

Supplementary Information

Development of Highly Efficient Platinum Catalysts for Hydroalkoxylation and Hydroamination of Unactivated Alkenes

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Supplementary Information

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1. General Information

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1260 LCMS analyses. HPLC analysis was conducted on Agilent 1260 or Shimadzu LC-20A instrument using chiral column described below in detail. TLC was performed using 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm). Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). ^1H NMR (400 MHz, 600 MHz), ^{13}C NMR (101 MHz, 151 MHz), ^{31}P NMR (162 MHz, 243 MHz) and ^{19}F NMR (376 MHz, 565 MHz) spectra were recorded on a Bruker AV III HD spectrometer, and were reported in terms of chemical shift relative to residual CDCl_3 (δ 7.26 and δ 77.16 ppm, respectively), CD_2Cl_2 (δ 5.32 ppm and δ 53.84 ppm, respectively). Data for ^1H NMR spectra is reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Abbreviations are used as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet. High-resolution mass spectra (HRMS) was obtained from the SUSTech Mass Spectral Facility using Thermo ScientificTM Q ExactiveTM Quadrupole-Orbitrap Mass Spectrometer. Reagents were purchased from commercial vendors as follows: Dichloro(1,5-cyclooctadiene)Platinum, silver salts (silver trifluoromethanesulfonate) were purchased from Sigma-Aldrich and stored in an argon-filled glovebox. Alcohols (methanol, ethanol) were commercial available.

2. Synthesis of Catalysts

General Procedure

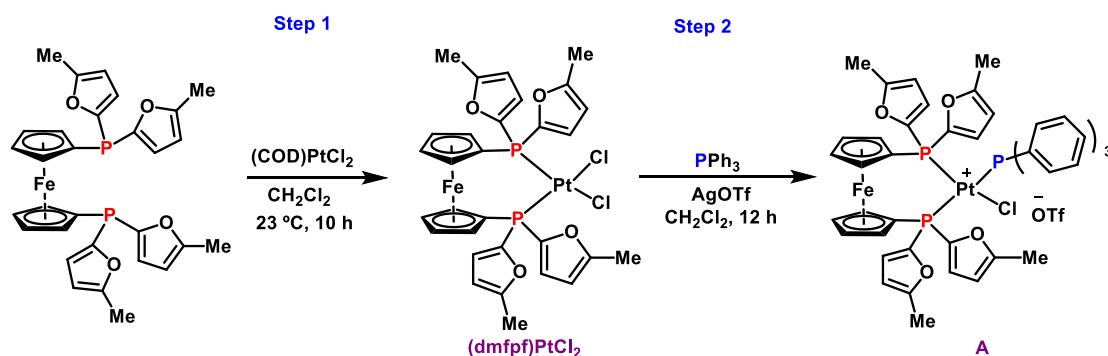
Step 1: In an argon filled glovebox, to a 20 mL scintillation vial with a magnetic stir bar were added 1,1'-bis[bis(5-methyl-2-furanyl)phosphino]ferrocene (182 mg, 0.32 mmol), (COD)PtCl₂ (120 mg, 0.32 mmol) and 3 mL CH₂Cl₂, then the vial was taken outside of the dry box and the mixture was stirred at room temperature (23 °C) for 10 h. The yellow solution was filtered and then evaporated to provide yellow solid, which was recrystallized through 1 mL CH₂Cl₂ and 1 mL hexane to give yellow precipitate. The solid was collected and dried in *vacuo* to yield (dmfpf)PtCl₂ (220 mg, 82% yield).

¹H NMR (600 MHz, CDCl₃): δ 7.16 (s, 4H), 6.12 (d, J = 2.6 Hz, 4H), 4.37 (d, J = 15.9 Hz, 8H), 2.35 (s, 12H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 158.7, 140.8(dd, J = 102.0, 2.1 Hz), 126.2 – 126.1 (m), 107.9 – 107.7 (m), 75.3 – 75.2 (m), 73.7 – 73.6 (m), 14.21 ppm

³¹P NMR (243 MHz, CDCl₃): δ -24.7 (d, $^1J_{\text{Pt-P}}$ = 3764 Hz) ppm

Step 2: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added (dmfpf)PtCl₂ (100 mg, 0.12 mmol), silver trifluoromethanesulfonate (31 mg, 0.12 mmol, 1.0 equiv.), monophosphine ligand (0.13 mmol, 1.5 equiv.) and 2 mL CH₂Cl₂. Then the vial was taken outside of the glovebox and the mixture was stirred at room temperature (23 °C) for 12 h. The orange solution was filtered and CH₂Cl₂ was evaporated to provide orange solid, which was recrystallized through CH₂Cl₂ and hexane to give yellow precipitate.



Yellow solid (130 mg, 89% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.51 – 7.43 (m, 9H), 7.35 – 7.31 (m, 6H), 7.07 – 7.05 (m, 2H), 6.43 – 6.42 (m, 2H), 6.20 – 6.20 (m, 2H), 5.97 – 5.96 (m, 2H), 4.56 – 4.56 (m, 2H), 4.47 – 4.46 (m, 4H), 4.06 – 4.06 (m, 2H), 2.42 (s, 6H), 2.10 (s, 6H) ppm

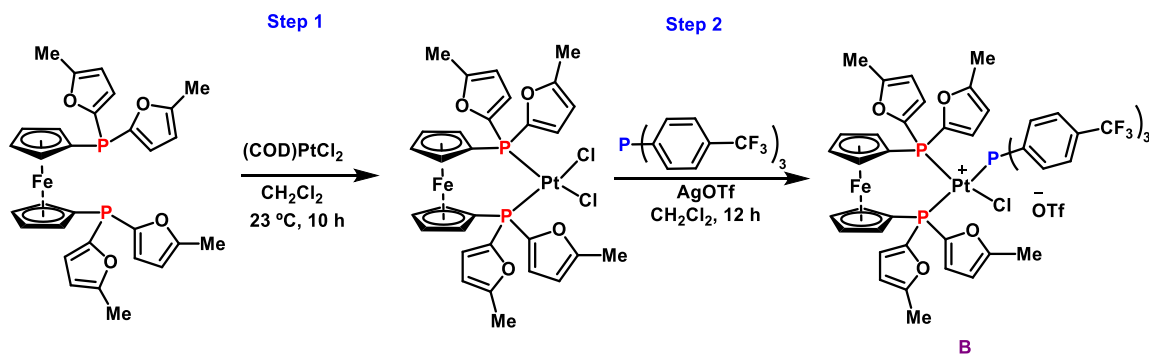
¹³C NMR (101 MHz, CDCl₃): δ 159.2 (dd, J = 46.7, 6.3 Hz), 139.4 (ddd, J = 105.3, 99.0, 3.0 Hz), 134.9 (dd, J = 10.2, 0.9 Hz), 134.0 (d, J = 16.1 Hz), 131.6 (d, J = 2.5 Hz), 129.2 (d, J = 10.0 Hz), 128.4 (d, J =

11.4 Hz), 126.1 (dd, $J = 35.8, 17.9$ Hz), 121.2 (q, $J = 332.4$ Hz), 108.8 (dd, $J = 81.8, 7.7$ Hz), 75.5 (d, $J = 13.8$ Hz), 75.3 – 74.8 (m), 14.3, 13.7 ppm

^{31}P NMR (243 MHz, CDCl_3): δ 23.3 (dd, $^2J_{\text{P-P}} = 445, 19$ Hz, $^1J_{\text{Pt-P}} = 2555$ Hz), -11.2 (dd, $^2J_{\text{P-P}} = 444, 19$ Hz, $^1J_{\text{Pt-P}} = 2504$ Hz), -23.7 (t, $^2J_{\text{P-P}} = 18$ Hz, $^1J_{\text{Pt-P}} = 3701$ Hz) ppm

^{19}F NMR (565 MHz, CDCl_3): δ -77.9 (s) ppm

HRMS (ESI⁺): calc'd for $\text{C}_{48}\text{H}_{43}\text{ClFeO}_4\text{P}_3\text{Pt}$ [M-OTf]⁺: 1062.1054, found 1062.1045.



