv. of H₂O₂. The resulting mixture was purified by column chromatography (silica gel, EA: hexane = 1: 6 (RSM and RSM epoxide isolated) → EA: hexane = 2: 3 (ketone mixture isolated) → EA: hexane = 2: 1 (alcohol mixture isolated). Site-selectivity was obtained by quantitative ¹H NMR analysis of each product mixture. **Run 1:** 26% RSM, 50% yield, alcohol: ketone = 1.5: 1, C4: C3 = 1.1: 1, epoxide 16%. **Run 2:** 30% RSM, 48% yield,

alcohol: ketone = 2.1: 1, C4: C3 = 1.2: 1, epoxide 15%. **Run 3:** 27% RSM, 48% yield, alcohol: ketone = 2.0: 1, C4: C3 = 1.3: 1, epoxide 17%. **Average:** 28% RSM $\pm$ 1.7%, 49% $\pm$ 1.3% yield, alcohol: ketone = 1.8: 1. C4: C3 = 1.2: 1, epoxide = 16% $\pm$ 0.7%. With catalyst **2** ((*S,R,R,S*)-Mn(MeCF₃-PDP)): **Run 1:** 20% RSM, 31% yield, alcohol: ketone = 1.5: 1, C4: C3 = 1: 1.2, epoxide 33%. **Run 2:** 19% RSM, 33% yield, alcohol: ketone = 1.3: 1, C4: C3 = 1: 1, epoxide 33%. **Average:** 20% RSM $\pm$ 0.6%, 32% $\pm$ 0.9% yield, alcohol: ketone = 1.4: 1. C4: C3 = 1: 1.1, epoxide = 33% $\pm$ 0.1%.

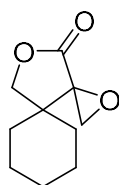
Separation and Identification of ketone 17-ketones. The ketone mixture was subsequently separated by MPLC (Teledyne Combiflash® system, EA: hexane = 5: 95 $\rightarrow$ 1: 3).



Separation and Identification of Alcohol Mixture 17-OH. To a stirred mixture of alcohol mixture **17-OH** (12 mg, 0.064 mmol, 1.0 equiv.) in THF (0.13M) was added 2,6-lutidine (0.01 mL, 0.1 mmol, 1.6 equiv.), DMAP (3 mg, 0.025 mmol, 0.4 equiv.) and TFA anhydride (0.02 mL, 0.15 mmol, 2.3 equiv.) at 0°C. The reaction was completed in 30min at 0°C (confirmed by TLC

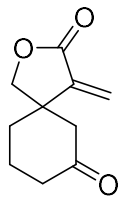
analysis, EA: hexane = 2: 1). Upon completion, the resulting mixture concentrated in vacuo and purified by column chromatography (ether: pentane = 1: 3), furnishing mixture **A** and **B** (10 mg in total, 0.036 mmol, 56% total yield). Each mixture contained a 3-TFA and a 4-TFA diastereomer. Each regioisomeric mixture was transferred into separate vials, and a mixture of pyridine: MeOH = 1: 5 (0.1 M) was added. The TFA deprotection reactions were monitored by TLC (silica, MTBE: MeOH = 50: 1). Upon completion, each reaction mixture was concentrated and purified separately by MPLC (Teledyne Combiflash® system, MTBE: MeOH = 100: 1) to afford the separated diastereomers of the alcohol products with approximately 80% TFA deprotection yield.

1,11-dioxadispiro[2.0.5⁴.3³]dodecan-12-one [S23]. ¹H NMR (500 MHz, CDCl₃) δ 4.46 (d, *J* =



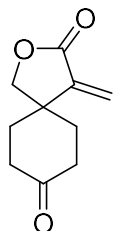
9.1 Hz, 1H), 4.18 (d, *J* = 9.1 Hz, 1H), 3.09 (d, *J* = 5.9 Hz, 1H), 3.02 (d, *J* = 5.9 Hz, 1H), 1.80 – 1.72 (m, 1H), 1.71 – 1.63 (m, 3H), 1.62 – 1.53 (m, 1H), 1.45 – 1.34 (m, 2H), 1.30 – 1.15 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.26, 74.38, 62.11, 49.59, 37.96, 31.94, 29.57, 25.27, 22.42, 21.93. MS (EI⁺) *m/z* calculated for C₁₀H₁₄O₃ [M]⁺: 182.0943, found 182.1.

4-methylene-2-oxaspiro[4.5]decane-3,7-dione [17-C3ketone]. ¹H NMR (500 MHz, CDCl₃) δ



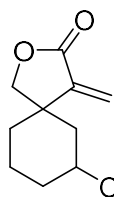
6.34 (s, 1H), 5.58 (s, 1H), 4.14 (d, *J* = 9.1 Hz, 1H), 4.02 (d, *J* = 9.2 Hz, 1H), 2.46 (s, 2H), 2.49 – 2.38 (m, 2H), 2.07 – 1.78 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 208.25, 169.86, 141.45, 122.78, 75.21, 49.96, 46.21, 40.93, 34.50, 21.75. HRMS (TOF ESI⁺) *m/z* calculated for C₁₀H₁₃O₃ [M+H]⁺: 181.0865, found 181.0871.

4-methylene-2-oxaspiro[4.5]decane-3,8-dione [17-C4ketone]. ^1H NMR (500 MHz, CDCl_3) δ



6.35 (s, 1H), 5.65 (s, 1H), 4.38 (s, 2H), 2.55 – 2.47 (m, 2H), 2.47 – 2.38 (m, 2H), 2.14 – 2.07 (m, 2H), 2.01 (app td, $J = 13.1, 5.1$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.44, 170.18, 142.18, 122.12, 74.34, 41.72, 37.67, 35.76. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{13}\text{O}_3$ $[\text{M}+\text{H}]^+$: 181.0865, found 181.0861.

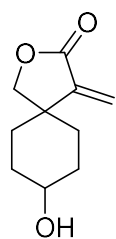
7-hydroxy-4-methylene-2-oxaspiro[4.5]decan-3-one [17-C3OH-ds1]. ^1H NMR (500 MHz,



CDCl_3) δ 6.28 (s, 1H), 5.58 (s, 1H), 4.16 (d, $J = 9.1$ Hz, 1H), 4.12 (dd, $J = 9.1, 1.2$ Hz, 1H), 3.61 (tt, $J = 11.2, 4.2$ Hz, 1H), 2.08 – 1.99 (m, 2H), 1.90 – 1.81 (m, 1H), 1.75 – 1.69 (m, 1H), 1.46 (t, $J = 12.0$ Hz, 1H), 1.42 – 1.35 (m, 1H), 1.35 – 1.24 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.75, 143.27, 121.47, 74.99, 67.71, 44.76, 43.71, 35.88, 34.79, 21.02. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 183.1021, found 183.1018.

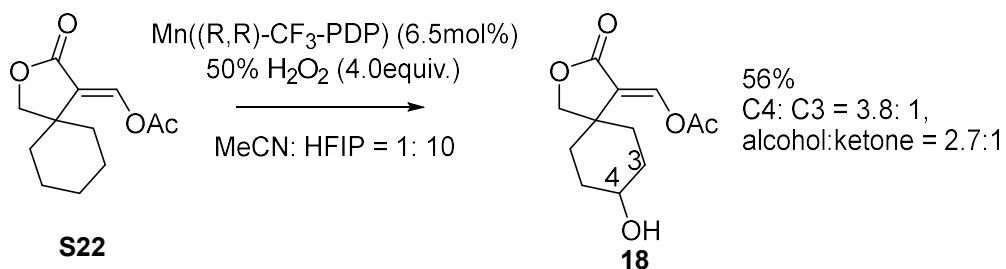
[17-C3OH-ds2]. ^1H NMR (500 MHz, CDCl_3) δ 6.24 (s, 1H), 5.52 (s, 1H), 4.36 (d, $J = 9.6$ Hz, 1H), 4.29 (dd, $J = 9.5, 1.3$ Hz, 1H), 4.24 (quint, $J = 4.1$ Hz, 1H), 1.90 – 1.74 (m, 4H), 1.73 – 1.63 (m, 2H), 1.61 – 1.54 (m, 2H), 1.39 – 1.31 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.15, 144.51, 120.66, 76.69, 66.55, 42.17, 40.70, 36.46, 32.99, 17.28. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 183.1021, found 183.1022.

8-hydroxy-4-methylene-2-oxaspiro[4.5]decan-3-one [17-C4OH-ds1]. ^1H NMR (500 MHz,



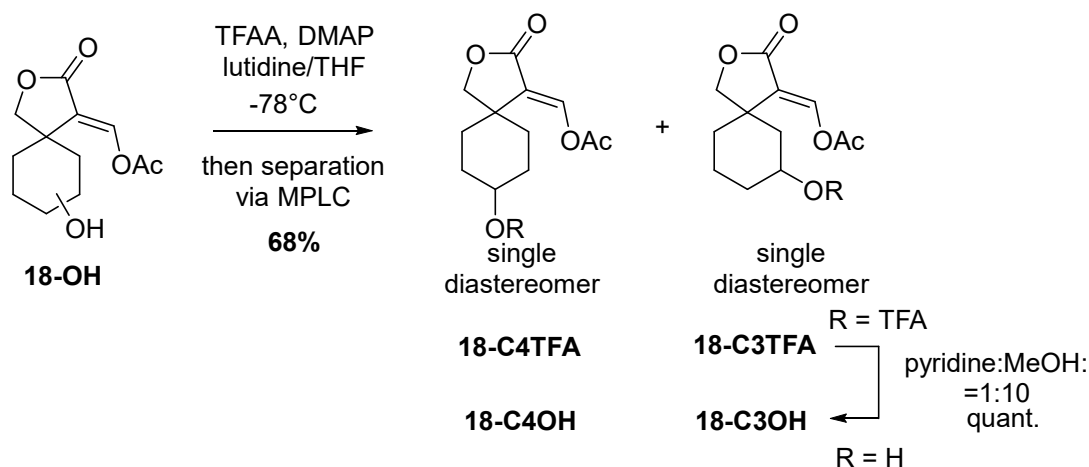
CDCl_3) δ 6.25 (s, 1H), 5.54 (s, 1H), 4.19 (s, 2H), 3.72 (tt, $J = 10.6, 4.3$ Hz, 1H), 2.04 – 1.96 (m, 2H), 1.85 – 1.77 (m, 2H), 1.59 – 1.49 (m, 3H), 1.40 – 1.28 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.95, 143.53, 121.13, 75.03, 69.46, 41.73, 34.62, 31.92. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 183.1021, found 183.1025. **[17-**

C4OH-ds2]. ^1H NMR (500 MHz, CDCl_3) δ 6.27 (s, 1H), 5.67 (s, 1H), 4.14 (s, 2H), 4.07 – 4.02 (m, 1H), 1.95 (ddd, $J = 13.6, 11.8, 3.9$ Hz, 2H), 1.83 – 1.76 (m, 2H), 1.65 (ddt, $J = 14.9, 11.7, 3.4$ Hz, 2H), 1.56 – 1.50 (m, 3H, containing H_2O peak). ^{13}C NMR (126 MHz, CDCl_3) δ 171.18, 143.86, 121.64, 75.30, 65.53, 42.05, 30.48, 29.63. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 183.1021, found 183.1023.



Oxidation of (E)-(3-oxo-2-oxaspiro[4.5]decan-4-ylidene)methyl acetate [S22]. (E)-(3-oxo-2-oxaspiro[4.5]decan-4-ylidene)methyl acetate **S22** (0.4 mmol) in HFIP was oxidized according to the Standard conditions with 6.5 mol% (*R,R*)- $\text{Mn}(\text{CF}_3\text{-PDP})$ and 4 equiv. of H_2O_2 . Immediately after the H_2O_2 addition was complete, the reaction mixture was directly filtered through a silica pad using a large volume of ethyl acetate (ca. 300 mL) to prevent product decomposition. The resulting crude product was concentrated and purified by flash column chromatography (silica, EA: DCM=1: 1). The ketone product mixture was further purified by flash column

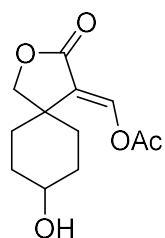
chromatography (silica, acetone:benzene= 1: 6), and the alcohol product mixture was further purified by flash column chromatography (silica, acetone:benzene= 1: 3). Site-selectivity was obtained by quantitative ^1H NMR analysis of each product mixture. **Run 1:** 56% yield, alcohol: ketone = 2.9: 1. C4: C3 = 3.8: 1. **Run 2:** 57% yield, alcohol: ketone = 2.6: 1. C4: C3 = 3.8: 1. **Run 3:** 58% yield, alcohol: ketone = 3.2: 1. C4: C3 = 3.8: 1. **Average:** 56% yield $\pm$ 0.2%, alcohol: ketone = 2.7: 1. C4: C3 = 3.8: 1.



Separation and Identification of alcohol mixture 18-OH. To a stirred solution of alcohol mixture **18-OH** (39.5 mg, 0.164 mmol, 1.0 equiv.) in THF (0.8 mL, 0.2 M) was added 2,6-lutidine (0.08 mL, 0.8 mmol, 4.9 equiv.), DMAP (10 mg, 0.08 mmol, 0.5 equiv.), and TFA anhydride (0.1 mL, 0.8 mmol, 4.9 equiv.) at -78°C . The reaction was completed within 10 minutes at -78°C , confirmed by TLC analysis (EA: DCM = 1: 3). Upon completion, the resulting mixture concentrated in vacuo and purified by MPLC (Teledyne Combiflash® system, hexane $\rightarrow$ EA: hexane = 1: 3), furnishing C4-TFA (24 mg, white solid) and C3-TFA (13 mg, colorless oil), with a total mass of 37 mg (0.11 mmol, 67%). A single diastereomer was observed for each constitutional isomer of the TFA esters. Each TFA ester was subjected to a mixture of pyridine:

MeOH = 1: 10 mixture at room temperature. Full deprotection of TFA was confirmed with TLC analysis (EA: DCM = 1: 1). The resulting mixtures were concentrated and purified by flash column chromatography (EA: DCM: MeOH = 10: 10: 1) to furnish the separated diastereomers of the alcohol products C4-OH and C3-OH, with approximately quantitative yield for the TFA deprotection step.

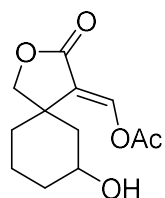
(E)-(8-hydroxy-3-oxo-2-oxaspiro[4.5]decan-4-ylidene)methyl acetate [18-C4OH]. ^1H NMR



(500 MHz, CDCl_3) δ 8.23 (s, 1H), 4.18 (s, 2H), 3.70 (tt, J = 10.8, 4.2 Hz, 1H), 2.27 (s, 3H), 2.09 – 1.98 (m, 4H), 1.77 – 1.71 (m, 2H), 1.61 (s, 1H), 1.32 – 1.23 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.41, 165.93, 143.38, 117.71, 74.92, 69.61, 41.88, 31.96, 31.86, 20.68. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{17}\text{O}_5$ $[\text{M}+\text{H}]^+$:

241.1076, found 241.1073.

(E)-(7-hydroxy-3-oxo-2-oxaspiro[4.5]decan-4-ylidene)methyl acetate [18-C3OH].

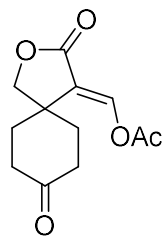


^1H NMR (600 MHz, CDCl_3) δ 8.26 (s, 1H), 4.14 (d, J = 9.1 Hz, 1H), 4.12 (dd, J = 9.1, 1.2 Hz, 1H), 3.61 – 3.53 (m, 1H), 2.29 (s, 3H), 2.07 – 1.96 (m, 3H), 1.87 – 1.78 (m, 2H), 1.68 – 1.60 (m, 1H), 1.53 (app s, 1H), 1.41 – 1.26 (m, 2H). ^{13}C NMR (151

MHz, CDCl_3) δ 171.08, 165.83, 143.55, 117.21, 74.88, 67.53, 43.56, 42.10, 34.60, 32.53, 20.72, 20.58. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{17}\text{O}_5$ $[\text{M}+\text{H}]^+$: 241.1076, found 241.1071.

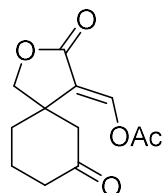
Identification of ketone mixture 18-ketones. The 4-ketone and 3-ketone isomers were prepared by Dess-Martin Periodinane oxidation of the obtained alcohol products. The site-selectivity of the ketone mixture resulting from C-H oxidation was quantified based on the quantitative ^1H NMR spectrum, using peaks identified from authentic ketone samples.

(E)-(3,8-dioxo-2-oxaspiro[4.5]decan-4-ylidene)methyl acetate [18-C4ketone]. ^1H NMR (600

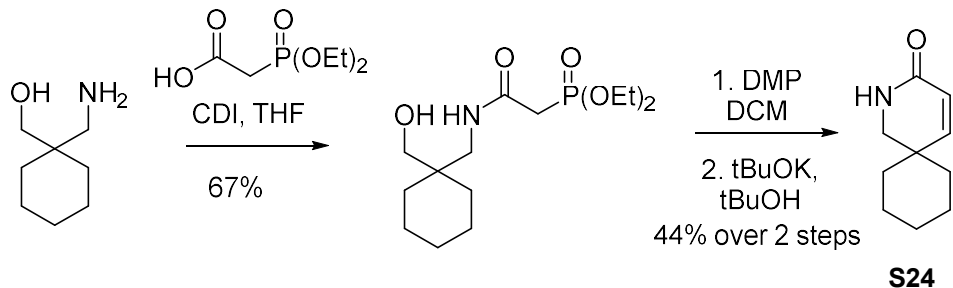


MHz, CDCl_3) δ 8.30 (s, 1H), 4.39 (s, 2H), 2.52 – 2.38 (m, 6H), 2.26 (s, 3H), 2.08 – 2.04 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 209.01, 170.76, 165.75, 144.00, 116.35, 74.30, 41.91, 37.71, 33.10, 20.70. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{15}\text{O}_5$ $[\text{M}+\text{H}]^+$: 239.0919, found 239.0920.

(E)-(3,7-dioxo-2-oxaspiro[4.5]decan-4-ylidene)methyl acetate [18-C3ketone]. ^1H NMR (600



MHz, CDCl_3) δ 8.33 (s, 1H), 4.15 (d, $J = 8.9$ Hz, 1H), 3.96 (d, $J = 8.9$ Hz, 1H), 2.77 (dt, $J = 15.3, 1.5$ Hz, 1H), 2.54 – 2.48 (m, 1H), 2.40 – 2.33 (m, 2H), 2.27 – 2.22 (m, 1H), 2.23 (s, 3H), 1.96 – 1.80 (m, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 207.72, 170.59, 165.81, 144.08, 116.48, 76.09, 47.50, 46.09, 40.82, 34.52, 21.78, 20.62. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{15}\text{O}_5$ $[\text{M}+\text{H}]^+$: 239.0919, found 239.0916.



Synthesis of 2-azaspiro[5.5]undec-4-en-3-one [S24]. (1-(aminomethyl)cyclohexyl)methanol was prepared according to the reported literature²⁶. To a stirred solution of 2-

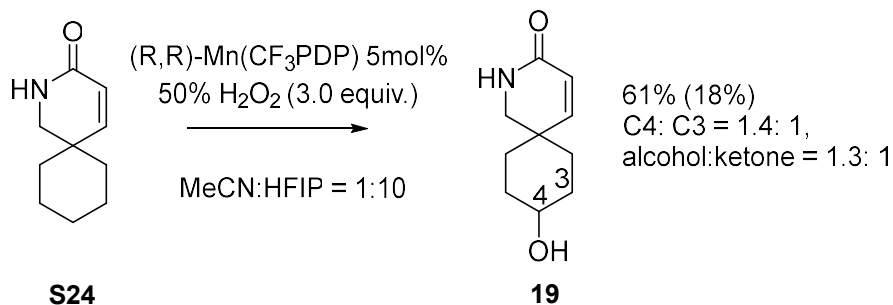
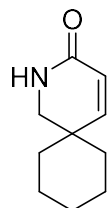
(diethoxyphosphinyl)acetic acid (96% purity, 1.7 g, 8.1 mmol, 1.0 equiv.) in THF (1 ml, 8 M) was added CDI (1.3 g, 8.1 mmol, 1.0 equiv.) at room temperature under open air. Once effervescence ceased, the reaction mixture was sealed with a septum and stirred for 30 minutes under nitrogen atmosphere. (1-(aminomethyl)cyclohexyl)methanol (1.2 g, 8.1 mmol, 1.0 equiv.) was introduced to the activated acid and rinsed with ca. 0.5 ml of THF. The resulting mixture was stirred for 15 hours at room temperature, and the reaction was monitored by TLC (silica gel, EA: DCM: MeOH = 10: 10: 1). Upon completion, the reaction was concentrated in vacuo and purified by flash column chromatography (silica gel, EA: DCM = 1: 1 $\rightarrow$ EA: DCM: MeOH = 10: 10: 1) to afford diethyl (2-(((1-(hydroxymethyl)cyclohexyl)methyl)amino)-2-oxoethyl)phosphonate (1.7 g, 5.4 mmol, 67% yield) as a yellow oil.

To a stirred solution of diethyl (2-(((1-(hydroxymethyl)cyclohexyl)methyl)amino)-2-oxoethyl)phosphonate (3 g, 9.3 mmol, 1.0 equiv.) in DCM (47 ml, 0.2 M) was added Dess-Martin Periodinane (4.4 g, 10.3 mmol, 1.1 equiv.) at 0°C. The reaction mixture was sealed with a septum and gradually warmed to room temperature over 24 hours under nitrogen atmosphere, with progress monitored by TLC (silica gel, EA: DCM: MeOH = 10: 10: 1). Upon completion, the reaction was quenched with saturated NaHCO₃ aqueous solution, and the organic layer was extracted with DCM and dried over Na₂SO₄. The crude product was concentrated in vacuo and filtered through syringe filter (2 μ m) and used directly without further purification as a yellow oil.

To a stirred solution of yellow oil (ca. 2.9 g) in tBuOH (45 ml, 0.2 M) was added tBuOK (1.25 g, 11.2 mmol, 1.2 equiv.) at room temperature. The reaction mixture was sealed with a septum and stirred for 24 hours under nitrogen atmosphere, with progress monitored by TLC (silica gel, EA: DCM: MeOH = 5: 5: 1). Upon completion, the reaction was quenched with saturated NH₄Cl aqueous solution, and the organic layer was extracted with EA and dried over Na₂SO₄. The

crude product was concentrated in vacuo and purified by flash column chromatography (silica gel, acetone: hexane = 1: 1) to afford lactam **S24** (679 mg, 4.1 mmol, 44% yield over 2 steps) as a white solid.

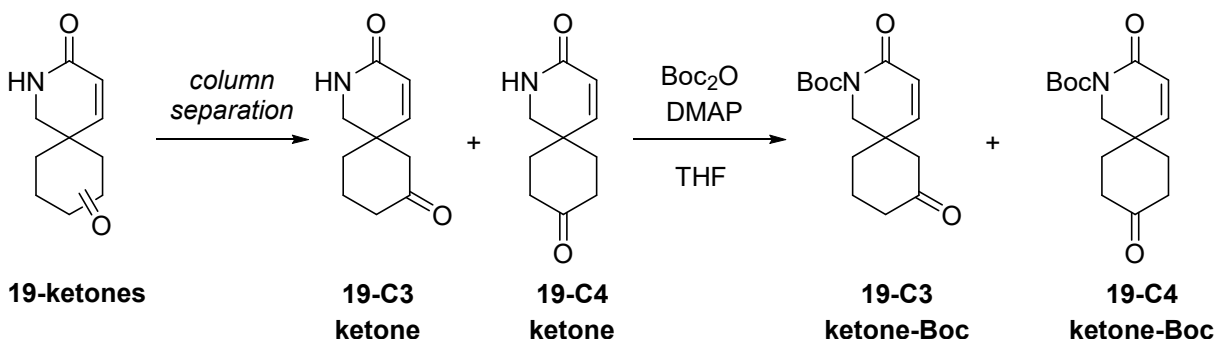
2-azaspiro[5.5]undec-4-en-3-one [S24]. ^1H NMR (500 MHz, CDCl_3) δ 6.73 (br s, 1H), 6.49 (d, $J = 10.0$ Hz, 1H), 5.75 (dd, $J = 10.1, 1.8$ Hz, 1H), 3.22 (d, $J = 2.6$ Hz, 2H), 1.57 – 1.33 (m, 10H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.68, 151.16, 122.38, 49.50, 35.21, 34.21, 25.87, 21.59. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: 166.1232, found 166.1232.



Oxidation of 2-azaspiro[5.5]undec-4-en-3-one [S24]. 2-azaspiro[5.5]undec-4-en-3-one **S24** in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF_3 -PDP) and 3.0 equiv. of H_2O_2 . The resulting mixture was purified with column chromatography (EA: DCM: MeOH = 4: 4: 1). The ketone products were Boc-protected, and the alcohol products were acetyl-protected for quantitative ^1H NMR analysis to calculate site-selectivity (vide infra). **Run 1:** 18% RSM, 63% yield, alcohol: ketone = 1.2: 1. C4: C3 = 1.4: 1. **Run 2:** 18% RSM, 64% yield, alcohol: ketone = 1.2: 1. C4: C3 = 1.4: 1. **Run 3:** 18% RSM, 58% yield, alcohol: ketone = 1.3: 1. C4: C3

= 1.4: 1. **Average:** 18% RSM $\pm$ 0.1%, 61% $\pm$ 2.7% yield, alcohol: ketone = 1.3: 1. C4: C3 = 1.4:

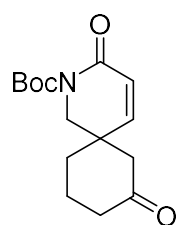
1.



Identification of ketone products. Two ketone constitutional isomers **19-C3ketone** and **19-C4ketone** were obtained via column separation of ketone mixture **19-ketones** (EA: DCM = 1: 1 $\rightarrow$ EA: DCM: MeOH = 5: 5: 1). Each ketone was separately Boc-protected to obtain clean NMR spectrum.

To a stirred solution of keto lactam (11 mg, 0.06 mmol, 1.0 equiv.) in THF (1 ml, 8 M) were added Boc_2O (26 mg, 0.12 mmol, 2.0 equiv.) and DMAP (7.3 mg, 0.06 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred for 30 minutes under open air, and the reaction was monitored by TLC (silica gel, EA: hexane = 1: 1). Upon completion, the reaction was concentrated in vacuo and purified by flash column chromatography (silica gel, EA: hexane = 1: 2) to afford Boc-protected keto lactam with the yield ranging from 40% to 60%.

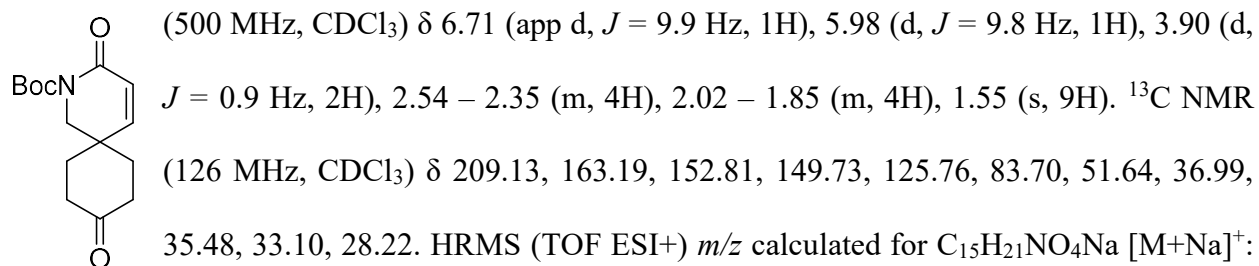
tert-butyl 3,8-dioxo-2-azaspiro[5.5]undec-4-ene-2-carboxylate [19-C3ketone-Boc]. ^1H NMR



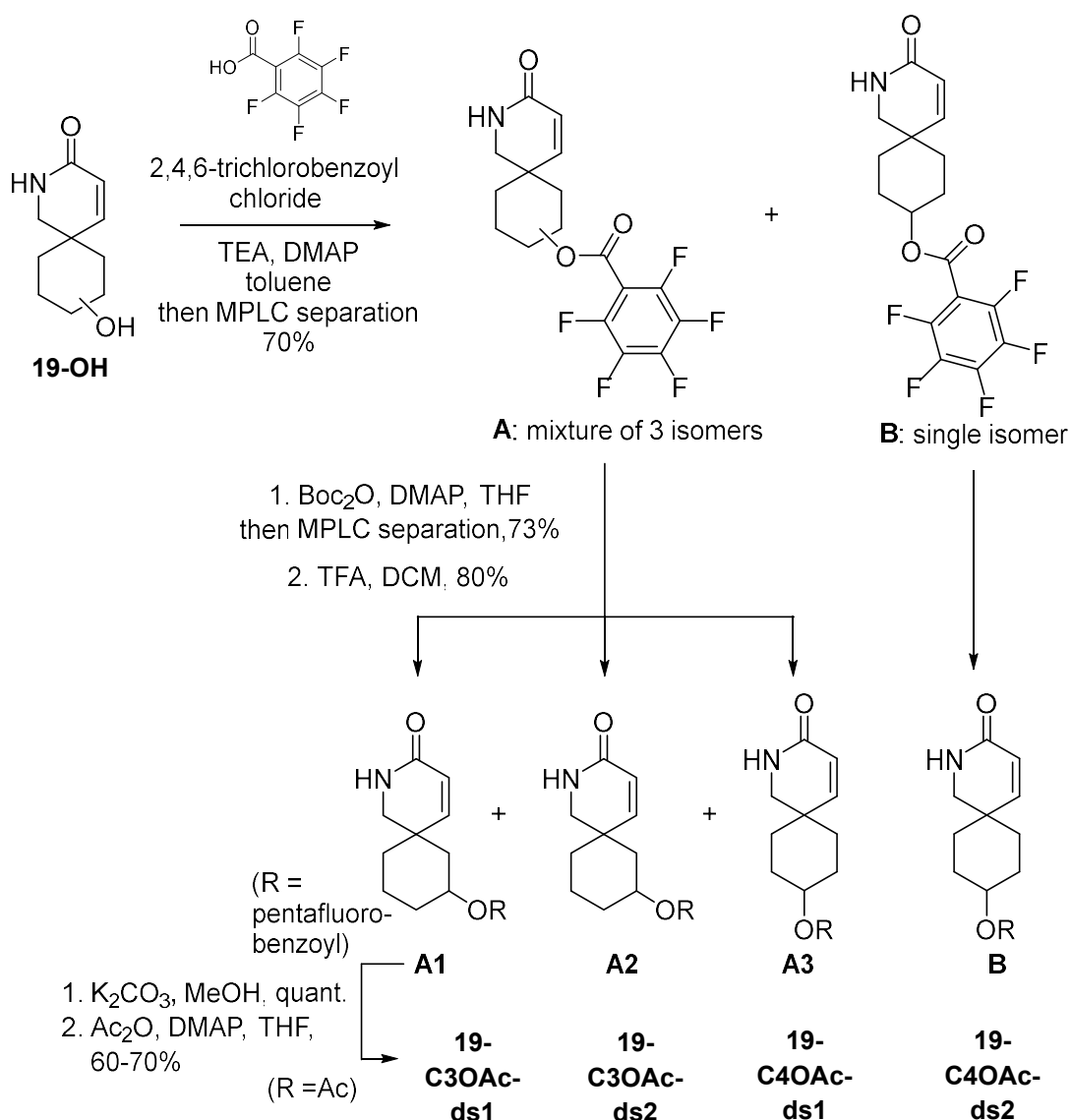
(500 MHz, CDCl_3) δ 6.52 (app d, J = 9.8 Hz, 1H), 5.89 (d, J = 9.8 Hz, 1H), 3.81 (dd, J = 13.3, 1.2 Hz, 1H), 3.60 (d, J = 13.2 Hz, 1H), 2.41 (app t, J = 6.5 Hz, 2H), 2.36 (s, 2H), 1.99 – 1.89 (m, 3H), 1.84 – 1.78 (m, 1H), 1.54 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.08, 162.92, 152.45, 149.13, 125.25, 83.62, 52.55, 48.45,

40.97, 40.76, 32.73, 28.17, 21.88. HRMS (TOF ESI+) m/z calculated for $C_{15}H_{21}NO_4Na$ $[M+Na]^+$: 302.1368, found 302.1368.

tert-butyl 3,9-dioxo-2-azaspiro[5.5]undec-4-ene-2-carboxylate [19-C4ketone-Boc]. 1H NMR



302.1368, found 302.1367.



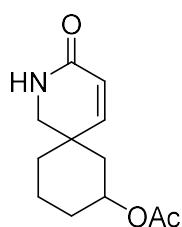
Separation and Identification of alcohol mixture 19-OH. To a stirred solution of pentafluorobenzoic acid (48 mg, 0.22 mmol, 1.5 equiv.) in toluene (1.5 ml, 0.1 M) were added 2,4,6-trichlorobenzoyl chloride (55 mg, 0.22 mmol, 2.0 equiv.) and TEA (0.03 ml, 0.22 mmol, 1.5 equiv.) at room temperature. The mixture was stirred for 15 minutes. The mixture of amide alcohol products (26 mg, 0.14 mmol, 1.0 equiv.) was introduced to the activated acid followed by addition of DMAP (21 mg, 0.17 mmol, 1.2 equiv.). The mixture was stirred for 30 min, and the reaction was monitored by TLC (silica gel, EA: DCM: MeOH = 5: 5: 1). Upon completion, the reaction mixture was quenched with water, extracted with EA, and concentrated in vacuo. The resulting

crude was purified with MPLC (Teledyne Combiflash® system, EA: DCM = 1: 10 → 1: 1.5), furnishing mixture **A** (mixture of 3 isomers) and single isomer pentafluorobenzoyl ester **B** (total mass 36 mg, 0.098 mmol, 70% yield, A:B = 4: 1).

To a stirred solution of mixture **A** (27 mg, 0.072 mmol, 1.0 equiv.) in THF (0.7 mL, 0.1 M), Boc₂O (47 mg, 0.22 mmol, 3.0 equiv.) and DMAP (13 mg, 0.11 mmol, 1.5 equiv.) were added at room temperature. The reaction mixture was stirred for 40 minutes under open air, with progress monitored by TLC (silica gel, EA: DCM = 1: 1). Upon completion, the reaction was filtered through a silica plug using EA and concentrated in vacuo. The resulting yellow oil was purified by MPLC (Teledyne Combiflash® system, hexane only → EA: hexane = 1: 3) to afford three separated Boc-protected isomers (1st isomer: 9 mg, 2nd isomer: 7.2 mg, 3rd isomer: 8.9 mg, total mass: 25 mg, 0.053 mmol, 73% yield). Each Boc-protected isomer was dissolved in DCM (0.05 M) and treated with TFA (2 equiv.). The resulting crude products were purified by column chromatography (EA: DCM = 3: 1), yielding pentafluorobenzoyl ester **A1-3** (80% yield).

Pentafluorobenzoyl ester **A1-3** and **B** were separately dissolved in MeOH (0.1 M) and treated with K₂CO₃ (2.0 equiv.) at room temperature. Upon completion, the reaction mixtures were quenched with saturated NaHCO₃ solution, extracted with DCM, and dried over Na₂SO₄. The crude products were concentrated in vacuo and stored under vacuum for 1 hour, yielding diastereomerically pure hydroxy lactams in quantitative yield. To a stirred solution of the hydroxy lactam in THF (0.03 M) were added acetic anhydride (1.3 equiv.) and DMAP (0.5 equiv.) at room temperature. The reaction mixture was stirred for 30 minutes. Upon completion, the reaction was quenched with saturated NaHCO₃ solution, extracted with DCM, and dried over Na₂SO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (silica gel, ether: MeOH = 10: 1) to afford acetoxylactam with yields ranging from 60% to 70%.

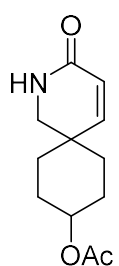
3-oxo-2-azaspiro[5.5]undec-4-en-8-yl acetate. Diastereomer 1 [19-C3OAc-ds1]. ^1H NMR



(600 MHz, CDCl_3) δ 6.44 (d, $J = 10.0$ Hz, 1H), 5.80 (dd, $J = 10.0$, 1.9 Hz, 1H), 5.55 (br s, 1H), 4.85 (tt, $J = 9.0$, 4.1 Hz, 1H), 3.32 (br s, 2H), 2.03 (s, 3H), 1.94 – 1.87 (m, 2H), 1.81 – 1.75 (m, 1H), 1.66 – 1.63 (m, 1H, mixed with H_2O (1.63ppm), 1.56 (dd, $J = 13.3$, 9.7 Hz, 1H), 1.53 – 1.38 (m, 3H). ^{13}C NMR (151 MHz, CDCl_3)

δ 170.48, 165.93, 151.00, 122.66, 69.06, 48.42, 38.46, 36.77, 32.45, 30.99, 21.48, 19.42. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{18}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 224.1287, found 224.1286. **Diastereomer 2 [19-C3OAc-ds2].** ^1H NMR (600 MHz, CDCl_3) δ 6.60 (d, $J = 10.1$ Hz, 1H), 5.86 (dd, $J = 10.1$, 2.2 Hz, 1H), 5.55 (br s, 1H), 4.96 (tt, $J = 8.6$, 4.0 Hz, 1H), 3.32 (dd, $J = 12.2$, 3.0 Hz, 1H), 3.25 (dd, $J = 12.3$, 2.7 Hz, 1H), 2.03 (s, 3H), 1.99 – 1.87 (m, 2H), 1.79 – 1.70 (m, 1H), 1.68 – 1.63 (m, 1H), 1.61 – 1.54 (m, 1H, mixed with H_2O (1.58ppm), 1.52 – 1.45 (m, 2H), 1.44 – 1.38 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.38, 165.70, 148.73, 123.54, 69.28, 51.66, 39.36, 36.46, 33.41, 31.12, 21.50, 18.92. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{18}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 224.1287, found 224.1286.

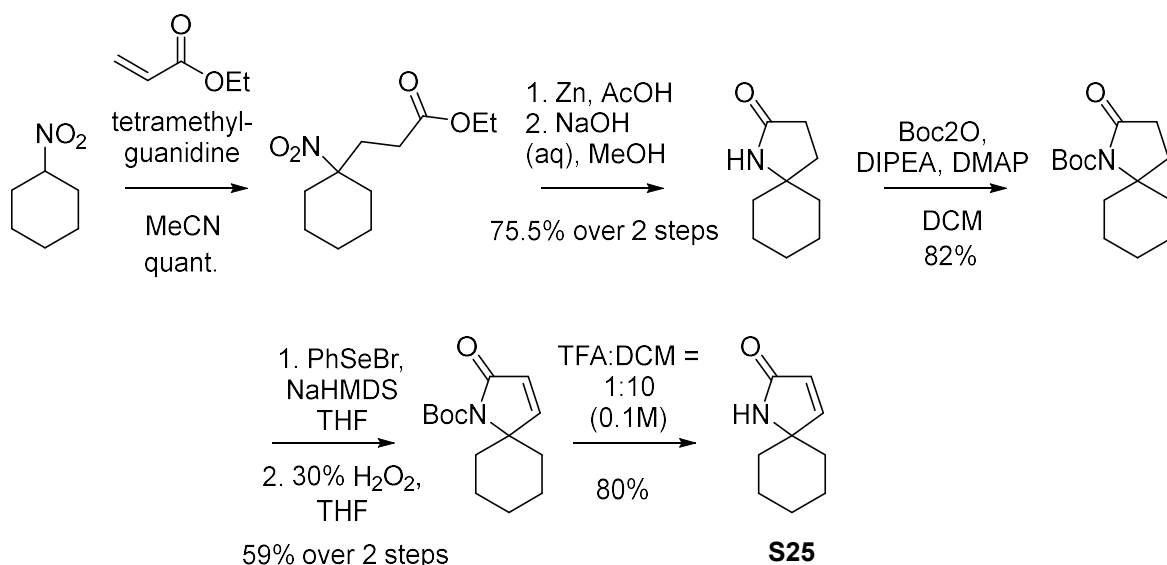
3-oxo-2-azaspiro[5.5]undec-4-en-9-yl acetate. Diastereomer 1 [19-C4OAc-ds1]. ^1H NMR (600



MHz, CDCl_3) δ 6.44 (d, $J = 10.0$ Hz, 1H), 5.84 (dd, $J = 10.0$, 2.1 Hz, 1H), 5.57 (br s, 1H), 4.84 – 4.78 (m, 1H), 3.33 (d, $J = 2.9$ Hz, 2H), 2.05 (s, 3H), 1.89 – 1.80 (m, 2H), 1.79 – 1.70 (m, 2H), 1.57 – 1.50 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.62, 166.02, 150.30, 123.32, 71.11, 48.52, 34.79, 30.80, 26.64, 21.49. HRMS (TOF ESI+)

m/z calculated for $\text{C}_{12}\text{H}_{18}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 224.1287, found 224.1285. **Diastereomer 2 [19-C4OAc-ds2].** ^1H NMR (600 MHz, CDCl_3) δ 6.69 (dd, $J = 10.0$, 3.0 Hz, 1H), 5.97 (br s, 1H), 5.88 (dd, $J = 10.2$, 2.1 Hz, 1H), 4.86 – 4.79 (m, 1H), 3.25 (br s, 2H), 2.06 (s, 3H), 1.86 – 1.78 (m, 4H), 1.70 –

1.62 (m, 2H), 1.50 – 1.41 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.65, 166.21, 149.72, 122.86, 70.93, 50.31, 34.61, 31.10, 26.46, 21.49. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{18}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 224.1287, found 224.1287.



Synthesis of 1-azaspiro[4.5]dec-3-en-2-one [S25]. To a stirred solution of nitrocyclohexane (2.5 g, 20.6 mmol, 1.0 equiv.) in MeCN (5.6 ml, 4.0 M) were added ethyl acrylate (2.2 ml, 20.6 mmol, 1.0 equiv.) and tetramethyl guanidine (0.4 ml, 3.1 mmol, 0.15 equiv.) at room temperature. The reaction mixture was stirred for 15 hours under argon atmosphere, and the reaction was monitored by TLC (silica gel, $\text{EA}:\text{hexane} = 1:5$). Upon completion, the reaction was concentrated in vacuo and purified by flash column chromatography ($\text{EA}:\text{hexane} = 1:5$) to afford ethyl 3-(1-nitrocyclohexyl)propanoate (4.7g, 20 mmol, quantitative).

To a stirred solution of ethyl 3-(1-nitrocyclohexyl)propanoate (4.7 g, 20 mmol, 1.0 equiv.) in acetic acid (40 mL, 0.5 M) was added zinc metal powder (8.1 g, 124 mmol, 6.0 equiv.) portionwise at 10-15°C. The mixture gradually warmed to room temperature and was stirred for

1.5 days. The resulting mixture was filtered through a Celite pad using ethyl acetate and concentrated in vacuo. Heptane was introduced to the mixture and evaporated multiple times to remove residual acetic acid, resulting in a dark pink oil. To a stirred solution of the crude oil in methanol (29 mL, 0.7 M), 1.8 M NaOH (67 mL, 6.0 equiv.) was added at 0°C. The mixture was gradually warmed to room temperature and stirred for 17 hours. The reaction was then acidified with 1N HCl solution, extracted with DCM five times, and dried over Na₂SO₄. The resulting yellow oil was stored under vacuum, where it spontaneously solidified to yield 1-azaspiro[4.5]decan-2-one (2.3 g, 15.1 mmol, 76% yield over 2 steps). Spectroscopic data matched the published literature²⁸.

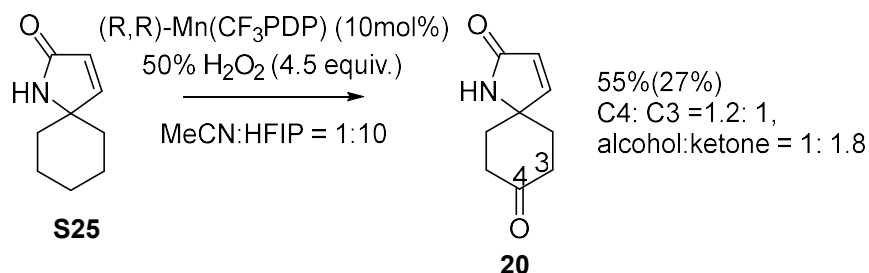
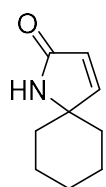
To a stirred solution of 1-azaspiro[4.5]decan-2-one (2.3 g, 15.1 mmol, 1.0 equiv.) in DCM (50 mL, 0.3 M) were added Boc₂O (6.5 mg, 30 mmol, 2.0 equiv.) DIPEA (14 mL, 7.5 mmol, 5.0 equiv.) and DMAP (550 mg, 4.5 mmol, 0.3 equiv.) at room temperature. The reaction mixture was stirred for 15 hours. The reaction was then quenched with NH₄Cl aqueous solution, extracted with DCM, and dried over MgSO₄. The resulting crude was purified by flash column chromatography (silica, EA: hexane = 1: 5) to afford tert-butyl 2-oxo-1-azaspiro[4.5]decane-1-carboxylate (3.1 g, 12.4 mmol, 82% yield) as a yellow solid.

To a stirred solution of tert-butyl 2-oxo-1-azaspiro[4.5]decane-1-carboxylate (1 g, 4.0 mmol, 1.0 equiv.) in THF (13 mL, 0.3 M) was added 1M NaHMDS (9.9 mL, 9.9 mmol, 2.5 equiv.) at -78°C. The reaction mixture was stirred for 30 minutes at -78°C, followed by the addition of PhSeBr (1.9 g, 7.9 mmol, 2.0 equiv.). The reaction was stirred for an additional 20 minutes and monitored by TLC (silica gel, EA: hexane = 1: 4). Upon completion, the reaction was quenched with NH₄Cl aqueous solution, extracted with ethyl acetate (EA), and dried over MgSO₄. The resulting crude product was concentrated in vacuo to afford a yellow oil. To a stirred solution of

the crude oil in THF (30 mL, 0.13 M) was added 30% H₂O₂ solution (1.12 mL, 9.9 mmol, 2.5 equiv.) at 0°C. The reaction was stirred for 1 hour at 0°C, with progress monitored by TLC (silica gel, EA: hexane = 1: 4). Upon completion, the reaction was diluted with water, extracted with EA, and dried over MgSO₄. The crude product was concentrated in vacuo and purified by flash column chromatography (silica, EA: hexane = 1: 4), affording tert-butyl 2-oxo-1-azaspiro[4.5]dec-3-ene-1-carboxylate (589 mg, 2.3 mmol, 59% yield over two steps) as a white solid with a slight red tint.

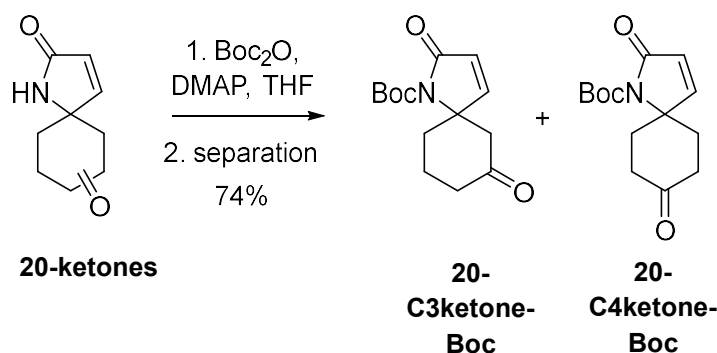
Tert-butyl 2-oxo-1-azaspiro[4.5]dec-3-ene-1-carboxylate (589 mg, 2.3 mmol, 1.0 equiv.) was dissolved in a TFA: DCM = 1: 10 mixture (22.3 mL, 0.1 M), and the solution was cooled to 0°C. The reaction was stirred at 0°C for 3 hours. After completion, the reaction was quenched with saturated NaHCO₃ aqueous solution, extracted with DCM, and dried over MgSO₄. The crude product was concentrated in vacuo and spontaneously solidified into a yellow solid. The solid was rinsed with ether 7 times, affording lactam **S25** (283 mg, 1.9 mmol, 80% yield) as a white powder.

1-azaspiro[4.5]dec-3-en-2-one [S25]. ¹H NMR (500 MHz, CDCl₃) δ 7.60 (s, 1H), 7.08 (dd, *J* = 5.7, 1.8 Hz, 1H), 5.99 (dd, *J* = 5.8, 1.6 Hz, 1H), 1.73 – 1.52 (m, 9H), 1.44 – 1.35 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 173.34, 155.59, 125.21, 64.71, 35.18, 25.07, 23.61. HRMS (TOF ESI+) *m/z* calculated for C₉H₁₄NO [M+H]⁺: 152.1075, found 152.1082.



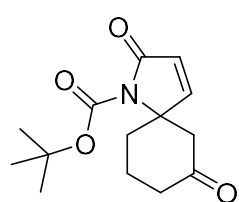
Oxidation of 1-azaspiro[4.5]dec-3-en-2-one [S25]. 1-azaspiro[4.5]dec-3-en-2-one **S25** in HFIP was oxidized according to the Standard conditions with 10mol% (*R,R*)-Mn(CF₃-PDP) and 4.5

equiv. of H₂O₂. The resulting mixture was purified by column chromatography (silica gel, EA: DCM: MeOH = 7: 7: 1) to obtain ketone and alcohol products. The RSM portion was further purified by column chromatography (silica, acetone:benzene = 1: 2). The ketone products were Boc-protected, and the alcohol products were acetyl-protected for quantitative ¹H NMR analysis to calculate site-selectivity (vide infra). **Run 1:** 30% RSM, 53% yield, alcohol: ketone = 1: 1.6. C4: C3 = 1.3: 1. **Run 2:** 26% RSM, 56% yield, alcohol: ketone = 1: 1.4. C4: C3 = 1.3: 1. **Run 3:** 25% RSM, 55% yield, alcohol: ketone = 1: 2.6. C4: C3 = 1.2: 1. **Average:** 27% RSM ± 2.2%, 55% yield ± 1.3%, alcohol: ketone = 1: 1.8. C4: C3 = 1.2: 1.



Identification of 20 ketones. To a stirred solution of keto lactam (30 mg, 0.18 mmol, 1.0 equiv.) in THF (1.8 ml, 0.1 M) were added Boc₂O (194 mg, 0.9 mmol, 5.0 equiv.) and DMAP (33 mg, 0.27 mmol, 1.5 equiv.) at room temperature. The reaction mixture was stirred for 30 minutes under open air, and the reaction was monitored by TLC (silica gel, EA: hexane = 1: 2). Upon completion, the reaction was concentrated in vacuo and purified by flash column chromatography (silica gel, EA: hexane = 1: 1 → 2: 1) to afford separated 4-keto isomer and 3-keto isomer (total 36mg, 0.13 mmol, 74% total yield, 4-keto isomer: 3-keto isomer = 2.2: 1).

tert-butyl 2,7-dioxo-1-azaspiro[4.5]dec-3-ene-1-carboxylate [20-C3ketone-Boc]. ^1H NMR



(500 MHz, CDCl_3) δ 7.20 (d, $J = 6.2$ Hz, 1H), 6.09 (d, $J = 6.2$ Hz, 1H), 3.69

(d, $J = 13.7$ Hz, 1H), 2.95 (td, $J = 13.2, 4.2$ Hz, 1H), 2.52 – 2.38 (m, 2H),

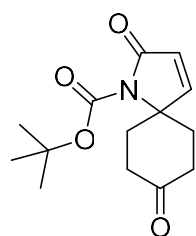
2.23 (dt, $J = 13.8, 2.0$ Hz, 1H), 2.18 – 2.11 (m, 1H), 1.82 – 1.67 (m, 2H), 1.58

(s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 207.80, 167.72, 152.87, 149.94, 125.52, 83.88, 69.96,

48.32, 40.19, 31.74, 28.32, 21.15. HRMS (TOF ESI $^+$) m/z calculated for $\text{C}_{14}\text{H}_{19}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$:

288.1212, found 288.1214.

tert-butyl 2,8-dioxo-1-azaspiro[4.5]dec-3-ene-1-carboxylate [20-C4ketone-Boc]. ^1H NMR



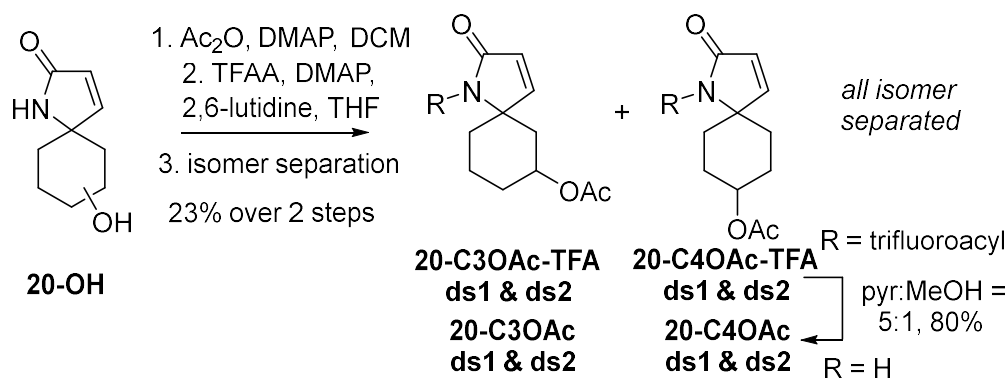
(500 MHz, CDCl_3) δ 7.72 (d, $J = 6.2$ Hz, 1H), 6.21 (d, $J = 6.3$ Hz, 1H), 3.06 (td,

$J = 13.3, 5.5$ Hz, 2H), 2.64 – 2.44 (m, 4H), 1.80 (ddt, $J = 13.6, 6.0, 2.7$ Hz, 2H),

1.56 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.36, 168.22, 152.31, 149.77,

126.23, 83.76, 67.30, 38.12, 31.20, 28.31. HRMS (TOF ESI $^+$) m/z calculated for

$\text{C}_{14}\text{H}_{19}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$: 288.1212, found 288.1207.

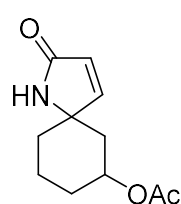


Identification of alcohols 20-OH. To a stirred solution of the alcohol mixture (45 mg, 0.3 mmol, 1.0 equiv.) in DCM (1.5 mL, 0.2 M) was added Ac_2O (92 mg, 0.9 mmol, 3.0 equiv.) and DMAP (27 mg, 0.23 mmol, 0.75 equiv.) at room temperature. The reaction mixture was stirred for 15 hours, with progress monitored by TLC (silica gel, EA: DCM: MeOH = 5: 5: 1). Upon completion,

the reaction was quenched with NH₄Cl aqueous solution, extracted with DCM, and dried over MgSO₄. The crude product was concentrated and used directly without further purification.

To a stirred solution of the crude mixture in THF (1 mL, 0.3 M) was added 2,6-lutidine (0.05 mL, 0.4 mmol, 1.3 equiv.), DMAP (18 mg, 0.15 mmol, 0.5 equiv.), and trifluoroacetic anhydride (TFAA, 0.075 mL, 0.54 mmol, 1.8 equiv.) at 0°C. The reaction mixture was stirred for 10 minutes, with progress monitored by TLC (silica gel, EA: hexane = 1: 2). Upon completion, the reaction was concentrated in vacuo and purified by flash column chromatography (silica gel, EA: hexane = 1: 1.5 → 1: 1) to afford a mixture of 3-OH-TFA ds1 & ds2 (11.3 mg), 4-OH-TFA ds1 (2.9 mg), and 4-OH-TFA ds2 (6.5 mg), for a total of 21 mg (0.069 mmol), corresponding to a 23% yield over two steps. The mixture of 3-OH-TFA ds1 & ds2 was further purified by MPLC (Teledyne Combiflash® system, EA only → EA: MeOH = 20: 1) to afford 3-OH-TFA ds1 & ds2 as separated single isomers. Each TFA ester isomer was dissolved in a pyridine: MeOH = 5: 1 mixture (0.1M) separately for TFA deprotection, yielding single isomers of 3-OH ds1, 3-OH ds2, 4-OH-ds1, and 4-OH-ds2 with an approximate 80% TFA deprotection yield.

2-oxo-1-azaspiro[4.5]dec-3-en-7-yl acetate [20-C3OAc-ds1]. ¹H NMR (500 MHz, CDCl₃) δ



7.12 (d, *J* = 5.7 Hz, 1H), 6.95 (s, 1H), 6.02 (dd, *J* = 5.7, 1.2 Hz, 1H), 5.00 (tt, *J* = 8.5, 3.9 Hz, 1H), 2.05 (s, 3H), 1.96 – 1.82 (m, 3H), 1.76 (dd, *J* = 13.2, 8.7 Hz, 1H), 1.71 – 1.63 (m, 2H), 1.63 – 1.50 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 172.93,

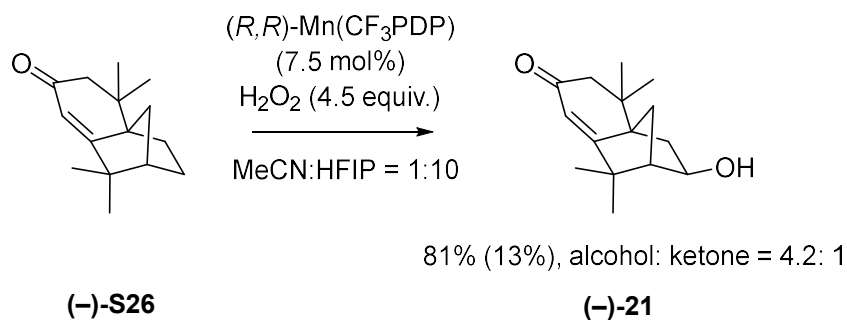
170.20, 154.79, 125.56, 70.23, 64.39, 39.62, 34.49, 30.10, 21.46, 20.76. HRMS (TOF ESI+) *m/z* calculated for C₁₁H₁₆NO₃ [M+H]⁺: 210.1130, found 210.1129. **[20-C3OAc-ds2].** ¹H NMR (500 MHz, CDCl₃) δ 6.99 (dd, *J* = 5.8, 1.8 Hz, 1H), 6.53 (s, 1H), 6.04 (dd, *J* = 5.8, 1.6 Hz, 1H), 5.23 – 5.16 (m, 1H), 2.11 (s, 3H), 1.92 (dd, *J* = 14.1, 3.4 Hz, 1H), 1.88 – 1.81 (m, 1H), 1.79 – 1.55 (m,

6H, containing H₂O peak). ¹³C NMR (126 MHz, CDCl₃) δ 172.47, 170.03, 154.83, 126.16, 69.02, 63.16, 37.92, 34.58, 29.18, 21.62, 18.59. HRMS (TOF ESI+) *m/z* calculated for C₁₁H₁₆NO₃ [M+H]⁺: 210.1130, found 210.1133.

2-oxo-1-azaspiro[4.5]dec-3-en-8-yl acetate [20-C4OAc-ds1]. ¹H NMR (500 MHz, CDCl₃) δ

7.19 (d, *J* = 5.8 Hz, 1H), 6.61 (br s, 1H), 6.05 (d, *J* = 5.9 Hz, 1H), 4.99 (quint, *J* = 4.9 Hz, 1H), 2.07 (s, 3H), 1.95 – 1.82 (m, 6H), 1.62 – 1.55 (m, 2H, containing H₂O peak). ¹³C NMR (126 MHz, CDCl₃) δ 172.78, 170.54, 154.39, 125.86, 69.19, 63.57, 31.16, 28.00, 21.47. HRMS (TOF ESI+) *m/z* calculated for C₁₁H₁₆NO₃ [M+H]⁺: 210.1130, found 210.1130.

[20-C4OAc-ds2]. ¹H NMR (500 MHz, CDCl₃) δ 7.07 (d, *J* = 5.8 Hz, 1H), 6.81 (s, 1H), 6.04 (d, *J* = 5.8 Hz, 1H), 4.84 (tt, *J* = 8.8, 4.0 Hz, 1H), 2.07 (s, 3H), 2.01 (dq, *J* = 13.7, 4.4 Hz, 2H), 1.79 – 1.67 (m, 4H), 1.65 – 1.59 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 172.90, 170.66, 154.66, 125.91, 70.27, 63.29, 32.41, 28.66, 21.48. HRMS (TOF ESI+) *m/z* calculated for C₁₁H₁₆NO₃ [M+H]⁺: 210.1130, found 210.1131.

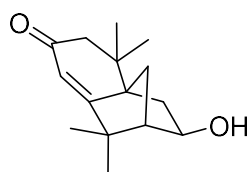


Oxidation of (-)-isolongifolenone [(-)-S26]. (-)-Isolongifolenone was prepared from (-)-isolongifolene according to the reported literature²⁹. The spectroscopic data matched those

reported in the literature. (–)-Isolongifolenone in HFIP was oxidized according to the Standard conditions with 7.5 mol% (*R,R*)-Mn(CF₃-PDP) and 4.5 equiv. H₂O₂. The resulting mixture was purified with column chromatography (1: 2 EtOAc: hexanes → 2: 1 EtOAc: hexanes → EtOAc). **Run 1:** 12% RSM, 84% yield, alcohol: ketone = 4.3: 1. **Run 2:** 12% RSM, 79% yield, alcohol: ketone = 4.3: 1. **Run 3:** 15% RSM, 81% yield, alcohol: ketone = 4.1: 1. **Average:** 13% RSM ± 1.7%, 81% yield ± 2.1%, alcohol: ketone = 4.2: 1. With 7.5mol% (*S,S*)-Mn(CF₃-PDP), 4.5 equiv. H₂O₂: 2% RSM, 77% yield, alcohol: ketone = 8.6: 1.

(2*S*,3*R*,4*aR*)-3-hydroxy-1,1,5,5-tetramethyl-1,2,3,4,5,6-hexahydro-7*H*-2,4*a*-

methanonaphthalen-7-one [(–)-21-OH]. ¹H NMR (600 MHz, CDCl₃) δ 5.71 (s, 1H), 4.32 (d, *J*



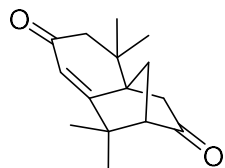
= 6.5 Hz, 1H), 2.33 (d, *J* = 16.2 Hz, 1H), 2.07 (d, *J* = 16.2 Hz, 1H), 1.96 (s, 1H), 1.89 (d, *J* = 10.5 Hz, 1H), 1.81 (ddd, *J* = 13.0, 6.6, 2.5 Hz, 1H), 1.75 (app d, *J* = 13.0 Hz, 1H), 1.60 (d, *J* = 1.9 Hz, 1H), 1.12 (s, 3H), 1.10 (s, 3H),

1.07 (s, 3H), 0.99 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 200.04, 182.03, 117.68, 70.38, 58.11, 54.53, 49.94, 42.25, 40.27, 34.25, 32.96, 27.34, 26.04, 25.40, 24.39. [α]_D²³ = -93.95 (c=1.0, CHCl₃).

HRMS (TOF MS EI⁺) *m/z* calculated for C₁₅H₂₃O₂ [M+H]⁺: 235.1698, found 235.1695.

(2*S*,4*aR*)-1,1,5,5-tetramethyl-1,2,5,6-tetrahydro-7*H*-2,4*a*-methanonaphthalene-3,7(4*H*)-

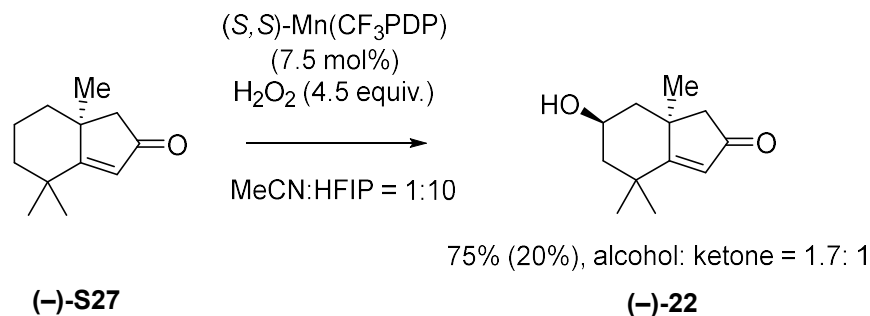
dione [(–)-21-ketone]. ¹H NMR (500 MHz, CDCl₃) δ 5.88 (s, 1H), 2.43 (s, 1H), 2.37 (d, *J* = 17.9



Hz, 1H), 2.34 (d, *J* = 17.7 Hz, 1H), 2.16 (d, *J* = 16.5 Hz, 1H), 2.05 – 1.93 (m, 2H), 1.81 (d, *J* = 10.8 Hz, 1H), 1.20 (s, 3H), 1.13 (s, 3H), 1.08 (s, 3H), 1.04 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 212.93, 198.89, 177.18, 119.60, 61.14,

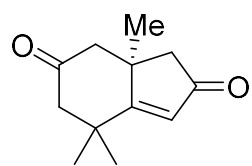
56.95, 49.75, 43.31, 43.05, 35.55, 34.42, 26.22, 25.90, 25.84, 23.94. $[\alpha]_D^{23} = -58.42$ ($c=1.0$, CHCl_3).

HRMS (TOF EI+) m/z calculated for $\text{C}_{15}\text{H}_{20}\text{O}_2$ $[M^+]$: 232.1463, found 232.1470.



Oxidation of (S)-4,4,7a-trimethyl-1,4,5,6,7,7a-hexahydro-2H-inden-2-one [(-)-S27]. (S)-4,4,7a-trimethyl-1,4,5,6,7,7a-hexahydro-2H-inden-2-one was prepared according to the reported literature³⁰. The spectroscopic data matched those reported in the literature. (S)-4,4,7a-trimethyl-1,4,5,6,7,7a-hexahydro-2H-inden-2-one in HFIP was oxidized according to the Standard conditions with 7.5 mol% (S,S)-Mn(CF₃-PDP) and 4.5 equiv. H₂O₂. The resulting mixture was purified with column chromatography (1: 1 EtOAc: hexanes → 2: 1 EtOAc). **Run 1:** 18% RSM, 73% yield, alcohol: ketone = 1.8: 1. **Run 2:** 21% RSM, 77% yield, alcohol: ketone = 1.7: 1. **Run 3:** 20% RSM, 74% yield, alcohol: ketone = 1.6: 1. **Average:** 20% RSM ± 1.2%, 75% yield ± 1.7%, alcohol: ketone = 1.7: 1. With 5 mol% (R,R)-Mn(CF₃-PDP), 3.0 equiv. H₂O₂: 48% RSM, 52% yield, alcohol: ketone = 2.1: 1. With 5 mol% (S,S)-Mn(CF₃-PDP), 3.0 equiv. H₂O₂: 40% RSM, 60% yield, alcohol: ketone = 2.1: 1.

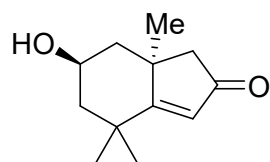
(S)-4,4,7a-trimethyl-4,5,7,7a-tetrahydro-1H-indene-2,6-dione [(-)-22-ketone]. ¹H NMR (600



MHz, CDCl₃) δ 6.05 (s, 1H), 2.64 (d, *J* = 14.8 Hz, 1H), 2.53 (d, *J* = 14.8 Hz, 1H), 2.49 (d, *J* = 14.7 Hz, 1H), 2.46 – 2.39 (m, 3H), 1.39 (s, 3H), 1.33 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 208.02, 206.34, 189.33, 127.78, 53.60,

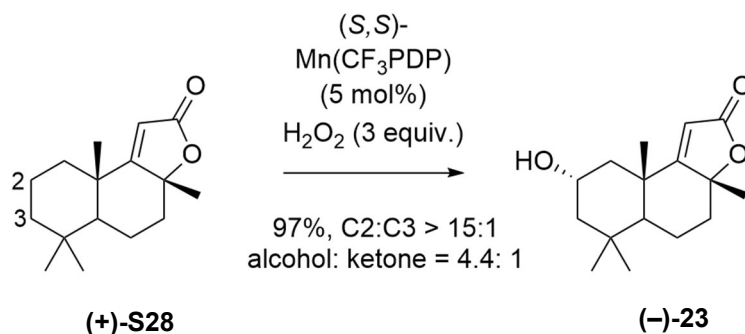
53.41, 52.77, 45.91, 38.28, 31.83, 29.17, 28.73. [α]_D^{23.6} = -137.28° (c = 1.00, CHCl₃). HRMS (TOF MS EI⁺) *m/z* calculated for C₁₂H₁₇O₂ [M+H]⁺: 193.1229, found 193.1232.

(6R,7aS)-6-hydroxy-4,4,7a-trimethyl-1,4,5,6,7,7a-hexahydro-2H-inden-2-one [(-)-22-OH].



¹H NMR (600 MHz, CDCl₃) δ 5.86 (s, 1H), 4.20 (app t, *J* = 11.4 Hz, 1H), 2.35 (d, *J* = 18.0 Hz, 1H), 2.30 (d, *J* = 18.7 Hz, 1H), 2.24 (app br d, *J* = 12.0 Hz, 1H), 1.98 (app br d, *J* = 12.7 Hz, 1H), 1.95 (br s, 1H), 1.39 – 1.30

(m, 2H), 1.37 (s, 3H), 1.28 (s, 3H), 1.24 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 207.81, 191.83, 126.82, 64.32, 54.81, 49.83, 48.68, 44.74, 36.77, 31.34, 28.52, 27.24. [α]_D^{24.4} = -69.6° (c = 1.00, CHCl₃). HRMS (TOF MS EI⁺) *m/z* calculated for C₁₂H₁₉O₂ [M+H]⁺: 195.1385, found 195.1386.



Oxidation of (3aR,9aS)-3a,6,6,9a-tetramethyl-4,5,5a,6,7,8,9,9a-octahydronaphtho[2,1-b] furan-2(3aH)-one [(+)-S28]. (3aR,9aS)-3a,6,6,9a-tetramethyl-4,5,5a,6,7,8,9,9a-

octahydronaphtho[2,1-b]furan-2(3aH)-one was prepared according to the reported literature³¹. **S28** in HFIP was oxidized according to the Standard conditions with 5 mol% (*S,S*)-Mn(CF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (1: 2 EtOAc: hexanes → 1: 1 EtOAc: hexanes → 2: 1 EtOAc: hexanes). **Run 1:** 95% yield, alcohol: ketone = 3.8: 1, C2: C3 >15: 1. **Run 2:** 98% yield, alcohol: ketone = 4.8: 1, C2: C3 > 15: 1. **Run 3:** 97% yield, alcohol: ketone = 4.7: 1, C2: C3 >15: 1. **Average:** 97% yield ± 1.2%, alcohol: ketone = 4.4: 1, C2: C3 >15: 1. With 5mol% (*R,R*)-Mn(CF₃-PDP), 3.0 equiv. H₂O₂: 91% yield, alcohol: ketone = 8: 1, C2: C3 = 6: 1.

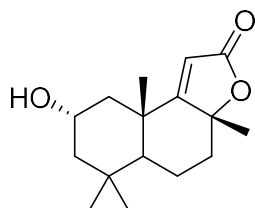
(3aR,9aS)-3a,6,6,9a-tetramethyl-3a,4,5,5a,6,7,9,9a-octahydronaphtho[2,1-b]furan-2,8-dione

[(-)-23-C2ketone]. ¹H NMR (600 MHz, CDCl₃) δ 5.52 (s, 1H), 2.64 (d, *J* = 12.4 Hz, 1H), 2.51 (dd, *J* = 12.3, 2.3 Hz, 1H), 2.40 – 2.35 (m, 1H), 2.32 (d, *J* = 13.8 Hz, 1H), 2.25 (dd, *J* = 13.7, 2.3 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.64 – 1.54 (m, 3H), 1.56 (s, 3H), 1.18 (s, 3H), 1.09 (s, 3H), 0.97 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 208.58, 181.29, 171.50, 110.55, 86.91, 56.18, 55.09, 52.93, 43.73, 40.28, 39.04, 33.53, 24.98,

23.17, 19.87, 19.47. $[\alpha]_D^{26.6} = -138.6^\circ$ ($c = 1.00$, CHCl_3). HRMS (TOF EI+) m/z calculated for $\text{C}_{16}\text{H}_{23}\text{O}_3$ $[\text{M}+\text{H}]^+$: 263.1647, found 263.1643.

(3aR,8S,9aS)-8-hydroxy-3a,6,6,9a-tetramethyl-4,5,5a,6,7,8,9,9a-octahydronaphtho[2,1-

b]furan-2(3aH)-one [(-)-23-C2OH]. ^1H NMR (600 MHz, CDCl_3) δ 5.55 (s, 1H), 4.11 – 4.03 (m,

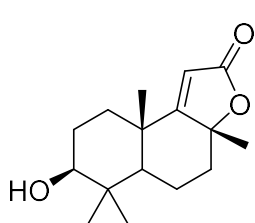


1H), 2.35 – 2.28 (m, 1H), 2.17 (app d, $J = 11.9$ Hz, 1H), 1.88 – 1.80 (m, 2H), 1.66 (br s, 1H), 1.55 (s, 3H), 1.54 – 1.40 (m, 3H), 1.22 (s, 3H), 1.17 (app t, $J = 12.1$ Hz, 1H), 0.96 (s, 3H), 0.95 (s, 3H), 0.97 – 0.94 (m, 1H). ^{13}C NMR

(151 MHz, CDCl_3) δ 183.43, 172.28, 109.87, 87.17, 64.44, 55.33, 50.97, 46.19, 41.20, 40.76, 35.47, 33.55, 25.53, 22.57, 19.29, 19.19. $[\alpha]_D^{25.7} = -134.0^\circ$ ($c = 1.00$, CHCl_3). HRMS (TOF EI+) m/z calculated for $\text{C}_{16}\text{H}_{25}\text{O}_3$ $[\text{M}+\text{H}]^+$: 265.1804, found 265.1805.

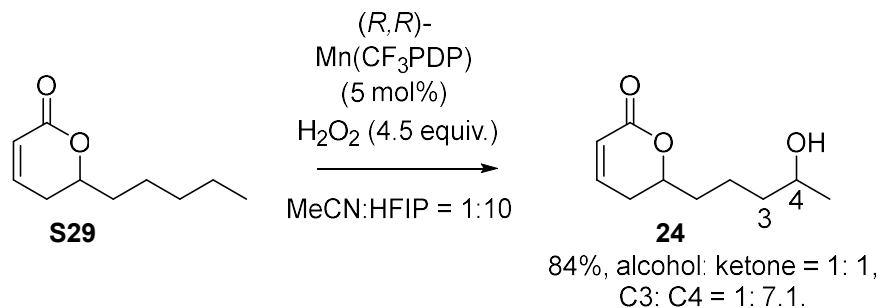
(3aR,7S,9aS)-7-hydroxy-3a,6,6,9a-tetramethyl-4,5,5a,6,7,8,9,9a-octahydronaphtho[2,1-

b]furan-2(3aH)-one [23-C3OH]. ^1H NMR (600 MHz, CDCl_3) δ 5.52 (s, 1H), 3.26 (dd, $J = 11.3$,



4.5 Hz, 1H), 2.31 (dt, $J = 12.4$, 3.0 Hz, 1H), 1.91 – 1.78 (m, 3H), 1.78 – 1.72 (m, 1H), 1.66 (td, $J = 13.0$, 4.2 Hz, 1H), 1.60 – 1.53 (m, 1H), 1.56 (s, 3H), 1.50 (dd, $J = 12.7$, 4.1 Hz, 1H), 1.47 – 1.40 (m, 1H), 1.20 (s, 3H), 1.02 (s, 3H), 0.93 (dd, $J = 12.1$, 2.5 Hz, 1H), 0.89 (s, 3H). ^{13}C NMR (151 MHz,

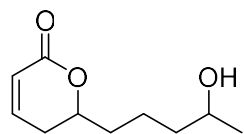
CDCl_3) δ 183.96, 172.33, 109.93, 87.21, 78.20, 54.77, 40.62, 39.78, 39.54, 35.37, 28.34, 27.02, 25.42, 19.43, 18.32, 15.63. HRMS (TOF EI+) m/z calculated for $\text{C}_{16}\text{H}_{25}\text{O}_3$ $[\text{M}+\text{H}]^+$: 265.1804, found 265.1805.



Oxidation of 6-pentyl-5,6-dihydro-2H-pyran-2-one [S29]. S29 is commercially available. 6-pentyl-5,6-dihydro-2H-pyran-2-one in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) and 4.5 equiv. of H₂O₂. The resulting mixture was purified with column chromatography (2: 1 EtOAc: hexanes → 4: 1 EtOAc: hexanes). **Run 1:** 86% yield, alcohol: ketone = 1: 1, C3: C4 = 1: 7.1. **Run 2:** 86% yield, alcohol: ketone = 1: 1, C3: C4 = 1: 7.1. **Run 3:** 81% yield, alcohol: ketone = 1: 1, C3: C4 = 1: 7.1. **Average:** 84% yield ± 2.4%, alcohol: ketone = 1: 1, C3: C4 = 1: 7.1.

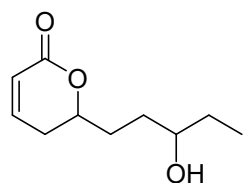
6-(4-oxopentyl)-5,6-dihydro-2H-pyran-2-one [24-C4ketone]. Ketones isolated as a 15: 1 mixture of constitutional isomers. ¹H NMR (500 MHz, CDCl₃) δ 6.87 (ddd, *J* = 9.8, 5.0, 3.7 Hz, 1H), 6.01 (d, *J* = 9.8 Hz, 1H), 4.42 (app dq, *J* = 10.4, 6.0 Hz, 1H), 2.50 (t, *J* = 6.5 Hz, 2H), 2.37 – 2.30 (m, 2H), 2.14 (s, 3H), 1.85 – 1.64 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 208.49, 164.47, 145.11, 121.53, 77.84, 43.08, 34.18, 30.10, 29.39, 19.17. HRMS (TOF ES⁺) *m/z* calculated for C₁₀H₁₄O₃Na [M+Na]⁺: 205.0841, found 205.0845.

6-(4-hydroxypentyl)-5,6-dihydro-2H-pyran-2-one [24-C4OH]. Product isolated as a mixture of

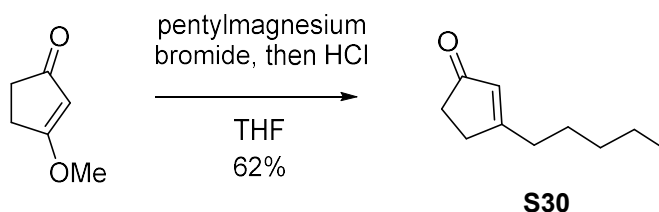


diastereomers. ^1H NMR (500 MHz, CDCl_3) δ 6.87 (ddd, $J = 9.0, 4.9, 3.4$ Hz, 1H), 6.03 – 5.98 (m, 1H), 4.46 – 4.38 (m, 1H), 3.84 – 3.77 (m, 1H), 2.35 – 2.29 (m, 2H), 1.87 – 1.76 (m, 1H), 1.72 – 1.41 (m, 6H), 1.19 (d, $J = 6.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.67, 145.20, 121.52, 78.05, (77.96), 67.95, (67.90), 38.99, (38.88), 34.95, (34.86), 29.50, (29.45), 23.73, (21.31), 21.16. HRMS (TOF ES+) m/z calculated for $\text{C}_{10}\text{H}_{16}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^{+}$: 207.0997, found 207.1001.

6-(3-hydroxypentyl)-5,6-dihydro-2H-pyran-2-one [24-C3OH]. Product isolated as a mixture of



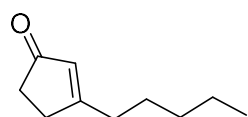
diastereomers. ^1H NMR (500 MHz, CDCl_3) δ 6.82 (ddd, $J = 9.0, 4.9, 3.4$ Hz, 1H), 5.98 – 5.93 (m, 1H), 4.42 – 4.32 (m, 1H), 3.80 – 3.70 (m, 1H), 2.30 – 2.24 (m, 2H), 1.82 – 1.69 (m, 1H), 1.68 – 1.33 (m, 6H), 1.14 (d, $J = 6.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.67, 145.20, 121.52, 78.05, (77.96), 67.95, (67.90), 38.99, (38.88), 34.95, (34.86), 29.50, (29.45), 23.73, (21.31), 21.16. HRMS (TOF ES+) m/z calculated for $\text{C}_{10}\text{H}_{16}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^{+}$: 207.0997, found 207.1001.



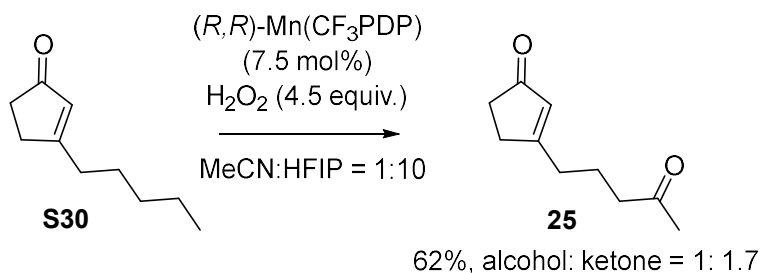
Preparation of 3-pentylcyclopent-2-en-1-one [S30]. A solution of 3-methoxycyclopent-2-en-1-one (1.00 g, 8.92 mmol, 1.0 equiv.) in THF (18 mL) was added dropwise to a 1M solution of

pentylmagnesium bromide (17.8 mmol, 2.0 equiv.) in THF (17.8 mL) at 0 °C. The reaction was warmed to room temperature and stirred for 4h until completion was verified by TLC analysis (EtOAc: hexanes = 1: 9), at which point it was quenched with 18 mL of 1M HCl. The mixture was stirred for 30 minutes, then extracted 3x with diethyl ether. Combined organics were dried over magnesium sulfate, filtered, then concentrated under reduced pressure. The crude reaction mixture was purified by silica flash column chromatography (EtOAc: hexanes = 1: 9), then purified by vacuum distillation to give 3-pentylcyclopent-2-en-1-one (846 mg, 5.56 mmol, 62% yield).

3-pentylcyclopent-2-en-1-one [S30]. The spectroscopic data of **S30** matched those reported in the

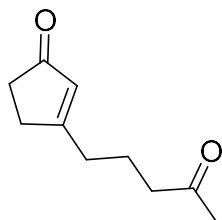


literature³².



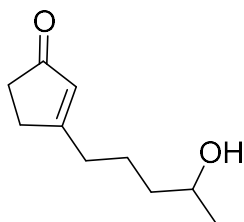
Oxidation of 3-pentylcyclopent-2-en-1-one [S30]. 3-pentylcyclopent-2-en-1-one in HFIP was oxidized according to the Standard conditions with 7.5 mol% (*R,R*)-Mn(CF₃-PDP) and 4.5 equiv. of H₂O₂. The resulting mixture was purified with column chromatography (2: 1 EtOAc: hexanes → 66: 33: 2 EtOAc: hexanes: MeOH). **Run 1:** 62% yield, alcohol: ketone = 0.5: 1. **Run 2:** 64% yield, alcohol: ketone = 1: 1.7. **Run 3:** 59% yield, alcohol: ketone = 1: 1.7. **Average:** 62% yield ± 2.1%, alcohol: ketone = 1: 1.7.

3-(4-oxopentyl)cyclopent-2-en-1-one [25-ketone]. ^1H NMR (500 MHz, CDCl_3) δ 5.92 (s, 1H),



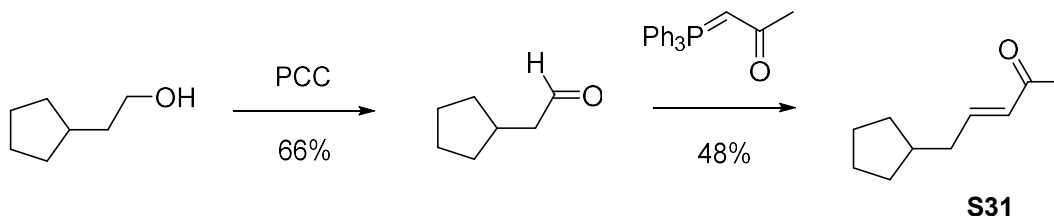
2.58 – 2.53 (m, 2H), 2.48 (t, $J = 7.2$ Hz, 2H), 2.42 – 2.35 (m, 4H), 2.12 (s, 3H), 1.84 (quint, $J = 7.3$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.02, 207.94, 181.96, 129.77, 42.69, 35.36, 32.74, 31.51, 30.13, 20.90. HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 167.1072, found 167.1066.

3-(4-hydroxypentyl)cyclopent-2-en-1-one [25-OH]. Alcohol was isolated as a 13: 1 mixture with



a minor alcohol isomer. ^1H NMR (500 MHz, CDCl_3) δ 5.94 (s, 1H), 3.87 – 3.76 (m, 1H), 2.61 – 2.55 (m, 2H), 2.47 – 2.35 (m, 4H), 2.00 – 1.54 (m, 2H), 1.54 – 1.43 (m, 2H), 1.22 – 1.16 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.39, 183.07, 129.64, 67.68, 38.80, 35.41, 33.54, 31.61, 23.81, 23.39.

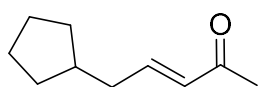
HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 169.1229, found 169.1221.



Preparation of (E)-5-cyclopentylpent-3-en-2-one [S31]. To a 1 L round bottom flask equipped with a stir bar was added 2-cyclopentylethanol (2.5g, 21.89 mmol, 1.0 equiv.), PCC (6.135 g, 28.46 mmol, 1.3 equiv.), and dichloromethane (218 mL). The reaction was stirred for 3 hours until completion was confirmed by TLC analysis (Et_2O : pentane = 1: 4). 200 mL of diethyl ether were added, the reaction was filtered through celite, and the filtrate concentrated under reduced pressure to yield crude aldehyde, which was used in the next step without further purification. Crude

aldehyde (1.6 g, 14.21 mmol, 1.3 equiv.) and acetylmethyl triphenylphosphorane (5.9 g, 18.54 mmol, 1.3 equiv.) were dissolved in 30 mL of benzene in a 100 mL round bottom flask equipped with a reflux condenser and stirbar. The reaction was heated to 100 °C and stirred for 4 hours until completion was confirmed by TLC analysis (ethyl ether:pentane = 1: 4). The reaction was cooled to room temperature and allowed to stand overnight, then filtered through celite and concentrated under reduced pressure to remove benzene. The crude reaction mixture was taken up in 250 mL hexanes and added to an ice bath to precipitate the remaining phosphine oxide, then filtered once more through celite. Hexane was removed under reduced pressure and the crude mixture was purified by silica flash column chromatography (ethyl ether:pentane = 1: 4) to furnish (E)-5-cyclopentylpent-3-en-2-one (1.05 g, 6.89 mmol, 48% yield).

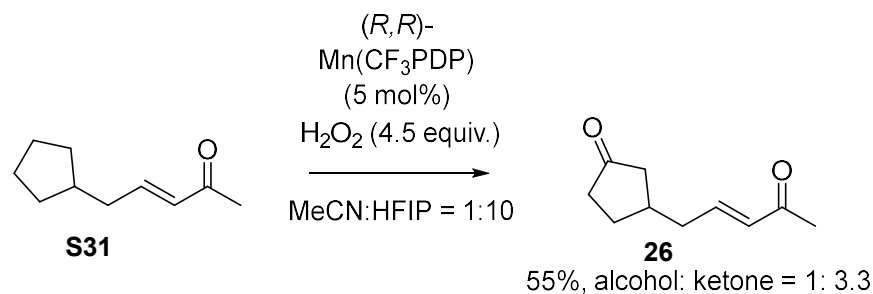
(E)-5-cyclopentylpent-3-en-2-one [S31]. ^1H NMR (500 MHz, CDCl_3) δ 6.78 (dt, $J = 15.9$, 7.2



Hz, 1H), 6.06 (d, $J = 15.9$ Hz, 1H), 2.24 (s, 3H), 2.25 – 2.20 (m, 2H), 1.94 (hept, $J = 7.6$ Hz, 1H), 1.82 – 1.72 (m, 2H), 1.67 – 1.47 (m, 4H), 1.20 – 1.09

(m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.93, 148.08, 131.82, 39.08, 38.96, 32.52, 26.99, 25.18.

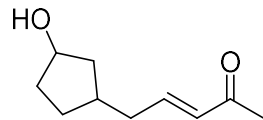
HRMS (TOF ESI+) m/z calculated for $\text{C}_{10}\text{H}_{17}\text{O}$ $[\text{M}+\text{H}]^+$: 153.1279, found 153.1277.



Oxidation of (E)-5-cyclopentylpent-3-en-2-one [S31]. (E)-5-cyclopentylpent-3-en-2-one in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) and 4.5 equiv. of H₂O₂. The resulting mixture was purified with column chromatography (2: 3 EtOAc: hexanes → 1: 1 EtOAc: hexanes). **Run 1:** 54% yield, alcohol: ketone = 1: 3.3. **Run 2:** 56% yield, alcohol: ketone = 1: 2.5. **Run 3:** 55% yield, alcohol: ketone = 1: 3.3. **Average:** 55% yield ± 0.8%, alcohol: ketone = 1: 3.3.

(E)-3-(4-oxopent-2-en-1-yl)cyclopentan-1-one [26-ketone]. ¹H NMR (500 MHz, CDCl₃) ¹H NMR (500 MHz, CDCl₃) δ 6.79 – 6.69 (m, 1H), 6.10 (d, *J* = 16.1 Hz, 1H), 2.43 – 2.25 (m, 5H), 2.22 (s, 3H), 2.21 – 2.11 (m, 2H), 1.84 (dd, *J* = 17.3, 7.8 Hz, 1H), 1.62 – 1.51 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 218.27, 198.25, 145.00, 132.60, 44.63, 38.22, 38.08, 36.10, 29.19, 27.25. HRMS (TOF ESI+) *m/z* calculated for C₁₀H₁₅O₂ [M+H]⁺: 167.1072, found 167.1067.

(E)-5-(3-hydroxycyclopentyl)pent-3-en-2-one [26-OH]. Alcohols were isolated as a 0.7:0.3



mixture of diastereomers. ^1H NMR (500 MHz, C_6D_6) δ 6.81 – 6.70 (m, 1H),

6.10 – 6.02 (m, 1H), 4.38 – 4.26 (m, 1H), 2.34 – 2.29 (m, 1H), 2.25 – 2.19

(m, 4H), 2.18 – 2.04 (m, 1H), 2.03 – 1.86 (m, 2.3H), 1.86 – 1.70 (m, 1.7H), 1.66 – 1.52 (m, 1H),

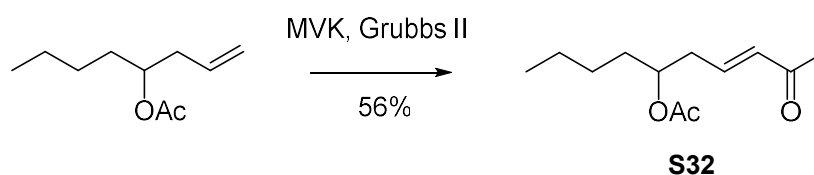
1.77-1.71 (m, 1.4H), 1.72 – 1.67 (m, 0.6H), 1.65 – 1.47 (m, 1.7H), 1.44 – 1.32 (m, 2H), 1.49 –

1.32 (m, 1H), 1.27 – 1.13 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.95, (198.89), 147.46,

(147.40), 131.98, (131.93), 73.55, (73.48), 42.29, (41.83), 39.44, (38.80), 37.28, (36.46), 35.47,

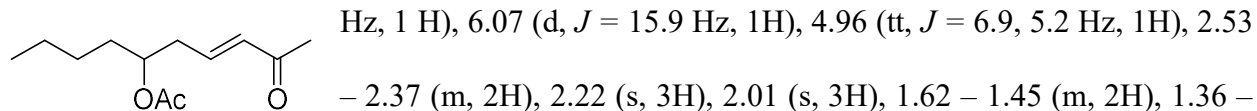
(35.11), 30.23, (30.09), 27.02, (26.98). HRMS (ESI $^+$) m/z calculated for $\text{C}_{10}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 168.1150,

found 168.1146.

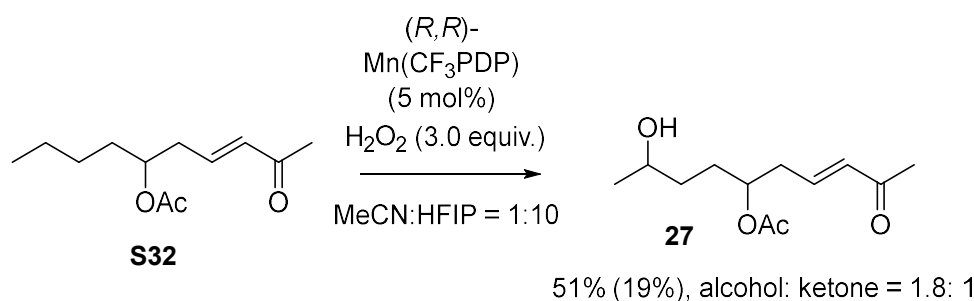


Preparation of (E)-9-oxodec-7-en-5-yl acetate [S32]. Oct-1-en-4-yl acetate was prepared according to the reported literature procedure³³. The spectroscopic data matched those reported in the literature. To a flame-dried round bottom flask under argon was added copper (I) iodide (22.9 mg, 0.12 mmol, 3 mol%), oct-1-en-4-yl acetate (681 mg, 4.0 mmol, 1.0 equiv.) methyl vinyl ketone (1 mL, 12.0 mmol, 3.0 equiv.), and Grubbs II (67.9 mg, 0.08 mmol, 2 mol%). The reaction was stirred at room temperature for 16 h until completion was confirmed with TLC analysis (ethyl acetate: hexanes 1: 9). Solvent was removed under reduced pressure and the crude reaction mixture was purified by silica flash column chromatography (ethyl acetate: hexanes 1: 9) to furnish (E)-9-oxodec-7-en-5-yl acetate (484 mg, 2.28 mmol, 56% yield).

(E)-9-oxodec-7-en-5-yl acetate [S32]. ^1H NMR (500 MHz, CDCl_3) δ 6.69 (ddd, $J = 16.0, 7.8, 6.8$

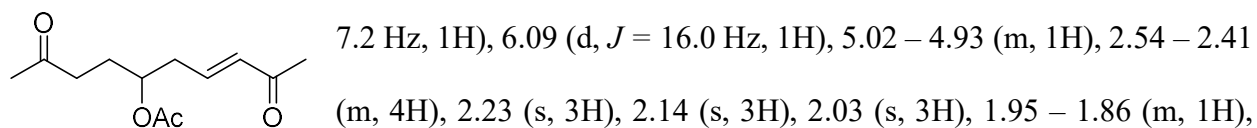


1.19 (m, 4H), 0.87 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.38, 170.76, 143.03, 133.75, 72.51, 37.39, 33.64, 27.54, 26.97, 22.53, 21.23, 14.03. HRMS (TOF ES+) m/z calculated for $\text{C}_{12}\text{H}_{20}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 235.1310, found 235.1314.



Oxidation of (E)-9-oxodec-7-en-5-yl acetate [S32]. (E)-9-oxodec-7-en-5-yl acetate in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)- $\text{Mn}(\text{CF}_3\text{-PDP})$ and 3.0 equiv. of H_2O_2 . The resulting mixture was purified with column chromatography (1: 2 EtOAc: hexanes $\rightarrow$ 1: 1 EtOAc: hexanes). **Run 1:** 21% RSM, 54% yield, alcohol: ketone = 1.7: 1. **Run 2:** 22% RSM, 50% yield, alcohol: ketone = 1.5: 1. **Run 3:** 15% RSM, 50% yield, alcohol: ketone = 2.3: 1. **Average:** 19% $\pm$ 3.1% RSM, 51% yield $\pm$ 1.9%, alcohol: ketone = 1.8: 1.

(E)-2,9-dioxodec-7-en-5-yl acetate [27-ketone]. ^1H NMR (500 MHz, CDCl_3) δ 6.68 (dt, $J = 15.9,$

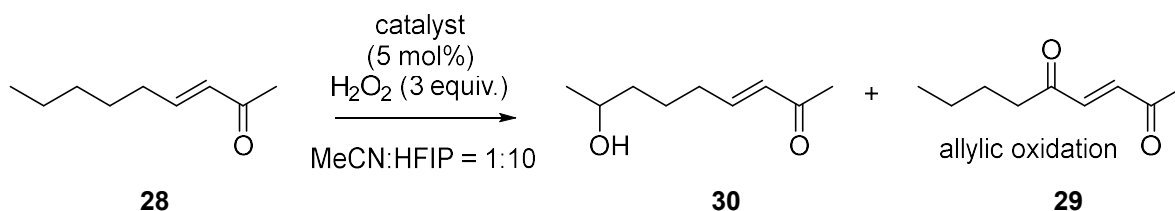


1.84 – 1.73 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 207.45, 198.31, 170.78, 142.30, 133.97, 71.77,

39.43, 37.63, 30.10, 27.88, 27.08, 21.17. HRMS (TOF ES⁺) m/z calculated for C₁₂H₁₈O₄Na [M+Na]⁺: 249.1103, found 249.1108.

(E)-2-hydroxy-9-oxodec-7-en-5-yl acetate [27-OH]. ¹H NMR (500 MHz, CDCl₃) δ 6.70 (dt, J =

16.0, 7.3 Hz, 1H), 6.08 (d, J = 16.0 Hz, 1H), 5.04 – 4.95 (m, 1H), 3.84 – 3.73 (m, 1H), 2.56 – 2.41 (m, 2H), 2.25 – 2.21 (m, 3H), 2.04 – 2.01 (s, 3H), 1.80 – 1.55 (m, 3H), 1.52 – 1.37 (m, 2H), 1.18 (app d, J = 6.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 198.44, 170.88, (170.86), 142.82, (142.77), 133.84, (133.82), 72.62, (72.32), 67.80, (67.58), 37.46, (37.45), 34.89, (34.66), 30.38, (30.16), 27.04, 23.82, 21.24, (21.23). HRMS (TOF ES⁺) m/z calculated for C₁₂H₂₀O₄Na [M+Na]⁺: 251.1259, found 251.1264.



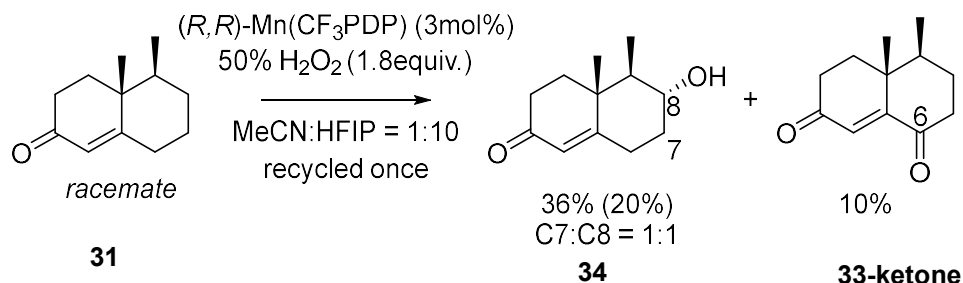
(*R,R*)-Mn(CF₃PDP):
 44% yield, alcohol:ketone = 1.3:1, 5% allylic oxidation
 (*S,R,R,S*)-Mn(MeCF₃PDP):
 30% yield (21% RSM), alcohol only, <5% allylic oxidation

Oxidation of (E)-non-3-en-2-one [28]. (E)-non-3-en-2-one was purchased from Ambeed (catalog number A386764) and used as received. (E)-non-3-en-2-one in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (1: 2 EtOAc: hexanes → 1: 1 EtOAc: hexanes). **Run 1:** 41% yield, alcohol: ketone = 1.3: 1, 6% allylic. **Run 2:** 45% yield, alcohol: ketone = 1.4:

1, 5% allylic. **Run 3:** 46% yield, alcohol: ketone = 1.2: 1, 5% allylic. **Average:** 44% yield $\pm$ 2.2%, alcohol: ketone = 1.3: 1, 5% $\pm$ 0.5% allylic. With 5 mol% (*S,R,R,S*)-Mn(MeCF₃-PDP) and 3.0 equiv. H₂O₂. **Run 1:** 21% RSM, 31%, yield, alcohol only, <5% allylic. **Run 2:** 21% RSM, 28%, yield, alcohol only, <5% allylic. **Average:** 21% RSM, 30% yield $\pm$ 1.5%, alcohol only, <5% allylic.

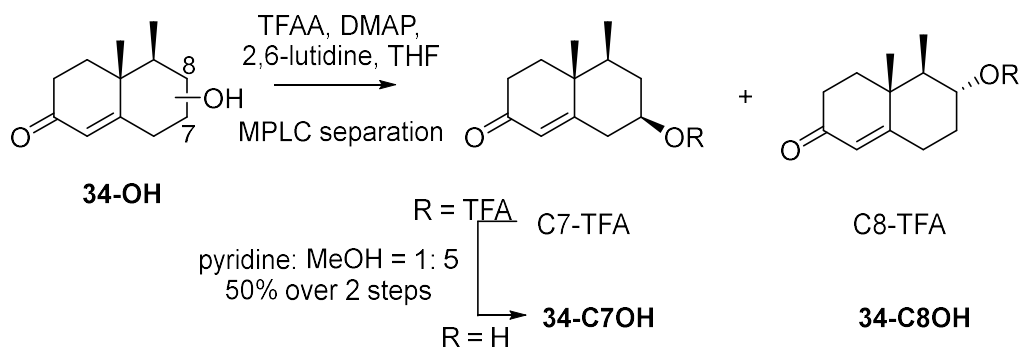
(E)-non-3-ene-2,8-dione [30-ketone]. ¹H NMR (500 MHz, CDCl₃) δ 6.75 (dt, *J* = 16.0, 6.9 Hz, 1H), 6.07 (d, *J* = 16.0 Hz, 1H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.28 – 2.19 (m, 2H), 2.23 (s, 3H), 2.13 (s, 3H), 1.76 (p, *J* = 7.3 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 208.25, 198.73, 147.35, 131.88, 42.71, 31.78, 30.15, 27.06, 21.98. HRMS (TOF EI+) *m/z* calculated for C₉H₁₄O₂ [M]⁺: 154.0994, found 154.1003.

(E)-8-hydroxynon-3-en-2-one [30-OH]. ¹H NMR (600 MHz, CDCl₃) δ 6.80 (dt, *J* = 15.9, 6.9 Hz, 1H), 6.08 (d, *J* = 16.0 Hz, 1H), 3.81 (sext, *J* = 6.1 Hz, 1H), 2.29 – 2.22 (m, 2H), 2.24 (s, 3H), 1.67 – 1.56 (m, 1H), 1.55 – 1.43 (m, 3H), 1.35 (br s, 1H), 1.20 (d, *J* = 6.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 198.85, 148.15, 131.64, 67.94, 38.75, 32.50, 27.04, 24.43, 23.82. HRMS (TOF EI+) *m/z* calculated for C₉H₁₆O₂ [M]⁺: 156.1150, found 156.1146.



Oxidation of (4aR,5S)-4a,5-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one [31].

(4aR,5S)-4a,5-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one was prepared according to the reported literature³⁴. Compound **31** (0.4 mmol) in HFIP was oxidized according to the Standard conditions with 3 mol% (*R,R*)-Mn(CF₃-PDP) and 1.8 equiv. of H₂O₂. The resulting mixture was purified by column chromatography (silica, acetone: hexane = 1: 6 → 1: 2), yielding recovered starting material (RSM) and a mixture of oxidation products. The RSM was resubjected to the same conditions (Standard conditions with 3 mol% (*R,R*)-Mn(CF₃-PDP) and 1.8 equiv. of H₂O₂). The resulting mixture, combined with the products from the first run, was purified by column chromatography (silica, acetone: hexane = 1: 6 → 1: 2). The RSM and yields (%) from both runs were combined to calculate the final result. Site-selectivity of alcohol mixture was obtained by quantitative ¹H NMR analysis. **Run 1:** first run - 33% RSM, after recycle - 20% RSM, 34% yield, alcohol only (C7: C8 = 1: 1), allylic oxidation 10%. **Run 2:** first run - 47% RSM, after recycle - 19% RSM, 36% yield, alcohol only (C7: C8 = 1: 1), allylic oxidation 11%. **Run 3:** first run - 47% RSM, after recycle - 20% RSM, 39% yield, alcohol only (C7: C8 = 1: 1), allylic oxidation 10%. **Average** (after recycle): 20% RSM ± 0.6%, 36% yield ± 1.8%, alcohol only (C7: C8 = 1: 1), allylic oxidation 10% ± 0.7%. With 3 mol% (*S,R,R,S*)-Mn(MeCF₃-PDP) and 1.8 equiv. of H₂O₂ after recycle: 20% RSM, 37% yield, alcohol: ketone = 1.8: 1, C7: C8 = 1: 1, allylic oxidation 5%.

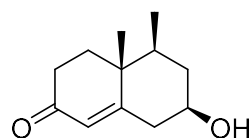


Separation and Identification of Alcohol Mixture. To a stirred solution of alcohol mixture **34** (18 mg, 0.09 mmol, 1.0 equiv.) in THF (1.0 mL, 0.1 M) was added 2,6-lutidine (0.02 mL, 0.19 mmol, 2.0 equiv.), DMAP (6 mg, 0.047 mmol, 0.5 equiv.), and TFAA (0.026 mL, 0.19 mmol, 2.0 equiv.) at -78°C . The reaction was completed in 30 minutes at -78°C , confirmed by TLC analysis (silica, EA: pentane = 1: 1). Upon completion, the resulting mixture concentrated in vacuo and purified by MPLC (Teledyne Combiflash® system, ether: pentane = 1: 4 $\rightarrow$ 1: 1), separating two constitutional isomers of TFA esters **C7-TFA** and **C8-TFA**.

Each TFA ester was transferred into separate vials, and a mixture of pyridine: MeOH = 1: 5 (0.1 M) was added. Each reaction mixture was stirred for 15 minutes at room temperature, then concentrated in vacuo and purified by column chromatography (acetone: hexane = 1: 3), resulting in the complete separation of the two alcohol isomers **C7-OH** and **C8-OH** as colorless oils with approximately 50% yield over two steps.

(4aR,5S,7R)-7-hydroxy-4a,5-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one

(racemic mixture) [34-C7OH]. ^1H NMR (600 MHz, CDCl_3) δ 5.78 (s, 1H), 3.74 (tt, J = 10.6, 4.8



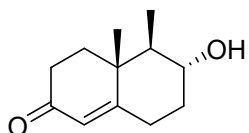
Hz, 1H), 2.56 (ddd, J = 13.7, 4.9, 2.3 Hz, 1H), 2.45 (ddd, J = 16.3, 14.5, 5.0

Hz, 1H), 2.38 – 2.32 (m, 2H), 2.05 (ddd, J = 13.5, 4.9, 3.0 Hz, 1H), 1.88 –

1.82 (m, 1H), 1.78 (br s, 1H), 1.68 (td, J = 14.1, 4.7 Hz, 1H), 1.54 – 1.45 (m, 2H), 1.12 (s, 3H),

0.95 (d, $J = 5.7$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 199.63, 167.79, 125.85, 69.68, 42.57, 40.25, 39.73, 38.12, 35.38, 34.05, 16.05, 15.06. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 195.1385, found 195.1386.

(4aR,5R,6R)-6-hydroxy-4a,5-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one



(racemic mixture) [34-C8OH]. ^1H NMR (600 MHz, CDCl_3) δ 5.77 (s, 1H),

3.62 (td, $J = 10.8, 4.3$ Hz, 1H), 2.47 (ddd, $J = 17.7, 14.4, 5.3$ Hz, 1H), 2.42 –

2.31 (m, 3H), 2.18 – 2.14 (m, 1H), 2.07 (ddd, $J = 13.5, 5.1, 3.4$ Hz, 1H), 1.75 (td, $J = 13.9, 5.0$

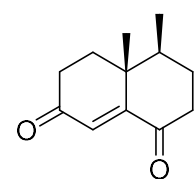
Hz, 1H), 1.54 – 1.39 (m, 2H), 1.33 (dq, $J = 13.5, 6.8$ Hz, 1H), 1.12 (s, 3H), 1.08 (d, $J = 6.7$ Hz,

3H). ^{13}C NMR (151 MHz, CDCl_3) δ 199.47, 168.89, 124.59, 71.36, 49.97, 39.32, 35.87, 35.41,

33.53, 31.40, 17.39, 10.66. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 195.1385,

found 195.1377.

(4S,4aR)-4,4a-dimethyl-2,3,4,4a,5,6-hexahydronaphthalene-1,7-dione (racemic mixture)



[33-ketone]. ^1H NMR (600 MHz, CDCl_3) δ 6.22 (d, $J = 1.1$ Hz, 1H), 2.69 (ddd,

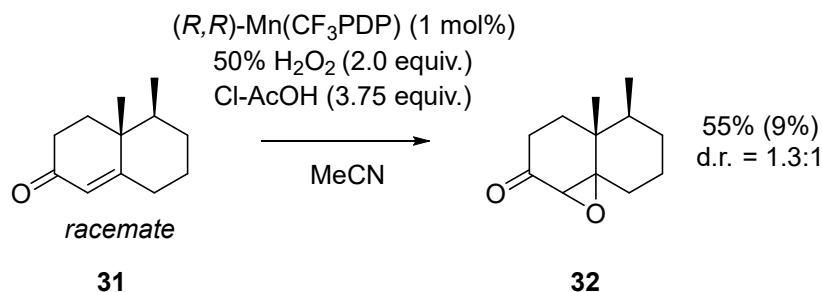
$J = 16.9, 5.0, 2.0$ Hz, 1H), 2.56 (ddd, $J = 17.5, 14.7, 5.2$ Hz, 1H), 2.51 – 2.44 (m,

2H), 2.13 (ddd, $J = 13.4, 5.2, 2.7$ Hz, 1H), 1.95 – 1.81 (m, 4H), 1.10 (s, 3H), 1.03

(d, $J = 6.2$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 202.48, 199.72, 160.53, 126.27, 41.00, 40.63,

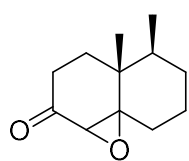
39.84, 35.76, 34.11, 27.97, 16.15, 14.81. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$:

193.1229, found 193.1267.



Comparison to PDP/carboxylic acid condition in MeCN. Compound **31** (0.4 mmol) in HFIP was oxidized according to PDP/carboxylic acid condition in MeCN outlined in Table S1, Entry 1, with 1 mol% $(R,R)\text{-Mn}(\text{CF}_3\text{-PDP})$, 2.0 equiv. of H_2O_2 , and 3.75 equiv. of chloroacetic acid. The resulting mixture was purified by column chromatography (silica, acetone: hexane = 1: 19 $\rightarrow$ 1: 4), yielding recovered starting material (RSM) and a mixture of epoxide products. **Run 1:** 10% RSM, 56% yield, d.r. = 1.3: 1. **Run 2:** 8% RSM, 53% yield, d.r. = 1.3: 1. **Average:** 9% RSM $\pm$ 1%, 55% yield $\pm$ 1.5%, d.r. = 1.3: 1.

(4aR,5S)-4a,5-dimethylhexahydro-3H-naphtho[1,8a-b]oxiren-2(1aH)-one [32]. Product



isolated as a 1.3: 1 mixture of diastereomers. ^1H NMR (600 MHz, CDCl_3) δ 3.02

(s, 0.6H), 2.98 (s, 0.4H), 2.38 (ddd, J = 19.8, 7.2, 1.5 Hz, 0.6H), 2.30 (ddd, J =

19.4, 6.1, 2.2 Hz, 0.4H), 2.25 (dd, J = 12.1, 7.7 Hz, 0.4H), 2.21 (dd, J = 8.1, 4.1

Hz, 0.4H), 2.19 – 2.10 (m, 1.2H), 1.89 – 1.79 (m, 1.4H), 1.76 – 1.71 (m, 0.6H), 1.71 – 1.65 (m,

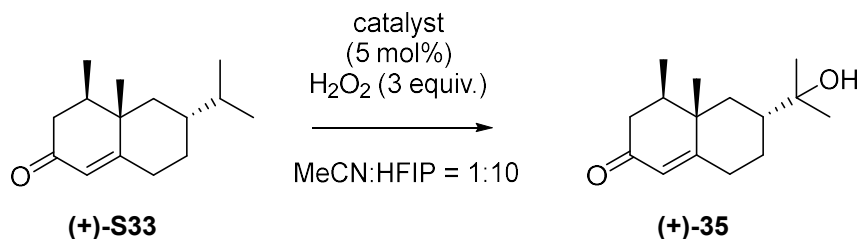
0.6H), 1.65 – 1.59 (m, 1H), 1.59 – 1.51 (m, 2H), 1.49 – 1.33 (m, 1.4H), 1.11 – 1.03 (m, 1H), 1.06

(s, 1.3H), 0.96 (s, 1.7H), 0.87 (d, J = 6.8 Hz, 1.7H), 0.85 (d, J = 6.8 Hz, 1.3H). ^{13}C NMR (151

MHz, CDCl_3) δ 207.33, 206.96, 70.36, 70.07, 62.81, 62.76, 40.01, 37.76, 37.19, 35.61, 33.36,

32.74, 30.39, 30.18, 30.06, 29.77, 29.09, 26.37, 24.87, 23.83, 17.41, 15.69, 15.24, 15.10. HRMS

(TOF ES $^+$) m/z calculated for $\text{C}_{12}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 195.1384, found: 195.1385.



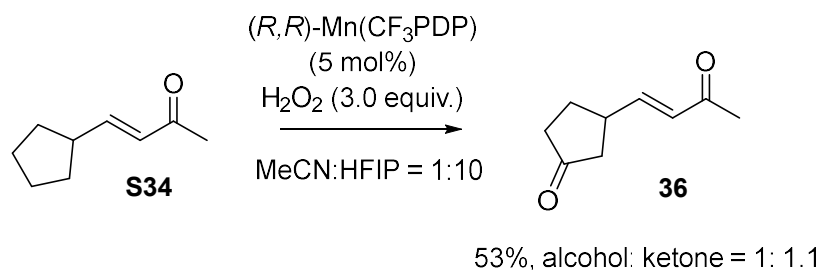
(R,S,S,R)-Mn(MeCF₃PDP): 47% yield
(S,S)-Mn(CF₃PDP): 33% yield

Oxidation of (4R,4aS,6R)-6-isopropyl-4,4a-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one [(+)-S33]. (4R,4aS,6R)-6-isopropyl-4,4a-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one was prepared according to the reported literature³⁵. The spectroscopic data matched those reported in the literature. (4R,4aS,6R)-6-isopropyl-4,4a-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,S,S,R*)-Mn(MeCF₃-PDP) and 3.0 equiv. of H₂O₂. The resulting mixture was purified with column chromatography (2: 3 EtOAc: hexanes). **Run 1:** 47%. **Run 2:** 48%. **Run 3:** 47%. **Average:** 47% yield $\pm$ 0.5%. Remainder of mass balance is a complex mixture of epoxides, including epoxidation resulting from a minor unsaturation pathway involving the isopropyl substituent. With 5 mol% (*S,S*)-Mn(CF₃-PDP) and 3.0 equiv. of H₂O₂: 33% yield.

(4R,4aS,6R)-6-(2-hydroxypropan-2-yl)-4,4a-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one [(+)-35]. ¹H NMR (500 MHz, CDCl₃) δ 5.74 (s, 1H), 2.51 – 2.40 (m, 1H), 2.36 (ddd, *J* = 15.0, 4.3, 2.3 Hz, 1H), 2.31 – 2.16 (m, 2H), 2.04 (d, *J* = 13.4 Hz, 1H), 2.01 – 1.93 (m, 2H), 1.71 (t, *J* = 12.5 Hz, 1H), 1.58 (br s, 1H), 1.27 – 1.10 (m, 1H), 1.19 (s, 3H), 1.17 (s, 3H), 1.07 (s, 3H), 1.01 – 0.92 (m, 1H). 0.95 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 199.84, 171.01, 124.52, 72.46, 43.97, 42.18, 40.66, 39.72, 39.26, 33.09,

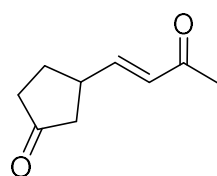
27.81, 27.42, 27.01, 17.01, 15.08. $[\alpha]_D^{24.3} = +155.03^\circ$ ($c = 1.00$, CHCl_3). HRMS (TOF MS EI+) m/z calculated for $\text{C}_{15}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$: 237.1855, found 237.1856.

Preparation of (E)-4-cyclopentylbut-3-en-2-one [S34]. (E)-4-cyclopentylbut-3-en-2-one was prepared according to the reported literature³⁶. The spectroscopic data matched those reported in the literature.



Oxidation of (E)-4-cyclopentylbut-3-en-2-one [S34]. (E)-4-cyclopentylbut-3-en-2-one in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (2: 3 EtOAc: hexanes → 1: 1 EtOAc: hexanes → 2: 1 EtOAc: hexanes). **Run 1:** 51% yield, alcohol: ketone = 1: 1.1, **Run 2:** 55% yield, alcohol: ketone = 1: 1.1. **Run 3:** 54% yield, alcohol: ketone = 1: 1.3. **Average:** 53% yield $\pm$ 1.7%, alcohol: ketone = 1: 1.1.

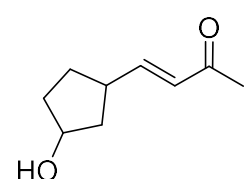
(E)-3-(3-oxobut-1-en-1-yl)cyclopentan-1-one [36-ketone]. ¹H NMR (500 MHz, CDCl₃) δ 6.78



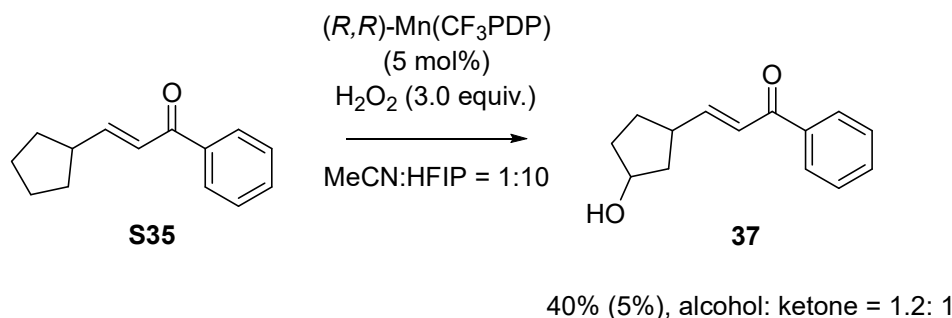
(dd, $J = 15.9, 7.2$ Hz, 1H), 6.13 (dd, $J = 15.9, 1.4$ Hz, 1H), 3.07 – 2.95 (m, 1H), 2.47 (dd, $J = 18.1, 7.5$ Hz, 1H), 2.42 – 2.33 (m, 1H), 2.26 (s, 3H), 2.31 – 2.18 (m, 2H), 2.10 (dd, $J = 18.2, 10.3$ Hz, 1H), 1.87 – 1.74 (m, 1H). ¹³C NMR (126

MHz, CDCl₃) δ 216.94, 198.27, 148.28, 130.57, 43.89, 39.61, 38.05, 29.07, 27.47. HRMS (TOF EI+) m/z calculated for C₉H₁₃O₂ [M+H]⁺: 153.0916, found 153.0910

(E)-4-(3-hydroxycyclopentyl)but-3-en-2-one [36-OH]. Product isolated as a 1: 1 mixture of

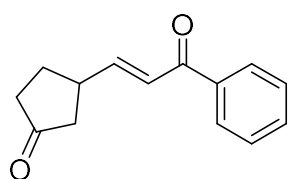
 diastereomers. ¹H NMR (500 MHz, CDCl₃) δ 6.81 (dd, J = 16.0, 8.1 Hz, 0.46H), 6.75 (dd, J = 15.9, 7.8 Hz, 0.54H), 6.07 (dd, J = 15.9, 0.9 Hz, 0.54H), 6.03 (dd, J = 15.9, 0.7 Hz, 0.46H), 4.46 – 4.41 (m, 0.54H), 4.41 – 4.36 (m, 0.46H), 2.98 (sext, J = 8.3 Hz, 0.54H), 2.66 (sext, J = 8.1 Hz, 0.46H), 2.25 – 2.19 (m, 3.46H), 2.09 – 2.02 (m, 1H), 1.92 – 1.80 (m, 1.54H), 1.75 – 1.57 (m, 3H), 1.51 – 1.41 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 199.18 (198.98), 152.53 (151.71), 129.77 (129.75), 73.65 (73.49), 42.27 (41.89), 41.43 (40.46), 35.81 (35.30), 30.35 (30.31), 27.18 (26.96). HRMS (TOF EI+) m/z calculated for C₉H₁₄O₂Na [M+Na]⁺: 177.0891, found 177.0899.

Preparation of (E)-3-cyclopentyl-1-phenylprop-2-en-1-one [S35]. (E)-4-cyclopentylbut-3-en-2-one was prepared according to the reported literature³⁷. The spectroscopic data matched those reported in the literature.



Oxidation of (E)-3-cyclopentyl-1-phenylprop-2-en-1-one [S35]. (E)-3-cyclopentyl-1-phenylprop-2-en-1-one in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (1: 2 EtOAc: hexanes → 1: 1 EtOAc: hexanes). **Run 1:** 4% RSM, 40% yield, alcohol: ketone = 1.2: 1. **Run 2:** 4% RSM, 43% yield, alcohol: ketone = 1.2: 1. **Run 3:** 6% RSM, 38% yield, alcohol: ketone = 1.1: 1. **Average:** 5% RSM ± 0.9%, 40% yield ± 2.1%, alcohol: ketone = 1.2: 1.

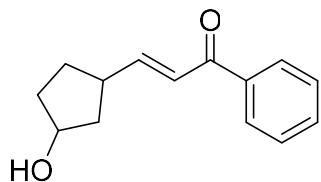
(E)-3-(3-oxo-3-phenylprop-1-en-1-yl)cyclopentan-1-one [37-ketone]. ¹H NMR (500 MHz,



CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 8.2 Hz, 2H), 7.06 (dd, *J* = 15.4, 7.2 Hz, 1H), 6.95 (d, *J* = 15.1 Hz, 1H), 3.12 (sext, *J* = 8.5 Hz, 1H), 2.52 (dd, *J* = 18.2, 7.5 Hz, 1H), 2.40 (dd, *J* =

17.9, 8.4 Hz, 1H), 2.35 – 2.13 (m, 3H), 1.96 – 1.82 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 217.15, 190.41, 149.82, 137.72, 133.08, 128.75, 128.63, 125.34, 44.00, 40.02, 38.04, 29.18. HRMS (TOF EI+) *m/z* calculated for C₁₄H₁₅O₂ [M+H]⁺: 215.1072, found 215.1073.

(E)-3-(3-hydroxycyclopentyl)-1-phenylprop-2-en-1-one [37-OH]. Alcohols were isolated as a

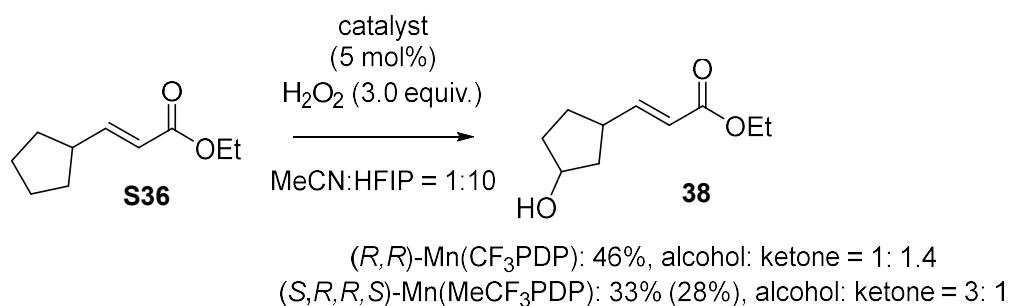


1.3: 1 mixture of diastereomers. Minor diastereomer reported in parentheses for ¹³C NMR. ¹H NMR (500 MHz, CDCl₃) δ 7.95 – 7.88

(m, 2H), 7.58 – 7.51 (m, 1H), 7.50 – 7.42 (m, 2H), 7.08 (dd, *J* = 15.3, 8.0 Hz, 0.56H), 7.01 (dd, *J* = 15.3, 8.0 Hz, 0.44H), 6.92 – 6.81 (m, 1H), 4.49 – 4.44 (m, 0.44H), 4.44 – 4.37 (m, 0.56H), 3.09 (sext, *J* = 8.1 Hz, 0.44H), 2.76 (sext, *J* = 8.4 Hz, 0.56H), 2.32 – 2.22 (m, 0.56H), 2.16 – 2.01 (m, 1H), 1.97 – 1.62 (m, 4.44H), 1.59 – 1.45 (m, 1H). ¹³C NMR (126 MHz,

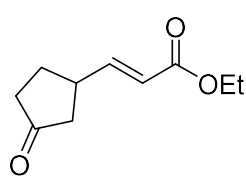
CDCl₃) δ 191.32, (191.12), 153.76, (153.28), 138.09, (138.07), 132.80, (132.75), 128.65, 128.63, 124.44, (124.37), 73.64, (73.59), 42.41, (41.97), 41.77, (40.91), 35.73, (35.35), 30.45, (30.32).
 HRMS (TOF EI+) m/z calculated for C₁₄H₁₇O₂ [M+H]⁺: 217.1229, found 217.1229

Preparation of ethyl (E)-3-cyclopentylacrylate [S36]. Ethyl (E)-3-cyclopentylacrylate was prepared according to the reported literature³⁸. The spectroscopic data matched those reported in the literature.



Oxidation of ethyl (E)-3-cyclopentylacrylate [S36]. Ethyl (E)-3-cyclopentylacrylate in HFIP was oxidized according to the Standard conditions with 5 mol% (R,R) -Mn(CF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (1: 4 EtOAc: hexanes → 1: 2 EtOAc: hexanes → 1: 1 EtOAc: hexanes). **Run 1:** 47% yield, alcohol: ketone = 1: 1.4. **Run 2:** 43% yield, alcohol: ketone = 1: 1.3. **Run 3:** 47% yield, alcohol: ketone = 1: 1.5. **Average:** 46% yield $\pm$ 1.9%, alcohol: ketone = 1: 1.4. With 5 mol% (S,R,R,S) -Mn(MeCF₃-PDP) and 3.0 equiv. H₂O₂: 28% RSM, 33% yield, alcohol: ketone = 3: 1.

ethyl (E)-3-(3-oxocyclopentyl)acrylate [38-ketone]. ^1H NMR (500 MHz, CDCl_3) δ 6.95 (dd, J



= 15.6, 7.2 Hz, 1H), 5.86 (d, J = 15.7 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 3.05

– 2.94 (m, 1H), 2.45 (dd, J = 18.2, 7.4 Hz, 1H), 2.40 – 2.30 (m, 1H), 2.30 –

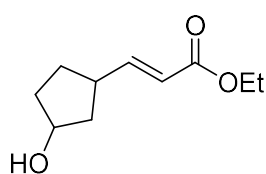
2.14 (m, 2H), 2.09 (dd, J = 18.2, 10.2 Hz, 1H), 1.85 – 1.73 (m, 1H), 1.28 (t,

J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 217.20, 166.44, 149.51, 121.40, 60.61, 43.83,

39.41, 38.03, 28.99, 14.36. HRMS (TOF EI+) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 183.1021,

found 183.1028.

ethyl (E)-3-(3-hydroxycyclopentyl)acrylate [38-OH]. ^1H NMR (600 MHz, CDCl_3) δ 6.98 (dd, J



= 15.6, 8.1 Hz, 0.45H), 6.90 (dd, J = 15.6, 7.9 Hz, 0.54H), 5.82 – 5.75 (m,

1H), 4.44 – 4.39 (m, 0.53H), 4.39 – 4.34 (m, 0.46H), 4.17 (app q, J = 7.1

Hz 2H), 2.96 (sext, J = 8.1 Hz, 0.53H), 2.64 (sext, J = 7.8 Hz, 0.47H), 2.24

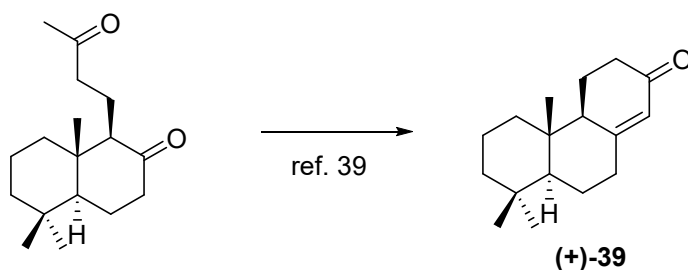
– 2.17 (m, 0.48H), 2.07 – 1.99 (m, 1H), 1.89 – 1.80 (m, 1.52H), 1.76 – 1.56 (m, 3H), 1.48 – 1.38

(m, 1H), 1.27 (app t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 167.02, (167.01), 153.05,

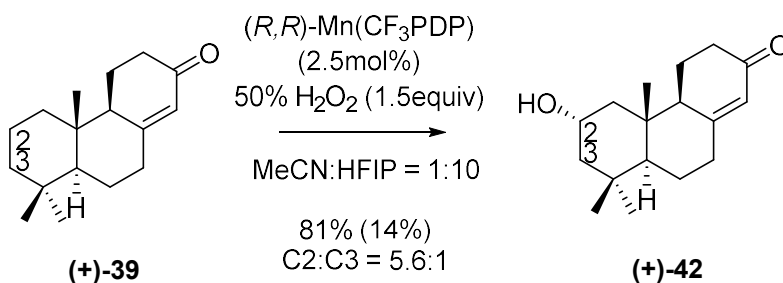
(152.62), 119.98, (119.84), 73.59, (73.49), 60.36, (60.35), 42.16, (41.79), 41.16, (40.24), 35.65,

(35.25), 30.22, (30.12), 14.39 (2C). HRMS (TOF EI+) m/z calculated for $\text{C}_{10}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$:

185.1178, found 185.1182.



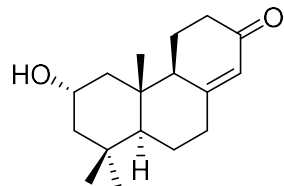
Preparation of podocarpinone [(+)-39]. (–)-(1R,4aS,8aS)-5,5,8a-trimethyl-1-(3-oxobutyl)octahydronaphthalen-2(1H)-one was prepared according to the reported procedure³⁹. Podocarpinone (+)-39 was prepared according to the reported procedure from (1R,4aS,8aS)-5,5,8a-trimethyl-1-(3-oxobutyl)octahydronaphthalen-2(1H)-one⁴⁰. The spectroscopic data matched those reported in the literature⁴¹.



Oxidation of podocarpinone. Podocarpinone 39 in HFIP was oxidized according to the Standard conditions to afford a separable mixture (C2: C3= 8: 1) of alcohols. The resulting mixture was purified with column chromatography (EA: hexane = 1: 6 → 1: 2) to afford diastereomerically pure C2 and C3 alcohols. **Run 1:** 13% RSM, 80% yield, C2:C3 = 5.2: 1. **Run 2:** 12% RSM, 83% yield, C2:C3 = 5.4: 1. **Run 3:** 16% RSM, 80% yield, C2:C3 = 6.3: 1. **Average:** 14% RSM $\pm$ 1.7%, 81% yield $\pm$ 1.4%, C2:C3 = 5.6: 1.

(4aS,4bS,6S,8aS)-6-hydroxy-4b,8,8-trimethyl-4,4a,4b,5,6,7,8,8a,9,10-

decahydrophenanthren-2(3H)-one [(+)-42-C2OH]. ^1H NMR (600 MHz, CDCl_3) δ 5.90 (app s,



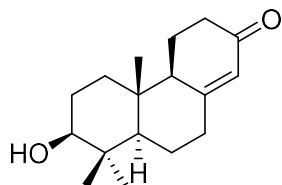
1H), 3.85 (tt, J = 11.5, 4.0 Hz, 1H), 2.56 (app dd, J = 15.8, 4.5 Hz, 1H), 2.41 (dt, J = 16.0, 4.3 Hz, 1H), 2.30 (td, J = 14.4, 6.6 Hz, 1H), 2.22 (ddd, J = 15.9, 14.0, 5.5 Hz, 1H), 2.14 (dd, J = 10.2, 5.7 Hz, 1H), 2.09 – 1.99

(m, 2H), 1.83 – 1.70 (m, 3H), 1.50 (br s, 1H), 1.45 (qd, J = 13.0, 4.9 Hz, 1H), 1.22 – 1.14 (m, 2H),

1.07 (t, $J = 11.7$ Hz, 1H), 0.99 (s, 3H), 0.92 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 199.84, 164.82, 126.53, 64.97, 53.33, 51.70, 50.85, 48.37, 40.48, 36.86, 35.57, 35.15, 33.83, 23.15, 21.68, 20.80, 16.33. $[\alpha]_{\text{D}}^{24} = +17.22$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{17}\text{H}_{27}\text{O}_2$ $[\text{M}+\text{H}]^+$: 263.2011, found 263.2010. The site selectivity and stereochemistry of the alcohol was assigned by ^1H NMR splitting pattern and coupling constant (triplet of triplet splitting, $J=11.5\text{Hz}$ for *trans*-coupling) analysis.

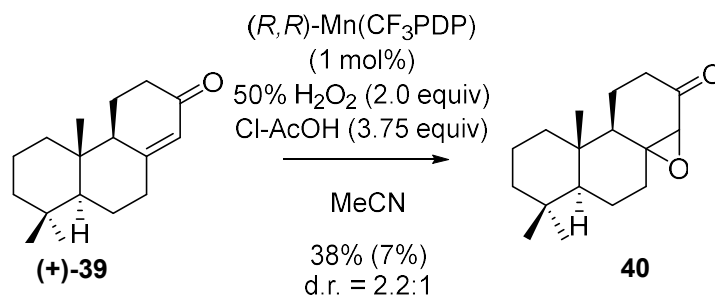
(4aS,4bR,7S,8aR)-7-hydroxy-4b,8,8-trimethyl-4,4a,4b,5,6,7,8,8a,9,10-

decahydrophenanthren-2(3H)-one [(+)-42-C3OH]. ^1H NMR (600 MHz, CDCl_3) δ 5.89 (t, $J =$



2.2 Hz, 1H), 3.30 (dd, $J = 11.7$, 4.1 Hz, 1H), 2.56 (ddd, $J = 15.6$, 4.8, 1.8 Hz, 1H), 2.40 (dt, $J = 16.0$, 4.2 Hz, 1H), 2.29 (dddt, $J = 15.2$, 13.0, 6.5, 1.8 Hz, 1H), 2.21 (ddd, $J = 15.9$, 13.7, 5.5 Hz, 1H), 2.08 – 2.02 (m, 1H),

2.02 – 1.95 (m, 1H), 1.83 – 1.66 (m, 4H), 1.62 – 1.49 (m, 3H), 1.26 (td, $J = 13.4$, 3.8 Hz, 1H), 1.18 (dd, $J = 12.5$, 2.7 Hz, 1H), 1.05 (s, 3H), 0.85 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 199.92, 165.00, 126.16, 78.81, 53.45, 51.52, 39.20, 38.89, 37.35, 36.89, 35.69, 28.62, 27.45, 21.72, 20.70, 15.82, 15.43. $[\alpha]_{\text{D}}^{24} = +2.92$ ($c=0.5$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{17}\text{H}_{27}\text{O}_2$ $[\text{M}+\text{H}]^+$: 263.2011, found 263.2004. The site selectivity and stereochemistry of the alcohol was assigned by ^1H NMR splitting pattern and coupling constant (triplet of triplet splitting, $J=11.5\text{Hz}$ for *trans*-coupling) analysis.

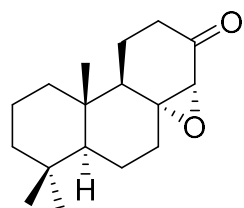


Oxidation of podocapenone. A 30 mL vial equipped with a stir bar was charged with **39** (73.9 mg, 0.3 mmol, 1 equiv.), chloroacetic acid (106.3 mg, 1.125 mmol, 3.75 equiv.), and acetonitrile (1.25 mL). A 0.096 M solution of hydrogen peroxide (50% w/w) in acetonitrile was prepared and 6.25 mL were drawn into a 10 mL syringe. A 0.0048 M solution of (*R,R*)-MnCF₃-PDP (4.1 mg, 0.003 mmol, 1 mol%) in acetonitrile was prepared and 0.625 mL were drawn into a 1 mL syringe. The oxidant solution and the catalyst solution were added dropwise over 3 hours by syringe pump. After the addition finished, the acetonitrile was removed under reduced pressure and the crude mixture was dissolved in dichloromethane and washed with sat. sodium bicarbonate. The aqueous layer was extracted 3x with dichloromethane, combined organics were dried over sodium sulfate, filtered, and concentrated under reduced pressure.

The resulting mixture was purified with column chromatography (EA: hexane = 3: 97 → 1: 19) to afford each epoxide. The major epoxide contained 10% of inseparable impurity. This was accounted for in the reported yield. The major epoxide was also synthesized according to the reported literature via Weitz-Scheffer protocol and the product matched ¹H and ¹³C NMR data of ours. **Run 1:** 8% RSM, 37% yield, d.r. = 2.1:1. **Run 2:** 6% RSM, 38% yield, d.r. = 2.2:1. **Average:** 7% RSM, 38% yield, d.r. = 2.2: 1.

(3aR,4aR,6aS,10aS,10bR)-7,7,10a-trimethyldecahydro-2H-phenanthro[1,10a-b]oxiren-

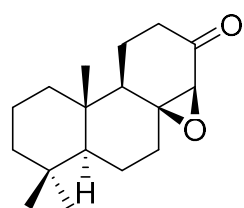
3(3aH)-one [40-ds1]. The spectroscopic data matched those reported in the literature⁴². ¹H NMR



(500 MHz, CDCl₃) δ 3.17 (s, 1H), 2.42 (ddd, J = 18.8, 10.4, 2.4 Hz, 1H), 2.21 (dt, J = 18.6, 9.1 Hz, 1H), 2.14 – 2.04 (m, 1H), 2.04 – 1.96 (m, 1H), 1.89 – 1.73 (m, 4H), 1.59 – 1.41 (m, 5H), 1.17 (td, J = 13.7, 4.3 Hz, 1H), 1.10 – 0.99

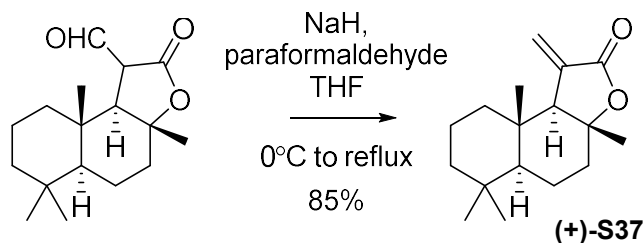
(m, 2H), 0.91 (s, 3H), 0.84 (s, 3H), 0.82 (s, 3H) ¹³C NMR (126 MHz, CDCl₃) δ 209.07, 67.43, 63.92, 54.53, 48.50, 41.92, 39.94, 39.94, 35.31, 33.92, 33.86, 33.44, 21.89, 21.53, 18.69, 16.89, 16.28. HRMS (TOF ESI+) m/z calculated for C₁₇H₂₇O₂ [M+H]⁺: 263.2011, found 263.2007.

(3aS,4aS,6aS,10aS,10bR)-7,7,10a-trimethyldecahydro-2H-phenanthro[1,10a-b]oxiren-

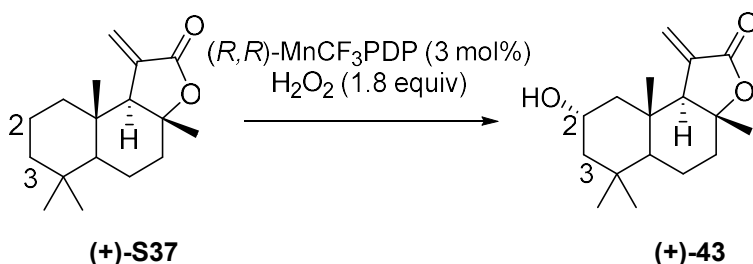


3(3aH)-one [(-)-40-ds2]. ¹H NMR (500 MHz, CDCl₃) δ 2.83 (s, 1H), 2.48 (app ddd, J = 18.5, 4.9, 1.9 Hz, 1H), 2.16 – 1.95 (m, 2H), 1.77 – 1.67 (m, 3H), 1.64 – 1.52 (m, 4H), 1.49 – 1.42 (m, 3H), 1.20 (td, J = 13.6, 4.0 Hz, 1H), 1.08

– 0.96 (m, 2H), 1.02 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 206.48, 63.16, 59.32, 54.54, 49.49, 42.03, 39.60, 38.19, 36.99, 34.31, 33.86, 33.48, 22.21, 20.10, 18.68, 15.67, 15.06. $[\alpha]_D^{23.4}$ = -147.7 (c=0.8, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₁₇H₂₇O₂ [M+H]⁺: 263.2011, found 263.2010.

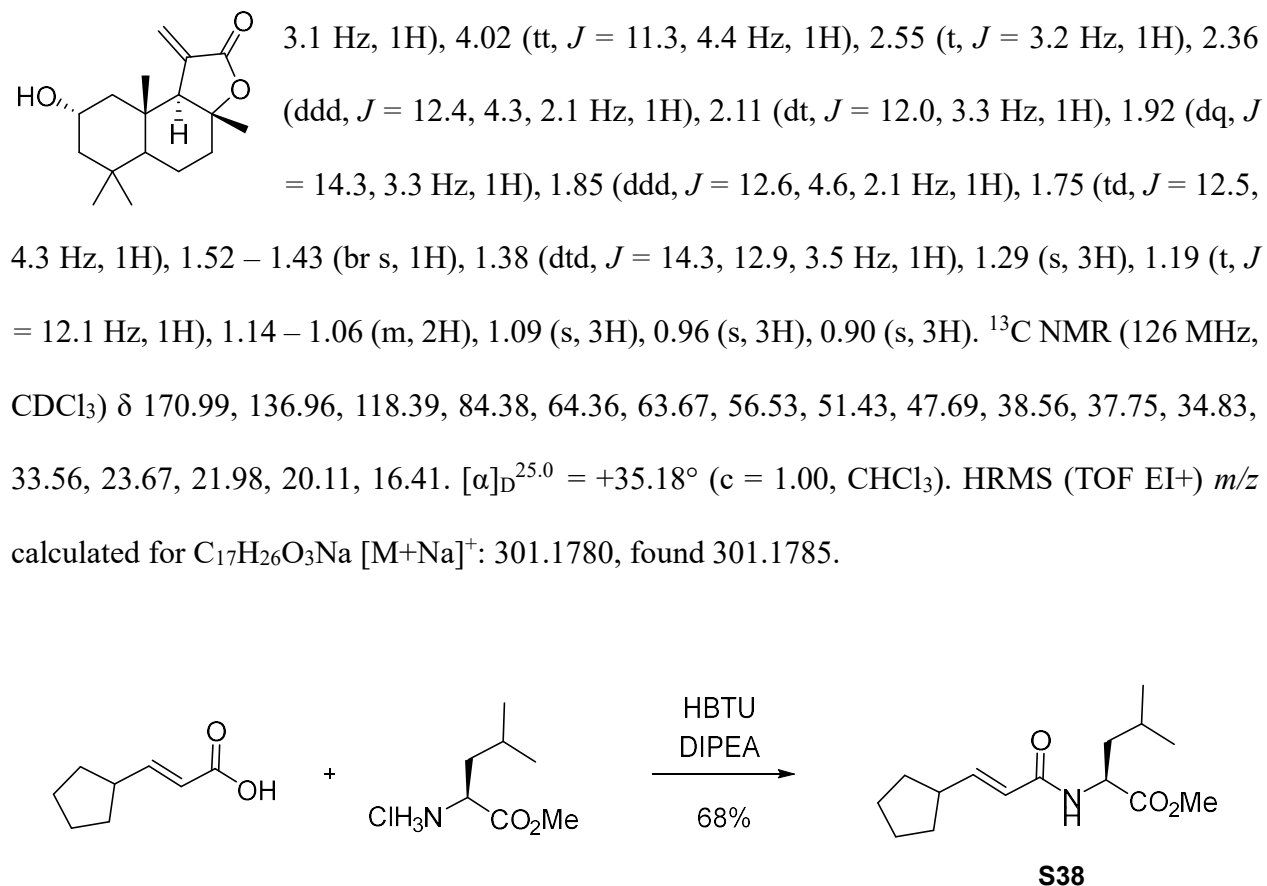


Preparation of (3aR,9aS,9bS)-3a,6,6,9a-tetramethyl-1-methylenedecahydronaphtho[2,1-b]furan-2(1H)-one [(+)-S37]. Formyl sclareolide was prepared according to the reported literature⁴³. The spectroscopic data matched those reported in the literature. A solution of formyl sclareolide (1.2 g, 4.31 mmol, 1.0 equiv.) in THF (4.5 mL) was added dropwise to a suspension of NaH (126 mg, 4.74 mmol, 1.1 equiv.) in THF (4.5 mL) at 0 °C. The reaction was removed from the ice bath and stirred at room temperature for 30 min to ensure full deprotonation. (*Note: when sodium salt forms, reaction becomes thick and maintaining stirring is difficult*) Paraformaldehyde (259 mg, 8.62 mmol, 2.0 equiv.) was added to the reaction, which was then heated to reflux for 3h. When TLC showed full consumption of SM, reaction cooled to rt and quenched with 1N HCl solution. The aqueous layer was extracted with Et₂O and combined organics were dried over MgSO₄. Solvents were removed under reduced pressure and the crude reaction mixture was purified by silica column chromatography (Ethyl acetate: hexanes = 1: 19) to furnish the title compound as a white solid (966 mg, 3.68 mmol, 85% yield). The NMR data of **(+)-S37** ($[\alpha]_{\text{D}}^{23.6} = +25.93^{\circ}$ (c = 1.00, CHCl₃)) matched those reported in the literature⁴⁴.



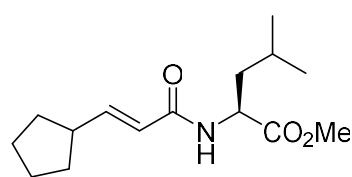
Oxidation of (3aR,9aS,9bS)-3a,6,6,9a-tetramethyl-1-methylenedecahydronaphtho[2,1-b]furan-2(1H)-one [(+)-S37]. (+)-S37 in HFIP was oxidized according to the Standard conditions with 3 mol% (*R,R*)-Mn(CF₃-PDP) and 1.8 equiv. H₂O₂. The resulting mixture was purified with column chromatography (1: 2 EtOAc: hexanes). **Run 1:** 76% yield, alcohol only, C2:C3 = 7.7: 1, epoxide 10.4%. **Run 2:** 71% yield, alcohol only, C2:C3 = 7.2: 1. **Run 3:** 72% yield, alcohol only, C2:C3 = 7.0: 1, epoxide 13 %. **Average:** 73% yield $\pm$ 2.2%, alcohol only, C2:C3 = 7.3: 1, epoxide 12 $\pm$ 1.1%. With 3mol% (*S,S*)-Mn(CF₃-PDP), 1.8 equiv. H₂O₂: 10% RSM, 58% yield, alcohol only, C2:C3 = 9: 1, epoxide 17%.

(3aR,8S,9aS,9bS)-8-hydroxy-3a,6,6,9a-tetramethyl-1-methylenedecahydronaphtho[2,1-b]furan-2(1H)-one [(+)-43]. ¹H NMR (500 MHz, CDCl₃) δ 6.16 (d, *J* = 3.2 Hz, 1H), 5.54 (d, *J* = 3.1 Hz, 1H), 4.02 (tt, *J* = 11.3, 4.4 Hz, 1H), 2.55 (t, *J* = 3.2 Hz, 1H), 2.36 (ddd, *J* = 12.4, 4.3, 2.1 Hz, 1H), 2.11 (dt, *J* = 12.0, 3.3 Hz, 1H), 1.92 (dq, *J* = 14.3, 3.3 Hz, 1H), 1.85 (ddd, *J* = 12.6, 4.6, 2.1 Hz, 1H), 1.75 (td, *J* = 12.5, 4.3 Hz, 1H), 1.52 – 1.43 (br s, 1H), 1.38 (dtd, *J* = 14.3, 12.9, 3.5 Hz, 1H), 1.29 (s, 3H), 1.19 (t, *J* = 12.1 Hz, 1H), 1.14 – 1.06 (m, 2H), 1.09 (s, 3H), 0.96 (s, 3H), 0.90 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 170.99, 136.96, 118.39, 84.38, 64.36, 63.67, 56.53, 51.43, 47.69, 38.56, 37.75, 34.83, 33.56, 23.67, 21.98, 20.11, 16.41. [α]_D^{25.0} = +35.18° (*c* = 1.00, CHCl₃). HRMS (TOF EI+) *m/z* calculated for C₁₇H₂₆O₃Na [M+Na]⁺: 301.1780, found 301.1785.



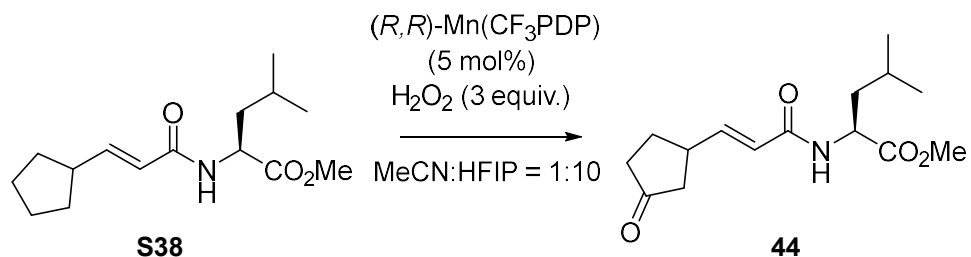
Preparation of methyl (E)-(3-cyclopentylacryloyl)-L-leucinate [S38]. To a solution of (E)-3-cyclopentylacrylic acid (280 mg, 2.0 mmol, 1.0 equiv.) in dichloromethane (12 mL) was added diisopropylethylamine (1.38 mL, 8.0 mmol, 4.0 equiv.) and the reaction was stirred for ten minutes, at which point HBTU (910 mg, 2.4 mmol, 1.2 equiv.) was added. The reaction was stirred for an additional 30 minutes, then leucine methyl ester HCl (400 mg, 2.2 mmol, 1.1 equiv.) was added and the reaction was stirred overnight (16 hours). After completion was verified by TLC analysis (ethyl acetate: hexanes 1: 4), the reaction was quenched with water and extracted 3x with dichloromethane. Combined organics were dried over sodium sulfate and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography (ethyl acetate: hexanes 1: 4) to give methyl (E)-(3-cyclopentylacryloyl)-L-leucinate as a white solid (365 mg, 1.37 mmol, 68% yield)

methyl (E)-(3-cyclopentylacryloyl)-L-leucinate [S38]. ^1H NMR (600 MHz, CDCl_3) δ 6.84 (dd,



$J = 15.2, 7.9$ Hz, 1H), 5.87 (br s, 1H), 5.77 (d, $J = 15.2$ Hz, 1H), 4.76 – 4.69 (m, 1H), 3.73 (s, 3H), 2.56 (sext, $J = 8.1$ Hz, 1H), 1.85 – 1.76 (m, 2H), 1.73 – 1.62 (m, 4H), 1.62 – 1.51 (m, 3H), 1.42 – 1.33 (m,

2H), 0.94 (d, $J = 9.6$ Hz, 3H), 0.93 (d, $J = 9.8$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 173.95, 166.01, 150.18, 121.18, 52.44, 50.71, 42.87, 42.05, 32.59, 25.35, 24.99, 22.96, 22.12. HRMS (TOF ESI+) m/z calculated for $\text{C}_{15}\text{H}_{26}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 268.1913, found 268.1906.



64%, alcohol: ketone = 1: 1.3

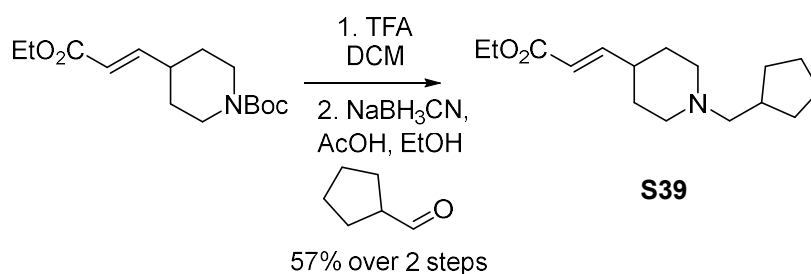
Oxidation of methyl (E)-3-(3-cyclopentylacryloyl)-L-leucinate [S38]. Ethyl (E)-3-cyclopentylacrylate in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (1: 1 EtOAc: hexanes → 2: 1 EtOAc: hexanes w/ 7% MeOH v/v). **Run 1:** 65% yield, alcohol: ketone = 1: 1.7. **Run 2:** 63% yield, alcohol: ketone = 1: 1.1. **Run 3:** 63% yield, 1: 1.1. **Average:** 64% yield ± 0.9%, alcohol: ketone = 1:1.3.

methyl ((E)-3-(3-oxocyclopentyl)acryloyl)-L-leucinate [44-ketone]. Product isolated as a 1.3: 1

mixture of two diastereomers. ¹H NMR (600 MHz, CDCl₃) δ 6.88 (dd, *J* = 15.3, 7.2 Hz, 1H), 6.02 (s, 1H), 5.86 (d, *J* = 15.2 Hz, 1H), 4.75 – 4.68 (m, 1H), 3.73 (s, 3H), 2.98 (sext, *J* = 8.5 Hz, 1H), 2.43 (dd, *J* = 18.2, 7.5 Hz, 1H), 2.39 – 2.30 (m, 1H), 2.26 – 2.16 (m, 2H), 2.09 (dd, *J* = 18.2, 10.3 Hz, 1H), 1.84 – 1.75 (m, 1H), 1.71 – 1.61 (m, 2H), 1.55 (quint, *J* = 9.4 Hz, 1H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.3 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 217.57 (217.53), 173.84 (173.80), 165.21 (165.19), 146.34 (146.32), 122.95 (122.93), 52.50, 50.81 (50.79), 43.96, 41.90 (41.87), 39.29, 38.02 (38.00), 29.10 (29.06), 24.97, 22.92, 22.04 (22.02). HRMS (TOF ESI+) *m/z* calculated for C₁₅H₂₄NO₄ [M+H]⁺: 282.1705, found 282.1696.

methyl ((E)-3-(3-hydroxycyclopentyl)acryloyl)-L-leucinate [44-OH]. Product isolated as a 1:

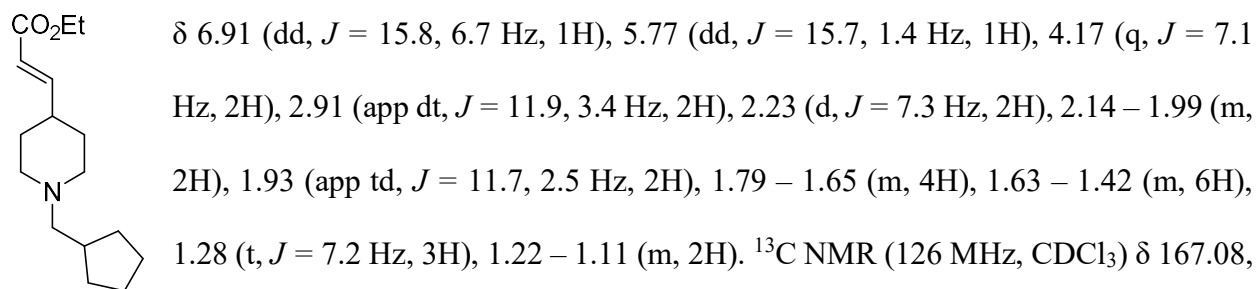
1.5: 2: 2 mixture of four diastereomers. ¹H NMR (600 MHz, CDCl₃) δ 6.88 (dd, *J* = 15.4, 7.8 Hz, 0.44H), 6.81 (dd, *J* = 15.2, 8.0 Hz, 0.56H), 6.00 (br s, 0.44H), 5.94 (br s, 0.56H), 5.80, 5.78 (overlapping doublets, *J* = 15.2 Hz, *J* = 15.4 Hz, 1H), 4.75 – 4.68 (m, 1H), 4.44 – 4.39 (m, 0.56H), 4.38 – 4.33 (m, 0.44H), 3.73 (s, 3H), 2.94 (sext, *J* = 8.1 Hz, 0.56H), 2.62 (sext, *J* = 7.9 Hz, 0.44H), 2.20 (app quint, *J* = 7.1 Hz, 0.44H), 2.08 – 1.97 (m, 1H), 1.88 – 1.49 (m, 7.56H), 1.48 – 1.38 (m, 1H), 0.94 (app t, *J* = 7.7 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 174.05 (174.02, 173.95, 173.94), 165.93 (165.92, 165.84, 165.83), 149.45 (149.42, 149.22, 149.20), 121.72, (121.58), 73.61, (73.57), 52.47, 50.74, 42.36, (42.34, 41.85, 41.82), 41.97, 41.01, (40.19), 35.64, (35.30, 35.27), 30.37, (30.17), 24.98, 22.95, 22.09. HRMS (TOF ESI⁺) *m/z* calculated for C₁₅H₂₆NO₄ [M+H]⁺: 284.1862, found 284.1857. Carbons assigned from HSQC correlations to diastereomeric protons.



Preparation of ethyl (E)-3-(1-(cyclopentylmethyl)piperidin-4-yl)acrylate [S39]. Tert-butyl (E)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)piperidine-1-carboxylate was prepared according to the reported literature⁴⁵. To a solution of tert-butyl (E)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)piperidine-1-carboxylate (2.26 g, 7.98 mmol, 1.0 equiv.) in dichloromethane (61 mL) was added trifluoroacetic acid (12.3 mL) and the solution was stirred for 4 hours, then concentrated under

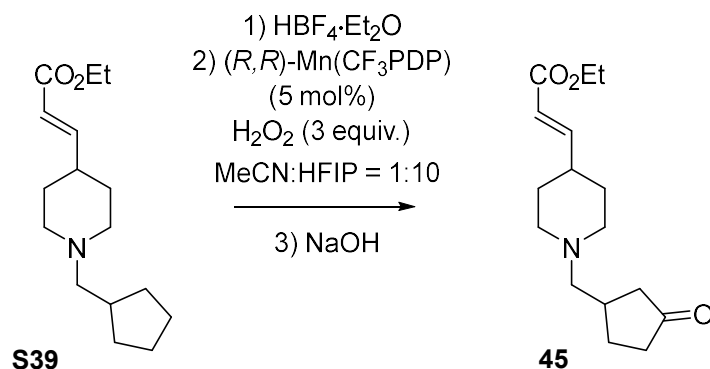
reduced pressure to furnish the trifluoroacetate salt, which was dissolved in diethyl ether in a separatory funnel and shaken for 30 seconds. The aqueous layer was extracted 3x with diethyl ether, then combined organics were dried over potassium carbonate and concentrated under reduced pressure to give the free amine (1.3683 g, 7.47 mmol, 94%), which was used in the next step without further purification. To a 100 mL round bottom flask equipped with a stir bar was added ethyl (E)-3-(piperidin-4-yl)acrylate (1.368 g, 7.47 mmol, 1.0 equiv.) ethanol (37 mL), cyclopentyl carboxaldehyde (0.8 mL, 7.47 mmol, 1.0 equiv.), acetic acid (2 mL), and sodium cyanoborohydride (938 mg, 14.94 mmol, 2.0 equiv.). The reaction was stirred overnight (16 hours) and completion was verified by alumina TLC analysis (ethyl acetate: hexanes 1: 19). Ethanol was removed under reduced pressure, the reaction mixture was dissolved in ethyl acetate, and this solution was added to a separatory funnel and shaken with saturated aqueous sodium bicarbonate. The aqueous layer was extracted 3x with ethyl acetate, then combined organics were dried over potassium carbonate and concentrated under reduced pressure. The crude mixture was purified by alumina (grade II) flash column chromatography (ethyl acetate: hexanes = 1: 19), furnishing ethyl (E)-3-(1-(cyclopentylmethyl)piperidin-4-yl)acrylate (1.1205 g, 4.22 mmol, 57% yield).

ethyl (E)-3-(1-(cyclopentylmethyl)piperidin-4-yl)acrylate [S39]. ^1H NMR (500 MHz, CDCl_3)



153.14, 119.62, 65.09, 60.33, 53.79, 38.93, 37.55, 31.73, 31.09, 25.32, 14.40. HRMS (TOF ESI+)

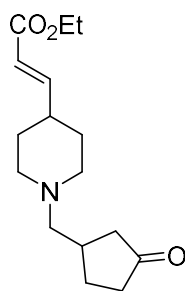
m/z calculated for $\text{C}_{16}\text{H}_{28}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 266.2114, found 266.2120.



64%, alcohol: ketone = 1: 1.3

Oxidation of ethyl (E)-3-(1-(cyclopentylmethyl)piperidin-4-yl)acrylate [S39]. Ethyl (E)-3-(1-(cyclopentylmethyl)piperidin-4-yl)acrylate was protected with HBF_4 . In HFIP, the imidazolium BF_4 salt was oxidized according to general the Standard conditions with 5 mol% $(R,R)\text{-Mn}(\text{CF}_3\text{-PDP})$ and 3.0 equiv. H_2O_2 , then freebased by stirring with aqueous NaOH . The resulting mixture was purified with column chromatography (1: 2 EtOAc: hexanes $\rightarrow$ 2: 1 EtOAc: hexanes $\rightarrow$ 70: 30: 15 EtOAc: hexanes: MeOH). **Run 1:** 61% yield, alcohol: ketone = 0.6: 1. **Run 2:** 64% yield, alcohol: ketone = 1.1: 1. **Run 3:** 66% yield, alcohol: ketone = 1: 1.7. **Average:** 64% yield $\pm$ 2.1%, alcohol: ketone = 1: 1.3. Without HBF_4 protection, $(R,R)\text{-Mn}(\text{CF}_3\text{-PDP})$ - 0% yield, 93% RSM.

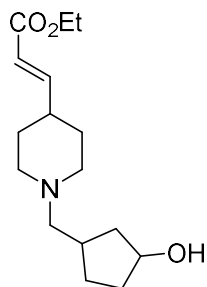
ethyl (E)-3-(1-((3-oxocyclopentyl)methyl)piperidin-4-yl)acrylate [45-ketone]. ¹H NMR (600



MHz,) δ 6.89 (dd, J = 15.8, 7.0 Hz, 1H), 5.76 (dd, J = 15.5, 1.2 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.87 (app d, J = 10.8 Hz, 2H), 2.42 (hept, J = 8.3 Hz, 1H), 2.38 – 2.21 (m, 4H), 2.20 – 2.05 (m, 3H), 2.03 – 1.95 (m, 2H), 1.91 (dd, J = 18.2, 8.7 Hz, 1H), 1.70 (app d, J = 13.0 Hz, 2H), 1.65 – 1.55 (m, 1H), 1.50 – 1.40 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (151 MHz,) δ 219.67, 166.97, 152.75, 119.74,

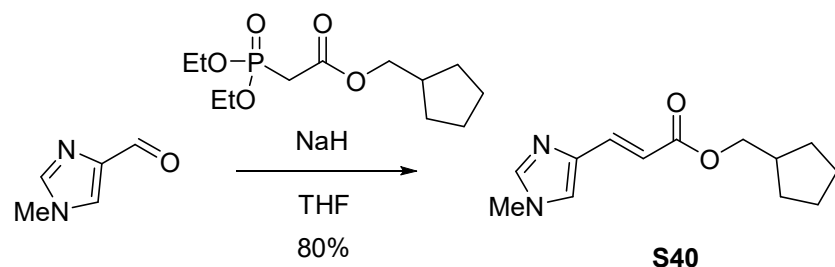
63.72, 60.34, 53.84, 53.72, 44.07, 38.68, 37.95, 34.74, 31.02, 31.00, 27.82, 14.36. HRMS (TOF ESI+) m/z calculated for C₁₆H₂₆NO₃ [M+H]⁺: 280.1913, found 280.1904.

ethyl (E)-3-(1-((3-hydroxycyclopentyl)methyl)piperidin-4-yl)acrylate [45-OH]. The product



was isolated as a ca. 1: 1 mixture of diastereomers. ¹H NMR (500 MHz, CDCl₃) δ 6.90(dd, J = 15.5, 7.9 Hz, 0.5H), 6.89 (dd, J = 15.8, 8.3 Hz, 0.5H), 5.77 (d, J = 15.8 Hz, 1H), 4.36 – 4.31 (m, 0.5H), 4.25 – 4.20 (m, 0.5H), 4.17 (q, J = 7.2, 1H), 4.16 (q, J = 7.2, 1H), 3.28 – 2.99 (br m, 1H), 2.99 – 2.86 (m, 2H), 2.47 – 2.34 (m, 0.5H), 2.41 (app d, J = 5.7, 1H), 2.27 (app d, J = 7.9 Hz, 1H), 2.24 –

2.05 (m, 2.5H), 2.05 – 1.86 (m, 2.5H), 1.83 – 1.74 (m, 1H), 1.74 – 1.63 (m, 3H), 1.60 – 1.46 (m, 3H), 1.45 – 1.35 (m, 1H), 1.32 – 1.17 (m, 3.5H). ¹³C NMR (126 MHz, CDCl₃) δ 167.04 (166.96), 152.86 (152.43), 119.97 (119.76), 73.69 (73.26), 64.73 (63.88), 60.37, 55.04 (54.85), 53.65 (53.52), 41.60 (40.44), 38.74 (38.30), 36.43 (34.84), 35.96 (35.06), 30.85 (2 overlapping peaks), 30.85 (30.78), 29.32 (28.15), 14.40 (14.38). Carbons assigned from HSQC correlations to diastereomeric protons. HRMS (TOF ESI+) m/z calculated for C₁₆H₂₈NO₃ [M+H]⁺: 282.2069, found 282.2066.

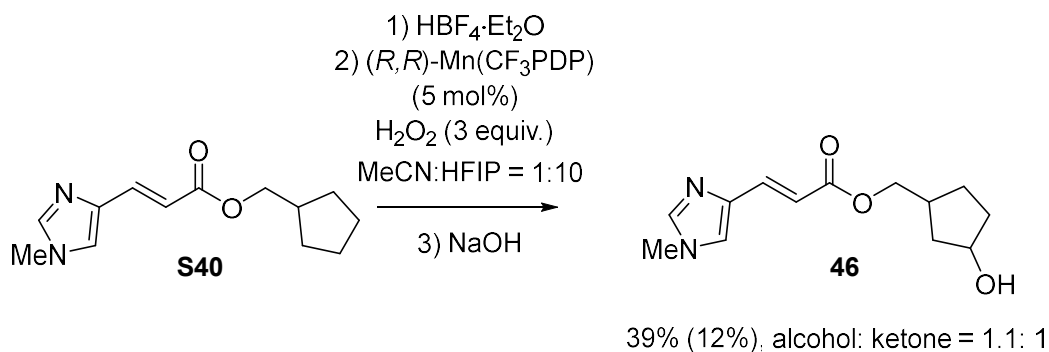


Preparation of cyclopentylmethyl (E)-3-(1-methyl-1H-imidazol-4-yl)acrylate [S40]. A flame-dried 25 mL round bottom flask equipped with a stir bar was charged with 90% sodium hydride (80 mg, 3.0 mmol, 1.2 equiv.) and THF (3 mL). The suspension was cooled to 0 °C in an ice bath, then a solution of cyclopentylmethyl 2-(diethoxyphosphoryl)acetate (835 mg, 3.0 mmol, 1.2 equiv.) in THF (3 mL) was added dropwise and the reaction was stirred for 30 minutes. A solution of 1-methyl-1H-imidazole-4-carbaldehyde (275.3 mg, 2.5 mmol, 1.0 equiv.) in THF (3 mL) was added dropwise over 5 minutes. The reaction was allowed to warm to room temperature and stir overnight (16 hours) before confirmation of completion by TLC (ethyl acetate:dichloromethane:methanol = 20: 77: 3). The reaction was quenched with saturated aqueous ammonium chloride and extracted 3x with ethyl acetate. Combined organics were dried over sodium sulfate and concentrated under reduced pressure. The crude reaction mixture was purified by silica flash column chromatography (ethyl acetate:dichloromethane:methanol = 20: 77: 3), furnishing cyclopentylmethyl (E)-3-(1-methyl-1H-imidazol-4-yl)acrylate as an off-white solid (1.027 g, 3.17 mmol, 80% yield).

cyclopentylmethyl (E)-3-(1-methyl-1H-imidazol-4-yl)acrylate [S40]. ¹H NMR (500 MHz,

CDCl₃) δ 7.51 (d, *J* = 15.6 Hz, 1H), 7.43 (s, 1H), 7.05 (s, 1H), 6.53 (d, *J* = 15.7 Hz, 1H), 4.04 (d, *J* = 7.0 Hz, 2H), 3.68 (s, 3H), 2.24 (hept, *J* = 7.5 Hz, 1H), 1.80 – 1.69 (m, 2H), 1.66 – 1.48 (m, 4H), 1.35 – 1.22 (m, 2H). ¹³C NMR

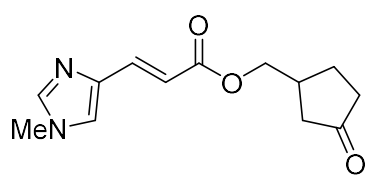
(126 MHz, CDCl₃) δ 167.97, 139.24, 138.76, 136.02, 122.46, 116.36, 68.32, 38.77, 33.71, 29.48, 25.49. HRMS (TOF ESI+) m/z calculated for C₁₃H₁₉N₂O₂ [M+H]⁺: 235.1447, found 235.1445.



Oxidation of cyclopentylmethyl (E)-3-(1-methyl-1H-imidazol-4-yl)acrylate [S40].

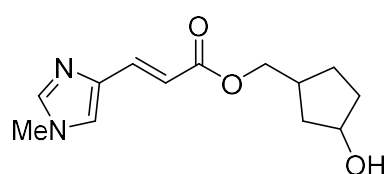
Cyclopentylmethyl (E)-3-(1-methyl-1H-imidazol-4-yl)acrylate was protected with HBF₄. In HFIP, the imidazolium BF₄ salt was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) and 3.0 equiv. H₂O₂, then freebased by stirring with aqueous NaOH. The resulting mixture was purified with column chromatography (20: 80: 3 EtOAc: DCM: MeOH → 5: 5: 1 EtOAc: DCM: MeOH). With (*R,R*)-Mn(CF₃-PDP) - **Run 1**: 37% yield, alcohol: ketone = 1.3: 1, 15% RSM. **Run 2**: 12% RSM, 40% yield, alcohol: ketone = 1: 1.1. **Run 3**: 10% RSM, 41% yield, alcohol: ketone = 1: 1. **Average**: 12% RSM $\pm$ 2.1%, 39% yield $\pm$ 1.7%, alcohol: ketone = 1.1: 1. With 5 mol% (*R,S,S,R*)-Mn(MeCF₃-PDP) - 65% RSM, 10% yield, alcohol only. With 10mol% (*R,S,S,R*)-Mn(MeCF₃-PDP) - 31% yield, alcohol: ketone = 1: 2.1. Without HBF₄ protection, (*R,R*)-Mn(CF₃-PDP) - 0% yield, 75% RSM.

(3-oxocyclopentyl)methyl (E)-3-(1-methyl-1H-imidazol-4-yl)acrylate [46-ketone]. ^1H NMR

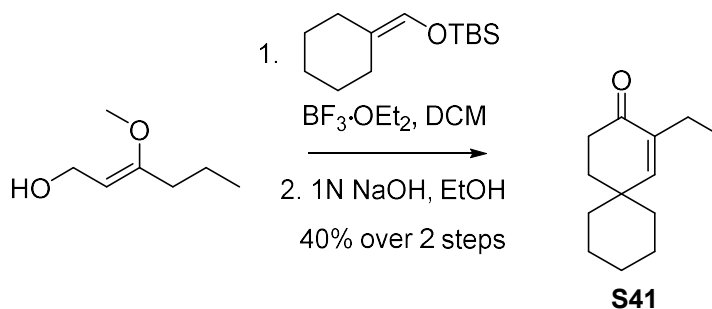


(600 MHz, CDCl_3) δ 7.53 (d, $J = 15.6$ Hz, 1H), 7.45 (s, 1H), 7.08 (s, 1H), 6.53 (d, $J = 15.6$ Hz, 1H), 4.22 (dd, 11.1, 6.3 Hz, 1H), 4.20 (dd, 11.1, 6.3 Hz, 1H), 3.70 (s, 3H), 2.62 (app hept, $J=7.8$ Hz, 1H), 2.41 (dd, $J = 18.4$, 7.8 Hz, 1H), 2.38 – 2.31 (m, 1H), 2.25 – 2.14 (m, 2H), 2.04 (ddd, $J = 18.4$, 9.4, 1.5 Hz, 1H), 1.80 – 1.70 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 218.46, 167.63, 139.38, 138.50, 136.65, 122.85, 115.58, 66.80, 41.94, 38.06, 36.18, 33.75, 26.14. HRMS (TOF ESI+) m/z calculated for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 249.1239, found 249.1238.

(E)-4-(3-hydroxycyclopentyl)but-3-en-2-one [46-OH]. Product isolated as a 1.3: 1 mixture of



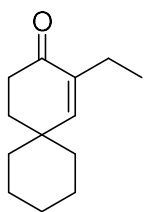
diastereomers. ^1H NMR (500 MHz, CDCl_3) δ 7.54 (d, $J = 15.6$ Hz, 0.4H), 7.52 (d, $J = 15.7$ Hz, 0.6H), 7.45 (s, 1H), 7.06 (s, 1H), 6.53 (d, $J = 15.6$ Hz, 1H), 4.40 (tt, $J = 5.5$, 2.9 Hz, 0.6H), 4.33 (tt, $J = 10.1$, 4.4 Hz, 0.4H), 4.17 (dd, $J = 10.7$, 6.9 Hz, 0.4H), 4.14 (dd, $J = 10.7$, 6.8 Hz, 0.4H), 4.10 (dd, 10.8, 6.6 Hz, 0.6H), 4.07 (dd, 10.8, 6.6 Hz, 0.6H), 3.70 (s, 3H), 2.58 (hept, $J = 7.5$ Hz, 0.6H), 2.32 (hept, $J = 7.5$ Hz, 0.4H), 2.15 – 2.07 (m, 0.6H), 2.06 – 1.88 (m, 1.4H), 1.86 – 1.74 (m, 1.4H), 1.66 – 1.52 (m, 2.6H), 1.45 – 1.31 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 167.91, (167.87), 139.30, 138.63, 136.20, (136.12), 122.58, 116.19, 73.78, (73.76), 68.51, (67.91), 39.25, (38.91), 37.17, (36.51), 35.43, (35.09), 33.74, 26.94, (26.89). HRMS (TOF ESI+) m/z calculated for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 251.1396, found 251.1396.



Preparation of 2-ethylspiro[5.5]undec-1-en-3-one [S41]. (Z)-3-methoxyhex-2-en-1-ol was prepared according to the reported literature⁴⁶. **S41** was prepared according to the reported procedure with slight modification. To a stirred solution of (Z)-3-methoxyhex-2-en-1-ol (1.7 g, 13 mmol, 1.0 equiv.) and tert-butyl(cyclohexylidenemethoxy)dimethylsilane (3.0 g, 13 mmol, 1.0 equiv.) in DCM (26 ml, 0.5 M) was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.3 mL, 3.3 mmol, 0.2 equiv.) at -78°C under nitrogen atmosphere. The reaction mixture was stirred at -78°C for 1 hour and monitored by TLC (silica gel, EA: hexane = 1: 7). Upon completion, the reaction mixture was filtered through a pad of silica with a mixture of ether:pentane = 1: 2. The resulting crude was concentrated and purified by column chromatography (EA: hexane = 1: 6) to furnish 1-(3-oxohexyl)cyclohexane-1-carbaldehyde (1.2 g, 5.6 mmol, 43% yield).

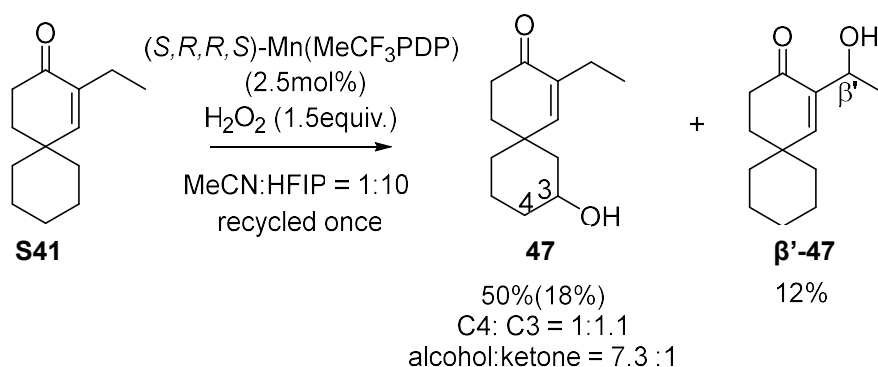
To a stirred solution of 1-(3-oxohexyl)cyclohexane-1-carbaldehyde (297 mg, 1.4 mmol, 1.0 equiv.) in ethanol (28 ml, 0.05 M) was added 1N NaOH (2.1 ml, 2.1 mmol, 1.5 equiv.) at room temperature. The mixture was stirred for 10 hours, and the reaction was concentrated, reducing the volume to approximately 10% of the original, removing most of the ethanol. The reaction mixture was then diluted with brine and the organic layer was extracted with DCM, dried over MgSO_4 , and concentrated in vacuo. The resulting crude was purified by column chromatography (ether: pentane = 1: 6) to afford enone **S41** (254 mg, 1.3 mmol, 94% yield) as a clear oil.

2-ethylspiro[5.5]undec-1-en-3-one [S41]. ^1H NMR (500 MHz, CDCl_3) δ 6.50 (s, 1H), 2.41 (app



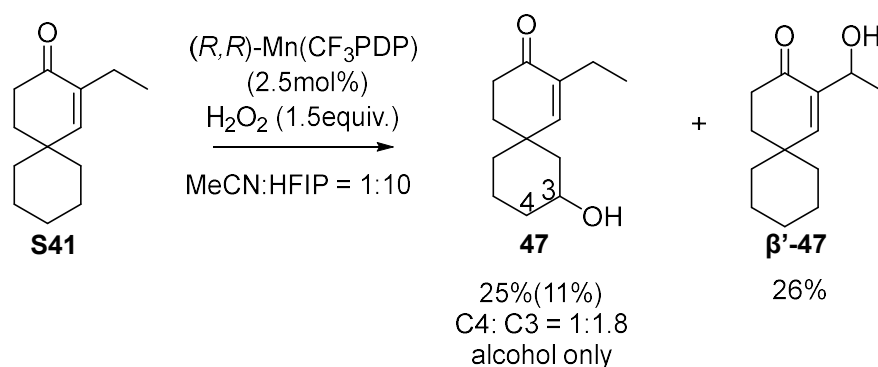
t, $J = 6.8$ Hz, 2H), 2.18 (qd, $J = 7.5, 1.3$ Hz, 2H), 1.86 (t, $J = 6.8$ Hz, 2H), 1.60 – 1.38 (m, 10H), 0.99 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.97, 152.93, 138.72, 36.42, 35.50, 34.27, 32.85, 26.17, 22.67, 21.88, 13.17. HRMS (TOF

ESI+) m/z calculated for $\text{C}_{13}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}]^+$: 193.1592, found 193.1593.



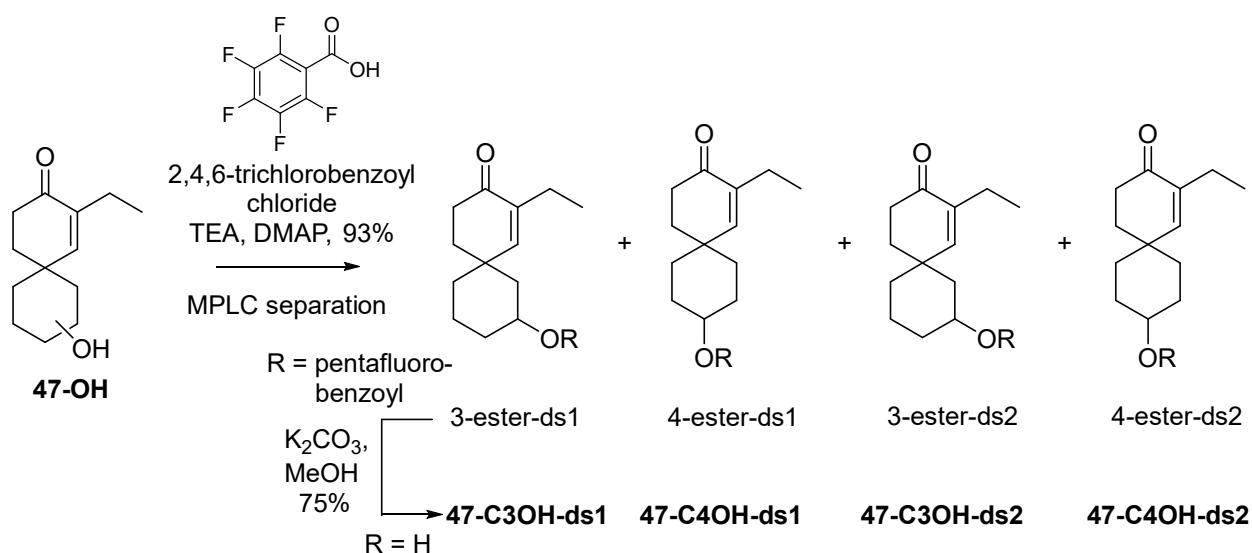
Oxidation of 2-ethylspiro[5.5]undec-1-en-3-one [S41]. With $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$: 2-ethylspiro[5.5]undec-1-en-3-one (0.4 mmol) in HFIP was oxidized according to the Standard conditions with 2.5 mol% $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$ and 1.5 equiv. of H_2O_2 . The resulting mixture was purified by column chromatography (silica, acetone: hexane = 1: 10 $\rightarrow$ 1: 3), yielding recovered starting material (RSM) and a mixture of oxidation products. The RSM was resubjected to the same oxidation condition (Standard conditions, 2.5 mol% $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$ and 1.5 equivalents of H_2O_2). The resulting mixture, combined with the products from the first run, was purified by column chromatography (silica, acetone: hexane = 1: 10 (to isolate RSM, allylic oxidation, and ketone product) $\rightarrow$ 1: 3 (to isolate the alcohol product)). The RSM and allylic oxidation products eluted as a mixture, which was further purified by column chromatography

(acetone: hexane = 1: 10). The RSM and yields (%) from both runs were combined to calculate the final result. Site-selectivity was obtained by quantitative ^1H NMR analysis of each product mixture. **Run 1:** first run - 43% RSM, after recycle - 19% RSM, 52% yield, alcohol: ketone = 10.5: 1. C4: C3 = 1: 1.3, allylic oxidation 13%. **Run 2:** first run - 36% RSM, after recycle - 18% RSM, 47% yield, alcohol: ketone = 6.6: 1. C4: C3 = 1: 1.1, allylic oxidation 12%. **Run 3:** first run - 19% RSM, after recycle - 17% RSM, 51% yield, alcohol: ketone = 5.9: 1. C4: C3 = 1: 1, allylic oxidation 11%. **Average** (after recycle): 18% RSM $\pm$ 0.6%, 50% $\pm$ 2.1% yield, alcohol: ketone = 7.3: 1. C4: C3 = 1: 1.1, allylic oxidation 12% $\pm$ 0.6%.



With $(R,R)\text{-Mn}(\text{CF}_3\text{-PDP})$: 2-ethylspiro[5.5]undec-1-en-3-one (0.4 mmol) in HFIP was oxidized according to the Standard conditions with 2.5 mol% $(R,R)\text{-Mn}(\text{CF}_3\text{-PDP})$ and 1.5 equiv. of H_2O_2 . The same purification and analysis methods as described for the procedure with catalyst **2** were applied. **Run 1:** 11% RSM, 25% yield, alcohol only, C4: C3 = 1: 2, allylic oxidation 26%. **Run 2:** 9% RSM, 24% yield, alcohol only, C4: C3 = 1: 1.5, allylic oxidation 26%. **Average:** 11% RSM $\pm$ 1.0%, 25% $\pm$ 0.6% yield, alcohol only, C4: C3 = 1: 1.8, allylic oxidation 26% $\pm$ 0.3%.

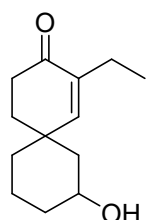
2-(1-hydroxyethyl)spiro[5.5]undec-1-en-3-one [β' -47]. ^1H NMR (500 MHz, CDCl_3) δ 6.70 (s, 1H), 4.53 – 4.99 (m, 1H), 3.06 – 2.94 (m, 1H), 2.44 (app tf, J = 6.9 Hz, 2H), 1.87 (app t, J = 6.8 Hz, 2H), 1.64 – 1.41 (m, 10H), 1.33 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 201.24, 153.51, 139.25, 67.12, 36.20, 36.02, 35.44, 34.49, 32.35, 26.05, 22.08, 21.78, 21.74. HRMS (TOF ESI+) m/z calculated for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 231.1361, found 231.1360.



Separation and Identification of Alcohol Mixture 47-OH. To a stirred solution of pentafluorobenzoic acid (52 mg, 0.25 mmol, 1.5 equiv.) in toluene (1.5 mL, 0.1 M) were added 2,4,6-trichlorobenzoyl chloride (60 mg, 0.25 mmol, 1.5 equiv.) and TEA (0.04 mL, 0.25 mmol, 1.5 equiv.) at room temperature. The mixture was stirred for 20 minutes. The alcohol product mixture (34 mg, 0.16 mmol, 1.0 equiv.) was then added to the activated acid, followed by DMAP (6 mg, 0.05 mmol, 0.3 equiv.). The reaction was stirred for 30 minutes, and progress was monitored by TLC (silica gel, ether: pentane = 1: 2). Upon completion, the reaction mixture was quenched with water, extracted with EA, and concentrated in vacuo. The resulting crude was purified by

MPLC (Teledyne Combiflash® system, ether: pentane = 1: 2, yielding three mixtures: mixture **A**: 3-ester-ds1 + 4-ester-ds1, mixture **B**: 3-ester-ds2, mixture **C**: 4-ester-ds2. The mixture **A** was further purified by MPLC (CPME:pentane = 1: 2.5), separating all four isomers as pentafluorobenzoyl esters, with a total mass of 61 mg (0.15 mmol, 93% yield). The pentafluorobenzoyl ester isomers were separately dissolved in methanol (0.1 M) and treated with K₂CO₃ (3.0 equiv.) at room temperature. The reaction was stirred for 2 hours, with progress monitored by TLC (silica gel, EA: hexane = 1: 5). Upon completion, the reaction mixtures were quenched with saturated NH₄Cl solution, extracted with ethyl acetate (EA), and dried over Na₂SO₄. The crude products were concentrated in vacuo and purified by flash column chromatography (silica gel, EA: hexane = 1: 1) to afford the single isomers of alcohols with approximately 75% yield.

2-ethyl-8-hydroxyspiro[5.5]undec-1-en-3-one [47-C3OH-ds1]: ¹H NMR (500 MHz, CDCl₃) δ



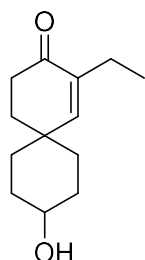
6.67 (s, 1H), 3.86 (tt, *J* = 10.5, 4.1 Hz, 1H), 2.56 – 2.42 (m, 2H), 2.19 (qd, *J* = 7.4, 1.3 Hz, 2H), 2.07 – 1.99 (m, 2H), 1.85 (t, *J* = 6.9 Hz, 2H), 1.80 – 1.73 (m, 1H), 1.67 – 1.53 (m, 3H), 1.34 – 1.24 (m, 3H), 0.99 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 199.18, 149.02, 139.62, 67.39, 45.91, 37.70, 37.10, 36.66, 35.61, 34.40,

22.90, 20.17, 13.16. HRMS (TOF ESI⁺) *m/z* calculated for C₁₃H₂₁O₂ [M+H]⁺: 209.1542, found

209.1540. **[47-C3OH-ds2]:** ¹H NMR (500 MHz, CDCl₃) δ 6.30 (s, 1H), 3.81 (tt, *J* = 9.8, 4.0 Hz, 1H), 2.47 – 2.33 (m, 2H), 2.17 (qd, *J* = 7.5, 1.3 Hz, 2H), 2.05 – 1.96 (m, 1H), 1.95 – 1.83 (m, 3H), 1.79 – 1.72 (m, 1H), 1.60 – 1.42 (m, 3H), 1.35 – 1.20 (m, 3H), 0.99 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 199.62, 153.24, 138.89, 66.95, 44.42, 37.39, 35.32, 34.64, 34.14, 30.65,

22.45, 20.25, 13.03. HRMS (TOF ESI+) m/z calculated for $C_{13}H_{21}O_2$ $[M+H]^+$: 209.1542, found 209.1542.

2-ethyl-9-hydroxyspiro[5.5]undec-1-en-3-one [47-C4OH-ds1]: 1H NMR (500 MHz, $CDCl_3$) δ

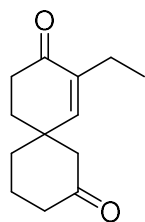


6.30 (s, 1H), 3.71 (tt, $J = 9.4, 4.1$ Hz, 1H), 2.44 (app t, $J = 6.8$ Hz, 2H), 2.17 (qd, $J = 7.5, 1.3$ Hz, 2H), 1.94 (app t, $J = 6.9$ Hz, 2H), 1.89 – 1.83 (m, 2H), 1.72 – 1.66 (m, 2H), 1.55 – 1.40 (m, 5H), 0.99 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.75, 152.76, 139.46, 69.81, 34.99, 34.21, 33.39, 30.64, 30.49, 22.57, 13.05.

HRMS (TOF ESI+) m/z calculated for $C_{13}H_{21}O_2$ $[M+H]^+$: 209.1542, found 209.1537. **[47-C4OH-ds2]:** 1H NMR (500 MHz, $CDCl_3$) δ 6.70 (s, 1H), 3.87 – 3.77 (m, 1H), 2.45 (app t, $J = 6.9$ Hz, 2H), 2.20 (qd, $J = 7.5, 1.4$ Hz, 2H), 1.88 – 1.77 (m, 6H), 1.63 – 1.57 (m, 2H), 1.45 (d, $J = 2.9$ Hz, 1H), 1.43 – 1.35 (m, 2H), 1.01 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.42, 150.21, 139.39, 69.16, 34.76, 34.63, 34.52, 33.60, 30.47, 22.80, 13.13. HRMS (TOF ESI+) m/z calculated for $C_{13}H_{21}O_2$ $[M+H]^+$: 209.1542, found 209.1538.

Identification of ketone mixture 47-ketones. The **47-C4ketone** and **47-C3ketone** isomers were prepared by Dess-Martin Periodinane oxidation of the obtained alcohol products. The site-selectivity of the ketone mixture resulting from C-H oxidation was quantified based on the quantitative 1H NMR spectrum, using peaks identified from authentic ketone samples.

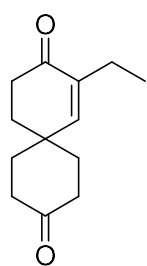
8-ethylspiro[5.5]undec-7-ene-2,9-dione [47-C3ketone]. 1H NMR (500 MHz, $CDCl_3$) δ 6.35 (s,



1H), 2.45 (t, $J = 6.9$ Hz, 2H), 2.44 (br-t, $J = 6.3$ Hz, 2H), 2.37 (s, 2H), 2.19 (qd, $J = 7.5, 1.4$ Hz, 2H), 2.04 – 1.75 (m, 6H), 0.99 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.80, 198.41, 148.66, 140.08, 51.11, 41.10, 40.67, 35.68, 34.01, 32.83,

22.57, 22.23, 12.93. HRMS (TOF ESI+) m/z calculated for $C_{13}H_{19}O_2$ $[M+H]^+$: 207.1385, found 207.1385.

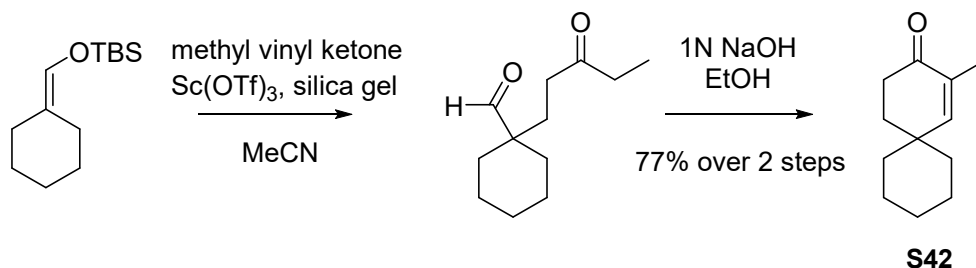
2-ethylspiro[5.5]undec-1-ene-3,9-dione [47-C4ketone]. 1H NMR (500 MHz, $CDCl_3$) δ 6.52 (app



s, 1H), 2.52 (dd, $J = 7.4, 6.2$ Hz, 2H), 2.45 (t, $J = 6.8$ Hz, 4H), 2.23 (qd, $J = 7.4, 1.4$ Hz, 2H), 2.07 (app t, $J = 6.9$ Hz, 2H), 1.98 – 1.86 (m, 4H), 1.02 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.38, 198.78, 149.19, 140.60, 37.50, 35.92, 34.86, 34.36, 31.68, 22.73, 13.06. HRMS (TOF ESI+) m/z calculated for $C_{13}H_{19}O_2$ $[M+H]^+$:

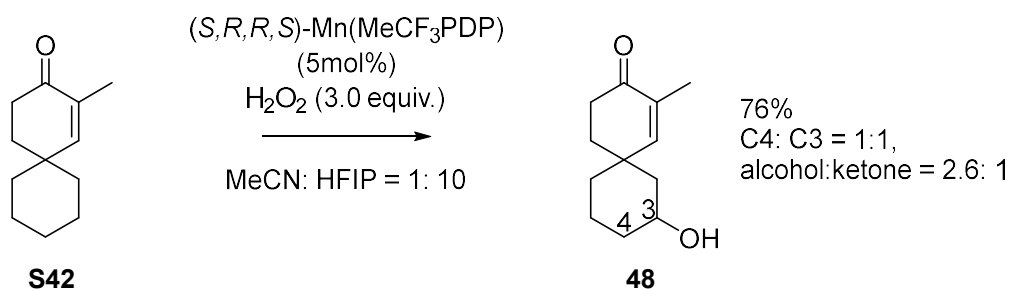
207.1385, found 207.1386.



Preparation of 2-methylspiro[5.5]undec-1-en-3-one [S42]. To a stirred solution of tert-butyl(cyclohexylidenemethoxy)dimethylsilane (3.7 g, 16.7 mmol, 1.0 equiv.) in MeCN (56 mL, 0.3 M), silica gel (13 g, 3.5× w/w) and freshly distilled ethyl vinyl ketone (2.6 mL, 25.1 mmol, 1.5 equiv.) were added at 0°C under a nitrogen atmosphere. $Sc(OTf)_3$ (330 mg, 0.67 mmol, 4 mol%) was then added at 0°C. The mixture was gradually warmed to room temperature over 3 hours, and the reaction was monitored by TLC (silica gel, EA: hexane = 1: 5). Upon completion, the mixture was filtered through a pad of silica with a mixture of EA: hexane = 1: 1. The resulting filtrate was concentrated in vacuo and stored under vacuum for 30 minutes to remove residual ethyl vinyl ketone to afford 1-(3-oxopentyl)cyclohexane-1-carbaldehyde (3.2 g, 16 mmol, 96% yield) as a

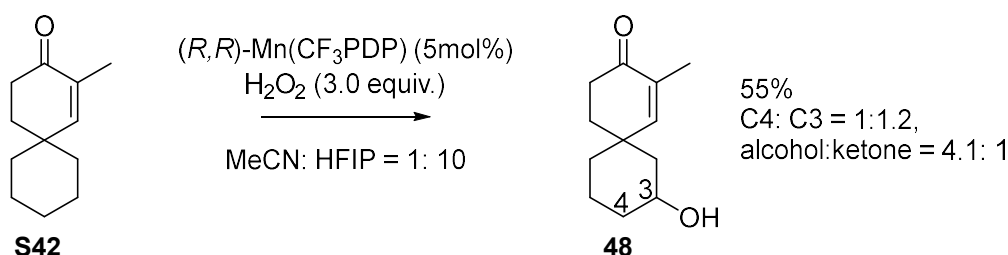
clear oil. 1-(3-oxopentyl)cyclohexane-1-carbaldehyde was used for the next step without further purification.

1-(3-oxopentyl)cyclohexane-1-carbaldehyde was dissolved in ethanol (322 mL, 0.05 M), and 1N NaOH solution (48 mL, 3.0 equiv.) was added at room temperature. The mixture was stirred for 15 hours, with progress monitored by TLC (silica, EA: hexane = 1: 3). After completion, the reaction mixture was concentrated to reduce the volume to approximately 20% of the original. The reaction was quenched with saturated NH_4Cl aqueous solution, and the organic layer was extracted with EA/hexane mixture (1: 9) and dried over MgSO_4 . The crude product was concentrated in vacuo and purified by flash column chromatography (EA: hexane = 1: 9) to afford spiroenone **S42** (2.2 g, 12.3 mmol, 77% yield over 2 steps) as a colorless oil. Spectroscopic data matched the published literature⁴⁷.



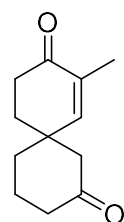
Oxidation of 2-methylspiro[5.5]undec-1-en-3-one [S42]. With catalyst **2** ($(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$): 2-methylspiro[5.5]undec-1-en-3-one **S42** (0.4 mmol) in HFIP was oxidized according to the Standard conditions with 5 mol% $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$ and 3.0 equiv. of H_2O_2 . The resulting mixture was purified by column chromatography (silica, acetone: hexane = 1: 10 to isolate ketone products, followed by 1: 2 to isolate the alcohol products). The ketone product mixture was further subjected to MPLC (EA: hexane = 1: 10 $\rightarrow$ 1: 4), resulting in fully separated C4- and C3-ketone isomers. Site-selectivity was determined by quantitative ^1H NMR analysis of

each product mixture. **Run 1:** 76% yield, alcohol: ketone = 2.7: 1. C4: C3 = 1: 1.1. **Run 2:** 76% yield, alcohol: ketone = 2.8: 1. C4: C3 = 1: 1. **Run 3:** 75% yield, alcohol: ketone = 2.3: 1. C4: C3 = 1.1: 1. **Average:** 76% yield $\pm$ 0.5%, alcohol: ketone = 2.6: 1. C4: C3 = 1: 1.



With catalyst **1** (*R,R*)-Mn(CF₃-PDP): 2-methylspiro[5.5]undec-1-en-3-one **S42** (0.4 mmol) in HFIP was oxidized according to the Standard conditions. The resulting mixture was purified by column chromatography (silica, acetone: hexane = 1: 10 to isolate ketone products, changed to 1: 2 to isolate the alcohol products). Site-selectivity was obtained by quantitative ¹H NMR analysis of each product mixture. **Run 1:** 52% yield, alcohol: ketone = 3.8: 1. C4: C3 = 1: 1.2. **Run 2:** 57% yield, alcohol: ketone = 4.4: 1. C4: C3 = 1: 1.1. **Average:** 55% yield $\pm$ 2.8%, alcohol: ketone = 4.1: 1. C4: C3 = 1: 1.2.

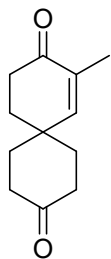
8-methylspiro[5.5]undec-7-ene-2,9-dione [48-C3ketone]. ¹H NMR (500 MHz, CDCl₃) δ 6.41



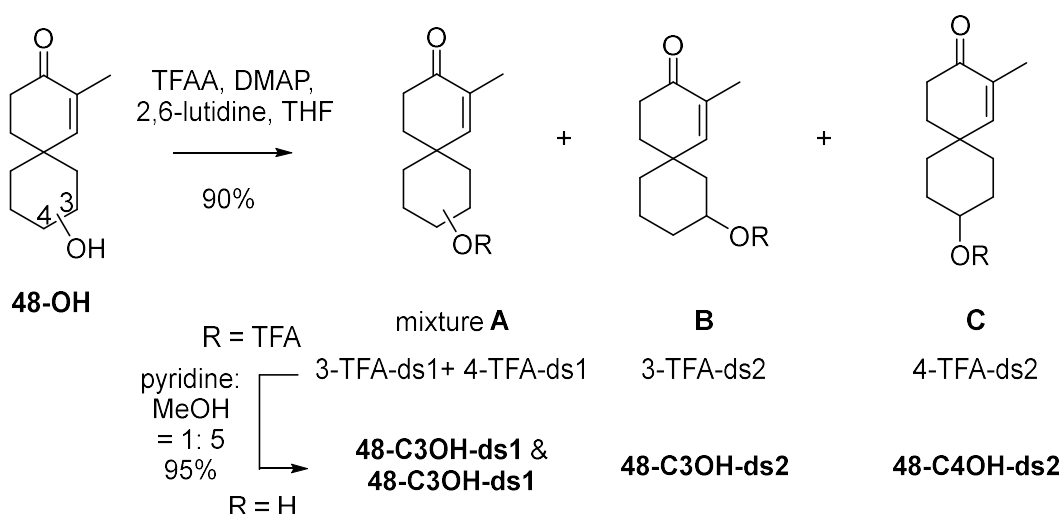
(app s, 1H), 2.46 (t, *J* = 7.0 Hz, 2H), 2.39 (app t, *J* = 6.6 Hz, 2H), 2.36 (s, 2H), 2.03 – 1.85 (m, 5H), 1.80 – 1.74 (m, 1H), 1.76 (d, *J* = 1.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 209.80, 198.84, 150.20, 134.63, 51.03, 41.08, 40.84, 35.57, 33.76, 33.08, 22.21, 16.23. HRMS (TOF ESI+) *m/z* calculated for C₁₂H₁₇O₂ [M+H]⁺: 193.1229,

found 193.1227.

2-methylspiro[5.5]undec-1-ene-3,9-dione [48-C4ketone]. ^1H NMR (500 MHz, CDCl_3) δ 6.60



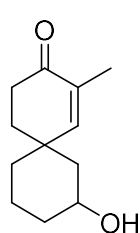
(app s, 1H), 2.52 (app t, $J = 6.8$ Hz, 2H), 2.44 (app t, $J = 7.1$ Hz, 4H), 2.07 (t, $J = 6.8$ Hz, 2H). 1.98 – 1.86 (m, 4H), 1.80 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 210.36, 199.22, 150.72, 135.11, 37.48, 35.84, 35.02, 34.10, 31.97, 16.39. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 193.1229, found 193.1229.



Separation and Identification of Alcohol Mixture 48-OH. To a stirred mixture of alcohol mixture **48** (60 mg, 0.26 mmol, 1.0 equiv.) in THF (0.26 mL, 0.1 M) was added 2,6-lutidine (0.12 mL, 1.0 mmol, 4.0 equiv.), DMAP (9 mg, 0.077 mmol, 0.3 equiv.) and TFA anhydride (0.11 mL, 0.77 mmol, 3.0 equiv.) at -78°C . The reaction was completed in 30min at -78°C (confirmed by TLC analysis, EA: hexane = 1: 2). Upon completion, the resulting mixture concentrated in vacuo and purified by MPLC (Teledyne Combiflash® system, hexane only $\rightarrow$ EA: hexane = 1: 10), furnishing three mixtures: mixture **A**: 3-TFA-ds1 + 4-TFA-ds1, **B**: 3-TFA-ds2, **C**: 4-TFA-ds2, with a total mass of 67 mg (0.23 mmol, 90% total yield).

Each mixture was transferred into separate vials, and a mixture of pyridine: MeOH = 1: 5 (0.1 M) was added. The TFA deprotection reactions were monitored by TLC (EA: hexane = 1: 2). The regioisomeric pair of alcohols from the TFA deprotection of mixture **A** was separated using MPLC (EA: hexane = 1: 8 $\rightarrow$ 1: 3), while the other two alcohols were purified by column chromatography (EA: hexane = 2: 1), resulting in the complete separation of all four alcohol isomers with approximately 80% yield for TFA deprotection.

8-hydroxy-2-methylspiro[5.5]undec-1-en-3-one [48-C3OH-ds1]: ^1H NMR (500 MHz, CDCl_3)

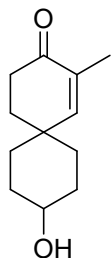


δ 6.73 (s, 1H), 3.85 (tt, J = 10.5, 4.2 Hz, 1H), 2.57 – 2.38 (m, 2H), 2.06 – 1.98 (m, 2H), 1.86 (t, J = 6.8 Hz, 2H), 1.79 – 1.72 (m, 1H), 1.76 (d, J = 1.4 Hz, 3H), 1.67 – 1.61 (m, 1H), 1.61 – 1.52 (m, 2H), 1.33 – 1.23 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.66, 150.67, 134.11, 67.33, 45.80, 37.88, 37.29, 36.57, 35.57, 34.15, 20.14,

16.60. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 195.1385, found 195.1381. **[48-**

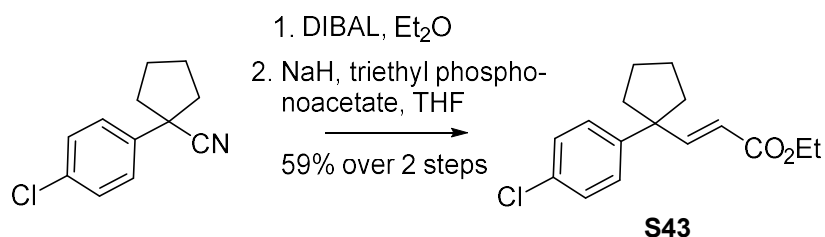
C3OH-ds2]: ^1H NMR (500 MHz, CDCl_3) δ 6.37 (s, 1H), 3.81 (tt, J = 10.4, 4.2 Hz, 1H), 2.46 – 2.34 (m, 2H), 2.03 – 1.96 (m, 1H), 1.95 – 1.85 (m, 3H), 1.79 – 1.71 (m, 1H), 1.74 (d, J = 1.3 Hz, 3H), 1.59 – 1.52 (m, 2H), 1.51 – 1.43 (m, 1H), 1.34 – 1.20 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 200.06, 154.85, 133.37, 66.89, 44.28, 37.54, 35.28, 34.54, 33.88, 30.87, 20.20, 16.13. HRMS (TOF ESI+) m/z calculated for $\text{C}_{12}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 195.1385, found 195.1381.

9-hydroxy-2-methylspiro[5.5]undec-1-en-3-one [48-C4OH-ds1]: ^1H NMR (500 MHz, CDCl_3)



δ 6.36 (s, 1H), 3.71 (tt, J = 9.4, 4.2 Hz, 1H), 2.41 (app t, J = 6.8 Hz, 2H), 1.95 (t, J = 6.8 Hz, 2H), 1.90 – 1.82 (m, 2H), 1.75 (d, J = 1.4 Hz, 3H), 1.72 – 1.65 (m, 2H), 1.54 – 1.38 (m, 5H). ^{13}C NMR (126 MHz, CDCl_3) δ 200.19, 154.38, 133.95, 69.72, 35.17,

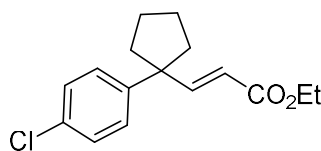
33.95, 33.26, 30.72, 30.58, 16.27. HRMS (TOF ESI+) m/z calculated for $C_{12}H_{19}O_2$ $[M+H]^+$: 195.1385, found 195.1381. **[48-C4OH-ds2]**: 1H NMR (500 MHz, $CDCl_3$) δ 6.77 (s, 1H), 3.80 (tt, $J = 8.7, 3.6$ Hz, 1H), 2.45 (app t, $J = 6.9$ Hz, 2H), 1.87 – 1.78 (m, 4H), 1.82 (app t, $J = 6.9$ Hz, 2H), 1.77 (d, $J = 1.4$ Hz, 3H), 1.62 – 1.45 (m, 3H), 1.42 – 1.34 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.88, 151.84, 133.89, 69.15, 34.98, 34.84, 34.28, 33.53, 30.46, 16.53. HRMS (TOF ESI+) m/z calculated for $C_{12}H_{19}O_2$ $[M+H]^+$: 195.1385, found 195.1382.



Preparation of ethyl (E)-3-(1-(4-chlorophenyl)cyclopentyl)acrylate [S43]. 1-(4-chlorophenyl)cyclopentane-1-carbonitrile was prepared according to the reported literature¹. To a solution of 1-(4-chlorophenyl)cyclopentane-1-carbonitrile (1.289 g, 6.267 mmol, 1.0 equiv.) in diethyl ether (22 mL) at -78 °C was added diisobutylaluminum hydride (1.0 M in hexanes, 10.0 mL, 10.0 mmol, 1.6 equiv.) dropwise over 10 minutes. The reaction was stirred for 1h at -78 °C until completion was confirmed by TLC analysis (ethyl acetate: hexanes 1: 19). A saturated aqueous solution of Rochelle's salt (20 mL) was added and the mixture was stirred for 2h until separation of the organic and aqueous layers was observed. The aqueous layer was extracted 3x with diethyl ether, then combined organics were dried over magnesium sulfate and concentrated under reduced pressure. The resulting crude mixture was purified by silica flash column chromatography (ethyl acetate: hexanes = 1: 39), furnishing 1-(4-chlorophenyl)cyclopentane-1-carbaldehyde (1.29 g, 6.18 mmol, 99%).

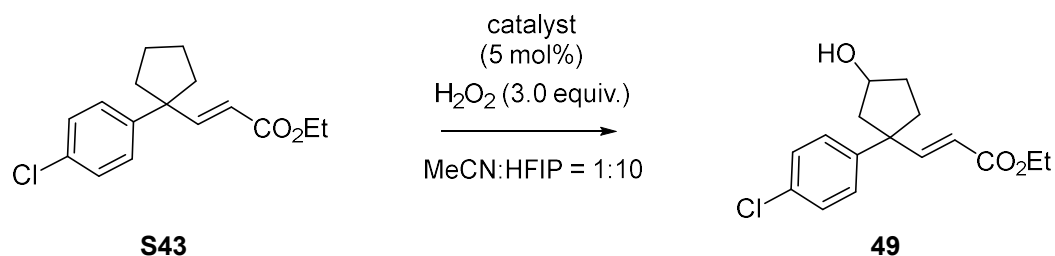
A flame-dried 50 mL round bottom flask equipped with a stir bar was charged with 90% sodium hydride (232 mg, 9.2 mmol, 1.5 equiv.) and tetrahydrofuran (14 mL). The suspension was cooled to 0 °C in an ice bath, then triethyl phosphonoacetate (2.062 g, 9.2 mmol, 1.5 equiv.) was added dropwise and the reaction was stirred for 30 minutes. A solution of 1-(4-chlorophenyl)cyclopentane-1-carbaldehyde (1.28 g, 6.13 mmol, 1.0 equiv.) in tetrahydrofuran (7 mL) was added dropwise over 5 minutes. The reaction was allowed to warm to room temperature and stir overnight (16 hours) before confirmation of completion by TLC (ethyl acetate: hexanes = 1: 39). The reaction was quenched with saturated aqueous ammonium chloride and extracted 3x with ethyl acetate. Combined organics were dried over sodium sulfate and concentrated under reduced pressure. The crude reaction mixture was purified by silica flash column chromatography (ethyl acetate: hexanes = 1: 99), furnishing ethyl (E)-3-(1-(4-chlorophenyl)cyclopentyl)acrylate as a white solid (1.021 g, 3.66 mmol, 60% yield).

ethyl (E)-3-(1-(4-chlorophenyl)cyclopentyl)acrylate [S43]. ^1H NMR (500 MHz, CDCl_3) δ 7.30



– 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 7.03 (d, $J = 15.8$ Hz, 1H), 5.58 (d, $J = 15.8$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 2.13 – 2.05 (m, 2H), 2.03 –

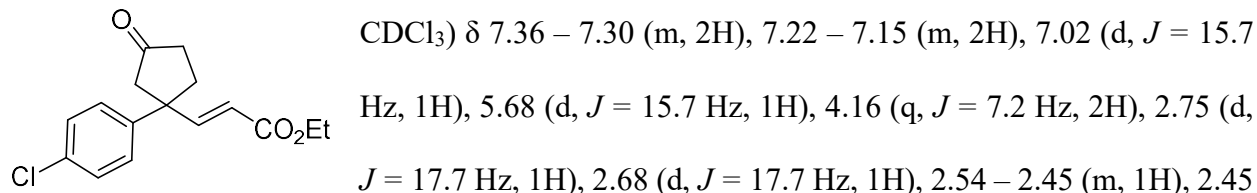
1.94 (m, 2H), 1.83 – 1.67 (m, 4H), 1.26 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.05, 155.48, 143.91, 132.33, 128.65, 128.59, 118.90, 60.49, 53.54, 37.42, 23.20, 14.37. HRMS (TOF ESI+) m/z calculated for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{Cl}$ $[\text{M}+\text{H}]^+$: 279.1152, found 279.1148.



(*S,R,R,S*)-Mn(MeCF₃PDP): 51% (18%), alcohol: ketone = 2: 1
 (*R,R*)-Mn(CF₃PDP): 0% yield, decomposition

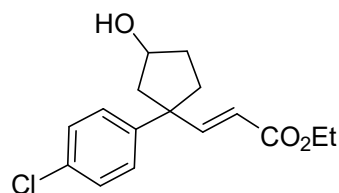
Oxidation of ethyl (E)-3-(1-(4-chlorophenyl)cyclopentyl)acrylate [S43]. Ethyl (E)-3-(1-(4-chlorophenyl)cyclopentyl)acrylate in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) or (*S,R,R,S*)-Mn(MeCF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (ethyl acetate: hexanes = 1: 2 → ethyl acetate: hexanes = 1: 1). With (*R,R*)-Mn(CF₃-PDP) - **Run 1:** 0%. **Run 2:** 0%. **Average:** 0%. With (*S,R,R,S*)-Mn(MeCF₃-PDP) - **Run 1:** 52% yield, alcohol: ketone = 1.9: 1, 19% RSM. **Run 2:** 48% yield, alcohol: ketone = 2.2: 1, 20% RSM. **Run 3:** 53% yield, alcohol: ketone = 1.9: 1, 16% RSM. **Average:** 51% yield ± 2.2%, alcohol: ketone = 2.0: 1, 18% ± 1.7% RSM.

ethyl (E)-3-(1-(4-chlorophenyl)-3-oxocyclopentyl)acrylate [49-ketone]. ¹H NMR (500 MHz,



– 2.39 (m, 1H), 2.38 – 2.27 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 215.31, 166.23, 152.29, 141.66, 133.40, 129.18, 128.08, 120.26, 60.84, 49.63, 49.41, 36.30, 33.78, 14.30. HRMS (TOF ESI⁺) *m/z* calculated for C₁₆H₁₈O₃Cl [M+H]⁺: 293.0944, found 293.0944.

ethyl (E)-3-(1-(4-chlorophenyl)-3-hydroxycyclopentyl)acrylate [49-OH]. Alcohols were



isolated as a 3: 1 mixture of diastereomers. Minor diastereomer

reported in parentheses for ^{13}C NMR. ^1H NMR (600 MHz, CDCl_3) δ

7.30 – 7.25 (m, 2H), 7.22 – 7.13 (m, 2.25H), 6.95 (d, J = 15.8 Hz,

0.75H), 5.61 – 5.53 (m, 1H), 4.52 – 4.45 (m, 0.75H), 4.44 – 4.38 (m, 0.25H), 4.15 (q, J = 7.1 Hz,

2H), 2.57 – 2.51 (m, 0.75H), 2.48 – 2.42 (m, 0.25H), 2.26 (m, 1H), 2.16 – 2.02 (m, 3H), 1.90 (br

s, 1H), 1.75 – 1.68 (m, 1H), 1.25 (t, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ (167.03),

166.85, (155.93), 154.89, 143.99, (143.33), (132.53), 132.52, (128.73), 128.71, (128.47), 128.39,

(119.17), 118.75, (72.56), 72.47, 60.64, (60.57), (52.65), 52.56, (47.33), 46.90, (36.25), 35.56,

(34.43), 34.33, 14.32, (14.32). HRMS (TOF ESI+) m/z calculated for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Cl}$ $[\text{M}+\text{H}]^+$:

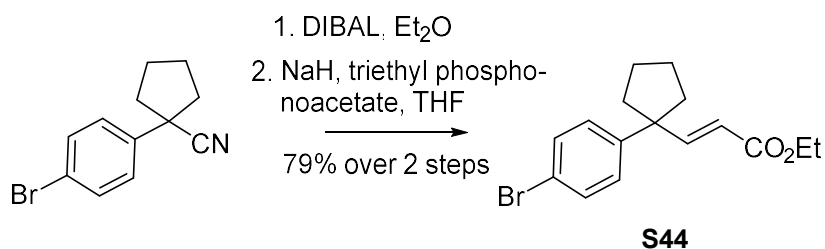
295.1101, found 295.1106. Major diastereomer: δ 7.29 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.6 Hz,

2H), 6.96 (d, J = 15.6 Hz, 1H), 5.59 (d, J = 15.6 Hz, 1H), 4.54 – 4.46 (m, 1H), 4.15 (q, J = 7.1

Hz, 2H), 2.55 (dd, J = 13.7, 6.8 Hz, 1H), 2.33 – 2.21 (m, 1H), 2.18 – 2.09 (m, 2H), 2.06 (dd, J =

13.8, 5.5 Hz, 1H), 1.77 – 1.68 (m, 1H), 1.65 (br s, 1H), 1.26 (t, J = 7.1 Hz, 3H). HRMS (TOF

ESI+) m/z calculated for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Cl}$ $[\text{M}+\text{H}]^+$: 295.1101, found 295.1106.



Preparation of ethyl (E)-3-(1-(4-bromophenyl)cyclopentyl)acrylate [S44]. 1-(4-

bromophenyl)cyclopentane-1-carbonitrile was prepared according to the reported literature¹. To a

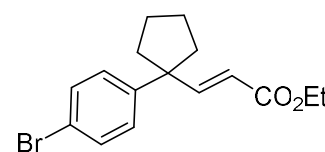
solution of 1-(4-bromophenyl)cyclopentane-1-carbonitrile (1 g, 4.0 mmol, 1.0 equiv.) in diethyl

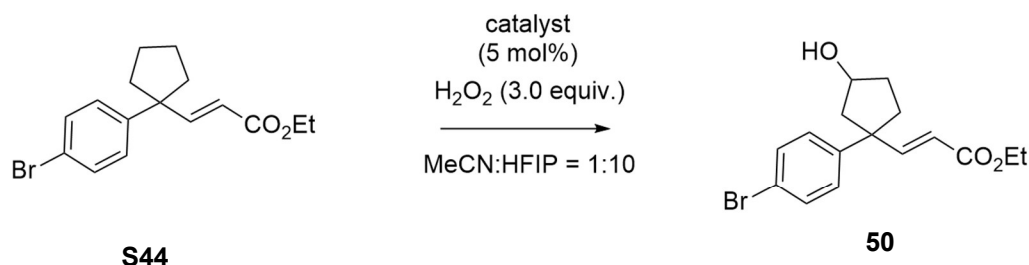
ether (14 mL) at -78 °C was added diisobutylaluminum hydride (1.0 M in hexanes, 6.4 mL, 6.4

mmol, 1.6 equiv.) dropwise over 10 minutes. The reaction was stirred for 1h at -78 °C until completion was confirmed by TLC analysis (ethyl acetate: hexanes 1: 19). A saturated aqueous solution of Rochelle's salt (14 mL) was added and the mixture was stirred for 2h until separation of the organic and aqueous layers was observed. The aqueous layer was extracted 3x with diethyl ether, then combined organics were dried over magnesium sulfate and concentrated under reduced pressure. The resulting crude mixture was purified by silica flash column chromatography (ethyl acetate: hexanes = 1: 39), furnishing 1-(4-bromophenyl)cyclopentane-1-carbaldehyde (1.002 g, 3.96 mmol, 99%).

A flame-dried 50 mL round bottom flask equipped with a stir bar was charged with 90% sodium hydride (149 mg, 5.59, 1.4 equiv.) and dichloromethane (8 mL). The suspension was cooled to 0 °C in an ice bath, then triethyl phosphonoacetate (1.19 mL, 5.98 mmol, 1.5 equiv.) was added dropwise and the reaction was stirred for 30 minutes. A solution of 1-(4-bromophenyl)cyclopentane-1-carbaldehyde (1.002 g, 3.96 mmol, 1.0 equiv.) in dichloromethane (5 mL) was added dropwise over 5 minutes. The reaction was allowed to warm to room temperature and stir overnight (16 hours) before confirmation of completion by TLC (ethyl acetate: hexanes = 1: 39). The reaction was quenched with saturated aqueous ammonium chloride and extracted 3x with ethyl acetate. Combined organics were dried over sodium sulfate and concentrated under reduced pressure. The crude reaction mixture was purified by silica flash column chromatography (ethyl acetate: hexanes = 1: 99), furnishing ethyl (E)-3-(1-(4-bromophenyl)cyclopentyl)acrylate as a white solid (1.027 g, 3.17 mmol, 80% yield).

ethyl (E)-3-(1-(4-chlorophenyl)cyclopentyl)acrylate [S44]. ^1H NMR (500 MHz, CDCl_3) δ 7.43

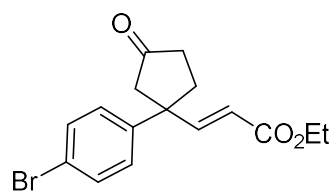
 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 15.8 Hz, 1H), 5.58 (d, J = 15.8 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.13 – 2.03 (m, 2H), 2.03 – 1.94 (m, 2H), 1.83 – 1.68 (m, 4H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.92, 155.27, 144.34, 131.44, 128.93, 120.32, 118.83, 60.38, 53.49, 37.27, 23.08, 14.25. HRMS (TOF ESI+) m/z calculated for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{Br}$ $[\text{M}+\text{H}]^+$: 323.0647, found 323.0645.



(*S,R,R,S*)-Mn(MeCF₃PDP): 63% (7%), alcohol: ketone = 1.3: 1
 (*R,R*)-Mn(CF₃PDP): 56%, alcohol: ketone = 1: 1

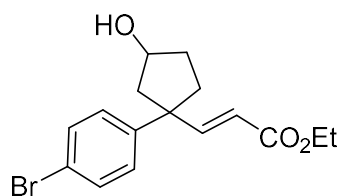
Oxidation of ethyl (E)-3-(1-(4-bromophenyl)cyclopentyl)acrylate [S44]. Ethyl (E)-3-(1-(4-bromophenyl)cyclopentyl)acrylate in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) or (*S,R,R,S*)-Mn(MeCF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (ethyl acetate: hexanes = 1: 2 → ethyl acetate: hexanes = 1: 1). (*R,R*)-Mn(CF₃-PDP) - **Run 1**: 57% yield, alcohol: ketone = 1: 1. **Run 2**: 55% yield, alcohol: ketone = 1: 1. **Average**: 56% yield $\pm$ 1%. alcohol: ketone = 1: 1. (*S,R,R,S*)-Mn(MeCF₃-PDP) - **Run 1**: 6% RSM, 63% yield, alcohol: ketone = 1.2: 1. **Run 2**: 6% RSM, 62% yield, alcohol: ketone = 1.4: 1. **Run 3**: 8% RSM, 63% yield, alcohol: ketone = 1.2: 1. **Average**: 7% RSM $\pm$ 0.9%, 63% yield $\pm$ 0.6%, alcohol: ketone = 1.3:1.

ethyl (E)-3-(1-(4-chlorophenyl)-3-oxocyclopentyl)acrylate [50-ketone]. ^1H NMR (500 MHz,

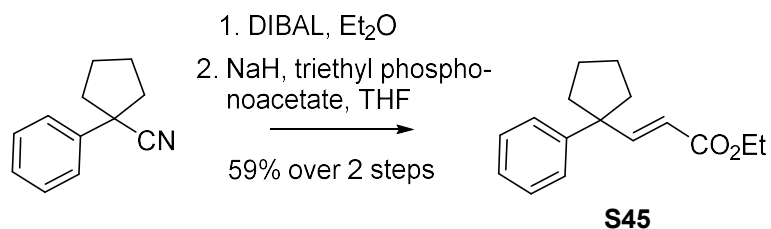


CDCl_3) δ 7.49 (d, J = 8.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 7.02 (d, J = 15.8 Hz, 1H), 5.68 (d, J = 15.9 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.75 (d, J = 17.7 Hz, 1H), 2.68 (d, J = 17.7 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.45 – 2.27 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 215.31, 166.23, 152.21, 142.19, 132.15, 128.44, 121.50, 120.30, 60.86, 49.70, 49.35, 36.30, 33.73, 14.31. HRMS (TOF ESI+) m/z calculated for $\text{C}_{16}\text{H}_{18}\text{O}_3\text{Br}$ $[\text{M}+\text{H}]^+$: 337.0439, found 337.0432.

ethyl (E)-3-(1-(4-chlorophenyl)-3-hydroxycyclopentyl)acrylate [50-OH]. Alcohols were



isolated as a 4: 1 mixture of diastereomers. Minor diastereomer reported in parentheses for ^{13}C NMR. ^1H NMR (600 MHz, CDCl_3) δ 7.43 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.6 Hz, 1.6H), 7.10 (d, J = 8.6 Hz, 0.4H), 6.95 (d, J = 15.8 Hz, 1H), 5.58 (d, J = 15.8 Hz, 0.8H), 5.57 (d, J = 15.8 Hz, 0.2H), 4.52 – 4.45 (m, 0.8H), 4.45 – 4.38 (m, 0.2H), 4.18 – 4.12 (m, 2H), 2.53 (dd, J = 13.7, 6.7 Hz, 0.8H), 2.44 (dd, J = 13.9, 7.1 Hz, 0.2H), 2.32 – 2.20 (m, 1H), 2.16 – 2.01 (m, 3H), 1.90 (br s, 1H), 1.75 – 1.68 (m, 1H), 1.25 (t, J = 7.1 Hz, 0.6H), 1.25 (t, J = 7.0 Hz, 2.4H). ^{13}C NMR (126 MHz, CDCl_3) δ (167.02), 166.83, (155.86), 154.80, 144.53, (143.85), (131.66), 131.64, (128.84), 128.76, 120.61, (119.16), 118.74, (72.48), 72.39, 60.64, (60.56), (52.67), 52.57, (47.26), 46.81, (36.18), 35.49, (34.38), 34.27, 14.30. HRMS (TOF ESI+) m/z calculated for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Br}$ $[\text{M}+\text{H}]^+$: 339.0596, found 339.0599.



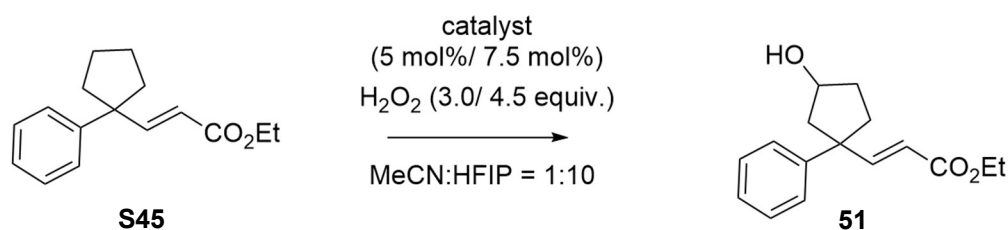
Preparation of ethyl (E)-3-(1-phenylcyclopentyl)acrylate [S45]. 1-phenylcyclopentane-1-carbonitrile was prepared according to the reported literature¹. To a solution of 1-phenylcyclopentane-1-carbonitrile (1.00 g, 5.84 mmol, 1.0 equiv.) in diethyl ether (31 mL) at -78 °C was added diisobutylaluminum hydride (1.0 M in hexanes, 9.3 mL, 9.3 mmol, 1.6 equiv.) dropwise over 10 minutes. The reaction was stirred for 1h at -78 °C until completion was confirmed by TLC analysis (ethyl acetate: hexanes 1: 19). A saturated aqueous solution of Rochelle's salt (30 mL) was added and the mixture was stirred for 2h until separation of the organic and aqueous layers was observed. The aqueous layer was extracted 3x with diethyl ether, then combined organics were dried over magnesium sulfate and concentrated under reduced pressure. The resulting crude mixture was purified by silica flash column chromatography (ethyl acetate: hexanes = 1: 39), furnishing 1-phenylcyclopentane-1-carbaldehyde (1.00 g, 5.74 mmol, 98%).

A flame-dried 50 mL round bottom flask equipped with a stir bar was charged with 90% sodium hydride (230 mg, 8.61 mmol, 1.5 equiv.) and tetrahydrofuran (13 mL). The suspension was cooled to 0 °C in an ice bath, then triethyl phosphonoacetate (1.93 g, 8.61 mmol, 1.5 equiv.) was added dropwise and the reaction was stirred for 30 minutes. A solution of 1-phenylcyclopentane-1-carbaldehyde (1.00 g, 5.74 mmol, 1.0 equiv.) in tetrahydrofuran (7 mL) was added dropwise over 5 minutes. The reaction was allowed to warm to room temperature and stir overnight (16 hours) before confirmation of completion by TLC (ethyl acetate: hexanes = 1: 39). The reaction was quenched with saturated aqueous ammonium chloride and extracted 3x with

ethyl acetate. Combined organics were dried over sodium sulfate and concentrated under reduced pressure. The crude reaction mixture was purified by silica flash column chromatography (ethyl acetate: hexanes = 1: 99), furnishing ethyl (E)-3-(1-phenylcyclopentyl)acrylate as a white solid (833 mg, 3.41 mmol, 60% yield).

ethyl (E)-3-(1-phenylcyclopentyl)acrylate [S45]. ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.26 (m,

4H), 7.21 (t, J = 7.0 Hz, 1H), 7.07 (d, J = 15.8 Hz, 1H), 5.61 (d, J = 15.9 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.16 – 1.98 (m, 4H), 1.83 – 1.69 (m, 4H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.25, 156.13, 145.46, 128.50, 127.21, 126.50, 118.53, 60.41, 53.93, 37.31, 23.25, 14.39. HRMS (TOF ESI+) m/z calculated for $\text{C}_{16}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$: 245.1542, found 245.1538.



$(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{PDP})$: 41% (18%), alcohol: ketone = 1: 1
 $(R,R)\text{-Mn}(\text{CF}_3\text{PDP})$: 33% (9%), alcohol only

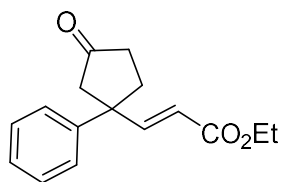
Oxidation of ethyl (E)-3-(1-phenylcyclopentyl)acrylate [S45]. Ethyl (E)-3-(1-phenylcyclopentyl)acrylate in HFIP was oxidized following Procedure A with 5 mol% (R,R) - $\text{Mn}(\text{CF}_3\text{-PDP})$. The resulting mixture was purified with column chromatography (2: 1 EtOAc:

hexanes → EtOAc). With (*R,R*)-Mn(CF₃-PDP) - **Run 1**: 33% yield, alcohol only, 8% RSM. **Run 2**: 33% yield, alcohol only, 9% RSM. **Average**: 33% yield, alcohol only, 9% ± 0.5% RSM.

Ethyl (E)-3-(1-phenylcyclopentyl)acrylate in HFIP was oxidized following Procedure A with 7.5 mol% (*S,R,R,S*)-Mn(MeCF₃-PDP) and 4.5 equivalents of H₂O₂. The resulting mixture was purified by silica flash column chromatography (2: 1 EtOAc: hexanes → EtOAc), separating RSM, ketone, and alcohols. The RSM was then resubjected to the same oxidation conditions (Procedure A, 7.5 mol% (*S,R,R,S*)-Mn(MeCF₃-PDP) and 4.5 equivalents of H₂O₂). The combined mixtures were purified under the same conditions (column chromatography, silica, 2: 1 EtOAc: hexanes → EtOAc). RSM and yields were calculated relative to the initial starting amount.

With (*S,R,R,S*)-Mn(MeCF₃-PDP): **Run 1**: 45% yield, alcohol: ketone = 1.1: 1, 18% RSM. **Run 2**: 41% yield, alcohol: ketone = 1: 1.1, 16% RSM. **Run 3**: 37% yield, alcohol: ketone = 1.1: 1, 20% RSM. **Average**: 41% ± 3.3%, alcohol: ketone = 1: 1, 18% ± 1.6% RSM.

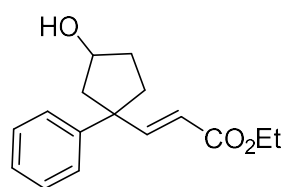
ethyl (E)-3-(3-oxo-1-phenylcyclopentyl)acrylate [51-ketone]. ¹H NMR (500 MHz, CDCl₃) δ



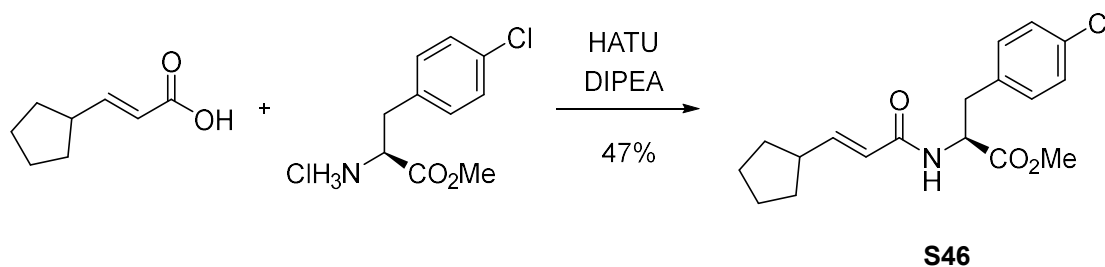
7.36 (app t, *J* = 7.6 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.07 (d, *J* = 15.8 Hz, 1H), 5.70 (d, *J* = 15.8 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.78 (d, *J* = 18.0 Hz, 1H), 2.73 (d, *J* = 17.8 Hz, 1H), 2.56 – 2.28 (m, 4H), 1.26 (t, *J* = 7.1

Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 215.94, 166.43, 152.95, 143.14, 129.06, 127.46, 126.65, 119.90, 60.76, 50.04, 49.48, 36.40, 33.77, 14.33. HRMS (EI⁺) *m/z* calculated for C₁₆H₁₈O₃ [M]⁺: 258.1256, found 258.1266.

ethyl (E)-3-(3-hydroxy-1-phenylcyclopentyl)acrylate [51-OH]. Alcohols were isolated as a 2.7:



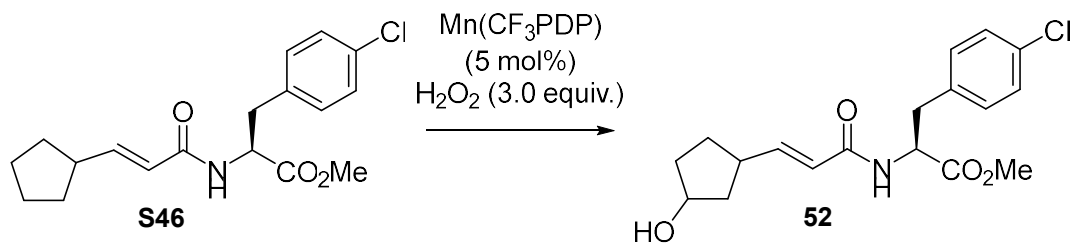
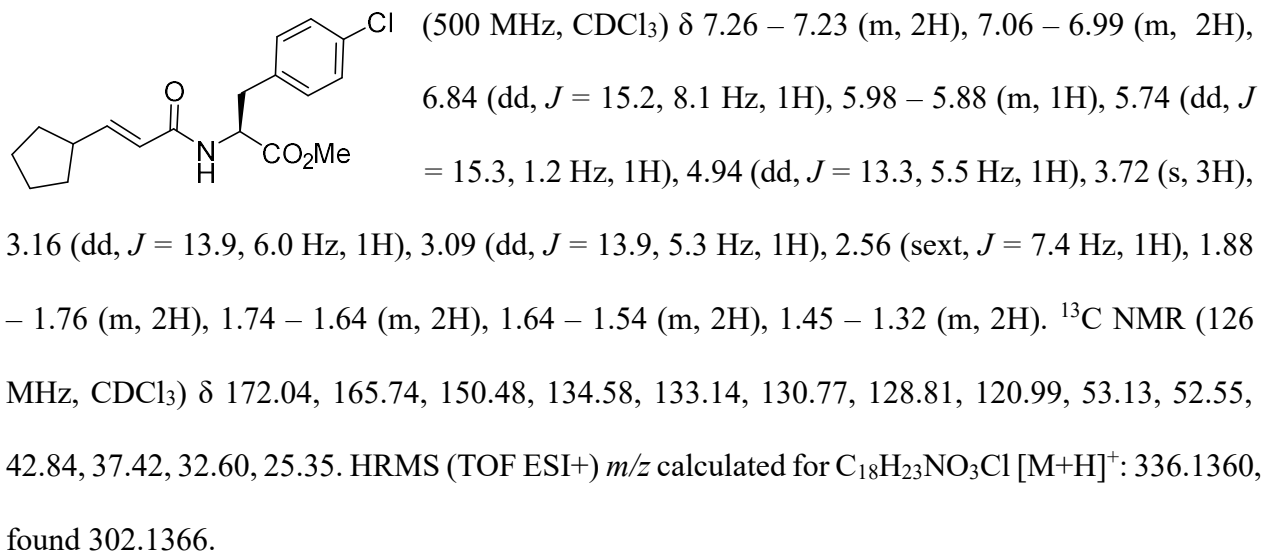
1 mixture of diastereomers. Minor diastereomer reported in parentheses for ^{13}C NMR. ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.19 (m, 5.3H), 7.00 (d, J = 15.8 Hz, 0.7H), 5.62 (d, J = 15.8 Hz, 0.3H), 5.62 (d, J = 15.7 Hz, 0.7H), 4.53 – 4.47 (m, 0.7H), 4.47 – 4.41 (m, 0.3H), 4.15 (q, J = 7.2 Hz, 1.4H), 4.15 (q, J = 7.2 Hz, 0.6H), 2.58 (dd, J = 13.6, 6.8 Hz, 0.7H), 2.53 (dd, J = 13.9, 7.2 Hz, 0.3H), 2.39 – 2.24 (m, 1H), 2.20 – 2.06 (m, 3H), 1.80 – 1.68 (m, 1H), 1.59 (br s, 1H), 1.26 (t, J = 7.1 Hz, 2.1H), 1.25 (t, J = 7.1 Hz, 0.9H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.14, (167.00), 156.44, (155.47), 145.41, (144.82), 128.68, (128.65), 127.03, (126.96), 126.75, (126.70), 118.91, (118.49), 72.81, (72.69), 60.56, (60.48), 53.04, (53.00), 47.34, (46.96), 36.15, (35.44), 34.55, (34.40), 14.37. HRMS (TOF ESI+) m/z calculated for $\text{C}_{16}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$: 261.1491, found 261.1487.



Preparation of methyl (S,E)-3-(4-chlorophenyl)-2-(3-cyclopentylacrylamido)propanoate [S46]. To a solution of (E)-3-cyclopentylacrylic acid (563 mg, 4.02 mmol, 1.0 equiv.) in dichloromethane (24 mL) was added diisopropylethylamine (2.78 mL, 16.08 mmol, 4.0 equiv.) and the reaction was stirred for ten minutes, at which point HATU (1.834 g, 4.82 mmol, 1.2 equiv.) was added. The reaction was stirred for an additional 30 minutes, then L-p-chlorophenylalanine methyl ester HCl (1.105 g, 4.42 mmol, 1.1 equiv.) was added and the reaction was stirred overnight (16 hours). After completion was verified by TLC analysis (ethyl acetate: hexanes 1: 2), the

reaction was quenched with water and extracted 3x with dichloromethane. Combined organics were dried over sodium sulfate and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography (ethyl acetate: hexanes 1: 4 $\rightarrow$ 1: 2) to give methyl (S,E)-3-(4-chlorophenyl)-2-(3-cyclopentylacrylamido)propanoate as a white solid (633 mg, 1.88 mmol, 47% yield).

methyl (R,E)-3-(4-chlorophenyl)-2-(3-cyclopentylacrylamido)propanoate [S46]. ^1H NMR

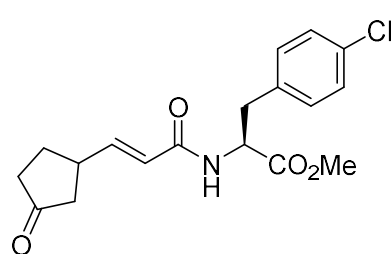


(S,*R*,*R*,S)-Mn(MeCF₃PDP): 66% (14%), alcohol: ketone = 1.2: 1
(R,*R*)-Mn(CF₃PDP): 66% (5%), alcohol: ketone = 1.1: 1

Oxidation of methyl (R,E)-3-(4-chlorophenyl)-2-(3-cyclopentylacrylamido)propanoate [S46].

Methyl (R,E)-3-(4-chlorophenyl)-2-(3-cyclopentylacrylamido)propanoate in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) or (*S,R,R,S*)-Mn(MeCF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (2: 1 EtOAc: hexanes → EtOAc). With (*R,R*)-Mn(CF₃-PDP) - **Run 1**: 4% RSM, 64% yield, alcohol: ketone = 1.2: 1. **Run 2**: 5% RSM, 68% yield, alcohol: ketone = 0.9: 1. **Average**: 5% RSM ± 0.5%, 66% yield ± 2%, alcohol: ketone = 1.1: 1. With (*S,R,R,S*)-Mn(MeCF₃-PDP) - **Run 1**: 15% RSM, 67% yield, alcohol: ketone = 1.1: 1. **Run 2**: 13% RSM, 66% yield, alcohol: ketone = 1.2: 1. **Run 3**: 15% RSM, 66% yield, alcohol: ketone = 1.3: 1. **Average**: 14% RSM ± 0.9%, 66% yield ± 0.5%, alcohol: ketone = 1.2: 1.

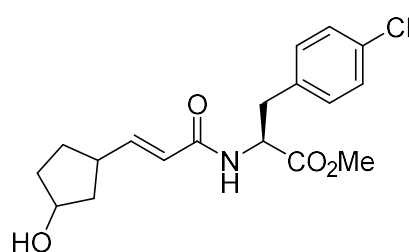
methyl (2R)-3-(4-chlorophenyl)-2-((E)-3-(3-oxocyclopentyl)acrylamido)propanoate [52-



ketone]. Product was isolated as a mixture of two diastereomers.

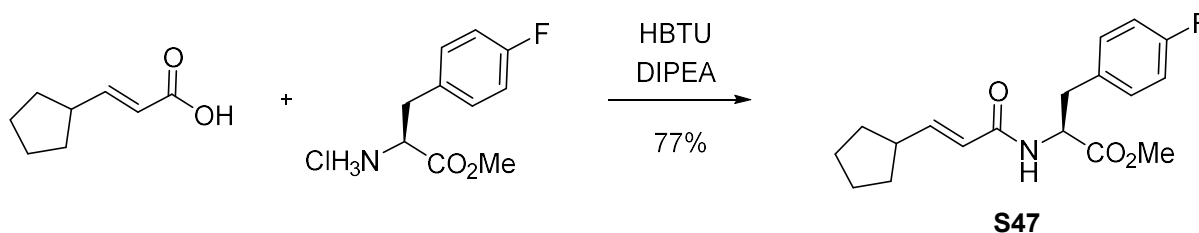
¹H NMR (500 MHz, CDCl₃) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.88 (dd, *J* = 15.2, 7.2 Hz, 1H), 6.00 (br s, 1H), 5.83 (d, *J* = 15.2 Hz, 1H), 4.94 (dd, *J* = 12.3, 6.0 Hz, 1H), 3.74 (s, 3H), 3.17 (dd, *J* = 13.9, 4.7 Hz, 1H), 3.10 (dd, *J* = 13.8, 5.1 Hz, 1H), 2.98 (sext, *J* = 8.1 Hz, 1H), 2.49 – 2.33 (m, 2H), 2.29 – 2.15 (m, 2H), 2.14 – 2.02 (m, 1H), 1.85 – 1.74 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 217.32, 171.89, 164.91, 146.72, 134.41, 133.22, 130.72, 128.86, 122.72, 53.20, 52.63, 43.93, 39.30, 38.00, 37.33, 29.09. HRMS (TOF ESI+) *m/z* calculated for C₁₈H₂₁NO₄Cl [M+H]⁺: 350.1159, found 350.1158.

methyl (2R)-3-(4-chlorophenyl)-2-((E)-3-(3-hydroxycyclopentyl)acrylamido)propanoate



[52-OH]. Product isolated as a mixture of four diastereomers.

^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 6.88 (dd, $J = 15.3, 7.9$ Hz, 0.44H), 6.81 (dd, $J = 15.3, 8.1$ Hz, 0.56H), 6.00 (br s, 1H), 5.76 (d, $J = 15.3$ Hz, 0.56H), 5.75 (d, $J = 15.3$ Hz, 0.44H), 4.93 (dd, $J = 13.3, 5.8$ Hz, 1H), 4.41 (app br s, 0.56H), 4.35 (app br s, 0.44H), 3.72 (s, 3H), 3.15 (dd, $J = 13.9, 6.0$ Hz, 1H), 3.09 (dd, $J = 14.0, 5.6$ Hz, 1H), 2.94 (sext, $J = 8.1$ Hz, 0.56H), 2.61 (sext, $J = 8.0$ Hz, 0.44H), 2.25 – 2.14 (m, 0.56H), 2.09 – 1.96 (m, 1H), 1.91 – 1.52 (m, 4.44H), 1.49 – 1.37 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.05, 165.60, 149.86, (149.54), 134.53, 133.16, 130.75, 128.83, 121.50, (121.35), 73.55, 53.15, 52.58, 42.32, (41.85), 41.02, (40.16), 37.39, 35.64, (35.27), 30.36, (30.19). HRMS (TOF ESI+) m/z calculated for $\text{C}_{18}\text{H}_{23}\text{NO}_4\text{Cl}$ $[\text{M}+\text{H}]^+$: 352.1316, found 352.1313. Carbons assigned from HSQC correlations to diastereomeric protons.

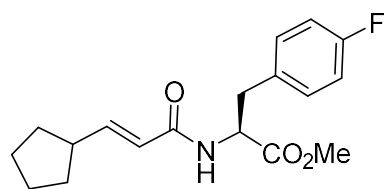


Preparation of methyl (S,E)-2-(3-cyclopentylacrylamido)-3-(4-fluorophenyl)propanoate

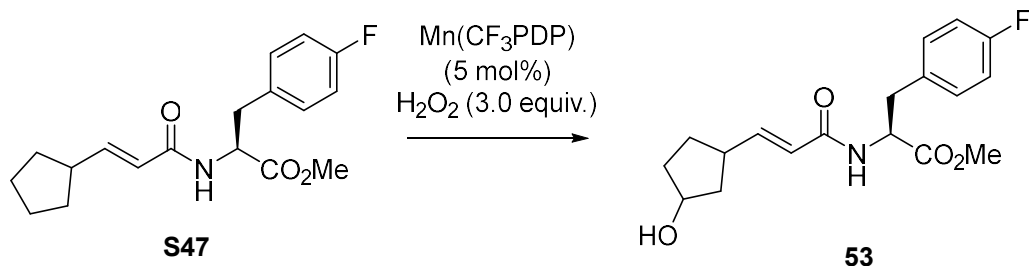
[S47]. To a solution of (E)-3-cyclopentylacrylic acid (493 mg, 3.2 mmol, 1.0 equiv.) in dichloromethane (19 mL) was added diisopropylethylamine (2.7 mL, 15.68 mmol, 4.9 equiv.) and the reaction was stirred for ten minutes, at which point HBTU (1.78 g, 4.70 mmol, 1.47 equiv.) was added. The reaction was stirred for an additional 30 minutes, then L-p-fluorophenylalanine

methyl ester HCl (1.00 g, 4.28 mmol, 1.34 equiv.) was added and the reaction was stirred overnight (16 hours). After completion was verified by TLC analysis (ethyl acetate: hexanes 1: 2), the reaction was quenched with water and extracted 3x with dichloromethane. Combined organics were dried over sodium sulfate and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography (ethyl acetate: hexanes 1: 4 $\rightarrow$ 1: 2) to give methyl (S,E)-2-(3-cyclopentylacrylamido)-3-(4-fluorophenyl)propanoate as a white solid (787 mg, 2.46 mmol, 77% yield).

methyl (S,E)-3-(4-fluorophenyl)-2-(3-cyclopentylacrylamido)propanoate [S47]. ^1H NMR



(500 MHz, CDCl_3) δ 7.09 – 7.00 (m, 2H), 7.01 – 6.91 (m, 2H), 6.83 (dd, J = 15.2, 7.8 Hz, 1H), 5.92 (d, J = 7.8 Hz, 1H), 5.74 (d, J = 15.2 Hz, 1H), 4.93 (dt, J = 7.7, 5.6 Hz, 1H), 3.72 (s, 3H), 3.13 (qd, J = 14.0, 5.6 Hz, 2H), 2.56 (h, J = 8.1 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.74 – 1.64 (m, 2H), 1.64 – 1.53 (m, 2H), 1.44 – 1.32 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.14, 165.74, 162.15 (d, J = 245.5 Hz), 150.43, 131.78 (d, J = 3.3 Hz), 130.92 (d, J = 8.0 Hz), 121.03, 115.54 (d, J = 21.4 Hz), 53.27, 52.51, 42.84, 37.29, 32.60, 25.35. ^{19}F NMR (471 MHz, CDCl_3) δ -115.65. HRMS (TOF ESI+) m/z calculated for $\text{C}_{18}\text{H}_{23}\text{NO}_3\text{F}$ $[\text{M}+\text{H}]^+$: 320.1662, found 320.1663.



(S,R,R,S)-Mn(MeCF₃PDP): 29% (24%), alcohol only.
(R,R)-Mn(CF₃PDP): 21% (8%), alcohol only.

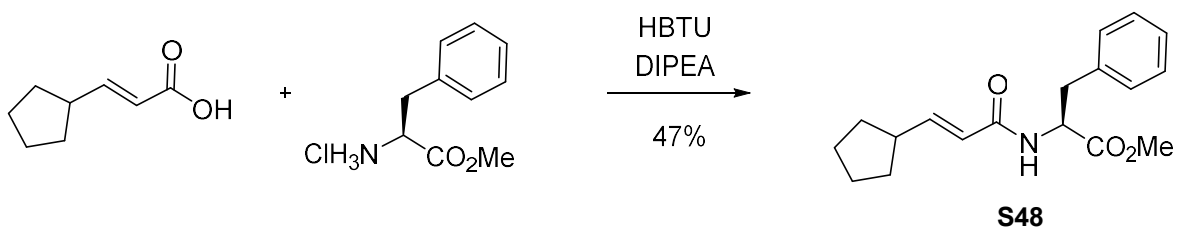
Oxidation of methyl (*S,E*)-2-(3-cyclopentylacrylamido)-3-(4-fluorophenyl)propanoate [S47].

Methyl (*R,E*)-2-(3-cyclopentylacrylamido)-3-(4-fluorophenyl)propanoate in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) or (*S,R,R,S*)-Mn(MeCF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (2: 1 EtOAc: hexanes → EtOAc). With (*R,R*)-Mn(CF₃-PDP) - **Run 1**: 7% RSM, 19% yield. **Run 2**: 8% RSM, 23% yield. **Average**: 8% RSM ± 0.5%, 21% yield ± 2.0%. With (*S,R,R,S*)-Mn(MeCF₃-PDP) - **Run 1**: 25% RSM, 28% yield. **Run 2**: 25% RSM, 27% yield. **Run 3**: 23% RSM, 31% yield. **Average**: 24% RSM ± 0.9%, 29% yield ± 1.7%.

methyl (2*S*)-3-(4-fluorophenyl)-2-((*E*)-3-(3-hydroxycyclopentyl)acrylamido)propanoate

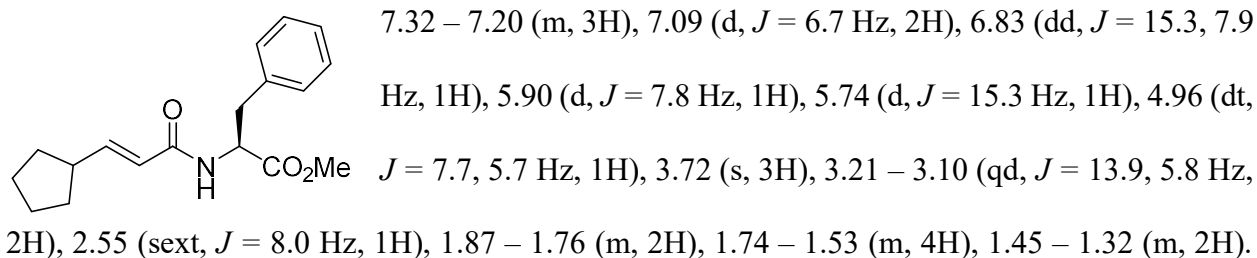
[**53-OH**]. Product was isolated as a mixture of four diastereomers. ¹H NMR (500 MHz, CDCl₃) δ 7.10 – 7.02 (m, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 6.88 (dd, *J* = 15.3, 7.9 Hz, 0.4H), 6.81 (dd, *J* = 15.2, 8.0 Hz, 0.6H), 6.05 – 5.96 (m, 1H), 5.77 (d, *J* = 15.1 Hz, 0.6H), 5.75 (d, *J* = 15.4 Hz, 0.4H), 4.93 (dt, *J* = 6.9, 5.9 Hz, 1H), 4.45 – 4.38 (m, 0.6H), 4.38 – 4.32 (m, 0.4H), 3.72 (s, 3H), 3.12 (qd, *J* = 14.0, 5.7 Hz, 2H), 2.94 (h, *J* = 8.1 Hz, 0.6H), 2.61 (h, *J* = 8.0 Hz, 0.4H), 2.25 – 2.15 (m, 0.4H), 2.08 – 1.96 (m, 1.6H), 1.89 – 1.54 (m, 4.4H), 1.49 – 1.36 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 172.18, (172.14), 165.63, (165.58), 162.15

(d, $J = 245.6$ Hz), 149.76, (149.49), (149.46), 131.73 (d, $J = 3.4$ Hz), 130.90 (d, $J = 8.0$ Hz), 121.54, (121.39), 115.56 (d, $J = 21.2$ Hz), 73.59, (73.53), 53.29, 52.54, 42.33, (41.86), 41.02, (40.17), 37.27, 35.65, (35.28), 30.37, (30.19). ^{19}F NMR (471 MHz, CDCl_3) δ -115.59, (-115.61). HRMS (TOF ESI+) m/z calculated for $\text{C}_{18}\text{H}_{23}\text{NO}_4\text{F}$ $[\text{M}+\text{H}]^+$: 336.1611, found 336.1606.

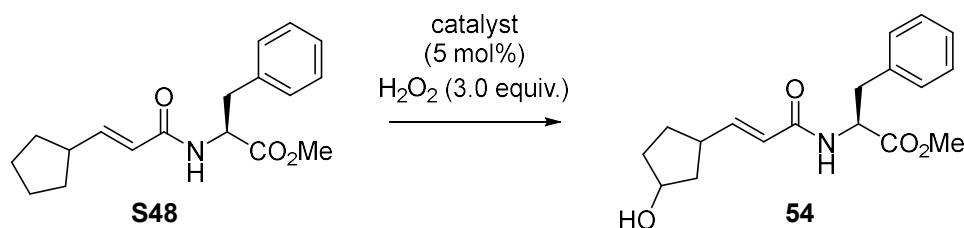


Preparation of methyl (E)-(3-cyclopentylacryloyl)-L-phenylalaninate [S48]. To a solution of (E)-3-cyclopentylacrylic acid (1.05 g, 7.52 mmol, 1.0 equiv.) in dichloromethane (44 mL) was added diisopropylethylamine (6.3 mL, 36.86 mmol, 4.9 equiv.) and the reaction was stirred for ten minutes, at which point HBTU (4.19 g, 11.06 mmol, 1.47 equiv.) was added. The reaction was stirred for an additional 30 minutes, then L-phenylalanine methyl ester HCl (2.19 g, 10.1 mmol, 1.34 equiv.) was added and the reaction was stirred overnight (16 hours). After completion was verified by TLC analysis (ethyl acetate: hexanes 1: 2), the reaction was quenched with water and extracted 3x with dichloromethane. Combined organics were dried over sodium sulfate and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography (ethyl acetate: hexanes 1: 4 $\rightarrow$ 1: 2) to give methyl (E)-(3-cyclopentylacryloyl)-L-phenylalaninate as a white solid (633 mg, 1.88 mmol, 47% yield).

methyl (E)-(3-cyclopentylacryloyl)-D-phenylalaninate [S48]. ^1H NMR (500 MHz, CDCl_3) δ



^{13}C NMR (126 MHz, CDCl_3) δ 172.26, 165.75, 150.24, 136.03, 129.43, 128.69, 127.23, 121.14, 53.21, 52.44, 42.83, 38.07, 32.60, 25.34. HRMS (TOF ESI+) m/z calculated for $\text{C}_{18}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 302.1756, found 302.1752.



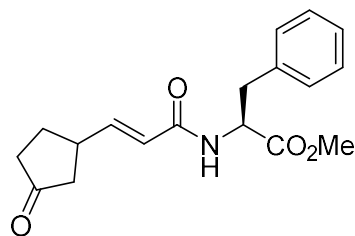
$(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{PDP})$: 38% (22%), alcohol: ketone = 5.6: 1
 $(R,R)\text{-Mn}(\text{CF}_3\text{PDP})$: 39% (12%), alcohol: ketone = 2.9: 1

Oxidation of methyl (E)-(3-cyclopentylacryloyl)-D-phenylalaninate [S48]. Methyl (E)-(3-cyclopentylacryloyl)-D-phenylalaninate in HFIP was oxidized according to the Standard conditions with 5 mol% $(R,R)\text{-Mn}(\text{CF}_3\text{-PDP})$ or $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$ and 3.0 equiv. H_2O_2 . The resulting mixture was purified with column chromatography (2: 1 EtOAc: hexanes $\rightarrow$ EtOAc). With $(R,R)\text{-Mn}(\text{CF}_3\text{-PDP})$ - **Run 1**: 10% RSM, 37% yield, alcohol: ketone = 2.7: 1. **Run 2**: 13% RSM, 40% yield, alcohol: ketone = 3: 1. **Average**: 12% RSM $\pm$ 1.5%, 39% yield $\pm$ 1.5%, alcohol: ketone = 2.9: 1. With $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$ - **Run 1**: 22% RSM, 40% yield. Alcohol: ketone = 5.7: 1, **Run 2**: 19% RSM, 36% yield, Alcohol: ketone = 8: 1, **Run 3**: 24% RSM, 37% yield,

Alcohol: ketone = 4.3: 1, **Average:** 22% RSM $\pm$ 2.5%, 38% yield $\pm$ 2.1%, Alcohol: ketone = 5.6:

1.

methyl ((E)-3-(3-oxocyclopentyl)acryloyl)-L-phenylalaninate [54-ketone]. Product isolated as



a mixture of two diastereomers. ^1H NMR (500 MHz, CDCl_3) δ 7.29

(t, J = 7.1 Hz, 2H), 7.24 (d, J = 7.3 Hz, 1H), 7.09 (d, J = 6.9 Hz, 1H),

6.88 (ddd, J = 15.3, 7.3, 2.1 Hz, 1H), 5.94 (br s, 1H), 5.82 (d, J =

15.3 Hz, 1H), 4.97 (q, J = 6.3 Hz, 1H), 3.74 (s, 3H), 3.17 ((qd, J =

13.9, 5.8 Hz, 2H)), 2.98 (sext, J = 8.1 Hz, 1H), 2.50 – 2.31 (m, 2H), 2.29 – 2.15 (m, 2H), 2.15 –

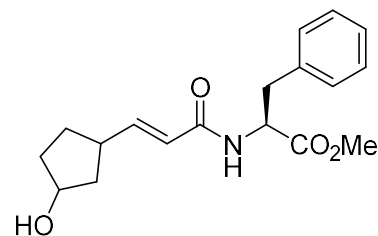
2.04 (m, 1H), 1.85 – 1.72 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 217.27, (217.24), 171.99,

(171.97), 164.80, 146.42, (146.39), 135.74, (135.73), 129.28, 128.64, 127.21, 122.76, (122.74),

53.17, 52.43, 43.87, (43.85), 39.22, (39.19), 37.92, (37.86), 29.71, 29.03, (28.99). HRMS (TOF

ESI+) m/z calculated for $\text{C}_{18}\text{H}_{22}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 316.1549, found 316.1544.

methyl ((E)-3-(3-hydroxycyclopentyl)acryloyl)-L-phenylalaninate [54-OH]. Product isolated



as a mixture of four diastereomers. ^1H NMR (600 MHz, CDCl_3) δ

7.29 (t, J = 7.2 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.09 (d, J = 7.1 Hz,

2H), 6.88 (dd, J = 15.3, 7.9 Hz, 0.5H), 6.81 (dd, J = 15.2, 8.0 Hz,

0.5H), 5.91 (t, J = 7.6 Hz, 1H), 5.75 (dd, J = 15.2, 8.6 Hz, 1H),

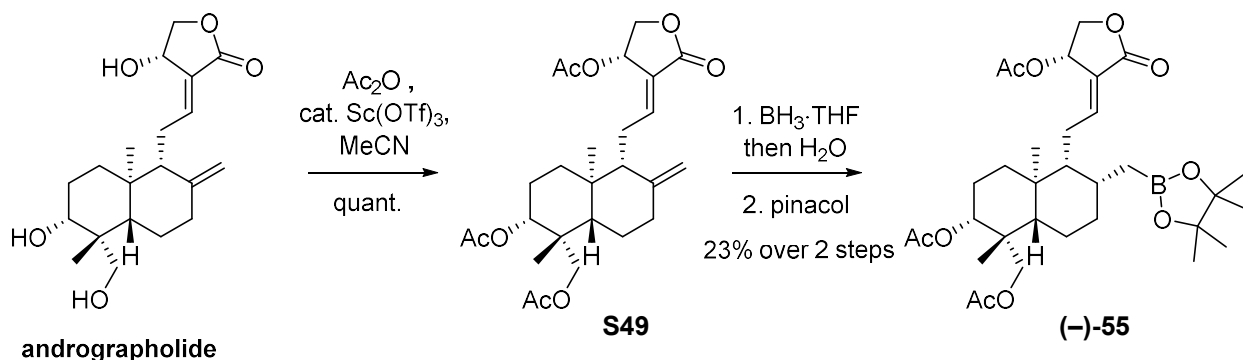
4.96 (dt, J = 7.9, 5.7 Hz, 1H), 4.45 – 4.39 (m, 0.5H), 4.39 – 4.34 (m, 0.5H), 3.73 (s, 3H), 3.16 (qd,

J = 14.0, 5.6 Hz, 2H), 2.94 (h, J = 8.0 Hz, 0.5H), 2.62 (h, J = 8.1 Hz, 0.5H), 2.24 – 2.17 (m, 0.5H),

2.10 – 1.97 (m, 1H), 1.89 – 1.79 (m, 1.5H), 1.75 – 1.56 (m, 3H), 1.49 – 1.38 (m, 1H). ^{13}C NMR

(151 MHz, CDCl₃) δ 172.25, (172.23), 165.59, (165.56), 149.53, (149.31, 149.28), 135.99, (135.98), 129.44, 128.73, 127.27, 121.67, (121.66, 121.56), 73.67, (73.65, 73.60), 53.24, 52.48, 42.38, (42.36), 41.95, (41.93), 41.06, 40.17, (40.15), 38.06, 35.68, (35.32, 35.32), 30.39, (30.38, 30.22, 30.21). HRMS (TOF ESI+) m/z calculated for C₁₈H₂₄NO₄ [M+H]⁺: 318.1705, found 318.1707. Carbons assigned from HSQC correlations to diastereomeric protons.

VII. Experimental Procedures and Compound Characterization for Figure 3

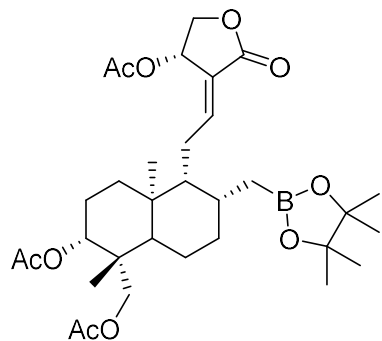


Preparation of (1R,2R,4aS,5R,6R)-5-((E)-2-((S)-4-acetoxy-2-oxodihydrofuran-3(2H)-ylidene)ethyl)-1-(acetoxymethyl)-1,4a-dimethyl-6-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)decahydronaphthalen-2-yl acetate [(-)-55]. To a stirred solution of andrographolide (2 g, 5.7 mmol, 1.0 equiv.) in MeCN (11.4 mL, 0.5 M) was added Ac₂O (4.3 mL, 45.6 mmol, 8.0 equiv.). A solution of Sc(OTf)₃ (56 mg, 0.11 mmol, 2 mol%) in MeCN (4 mL, 0.03 M) was added dropwise over 2 hours at room temperature using a syringe pump. After the addition was complete, the mixture was concentrated to remove acetonitrile. The resulting crude product was diluted with DCM and quenched with saturated NaHCO₃ aqueous solution. The

organic layer was extracted with DCM, dried over MgSO_4 , and concentrated in vacuo. The crude product was triturated with EA and pentane, yielding acetate (**S49**) (2.8 g, 5.7 mmol, quantitative yield) as a white solid. A round-bottom flask was charged with acetate **S49** (1.6 g, 3.4 mmol, 1.0 equiv.). A 1M BH_3 -THF solution (3.7 mL, 3.7 mmol, 1.1 equiv.) was added directly to the solid at 0°C , and the mixture was stirred for 2 hours at 0°C . The reaction progress was monitored by TLC (silica, EA: hexane = 2: 1). Upon full consumption of acetate **S49**, water (3.7 mL) was added at 0°C , and the mixture was gradually warmed to room temperature over 2 hours, monitored by TLC (silica, acetone: hexane = 1: 1). Upon completion, the mixture was filtered through a silica pad using acetone. The filtrate was concentrated in vacuo and purified by column chromatography (silica, acetone: hexane = 1: 2 $\rightarrow$ acetone only) to afford the hydroboration product (ca. 1.1 g). The crude hydroboration product (ca. 2 mmol) was dissolved in benzene (20 mL, 0.1 M), and pinacol (263 mg, 2.2 mmol, 1.1 equiv.) was added at room temperature. The mixture was stirred for 2 hours, monitored by TLC (silica, acetone: hexane = 1.5: 1). Upon completion, the mixture was concentrated in vacuo and purified by column chromatography (silica, hexane $\rightarrow$ tBuOH: hexane = 1: 3) to yield a white foamy solid. This solid was further purified by MPLC (Teledyne Combiflash® system, silica, ether: benzene = 1: 5) to remove residual pinacol, yielding (–)-**55** (460 mg, 0.76 mmol, 22% yield over two steps) as a white solid.

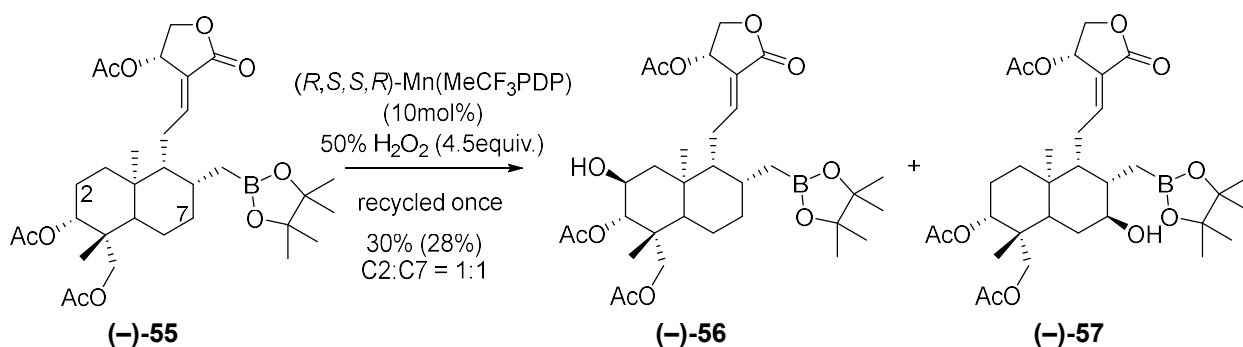
(1R,2R,4aS,5R,6R)-5-((E)-2-((S)-4-acetoxy-2-oxodihydrofuran-3(2H)-ylidene)ethyl)-1-(acetoxyethyl)-1,4a-dimethyl-6-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)methyl)decahydronaphthalen-2-yl acetate [(-)-55]. ¹H NMR (600 MHz, CDCl₃) δ 7.09 (t, *J*



= 7.6 Hz, 1H), 5.87 (d, *J* = 5.8 Hz, 1H), 4.57 – 4.48 (m, 2H), 4.34 (d, *J* = 11.6 Hz, 1H), 4.21 (d, *J* = 11.2 Hz, 1H), 4.08 (d, *J* = 11.8 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.23 (dt, *J* = 16.3, 9.1 Hz, 1H), 2.11 (s, 3H), 2.05 – 1.99 (m, 1H), 2.04 (s, 3H), 2.01 (s, 3H), 1.72 – 1.63 (m, 4H), 1.60 (app d, *J* = 13.5 Hz, 1H), 1.53 (app d, *J* = 13.6 Hz,

1H), 1.51 – 1.43 (m, 1H), 1.38 (dt, *J* = 9.1, 4.2 Hz, 1H), 1.19 (s, 12H), 1.15 – 1.07 (m, 1H), 1.03 (d, *J* = 10.0 Hz, 1H), 0.98 (s, 3H), 0.89 (s, 3H), 0.84 (app d, *J* = 15.9 Hz, 1H), 0.71 (dd, *J* = 16.0, 12.0 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 171.08, 170.67, 170.59, 169.03, 150.18, 124.50, 83.22 (2C), 79.88, 71.77, 67.77, 65.14, 56.28, 54.39, 41.24, 37.89 (2C), 34.42, 32.11, 27.50, 24.91 (2C), 24.79 (2C), 23.43, 22.60, 21.27 (2C), 20.88, 18.10, 16.22, 11.21. [α]_D²³ = -83.3 (c=1.0, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₃₂H₅₀BO₁₀ [M+H]⁺: 605.3497, found 605.3498.



Oxidation of andrographolide analogue [(-)-55]. With (*R,S,S,R*)-Mn(MeCF₃-PDP) 10 mol% and H₂O₂ 4.5 equiv.: Boronate (121 mg, 0.2 mmol) in HFIP was oxidized following Standard conditions, using 10 mol% (*R,S,S,R*)-Mn(MeCF₃-PDP) and 4.5 equivalents of H₂O₂. The resulting

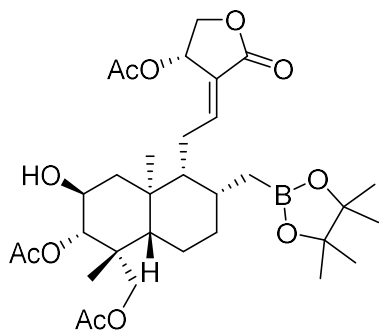
mixture was purified by column chromatography (silica, acetone: benzene = 1: 10 (to isolate RSM) → 1: 4 (to isolate (-)-**56** and (-)-**57**). The RSM was then resubjected to the same oxidation conditions (Standard conditions, 10 mol% (*R,S,S,R*)-Mn(MeCF₃-PDP) and 4.5 equivalents of H₂O₂). The mixture was purified under the same conditions (column chromatography, silica, acetone: benzene = 1: 10 → 1: 4). RSM and yield percentages were calculated cumulatively after each sequential run, relative to the initial starting amount. **Run 1:** first run - 59% RSM (71 mg, 0.12 mmol), (-)-**56** 10.4% (13 mg, 0.021 mmol), (-)-**57** 9.8% (12 mg, 0.02 mmol), total alcohol products 20.2% (25 mg, 0.04 mmol). After recycle - 26% RSM (32 mg, 0.05 mmol), (-)-**56** 14.1% (18 mg, 0.028 mmol), (-)-**57** 14.2% (18 mg, 0.028 mmol), total alcohol products 28.3% (35 mg, 0.057 mmol). **Run 2:** first run - 59% RSM (72 mg, 0.12 mmol), (-)-**56** 11.4% (14 mg, 0.022 mmol), (-)-**57** 9% (11 mg, 0.02 mmol), total alcohol products 20.4% (25 mg, 0.04 mmol). After recycle - 28% RSM (33 mg, 0.055 mmol), (-)-**56** 15.8% (20 mg, 0.031 mmol), (-)-**57** 14.9% (19 mg, 0.030 mmol), total alcohol products 30.7% (38 mg, 0.061 mmol). **Run 3:** first run - 54% RSM (65 mg, 0.11 mmol), (-)-**56** 10.7% (13 mg, 0.021 mmol), (-)-**57** 10.6% (13.2 mg, 0.021 mmol), total alcohol products 21.4% (27 mg, 0.04 mmol). After recycle - 31% RSM (38 mg, 0.06 mmol), (-)-**56** 13.8% (17 mg, 0.028 mmol), (-)-**57** 16.8% (21 mg, 0.034 mmol), total alcohol products 30.6% (38 mg, 0.061 mmol). **Average:** 57% RSM ± 2.4%, (-)-**56** 11% ± 0.4%, (-)-**57** 10% ± 0.7%, total alcohol products 21% ± 0.5%. After recycle - 28% RSM ± 2.0%, (-)-**56** 15% ± 0.9%, (-)-**57** 15% ± 1.1%, total alcohol products 30% ± 1.1%.

Comparison to other catalysts.

catalyst	H ₂ O ₂ equiv.	rsm	C-H oxidation yield	C7-OH:C2-OH
(<i>R,S,S,R</i>)- 2 5 mol%	3.0	70%	11%	1: 1
(<i>R,S,S,R</i>)- 2 10mol%	4.5	57%	21%	1: 1.1
(<i>R,S,S,R</i>)- 2 10mol%*	4.5	28%	30%	1: 1
(<i>S,S</i>)- 1 5 mol%	3.0	87%	-	-
(<i>S,R,R,S</i>)- 2 5 mol%	3.0	66%	14%	C7-OH only

Table S46. Oxidation of (**-**)-**55**. *recycled once.

(**1R,2S,3S,4aS,5R,6R,8aS**)-**5**-((**E**)-2-((*S*)-4-acetoxy-2-oxodihydrofuran-3(2H)-ylidene)ethyl)-1-(acetoxymethyl)-3-hydroxy-1,4a-dimethyl-6-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)decahydronaphthalen-2-yl acetate [(**-**)-**56**]. ¹H NMR (600 MHz, CDCl₃) δ 7.10 (t, *J*



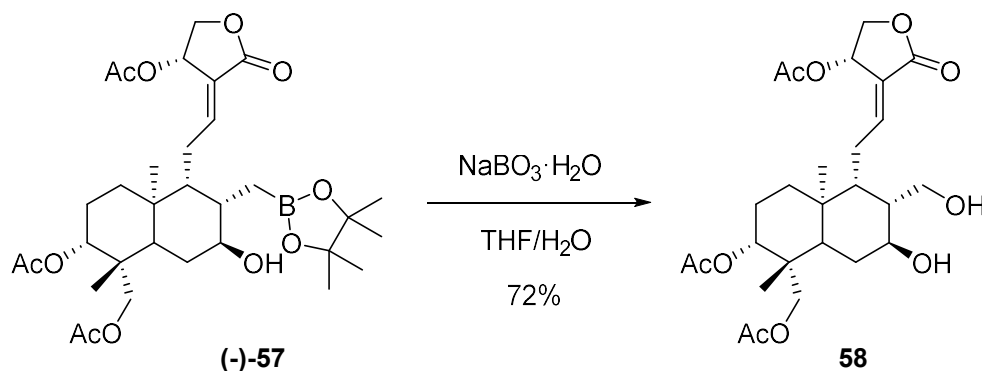
= 7.5 Hz, 1H), 5.90 (d, *J* = 6.0 Hz, 1H), 4.58 (d, *J* = 10.2 Hz, 1H), 4.55 (dd, *J* = 11.0, 6.3 Hz, 1H), 4.27 (d, *J* = 11.8 Hz, 1H), 4.23 (d, *J* = 11.1 Hz, 1H), 4.06 (d, *J* = 11.8 Hz, 1H), 3.86 (td, *J* = 10.9, 4.4 Hz, 1H), 2.49 – 2.43 (m, 1H), 2.30 (dt, *J* = 15.5, 9.2 Hz, 1H), 2.15 – 2.10 (m, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.08 –

2.03 (m, 1H), 2.06 (s, 3H), 1.79 – 1.68 (br s, 1H), 1.72 (app d, *J* = 12.8 Hz, 1H), 1.65 – 1.44 (m, 4H), 1.21 (s, 12H), 1.15 (d, *J* = 11.3 Hz, 1H), 1.09 – 1.04 (m, 1H), 1.02 (s, 3H), 0.96 (s, 3H), 0.86 (d, *J* = 15.7 Hz, 1H), 0.71 (dd, *J* = 15.9, 12.2 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 171.86, 170.93, 170.73, 169.04, 149.66, 124.85, 83.80, 83.32 (2C), 71.82, 67.84, 66.69, 65.35, 56.11, 54.28, 47.34, 42.91, 39.02, 34.35, 31.94, 27.38, 24.94 (2C), 24.84 (2C), 23.11, 21.25, 21.19, 20.93,

18.23, 17.35, 11.30. $[\alpha]_D^{22} = -54.3$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{32}\text{H}_{50}\text{BO}_{11}$ $[\text{M}+\text{H}]^+$: 621.3446, found 621.3451.

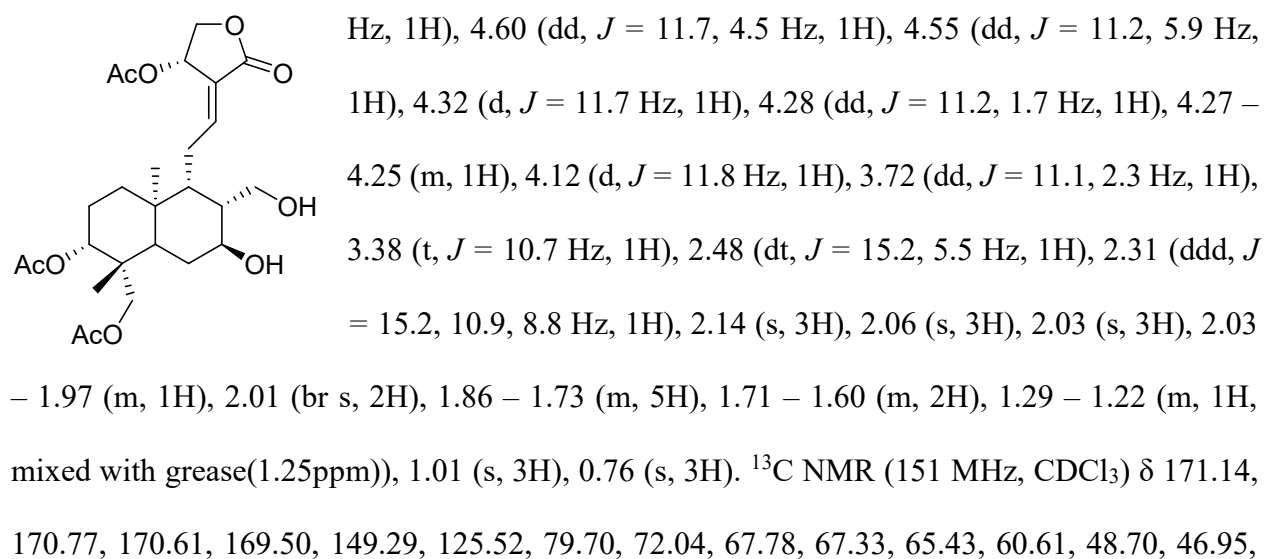
(1R,2R,4aS,5R,6S,7S,8aS)-5-((E)-2-((S)-4-acetoxy-2-oxodihydrofuran-3(2H)-ylidene)ethyl)-1-(acetoxymethyl)-7-hydroxy-1,4a-dimethyl-6-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)decahydronaphthalen-2-yl acetate [(-)-57]. ^1H NMR (600 MHz, CDCl_3) δ 7.09 (t, J

= 7.6 Hz, 1H), 5.89 (d, $J = 5.8$ Hz, 1H), 4.60 (dd, $J = 11.4$, 4.6 Hz, 1H), 4.53 (dd, $J = 11.2$, 5.9 Hz, 1H), 4.34 (d, $J = 11.7$ Hz, 1H), 4.22 (d, $J = 11.1$ Hz, 1H), 4.11 (d, $J = 11.7$ Hz, 1H), 3.89 – 3.86 (m, 1H), 2.48 – 2.42 (m, 1H), 2.27 – 2.20 (m, 1H), 2.13 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.94 – 1.86 (m, 2H), 1.82 – 1.65 (m, 6H), 1.50 (br s, 1H), 1.21 (s, 12H), 1.26 – 1.18 (m, 1H), 0.99 (s, 3H), 0.92 (d, $J = 16.3$ Hz, 1H), 0.88 (s, 3H), 0.51 (dd, $J = 16.3$, 11.8 Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.12, 170.71, 170.57, 169.03, 149.69, 124.85, 83.52 (2C), 79.84, 71.83, 71.31, 67.81, 65.44, 47.69, 46.71, 40.71, 40.22, 37.85, 37.63, 26.75, 25.02, 24.87 (4C), 23.44, 22.36, 21.30 (2C), 20.91, 15.56, 10.66. $[\alpha]_D^{22} = -44.9$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{32}\text{H}_{50}\text{BO}_{11}$ $[\text{M}+\text{H}]^+$: 621.3446, found 621.3446.



Confirmation of the Structural Elucidation of (-)-57. To further confirm the stereochemistry of C7-OH, (-)-57 was oxidized with $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ to afford diol **58**. To a stirred solution of (-)-57 (17 mg, 0.027 mmol, 1.0 equiv.) in a THF: water = 2: 1 mixture (0.3 mL, 0.1 M) was added $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ (4.9 mg, 0.049 mmol, 1.8equiv.) at 0°C. The mixture was gradually warmed to room temperature over 9 hours, with progress monitored by TLC (silica gel, EA only). Upon completion, the reaction mixture was concentrated in vacuo and directly purified by column chromatography (silica, acetone: hexane = 2: 1), affording diol **58** (10 mg, 0.02 mmol, 72% yield) as a white solid. Diol **58** was dissolved in toluene, and slow evaporation of toluene over 3 days yielded a single crystal. The stereochemistry of C7 was confirmed by X-ray crystallography of **58**.

(1R,2R,4aS,5R,6R,7S,8aS)-5-((E)-2-((S)-4-acetoxy-2-oxodihydrofuran-3(2H)-ylidene)ethyl)-1-(acetoxymethyl)-7-hydroxy-6-(hydroxymethyl)-1,4a-dimethyldecahydronaphthalen-2-yl acetate [58]. ^1H NMR (600 MHz, CDCl_3) δ 7.09 (ddd, J = 8.4, 6.4, 1.7 Hz, 1H), 5.91 (d, J = 5.8



46.85, 40.70, 37.46, 37.29, 26.54, 26.02, 23.68, 22.39, 21.32, 21.28, 20.87, 14.92. HRMS (TOF ESI+) m/z calculated for $C_{26}H_{38}O_{10}Na$ $[M+Na]^+$: 533.2363, found 533.2362.

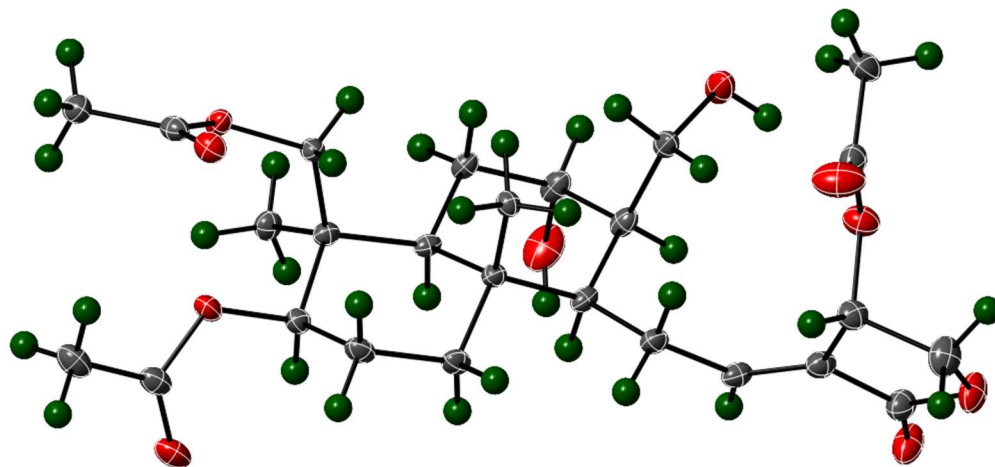
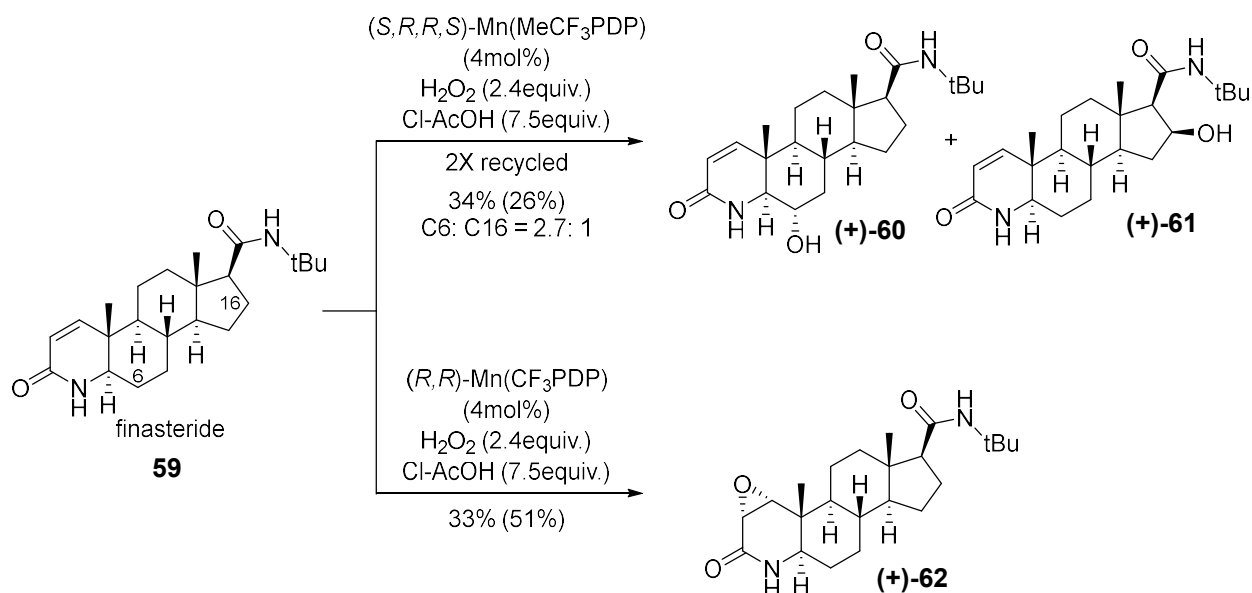


Figure S30. X-ray Crystal Data of **58**.

Identification code	6333ds_sq	
Empirical formula	C ₂₆ H ₃₈ O ₁₀	
Formula weight	510.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2	
Unit cell dimensions	$a = 28.1811(5)$ Å	$a = 90^\circ$.

	$b = 7.3469(2) \text{ \AA}$	$b = 90^\circ$.
	$c = 13.3487(3) \text{ \AA}$	$g = 90^\circ$.
Volume	$2763.76(11) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.227 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	1096	
Crystal size	$0.119 \times 0.117 \times 0.043 \text{ mm}^3$	
Theta range for data collection	2.651 to 25.382° .	
Index ranges	$-33 \leq h \leq 33$, $-8 \leq k \leq 8$, $-16 \leq l \leq 16$	
Reflections collected	74579	
Independent reflections	5066 [$R(\text{int}) = 0.0582$]	
Completeness to $\theta = 25.242^\circ$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.7052	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5066 / 3 / 336	
Goodness-of-fit on F^2	1.071	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0332$, $wR2 = 0.0794$	
R indices (all data)	$R1 = 0.0362$, $wR2 = 0.0812$	
Absolute structure parameter	0.3(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.151 and $-0.160 \text{ e.\AA}^{-3}$	



Oxidation of finasteride with PDP/carboxylic acid condition in HFIP. PDP/carboxylic acid condition in HFIP with catalyst **2** ($(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$). Finasteride (**59**, 224 mg (0.6 mmol) or 149 mg (0.4 mmol), 1.0 equiv.) in HFIP was oxidized according to the PDP/carboxylic acid condition in HFIP with 4 mol% $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$, 7.5equiv. of Cl-AcOH and 2.4 equiv. of H_2O_2 . The resulting mixture was purified by column chromatography (silica, DCM: EA: MeOH = 10: 10: 1 $\rightarrow$ 5: 5: 1), yielding recovered starting material (RSM) and a mixture of oxidation products. The RSM was resubjected to the same oxidation conditions (PDP/carboxylic acid condition in HFIP, 4 mol% $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$, 7.5 equivalents of Cl-AcOH , and 2.4 equivalents of H_2O_2). The mixture was purified under the same conditions (silica gel column chromatography, DCM:EA: MeOH = 10: 10: 1 $\rightarrow$ 5: 5: 1), and RSM was again collected. The RSM was resubjected to a third oxidation run under the same conditions (PDP/carboxylic acid condition in HFIP, 4 mol% $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$, 7.5equiv. of Cl-AcOH and 2.4 equiv. of H_2O_2). The final mixture, combined with products from the first and second runs, was purified by

column chromatography (silica column chromatography, DCM: EA: MeOH = 10: 10: 1 → 5: 5: 1). RSM and yield percentages were calculated cumulatively after each sequential run, relative to the initial starting amount. Site-selectivity was determined by HPLC analysis on alcohol product mixture (*vide infra*). **Run 1** (0.4 mmol scale, 149 mg starting material): first run - 70% RSM (104 mg, 0.28 mmol), alcohol product 16% (24 mg, 0.064 mmol). second run - 40% RSM (60 mg, 0.16 mmol), alcohol product 30% (44 mg, 0.12 mmol). final run - 22% RSM (33 mg, 0.09 mmol), alcohol product 37% (55 mg, 0.15 mmol). **Run 2** (0.6 mmol scale, 224 mg starting material): first run - 76% RSM (170 mg, 0.46 mmol), alcohol product 14% (31 mg, 0.083 mmol). second run - 36% RSM (80 mg, 0.21 mmol), alcohol product 27% (59 mg, 0.16 mmol). final run - 29% RSM (65 mg, 0.17 mmol), alcohol product 32% (70 mg, 0.19 mmol). **Run 3** (0.6 mmol scale, 224 mg starting material): first run - 70% RSM (156 mg, 0.42 mmol), alcohol product 17% (38 mg, 0.1 mmol). second run - 46% RSM (103 mg, 0.28 mmol), alcohol product 26% (57 mg, 0.16 mmol). final run - 27% RSM (61 mg, 0.16 mmol), alcohol product 33% (73 mg, 0.2 mmol). **Average:** 26% RSM $\pm$ 2.9%, alcohol product 34% $\pm$ 2.4% yield. PDP/carboxylic acid condition in HFIP with catalyst **1** ((*R,R*)-Mn(CF₃-PDP)): Finasteride (224 mg (0.6 mmol)) in HFIP was oxidized according to the PDP/carboxylic acid condition in HFIP with 4 mol% (*R,R*)-Mn(CF₃-PDP), 7.5equiv. of Cl-AcOH and 2.4 equiv. of H₂O₂. The resulting mixture was purified by column chromatography (silica, EA: DCM = 1: 1 → EA: DCM: MeOH = 10: 10: 1). **Run 1:** 51% RSM (115 mg, 0.31 mmol), epoxide 31% (71 mg, 0.18 mmol). **Run 2:** 49% RSM (110 mg, 0.30 mmol), epoxide 35% (80 mg, 0.21 mmol). **Average:** 51% RSM $\pm$ 1.1%, epoxide 33% yield $\pm$ 2.0%.

Oxidation of finasteride with Standard conditions. Finasteride (149 mg (0.4 mmol), 1.0 equiv.) in HFIP was oxidized according to the Standard conditions with 4 mol% (*R,R*)-Mn(MeCF₃-PDP)

or (*S,R,R,S*)-Mn(MeCF₃-PDP) and 2.4 equiv. of H₂O₂. The resulting mixture was purified by column chromatography (silica, DCM: EA: MeOH = 10: 10: 1 → 5: 5: 1), furnishing recovered starting material (RSM) without any isolable C-H oxidation product formation for both catalysts. With catalyst **1** ((*R,R*)-Mn(MeCF₃-PDP)). **Run 1**: 78% RSM. **Run 2**: 81% RSM. **Average**: 80% RSM ± 1.5%. With catalyst **2** (*S,R,R,S*)-Mn(MeCF₃-PDP). **Run 1**: 98% RSM. **Run 2**: 96% RSM. **Average**: 97% RSM ± 1.0%.

Determination of monohydroxylated product ratio. Alcohol product ratio was determined by HPLC (Agilent Poroshell 120, EC-C18 2.7μm, 4.6*100mm) with the following method (flow = 1ml/min). The calculated peak ratio was **60** (C6): **61** (C16) = 2.7: 1.

time(min)	water (%)	acetonitrile (%)
0	70	30
3	70	30
12	20	80
12.5	20	80
13	20	80
14	70	30

Table S47. HPLC Method for Finasteride Oxidation Product Separation

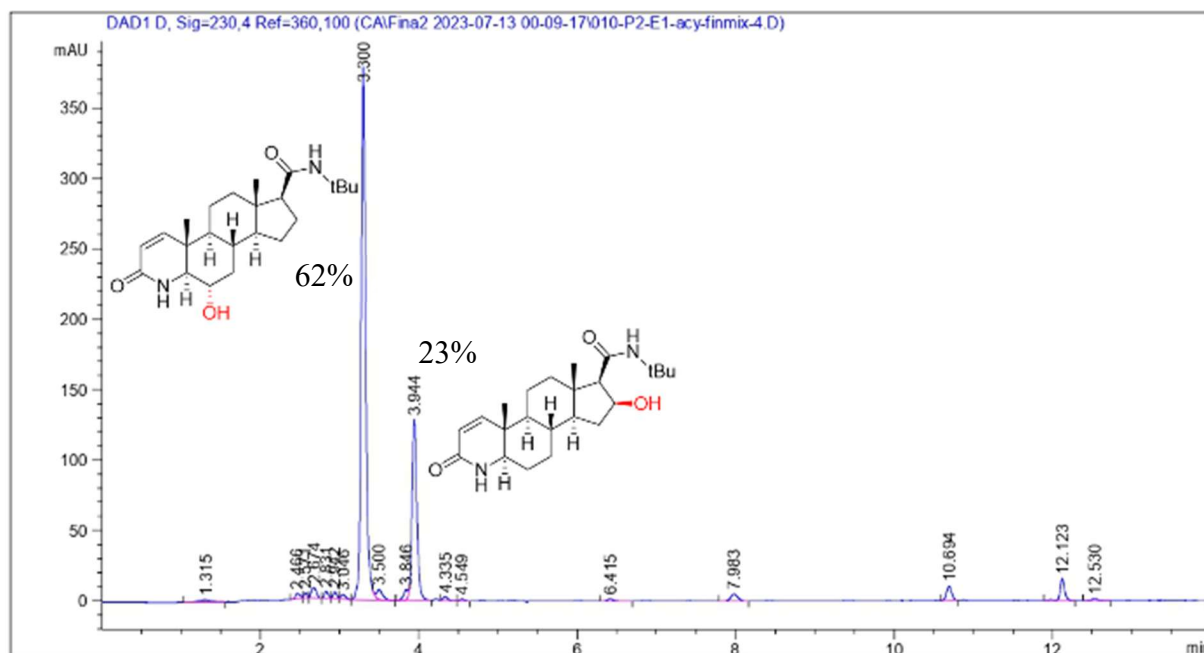
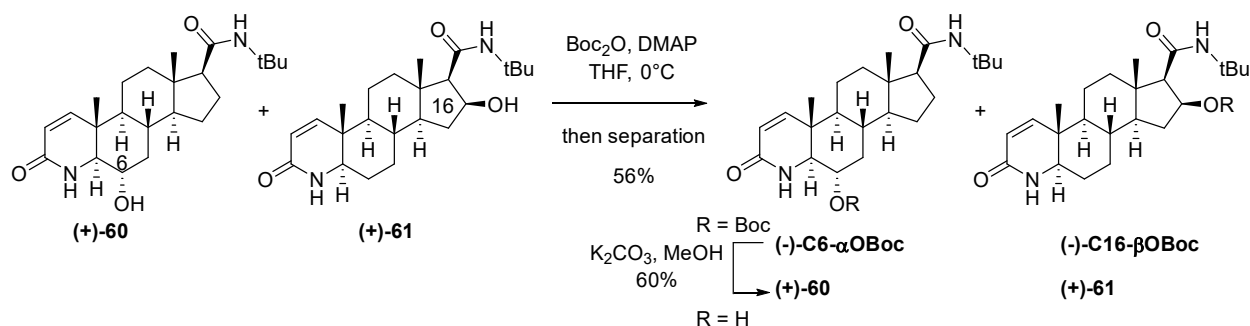


Figure S31. HPLC profile of Finasteride Oxidation Products



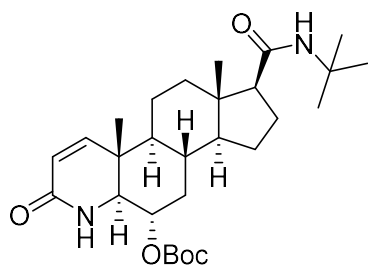
Separation and Identification of monohydroxylated finasterides. To a stirred solution of a mixture of monohydroxylated finasterides (70 mg, 0.18 mmol, 1.0 equiv.) was added Boc anhydride (79 mg, 0.36 mmol, 2.0 equiv.) and DMAP (33 mg, 0.27 mmol, 1.5 equiv.) at 0°C . The mixture was stirred for 2 hours at 0°C , after which an additional portion of Boc anhydride (79 mg, 0.36 mmol, 2.0 equiv.) and DMAP (33 mg, 0.27 mmol, 1.5 equiv.) was added, and the reaction was stirred for another 2 hours. The reaction progress was monitored by TLC (EA: DCM: MeOH = 5: 5: 1). The resulting mixture was concentrated *in vacuo* and purified by flash column

chromatography (silica, EA: DCM = 1: 1 → EA: DCM: MeOH = 5: 5: 1), yielding fully separated C6- α OBoc (29 mg, 0.06 mmol, 33% yield) and C16- β OBoc finasteride (20 mg, 0.04 mmol, 23% yield), for a combined yield of 56%.

Each Boc-protected product was transferred into separate vials. A stirred solution of the Boc-protected product (1.0 equiv.) in MeOH (0.1 M) was treated with K₂CO₃ (3.0 equiv.) at 0°C. For C6- α OBoc, the mixture was gradually warmed to room temperature over 2 hours until complete reaction was confirmed. For C16- β OBoc, the mixture was gradually warmed to 50°C and stirred for 2 hours until complete reaction was confirmed. The completion of both reactions was monitored by TLC (EA: DCM: MeOH = 5: 5: 1). Upon completion, each reaction was quenched with aqueous NH₄Cl solution, and the organic layer was extracted with EA, dried over MgSO₄, and concentrated in vacuo. The resulting crude products were purified by flash column chromatography (silica, Et₂O: MeOH = 20: 1 → 10: 1) to furnish (+)-**60** and (+)-**61** with approximately 60% yield each. Spectroscopic data for (+)-**60** finasteride matched the reported literature⁴⁸. The structure of (+)-**61** was confirmed by X-ray crystallography (*vide infra*).

tert-butyl ((4aR,4bS,6aS,7S,9aS,9bS,11S,11aS)-7-(tert-butylcarbamoyl)-4a,6a-dimethyl-2-oxo-2,4a,4b,5,6,6a,7,8,9,9a,9b,10,11,11a-tetradecahydro-1H-indeno[5,4-f]quinolin-11-yl) carbonate [60-OBoc].

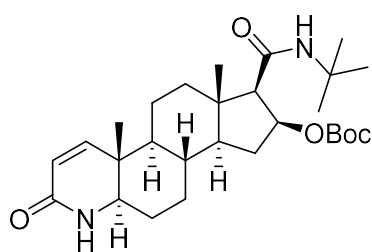
¹H NMR (600 MHz, CDCl₃) δ 6.75 (d, *J* = 9.9 Hz, 1H), 5.84 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.81 (br s, 1H), 5.08 (s, 1H), 4.64 (td, *J* = 10.9, 4.6 Hz, 1H), 3.39 (d, *J* = 11.0 Hz, 1H), 2.20 – 2.10 (m, 2H), 2.04 (t, *J* = 9.2 Hz, 1H), 2.00 (dt, *J* = 12.3, 3.5 Hz, 1H), 1.79 – 1.55 (m, 4H), 1.49 (s, 9H), 1.48 – 1.39 (m, 1H), 1.34 (s, 9H), 1.33 – 1.22 (m, 2H), 1.22 – 1.04 (m, 3H), 1.03 (s, 3H), 0.69 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.53, 166.21, 153.03,



149.77, 123.41, 83.31, 73.03, 62.11, 57.45, 55.44, 51.29, 47.31, 44.04, 40.33, 38.31, 35.39, 34.15, 29.16, 27.86, 24.39, 23.37, 21.21, 13.35, 13.22. $[\alpha]_D^{23} = -17.08$ (c=1.0, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₂₈H₄₅N₂O₅ [M+H]⁺: 489.3328, found 489.3322.

tert-butyl ((4aR,4bS,6aS,7R,8S,9aS,9bS,11aR)-7-(tert-butylcarbamoyl)-4a,6a-dimethyl-2-oxo-2,4a,4b,5,6,6a,7,8,9,9a,9b,10,11,11a-tetradecahydro-1H-indeno[5,4-f]quinolin-8-yl)

carbonate [61-OBoc]. ¹H NMR (600 MHz, CDCl₃) δ 6.80 (d, $J = 9.9$ Hz, 1H), 6.18 (s, 1H), 5.80



(dd, $J = 9.9, 1.9$ Hz, 1H), 5.56 – 5.48 (m, 1H), 5.18 (td, $J = 7.9, 4.8$ Hz, 1H), 3.32 (br dd, $J = 8.4, 7.7$ Hz, 1H), 2.39 (dt, $J = 13.5, 7.6$ Hz, 1H), 2.16 (d, $J = 7.7$ Hz, 1H), 2.09 (dt, $J = 12.9, 3.4$ Hz, 1H), 1.76 – 1.71 (m, 2H, mixed with H₂O (1.70ppm)), 1.61 – 1.57 (m,

2H), 1.57 – 1.51 (m, 1H), 1.47 (s, 9H), 1.46 – 1.39 (m, 2H), 1.33 (s, 9H), 1.26 (ddd, $J = 12.9, 8.1, 4.5$ Hz, 1H, mixed with grease H (1.26ppm)), 1.08 – 1.02 (m, 2H), 1.01 – 1.94 (m, 1H), 0.98 (s, 3H), 0.97 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 168.51, 166.65, 152.92, 151.05, 123.09, 82.66, 75.94, 61.12, 59.73, 52.68, 51.17, 47.84, 44.07, 39.65, 38.13, 35.04, 34.79, 29.43, 28.92, 27.97, 26.06, 20.98, 14.56, 12.20. $[\alpha]_D^{23} = -1.0$ (c=1.0, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₂₈H₄₅N₂O₅ [M+H]⁺: 489.3328, found 489.3322.

(4aR,4bS,6aS,7S,9aS,9bS,11S,11aS)-N-(tert-butyl)-11-hydroxy-4a,6a-dimethyl-2-oxo-2,4a,4b,5,6,6a,7,8,9,9a,9b,10,11,11a-tetradecahydro-1H-indeno[5,4-f]quinoline-7-carboxamide [(+)-60].

¹H NMR (600 MHz, CDCl₃) δ 6.92 (s, 1H), 6.75 (d, *J* = 9.9 Hz, 1H), 5.81 (dd, *J* = 9.9, 2.1 Hz, 1H), 5.11 (s, 1H), 3.74 (td, *J* = 10.6, 4.6 Hz, 1H), 3.14 (d, *J* = 10.4 Hz, 1H), 2.19 – 2.12 (m, 1H), 2.07 – 2.00 (m, 2H), 1.98 (dt, *J* = 12.1, 3.4 Hz, 1H), 1.77 – 1.66 (m, 3H), 1.54 (app qd, *J* = 10.9, 3.9 Hz, 1H), 1.43 (qd, *J* = 13.1, 3.8 Hz, 1H), 1.34 (s, 9H), 1.32 – 1.23 (m, 3H), 1.20 – 1.15 (m, 1H), 1.12 – 1.02 (m, 2H), 0.96 (s, 3H), 0.69 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.72, 167.01, 150.56, 123.20, 66.87, 65.01, 57.53, 55.53, 51.30, 47.42, 44.04, 39.94, 39.10, 38.39, 34.38, 29.18, 24.44, 23.38, 21.24, 13.41, 13.18. [α]_D²³ = +13.36 (c=0.5, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₂₃H₃₇N₂O₃ [M+H]⁺: 389.2804, found 389.2805.

(4aR,4bS,6aS,7R,8S,9aS,9bS,11aR)-N-(tert-butyl)-8-hydroxy-4a,6a-dimethyl-2-oxo-2,4a,4b,5,6,6a,7,8,9,9a,9b,10,11,11a-tetradecahydro-1H-indeno[5,4-f]quinoline-7-carboxamide [(+)-61]. [α]_D²³ = +15.8 (c=0.2, CHCl₃).

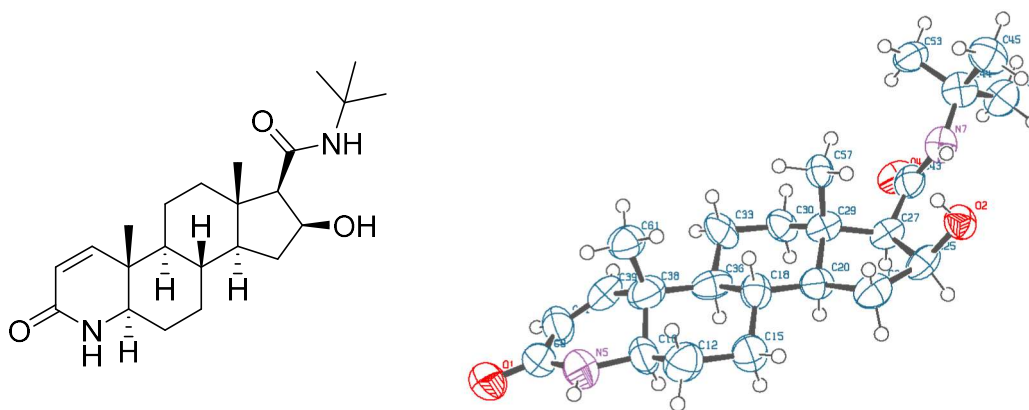


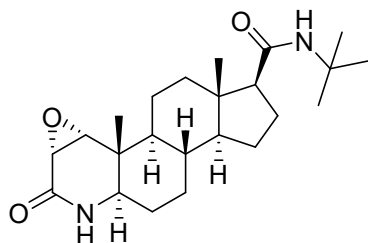
Figure S32. X-ray Crystal Data of **61**.

Identification code	ed76xs	
Empirical formula	C ₂₄ H ₃₆ Cl ₃ D N ₂ O ₃	
Formula weight	508.91	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 6.0574(4) Å	a = 90°.
	b = 11.8369(8) Å	b = 90°.
	c = 35.829(2) Å	g = 90°.
Volume	2568.9(3) Å ³	
Z	4	
Density (calculated)	1.316 Mg/m ³	
Absorption coefficient	3.450 mm ⁻¹	
F(000)	1080	
Crystal size	0.322 x 0.064 x 0.030 mm ³	
Theta range for data collection	2.466 to 59.081°.	
Index ranges	-6 ≤ h ≤ 6, -12 ≤ k ≤ 12, -39 ≤ l ≤ 39	
Reflections collected	20516	
Independent reflections	3630 [R(int) = 0.1416]	
Completeness to theta = 59.081°	98.4 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7516 and 0.4520
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3630 / 110 / 338
Goodness-of-fit on F ²	1.074
Final R indices [I>2sigma(I)]	R1 = 0.1409, wR2 = 0.3519
R indices (all data)	R1 = 0.1618, wR2 = 0.3660
Absolute structure parameter	0.14(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.324 and -0.464 e.Å ⁻³

(2aR,3aR,3bR,3cS,5aS,6S,8aS,8bS,10aR)-N-(tert-butyl)-3b,5a-dimethyl-2-

oxohexadecahydro-1H-indeno[5,4-f]oxireno[2,3-c]quinoline-6-carboxamide [(+)-62]. ¹H



NMR (600 MHz, CDCl₃) δ 5.76 (s, 1H), 5.08 (s, 1H), 3.42 (d, *J* = 4.2 Hz, 1H), 3.38 (dd, *J* = 4.2, 2.4 Hz, 1H), 3.24 (dd, *J* = 12.8, 3.2 Hz, 1H), 2.20 – 2.13 (m, 1H), 2.03 (t, *J* = 9.1 Hz, 1H), 1.96 (dt, *J* = 12.2, 3.5 Hz, 1H), 1.84 (dq, *J* = 13.5, 3.7 Hz, 1H), 1.75

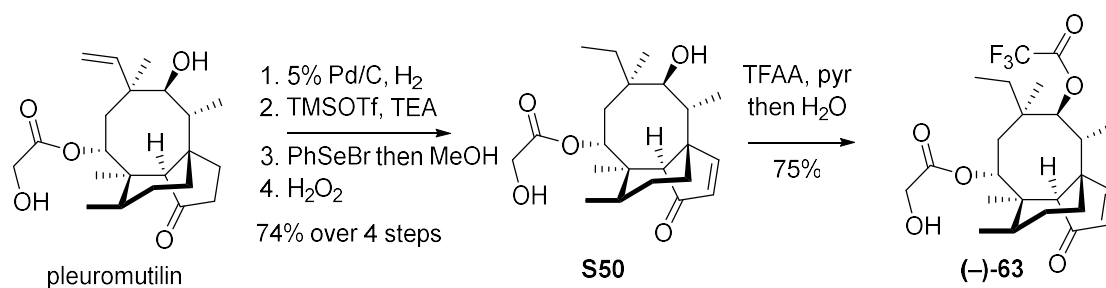
– 1.64 (m, 3H), 1.61 – 1.41 (m, 4H), 1.34 (s, 9H), 1.33 – 1.21 (m, 3H, containing grease(1.24ppm)),

1.14 – 1.08 (m, 1H), 1.01 (qd, *J* = 13.1, 4.3 Hz, 1H), 0.89 (s, 3H), 0.69 (s, 3H). ¹³C NMR (151

MHz, CDCl₃) δ 171.72, 168.28, 58.62, 57.62, 55.55, 52.68, 51.53, 51.25, 46.92, 43.92, 39.02,

38.38, 35.31, 29.49, 29.18, 25.85, 24.46, 23.32, 22.01, 13.37, 10.50. [α]_D²³ = +45.1 (c=0.2, CHCl₃).

HRMS (TOF ESI+) *m/z* calculated for C₂₃H₃₇N₂O₃ [M+H]⁺: 389. 2804, found 389.2798.



Preparation of pleuromutilin analogue. To a stirred solution of pleuromutilin (3.8 g, 10 mmol, 1.0 equiv.) in a MeOH: DCM = 4: 1 mixture (35 mL, 0.3 M) was added 5% Pd/C (636 mg, 0.3 mmol, 3 mol% Pd) under a nitrogen atmosphere. The headspace was evacuated and backfilled with H₂ three times. The reaction was stirred under H₂ (1 atm, balloon) for 12 hours at room temperature, with completion confirmed by TLC (silica, EA: hexane = 1: 2, developed twice). Upon completion, the reaction was filtered through a Celite pad with EA and concentrated in vacuo, yielding hydrogenated pleuromutilin (3.8 g, 10 mmol, quantitative yield) as a white foamy solid.

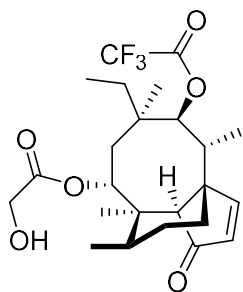
To a stirred solution of the hydrogenated pleuromutilin (2 g, 4 mmol, 1.0 equiv.) and TMSOTf (4 mL, 21 mmol, 5.3 equiv.) in benzene (4 mL, 1.0 M) was added TEA (4.2 mL, 30 mmol, 7.5 equiv.) at 0°C under a nitrogen atmosphere. The reaction mixture was gradually warmed to room temperature over 15 hours and monitored by TLC (silica, EA: hexane = 1: 8). Upon completion, the reaction was diluted with EA and quenched with saturated NH₄Cl solution. The organic layer was extracted with EA, dried over Na₂SO₄, and concentrated in vacuo. The resulting crude mixture was filtered through a silica pad (EA: hexane = 1: 8) and concentrated in vacuo, furnishing the crude mixture of silyl enol ethers as a colorless oil. To the mixture of crude in THF (20 mL, 0.2 M) was added PhSeBr (944 mg, 4 mmol, 1.0 equiv.) at room temperature. The reaction was stirred for 15 hours, monitored by TLC (silica, EA: hexane = 1: 8). Upon completion, the mixture was concentrated in vacuo, diluted with MeOH (5 mL) and stirred for 5 minutes to remove any trimethylsilyl groups. The concentrated crude was purified by flash column chromatography

(benzene → EA: benzene = 1: 4) to afford α -selenyl ketone (1.7 g, 3.1 mmol, 78% yield over two steps) as a white foamy solid.

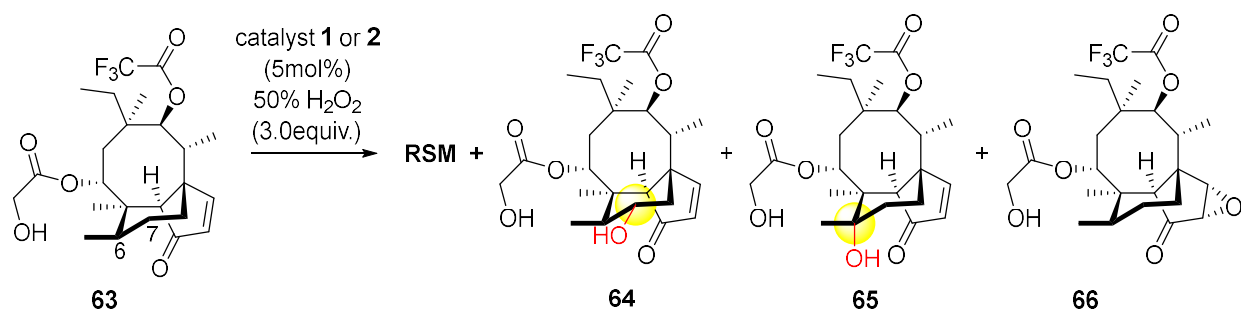
To a stirred solution of α -selenyl ketone (1.7 g, 3.1 mmol, 1.0 equiv.) in THF (8 mL, 0.4 M) was added 30% H₂O₂ (0.7 mL, 6.2 mmol, 2.0 equiv.) at 0°C. The reaction mixture was gradually warmed to room temperature over 3 hours and monitored by TLC (silica, EA: hexane = 1: 2). Upon completion, the reaction was quenched with saturated Na₂S₂O₃ solution. The organic portion was extracted with EA, dried over MgSO₄ and concentrated in vacuo. The crude product was purified by flash column chromatography (hexane → EA: hexane = 1: 3) to afford cyclopentenone **S50** (1.1 g, 3.0 mmol, 95% yield, 74% yield over four steps from pleuromutilin) as a white foamy solid.

To a stirred solution of cyclopentenone **S50** (662 mg, 1.7 mmol, 1.0 equiv.) and pyridine (0.8 mL, 10.4 mmol, 6.0 equiv.) in THF (17 mL, 0.1 M) was added TFA anhydride (0.5 mL, 3.5 mmol, 2.0 equiv.) at 0°C. The reaction mixture was gradually warmed to room temperature over 2 hours and monitored by TLC (silica, EA: hexane = 1: 2). Upon full consumption of the starting material, 10 mL of water was added, and the mixture was stirred for 15 hours to remove the TFA group from the glycolate appendage. The organic layer was extracted with EA, and dried over MgSO₄. Residual pyridine was removed by repeated addition and evaporation of heptane (three times). The crude product was purified by flash column chromatography (EA: hexane = 1: 1) to afford TFA ester (621 mg, 1.3 mmol, 75% yield) as a white solid.

(3aR,4R,5R,7R,8S,9R,9aS,12R)-7-ethyl-5-(2-hydroxyacetoxy)-4,7,9,12-tetramethyl-3-oxo-3,3a,4,5,6,7,8,9-octahydro-4,9a-propanocyclopenta[8]annulen-8-yl 2,2,2-trifluoroacetate [(–)-63].



¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, *J* = 6.2 Hz, 1H), 6.10 (d, *J* = 6.1 Hz, 1H), 5.71 (d, *J* = 8.5 Hz, 1H), 4.65 (d, *J* = 7.1 Hz, 1H), 4.12 (dd, *J* = 17.1, 5.5 Hz, 1H), 4.05 (dd, *J* = 17.1, 5.3 Hz, 1H), 2.59 (quint, *J* = 7.2 Hz, 1H), 2.39 – 2.32 (m, 2H), 2.23 (dq, *J* = 14.4, 3.0 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.75 – 1.65 (m, 2H), 1.65 – 1.57 (m, 1H), 1.53 (s, 3H), 1.46 – 1.38 (m, 1H), 1.44 (d, *J* = 16.3 Hz, 1H), 1.07 – 0.96 (m, 1H), 1.02 (d, *J* = 7.1 Hz, 3H), 0.85 (s, 3H), 0.81 (t, *J* = 7.4 Hz, 3H), 0.76 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 206.32, 172.50, 164.31, 157.27 (q, *J* = 42.1 Hz), 132.85, 114.85 (q, *J* = 286.1 Hz), 84.20, 69.58, 61.43, 58.84, 50.57, 42.36, 41.31, 40.84, 38.77, 37.95, 33.24, 26.91, 25.39, 22.23, 16.19, 14.41, 11.45, 8.19. ¹⁹F NMR (471 MHz, CDCl₃) δ -74.85. [α]_D²³ = -37.62 (c=1.0, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₂₄H₃₄O₆F₃ [M+H]⁺: 475.2307, found 475.2309.



catalyst	RSM	C-H oxidation products	epoxide	enone: epoxide
(<i>S,R,R,S</i>)- 2	42%	29% ^a	-	>20:1
(<i>S,R,R,S</i>)- 2 *	19%	41% ^a	-	>20:1
(<i>R,R</i>)- 1	36%	15% ^b	12%	1.2:1
(<i>R,S,S,R</i>)- 2	34%	17% ^c	22%	1:1.3
(<i>S,S</i>)- 1	34%	13% ^d	4%	3.6:1

Table S48. Oxidation of (**-**)-**63**. *recycled once. C7OH: C6OH ratio = ^a2.8:1. ^b4:1. ^c1.8:1. ^d1.4:1

Oxidation of pleuromutilin analogue (**-**)-**63**.

With catalyst **2** ((*S,R,R,S*)-Mn(MeCF₃-PDP)). Pleuromutilin analogue (**-**)-**63** (190 mg, 0.4 mmol) in HFIP was oxidized following Standard conditions, using 5 mol% (*S,R,R,S*)-Mn(MeCF₃-PDP) and 3.0 equivalents of H₂O₂. The resulting mixture was purified by column chromatography (silica, DCM only → acetone: DCM = 1: 5), separating RSM, (+)-**64** (C7OH) and (**-**)-**65** (C6OH). The RSM was then resubjected to the same oxidation conditions (Standard conditions, 5 mol% (*S,R,R,S*)-Mn(MeCF₃-PDP) and 3.0 equivalents of H₂O₂). The mixture was purified under the same conditions (column chromatography, silica, DCM only → acetone: DCM = 1: 5). RSM and yield percentages were calculated cumulatively after each sequential run, relative to the initial

starting amount. **Run 1:** first run - 43% RSM (82 mg, 0.17 mmol), (+)-**64** (C7OH) 22% (43 mg, 0.087 mmol), (-)-**65** (C6OH) 8% (15 mg, 0.03 mmol), total alcohol products 29% (58 mg, 0.12 mmol). After recycle - 19% RSM (37 mg, 0.077 mmol), (+)-**64** (C7OH) 31% (62 mg, 0.13 mmol), (-)-**65** (C6OH) 11% (21 mg, 0.043 mmol), total alcohol products 42% (83 mg, 0.17 mmol). **Run 2:** first run - 40% RSM (76 mg, 0.16 mmol), (+)-**64** (C7OH) 20% (40 mg, 0.082 mmol), (-)-**65** (C6OH) 8% (15 mg, 0.03 mmol), total alcohol products 28% (55 mg, 0.11 mmol). After recycle - 18% RSM (34 mg, 0.072 mmol), (+)-**64** (C7OH) 30% (58 mg, 0.12 mmol), (-)-**65** (C6OH) 11% (22 mg, 0.044 mmol), total alcohol products 41% (80 mg, 0.16 mmol). **Average:** first run - RSM $41.8\% \pm 1.6\%$, (+)-**64** (C7OH) $21.1\% \pm 0.7\%$, (-)-**65** (C6OH) $7.7\% \pm 0.08\%$, total alcohol products $29.4\% \pm 0.6\%$. after recycle - RSM $18.6\% \pm 0.6\%$, (+)-**64** (C7OH) $30.5\% \pm 0.9\%$, (-)-**65** (C6OH) $10.9\% \pm 0.05\%$, total alcohol products $41.4\% \pm 0.9\%$.

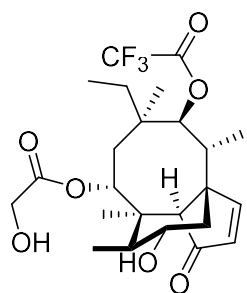
With catalyst 1 ((R,R)-Mn(MeCF₃-PDP)). Pleuromutilin analogue (-)-**63** (190 mg, 0.4 mmol) in HFIP was oxidized following Standard conditions, using 5 mol% (R,R)-Mn(CF₃-PDP) and 3.0 equivalents of H₂O₂. The resulting mixture was purified by column chromatography (silica, DCM only → acetone: DCM = 1: 5), separating three portions: a mixture of RSM and epoxide, (+)-**64** (C7OH) and (-)-**65** (C6OH). RSM and epoxide were separated by another column chromatography (silica, hexane only → acetone: hexane = 1: 5). **Run 1:** 36% RSM (69 mg, 0.14 mmol), (+)-**64** (C7OH) 12% (23 mg, 0.047 mmol), (-)-**65** (C6OH) 3% (6 mg, 0.012 mmol), total alcohol products 15% (29 mg, 0.059 mmol), epoxide 11% (21 mg, 0.043 mmol). **Run 2:** 35% RSM (67 mg, 0.14 mmol), (+)-**64** (C7OH) 12% (23 mg, 0.048 mmol), (-)-**65** (C6OH) 2% (5 mg, 0.01 mmol), total alcohol products 14% (28 mg, 0.057 mmol), epoxide 12% (24 mg, 0.05 mmol). **Average:** 36% RSM $\pm 0.5\%$, (+)-**64** (C7OH) $12\% \pm 0.08\%$, (-)-**65** (C6OH) $3\% \pm 0.3\%$, total alcohol products $15\% \pm 0.2\%$, epoxide $12\% \pm 0.8\%$.

With catalyst **2** ((*R,S,S,R*)-Mn(MeCF₃-PDP)). Pleuromutilin analogue **(-)-63** (190 mg, 0.4 mmol) in HFIP was oxidized following Standard conditions, using 5 mol% (*R,S,S,R*)-Mn(MeCF₃-PDP) and 3.0 equivalents of H₂O₂. The resulting mixture was purified by column chromatography (silica, DCM only → acetone: DCM = 1: 5), separating three portions: a mixture of RSM and epoxide, **(+)-64** (C7OH) and **(-)-65** (C6OH). RSM and epoxide were separated by another column chromatography (silica, hexane only → acetone: hexane = 1: 5). **Run 1:** 33% RSM (63 mg, 0.13 mmol), **(+)-64** (C7OH) 11% (21 mg, 0.043 mmol), **(-)-65** (C6OH) 6% (11 mg, 0.023 mmol), total alcohol products 16% (32 mg, 0.066 mmol), epoxide 22% (44 mg, 0.089 mmol). **Run 2:** 34% RSM (65 mg, 0.14 mmol), **(+)-64** (C7OH) 12% (23 mg, 0.046 mmol), **(-)-65** (C6OH) 6% (13 mg, 0.026 mmol), total alcohol products 18% (35 mg, 0.072 mmol), epoxide 21% (41 mg, 0.084 mmol). **Average:** 34% RSM ± 0.6%, **(+)-64** (C7OH) 11% ± 0.4%, **(-)-65** (C6OH) 6% ± 0.4%, total alcohol products 17% ± 0.8%, epoxide 22% ± 0.6%.

With catalyst **1** ((*S,S*)-Mn(MeCF₃-PDP)). Pleuromutilin analogue **(-)-63** (190 mg, 0.4 mmol) in HFIP was oxidized following Standard conditions, using 5 mol% (*S,S*)-Mn(CF₃-PDP) and 3.0 equivalents of H₂O₂. The resulting mixture was purified by column chromatography (silica, DCM only → acetone: DCM = 1: 5), separating three portions: a mixture of RSM and epoxide, **(+)-64** (C7OH) and **(-)-65** (C6OH). RSM and epoxide were separated by another column chromatography (silica, hexane only → acetone: hexane = 1: 5). **Run 1:** 32% RSM (61 mg, 0.13 mmol), **(+)-64** (C7OH) 9% (17 mg, 0.034 mmol), **(-)-65** (C6OH) 5% (10 mg, 0.021 mmol), total alcohol products 14% (27 mg, 0.055 mmol), epoxide 5% (9 mg, 0.019 mmol). **Run 2:** 36% RSM (69 mg, 0.15 mmol), **(+)-64** (C7OH) 6% (13 mg, 0.026 mmol), **(-)-65** (C6OH) 5% (10 mg, 0.021 mmol), total alcohol products 12% (23 mg, 0.047 mmol), epoxide 2% (5 mg, 0.009 mmol). **Average:** 34%

RSM $\pm$ 2.2%, (+)-**64** (C7OH) 8% $\pm$ 1.1%, (-)-**65** (C6OH) 5% $\pm$ 0.0%, total alcohol products 13% $\pm$ 1.1%, epoxide 4% $\pm$ 1.2%.

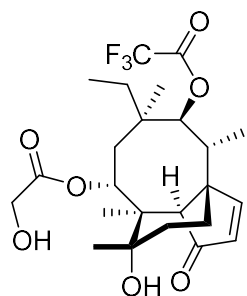
(3aR,4R,5R,7R,8S,9R,9aS,11S,12S)-7-ethyl-11-hydroxy-5-(2-hydroxyacetoxy)-4,7,9,12-tetramethyl-3-oxo-3,3a,4,5,6,7,8,9-octahydro-4,9a-propanocyclopenta[8]annulen-8-yl 2,2,2-trifluoroacetate [(+)-64]. ¹H NMR (600 MHz, CDCl₃) δ 7.64 (d, *J* = 6.2 Hz, 1H), 6.15 (d, *J* = 6.1



Hz, 1H), 5.58 (d, *J* = 8.4 Hz, 1H), 4.65 (d, *J* = 7.2 Hz, 1H), 4.15 (d, *J* = 17.1 Hz, 1H), 4.09 (d, *J* = 17.3 Hz, 1H), 3.83 (td, *J* = 11.2, 4.3 Hz, 1H), 2.58 – 2.50 (m, 2H), 2.38 (s, 1H), 1.95 (dd, *J* = 16.7, 8.4 Hz, 1H), 1.82 (dq, *J* = 14.4, 7.4 Hz, 1H), 1.67 (dq, *J* = 14.6, 7.5 Hz, 1H), 1.60 – 1.55 (m, 1H), 1.57 (s,

3H), 1.43 (d, *J* = 16.6 Hz, 1H), 1.09 (d, *J* = 7.1 Hz, 3H), 0.97 – 0.90 (m, 1H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.85 (s, 3H), 0.79 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 205.61, 172.60, 163.48, 157.28 (q, *J* = 42.3 Hz), 133.12, 114.82 (q, *J* = 286.0 Hz), 83.86, 70.41, 69.06, 61.45, 58.29, 50.89, 47.03, 44.84, 42.84, 41.26, 40.53, 34.64, 25.33, 22.19, 14.62, 11.72, 11.67, 8.12. ¹⁹F NMR (471 MHz, CDCl₃) δ -74.84. [α]_D²³ = 5.28 (c=0.5, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₂₄H₃₄O₇F₃ [M+H]⁺: 491.2257, found 491.2259.

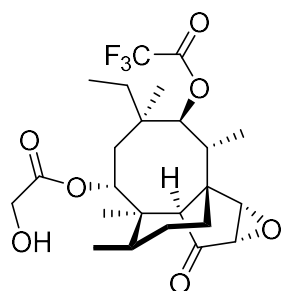
(3aR,4R,5R,7R,8S,9R,9aS,12S)-7-ethyl-12-hydroxy-5-(2-hydroxyacetoxy)-4,7,9,12-tetramethyl-3-oxo-3,3a,4,5,6,7,8,9-octahydro-4,9a-propanocyclopenta[8]annulen-8-yl 2,2,2-trifluoroacetate [(-)-65]. ¹H NMR (600 MHz, CDCl₃) δ 7.60 (d, *J* = 6.1 Hz, 1H), 6.12 (d, *J* = 6.1 Hz, 1H), 5.58 (d, *J* = 8.6 Hz, 1H), 4.63 (d, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 17.2 Hz, 2H), 2.54 (quint, *J* = 7.2 Hz, 1H), 2.24 (s, 1H), 2.03 – 1.92 (m, 3H), 1.88 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.72 (dq, *J* =



14.7, 7.4 Hz, 1H), 1.59 (s, 3H), 1.61 – 1.51 (m, 2H), 1.48 (d, $J = 16.5$ Hz, 1H), 1.03 (d, $J = 7.1$ Hz, 3H), 1.01 (s, 3H), 0.86 (s, 3H), 0.80 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 207.69, 172.56, 164.40, 157.20 (q, $J = 41.8$ Hz), 132.59, 114.81 (q, $J = 286.1$ Hz), 83.77, 73.62, 71.81, 61.28, 55.63, 49.95, 47.86, 42.16, 41.00, 33.40, 32.93, 32.13, 25.65, 25.34, 22.27, 11.56,

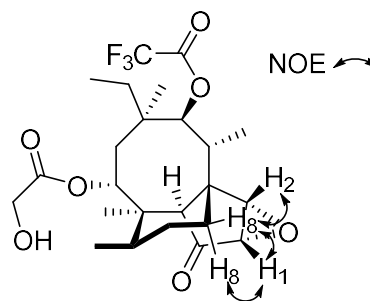
9.61, 8.22. ^{19}F NMR (565 MHz, CDCl_3) δ -74.85. $[\alpha]_{\text{D}}^{22} = -25.18$ ($c=0.8$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{24}\text{H}_{34}\text{O}_7\text{F}_3$ $[\text{M}+\text{H}]^+$: 491.2257, found 491.2260.

(1aS,1bS,2R,3S,4R,6R,7R,7aS,8aS,9R)-4-ethyl-6-(2-hydroxyacetoxy)-2,4,7,9-tetramethyl-8-oxodecahydro-7,1b-propanocycloocta[3,4]cyclopenta[1,2-b]oxiren-3-yl **2,2,2-trifluoroacetate** **(-)-66**

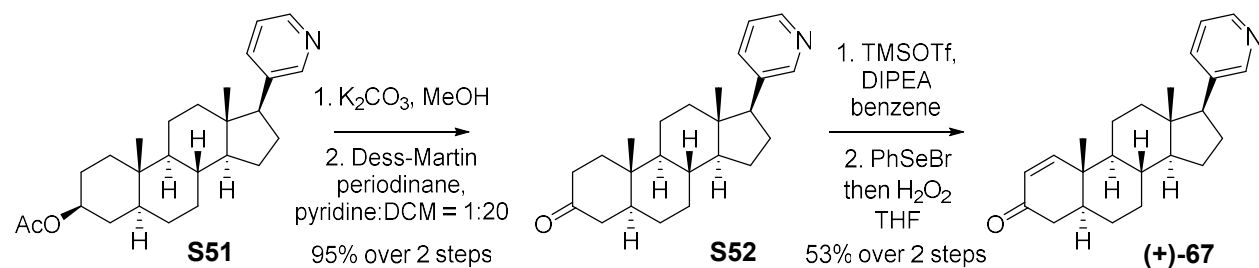


^1H NMR (500 MHz, CDCl_3) δ 5.62 (d, $J = 8.2$ Hz, 1H), 5.41 (d, $J = 7.4$ Hz, 1H), 4.10 (d, $J = 17.2$ Hz, 1H, contains an ethyl acetate signal), 4.03 (d, $J = 17.1$ Hz, 1H), 3.62 (d, $J = 3.1$ Hz, 1H), 3.25 (d, $J = 3.1$ Hz, 1H), 2.65 – 2.59 (m, 2H), 1.94 – 1.83 (m, 3H), 1.78 – 1.71 (m, 1H), 1.71 – 1.64 (m, 1H), 1.61 – 1.53 (m, 1H, contains a broad H_2O signal), 1.43 – 1.36 (m, 2H), 1.36 (s, 3H), 1.11 (d, $J = 7.1$ Hz, 3H), 1.02 – 0.97 (m, 1H), 0.87 (s, 3H), 0.78 (t, $J = 7.5$ Hz, 3H), 0.72 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.40, 172.43, 156.84 (app d, $J = 42.0$ Hz), 115.00 (app d, $J = 286.1$ Hz), 83.09, 69.34, 61.42, 59.48,

51.85, 48.00, 43.55, 40.72, 40.70, 40.30, 36.42, 33.62, 30.79, 25.74, 25.42, 21.73, 16.33, 15.18, 11.96, 8.13. ^{19}F NMR (471 MHz, CDCl_3) δ -74.74. $[\alpha]_{\text{D}}^{22} = -44.68$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{24}\text{H}_{34}\text{O}_7\text{F}_3$ $[\text{M}+\text{H}]^+$: 491.2257,



found 491.2249. Stereochemistry of epoxide was confirmed by NOE signal between epoxide protons (H1 and H2) and H8.



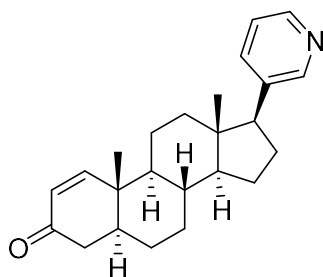
Preparation of abiraterone analogue. S51 was prepared according to the reported literature⁴⁹. To a stirred solution of acetate (1.7 g, 4.1 mmol, 1.0 equiv.) in MeOH (41 mL, 0.1 M), oven-dried K_2CO_3 (1.7 g, 12.3 mmol, 3.0 equiv.) was added at 0°C . The reaction mixture was stirred for 10 hours, gradually warming to room temperature. Reaction completion was confirmed by TLC (silica, EA: DCM = 1: 3). Upon completion, the reaction was quenched with aqueous NH_4Cl and extracted with EA. The combined organic layers were dried over MgSO_4 and concentrated in vacuo. The resulting white solid was dissolved in pyridine: DCM = 1: 20 (40 mL, 0.1M). Dess-Martin periodinane (2.0 g, 4.8 mmol, 1.2 equiv.) was added at room temperature, and the reaction was stirred for 6 hours, with completion confirmed by TLC (silica, EA: hexane = 1: 1). Upon completion, the mixture was concentrated in vacuo and purified by flash column chromatography (DCM only $\rightarrow$ EA: DCM = 1: 6), yielding the product **S52** (1.4 g, 3.9 mmol, 95% yield over two steps) as a white solid.

To a stirred solution of the **S52** (602 mg, 1.7 mmol, 1.0 equiv.) in benzene (17 mL, 0.1 M) was added TMSOTf (0.6 mL, 3.4 mmol, 2.0 equiv.), followed by DIPEA (0.9 mL, 5.1 mmol, 3.0 equiv.) at room temperature. The reaction mixture was stirred for 3.5 hours, with completion

confirmed by TLC (silica, EA: hexane = 1: 2). Upon completion, the reaction mixture was filtered through a silica pad using EA: hexane = 1: 1, and the filtrate was concentrated in vacuo and used for the next step without further purification.

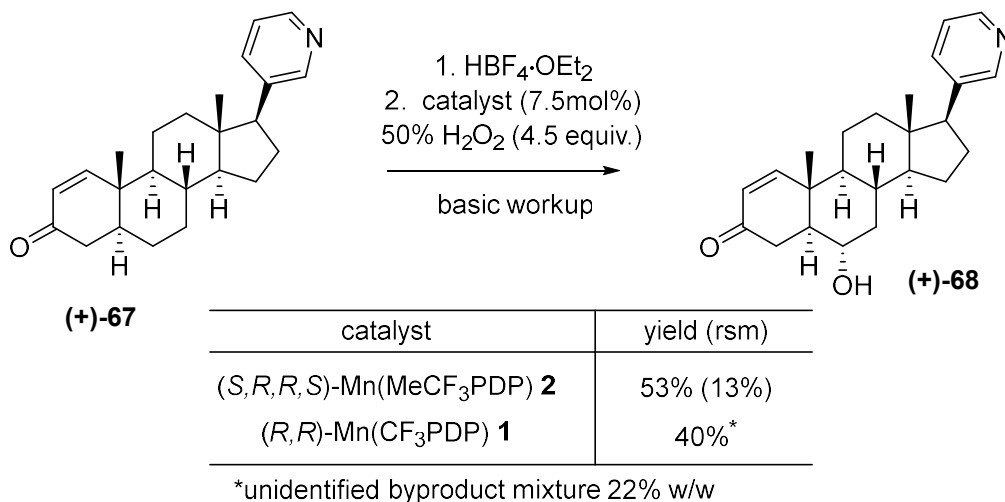
To a solution of the crude product (750 mg, ca. 1.8 mmol, 1.0 equiv.) in THF (18 mL, 1.0 M) was added PhSeBr (460 mg, 2.0 mmol, 1.1 equiv.) at -78°C. The mixture was stirred for 20 minutes at -78°C, monitored by TLC (silica, EA: hexane = 1: 1). Once the starting material was consumed, the mixture was diluted with THF (100 mL, 0.015 M), and 30% H₂O₂ (0.5 mL, 4.5 mmol, 2.5 equiv.) was introduced at -78°C. The reaction was warmed to room temperature over 1 hour. Upon completion, the mixture was quenched with water and extracted with EA. The organic layer was treated with saturated Na₂SO₃ and extracted with EA. The resulting organic portion was dried over MgSO₄ and concentrated in vacuo. Subsequent flash column chromatography (silica, acetone: hexane = 1: 3) furnished the desired abiraterone analogue **67** (330 mg, 0.94 mmol, 53% yield over 2 steps) as a white solid.

(5S,8S,9S,10R,13S,14S,17S)-10,13-dimethyl-17-(pyridin-3-yl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one [(+)-67].



¹H NMR (600 MHz, CDCl₃) δ 8.51 – 8.38 (m, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.13 (d, *J* = 10.2 Hz, 1H), 5.85 (d, *J* = 10.1 Hz, 1H), 2.69 (t, *J* = 9.9 Hz, 1H), 2.37 (dd, *J* = 17.6, 14.2 Hz, 1H), 2.23 (dd, *J* = 17.7, 4.0 Hz, 1H), 2.09 (dtd, *J* = 14.3, 10.8, 3.4 Hz, 1H), 2.03 – 1.90 (m, 2H), 1.87 – 1.74 (m, 3H), 1.61 (dt, *J* = 12.2, 3.3 Hz, 1H), 1.52 (qd, *J* = 10.9, 4.0 Hz, 1H), 1.47 – 1.40 (m, 2H), 1.42 – 1.25 (m, 4H), 1.10 – 1.02 (m, 2H), 1.00 (s,

3H), 0.51 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 200.27, 158.42, 150.26, 147.54, 136.41, 135.93, 127.58, 122.99, 56.24, 54.52, 50.25, 44.68, 44.49, 41.10, 39.19, 37.47, 36.24, 31.45, 27.71, 25.94, 24.45, 20.94, 13.19, 13.02. $[\alpha]_{\text{D}}^{24} = +45.38$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{24}\text{H}_{32}\text{NO}$ $[\text{M}+\text{H}]^+$: 350.2484, found 350.2472.



Oxidation of abiraterone analogue [(+)-67].

HBF₄ protection. To a stirred solution of the abiraterone analogue **67** (228 mg, 0.6 mmol, 1.0 equiv.) in DCM (2.4 mL, 0.25 M) was added HBF₄·OEt₂ (100 mg, 0.63 mmol, 1.03 equiv.) at 0°C under argon atmosphere. The mixture was stirred for 1 hour at 0°C, then concentrated in vacuo and stored under vacuum for 24 hours. The resulting white foamy solid was used for oxidation without further purification.

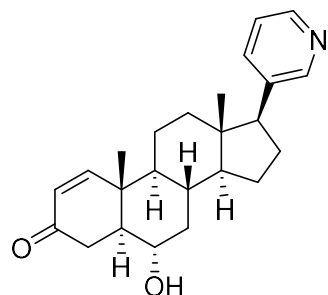
With catalyst 2 ((*S,R,R,S*)-Mn(MeCF₃-PDP)). HBF₄-protected abiraterone analogue (88 mg, 0.2 mmol) in HFIP was oxidized according to the Standard conditions with 7.5 mol% (*S,R,R,S*)-Mn(MeCF₃-PDP) and 4.5 equiv. of H₂O₂. After completing the H₂O₂ addition, the reaction mixture was diluted with DCM and quenched with saturated NaHCO₃ aqueous solution. The organic layer was extracted with DCM, dried over Na₂SO₄, and the resulting crude product was purified by column chromatography (silica, EA: DCM = 1: 1 → EA: DCM: MeOH = 10: 10: 1). **Run 1:** 12%

RSM, 55% yield. **Run 2:** 14% RSM, 53% yield. **Run 3:** 12% RSM, 51% yield. **Average:** 13% RSM $\pm$ 0.9%, 53% yield $\pm$ 1.3%.

With catalyst **1** (*(R,R)*-Mn(CF₃-PDP)). HBF₄-protected abiraterone analogue (88 mg, 0.2 mmol) in HFIP was oxidized according to the Standard conditions with 7.5 mol% (*R,R*)-Mn(CF₃-PDP) and 4.5 equiv. of H₂O₂. The same workup and purification methods as described for the procedure with catalyst **2** were applied. **Run 1:** 39% yield, unidentifiable byproduct mixture 16mg (18% w/w). **Run 2:** 40% yield, unidentifiable byproduct mixture 23mg (26% w/w). **Average:** 40% yield $\pm$ 0.9%, unidentifiable byproduct mixture 20% $\pm$ 4% w/w.

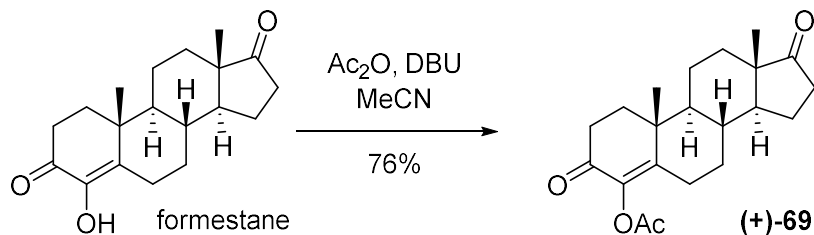
(5S,6S,8S,9S,10R,13S,14S,17S)-6-hydroxy-10,13-dimethyl-17-(pyridin-3-yl)-

4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one



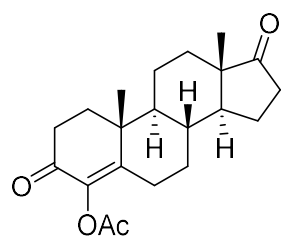
[(+)-68]. ¹H NMR (600 MHz, CDCl₃) δ 8.44 – 8.39 (m, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.21 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.07 (d, *J* = 10.2 Hz, 1H), 5.86 (d, *J* = 10.2 Hz, 1H), 3.60 (dt, *J* = 10.8, 5.4 Hz, 1H), 2.85 (dd, *J* = 17.9, 4.0 Hz, 1H), 2.82 (br s, 1H), 2.70 (t, *J* = 9.9 Hz, 1H),

2.30 (dd, *J* = 17.8, 14.0 Hz, 1H), 2.14 – 2.04 (m, 2H), 2.04 – 1.95 (m, 1H), 1.87 – 1.75 (m, 3H), 1.63 – 1.53 (m, 2H), 1.45 – 1.26 (m, 4H), 1.11 – 1.02 (m, 2H), 0.98 (s, 3H), 0.49 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 199.82, 157.47, 150.17, 147.54, 136.22, 135.88, 127.75, 123.01, 68.36, 55.91, 54.37, 50.84, 49.69, 44.60, 41.18, 39.71, 37.25, 36.05, 34.70, 25.83, 24.40, 20.83, 14.13, 12.94. $[\alpha]_D^{24} = +53.18$ (c=1.0, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₂₄H₃₂NO₂ [M+H]⁺: 366.2433, found 366.2426.

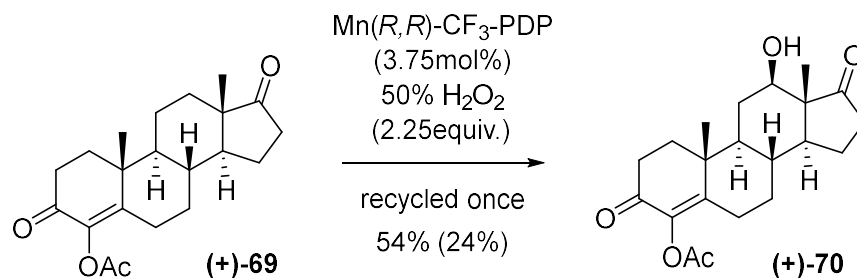


Preparation of (8R,9S,10R,13S,14S)-10,13-dimethyl-3,17-dioxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-4-yl acetate [(+)-69]. To a stirred solution of formestane **77** in MeCN (0.2M) was added Acetic anhydride (2.0equiv.) and DBU (2.0equiv.) at rt. The mixture was stirred for 5hr. The completion of the reaction was confirmed by TLC analysis (silica, EA: hexane = 1: 2). Upon completion, the mixture was concentrated *in vacuo* and directly purified with column chromatography (silica, EA: hexane = 1: 2) to furnish the desired Ac-formestane as a white solid (75.7% yield).

(8R,9S,10R,13S,14S)-10,13-dimethyl-3,17-dioxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-4-yl acetate [(+)-69]. ¹H NMR (600 MHz,



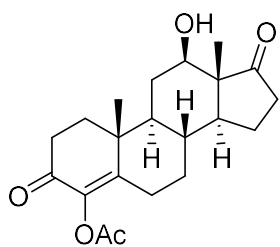
CDCl₃) δ 2.72 (app dt, J = 14.8, 4.2 Hz, 1H), 2.54 (ddd, J = 17.3, 14.2, 5.0 Hz, 1H), 2.49 – 2.43 (m, 2H), 2.23 (s, 3H), 2.09 (dt, J = 18.9, 9.1 Hz, 1H), 2.05 – 1.93 (m, 4H), 1.86 (dt, J = 13.1, 3.4 Hz, 1H), 1.79 (td, J = 13.9, 4.8 Hz, 1H), 1.74 – 1.67 (m, 2H), 1.56 (tt, J = 12.5, 9.1 Hz, 1H), 1.44 (qd, J = 13.2, 4.1 Hz, 1H), 1.31 – 1.25 (m, 2H), 1.26 (s, 3H), 1.12 – 1.02 (m, 2H), 0.91 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 220.36, 190.59, 168.75, 155.16, 139.41, 53.90, 50.86, 47.59, 39.26, 35.86, 34.80, 34.71, 33.46, 31.36, 29.87, 24.01, 21.84, 20.47, 20.38, 17.80, 13.82. $[\alpha]_D^{24}$ = +171.84 (c=1.0, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₂₁H₂₉O₄ [M+H]⁺: 345.2066, found 345.2067.



Oxidation of Ac-formestane [(+)-69]. Formestane (0.3 mmol) in HFIP was oxidized according to the Standard conditions with 3.75 mol% (*R,R*)-Mn(CF₃-PDP) and 2.25 equiv. of H₂O₂. The resulting mixture was purified by MPLC(silica, ether only → 5 % MeOH in Et₂O) yielding recovered starting material (RSM) and **70**. The RSM was resubjected to the same oxidation condition (Standard conditions, 3.75 mol% (*R,R*)-Mn(CF₃-PDP) and 2.25 equiv. of H₂O₂). The resulting mixture, combined with the products from the first run was purified by MPLC(silica, ether only → 5 % MeOH in Et₂O). The RSM and yields(%) from both runs were combined to calculate the final result. **Run 1:** first run - 51% RSM, after recycle - 21% RSM, 57% yield. **Run 2:** first run - 53% RSM, after recycle - 25% RSM, 53% yield. **Run 3:** first run - 56% RSM, after recycle - 26% RSM, 52% yield. **Average** (after recycle): 24% RSM ± 2.1%, 54% ± 2.2% yield.

(8*R*,9*S*,10*R*,12*R*,13*R*,14*S*)-12-hydroxy-10,13-dimethyl-3,17-dioxo-

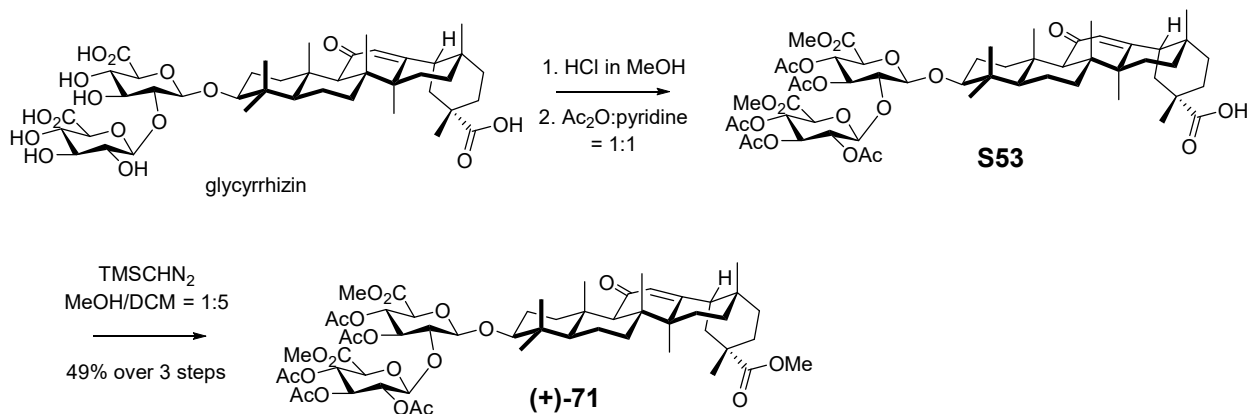
2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-4-yl



acetate [(+)-70]. ¹H NMR (600 MHz, CDCl₃) δ 3.78 (dd, *J* = 11.2, 4.7 Hz, 1H), 3.02 (br s, 1H), 2.72 (ddd, *J* = 14.9, 4.2, 2.4 Hz, 1H), 2.57 – 2.43 (m, 3H), 2.22 (s, 3H), 2.12 (dt, *J* = 19.6, 9.0 Hz, 1H), 2.04 – 1.92 (m, 4H), 1.82 (dt, *J* = 13.0, 4.4 Hz, 1H), 1.82 – 1.75 (m, 1H), 1.72 – 1.64

(m, 2H), 1.40 (td, *J* = 12.9, 11.1 Hz, 1H), 1.28 – 1.21 (m, 1H), 1.26 (s, 3H), 1.17 (ddd, *J* = 12.7,

10.7, 4.0 Hz, 1H), 1.03 (app qd, $J = 12.8, 4.2$ Hz, 1H), 0.97 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 222.08, 190.42, 168.69, 154.27, 139.56, 72.35, 52.24, 51.51, 48.53, 39.17, 35.74, 34.66, 33.83, 33.41, 29.30, 27.99, 23.93, 21.71, 20.44, 17.62, 8.31. $[\alpha]_{\text{D}}^{24} = +135.82$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{21}\text{H}_{29}\text{O}_5$ $[\text{M}+\text{H}]^+$: 361.2015, found 361.2003. The site selectivity of the alcohol was assigned by HSQC, HMBC and COSY analysis. The stereochemistry of the alcohol **70** was assigned by 2D NOE analysis.

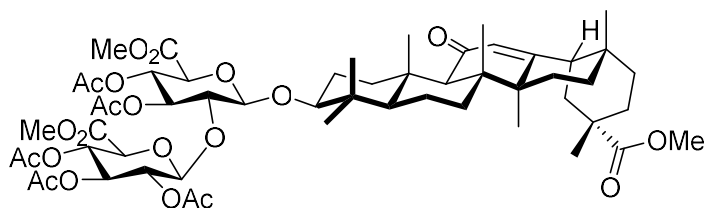


Preparation of glycyrrhizin analogue [(+)-71]. Pentaacetate **S53** was prepared according to the reported literature with a slight modification to the procedure⁵⁰. A round-bottom flask covered with aluminium foil was charged with glycyrrhizin (80% purity, 2 g, 1.9 mmol, 1.0 equiv.). A 1.2 M HCl solution in MeOH (47 mL, 57 mmol, 30 equiv.) was added to the solid at 0°C, and the mixture was gradually warmed to room temperature over 5 hours. Ag_2CO_3 (8.3 g, 30 mmol, 16 equiv.) was added at 0°C, and the mixture was stirred for 30 minutes at 0°C. The reaction progress was monitored by TLC (silica, EA: DCM: MeOH = 3: 3: 2). The reaction mixture was filtered through a Celite pad with MeOH, and the organic filtrate was concentrated in vacuo. The resulting crude was purified by column chromatography (silica, EA: DCM: MeOH = 3: 3: 2). The resulting

crude was transferred into a round-bottom flask and dissolved in a mixture of Ac₂O: pyridine = 1: 1 (80 mL, 0.024M). The reaction mixture was stirred for 15 hours at room temperature. Water (100 mL) was added at 0°C, resulting in precipitation. The resulting solid was collected by filtration and dried under vacuum, yielding a crude mixture (1.9 g, ca. 95% yield over 2 steps) as a white solid.

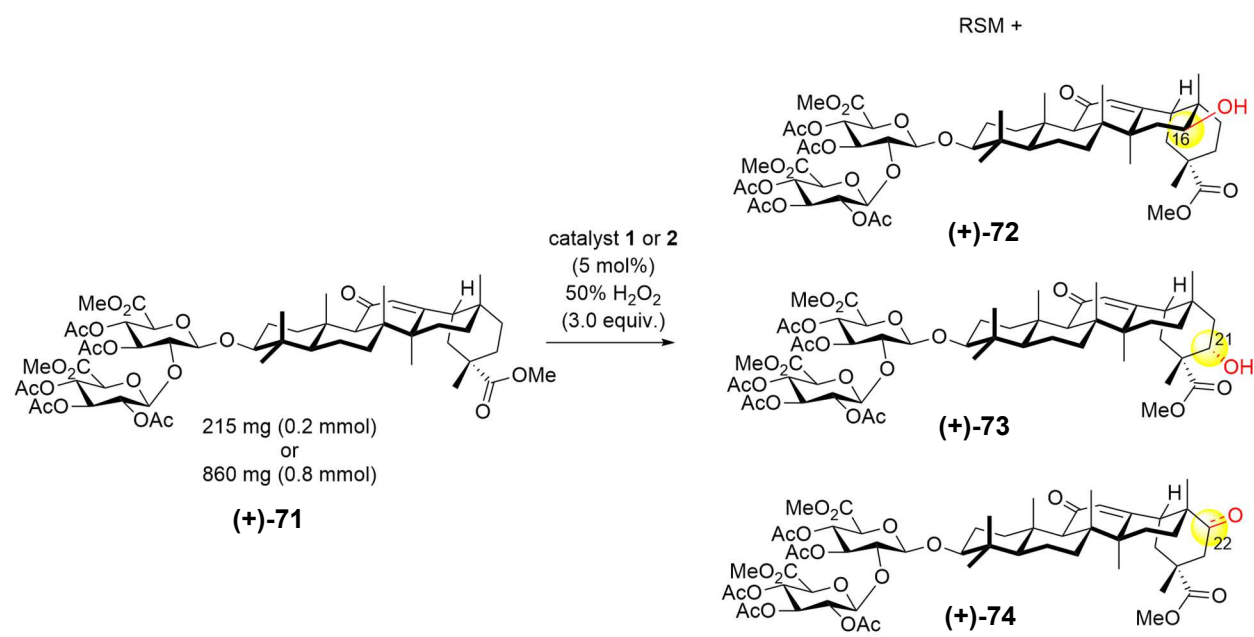
To a stirred solution of this solid (1.9g, ca. 1.8 mmol, 1.0 equiv.) in MeOH: DCM = 1: 5 mixture (0.1 M, 18 mL) was added 2 M TMS-diazomethane (1.2 mL, 2.3 mmol, 1.3 equiv.) at room temperature. An additional 2 M TMS-diazomethane (0.45 mL, 0.9 mmol, 0.5 equiv.) was then added. When the yellow color of TMS-diazomethane persisted, the reaction was monitored by TLC (silica, EA: hexane = 1: 1, developed three times) to confirm full conversion. Upon completion, acetic acid was added to quench residual TMS-diazomethane, and the reaction mixture was concentrated in vacuo. The resulting crude product was filtered through a short silica pad with acetone, concentrated again, and purified by MPLC (Teledyne Combiflash® system, silica, acetone: DCM = 1: 20 → 1: 10) to afford ester **71** (1 g, 0.94 mmol, 49% over three steps) as a white foamy solid. The spectroscopic data matched the published literature^{51,52}.

(2R,3R,4S,5S,6S)-2-(((2R,3R,4S,5S,6S)-4,5-diacetoxy-6-(methoxycarbonyl)-2-(((3S,4aR,6aR,6bS,8aS,11S,12aR,14aR,14bS)-11-(methoxycarbonyl)-4,4,6a,6b,8a,11,14b-heptamethyl-14-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydricen-3-yl)oxy)tetrahydro-2H-pyran-3-yl)oxy)-6-(methoxycarbonyl)tetrahydro-2H-pyran-3,4,5-



triyl triacetate [(+)-71]. ¹H NMR (600 MHz, CDCl₃) δ 5.63 (s, 1H), 5.21 (app t, *J* = 9.6 Hz, 1H), 5.18 (app t, *J* = 9.5 Hz,

1H), 5.12 (t, $J = 9.5$ Hz, 1H), 5.08 (t, $J = 9.7$ Hz, 1H), 4.90 (dd, $J = 9.6, 8.0$ Hz, 1H), 4.71 (d, $J = 8.1$ Hz, 1H), 4.48 (d, $J = 7.6$ Hz, 1H), 3.98 (d, $J = 9.6$ Hz, 1H). 3.96 (d, $J = 9.8$ Hz, 1H), 3.82 (dd, $J = 9.4, 7.5$ Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.09 (app t, $J = 9.4$ Hz, 1H), 2.75 (dt, $J = 13.5, 3.7$ Hz, 1H), 2.29 (s, 1H), 2.09 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.97 (s, 3H), 2.07 – 1.96 (m, 3H), 1.93 – 1.87 (m, 1H), 1.85 – 1.75 (m, 3H), 1.66 – 1.54 (m, 3H), 1.42 – 1.35 (m, 3H), 1.33 (s, 3H), 1.31 – 1.24 (m, 2H), 1.20 – 1.15 (m, 1H), 1.13 (s, 3H), 1.11 (s, 3H), 1.09 (s, 3H), 1.00 (s, 3H), 1.03 – 0.97 (m, 1H), 0.94 – 0.87 (m, 1H), 0.80 (s, 3H), 0.78 (s, 3H), 0.69 – 0.63 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 200.37, 177.04, 170.29, 169.99, 169.63, 169.57, 169.33 (2C), 167.35, 166.52, 128.63, 103.39, 100.76, 91.27, 76.88, 74.31, 72.86, 72.60, 72.26, 71.21, 69.83, 69.35, 61.91, 55.45, 52.93, 52.81, 51.89, 48.50, 45.51, 44.15, 43.26, 41.18, 39.58, 39.21, 37.85, 36.85, 32.83, 31.93, 31.23, 28.61, 28.45, 27.63, 26.55, 26.51, 25.84, 23.48, 21.00, 20.68, 20.62 (2C), 20.51, 18.77, 17.41, 16.49, 16.00. $[\alpha]_{\text{D}}^{25} = +37.26$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{55}\text{H}_{79}\text{O}_{21}$ $[\text{M}+\text{H}]^+$: 1075.5114, found 1075.5100.



catalyst	RSM	(+)- 72 (C16)	(+)- 73 (C21)	(+)- 74 (C22)	total C-H oxidation
(<i>R,S,S,R</i>)- 2	36%	14%	11%	29% ^a	54%
(<i>S,S</i>)- 1	28%	13%	11%	21% ^b	45%
(<i>S,R,R,S</i>)- 2	45%	20%	7%	20% ^c	47%
(<i>R,R</i>)- 1	55%	8%	20%	9% ^d	37%

Table S49. Oxidation of **71**. alcohol: ketone ratio = ^a2.1:1. ^b3.9:1. ^c2.8:1. ^d6.9:1.

Oxidation of glycyrrhizin analogue [(+)-71**].** Glycyrrhizin analogue **71** (0.2 mmol or 0.8 mmol) in HFIP was oxidized following Standard conditions, using 5 mol% catalyst and 3.0 equivalents of H₂O₂. The resulting mixture was purified by column chromatography (silica, acetone: DCM = 1: 15 → 1: 10 → 1: 3), yielding three fractions: recovered starting material (RSM), mixture A (**74** (C22) ketone + **73** (C21) OH), and mixture B (**72** (C16) OH + **74** (C22) OH). Mixture A was further purified by column chromatography (silica, EA: hexane = 1: 1), separating **74** (C22) ketone and **73** (C21) OH. Mixture B also was further purified by column chromatography (silica, acetone: DCM = 1: 8), separating **72** (C16) OH and **74** (C22) OH. Each catalytic run was performed twice, once on a 0.2 mmol scale and once on a 0.8 mmol scale.

*With catalyst 2 ((*R,S,S,R*)-Mn(MeCF₃-PDP)).* **Run 1 (0.2 mmol scale, 215 mg starting material):** 39% RSM (84.2 mg, 0.078 mmol), **74** (C22)-ketone 9% (19 mg, 0.018 mmol), **73** (C21) OH 12% (25 mg, 0.023 mmol), **72** (C16) OH 15% (32 mg, 0.029 mmol), **74** (C22) OH 18% (40 mg, 0.037 mmol), total C-H oxidation 53% (116 mg, 0.107 mmol), mixture of unidentified byproducts (6 mg, 3% w/w). **Run 2 (0.8 mmol scale, 860 mg starting material):** 33% RSM (286 mg, 0.27 mmol), **74** (C22)-ketone 10% (86 mg, 0.08 mmol), **73** (C21) OH 11% (95 mg, 0.087 mmol), **72** (C16) OH 14% (118 mg, 0.11 mmol), **74** (C22) OH 20% (177 mg, 0.16 mmol), total C-H oxidation

55% (477 mg, 0.44 mmol), mixture of unidentified byproducts (16 mg, 2% w/w). **Average:** 36% RSM $\pm$ 2.9%, **74** (C22)-ketone 9% $\pm$ 0.5%, **73** (C21) OH 11% $\pm$ 0.3%, **72** (C16) OH 14% $\pm$ 0.5%, **74** (C22) OH 19% $\pm$ 1.0%, total C-H oxidation 54% $\pm$ 0.7%, mixture of unidentified byproducts 2 % w/w $\pm$ 0.4%.

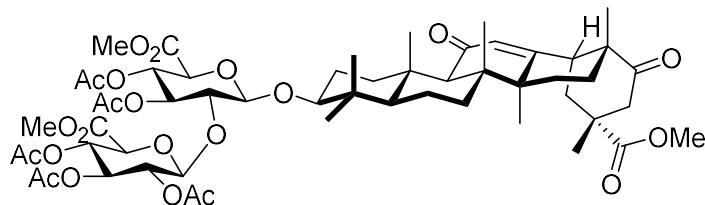
With catalyst 1 ((S,S)-Mn(MeCF₃-PDP)). **Run 1 (0.2 mmol scale, 215 mg starting material):** 29% RSM (63 mg, 0.058 mmol), **74** (C22)-ketone 3% (6 mg, 0.0058 mmol), **73** (C21) OH 12% (25 mg, 0.023 mmol), **72** (C16) OH 12% (26 mg, 0.024 mmol), **74** (C22) OH 17% (37 mg, 0.033 mmol), total C-H oxidation 43% (94 mg, 0.087 mmol), mixture of unidentified byproducts (37 mg, 17% w/w). **Run 2 (0.8 mmol scale, 860 mg starting material):** 27% RSM (234 mg, 0.22 mmol), **74** (C22)-ketone 6% (50 mg, 0.046 mmol), **73** (C21) OH 10% (86 mg, 0.079 mmol), **72** (C16) OH 15% (131 mg, 0.12 mmol), **74** (C22) OH 17% (149 mg, 0.14 mmol), total C-H oxidation 48% (416 mg, 0.38 mmol), mixture of unidentified byproducts (158 mg, 18% w/w). **Average:** 28% RSM $\pm$ 1.0%, **74** (C22)-ketone 4% $\pm$ 1.4%, **73** (C21) OH 11% $\pm$ 0.9%, **72** (C16) OH 13% $\pm$ 1.5%, **74** (C22) OH 17% $\pm$ 1.6%, total C-H oxidation 45% $\pm$ 2.2%, mixture of unidentified byproducts 18% w/w $\pm$ 0.7%.

With catalyst 2 ((S,R,R,S)-Mn(MeCF₃-PDP)). **Run 1 (0.2 mmol scale, 215 mg starting material):** 48% RSM (103 mg, 0.096 mmol), **74** (C22)-ketone 5% (11 mg, 0.01 mmol), **73** (C21) OH 7% (14 mg, 0.013 mmol), **72** (C16) OH 19% (40 mg, 0.037 mmol), **74** (C22) OH 16% (35 mg, 0.032 mmol), total C-H oxidation 46% (100 mg, 0.092 mmol), mixture of unidentified byproducts (0 mg, 0% w/w). **Run 2 (0.8 mmol scale, 860 mg starting material):** 42% RSM (357 mg, 0.33 mmol), **74** (C22)-ketone 6% (49 mg, 0.045 mmol), **73** (C21) OH 7% (62 mg, 0.057 mmol), **72** (C16) OH 21% (186 mg, 0.17 mmol), **74** (C22) OH 14% (119 mg, 0.11 mmol), total C-H oxidation 48% (416 mg, 0.38 mmol), mixture of unidentified byproducts (67 mg, 8% w/w). **Average:** 45%

RSM $\pm$ 3.2%, **74** (C22)-ketone 5% $\pm$ 0.3%, **73** (C21) OH 7% $\pm$ 0.3%, **72** (C16) OH 20% $\pm$ 1.4%, **74** (C22) OH 15% $\pm$ 1.1%, total C-H oxidation 47% $\pm$ 0.8%, mixture of unidentified byproducts 4% w/w $\pm$ 4%.

With catalyst 1 ((R,R)-Mn(MeCF₃-PDP)). **Run 1 (0.2 mmol scale, 215 mg starting material):** 56% RSM (120 mg, 0.11 mmol), **74** (C22)-ketone 0% (0 mg, 0 mmol), **73** (C21) OH 19% (41 mg, 0.038 mmol), **72** (C16) OH 8% (17 mg, 0.016 mmol), **74** (C22) OH 9% (19 mg, 0.017 mmol), total C-H oxidation 36% (78 mg, 0.071 mmol), mixture of unidentified byproducts (8 mg, 4% w/w). **Run 2 (0.8 mmol scale, 860 mg starting material):** 53% RSM (459 mg, 0.43 mmol), **74** (C22)-ketone 2% (20 mg, 0.018 mmol), **73** (C21) OH 21% (188 mg, 0.17 mmol), **72** (C16) OH 8% (72 mg, 0.067 mmol), **74** (C22) OH 7% (63 mg, 0.058 mmol), total C-H oxidation 39% (344 mg, 0.32 mmol), mixture of unidentified byproducts (35 mg, 4% w/w). **Average:** 55% RSM $\pm$ 1.2%, **74** (C22)-ketone 1% $\pm$ 1%, **73** (C21) OH 20% $\pm$ 1.2%, **72** (C16) OH 8% $\pm$ 0.2%, **74** (C22) OH 8% $\pm$ 0.7%, total C-H oxidation 37% $\pm$ 1.8%, mixture of unidentified byproducts 4% w/w $\pm$ 0.2%.

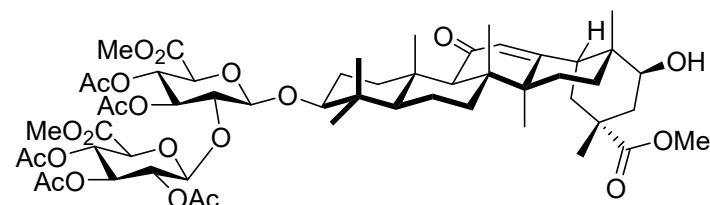
(2R,3R,4S,5S,6S)-2-(((2R,3R,4S,5S,6S)-4,5-diacetoxy-6-(methoxycarbonyl)-2-(((3S,4aR,6aR,6bS,8aR,11R,12aS,14aR,14bS)-11-(methoxycarbonyl)-4,4,6a,6b,8a,11,14b-heptamethyl-9,14-dioxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydropicen-3-yl)oxy)tetrahydro-2H-pyran-3-yl)oxy)-6-(methoxycarbonyl)tetrahydro-



2H-pyran-3,4,5-triyl triacetate [(+)-**74**-ketone]. ¹H NMR (600 MHz, CDCl₃) δ 5.60 (s, 1H), 5.22 (t, *J* = 9.2 Hz, 1H), 5.19 (t, *J* = 9.5 Hz, 1H), 5.13 (t, *J* = 9.5 Hz, 1H), 5.09 (t, *J* = 9.7 Hz, 1H), 4.91 (t, *J* = 8.8 Hz, 1H),

4.72 (d, $J = 8.1$ Hz, 1H), 4.48 (d, $J = 7.5$ Hz, 1H), 3.98 (app t, $J = 9.3$ Hz, 2H), 3.84 (app t, $J = 9.4$ Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 3.09 (t, $J = 8.2$ Hz, 1H), 2.78 – 2.68 (m, 2H), 2.38 – 2.18 (m, 3H), 2.14 – 2.08 (m, 1H), 2.10 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.98(s, 3H), 1.99 – 1.93 (m, 2H), 1.87 – 1.78 (m, 3H), 1.65 – 1.58 (m, 2H, mixed with H₂O (1.62ppm)), 1.44 – 1.34 (m, 3H), 1.40 (s, 3H), 1.30 – 1.24 (m, 1H), 1.28 (s, 3H), 1.12 (s, 3H), 1.10 (s, 3H), 1.02 (s, 3H), 1.01 (s, 3H), 0.95 – 0.89 (m, 1H), 0.81 (s, 3H), 0.67 (d, $J = 11.7$ Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 212.31, 199.97, 176.05, 170.32, 170.02, 169.66, 169.62, 169.37, 167.39, 166.54, 164.81, 129.52, 103.41, 100.80, 91.21, 76.87, 74.32, 72.89, 72.61, 72.32, 71.22, 69.85, 69.37, 61.98, 55.50, 52.97, 52.85, 52.52, 48.05, 46.60, 46.50, 45.70, 45.24, 43.44, 42.48, 39.60, 39.22, 36.96, 32.90, 27.67, 27.32, 26.36, 25.83, 25.36, 22.67, 21.55, 21.03, 20.70, 20.64 (2C), 20.54, 18.79, 17.40, 16.53, 16.04. $[\alpha]_D^{24} = +10.58$ (c=1.0, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₅₅H₇₇O₂₂ $[M+H]^+$: 1089.4906, found 1089.4874.

**(2R,3R,4S,5S,6S)-2-(((2R,3R,4S,5S,6S)-4,5-diacetoxy-2-
(((3S,4aR,6aR,6bS,8aR,9S,11R,12aS,14aR,14bS)-9-hydroxy-11-(methoxycarbonyl)-
4,4,6a,6b,8a,11,14b-heptamethyl-14-oxo-
1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydricen-3-yl)oxy)-6-
(methoxycarbonyl)tetrahydro-2H-pyran-3-yl)oxy)-6-(methoxycarbonyl)tetrahydro-2H-**



pyran-3,4,5-triyl triacetate [(+)-74-

OH]. ¹H NMR (600 MHz, CDCl₃) δ 5.64

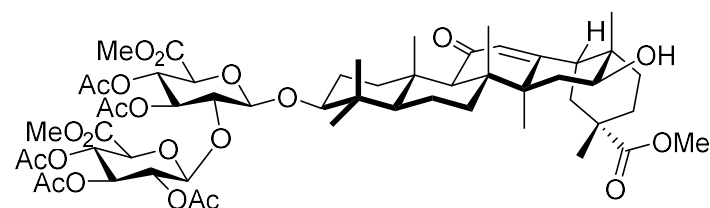
(s, 1H), 5.22 (t, $J = 9.4$ Hz, 1H). 5.19 (t,

$J = 9.7$ Hz, 1H). 5.13 (t, $J = 9.5$ Hz, 1H), 5.09 (t, $J = 9.7$ Hz, 1H), 4.91 (t, $J = 8.7$ Hz, 1H), 4.72

(d, $J = 8.0$ Hz, 1H), 4.49 (d, $J = 7.4$ Hz, 1H), 3.99 (d, $J = 7.5$ Hz, 1H), 3.97 (d, $J = 7.6$ Hz, 1H),

3.84 (t, J = 8.4 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.69 (s, 3H), 3.40 (dd, J = 12.2, 4.3 Hz, 1H), 3.10 (t, J = 8.2 Hz, 1H), 2.75 (dt, J = 13.6, 3.7 Hz, 1H), 2.31 (s, 1H), 2.21 – 2.16 (m, 1H), 2.10 (s, 3H), 2.07 – 2.03 (m, 1H), 2.01 (s, 3H), 1.99 – 1.97 (3s, 9H), 1.92 – 1.87 (m, 1H), 1.81 – 1.77 (m, 2H), 1.75 – 1.69 (m, 2H), 1.68 – 1.58 (4H, mixed with H₂O (1.58ppm)), 1.53 – 1.47 (m, 1H), 1.44 – 1.34 (m, 3H), 1.36 (s, 3H), 1.25 – 1.22 (m, 1H), 1.18 (s, 3H), 1.11 (2s, 6H), 1.01 (s, 3H), 0.94 (s, 3H), 0.92 – 0.87 (m, 1H), 0.81 (s, 3H), 0.67 (d, J = 11.8 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 200.39, 176.77, 170.34, 170.03, 169.68, 169.62, 169.38, 167.59, 167.40, 166.56, 128.91, 103.42, 100.79, 91.28, 76.89, 75.84, 74.33, 72.89, 72.62, 72.30, 71.23, 69.86, 69.38, 62.01, 55.45, 52.96, 52.85, 52.18, 48.26, 45.63, 43.99, 43.88, 40.64, 39.61, 39.24, 39.01, 37.35, 36.87, 32.77, 28.42, 27.66, 26.09, 25.86, 25.08, 23.68, 21.03, 20.71, 20.65 (2C), 20.54, 19.31, 18.74, 17.42, 16.52, 16.03. $[\alpha]_D^{24}$ = +25.86 (c=1.0, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₅₅H₇₉O₂₂ [M+H]⁺: 1091.5063, found 1091.5048.

**(2R,3R,4S,5S,6S)-2-(((2R,3R,4S,5S,6S)-4,5-diacetoxy-2-
(((3S,4aR,6aR,6bS,8S,8aS,11S,12aS,14aR,14bS)-8-hydroxy-11-(methoxycarbonyl)-
4,4,6a,6b,8a,11,14b-heptamethyl-14-oxo-
1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydricen-3-yl)oxy)-6-
(methoxycarbonyl)tetrahydro-2H-pyran-3-yl)oxy)-6-(methoxycarbonyl)tetrahydro-2H-**



pyran-3,4,5-triyl triacetate [(+)-72]. ¹H

NMR (600 MHz, CDCl₃) δ 5.69 (s, 1H),

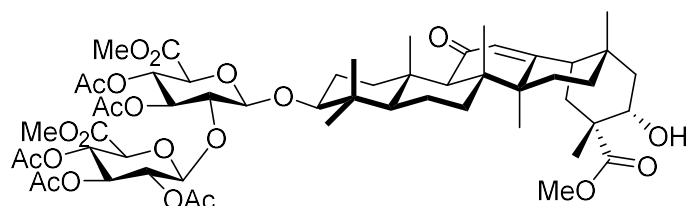
5.22(t, J = 9.6Hz, 1H), 5.19 (t, J =

9.4Hz, 1H), 5.13 (t, J = 9.5Hz, 1H), 5.09 (t, J = 9.7Hz, 1H), 4.91 (app t, J = 8.8 Hz, 1H), 4.72 (d,

J = 8.0 Hz, 1H), 4.49 (d, J = 7.5 Hz, 1H), 4.22 (dd, J = 11.4, 5.1 Hz, 1H), 3.99 (d, J = 7.5 Hz,

1H), 3.97 (d, $J = 7.6$ Hz, 1H), 3.84 (dd, $J = 9.2, 7.3$ Hz, 1H), 3.73 (s, 3H), 3.69 (2s, 6H), 3.09 (app t, $J = 8.2$ Hz, 1H), 2.75 (dt, $J = 13.5, 3.7$ Hz, 1H), 2.31 – 2.27 (m, 1H), 2.26 (s, 1H), 2.10 (s, 3H), 2.07 – 2.01 (m, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.99 – 1.94 (m, 2H), 1.83 – 1.75 (m, 2H), 1.72 (app t, $J = 12.3$ Hz, 1H), 1.65 – 1.58 (m, 3H), 1.50 (dd, $J = 13.0, 5.0$ Hz, 1H), 1.45 – 1.36 (m, 2H), 1.43 (s, 3H), 1.36 – 1.30 (m, 1H), 1.15 (s, 3H), 1.13 (s, 3H), 1.12 (s, 3H), 1.07 – 0.98 (m, 1H), 1.01 (s, 3H), 0.94 – 0.87 (m, 1H), 0.81 (s, 3H), 0.76 (s, 3H), 0.66 (d, $J = 11.6$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 200.09, 176.92, 170.33, 170.02, 169.68, 169.62, 169.37, 167.39, 167.15, 166.55, 128.69, 103.41, 100.80, 91.21, 76.91, 74.33, 72.90, 72.63, 72.30, 71.24, 69.86, 69.38, 65.39, 61.24, 55.47, 52.96, 52.85, 52.04, 50.32, 45.85, 45.52, 44.07, 40.95, 39.61, 39.22, 36.84, 36.71, 35.83, 32.90, 31.72, 30.77, 28.40, 27.66, 25.85, 24.63, 21.92, 21.03, 20.71, 20.65, 20.64, 20.55, 18.79, 17.42, 16.56, 16.03. $[\alpha]_{\text{D}}^{25} = +28.28$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{55}\text{H}_{79}\text{O}_{22}$ $[\text{M}+\text{H}]^+$: 1091.5063, found 1091.5045.

(2R,3R,4S,5S,6S)-2-(((2R,3R,4S,5S,6S)-4,5-diacetoxy-2-(((3S,4aR,6aR,6bS,8aS,10R,11R,12aR,14aR,14bS)-10-hydroxy-11-(methoxycarbonyl)-4,4,6a,6b,8a,11,14b-heptamethyl-14-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydricen-3-yl)oxy)-6-(methoxycarbonyl)tetrahydro-2H-pyran-3-yl)oxy)-6-(methoxycarbonyl)tetrahydro-2H-



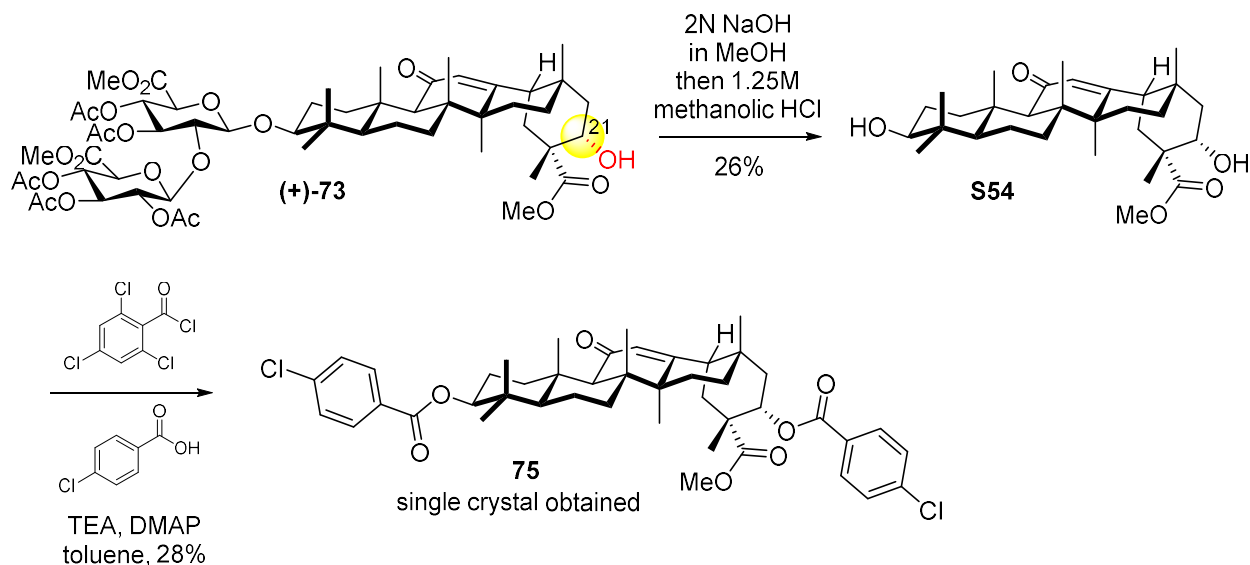
pyran-3,4,5-triyl triacetate [(+)-73]. ^1H

NMR (600 MHz, CDCl_3) δ 5.59 (s, 1H),

5.20 (t, $J = 9.8$ Hz, 1H), 5.18 (t, $J = 9.4$ Hz,

1H), 5.12 (t, $J = 9.5$ Hz, 1H), 5.08 (t, $J = 9.7$ Hz, 1H), 4.90 (t, $J = 8.8$ Hz, 1H), 4.71 (d, $J = 8.0$ Hz, 1H), 4.47 (d, $J = 7.5$ Hz, 1H), 3.98 (d, $J = 7.9$ Hz, 1H), 3.96 (d, $J = 7.4$ Hz, 1H), 3.82 (app t,

$J = 8.2$ Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 3.48 – 3.35 (m, 2H), 3.09 (t, $J = 8.1$ Hz, 1H), 2.74 (app d, $J = 13.3$ Hz, 1H), 2.29 (s, 1H), 2.09 (s, 3H), 2.00 (s, 3H), 1.98 – 1.88 (m, 12H), 1.82 – 1.73 (m, 4H), 1.69 (t, $J = 13.4$ Hz, 1H), 1.64 – 1.54 (m, 2H), 1.46 (t, $J = 12.3$ Hz, 1H), 1.42 – 1.35 (m, 2H), 1.31 (2s, 6H), 1.18 (app t, $J = 11.6$ Hz, 2H), 1.10 (s, 3H), 1.08 (s, 3H), 1.00 (s, 3H), 0.93 – 0.87 (m, 1H), 0.83 (s, 3H), 0.80 (s, 3H), 0.65 (d, $J = 11.8$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 200.25, 177.52, 170.30, 169.98, 169.64, 169.58, 169.34, 167.88, 167.37, 166.52, 128.97, 103.39, 100.76, 91.22, 76.85, 74.29, 73.18, 72.86, 72.58, 72.28, 71.20, 69.83, 69.35, 61.95, 55.43, 52.93, 52.82, 52.11, 48.59 (2C), 46.73, 45.47, 43.24, 41.82, 39.58, 39.18, 36.86, 34.74, 32.82, 28.57, 27.63, 27.46, 26.44, 25.83, 24.65, 23.34, 21.00, 20.68, 20.62, 20.61, 20.51, 18.77, 17.38, 16.49, 16.00. $[\alpha]_{\text{D}}^{25} = +36.24$ ($c=1.0$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{55}\text{H}_{79}\text{O}_{22}$ $[\text{M}+\text{H}]^+$: 1091.5063, found 1091.5051. The structure of **73** was confirmed by X-ray crystallography analysis of 4-chlorobenzoyl ester **75**.



Preparation of 4-chlorobenzoyl ester 75. To a stirred solution of **73** (C21)–OH (283 mg, 0.26 mmol, 1.0 equiv.) in MeOH (4.6 mL, 0.056 M) was added 2N NaOH (1.4 mL, 11 equiv.) at room temperature. The reaction was stirred for 50 hours and then concentrated in vacuo. Water was

added to the crude mixture, and the organic portion was extracted with DCM. The resulting organic solution was dried over Na₂SO₄ and concentrated in vacuo. To the crude, 1.25 M methanolic HCl (2 mL) was directly added, and the reaction was stirred for 15 hours at room temperature. Water was added to the mixture, and the organic portion was extracted with DCM. The organic solution was dried over Na₂SO₄ and concentrated in vacuo, affording aglycone **S54** (34 mg, 0.068 mmol, 26% yield over two steps).

To a stirred solution of *p*-chlorobenzoic acid (21 mg, 0.14 mmol, 2.0 equiv.) in toluene (6 mL, 0.01 M) were added 2,4,6-trichlorobenzoyl chloride (0.02 mL, 0.14 mmol, 2.0 equiv.) and TEA (0.02 mL, 0.14 mmol, 2.0 equiv.) at room temperature. The mixture was stirred for 15 minutes. Aglycone **S54** (33 mg, 0.068 mmol, 1.0 equiv.) was then introduced, followed by the addition of DMAP (4 mg, 0.034 mmol, 0.5 equiv.). The mixture was stirred for 15 hours and monitored by TLC (silica gel, acetone: hexane = 3: 1 → 1: 4, developed twice). Upon completion, the reaction was quenched with saturated NH₄Cl aqueous solution, extracted with DCM, dried over MgSO₄, and concentrated in vacuo. The resulting crude was purified by flash column chromatography (silica, acetone: hexane = 1: 5), furnishing dibenzoate **75** (15 mg, 0.019 mmol, 28% yield). Dibenzoate **75** was dissolved in EA with a drop of benzene, and slow solvent evaporation furnished a single crystal for X-ray crystallography.

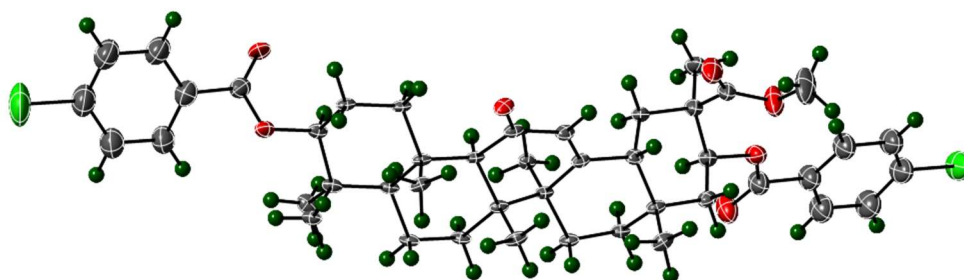
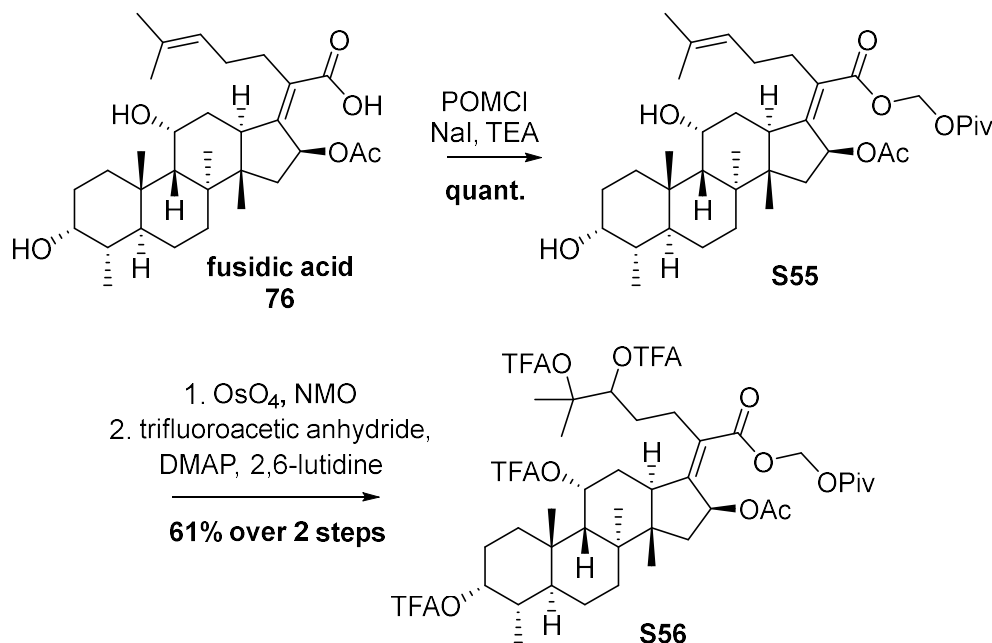


Figure S33. X-ray Crystal Data of **75**.

Identification code	7897dsa	
Empirical formula	C ₄₅ H ₅₄ Cl ₂ O ₇	
Formula weight	777.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁	
Unit cell dimensions	a = 7.3866(3) Å	a = 90°.
	b = 11.2901(4) Å	b = 91.7779(12)°.
	c = 24.4557(9) Å	g = 90°.
Volume	2038.51(13) Å ³	
Z	2	
Density (calculated)	1.267 Mg/m ³	
Absorption coefficient	0.209 mm ⁻¹	
F(000)	828	
Crystal size	0.835 x 0.462 x 0.080 mm ³	
Theta range for data collection	1.987 to 26.441°.	
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 13, -30 ≤ l ≤ 30	
Reflections collected	41965	
Independent reflections	8323 [R(int) = 0.0720]	
Completeness to theta = 25.242°	99.9 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7347
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8323 / 1033 / 635
Goodness-of-fit on F^2	1.028
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0713$, $wR_2 = 0.1986$
R indices (all data)	$R_1 = 0.0757$, $wR_2 = 0.2053$
Absolute structure parameter	0.05(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.710 and -0.535 e. $\text{\AA}^{-3}$

VIII. Oxidative Derivatization of Fusidic Acid



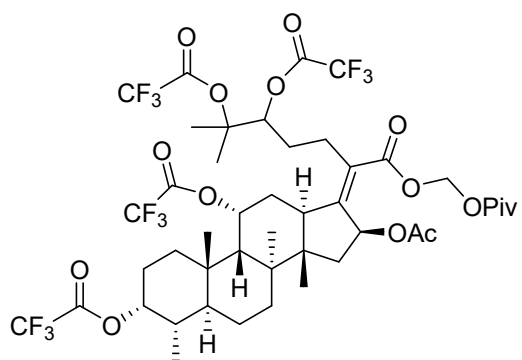
Preparation of oxidation substrate S56. To a stirred solution of fusidic acid **76** (1.2 g, 2.3 mmol, 1.0 equiv.) in DMF (5.8 mL, 0.4 M) were added chloromethyl pivalate (POM-Cl, 97% purity, 1.0 mL, 7 mmol, 3.0 equiv.) and NaI (105 mg, 0.7 mmol, 0.3 equiv.). The reaction mixture was stirred at room temperature for 18 hours, and monitored by TLC (silica, EA: hexane = 1: 1). Upon completion, brine was added to the mixture. The organic portion was extracted with EA, dried over MgSO₄, and concentrated in vacuo. The resulting pivalate **S55** (1.5 g, 2.3 mmol, quantitative yield, yellow-white foamy solid) was used for the next step without further purification.

To a stirred solution of pivalate **S55** (1.5 g, 2.3 mmol, 1.0 equiv.) in acetone: water = 13: 1 mixture (14 mL, 0.15 M) were added NMO (404 mg, 3.5 mmol, 1.5 equiv.) and 0.02 M OsO₄ solution in acetonitrile (3.5 mL, 0.07 mmol, 3 mol%). The reaction was stirred for 6 hours at room temperature, and monitored by TLC (silica, EA: hexane = 1: 1). Upon completion, the reaction was quenched with saturated Na₂S₂O₃ aqueous solution. The organic portion was extracted with

EA, dried over MgSO_4 , and concentrated in vacuo. The resulting crude was purified by flash column chromatography (silica, DCM: MeOH = 20: 1) to afford diol **77** (1.4 g, 2.1 mmol, 93% yield over two steps).

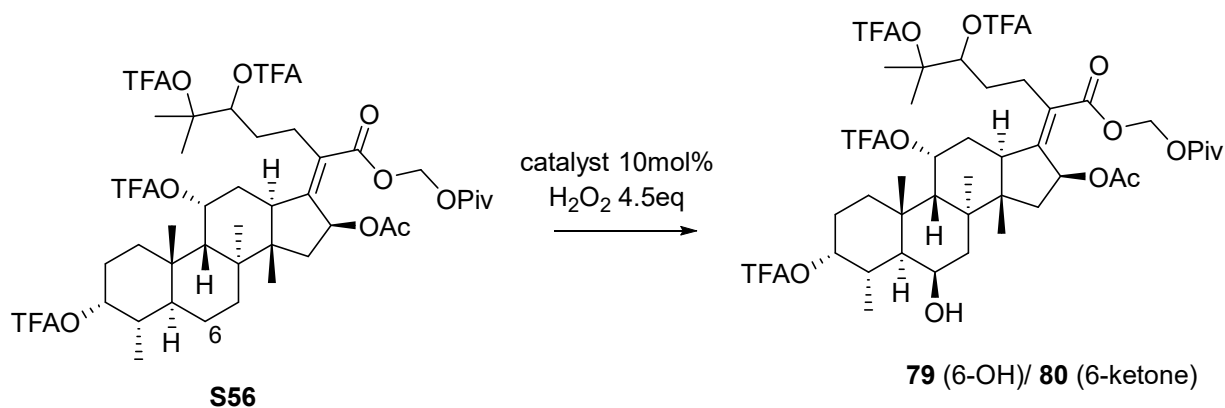
To a stirred solution of the diol **77** (1.4 g, 2.1 mmol, 1.0 equiv.), 2,6-lutidine (1.5 mL, 12.8 mmol, 6.0 equiv.) and DMAP (78 mg, 0.64 mmol, 0.3 equiv.) in THF (21 mL, 0.1 M) was slowly added trifluoroacetic anhydride (1.8 mL, 12.8 mmol, 6.0 equiv.) at -78°C . The reaction was stirred for 10 minutes at -78°C , and monitored by TLC (silica, EA: hexane = 1: 1 $\rightarrow$ EA only). Upon completion, the reaction was quenched with saturated NH_4Cl aqueous solution. The organic portion was extracted with EA, dried over Na_2SO_4 , and concentrated in vacuo. The resulting crude was purified by flash column chromatography (silica, EA: DCM: MeOH = 1: 2: 6) to afford TFA ester **S57** (2.1 g, 2.0 mmol, 93% yield) as a white foamy solid.

(3R,4S,5S,8S,9S,10S,11R,13R,14S,16S,Z)-16-acetoxy-4,8,10,14-tetramethyl-17-(6-methyl-1-oxo-1-((pivaloyloxy)methoxy)-5,6-bis(2,2,2-trifluoroacetoxy)heptan-2-ylidene)hexadecahydro-1H-cyclopenta[a]phenanthrene-3,11-diyl bis(2,2,2-trifluoroacetate)



[S56]. Diastereomeric mixture (d.r. = 0.3: 0.7) ^1H NMR (500 MHz, CDCl_3) δ 5.86 (d, J = 8.5 Hz, 0.3H), 5.82 (d, J = 8.5 Hz, 0.7H), 5.78 (d, J = 5.4 Hz, 0.7H), 5.76 (d, J = 5.5 Hz, 0.3H), 5.68 (d, J = 5.5 Hz, 0.3H), 5.66 (d, J = 5.4 Hz, 0.7H), 5.47 (app s, 0.3H), 5.43 (app s, 0.7H), 5.32 (dd, J = 10.1, 2.7 Hz, 0.7H), 5.24 (dd, J = 10.6, 2.2 Hz, 0.3H), 5.15 - 5.19 (m, 1H), 2.86 - 2.78 (m, 1H), 2.50 - 2.24 (m, 3H), 2.23 - 2.11 (m, 2H), 1.98 - 1.97 (2s, 3H), 1.92 - 1.64 (m, 10H), 1.62 - 1.61 (2s, 3H), 1.59 (s, 0.9H), 1.54 (s, 2.1H), 1.36 (d, J = 14.5 Hz, 1H), 1.33 (s,

3H), 1.31 – 1.23 (m, 2H), 1.20 – 1.19 (2s, 9H), 1.18 – 1.11 (m, 1H), 1.04 - 1.03 (2s, 3H), 0.94 - 0.93 (2s, 3H), 0.87 (app d, $J = 6.7$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.15, 170.10 (170.07), 167.26 (167.11), 157.22 (q, $J = 41.8$ Hz). 157.12 (q, $J = 43.3$ Hz), 156.76 (q, $J = 42.8$ Hz), 155.66 (q, $J = 42.3$ Hz), 151.56 (151.21), 128.15 (127.81), 114.77 (q, $J = 285.6$ Hz), 114.62 (q, $J = 285.6$ Hz), 114.53 (q, q, $J = 285.6$ Hz), 114.2 (q, $J = 287.1$ Hz), 87.77 (87.68), 80.87 (80.62), 80.62 (80.17), 79.45 (79.40), 75.61 (75.50), 73.83 (73.74), 48.66 (48.64), 48.53, 44.46 (44.44), 39.64, 38.88, 38.84, 37.00 (36.98), 36.68, 35.31 (35.27), 31.67 (31.63), 31.53 (31.48), 29.42 (29.40), 28.26, 27.01 (26.91), 26.94 (26.87), 25.44 (25.34), 23.18 (23.13), 22.93 (22.90), 22.00 (21.71), 20.84 (20.81), 20.62 (20.49), 20.52 (20.46), 17.86 (17.80), 15.36. ^{19}F NMR (471 MHz, CDCl_3) δ -75.03 (-75.07), -75.55 (m), -75.80 (-75.86), -75.91 (m) (-75.99 (m)). ^{19}F NMR peak multiplicity indicates this compound contains rotational isomers. HRMS (TOF ESI+) m/z calculated for $\text{C}_{45}\text{H}_{56}\text{F}_{12}\text{NaO}_{14}$ $[\text{M}+\text{Na}]^+$: 1071.3376, found 1071.3379.

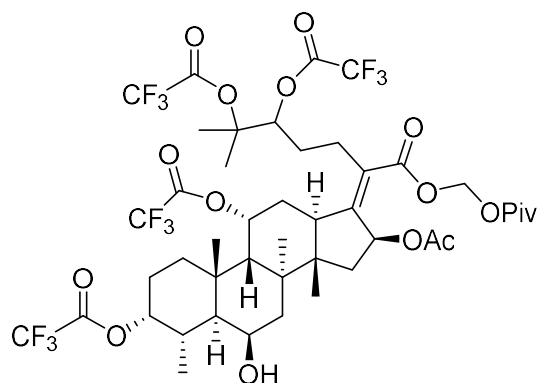


catalyst	yield (rsm)
(<i>S,R,R,S</i>)- 2	56% (18%) ^a
(<i>R,R</i>)- 1	14% (49%) ^b

alcohol **79** : ketone **80** ratio = ^a1.7: 1, ^b1.6: 1

Oxidation of S56. TFA ester **S56** in HFIP was oxidized according to the Standard conditions with 10 mol% catalyst and 4.5 equiv. H₂O₂. The resulting mixture was purified with MPLC (Teledyne Combiflash® system, silica, hexane only → EA: hexane = 1: 3), separating RSM, **79** (C6–OH) and **80** (C6-ketone). With catalyst **2** ((*S,R,R,S*)-Mn(MeCF₃-PDP)). **Run 1 (0.4 mmol scale, 420 mg starting material):** 20% RSM (83 mg, 0.079 mmol), **80** (C6-ketone) 23% (98 mg, 0.092 mmol), **79** (C6–OH) 36% (154 mg, 0.14 mmol), total C-H oxidation 59% (252 mg, 0.24 mmol). **Run 2 (0.37 mmol scale, 393 mg starting material):** 20% RSM (77 mg, 0.073 mmol), **80** (C6-ketone) 22% (79 mg, 0.082 mmol), **79** (C6–OH) 34% (134 mg, 0.13 mmol), total C-H oxidation 56% (221 mg, 0.21 mmol). **Run 3 (0.5 mmol scale, 525 mg starting material):** 15% RSM (80 mg, 0.076 mmol), **80** (C6-ketone) 17% (90 mg, 0.085 mmol), **79** (C6–OH) 36% (190 mg, 0.18 mmol), total C-H oxidation 53% (280 mg, 0.26 mmol). **Average:** 18% RSM ± 2.3%, **80** (C6-ketone) 21% ± 2.6%, **79** (C6–OH) 35% ± 0.9%, total C-H oxidation 56% ± 2.5%. With catalyst **1** ((*R,R*)-Mn(MeCF₃-PDP)). **Run 1 (0.4 mmol scale, 420 mg starting material):** 46% RSM (194 mg, 0.19 mmol), **80** (C6-ketone) 6% (24 mg, 0.022 mmol), **79** (C6–OH) 8% (36 mg, 0.034 mmol), total C-H oxidation 14% (60 mg, 0.056 mmol). **Run 2 (0.4 mmol scale, 420 mg starting material):** 52% RSM (218 mg, 0.21 mmol), **80** (C6-ketone) 5% (23 mg, 0.022 mmol), **79** (C6–OH) 9% (38 mg, 0.035 mmol), total C-H oxidation 14% (61 mg, 0.057 mmol). **Average:** 49% RSM ± 2.9%, **80** (C6-ketone) 6% ± 0.2%, **79** (C6–OH) 9% ± 0.3%, total C-H oxidation 14% ± 0.1%.

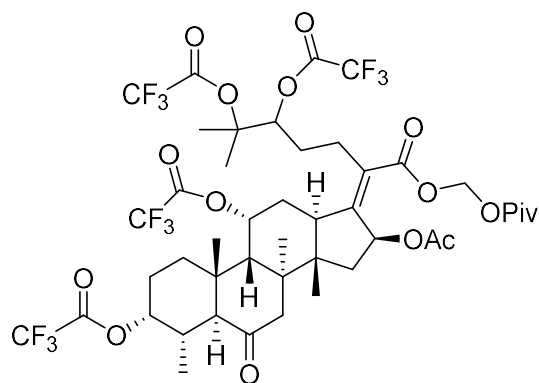
(3R,4S,5S,6R,8S,9S,10S,11R,13R,14S,16S,Z)-16-acetoxy-6-hydroxy-4,8,10,14-tetramethyl-17-(6-methyl-1-oxo-1-((pivaloyloxy)methoxy)-5,6-bis(2,2,2-trifluoroacetoxy)heptan-2-ylidene)hexadecahydro-1H-cyclopenta[a]phenanthrene-3,11-diyl bis(2,2,2-trifluoroacetate)



[79]. Diastereomeric mixture (d.r. = 0.1: 0.9). ^1H NMR (500 MHz, CDCl_3) δ 5.87 (d, J = 8.5 Hz, 0.1H), 5.84 (d, J = 8.4 Hz, 0.9H), 5.77 (d, J = 5.6 Hz, 0.1H), 5.69 (d, J = 5.5 Hz, 0.1H), 5.79 (d, J = 5.4 Hz, 0.9H), 5.67 (d, J = 5.4 Hz, 0.9H), 5.50 (app s, 0.1H), 5.47 (app s, 0.9H), 5.32 (dd, J = 10.3, 2.5 Hz, 0.9H), 5.25

(dd, J = 10.6, 2.3 Hz, 0.1H), 5.22 (app s, 1H), 4.27 – 4.18 (m, 1H), 2.82 (app d, J = 11.0 Hz, 1H), 2.54 – 2.35 (m, 3H), 2.30 – 2.17 (m, 3H), 2.10 – 2.05 (m, 1H), 1.99 (s, 3H), 1.94 – 1.64 (m, 8H), 1.62 (s, 3H), 1.59 (s, 0.3H), 1.54 (s, 2.7H), 1.39 (d, J = 14.5 Hz, 1H), 1.29 (s, 3H), 1.26 (s, 3H), 1.27 – 1.22 (m, 1H), 1.21 (s, 9H), 1.03 (d, J = 5.5 Hz, 3H), 1.00 (s, 0.3H), 0.99 (s, 2.7H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.15, 170.13, 167.06, 157.67 – 156.16 (m, 3C), 155.68 (d, J = 42.8 Hz), 150.94, 128.40, 114.76 (q, J = 285.6 Hz), 114.63 (q, J = 286.1 Hz), 114.52 (q, J = 286.1 Hz), 114.20 (q, J = 287.1 Hz), 87.74, 80.65 (s, 2C), 80.09, 75.28, 73.77, 65.75, 48.65, 48.31, 44.18, 43.54, 40.99, 38.90, 38.89, 38.73, 36.22, 31.81, 31.45, 30.57, 28.20, 26.96 (26.93), 26.84, 25.90, 25.39, 22.11, 21.72, 20.86, 20.49, 18.33, 15.71. ^{19}F NMR (471 MHz, CDCl_3) δ -74.99 (-75.04), -75.52 (m), -75.77 (-75.83), -75.88 (m) (-75.97 (m)). ^{19}F NMR peak multiplicity indicates this compound contains rotational isomers. HRMS (TOF ESI+) m/z calculated for $\text{C}_{45}\text{H}_{56}\text{F}_{12}\text{NaO}_{15}$ $[\text{M}+\text{Na}]^+$: 1087.3325, found 1087.3323.

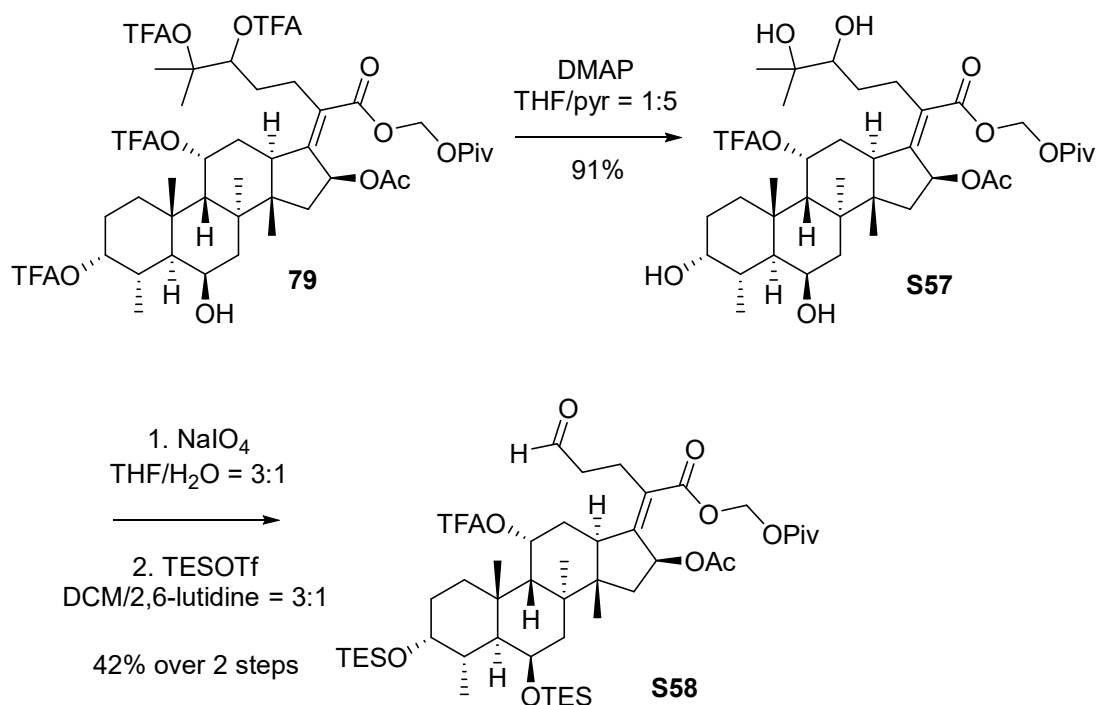
(3R,4S,5S,8S,9S,10R,11R,13R,14S,16S,Z)-16-acetoxy-4,8,10,14-tetramethyl-17-(6-methyl-1-oxo-1-((pivaloyloxy)methoxy)-5,6-bis(2,2,2-trifluoroacetoxy)heptan-2-ylidene)-6-oxohexadecahydro-1H-cyclopenta[a]phenanthrene-3,11-diyl bis(2,2,2-trifluoroacetate) [80].



Major diastereomer. ^1H NMR (500 MHz, CDCl_3) δ 5.86 (d, $J = 8.4$ Hz, 1H), 5.78 (d, $J = 5.4$ Hz, 1H), 5.67 (d, $J = 5.5$ Hz, 1H), 5.42 (m, 1H), 5.32 (dd, $J = 10.5$, 2.4 Hz, 1H), 5.16 (m, 1H), 3.39 (d, $J = 10.8$ Hz, 1H), 2.86 (d, $J = 11.9$ Hz, 1H), 2.56 (d, $J = 18.5$ Hz, 1H), 2.53 – 2.41 (m, 3H), 2.26 – 2.16 (m, 2H), 2.10 (d, $J =$

18.3 Hz, 1H), 2.07 – 2.00 (m, 1H), 1.99 (s, 3H), 1.92 – 1.82 (m, 4H), 1.78 – 1.65 (m, 2H), 1.62 (2s, 6H), 1.54 (s, 3H), 1.36 (d, $J = 14.5$ Hz, 1H), 1.31 – 1.27 (m, 1H), 1.21 (s, 9H), 1.0 (d, $J = 7.0$ Hz, 3H), 0.99 (s, 3H), 0.978 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.96, 177.14, 170.06, 166.84, 157.16 (q, $J = 42.8$ Hz), 156.79 (q, $J = 42.3$ Hz), 156.55 (q, $J = 42.8$ Hz), 155.65 (q, $J = 42.3$ Hz), 150.14, 129.01, 114.73 (q, $J = 286.1$ Hz), 114.61 (q, $J = 286.1$ Hz), 114.49 (q, $J = 285.6$ Hz), 114.19 (q, $J = 286.6$ Hz), 87.68, 80.71, 80.68, 78.81, 74.63, 73.41, 52.64, 51.25, 48.85, 48.32, 44.32, 41.63, 40.09, 39.01, 38.90, 31.17, 30.08, 28.98, 28.01, 26.95, 26.59, 25.51, 24.19, 23.92, 21.72, 20.81, 20.48, 19.14, 15.50. ^{19}F NMR (471 MHz, CDCl_3) δ -75.00, -75.55, -75.84, -75.91.

HRMS (TOF ESI+) m/z calculated for $\text{C}_{45}\text{H}_{54}\text{F}_{12}\text{NaO}_{15}$ $[\text{M}+\text{Na}]^+$: 1085.3169, found 1085.3179.



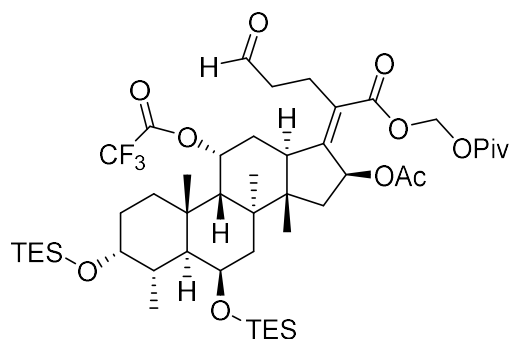
Synthesis of aldehyde intermediate [S58]. To a stirred solution of **79** (418 mg, 0.4 mmol, 1.0equiv.) in pyridine: MeOH = 1: 5 mixture (4 mL, 0.1 M) was added DMAP (238 mg, 2.0 mmol, 5.0 equiv.) at 0°C. The stirred mixture was gradually warmed to room temperature over 3 hours, and monitored by TLC (silica, DCM: EA = 2: 1). Upon completion, the reaction was quenched with saturated NH₄Cl solution. The organic portion was extracted with EA, dried over MgSO₄, and concentrated in vacuo. Heptane was introduced to the mixture and evaporated three times to remove residual pyridine. The resulting crude was purified by flash column chromatography (silica, DCM: EA: MeOH = 10: 10: 1) to afford **S57** (275 mg, 0.35 mmol, 91% yield) as a white foamy solid.

To a stirred solution of **S57** (275 mg, 0.35 mmol, 1.0 equiv.) in THF: water = 3: 1 mixture (1.7 mL, 0.2 M) were added NaIO₄ (299 mg, 1.4 mmol, 4.0 equiv.) at room temperature. The reaction was stirred for 20 minutes at room temperature, and monitored by TLC (silica, DCM: EA = 2: 1). Upon completion, the reaction was diluted with EA (10 mL), quenched with saturated

Na₂S₂O₃ aqueous solution, and diluted with brine. The organic portion was extracted with EA, dried over Na₂SO₄, and concentrated in vacuo. The resulting crude containing aldehyde was used for the next step without further purification.

To a stirred solution of crude (ca. 0.34 mmol, 1.0equiv.) in 2,6-lutidine: DCM = 1: 3 mixture (3.4 mL, 0.1 M) was added TESOTf (0.23 mL, 1.04 mmol, 3.0 equiv.) at -78°C. The mixture was stirred for 30 minutes at -78°C, followed by addition of another TESOTf (0.23 mL, 1.04 mmol, 3.0 equiv.) at -78°C. The reaction was monitored by TLC (silica, EA: hexane = 1: 6). Upon completion, the cold reaction mixture was directly filtered through a pad of silica using a large volume of EA (ca. 100 mL). The organic filtrate was concentrated in vacuo, and purified by flash column chromatography (silica, EA: hexane = 1: 6) to afford TES ether aldehyde **S58** (220 mg, 0.23 mmol, 67% yield over two steps) as a white foamy solid.

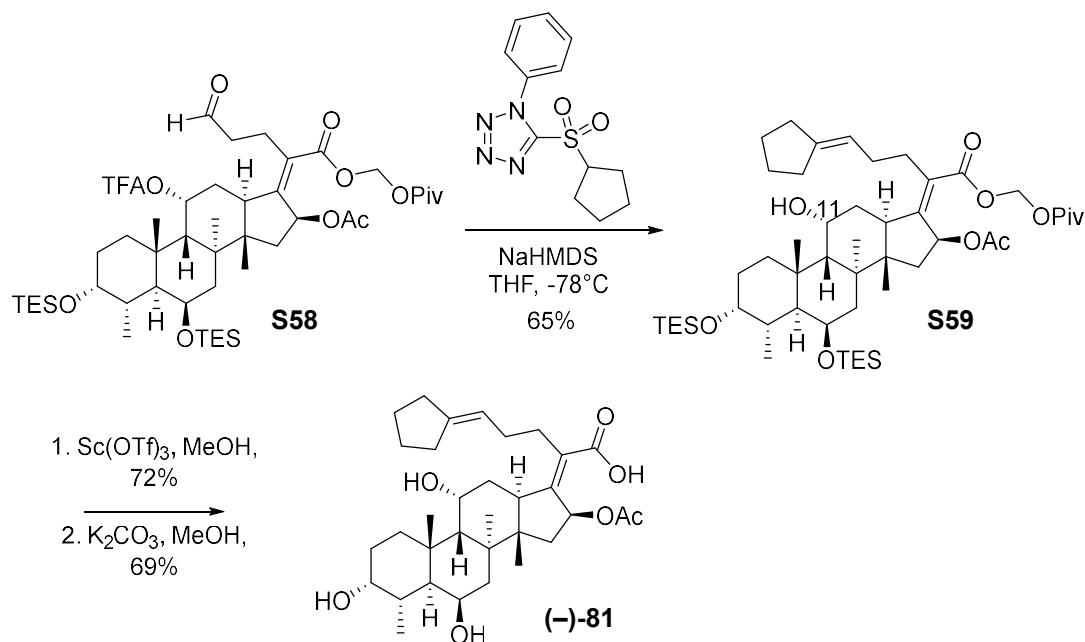
(pivaloyloxy)methyl (Z)-2-((3R,4S,5S,6R,8S,9S,10S,11R,13R,14S,16S)-16-acetoxy-4,8,10,14-tetramethyl-3,6-bis((triethylsilyl)oxy)-11-(2,2,2-trifluoroacetoxy)hexadecahydro-17H-cyclopenta[a]phenanthren-17-ylidene)-5-oxopentanoate [S58]. ¹H NMR (500 MHz, CDCl₃) δ



9.70 (s, 1H), 5.87 (d, *J* = 8.2 Hz, 1H), 5.78 (d, *J* = 5.4 Hz, 1H), 5.70 (d, *J* = 5.4 Hz, 1H), 5.52 (m, 1H), 4.16 (dt, *J* = 7.6, 2.6 Hz, 1H), 3.77 (m, 1H), 2.87 – 2.82 (m, 1H), 2.78 – 2.70 (m, 1H), 2.64 – 2.55 (m, 3H), 2.52 – 2.43 (m, 1H), 2.20 – 2.10 (m, 3H), 2.00 (s, 3H), 1.98 –

1.78 (m, 4H), 1.73 – 1.65 (m, 1H), 1.60 (dd, *J* = 14.6, 7.5 Hz, 1H), 1.54 – 1.48 (m, 1H), 1.37 (d, *J* = 14.3 Hz, 1H), 1.29 (s, 3H), 1.23 (s, 3H), 1.21 (s, 9H), 0.98 (1H, s), 0.96-0.89 (m, 21H), 0.87 – 0.82 (m, 1H), 0.61 – 0.51 (m, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 200.01, 177.21, 170.31, 167.35,

157.05 (q, $J = 42.3$ Hz), 151.13, 128.59, 114.67 (q, $J = 286.1$ Hz), 80.05, 76.06, 74.17, 72.41, 67.40, 48.63, 47.44, 45.36, 44.74, 43.10, 39.95, 39.17, 39.05, 38.93, 36.88, 33.76, 31.68, 31.30, 30.94, 27.03, 24.87, 23.42, 21.36, 20.98, 19.63, 16.68, 7.20, 7.01, 5.50, 5.18. ^{19}F NMR (471 MHz, CDCl_3) δ -75.71. HRMS (TOF ESI+) m/z calculated for $\text{C}_{48}\text{H}_{79}\text{F}_3\text{NaO}_{11}\text{Si}_2$ $[\text{M}+\text{Na}]^+$: 967.5011, found 967.5015.



Synthesis of FA-alcohol [(-)-81]. To a stirred solution of 5-(cyclopentylsulfonyl)-1-phenyl-1H-tetrazole (324 mg, 1.2 mmol, 5.0 equiv.) in THF (2 mL) was added 1M NaHMDS (1.04 mL, 1.04 mmol, 4.5 equiv.) at -78°C under argon atmosphere. The reaction mixture was stirred for 1 hour at -78°C . To the stirred solution, a solution of TES ether aldehyde **S58** (218 mg, 0.23 mmol, 1.0 equiv.) in THF (2.5 mL) was slowly added over 3 minutes at -78°C . The reaction mixture was stirred for 10 minutes at -78°C , and monitored by TLC (silica, EA: hexane = 1: 9, developed twice). Upon completion, the cold reaction mixture was directly poured into a saturated NH_4Cl solution. The organic layer was extracted with ether, dried over Na_2SO_4 , and concentrated in vacuo. The

resulting crude product was purified by flash column chromatography (silica, EA: hexane = 1: 9) to afford TES alkene **S59** (134 mg, 0.15 mmol, 65%) as a colorless foamy gel. (*Note: If C11-TFA formation does not occur simultaneously with olefination, the product can be treated with 2.0 equivalents of NaBH₄ in MeOH (0.5 M) and stirred for 15 minutes at room temperature to yield alkene S59.*)

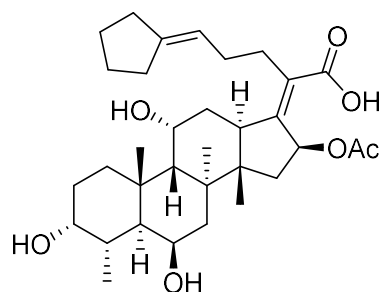
To a stirred solution of TES alkene **S59** (111 mg, 0.12 mmol, 1.0 equiv.) in MeOH (2.5 mL, 0.05 M) was added Sc(OTf)₃ (48 mg, 0.098 mmol, 0.8 equiv.) at 0°C under nitrogen atmosphere. The reaction mixture was stirred at 0°C for 4.5 hours, after which additional Sc(OTf)₃ (24 mg, 0.049 mmol, 0.4 equiv.) was added. The mixture was stirred for another 30 minutes at 0°C, with progress monitored by TLC (silica, EA: DCM = 1: 1). Upon completion, the reaction was quenched by adding saturated NaHCO₃ solution, and the organic layer was extracted with DCM. The organic layer was dried over Na₂SO₄, concentrated in vacuo, and purified by flash column chromatography (silica, EA: DCM = 1: 2 → 1: 1) to afford POM ester triol ((pivaloyloxy)methyl (Z)-2-((3R,4S,5S,6R,8S,9S,10S,11R,13R,14S,16S)-16-acetoxy-3,6,11-trihydroxy-4,8,10,14-tetramethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-ylidene)-5-cyclopentylidenepentanoate, 59 mg, 0.088 mmol, 72% yield) as a sticky gel, which transformed into a white foamy solid under vacuum.

To a stirred solution of the triol (56 mg, 0.083 mmol, 1.0 equiv.) in MeOH (0.8 mL, 0.1 M) was added oven-dried K₂CO₃ (23 mg, 0.17 mmol, 2.0 equiv.) at 0°C under nitrogen atmosphere. The reaction mixture was stirred for 3 hours at 0°C, with progress monitored by TLC (silica, after a mini workup with EA/NH₄Cl (aq.). DCM: EA: MeOH = 3: 3: 1). Upon completion, the reaction mixture was diluted with EA and water, and the aqueous layer was acidified with HCl solution to pH 2. The organic layer was extracted with EA, dried over Na₂SO₄, and concentrated

in vacuo to afford a white solid. This solid was dissolved in a small amount of EA and triturated by slow addition of hexane. The resulting white solid was obtained by decanting the aliquot, then rinsed with hexane and dried to afford **(-)-81** (32 mg, 0.057 mmol, 69% yield) as white flakes.

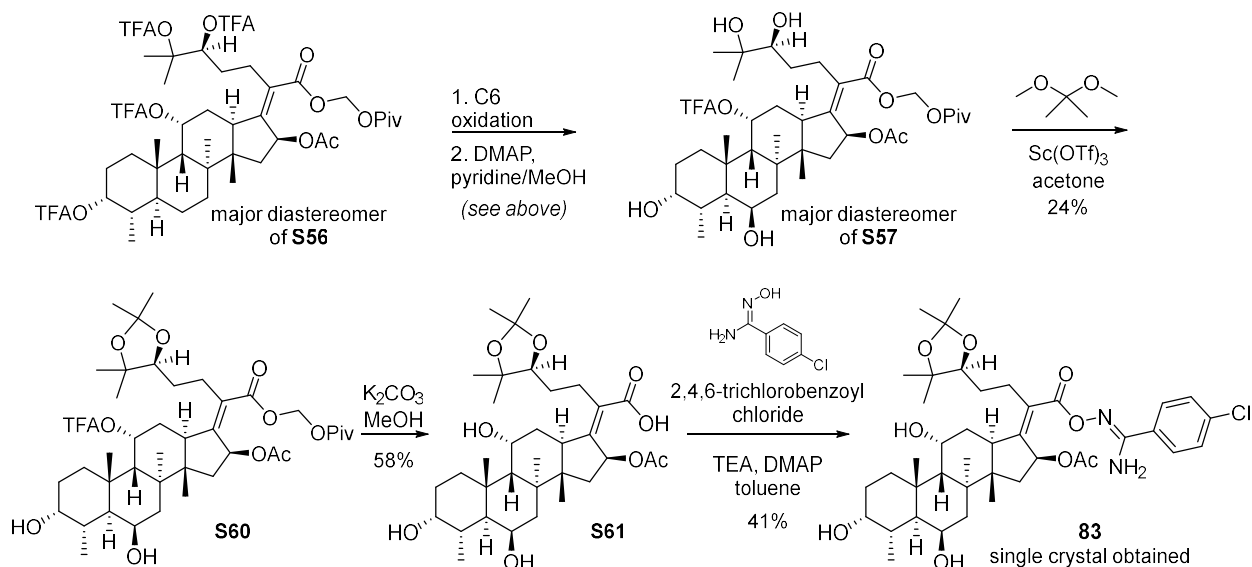
(Z)-2-((3R,4S,5S,6R,8S,9S,10S,11R,13R,14S,16S)-16-acetoxy-3,6,11-trihydroxy-4,8,10,14-tetramethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-ylidene)-5-

cyclopentylidenepentanoic acid [(-)-81]. ¹H NMR (500 MHz, CD₃OD) δ 5.82 (d, *J* = 8.5 Hz,



1H), 5.25 (m, 1H), 4.32 (m, 1H), 4.11 (td, *J* = 7.1, 4.6 Hz, 1H), 3.75 (m, 1H), 3.07 (app d, *J* = 11.4 Hz, 1H), 2.62 – 2.51 (m, 1H), 2.43 – 2.36 (m, 1H), 2.36 – 2.28 (m, 2H), 2.25 – 2.04 (m, 8H), 1.97 (s, 3H), 1.99 – 1.92 (m, 1H), 1.89 – 1.79 (m, 3H), 1.75 – 1.56 (m, 7H), 1.42 (ddd, *J* = 13.3, 4.4, 2.8 Hz, 1H), 1.34 (s, 3H), 1.27 (d, *J*

= 14.1 Hz, 1H), 1.18 (s, 3H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.98 (s, 3H). ¹³C NMR (126 MHz, CD₃OD) δ 174.52, 172.63, 148.21, 145.16, 132.74, 119.86, 75.78, 72.85, 68.28, 67.46, 50.74, 49.62, 44.66, 44.41, 41.00, 40.05, 39.72, 37.43, 37.37, 34.49, 34.33, 32.27, 30.99, 30.82, 29.73, 29.48, 27.37 (2C), 26.49, 23.28, 20.71, 18.53, 16.72. [α]_D²⁵ = -10.2 (c=0.17, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₃₃H₅₀F₃NaO₇ [M+Na]⁺: 581.3454, found 581.3448. The stereochemistry of C6-hydroxyl group was confirmed by X-ray crystallography analysis of analogue **83**.



Preparation of FA-C6–OH analogue 83. Diastereomerically pure **S57** was obtained following the procedure described above, through oxidation of the major diastereomer of TFA ester **S56**. To a stirred solution of diastereomerically pure **S57** (78 mg, 0.1 mmol, 1.0 equiv.) in 2,2-dimethoxypropane: acetone = 1: 2 mixture (1.0 mL, 0.1 M) was added $\text{Sc}(\text{OTf})_3$ (5 mg, 0.01 mmol, 0.1 equiv.) at room temperature. The mixture was stirred for 10 minutes, with progress monitored by TLC (silica, EA: hexane = 1: 1). Upon completion, the reaction mixture was filtered directly through a silica pad with acetone (*Note: concentrating the reaction mixture induced product decomposition*). The filtrate was collected, concentrated, and purified by flash column chromatography (silica, acetone: hexane = 1: 3) to afford **S60** (20 mg, 0.024 mmol, 24% yield) as a transparent oil.

To a stirred solution of **S60** (20 mg, 0.024 mmol, 1.0 equiv.) in MeOH (2.4 mL, 0.01 M) was added oven-dried K_2CO_3 (13 mg, 0.096 mmol, 4.0 equiv.) at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 1 hour, with progress monitored by TLC (silica, acetone only). Upon completion, the reaction mixture was quenched with saturated NH_4Cl solution, and the organic layer was extracted with DCM five times. The remaining aqueous layer

was acidified with 4N HCl to pH 2 and quickly extracted with DCM three times. The combined organic layer was dried over Na₂SO₄ and concentrated in vacuo to afford **S61** (8.4 mg, 0.014 mmol, 58 % yield) as a white foamy solid. **S61** was used directly in the next step without further purification. To the solution of **S61** (8.4 mg, 0.014 mmol, 1.2 equiv.) in toluene (1.4 ml, 0.01 M) were added 2,4,6-trichlorobenzoyl chloride (4 mg, 0.017 mmol, 1.2 equiv.) and TEA (0.004 ml, 0.025 mmol, 1.8 equiv.) at room temperature. The mixture was stirred for 5 minutes, with full consumption of **S61** confirmed by TLC (silica, acetone: hexane = 1.5: 1). 4-chloro-N-hydroxybenzimidamide (4.8 mg, 0.028 mmol, 2.0 equiv.) was then added, followed by DMAP (21 mg, 0.17 mmol, 1.2 equiv.). The mixture was stirred for 30 minutes, with progress monitored by TLC (silica gel, acetone: hexane = 1.5: 1). Upon completion, the reaction mixture was concentrated in vacuo and purified by flash column chromatography (silica, acetone: hexane = 1: 1.5) to afford ester **83** (5 mg, 0.006 mmol, 41% yield) as a white solid. **83** was dissolved in a small amount of EA, and a single crystal was obtained by EA-toluene diffusion.

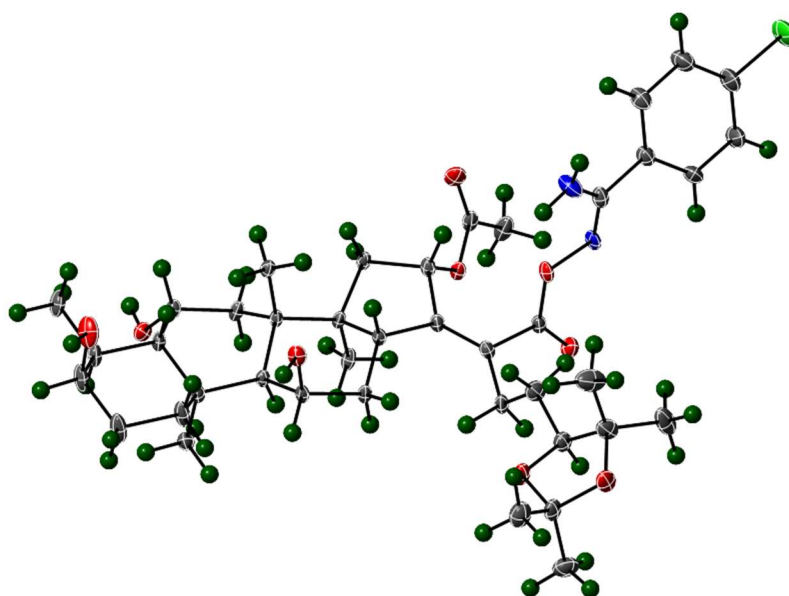
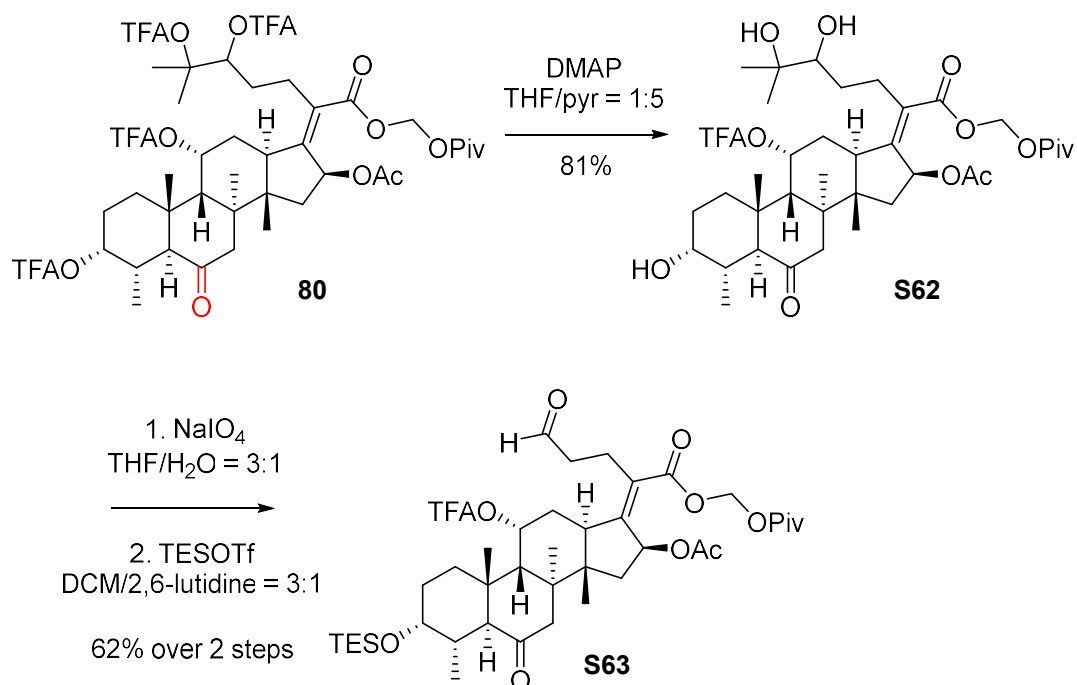


Figure S34. X-ray Crystal Data of **83**.

Identification code	8039ds	
Empirical formula	C ₅₅ H ₇₅ Cl N ₂ O ₉	
Formula weight	943.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	$a = 20.1695(6)$ Å	$a = 90^\circ$.
	$b = 14.6512(4)$ Å	$b = 118.9602(8)^\circ$.
	$c = 20.3624(8)$ Å	$c = 90^\circ$.
Volume	5264.8(3) Å ³	
Z	4	

Density (calculated)	1.190 Mg/m ³
Absorption coefficient	0.128 mm ⁻¹
F(000)	2032
Crystal size	0.314 x 0.074 x 0.048 mm ³
Theta range for data collection	2.286 to 25.411°.
Index ranges	-24 ≤ h ≤ 24, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24
Reflections collected	64405
Independent reflections	9676 [R(int) = 0.0463]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6744
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9676 / 605 / 699
Goodness-of-fit on F ²	1.068
Final R indices [I > 2σ(I)]	R1 = 0.0533, wR2 = 0.1394
R indices (all data)	R1 = 0.0577, wR2 = 0.1430
Absolute structure parameter	0.01(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.544 and -0.385 e.Å ⁻³



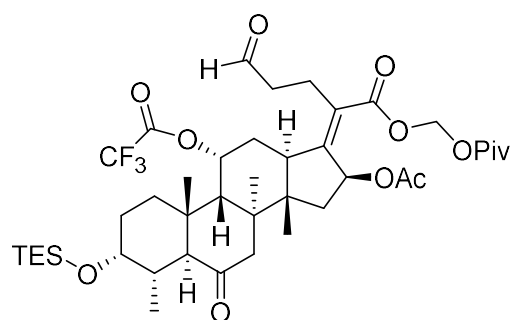
Synthesis of aldehyde intermediate S63. To a stirred solution of **80** (C6-ketone) (505 mg, 0.48 mmol, 1.0equiv.) in pyridine: MeOH = 1: 5 mixture (4.8 mL, 0.1 M) was added DMAP (290 mg, 2.4 mmol, 5.0 equiv.) at 0°C. The stirred mixture was gradually warmed to room temperature over 3 hours, and monitored by TLC (silica, DCM: EA = 2: 1). Upon completion, the reaction was quenched with saturated NH_4Cl solution. The organic portion was extracted with EA, dried over MgSO_4 , and concentrated in vacuo. Heptane was introduced to the mixture and evaporated three times to remove residual pyridine. The resulting crude was purified by flash column chromatography (silica, DCM: EA: MeOH = 25: 5: 1) to afford **S62** (299 mg, 0.39 mmol, 81% yield) as a white foamy solid.

To a stirred solution of **S62** (280 mg, 0.36 mmol, 1.0 equiv.) in THF: water = 3: 1 mixture (1.8 mL, 0.2 M) were added NaIO_4 (309 mg, 1.45 mmol, 4.0 equiv.) at room temperature. The reaction was stirred for 25 minutes at room temperature, and monitored by TLC (silica, DCM: EA: MeOH = 4: 1: 0.3). Upon completion, the reaction was diluted with EA (10 mL), quenched with

saturated Na₂S₂O₃ aqueous solution, and diluted with brine. The organic portion was extracted with EA, dried over Na₂SO₄, and concentrated in vacuo. The resulting crude containing aldehyde was used for the next step without further purification.

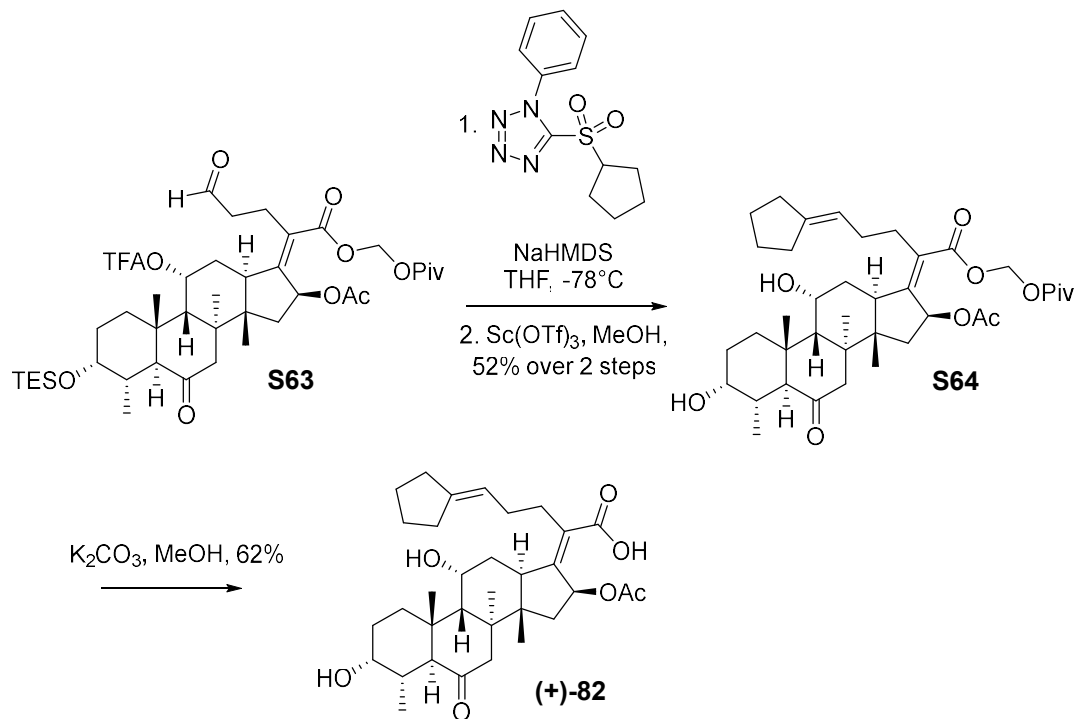
To a stirred solution of crude (ca. 0.36 mmol, 1.0equiv.) in 2,6-lutidine: DCM = 1: 3 mixture (3.6 mL, 0.1 M) was added TESOTf (0.04 mL, 0.18 mmol, 0.5 equiv.) at -78°C. The mixture was stirred for 10 minutes at -78°C, followed by addition of another TESOTf (0.04 mL, 0.18 mmol, 0.5 equiv.) at -78°C. The reaction was monitored by TLC (silica, DCM: EA = 4: 1). Upon completion, the cold reaction mixture was directly filtered through a pad of silica with DCM: EA = 4: 1, followed by EA. The organic filtrate was concentrated in vacuo, and purified by flash column chromatography (silica, EA: DCM = 1: 20) to afford TES ether aldehyde **S63** (186 mg, 0.22 mmol, 62% yield over two steps) as a white foamy solid.

(pivaloyloxy)methyl (Z)-2-((3R,4S,5S,8S,9S,10R,11R,13R,14S,16S)-16-acetoxy-4,8,10,14-tetramethyl-6-oxo-3-((triethylsilyl)oxy)-11-(2,2,2-trifluoroacetoxy)hexadecahydro-17H-cyclopenta[a]phenanthren-17-ylidene)-5-oxopentanoate [S63]. ¹H NMR (500 MHz, CDCl₃) δ



9.69 (s, 1H), 5.89 (d, *J* = 8.2 Hz, 1H), 5.77 (d, *J* = 5.4 Hz, 1H), 5.70 (d, *J* = 5.3 Hz, 1H), 5.46 (m, 1H), 3.74 (m, 1H), 3.53 (br-d, *J* = 10.5 Hz, 1H), 2.92 (app d, *J* = 12.6 Hz, 1H), 2.80 – 2.74 (m, 2H), 2.64 – 2.43 (m, 4H), 2.31 – 2.13 (m, 2H), 2.05 (d, *J* = 18.0 Hz, 1H), 1.98 (s, 3H), 1.92 – 1.84 (m, 2H), 1.77 (m, 1H), 1.64 (s, 3H), 1.69 – 1.57 (m, 2H), 1.35 (d, *J* = 14.3 Hz, 1H), 1.21 (s, 9H), 1.05 (m, 1H), 0.98 (br-s, 3H). 0.97 – 0.89 (m, 15H), 0.57 (3q, *J* = 7.9 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 212.34, 199.97, 177.19, 170.16, 167.16, 156.91 (q, *J* = 42.8 Hz),

149.99, 129.29, 114.63 (q, $J = 286.0$ Hz), 80.09, 75.18, 73.76, 71.04, 51.95, 51.78, 48.98, 48.58, 44.73, 42.71, 42.20, 40.87, 39.01, 38.93, 31.92, 31.26, 30.53, 28.99, 27.02, 23.99, 23.81, 21.32, 20.86, 19.71, 16.29, 6.98, 5.09. ^{19}F NMR (471 MHz, CDCl_3) δ -75.56. HRMS (TOF ESI+) m/z calculated for $\text{C}_{42}\text{H}_{64}\text{F}_3\text{O}_{11}\text{Si}$ $[\text{M}+\text{H}]^+$: 829.4170, found 829.4154.



Synthesis of FA-ketone [(+)-82]. To a stirred solution of 5-(cyclopentylsulfonyl)-1-phenyl-1H-tetrazole (324 mg, 1.2 mmol, 5.8 equiv.) in THF (2 mL) was added 1M NaHMDS (1.04 mL, 1.04 mmol, 5.2 equiv.) at -78°C under argon atmosphere. The reaction mixture was stirred for 2 hour at -78°C . To the stirred solution, a solution of TES ether aldehyde **S63** (166 mg, 0.2 mmol, 1.0 equiv.) in THF (2.5 mL) was slowly added over 3 minutes at -78°C . The reaction mixture was stirred for 5 minutes at -78°C , and monitored by TLC (silica, EA: hexane = 1: 3). Upon completion, the cold reaction mixture was directly poured into a saturated NH_4Cl solution. The organic layer was extracted with ether, dried over MgSO_4 , and concentrated in vacuo. The resulting crude

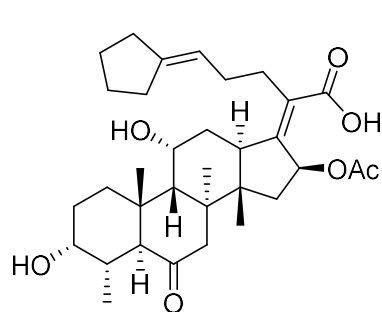
product was purified by flash column chromatography (silica, EA: hexane = 1: 6 → 1: 4) to afford TES alkene mixed with 5-(cyclopentylsulfonyl)-1-phenyl-1H-tetrazole (62% yield based on quantitative ^1H NMR). The mixture was used for the next step without further purification.

To a stirred solution of a mixture containing TES alkene (ca. 0.12 mmol, 1.0 equiv.) in MeOH (2.5 mL, 0.05 M) was added $\text{Sc}(\text{OTf})_3$ (24 mg, 0.05 mmol, 0.4 equiv.) at 0°C under nitrogen atmosphere. The reaction mixture was stirred at 0°C for 1 hour, after which additional $\text{Sc}(\text{OTf})_3$ (12 mg, 0.025 mmol, 0.2 equiv.) was added. The mixture was stirred for another 30 minutes at 0°C , with progress monitored by TLC (silica, EA: hexane = 1: 5). Upon completion, the reaction was quenched by adding saturated NaHCO_3 solution, and the organic layer was extracted with DCM. The organic layer was dried over MgSO_4 , concentrated in vacuo, and purified by flash column chromatography (silica, EA: DCM = 1: 3) to afford **S64** (70 mg, 0.104 mmol, 52% yield over two steps) as a white foamy solid.

To a stirred solution of **S64** (60 mg, 0.089 mmol, 1.0 equiv.) in MeOH (0.9 mL, 0.1 M) was added oven-dried K_2CO_3 (25 mg, 0.18 mmol, 2.0 equiv.) at 0°C under nitrogen atmosphere. The reaction mixture was stirred for 3.5 hours at 0°C , with progress monitored by TLC (silica, after a mini workup with EA/ NH_4Cl (aq.). DCM: EA: MeOH = 10: 10: 1). Upon completion, the reaction mixture was diluted with EA and water, and the aqueous layer was acidified with HCl solution to pH 2. The organic layer was extracted with EA, dried over Na_2SO_4 , and concentrated in vacuo to afford a white solid. This solid was dissolved in a small amount of EA: ether = 1: 1 mixture, and triturated by slow addition of pentane. The resulting white solid was obtained by decanting the aliquot, then rinsed with pentane and dried to afford (+)-**82** (31 mg, 0.055 mmol, 62% yield) as a white solid.

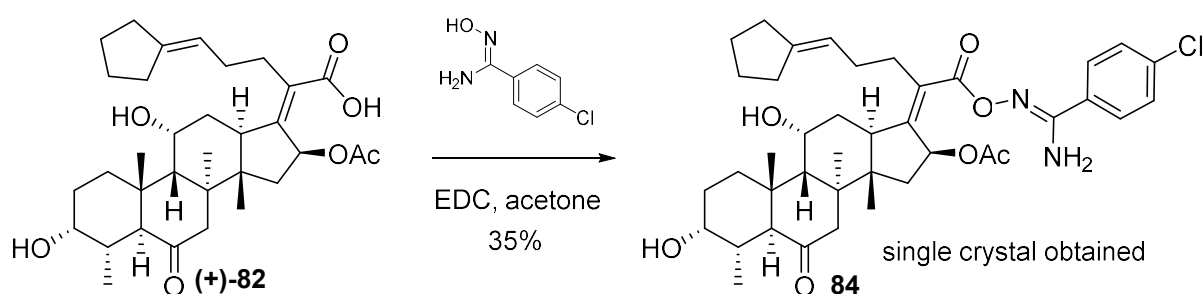
(Z)-2-((3R,4S,5S,8S,9S,10R,11R,13R,14S,16S)-16-acetoxy-3,11-dihydroxy-4,8,10,14-tetramethyl-6-oxohexadecahydro-17H-cyclopenta[a]phenanthren-17-ylidene)-5-

cyclopentylidenepentanoic acid [(+)-82]. ^1H NMR (500 MHz, CD_3OD) δ 5.86 (d, J = 8.3 Hz,



1H), 5.25 (m, 1H), 4.26 (m, 1H), 3.72 – 3.69 (m, 1H), 3.53 (br-d, J = 10.7 Hz, 1H), 3.16 (app d, J = 11.5 Hz, 1H), 2.67 – 2.53 (m, 2H), 2.47 (d, J = 18.0 Hz, 1H), 2.45 – 2.31 (m, 2H), 2.29 – 2.04 (m, 7H), 2.01 (d, J = 18.0 Hz, 1H), 1.96 (s, 3H), 1.94 – 1.72 (m, 4H), 1.68 (s, 3H), 1.70 – 1.50 (m, 6H), 1.27 (d, J = 14.0 Hz, 1H),

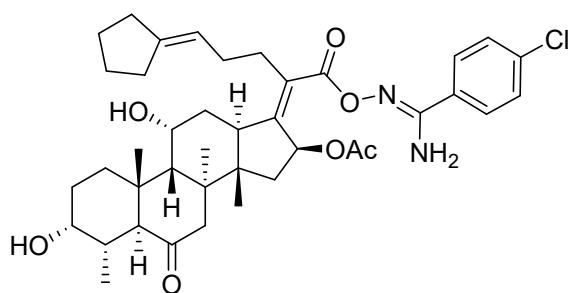
0.98 (d, J = 6.6 Hz, 3H), 0.95 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (126 MHz, CD_3OD) δ 217.18, 173.96, 172.53, 148.45, 145.29, 132.93, 119.74, 75.53, 71.23, 67.47, 53.50, 53.05, 50.90, 49.66, 44.99, 43.43, 42.28, 40.17, 37.09, 34.50, 32.42, 31.23, 30.82, 30.75, 29.72, 29.48, 27.38, 27.36, 25.18, 24.13, 20.67, 19.39, 16.33. $[\alpha]_{\text{D}}^{25}$ = +18.24 (c =0.25, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{33}\text{H}_{48}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$: 579.3298, found 579.3287. The structure of the FA-C6-ketone was confirmed by X-ray crystallography analysis of its analogue **84**.



Preparation of ketone analogue 84. To a stirred solution of **82** (29 mg, 0.052 mmol, 1.0 equiv.) in acetone (2.6 mL, 0.02 M) was added EDC (60 mg, 0.31 mmol, 6.0 equiv.) at room temperature. The mixture was stirred for 1 hour, followed by the addition of 4-chloro-N-hydroxybenzimidamide

(44 mg, 0.26 mmol, 5.0 equiv.). The reaction was monitored by TLC (silica, EA: DCM: MeOH = 5: 5: 1). Upon completion, brine was added to the mixture. The organic portion was extracted with EA, dried over Na₂SO₄ and concentrated *in vacuo*. The resulting crude was purified by flash column chromatography (silica, EA: DCM: MeOH = 5: 5: 1) to afford a mixture of ester **84** and benzimidamide reagent (37 mg) as a white solid. The mixture was dissolved in a mixture of isopropyl ether and benzene and kept at a low temperature until spontaneous solidification occurred. The solution was decanted, and the remaining solid was rinsed with ether to afford **84** (13 mg, 0.018 mmol, 35% yield) as a white solid. A single crystal of ester **84** was obtained by dissolving approximately 10 mg of ester **84** in 0.1 mL of acetonitrile with a drop of benzene, followed by slow diffusion of diethyl ether into the solution over 2 days.

(3R,4S,5S,8S,9S,10R,11R,13R,14S,16S,Z)-17-(1-((((Z)-amino(4-chlorophenyl)methylene)amino)oxy)-5-cyclopentylidene-1-oxopentan-2-ylidene)-3,11-dihydroxy-4,8,10,14-tetramethyl-6-oxohexadecahydro-1H-cyclopenta[a]phenanthren-16-yl



acetate [84]. ¹H NMR (500 MHz, CDCl₃) δ 7.62

(app d, *J* = 8.6 Hz, 2H), 7.39 (app d, *J* = 8.5 Hz,

2H), 5.80 (d, *J* = 8.8 Hz, 1H), 5.23 (m, 1H), 5.04 –

4.83 (m, 2H), 4.37 – 4.30 (m, 1H), 3.85 – 3.77 (m,

1H), 3.46 (d, *J* = 10.6 Hz, 1H), 3.16 (d, *J* = 12.1 Hz, 1H), 2.62 – 2.46 (m, 4H), 2.37 (app dt, *J* =

13.2, 3.3 Hz, 1H), 2.30 (dd, *J* = 14.3, 9.1 Hz, 1H), 2.25 – 2.10 (m, 6H), 2.04 – 1.95 (m, 5H), 1.92

– 1.79 (m, 3H), 1.67 (s, 3H), 1.66 – 1.51 (m, 6H), 1.26 (d, *J* = 14.6 Hz, 1H), 1.05 (d, *J* = 6.6 Hz,

3H), 0.96 (s, 3H), 0.93 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 213.00, 171.08, 167.59, 155.56,

146.85, 144.80, 137.25, 130.07, 129.90, 129.15, 128.21, 118.49, 74.07, 70.59, 67.63, 52.03, 51.99,

49.95, 48.60, 43.57, 42.13, 41.05, 39.31, 35.41, 33.78, 31.17, 30.41, 29.87, 29.82, 29.24, 28.96, 26.53 (2C), 25.05, 24.01, 21.09, 19.16, 15.98. HRMS (TOF ESI+) m/z calculated for $C_{40}H_{54}ClN_2O_7$ $[M+H]^+$: 709.3620, found 709.3619.

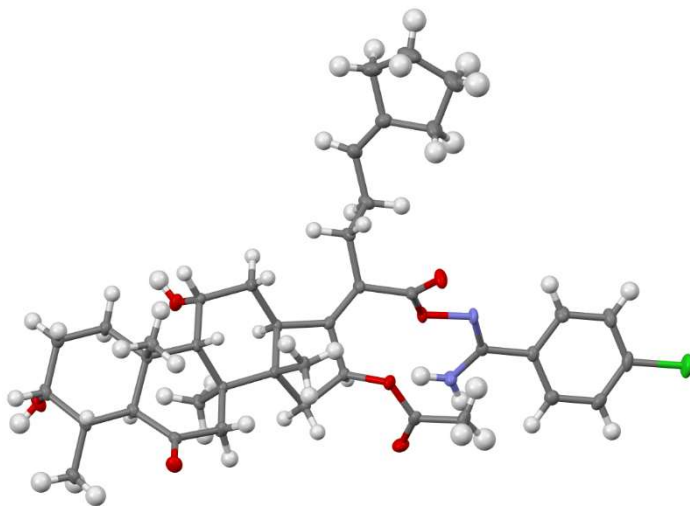
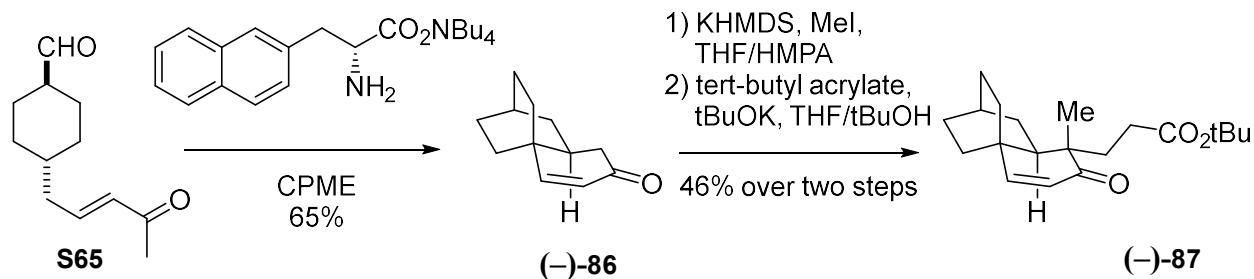


Figure S35 X-ray Crystal Data of **84**.

Identification code	ed80ks_sq	
Empirical formula	C ₄₀ H ₅₃ Cl N ₂ O ₇	
Formula weight	709.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁	
Unit cell dimensions	$a = 12.5410(3)$ Å	$a = 90^\circ$.
	$b = 8.0366(2)$ Å	$b = 96.8652(6)^\circ$.
	$c = 21.9163(5)$ Å	$c = 90^\circ$.

Volume	2193.04(9) Å ³
Z	2
Density (calculated)	1.074 Mg/m ³
Absorption coefficient	0.131 mm ⁻¹
F(000)	760
Crystal size	0.356 x 0.109 x 0.091 mm ³
Theta range for data collection	2.334 to 27.495°.
Index ranges	-16<=h<=16, -10<=k<=10, -28<=l<=28
Reflections collected	76994
Independent reflections	10047 [R(int) = 0.0383]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7157
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10047 / 164 / 514
Goodness-of-fit on F ²	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0295, wR2 = 0.0720
R indices (all data)	R1 = 0.0313, wR2 = 0.0735
Absolute structure parameter	-0.004(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.204 and -0.216 e.Å ⁻³

IX. Synthesis of Platencin and Its Analogues

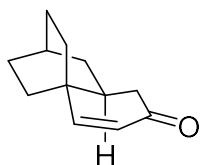


Preparation of oxidation substrate [(-)-87]. The procedure of Yamamoto et al.⁴⁵ was scaled up for multigram synthesis. Aldehyde **S65** was prepared in 7 steps from [(1R,4R)-4-{[(tert-butyl)dimethylsilyl]oxy}methyl}cyclohexyl]methanol (commercially available from Aldrich, CAS: 180046-62-2). Aldehyde **S65** (2.944 g, 15.16 mmol, 1 eq) and silica gel absorbed tetrabutylammonium salt of (S)-3-(2-naphthyl)-D-alanine (formal “molecular weight” = 1684 mg/mmol, 12.76 g, 50 mol%) were suspended in 152 mL cyclopentyl methyl ether and stirred at room temperature for 5 days. The reaction mixture was then diluted with Et₂O and filtered with Et₂O washing. The mixture was concentrated and the crude residue dissolved in ethanol (300 mL). Sodium hydroxide (1.8 g) was added and the solution was stirred for 24 hours, after which ethanol was removed under reduced pressure. The residue was dissolved in EtOAc, washed with water and brine, and dried over Na₂SO₄. The crude material was purified by column chromatography (1: 19 EtOAc/Hexanes) to furnish (-)-(2S,4aS,8aS)-1,2,3,4,8,8a-hexahydro-7H-2,4a-ethanonaphthalen-7-one **86** (1.7307 g, 9.82 mmol, 65%).

0.5 M KHMDS in toluene (29.3 mL, 14.67 mmol, 1.5 equiv.) was added slowly to a solution of 1,2,3,4,8,8a-hexahydro-7H-2,4a-ethanonaphthalen-7-one **86** (1.728 g, 9.78 mmol, 1.0 equiv.) in THF (98 mL) at -78 °C. The solution was stirred for 45 min and treated with HMPA (9.8 mL) and MeI (4.9 mL, 78.24 mmol, 8.0 equiv.) sequentially. The reaction mixture was stirred at -

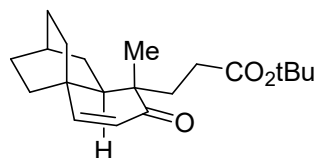
78 °C for one hour, then allowed to warm to 23 °C. The reaction was quenched with saturated aqueous NaHCO₃ solution and extracted three times with EtOAc. The combined organic layers were washed twice with H₂O, brine, dried over MgSO₄, and concentrated. Flash chromatography (19: 1 hexanes/EtOAc) afforded corresponding methyl enones (1.666 g, 8.76 mmol, 90% yield) as a mixture of diastereomers, which were both used for the next step. To a solution of the mixture of methyl enones (500 mg, 2.63 mmol, 1.0 equiv.) in THF (26 mL) was added a solution of potassium tert-butoxide (590 mg, 5.26 mmol, 2.0 equiv.) in tert-butanol (5.3 mL). The mixture was stirred for 15 minutes, then tert-butyl acrylate (0.77 mL, 5.26 mmol, 2.0 equiv.) was added and the reaction was stirred for 30 minutes. The reaction was quenched with saturated aqueous ammonium chloride, extracted 3x with diethyl ether, and combined organics were dried over magnesium sulfate. The crude reaction mixture was purified by silica column chromatography (1: 9 EtOAc: hexanes), furnishing 720 mg of a mixture of diastereomers (d.r. = 2.3: 1). The major diastereomer was isolated using a Teledyne Combiflash automated flash column chromatography system (3: 97 EtOAc: hexanes), furnishing the desired oxidation substrate (–)-**87** (427 mg, 1.34 mmol, 51% yield).

(–)-(2S,4aS,8aS)-1,2,3,4,8,8a-hexahydro-7H-2,4a-ethanonaphthalen-7-one [(–)-**86**]. The



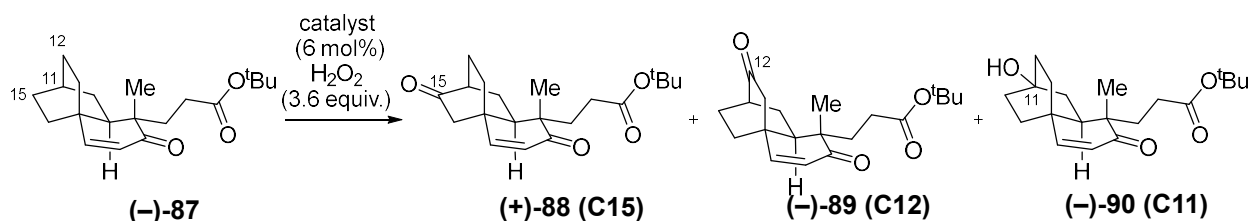
spectroscopic data of **86** matched those reported in the literature⁵³. 92% e.e. (HPLC). $[\alpha]_D^{22.5} = -99.8$ (c=1.0, CHCl₃).

tert-butyl 3-((2S,4aS,8S,8aR)-8-methyl-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoate [(-)-87]. ¹H NMR (600 MHz, CDCl₃) δ 6.39 (d, *J* = 10.0 Hz,



1H), 5.77 (d, *J* = 10.1 Hz, 1H), 2.20 – 2.09 (m, 2H), 2.09 – 1.99 (m, 2H), 1.93 – 1.85 (m, 1H), 1.82 (br s, 1H), 1.69 – 1.47 (m, 7H), 1.45 – 1.39 (m, 2H), 1.43 (s, 9H), 1.37 – 1.28 (m, 1H), 1.12 (s, 3H). ¹³C NMR

(151 MHz, CDCl₃) δ 204.85, 173.21, 155.87, 125.88, 80.21, 47.32, 38.77, 35.74, 33.62, 30.75, 29.84, 28.25, 27.10, 26.80, 25.57, 24.99, 24.92, 21.46. HRMS (TOF ESI+) *m/z* calculated for C₂₀H₃₁O₃ [M+H]⁺: 319.2273, found 319.2267. [α]_D^{23.6} = -66.14° (c = 1.00, CHCl₃)

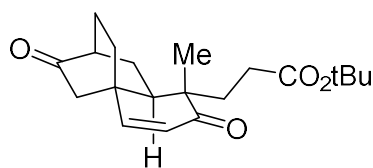


catalyst	yield	C11: C12: C15
(<i>R,R</i>)- 1	73%	1.8: 2.6: 1
(<i>S,S</i>)- 1	77%	1.2: 2.4: 1
(<i>S,R,R,S</i>)- 2	72%	1 : 2.6: 1.5
(<i>R,S,S,R</i>)- 2	66%	1 : 3 : 1.7

Oxidation of tert-butyl 3-((2S,4aS,8S,8aR)-8-methyl-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoate [(-)-87]. Tert-butyl 3-((2S,4aS,8S,8aR)-8-methyl-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoate was oxidized with slight modification to the Standard conditions (6 mol% catalyst, 3.6 equiv. hydrogen peroxide). Purification by flash column chromatography (2: 3 → 2: 1 EtOAc: hexanes) furnished two mixtures: a diastereomeric mixture of ketones (C15 & C12) and a mixture of alcohols (C11, C15, and C12 hydroxylated products). Ratios were determined by ¹H NMR analysis of each mixture. Secondary alcohols were observed to be a complex diastereomeric mixture, so the alcohol mixture

was subjected to DMP oxidation (1.2 equiv. DMP, 0.1 M in dichloromethane, stirred for 1h before purification by flash column chromatography [1: 1 → 2: 1 EtOAc: hexanes] which furnished clean C11 alcohol and a mixture of ketone diastereomers). Ketone diastereomers were separated using a Teledyne Combiflash automated chromatography system (3: 97 iPrOH: hexanes). With (*R,R*)-MnCF₃-PDP. **Run 1**: 74% yield, C11:C12:C15 = 1.8: 2.6: 1. **Run 2**: 72% yield, C11:C12:C15 = 1.8: 2.6: 1. **Average**: 73% ± 1%. With (*S,S*)-MnCF₃-PDP. **Run 1**: 77% yield, C11:C12:C15 = 1.2: 2.4: 1. **Run 2**: 77% yield, C11:C12:C15 = 1.2: 2.4: 1. **Average**: 77%. With (*S,R,R,S*)-MnMeCF₃-PDP. **Run 1**: 72% yield, C11:C12:C15 = 1: 2.6: 1.5. **Run 2**: 71% yield, C11:C12:C15 = 1: 2.6: 1.5. **Average**: 71.5% ± 0.5%. (*R,S,S,R*)-MnMeCF₃-PDP. **Run 1**: 68% yield, C11:C12:C15 = 1: 3: 1.7. **Run 2**: 63% yield, C11:C12:C15 = 1: 3: 1.7. **Average**: 65.5% ± 2.5%.

tert-butyl 3-((2*S*,4*aS*,8*S*,8*aR*)-8-methyl-3,7-dioxo-1,3,4,7,8,8*a*-hexahydro-2*H*-2,4*a*-ethanonaphthalen-8-yl)propanoate [(+)-88]. ¹H NMR (500 MHz, CDCl₃) δ 6.48 (d, *J* = 10.2 Hz,



1H), 5.90 (d, *J* = 10.1 Hz, 1H), 2.50 (br s, 1H), 2.31 (d, *J* = 18.1 Hz, 1H), 2.17 – 2.07 (m, 3H), 2.07 – 1.98 (m, 3H), 1.97 – 1.87 (m, 3H), 1.73 (dd, *J* = 12.4, 10.6 Hz, 1H), 1.69 – 1.60 (m, 1H), 1.58 –

1.52 (m, 1H), 1.41 (s, 9H), 1.20 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 213.65, 203.06, 172.69, 151.60, 127.23, 80.50, 52.69, 47.33, 43.01, 39.96, 38.10, 30.57, 30.06, 28.21, 25.79, 25.28, 23.13, 21.05. [α]_D^{19.6} = +10.95° (*c* = 1.30, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₂₀H₂₈O₄Na [M+Na]⁺: 355.1885, found 355.1881.

tert-butyl 3-((2R,4aR,8S,8aR)-8-methyl-3,7-dioxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoate [(-)-89**].** ^1H NMR (600 MHz, CDCl_3) δ 6.45 (d, $J = 10.1$ Hz, 1H), 5.90 (d, $J = 10.1$ Hz, 1H), 2.66 (dd, $J = 19.1, 3.1$ Hz, 1H), 2.50 – 2.45 (m, 1H), 2.33 – 2.18 (m, 2H), 2.18 – 2.05 (m, 3H), 2.02 – 1.87 (m, 3H), 1.76 – 1.68 (m, 1H), 1.67 – 1.47 (m, 3H), 1.44 (s, 9H), 1.07 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 213.38, 203.12, 172.79, 150.90, 127.01, 80.54, 47.11, 44.53, 42.55, 37.89, 37.78, 35.43, 30.62, 29.70, 28.24, 24.21, 22.44, 21.25. HRMS (TOF ESI+) m/z calculated for $\text{C}_{20}\text{H}_{28}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 355.1885, found 355.1883. $[\alpha]_{\text{D}}^{19.6} = -77.09^\circ$ ($c = 1.30$, CHCl_3). The structure of **89** was confirmed by single-crystal X-ray diffraction of **S66**, an analogue of ent-**89**.

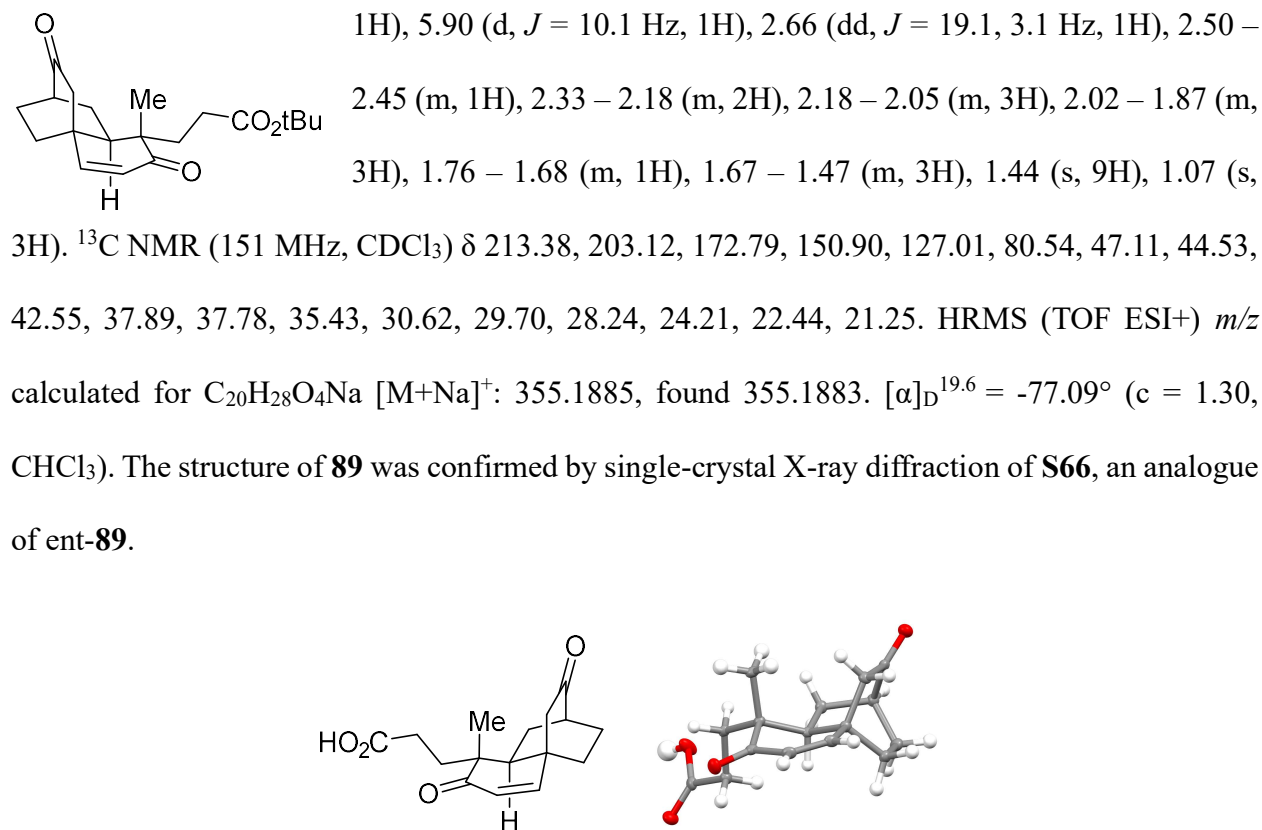
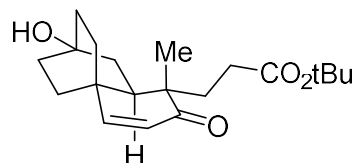


Figure S36. X-ray Crystal Data of **S66** (analogue of ent-**89**).

Empirical formula	C16 H20 O4	
Formula weight	276.32	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	$a = 8.8645(2)$ Å	$a = 90^\circ$.

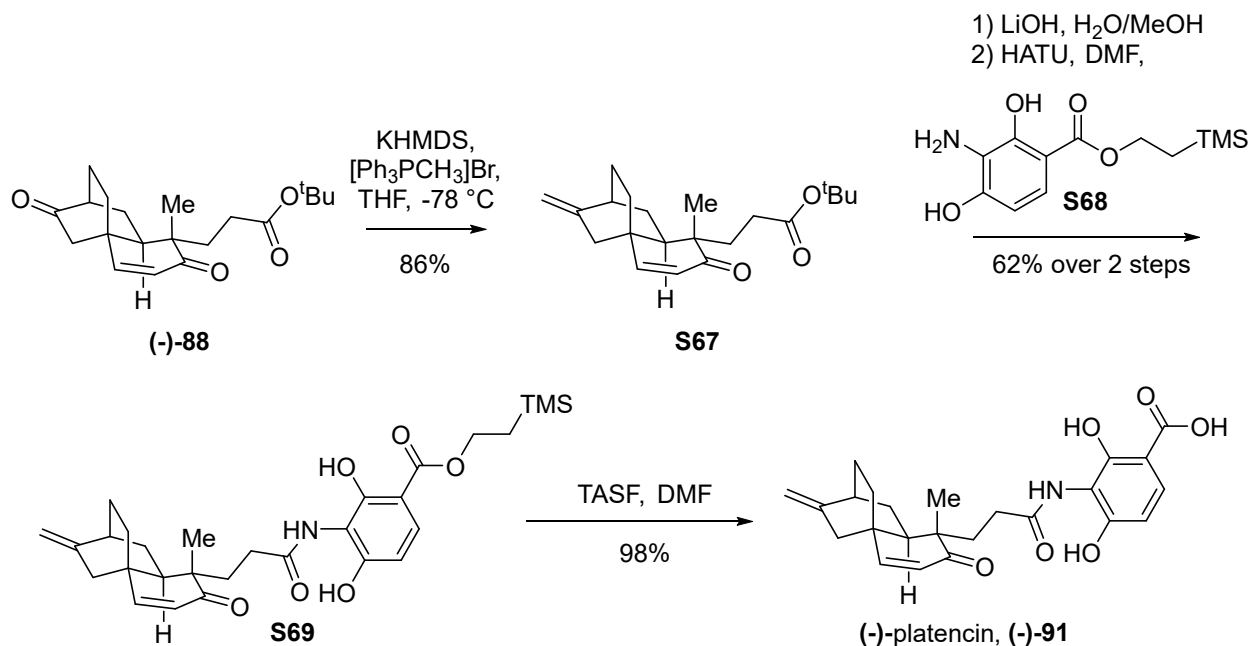
	$b = 10.2726(2) \text{ \AA}$	$b = 90^\circ$.
	$c = 14.7196(3) \text{ \AA}$	$g = 90^\circ$.
Volume	$1340.39(5) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.369 Mg/m^3	
Absorption coefficient	0.796 mm^{-1}	
F(000)	592	
Crystal size	$0.507 \times 0.441 \times 0.422 \text{ mm}^3$	
Theta range for data collection	$5.251 \text{ to } 74.496^\circ$.	
Index ranges	$-11 \leq h \leq 11, -11 \leq k \leq 12, -18 \leq l \leq 18$	
Reflections collected	20104	
Independent reflections	2731 [$R(\text{int}) = 0.0288$]	
Completeness to $\theta = 67.679^\circ$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6831	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2731 / 0 / 186	
Goodness-of-fit on F^2	1.079	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0266, wR2 = 0.0689$	
R indices (all data)	$R1 = 0.0267, wR2 = 0.0689$	
Absolute structure parameter	-0.06(4)	
Extinction coefficient	$0.0069(8)$	
Largest diff. peak and hole	$0.226 \text{ and } -0.140 \text{ e.\AA}^{-3}$	

tert-butyl 3-((8S,8aR)-2-hydroxy-8-methyl-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoate [(-)-90]. ¹H NMR (600 MHz, CDCl₃) δ 6.44 (d, *J* = 10.1 Hz,



1H), 5.80 (d, *J* = 10.0 Hz, 1H), 2.23 – 2.02 (m, 5H), 1.78 – 1.67 (m, 4H), 1.67 – 1.47 (m, 7H), 1.42 (s, 9H), 1.15 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 203.54, 172.91, 154.39, 126.47, 80.35, 70.04, 46.99,

40.44, 36.66, 34.90, 33.78, 33.44, 33.06, 30.70, 29.89, 28.70, 28.24, 21.48. [α]_D^{25.5} = -55.90° (*c* = 1.0, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₂₀H₃₀O₄Na [M+Na]⁺: 357.2042, found 357.2039.



Completion of the total synthesis of platencin [(-)-91]. To a solution of methyltriphenylphosphonium bromide (118 mg, 0.33 mmol, 3.0 equiv.) in dry THF (1.8 mL) was

added KHMDS (0.5 M in toluene, 0.66 mL, 0.33 mmol, 3.0 equiv.) dropwise at room temperature. The reaction was stirred at room temperature for 45 minutes, at which point it was cooled to -78 °C in an acetone/dry ice bath and a solution of diketone **88** (37 mg, 0.11 mmol, 1.0 equiv.) in dry THF (0.7 mL) was added dropwise. The reaction was stirred at -78 °C for 1 hour, warmed slowly to room temperature and stirred for another 2 hours, then quenched with saturated ammonium chloride solution. The aqueous layer was extracted 5x with diethyl ether, then combined organics were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by silica flash column chromatography (1: 9 EtOAc: hexanes), furnishing **S67** (28 mg, 0.08 mmol, 86% yield).

To a solution of **S67** (28 mg, 0.08 mmol) in MeOH (1.4 mL) at room temperature was added aq. LiOH (1 M, 1.4 mL). The resulting suspension was stirred at 50 °C for 6 h, then concentrated under vacuum to remove MeOH. Water was added and the aqueous solution was washed with EtOAc to remove organic impurities. The aqueous layer was acidified with aq. HCl (1 M) and extracted 3x with EtOAc. Combined organics were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by silica flash column chromatography (1: 9 EtOAc: hexanes), furnishing 22.8 mg 3-((2S,4aS,8S,8aR)-8-methyl-3-methylene-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoic acid (98% yield).

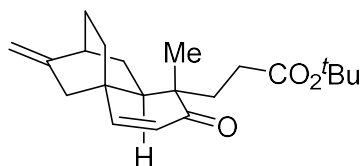
To a solution of 3-((2S,4aS,8S,8aR)-8-methyl-3-methylene-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoic acid (7 mg, 0.026 mmol, 1.0 equiv.) in dry DMF (100 µL) at room temperature was added triethylamine (15 µL, 0.109 mmol, 4.2 equiv.), and the reaction was stirred for ten minutes. HATU (31 mg, 0.082 mmol, 3.2 equiv.) was added, and the reaction was stirred for a further 45 minutes before the addition of aniline **S68** (22 mg, 0.082 mmol, 3.2

equiv.). The mixture was stirred for 13 h, then brine was added. The resulting mixture was extracted 10x with CHCl₃, and combined organics were dried over sodium sulfate, filtered, and concentrated. The crude residue was purified by silica flash column chromatography (15% EtOAc in hexanes) furnishing 8.5 mg of **S69** (63% yield).

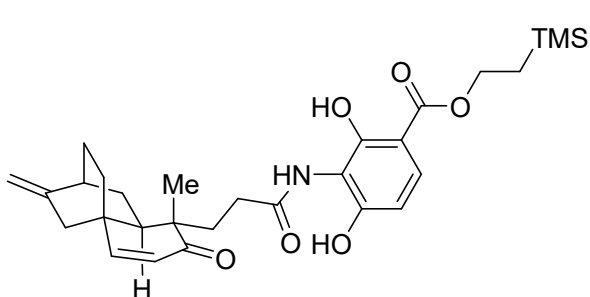
To a solution of **S69** (15.3 mg, 0.029 mmol, 1.0 equiv.) in DMF (0.26 mL) at room temperature was added tris(dimethylamino)sulfonium difluorotrimethyl-silicate (16 mg, 0.058 mmol, 2.0 equiv.), and the reaction was stirred at 40 °C for 40 min. The reaction was then cooled to room temperature and brine added. The mixture was extracted with CHCl₃ (10 × 1.5 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated. The crude reaction mixture was purified by silica column chromatography (80: 20:0.5: 1:0.5 EtOAc: hexanes:acetic acid:methanol:water), furnishing platencin **91** as a white solid (12 mg, 0.028 mmol, 98% yield).

tert-butyl 3-((2S,4aS,8S,8aR)-8-methyl-3-methylene-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoate [(+)-S67]. ¹H NMR (600 MHz, CDCl₃) δ 6.45 (d, *J* = 10.1

Hz, 1H), 5.82 (d, *J* = 10.1 Hz, 1H), 4.84 (br s, 1H), 4.67 (br s, 1H), 2.44 – 2.39 (m, 1H), 2.31 (app d, *J* = 16.1 Hz, 1H), 2.17 – 2.02 (m, 4H), 2.00 – 1.92 (m, 2H), 1.76 – 1.66 (m, 3H), 1.58 – 1.44 (m, 3H), 1.42 (s, 9H), 1.15 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 204.36, 173.08, 154.44, 149.07, 126.44, 107.40, 80.27, 47.32, 44.67, 39.58, 36.19, 36.05, 30.65, 29.91, 28.24, 28.12, 26.77, 26.04, 21.38. [α]_D^{22.6} = +11.10° (*c* = 1.09, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₂₁H₃₀O₃Na [M+H]⁺: 353.2093, found 353.2092.

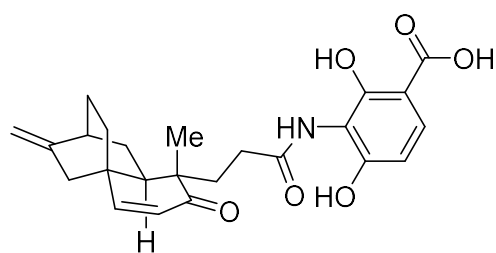


2-(trimethylsilyl)ethyl 2,4-dihydroxy-3-(3-((2S,4aS,8S,8aR)-8-methyl-3-methylene-7-oxo-1,3,4,7,8, 8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanamido)benzoate [(-)-S69].

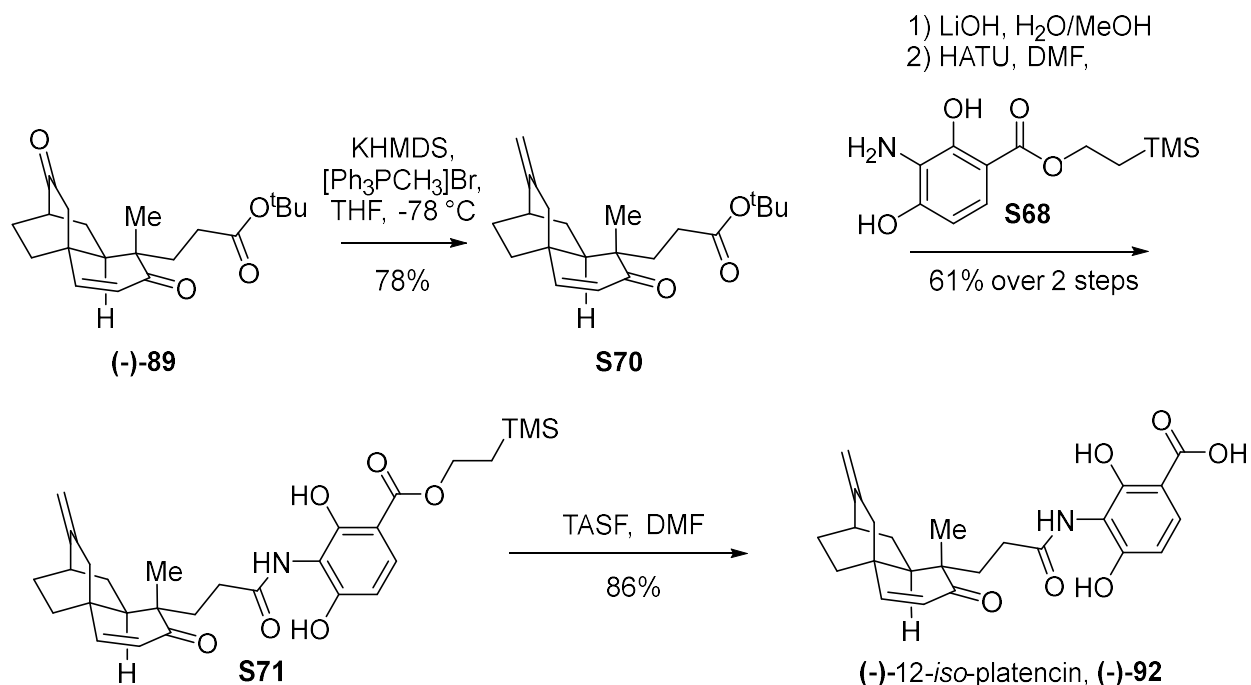


^1H NMR (500 MHz, CDCl_3) δ 11.81 (s, 1H), 11.08 (s, 1H), 8.14 (s, 1H), 7.55 (d, $J = 8.9$ Hz, 1H), 6.51 (d, $J = 10.1$ Hz, 1H), 6.50 (d, $J = 9.0$ Hz, 1H), 5.89 (d, $J = 10.1$ Hz, 1H), 4.85 (s, 1H), 4.68 (s, 1H), 4.44 – 4.39 (m, 2H), 2.48 – 2.43 (m, 1H), 2.43 – 2.37 (m, 2H), 2.34 (d, $J = 16.2$ Hz, 1H), 2.21 – 2.12 (m, 1H), 2.09 (d, $J = 16.0$ Hz, 1H), 2.04 – 1.95 (m, 2H), 1.84 – 1.69 (m, 4H), 1.63 – 1.46 (m, 2H), 1.21 (s, 3H), 1.17 – 1.09 (m, 2H), 0.08 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 204.78, 174.21, 170.65, 154.88, 154.79, 154.06, 148.65, 127.47, 126.29, 114.52, 111.24, 107.75, 104.57, 63.89, 47.78, 44.63, 39.79, 36.35, 35.96, 32.54, 31.04, 28.20, 26.68, 25.95, 21.13, 17.50, -1.31. $[\alpha]_{\text{D}}^{21.5} = -25.15^\circ$ ($c = 0.82$, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{29}\text{H}_{40}\text{NO}_6\text{Si}$ $[\text{M}+\text{H}]^+$: 526.2625, found 526.2622.

(-)-platencin [(-)-91]. ^1H NMR (500 MHz, CDCl_3) δ 11.69 (s, 1H), 11.26 (s, 1H), 8.26 (s, 1H),



7.62 (d, $J = 9.0$ Hz, 1H), 6.60 (d, $J = 10.0$ Hz, 1H), 6.51 (d, $J = 8.9$ Hz, 1H), 5.94 (d, $J = 10.0$ Hz, 1H), 4.87 (s, 1H), 4.70 (s, 1H), 2.53 – 2.39 (m, 3H), 2.39 – 2.30 (m, 1H), 2.20 – 2.07 (m, 2H), 2.07 – 1.96 (m, 2H), 1.89 – 1.68 (m, 4H), 1.64 – 1.49 (m, 2H), 1.24 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 206.56, 174.24, 173.10, 156.68, 155.61, 154.61, 148.38, 128.42, 126.05, 114.49, 111.42, 107.92, 103.48, 47.82, 44.51, 39.45, 36.51, 35.91, 32.35, 31.23, 28.10, 26.68, 25.89, 21.44. $[\alpha]_{\text{D}}^{24.8} = -20.99^\circ$ ($c = 0.465$, MeOH). HRMS (TOF ESI+) m/z calculated for $\text{C}_{24}\text{H}_{28}\text{NO}_6$ $[\text{M}+\text{H}]^+$: 426.1917, found 426.1910.



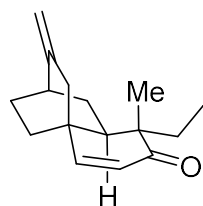
Completion of the synthesis of 12-iso-platencin [(-)-92]. To a solution of methyltriphenylphosphonium bromide (0.38 mmol, 136 mg) in dry THF (2.1 mL) was added KHMDS (0.5 M in toluene, 0.76 mL), dropwise at room temperature. The reaction was stirred at room temperature for 45 minutes, at which point it was cooled to $-78\text{ }^\circ\text{C}$ in an acetone/dry ice bath and a solution of diketone **89** (0.13 mmol, 42.1 mg) in dry THF (0.7 mL) was added dropwise. The reaction was stirred at $-78\text{ }^\circ\text{C}$ for 1 hour, warmed slowly to room temperature and stirred for another 2 hours, then quenched with saturated ammonium chloride solution. The aqueous layer was extracted 5x with diethyl ether, then combined organics were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by silica flash column chromatography (1: 9 EtOAc: hexanes), furnishing 33 mg **S70** (78% yield).

To a solution of **S70** (61.5 mg, 0.186 mmol) in MeOH (3 mL) at room temperature was added aq. LiOH (1 M, 3 mL). The resulting suspension was stirred at $50\text{ }^\circ\text{C}$ for 6 h, then concentrated under vacuum to remove MeOH. Water was added and the aqueous solution was

washed with EtOAc to remove organic impurities. The aqueous layer was acidified with aq. HCl (1 M) and extracted 3x with EtOAc. Combined organics were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by silica flash column chromatography (1: 9 EtOAc: hexanes), furnishing 46 mg 3-((2R,4aR,8S,8aR)-8-methyl-3-methylene-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoic acid (90% yield). To a solution of 3-((2R,4aR,8S,8aR)-8-methyl-3-methylene-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoic acid (19.8 mg, 0.072 mmol) in dry DMF (120 μ L) at room temperature was added triethylamine (42 μ L, 0.303 mmol), and the reaction was stirred for ten minutes. HATU (87.8 mg, 0.231 mmol) was added, and the reaction was stirred for a further 45 minutes before the addition of aniline **S68** (62.2 mg, 0.231 mmol). The mixture was stirred for 13 h, then brine was added. The resulting mixture was extracted 10x with CHCl₃, and combined organics were dried over sodium sulfate, filtered, and concentrated. The crude residue was purified by silica flash column chromatography (15% EtOAc in hexanes) furnishing 26 mg of **S71** (68% yield).

To a solution of **S71** (23 mg, 0.044 mmol) in DMF (0.4 mL) at room temperature was added tris(dimethylamino)sulfonium difluorotrimethyl-silicate (24 mg, 0.087 mmol), and the reaction was stirred at 40 °C for 40 min. The reaction was then cooled to room temperature and brine added. The mixture was extracted with CHCl₃ (10 $\times$ 1.5 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated to furnish (-)-12-isoplatencin (**92**).

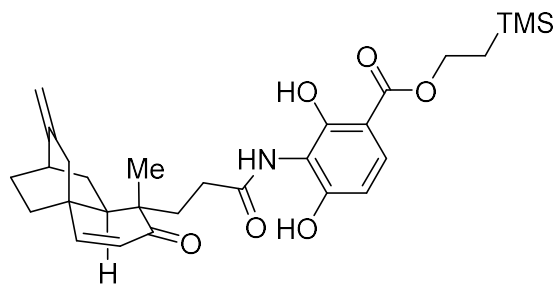
tert-butyl 3-((2R,4aR,8S,8aR)-8-methyl-3-methylene-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoate [(-)-S70]. ^1H NMR (500 MHz, CDCl_3) δ 6.44 (d, J =



10.1 Hz, 1H), 5.82 (d, J = 10.1 Hz, 1H), 4.85 – 4.80 (m, 1H), 4.66 – 4.61 (m, 1H), 2.66 (app dq, J = 17.4, 2.8 Hz, 1H), 2.44 – 2.38 (m, 1H), 2.23 – 2.01 (m, 5H), 1.82 – 1.66 (m, 3H), 1.58 – 1.47 (m, 3H), 1.43 (s,

9H), 1.46 – 1.35 (m, 1H), 1.08 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 204.39, 173.10, 154.29, 149.18, 126.36, 105.98, 80.29, 47.26, 38.49, 36.07, 36.05 (2C), 35.92, 30.75, 29.86, 28.26, 27.27, 25.77, 21.40. *Peak at 36.05 contains two overlapping methylene carbons (based on HSQC). $[\alpha]_{\text{D}}^{22.6} = -137.72^\circ$ (c = 0.58, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{21}\text{H}_{30}\text{O}_3\text{Na}$ $[\text{M}+\text{H}]^+$: 353.2093, found 353.2091.

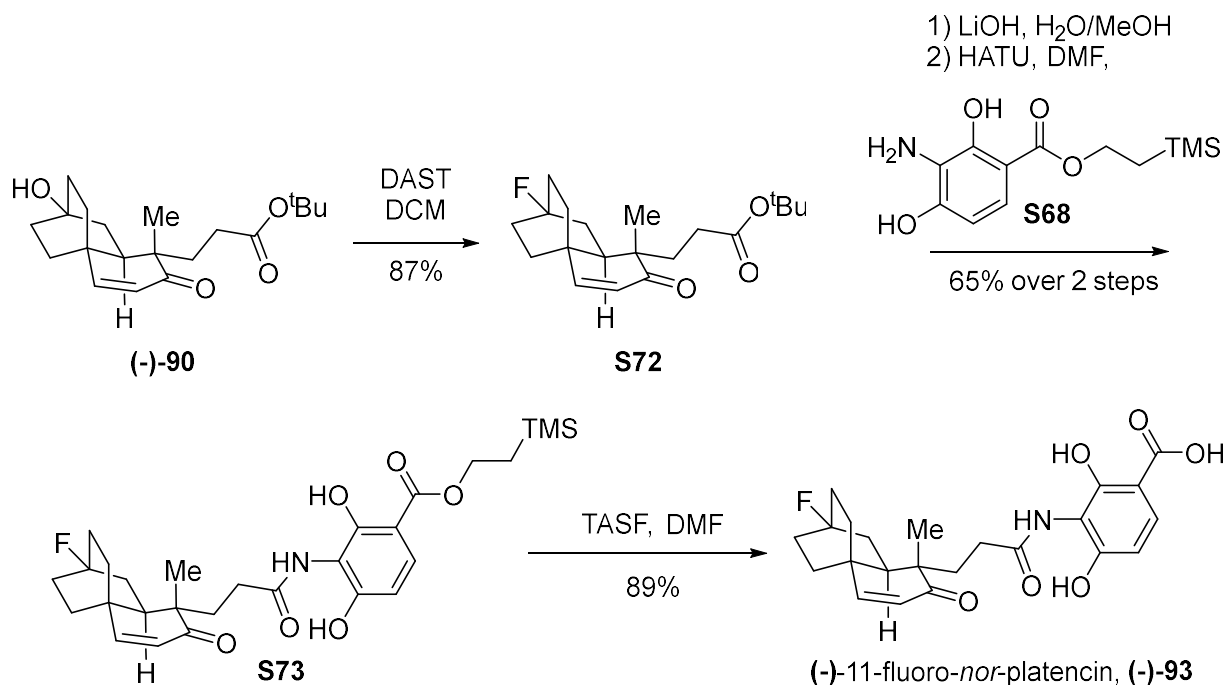
2-(trimethylsilyl)ethyl 2,4-dihydroxy-3-(3-((2R,4aR,8S,8aR)-8-methyl-3-methylene-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanamido)benzoate [(-)-S71]. ^1H



NMR (500 MHz, CDCl_3) δ 11.82 (s, 1H), 11.07 (s, 1H), 8.18 (s, 1H), 7.55 (d, J = 8.9 Hz, 1H), 6.50 (app d, J = 9.6 Hz, 2H), 5.88 (d, J = 10.1 Hz, 1H), 4.85 (br s, 1H), 4.65 (br s, 1H), 4.41 (app t, J = 8.5 Hz,

2H), 2.69 (app d, J = 17.4 Hz, 1H), 2.49 – 2.37 (m, 3H), 2.21 (app d, J = 18.0 Hz, 1H), 2.18 – 2.09 (m, 2H), 1.86 – 1.70 (m, 4H), 1.60 – 1.48 (m, 2H), 1.46 – 1.37 (m, 1H), 1.14 (s, 3H), 1.15 – 1.09 (m, 2H), 0.08 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 204.86, 174.25, 170.63, 154.79, 154.78, 154.06, 148.82, 127.48, 126.19, 114.50, 111.23, 106.20, 104.58, 63.89, 47.74, 38.65, 36.05, 35.99, 35.98, 35.93, 32.60, 30.98, 27.24, 25.70, 21.12, 17.48, -1.32. HRMS (TOF ESI+) m/z calculated for $\text{C}_{29}\text{H}_{40}\text{NO}_6\text{Si}$ $[\text{M}+\text{H}]^+$: 526.2625, found 526.2621. $[\alpha]_{\text{D}}^{21.6} = -124.65^\circ$ (c = 0.55, CHCl_3)

12-iso-platencin [(-)-92]. ^1H NMR (500 MHz, CDCl_3) δ 11.73 (s, 1H), 11.23 (s, 1H), 8.31 (s, 1H), 7.62 (d, J = 8.9 Hz, 1H), 6.60 (d, J = 10.1 Hz, 1H), 6.51 (d, J = 8.9 Hz, 1H), 5.93 (d, J = 10.1 Hz, 1H), 4.87 (s, 1H), 4.67 (s, 1H), 2.70 (d, J = 17.5 Hz, 1H), 2.60 – 2.39 (m, 3H), 2.23 (d, J = 17.5 Hz, 1H), 2.19 – 2.11 (m, 2H), 1.90 – 1.80 (m, 2H), 1.80 – 1.68 (m, 2H), 1.62 – 1.51 (m, 2H), 1.49 – 1.37 (m, 1H), 1.17 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 206.75, 174.28, 173.18, 156.73, 155.58, 154.62, 148.50, 128.47, 125.93, 114.46, 111.40, 106.44, 103.59, 47.77, 38.32, 36.23, 35.93, 35.90, 35.87, 32.39, 31.21, 27.14, 25.67, 21.48. $[\alpha]_{\text{D}}^{20.4} = -163.35^\circ$ (c = 1.07, CHCl_3). HRMS (TOF ESI+) m/z calculated for $\text{C}_{24}\text{H}_{28}\text{NO}_6$ $[\text{M}+\text{H}]^+$: 426.1917, found 426.1913.



Completion of the synthesis of 11-fluoro-nor-platencin [(-)-93]. To a solution of alcohol **90** (31 mg, 0.093 mmol, 1.0 equiv.) and sodium fluoride (8 mg, 0.186 mmol, 2.0 equiv.) in dichloromethane (1 mL) at -78°C was added DAST (14 μL , 0.11 mmol, 1.2 equiv.), and the

reaction was stirred at -78 °C for 40 min. The reaction was then warmed to room temperature and brine added. The mixture was extracted with CHCl₃ (10 × 1.5 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated. The crude reaction mixture was purified by silica flash column chromatography (Ethyl acetate: hexanes = 1: 9), furnishing **S72** as a clear oil (26.8 mg, 0.080 mmol, 87% yield).

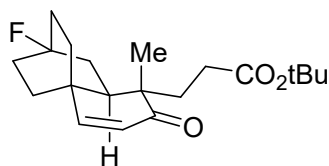
To a solution of **S72** (40 mg, 0.119 mmol) in MeOH (1.9 mL) at room temperature was added aq. LiOH (1 M, 1.9 mL). The resulting suspension was stirred at 50 °C for 6 h, then concentrated under vacuum to remove MeOH. Water was added and the aqueous solution was washed with EtOAc to remove organic impurities. The aqueous layer was acidified with aq. HCl (1 M) and extracted 3x with EtOAc. Combined organics were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by silica flash column chromatography (49: 50: 1 EtOAc: hexanes:acetic acid), furnishing 29.9 mg 3-((2R,4aR,8S,8aR)-2-fluoro-8-methyl-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoic acid (90% yield).

To a solution of 3-((2R,4aR,8S,8aR)-2-fluoro-8-methyl-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoic acid (29.9 mg, 0.107 mmol, 1.0 equiv.) in dry DMF (0.38 mL) at room temperature was added triethylamine (62 µL, 0.448 mmol, 4.2 equiv.), and the reaction was stirred for ten minutes. HATU (105.7 mg, 0.278 mmol, 2.6 equiv.) was added, and the reaction was stirred for a further 45 minutes before the addition of aniline **S68** (75 mg, 0.278 mmol, 2.6 equiv.). The mixture was stirred for 13 h, then brine was added. The resulting mixture was extracted 10x with CHCl₃, and combined organics were dried over sodium sulfate, filtered, and concentrated. The crude residue was purified by silica flash column chromatography (15%

EtOAc in hexanes), then by preparative TLC (silica, 15% EtOAc in hexanes), furnishing 40.7 mg of **S73** (72% yield).

To a solution of **S73** (25.2 mg, 0.047 mmol) in DMF (0.4 mL) at room temperature was added tris(dimethylamino)sulfonium difluorotrimethyl-silicate (26.1 mg, 0.095 mmol), and the reaction was stirred at 40 °C for 40 min. The reaction was then cooled to room temperature and brine added. The mixture was extracted with CHCl₃ (10 × 1.5 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated. The crude reaction mixture was purified by silica column chromatography (80: 20:0.5: 1:0.5 EtOAc: hexanes:acetic acid:methanol:water), furnishing 11-fluoro-nor-platencin ((-)-**93**) as a white solid (18 mg, 0.042 mmol, 89% yield).

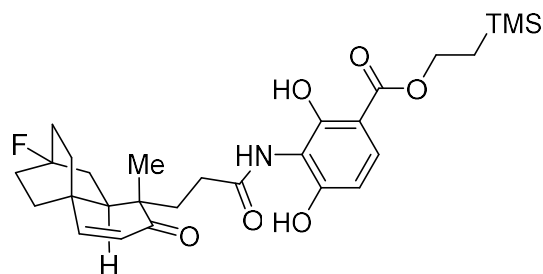
tert-butyl 3-((8S,8aR)-2-fluoro-8-methyl-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanoate [(-)-S72]. ¹H NMR (500 MHz, CDCl₃) δ 6.43 (d, *J* = 10.2



Hz, 1H), 5.83 (d, *J* = 10.2 Hz, 1H), 2.26 (t, *J* = 10.0 Hz, 1H), 2.22 – 2.05 (m, 4H), 1.94 – 1.73 (m, 7H), 1.71 – 1.62 (m, 1H), 1.60 – 1.52 (m, 2H), 1.44 (s, 9H), 1.17 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ

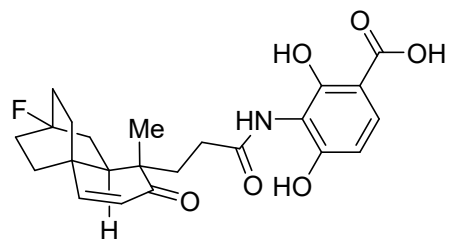
202.99, 172.77, 153.51 (d, *J* = 4.8 Hz), 126.77, 94.32 (d, *J* = 185.5 Hz), 80.44, 46.98, 40.85 (d, *J* = 9.3 Hz), 36.53 (d, *J* = 10.5 Hz), 33.78 (d, *J* = 3.4 Hz), 32.28 (d, *J* = 19.8 Hz), 30.79 (d, *J* = 19.6 Hz), 30.74, 30.35 (d, *J* = 19.6 Hz), 29.95, 28.92 (d, *J* = 10.2 Hz), 28.26, 21.46. ¹⁹F NMR (471 MHz, CDCl₃) δ -150.61. [α]_D^{22.3} = -69.6 (c 0.97, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₂₀H₂₉O₃FN_a [M+Na]⁺: 359.1998, found 359.1996.

2-(trimethylsilyl)ethyl 3-(3-((8S,8aR)-2-fluoro-8-methyl-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanamido)-2,4-dihydroxybenzoate [(-)-S73].



¹H NMR (500 MHz, CDCl₃) δ 11.83 (s, 1H), 11.03 (s, 1H), 8.14 (s, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 6.50 (d, *J* = 9.0 Hz, 1H), 6.48 (d, *J* = 10.4 Hz, 1H), 5.88 (d, *J* = 10.4 Hz, 1H), 4.44 – 4.39 (m, 2H), 2.44 (dd, *J* = 8.8, 7.3 Hz, 2H), 2.29 (t, *J* = 10.0 Hz, 1H), 2.23 – 2.11 (m, 2H), 1.96 – 1.86 (m, 4H), 1.86 – 1.71 (m, 4H), 1.69 (app t, *J* = 12.7 Hz, 1H), 1.62 – 1.53 (m, 1H), 1.22 (s, 3H), 1.15 – 1.10 (m, 2H), 0.08 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 203.45, 173.89, 170.63, 154.78, 154.04, 154.04 (d, *J* = 4.2 Hz), 127.52, 126.61, 114.45, 111.26, 104.58, 94.09 (d, *J* = 186.0 Hz), 63.90, 47.40, 41.00 (d, *J* = 9.1 Hz), 36.46 (d, *J* = 10.4 Hz), 33.91 (d, *J* = 3.3 Hz), 32.51, 32.27 (d, *J* = 20.2 Hz), 31.01, 30.72 (d, *J* = 19.6 Hz), 30.30 (d, *J* = 19.7 Hz), 28.82 (d, *J* = 10.2 Hz), 21.16, 17.48, -1.33. ¹⁹F NMR (471 MHz, CDCl₃) δ -150.71. [α]_D^{23.8} = -73.9° (c = 1.00, CHCl₃). HRMS (TOF ESI+) *m/z* calculated for C₂₈H₃₉NO₆FSi [M+H]⁺: 532.2531, found 532.2524.

3-(3-((8S,8aR)-2-fluoro-8-methyl-7-oxo-1,3,4,7,8,8a-hexahydro-2H-2,4a-ethanonaphthalen-8-yl)propanamido)-2,4-dihydroxybenzoic acid (11-fluoro-norplatencin) [(-)-93].

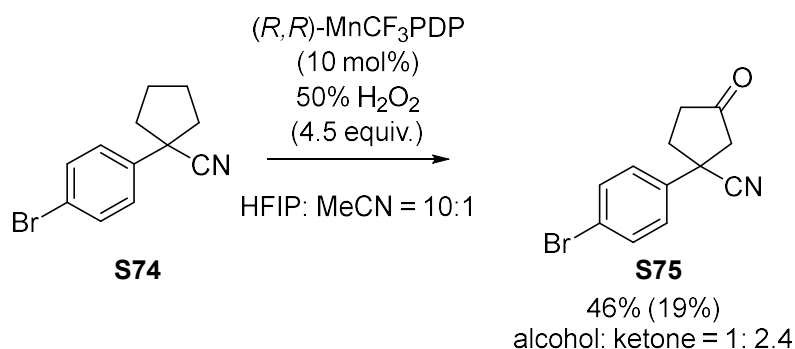


(600 MHz, CDCl₃) δ 11.64 (s, 1H), 11.20 (br s, 1H), 8.26 (s, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 6.57 (d, *J* = 10.1 Hz, 1H), 6.52 (d, *J* = 9.0 Hz, 1H), 5.93 (d, *J* = 10.1 Hz, 1H), 2.56 – 2.41 (m, 2H), 2.32 (t, *J* = 10.3 Hz, 1H), 2.22 – 2.12 (m, 2H), 1.98 – 1.78 (m, 8H), 1.71 (t, *J* = 13.0 Hz, 1H), 1.60 (br s, 1H), 1.25 (s, 3H). ¹³C NMR (151 MHz, CDCl₃)

δ 205.10, 174.00, 173.31, 155.68, 155.68, 154.59, 128.52, 126.37, 114.46, 111.53, 103.48, 94.02
(d, $J = 186.5$ Hz), 47.46, 40.67 (d, $J = 6.4$ Hz), 36.39 (d, $J = 8.6$ Hz), 34.05, 32.35, 32.16 (d, $J =$
20.3 Hz), 31.21, 30.66 (d, $J = 19.8$ Hz), 30.27 (d, $J = 19.8$ Hz), 28.80 (d, $J = 10.2$ Hz), 21.46. ^{19}F
NMR (471 MHz, CDCl_3) δ -150.86. HRMS (TOF ESI+) m/z calculated for $\text{C}_{23}\text{H}_{27}\text{NO}_6\text{F}$ $[\text{M}+\text{H}]^+$:
432.1822, found 432.1825. $[\alpha]_{\text{D}}^{22.8} = -114.2^\circ$ ($c = 0.7$, CHCl_3).

X. Unsuccessful Substrates

Aromatic Substrates with nitrile instead of α,β -unsaturated ester. Standard Procedure was tested on aromatic substrates previously used to demonstrate high aromatic tolerance of PDP/carboxylic acid condition in MeCN¹. Under Standard Procedure, the p-bromo and p-chloro analogues afforded yields of 46% and 42%, respectively, whereas the unsubstituted phenyl substrate gave 13% yield (23% RSM).

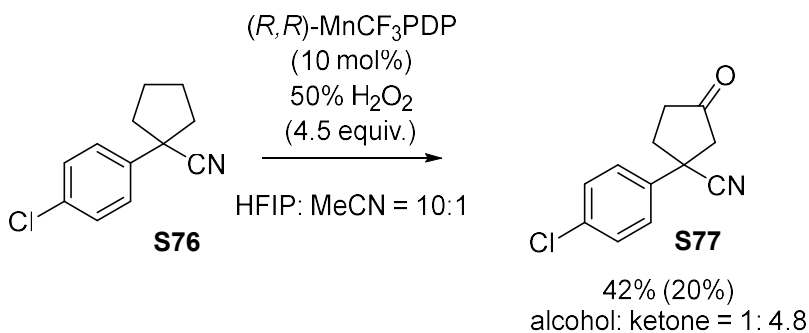


Oxidation of 1-(4-bromophenyl)cyclopentane-1-carbonitrile [S74]. 1-(4-bromophenyl)cyclopentane-1-carbonitrile (0.3 mmol) in HFIP was oxidized according to Standard Procedure with 10 mol% (R,R) -Mn(CF₃-PDP) or (S,R,R,S) -Mn(MeCF₃-PDP) and 4.5 equiv. H₂O₂. The resulting mixture was concentrated in vacuo and purified via flash column chromatography (silica, 1: 3 → 1: 1 EtOAc: Hexanes) affording **S75-ketone** and **S75-OH**. With (R,R) -Mn(CF₃-PDP) - **Run 1**: 36% yield, alcohol: ketone = 1: 2.2, 27% RSM, **Run 2**: 33% yield, alcohol: ketone = 1: 2.2, 23% RSM. **Average**: 35% $\pm$ 2.1% yield, alcohol: ketone = 1: 2.2, 25% $\pm$ 2.8% RSM. With (S,R,R,S) -Mn(MeCF₃-PDP) - **Run 1**: 48% yield, alcohol: ketone = 1: 2.2, 16% RSM. **Run 2**: 43% yield, alcohol: ketone = 1: 2.5, 20% RSM. **Run 3**: 47% yield, alcohol: ketone = 1: 2.6, 21%

RSM. **Average:** 46% yield $\pm$ 2.2%, alcohol: ketone = 1: 2.4, 19% $\pm$ 2.2% RSM. Spectroscopic data of **S75-ketone** matched the published literature¹¹

1-(4-bromophenyl)-3-hydroxycyclopentane-1-carbonitrile [S75-OH]. Alcohols were isolated

as a 1.8: 1 mixture of diastereomers. ¹H NMR (500 MHz, CDCl₃) δ 7.53 – 7.49 (m, 2H), 7.44 (app dt, J = 8.7, 2.4 Hz, 0.7H), 7.30 (app dt, J = 8.6, 2.8 Hz, 1.3H), 4.69 (tt, J = 5.8, 2.8 Hz, 0.35H), 4.61 (tt, J = 6.2, 3.0 Hz, 0.65H), 2.86 (dd, J = 14.4, 6.1 Hz, 0.35H), 2.76 – 2.69 (m, 0.65H), 2.59 – 2.54 (m, 0.65H), 2.47 (ddd, J = 12.4, 6.9, 2.5 Hz, 0.35H), 2.38 – 2.22 (m, 2H), 2.18 – 2.02 (m, 1.65H), 2.01 – 1.95 (m, 0.35H), 1.73 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 139.27 (139.25), 132.27 (132.15), 128.01 (127.67), 124.31 (124.12), 122.13 (121.99), 72.85 (72.50), 49.94 (49.91), 46.76 (45.15), 40.01 (39.27), 35.82 (35.54). HRMS (EI⁺) m/z calculated for C₁₂H₁₂BrNO [M]⁺: 265.0102, found 265.0107.

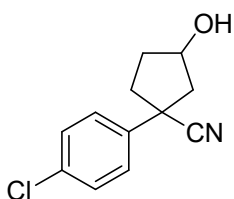


Oxidation of 1-(4-chlorophenyl)cyclopentane-1-carbonitrile [S76]. 1-(4-

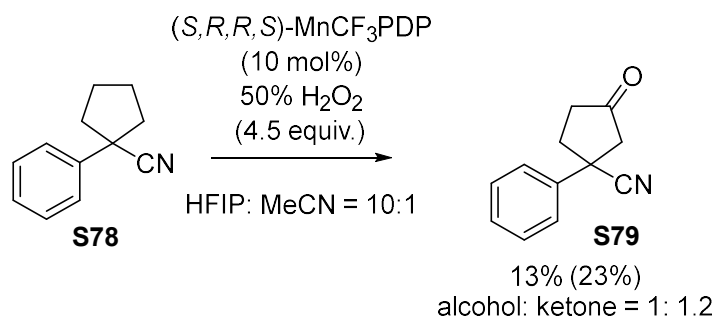
chlorophenyl)cyclopentane-1-carbonitrile (0.3 mmol) in HFIP was oxidized according to Standard Procedure with 10 mol% (*R,R*)-Mn(CF₃-PDP) or (*S,R,R,S*)-Mn(MeCF₃-PDP) and 4.5 equiv. of H₂O₂. The resulting mixture was concentrated in vacuo and purified via flash column chromatography (silica, 1: 3 $\rightarrow$ 1: 1 EtOAc: Hexanes) affording **S77-ketone** and **S77-OH**. With

(*R,R*)-Mn(CF₃-PDP) - **Run 1**: 26% RSM, 31% yield, alcohol: ketone = 1: 2.9. **Run 2**: 23% RSM, 35% yield, alcohol: ketone = 1: 2.9. **Average**: 24.5% $\pm$ 1.5% RSM, 33% $\pm$ 2% yield, alcohol: ketone 1: 2.9. With (*S,R,R,S*)-Mn(MeCF₃-PDP) - **Run 1**: 22% RSM, 43% yield, alcohol: ketone = 1: 5.1. **Run 2**: 19% RSM, 41% yield, alcohol: ketone = 1: 4.9. **Run 3**: 18% RSM, 43% yield, alcohol: ketone = 1: 4.4. **Average**: 20% RSM $\pm$ 1.7%, 42% yield $\pm$ 0.9%, alcohol: ketone = 1: 4.8. Spectroscopic data of **S77-ketone** matched the published literature¹.

1-(4-chlorophenyl)-3-hydroxycyclopentane-1-carbonitrile [S77-OH]. Alcohols were isolated

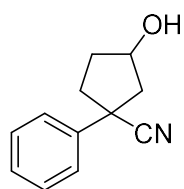


as a 1.5: 1 mixture of diastereomers. ¹H NMR (500 MHz, CDCl₃) ¹H NMR (500 MHz, CDCl₃) δ 7.49 (app dt, J = 8.6, 2.7 Hz, 0.8H), 7.38 – 7.34 (m, 3.2H), 4.69 (tt, J = 5.9, 2.6 Hz, 0.4H), 4.61 (tt, J = 6.3, 3.7 Hz, 0.6H), 2.86 (dd, J = 14.5, 6.3 Hz, 0.4H), 2.72 (dddd, J = 12.7, 8.1, 6.5, 1.2 Hz, 0.6H), 2.56 (m, 0.6H), 2.47 (ddd, J = 12.8, 7.0, 2.6 Hz, 0.4H), 2.39 – 2.22 (m, 2H), 2.18 – 2.02 (m, 1.6H), 2.01 – 1.94 (m, 0.4H), 1.78 (s, 1H). ¹³C NMR (126 MHz) ¹³C NMR (126 MHz, CDCl₃) δ 138.72 (138.69), 134.07 (133.91), 129.30 (129.17), 127.67 (127.34), 124.41 (124.19), 72.84 (72.48), 49.96 (49.93), 46.68 (45.07), 40.01 (39.29), 35.79 (35.52). HRMS (EI⁺) m/z calculated for C₁₂H₁₂ClNO [M]⁺: 221.0607, found 221.0615.



Oxidation of 1-phenylcyclopentane-1-carbonitrile [S78]. 1-phenylcyclopentane-1-carbonitrile (0.3 mmol) in HFIP was oxidized according to Standard Procedure with 10 mol% (*R,R*)-Mn(CF₃-PDP) or (*S,R,R,S*)-Mn(MeCF₃-PDP) and 4.5 equiv. of H₂O₂. The resulting mixture was concentrated in vacuo and purified via flash column chromatography (silica, 1: 3 → 1: 1 EtOAc: Hexanes) affording **S79-ketone** and **S79-OH**. With (*R,R*)-Mn(CF₃-PDP) - **Run 1**: 9% yield, alcohol: ketone = 1: 1.1. **Run 2**: 8% yield, alcohol: ketone = 1: 1.1. **Average**: 9% ± 0.7% yield, alcohol: ketone = 1: 1.1. With (*S,R,R,S*)-Mn(MeCF₃-PDP) - **Run 1**: 25% RSM, 11% yield, alcohol: ketone = 1: 1.2. **Run 2**: 23% RSM, 13% yield, alcohol: ketone = 1: 1. **Run 3**: 21% RSM, 16% yield, alcohol: ketone = 1: 1.3. **Average**: 23% RSM ± 2%, 13% yield ± 2.5%, alcohol: ketone = 1: 1.2. Spectroscopic data of **S79-ketone** matched the published literature¹.

3-hydroxy-1-phenylcyclopentane-1-carbonitrile [S79-OH]. Alcohols were isolated as a 1.1: 1

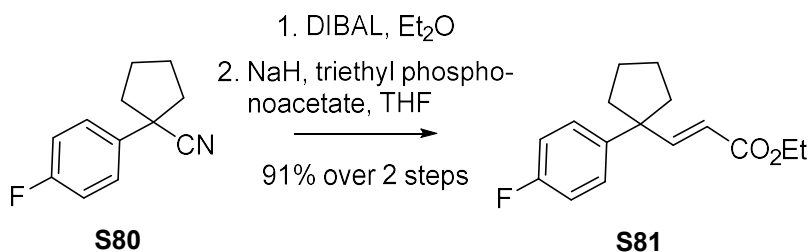


mixture of diastereomers. ¹H NMR (500 MHz, CDCl₃) δ 7.58 – 7.53 (m, 0.94H), 7.46 – 7.42 (m, 1.06H), 7.41 – 7.37 (m, 2H), 7.34 – 7.29 (m, 1H), 4.70 (tdd, *J* = 6.2, 4.0, 2.8 Hz, 0.47H), 4.61 (tdd, *J* = 6.4, 3.9, 2.7 Hz, 0.53H), 2.88 (dd, *J* = 14.6, 6.1 Hz, 0.47H), 2.72 (dddd, *J* = 13.3, 7.3, 5.6, 1.3 Hz, 0.53H), 2.61 – 2.54 (m, 0.53H), 2.47 (ddd, *J* = 12.9, 7.3, 2.9 Hz, 0.47H), 2.43 – 2.24 (m, 2H), 2.22 – 2.13 (m, 1H), 2.10 – 2.02 (m, 0.53H), 2.01 – 1.94 (m, 0.47H), 1.80 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 140.14 (139.95), 129.15

(129.06), 128.04 (127.95), 126.15 (125.88), 124.84 (124.54), 72.95 (72.50), 49.96 (49.86), 47.14 (45.47), 39.70 (39.27), 35.65 (35.56). HRMS (EI⁺) *m/z* calculated for C₁₂H₁₃NO [M]⁺: 187.0997, found 187.1004.

Further Study on Aromatic Tolerance of Fluoroarenes

Aromatic oxidation becomes more pronounced in fluorinated aromatics likely due to the mesomeric electron-donating effects of fluorine substituents⁵⁴.

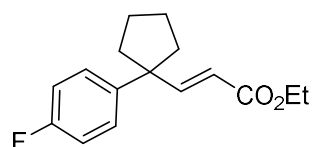


Preparation of ethyl (E)-3-(1-(4-fluorophenyl)cyclopentyl)acrylate [S81]. 1-(4-fluorophenyl)cyclopentane-1-carbonitrile was prepared according to the reported literature¹. To a solution of 1-(4-fluorophenyl)cyclopentane-1-carbonitrile (1.6728 g, 8.84 mmol, 1.0 equiv.) in diethyl ether (31 mL) at -78 °C was added diisobutylaluminum hydride (1.0 M in hexanes, 14.1 mL, 14.1 mmol, 1.6 equiv.) dropwise over 10 minutes. The reaction was stirred for 1h at -78 °C until completion was confirmed by TLC analysis (ethyl acetate: hexanes 1: 19). A saturated aqueous solution of Rochelle's salt (30 mL) was added and the mixture was stirred for 2h until separation of the organic and aqueous layers was observed. The aqueous layer was extracted 3x with diethyl ether, then combined organics were dried over magnesium sulfate and concentrated

under reduced pressure. The resulting crude mixture was purified by silica flash column chromatography (ethyl acetate: hexanes = 1: 39), furnishing 1-(4-fluorophenyl)cyclopentane-1-carbaldehyde (1.644 g, 8.55 mmol, 97%).

A flame-dried 50 mL round bottom flask equipped with a stir bar was charged with 90% sodium hydride (318 mg, 11.9 mmol, 1.4 equiv.) and dichloromethane (18 mL). The suspension was cooled to 0 °C in an ice bath, then triethyl phosphonoacetate (2.54 mL, 12.8 mmol, 1.5 equiv.) was added dropwise and the reaction was stirred for 30 minutes. A solution of 1-(4-fluorophenyl)cyclopentane-1-carbaldehyde (1.615 g, 8.4 mmol, 1.0 equiv.) in dichloromethane (10 mL) was added dropwise over 5 minutes. The reaction was allowed to warm to room temperature and stir overnight (16 hours) before confirmation of completion by TLC (ethyl acetate: hexanes = 1: 39). The reaction was quenched with saturated aqueous ammonium chloride and extracted 3x with ethyl acetate. Combined organics were dried over sodium sulfate and concentrated under reduced pressure. The crude reaction mixture was purified by silica flash column chromatography (ethyl acetate: hexanes = 1: 99), furnishing ethyl (E)-3-(1-(4-fluorophenyl)cyclopentyl)acrylate as a white solid (2.072 g, 7.90 mmol, 94% yield).

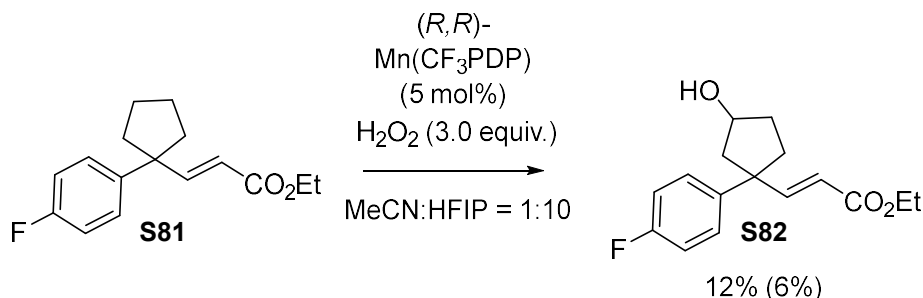
ethyl (E)-3-(1-(4-fluorophenyl)cyclopentyl)acrylate [S81]. ¹H NMR (500 MHz, CDCl₃) δ 7.19



– 7.11 (m, 2H), 6.96 (d, *J* = 15.8 Hz, 1H), 6.96 – 6.88 (m, 2H), 5.51 (d, *J* = 15.9 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.08 – 1.96 (m, 2H), 1.98 – 1.88 (m, 2H), 1.76 – 1.61 (m, 4H), 1.19 (t, *J* = 7.2 Hz, 3H). ¹³C NMR

(126 MHz, CDCl₃) δ 167.14, 161.52 (d, *J* = 245.0 Hz), 155.84, 141.11 (d, *J* = 3.3 Hz), 128.74 (d, *J* = 7.7 Hz), 118.68, 115.22 (d, *J* = 21.1 Hz), 60.47, 53.44, 37.55, 23.22, 14.38. ¹⁹F NMR (471

MHz, CDCl₃) δ -116.81. HRMS (TOF ESI+) m/z calculated for C₁₆H₂₀O₂F [M+H]⁺: 263.1447, found 263.1447.

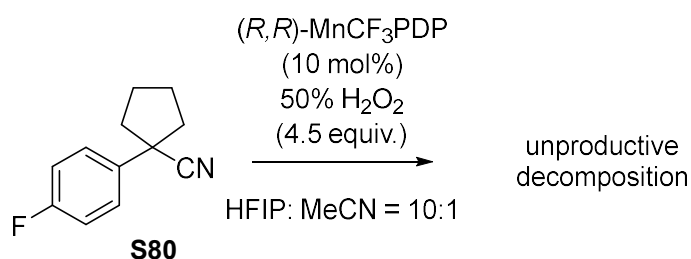


Oxidation of ethyl (E)-3-(1-(4-fluorophenyl)cyclopentyl)acrylate [S81]. Ethyl (E)-3-(1-(4-chlorophenyl)cyclopentyl)acrylate in HFIP was oxidized according to the Standard conditions with 5 mol% (*R,R*)-Mn(CF₃-PDP) or (*S,R,R,S*)-Mn(MeCF₃-PDP) and 3.0 equiv. H₂O₂. The resulting mixture was purified with column chromatography (2: 1 EtOAc: hexanes → EtOAc) to furnish **S77**. With (*R,R*)-Mn(CF₃-PDP) - **Run 1**: 14% yield, 5% RSM. **Run 2**: 13% yield, 5% RSM. **Run 3**: 9% yield, 8% RSM. **Average**: 12% ± 2.6%, 6% ± 1.7% RSM. With (*S,R,R,S*)-Mn(MeCF₃-PDP) - **Run 1**: 0%. **Run 2**: 0%. **Run 3**: 0%. **Average**: 0%.

ethyl (E)-3-(1-(4-fluorophenyl)-3-hydroxycyclopentyl)acrylate [S82]. Alcohols were isolated

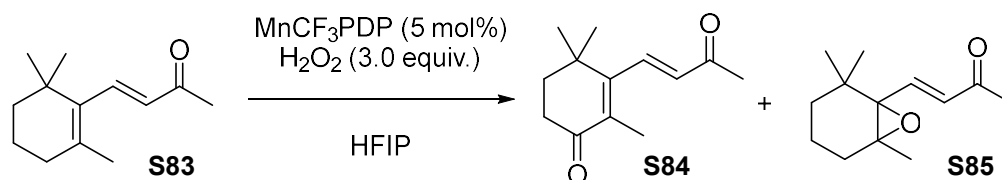
as a 2.3: 1 mixture of diastereomers. ¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.16 (m, 2.3H), 7.08 – 6.92 (m, 2.7H), (appt. d, J = 15.7 Hz, 1H), 4.51 (m, 0.7H), 4.44 (m, 0.3H), 4.16 (q, J = 7.1 Hz, 1.4H), 4.15 (q, J = 7.1 Hz, 0.6H), 2.56 (dd, J = 13.6, 6.7 Hz, 0.7H), 2.47 (dd, J = 13.8, 7.1 Hz, 0.3H), 2.34 – 2.23 (m, 1H), 2.19 – 2.03 (m, 3H), 1.60 (br. s, 1H), 1.81 – 1.68 (m, 1H), 1.26 (t, J = 7.1 Hz, 2.1H), 1.25 (t, J = 7.1 Hz, 0.9H) ¹³C NMR (126 MHz) δ 167.04 (166.90), 161.61 (d, J = 245.6 Hz) (161.59 (d,

$J = 245.8$ Hz)), 156.18 (155.19), 141.21 (d, $J = 3.3$ Hz) (140.54 (d, $J = 3.2$ Hz)), 128.65 (d, $J = 7.9$ Hz) (128.55 (d, $J = 8.1$ Hz)), 119.06 (118.61), 115.41 (d, $J = 21.1$ Hz), 72.73 (72.65), 60.63 (60.55), 52.58 (52.51), 47.54 (47.13), 36.42 (35.74), 34.54 (34.45), 14.36. ^{19}F NMR (471 MHz, CDCl_3) δ -116.33 – 116.45 (m). HRMS (ESI+) m/z calculated for $\text{C}_{10}\text{H}_{20}\text{FO}_3$ $[\text{M}+\text{H}]^+$: 279.1396, found 279.1396.



Oxidation of 1-(4-fluorophenyl)cyclopentane-1-carbonitrile [S80]. 1-(4-fluorophenyl)cyclopentane-1-carbonitrile (0.3 mmol) in HFIP was oxidized according to Standard Procedure with 10 mol% $(R,R)\text{-Mn}(\text{CF}_3\text{-PDP})$ or $(S,R,R,S)\text{-Mn}(\text{MeCF}_3\text{-PDP})$ and 4.5 equiv. of H_2O_2 . The resulting mixture, in all cases, was determined to contain no methylene oxidation products or unreacted starting material.

Oxidation of $\alpha,\beta,\gamma,\delta$ -Unsaturated carbonyl compound: β -ionone **S83**



Oxidation of β -ionone [S83]. β -Ionone was oxidized using the according to the Standard Procedure with 5 mol% (*R,R*)- $\text{Mn}(\text{CF}_3\text{-PDP})$ and 3.0 equiv. H_2O_2 . The resulting mixture was purified with column chromatography (1: 2 EtOAc: hexanes). The products shown were identified, and the remainder of the mass balance was isolated as an inseparable mixture of several oxidized products, which did not contain peaks corresponding to remote oxidation products. Spectroscopic data of oxidation products **S84** and **S85** matched the published literature⁵⁵. **Run 1:** 32% dione, 13% epoxide. **Run 2:** 33% dione, 11% epoxide. **Average:** 33% dione, 12% epoxide.

XI. Site Selectivity Prediction in PDP Oxidation

1. Predictable Site Selectivity from Literature Precedents

a) C4 Selectivity in Linear Substrates

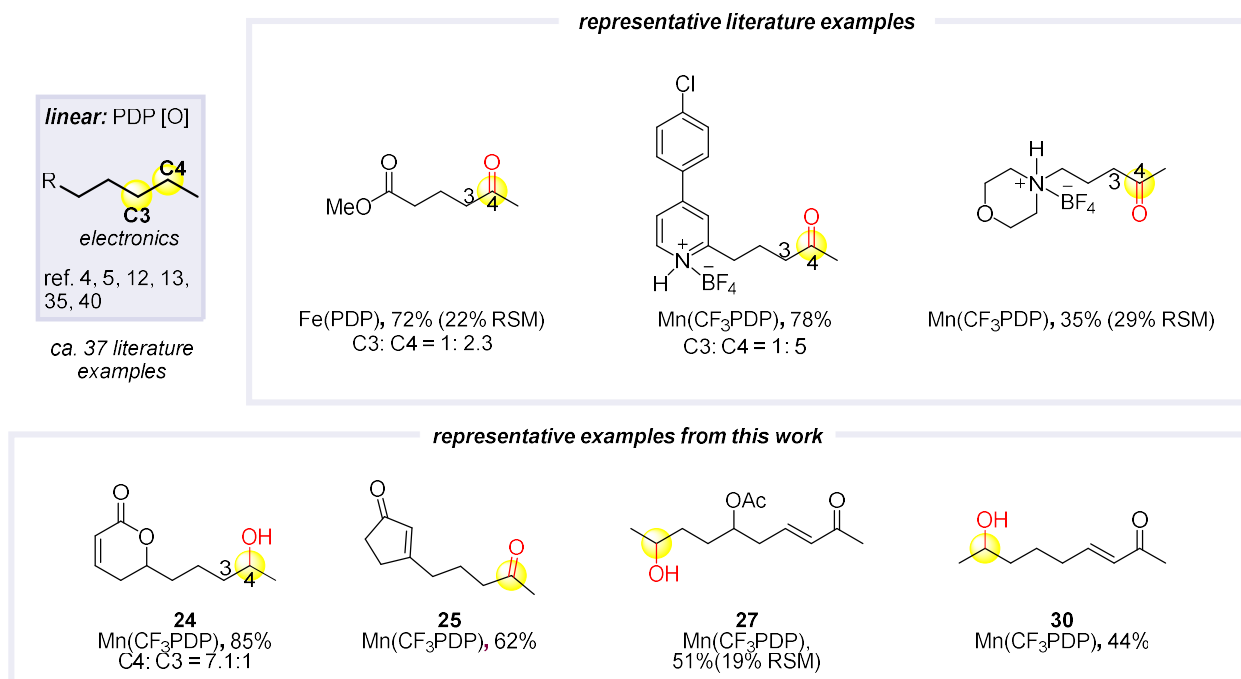


Figure S37. Predictable Site Selectivities of Linear Substrates Based on Literature Examples. See the manuscript for reference 4, 5, 12, 13, 35, 40.

C-H oxidation of linear aliphatic chain prefers methylene sites most distal from electron withdrawing functionalities, consistent with the electronic and steric trends described above^{1,56,57}.

b) C3 Selectivity in Cyclopentyl Substrates

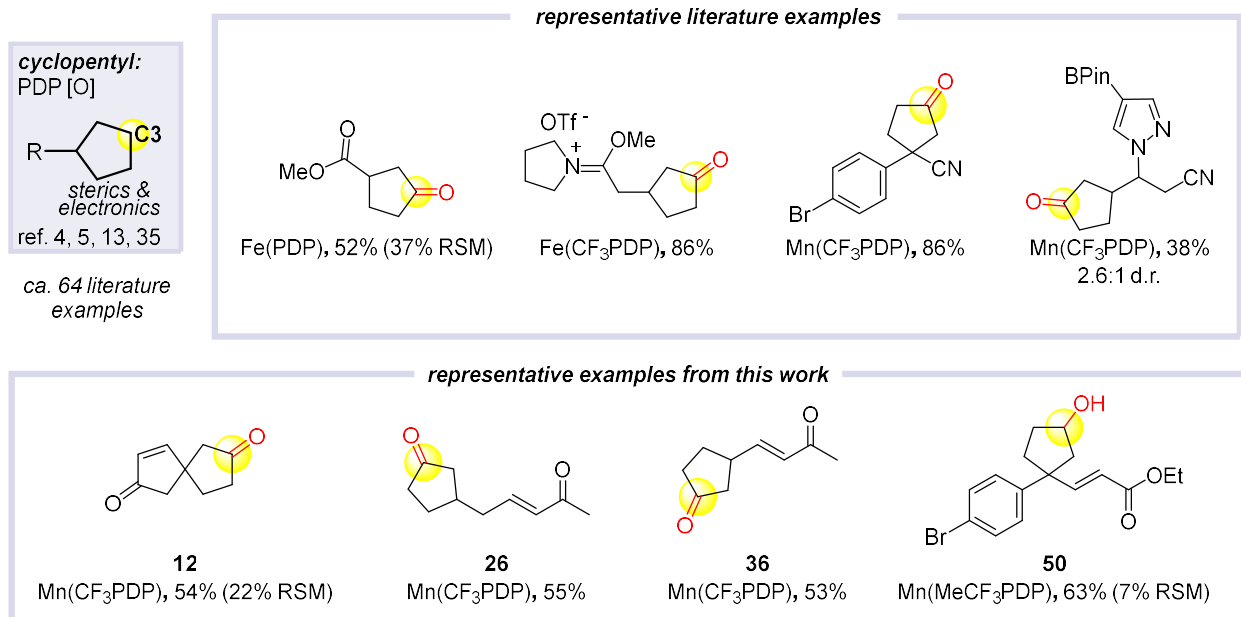


Figure S38. Predictable Site Selectivities of Cyclopentyl Substrates Based on Literature Examples. See the manuscript for reference 4, 5, 13, 35.

Numerous studies have demonstrated that C3 is the preferred oxidation site on cyclopentyl groups^{1,57}. This selectivity can be rationalized by the presence of substituent at C1, which is typically electron-deficient, resulting in increased steric hindrance and reduced electron richness at C2 relative to C3.

c) C3 vs. C4 Selectivity in Cyclohexyl Substrates

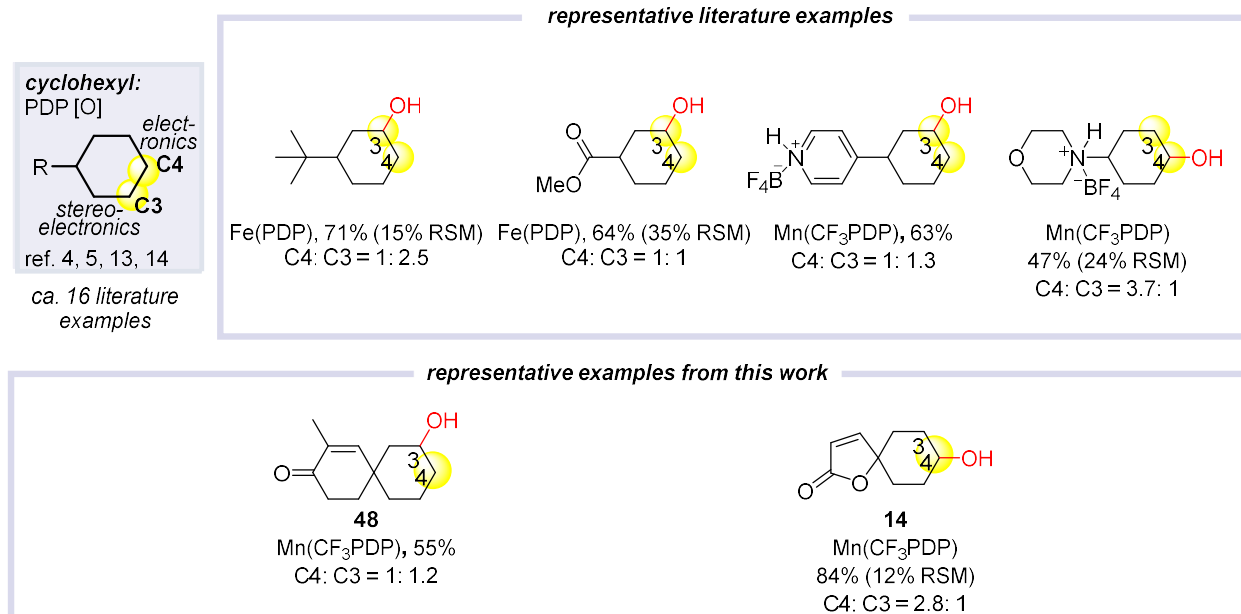


Figure S39. Predictable Site Selectivities of Cyclohexyl Substrates Based on Literature Examples. See the manuscript for reference 4, 5, 13, 14.

Several studies have reported a preference for C3 oxidation, particularly when only the C1 position is substituted on the cyclohexyl group^{56,57}. This selectivity was rationalized by torsional strain resulting from planarization due to the bulky C1 substituent⁵⁸. However, when the C1 substituent is electron withdrawing, oxidation can equally or preferentially occur at C4 due to an inductive effect, as the closer C3 site becomes more electronically deactivated relative to C4^{56,57}.

d) C3 vs. C4 Selectivity in Cycloheptyl Substrates

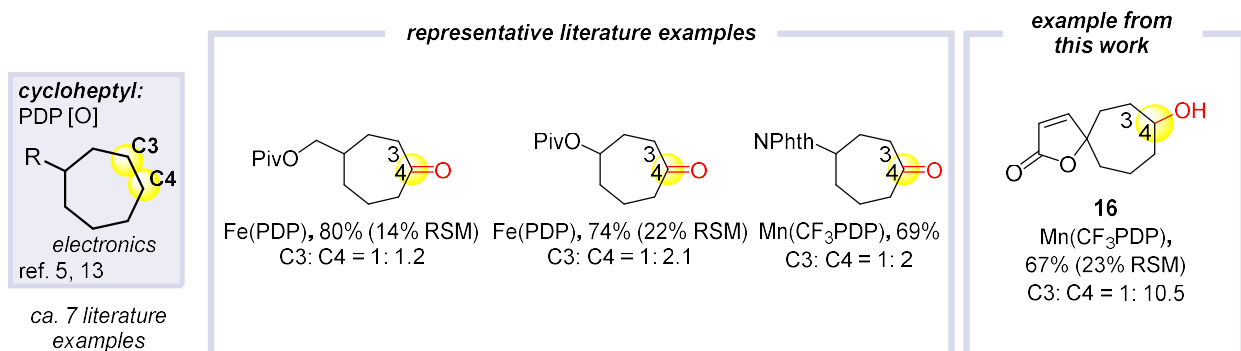


Figure S40. Predictable Site Selectivities of Cycloheptyl Substrates Based on Literature Examples. See the manuscript for reference 5, 13.

With electron-withdrawing substituent at C1, oxidation on cycloheptyl group predominantly occurs at the most distal C4 position, with minor oxidation at C3^{56,57}. Similar to cyclopentanes, this selectivity can be rationalized by inductive electron-withdrawing and steric effects from the substituent at C1. Substrate **16** demonstrates notably higher C4 selectivity (C3:C4 = 1:10.5) compared to previously reported examples, possibly due to enhanced inductive deactivation by solvent H-bonding to butanolide.

e) C3 Selectivity in Bornane Core

The major site of oxidation in isolongifolenone **21** is C4 which has been previously reported for the longiborneol analogues with PDP catalysis⁵⁹.

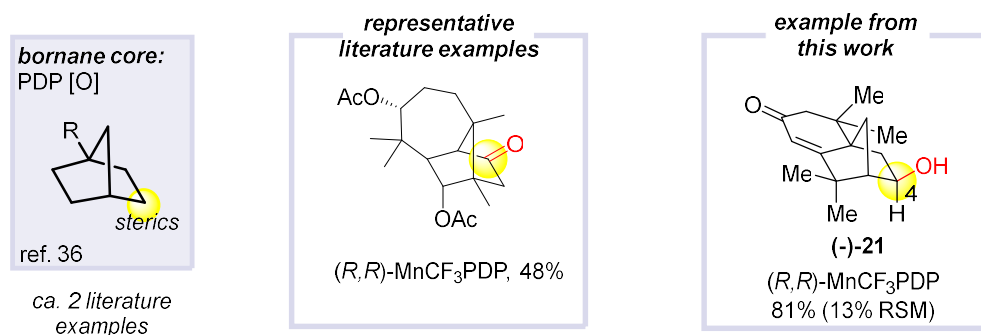


Figure S41. Predictable Site Selectivities of Bornane Cores Based on Literature Examples. See the manuscript for reference 36.

f) C2 Selectivity in Drimane Substrates

Previously reported PDP oxidations on substrates containing the drimane core show site-selectivity preference for C2 based primarily on a steric and stereoelectronic preference. The observation was first reported in 2010 in the oxidation of manool analogue and sclareolide and has most recently been demonstrated in the total synthesis of *ent*-beyerane by the de Lucca group⁶⁰. This precedent is fully consistent with site selectivities observed for substrates containing the drimane core in this work (**22**, **23**, **42**, **43**, **56**).

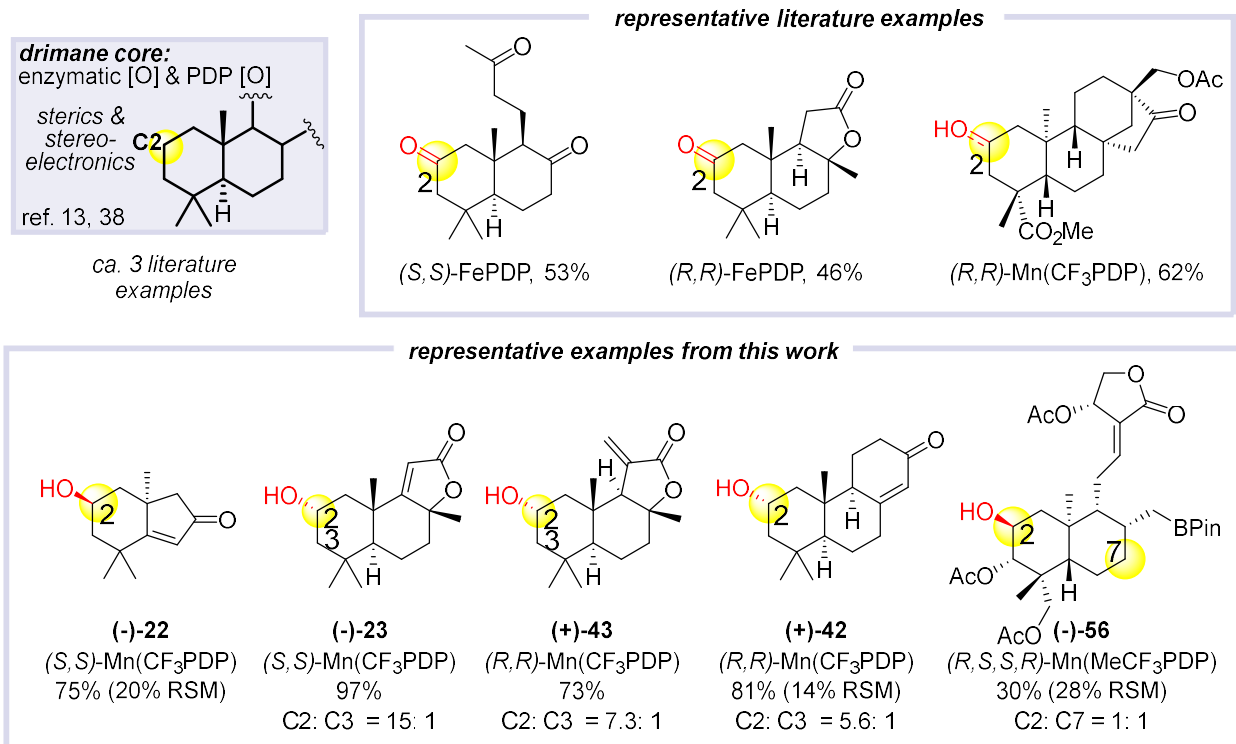
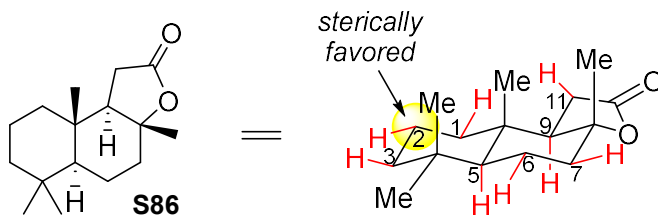


Figure S42. Predictable Site Selectivities of Drimanes Based on Literature Examples. See the manuscript for reference 13, 38.

Parameterization of electronics and sterics/stereoelectronics. Consistent with these empirical observations, reported calculations of electronic and sterics/stereoelectronics parameters for sclareolide **S86** show that C2 is the sterically and stereoelectronically preferred site⁶¹.



sites sorted by electronics	electronic parameter (E)	sites sorted by sterics	steric/ stereoelectronic parameter (S)	local sterics (L)	through space (TS)	stereoelectronics (SE)
5	0.19597	2	5.215	Et,Et	-	2Me
3	0.20279	11	6.36	C(O)Me,iPr	gauche	-
1	0.20391	6	7.435	Et,iPr	2gauche	2Me
2	0.20487	3	8.69	Et,tBu	-	-
9	0.20695	7	8.69	Et,tBu	-	-
7	0.21047	1	9.59	Et,tBu	gauche	-
6	0.21267	9	15.59	Et,tBu,tBu	2 H-H 1,3	-
11	0.23517	5	16.59	Et,tBu,tBu	4 H-H 1,3	-

Table S50. Electronic and Sterics/Stereoelectronics Parameters for Sclareolide **S86** Obtained from Ref. 61.

g) C6 & C12 Selectivity in Steroid Substrates

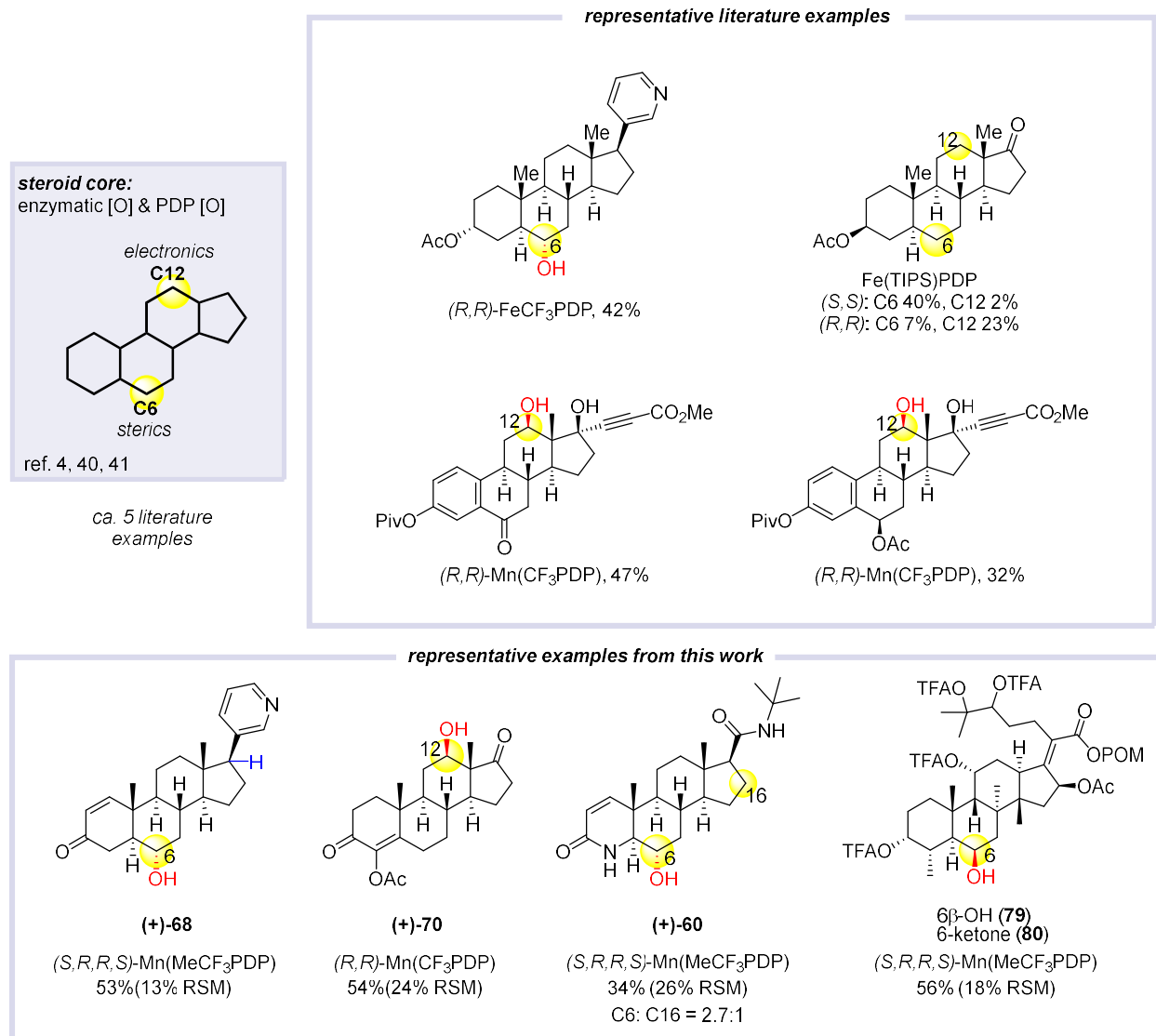
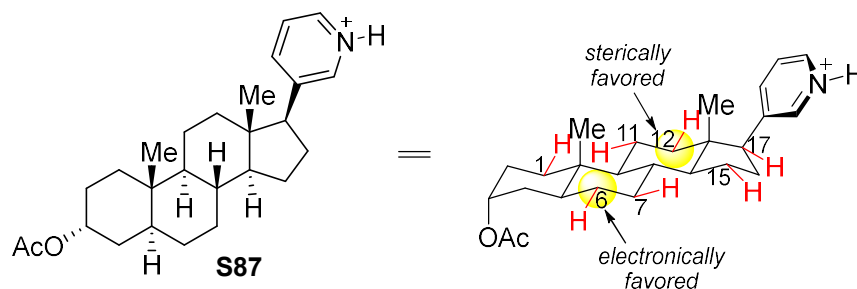


Figure S43. Predictable Site Selectivities of Steroid Cores Based on Literature Examples. See the manuscript for reference 4, 40, 41.

Numerous reported PDP oxidations on substrates with the steroid core have shown a predictable preference for either C6 or C12. When C6 is electronically accessible, it is the major site preferred based on sterics with bulky PDP catalysts. When C6 is sterically and/or electronically disfavored, C12 is preferred site of oxidation based primarily on electronics. Consistent with this precedent, our work with PDP catalysis shows the major site of oxidation is C6 on steroid scaffolds

(**68**, **60**, **79** and **80**). In the presence of a sterically bulky and electron withdrawing group proximal to C6, oxidation at C12 was favored (**70**).

Parameterization of electronics and sterics/ stereoelectronics. Consistent with these empirical observations, reported calculations of electronic and sterics/stereoelectronics parameters for steroid substrate **S87** indicate that C6 is electronically favored, while C12 is sterically favored⁶². Parameters were calculated based on the workflow reported for the PDP oxidation site-selectivity prediction model⁶¹.



sites sorted by electronics	electronic parameter (E)	sites sorted by sterics	steric/ stereoelectronic parameter (S)	local sterics (L)	through space (TS)	stereoelectronics (SE)
12	0.1957	6	5.82	Et,iPr	-	Me
1	0.2013	15	6.72	Et,iPr	gauche	Me
7	0.203	7	6.9	Et,iPr	gauche	-
6	0.2098	11	7.44	Et,iPr	2gauche	2Me
11	0.2147	1	9.41	Et,tBu	gauche	OAc
15	0.2201	12	9.49	Et,tBu	gauche	-
17	0.2212	17	12.59	Et,Ph,tBu	-	-

Table S51. Electronic and Sterics/Stereoelectronics Parameters for Steroid **S87** Obtained from Ref. 62.

h) C7 Selectivity in Pleuromutilin Analogues

The major site of oxidation in novel enone pleuromutilin analog **63** is C7 which has been previously reported for the pleuromutilin analogue with PDP catalysis⁵⁶.

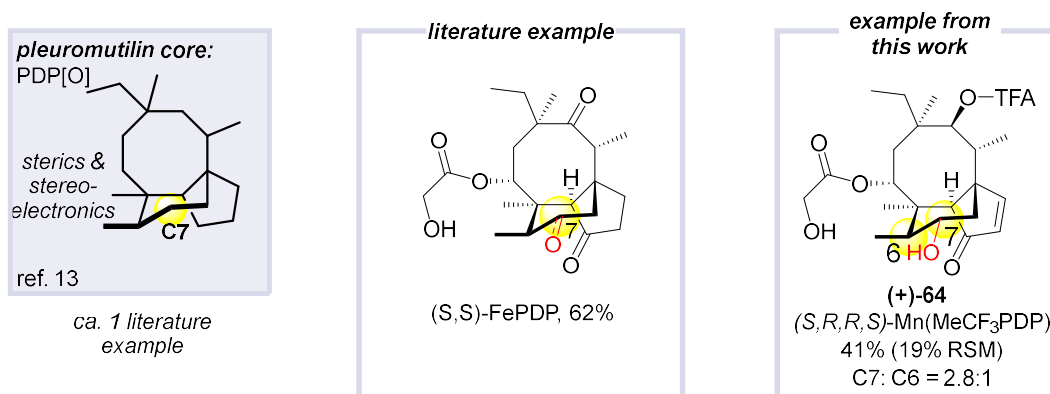


Figure S44. Predictable Site Selectivities of Pleuromutilin Analogues Based on Literature Examples. See the manuscript for reference 13.

2. Site Selectivity Predictions Based on Electronic and Steric/ Stereoelectronic Parameter Calculations

Site-selectivities observed in this work follow the empirical selectivities that are well-precedented in the literature for PDP oxidation in C1-substituted cyclohexane (10 examples), steroid (4 examples) and drimane (5 examples, *vide supra*) cores. This indicates that despite the change in active oxidant under these reported Mn(CF₃PDP) **1**/ HFIP conditions, the site-selectivity rules for PDP catalysis remain the same. Mn(CF₃PDP) **1** and Mn(MeCF₃PDP) **2**/ HFIP catalyzed C—H oxidations favor electron-rich, sterically accessible, and stereoelectronically activated sites consistent with prior reports⁵⁶. Accordingly, parameterization of electronic, steric, and stereoelectronic properties of C—H bonds⁶¹ provides rapid insights into predicting new sites of oxidation for this work. Site selectivities that have not been previously demonstrated in the

literature were rationalized using C—H bond parameterization calculated according to the reported procedure⁶¹. DFT Calculations were performed using B3LYP method in combination with 6-311++g(d,p) basis set and polarizable continuum solvent model for HFIP ($\epsilon_s=16.7$, $\epsilon_{\text{sinf}}=1.625625$)^{63,64}. Natural population analysis (NPA) charge was calculated by natural bonding orbital (NBO) analysis and used as electronic parameter. Steric/stereoelectronic parameters were derived from DFT-optimized geometries based on the reported procedure⁶¹ (**Table S52**). H-Me eclipse interaction was considered in **63** to describe through-space interaction in non-6-membered chair conformation. Methyl groups, C-H bonds α to heteroatoms, and axial methylenic C-H bonds on conformationally rigid 6-membered rings were excluded from the analysis. Methinyl sites that are axial and electron rich are considered. For conformationally flexible methylene sites, the average NPA and steric values were used.

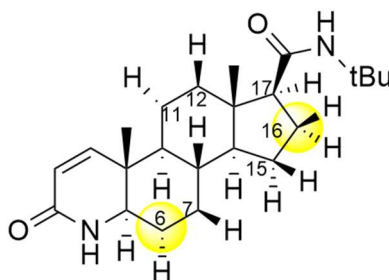
substituent	adjusted A-values for local sterics (L)	through space interaction types	values for through space (TS)
H	1	gauche(=syn pentane)	0.9
OMe	1.78	H-H 1,3	0.5
C(O)Me	2.25	H-Me 1,3	0.9
Me	2.74	H-Me eclipse	1.3
Et	2.79		
iPr	3.21		
tBu	5.8		

stereoelectronics interaction types	values for stereoelectronics (SE)
H-Me 1,3	0.18

Table S52. Values Used for the Steric/Stereoelectronic Parameter Calculation

a) Finasteride (59): Rationale for C16 selectivity

Consistent with our empirical findings and literature precedent, calculations show that C16 and with C6 are the top preferred sites of oxidation based on sterics with sterically bulky PDP catalysis.

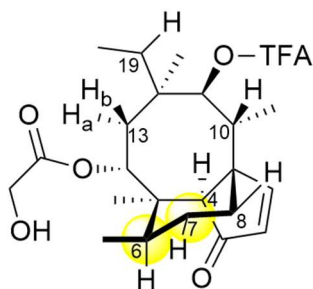


sites sorted by electronics	electronic parameter (E)	sites sorted by sterics	steric/ stereoelectronic parameter (S)	local sterics (L)	through space (TS)	stereo-electronics (SE)
15	0.20302	6	5.82	iPr, Et	-	Me
12	0.20615	16	6	Et, iPr/ Et, iPr	-/-	-/-
11	0.20691	15	6.45	Et, iPr/ Et, iPr	gauche/ -	-/-
16	0.21071	11	6.54	Et, iPr	gauche	2Me
7	0.21103	7	6.9	Et, iPr	gauche	-
6	0.2121	17	8.59	Et, tBu	-	-
17	0.21667	12	9.49	Et, tBu	gauche	-

Table S53. Electronic and Sterics/Stereoelectronics Parameters for **59**

b) Pleuromutilin 63: Rationale for C6 selectivity.

Consistent with previously reported site-selectivities, calculations support that C7 is the sterically preferred site of oxidation on the pleuromutilin core and indicate that C6 is the electronically favored site. This is consistent with our observations that C7 is the major site of oxidation in pleuromutilin analogue **63** and C6 is the minor site of oxidation.

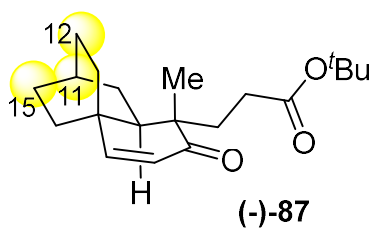


sites sorted by electronics	electronic parameter (E)	sites sorted by sterics	steric/ stereoelectronic parameter (S)	local sterics (L)	through space (TS)	stereoelectronics (SE)
6	0.20285	7	5.82	iPr, Et	-	H-Me 1,3
19	0.21245	13a	8.88	OAc, tBu	H-Me eclipse	-
8	0.21298	13b	8.88	OAc, tBu	H-Me eclipse	-
7	0.21354	19	9.44	Me, tBu/ Me, tBu	-/ 2 gauche	-/ -
13a	0.21895	8	9.89	tBu, Et	H-Me eclipse	-
10	0.21955	6	12.23	Me, tBu, Et	H-Me 1,3	-
13b	0.2337	10	12.65	Me, tBu, iPr	gauche	-
4	0.25924	4	16.05	C(O)Me, tBu, tBu	gauche, H-Me eclipse	-

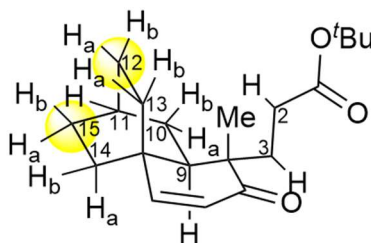
Table S54. Electronic and Sterics/Stereoelectronics Parameters for **63**

c) Platencin Core **87**: Rationale for C12 and C15 selectivity

The major sites of oxidation in platencin core **87** are predicted to be C12 and C15 based on electronics and C2, C12, and C15 based on sterics and stereoelectronics. C2 is highly disfavored electronically. Consistent with these predictions, Mn(CF₃PDP) **1** and Mn(MeCF₃PDP) **2** oxidations showed C12 to be the major site of oxidation and C15 the minor site. The calculations failed to predict tertiary C11, the other minor observed site of oxidation. This is likely due to overestimation of steric hinderance since the reported parameterization is unable to capture steric environment of bridgehead position of [2.2.2] bicycle. Examples of bridgehead tertiary C-H oxidation have been reported⁶⁵ despite their low NPA charges attributed to increased s-character⁶⁶.



catalyst	yield	site-selectivity
(<i>S,S</i>)- 1	77%	C15: C12 : C11 = 1.0: 2.4 : 1.2
(<i>R,S,S,R</i>)- 2	66%	C15: C12 : C11 = 1.7: 3.0 : 1.0
(<i>R,R</i>)- 1	73%	C15: C12 : C11 = 1.0: 2.6 : 1.8
(<i>S,R,R,S</i>)- 2	72%	C15: C12 : C11 = 1.5: 2.6 : 1.0
average ratio		C15: C12: C11 = 1.0: 2.1 : 1.0



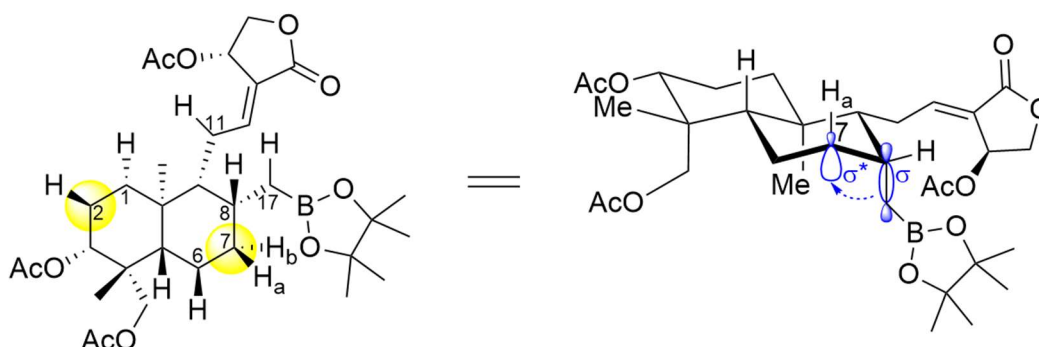
sites sorted by electronics	electronic parameter (E)	sites sorted by sterics	steric/ stereoelectronic parameter (S)	local sterics (L)	through space (TS)	stereoelectronics (SE)
15a	0.2021	2	5.49	Et, C(O)Me/ Et, C(O)Me	-/ gauche	-/-
12a	0.20228	15a	6.5	iPr, Et	H-H 1,3	-
12b	0.20495	15b	6.5	`	H-H 1,3	-
10b	0.20551	12a	6.9	Et, iPr	H-H 1,3	-
14b	0.20611	12b	7	Et, iPr	2 H-H 1,3	-
15b	0.20692	10a	7.82	iPr, iPr	H-H 1,3, gauche	-
13a	0.20797	11	8.37	Et, Et, Et	-	-
10a	0.20835	3	9.04	tBu, Et/ tBu, Et	-/ gauche	-/-
14a	0.2085	14a	9.09	tBu, Et	H-H 1,3	-
11	0.20991	10b	9.12	iPr, iPr	gauche, H-H 1,3	-
13b	0.21047	13b	9.49	tBu, Et	gauche	-
9	0.21346	14b	9.59	tBu, Et	2 H-H 1,3	-
3	0.21804	13a	9.59	tBu, Et	2 H-H 1,3	-
2	0.23577	9	15.79	tBu, tBu, Et	gauche, H-H 1,3	-

Table S55. Electronic and Sterics/Stereoelectronics Parameters for **87**

d) Andrographolide analogue 55: Rationale for C7 selectivity

Consistent with literature precedent and our observations, calculations predict that C2 is a major site of oxidation with PDP catalysis based on sterics. Consistent with the observations in this work, calculations predict that the C7 site is the electronically preferred site of oxidation. If the C7 axial (7a) site is considered, it is predicted to be more electronically activated than the C7

equatorial (7b) site and comparable sterically. The preferential electronic activation of 7a is likely due in part to hyperconjugative activation of the adjacent alkyl borane substituent which is antiperiplanar to 7a according to the energy minimized structure.

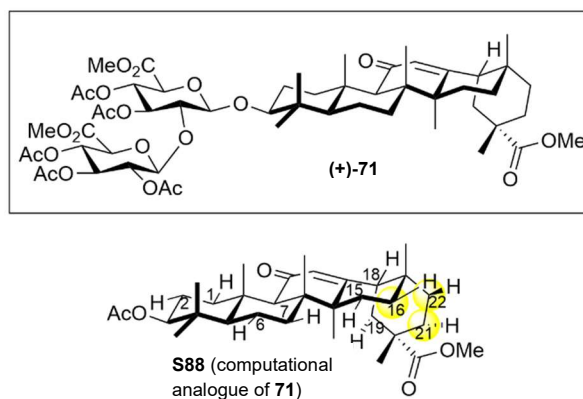


sites sorted by electronics	electronic parameter (E)	sites sorted by sterics	steric/ stereoelectronic parameter (S)	local sterics (L)	through space (TS)	stereoelectronics (SE)
7a	0.19439	2	5.64	Et, iPr	-	2 H-Me 1,3
7b	0.20297	6	6.36	iPr, Et	gauche	3 H-Me 1,3
8	0.20753	17	6.36	iPr, C(O)Me/ iPr, C(O)Me	gauche/ 2gauche	- / -
6	0.20861	11	6.81	iPr, C(O)Me/ iPr, C(O)Me	gauche/ gauche	- / -
1	0.21261	7b	6.9	iPr, Et	gauche	-
2	0.21724	7a	7	iPr, Et	2 H-H 1,3	-
17	0.23107	1	9.49	tBu, Et	gauche	-
11	0.23449	8	10.59	Et, Et, iPr	2 gauche	-

Table S56. Electronic and Sterics/Stereoelectronics Parameters for **55**

e) Glycyrrhizin analogue 71: Rationale for C16, C22 selectivity.

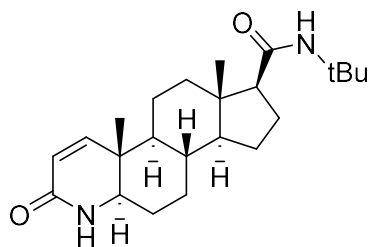
An acetate version **S88** (C3-acetoxy) of glycyrrhizin analogue **71** (C3-glycosyl) was used computationally for geometry optimization to reduce computational cost and time. Doing so underestimates the steric hindrance at C6 and C2 due to the absent bulky C3 substituent. Consistent with our experimental observations, C16 and C22 are calculated to be among the top electronically activated and sterically accessible sites for PDP oxidation and C21 is calculated to be as sterically favored as C22.



sites sorted by electronics	electronic parameter (E)	sites sorted by sterics	steric/ stereoelectronic parameter (S)	local sterics (L)	through space (TS)	stereoelectronics (SE)
7	0.2085	6	6.36	Et, iPr	gauche	3 H-Me 1,3
22	0.20966	2	6.54	Et, iPr	gauche	2 H-Me 1,3
16	0.20981	16	8.05	tBu, Et	-	3 H-Me 1,3
6	0.21064	22	8.41	tBu, Et	-	H-Me 1,3
15	0.2115	21	8.41	tBu, Et	-	H-Me 1,3
2	0.21444	19	8.65	tBu, iPr	-	2 H-Me 1,3
18	0.21815	15	9.13	tBu, Et	gauche	2 H-Me 1,3
21	0.2196	7	9.31	tBu, Et	gauche	H-Me 1,3
19	0.22237	18	9.45	C(O)Me, tBu	H-H 1,3, H-Me 1,3	-
1	0.22973	1	9.49	tBu, Et	gauche	-

Table S57. Electronic and Sterics/Stereoelectronics Parameters for **S88**

3. Gaussian optimization data



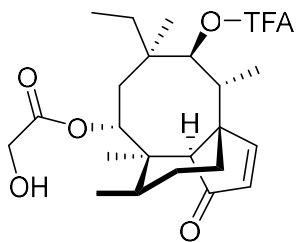
finasteride **59**

59

E(RB3LYP) = -1158.48200382

Center number	Atomic number	X	Y	Z
1	7	5.512099	0.114043	-0.16631
2	8	7.185968	-1.41678	-0.41896
3	7	-4.22334	-0.57035	-0.54899
4	8	-4.4076	1.24188	0.821939
5	6	4.930756	-2.19128	-0.47038
6	6	5.981259	-1.14731	-0.36709
7	6	4.104053	0.449459	-0.40704
8	6	3.177575	-0.57715	0.295514
9	6	3.650326	-1.94559	-0.16037
10	6	3.78655	1.892456	-0.03454
11	6	2.344336	2.213015	-0.44806
12	6	1.323442	1.218085	0.133664
13	6	1.716996	-0.26034	-0.17097
14	6	-0.08899	1.461653	-0.41354
15	6	-1.16698	0.520173	0.189413
16	6	-0.76839	-0.92766	-0.13602
17	6	0.656333	-1.24857	0.360356
18	6	-0.7216	2.860668	-0.32268
19	6	-2.23821	2.602918	-0.56258
20	6	-2.425	1.061117	-0.57167
21	6	3.315912	-0.54699	1.839475
22	6	-1.34115	0.699502	1.712069
23	6	-3.78119	0.603921	-0.02584
24	6	-5.47915	-1.29077	-0.21939
25	6	-6.69921	-0.42271	-0.57458
26	6	-5.48043	-2.56247	-1.08061
27	6	-5.50184	-1.67469	1.270215
28	1	6.196821	0.860016	-0.2029

29	1	-3.64469	-0.98953	-1.26268
30	1	5.276174	-3.18135	-0.74616
31	1	3.910434	0.341945	-1.48482
32	1	2.936653	-2.76405	-0.17033
33	1	3.927101	2.049627	1.039899
34	1	4.483754	2.562503	-0.55029
35	1	2.277465	2.19609	-1.54407
36	1	2.089474	3.229472	-0.13438
37	1	1.307098	1.359219	1.220396
38	1	1.722929	-0.35614	-1.26693
39	1	-0.04751	1.208814	-1.48413
40	1	-1.47429	-1.63911	0.306675
41	1	-0.80986	-1.07083	-1.2235
42	1	0.906174	-2.26701	0.049904
43	1	0.66674	-1.25221	1.453942
44	1	-0.30339	3.551656	-1.05806
45	1	-0.55354	3.30233	0.664543
46	1	-2.84822	3.042619	0.227647
47	1	-2.57684	3.032991	-1.50871
48	1	-2.34138	0.696472	-1.60099
49	1	4.366766	-0.61	2.130793
50	1	2.898833	0.36413	2.271751
51	1	2.797172	-1.39754	2.287534
52	1	-0.42047	0.48277	2.256205
53	1	-1.64966	1.712581	1.976499
54	1	-2.11006	0.017725	2.086649
55	1	-7.62178	-0.97246	-0.36615
56	1	-6.70515	0.498782	0.009121
57	1	-6.68882	-0.16258	-1.63731
58	1	-4.61674	-3.19377	-0.84948
59	1	-5.45399	-2.31483	-2.14655
60	1	-6.38629	-3.1424	-0.8893
61	1	-4.63879	-2.2992	1.519416
62	1	-5.48282	-0.78636	1.902765
63	1	-6.41012	-2.24176	1.494166



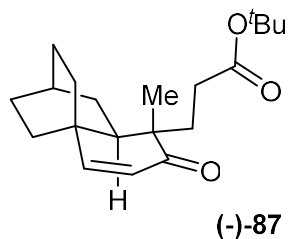
(-)-63

63

E(RB3LYP) = -1685.78884421

Center number	Atomic number	X	Y	Z
1	6	0.552163	0.754262	1.959982
2	6	0.750181	1.229938	0.51036
3	6	2.091729	0.804609	-0.1981
4	6	2.464694	-0.66499	0.190815
5	6	1.496754	-1.80907	-0.26106
6	6	0.422876	-2.3032	0.78751
7	6	-0.76952	-1.42486	1.262904
8	6	-0.64892	-0.19379	2.226845
9	6	3.871462	-1.19183	-0.22035
10	6	3.740977	-2.63485	-0.45419
11	6	2.450931	-2.9788	-0.4546
12	6	-1.96185	0.650045	2.175851
13	6	-3.2694	-0.04376	2.579257
14	6	-0.48434	-0.71108	3.677155
15	8	-1.51997	-0.99218	0.044919
16	6	1.083644	-2.97303	2.011154
17	1	2.542539	-0.72105	1.280532
18	6	0.943753	-1.56265	-1.71876
19	6	0.777552	-0.11017	-2.18874
20	6	1.922264	0.82356	-1.75539
21	6	1.75209	2.202077	-2.41106
22	6	3.219935	1.749087	0.271859
23	8	0.713631	2.709585	0.533469
24	6	-2.44619	-1.79924	-0.42565
25	8	-2.76586	-2.8921	-0.03431
26	8	4.916992	-0.56777	-0.29178
27	6	-0.34796	3.376154	0.10064
28	6	-0.18179	4.873546	0.283909
29	8	-1.34924	2.897787	-0.39331
30	8	-1.32859	5.568842	-0.16944
31	6	-3.16124	-1.19254	-1.66751
32	9	-2.99438	0.127884	-1.79911

33	9	-4.48046	-1.43987	-1.59671
34	9	-2.69569	-1.78418	-2.79004
35	1	1.461781	0.295088	2.344233
36	1	0.397601	1.63837	2.583031
37	1	-0.09925	0.927605	-0.09003
38	1	-0.08322	-3.11543	0.252789
39	1	-1.43883	-2.12431	1.763046
40	1	4.59231	-3.27488	-0.64947
41	1	2.065129	-3.97523	-0.64565
42	1	-2.07843	1.08446	1.182445
43	1	-1.80251	1.491295	2.859076
44	1	-3.24919	-0.39325	3.614565
45	1	-3.51765	-0.90088	1.94816
46	1	-4.09805	0.665792	2.492053
47	1	-1.23917	-1.45703	3.934505
48	1	0.497238	-1.14851	3.854392
49	1	-0.5969	0.129993	4.367948
50	1	0.326941	-3.30374	2.725594
51	1	1.642858	-3.85899	1.706361
52	1	1.774968	-2.31055	2.53462
53	1	1.655281	-2.02605	-2.40768
54	1	0.013435	-2.11906	-1.85067
55	1	-0.17933	0.302066	-1.86314
56	1	0.732853	-0.12203	-3.283
57	1	2.858339	0.408633	-2.15039
58	1	2.528831	2.907042	-2.10744
59	1	1.816286	2.093087	-3.49848
60	1	0.778693	2.648669	-2.19493
61	1	2.961371	2.791211	0.098306
62	1	3.402996	1.626495	1.344796
63	1	4.148824	1.524595	-0.24557
64	1	0.707218	5.195542	-0.27064
65	1	-0.00602	5.079679	1.345558
66	1	-1.93663	4.89723	-0.51555

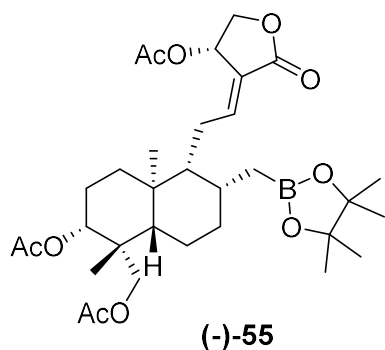


87

E(RB3LYP) = -1006.19261698

Center number	Atomic number	X	Y	Z
1	6	-1.75962	-0.19728	-0.01443
2	6	-3.13884	0.001074	0.679648
3	6	-3.3082	-1.1904	1.669392
4	6	-1.85078	-1.4183	-0.96954
5	6	-3.09477	-2.53245	0.914354
6	6	-3.08172	-2.27196	-0.60379
7	6	-4.33208	-0.09337	-0.31768
8	6	-4.35431	-1.49643	-0.98677
9	6	-3.18976	1.288825	1.435381
10	6	-1.09814	1.077809	-0.62422
11	6	-2.27087	2.263229	1.345455
12	6	-1.12202	2.206043	0.424579
13	8	-0.26218	3.079596	0.454383
14	6	0.356694	0.787206	-1.07603
15	6	1.297596	0.226905	-0.00715
16	6	2.727685	0.072861	-0.49075
17	8	3.09841	0.239521	-1.63348
18	6	-1.84281	1.663764	-1.85468
19	8	3.522649	-0.28873	0.530439
20	6	4.980425	-0.54289	0.375334
21	6	5.686994	0.733982	-0.08248
22	6	5.206989	-1.71527	-0.58038
23	6	5.404596	-0.91436	1.795561
24	1	-1.09482	-0.48233	0.808093
25	1	-2.59375	-1.09032	2.491703
26	1	-4.31093	-1.14237	2.105953
27	1	-1.93842	-1.10034	-2.01285
28	1	-0.9383	-2.01783	-0.89845
29	1	-3.88943	-3.24125	1.1665
30	1	-2.14967	-2.9953	1.216088
31	1	-3.04723	-3.22146	-1.14656
32	1	-5.25888	0.085445	0.236155

33	1	-4.26084	0.693129	-1.06825
34	1	-4.41497	-1.39561	-2.07471
35	1	-5.23767	-2.06016	-0.66953
36	1	-4.03139	1.417308	2.114872
37	1	-2.34422	3.162077	1.950894
38	1	0.318807	0.096909	-1.923
39	1	0.777957	1.719229	-1.45739
40	1	1.317108	0.862701	0.882289
41	1	0.980873	-0.76326	0.335811
42	1	-2.82583	2.060455	-1.59845
43	1	-1.25566	2.481946	-2.28071
44	1	-1.97052	0.906294	-2.63124
45	1	6.768519	0.575083	-0.04948
46	1	5.408433	1.006443	-1.09999
47	1	5.446519	1.56557	0.585852
48	1	4.92177	-1.46414	-1.60161
49	1	4.635703	-2.58993	-0.25672
50	1	6.267464	-1.98239	-0.57265
51	1	6.476123	-1.1282	1.817324
52	1	5.202021	-0.09297	2.487674
53	1	4.867902	-1.80183	2.140755



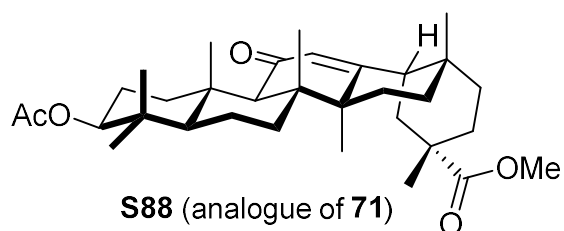
55

E(RB3LYP) = -2026.80356616

Center number	Atomic number	X	Y	Z
1	6	-3.91602	-2.16213	0.459389
2	6	-4.63726	-1.20937	-0.48322
3	6	-4.07839	0.23895	-0.48545
4	6	-2.54106	0.099552	-0.81224
5	6	-1.69784	-0.8883	0.079764
6	6	-2.42886	-2.25705	0.100716
7	6	-1.7985	1.431635	-1.02957
8	6	-0.46681	1.197368	-1.75124
9	6	0.460925	0.231462	-0.99266
10	6	-0.31756	-1.07681	-0.66169
11	6	-4.78204	1.00493	-1.62838
12	6	-4.44733	0.913633	0.848495
13	6	-1.50259	-0.41221	1.539543
14	6	0.599349	-2.14646	-0.02181
15	6	1.741325	-2.5465	-0.90366
16	6	2.938177	-3.00589	-0.51424
17	6	3.9706	-3.46113	-1.4756
18	8	4.964286	-4.08742	-0.79089
19	6	4.605454	-4.24109	0.609786
20	6	3.462515	-3.25331	0.871283
21	8	4.012216	-3.33667	-2.67729
22	6	1.17968	0.938432	0.180487
23	5	2.314349	1.937623	-0.2464
24	8	2.756022	2.959503	0.562885
25	6	3.698482	3.780112	-0.20219
26	6	4.143545	2.793887	-1.35369
27	8	3.005203	1.87418	-1.43176
28	6	5.36803	1.946357	-0.99589
29	6	4.337263	3.440497	-2.72079

30	6	2.913783	4.995902	-0.70507
31	6	4.817205	4.230876	0.730599
32	1	-2.55425	-0.38747	-1.79849
33	1	-4.56597	-1.5909	-1.5029
34	1	1.248111	-0.07161	-1.69286
35	8	-3.99972	2.295781	0.843374
36	8	-4.95234	2.623607	2.858988
37	6	-4.32223	3.045466	1.911608
38	6	-3.79602	4.448551	1.774966
39	8	-6.05554	-1.17323	-0.12997
40	8	-6.59759	-2.69593	-1.7114
41	6	-6.91866	-1.95904	-0.80347
42	6	-8.3177	-1.80319	-0.27199
43	8	3.969882	-1.99372	1.408176
44	8	4.033746	-2.8986	3.473744
45	6	4.220621	-1.95434	2.738361
46	6	4.752795	-0.61292	3.154344
47	1	-4.05226	-1.83941	1.495363
48	1	-4.37231	-3.15336	0.376694
49	1	-1.94671	-2.93315	0.812141
50	1	-2.33848	-2.72225	-0.88876
51	1	-1.63166	1.939809	-0.07752
52	1	-2.40808	2.109882	-1.62964
53	1	0.043435	2.152973	-1.91556
54	1	-0.67685	0.782087	-2.74527
55	1	-0.59469	-1.48583	-1.64371
56	1	-4.52201	0.573102	-2.59925
57	1	-5.86764	0.948849	-1.51169
58	1	-4.50933	2.059941	-1.64005
59	1	-5.53084	0.912791	0.969165
60	1	-4.01271	0.418676	1.712606
61	1	-0.65135	-0.91755	2.001627
62	1	-1.32598	0.660278	1.617688
63	1	-2.37038	-0.64681	2.157818
64	1	0.015625	-3.05979	0.147052
65	1	0.968023	-1.839	0.95844
66	1	1.566611	-2.50486	-1.97789
67	1	4.276478	-5.27024	0.765796
68	1	5.495112	-4.04274	1.203978
69	1	2.728069	-3.65579	1.564761
70	1	0.472298	1.463214	0.828186
71	1	1.66344	0.197122	0.830714

72	1	5.497153	1.172325	-1.7565
73	1	6.276397	2.553016	-0.96896
74	1	5.249332	1.45479	-0.02761
75	1	4.617036	2.67519	-3.44959
76	1	3.428041	3.929587	-3.07189
77	1	5.140747	4.181381	-2.68532
78	1	2.491862	5.524335	0.153636
79	1	3.560486	5.689738	-1.24757
80	1	2.090907	4.702948	-1.36145
81	1	5.575161	4.793618	0.178703
82	1	4.406379	4.887213	1.502448
83	1	5.300595	3.386404	1.222856
84	1	-4.1413	5.05586	2.610039
85	1	-2.70256	4.431159	1.764481
86	1	-4.12861	4.888097	0.8316
87	1	-9.01742	-2.34404	-0.9071
88	1	-8.36608	-2.204	0.744703
89	1	-8.59293	-0.74723	-0.22434
90	1	4.051311	0.175932	2.873434
91	1	5.695936	-0.416	2.637479
92	1	4.914726	-0.59932	4.230743



S88 (analogue of 71)

E(RB3LYP) = -1664.26879705

Center number	Atomic number	X	Y	Z
1	6	4.568556	1.660575	-0.65446
2	6	5.20361	0.696546	0.33554
3	6	4.837353	-0.78934	0.105732
4	6	3.265297	-0.86046	0.074242
5	6	2.520581	0.110311	-0.91246
6	6	3.040252	1.546868	-0.62261
7	6	2.704473	-2.28511	-0.03782
8	6	1.241362	-2.32186	0.417881
9	6	0.311107	-1.35719	-0.3577

10	6	0.992962	0.054659	-0.51478
11	6	5.52528	-1.36549	-1.14889
12	6	5.352619	-1.58323	1.328991
13	6	2.753474	-0.21515	-2.4098
14	1	2.97219	-0.50312	1.073036
15	6	-1.06631	-1.14694	0.441591
16	6	-1.9459	-0.15602	-0.32881
17	6	-1.38399	0.79307	-1.10266
18	6	0.057632	0.966386	-1.31663
19	8	0.44714	1.83813	-2.09084
20	6	-1.79017	-2.5091	0.666916
21	6	-3.2922	-2.39889	0.964904
22	6	-4.06223	-1.59621	-0.10452
23	6	-3.46512	-0.16104	-0.18011
24	6	0.055487	-1.99247	-1.74909
25	6	-0.83448	-0.52823	1.85746
26	6	-5.57292	-1.52596	0.229303
27	6	-5.95067	-0.61795	1.403824
28	6	-5.41665	0.816459	1.232721
29	6	-3.89138	0.745468	1.008342
30	6	-3.935	-2.27918	-1.48129
31	1	-3.86319	0.311512	-1.08548
32	6	-6.15845	1.527532	0.092253
33	8	-7.27762	1.254013	-0.28604
34	8	-5.45708	2.558897	-0.41244
35	6	-6.10508	3.350025	-1.43275
36	6	-5.70811	1.647673	2.505373
37	1	0.97145	0.498112	0.488309
38	8	6.659994	0.835097	0.267261
39	8	6.721841	2.260607	2.022016
40	6	7.284688	1.641456	1.142698
41	6	8.766702	1.681911	0.87895
42	1	4.958509	1.4689	-1.65833
43	1	4.860785	2.68294	-0.39416
44	1	4.900606	0.972214	1.347573
45	1	2.690995	1.851241	0.372523
46	1	2.606458	2.246019	-1.3365
47	1	2.804621	-2.66376	-1.05841
48	1	3.269484	-2.97118	0.596934
49	1	0.853275	-3.34069	0.322164
50	1	1.23299	-2.08562	1.484053
51	1	5.366587	-0.76164	-2.04164

52	1	6.603518	-1.43466	-0.98489
53	1	5.159353	-2.37435	-1.35653
54	1	6.416425	-1.38539	1.486054
55	1	4.817305	-1.30168	2.24174
56	1	5.243296	-2.66085	1.189652
57	1	1.948162	0.191958	-3.02081
58	1	3.679496	0.234247	-2.77034
59	1	2.821599	-1.28434	-2.6095
60	1	-2.00823	1.502359	-1.64074
61	1	-1.29944	-3.02196	1.499301
62	1	-1.66191	-3.15351	-0.20169
63	1	-3.44889	-1.9472	1.948841
64	1	-3.71144	-3.41021	1.022922
65	1	0.99799	-2.18574	-2.25831
66	1	-0.44998	-2.95483	-1.65726
67	1	-0.54619	-1.36276	-2.40535
68	1	-1.74818	-0.59644	2.447596
69	1	-0.0654	-1.07346	2.405994
70	1	-0.55185	0.524965	1.822173
71	1	-5.93401	-2.54312	0.421419
72	1	-6.10527	-1.17724	-0.66243
73	1	-7.0375	-0.59997	1.518719
74	1	-5.53853	-1.01048	2.339184
75	1	-3.46191	0.375881	1.940763
76	1	-3.48707	1.746512	0.848826
77	1	-4.50686	-1.72716	-2.23405
78	1	-2.90282	-2.33641	-1.83156
79	1	-4.33186	-3.29963	-1.4417
80	1	-6.34718	2.733194	-2.29948
81	1	-7.01486	3.807847	-1.04124
82	1	-5.38361	4.117662	-1.70597
83	1	-5.31696	2.664794	2.416934
84	1	-6.78313	1.70615	2.699421
85	1	-5.23258	1.17286	3.368101
86	1	9.273439	2.203944	1.689173
87	1	9.166806	0.671194	0.774343
88	1	8.950816	2.210333	-0.06128

XII. References

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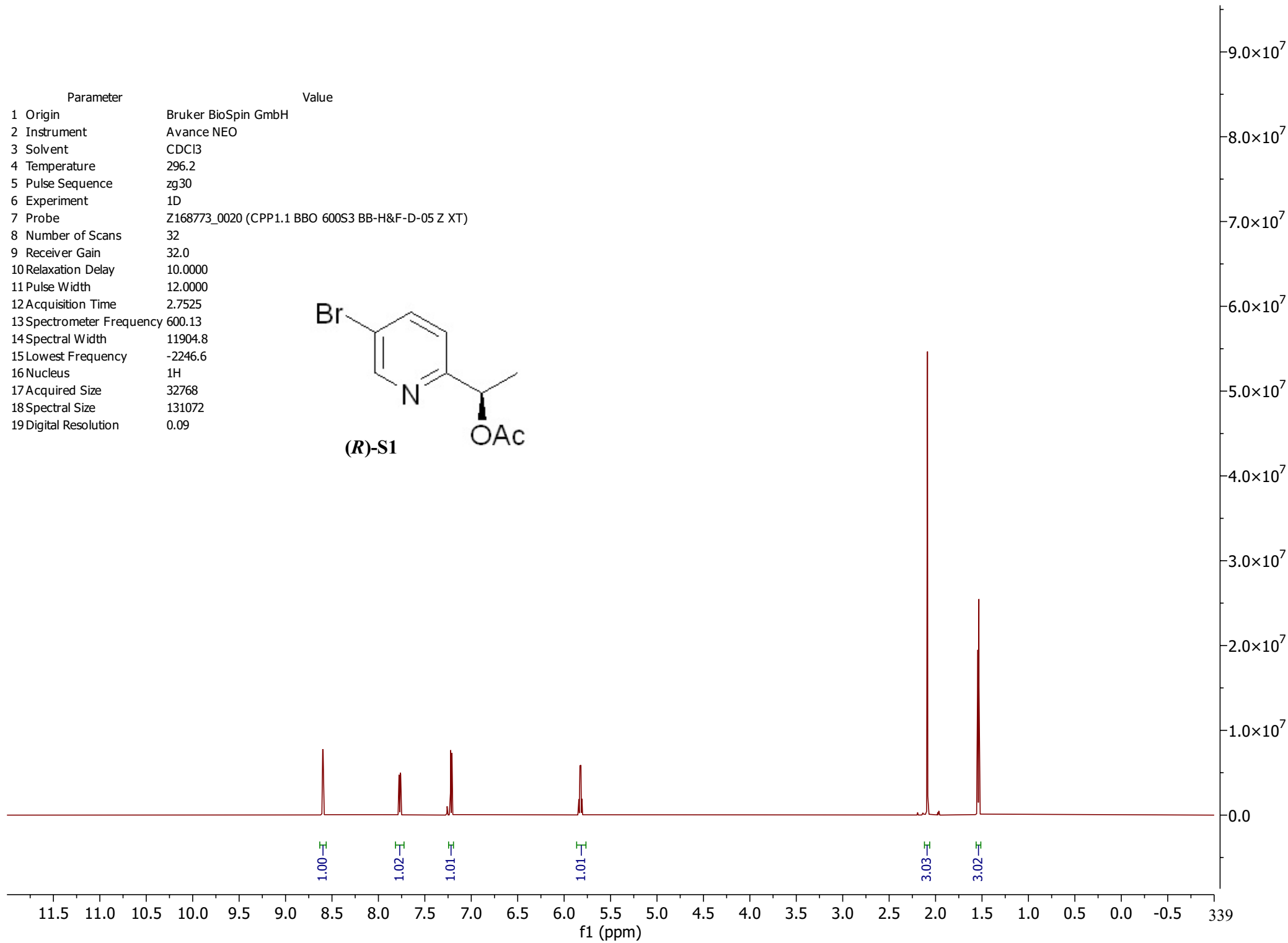
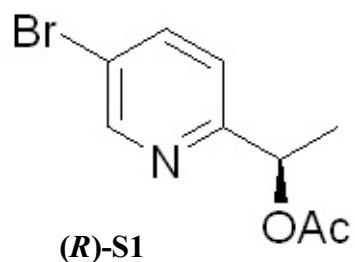
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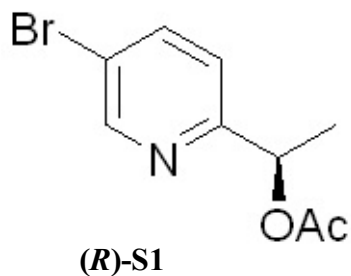
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XIII. Spectral Data

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

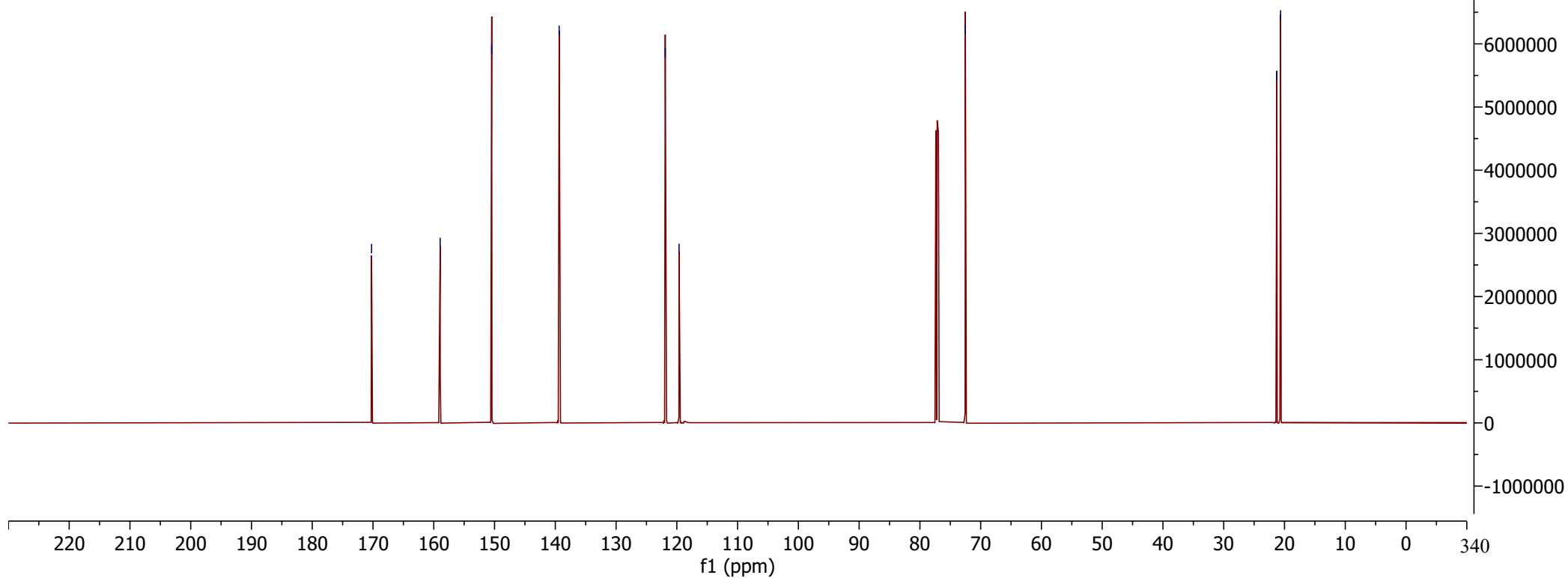


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
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10 Relaxation Delay	2.0000
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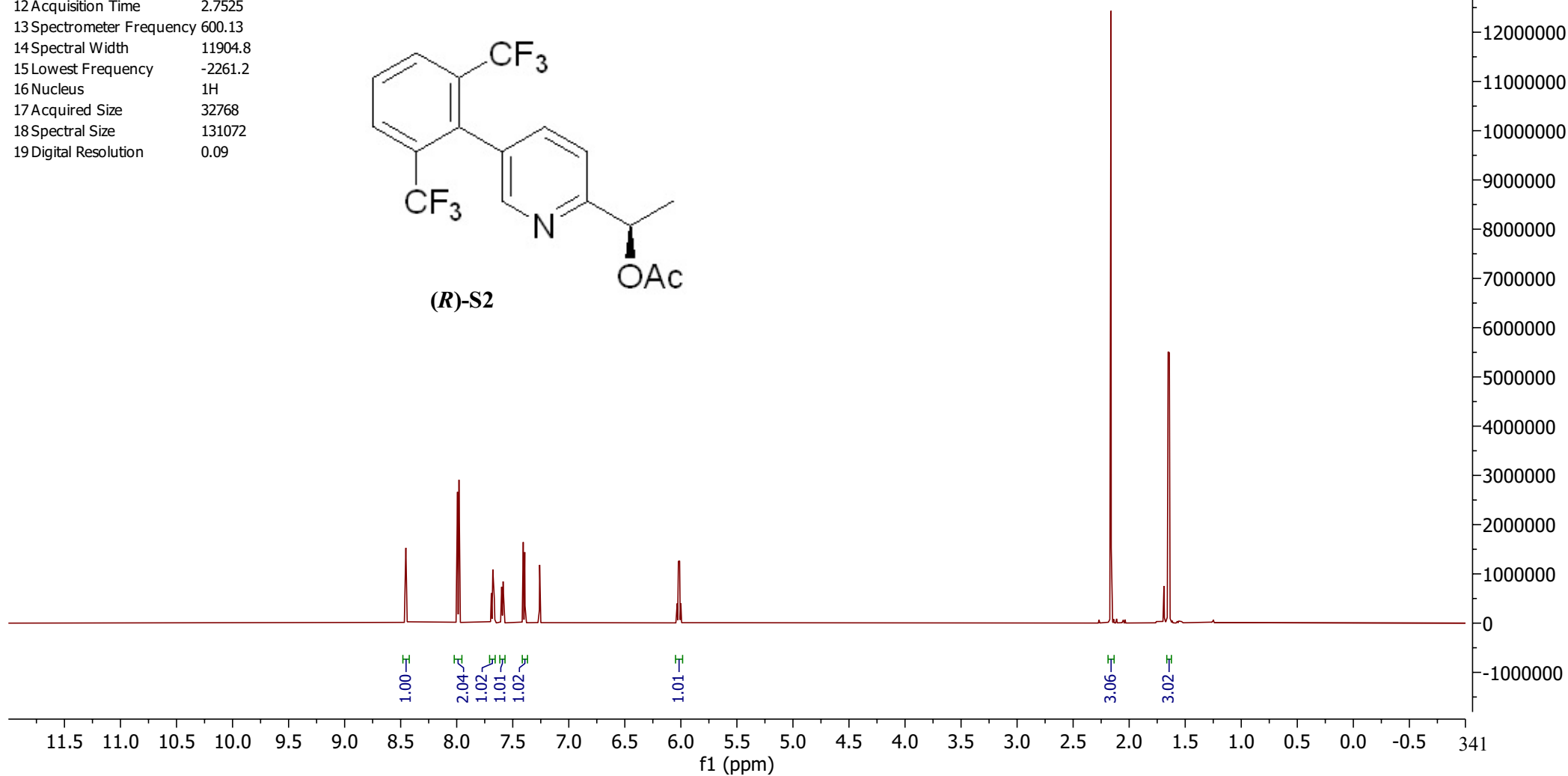
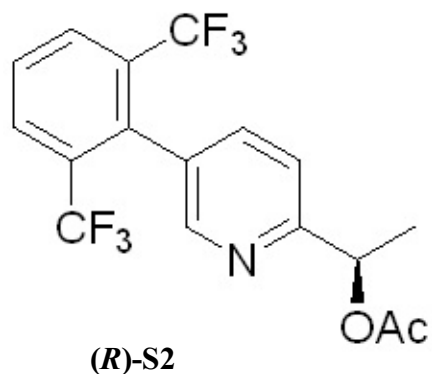


Peak chemical shifts (ppm):

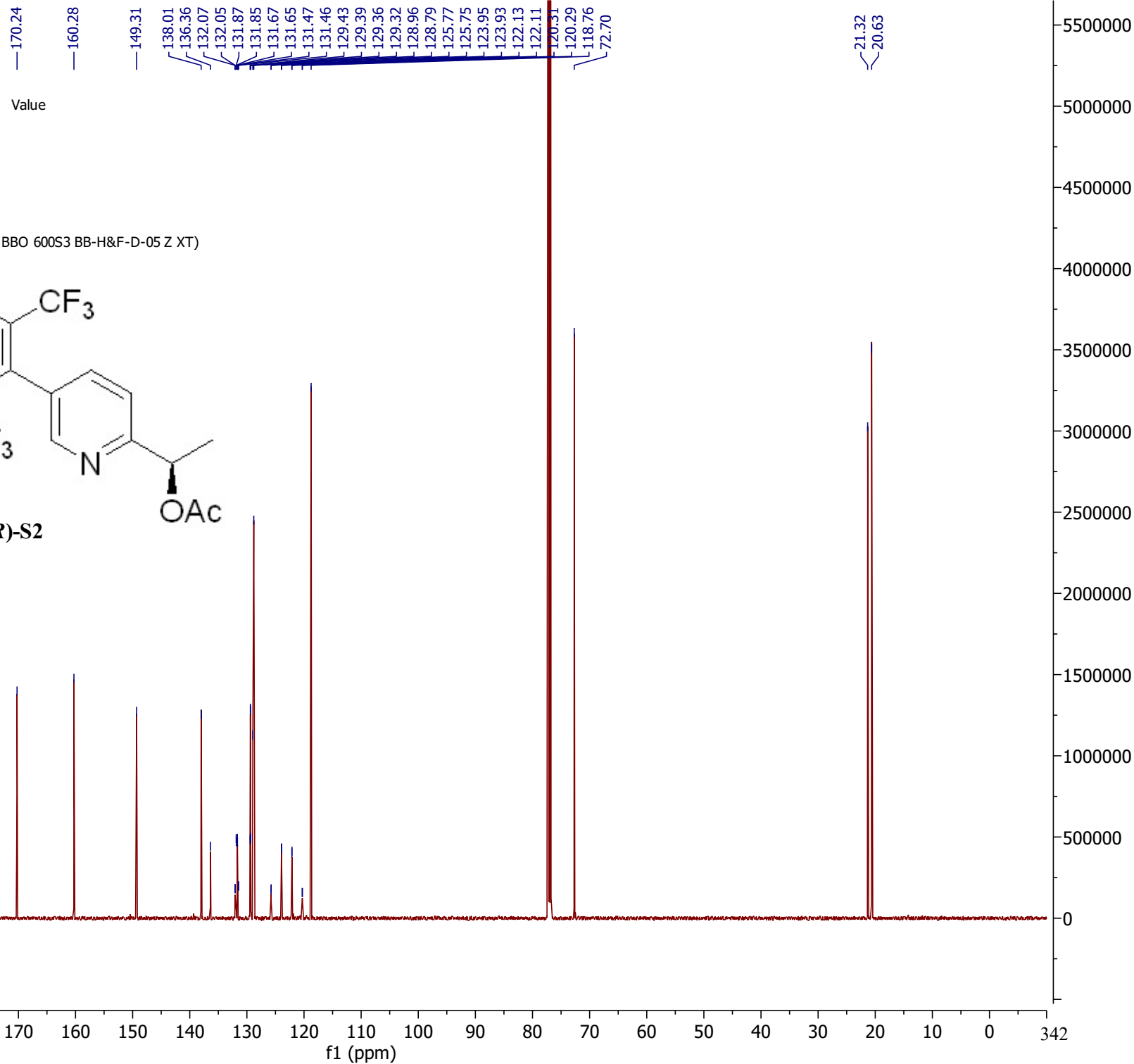
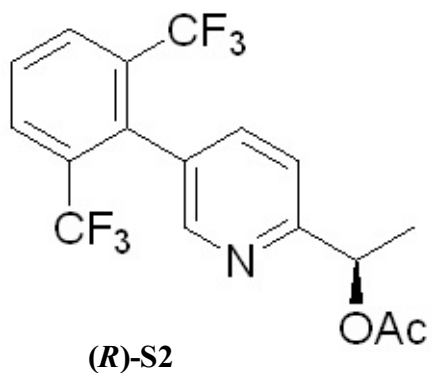
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- 158.95
- 150.47
- 139.37
- 121.91
- 119.64
- 72.53
- 21.26
- 20.64



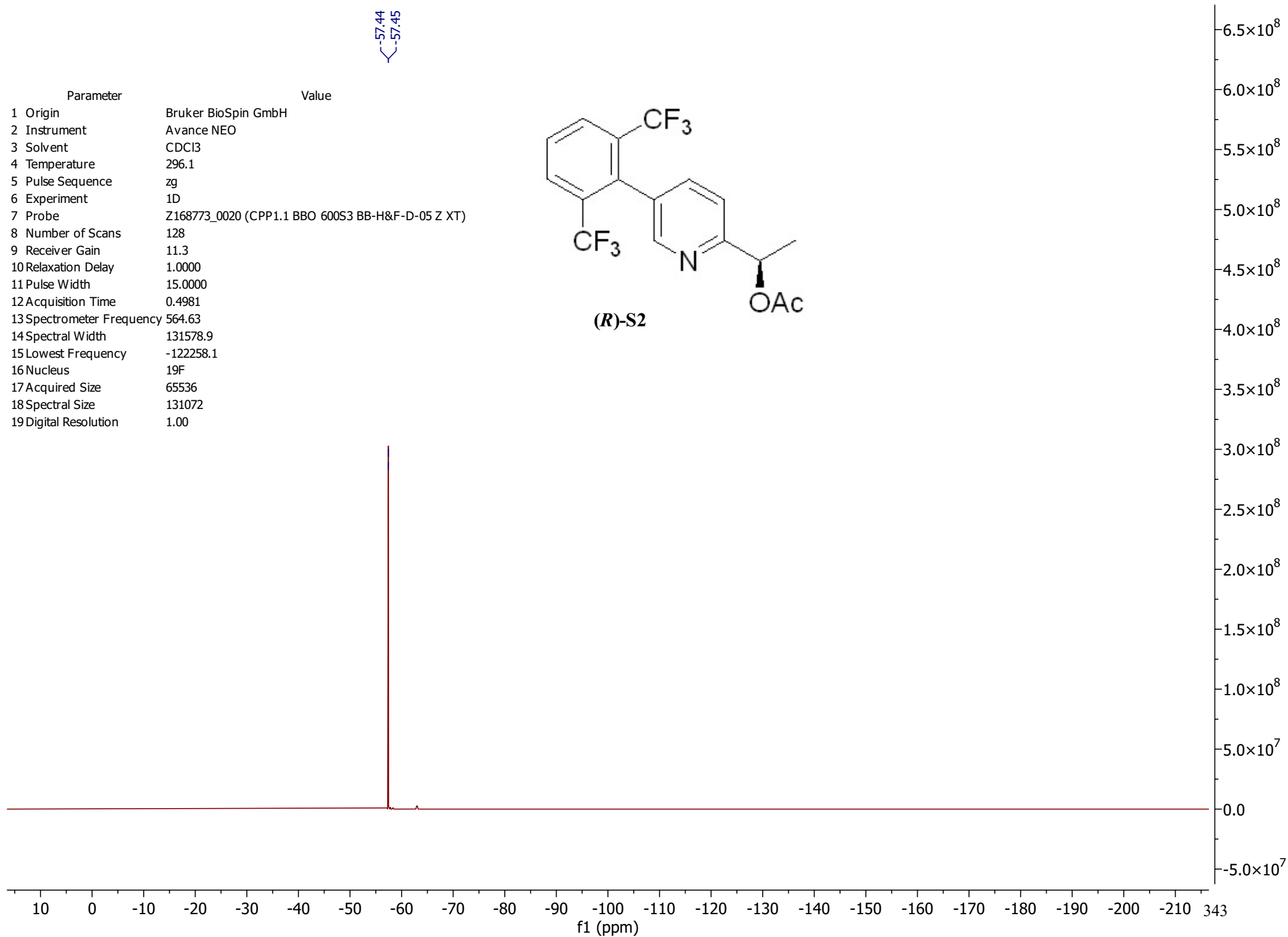
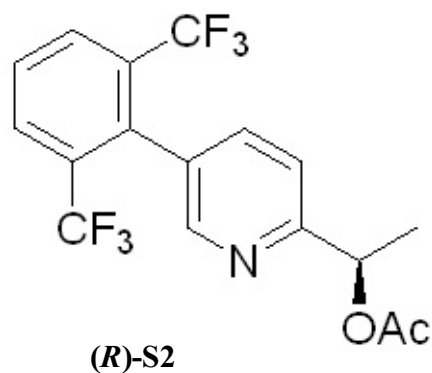
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



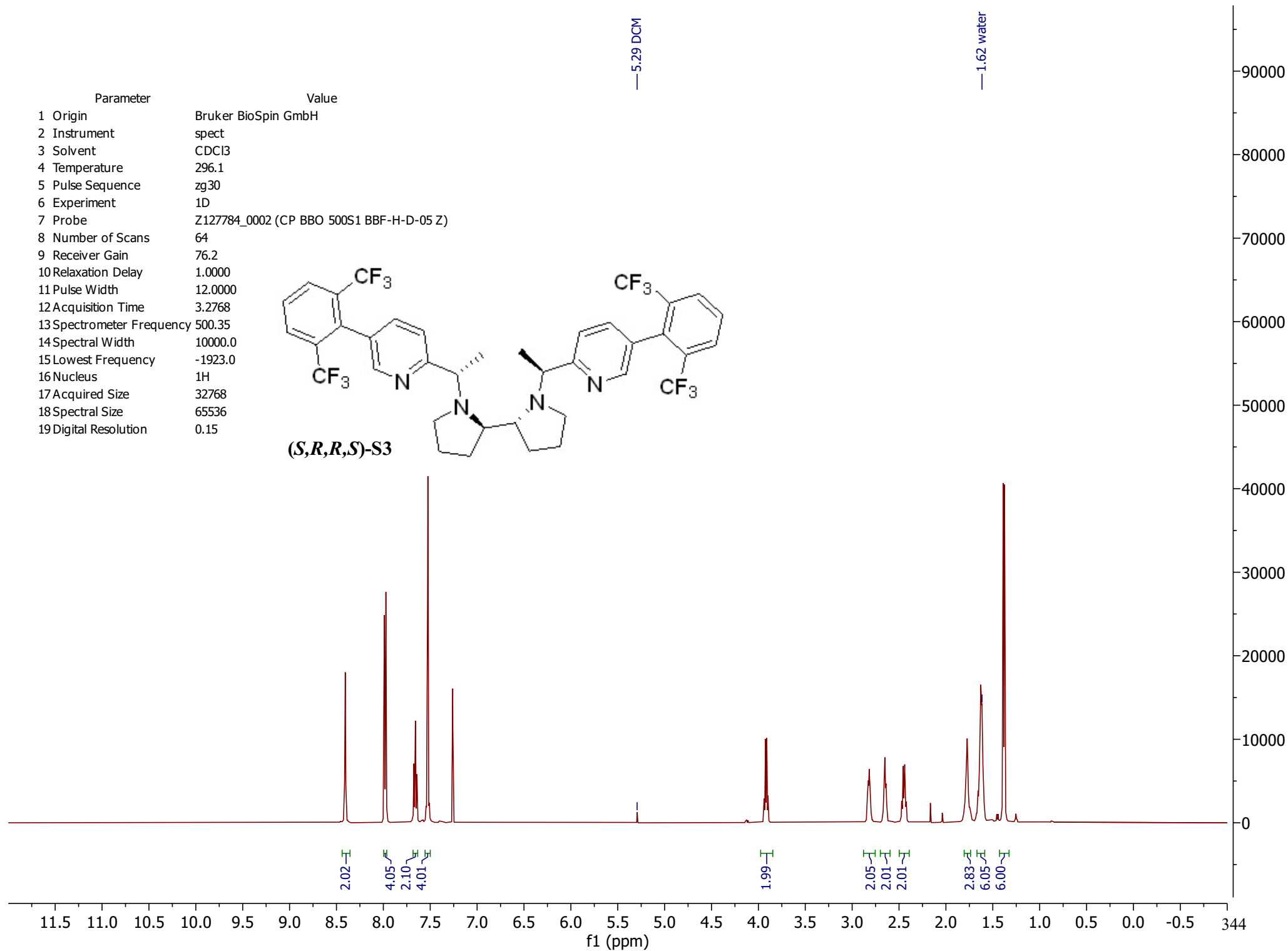
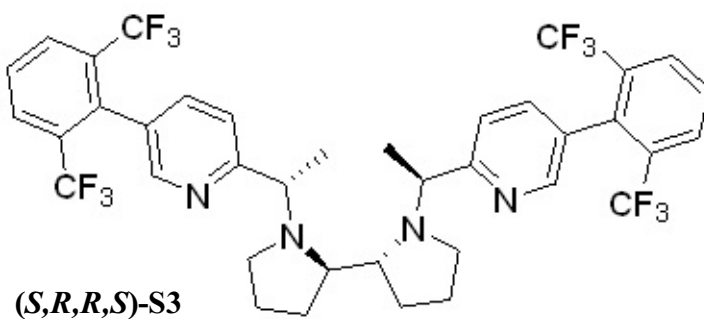
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 2 Instrument Avance NEO
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 5 Pulse Sequence zgpg30
 6 Experiment 1D
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 8 Number of Scans 1024
 9 Receiver Gain 101.0
 10 Relaxation Delay 2.0000
 11 Pulse Width 10.0000
 12 Acquisition Time 0.8847
 13 Spectrometer Frequency 150.92
 14 Spectral Width 37037.0
 15 Lowest Frequency -1919.2
 16 Nucleus ¹³C
 17 Acquired Size 32768
 18 Spectral Size 65536
 19 Digital Resolution 0.57



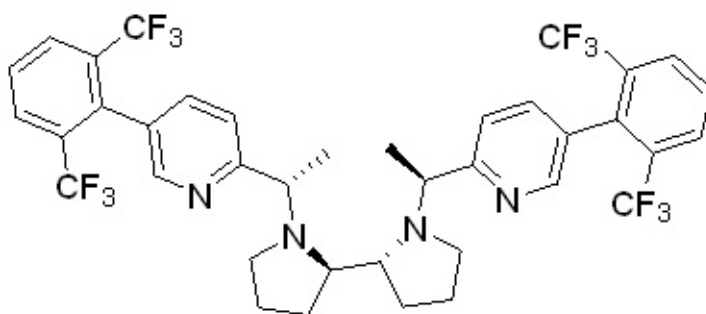
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	128
9 Receiver Gain	11.3
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.4981
13 Spectrometer Frequency	564.63
14 Spectral Width	131578.9
15 Lowest Frequency	-122258.1
16 Nucleus	19F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	1.00



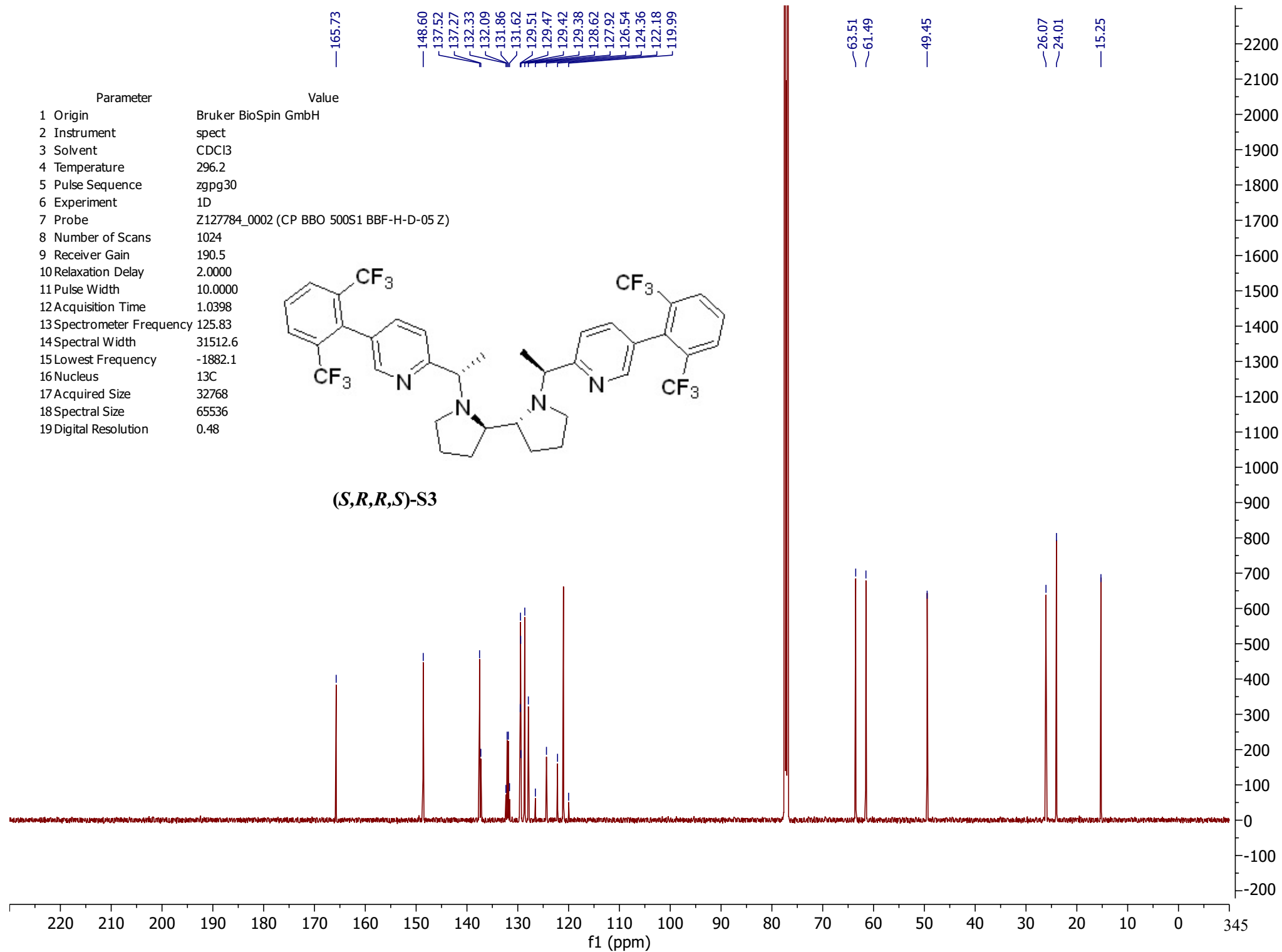
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



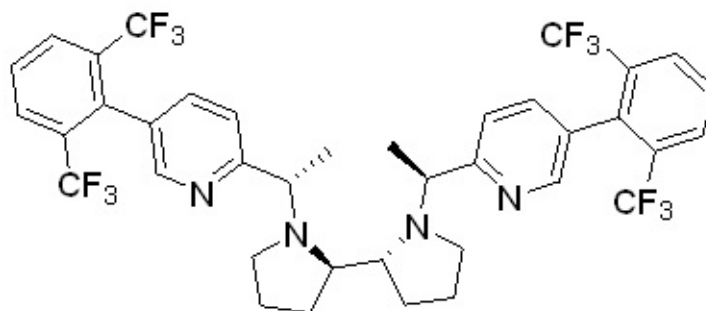
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1882.1
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



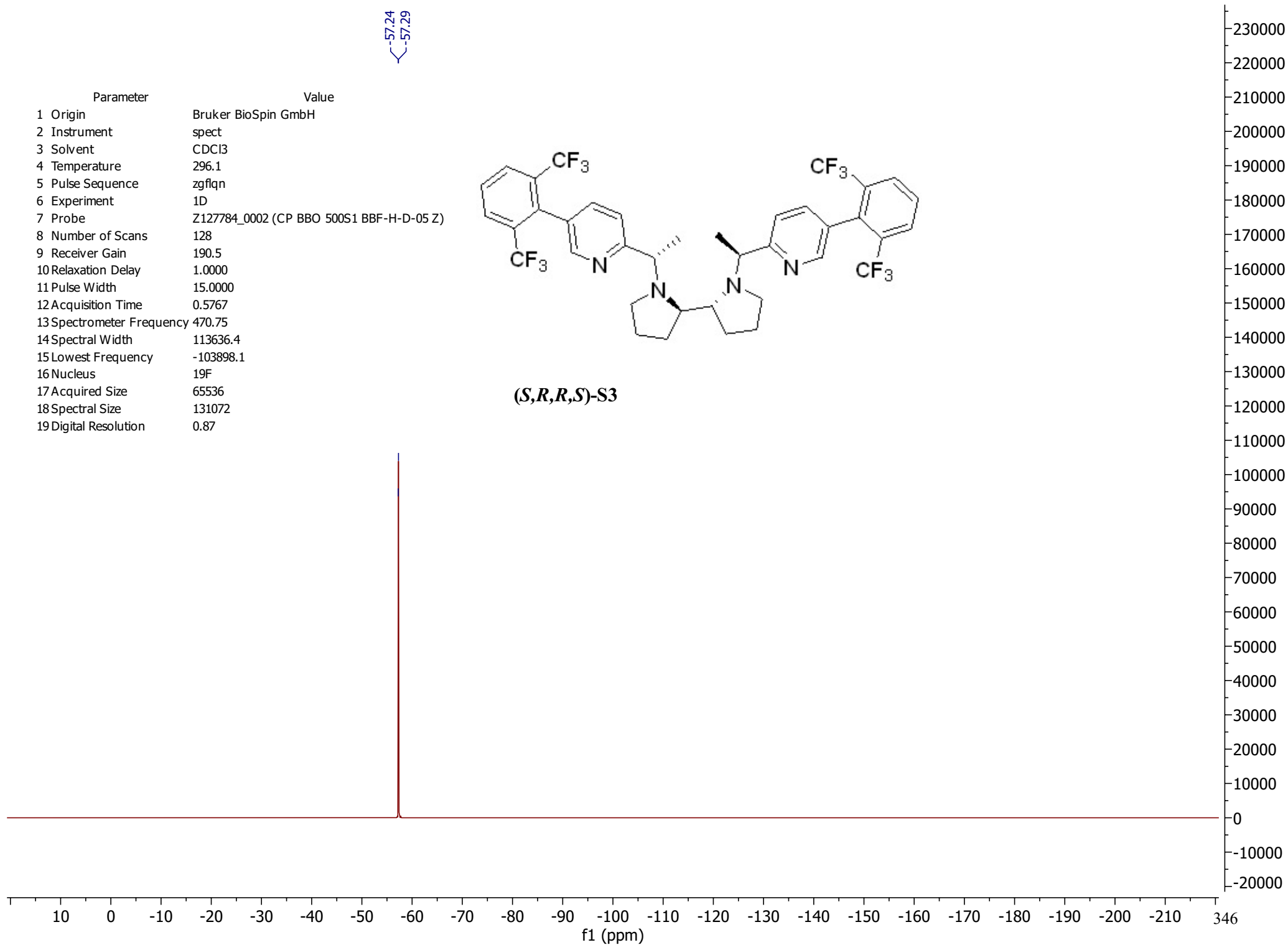
(S,R,R,S)-S3



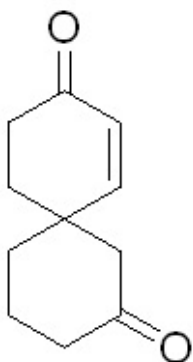
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	128
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	¹⁹ F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



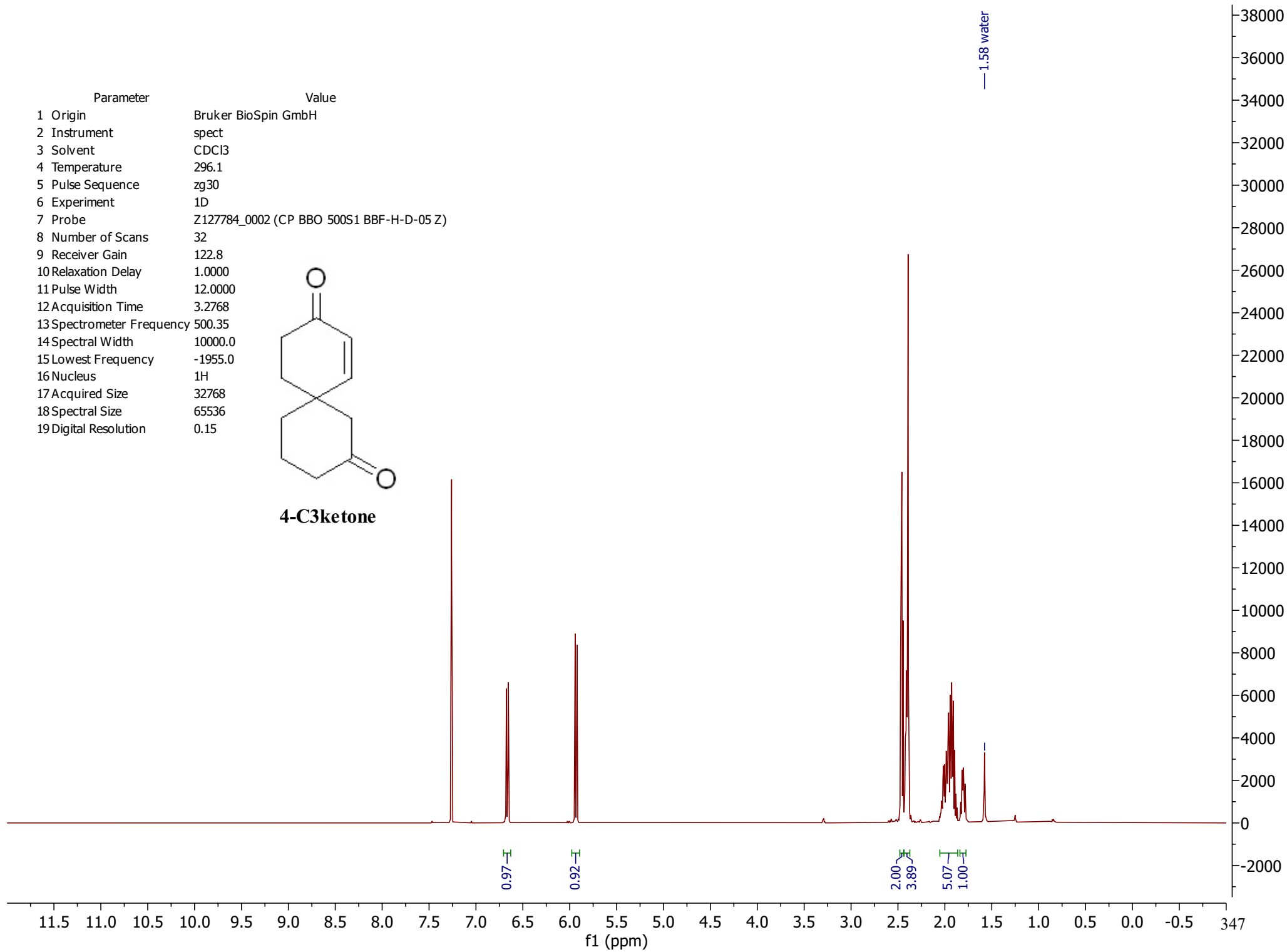
(S,R,R,S)-S3



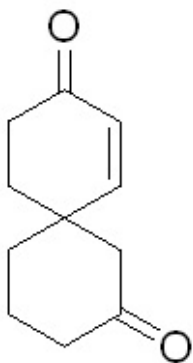
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	122.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1955.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



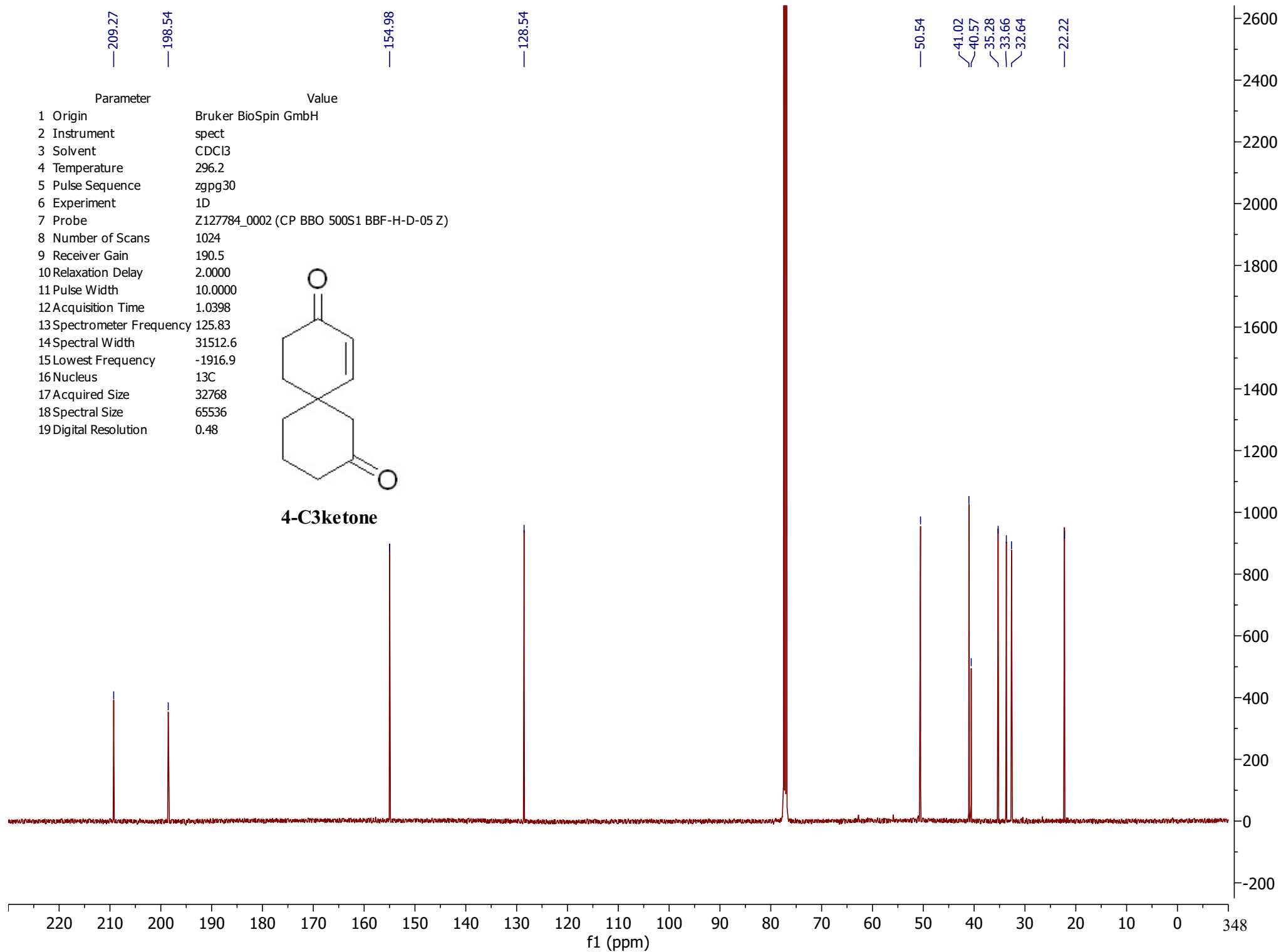
4-C3ketone



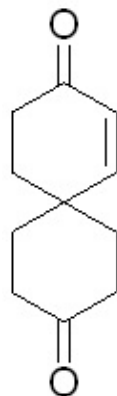
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



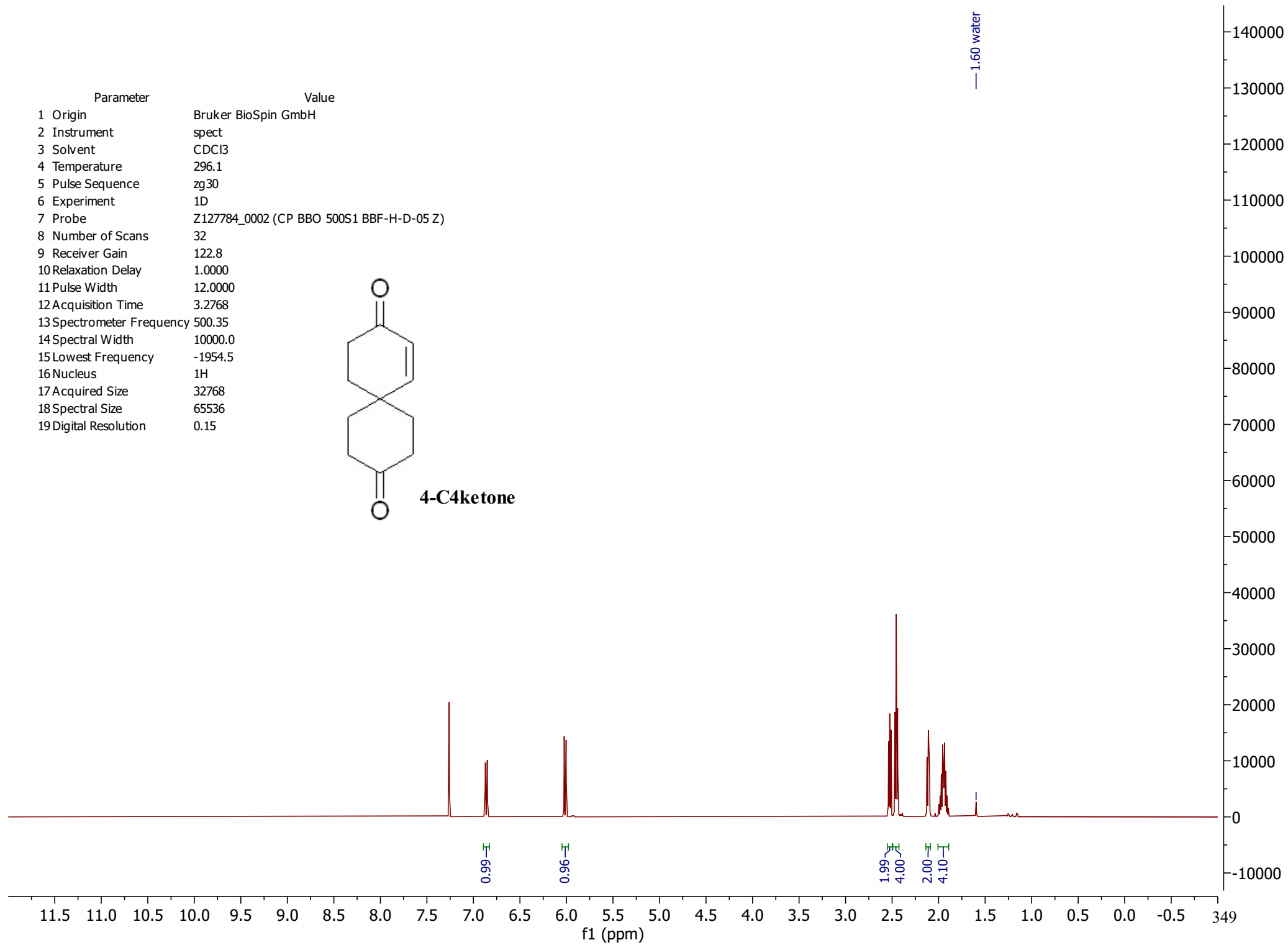
4-C3ketone

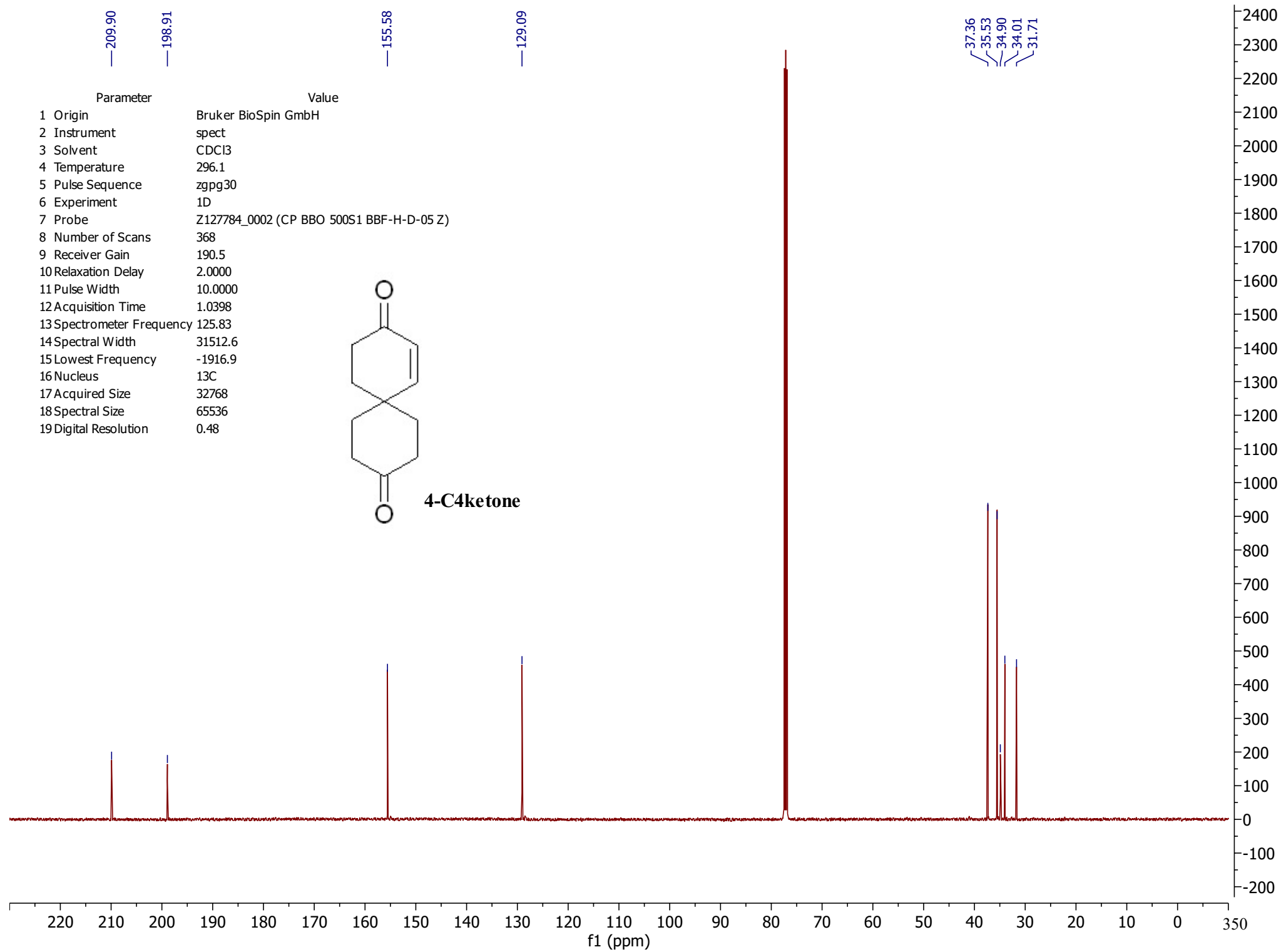


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	122.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1954.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

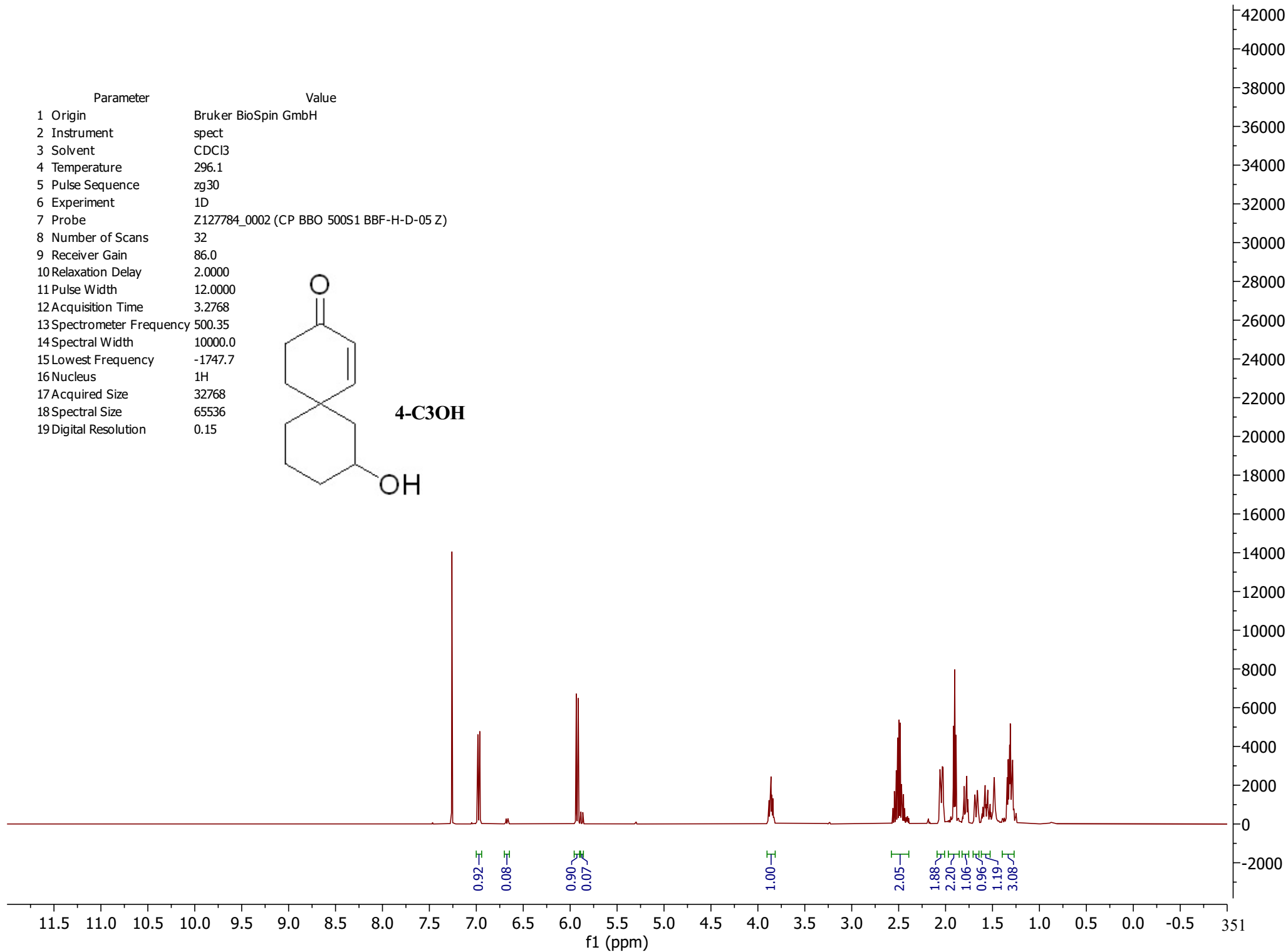
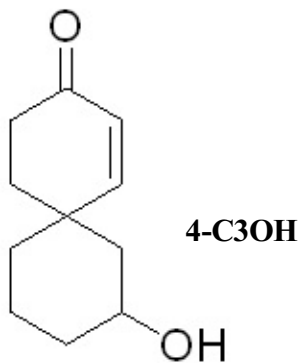


4-C4ketone

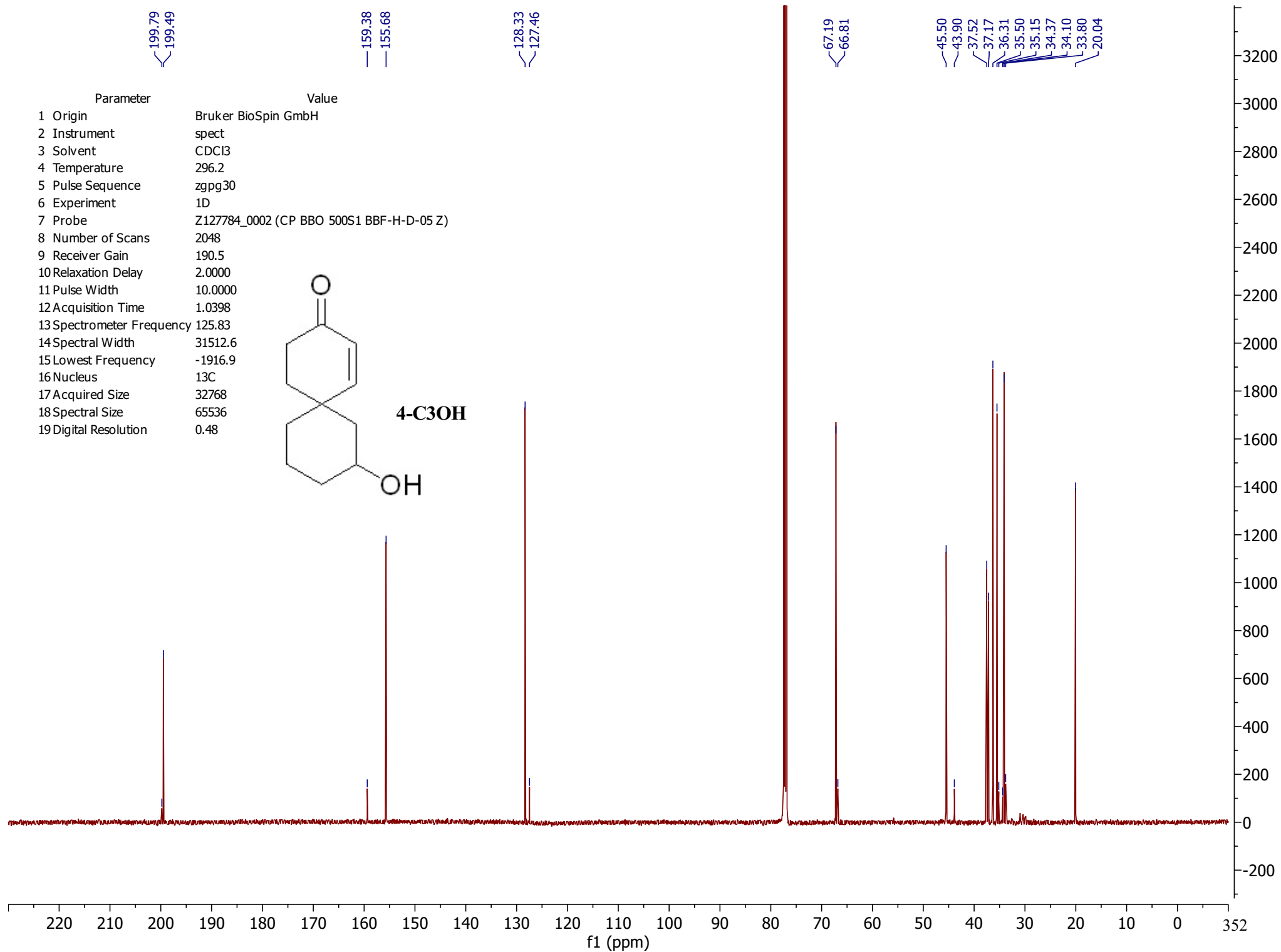
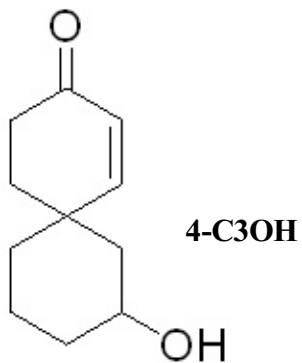




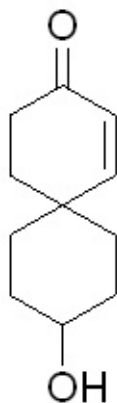
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



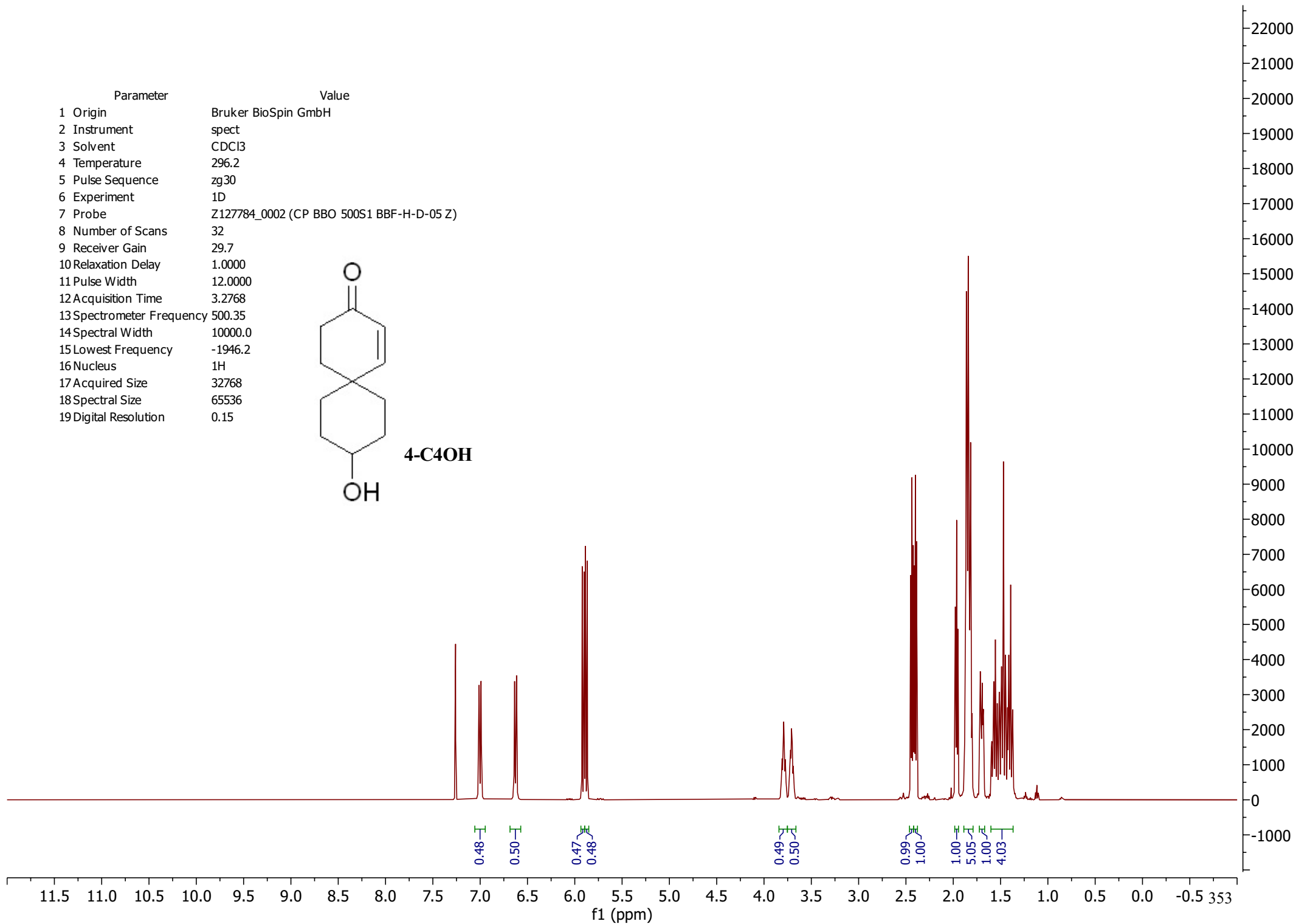
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



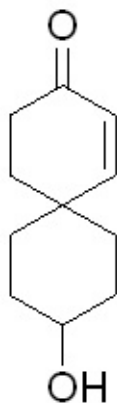
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1946.2
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



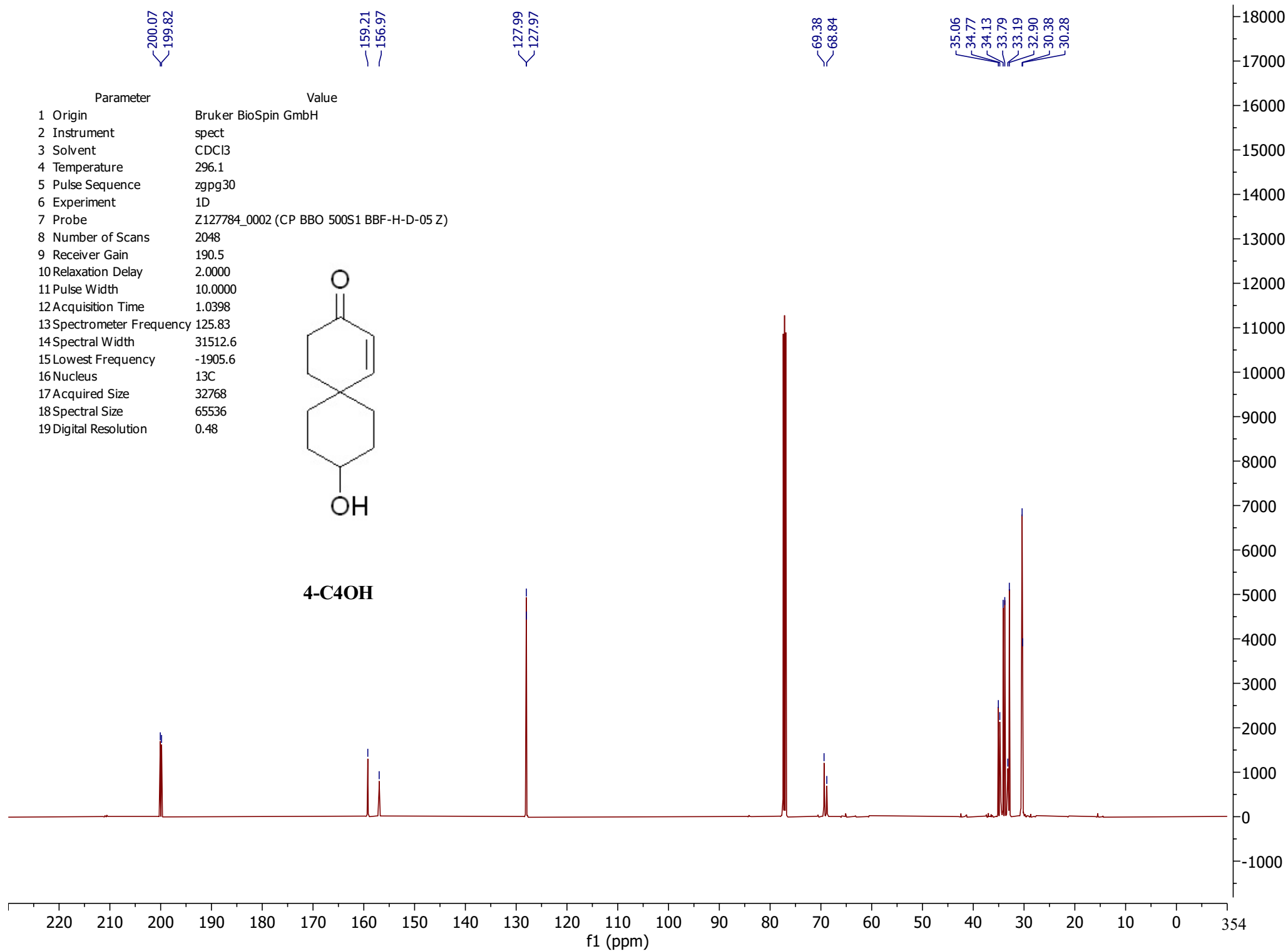
4-C4OH



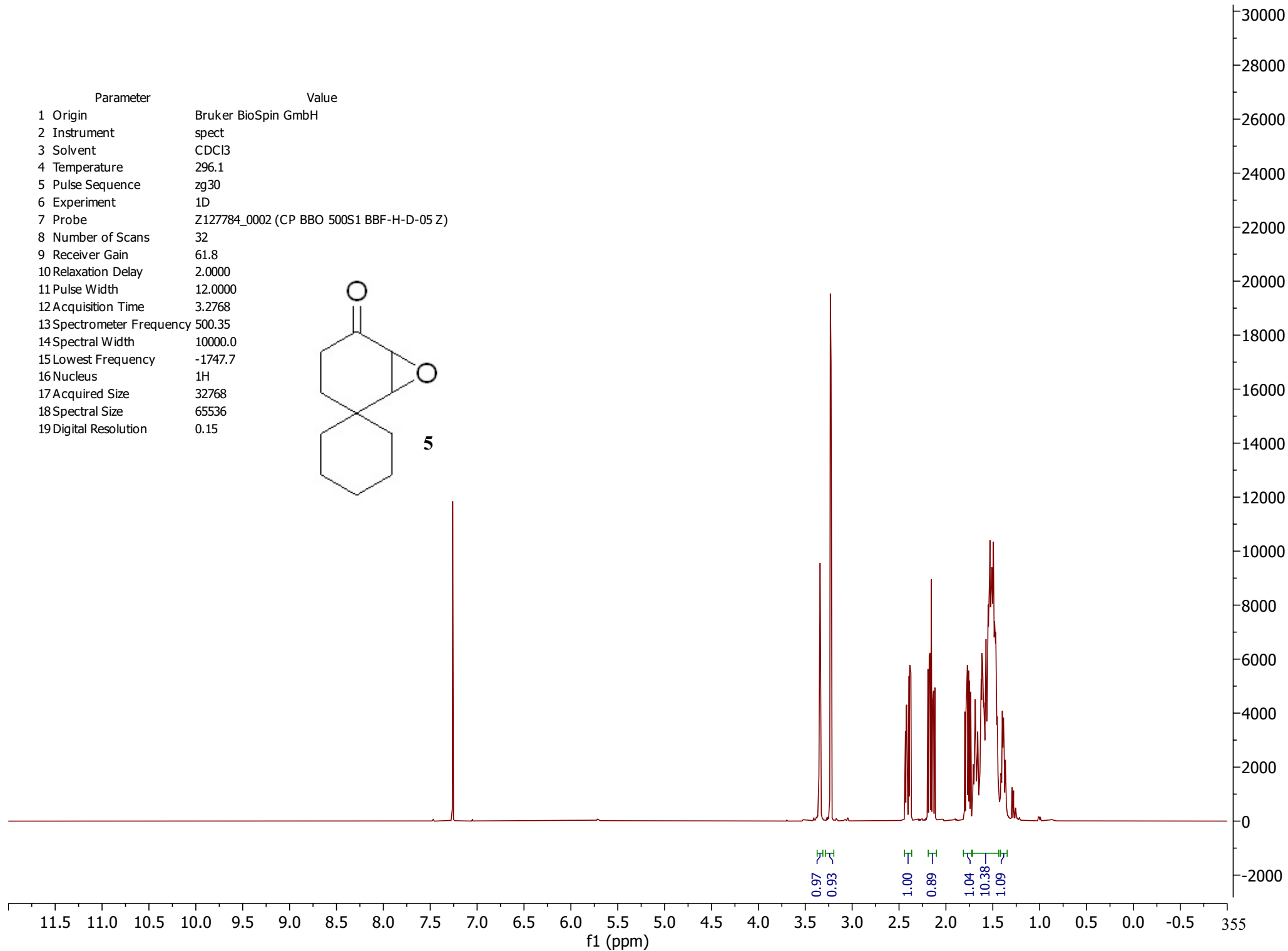
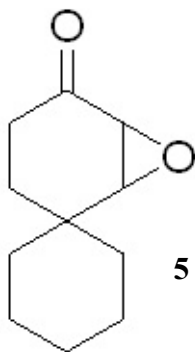
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1905.6
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



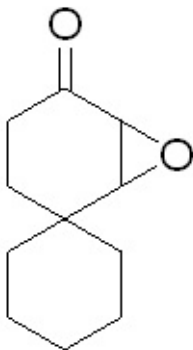
4-C4OH



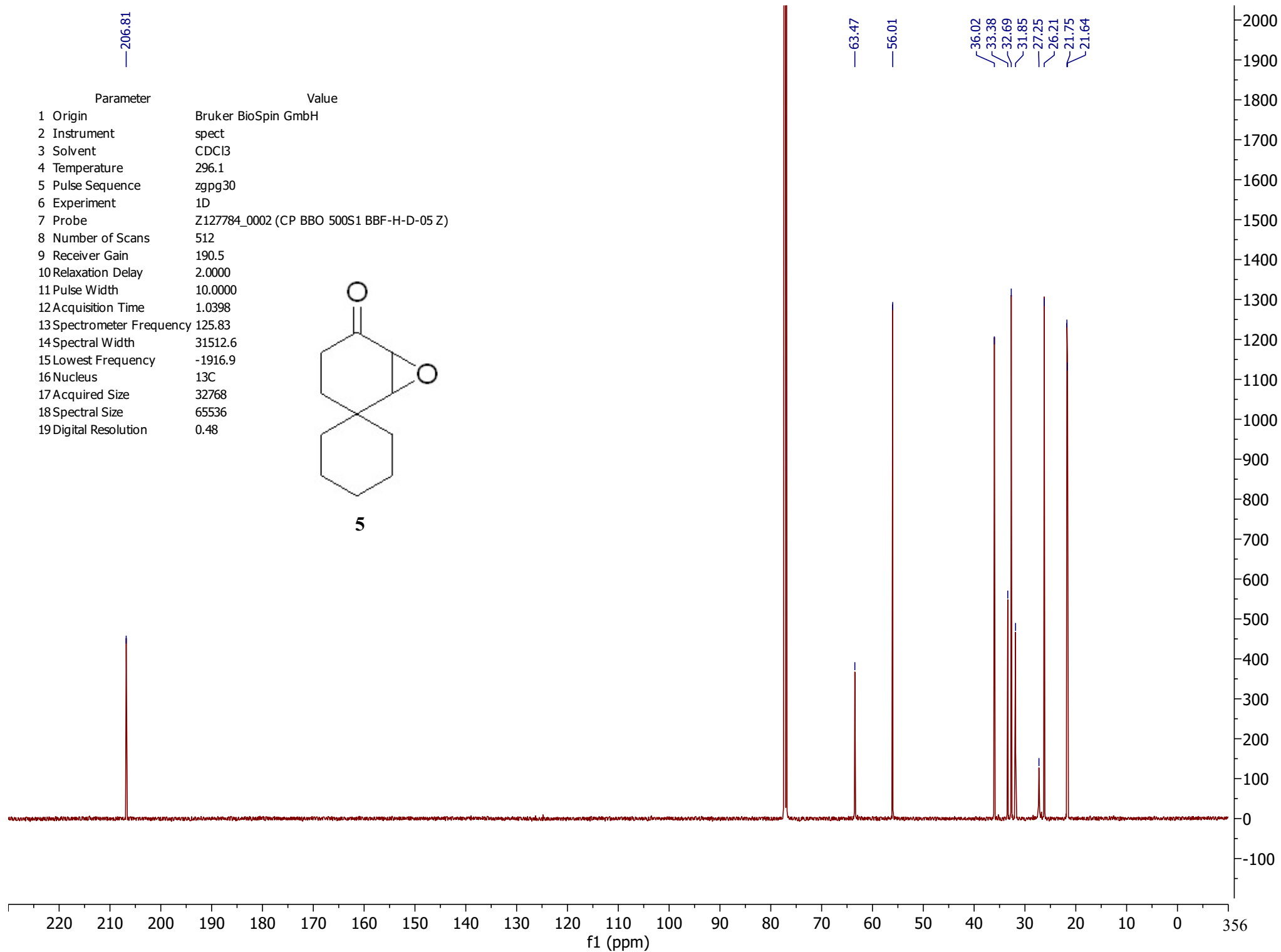
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	61.8
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



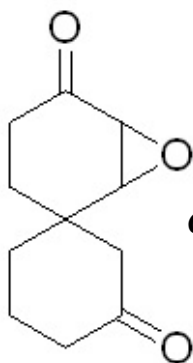
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	512
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



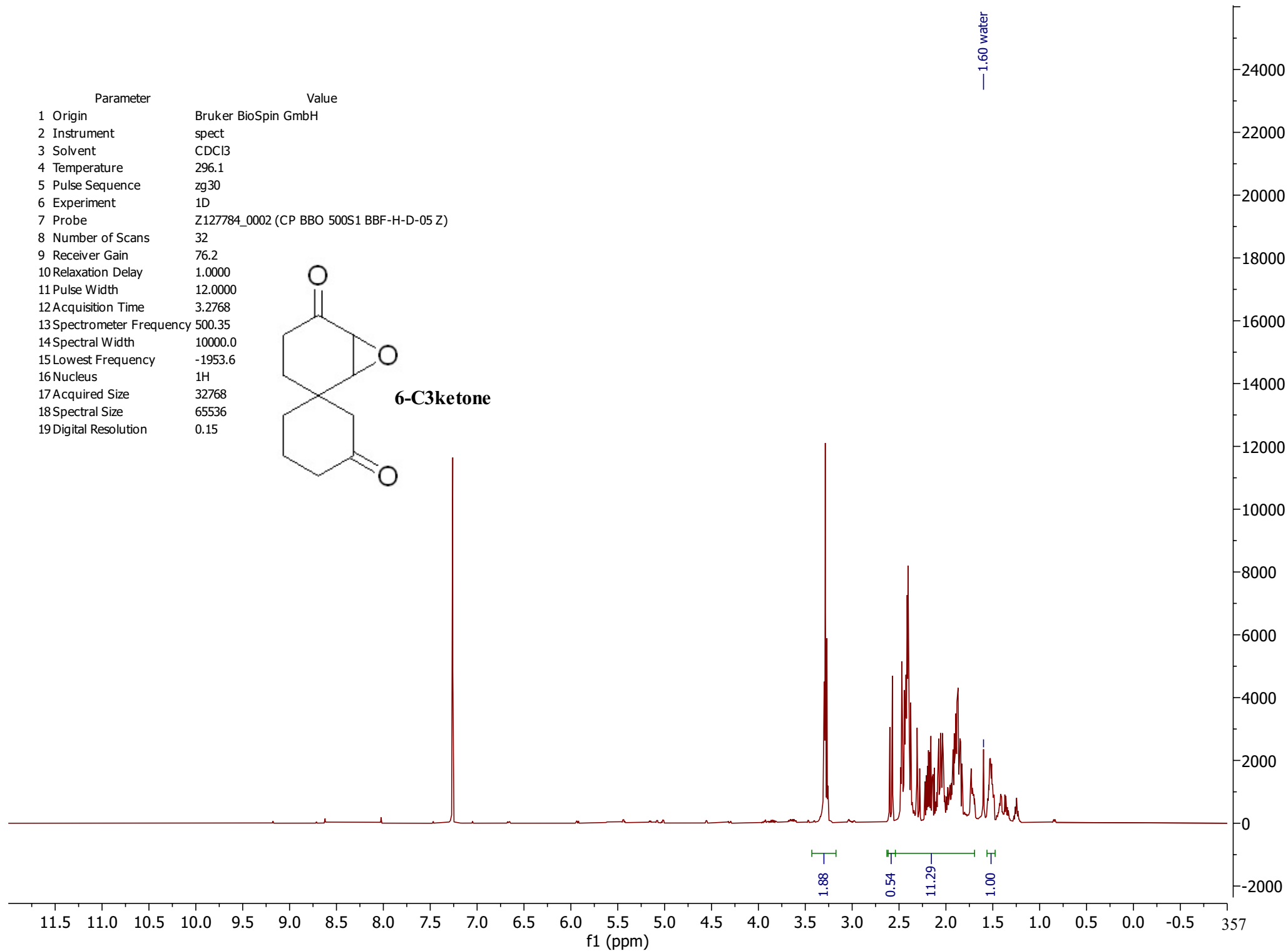
5



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1953.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

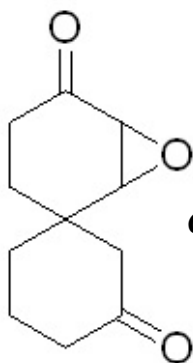


6-C3ketone



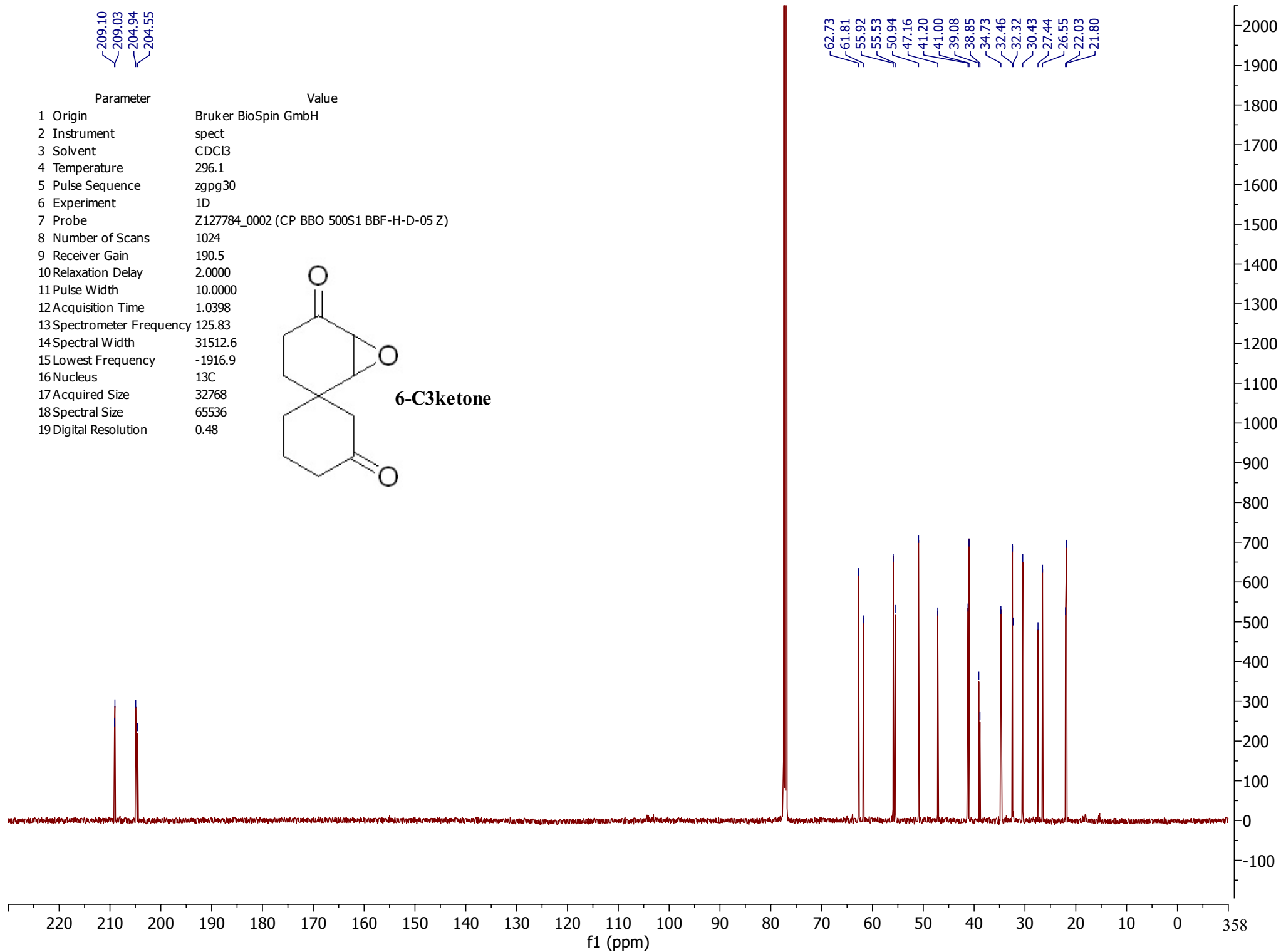
209.10
209.03
204.94
204.55

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

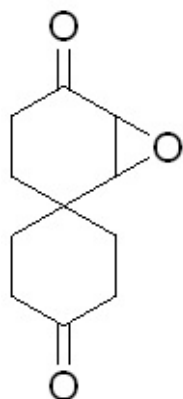


6-C3ketone

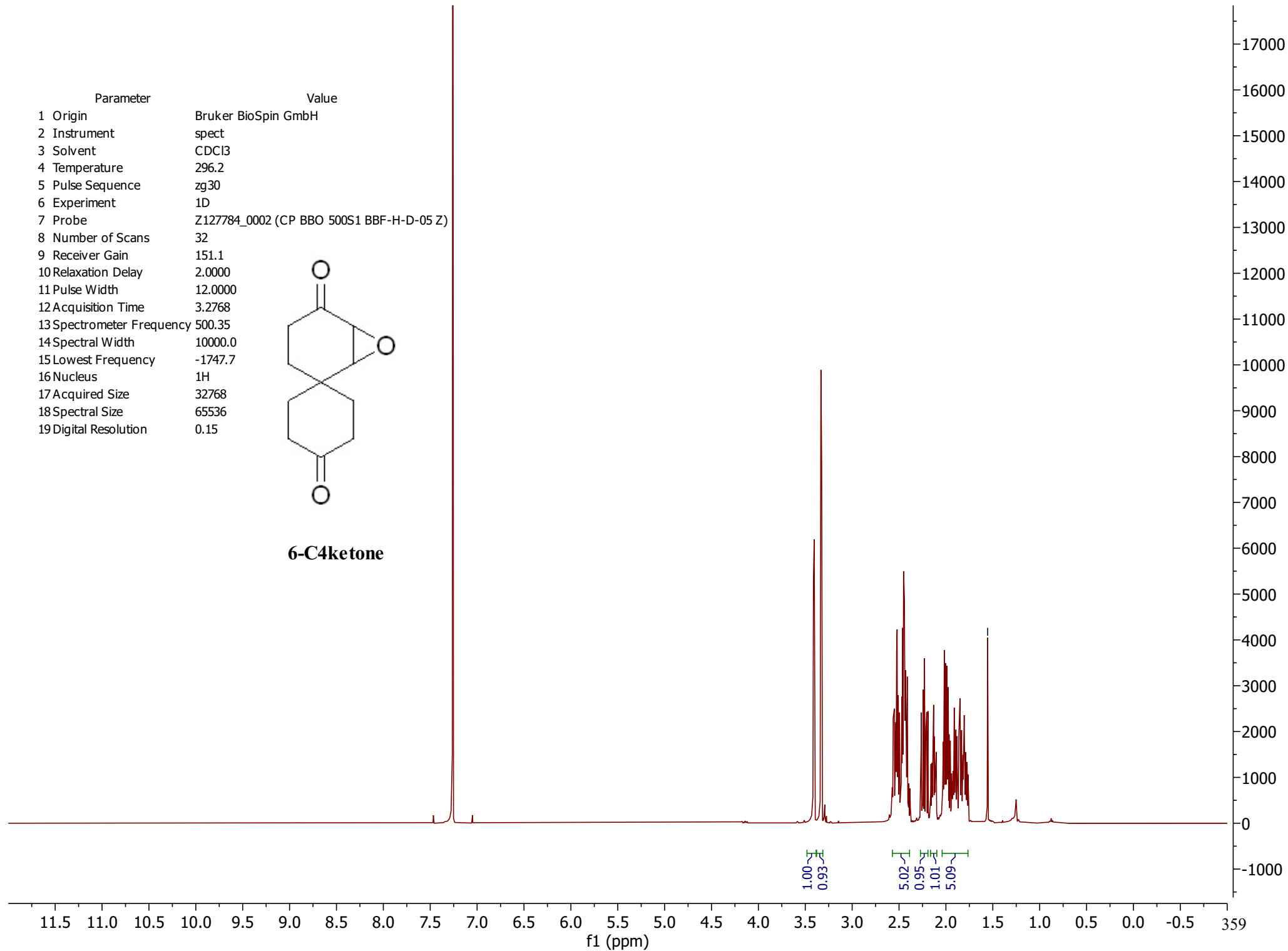
62.73
61.81
55.92
55.53
50.94
47.16
41.20
41.00
39.08
38.85
34.73
32.46
32.32
30.43
27.44
26.55
22.03
21.80



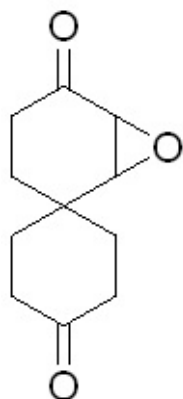
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	151.1
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



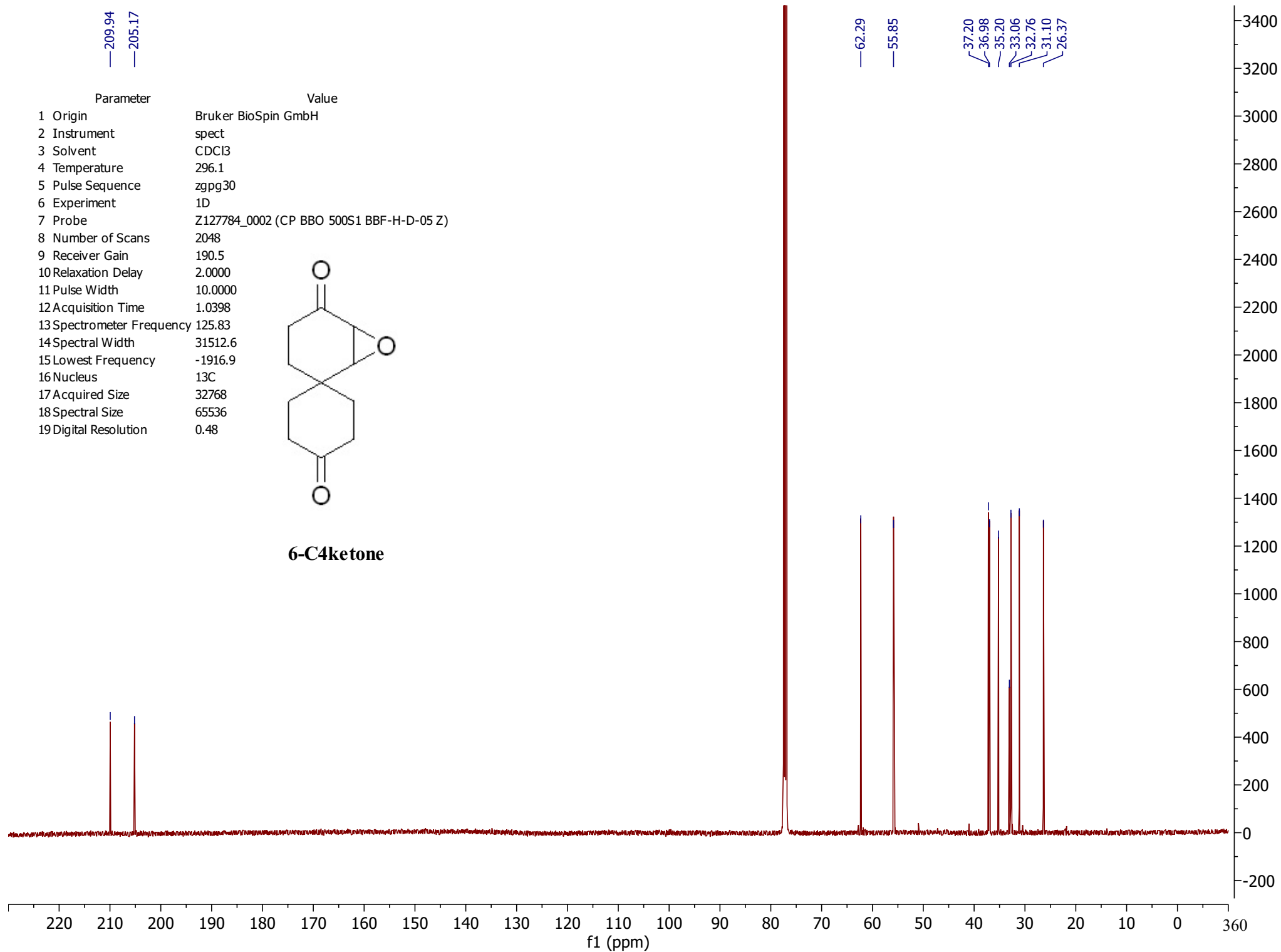
6-C4ketone



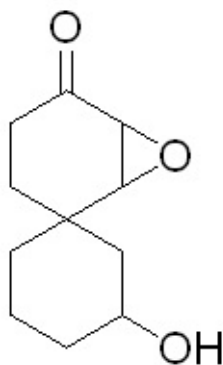
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



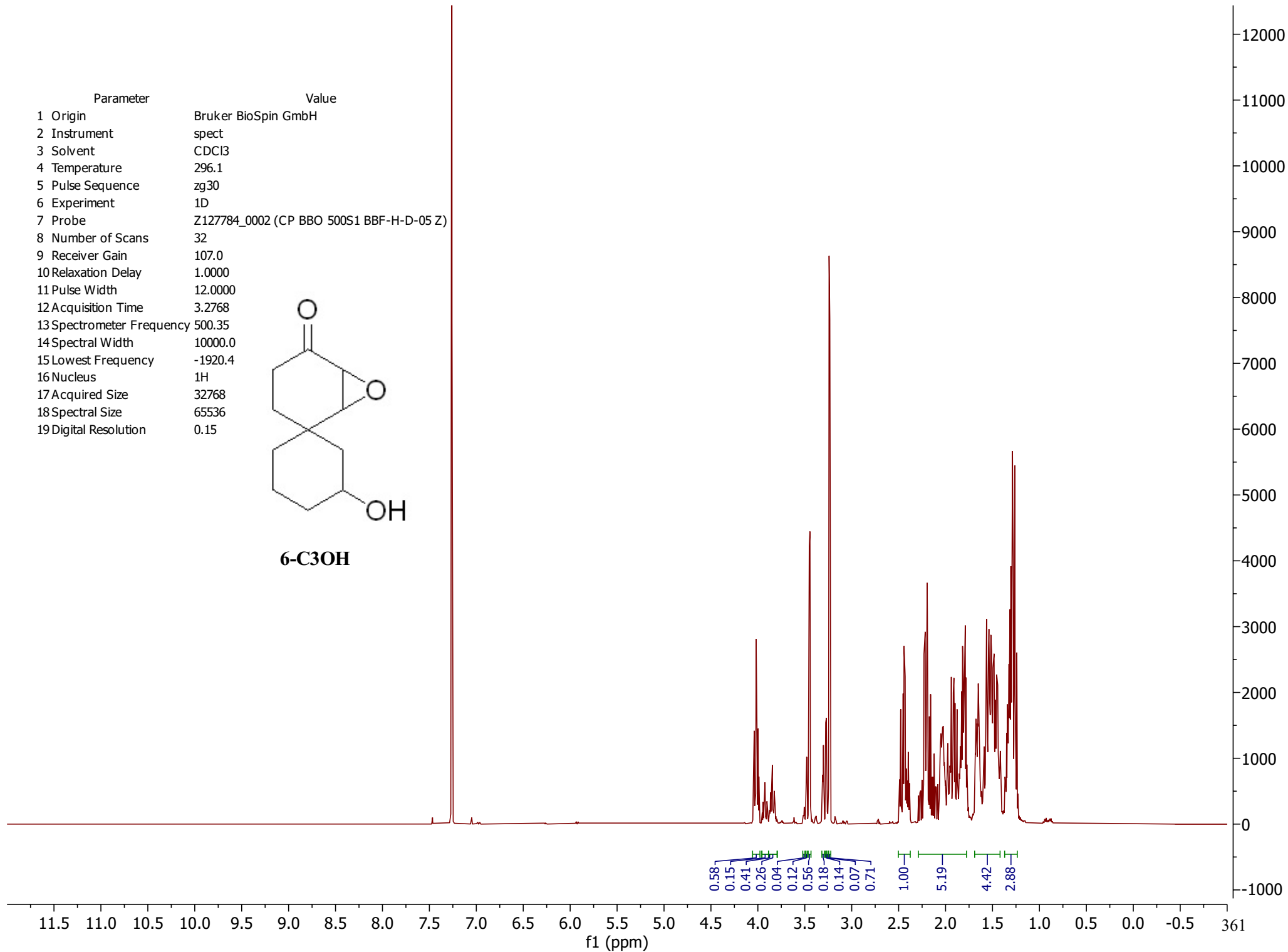
6-C4ketone



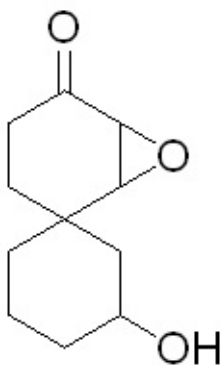
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	107.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1920.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



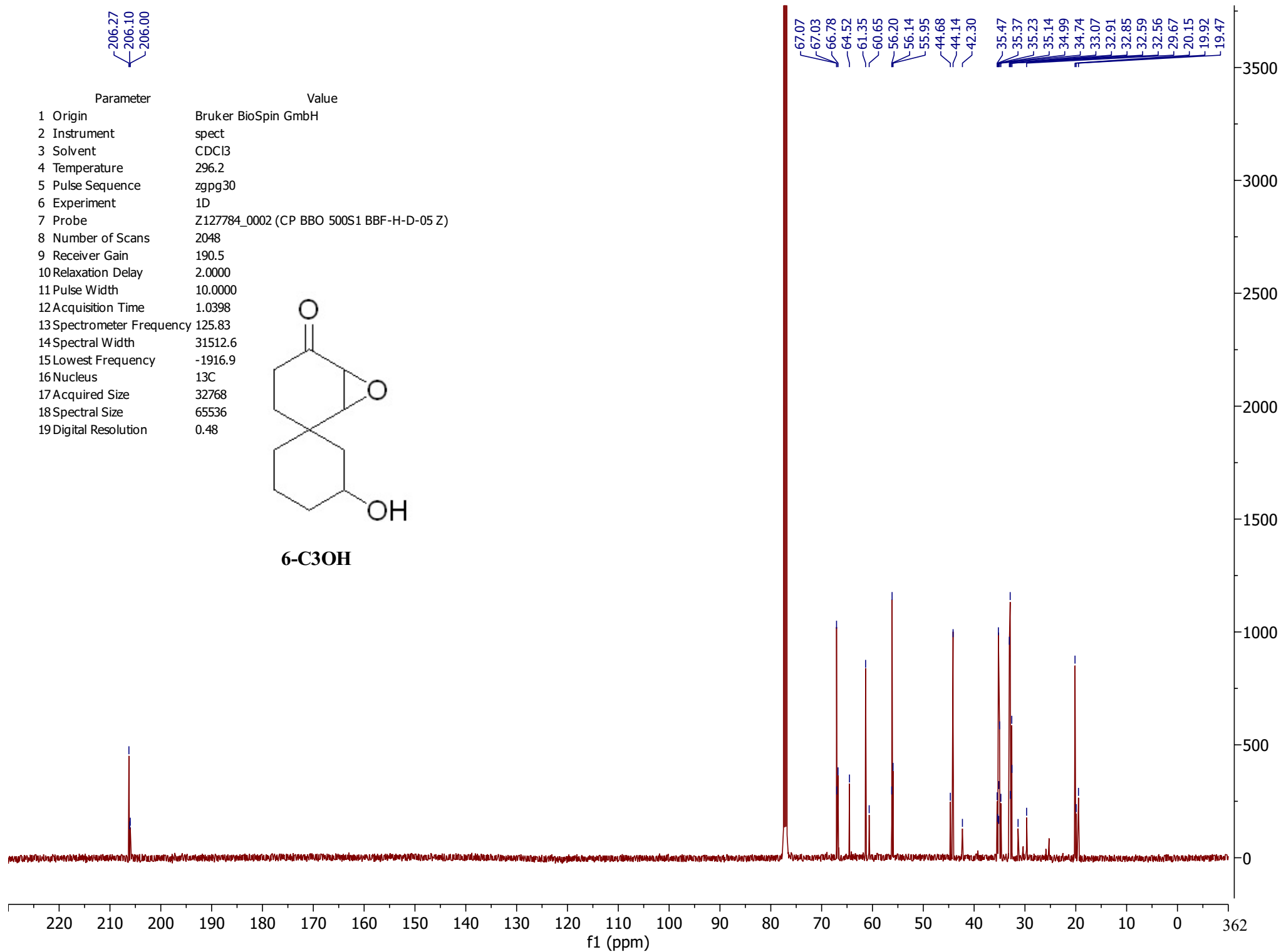
6-C3OH



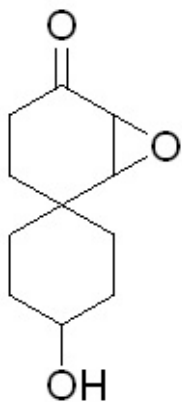
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



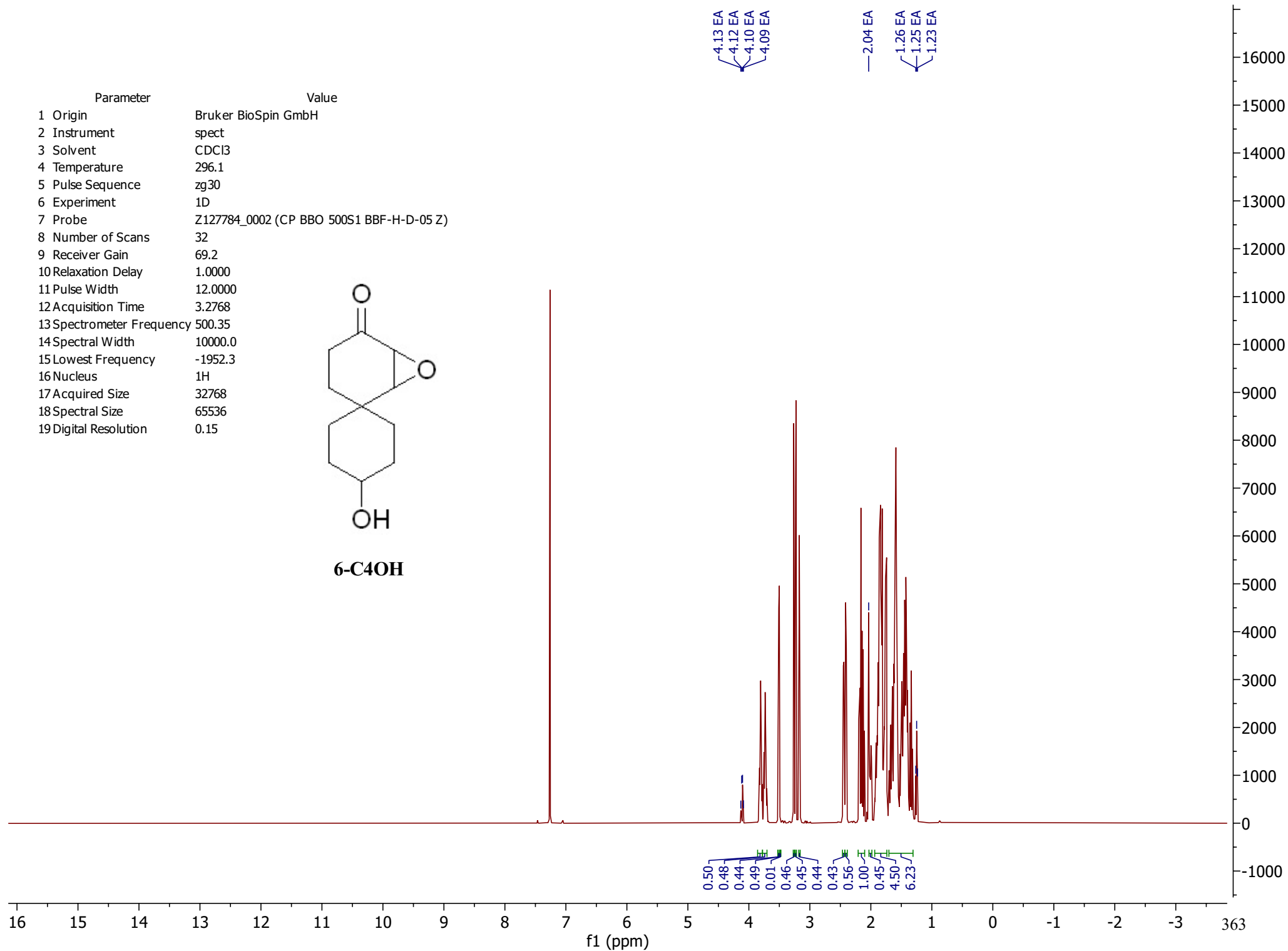
6-C3OH



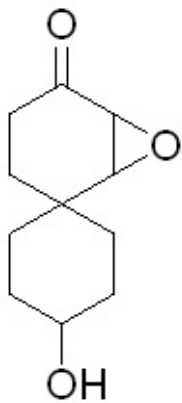
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1952.3
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



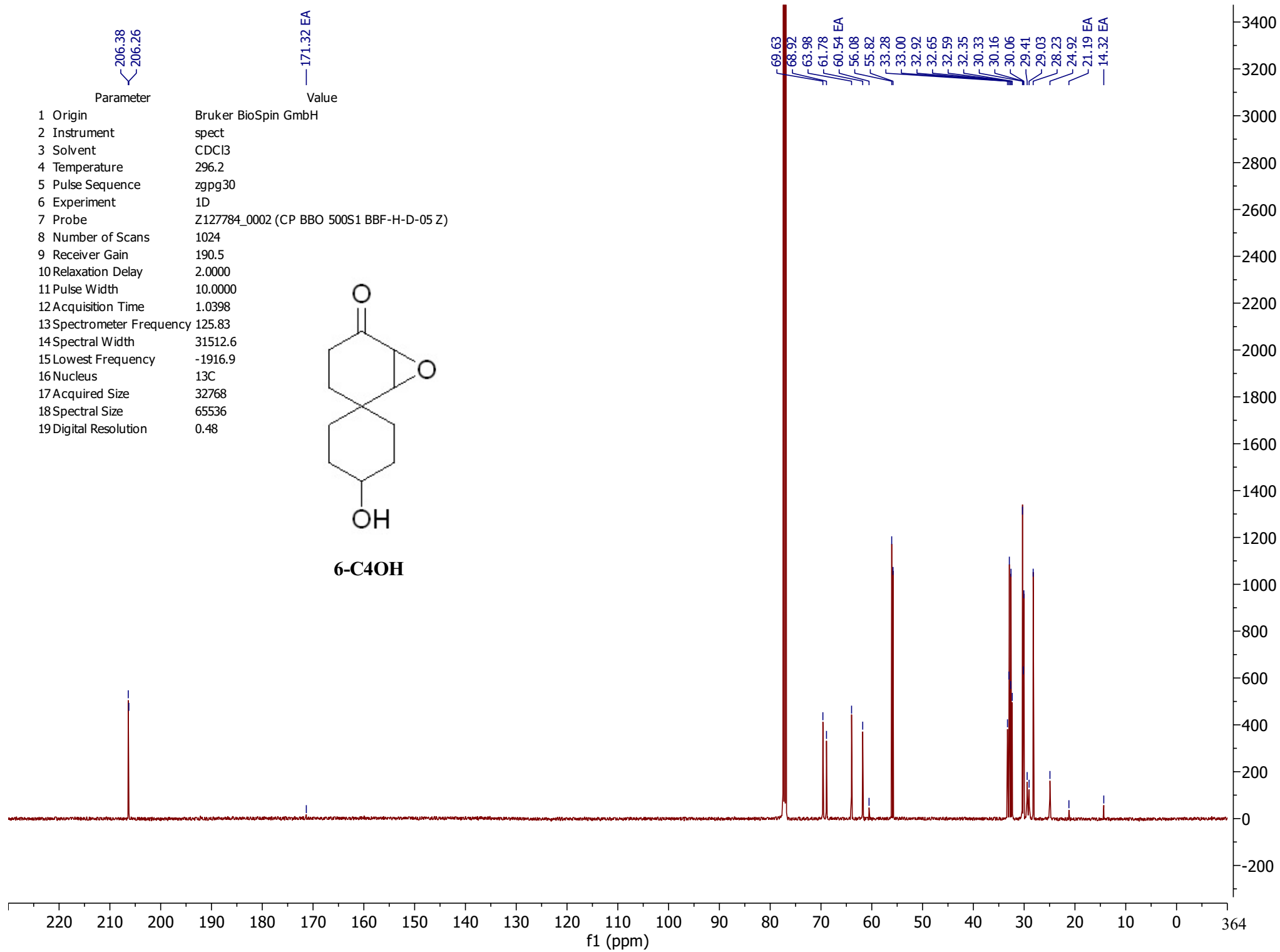
6-C4OH



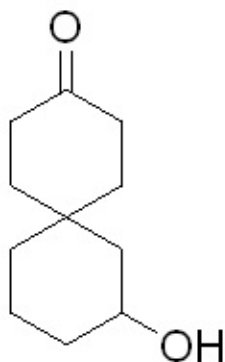
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



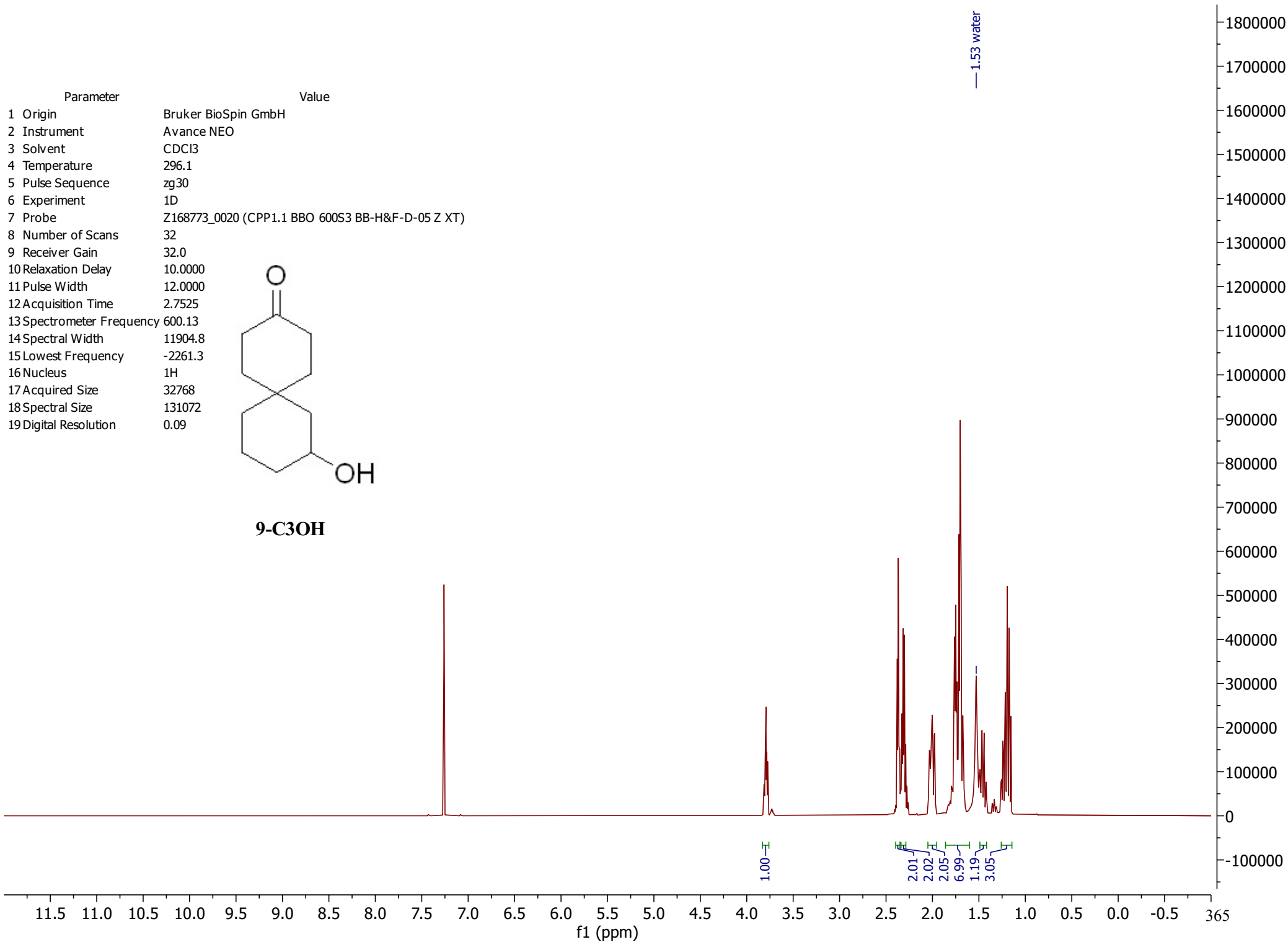
6-C4OH



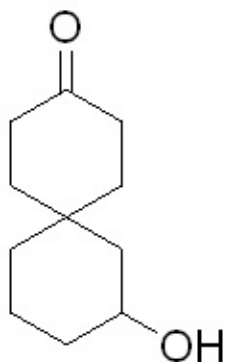
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.3
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



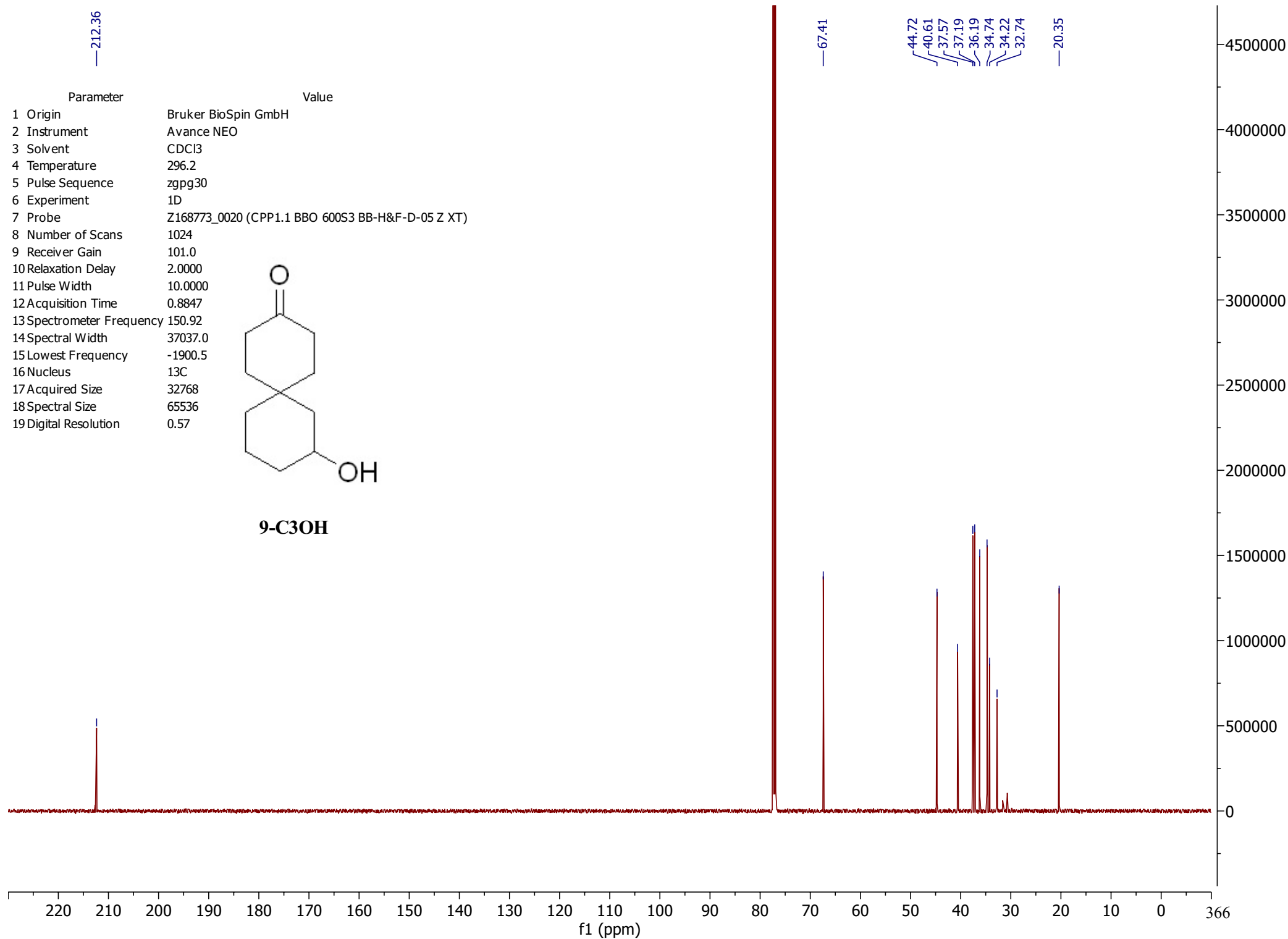
9-C3OH



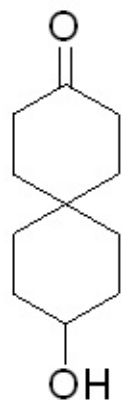
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	1024
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1900.5
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



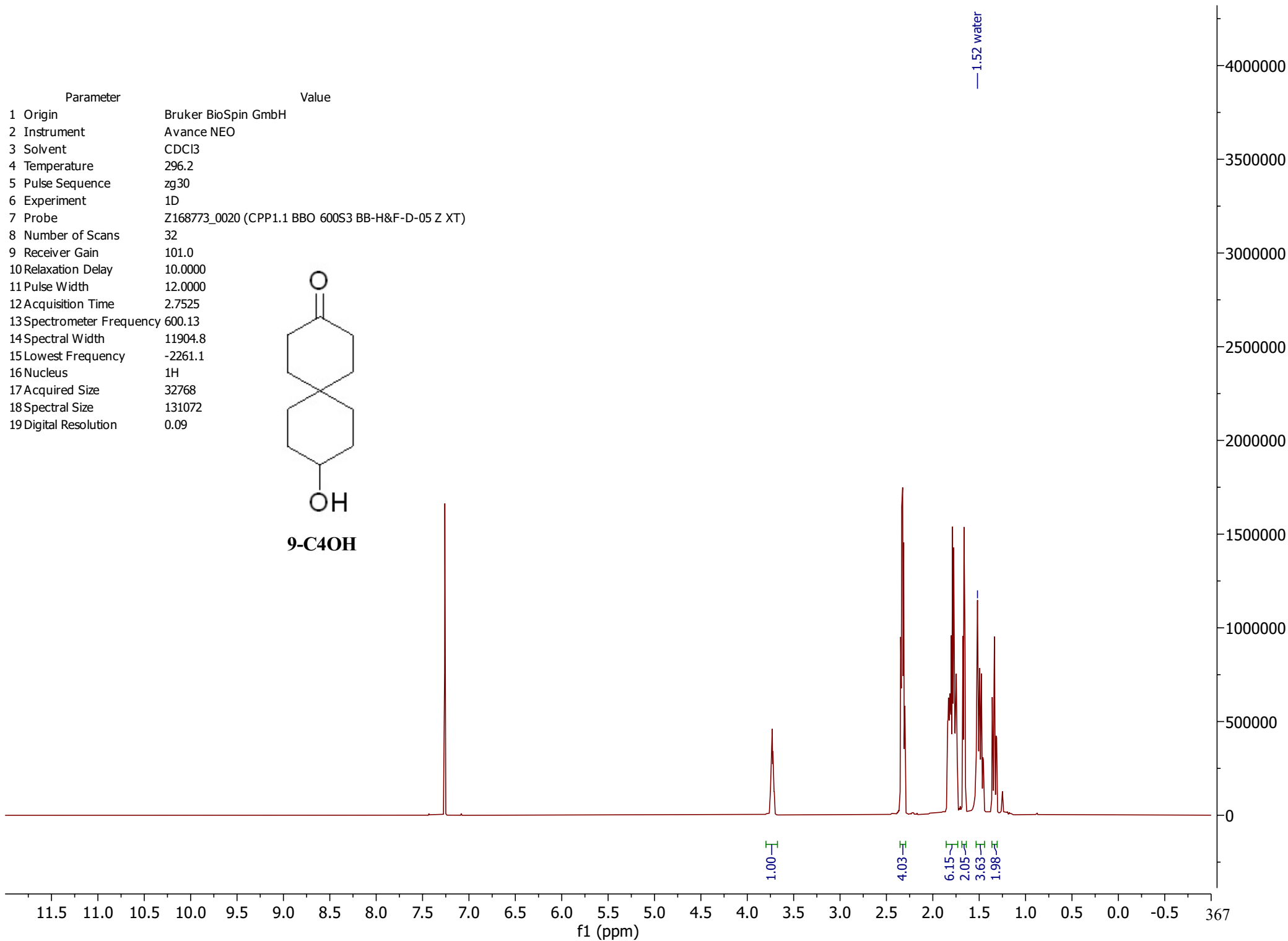
9-C3OH



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

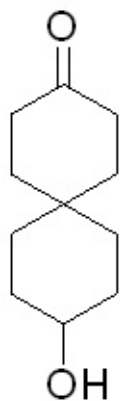


9-C4OH

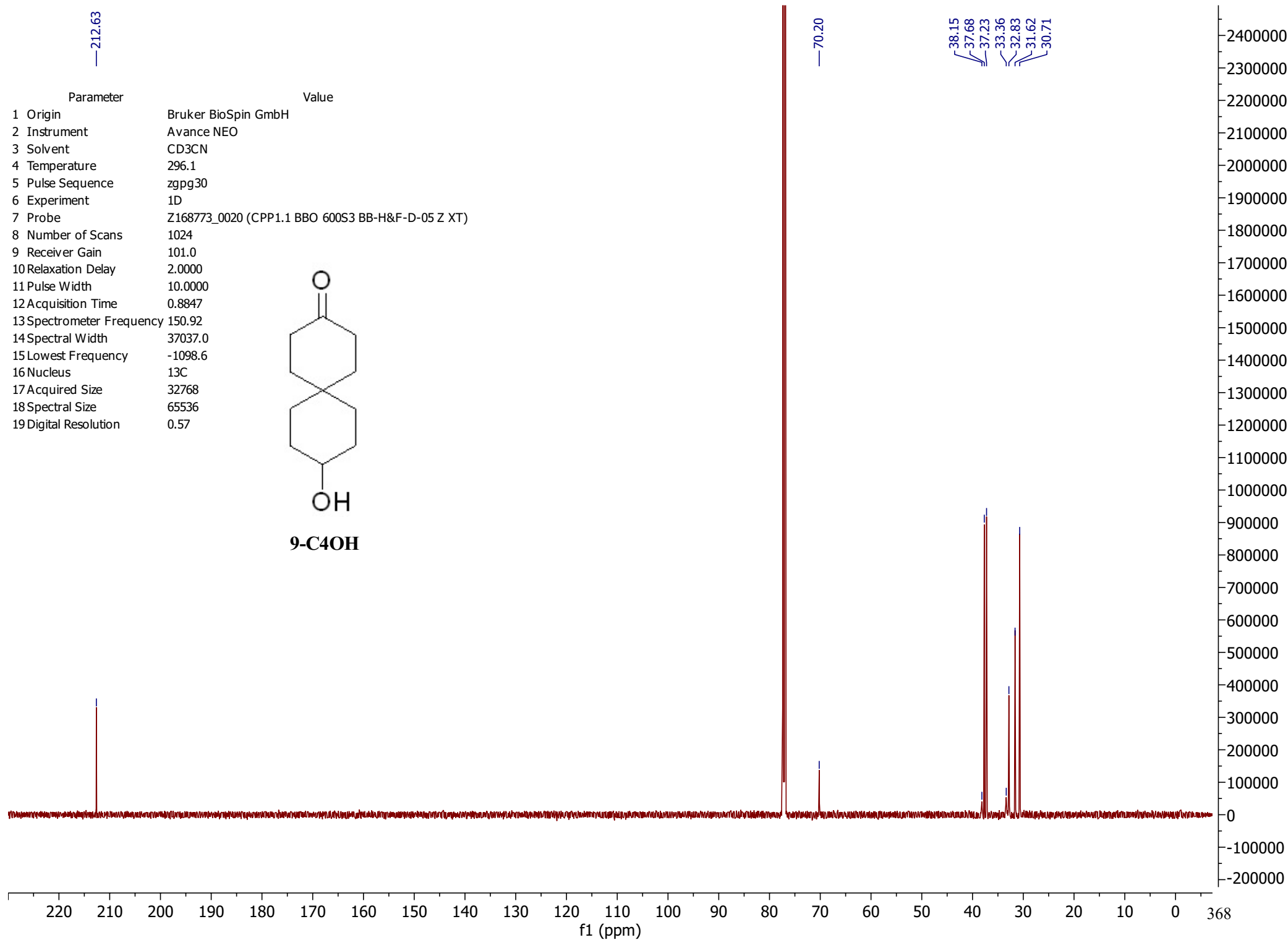


Parameter Value

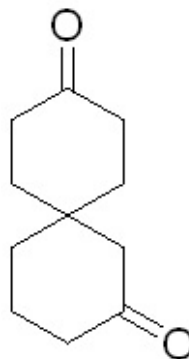
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CD3CN
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	1024
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1098.6
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



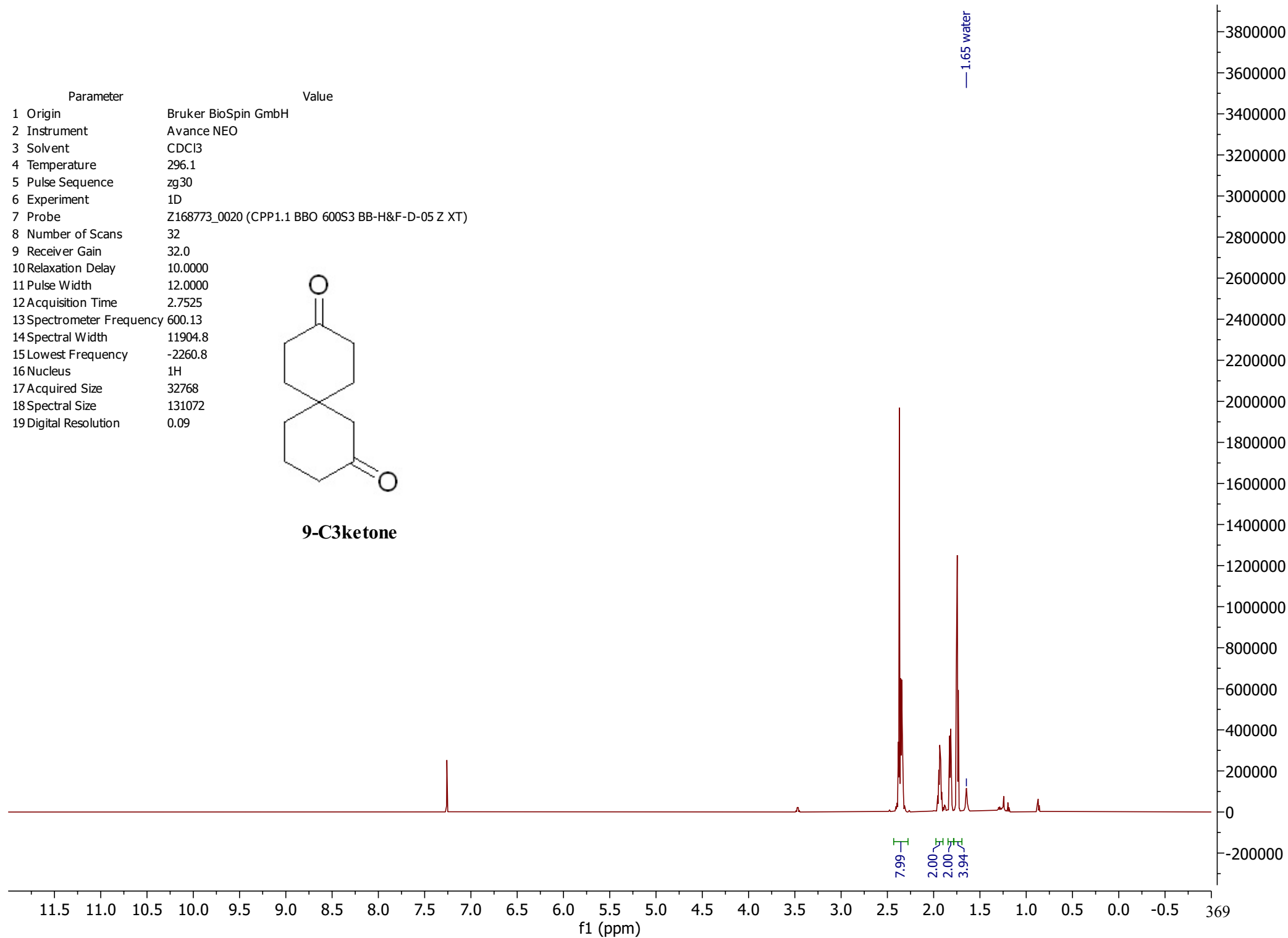
9-C4OH

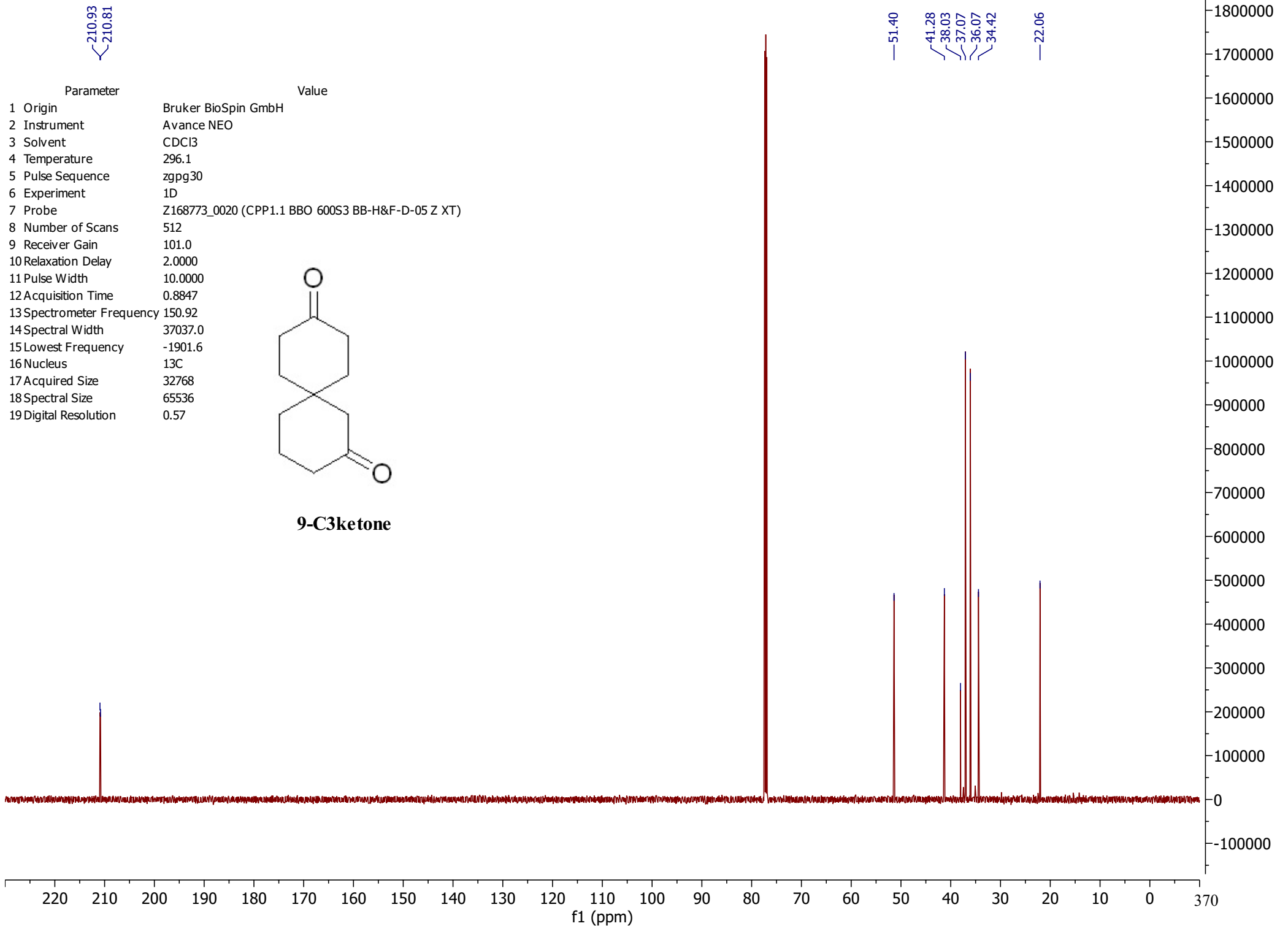


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



9-C3ketone

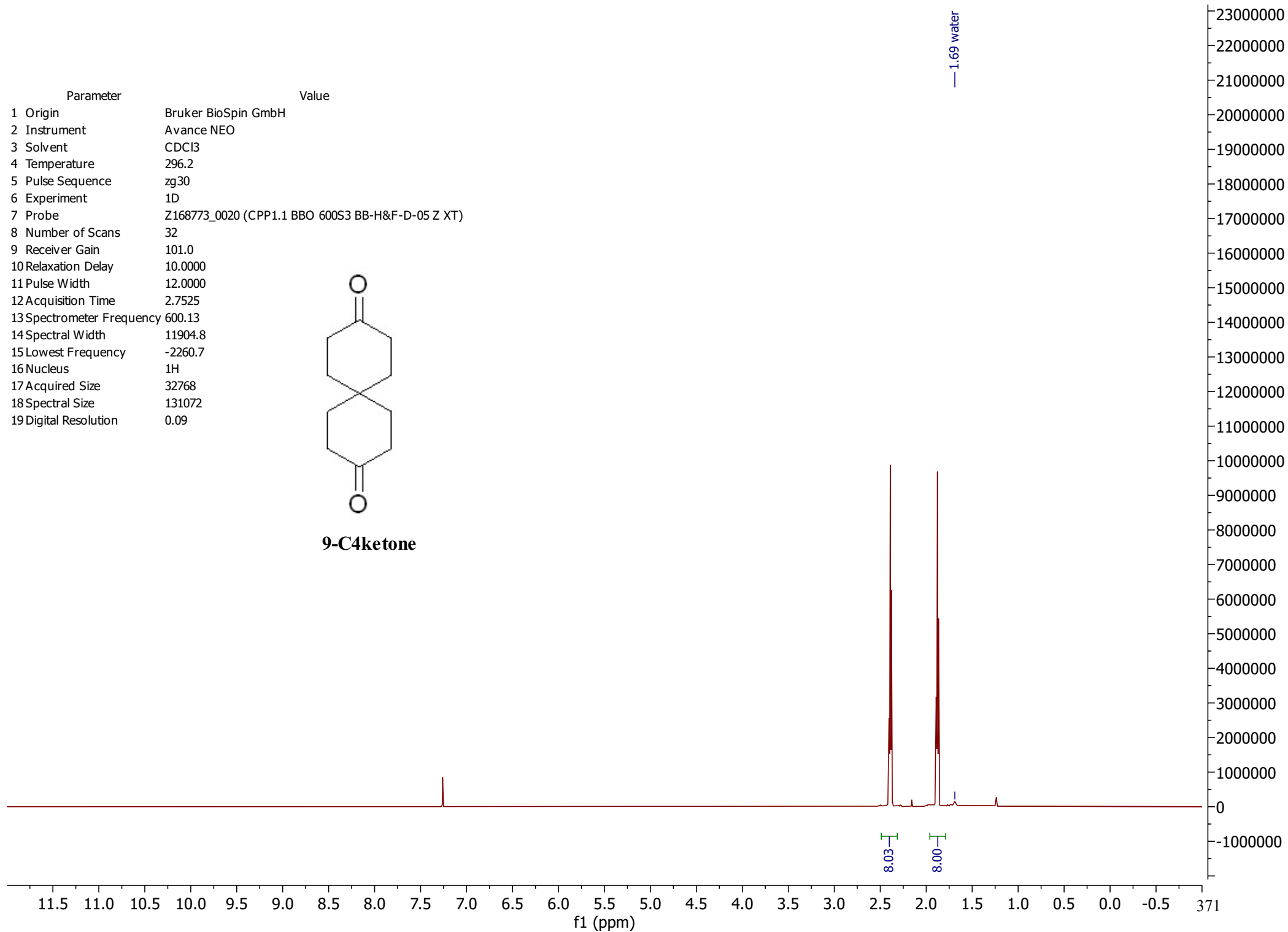


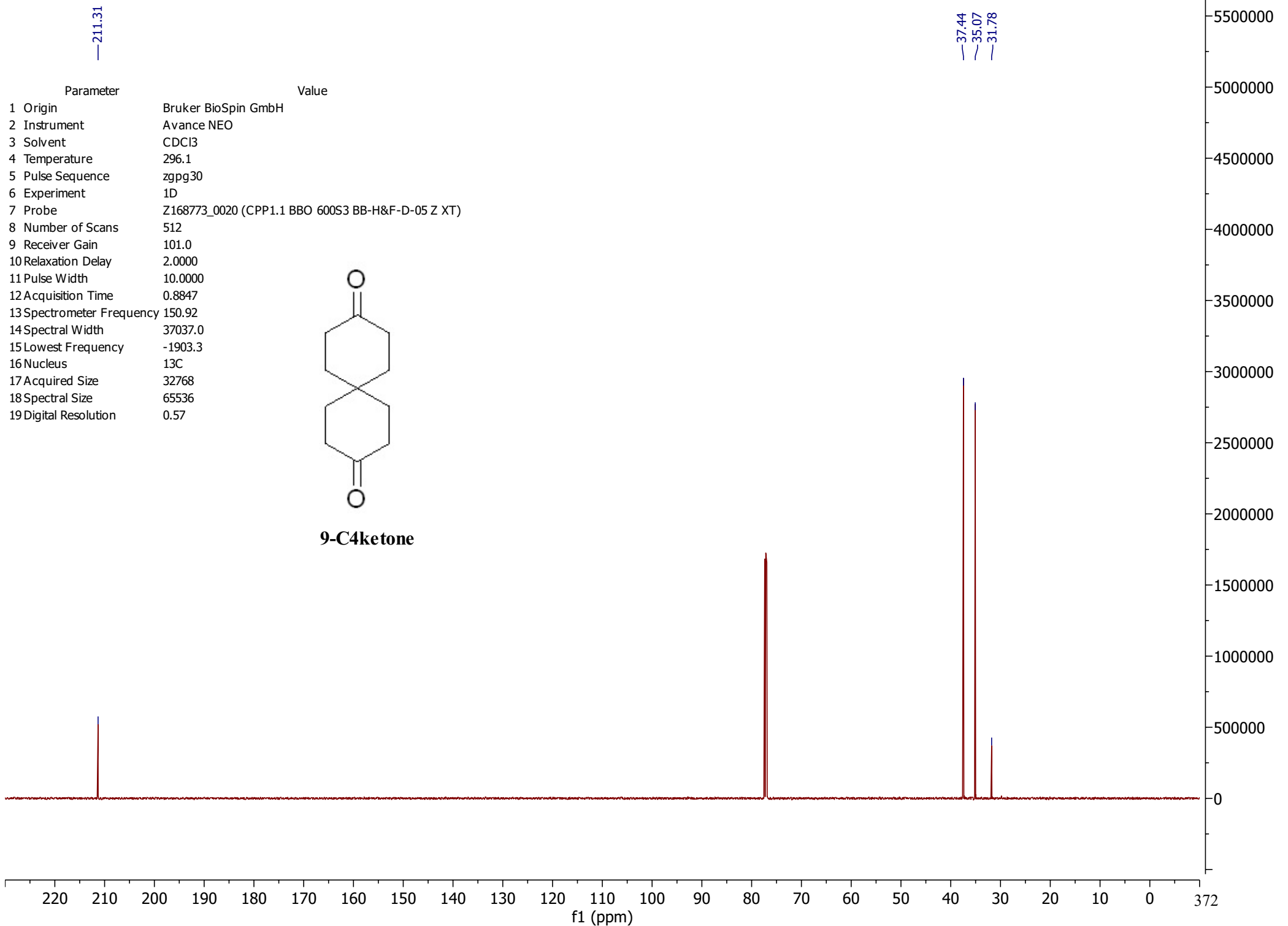


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

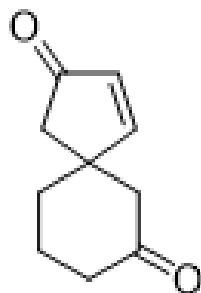


9-C4ketone

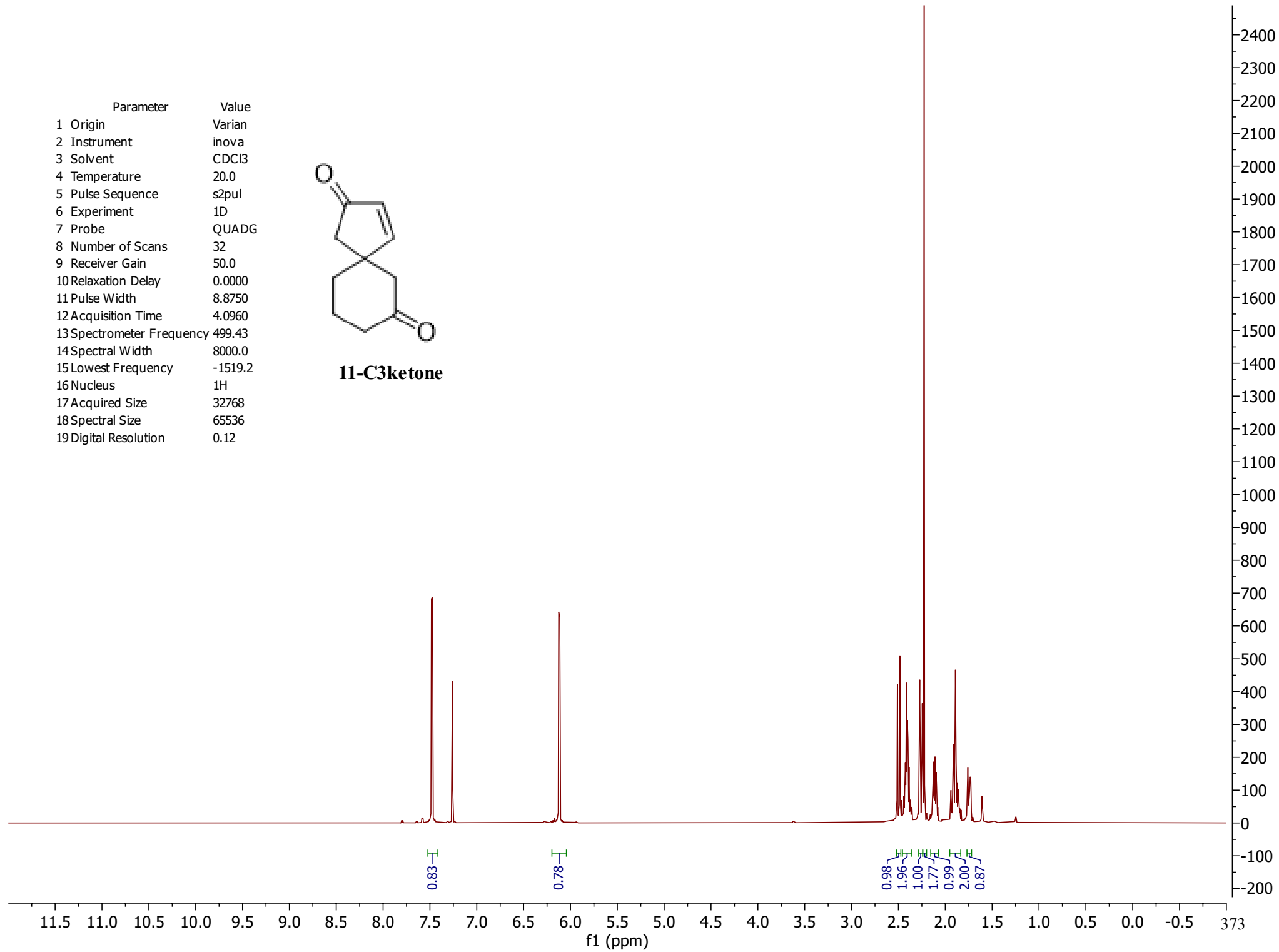


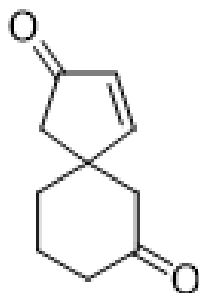


Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	QUADG
8 Number of Scans	32
9 Receiver Gain	50.0
10 Relaxation Delay	0.0000
11 Pulse Width	8.8750
12 Acquisition Time	4.0960
13 Spectrometer Frequency	499.43
14 Spectral Width	8000.0
15 Lowest Frequency	-1519.2
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12