Yellow solid (143 mg, 85% yield).

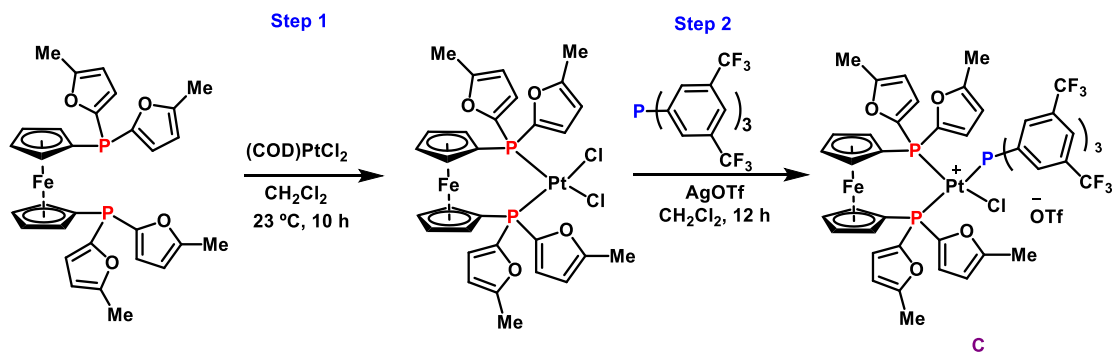
^1H NMR (400 MHz, CDCl_3): δ 7.71 – 7.64 (m, 12H), 7.13 – 7.12 (m, 2H), 6.62 – 6.61 (m, 2H), 6.26 – 6.24 (m, 2H), 6.05 – 6.04 (m, 2H), 4.58 (d, $J = 1.5$ Hz, 1H), 4.51 (d, $J = 1.5$ Hz, 1H), 4.45 (dd, $J = 4.0, 2.1$ Hz, 1H), 4.21 (dd, $J = 3.9, 2.0$ Hz, 1H), 2.42 (s, 6H), 2.12 (s, 6H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 159.6 (dd, $J = 55.6, 6.2$ Hz), 139.0 (ddd, $J = 75.1, 69.8, 3.1$ Hz), 135.4 (d, $J = 10.7$ Hz), 133.7 (dq, $J = 33.4, 3.0$ Hz), 131.62 (d, $J = 55.5$ Hz), 126.7 (dd, $J = 44.1, 18.2$ Hz), 125.8 – 125.4 (m), 123.3 (q, $J = 272.2$ Hz), 121.2 (q, $J = 322.3$ Hz), 109.13 (dd, $J = 83.4, 7.8$ Hz), 75.6 – 75.1 (m), 14.3, 13.7 ppm

^{19}F NMR (565 MHz, CDCl_3): δ -63.3 (s), -78.0 (s) ppm

^{31}P NMR (162 MHz, CDCl_3): δ 22.8 (dd, $^2J_{\text{P-P}} = 452, 19$ Hz, $^1J_{\text{Pt-P}} = 2508$ Hz), -10.9 (dd, $^2J_{\text{P-P}} = 451, 17$ Hz, $^1J_{\text{Pt-P}} = 2644$ Hz), -24.1 (t, $^2J_{\text{P-P}} = 18$ Hz, $^1J_{\text{Pt-P}} = 3656$ Hz) ppm

HRMS (ESI⁺): calc'd for $\text{C}_{51}\text{H}_{40}\text{ClF}_9\text{FeO}_4\text{FeP}_3\text{Pt}$ [M-OTf]⁺: 1266.0676, found 1266.0664.



Yellow solid (192 mg, 99% yield).

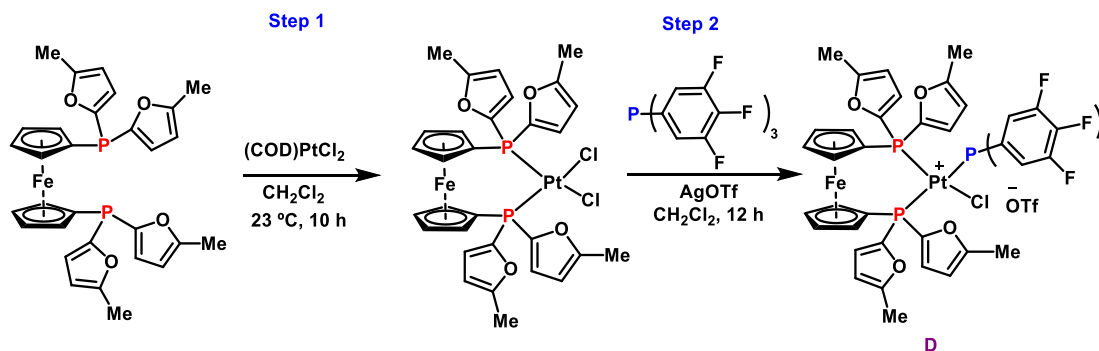
¹H NMR (400 MHz, CDCl₃): δ 8.08 (s, 3H), 7.96 (s, 3H), 7.93 (s, 3H), 6.96 (s, 2H), 6.47 (s, 2H), 6.22 (s, 2H), 6.02 (s, 2H), 4.73 (s, 2H), 4.64 (s, 2H), 4.61 (s, 2H), 4.07 (s, 2H), 2.40 (s, 6H), 2.00 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 160.1 (dd, *J* = 64.8, 6.6 Hz), 138.6 (ddd, *J* = 65.9, 62.0, 3.0 Hz), 134.1 (d, *J* = 8.4 Hz), 132.9 (qd, *J* = 34.5, 11.3 Hz), 129.4 (dd, *J* = 56.5, 2.9 Hz), 126.9 – 126.4 (m), 122.3 (q, *J* = 273.6 Hz), 121.0 (q, *J* = 324.3 Hz), 109.5 (dd, *J* = 181.5, 7.4 Hz), 76.6 – 74.9 (m), 14.0, 13.4 ppm

³¹P NMR (243 MHz, CDCl₃): δ 25.7 (dd, ²*J*_{P-P} = 458, 19 Hz, ¹*J*_{Pt-P} = 2507 Hz), -10.2 (dd, ²*J*_{P-P} = 459, 16 Hz, ¹*J*_{Pt-P} = 2760 Hz), -23.5 (t, ²*J*_{P-P} = 18 Hz, ¹*J*_{Pt-P} = 3536 Hz) ppm

¹⁹F NMR (565 MHz, CDCl₃): δ -63.2 (s), -78.2 (s) ppm

HRMS (ESI⁺): calc'd for C₅₄H₃₇ClF₁₈FeO₄P₃Pt [M-OTf]⁺: 1470.0297, found 1470.0295



Yellow solid (140 mg, 84% yield).