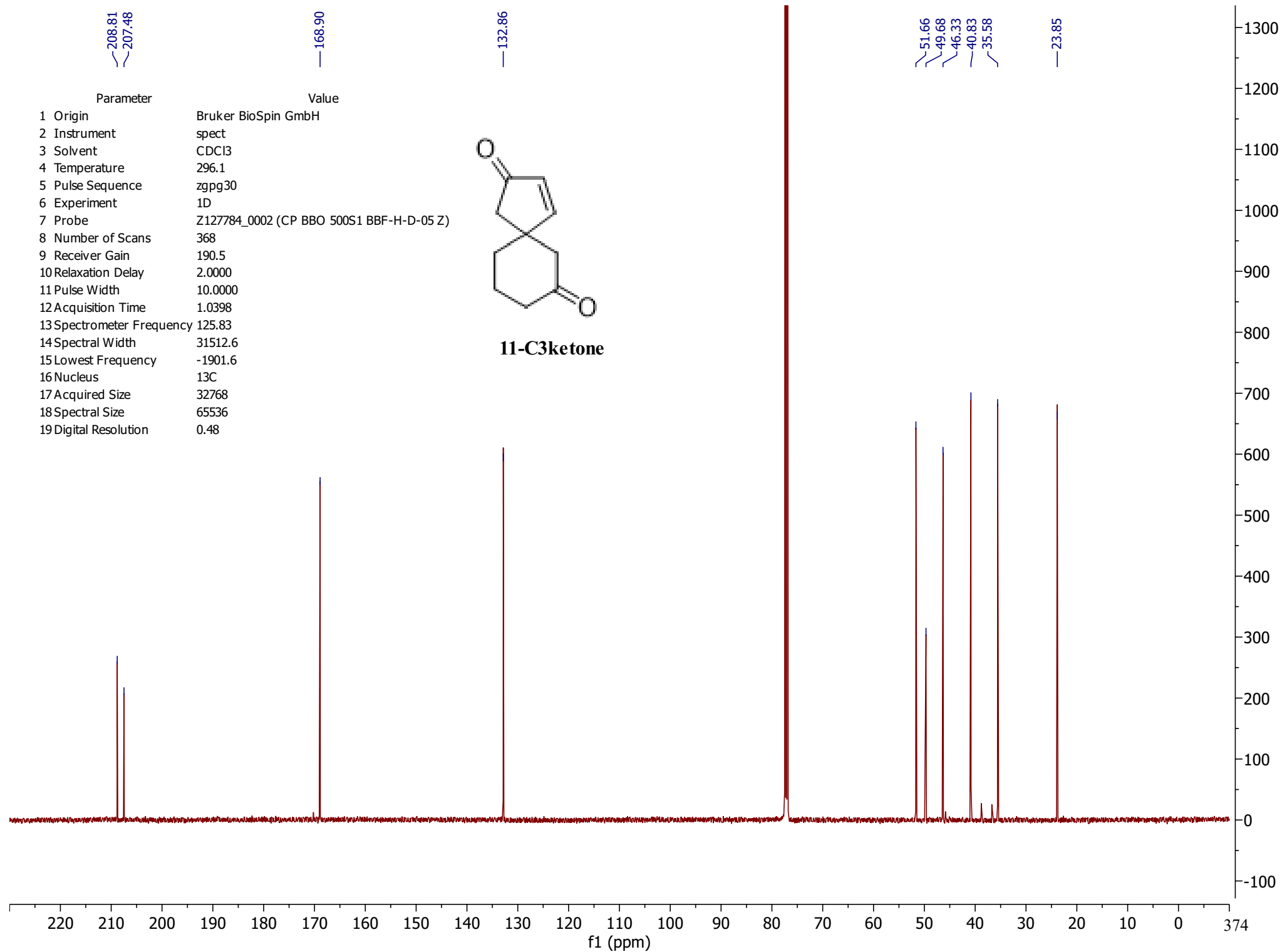


11-C3ketone

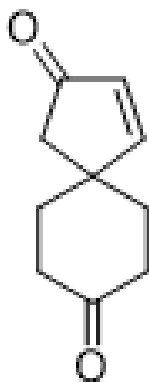




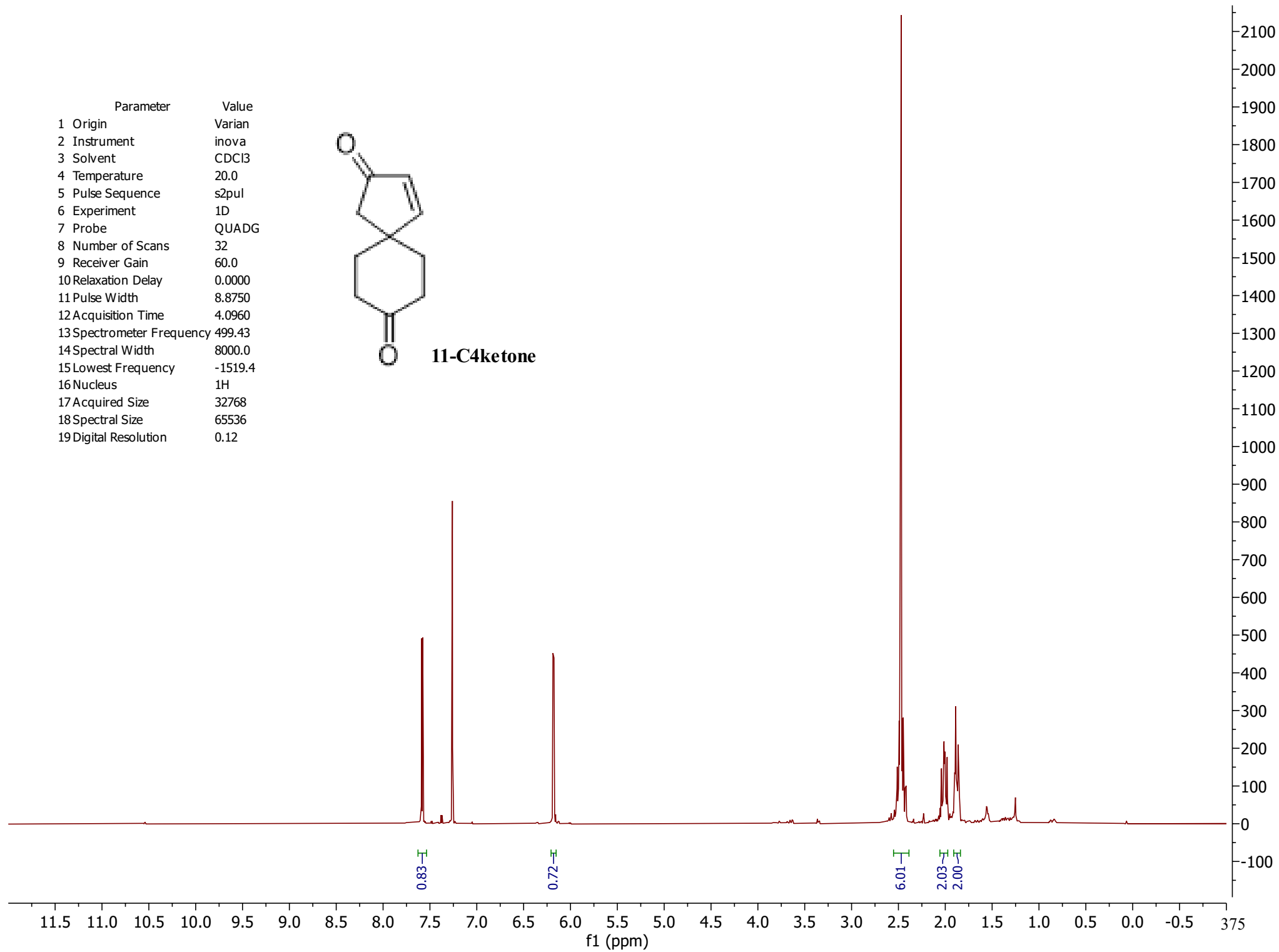
11-C3ketone



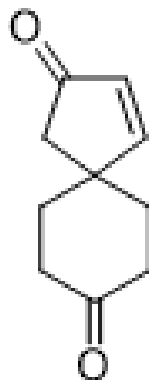
Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	QUADG
8 Number of Scans	32
9 Receiver Gain	60.0
10 Relaxation Delay	0.0000
11 Pulse Width	8.8750
12 Acquisition Time	4.0960
13 Spectrometer Frequency	499.43
14 Spectral Width	8000.0
15 Lowest Frequency	-1519.4
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12



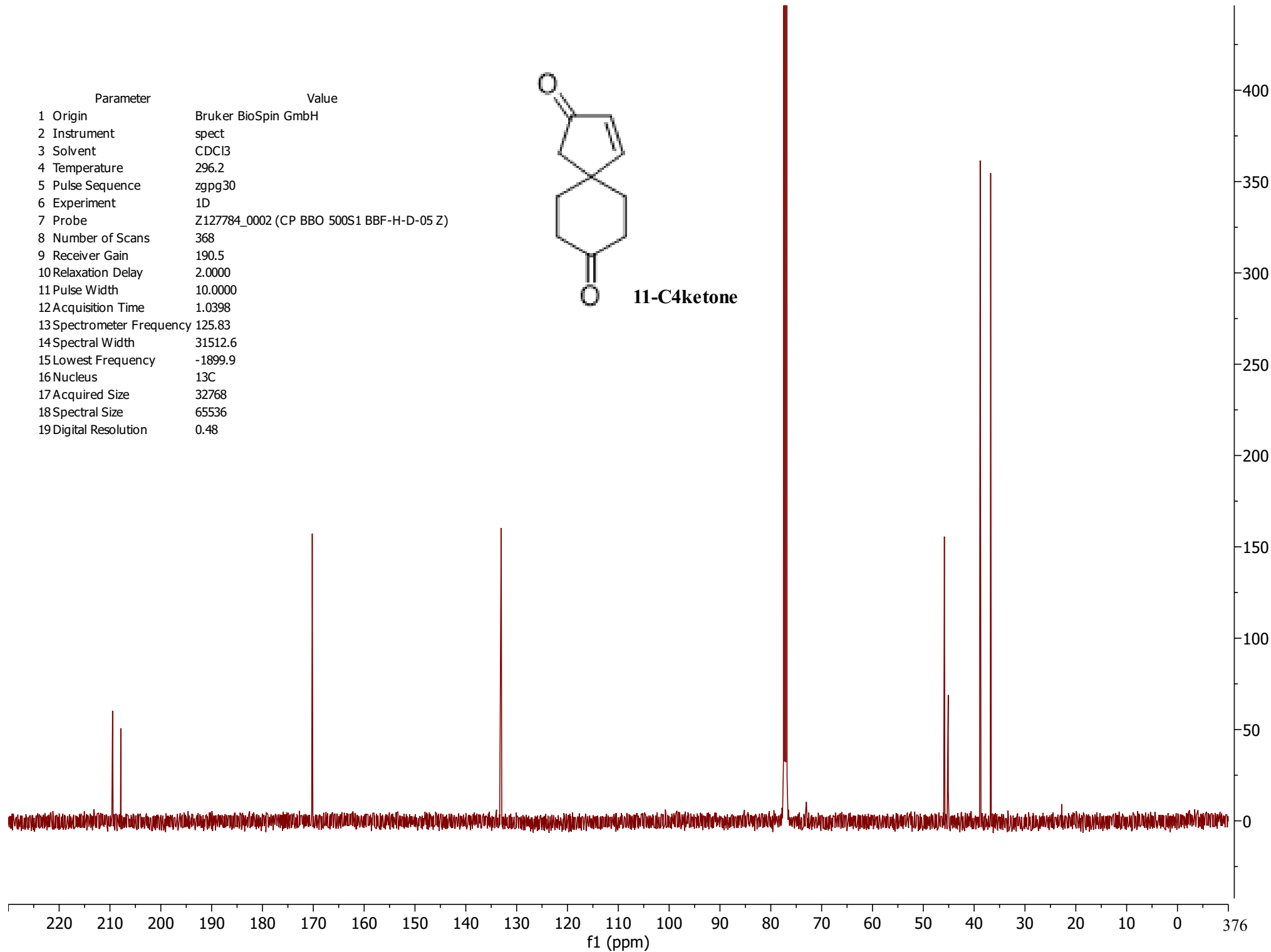
11-C4ketone



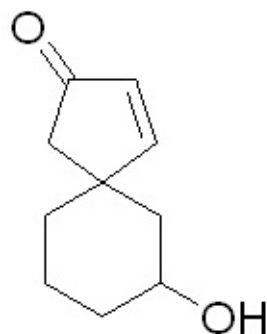
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1899.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



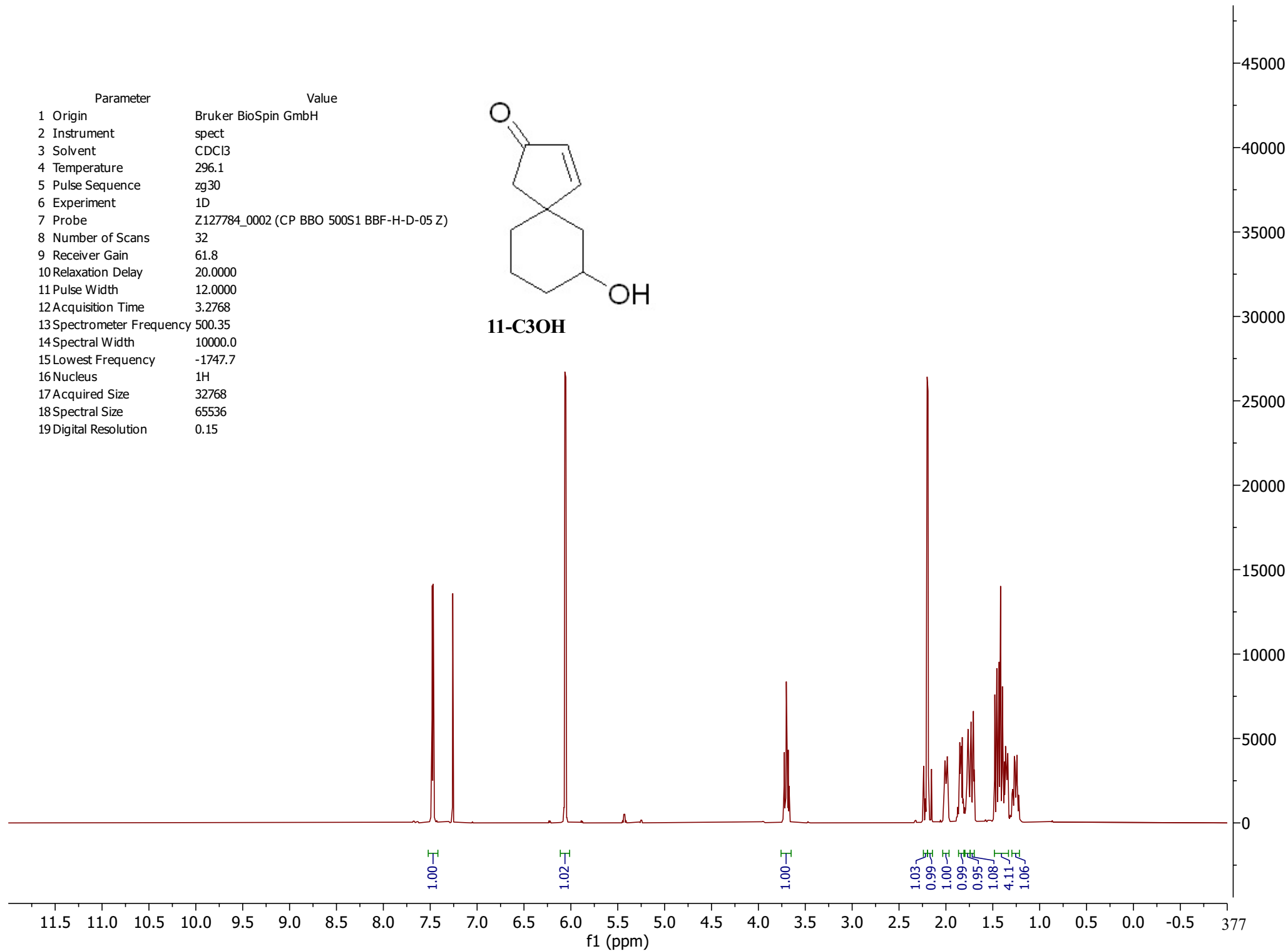
11-C4ketone



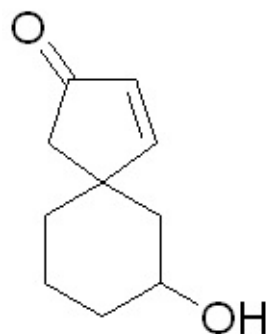
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	61.8
10 Relaxation Delay	20.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



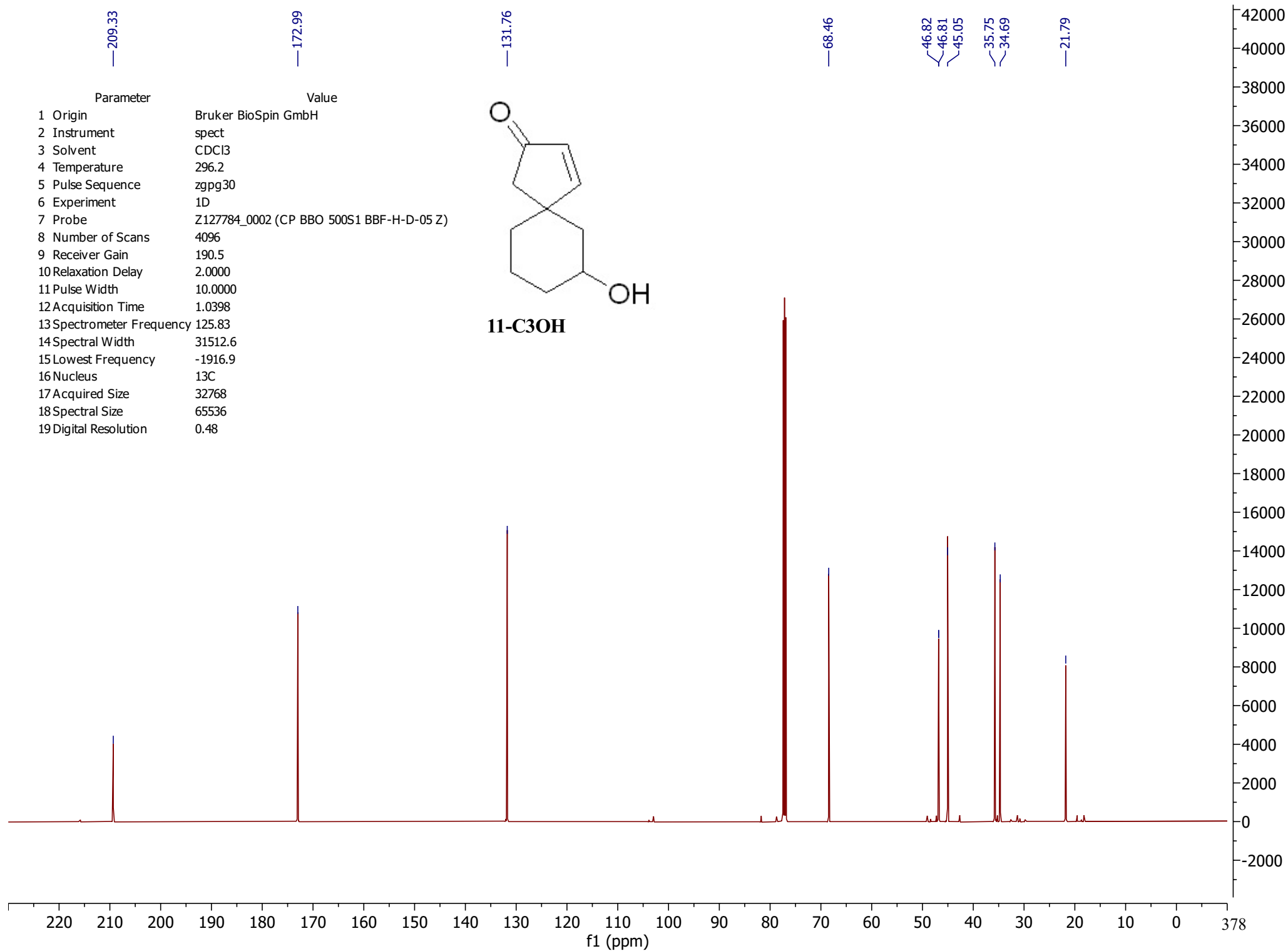
11-C3OH



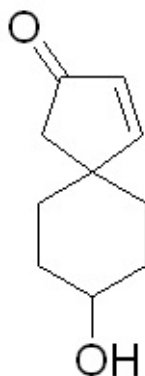
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	4096
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



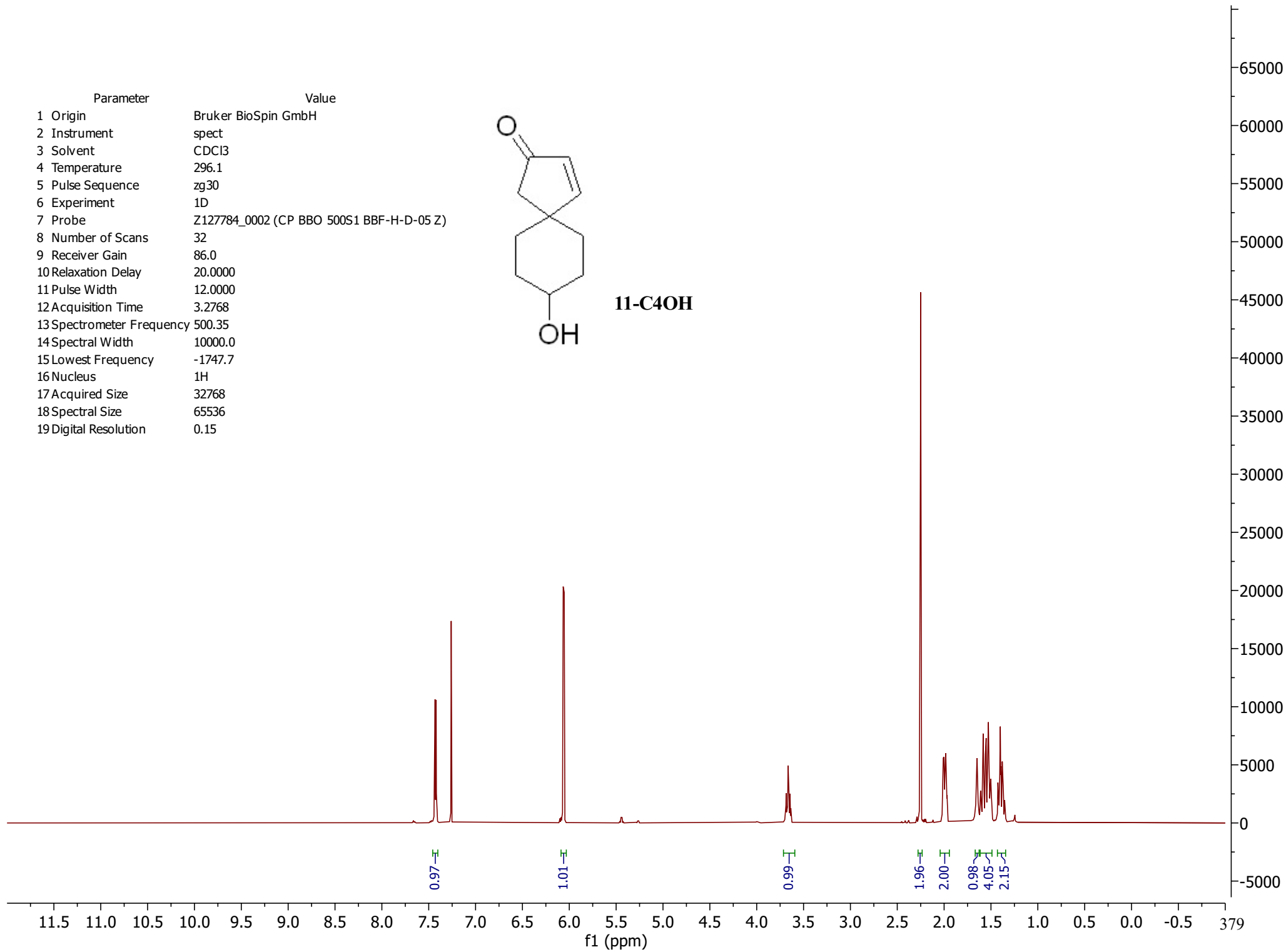
11-C3OH



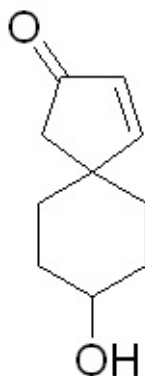
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	20.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



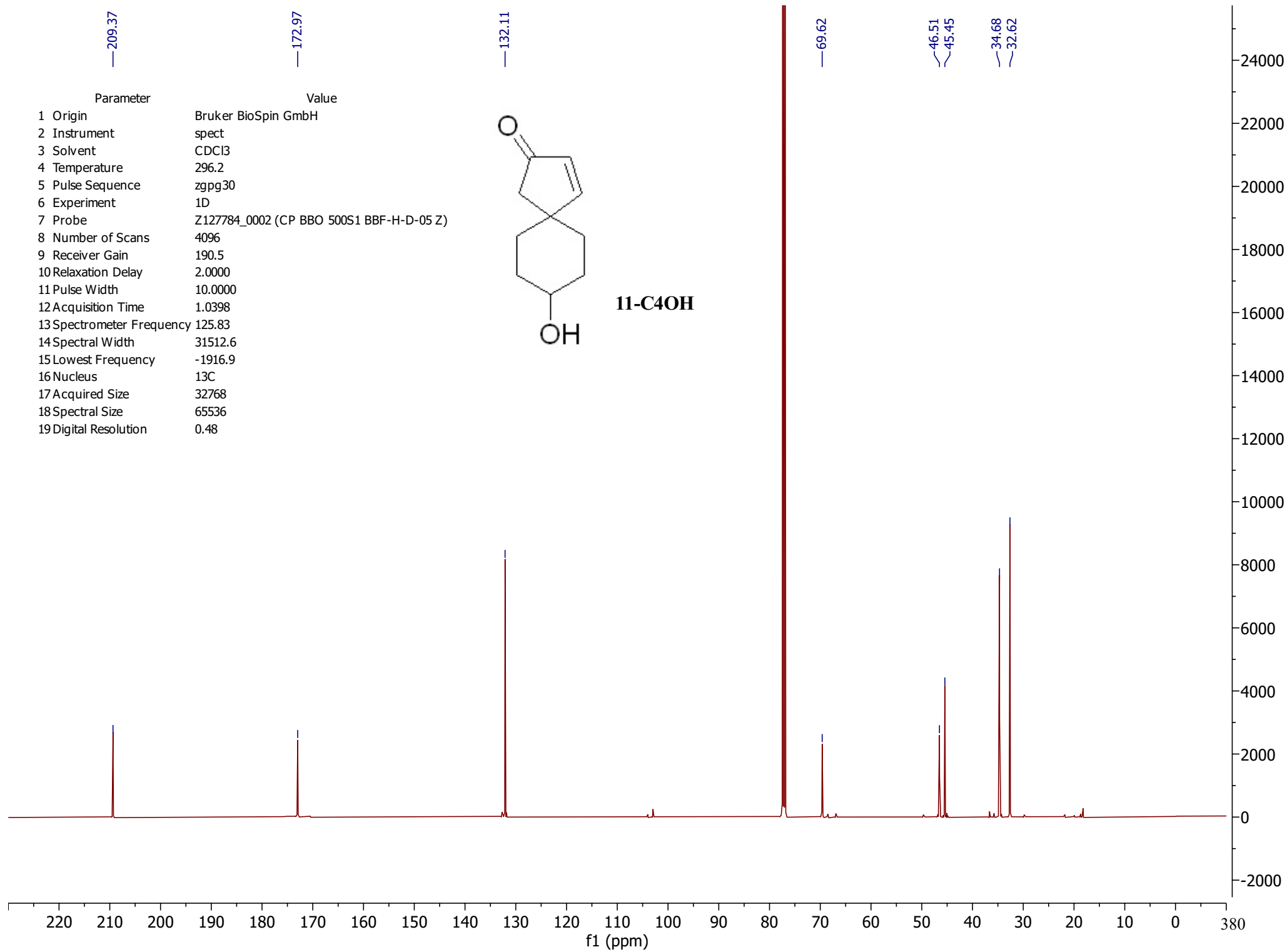
11-C40H



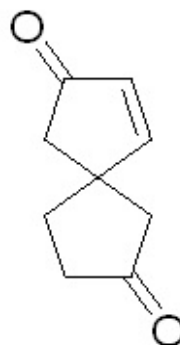
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	4096
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



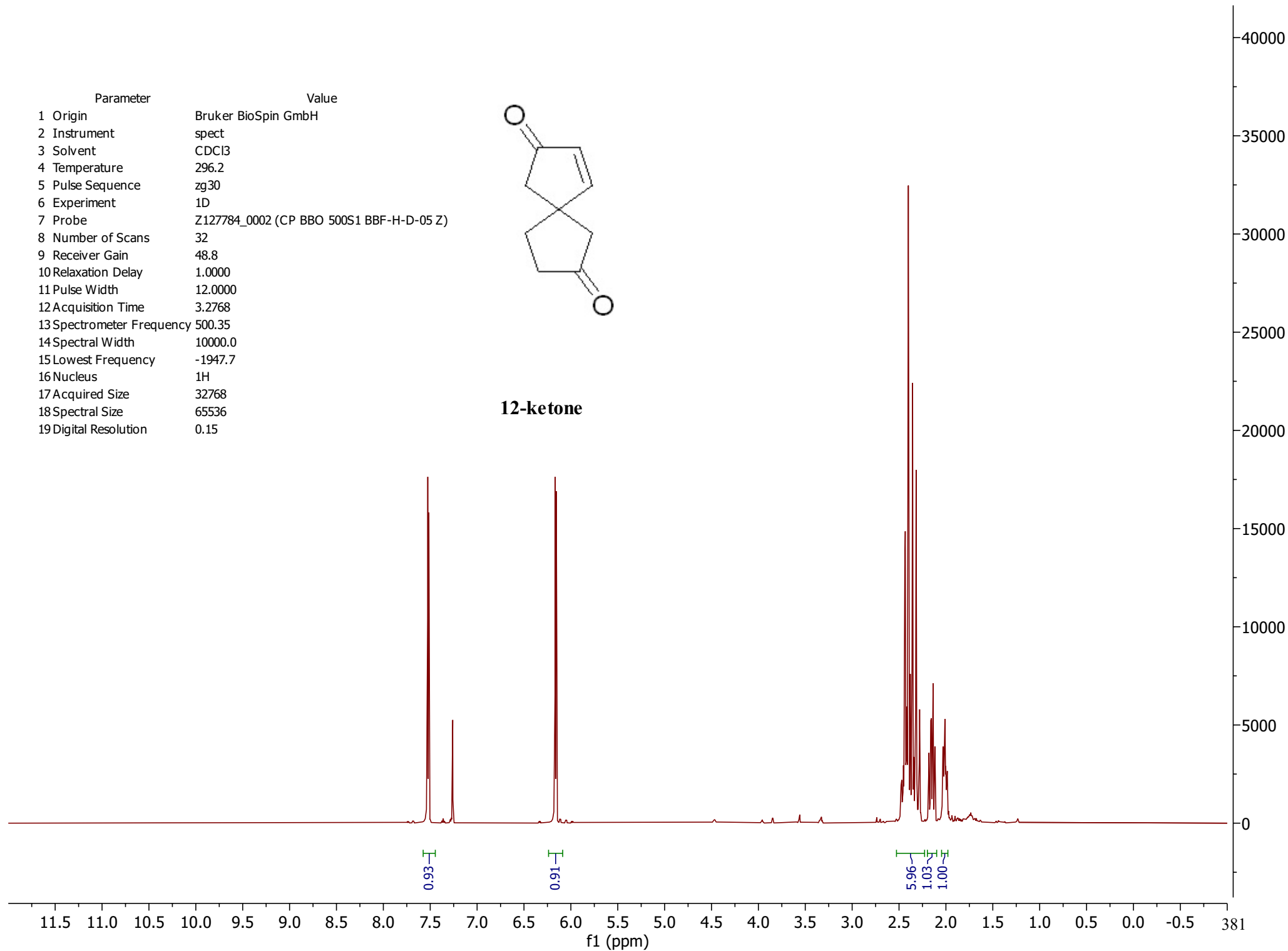
11-C4OH



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	48.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1947.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



12-ketone



215.82
207.69

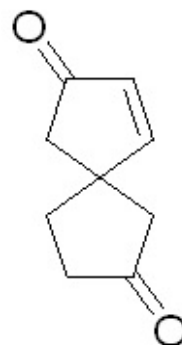
168.62

133.51

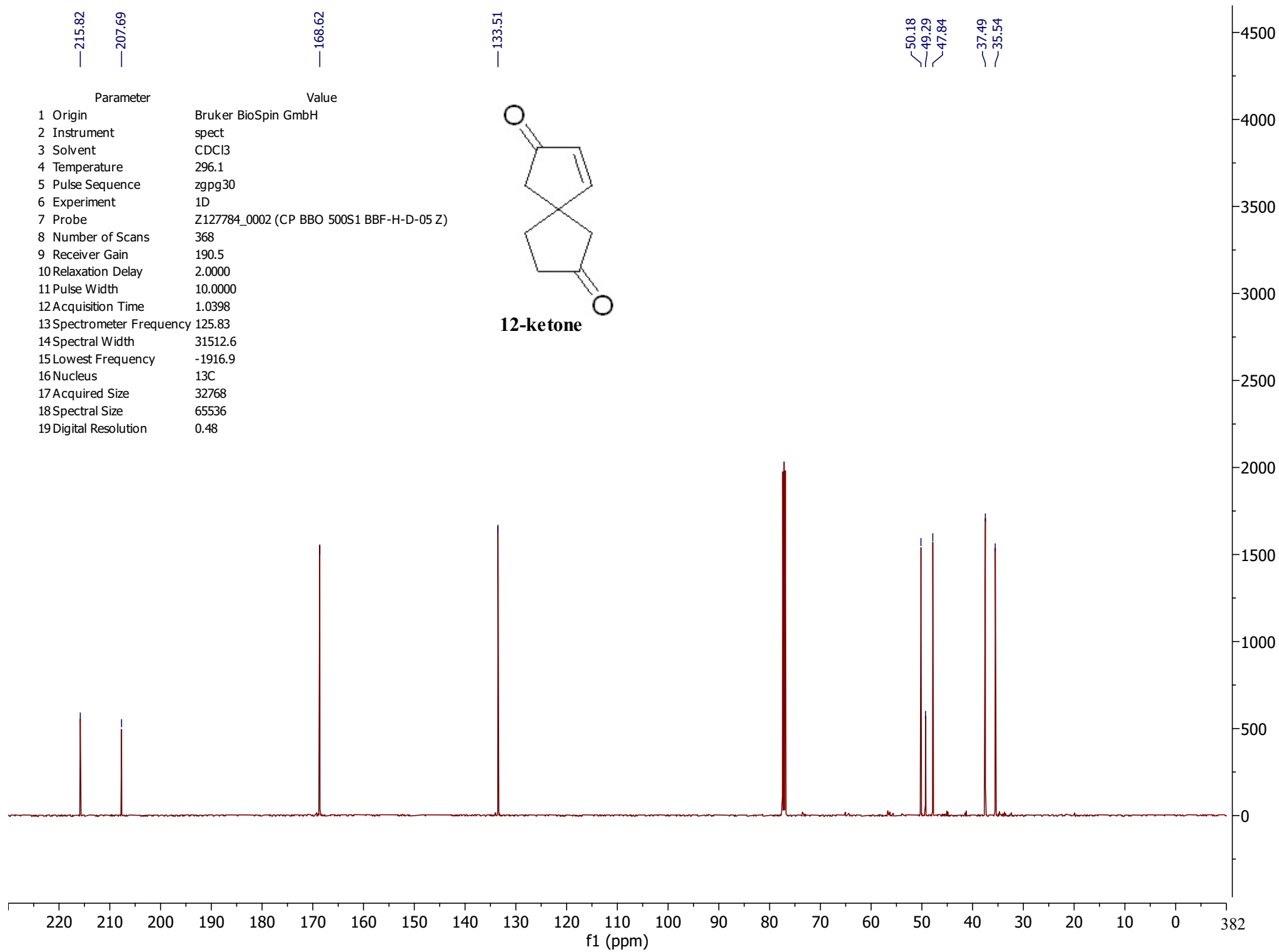
50.18
49.29
47.84

37.49
35.54

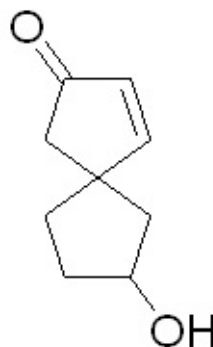
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



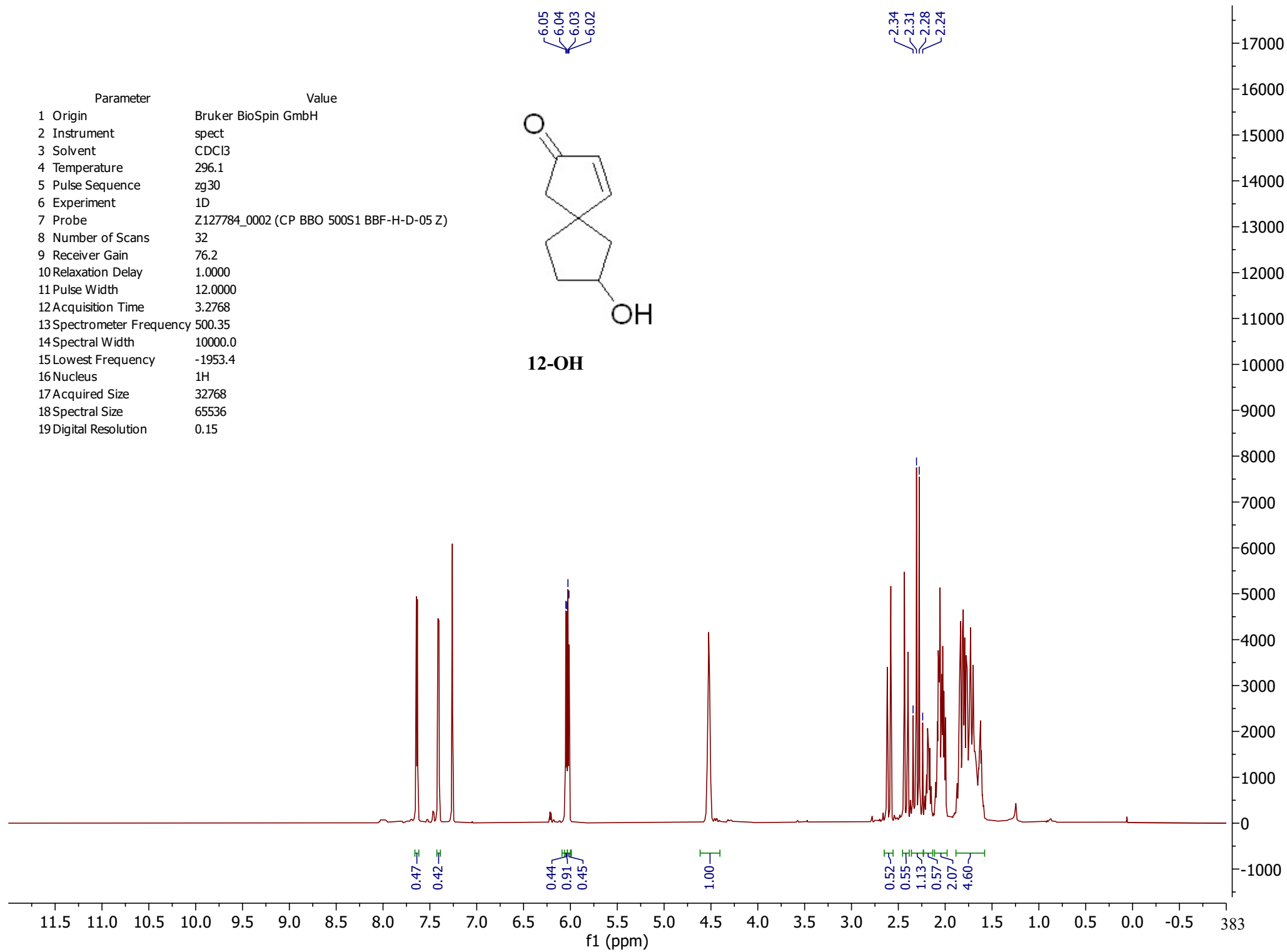
12-ketone



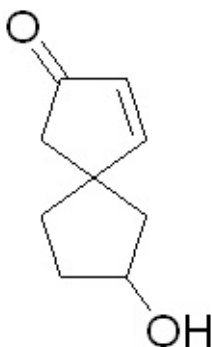
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1953.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



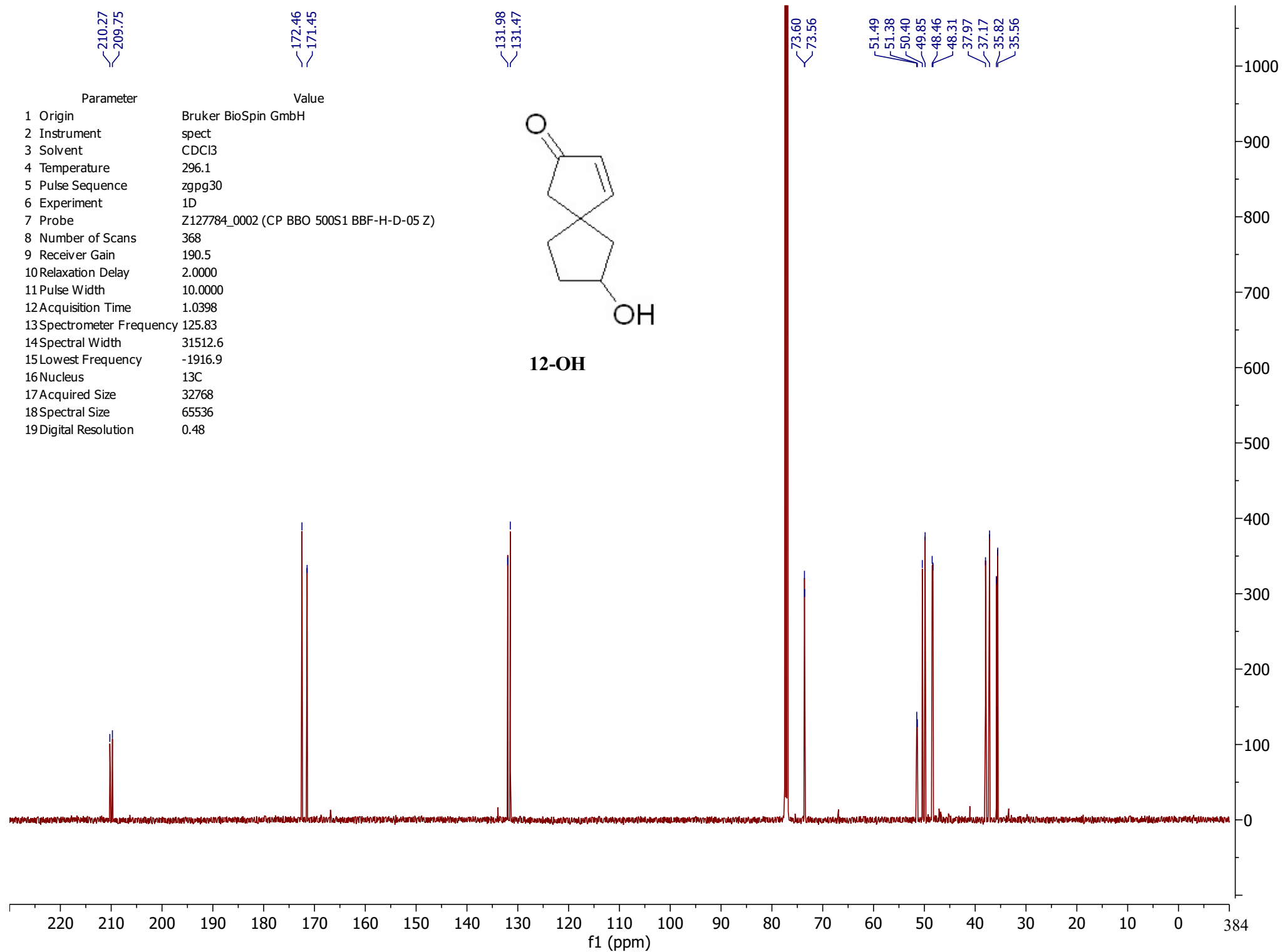
12-OH



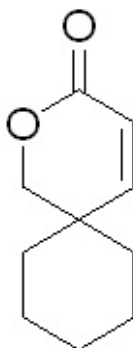
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



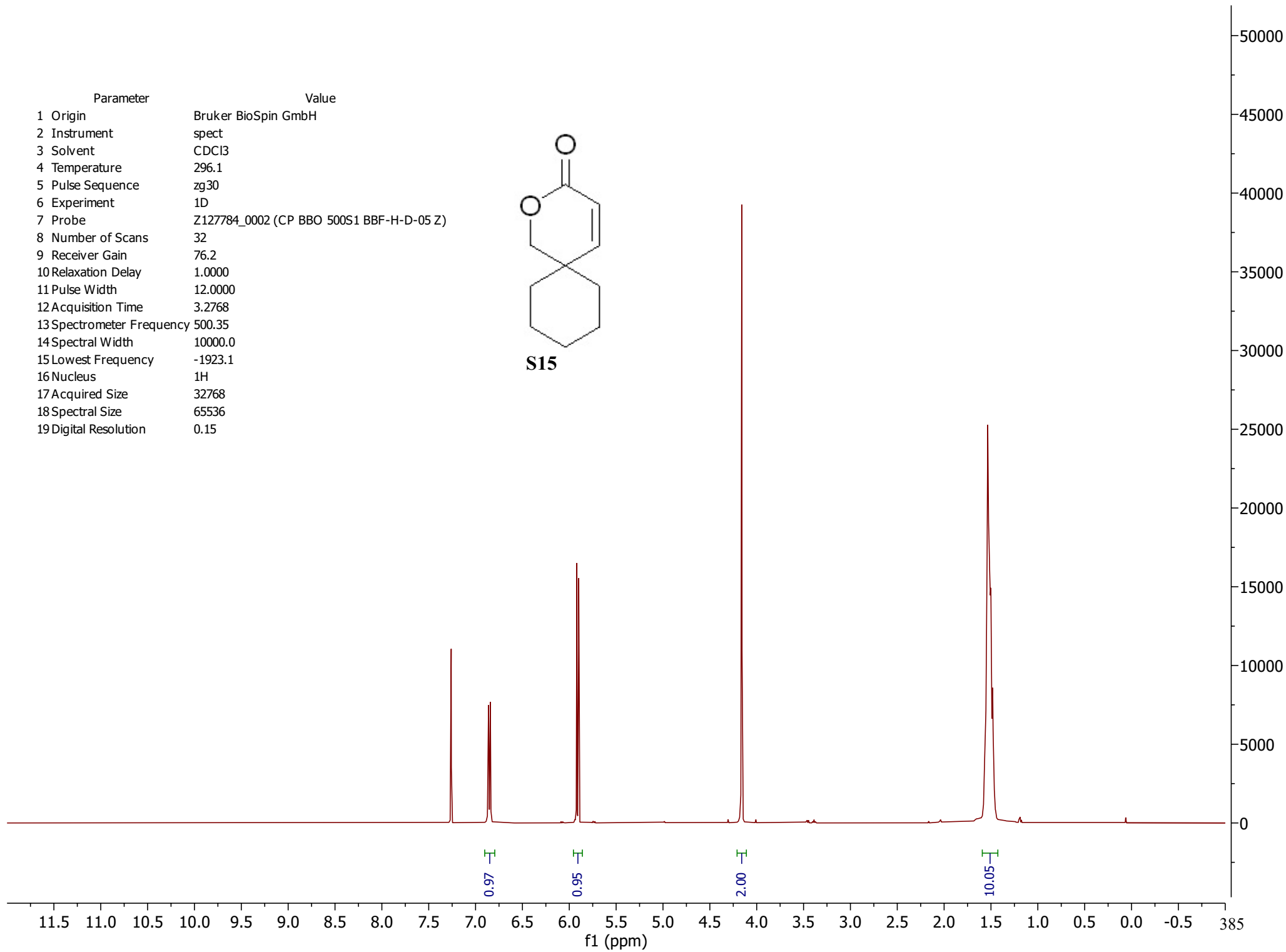
12-OH



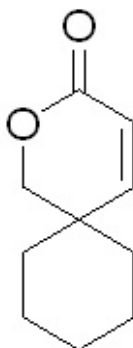
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



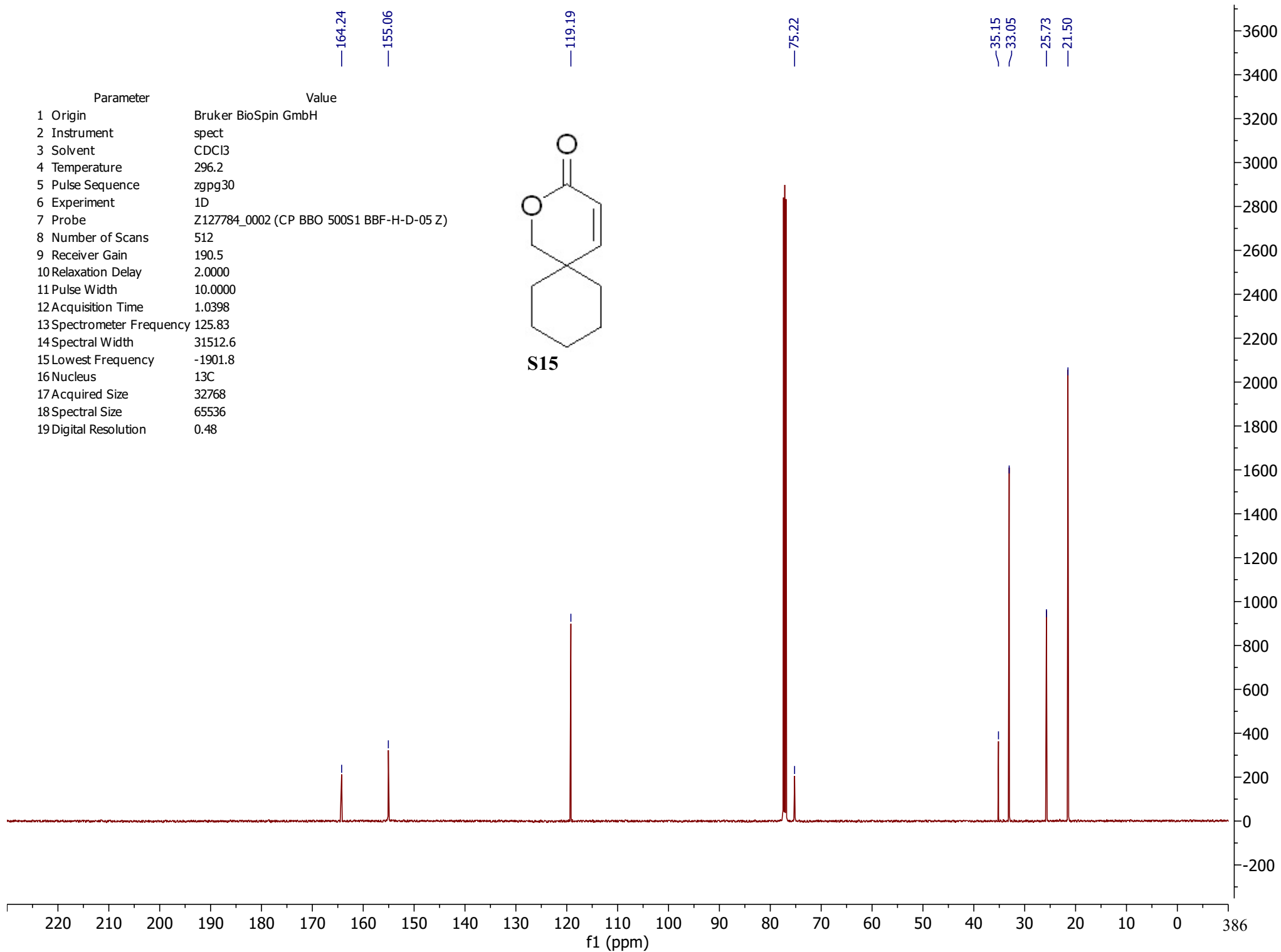
S15



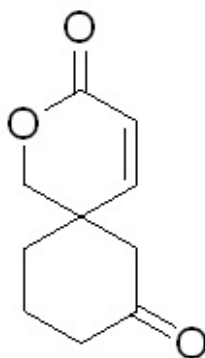
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	512
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1901.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



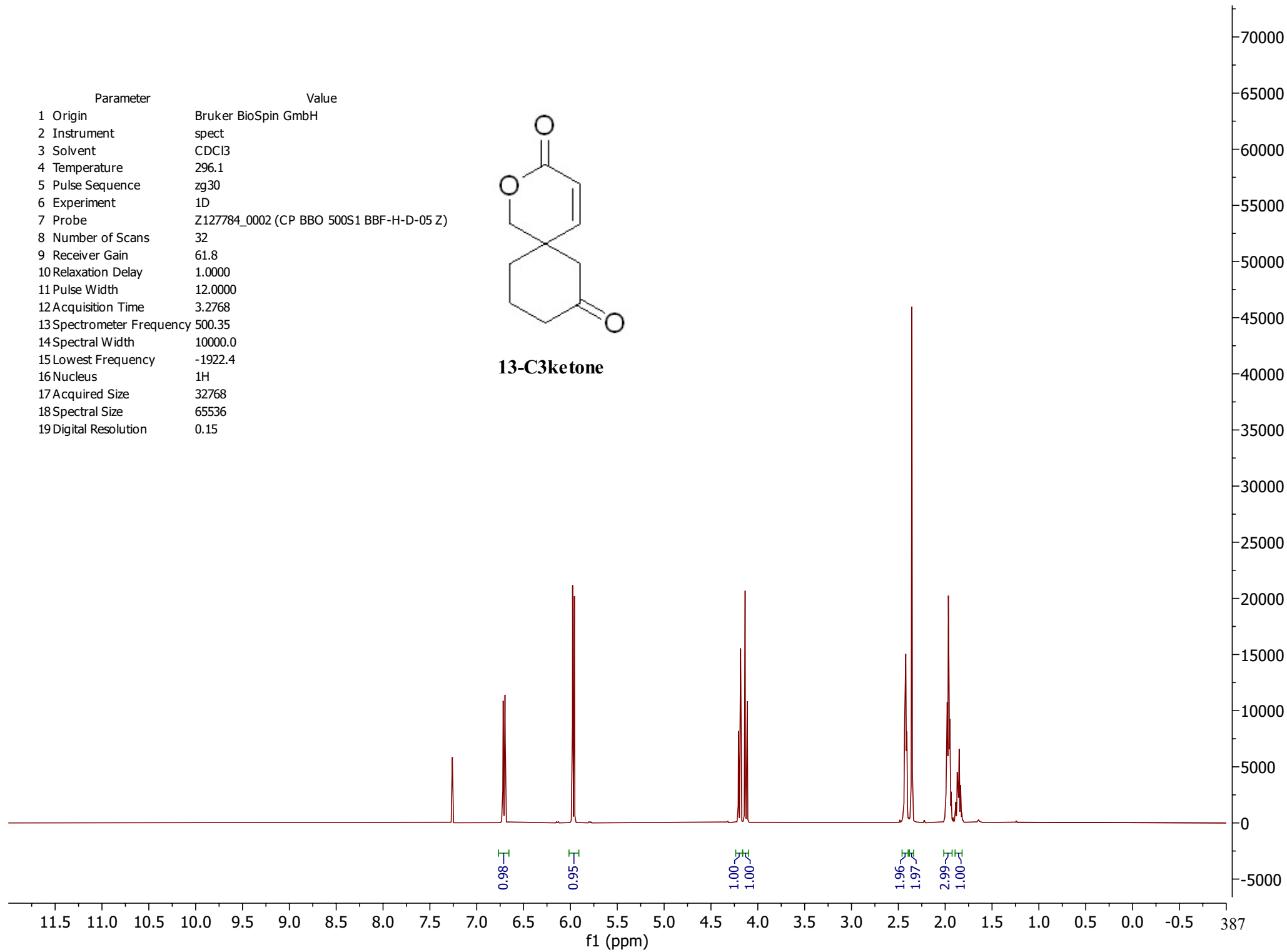
S15

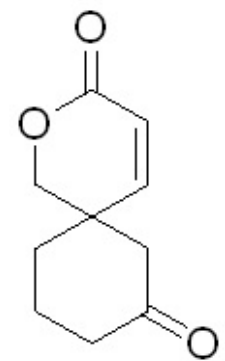


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	61.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.4
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



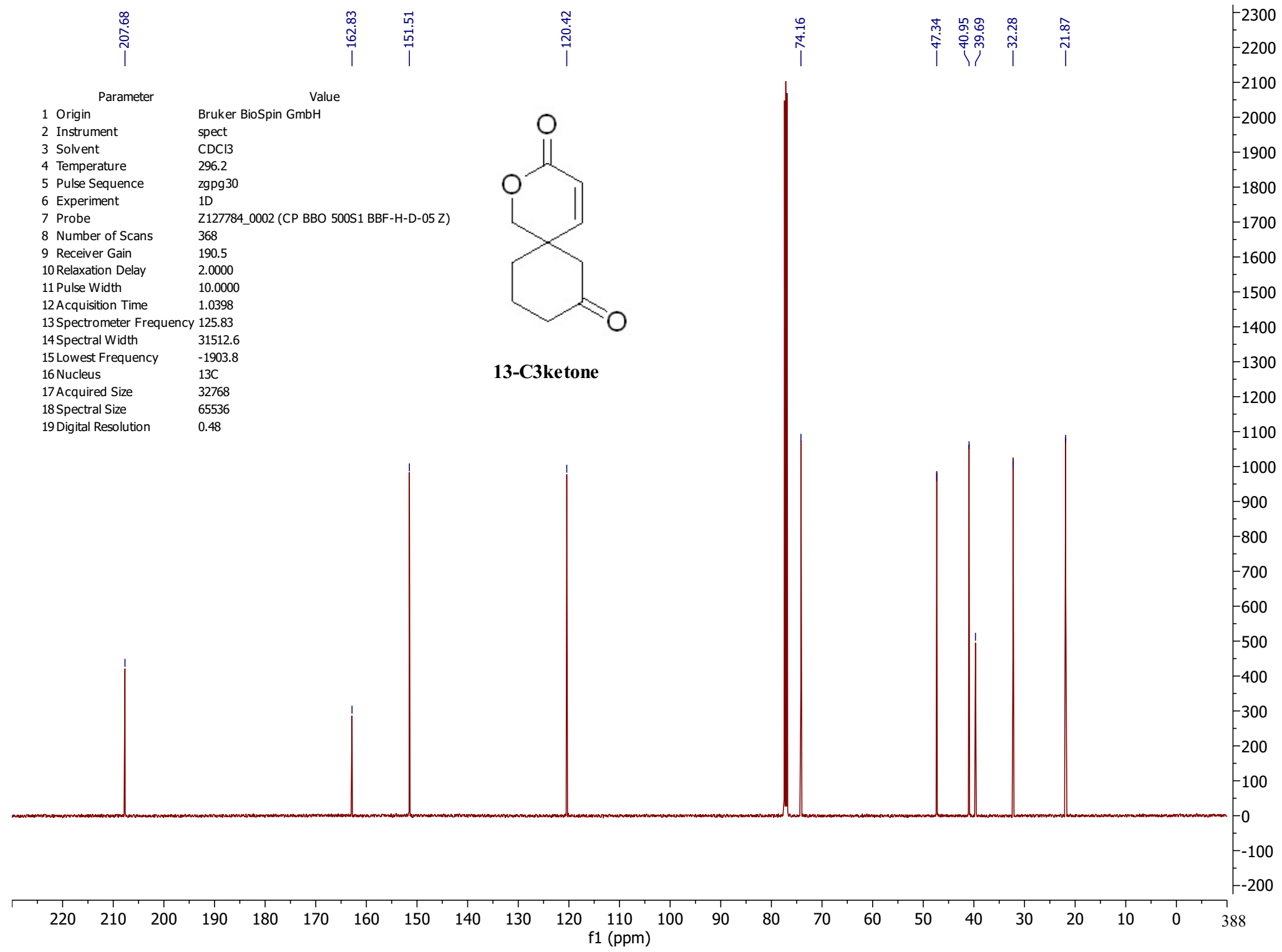
13-C3ketone



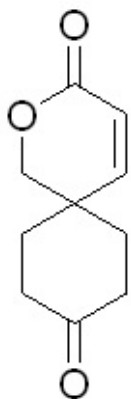


13-C3ketone

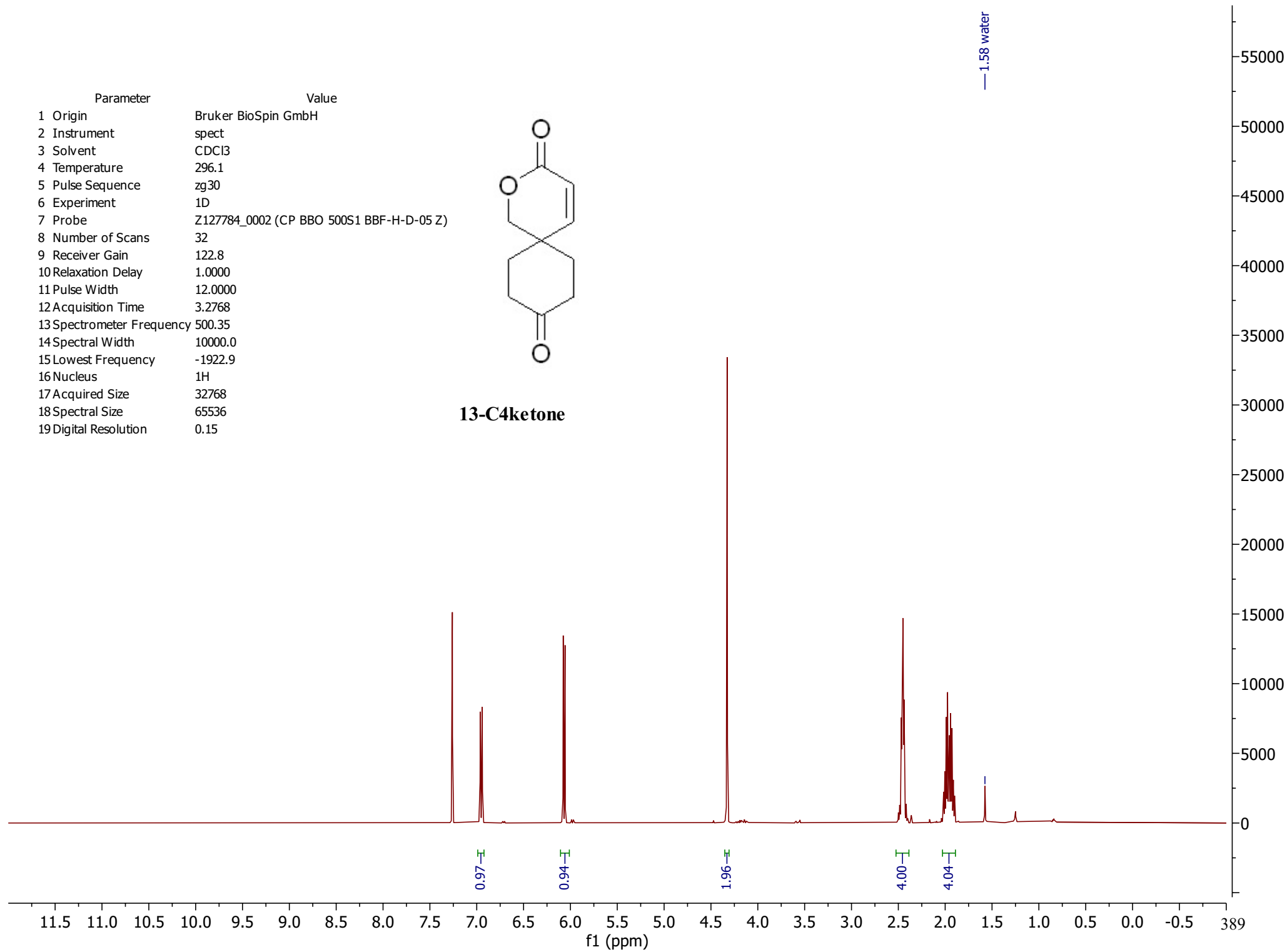
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCI3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1903.8
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



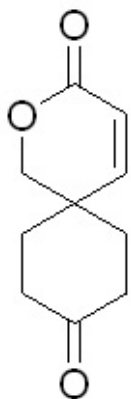
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	122.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



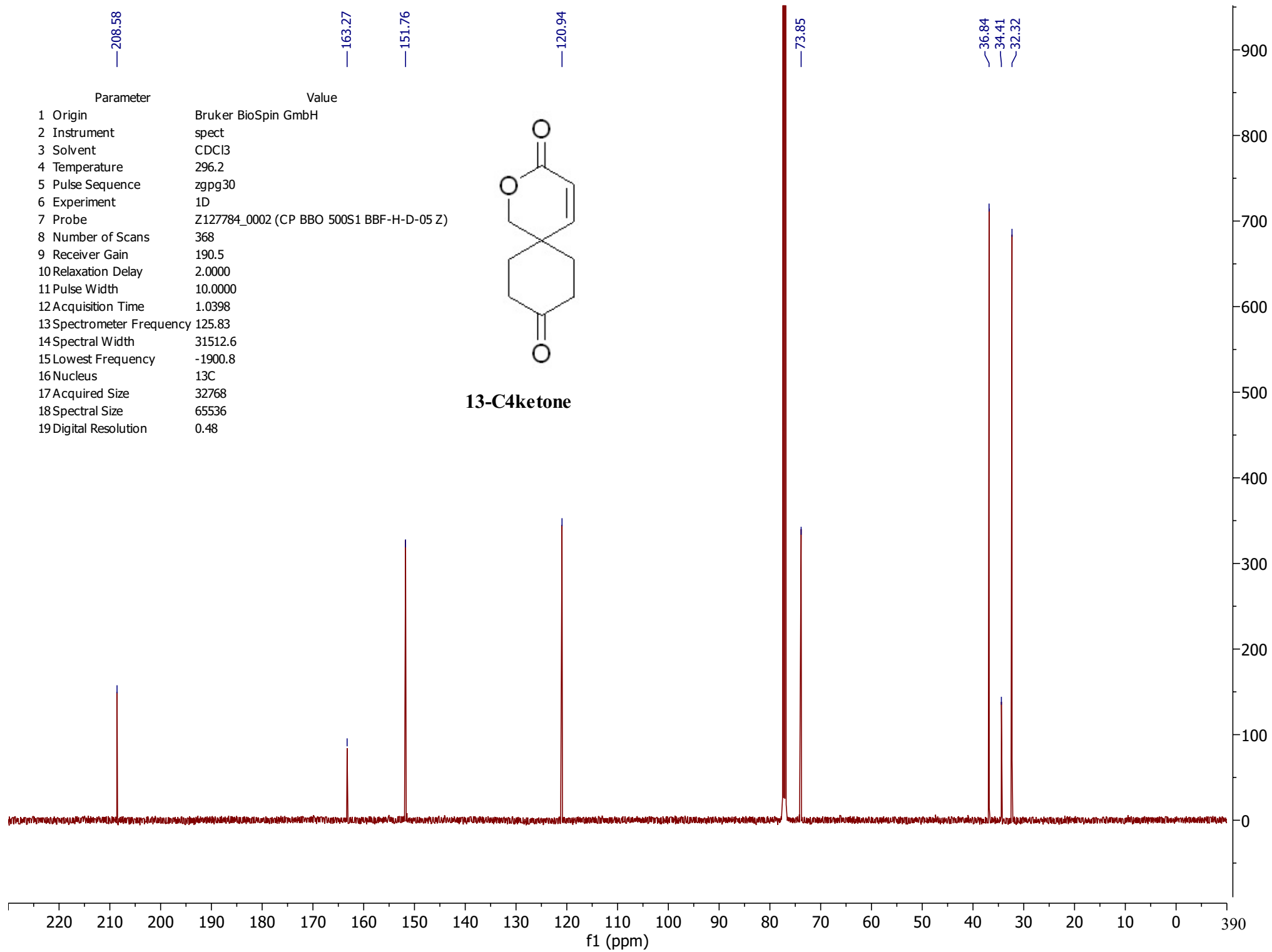
13-C4ketone



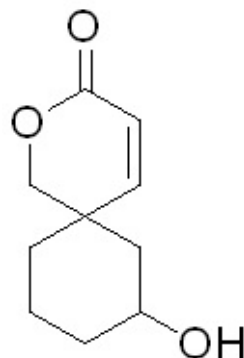
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



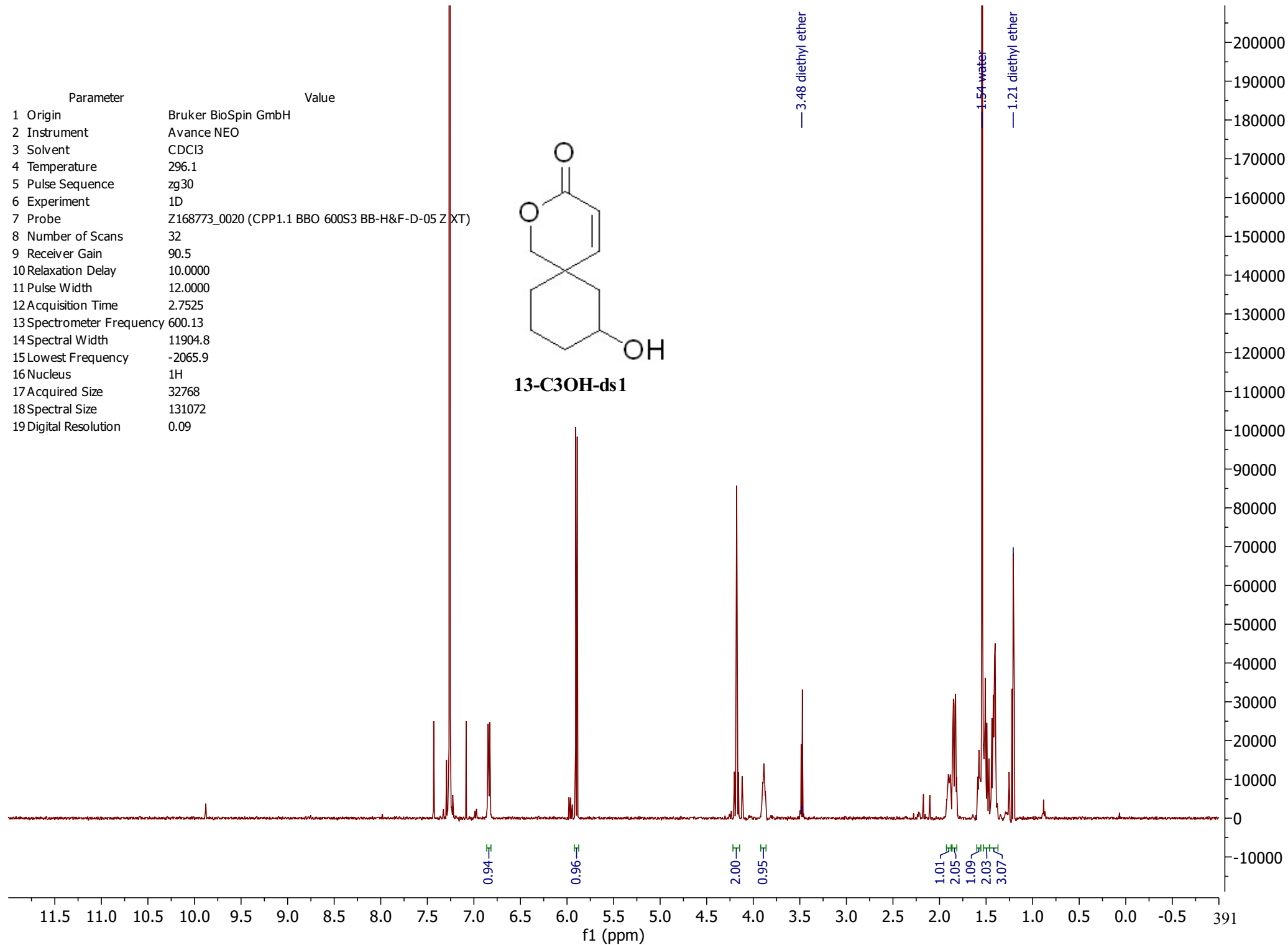
13-C4ketone



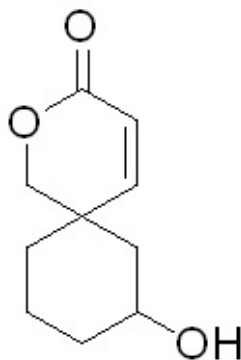
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	90.5
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2065.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



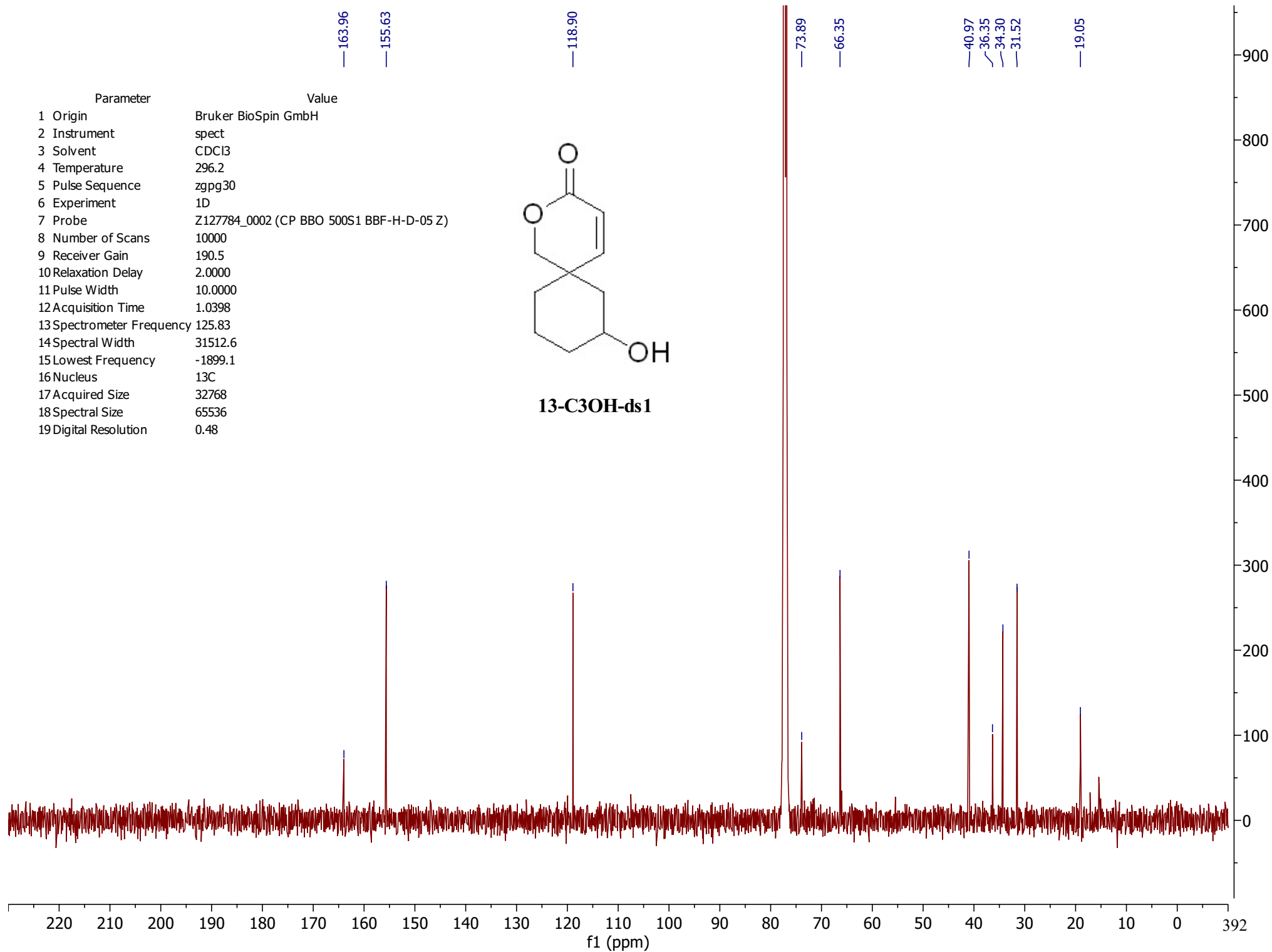
13-C3OH-ds1



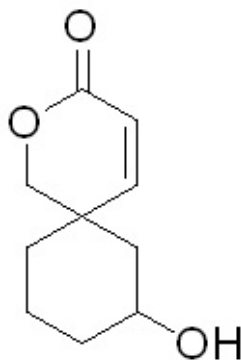
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	10000
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1899.1
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



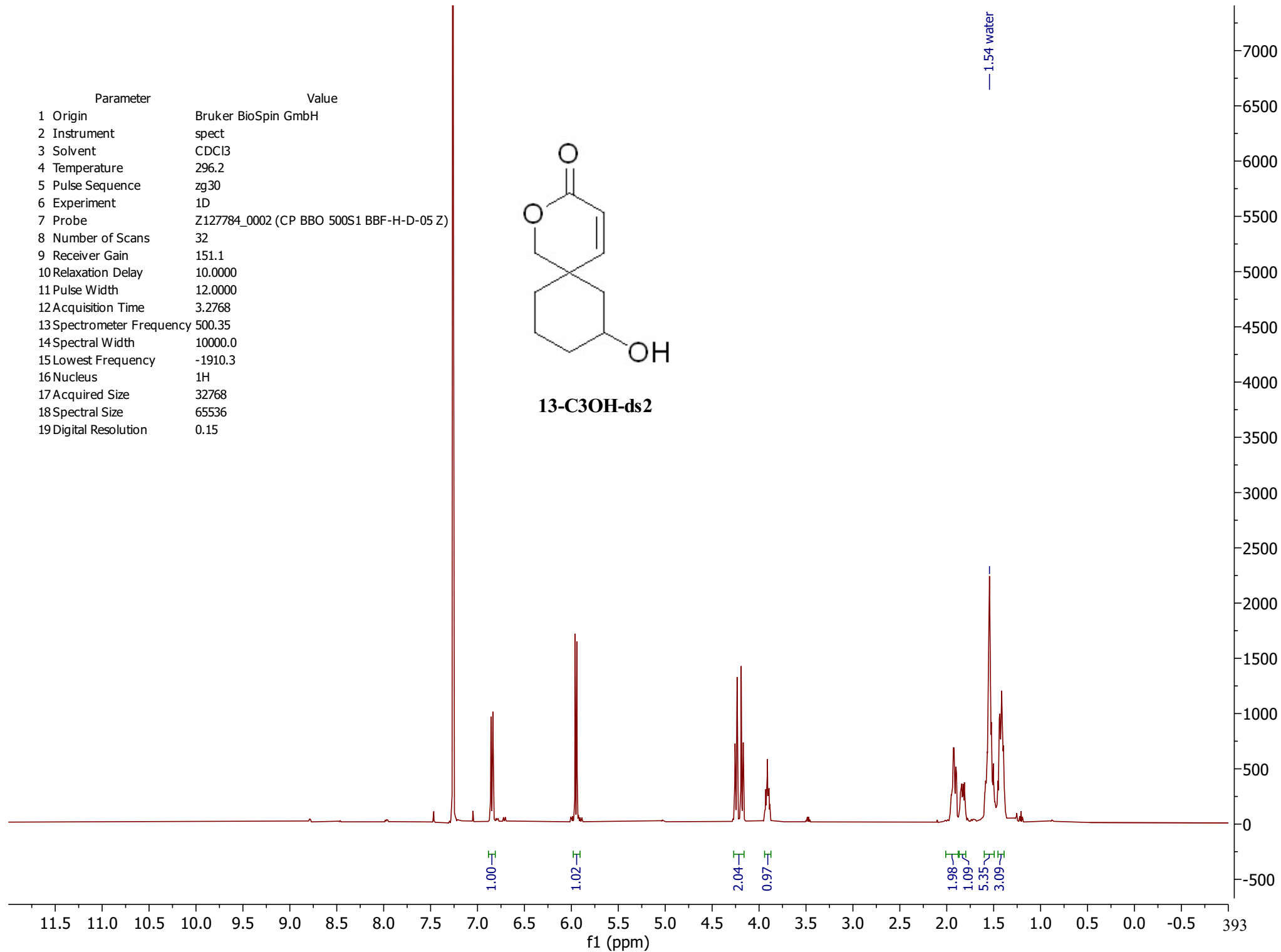
13-C3OH-ds1



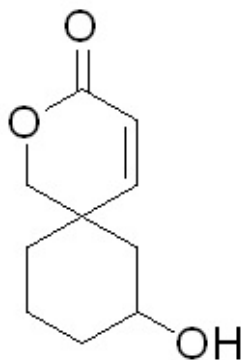
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	151.1
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1910.3
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



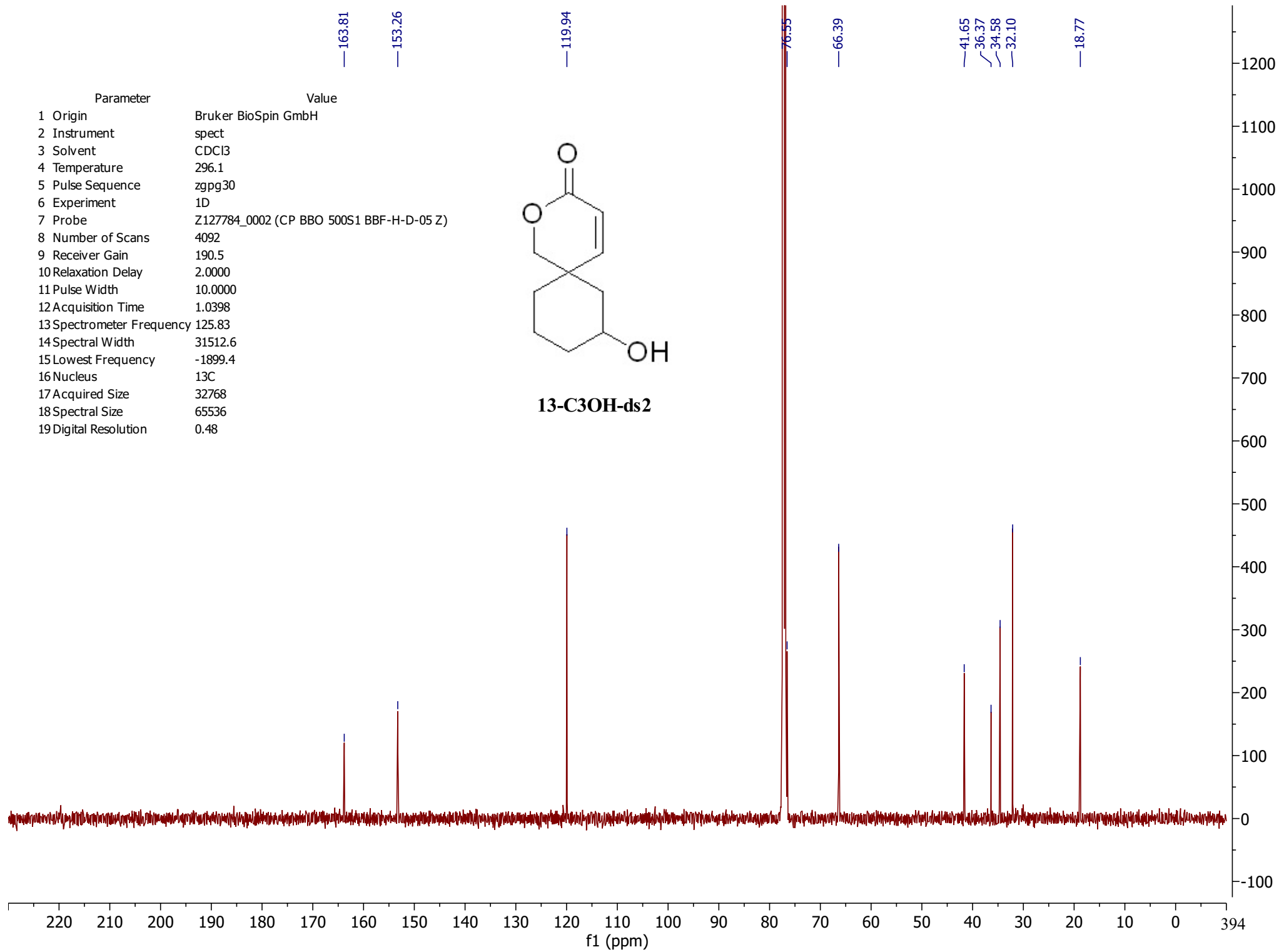
13-C3OH-ds2



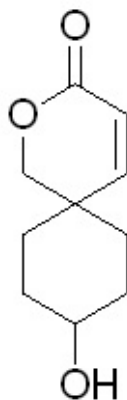
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	4092
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1899.4
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



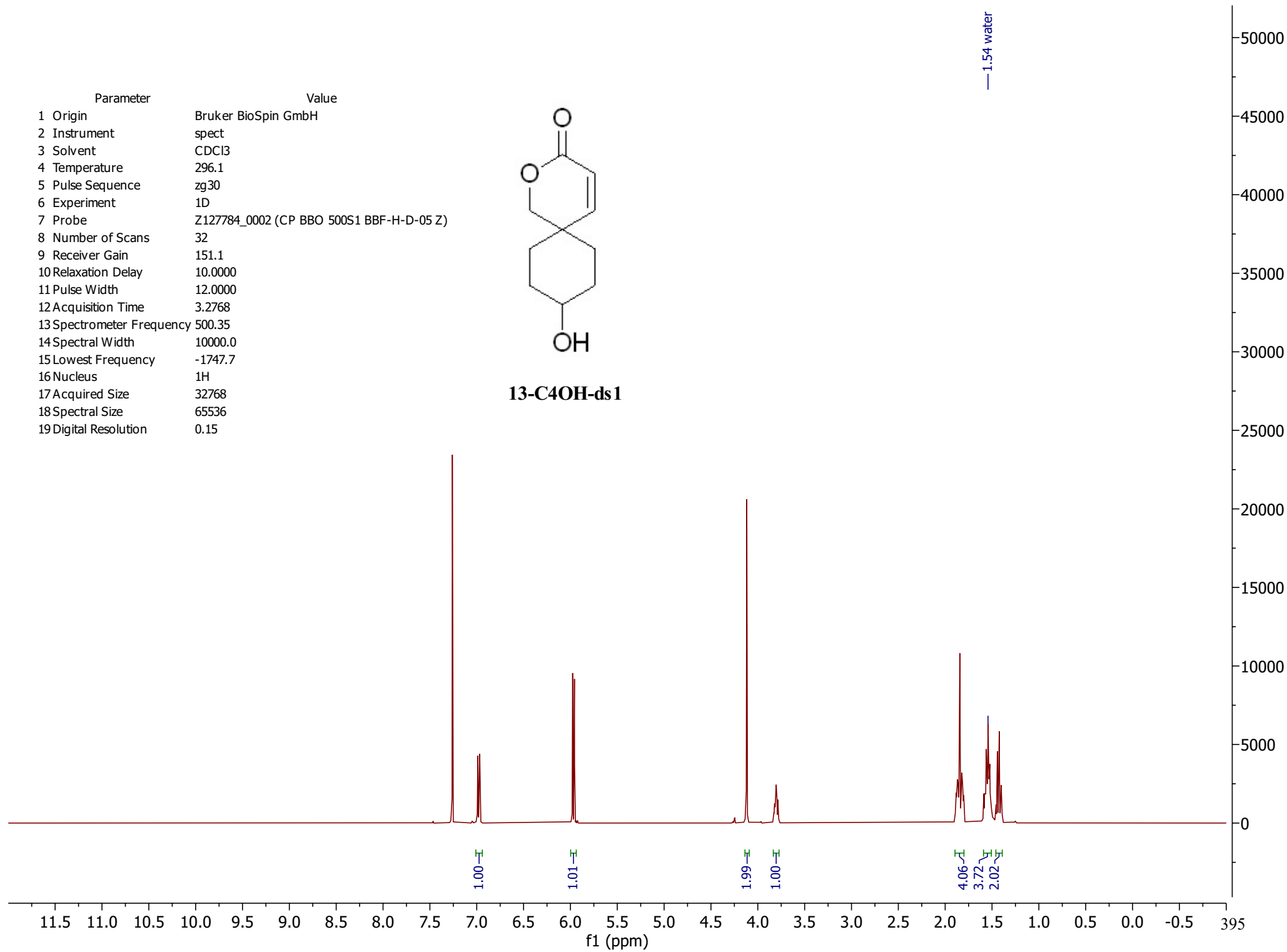
¹³C-3OH-ds2



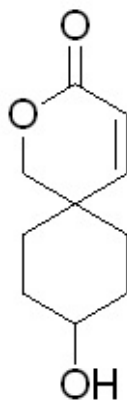
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	151.1
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



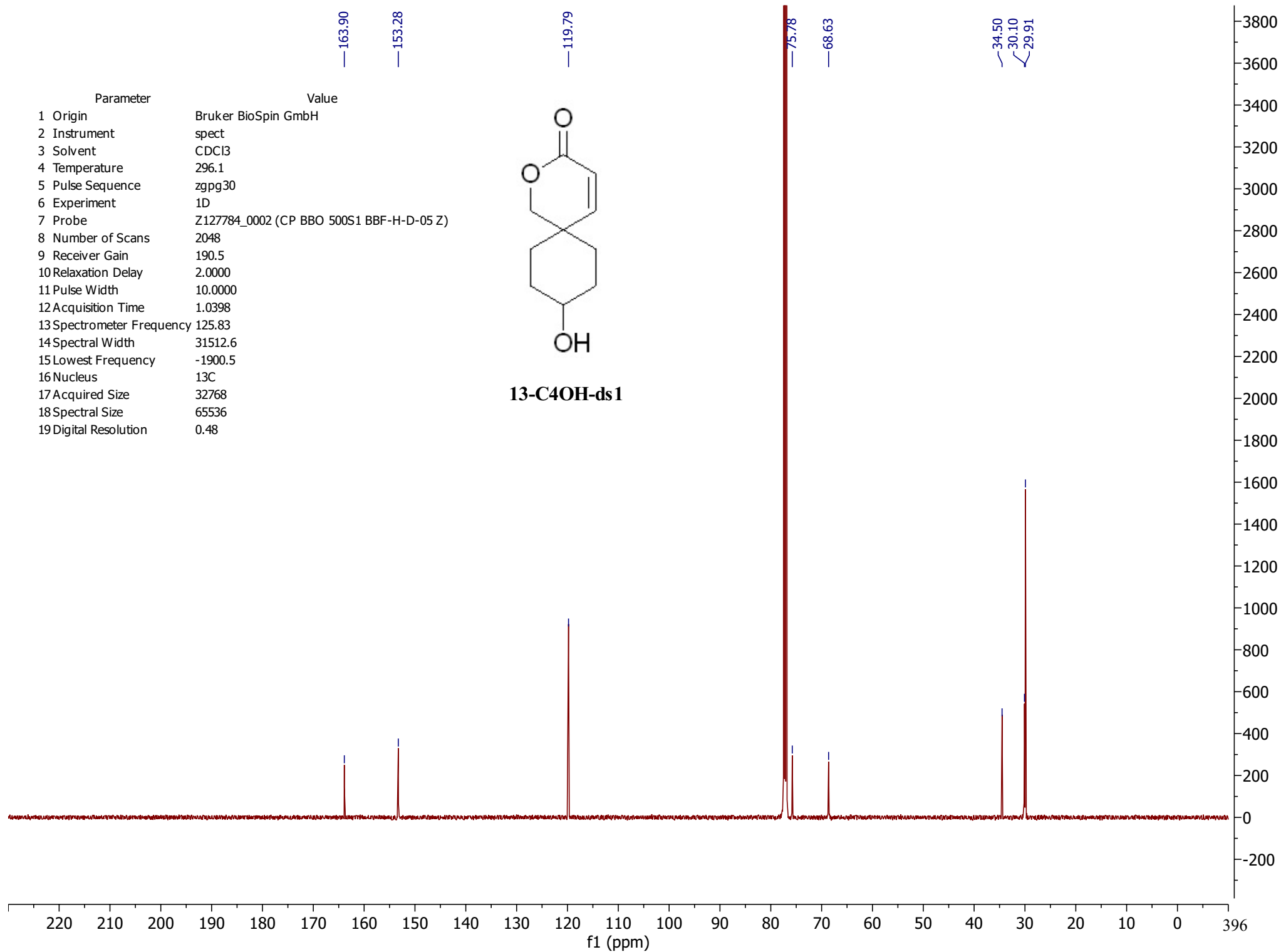
13-C4OH-ds1



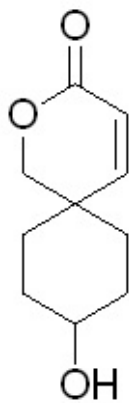
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.5
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



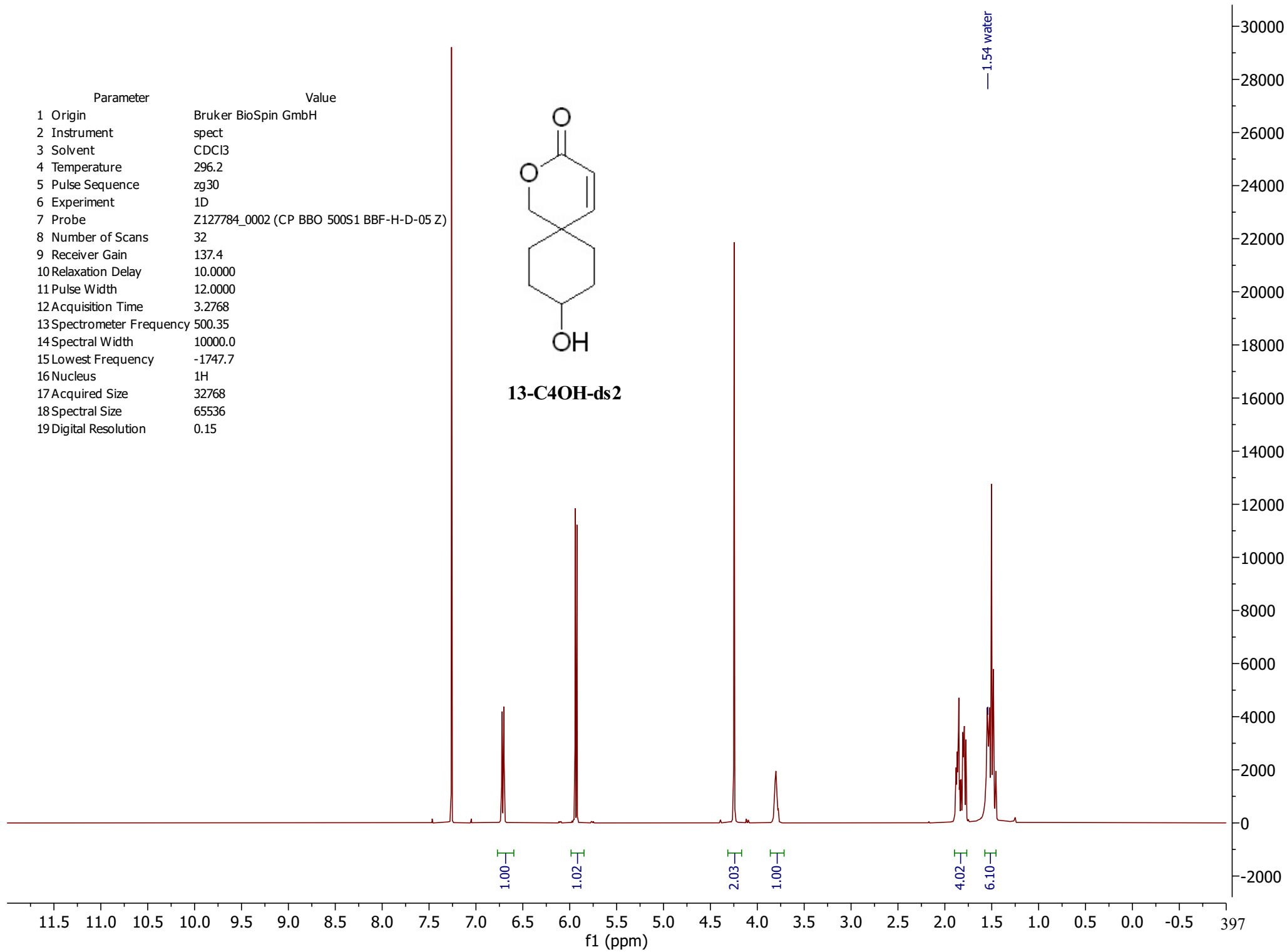
13-C4OH-ds1



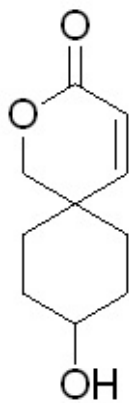
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	137.4
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



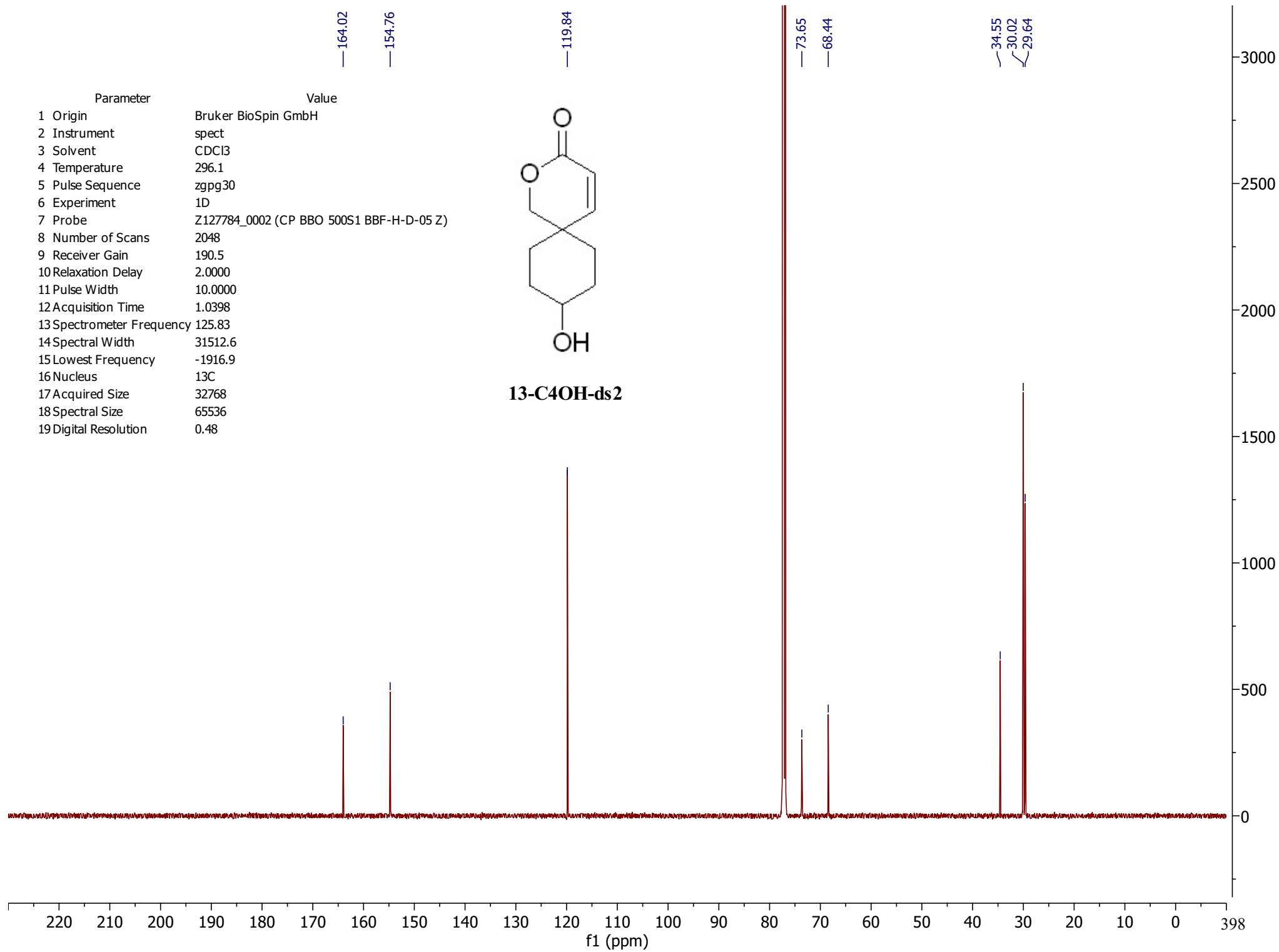
13-C4OH-ds2



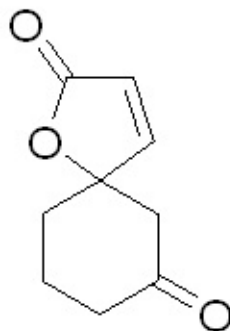
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



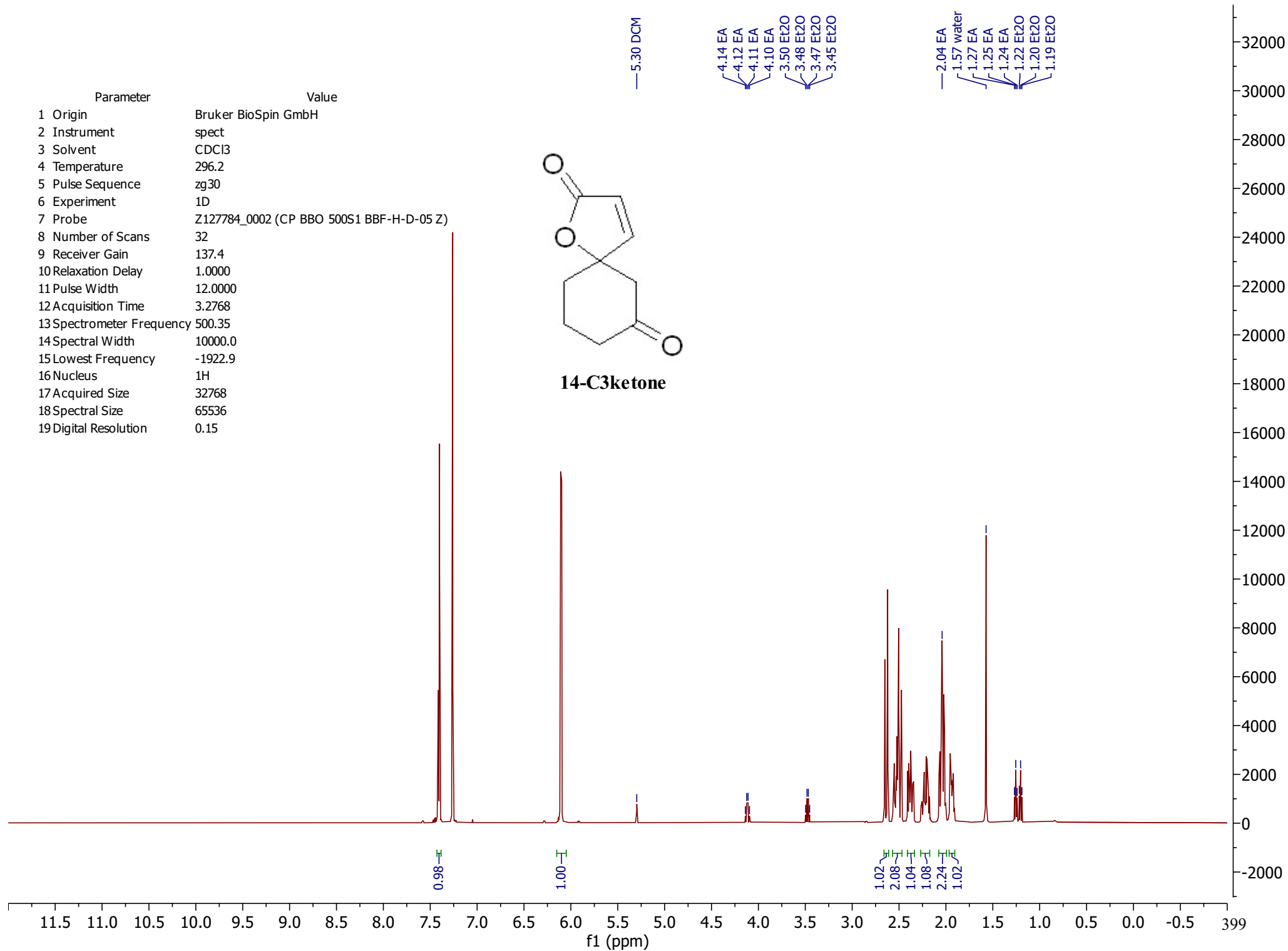
13-C4OH-ds2



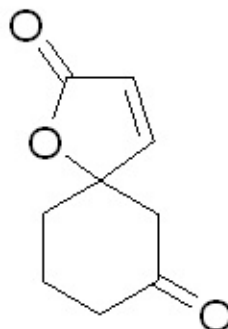
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	137.4
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



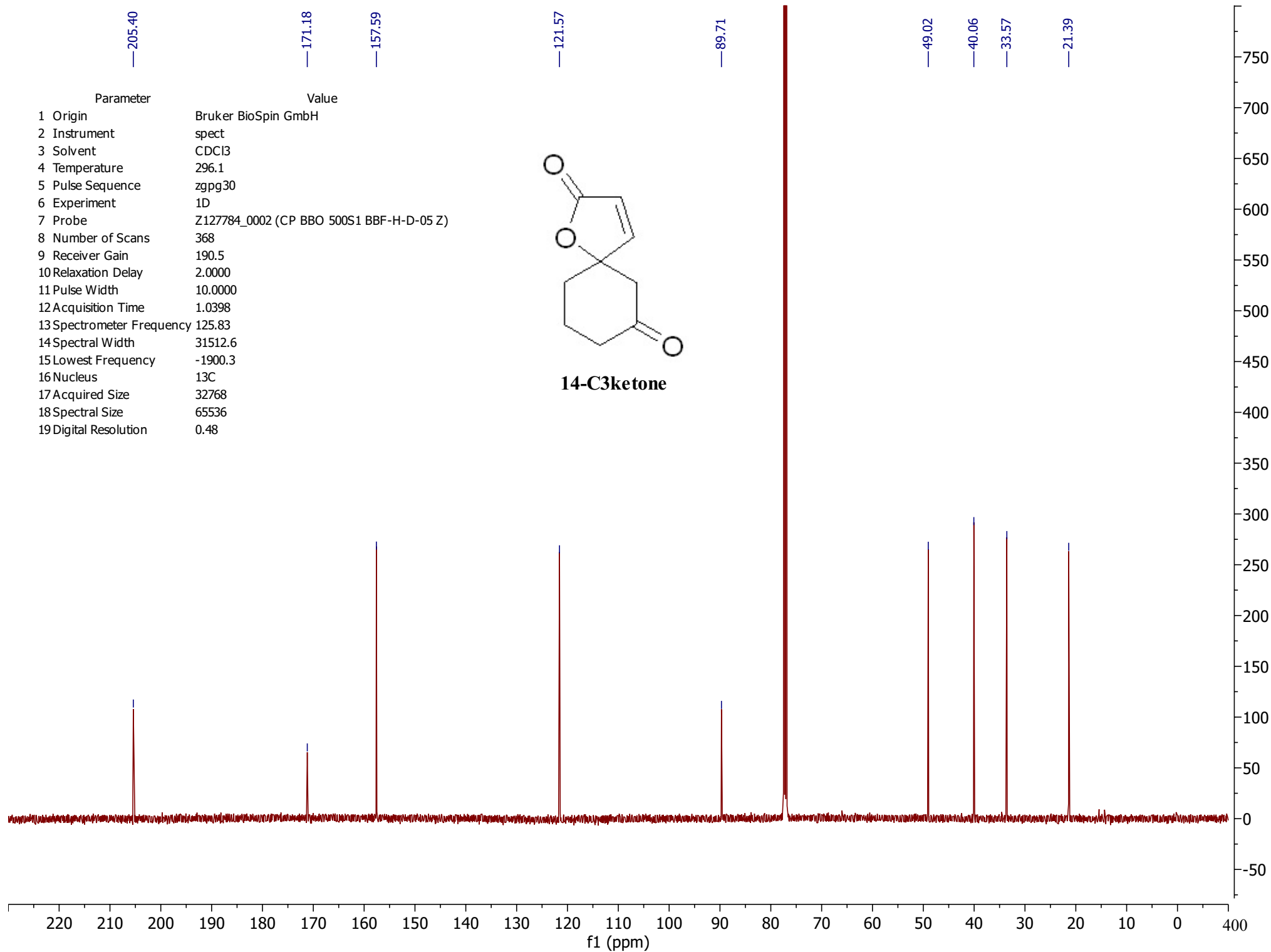
14-C3ketone



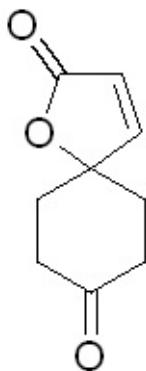
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.3
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



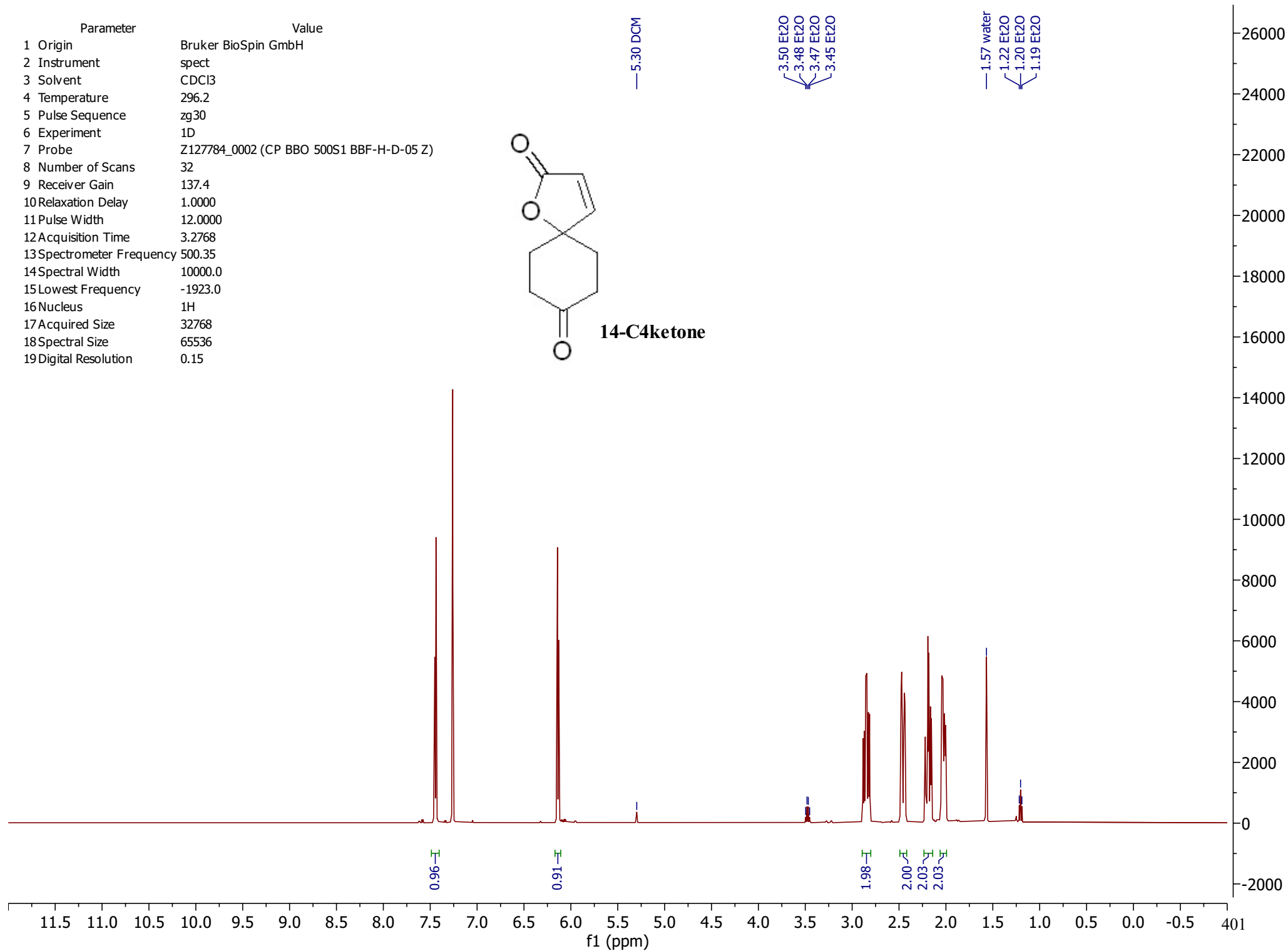
14-C3ketone



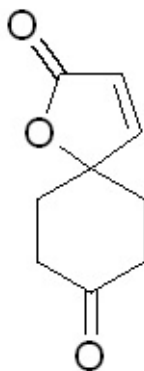
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	137.4
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



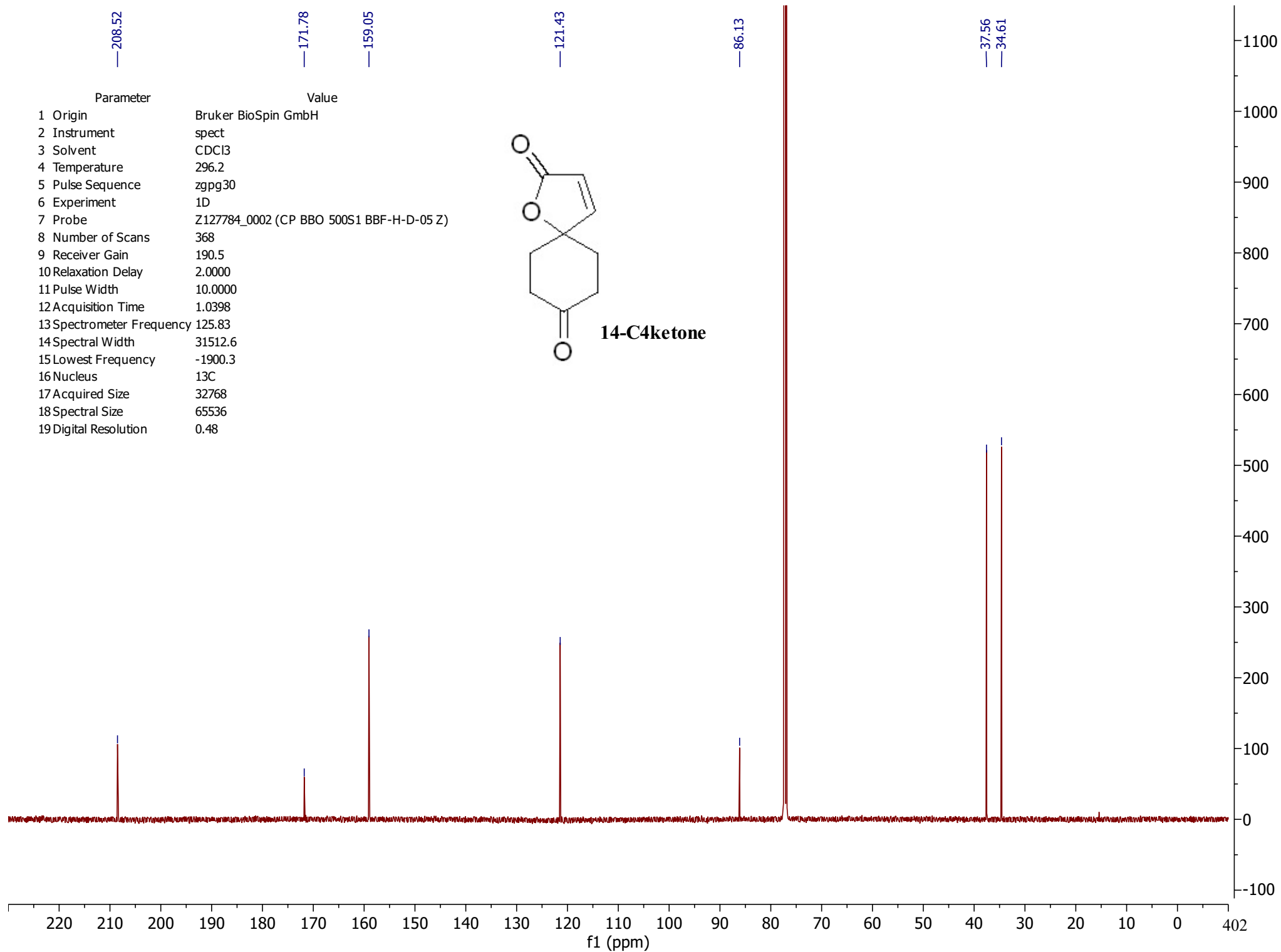
14-C4ketone



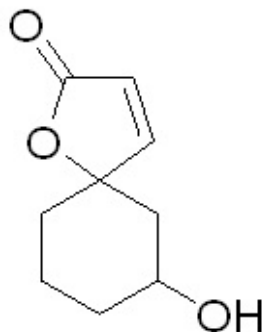
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.3
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



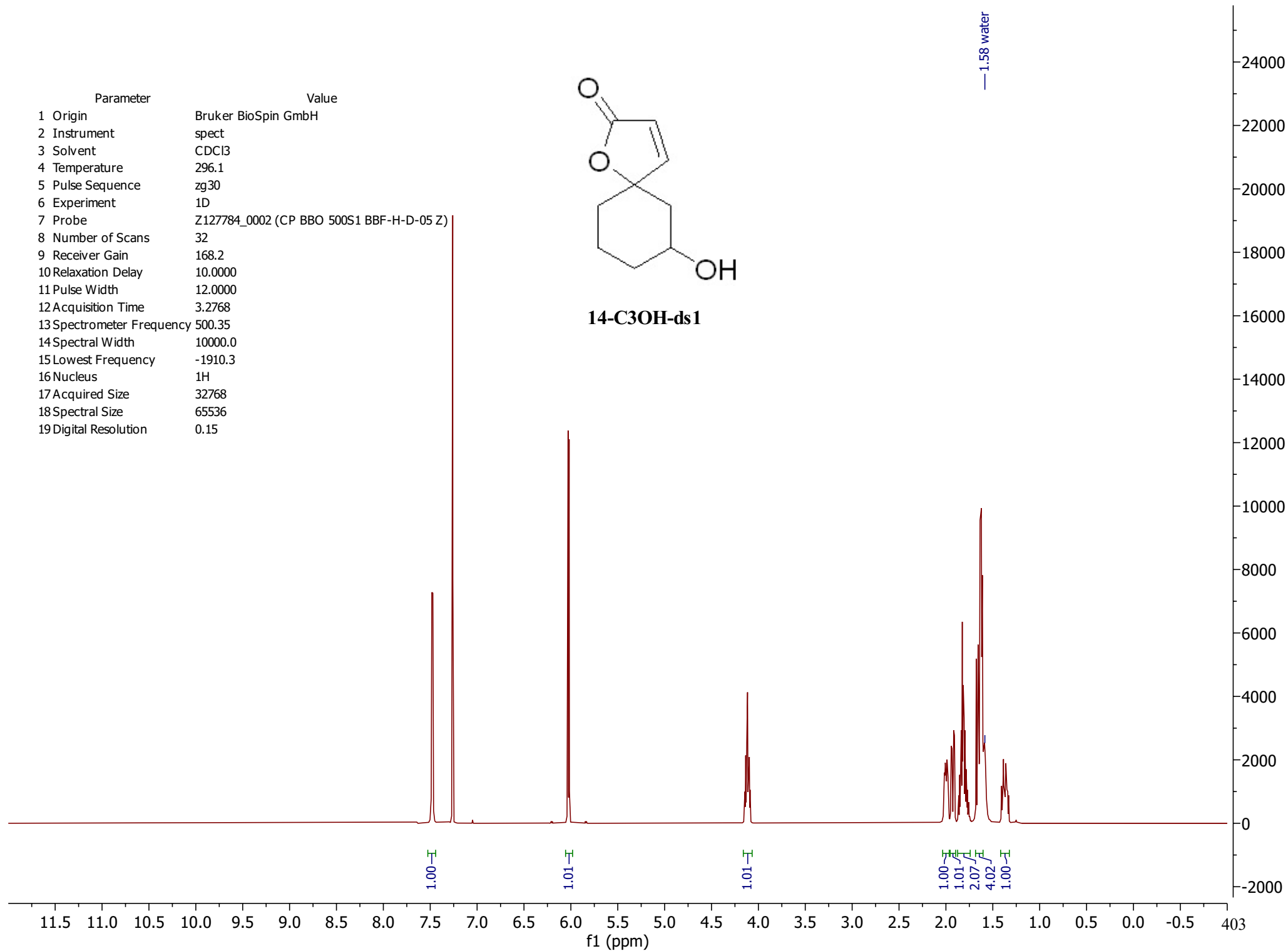
14-C4ketone



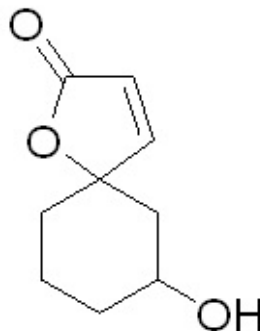
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	168.2
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1910.3
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



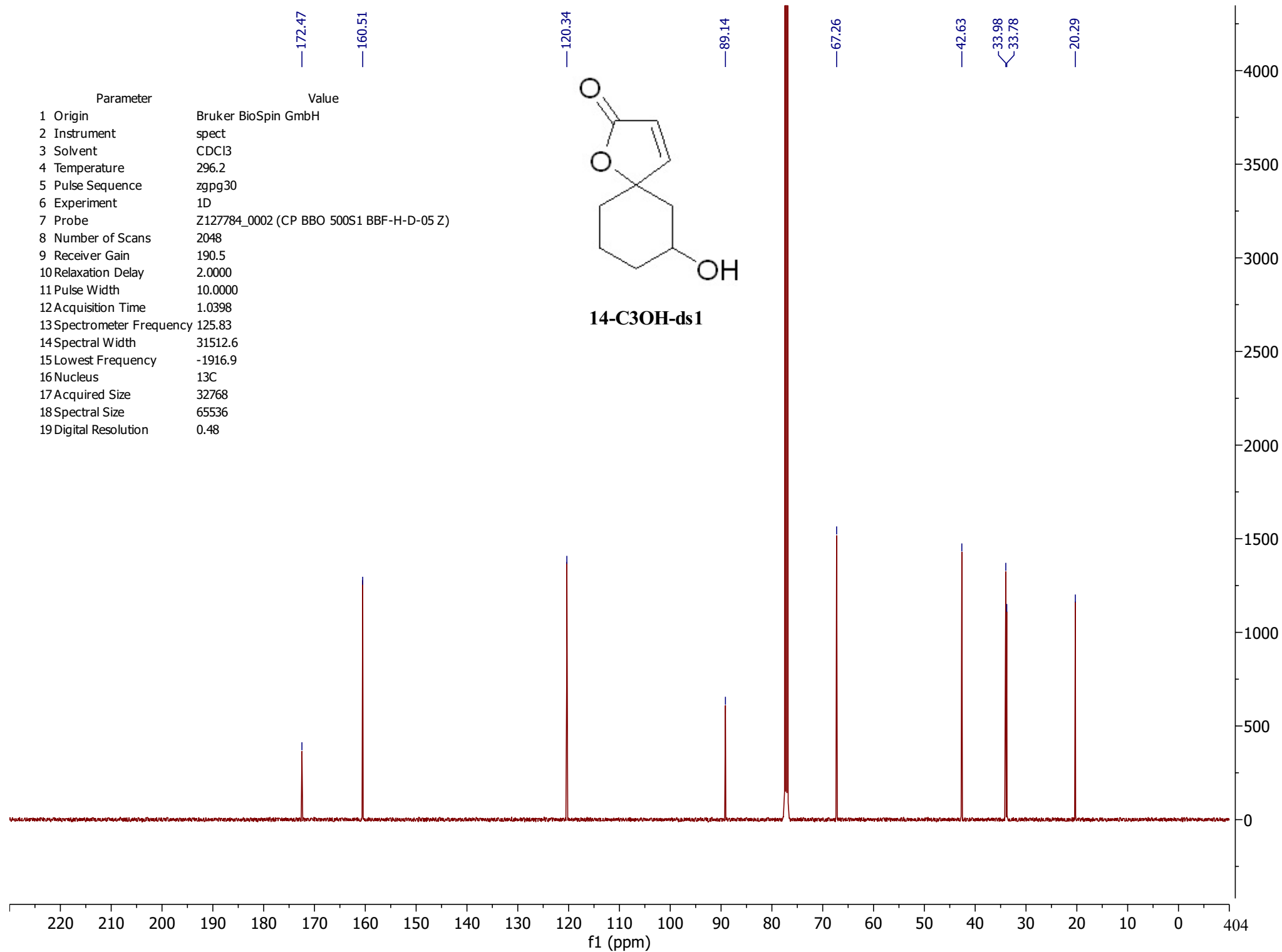
14-C3OH-ds1



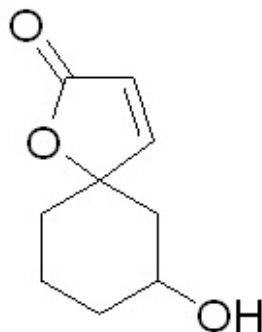
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



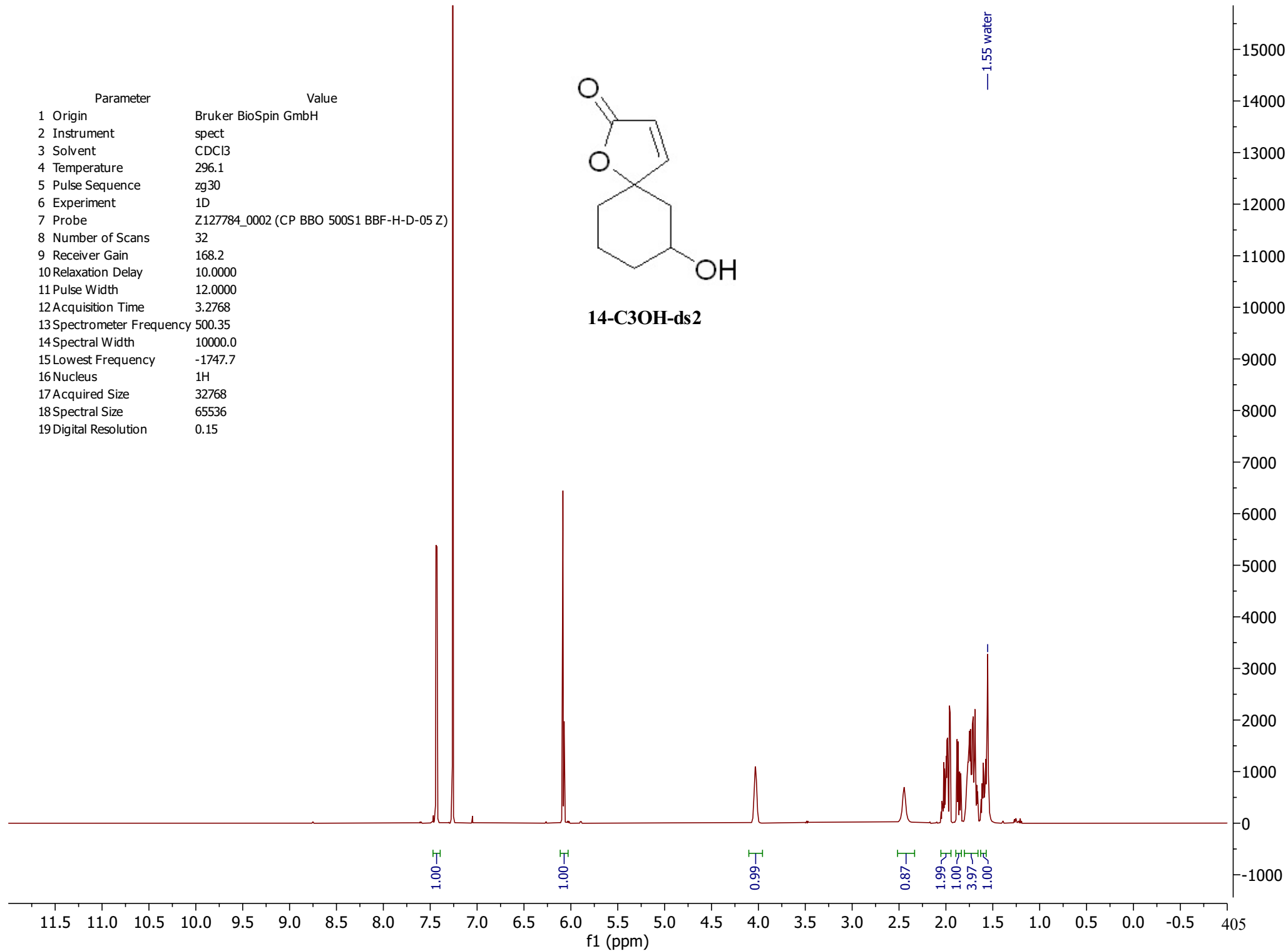
14-C3OH-ds1



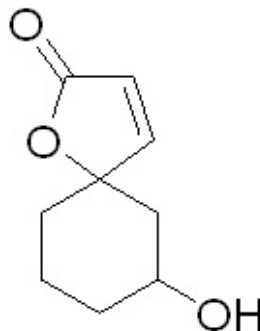
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	168.2
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



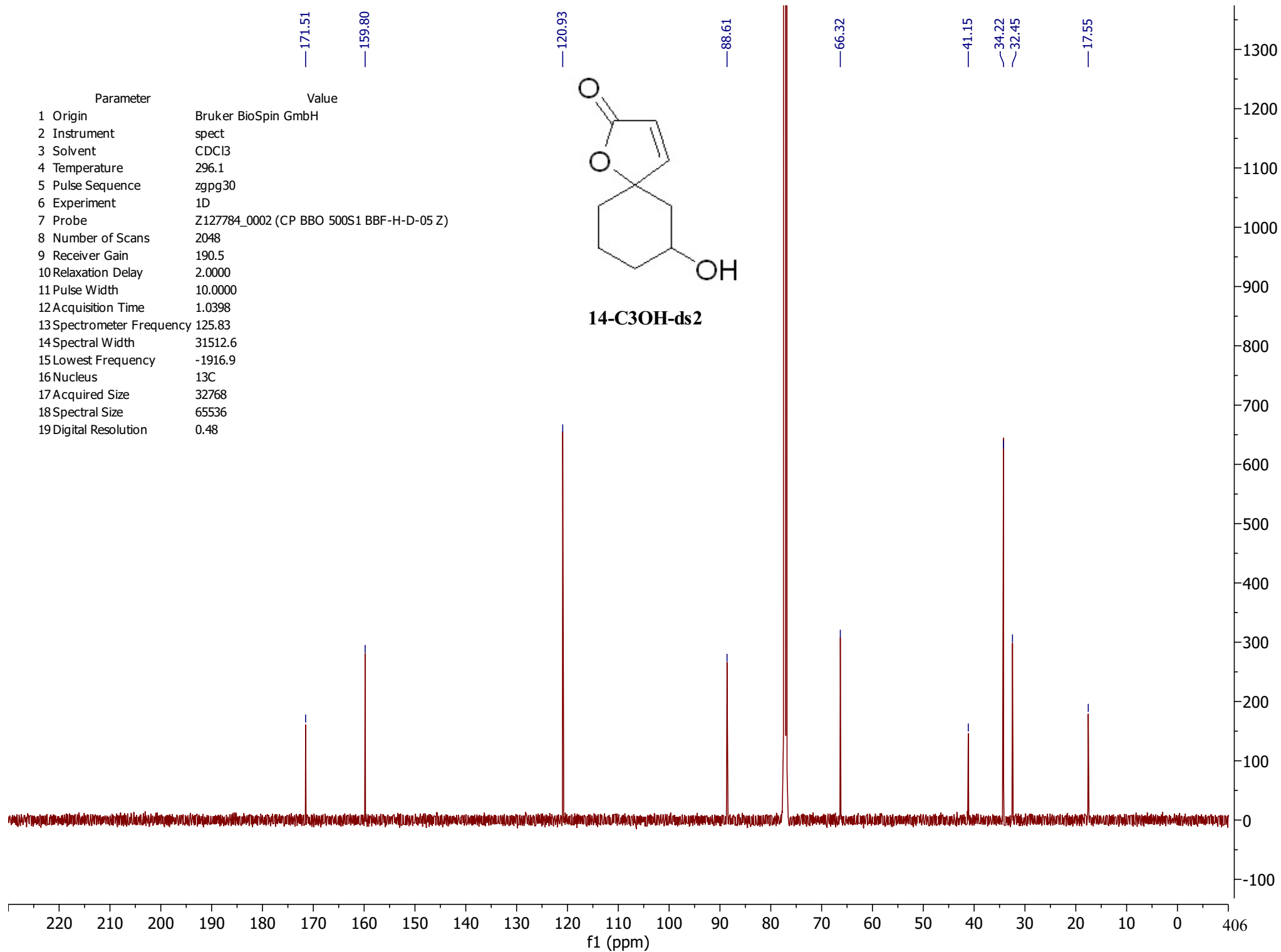
14-C3OH-ds2



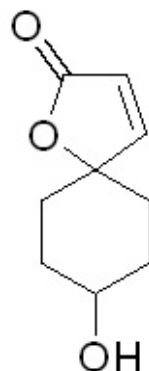
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



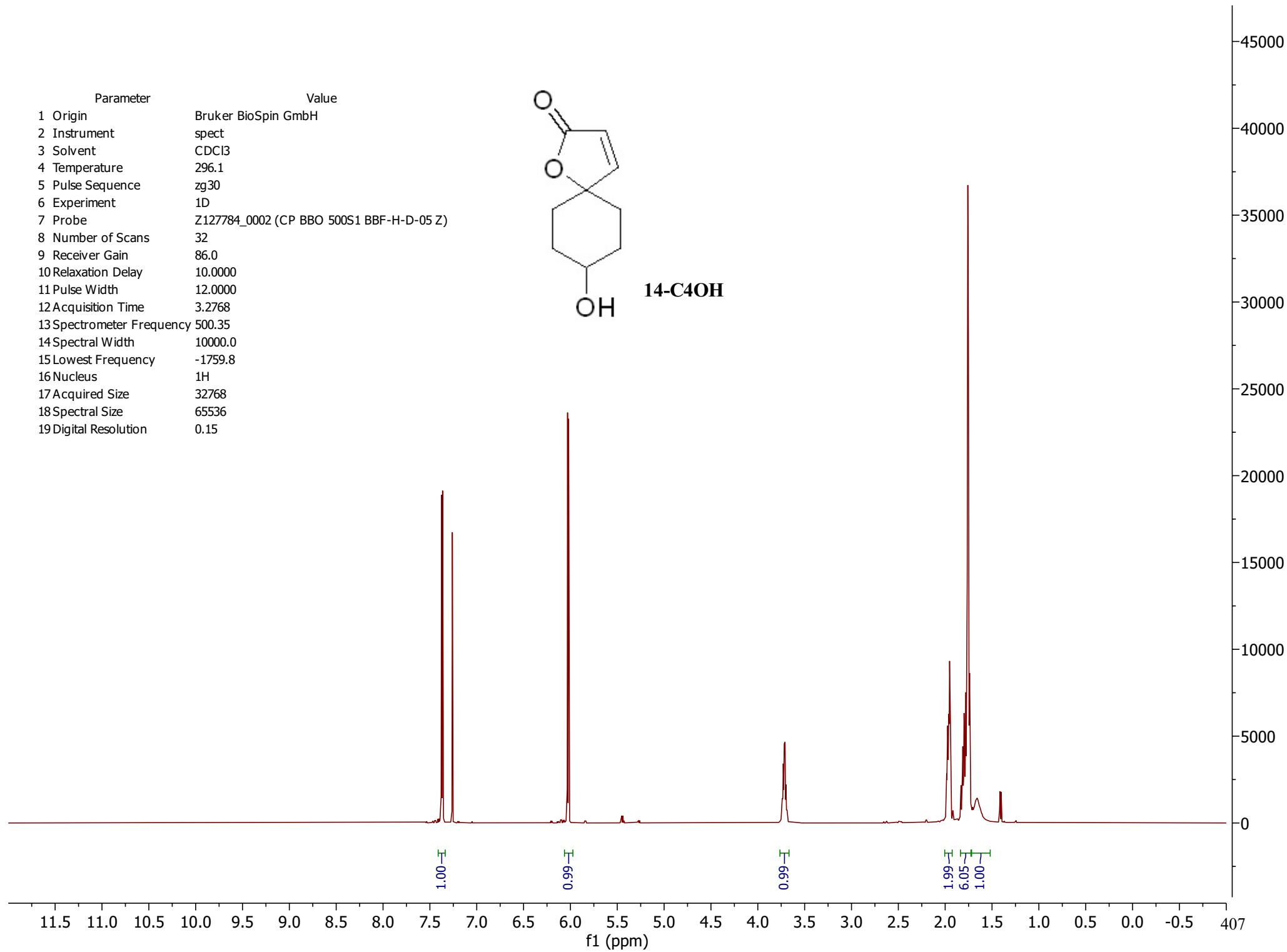
14-C3OH-ds2



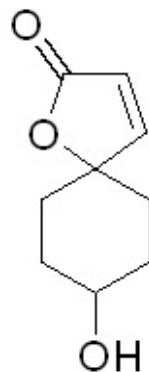
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1759.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



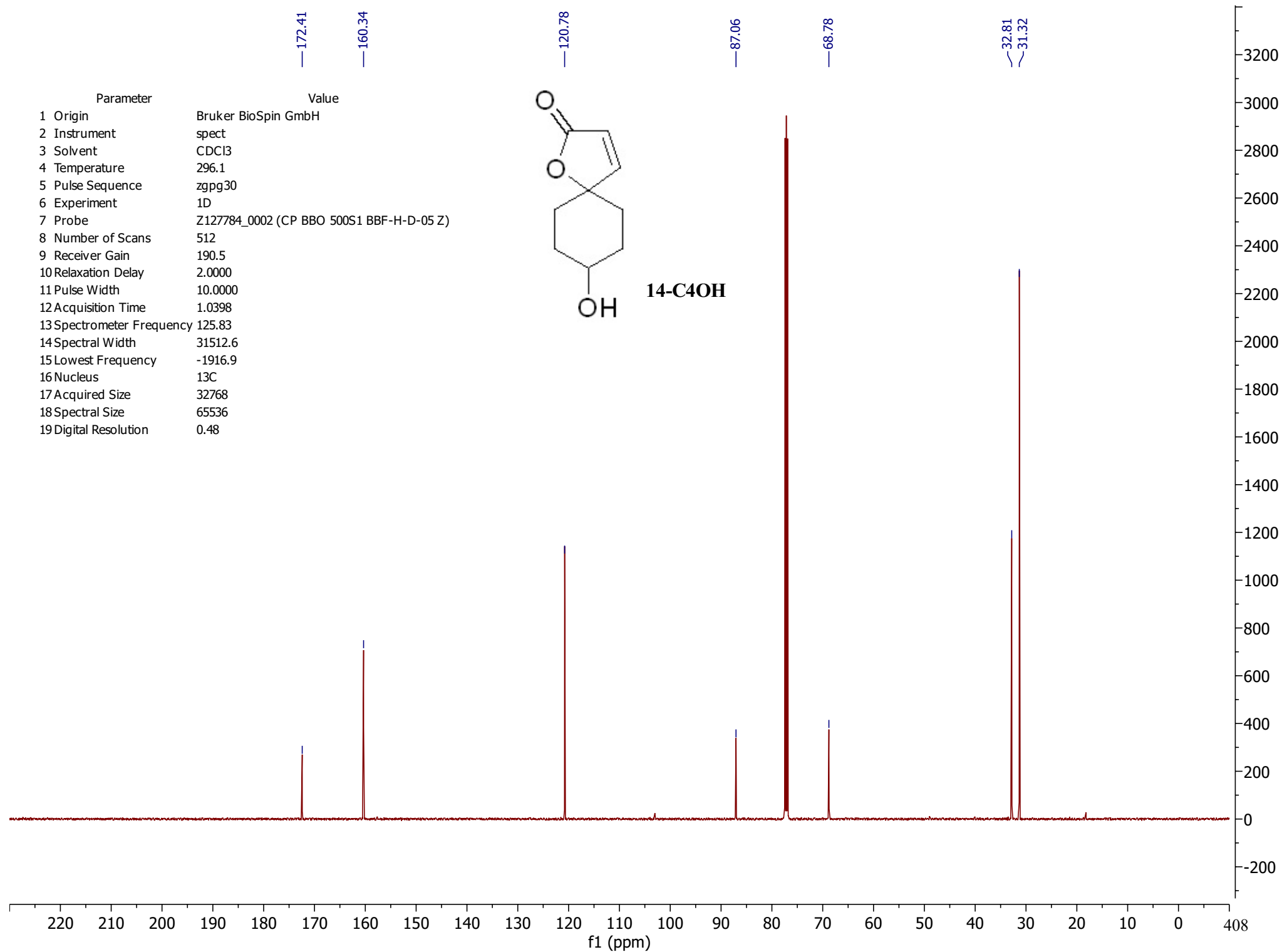
14-C4OH



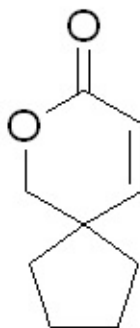
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	512
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



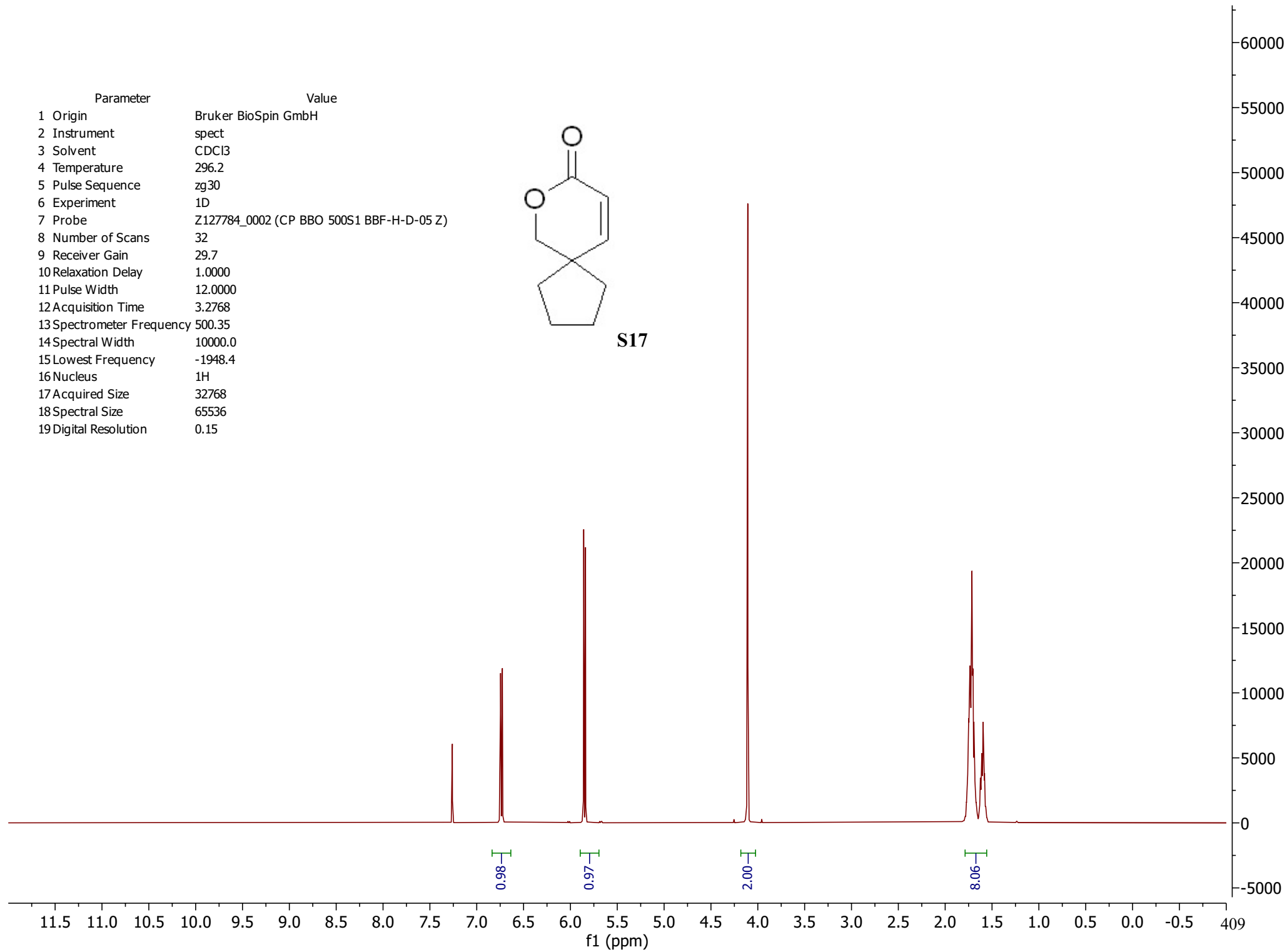
14-C4OH



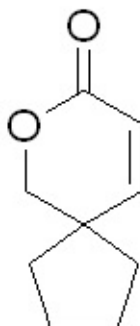
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1948.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



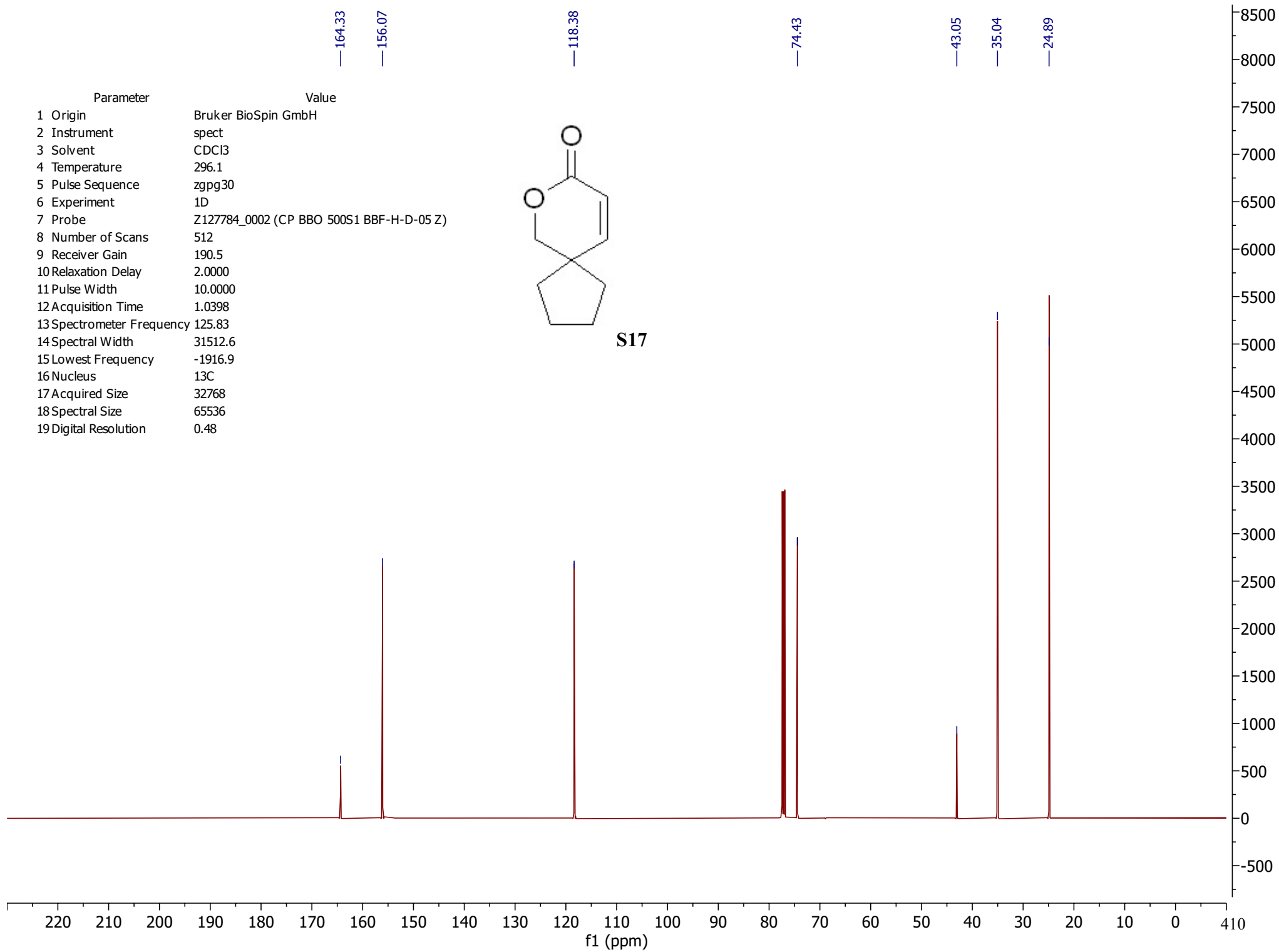
S17



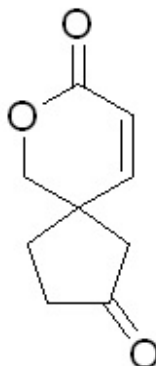
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	512
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



S17

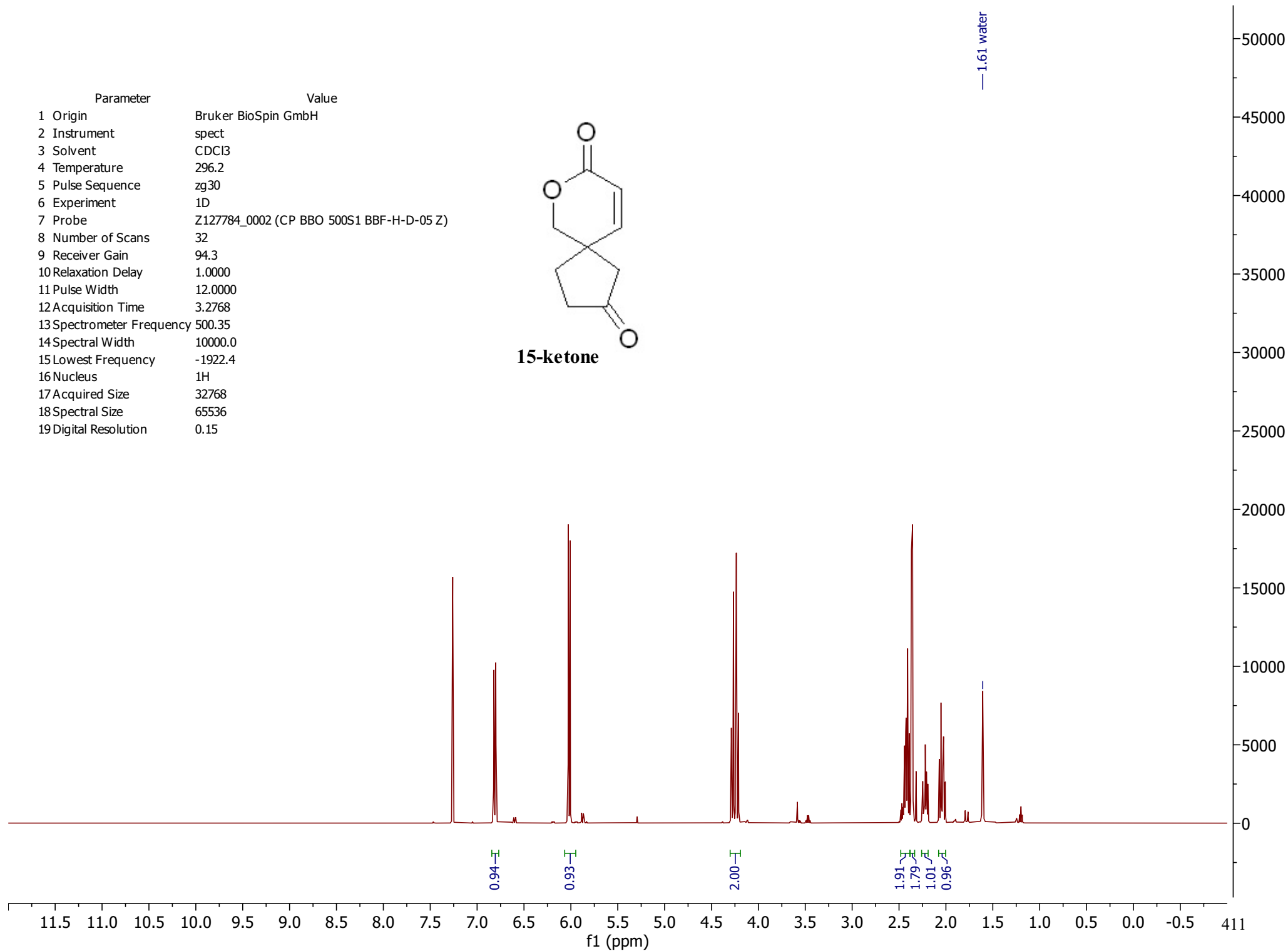


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	94.3
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.4
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

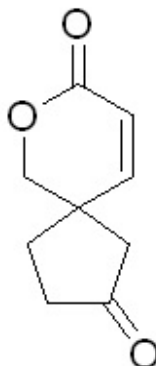


15-ketone

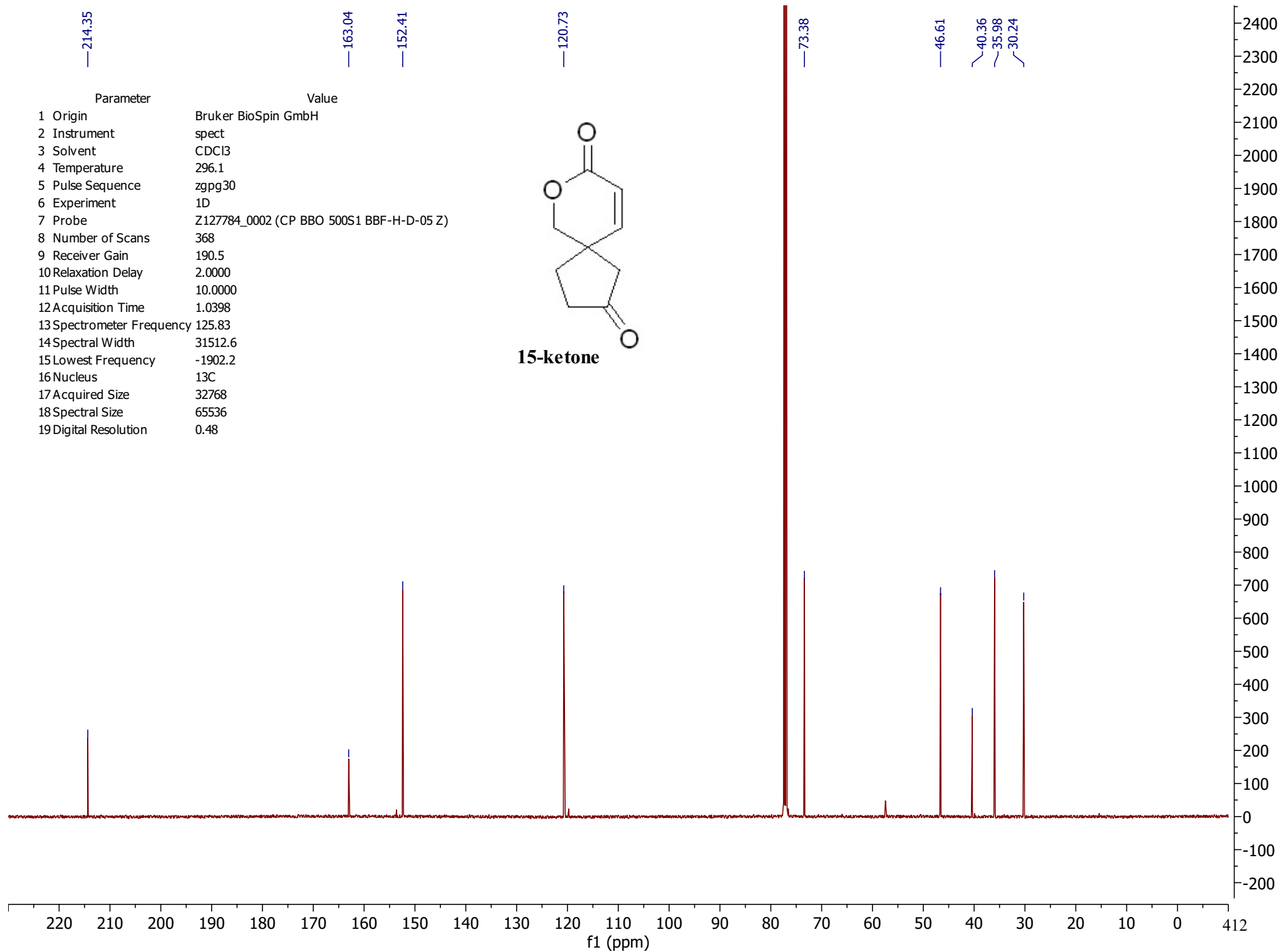
— 1.61 water



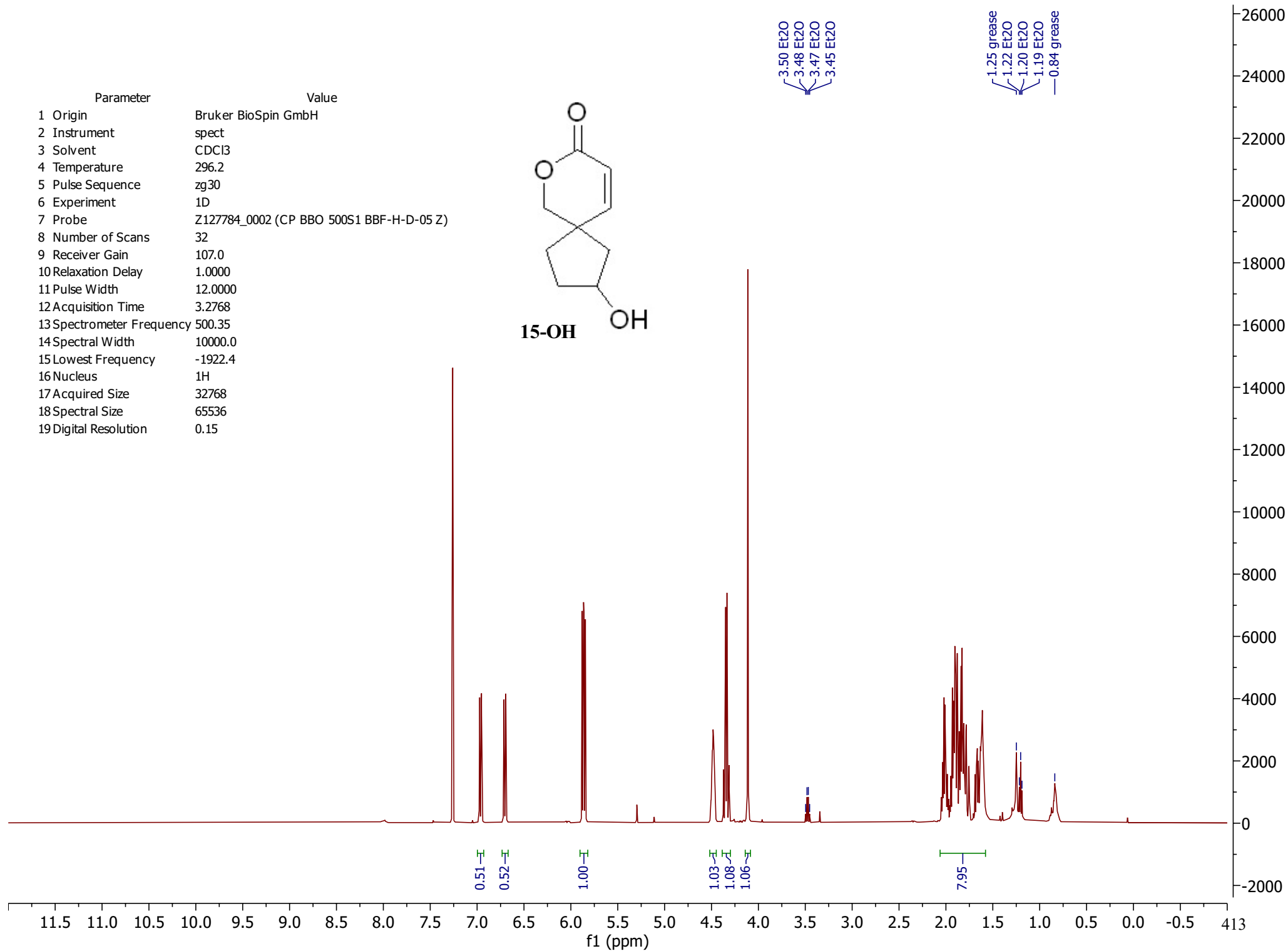
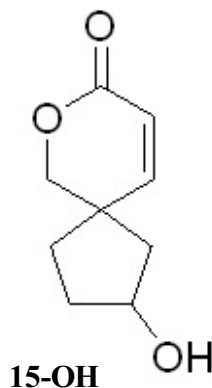
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1902.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



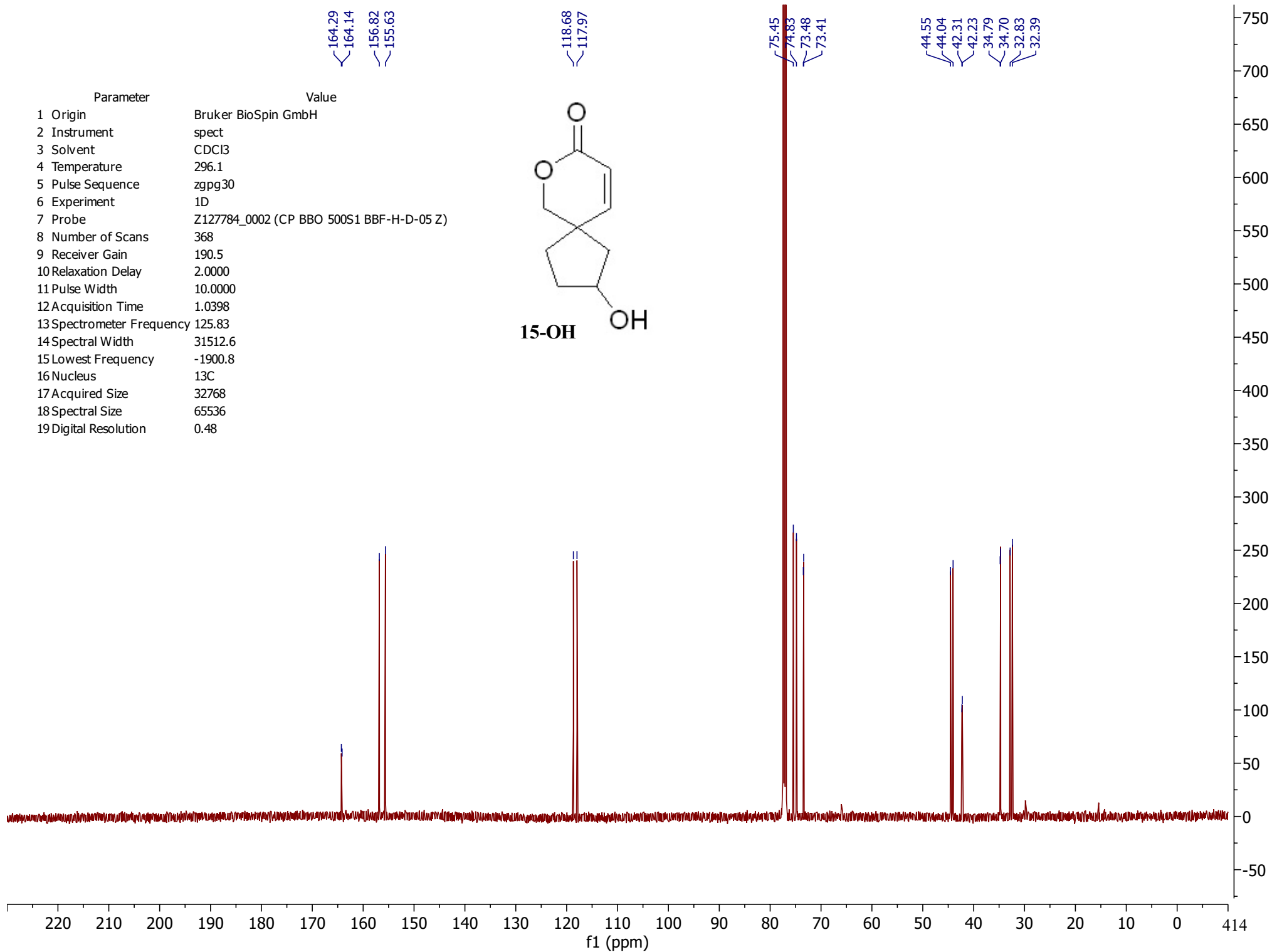
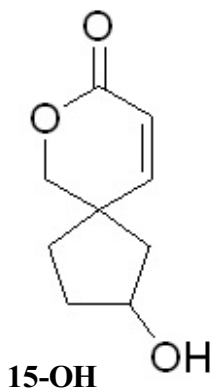
15-ketone



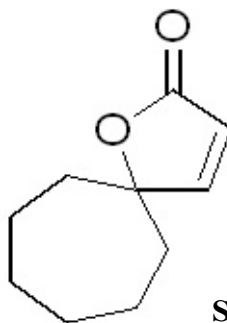
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	107.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

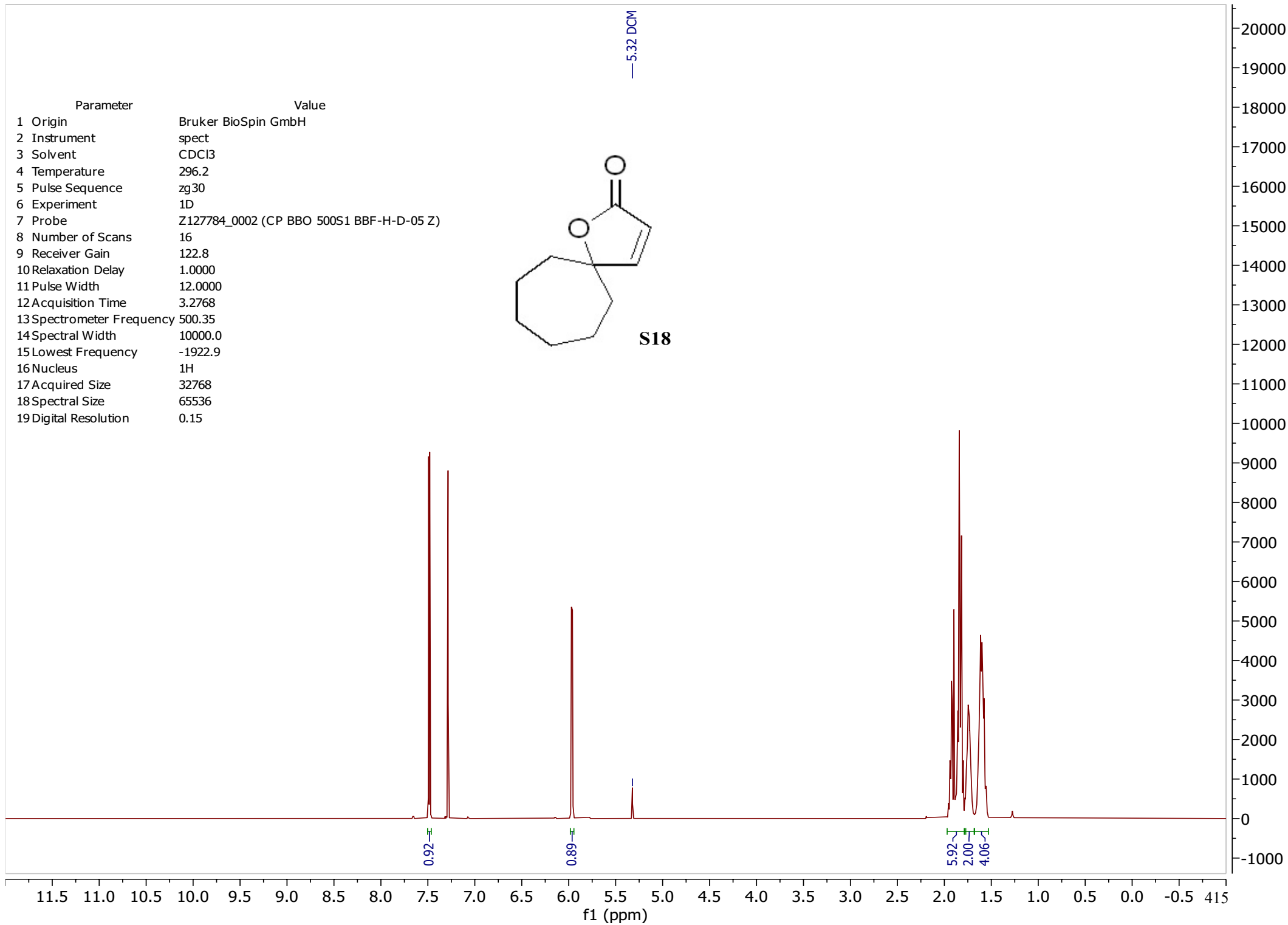


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	122.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

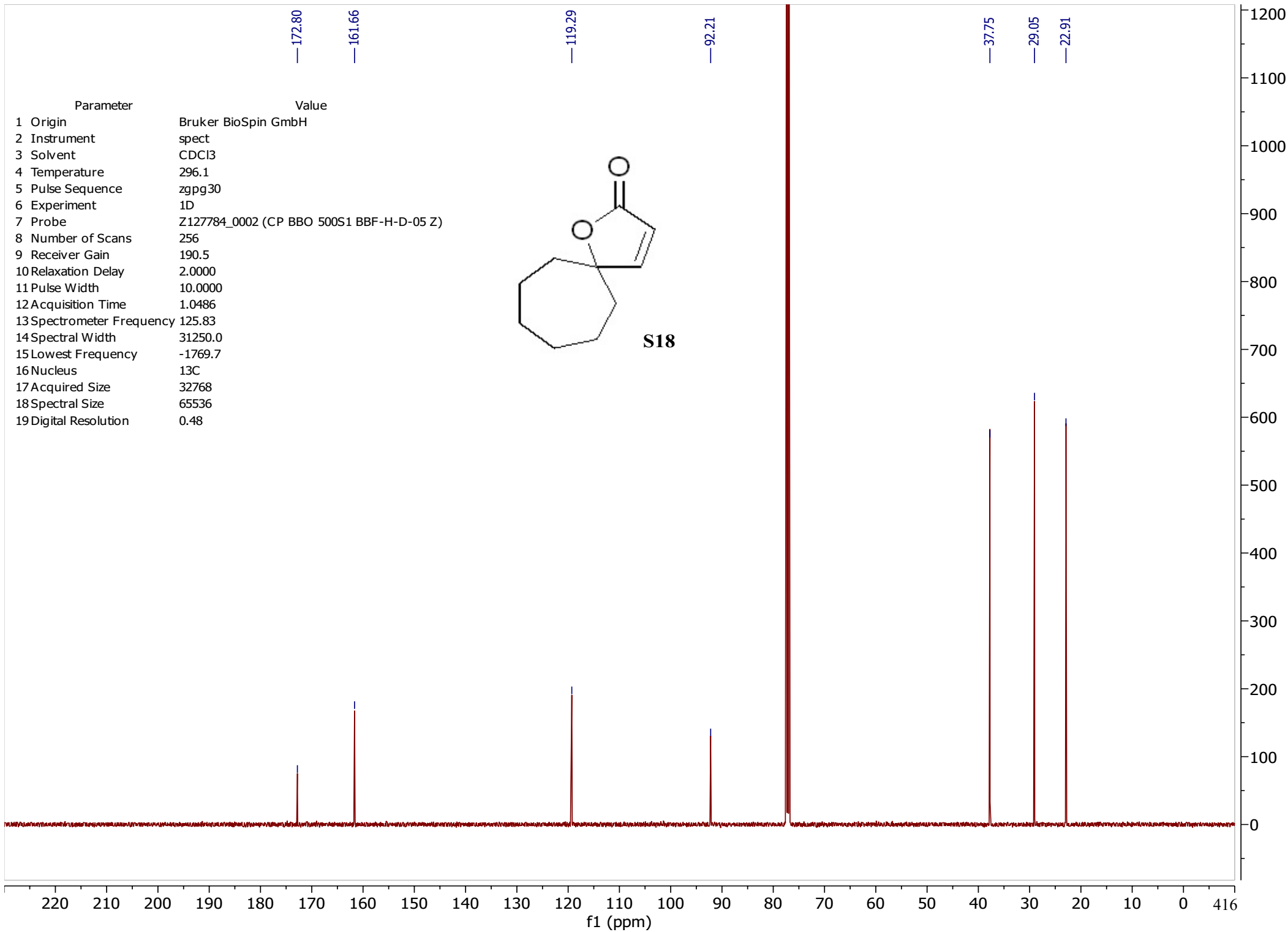
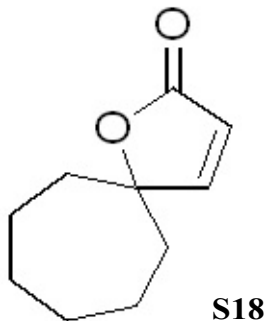


S18

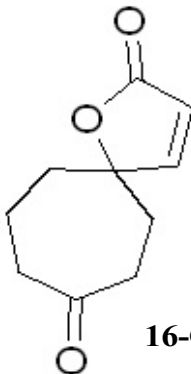
— 5.32 DCM



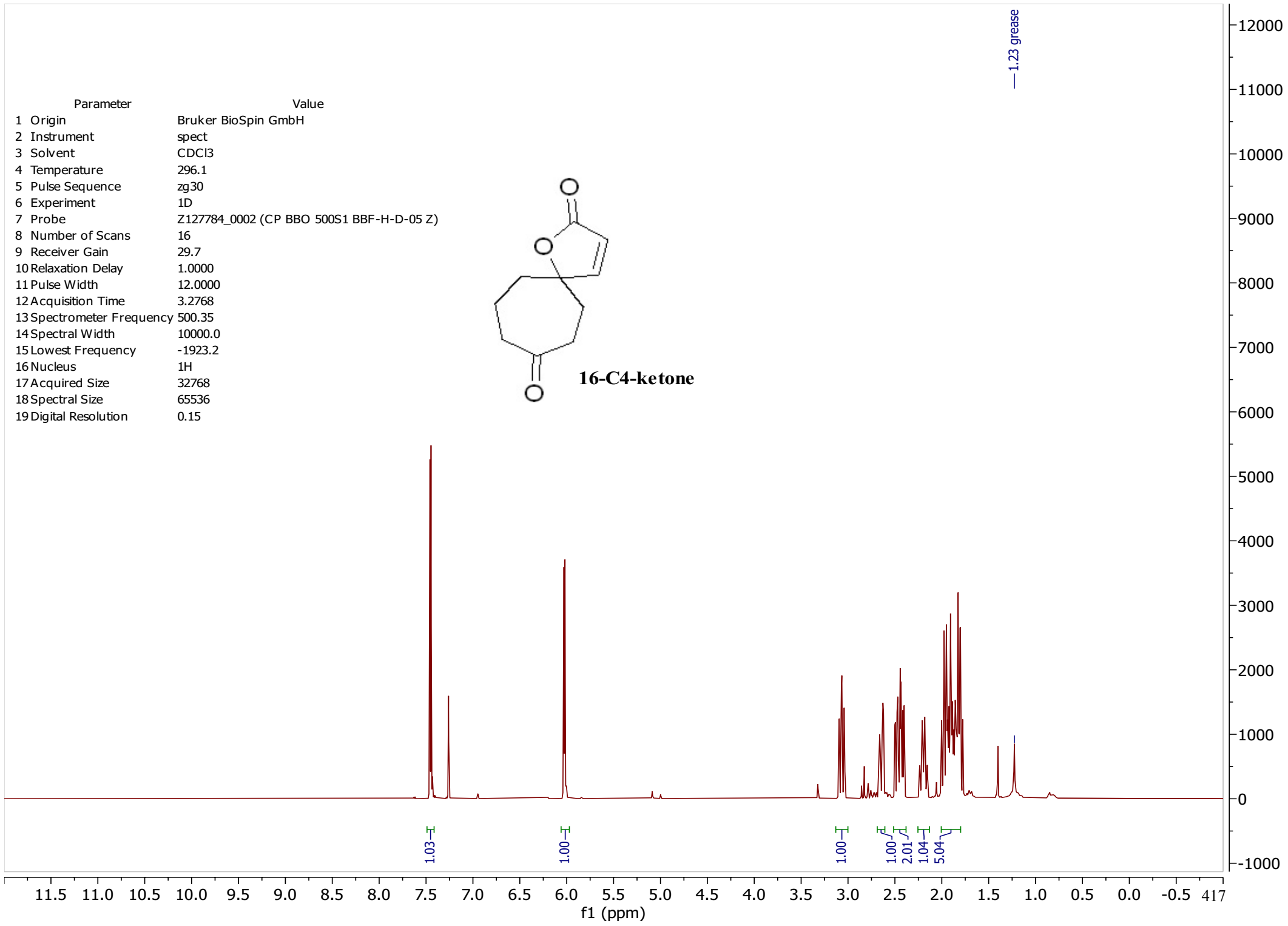
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1769.7
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

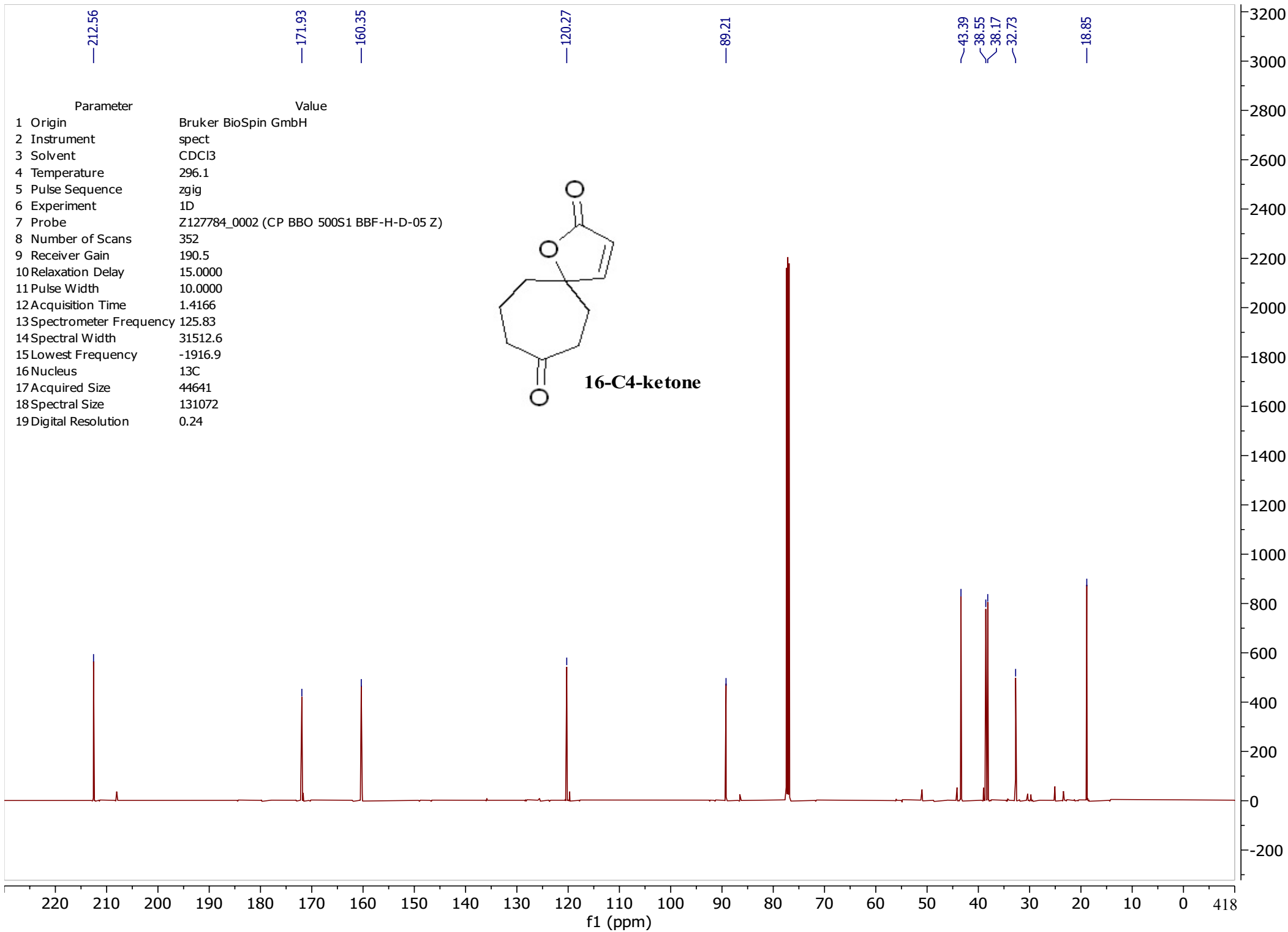


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.2
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

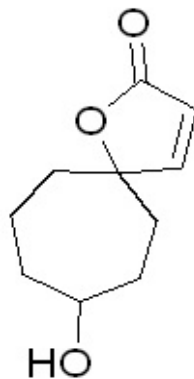


16-C4-ketone

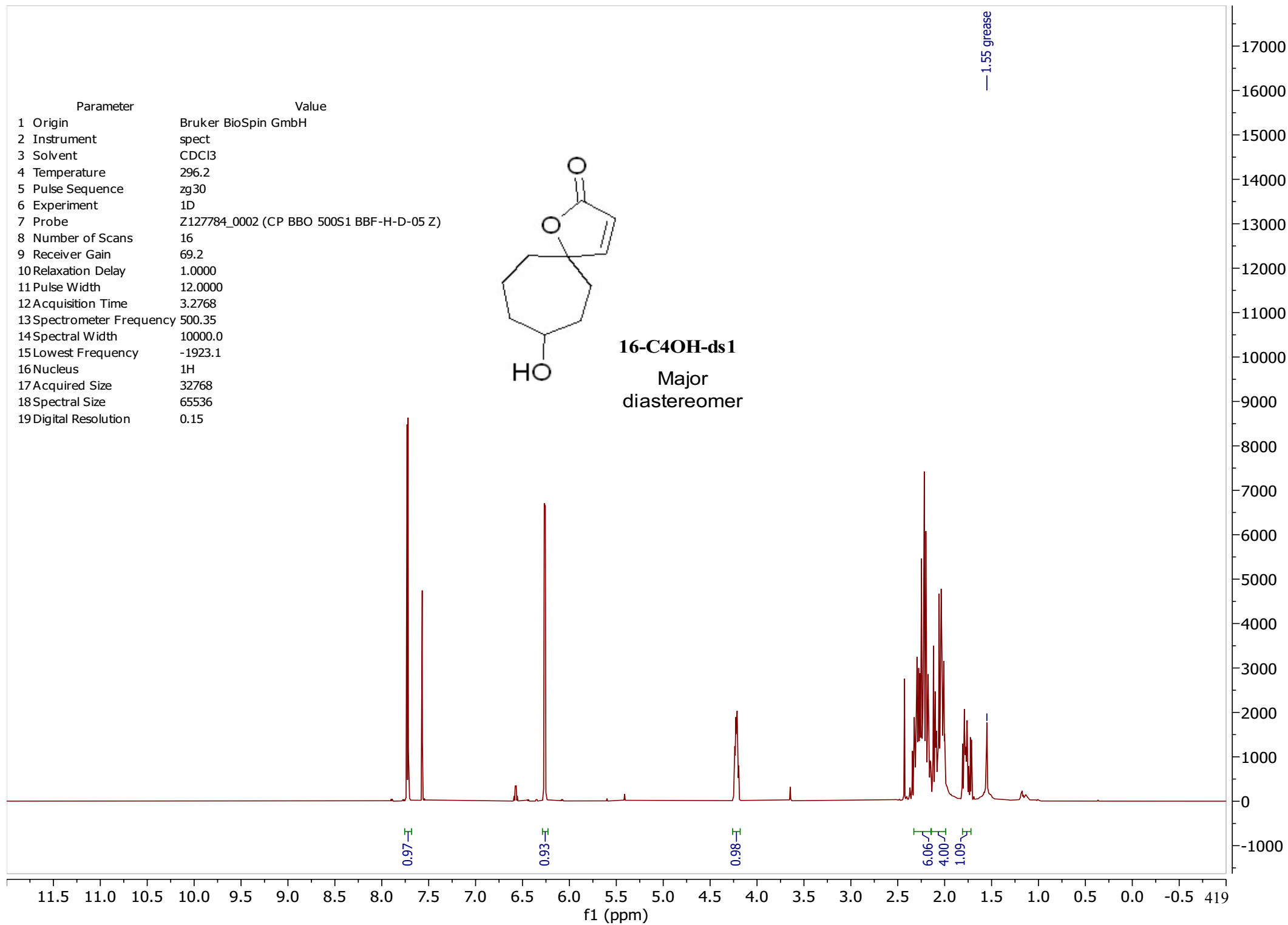


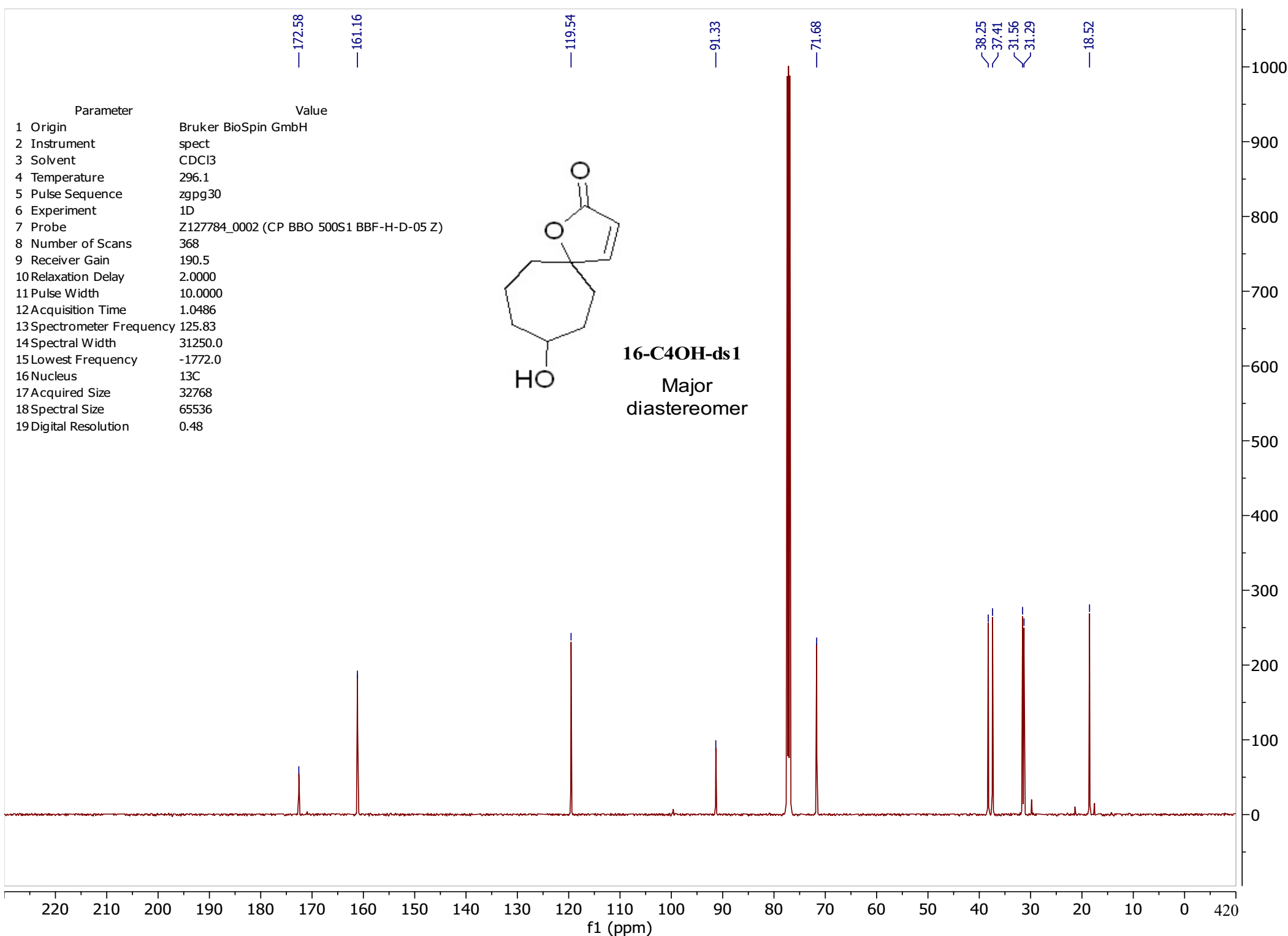


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

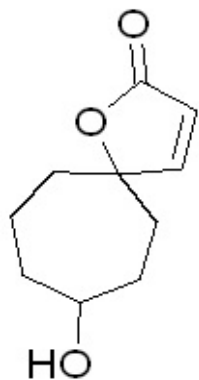


16-C4OH-ds1
Major
diastereomer

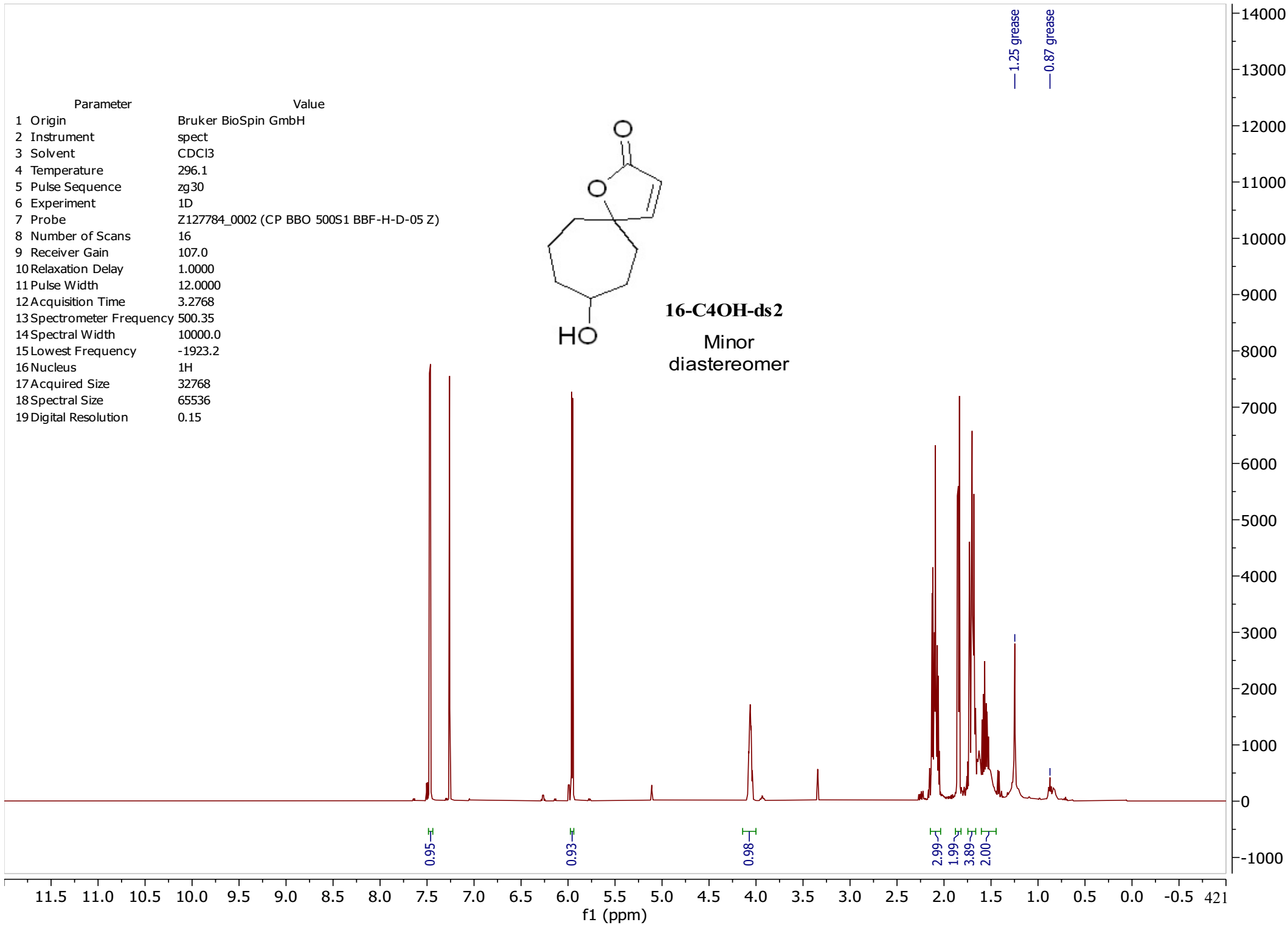




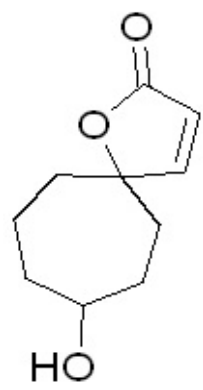
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	107.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



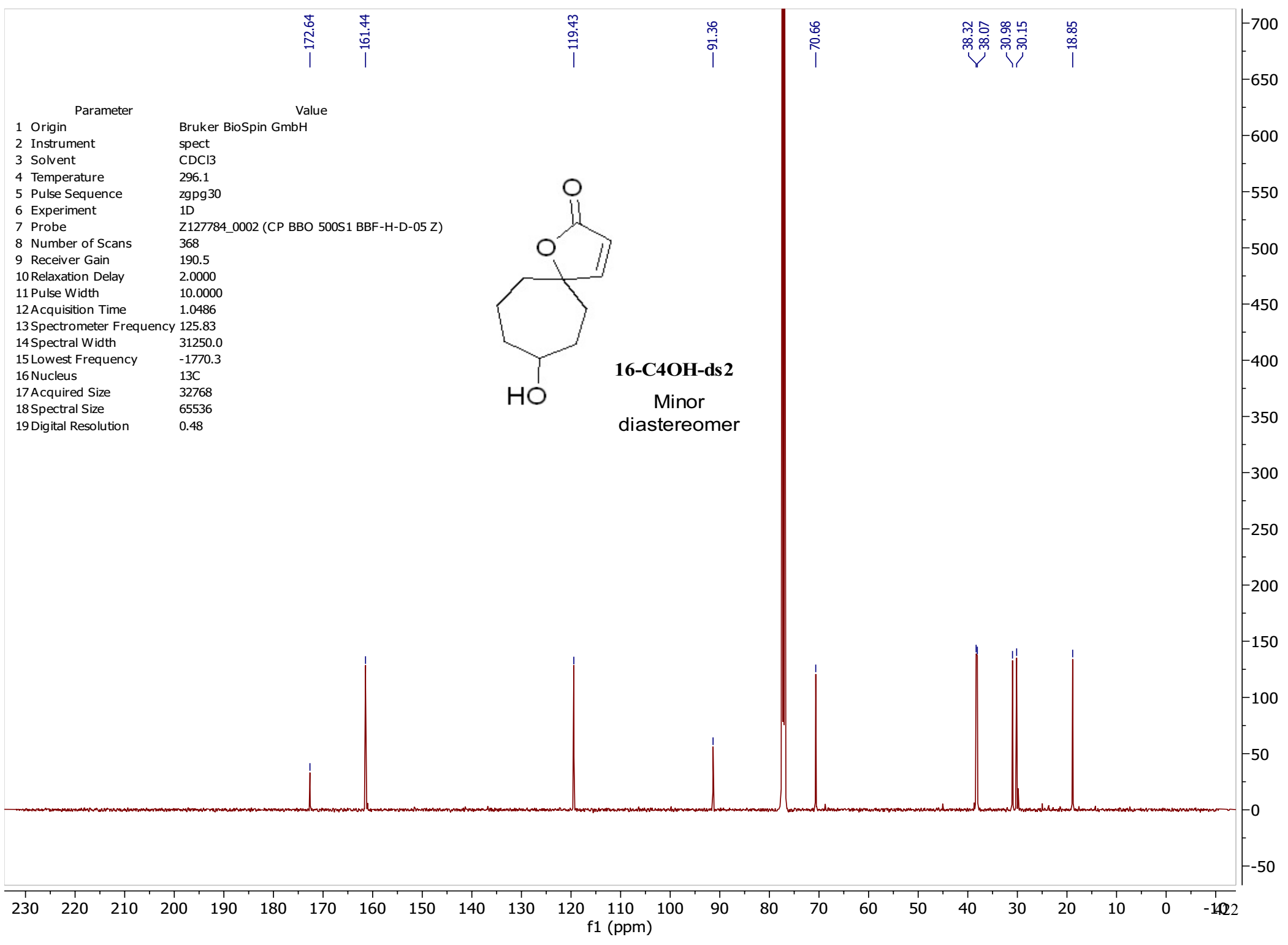
16-C4OH-ds2
Minor diastereomer



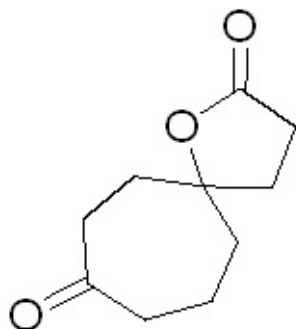
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1770.3
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



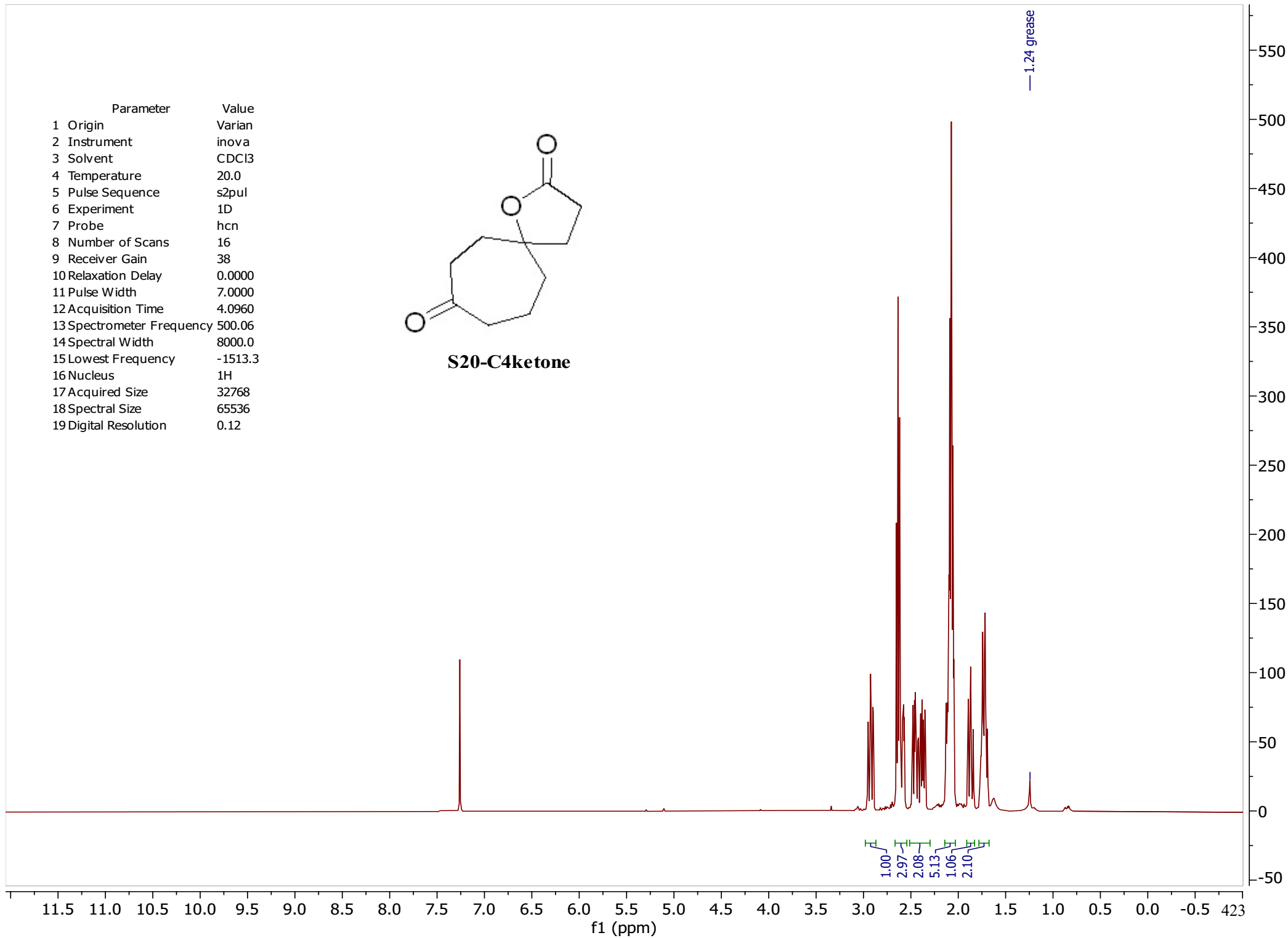
16-C4OH-ds2
Minor
diastereomer



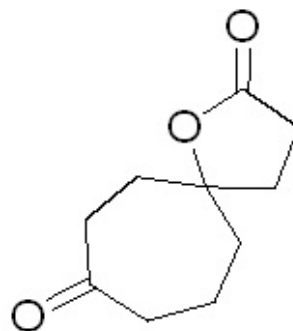
Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	hcn
8 Number of Scans	16
9 Receiver Gain	38
10 Relaxation Delay	0.0000
11 Pulse Width	7.0000
12 Acquisition Time	4.0960
13 Spectrometer Frequency	500.06
14 Spectral Width	8000.0
15 Lowest Frequency	-1513.3
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12



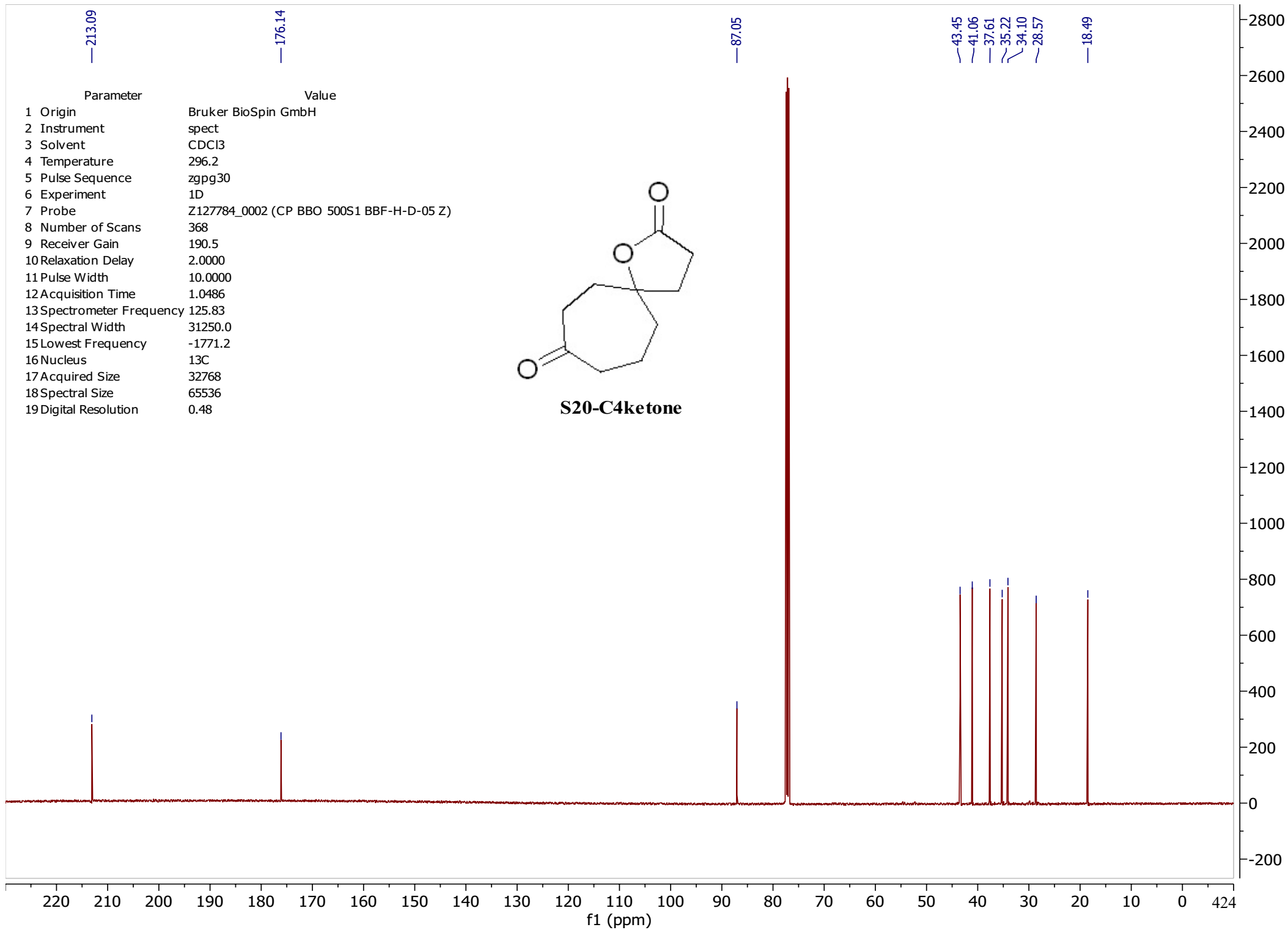
S20-C4ketone



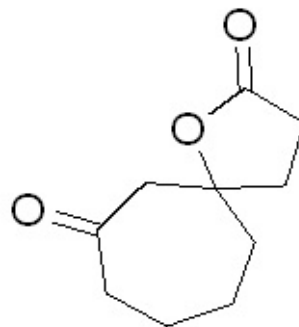
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1771.2
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



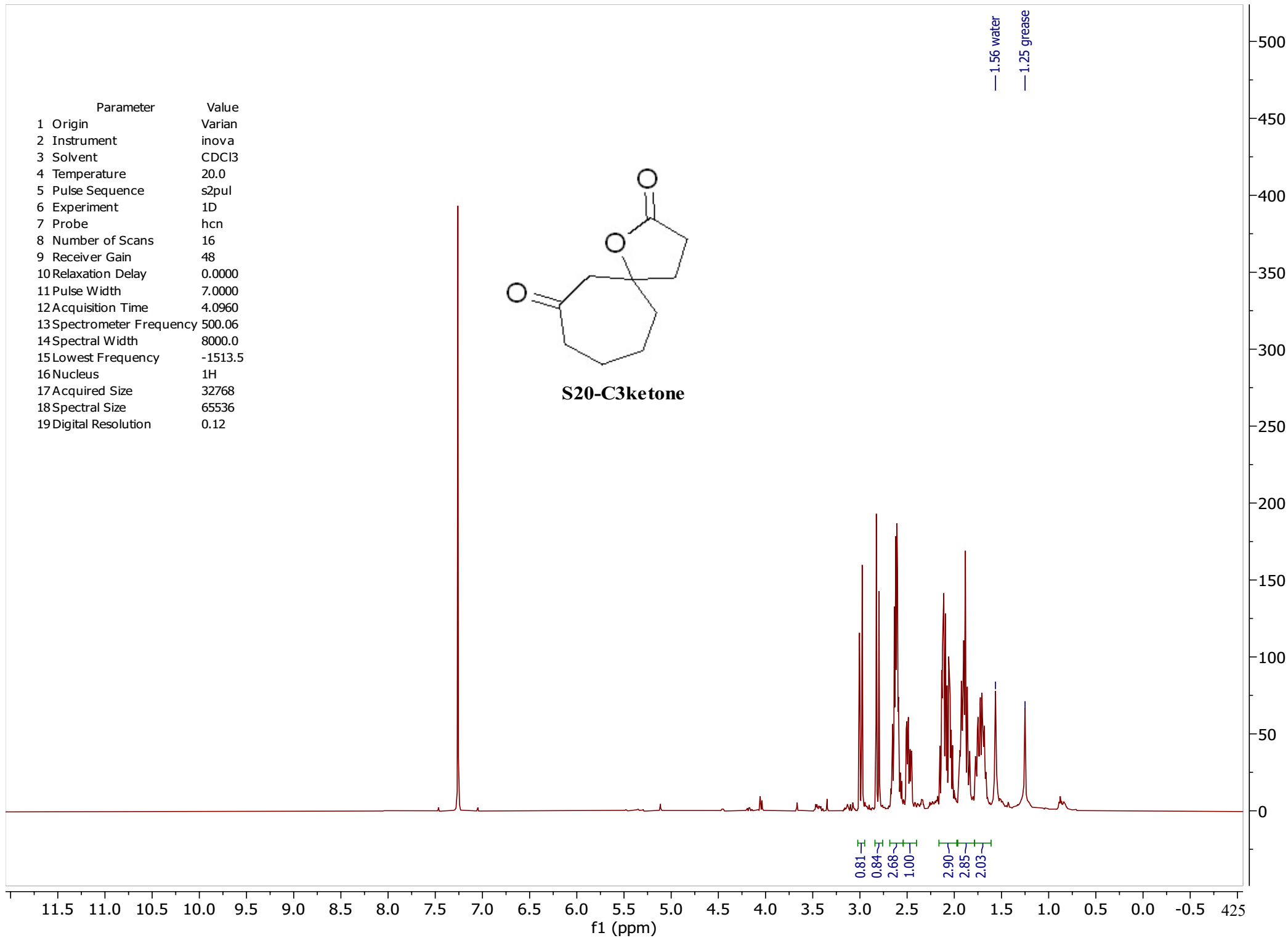
S20-C4ketone



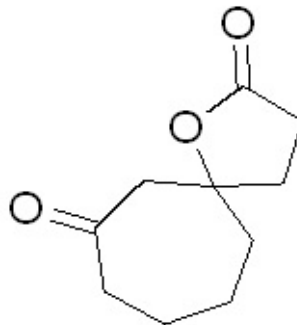
Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	hcn
8 Number of Scans	16
9 Receiver Gain	48
10 Relaxation Delay	0.0000
11 Pulse Width	7.0000
12 Acquisition Time	4.0960
13 Spectrometer Frequency	500.06
14 Spectral Width	8000.0
15 Lowest Frequency	-1513.5
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12



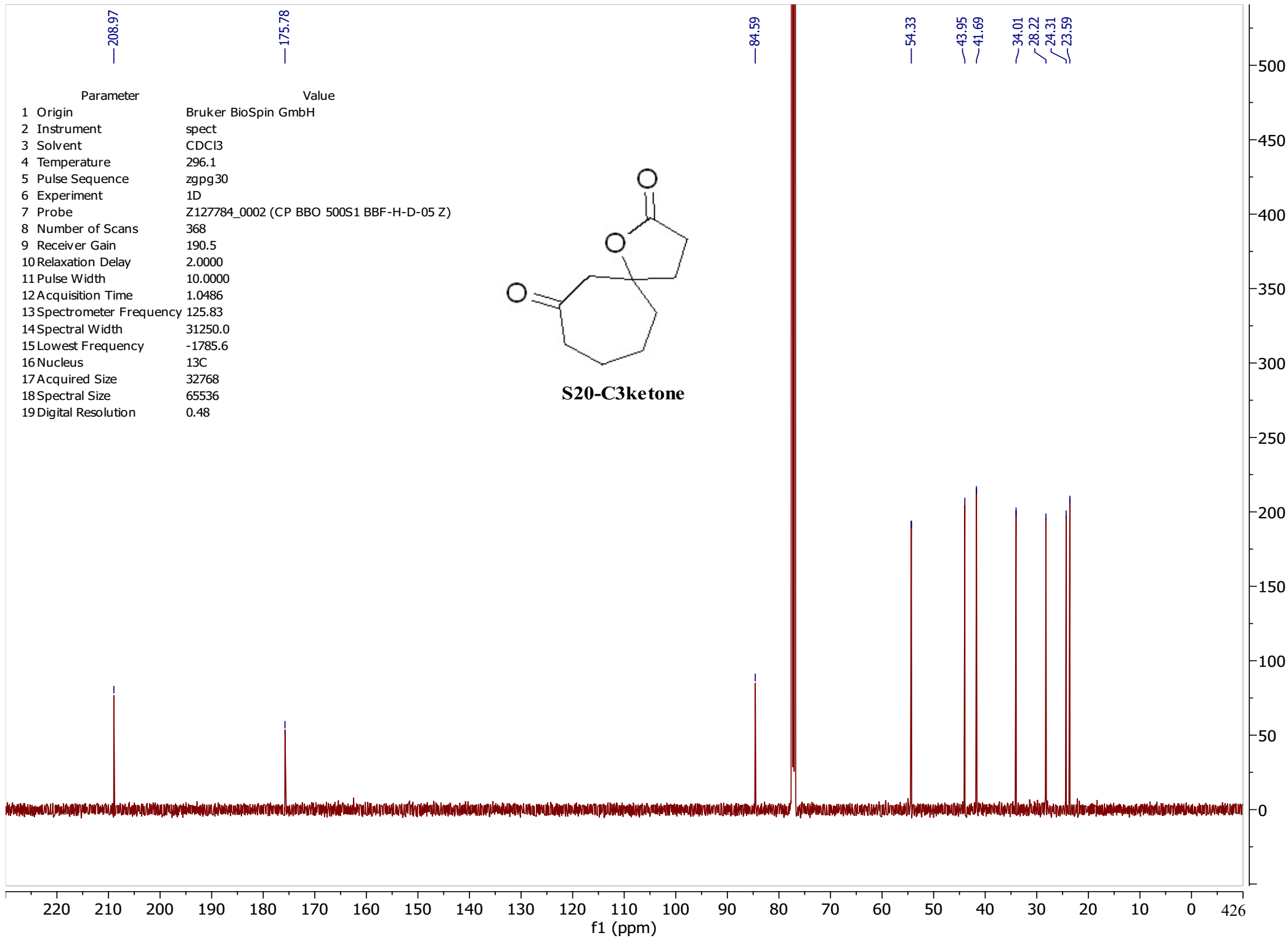
S20-C3ketone



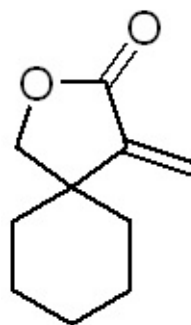
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



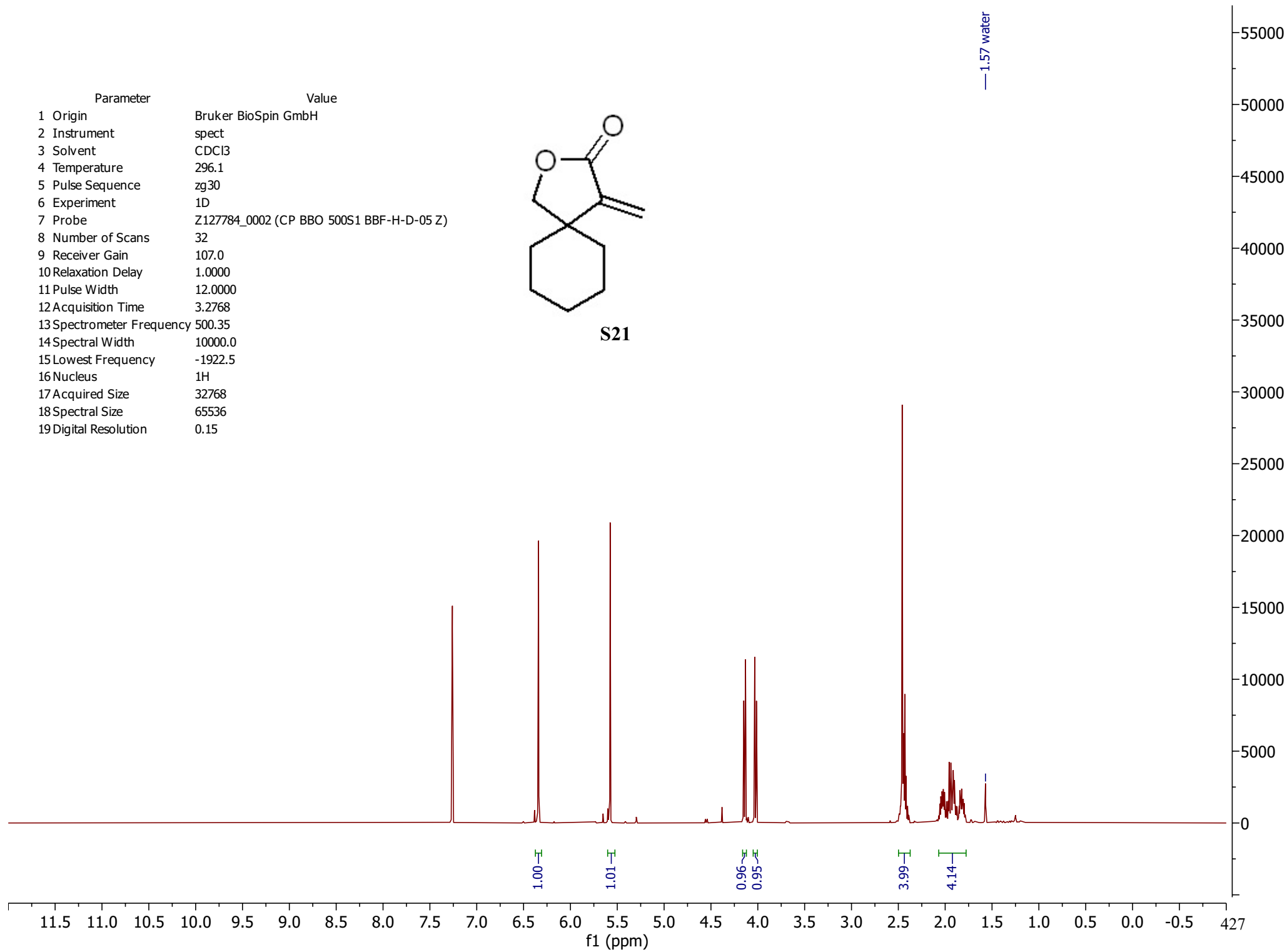
S20-C3ketone



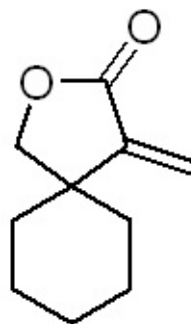
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	107.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



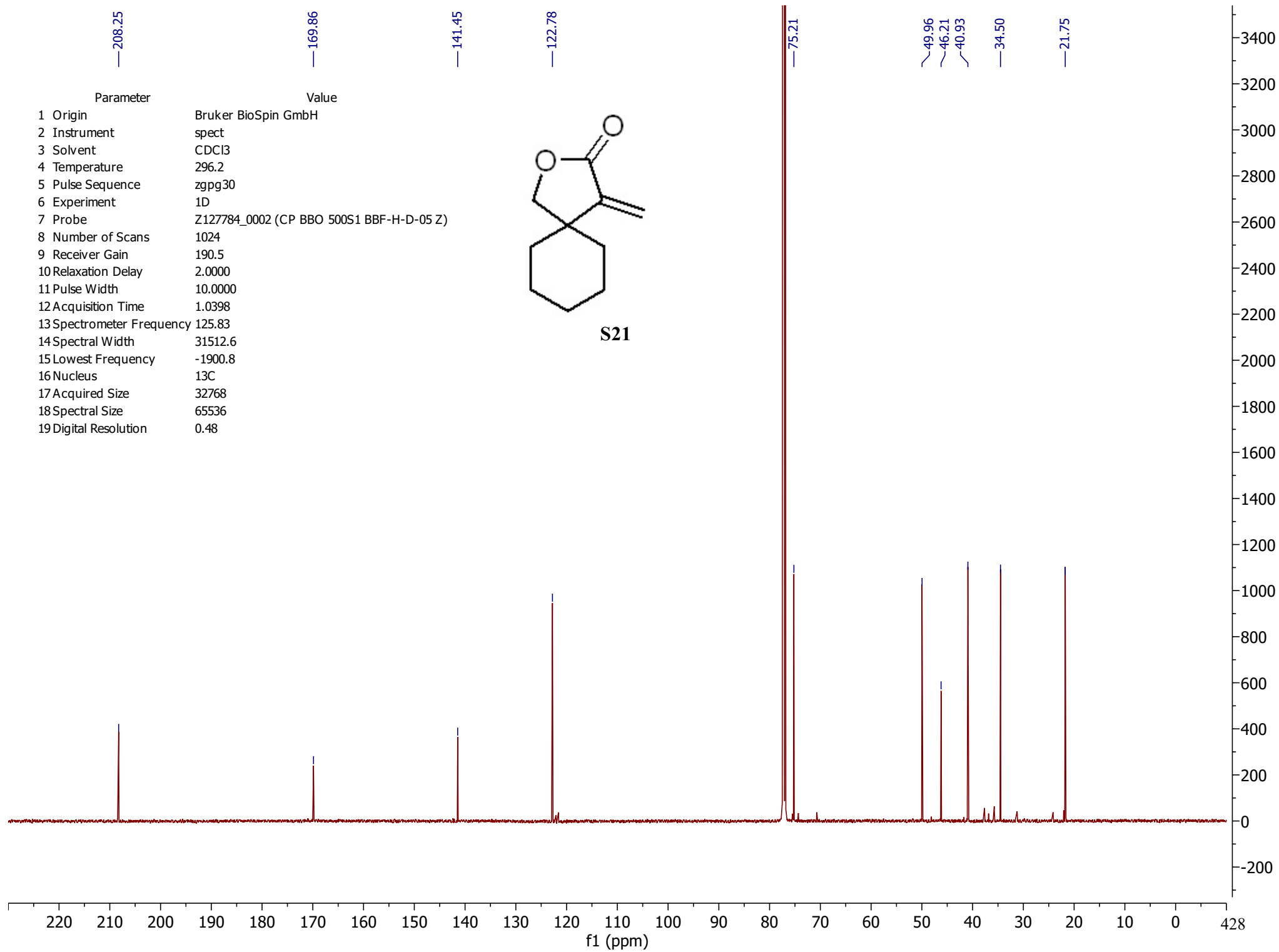
S21



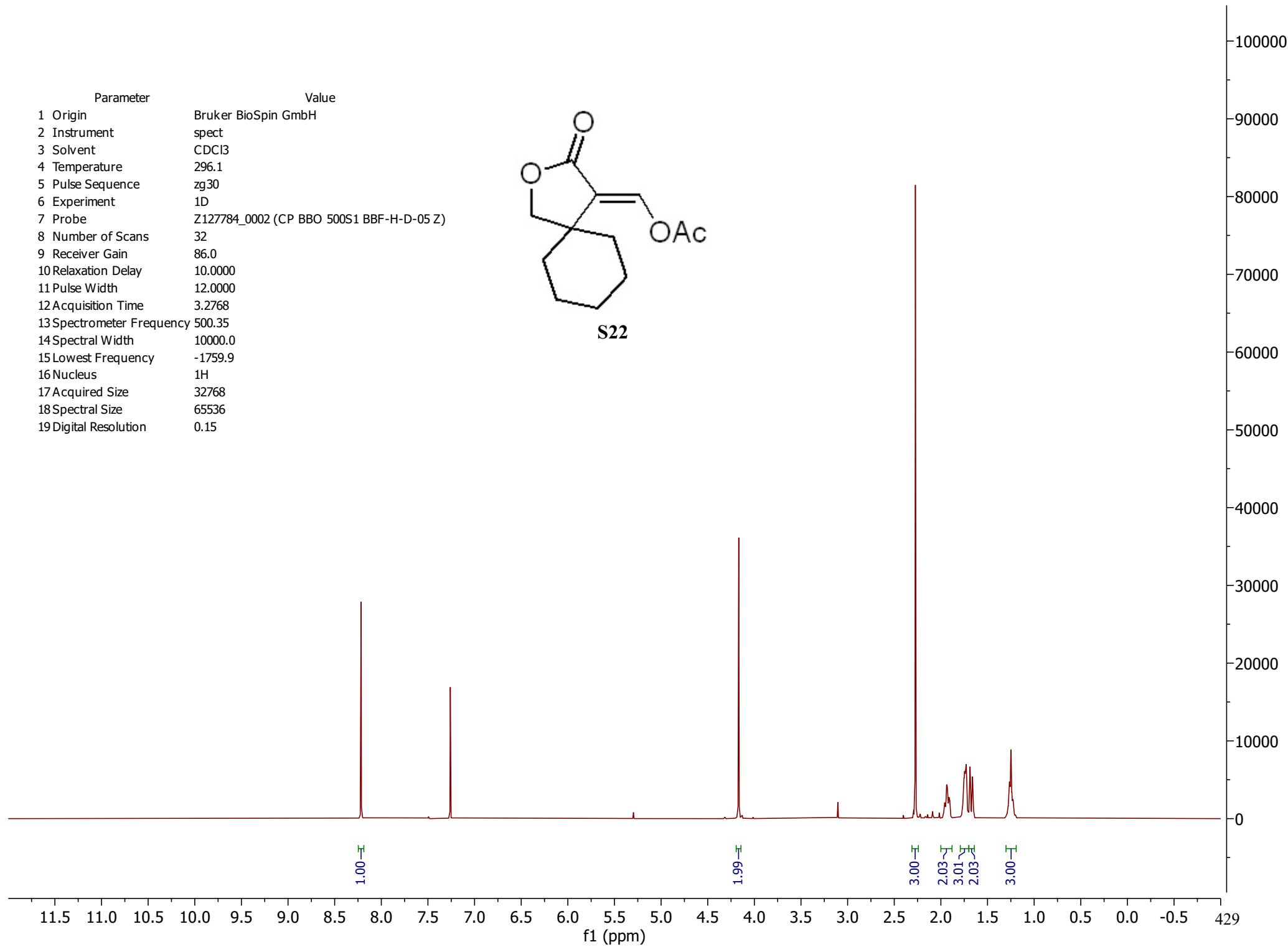
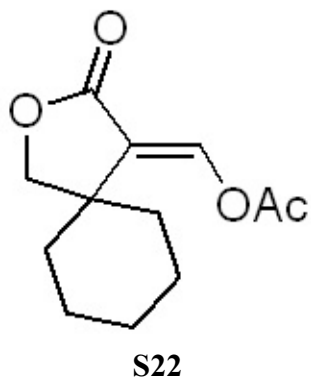
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



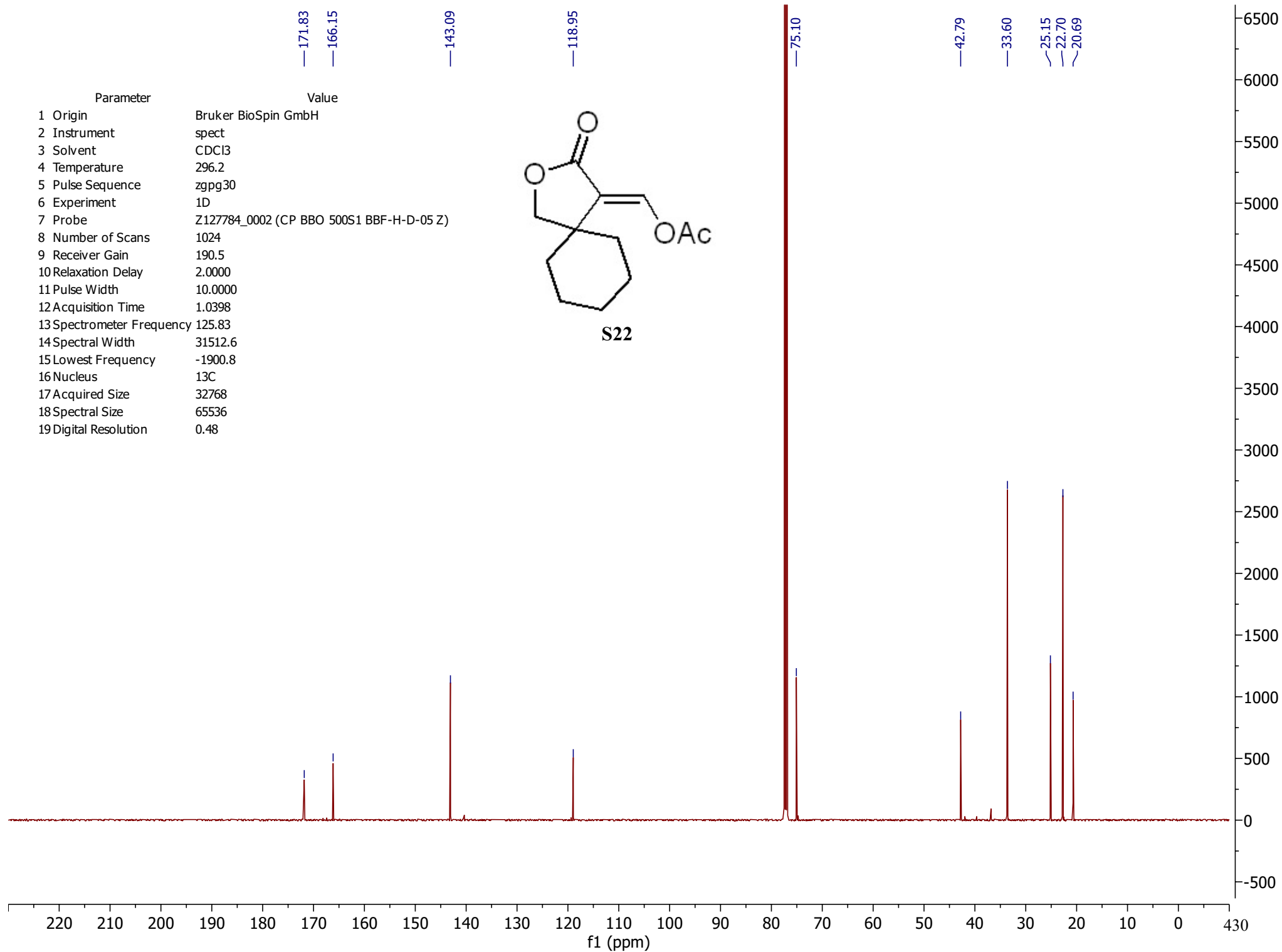
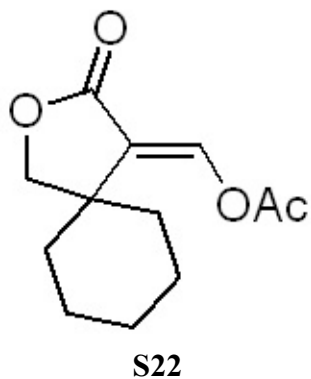
S21



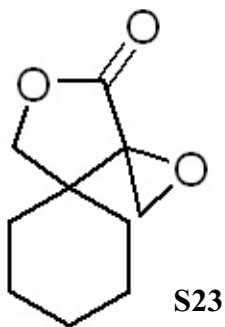
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1759.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



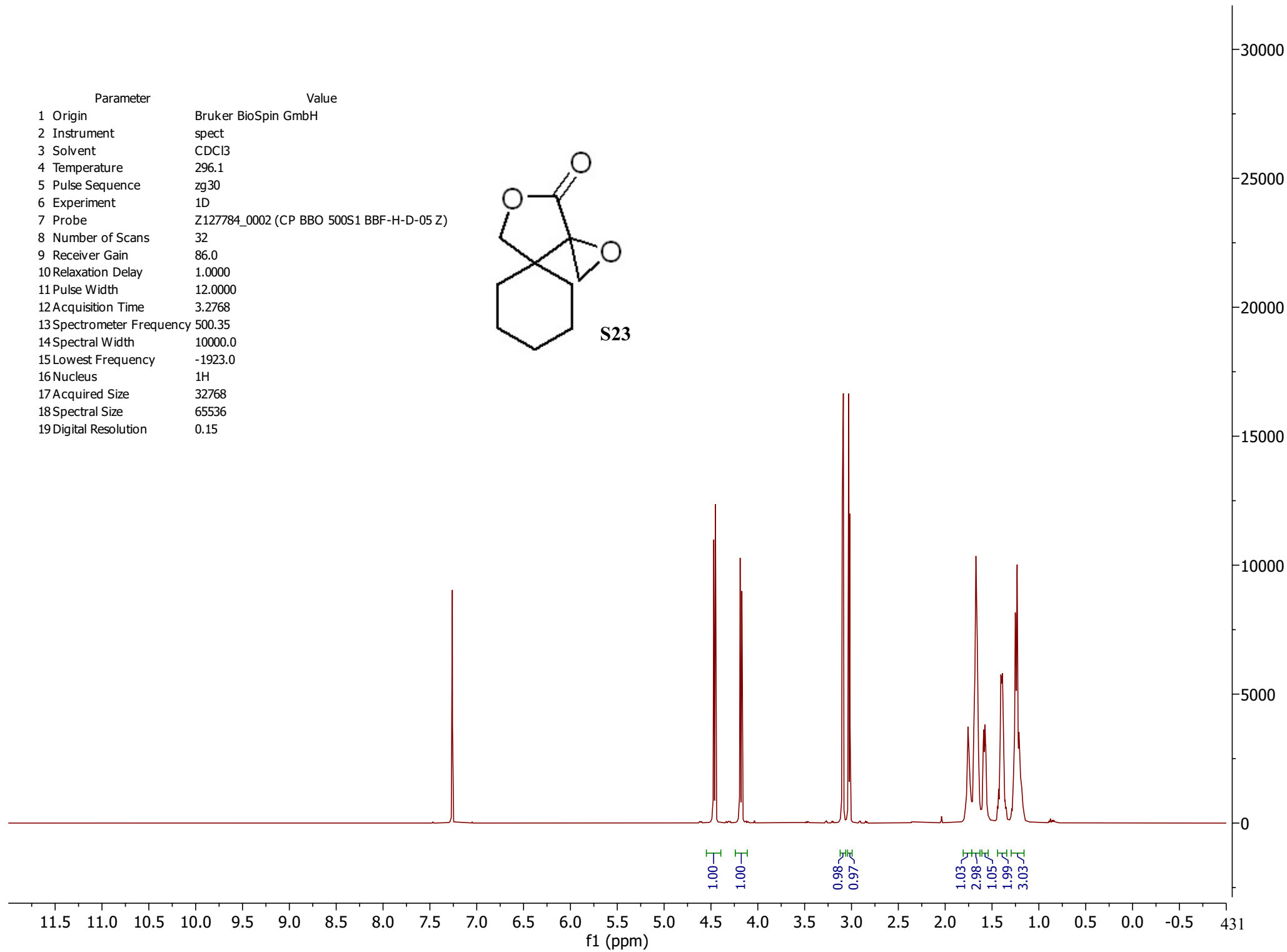
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



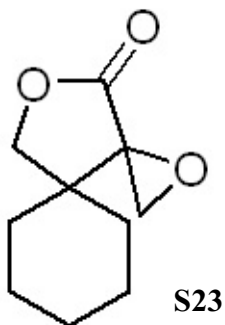
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



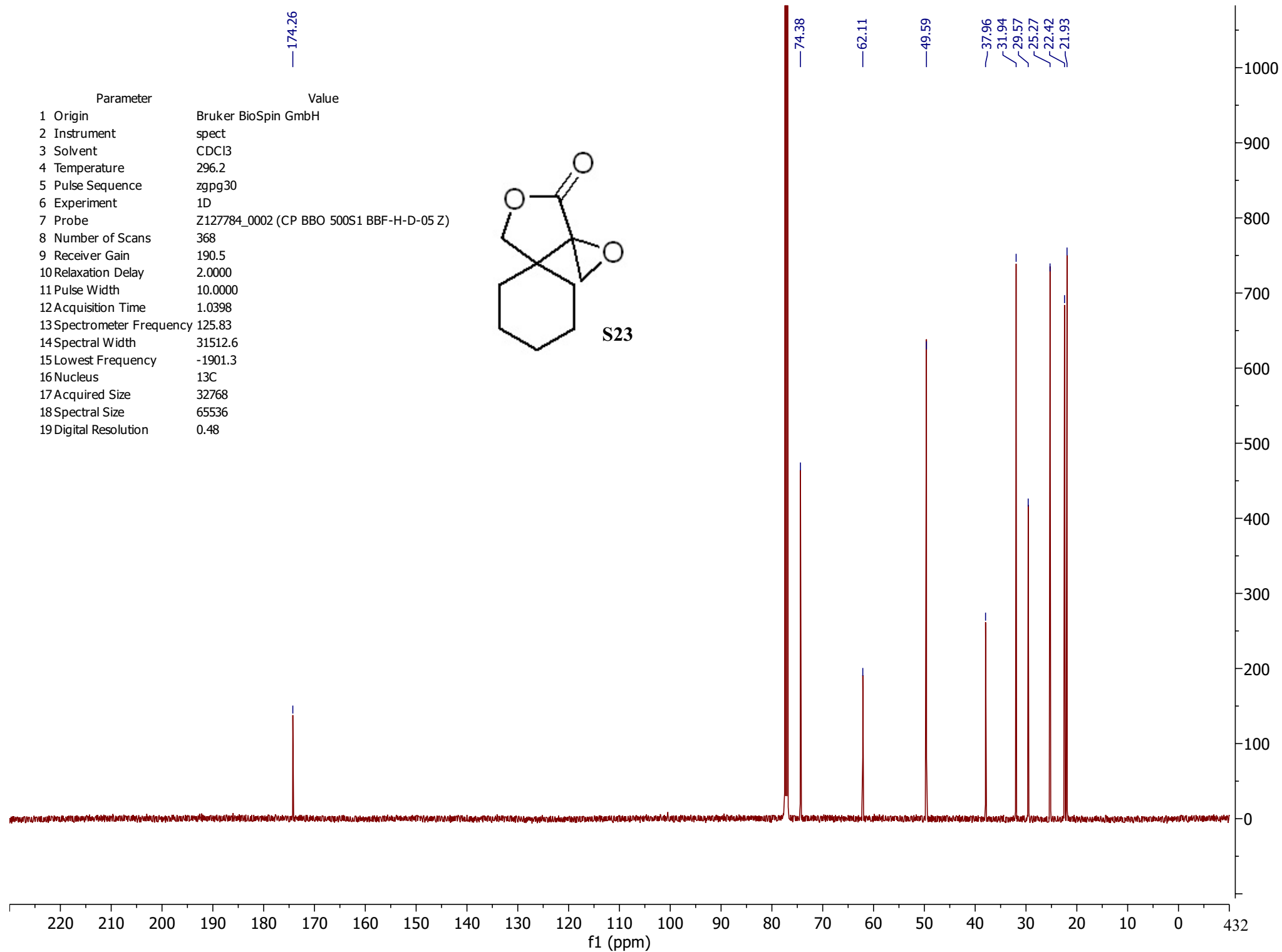
S23



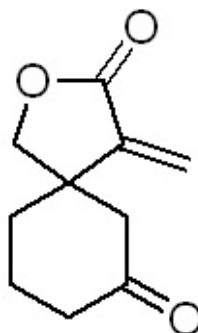
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1901.3
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



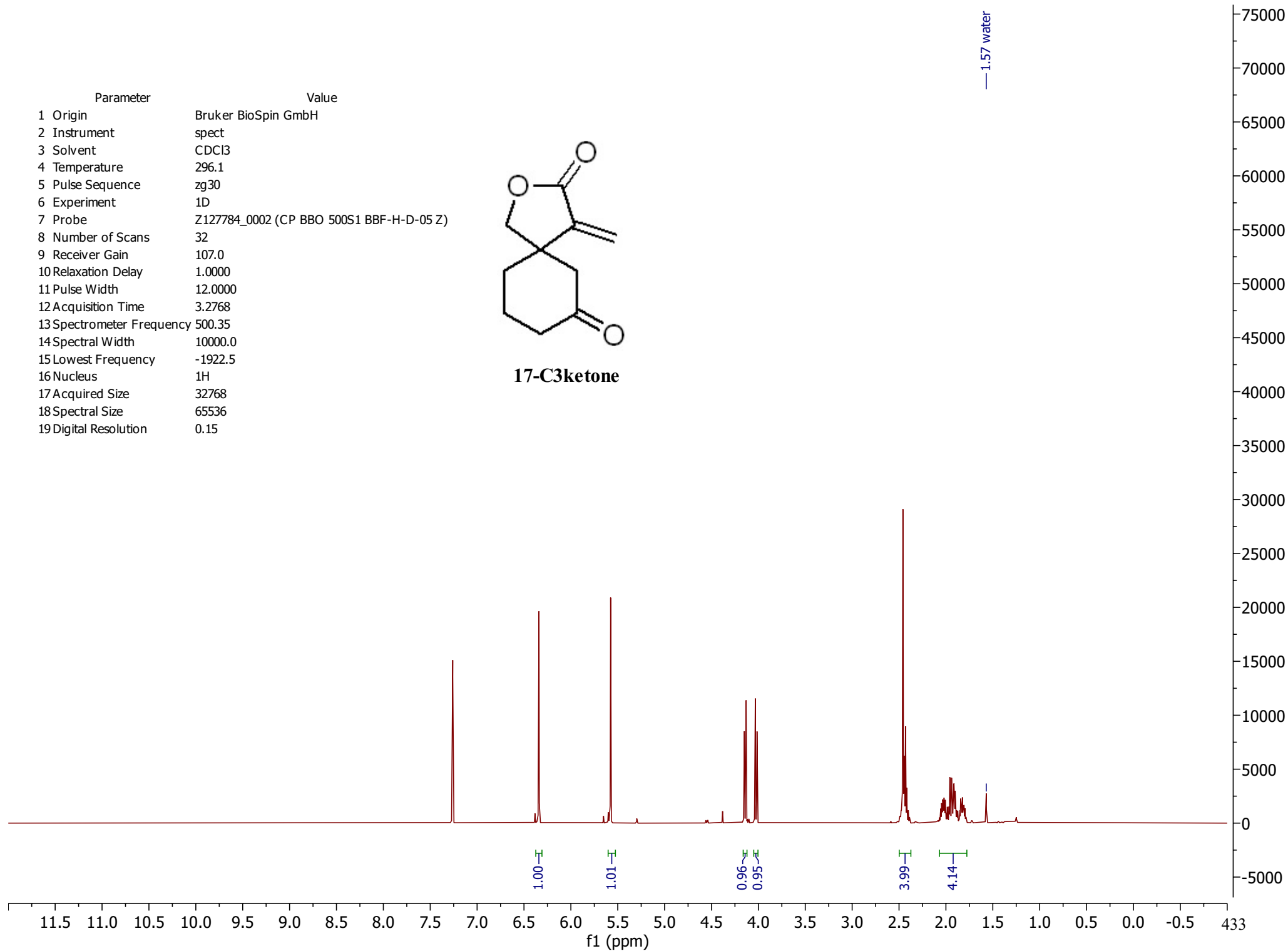
S23



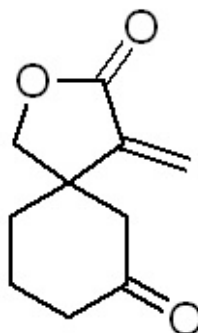
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	107.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



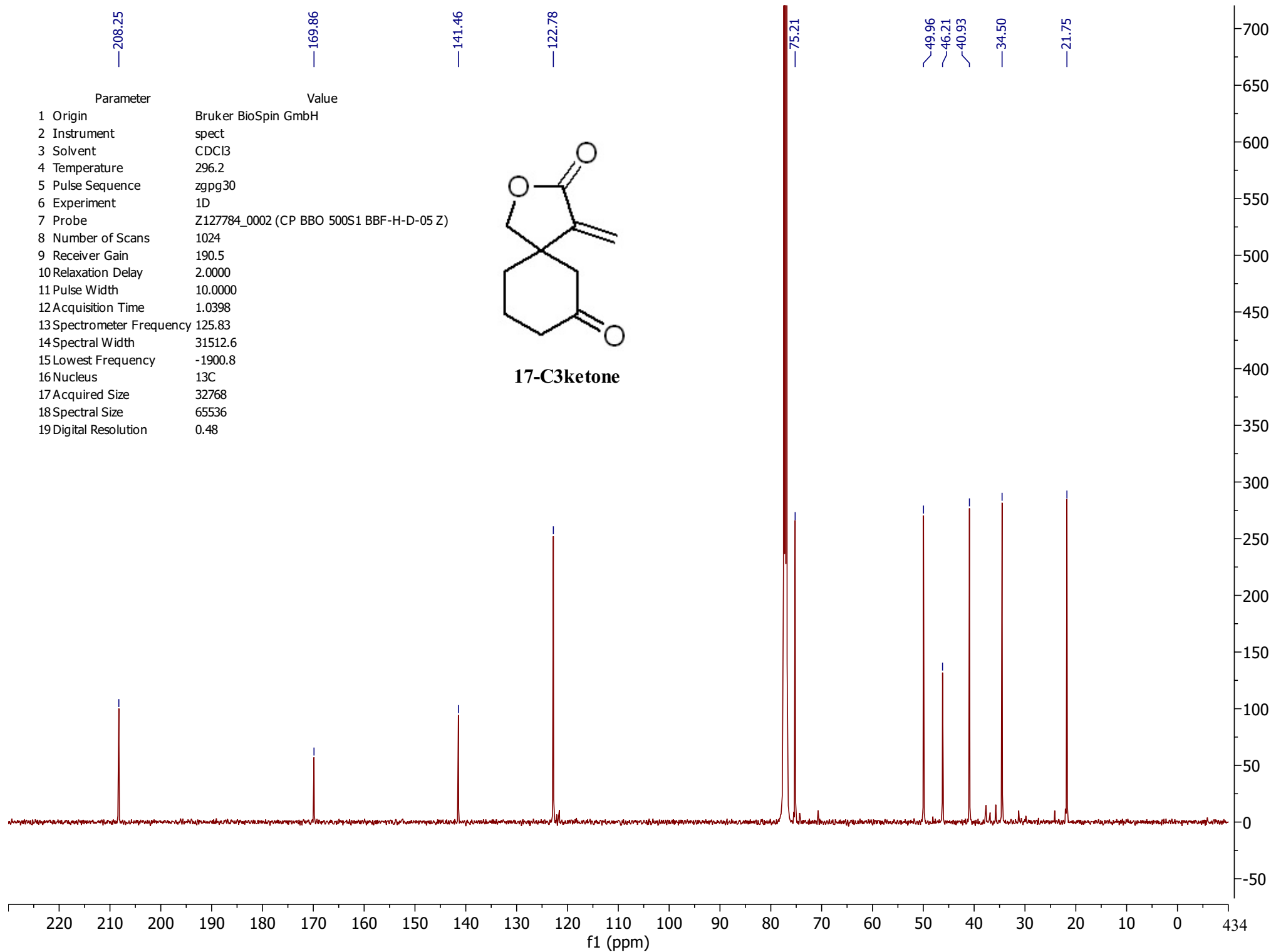
17-C3ketone



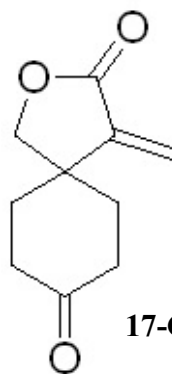
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



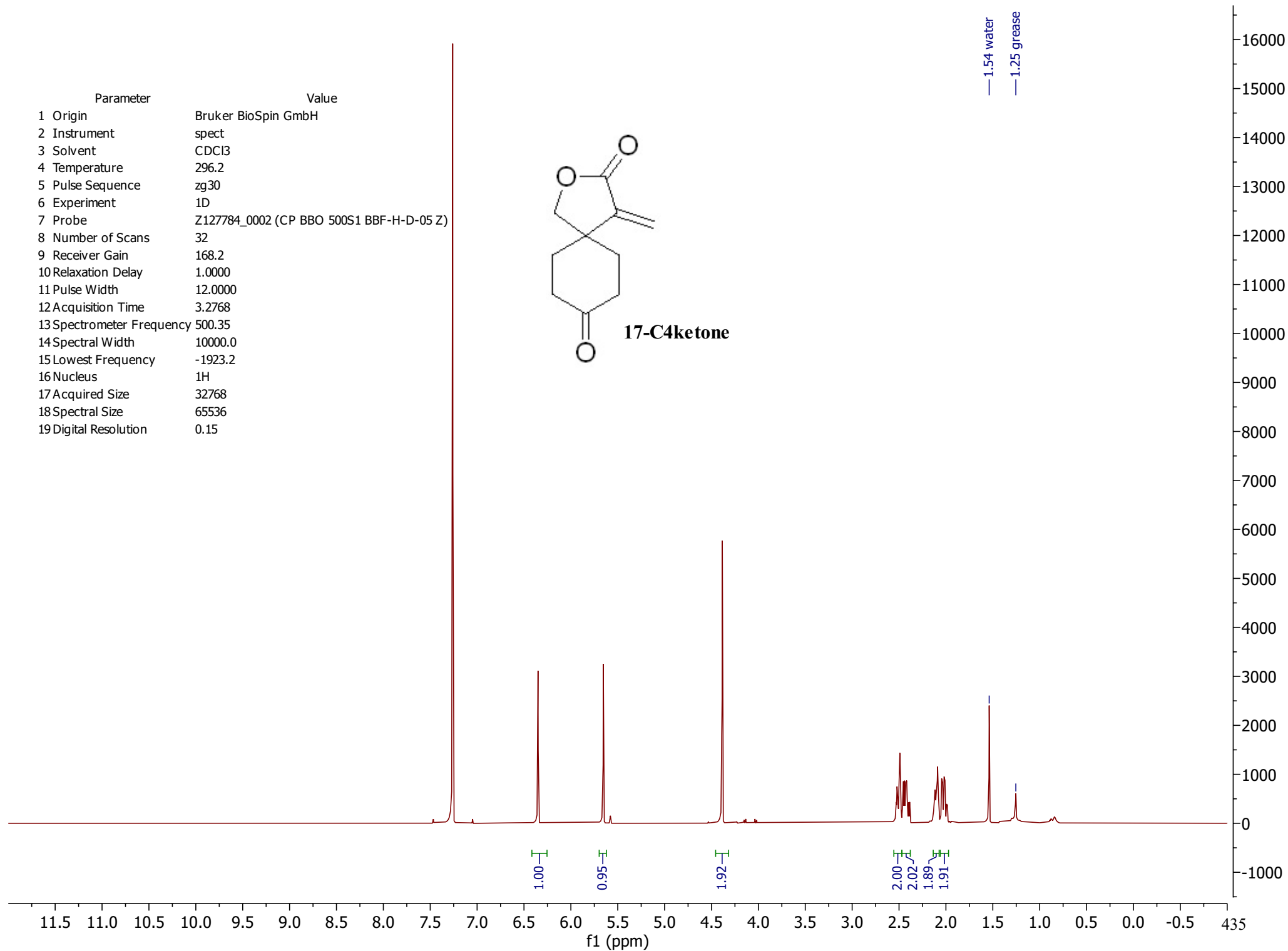
17-C3ketone



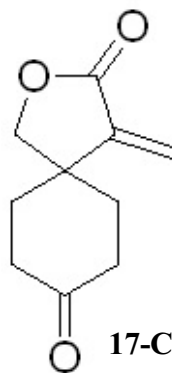
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	168.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.2
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



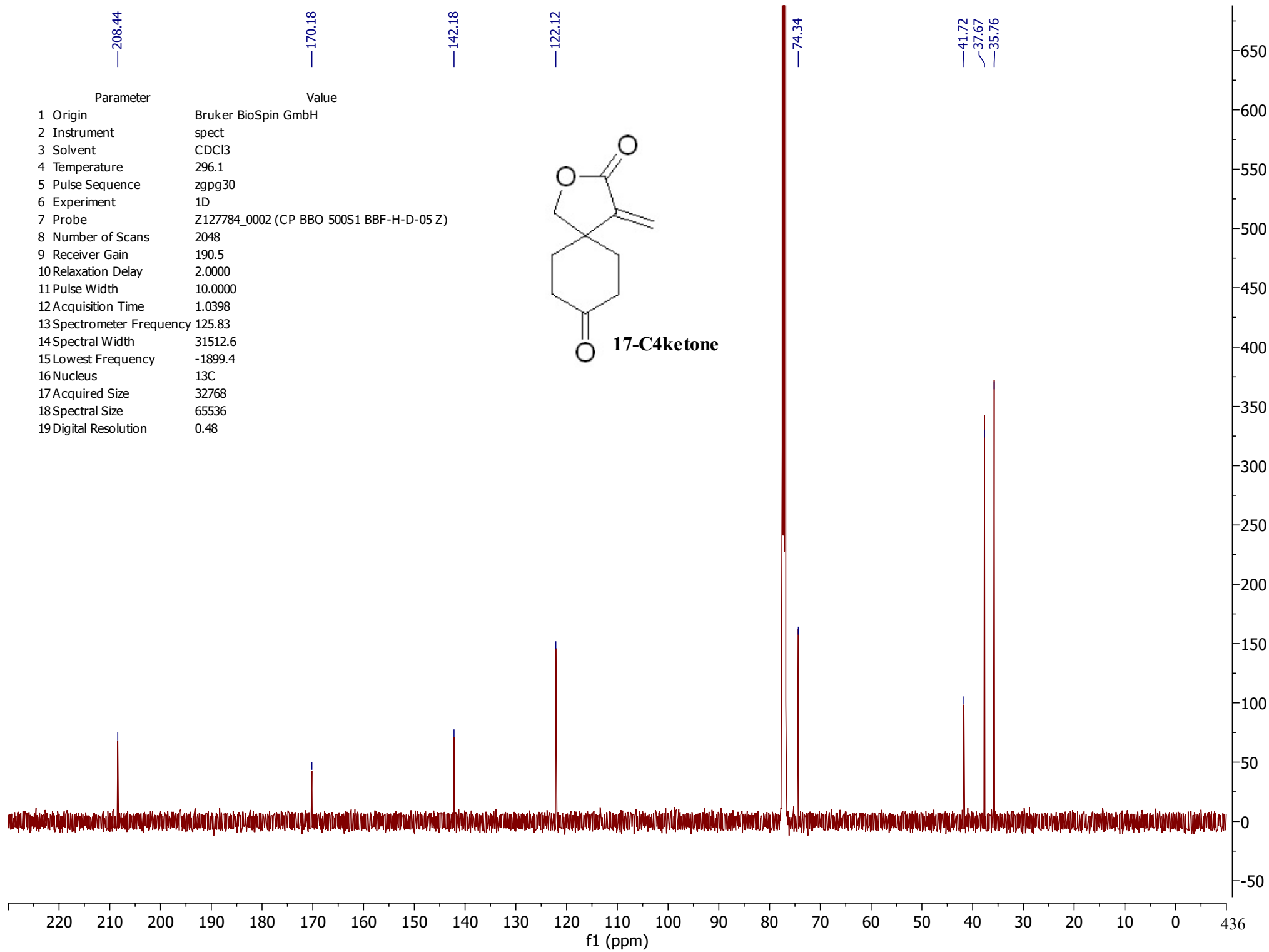
17-C4ketone



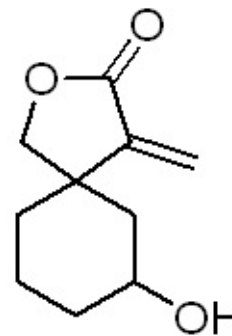
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1899.4
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



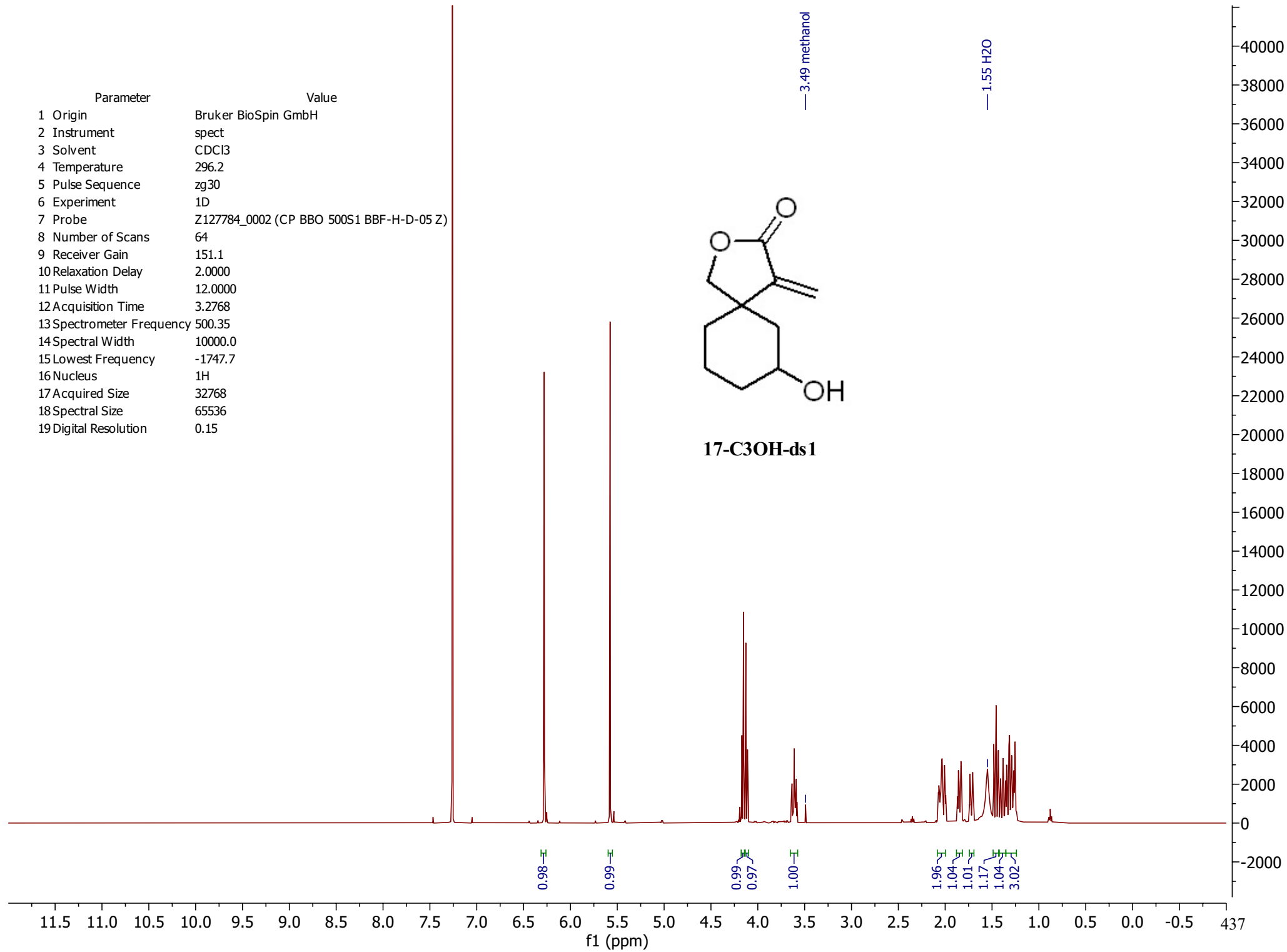
17-C4ketone



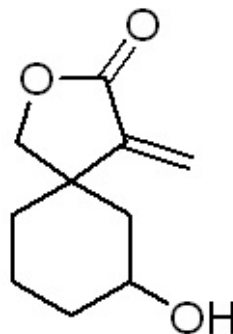
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	151.1
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



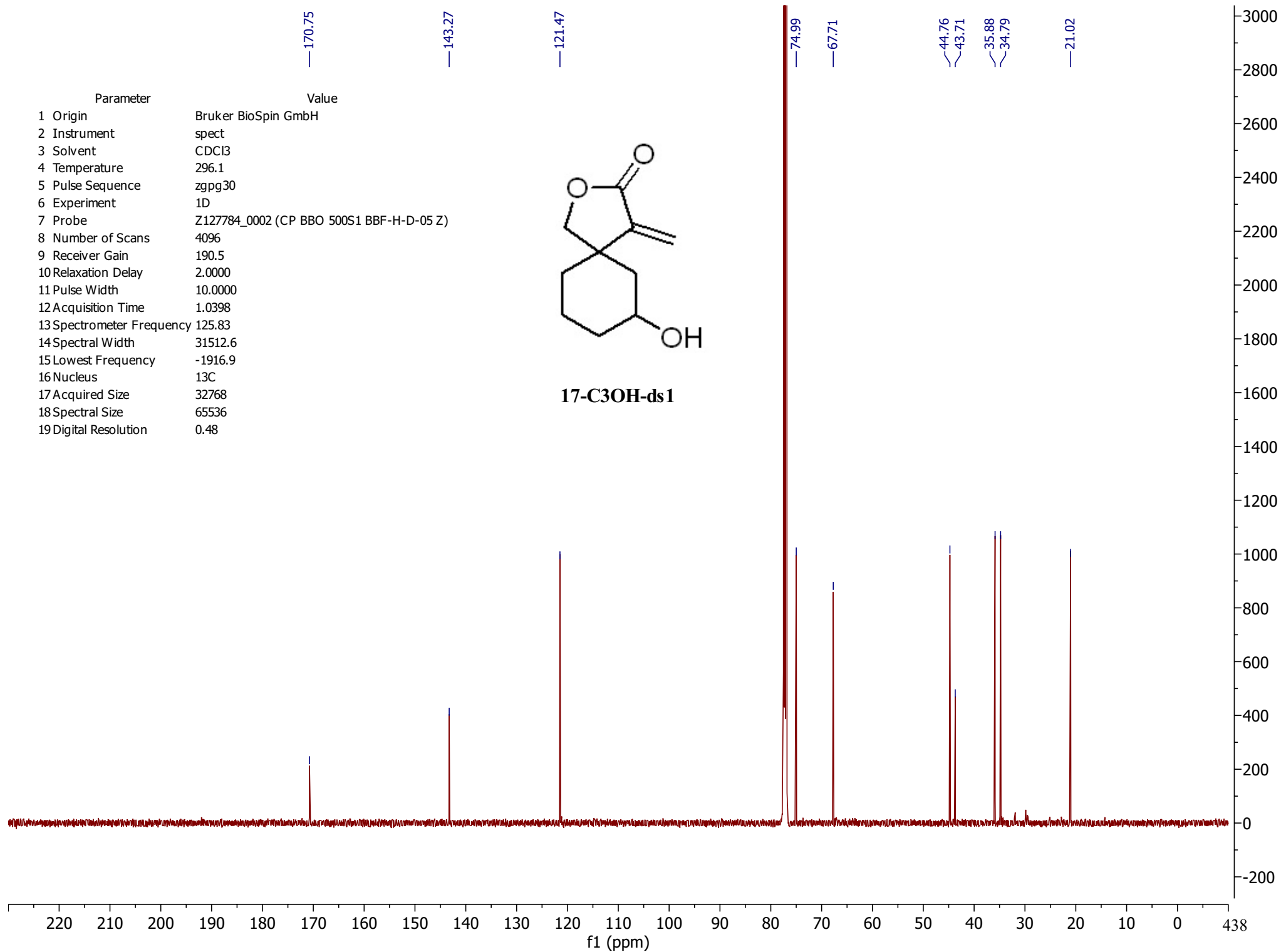
17-C3OH-ds1



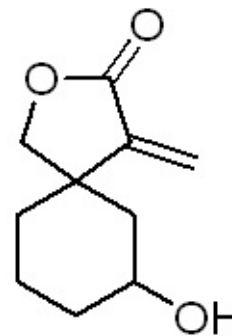
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	4096
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



17-C3OH-ds1

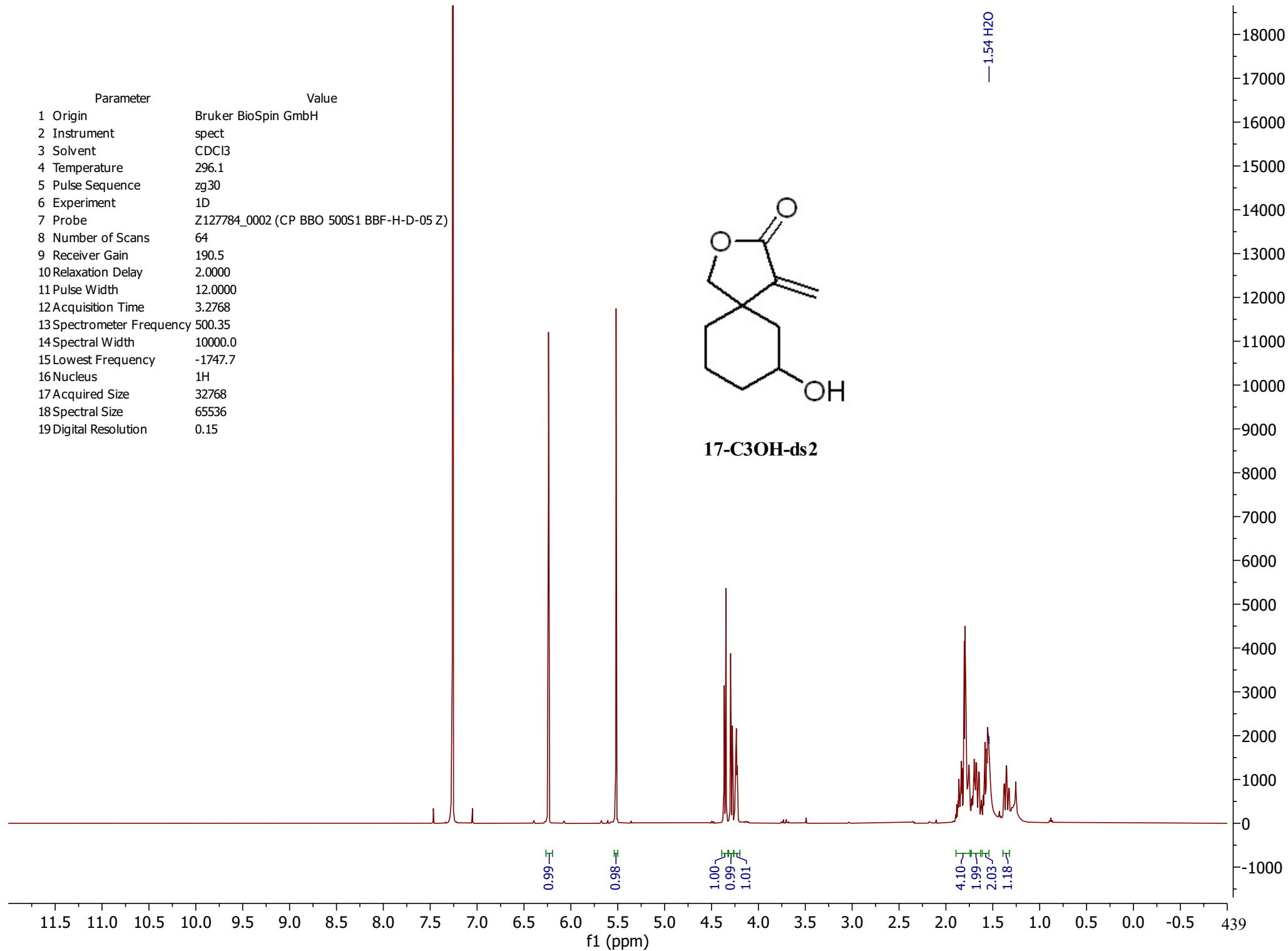


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

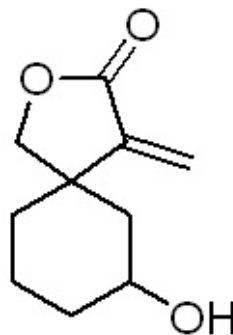


17-C3OH-ds2

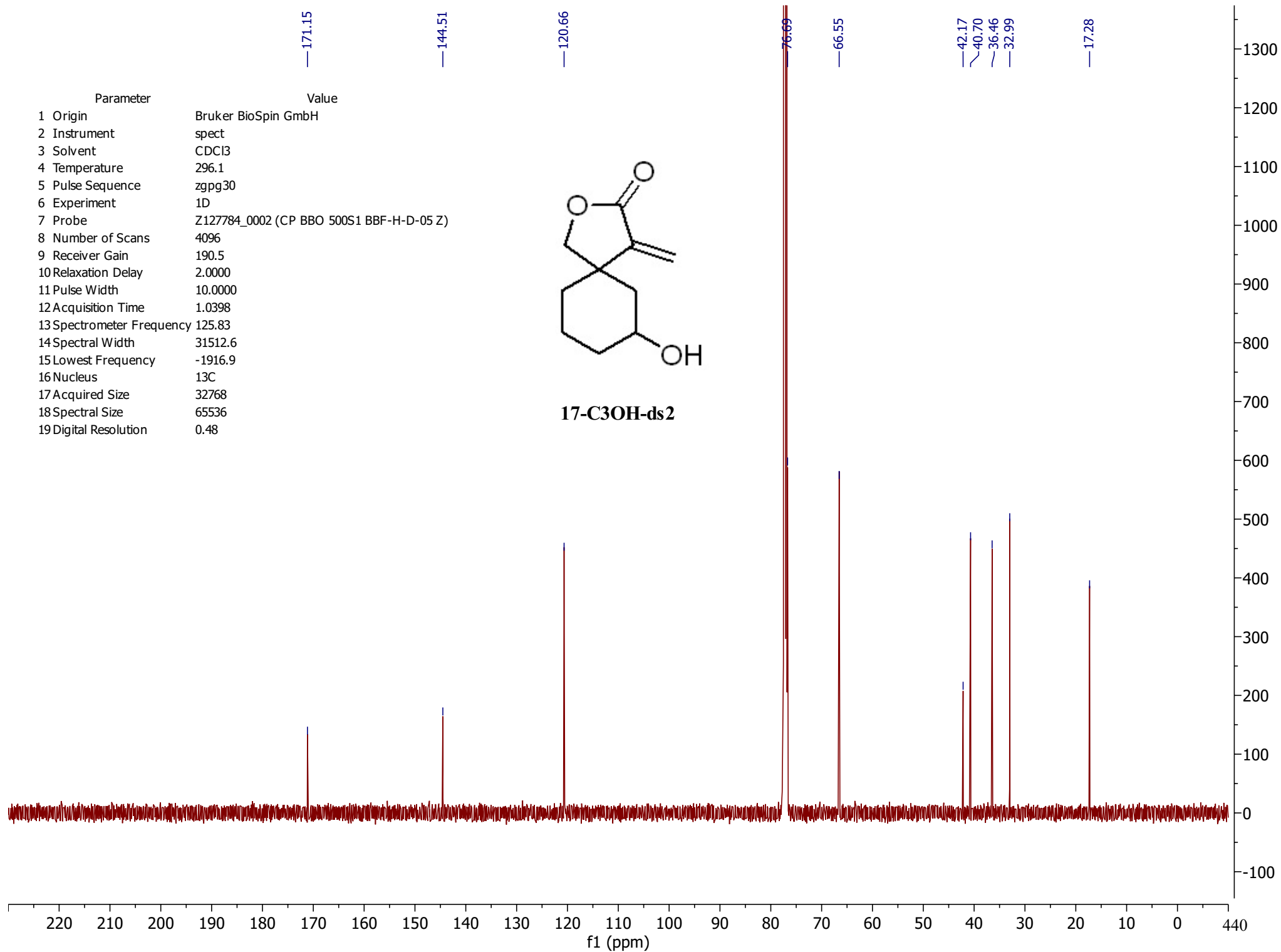
— 1.54 H₂O



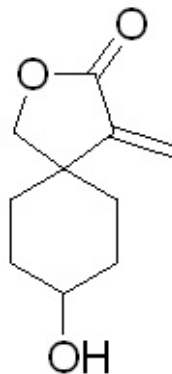
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	4096
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



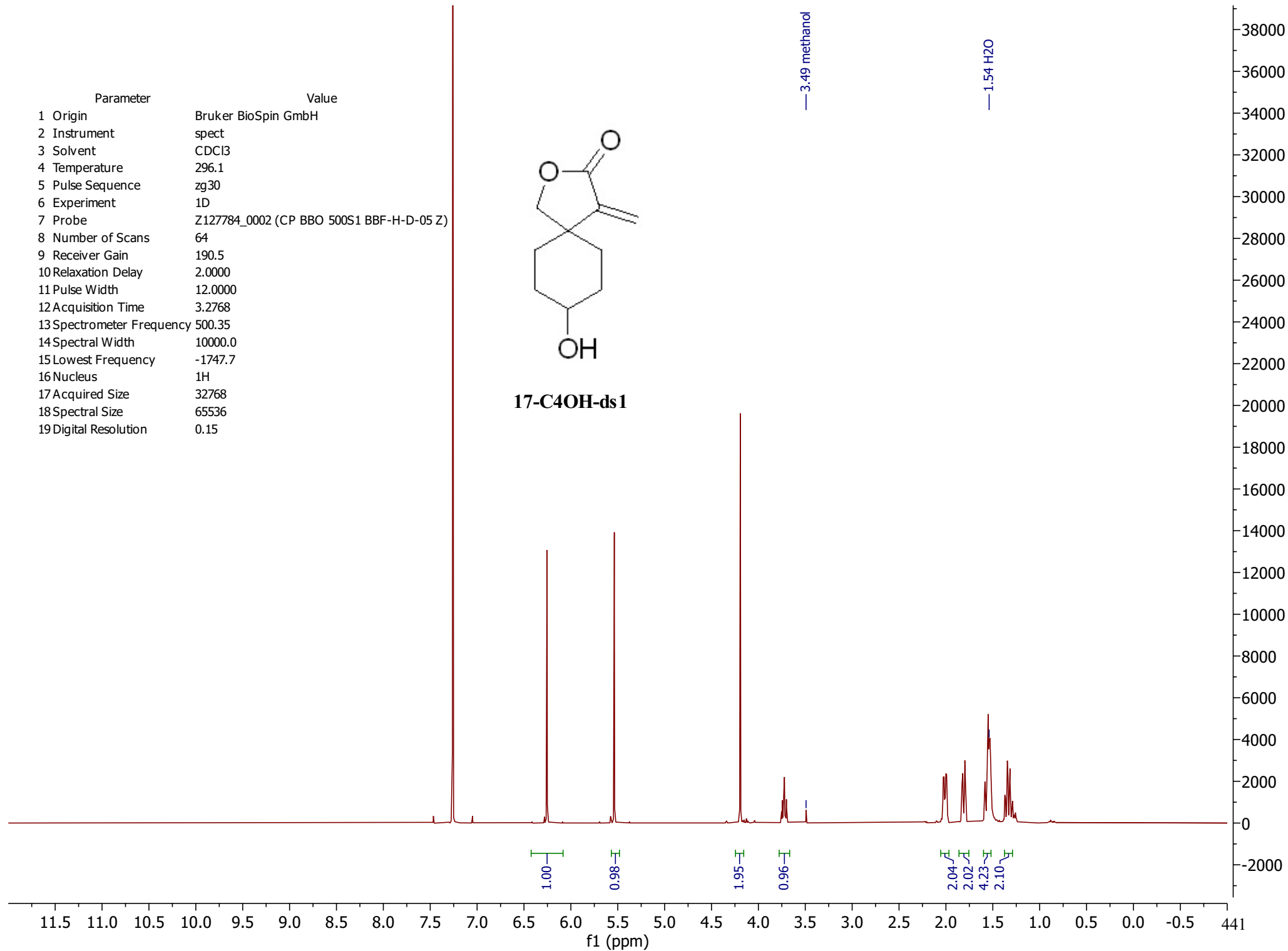
17-C3OH-ds2



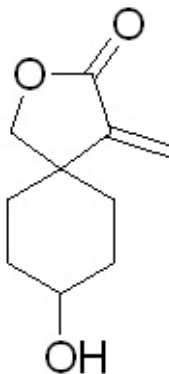
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



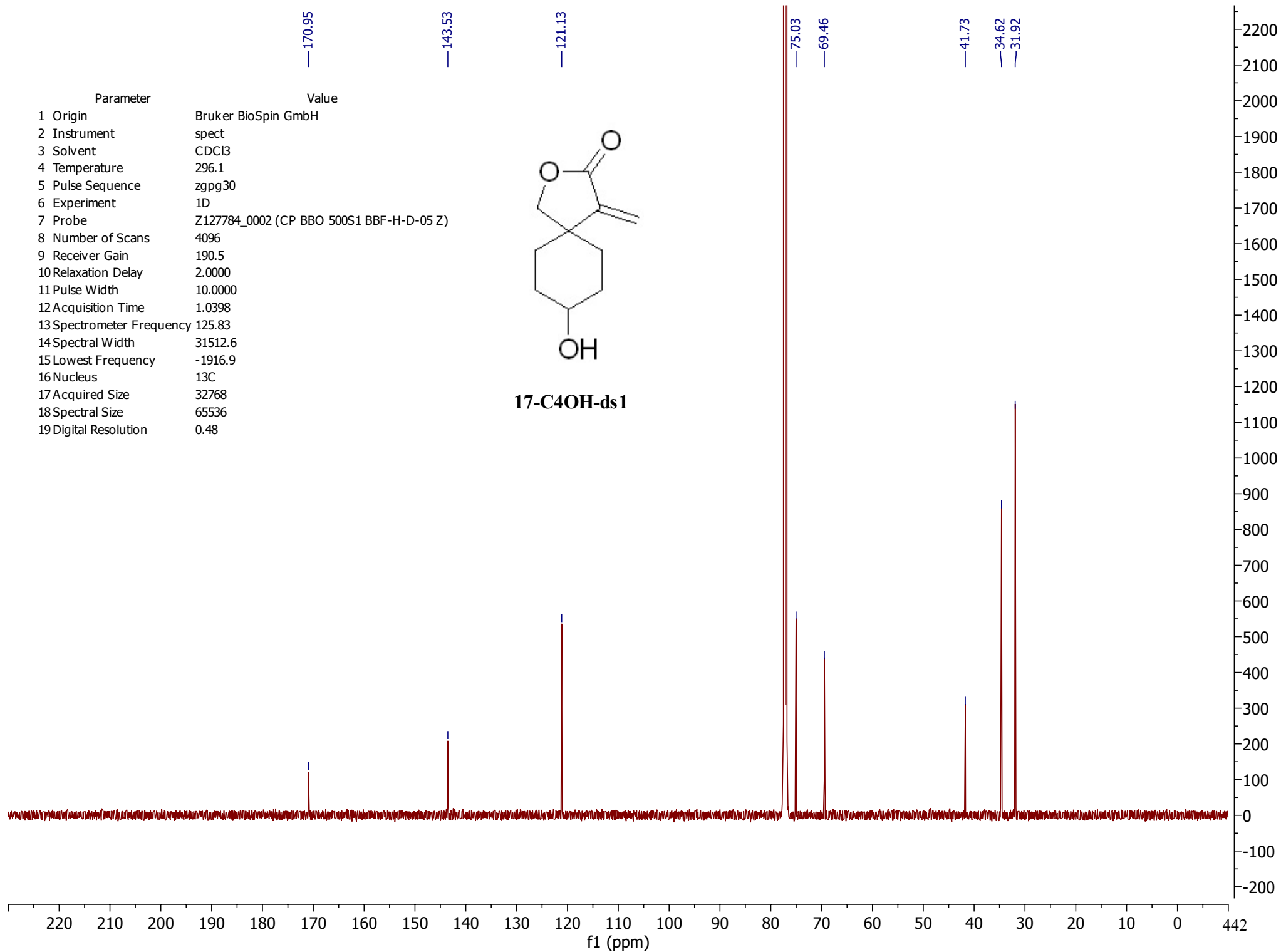
17-C4OH-ds1



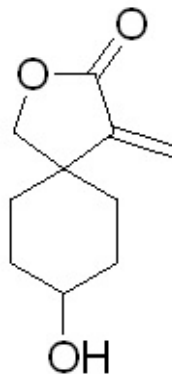
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	4096
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



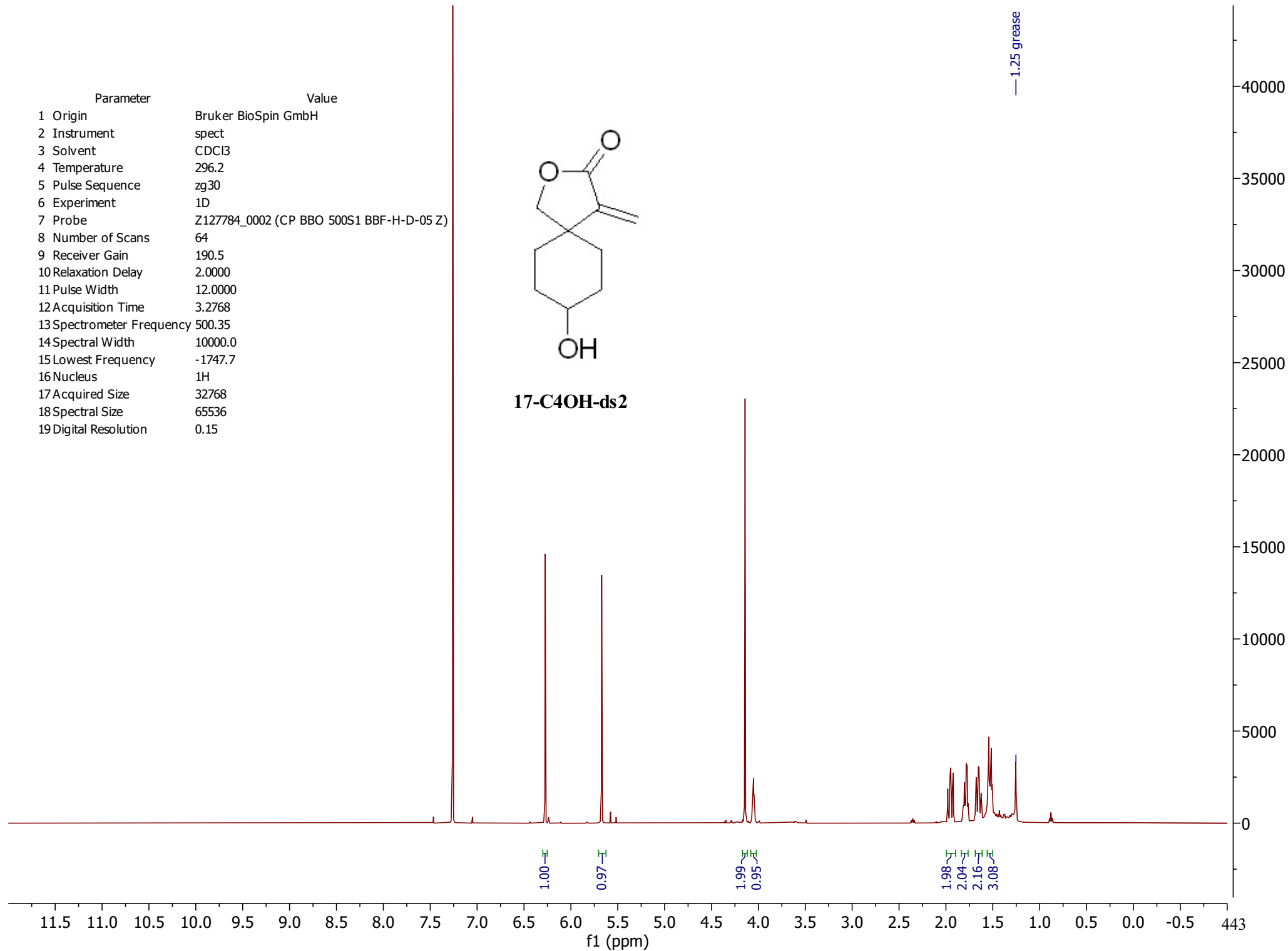
17-C4OH-ds1



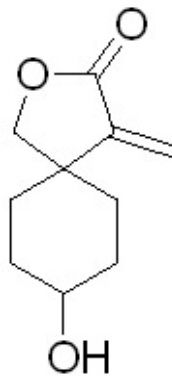
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



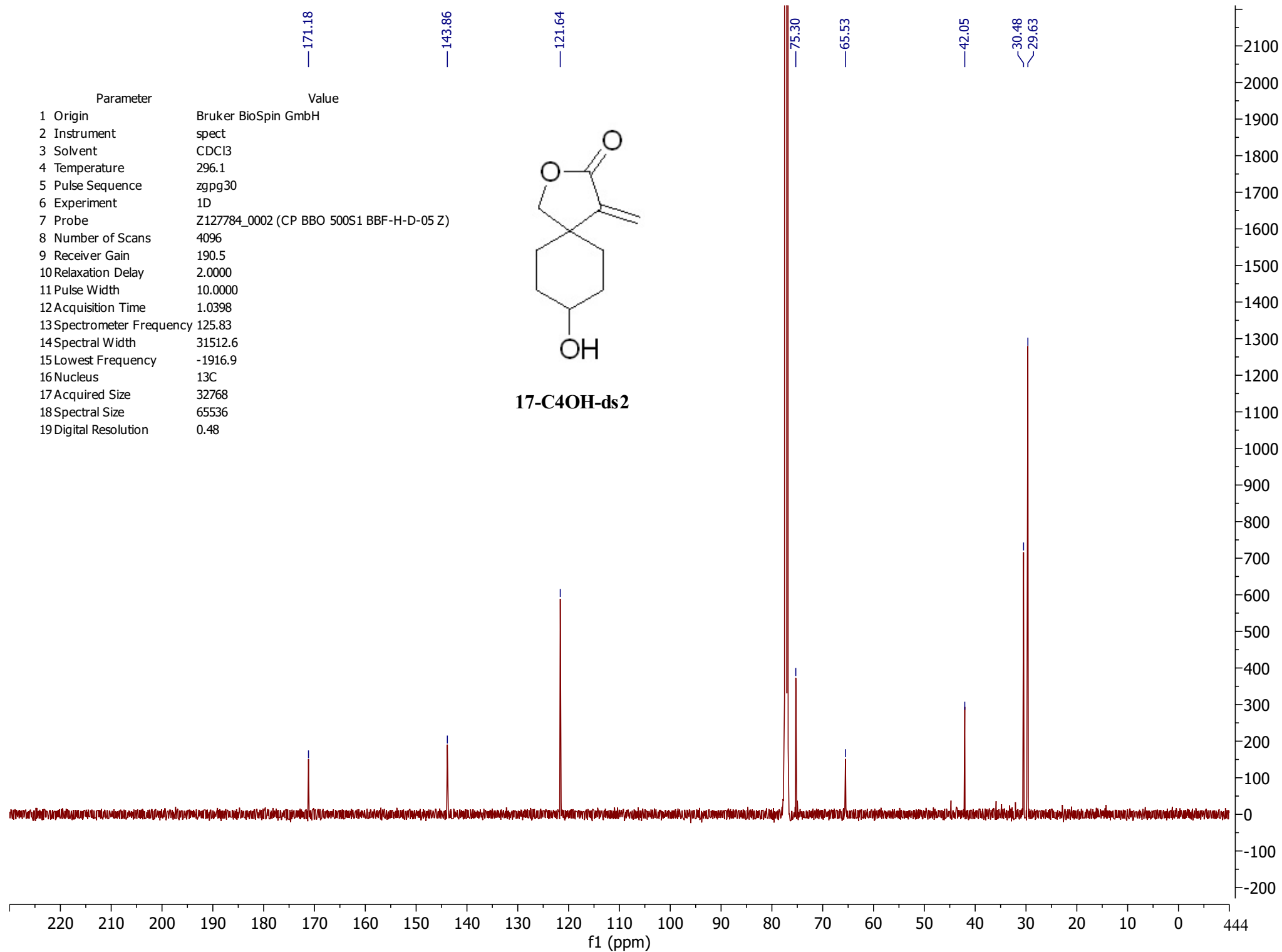
17-C4OH-ds2



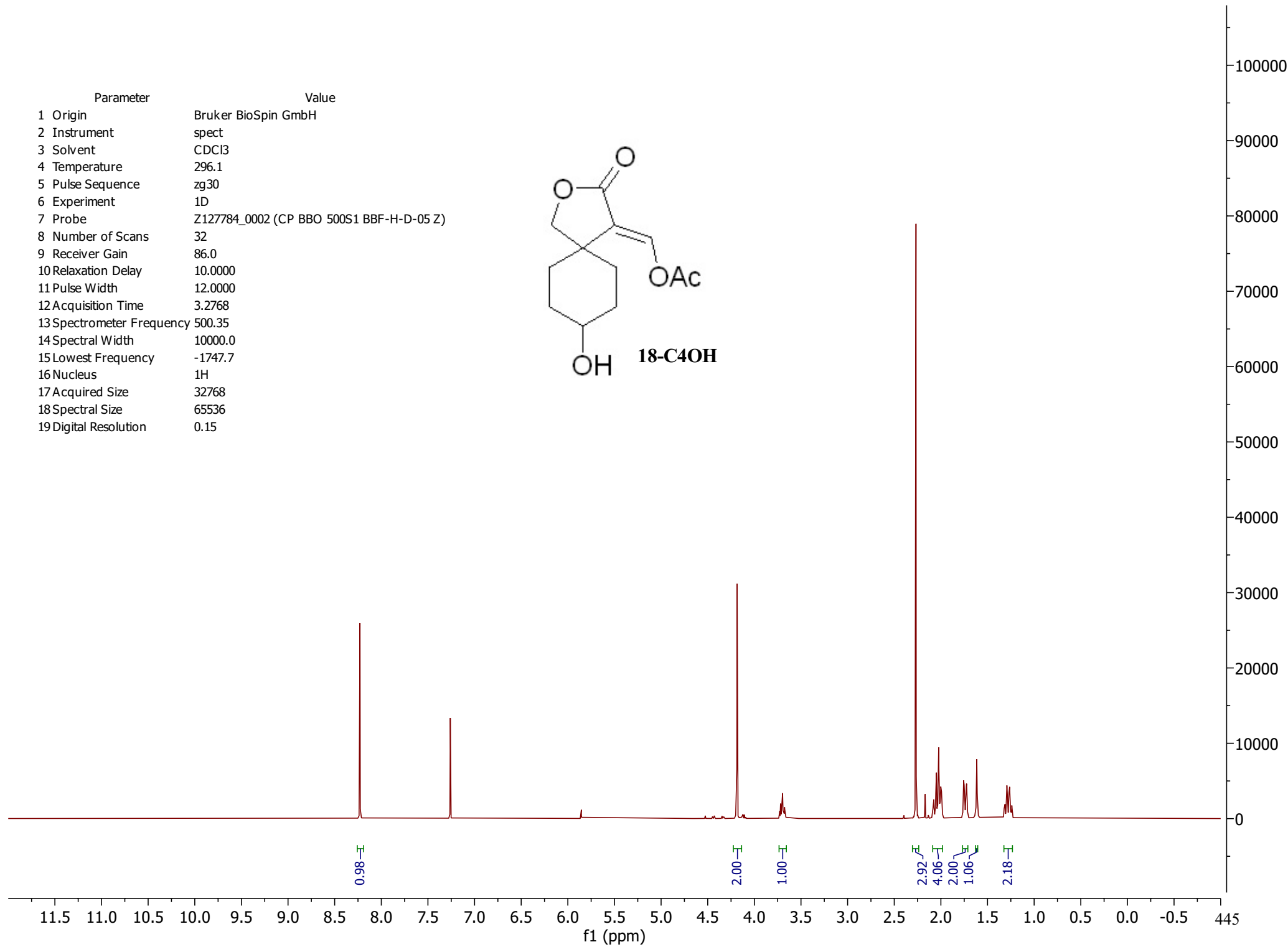
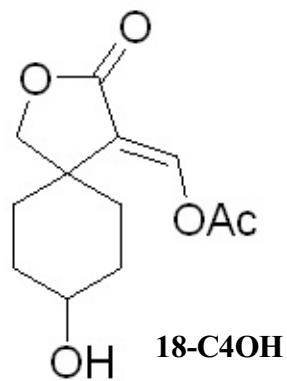
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	4096
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



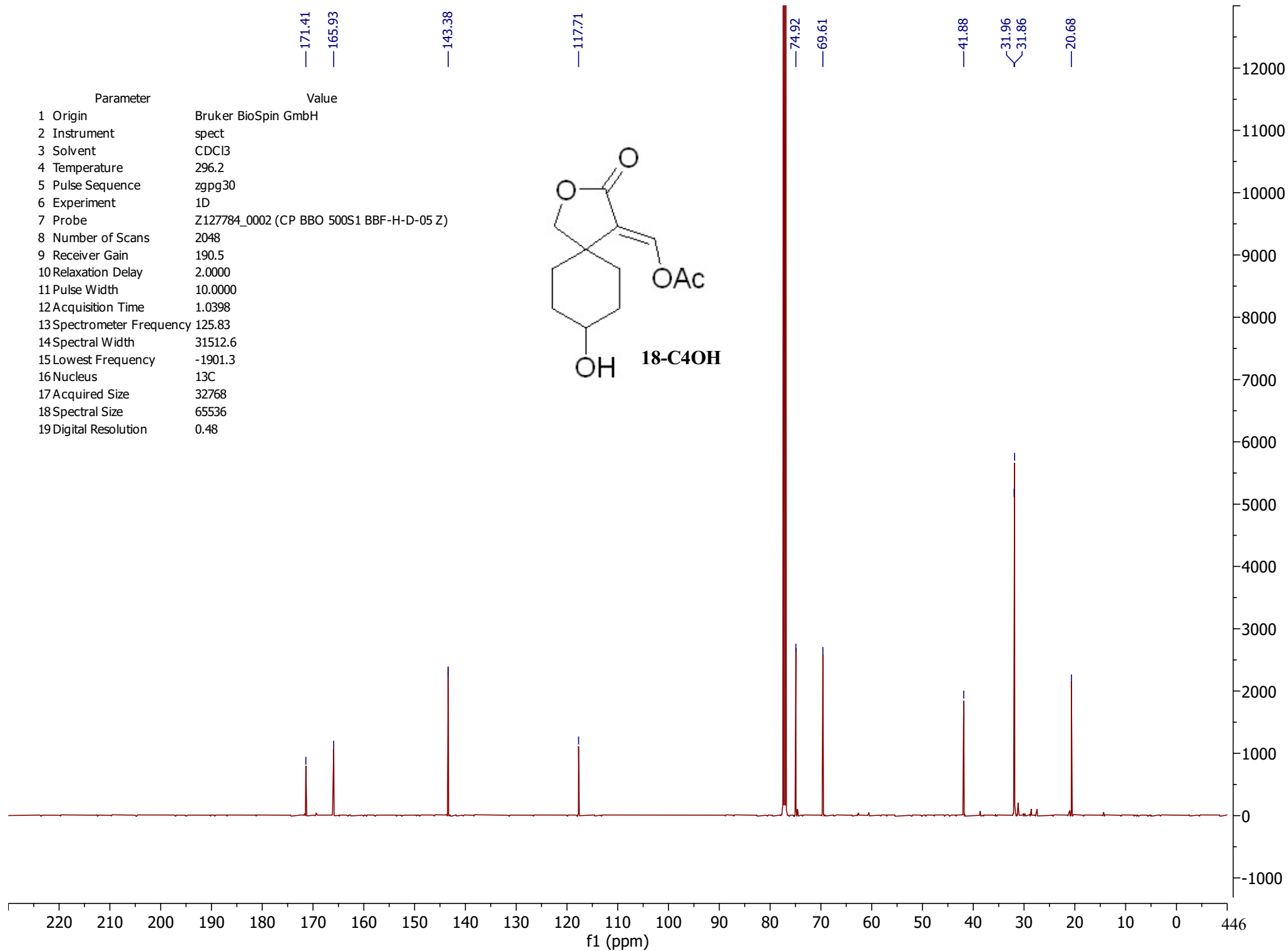
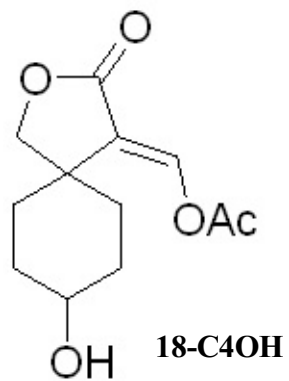
17-C4OH-ds2



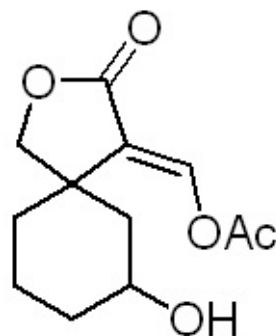
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



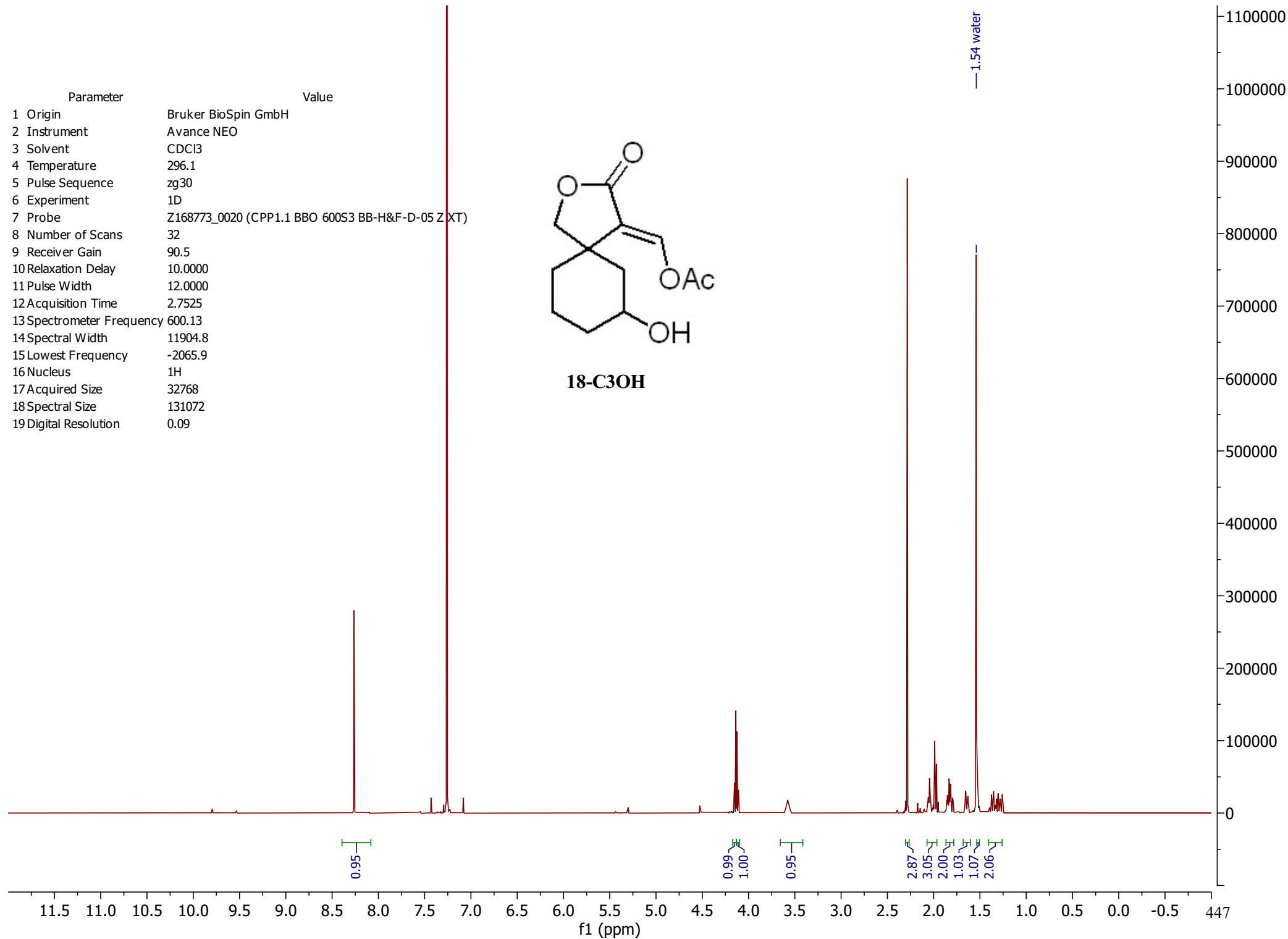
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1901.3
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



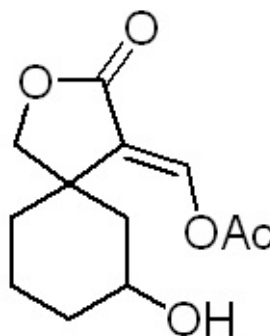
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	90.5
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2065.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



18-C3OH

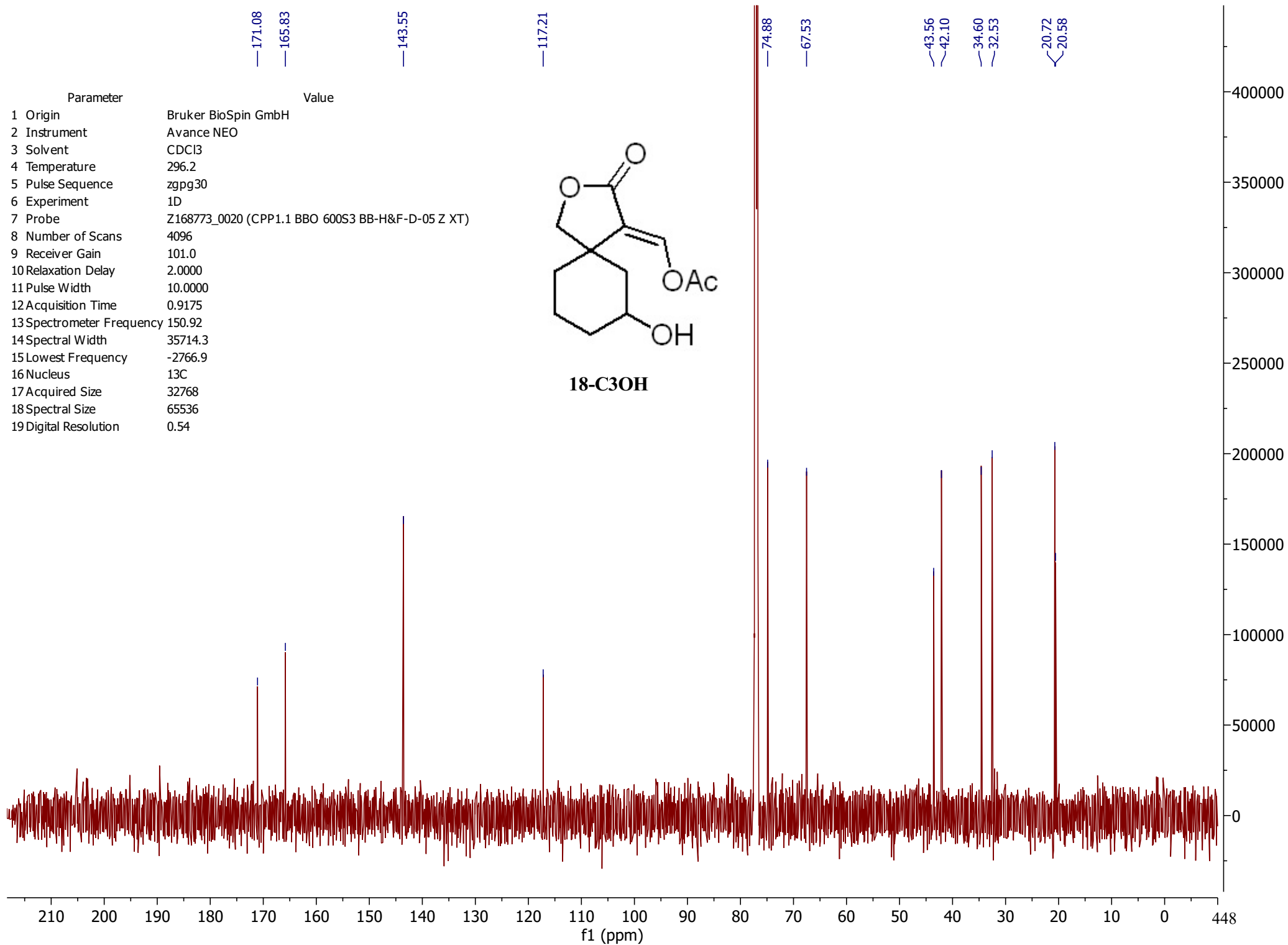


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4096
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.9175
13 Spectrometer Frequency	150.92
14 Spectral Width	35714.3
15 Lowest Frequency	-2766.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.54

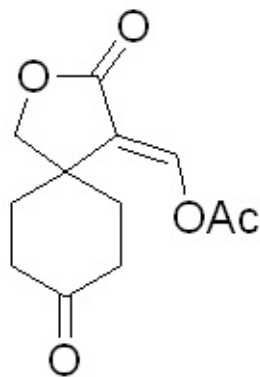


18-C3OH

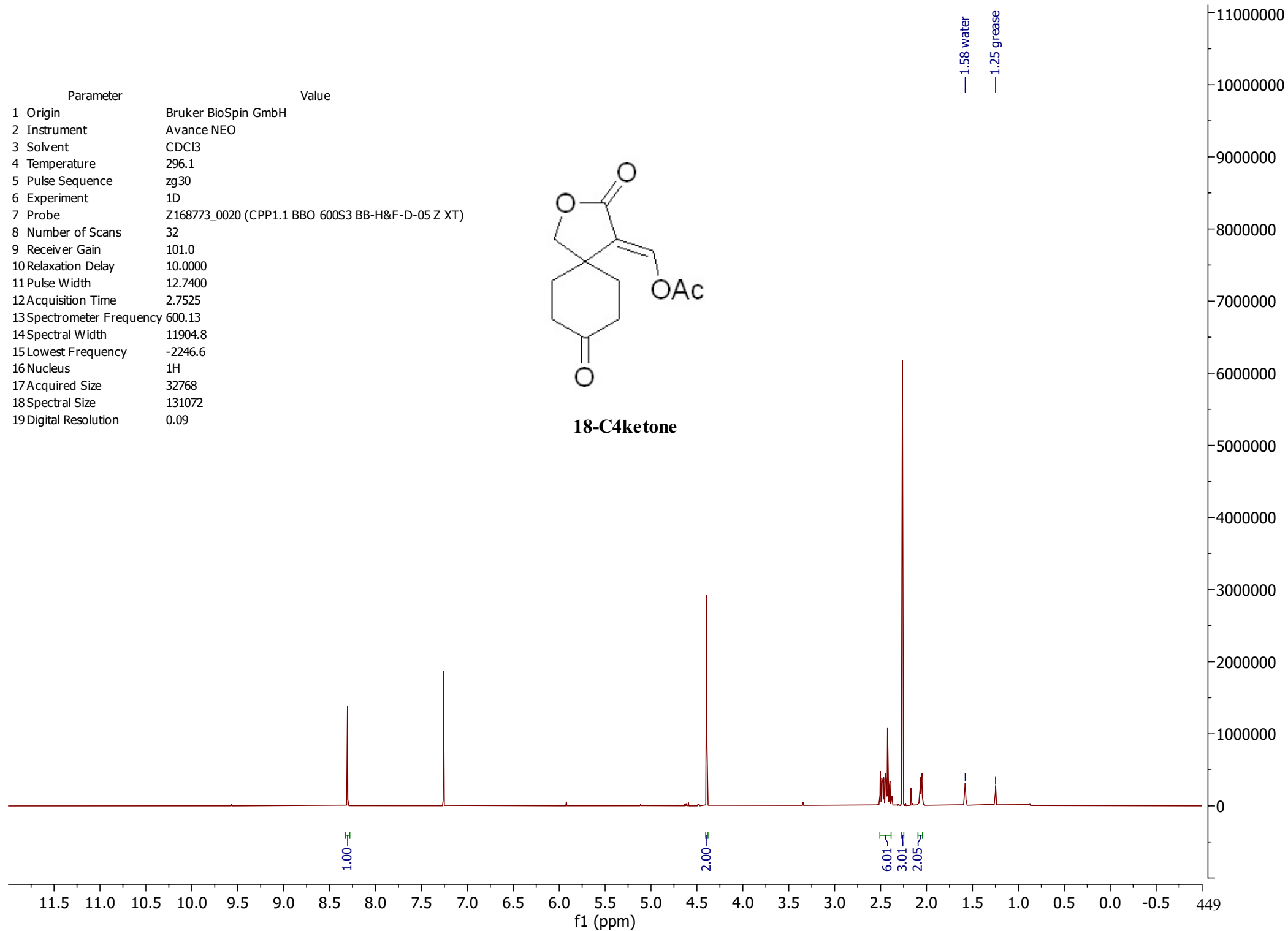
¹³C NMR chemical shifts (ppm): 171.08, 165.83, 143.55, 117.21, 74.88, 67.53, 43.56, 42.10, 34.60, 32.53, 20.72, 20.58.