Tris(3,4,5-trifluorophenyl)phosphane was prepared according to a literature procedure reported by Alexanian and coworkers.¹

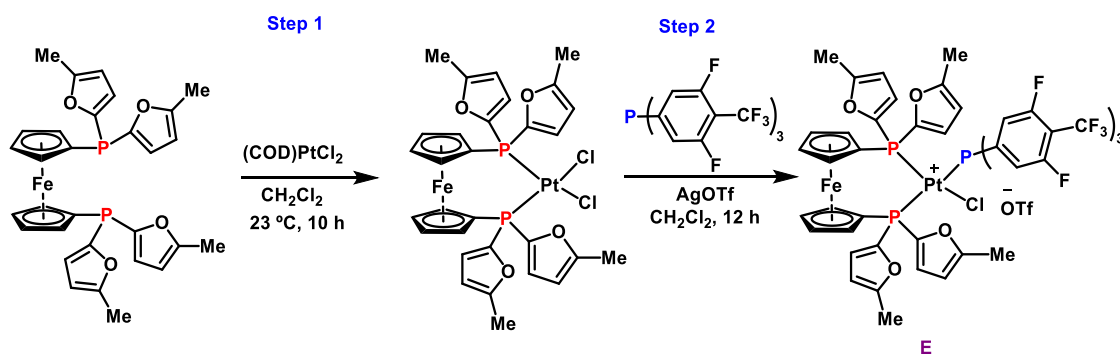
¹H NMR (400 MHz, CDCl₃): δ 7.09 – 7.08 (m, 2H), 7.05 – 7.01 (m, 6H), 6.95 – 6.94 (m, 2H), 6.28 – 6.28 (m, 2H), 6.24 – 6.24 (m, 2H), 4.60 (s, 2H), 4.55 (s, 2H), 4.46 – 4.45 (m, 2H), 4.22 (s, 2H), 2.47 (s, 6H), 2.39 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 160.2 (dd, *J* = 43.9, 6.5 Hz), 151.1 (dm, *J* = 257.9 Hz), 142.3 (dt, *J* = 263.0, 14.8 Hz), 138.8 (ddd, *J* = 102.4, 13.8, 3.0 Hz), 126.3 (dd, *J* = 41.6, 17.6 Hz), 122.9 (d, *J* = 52.6 Hz), 120.5 – 118.2 (m), 109.2 (dd, *J* = 97.9, 7.7 Hz), 75.6 – 74.2 (m), 14.1, 13.8 ppm

³¹P NMR (243 MHz, CDCl₃): δ 25.7 (dd, ²*J*_{P-P} = 461, 17 Hz, ¹*J*_{Pt-P} = 2475 Hz), -10.3 (dd, ²*J*_{P-P} = 461, 16 Hz, ¹*J*_{Pt-P} = 2747 Hz), 24.4 (t, ²*J*_{P-P} = 18 Hz, ¹*J*_{Pt-P} = 3642 Hz) ppm

¹⁹F NMR (565 MHz, CDCl₃): δ -78.9, -129.9 (d, *J* = 19.3 Hz), -151.4 (t, *J* = 20.2 Hz) ppm

HRMS (ESI⁺): calc'd for C₄₈H₃₄ClF₉FeO₄P₃Pt [M-OTf]⁺: 1224.0206, found 1224.0201.



Yellow solid (150 mg, 82% yield).

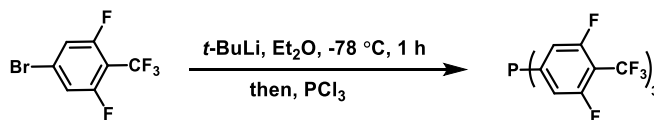
^1H NMR (600 MHz, CDCl_3): δ 7.16 (dd, $J = 11.8, 8.7$ Hz, 6H), 7.13 – 7.09 (m, 2H), 6.93 – 6.86 (m, 2H), 6.29 (d, $J = 3.1$ Hz, 2H), 6.22 (d, $J = 3.1$ Hz, 2H), 4.58 (dd, $J = 7.6, 1.3$ Hz, 4H), 4.41 (dd, $J = 3.8, 1.9$ Hz, 2H), 4.32 (dd, $J = 4.0, 2.1$ Hz, 2H), 2.46 (s, 6H), 2.36 (s, 6H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 160.9 (d, $J = 19.2$ Hz), 160.6 (d, $J = 6.1$ Hz), 160.4 (d, $J = 7.1$ Hz), 158.3 (d, $J = 20.2$ Hz), 139.2 (dd, $J = 37.8$ Hz, $J = 4.0$ Hz), 138.1 (dd, $J = 38.4$ Hz, $J = 3.0$ Hz), 133.2 (d, $J = 58.6$ Hz), 126.9 (d, $J = 17.2$ Hz), 126.5 (d, $J = 18.2$ Hz), 120.8 (q, $J = 275.7$ Hz), 122.64, 119.5, 119.2 (d, $J = 12.1$ Hz), 119.0 (d, $J = 11.1$ Hz), 112.3–111.2 (m), 109.9 (d, $J = 8.1$ Hz), 108.9 (d, $J = 7.1$ Hz), 75.7 (d, $J = 8.1$ Hz), 75.6 (d, $J = 13.1$ Hz), 74.8 (d, $J = 6.1$ Hz), 71.6 (d, $J = 90.9$ Hz), 67.3 (d, $J = 81.8$ Hz), 14.2, 13.8 ppm

^{19}F NMR (376 MHz, CDCl_3): δ -56.8 – -56.9 (m), -57.0 (s), -78.2 – -78.3 (m), -105.4 (qd, $J = 21.8, 4.0$ Hz) ppm

^{31}P NMR (243 MHz, CDCl_3): δ 24.9 (ddd, $^1J_{\text{Pt-P}} = 3691$ Hz, $^2J_{\text{P-P}} = 690$ Hz, $^2J_{\text{P-P}} = 27$ Hz), -10.3 (ddd, $^1J_{\text{Pt-P}} = 4238$ Hz, $^2J_{\text{P-P}} = 690$ Hz, $^2J_{\text{P-P}} = 24$ Hz), -24.8 (dt, $^1J_{\text{Pt-P}} = 5448$ Hz, $^2J_{\text{P-P}} = 24$ Hz) ppm

HRMS (ESI $^{+}$): calculated for $\text{C}_{51}\text{H}_{34}\text{ClF}_{15}\text{FeO}_4\text{P}_3\text{Pt}$ [M-OTf] $^{+}$: 1374.0111, found 1374.0126.



5-Bromo-1,3-difluoro-2-(trifluoromethyl)benzene (1.0 g, 3.8 mmol) was dissolved in 16 mL anhydrous ether, and cooled to -78 °C, *t*-BuLi (2.4 mL, 3.8 mmol) was added dropwise at this temperature. After stirred 1 h, freshly distilled PCl_3 (83 μL , 0.95 mmol) was added dropwise, and then the mixture was stirred at 23 °C overnight. The solution was quenched with saturated NH_4Cl aqueous solution, and extracted with EtOAc (3 $\times$ 25 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc/hexane = 0/100 to 5/95) to afford the desired tris(3,5-difluoro-4-(trifluoromethyl)phenyl)phosphine (333 mg, 61% yield) as white solid.