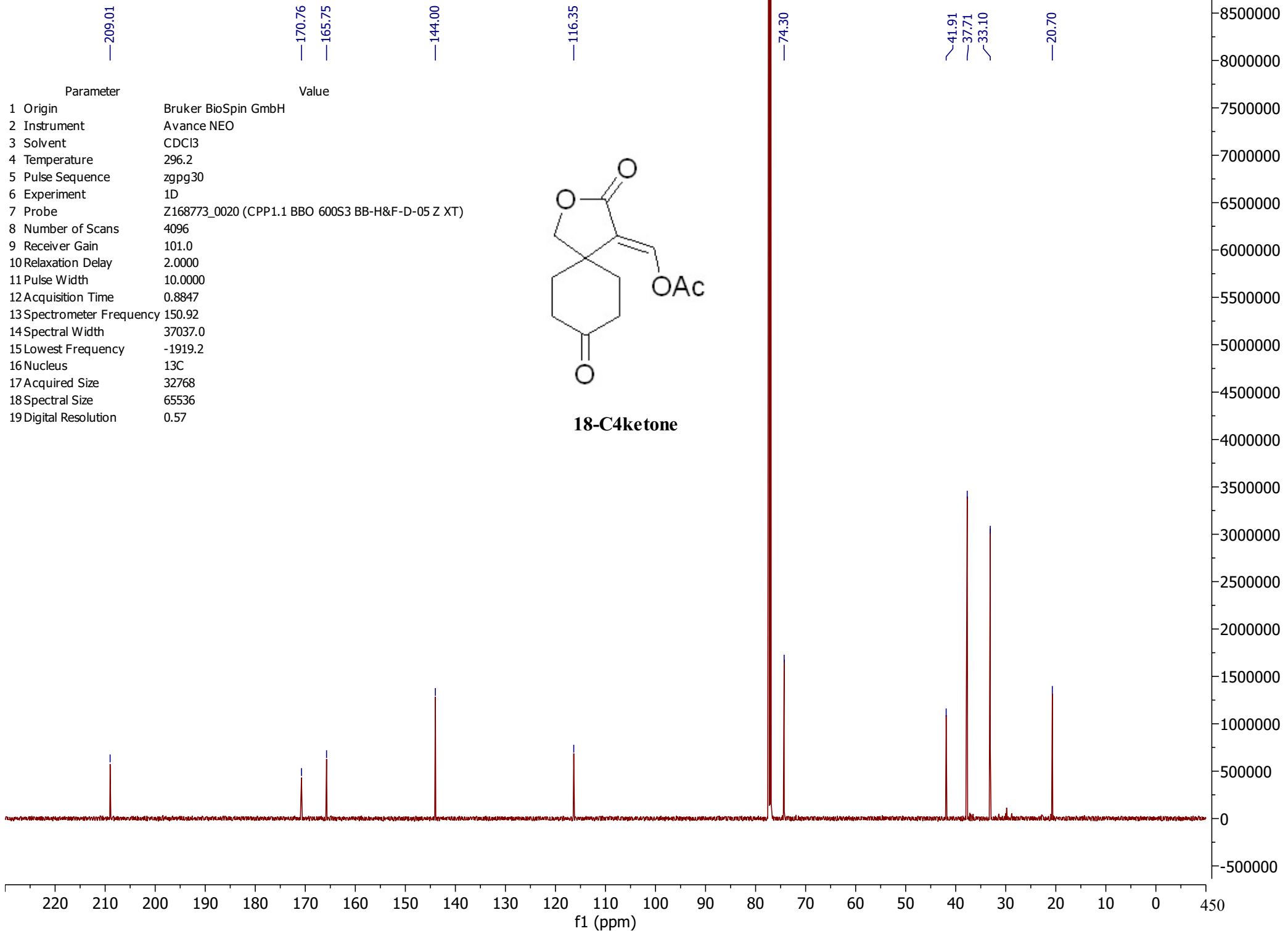


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.7400
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



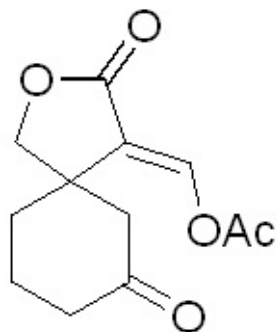
18-C4ketone



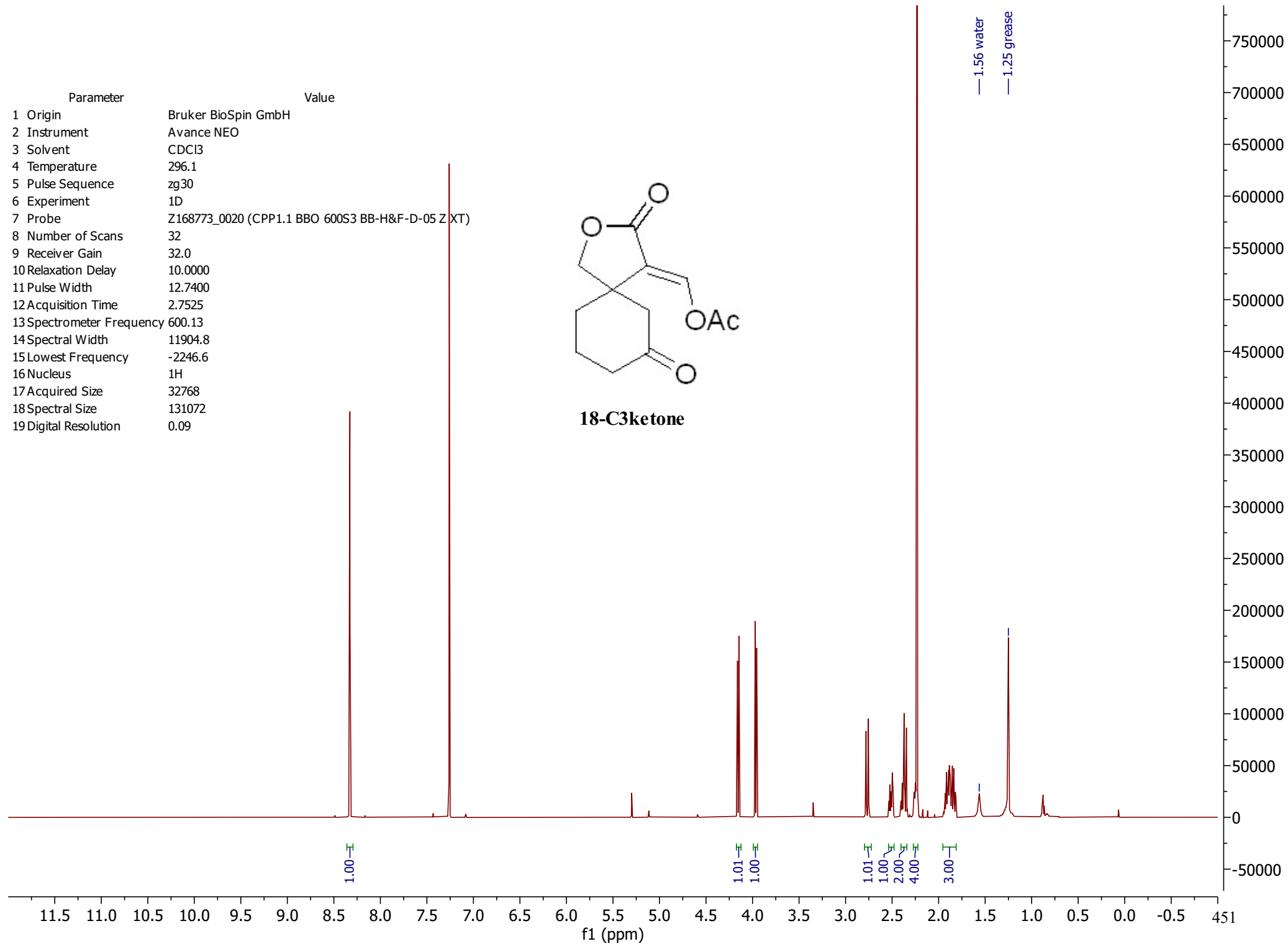


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4096
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1919.2
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57

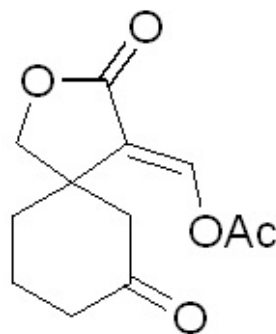
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.7400
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



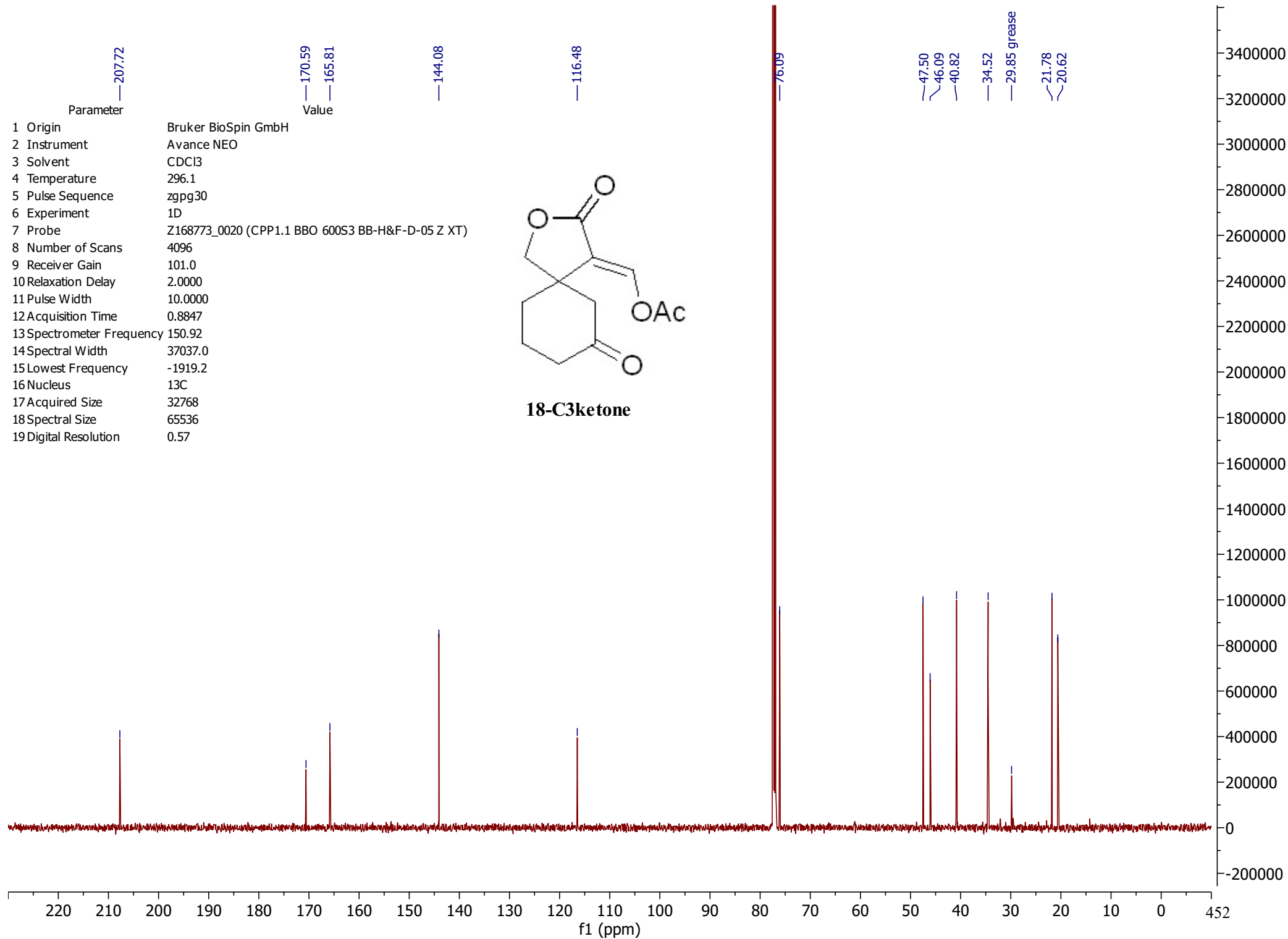
18-C3ketone



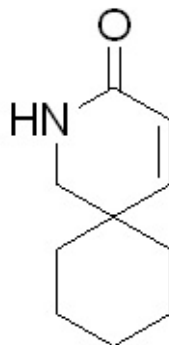
1	Origin	Bruker BioSpin GmbH
2	Instrument	Avance NEO
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8	Number of Scans	4096
9	Receiver Gain	101.0
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	0.8847
13	Spectrometer Frequency	150.92
14	Spectral Width	37037.0
15	Lowest Frequency	-1919.2
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536
19	Digital Resolution	0.57



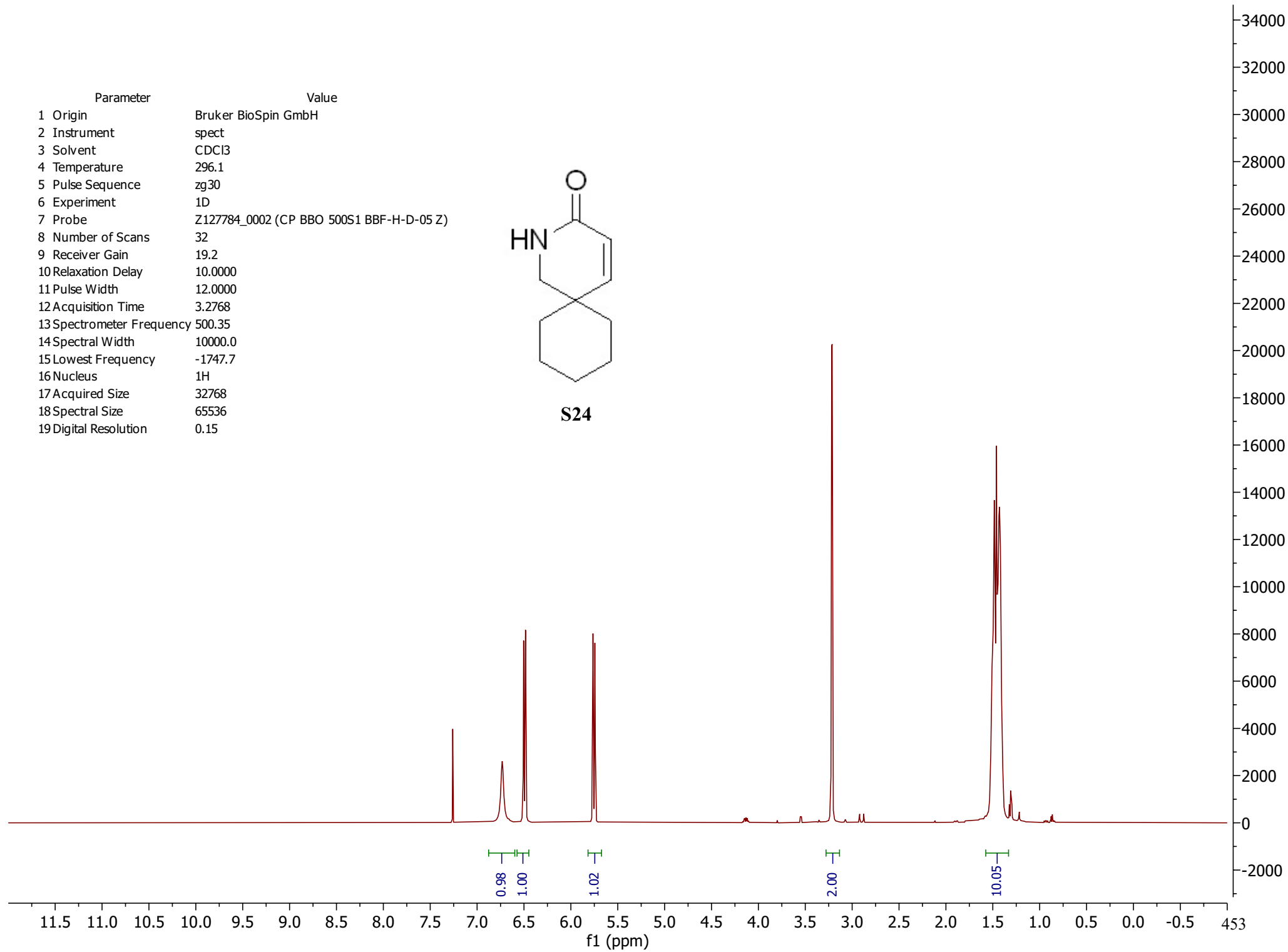
18-C3ketone



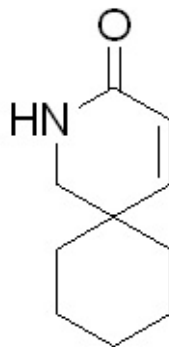
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	19.2
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



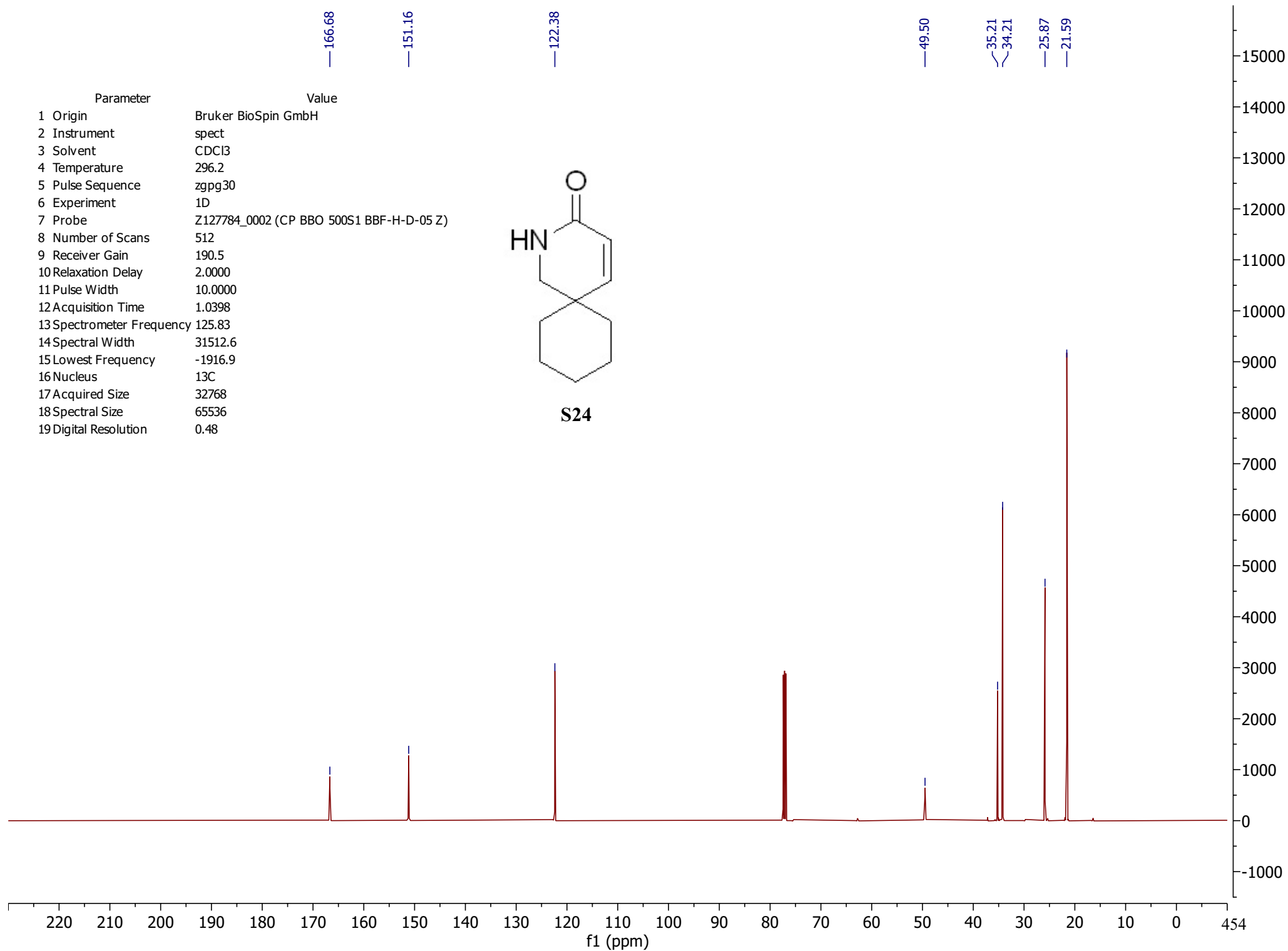
S24



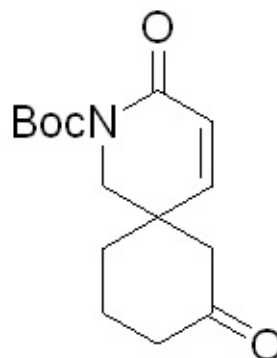
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	512
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



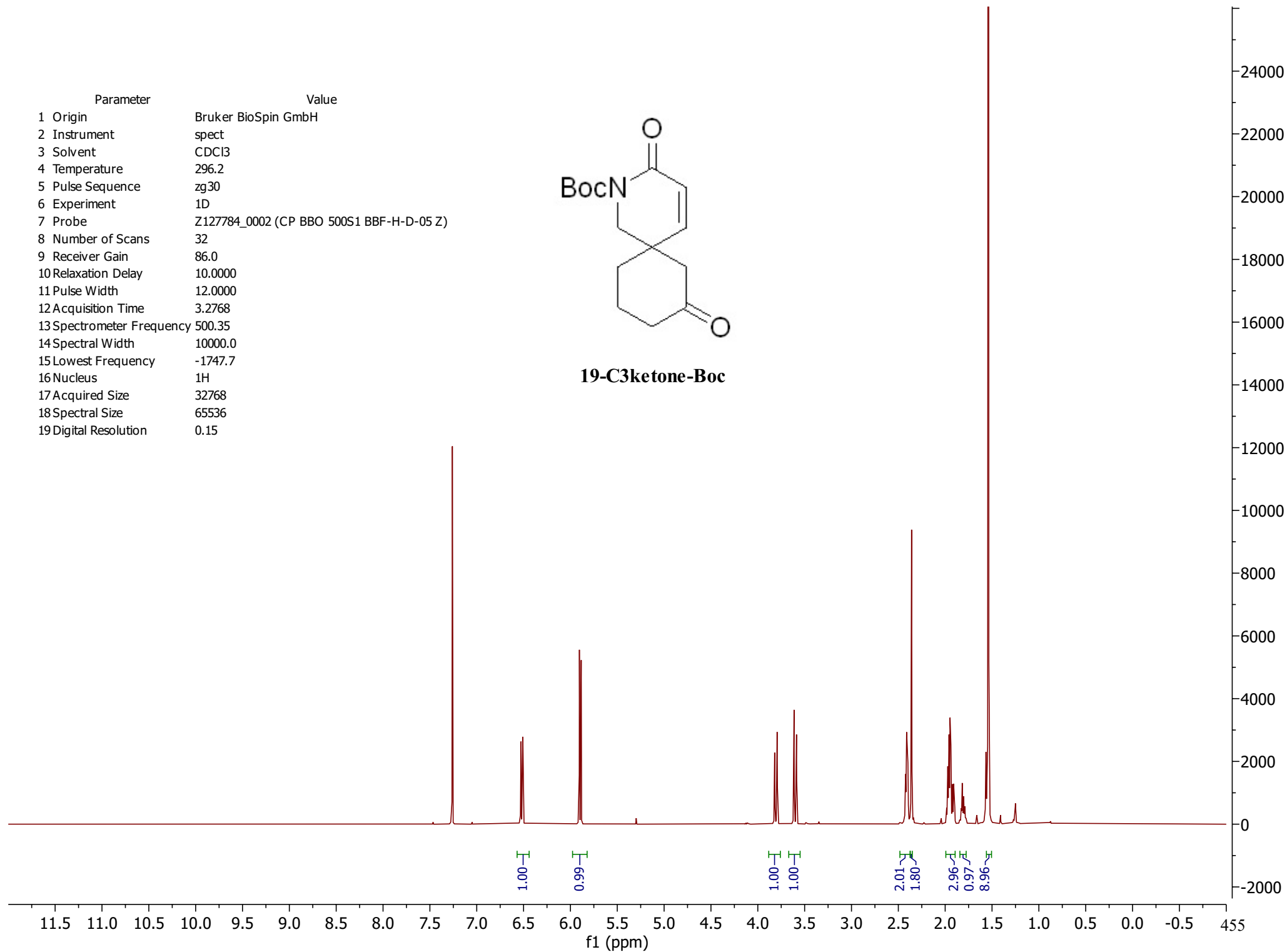
S24

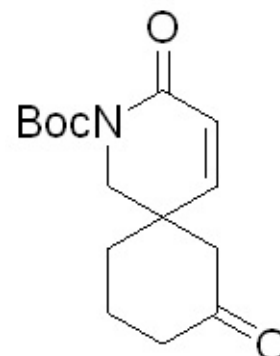


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

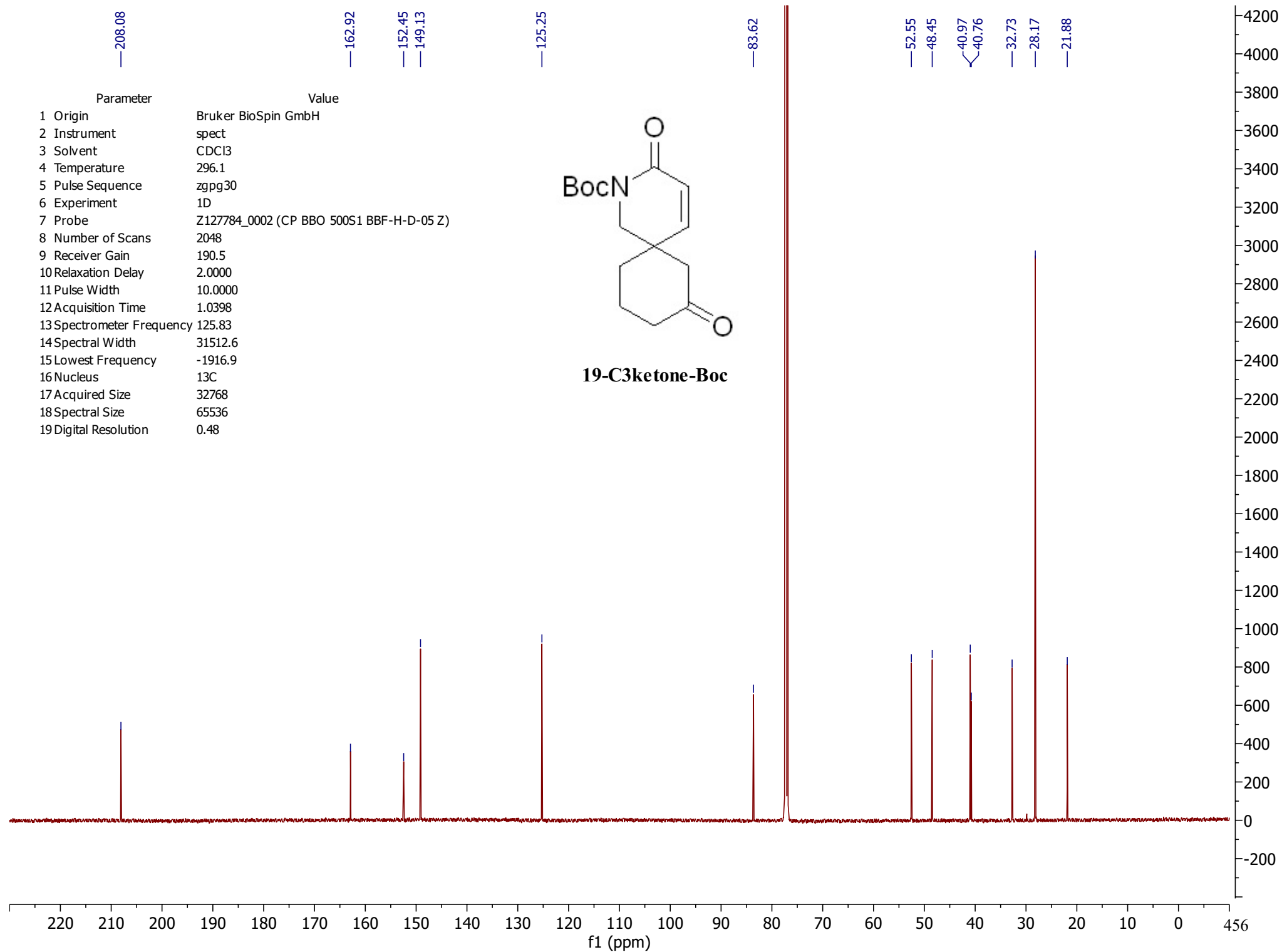


19-C3ketone-Boc

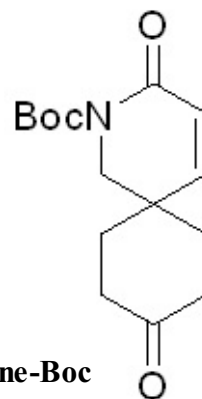




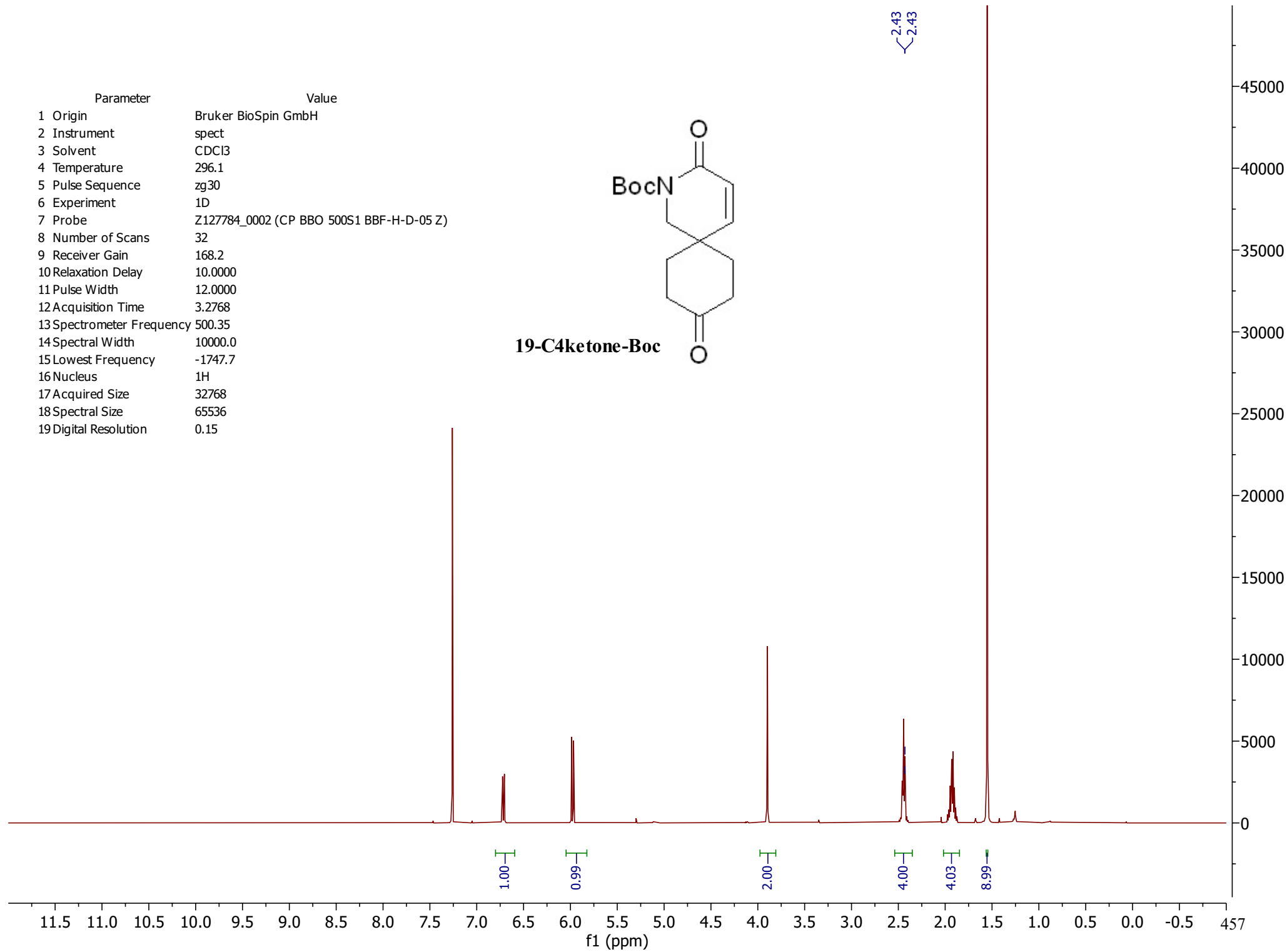
19-C3ketone-Boc



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	168.2
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

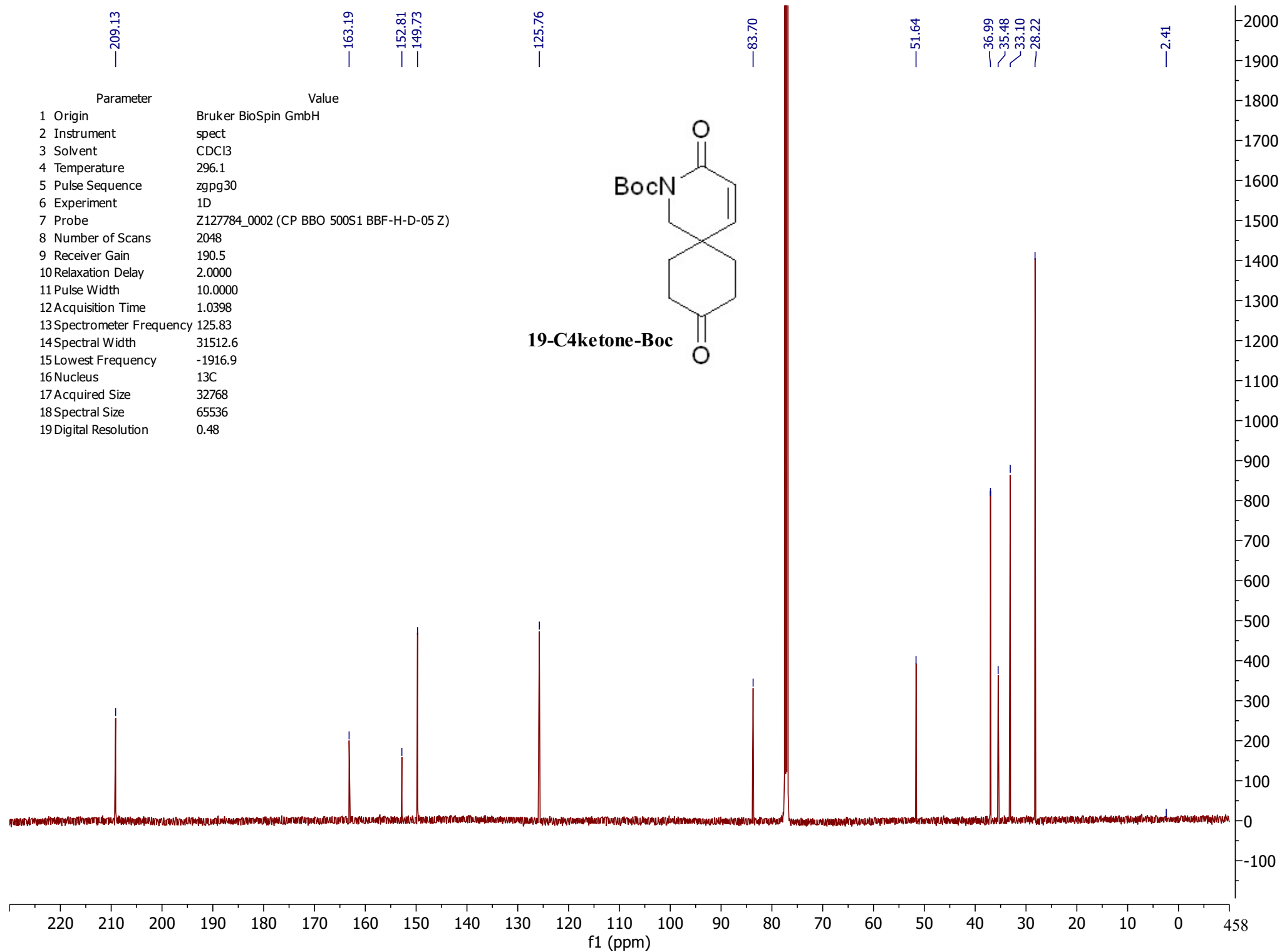
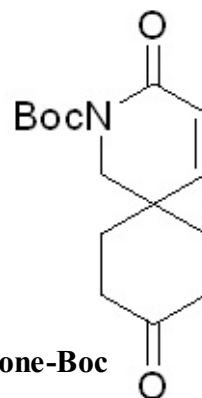


19-C4ketone-Boc

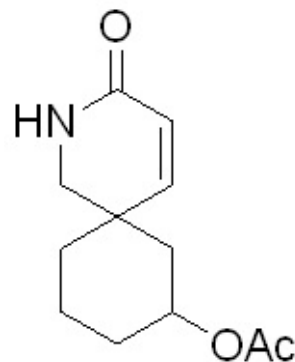


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

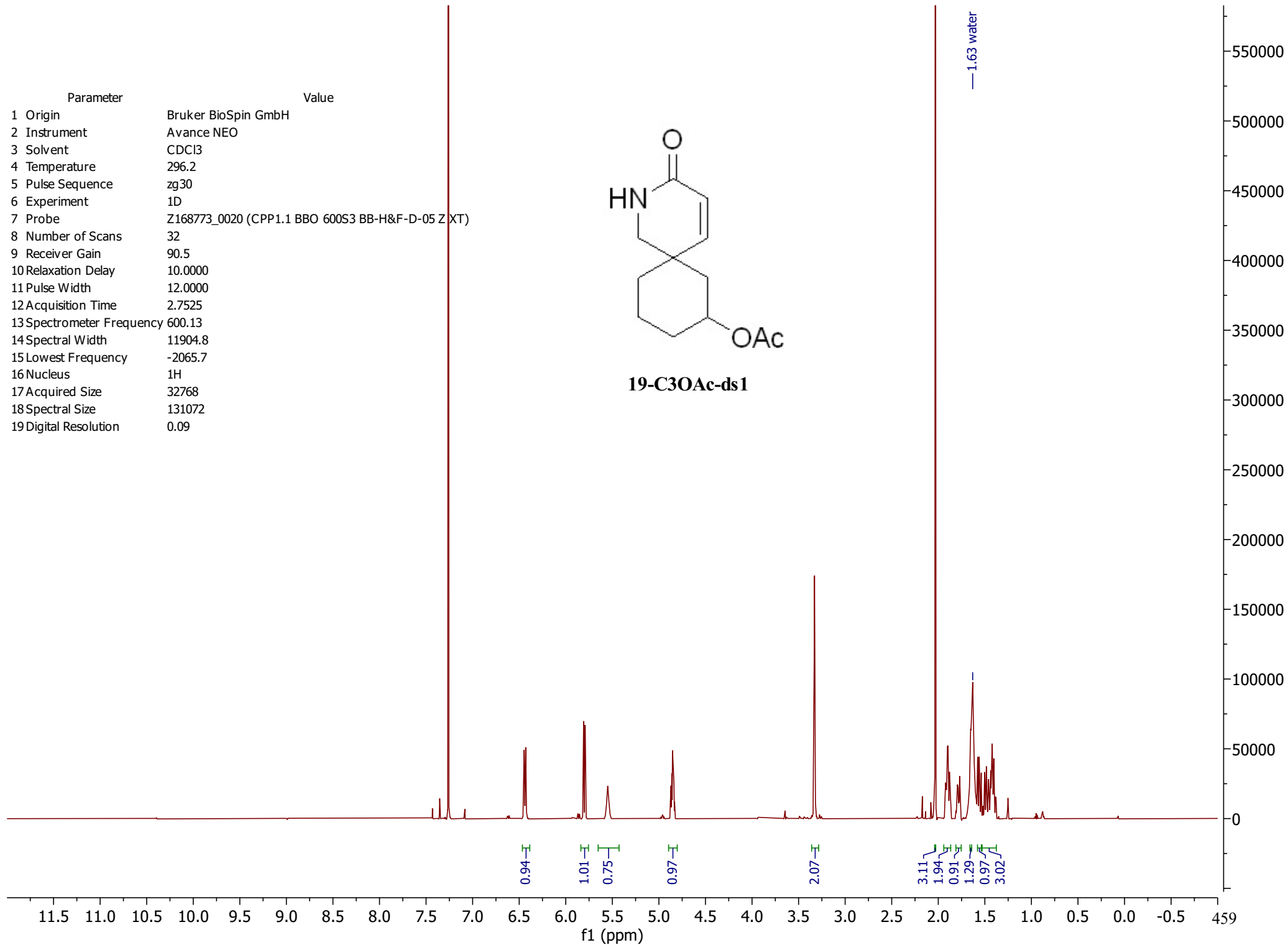
19-C4ketone-Boc



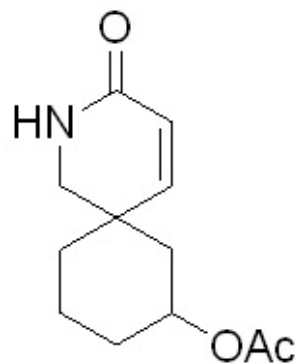
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	90.5
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2065.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



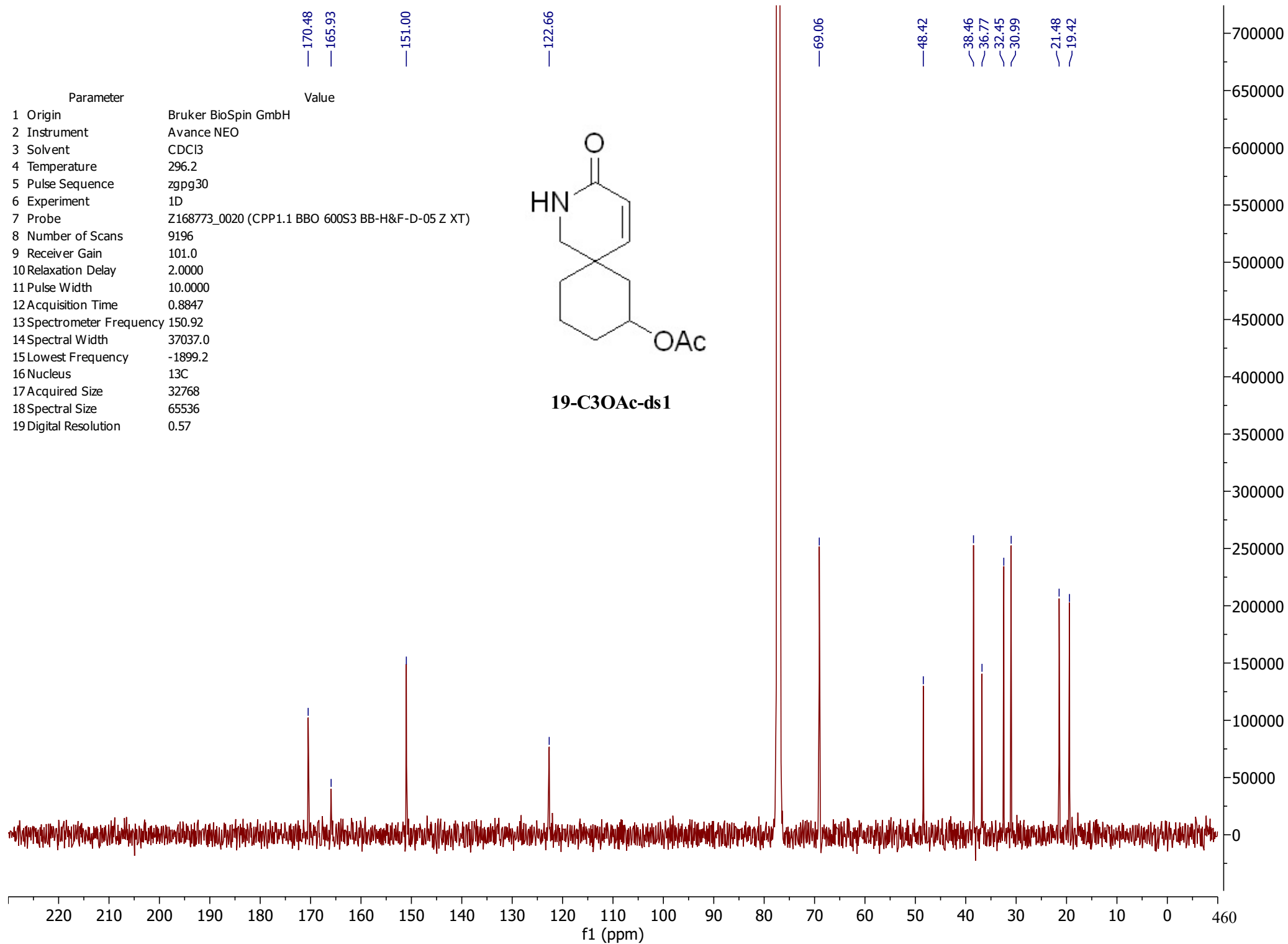
19-C3OAc-ds1



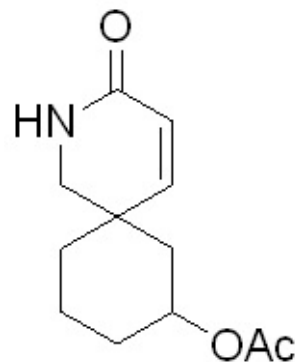
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	9196
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1899.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



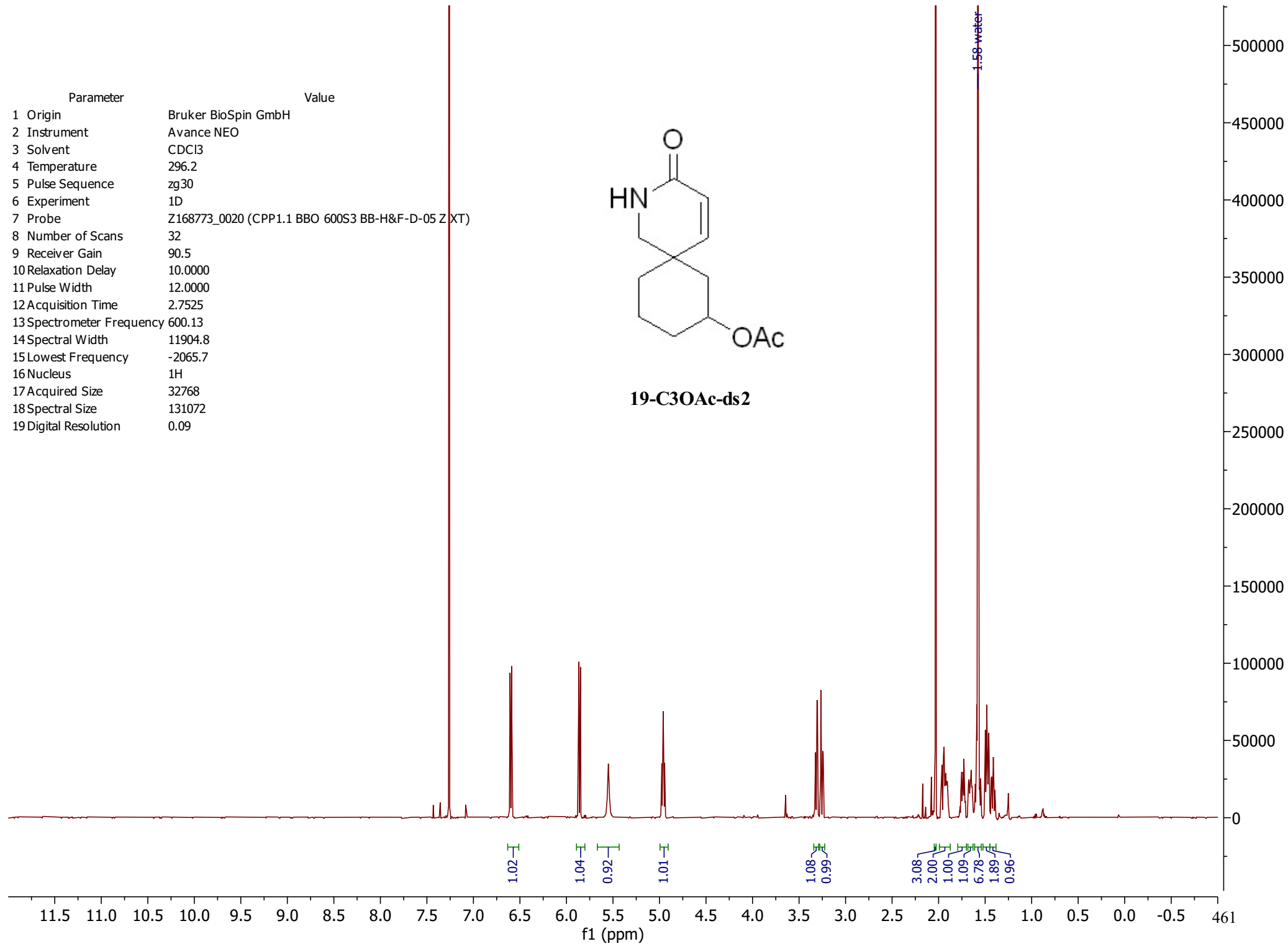
19-C3OAc-ds1



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	90.5
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2065.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

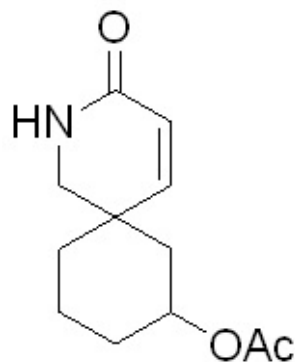


19-C3OAc-ds2

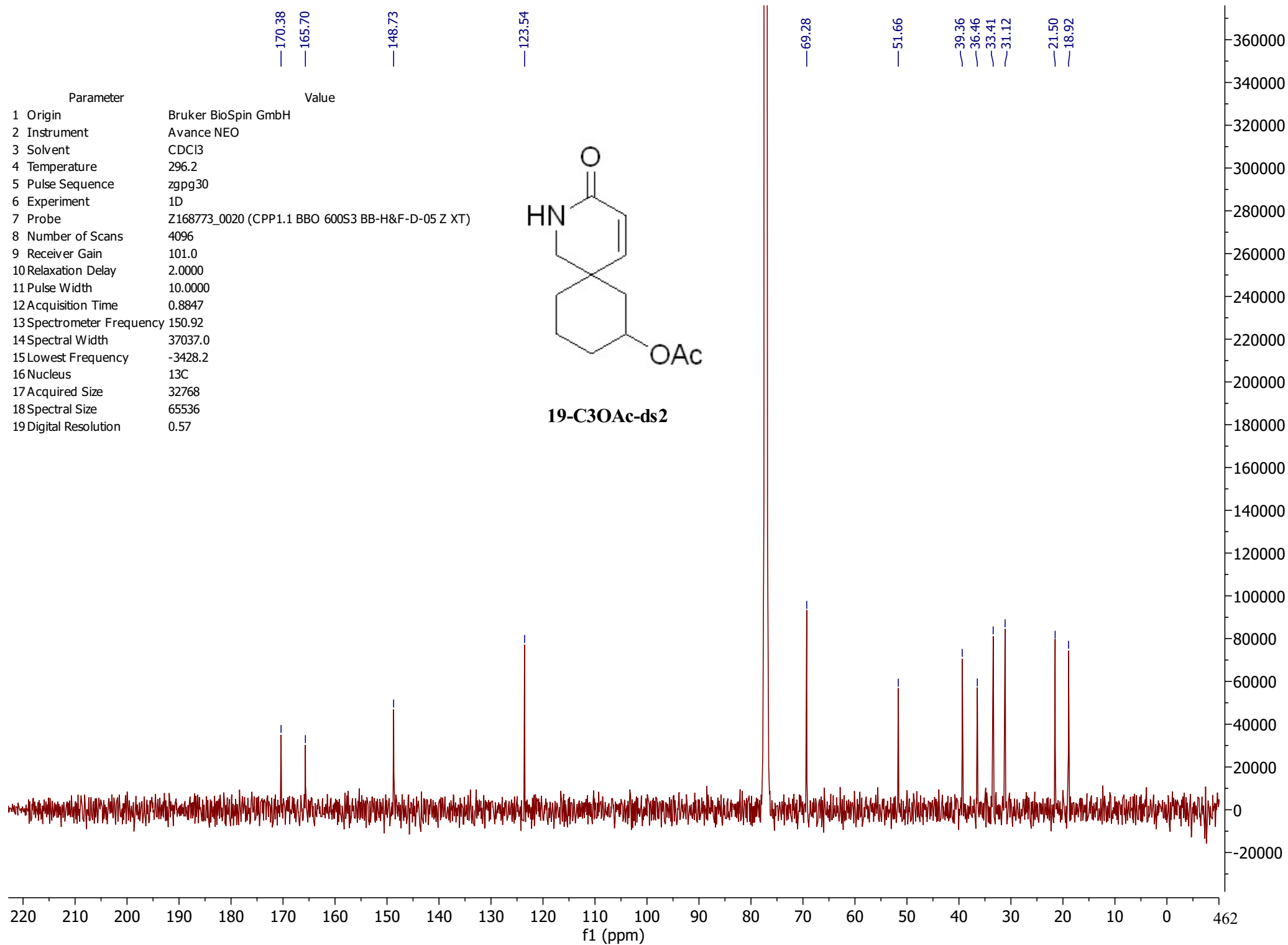


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4096
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-3428.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57

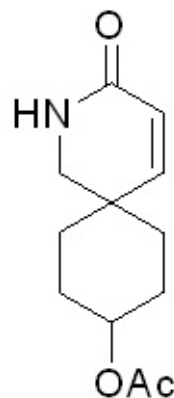
—	170.38
—	165.70
—	148.73
—	123.54
—	69.28
—	51.66
—	39.36
—	36.46
—	33.41
—	31.12
—	21.50
—	18.92



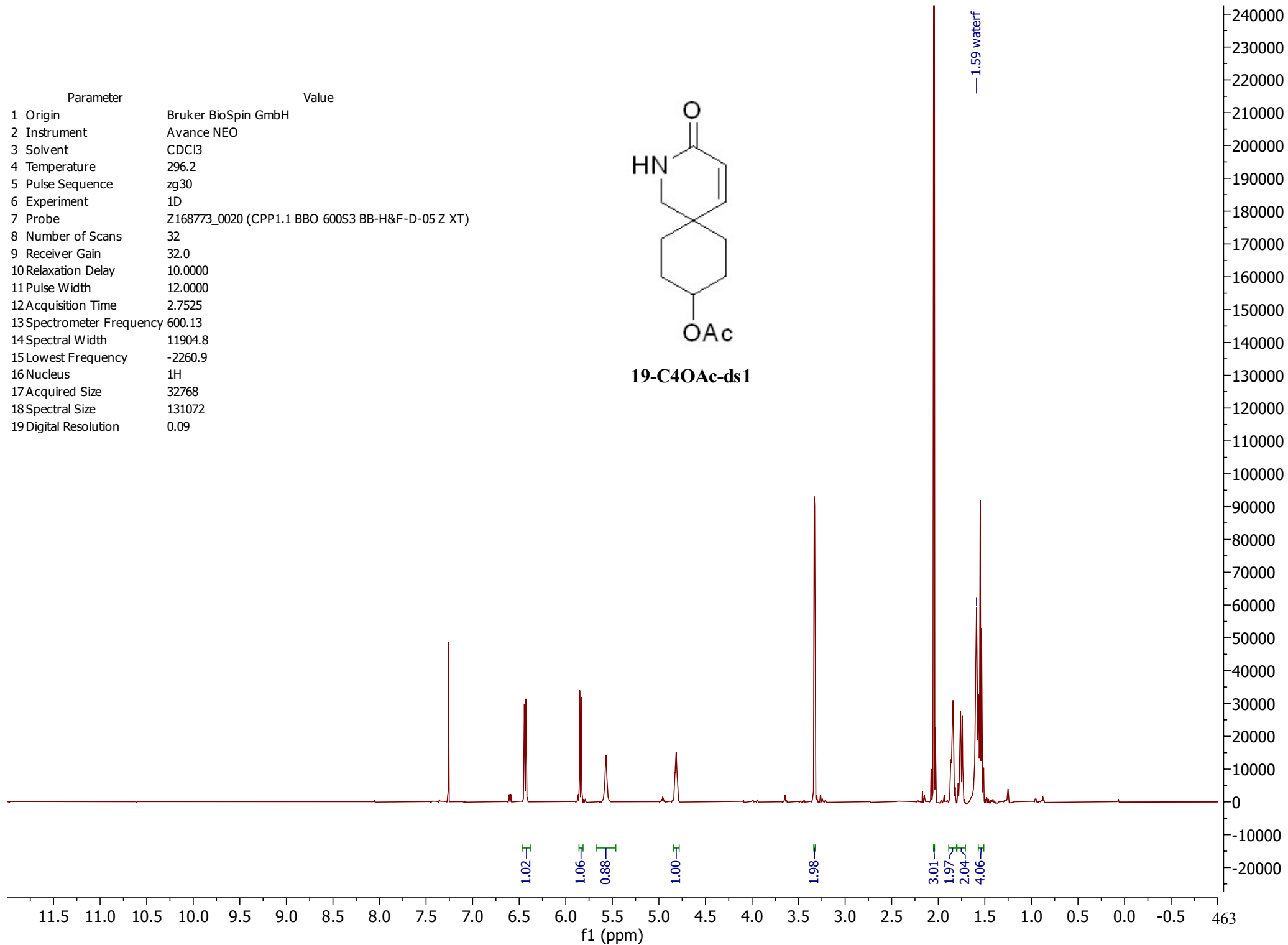
19-C3OAc-ds2



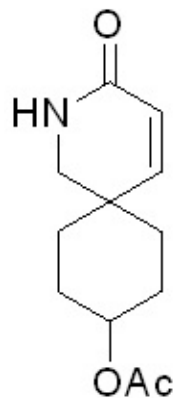
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



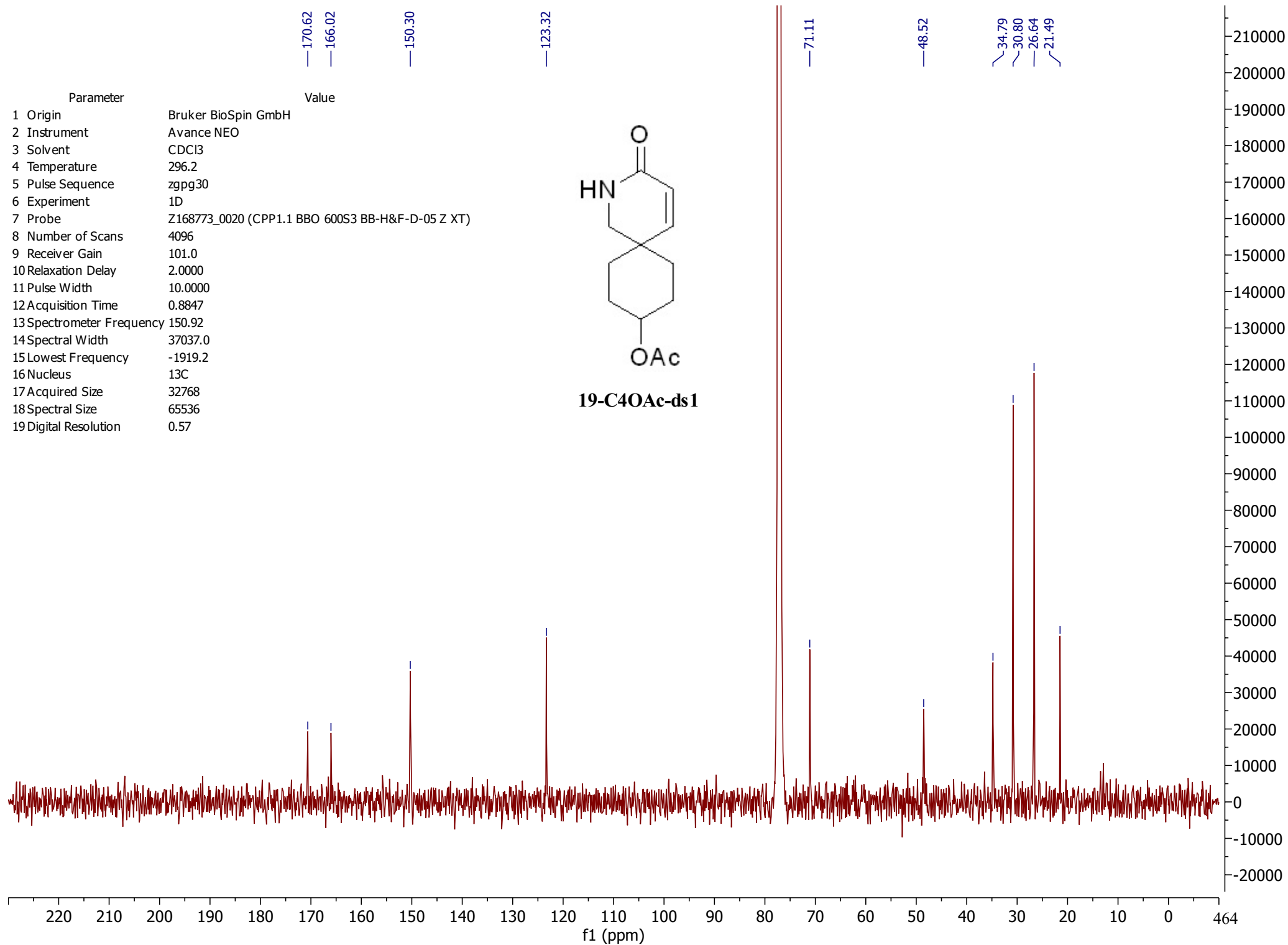
19-C4OAc-ds1



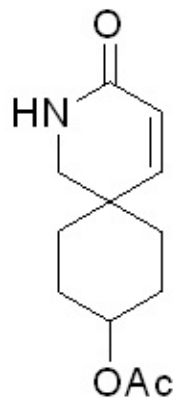
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4096
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1919.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



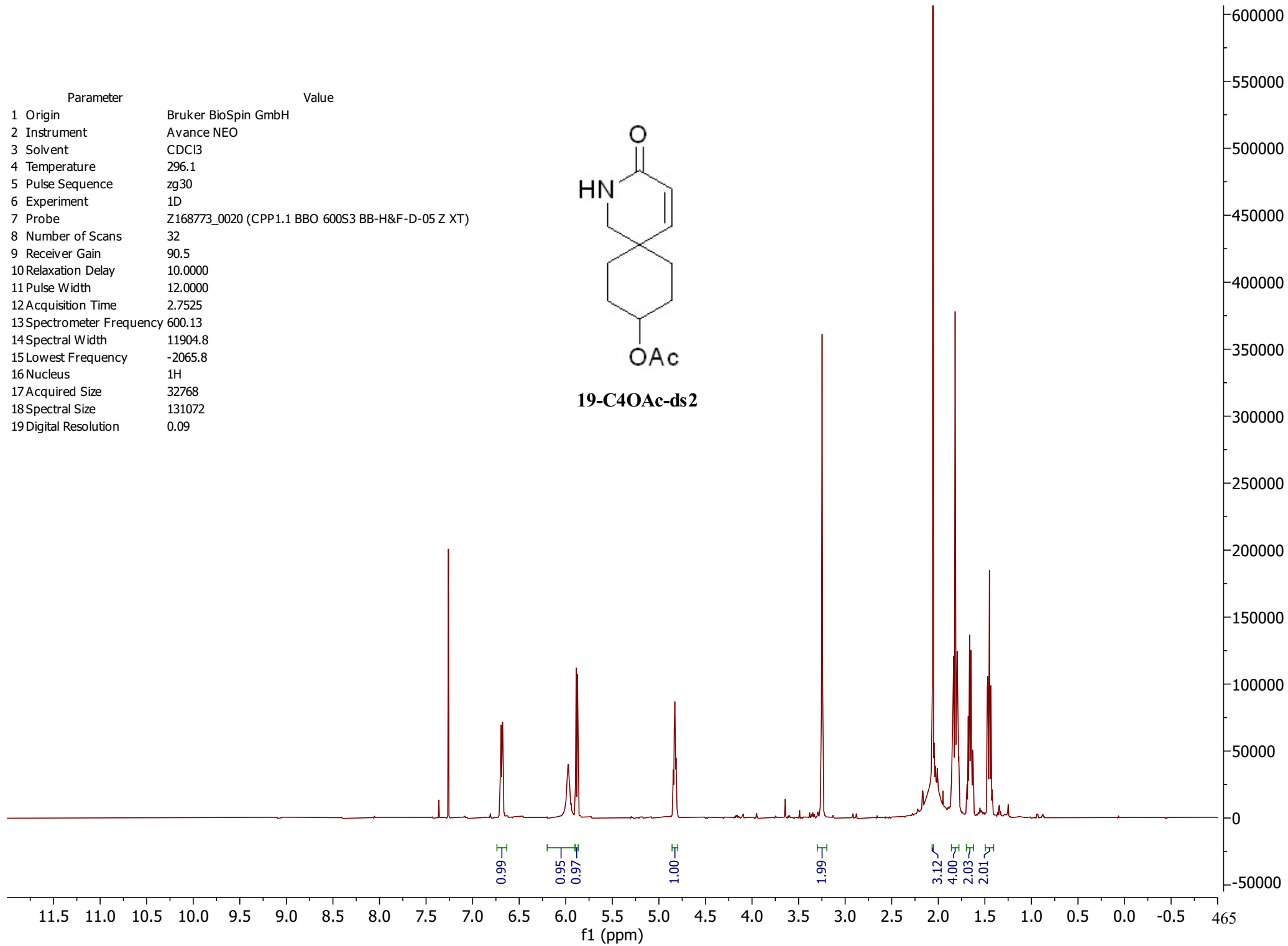
19-C4OAc-ds1



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	90.5
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2065.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



19-C4OAc-ds2



1 Origin Bruker BioSpin GmbH
 2 Instrument Avance NEO
 3 Solvent CDCl₃
 4 Temperature 296.2
 5 Pulse Sequence zgpg30
 6 Experiment 1D
 7 Probe Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
 8 Number of Scans 4096
 9 Receiver Gain 101.0
 10 Relaxation Delay 2.5000
 11 Pulse Width 10.0000
 12 Acquisition Time 0.8847
 13 Spectrometer Frequency 150.92
 14 Spectral Width 37037.0
 15 Lowest Frequency -1899.5
 16 Nucleus ¹³C
 17 Acquired Size 32768
 18 Spectral Size 65536
 19 Digital Resolution 0.57

Parameter Value
 170.65
 166.21

149.72

122.86

70.93

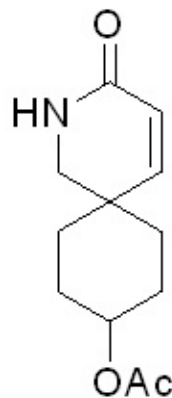
50.31

34.61

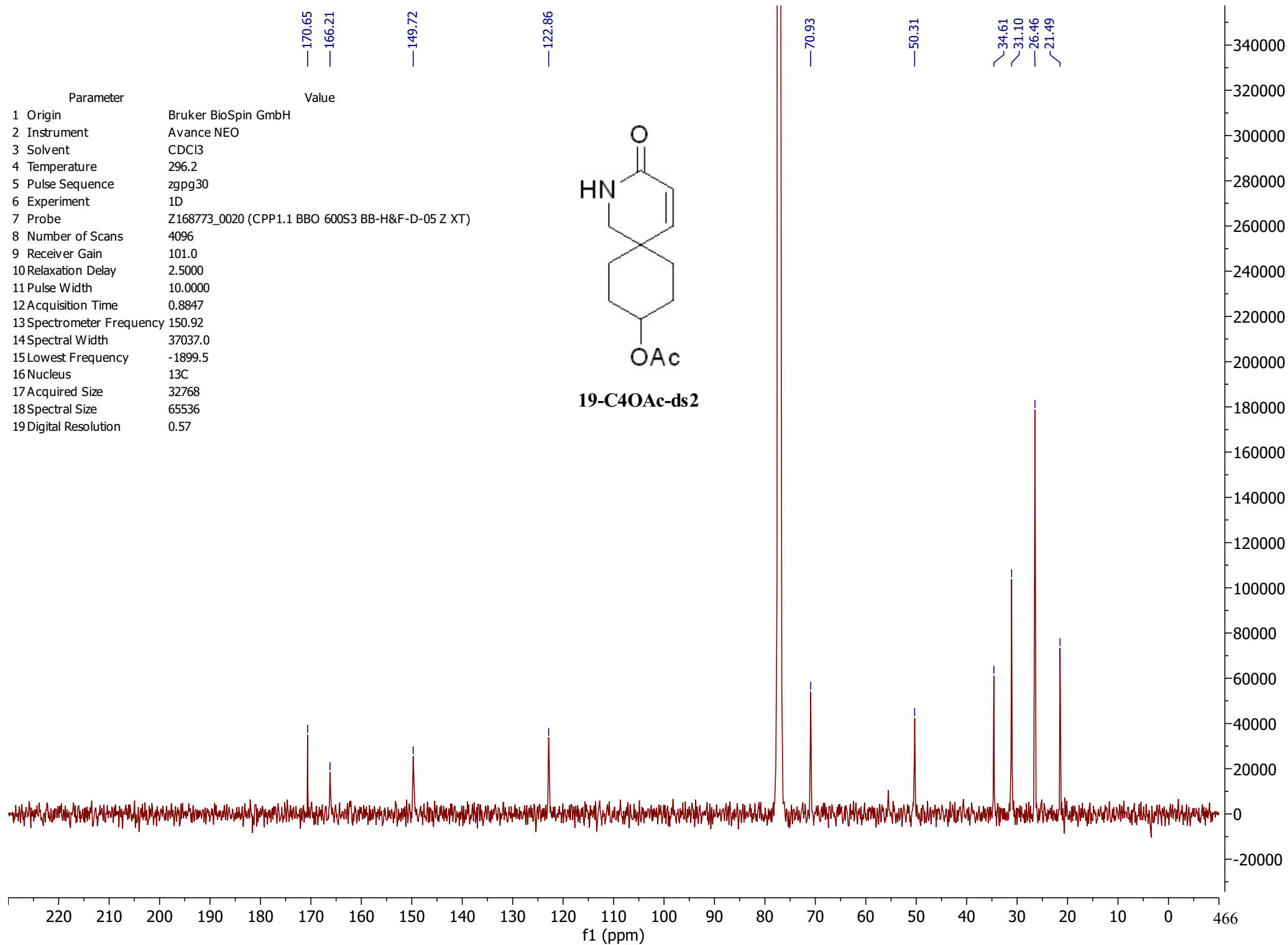
31.10

26.46

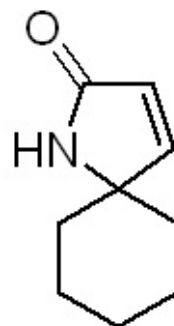
21.49



19-C4OAc-ds2

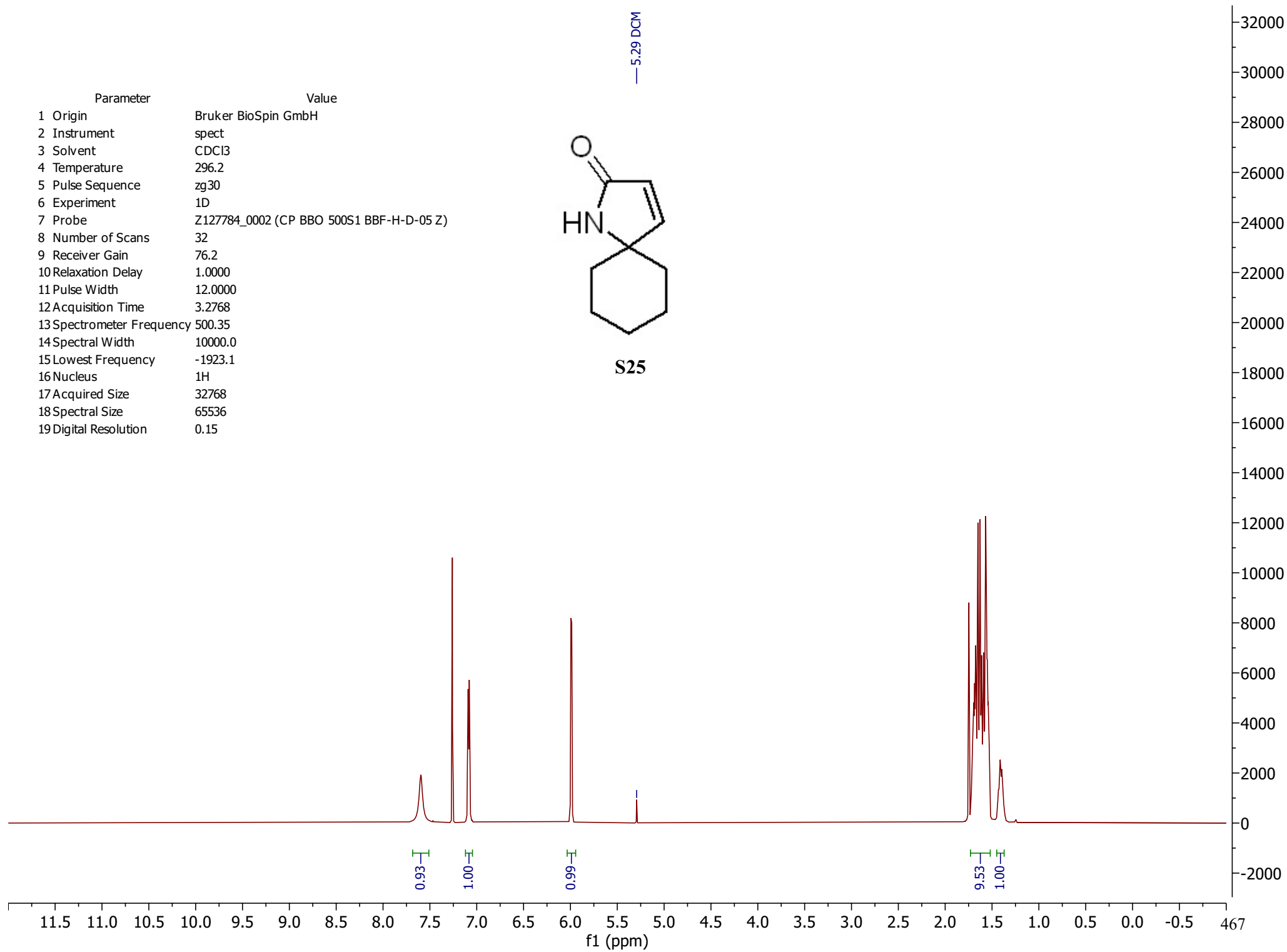


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

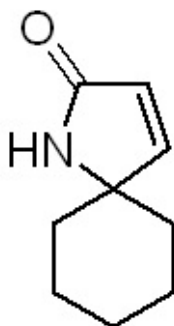


S25

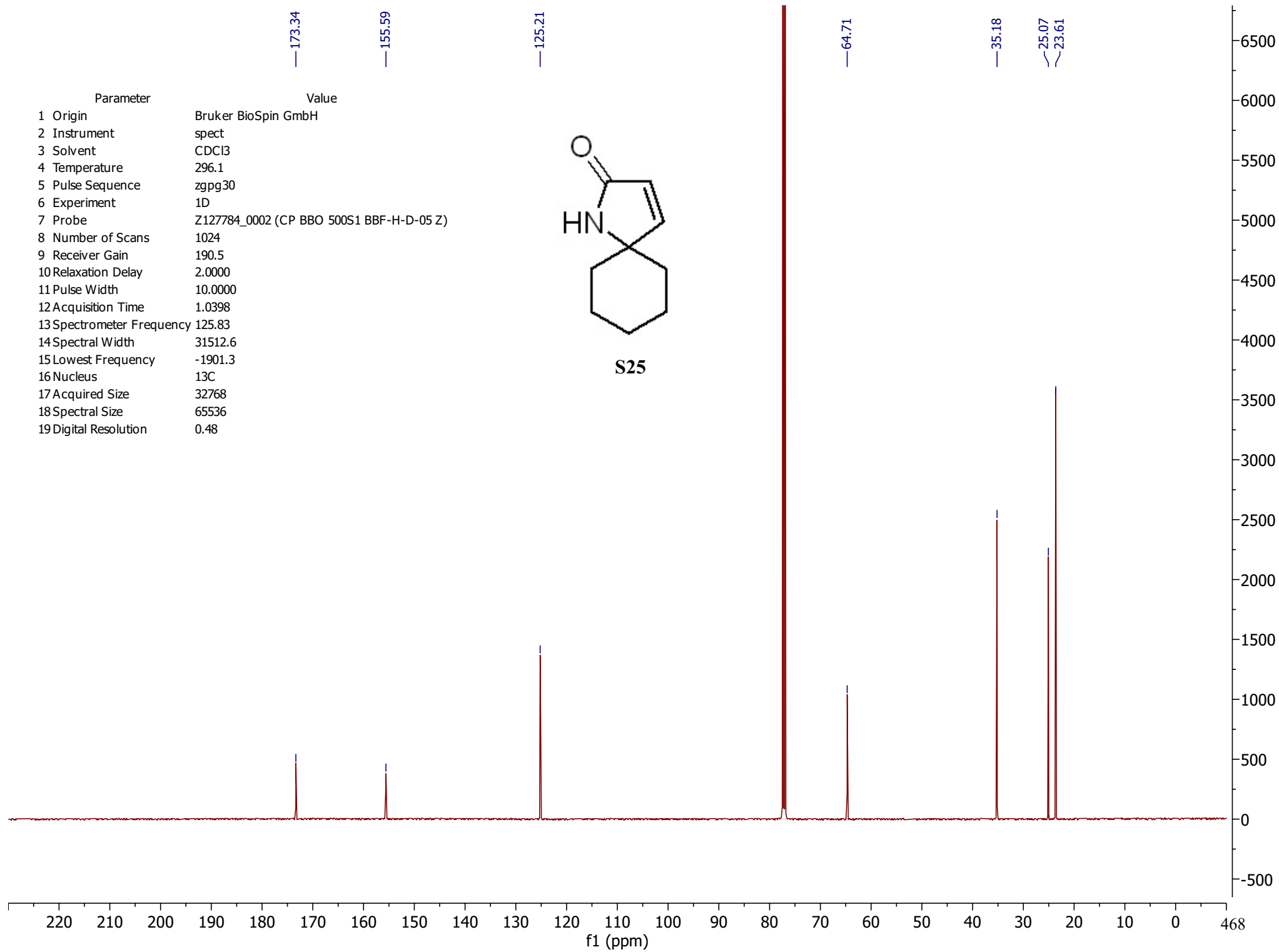
— 5.29 DCM



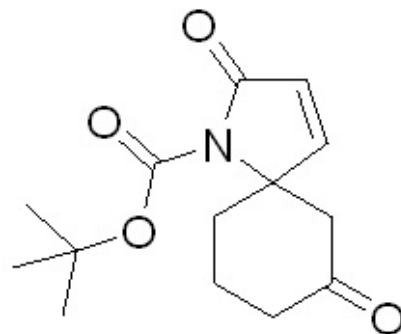
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1901.3
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



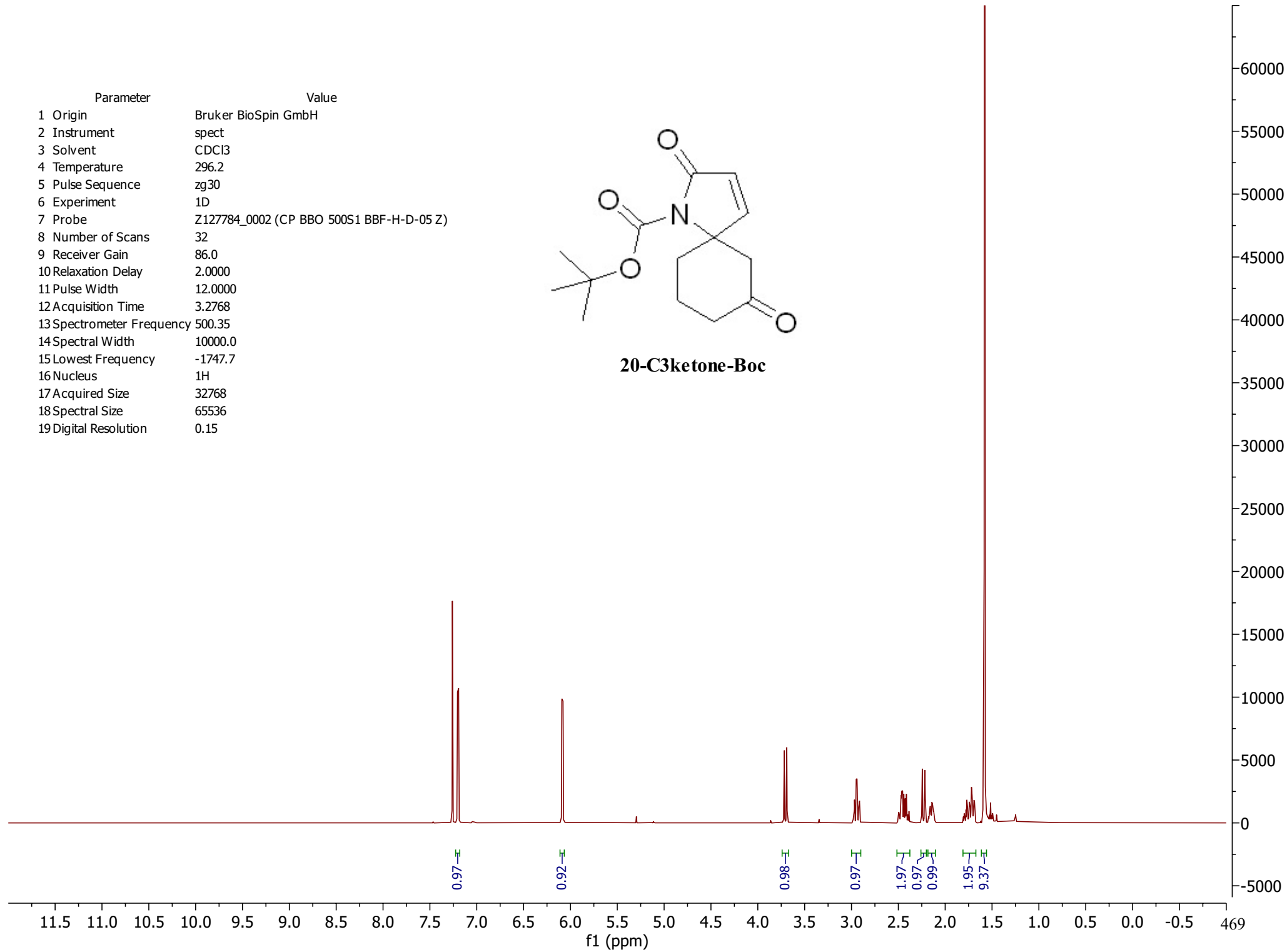
S25



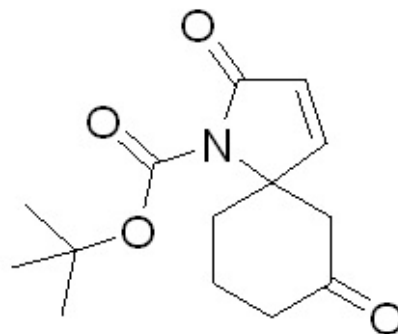
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



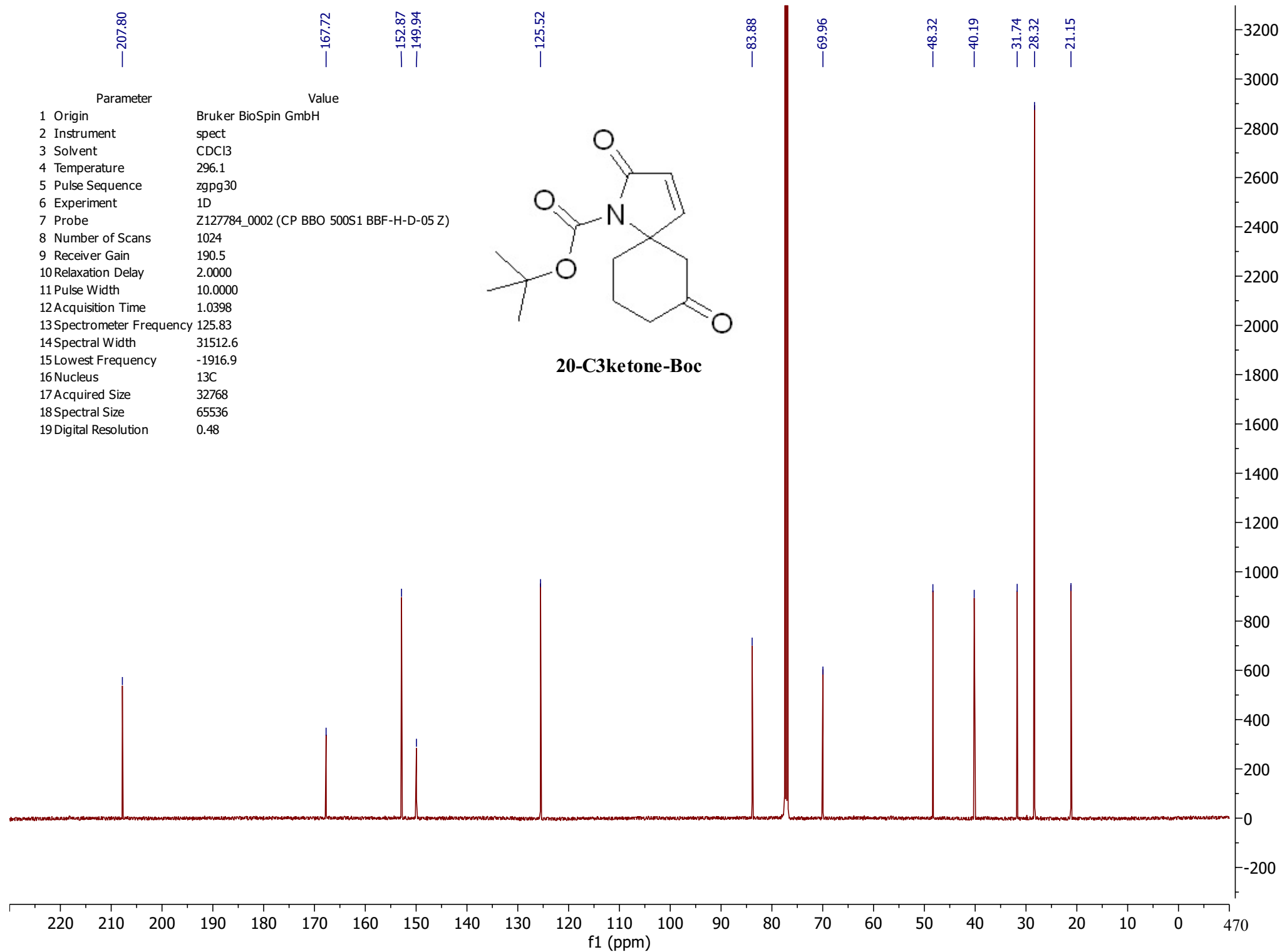
20-C3ketone-Boc



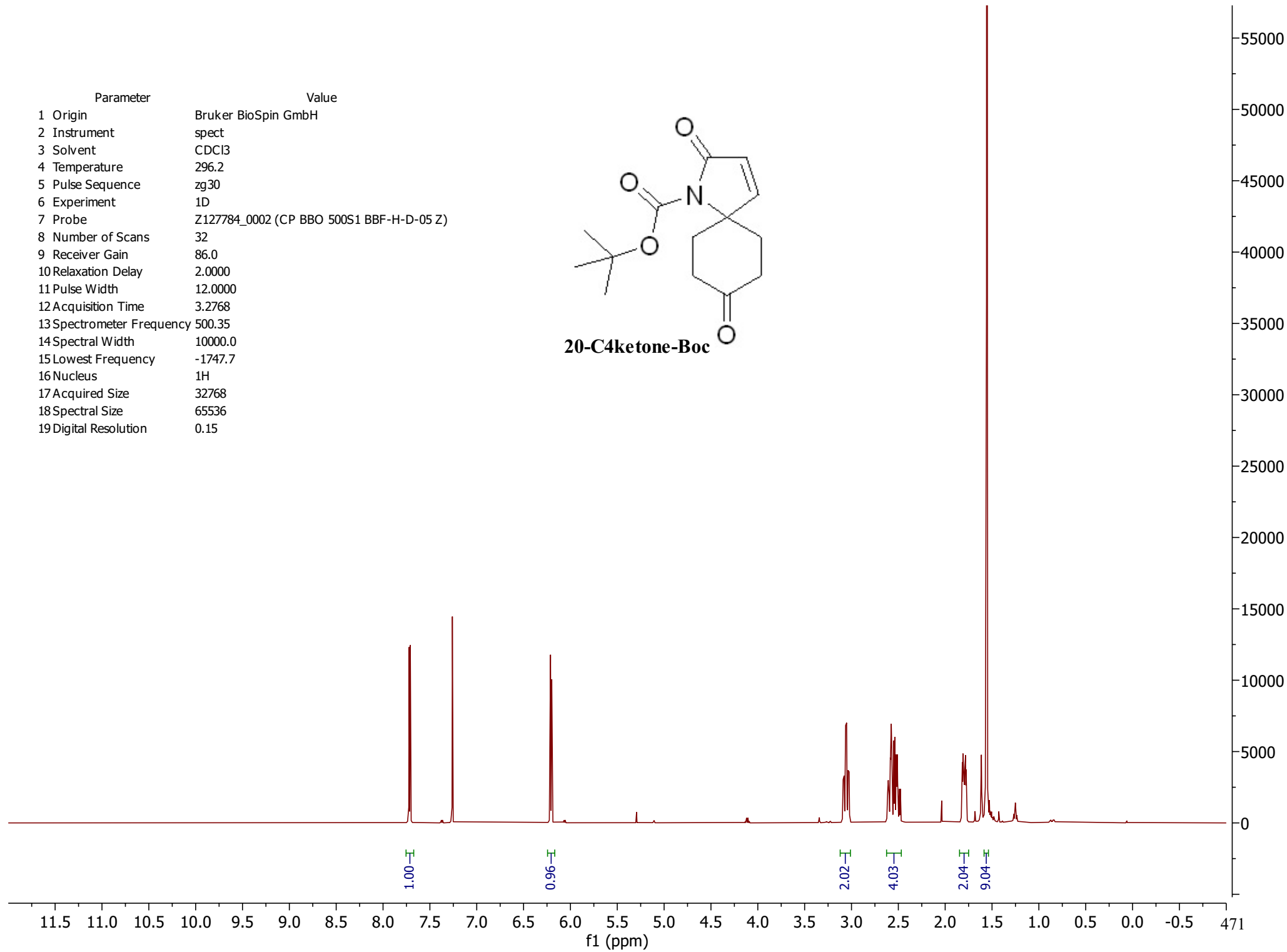
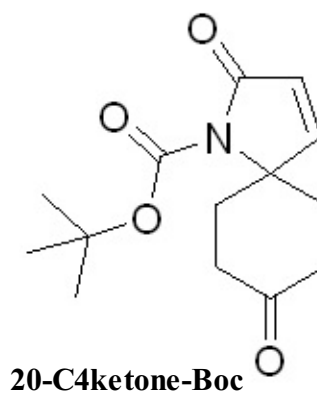
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

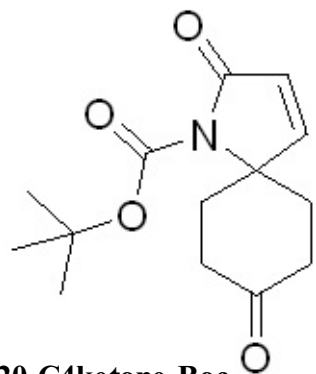


20-C3ketone-Boc



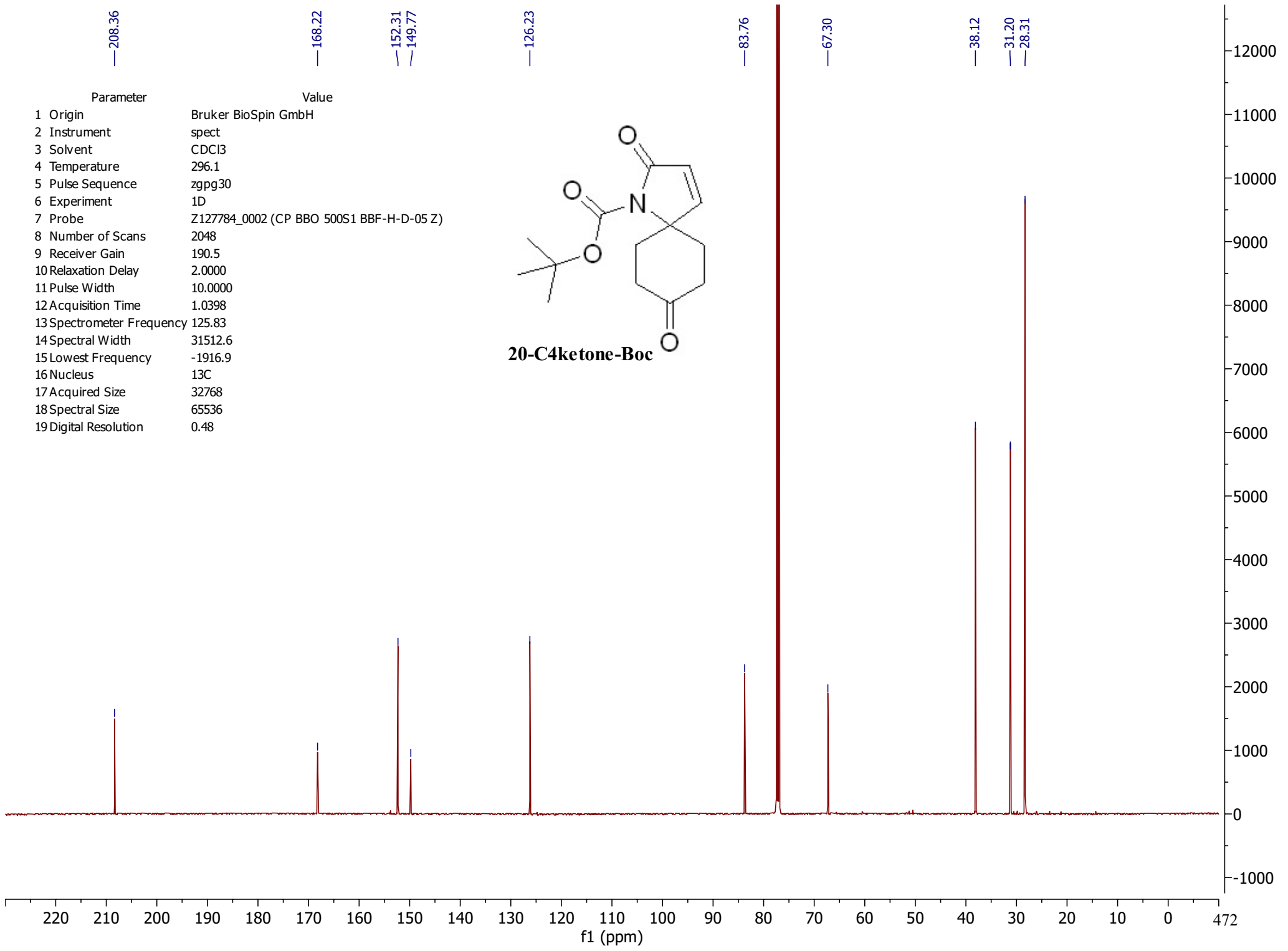
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



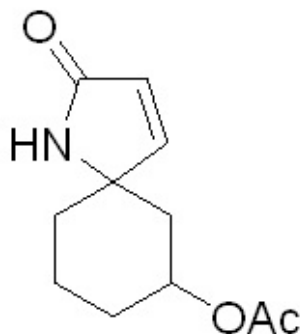


20-C4ketone-Boc

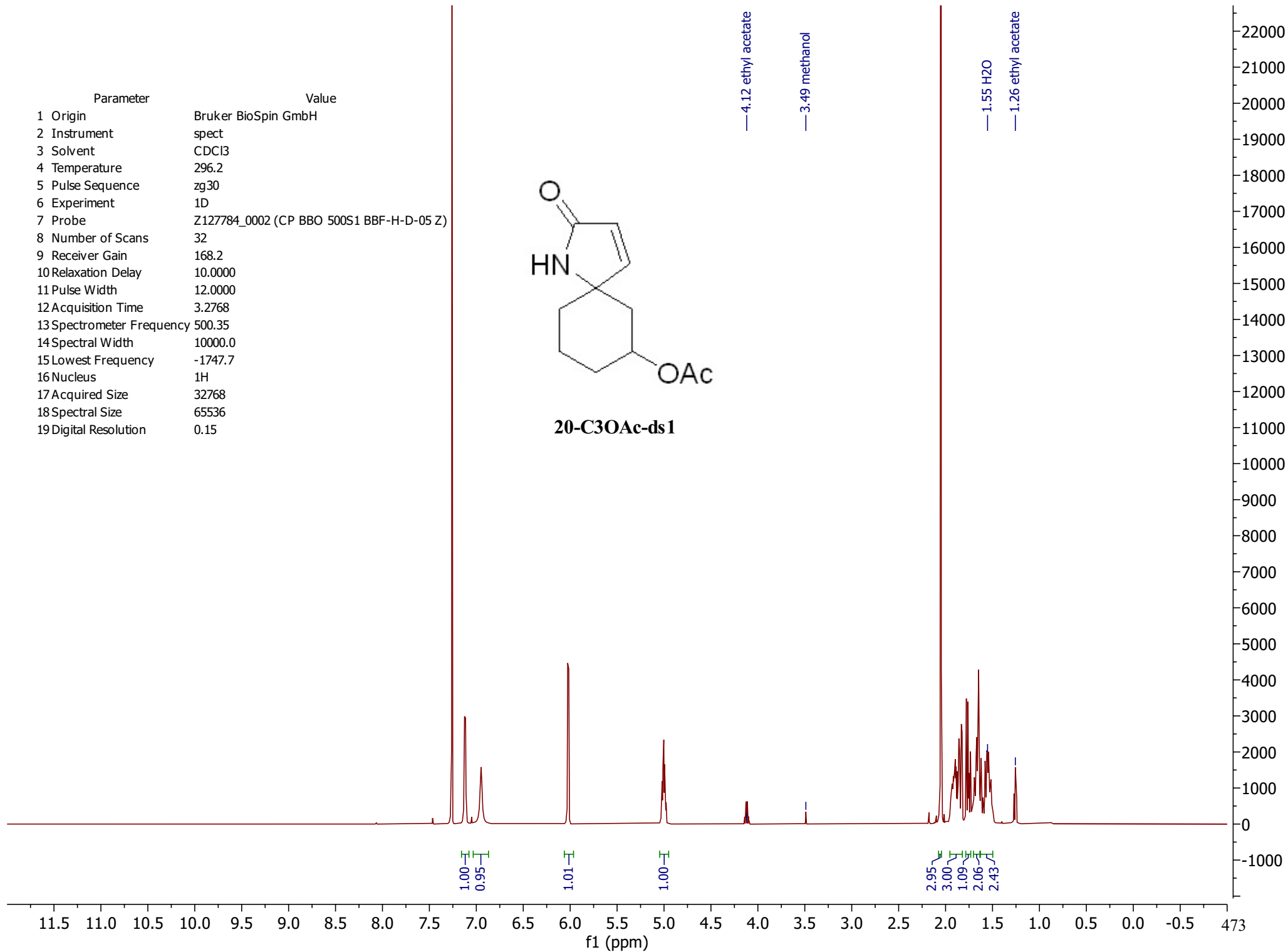
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



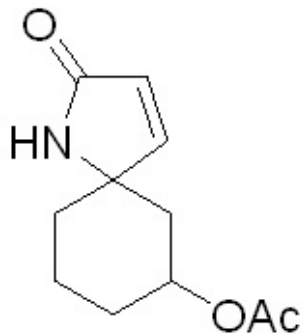
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	168.2
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



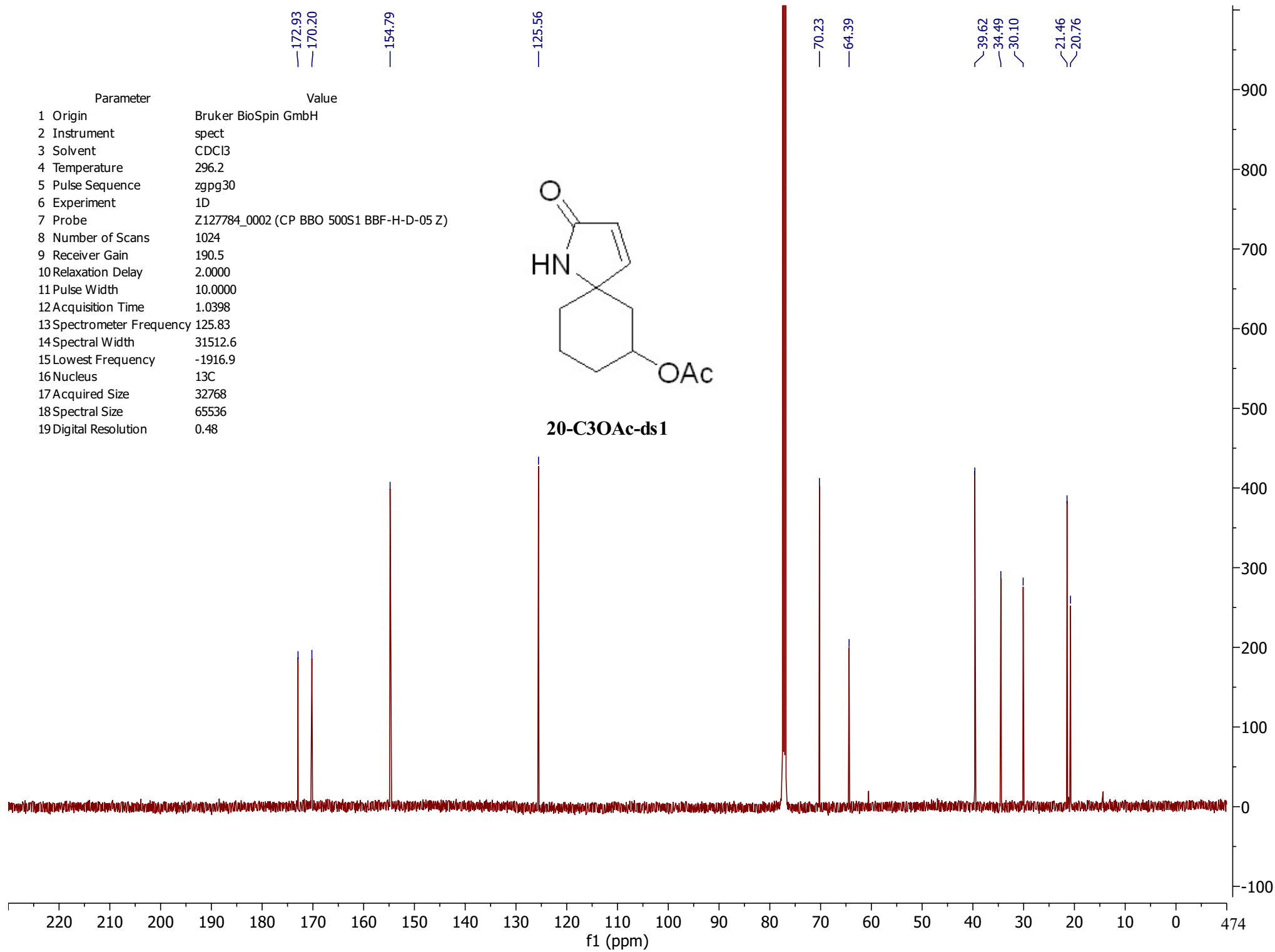
20-C3OAc-ds1



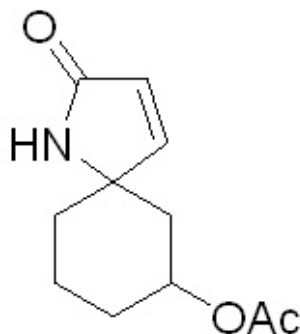
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



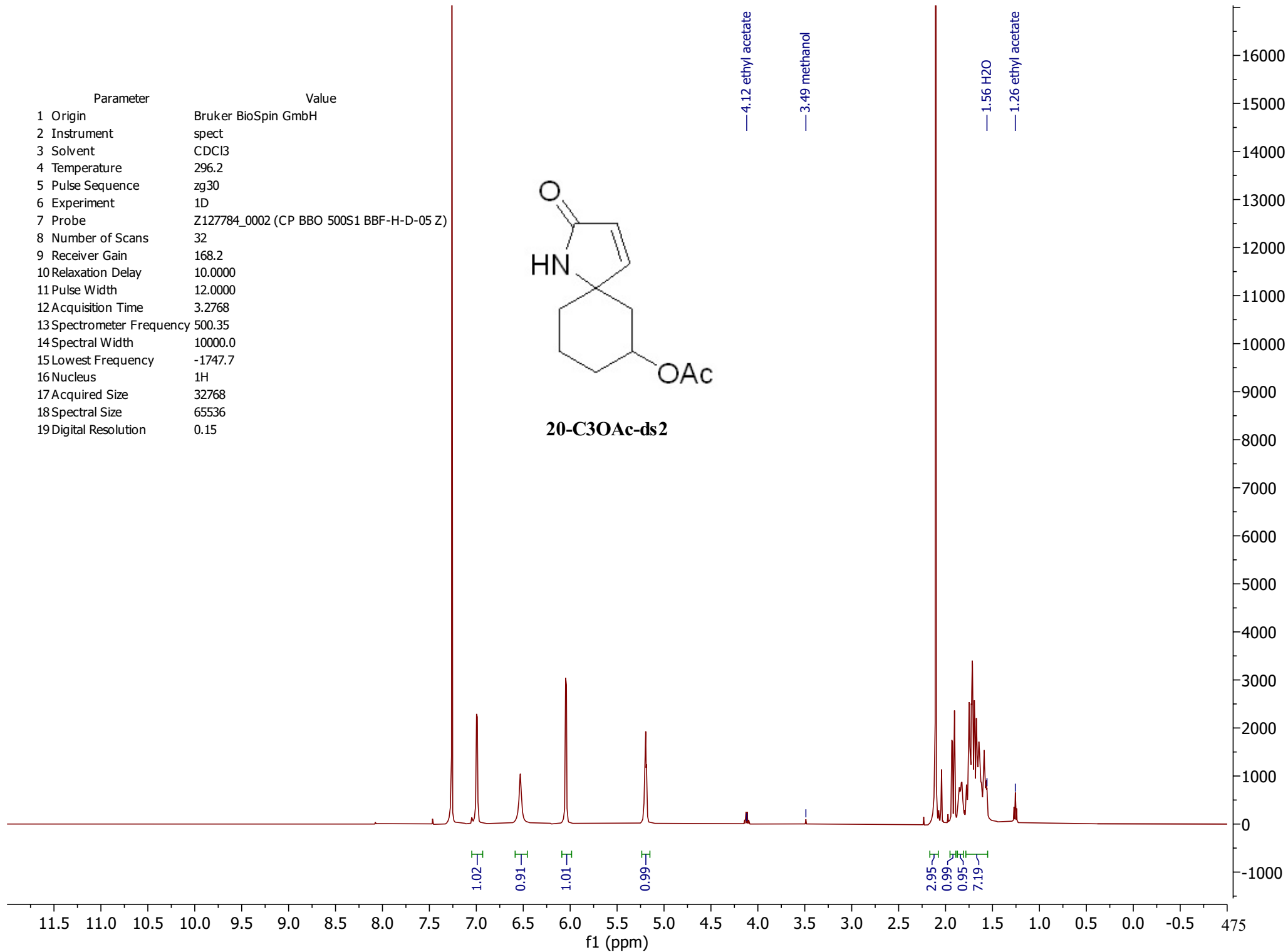
20-C3OAc-ds1



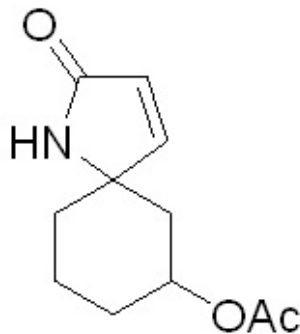
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	168.2
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



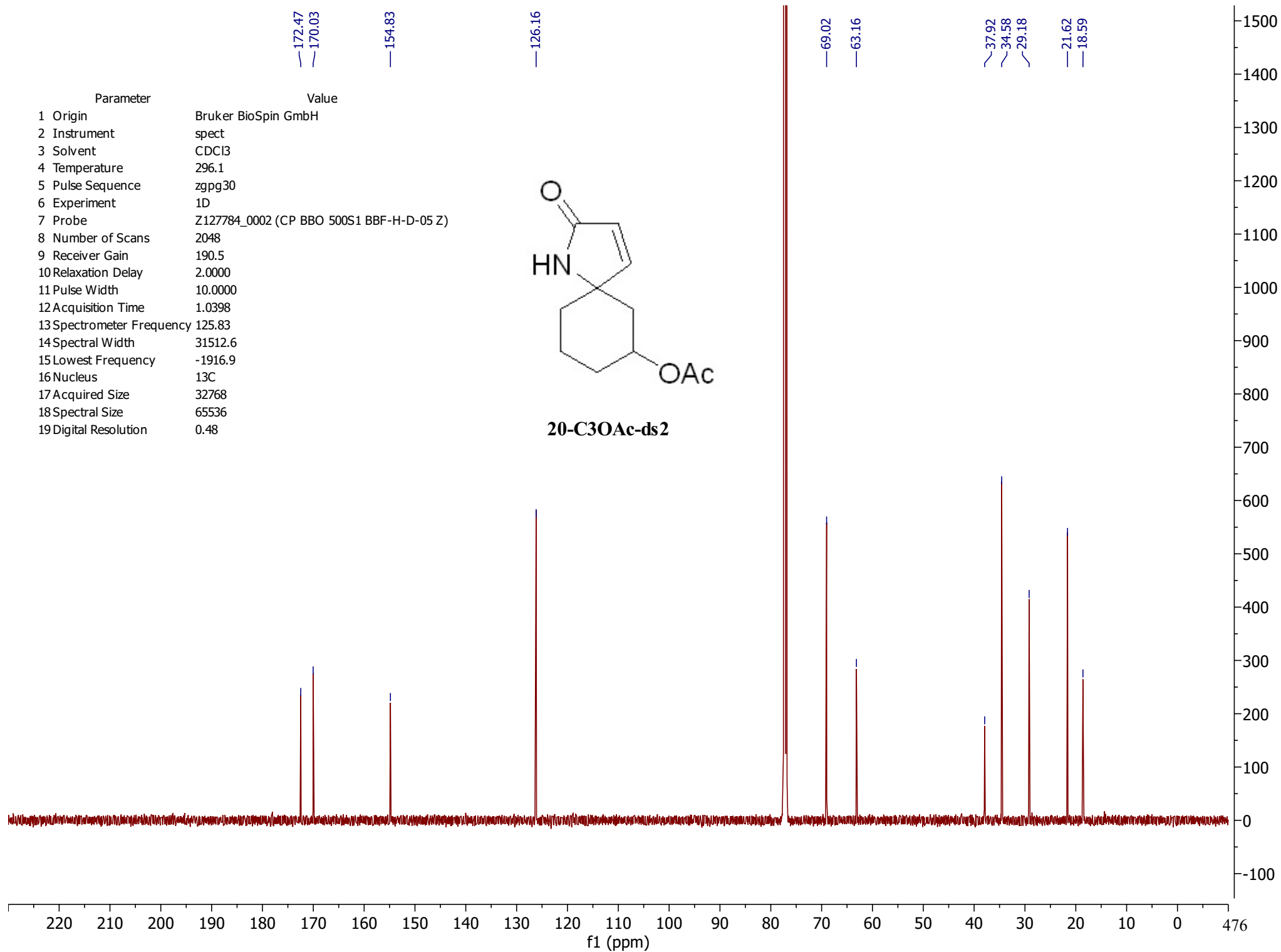
20-C3OAc-ds2



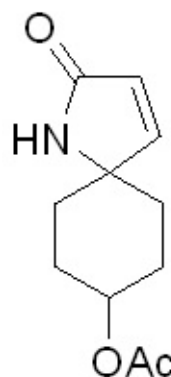
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



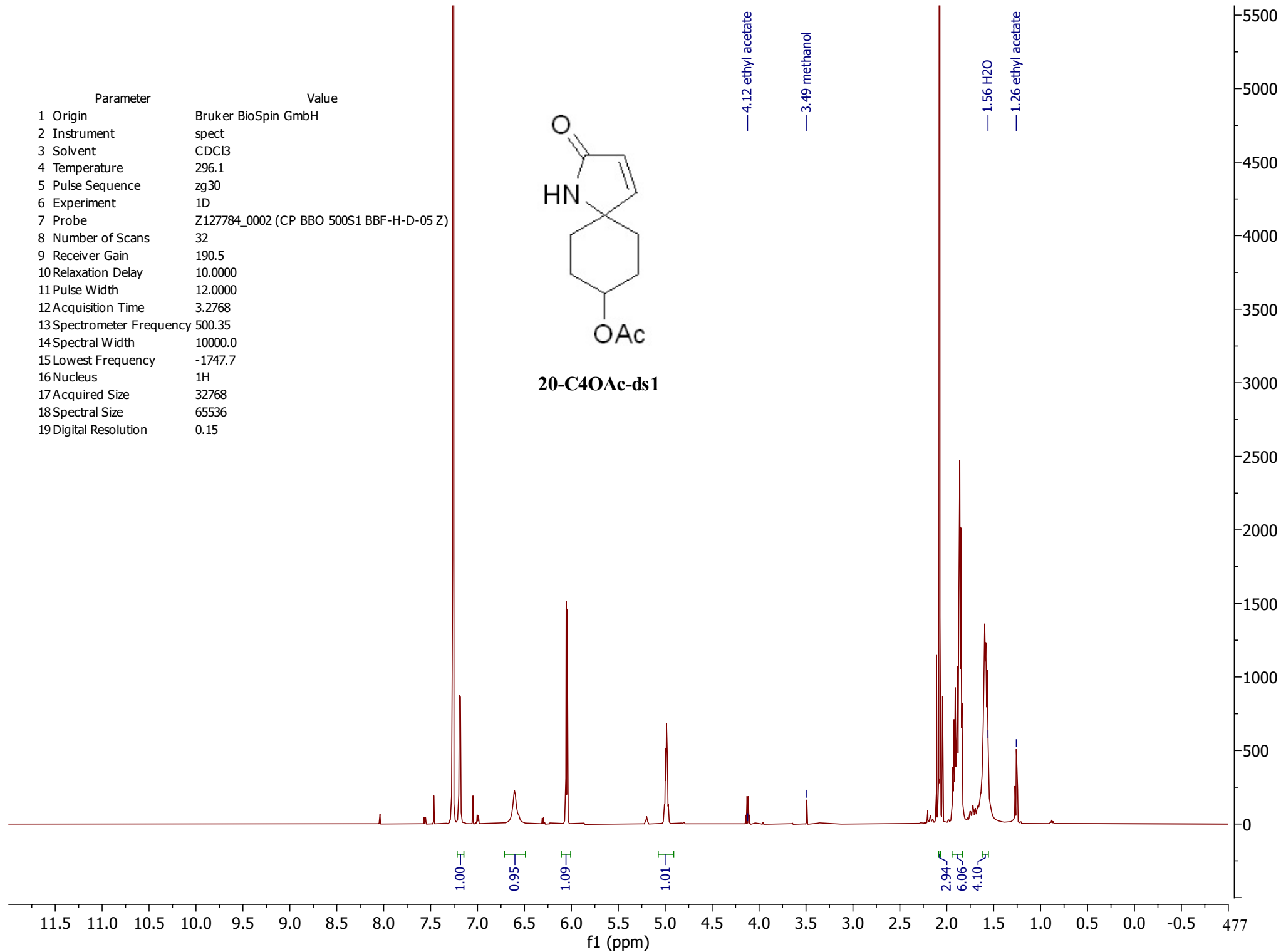
20-C3OAc-ds2



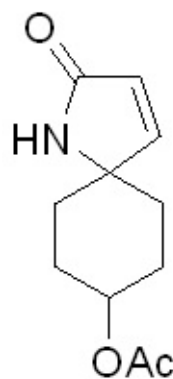
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	190.5
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



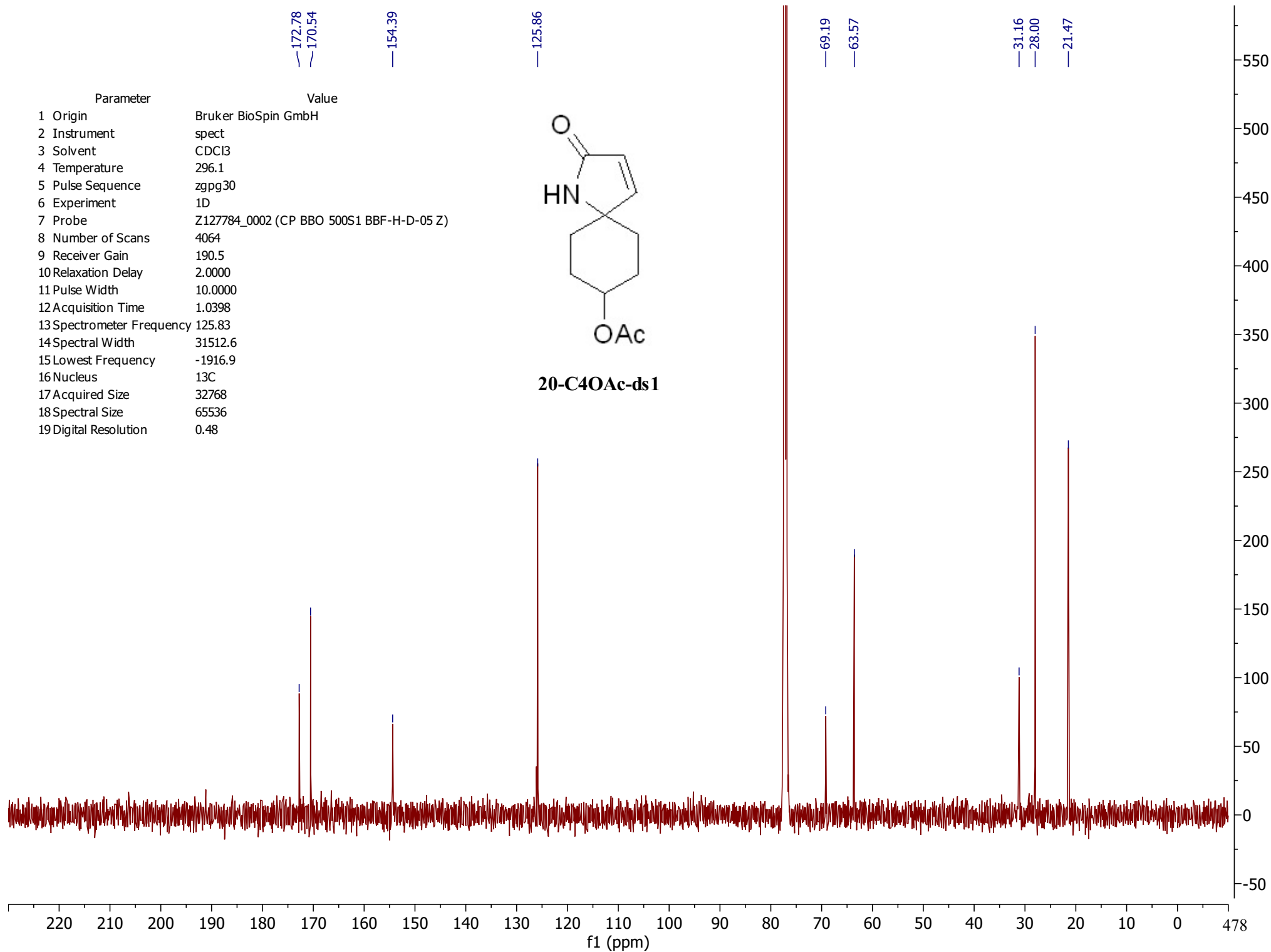
20-C4OAc-ds1



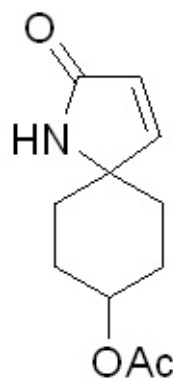
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	4064
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



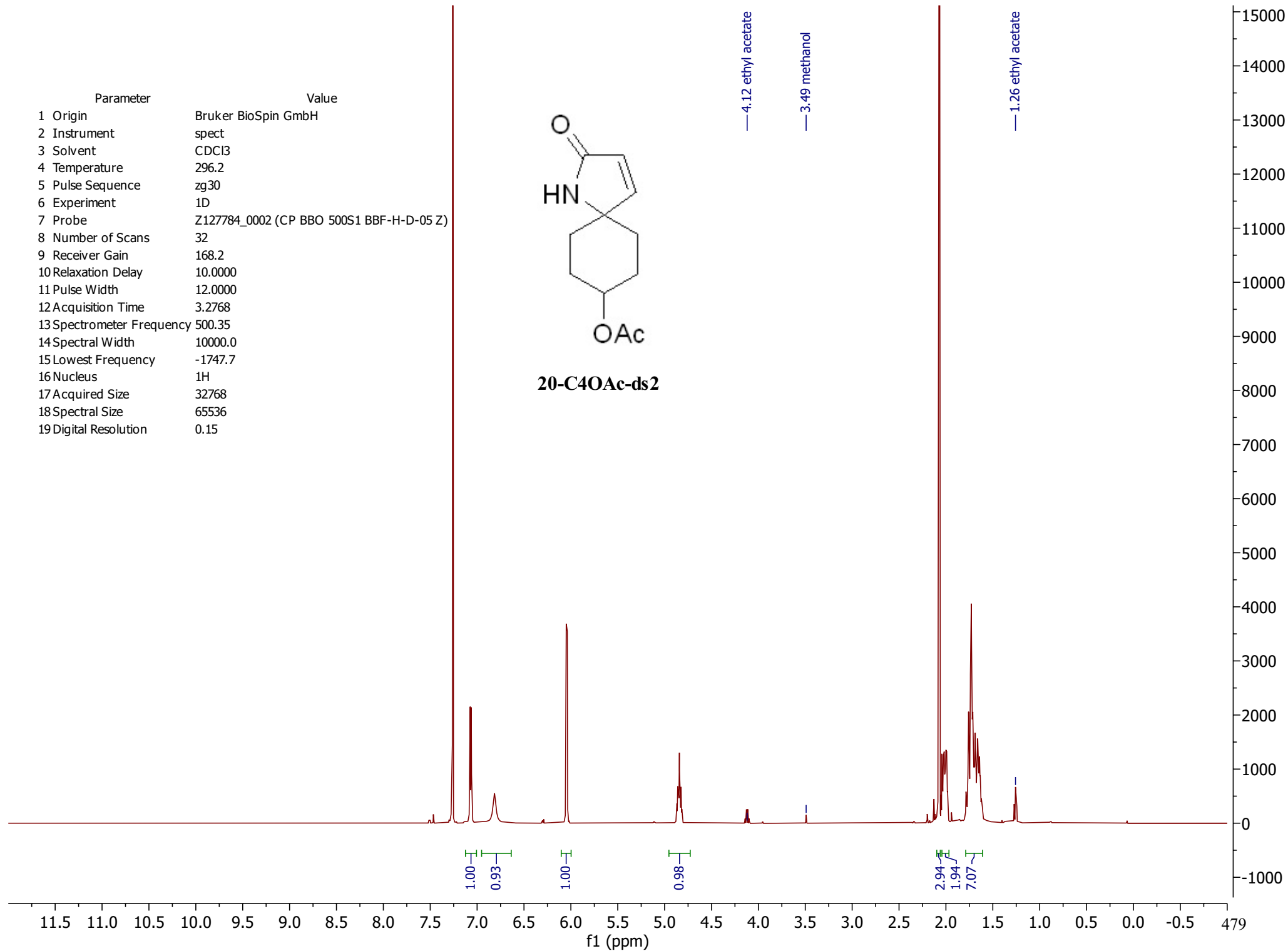
20-C4OAc-ds1



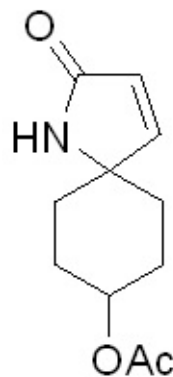
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	168.2
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



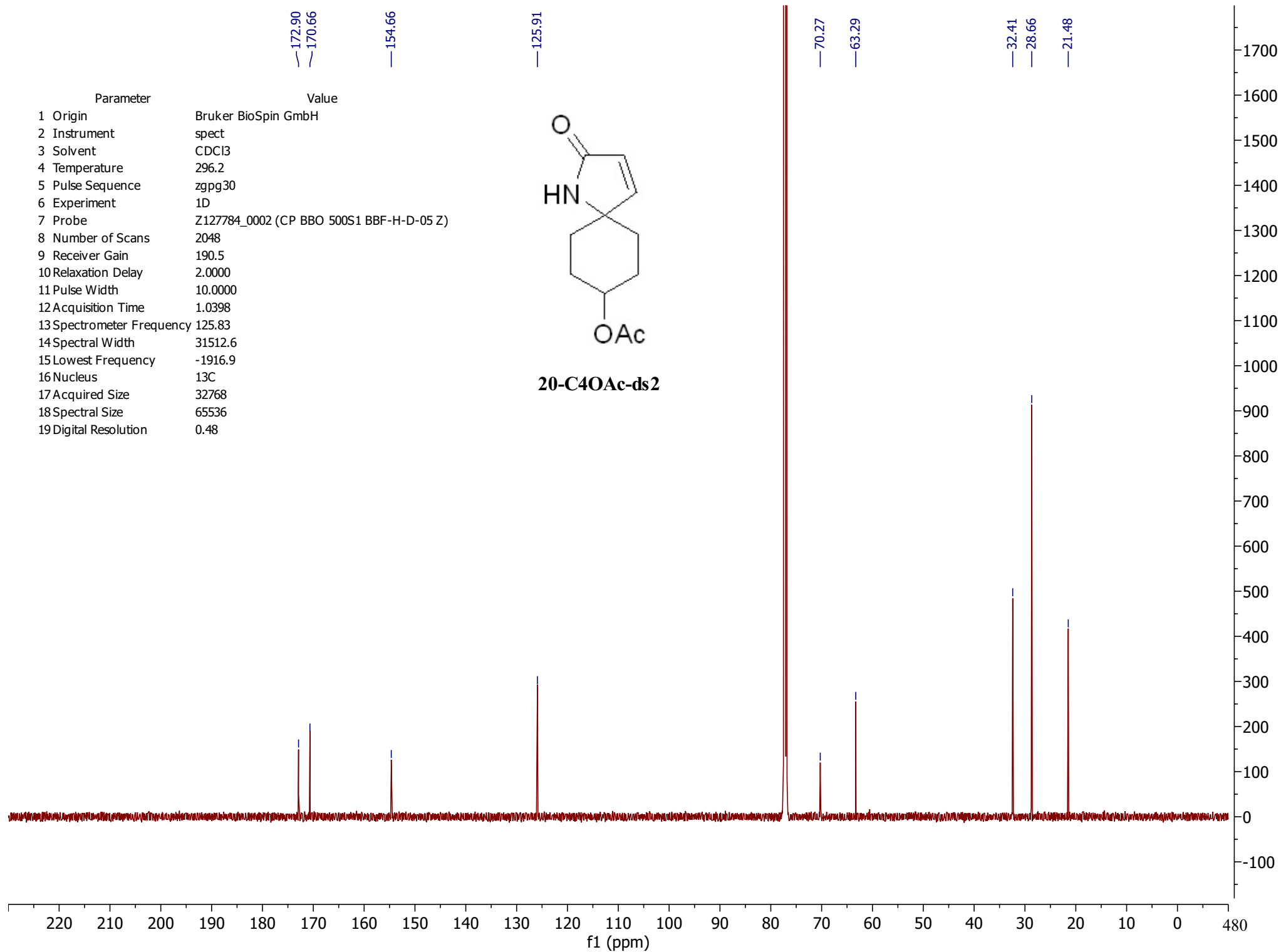
20-C4OAc-ds2



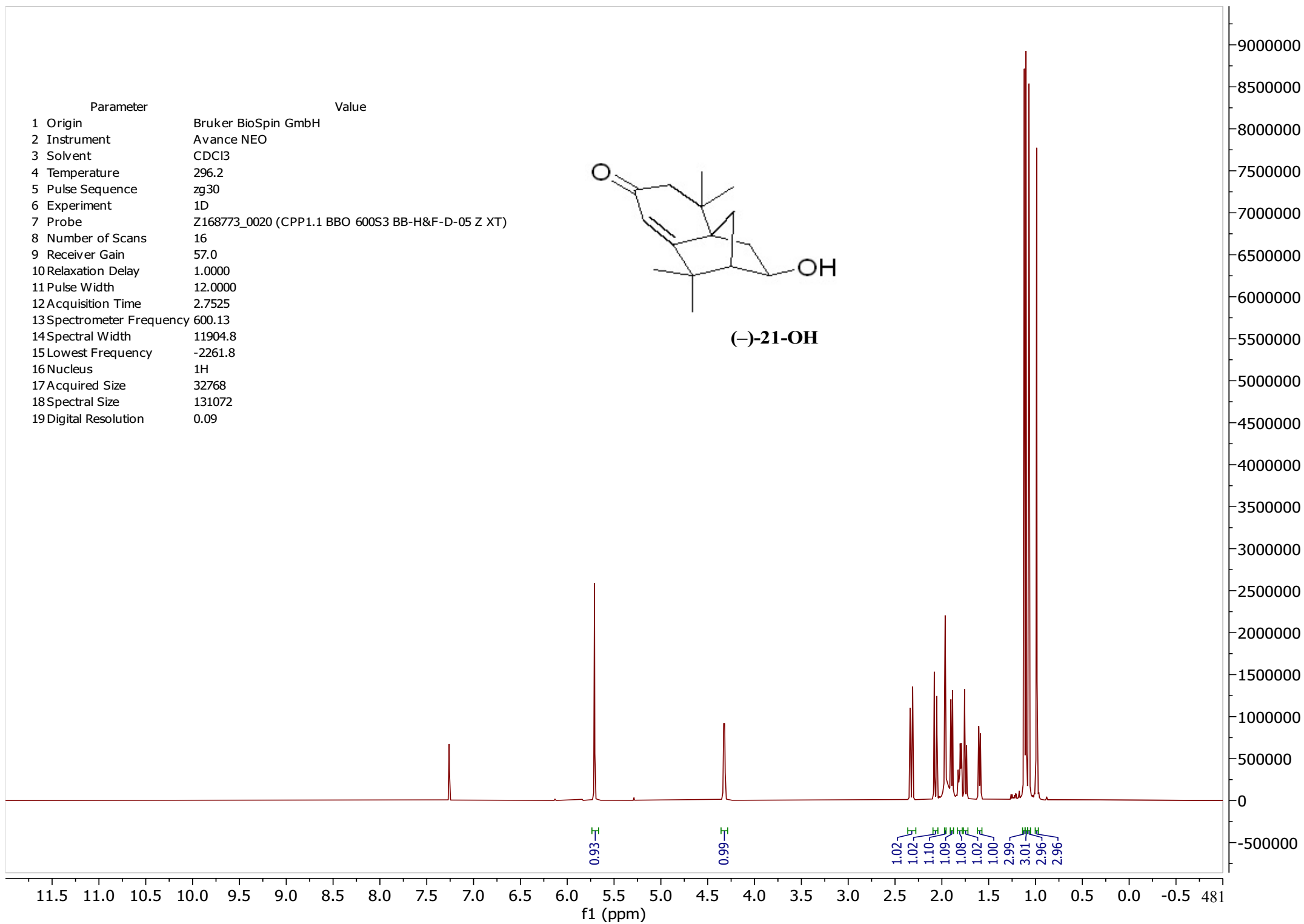
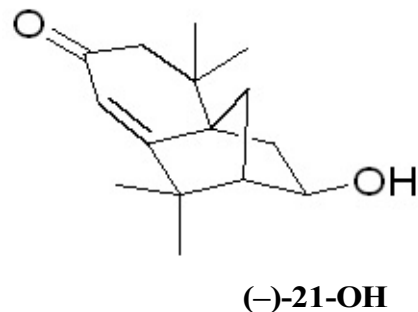
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



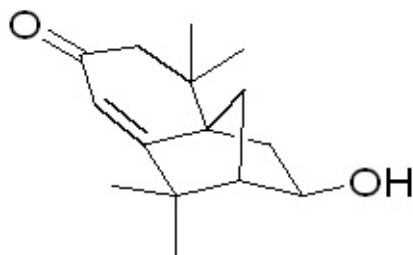
20-C4OAc-ds2



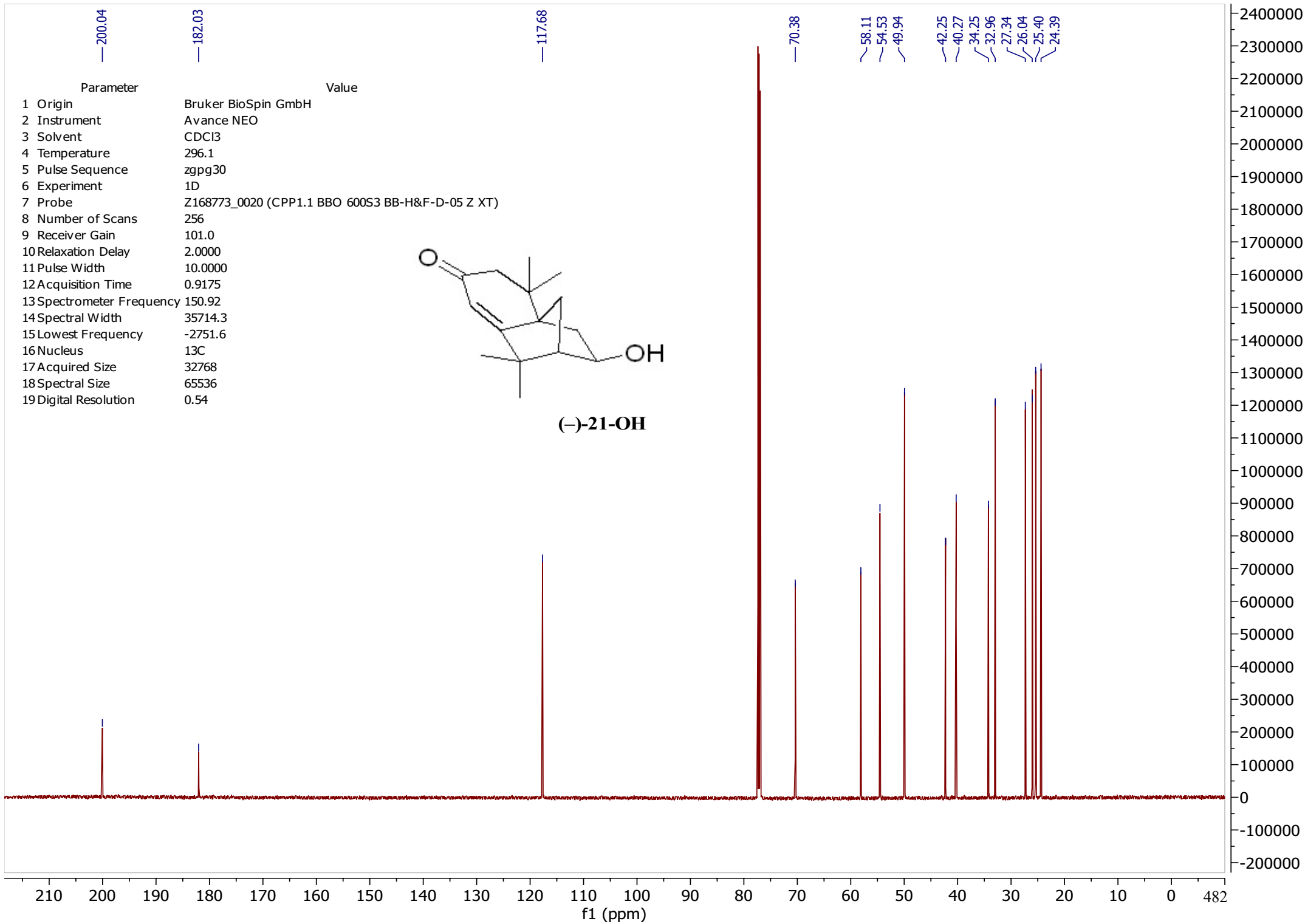
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	57.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.8
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



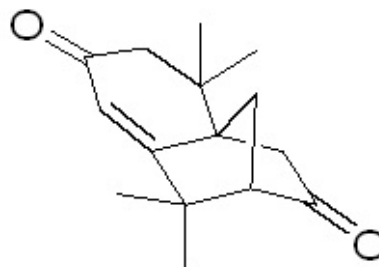
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	256
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.9175
13 Spectrometer Frequency	150.92
14 Spectral Width	35714.3
15 Lowest Frequency	-2751.6
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.54



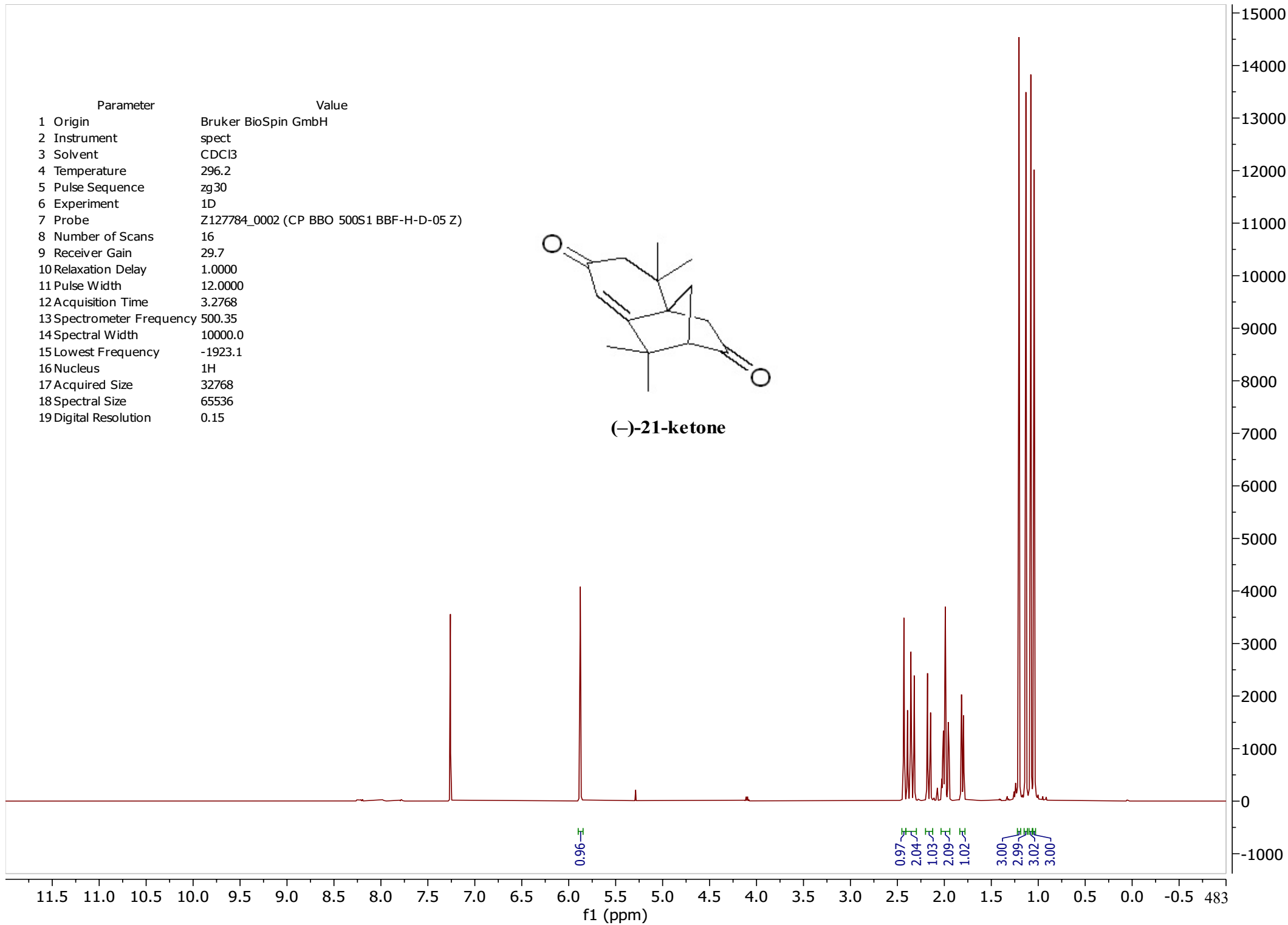
(-)-21-OH



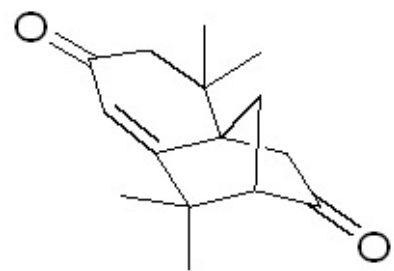
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.1
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



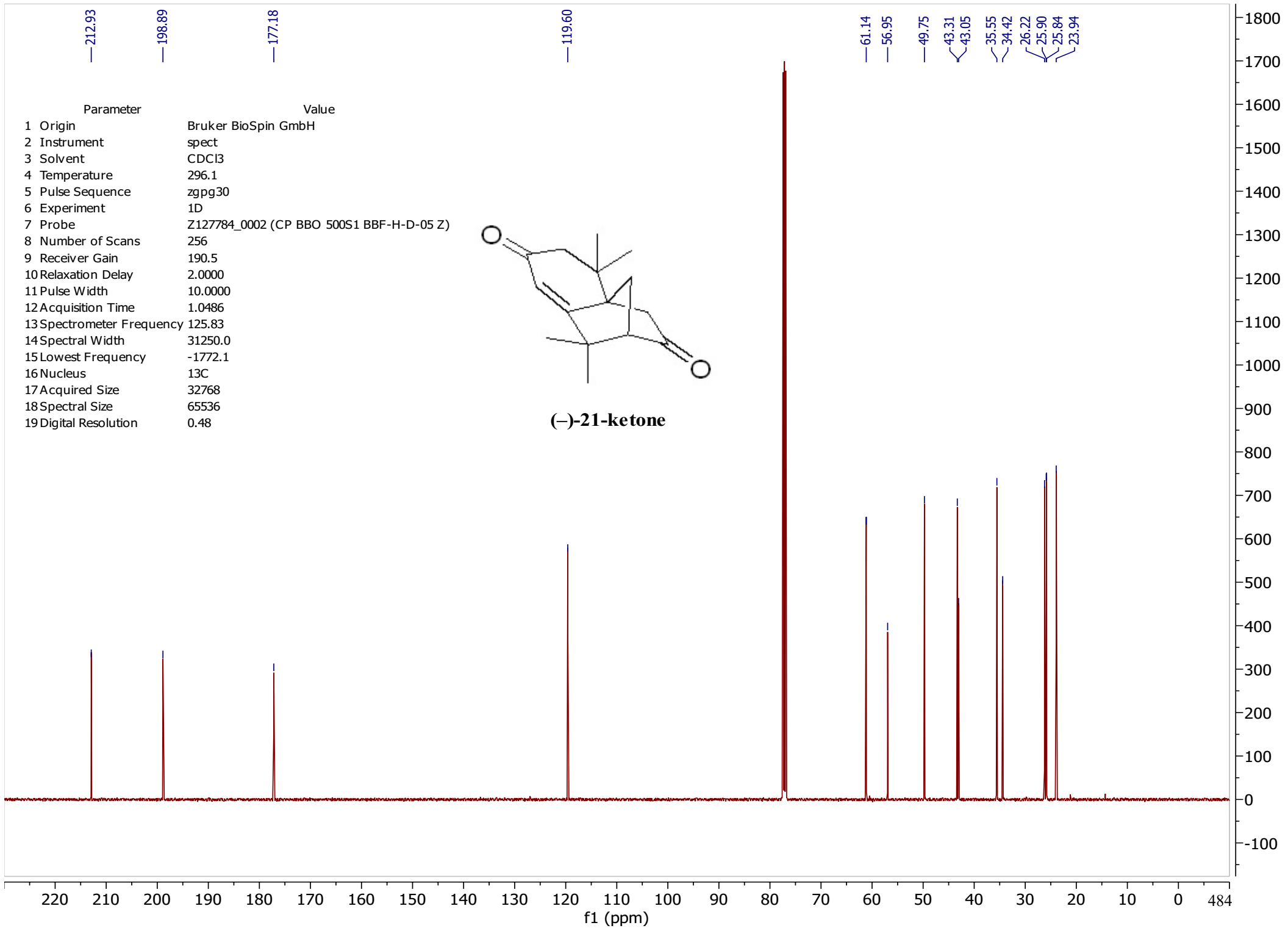
(-)-21-ketone



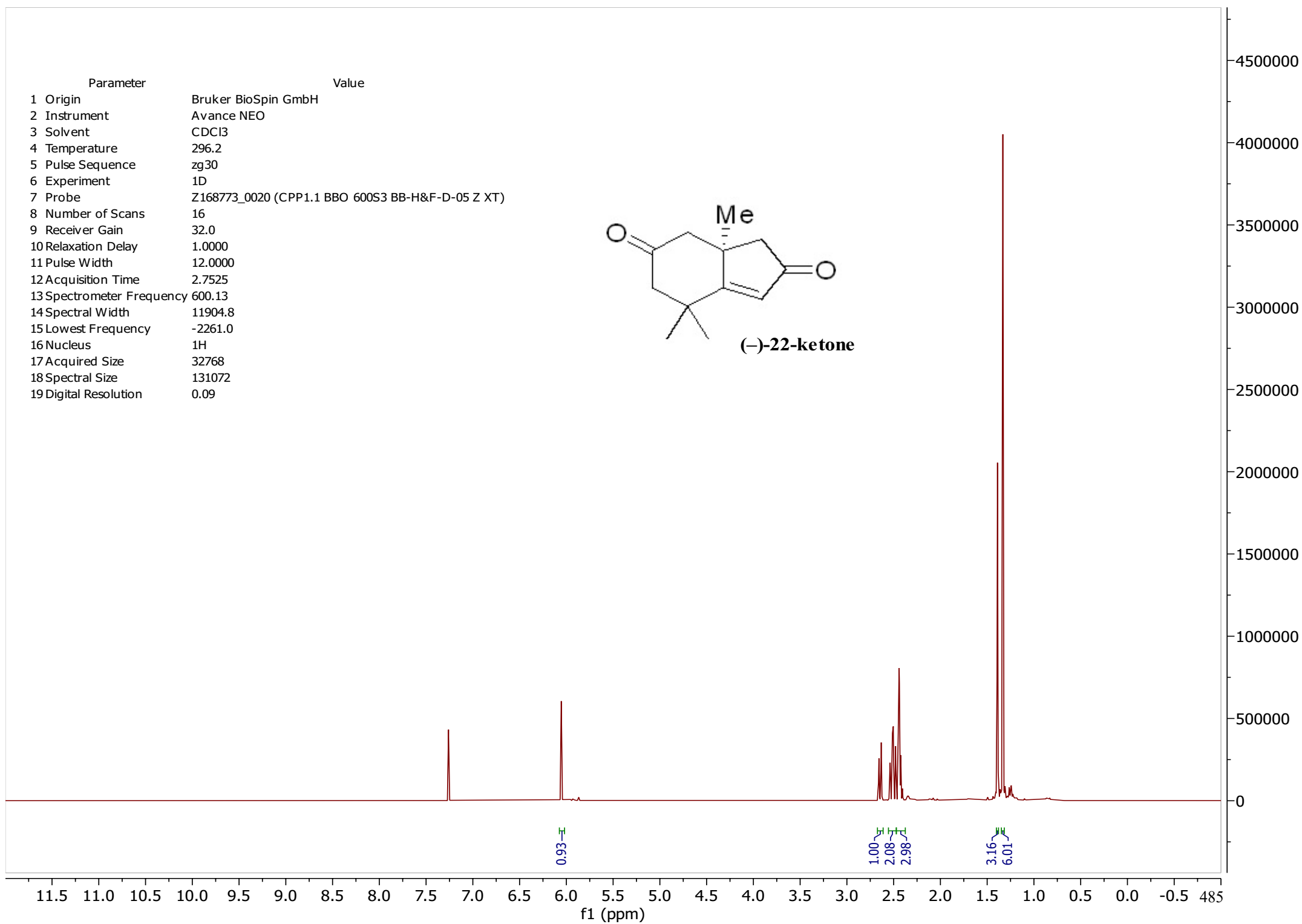
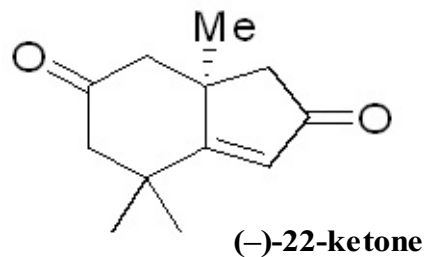
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1772.1
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



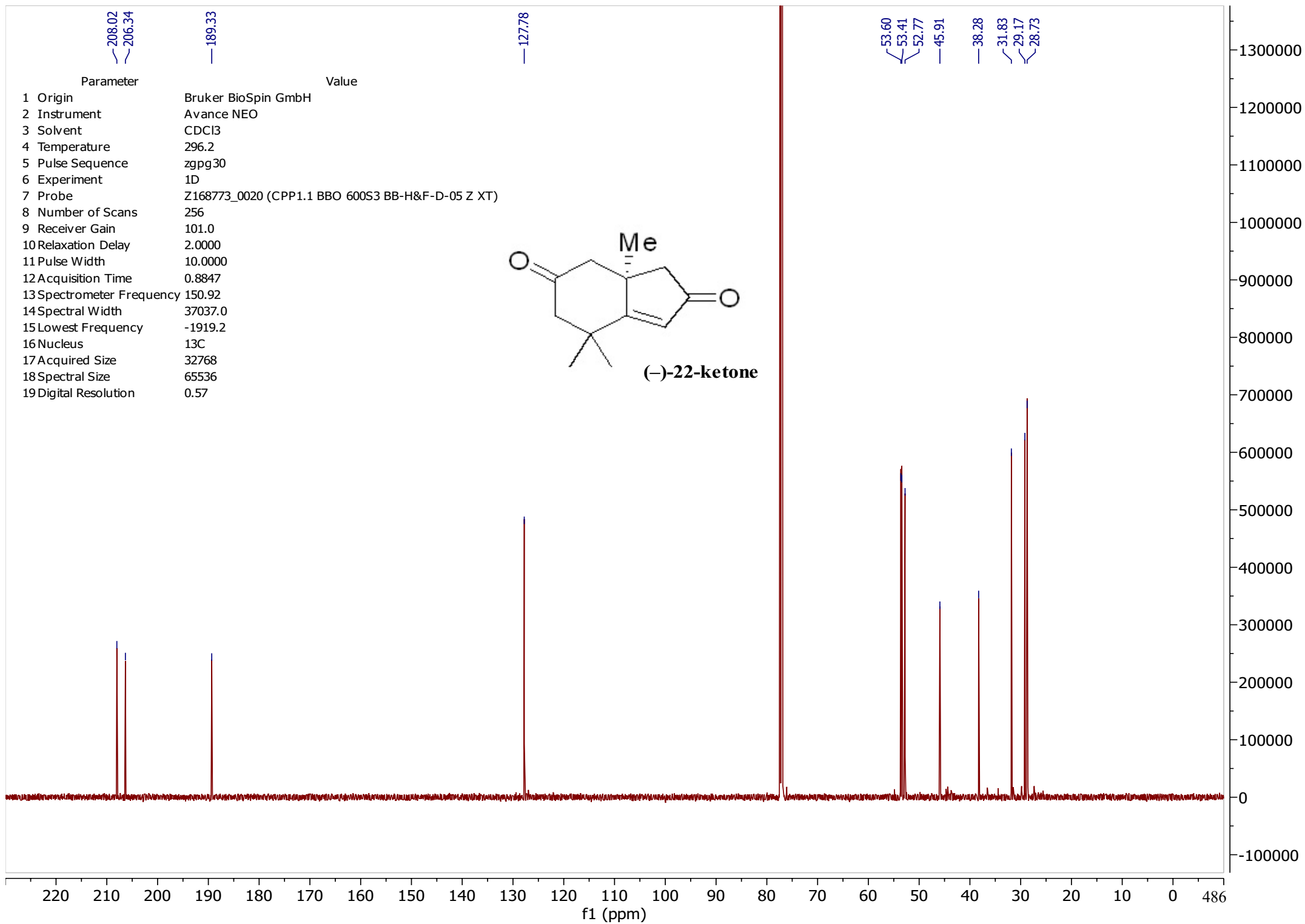
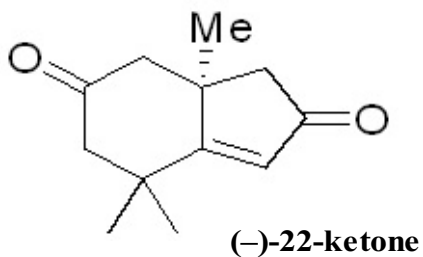
(-)-21-ketone



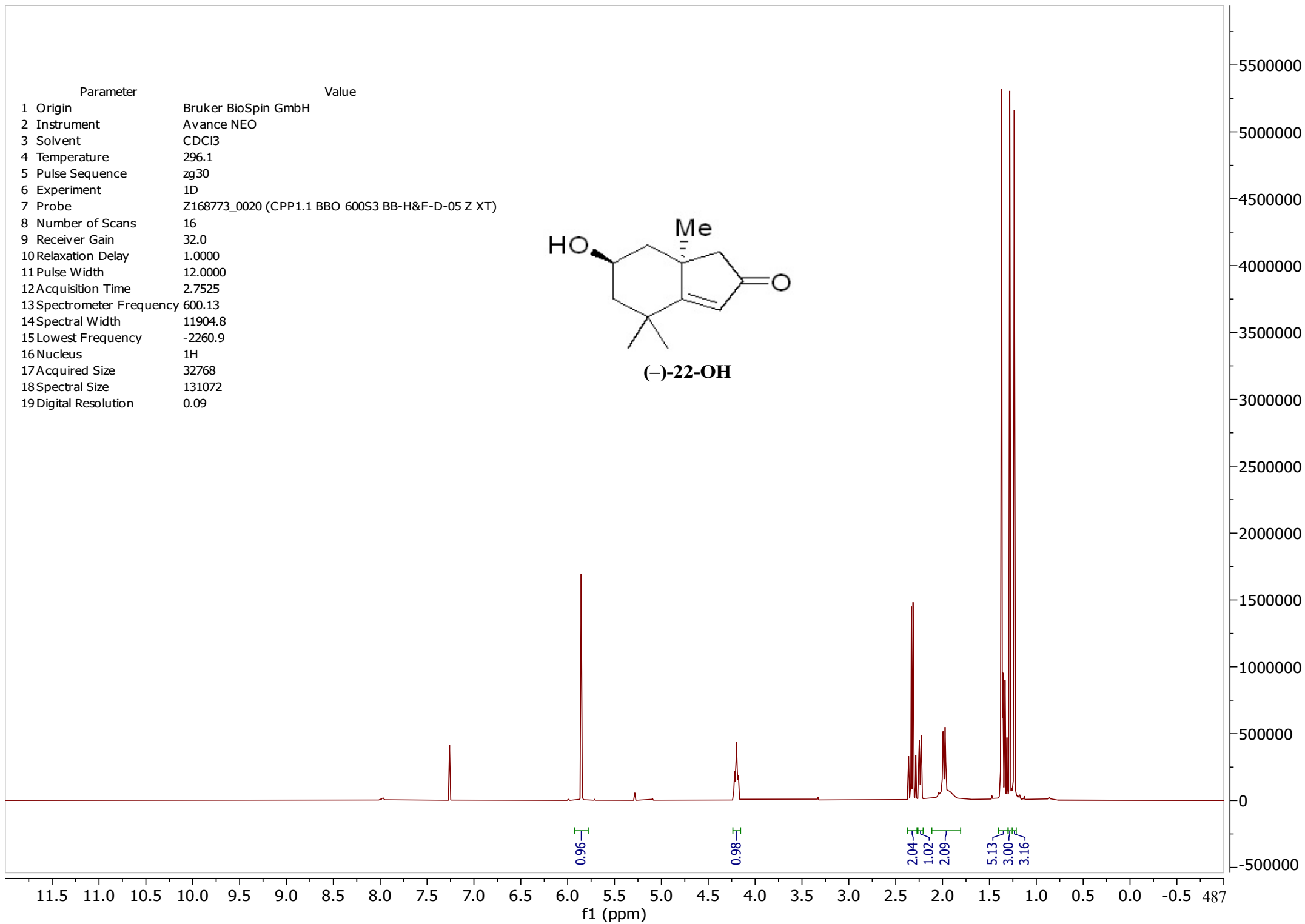
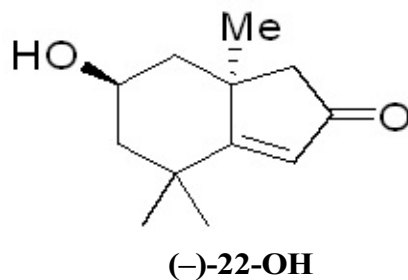
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



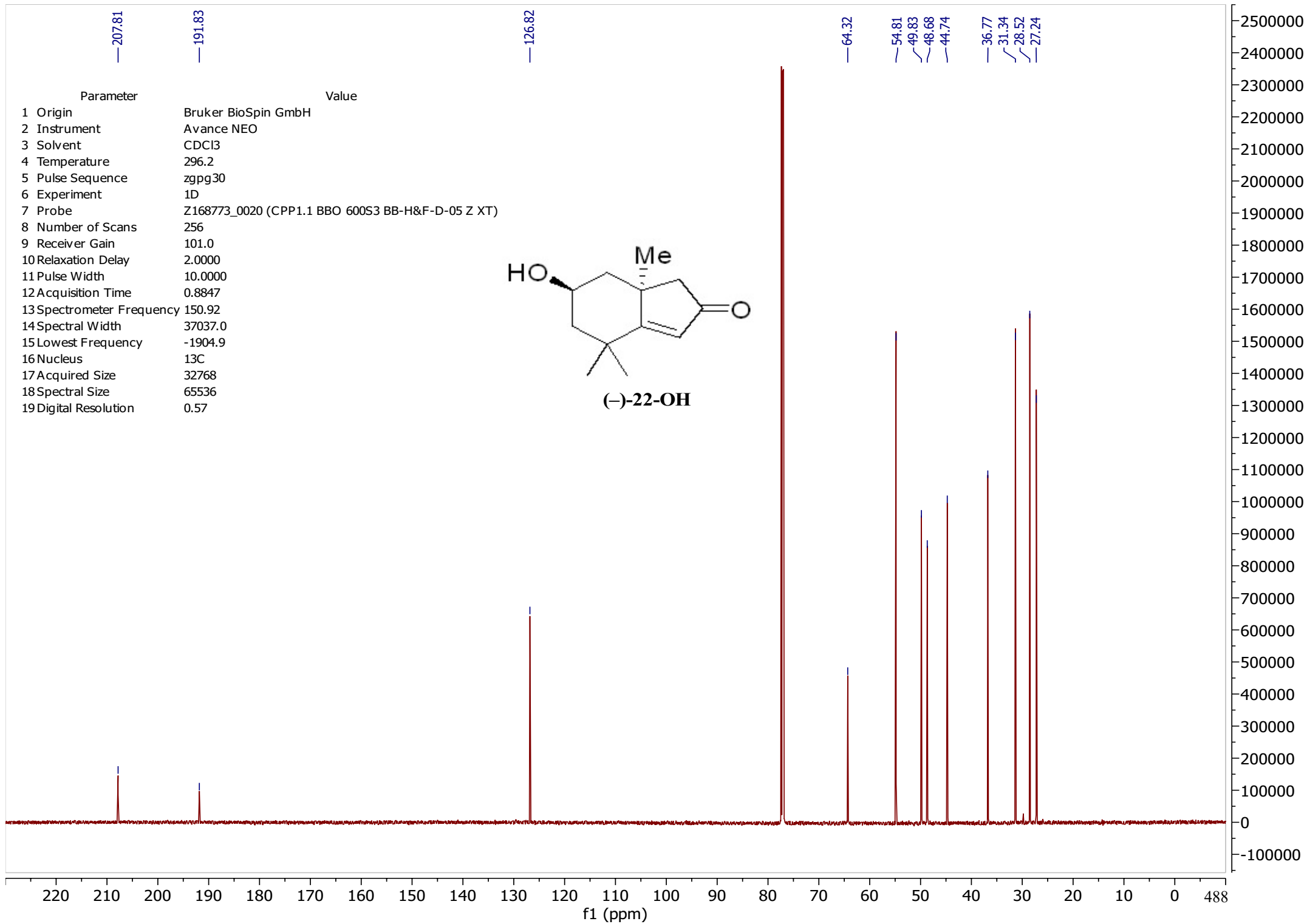
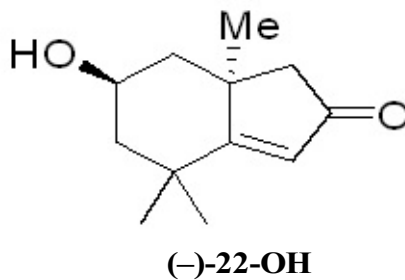
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	256
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1919.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



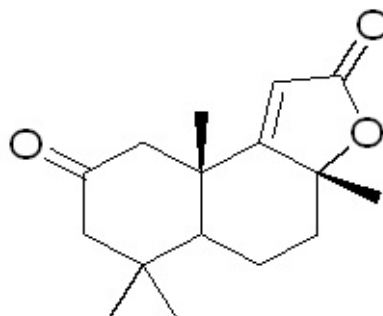
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



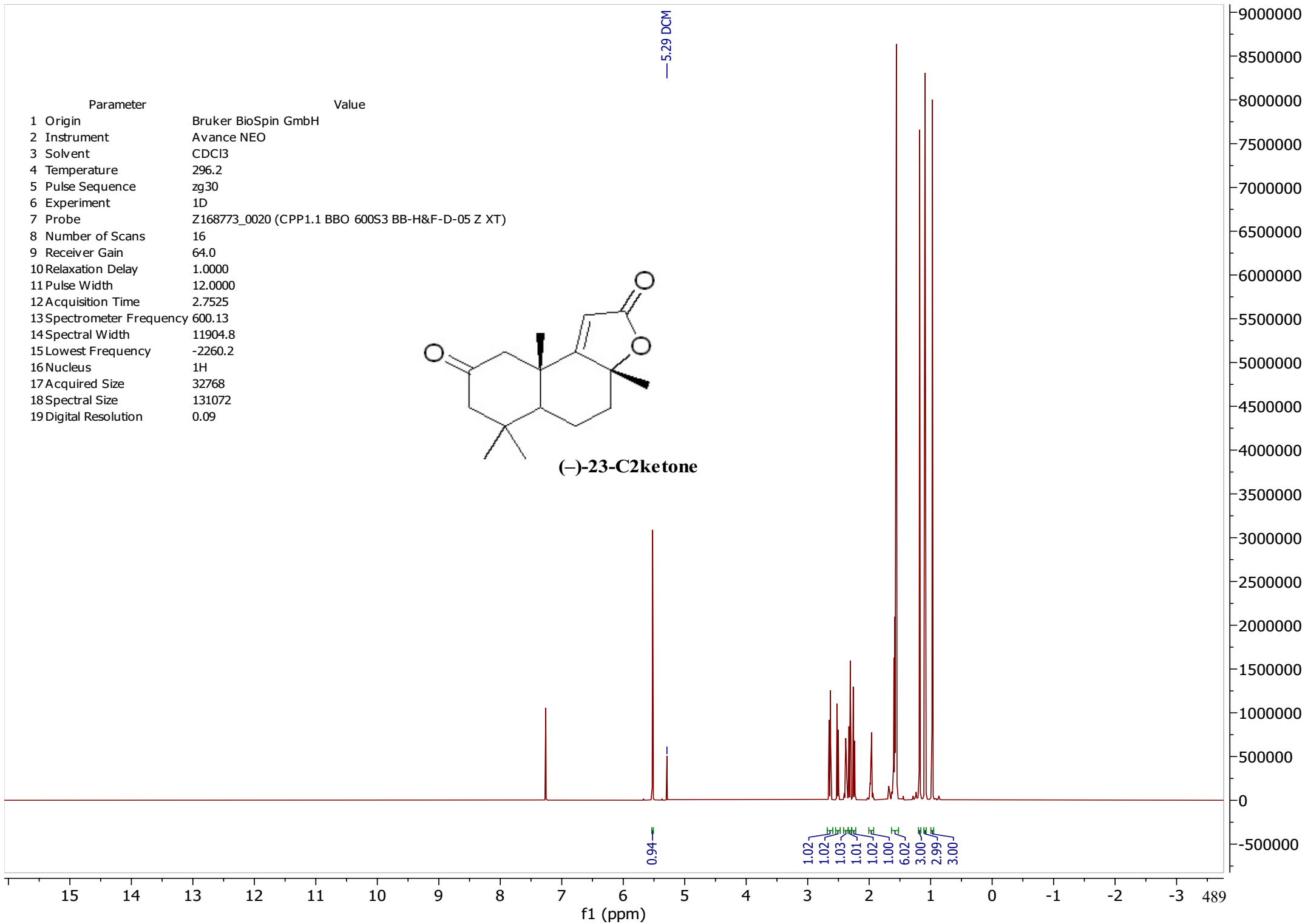
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	256
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1904.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57

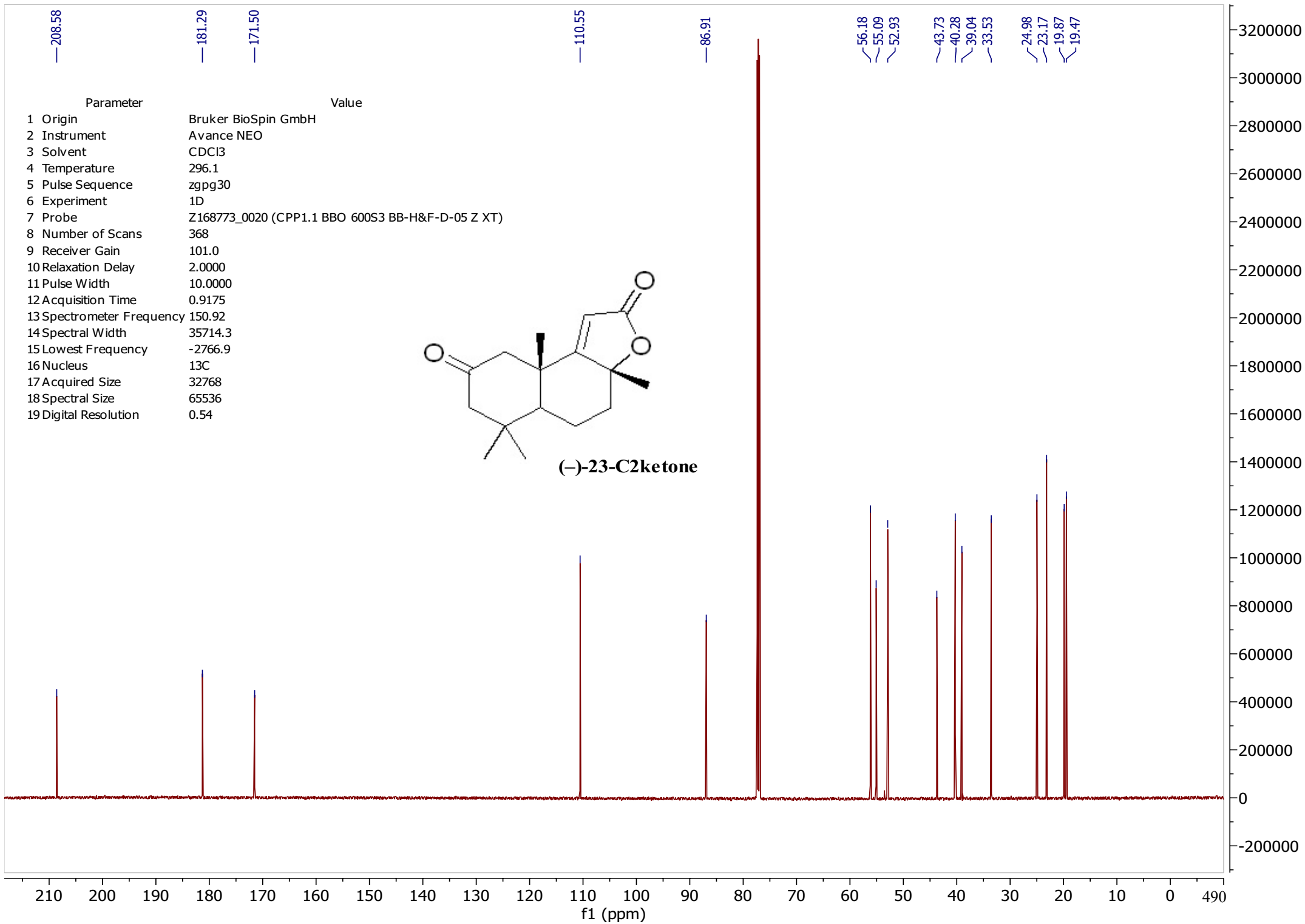


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

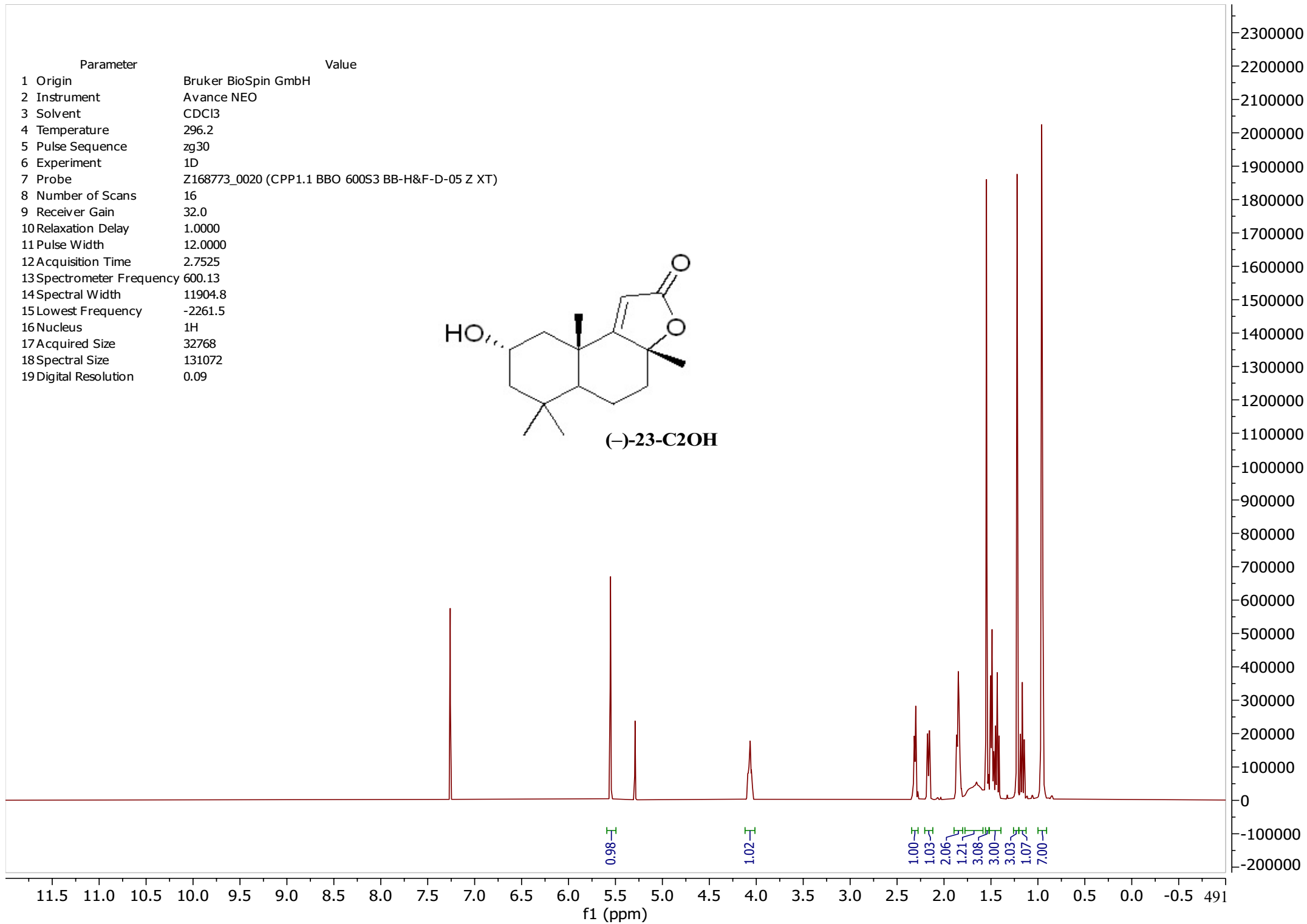
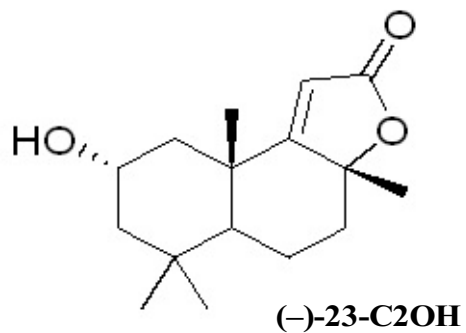


(-)-23-C2ketone

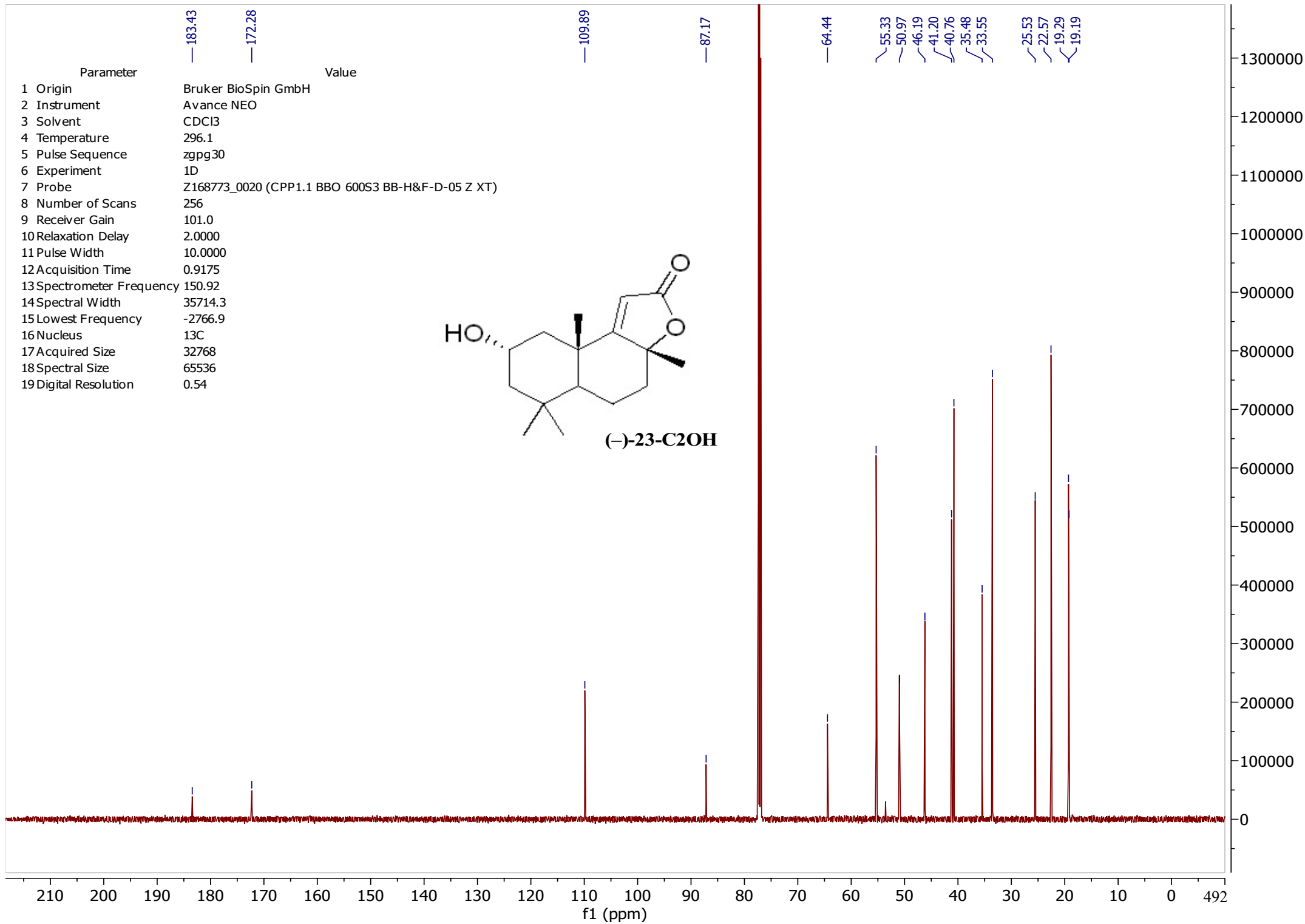
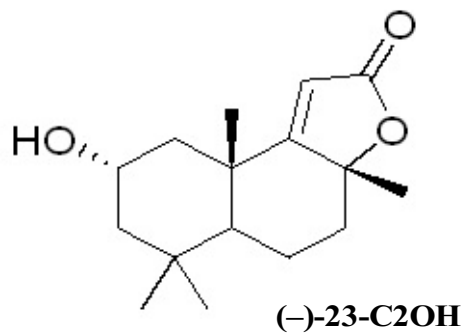




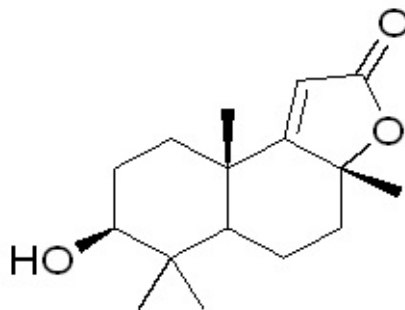
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	256
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.9175
13 Spectrometer Frequency	150.92
14 Spectral Width	35714.3
15 Lowest Frequency	-2766.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.54

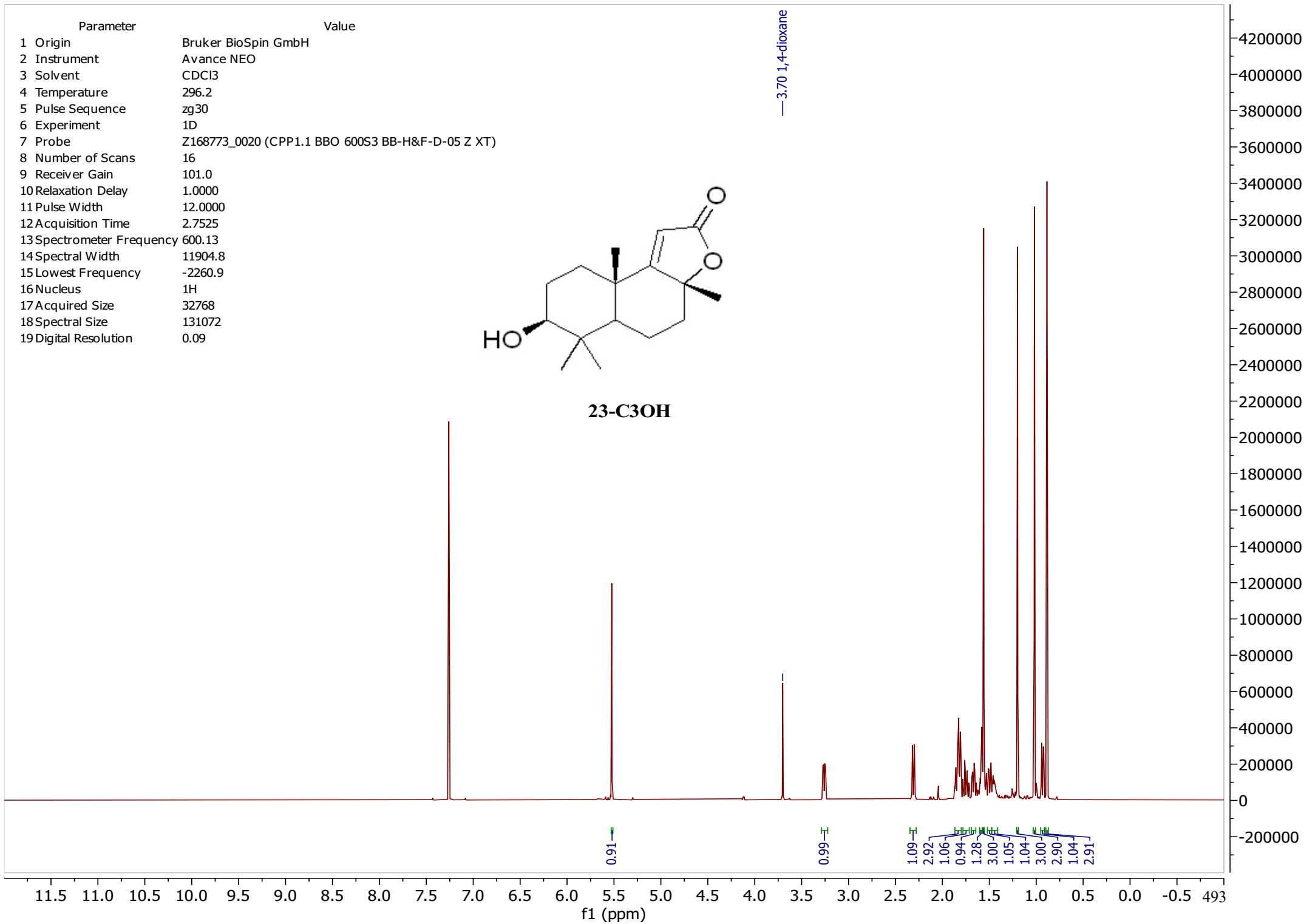


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

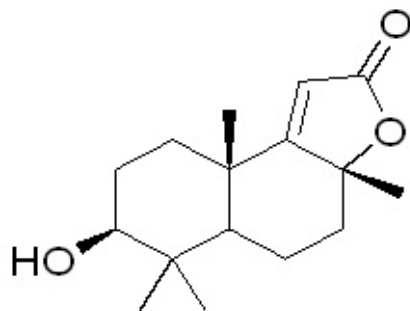


23-C3OH

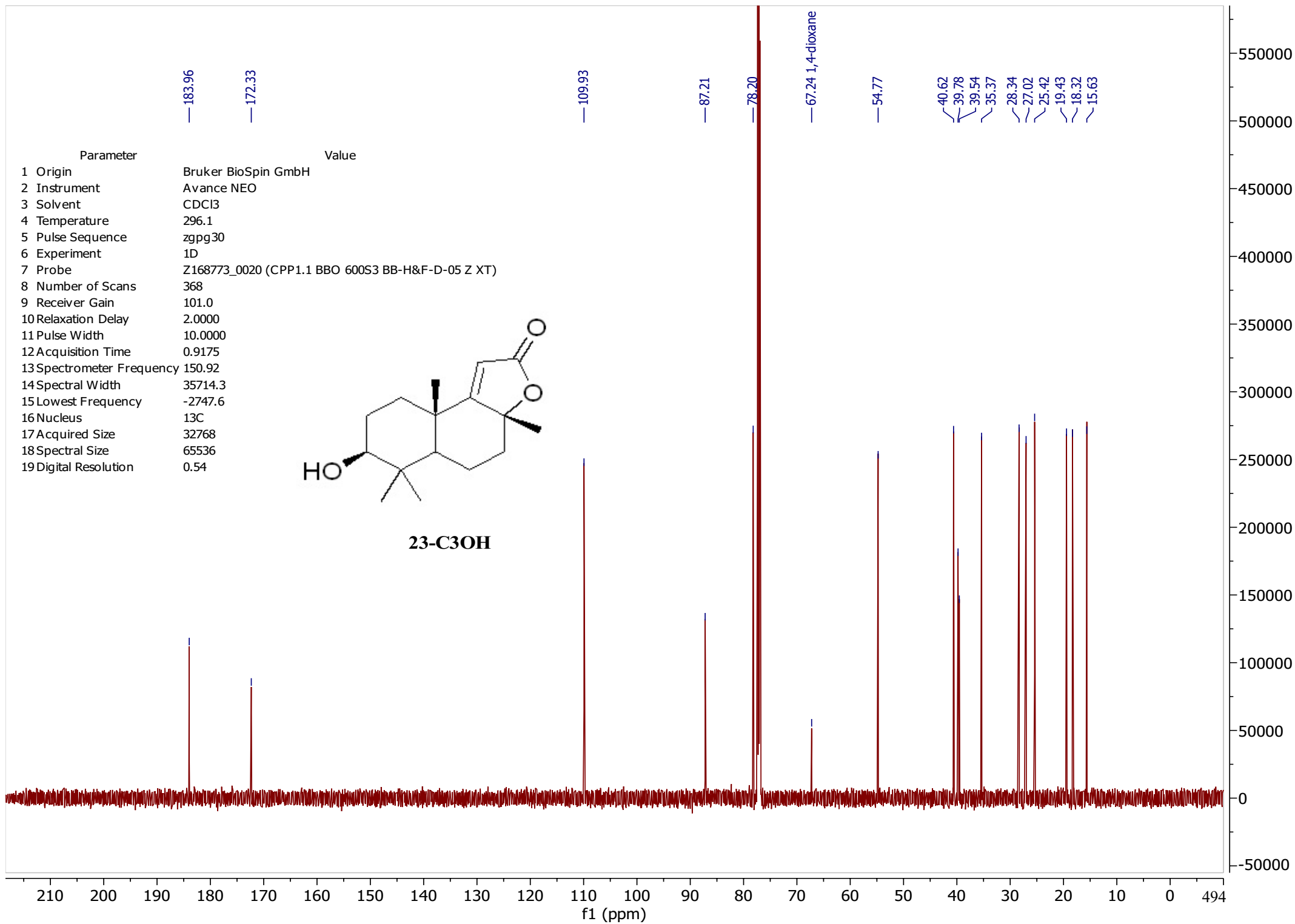
— 3.70 1,4-dioxane



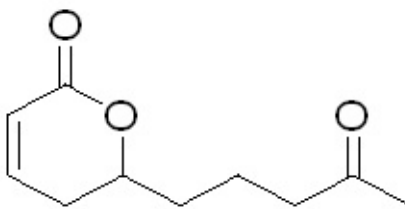
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	368
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.9175
13 Spectrometer Frequency	150.92
14 Spectral Width	35714.3
15 Lowest Frequency	-2747.6
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.54



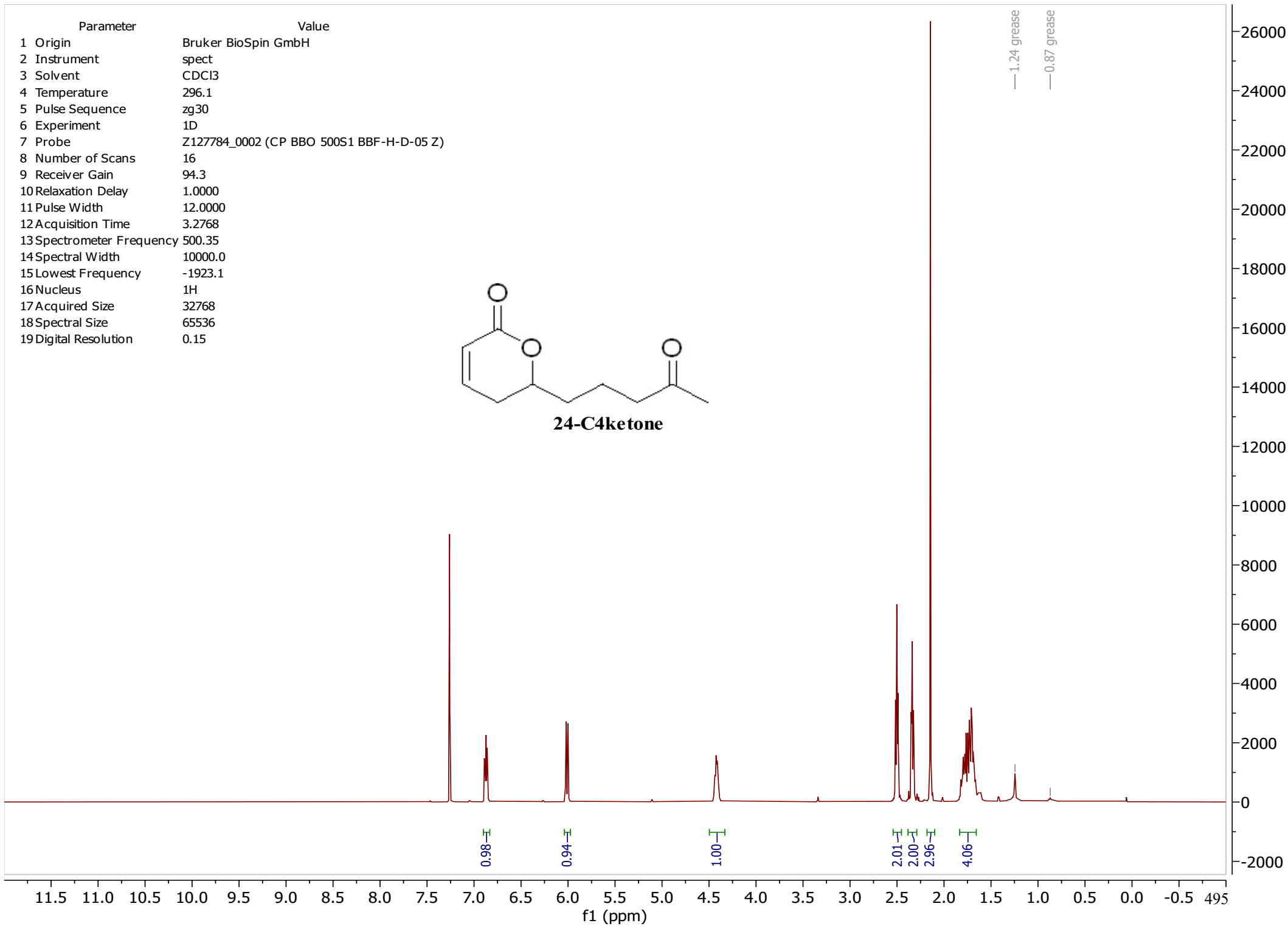
23-C3OH



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	94.3
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

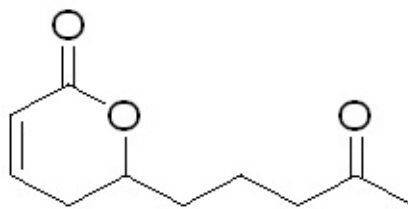


24-C4ketone



Parameter Value
1 Origin Bruker BioSpin GmbH
2 Instrument spect
3 Solvent CDCl3
4 Temperature 296.1
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Probe Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans 368
9 Receiver Gain 190.5
10 Relaxation Delay 2.0000
11 Pulse Width 10.0000
12 Acquisition Time 1.0486
13 Spectrometer Frequency 125.83
14 Spectral Width 31250.0
15 Lowest Frequency -1771.0
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
19 Digital Resolution 0.48

Value



24-C4ketone

f1 (ppm)

208.49

164.47

145.11

121.53

77.84

43.08

34.18

30.10

29.39

19.17

1300

1200

1100

1000

900

800

700

600

500

400

300

200

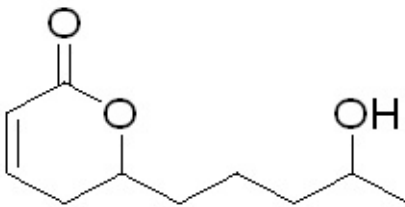
100

0

-100

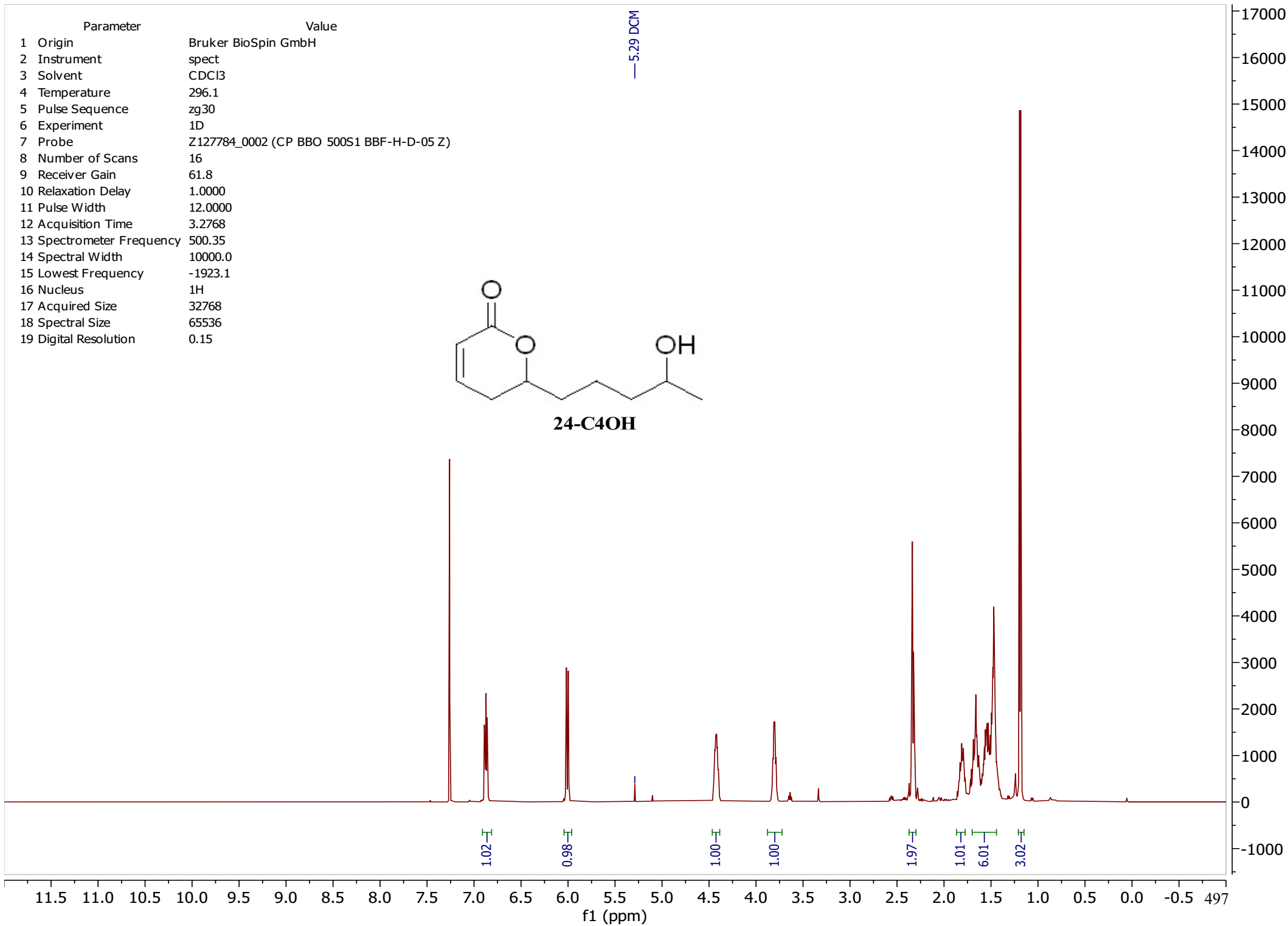
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 496

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	61.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

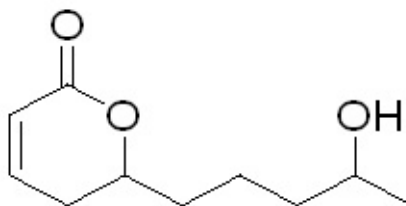


24-C4OH

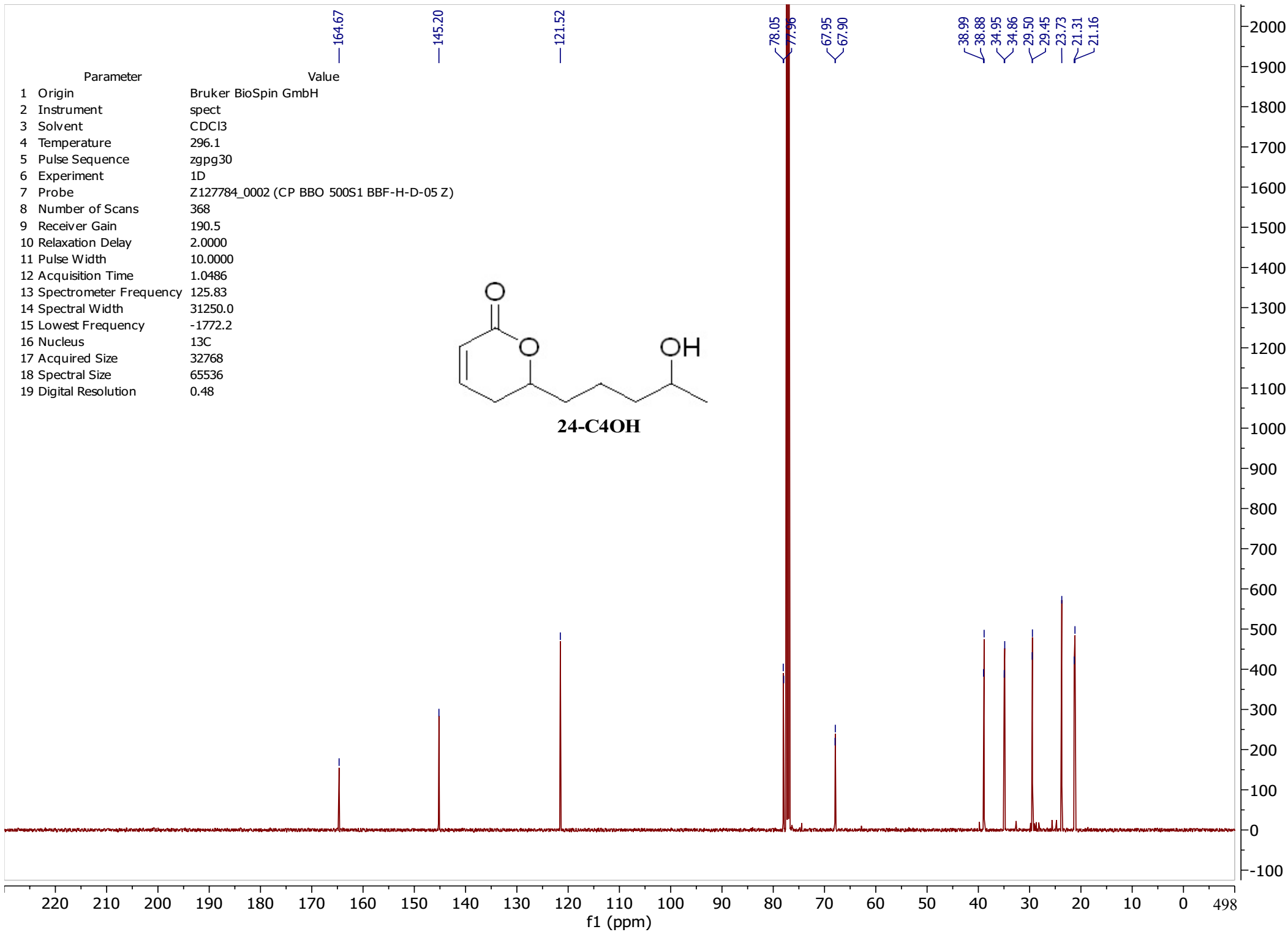
— 5.29 DCM



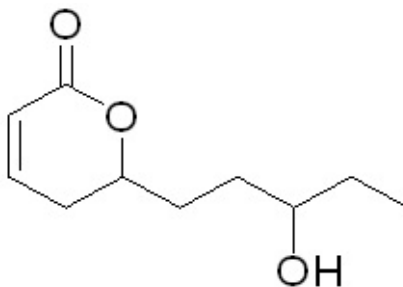
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1772.2
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



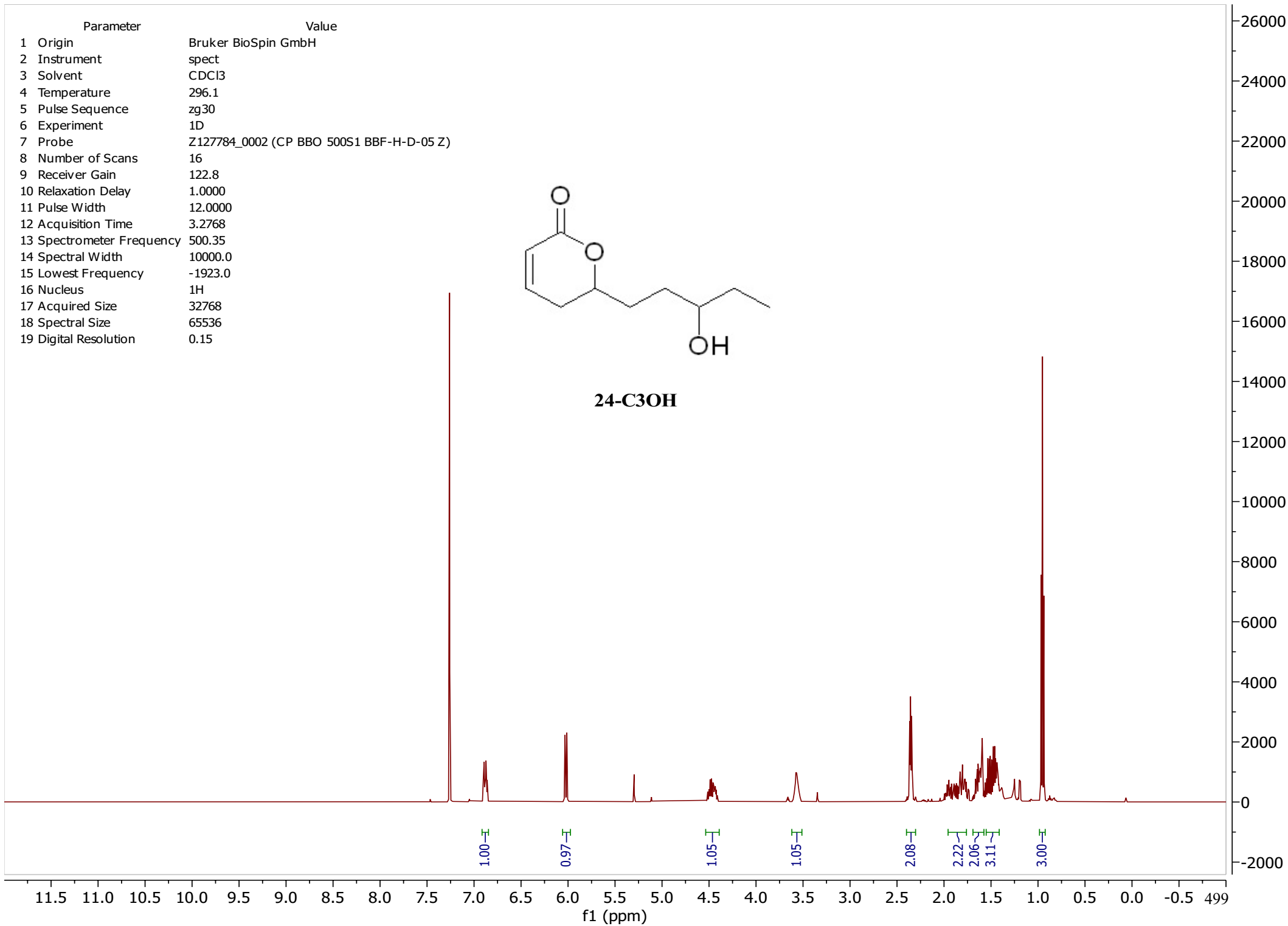
24-C4OH



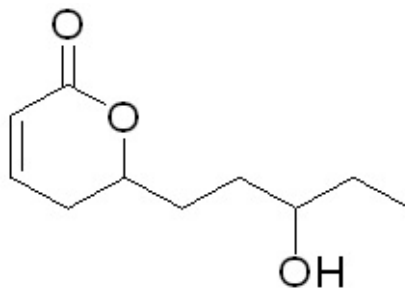
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	122.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



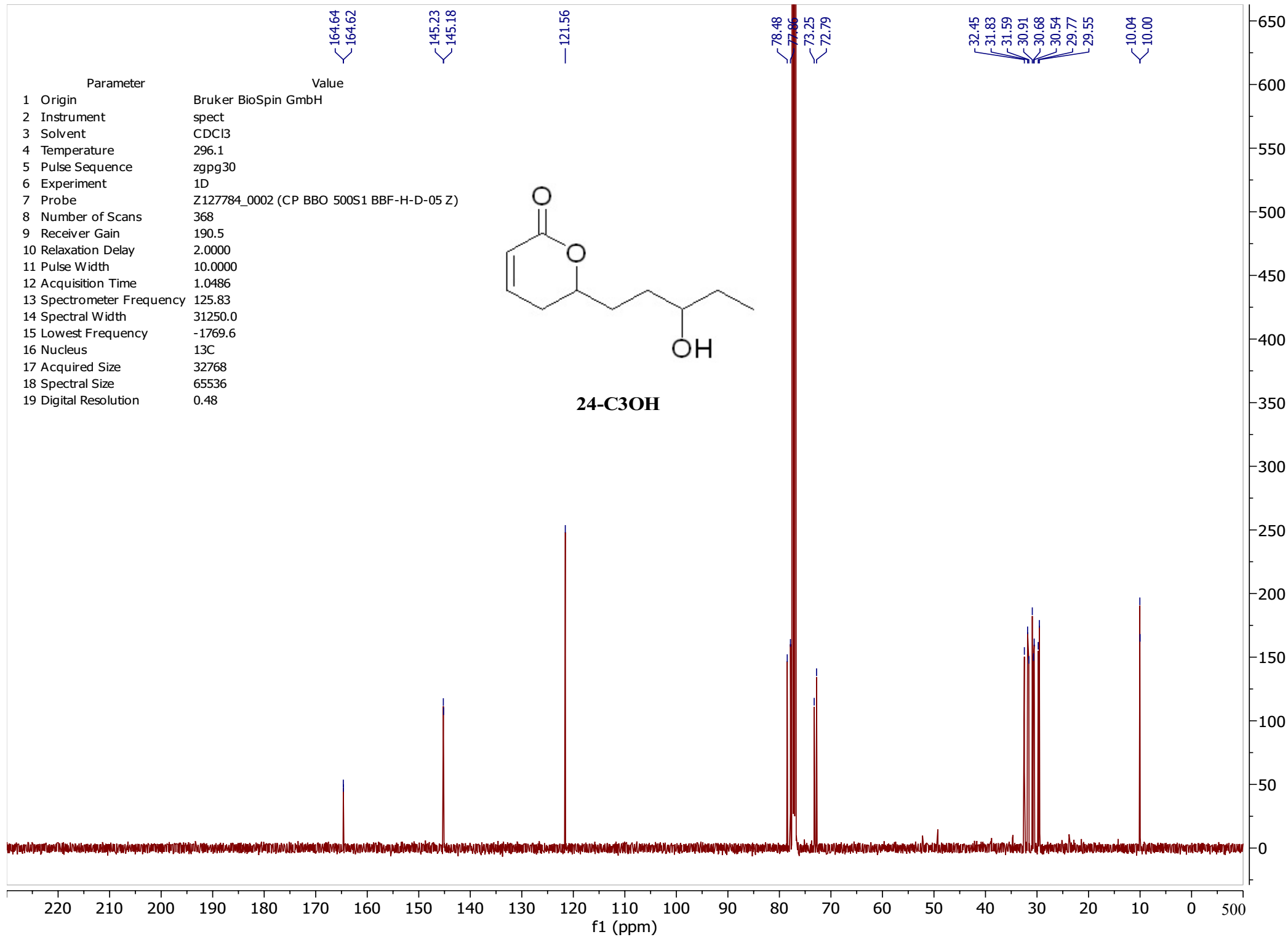
24-C3OH



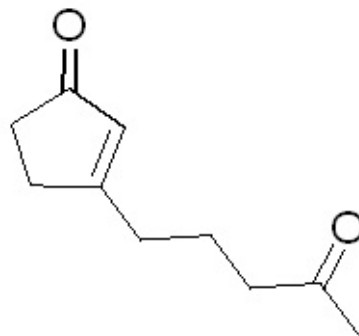
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1769.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



24-C3OH

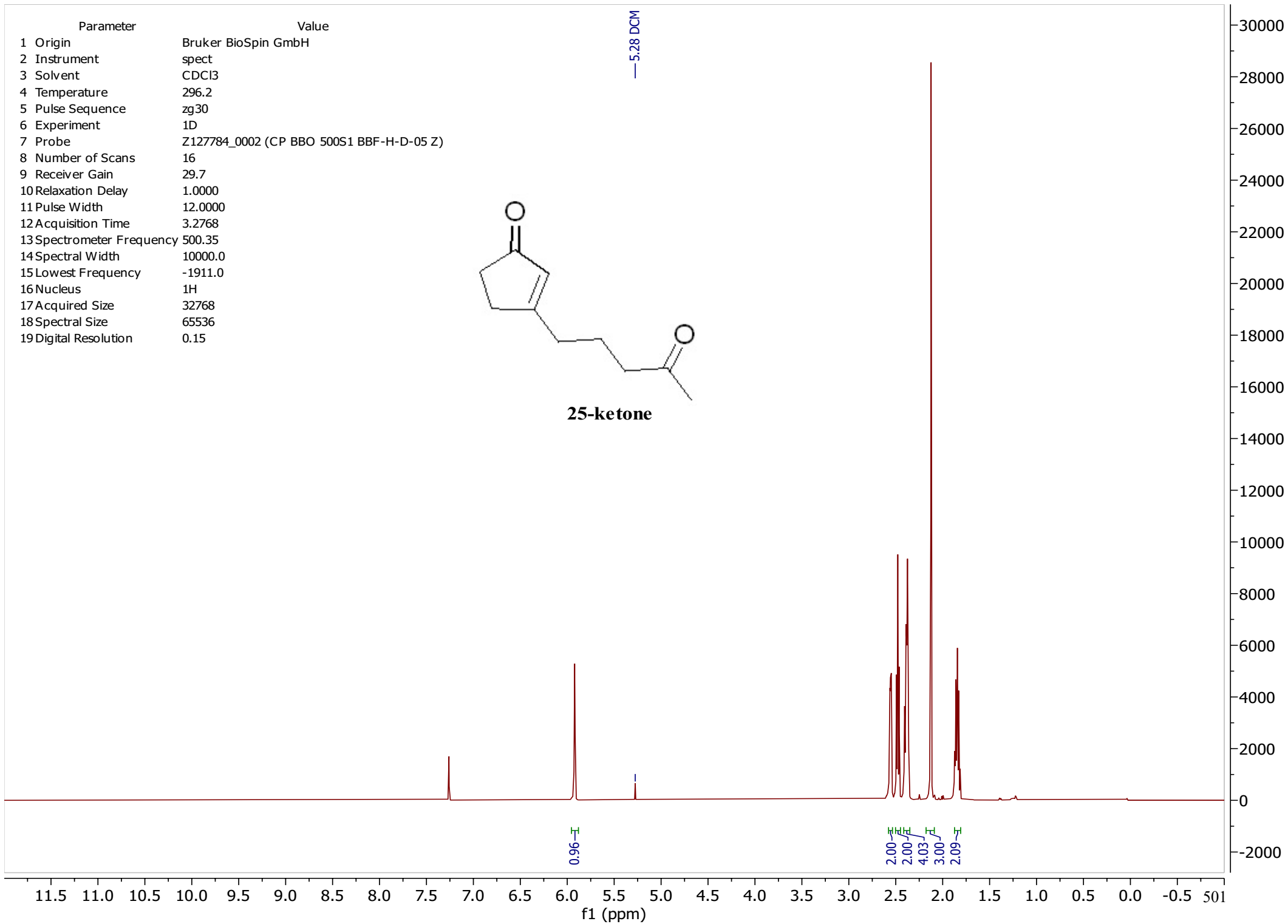


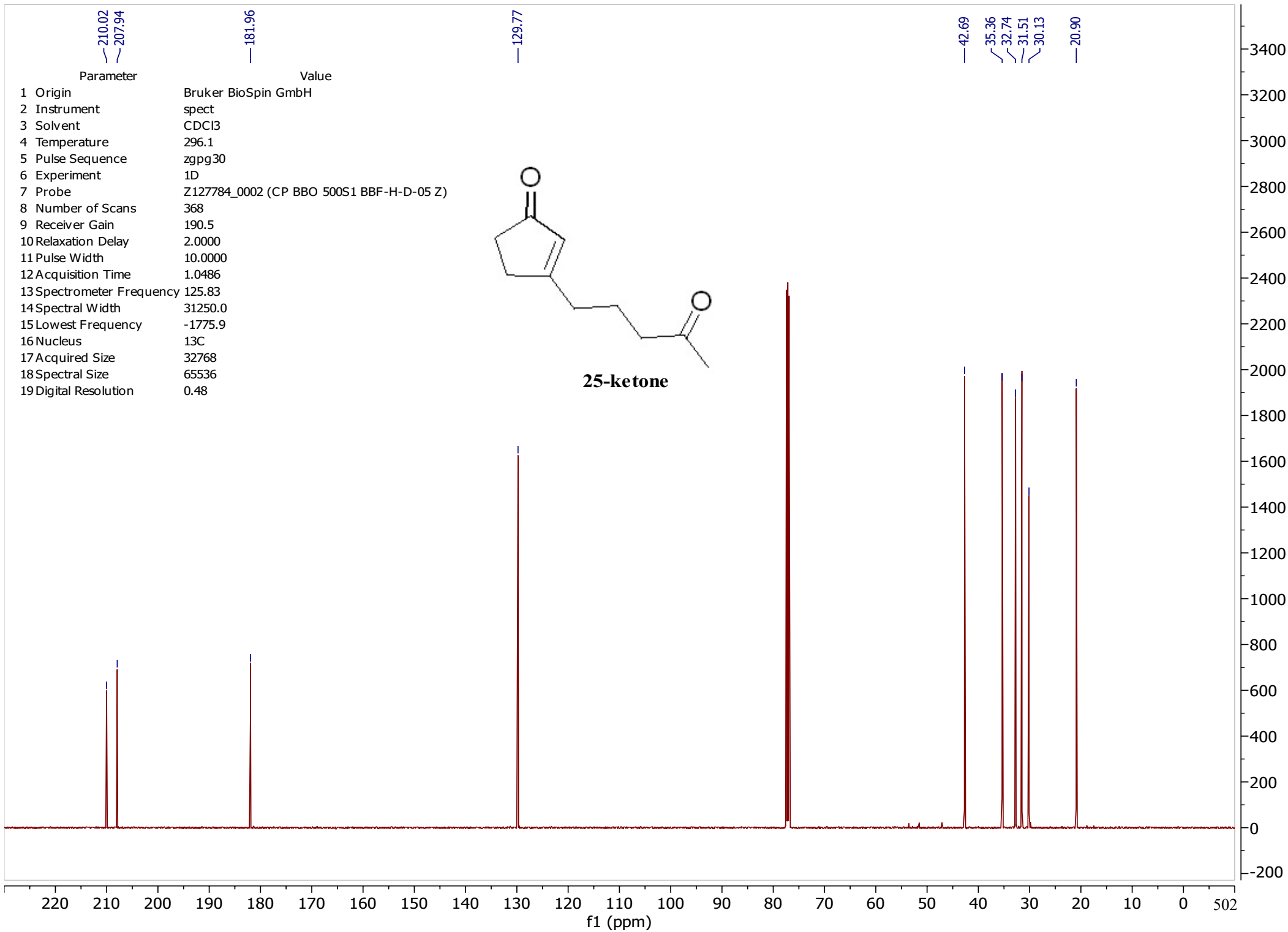
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1911.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



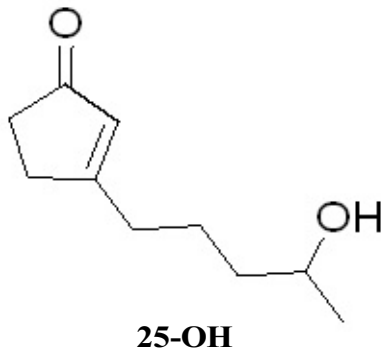
25-ketone

— 5.28 DCM

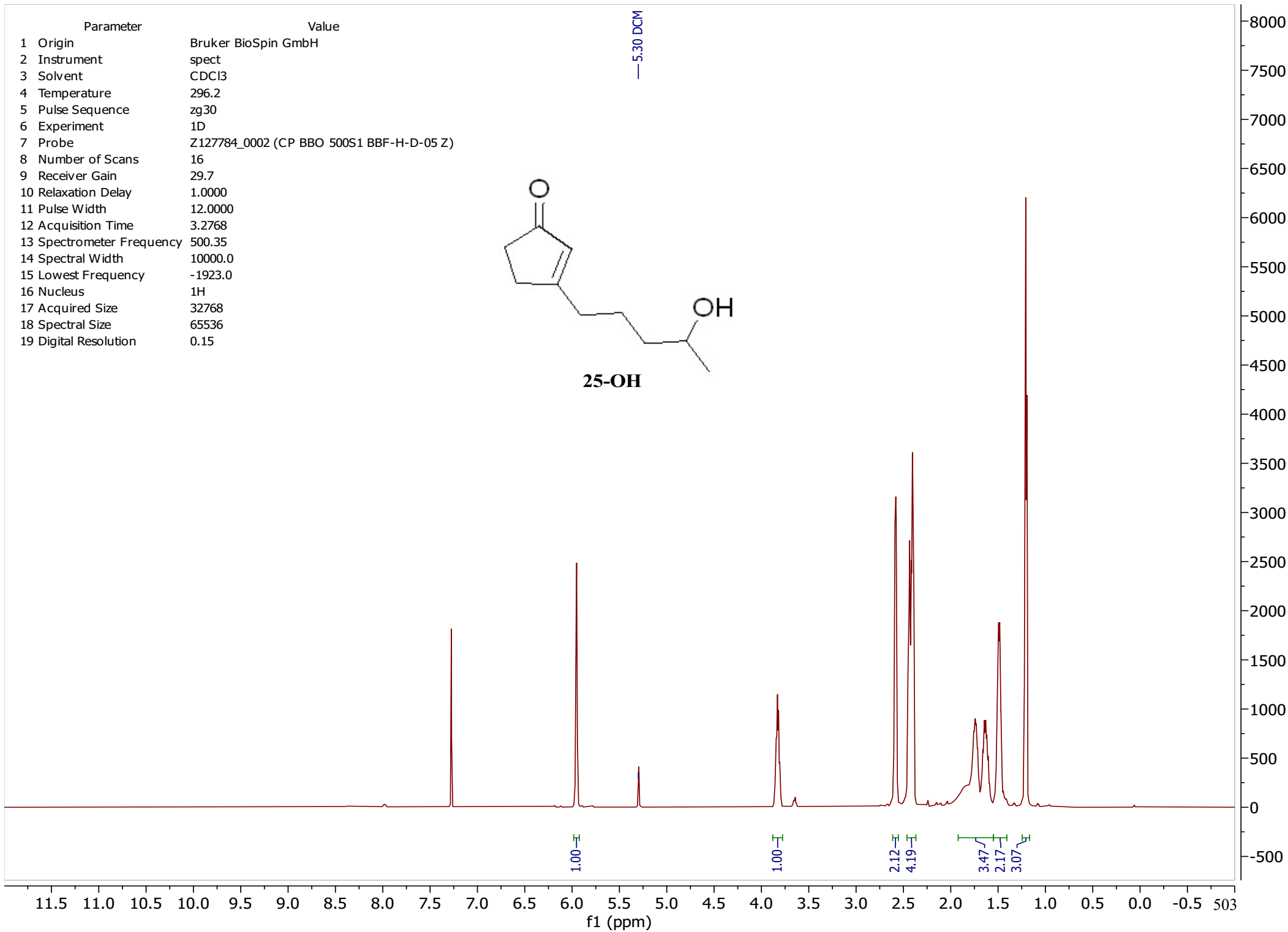




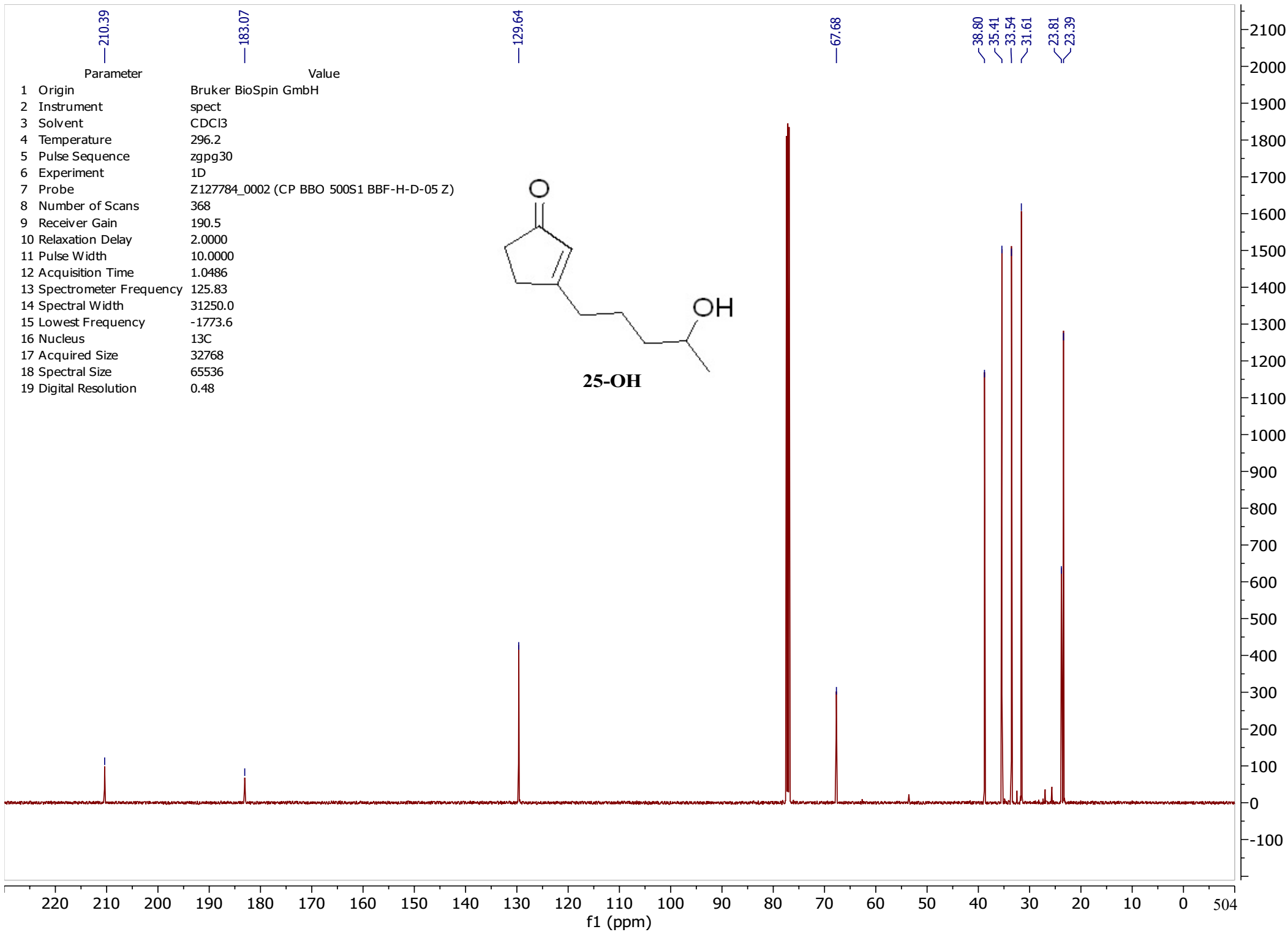
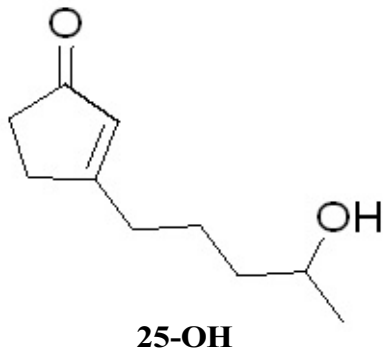
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



— 5.30 DCM



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1773.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

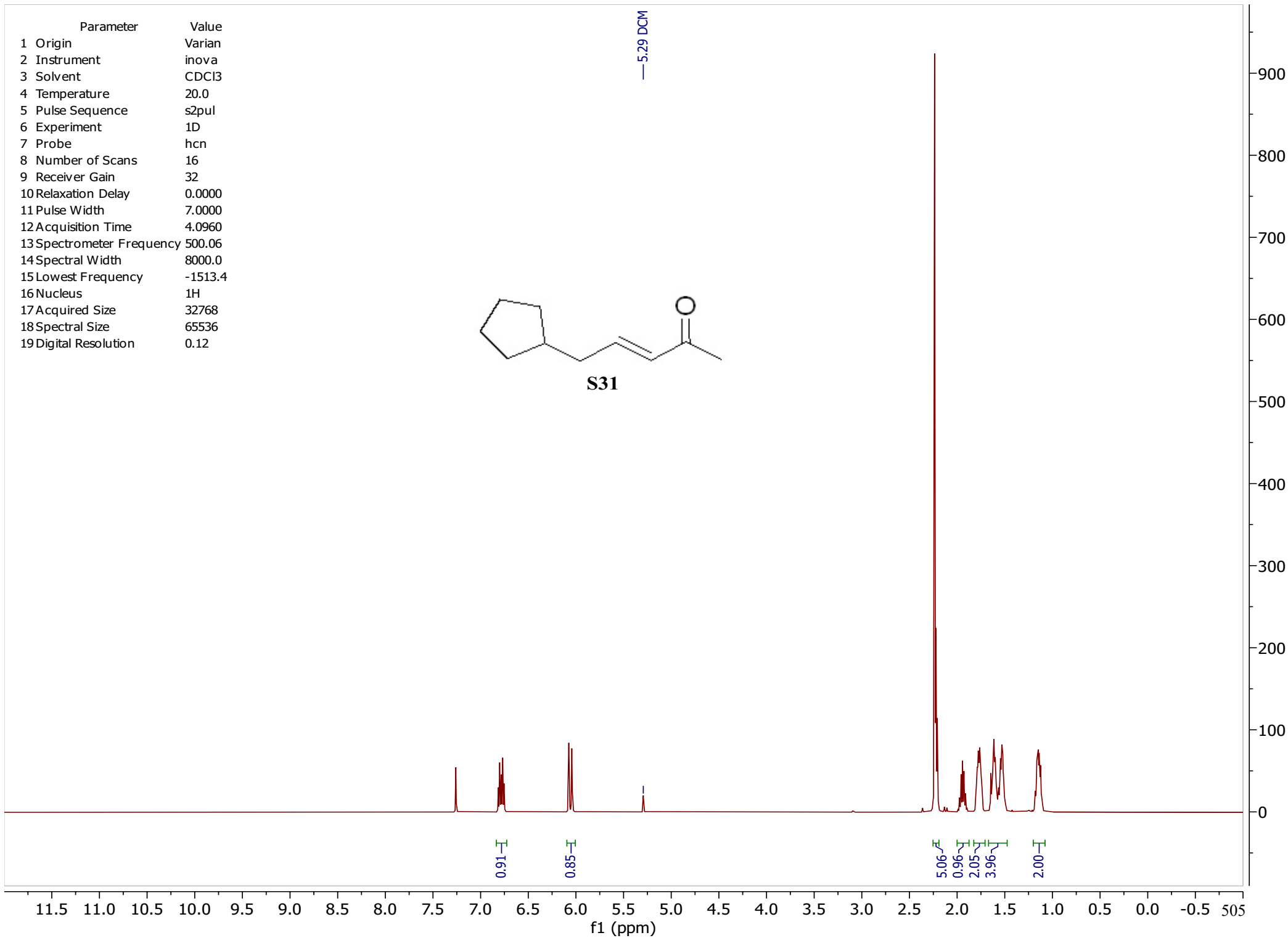


Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	hcn
8 Number of Scans	16
9 Receiver Gain	32
10 Relaxation Delay	0.0000
11 Pulse Width	7.0000
12 Acquisition Time	4.0960
13 Spectrometer Frequency	500.06
14 Spectral Width	8000.0
15 Lowest Frequency	-1513.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12

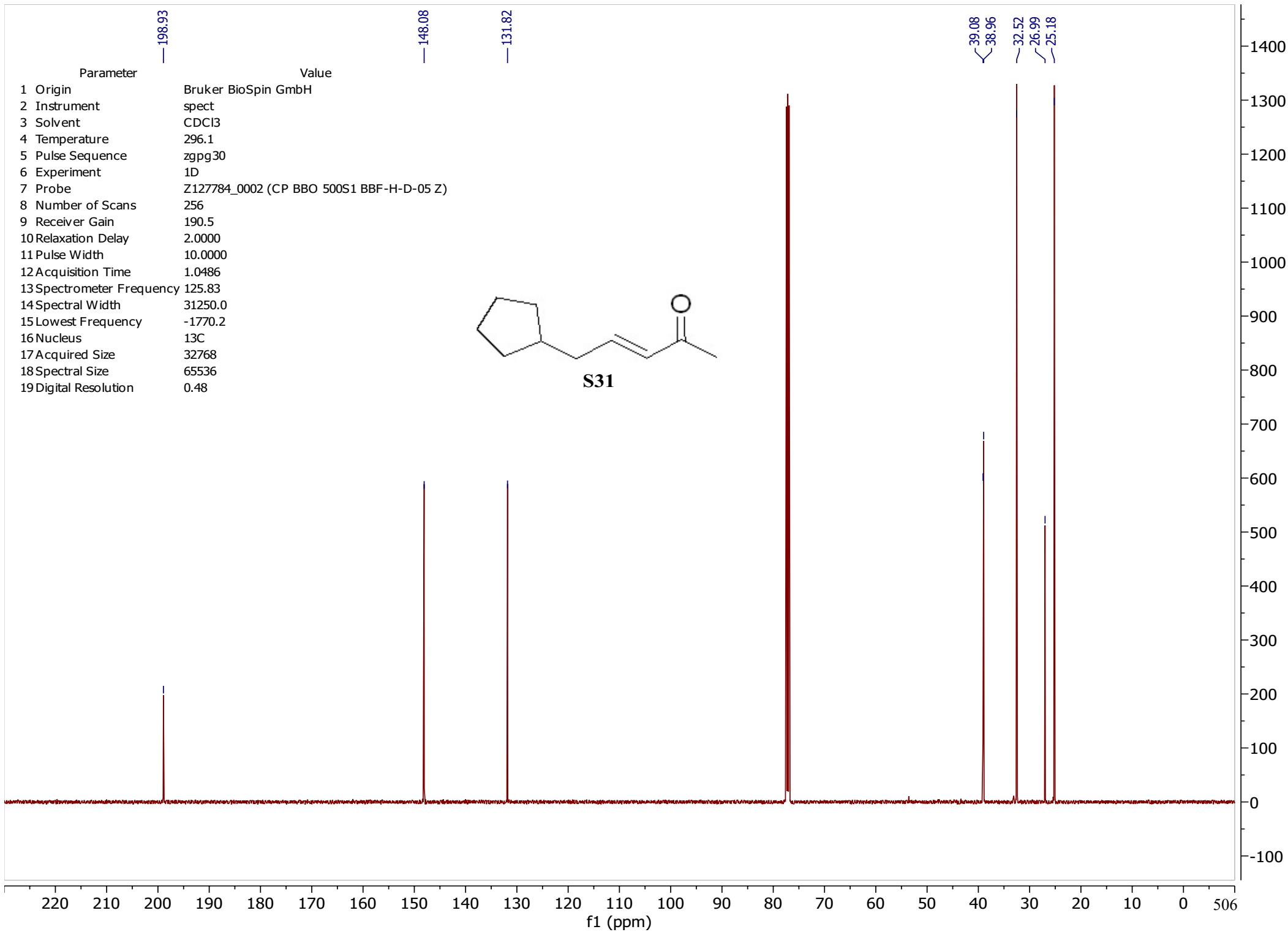


S31

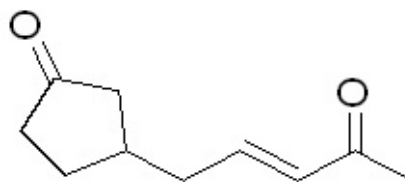
— 5.29 DCM



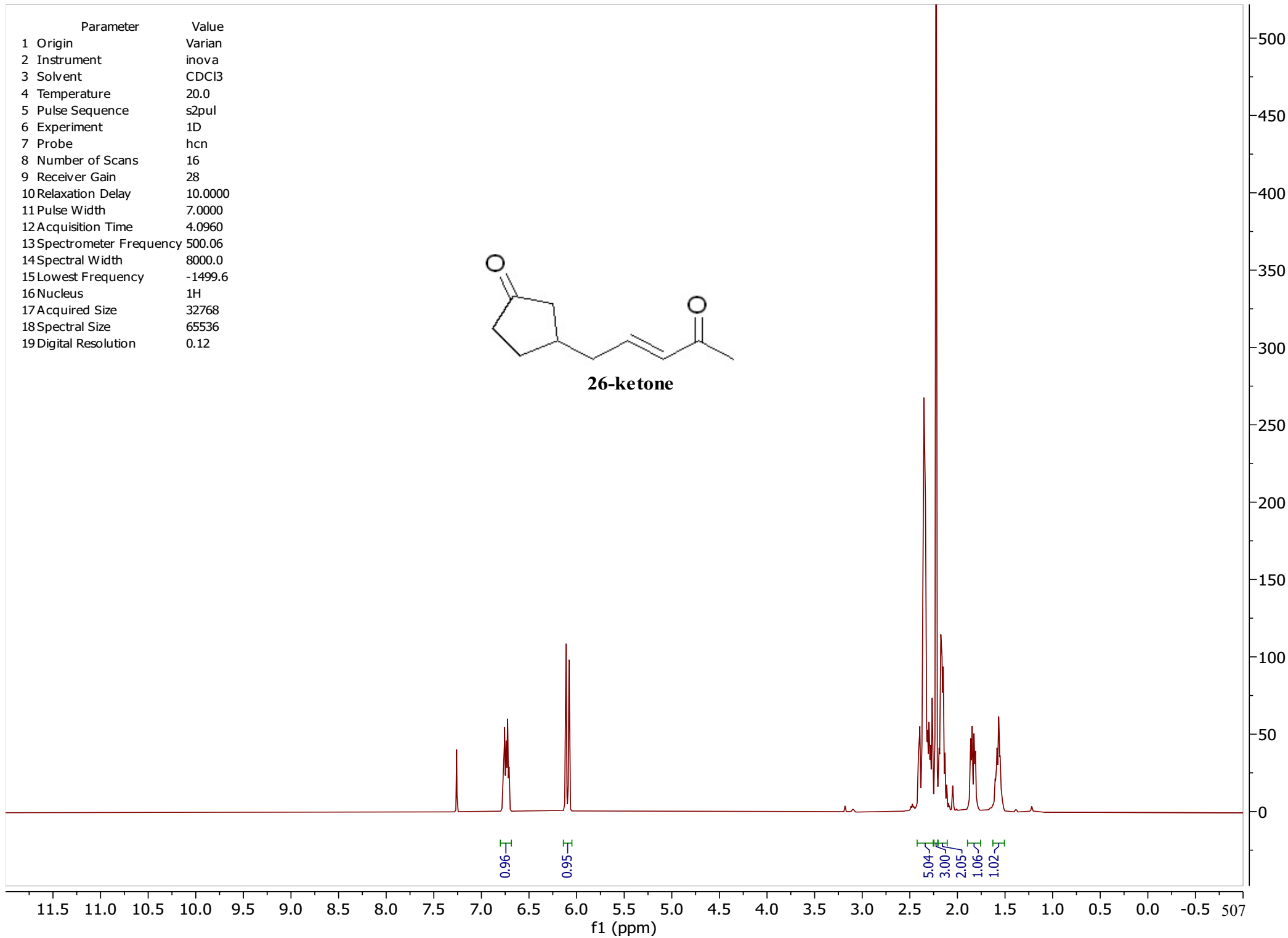
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1770.2
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

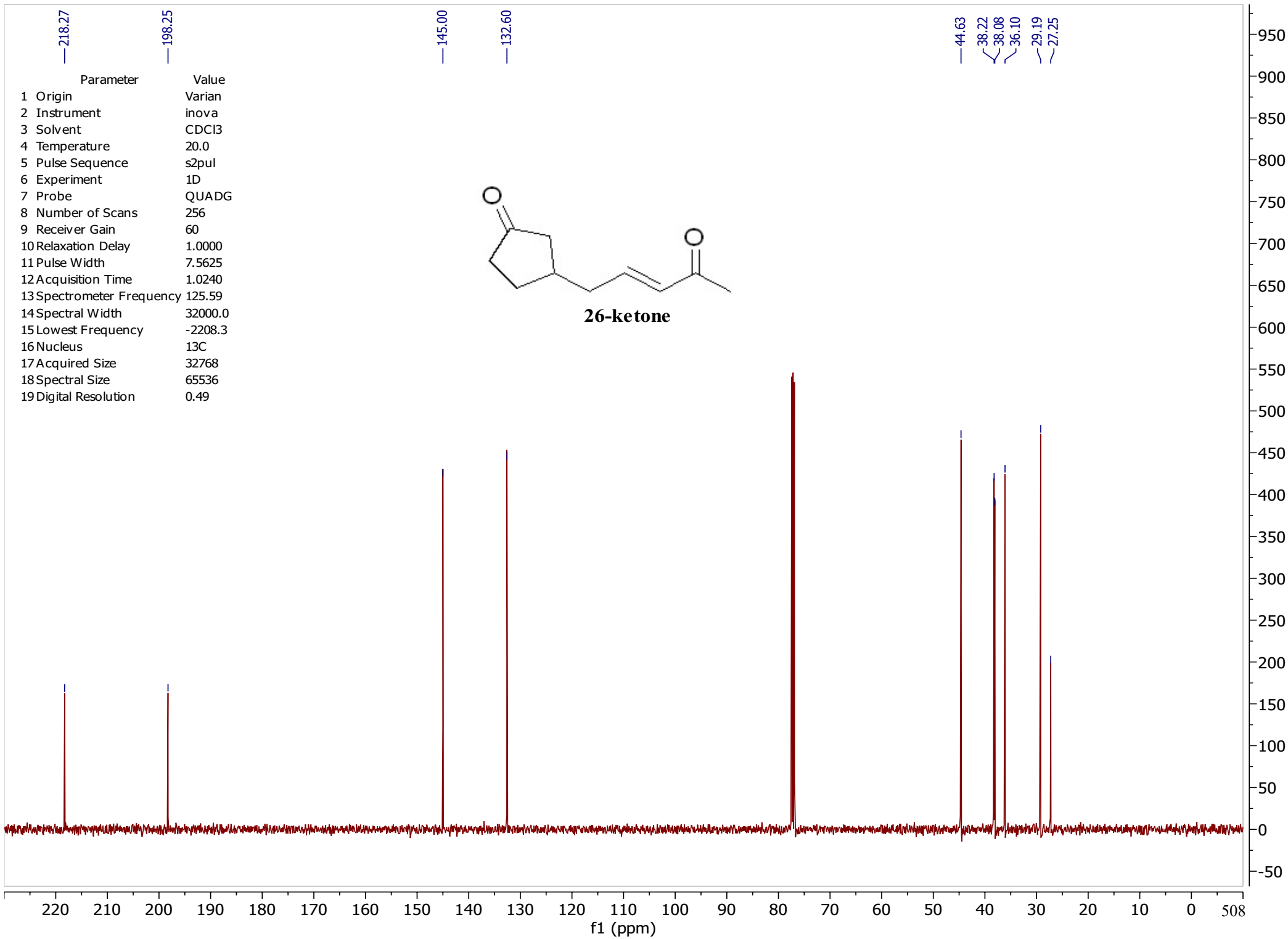


Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	hcn
8 Number of Scans	16
9 Receiver Gain	28
10 Relaxation Delay	10.0000
11 Pulse Width	7.0000
12 Acquisition Time	4.0960
13 Spectrometer Frequency	500.06
14 Spectral Width	8000.0
15 Lowest Frequency	-1499.6
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12

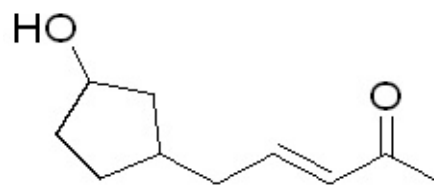


26-ketone

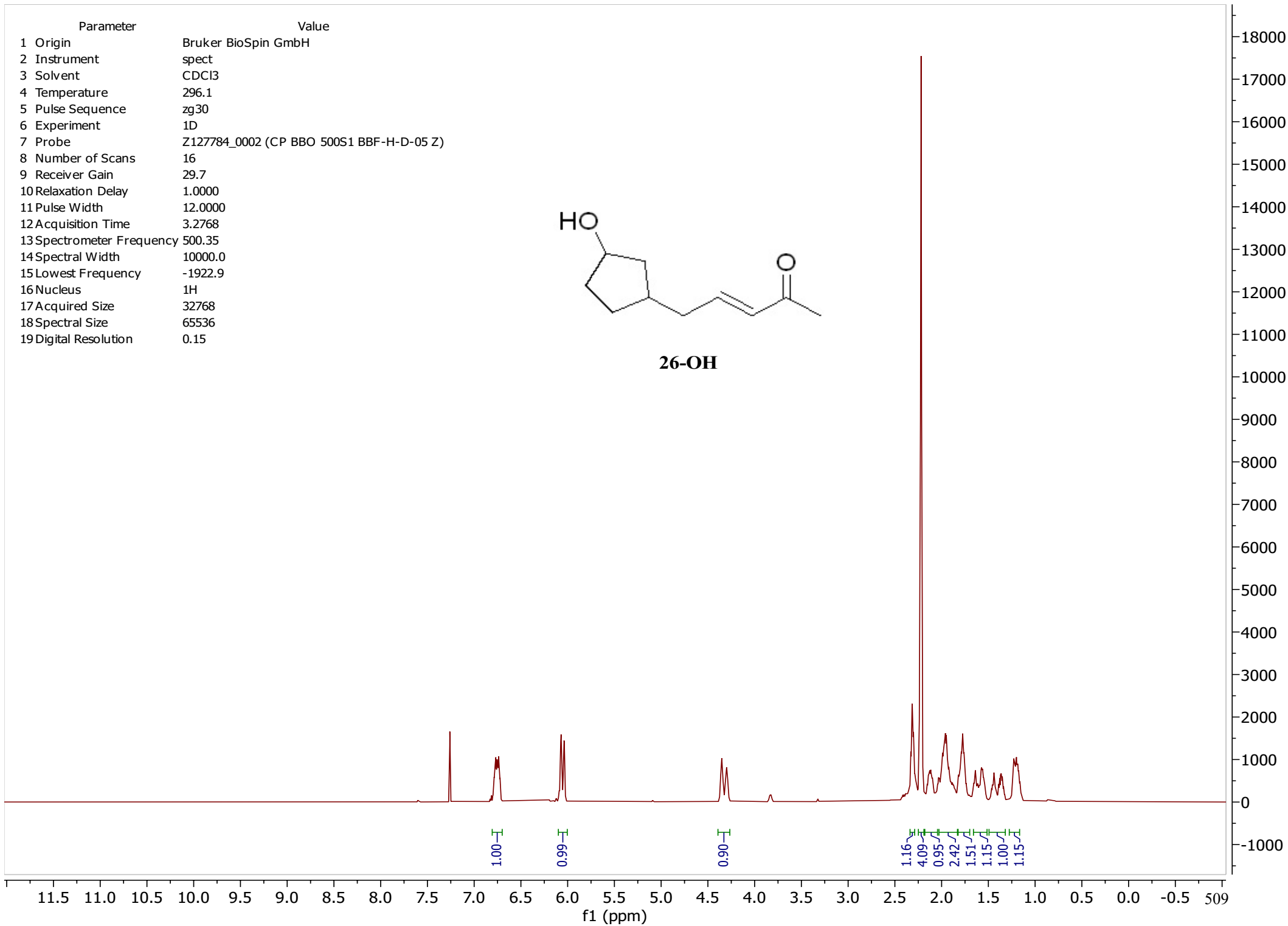




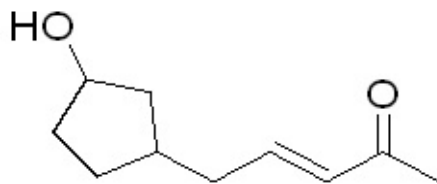
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.9
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



26-OH



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1774.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



26-OH

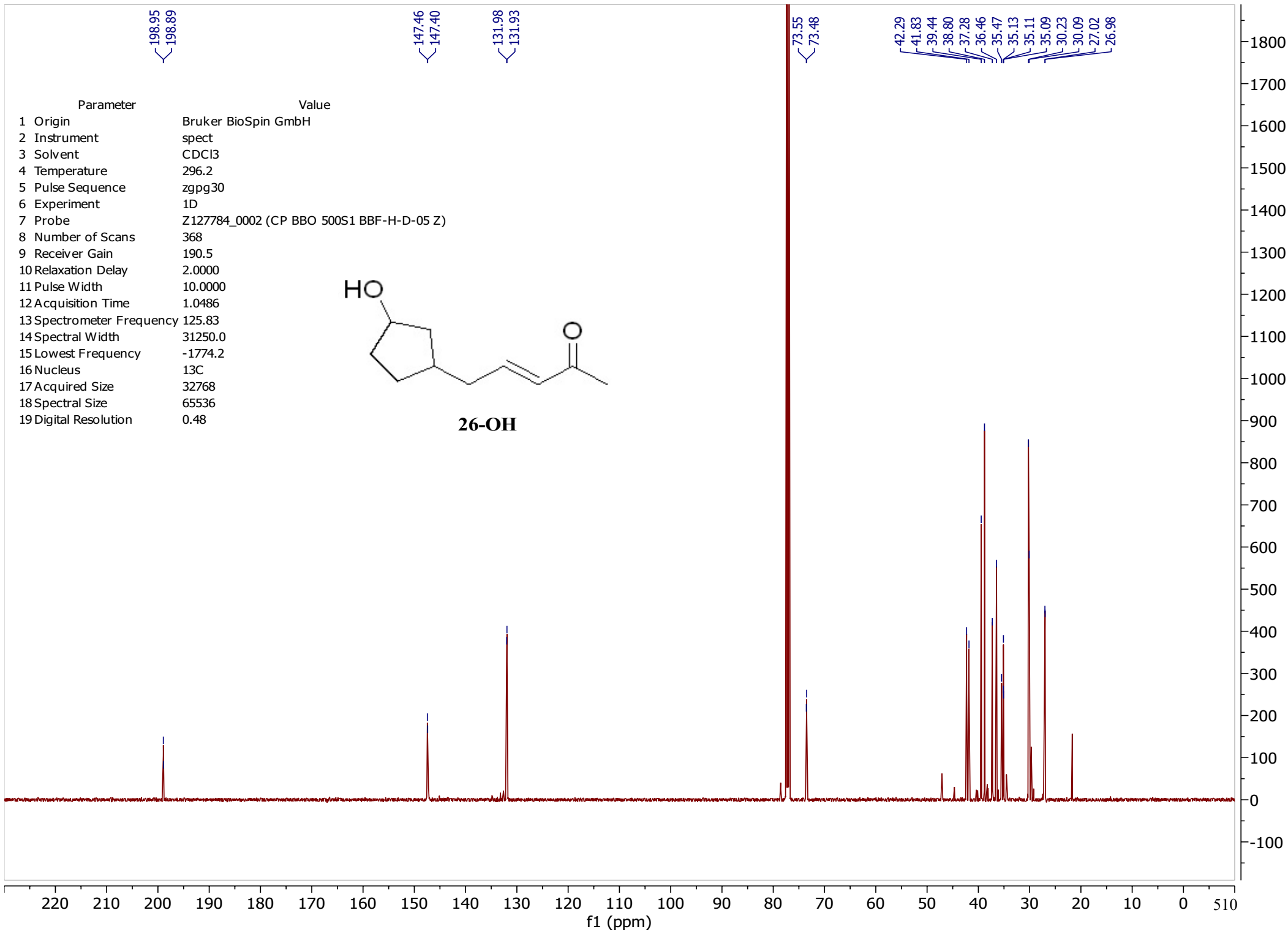
198.95
198.89

147.46
147.40

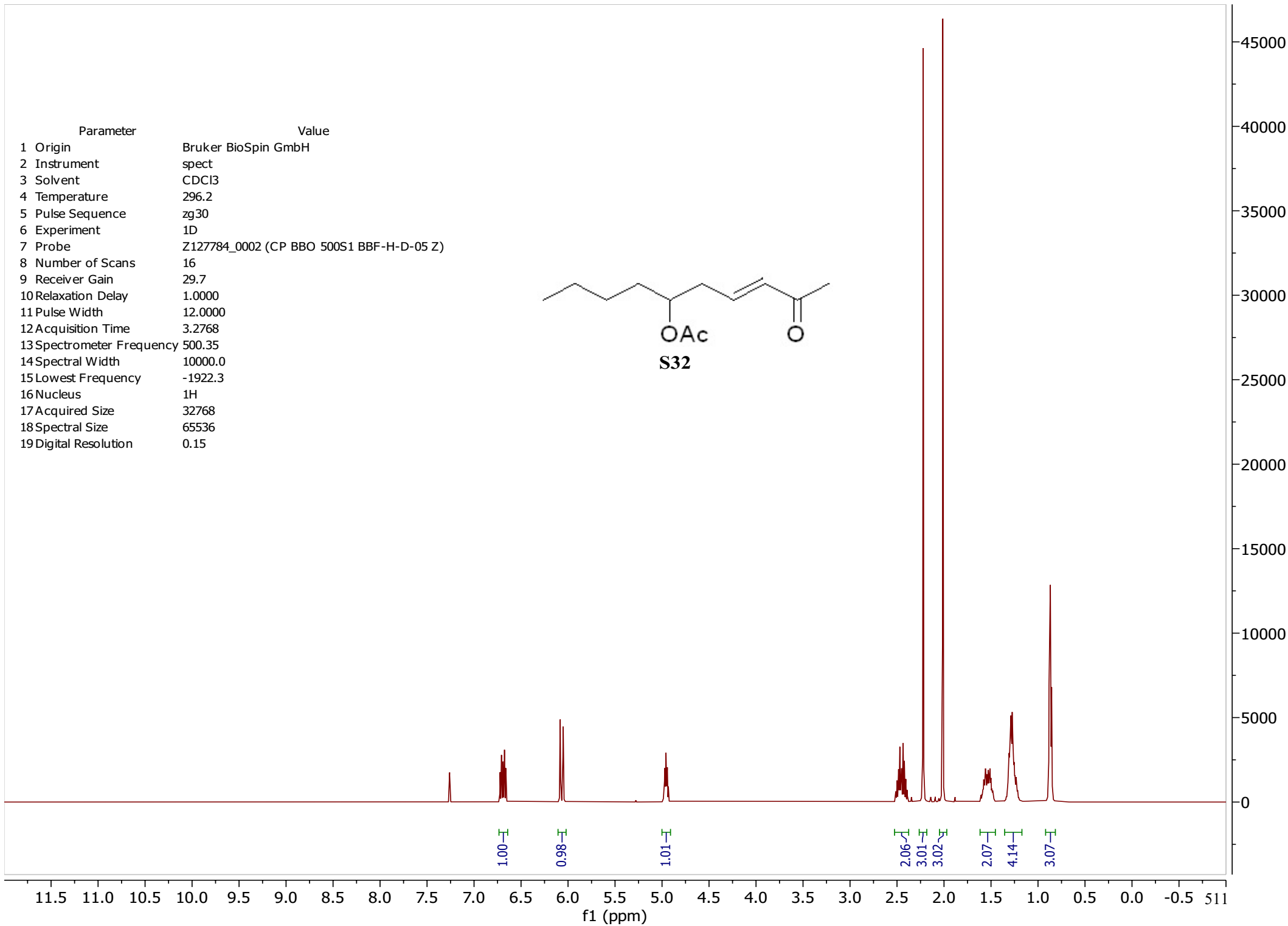
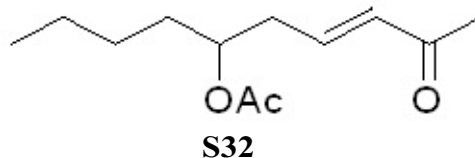
131.98
131.93

73.55
73.48

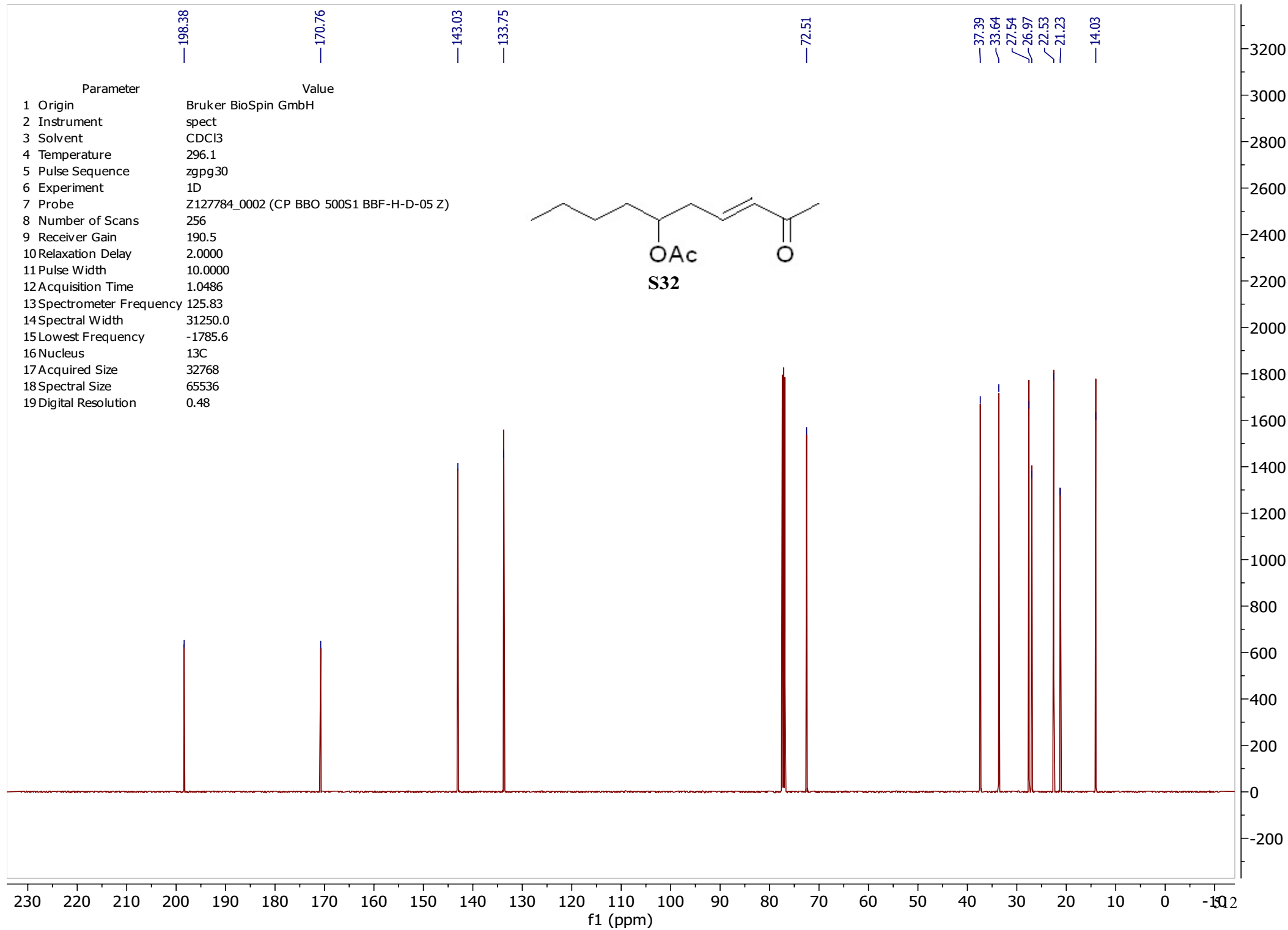
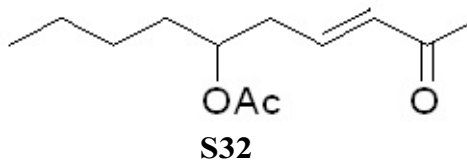
42.29
41.83
39.44
38.80
37.28
36.46
35.47
35.13
35.11
35.09
30.23
30.09
27.02
26.98



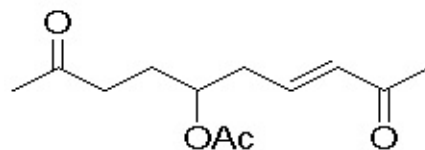
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.3
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



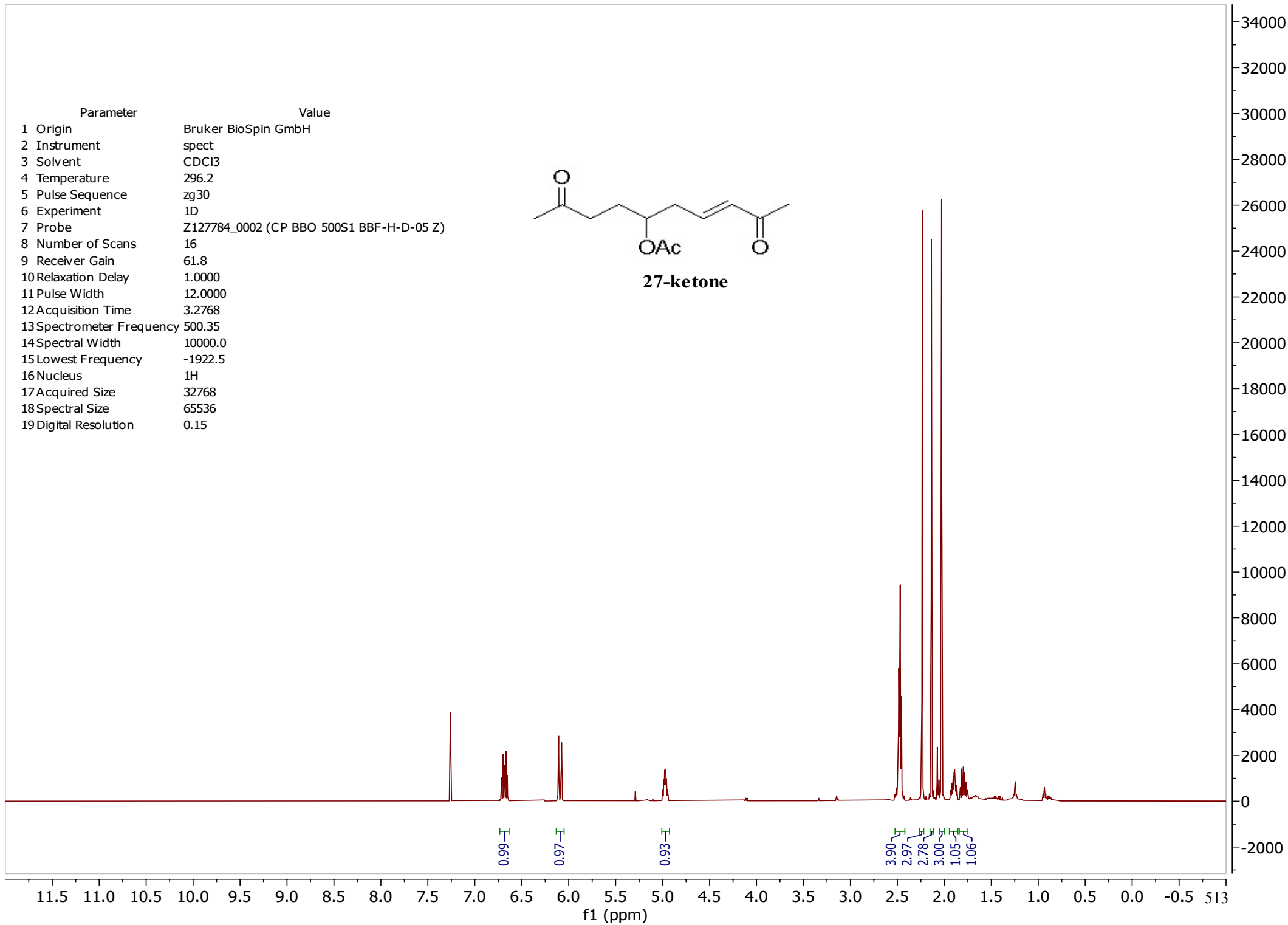
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	61.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.5
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



27-ketone



1 Origin Bruker BioSpin GmbH
2 Instrument spect
3 Solvent CDCl3
4 Temperature 296.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Probe Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans 368
9 Receiver Gain 190.5
10 Relaxation Delay 2.0000
11 Pulse Width 10.0000
12 Acquisition Time 1.0486
13 Spectrometer Frequency 125.83
14 Spectral Width 31250.0
15 Lowest Frequency -1770.7
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
19 Digital Resolution 0.48

Parameter Value

142.30

133.97

71.77

39.43

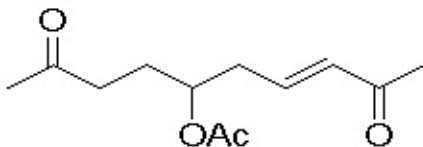
37.63

30.10

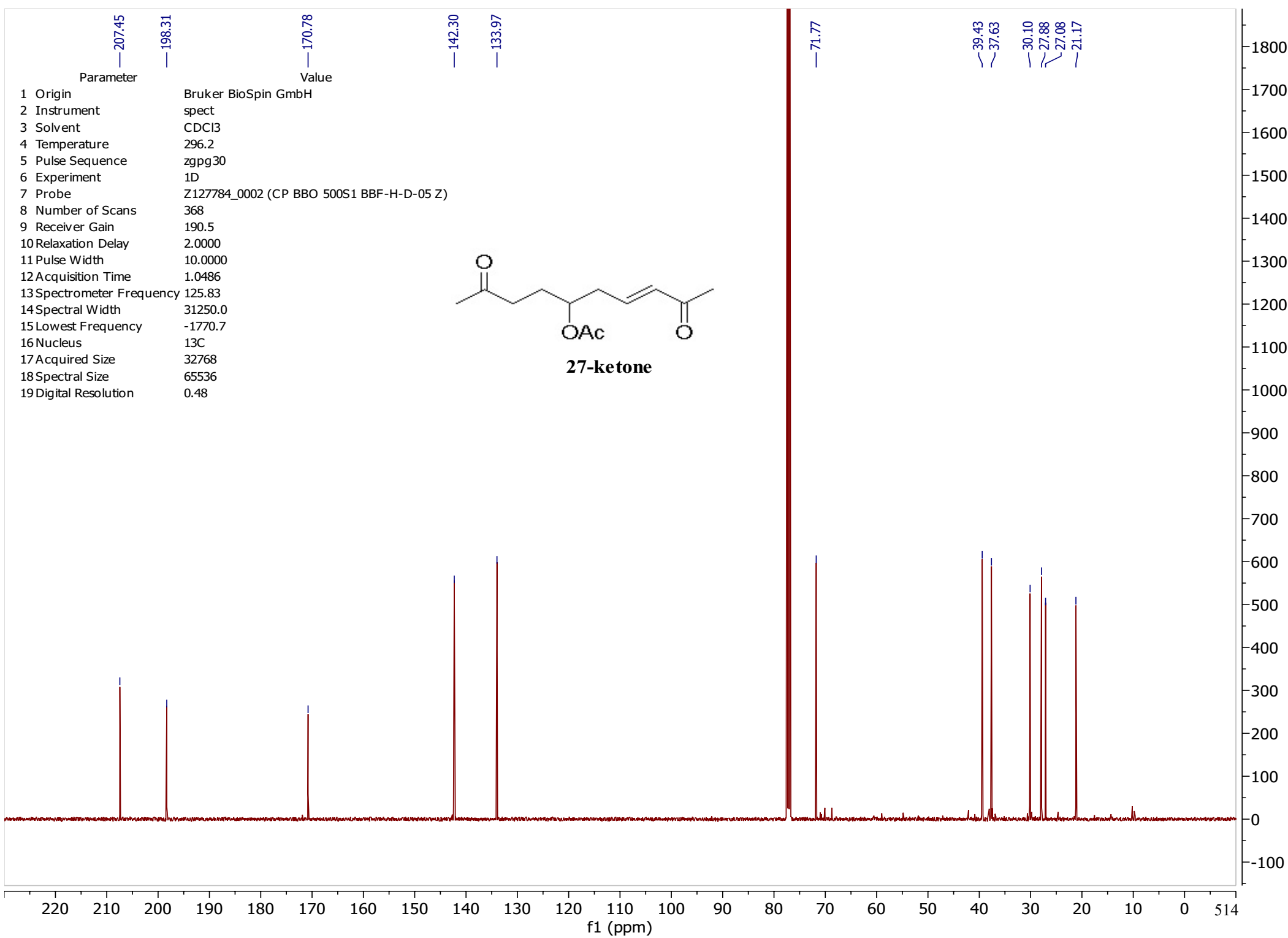
27.88

27.08

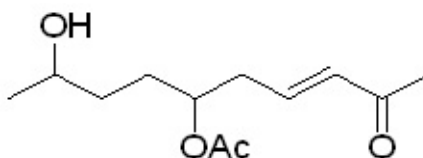
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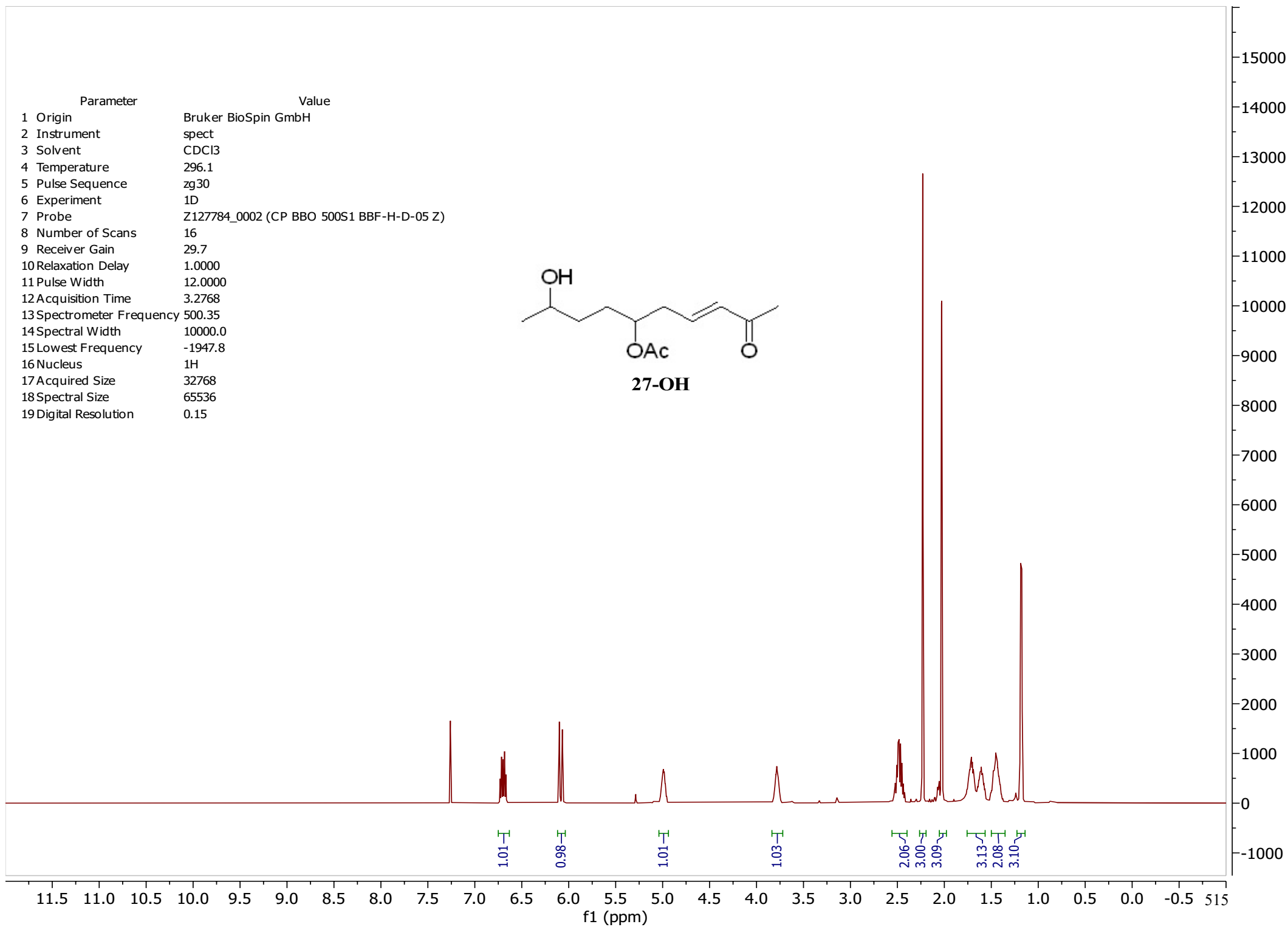
27-ketone



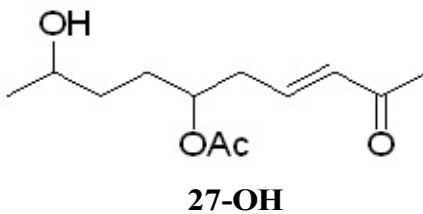
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1947.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



27-OH



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



198.44

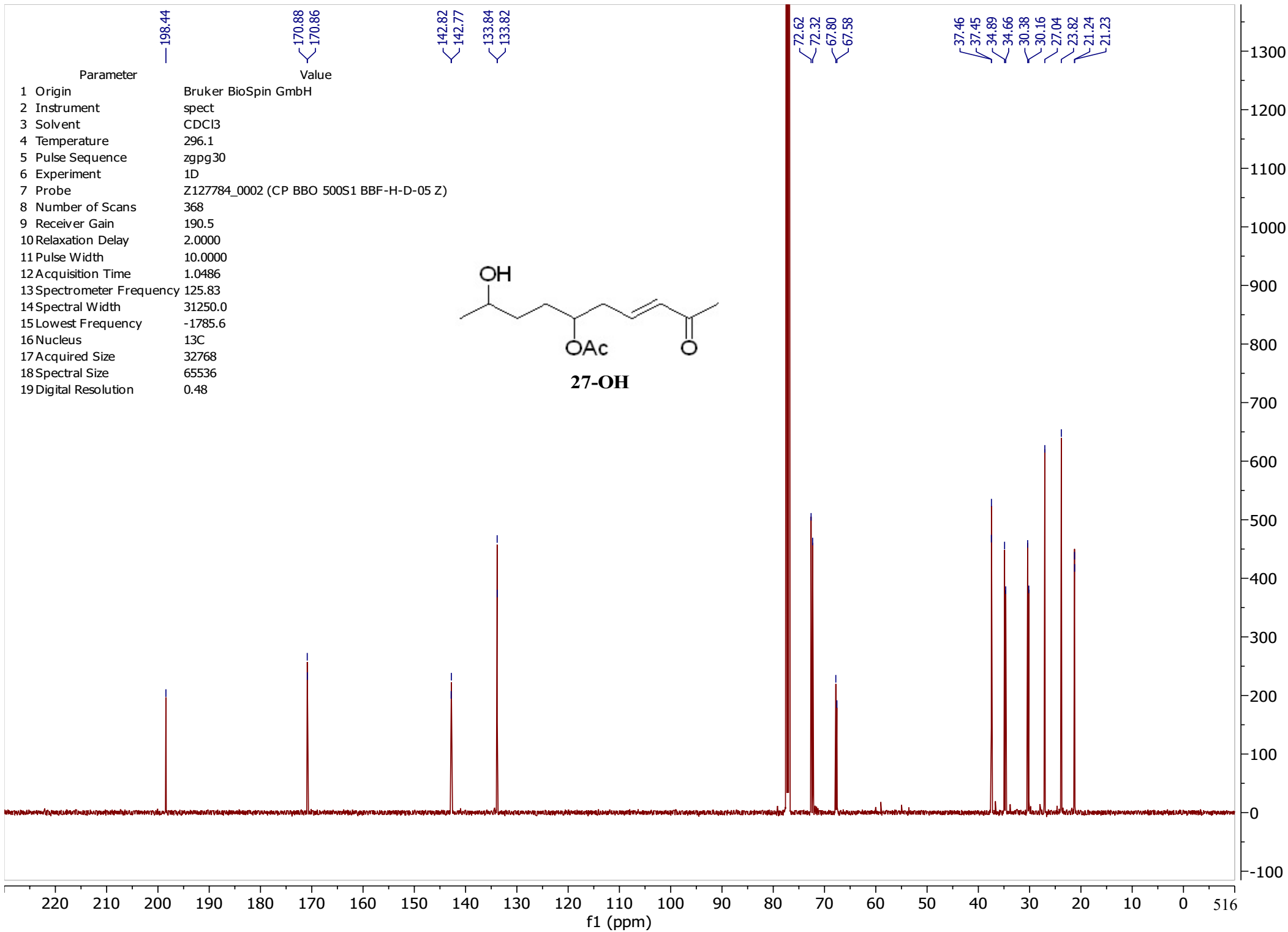
170.88
170.86

142.82
142.77

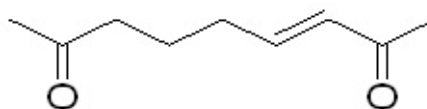
133.84
133.82

72.62
72.32
67.80
67.58

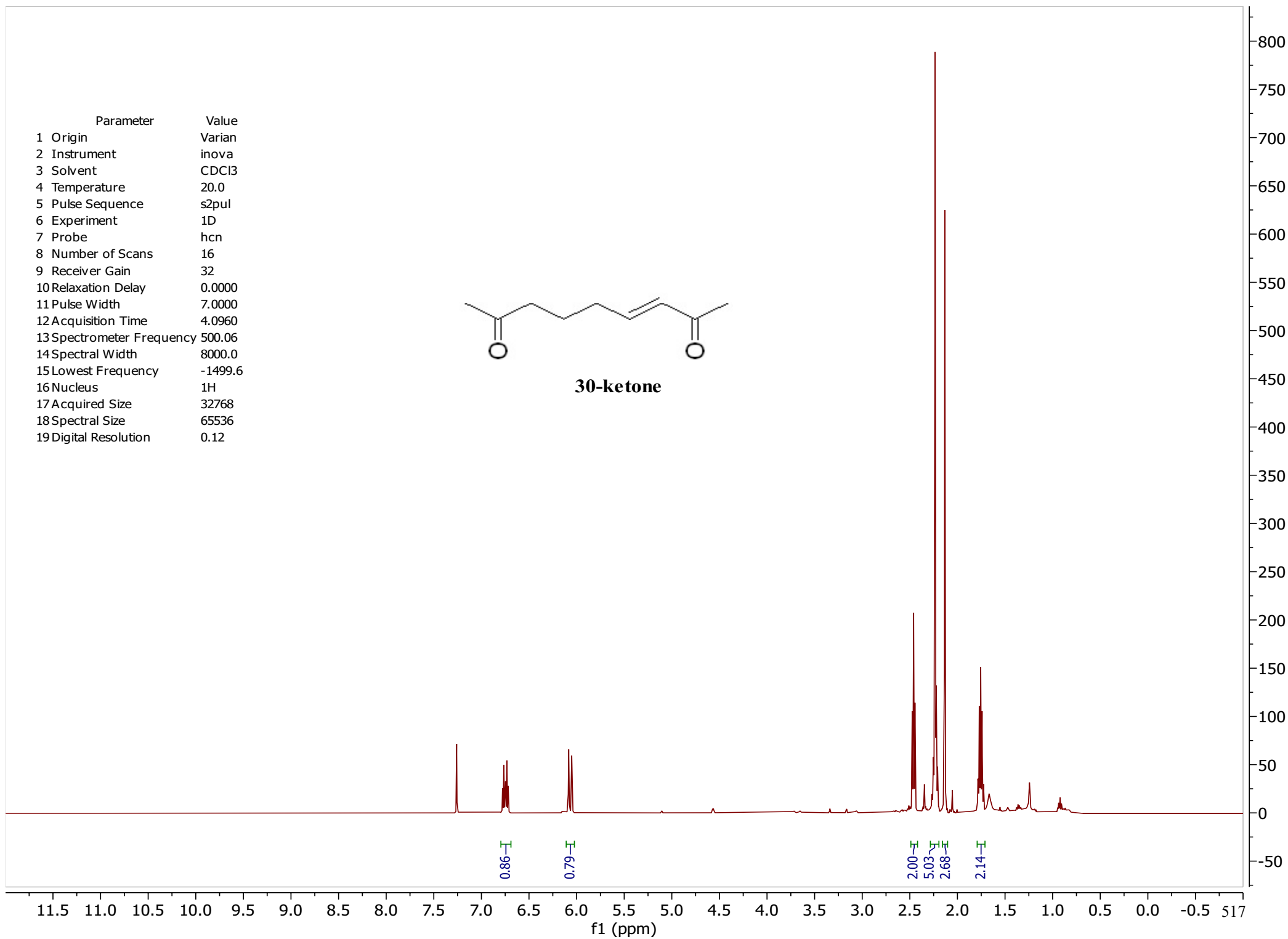
37.46
37.45
34.89
34.66
30.38
30.16
27.04
23.82
21.24
21.23

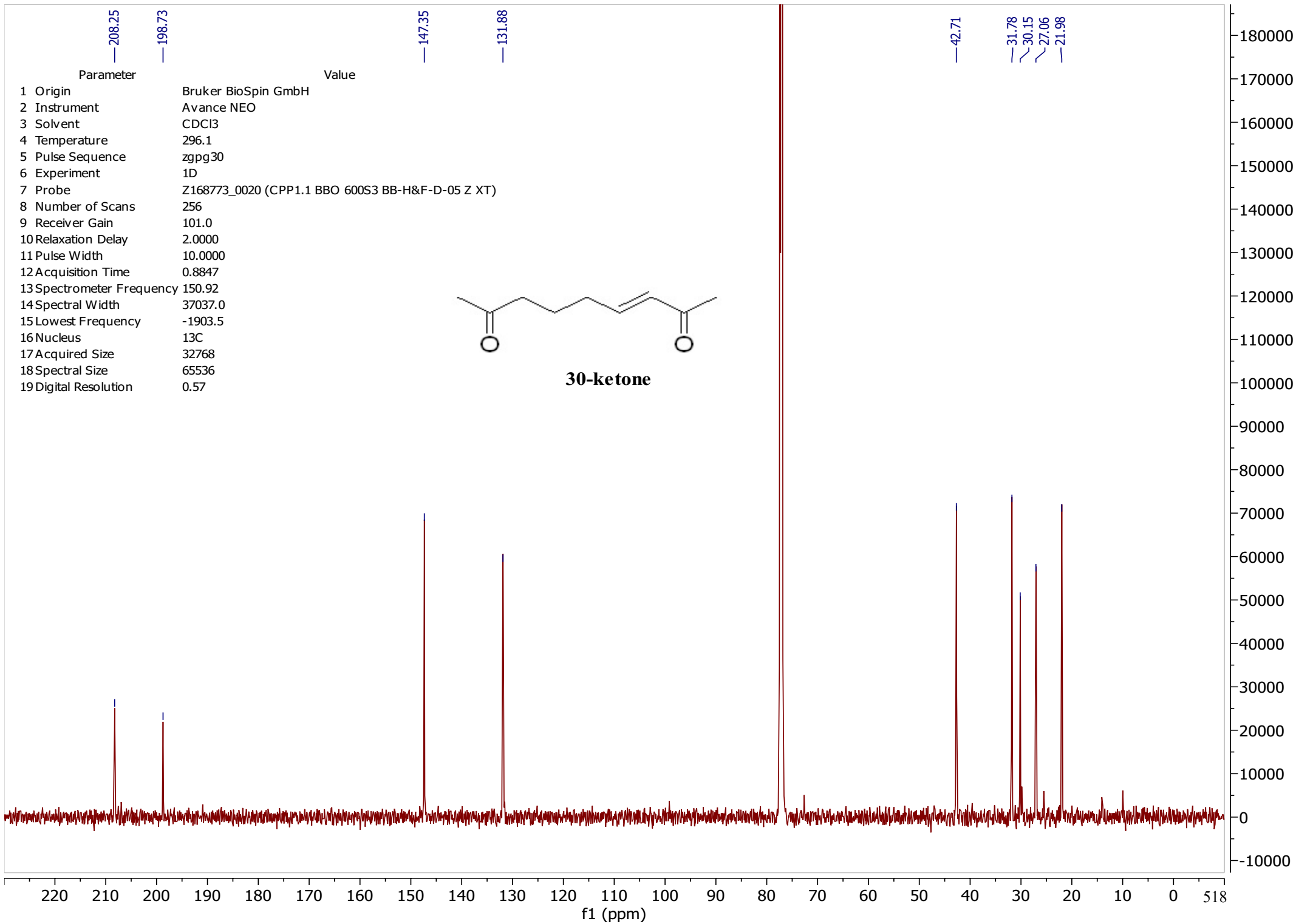


Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	hcn
8 Number of Scans	16
9 Receiver Gain	32
10 Relaxation Delay	0.0000
11 Pulse Width	7.0000
12 Acquisition Time	4.0960
13 Spectrometer Frequency	500.06
14 Spectral Width	8000.0
15 Lowest Frequency	-1499.6
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12

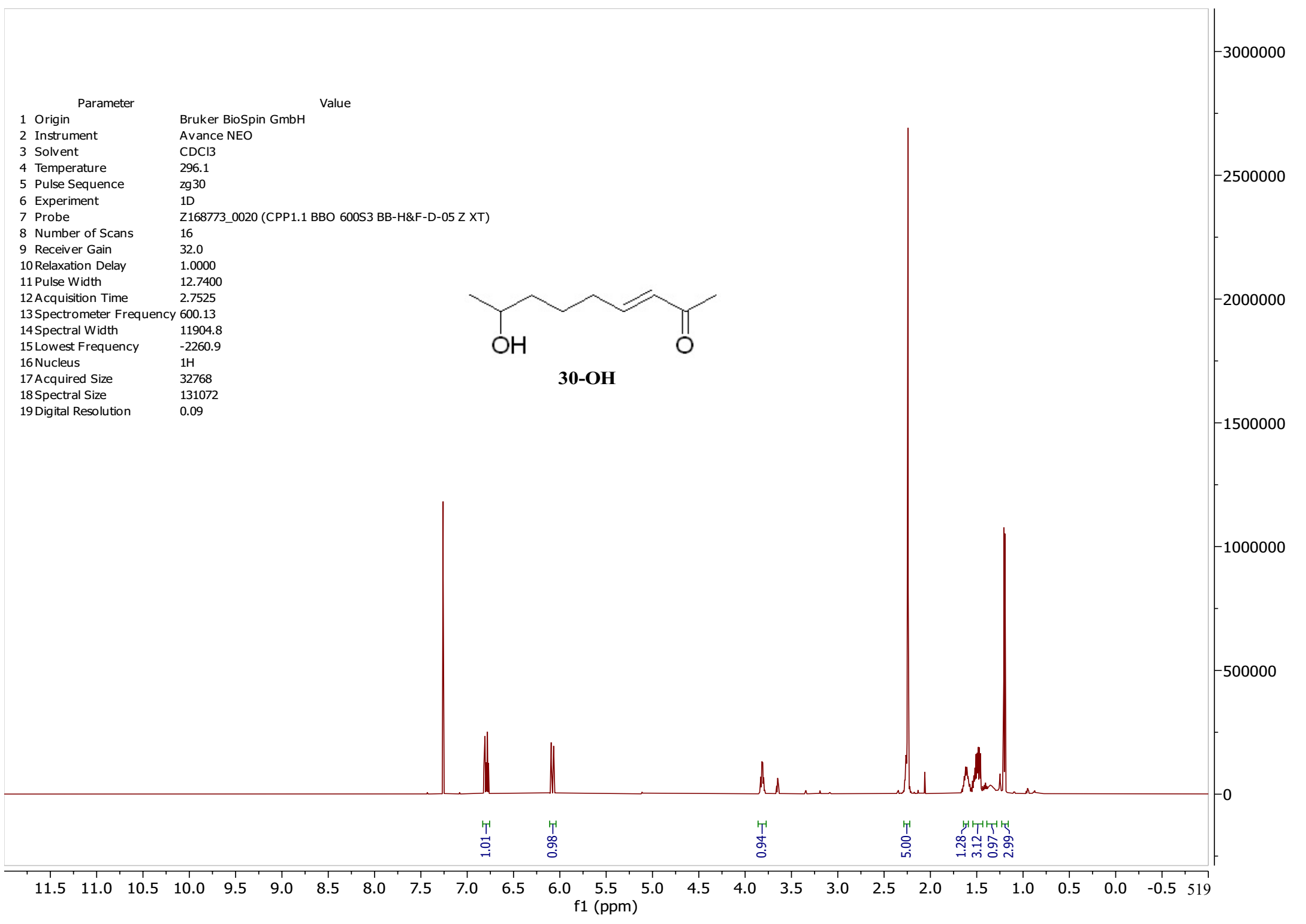
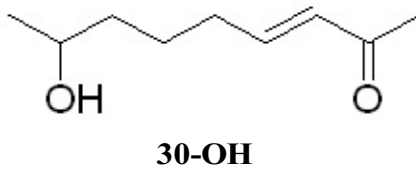


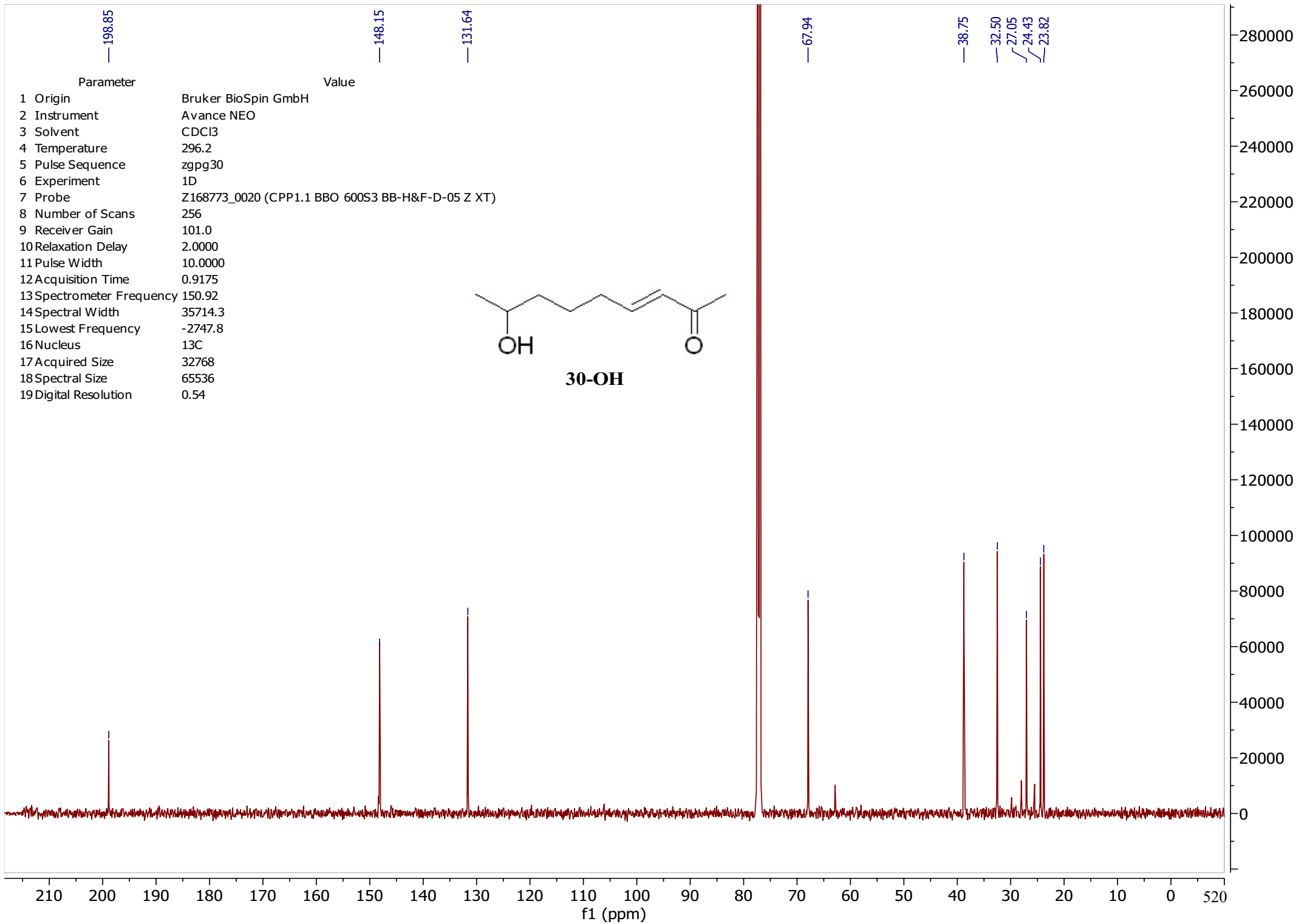
30-ketone



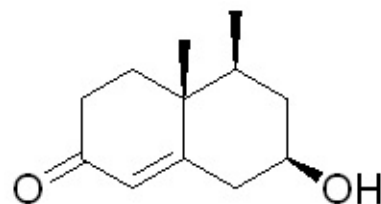


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.7400
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

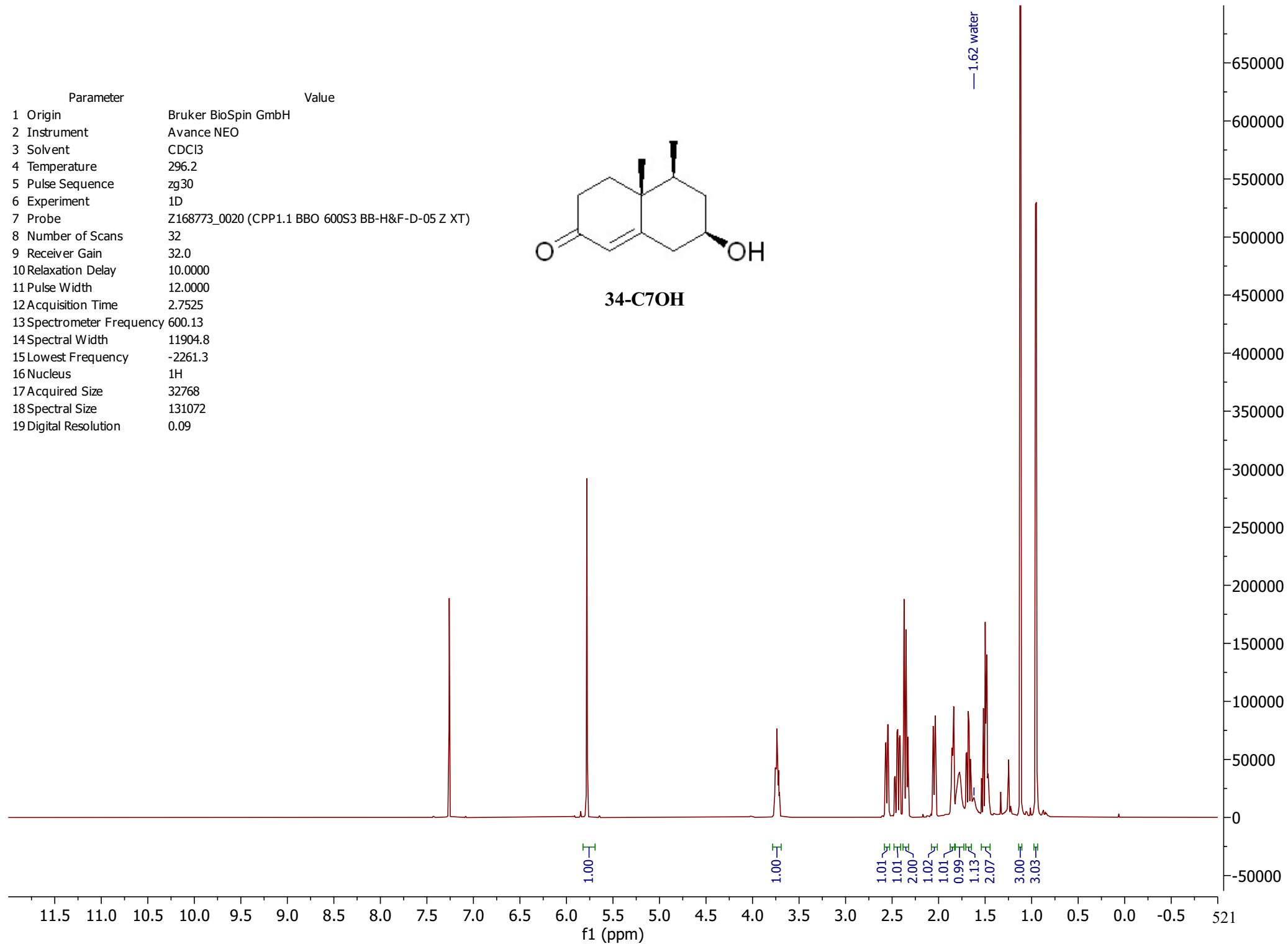




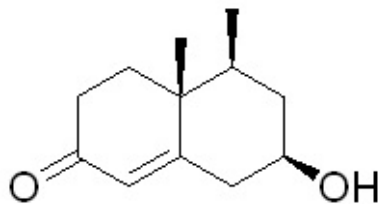
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.3
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



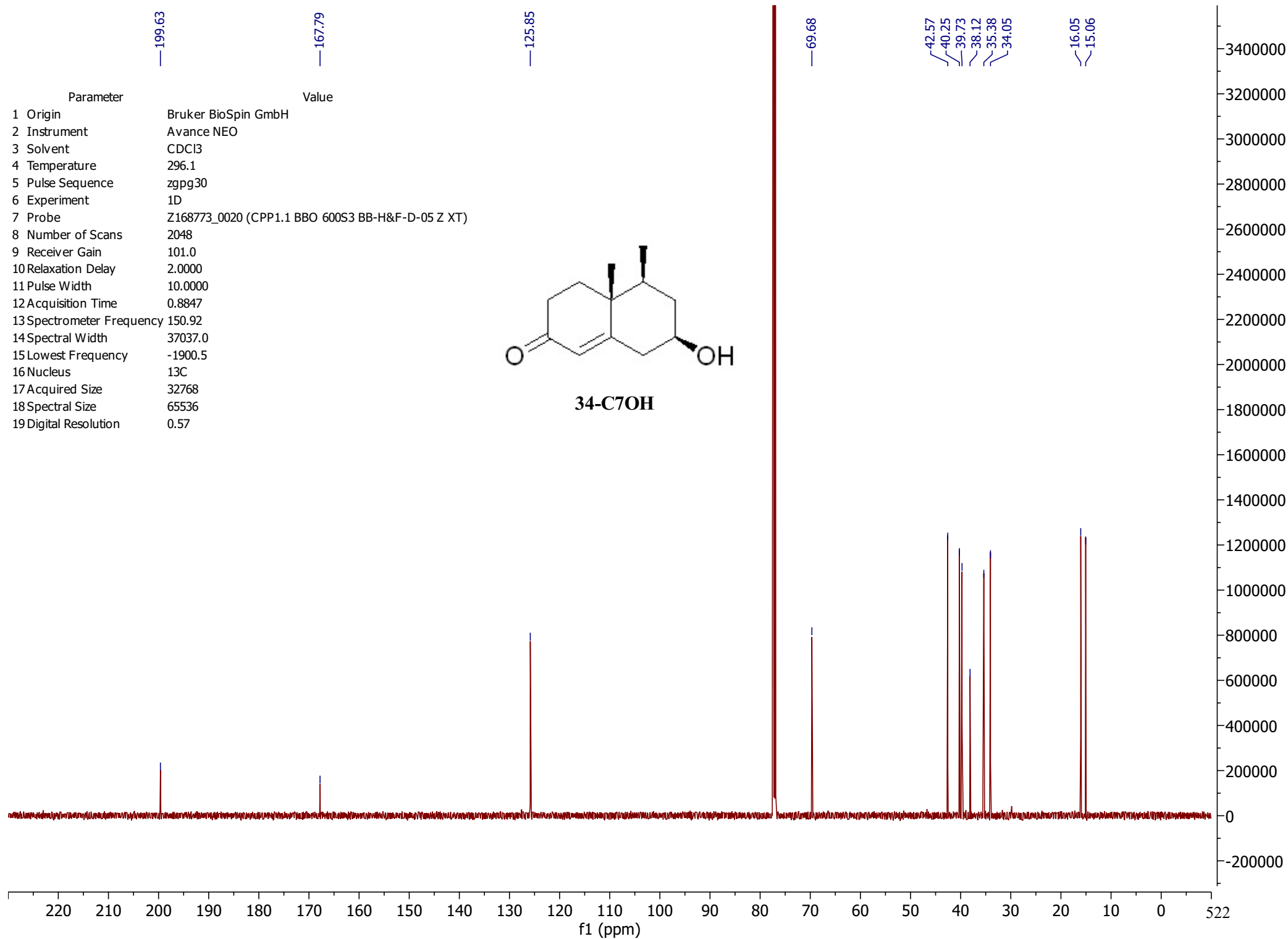
34-C7OH



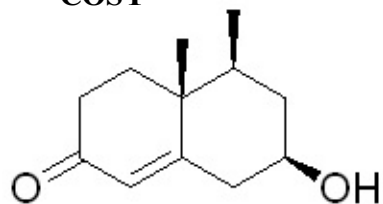
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	2048
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1900.5
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



34-C7OH

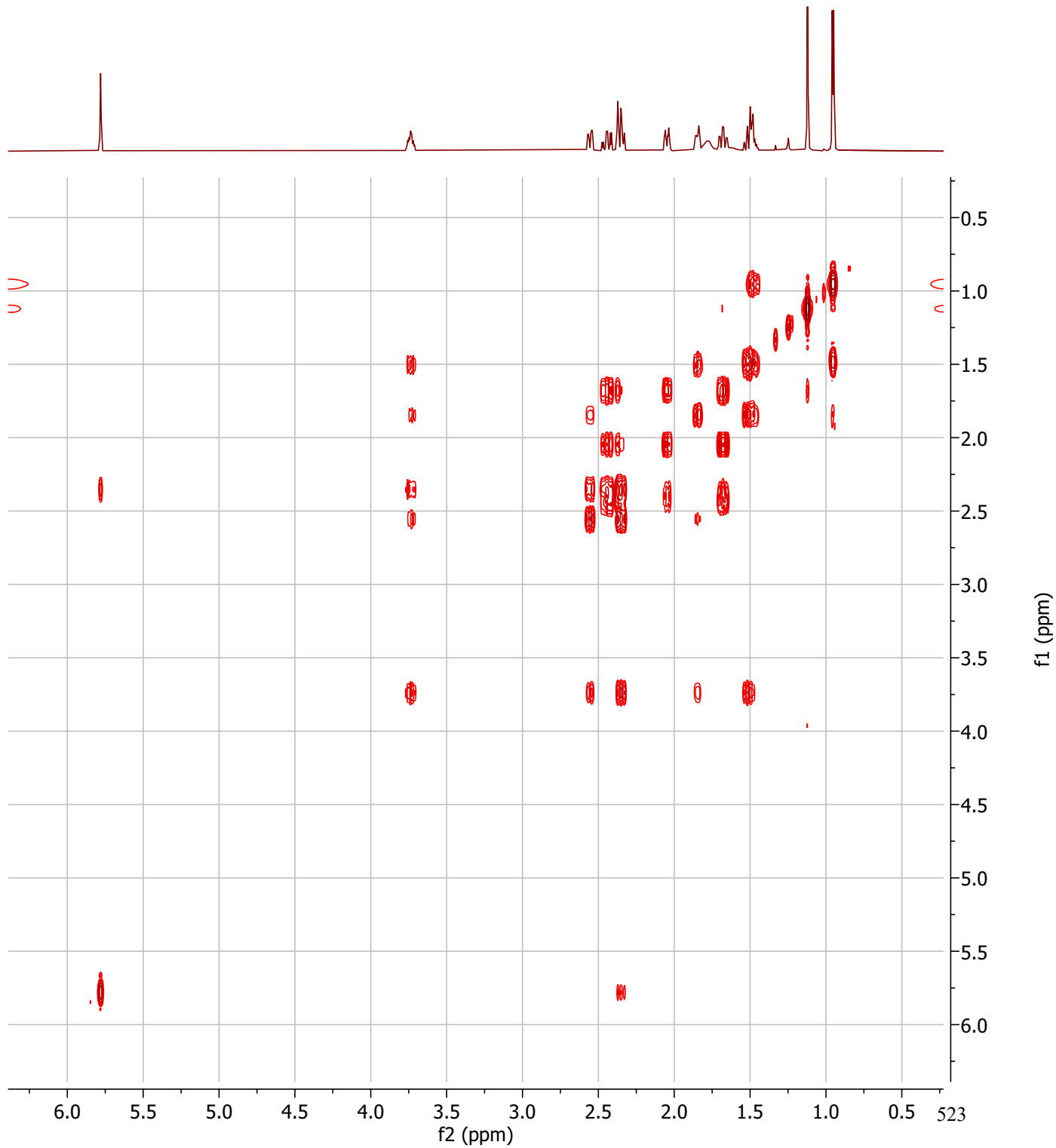
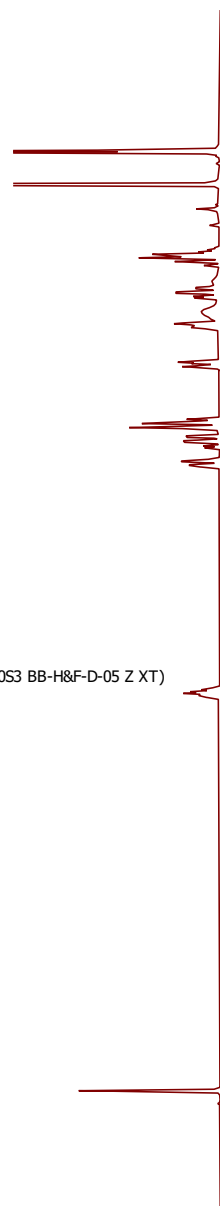


COSY

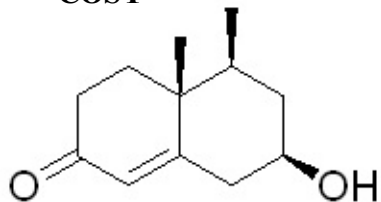


34-C7OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3587
11 Pulse Width	12.0000
12 Acquisition Time	0.2765
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3703.7, 3703.7)
15 Lowest Frequency	(131.6, 131.6)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.62, 3.62)

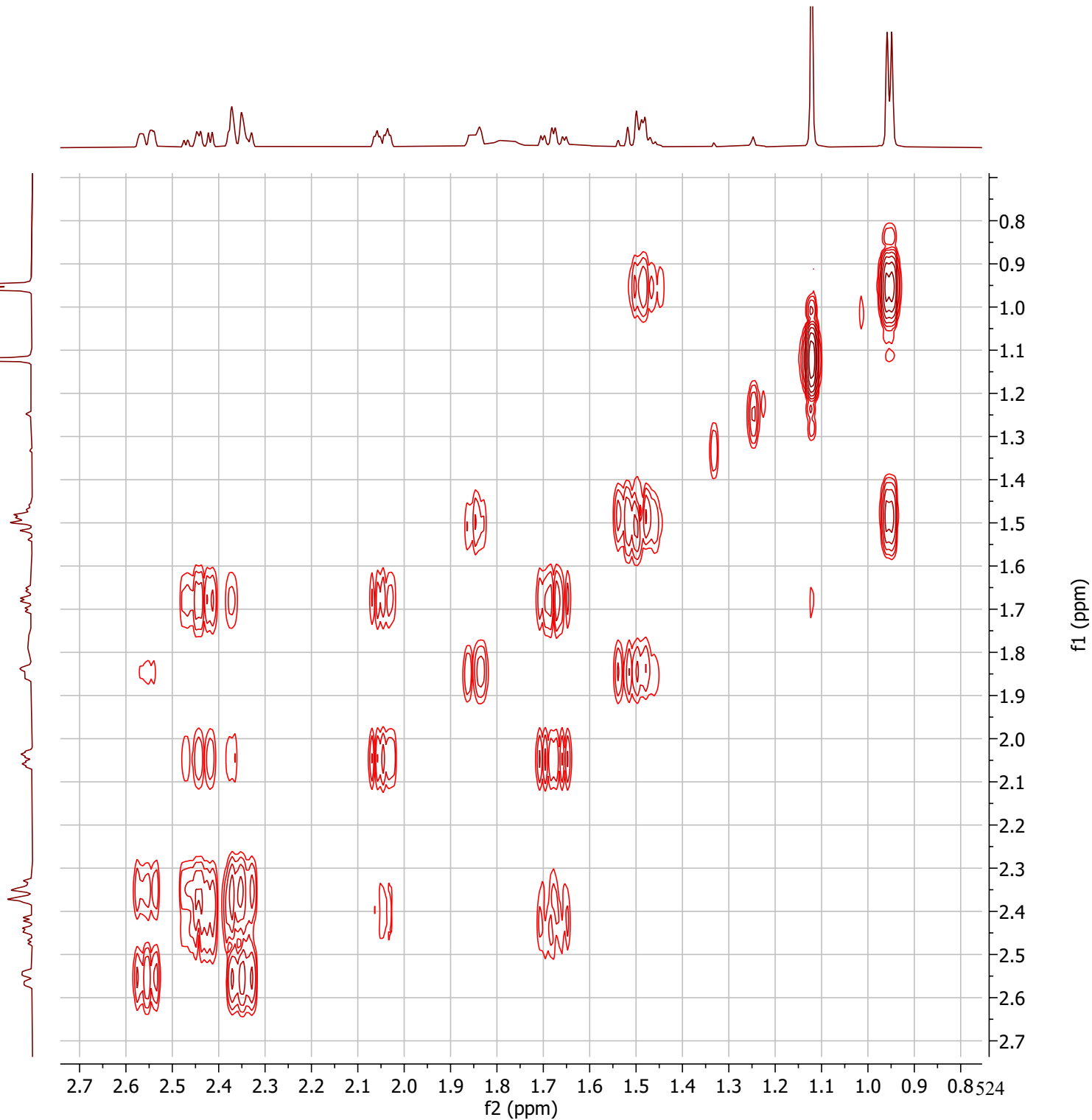


COSY

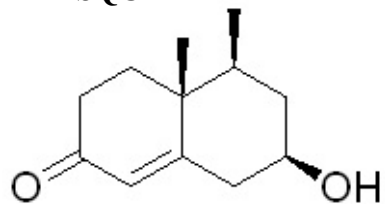


34-C7OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3587
11 Pulse Width	12.0000
12 Acquisition Time	0.2765
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(3703.7, 3703.7)
15 Lowest Frequency	(131.6, 131.6)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.62, 3.62)

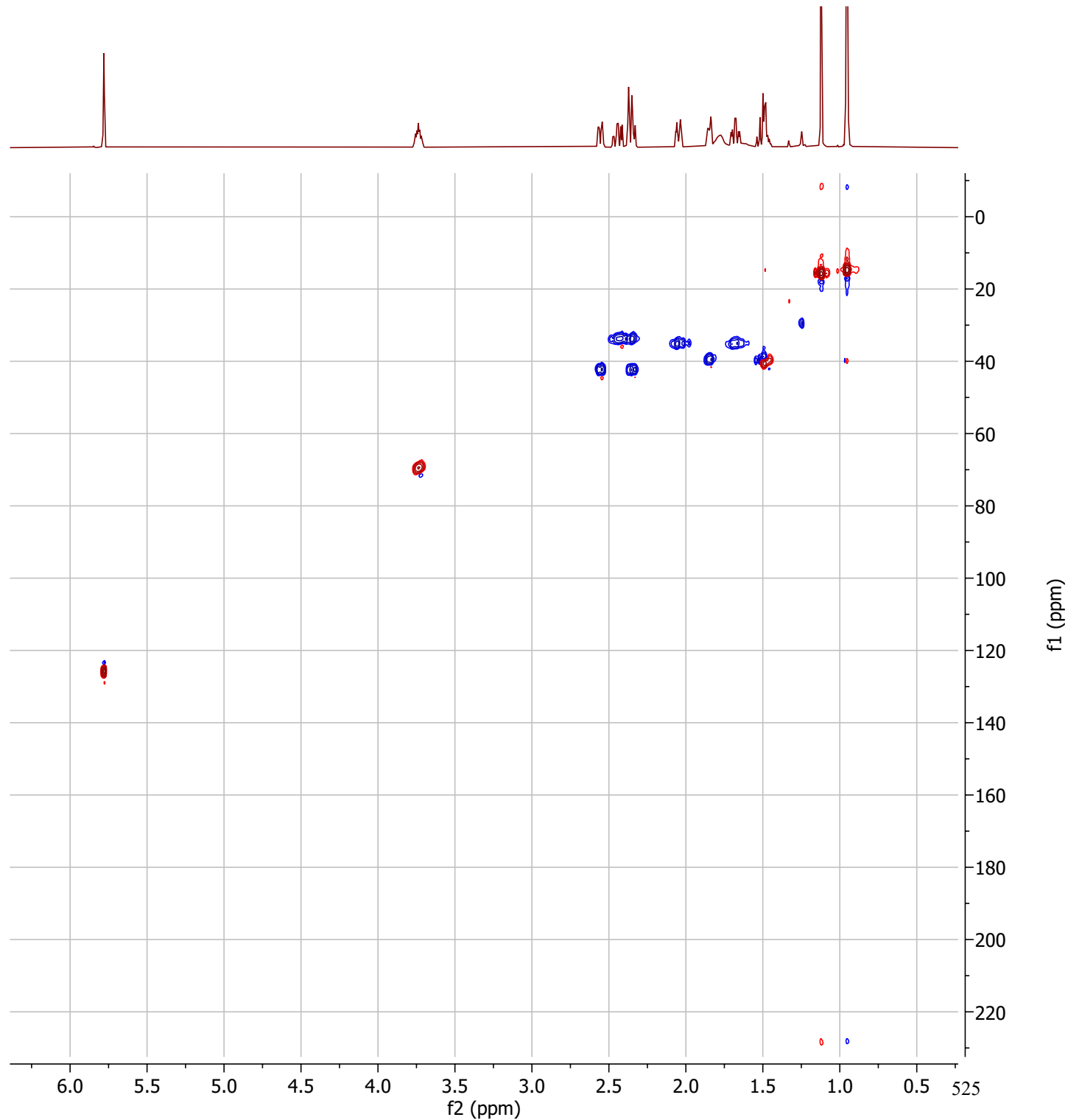


HSQC

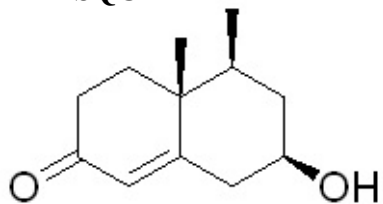


34-C7OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1382
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3703.7, 36974.0)
15 Lowest Frequency	(131.6, -1891.3)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.23, 72.21)

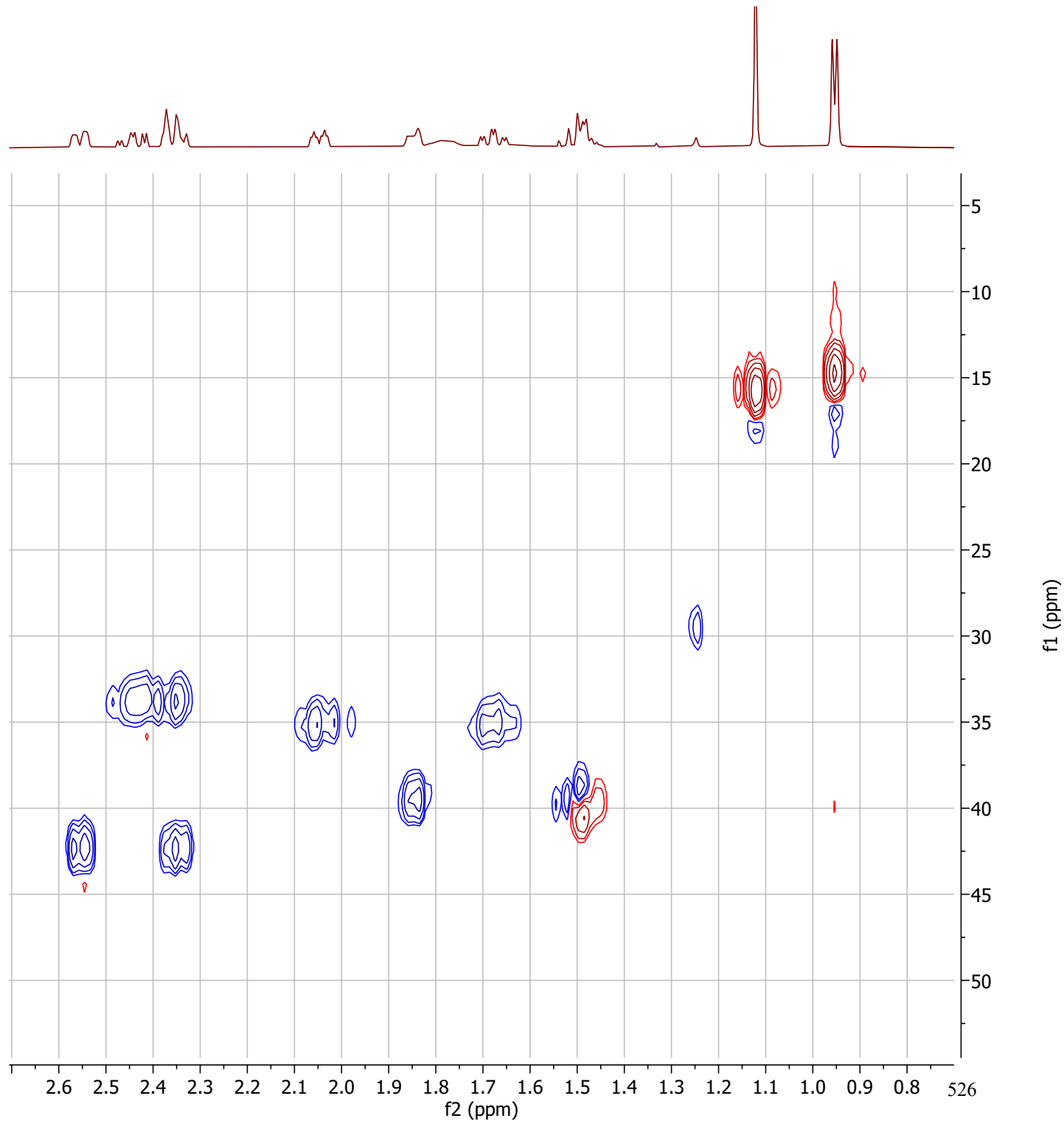


HSQC

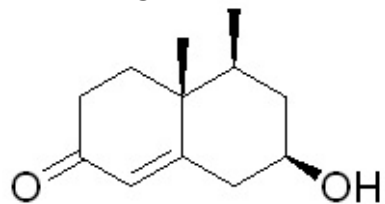


34-C7OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetdgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1382
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3703.7, 36974.0)
15 Lowest Frequency	(131.6, -1891.3)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.23, 72.21)

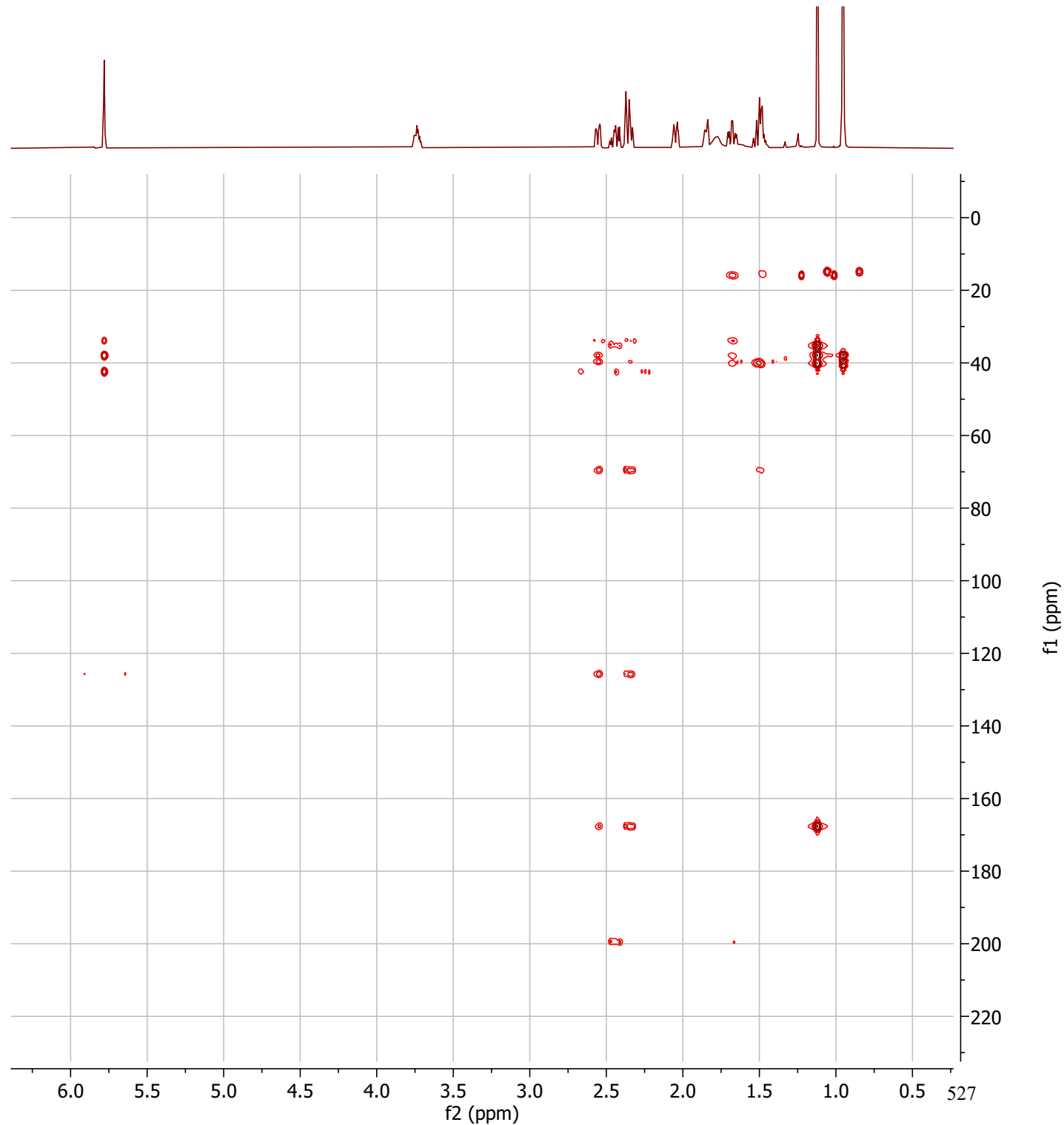


HMBC

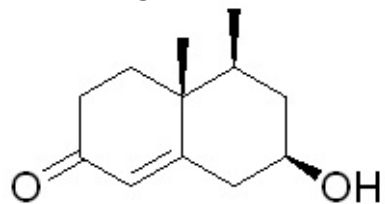


34-C7OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1382
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3703.7, 36974.9)
15 Lowest Frequency	(131.6, -1891.8)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.23, 72.22)

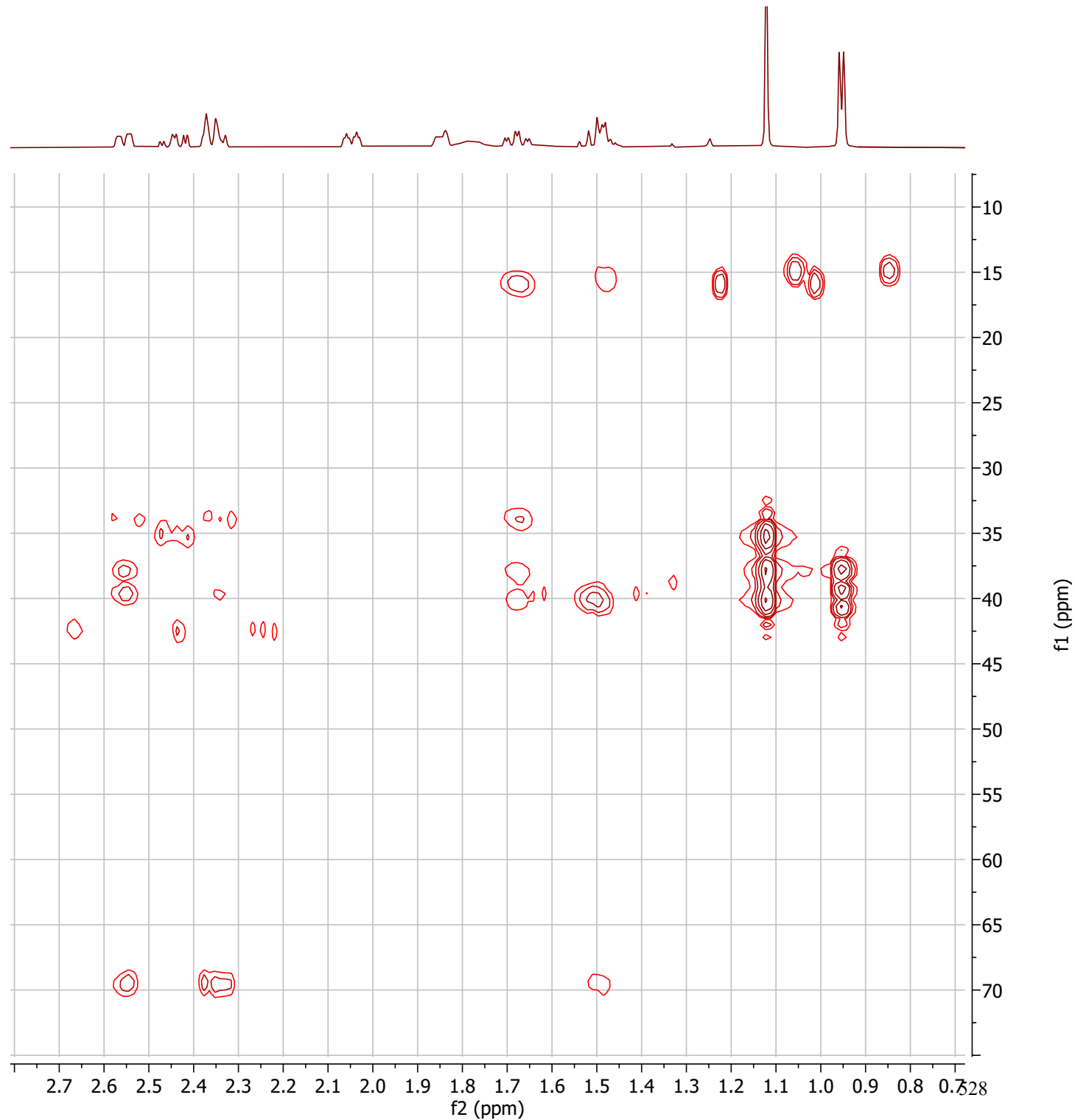


HMBC

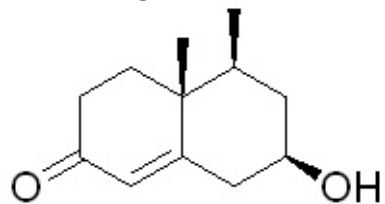


34-C7OH

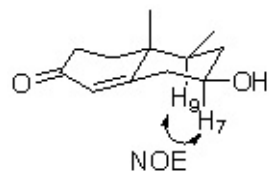
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1382
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3703.7, 36974.9)
15 Lowest Frequency	(131.6, -1891.8)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.23, 72.22)



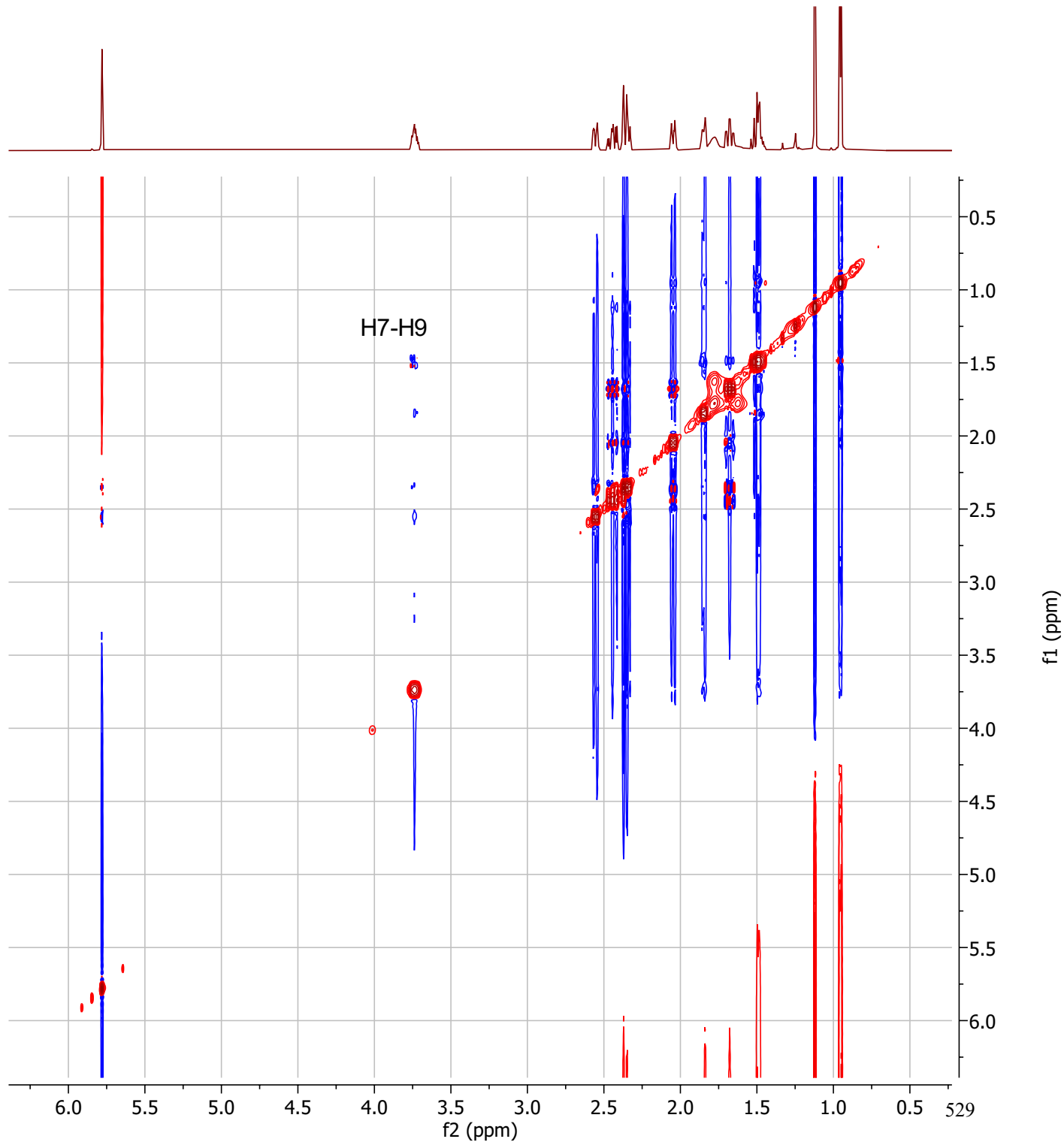
HMBC



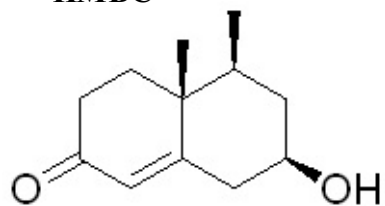
34-C7OH



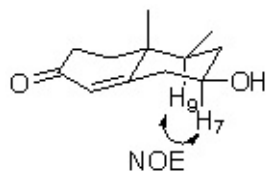
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	noesygp.php
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.9017
11 Pulse Width	12.0000
12 Acquisition Time	0.2765
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3703.7, 3703.7)
15 Lowest Frequency	(131.6, 131.6)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.62, 3.62)



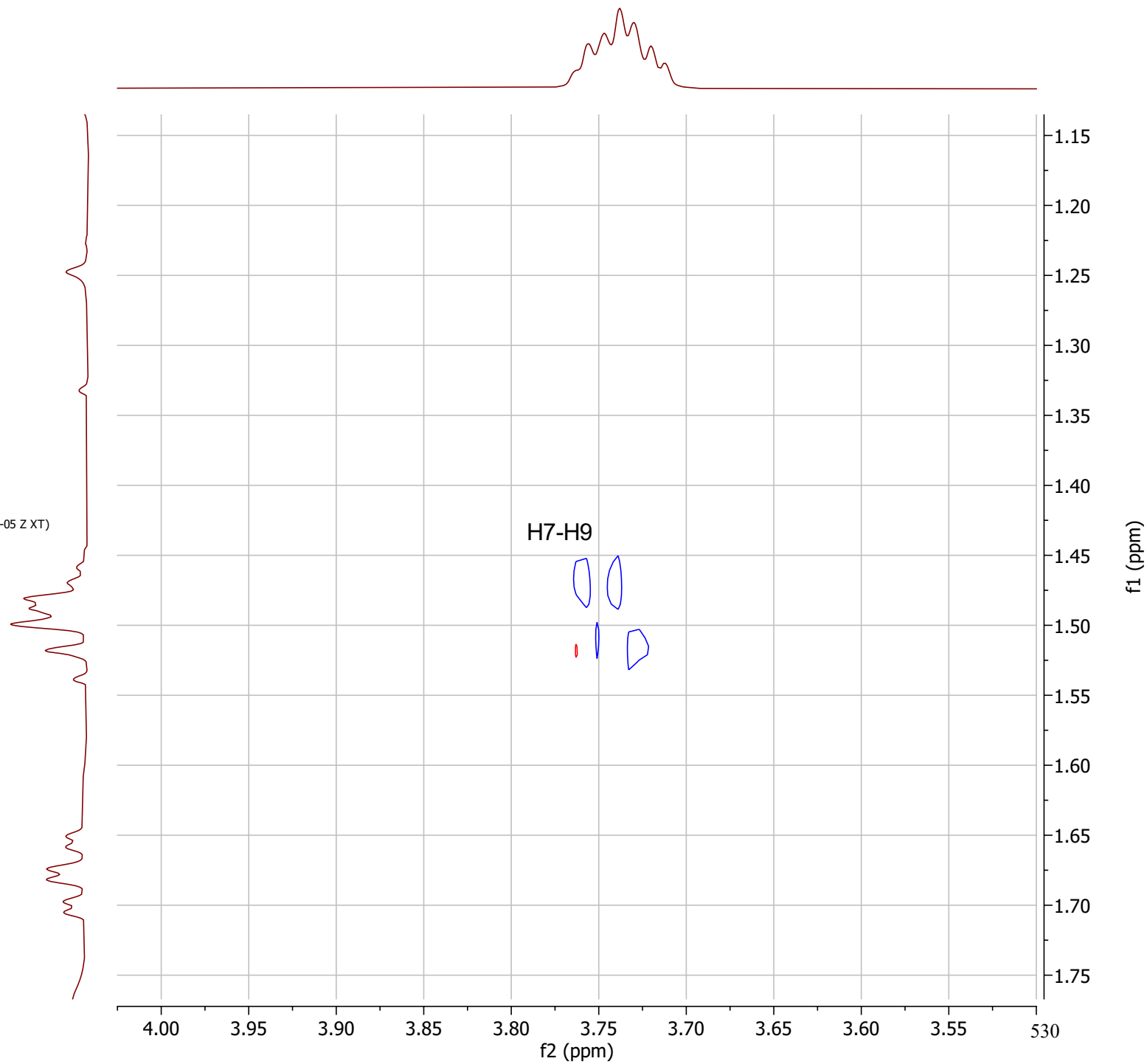
HMBC



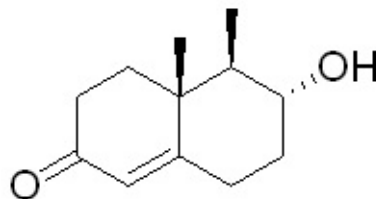
34-C7OH



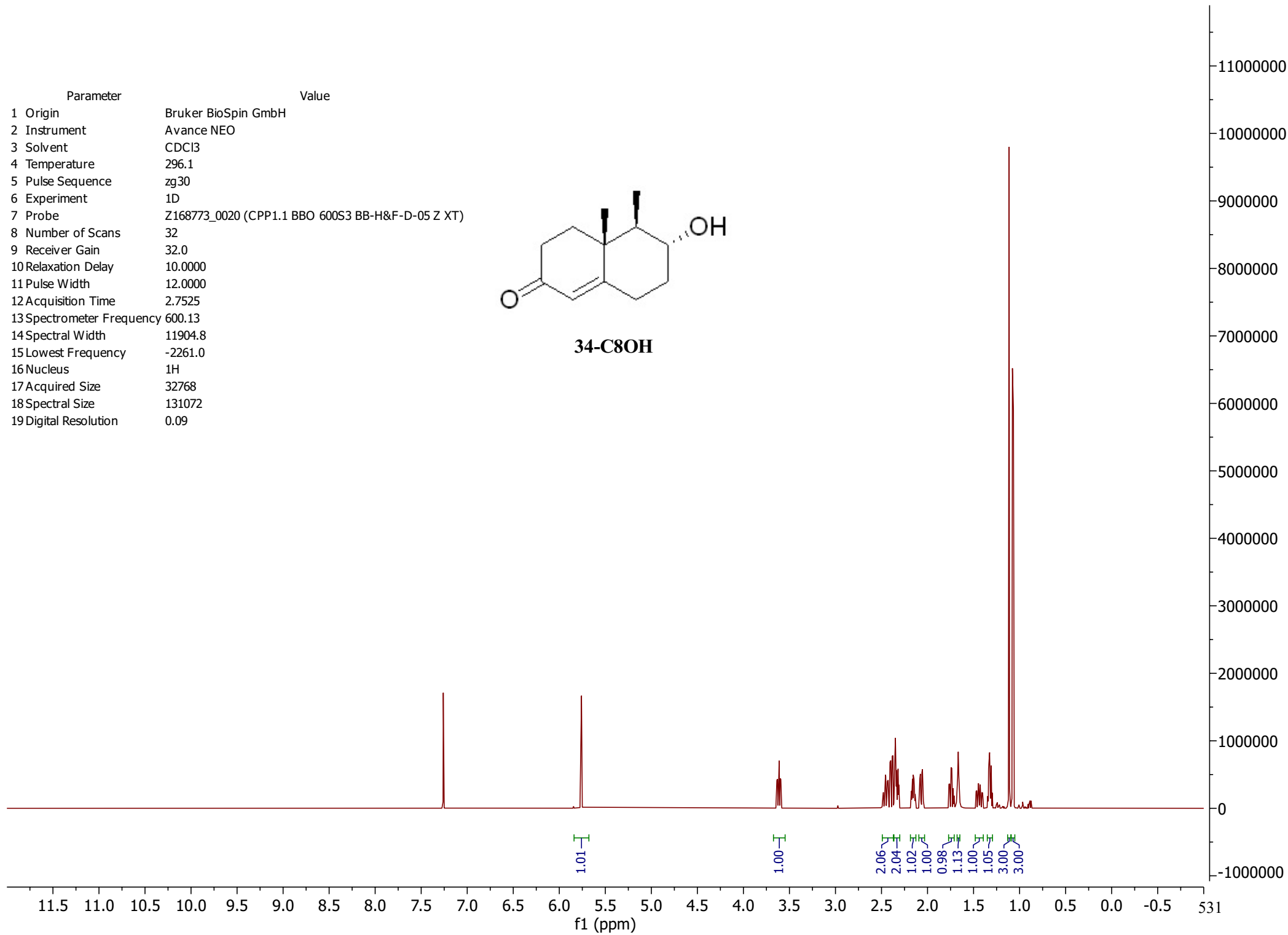
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	noesygpqhpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.9017
11 Pulse Width	12.0000
12 Acquisition Time	0.2765
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3703.7, 3703.7)
15 Lowest Frequency	(131.6, 131.6)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.62, 3.62)



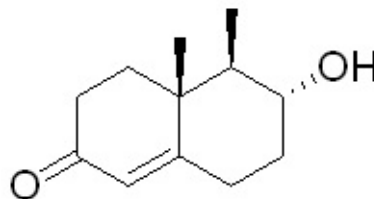
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



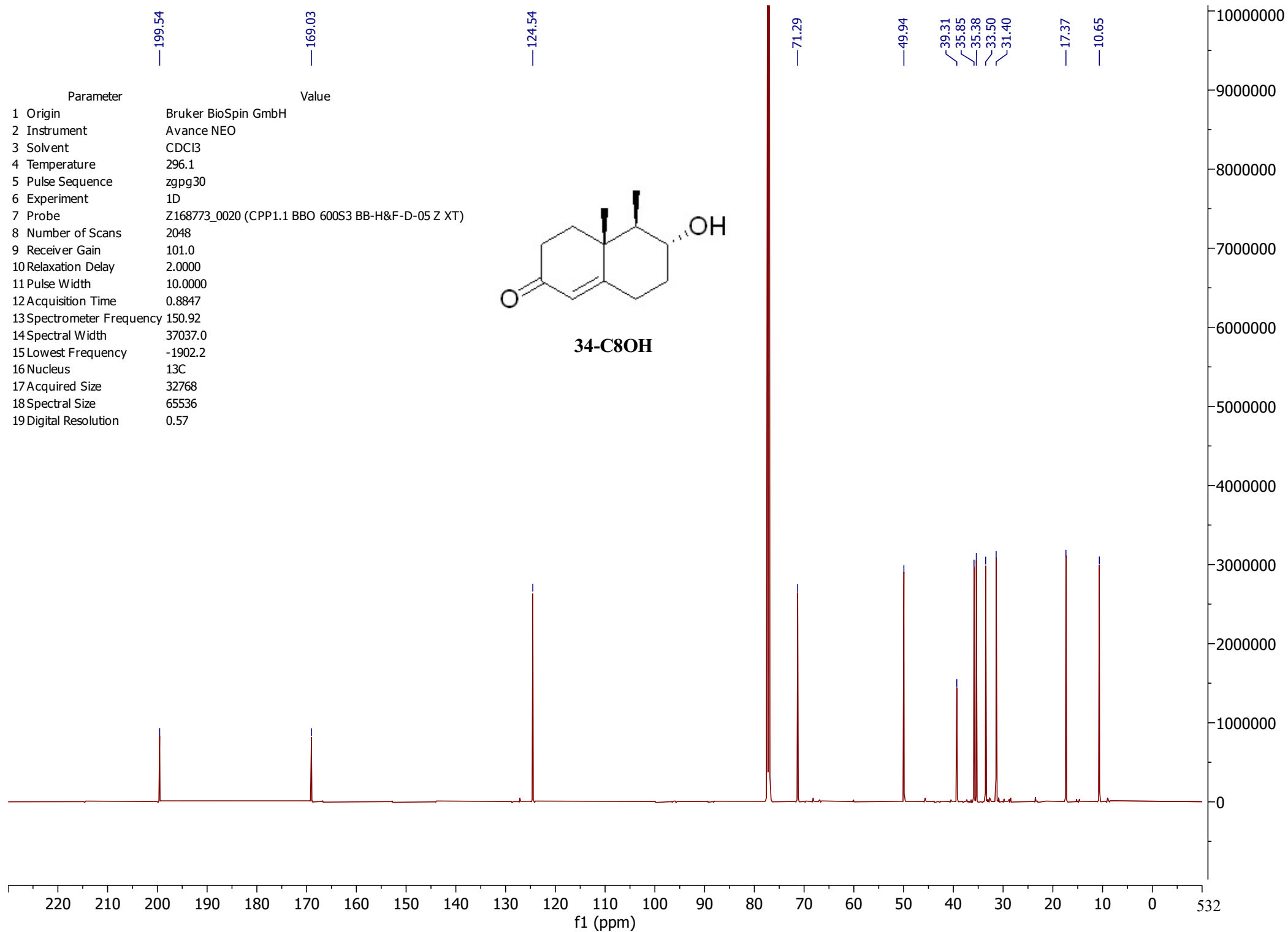
34-C8OH



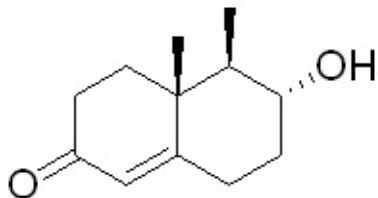
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	2048
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1902.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



34-C8OH

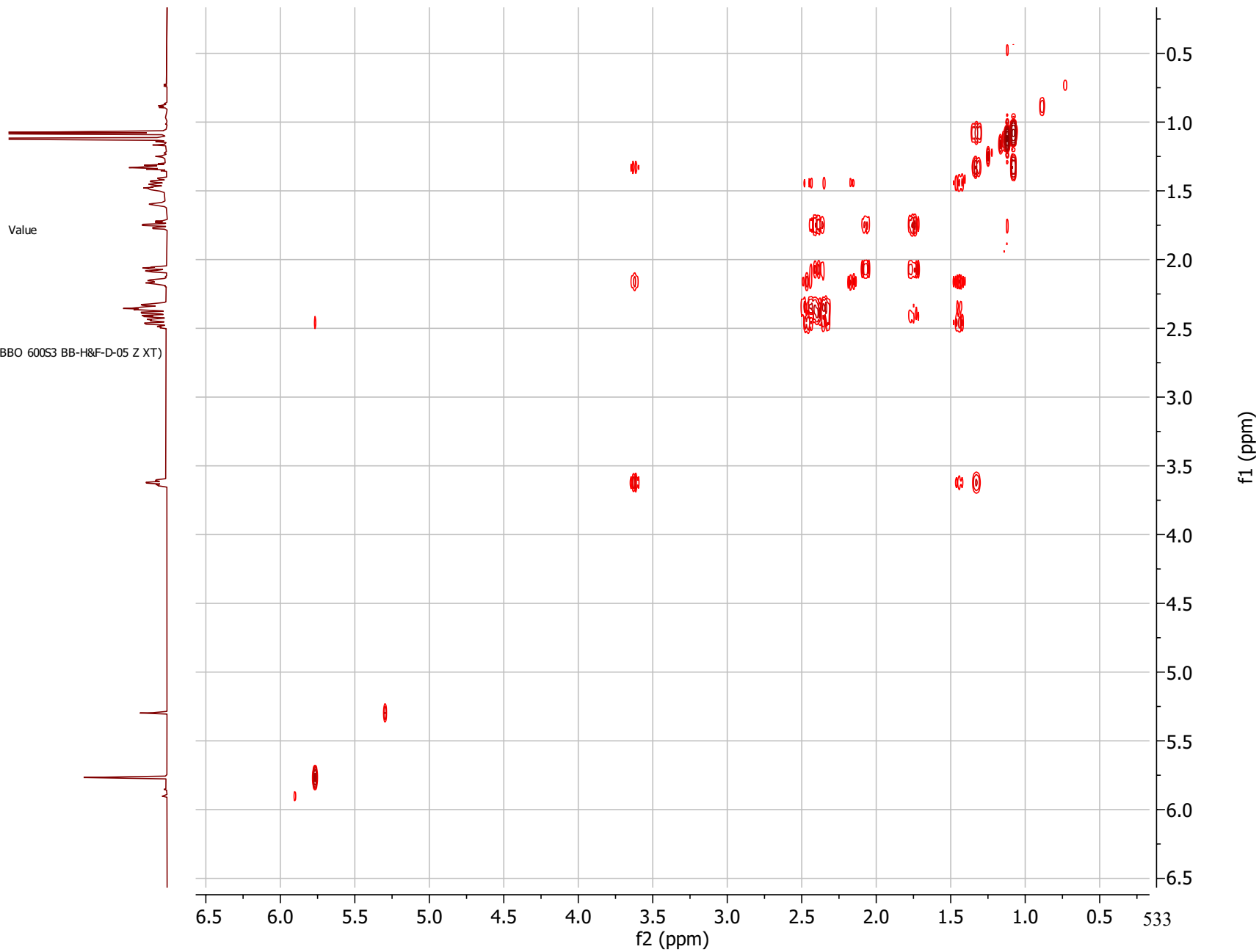


COSY

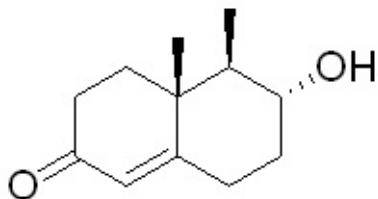


34-C8OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3628
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(95.6, 95.6)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)

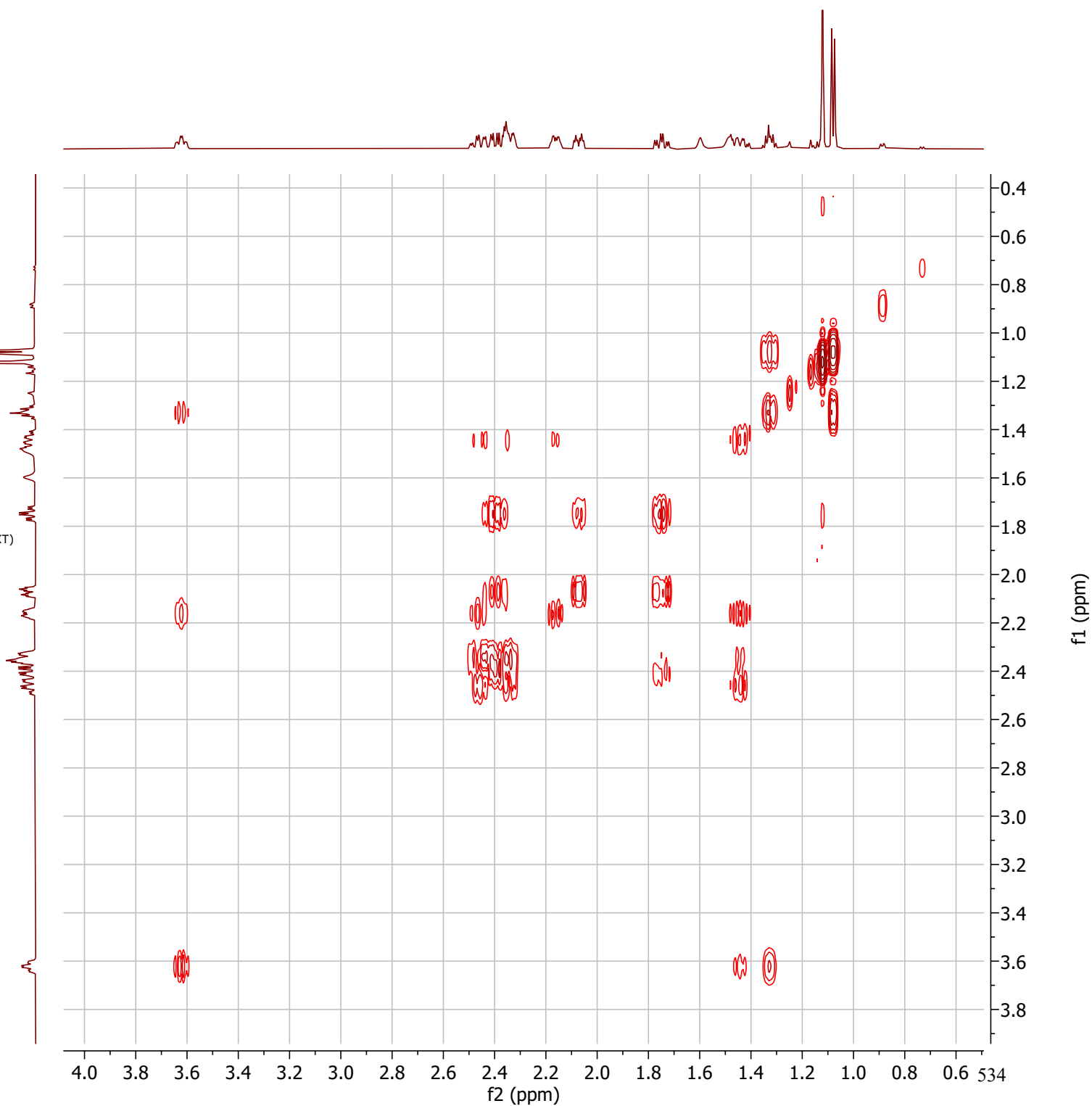


COSY

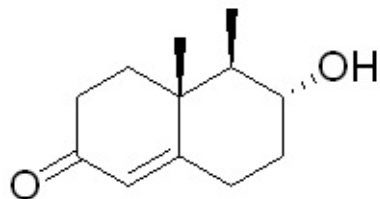


34-C8OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3628
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(95.6, 95.6)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)

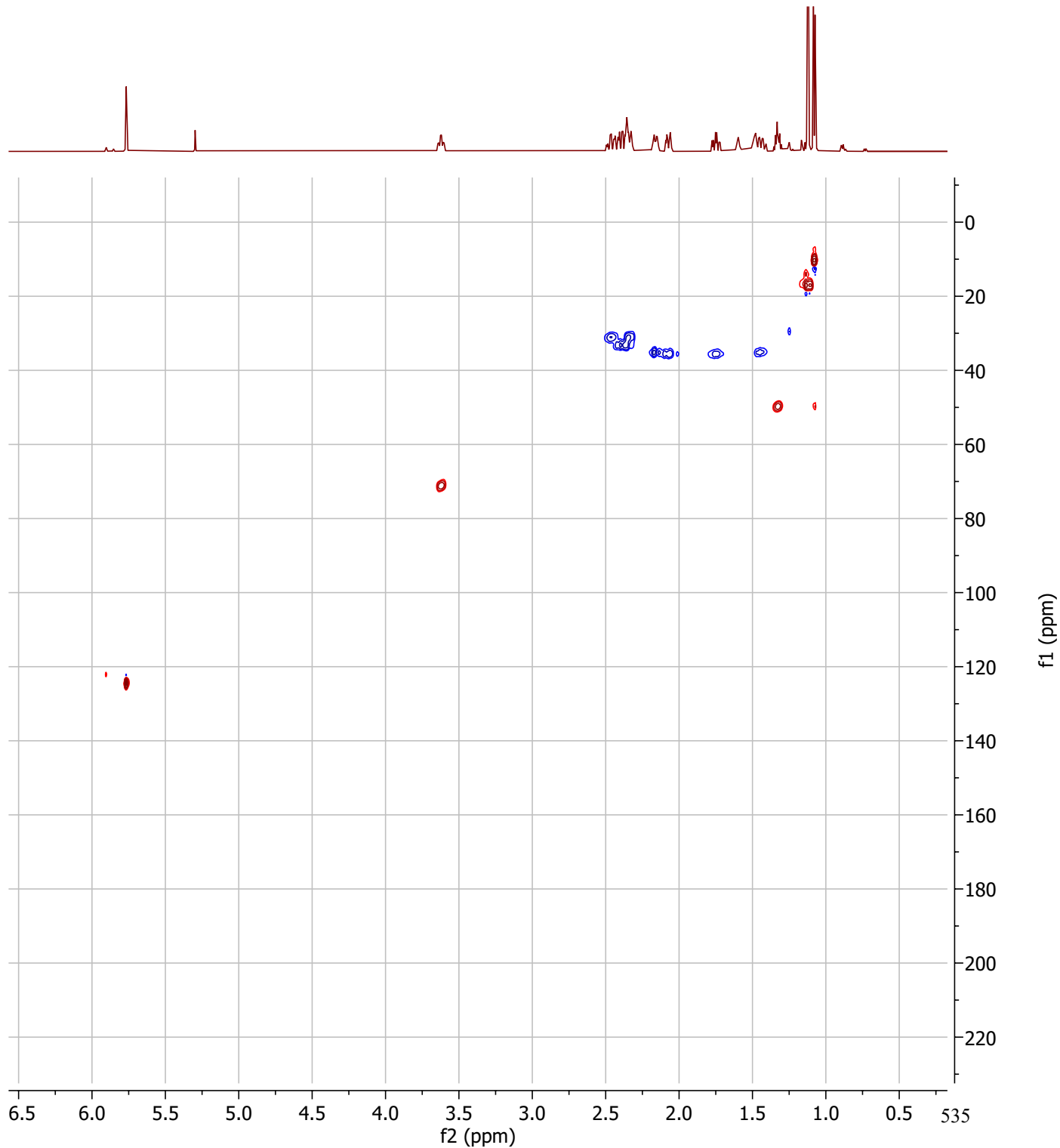


HSQC

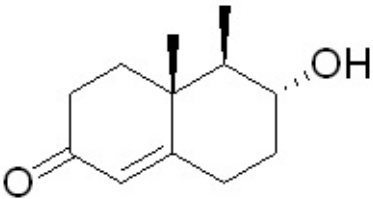


34-C8OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcedtgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(95.6, -1891.3)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)

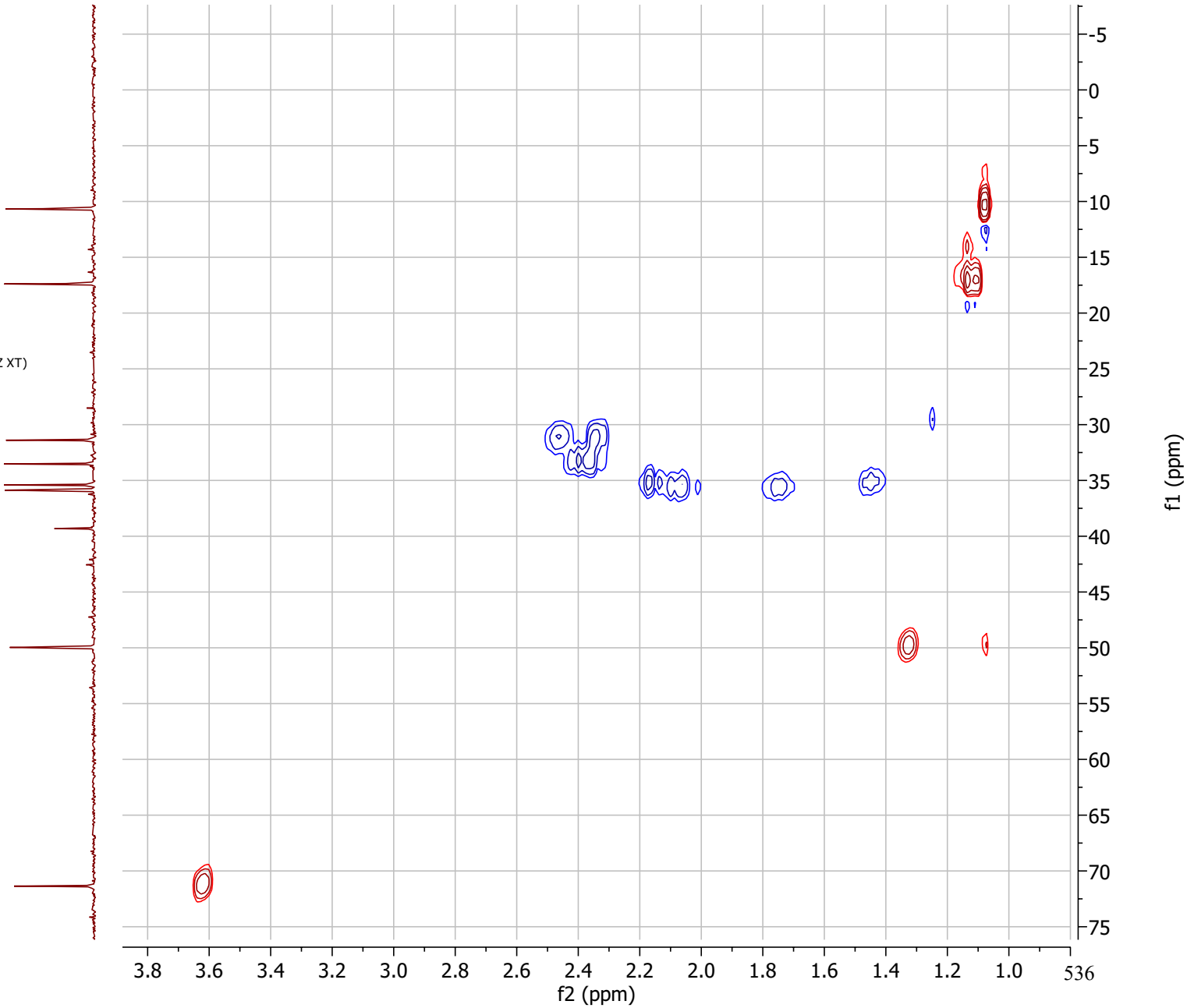


HSQC

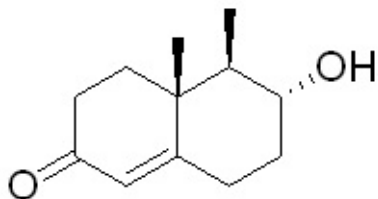


34-C8OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpgisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(95.6, -1891.3)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)

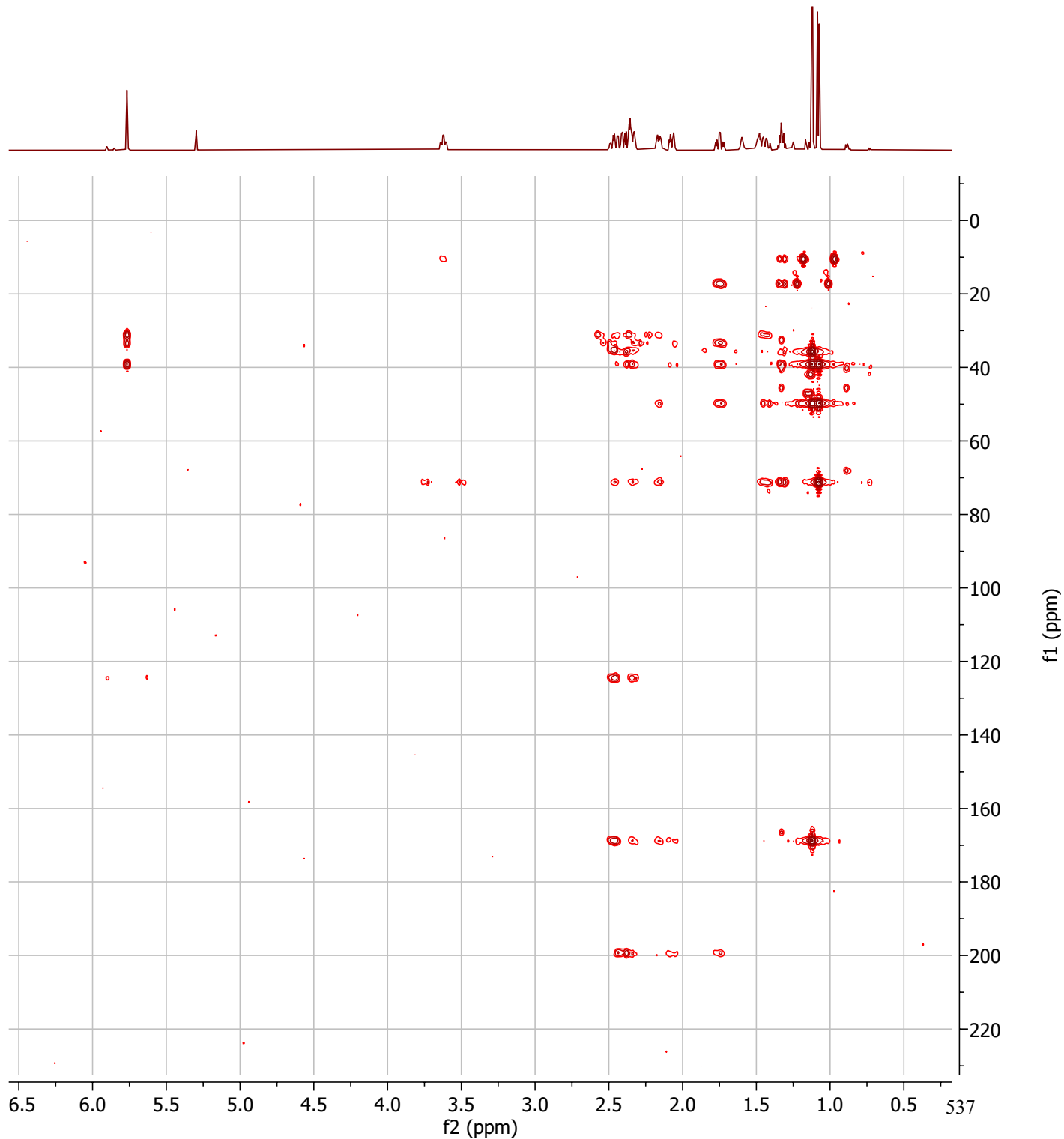


HMBC

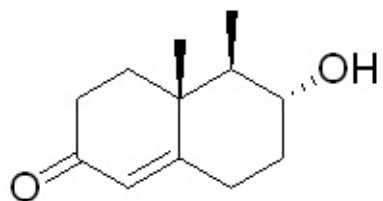


34-C8OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(95.6, -1891.8)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)

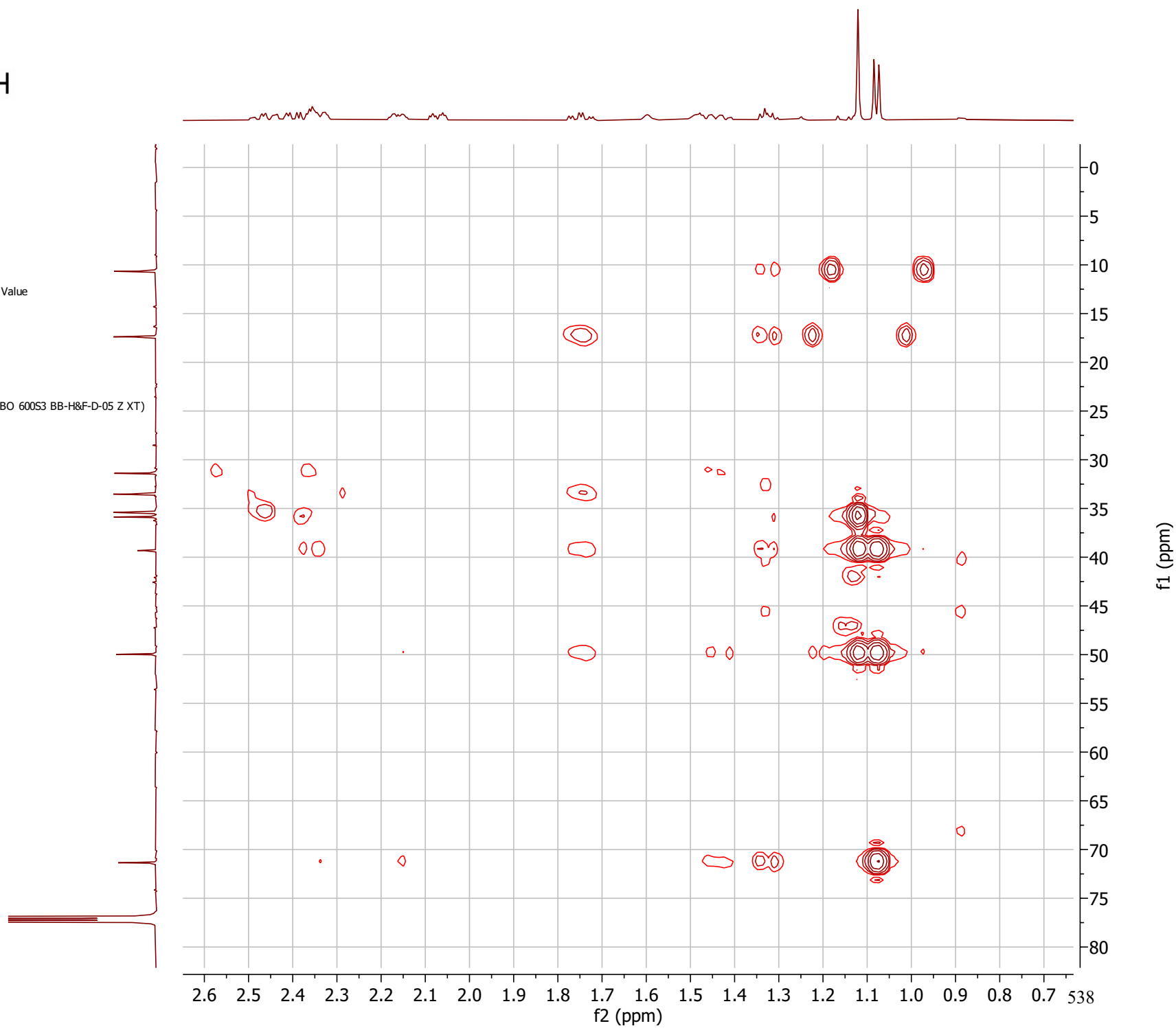


HMBC

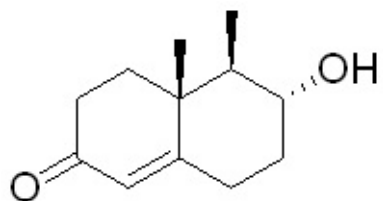


34-C8OH

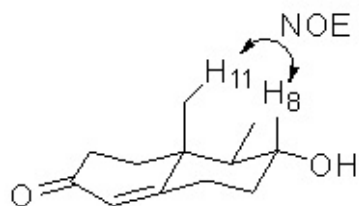
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(95.6, -1891.8)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



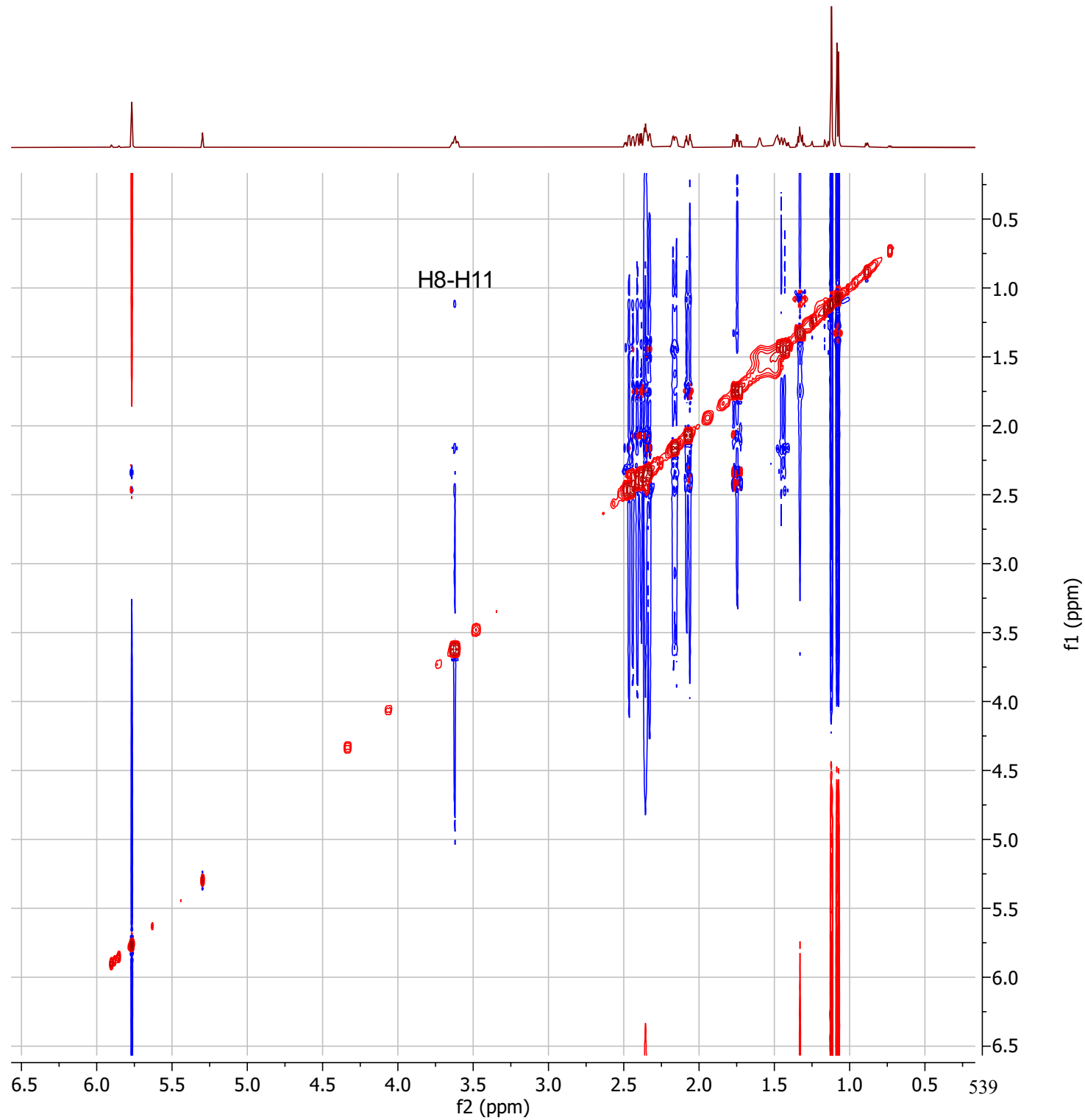
NOESY



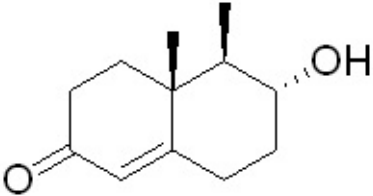
34-C8OH



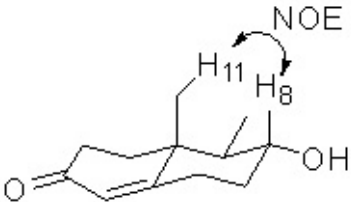
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.9058
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(95.6, 95.6)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



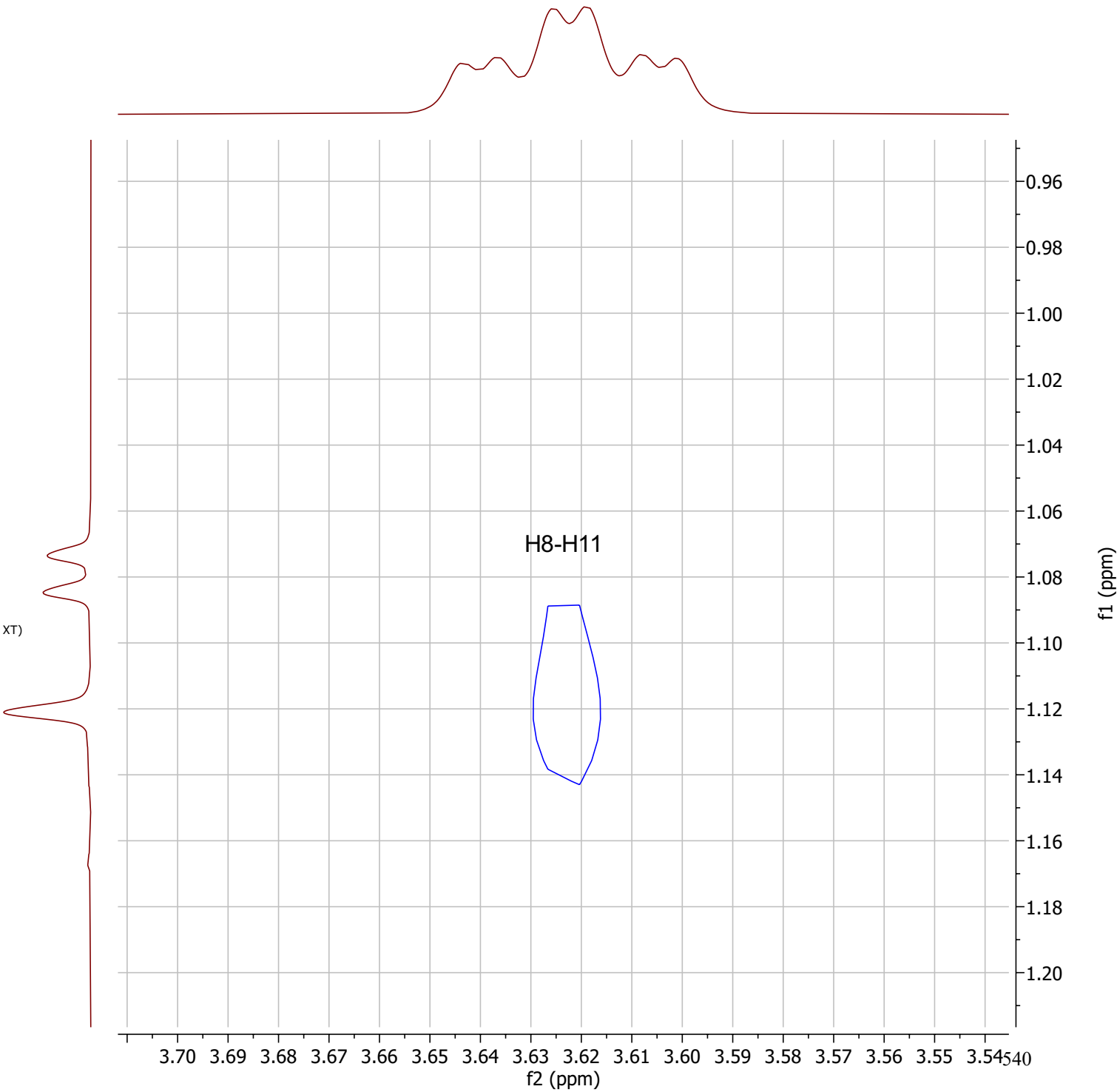
NOESY



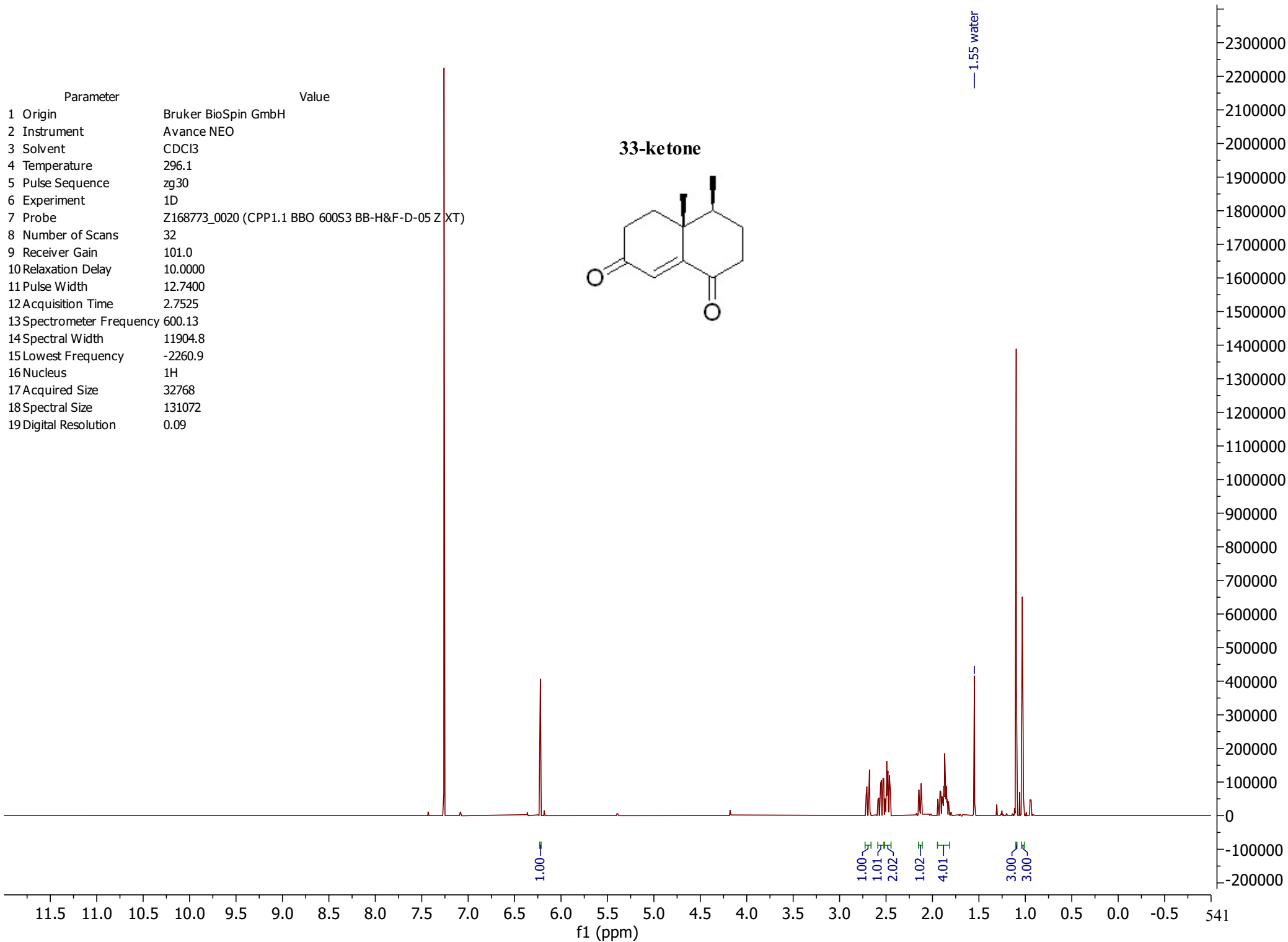
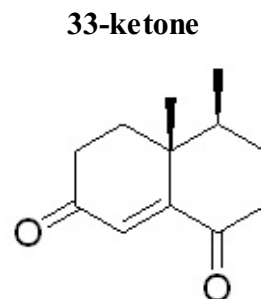
34-C8OH



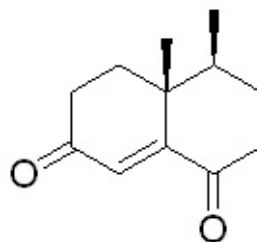
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.9058
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(95.6, 95.6)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



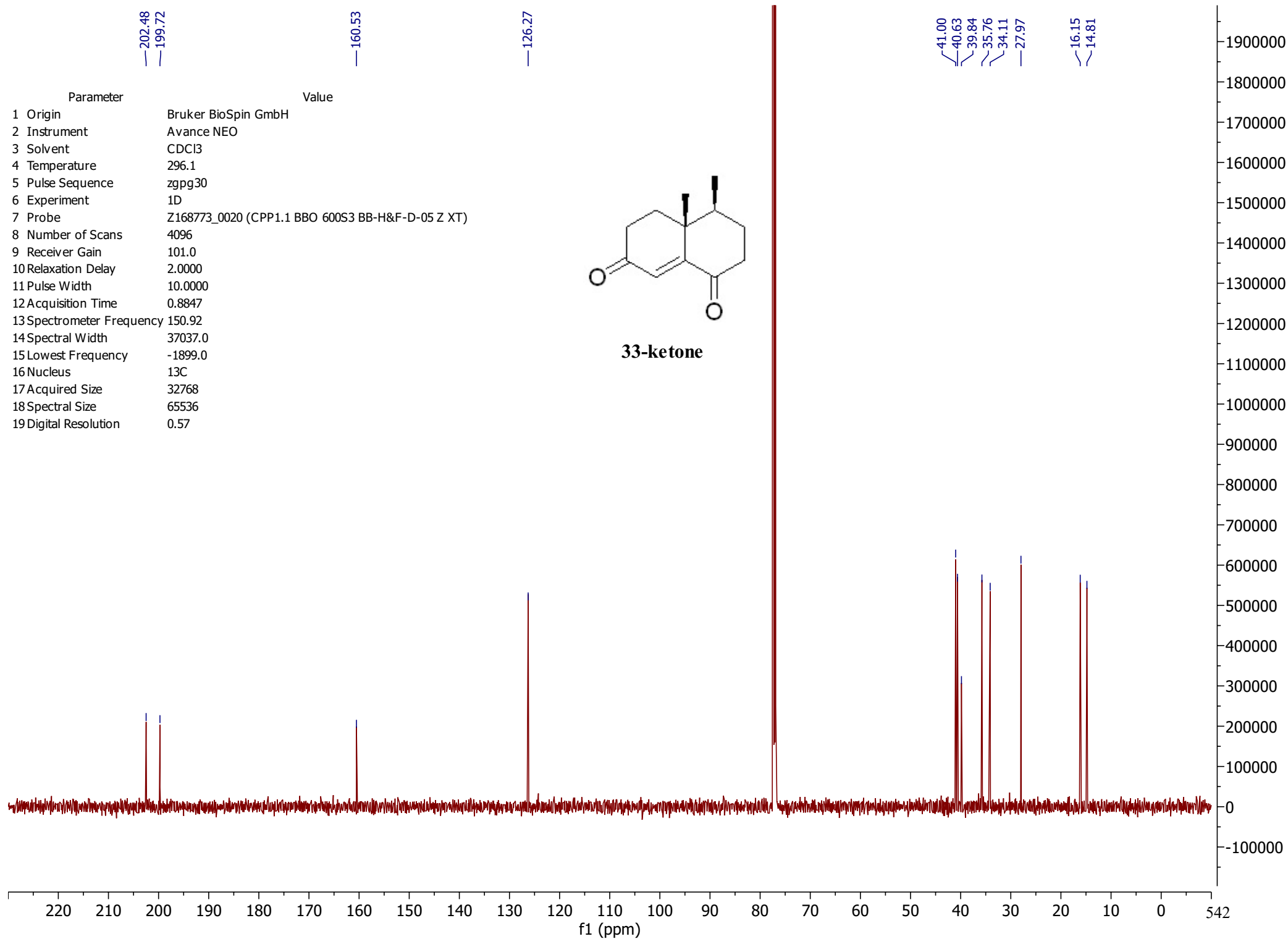
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.7400
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



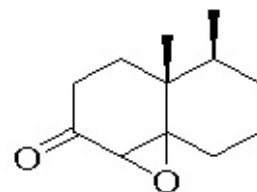
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4096
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1899.0
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



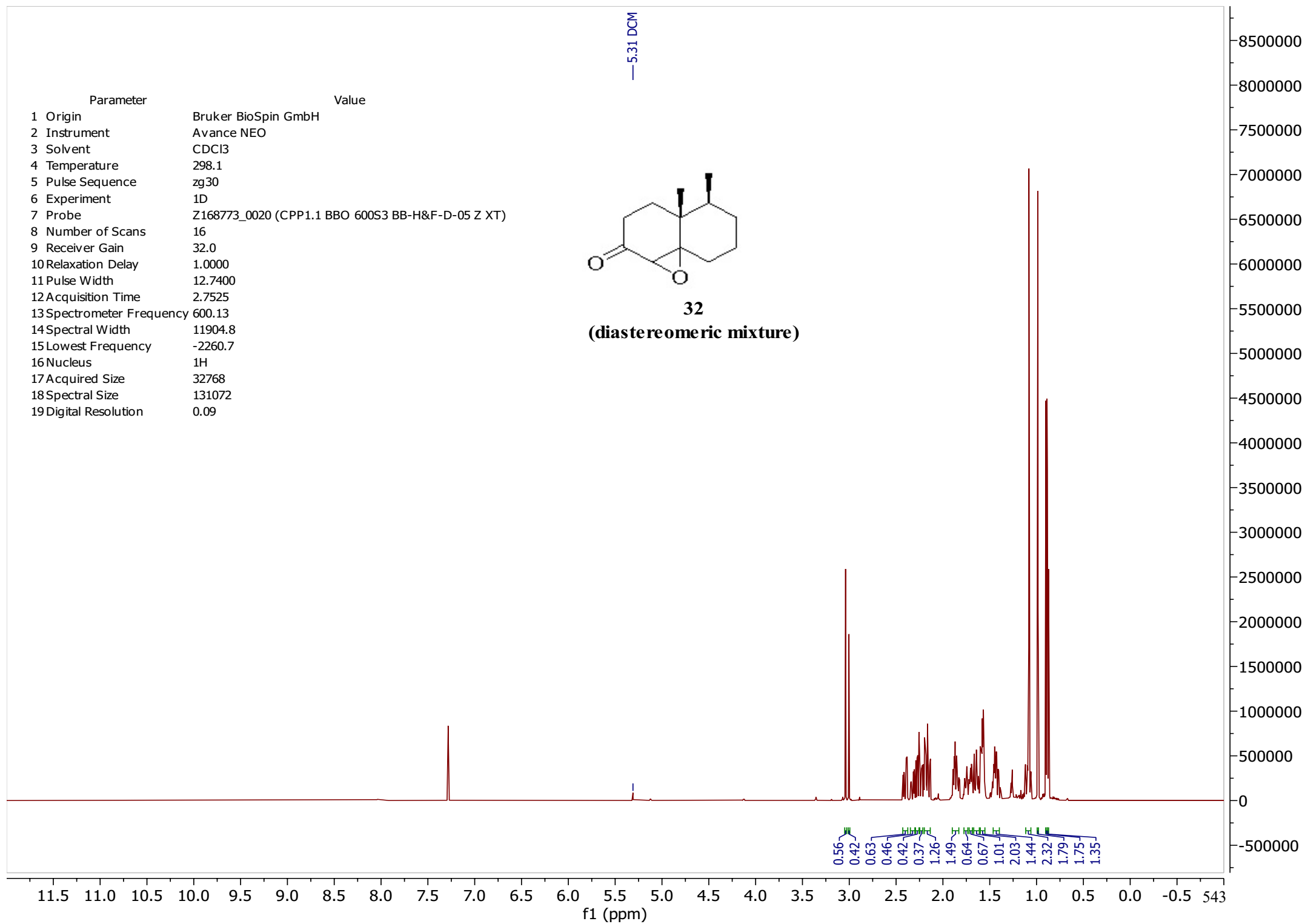
33-ketone



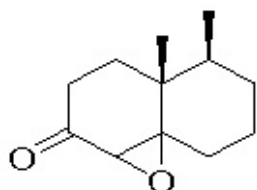
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	298.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.7400
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



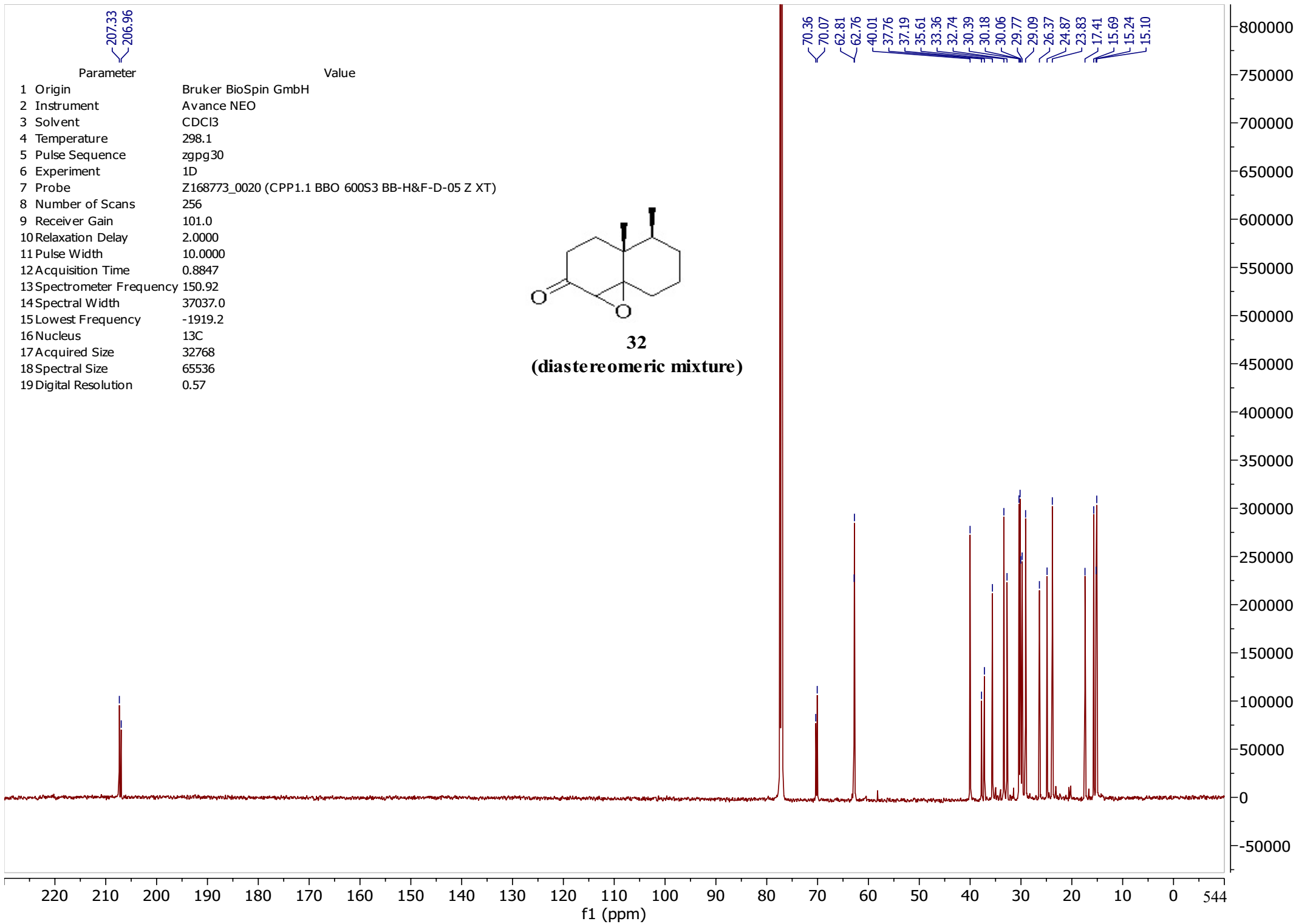
32
(diastereomeric mixture)



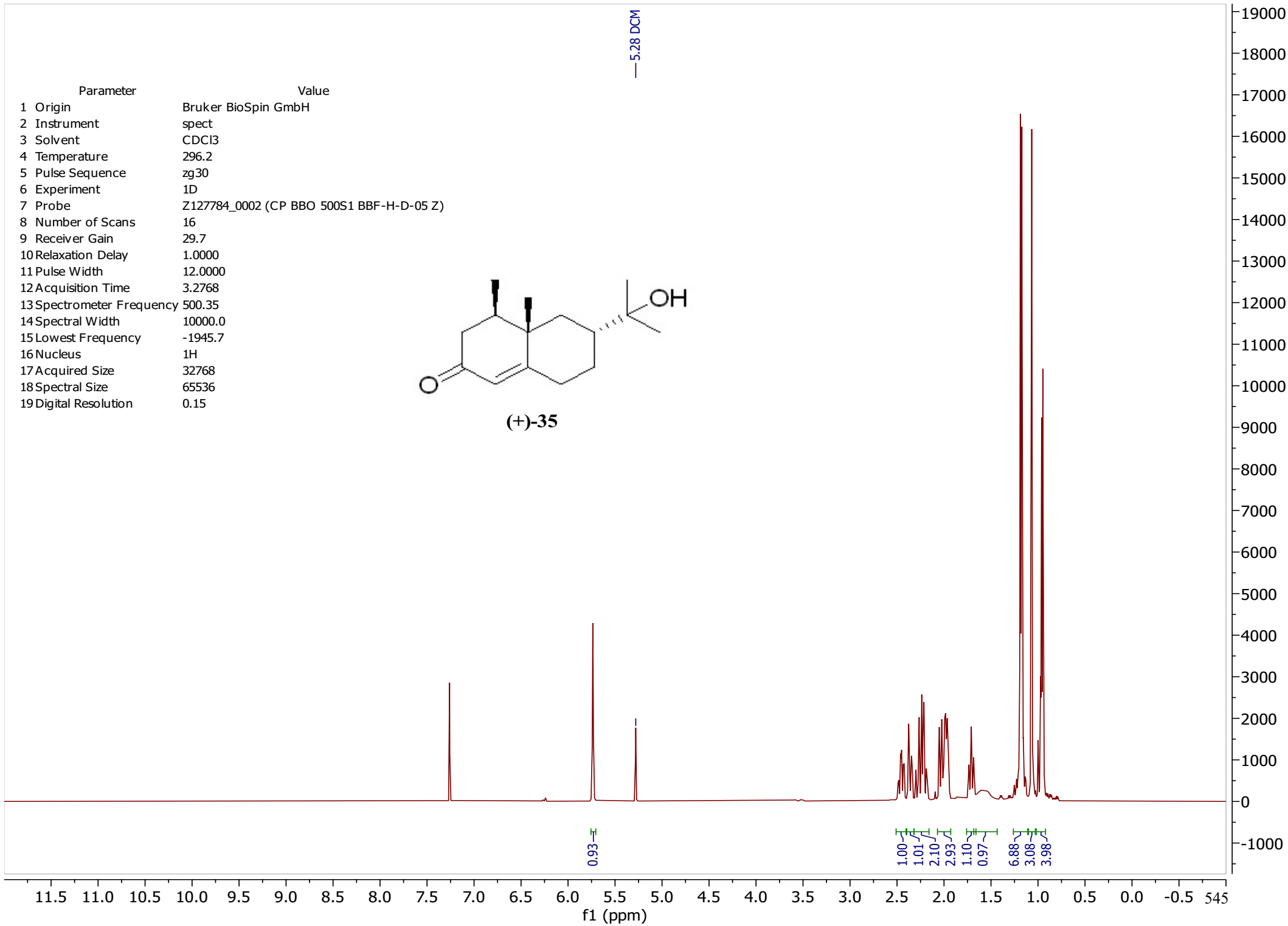
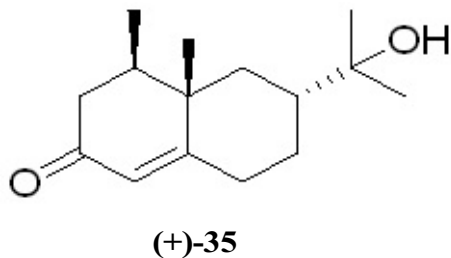
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	256
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1919.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



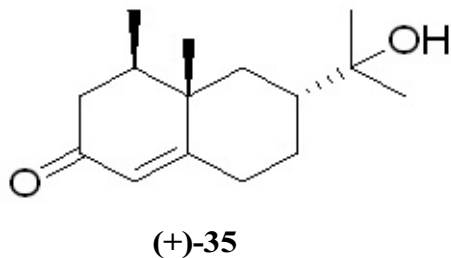
32
(diastereomeric mixture)



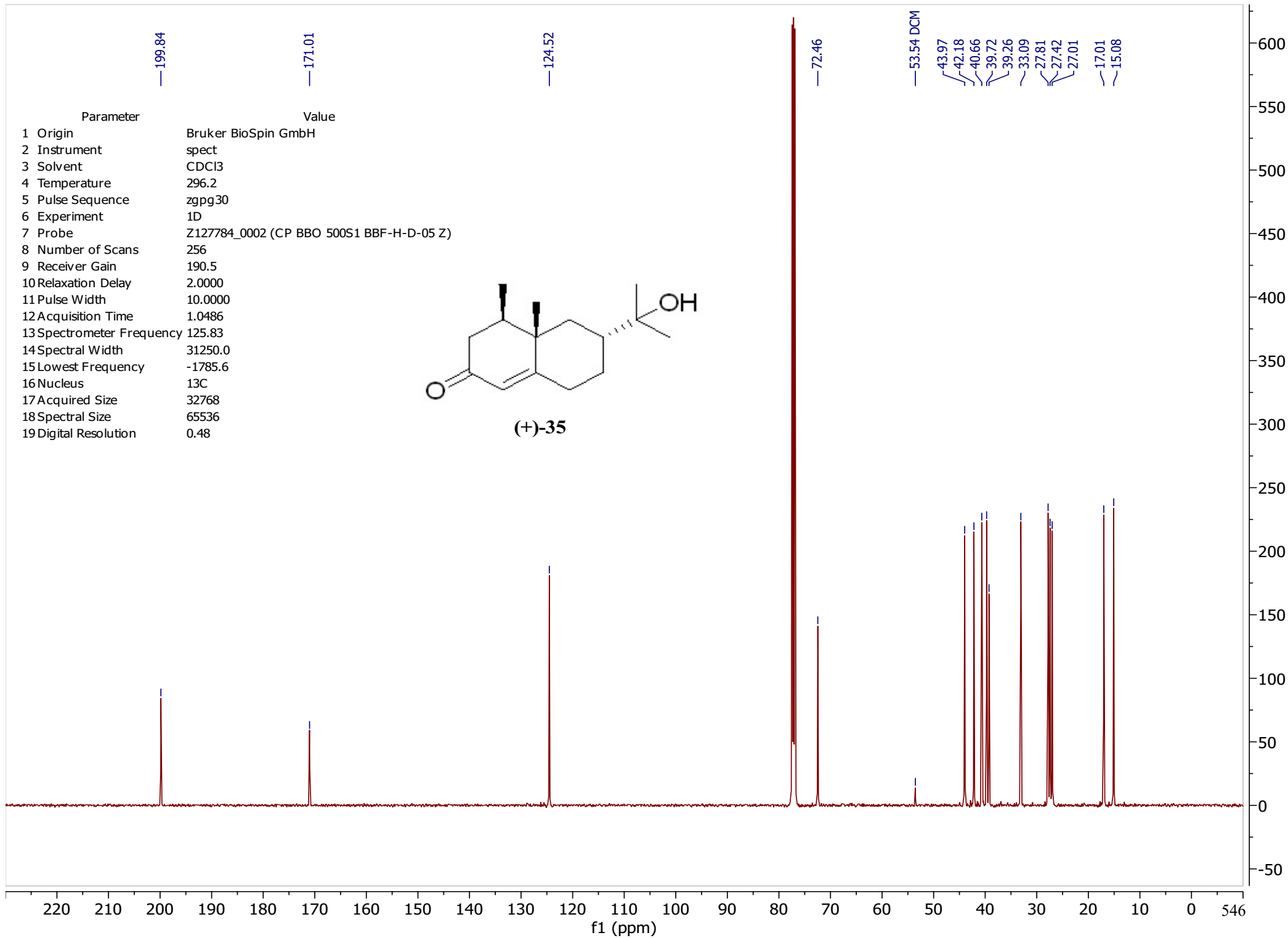
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1945.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



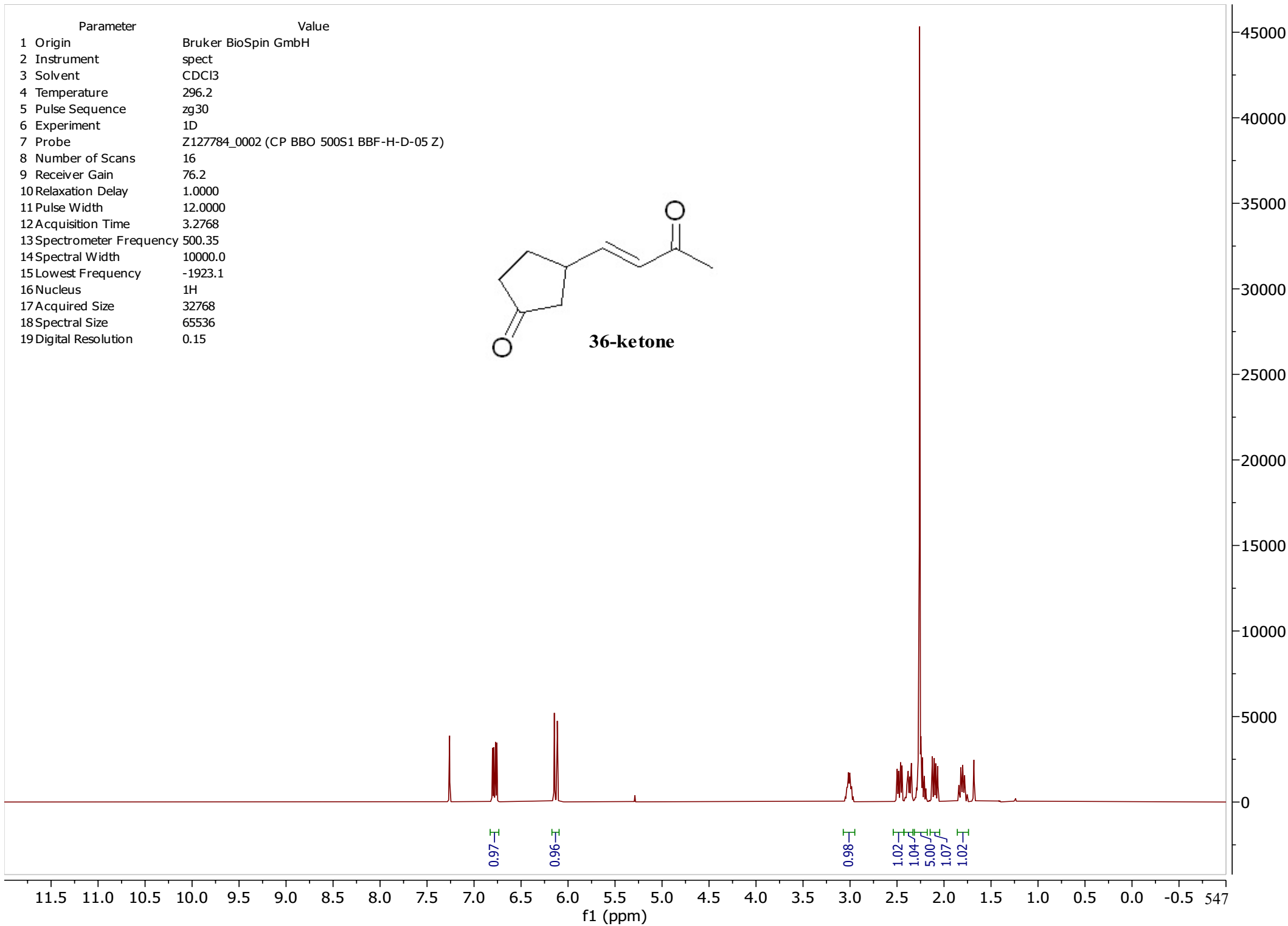
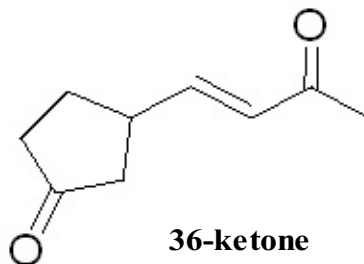
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



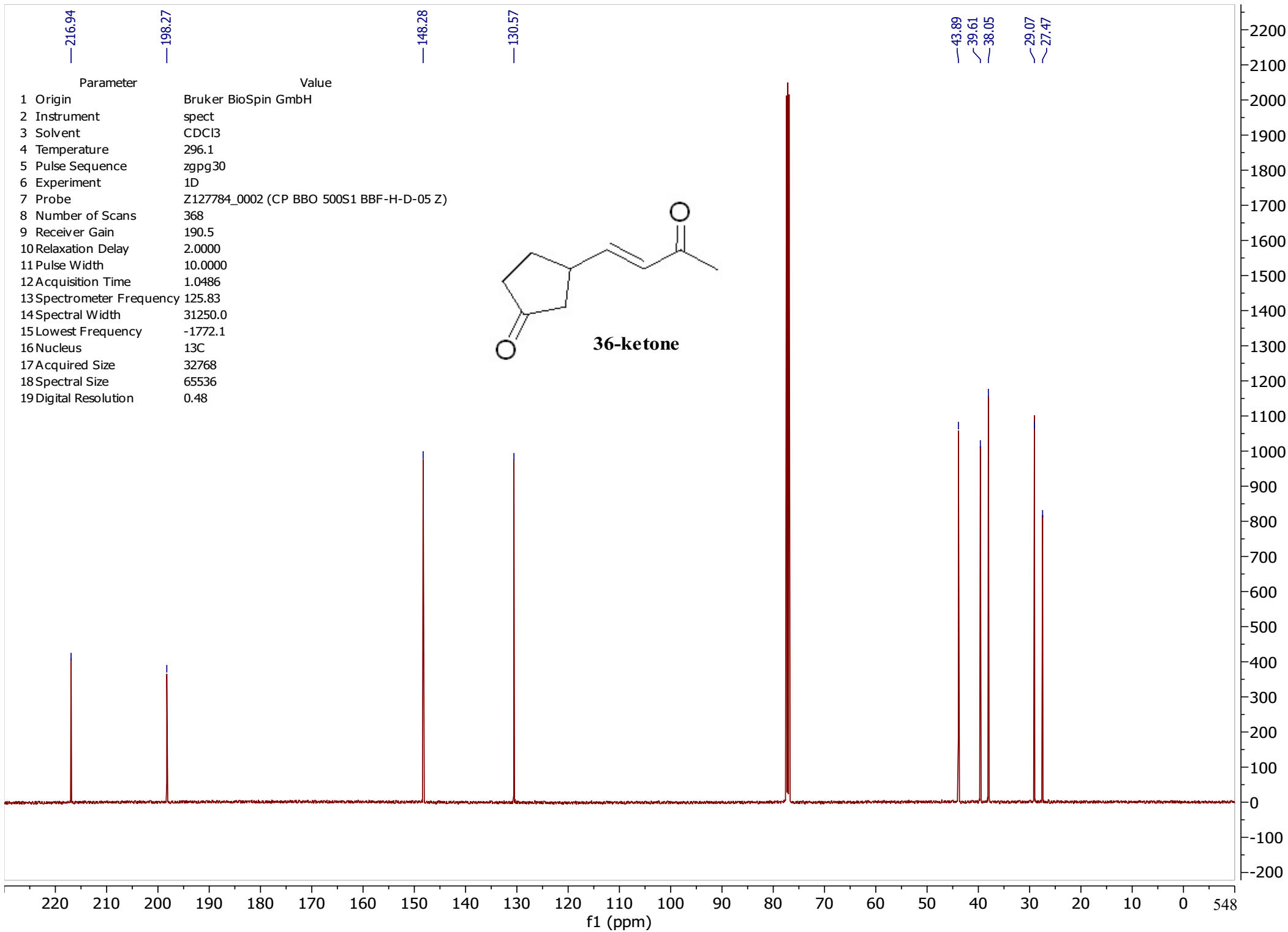
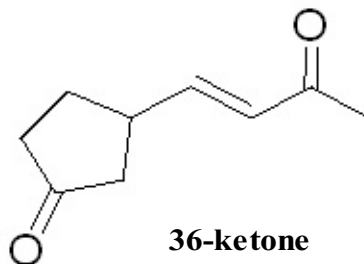
199.84
171.01
124.52
72.46
53.54 DCM
43.97
42.18
40.66
39.72
39.26
33.09
27.81
27.42
27.01
17.01
15.08



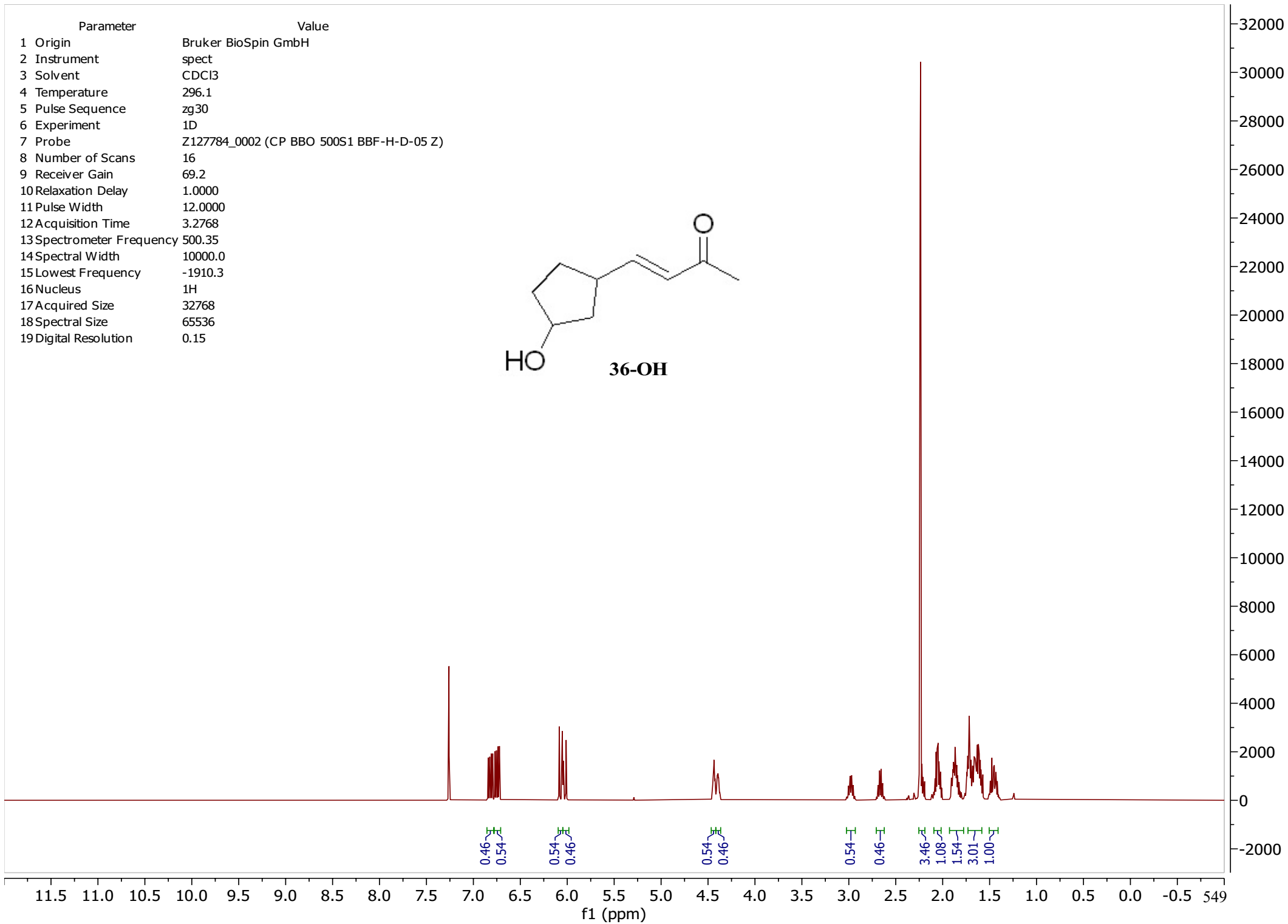
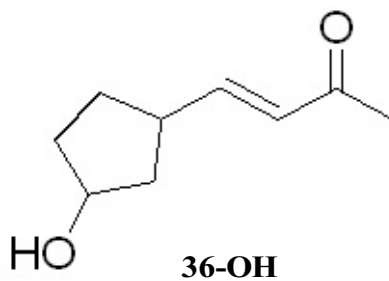
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



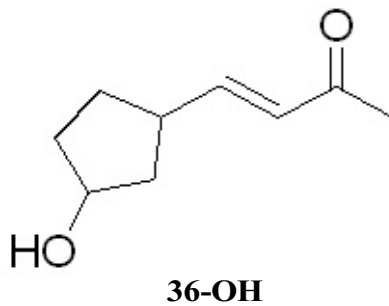
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1772.1
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1910.3
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



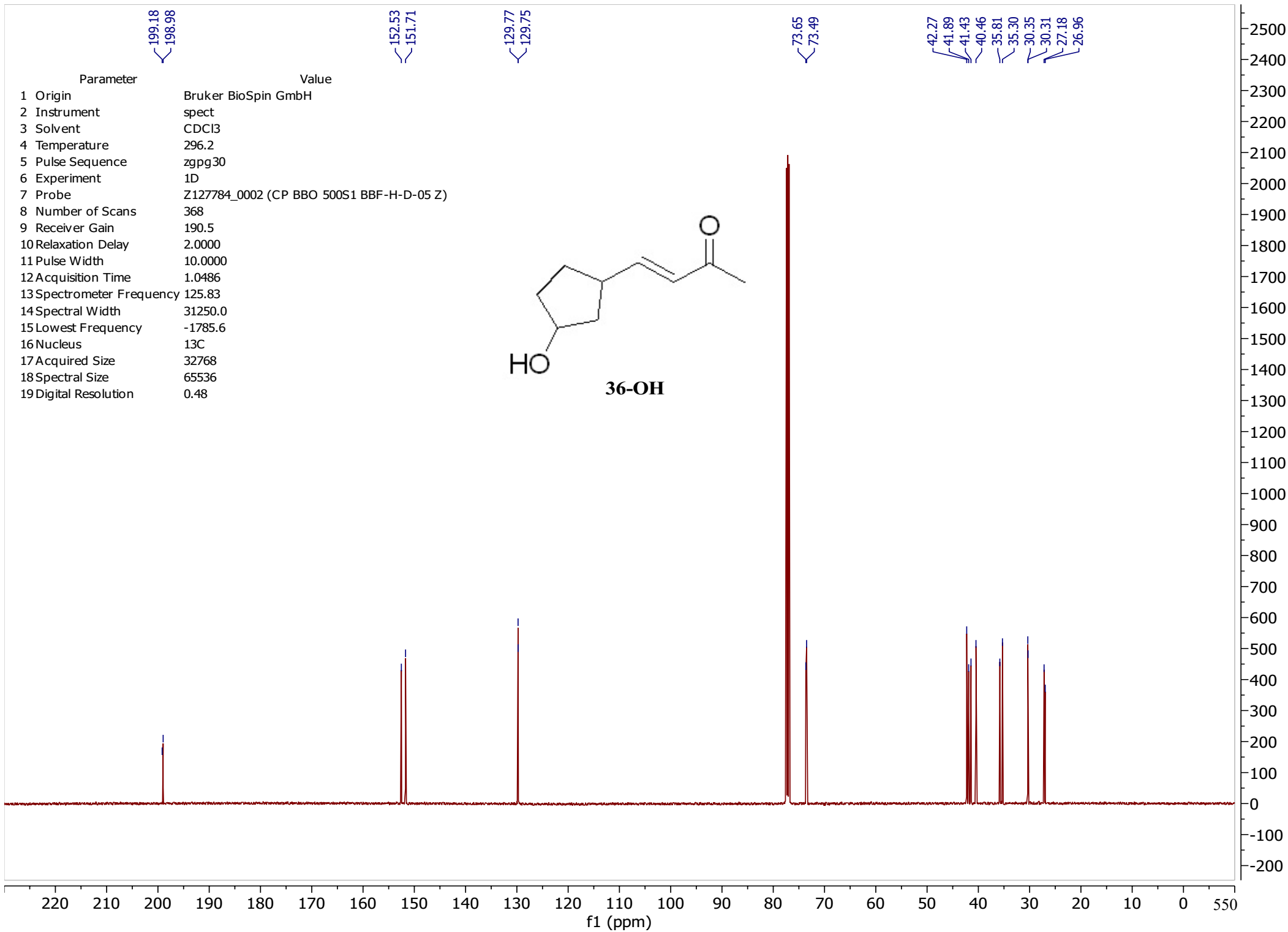
199.18
198.98

152.53
151.71

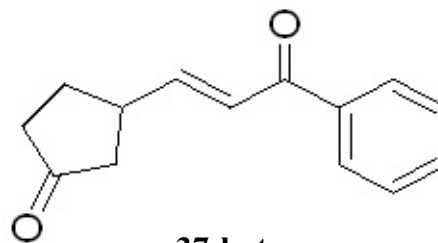
129.77
129.75

73.65
73.49

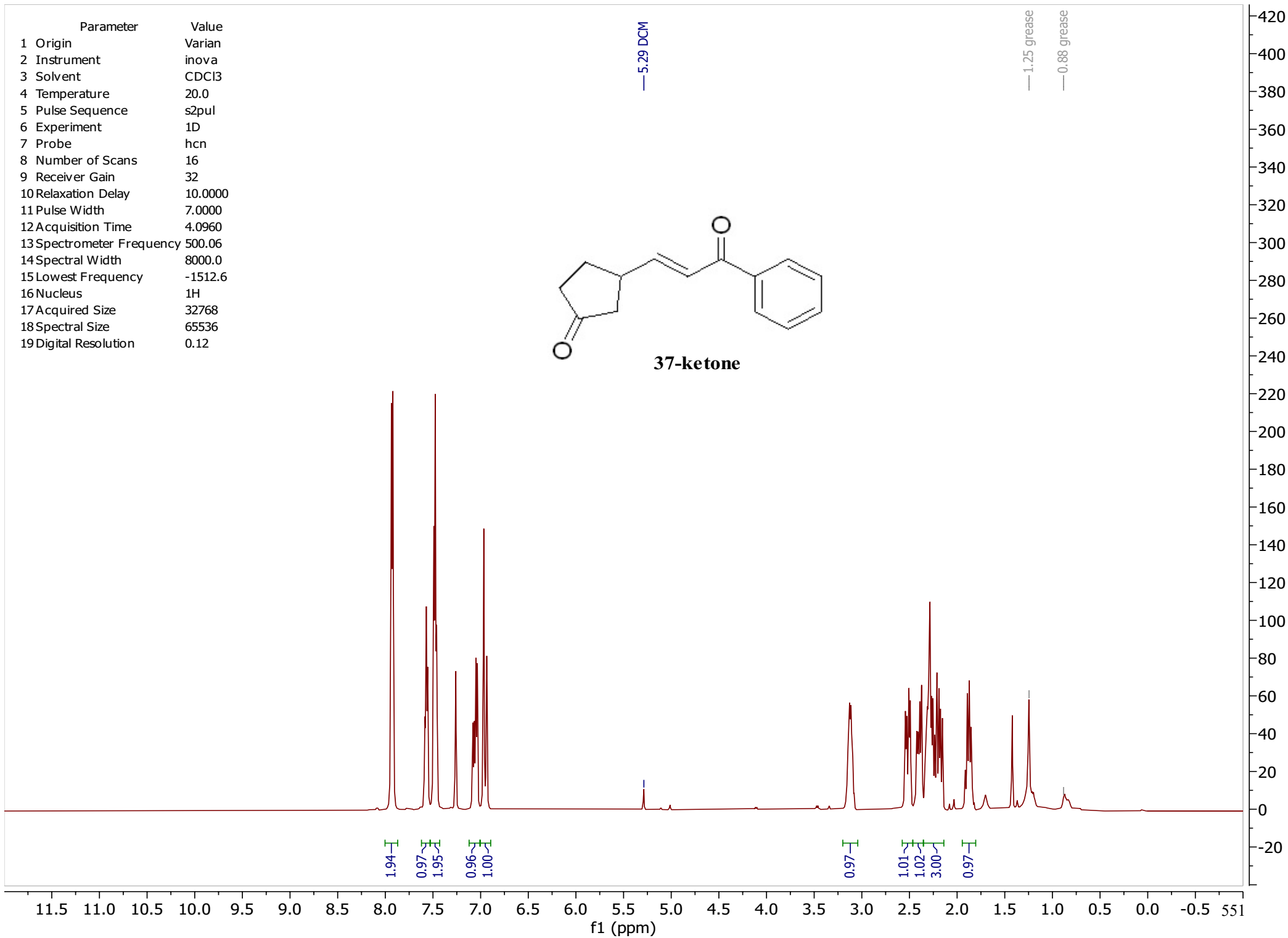
42.27
41.89
41.43
40.46
35.81
35.30
30.35
30.31
27.18
26.96