^1H NMR (400 MHz, CDCl_3): δ 6.94 (t, $J = 8.1$ Hz, 6H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 160.4 (d, J = 263 Hz) , 141.6 – 141.4 (m), 121.24 (q, J = 274.8 Hz), 117.6 (td, J = 22.6 Hz, J = 4.5 Hz), 110.25 – 109.86 (m) ppm

¹⁹F NMR (376 MHz, CDCl₃): δ -56.7 (t, J = 21.9 Hz), -107.2 (d, J = 22.1 Hz) ppm

³¹P NMR (162 MHz, CDCl₃): δ -2.6 (s) ppm

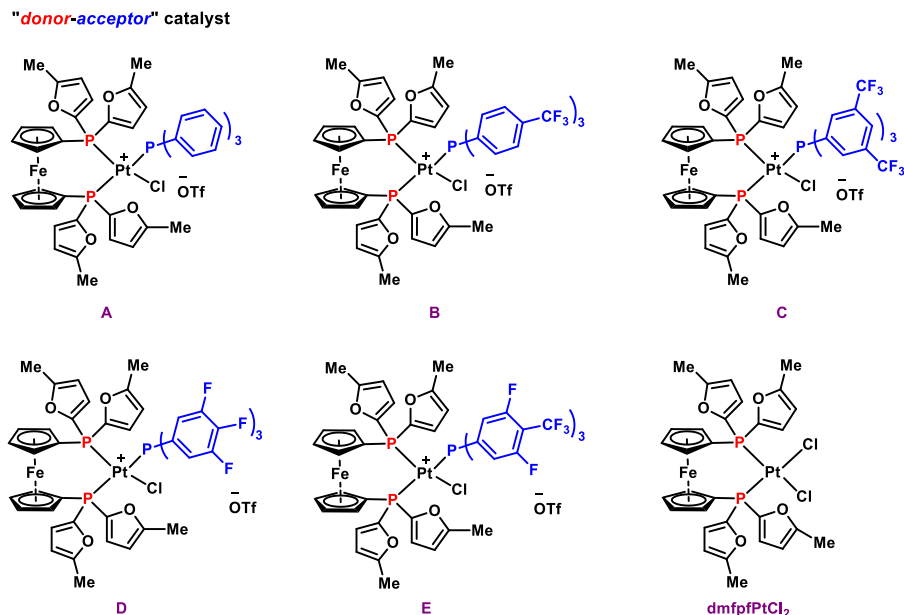
HRMS (ESI-): calculated for C₂₁H₆F₁₅PCl[M+Cl]⁻: 608.9651, found 608.9666.

3. Development of Reaction Condition

3.1 Evaluation of the Conditions for the Hydroalkoxylation of **1**

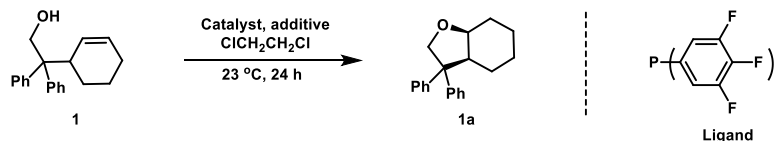
General Procedure

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst (0.0005mmol, 1 mol%), silver trifluoromethanesulfonate (0.3 mg, 0.001 mmol, 2 mol%), **1** (13.9 mg, 0.05 mmol, 1.0 equiv.), ClCH₂CH₂Cl (1 mL) and 4,4'-di-*tert*-butyl-1,1'-biphenyl (0.5 equiv.) used as an internal standard. Then the vial was taken outside of the glovebox and the mixture was stirred at room temperature (23 °C) for 24 h. The mixture was diluted with CH₂Cl₂, filtered through a pad of celite and concentrated. The yield of **1a** was determined by crude ¹H NMR analysis.



Supplementary Figure 1. Design of the Catalysts

Supplementary Table 1: Evaluation of the Conditions for the Hydroalkoxylation of 1



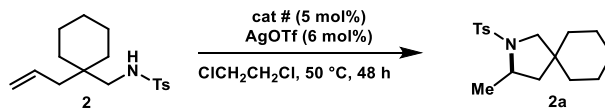
Entry	Catalyst	Additive	Yield (%) ^a	Entry	Catalyst	Additive	Yield (%) ^a
1	A (1 mol%)	AgOTf (1 mol%)	6	16	A (1 mol%)	AgOTf (2 mol%)	22
2	B (1 mol%)	AgOTf (1 mol%)	9	17	B (1 mol%)	AgOTf (2 mol%)	26
3	C (1 mol%)	AgOTf (1 mol%)	16	18	D (1 mol%)	AgOTf (2 mol%)	49
4	D (1 mol%)	AgOTf (1 mol%)	16	19	E (1 mol%)	AgOTf (2 mol%)	45
5	C (1 mol%)	AgOTf (2 mol%)	46	20	(dmfpf)PtCl ₂ (2 mol%)	AgOTf (4 mol%)	37
7	C (1 mol%)	AgOTf (3 mol%)	48	21	(COD)PtCl ₂ (2 mol%)	AgOTf (4 mol%)	17
6	C (1 mol%)	AgOTf (4 mol%)	50	22	D (2 mol%)	no additive	0
8	C (1 mol%)	AgOTf (5 mol%)	56	23	no catalyst	AgOTf (4 equiv.)	0
9	C (1 mol%)	AgOTf (6 mol%)	60	24 ^c	no catalyst	AgOTf (4 mol%) Ligand (4 mol%)	0
10	C (1 mol%)	AgOTf (8 mol%)	63	25	(dmfpf)PtCl ₂ (1 mol%)	AgBF ₄ (2 mol%) Ligand (1 mol%)	0
11	C (1 mol%)	AgOTf (10 mol%)	64	26	(dmfpf)PtCl ₂ (1 mol%)	AgPF ₆ (2 mol%) Ligand (1 mol%)	0
12	C (1 mol%)	AgOTf (30 mol%)	60	27	C (2 mol%)	AgOTf (4 mol%)	90 ^b
13	C (1 mol%)	AgOTf (50 mol%)	46	28	D (2 mol%)	AgOTf (4 mol%)	89 ^b
14	C (1 mol%)	AgOTf (80 mol%)	32	30 ^d	(dmfpf)PtCl ₂ (1 mol%)	AgOTf (1 mol%)	0
15	C (1 mol%)	AgOTf (100 mol%)	25	31	(dmfpf)PtCl ₂ (1 mol%)	AgOTf (1 mol%) Ligand (1 mol%)	0

^a Determined by ¹H NMR analysis using 4,4'-di-*tert*-butyl-1,1'-biphenyl as an internal standard. ^b Catalyst (2 mol%), AgOTf (4 mol%), 24 h. ^c Complex **H** (in the proposed mechanism in the manuscript) was made, but no reactivity was observed, indicating that complex **H** is not the catalytic active specie. ^d Complex **F** (in the proposed mechanism in the manuscript) was made, but no reactivity was observed.

3.2 Evaluation of the Conditions for the Hydroamination of 2

General Procedure

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst (0.005mmol, 5 mol%), silver trifluoromethanesulfonate (1.5 mg, 0.006 mmol, 6 mol%) and ClCH₂CH₂Cl (0.5 mL). The mixture was stirred at 23 °C for 1 h. To the mixture was added a solution of **2** (30.7 mg, 0.1 mmol, 1.0 equiv) and 4,4'-di-*tert*-butyl-1,1'-biphenyl (13.3 mg, 0.05 mmol) in ClCH₂CH₂Cl (0.5 mL). Then the vial was taken outside of the glovebox and the mixture was stirred at 50 °C for 48 h. The reaction mixture was diluted with CH₂Cl₂, filtered through a pad of celite and concentrated. The yield of **2a** was determined by crude ¹H NMR analysis.