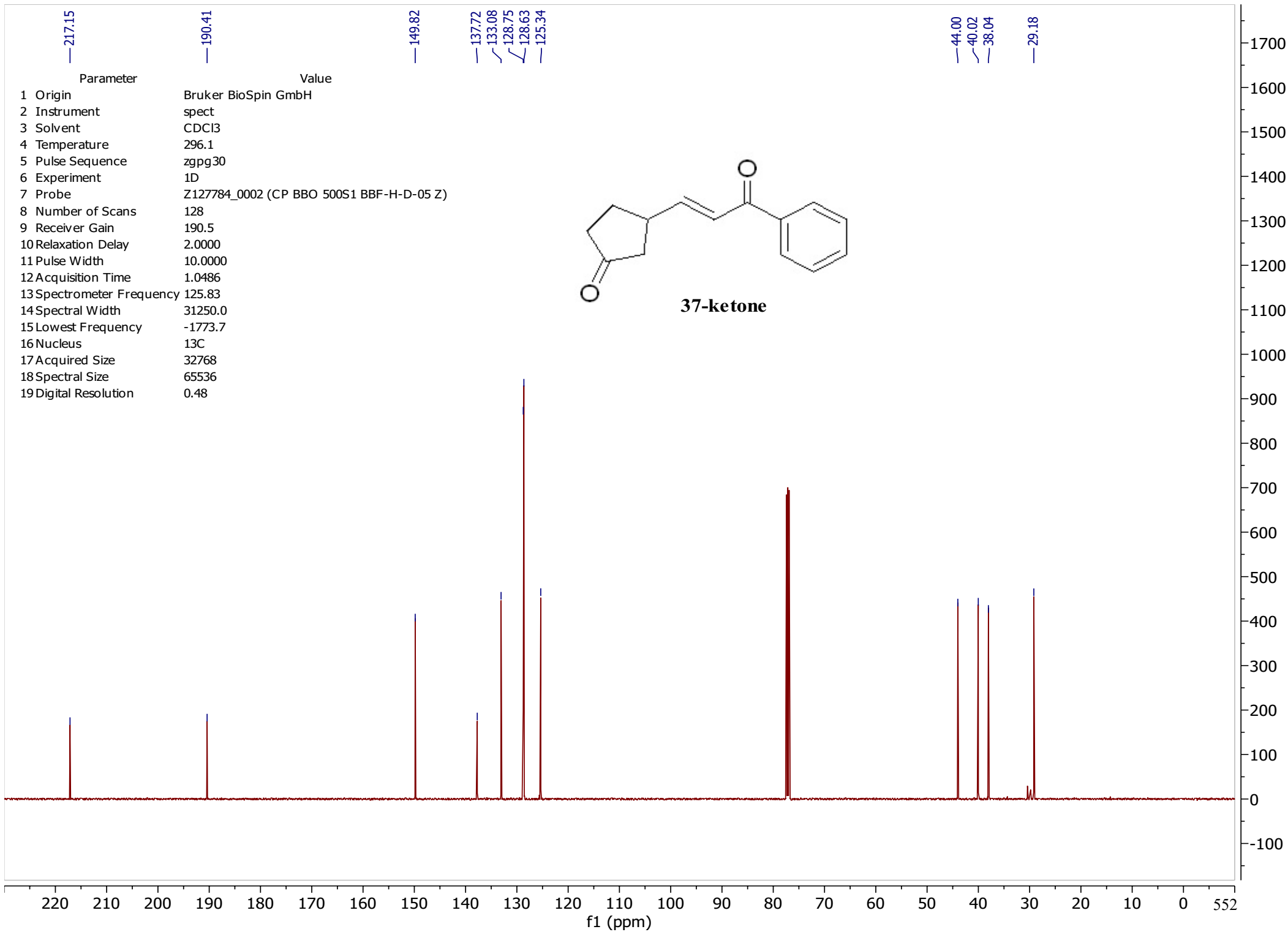


Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	hcn
8 Number of Scans	16
9 Receiver Gain	32
10 Relaxation Delay	10.0000
11 Pulse Width	7.0000
12 Acquisition Time	4.0960
13 Spectrometer Frequency	500.06
14 Spectral Width	8000.0
15 Lowest Frequency	-1512.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12

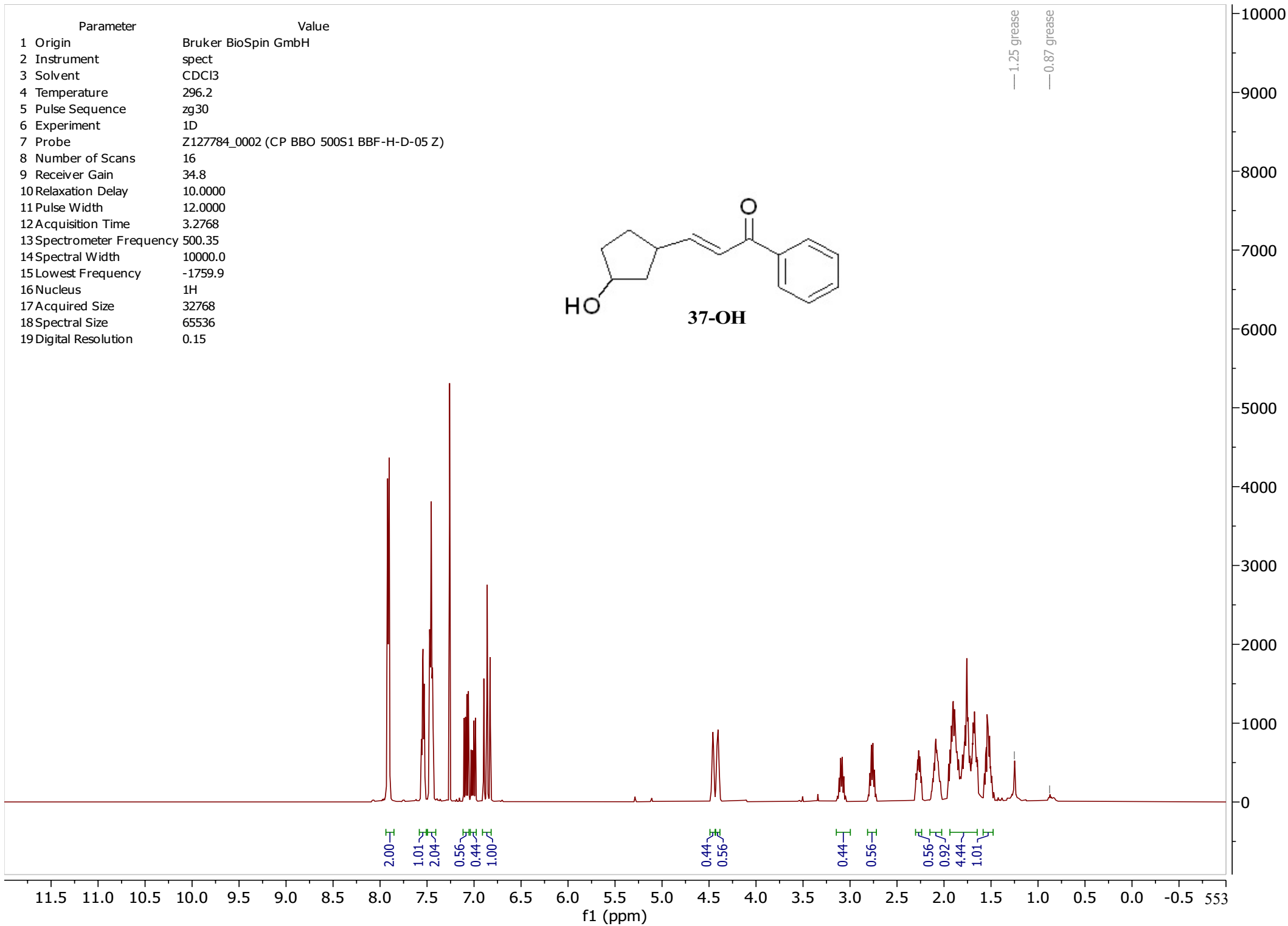
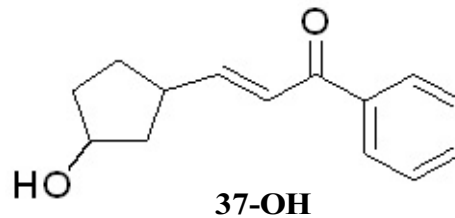


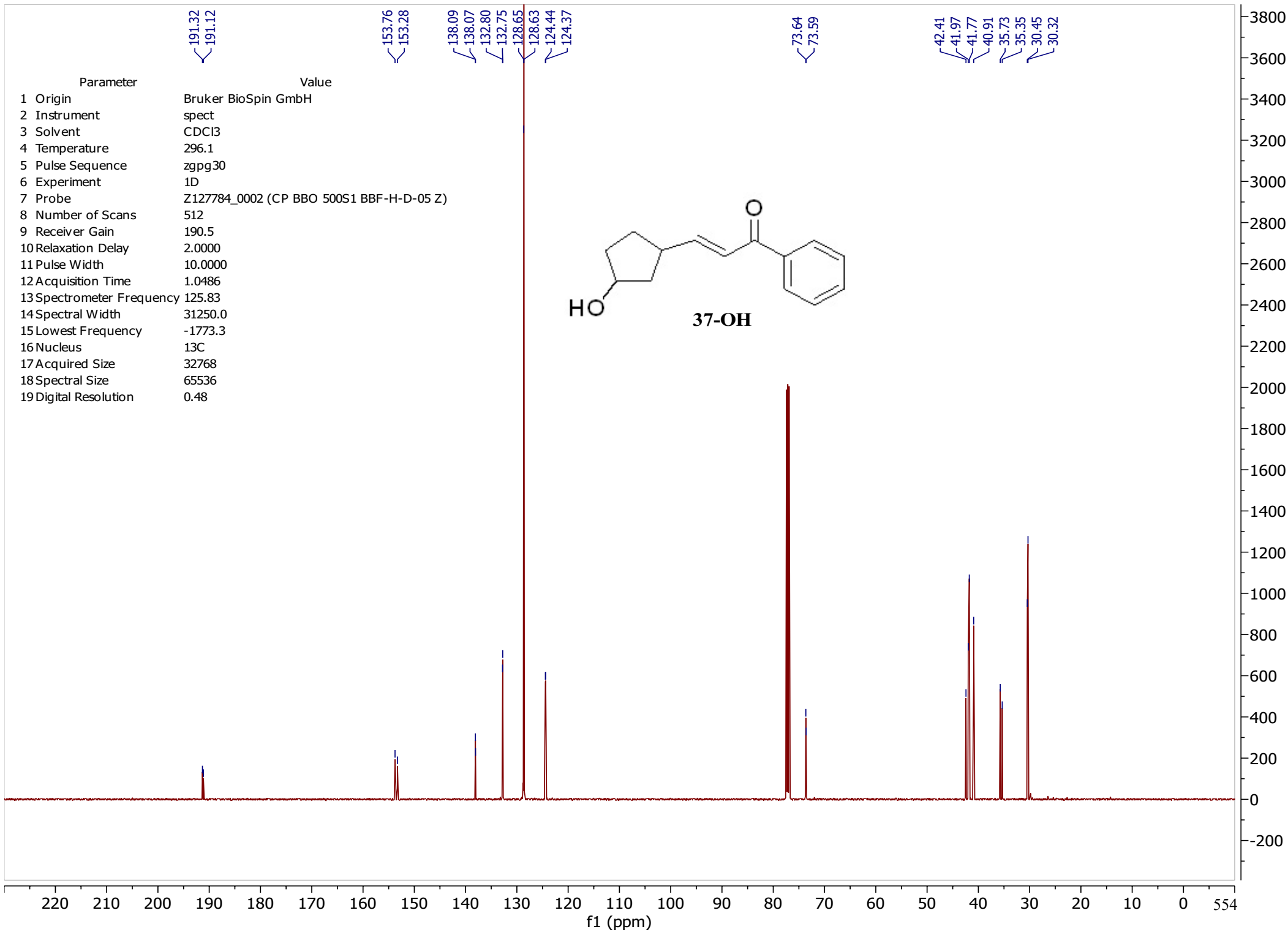
37-ketone



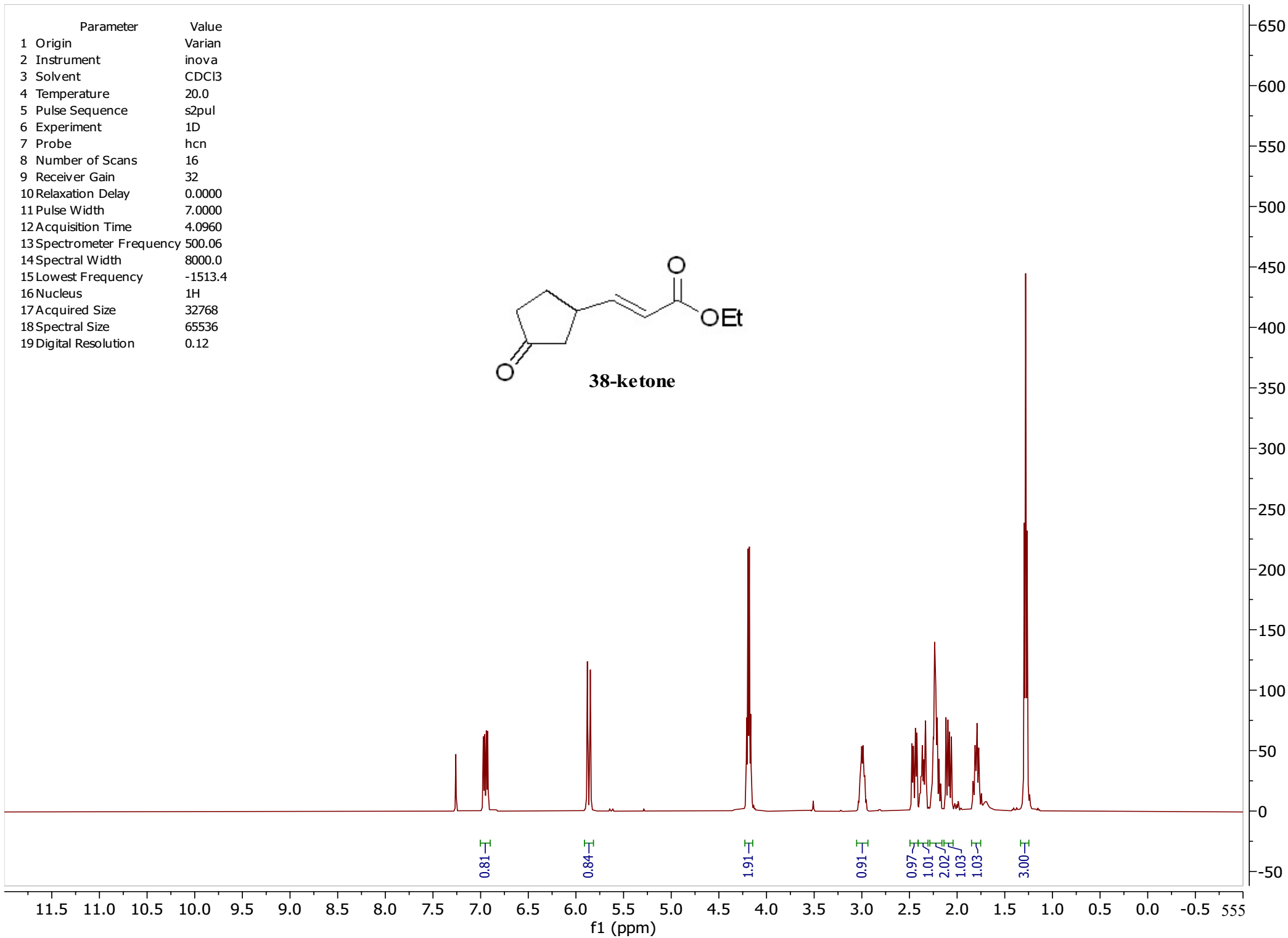
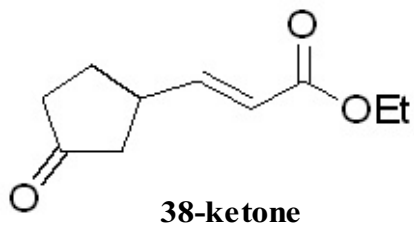


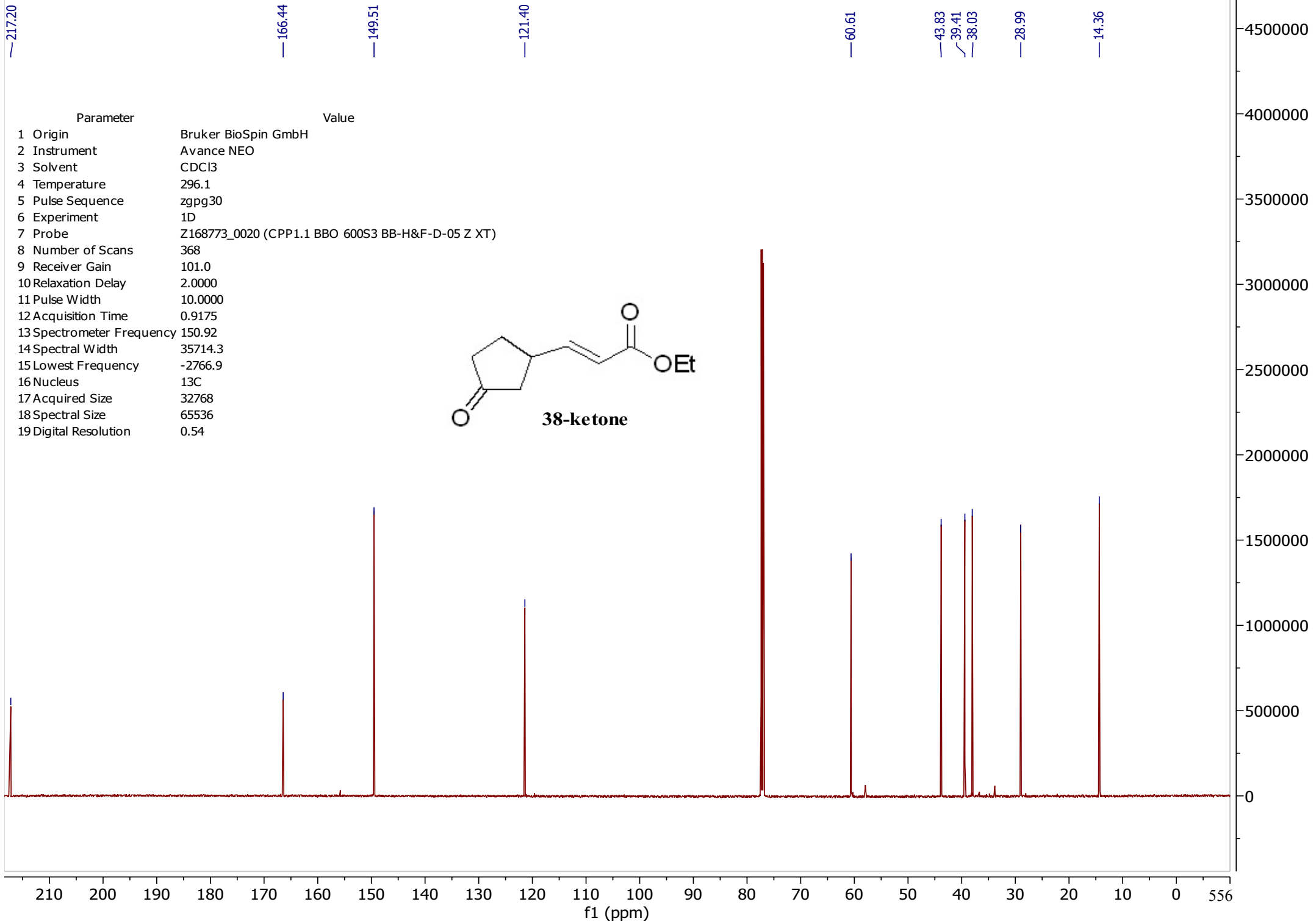
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	34.8
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1759.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15





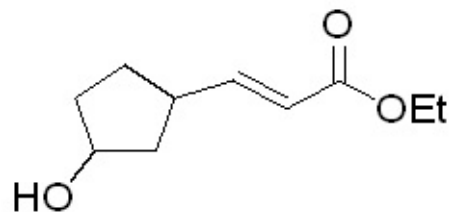
Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	hcn
8 Number of Scans	16
9 Receiver Gain	32
10 Relaxation Delay	0.0000
11 Pulse Width	7.0000
12 Acquisition Time	4.0960
13 Spectrometer Frequency	500.06
14 Spectral Width	8000.0
15 Lowest Frequency	-1513.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12



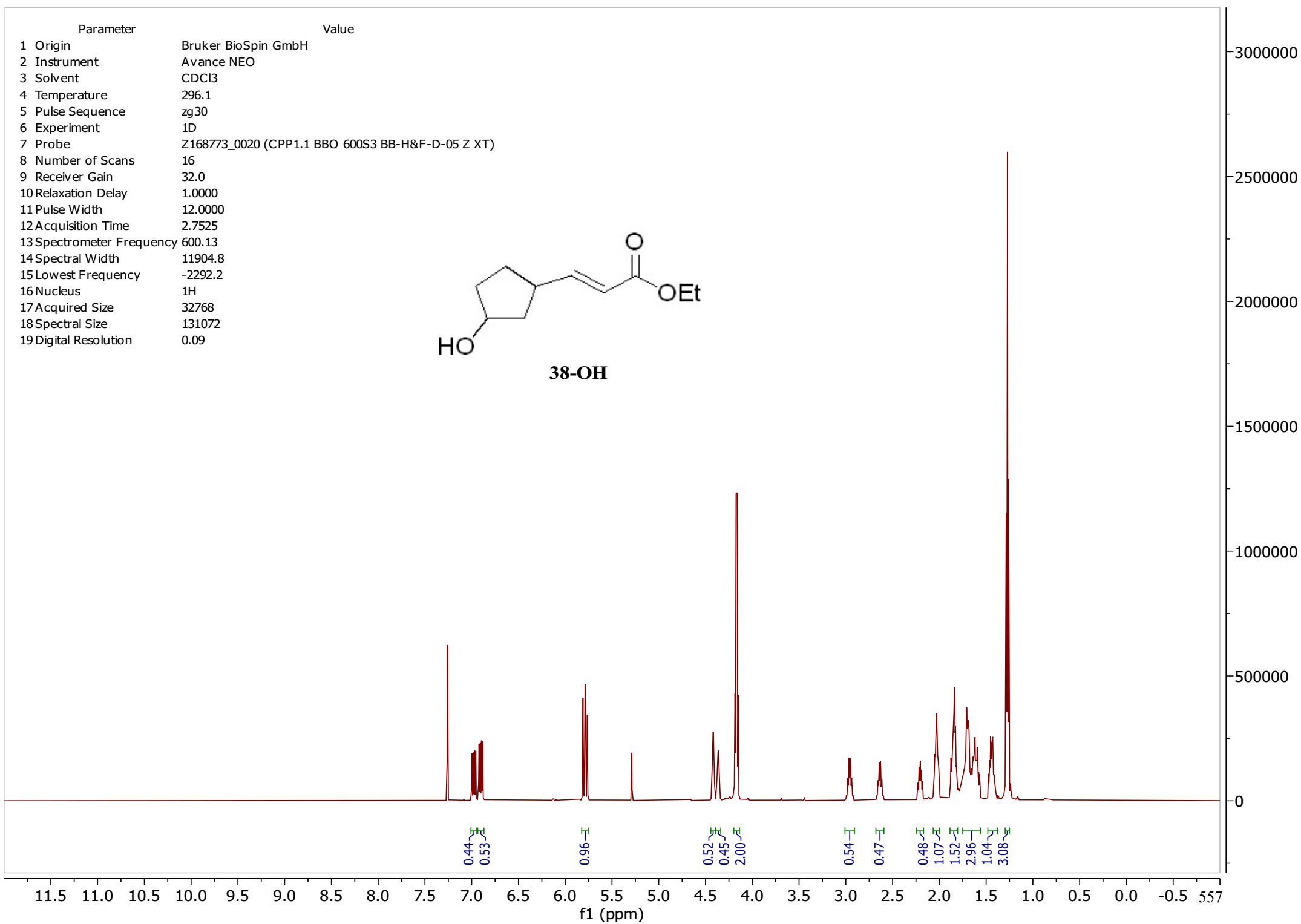


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	368
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.9175
13 Spectrometer Frequency	150.92
14 Spectral Width	35714.3
15 Lowest Frequency	-2766.9
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.54

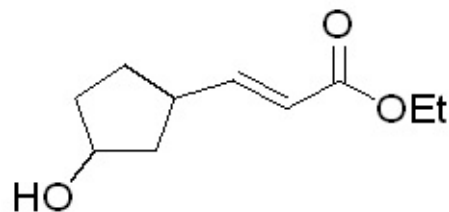
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2292.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



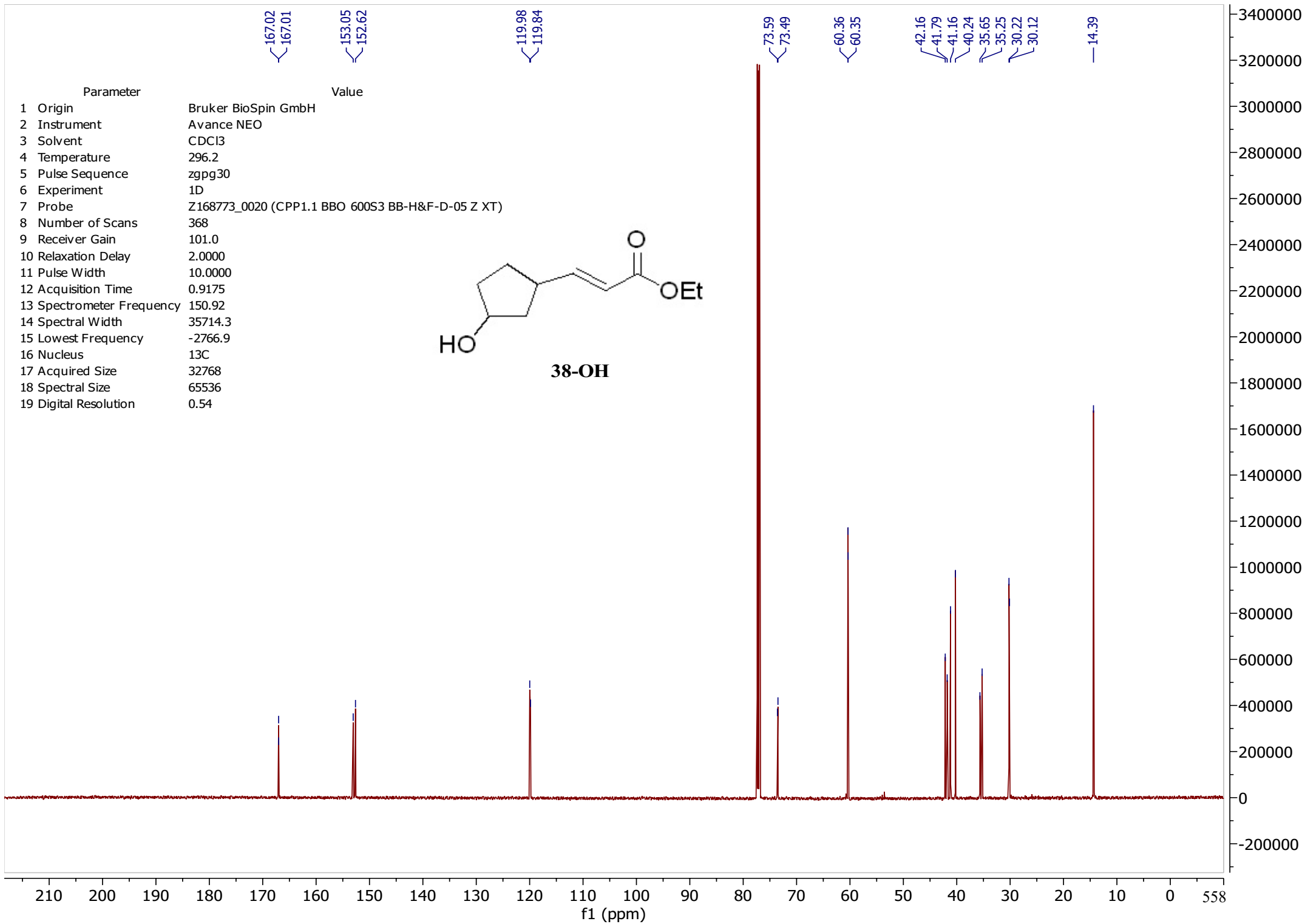
38-OH



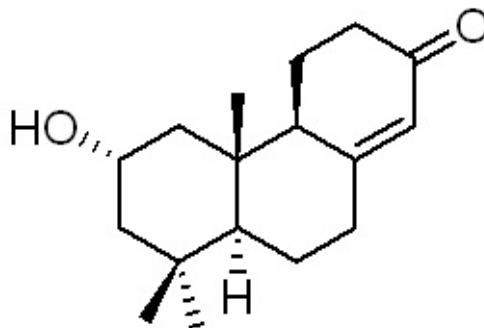
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	368
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.9175
13 Spectrometer Frequency	150.92
14 Spectral Width	35714.3
15 Lowest Frequency	-2766.9
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.54



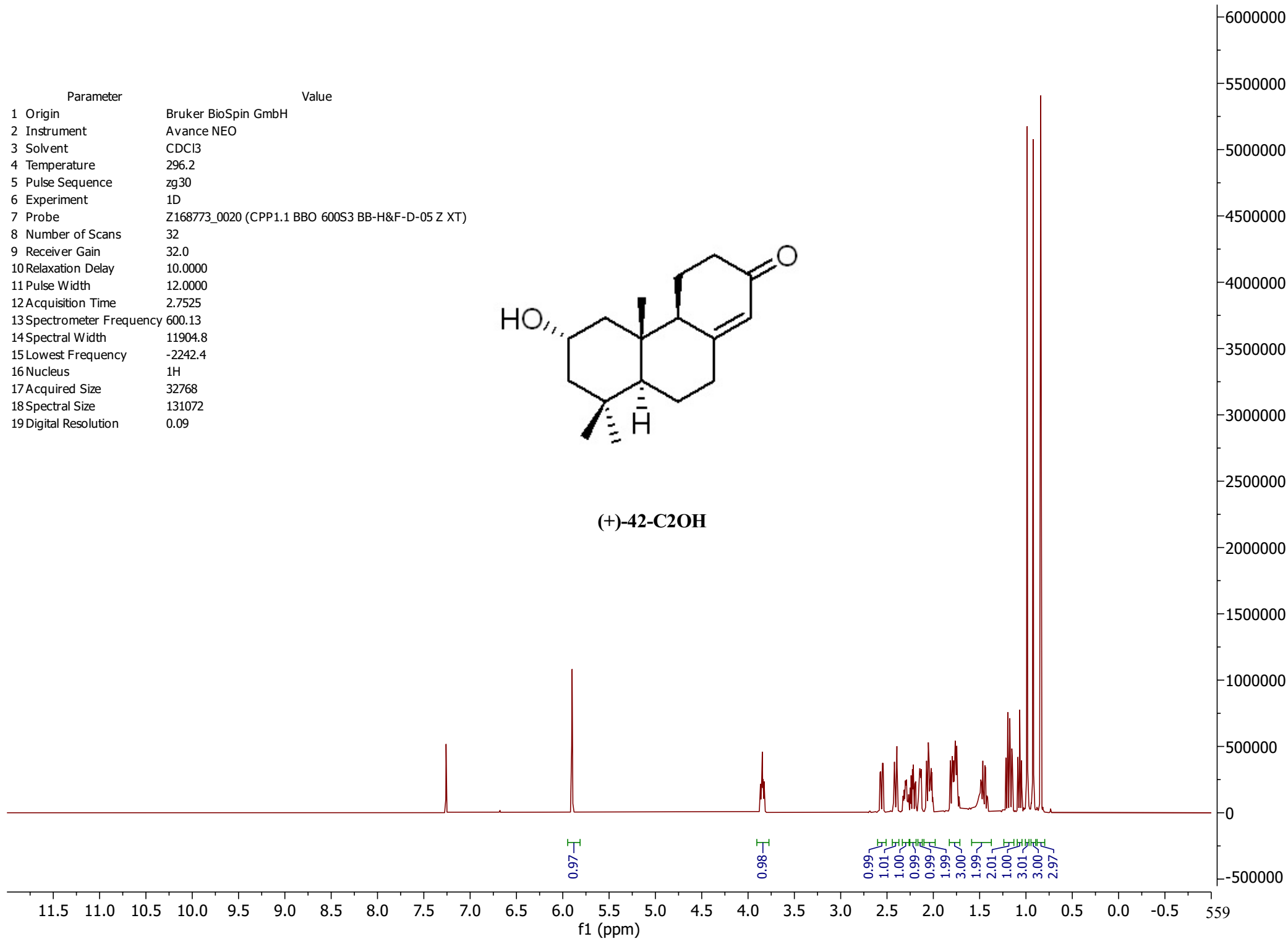
38-OH



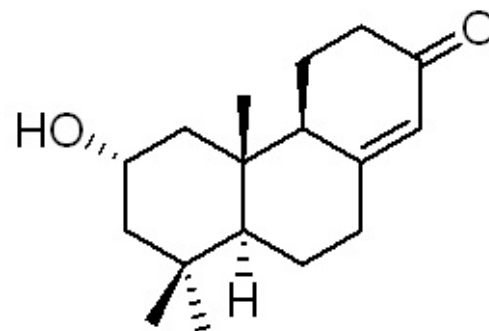
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2242.4
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



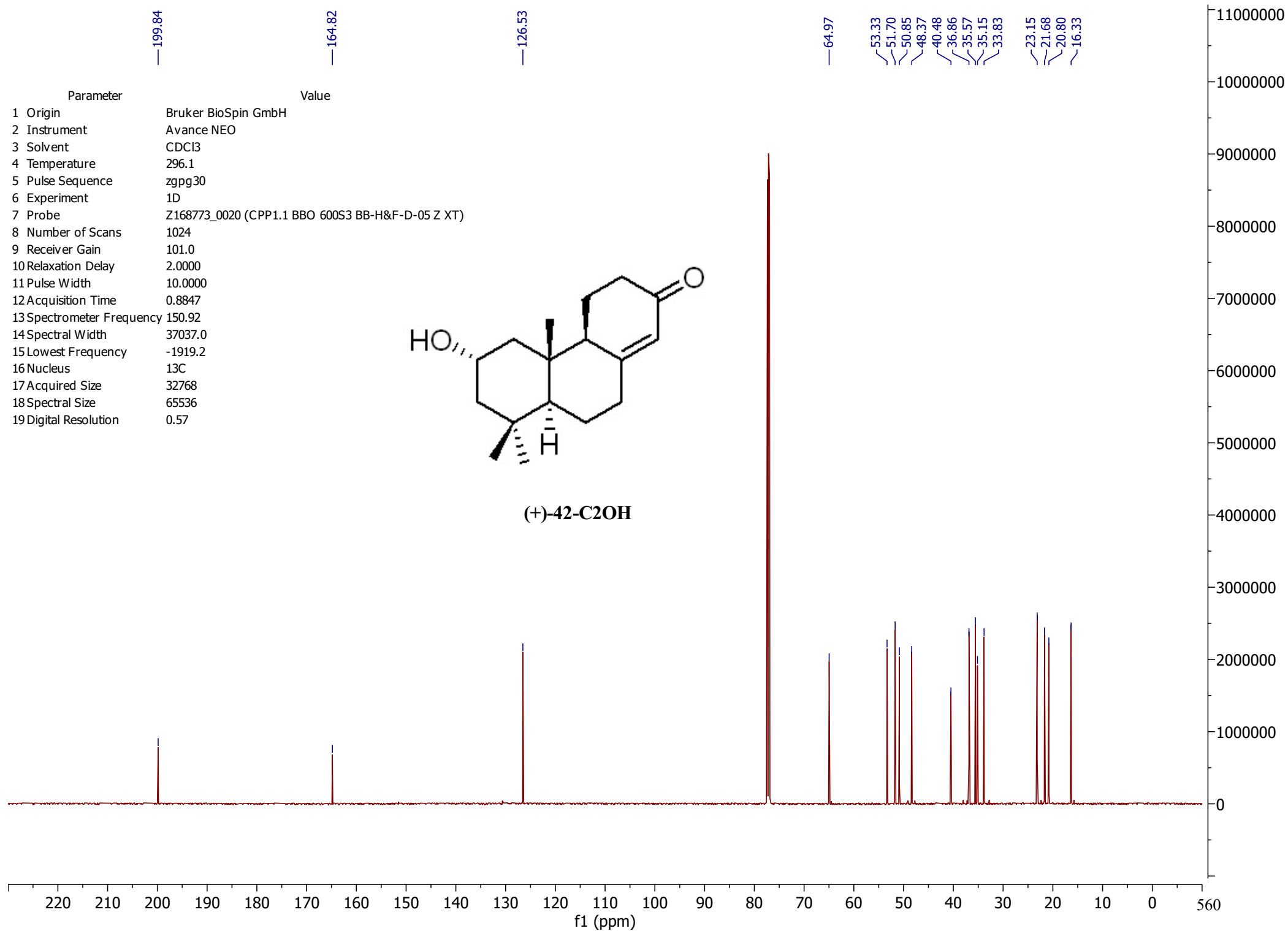
(+)-42-C2OH

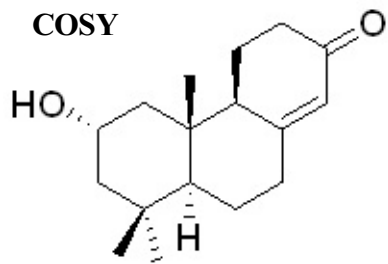


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	1024
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1919.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



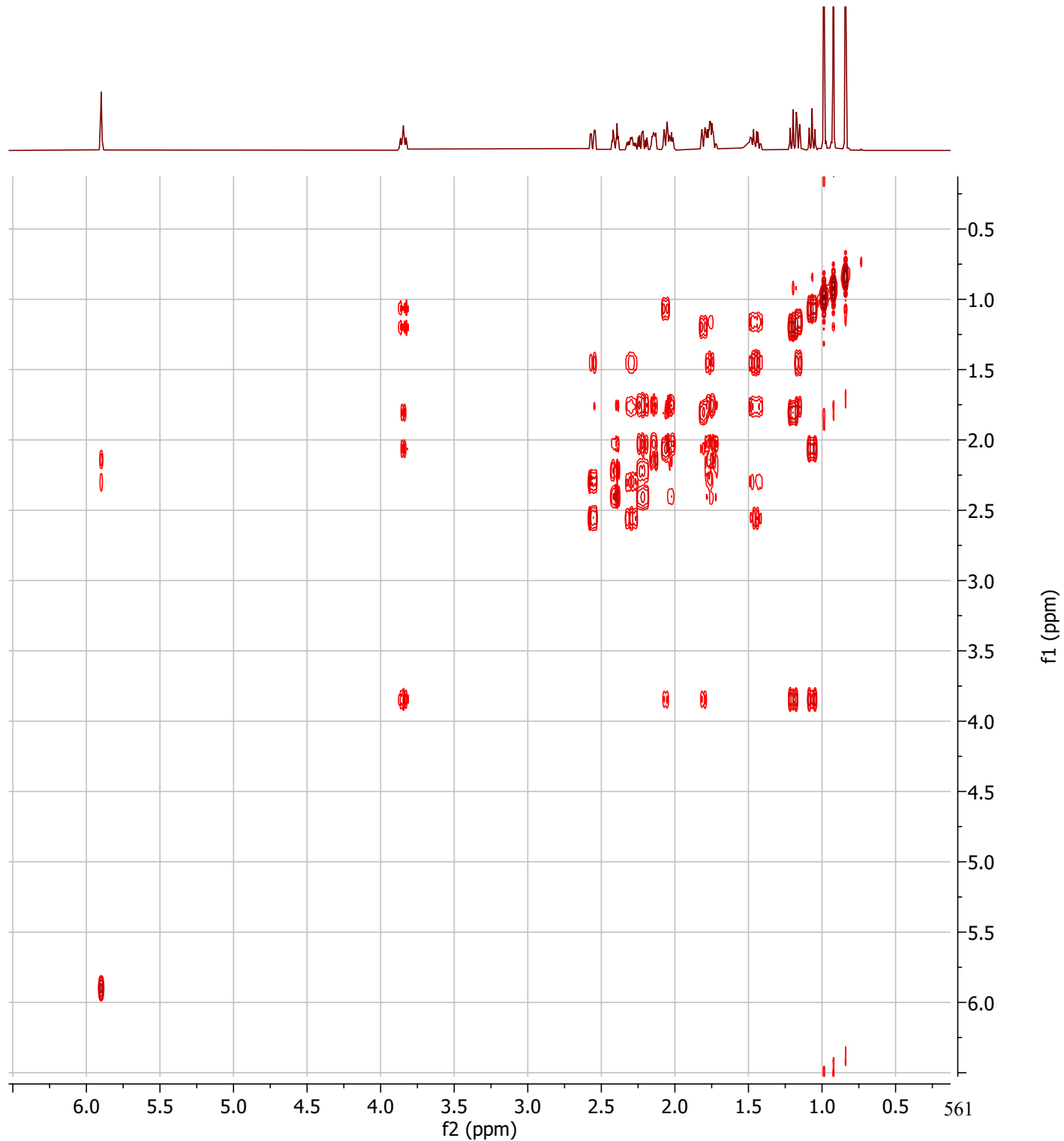
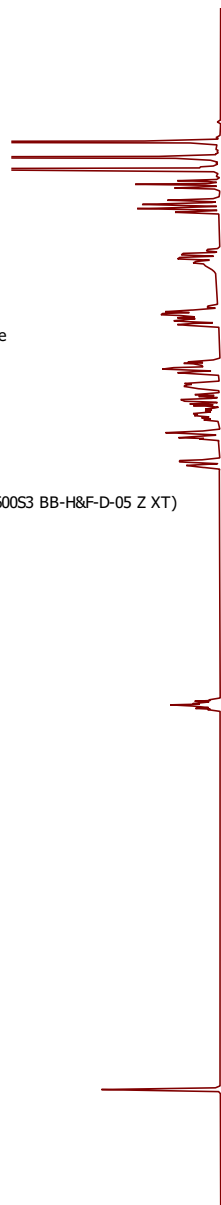
(+)-42-C2OH

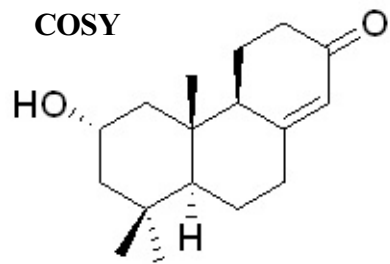




(+)-42-C2OH

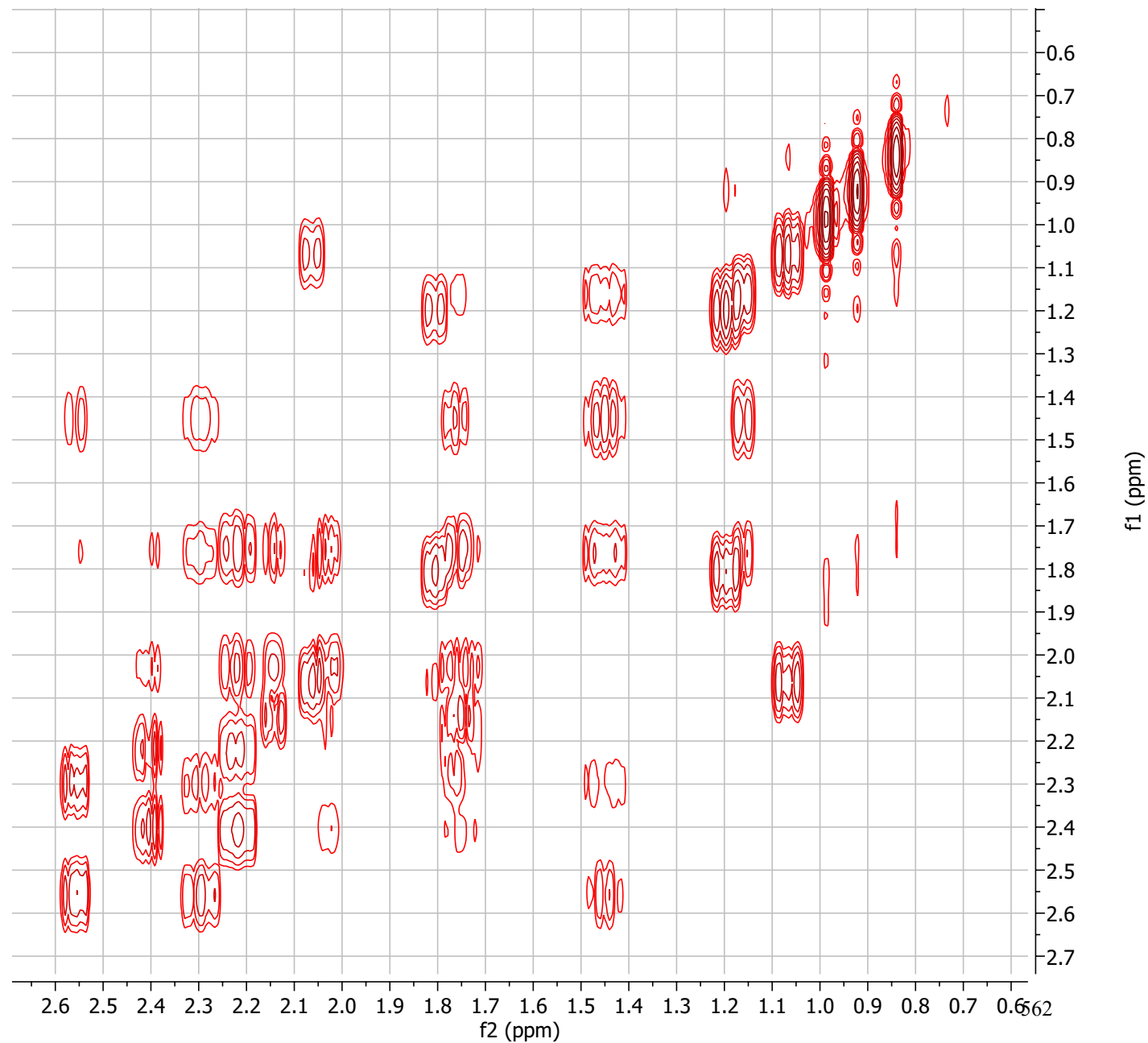
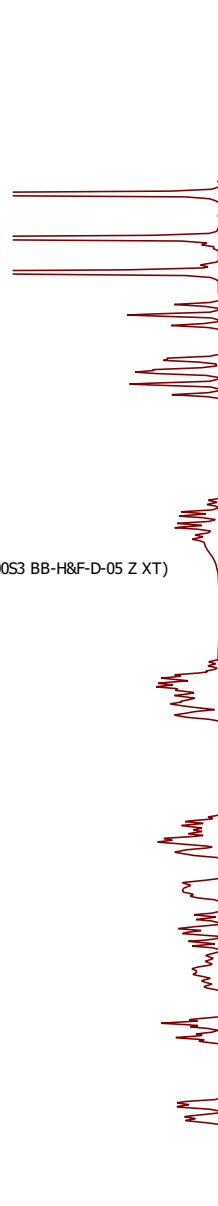
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3689
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(71.9, 71.9)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)

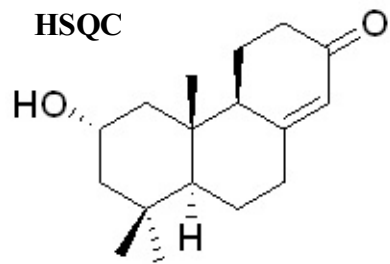




(+)-42-C2OH

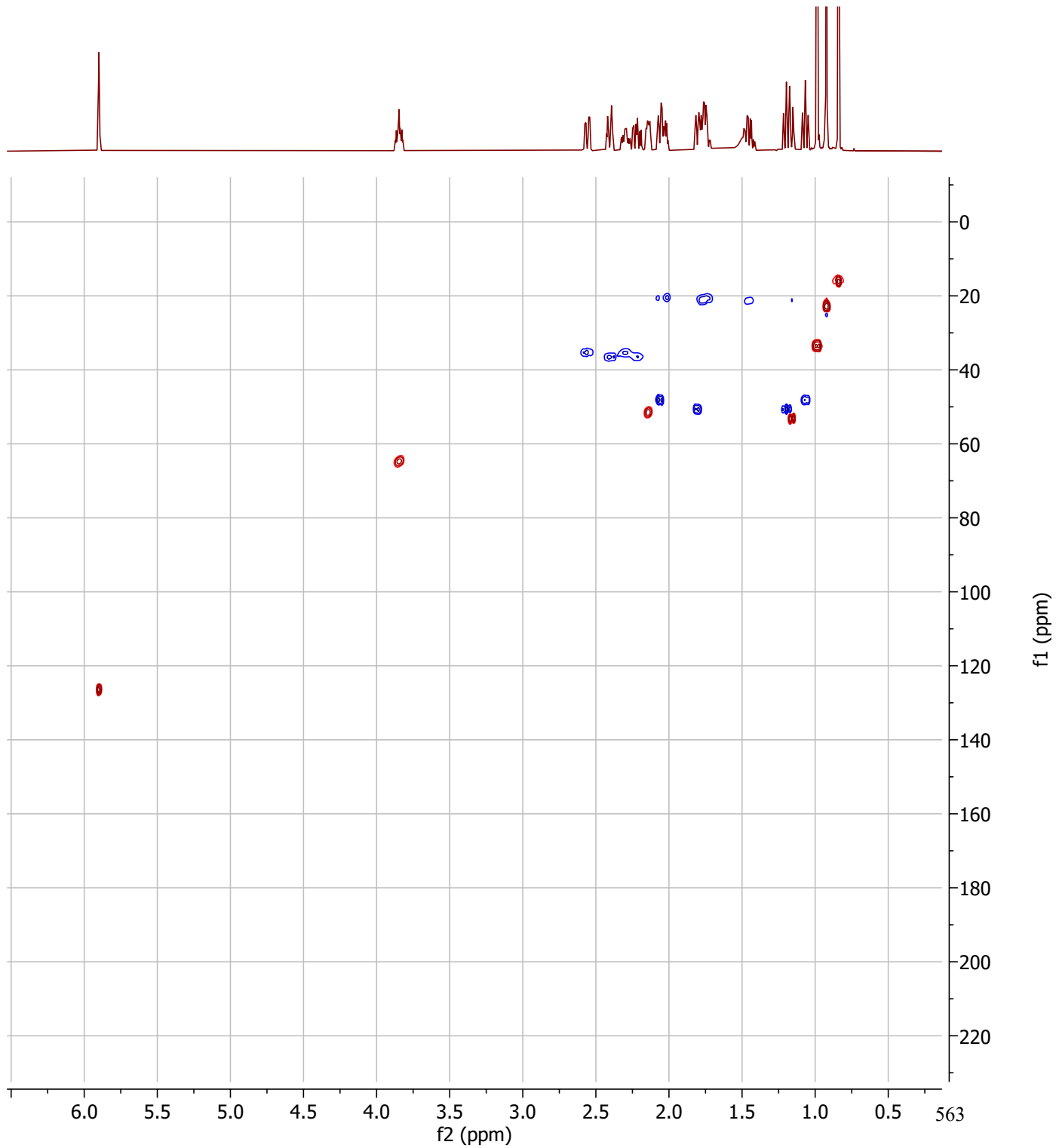
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3689
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(71.9, 71.9)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)





(+)-42-C2OH

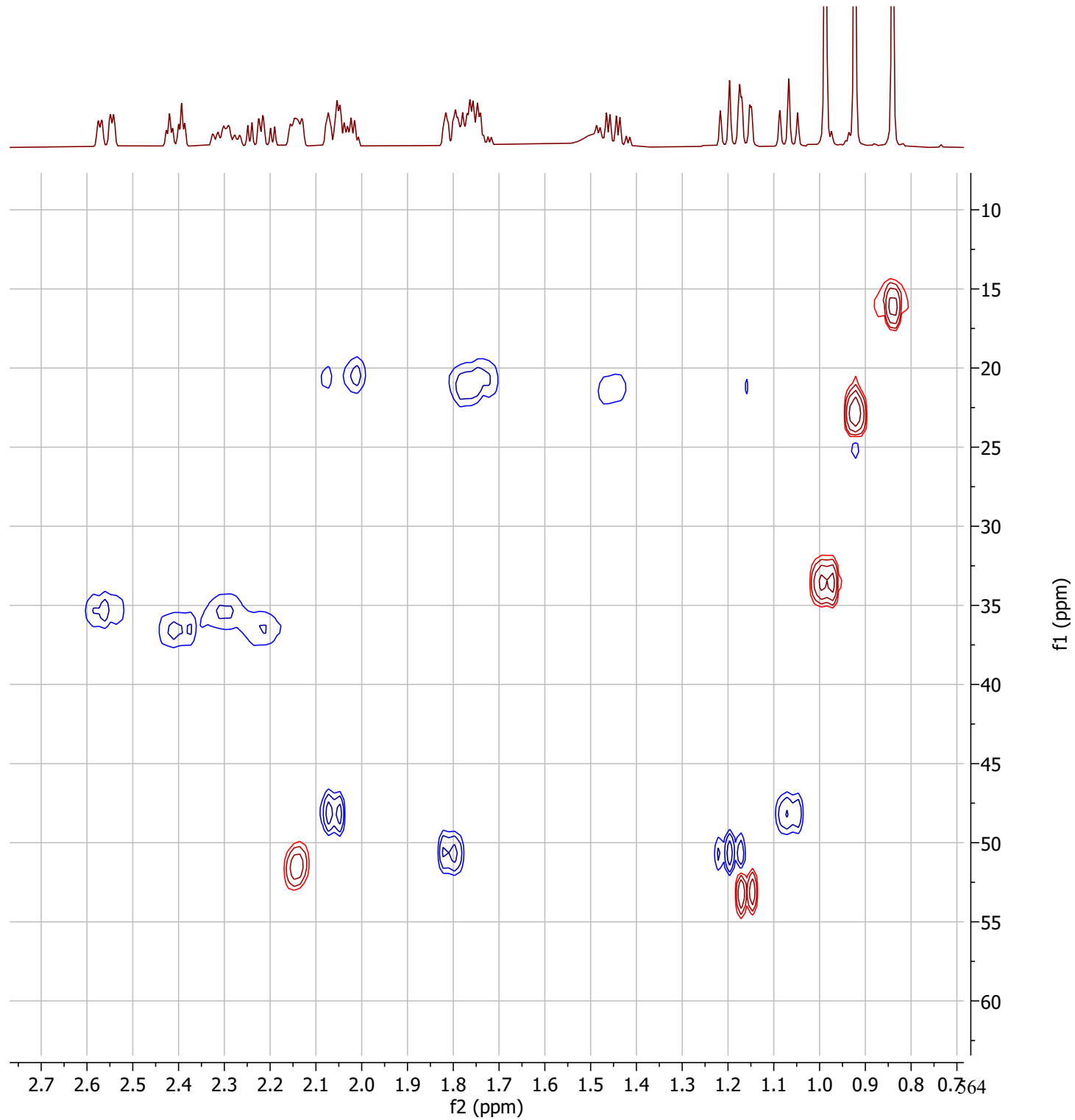
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetdgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(71.9, -1891.2)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)

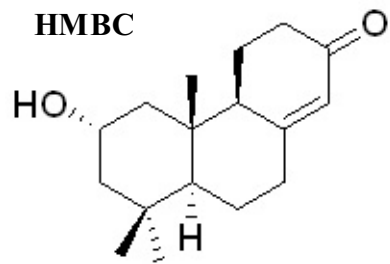


Chemical structure of compound 1, a pentacyclic steroid. It features a ketone group at C-3, a double bond at C-14, and a hydroxyl group at C-13. The structure is labeled with 'HSQC' and 'HO'.

(+)-42-C2OH

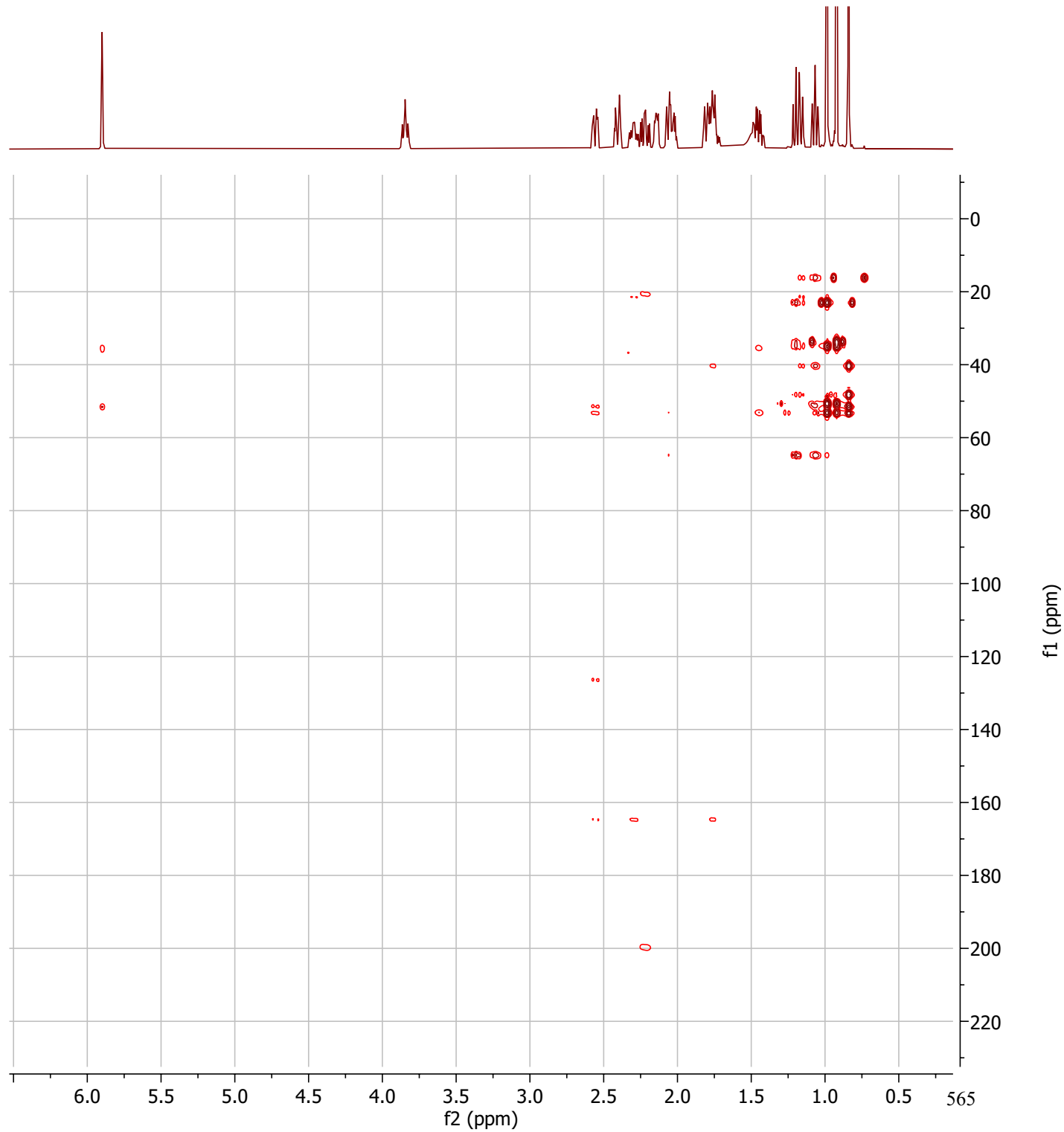
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcdegpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(71.9, -1891.2)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)

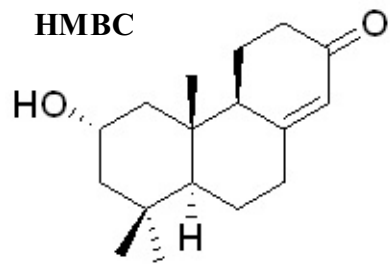




(+)-42-C2OH

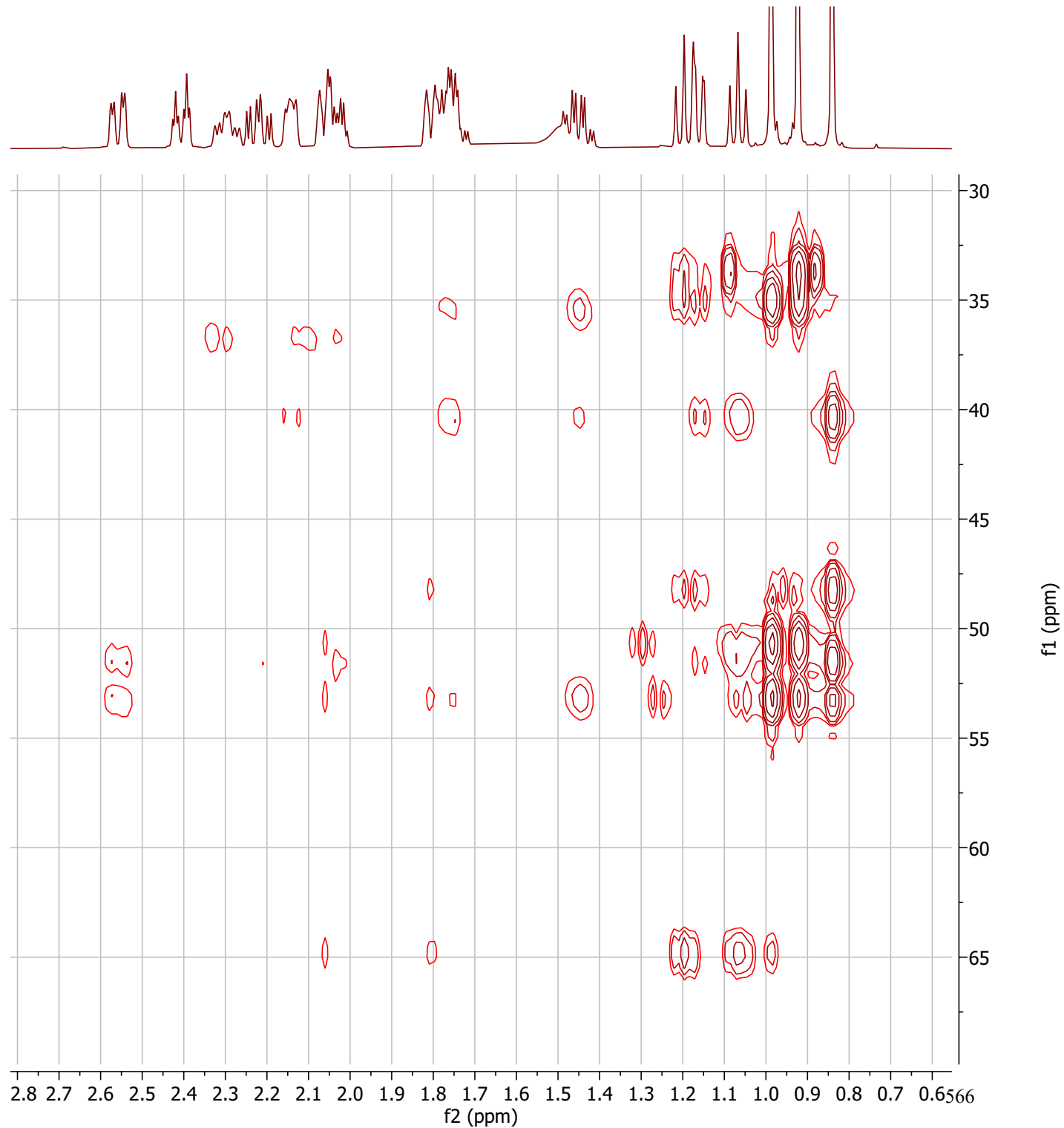
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(71.9, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



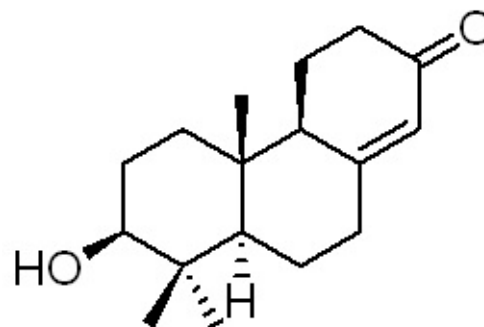


(+)-42-C2OH

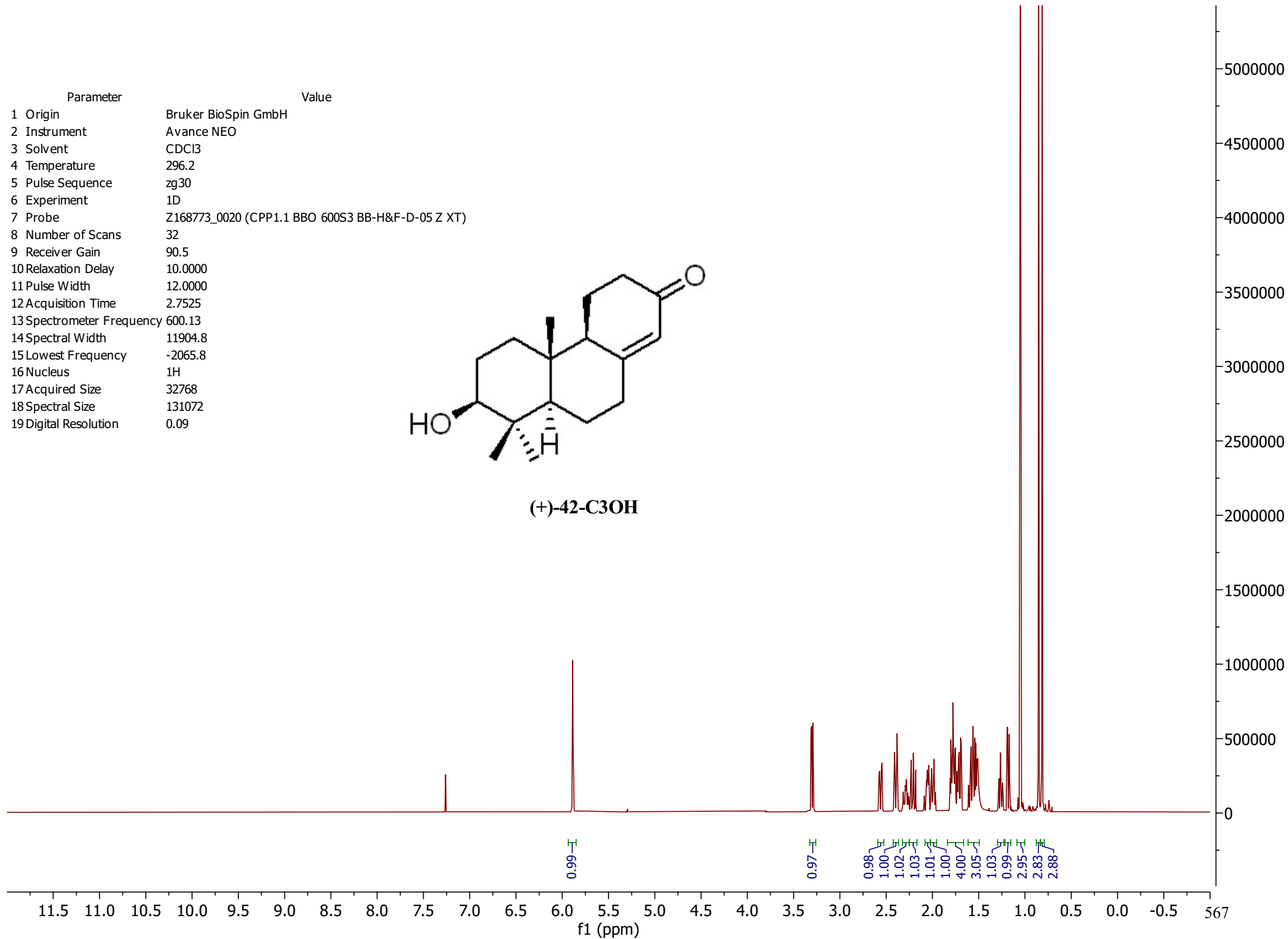
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(71.9, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)

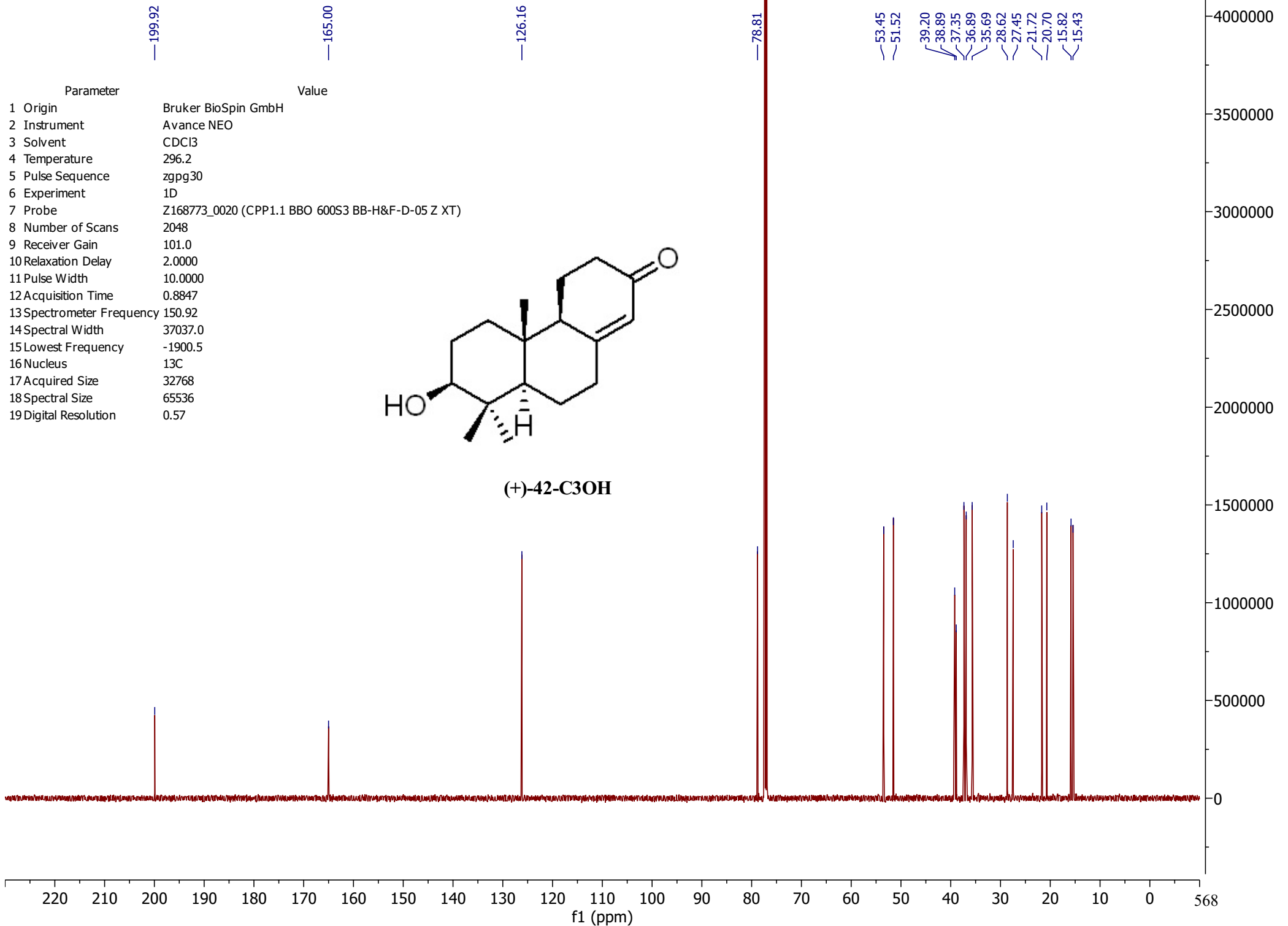


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	90.5
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2065.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



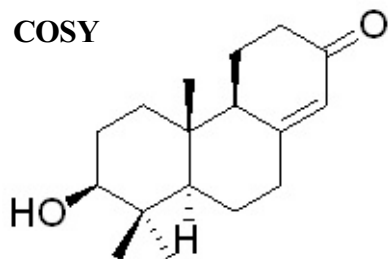
(+)-42-C3OH





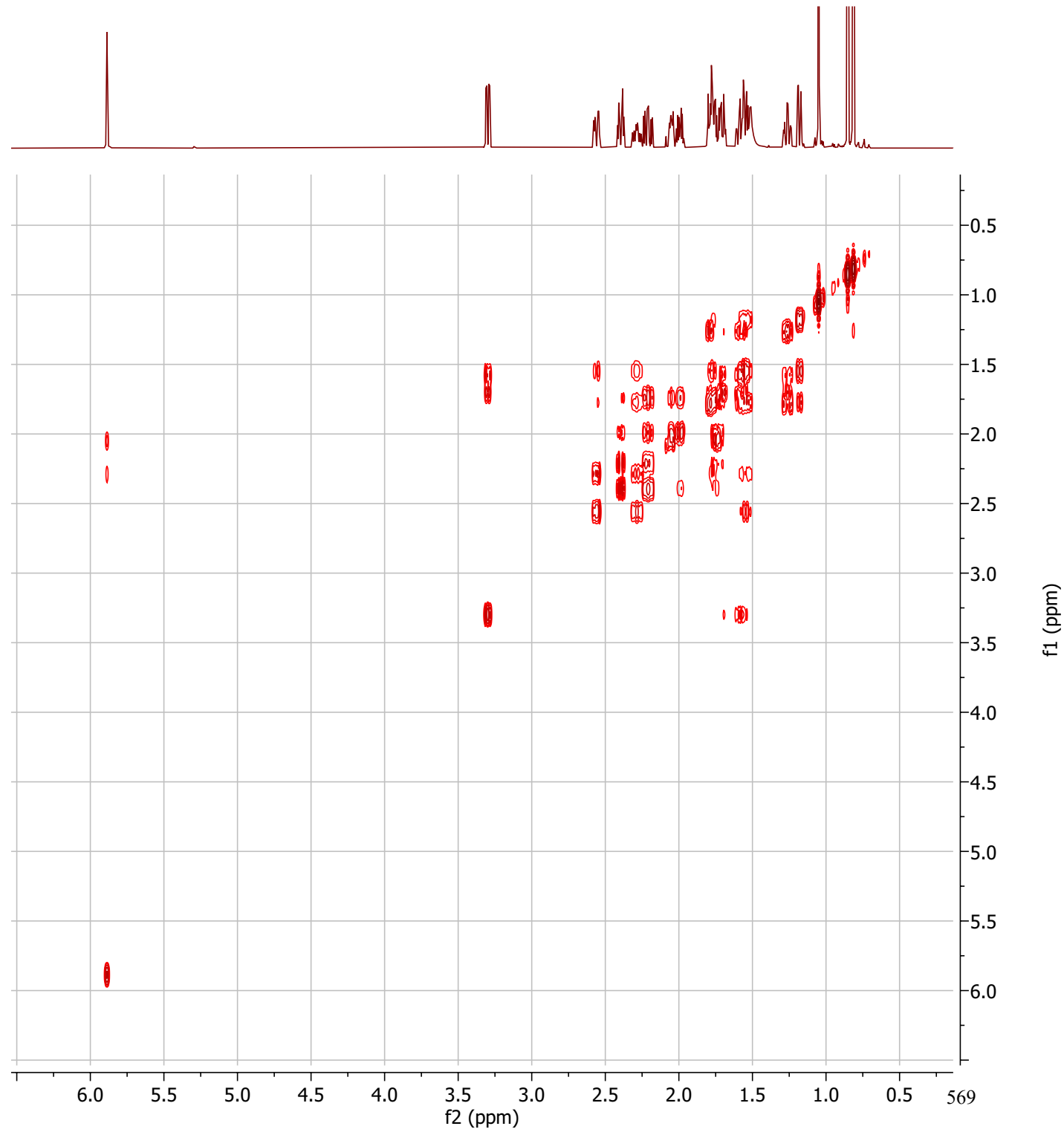
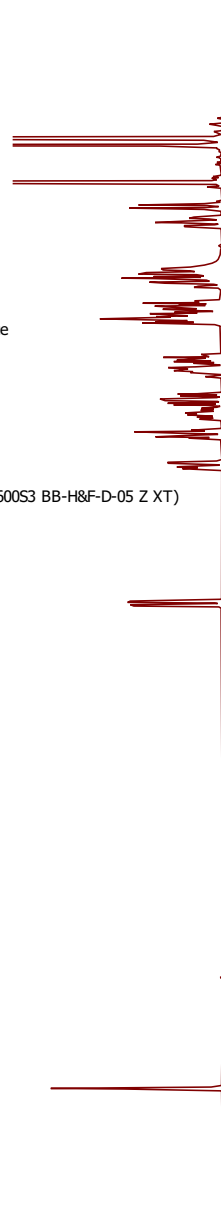
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	2048
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1900.5
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57

COSY

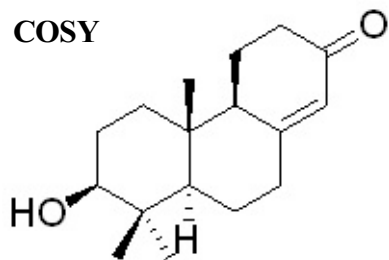


(+)-42-C3OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.3669
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(77.7, 77.7)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)

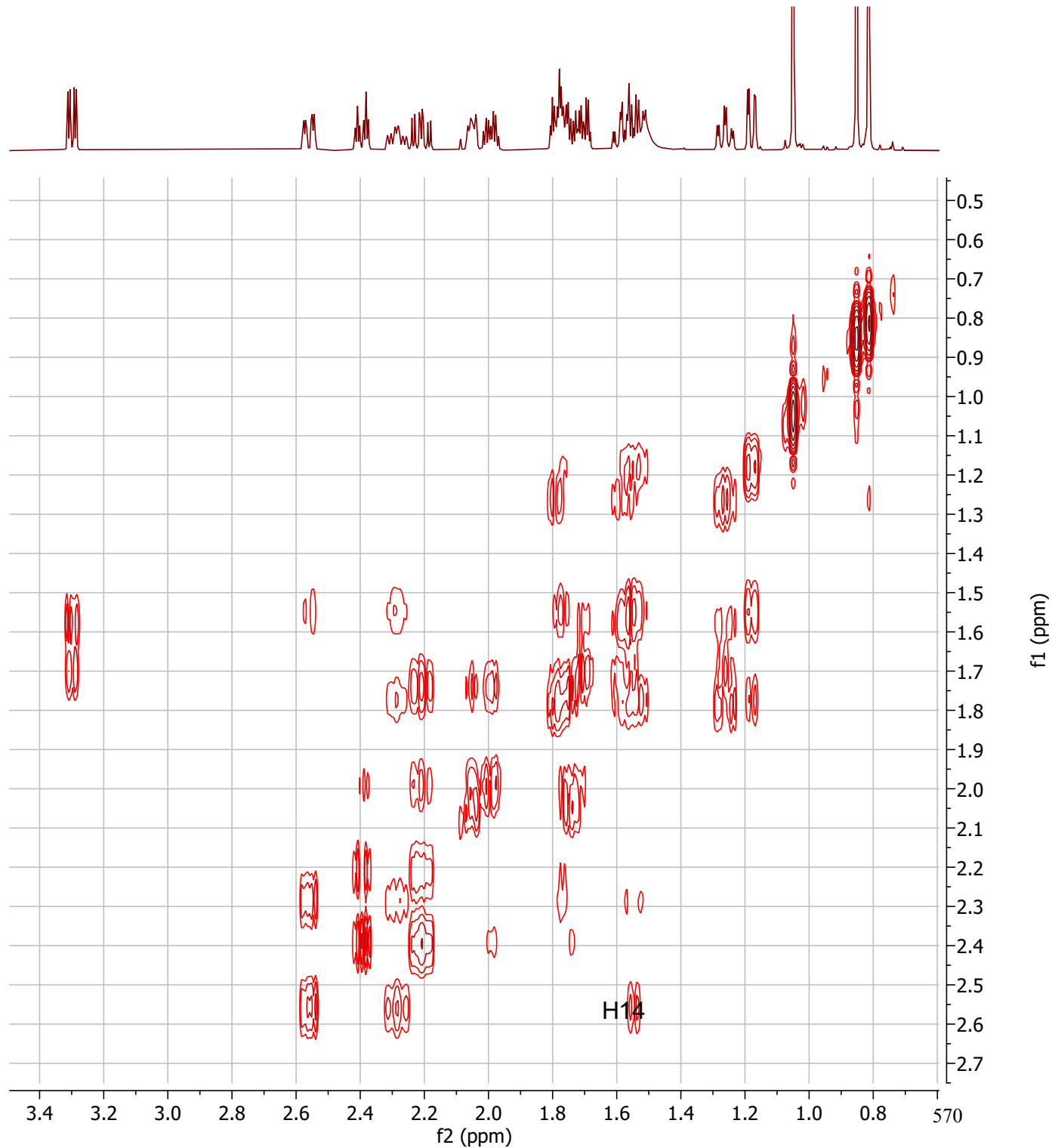
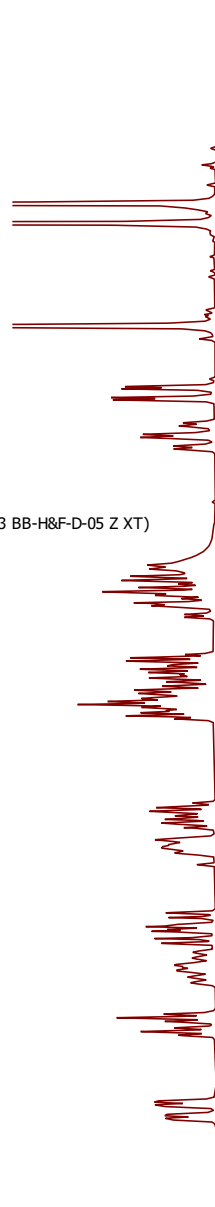


COSY

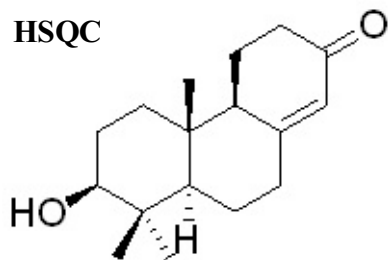


(+)-42-C3OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.3669
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(77.7, 77.7)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)

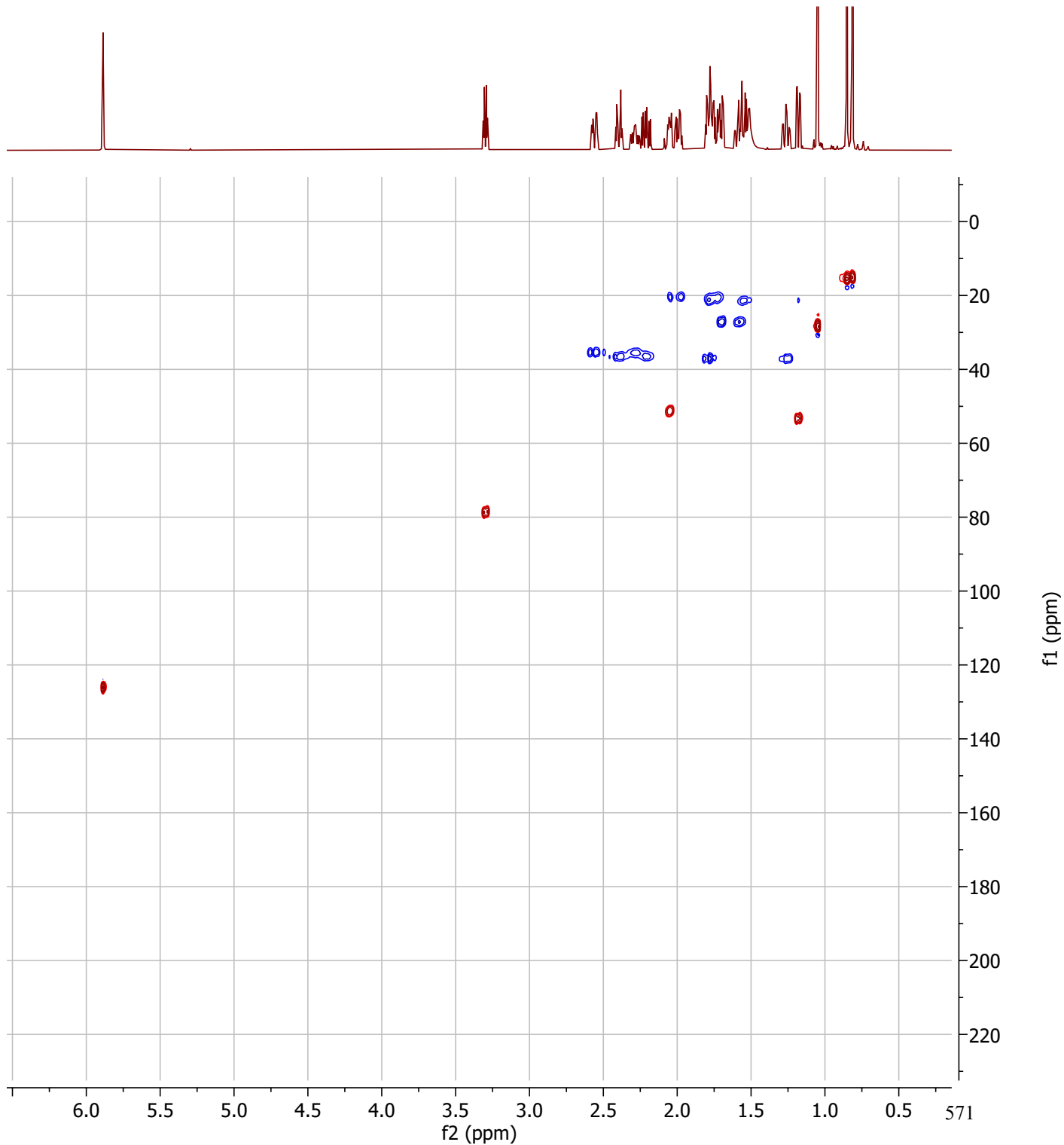


HSQC

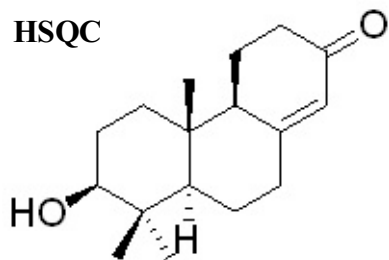


(+)-42-C3OH

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hsqcetdgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(77.7, -1891.3)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)

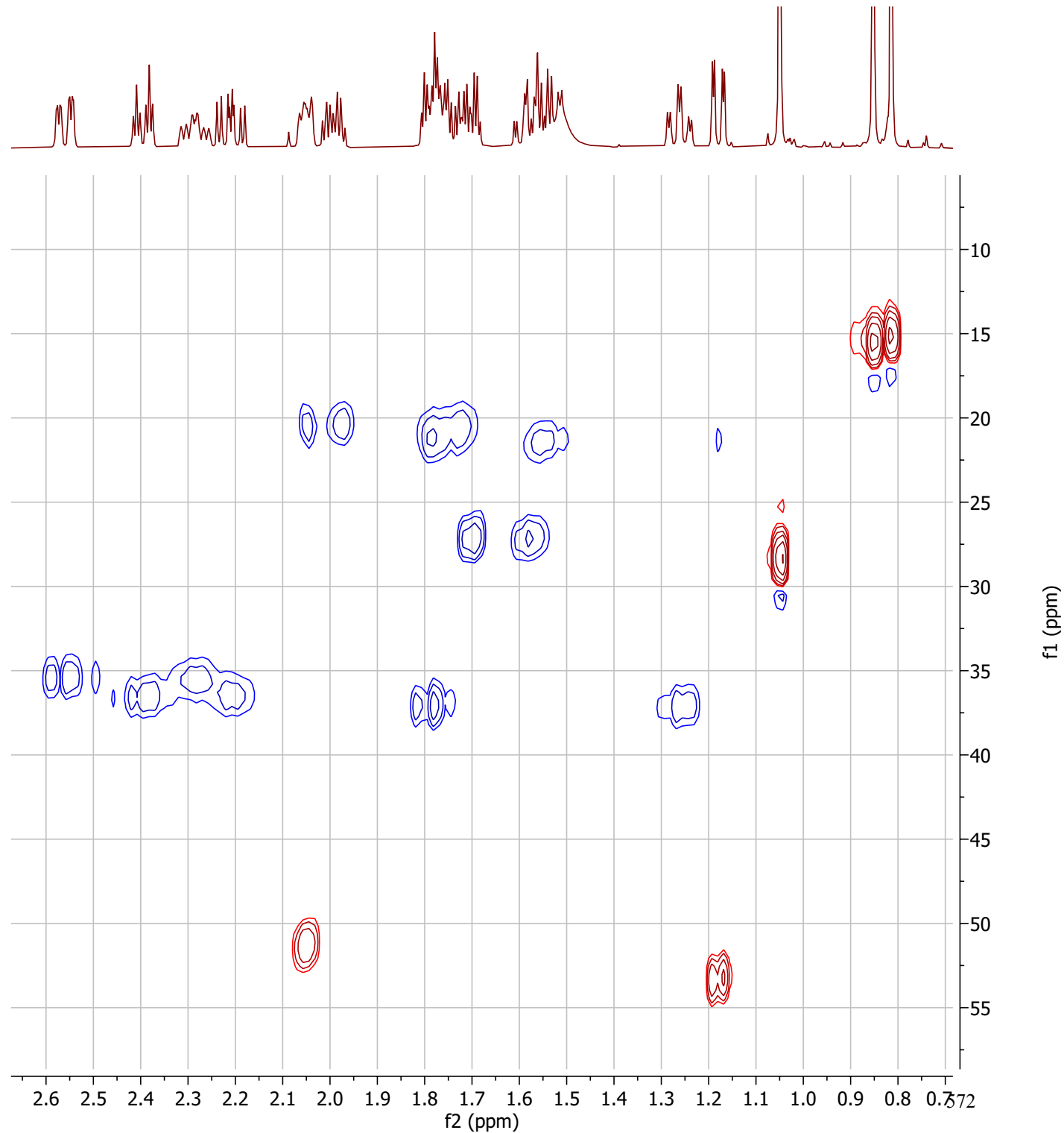


HSQC

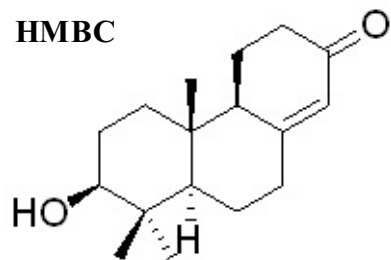


(+)-42-C3OH

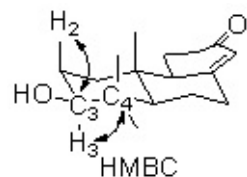
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	hsqcedetgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(77.7, -1891.3)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)



HMBC

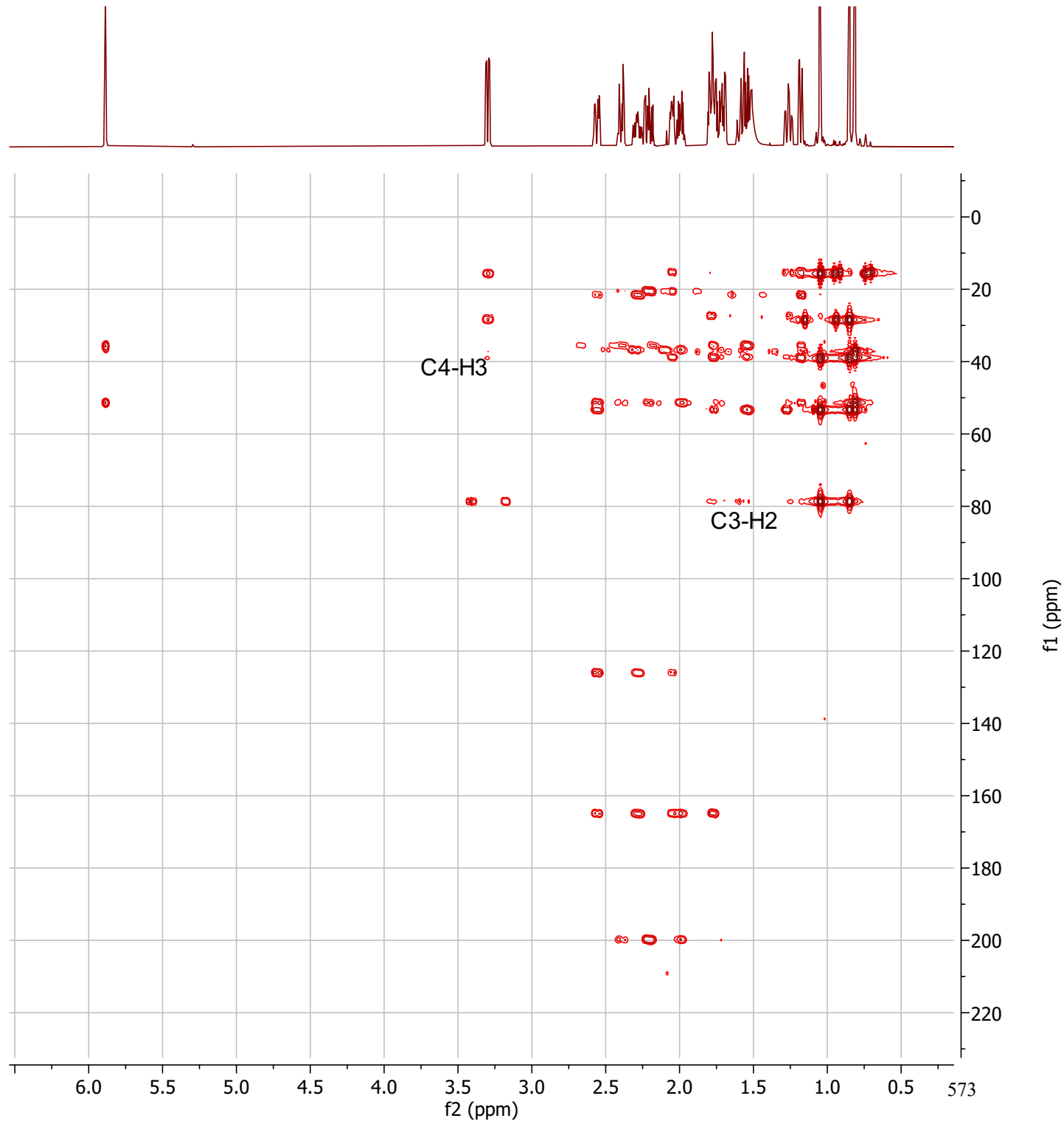


(+)-42-C3OH

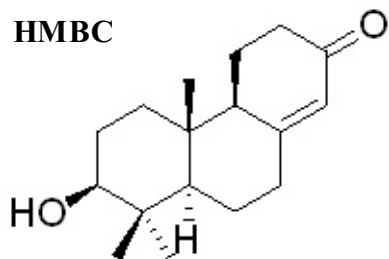


HMBC

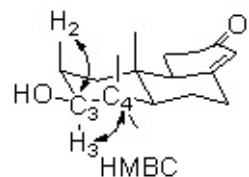
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(77.7, -1891.7)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



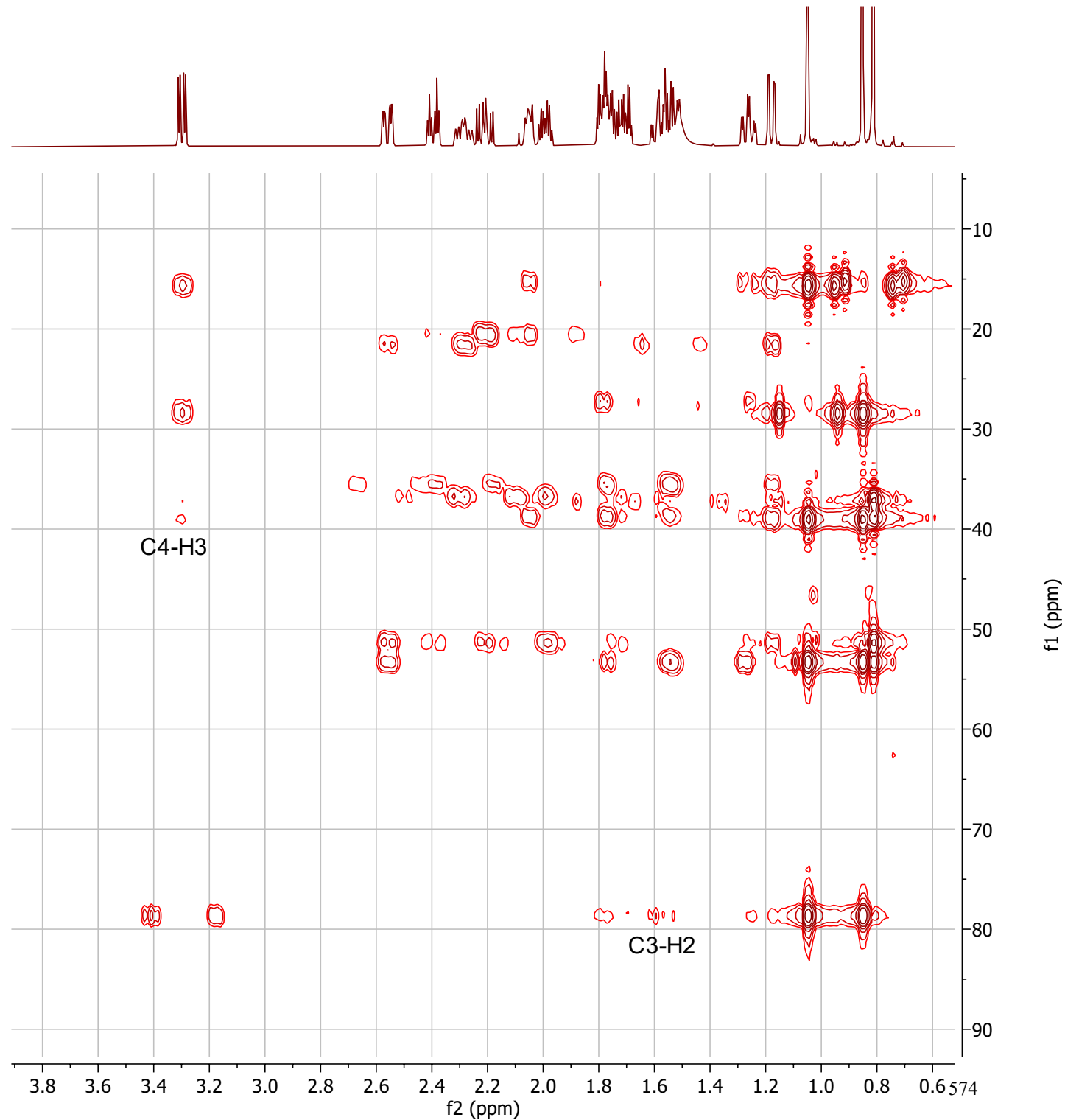
HMBC



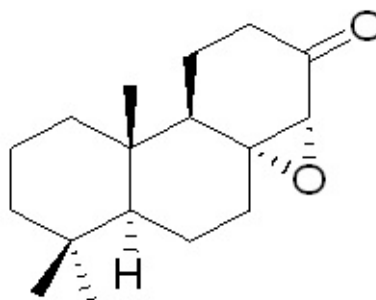
(+)-42-C3OH



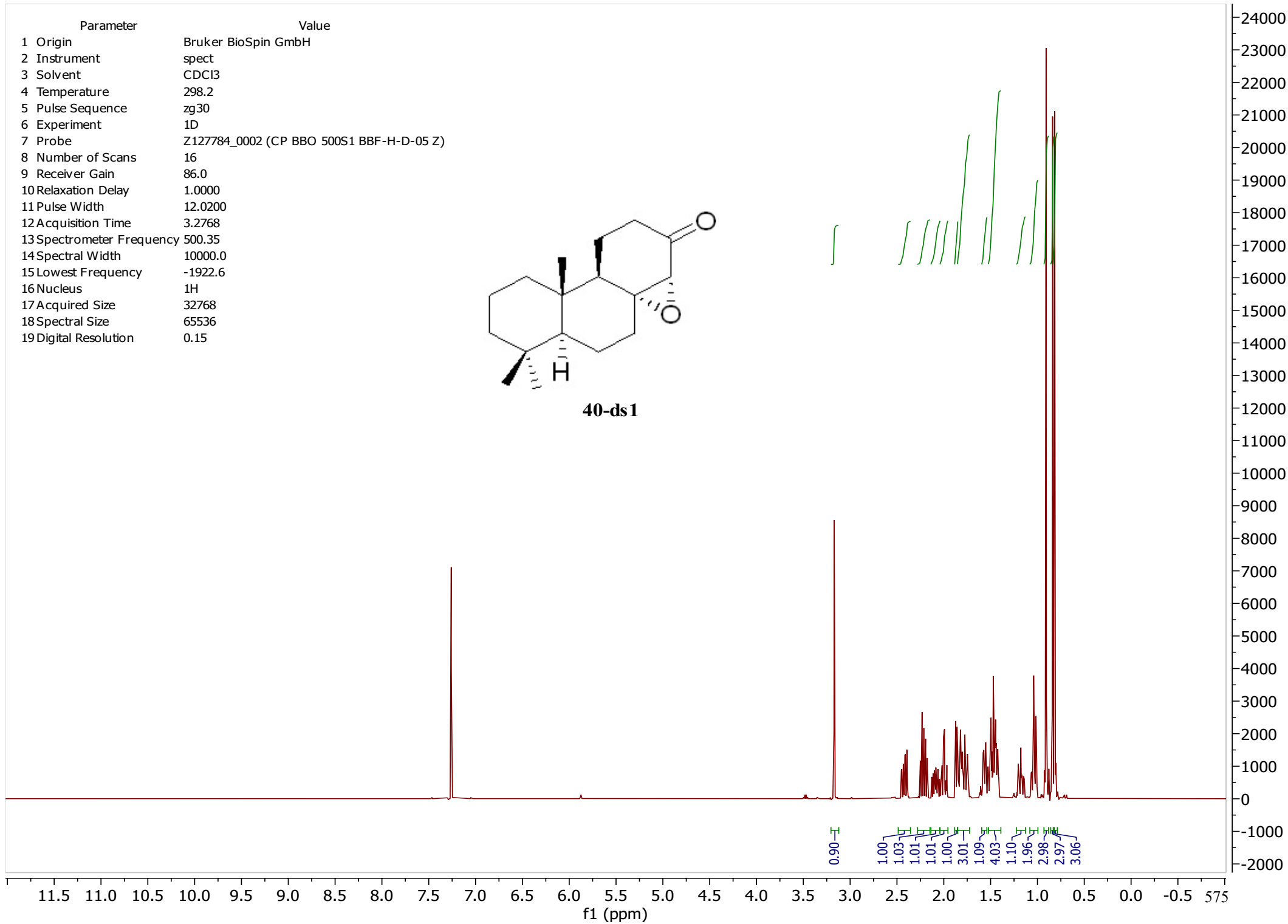
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3-BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(77.7, -1891.7)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



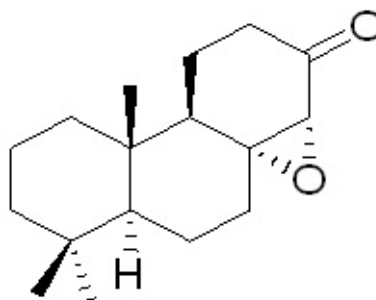
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	86.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0200
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



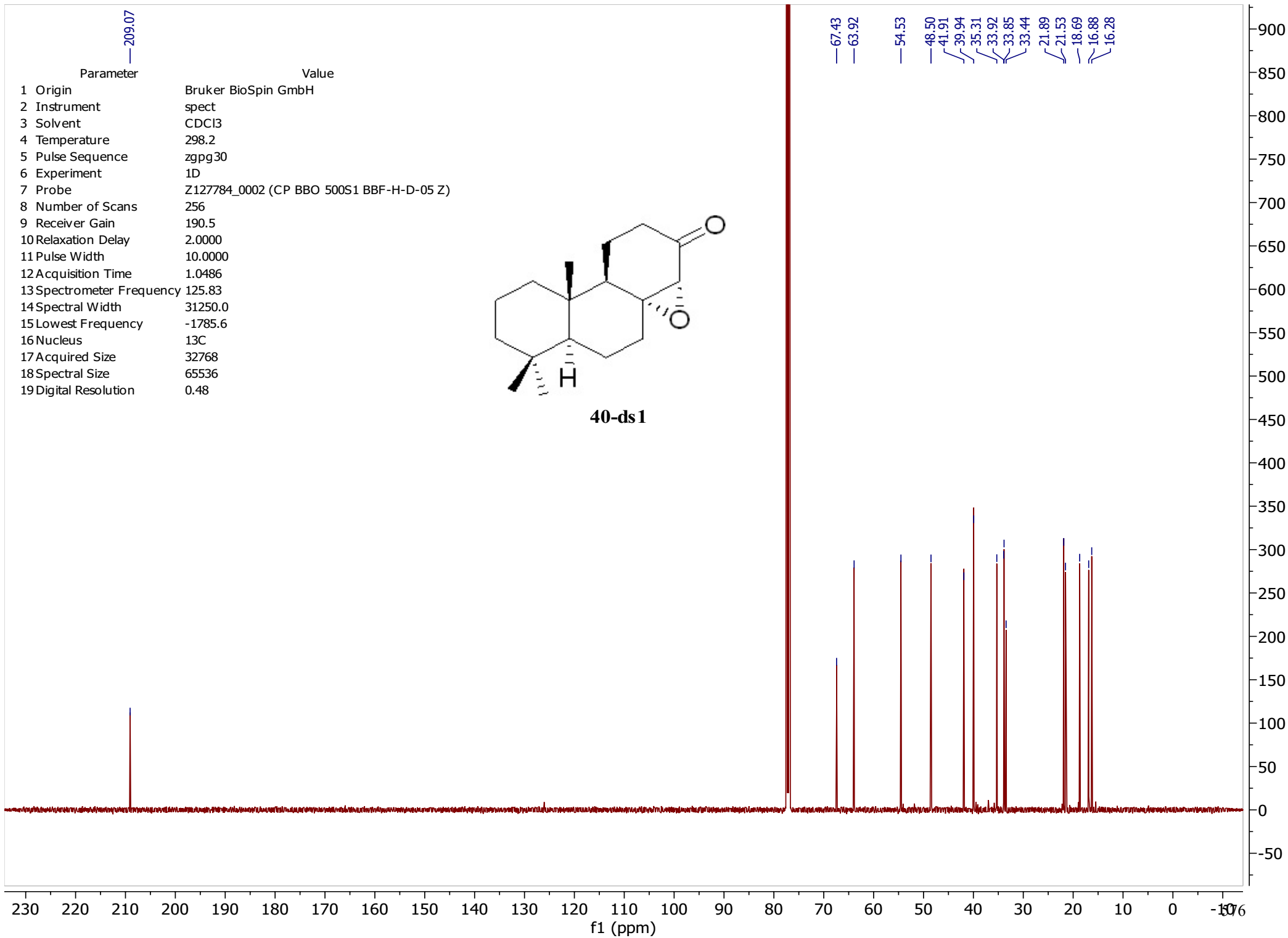
40-ds1



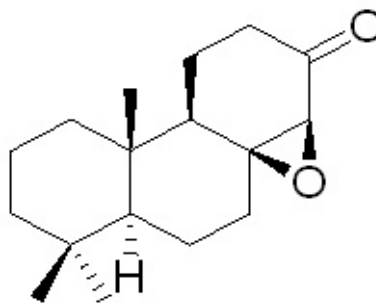
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



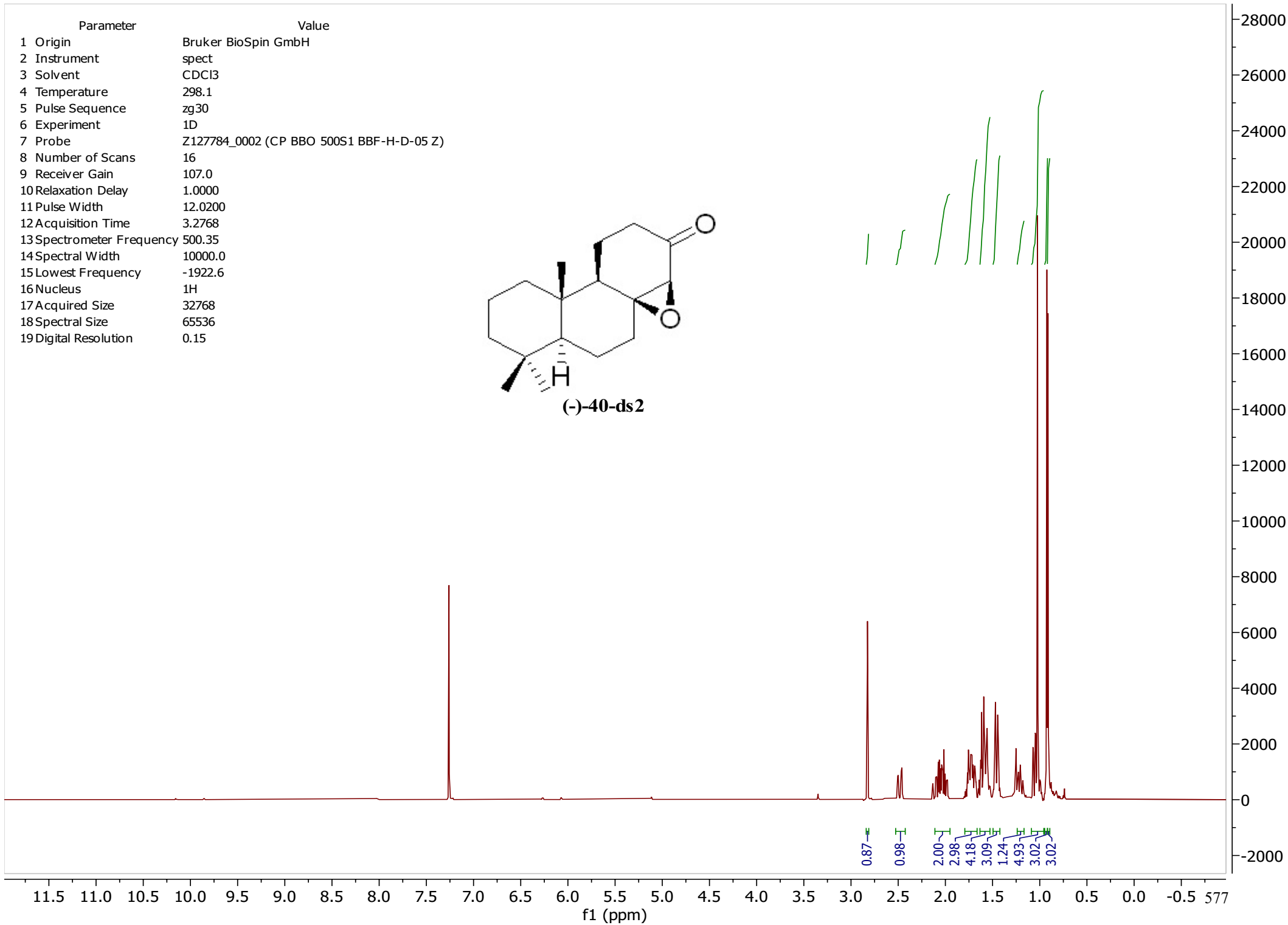
40-ds1



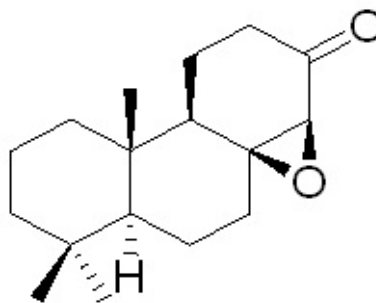
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	107.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0200
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.6
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



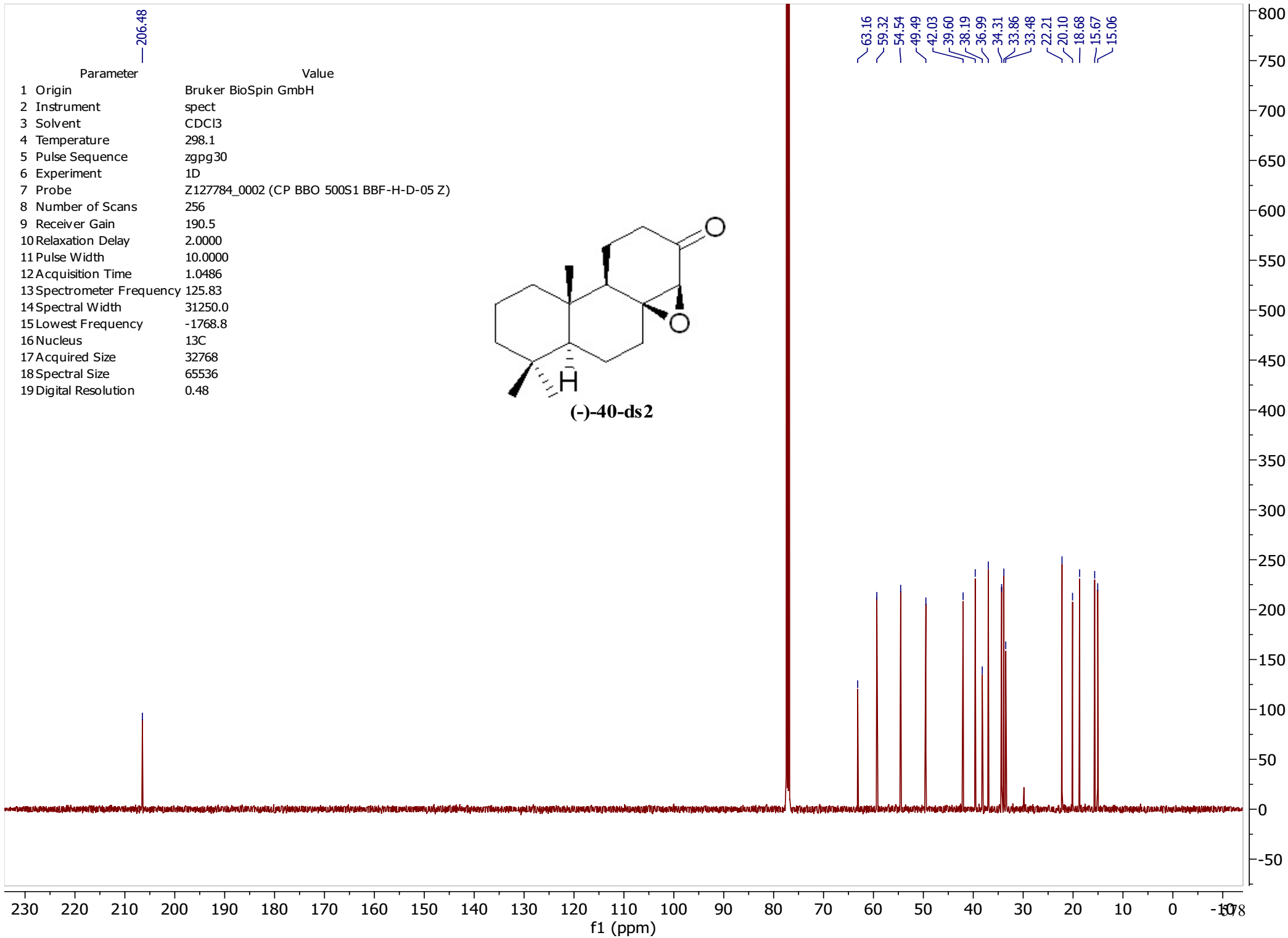
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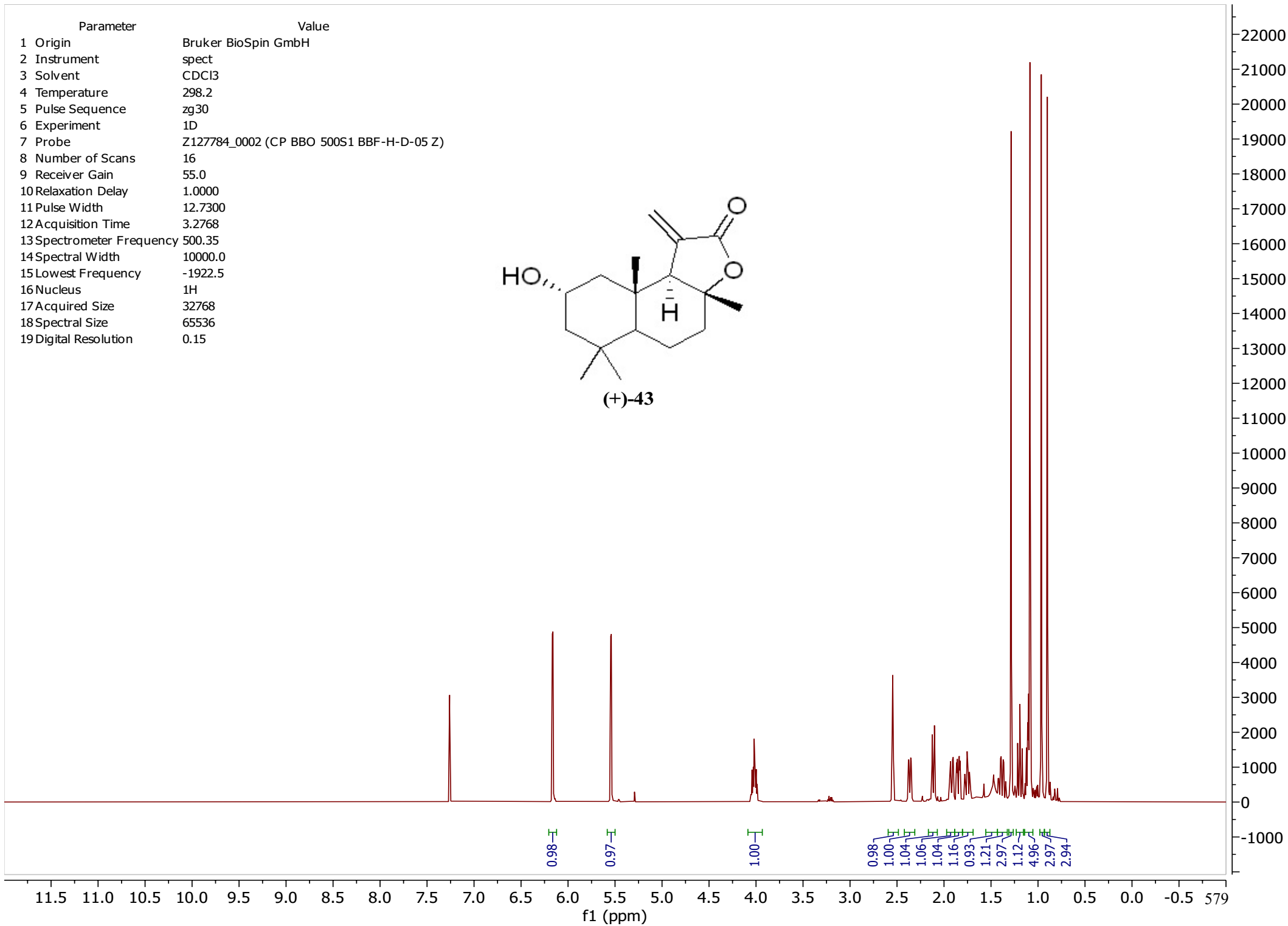
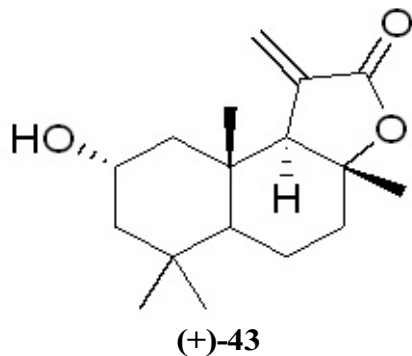
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1768.8
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



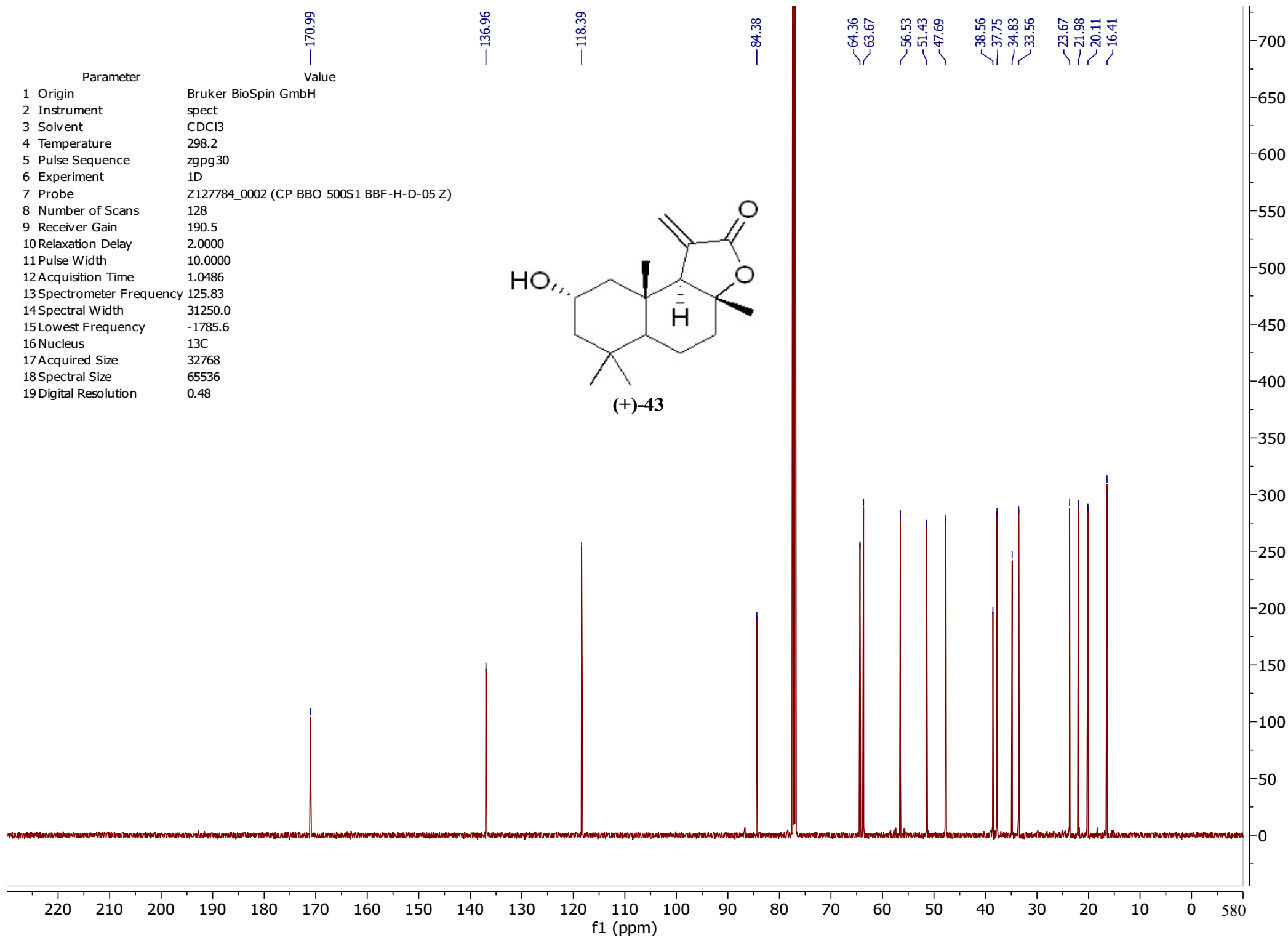
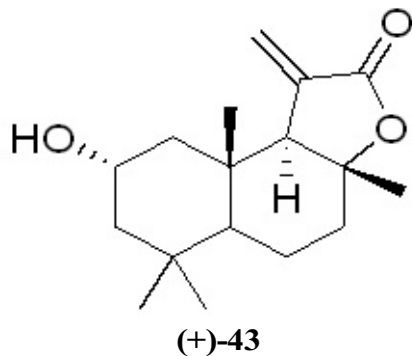
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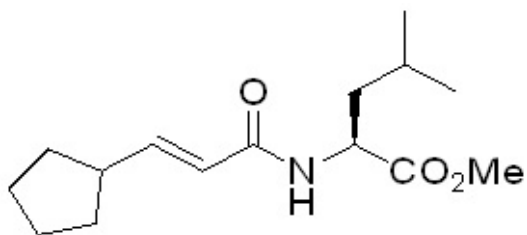
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	298.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	55.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.7300
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



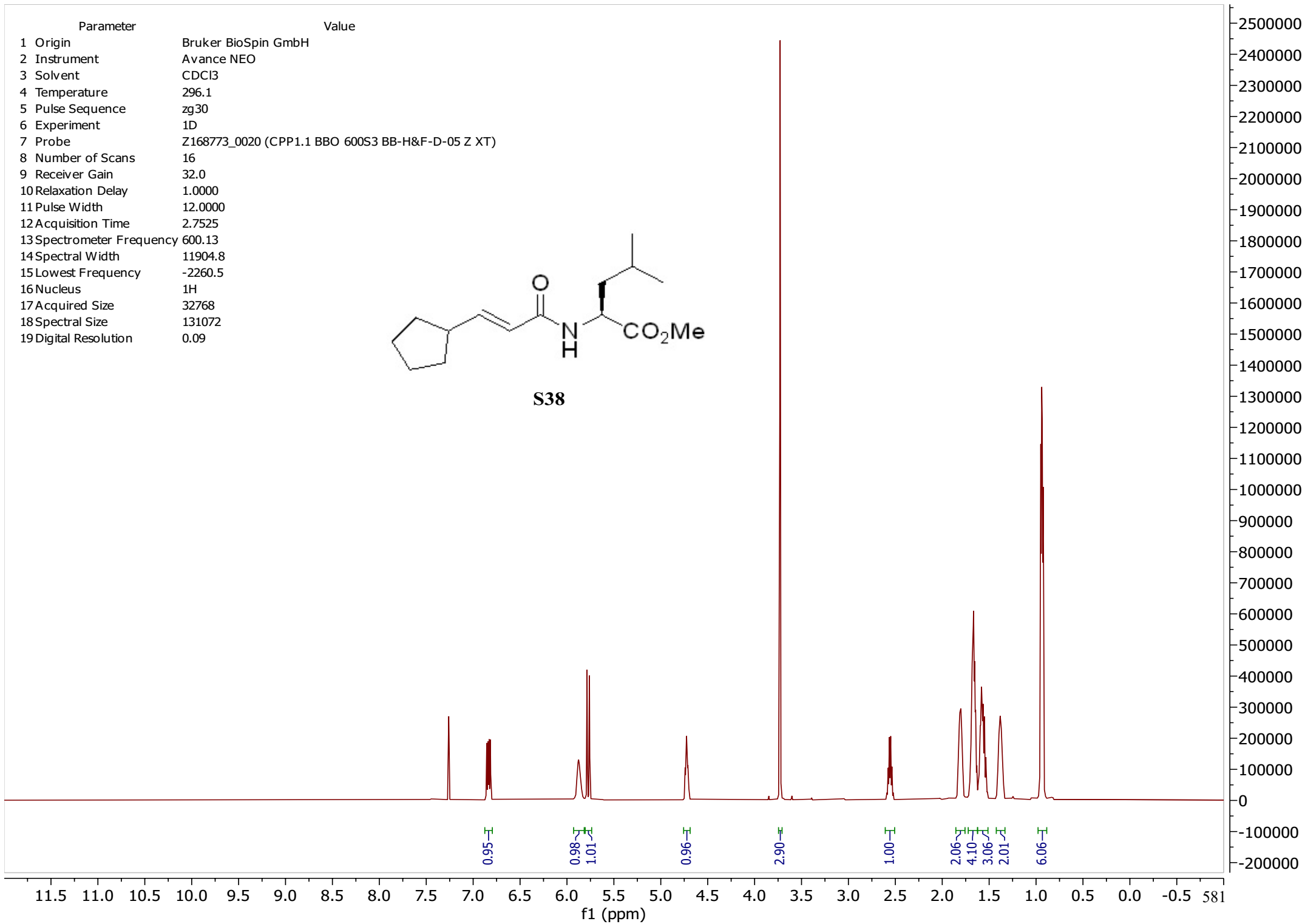
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	128
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



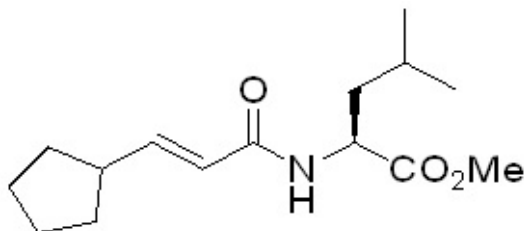
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



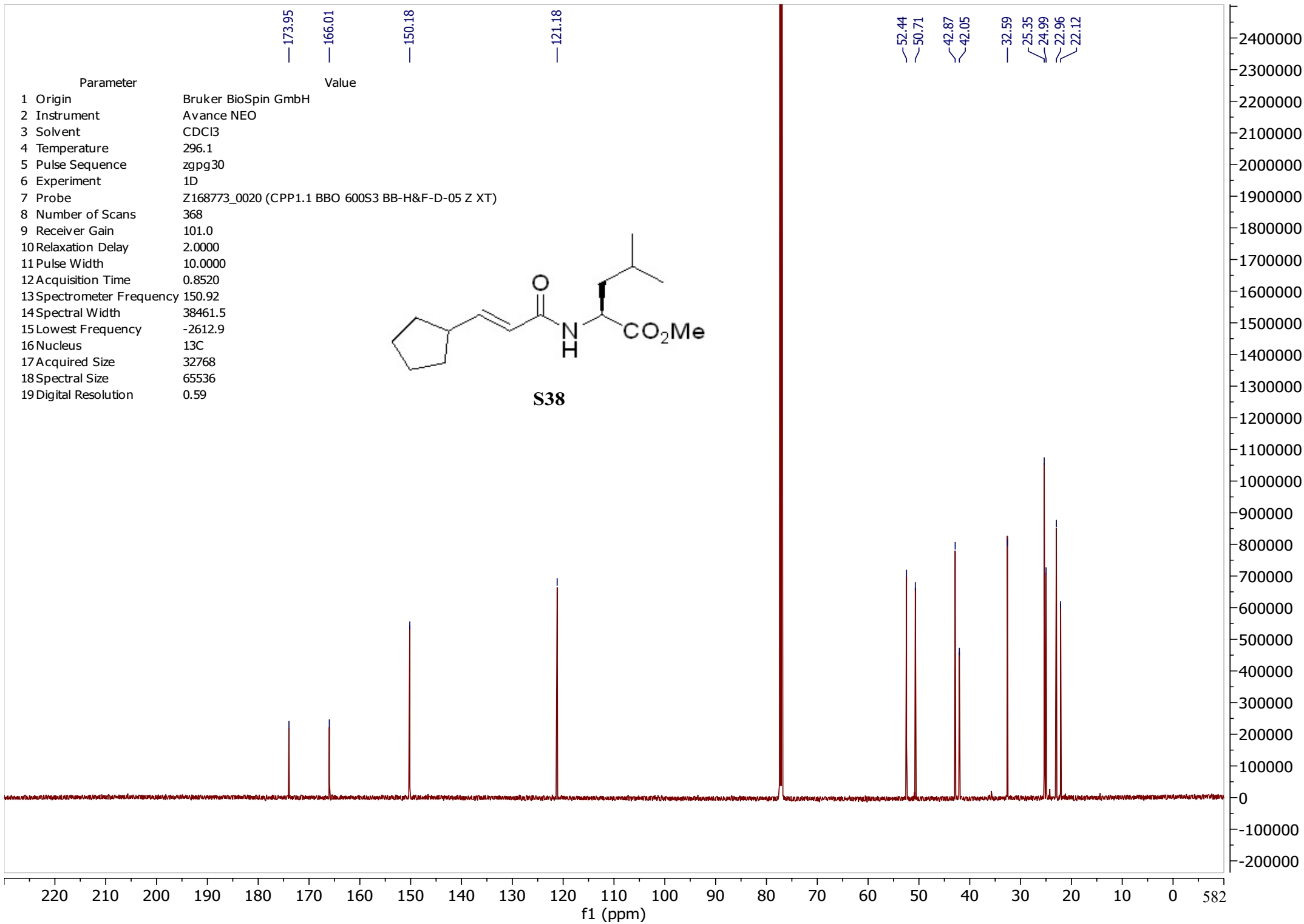
S38



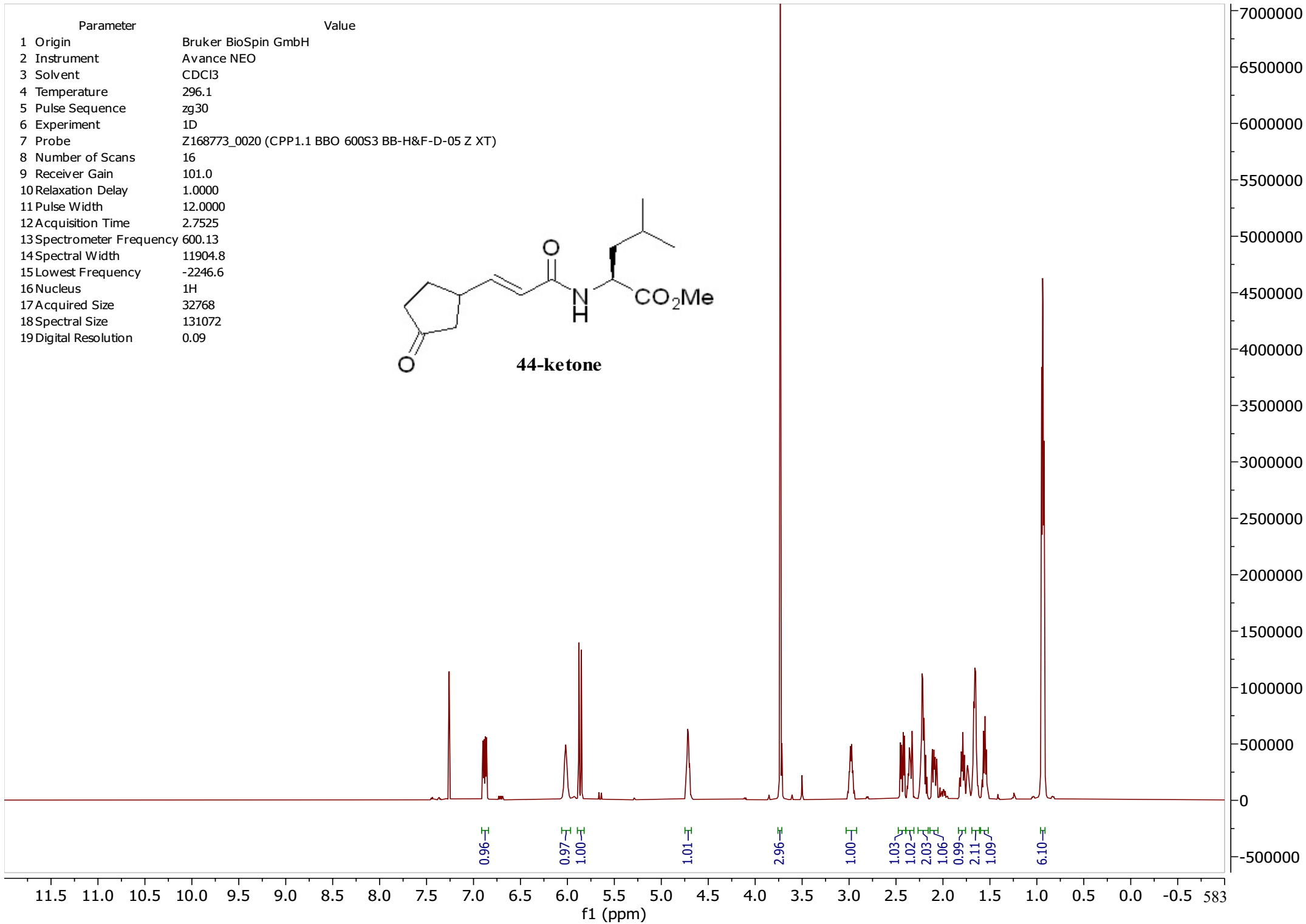
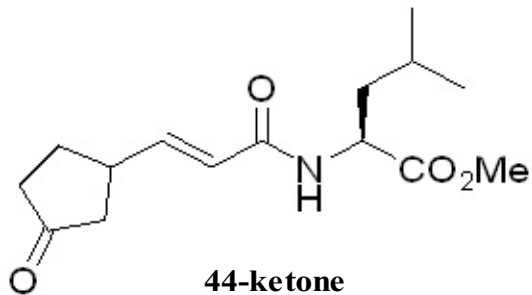
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	368
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8520
13 Spectrometer Frequency	150.92
14 Spectral Width	38461.5
15 Lowest Frequency	-2612.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.59



S38

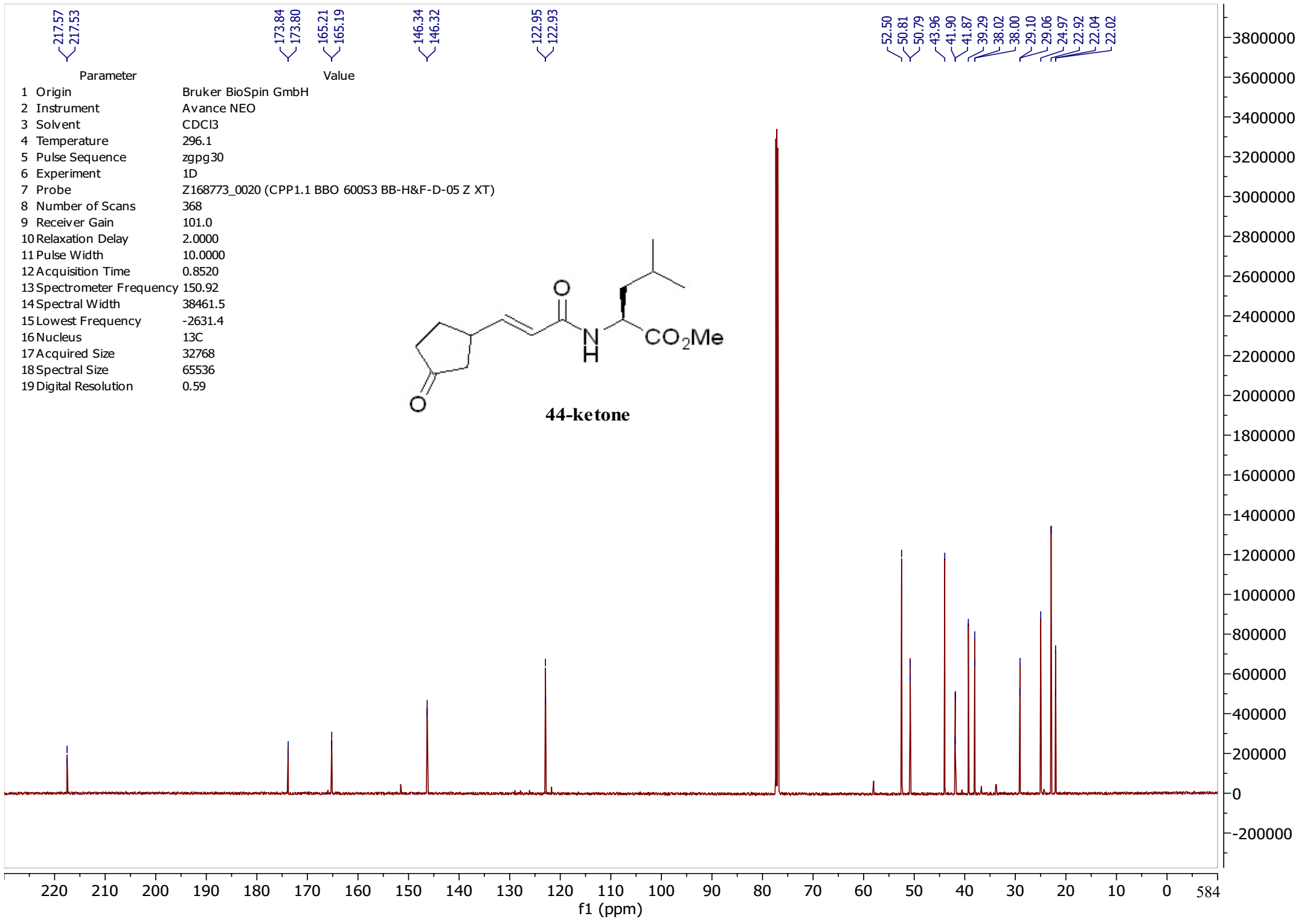
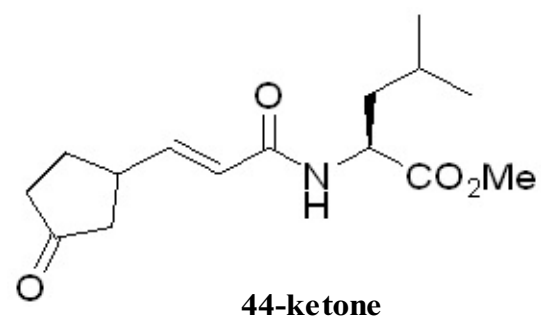


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

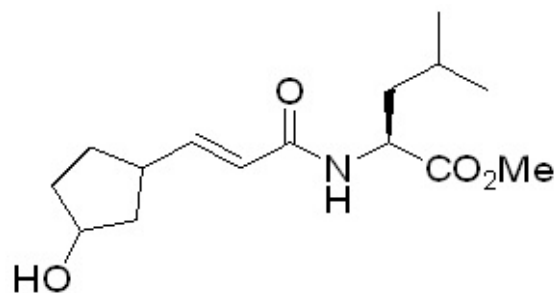


1 Origin Bruker BioSpin GmbH
2 Instrument Avance NEO
3 Solvent CDCl3
4 Temperature 296.1
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Probe Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans 368
9 Receiver Gain 101.0
10 Relaxation Delay 2.0000
11 Pulse Width 10.0000
12 Acquisition Time 0.8520
13 Spectrometer Frequency 150.92
14 Spectral Width 38461.5
15 Lowest Frequency -2631.4
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
19 Digital Resolution 0.59

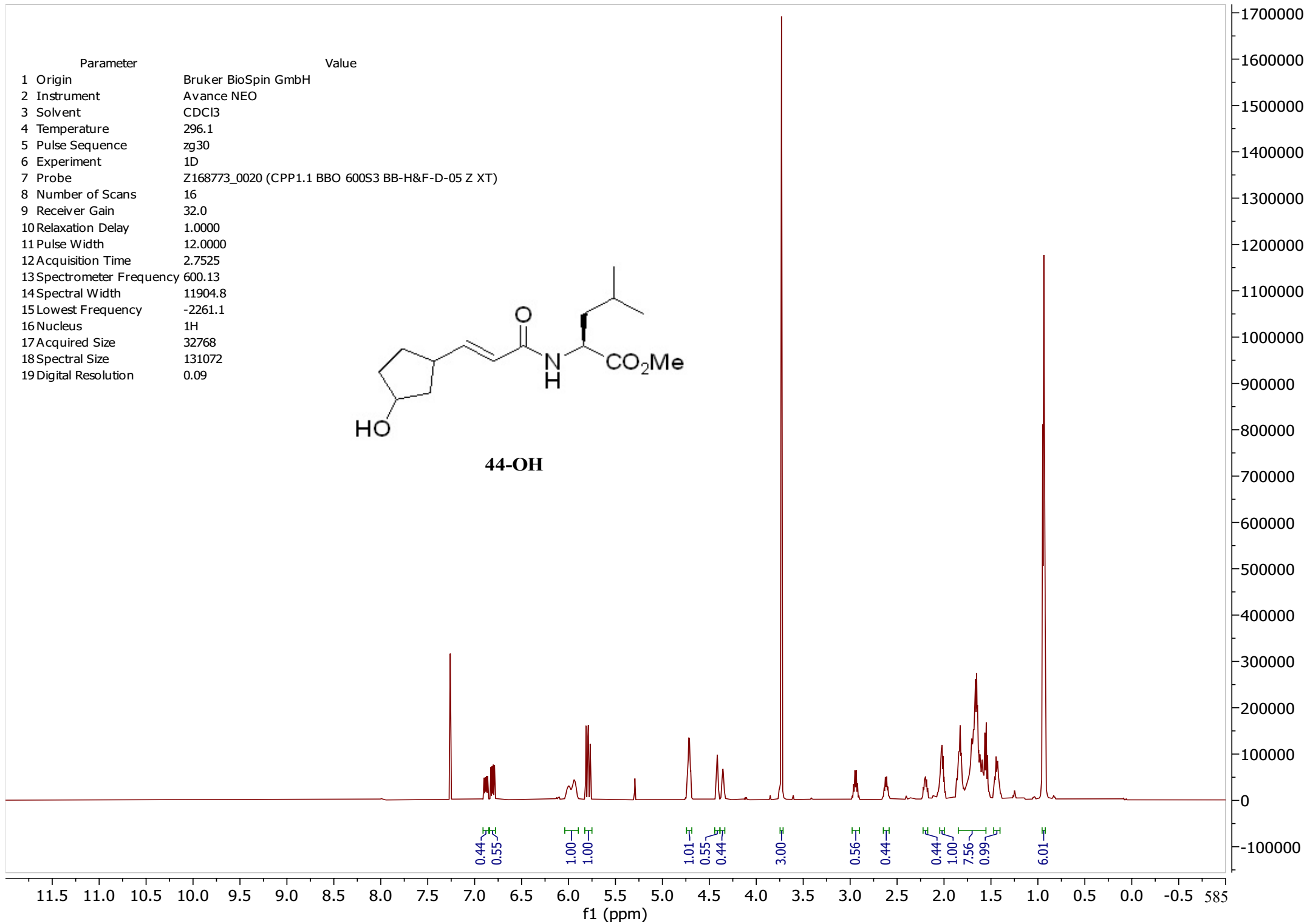
Parameter Value



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

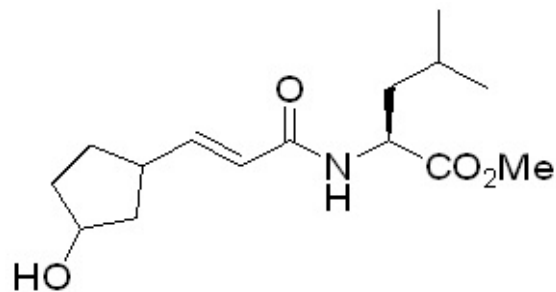


44-OH

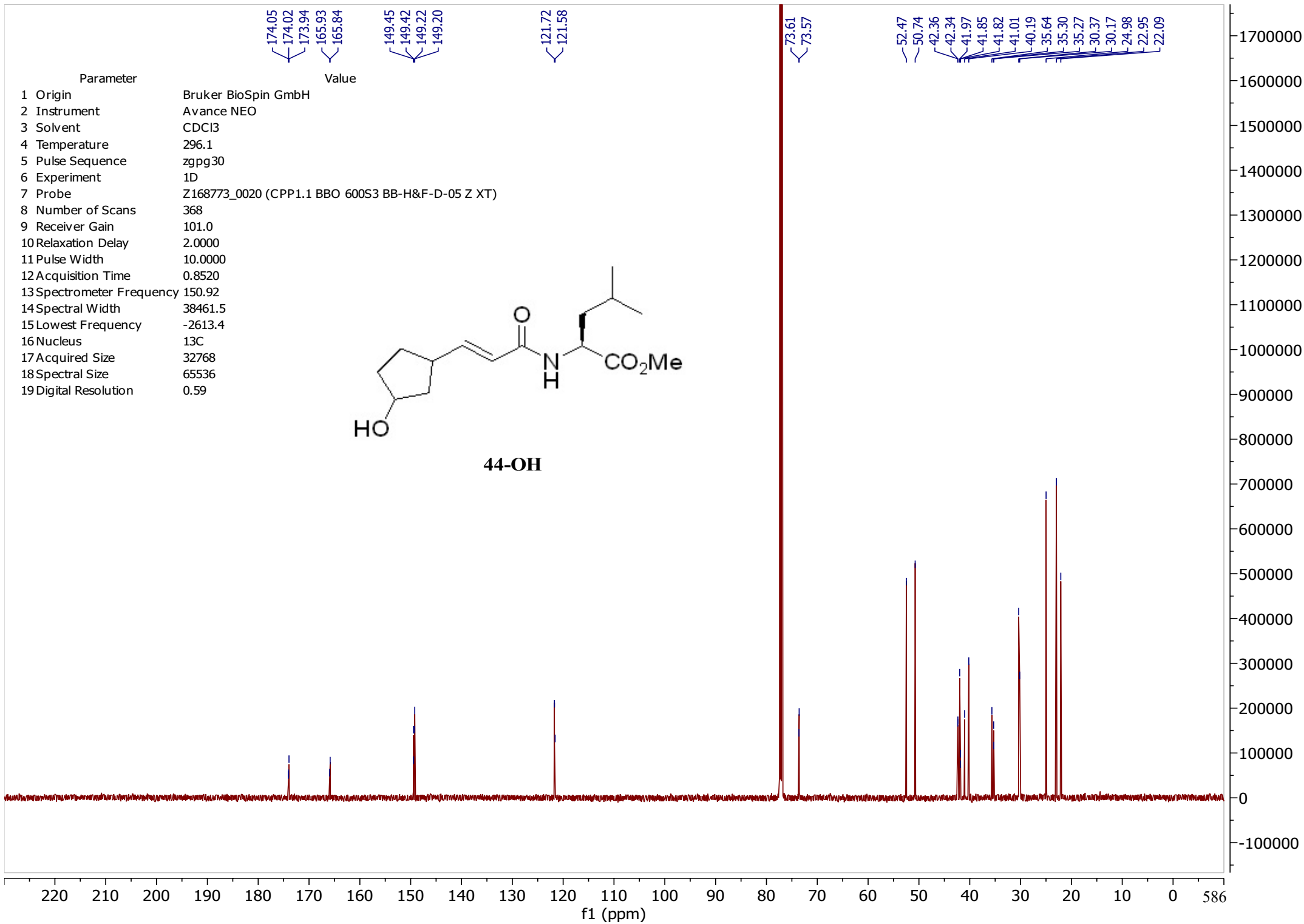


Parameter Value

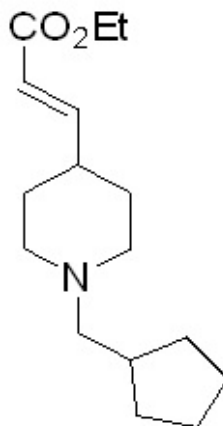
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	368
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8520
13 Spectrometer Frequency	150.92
14 Spectral Width	38461.5
15 Lowest Frequency	-2613.4
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.59



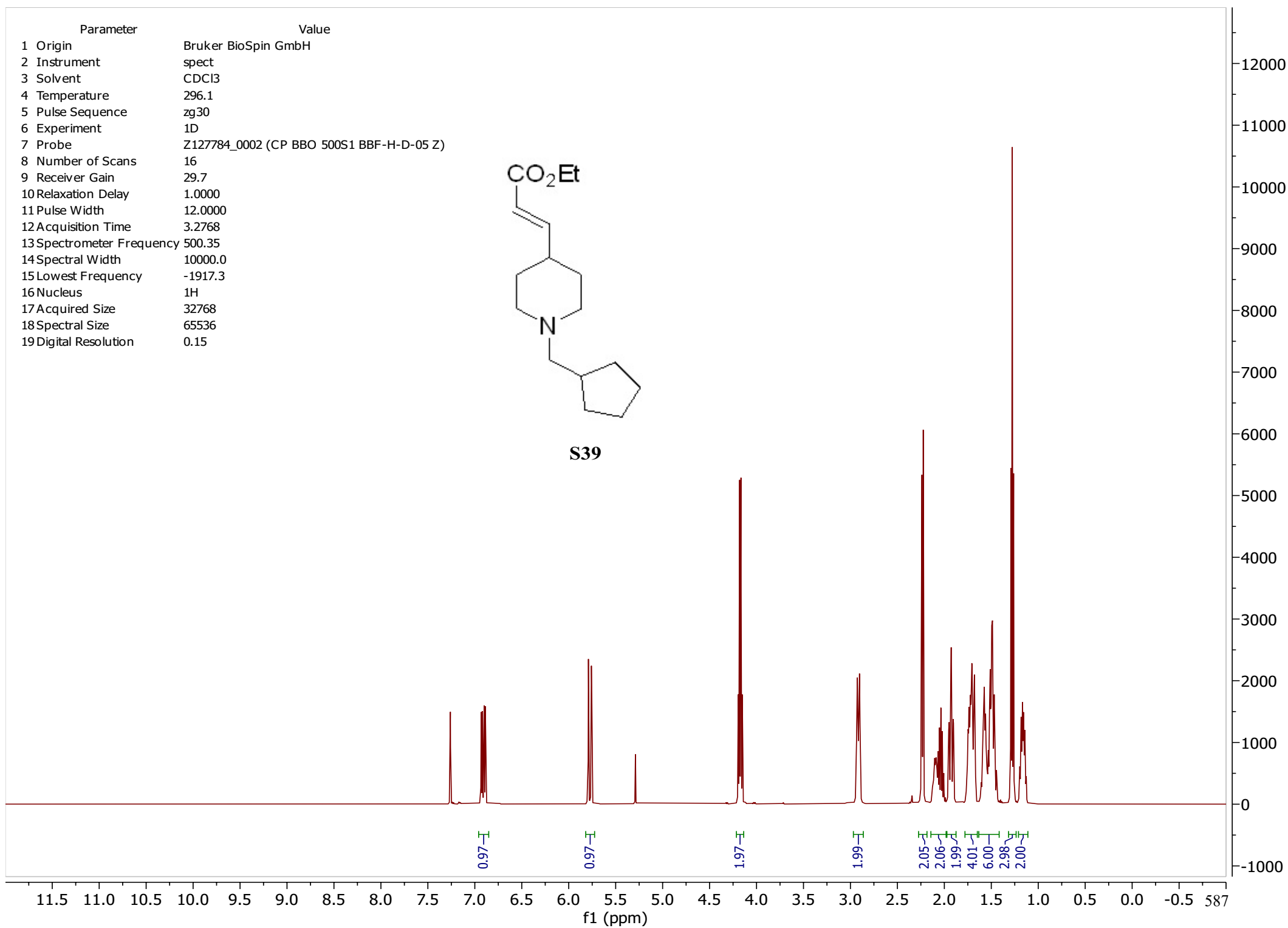
44-OH



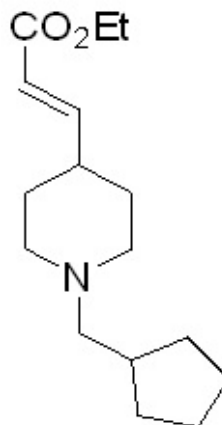
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1917.3
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



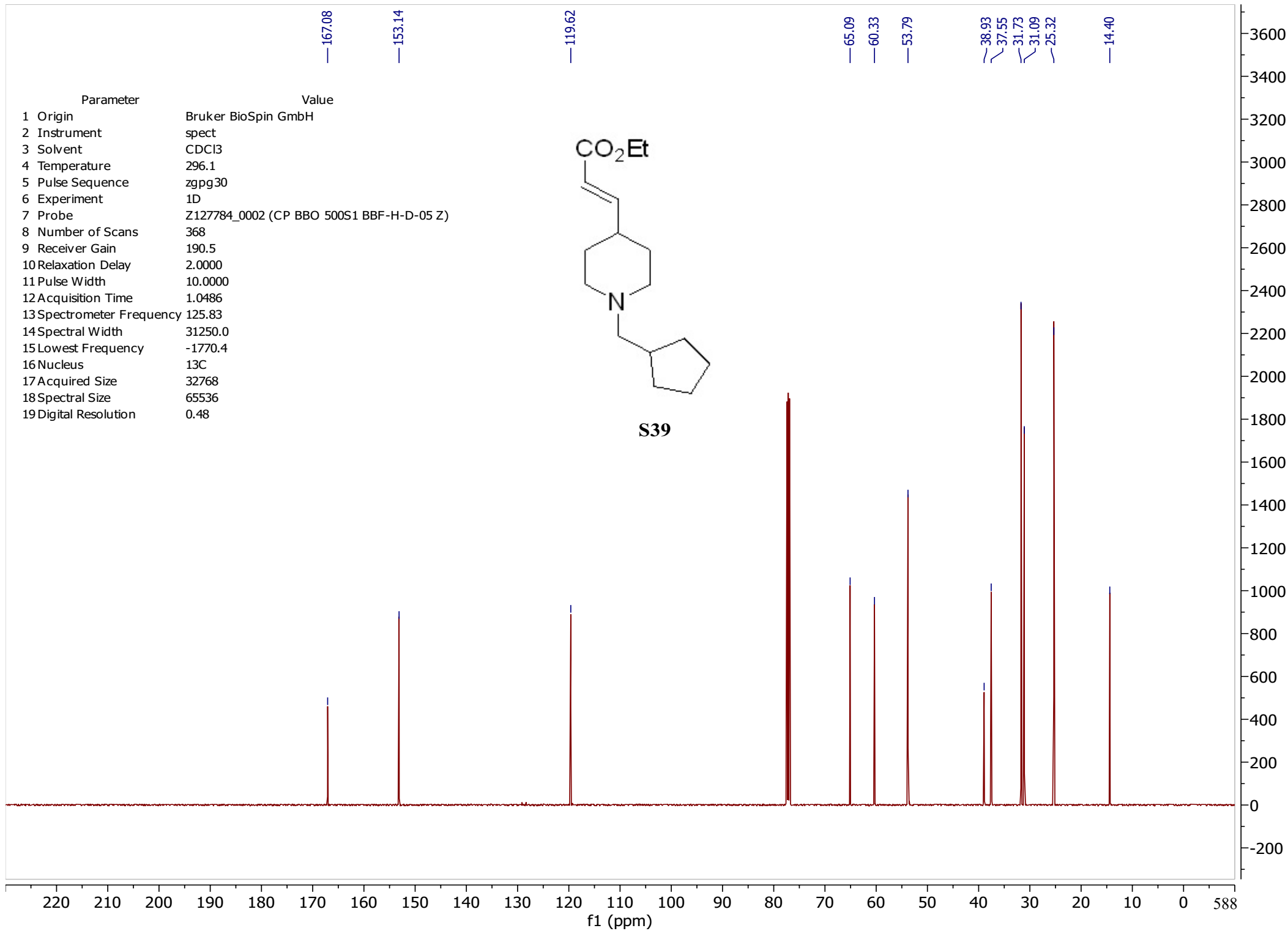
S39



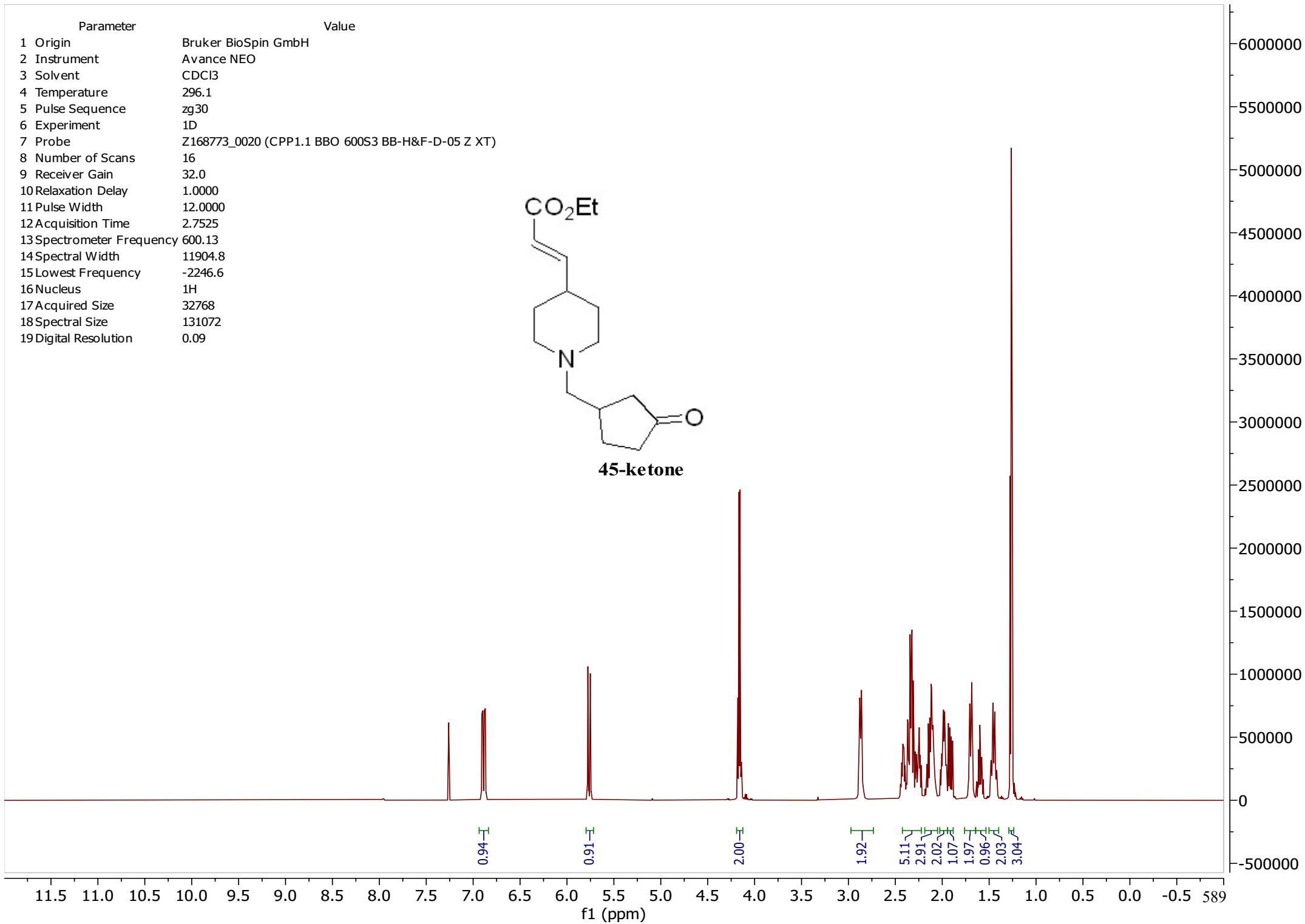
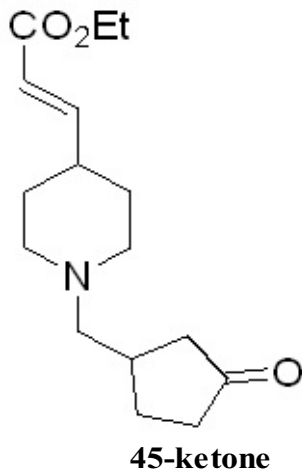
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1770.4
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



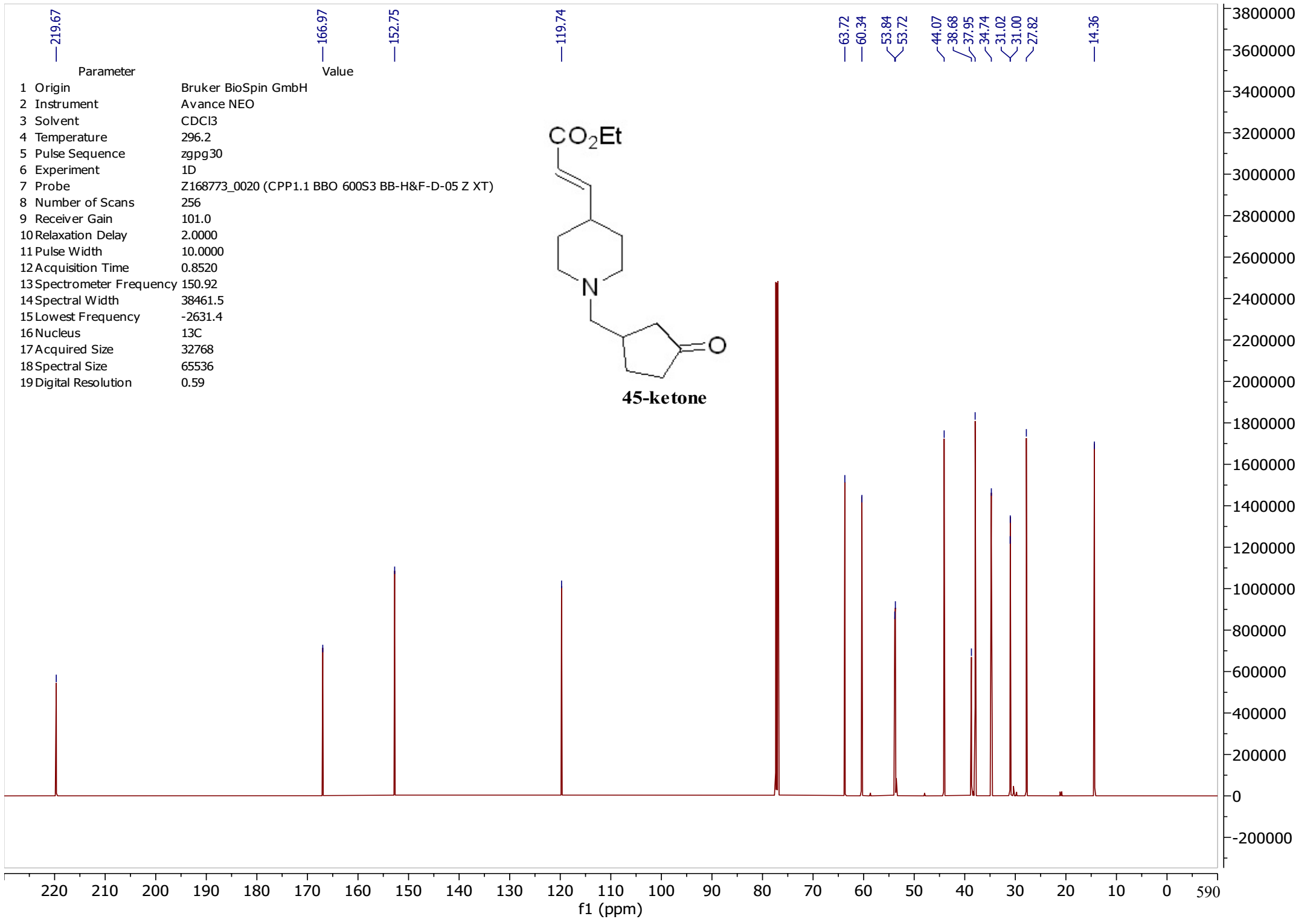
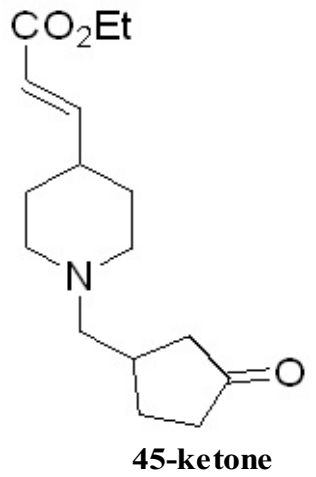
S39



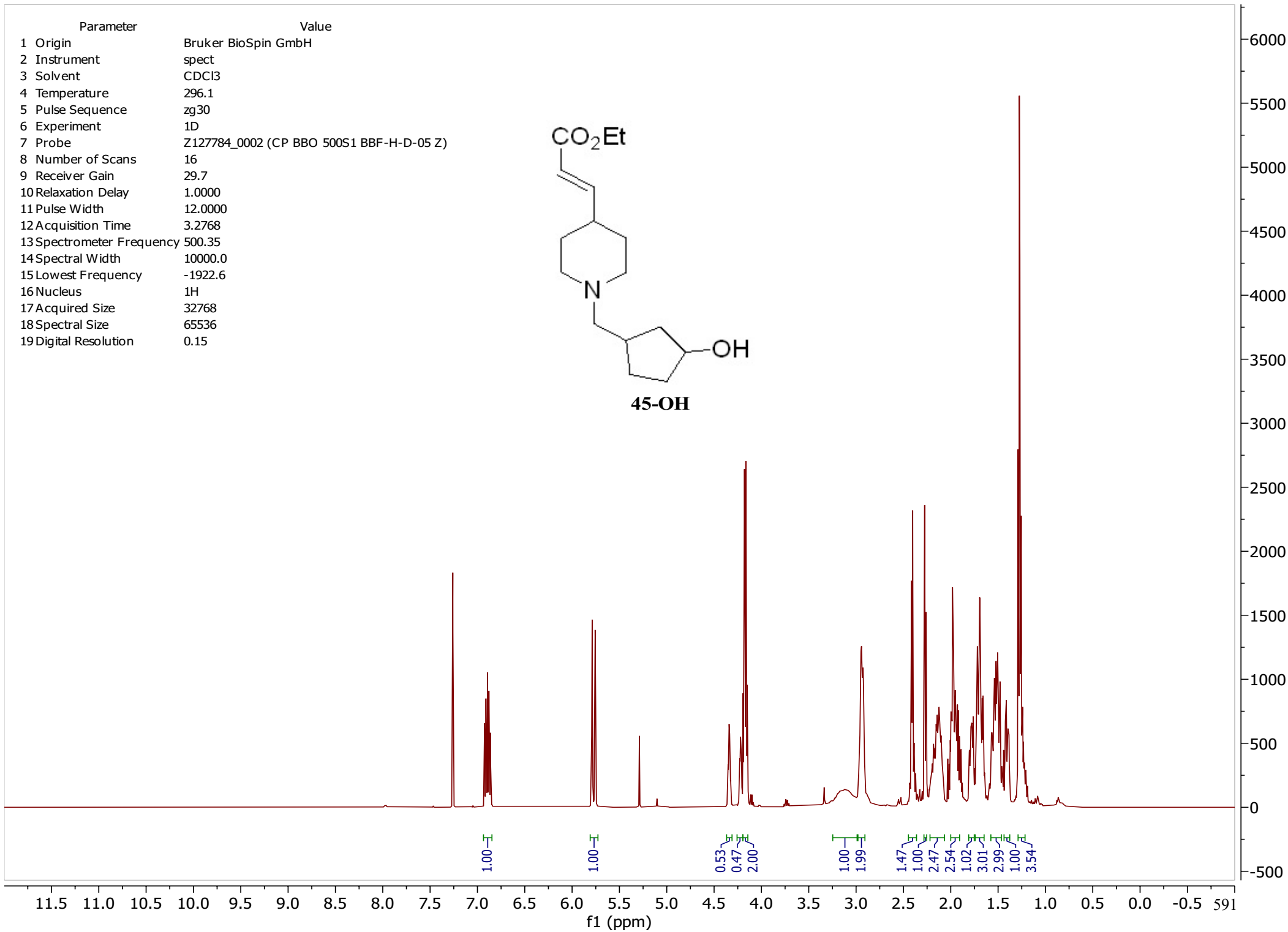
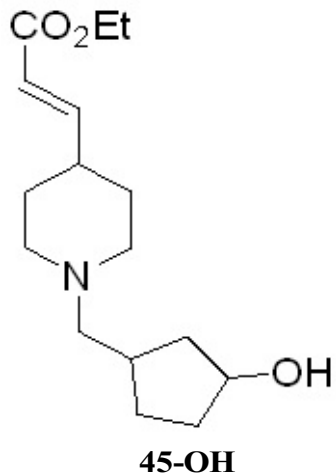
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	256
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8520
13 Spectrometer Frequency	150.92
14 Spectral Width	38461.5
15 Lowest Frequency	-2631.4
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.59



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



Parameter

1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	268
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1770.4
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

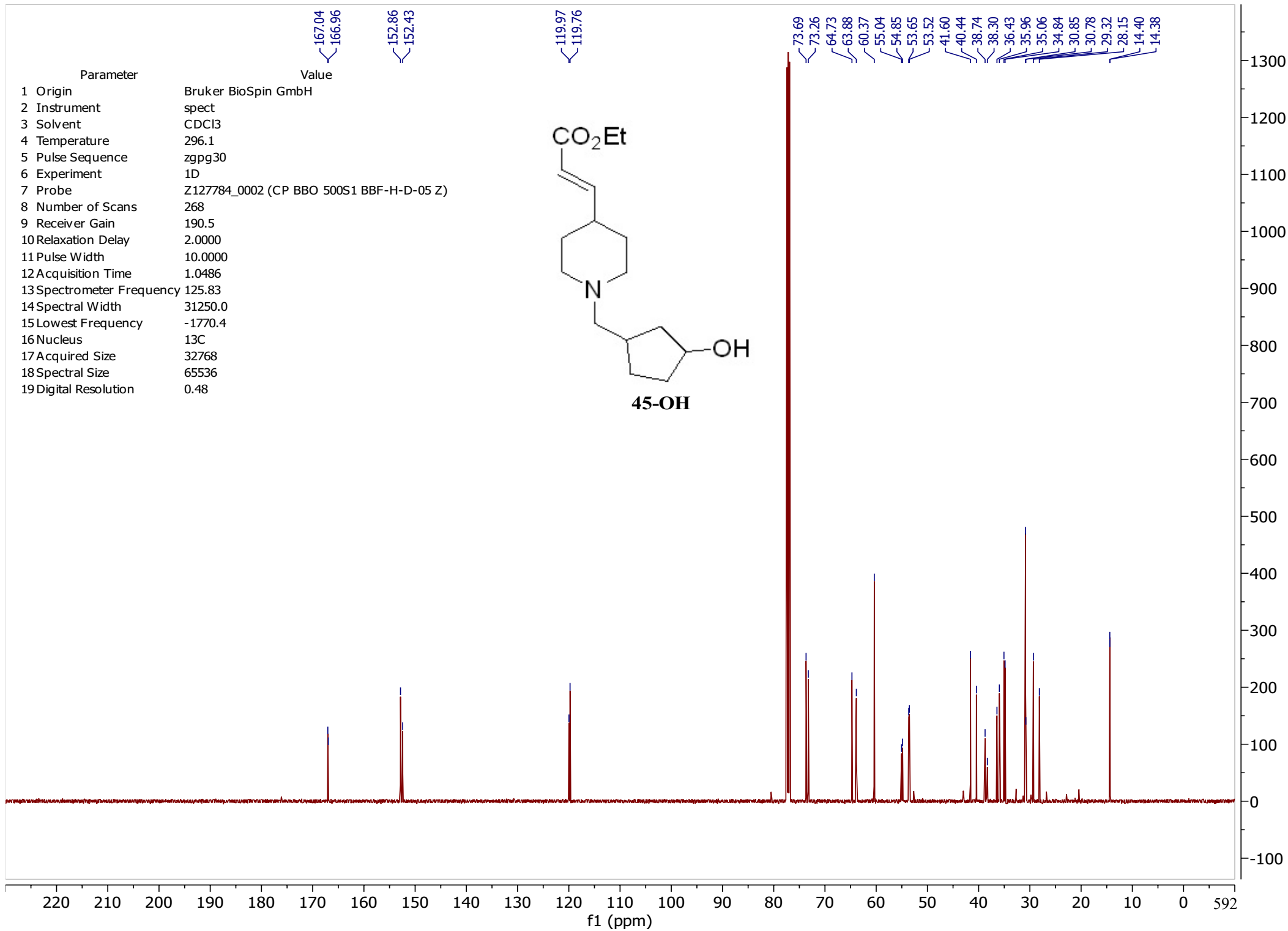
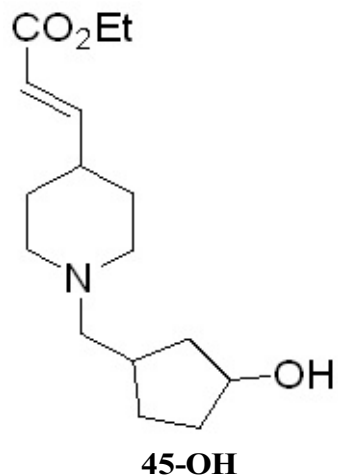
Value

167.04
166.96

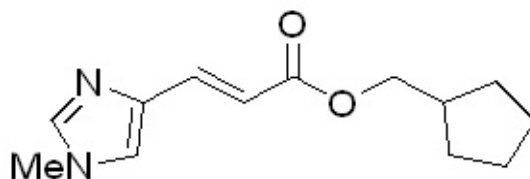
152.86
152.43

119.97
119.76

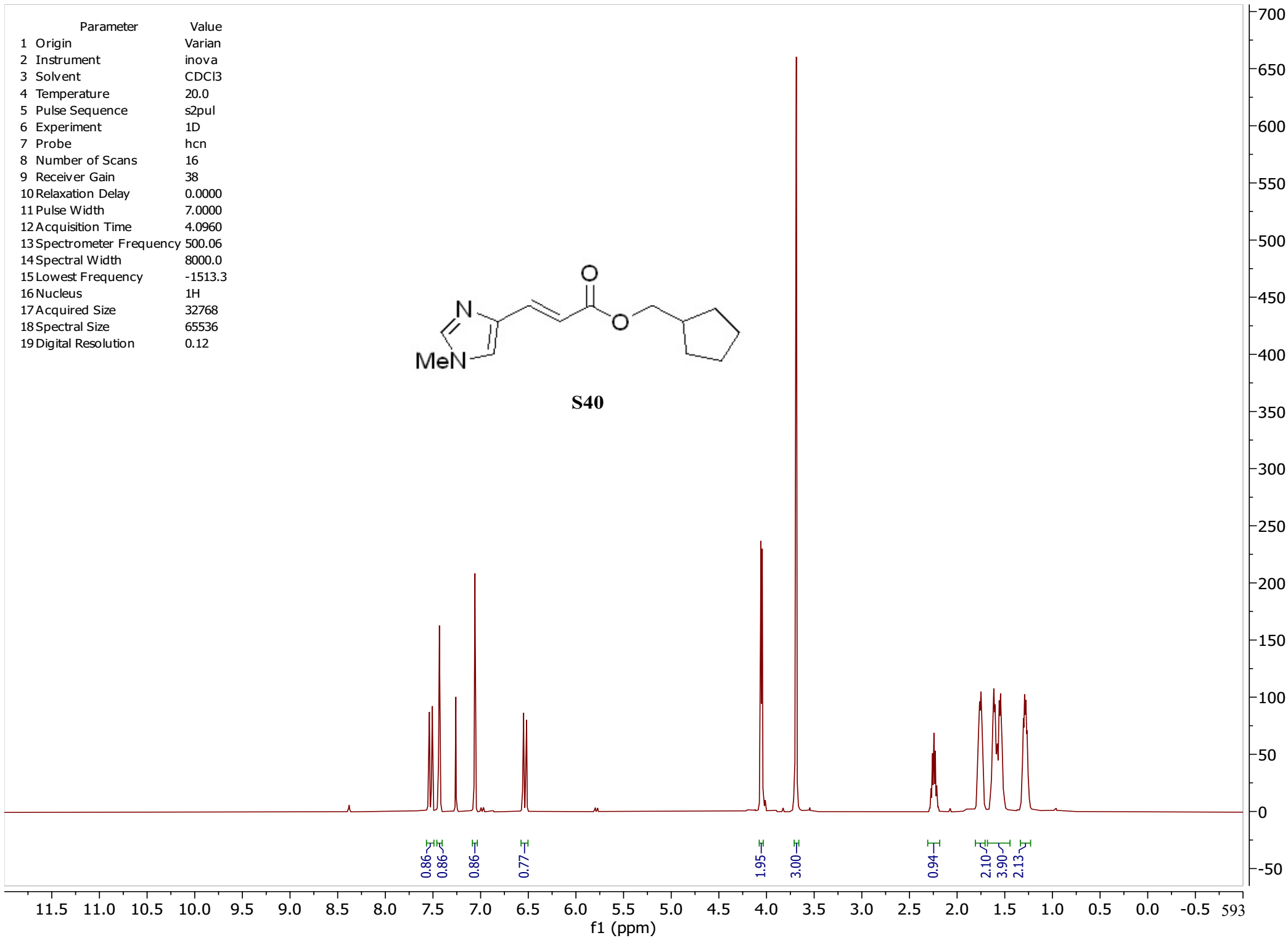
73.69
73.26
64.73
63.88
60.37
55.04
54.85
53.65
53.52
41.60
40.44
38.74
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35.96
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34.84
30.85
30.78
29.32
28.15
14.40
14.38



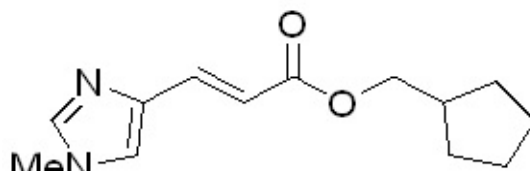
Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	hcn
8 Number of Scans	16
9 Receiver Gain	38
10 Relaxation Delay	0.0000
11 Pulse Width	7.0000
12 Acquisition Time	4.0960
13 Spectrometer Frequency	500.06
14 Spectral Width	8000.0
15 Lowest Frequency	-1513.3
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12



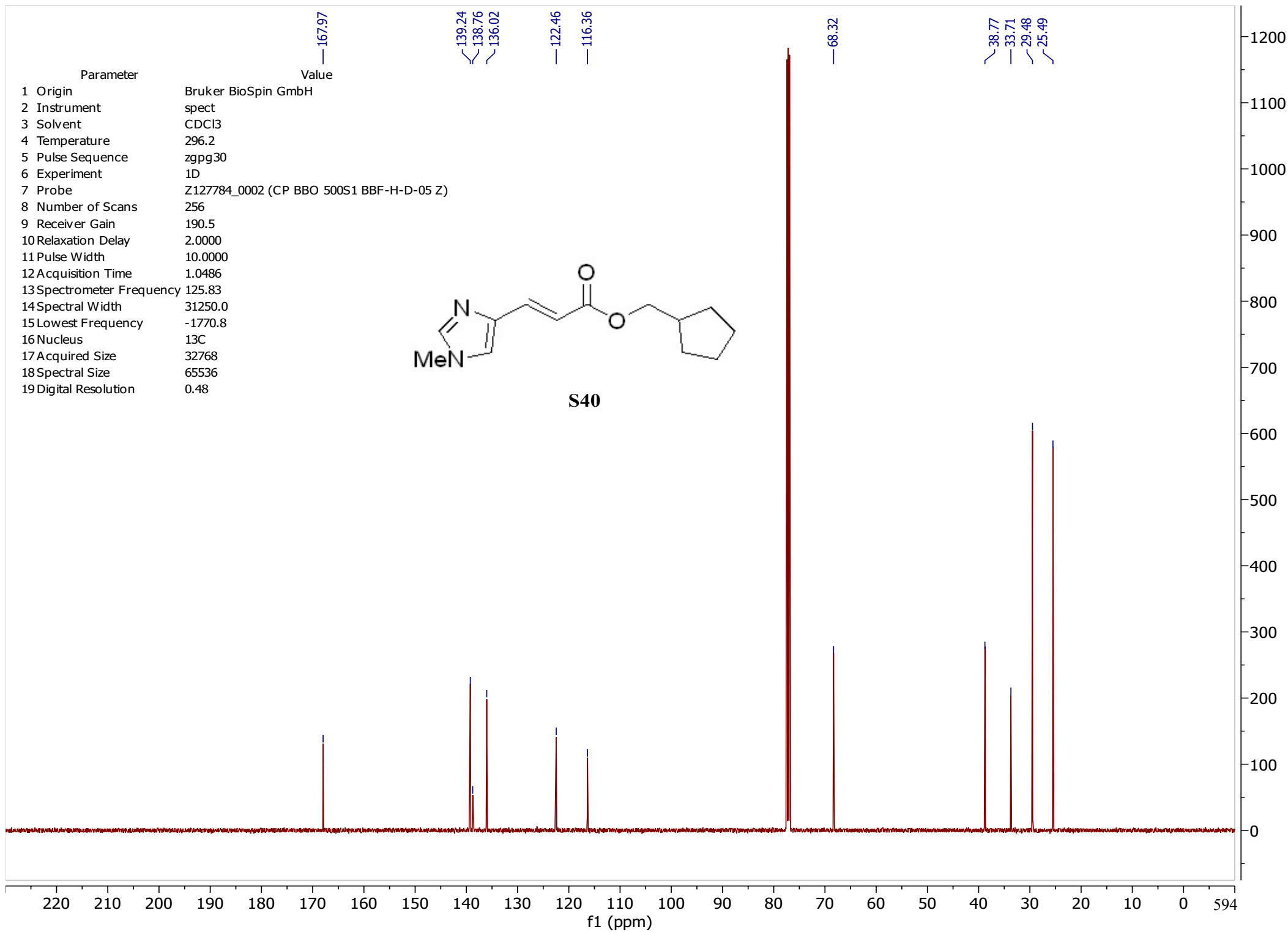
S40



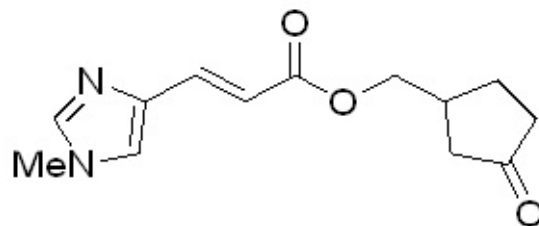
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1770.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



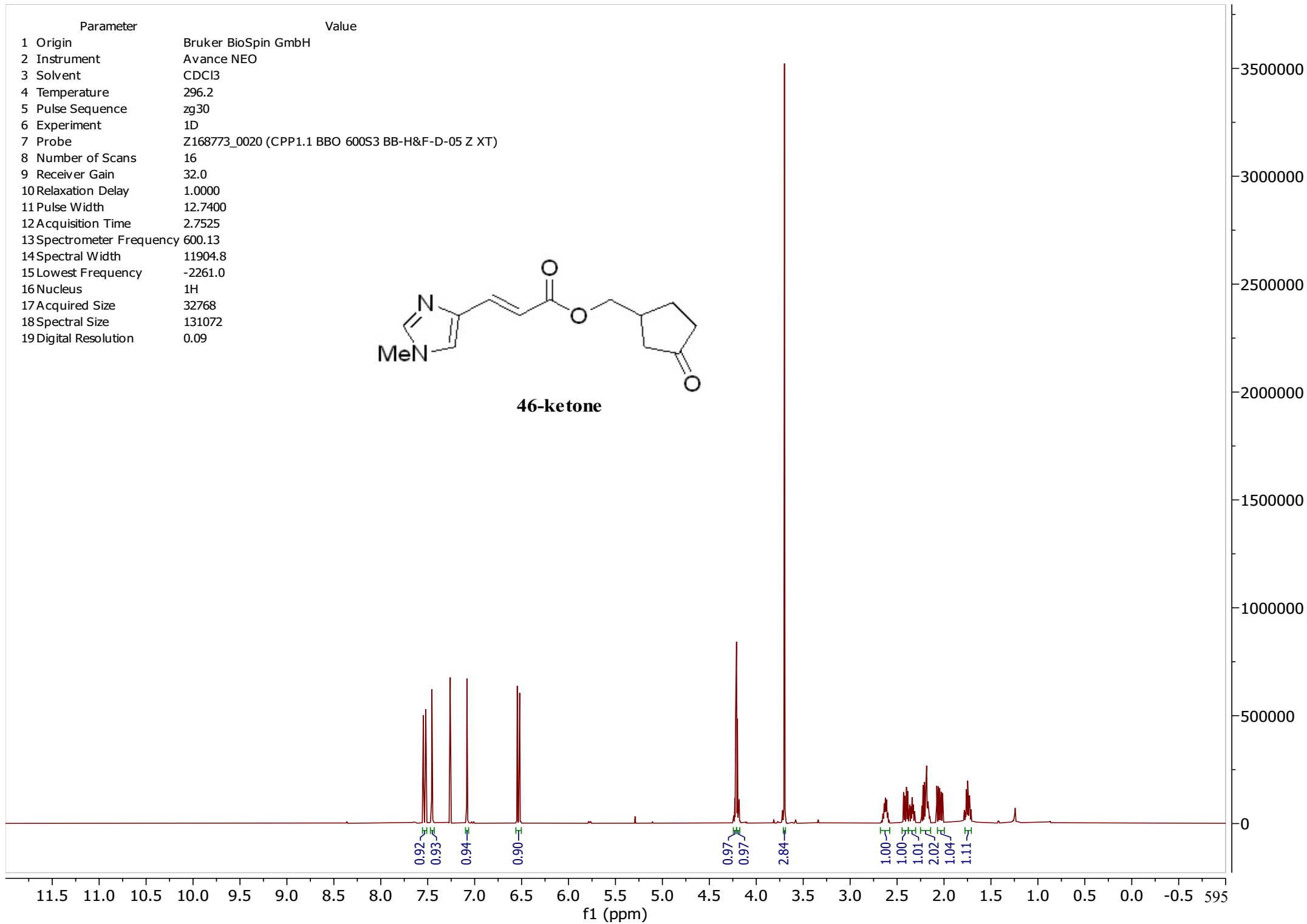
S40



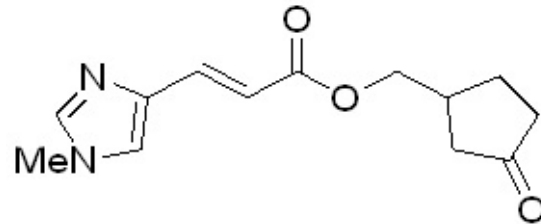
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.7400
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



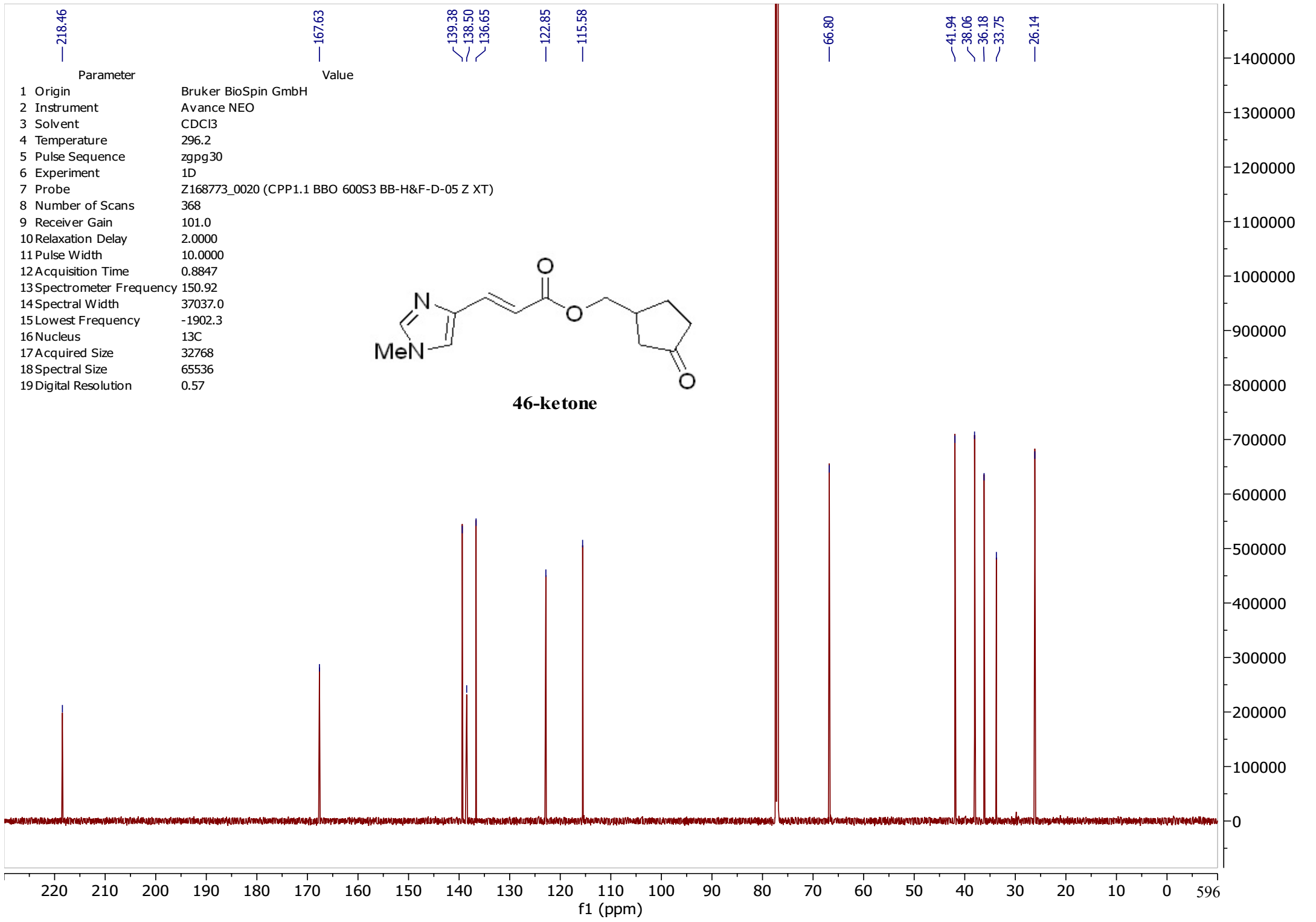
46-ketone



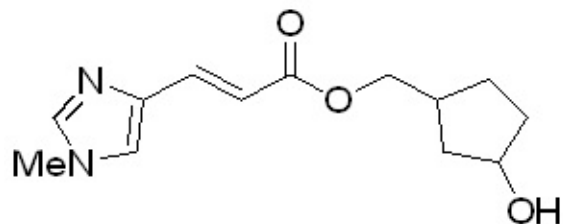
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	368
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1902.3
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



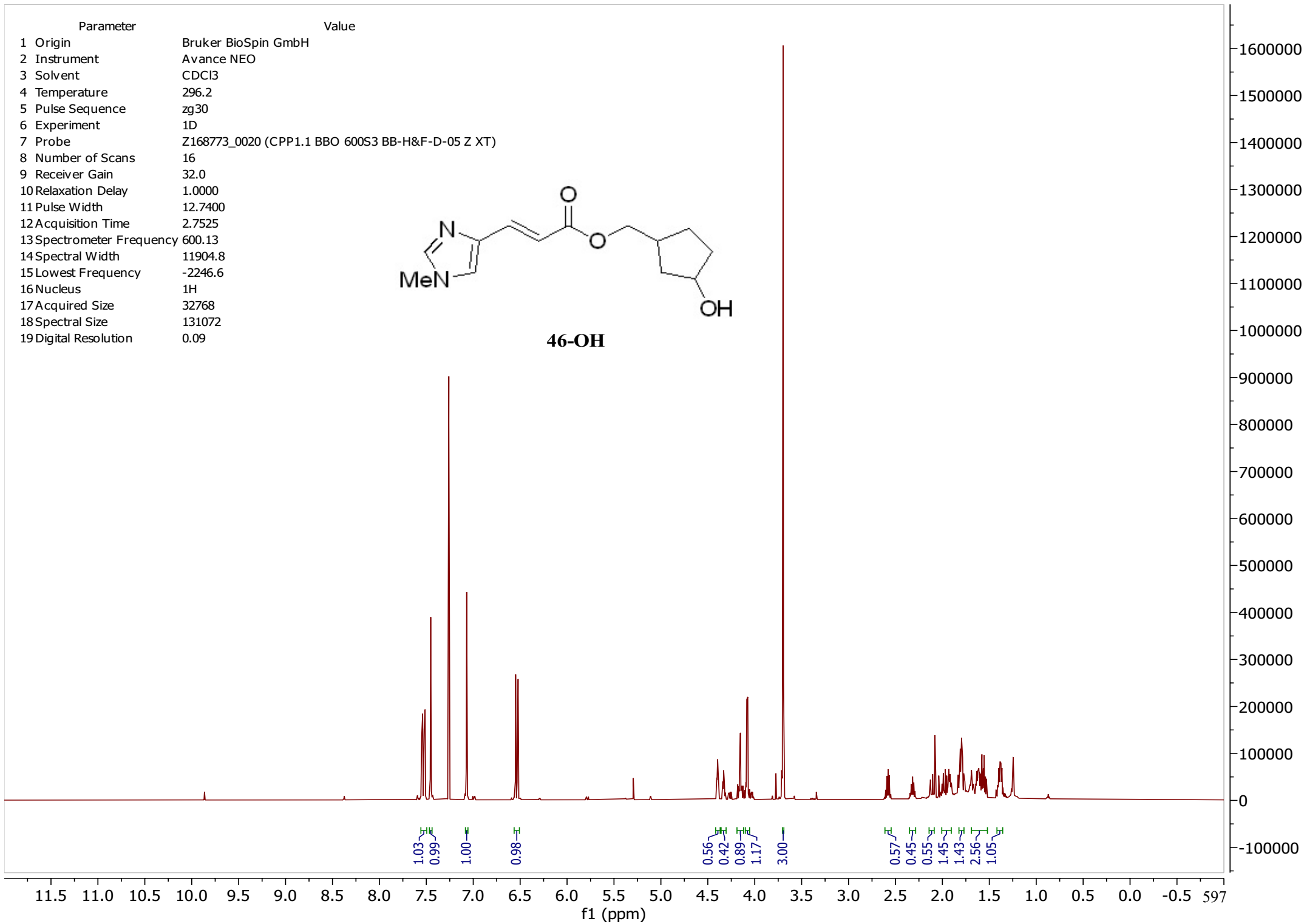
46-ketone



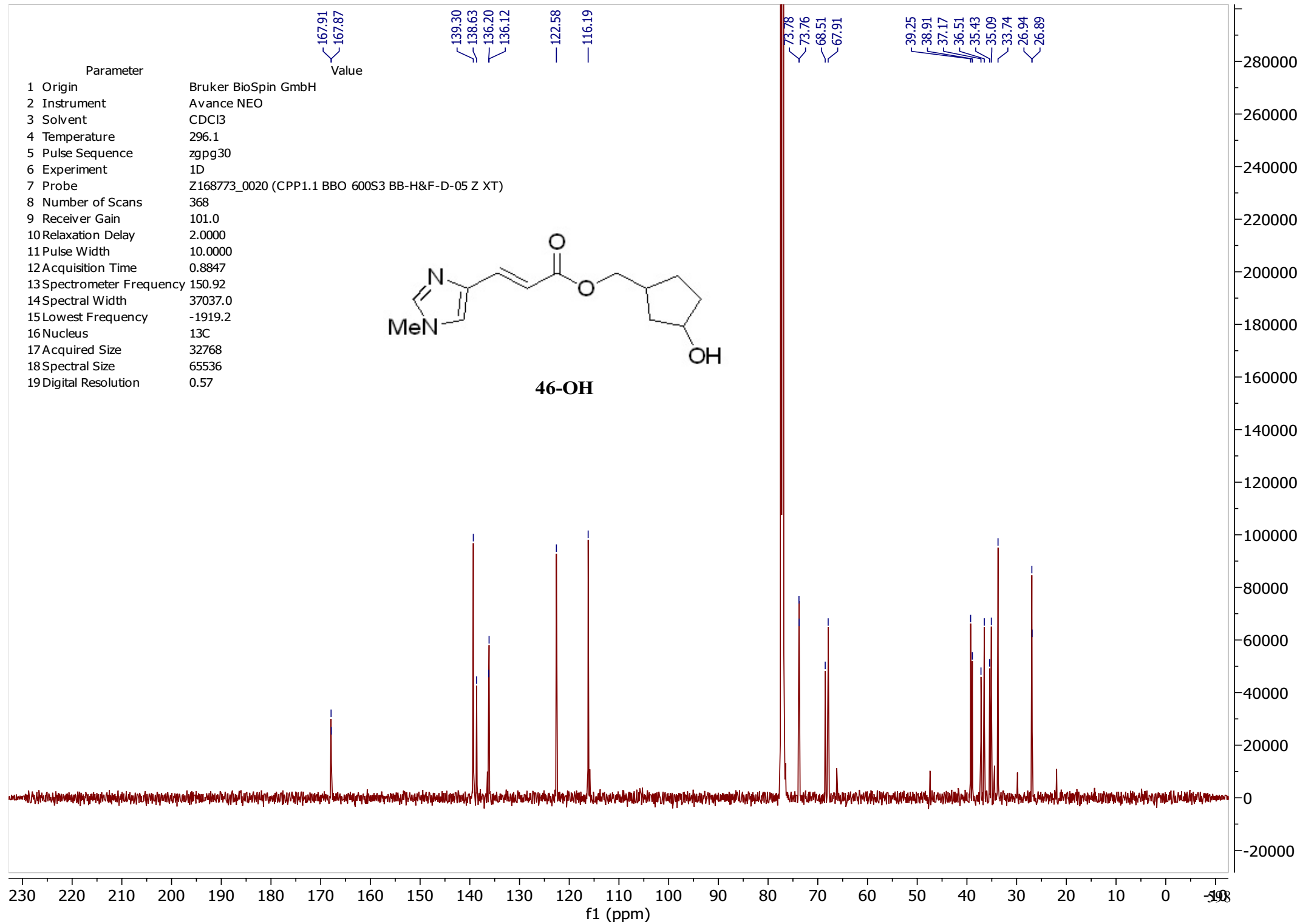
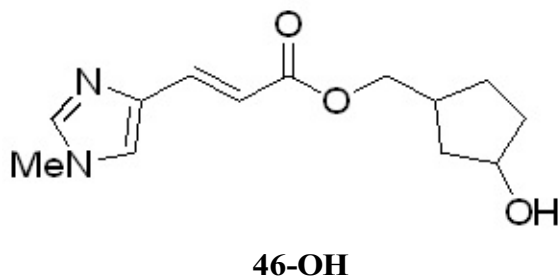
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.7400
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



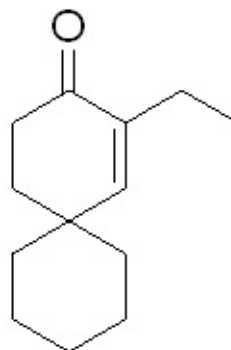
46-OH



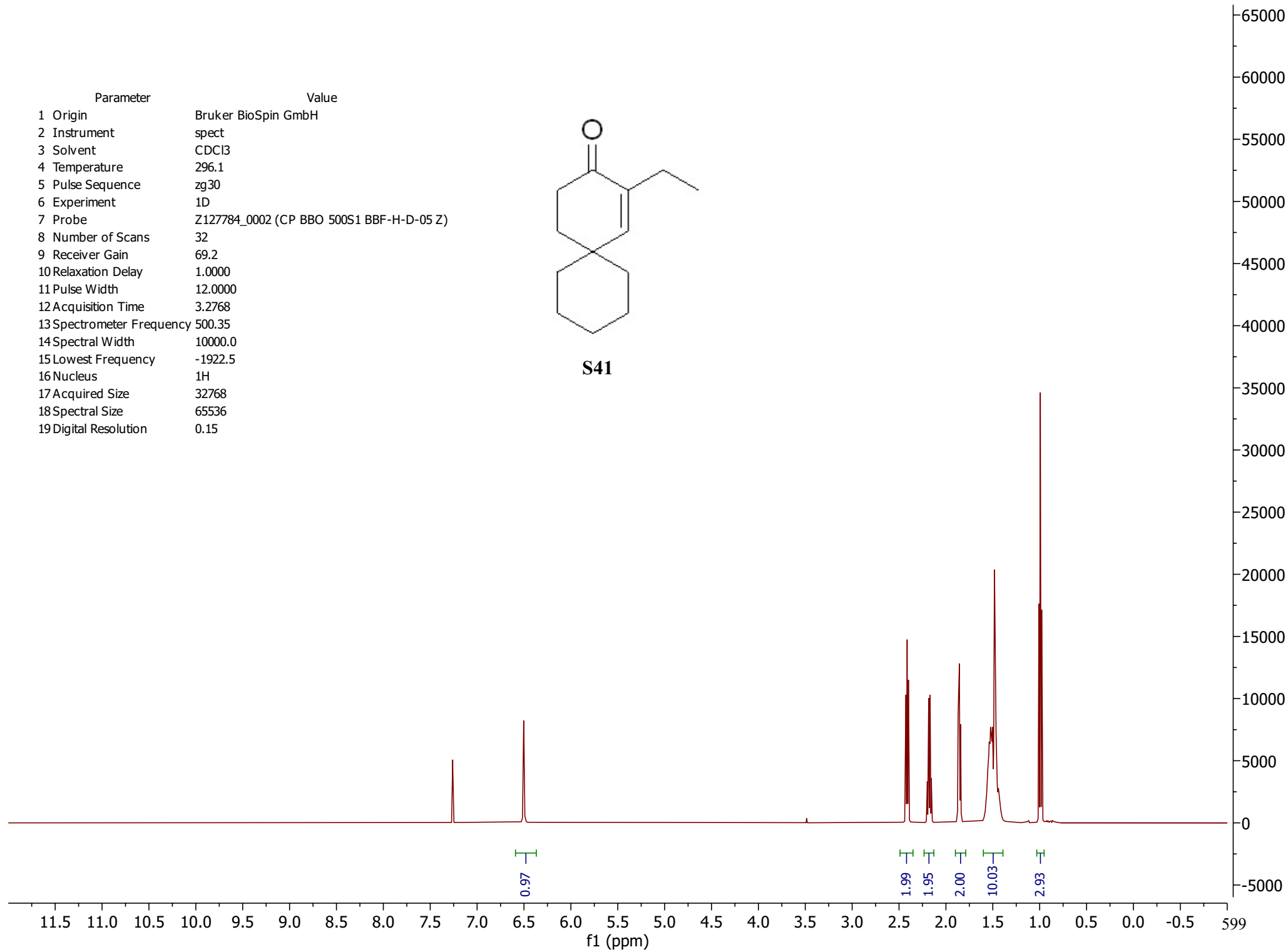
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	368
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1919.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



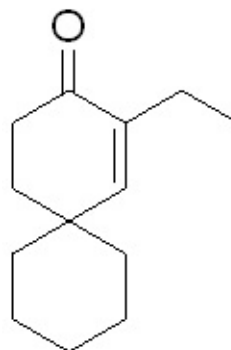
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



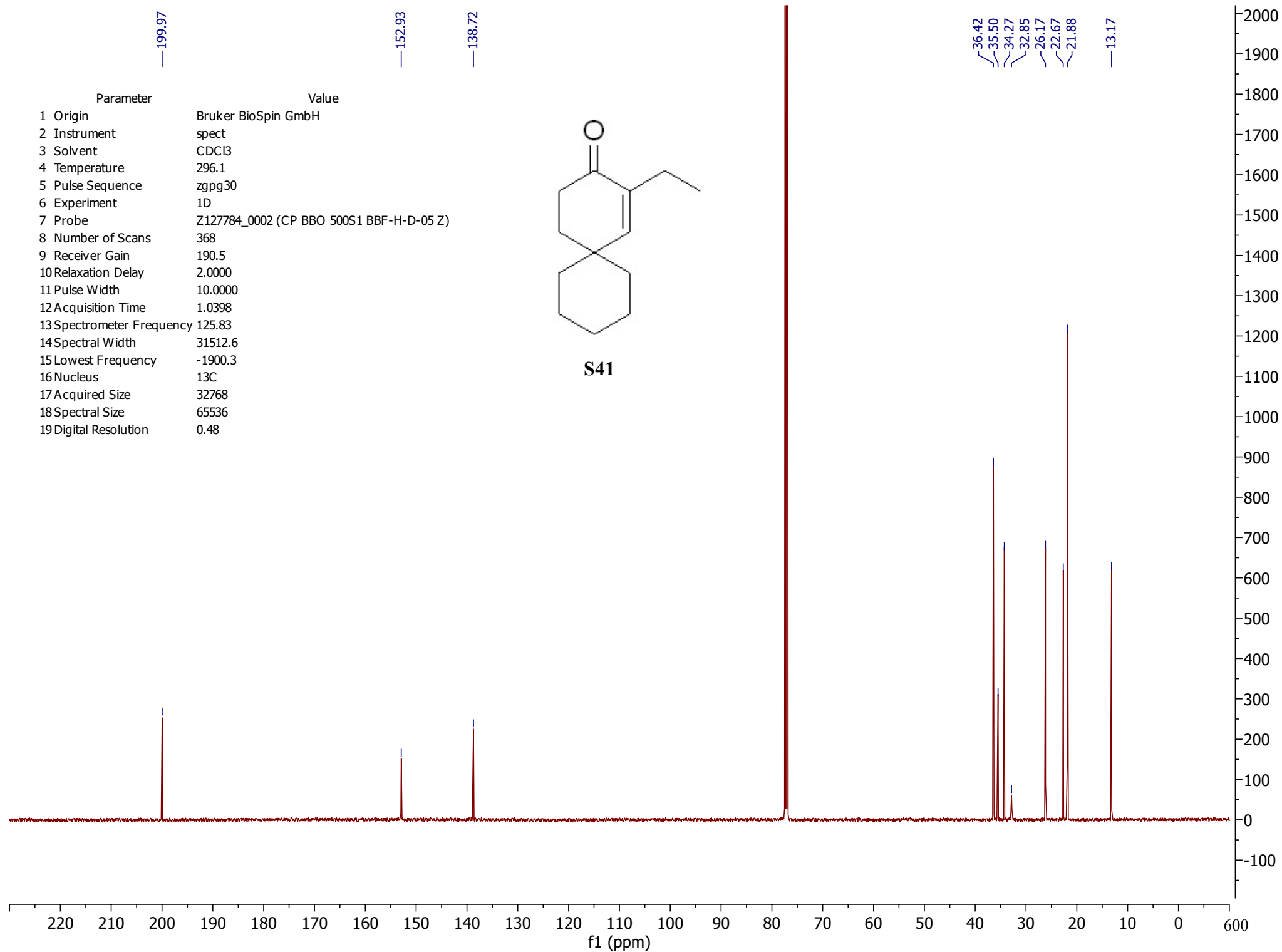
S41



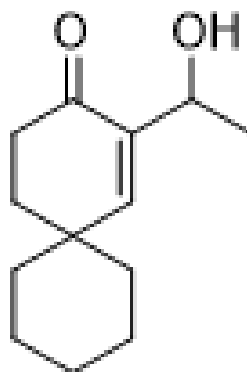
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.3
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



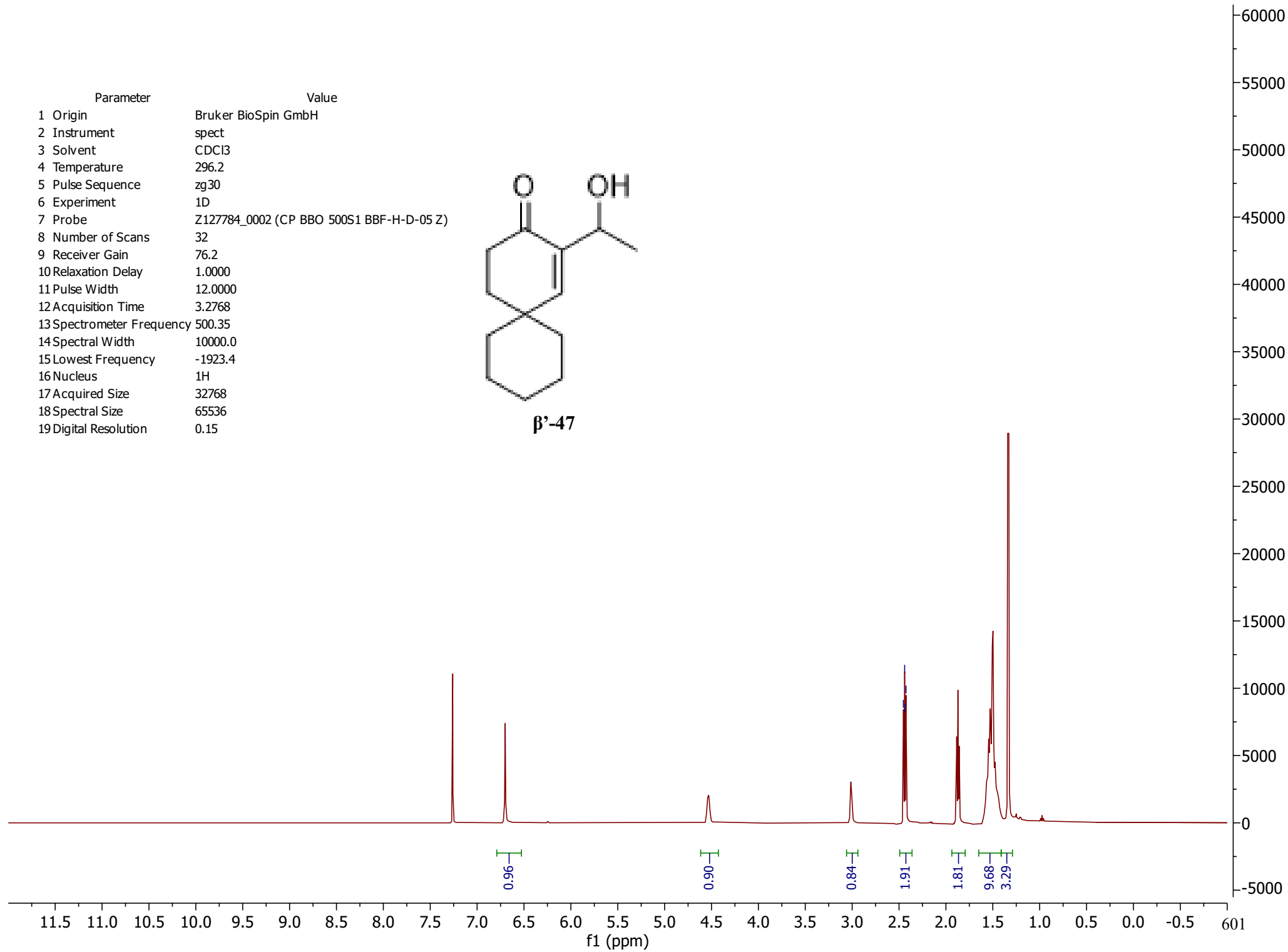
S41



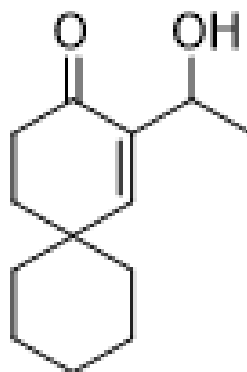
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



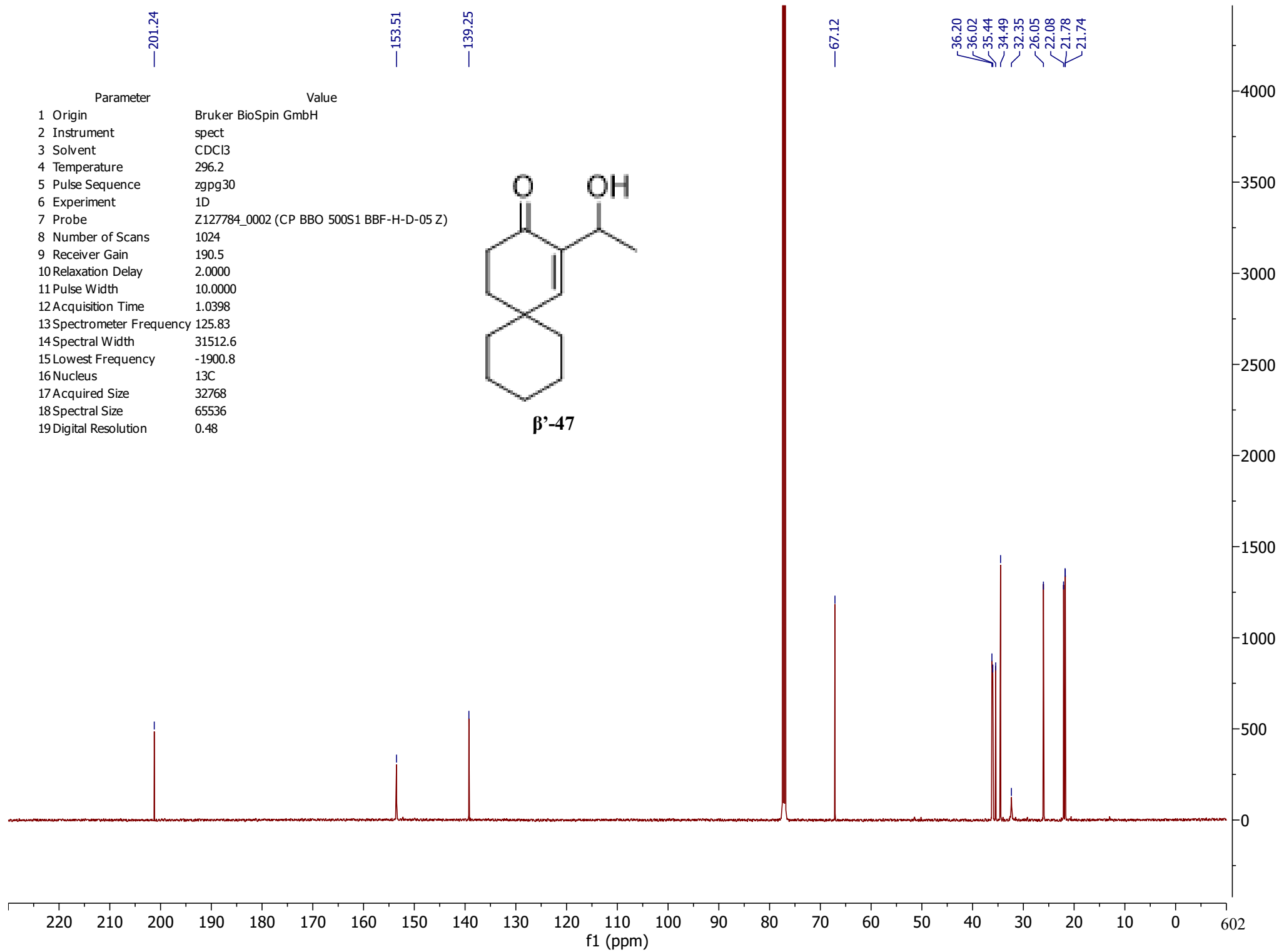
β'-47



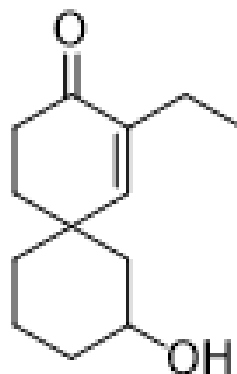
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



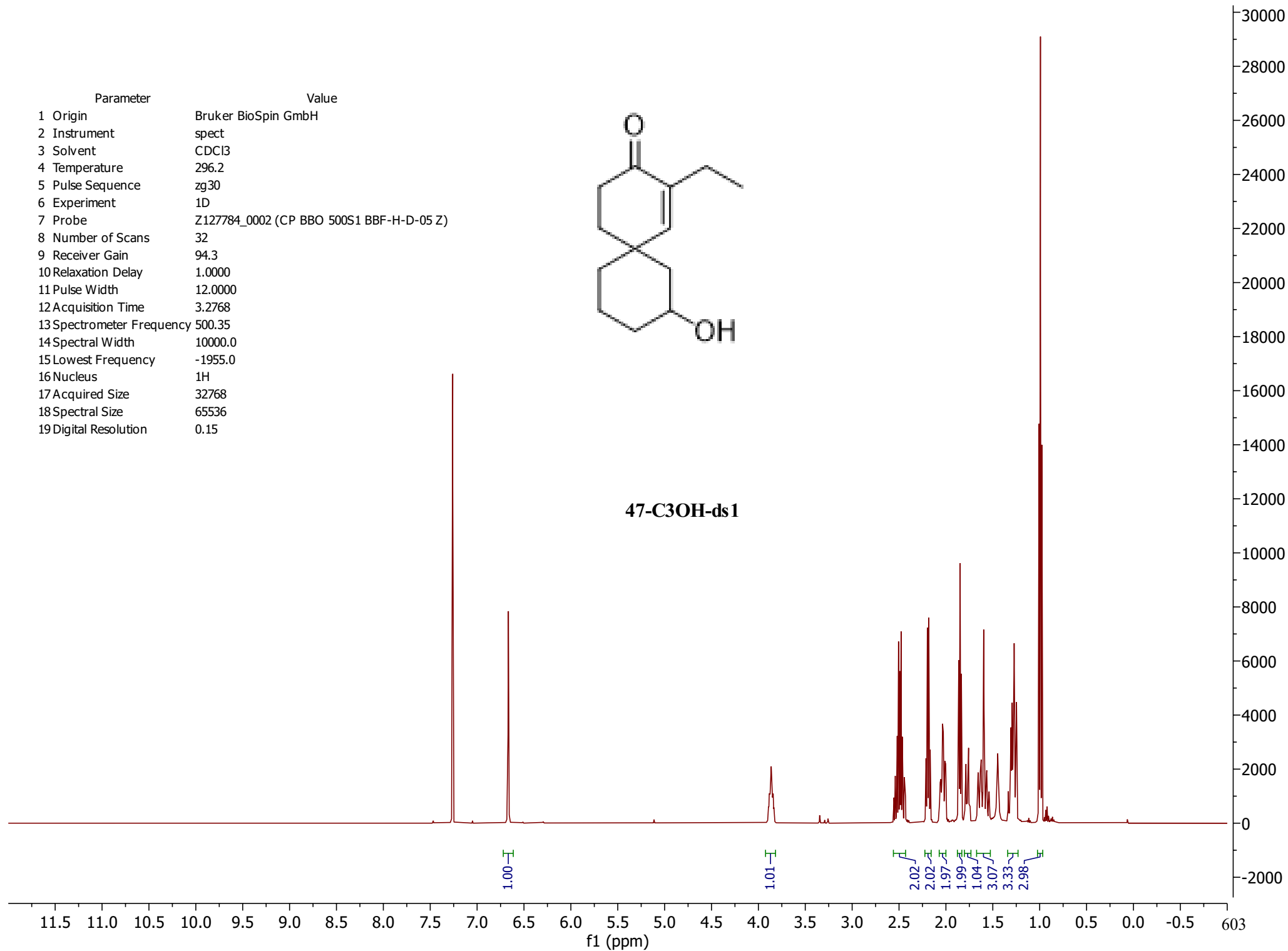
β' -47



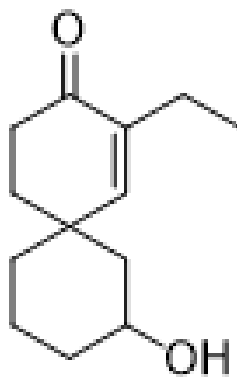
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	94.3
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1955.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



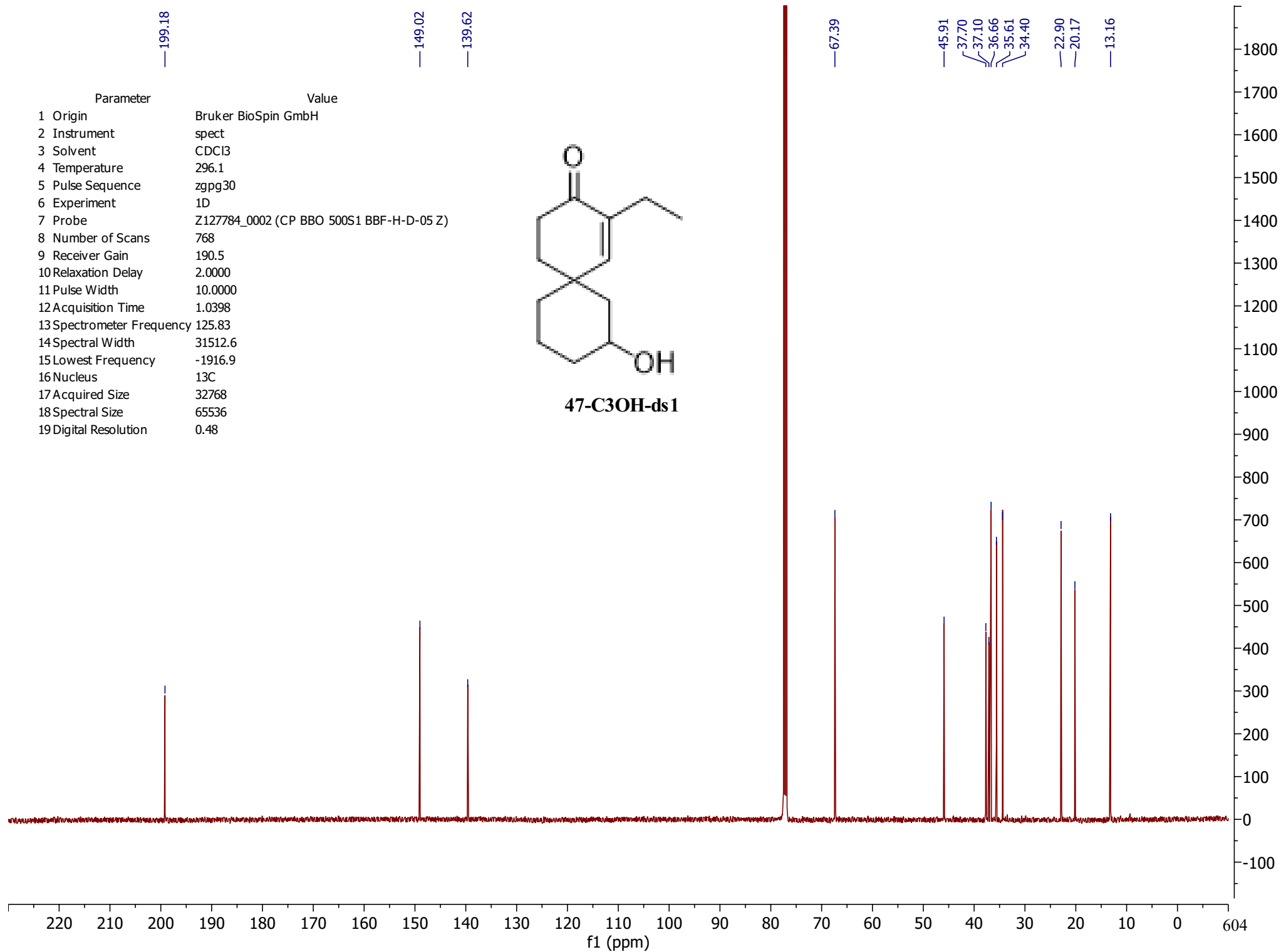
47-C3OH-ds1



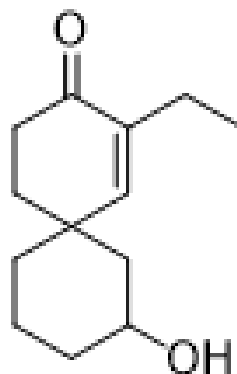
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	768
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



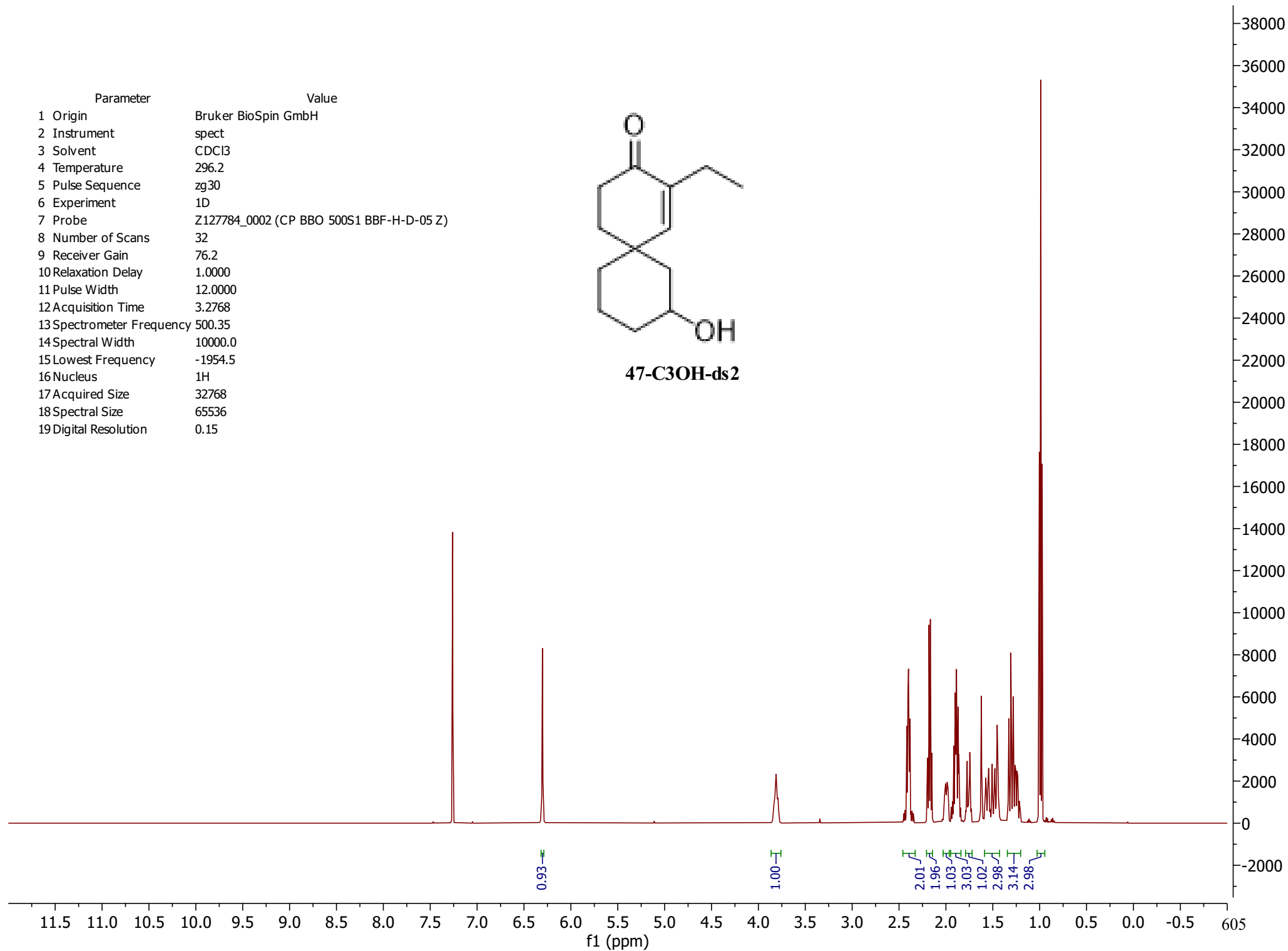
47-C3OH-ds1



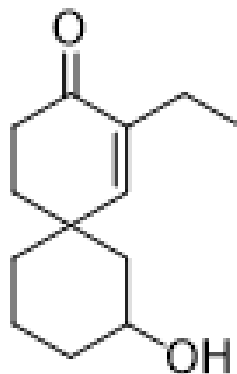
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1954.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



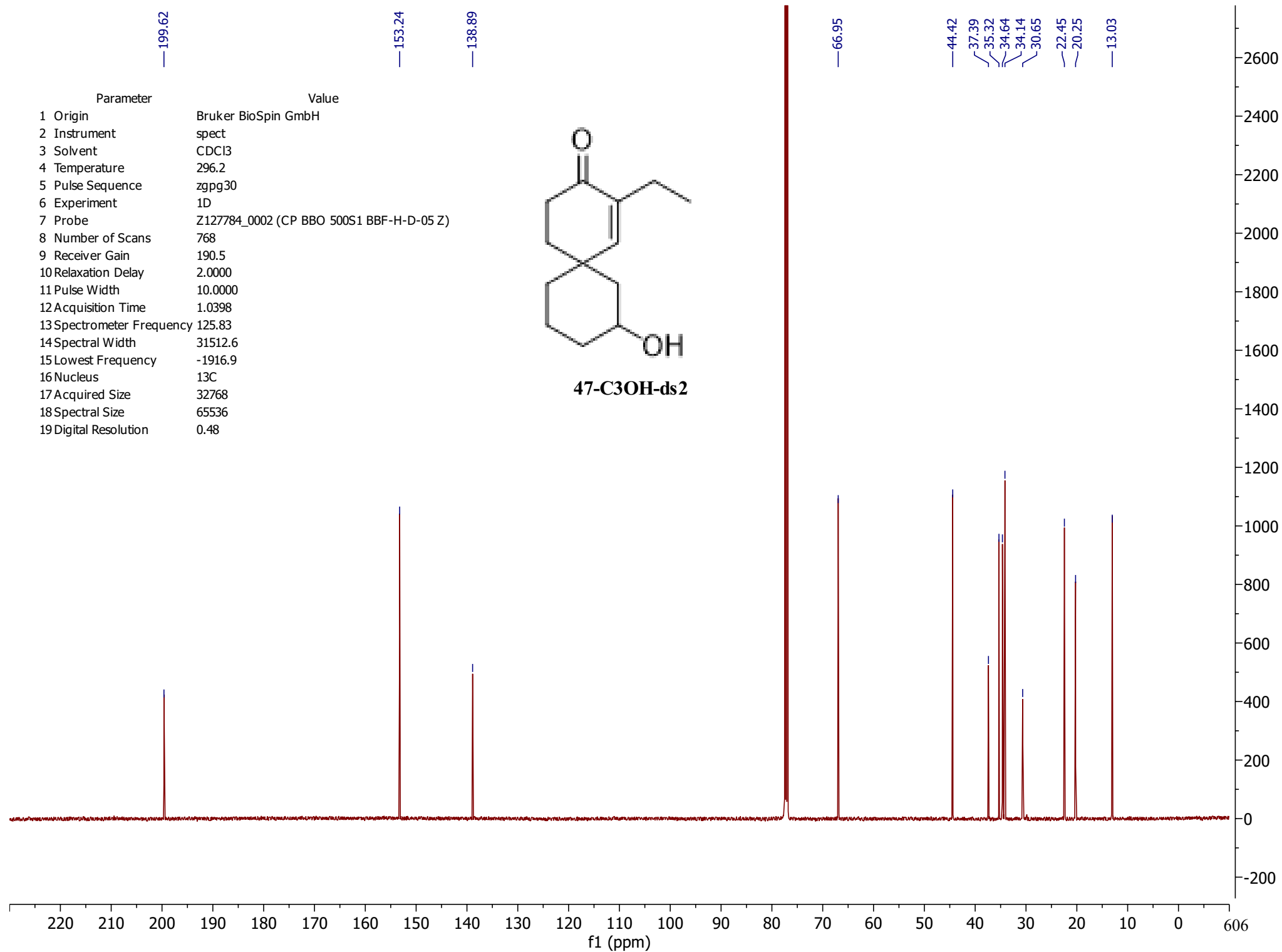
47-C3OH-ds2



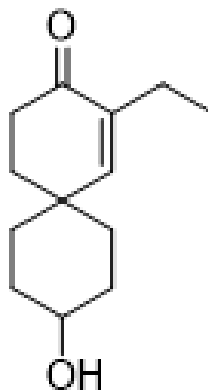
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	768
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



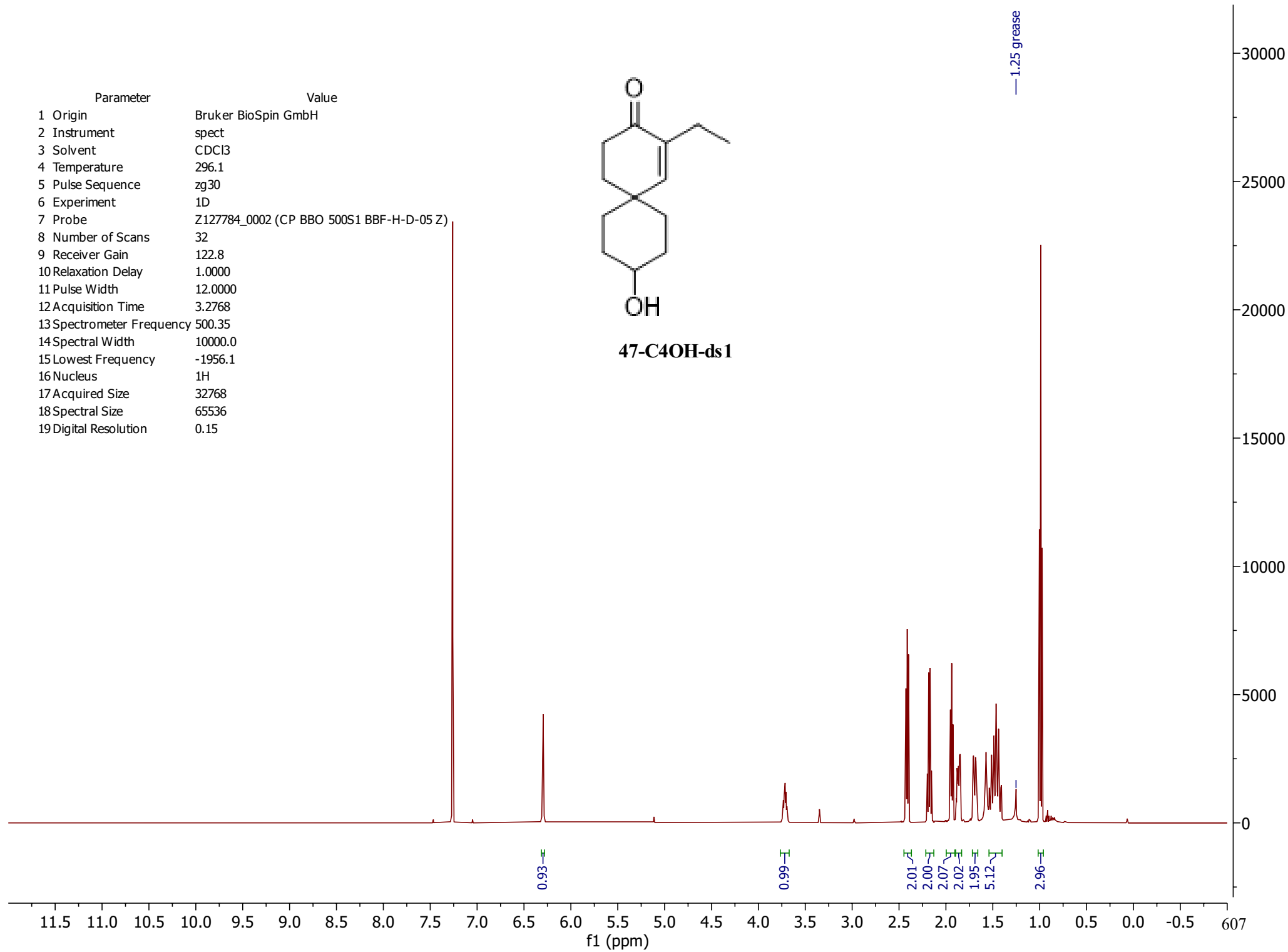
47-C3OH-ds2



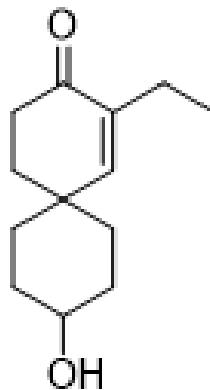
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	122.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1956.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



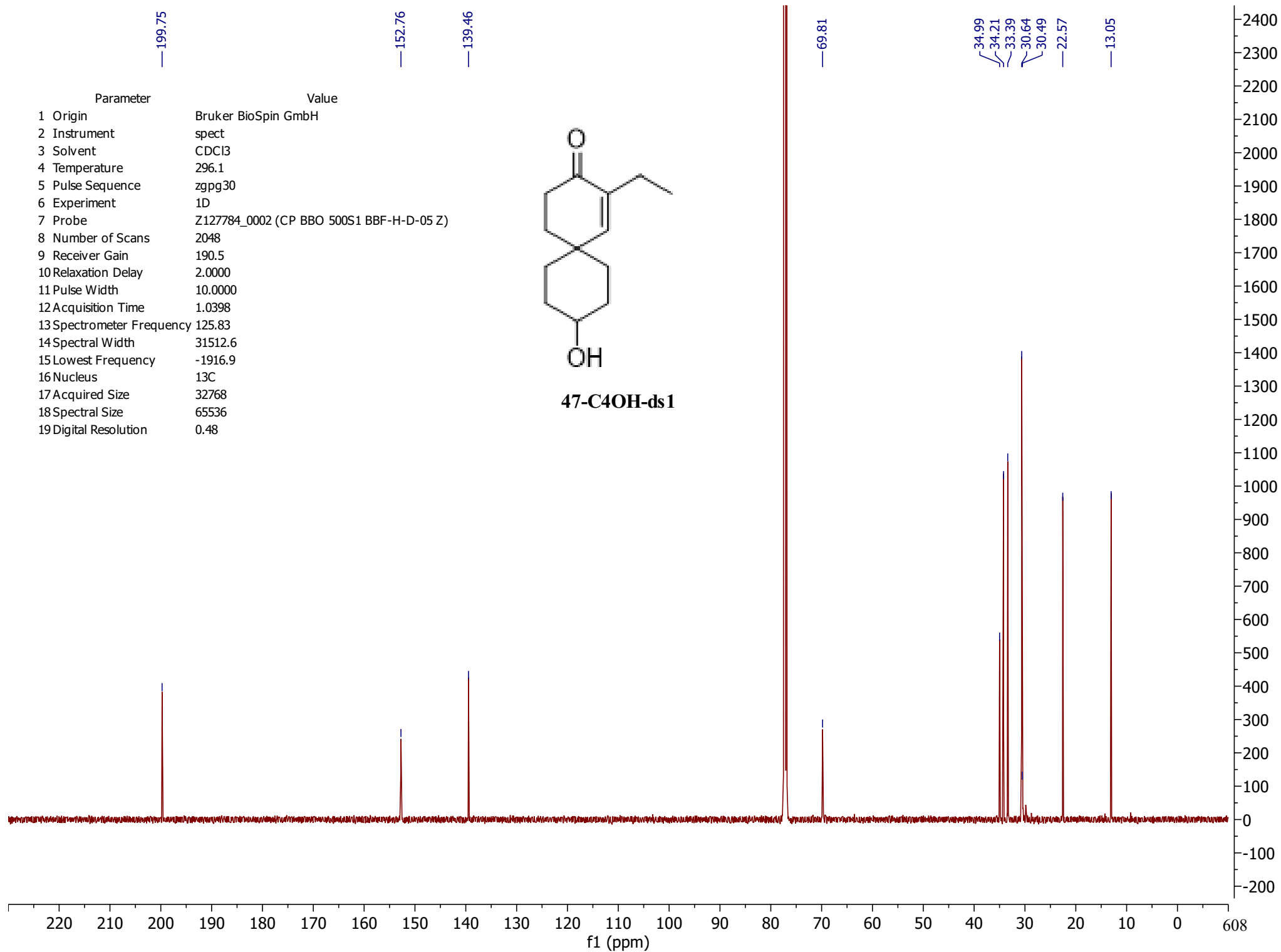
47-C4OH-ds1



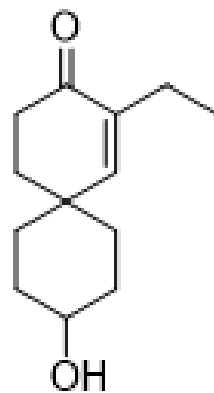
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



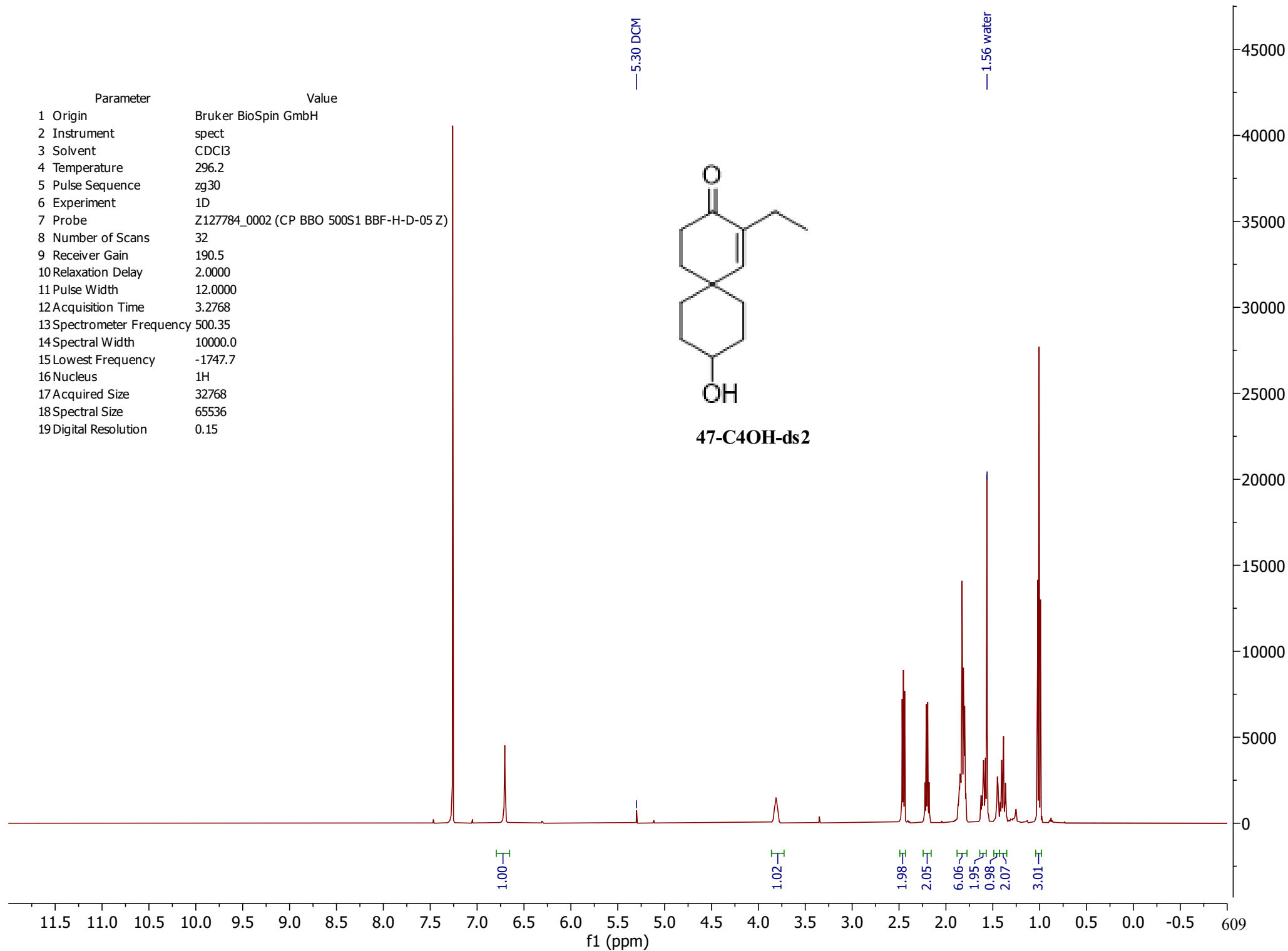
47-C4OH-ds1



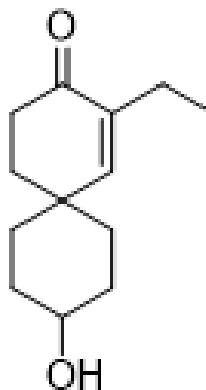
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



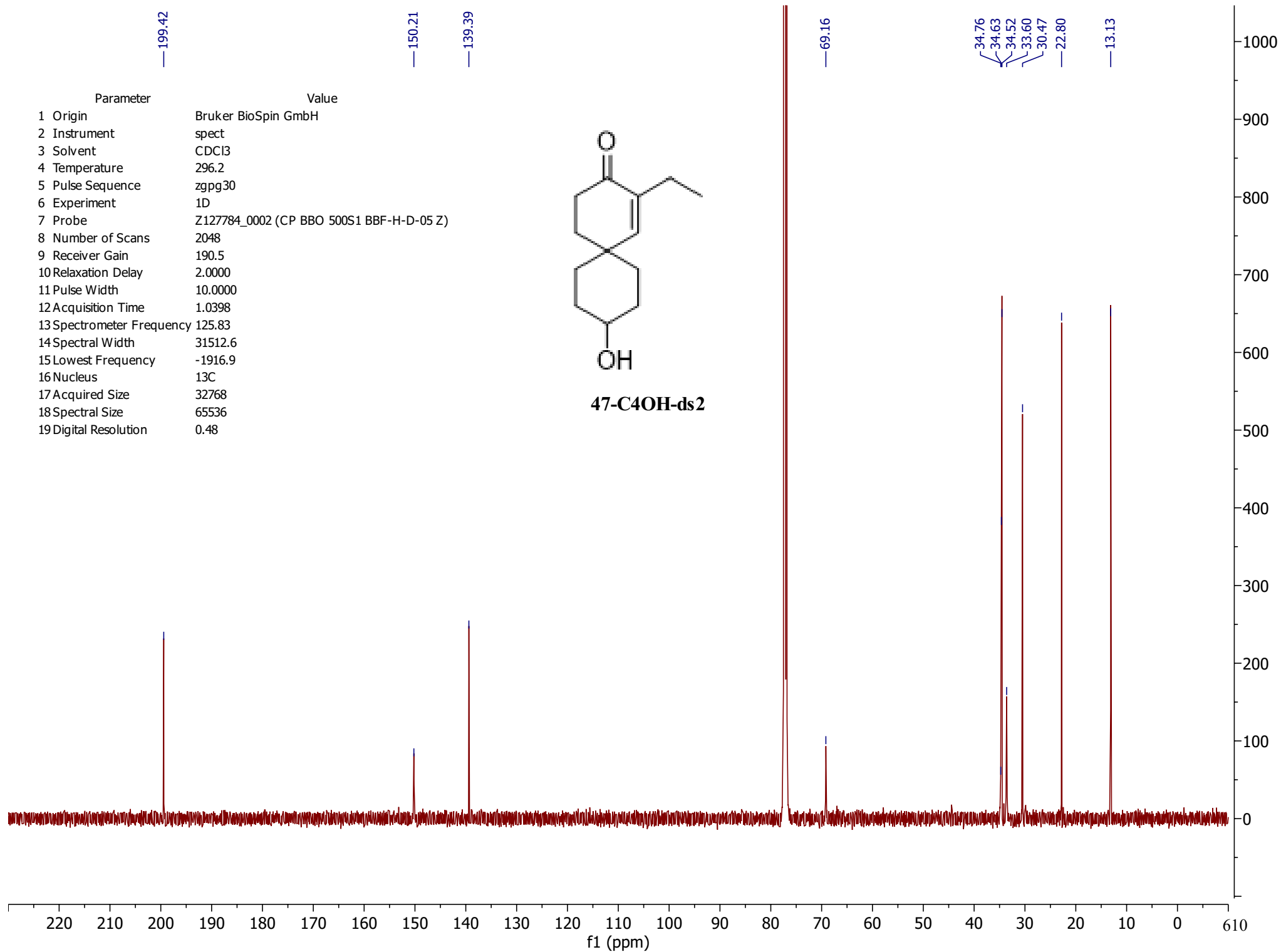
47-C4OH-ds2



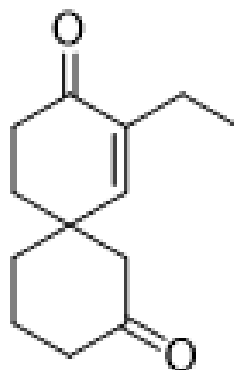
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



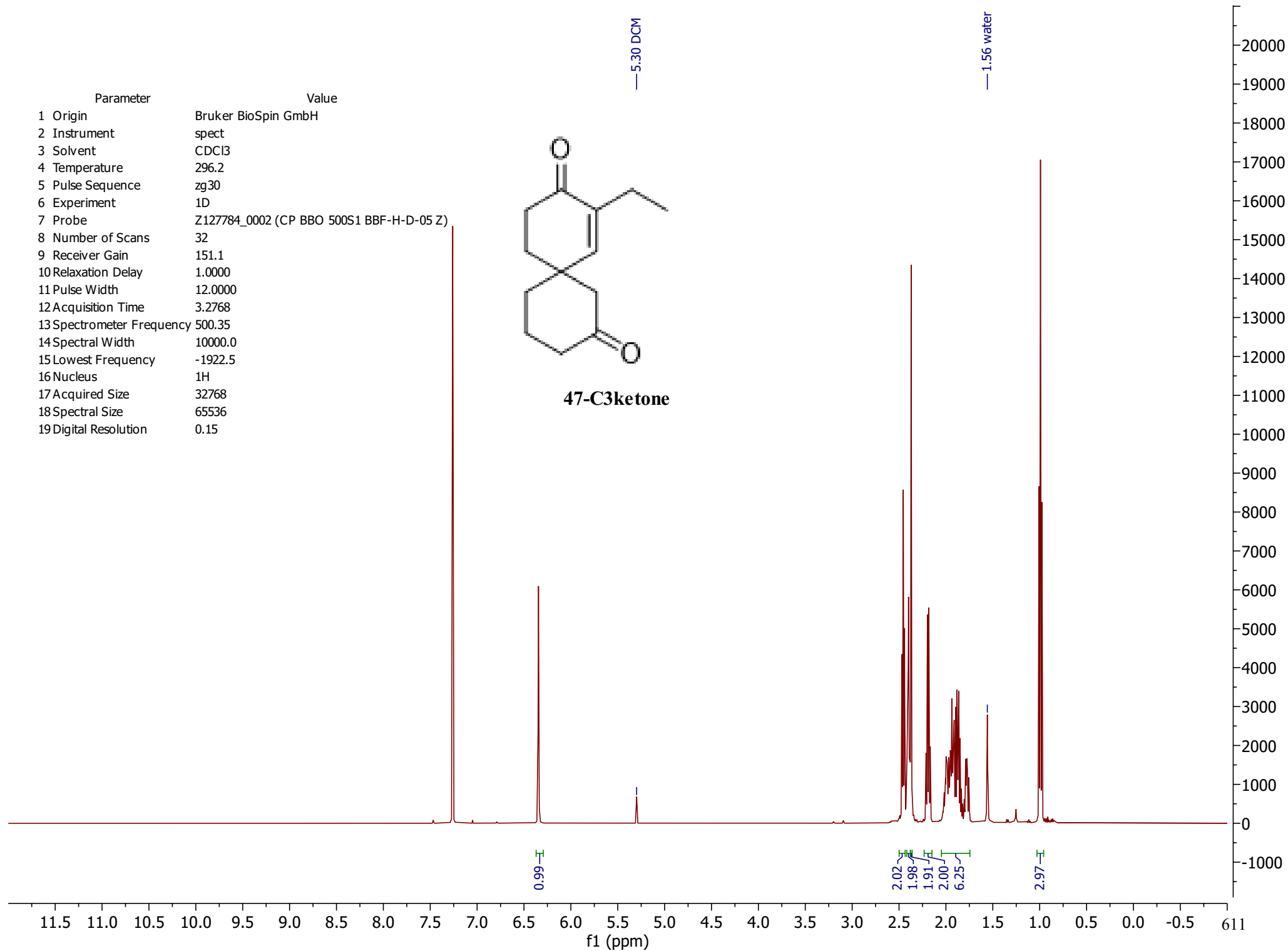
47-C4OH-ds2



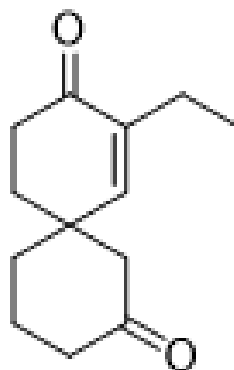
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	151.1
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



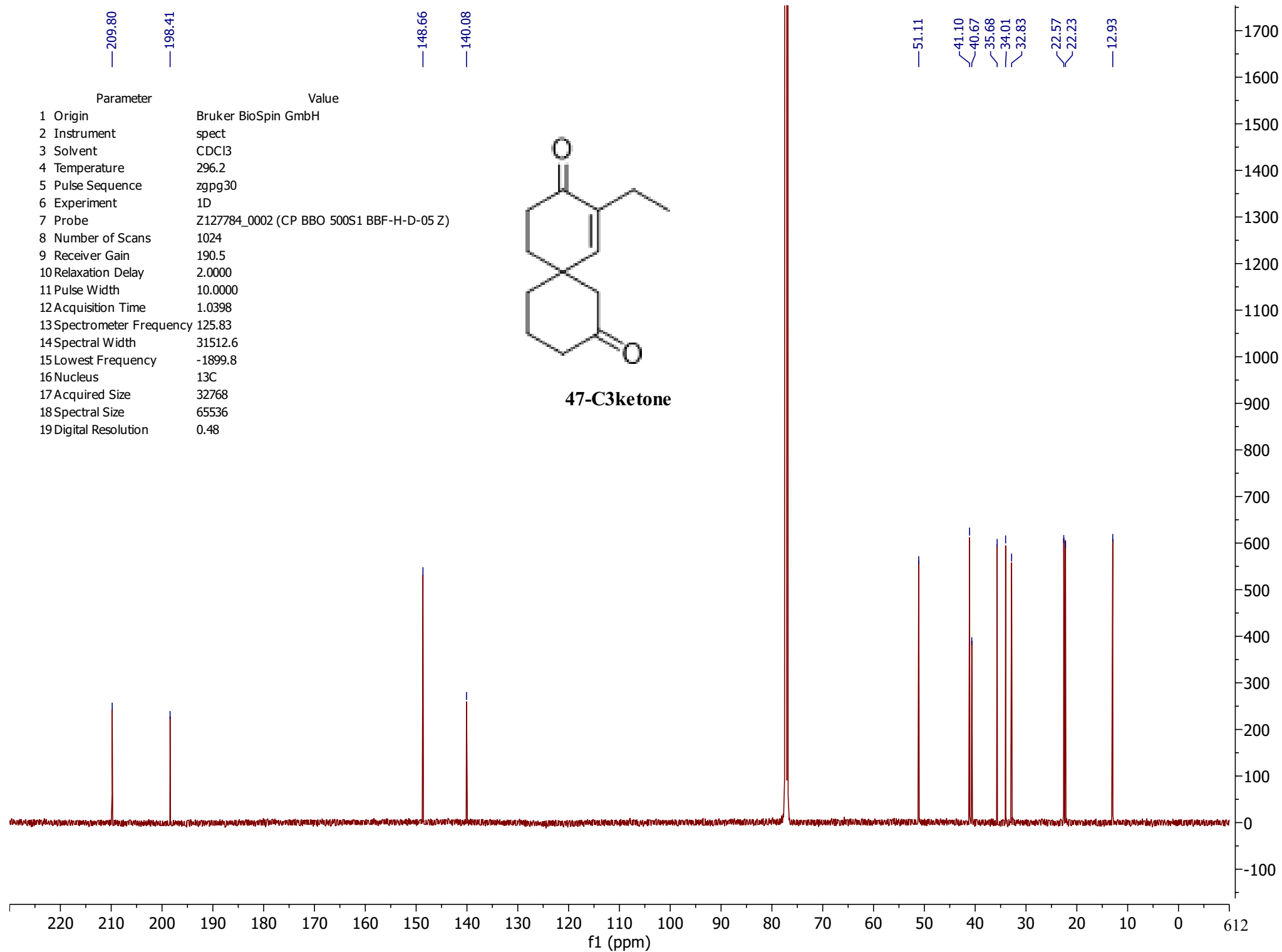
47-C3ketone



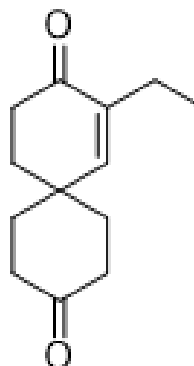
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1899.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



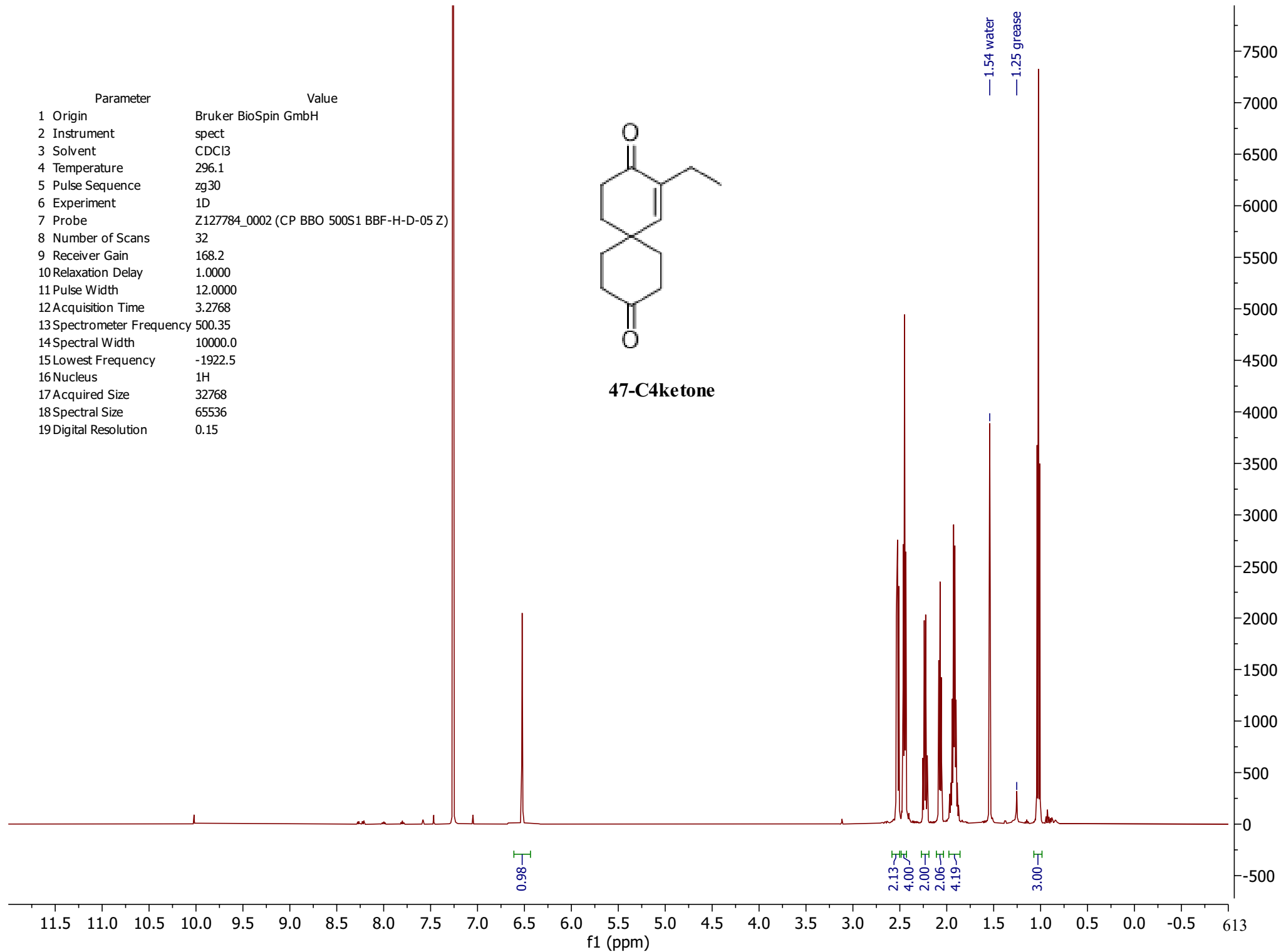
47-C3ketone

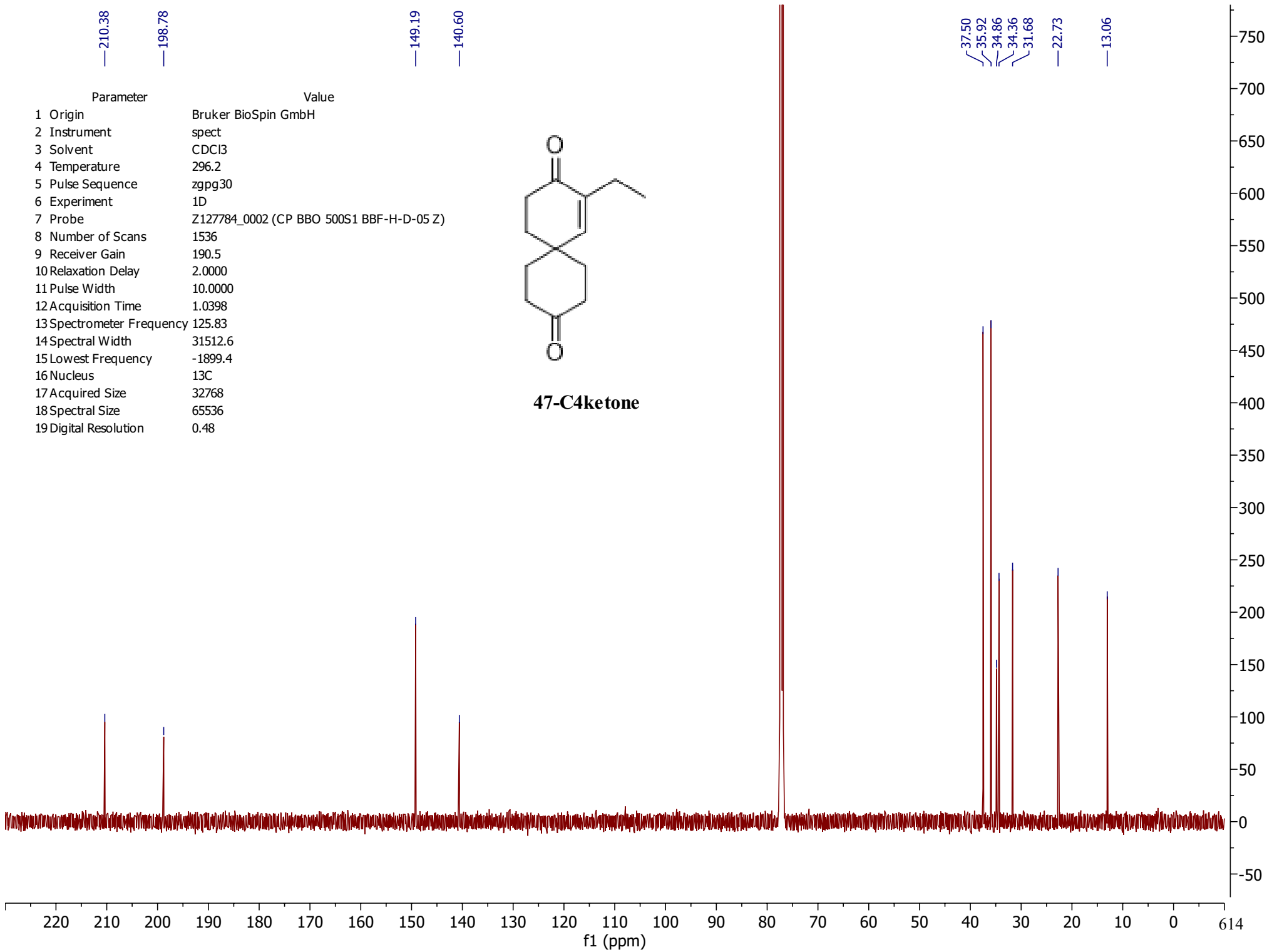


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	168.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

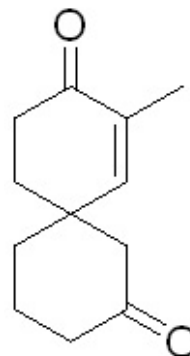


47-C4ketone

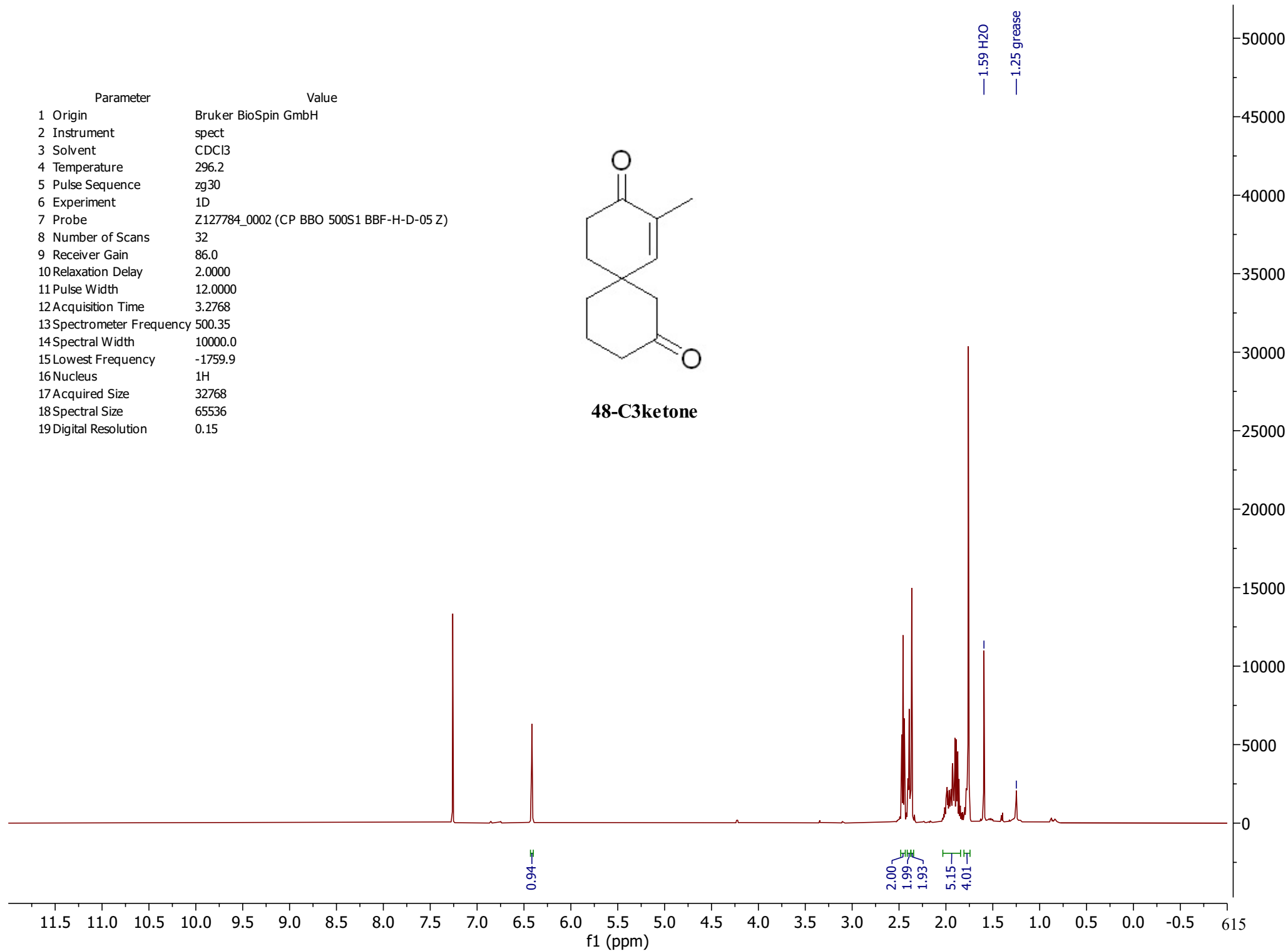




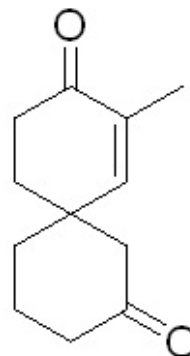
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1759.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



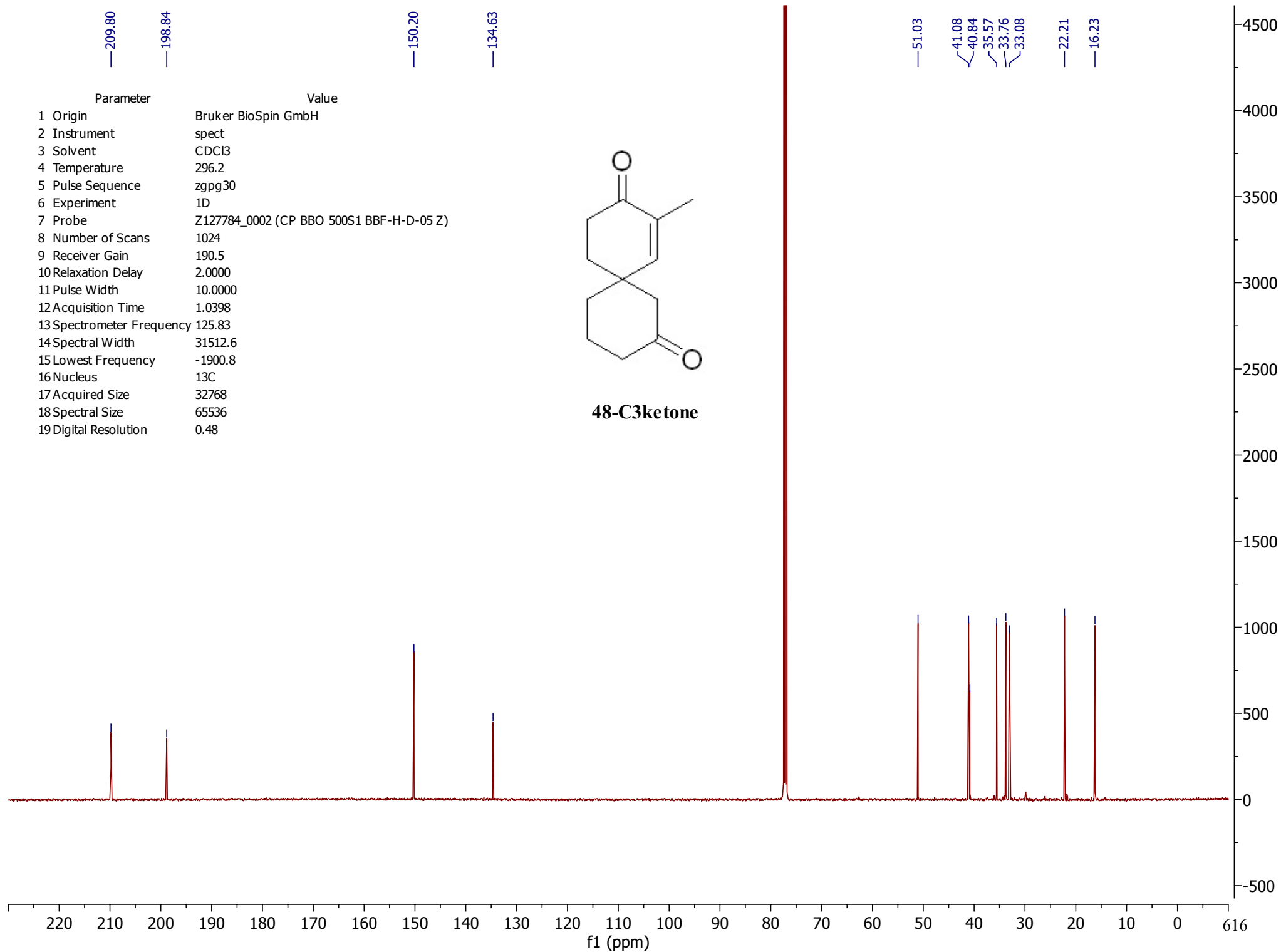
48-C3ketone



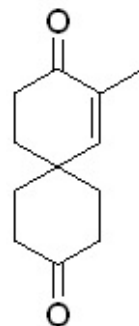
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



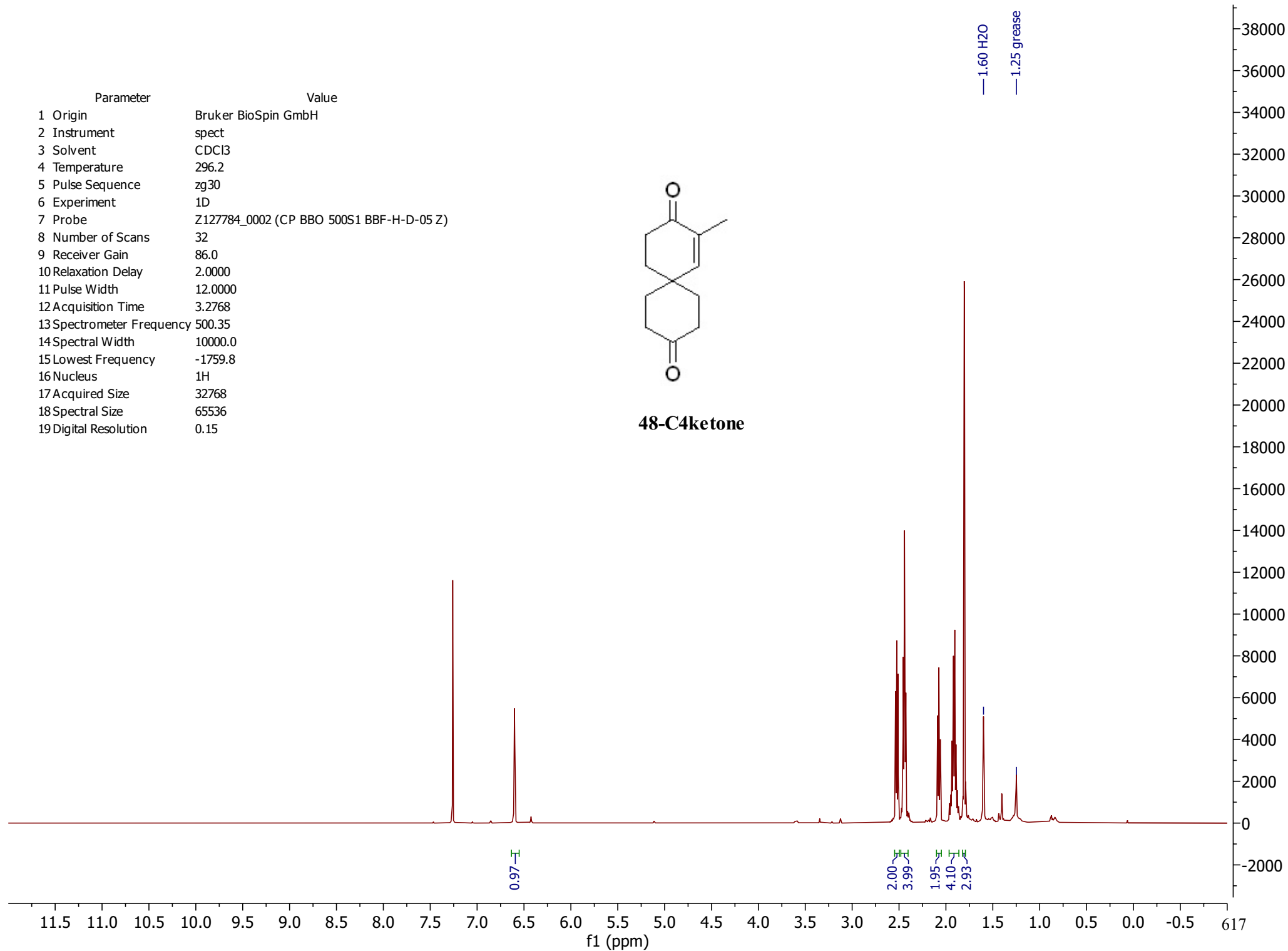
48-C3ketone



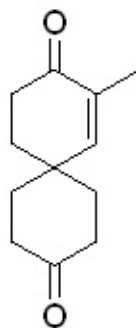
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1759.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



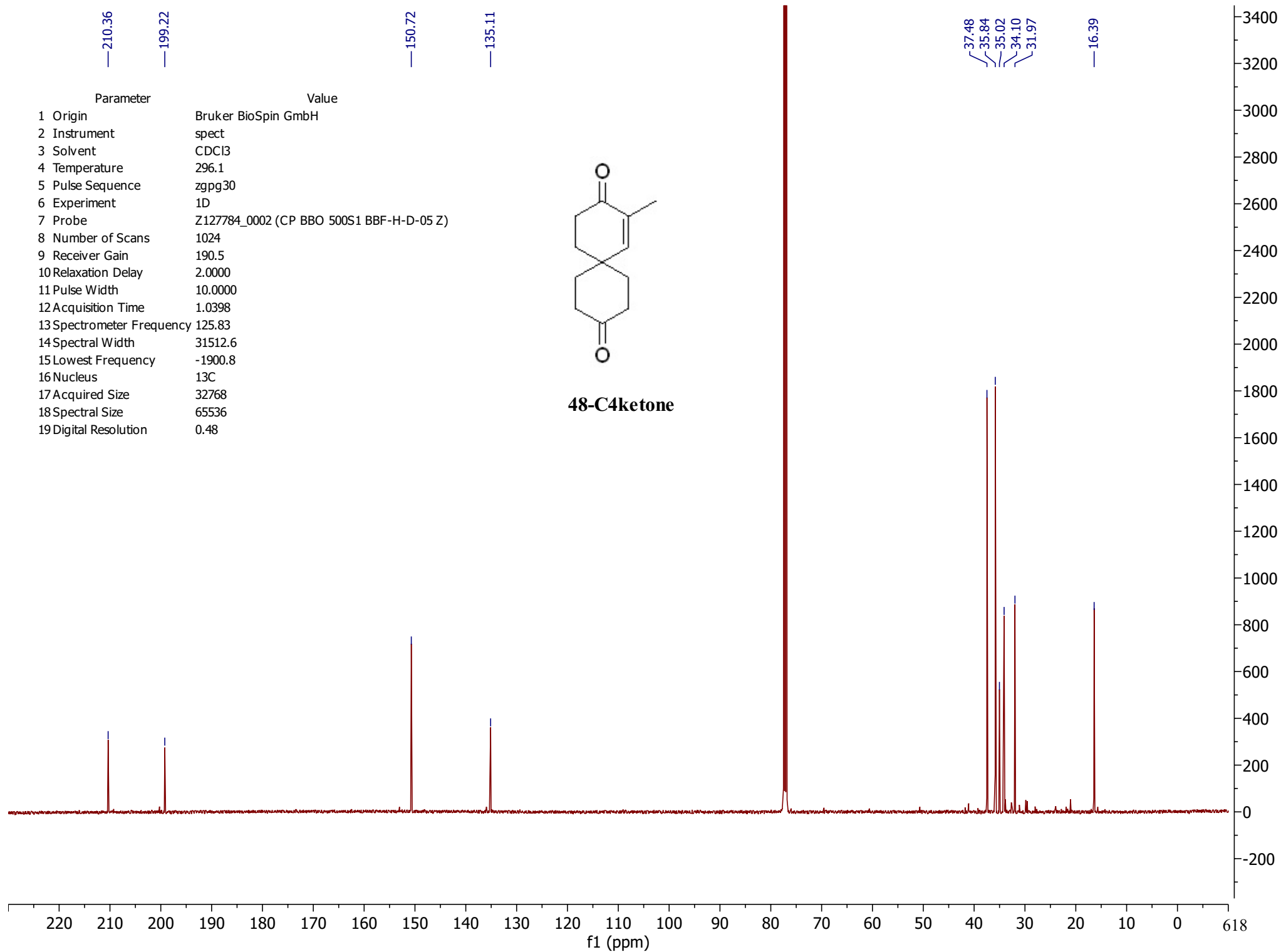
48-C4ketone



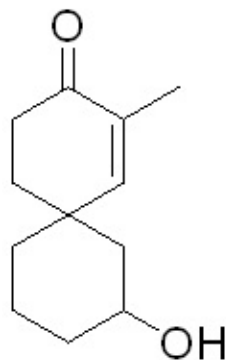
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



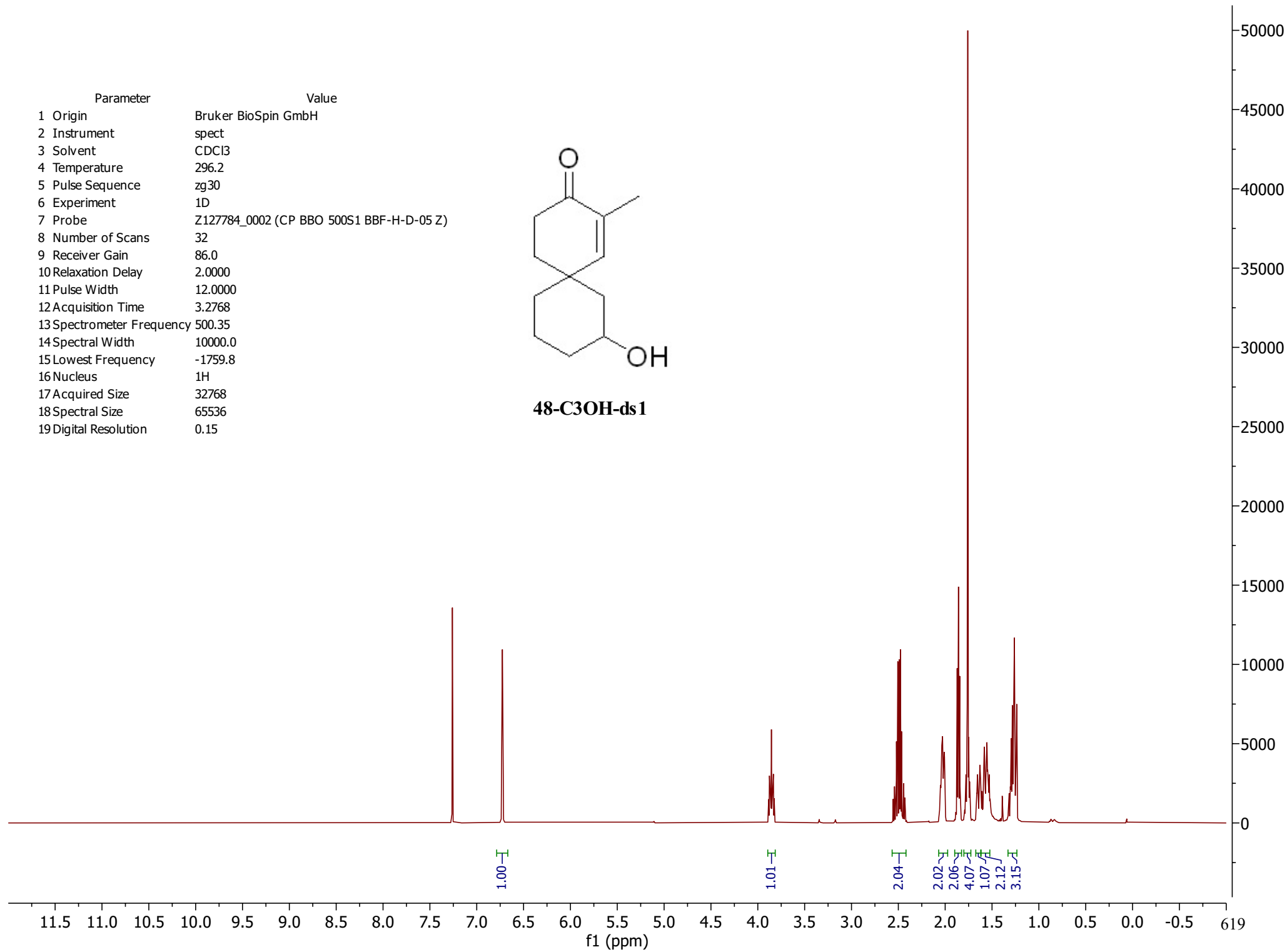
48-C4ketone



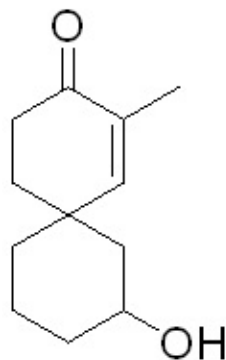
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1759.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



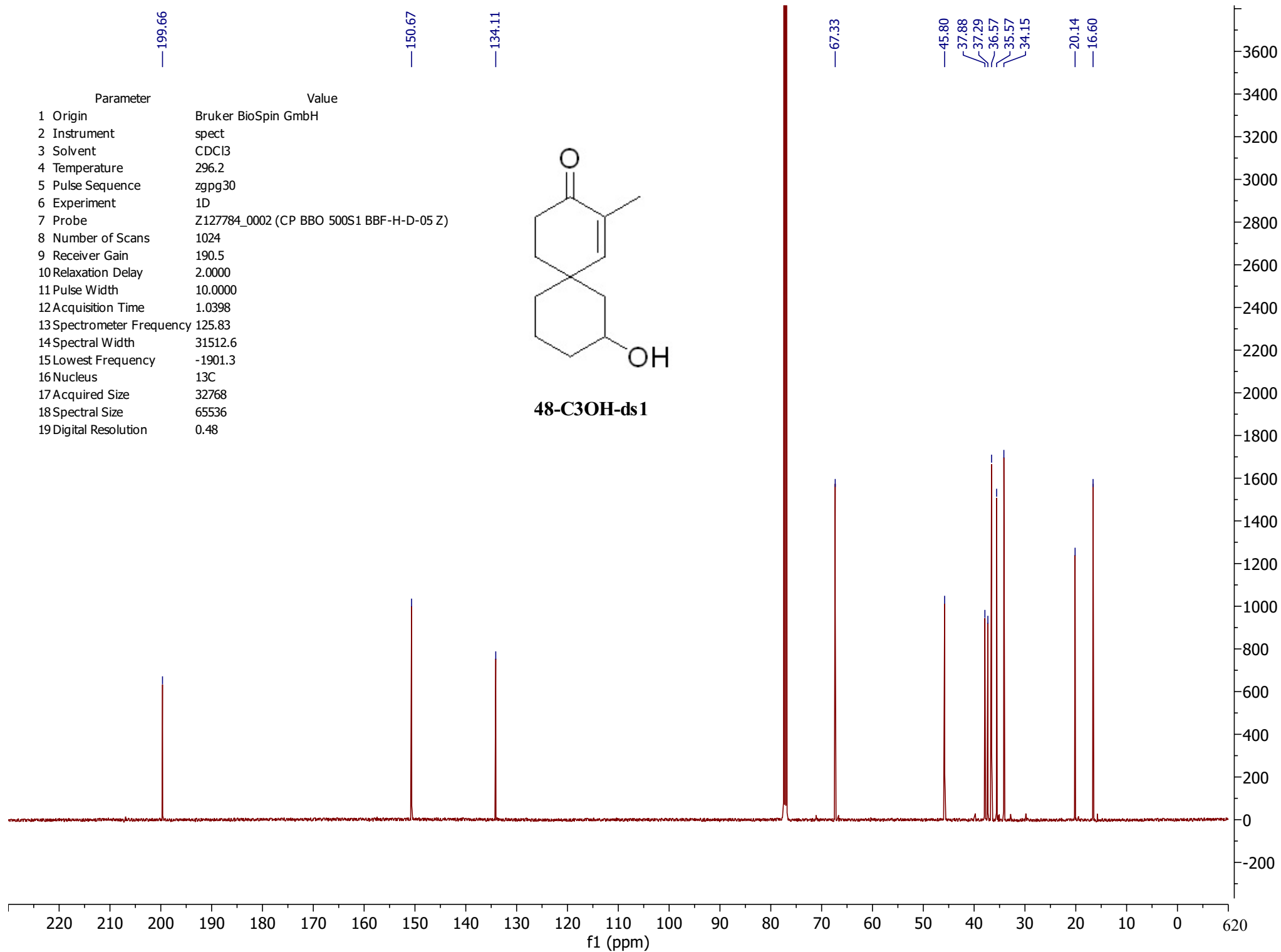
48-C3OH-ds1



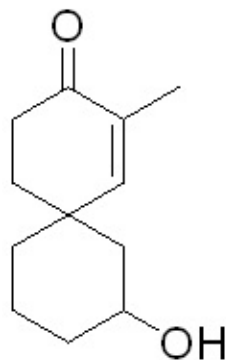
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1901.3
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



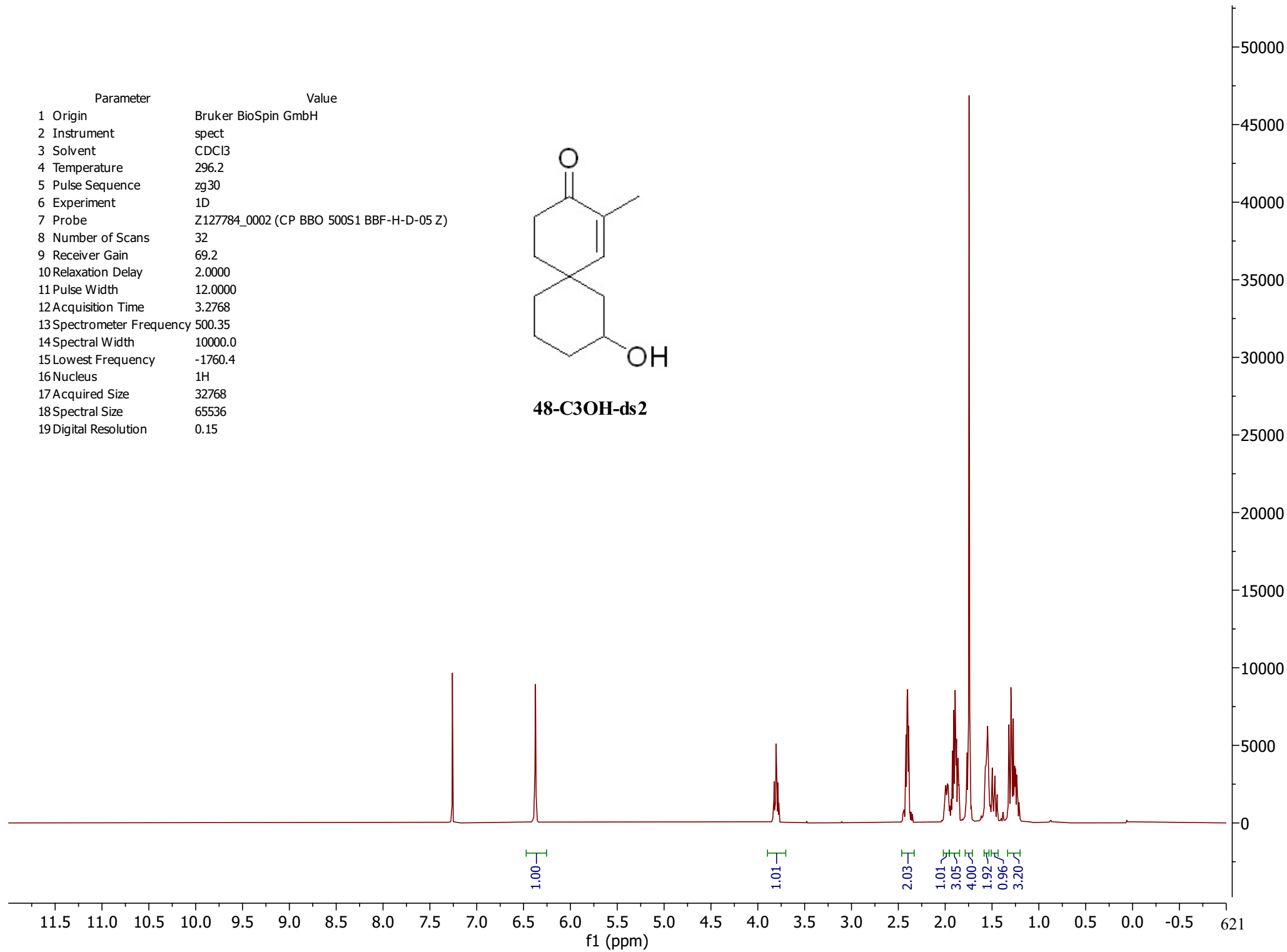
48-C3OH-ds1



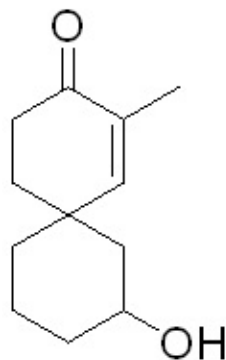
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	69.2
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1760.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



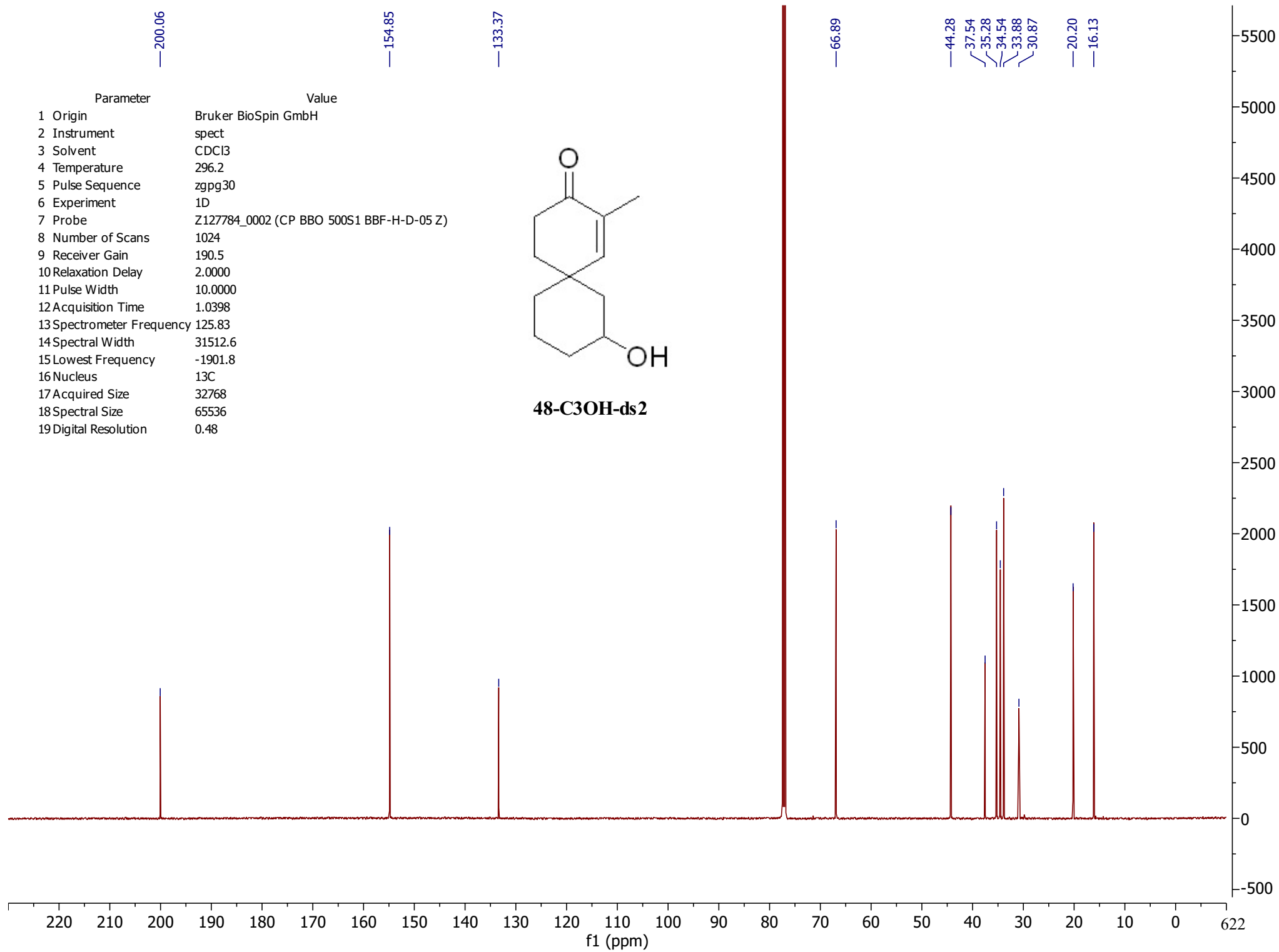
48-C3OH-ds2



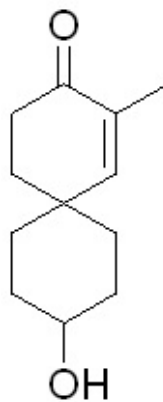
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1901.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



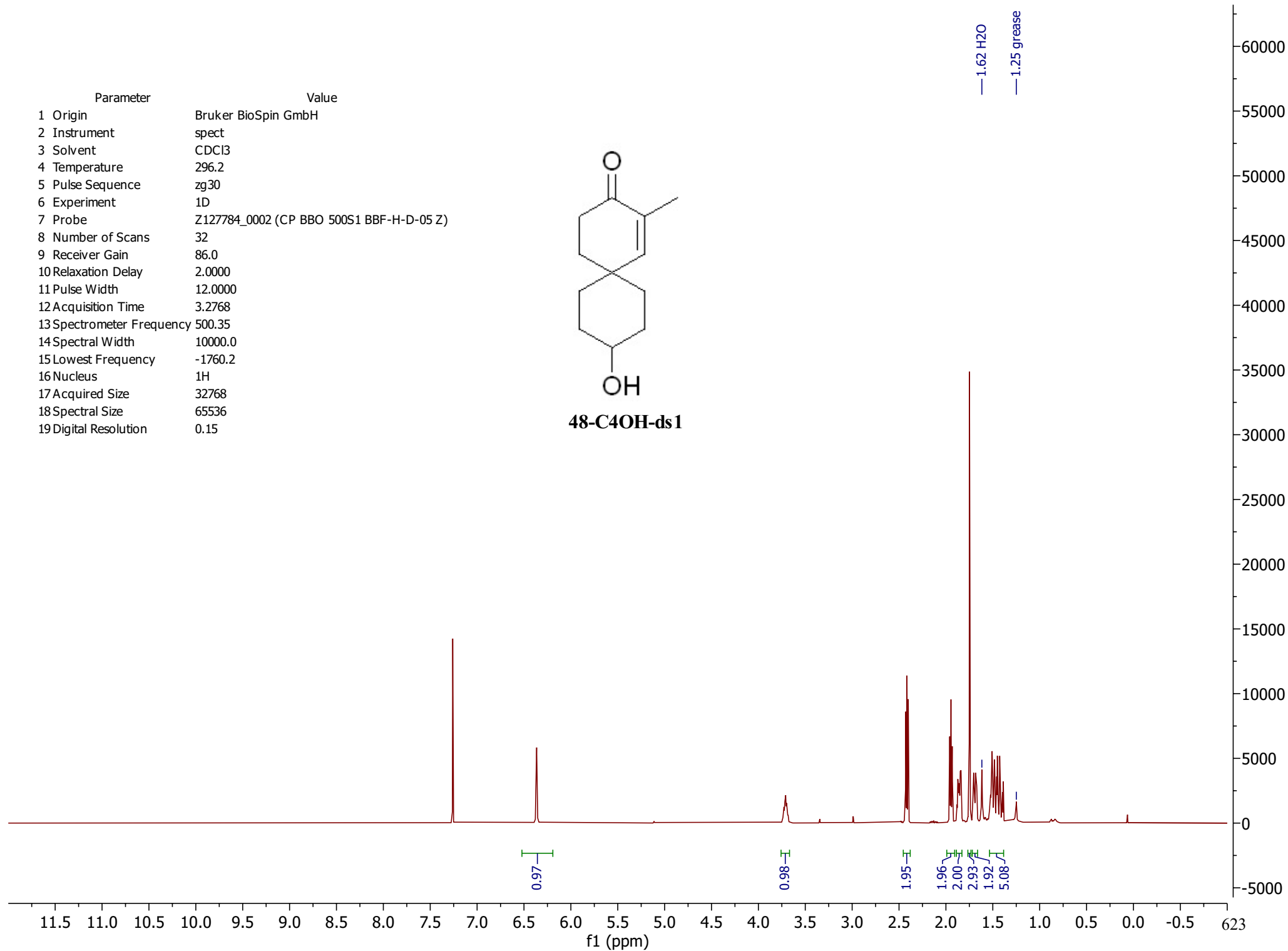
48-C3OH-ds2



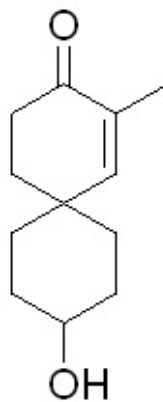
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1760.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



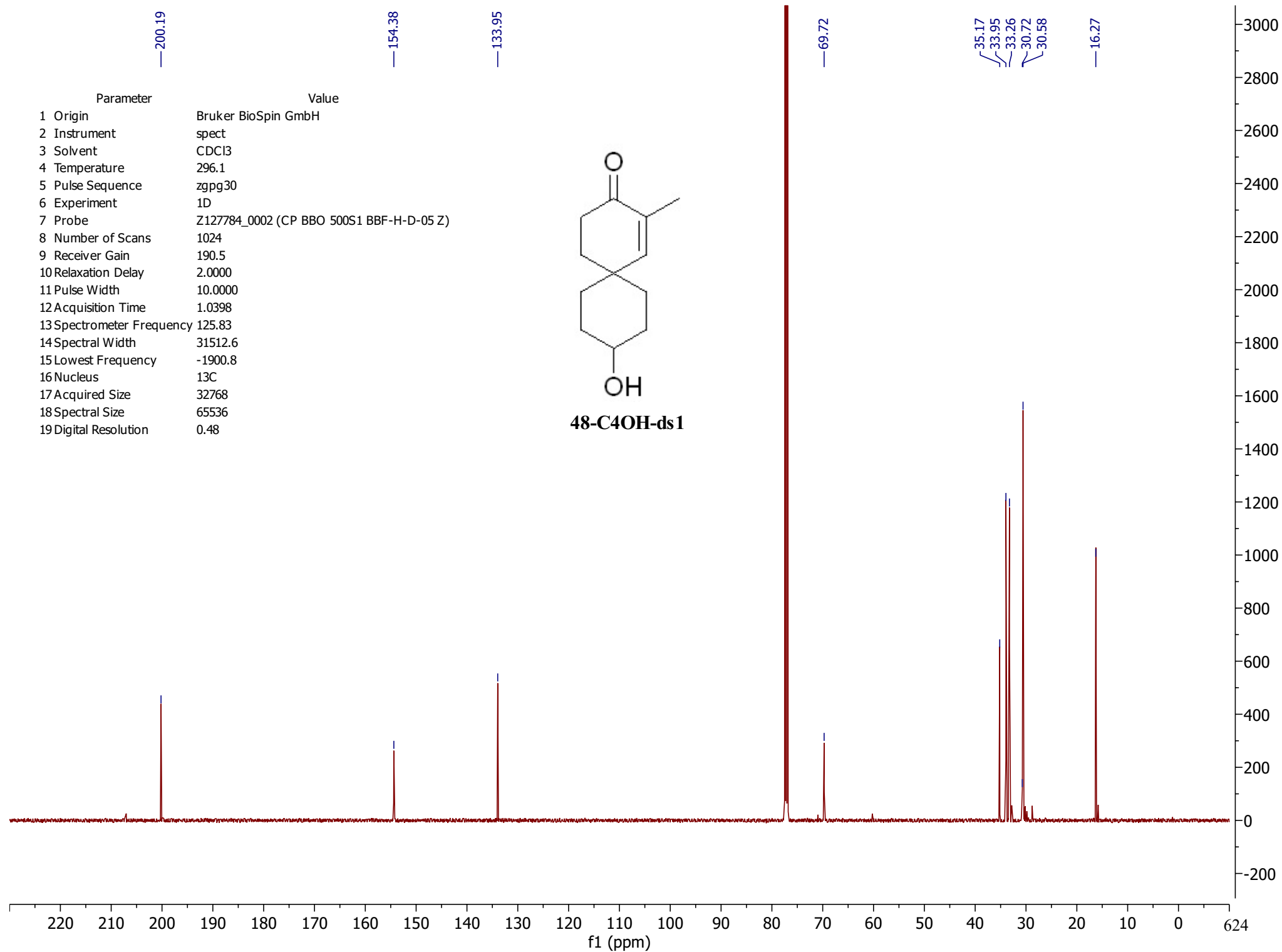
48-C4OH-ds1



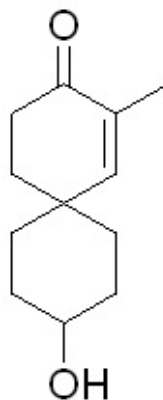
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.8
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



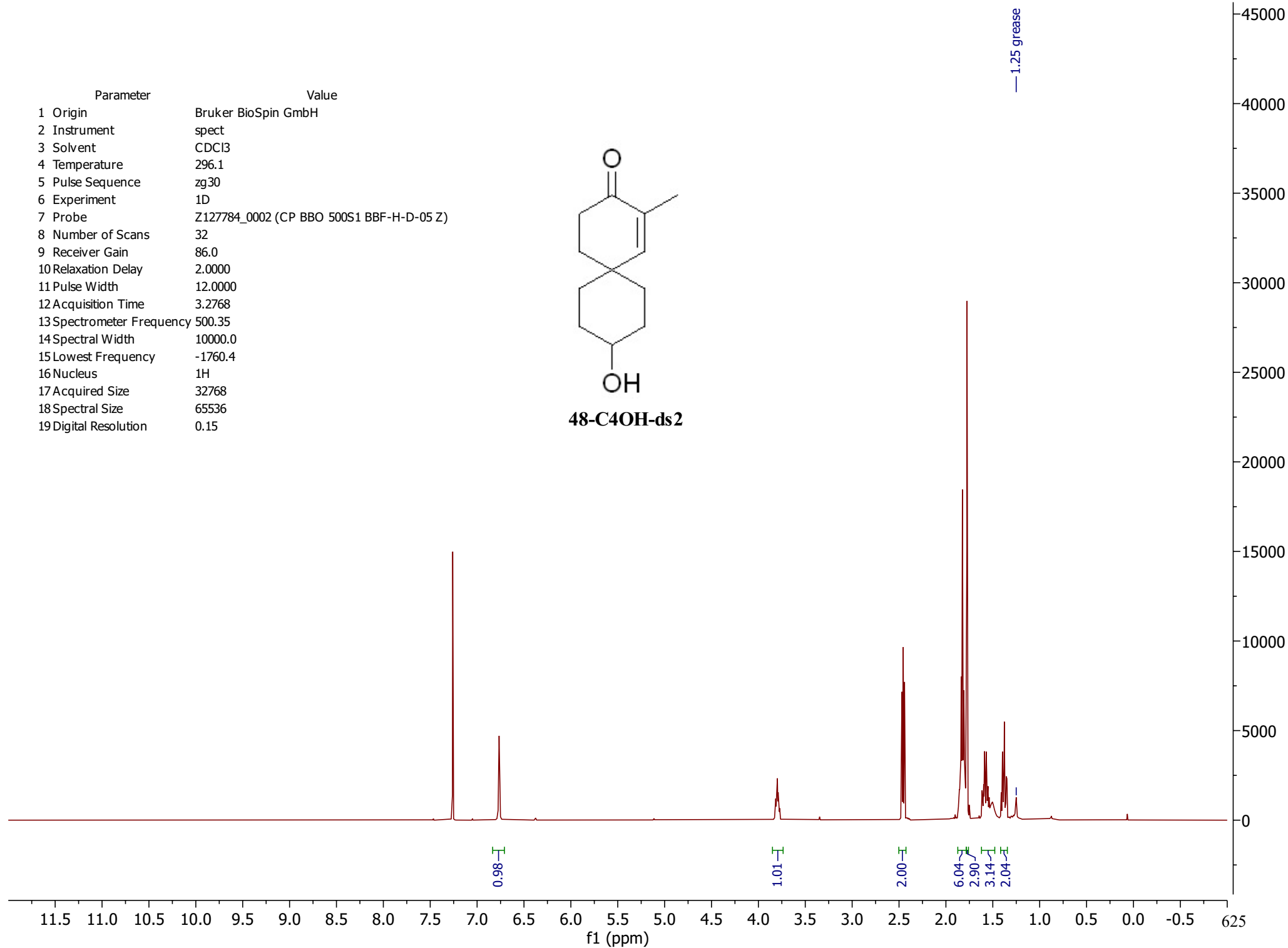
48-C4OH-ds1



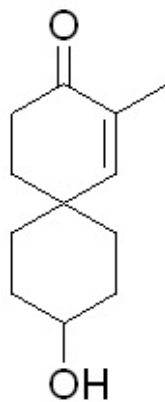
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1760.4
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



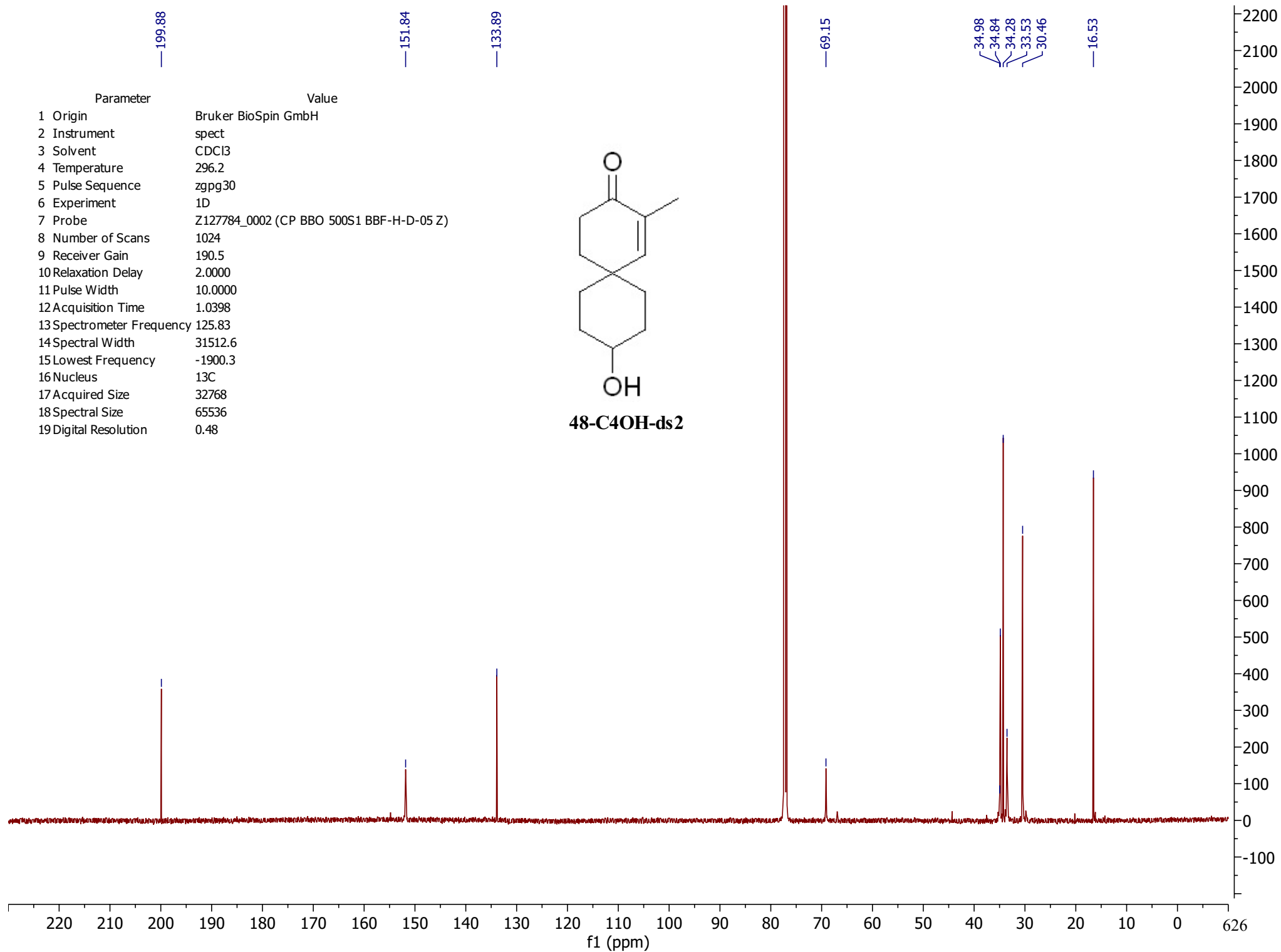
48-C4OH-ds2



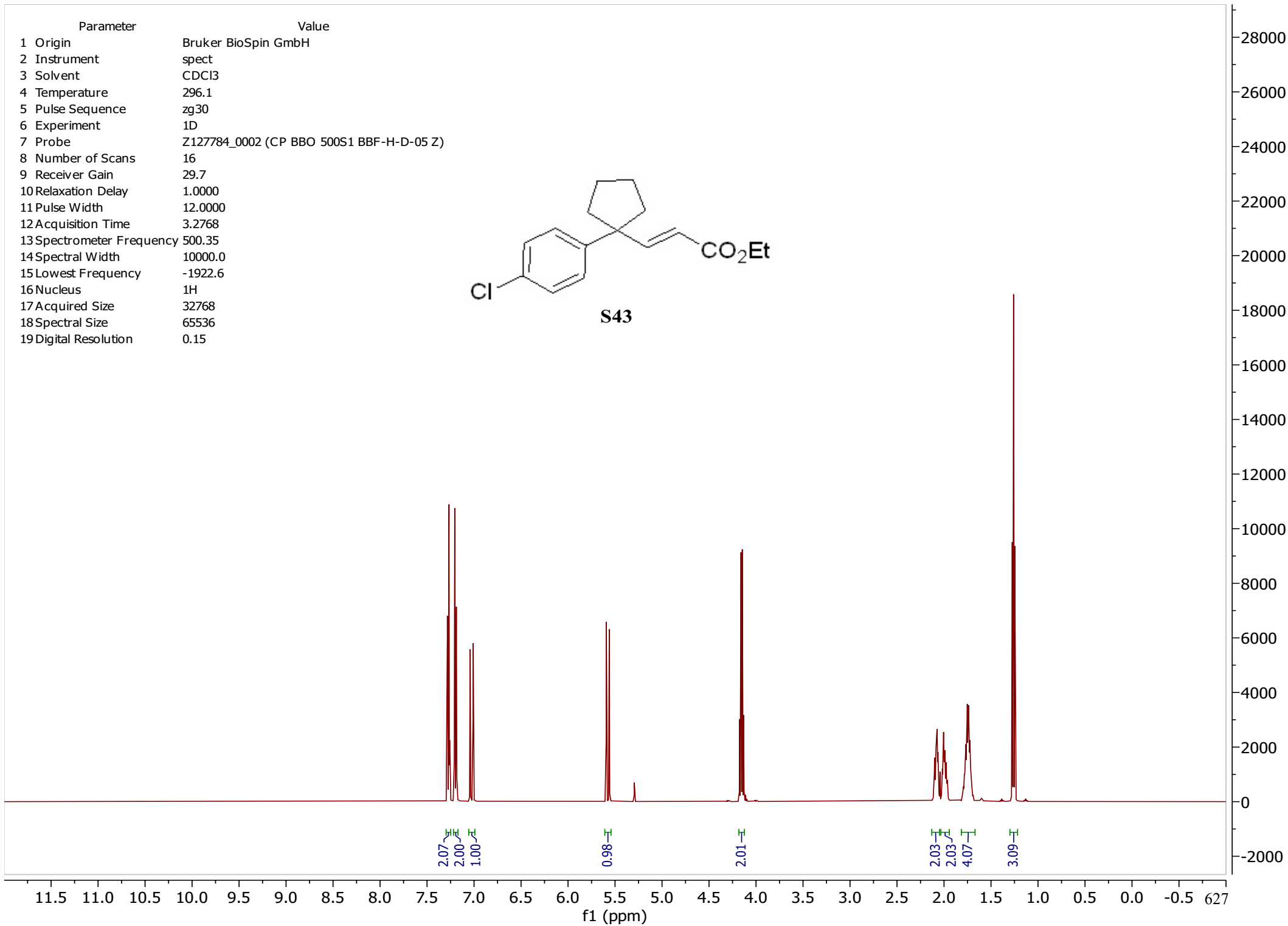
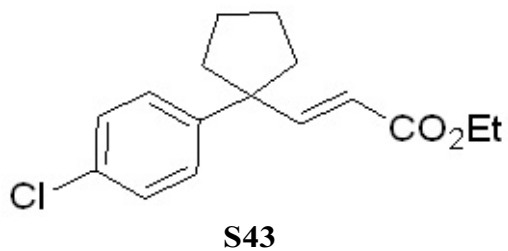
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.3
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



48-C4OH-ds2



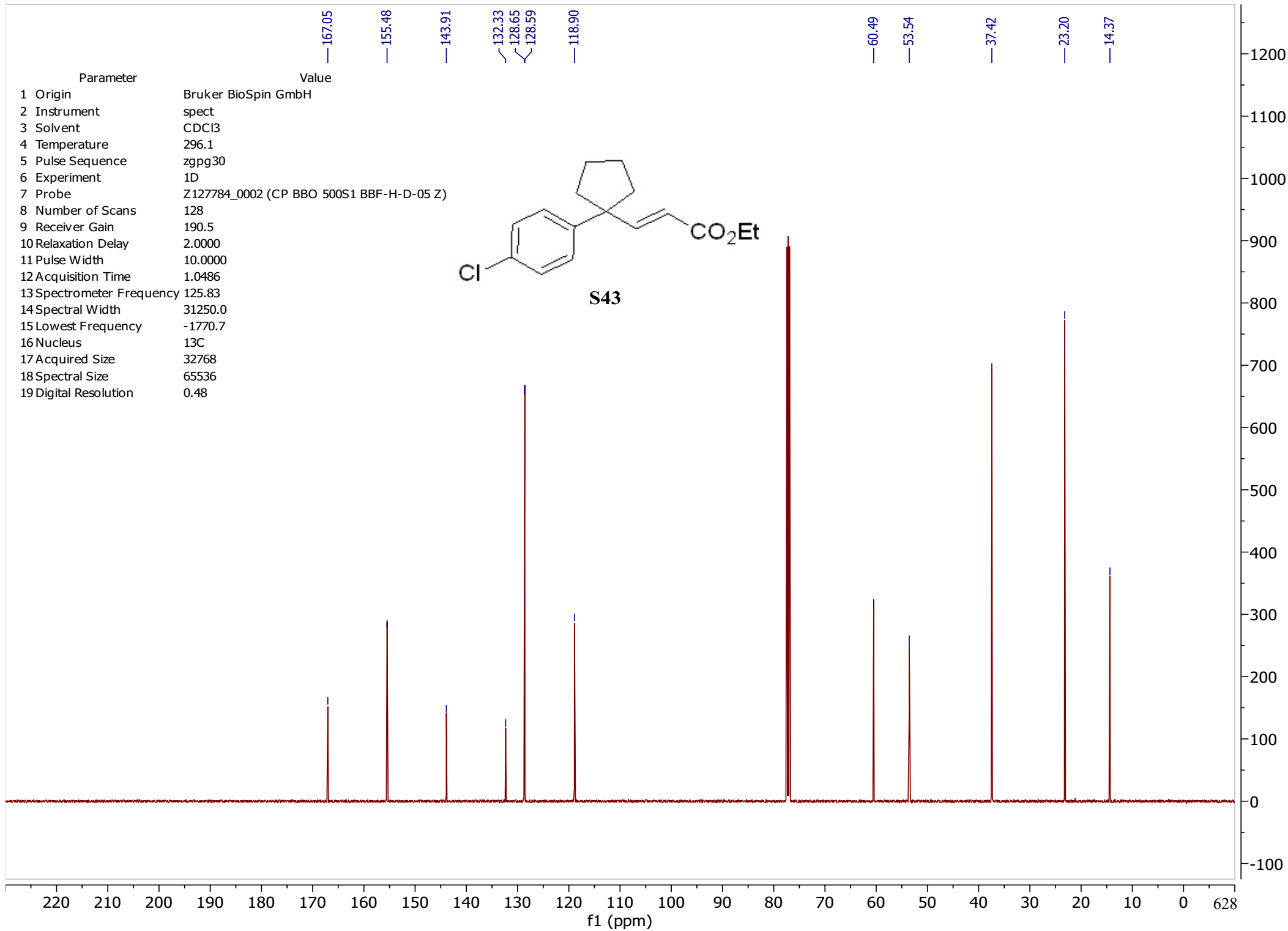
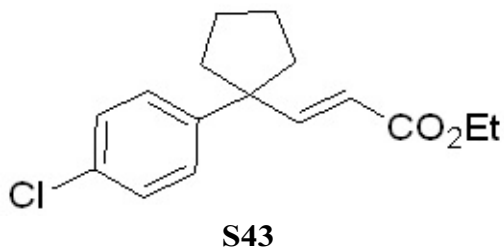
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



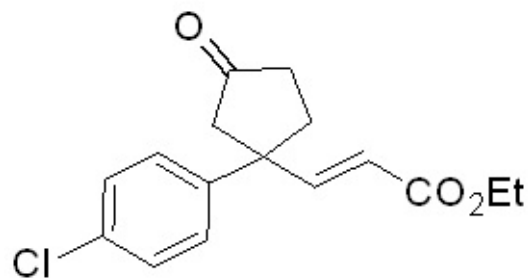
Parameter

Value

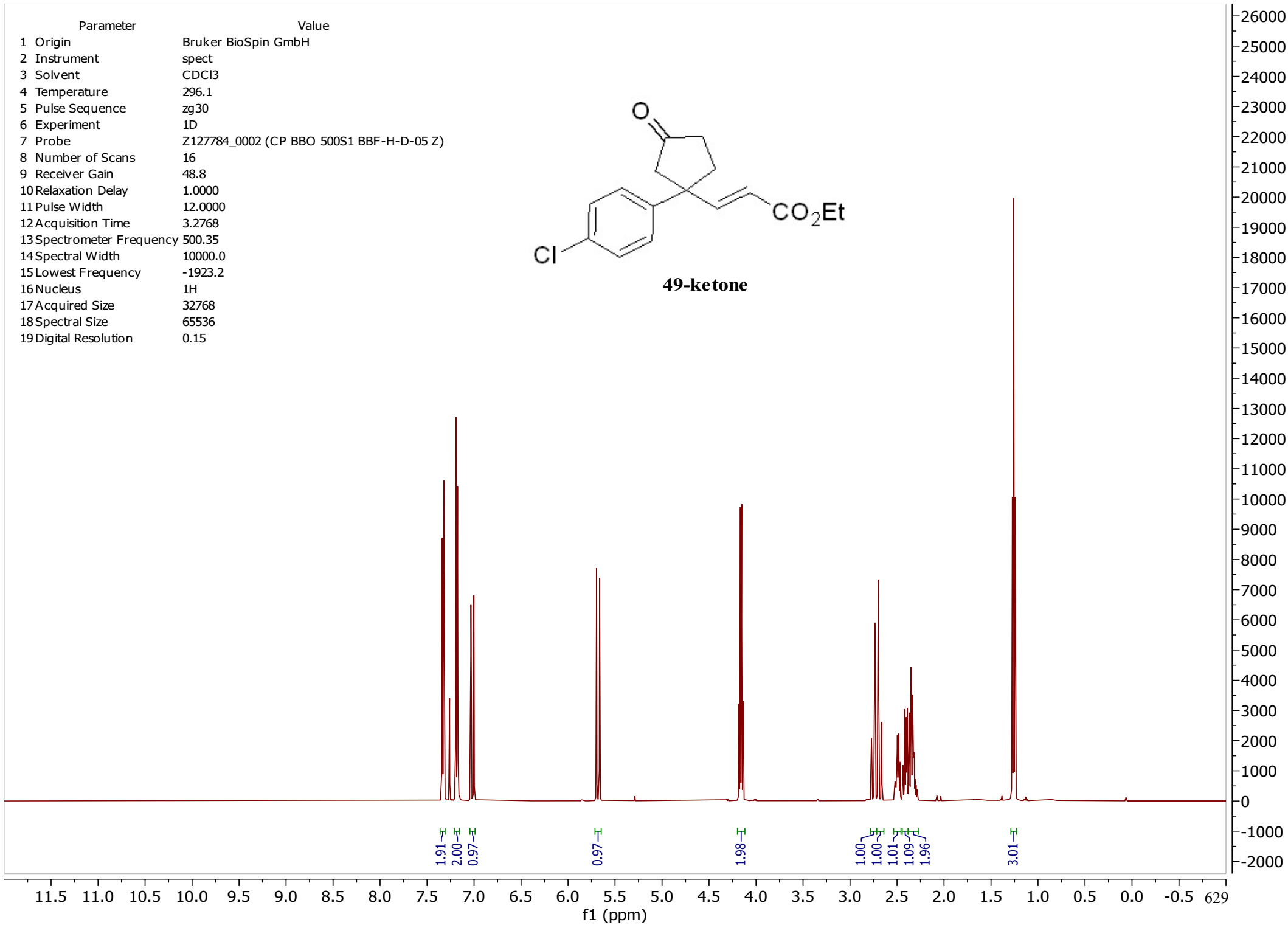
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	128
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1770.7
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

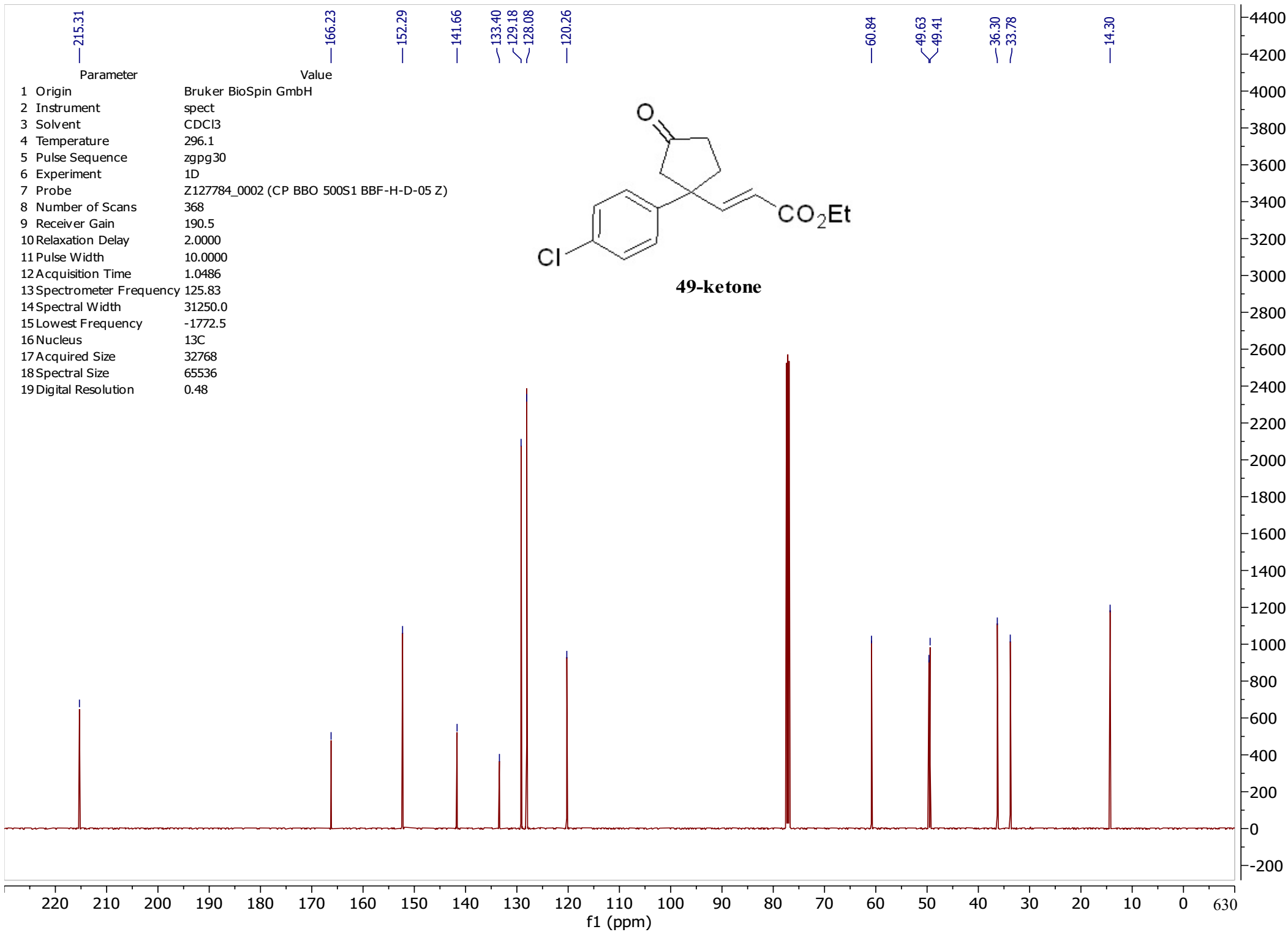


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	48.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

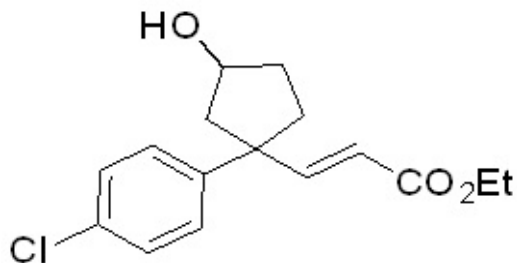


49-ketone

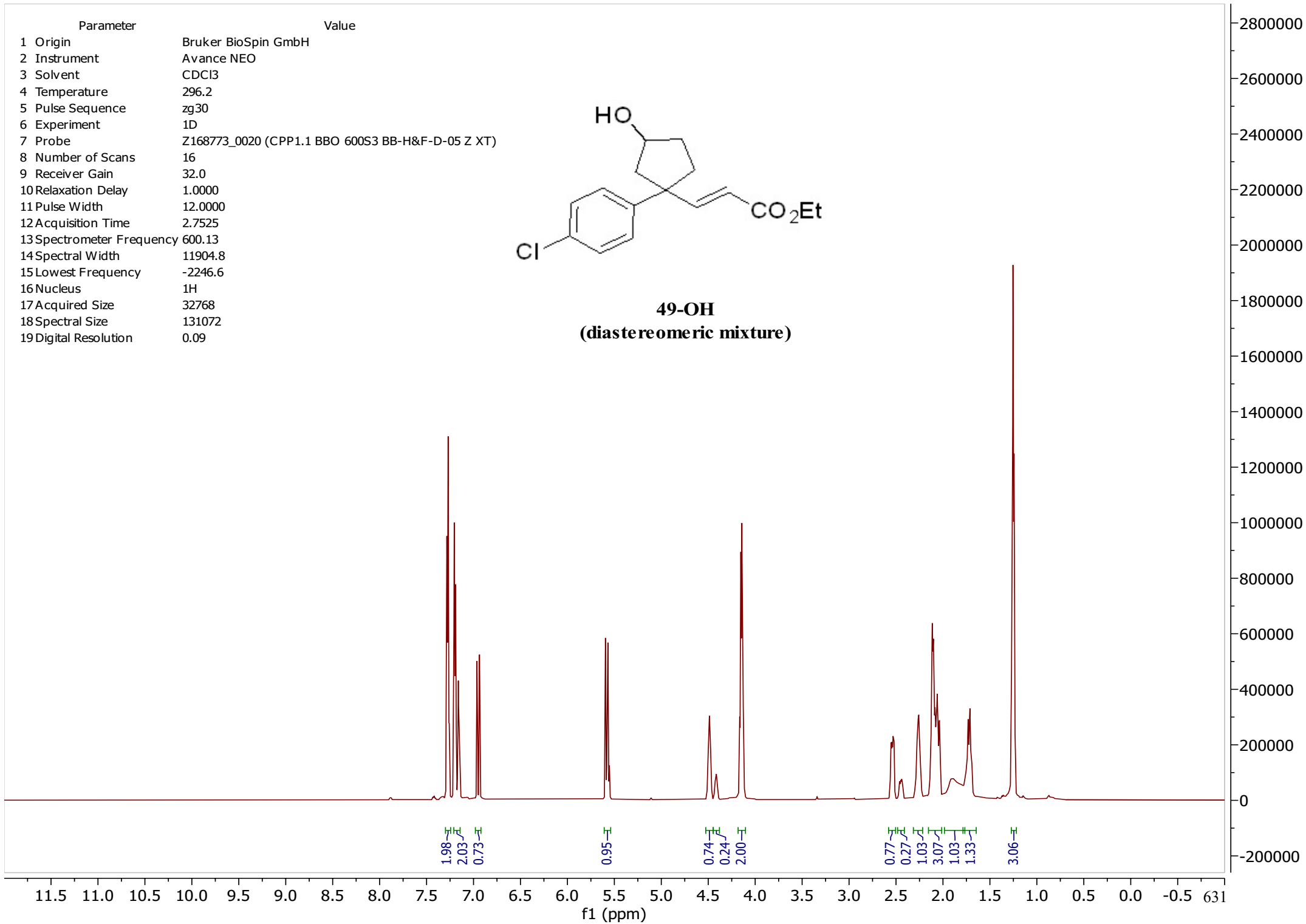




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



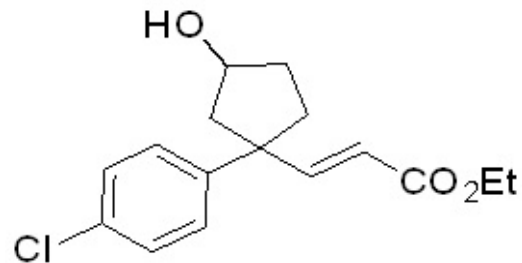
49-OH
(diastereomeric mixture)



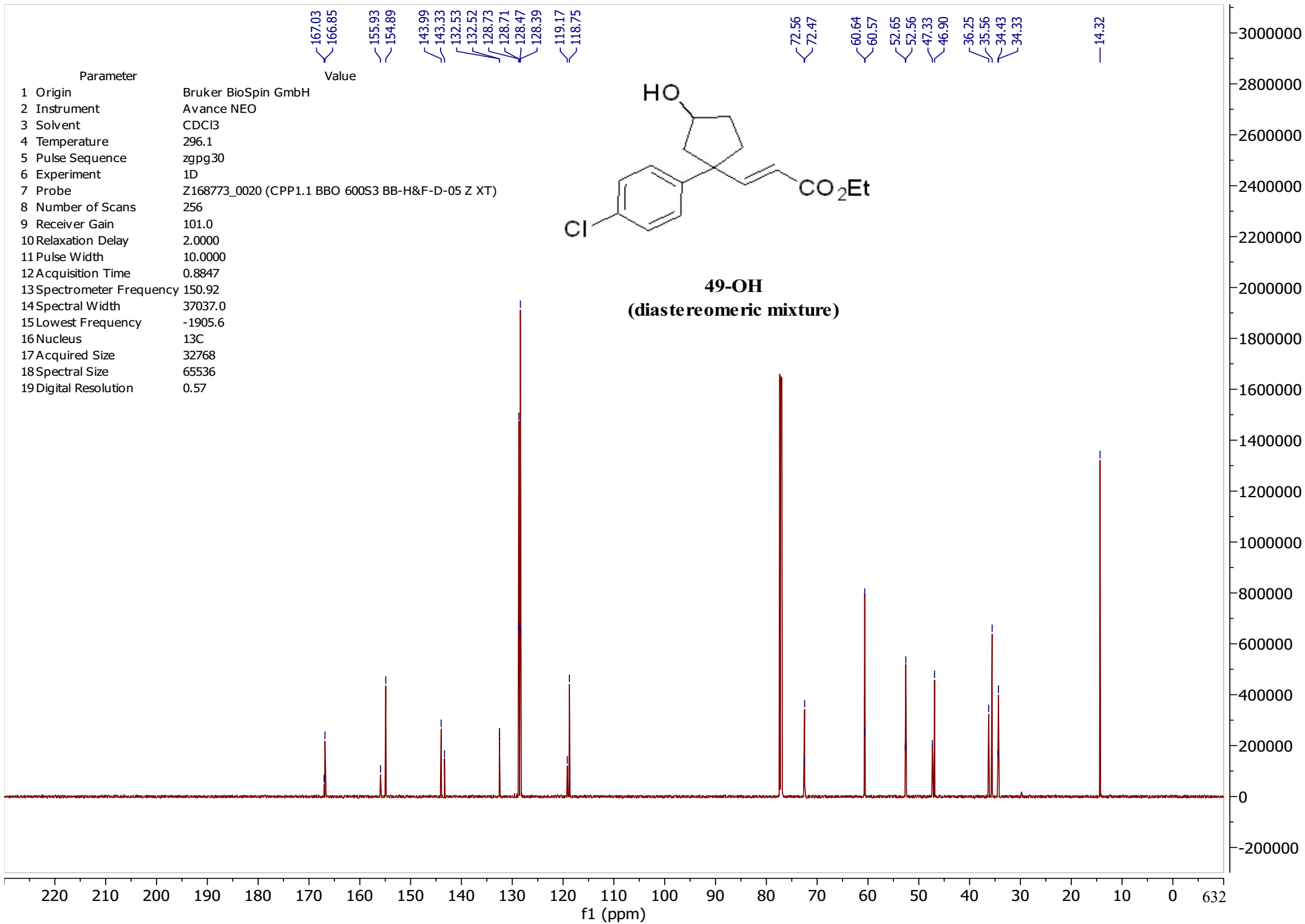
Parameter

1	Origin	Bruker BioSpin GmbH
2	Instrument	Avance NEO
3	Solvent	CDCl ₃
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8	Number of Scans	256
9	Receiver Gain	101.0
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	0.8847
13	Spectrometer Frequency	150.92
14	Spectral Width	37037.0
15	Lowest Frequency	-1905.6
16	Nucleus	¹³ C
17	Acquired Size	32768
18	Spectral Size	65536
19	Digital Resolution	0.57

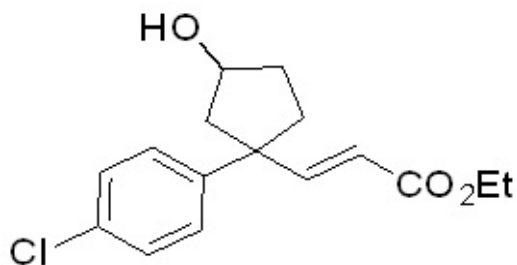
Value



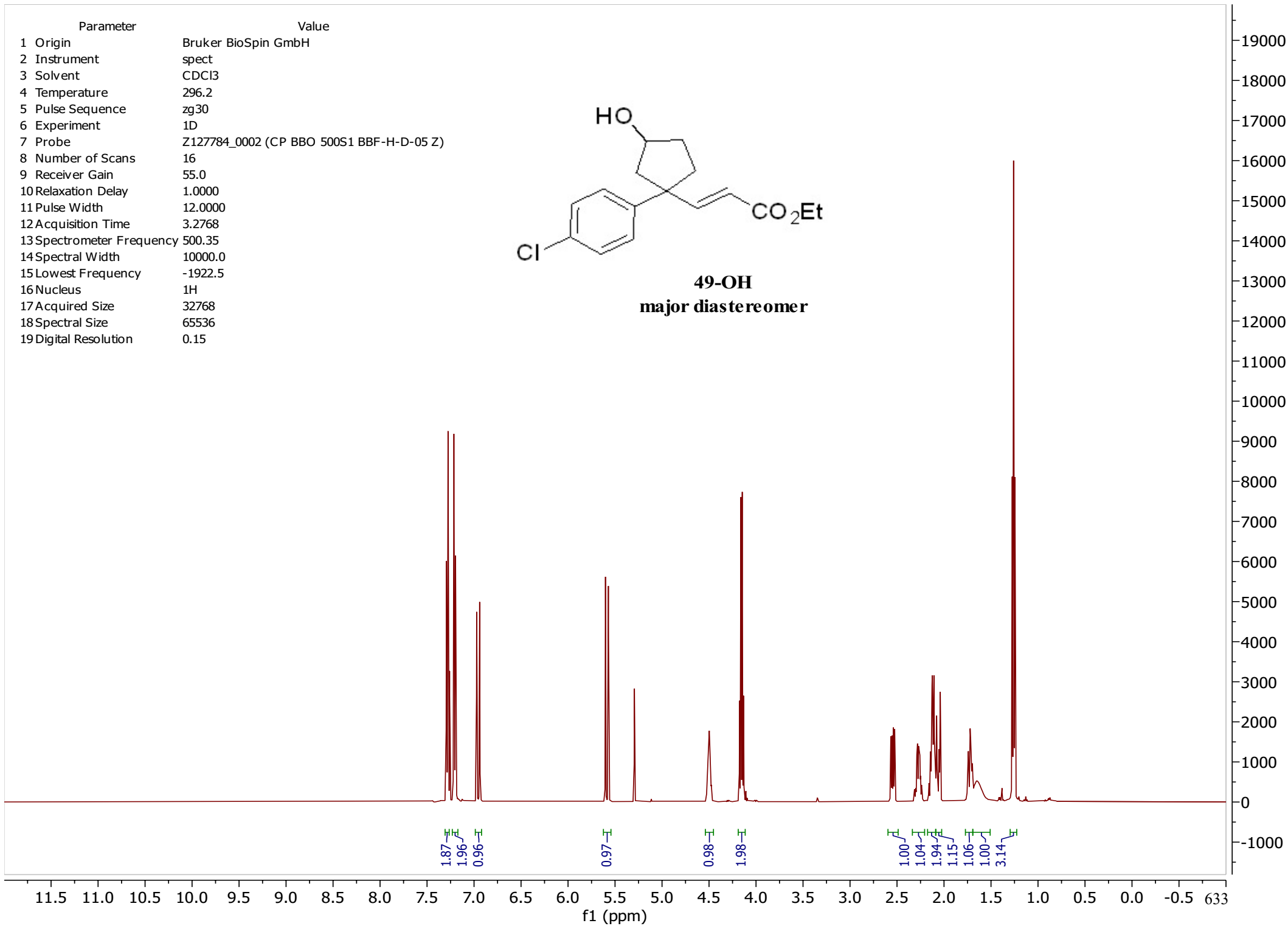
49-OH
(diastereomeric mixture)



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	55.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

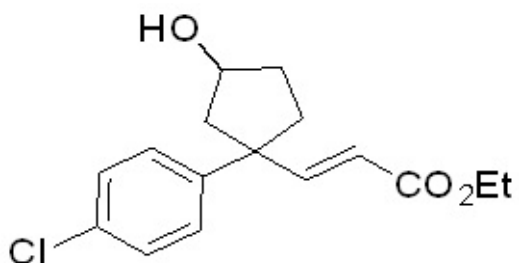


49-OH
major diastereomer

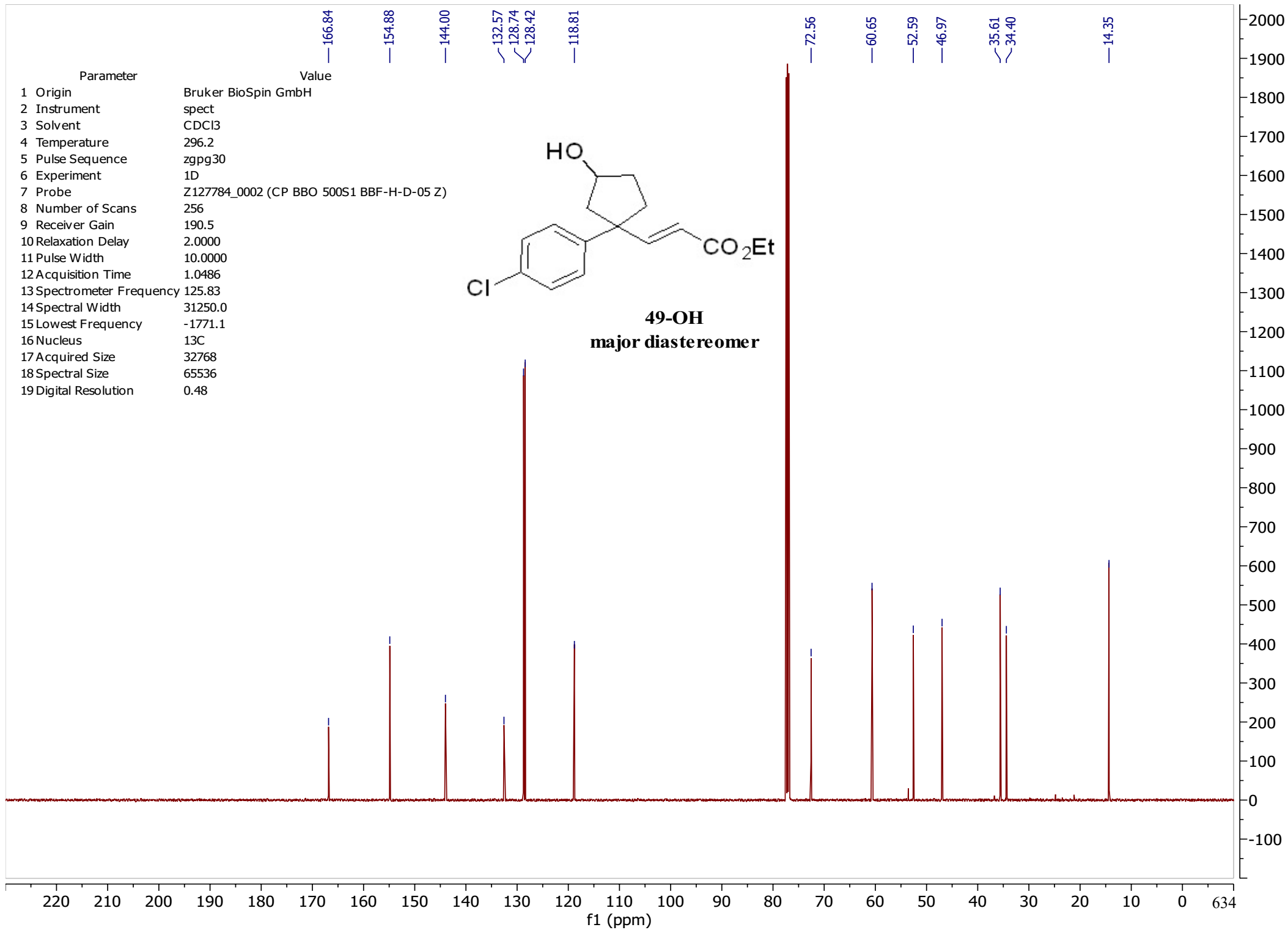


Parameter Value

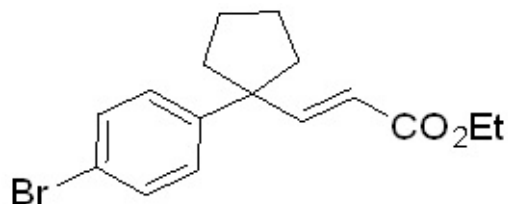
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1771.1
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



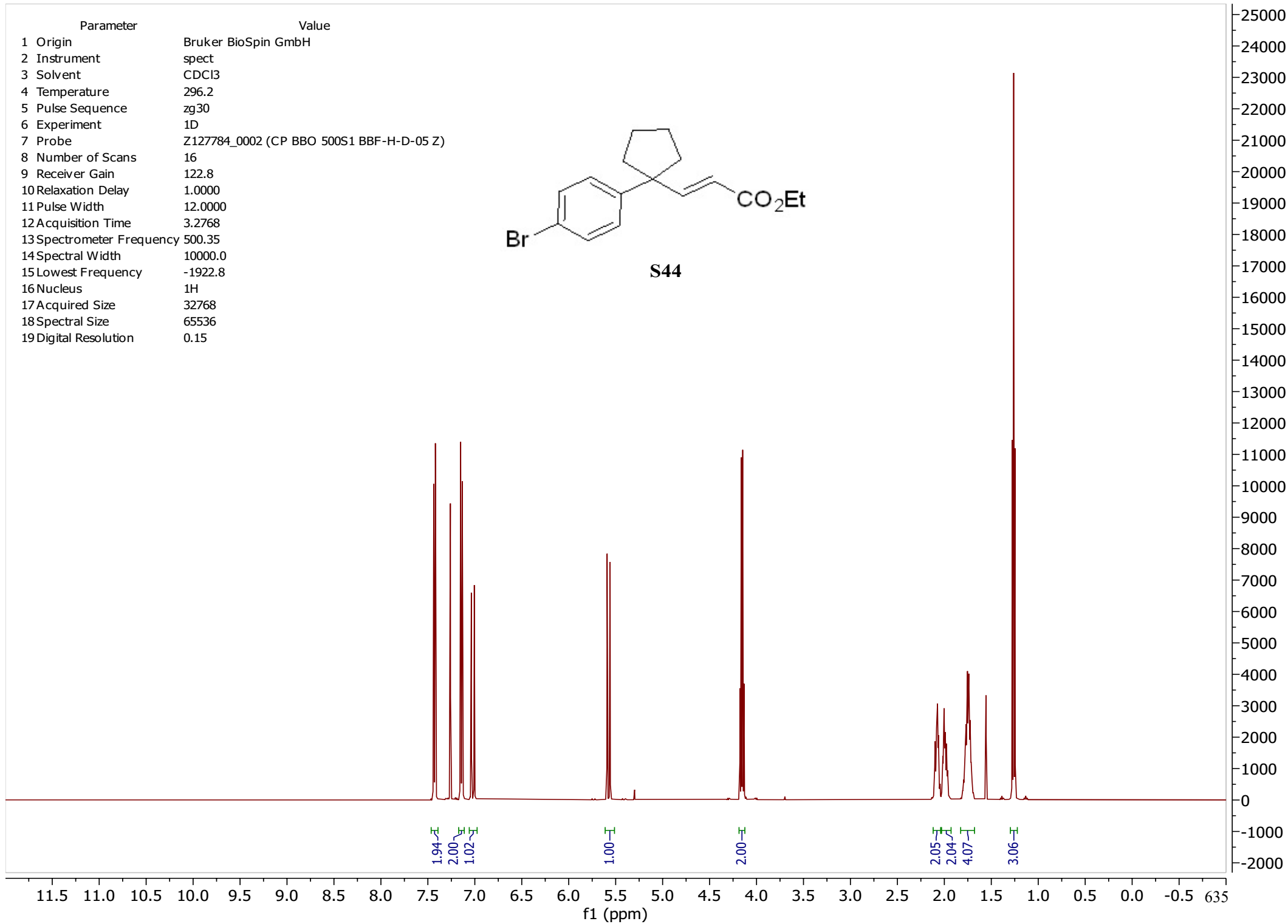
49-OH
major diastereomer



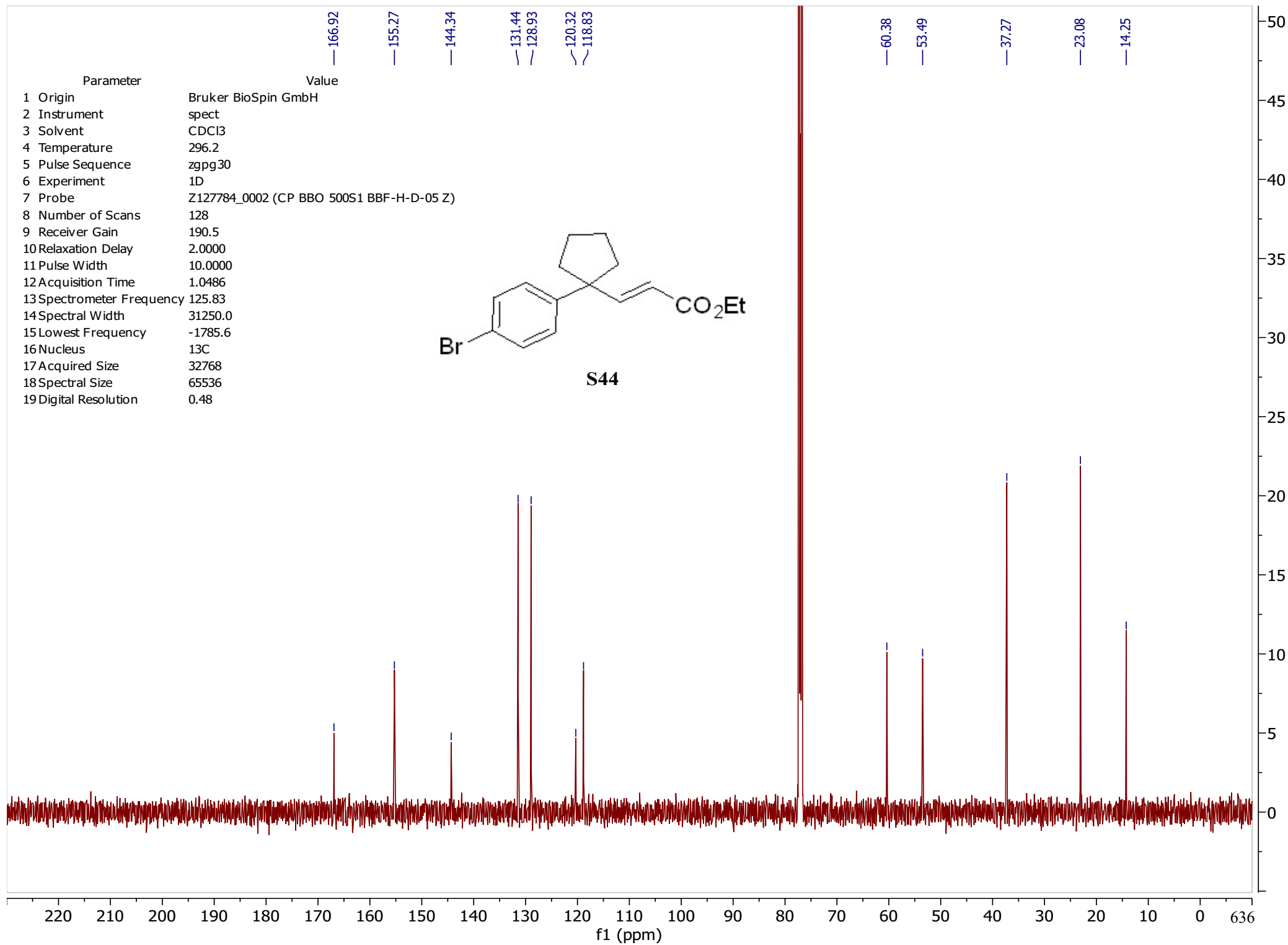
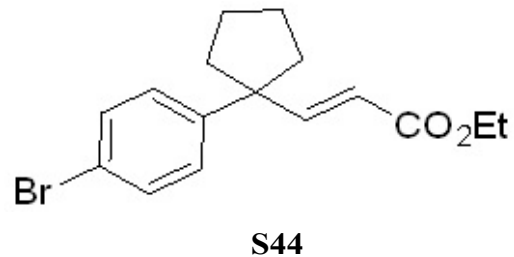
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	122.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



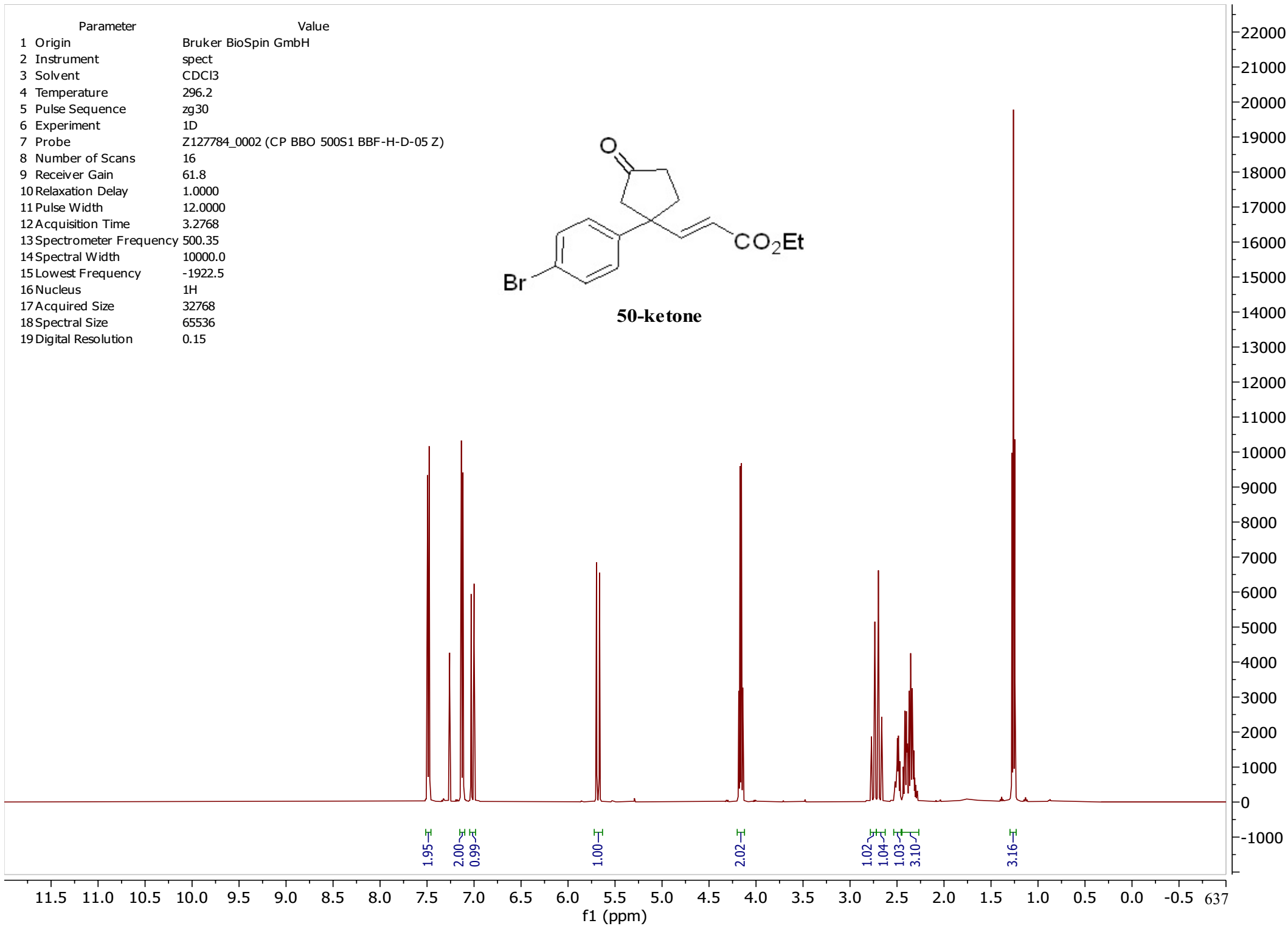
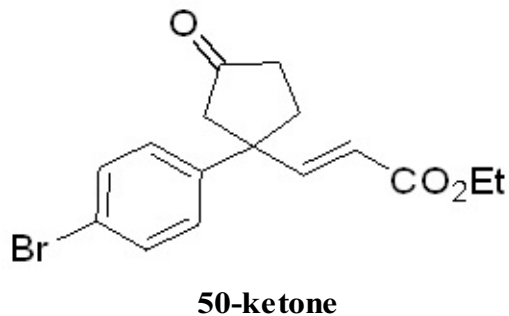
S44



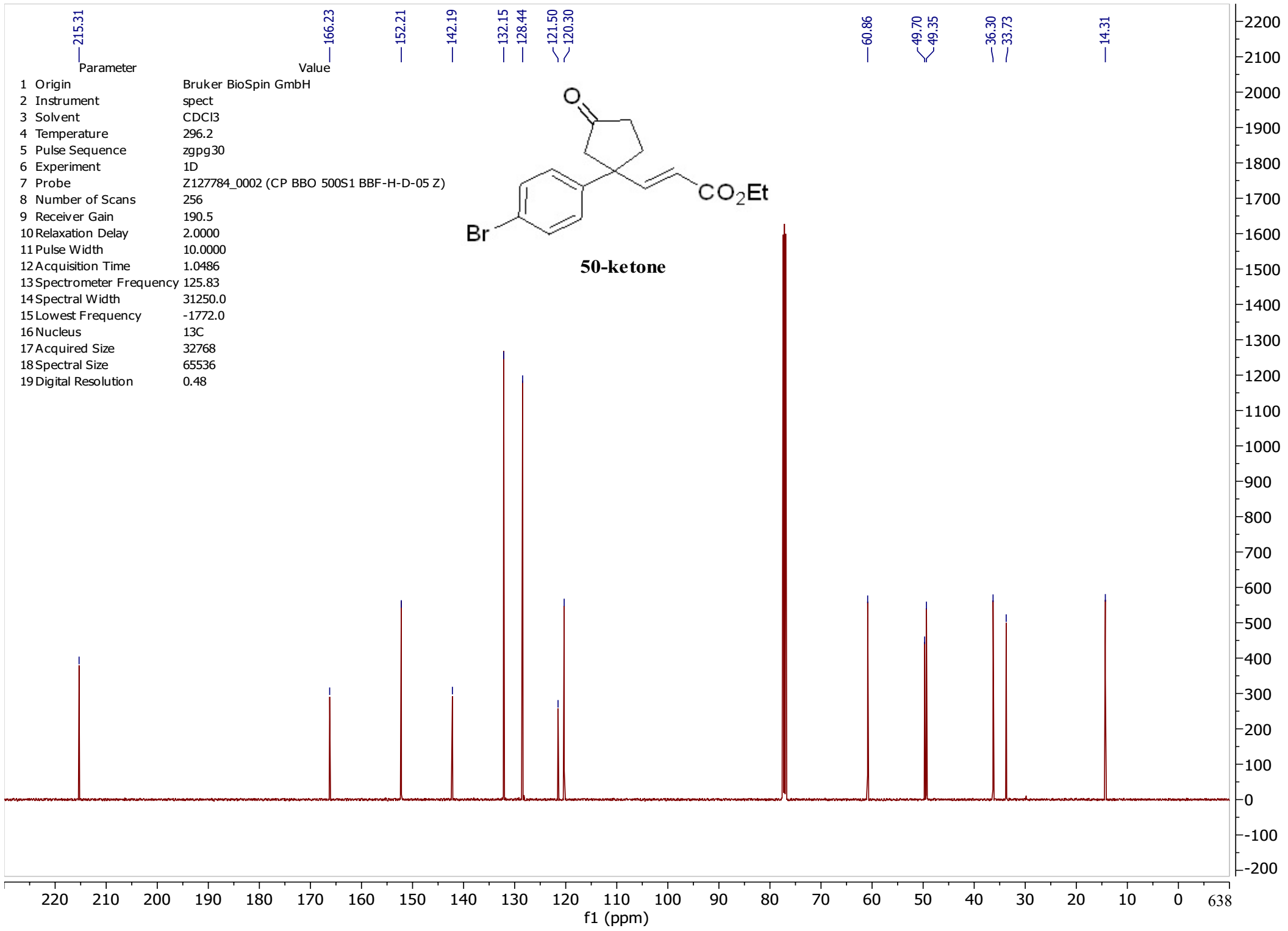
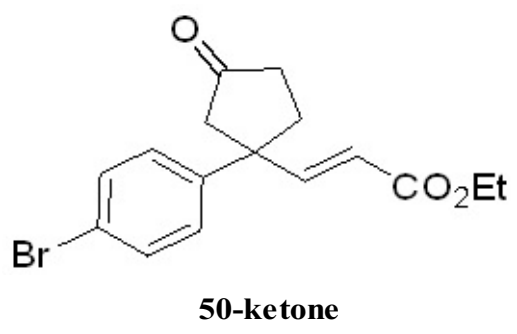
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	128
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



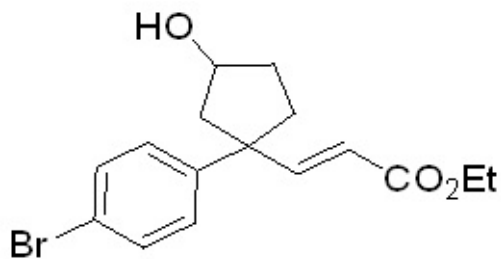
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	61.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



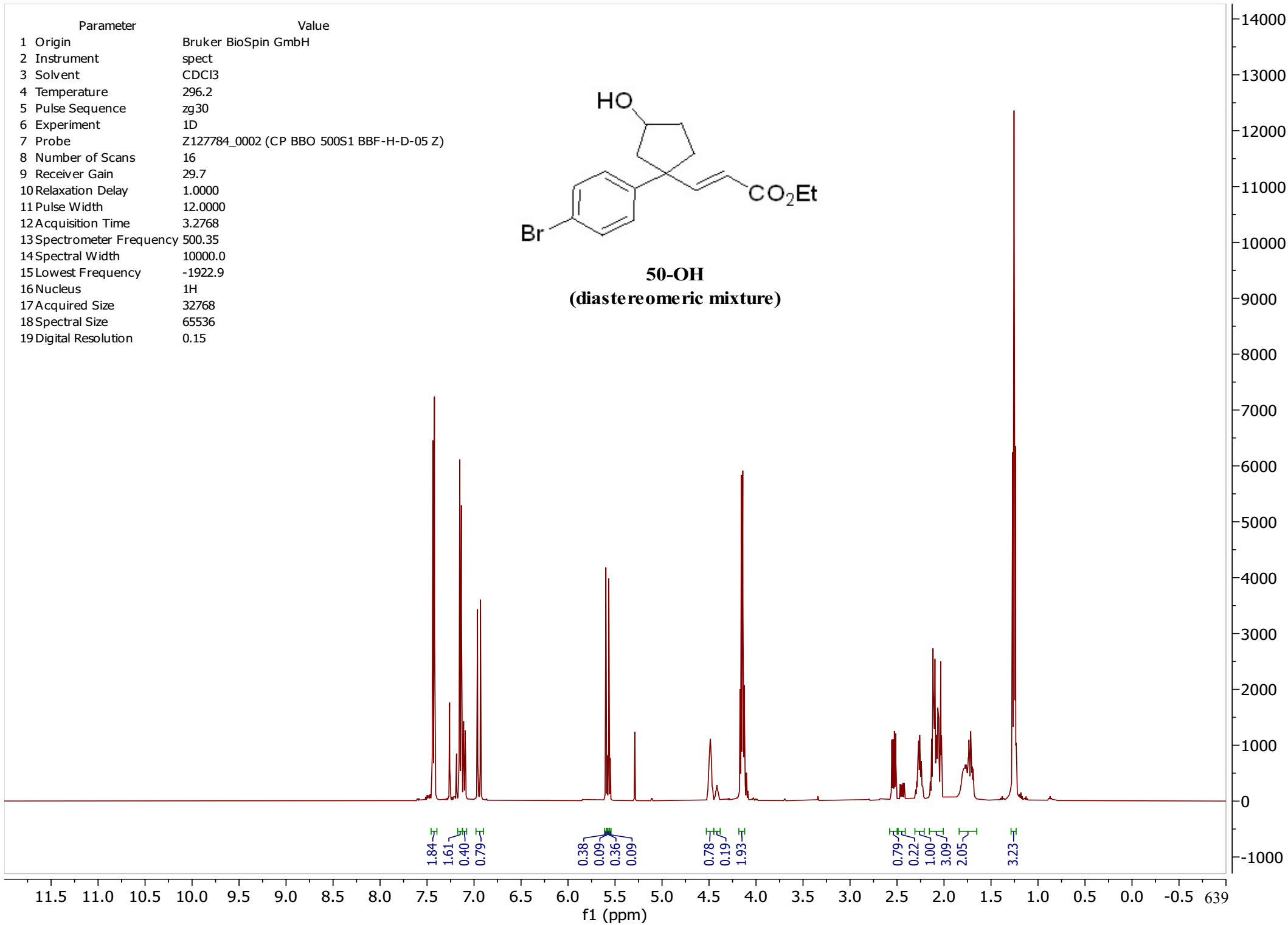
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1772.0
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



50-OH
(diastereomeric mixture)



Parameter

1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1777.4
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

Value

167.02
166.83

155.86
154.80

144.53
143.85

131.66
131.64

128.84
128.76

120.61
119.16
118.74

72.48
72.39

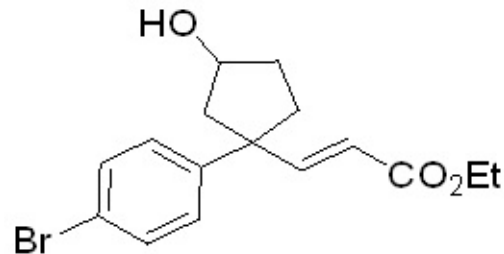
60.64
60.56

52.67
52.57

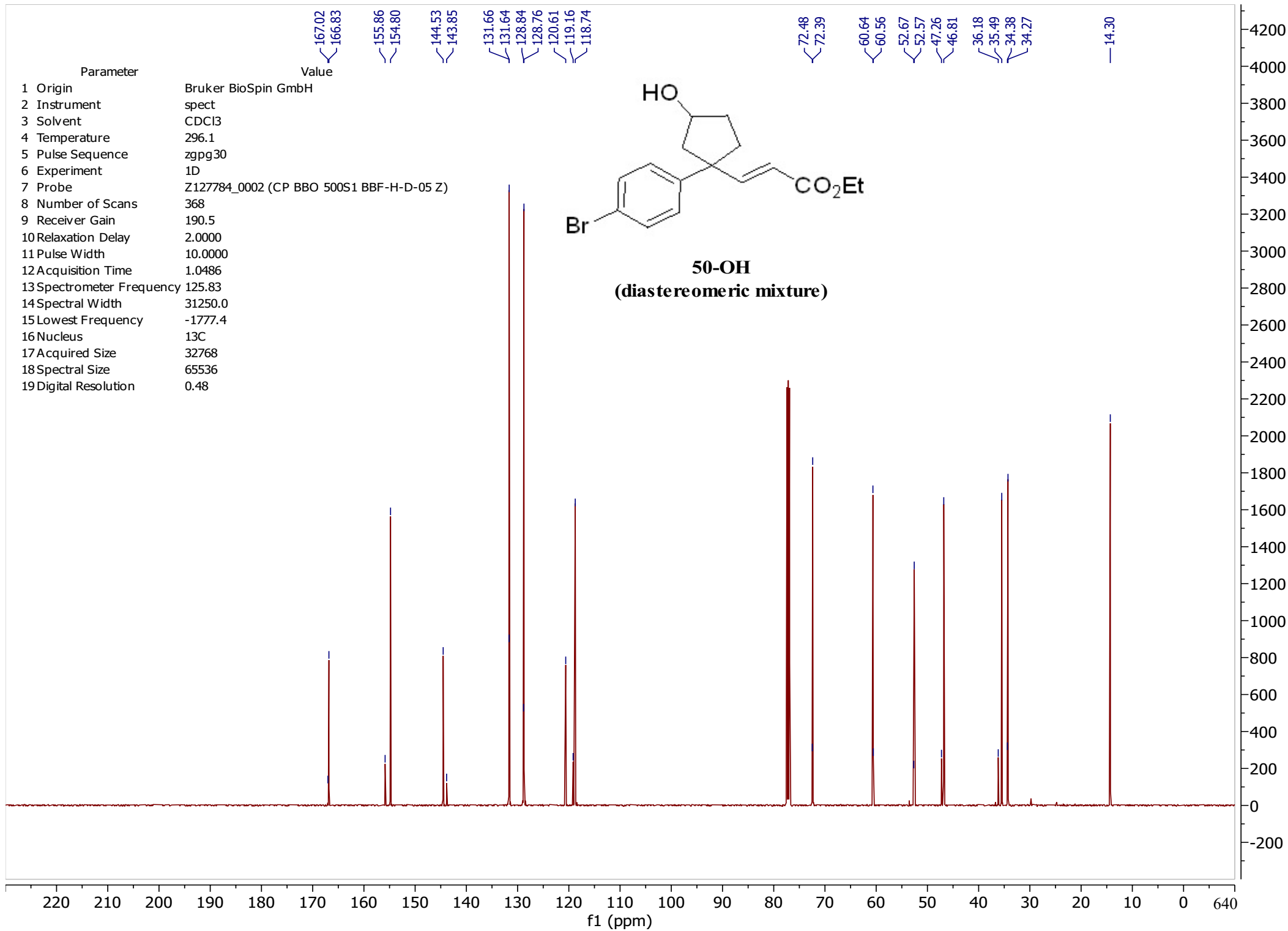
47.26
46.81

36.18
35.49
34.38
34.27

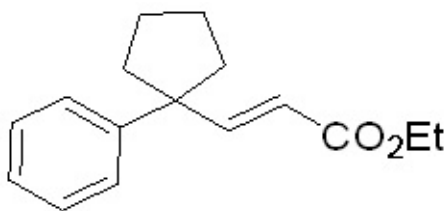
14.30



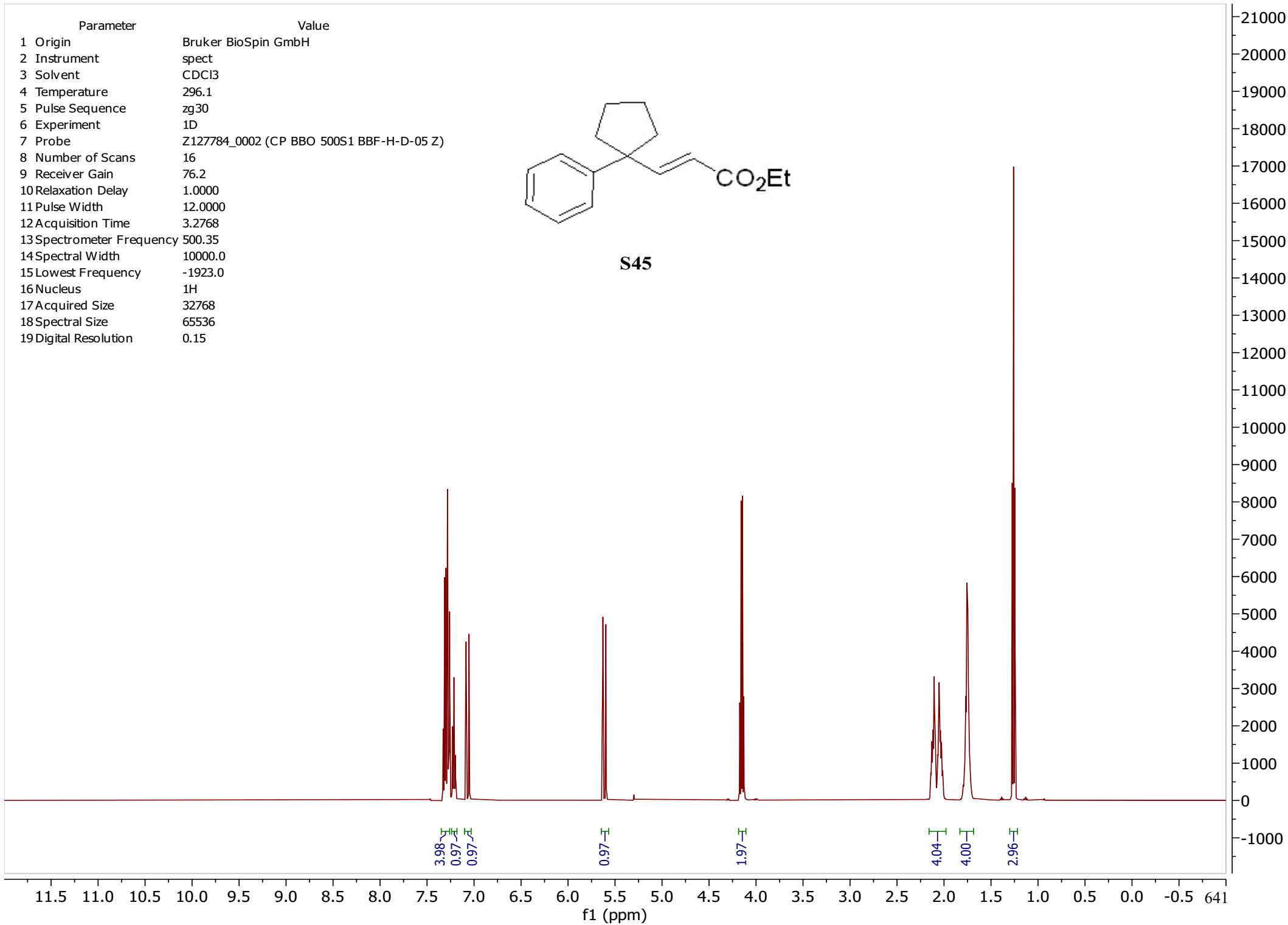
50-OH
(diastereomeric mixture)



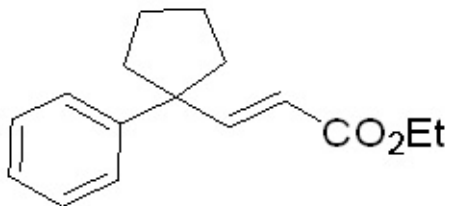
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



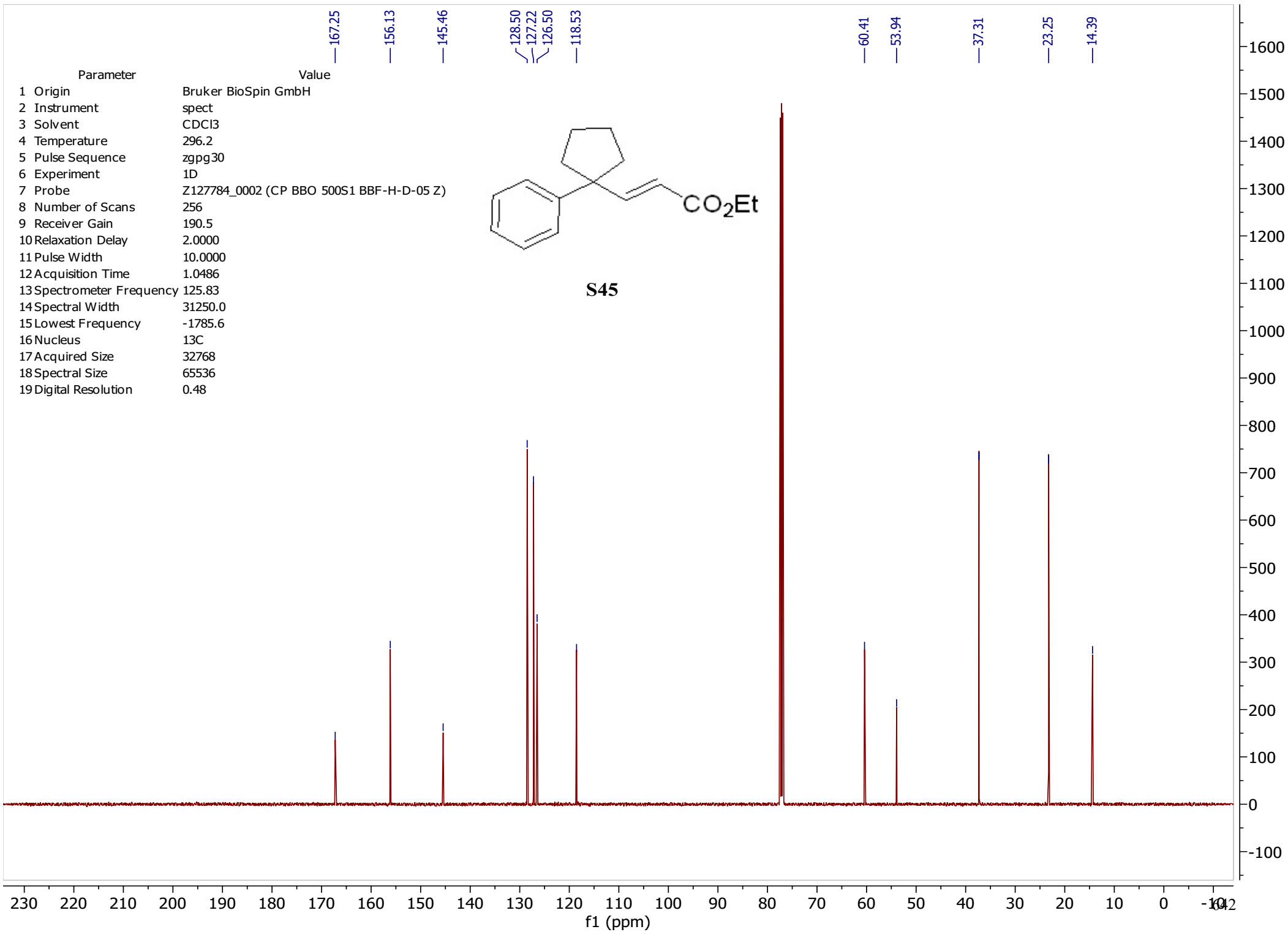
S45



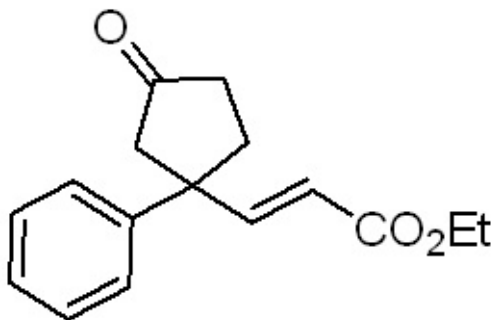
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



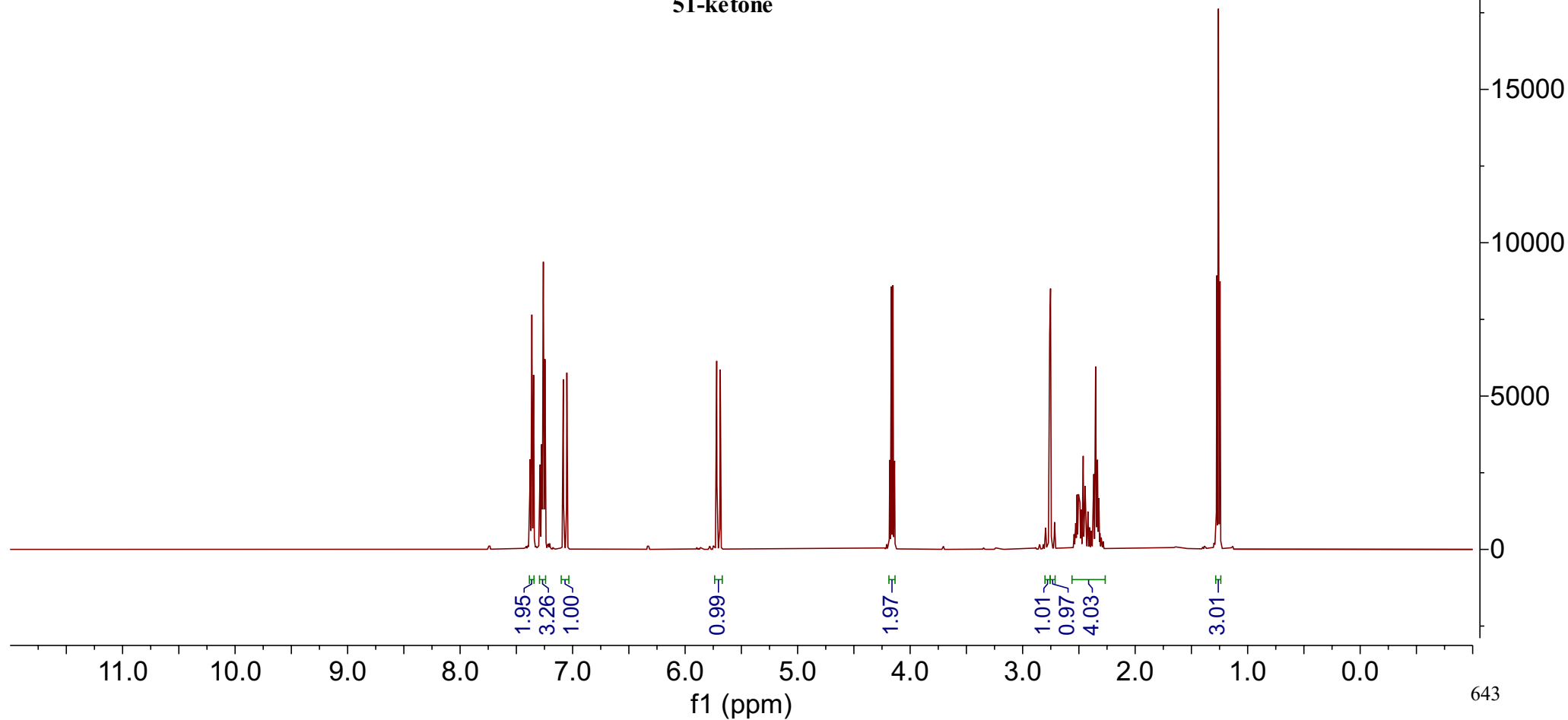
S45



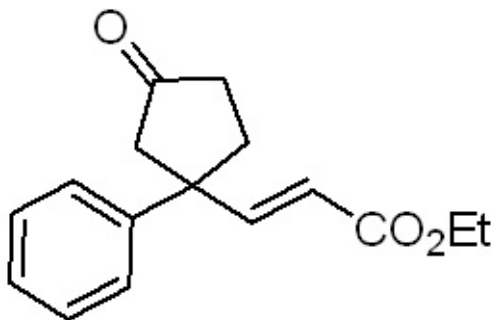
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	298.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	76.2
10 Relaxation Delay	10.0000
11 Pulse Width	12.7300
12 Spectrometer Frequency	500.35
13 Spectral Width	10000.0
14 Lowest Frequency	-1923.8
15 Nucleus	¹ H
16 Acquired Size	32768
17 Spectral Size	65536



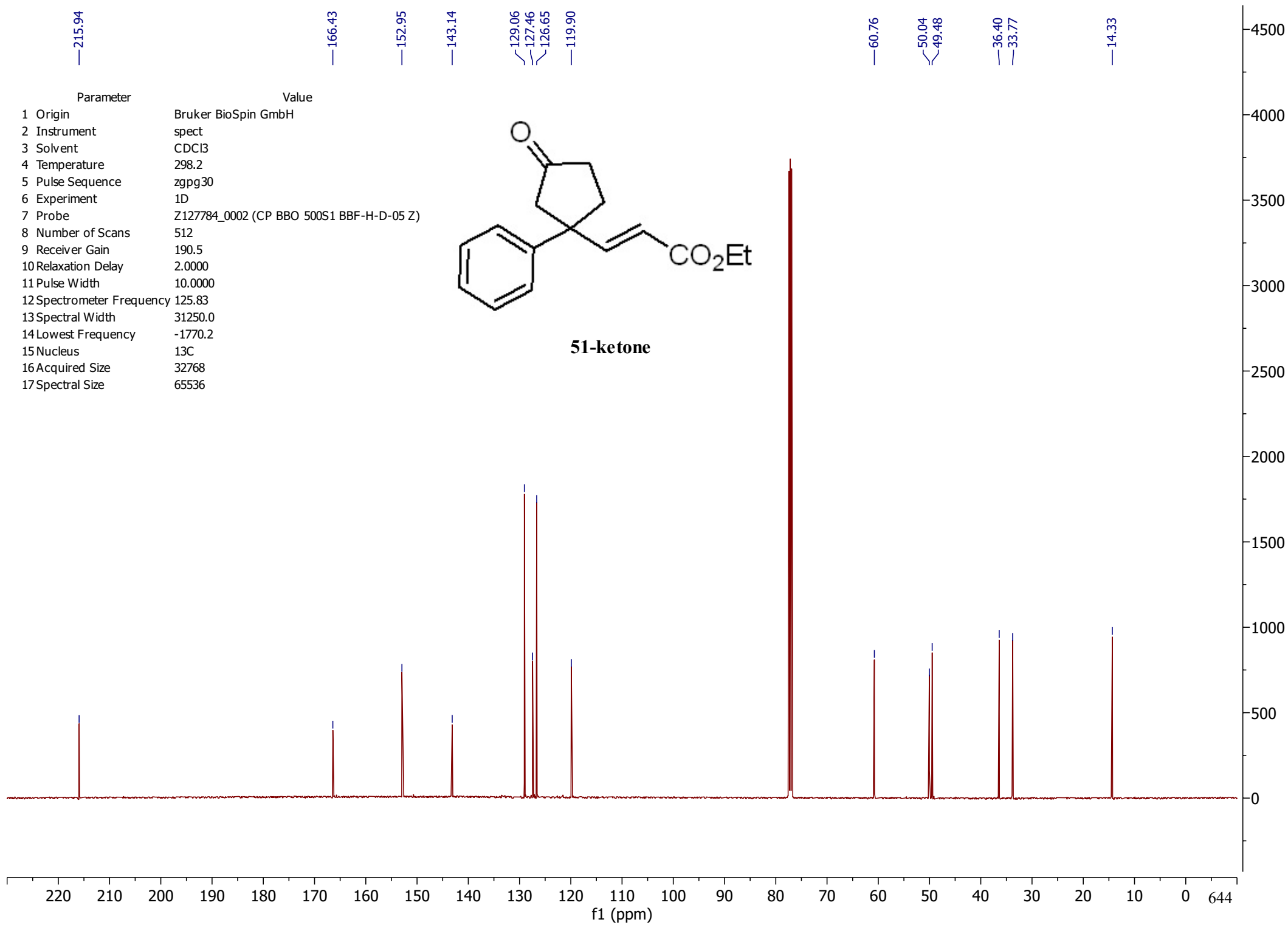
51-ketone



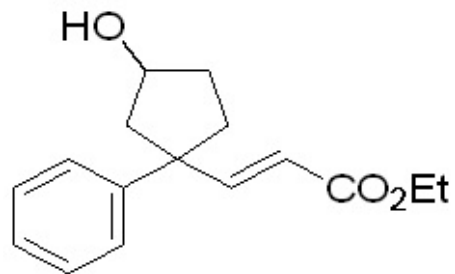
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	512
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Spectrometer Frequency	125.83
13 Spectral Width	31250.0
14 Lowest Frequency	-1770.2
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536



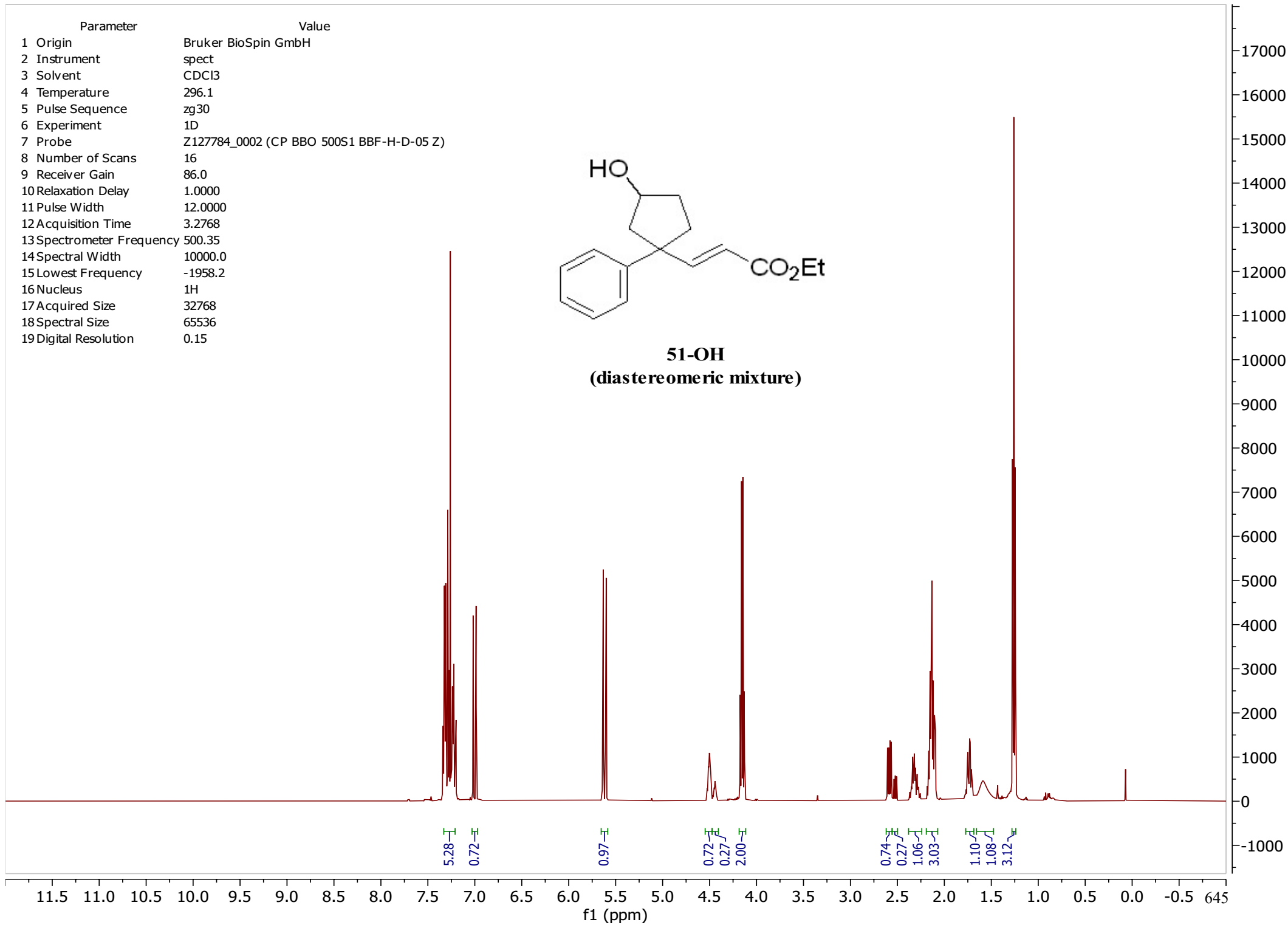
51-ketone



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	86.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1958.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



51-OH
(diastereomeric mixture)

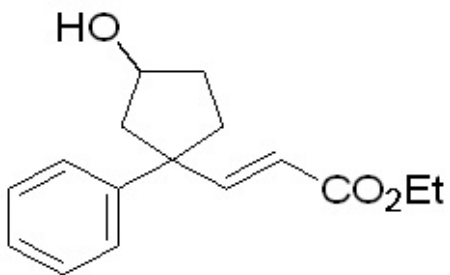


Parameter

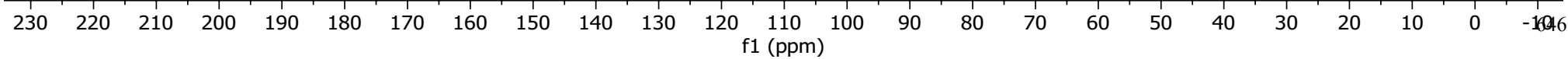
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

Value

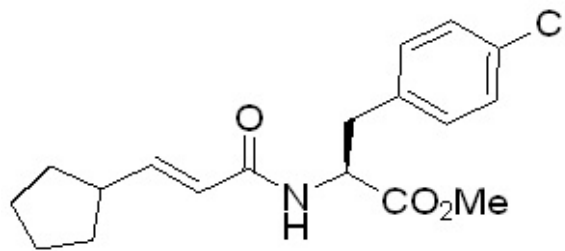
167.14	167.00	156.44	155.47	145.41	144.82	128.68	128.65	127.03	126.96	126.75	126.70	118.91	118.49	72.81	72.69	60.56	60.48	53.04	53.00	47.34	46.96	36.15	35.44	34.55	34.40	14.37
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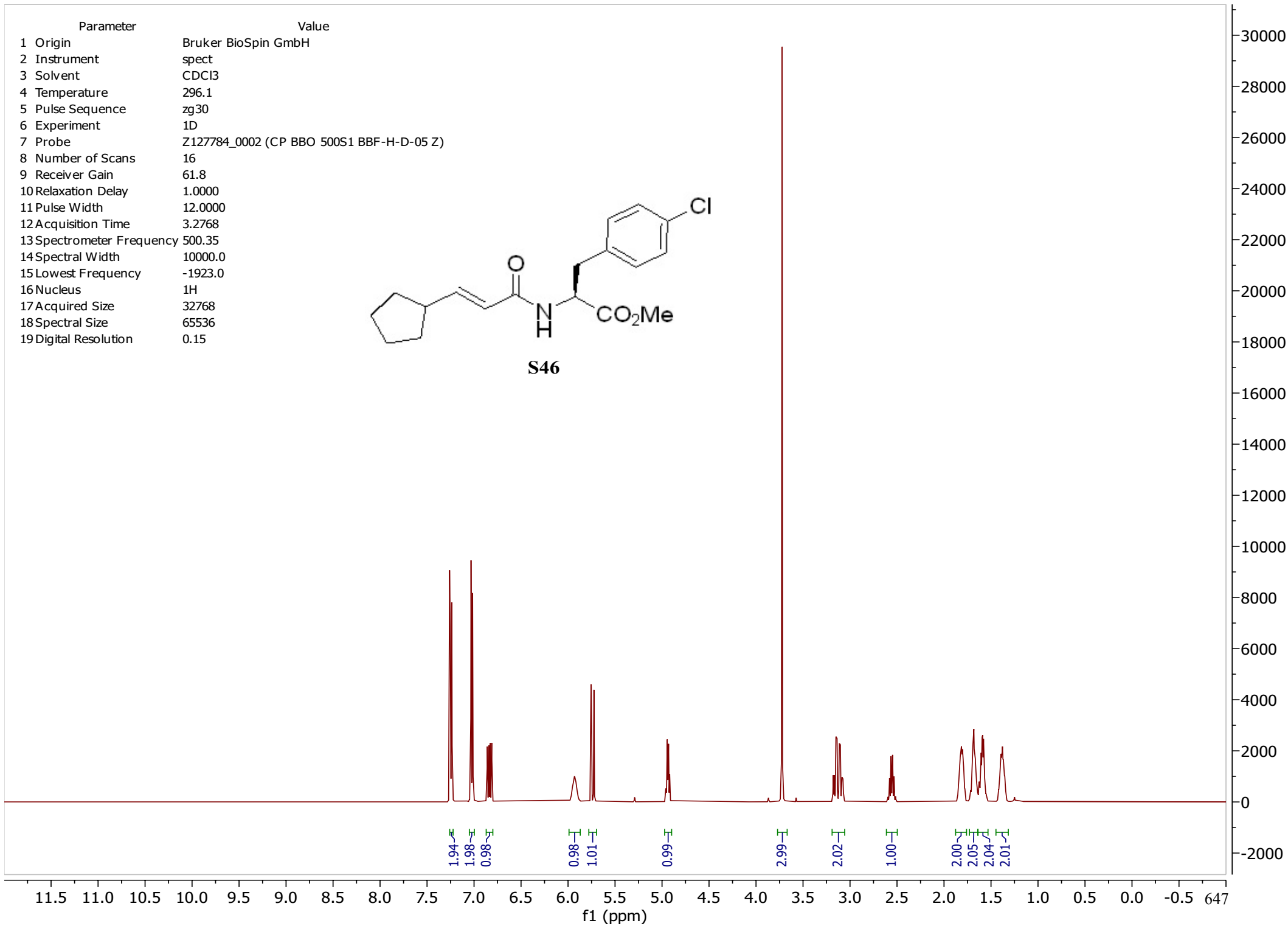
51-OH
(diastereomeric mixture)



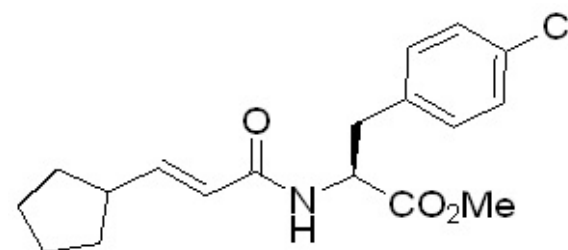
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	61.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



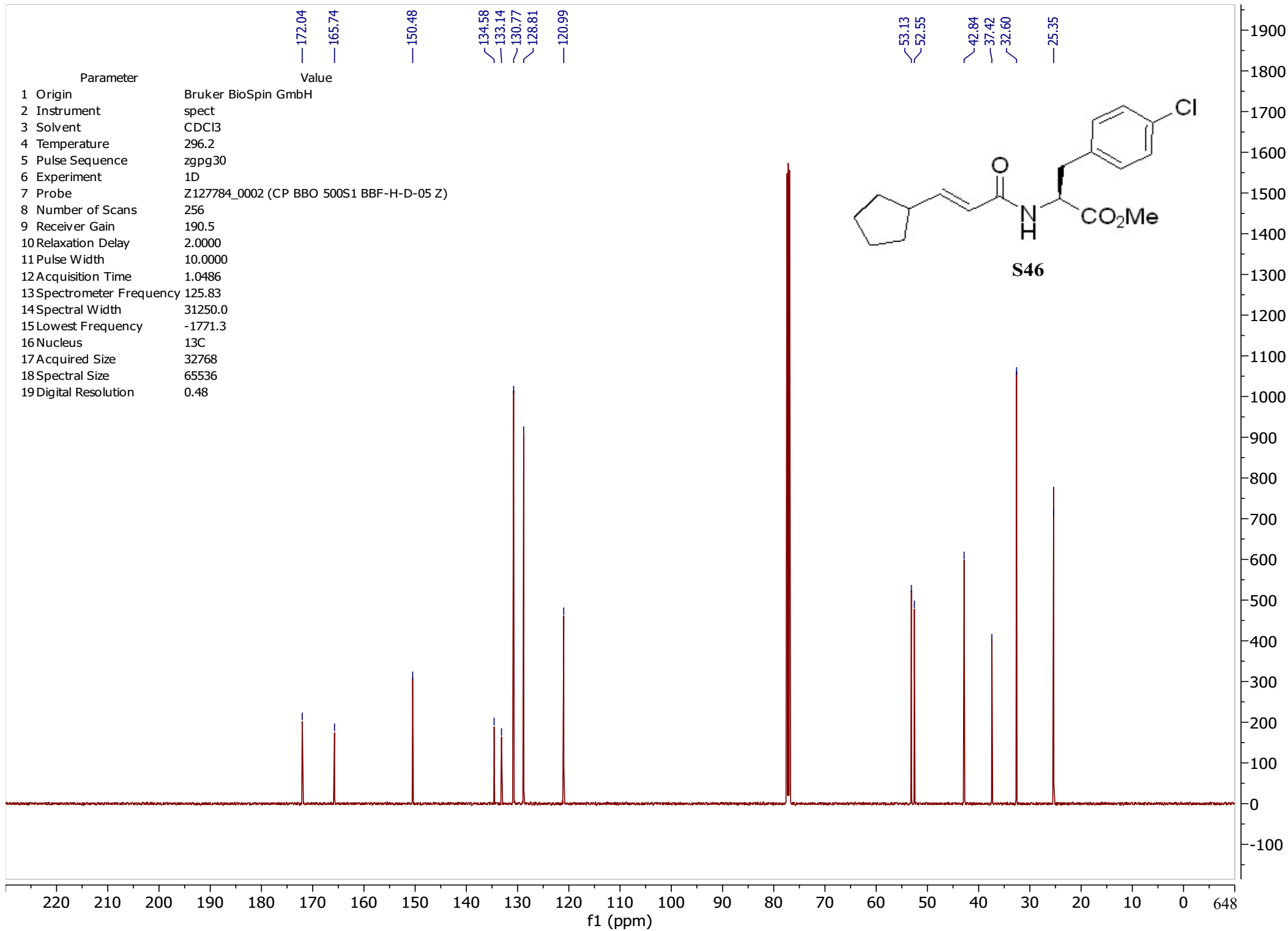
S46



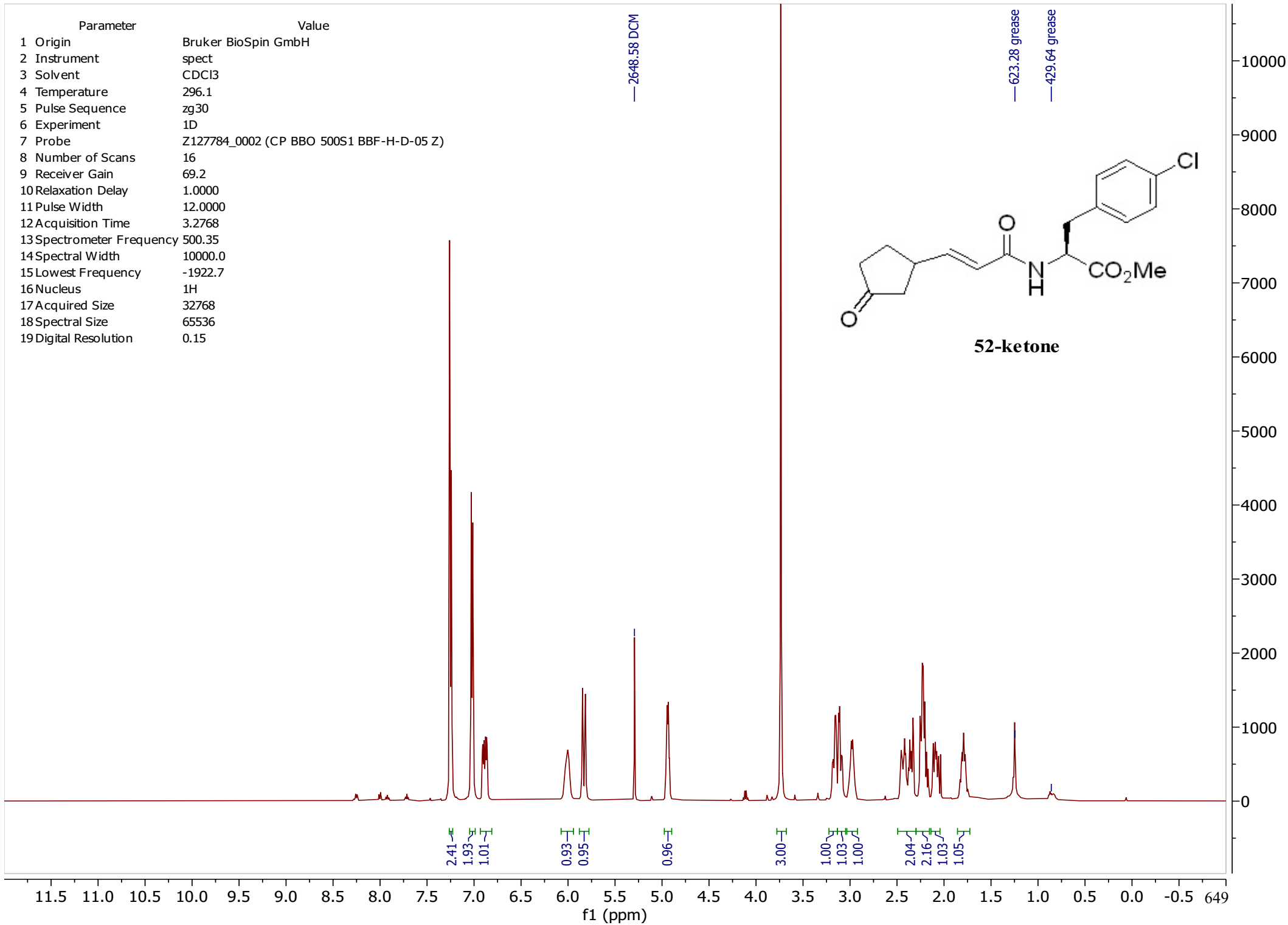
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1771.3
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

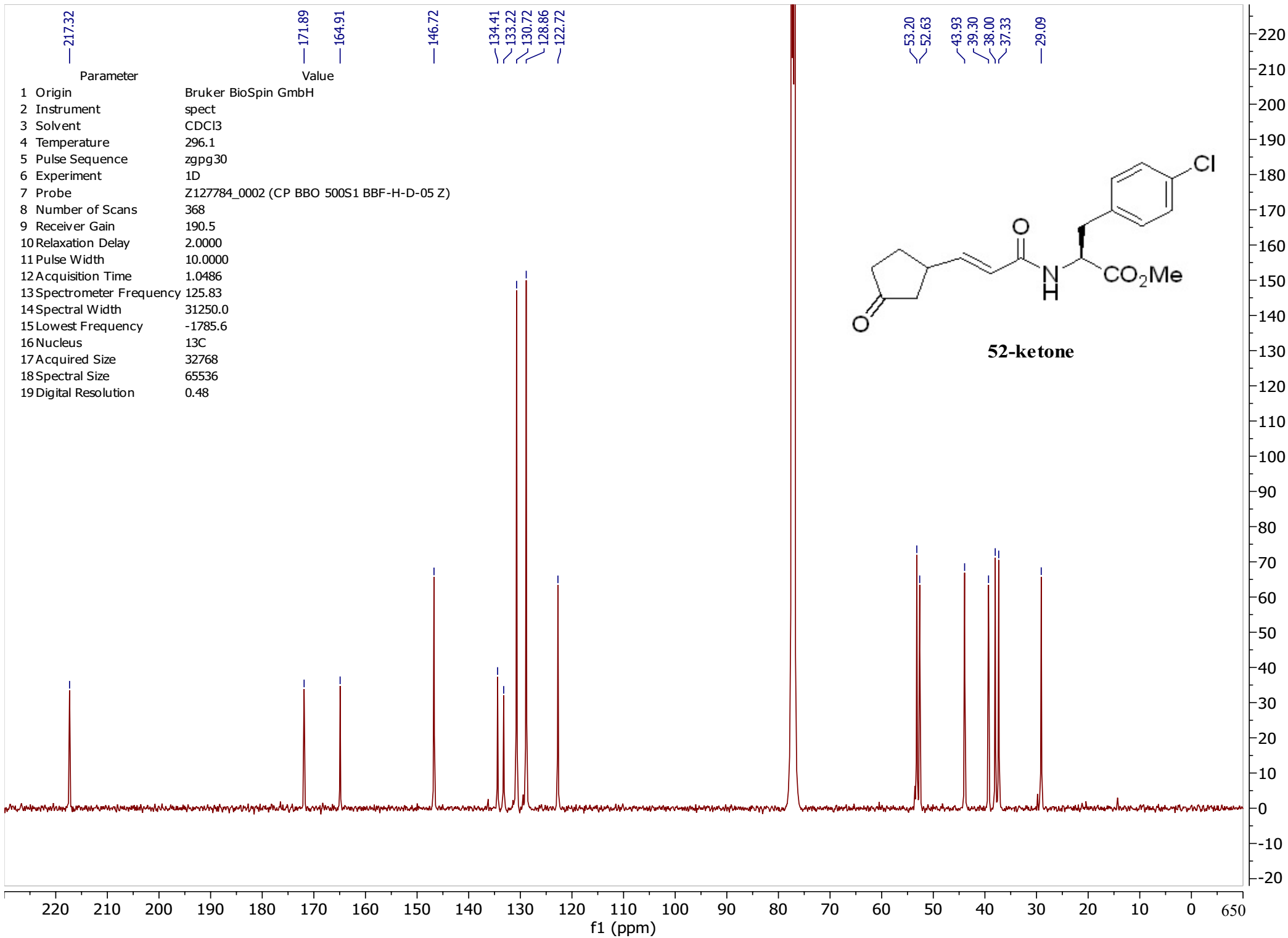


S46

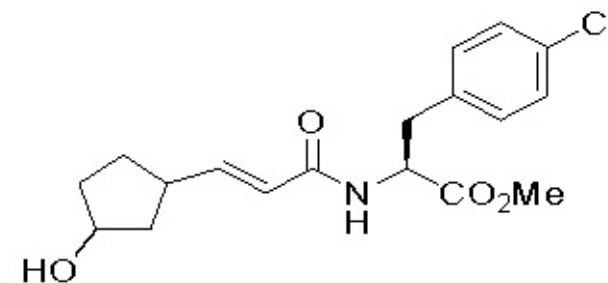


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

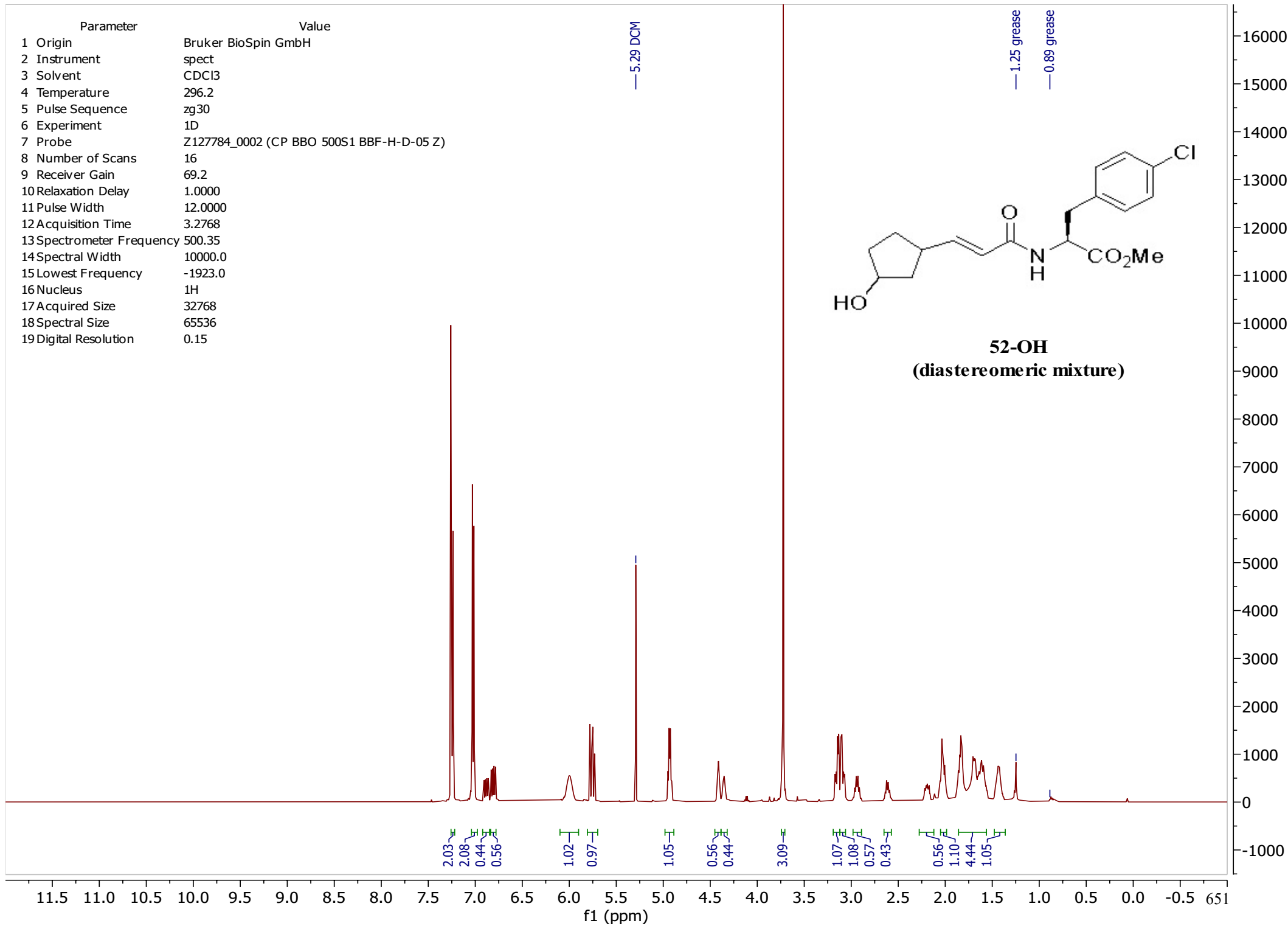




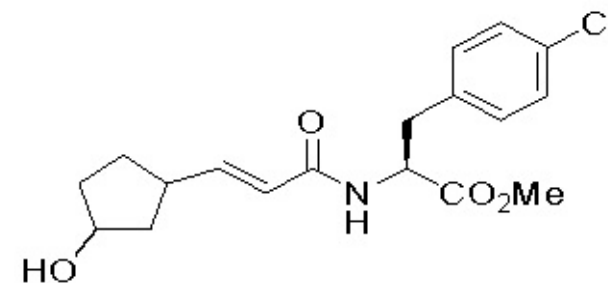
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



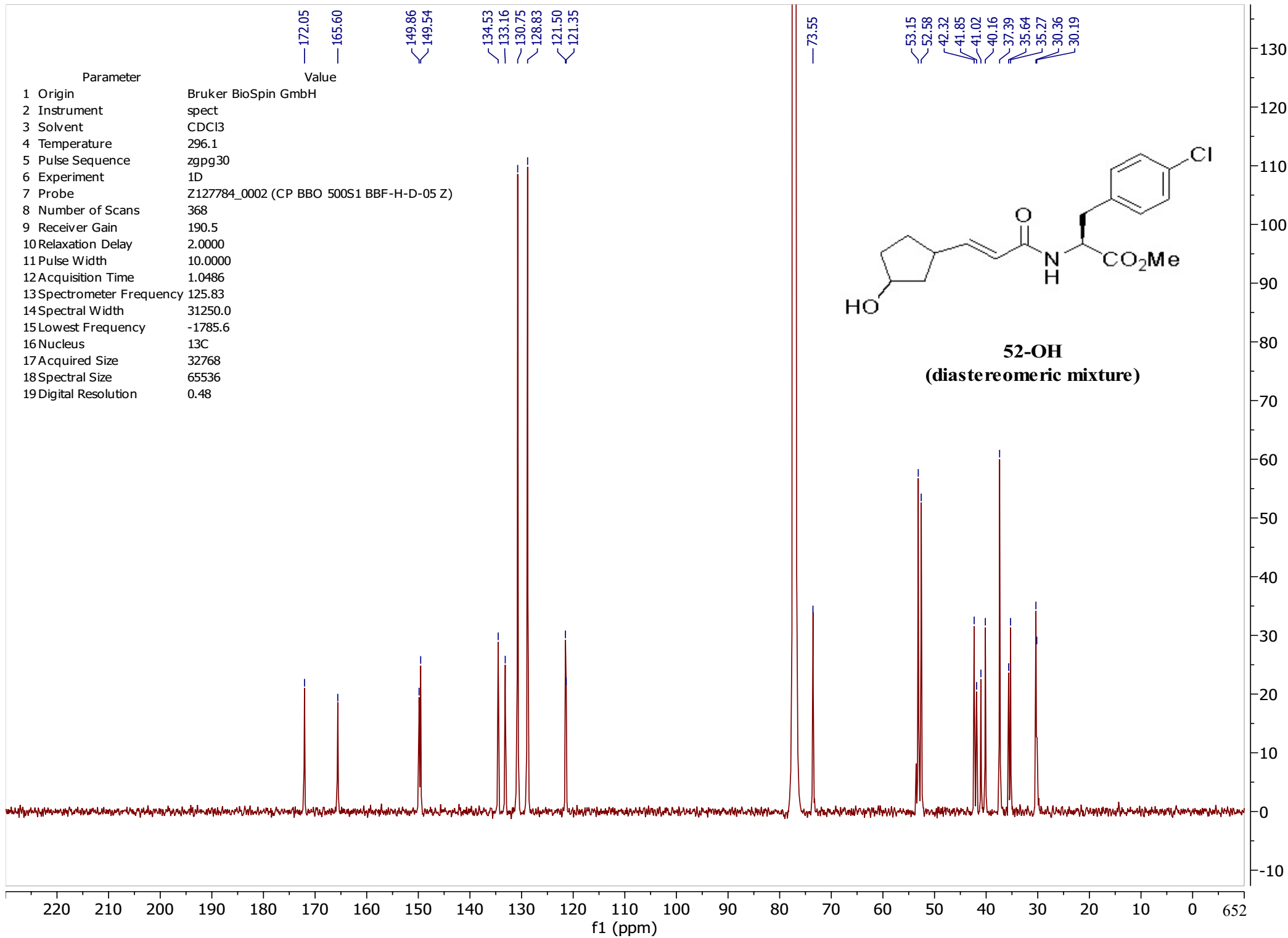
52-OH
(diastereomeric mixture)



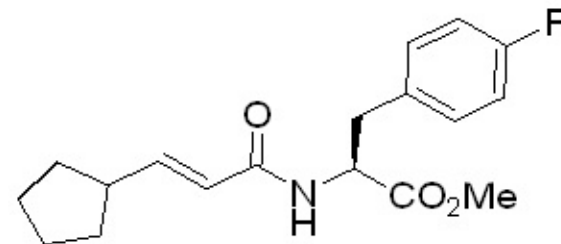
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



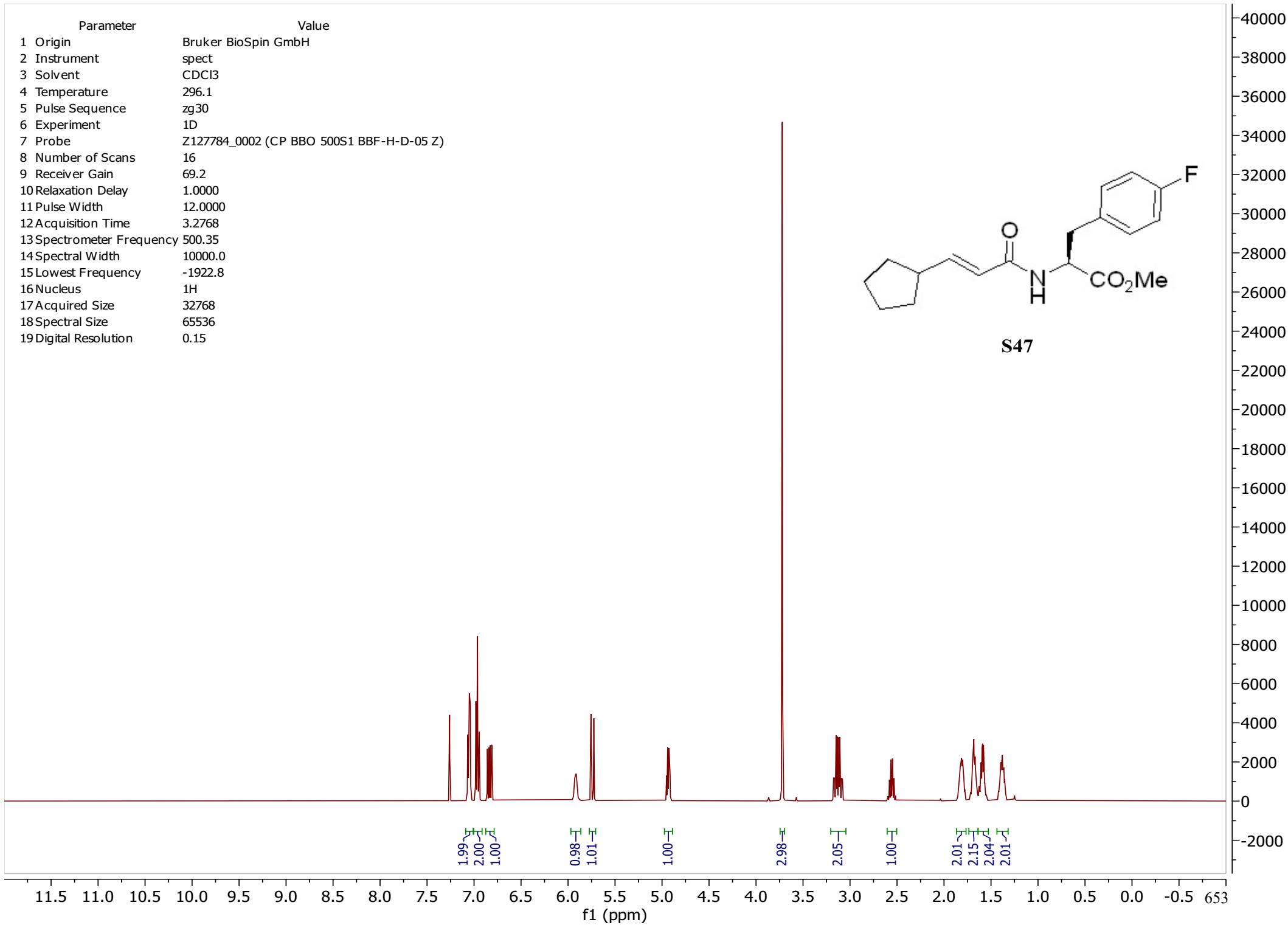
52-OH
(diastereomeric mixture)



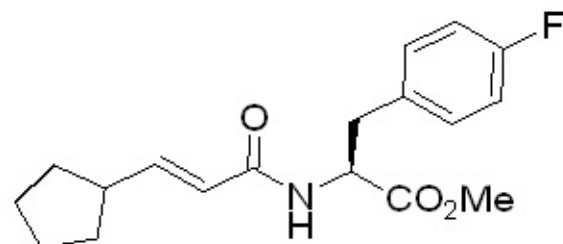
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



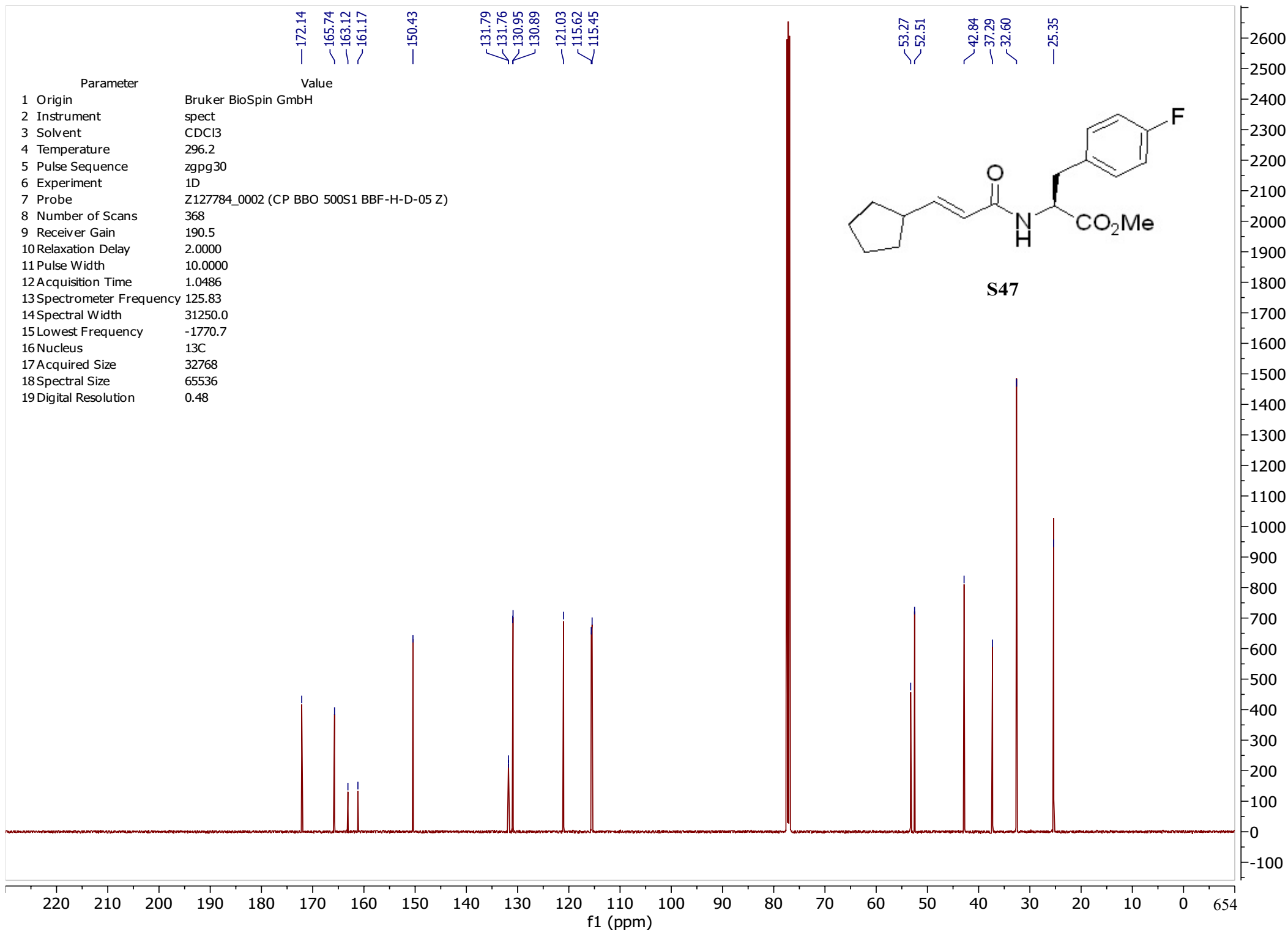
S47



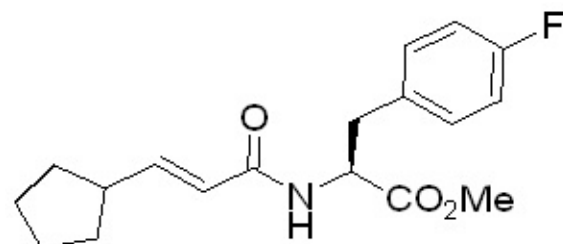
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1770.7
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



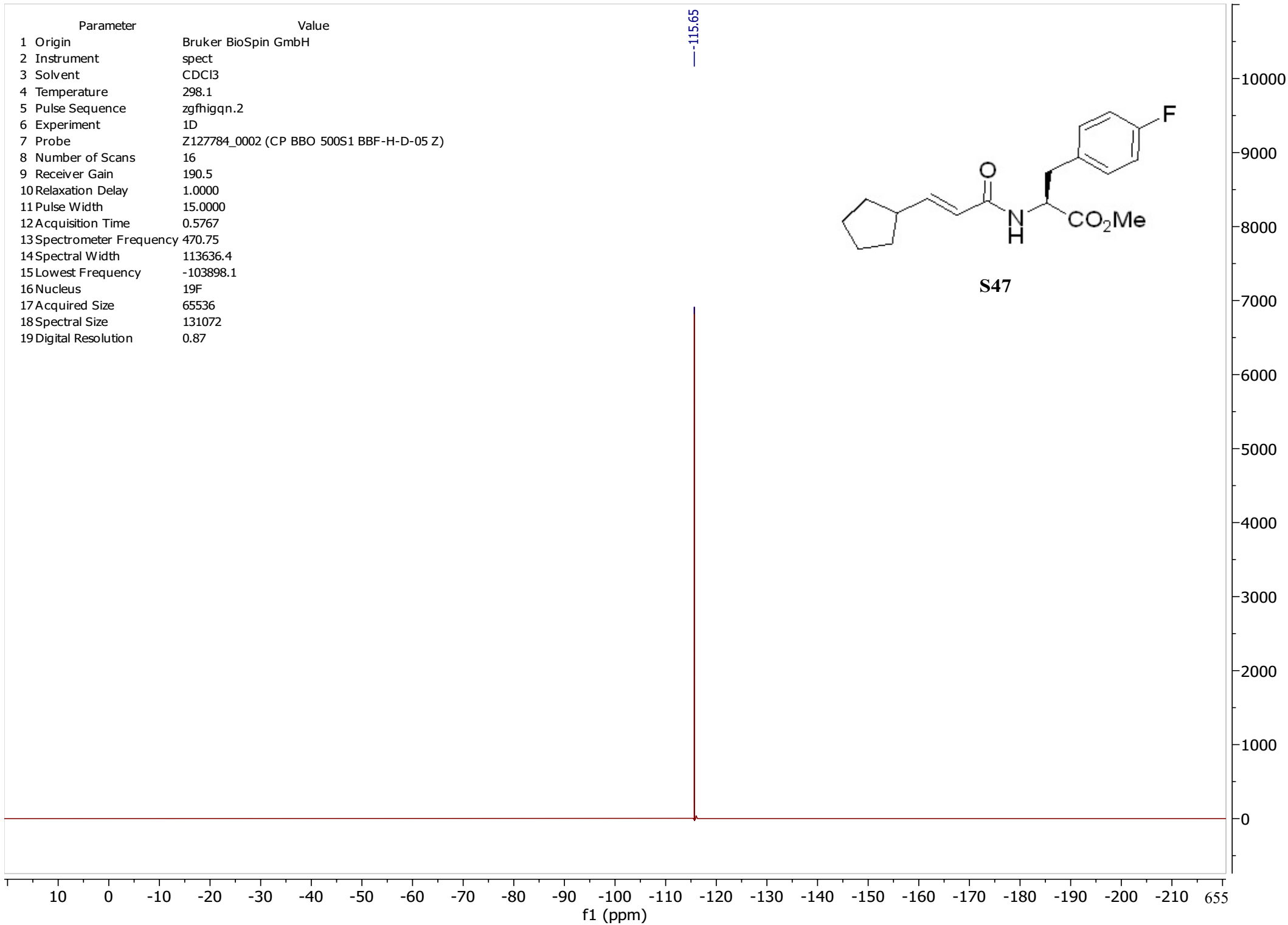
S47



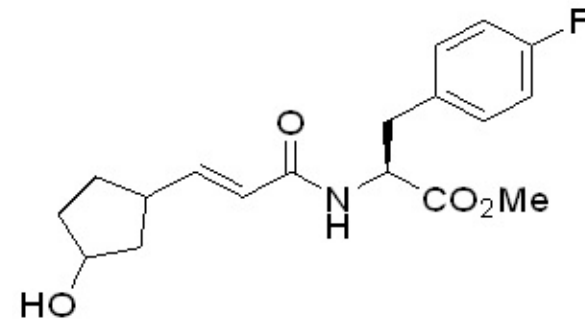
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	19F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



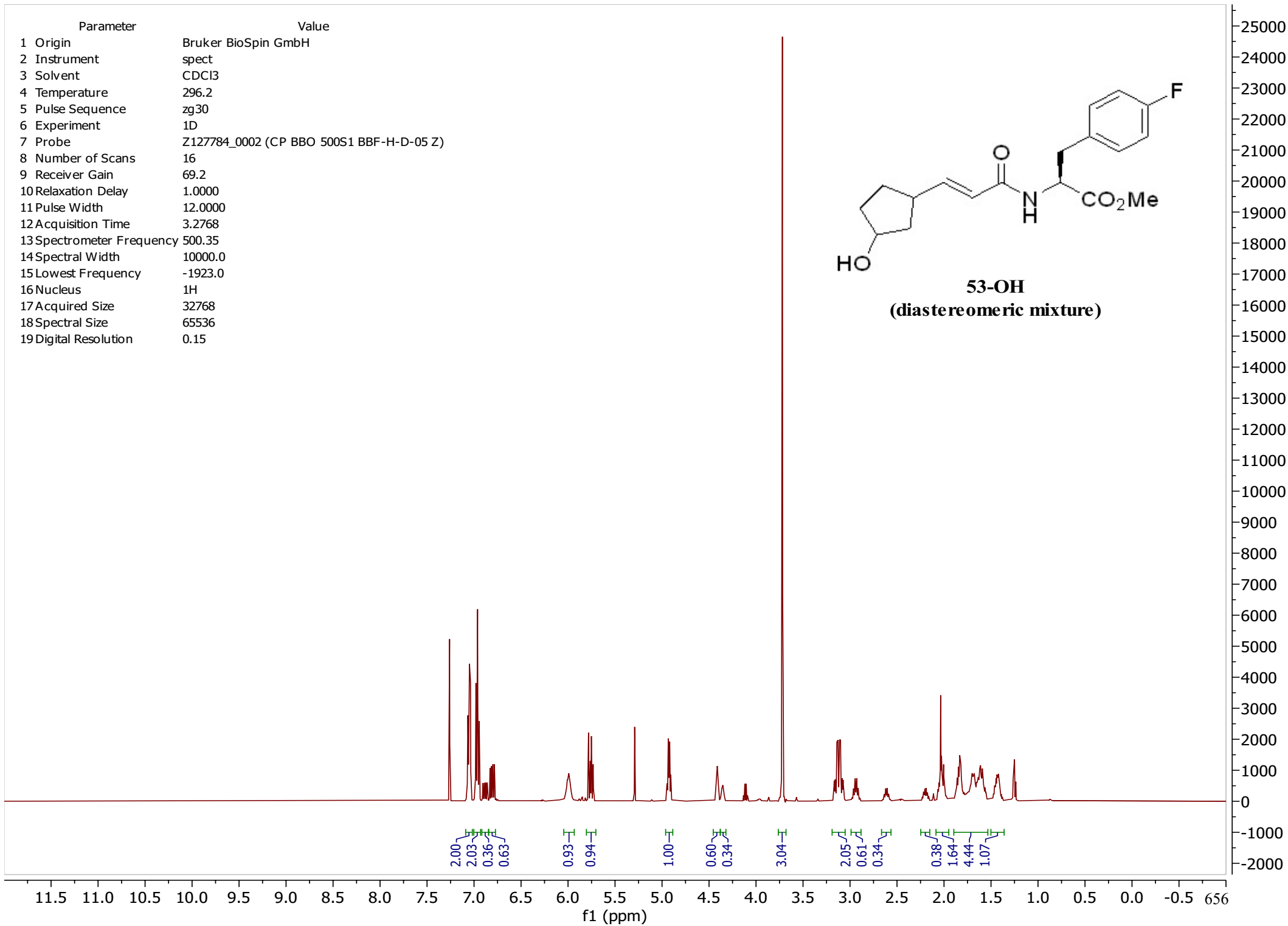
S47



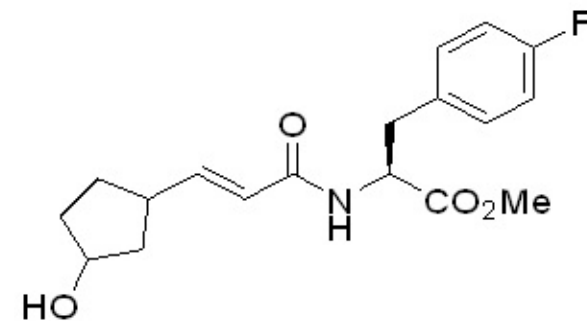
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



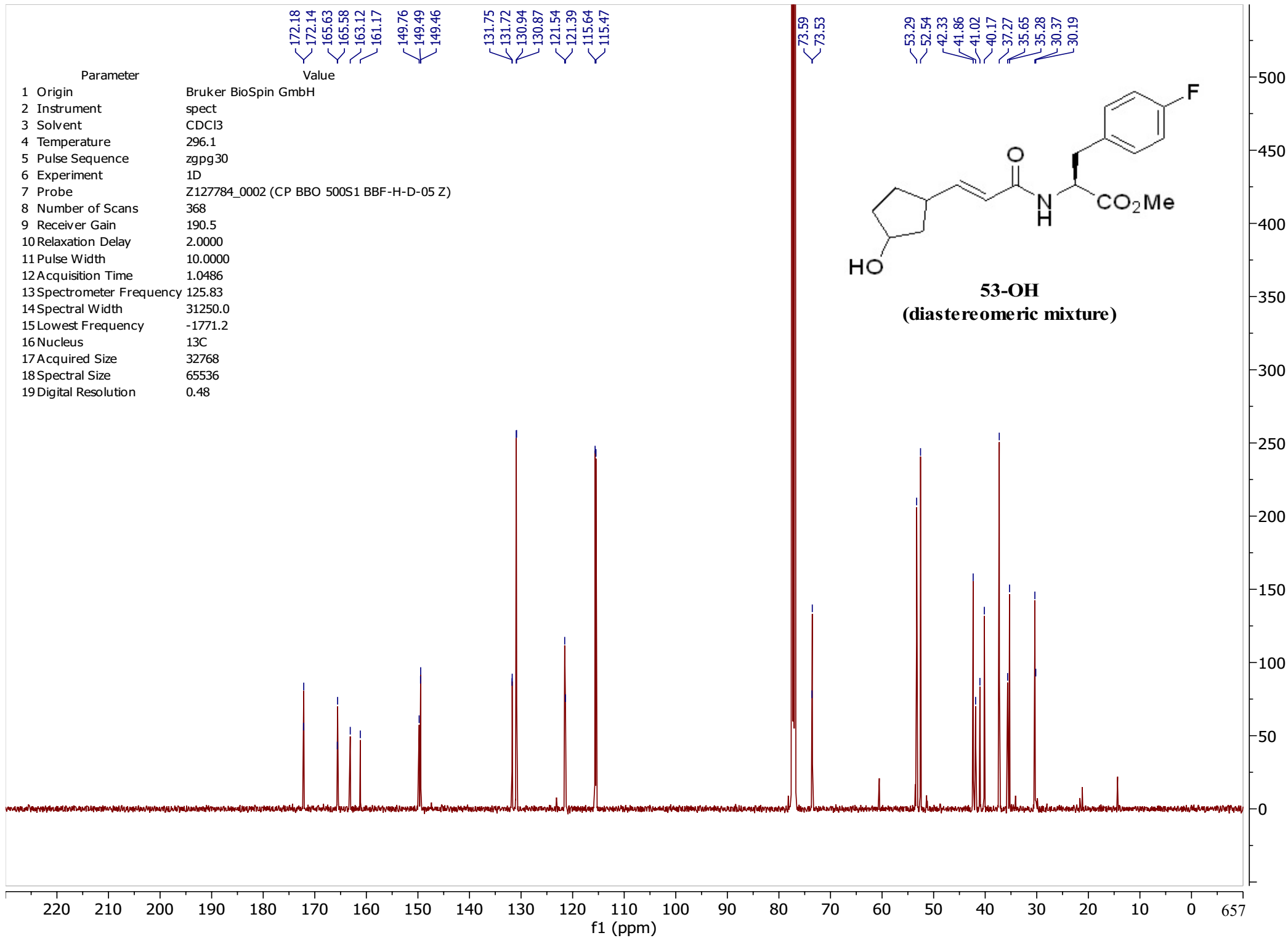
53-OH
(diastereomeric mixture)



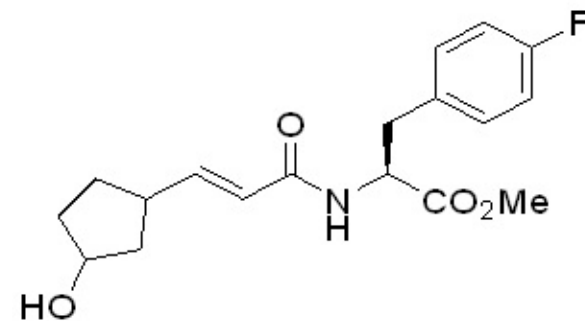
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1771.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



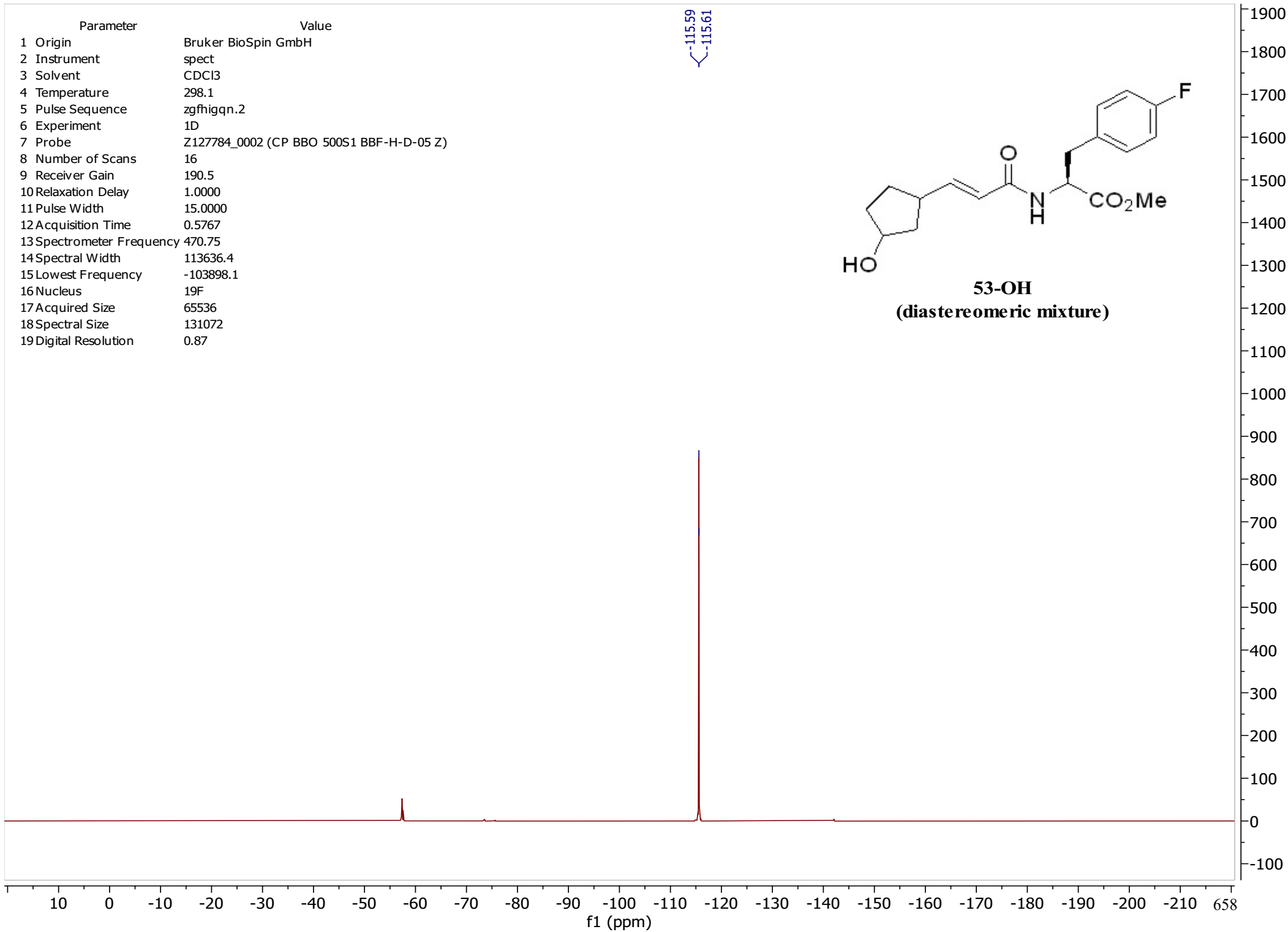
53-OH
(diastereomeric mixture)



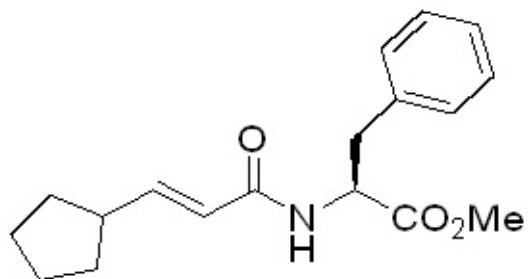
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	19F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



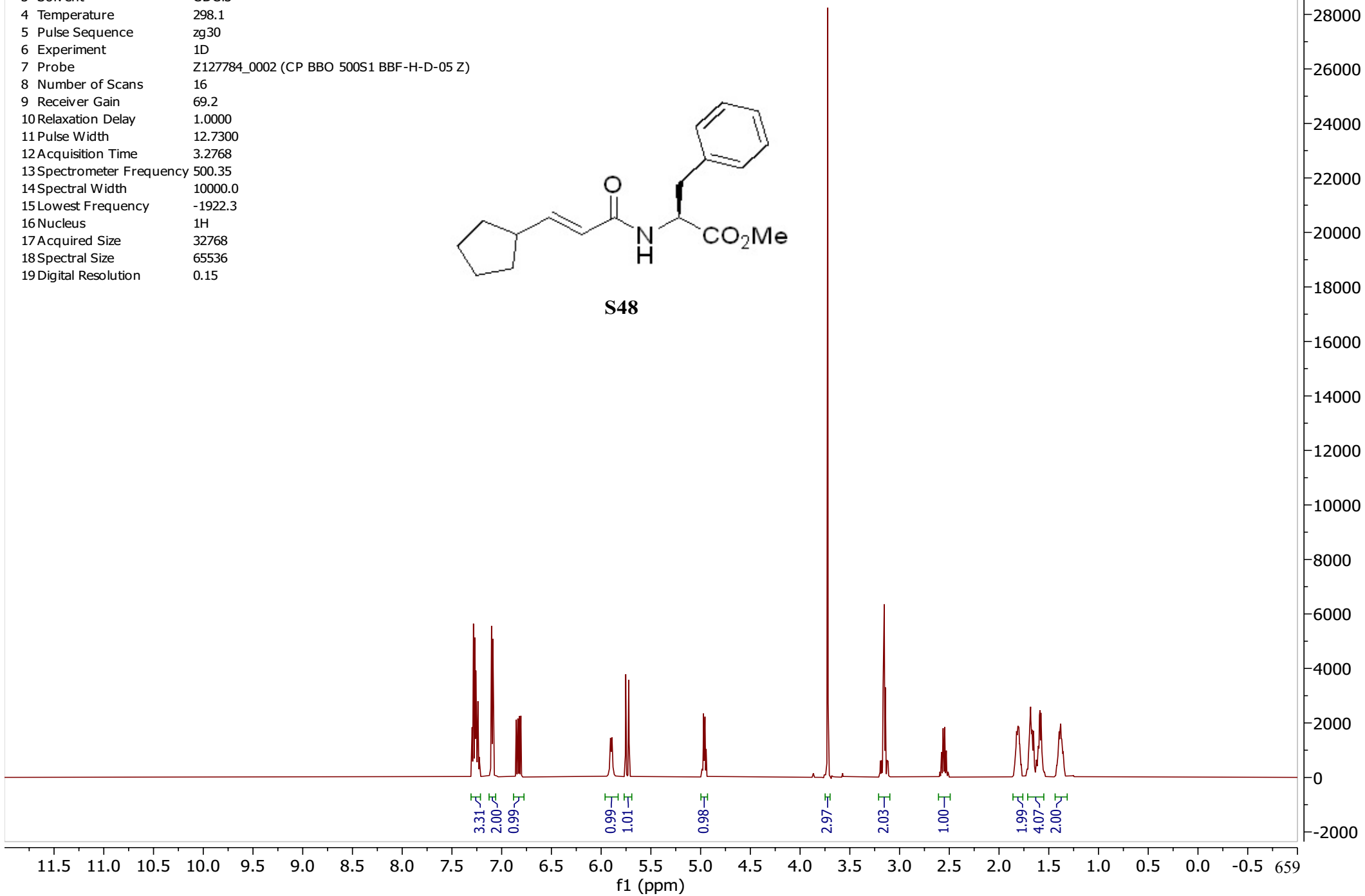
53-OH
(diastereomeric mixture)



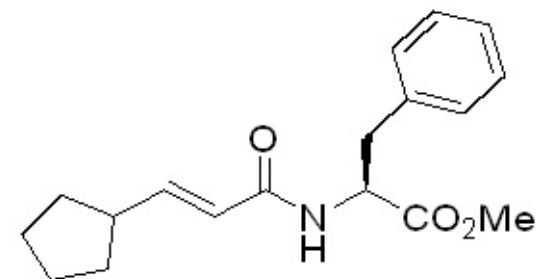
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.7300
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.3
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



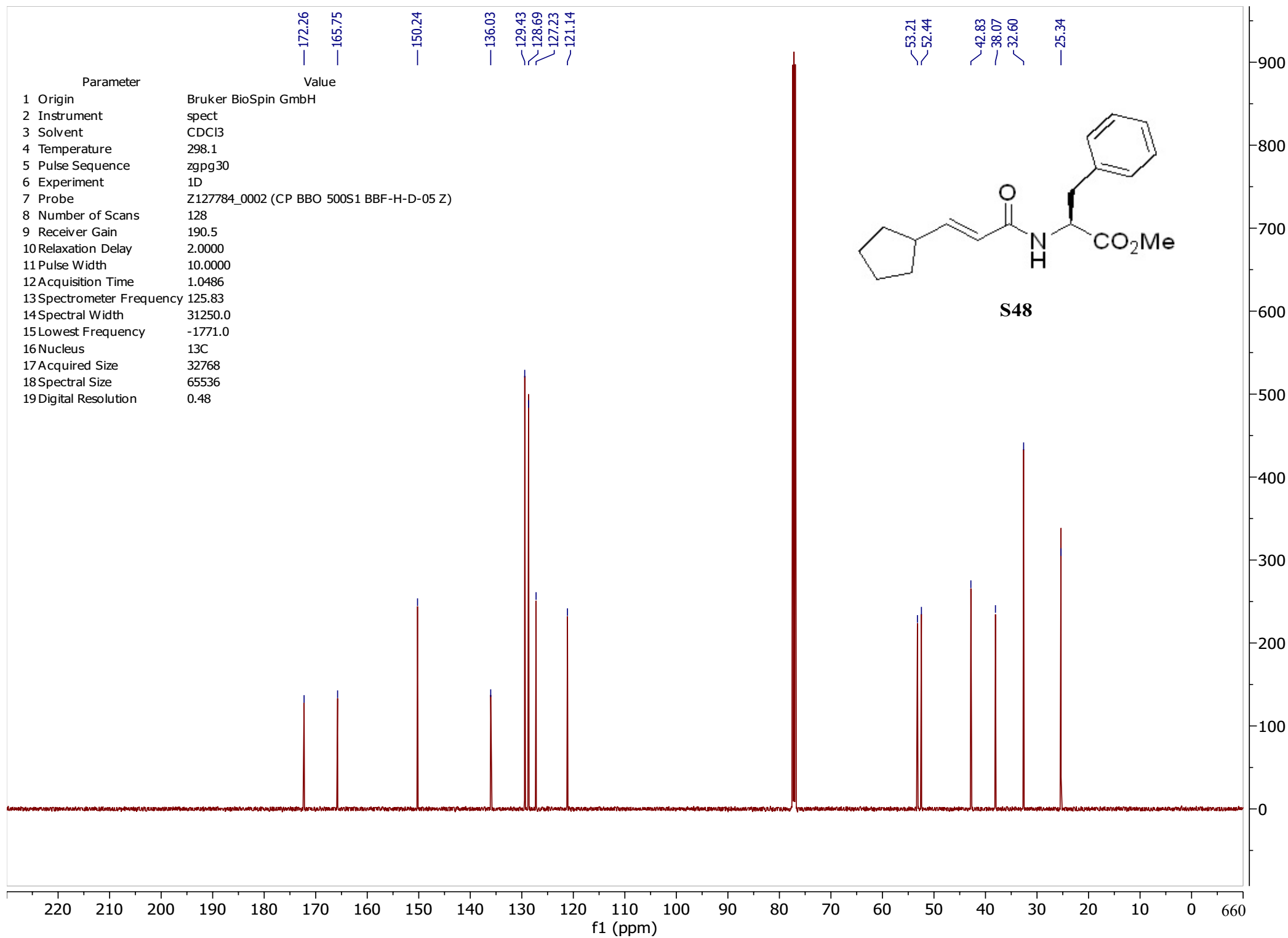
S48



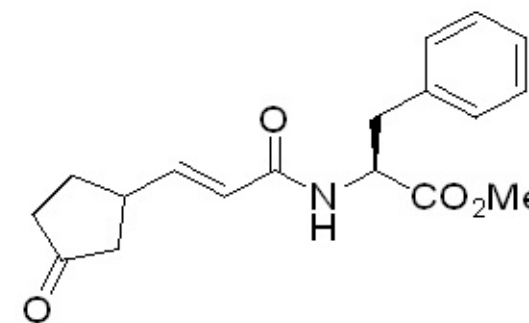
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	298.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	128
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1771.0
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



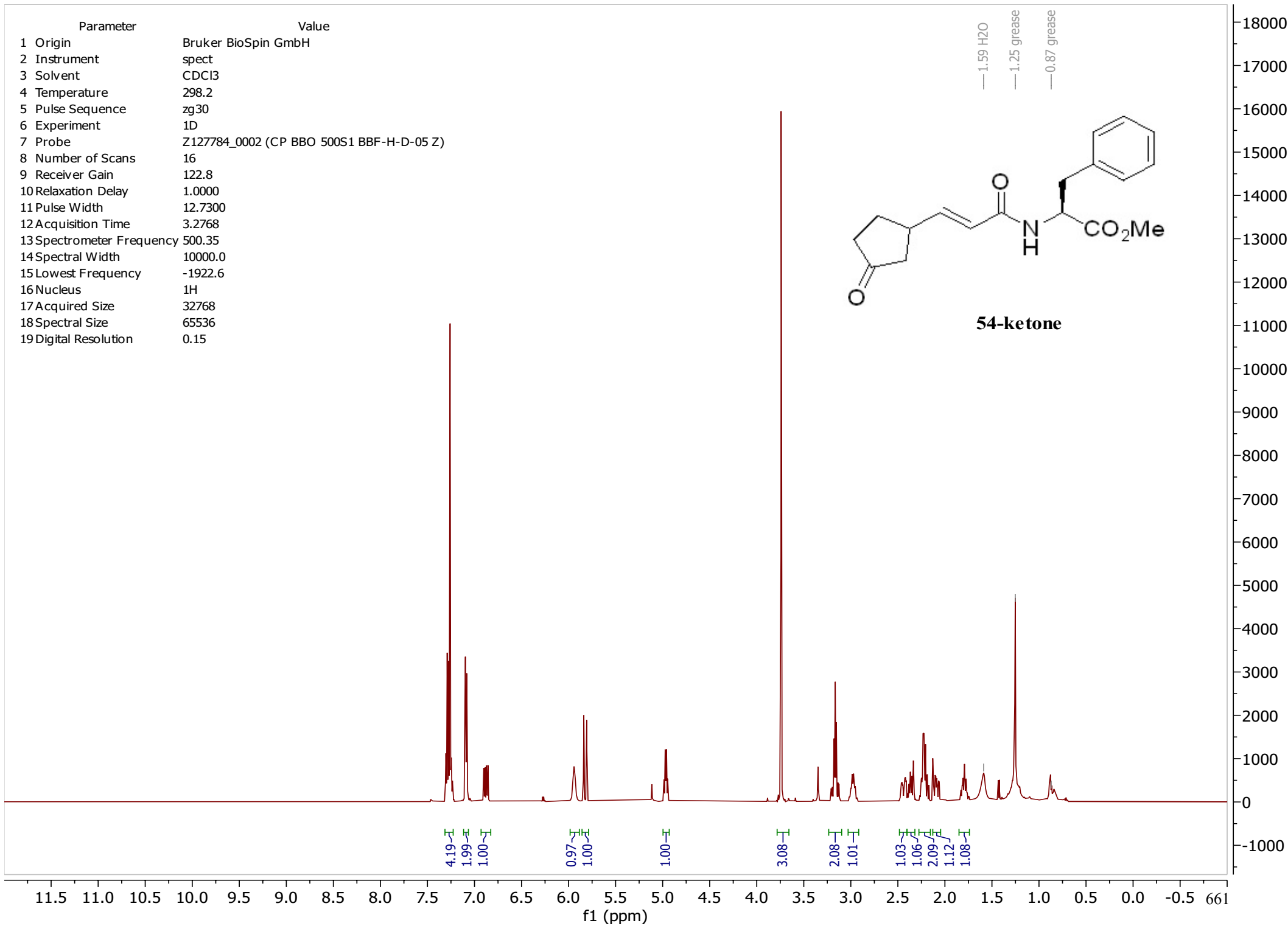
S48

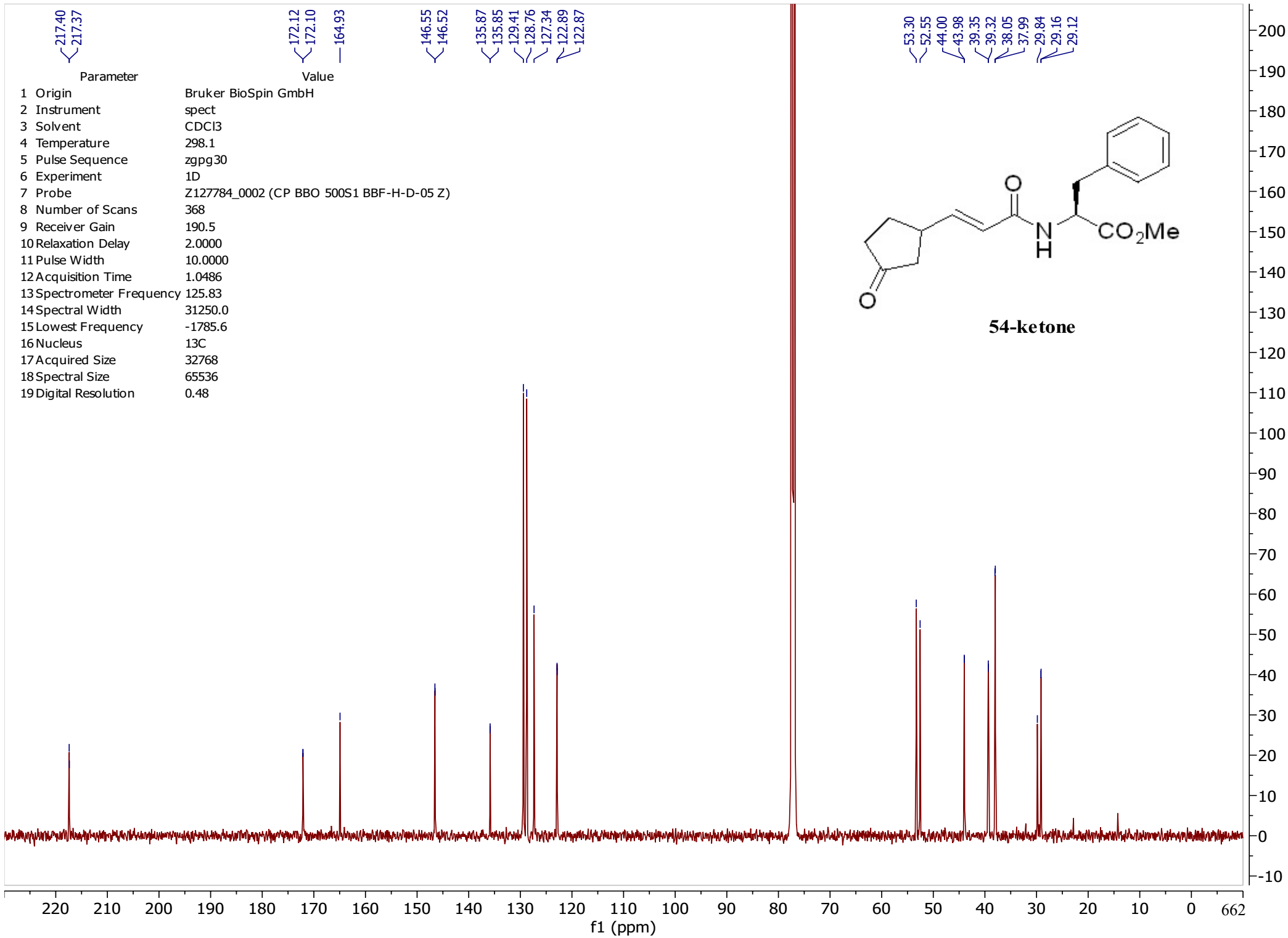


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	122.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.7300
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

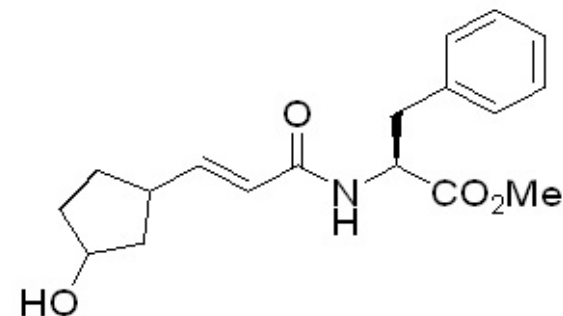


54-ketone

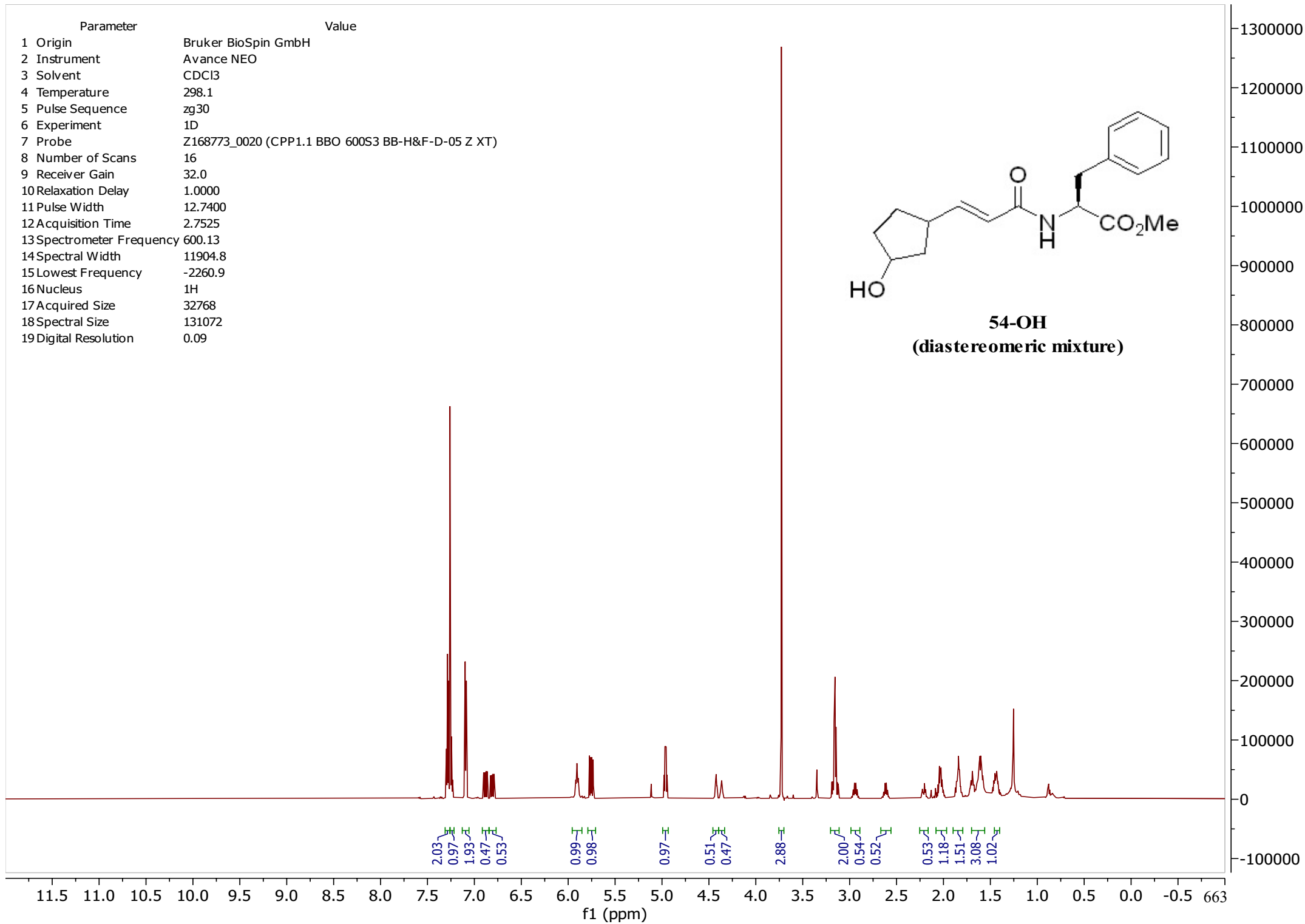


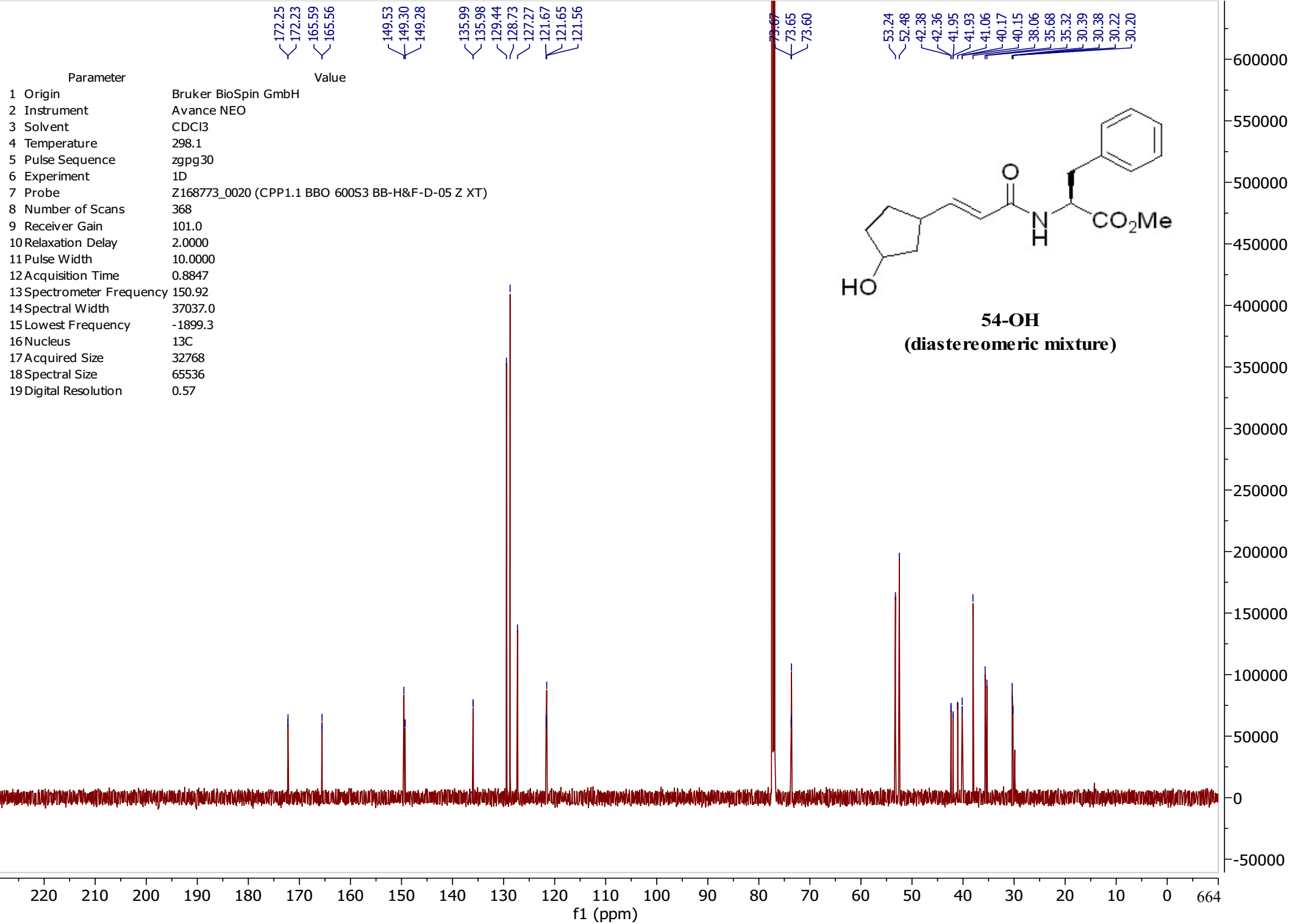


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	298.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.7400
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

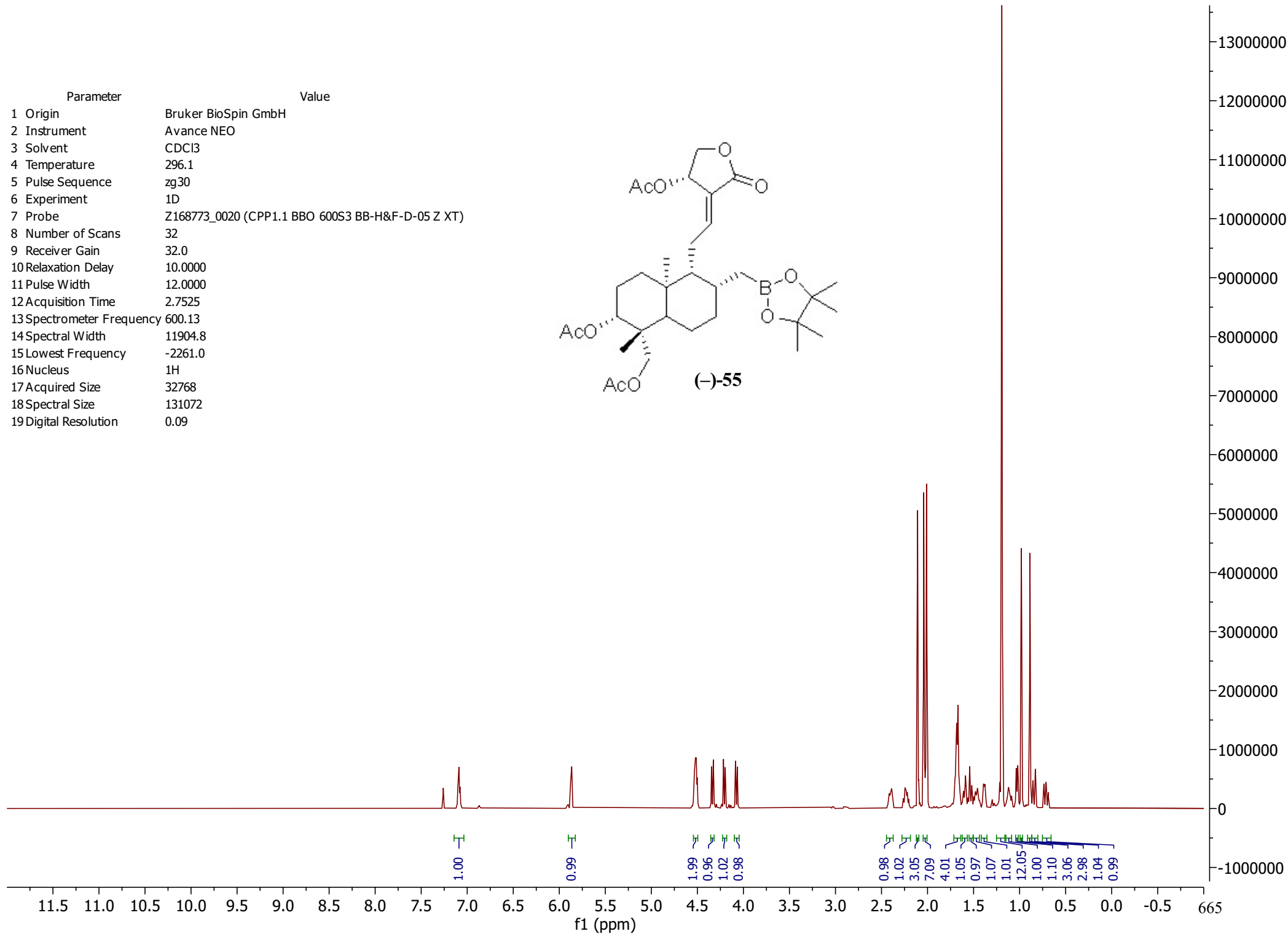
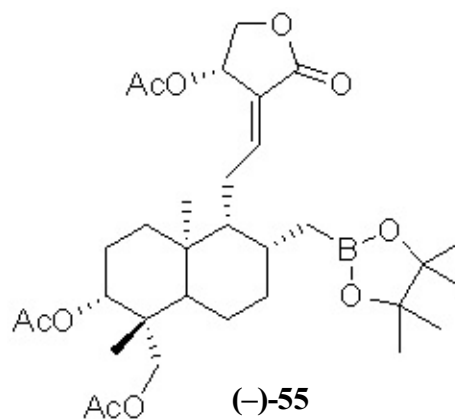


54-OH
(diastereomeric mixture)





Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



Parameter Value

1 Origin Bruker BioSpin GmbH

2 Instrument Avance NEO

3 Solvent CDCl₃

4 Temperature 296.2

5 Pulse Sequence zgpg30

6 Experiment 1D

7 Probe Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)

8 Number of Scans 1024

9 Receiver Gain 101.0

10 Relaxation Delay 2.0000

11 Pulse Width 10.0000

12 Acquisition Time 0.8847

13 Spectrometer Frequency 150.92

14 Spectral Width 37037.0

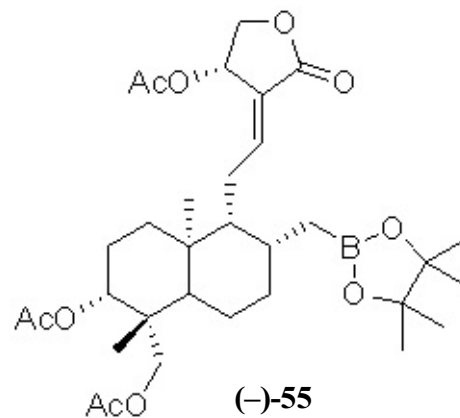
15 Lowest Frequency -1904.4

16 Nucleus ¹³C

17 Acquired Size 32768

18 Spectral Size 65536

19 Digital Resolution 0.57



171.08
170.67
170.59
169.03

150.18

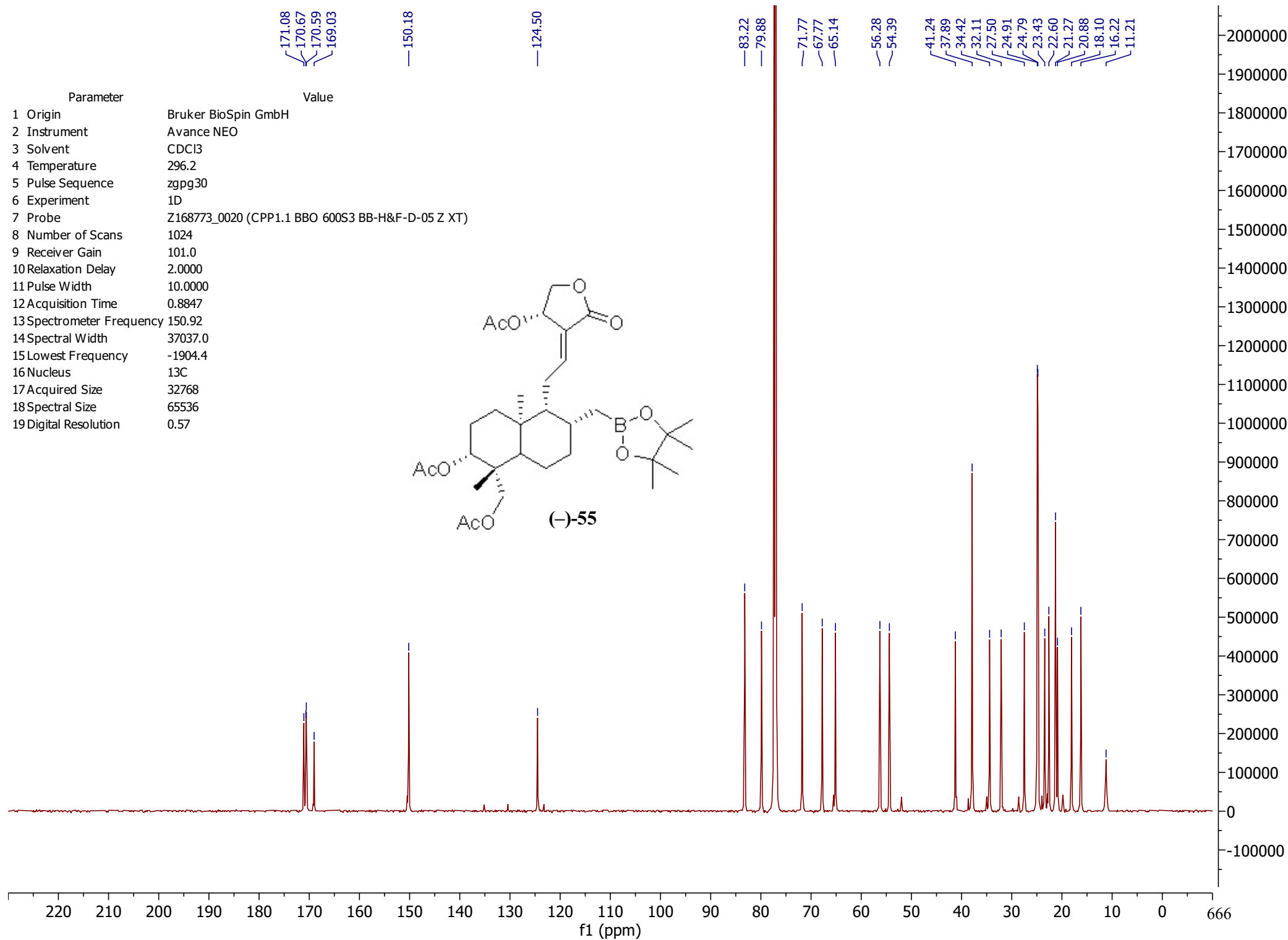
124.50

83.22
79.88

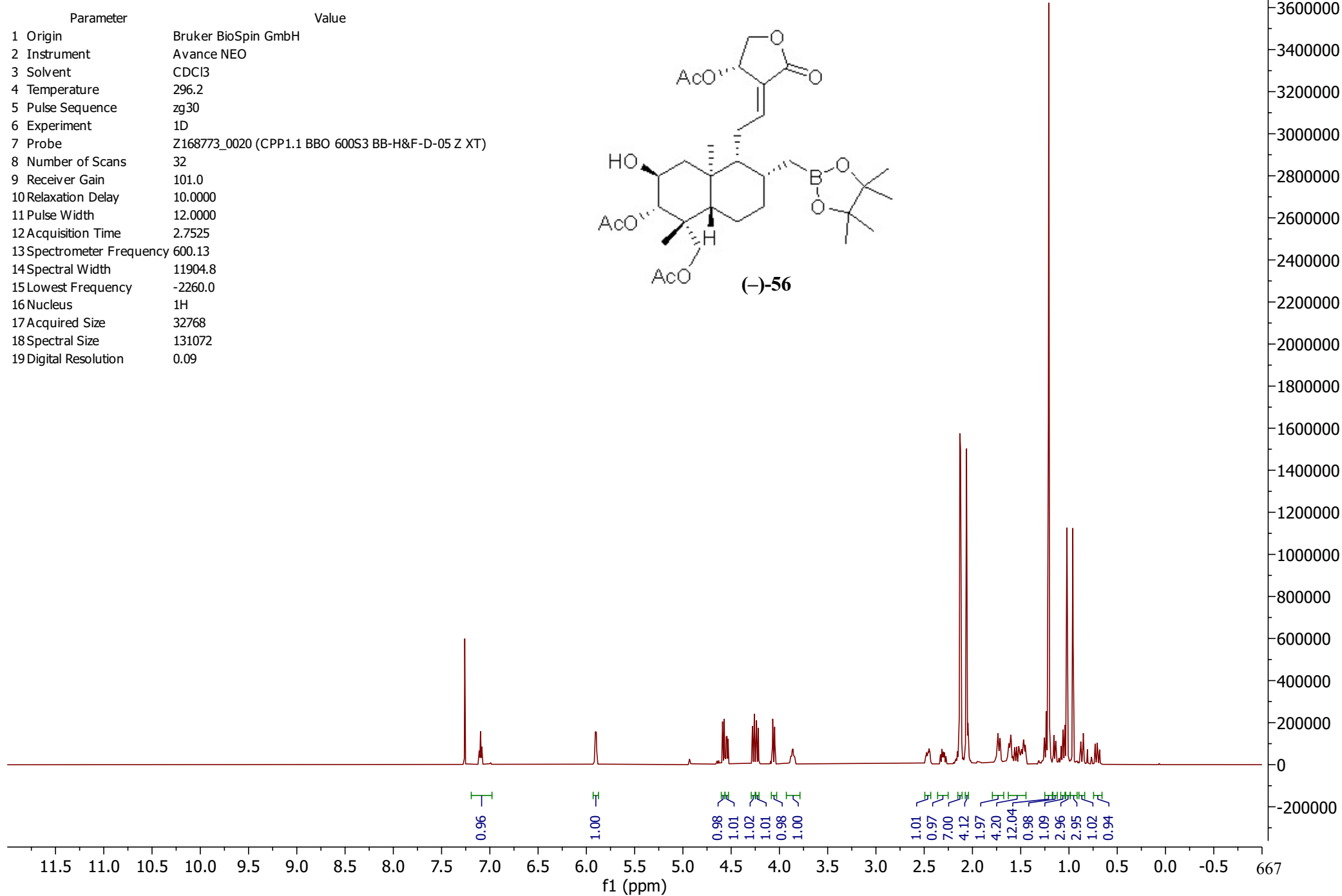
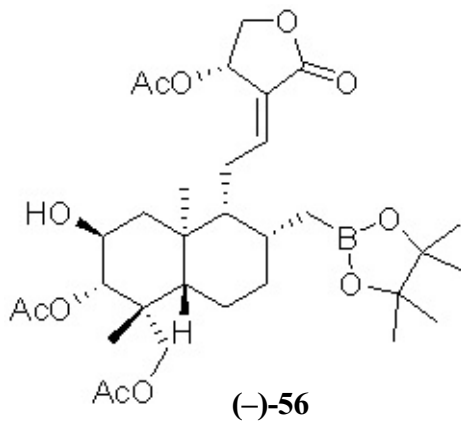
71.77
67.77
65.14

56.28
54.39

41.24
37.89
34.42
32.11
27.50
24.91
24.79
23.43
22.60
21.27
20.88
18.10
16.22
11.21



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



Parameter Value

1 Origin Bruker BioSpin GmbH

2 Instrument Avance NEO

3 Solvent CDCl3

4 Temperature 296.2

5 Pulse Sequence zgpg30

6 Experiment 1D

7 Probe Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)

8 Number of Scans 4096

9 Receiver Gain 101.0

10 Relaxation Delay 2.0000

11 Pulse Width 10.0000

12 Acquisition Time 0.8847

13 Spectrometer Frequency 150.92

14 Spectral Width 37037.0

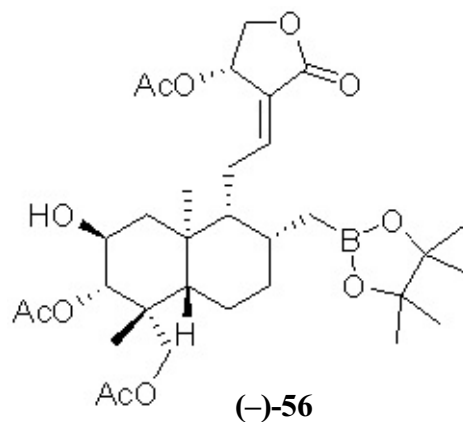
15 Lowest Frequency -1900.0

16 Nucleus 13C

17 Acquired Size 32768

18 Spectral Size 65536

19 Digital Resolution 0.57



171.86
170.93
170.73
169.04

149.66

124.85

83.80
83.32

71.82
67.84
66.69
65.35

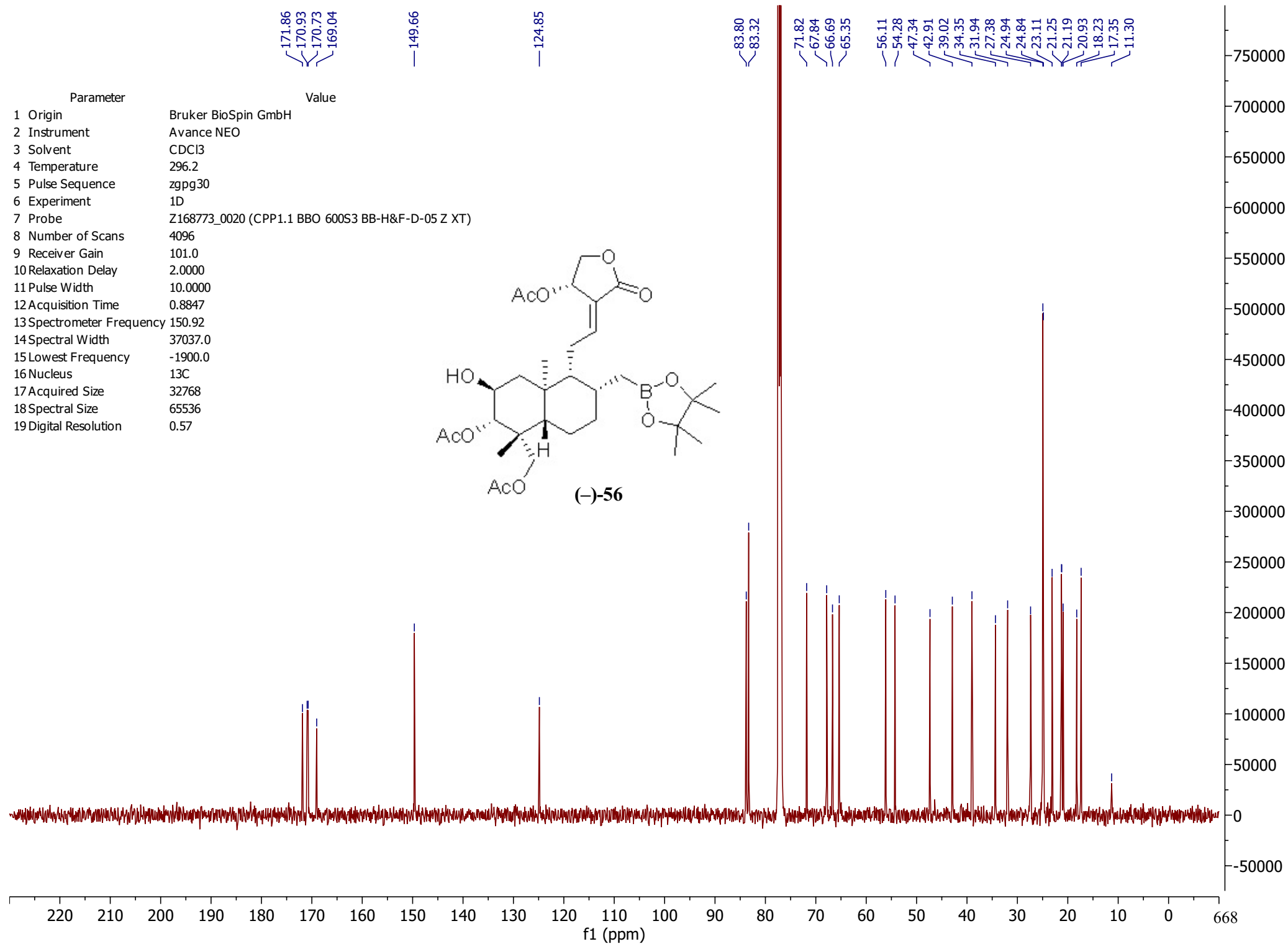
56.11
54.28
47.34

42.91
39.02
34.35

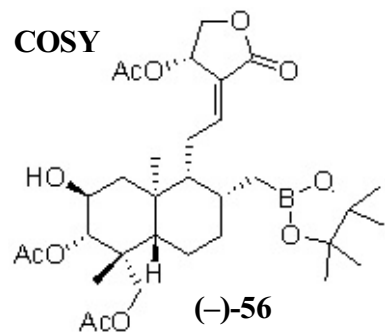
31.94
27.38
24.94
24.84

23.11
21.25
21.19

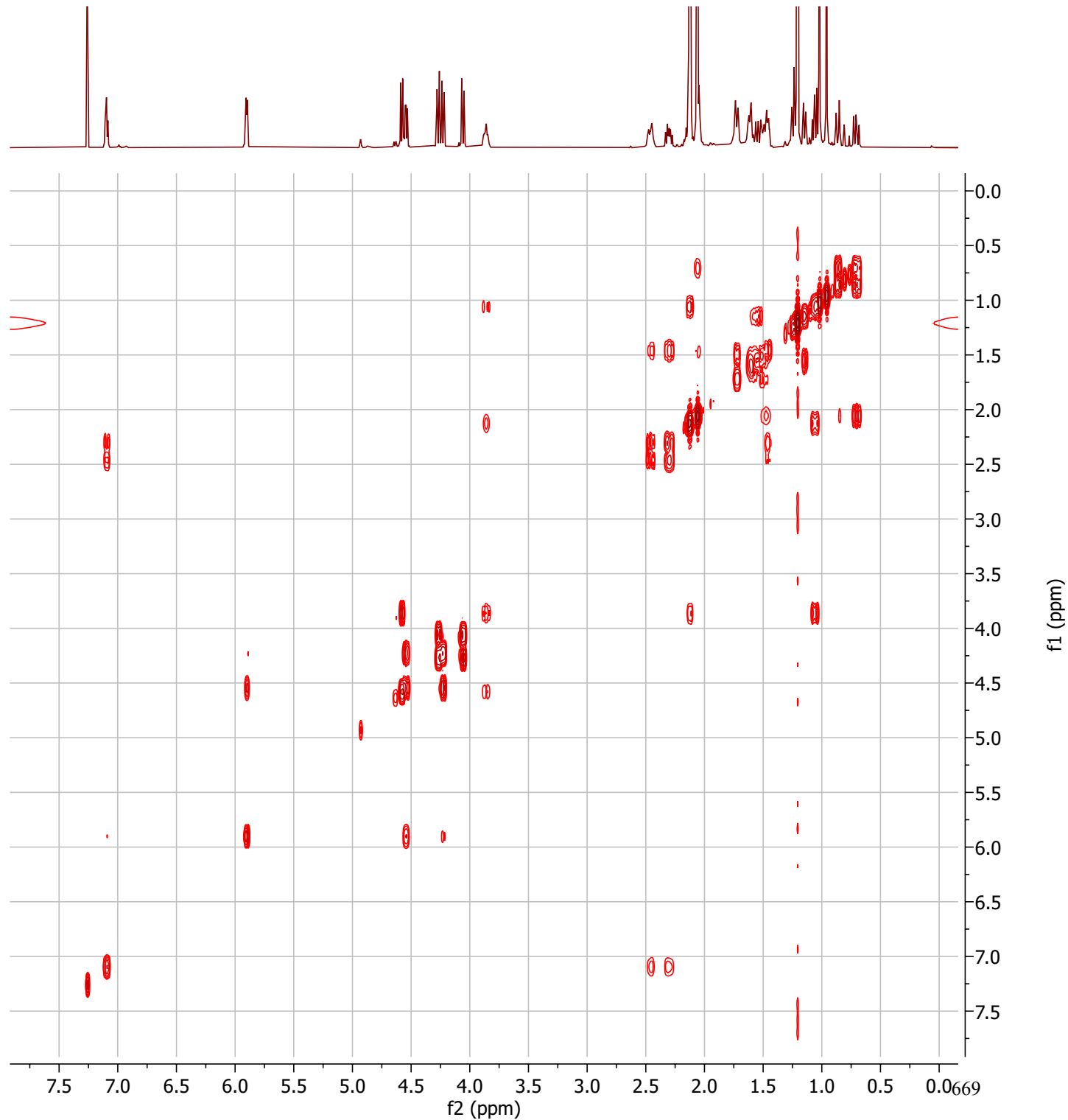
20.93
18.23
17.35
11.30



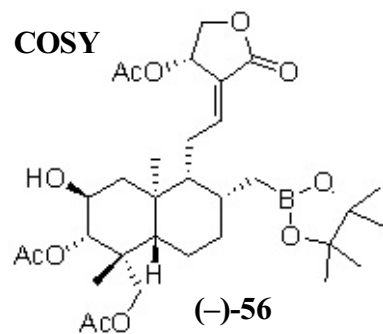
COSY



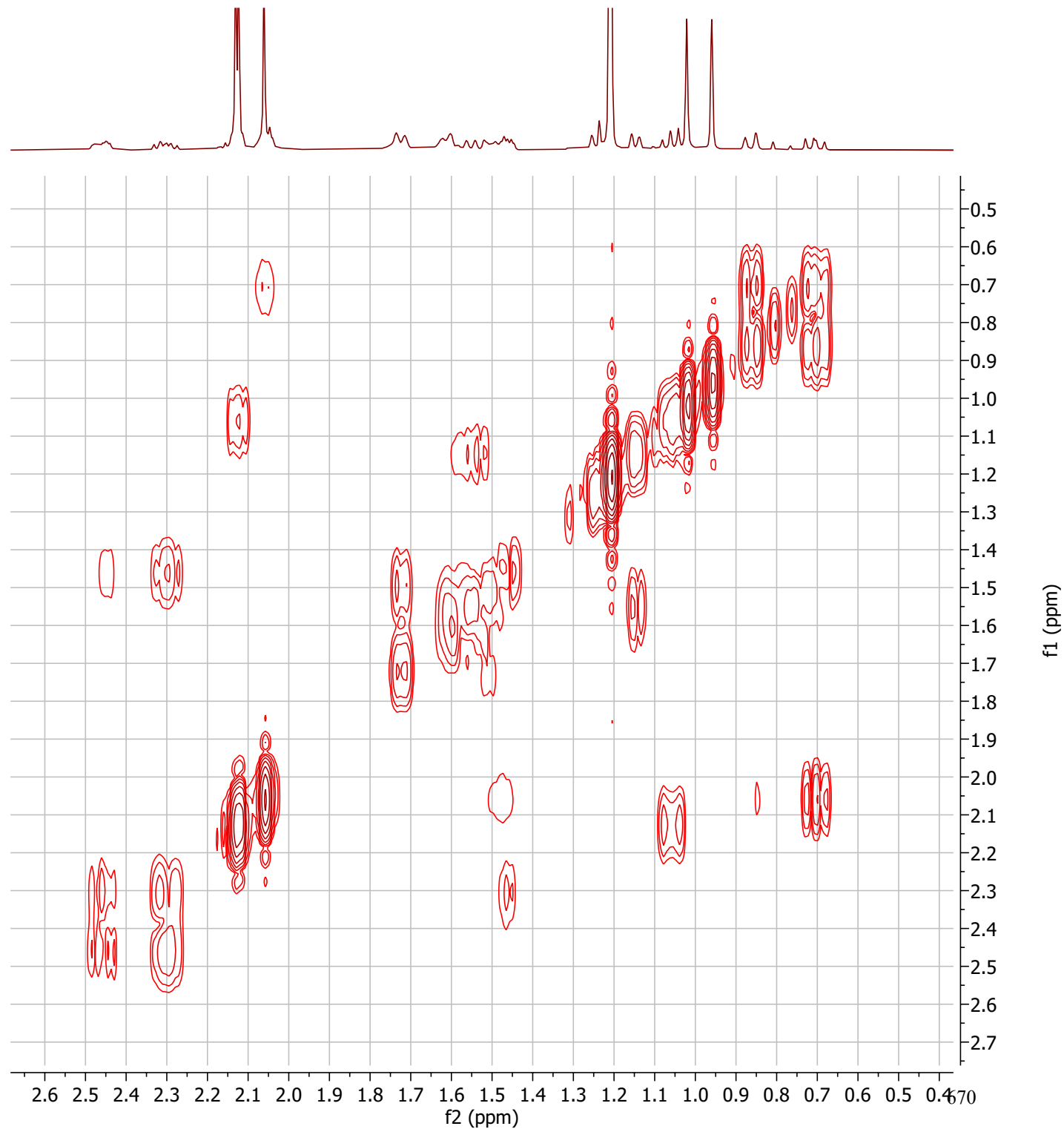
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.4181
11 Pulse Width	12.0000
12 Acquisition Time	0.2109
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(4854.4, 4854.4)
15 Lowest Frequency	(-101.9, -101.9)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.74, 4.74)

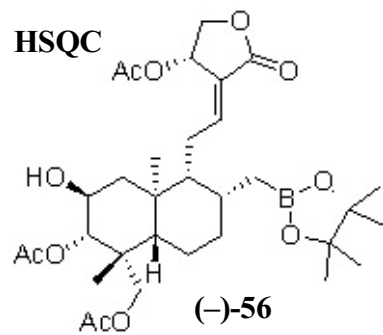


COSY

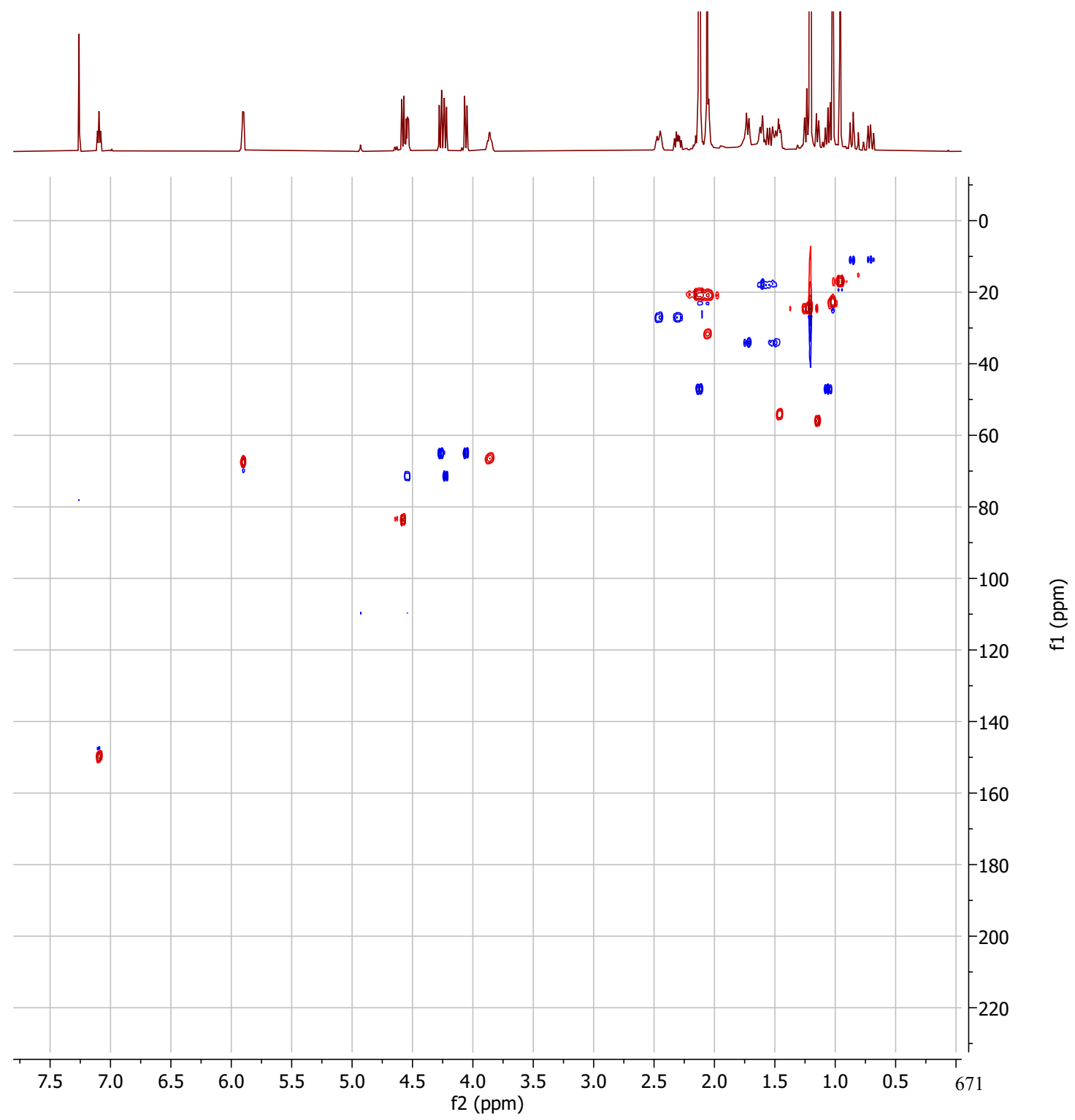


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.4181
11 Pulse Width	12.0000
12 Acquisition Time	0.2109
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(4854.4, 4854.4)
15 Lowest Frequency	(-101.9, -101.9)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.74, 4.74)

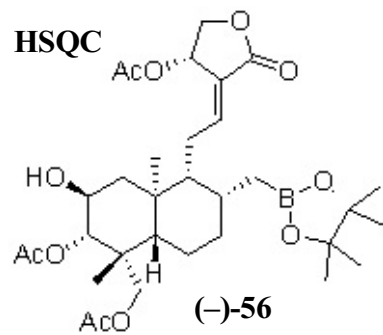




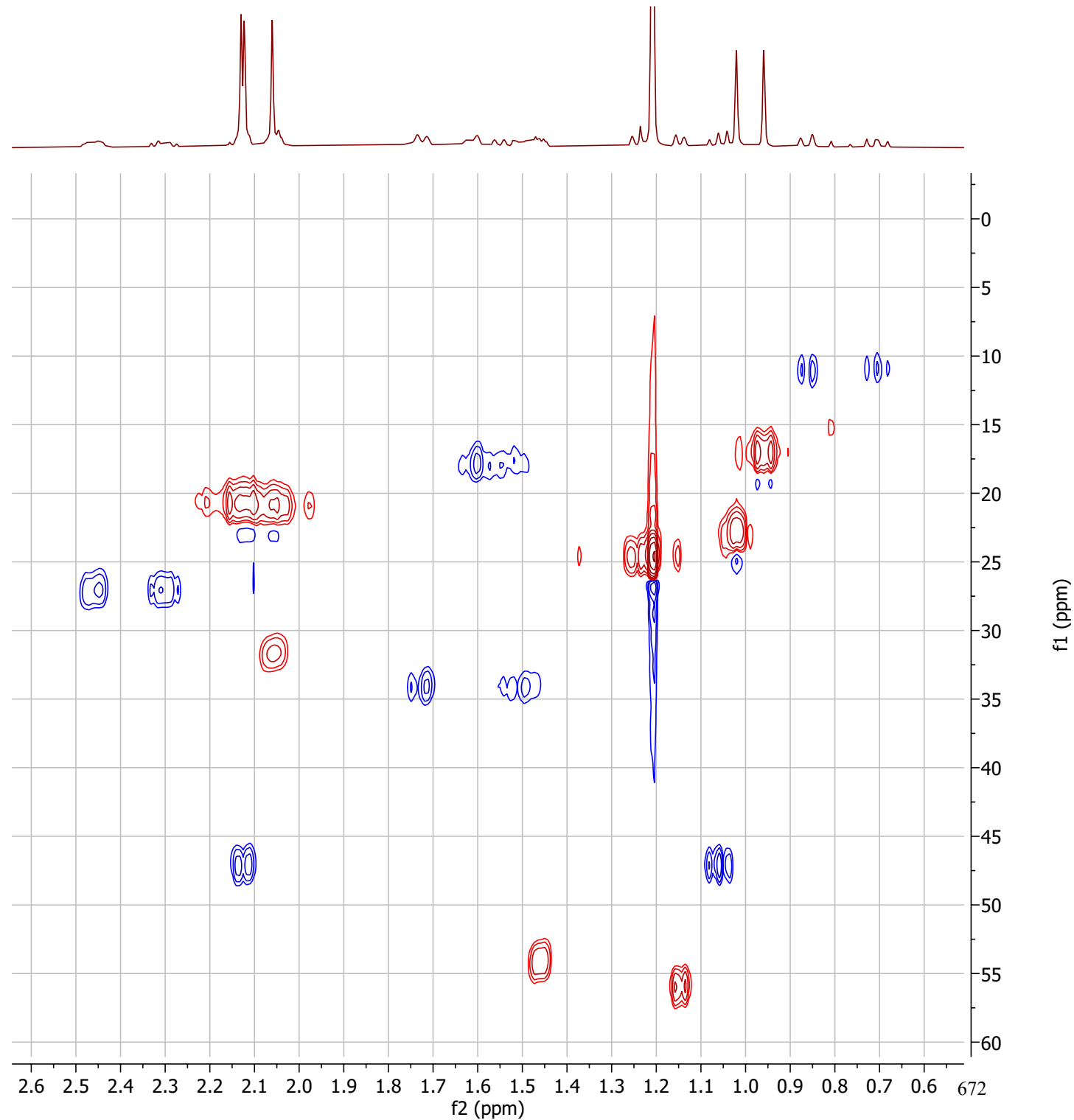
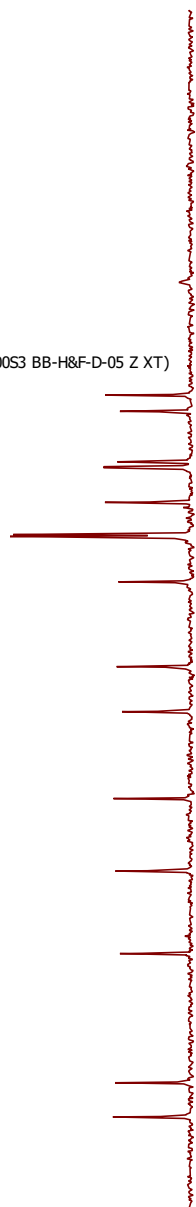
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpsi2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.2171
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4717.0, 36974.0)
15 Lowest Frequency	(-32.8, -1891.2)
16 Nucleus	(1H, 13C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.61, 36.11)



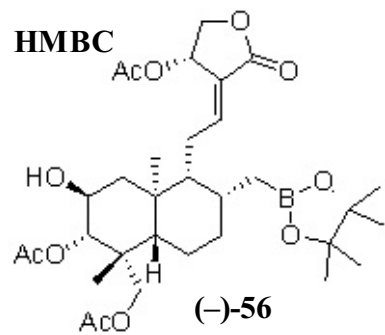
HSQC



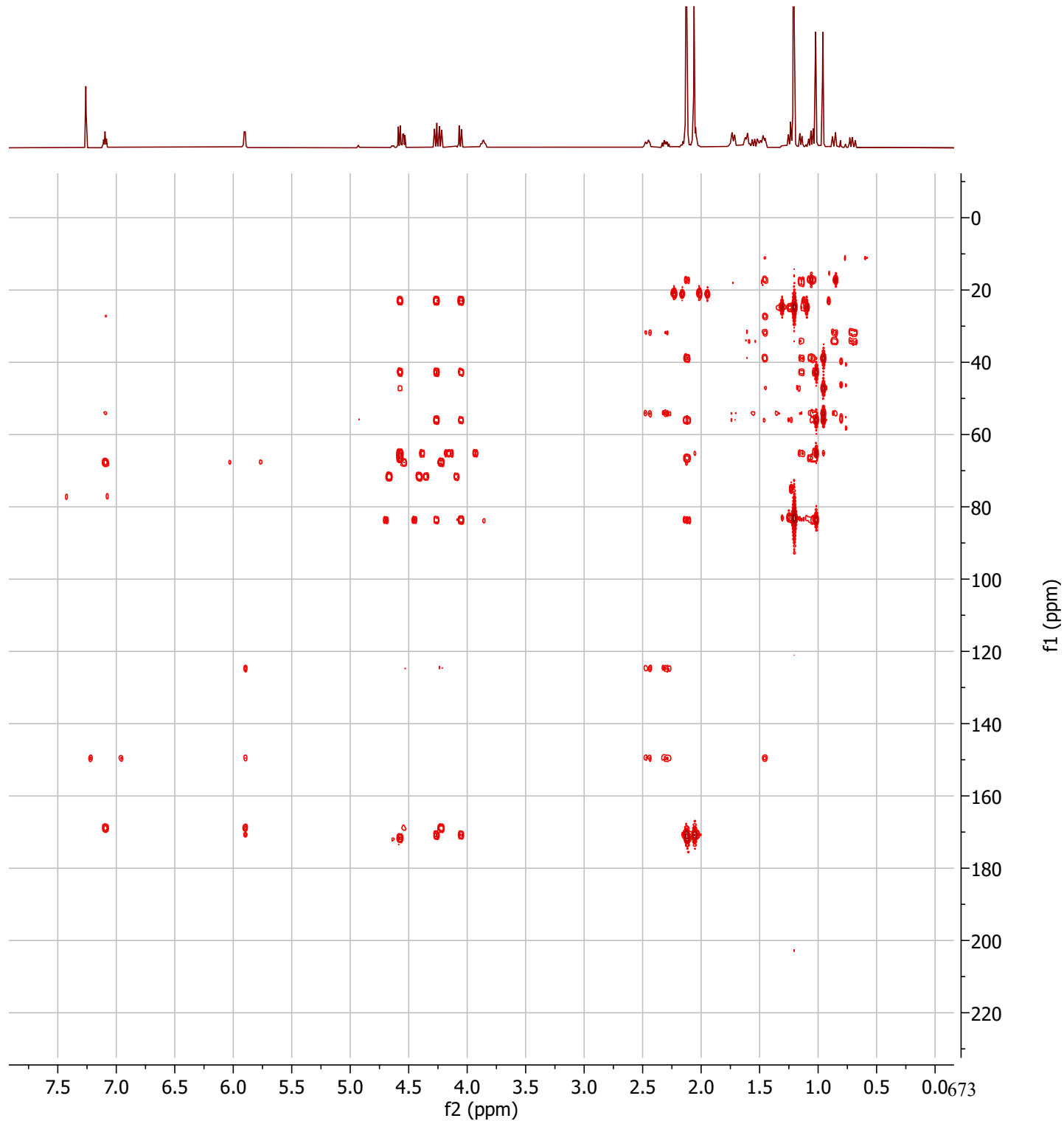
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpcisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.2171
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4717.0, 36974.0)
15 Lowest Frequency	(-32.8, -1891.2)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.61, 36.11)



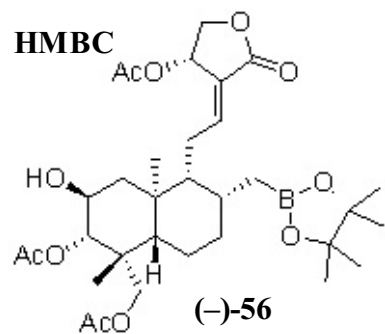
HMBC



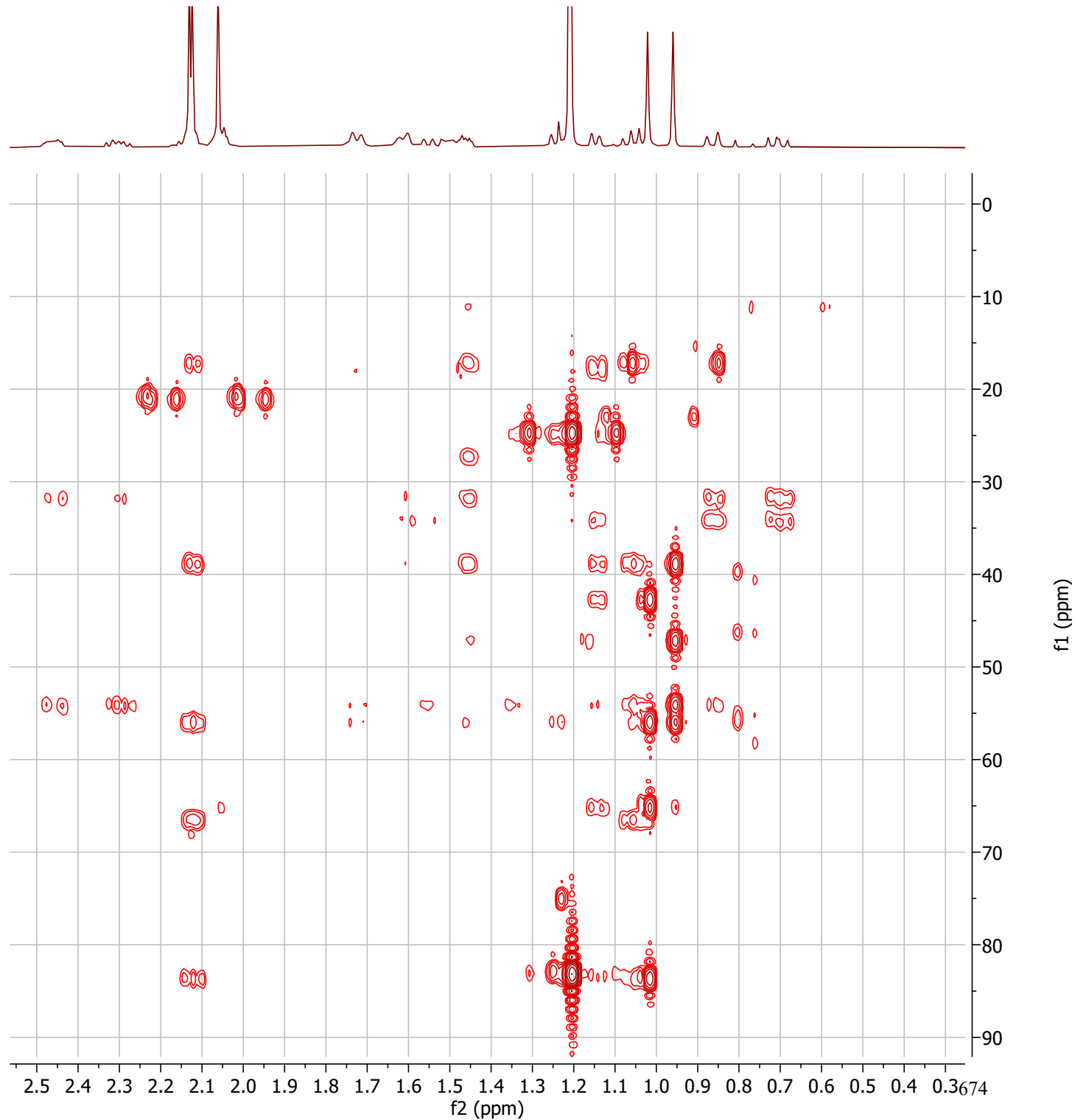
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.2109
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4854.4, 36974.9)
15 Lowest Frequency	(-101.9, -1891.5)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.74, 36.11)



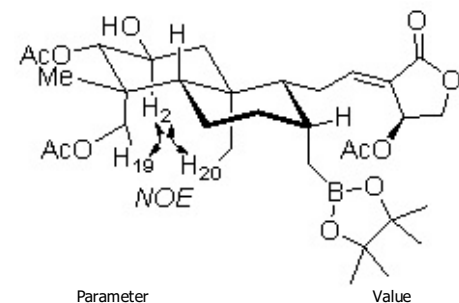
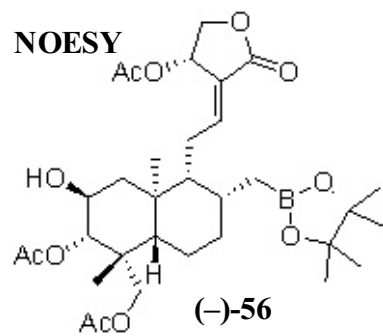
HMBC



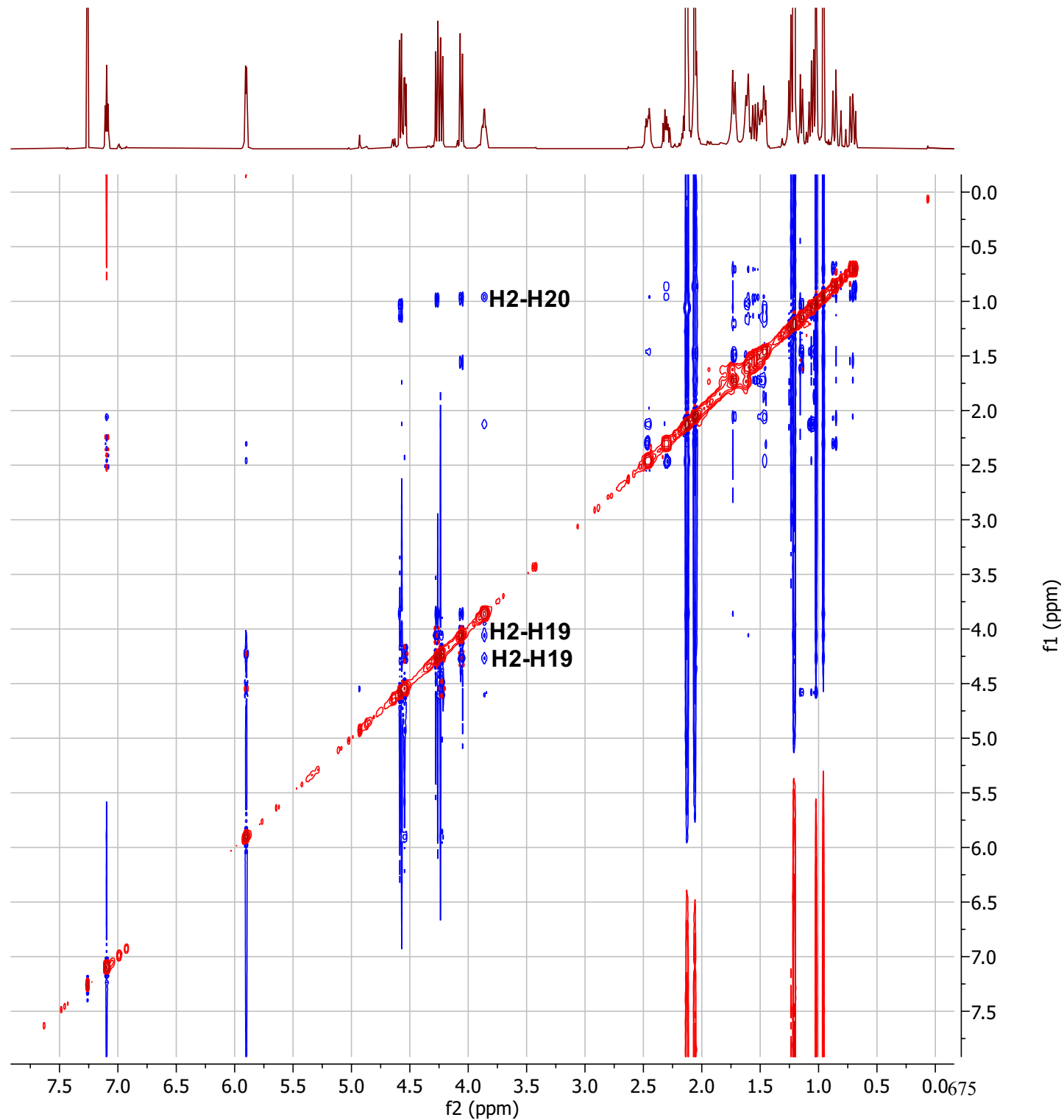
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.2109
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4854.4, 36974.9)
15 Lowest Frequency	(-101.9, -1891.5)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.74, 36.11)



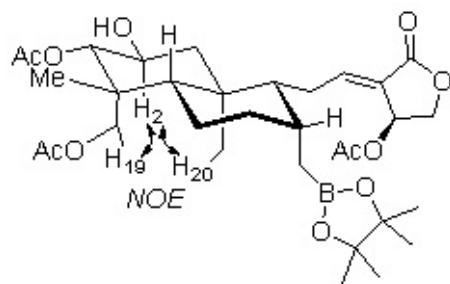
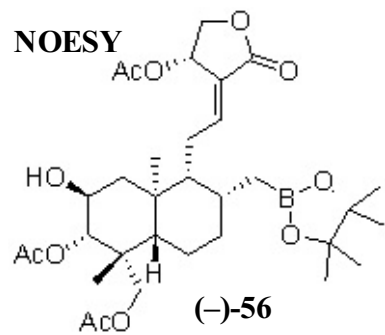
NOESY



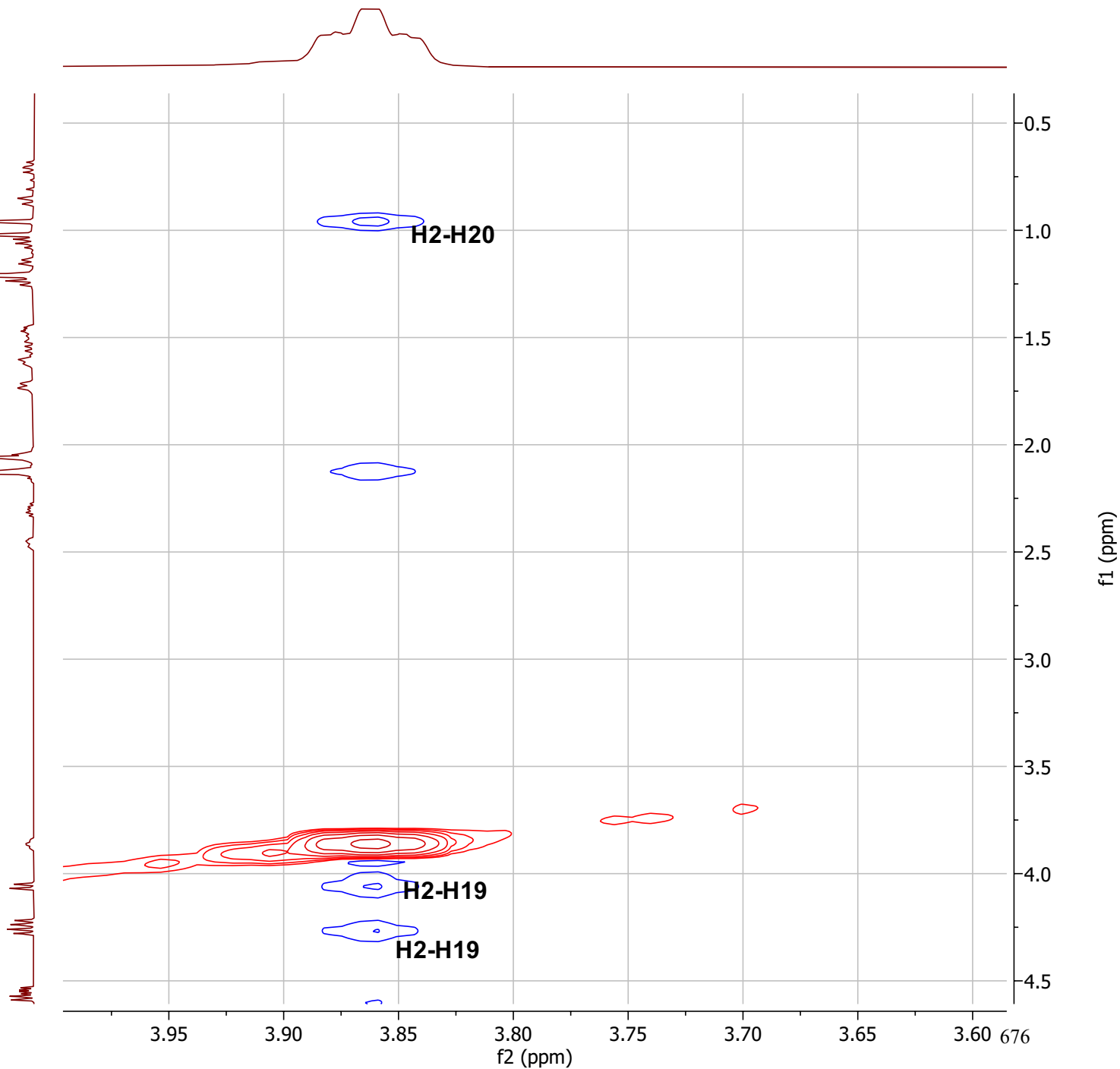
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.9611
11 Pulse Width	12.0000
12 Acquisition Time	0.2109
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(4854.4, 4854.4)
15 Lowest Frequency	(-101.9, -101.9)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.74, 4.74)



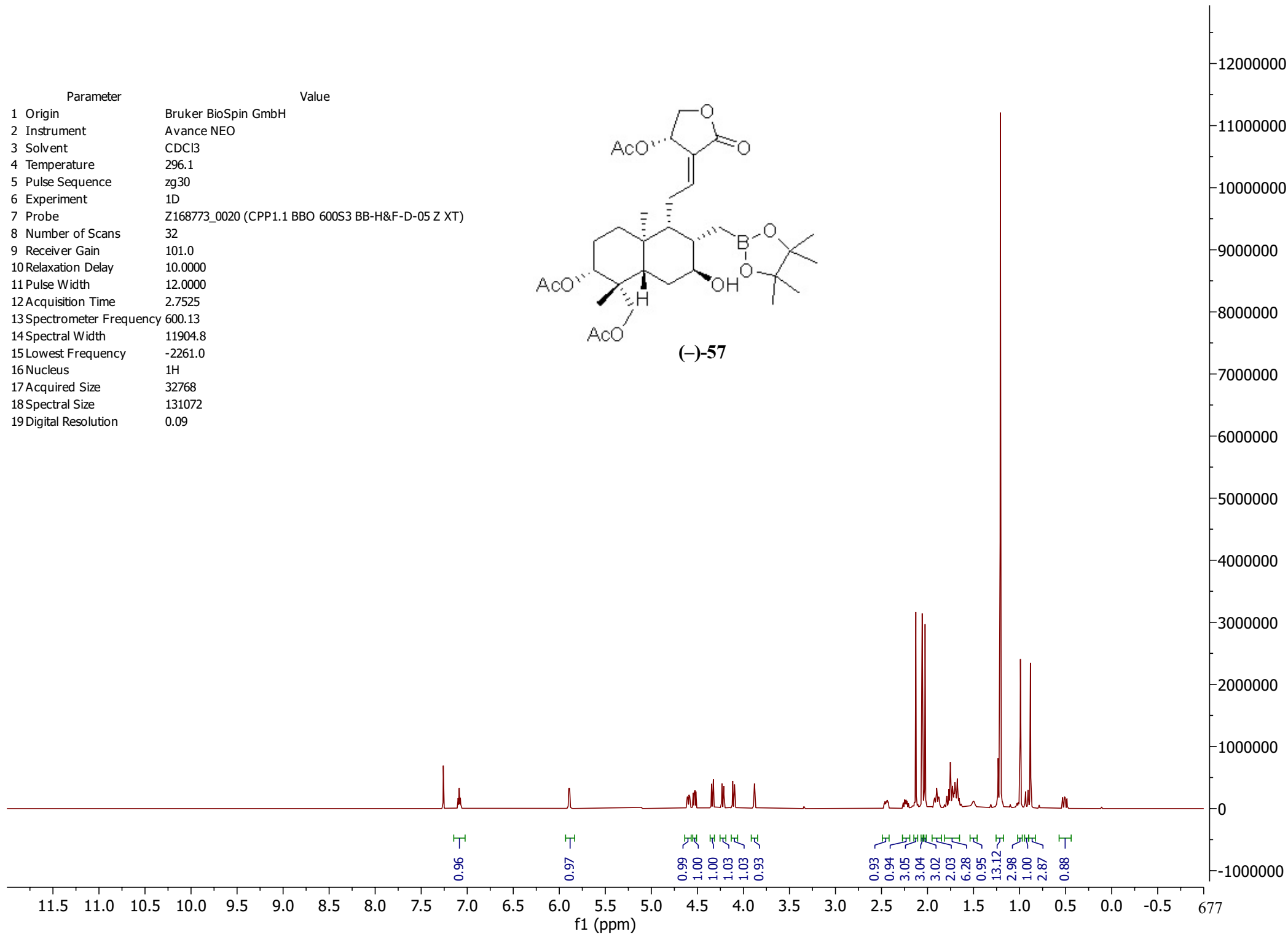
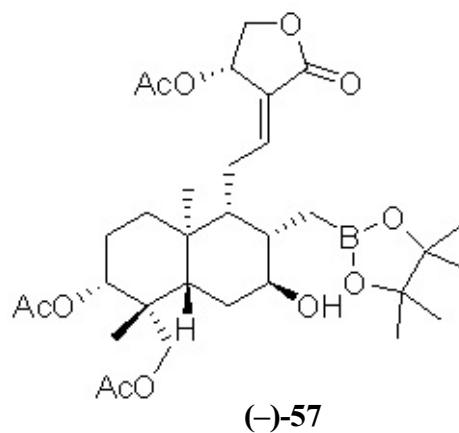
NOESY



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.9611
11 Pulse Width	12.0000
12 Acquisition Time	0.2109
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(4854.4, 4854.4)
15 Lowest Frequency	(-101.9, -101.9)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.74, 4.74)



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



Parameter Value

1 Origin Bruker BioSpin GmbH

2 Instrument Avance NEO

3 Solvent CDCl₃

4 Temperature 296.2

5 Pulse Sequence zgpg30

6 Experiment 1D

7 Probe Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)

8 Number of Scans 4096

9 Receiver Gain 101.0

10 Relaxation Delay 2.0000

11 Pulse Width 10.0000

12 Acquisition Time 0.8847

13 Spectrometer Frequency 150.92

14 Spectral Width 37037.0

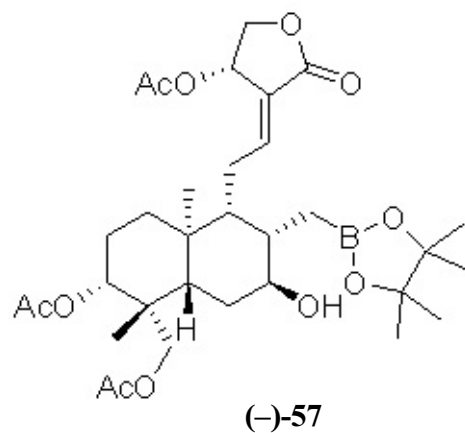
15 Lowest Frequency -1901.6

16 Nucleus ¹³C

17 Acquired Size 32768

18 Spectral Size 65536

19 Digital Resolution 0.57



171.12
170.71
170.57
169.03

149.69

124.85

83.52

79.84

71.83

71.31

67.81

65.44

47.69

46.71

40.71

40.22

37.85

37.63

26.75

24.87

23.44

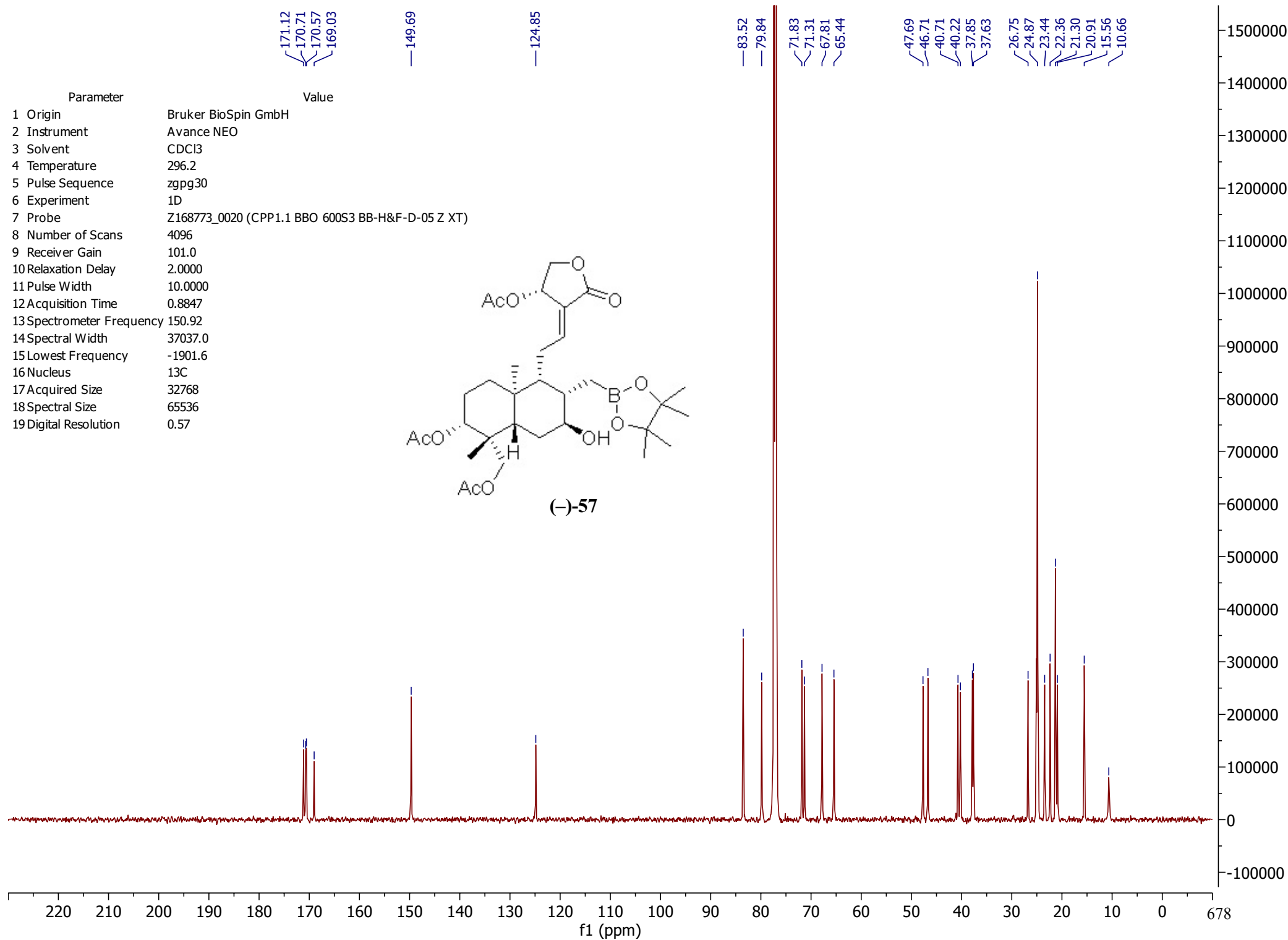
22.36

21.30

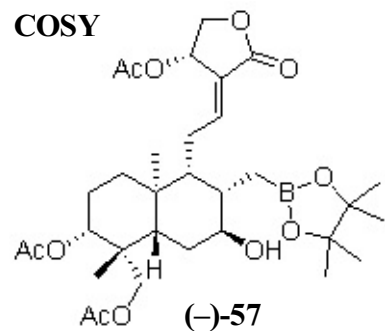
20.91

15.56

10.66



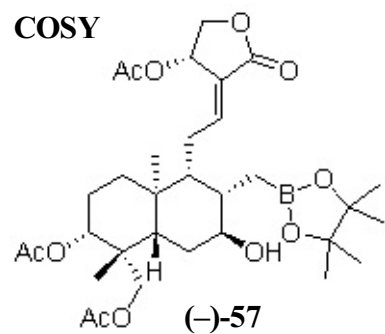
COSY



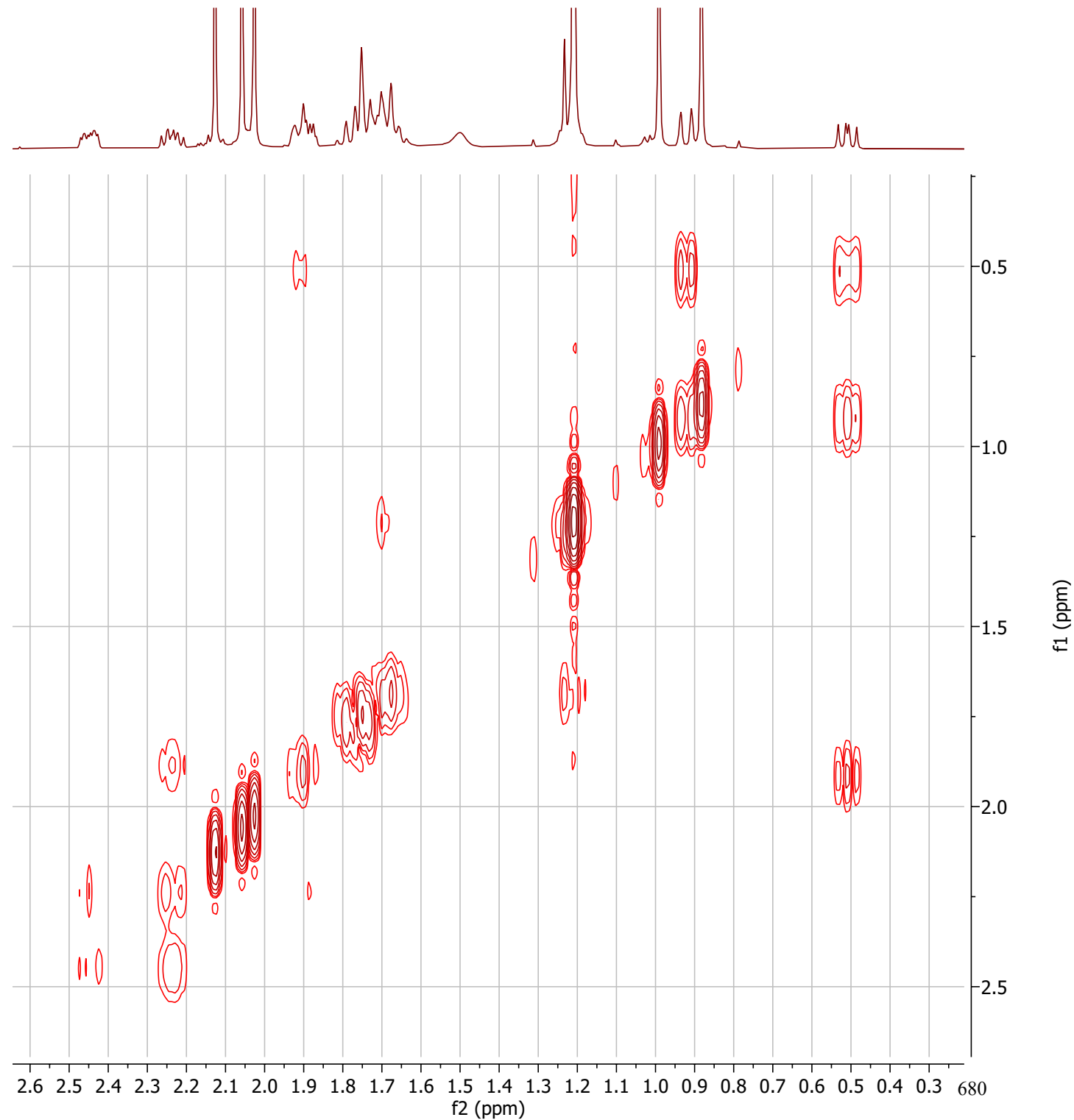
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.4242
11 Pulse Width	12.0000
12 Acquisition Time	0.2048
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(5000.0, 5000.0)
15 Lowest Frequency	(-234.4, -234.4)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.88, 4.88)



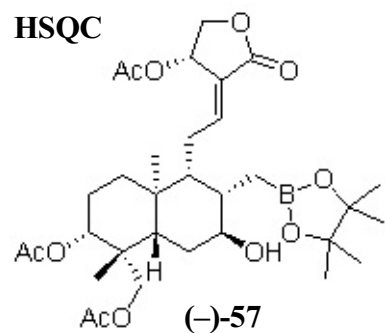
COSY



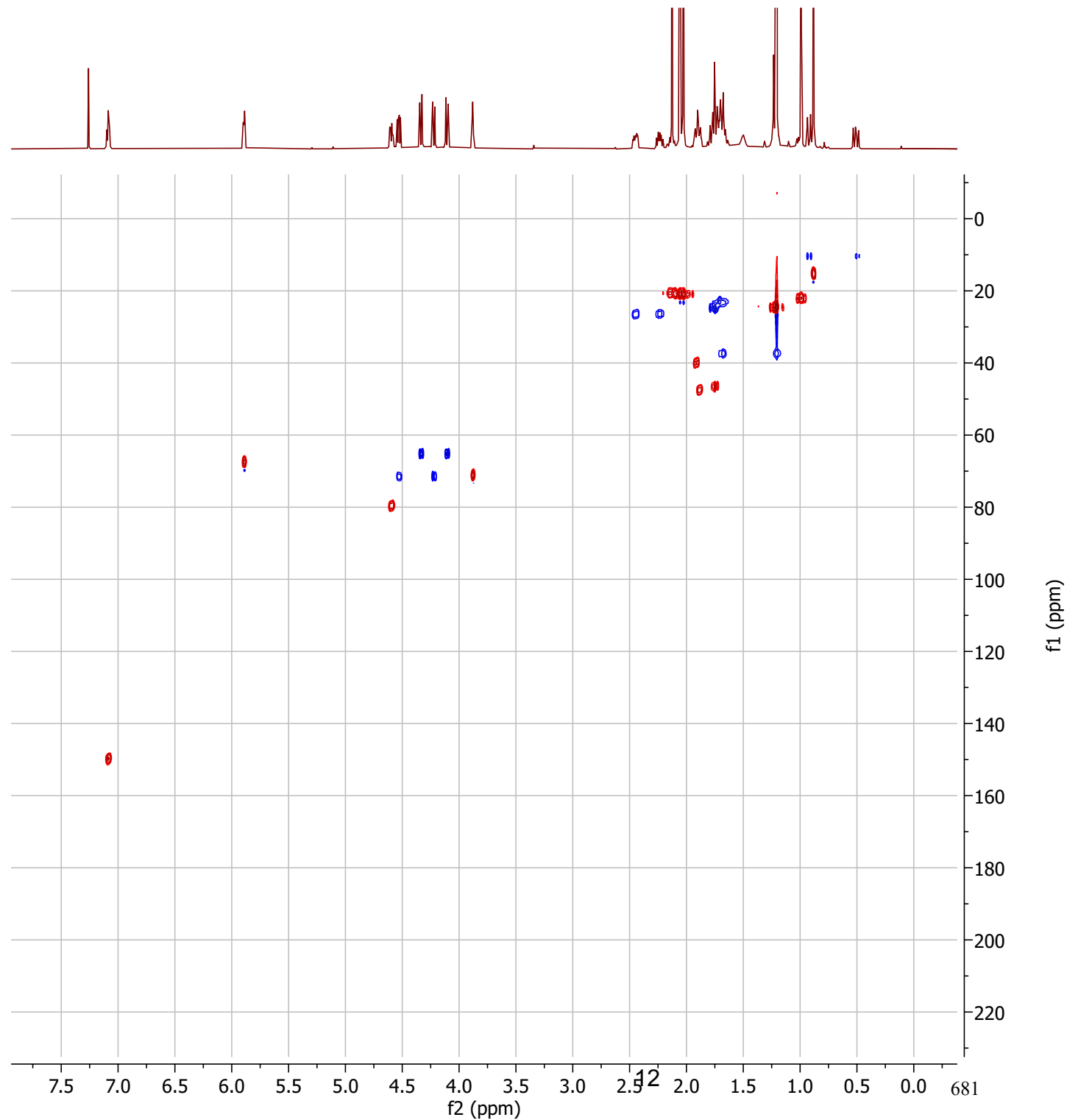
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.4242
11 Pulse Width	12.0000
12 Acquisition Time	0.2048
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(5000.0, 5000.0)
15 Lowest Frequency	(-234.4, -234.4)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.88, 4.88)



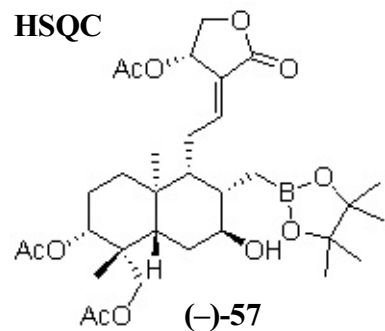
HSQC



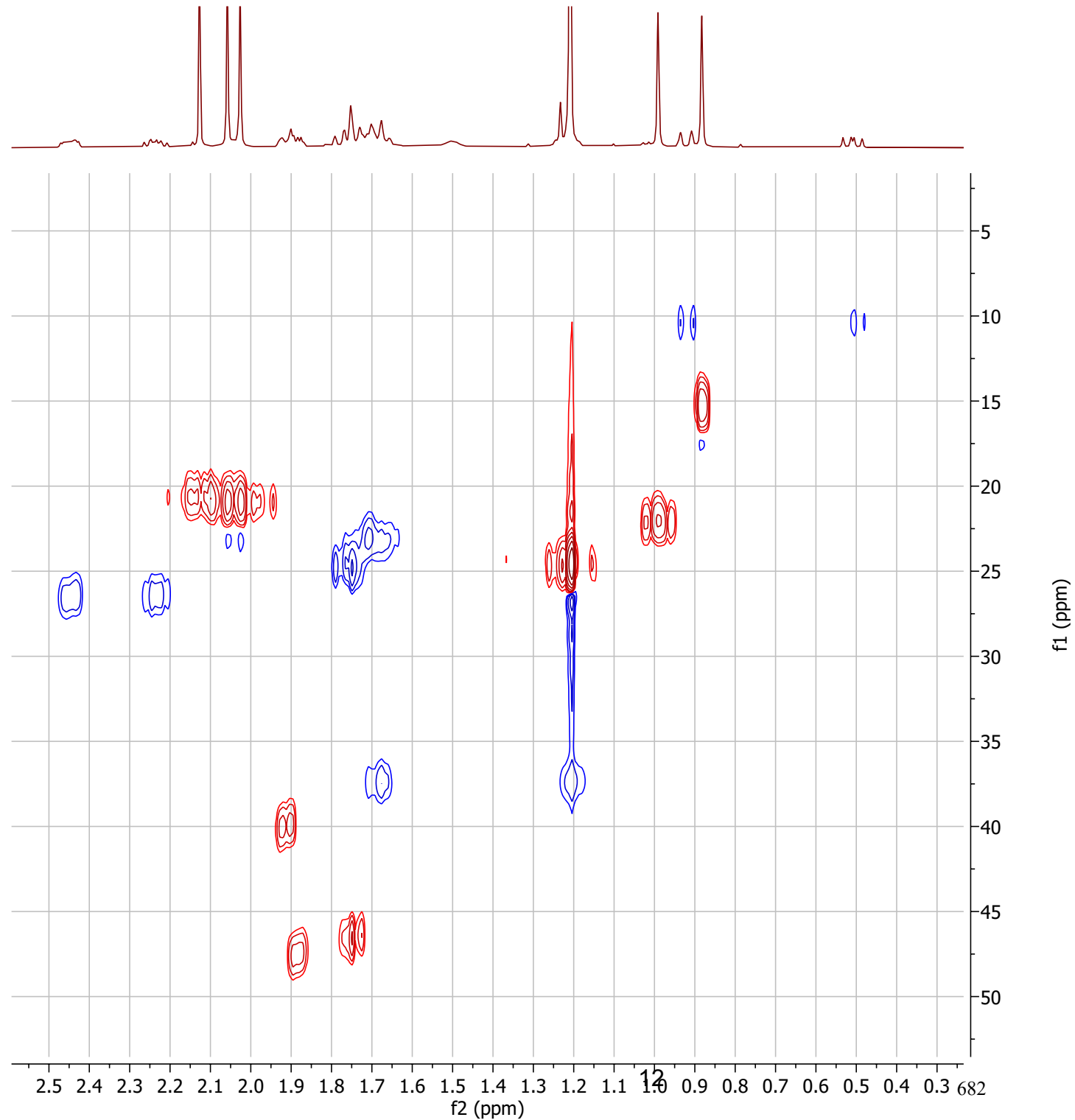
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hsqcetdgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.2048
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(5000.0, 36974.0)
15 Lowest Frequency	(-234.4, -1891.3)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.88, 36.11)



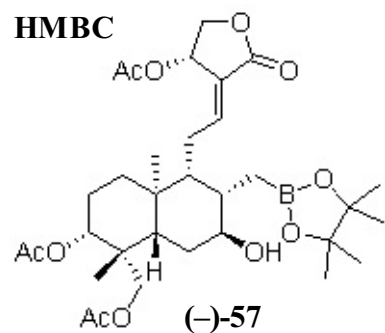
HSQC



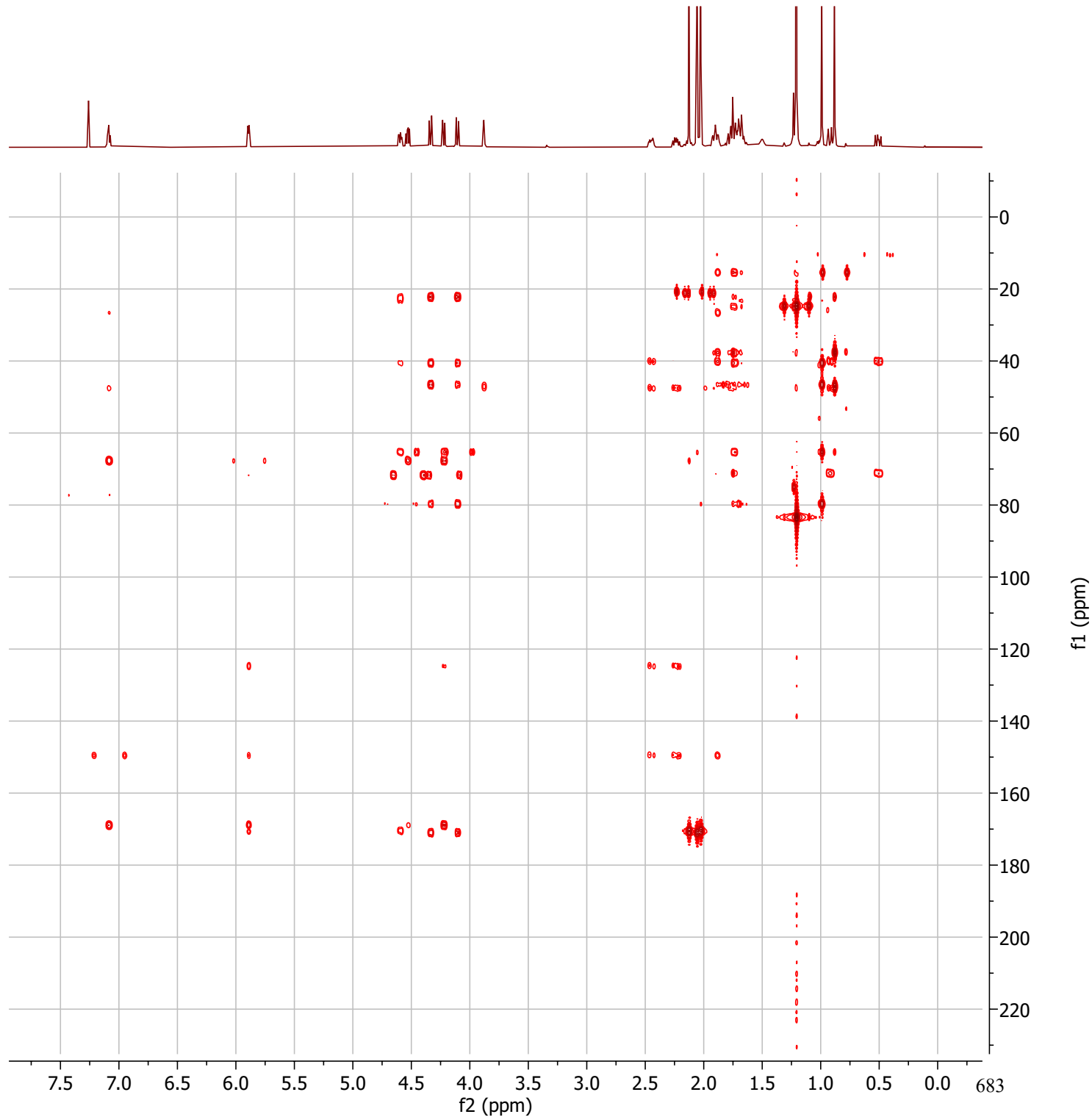
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hsqcetdgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.2048
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(5000.0, 36974.0)
15 Lowest Frequency	(-234.4, -1891.3)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.88, 36.11)



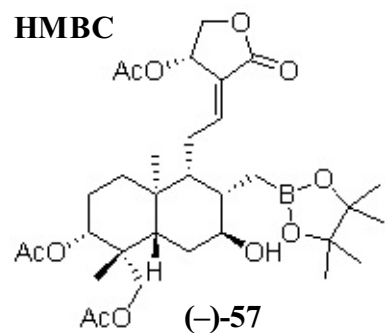
HMBC



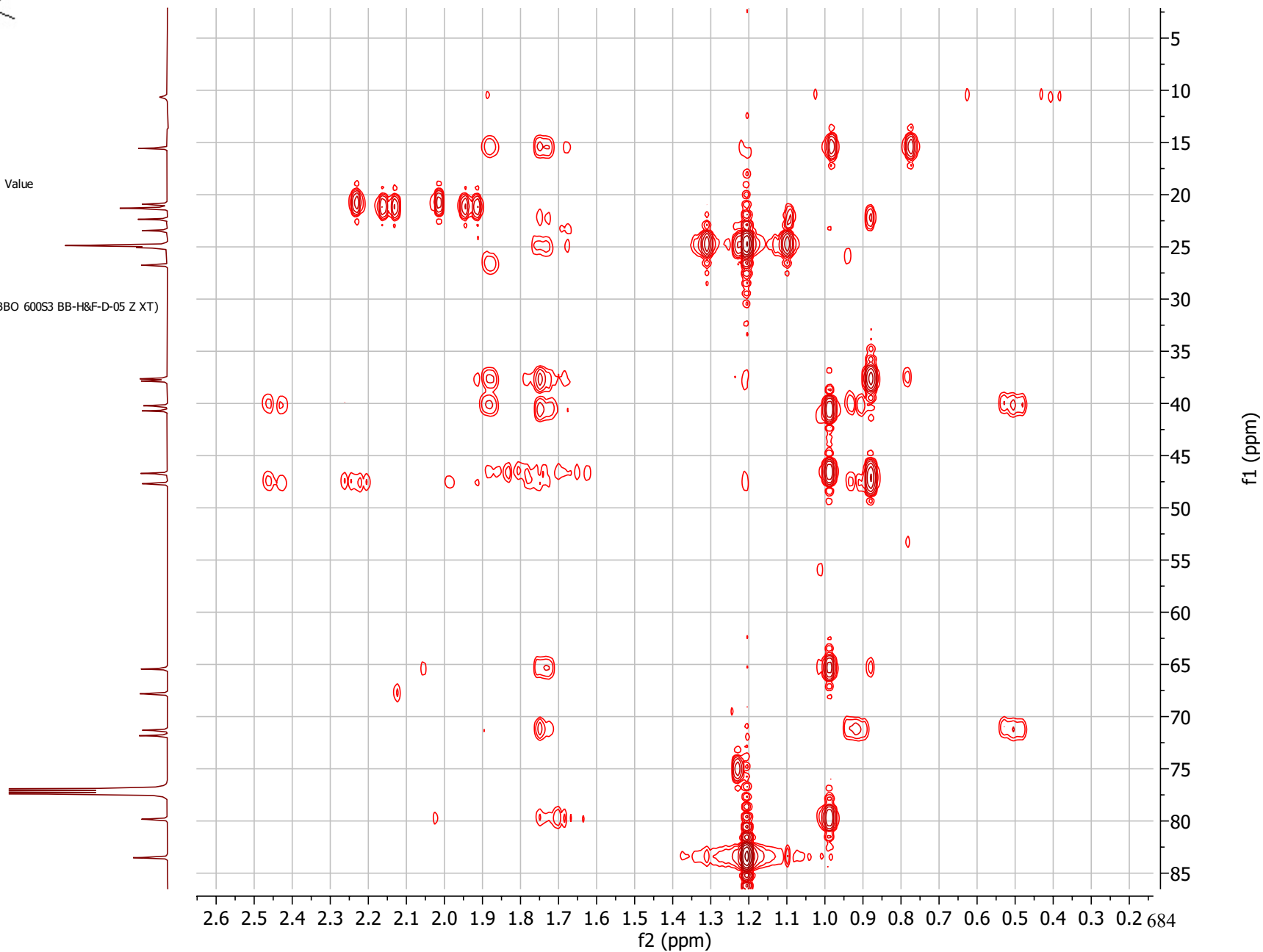
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.2048
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(5000.0, 36974.9)
15 Lowest Frequency	(-234.4, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.88, 36.11)



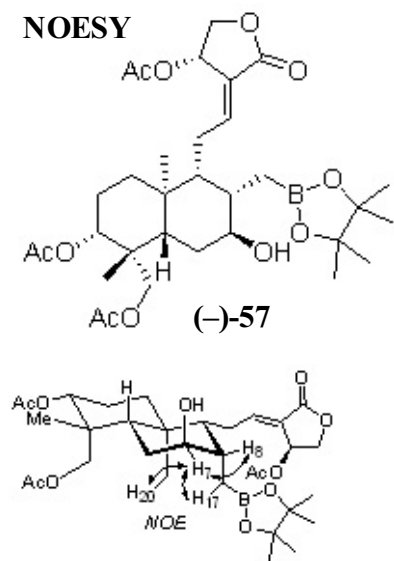
HMBC



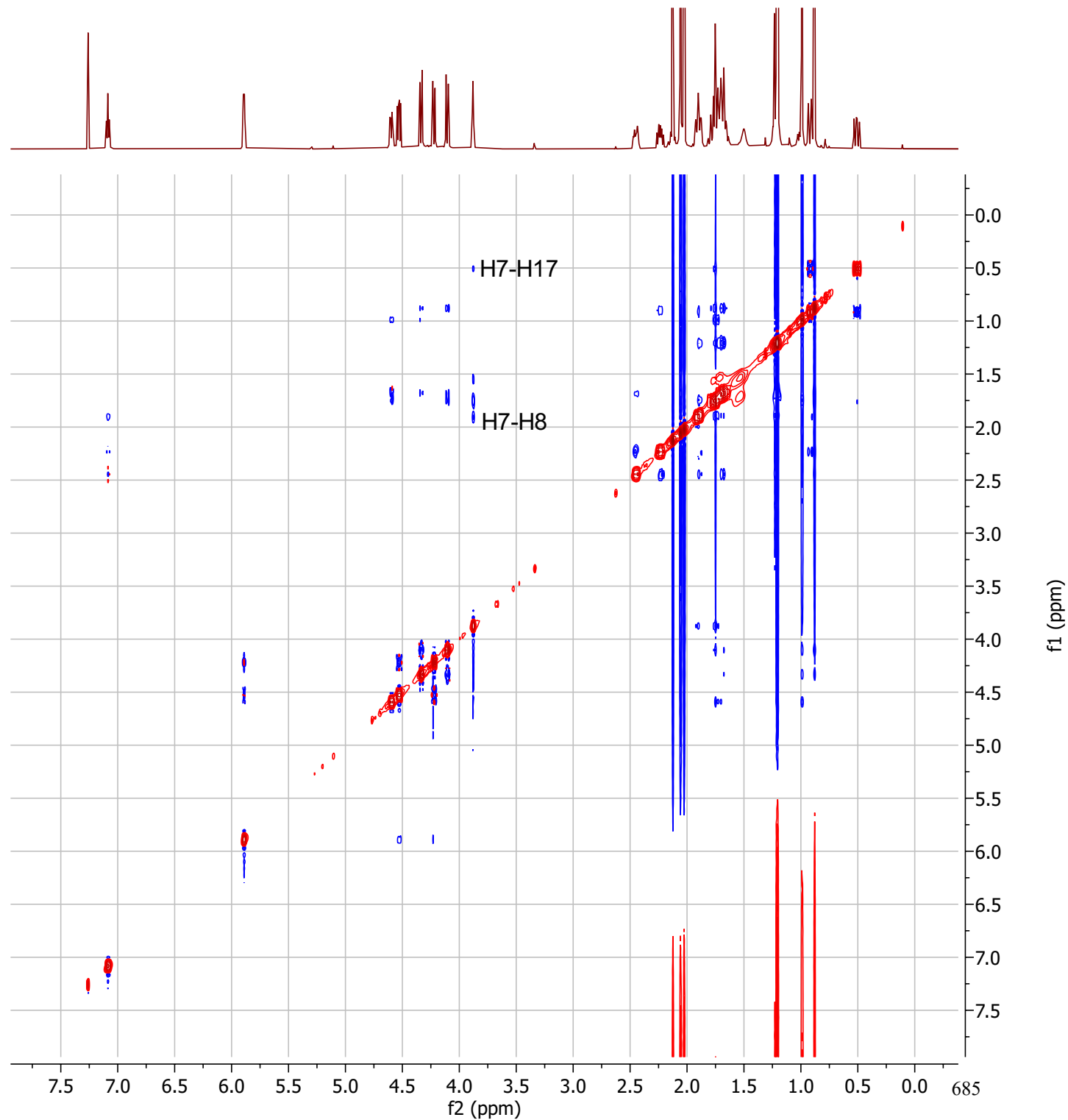
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.2048
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(5000.0, 36974.9)
15 Lowest Frequency	(-234.4, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.88, 36.11)



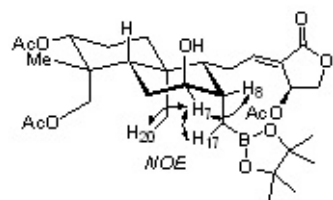
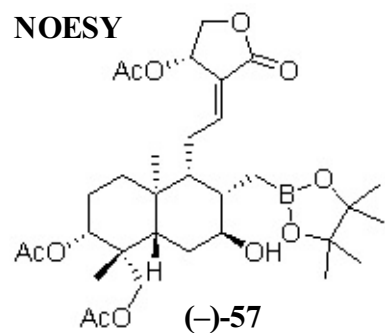
NOESY



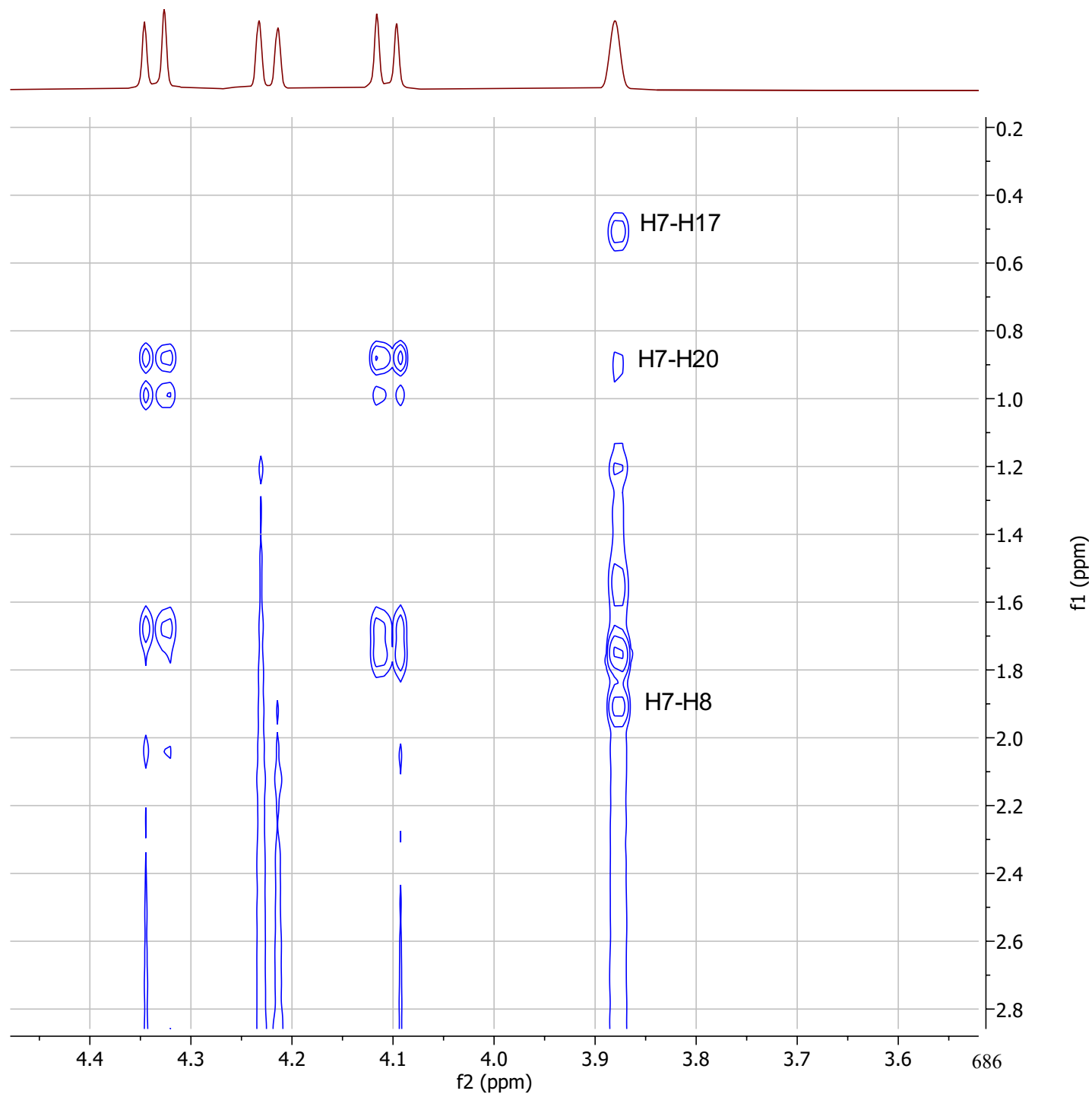
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.9672
11 Pulse Width	12.0000
12 Acquisition Time	0.2048
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(5000.0, 5000.0)
15 Lowest Frequency	(-234.4, -234.4)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.88, 4.88)



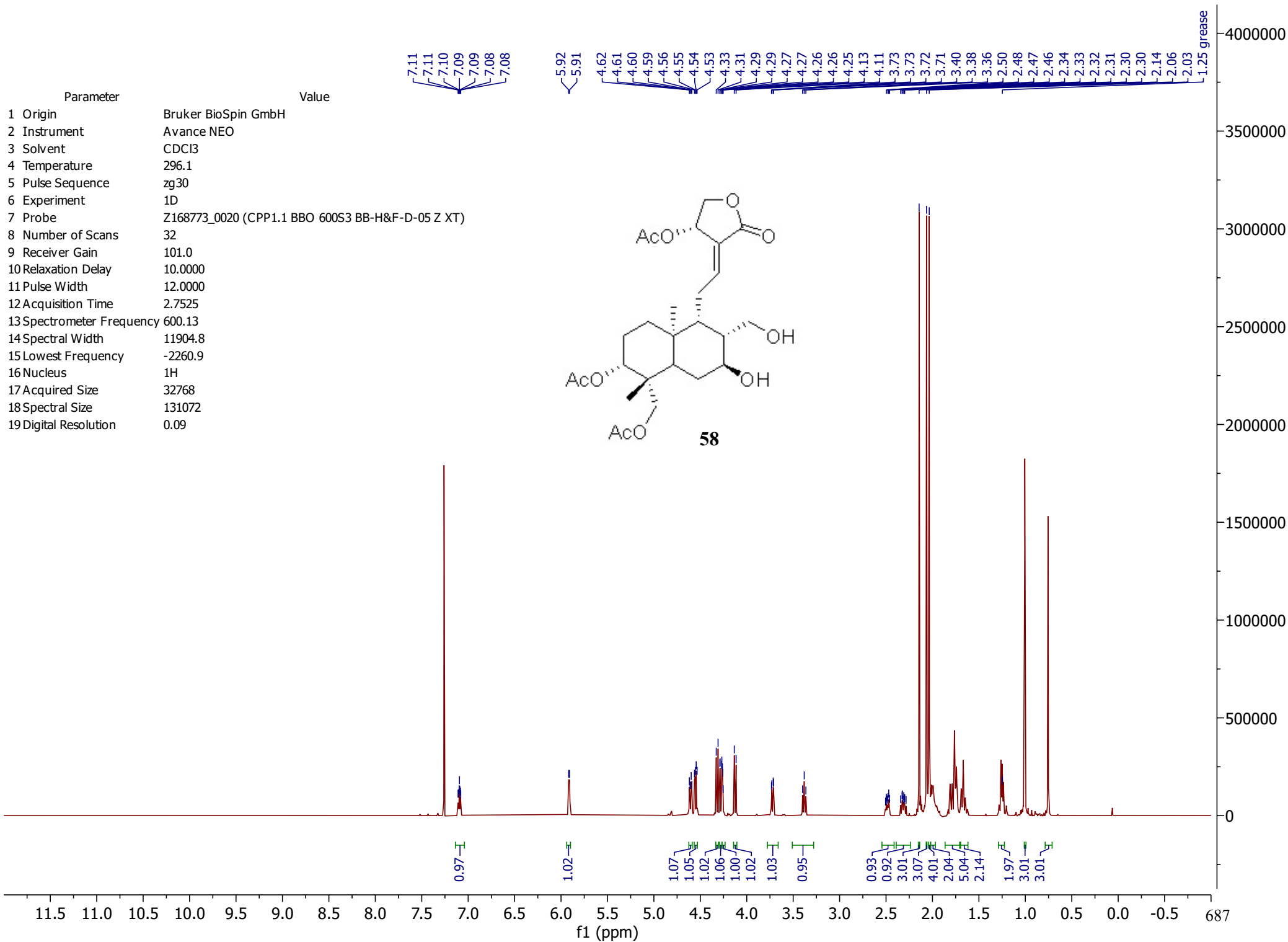
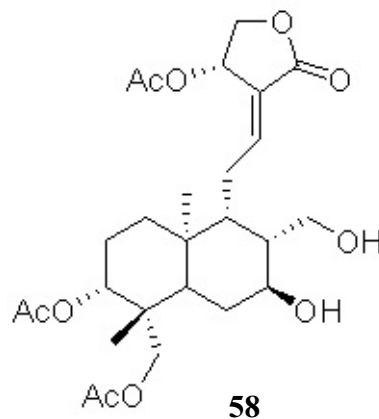
NOESY



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.9672
11 Pulse Width	12.0000
12 Acquisition Time	0.2048
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(5000.0, 5000.0)
15 Lowest Frequency	(-234.4, -234.4)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.88, 4.88)



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



1 Origin Bruker BioSpin GmbH
 2 Instrument Avance NEO
 3 Solvent CDCl₃
 4 Temperature 296.1
 5 Pulse Sequence zgpg30
 6 Experiment 1D
 7 Probe Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
 8 Number of Scans 1930
 9 Receiver Gain 101.0
 10 Relaxation Delay 2.0000
 11 Pulse Width 10.0000
 12 Acquisition Time 0.8847
 13 Spectrometer Frequency 150.92
 14 Spectral Width 37037.0
 15 Lowest Frequency -1900.5
 16 Nucleus ¹³C
 17 Acquired Size 32768
 18 Spectral Size 65536
 19 Digital Resolution 0.57

171.14
 170.77
 170.61
 169.50

149.29

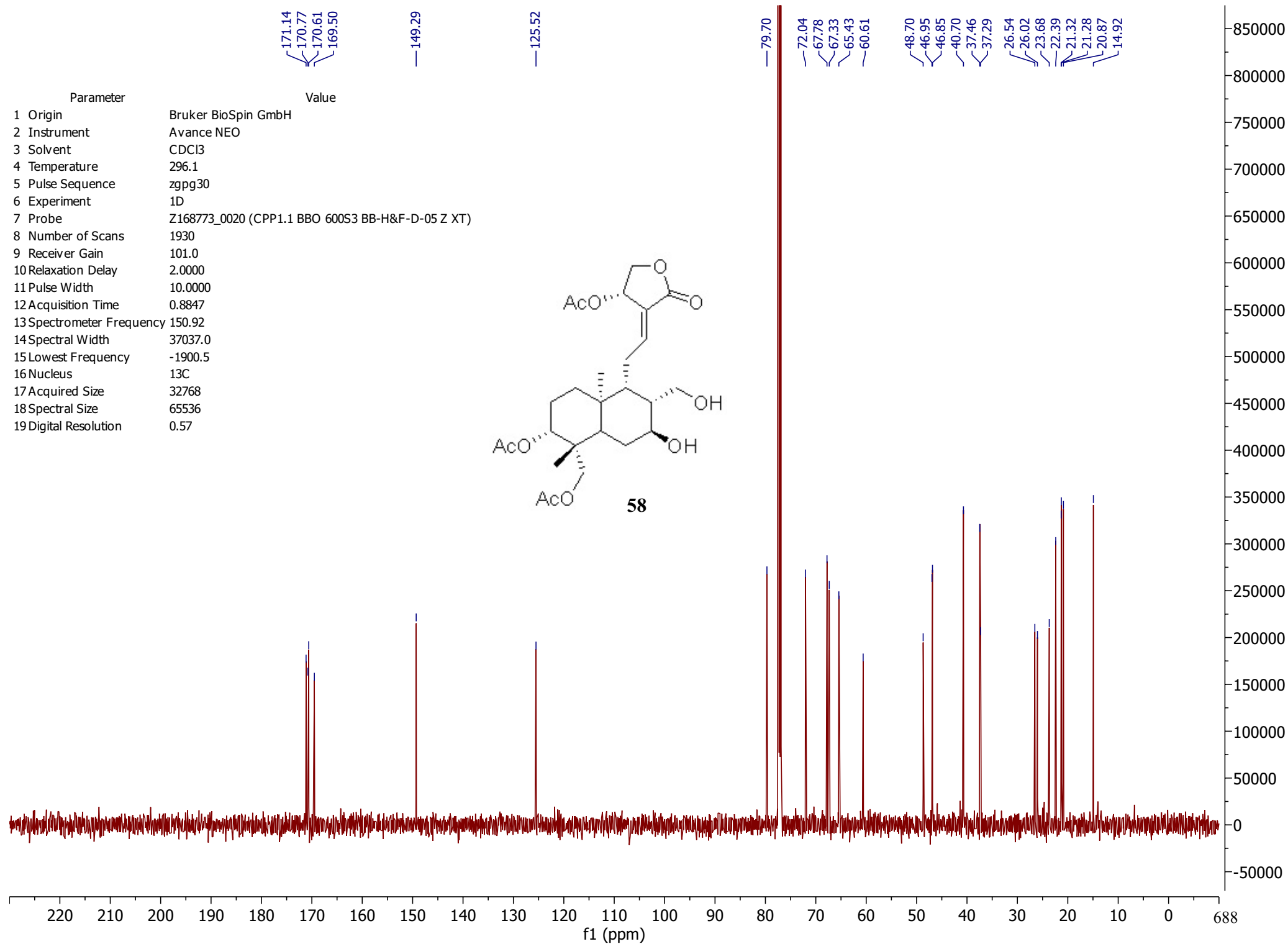
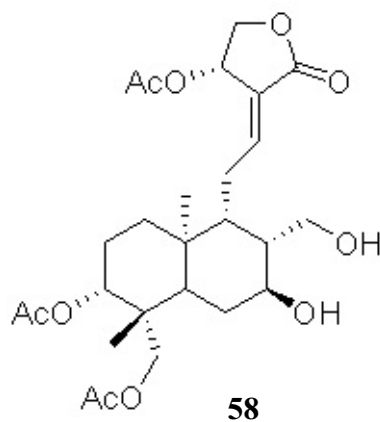
125.52

79.70

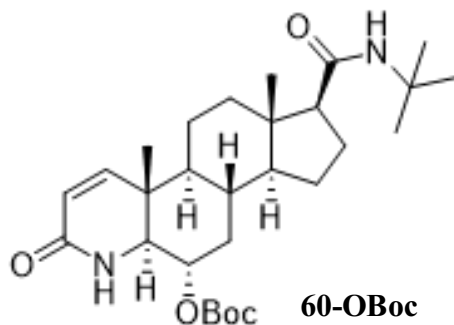
72.04
 67.78
 67.33
 65.43
 60.61

48.70
 46.95
 46.85
 40.70
 37.46
 37.29

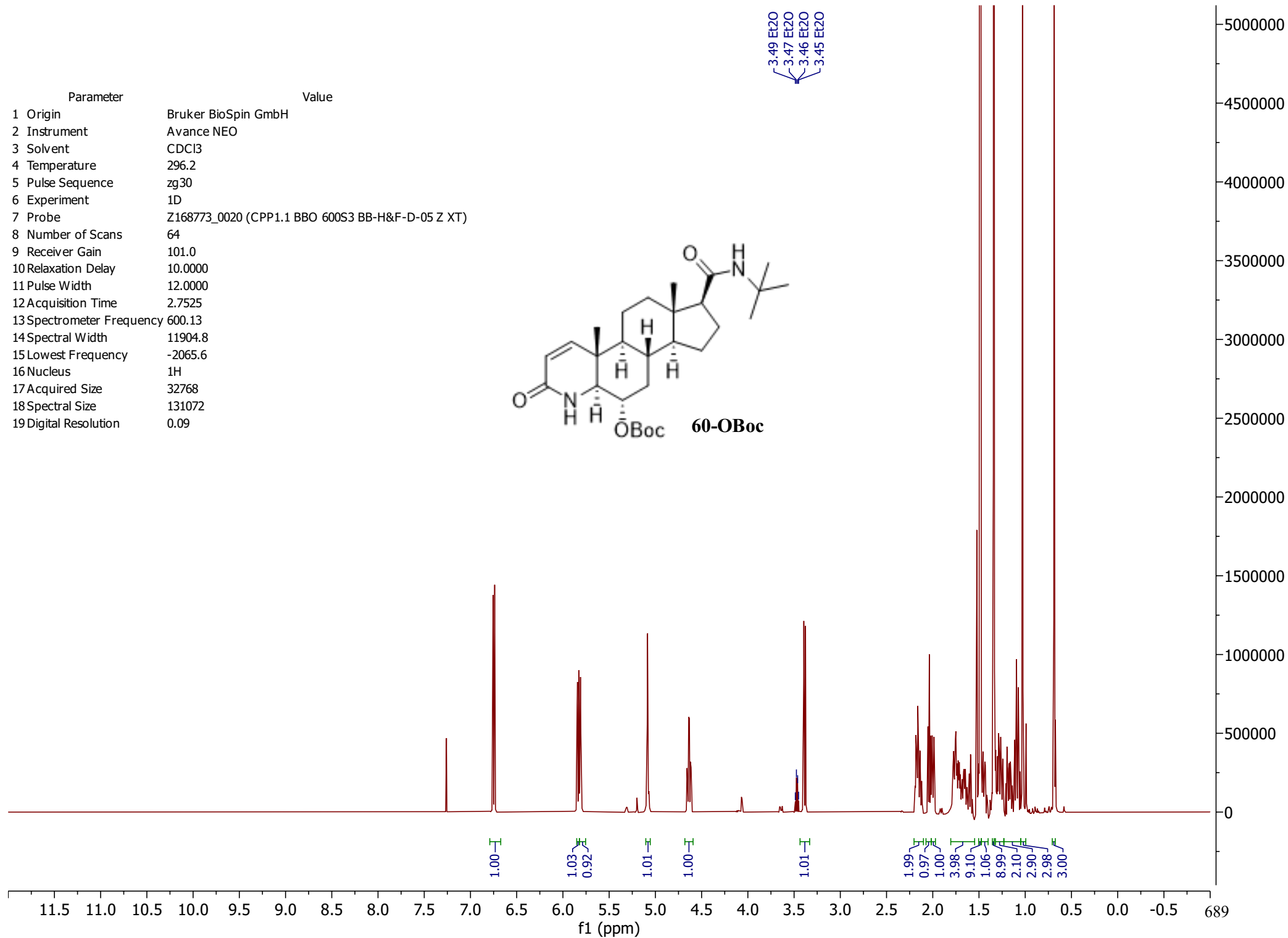
26.54
 26.02
 23.68
 22.39
 21.32
 21.28
 20.87
 14.92



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	64
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2065.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



3.49 Et2O
3.47 Et2O
3.46 Et2O
3.45 Et2O



Parameter Value

1 Origin Bruker BioSpin GmbH

2 Instrument Avance NEO

3 Solvent CDCl₃

4 Temperature 296.2

5 Pulse Sequence zgpg30

6 Experiment 1D

7 Probe Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)

8 Number of Scans 1024

9 Receiver Gain 101.0

10 Relaxation Delay 2.0000

11 Pulse Width 10.0000

12 Acquisition Time 0.8847

13 Spectrometer Frequency 150.92

14 Spectral Width 37037.0

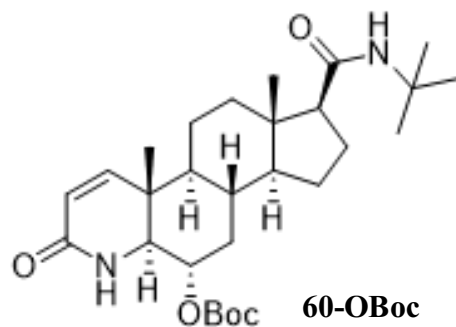
15 Lowest Frequency -1901.6

16 Nucleus ¹³C

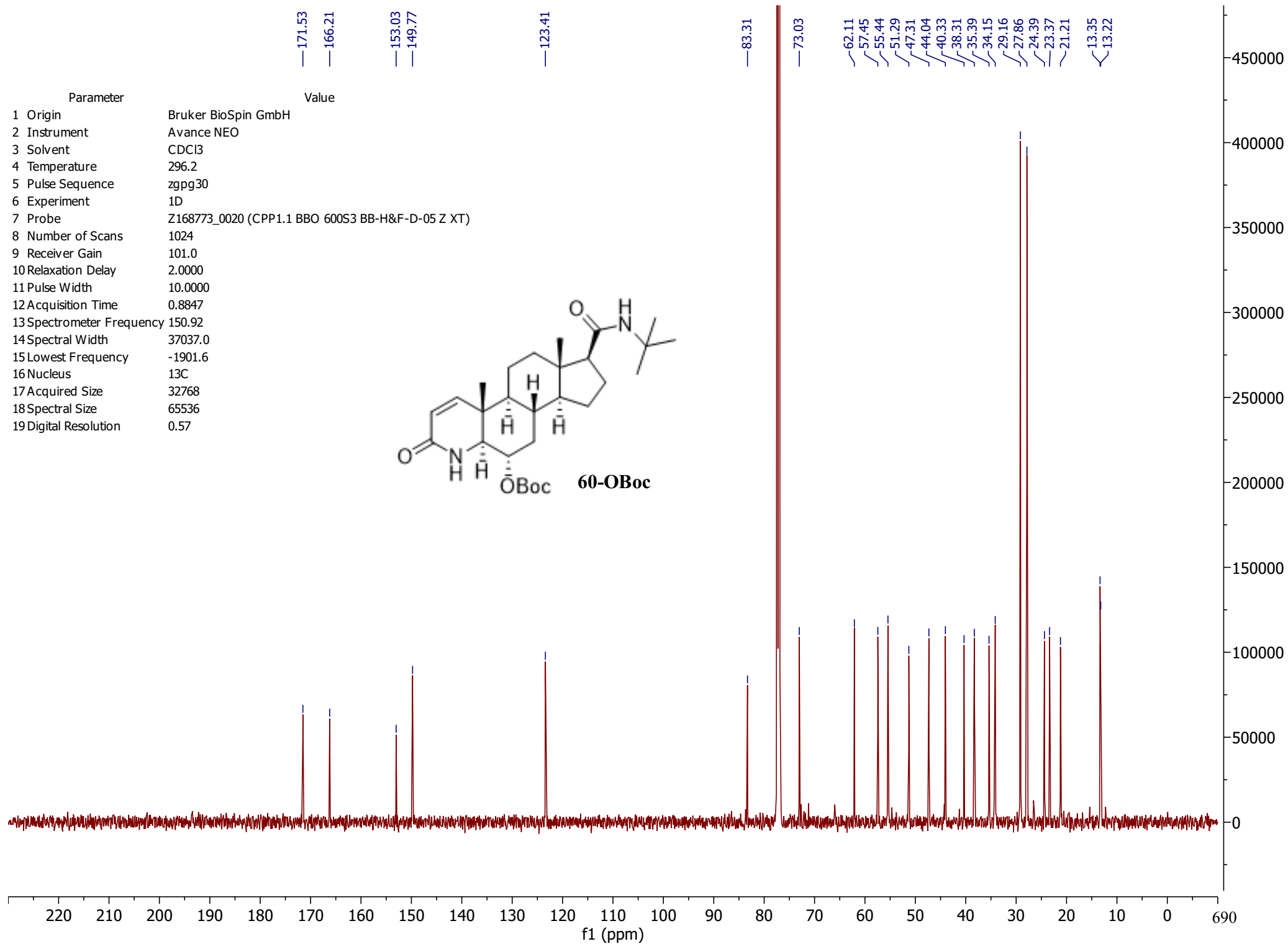
17 Acquired Size 32768

18 Spectral Size 65536

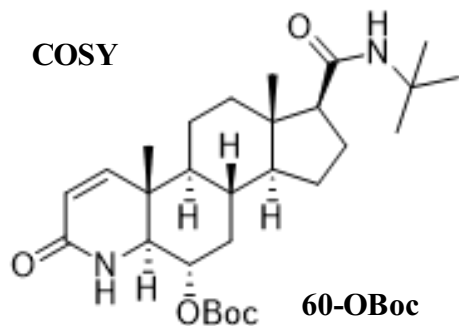
19 Digital Resolution 0.57



171.53 166.21 153.03 149.77 123.41 83.31 73.03 62.11 57.45 55.44 51.29 47.31 44.04 40.33 38.31 35.39 34.15 29.16 27.86 24.39 23.37 21.21 13.35 13.22



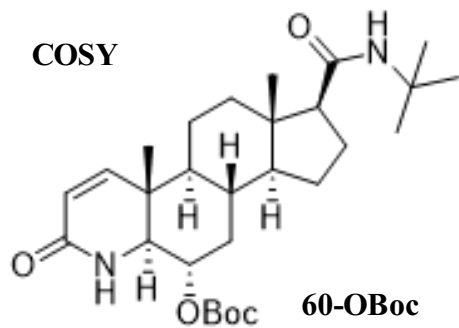
COSY



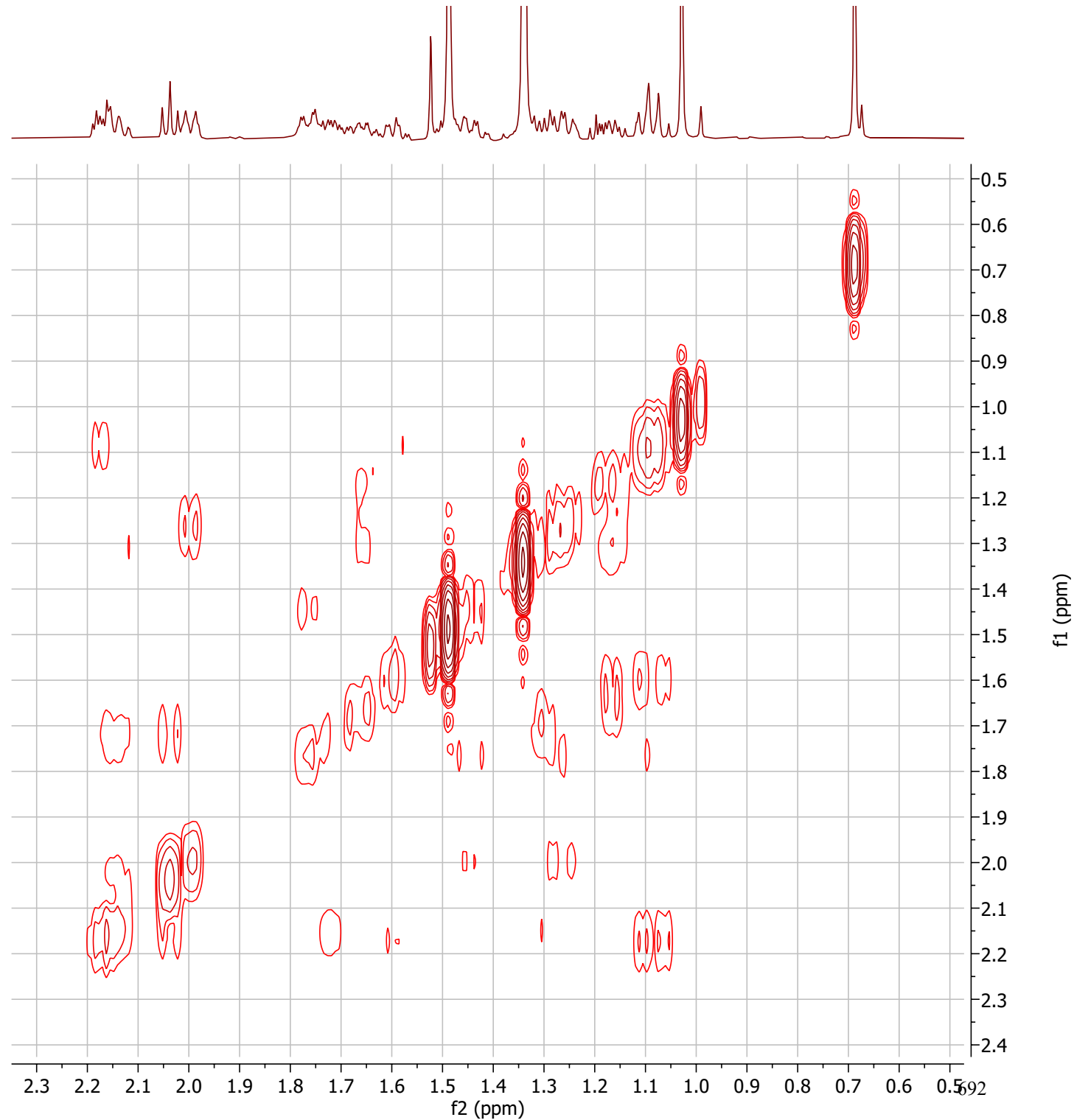
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.4078
11 Pulse Width	12.0000
12 Acquisition Time	0.2253
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(4545.5, 4545.5)
15 Lowest Frequency	(-51.6, -51.6)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.44, 4.44)



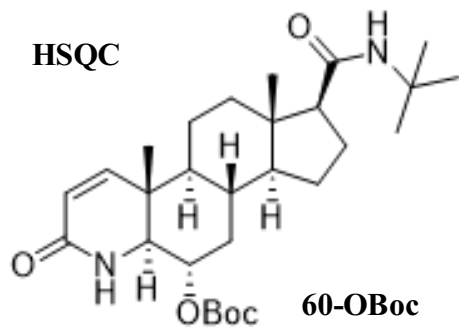
COSY



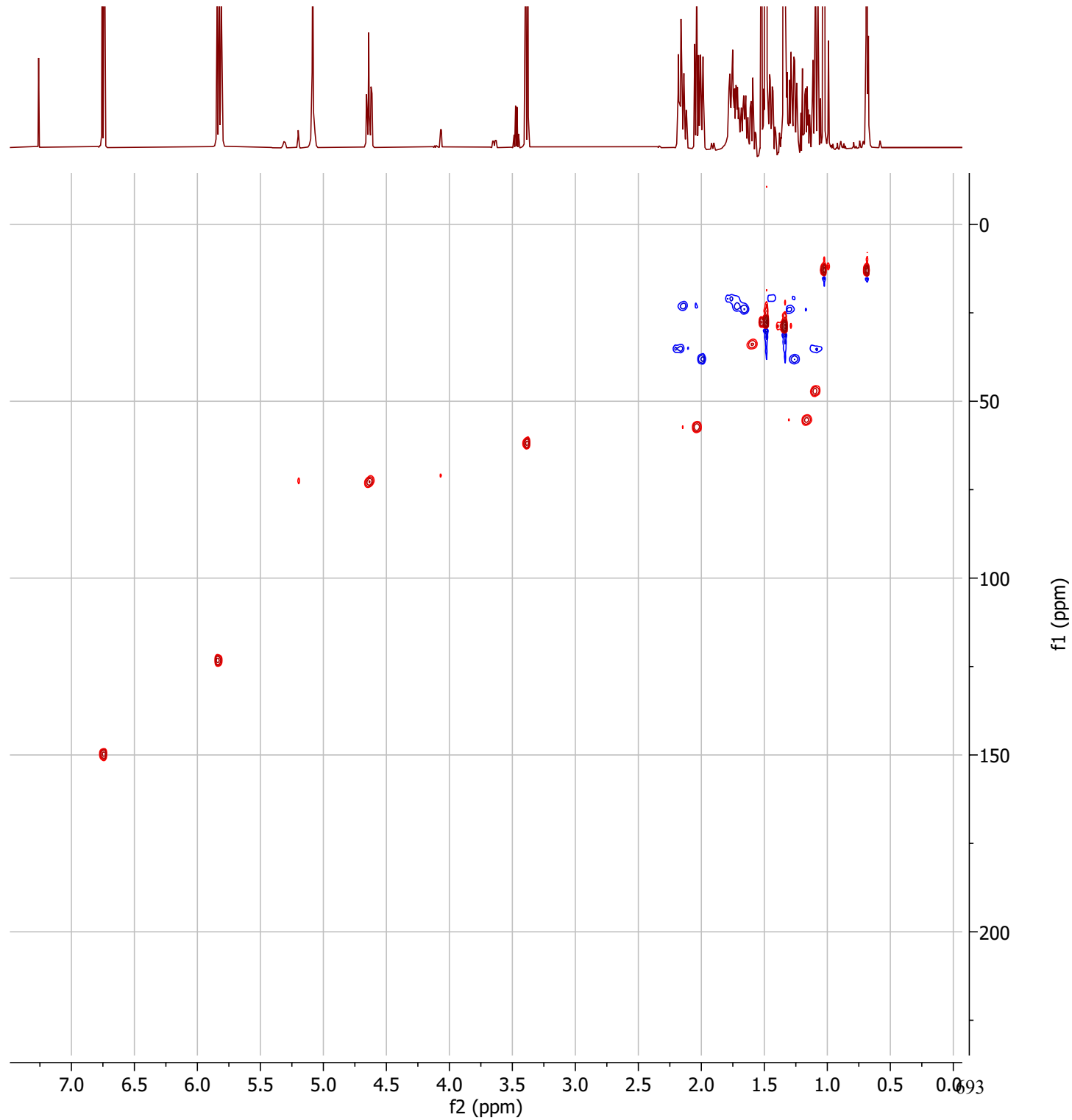
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.4078
11 Pulse Width	12.0000
12 Acquisition Time	0.2253
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(4545.5, 4545.5)
15 Lowest Frequency	(-51.6, -51.6)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.44, 4.44)



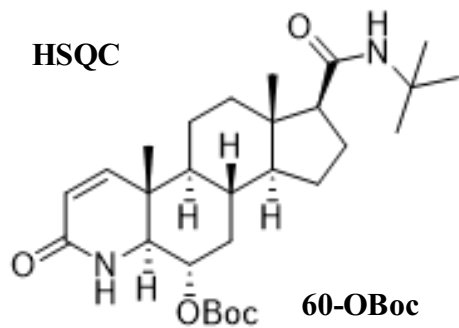
HSQC



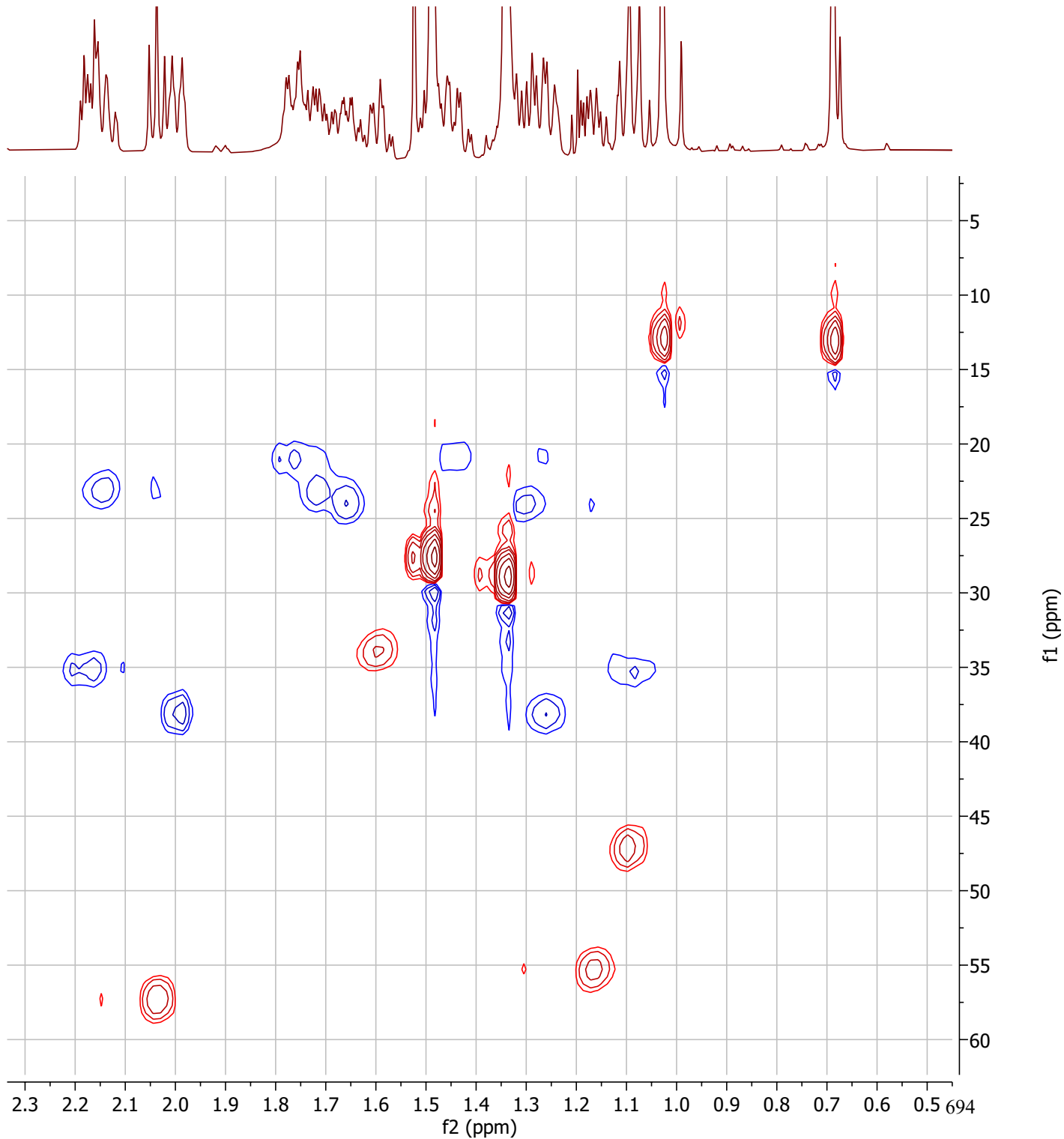
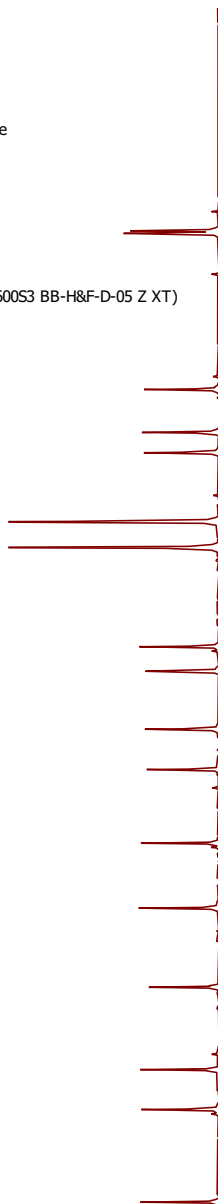
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcedetgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4545.5, 37728.5)
15 Lowest Frequency	(-51.6, -2268.5)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.88, 73.69)



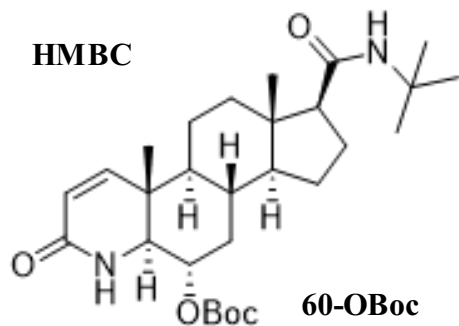
HSQC



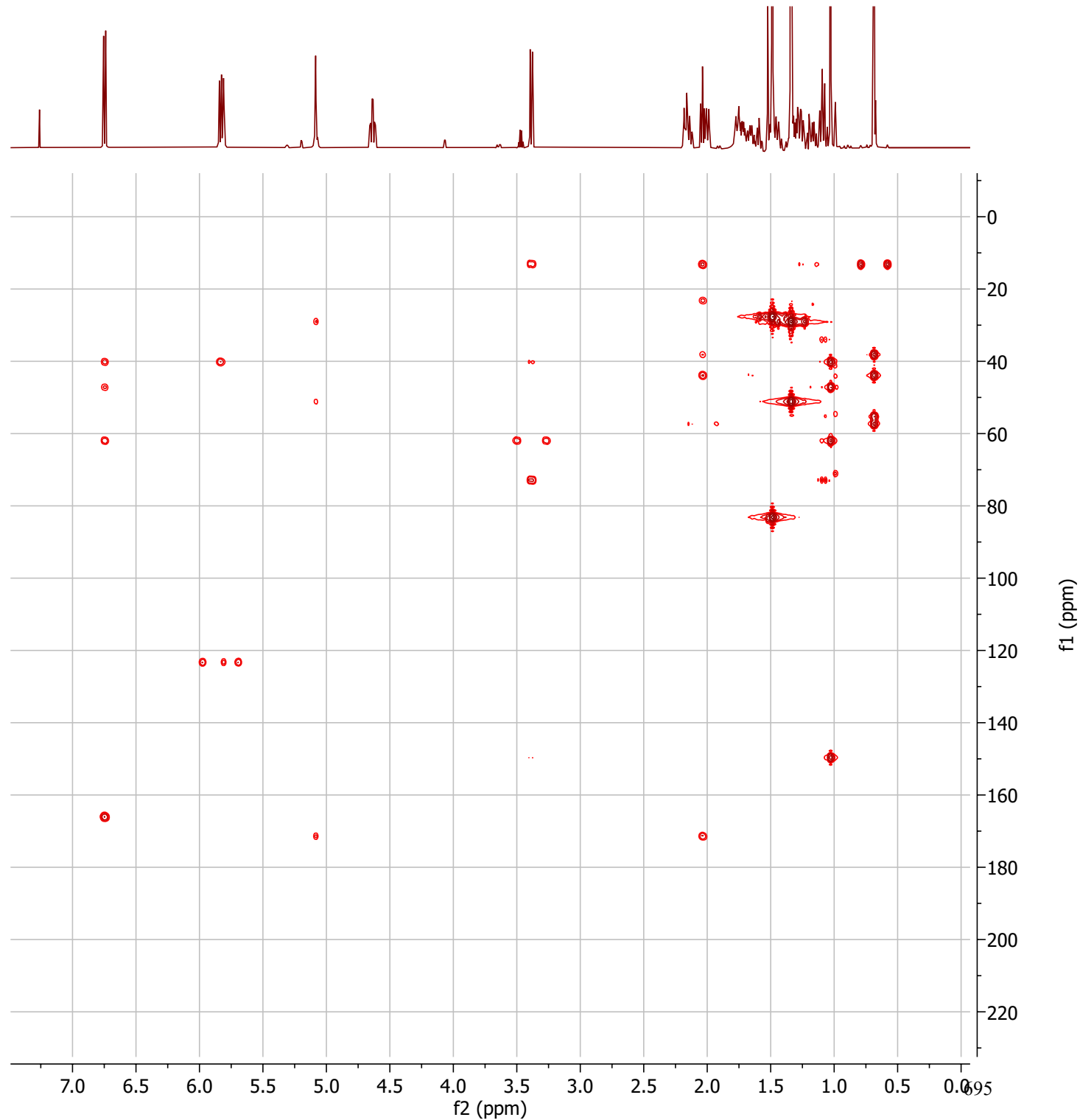
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetdgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4545.5, 37728.5)
15 Lowest Frequency	(-51.6, -2268.5)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.88, 73.69)



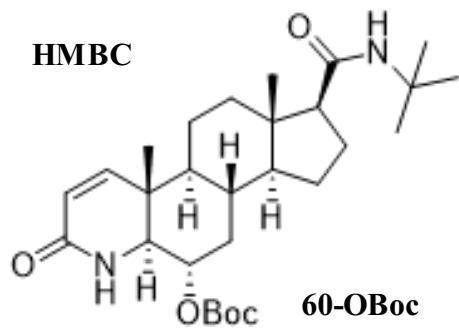
HMBC



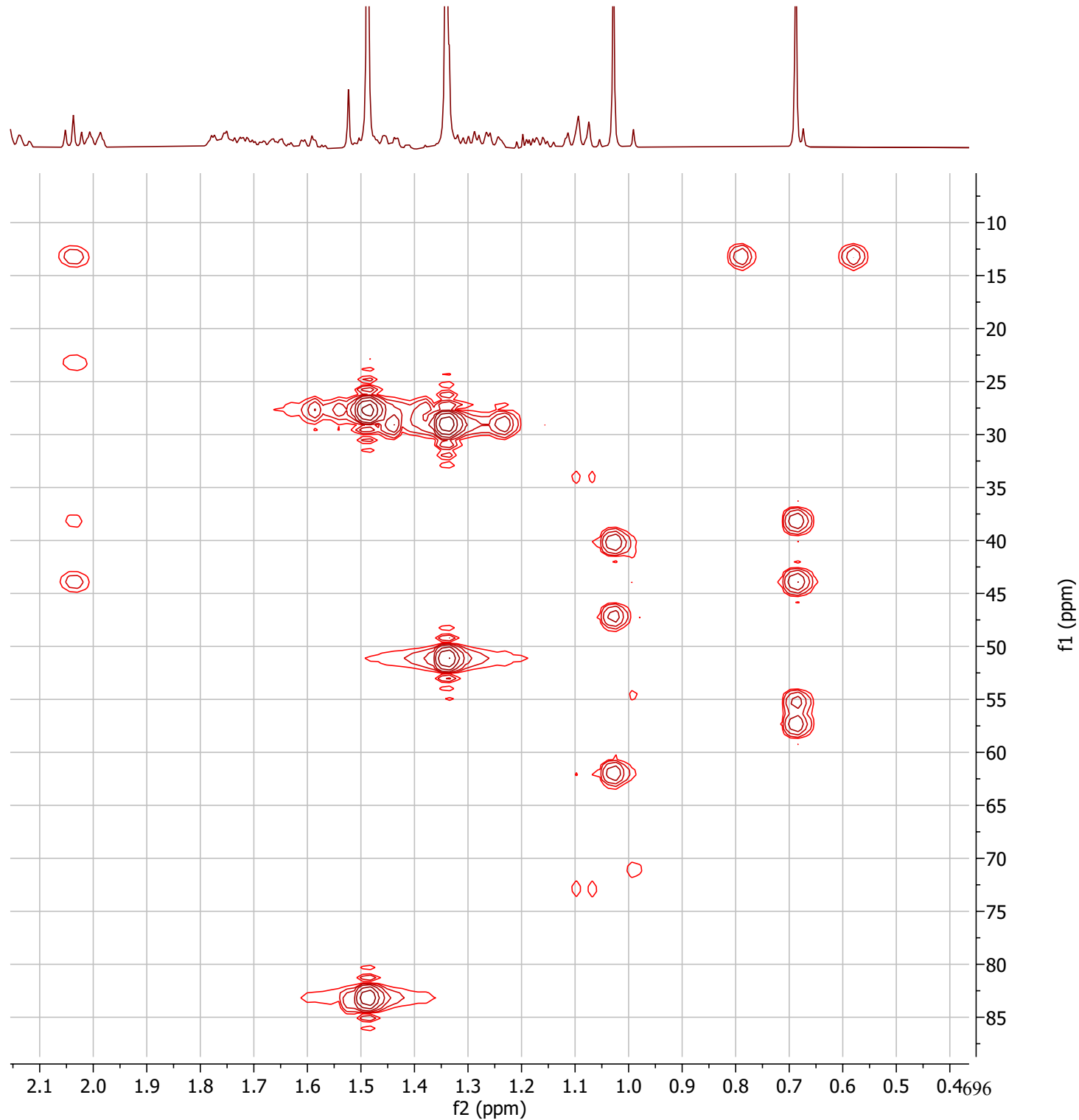
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4545.5, 36974.9)
15 Lowest Frequency	(-51.6, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.88, 72.22)



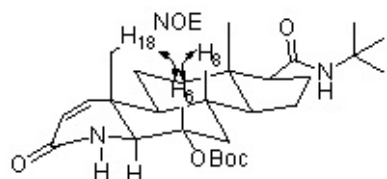
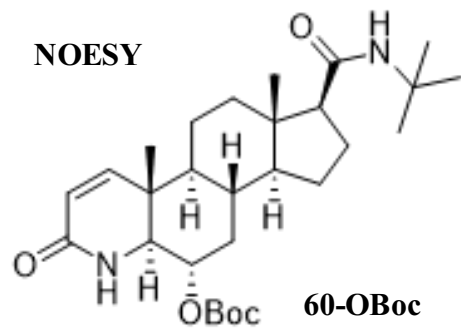
HMBC



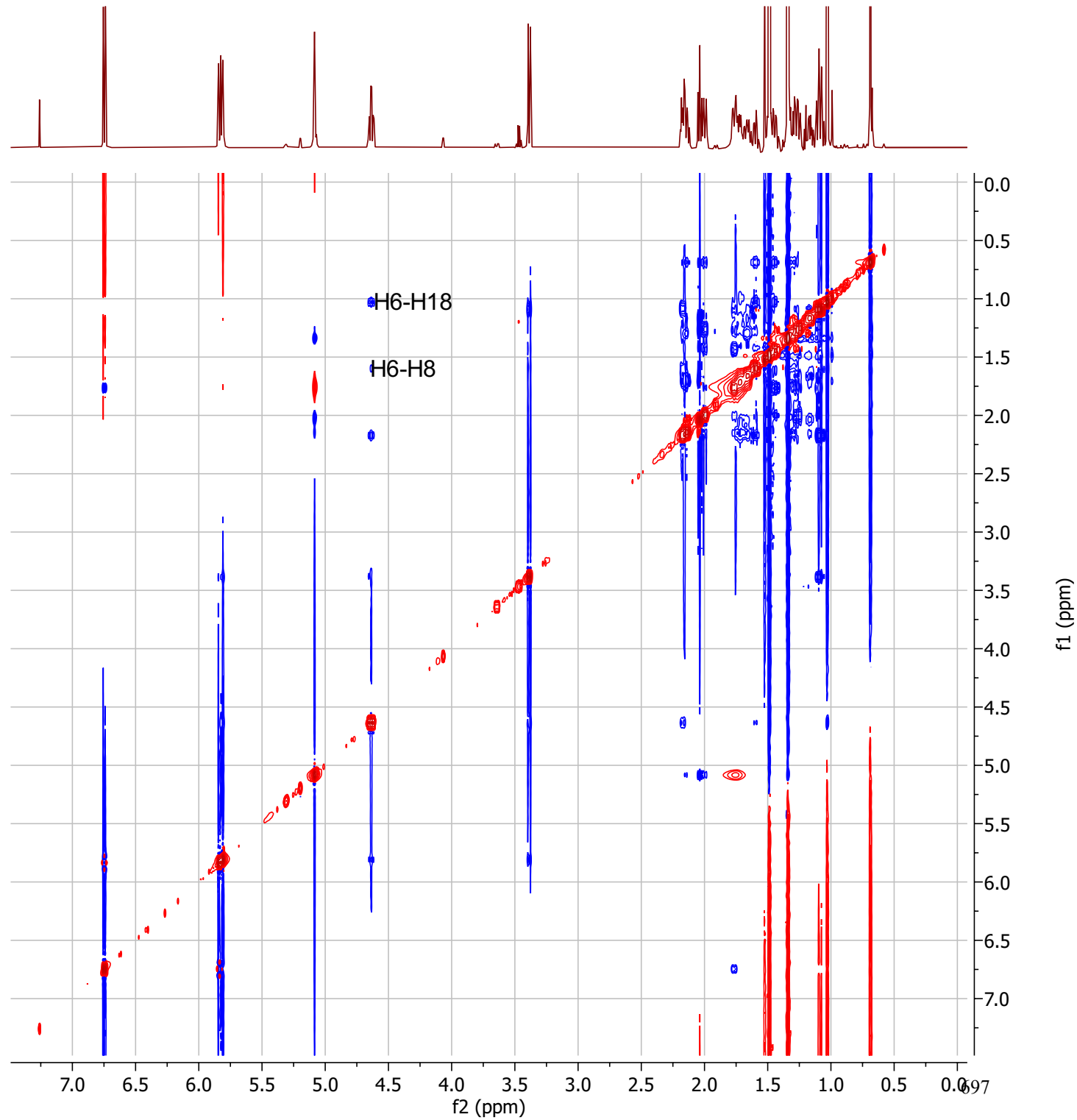
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4545.5, 36974.9)
15 Lowest Frequency	(-51.6, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.88, 72.22)



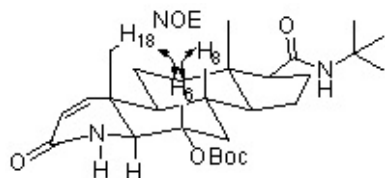
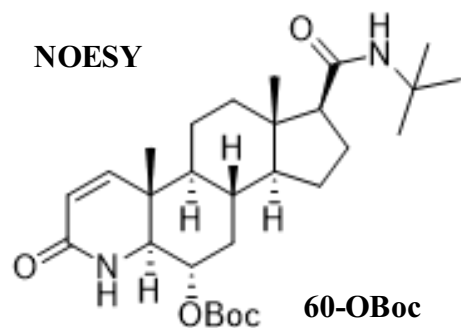
NOESY



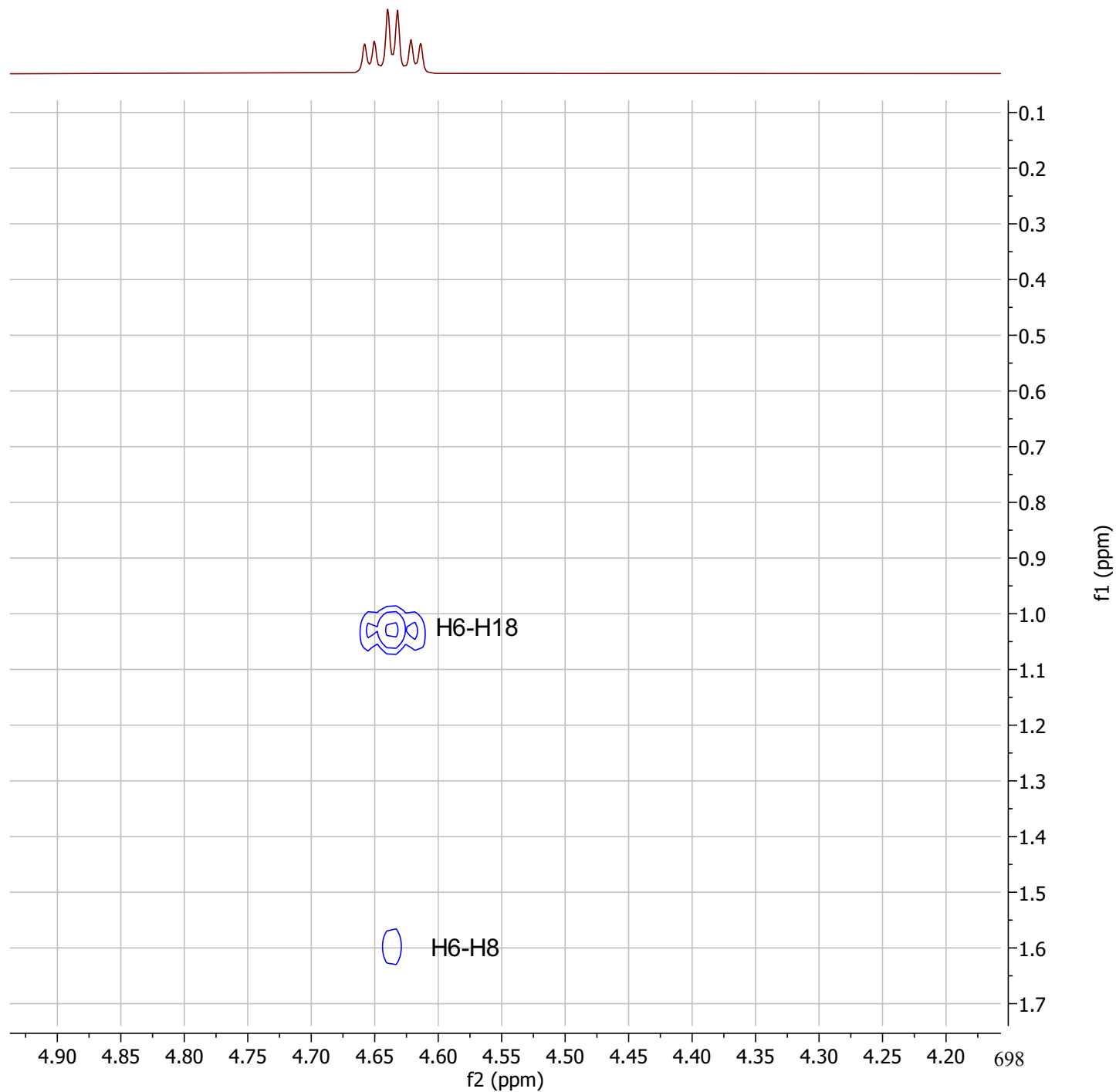
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	noesygpqhpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	64.0
10 Relaxation Delay	1.9508
11 Pulse Width	12.0000
12 Acquisition Time	0.2253
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(4545.5, 4545.5)
15 Lowest Frequency	(-51.6, -51.6)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.44, 4.44)



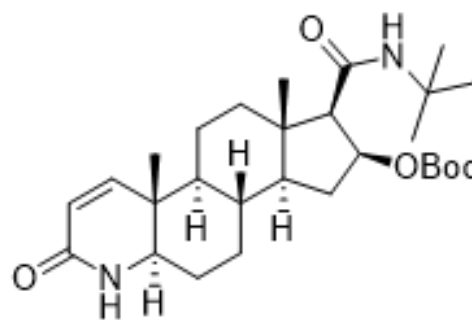
NOESY



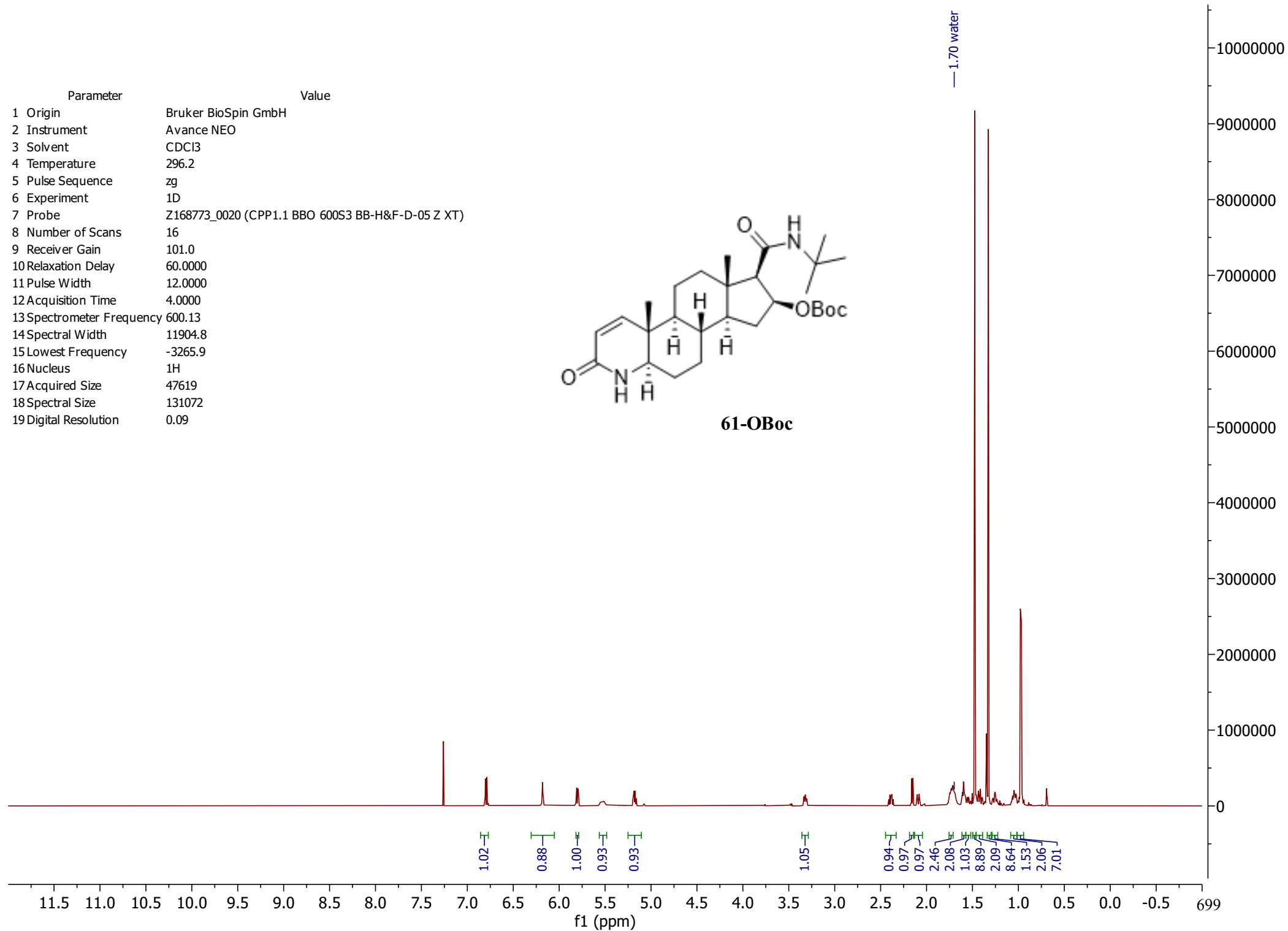
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	64.0
10 Relaxation Delay	1.9508
11 Pulse Width	12.0000
12 Acquisition Time	0.2253
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(4545.5, 4545.5)
15 Lowest Frequency	(-51.6, -51.6)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.44, 4.44)



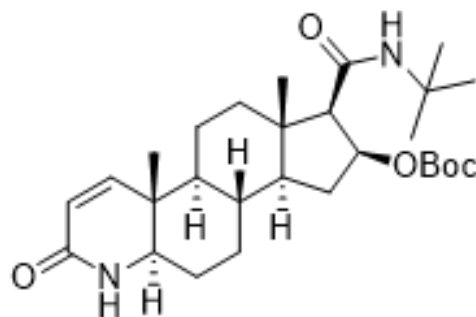
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	60.0000
11 Pulse Width	12.0000
12 Acquisition Time	4.0000
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-3265.9
16 Nucleus	¹ H
17 Acquired Size	47619
18 Spectral Size	131072
19 Digital Resolution	0.09



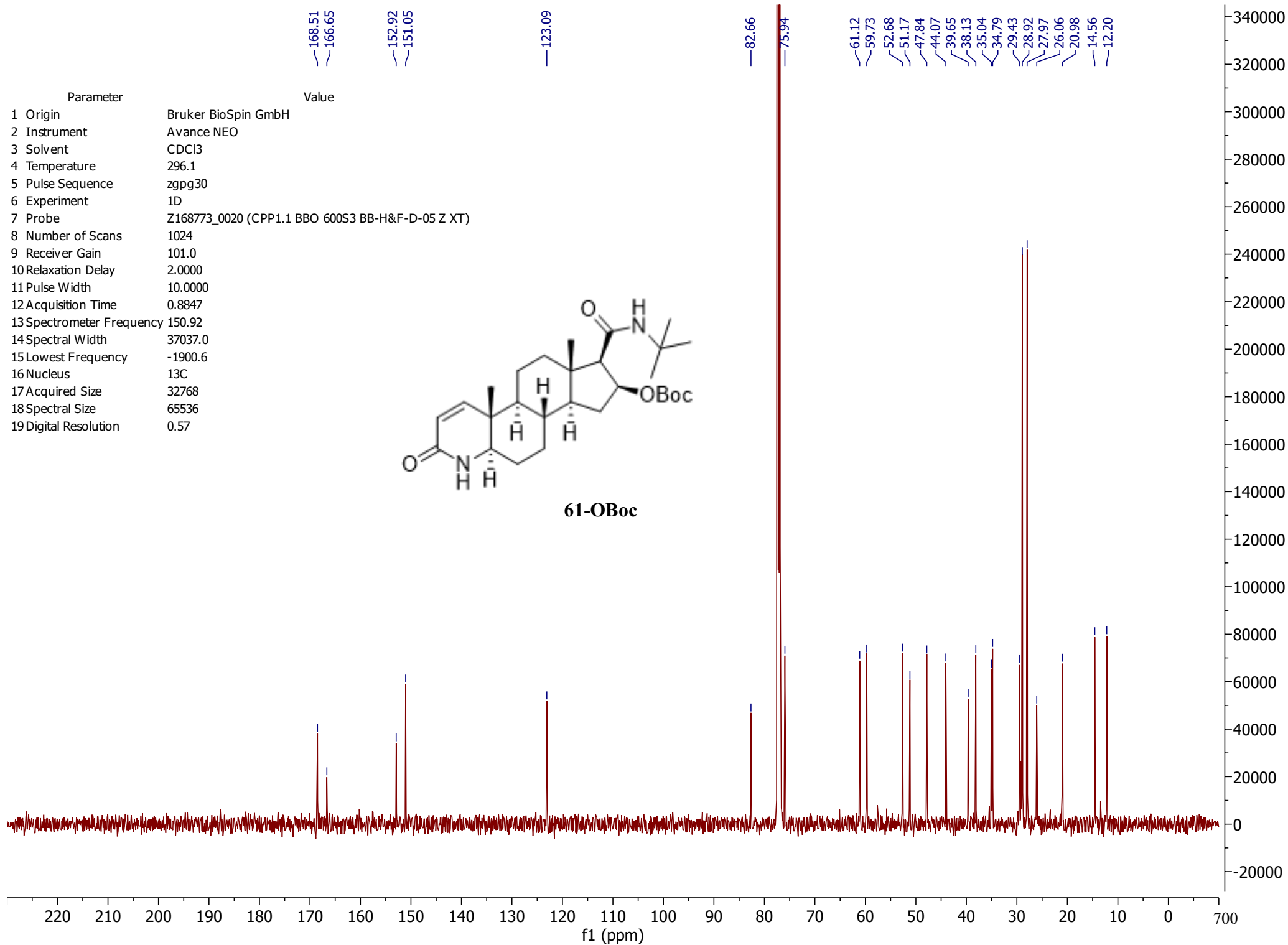
61-OBoc



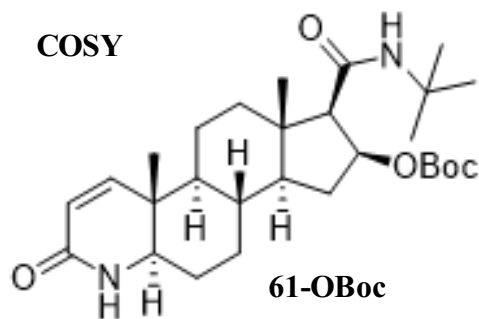
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	1024
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1900.6
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



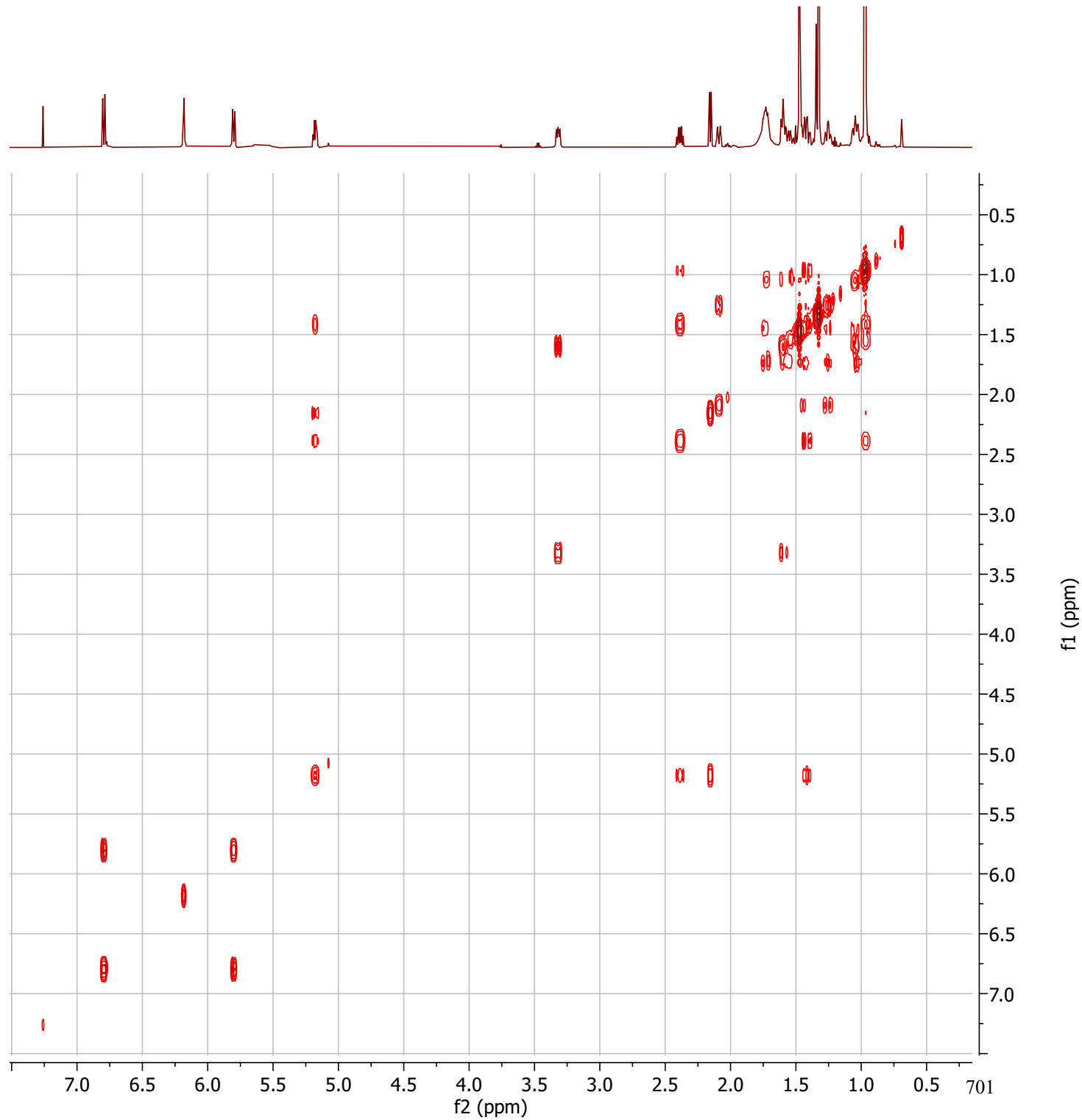
61-OBoc



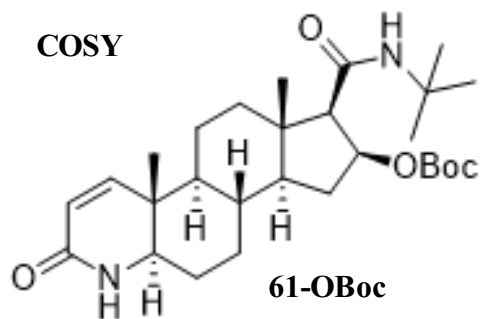
COSY



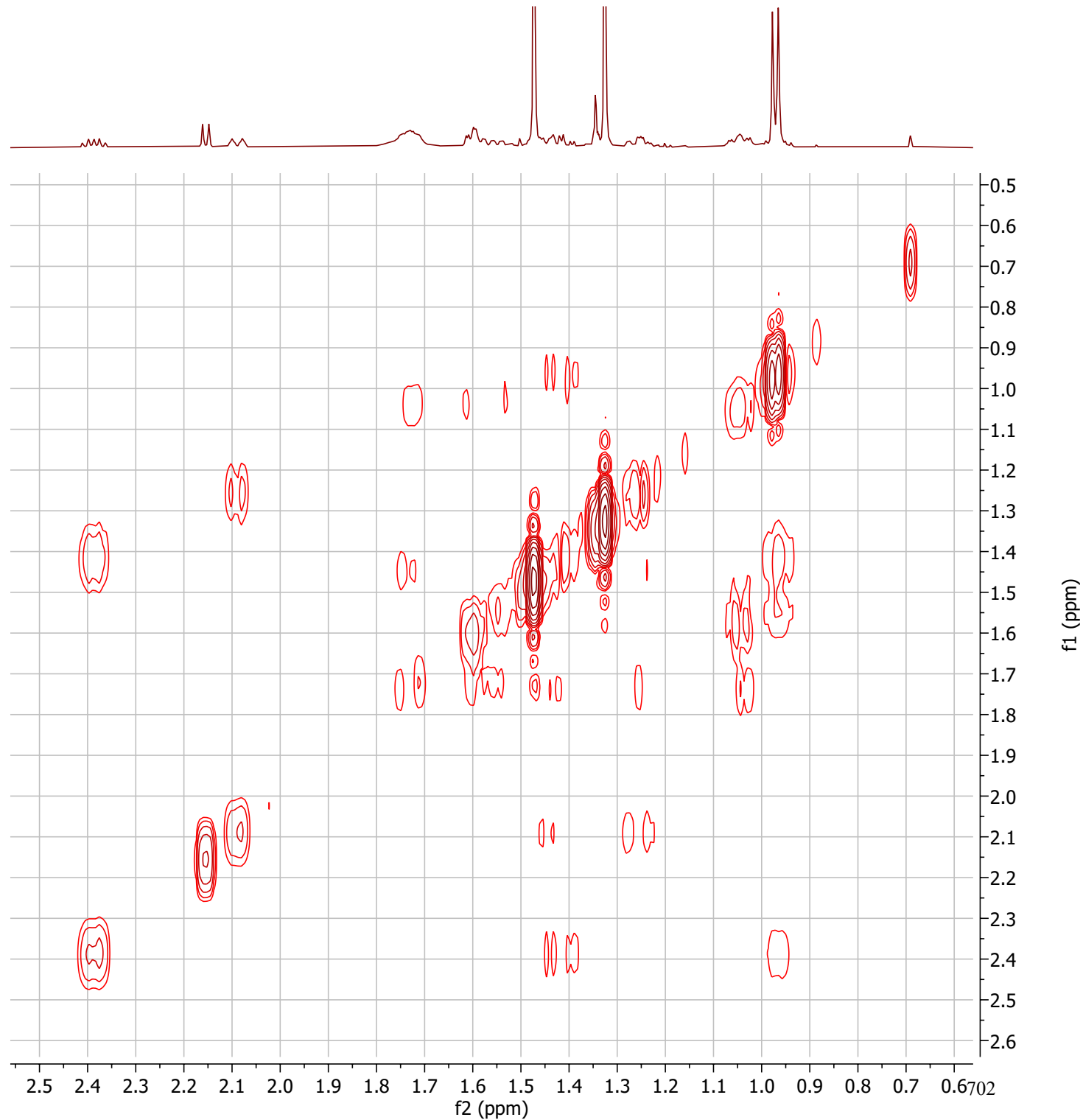
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.4017
11 Pulse Width	12.0000
12 Acquisition Time	0.2314
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(4424.8, 4424.8)
15 Lowest Frequency	(86.2, 86.2)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.32, 4.32)



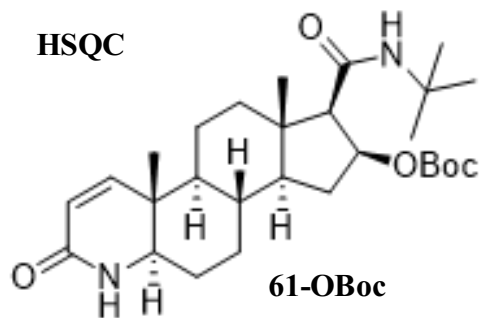
COSY



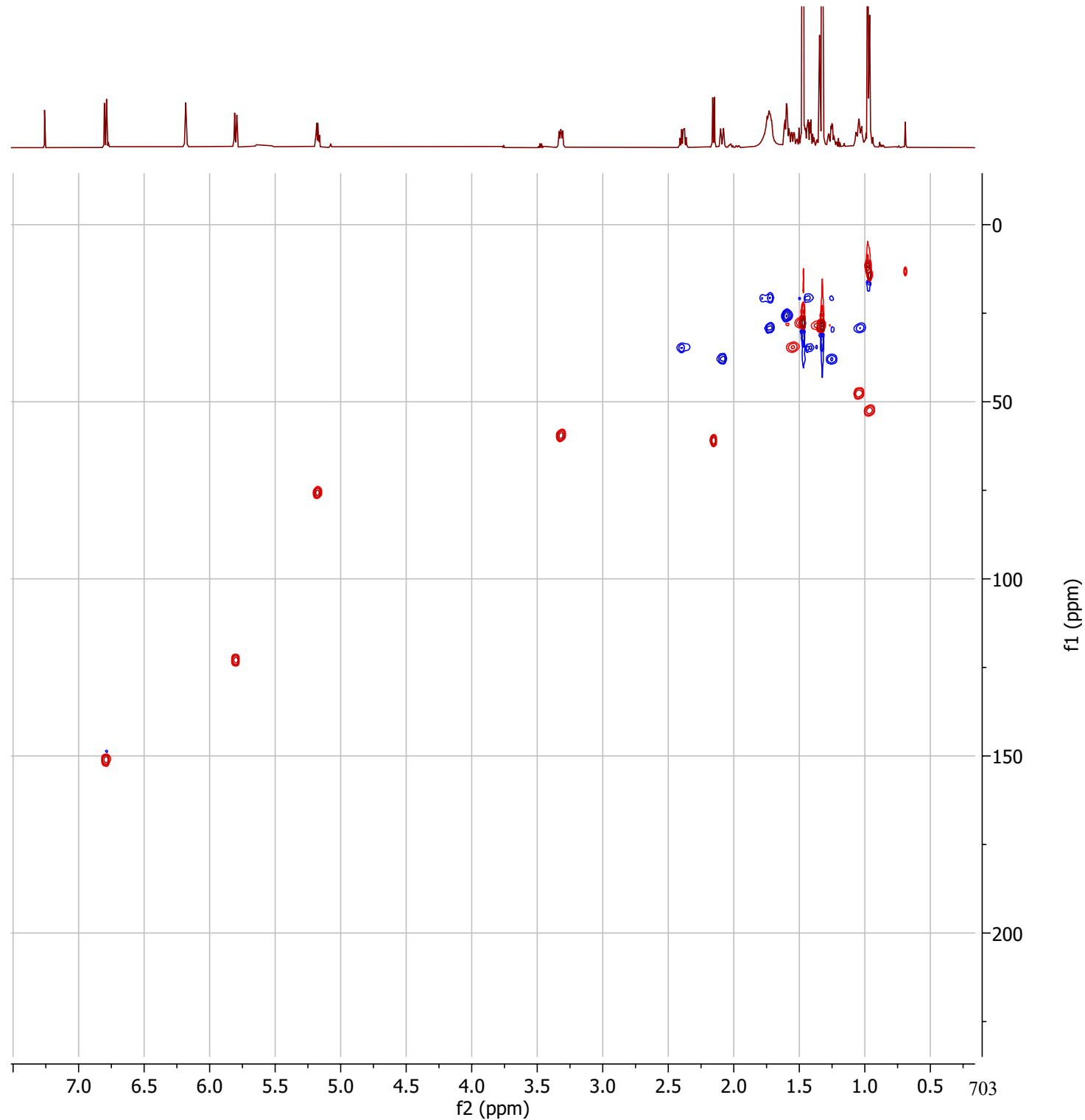
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosypppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.4017
11 Pulse Width	12.0000
12 Acquisition Time	0.2314
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(4424.8, 4424.8)
15 Lowest Frequency	(86.2, 86.2)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.32, 4.32)



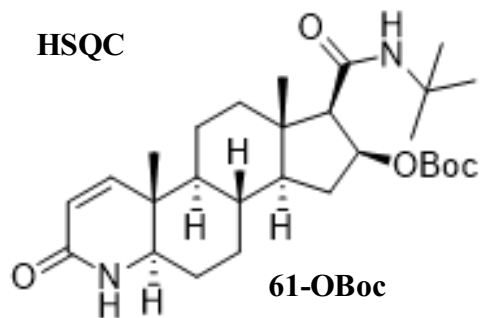
HSQC



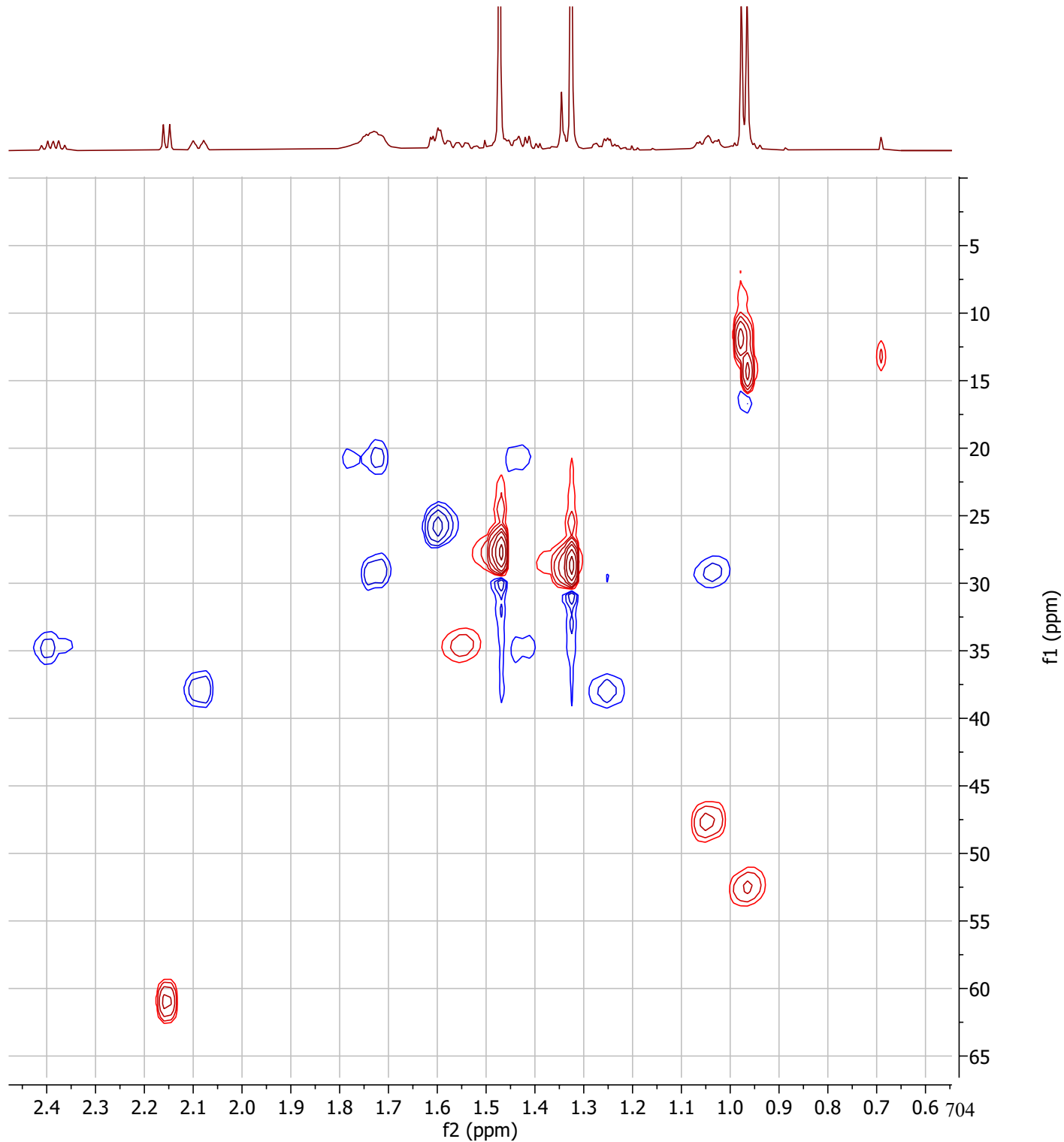
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpsi2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1157
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(4424.8, 37728.5)
15 Lowest Frequency	(86.2, -2268.5)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.64, 73.69)



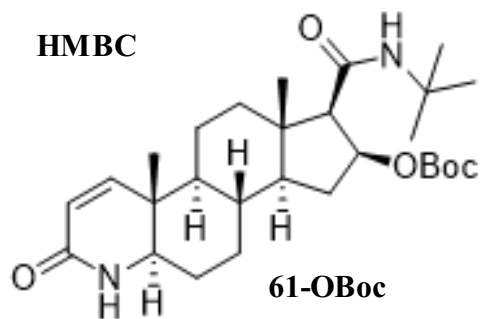
HSQC



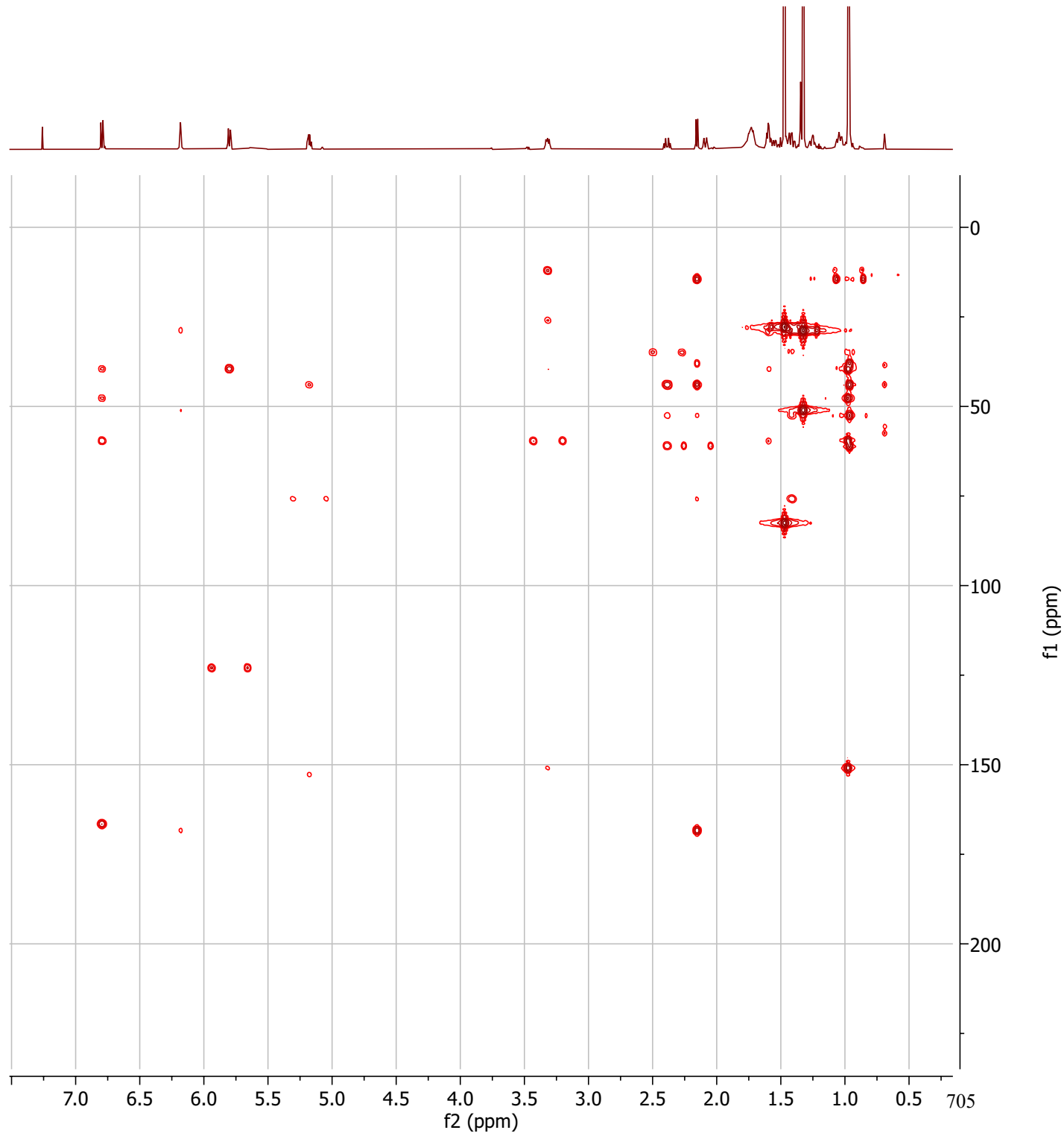
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpcisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1157
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4424.8, 37728.5)
15 Lowest Frequency	(86.2, -2268.5)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.64, 73.69)



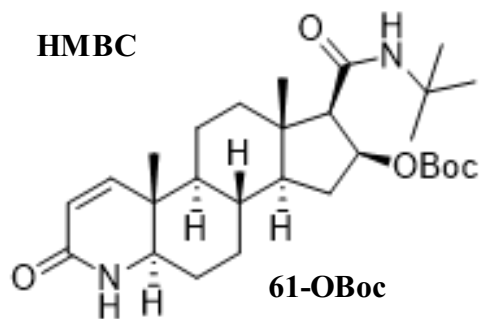
HMBC



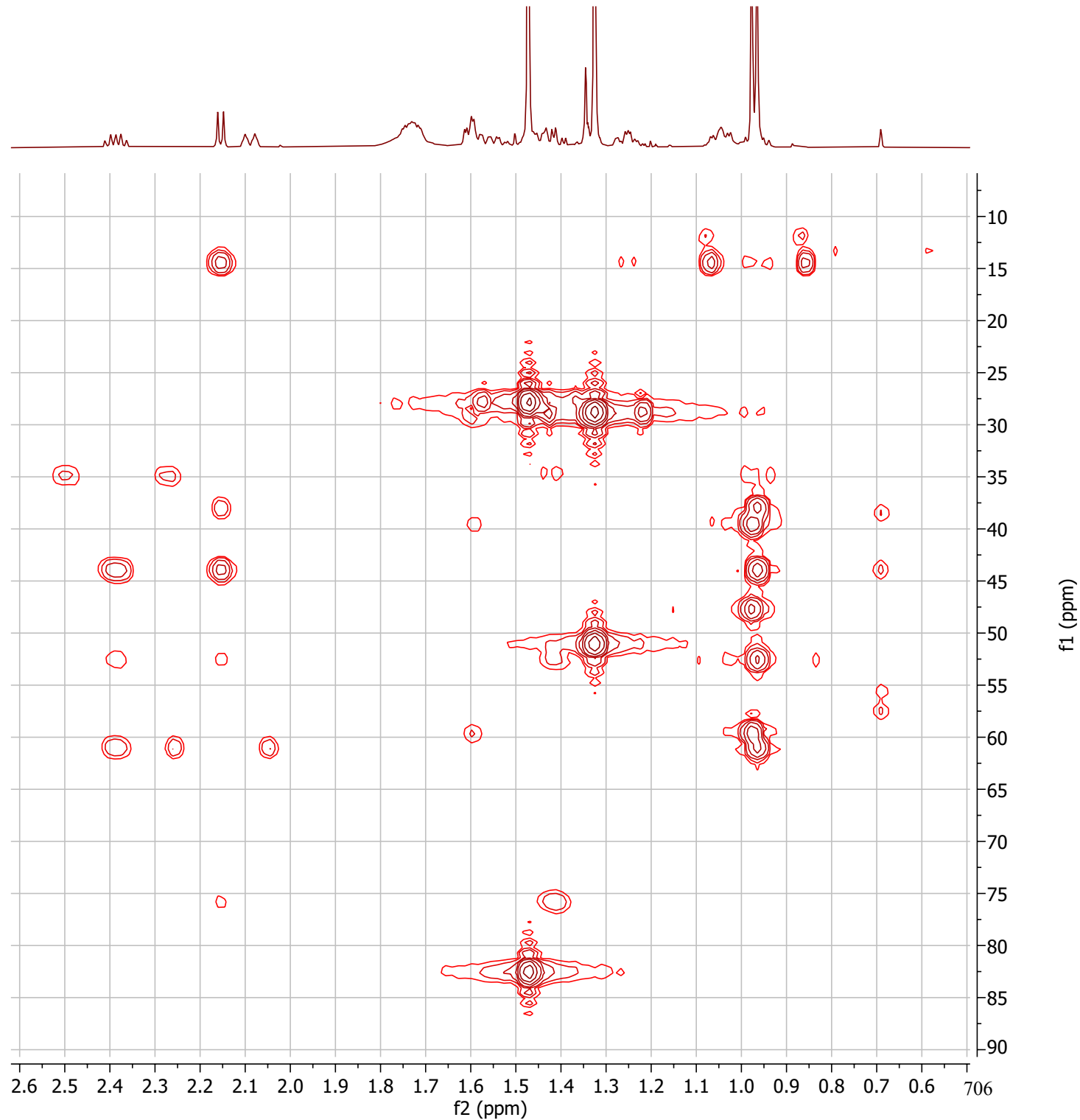
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1157
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(4424.8, 37729.5)
15 Lowest Frequency	(86.2, -2269.0)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.64, 73.69)



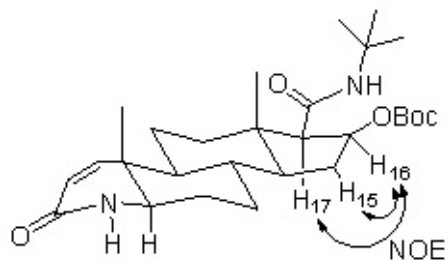
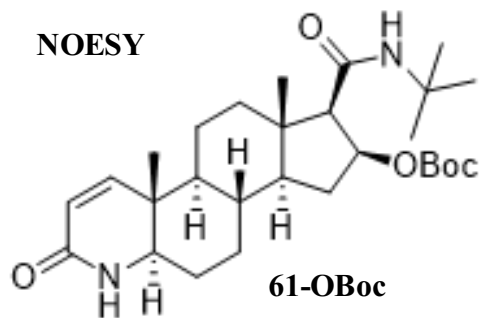
HMBC



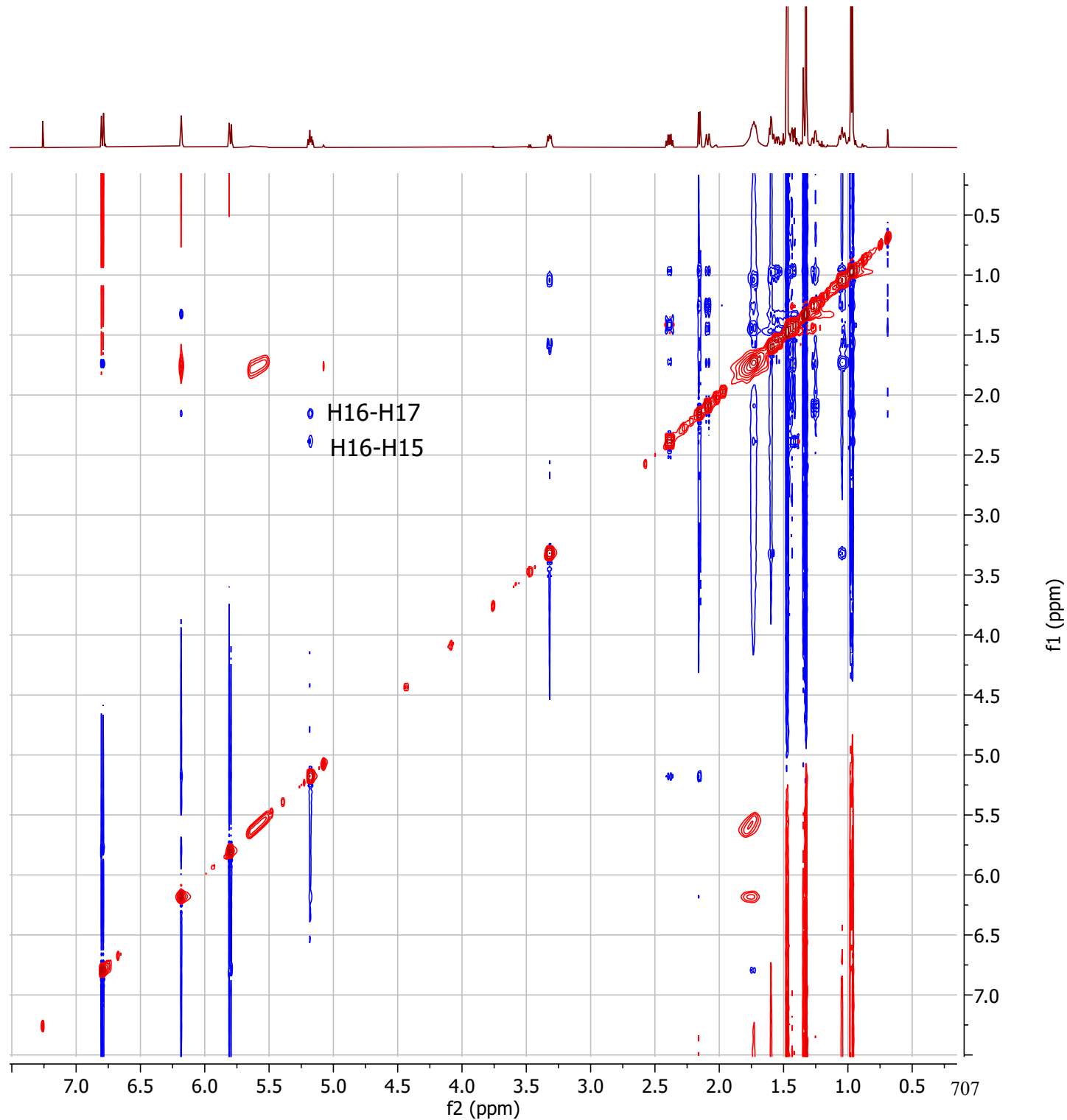
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1157
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(4424.8, 37729.5)
15 Lowest Frequency	(86.2, -2269.0)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.64, 73.69)



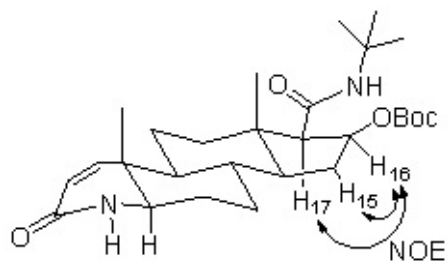
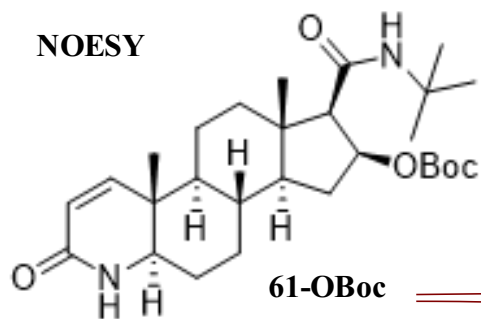
NOESY



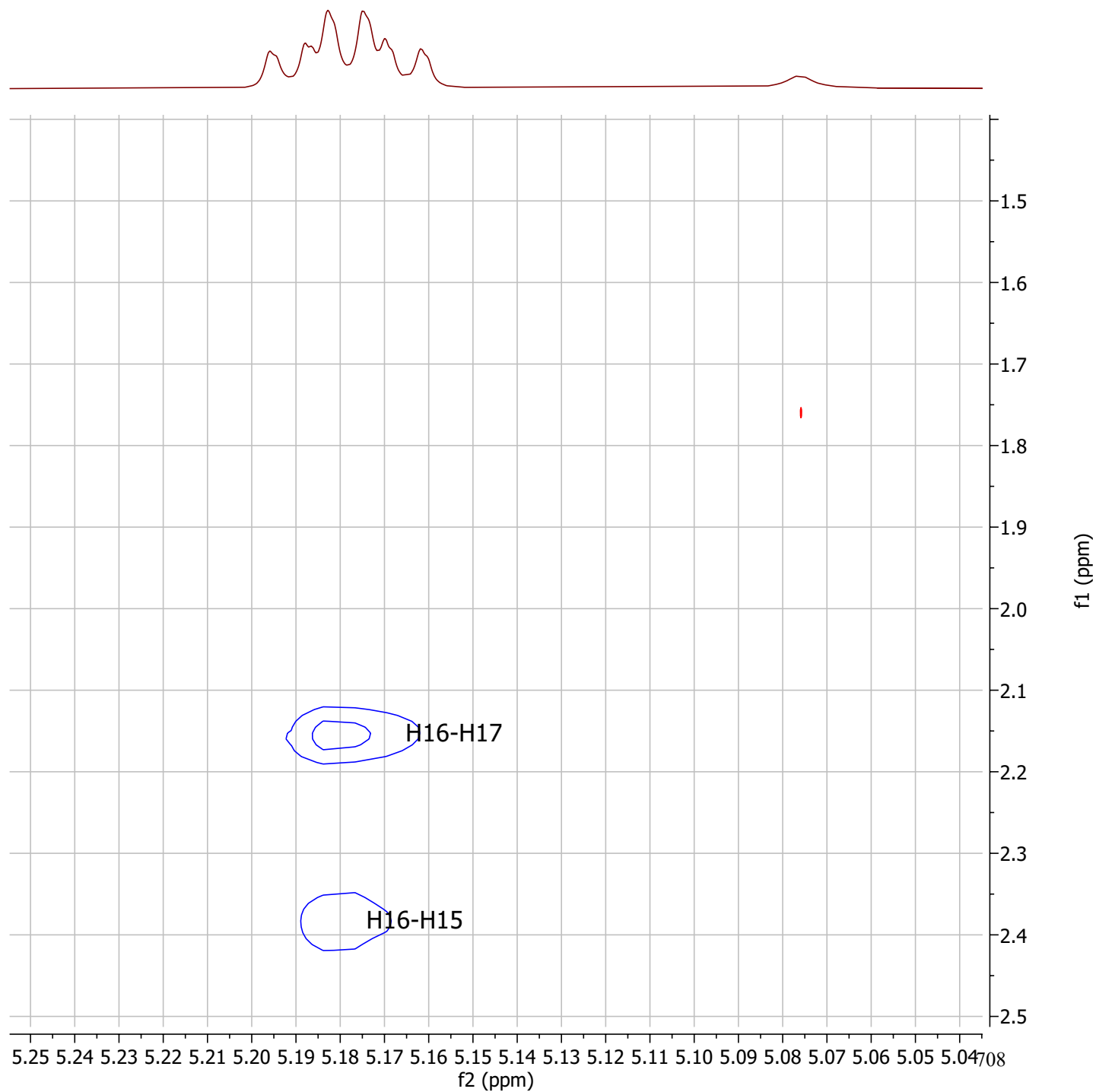
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	noesygpppp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	64.0
10 Relaxation Delay	1.9447
11 Pulse Width	12.0000
12 Acquisition Time	0.2314
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(4424.8, 4424.8)
15 Lowest Frequency	(86.2, 86.2)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.32, 4.32)



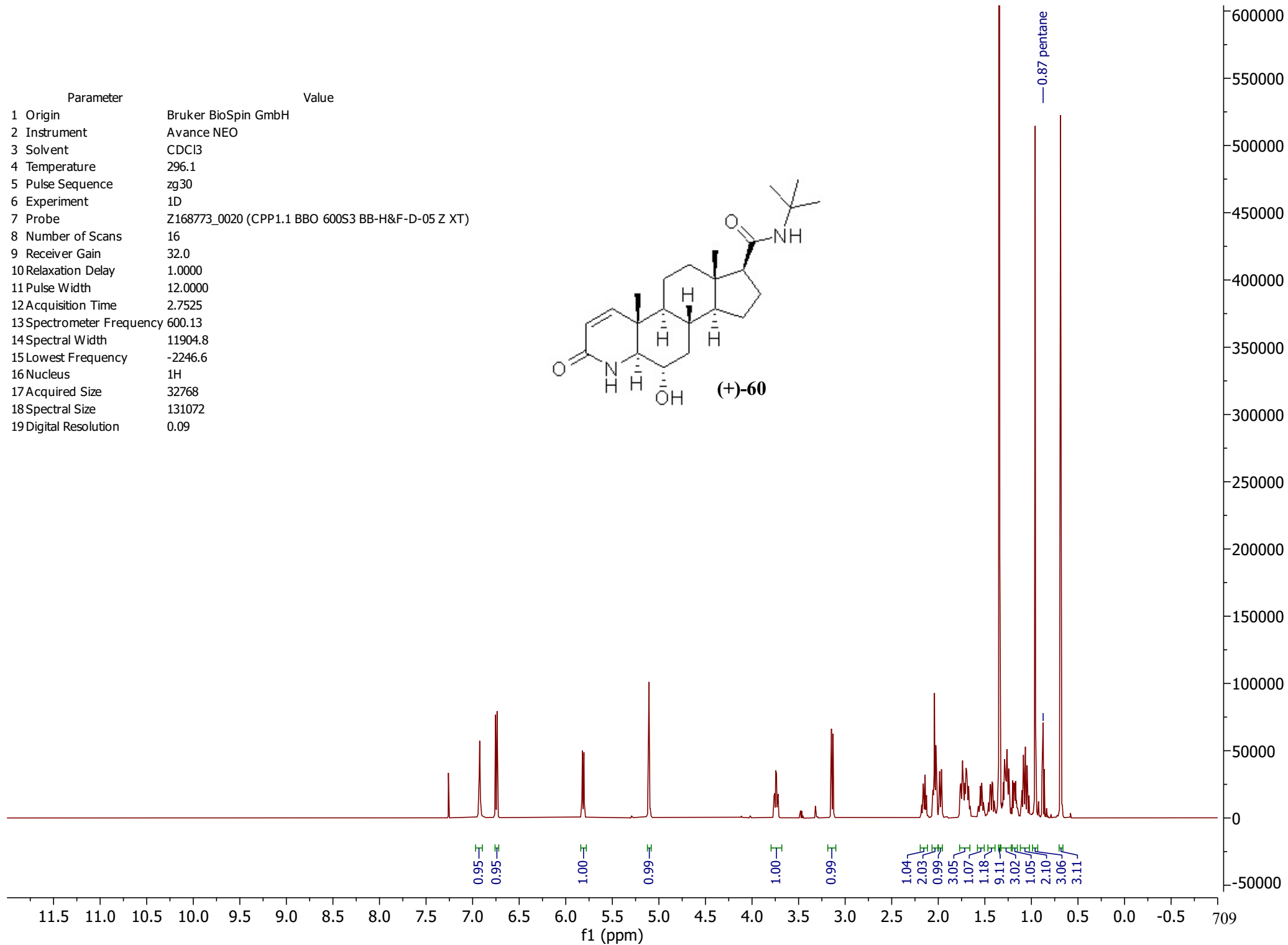
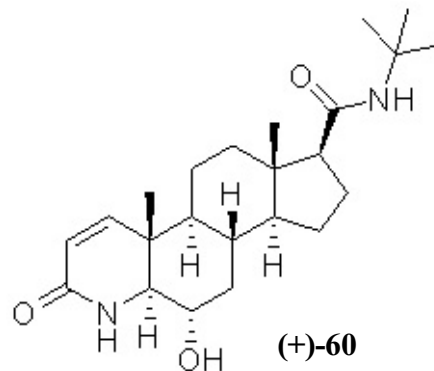
NOESY



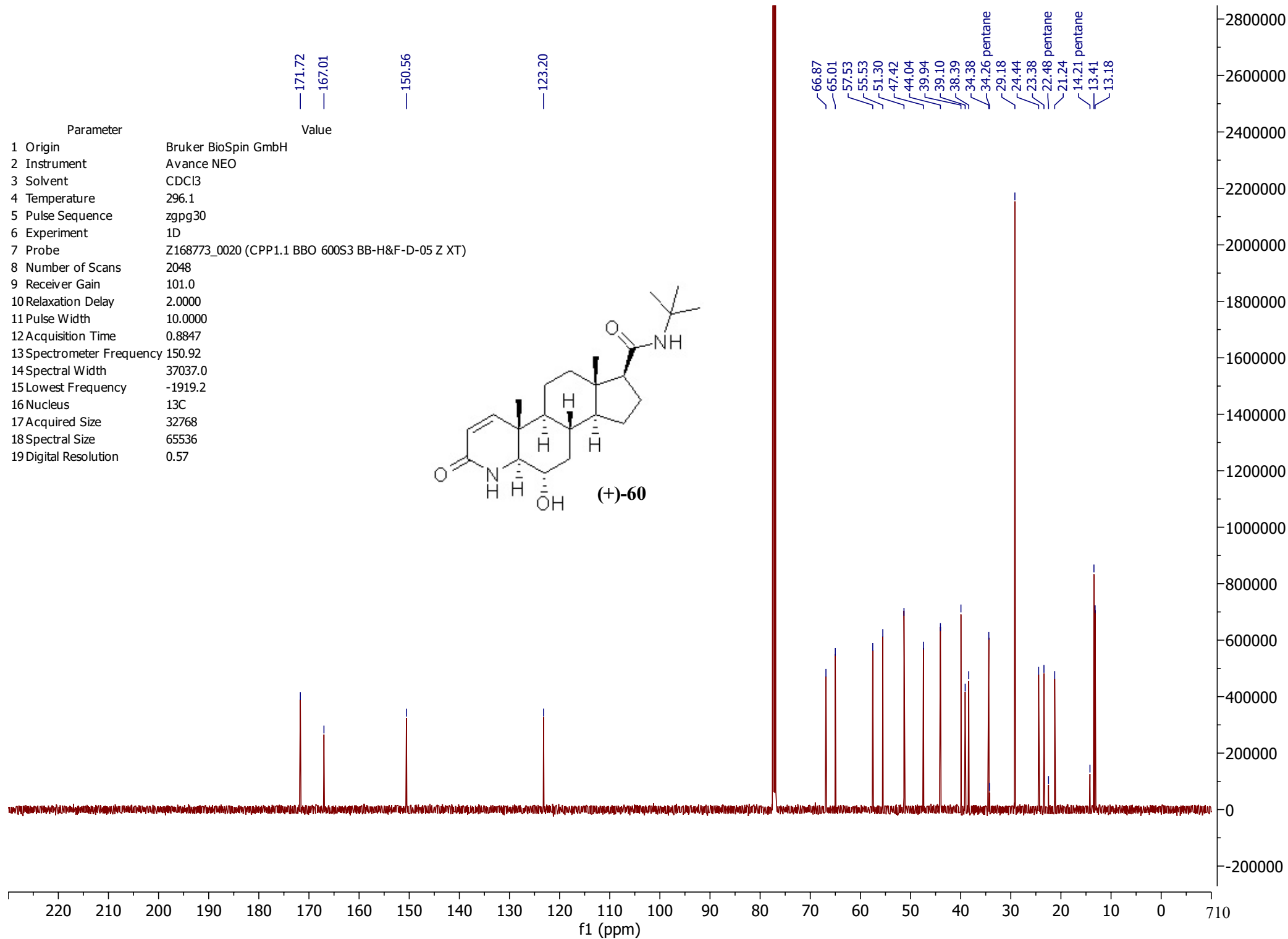
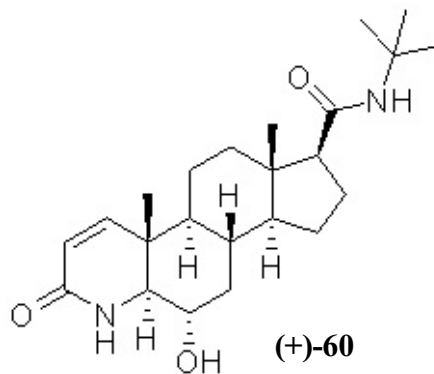
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	noesygp3pp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	64.0
10 Relaxation Delay	1.9447
11 Pulse Width	12.0000
12 Acquisition Time	0.2314
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(4424.8, 4424.8)
15 Lowest Frequency	(86.2, 86.2)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.32, 4.32)



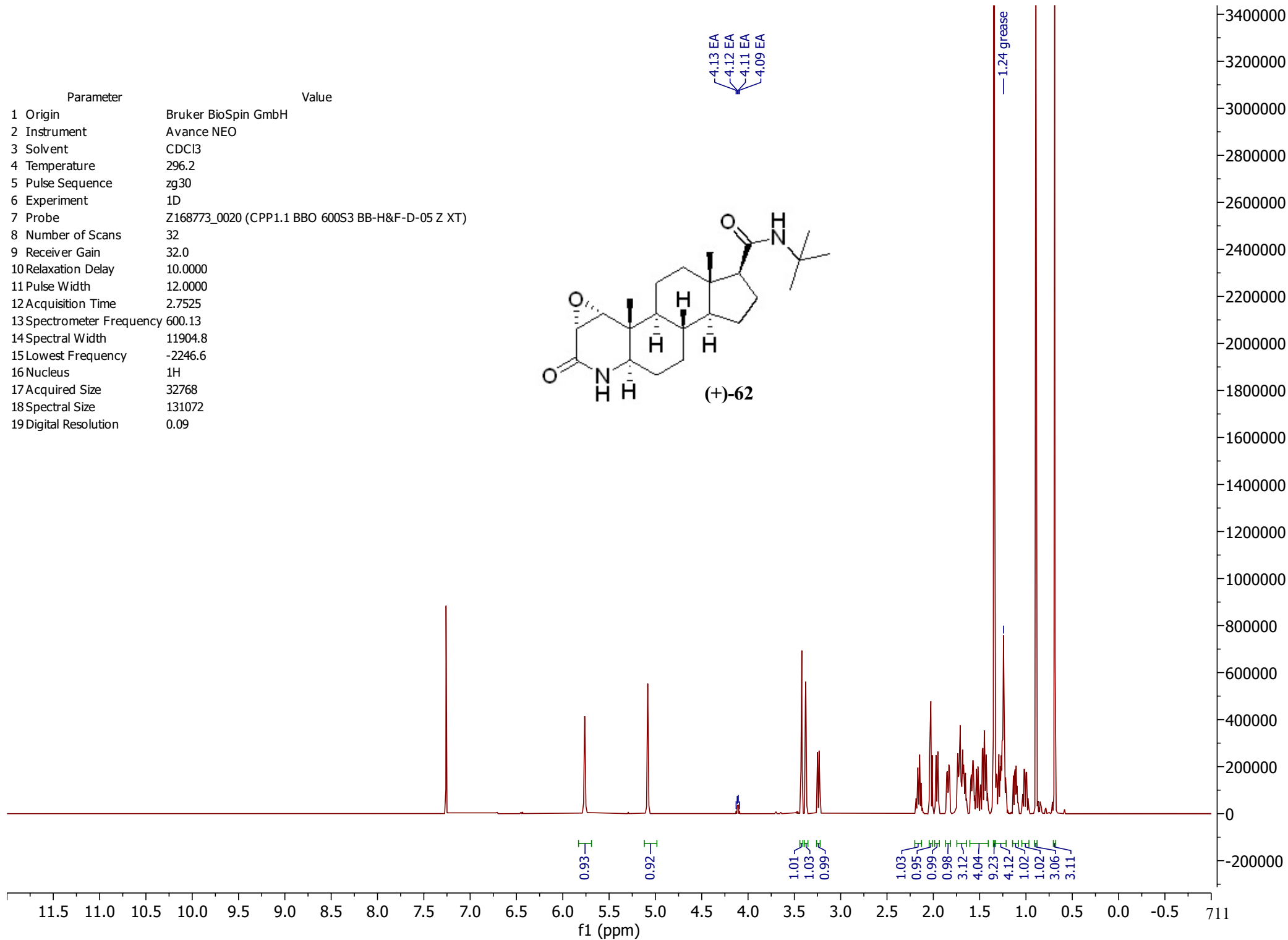
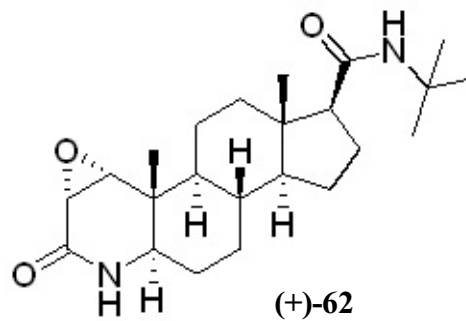
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	2048
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1919.2
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



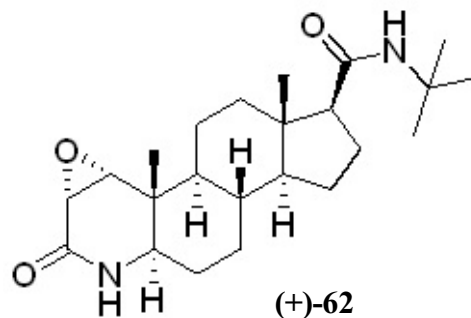
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



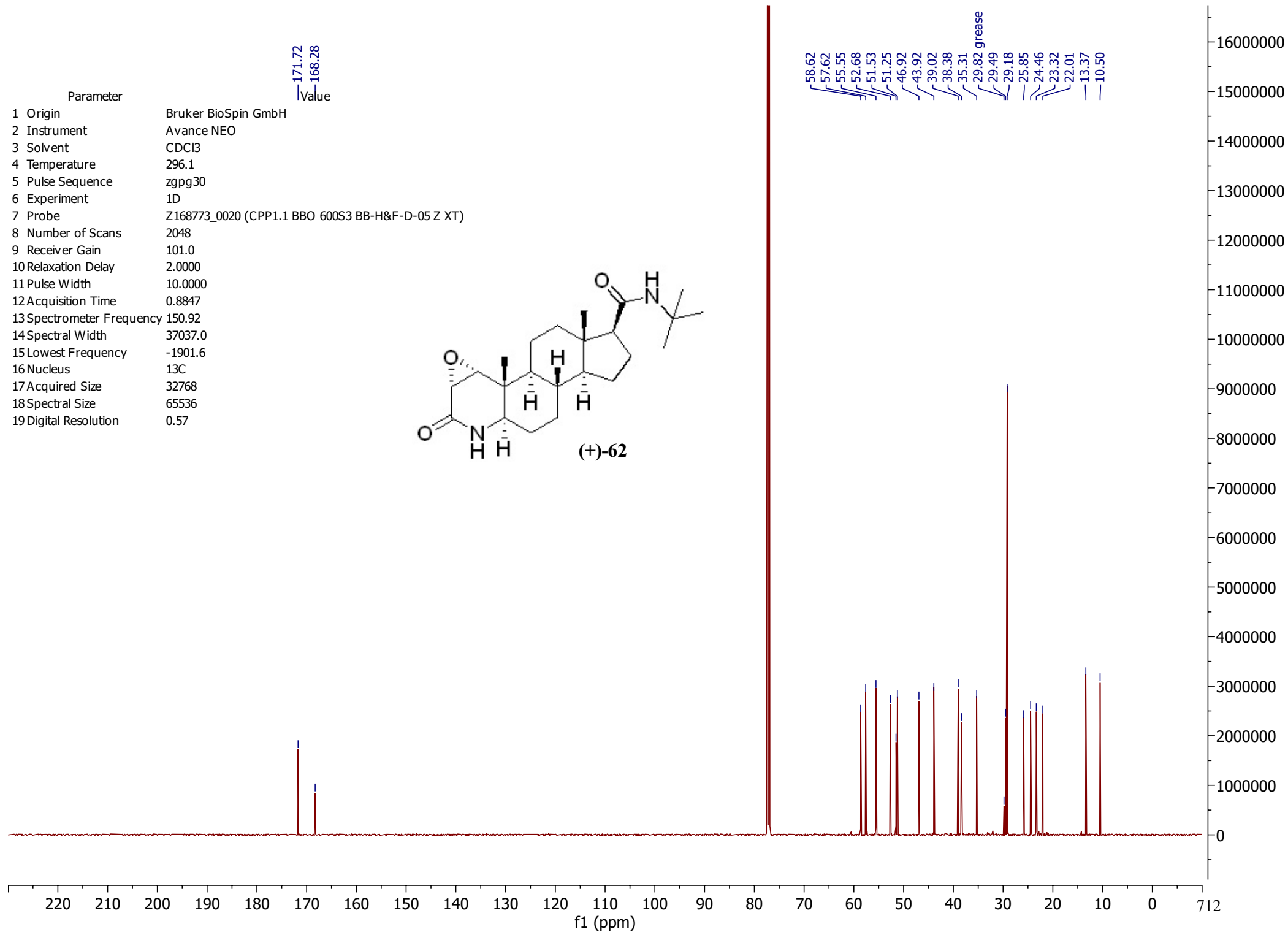
Parameter

1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	2048
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1901.6
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57

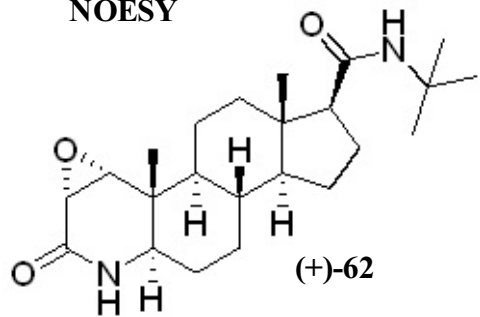
171.72
168.28
Value



58.62
57.62
55.55
52.68
51.53
51.25
46.92
43.92
39.02
38.38
35.31
29.82 grease
29.49
29.18
25.85
24.46
23.32
22.01
13.37
10.50

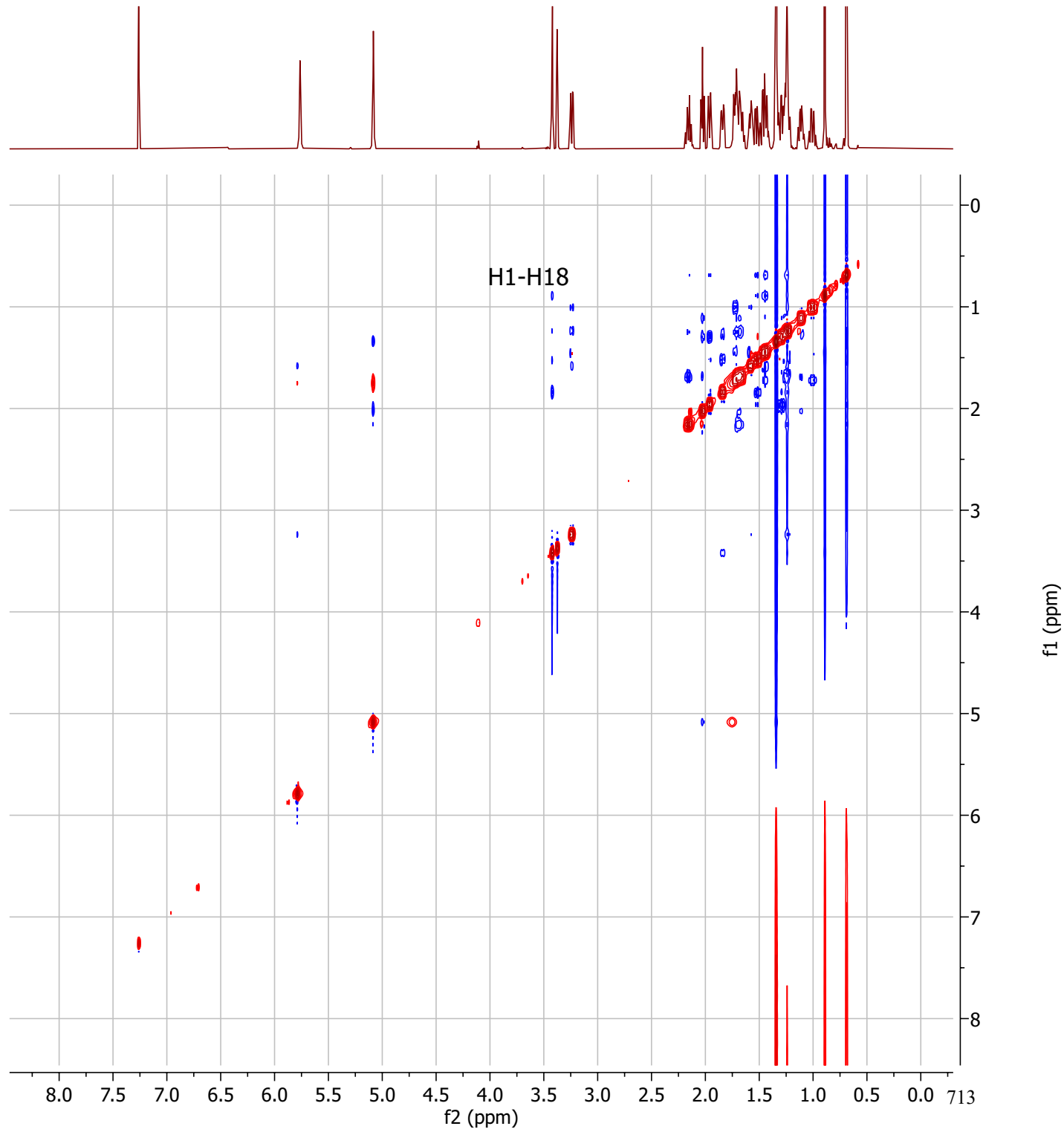


NOESY

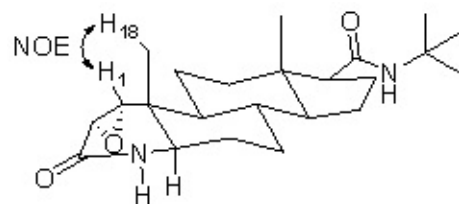
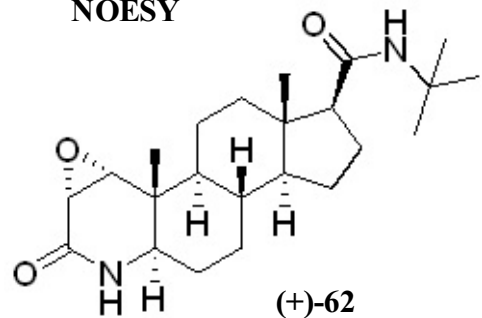


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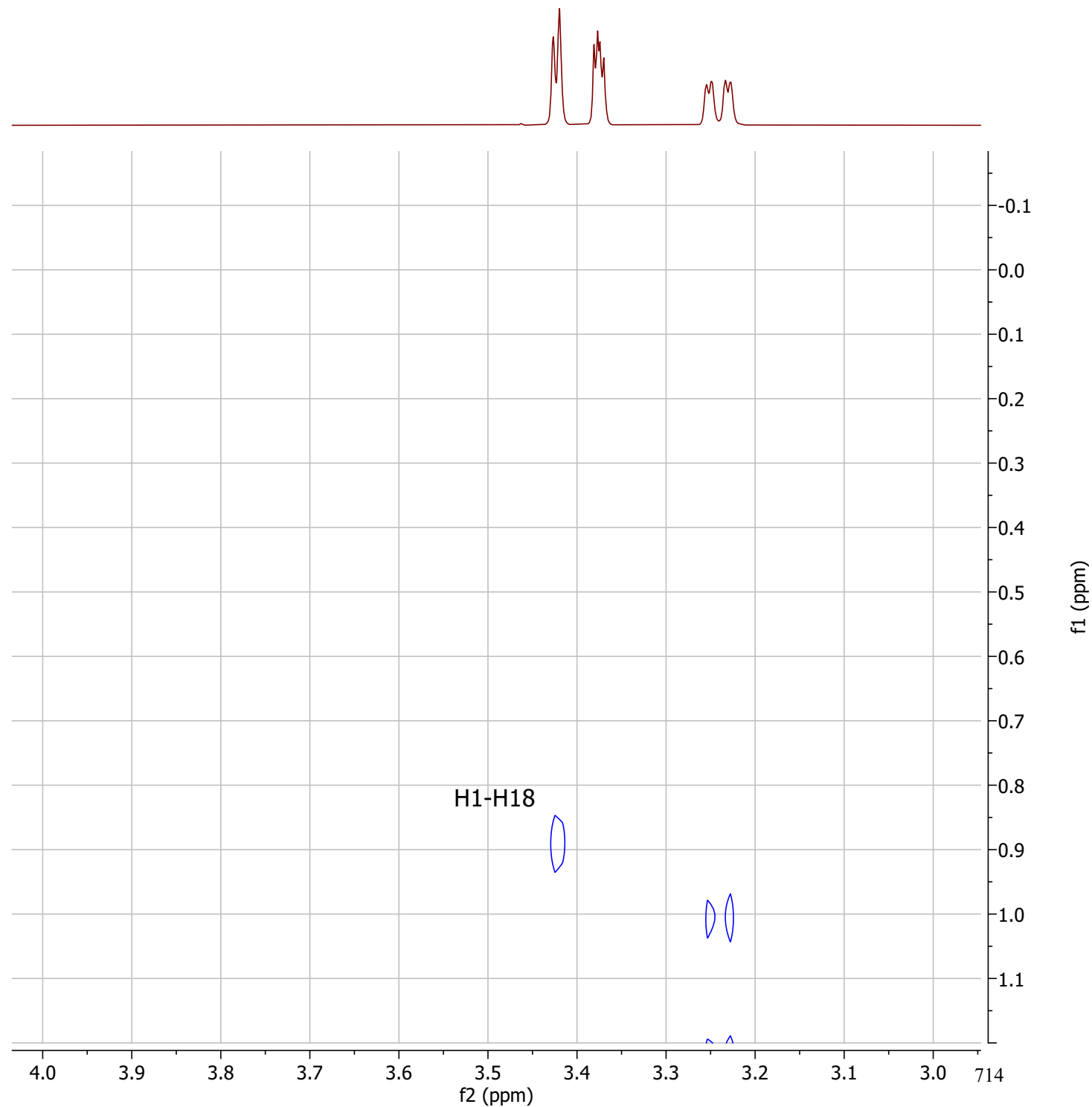
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.9754
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(5263.2, 5263.2)
15 Lowest Frequency	(-185.7, -185.7)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 5.14)



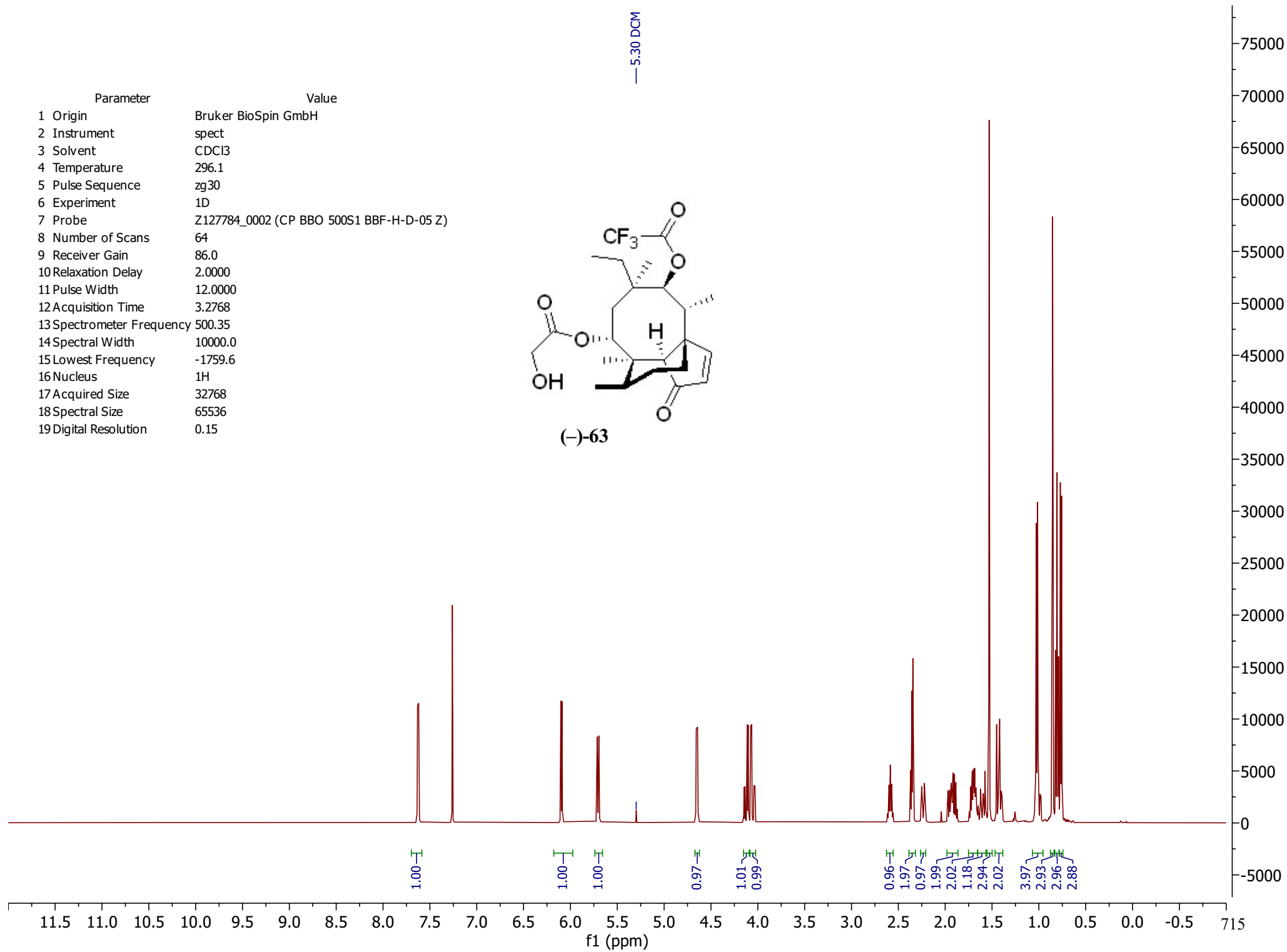
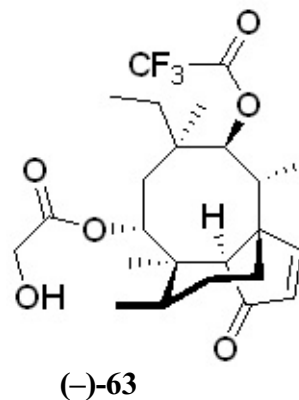
NOESY

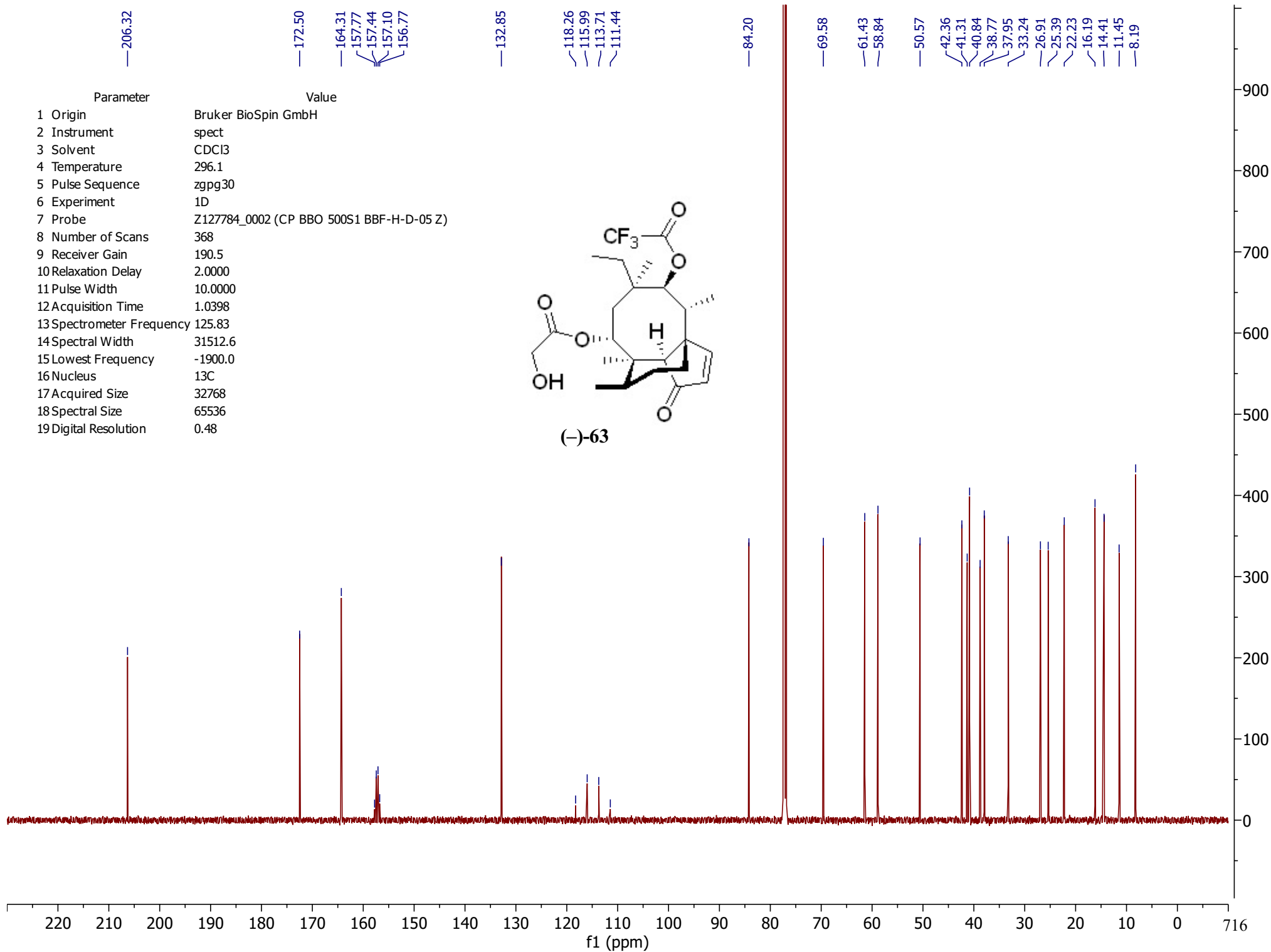


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.9754
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(5263.2, 5263.2)
15 Lowest Frequency	(-185.7, -185.7)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 5.14)

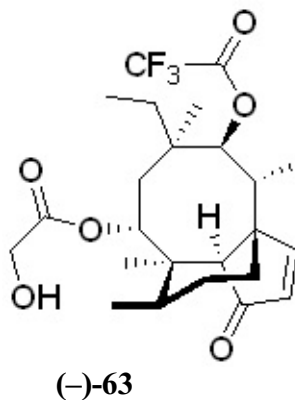


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1759.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

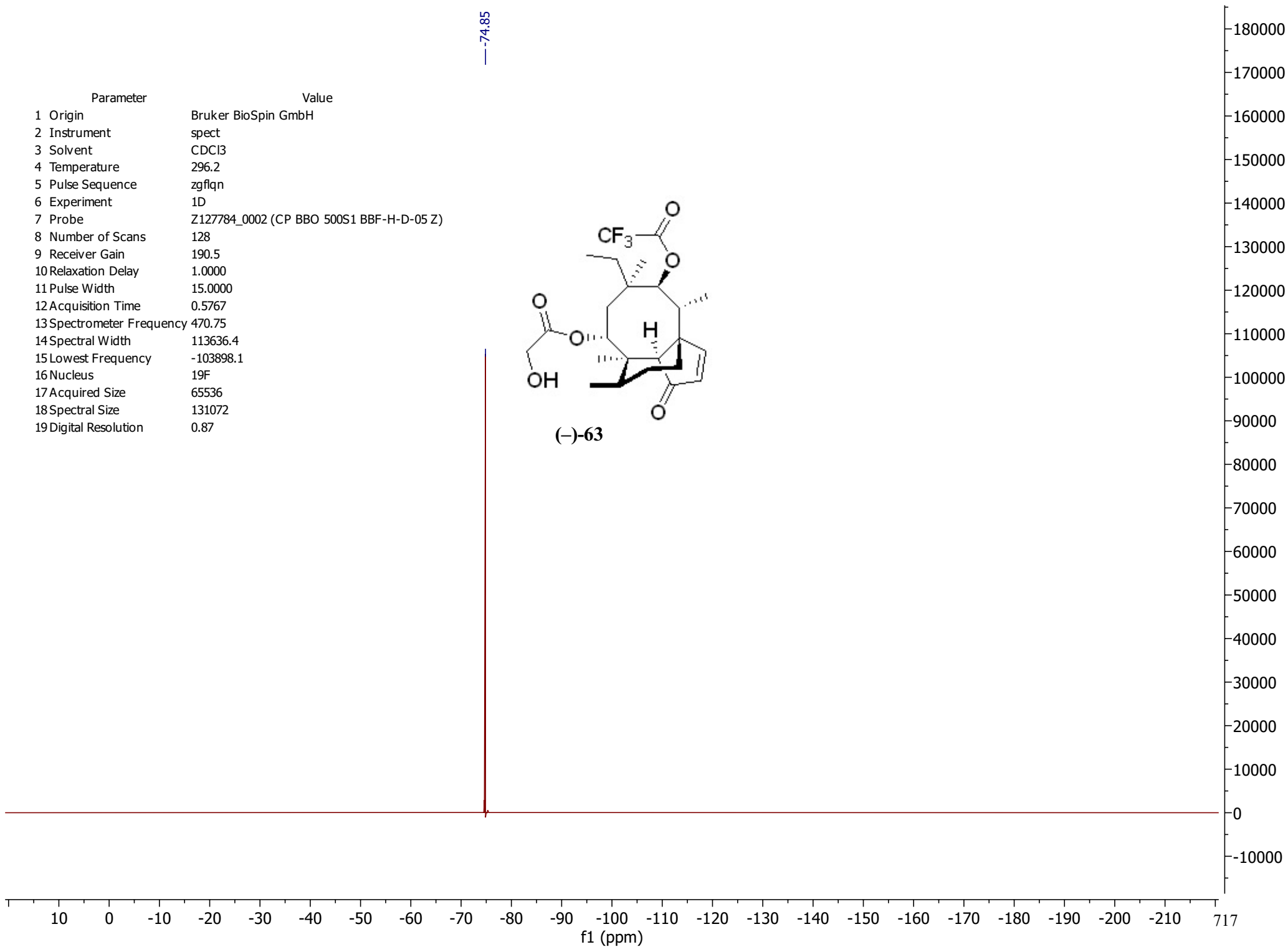




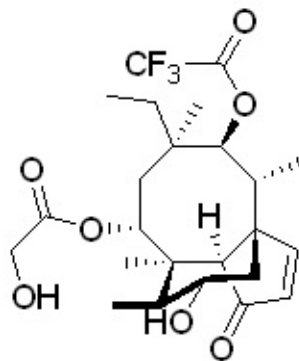
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgflqn
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	128
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	¹⁹ F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



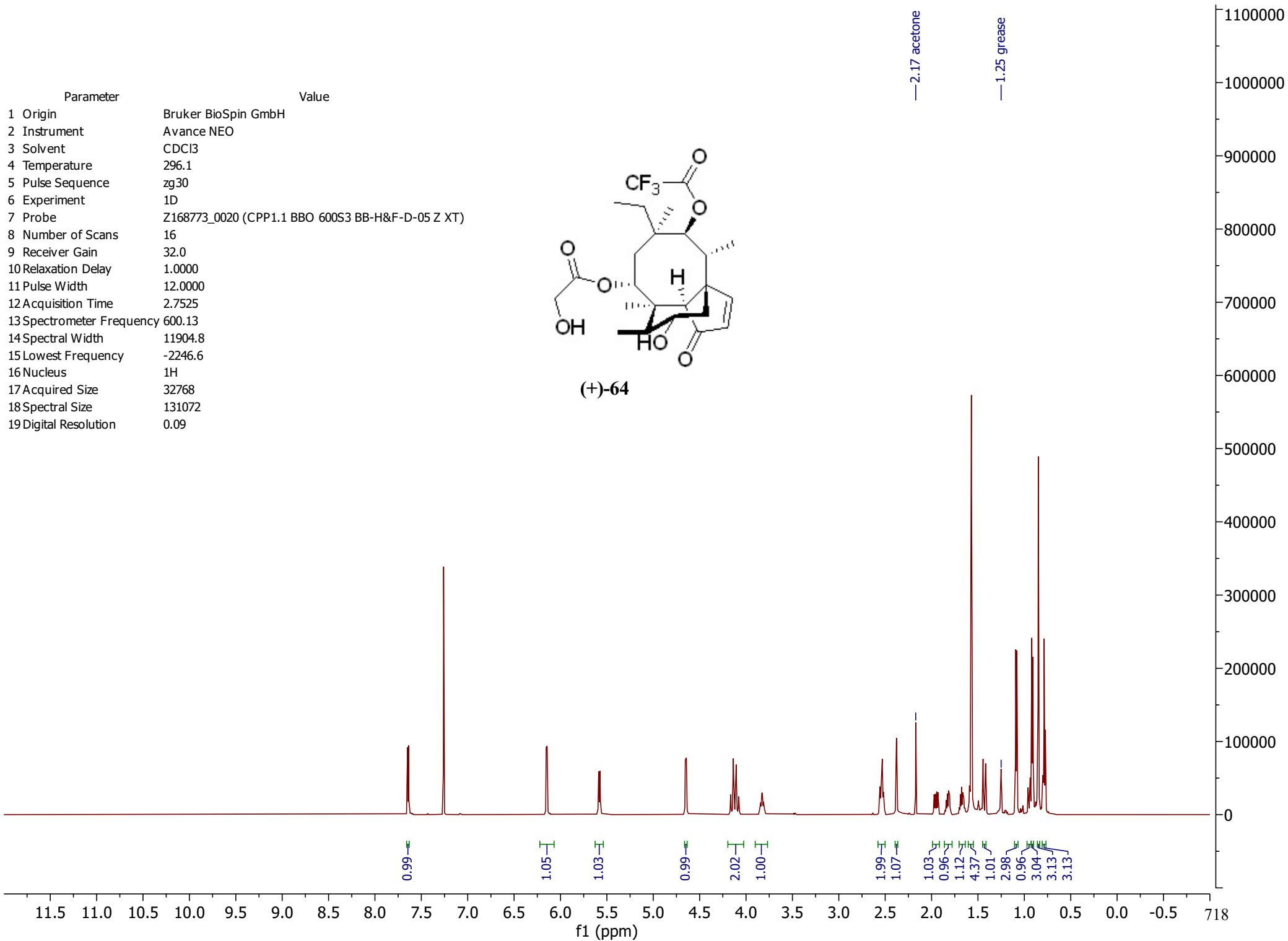
— -74.85



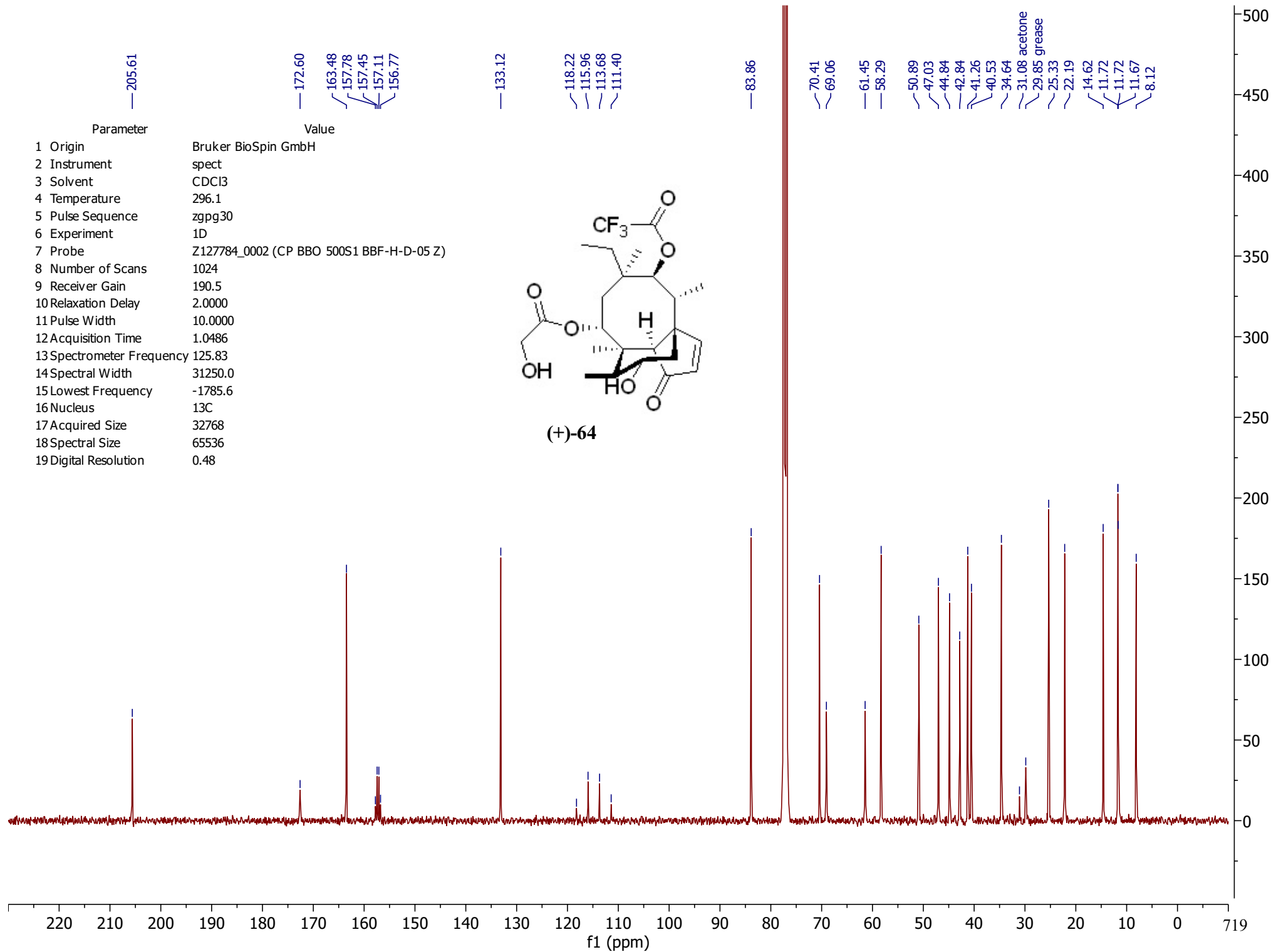
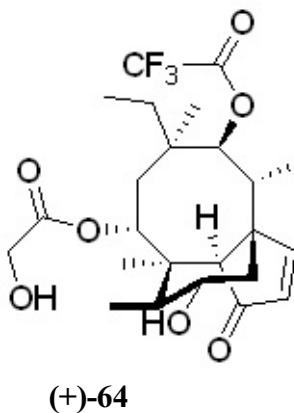
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



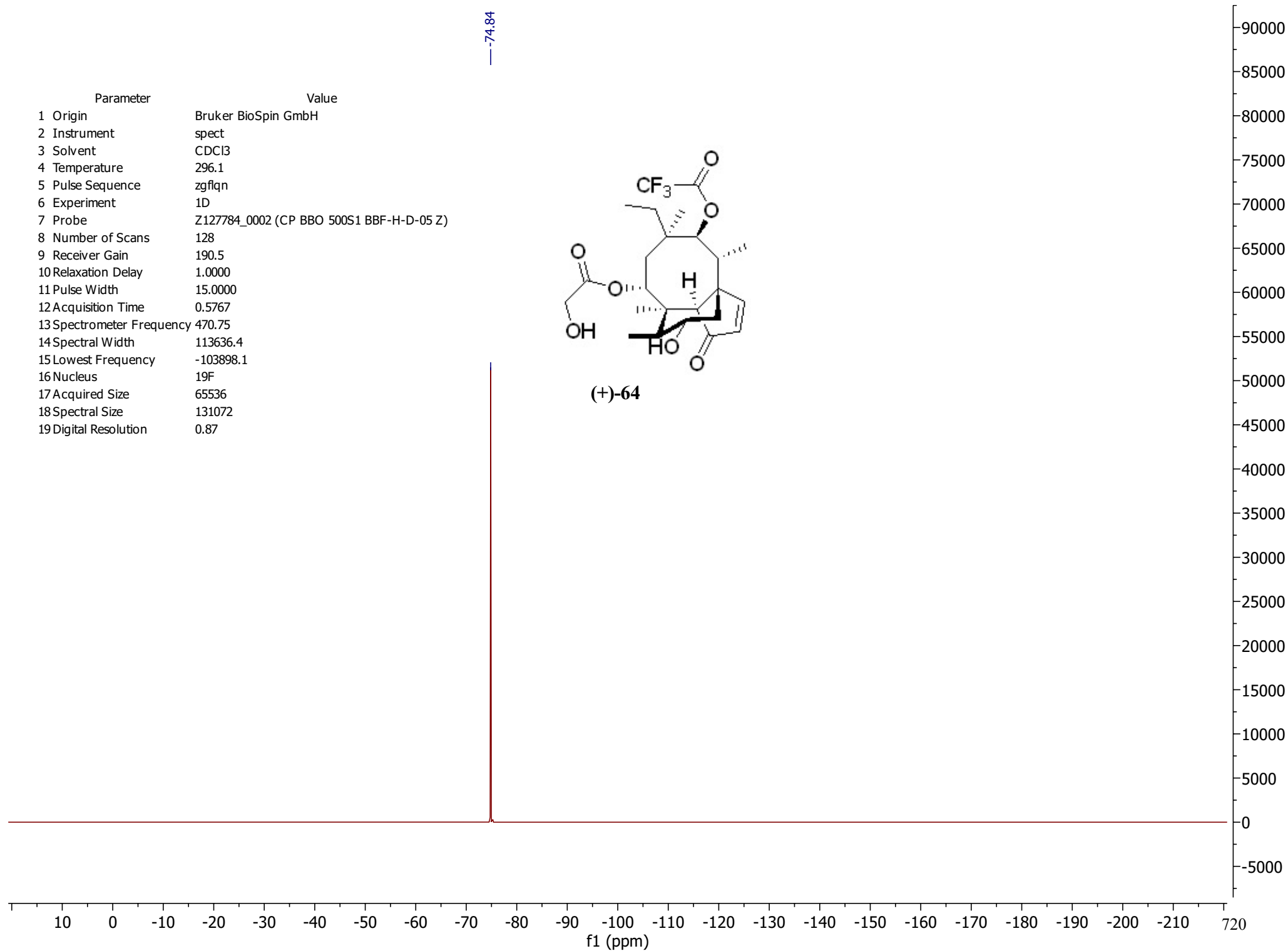
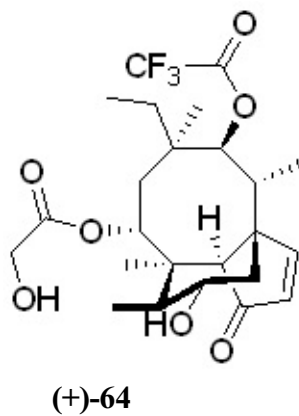
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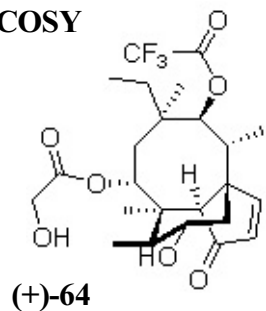
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	1024
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1785.6
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



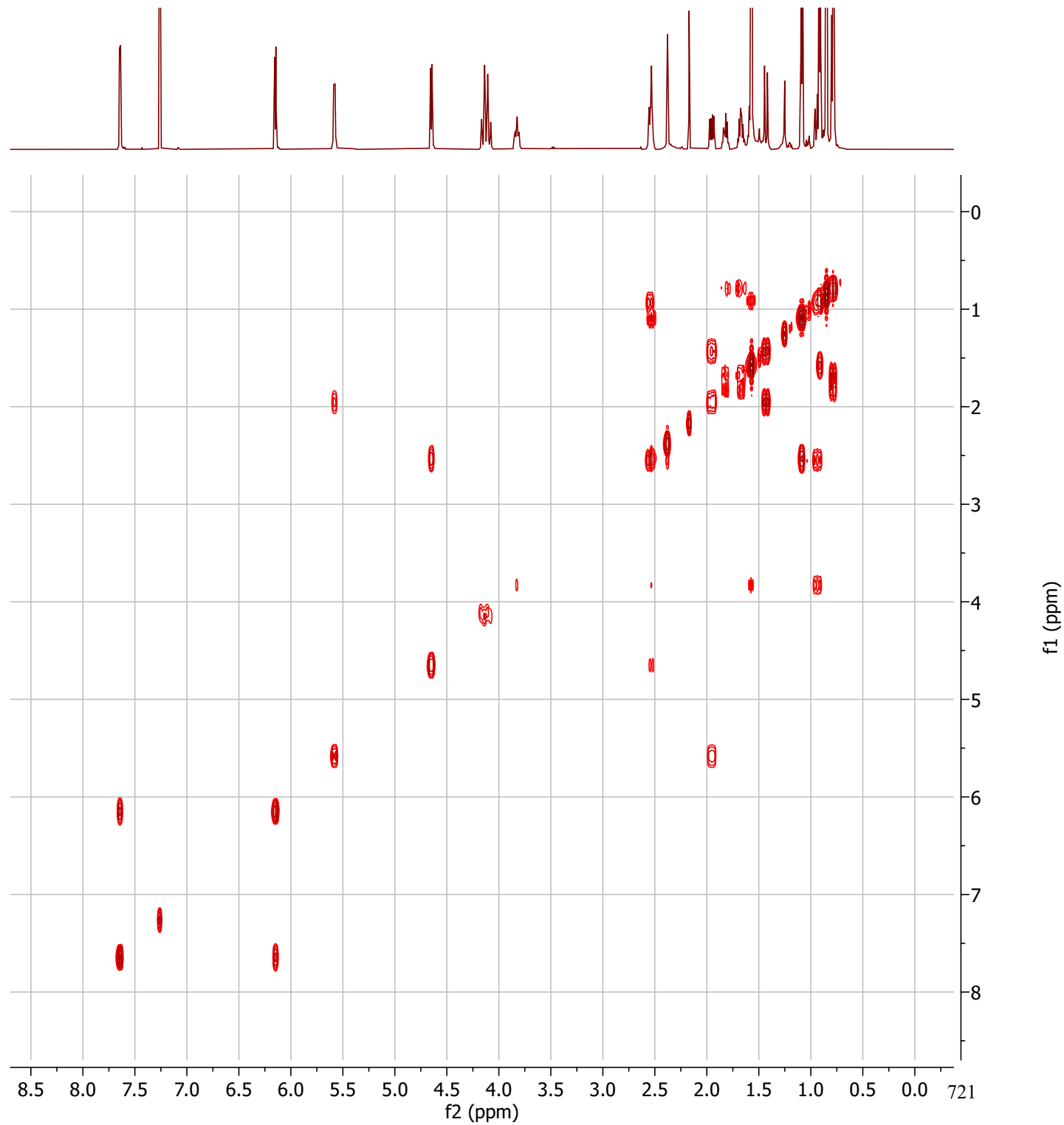
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	128
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	¹⁹ F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



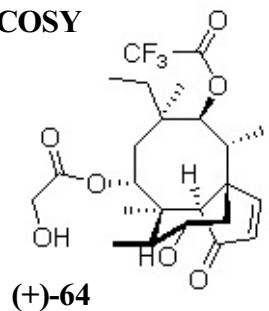
COSY



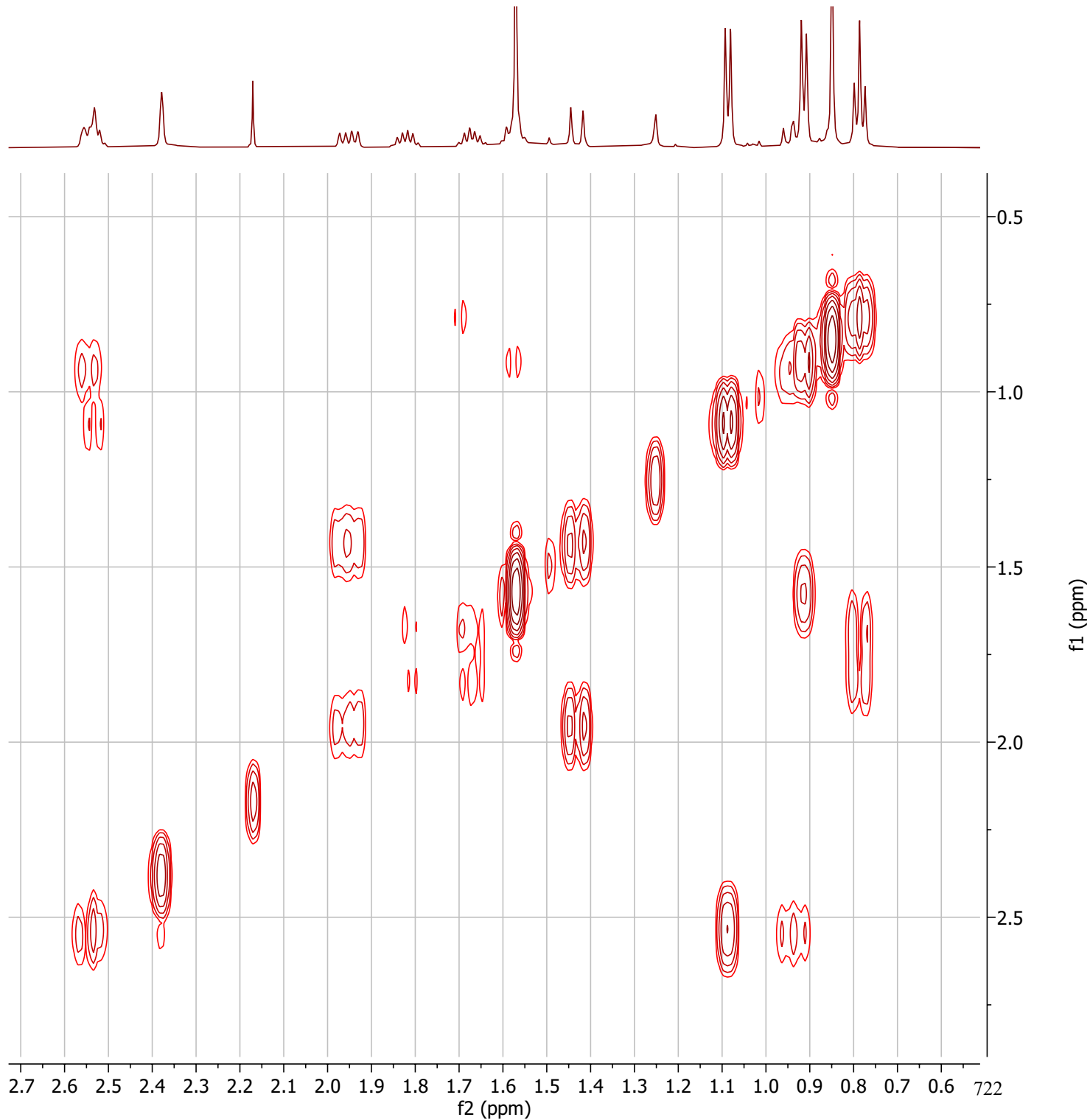
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	8
9 Receiver Gain	34.8
10 Relaxation Delay	1.9320
11 Pulse Width	12.0000
12 Acquisition Time	0.2253
13 Spectrometer Frequency (500.35, 500.35)	
14 Spectral Width	(4545.5, 4545.5)
15 Lowest Frequency	(-192.5, -192.3)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.44, 4.44)



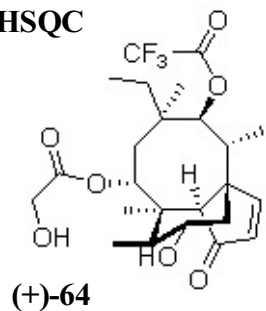
COSY



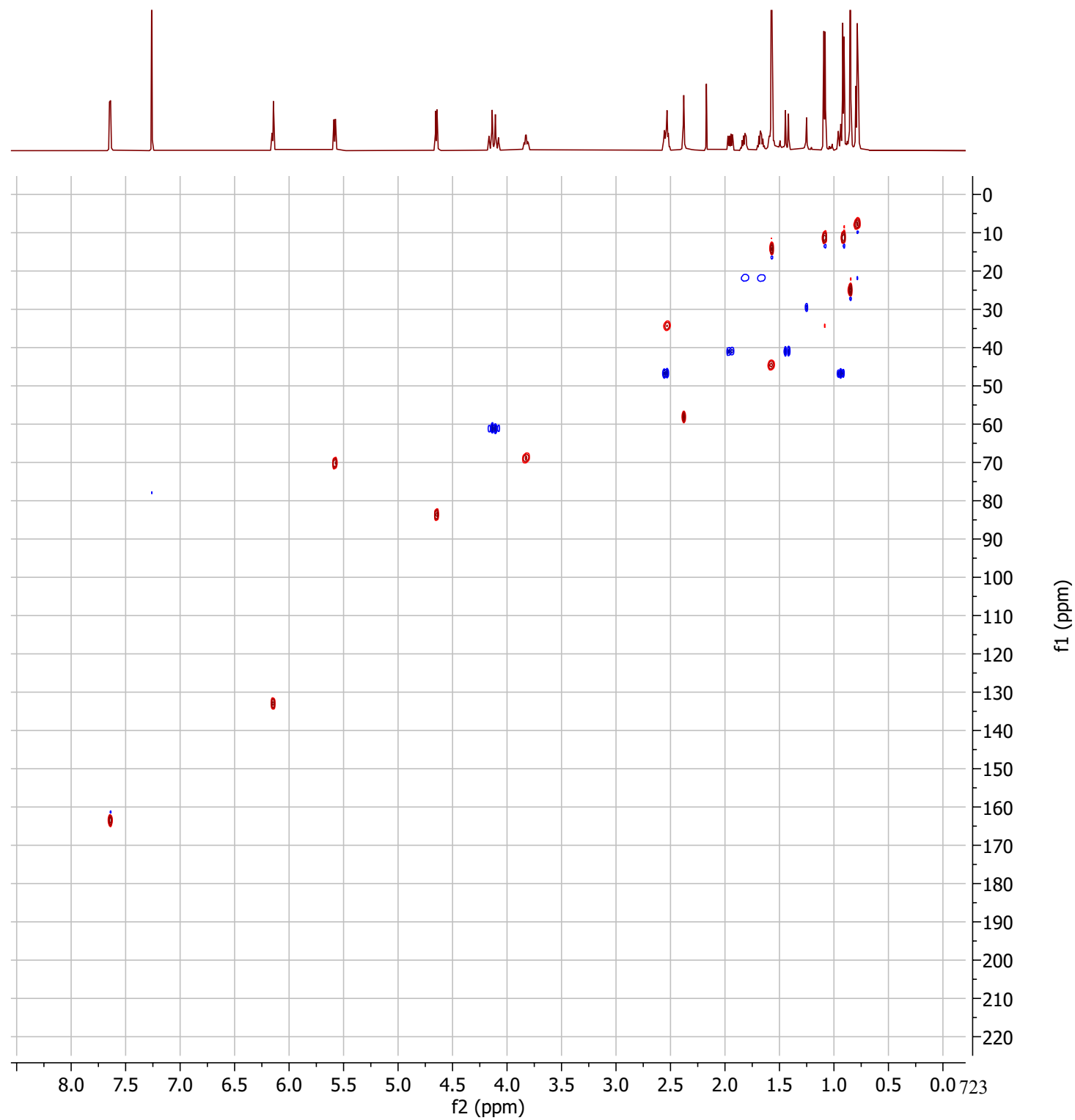
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	8
9 Receiver Gain	34.8
10 Relaxation Delay	1.9320
11 Pulse Width	12.0000
12 Acquisition Time	0.2253
13 Spectrometer Frequency (500.35, 500.35)	
14 Spectral Width	(4545.5, 4545.5)
15 Lowest Frequency	(-192.5, -192.3)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.44, 4.44)