Supplementary Table 2: Catalysts Screening by Intramolecular Hydroamination of **2**

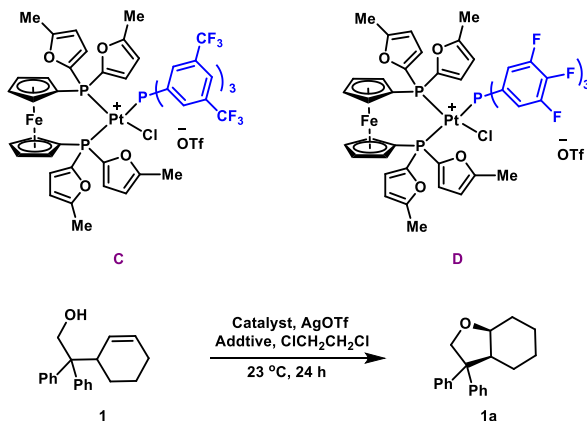
entry	cat #	additive	yield (%) ^a
1	E	AgOTf	62
2	A	AgOTf	23
3	B	AgOTf	28
4	C	AgOTf	44
5	D	AgOTf	46
6	none	AgOTf	n. r.
7	E	none	13

^a Determined by ¹H NMR analysis using 4,4'-di-*tert*-butyl-1,1'-biphenyl as an internal standard

3.3 The Effect of AgOTf on Catalytic Activity by Hydroalkoxylation of **1**

Procedure: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst (0.0005mmol, 1 mol%), silver trifluoromethanesulfonate, additive, ClCH₂CH₂Cl (1 mL) and 4,4'-di-*tert*-butyl-1,1'-biphenyl (0.5 equiv.) used as an internal standard. The mixture was stirred for 1 h and **1** (13.9 mg, 0.05 mmol, 1.0 equiv.) was added to the above solution. Then the vial was taken outside of the glovebox and the mixture was stirred at room temperature (23 °C) for 24 h. The reaction mixture was diluted with CH₂Cl₂, filtered through a pad of celite and concentrated. The yield of **1a** was determined by crude ¹H NMR analysis.

Supplementary Table 3: The Effect of AgOTf on Catalytic Activity



Entry	Catalyst	AgOTf (mol%)	Additive (mol%)	Yield (%) ^a	Entry	Catalyst	AgOTf (mol%)	Additive (mol%)	Yield (%) ^a
1	C (1 mol%)	1	--	16	6	C (1 mol%)	100	--	25
2	C (1 mol%)	2	--	46	7	D (1 mol%)	2	--	49
3	C (1 mol%)	5	--	56	8	D (1 mol%)	2	KOTf(10 mol%)	13
4	C (1 mol%)	10	--	64	9	D (1 mol%)	2	KOTf(30 mol%)	7
5	C (1 mol%)	50	--	46	10	D (1 mol%)	2	KOTf(50 mol%)	4

^a Determined by ¹H NMR analysis using 4,4'-di-*tert*-butyl-1,1'-biphenyl as an internal standard.

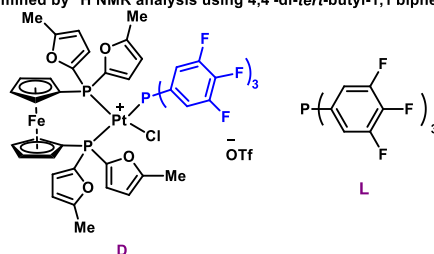
3.4 The Effect of Monodentate Phosphine Ligand on the Catalytic Activity

Procedure: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst **D** (0.0005 mmol, 1 mol%), silver trifluoromethanesulfonate (0.004 mmol, 2 mol%), L, $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1 mL) and 4,4'-di-*tert*-butyl-1,1'-biphenyl (0.5 equiv.) used as an internal standard. The mixture was stirred for 1 h and **1** (13.9 mg, 0.05 mmol, 1.0 equiv.) was added to the above solution. Then the vial was taken outside of the glovebox and the mixture was stirred at 23 °C for 24 h. The reaction mixture was diluted with CH_2Cl_2 , filtered through a pad of celite and concentrated. The yield of **1a** was determined by crude ¹H NMR analysis.

Supplementary Table 4: The Effect of Monodentate Phosphine Ligand on the Catalytic Activity

Entry	Catalyst	AgOTf (mol%)	L (mol%)	Yield (%) ^a
1	D (1 mol%)	2	--	49
2	D (1 mol%)	2	1	4
3	D (1 mol%)	2	2	0

^a Determined by ¹H NMR analysis using 4,4'-di-*tert*-butyl-1,1'-biphenyl as an internal standard.



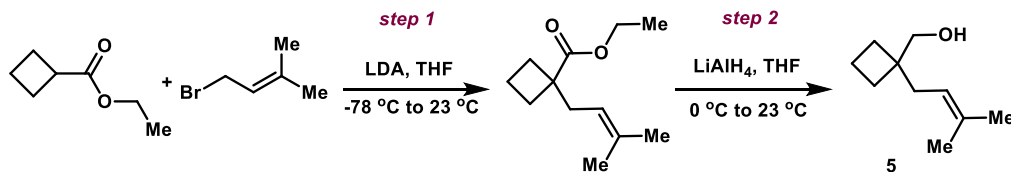
4. Synthesis of Substrates

4.1 Synthesis of Alcohols

Alcohols 2-(cyclohex-2-en-1-yl)-2,2-diphenylethan-1-ol(**1**), 5-methyl-2,2-diphenylhex-4-en-1-ol(**3**), 2,2-bis(2-methylallyl)propane-1,3-diol(**11**), 5-methyl-2,2-diphenylhex-5-en-1-ol(**14**), 2,2-diphenylpent-4-en-1-ol(**21**) were prepared according to a literature procedure reported by Widenhoefer and coworkers².

Alcohols (1-(3-methylbut-2-en-1-yl)cyclohexyl)methanol(**4**)³, 4-methyl-2-phenylpent-4-en-1-ol(**9**)²⁷, 4-methyl-1-phenylpent-4-en-1-ol(**10**)⁵, 2-(2-methylallyl)phenol(**13**)⁶, (1-(2-methylallyl)cyclohexyl)methanol(**15**)²⁸, 2,2,4-triphenylpent-4-en-1-ol(**16**)²⁹, (4-methylenecyclohexyl)methanol(**17**)⁹, 2-cinnamylphenol(**18**)¹⁰, (E)-2,2,5-triphenylpent-4-en-1-ol(**19**)¹¹, (1-allylcyclohexyl)methanol(**22**)⁴ were prepared according to literature procedures.

(1-(3-Methylbut-2-en-1-yl)cyclobutyl)methanol (**5**)



Step 1: A solution of ethyl cyclobutanecarboxylate (1.3 g, 10.0 mmol) in THF (5 mL) was added slowly to a solution of LDA [generated from diisopropylamine (1.2 g, 12.0 mmol) and *n*-BuLi (4.0 mL, 2.5 M in hexanes, 10.0 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$] over 30 min and the resulting solution was stirred for additional 15 minutes. 1-Bromo-3-methylbut-2-ene (1.8 g, 12.0 mmol) was added over 10 minutes and the resulting mixture was warmed to room temperature ($23\text{ }^{\circ}\text{C}$), stirred overnight, quenched with HCl (3 N, 10 mL), and extracted with ether ($4 \times 20\text{ mL}$). The combined ether extracts were washed with water

(20 mL), dried over anhydrous Na₂SO₄ and concentrated under vacuum. Column chromatography of the residue (hexane/ethyl acetate = 40:1) gave ethyl 1-(3-methylbut-2-en-1-yl)-cyclobutane-1-carboxylate (1.4 g, 71%) as a viscous colorless oil.