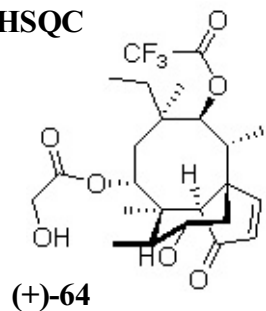
HSQC



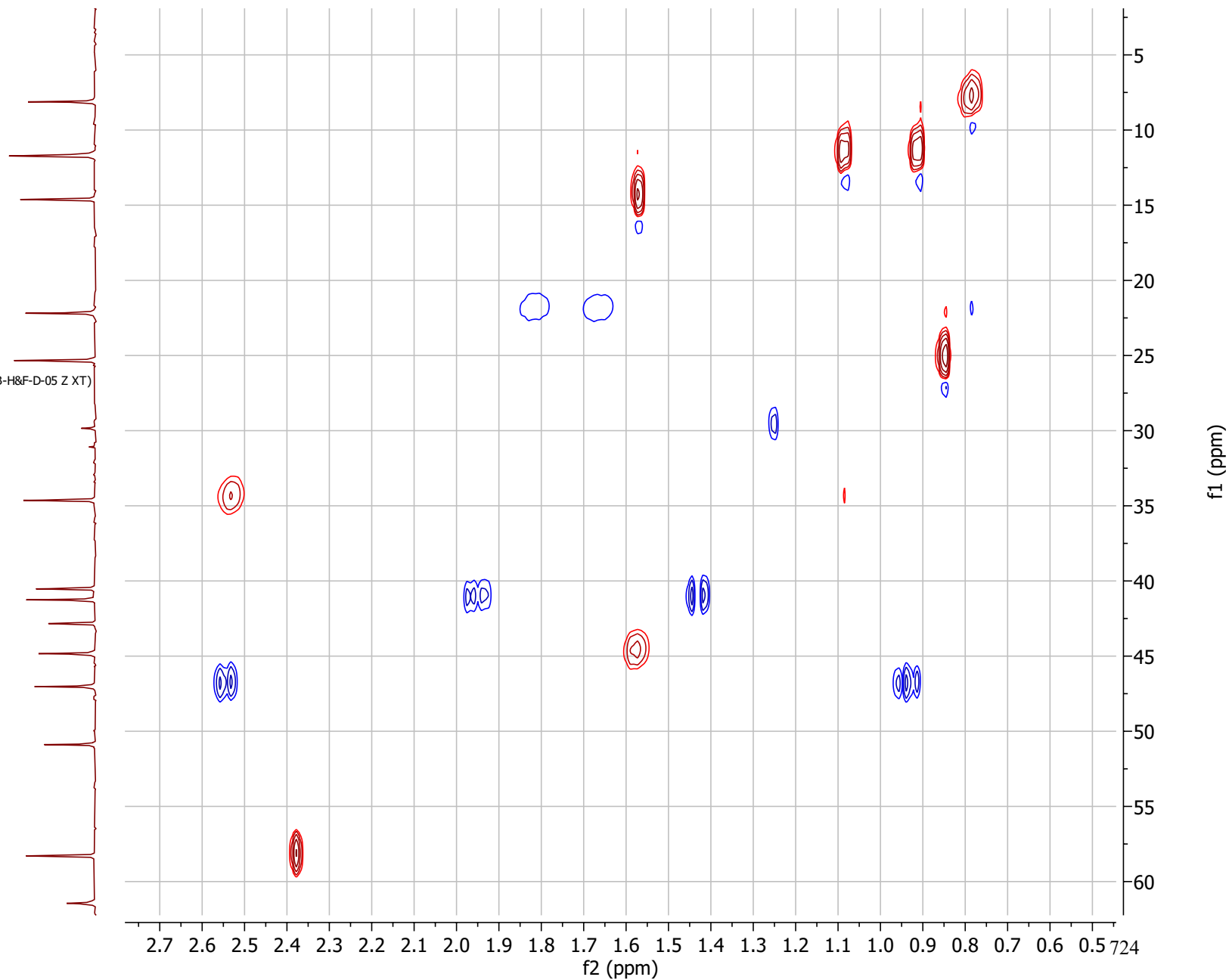
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcedetgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(5263.2, 34710.2)
15 Lowest Frequency	(-130.2, -759.5)
16 Nucleus	(1H, 13C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 33.90)



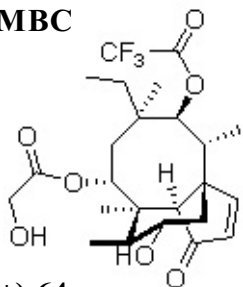
HSQC



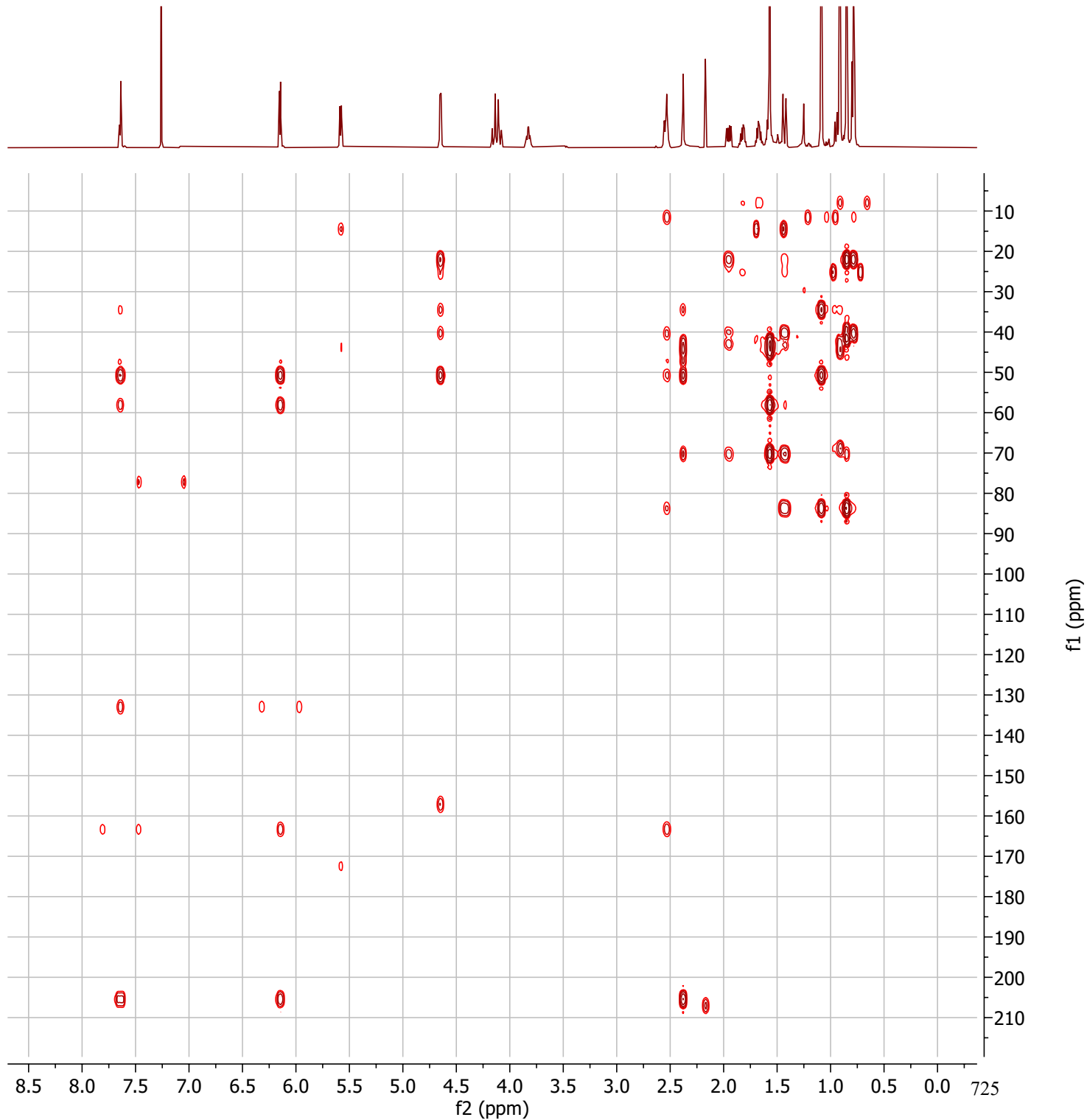
Parameter	Value
1 Origin	Brucker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpsi2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(5263.2, 34710.2)
15 Lowest Frequency	(-130.2, -759.5)
16 Nucleus	(1H, 13C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 33.90)



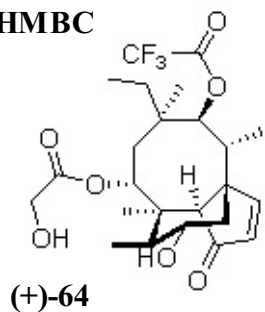
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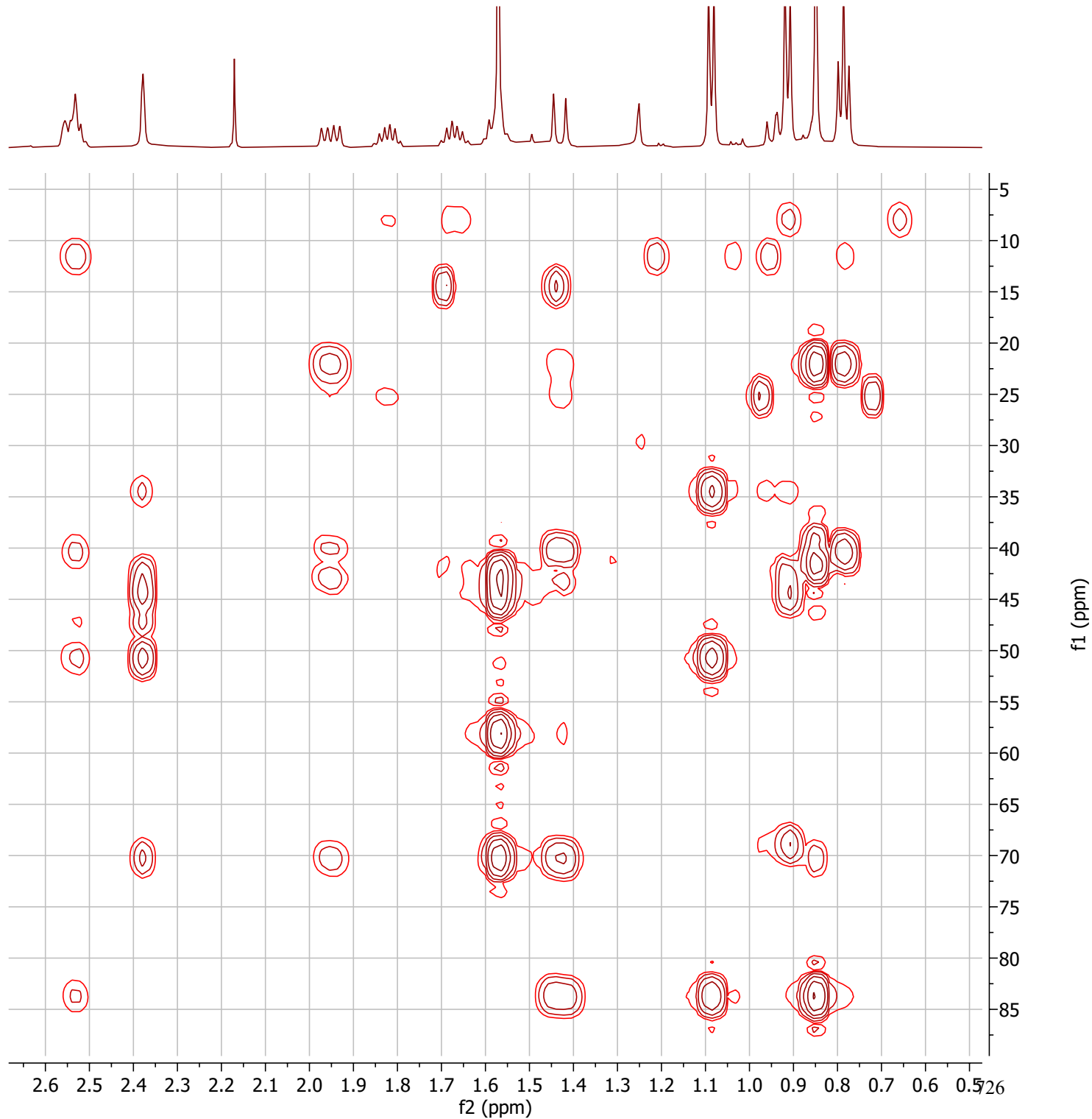
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hmbcgp1pndqf
6 Experiment	HMBC
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	8
9 Receiver Gain	190.5
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency	(500.35, 125.83)
14 Spectral Width	(4545.5, 27624.3)
15 Lowest Frequency	(-194.1, 23.4)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 128)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.88, 53.95)



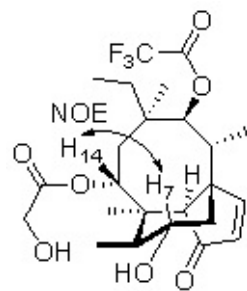
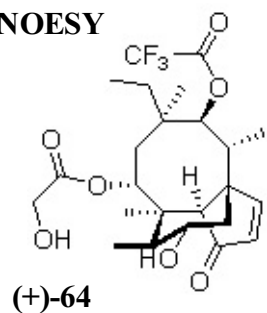
HMBC



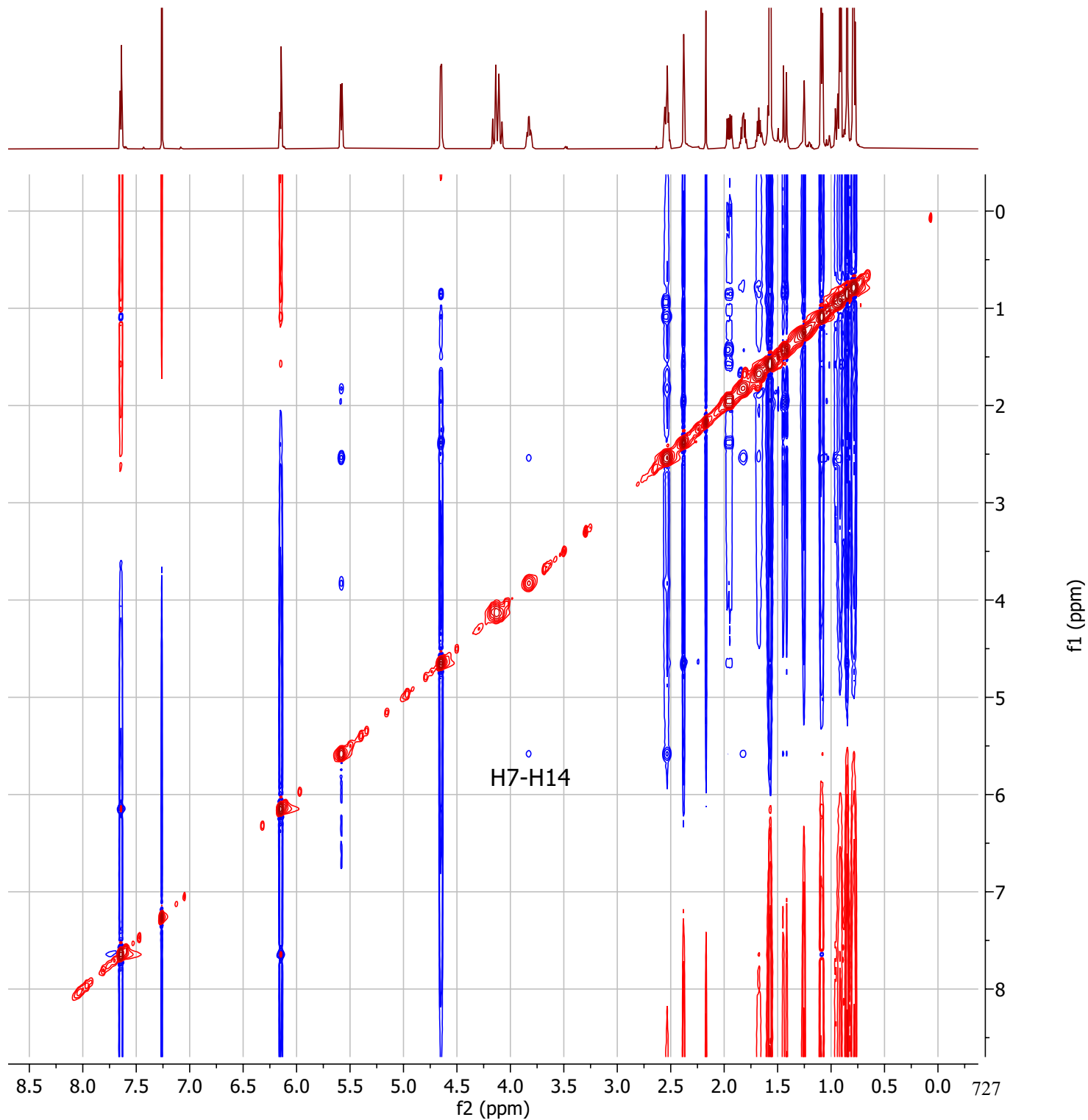
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hmbcgp1pndqf
6 Experiment	HMBC
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	8
9 Receiver Gain	190.5
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency (500.35, 125.83)	
14 Spectral Width	(4545.5, 27624.3)
15 Lowest Frequency	(-194.1, 23.4)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 128)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.88, 53.95)



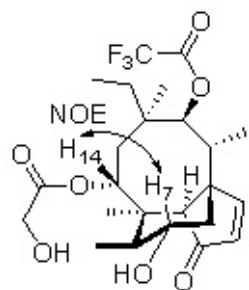
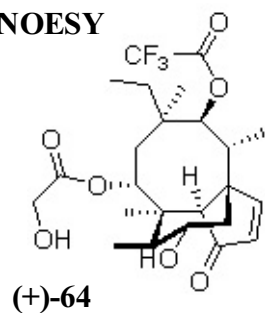
NOESY



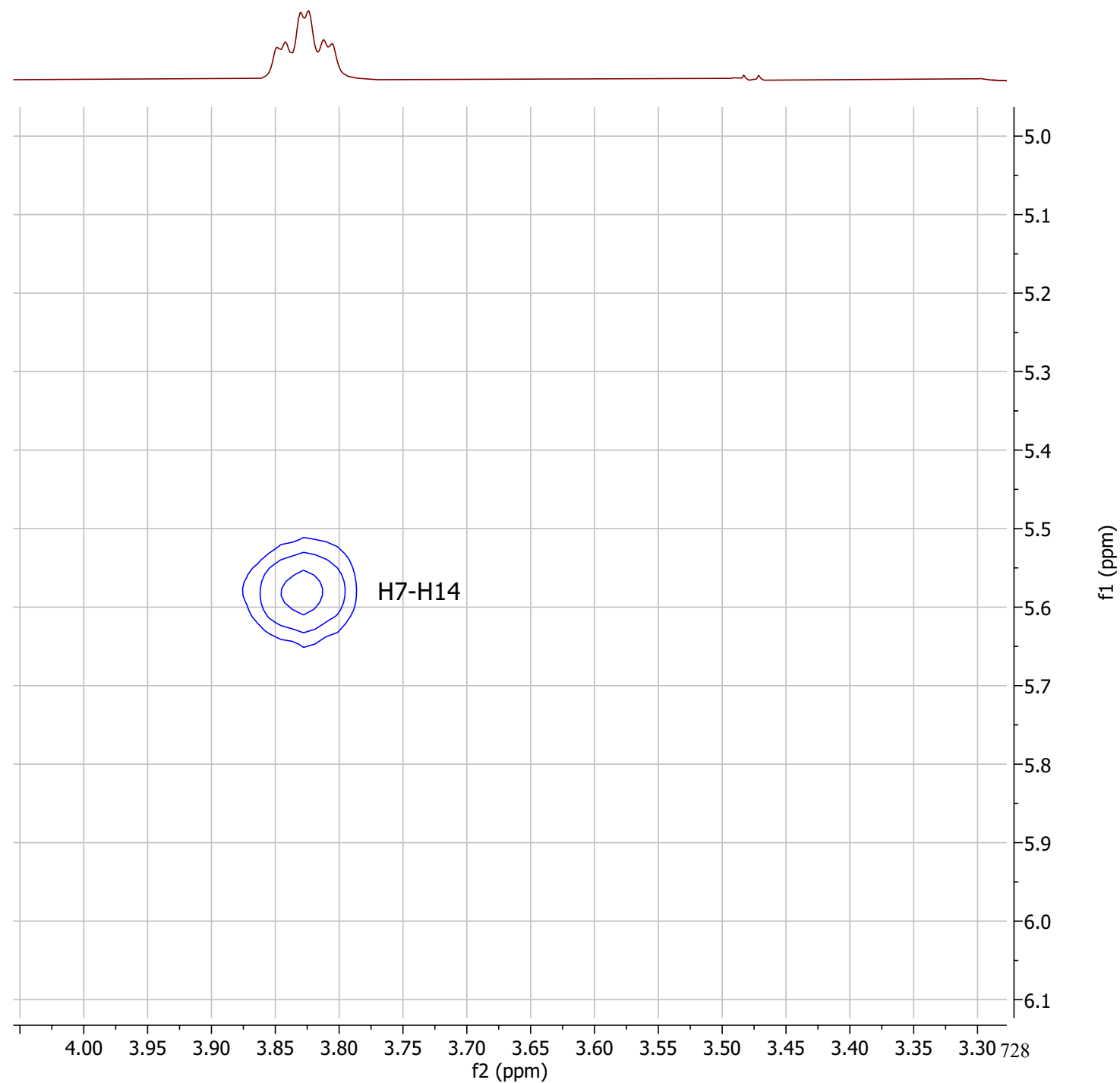
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCI3
4 Temperature	296.2
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	8
9 Receiver Gain	29.7
10 Relaxation Delay	1.9795
11 Pulse Width	12.0000
12 Acquisition Time	0.2253
13 Spectrometer Frequency (500.35, 500.35)	
14 Spectral Width	(4545.5, 4545.5)
15 Lowest Frequency	(-193.2, -192.8)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.44, 4.44)



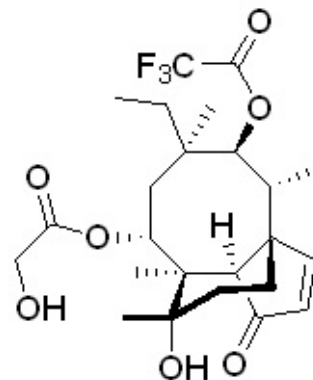
NOESY



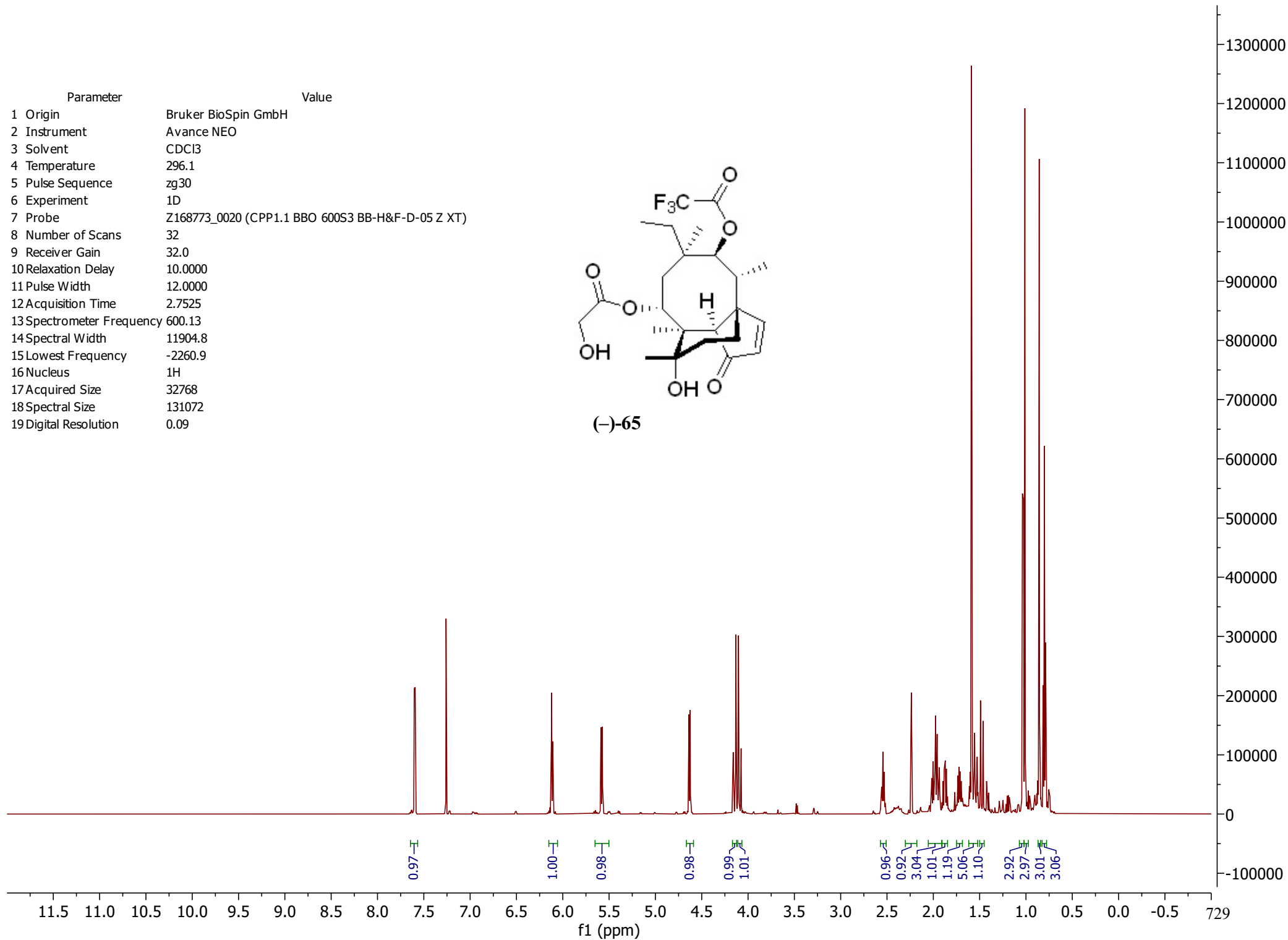
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	8
9 Receiver Gain	29.7
10 Relaxation Delay	1.9795
11 Pulse Width	12.0000
12 Acquisition Time	0.2253
13 Spectrometer Frequency	(500.35, 500.35)
14 Spectral Width	(4545.5, 4545.5)
15 Lowest Frequency	(-193.2, -192.8)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.44, 4.44)

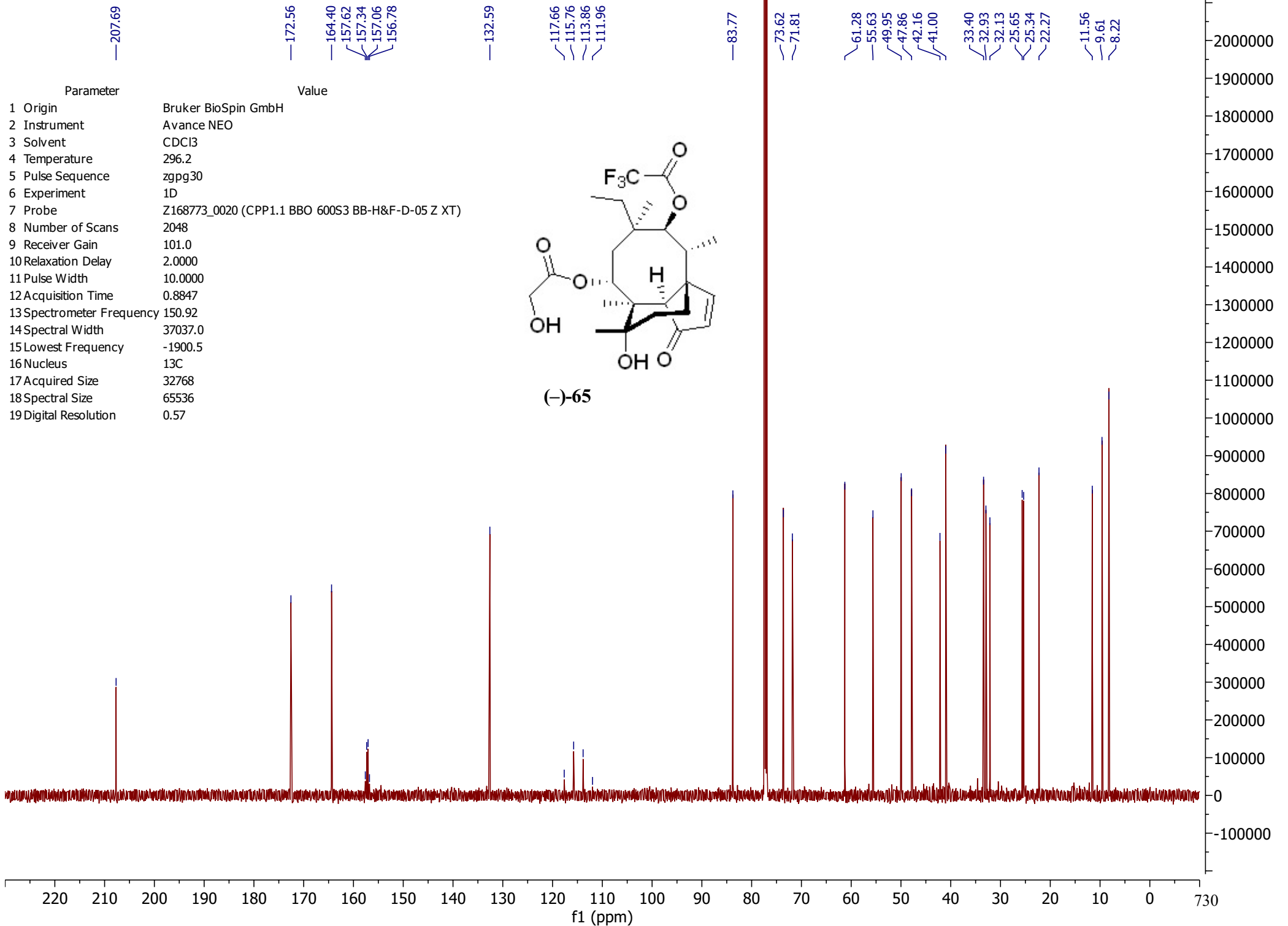


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

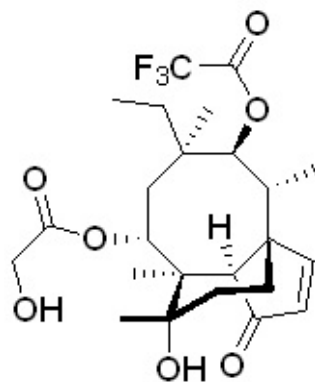


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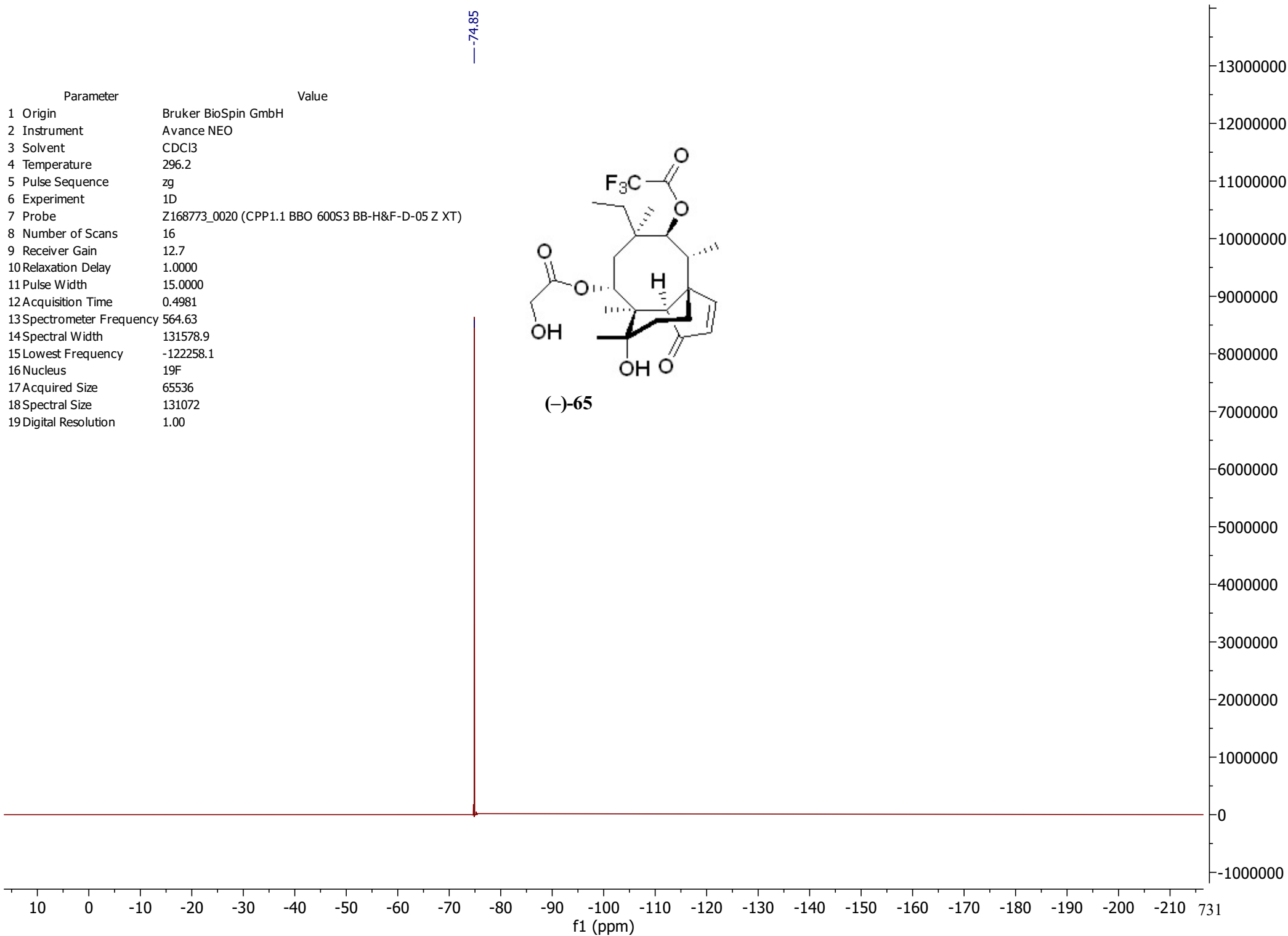


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	12.7
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.4981
13 Spectrometer Frequency	564.63
14 Spectral Width	131578.9
15 Lowest Frequency	-122258.1
16 Nucleus	¹⁹ F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	1.00

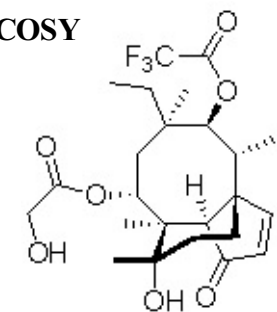


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— -74.85

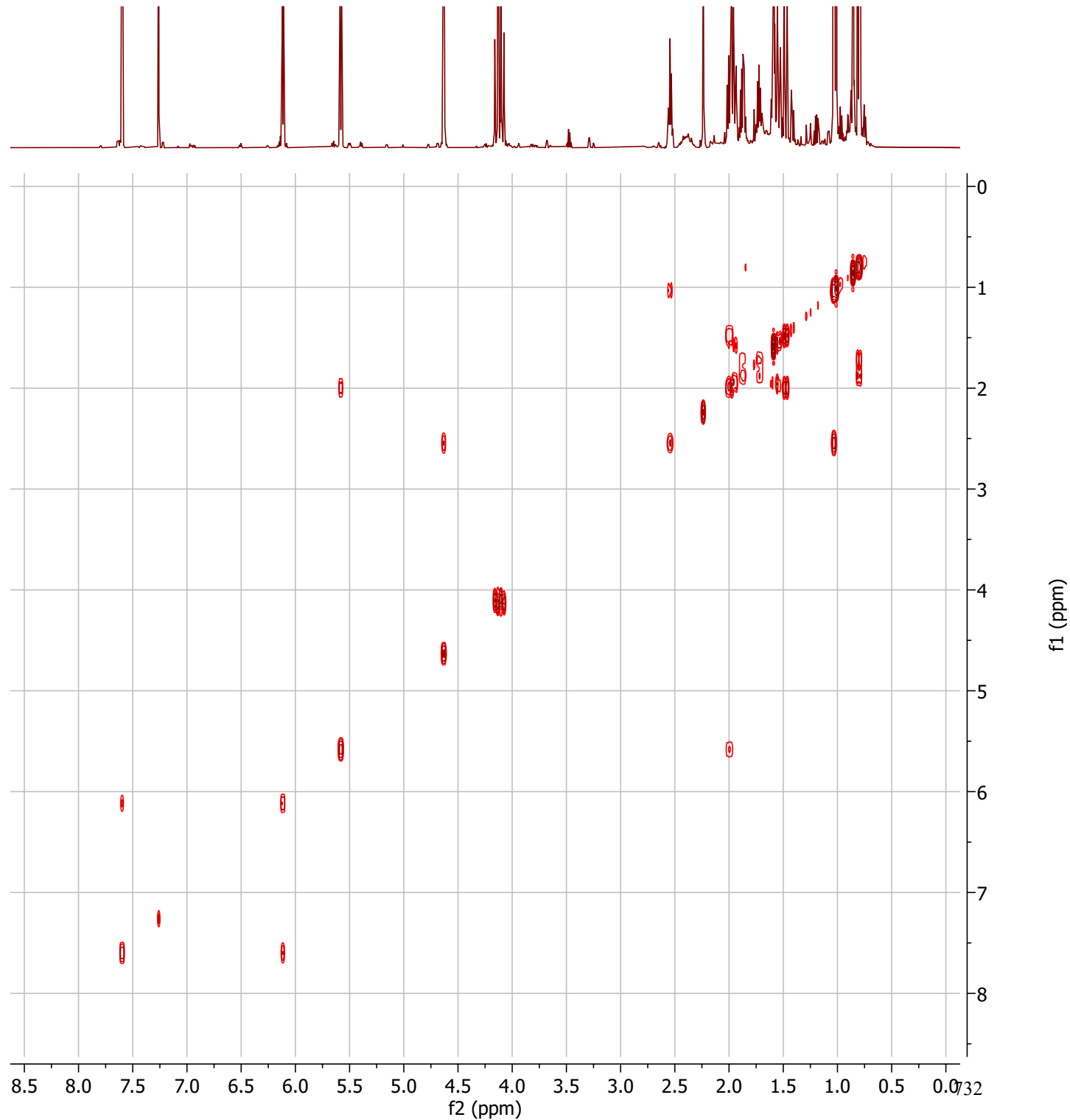
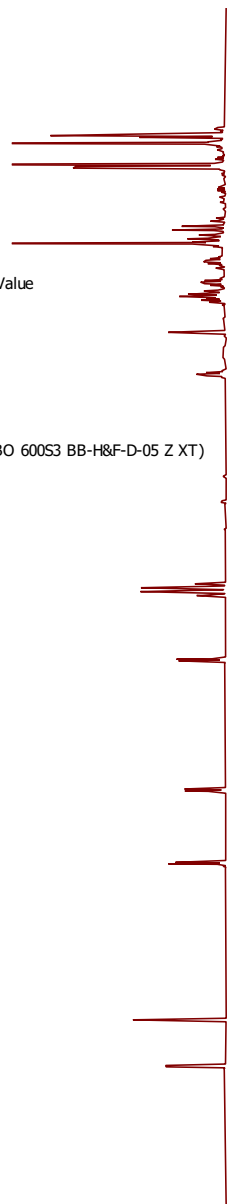


COSY

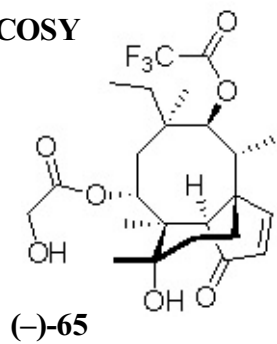


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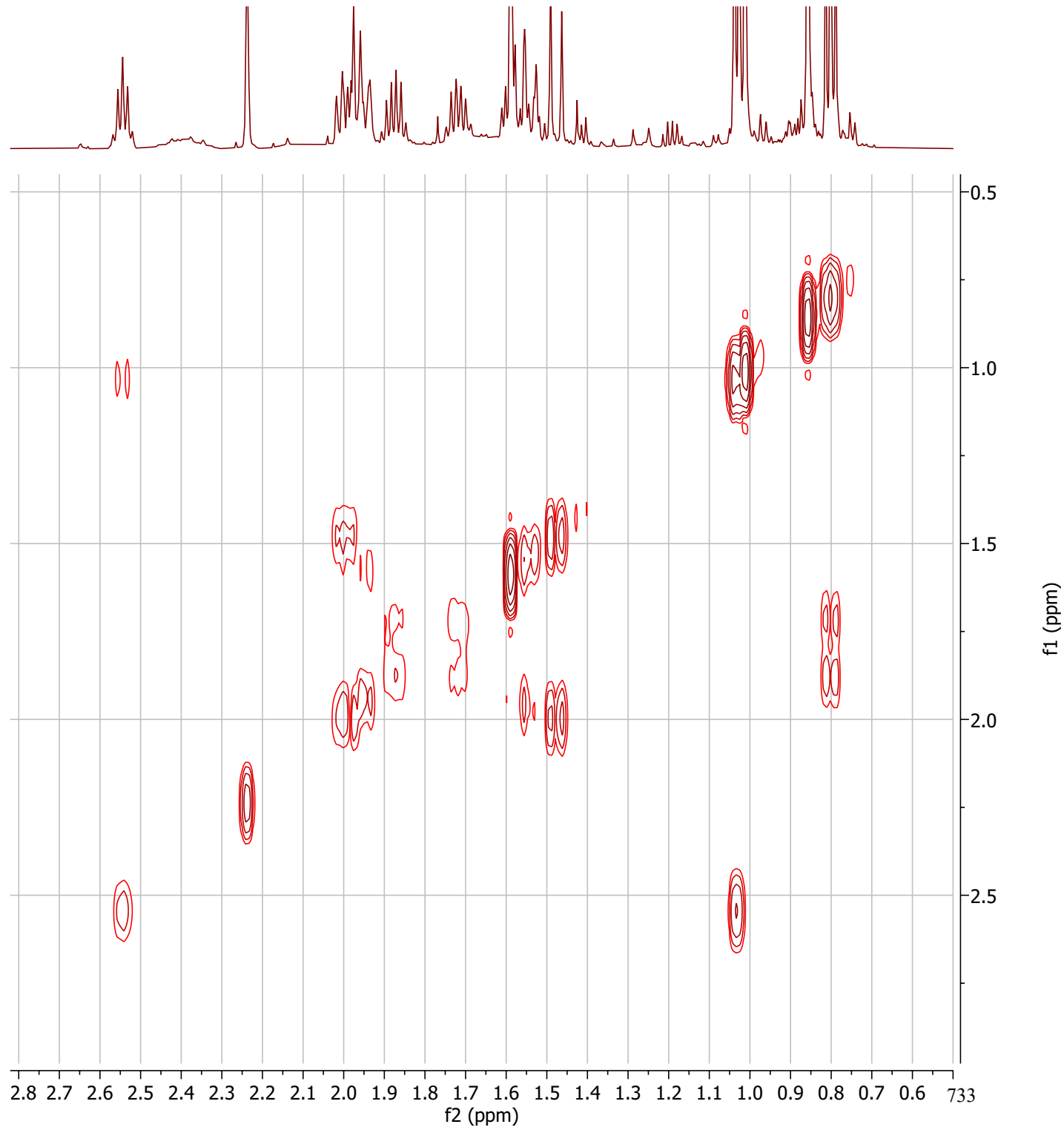
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.4386
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(5263.2, 5263.2)
15 Lowest Frequency	(-83.9, -83.9)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 5.14)



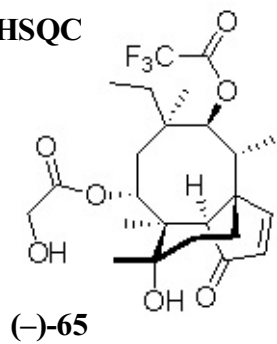
COSY



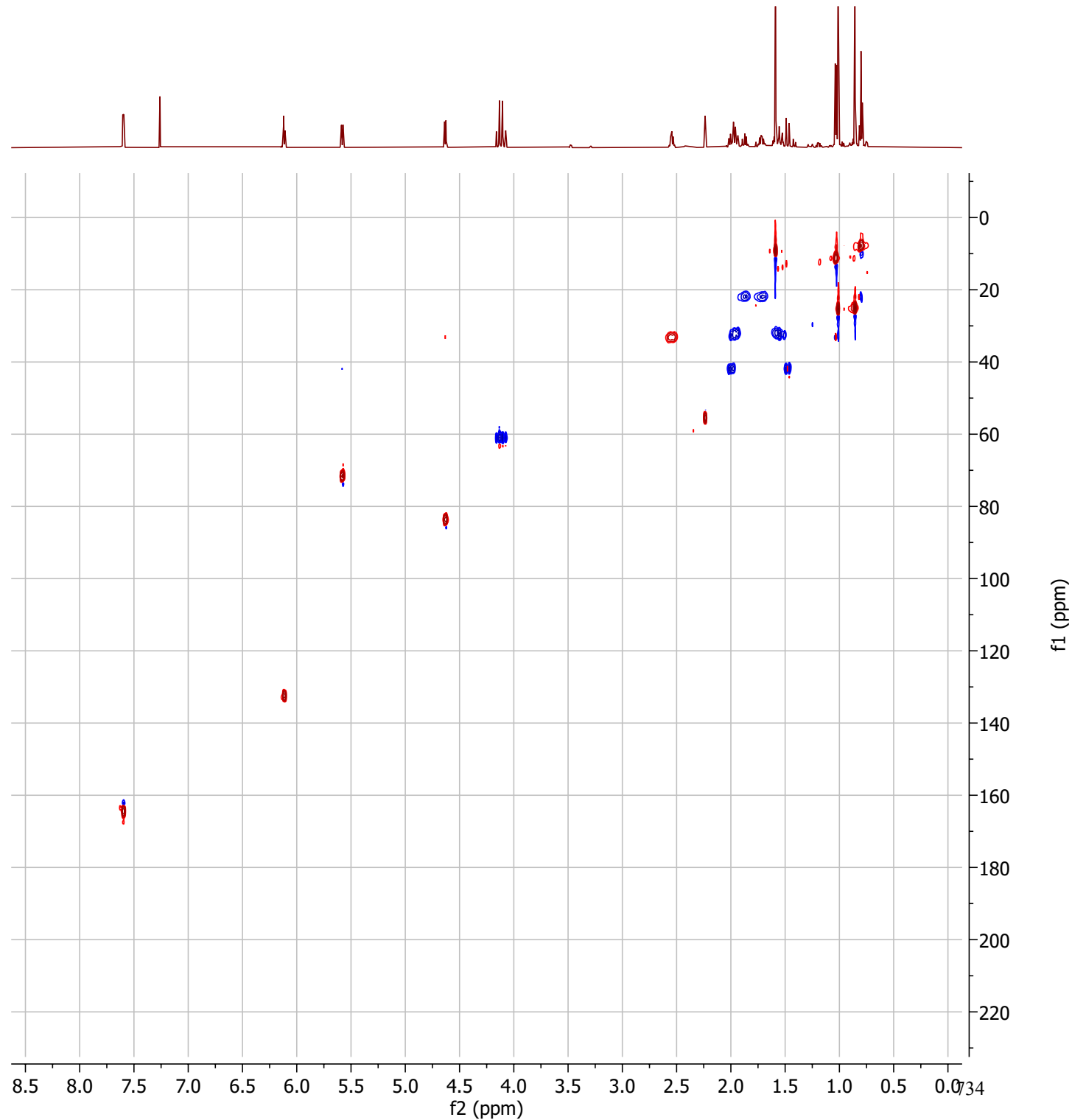
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.4386
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(5263.2, 5263.2)
15 Lowest Frequency	(-83.9, -83.9)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 5.14)



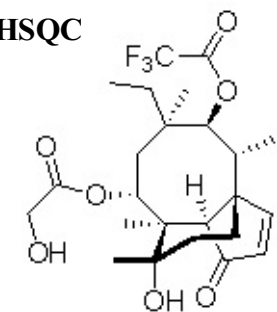
HSQC



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(5263.2, 36974.0)
15 Lowest Frequency	(-83.5, -1891.2)
16 Nucleus	(1H, 13C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 36.11)

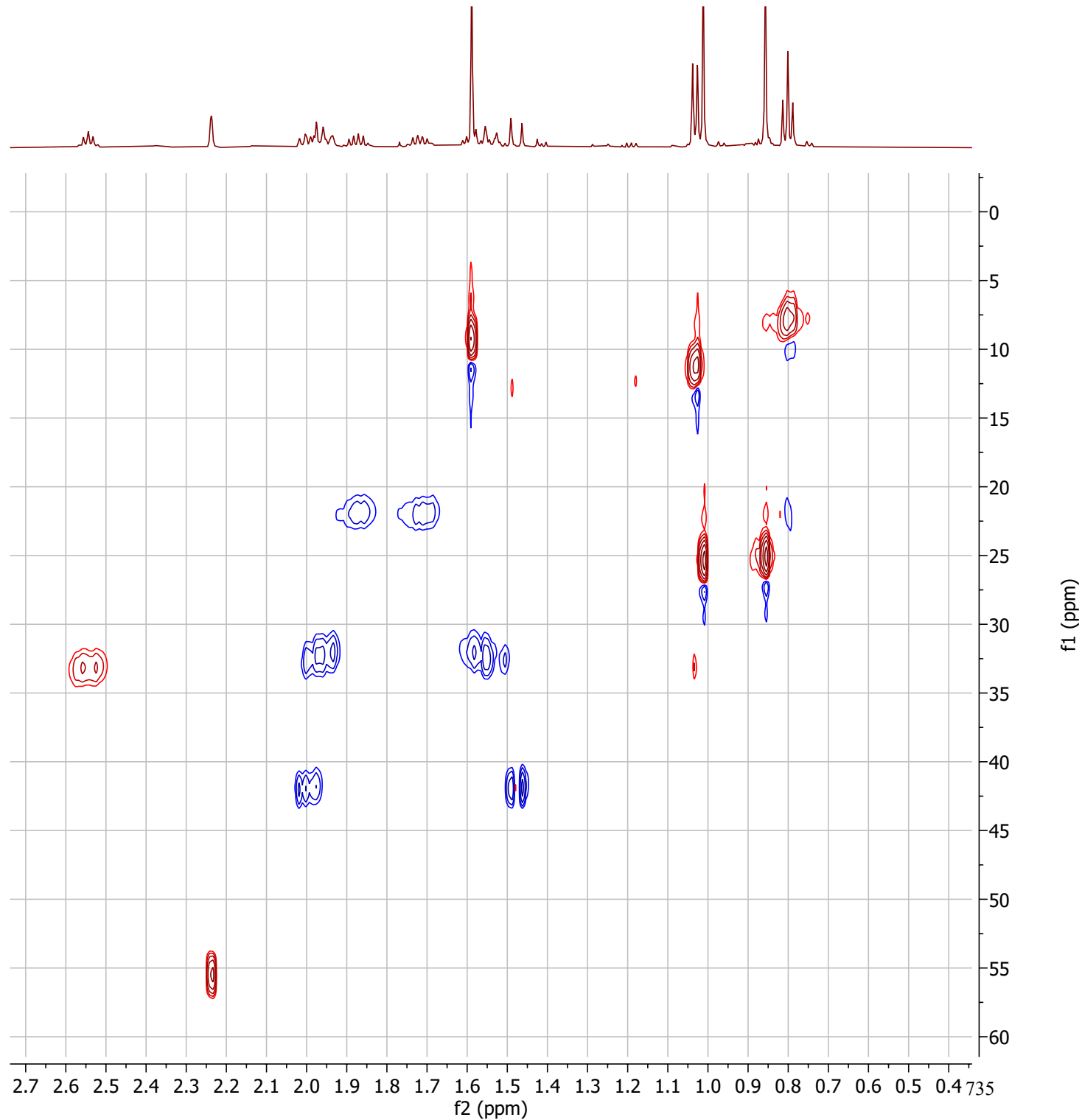


HSQC

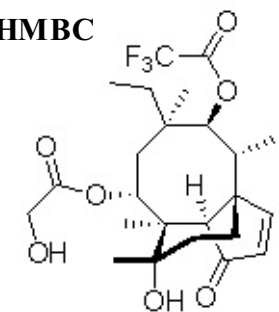


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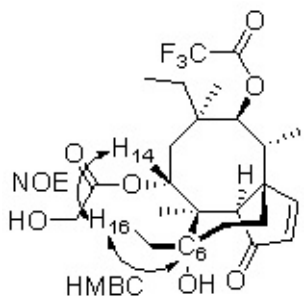
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcedetgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	6
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(5263.2, 36974.0)
15 Lowest Frequency	(-83.5, -1891.2)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 36.11)



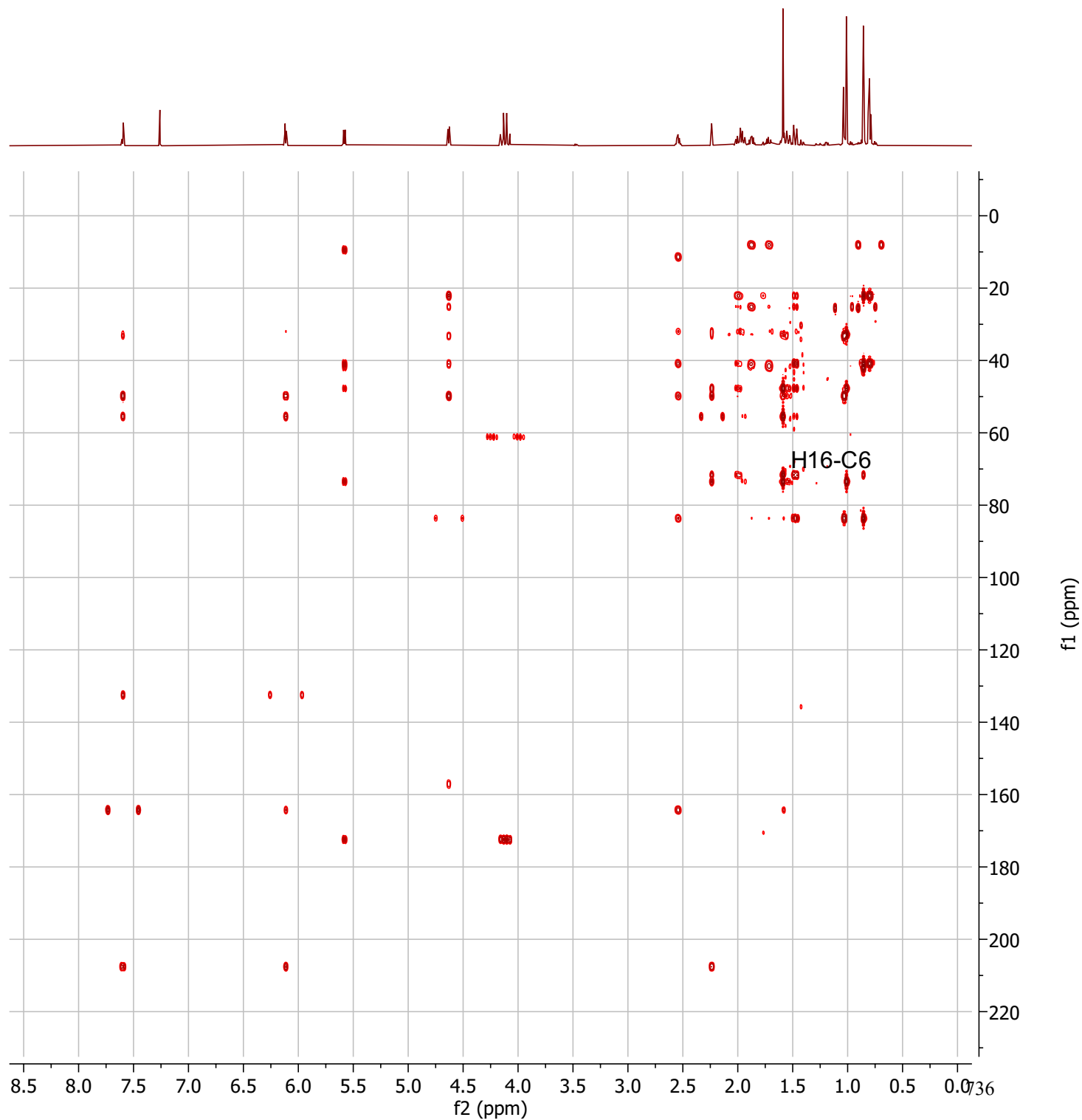
HMBC



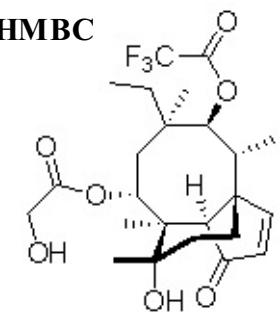
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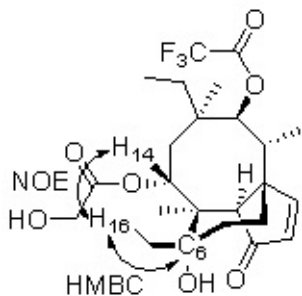
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(5263.2, 36974.9)
15 Lowest Frequency	(-83.9, -1891.7)
16 Nucleus	(1H, 13C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 36.11)



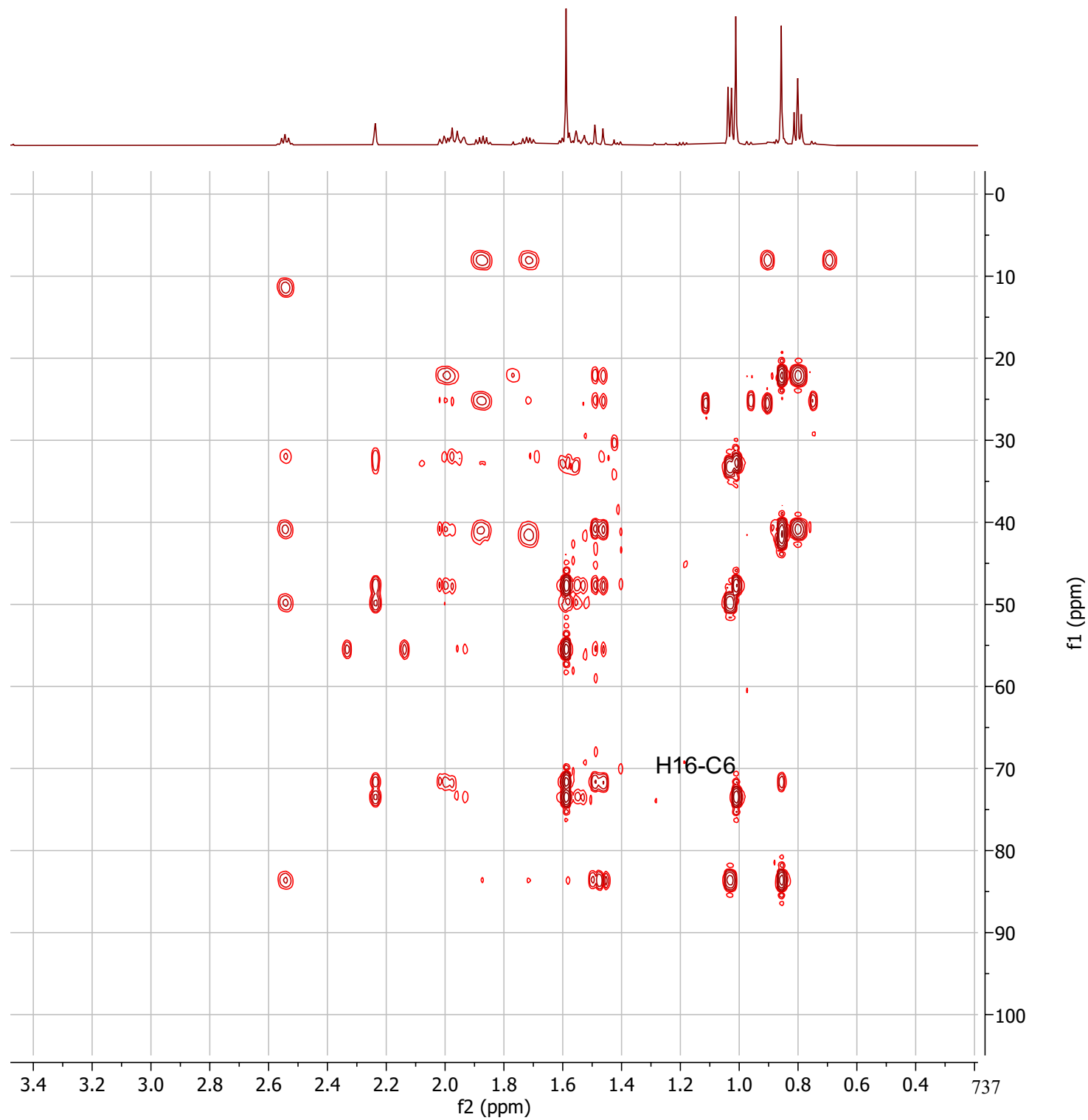
HMBC



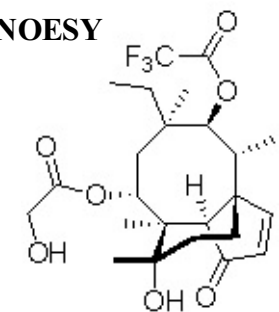
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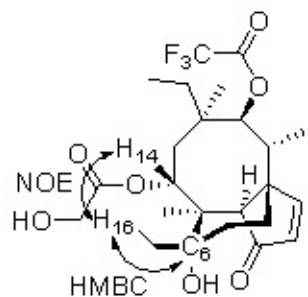
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(5263.2, 36974.9)
15 Lowest Frequency	(-83.9, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 36.11)



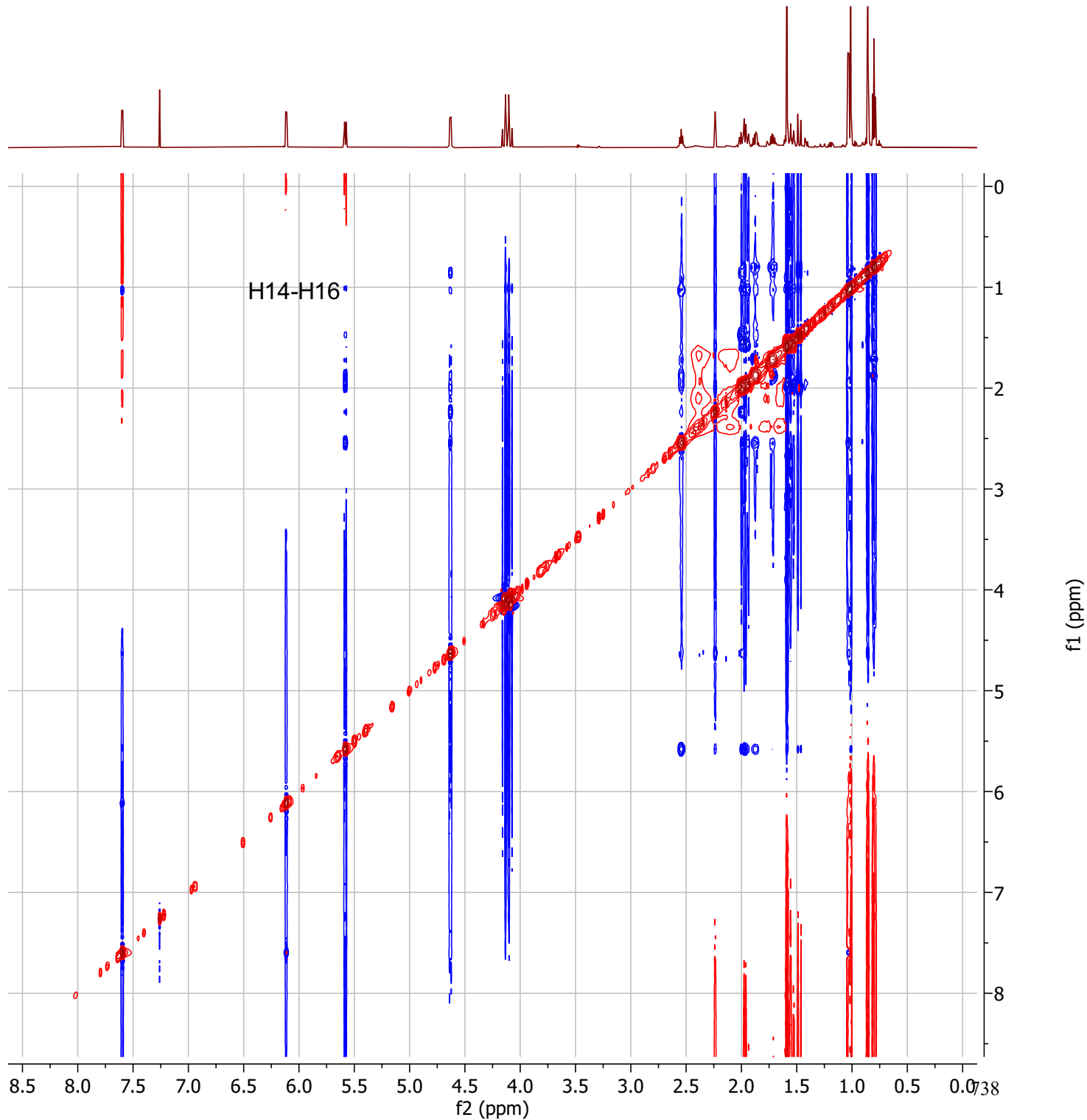
NOESY



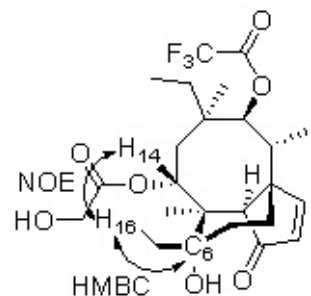
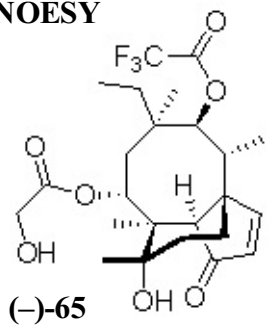
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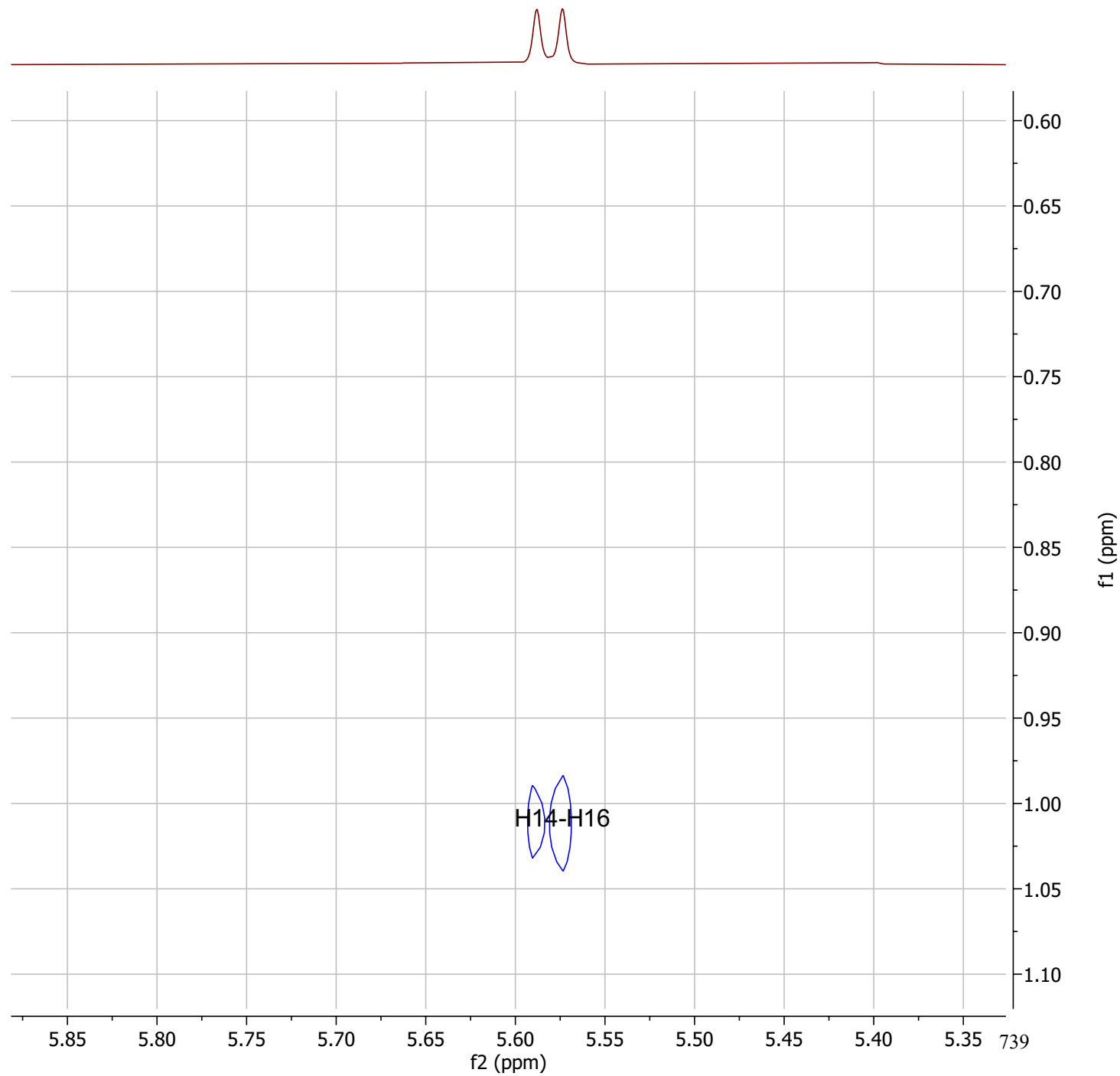
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.9816
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(5263.2, 5263.2)
15 Lowest Frequency	(-83.5, -83.5)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 5.14)



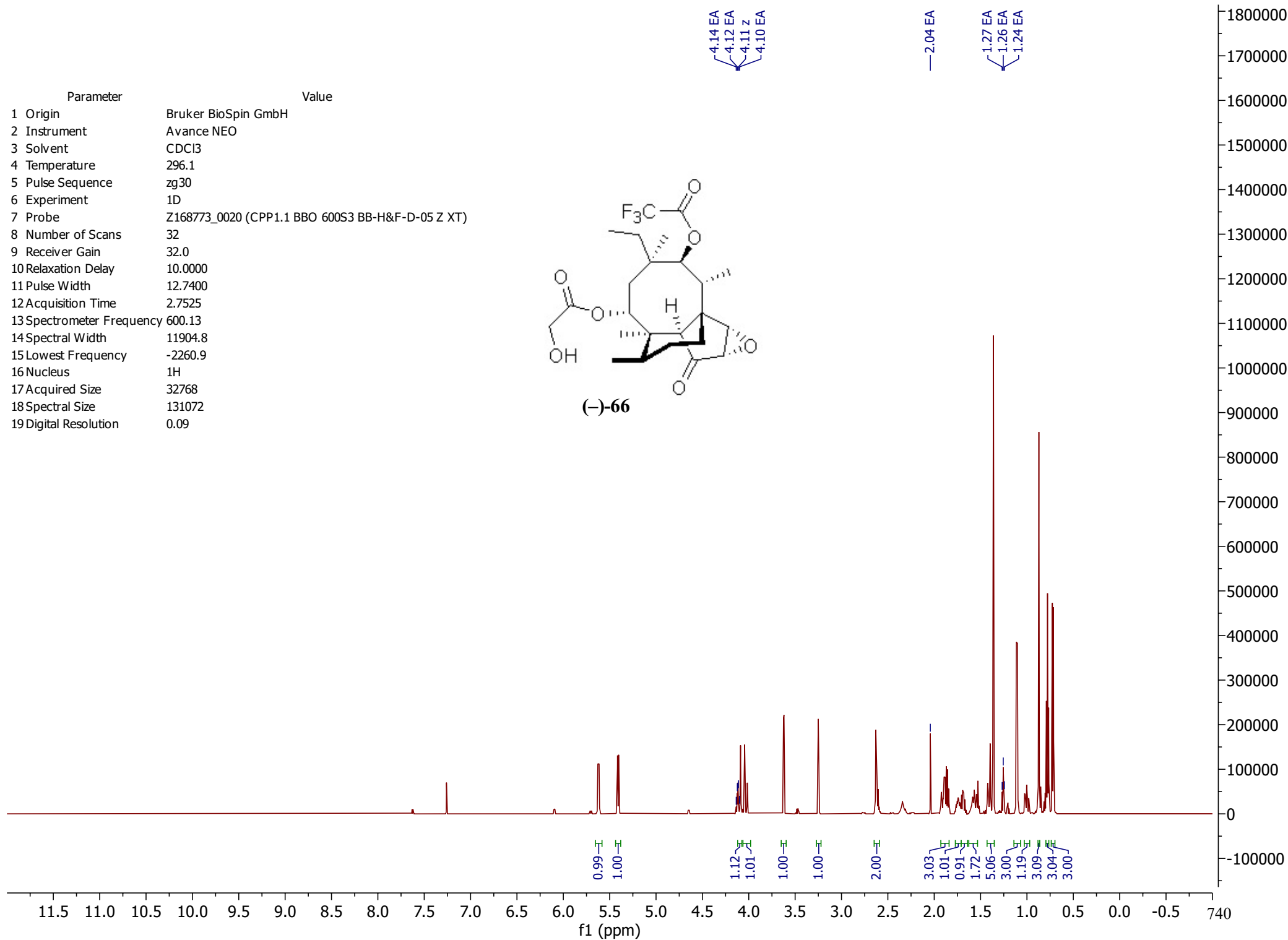
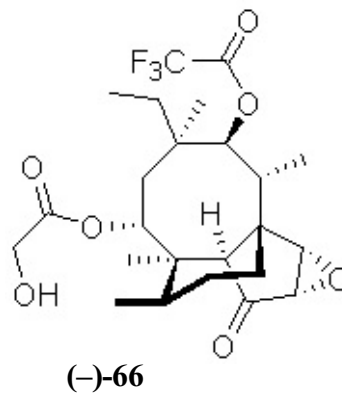
NOESY



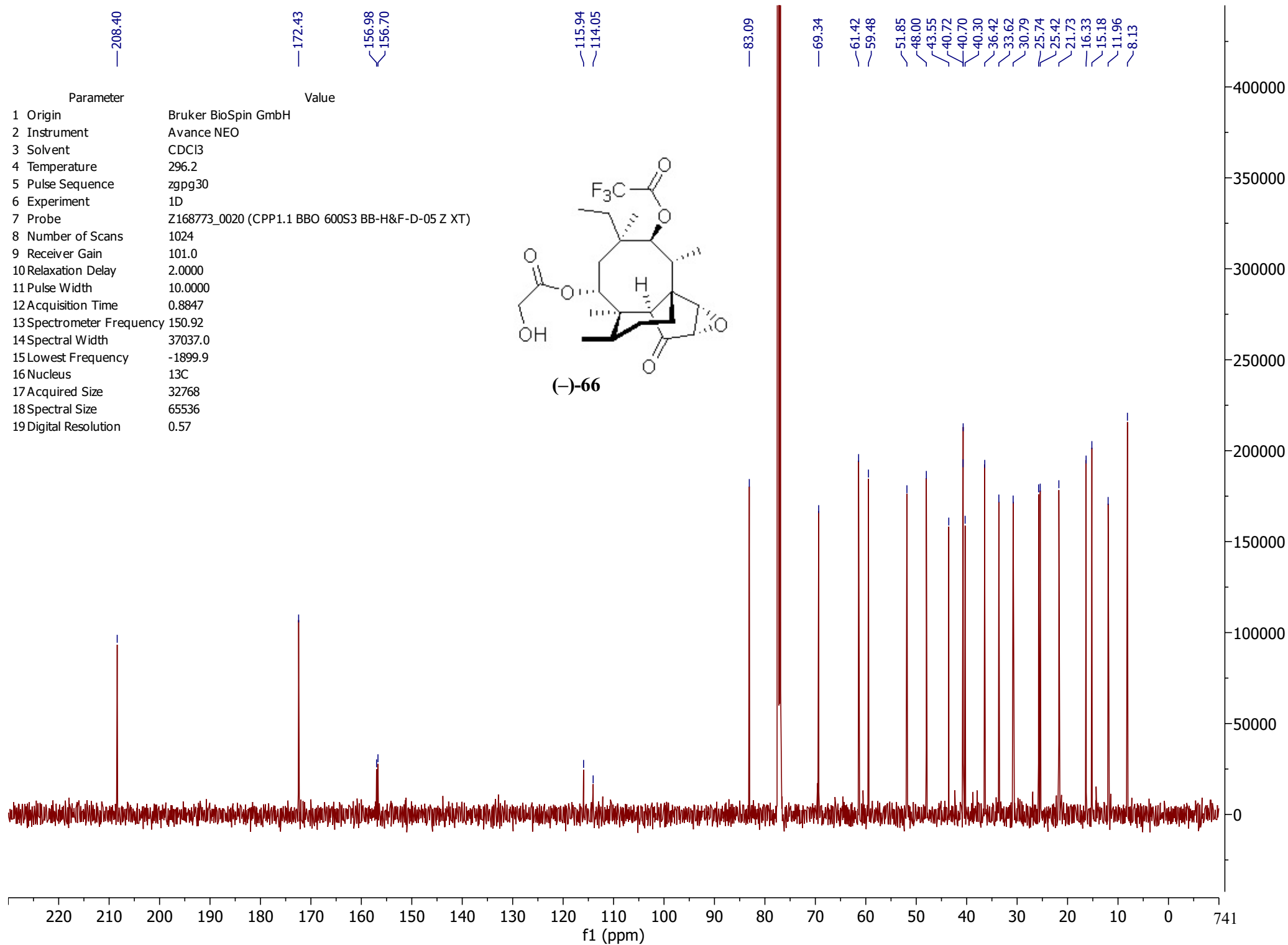
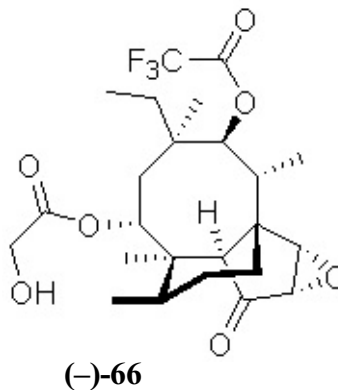
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.9816
11 Pulse Width	12.0000
12 Acquisition Time	0.1946
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(5263.2, 5263.2)
15 Lowest Frequency	(-83.5, -83.5)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.14, 5.14)



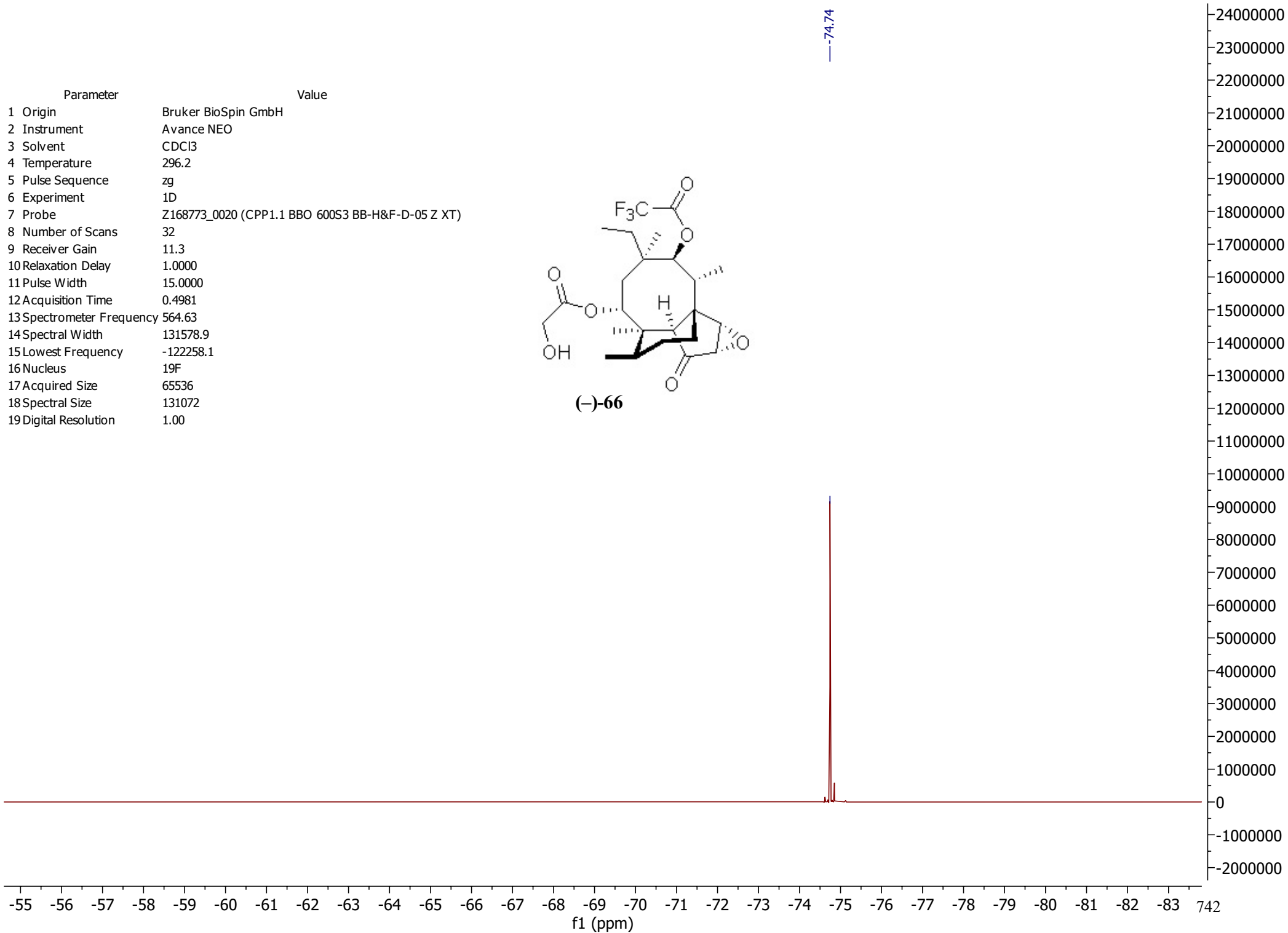
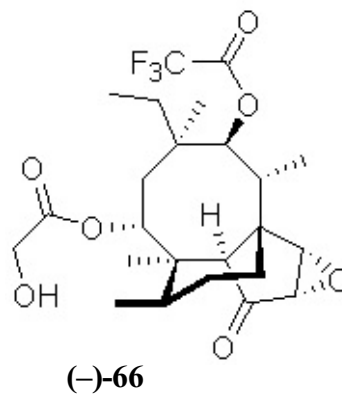
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.7400
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



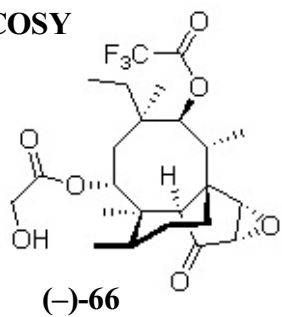
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	1024
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1899.9
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



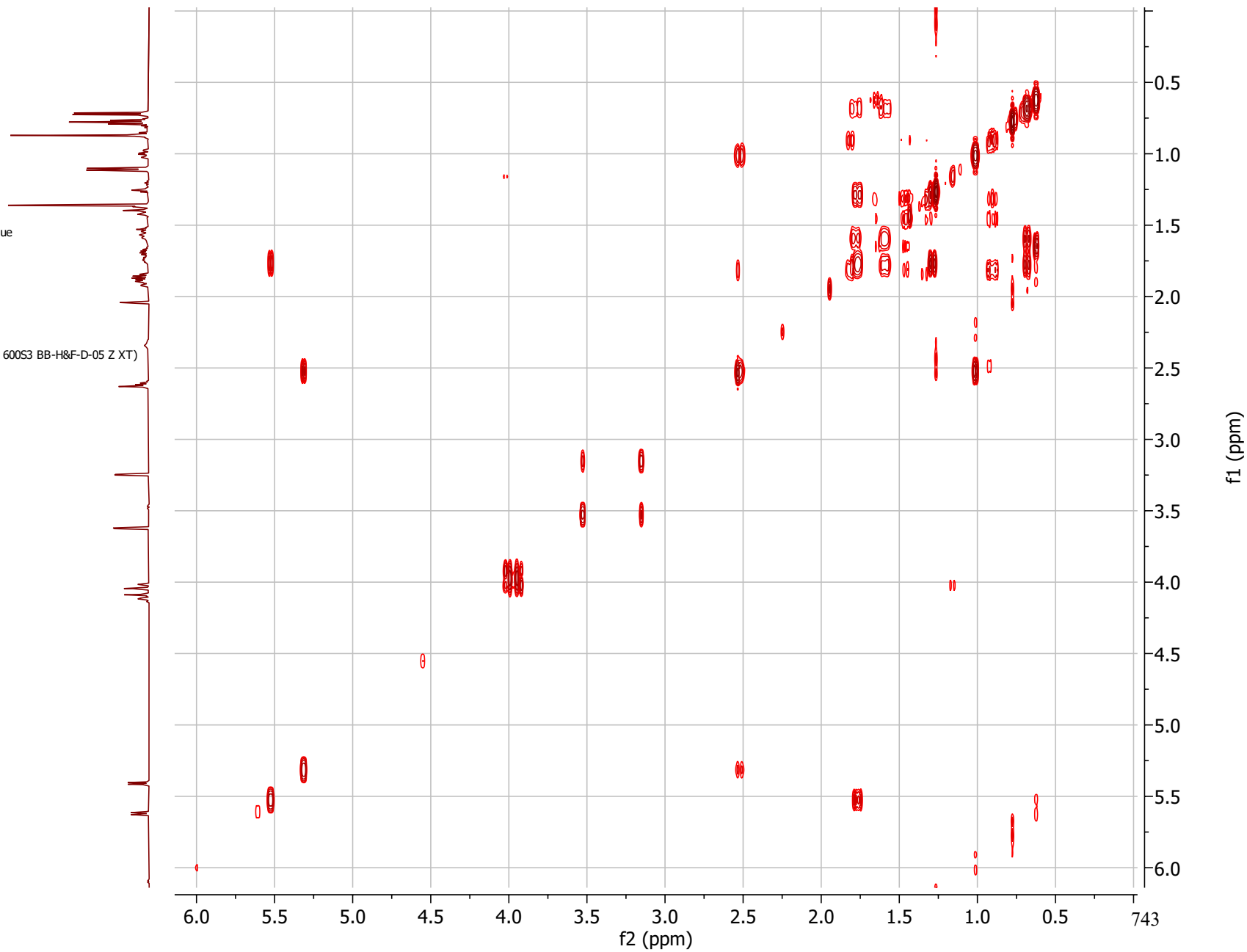
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	11.3
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.4981
13 Spectrometer Frequency	564.63
14 Spectral Width	131578.9
15 Lowest Frequency	-122258.1
16 Nucleus	¹⁹ F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	1.00



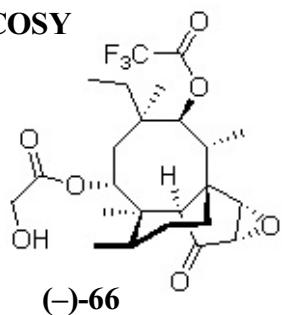
COSY



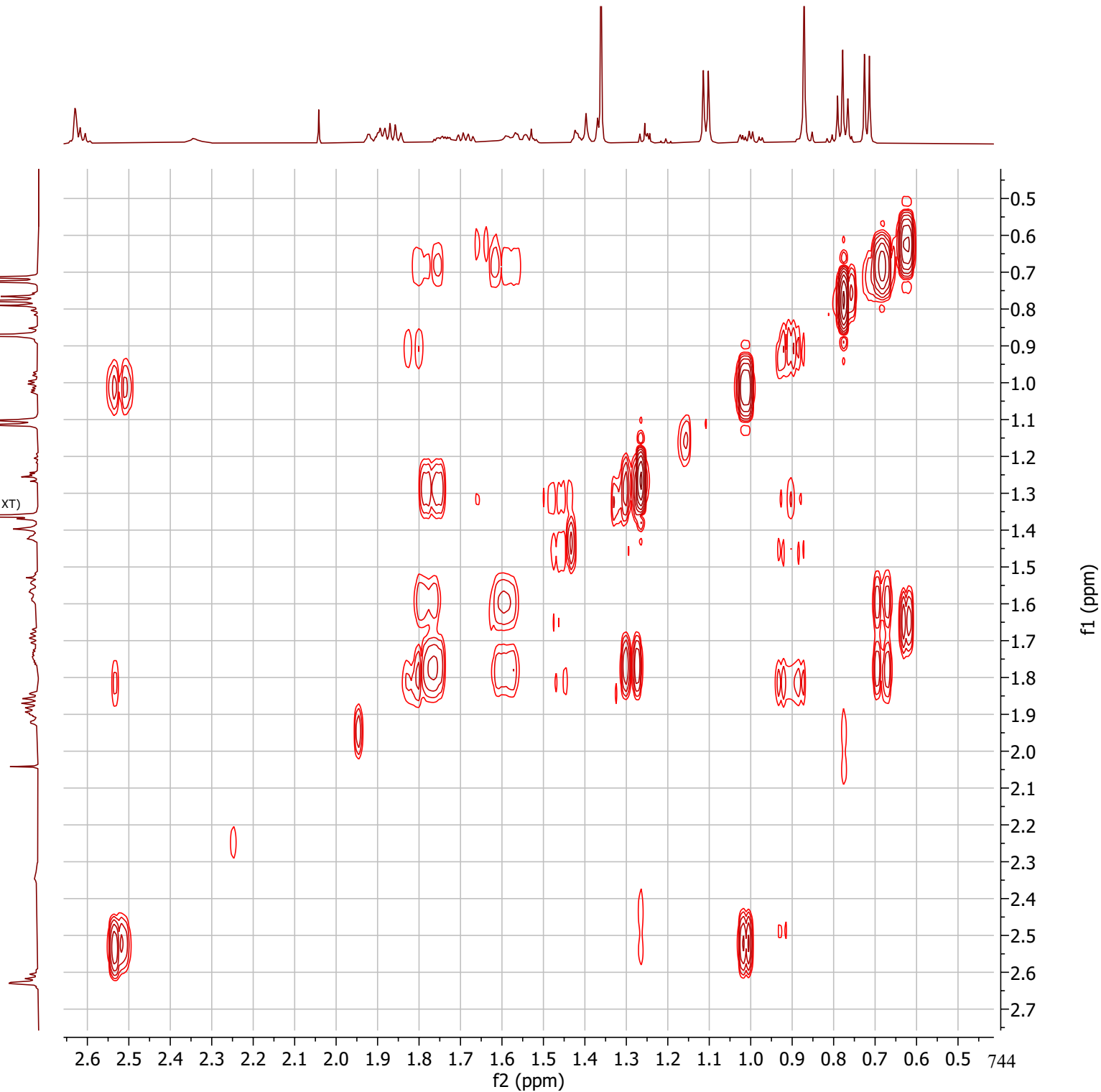
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.3587
11 Pulse Width	12.7400
12 Acquisition Time	0.2765
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3703.7, 3703.7)
15 Lowest Frequency	(-18.9, -18.9)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.62, 3.62)



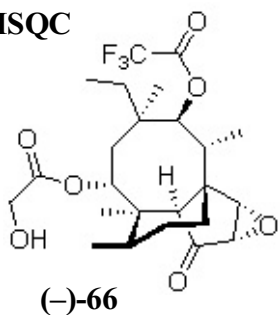
COSY



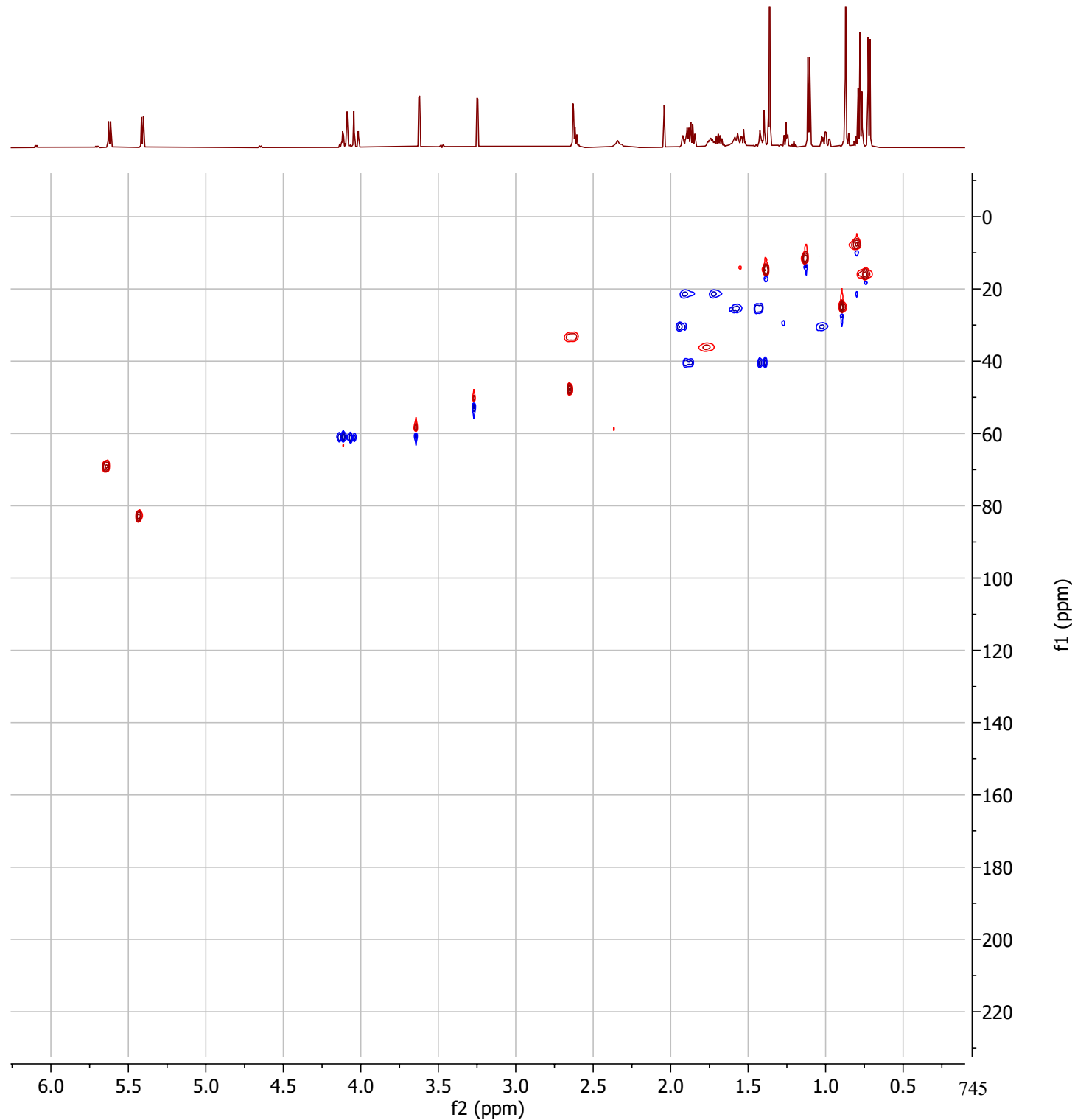
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.3587
11 Pulse Width	12.7400
12 Acquisition Time	0.2765
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3703.7, 3703.7)
15 Lowest Frequency	(-18.9, -18.9)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.62, 3.62)



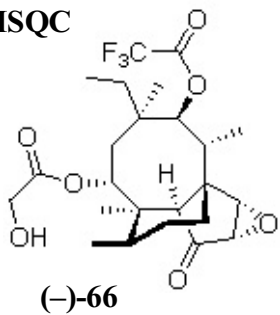
HSQC



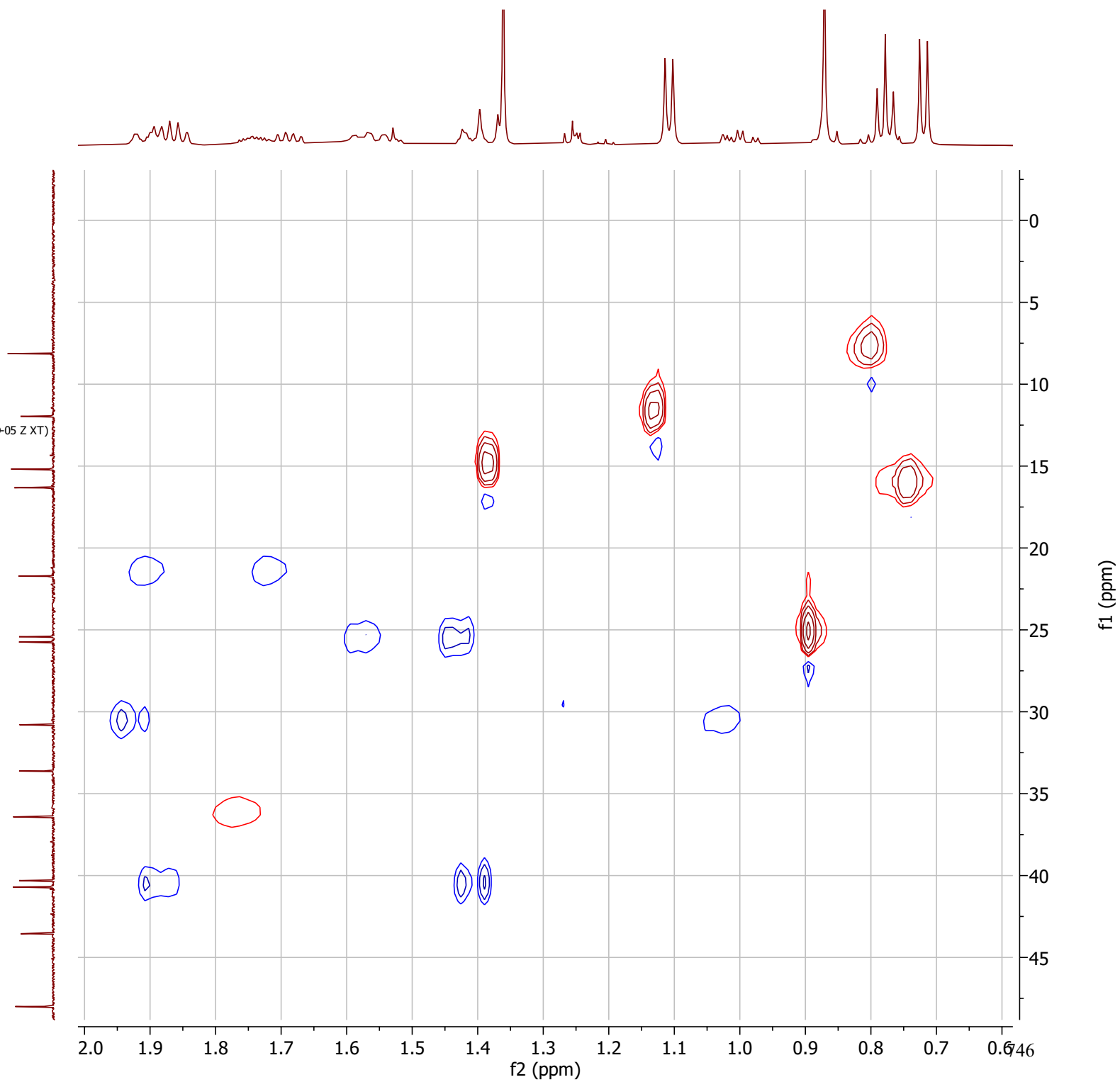
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hsqcetgpsi2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.7400
12 Acquisition Time	0.1382
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3703.7, 36974.0)
15 Lowest Frequency	(52.7, -1887.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.23, 72.21)



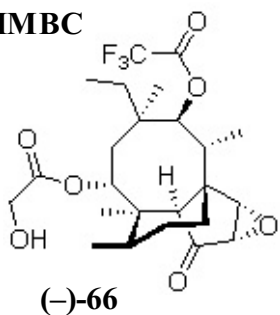
HSQC



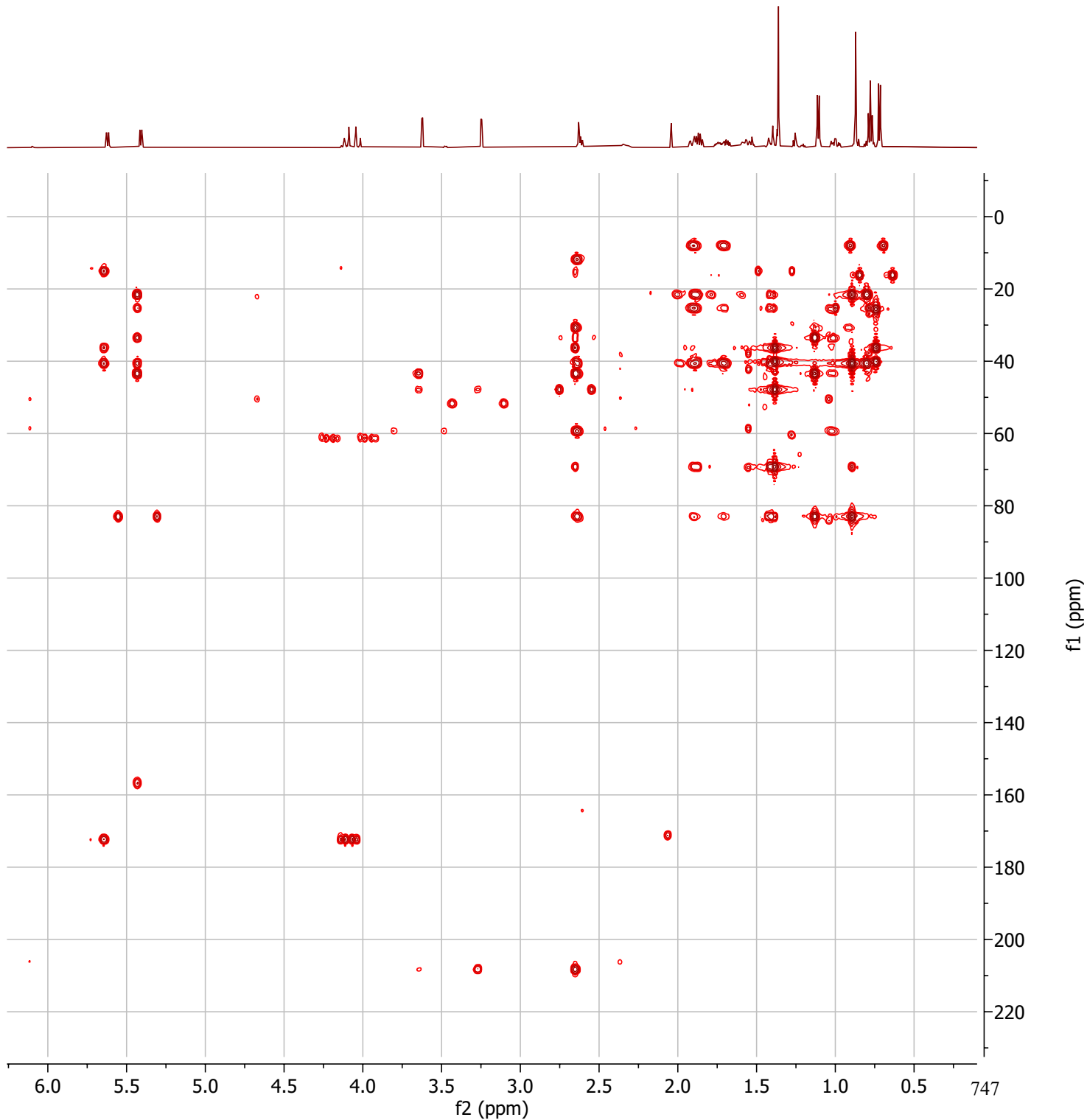
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	hsqcetdgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.7400
12 Acquisition Time	0.1382
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3703.7, 36974.0)
15 Lowest Frequency	(52.7, -1887.7)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.23, 72.21)



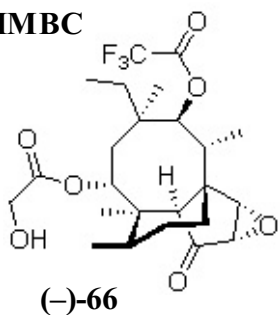
HMBC



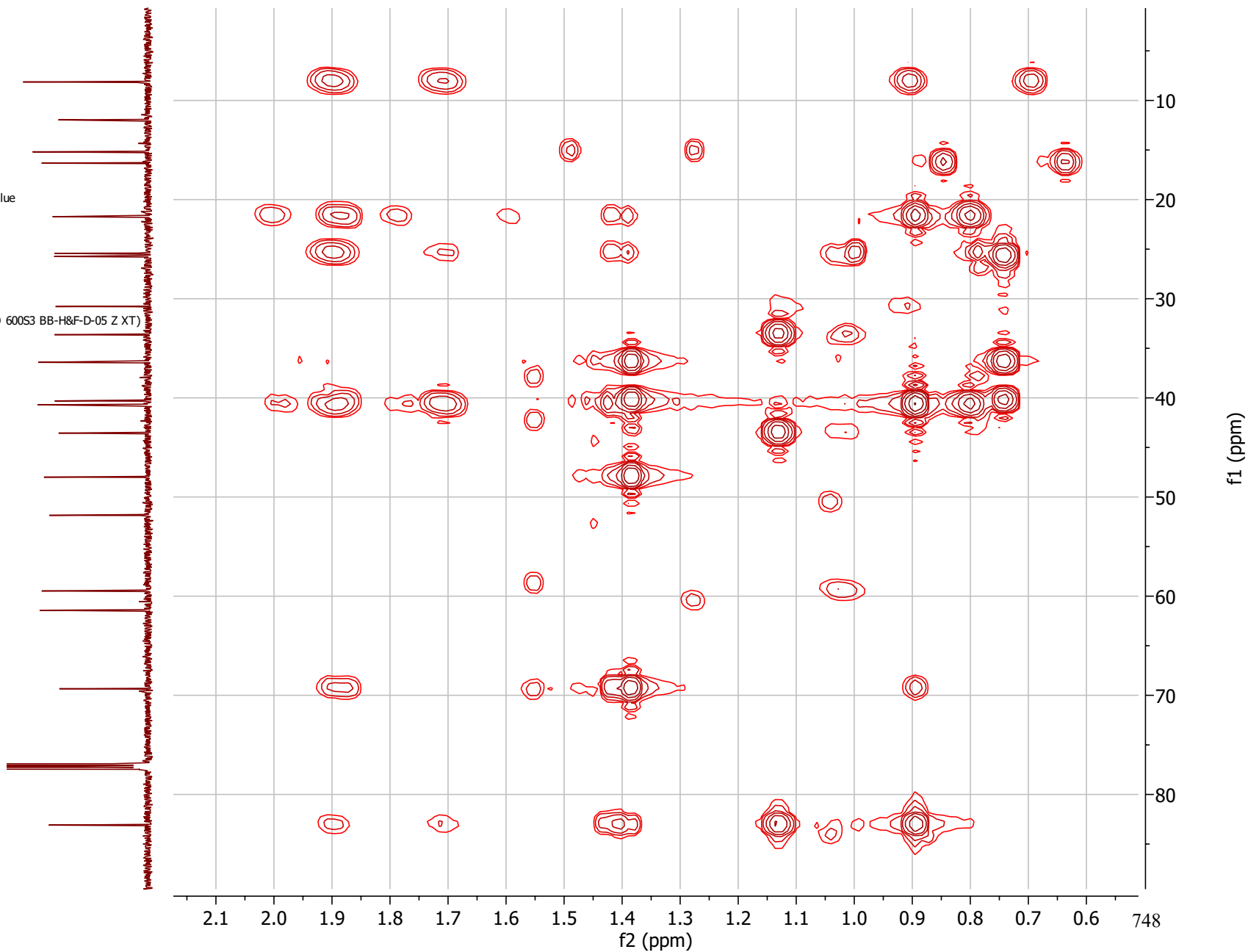
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.7400
12 Acquisition Time	0.1382
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3703.7, 36974.9)
15 Lowest Frequency	(52.7, -1888.1)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.23, 72.22)



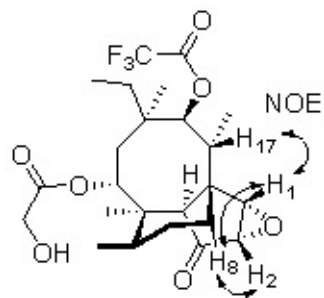
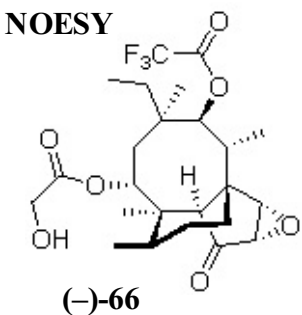
HMBC



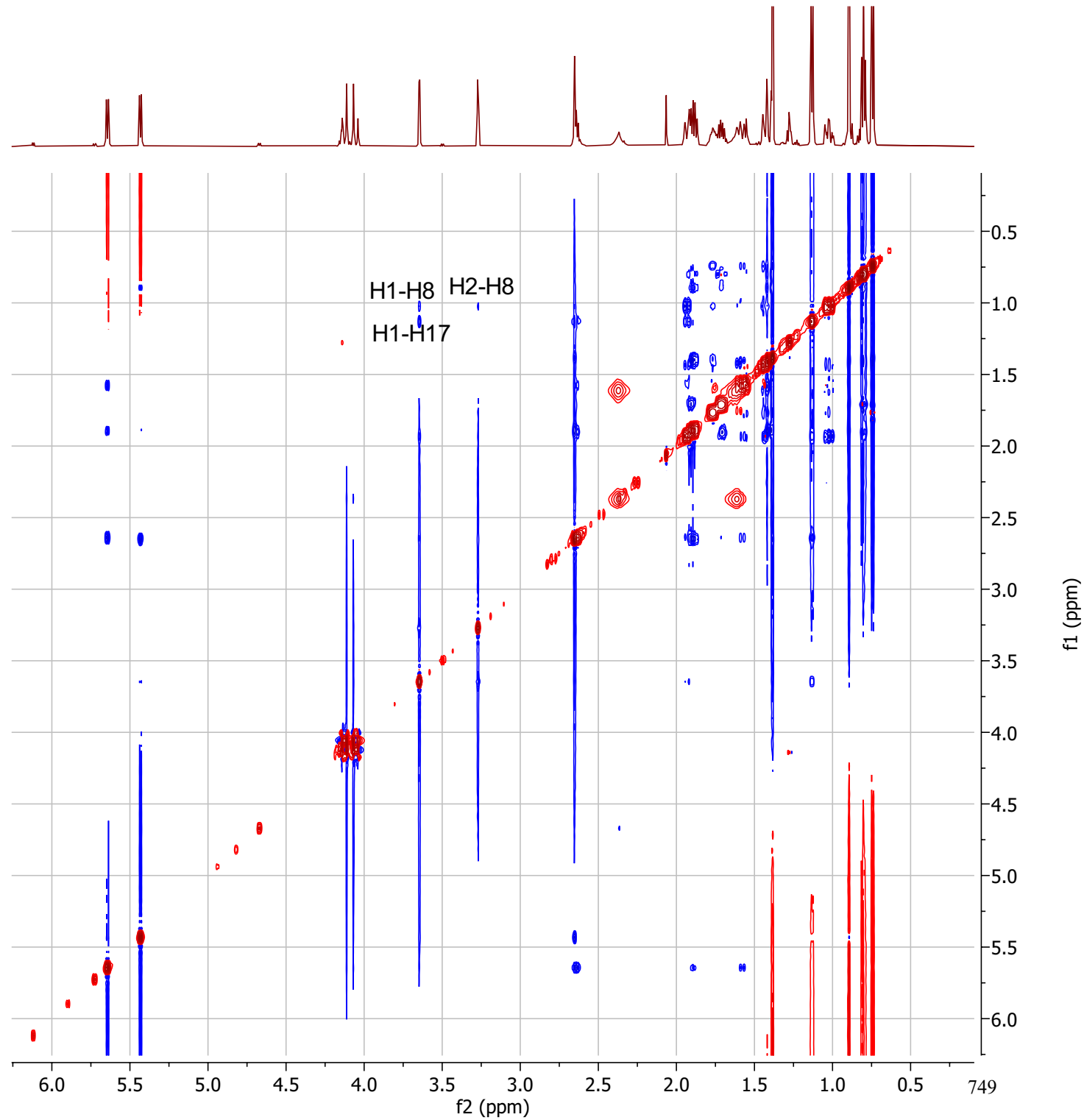
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.7400
12 Acquisition Time	0.1382
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3703.7, 36974.9)
15 Lowest Frequency	(52.7, -1888.1)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.23, 72.22)



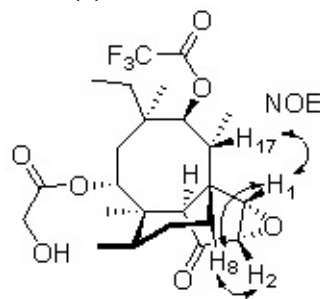
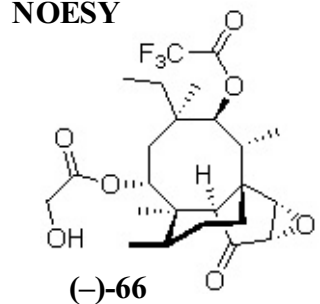
NOESY



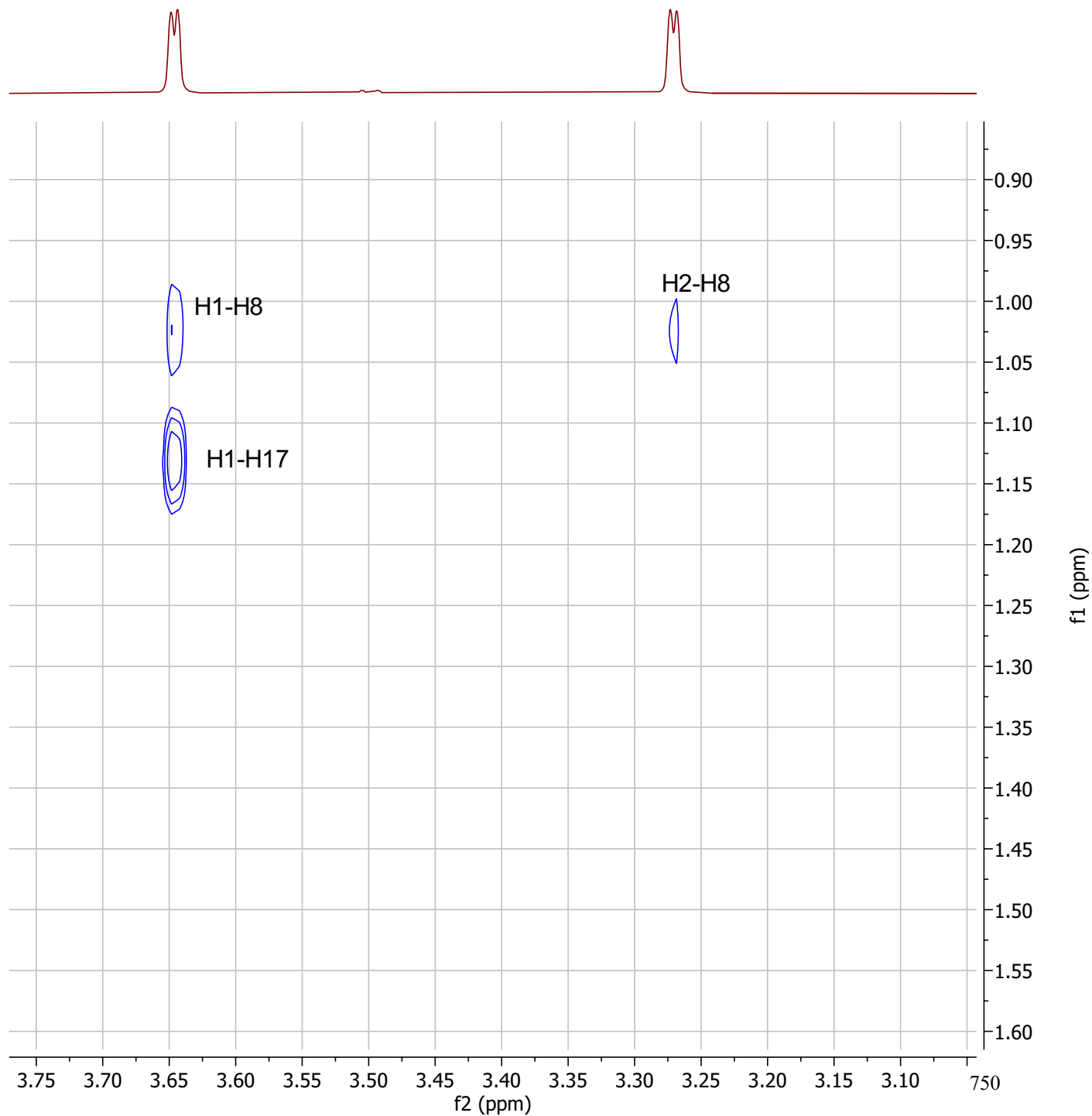
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.9017
11 Pulse Width	12.7400
12 Acquisition Time	0.2765
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3703.7, 3703.7)
15 Lowest Frequency	(51.8, 51.8)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.62, 3.62)



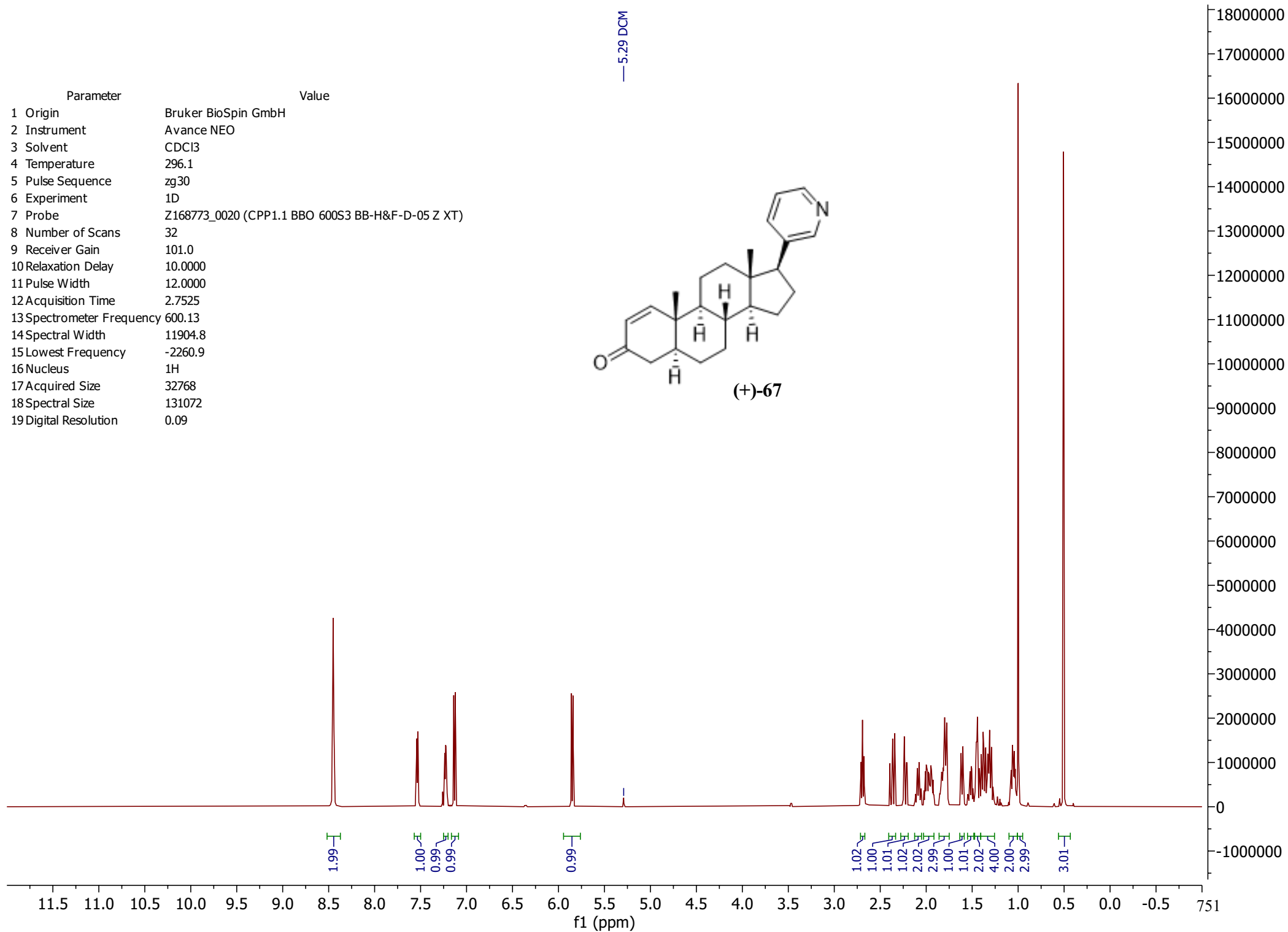
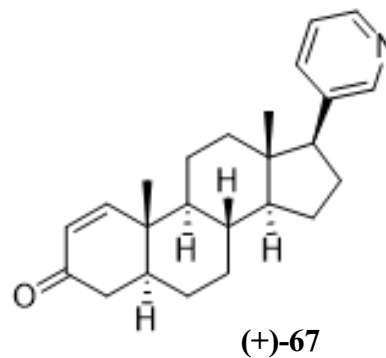
NOESY



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.9017
11 Pulse Width	12.7400
12 Acquisition Time	0.2765
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(3703.7, 3703.7)
15 Lowest Frequency	(51.8, 51.8)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.62, 3.62)

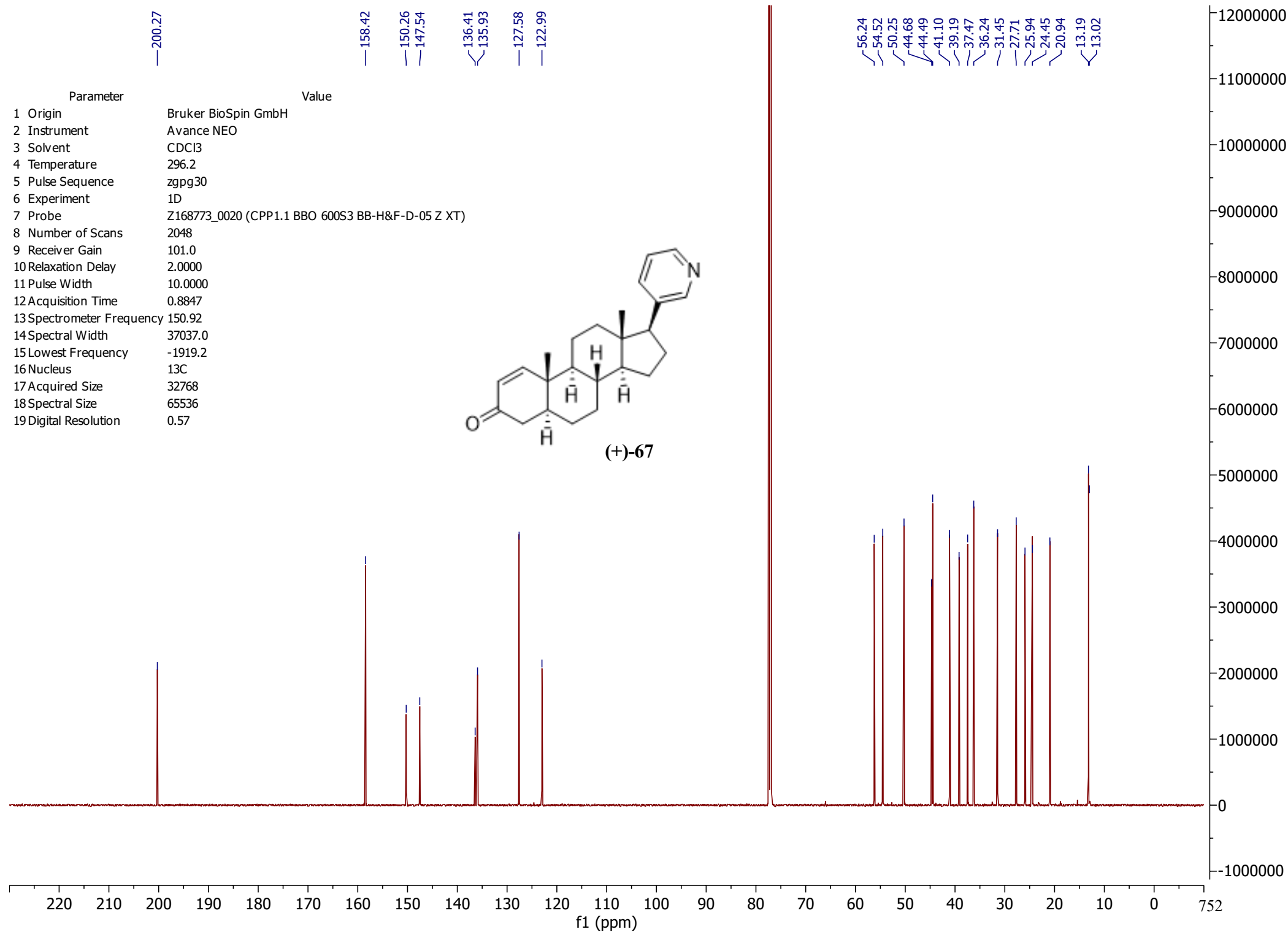
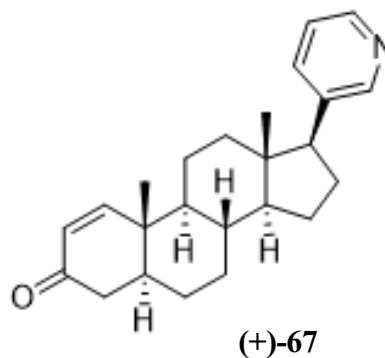


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

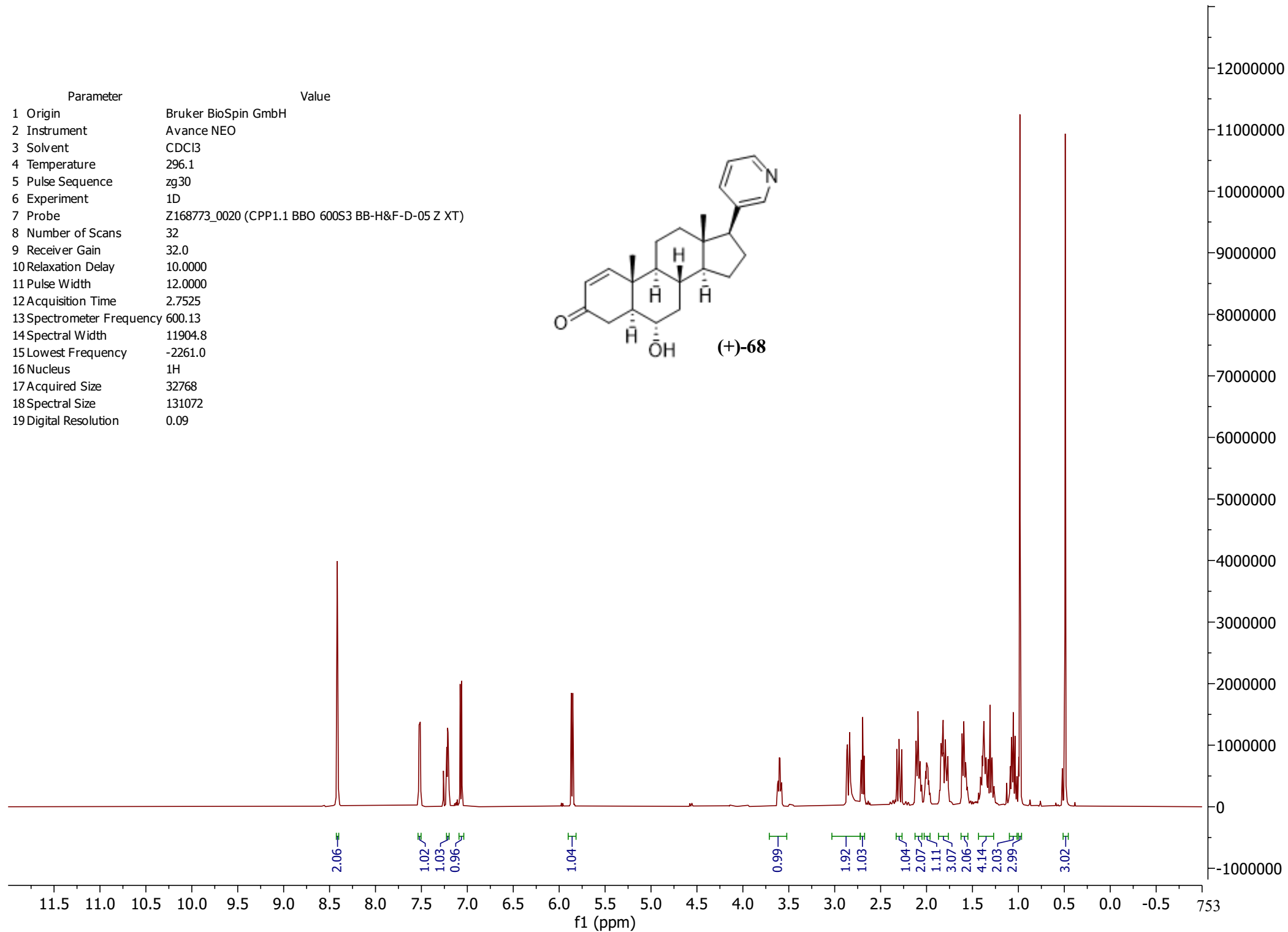
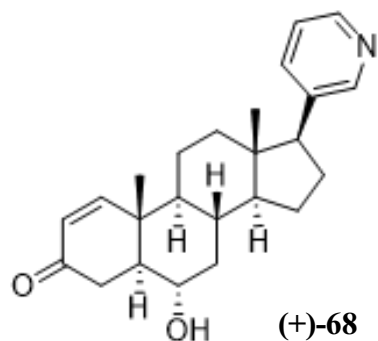


Parameter
1 Origin
2 Instrument
3 Solvent
4 Temperature
5 Pulse Sequence
6 Experiment
7 Probe
8 Number of Scans
9 Receiver Gain
10 Relaxation Delay
11 Pulse Width
12 Acquisition Time
13 Spectrometer Frequency
14 Spectral Width
15 Lowest Frequency
16 Nucleus
17 Acquired Size
18 Spectral Size
19 Digital Resolution

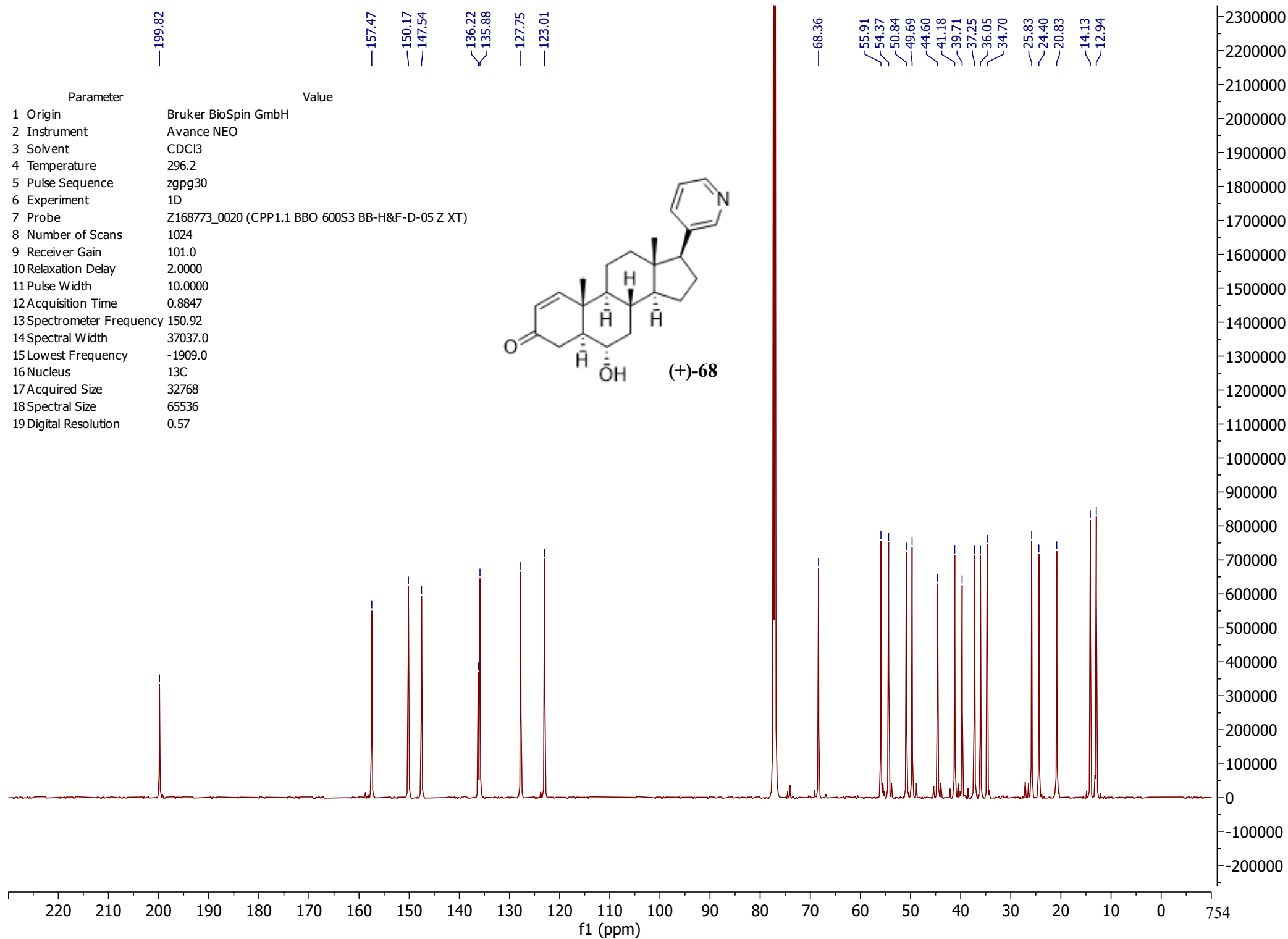
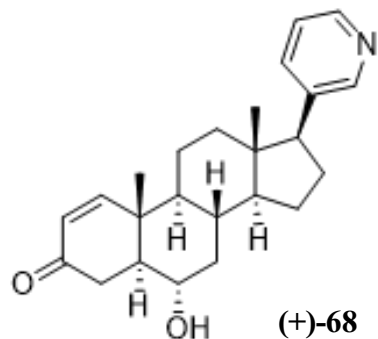
Value
Bruker BioSpin GmbH
Avance NEO
CDCl3
296.2
zgpg30
1D
Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
2048
101.0
2.0000
10.0000
0.8847
150.92
37037.0
-1919.2
13C
32768
65536
0.57



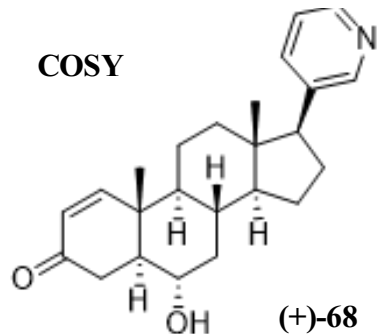
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



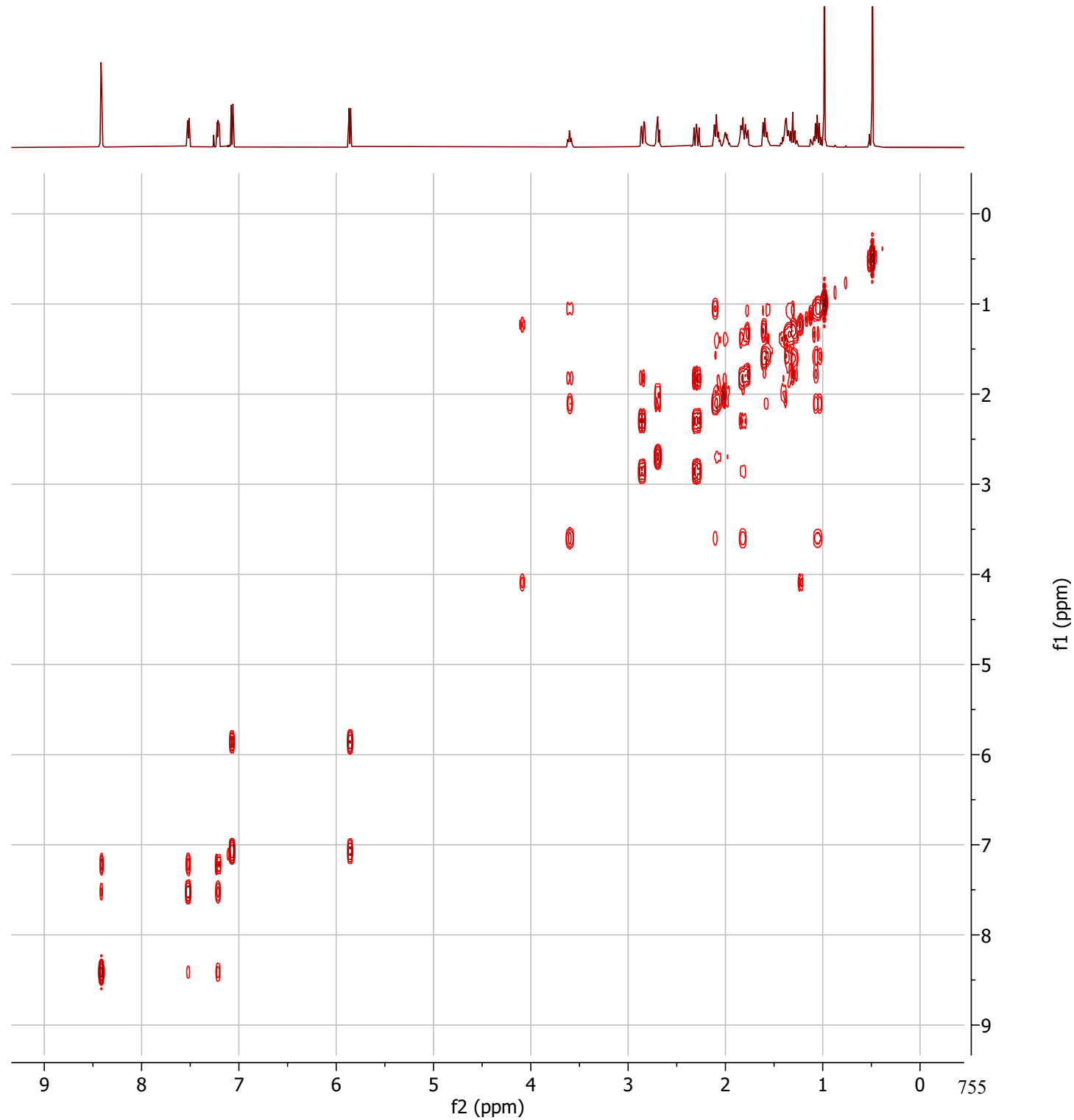
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	1024
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1909.0
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



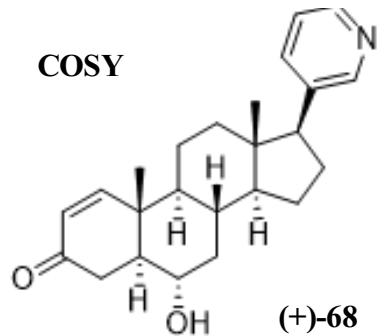
COSY



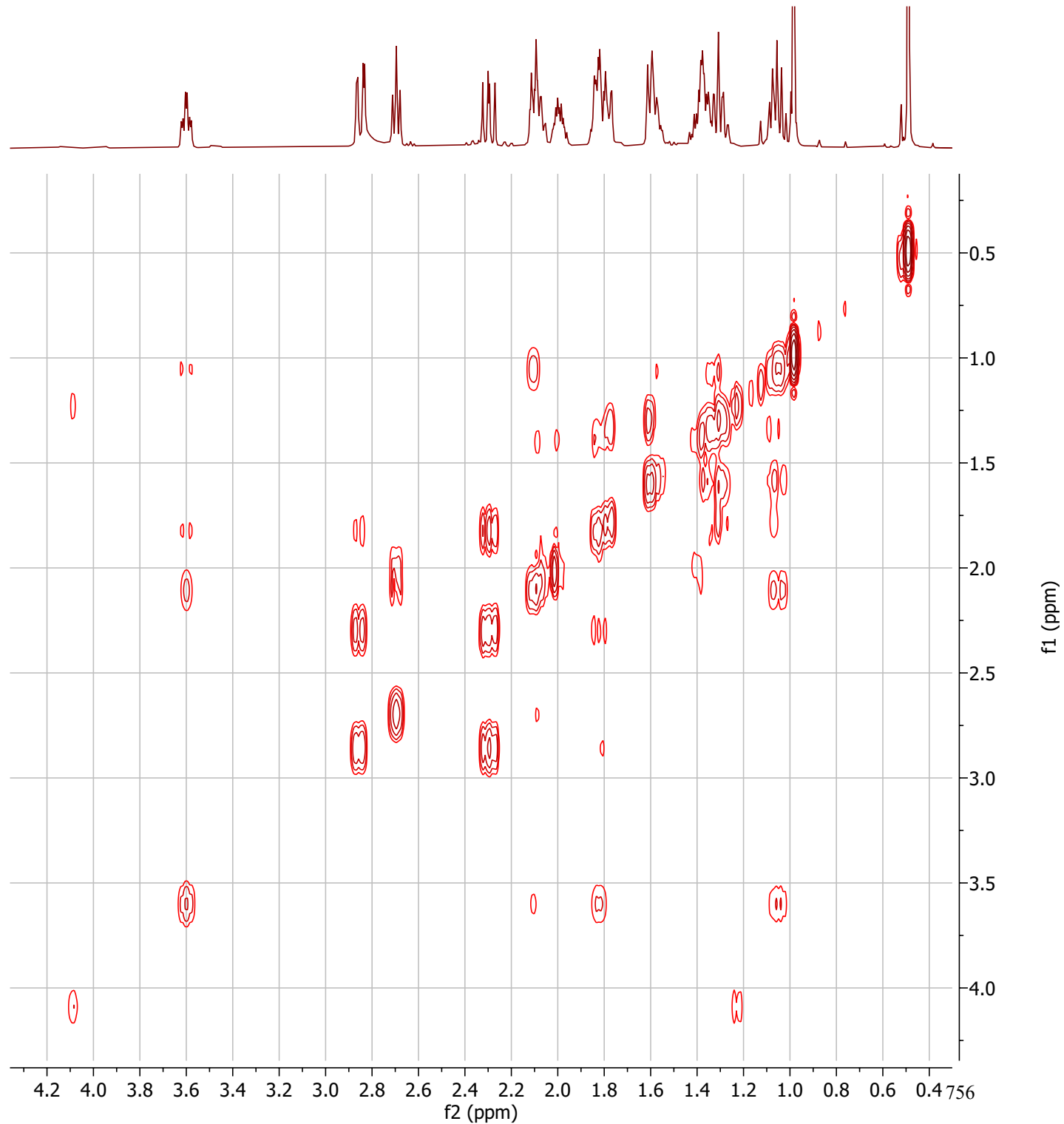
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.4611
11 Pulse Width	12.0000
12 Acquisition Time	0.1741
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(5882.4, 5882.4)
15 Lowest Frequency	(-278.2, -278.0)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.74, 5.74)



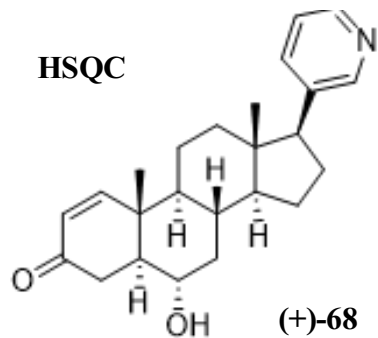
COSY



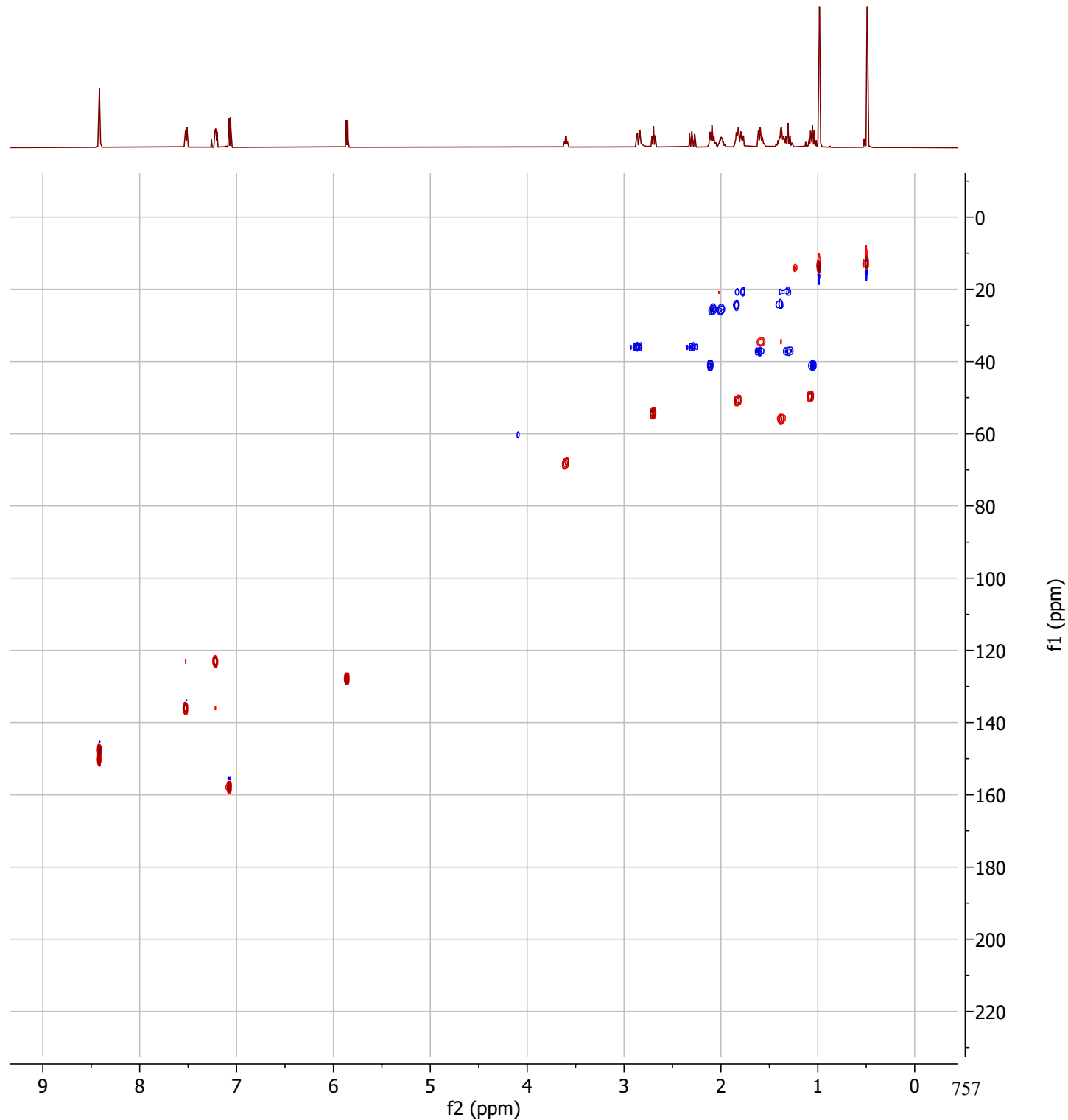
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.4611
11 Pulse Width	12.0000
12 Acquisition Time	0.1741
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(5882.4, 5882.4)
15 Lowest Frequency	(-278.2, -278.0)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.74, 5.74)



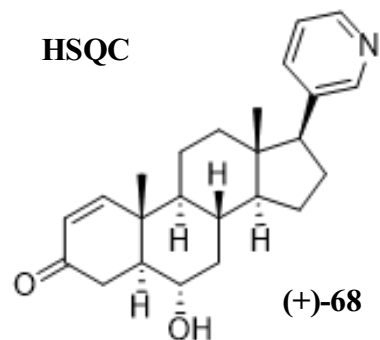
HSQC



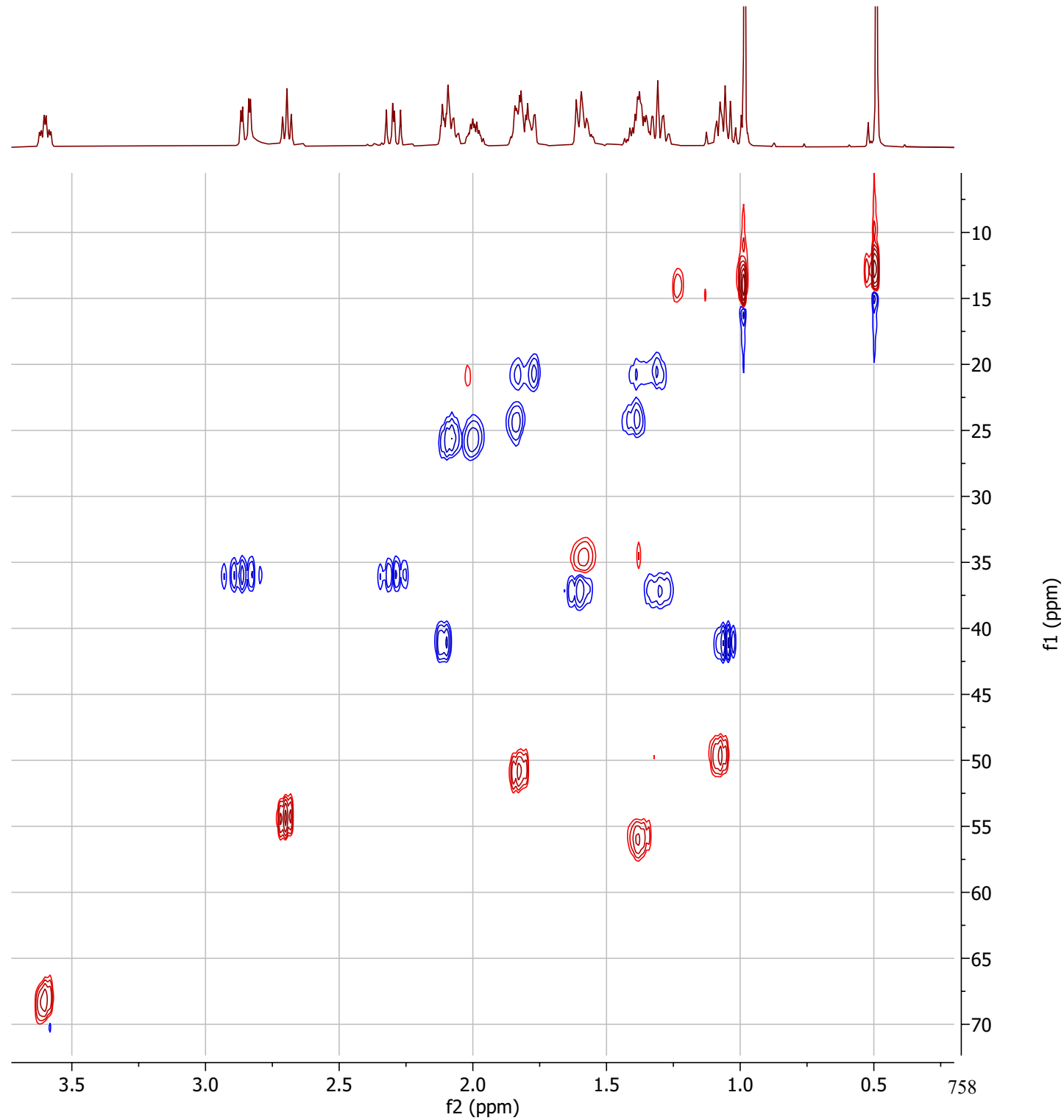
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpcisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1741
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(5882.4, 36974.0)
15 Lowest Frequency	(-275.0, -1872.9)
16 Nucleus	(1H, 13C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.74, 36.11)



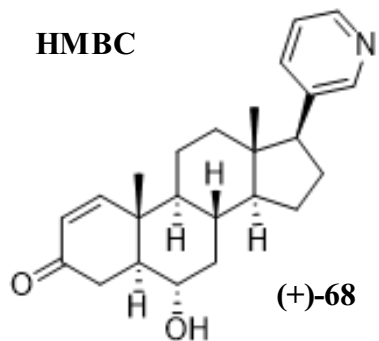
HSQC



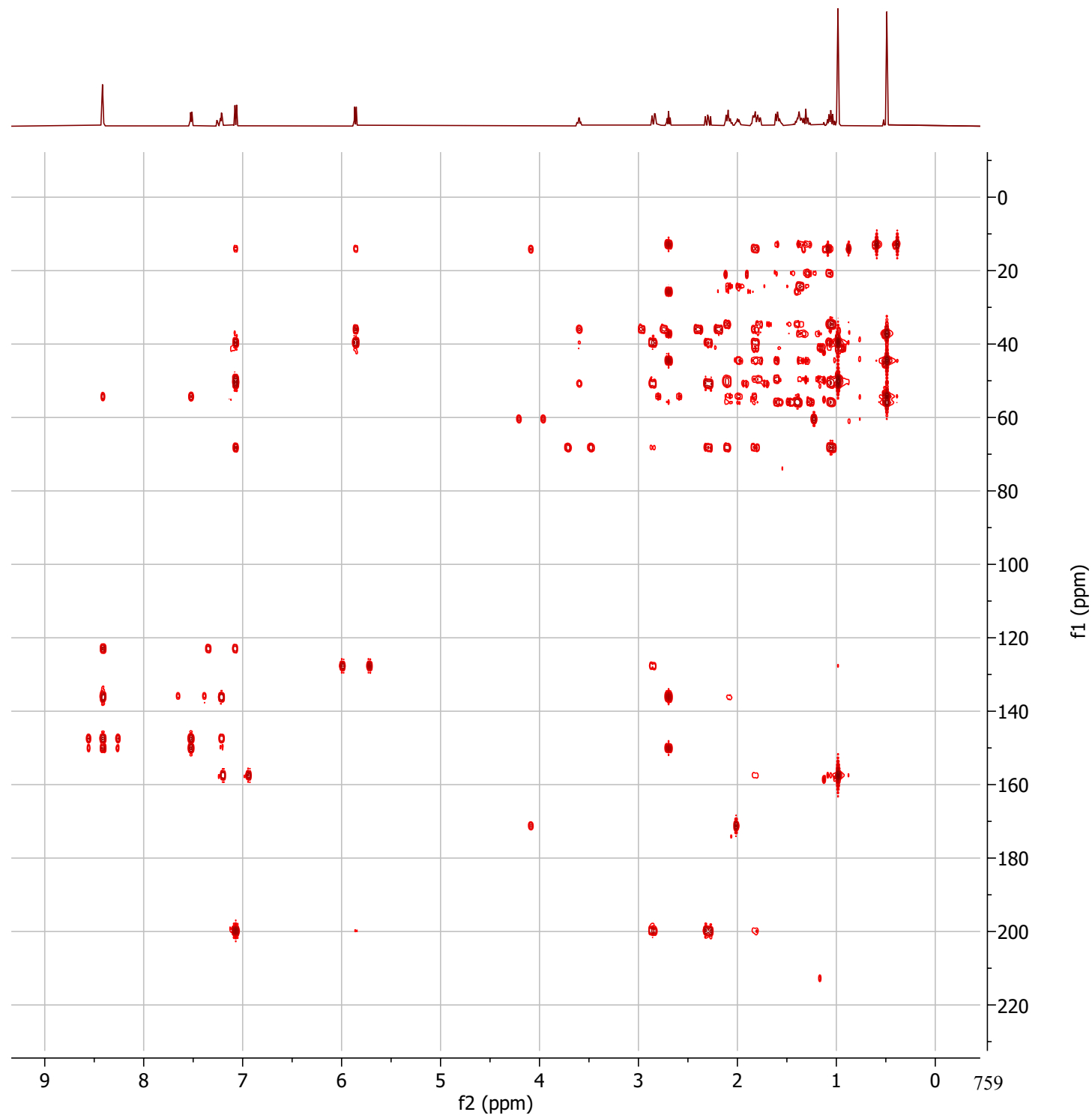
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpsi2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1741
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(5882.4, 36974.0)
15 Lowest Frequency	(-275.0, -1872.9)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.74, 36.11)



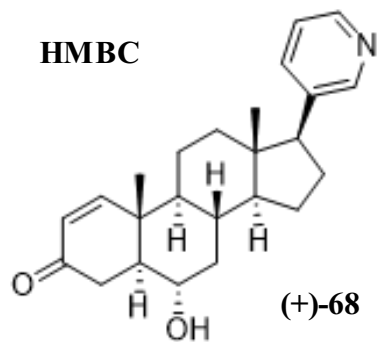
HMBC



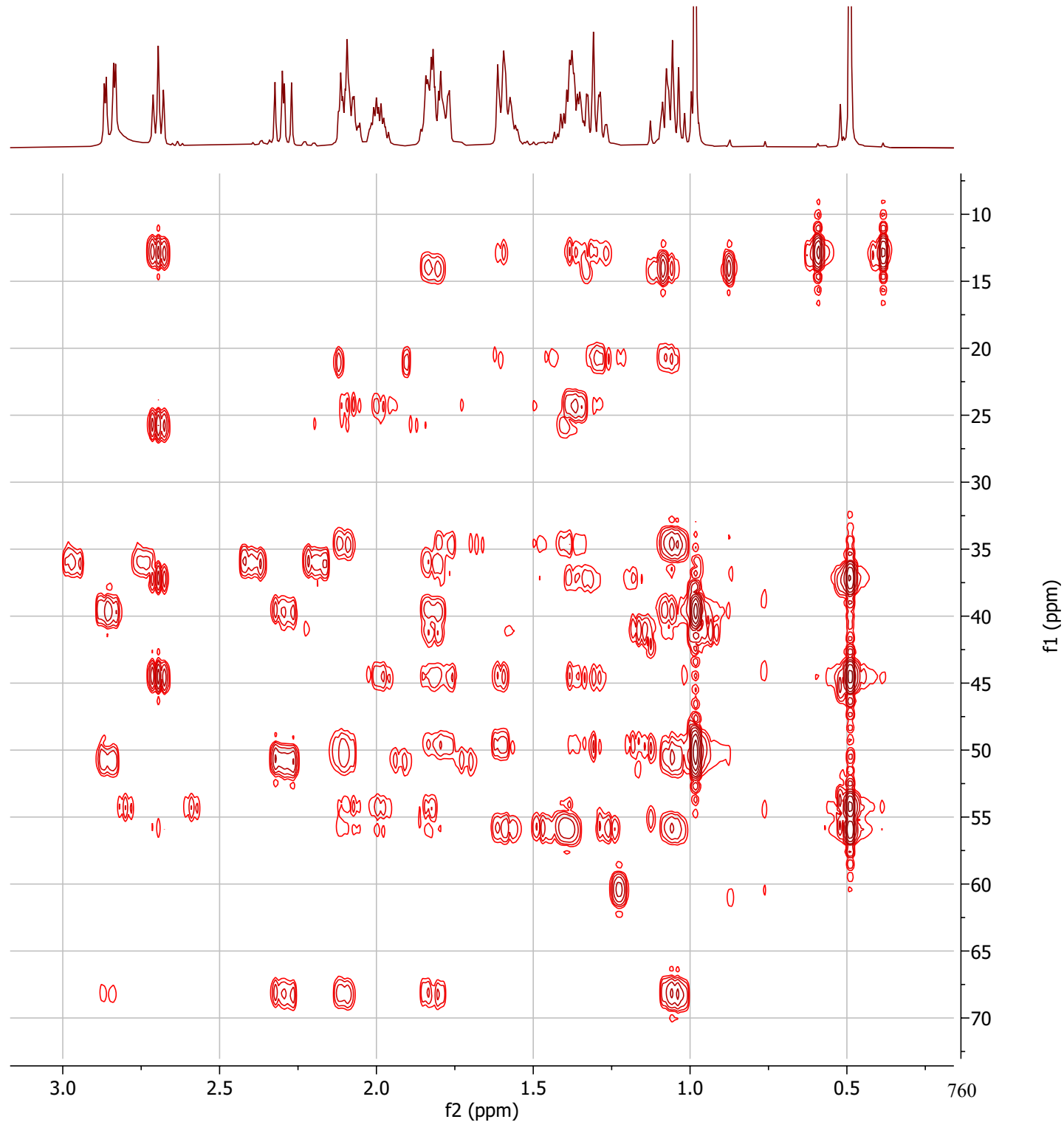
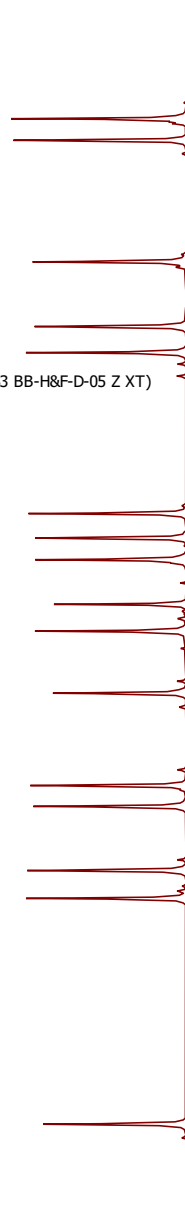
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCI3
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1741
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(5882.4, 36974.9)
15 Lowest Frequency	(-278.2, -1887.9)
16 Nucleus	(1H, 13C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.74, 36.11)



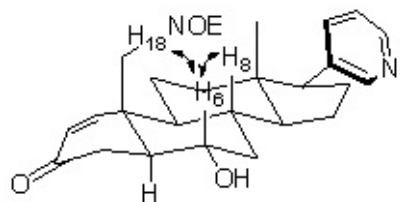
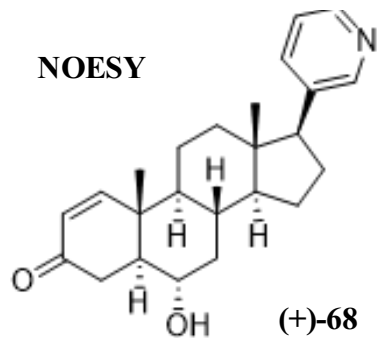
HMBC



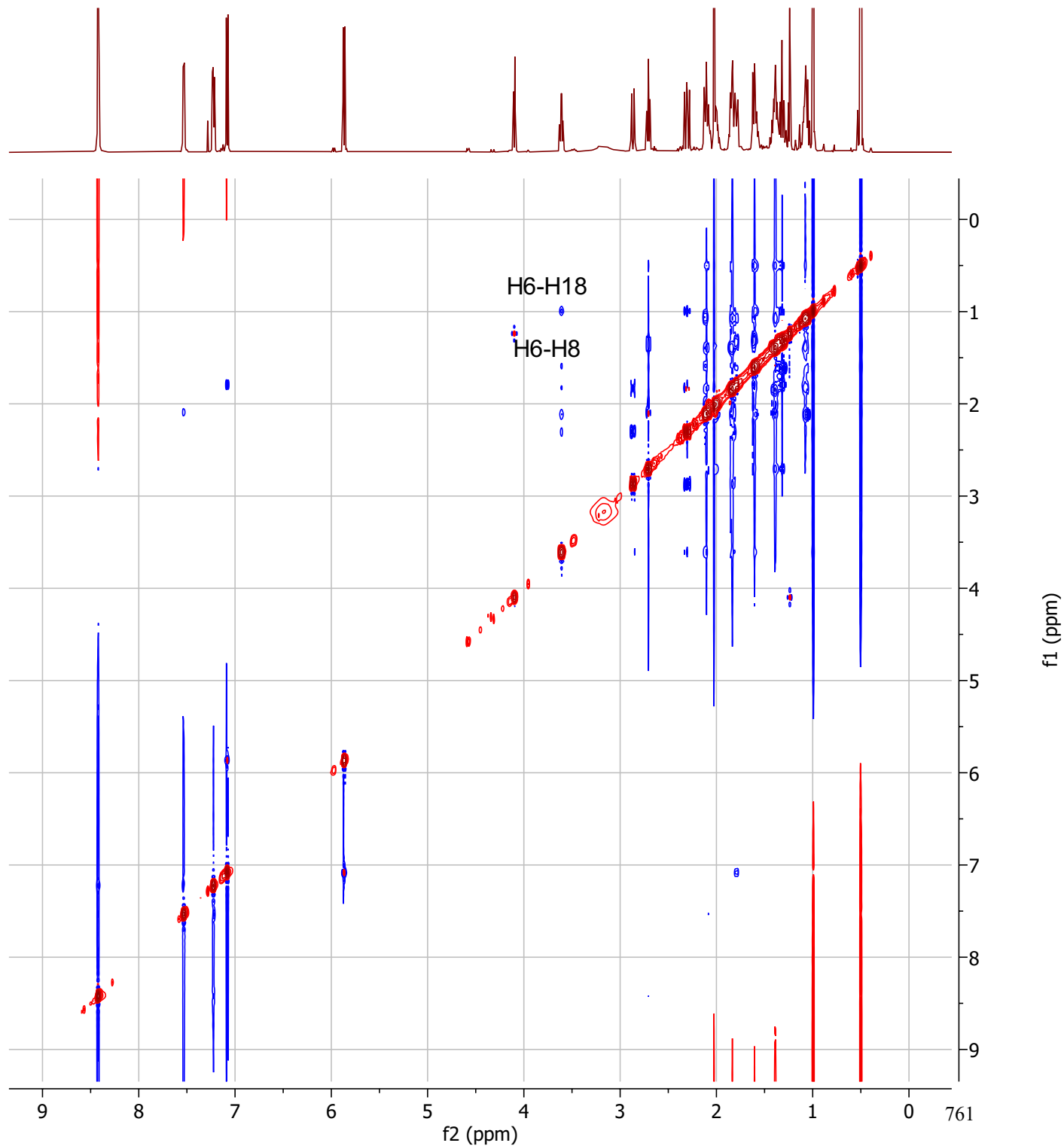
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1741
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(5882.4, 36974.9)
15 Lowest Frequency	(-278.2, -1887.9)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.74, 36.11)



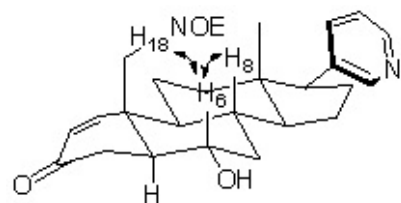
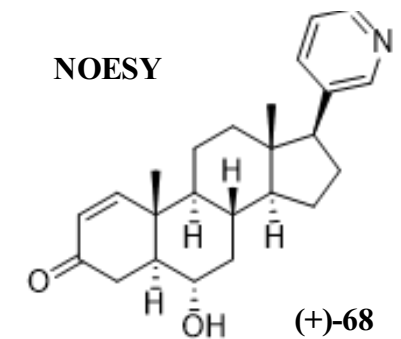
NOESY



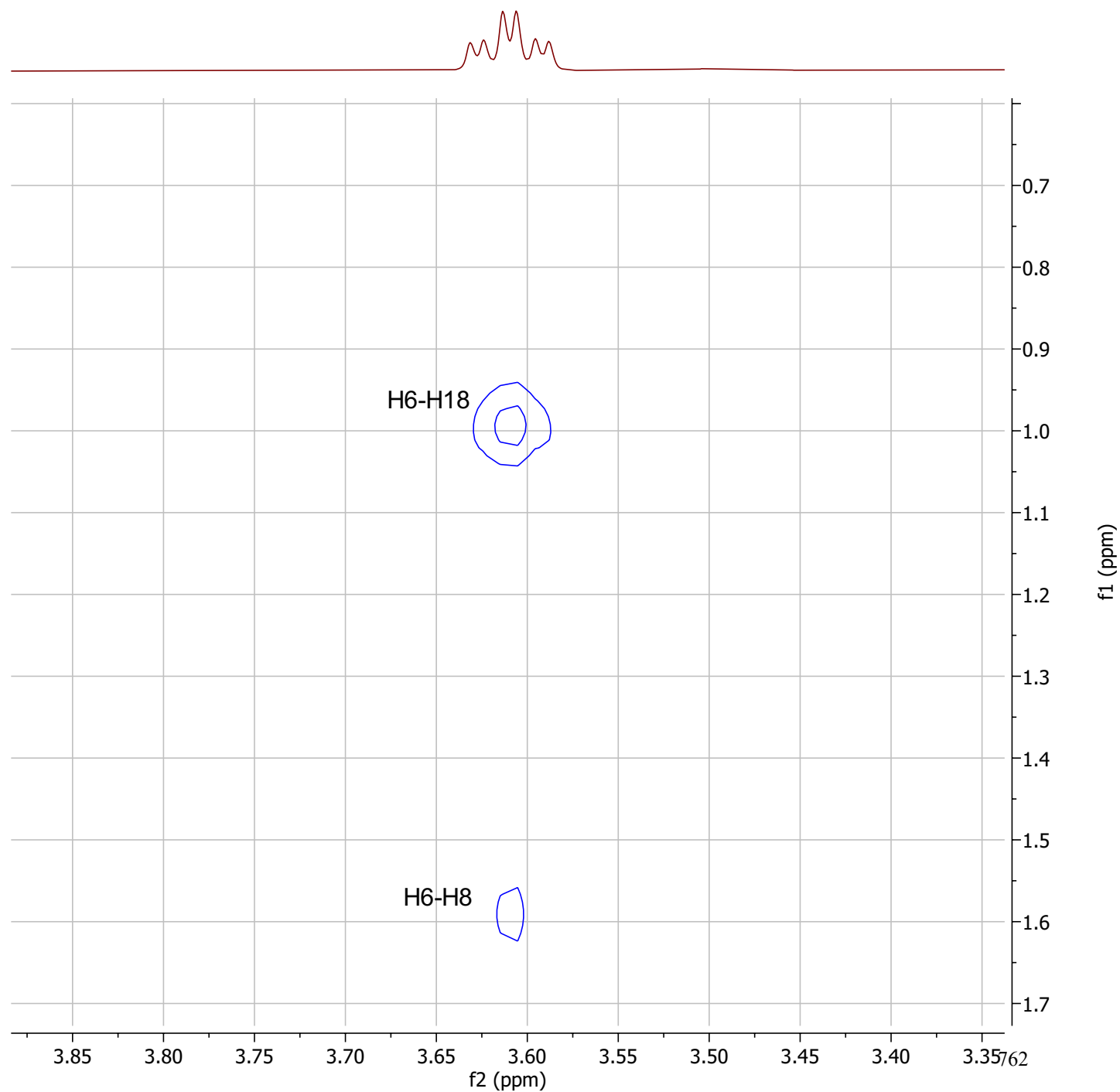
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDC13
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	2.0041
11 Pulse Width	12.0000
12 Acquisition Time	0.1741
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(5882.4, 5882.4)
15 Lowest Frequency	(-286.4, -286.4)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.74, 5.74)



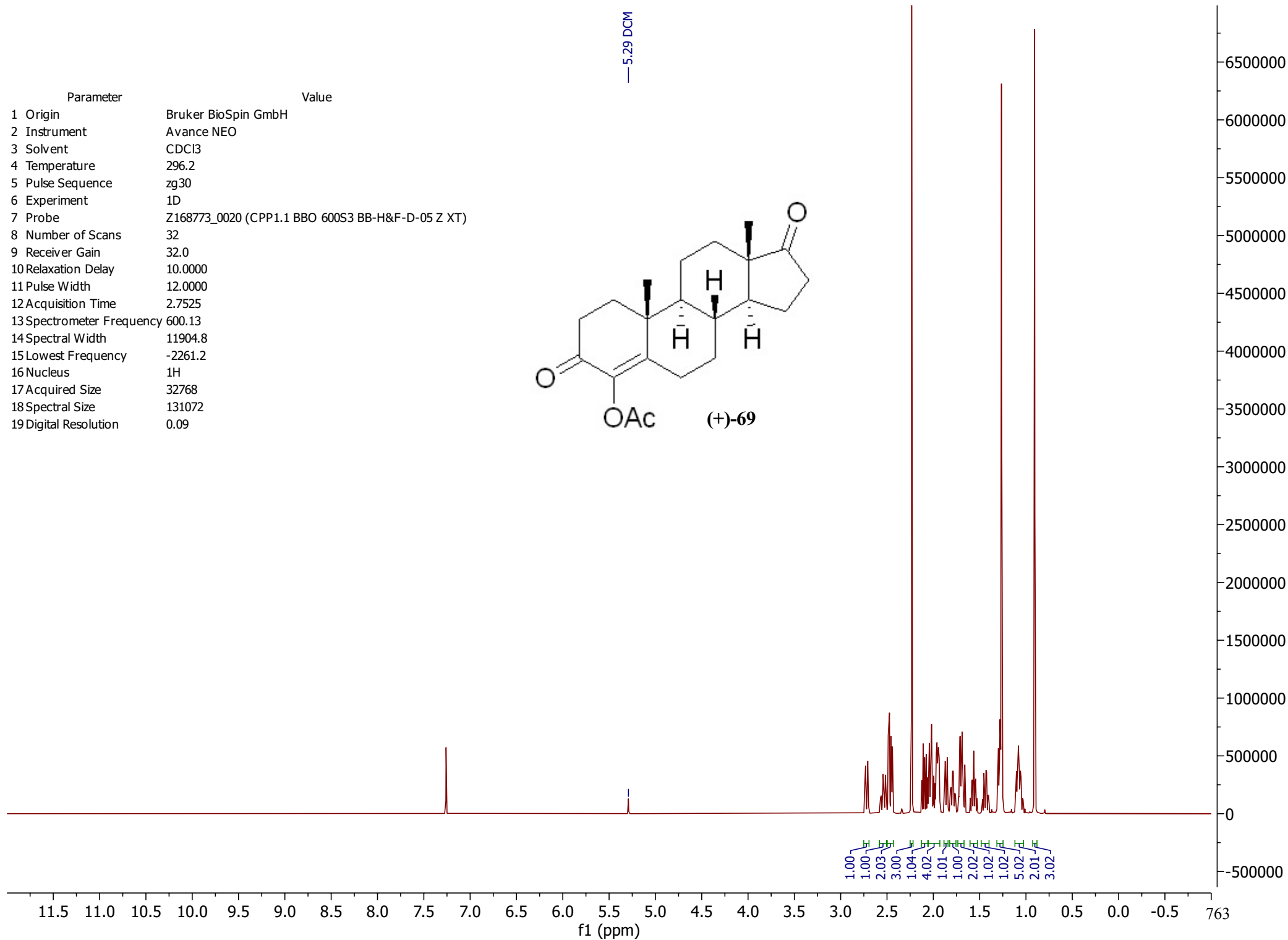
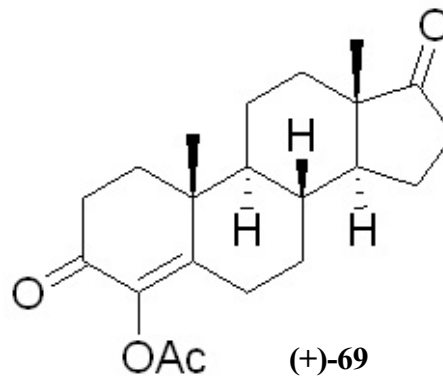
NOESY



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	2.0041
11 Pulse Width	12.0000
12 Acquisition Time	0.1741
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(5882.4, 5882.4)
15 Lowest Frequency	(-286.4, -286.4)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(5.74, 5.74)



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

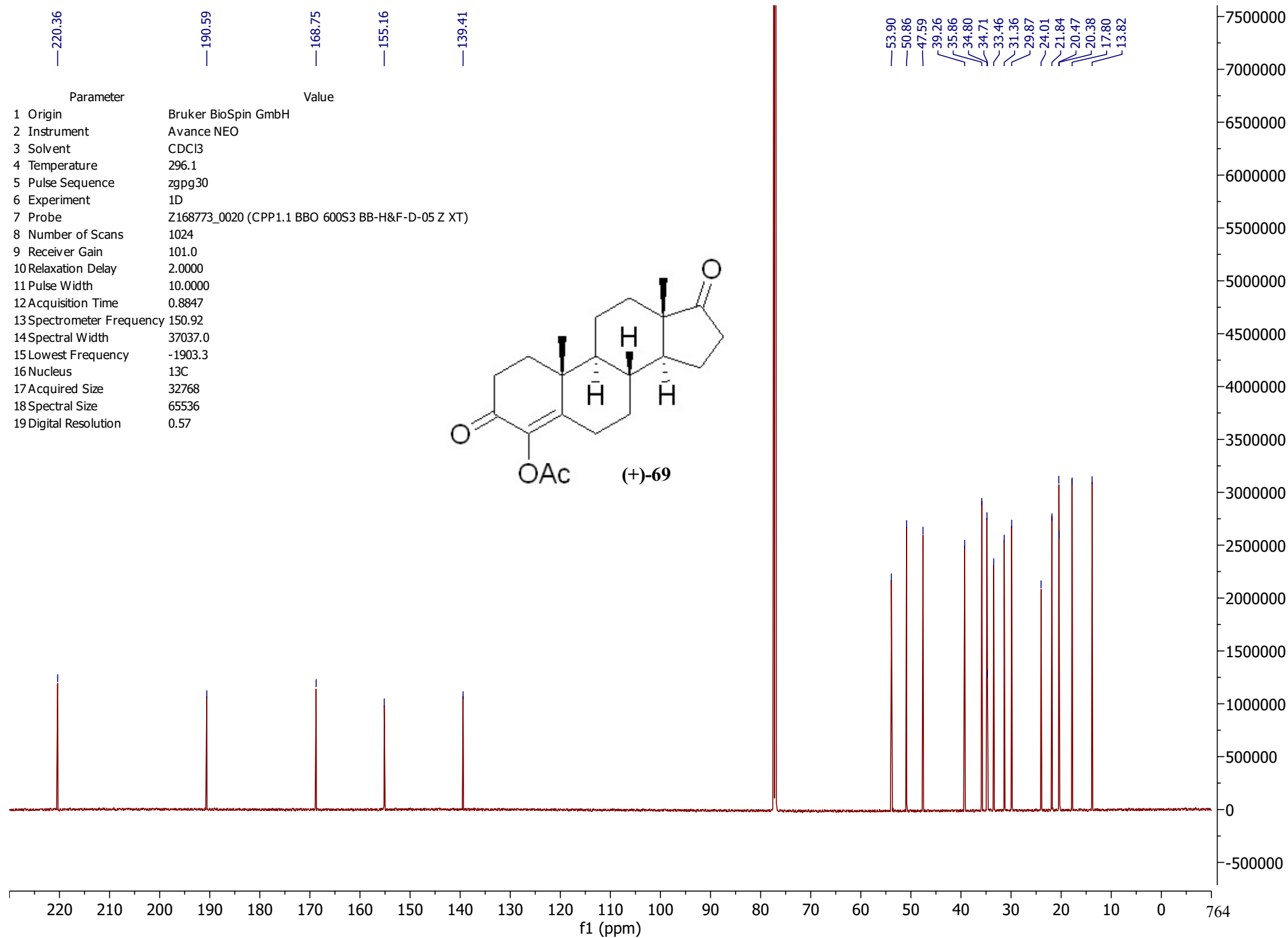
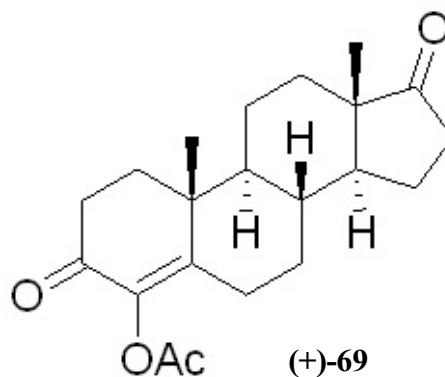


Parameter

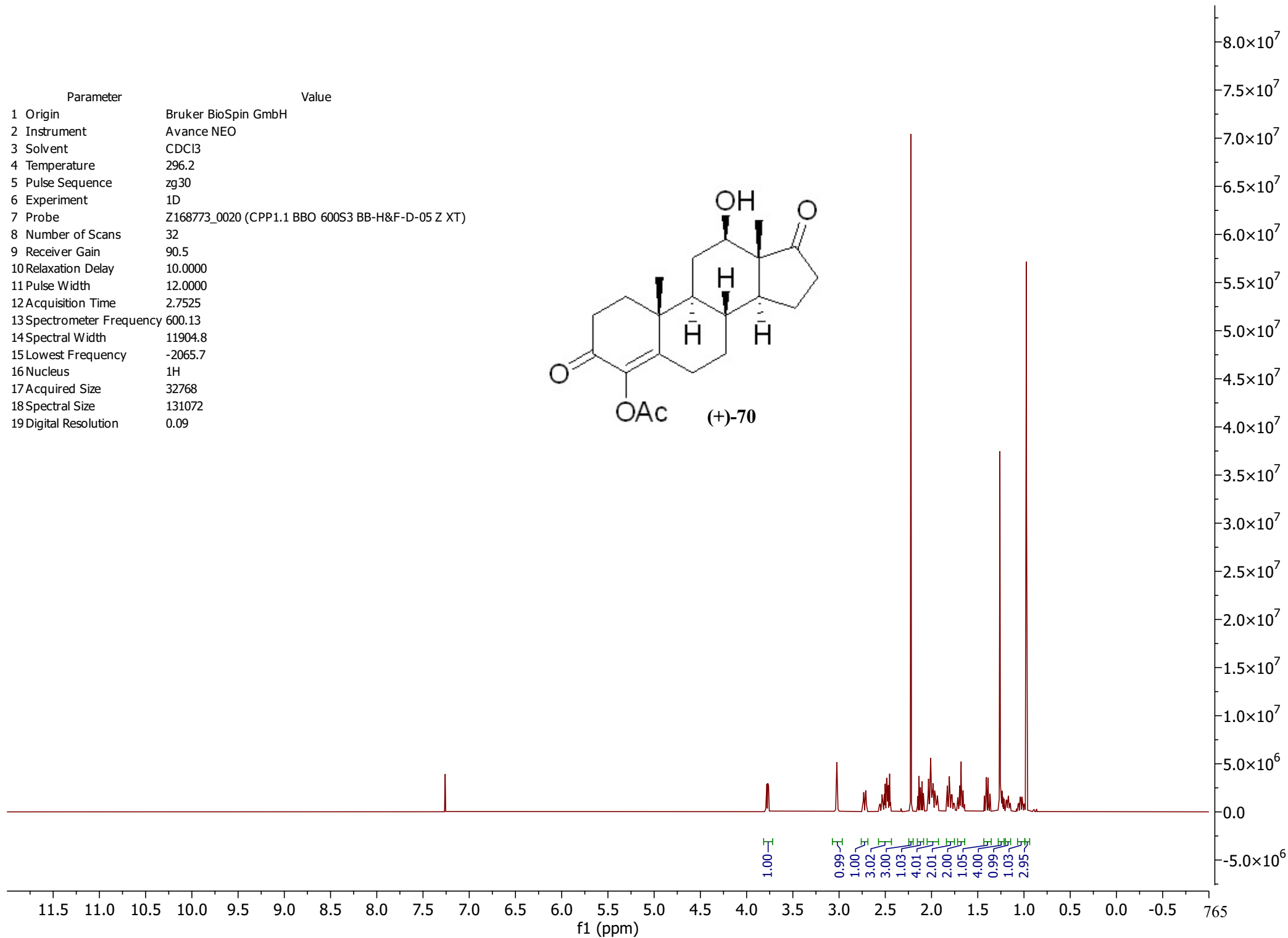
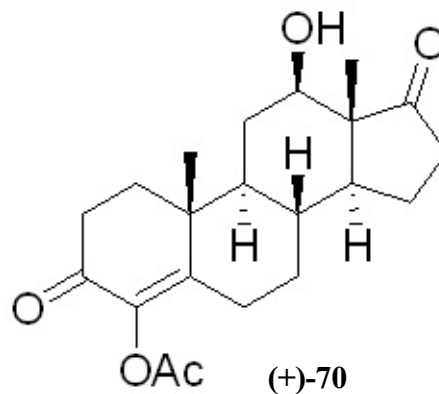
1 Origin
2 Instrument
3 Solvent
4 Temperature
5 Pulse Sequence
6 Experiment
7 Probe
8 Number of Scans
9 Receiver Gain
10 Relaxation Delay
11 Pulse Width
12 Acquisition Time
13 Spectrometer Frequency
14 Spectral Width
15 Lowest Frequency
16 Nucleus
17 Acquired Size
18 Spectral Size
19 Digital Resolution

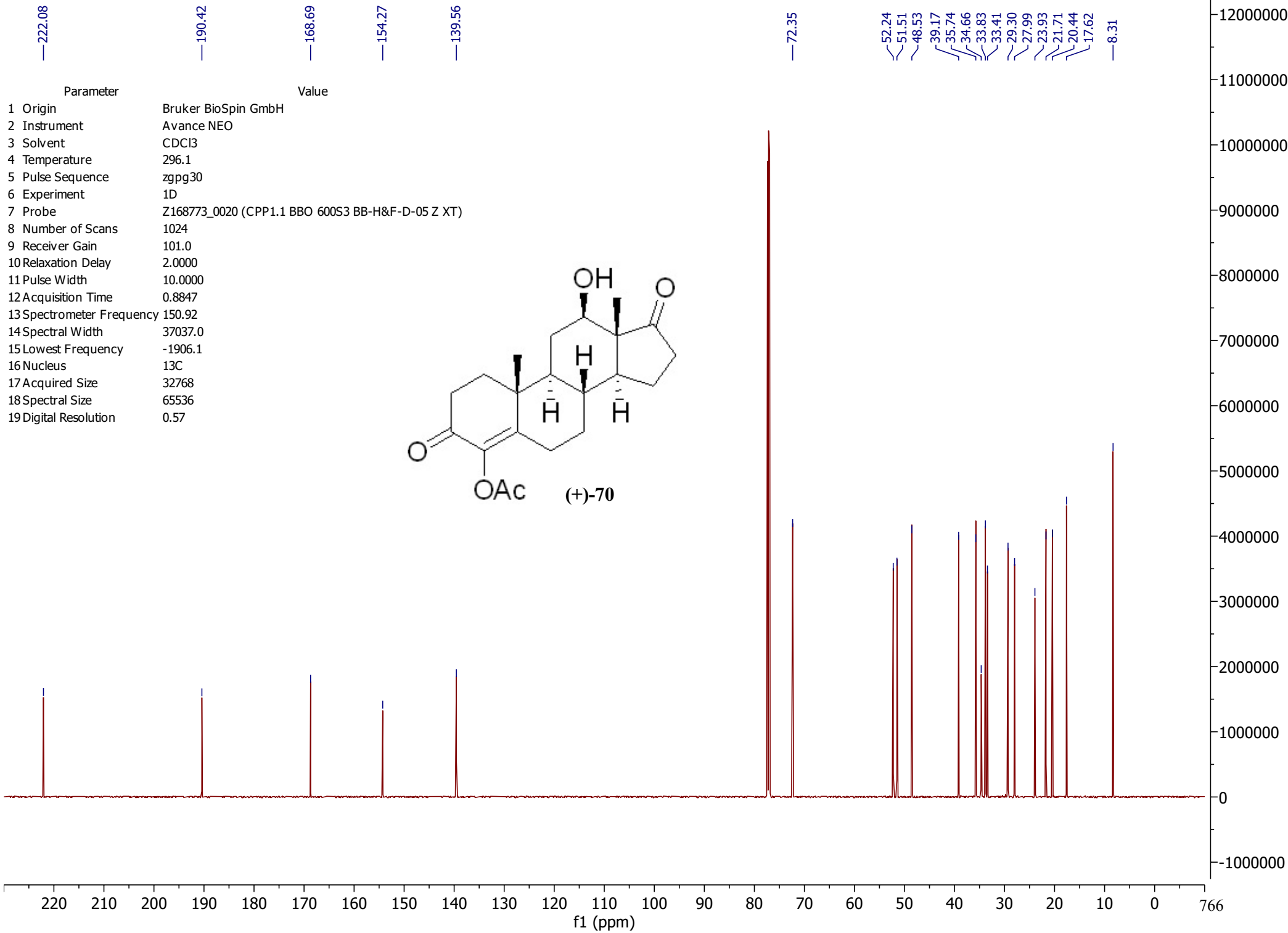
Value

Bruker BioSpin GmbH
Avance NEO
CDCl3
296.1
zgpg30
1D
Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
1024
101.0
2.0000
10.0000
0.8847
150.92
37037.0
-1903.3
13C
32768
65536
0.57

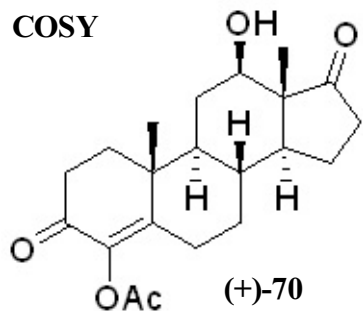


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	90.5
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2065.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

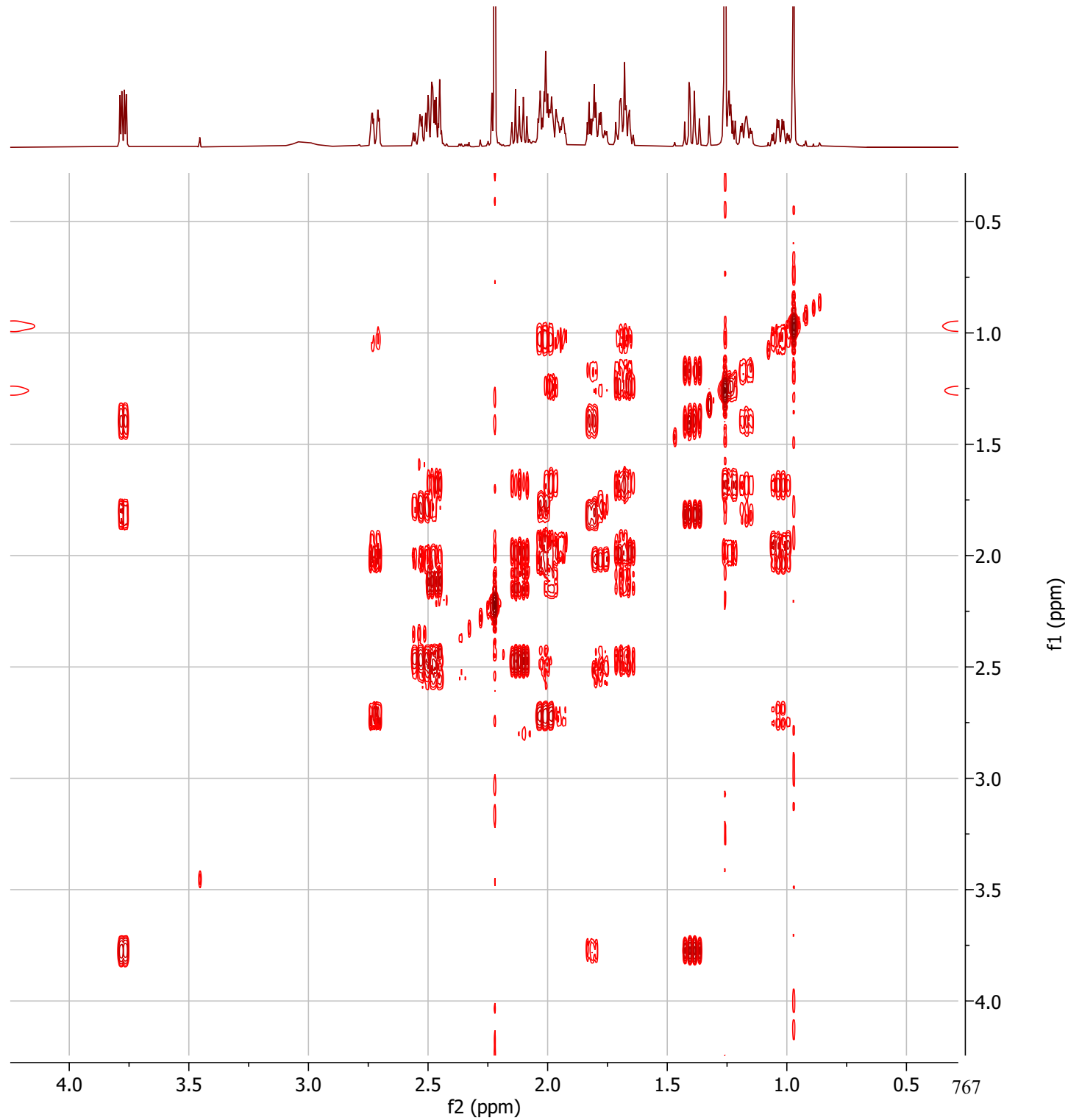




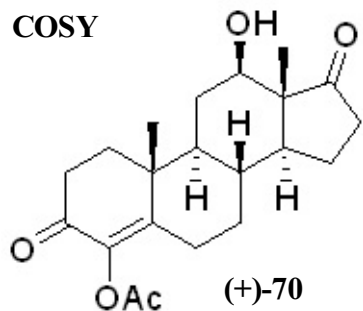
COSY



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	90.5
10 Relaxation Delay	1.2112
11 Pulse Width	12.0000
12 Acquisition Time	0.4301
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(2381.0, 2381.0)
15 Lowest Frequency	(167.7, 166.7)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(2.33, 2.33)

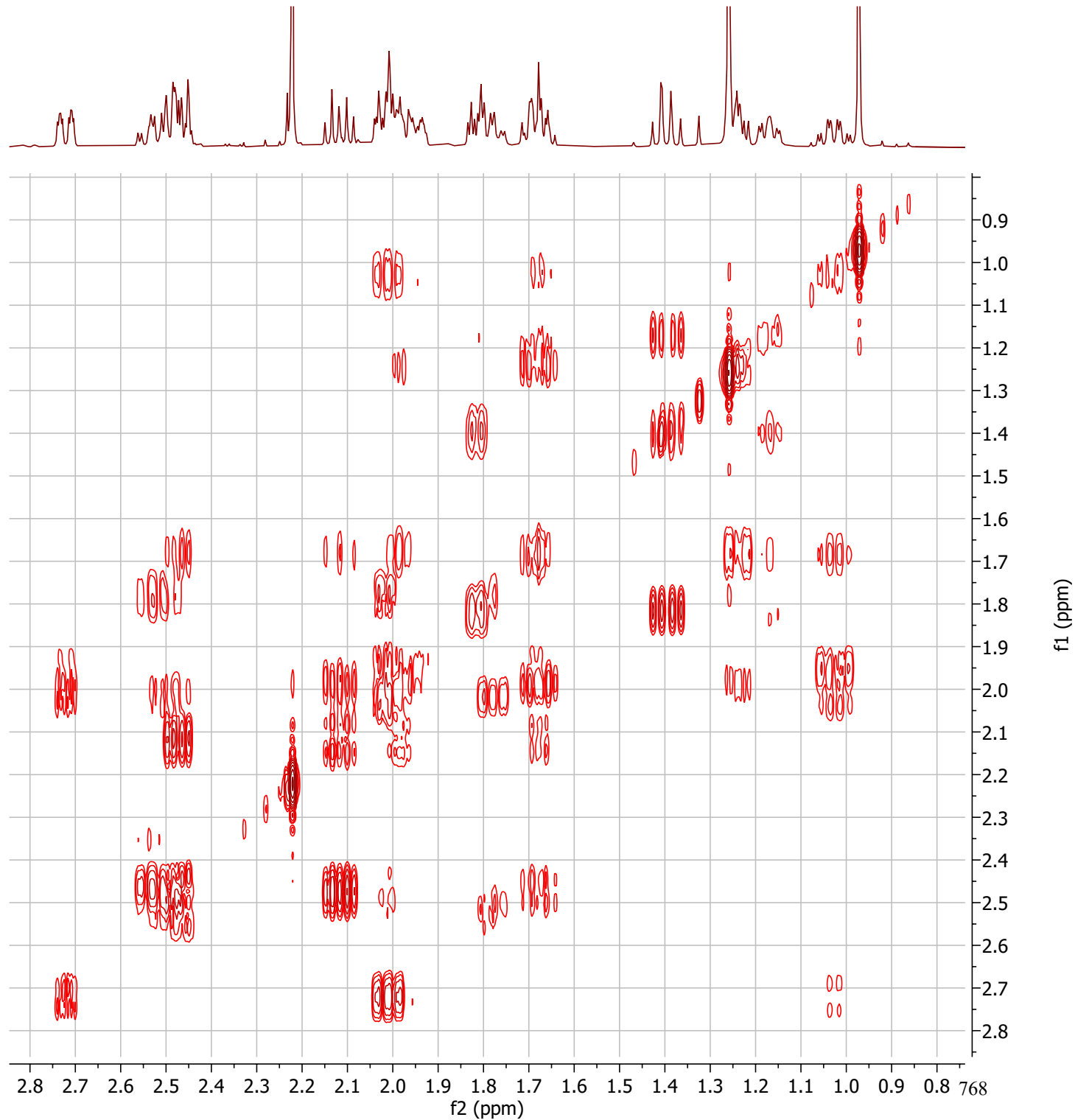


COSY

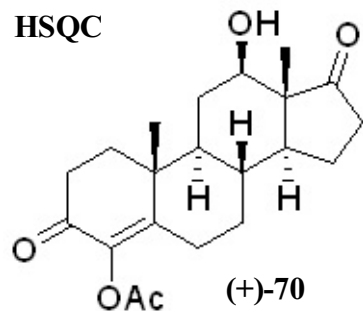


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Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	90.5
10 Relaxation Delay	1.2112
11 Pulse Width	12.0000
12 Acquisition Time	0.4301
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(2381.0, 2381.0)
15 Lowest Frequency	(167.7, 166.7)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(2.33, 2.33)

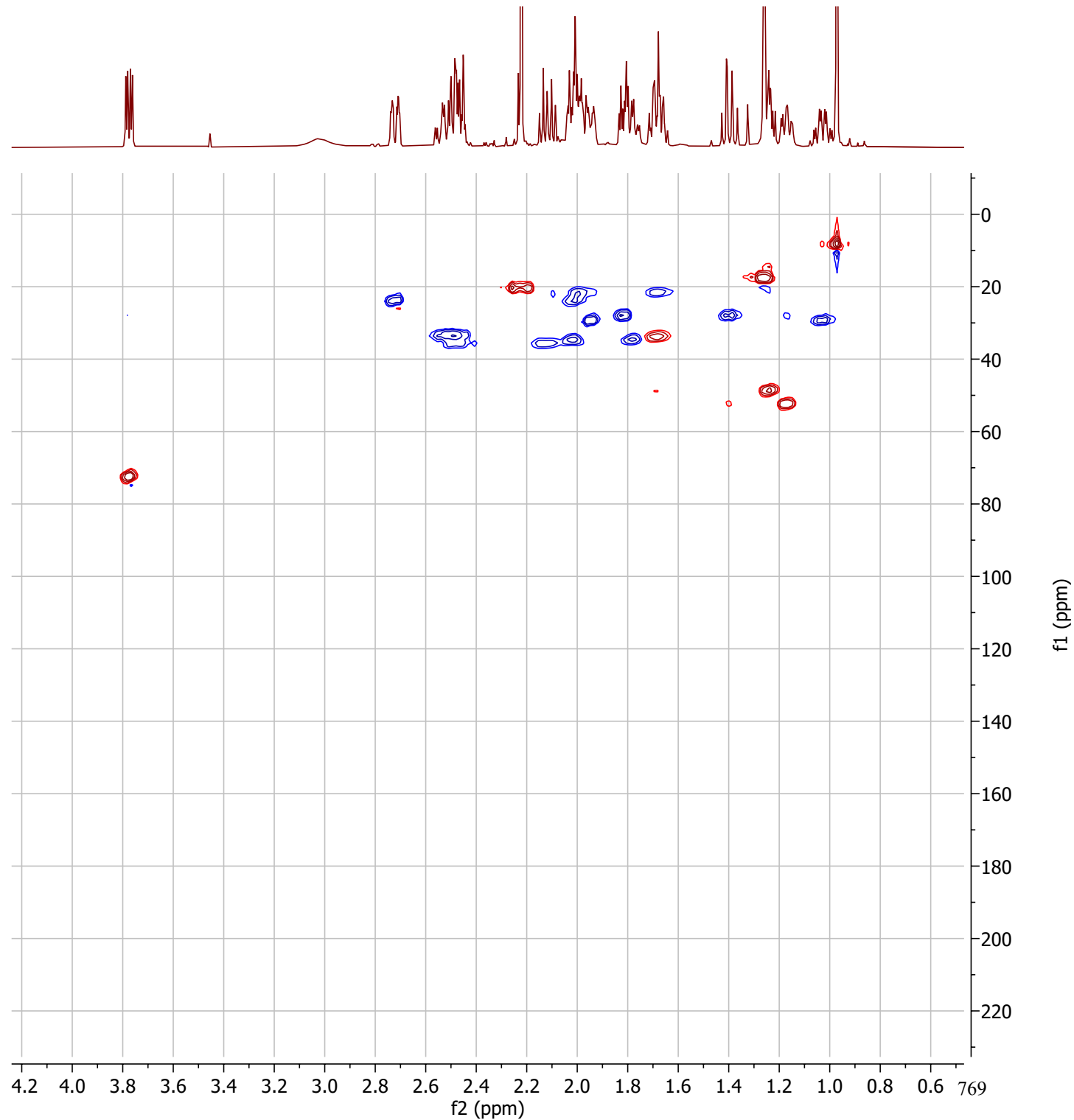


HSQC

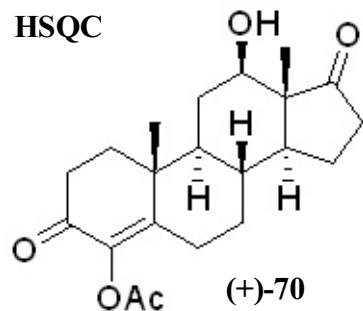


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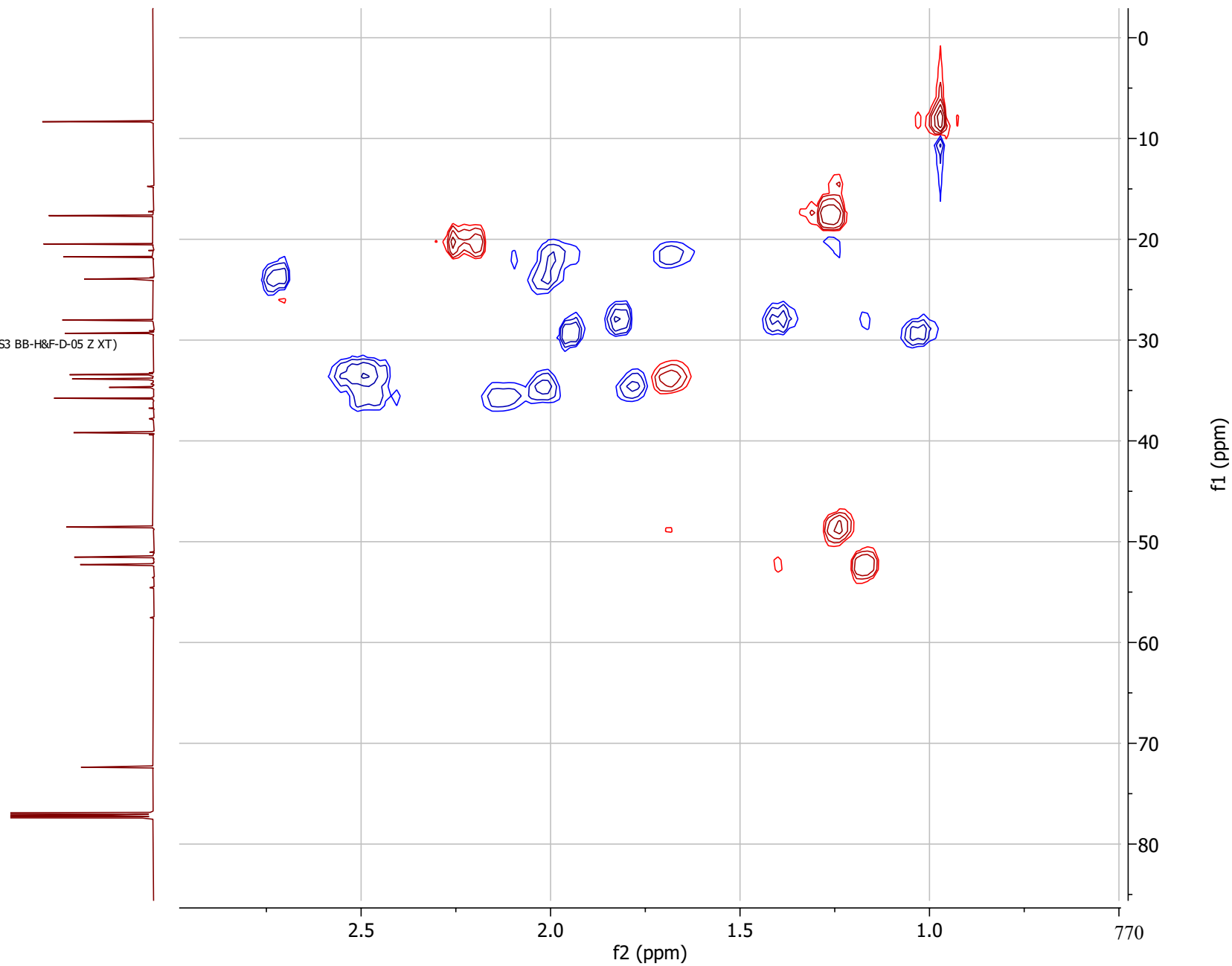
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hsqcetgpgisip2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(2272.7, 36974.0)
15 Lowest Frequency	(272.0, -1857.1)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(256, 256)
18 Spectral Size	(256, 256)
19 Digital Resolution	(8.88, 144.43)



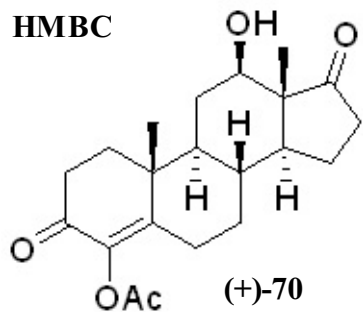
HSQC



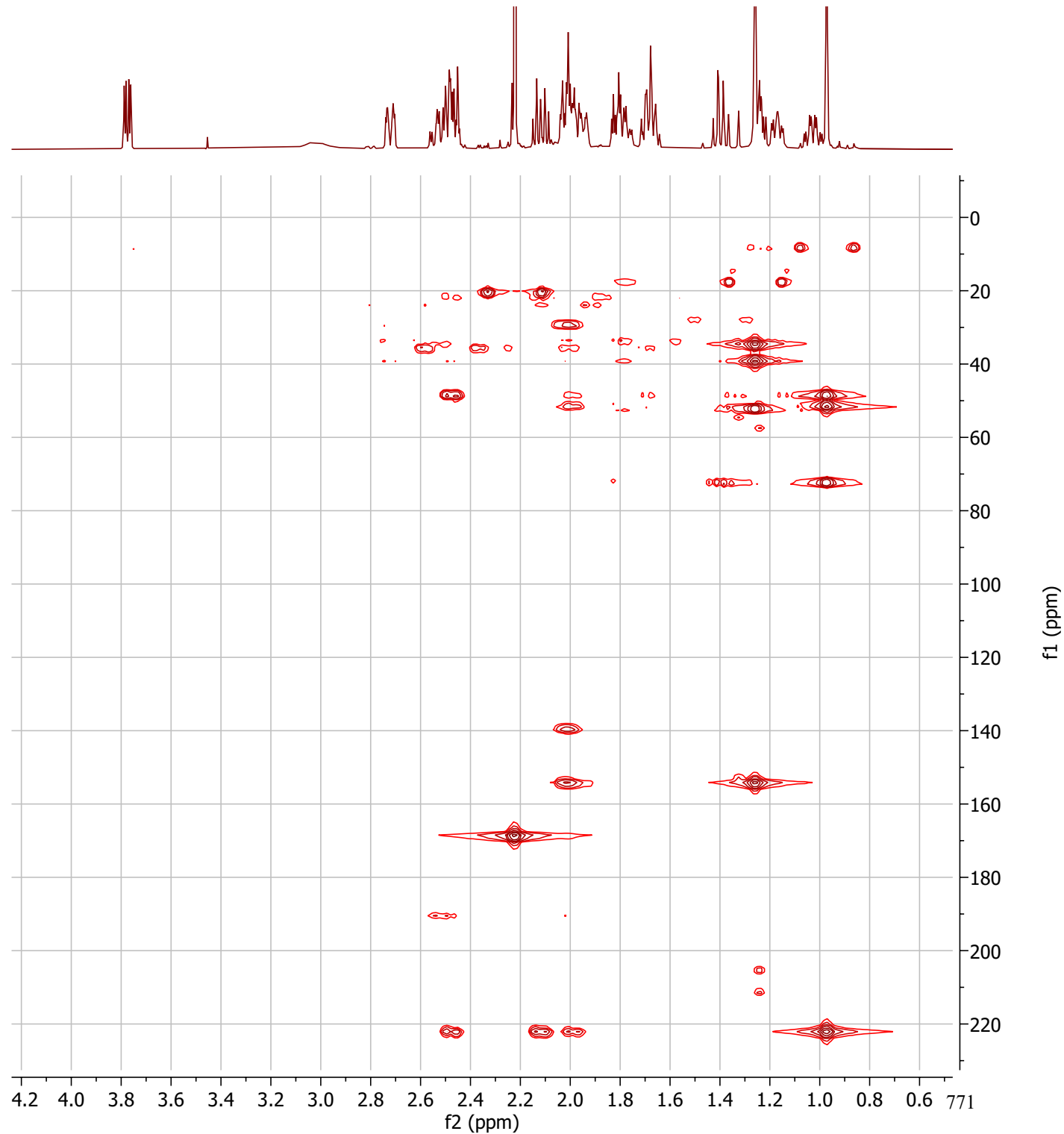
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hsqcetgpcisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(2272.7, 36974.0)
15 Lowest Frequency	(272.0, -1857.1)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(256, 256)
18 Spectral Size	(256, 256)
19 Digital Resolution	(8.88, 144.43)



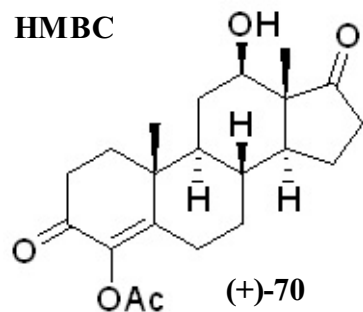
HMBC



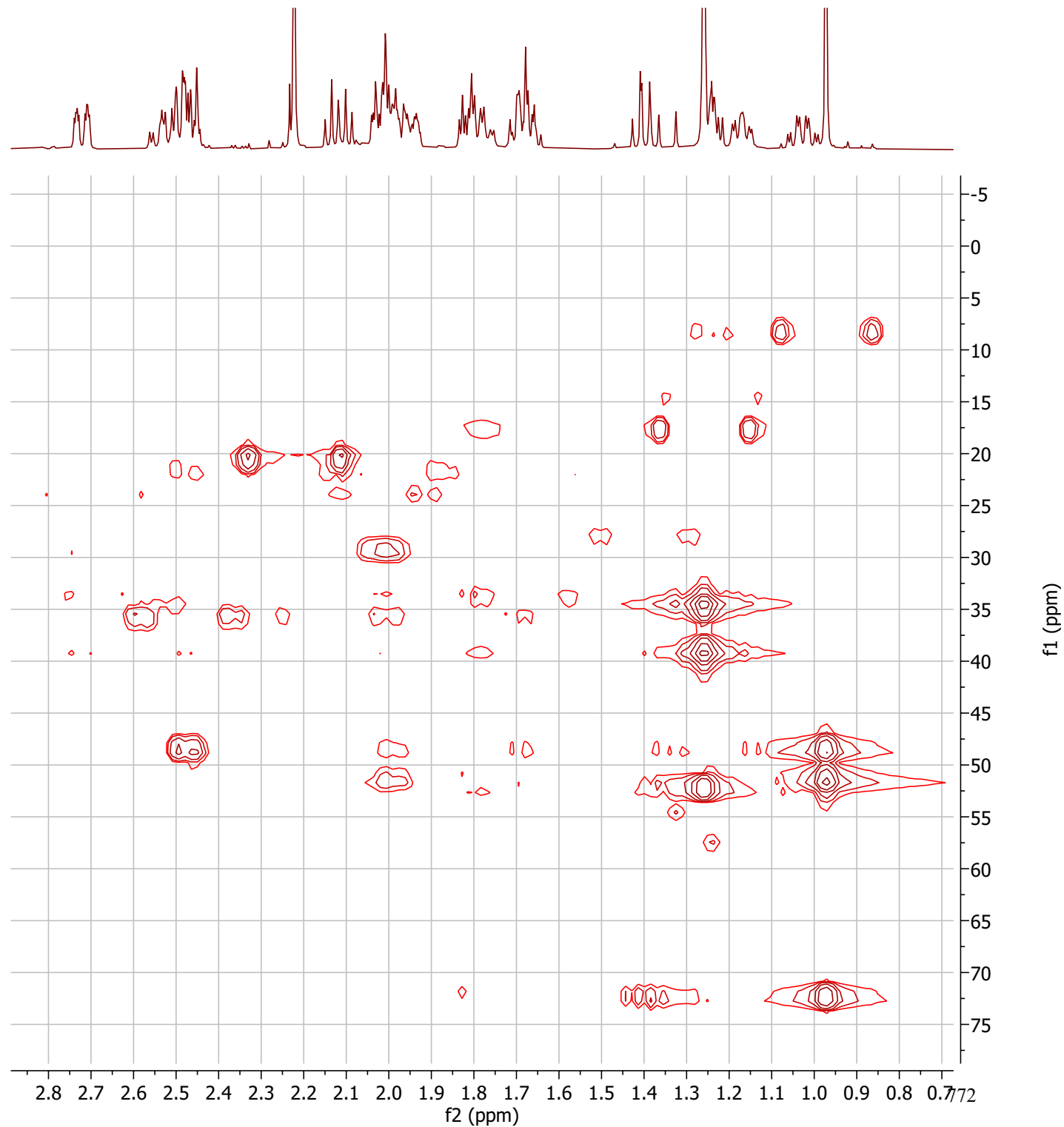
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(2272.7, 36974.9)
15 Lowest Frequency	(271.4, -1875.3)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(256, 256)
18 Spectral Size	(256, 256)
19 Digital Resolution	(8.88, 144.43)



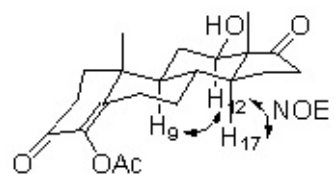
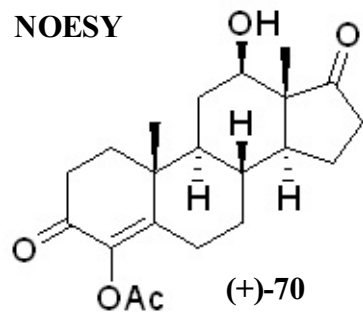
HMBC



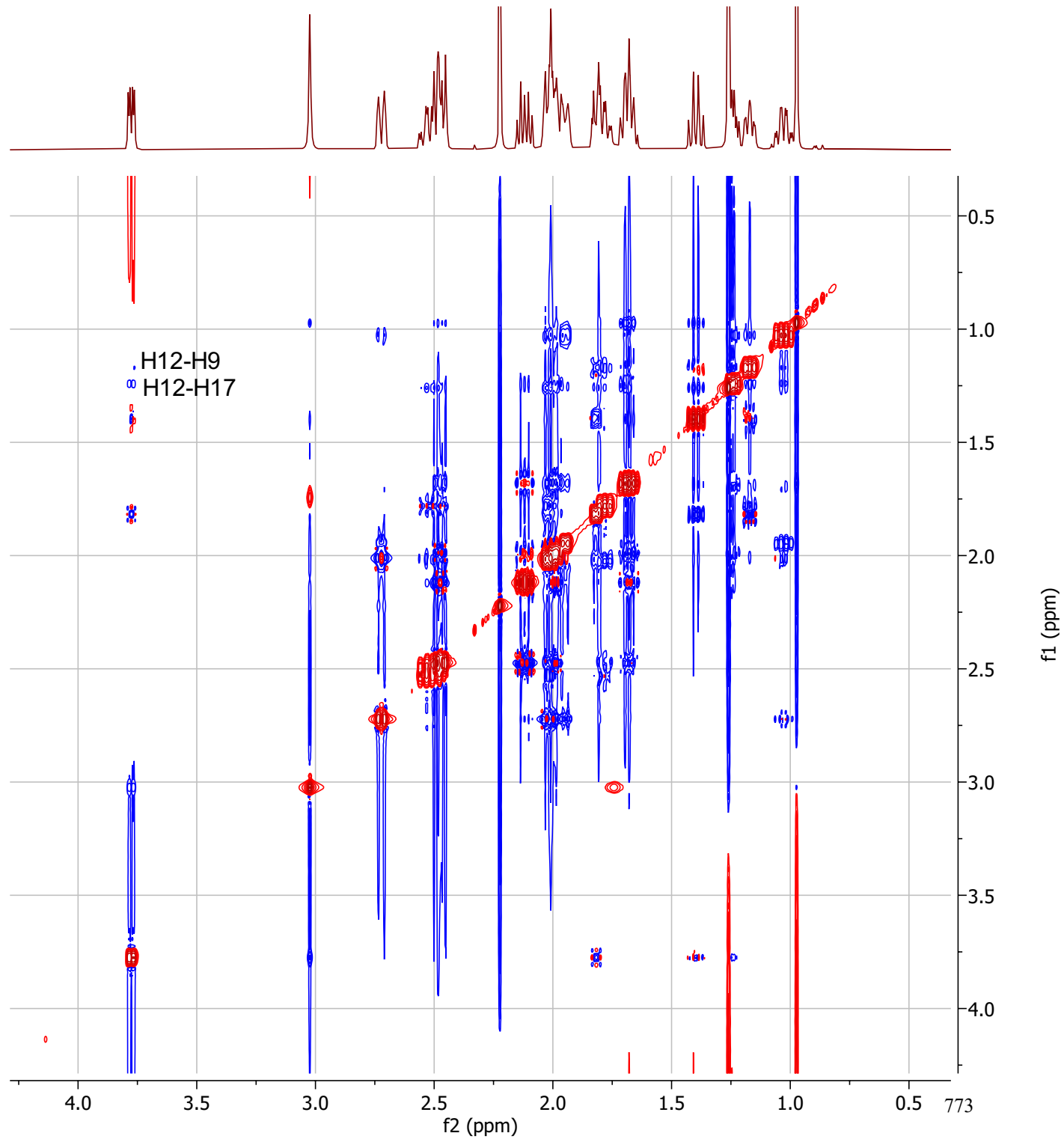
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1126
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(2272.7, 36974.9)
15 Lowest Frequency	(271.4, -1875.3)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(256, 256)
18 Spectral Size	(256, 256)
19 Digital Resolution	(8.88, 144.43)



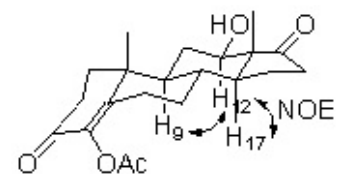
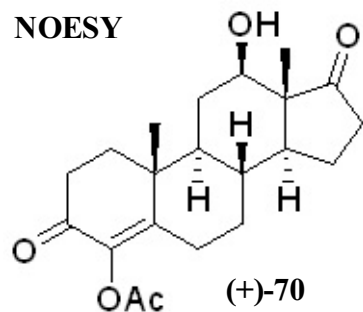
NOESY



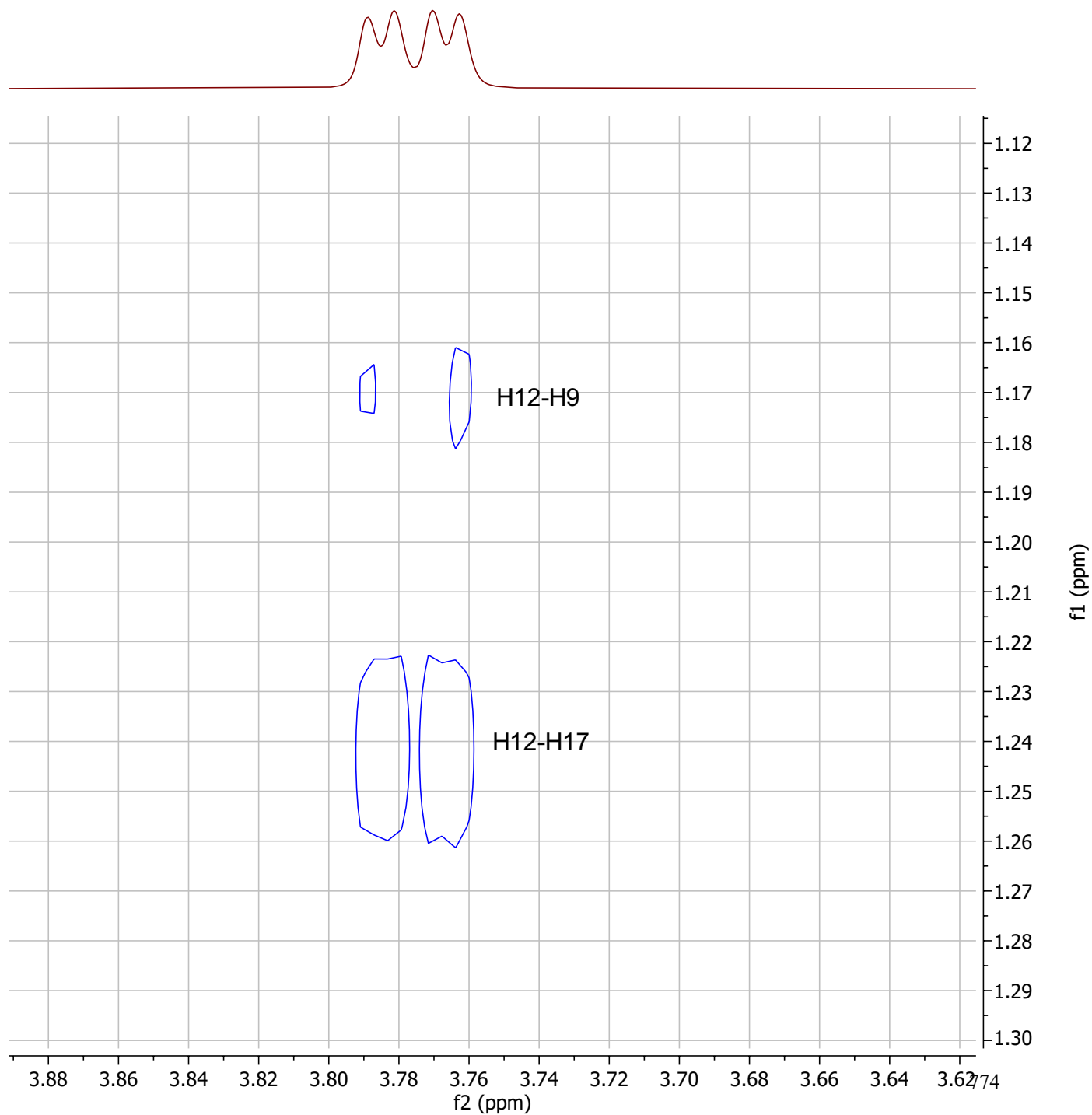
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	noesygpqhpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.7399
11 Pulse Width	12.0000
12 Acquisition Time	0.4301
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(2381.0, 2381.0)
15 Lowest Frequency	(191.7, 191.7)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(2.33, 2.33)



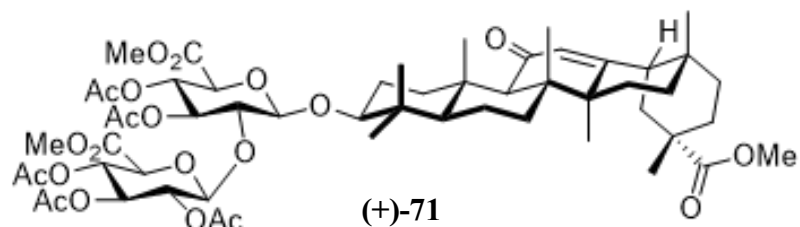
NOESY



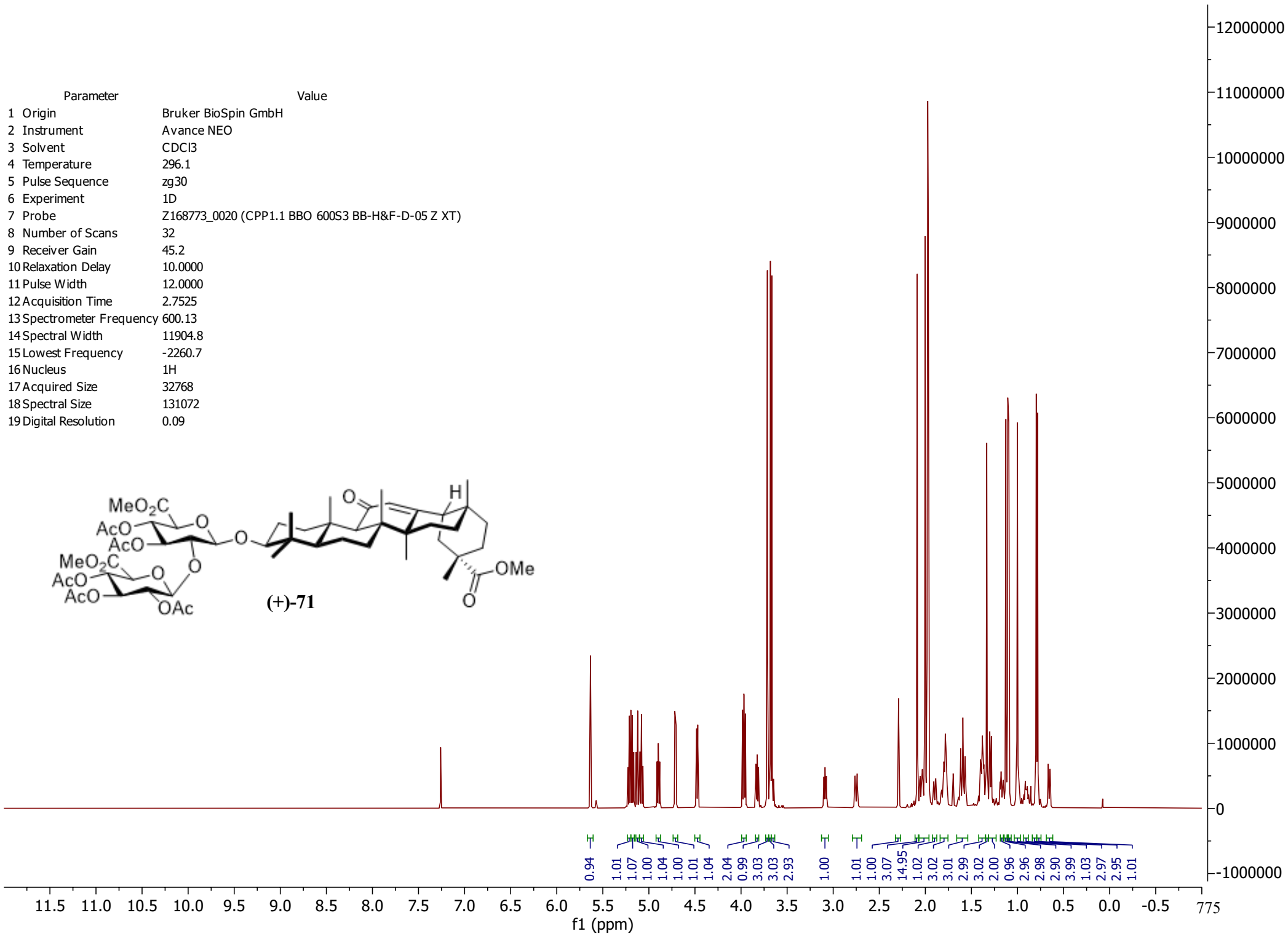
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	noesygp3pp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.7399
11 Pulse Width	12.0000
12 Acquisition Time	0.4301
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(2381.0, 2381.0)
15 Lowest Frequency	(191.7, 191.7)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(2.33, 2.33)



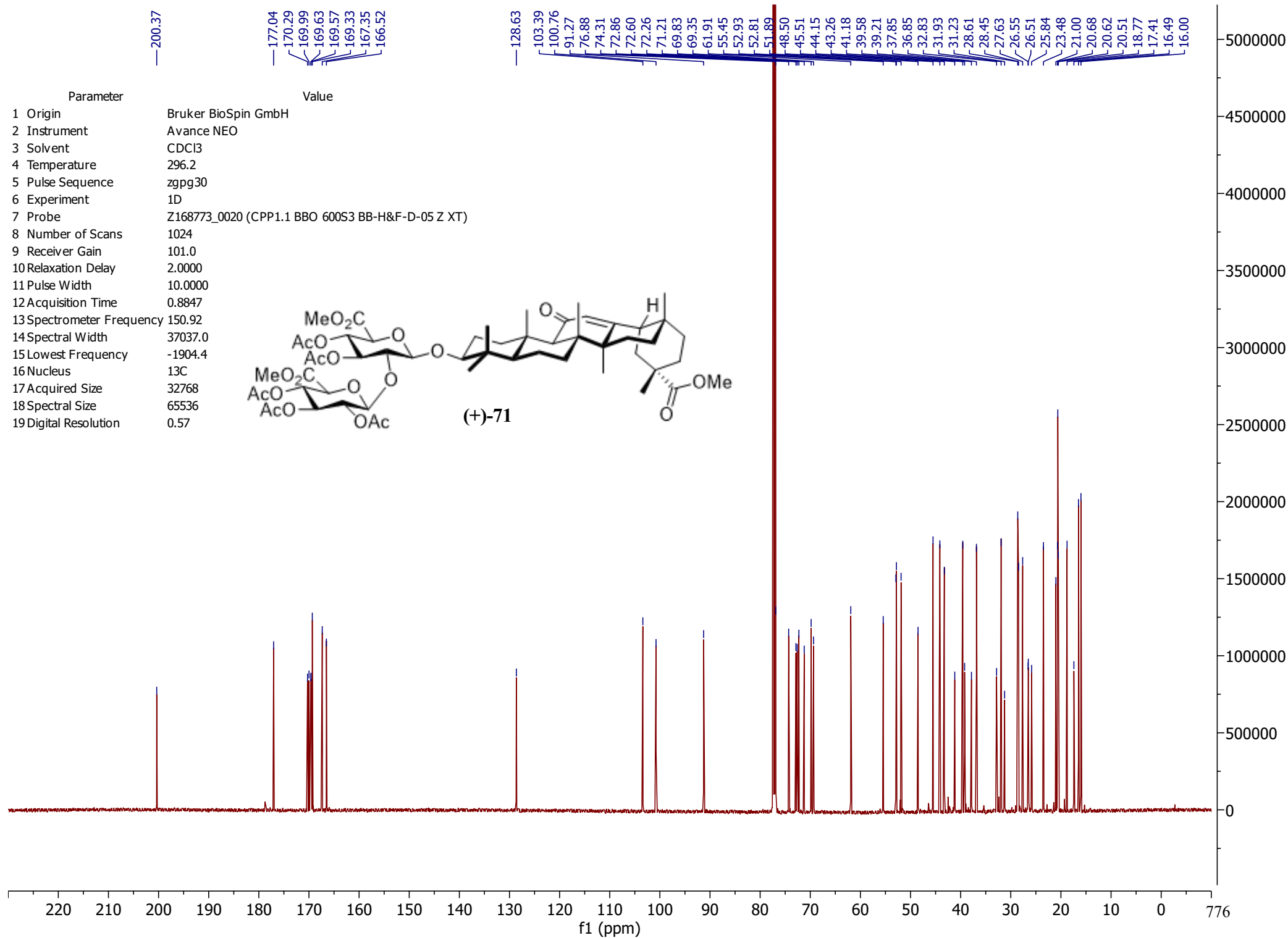
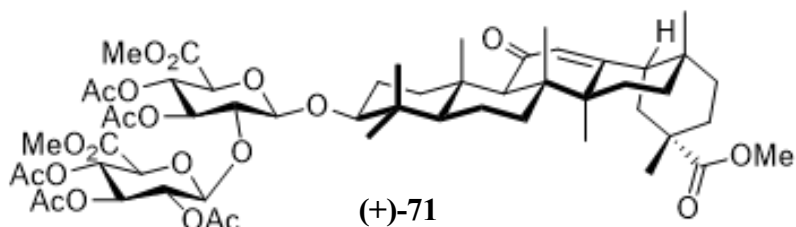
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	45.2
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



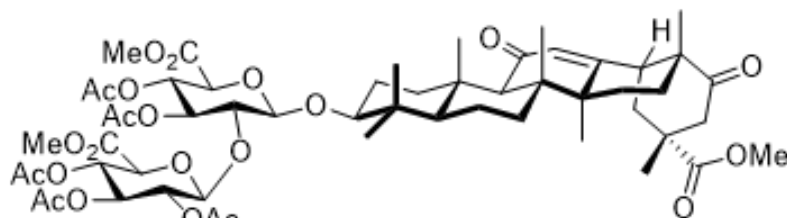
(+)-71



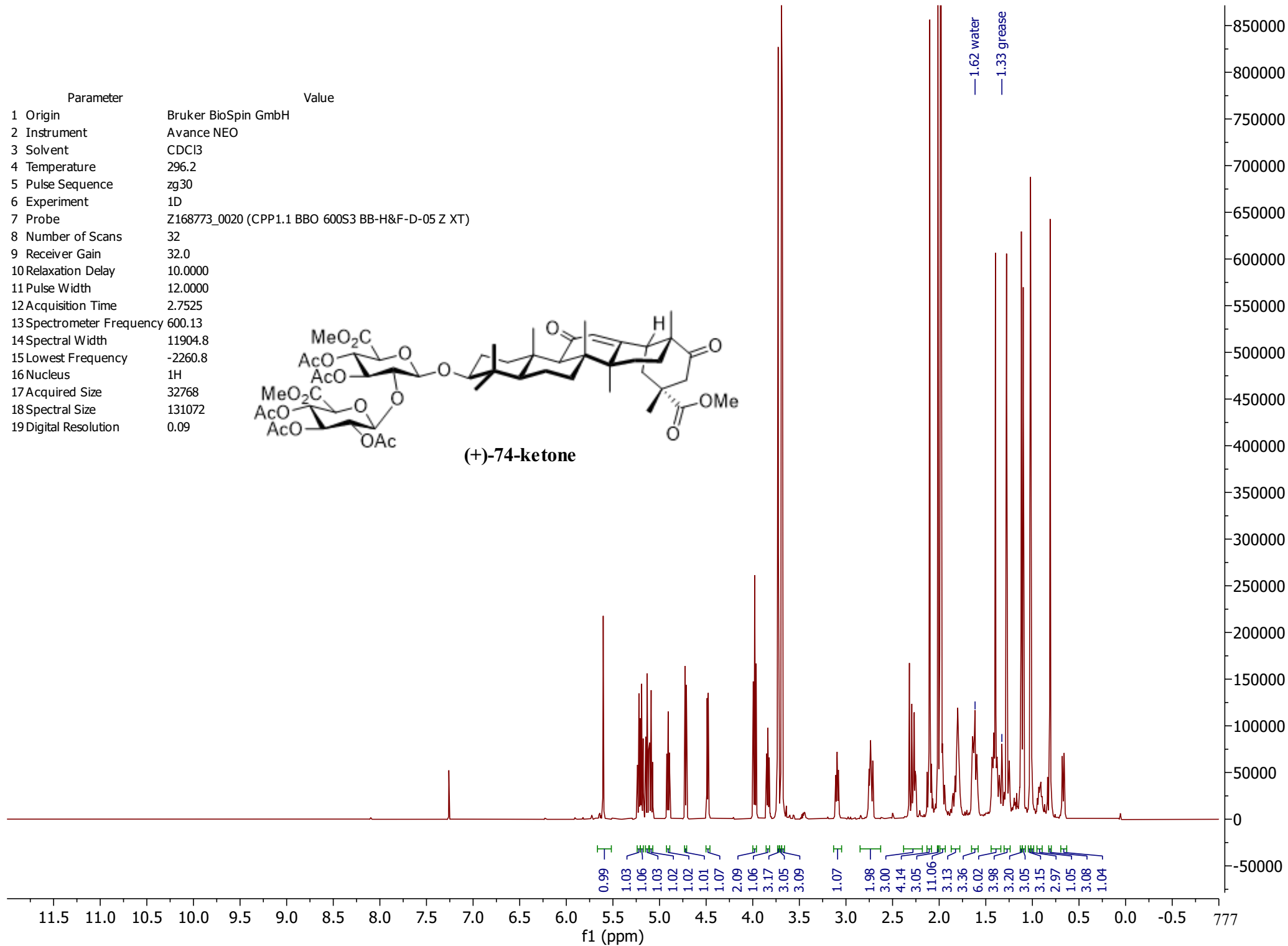
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	1024
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1904.4
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57

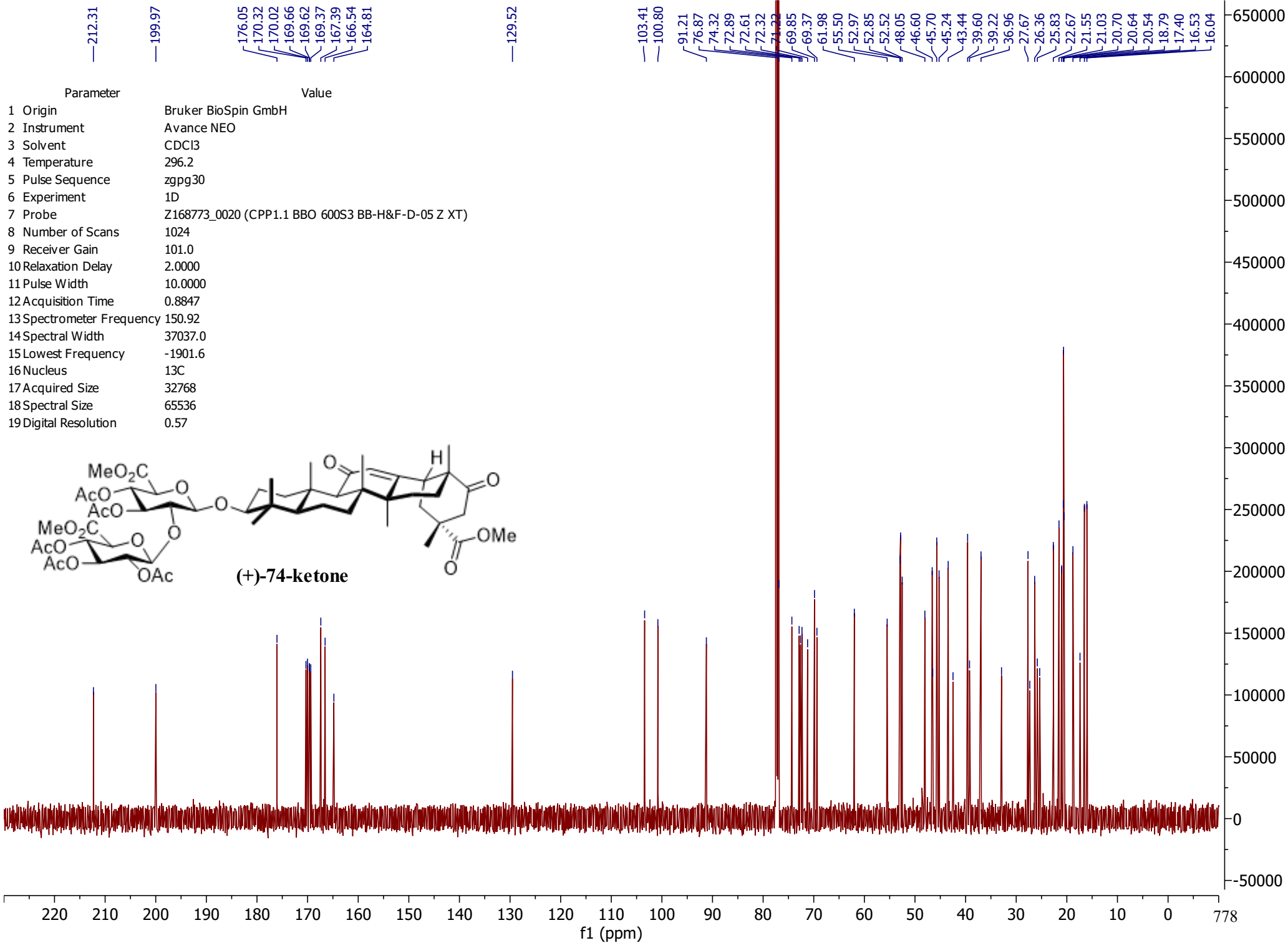


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

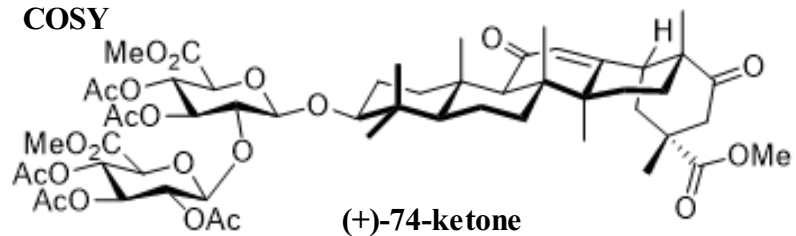


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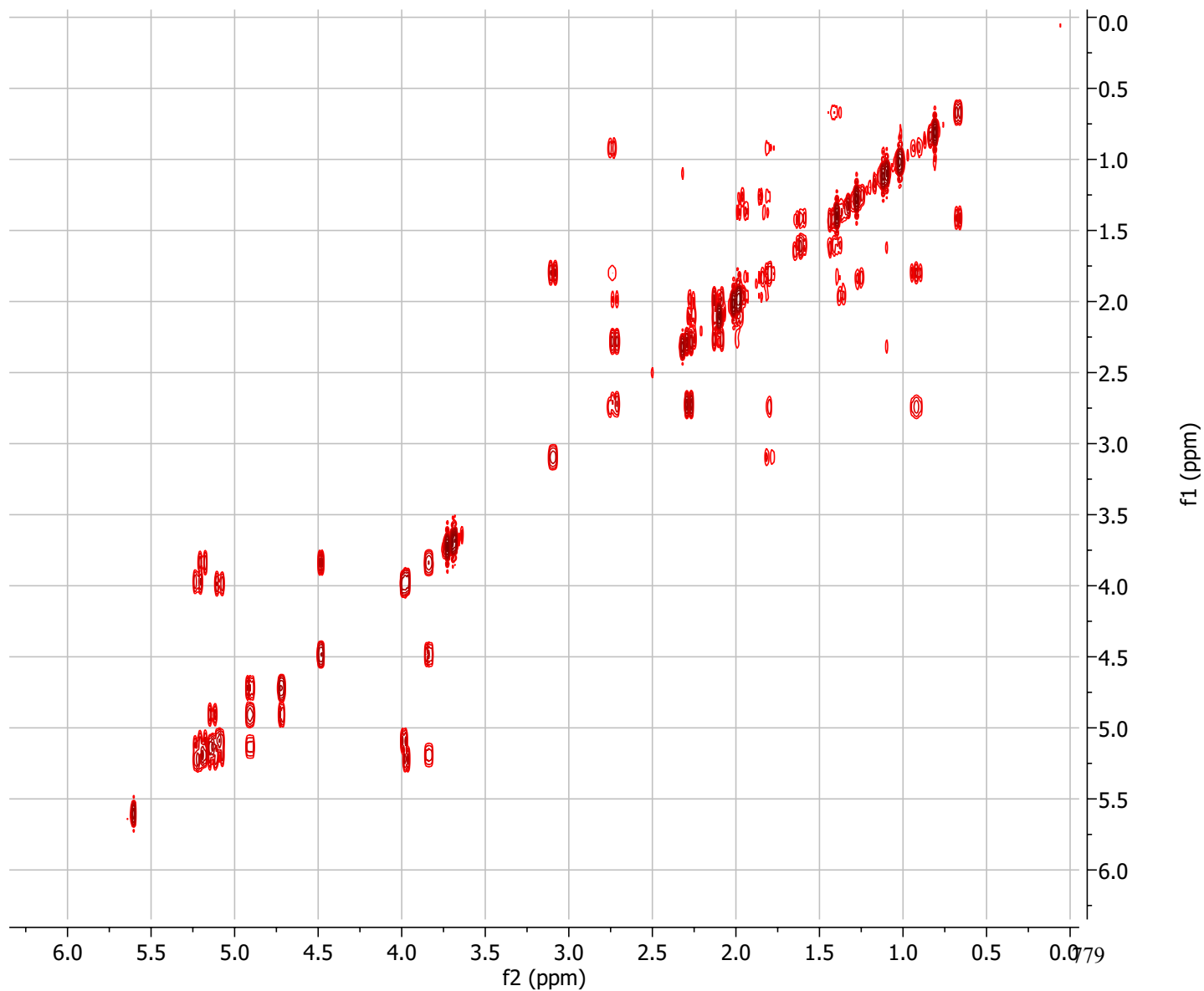




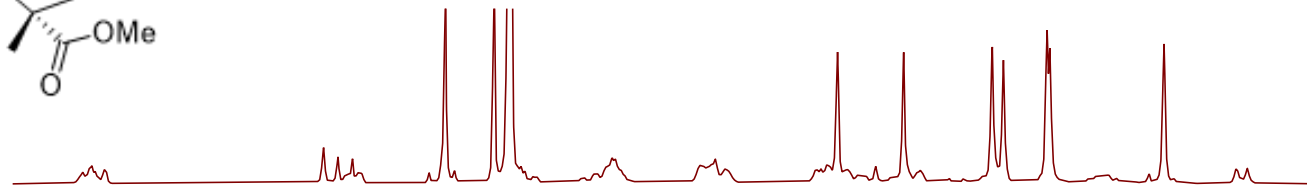
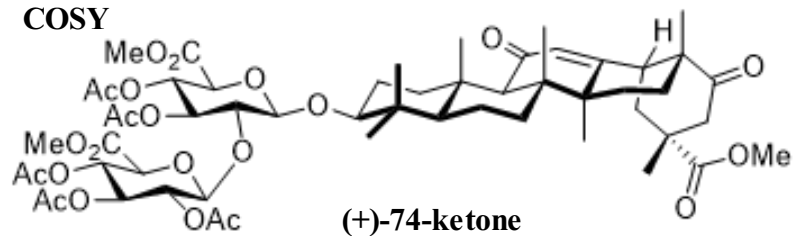
COSY



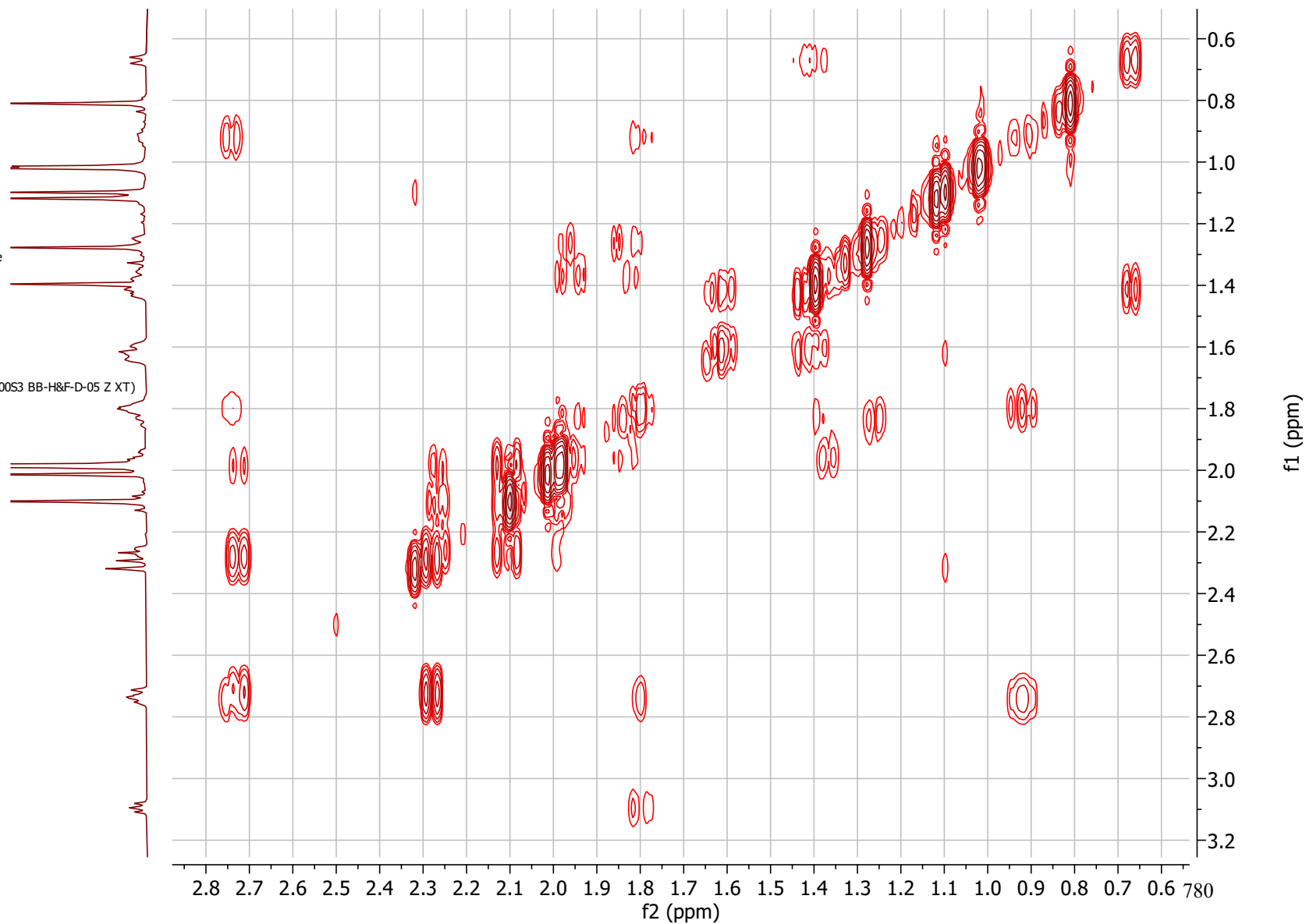
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3607
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(-36.4, -36.4)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



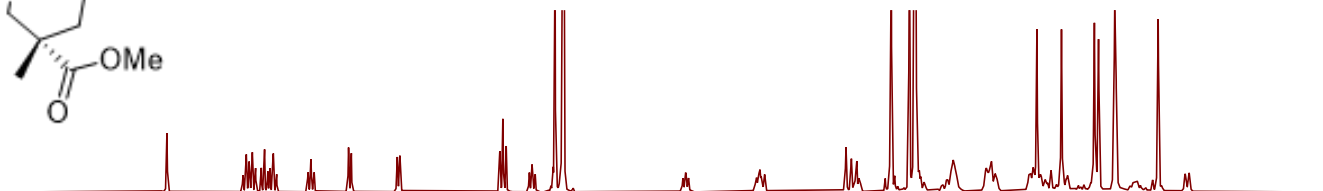
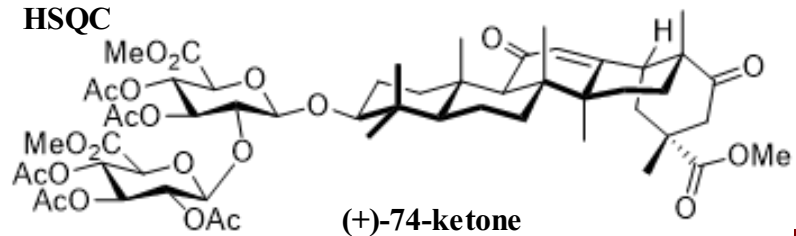
COSY



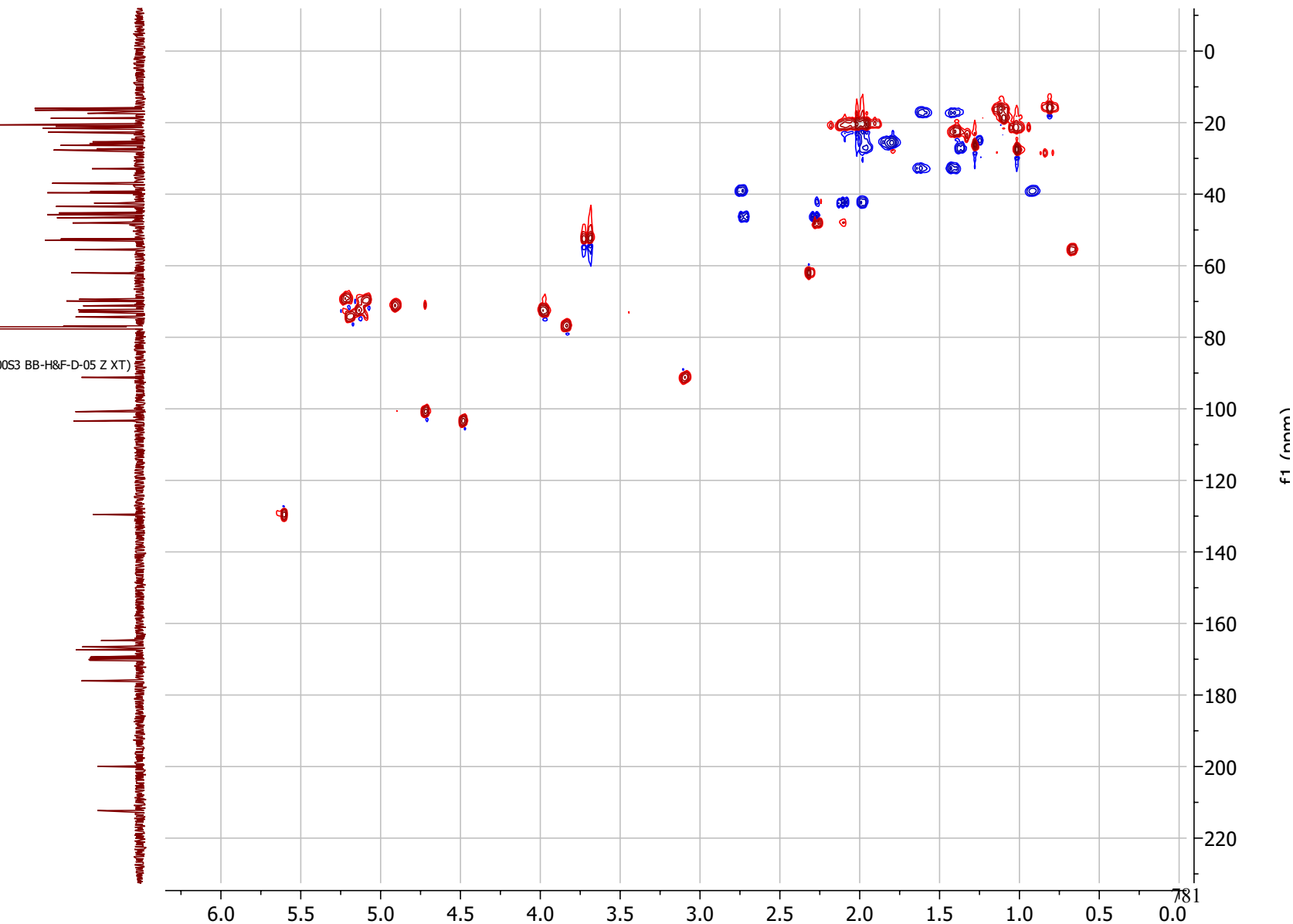
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3607
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(-36.4, -36.4)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



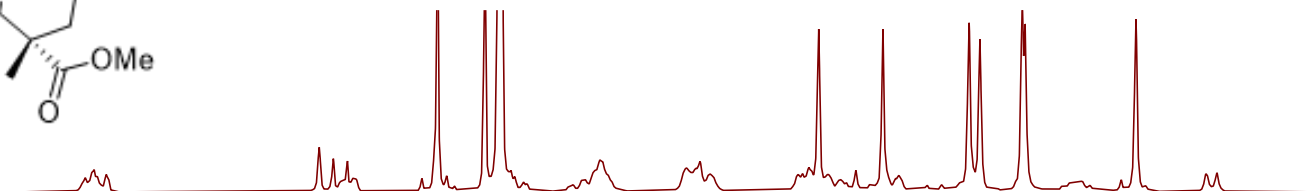
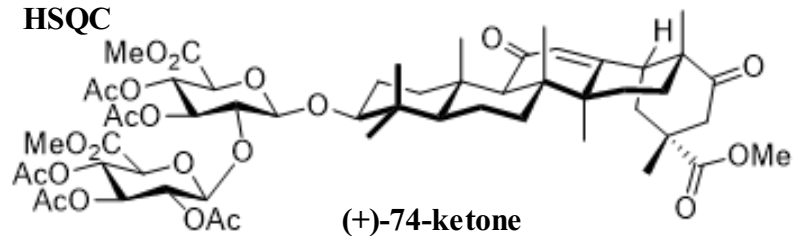
HSQC



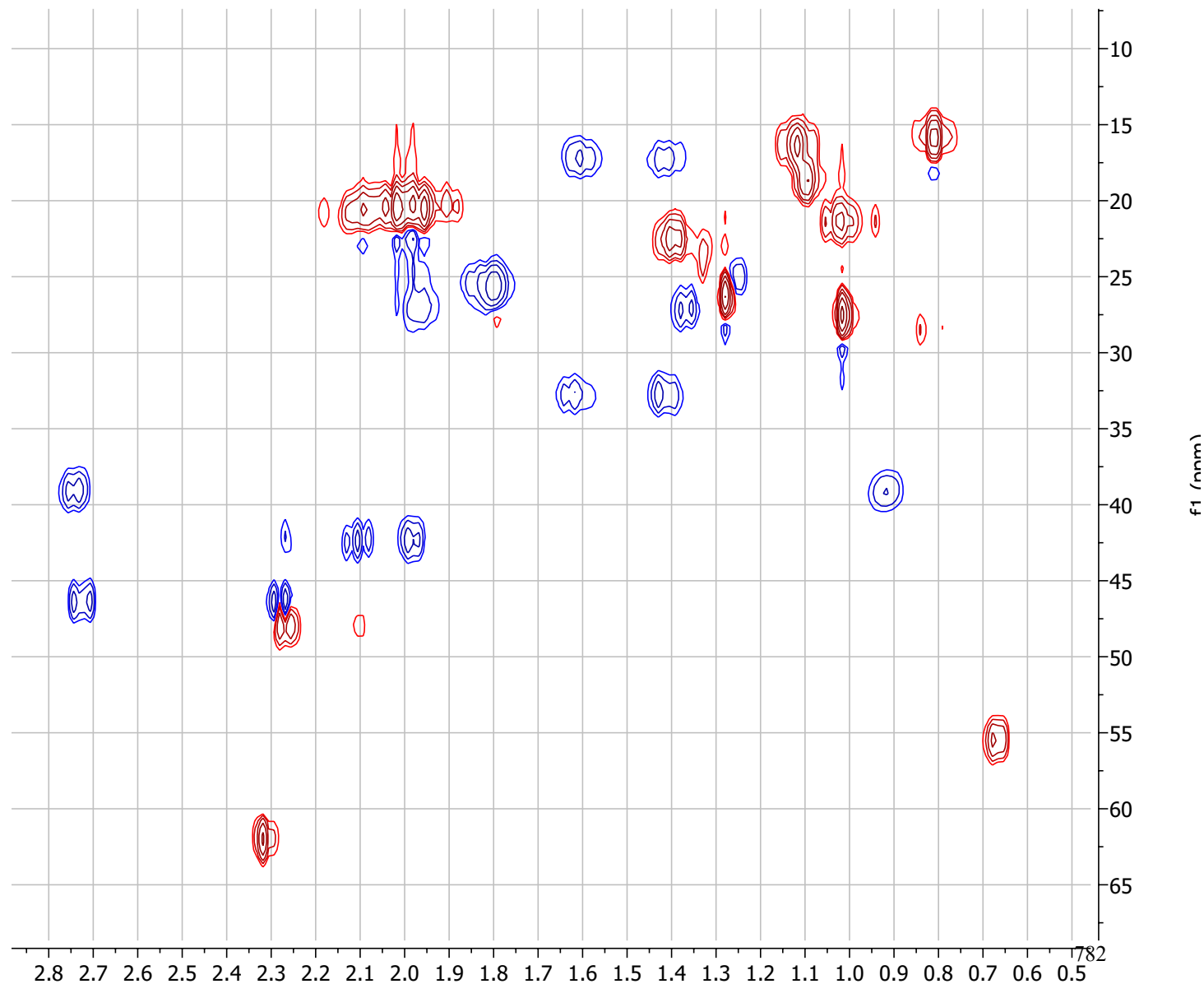
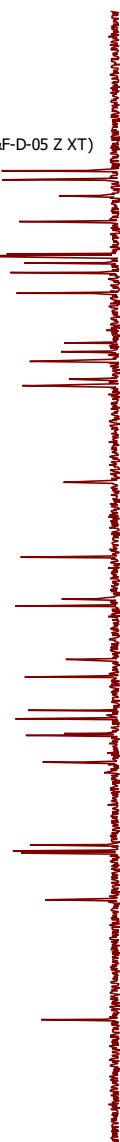
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpgisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(-35.9, -1874.5)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)



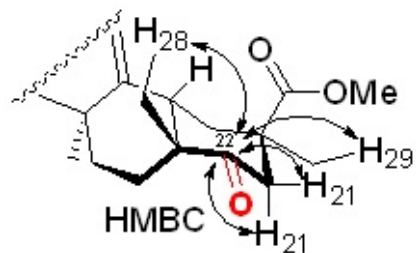
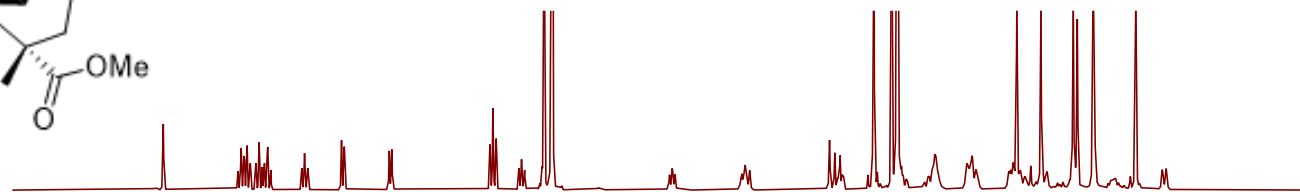
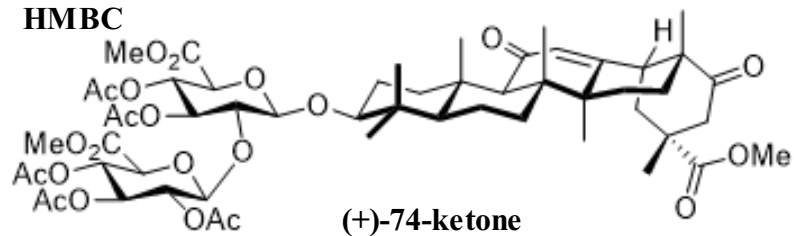
HSQC



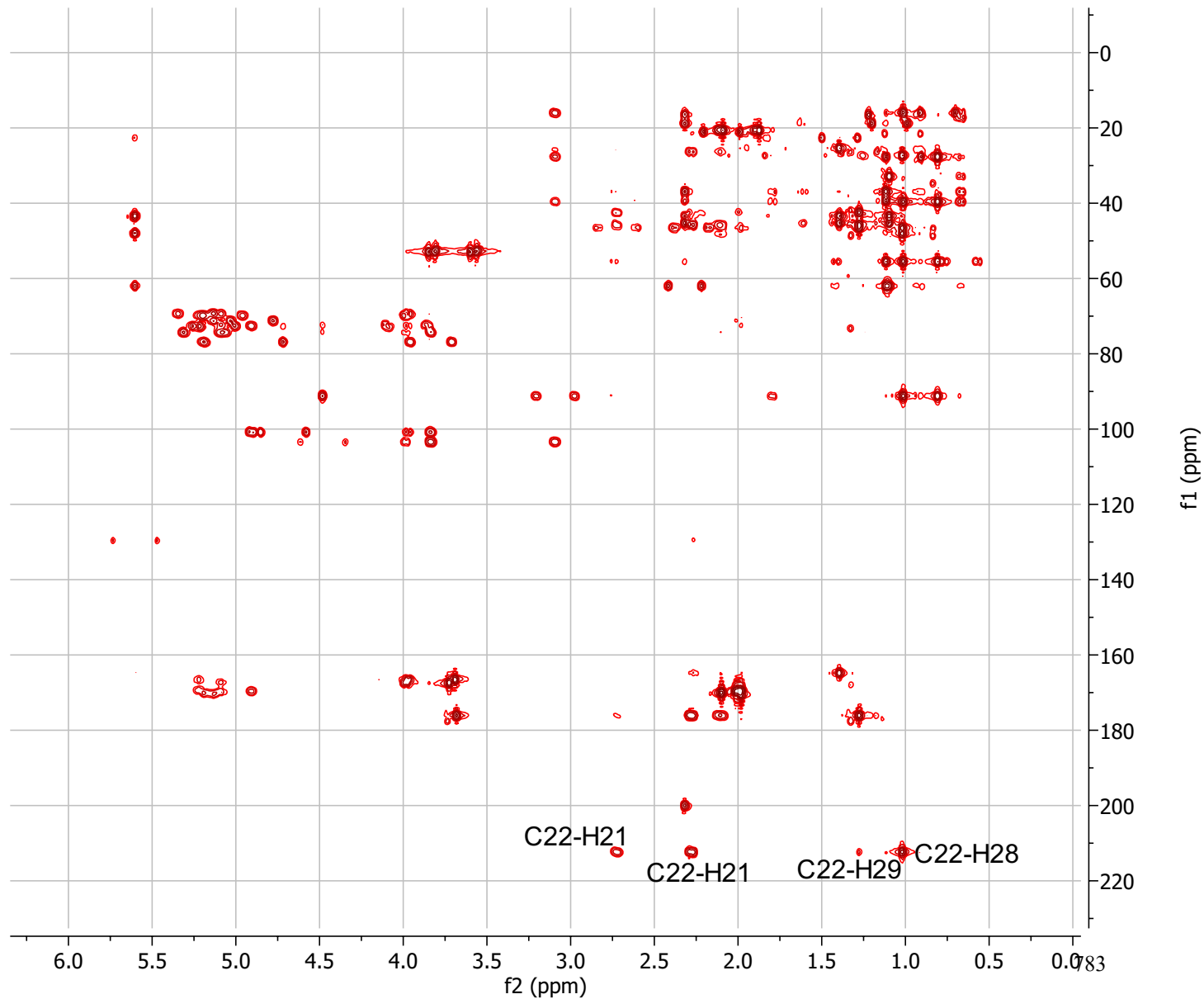
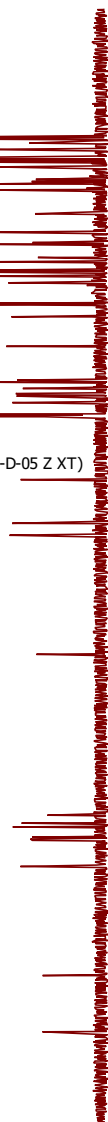
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpcisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(-35.9, -1874.5)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)



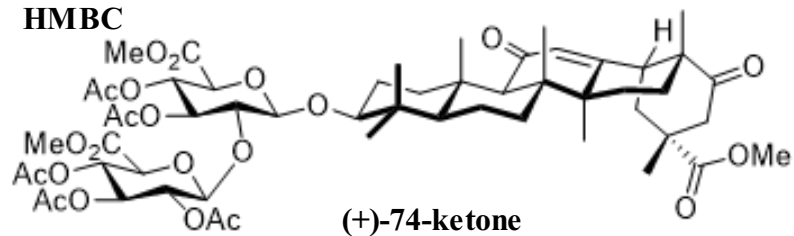
HMBC



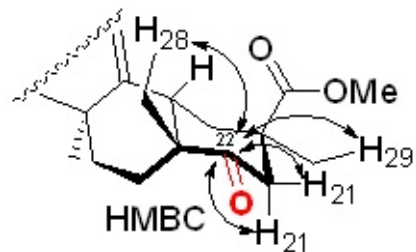
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-36.5, -1870.9)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



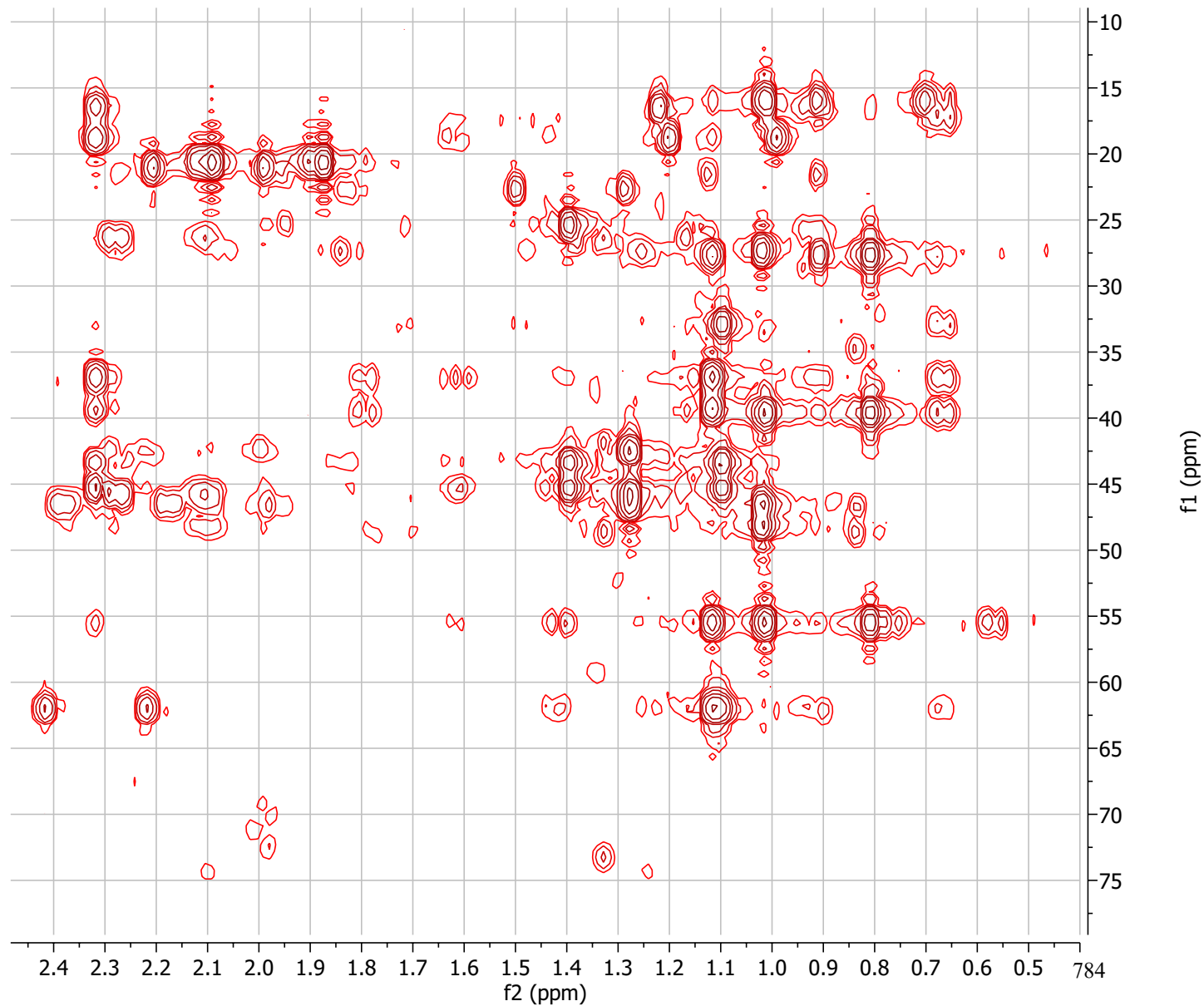
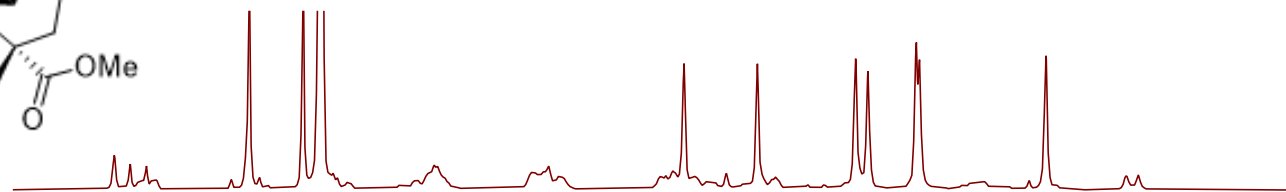
HMBC



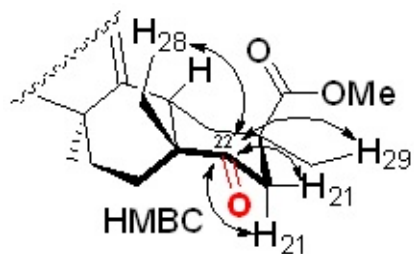
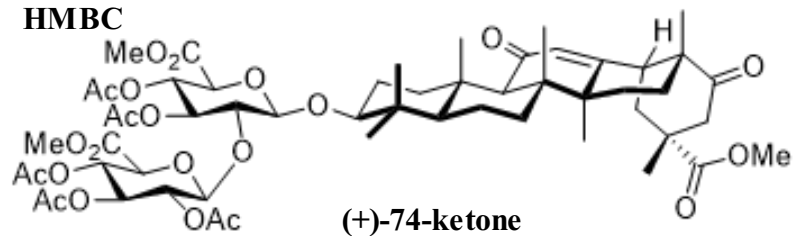
(+)-74-ketone



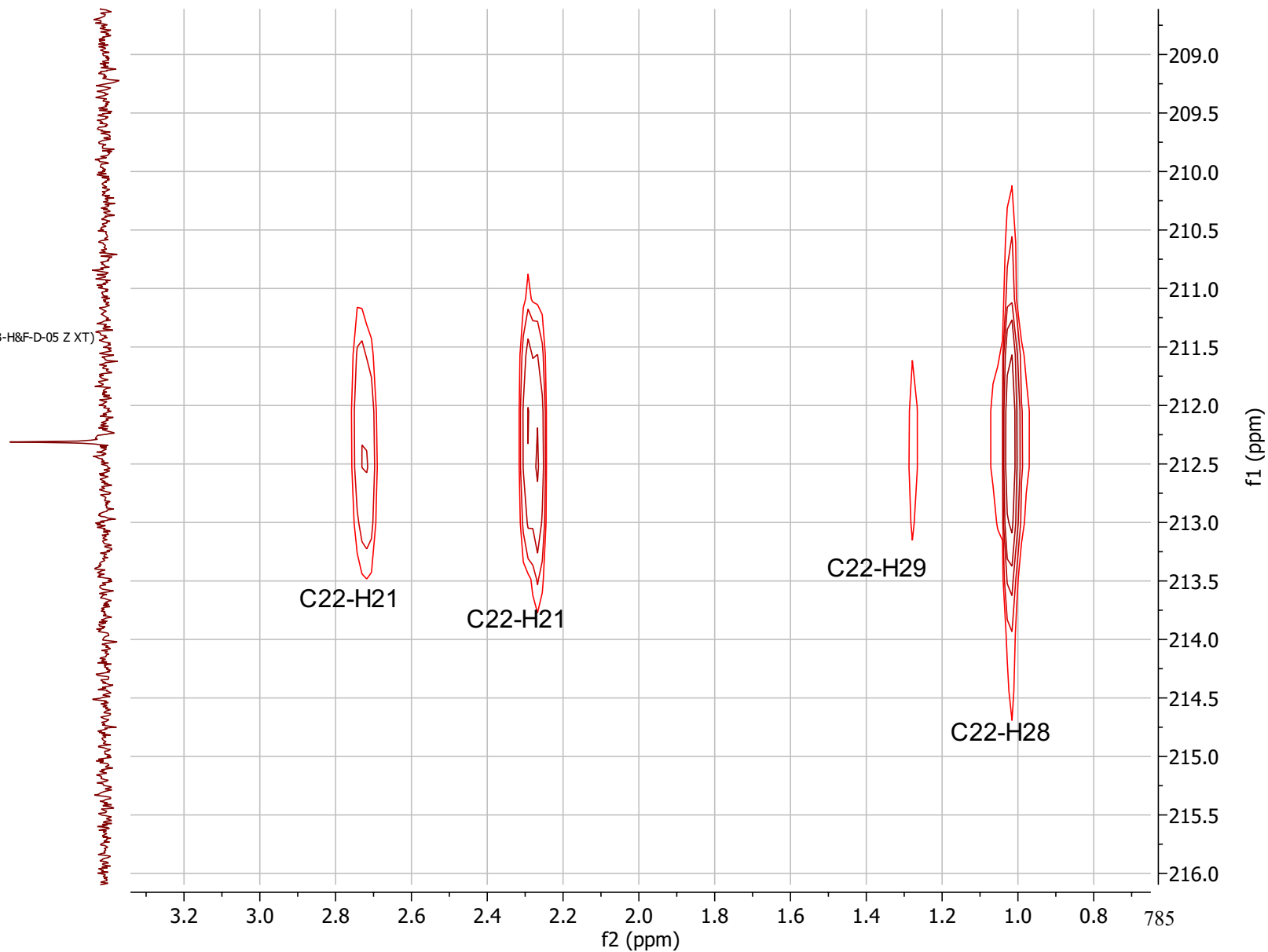
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-36.5, -1870.9)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



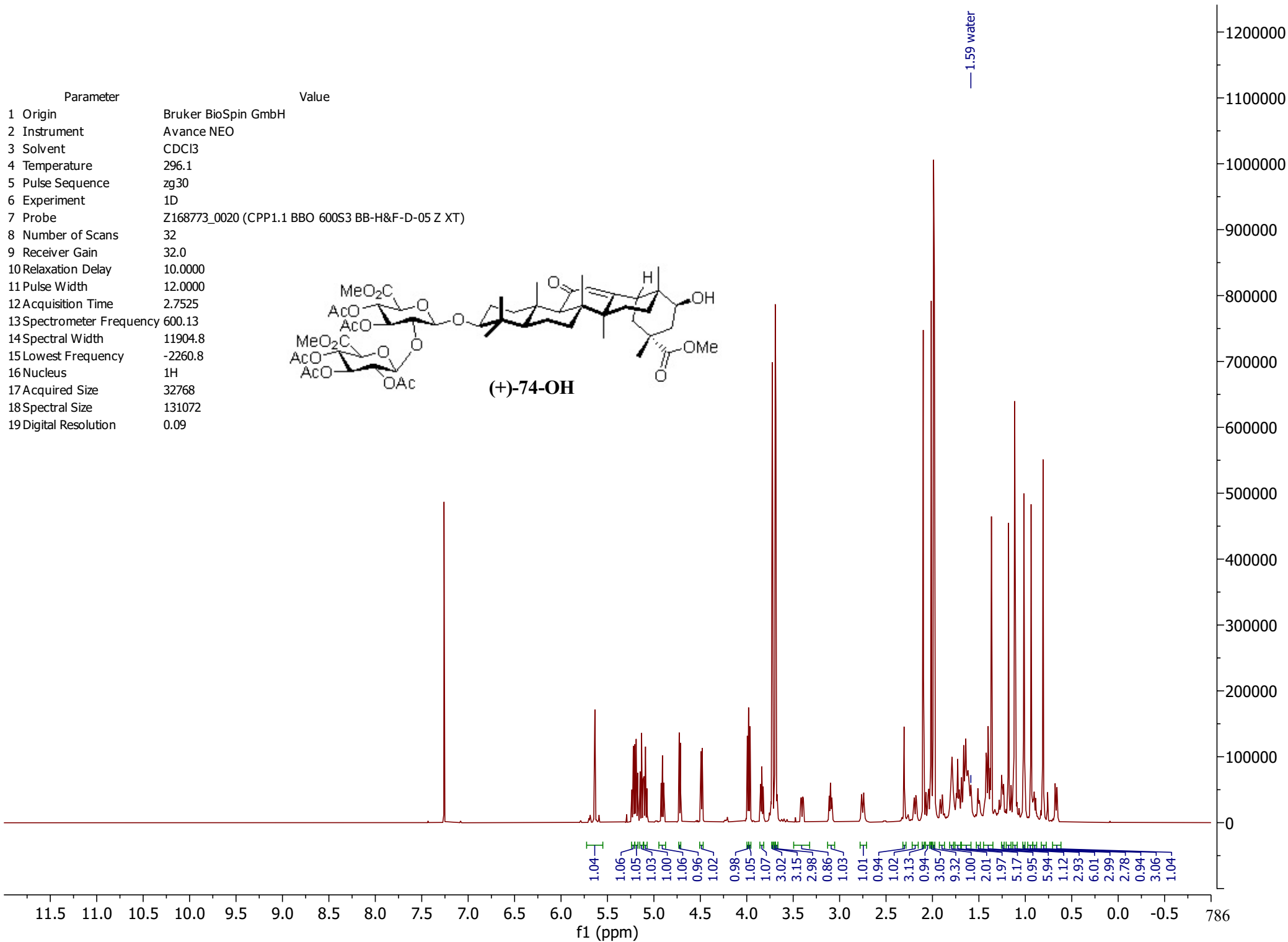
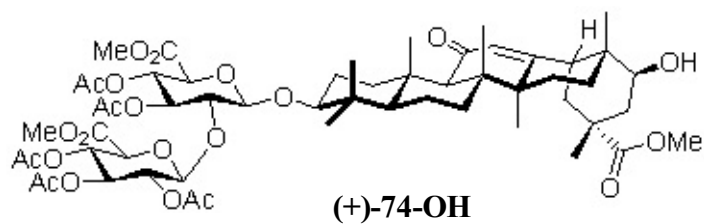
HMBC

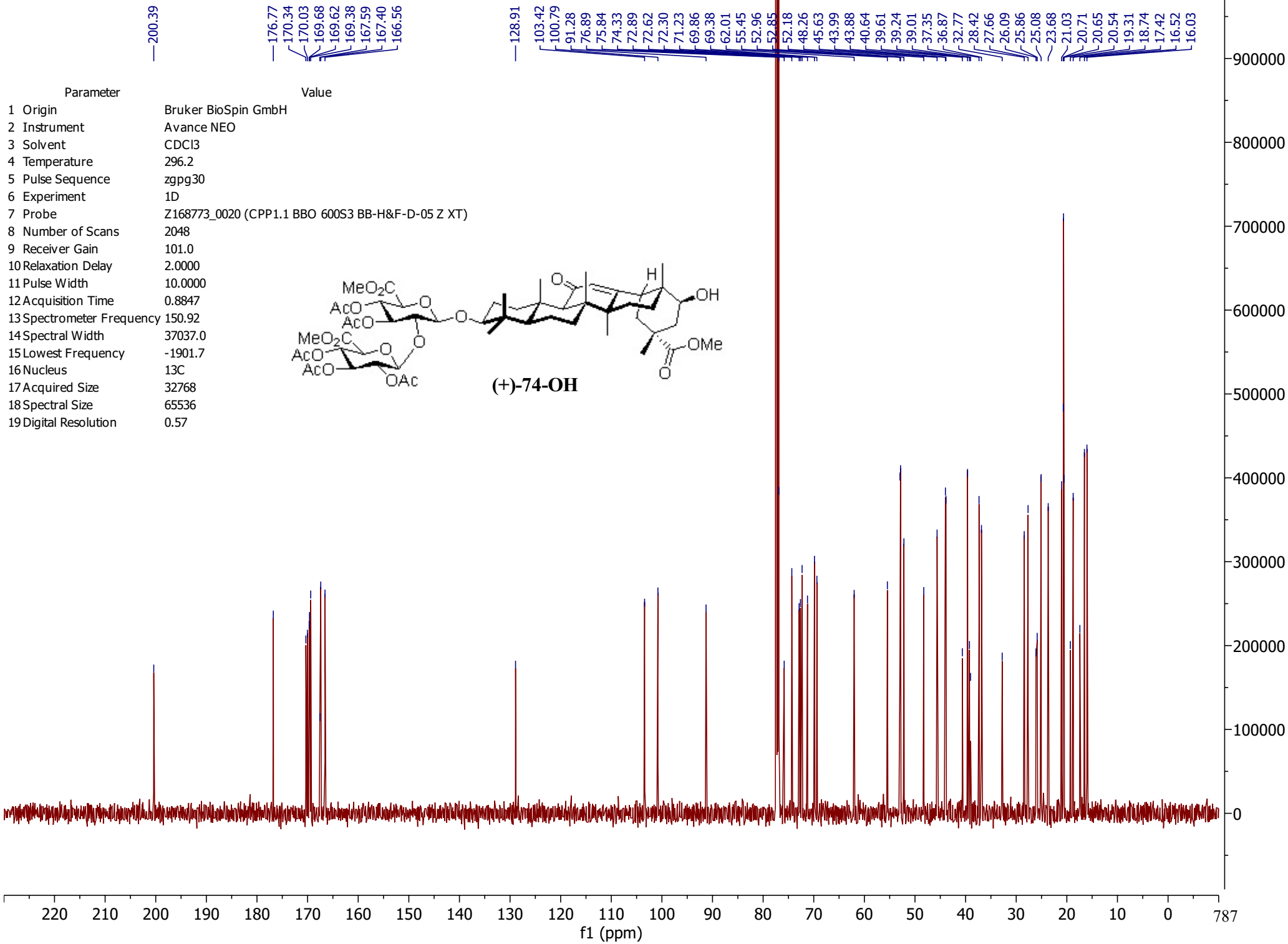


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-36.5, -1870.9)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)

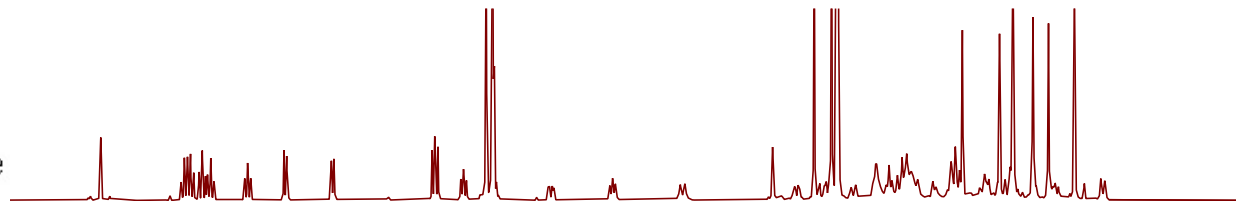
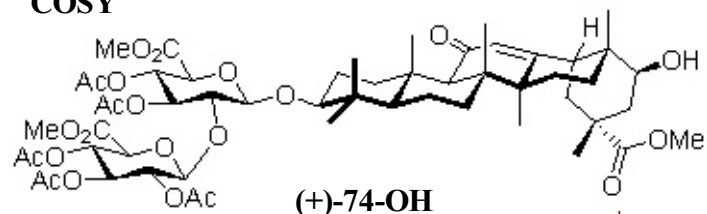


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.8
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

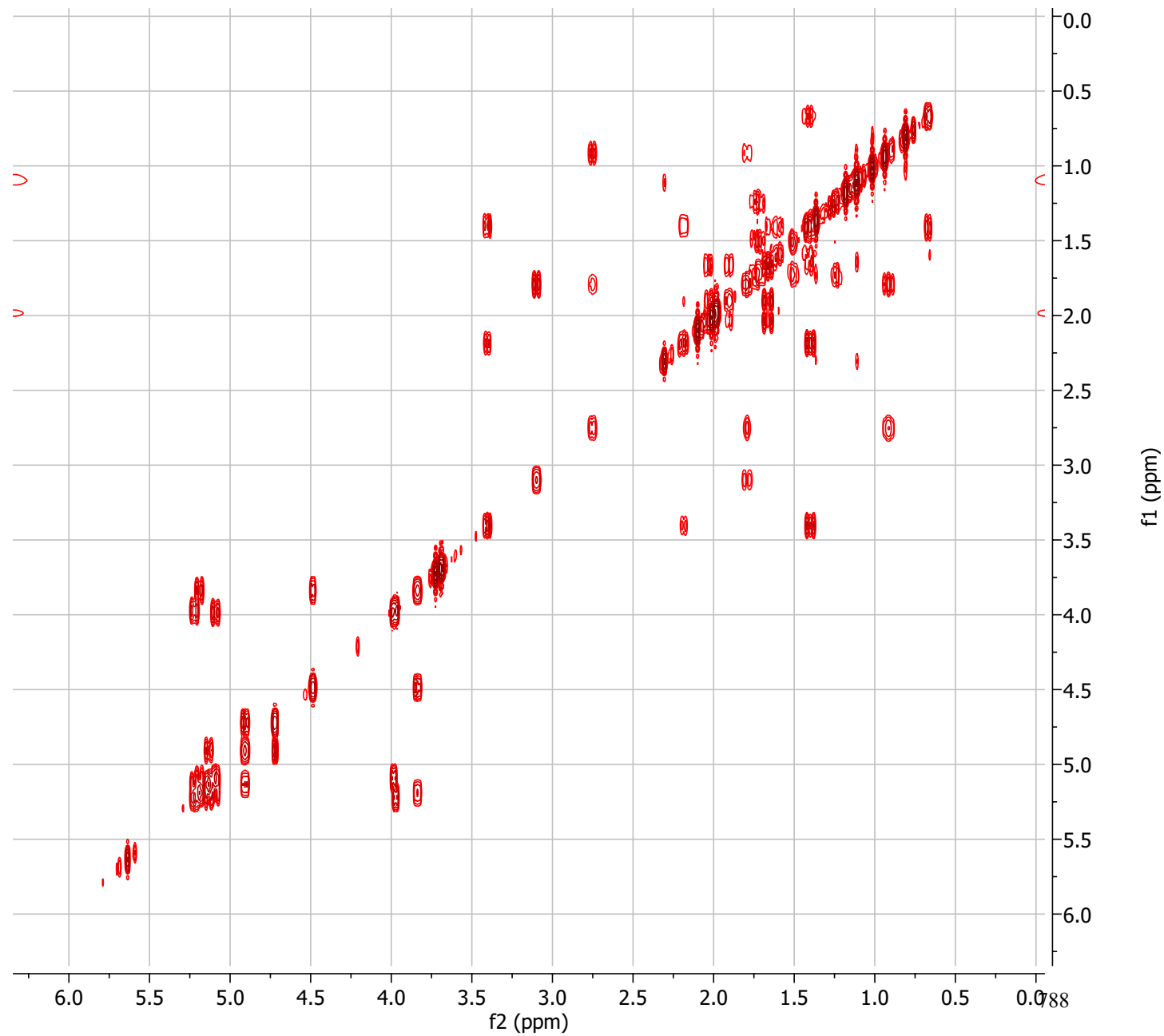




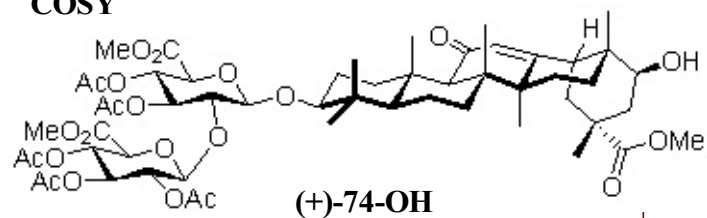
COSY



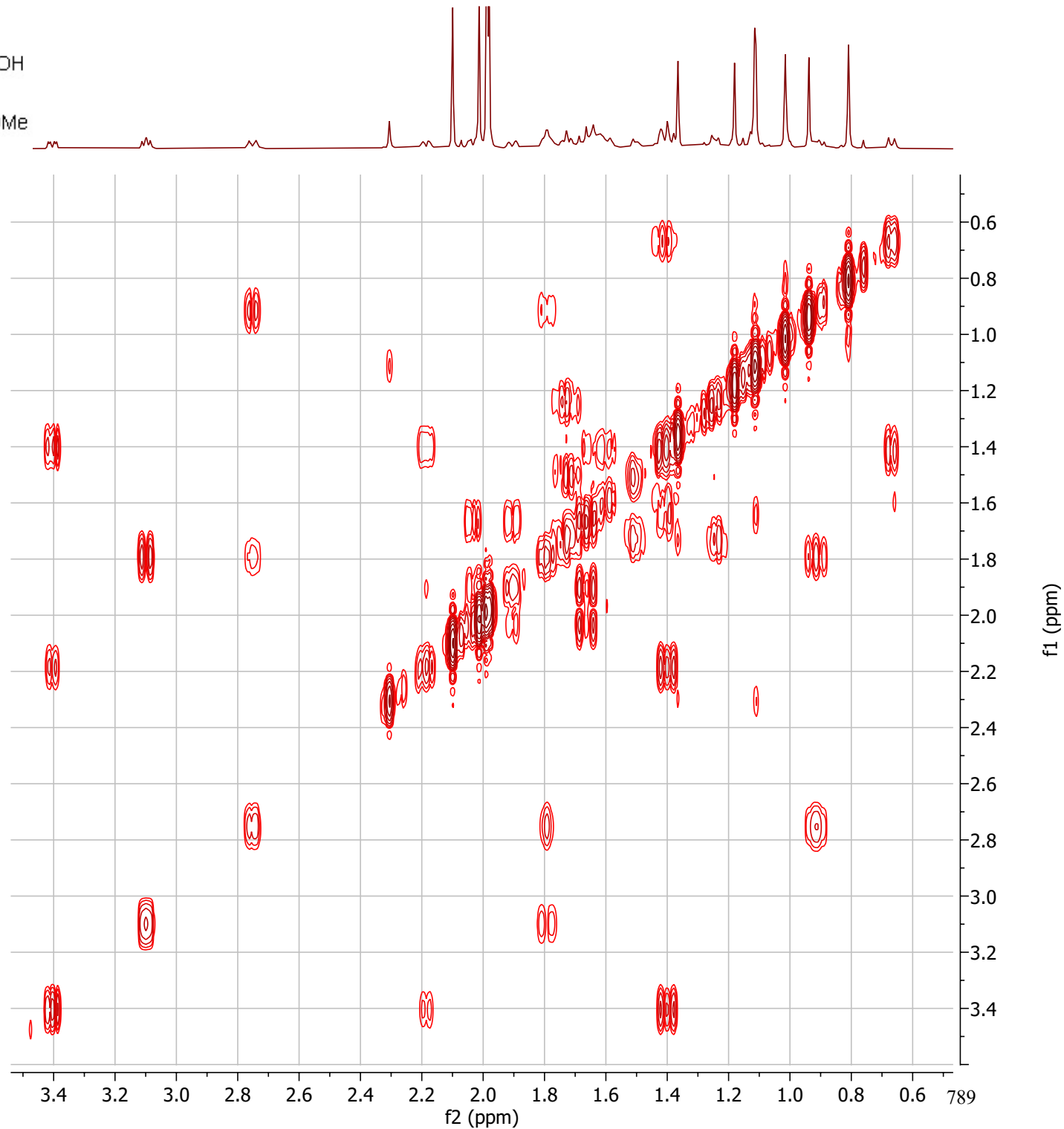
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3607
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(-36.8, -36.8)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



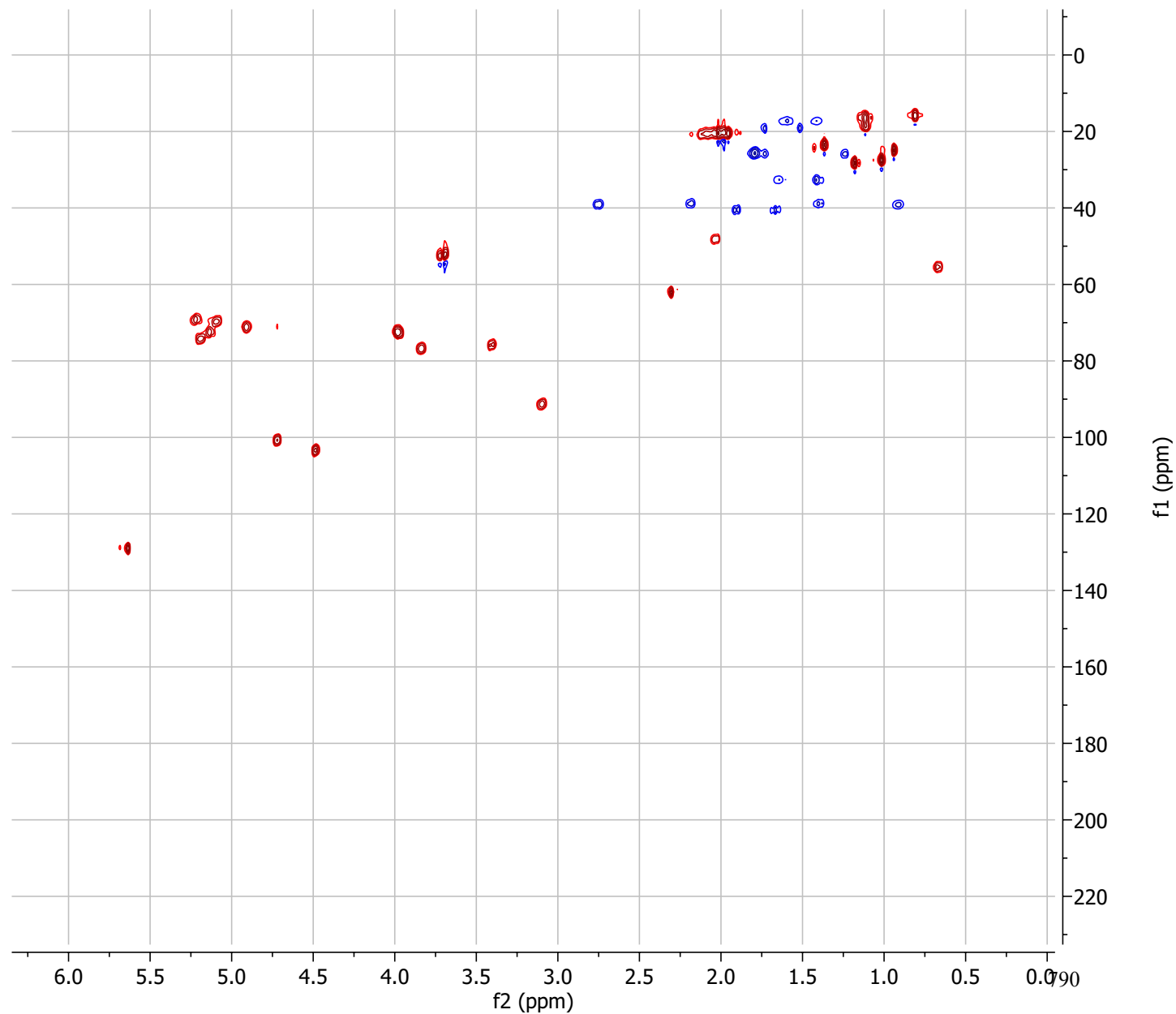
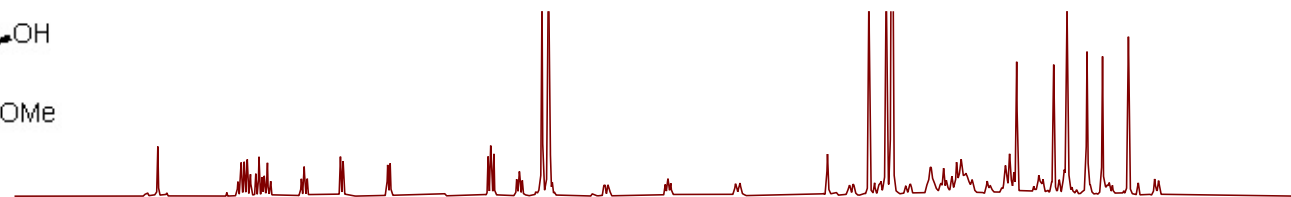
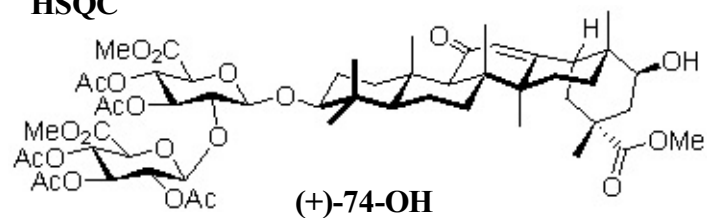
COSY



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.3607
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(-36.8, -36.8)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)

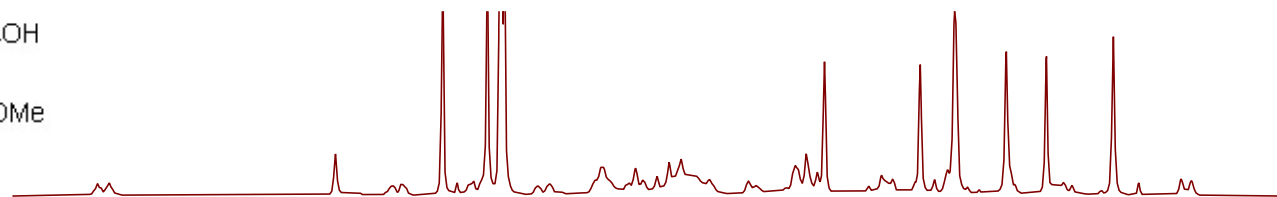
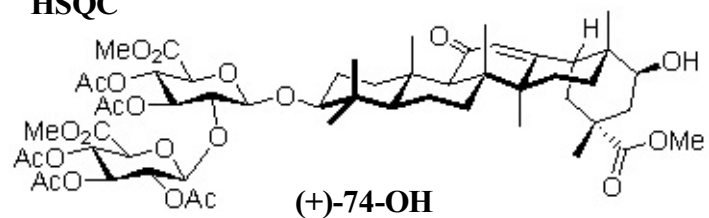


HSQC

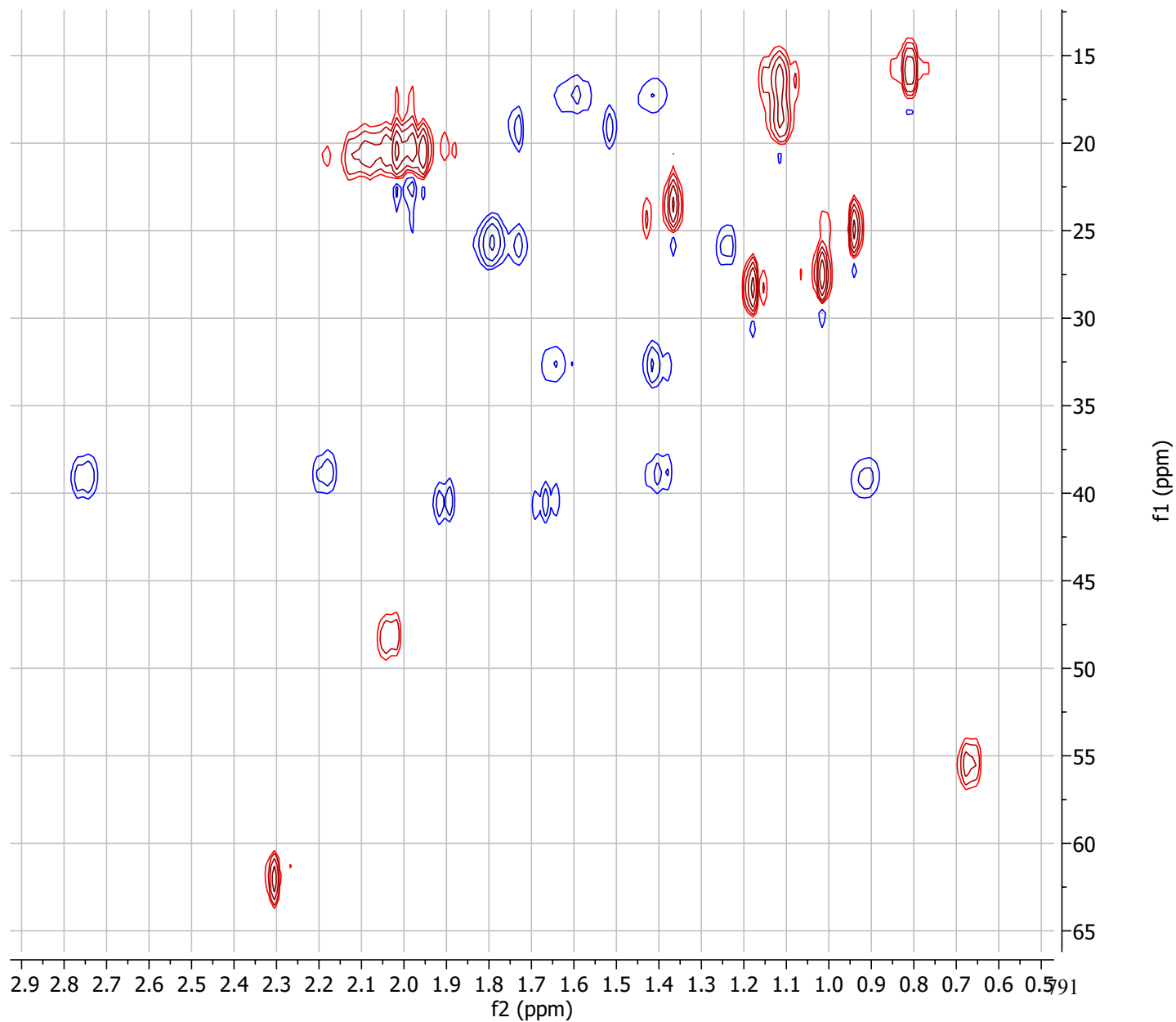
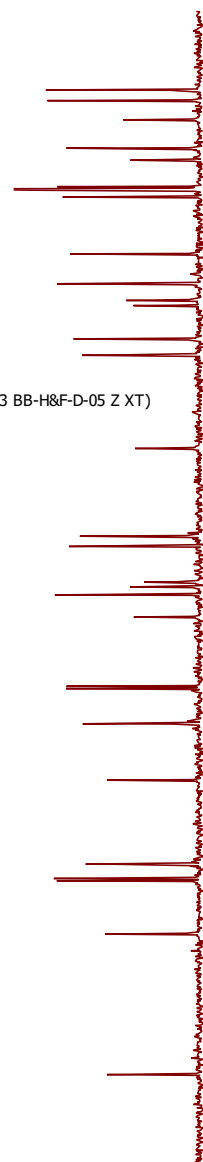


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hsqcedtgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(-36.4, -1871.6)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)

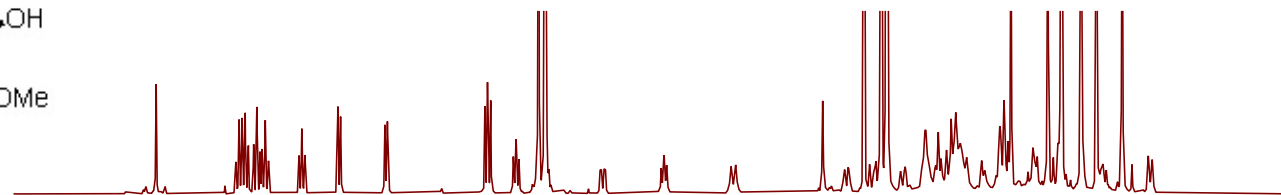
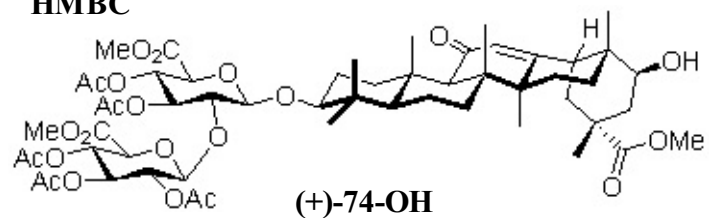
HSQC



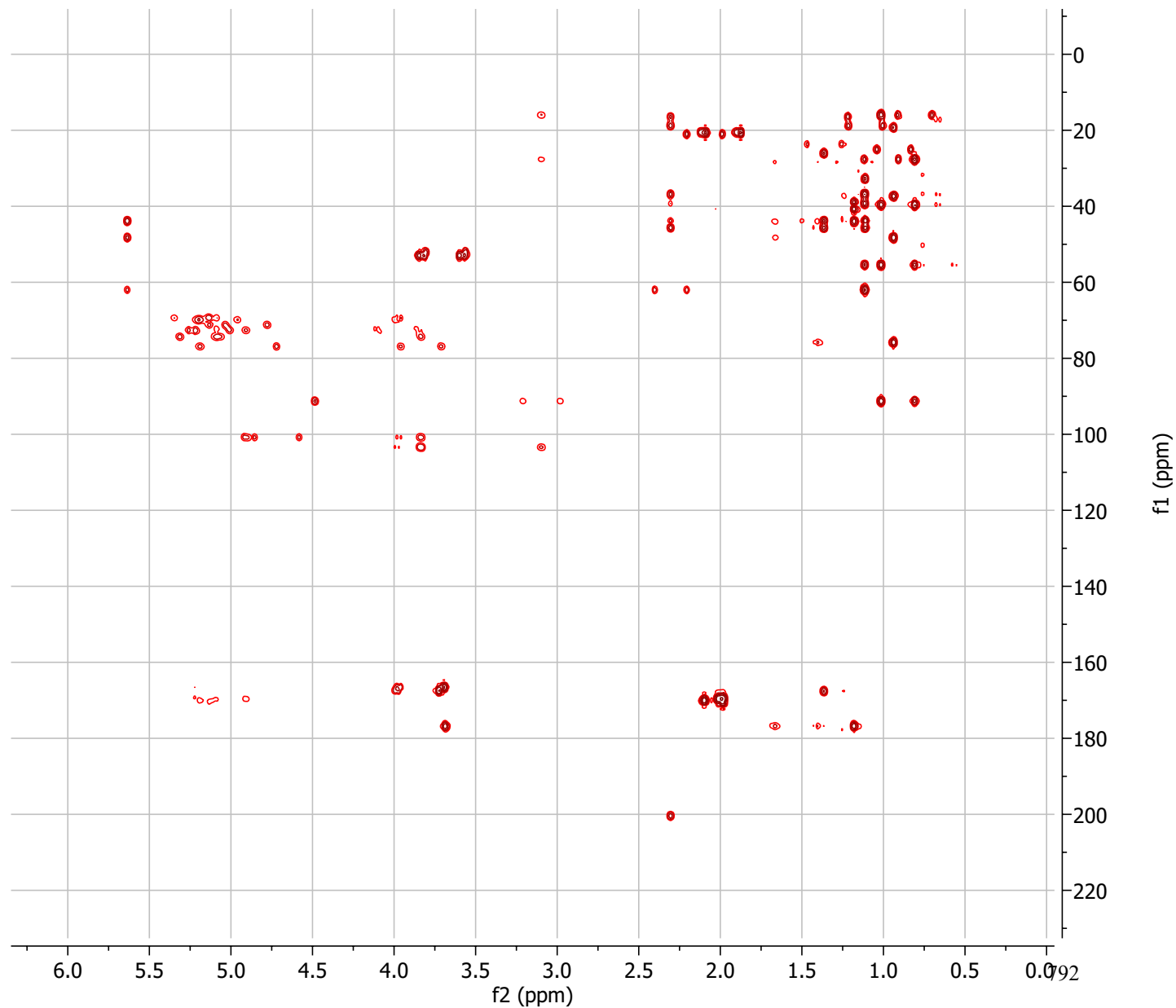
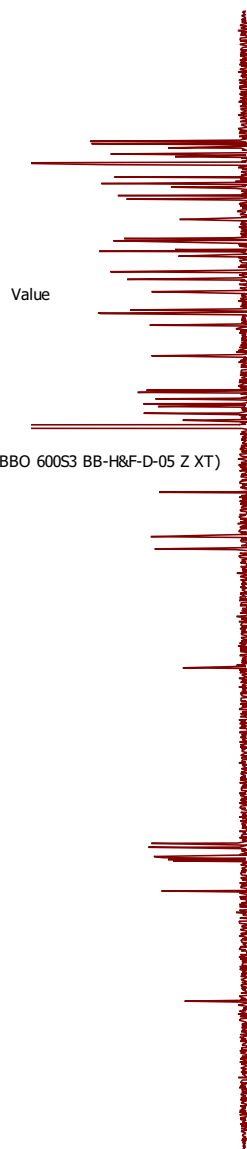
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hsqcedtgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(-36.4, -1871.6)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)



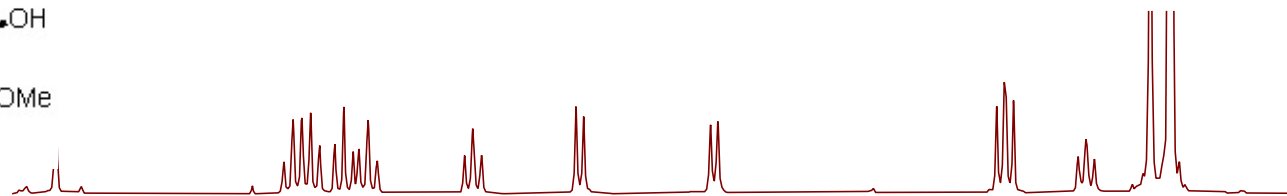
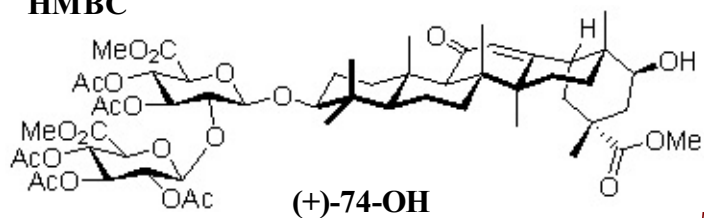
HMBC



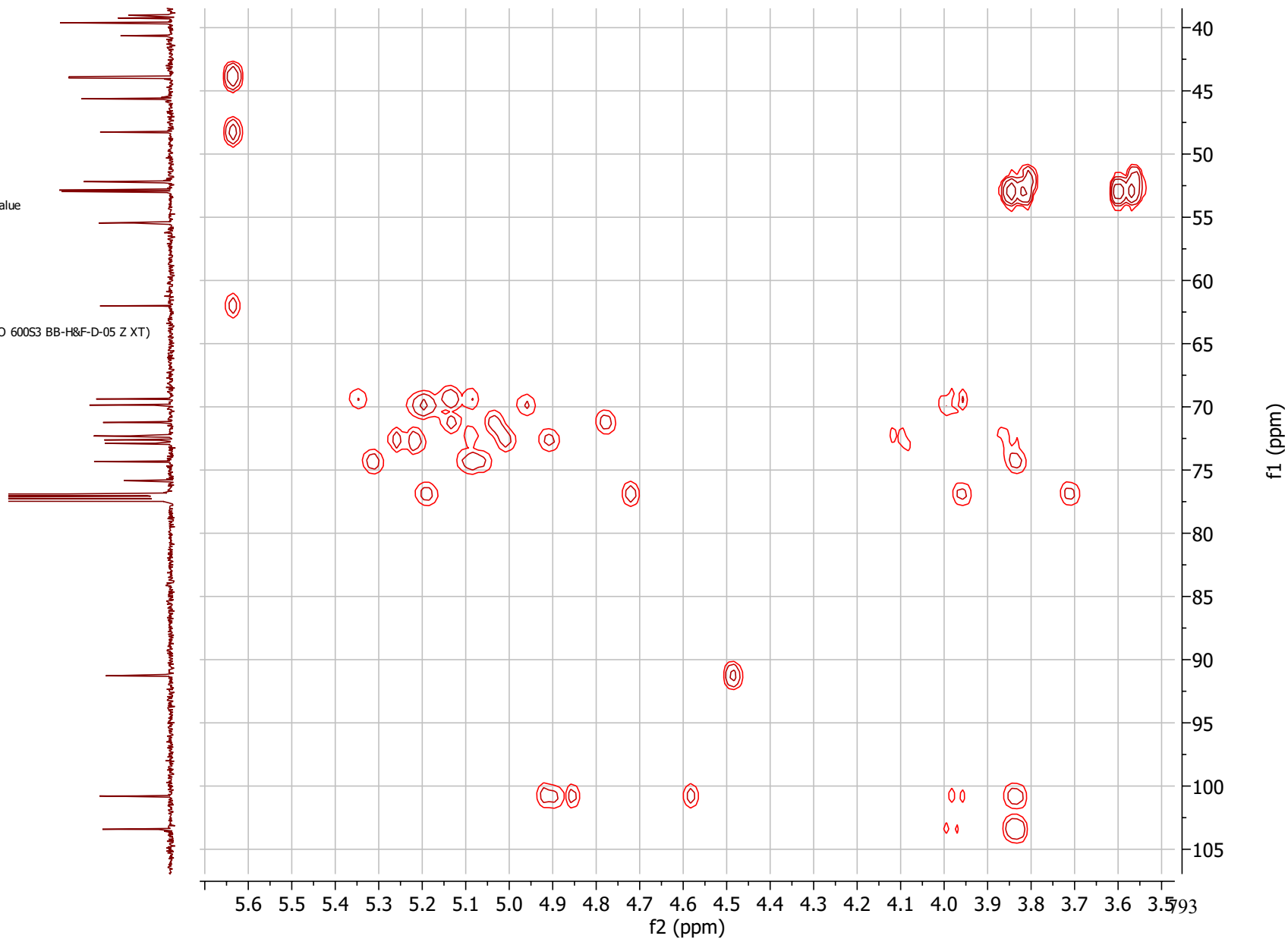
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-36.5, -1872.1)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



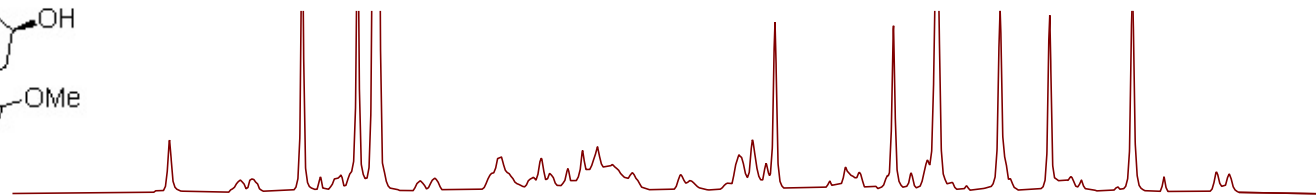
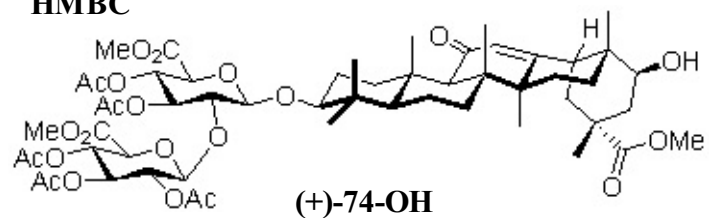
HMBC



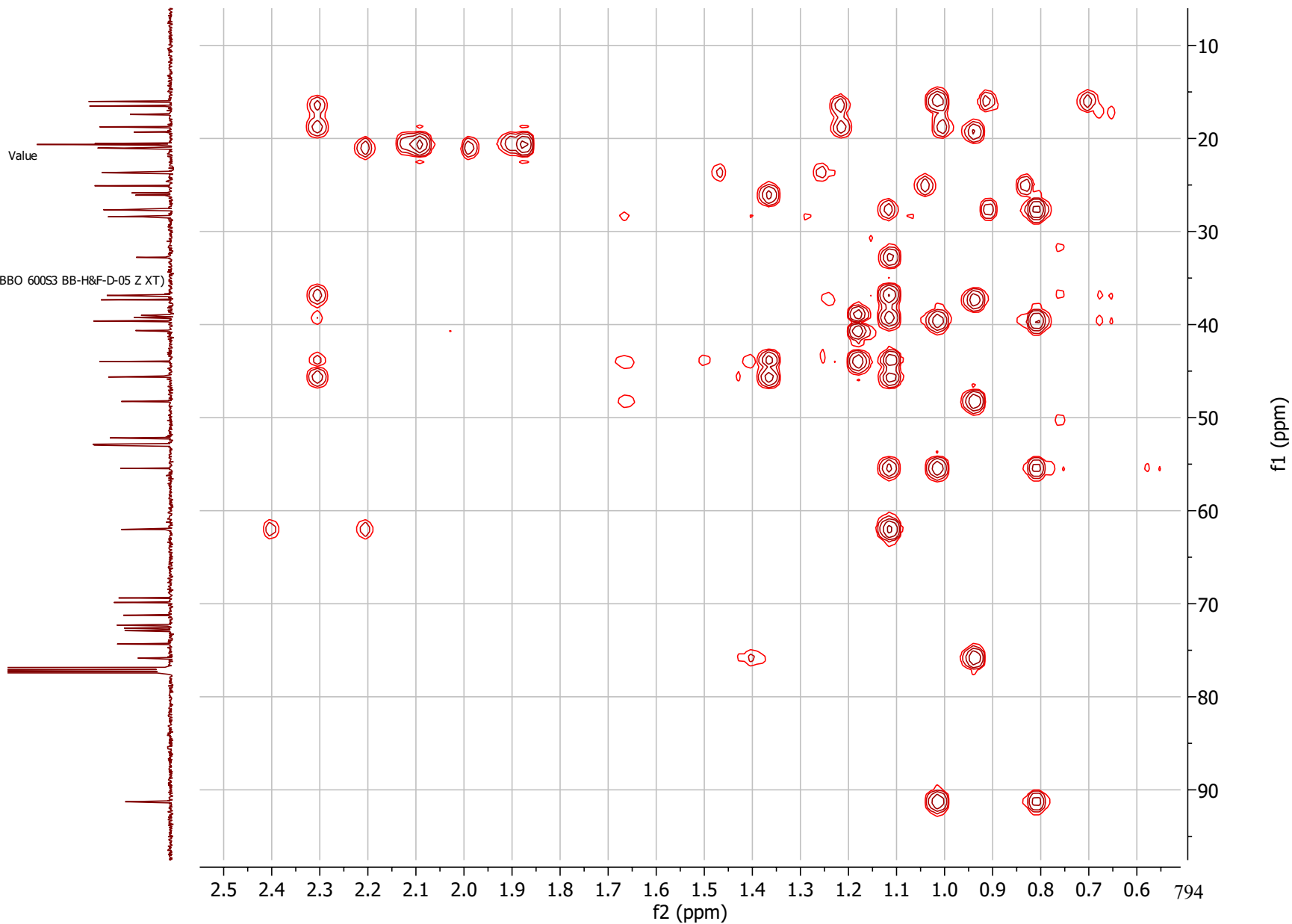
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency	(600.13, 150.92)
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-36.5, -1872.1)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



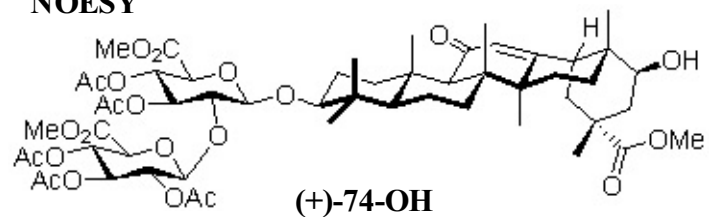
HMBC



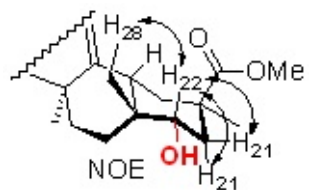
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-36.5, -1872.1)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



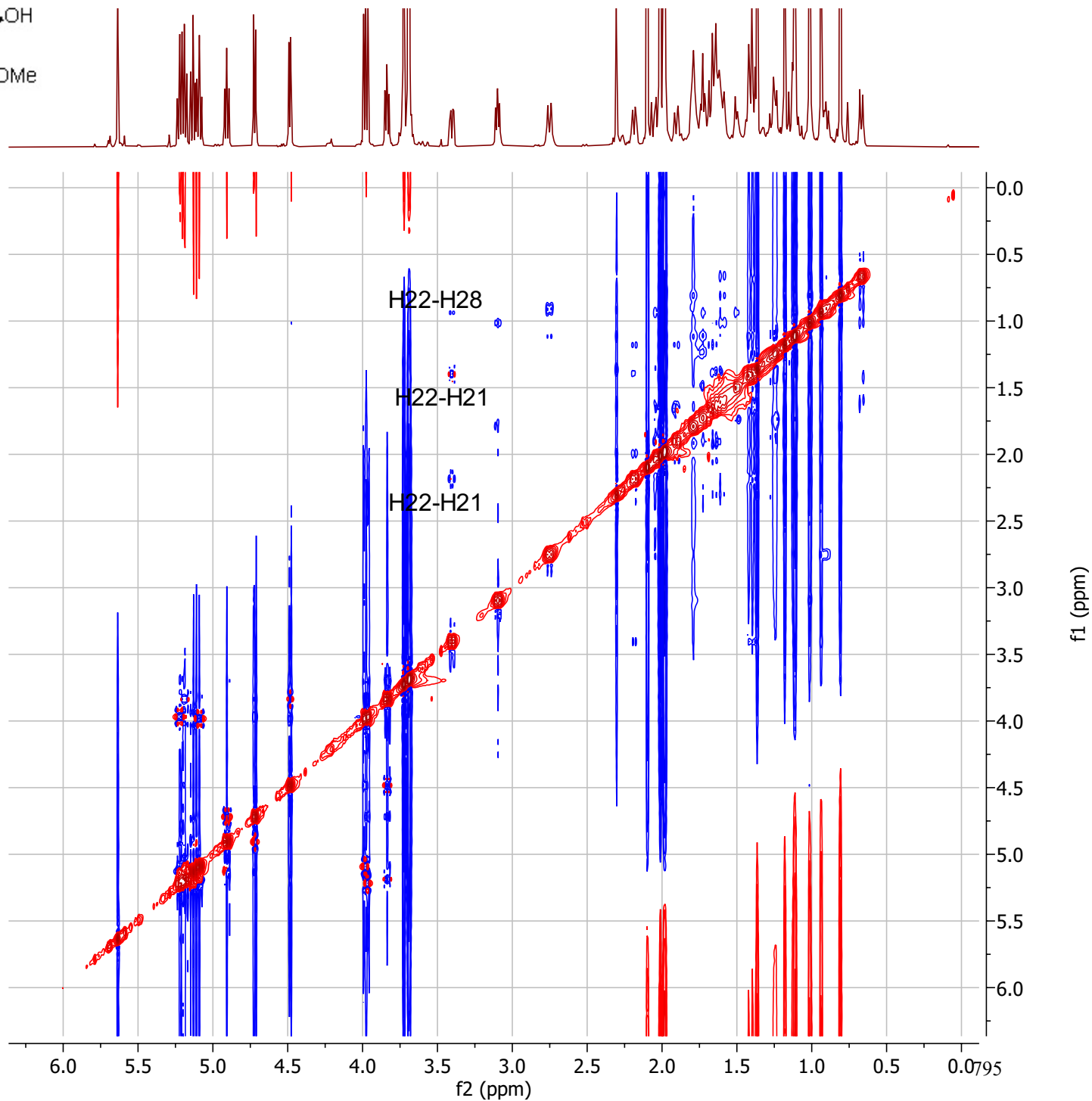
NOESY



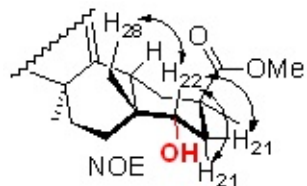
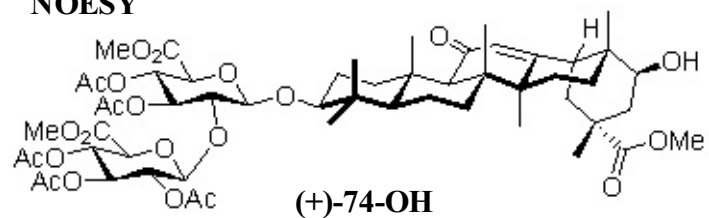
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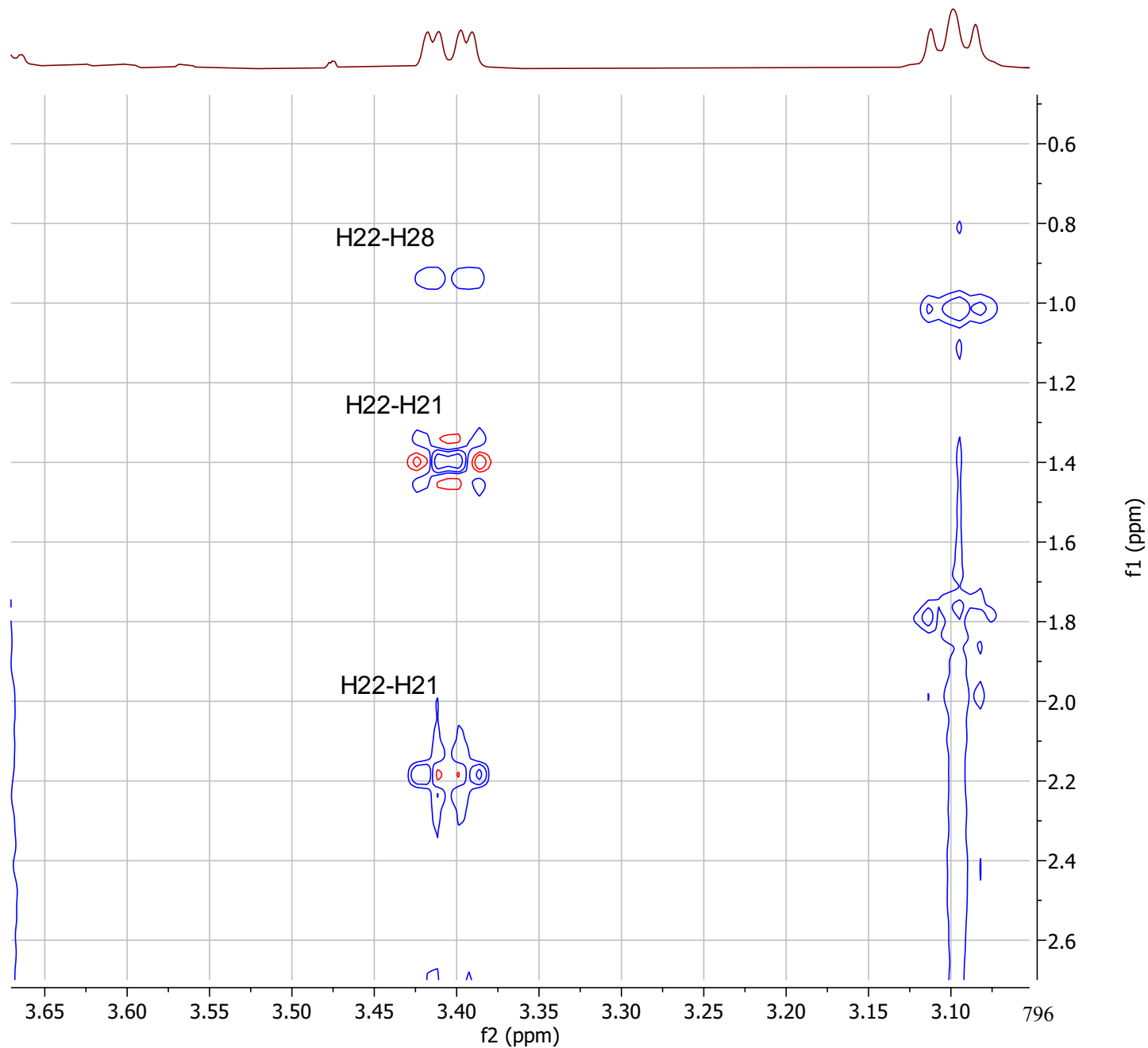
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCI ₃
4 Temperature	296.1
5 Pulse Sequence	noesygpqhpp
6 Experiment	NOESY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.8894
11 Pulse Width	12.0000
12 Acquisition Time	0.3154
13 Spectrometer Frequency (500.35, 500.35)	
14 Spectral Width	(3246.8, 3246.8)
15 Lowest Frequency	(-62.3, -62.1)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.17, 3.17)



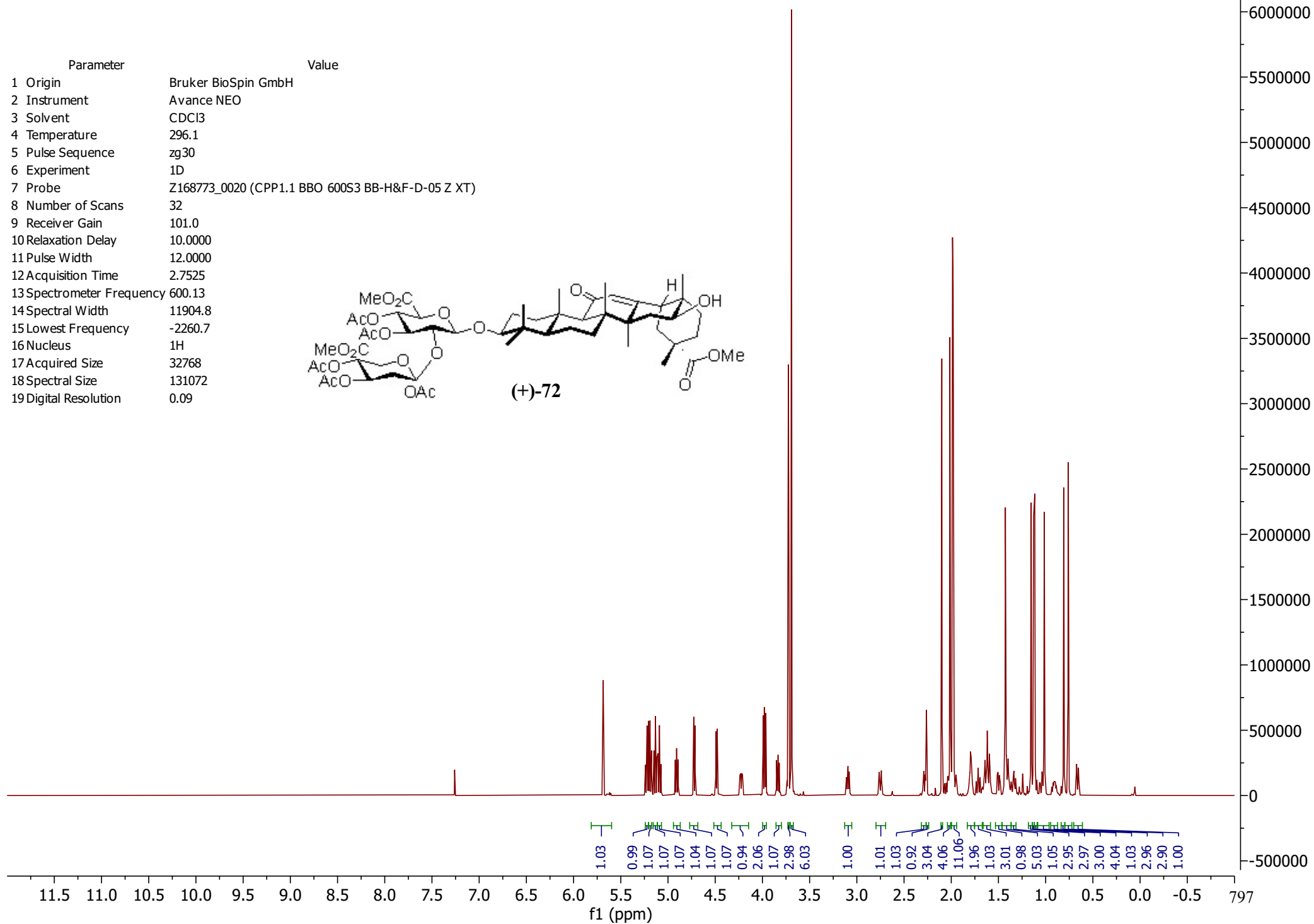
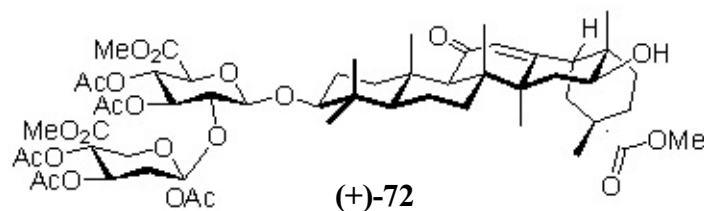
NOESY

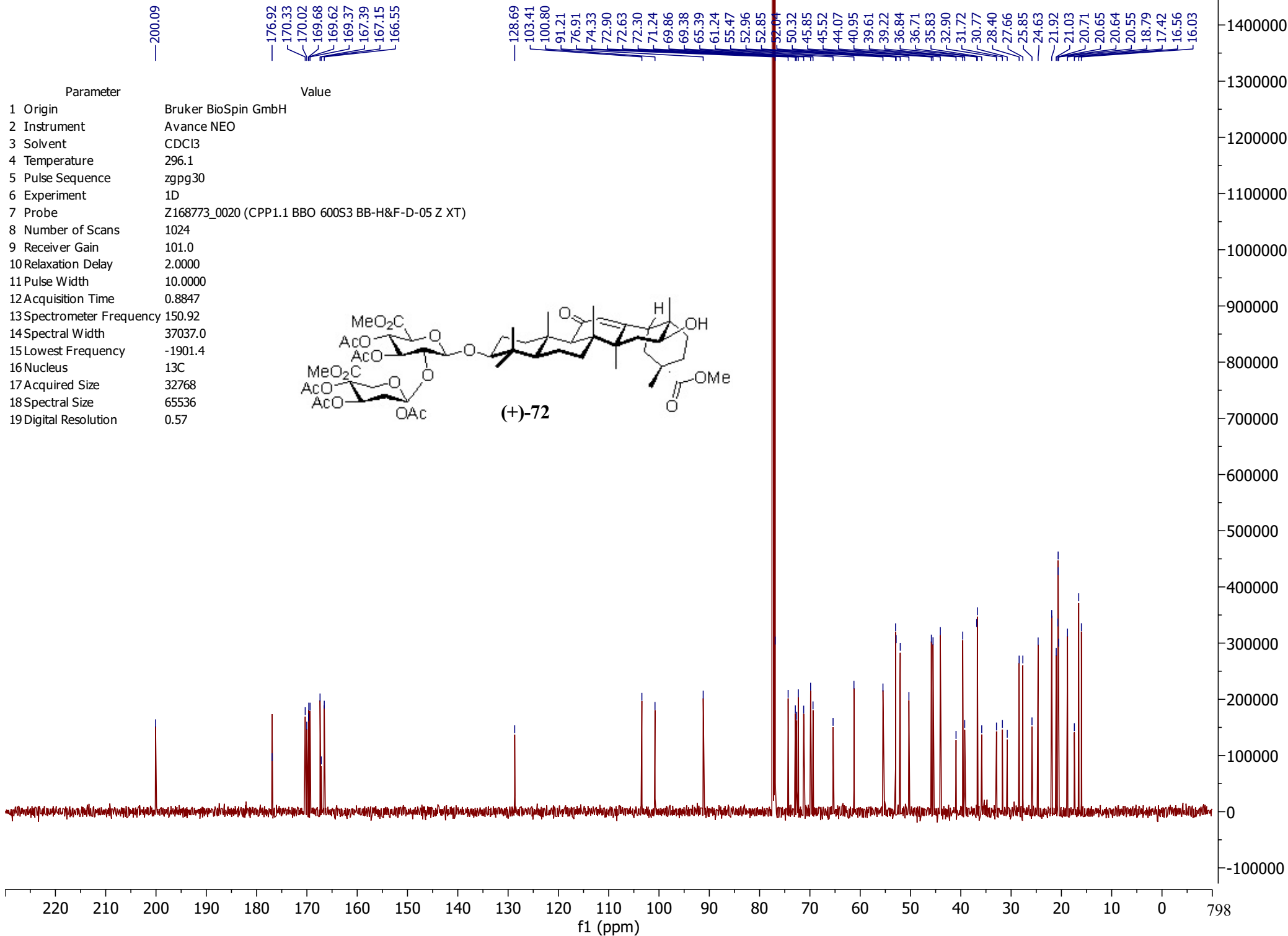


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCI3
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.8894
11 Pulse Width	12.0000
12 Acquisition Time	0.3154
13 Spectrometer Frequency (500.35, 500.35)	
14 Spectral Width	(3246.8, 3246.8)
15 Lowest Frequency	(-62.3, -62.1)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.17, 3.17)



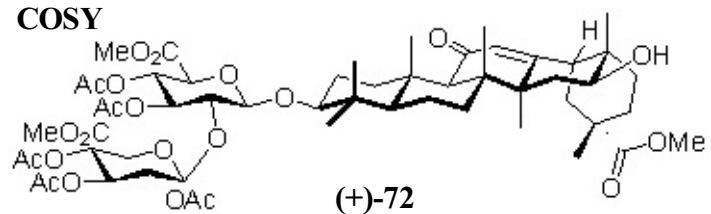
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	101.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.7
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



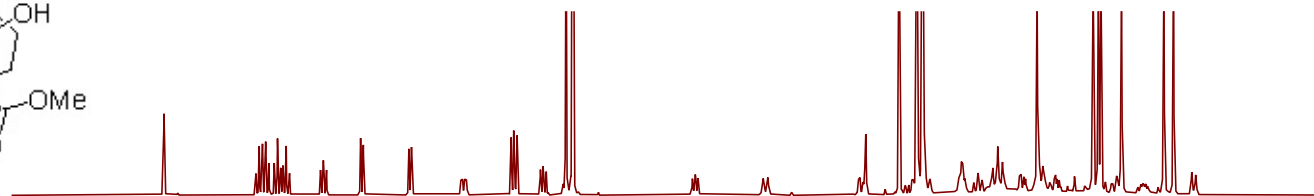


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	1024
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1901.4
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57

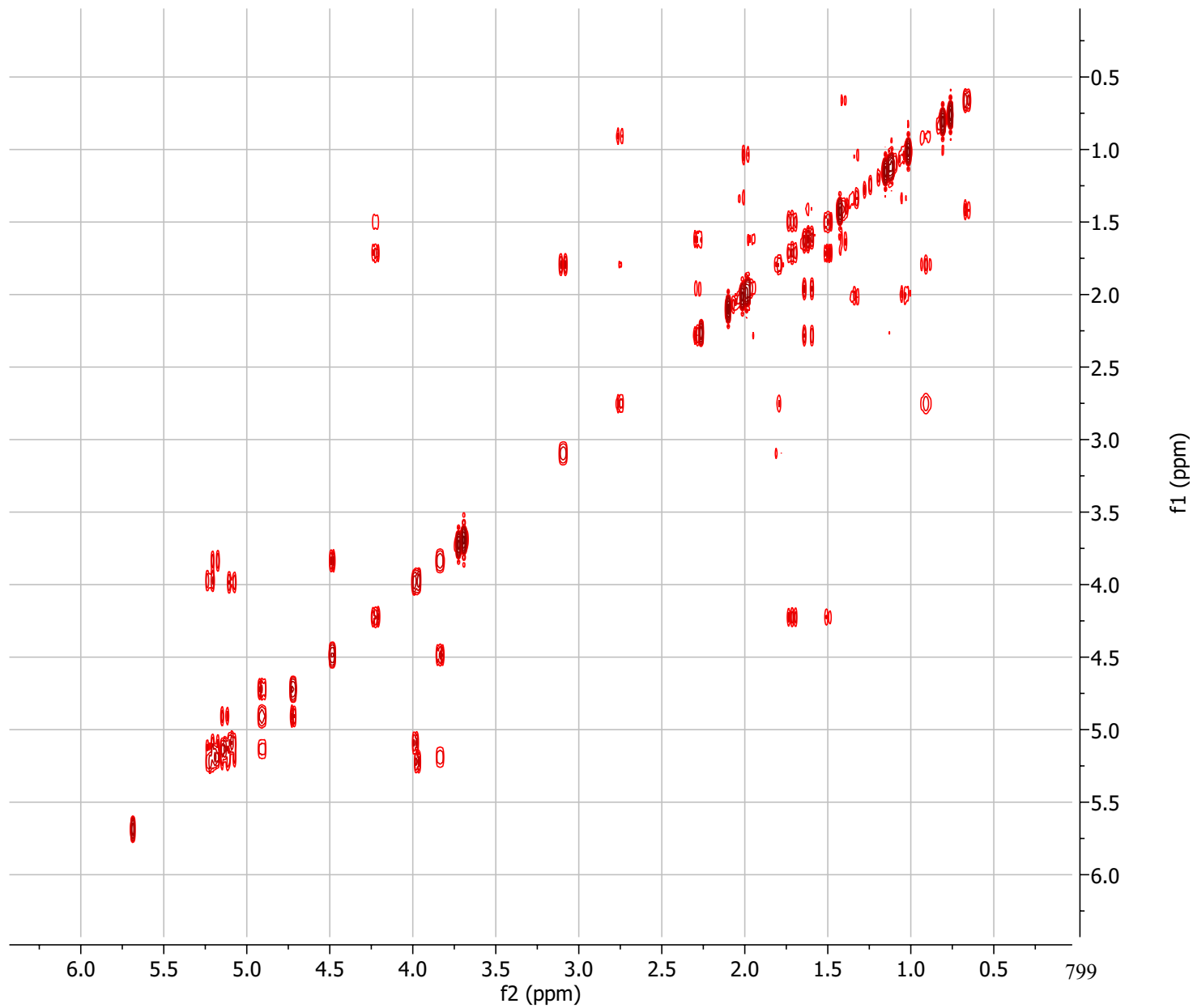
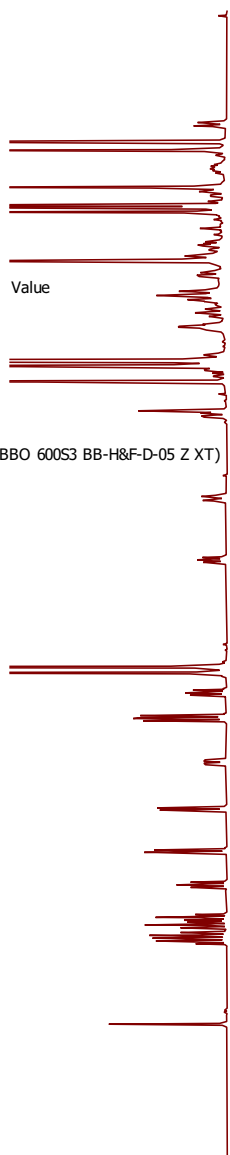
COSY



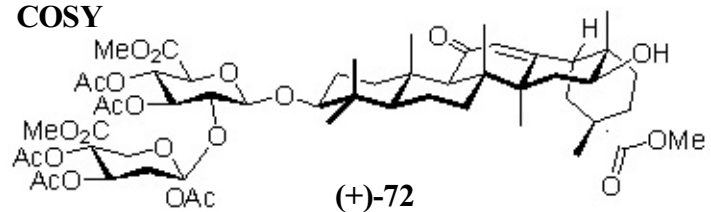
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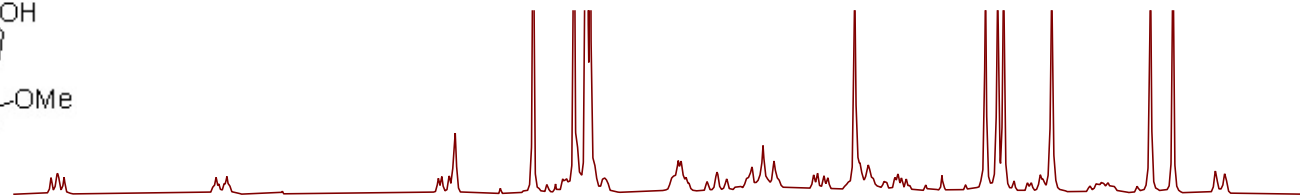
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.3689
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(12.9, 12.9)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



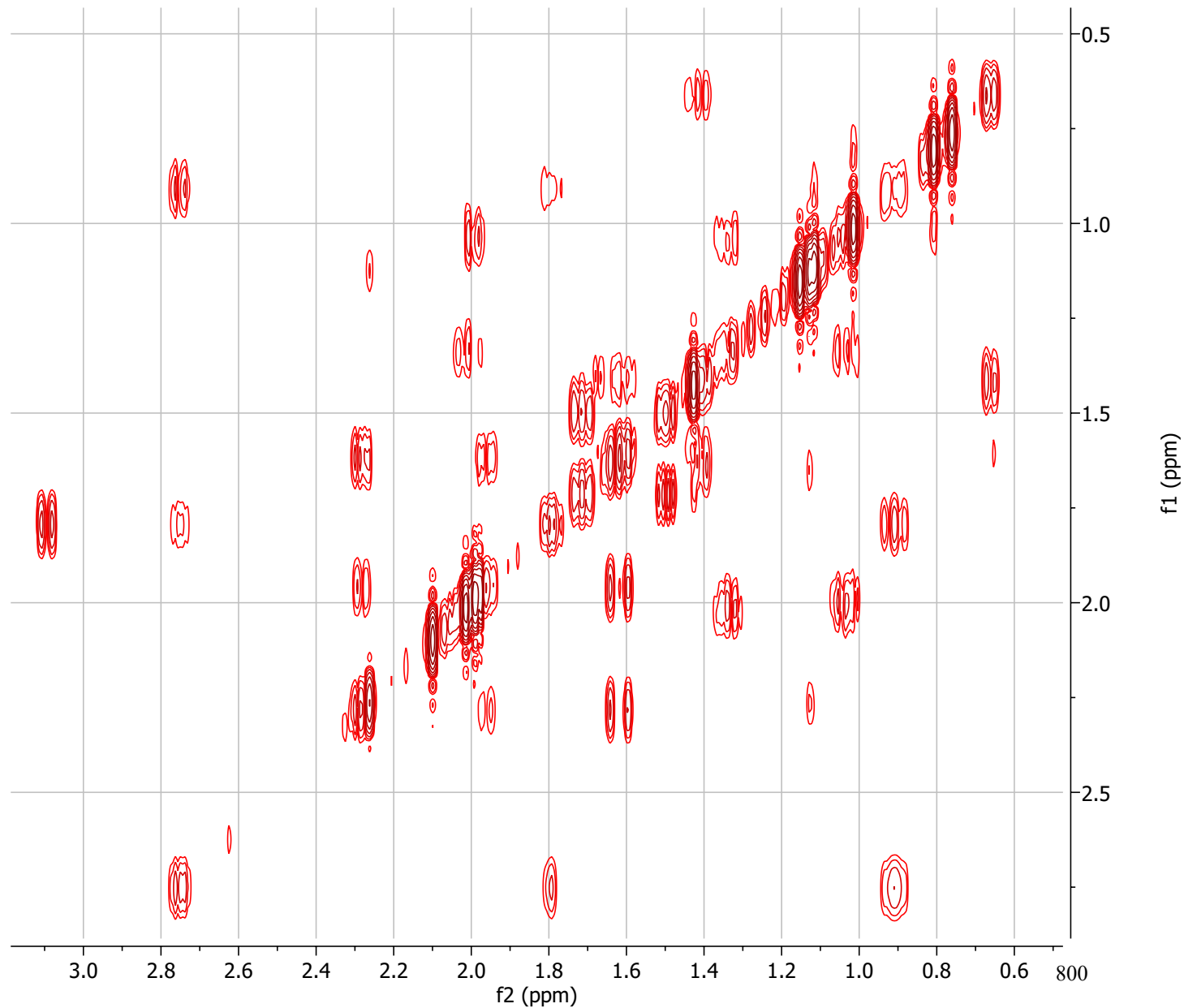
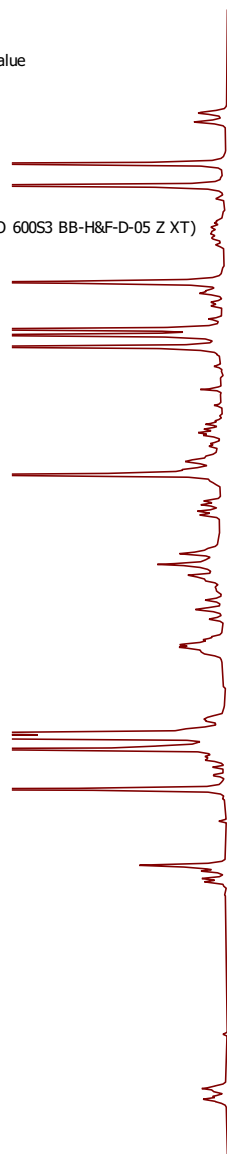
COSY



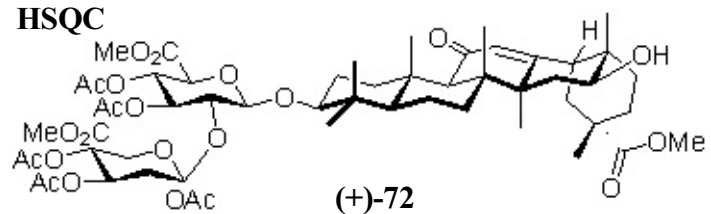
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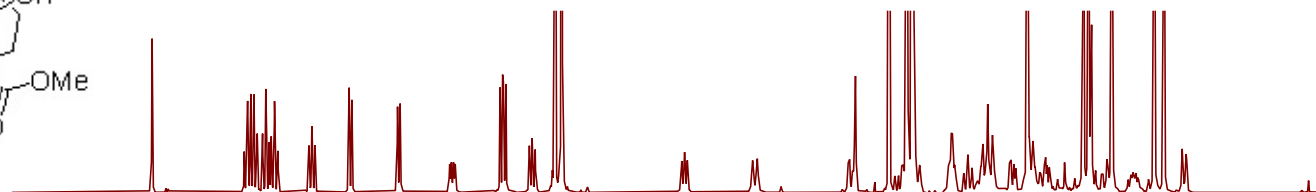
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	64.0
10 Relaxation Delay	1.3689
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency	(600.13, 600.13)
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(12.9, 12.9)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



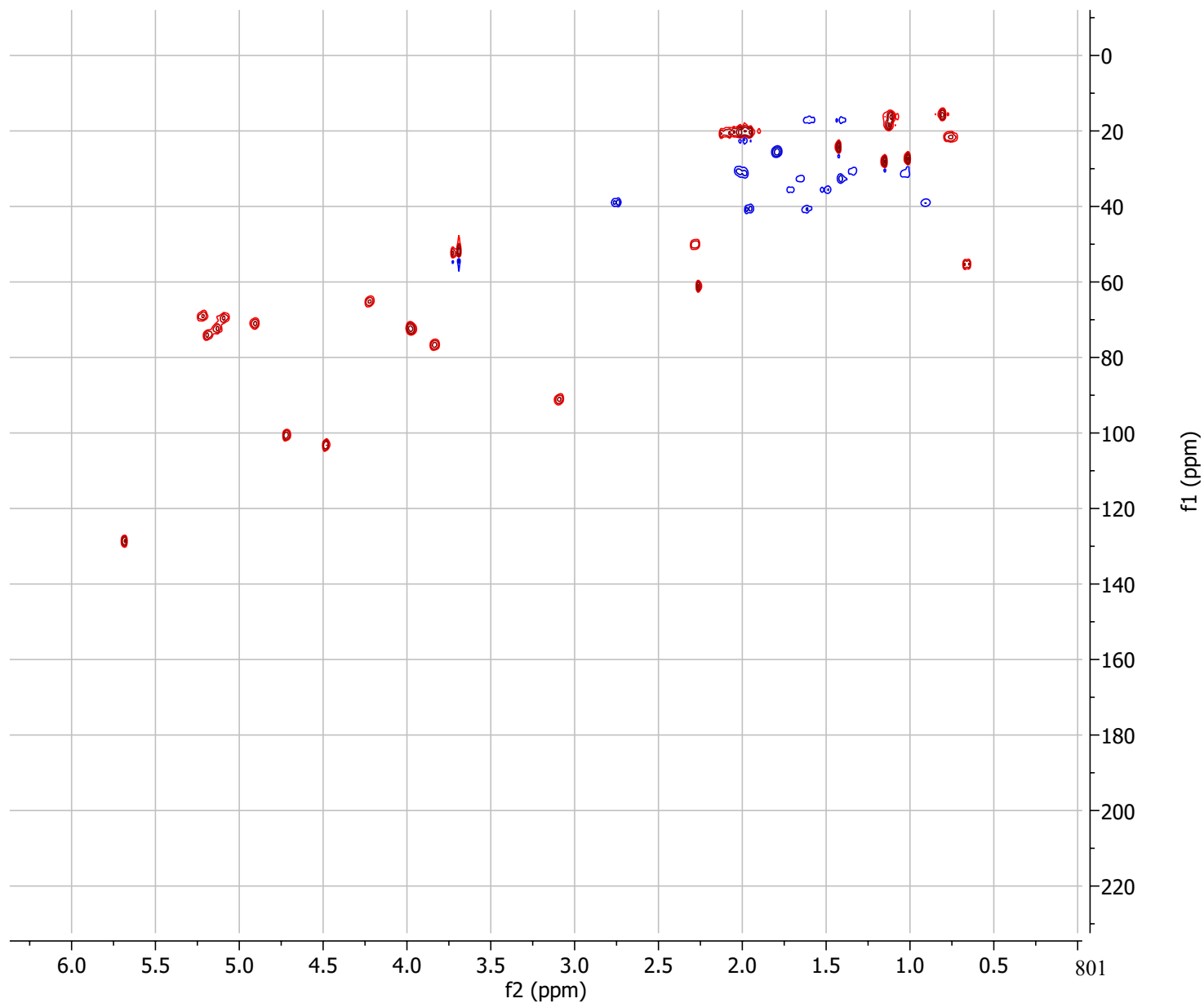
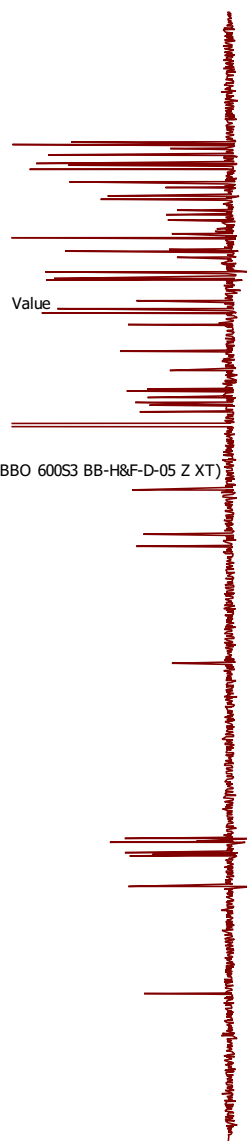
HSQC



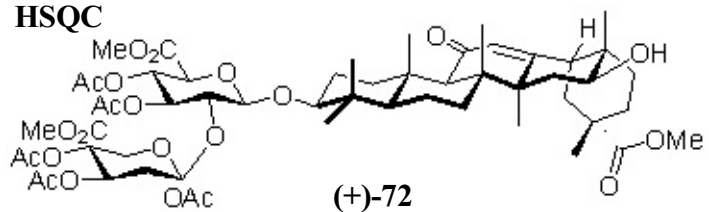
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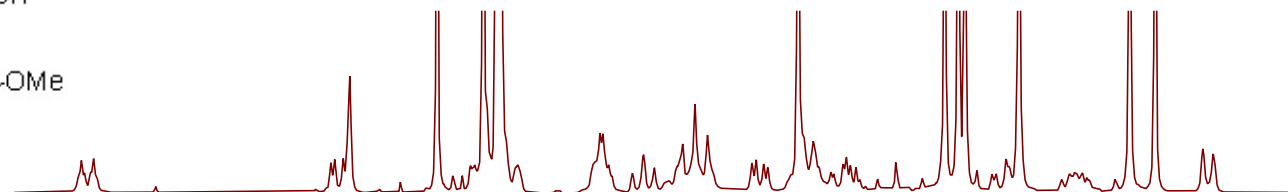
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpcisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(-24.0, -1891.2)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)