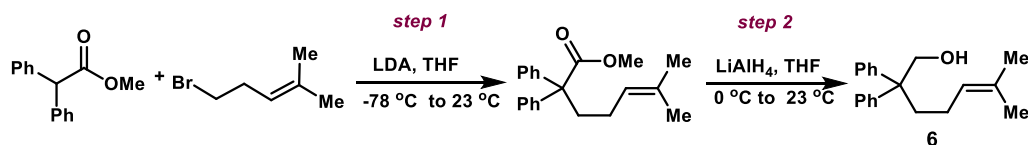
Step 2: A solution of ethyl 1-(3-methylbut-2-en-1-yl)-cyclobutane-1-carboxylate (1.4 g, 7.0 mmol) in THF (15 mL) was added slowly to a suspension of LiAlH₄ (532 mg, 14.0 mmol) in THF (10 mL) at 0 °C. The resulting mixture was stirred at room temperature (23 °C) overnight, quenched by sequential addition of water (0.5 mL) and aqueous NaOH (15%, 0.5 mL) and additional water (1.5 mL) at 0 °C. The resulting suspension was filtered through celite and eluted with ether. The ether eluant was dried over anhydrous Na₂SO₄ and concentrated under vacuum. Chromatography of the residue (hexane/ethyl acetate = 20:1) gave 2,2-diphenyl-4-penten-1-ol **5** (864 mg, 80%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.15 (tt, *J* = 7.4, 1.3 Hz, 1H), 3.50 (s, 2H), 2.18 (d, *J* = 7.4 Hz, 2H), 1.90 – 1.73 (m, 6H), 1.71 (s, 3H), 1.64 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 133.6, 120.6, 69.0, 43.5, 35.4, 28.0, 26.1, 18.1, 15.4 ppm

HRMS (ESI⁺): calc'd for C₁₀H₁₉O [M+H]⁺: 155.1430, found 155.1430.

6-Methyl-2,2-diphenylhept-5-en-1-ol (**6**)



Step 1: A solution of ethyl 2,2-diphenylacetate (2.3 g, 10.0 mmol) in THF (5 mL) was added slowly to a solution of LDA [generated from diisopropylamine (1.5 g, 15.0 mmol) and *n*-BuLi (4.8 mL, 2.5 M in hexanes, 12.0 mmol) in THF (10 mL) at –78 °C] over 30 min and the resulting solution was stirred for additional 15 min. 5-Bromo-2-methyl-2-pentene (2.0 g, 12.0 mmol) was added over 10 min and the resulting mixture was warmed to room temperature (23 °C), stirred overnight, quenched with HCl (3 N, 10 mL), and extracted with ether (4 × 20 mL). The combined ether extracts were washed with water (20 mL), dried over anhydrous Na₂SO₄, and concentrated under vacuum. Column chromatography of the residue (hexane/ethyl acetate = 40:1) gave ethyl 6-methyl-2,2-diphenylhept-5-enoate (1.8 g, 59%) as a viscous colorless oil.

Step 2: A solution of ethyl 6-methyl-2,2-diphenylhept-5-enoate (1.8 g, 5.8 mmol) in THF (15 mL) was added slowly to a suspension of LiAlH₄ (440 mg, 11.6 mmol) in THF (10 mL) at 0 °C. The resulting mixture was stirred at room temperature (23 °C) overnight, quenched by sequential addition of water (0.5 mL) and aqueous NaOH (15%, 0.5 mL) and additional water (1.5 mL) at 0 °C. The resulting suspension was filtered through celite and eluted with ether. The ether eluant was dried over anhydrous Na₂SO₄, and

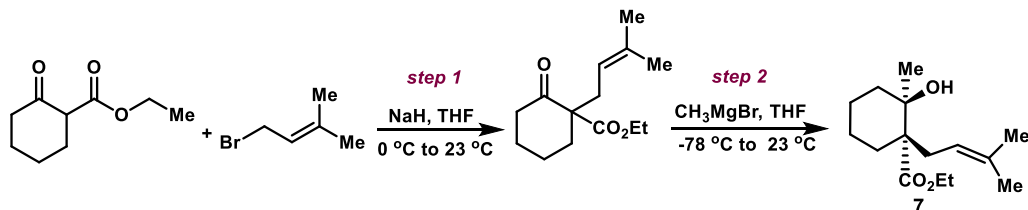
concentrated under vacuum. Chromatography of the residue (hexane/ethyl acetate = 20:1) gave 6-methyl-2,2-diphenylhept-5-en-1-ol **6** (1.2 g, 73%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.32 – 7.29 (m, 4H), 7.24 – 7.19 (m, 6H), 5.10 (tt, *J* = 7.1, 1.2 Hz, 1H), 4.18 (d, *J* = 6.9 Hz, 2H), 2.19 – 2.15 (m, 2H), 1.72 (q, *J* = 7.6 Hz, 2H), 1.65 (s, 3H), 1.44 (s, 3H), 1.12 (t, *J* = 6.9 Hz, 1H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 145.7, 131.9, 128.4, 128.3, 126.4, 124.4, 68.2, 52.2, 36.6, 25.8, 23.1, 17.6 ppm

HRMS (ESI⁺): calc'd for C₂₀H₂₅O [M+H]⁺: 281.1900, found 281.1901.

Ethyl -2-hydroxy-2-methyl-1-(3-methylbut-2-en-1-yl)cyclohexane-1-carboxylate (7**)**



Step 1: To a suspension of NaH (880 mg, 22.0 mmol) in THF (30 mL) at 0 °C under argon was added dropwise a solution of ethyl 2-oxocyclohexane-1-carboxylate (3.4 g, 20.0 mmol) in THF (20 mL). After stirring 30 min, a solution of 1-bromo-3-methylbut-2-ene (3.3 g, 22.0 mmol) in THF (10 mL) was added. The resulting mixture was warmed to room temperature (23 °C) and stirred overnight. The mixture was quenched with aqueous NH₄Cl (50 mL) and extracted with ether (2 x 60 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under vacuum. The product was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield 1.9 g of compound ethyl 1-(3-methylbut-2-en-1-yl)-2-oxocyclohexane-1-carboxylate (40% yield) as a colorless oil.

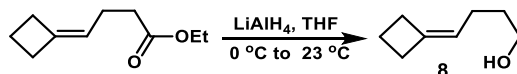
Step 2: To a suspension of ethyl 1-(3-methylbut-2-en-1-yl)-2-oxocyclohexane-1-carboxylate (263 mg, 1.1 mmol) in THF (5 mL) at -78 °C under argon was added dropwise a solution of CH₃MgBr in THF (1.2 mL, 1M, 1.2 mmol). The resulting mixture was warmed to room temperature (23 °C) and stirred for 2 h. The reaction was quenched with aqueous NH₄Cl (50 mL) and extracted with ether (2 x 60 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under vacuum. The product was purified by column chromatography (hexane/ethyl acetate = 20:1) yield 203 mg of compound ethyl -2-hydroxy-2-methyl-1-(3-methylbut-2-en-1-yl)cyclohexane-1-carboxylate **7** (73% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 4.90 – 4.85 (m, 1H), 4.22 – 4.07 (m, 2H), 3.47 (bs, 1H), 2.75 (dd, *J* = 14.8, 7.1 Hz, 1H), 2.39 (dd, *J* = 14.8, 7.7 Hz, 1H), 1.83 – 1.50 (m, 12H), 1.34 – 1.19 (m, 8H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 177.3, 134.4, 119.5, 72.8, 60.7, 54.2, 34.8, 27.8, 27.0, 26.1, 25.4, 22.8, 20.8, 18.1, 14.4 ppm

HRMS (ESI⁺): calc'd for C₁₅H₂₇O₃ [M+H]⁺: 255.1955, found 255.1953.

4-Cyclobutylidenebutan-1-ol (**8**)



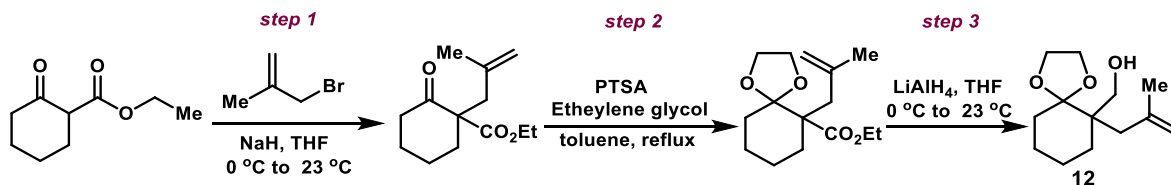
Ethyl 4-cyclobutylidenebutanoate was prepared according to a literature procedure reported by Shenvi and coworkers.¹⁶ A solution of ethyl 4-cyclobutylidenebutanoate (2.0 mmol, 336 mg) in anhydrous THF (5 mL) was added dropwise to a suspension of LiAlH₄ (4.0 mmol, 152 mg) in anhydrous THF (5 mL) at 0 °C. The resulting mixture was warmed to room temperature (23 °C) and stirred for 2 h, the reaction mixture was cooled to 0 °C, diluted with Et₂O (10 mL), quenched by the sequential addition of water (0.15 mL), a 15% aqueous NaOH solution (0.15 mL) and additional water (0.45 mL). The resulting white precipitate was filtered through a pad of celite and washed with Et₂O. The filtrate was dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. Purification by flash chromatography (hexane/ethyl acetate = 20:1) yielded 4-Cyclobutylidenebutan-1-ol **8** (215 mg, 85 %) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 5.08 – 5.02 (m, 1H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.64 – 2.60 (m, 4H), 1.97 – 1.88 (m, 4H), 1.62 – 1.55 (m, 2H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 140.8, 119.7, 62.8, 32.7, 31.0, 29.3, 24.5, 17.1 ppm

HRMS (ESI⁺): calc'd for C₈H₁₅O [M+H]⁺: 127.1117, found 127.118.

2-(Hydroxymethyl)-2-(2-methylallyl)cyclohexan-1-one (**12**)



Step 1: To a suspension of NaH (230 mg, 9.6 mmol) in THF (15 mL) at 0 °C under argon was added dropwise a solution of ethyl 2-oxocyclohexanecarboxylate (1.4 g, 8.0 mmol) in THF (10 mL). After 30 min, a solution of 3-Bromo-2-methylpropene (1.3 g, 9.6 mmol) in THF (5 mL) was added. The resulting mixture was warmed to room temperature (23 °C) and stirred overnight. The reaction was quenched with aqueous NH₄Cl (25 mL) and extracted with ether (2 x 50 mL). The combined organic layers were dried with anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The product was purified by column chromatography (hexane/ethyl acetate = 20:1) to yield 724 mg of compound ethyl 1-(2-methylallyl)-2-oxocyclohexanecarboxylate (40% yield) as a colorless oil.

Step 2: According to a procedure by Brimble and coworkers.⁷ A mixture of ethyl 1-(2-methylallyl)-2-oxocyclohexanecarboxylate (519 mg, 2.3 mmol), ethylene glycol (2 mL, 35.0 mmol), and *p*-toluenesulfonic acid monohydrate (7.9 mg, 2 mol%) in dry benzene (15 mL) was refluxed under argon for 8 h with azeotropic removal of water. The reaction mixture was diluted with ethyl ether (20 mL), washed

with saturated aqueous NaHCO₃ and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo to afford a crude product as a colorless oil. The crude product was used in the next step without further purification.

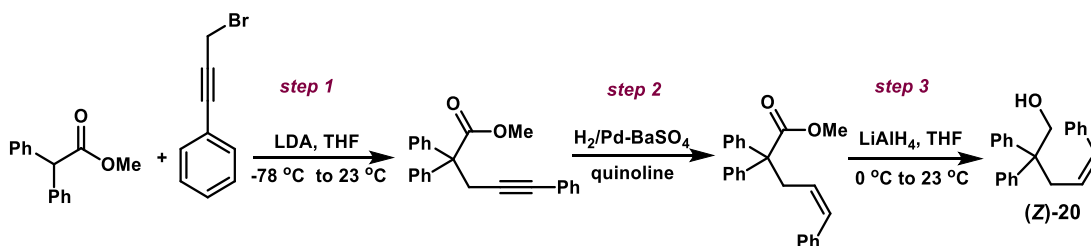
Step 3: A solution of ethyl 6-(2-methylallyl)-1,4-dioxaspiro[4.5]decane-6-carboxylate (1.8 mmol, 481 mg) in anhydrous THF (5 mL) was added dropwise to a suspension of LiAlH₄ (3.6 mmol, 137 mg) in anhydrous THF (5 mL) at 0 °C. The resulting mixture was warmed to room temperature (23 °C) and stirred for 2 h, the reaction mixture was cooled to 0 °C, diluted with Et₂O (10 mL), quenched by the sequential addition of water (0.14 mL), a 15 % aqueous NaOH solution (0.14 mL) and additional water (0.42 mL). The resulting white precipitate was filtered through a pad of celite and washed with Et₂O. The filtrate was dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. Purification by flash chromatography (hexane/ethyl acetate = 20:1) yielded 2-(hydroxymethyl)-2-(2-methylallyl)cyclohexan-1-one **12** (220 mg, 54 %) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 4.90 (s, 1H), 4.78 (s, 1H), 4.01 – 3.92 (m, 4H), 3.85 (d, *J* = 11.4 Hz, 1H), 3.42 (dd, *J* = 11.4, 8.4 Hz, 1H), 3.06 (dd, *J* = 8.4, 2.4 Hz, 1H), 2.41 (d, *J* = 13.1 Hz, 1H), 2.18 (d, *J* = 13.1 Hz, 1H), 1.81 (s, 3H), 1.69 – 1.38 (m, 8H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 142.6, 115.4, 113.8, 65.0, 64.8, 64.2, 45.3, 36.2, 30.5, 30.2, 25.7, 23.4, 20.6 ppm

HRMS (ESI⁺): calc'd for C₁₃H₂₃O₃ [M+H]⁺: 227.1642, found 227.1640.

(Z)-2,2,5-triphenylpent-4-en-1-ol [(Z)-20]



(3-bromoprop-1-yn-1-yl)benzene was synthesized from reported procedure and the analytical data was consistent with the literature.⁸

Step 1: A solution of methyl 2,2-diphenylacetate (2.3 g, 10.0 mmol) in THF (5 mL) was added slowly to a solution of LDA [generated from diisopropylamine (1.5 g, 15.0 mmol) and *n*-BuLi (4.8 mL, 2.5 M in hexanes, 12.0 mmol) in THF (10 mL) at –78 °C] over 30 min and the resulting solution was stirred for additional 15 min. (3-bromoprop-1-yn-1-yl)benzene (2.0 g, 10.0 mmol) was added over 10 min and the resulting mixture was warmed to room temperature (23 °C), stirred overnight, quenched with HCl (3 N, 10 mL), and extracted with ether (4 × 20 mL). The combined ether extracts were washed with water (20 mL), dried by anhydrous Na₂SO₄, and concentrated under vacuum. Column chromatography of the

residue (hexane/ethyl acetate = 40:1) gave methyl 2,2,5-triphenylpent-4-ynoate (3.2 g, 94%) as a yellow oil.