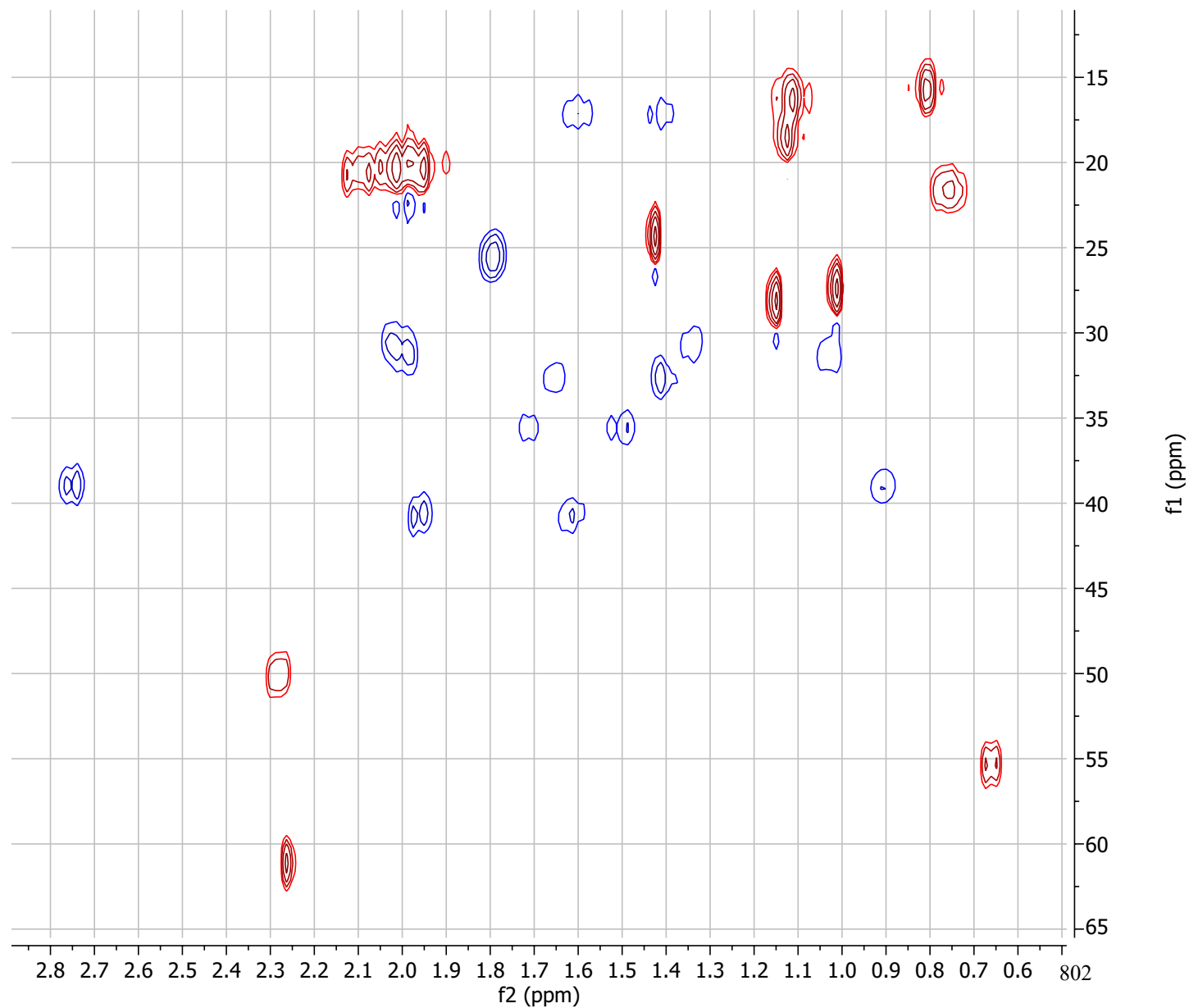
HSQC



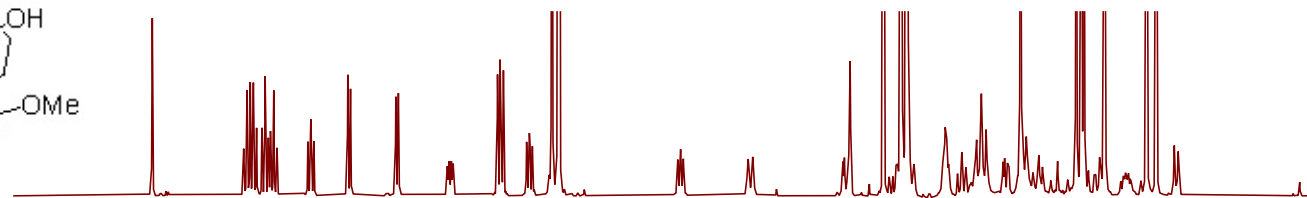
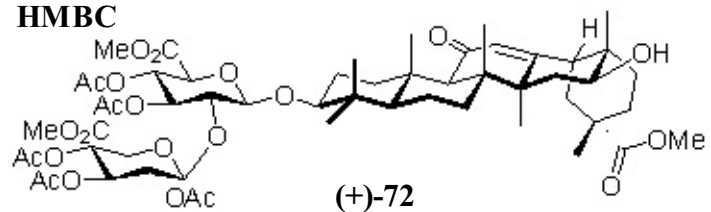
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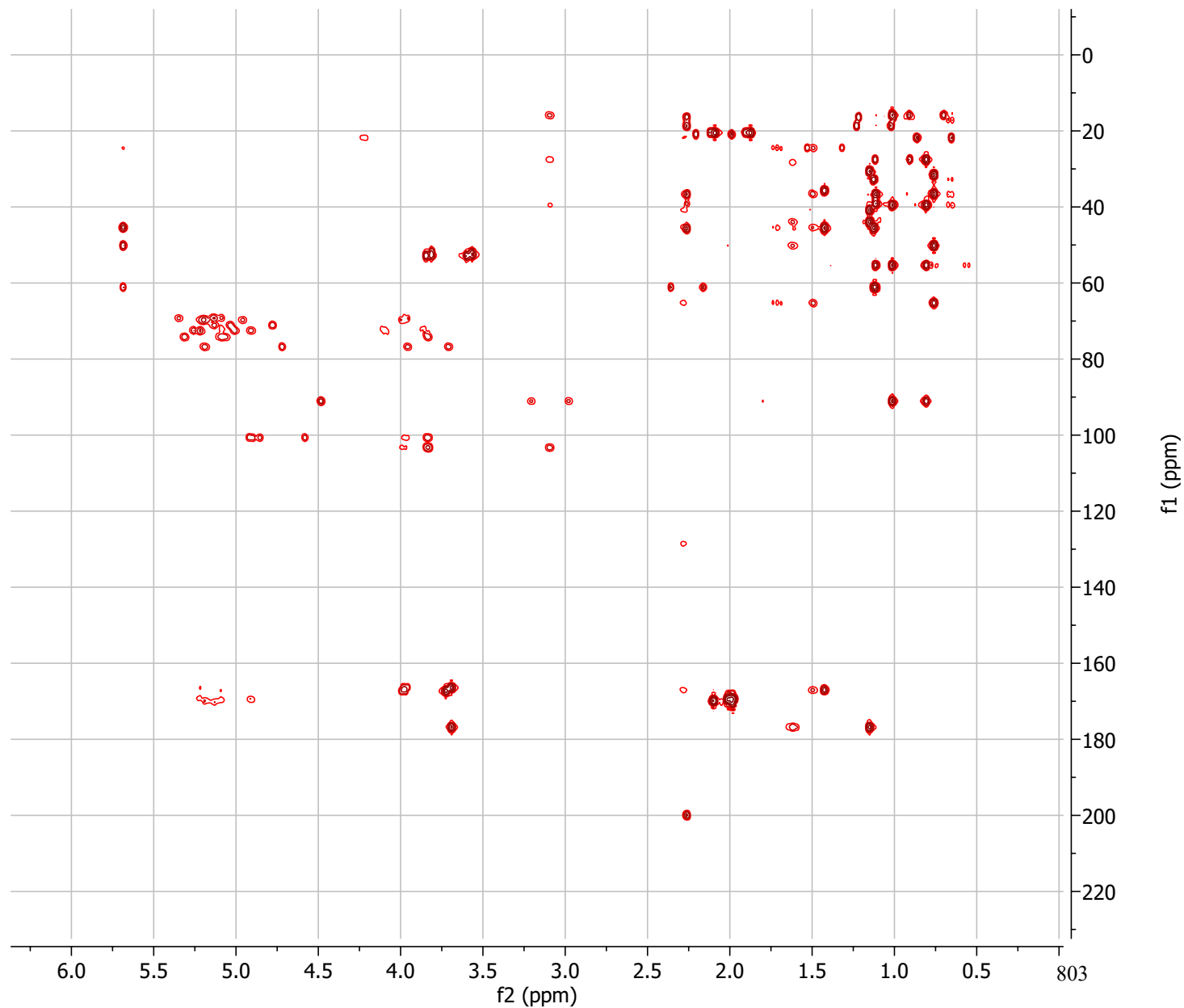
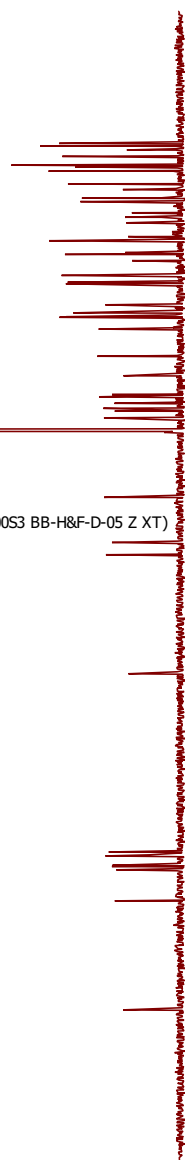
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetdgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(-24.0, -1891.2)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)



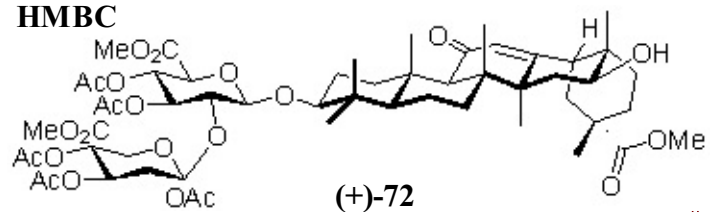
HMBC



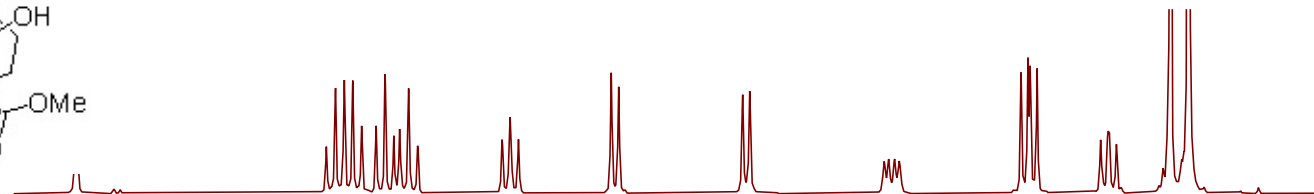
Parameter	Value
1 Origin	Brucker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-24.0, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



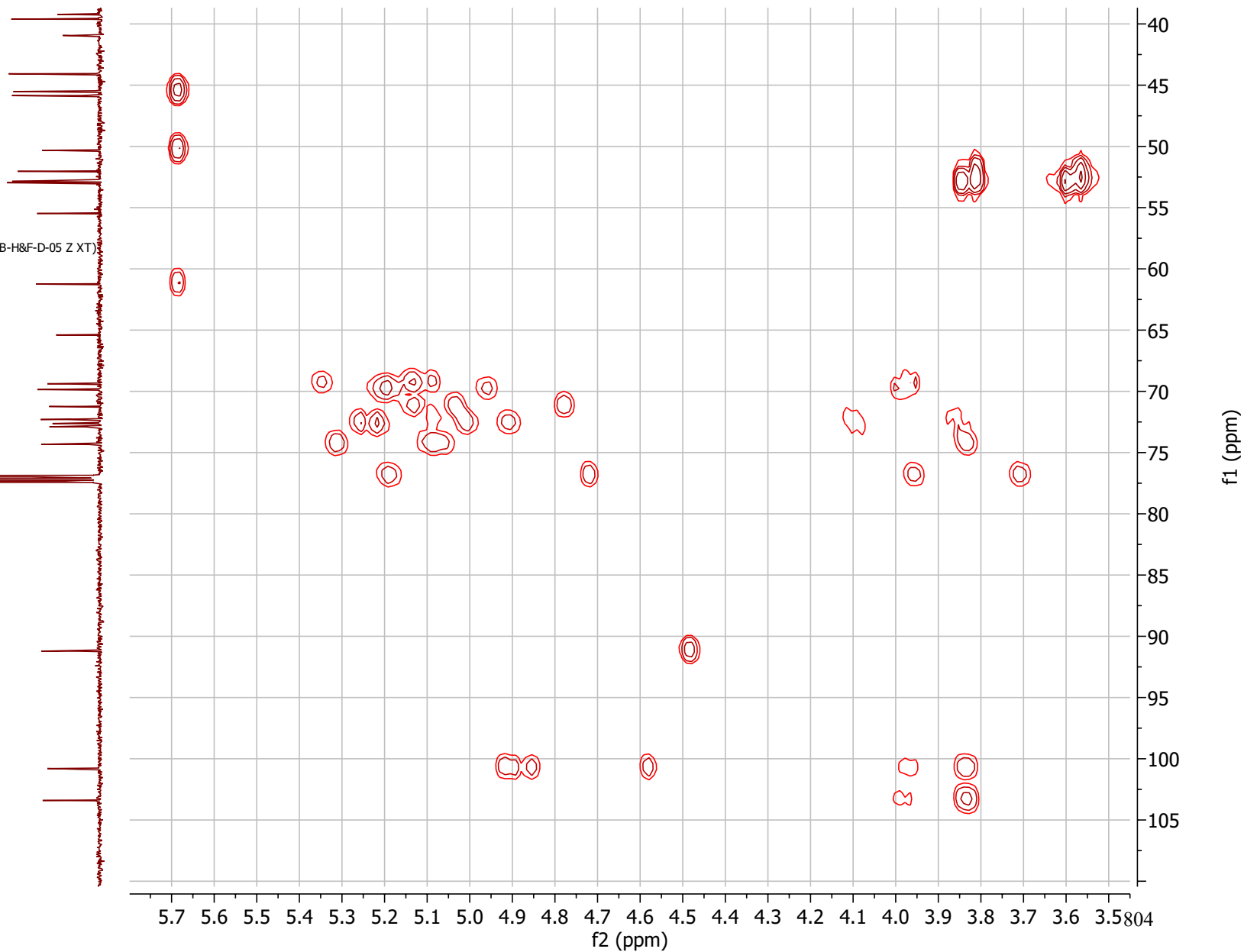
HMBC



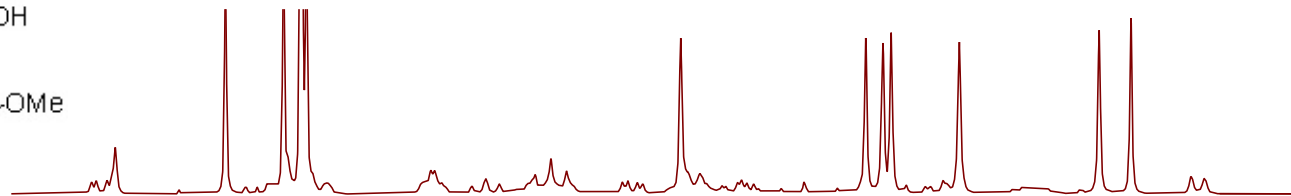
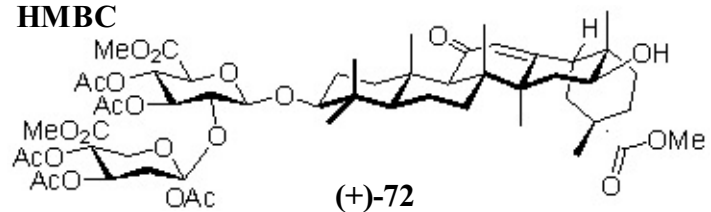
(+)-72



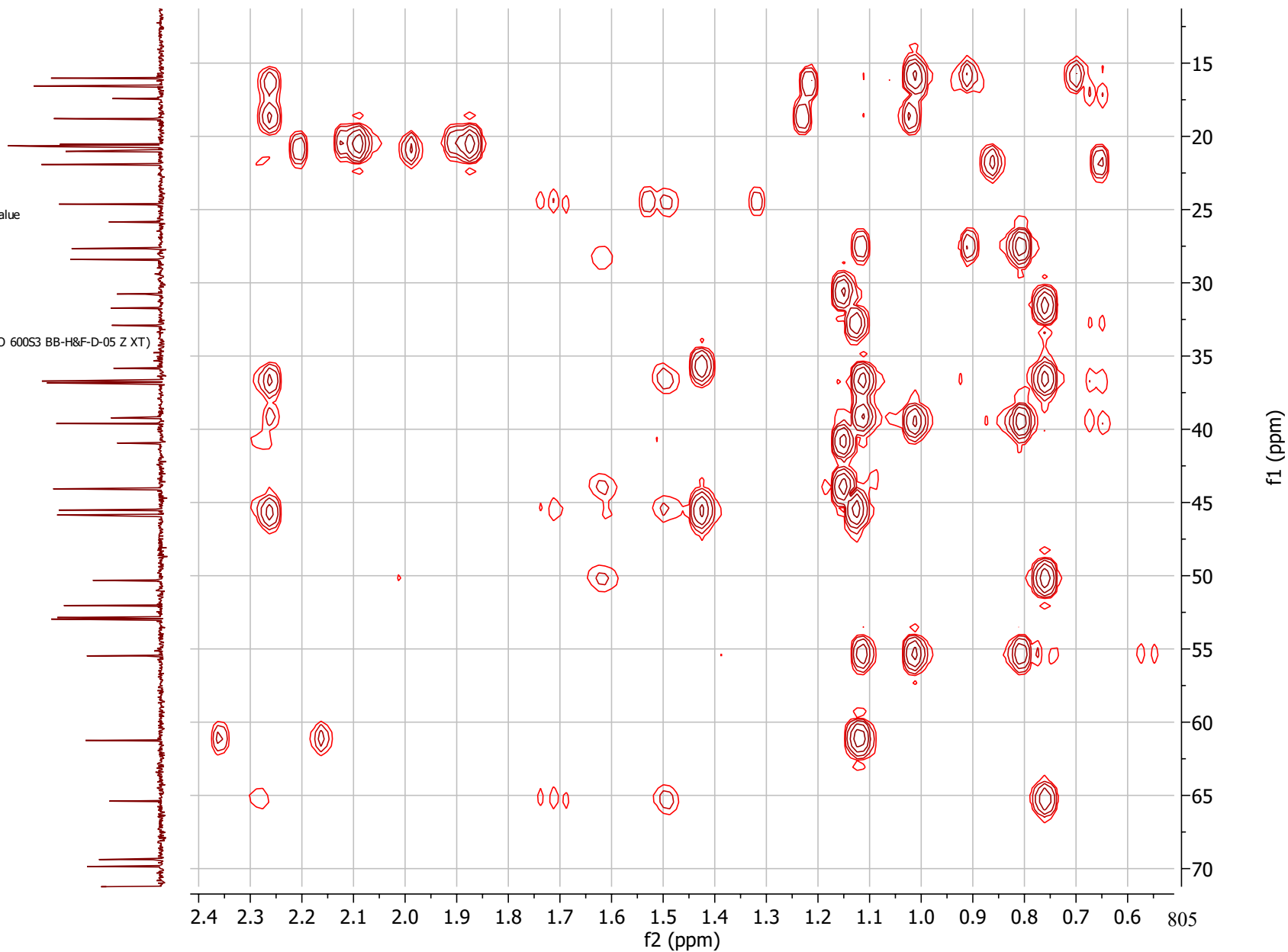
Parameter	Value
1 Origin	Brucker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-24.0, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



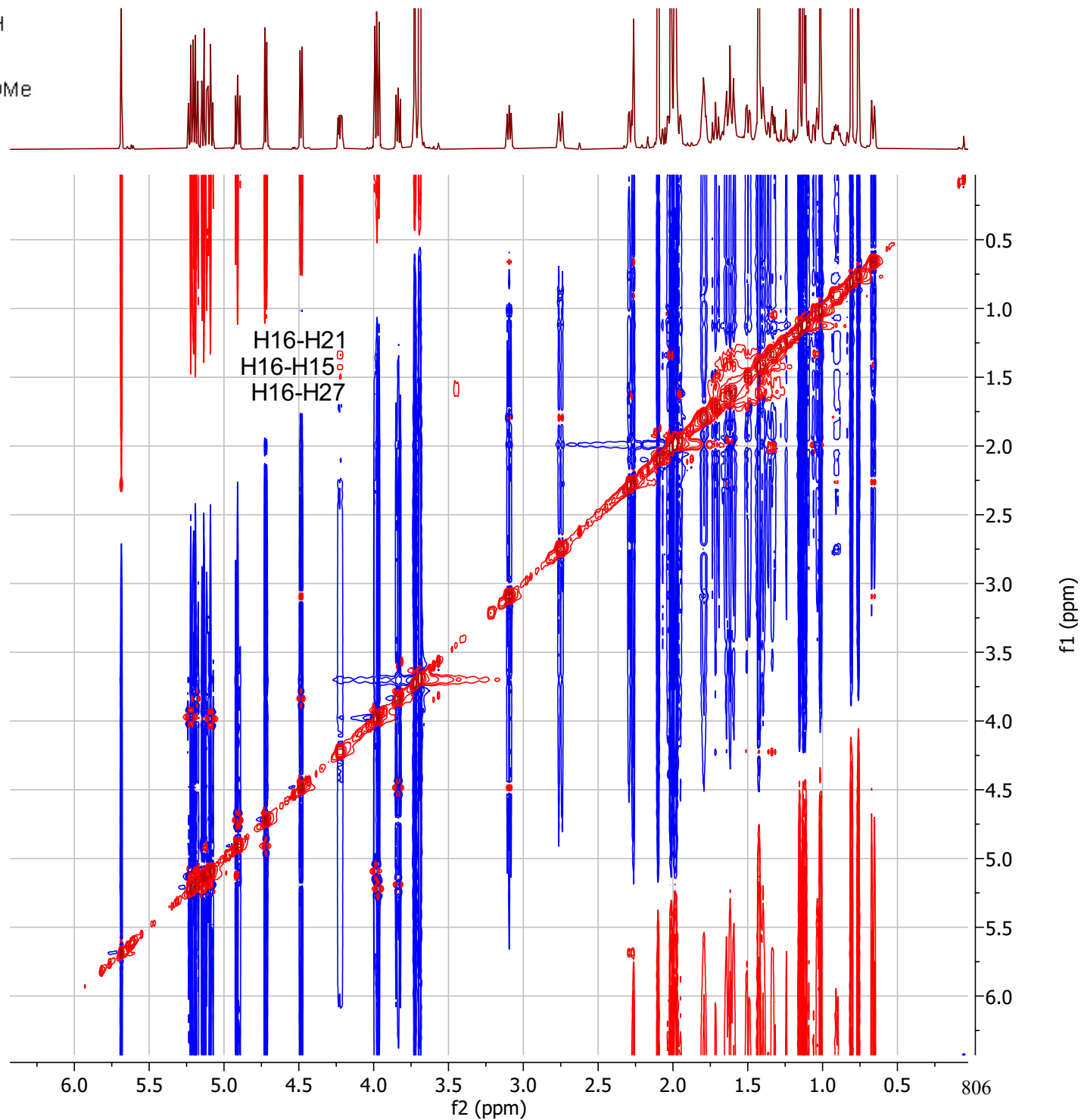
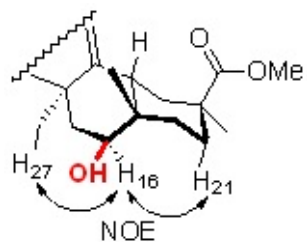
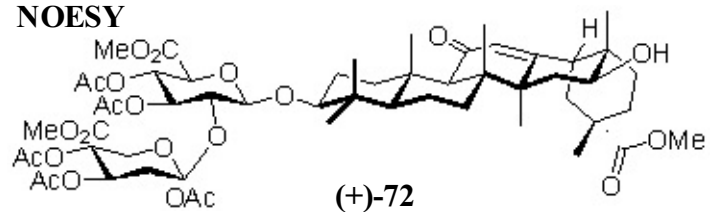
HMBC



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	4
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-24.0, -1891.7)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)

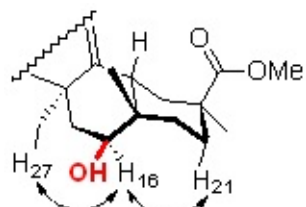
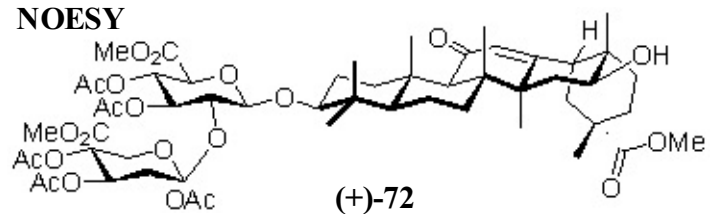


NOESY

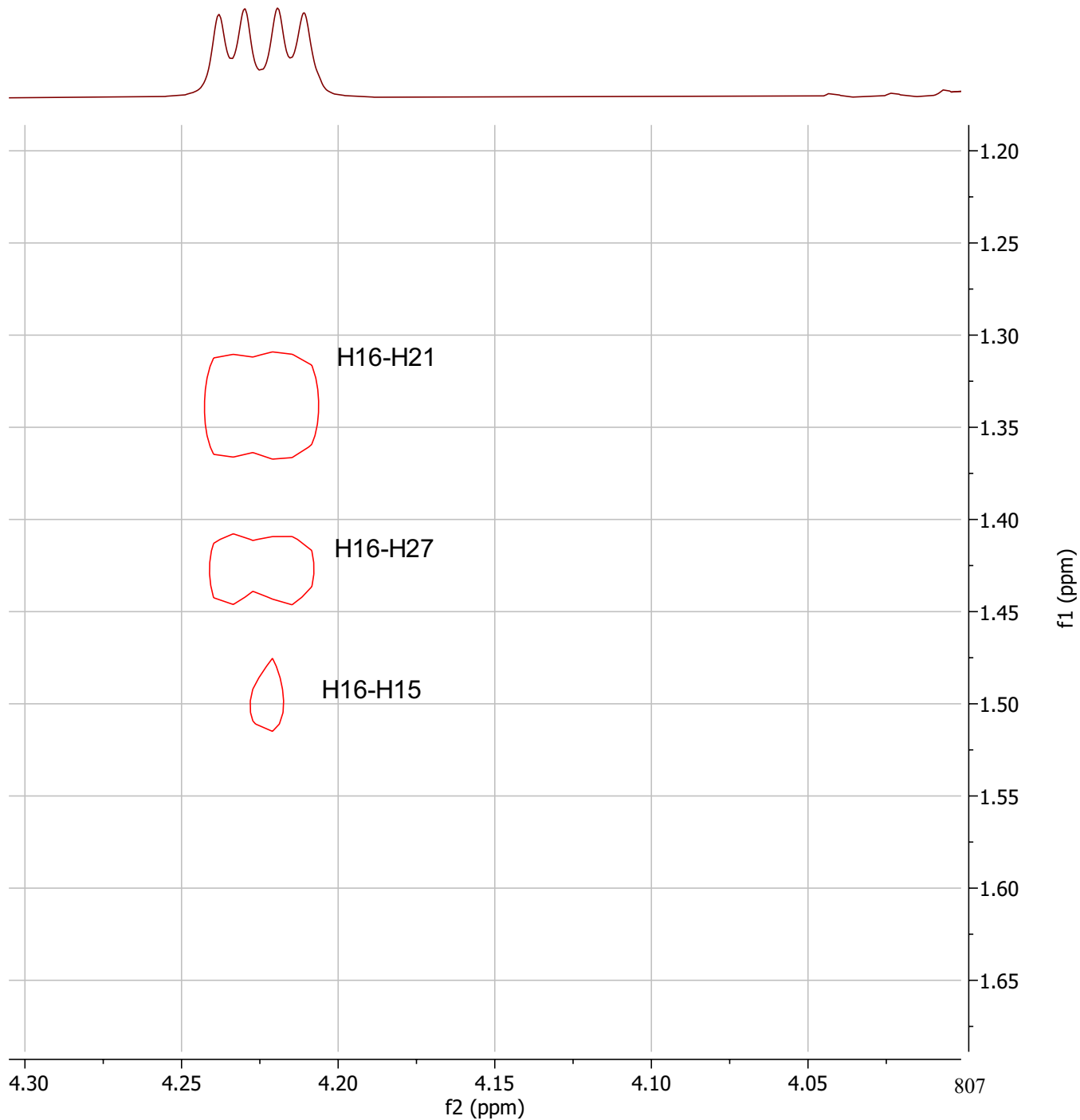


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	noesygpph
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.9119
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(12.9, 12.9)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)

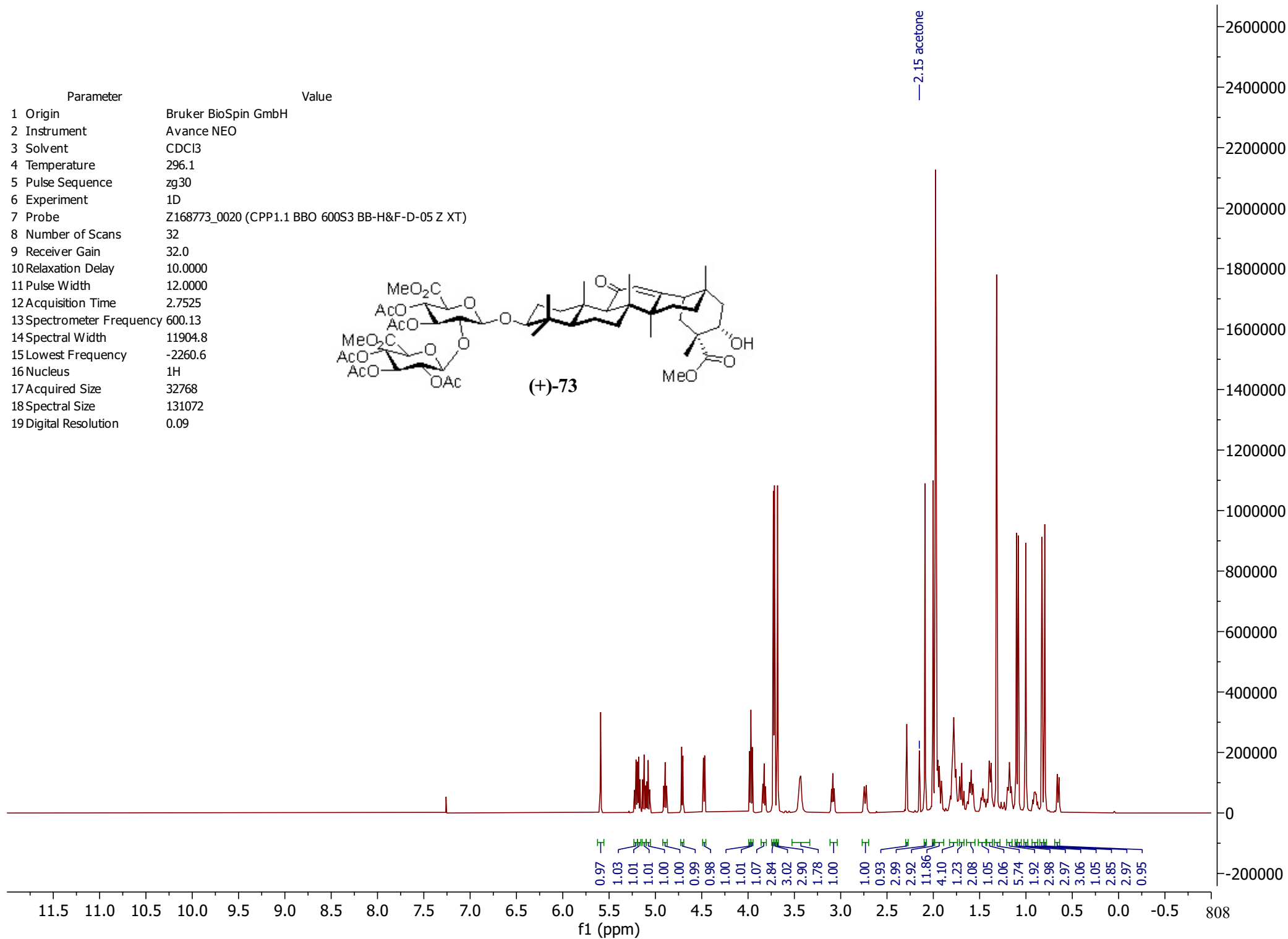
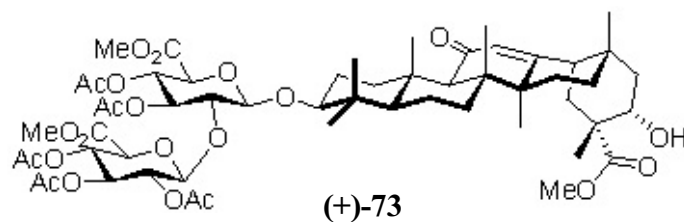
NOESY



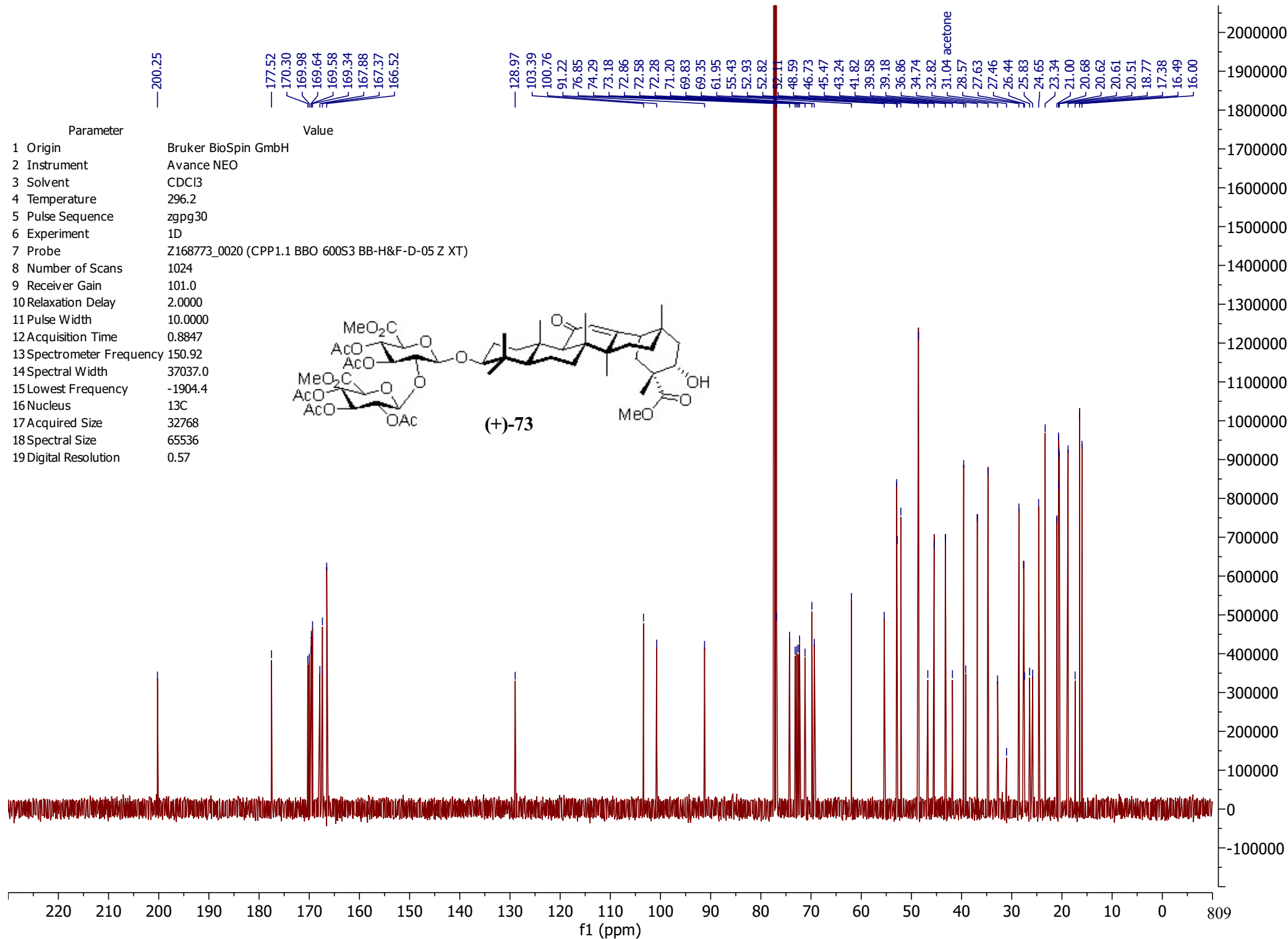
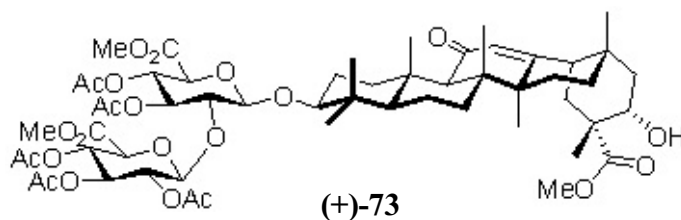
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	101.0
10 Relaxation Delay	1.9119
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(12.9, 12.9)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



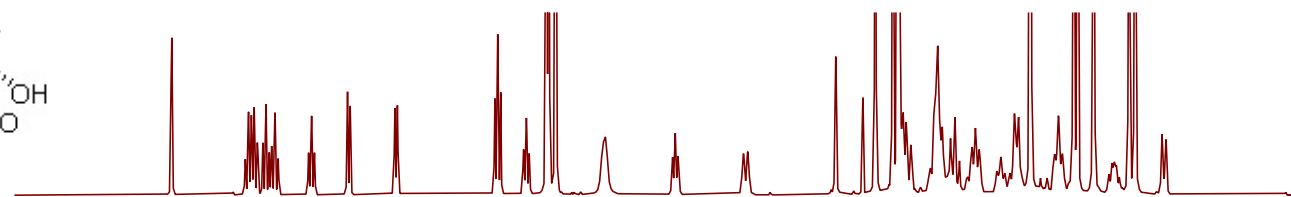
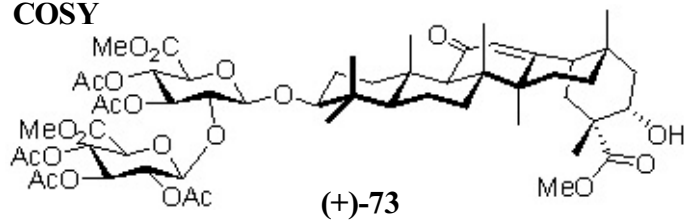
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	32
9 Receiver Gain	32.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



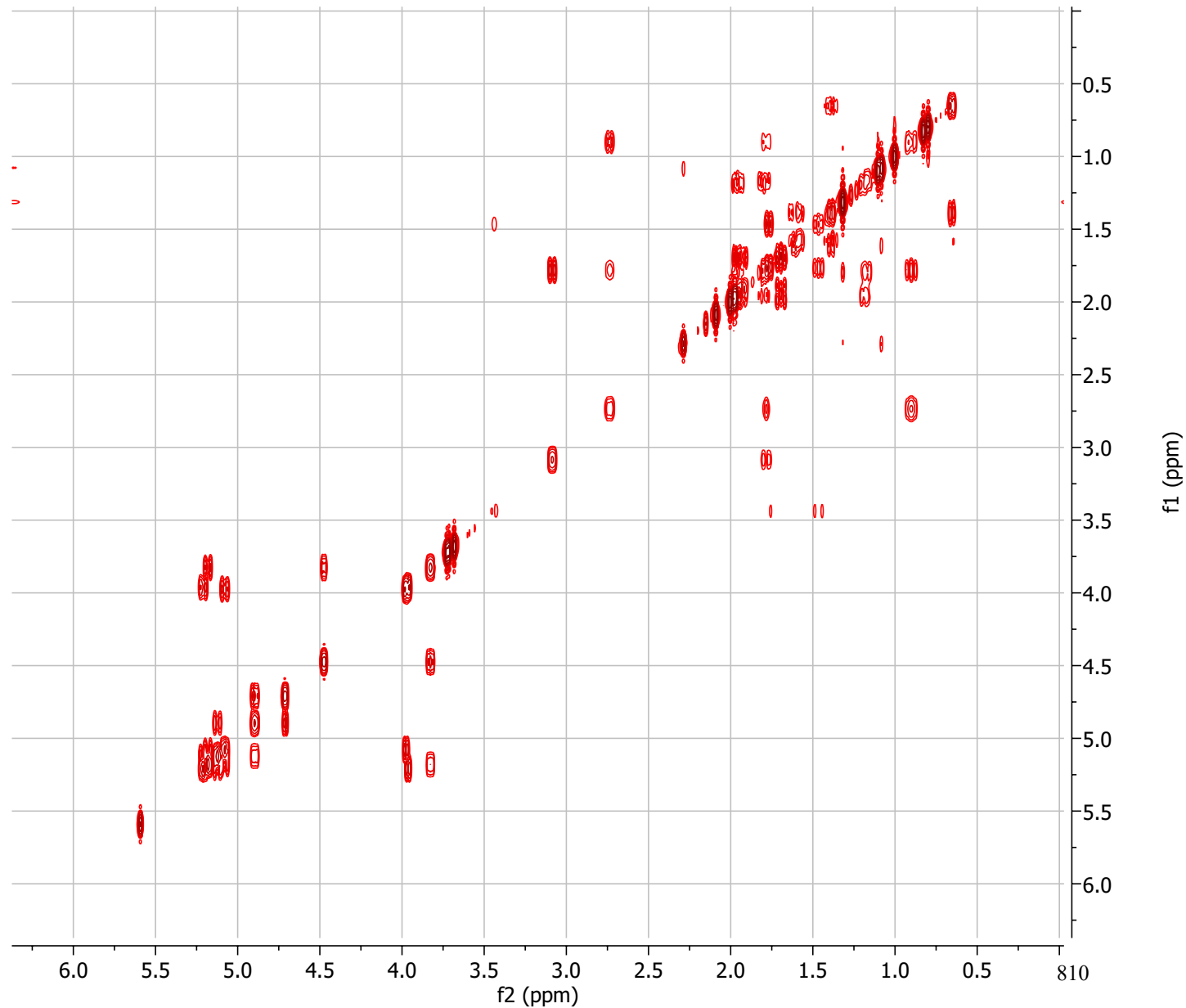
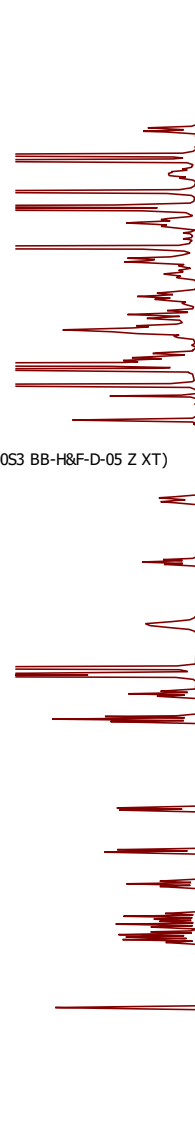
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	1024
9 Receiver Gain	101.0
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	0.8847
13 Spectrometer Frequency	150.92
14 Spectral Width	37037.0
15 Lowest Frequency	-1904.4
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.57



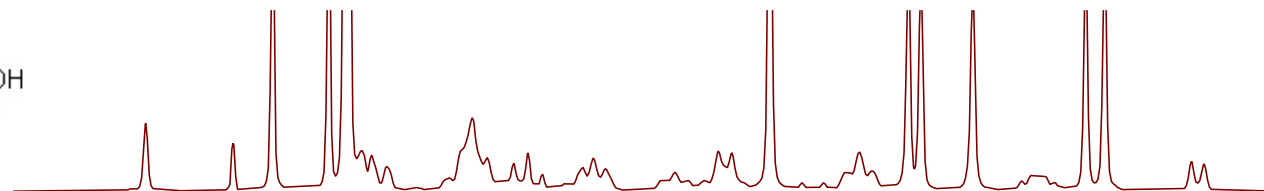
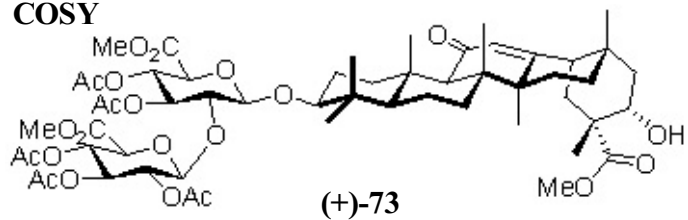
COSY



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.3648
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(-20.8, -21.8)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



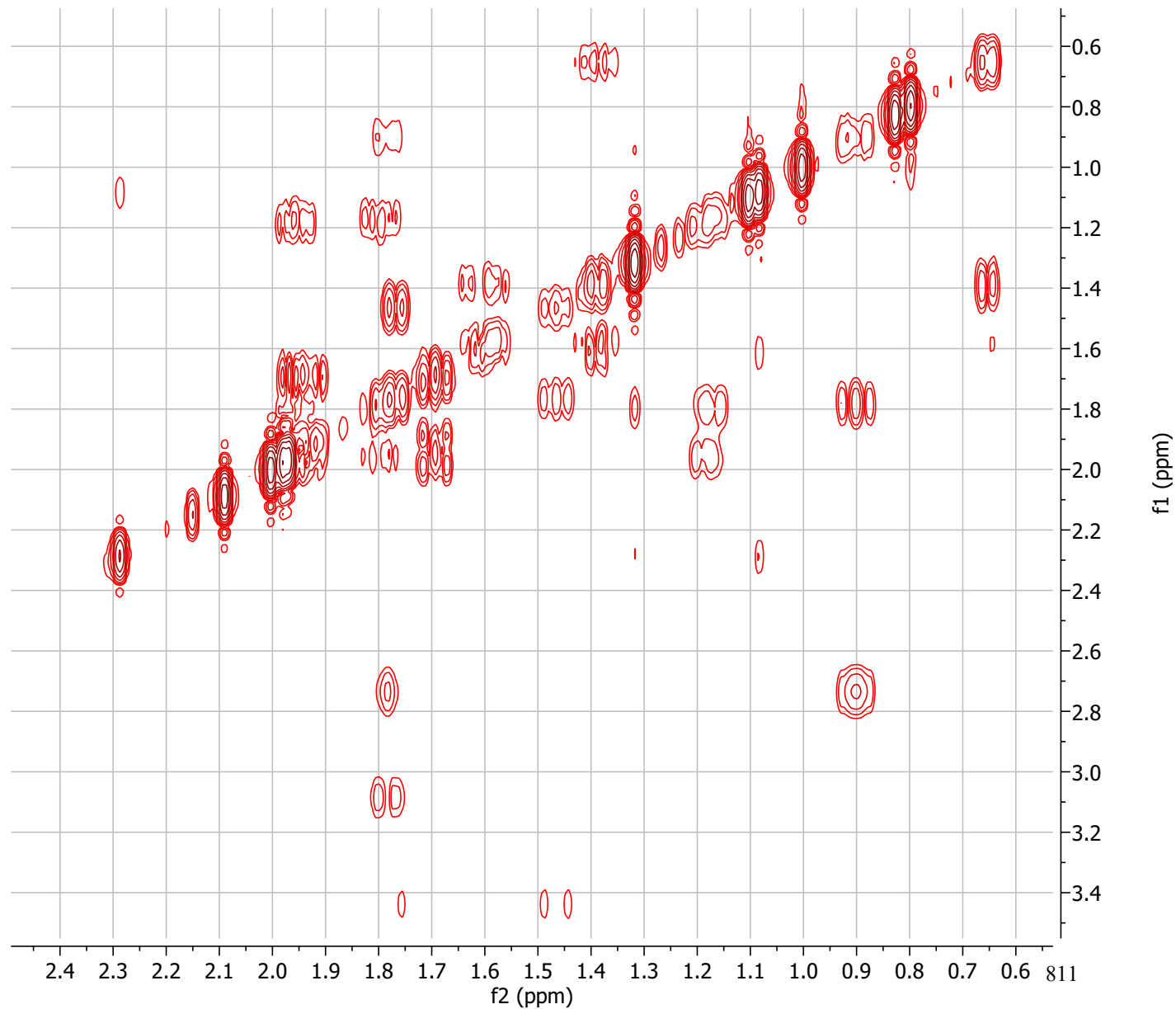
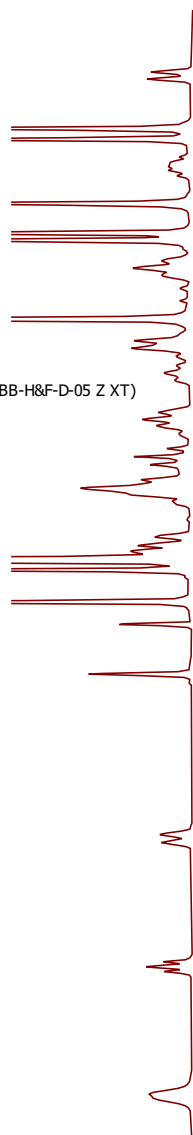
COSY



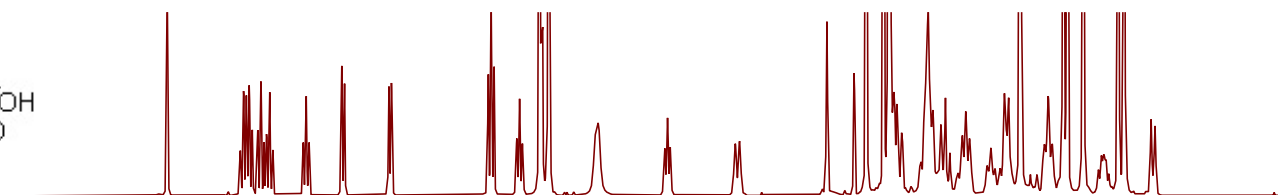
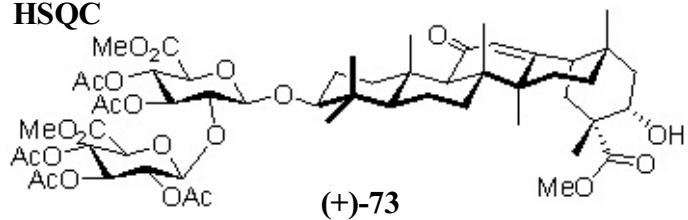
Parameter

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	64.0
10 Relaxation Delay	1.3648
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(-20.8, -21.8)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)

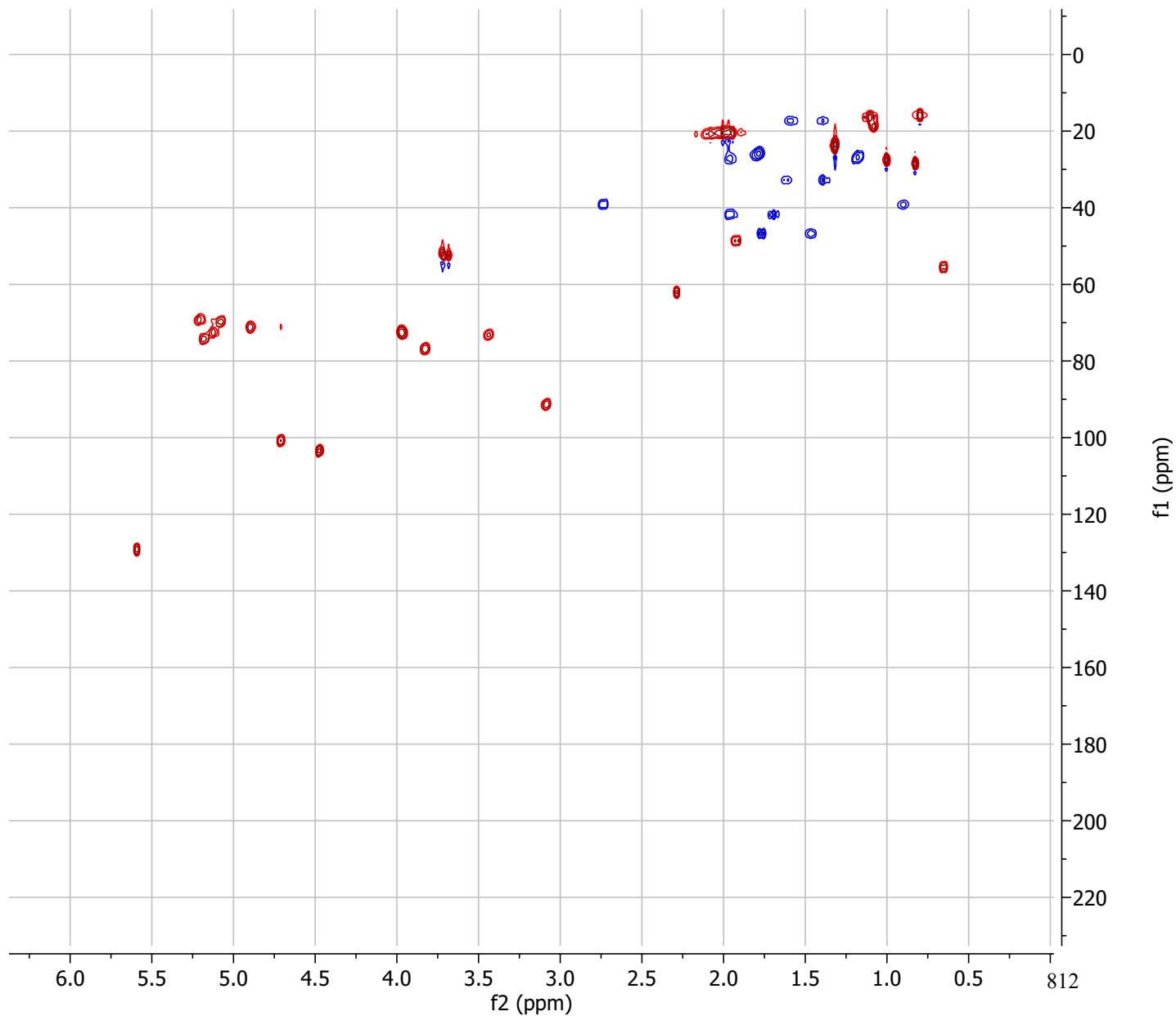
Value



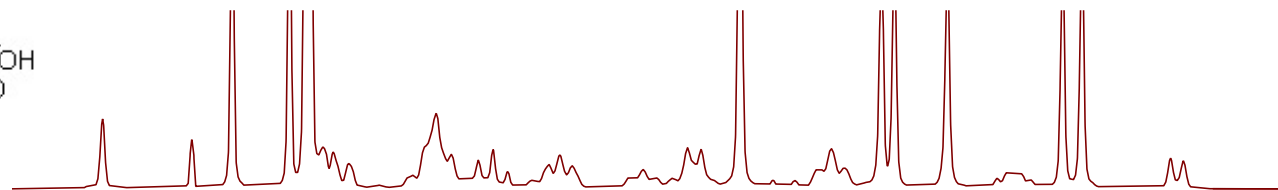
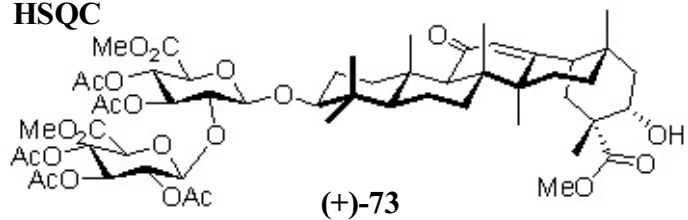
HSQC



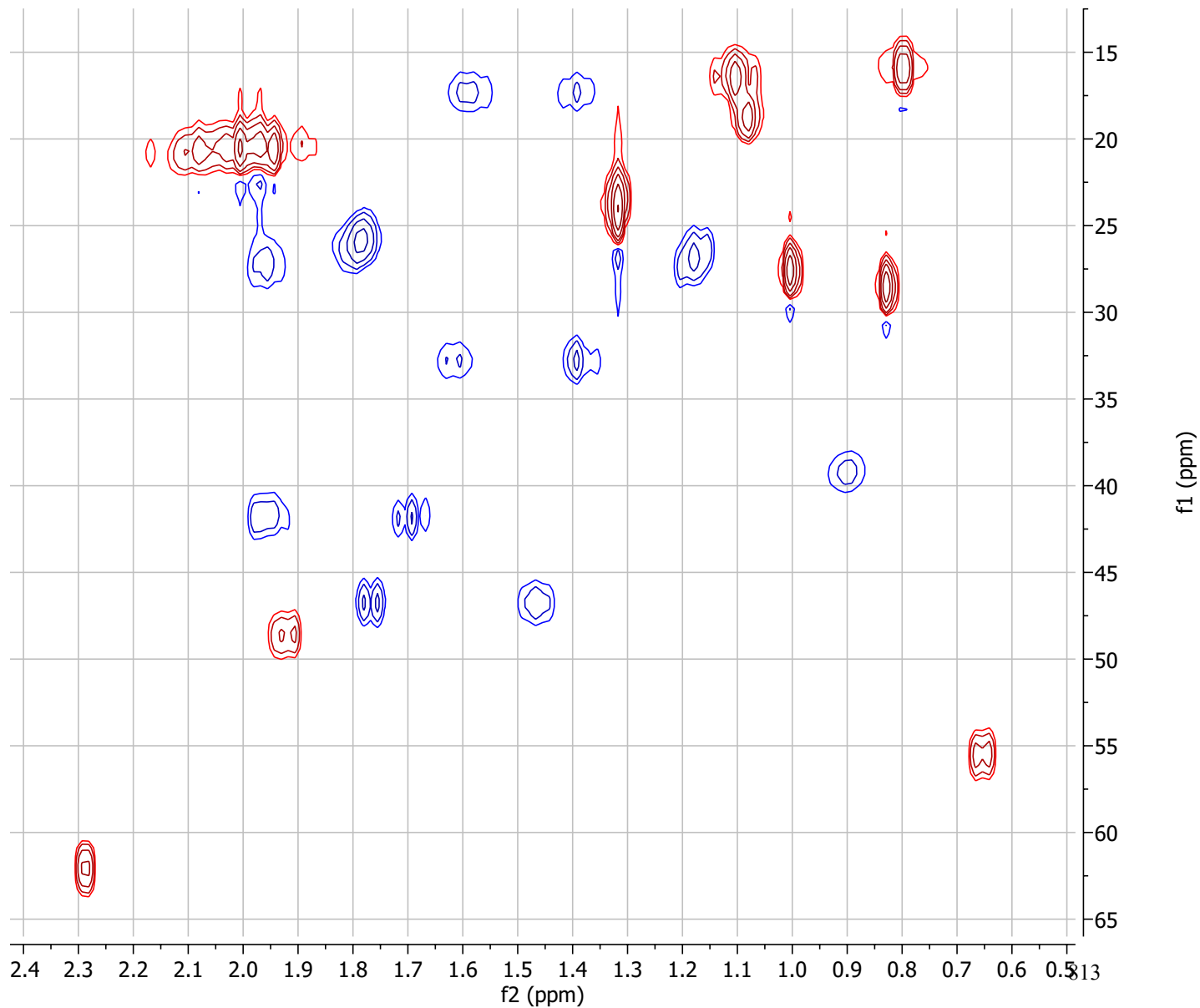
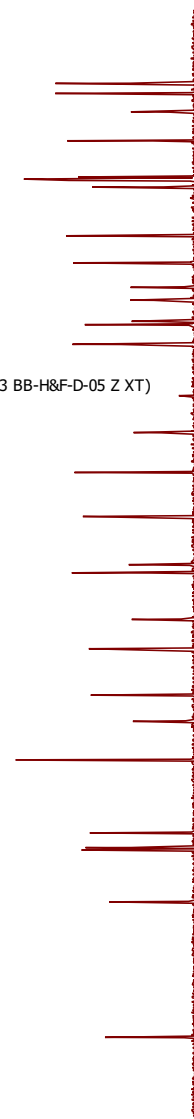
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpgpsisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(-20.8, -1860.0)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)



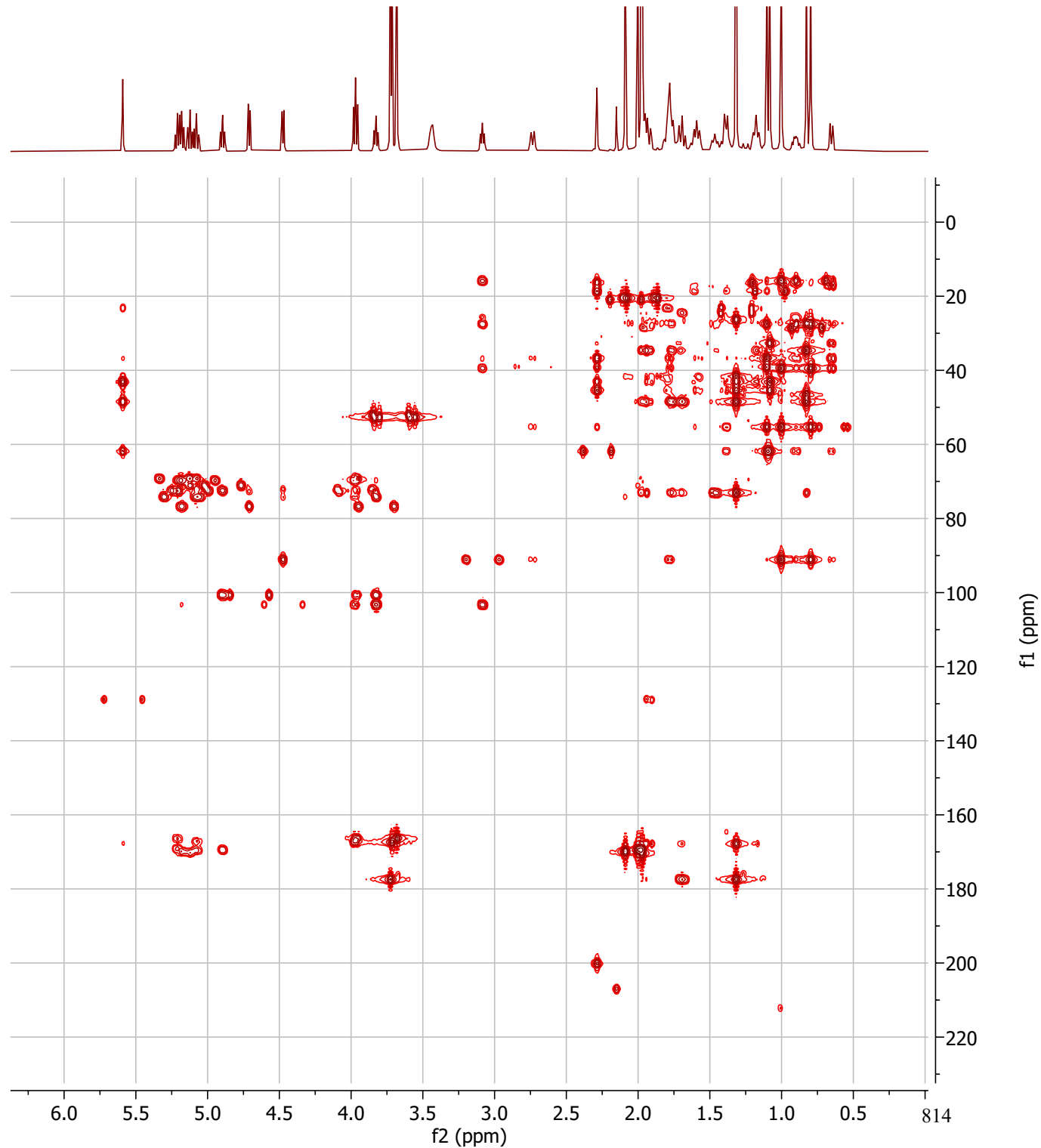
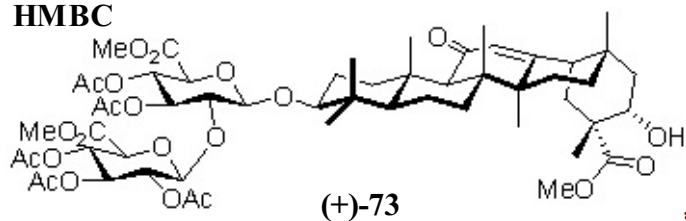
HSQC



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	hsqcetgpcisp2.3
6 Experiment	HSQC-EDITED
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.0)
15 Lowest Frequency	(-20.8, -1860.0)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.21)

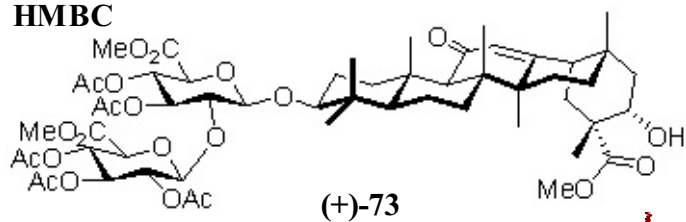


HMBC

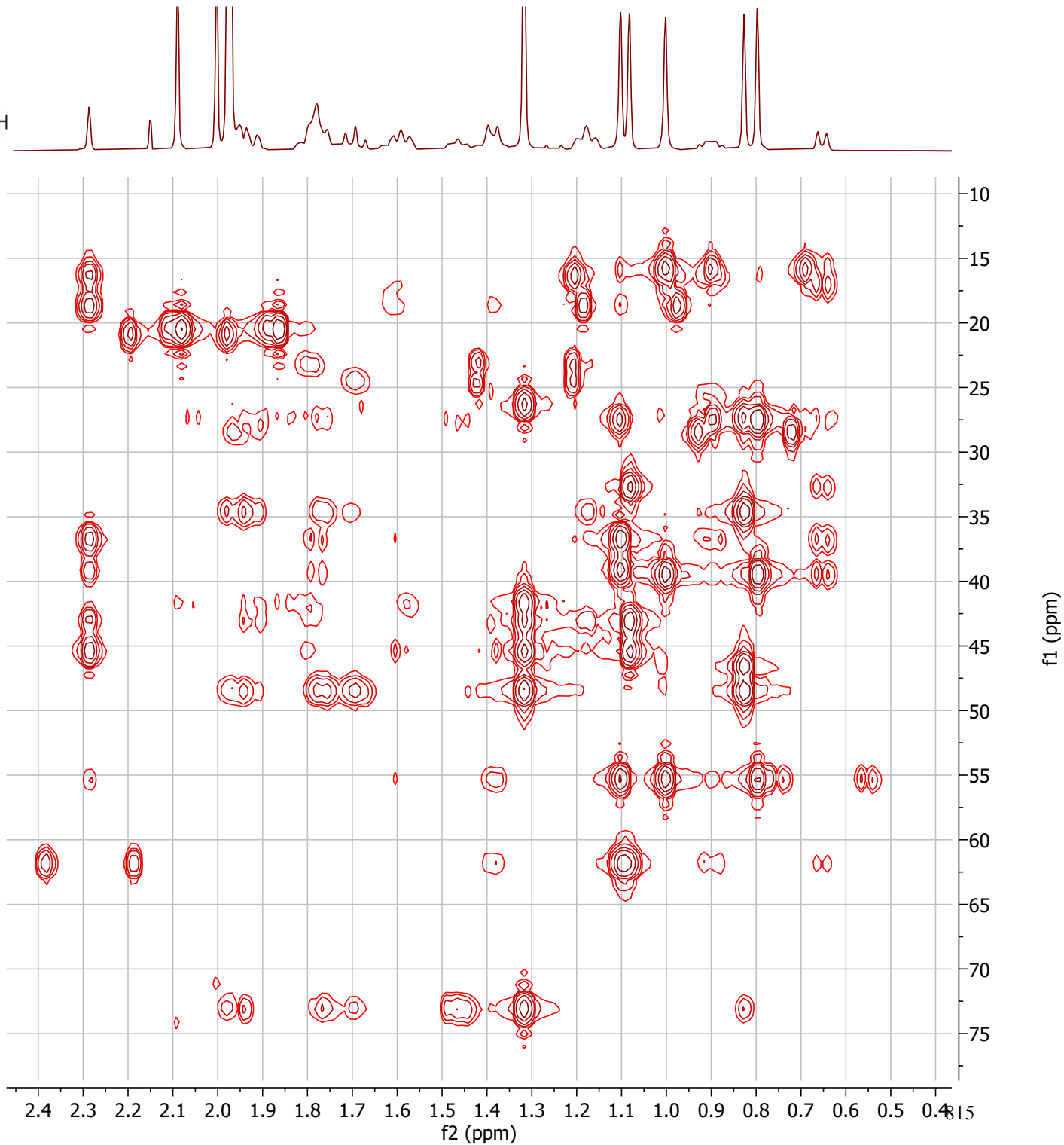


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-21.1, -1890.9)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)

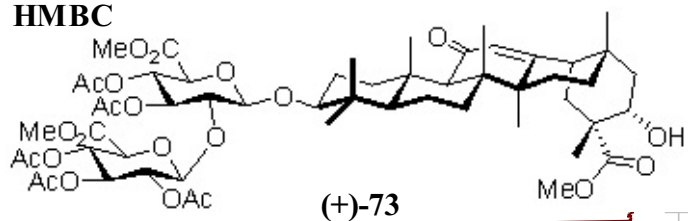
HMBC



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-21.1, -1890.9)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)

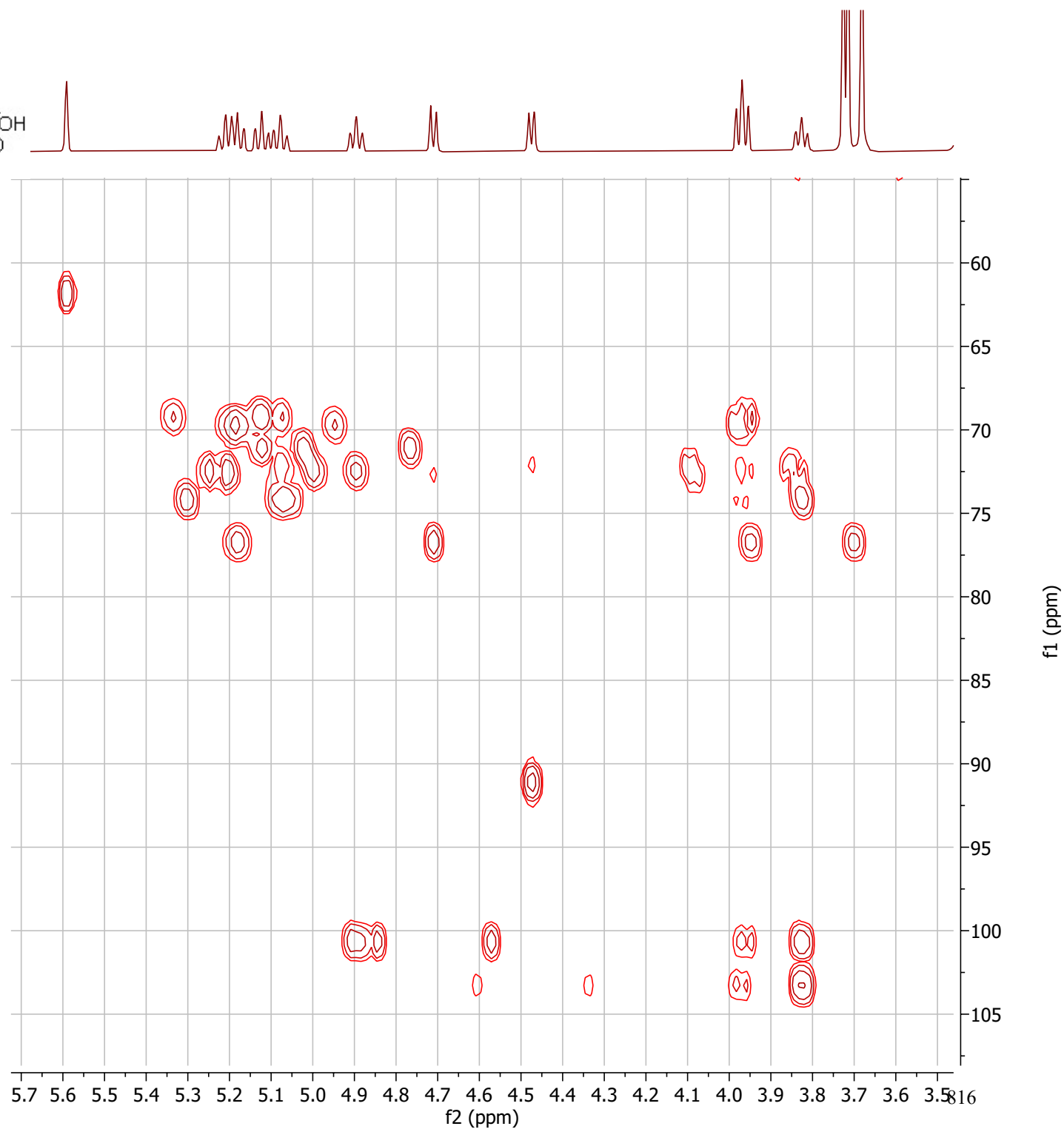


HMBC

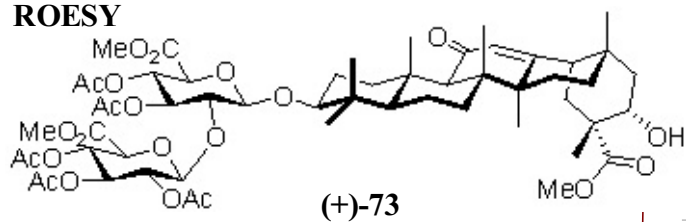


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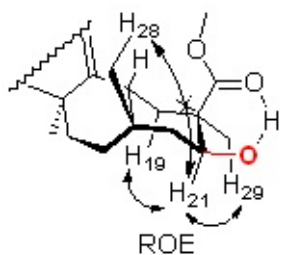
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	hmbcgpndqf
6 Experiment	HMBC
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	8
9 Receiver Gain	101.0
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1331
13 Spectrometer Frequency (600.13, 150.92)	
14 Spectral Width	(3846.2, 36974.9)
15 Lowest Frequency	(-21.1, -1890.9)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(7.51, 72.22)



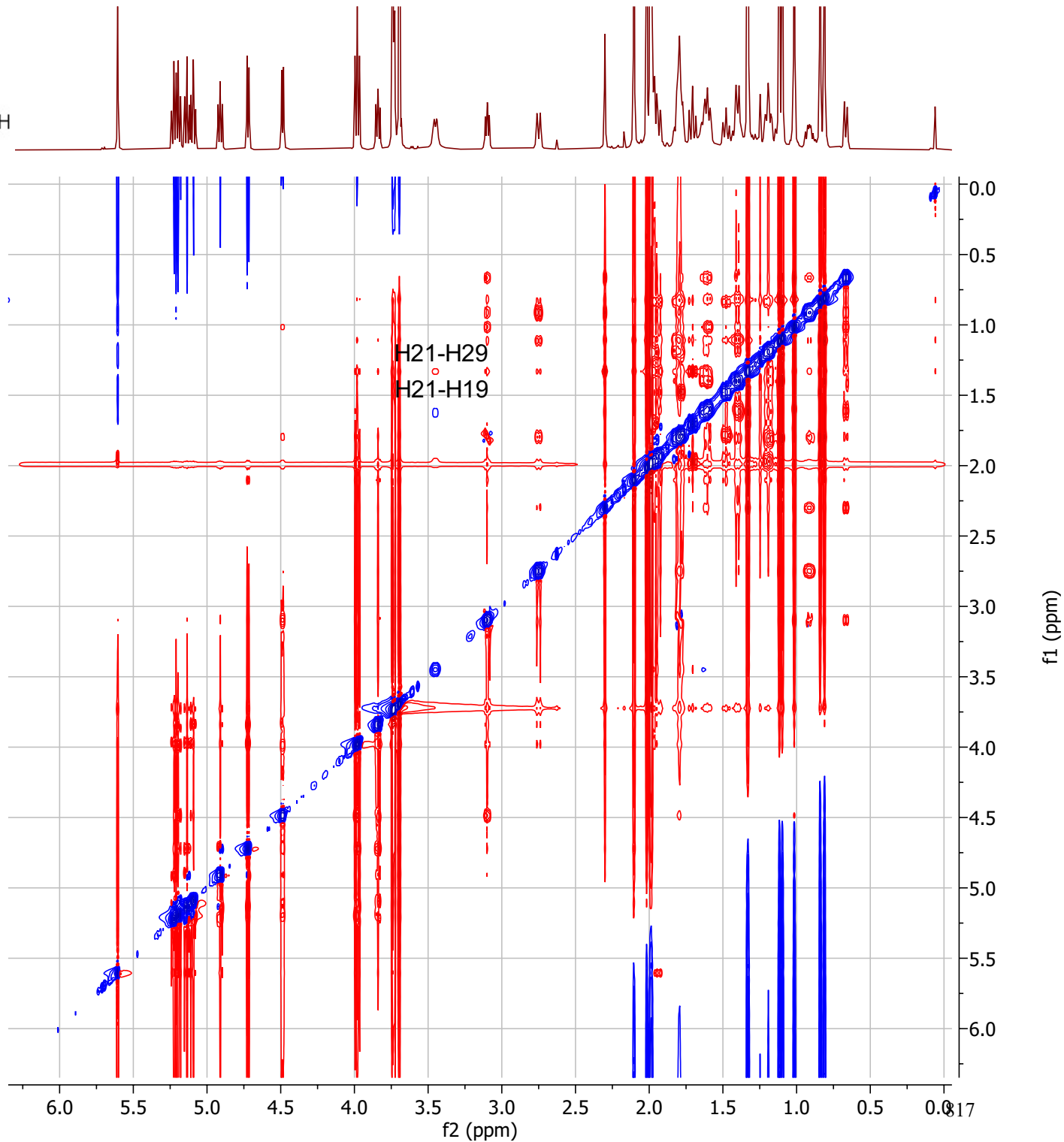
ROESY



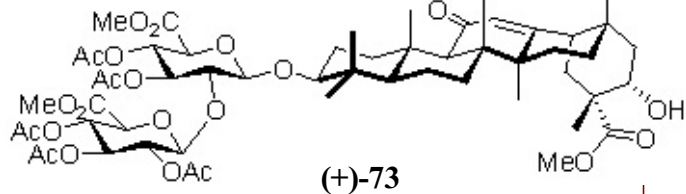
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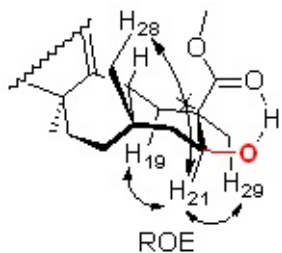
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	roesyphpp.2
6 Experiment	ROESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	20
9 Receiver Gain	101.0
10 Relaxation Delay	1.9037
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(-36.1, -36.1)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



ROESY

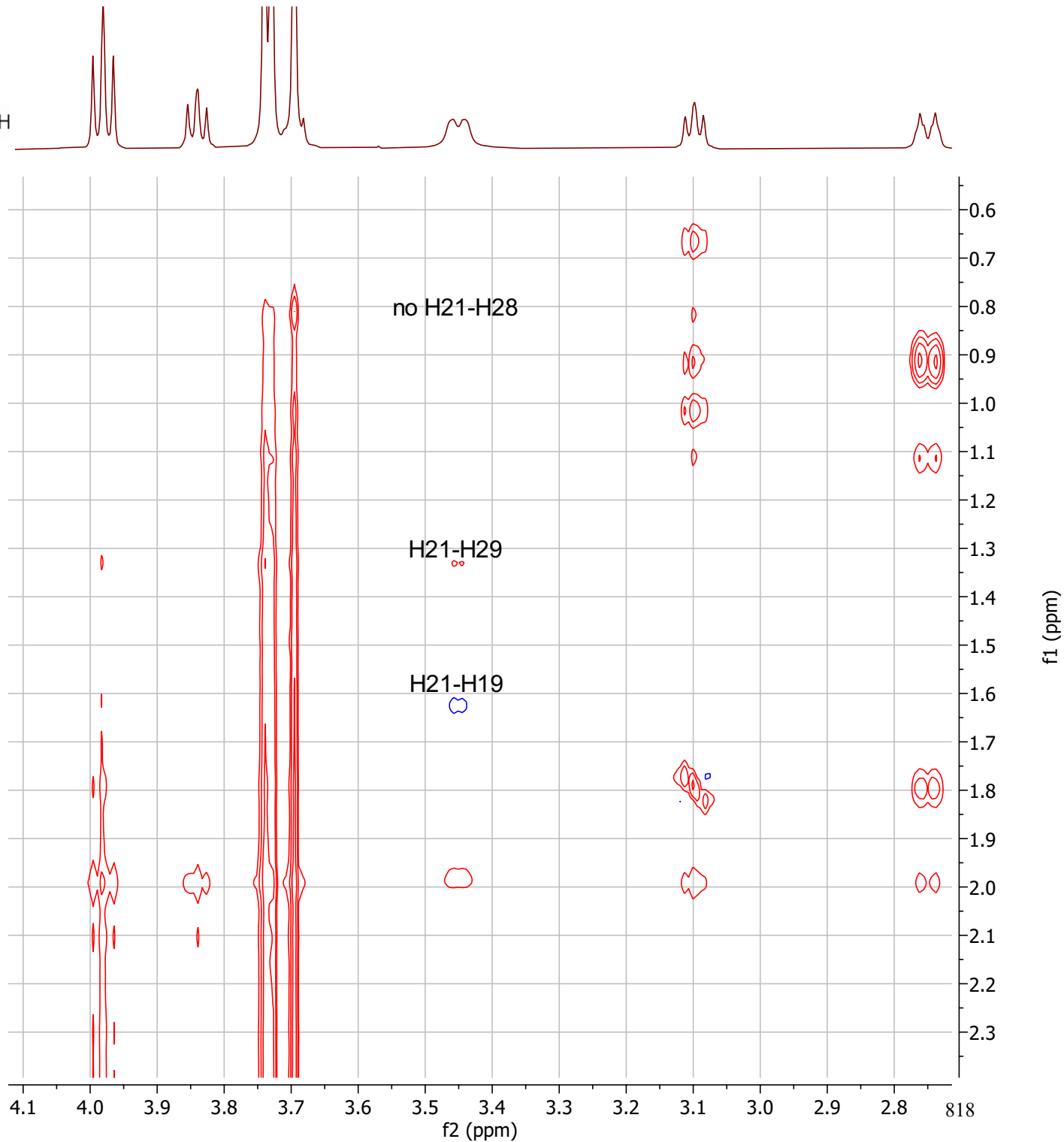


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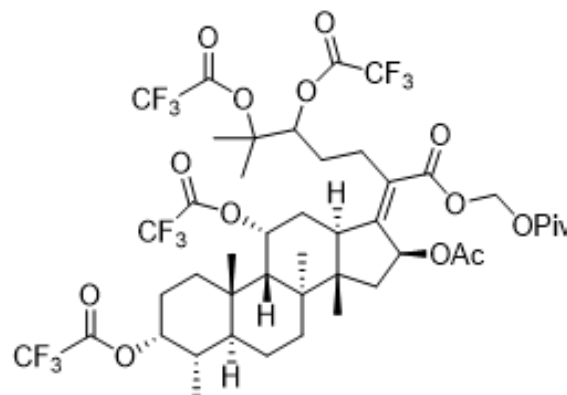


ROE

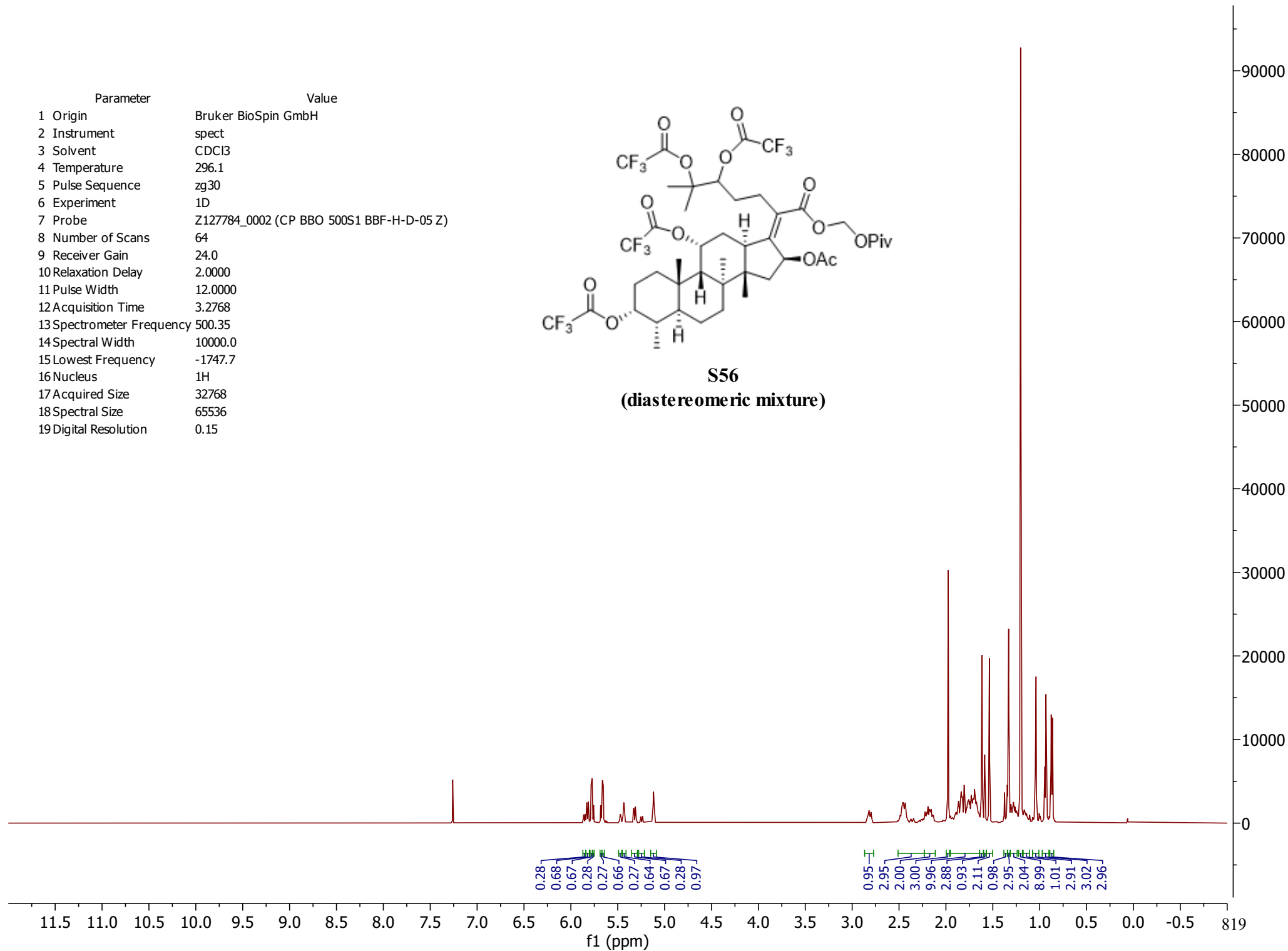
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	roesyphpp.2
6 Experiment	ROESY
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	20
9 Receiver Gain	101.0
10 Relaxation Delay	1.9037
11 Pulse Width	12.0000
12 Acquisition Time	0.2662
13 Spectrometer Frequency (600.13, 600.13)	
14 Spectral Width	(3846.2, 3846.2)
15 Lowest Frequency	(-36.1, -36.1)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.76, 3.76)



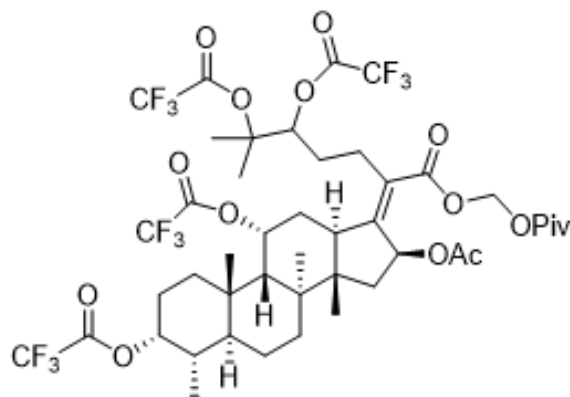
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	24.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



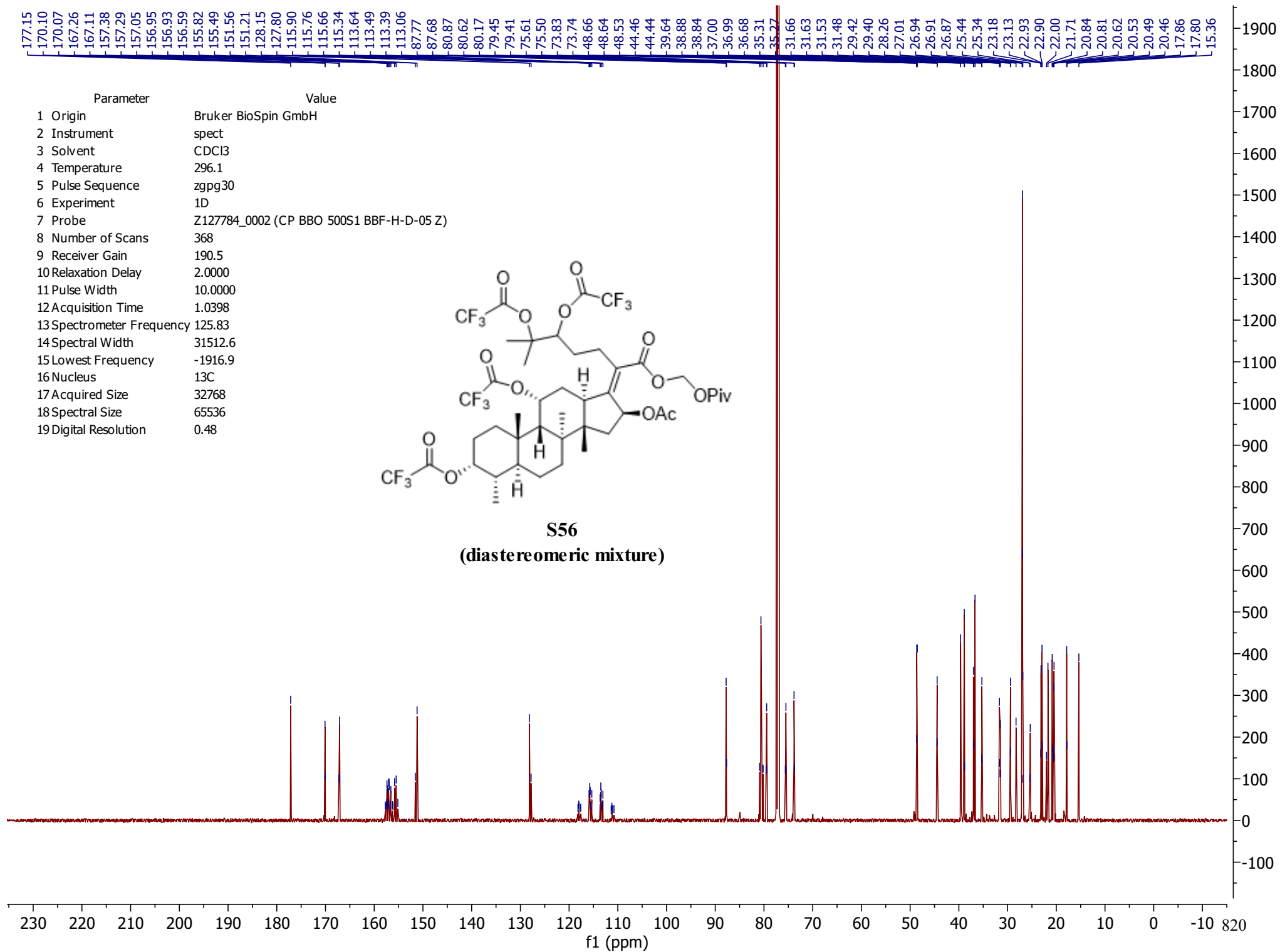
S56
(diastereomeric mixture)



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCI3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1916.9
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

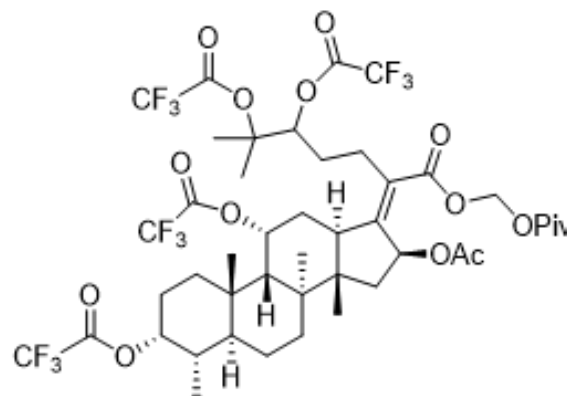


S56
(diastereomeric mixture)

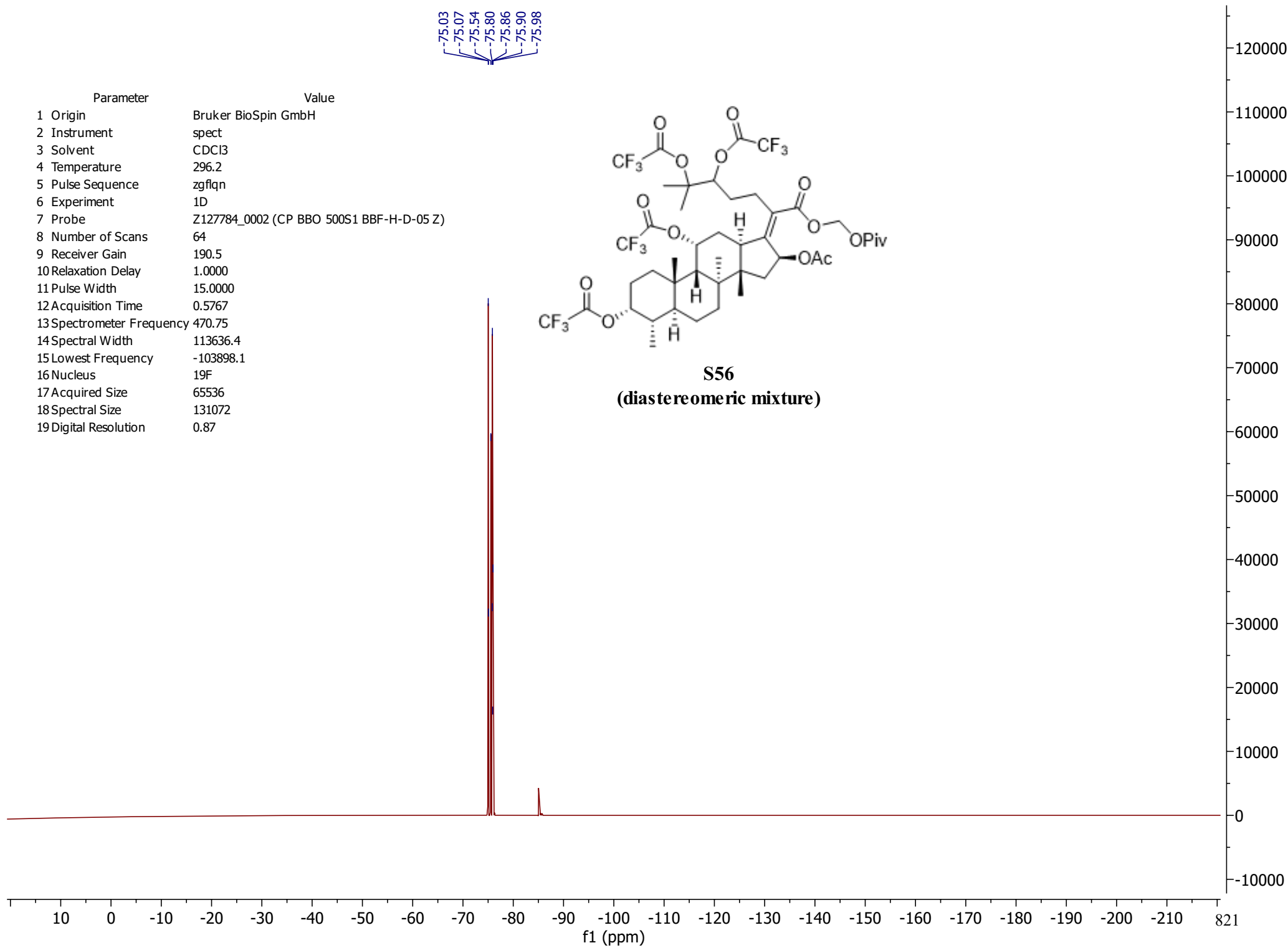


-75.03
-75.07
-75.54
-75.80
-75.86
-75.90
-75.98

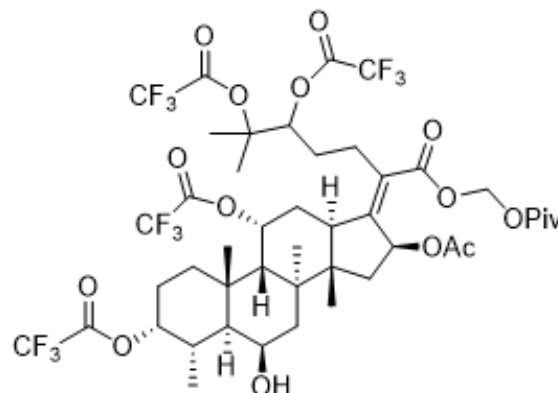
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgflqn
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	¹⁹ F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



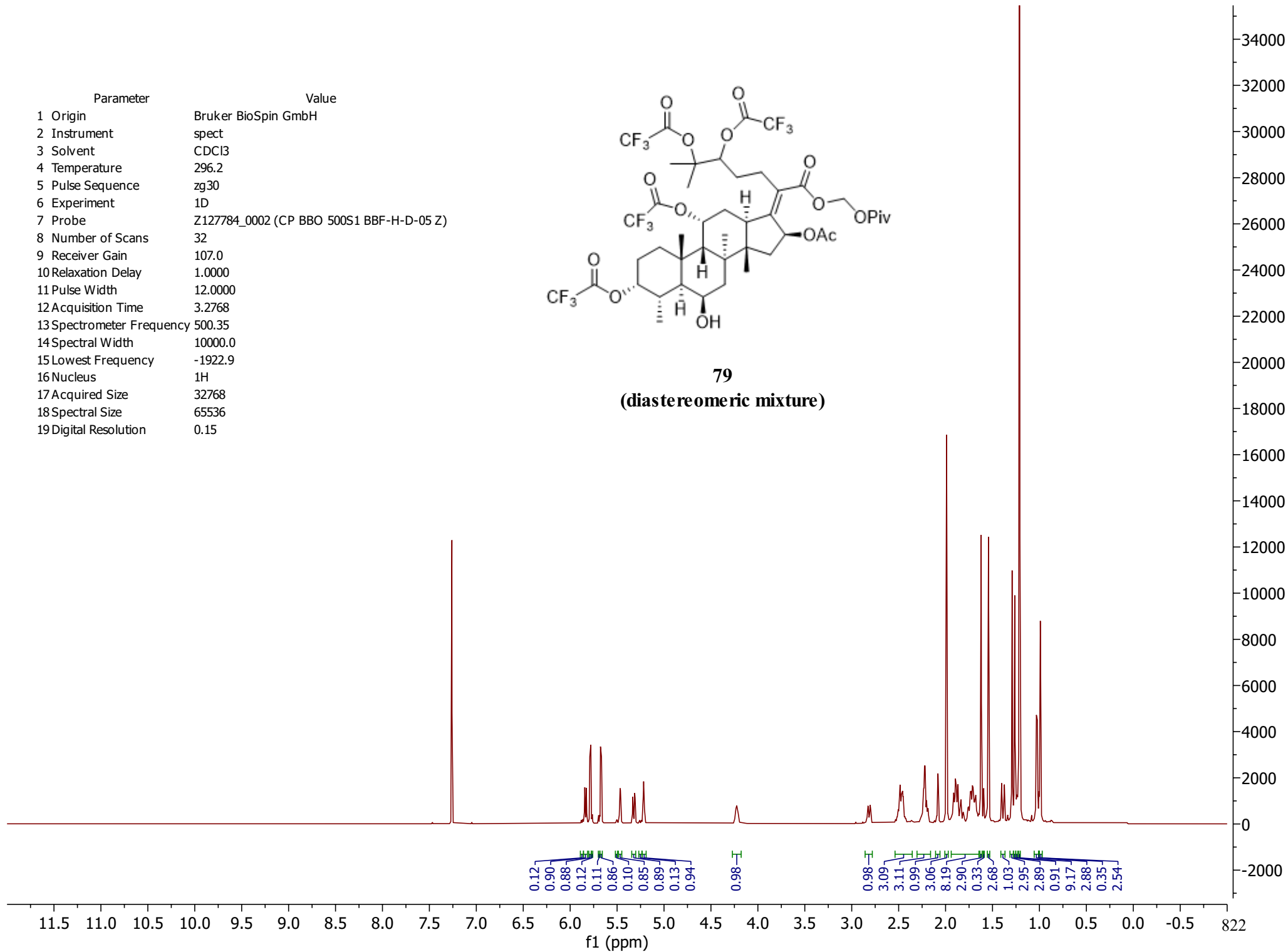
S56
(diastereomeric mixture)

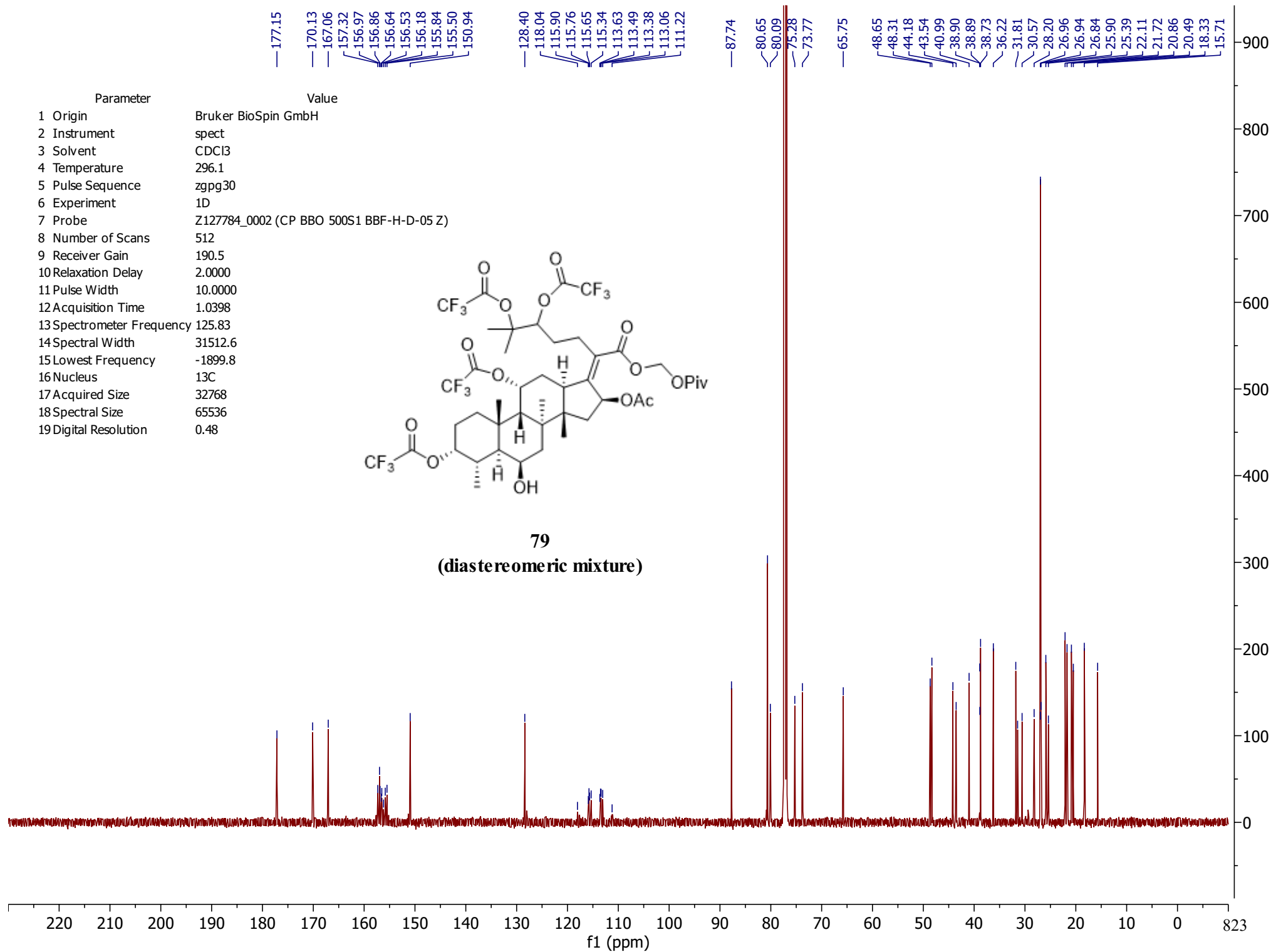


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	107.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



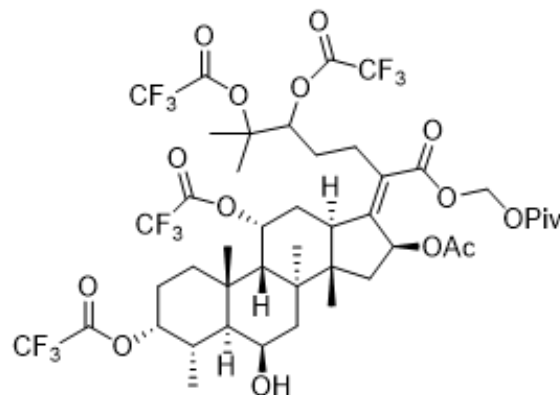
79
(diastereomeric mixture)



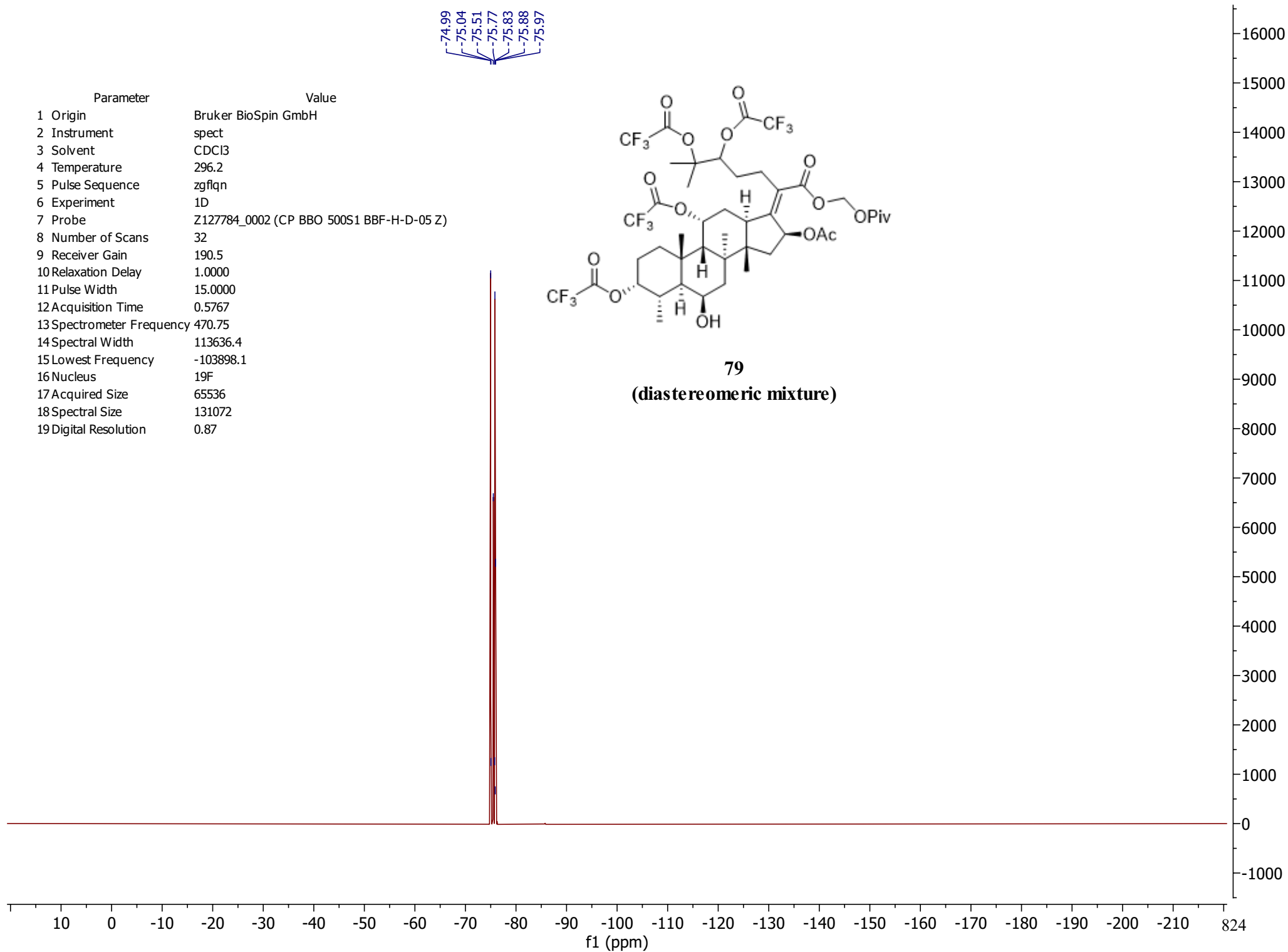


-74.99
-75.04
-75.51
-75.77
-75.83
-75.88
-75.97

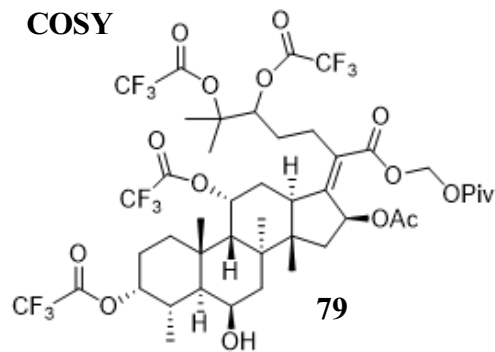
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	¹⁹ F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



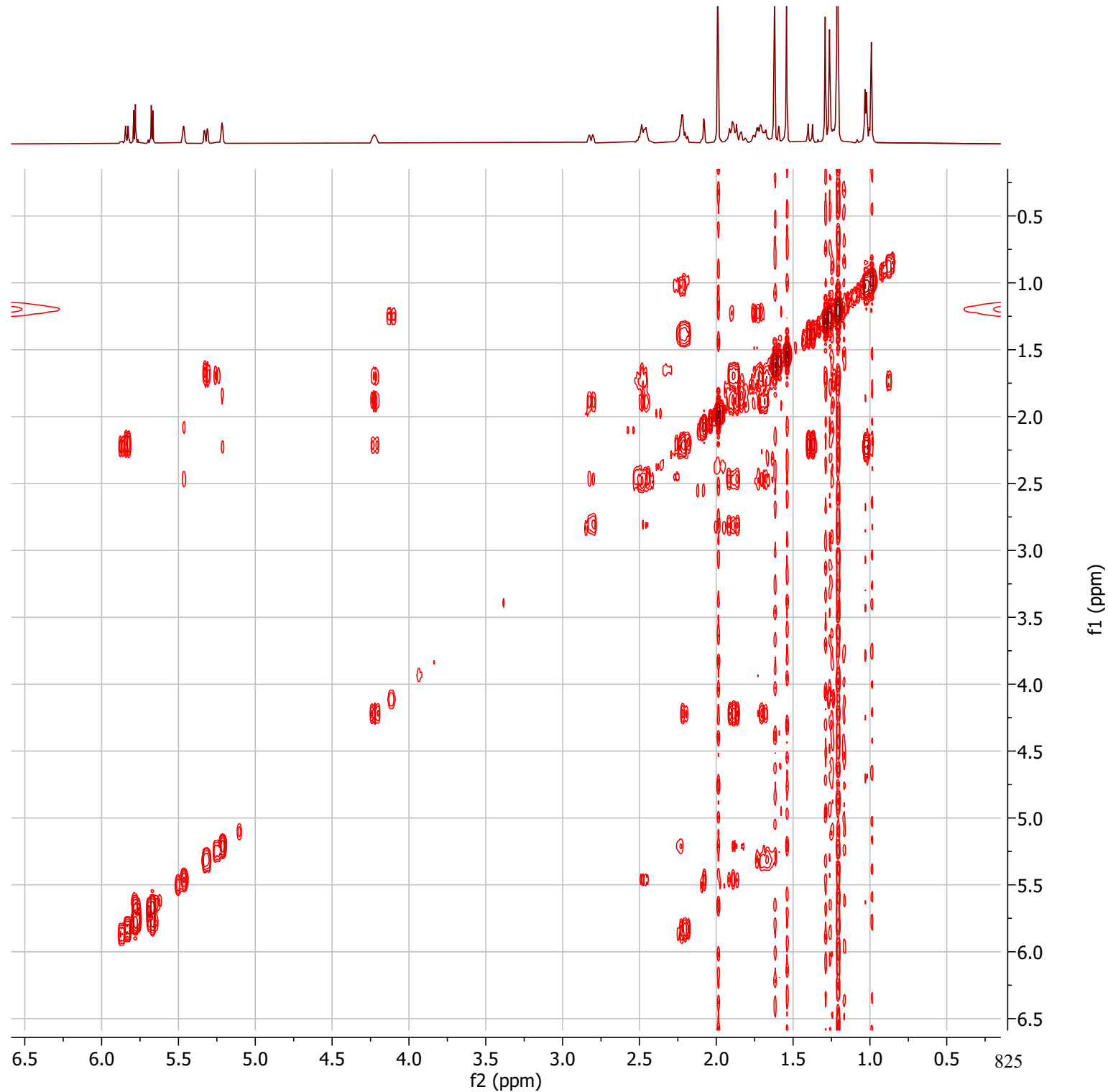
79
(diastereomeric mixture)



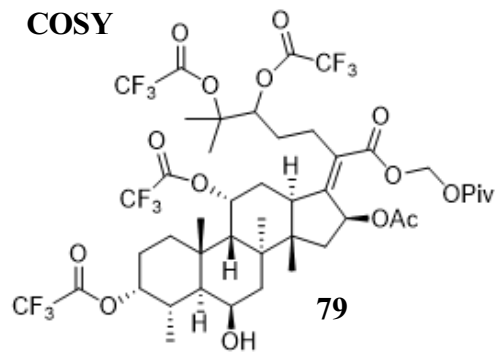
COSY



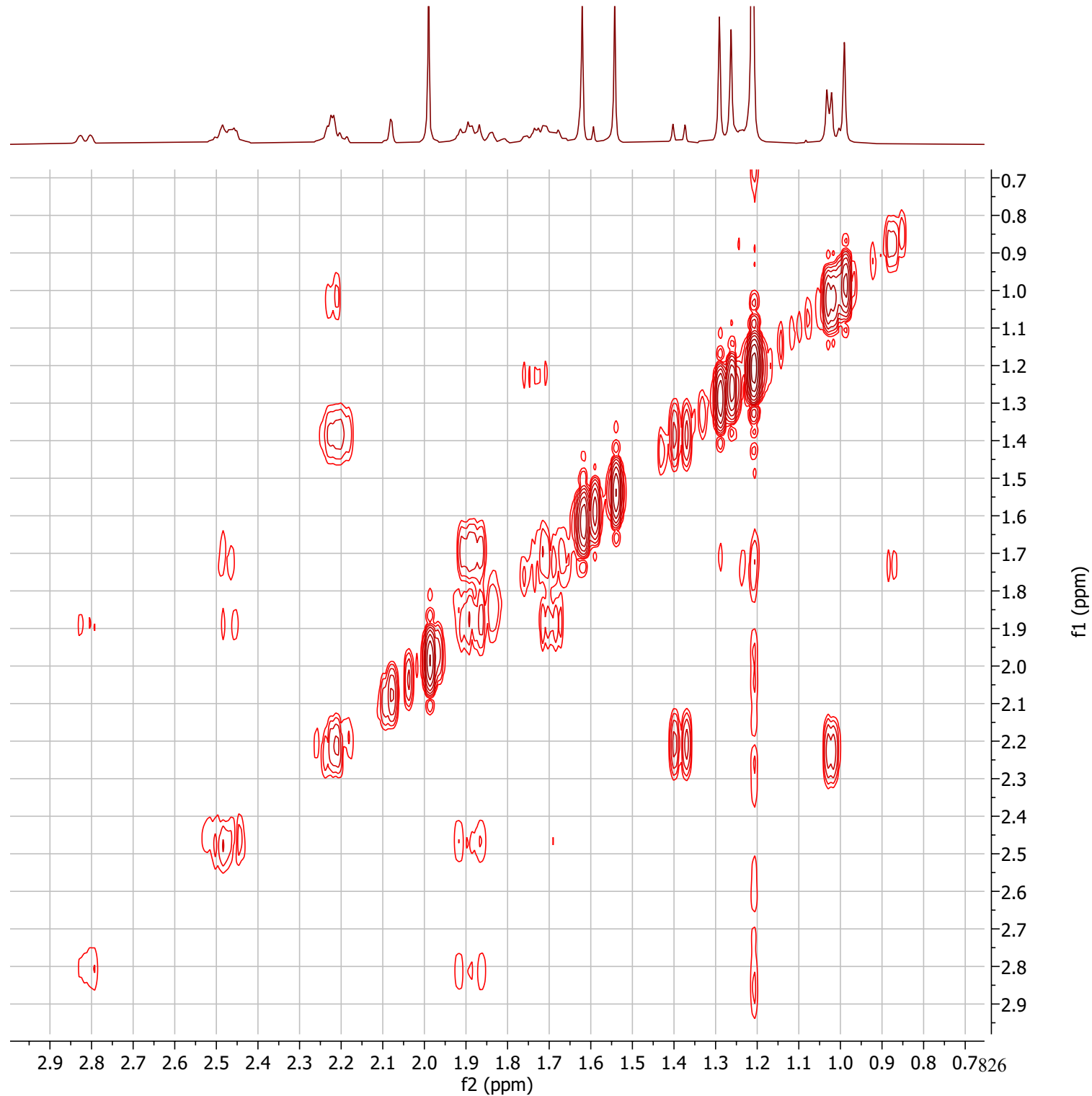
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	3
9 Receiver Gain	19.2
10 Relaxation Delay	1.8398
11 Pulse Width	12.0000
12 Acquisition Time	0.3174
13 Spectrometer Frequency (500.35, 500.35)	
14 Spectral Width	(3225.8, 3225.8)
15 Lowest Frequency	(70.9, 70.9)
16 Nucleus	(1H, 1H)
17 Acquired Size	(1024, 128)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(3.15, 3.15)



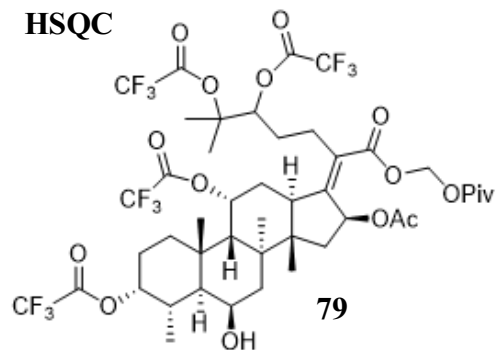
COSY



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	cosygpppqf
6 Experiment	COSY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	3
9 Receiver Gain	19.2
10 Relaxation Delay	1.8398
11 Pulse Width	12.0000
12 Acquisition Time	0.3174
13 Spectrometer Frequency (500.35, 500.35)	
14 Spectral Width (3225.8, 3225.8)	
15 Lowest Frequency (70.9, 70.9)	
16 Nucleus (1H, 1H)	
17 Acquired Size (1024, 128)	
18 Spectral Size (1024, 1024)	
19 Digital Resolution (3.15, 3.15)	

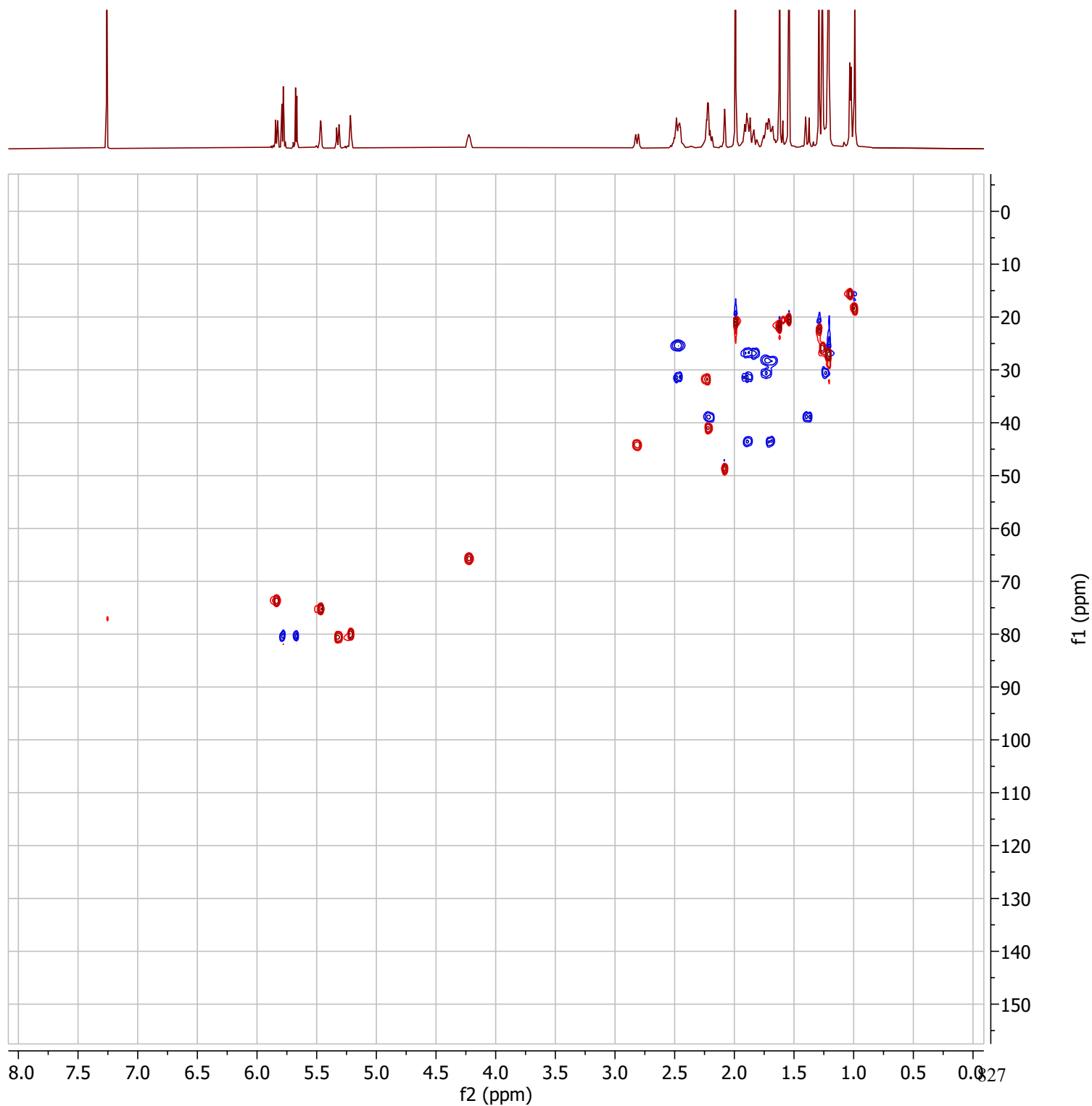


HSQC

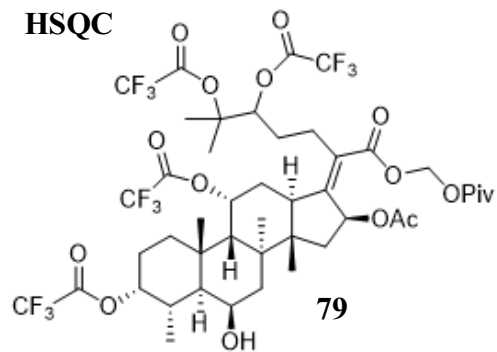


79

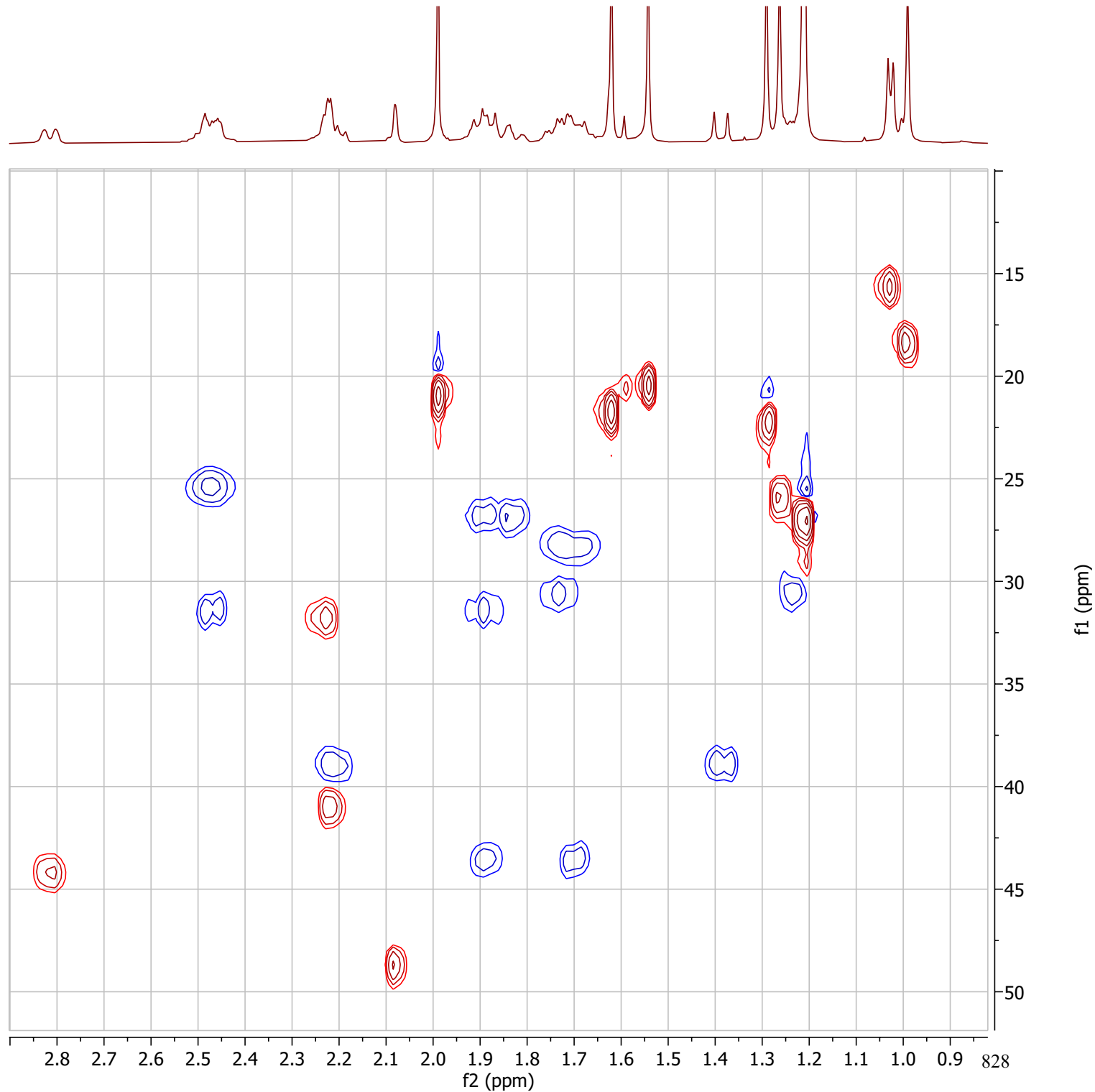
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetdgp
6 Experiment	HSQC-EDITED
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	8
9 Receiver Gain	190.5
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1249
13 Spectrometer Frequency (500.35, 125.82)	
14 Spectral Width	(4098.4, 20746.9)
15 Lowest Frequency	(-53.5, -927.3)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.00, 40.52)



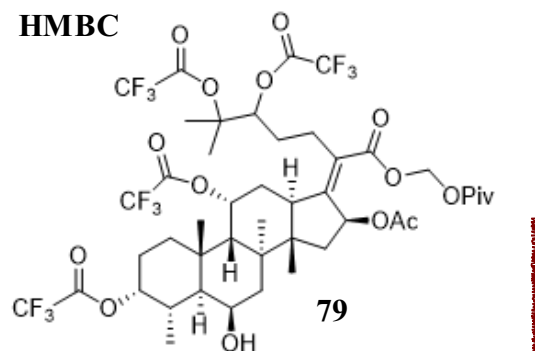
HSQC



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hsqcetdgp
6 Experiment	HSQC-EDITED
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	8
9 Receiver Gain	190.5
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1249
13 Spectrometer Frequency (500.35, 125.82)	
14 Spectral Width	(4098.4, 20746.9)
15 Lowest Frequency	(-53.5, -927.3)
16 Nucleus	(¹ H, ¹³ C)
17 Acquired Size	(512, 256)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.00, 40.52)

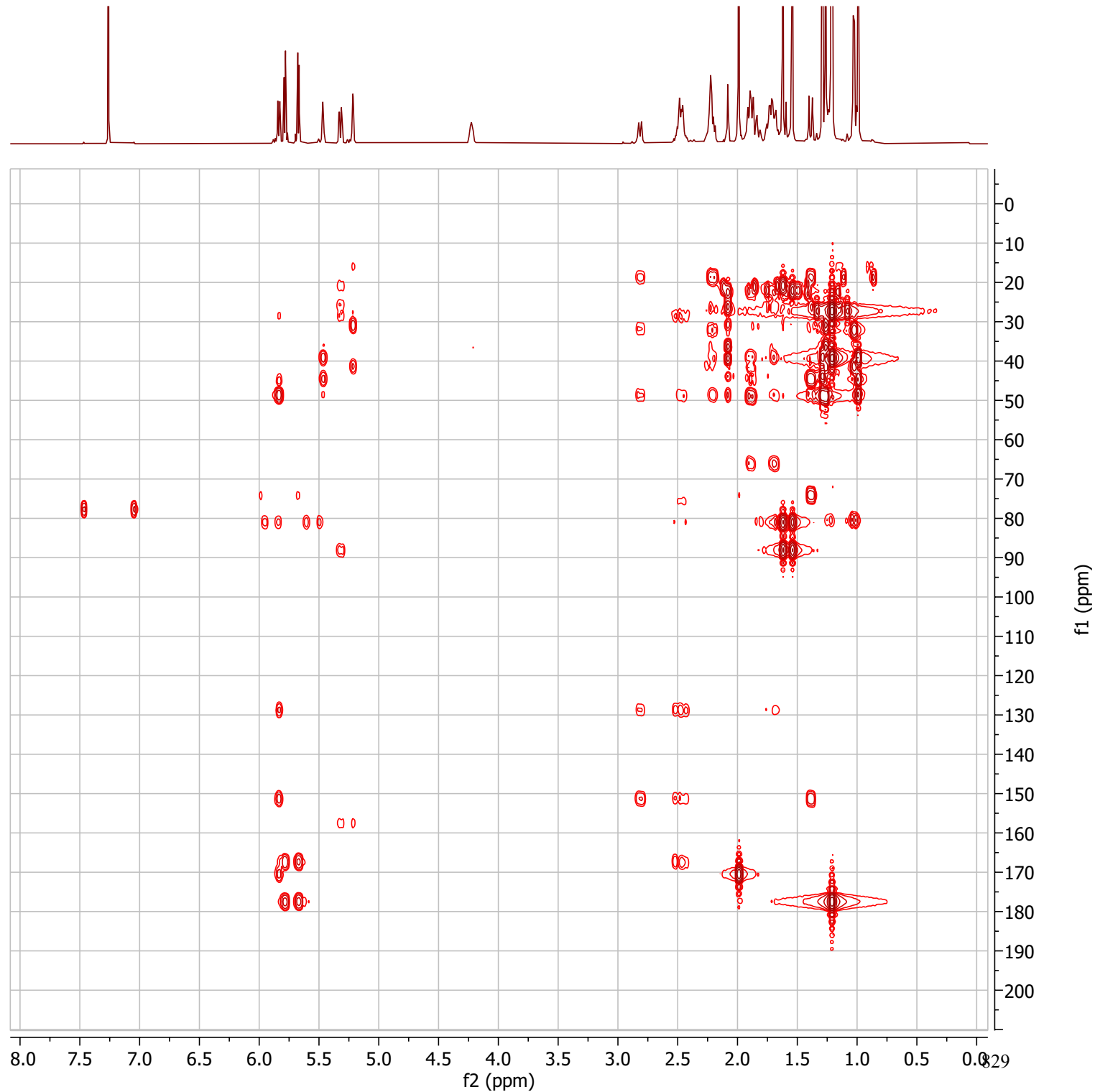


HMBC

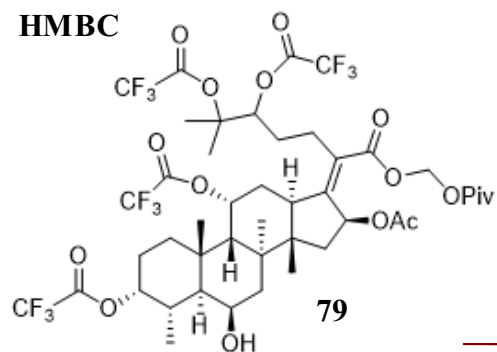


79

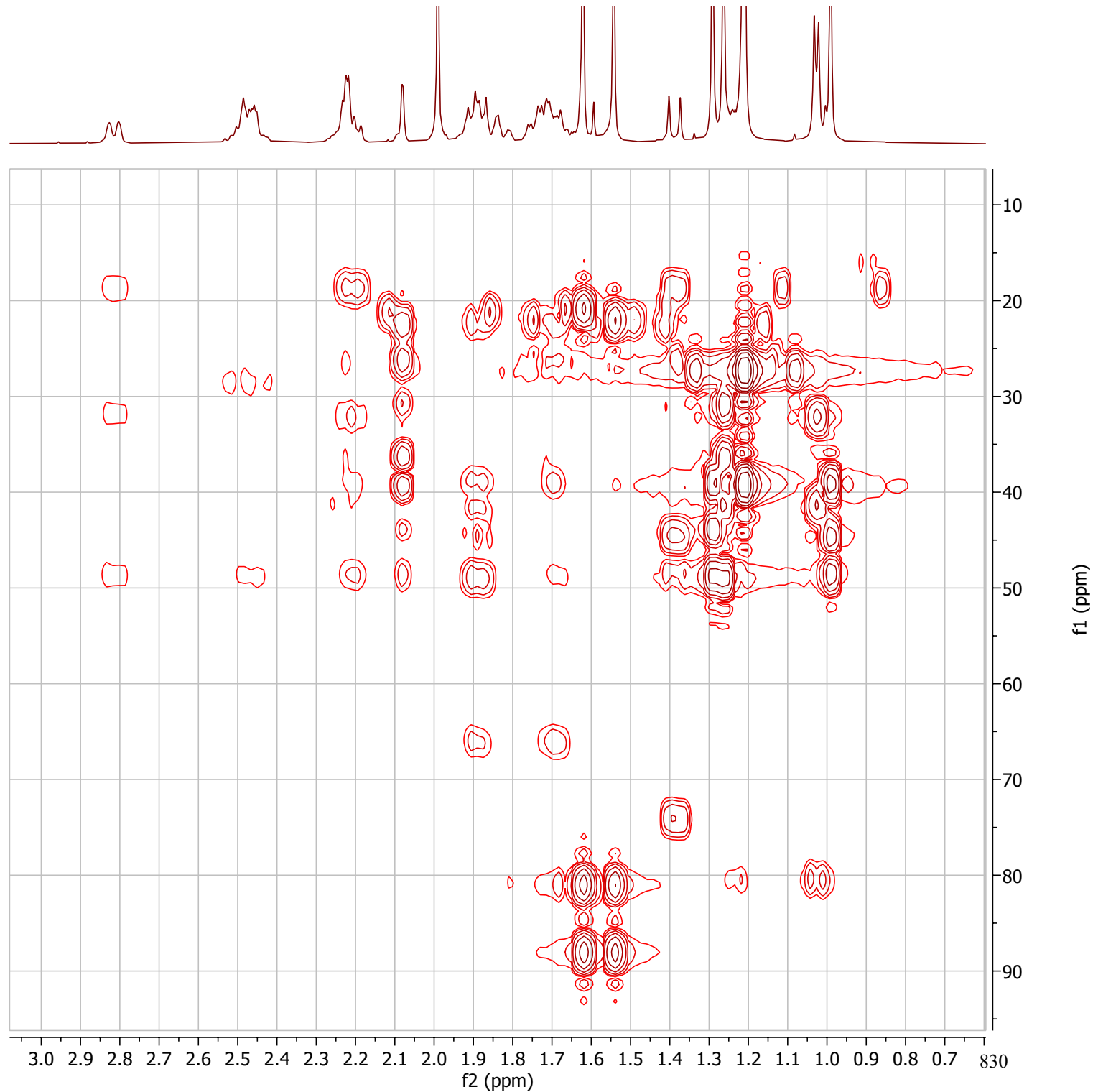
Parameter	Value
1 Origin	Brucker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgp1pndqf
6 Experiment	HMBC
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	12
9 Receiver Gain	190.5
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1249
13 Spectrometer Frequency (500.35, 125.83)	
14 Spectral Width	(4098.4, 27624.3)
15 Lowest Frequency	(-54.8, -1171.3)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 128)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.00, 53.95)



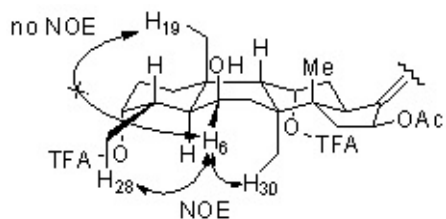
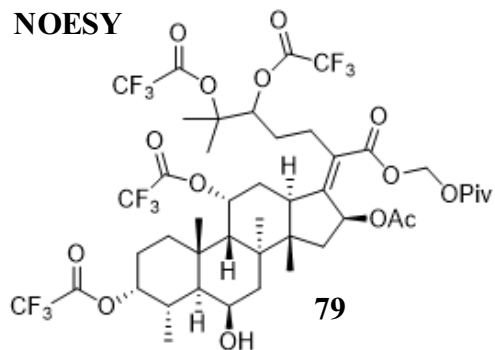
HMBC



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	hmbcgp1pndqf
6 Experiment	HMBC
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	12
9 Receiver Gain	190.5
10 Relaxation Delay	1.5000
11 Pulse Width	12.0000
12 Acquisition Time	0.1249
13 Spectrometer Frequency (500.35, 125.83)	
14 Spectral Width	(4098.4, 27624.3)
15 Lowest Frequency	(-54.8, -1171.3)
16 Nucleus	(1H, 13C)
17 Acquired Size	(512, 128)
18 Spectral Size	(512, 512)
19 Digital Resolution	(8.00, 53.95)

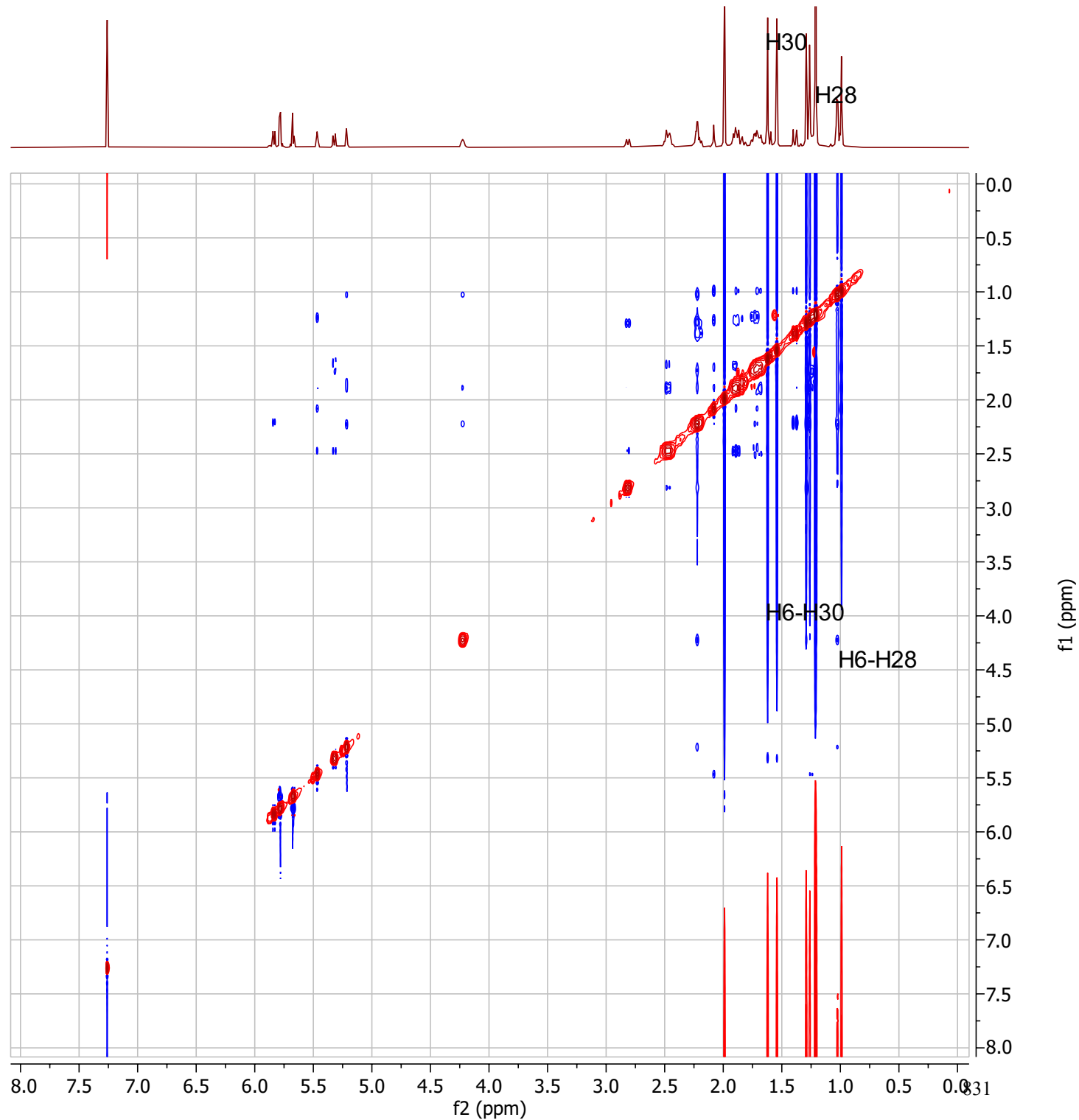


NOESY

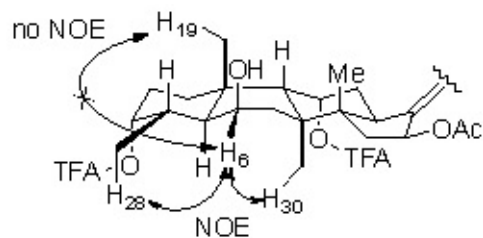
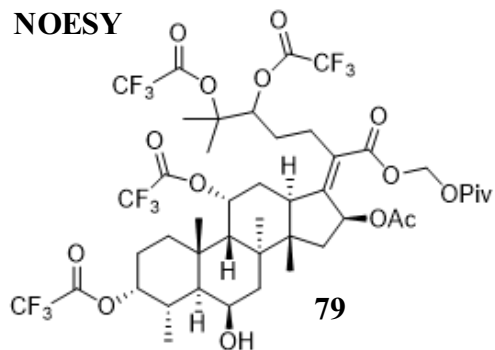


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	noesygpphpp
6 Experiment	NOESY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	12
9 Receiver Gain	34.8
10 Relaxation Delay	1.9549
11 Pulse Width	12.0000
12 Acquisition Time	0.2499
13 Spectrometer Frequency (500.35, 500.35)	
14 Spectral Width	(4098.4, 4098.4)
15 Lowest Frequency	(-53.5, -53.5)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.00, 4.00)

H6

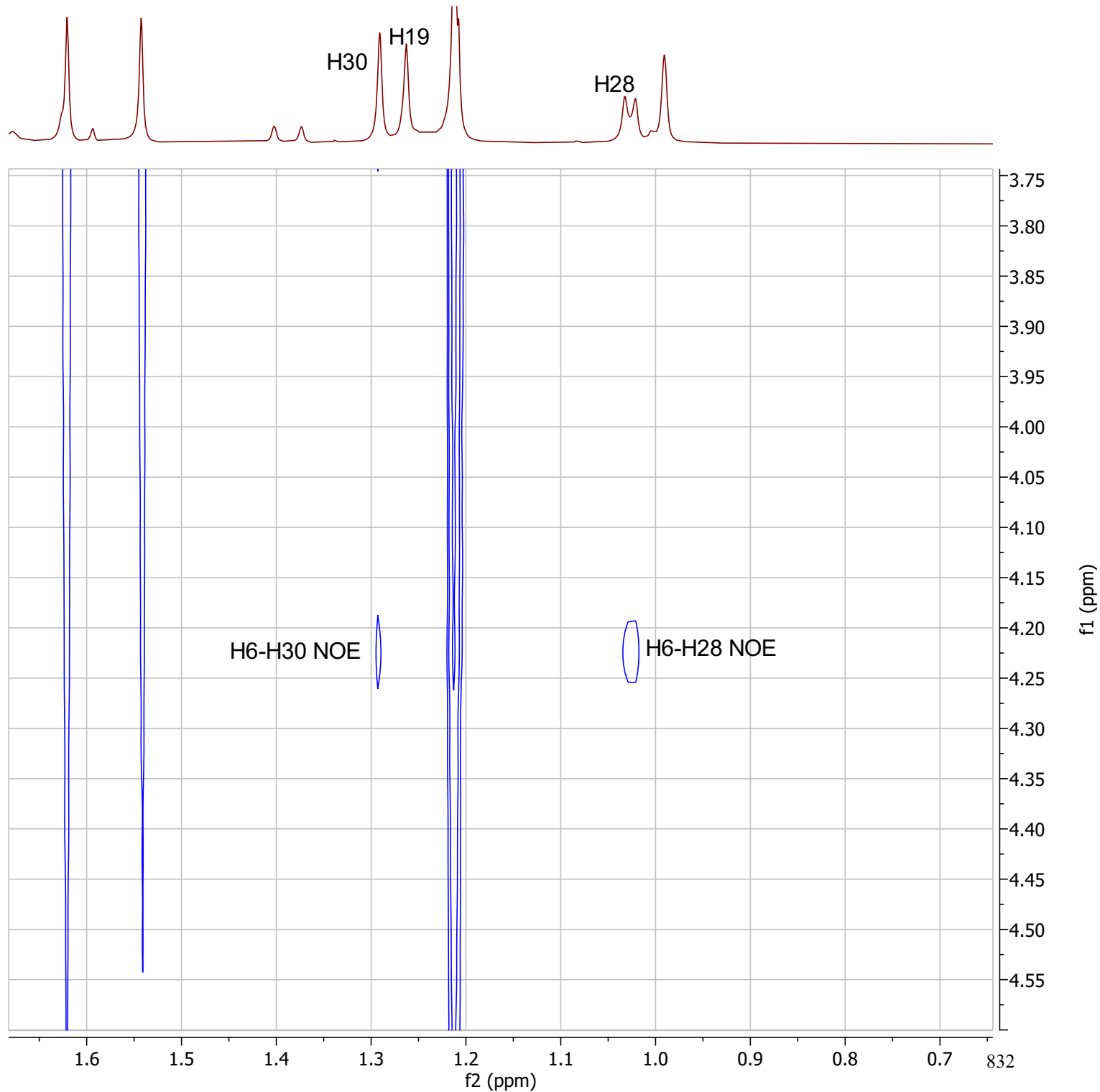


NOESY



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	noesygpph
6 Experiment	NOESY
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	12
9 Receiver Gain	34.8
10 Relaxation Delay	1.9549
11 Pulse Width	12.0000
12 Acquisition Time	0.2499
13 Spectrometer Frequency	(500.35, 500.35)
14 Spectral Width	(4098.4, 4098.4)
15 Lowest Frequency	(-53.5, -53.5)
16 Nucleus	(¹ H, ¹ H)
17 Acquired Size	(1024, 256)
18 Spectral Size	(1024, 1024)
19 Digital Resolution	(4.00, 4.00)

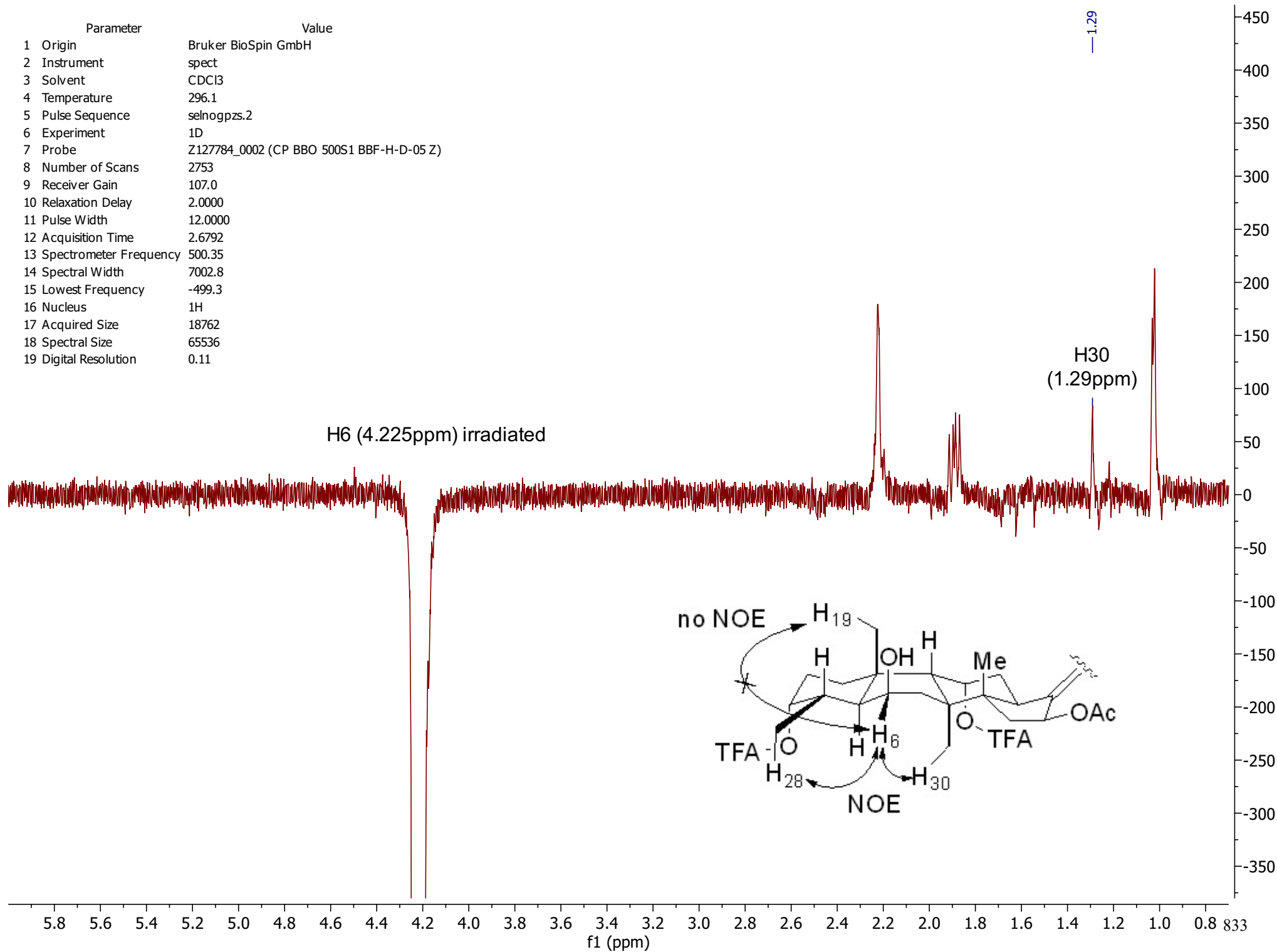
H6



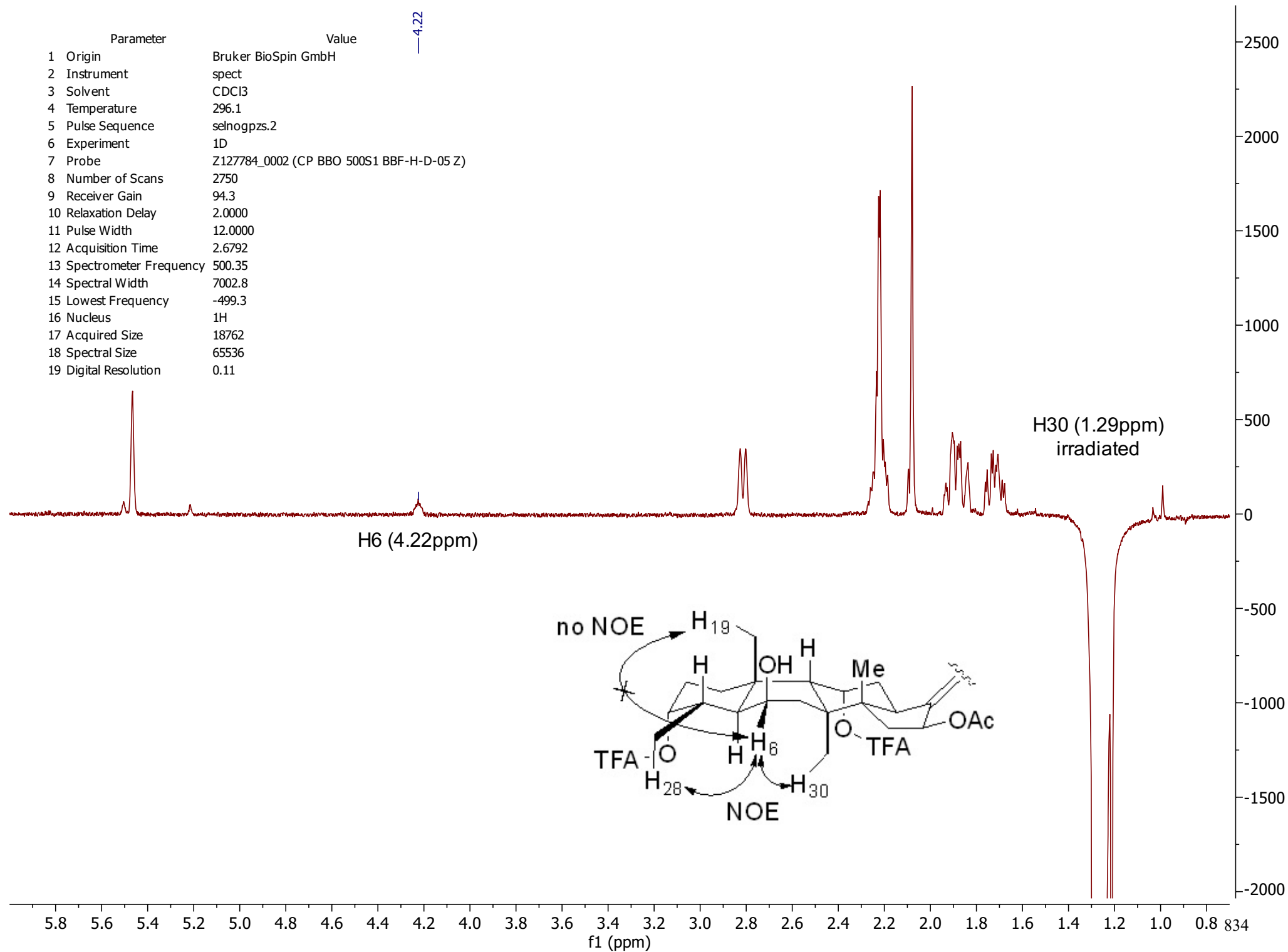
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	selnpgps.2
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2753
9 Receiver Gain	107.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.6792
13 Spectrometer Frequency	500.35
14 Spectral Width	7002.8
15 Lowest Frequency	-499.3
16 Nucleus	¹ H
17 Acquired Size	18762
18 Spectral Size	65536
19 Digital Resolution	0.11

H6 (4.225ppm) irradiated

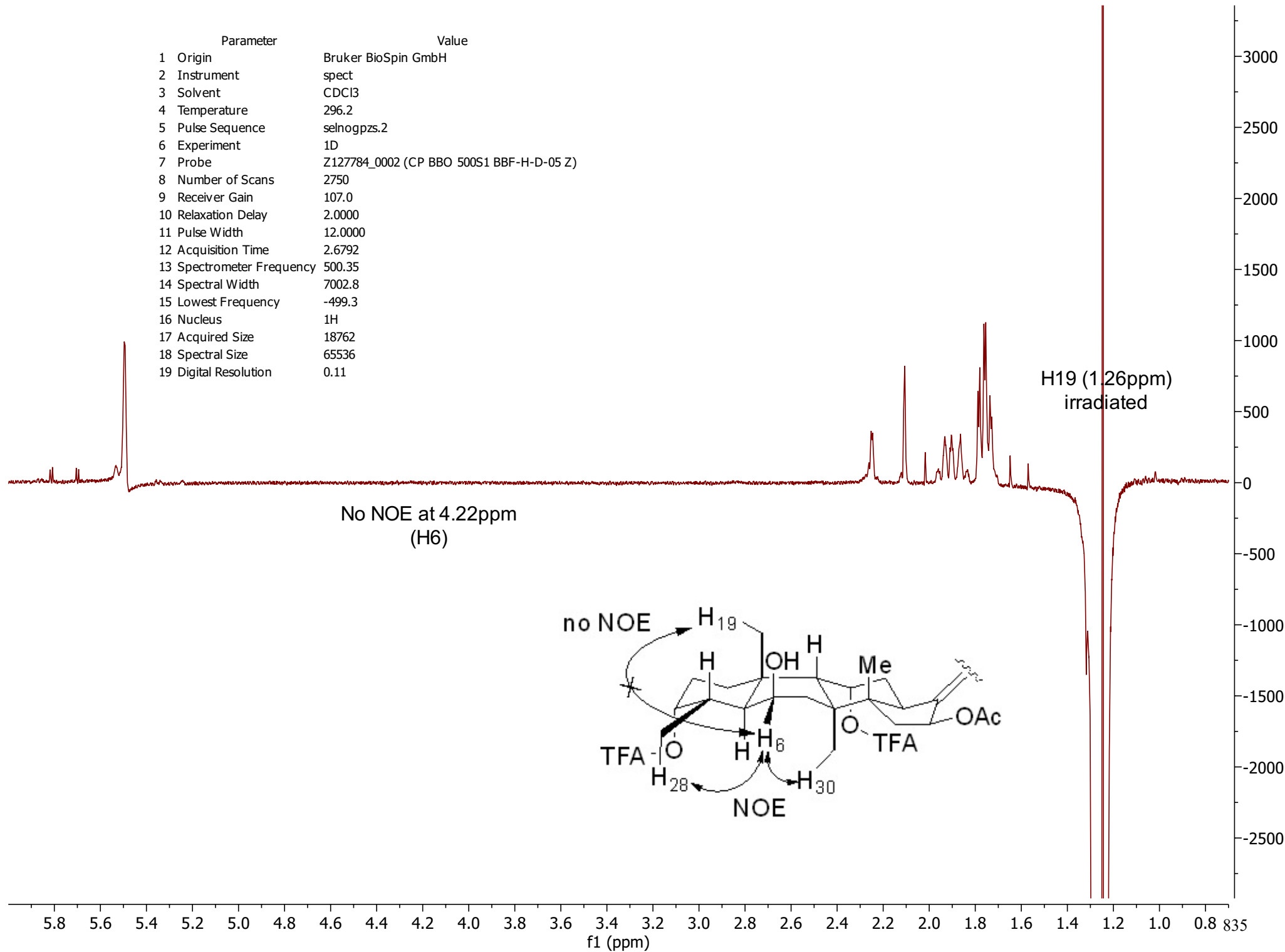
H30
(1.29ppm)



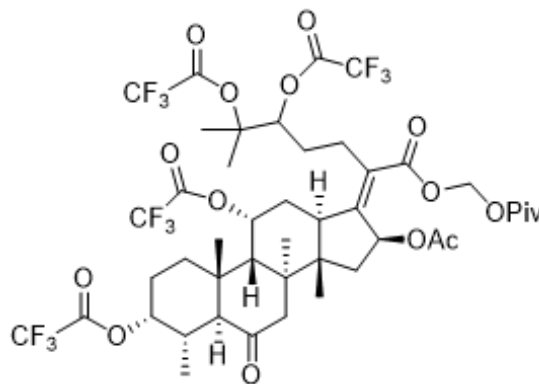
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	selnpgps.2
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2750
9 Receiver Gain	94.3
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.6792
13 Spectrometer Frequency	500.35
14 Spectral Width	7002.8
15 Lowest Frequency	-499.3
16 Nucleus	¹ H
17 Acquired Size	18762
18 Spectral Size	65536
19 Digital Resolution	0.11



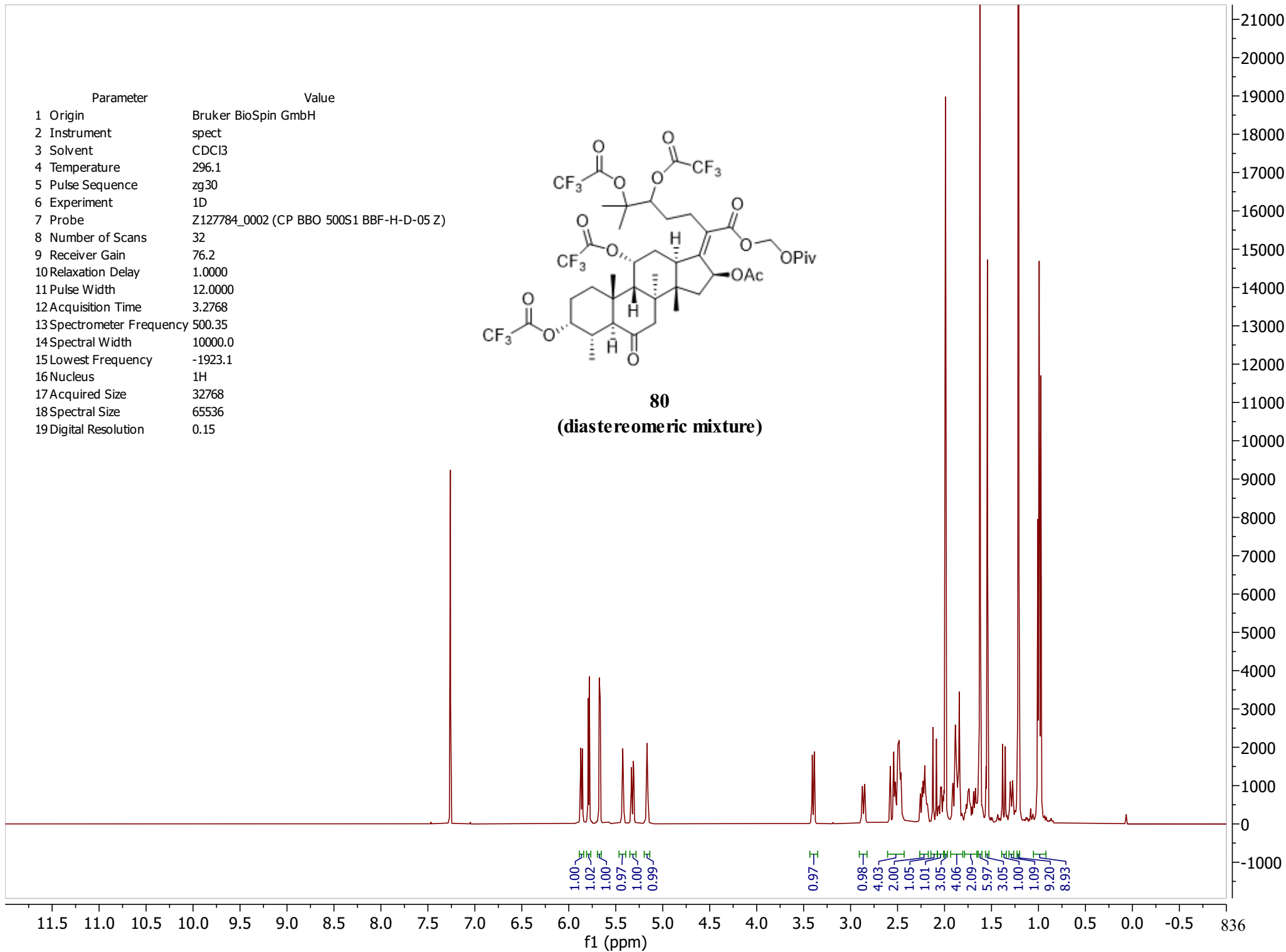
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	selnpgps.2
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2750
9 Receiver Gain	107.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.6792
13 Spectrometer Frequency	500.35
14 Spectral Width	7002.8
15 Lowest Frequency	-499.3
16 Nucleus	¹ H
17 Acquired Size	18762
18 Spectral Size	65536
19 Digital Resolution	0.11

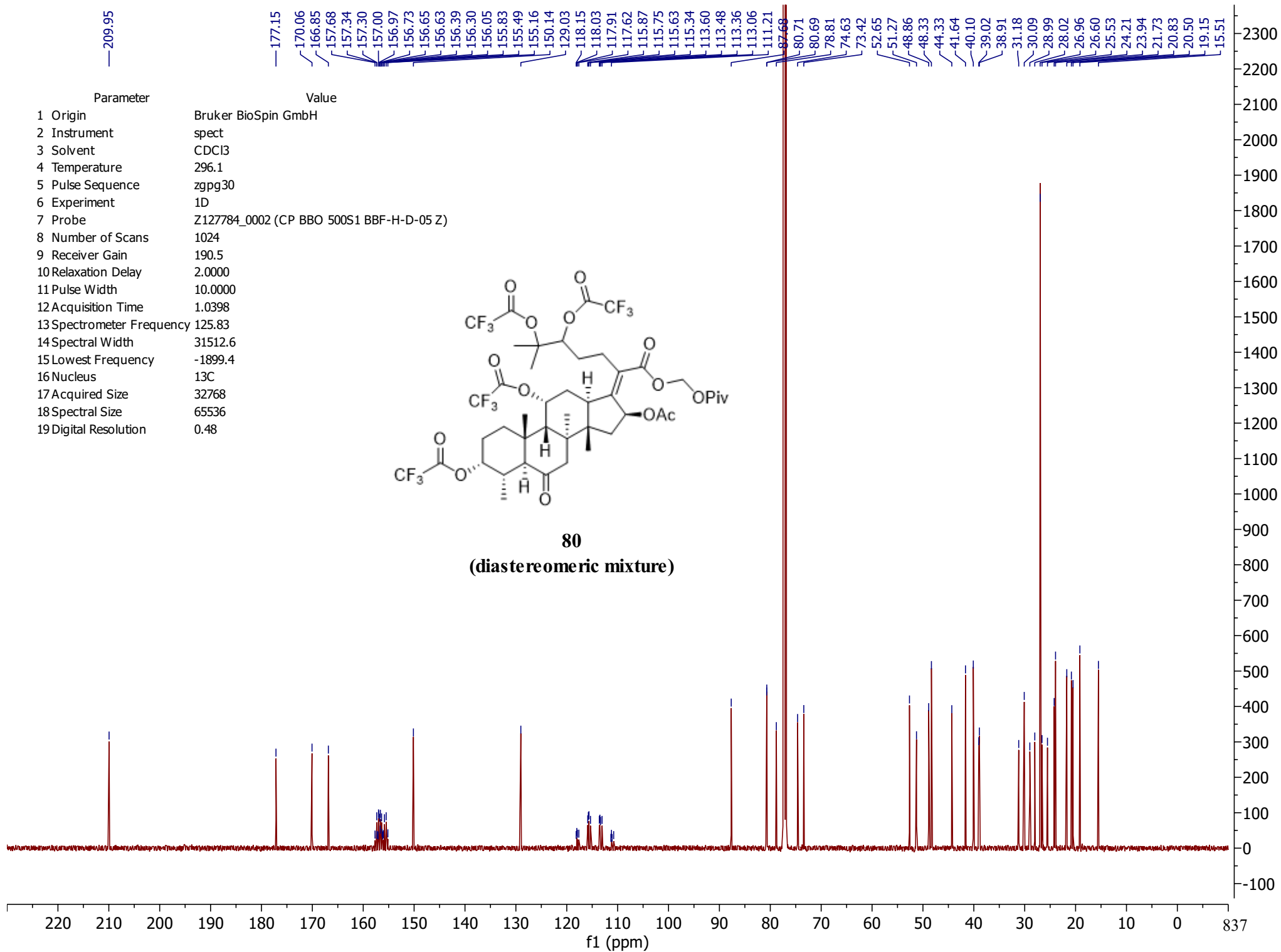


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



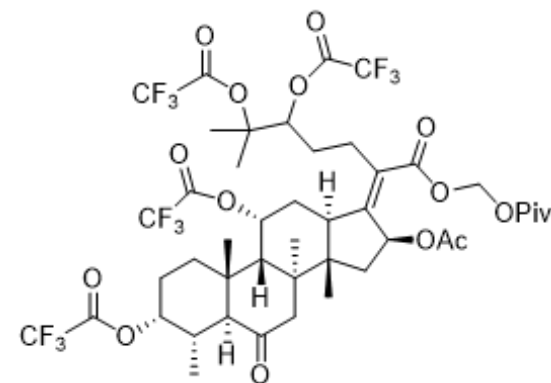
80
(diastereomeric mixture)



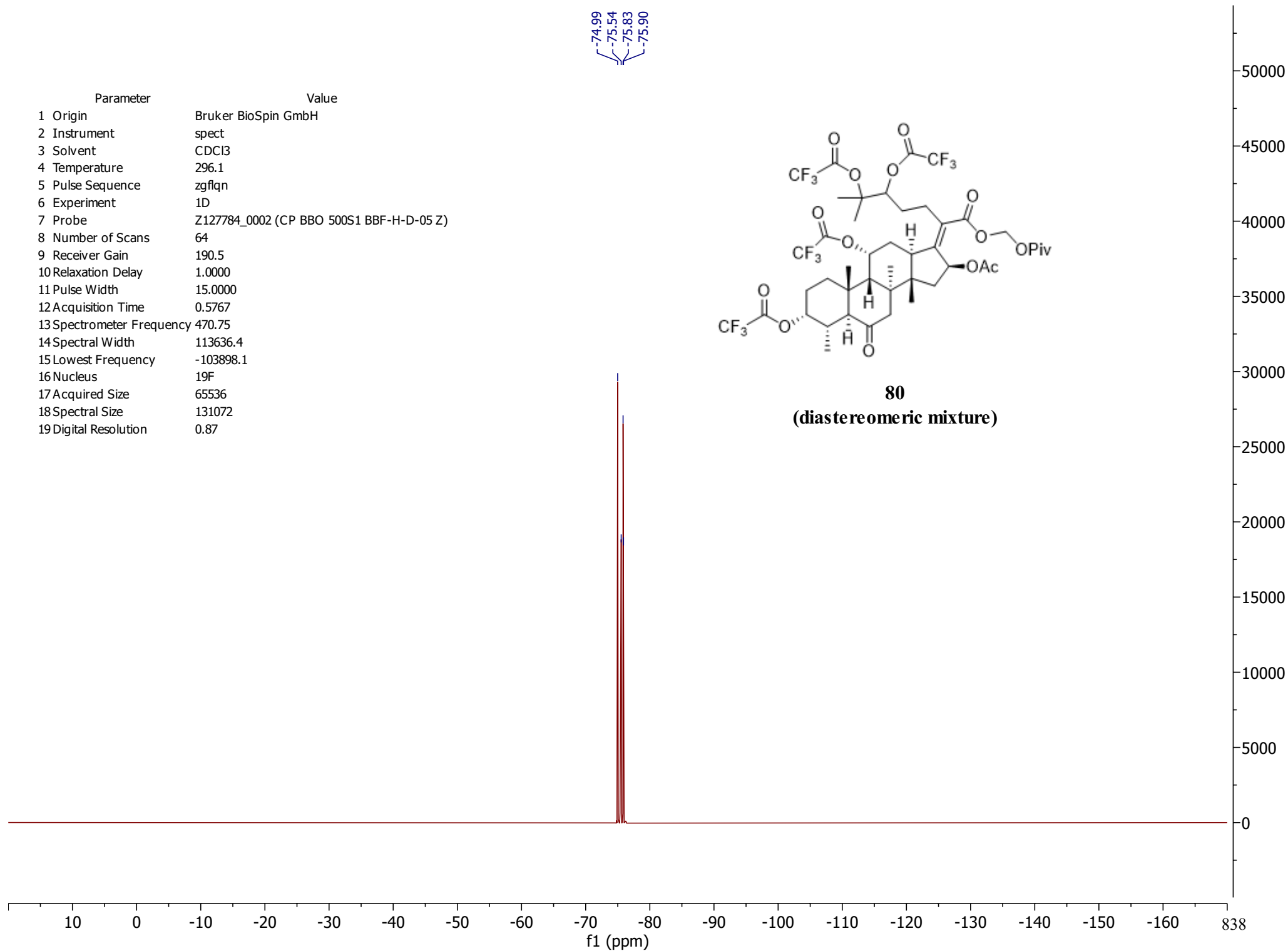


-74.99
-75.54
-75.83
-75.90

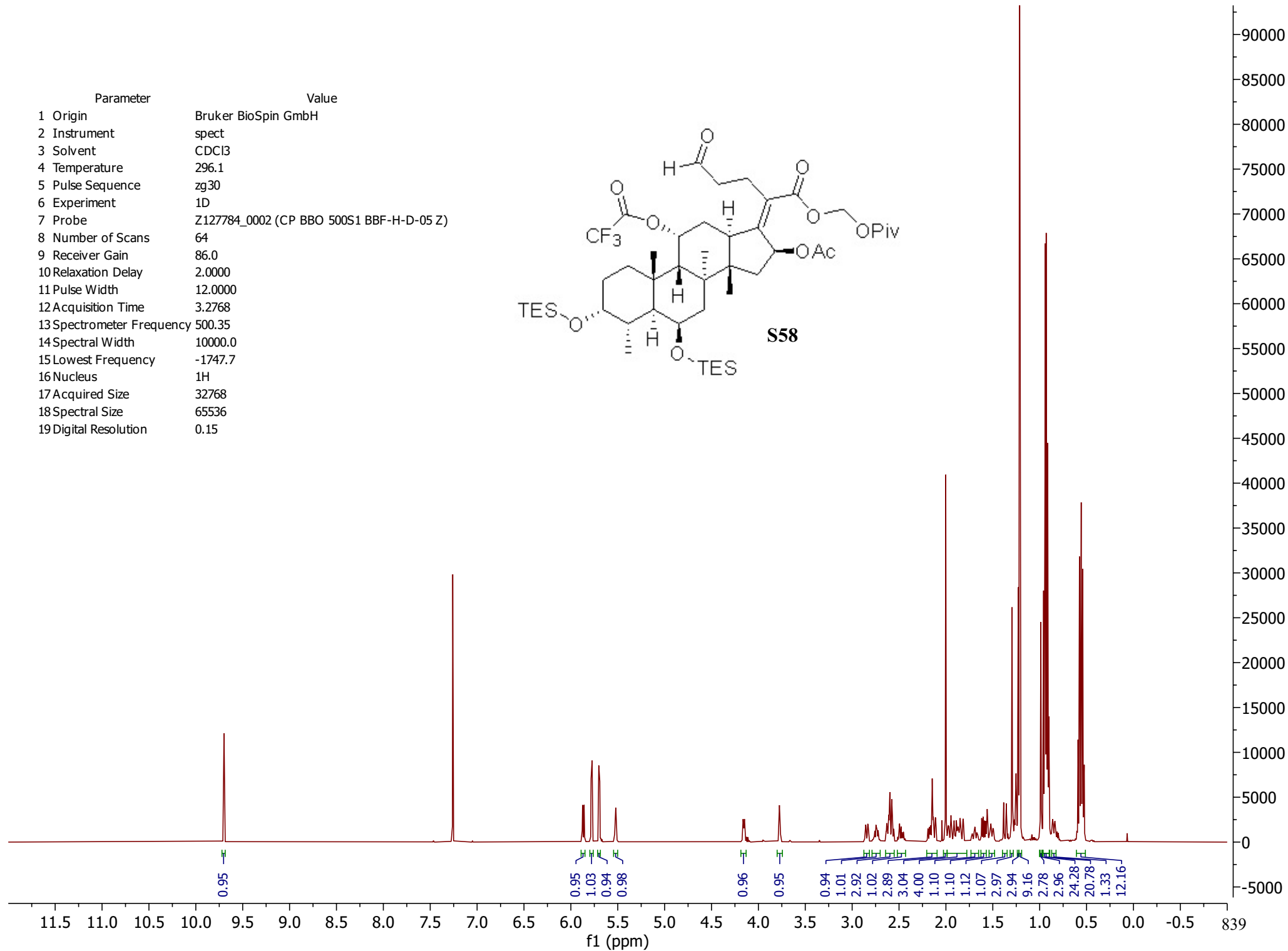
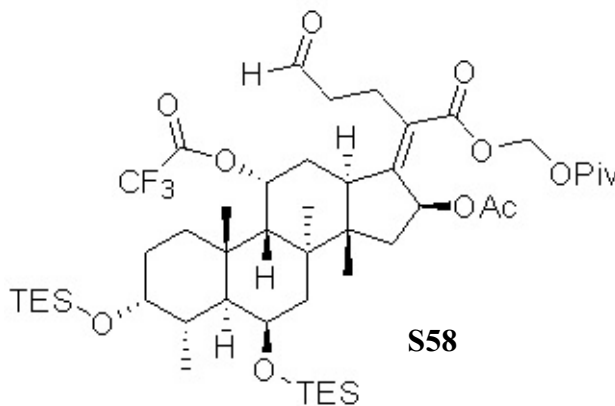
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgfgqn
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	¹⁹ F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



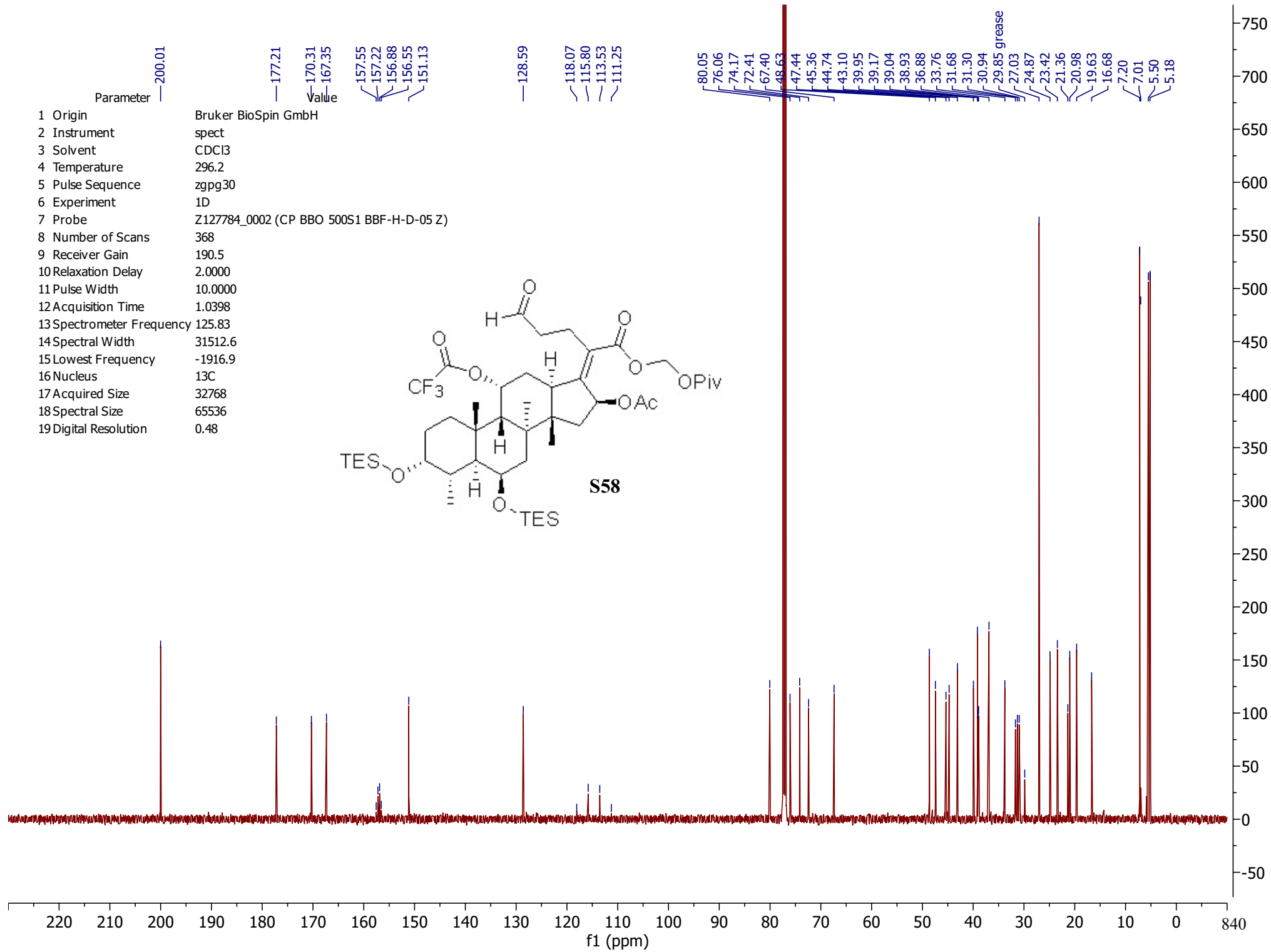
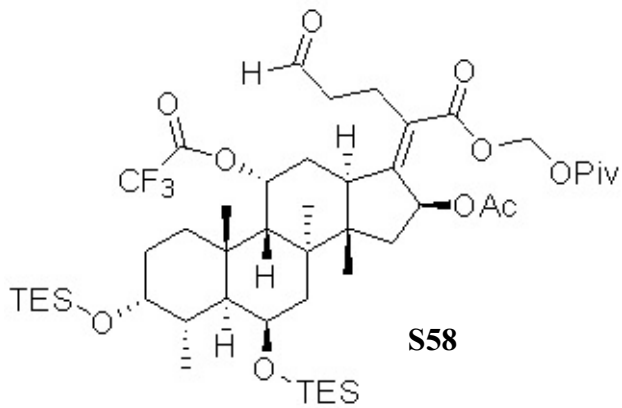
80
(diastereomeric mixture)



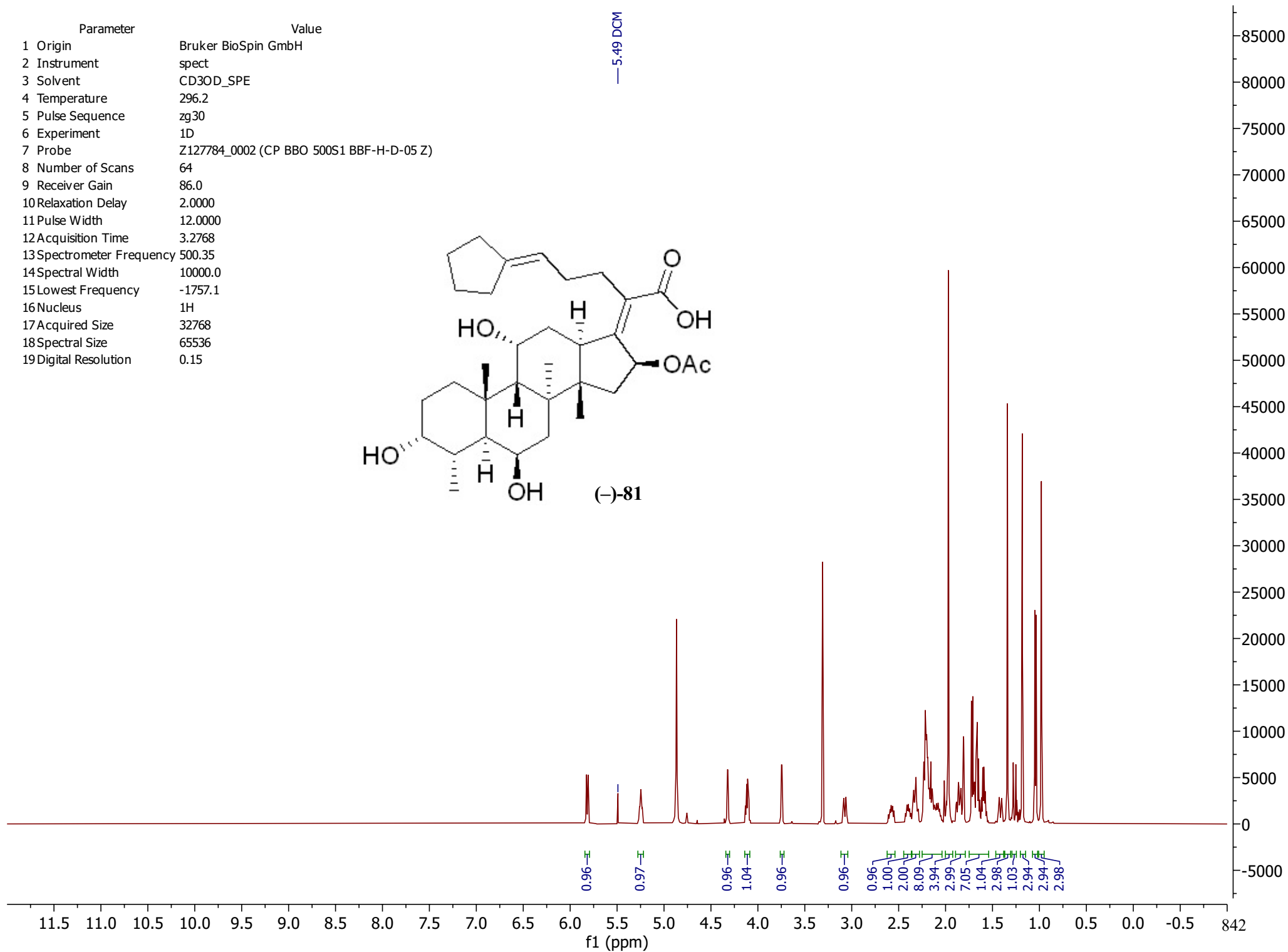
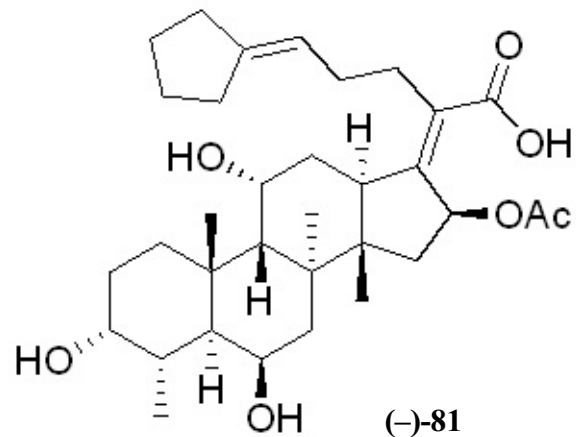
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



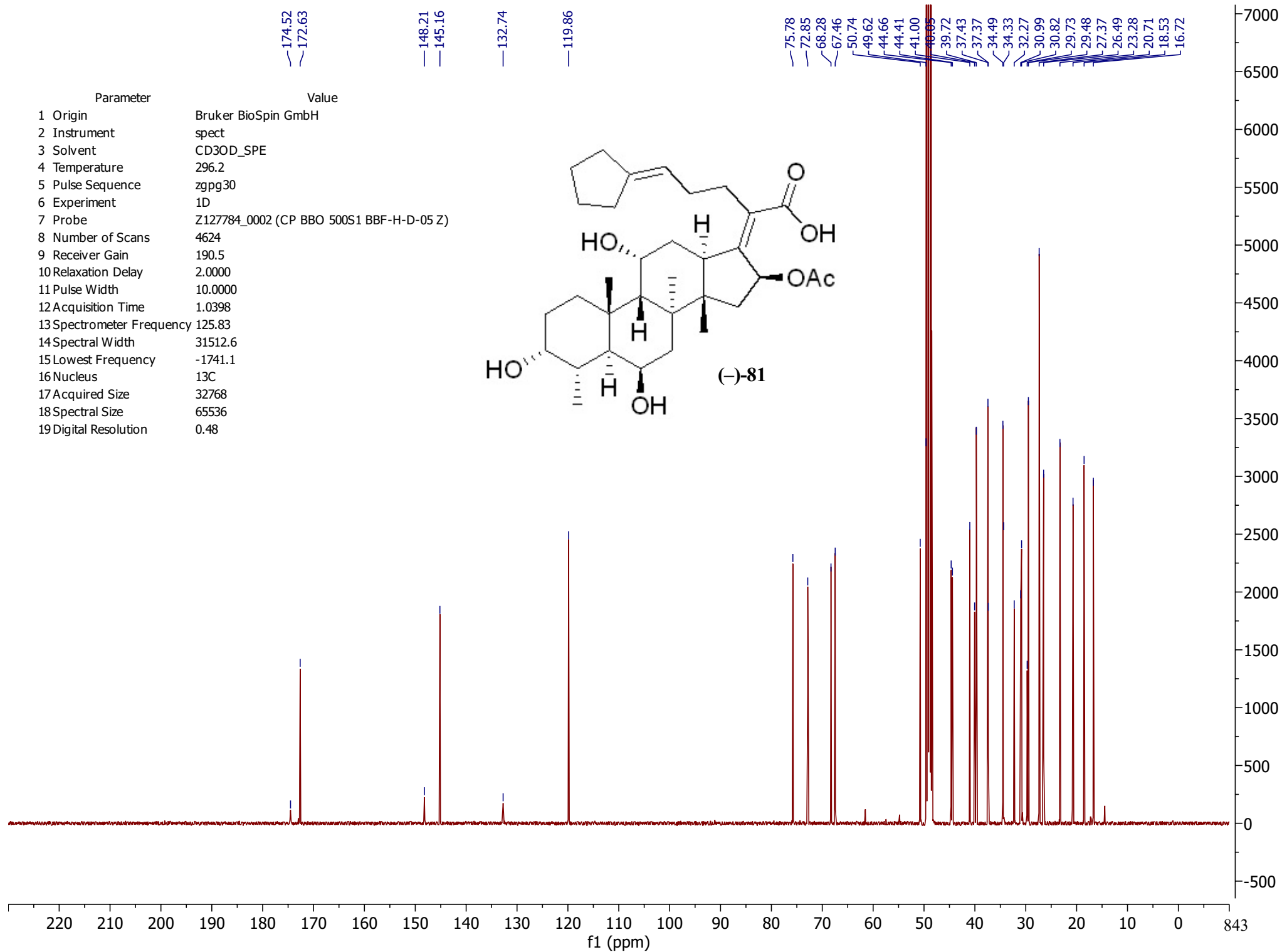
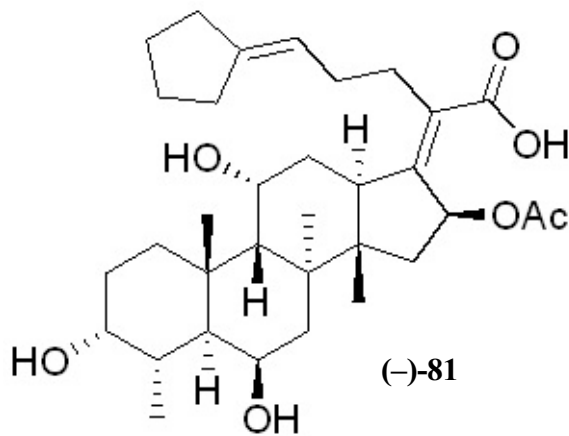
1	Origin	Bruker BioSpin GmbH
2	Instrument	spect
3	Solvent	CDCI3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1916.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536
19	Digital Resolution	0.48



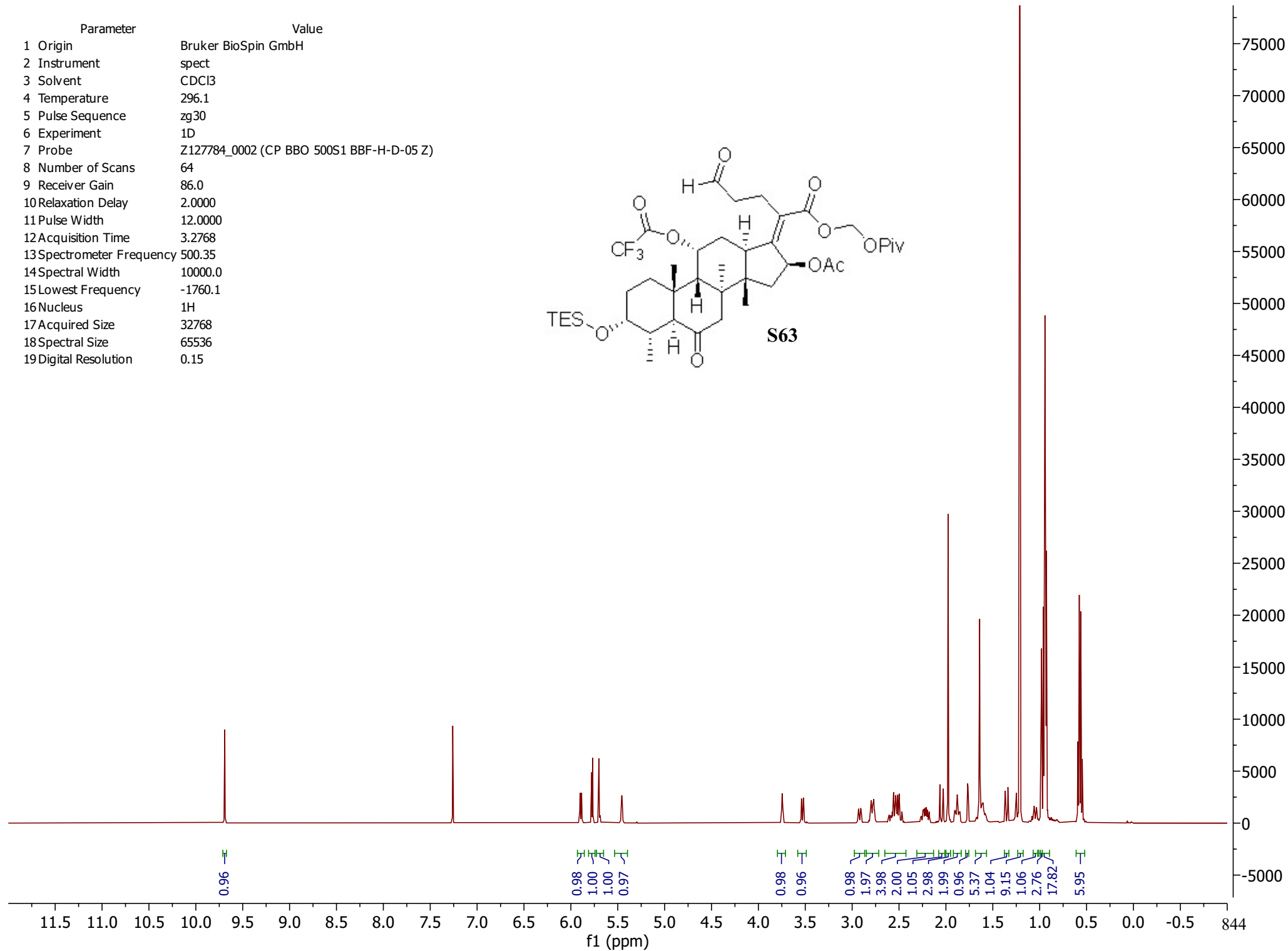
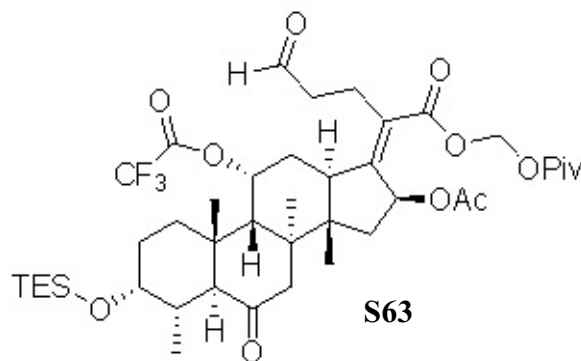
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CD3OD_SPE
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1757.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

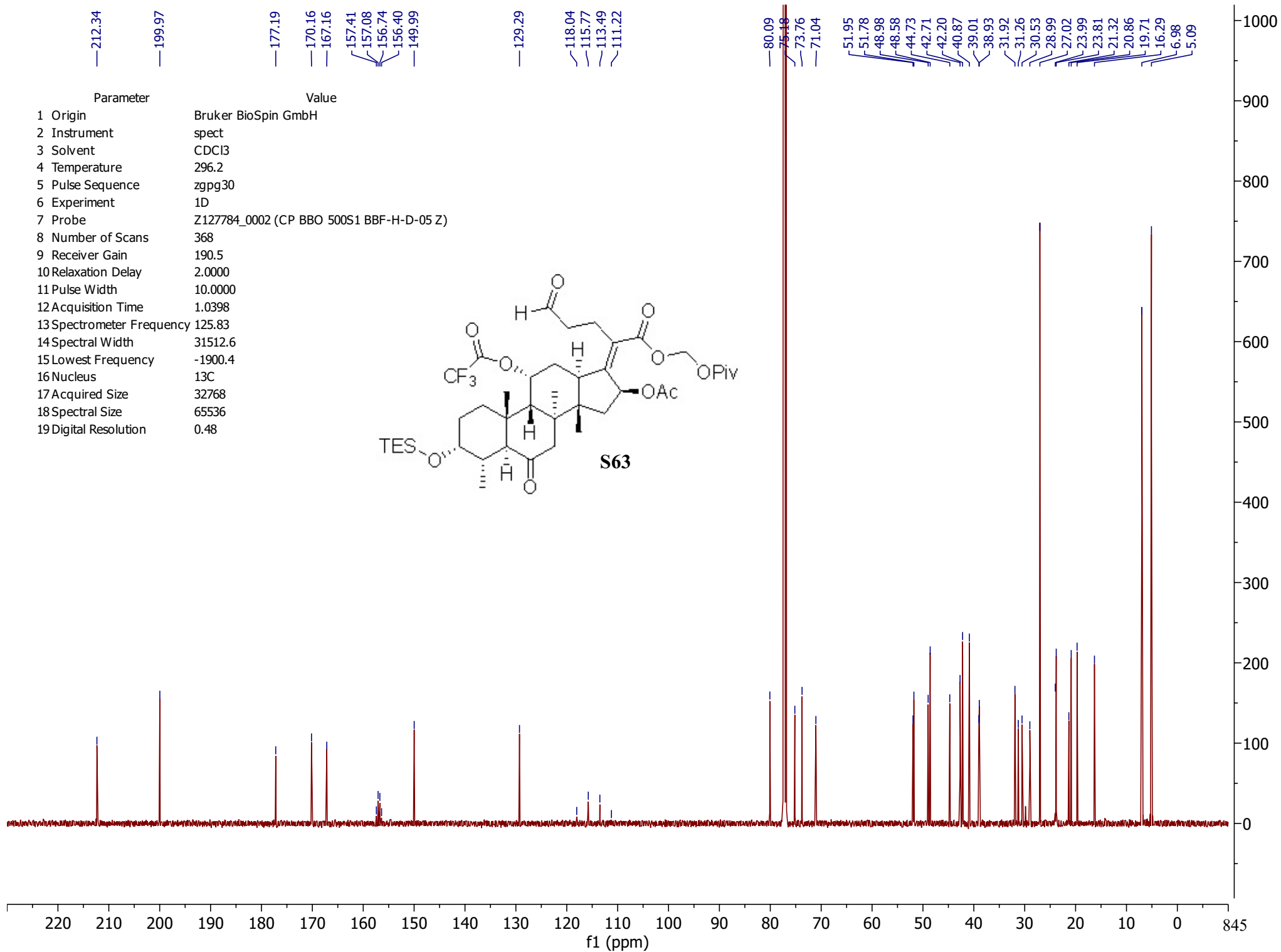


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CD3OD_SPE
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	4624
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1741.1
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



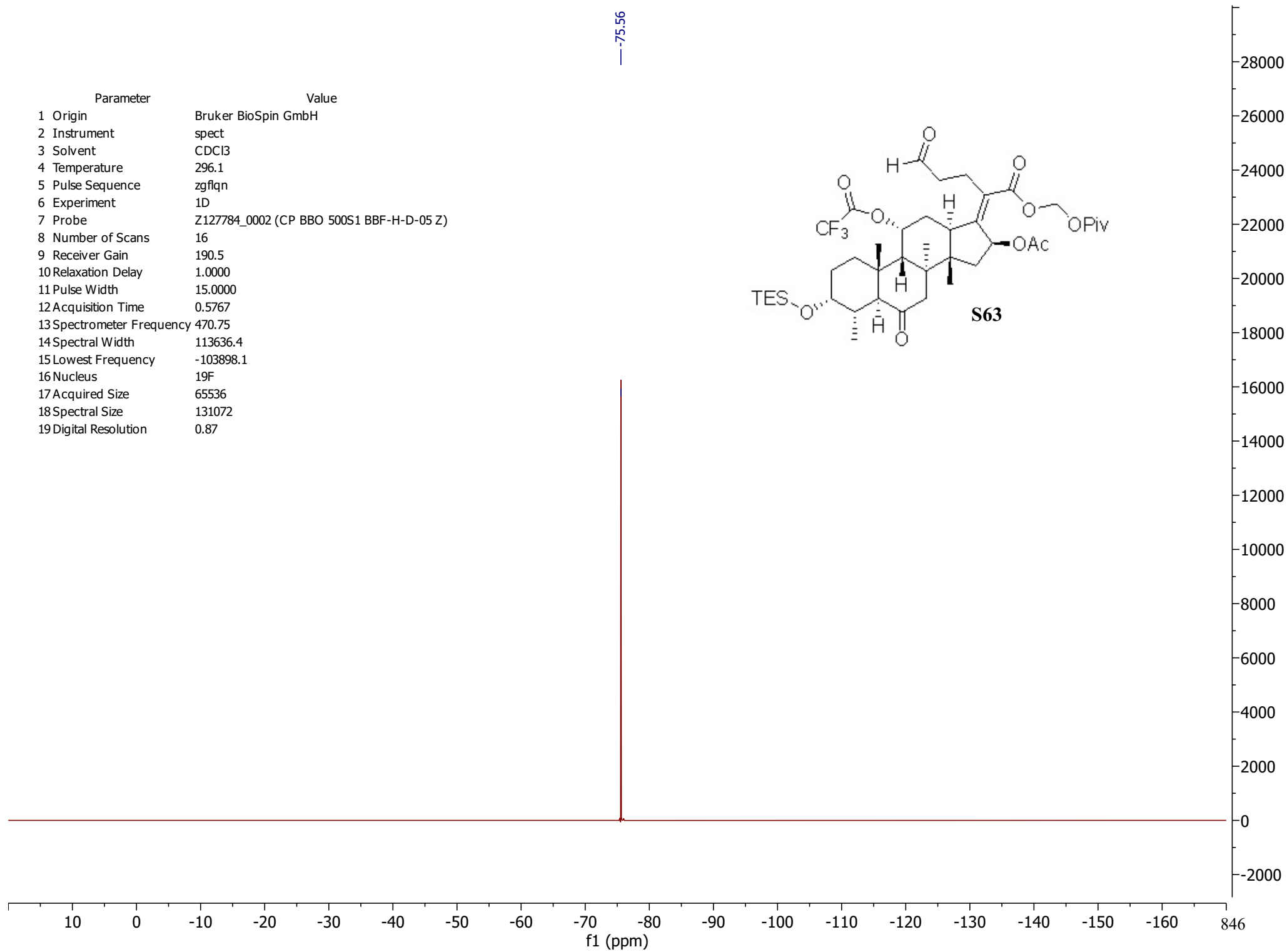
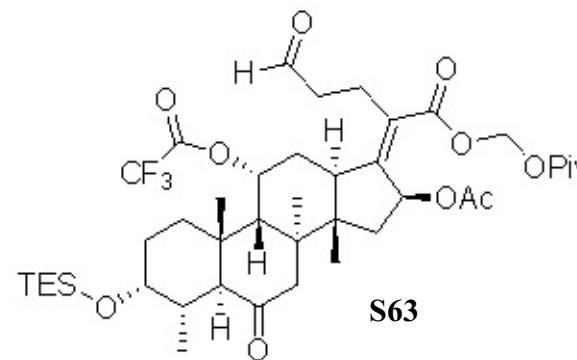
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	86.0
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1760.1
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



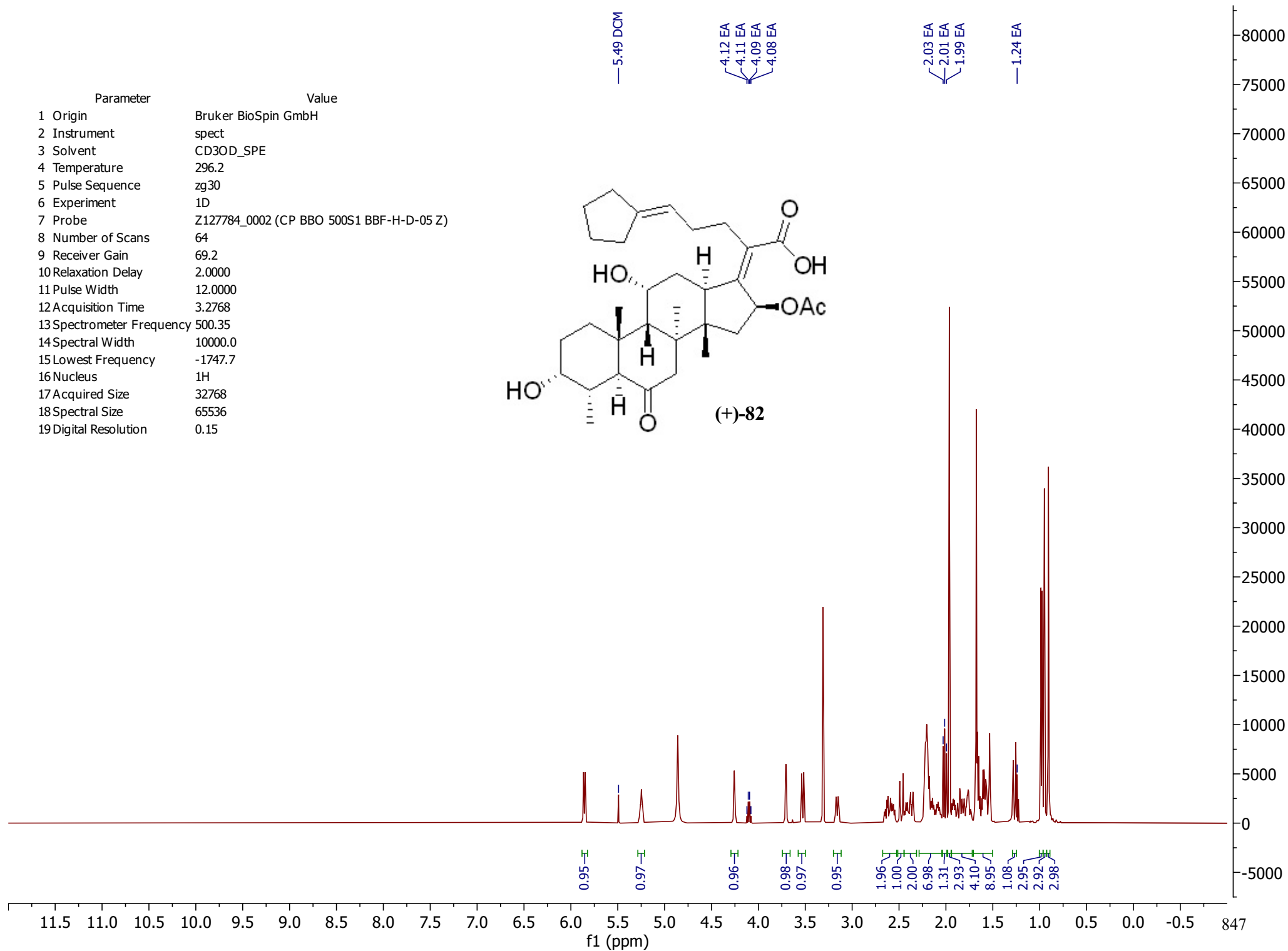
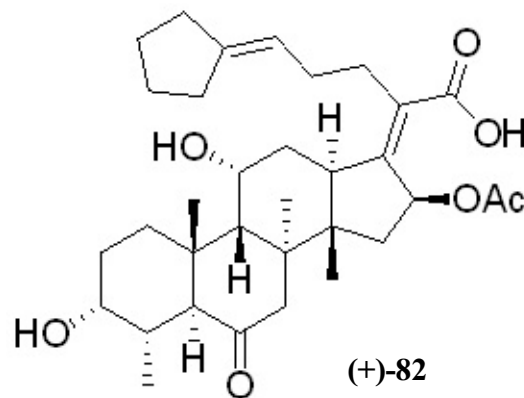


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	¹⁹ F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87

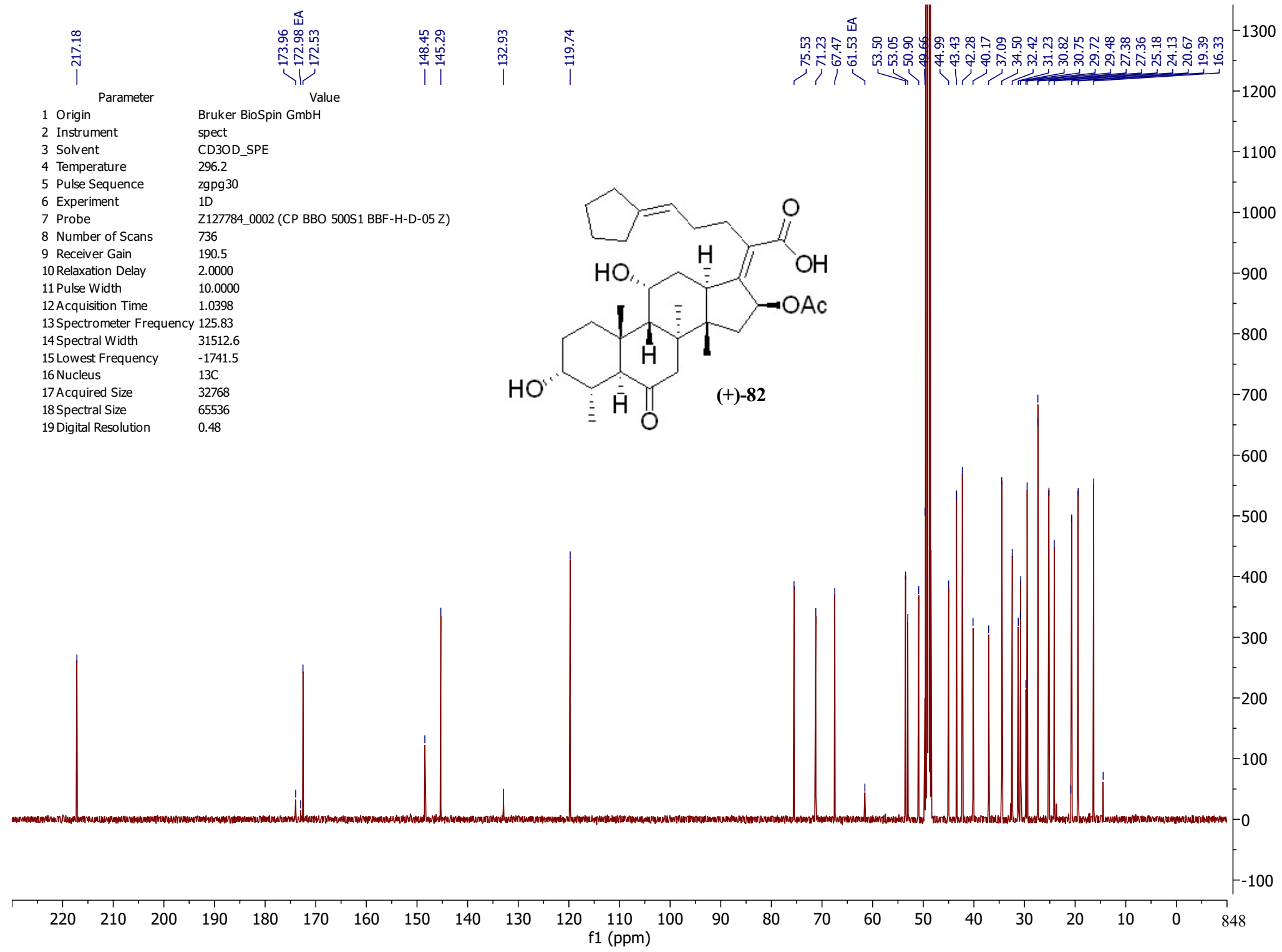
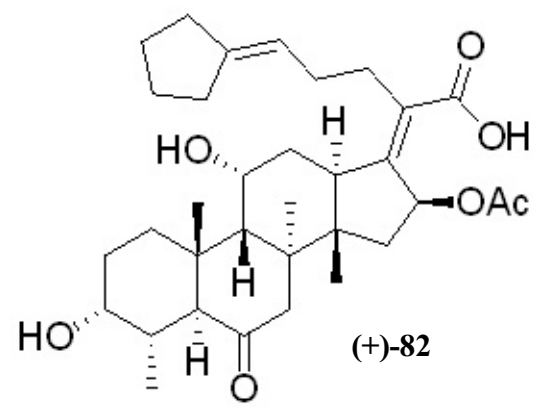
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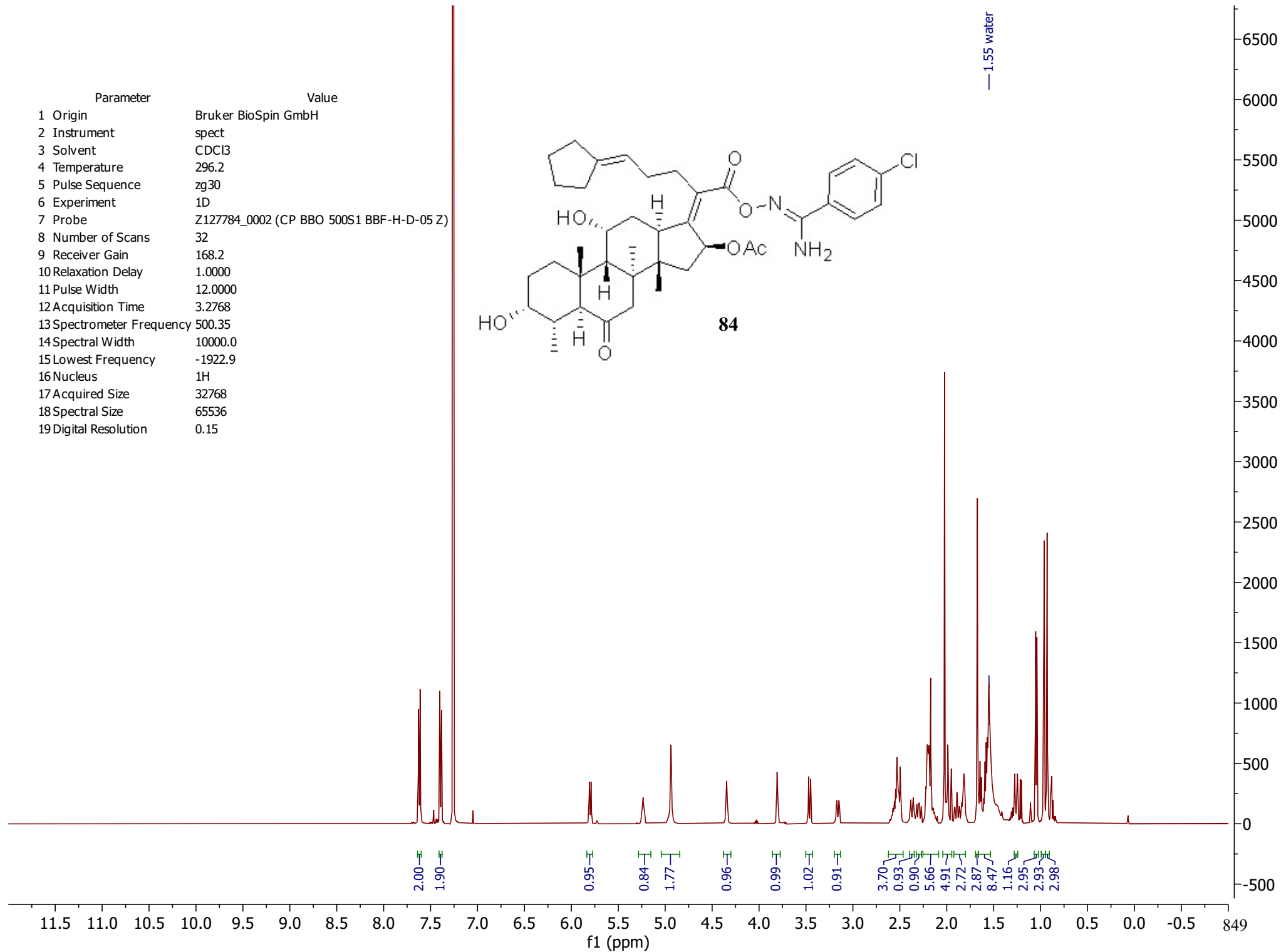
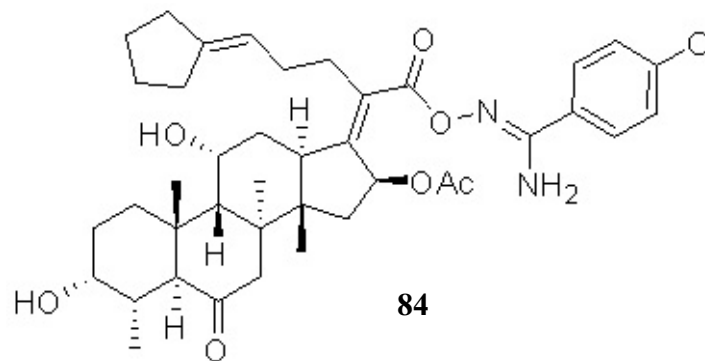
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CD3OD_SPE
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	69.2
10 Relaxation Delay	2.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1747.7
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



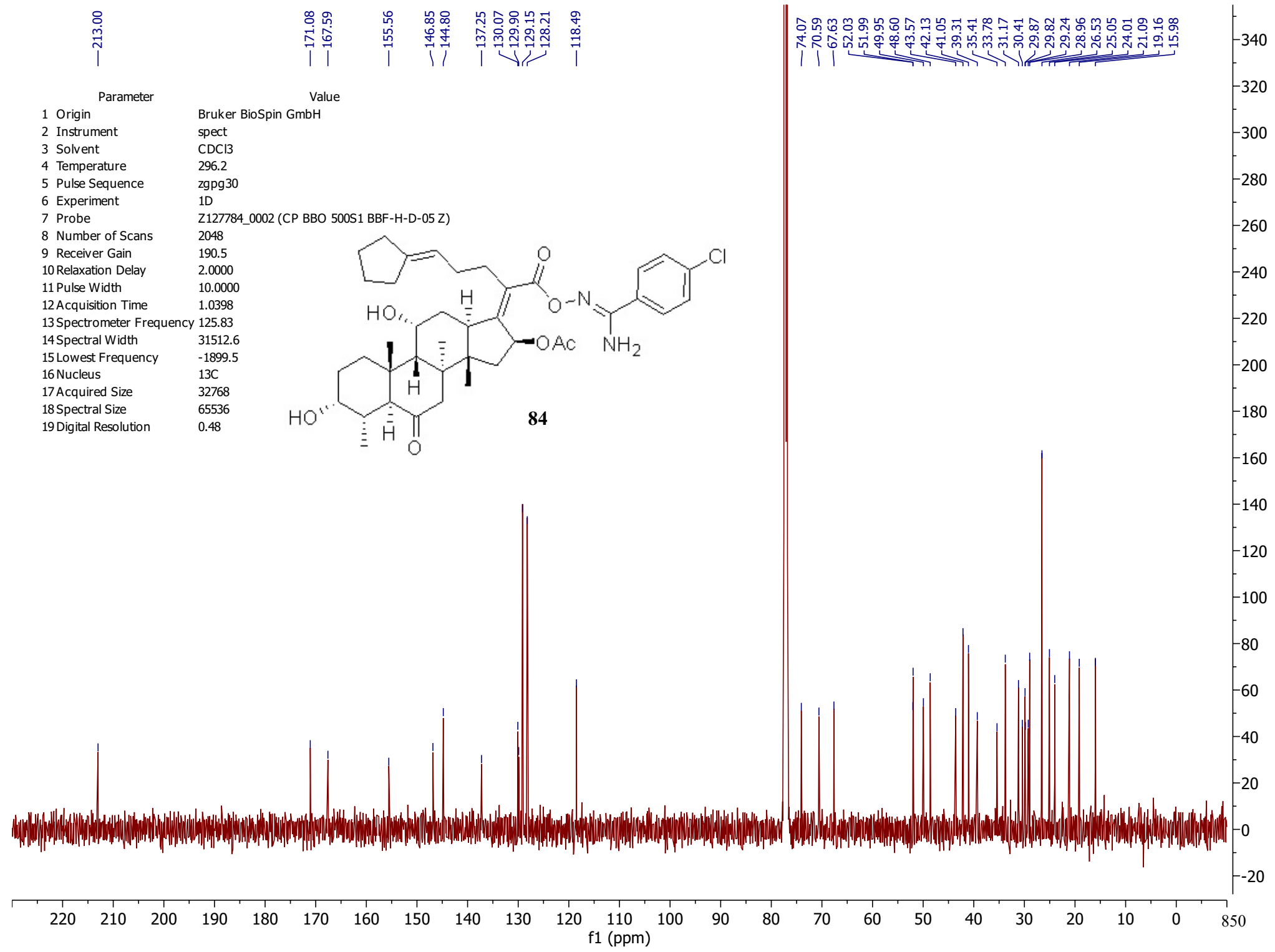
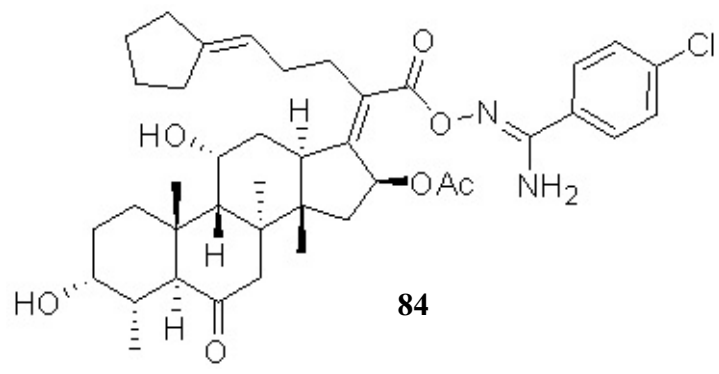
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CD3OD_SPE
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	736
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1741.5
16 Nucleus	¹³ C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



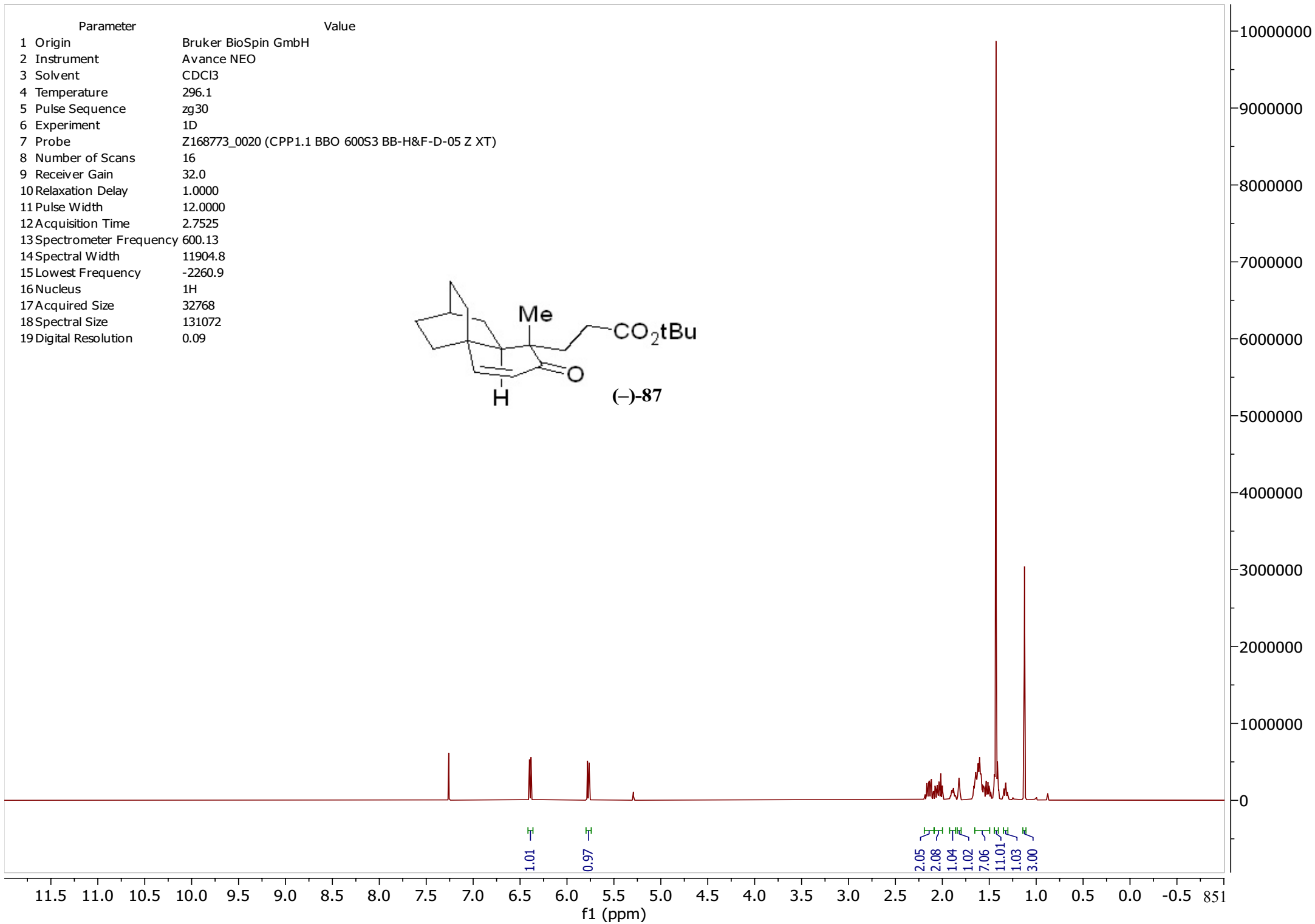
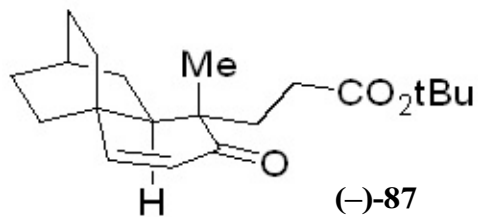
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	32
9 Receiver Gain	168.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.9
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

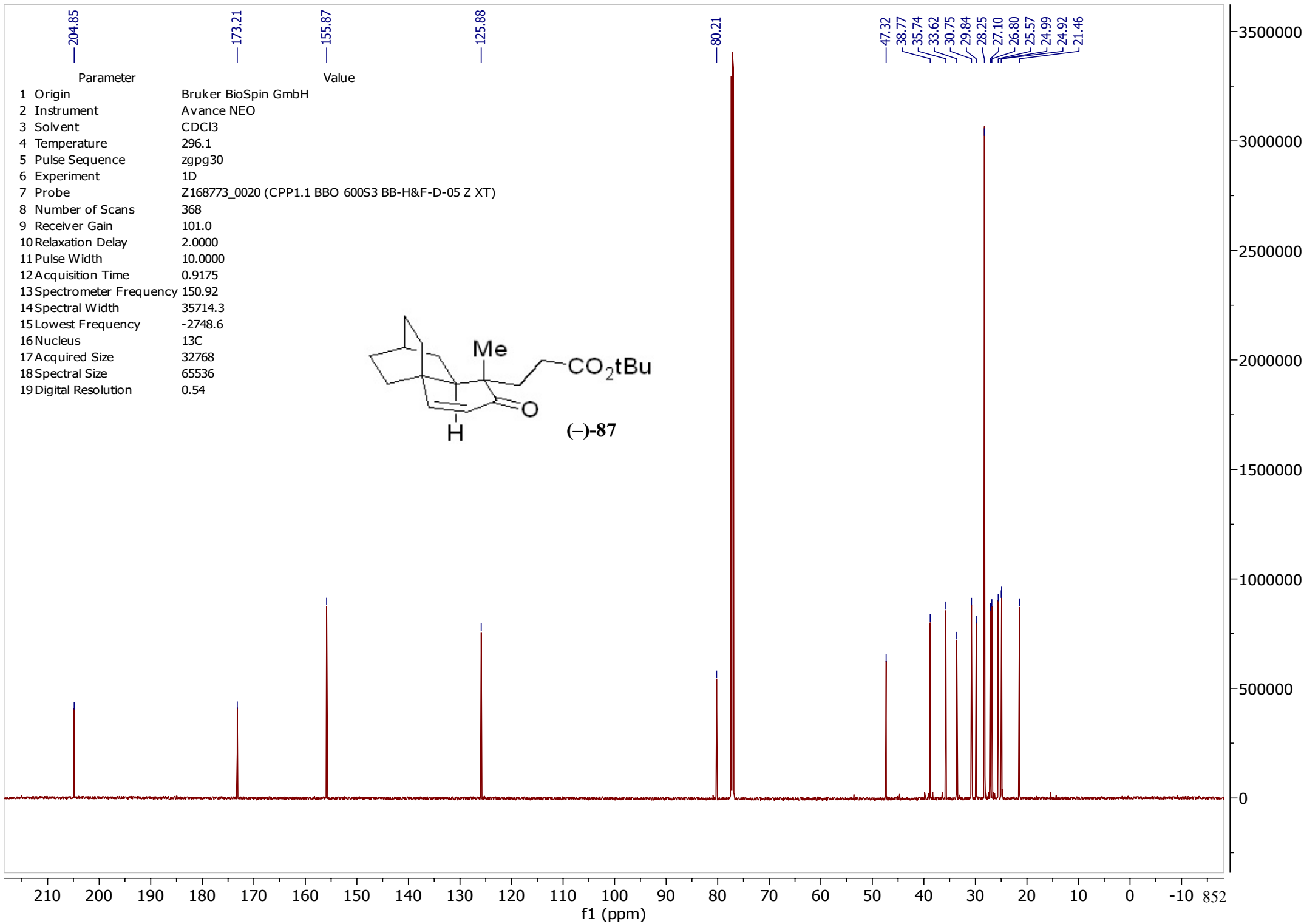


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	2048
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1899.5
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

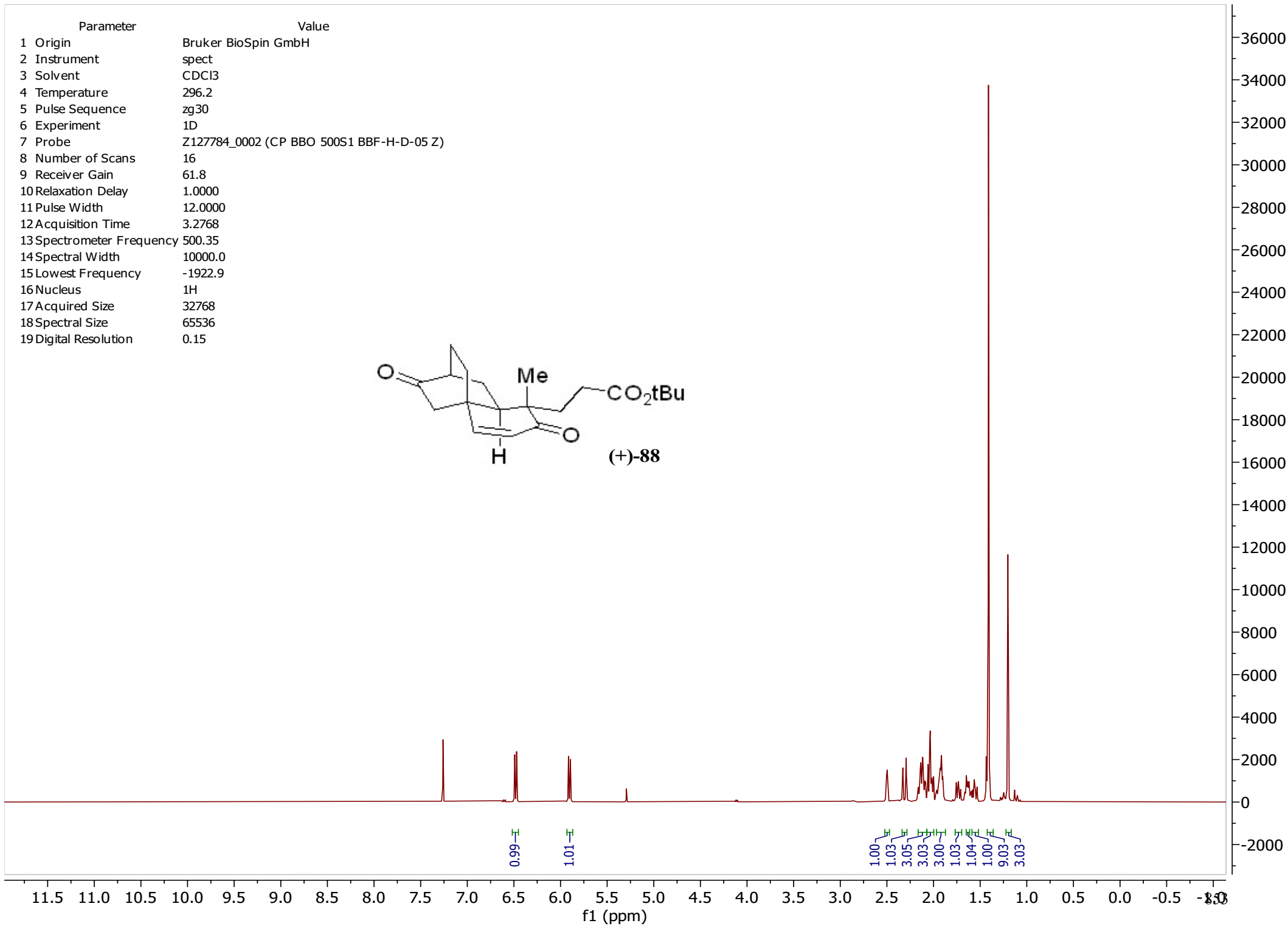
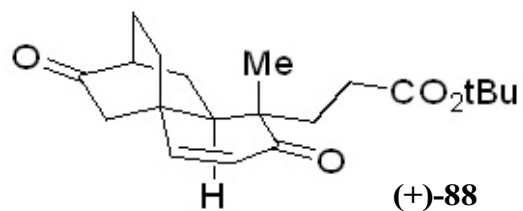


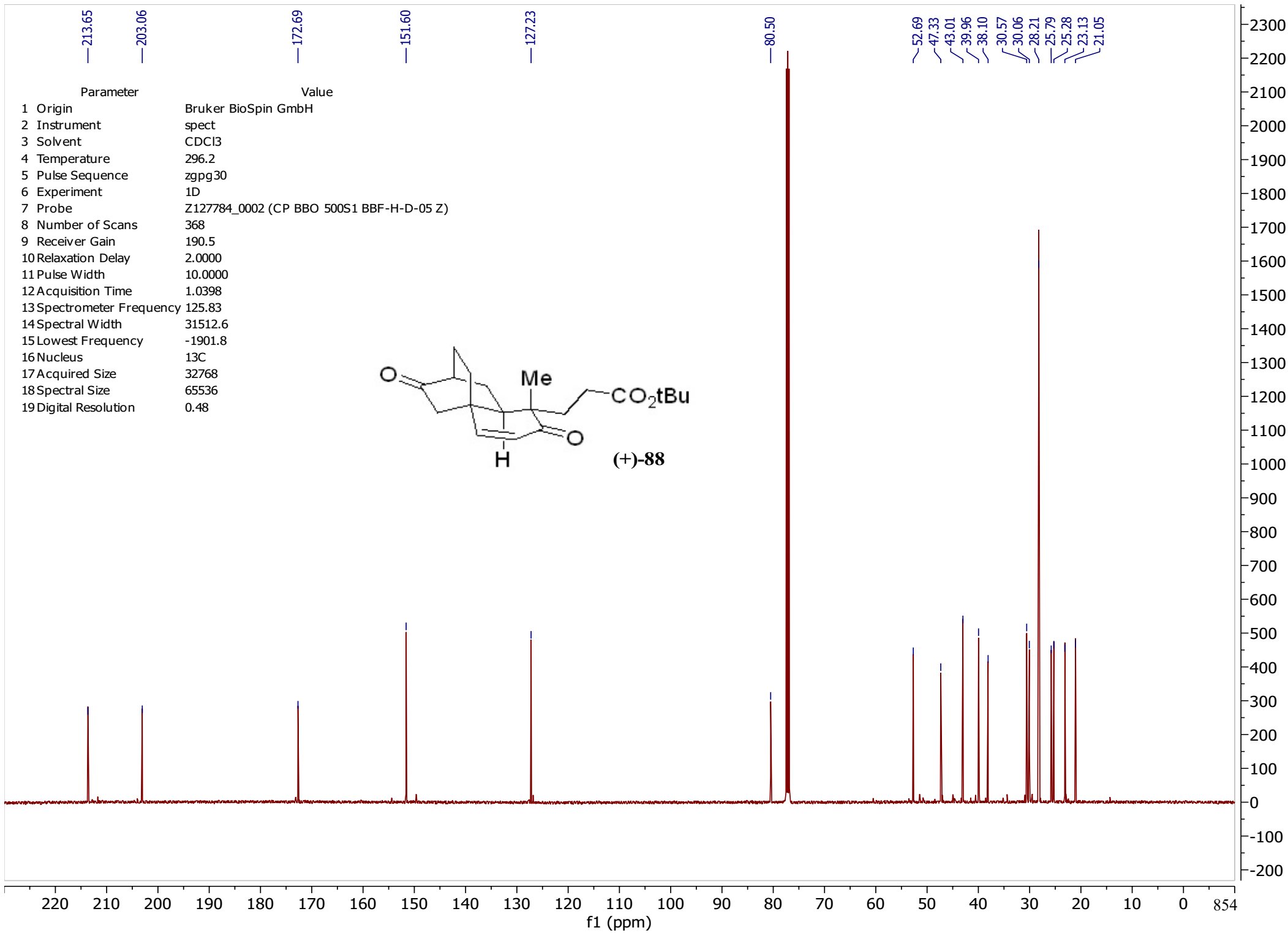
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



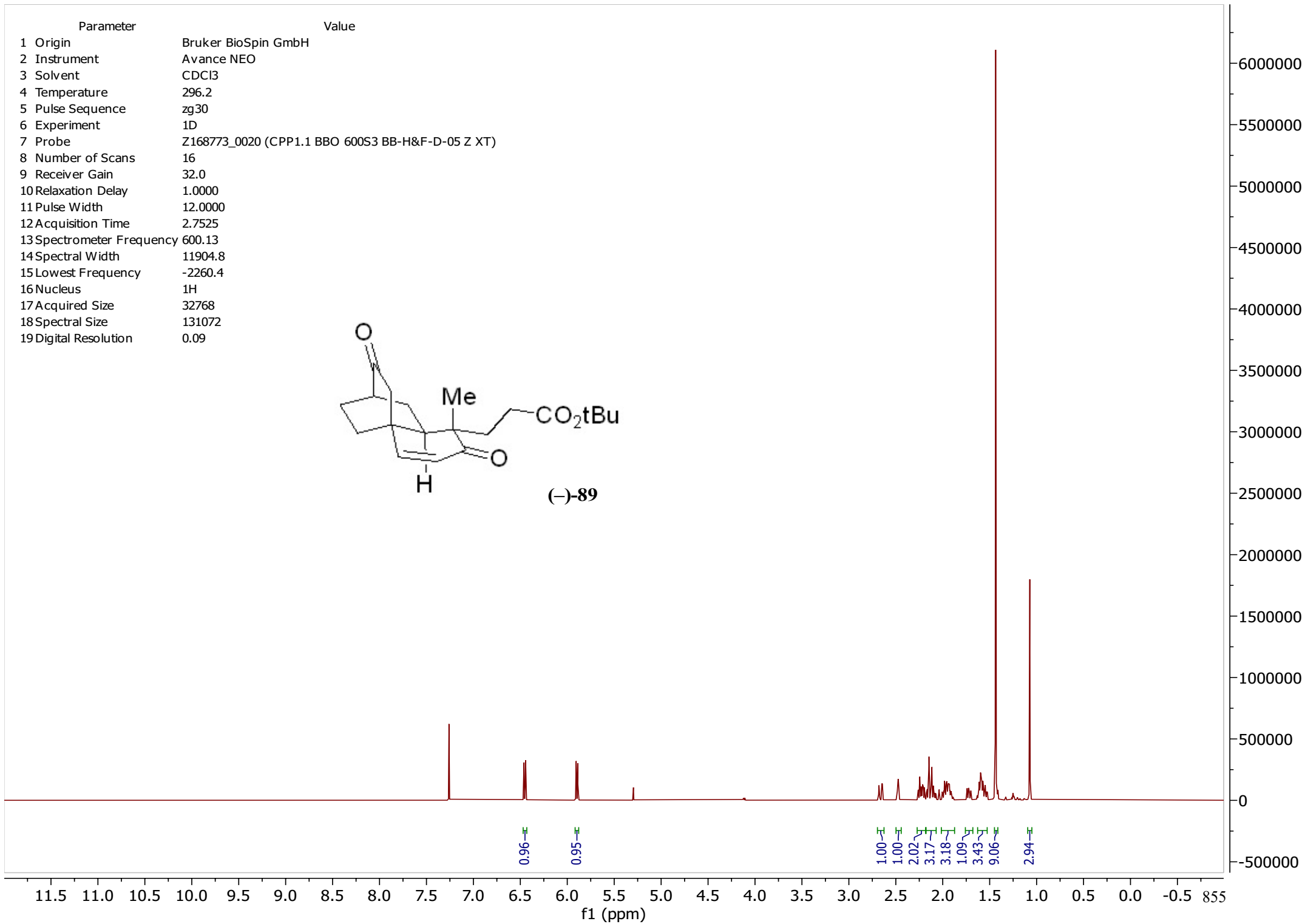
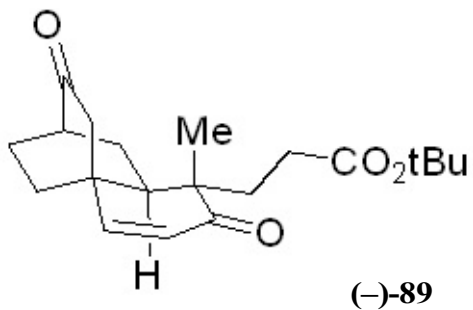


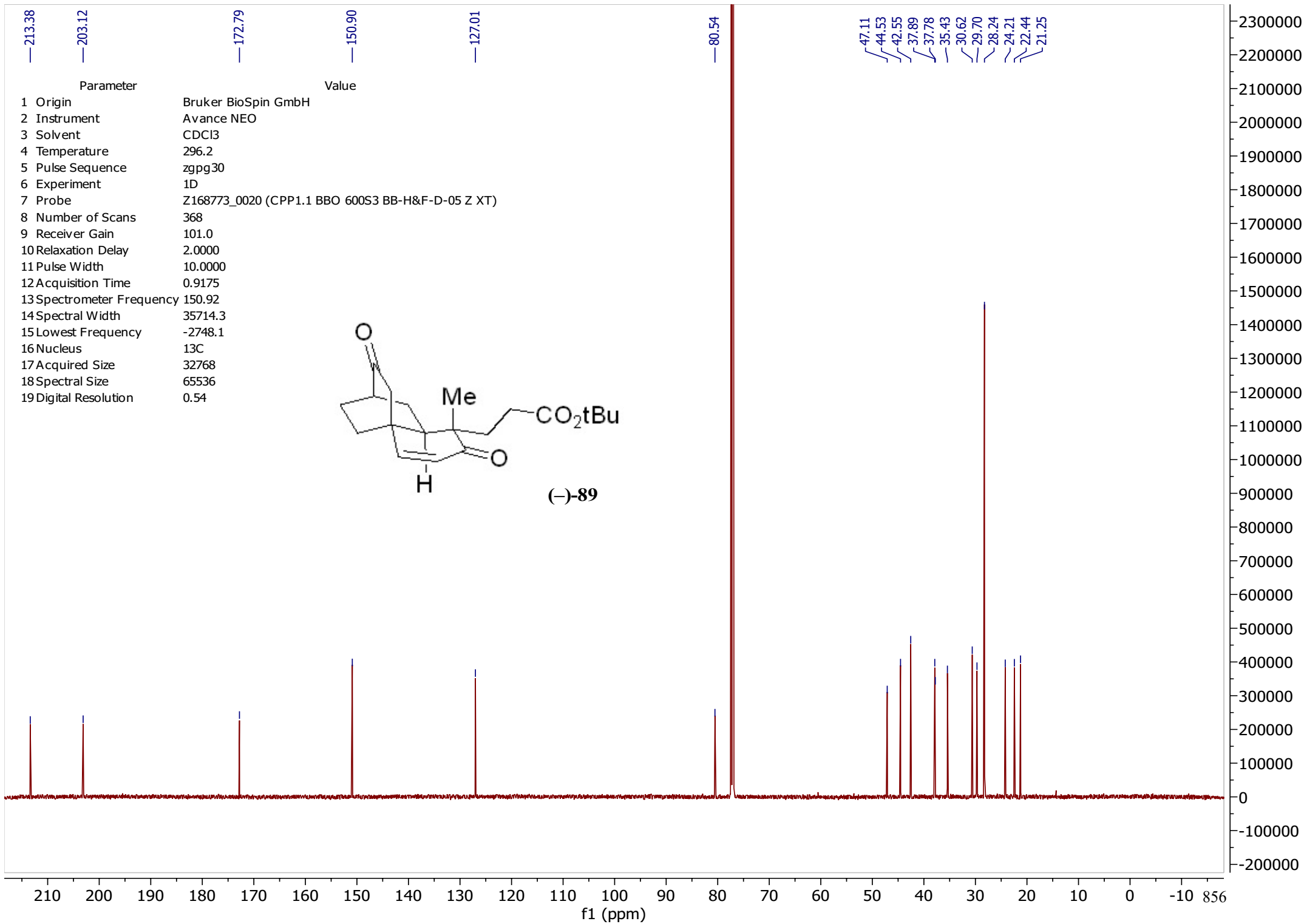
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	61.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.9
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



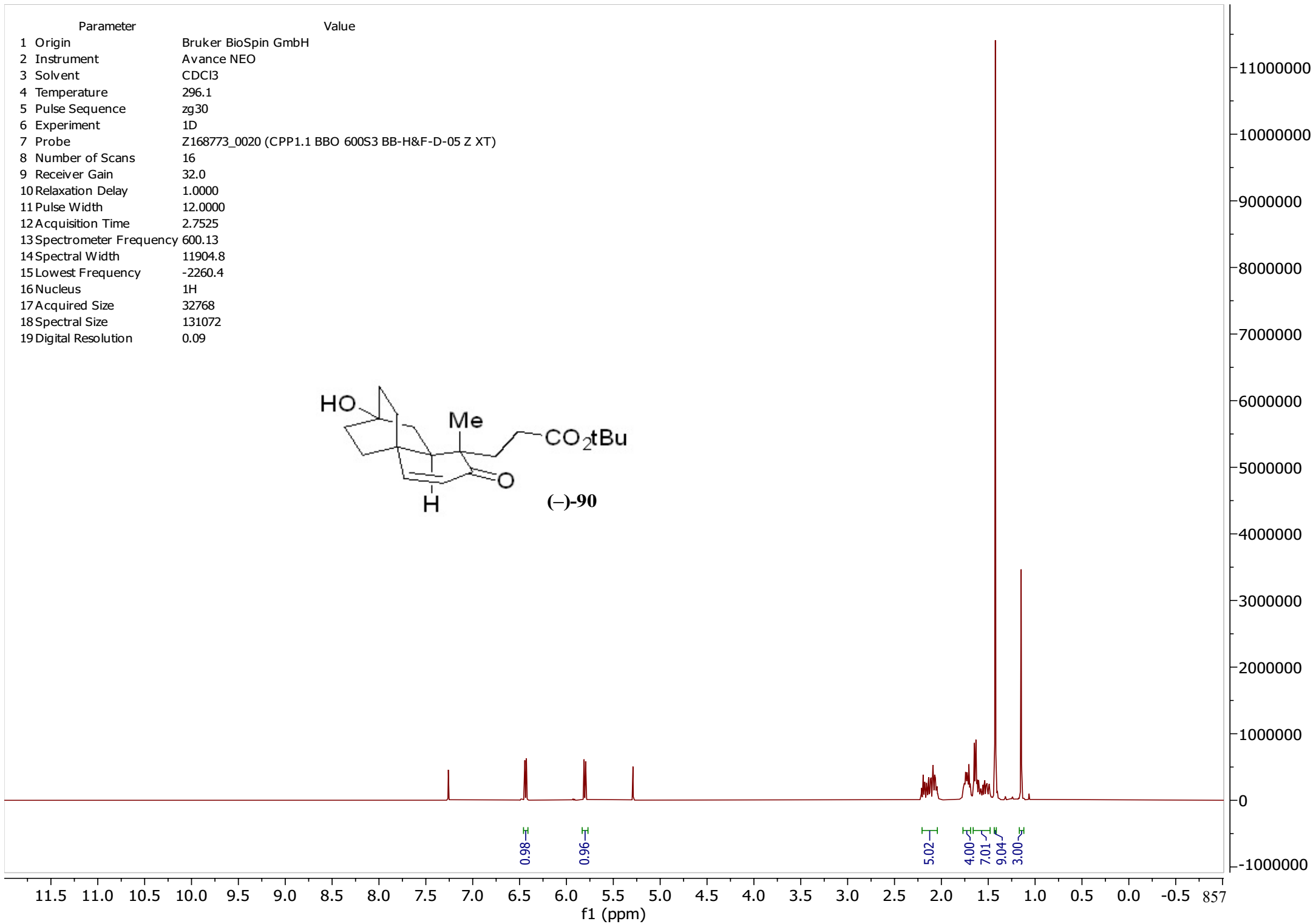
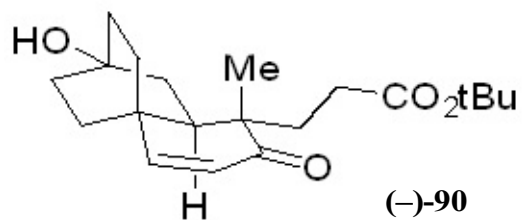


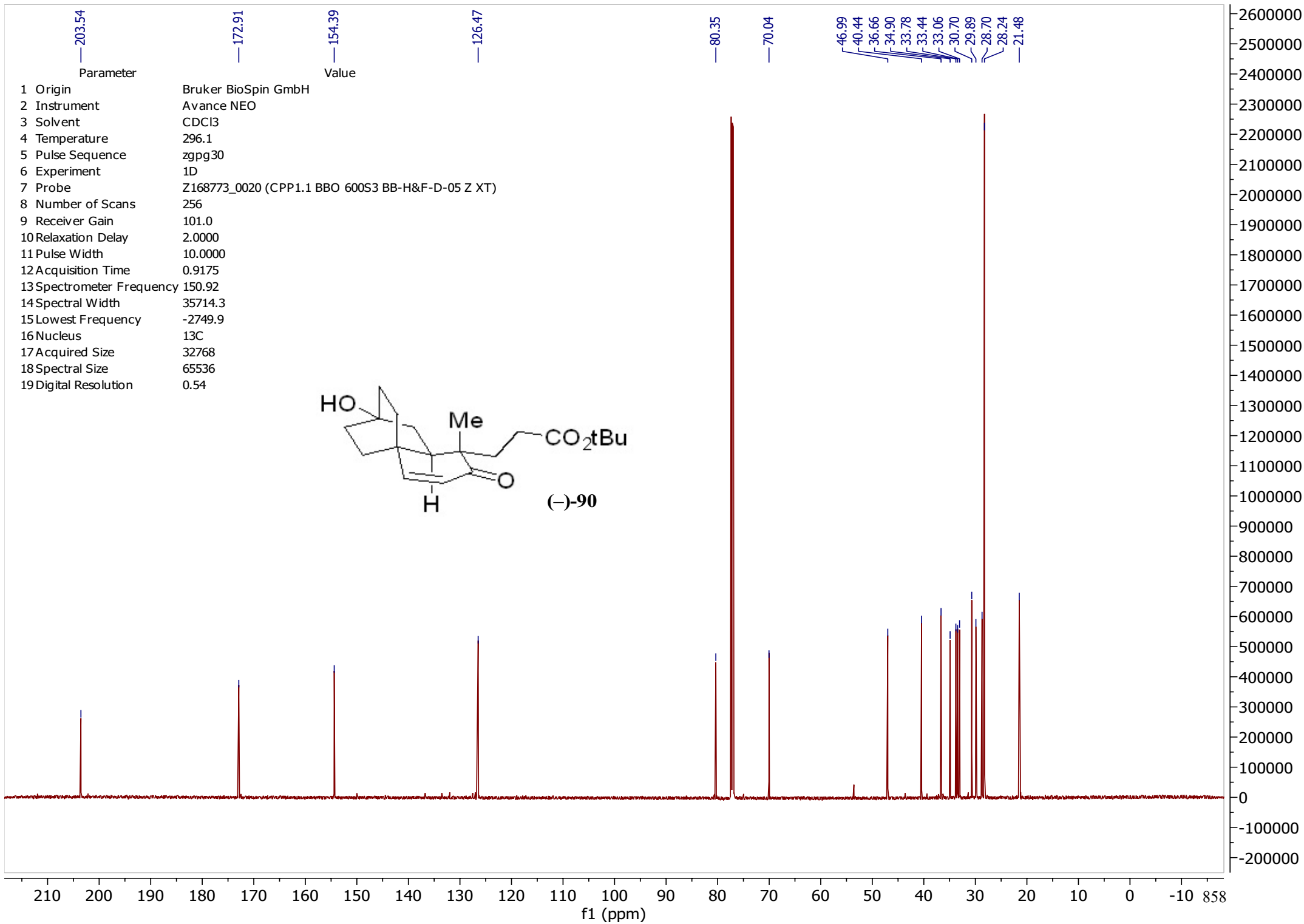
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



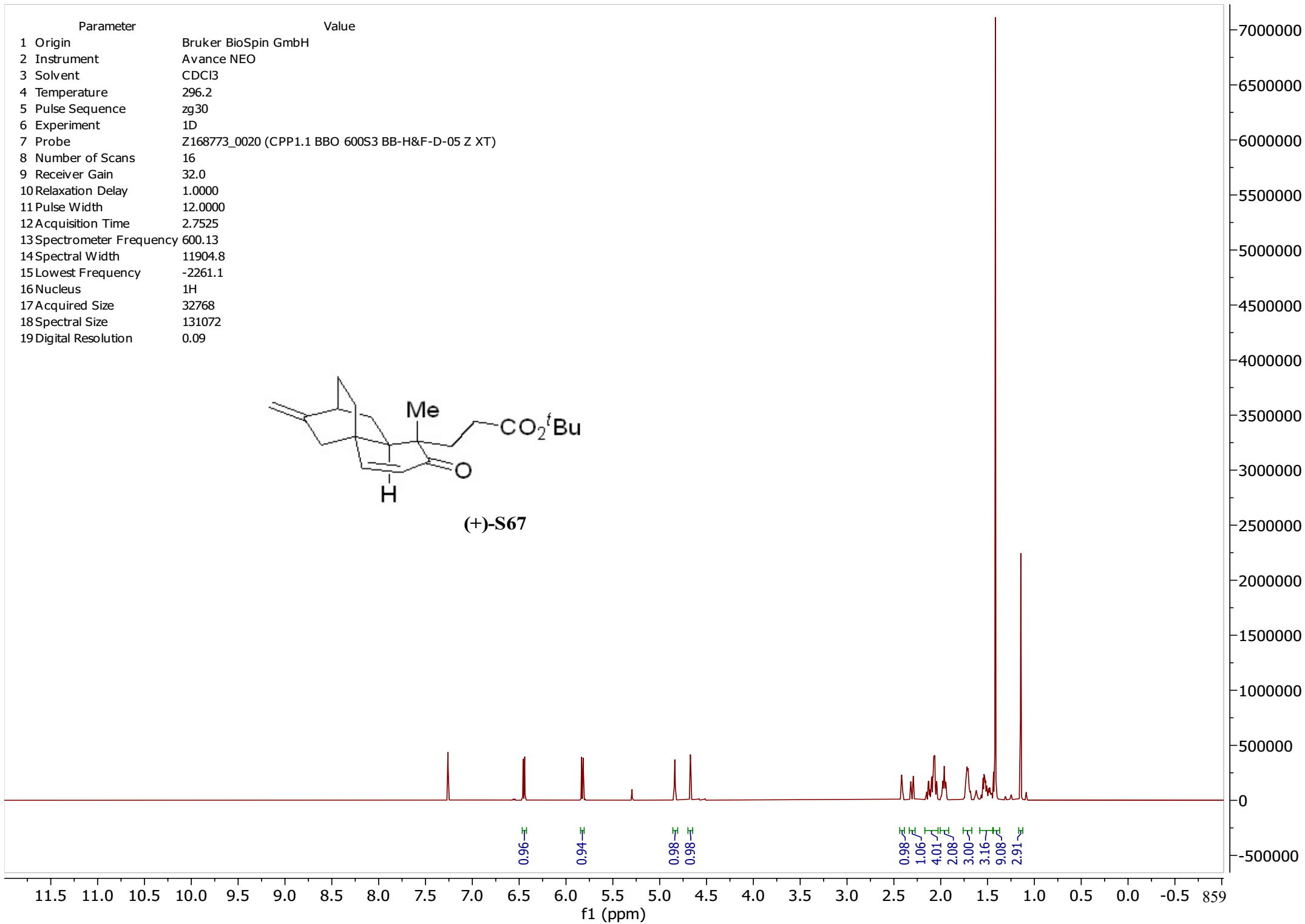
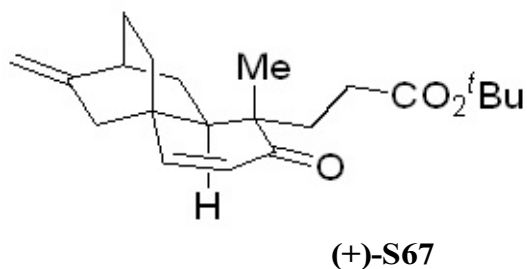


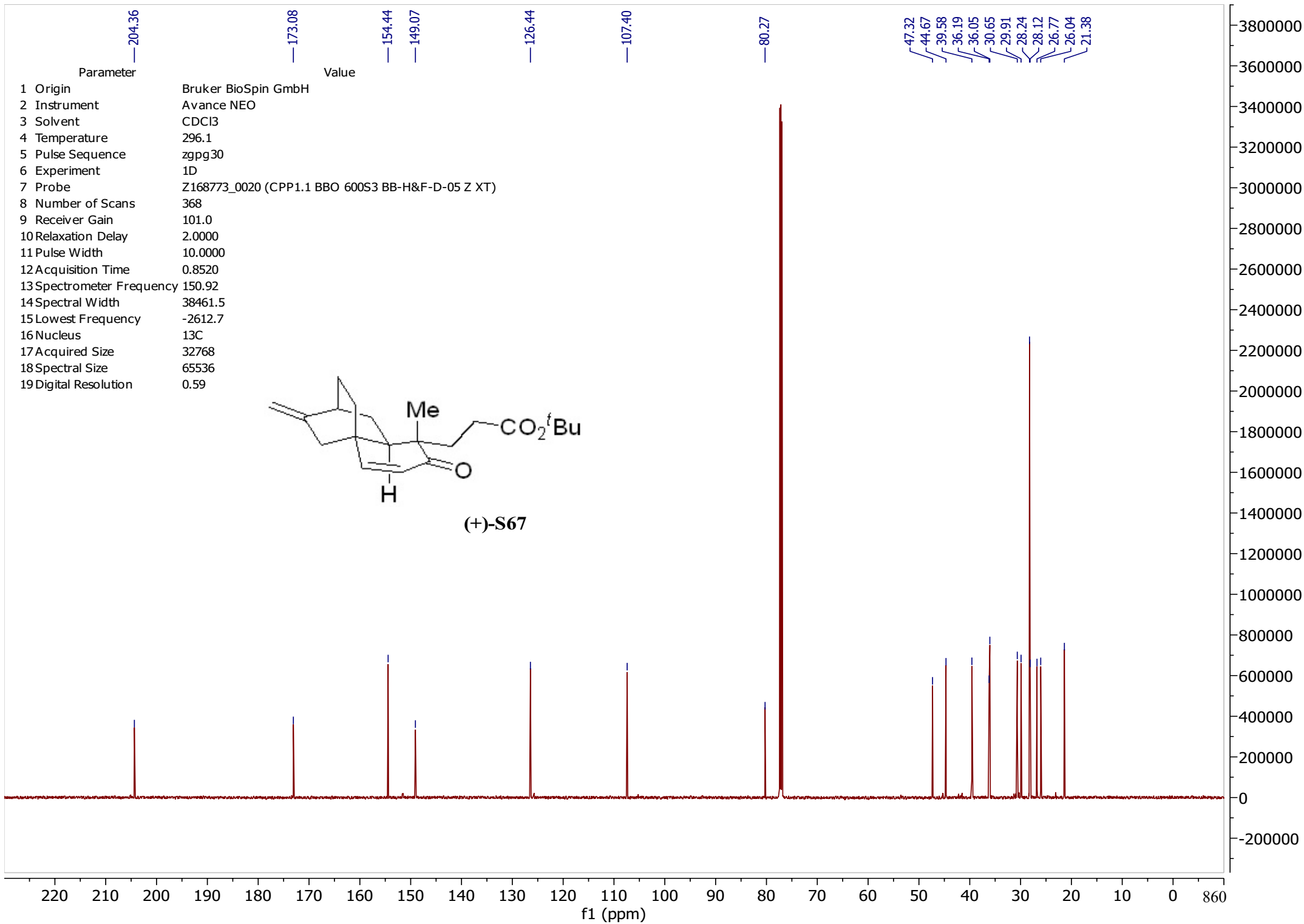
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2260.4
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09



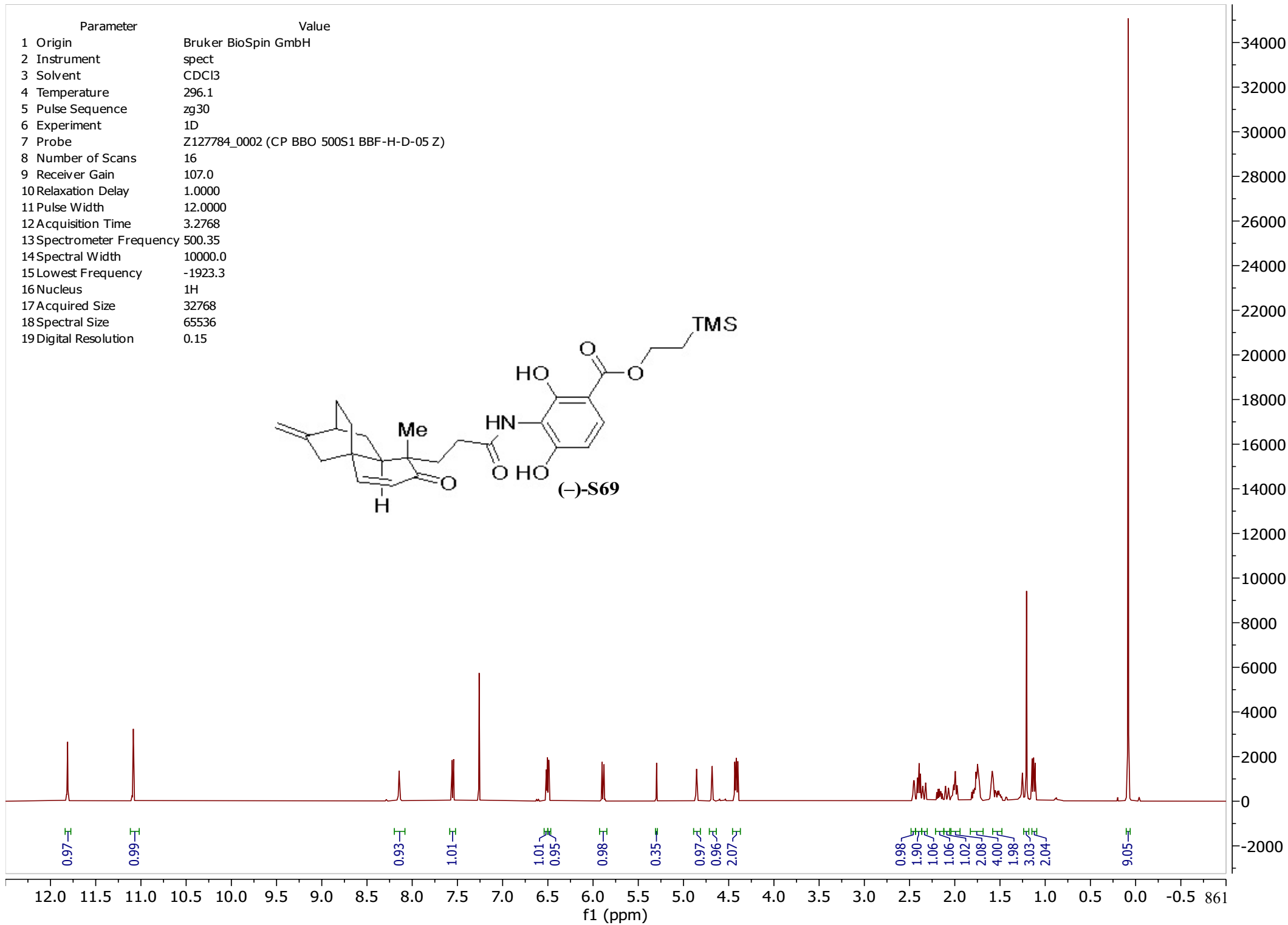
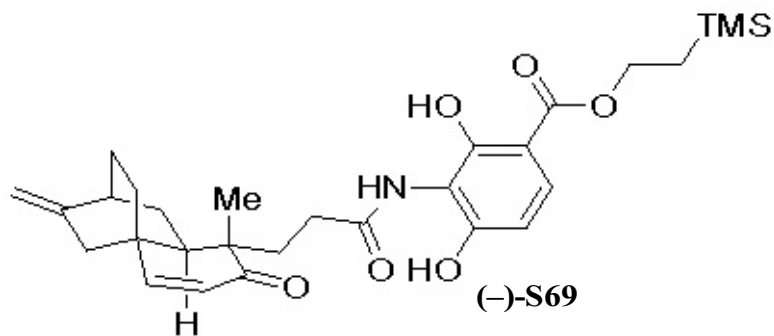


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2261.1
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

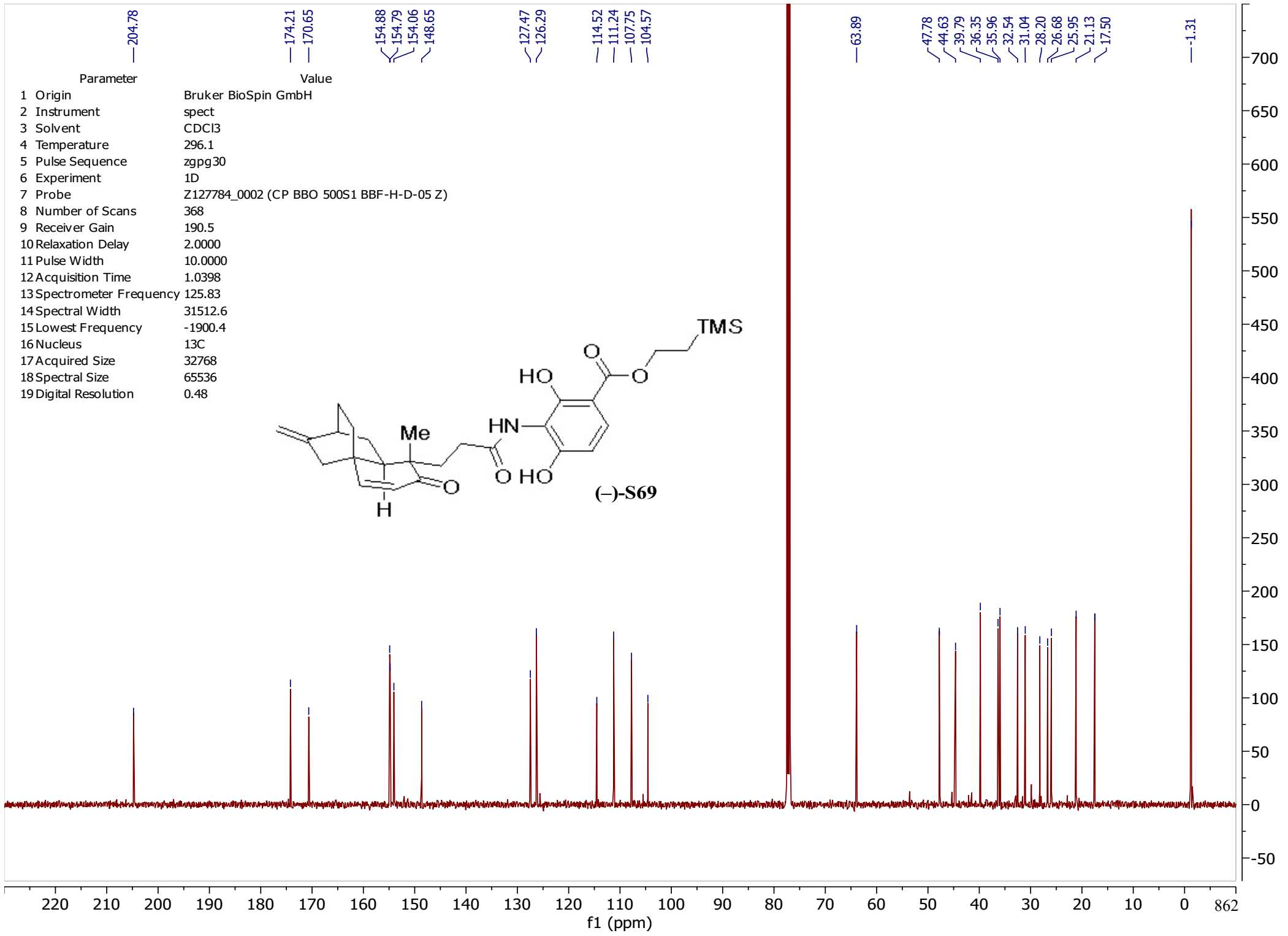
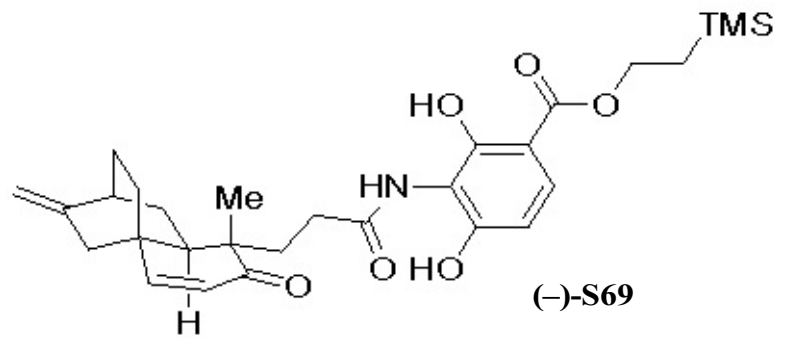




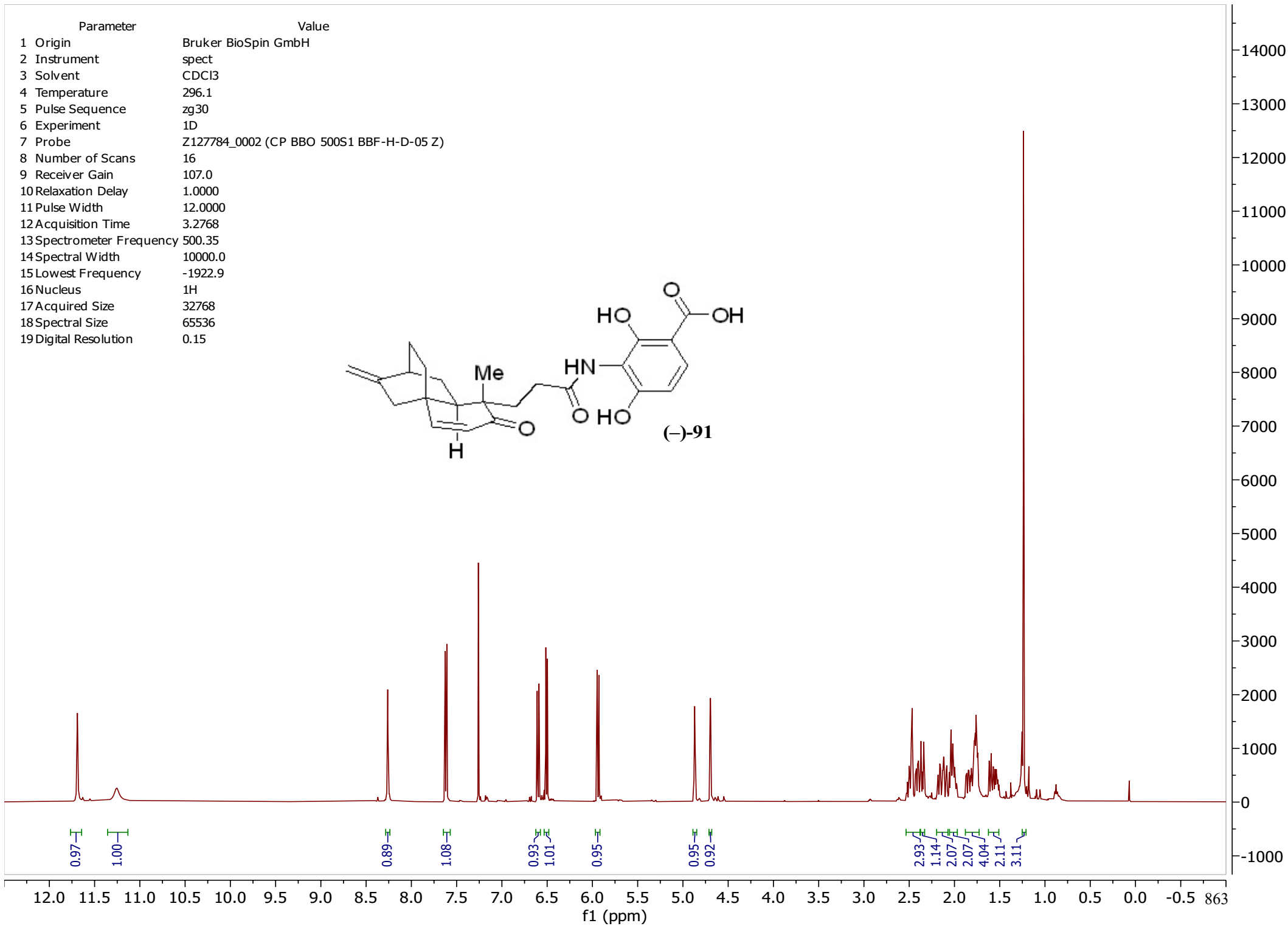
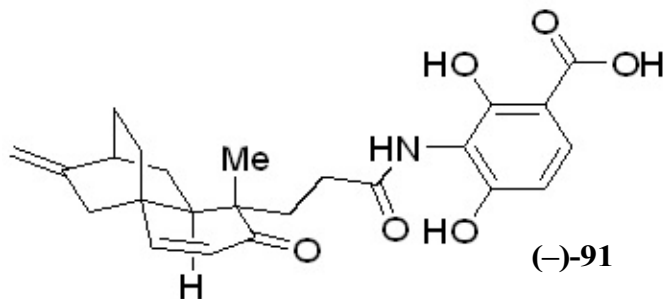
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	107.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.3
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

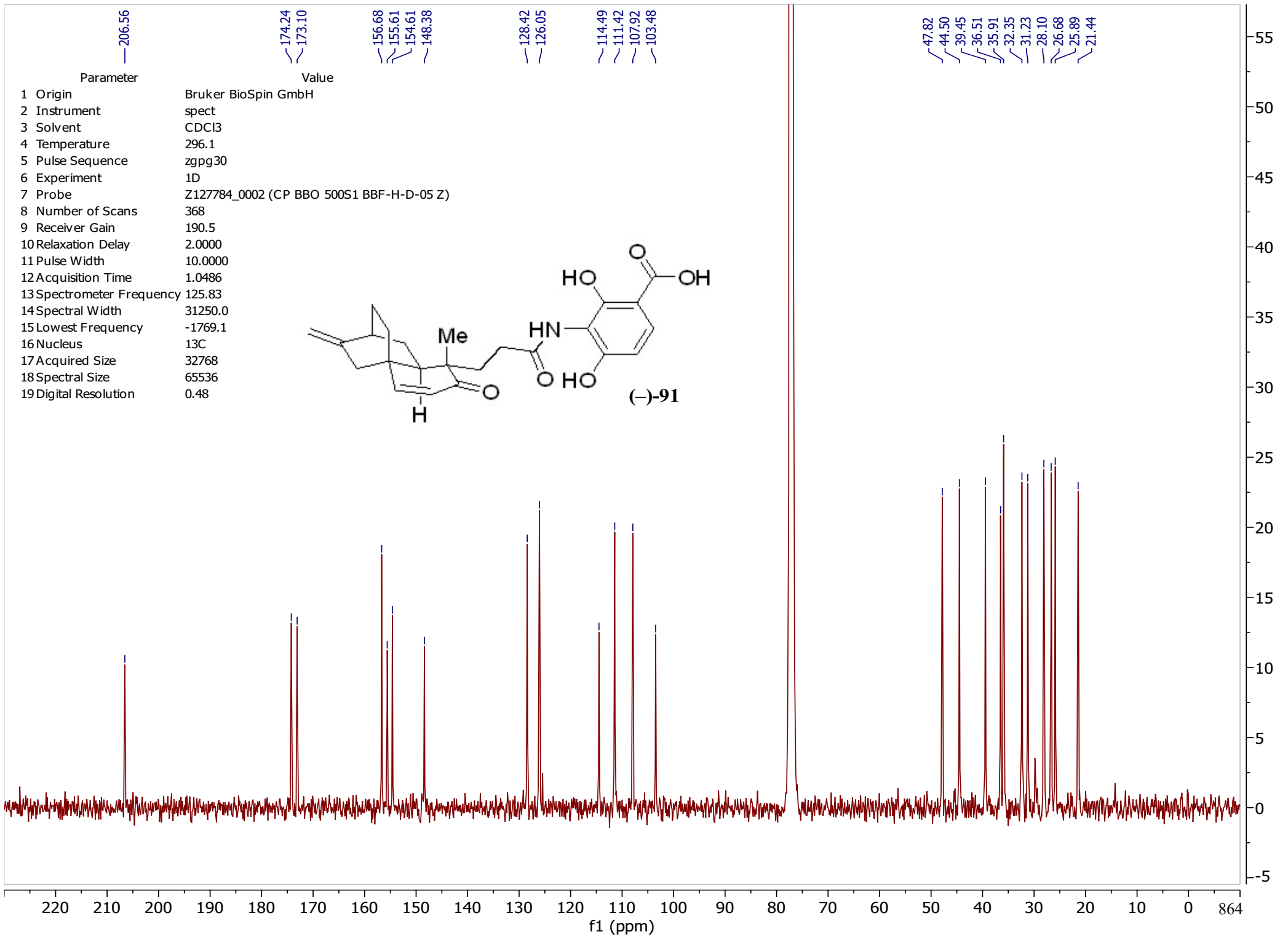


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	368
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0398
13 Spectrometer Frequency	125.83
14 Spectral Width	31512.6
15 Lowest Frequency	-1900.4
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48

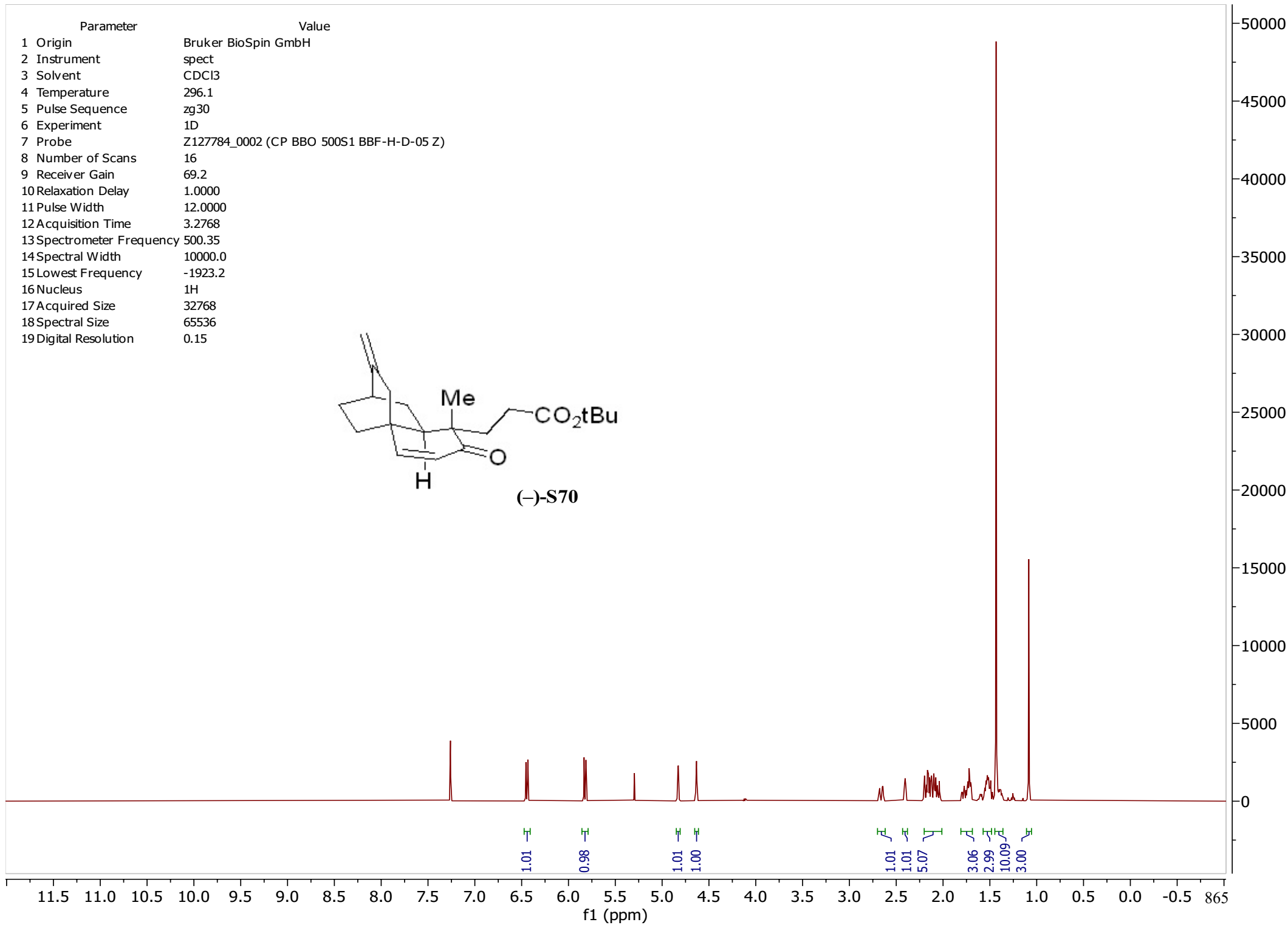
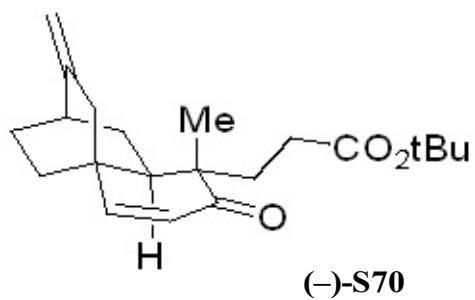


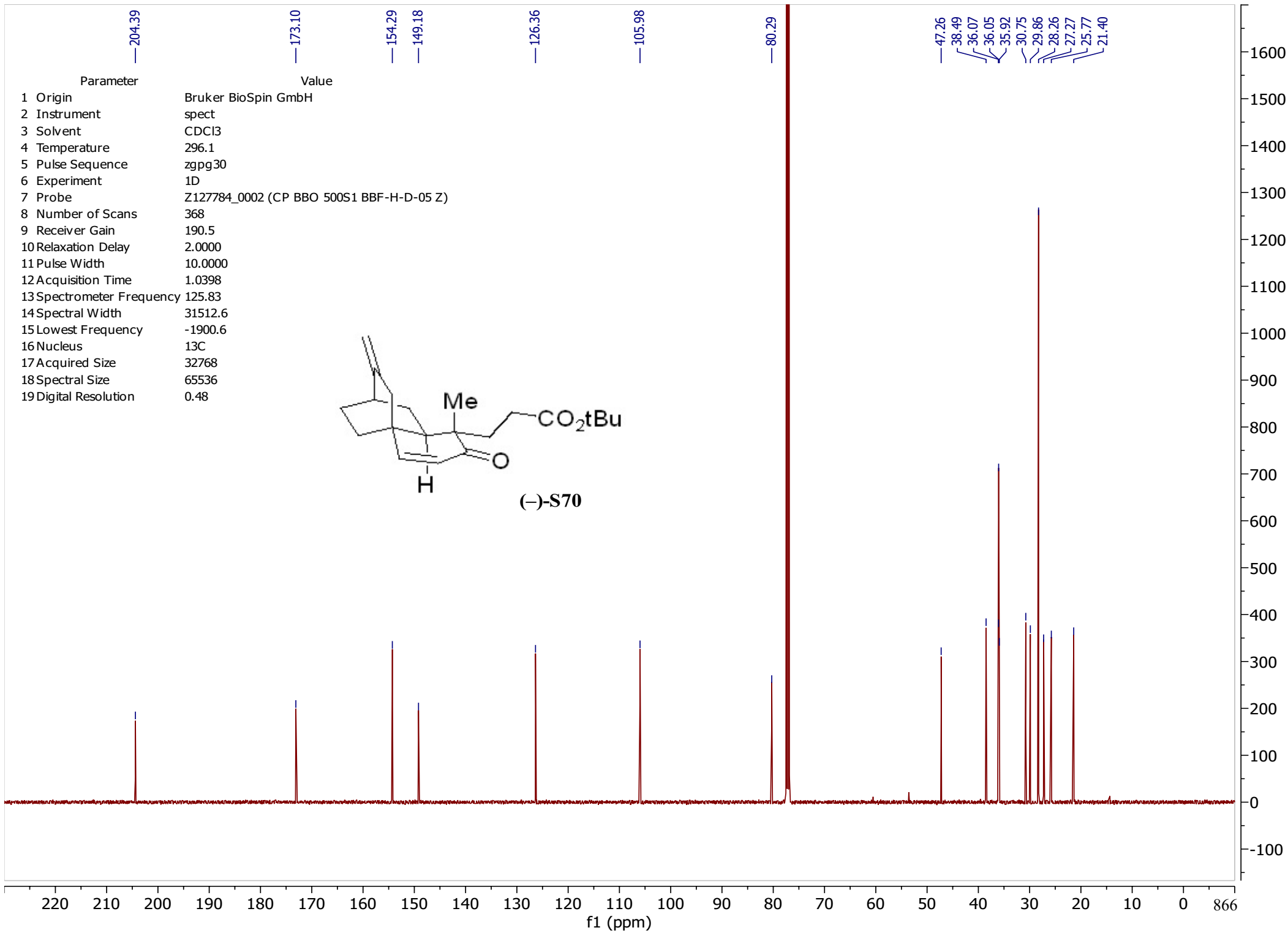
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	107.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.9
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



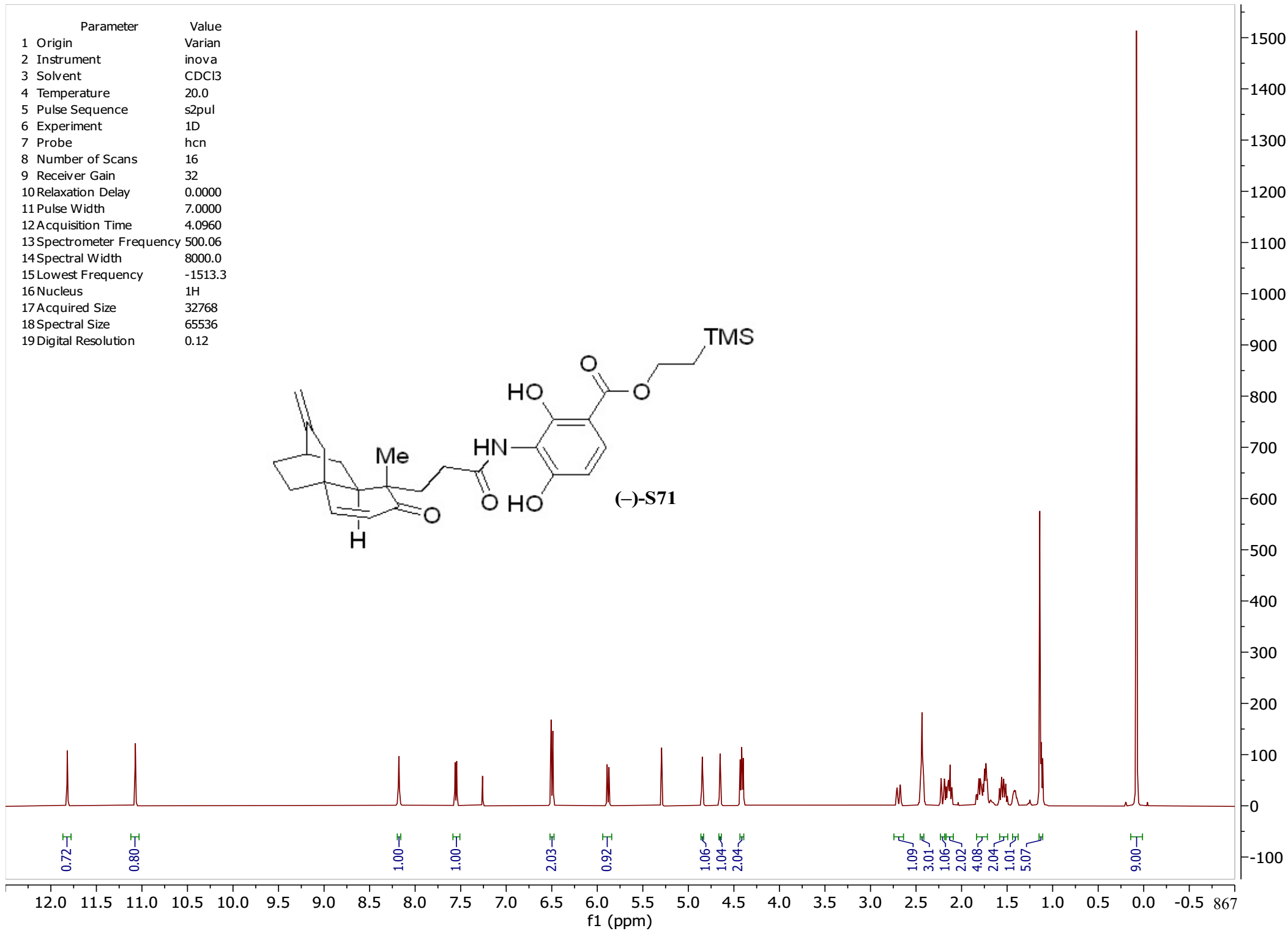
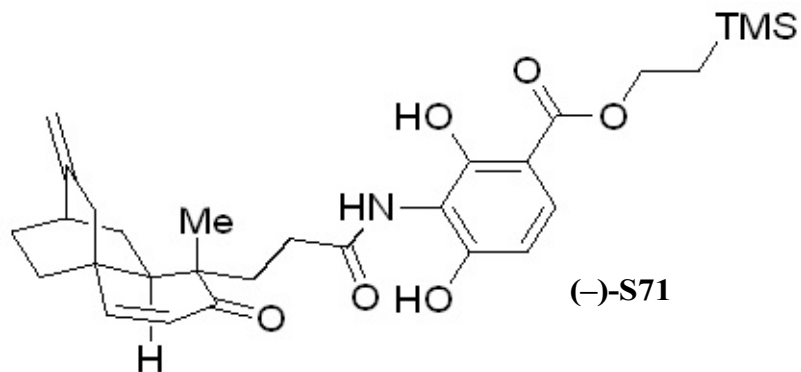


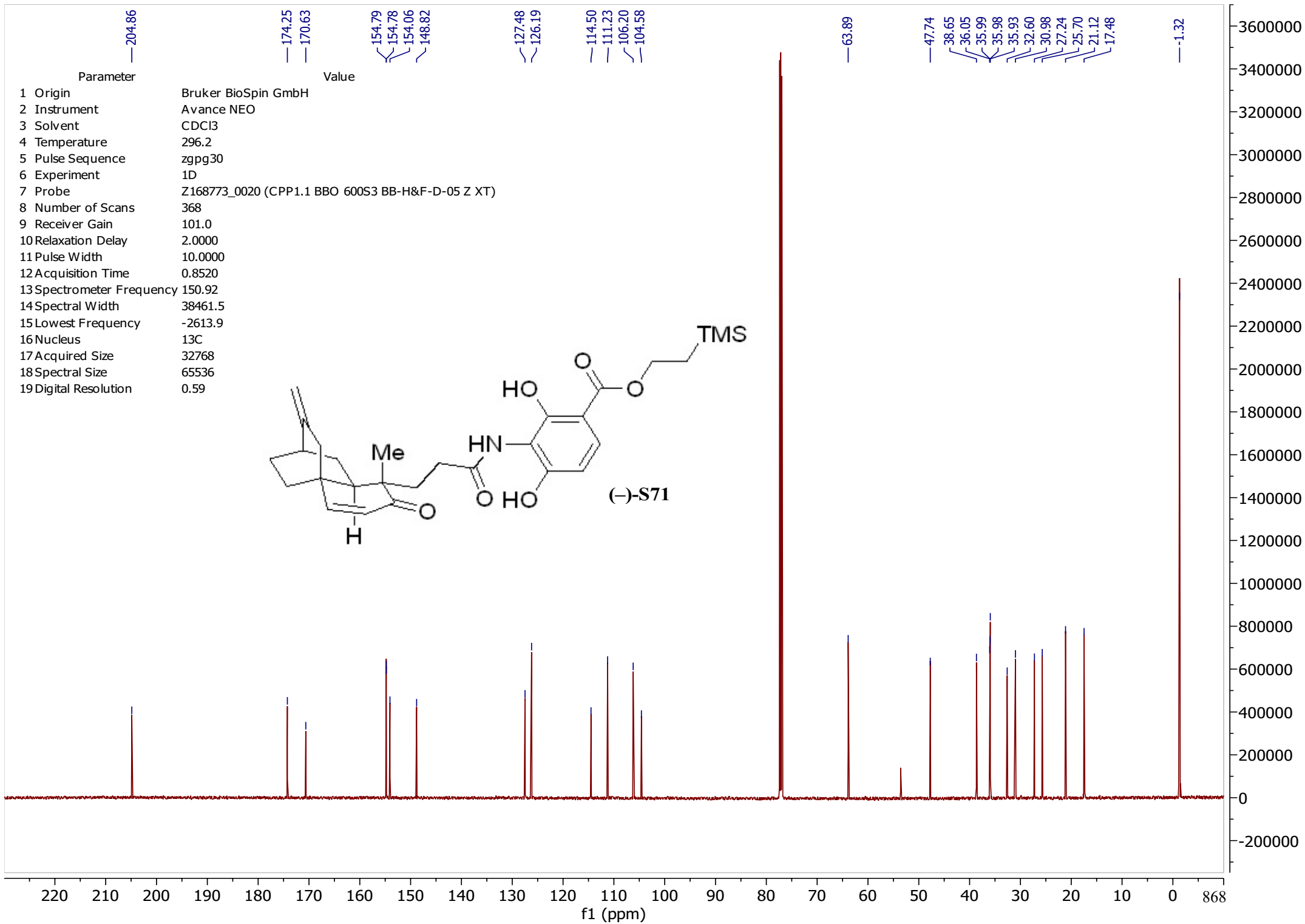
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	69.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



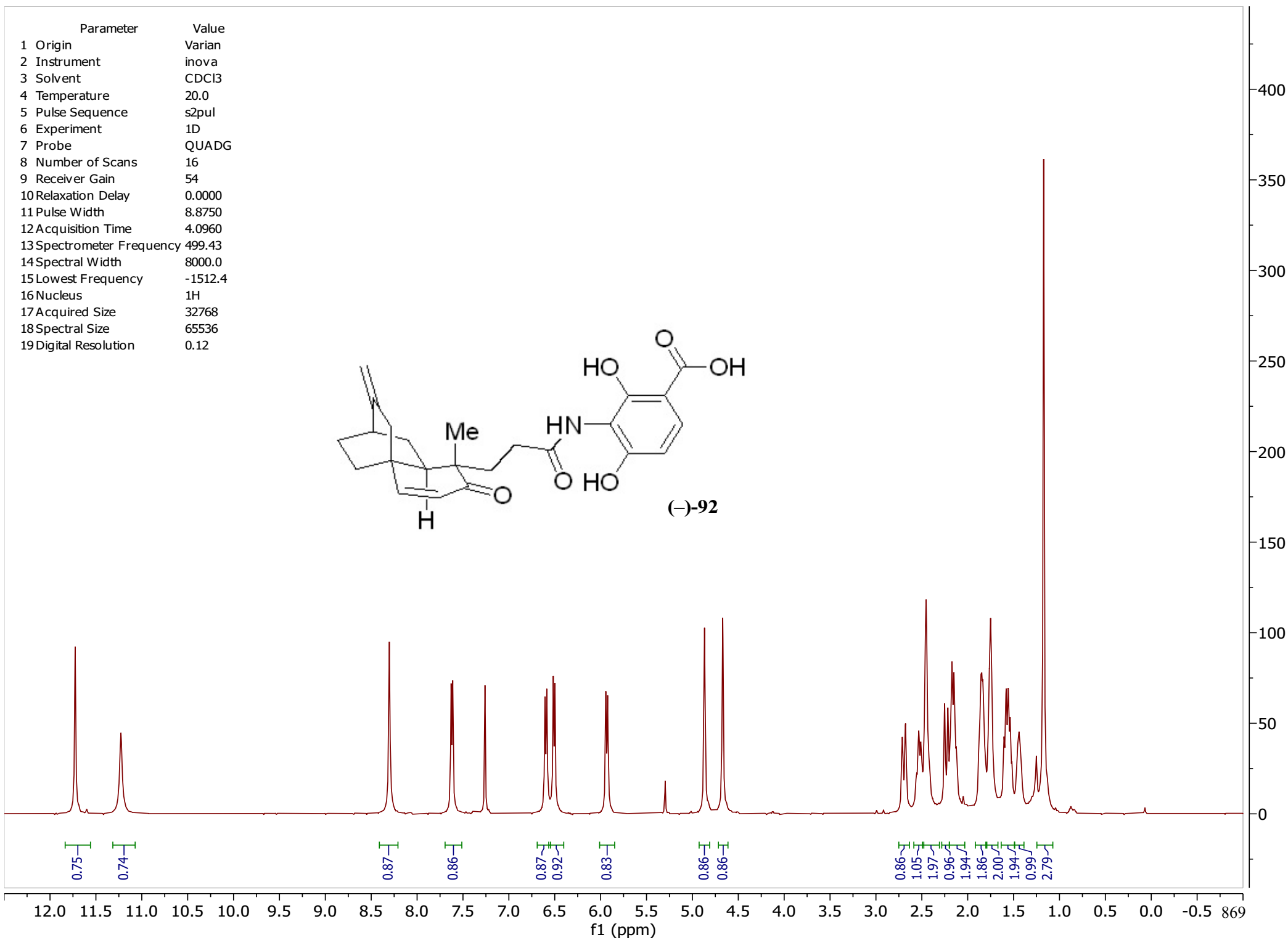
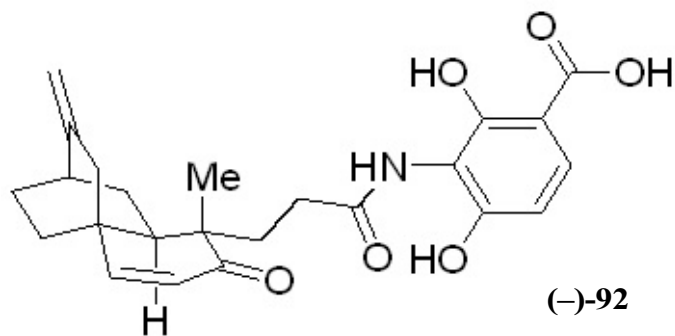


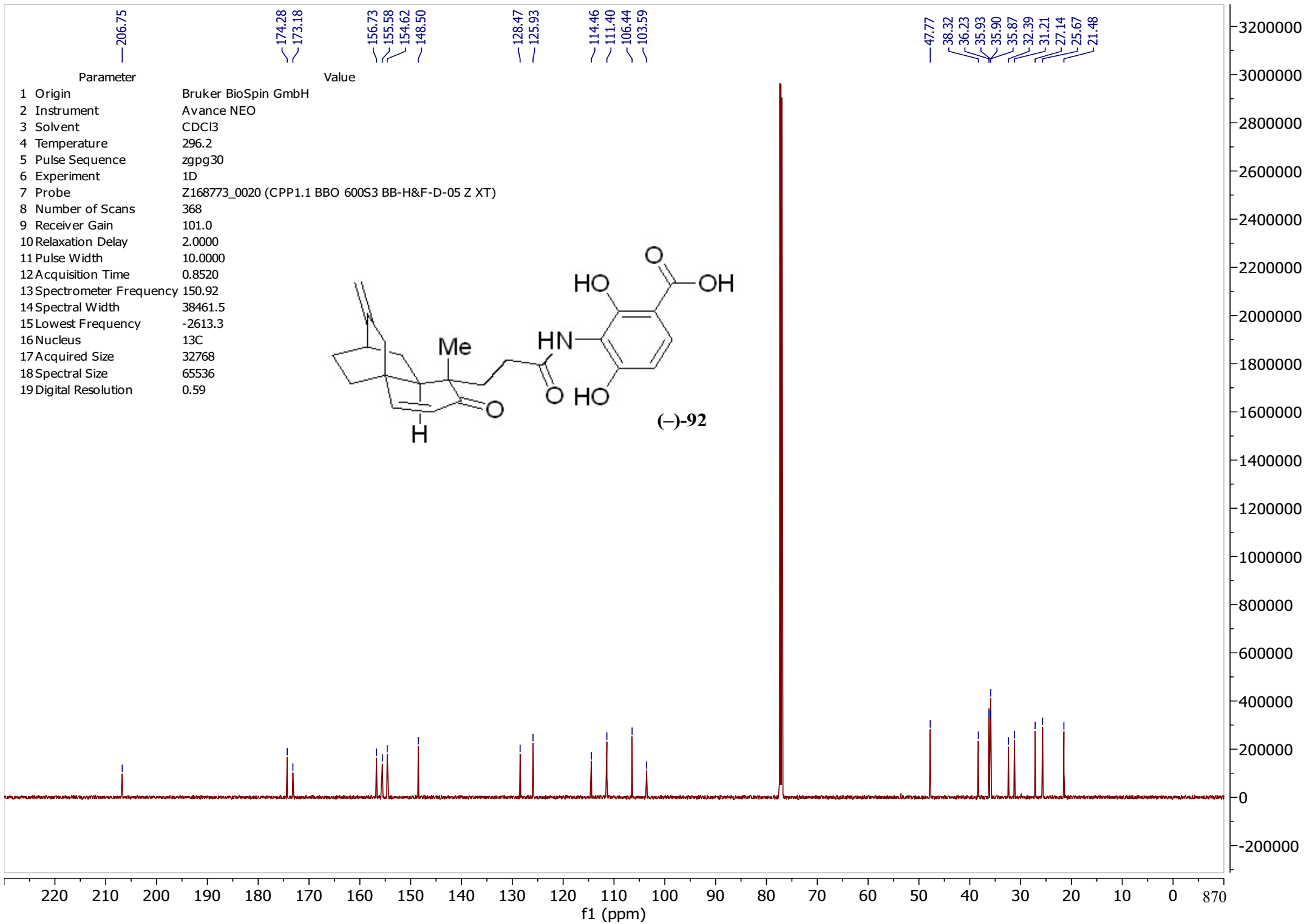
Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	hcn
8 Number of Scans	16
9 Receiver Gain	32
10 Relaxation Delay	0.0000
11 Pulse Width	7.0000
12 Acquisition Time	4.0960
13 Spectrometer Frequency	500.06
14 Spectral Width	8000.0
15 Lowest Frequency	-1513.3
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12



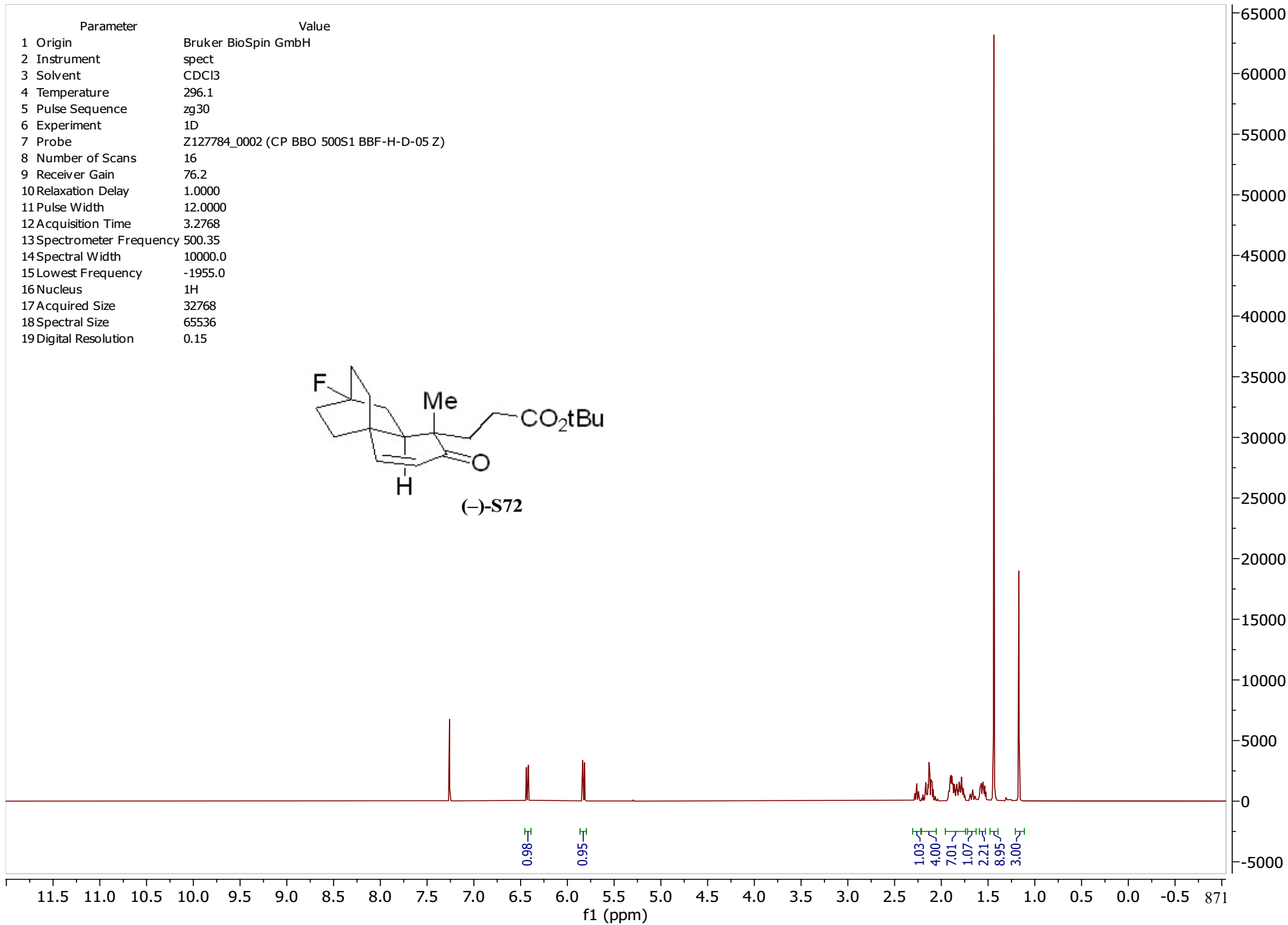
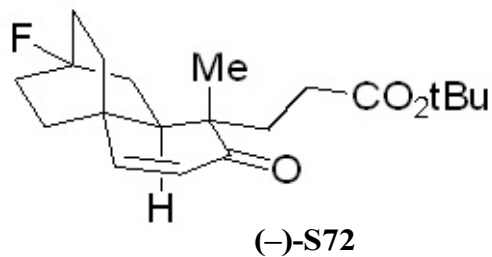


Parameter	Value
1 Origin	Varian
2 Instrument	inova
3 Solvent	CDCl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	QUADG
8 Number of Scans	16
9 Receiver Gain	54
10 Relaxation Delay	0.0000
11 Pulse Width	8.8750
12 Acquisition Time	4.0960
13 Spectrometer Frequency	499.43
14 Spectral Width	8000.0
15 Lowest Frequency	-1512.4
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.12

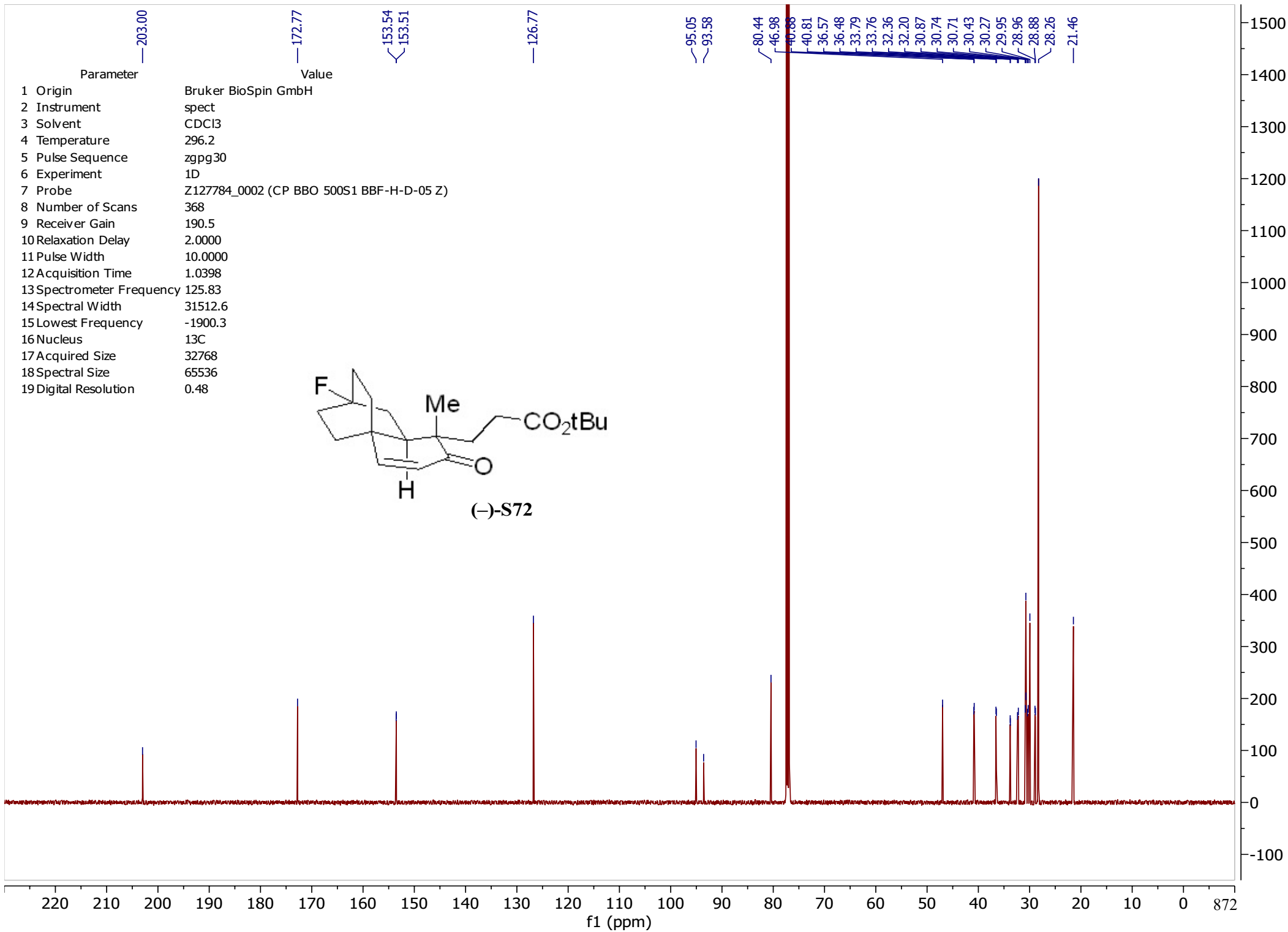
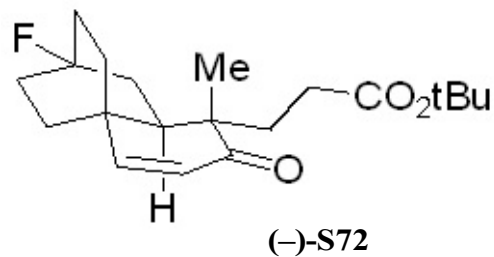




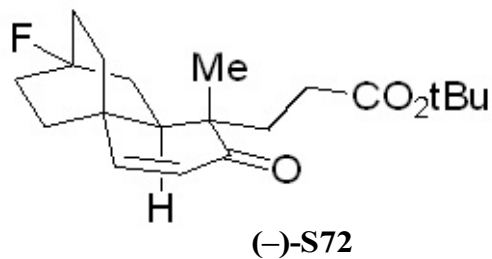
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	76.2
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1955.0
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



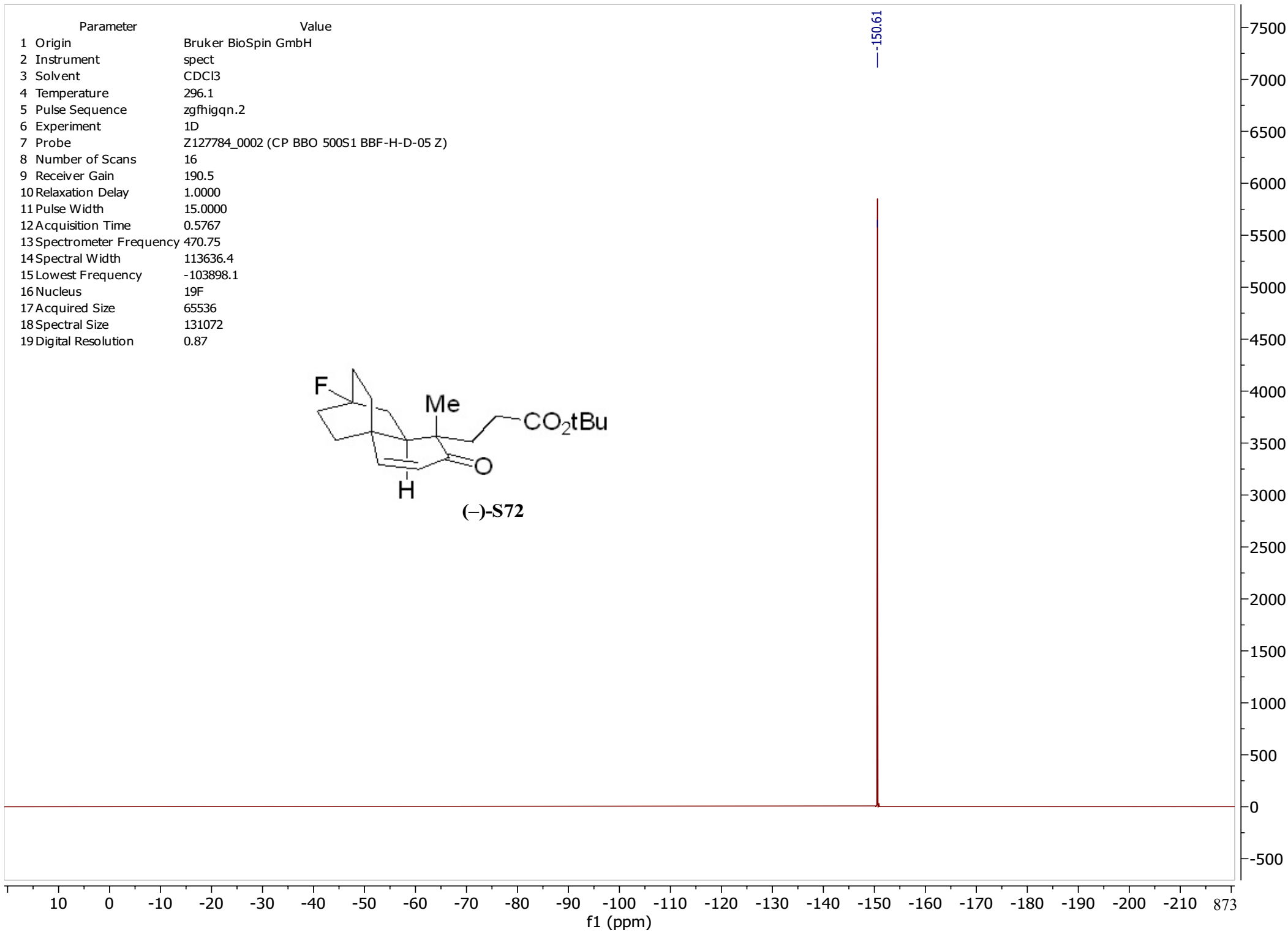
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Instrument spect
3 Solvent CDCl3
4 Temperature 296.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Probe Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans 368
9 Receiver Gain 190.5
10 Relaxation Delay 2.0000
11 Pulse Width 10.0000
12 Acquisition Time 1.0398
13 Spectrometer Frequency 125.83
14 Spectral Width 31512.6
15 Lowest Frequency -1900.3
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
19 Digital Resolution 0.48



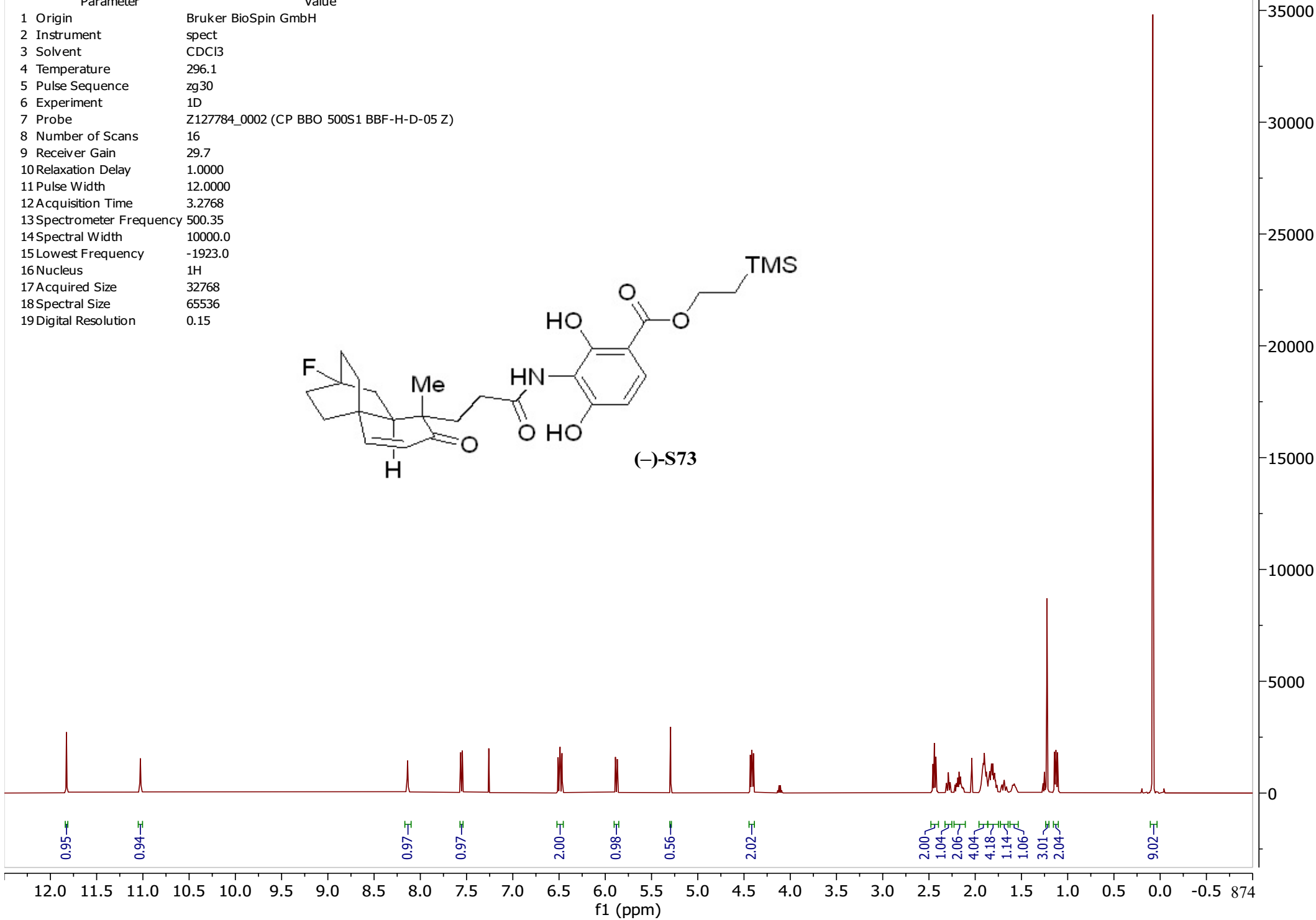
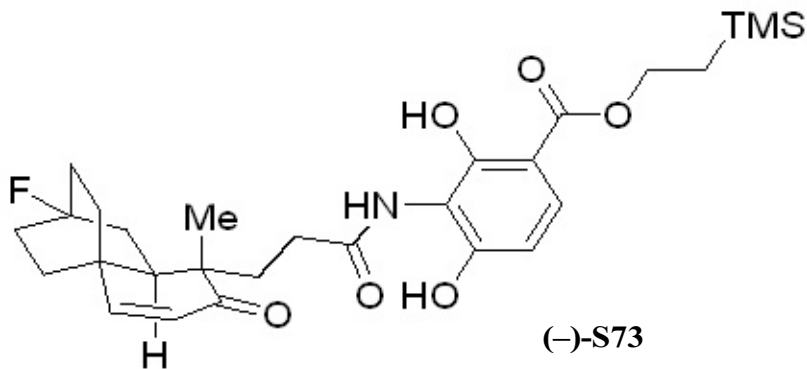
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	19F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



— -150.61

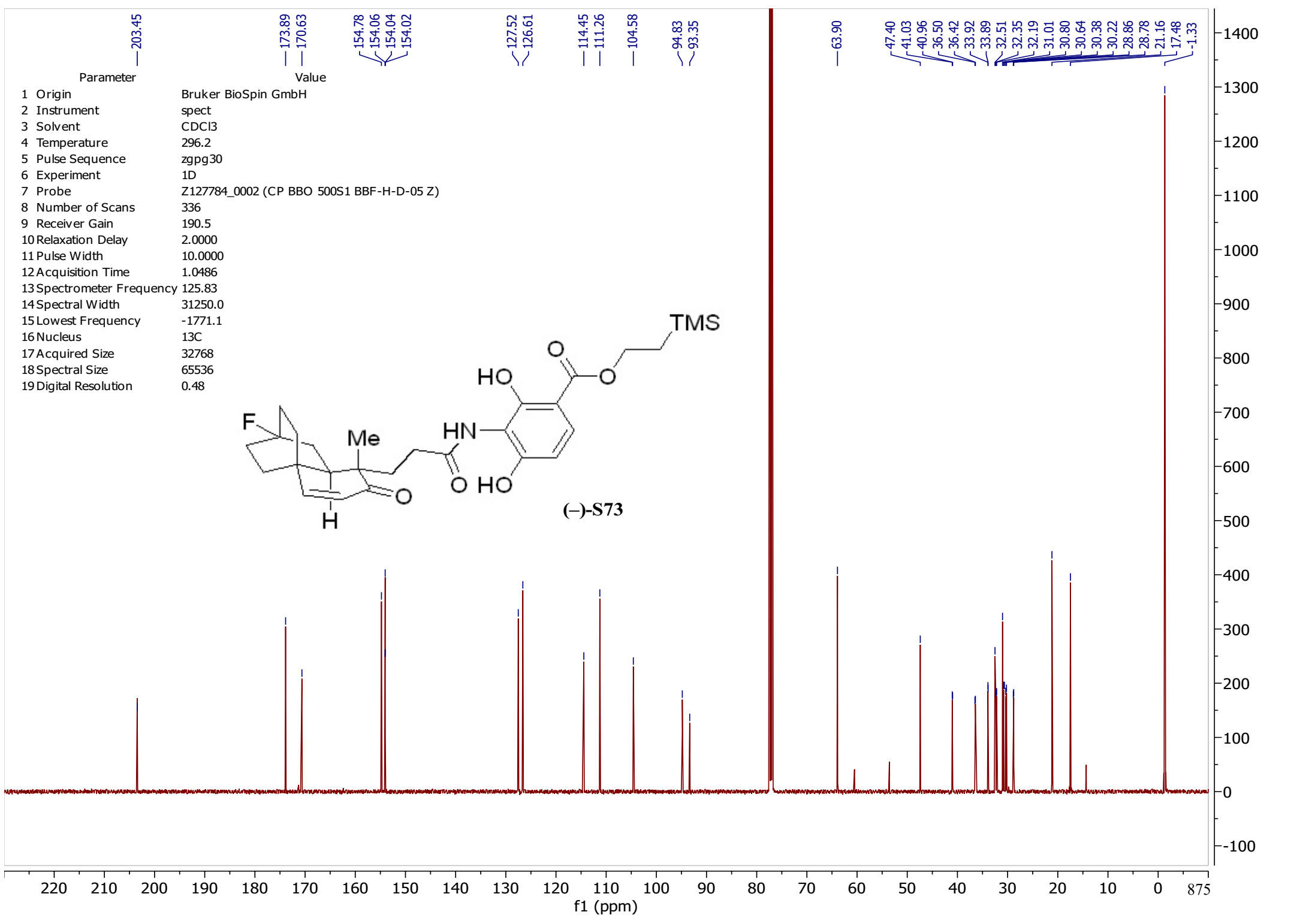
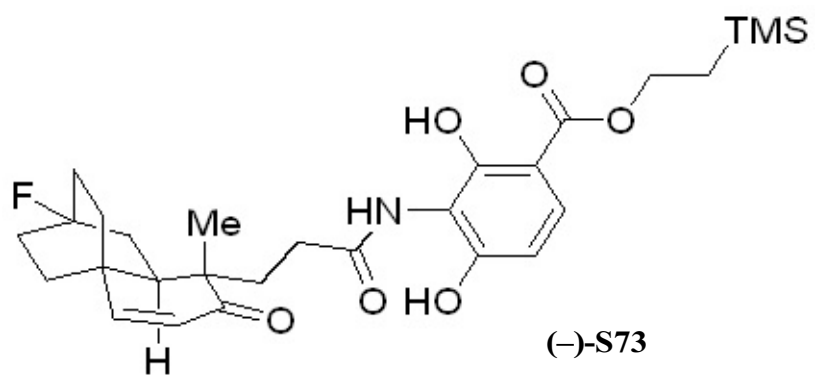


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	29.7
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1923.0
16 Nucleus	1H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15

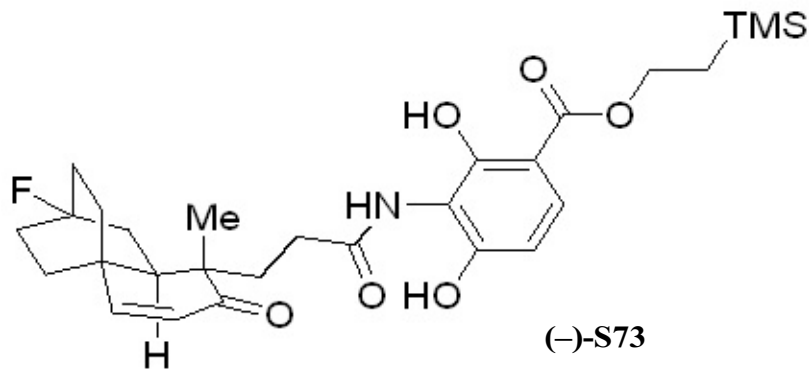


1 Origin Bruker BioSpin GmbH
 2 Instrument spect
 3 Solvent CDCl3
 4 Temperature 296.2
 5 Pulse Sequence zgpg30
 6 Experiment 1D
 7 Probe Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
 8 Number of Scans 336
 9 Receiver Gain 190.5
 10 Relaxation Delay 2.0000
 11 Pulse Width 10.0000
 12 Acquisition Time 1.0486
 13 Spectrometer Frequency 125.83
 14 Spectral Width 31250.0
 15 Lowest Frequency -1771.1
 16 Nucleus 13C
 17 Acquired Size 32768
 18 Spectral Size 65536
 19 Digital Resolution 0.48

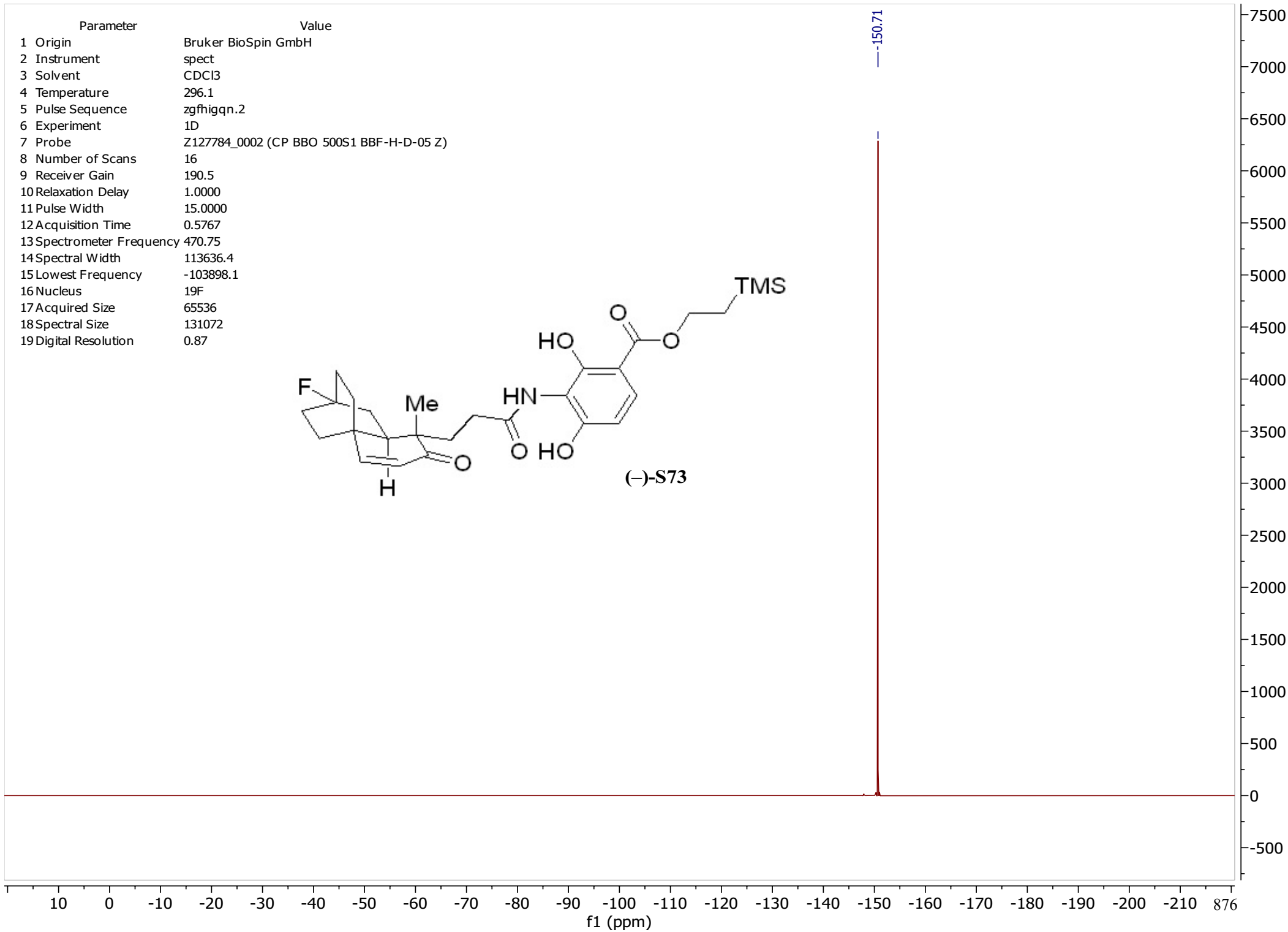
Parameter	Value
203.45	
173.89	
170.63	
154.78	
154.06	
154.04	
154.02	
127.52	
126.61	
114.45	
111.26	
104.58	
94.83	
93.35	
63.90	
47.40	
41.03	
40.96	
36.50	
36.42	
33.92	
33.89	
32.51	
32.35	
32.19	
31.01	
30.80	
30.64	
30.38	
30.22	
28.86	
28.78	
21.16	
17.48	
-1.33	



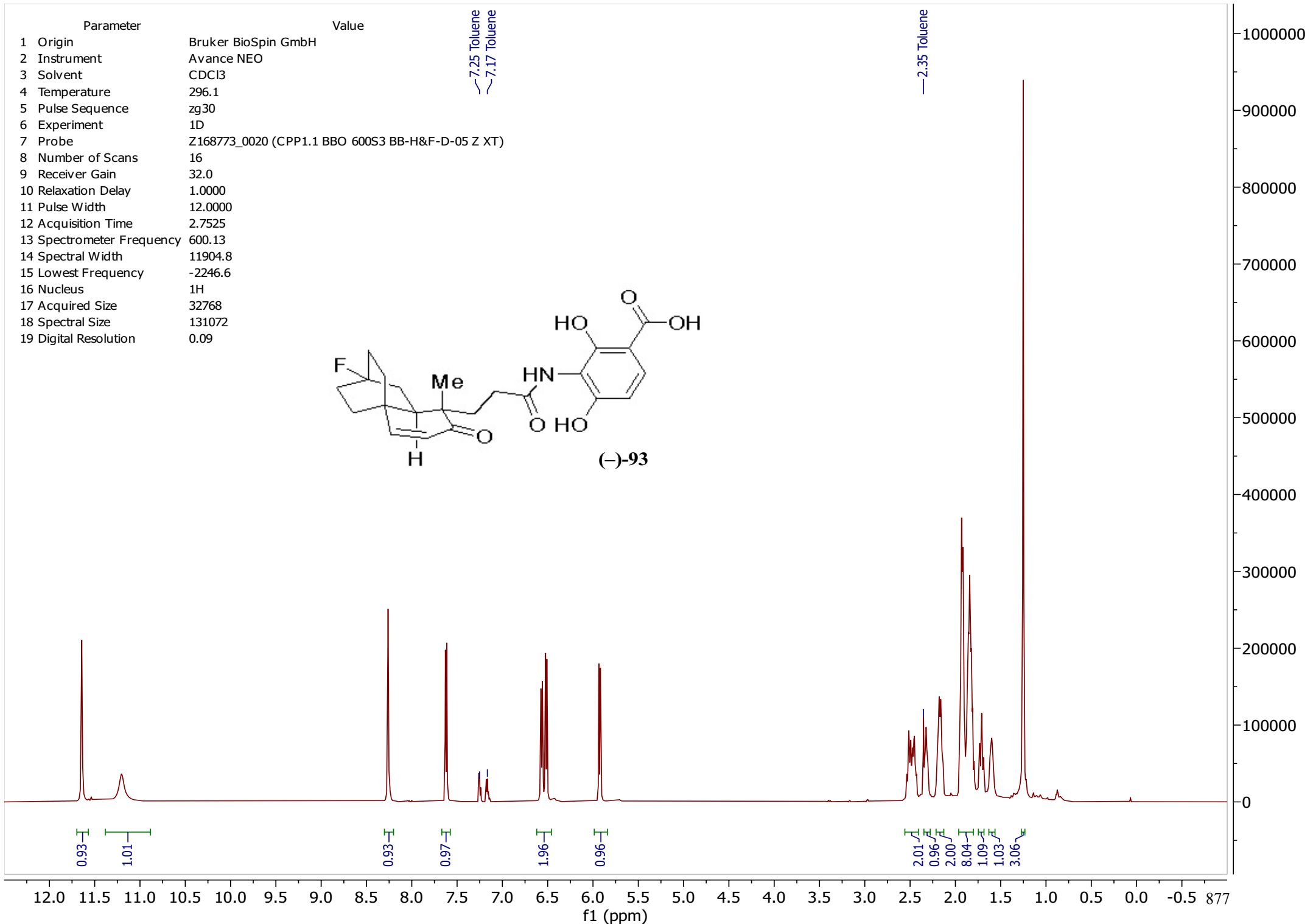
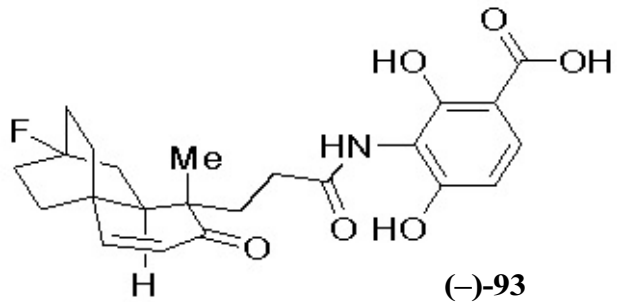
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	19F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87

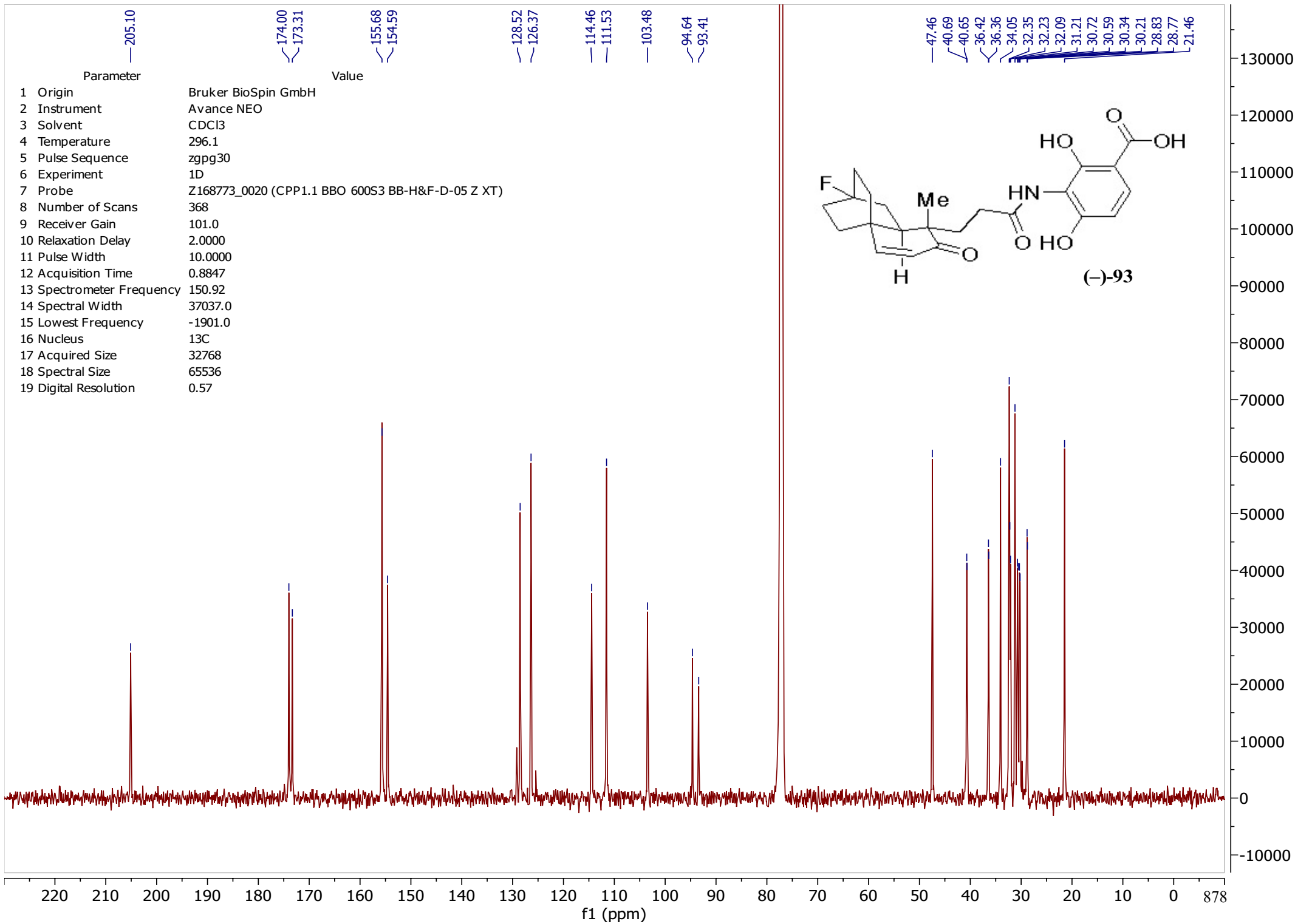


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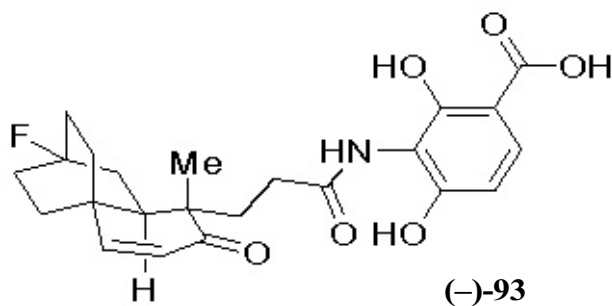


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance NEO
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z168773_0020 (CPP1.1 BBO 600S3 BB-H&F-D-05 Z XT)
8 Number of Scans	16
9 Receiver Gain	32.0
10 Relaxation Delay	1.0000
11 Pulse Width	12.0000
12 Acquisition Time	2.7525
13 Spectrometer Frequency	600.13
14 Spectral Width	11904.8
15 Lowest Frequency	-2246.6
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	131072
19 Digital Resolution	0.09

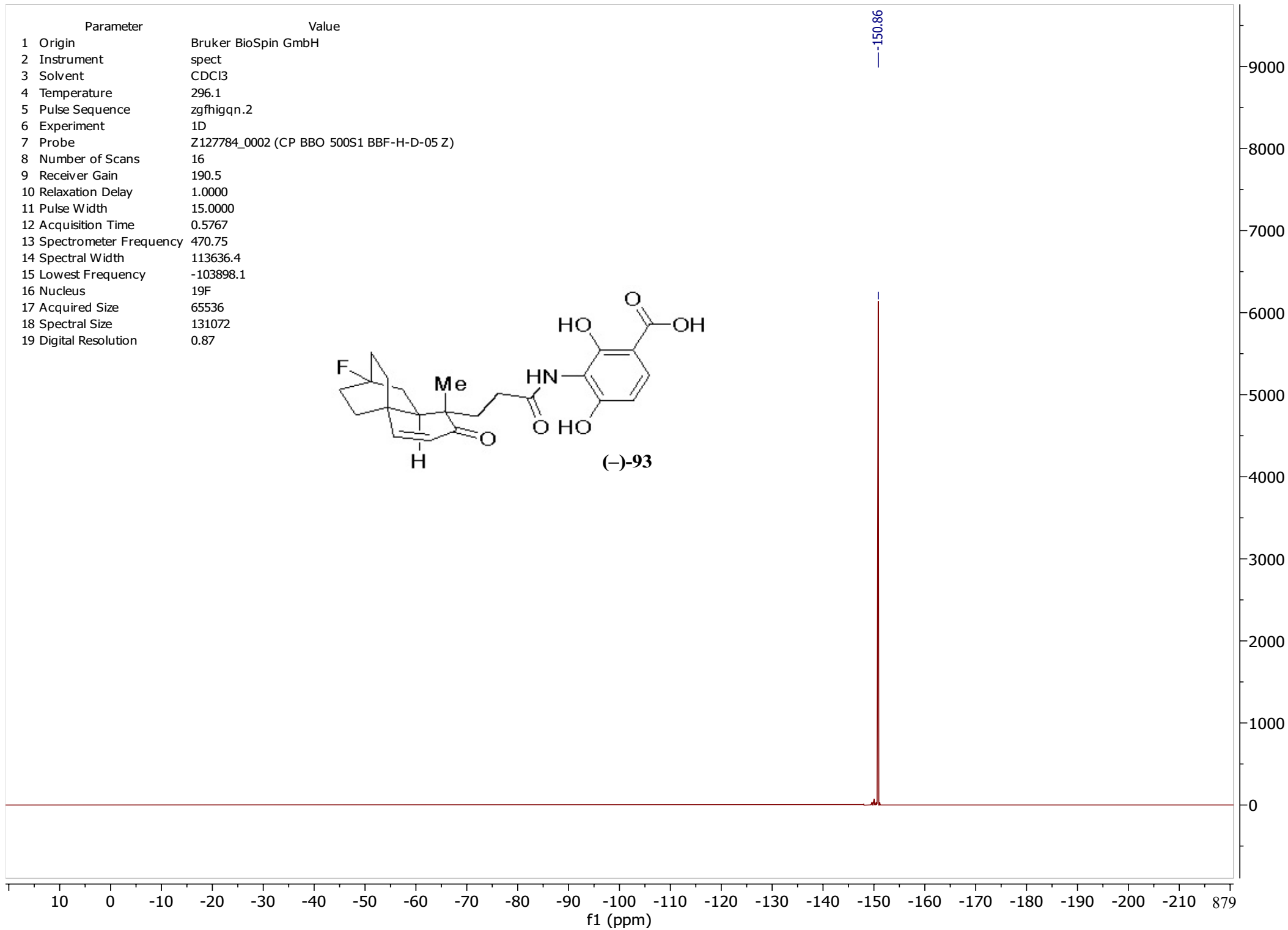




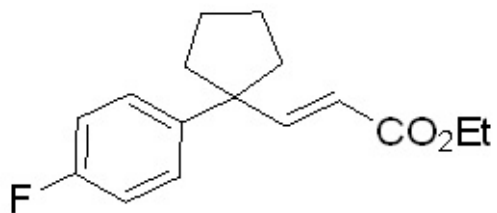
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	296.1
5 Pulse Sequence	zgfhgqn.2
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	19F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87



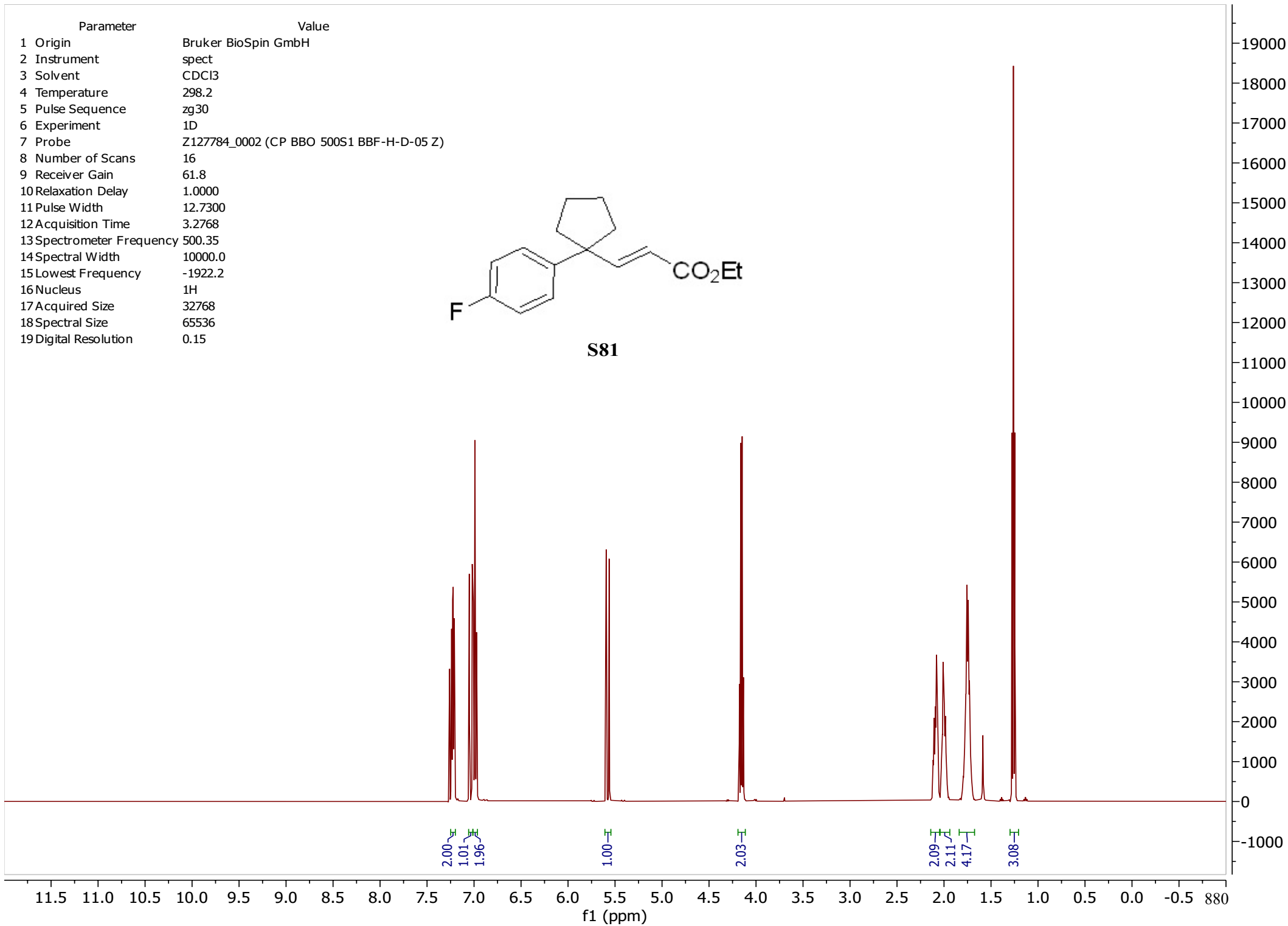
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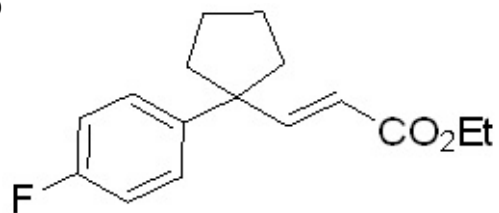
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	298.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	61.8
10 Relaxation Delay	1.0000
11 Pulse Width	12.7300
12 Acquisition Time	3.2768
13 Spectrometer Frequency	500.35
14 Spectral Width	10000.0
15 Lowest Frequency	-1922.2
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.15



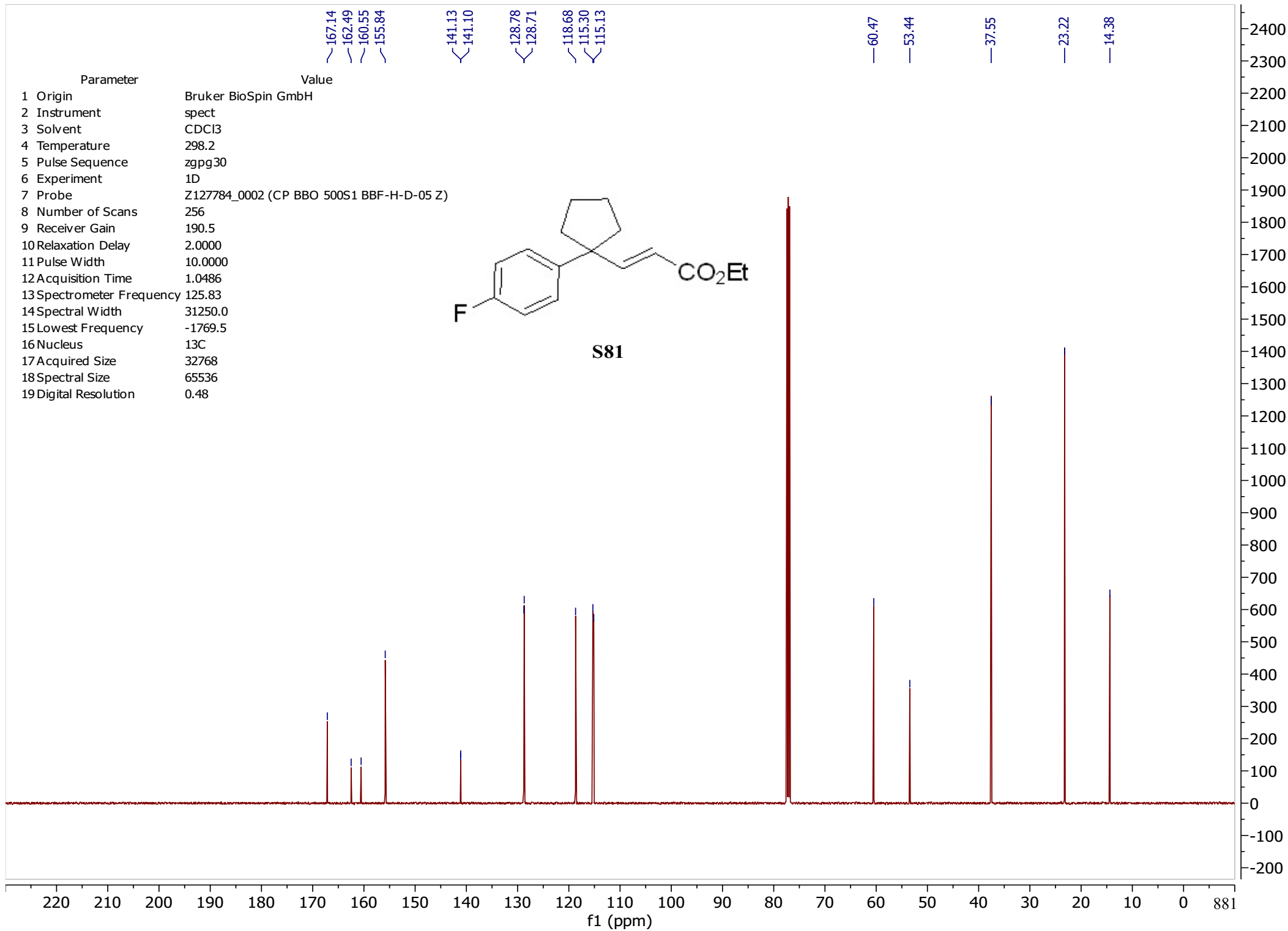
S81



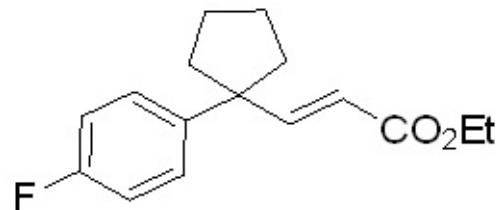
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	256
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Acquisition Time	1.0486
13 Spectrometer Frequency	125.83
14 Spectral Width	31250.0
15 Lowest Frequency	-1769.5
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536
19 Digital Resolution	0.48



S81

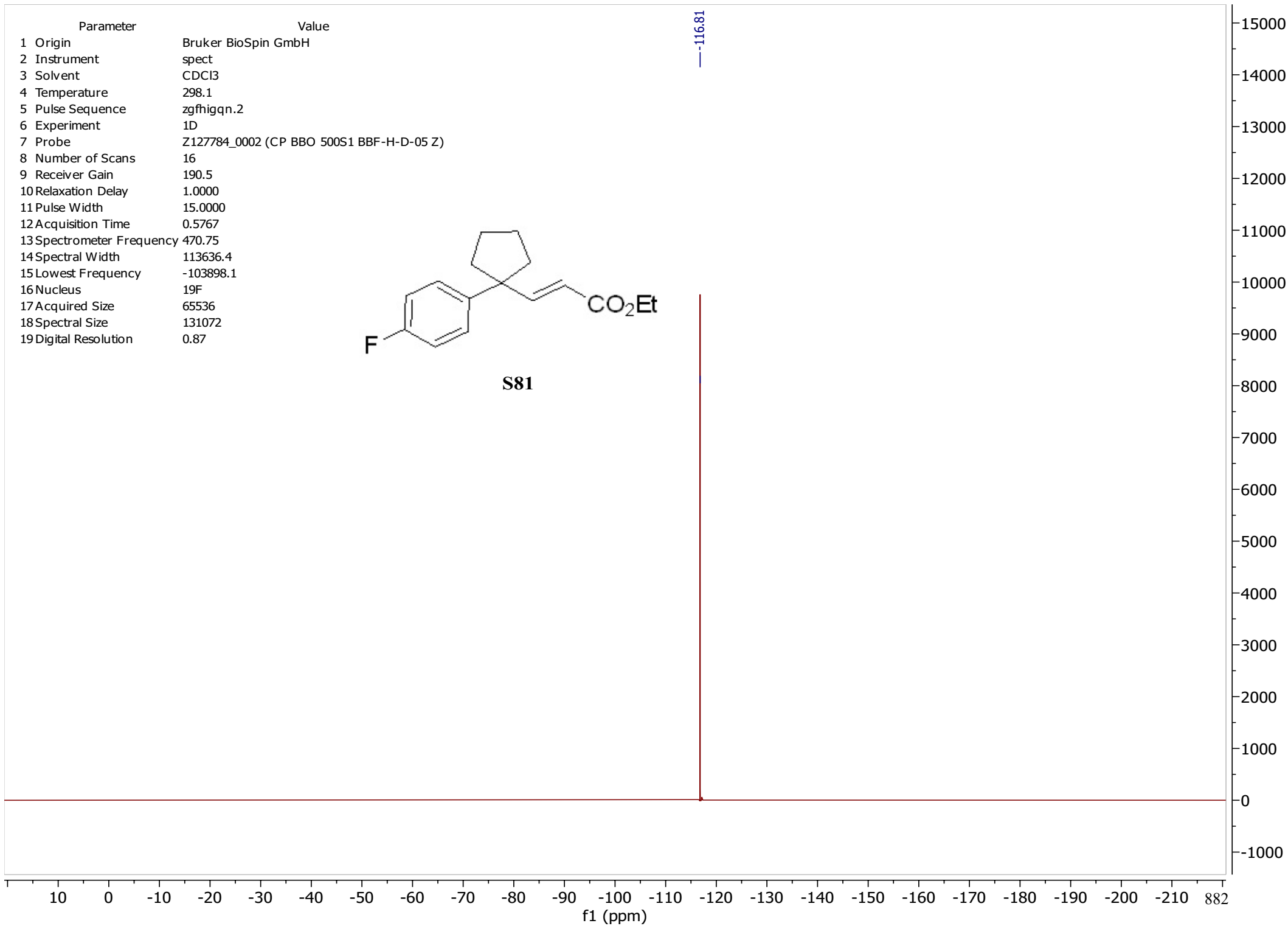


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zgfhigqn.2
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	190.5
10 Relaxation Delay	1.0000
11 Pulse Width	15.0000
12 Acquisition Time	0.5767
13 Spectrometer Frequency	470.75
14 Spectral Width	113636.4
15 Lowest Frequency	-103898.1
16 Nucleus	19F
17 Acquired Size	65536
18 Spectral Size	131072
19 Digital Resolution	0.87

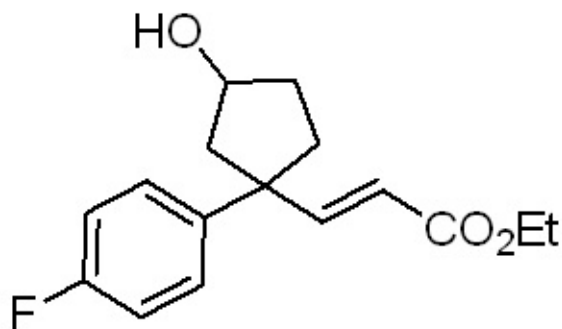


S81

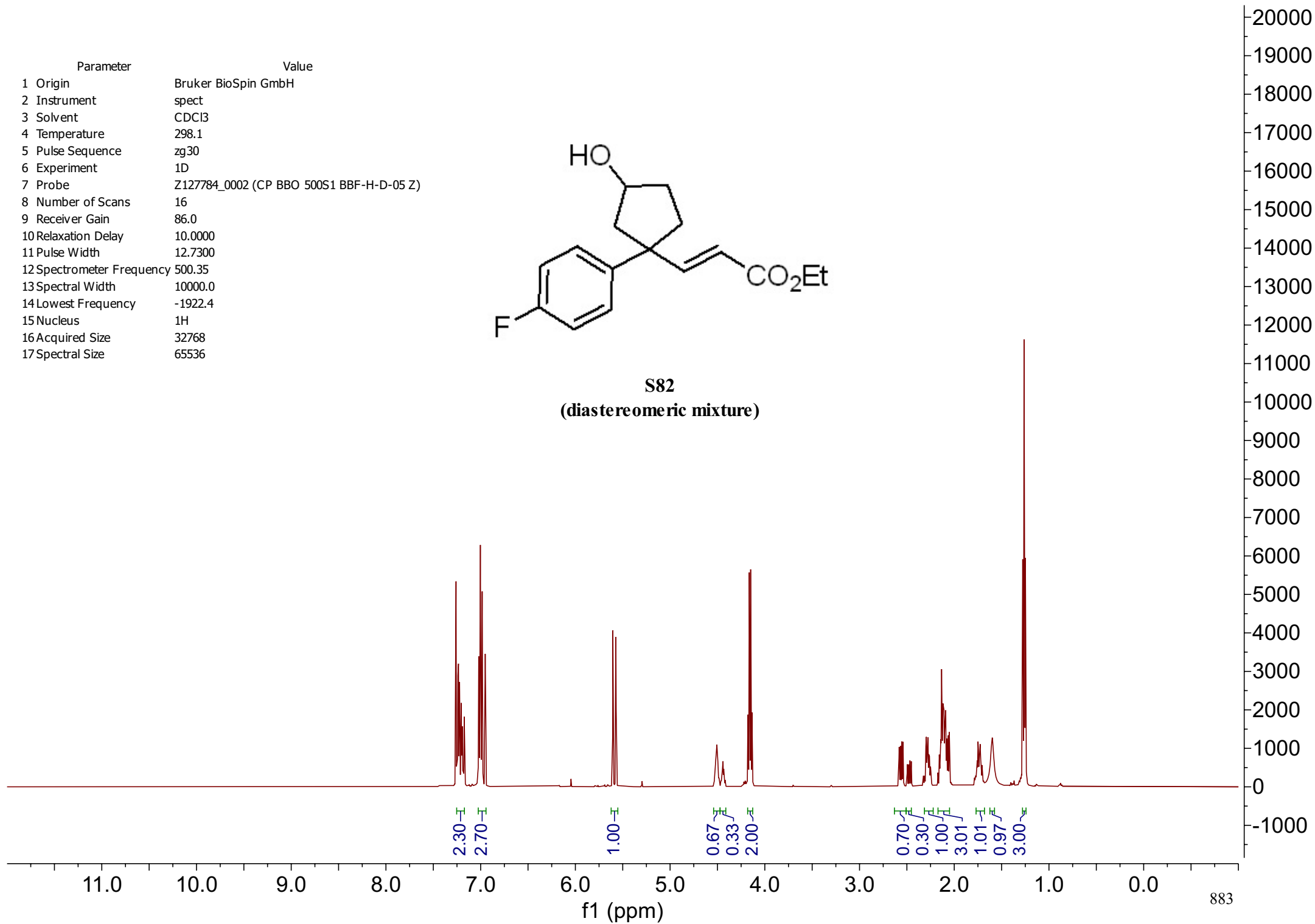
—116.81



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	298.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	16
9 Receiver Gain	86.0
10 Relaxation Delay	10.0000
11 Pulse Width	12.7300
12 Spectrometer Frequency	500.35
13 Spectral Width	10000.0
14 Lowest Frequency	-1922.4
15 Nucleus	¹ H
16 Acquired Size	32768
17 Spectral Size	65536



S82
(diastereomeric mixture)



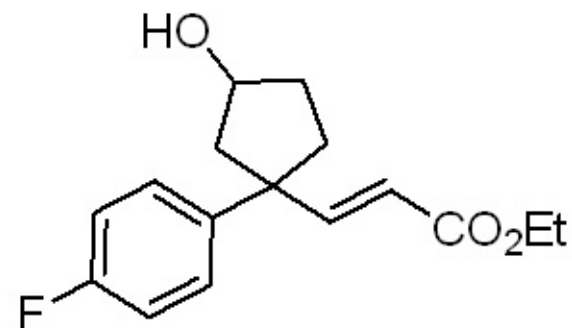
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl ₃
4 Temperature	298.2
5 Pulse Sequence	zgpg30
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	512
9 Receiver Gain	190.5
10 Relaxation Delay	2.0000
11 Pulse Width	10.0000
12 Spectrometer Frequency	125.83
13 Spectral Width	31250.0
14 Lowest Frequency	-1769.7
15 Nucleus	¹³ C
16 Acquired Size	32768
17 Spectral Size	65536

167.04
166.90
162.58
162.57
160.63
160.61
156.18
155.19
141.22
141.20
140.55
140.52
128.65
128.59
128.52
119.06
118.61
115.49
115.32

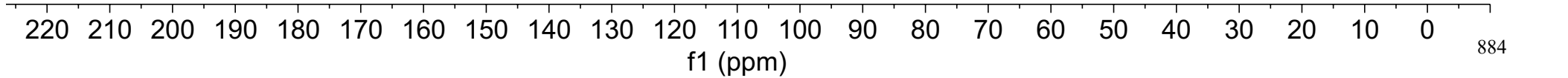
72.73
72.65

60.63
60.55
52.58
52.51
47.54
47.13
36.42
35.74
34.54
34.45

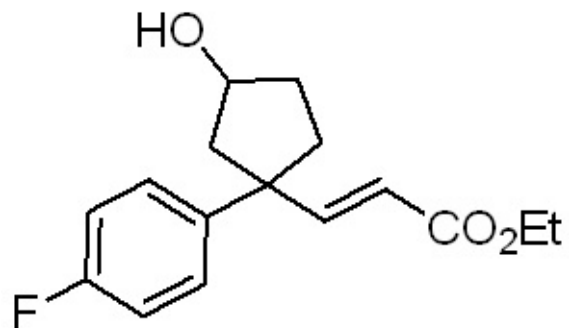
14.36



S82
(diastereomeric mixture)



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zgfgqn
6 Experiment	1D
7 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans	64
9 Receiver Gain	190.5
10 Relaxation Delay	10.0000
11 Pulse Width	15.0000
12 Spectrometer Frequency	470.75
13 Spectral Width	113636.4
14 Lowest Frequency	-103898.1
15 Nucleus	19F
16 Acquired Size	65536
17 Spectral Size	131072



S82
(diastereomeric mixture)

116.35
116.36
116.37
116.38
116.39
116.40
116.41
116.42
116.42
116.43
116.44