Step 2: To a stirred solution of methyl 2,2,5-triphenylpent-4-ynoate (681 mg, 2.0 mmol) in quinoline (2 mL) was added 5% Pd-BaSO₄ (424 mg, 0.2 mmol). The reaction mixture was stirred under H₂ balloon for 12 h at room temperature (23 °C). The resulting mixture was filtered through a celite pad and concentrated in vacuo. Methyl (Z)-2,2,5-triphenylpent-4-enoate (479 mg, 70 %) was obtained as a yellowish oil and used for next step without further purification.

Step 3: A solution of methyl (Z)-2,2,5-triphenylpent-4-enoate (213 g, 0.6 mmol) in THF (2 mL) was added slowly to a suspension of LiAlH₄ (45 mg, 1.2 mmol) in THF (2 mL) at 0 °C. The resulting mixture was stirred at room temperature (23 °C) overnight, quenched by sequential addition of water (0.05 mL) and aqueous NaOH (15%, 0.05 mL) and additional water (0.15 mL) at 0 °C. The resulting suspension was filtered through celite and eluted with ether. The ether eluant was dried by anhydrous Na₂SO₄ and concentrated under vacuum. Chromatography of the residue (hexane/ethyl acetate = 20:1) gave (Z)-2,2,5-triphenylpent-4-en-1-ol (**Z**)-**20** (131 mg, 70%) as a yellow oil.

¹H NMR (600 MHz, CDCl₃): δ 7.34 – 7.19 (m, 15H), 6.42 (d, J = 11.8 Hz, 1H), 5.43 (dt, J = 11.8, 6.9 Hz, 1H), 4.14 (d, J = 6.5 Hz, 2H), 3.24 (dd, J = 6.9, 2.0 Hz, 2H) 1.14 (t, J = 6.8 Hz, 1H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 145.1, 137.6, 131.3, 128.9, 128.5, 128.41, 128.4, 128.3, 126.9, 126.6, 68.8, 52.4, 35.4 ppm

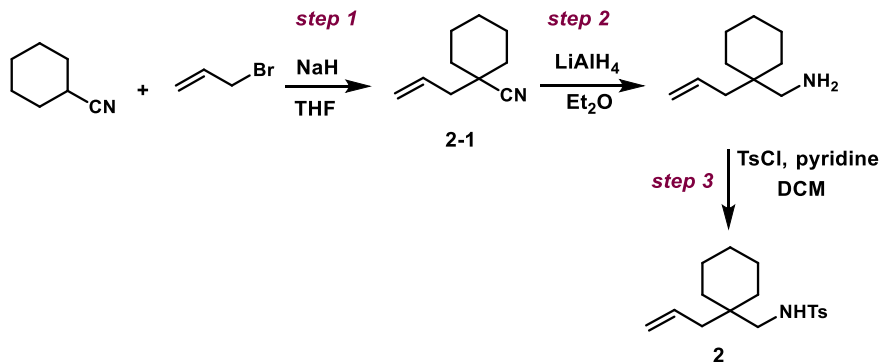
4.2 Synthesis of Alkenes

Norbornylene(**23**), Comphene(**24**), 1-methylcyclohex-1-ene(**43**) and 1-methylcyclopent-1-ene (**44**), styrene(**48**), (Z)-cyclooctene(**49**) were purchased from commercial sources.

Alkenes ethyl 4-cyclobutylidenebutanoate(**25**)¹⁶, 3,7-dimethyloct-6-en-1-yl benzoate(**26**)¹⁴, (5-methylhex-5-en-1-yl)benzene(**27**)¹⁵ were prepared according to literature procedures.

4.3 Synthesis of Amines

N-((1-allylcyclohexyl)methyl)-4-methylbenzenesulfonamide (**2**)



Step 1: The above alkene-substituted nitrile **2-1** was prepared by following a reported procedure.¹⁸ To a

freshly prepared LDA (from 21.0 mmol *n*-BuLi and 24.0 mmol diisopropyl amine at 0 °C for 30 min) in THF (40 mL) was added nitrile (20.0 mmol, 1.0 equiv.) dropwise at -78 °C. The resulting mixture was stirred at the same temperature for 30 min. Allyl bromide (28.0 mmol, 1.4 equiv.) was added to the reaction mixture dropwise before allowing the reaction mixture to warm up to 23 °C. After stirring overnight, the reaction mixture was quenched with water at 0 °C and extracted with EtOAc. The combined extracts were washed with brine, dried over MgSO₄, and concentrated. The crude product was used in the next step directly without further purification.

Step 2: The procedure analogous to that used to synthesize **31-2**

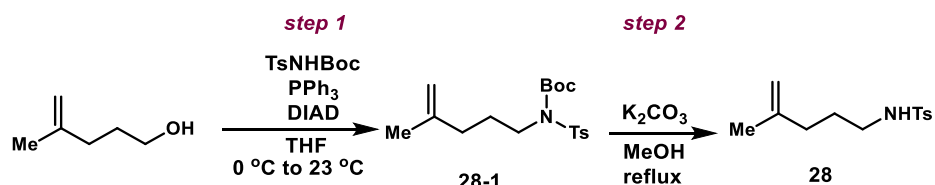
Step 3: The procedure analogous to that used to synthesize **29-1**.

¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.70 (ddt, *J* = 17.7, 10.2, 7.5 Hz, 1H), 5.07 – 4.94 (m, 2H), 4.90 (t, *J* = 6.8 Hz, 1H), 2.73 (d, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 2.04 (d, *J* = 7.5 Hz, 2H), 1.48 – 1.20 (m, 10H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 143.3, 137.1, 134.2, 129.7, 127.2, 117.9, 49.5, 40.4, 36.4, 33.3, 26.1, 21.6, 21.3 ppm

HRMS (ESI⁺): calculated for C₁₇H₂₆NO₂S[M+H]⁺: 308.1679, found 308.1680.

4-Methyl-N-(4-methylpent-4-en-1-yl)benzenesulfonamide (**28**)



Step 1: The above compounds 4-methyl-N-(4-methylpent-4-en-1-yl)benzenesulfonamide was prepared by following a reported procedure.¹² A mixture of Ts-NH-Boc (1.63 g, 6.0 mmol, 1.2 equiv.), PPh₃ (1.70 g, 6.5 mmol, 1.3 equiv) and alcohol (4.52 g, 5 mmol, 1.0 equiv.) in THF (25 mL) was cooled to 0 °C and DIAD (1.28 mL, 6.5 mmol, 1.3 equiv.) was added dropwise. After stirring for 5 min at 0 °C, the mixture was allowed to warm up to 23 °C and stirred overnight. The solvent was removed and the residue was purified by flash column chromatography on silica gel (hexanes/EtOAc 20:1–10:1) to give **28-1** as white solid (1.59 g, 90%).

¹H NMR (600 MHz, CDCl₃): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.74 (d, *J* = 6.7 Hz, 2H), 3.87 – 3.67 (m, 2H), 2.43 (s, 3H), 2.08 (t, *J* = 7.5 Hz, 2H), 1.97 – 1.81 (m, 2H), 1.75 (s, 3H), 1.33 (s, 9H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 151.1, 144.7, 144.2, 137.7, 129.4, 127.9, 110.6, 84.2, 47.1, 35.0, 28.0, 22.5, 21.7 ppm

HRMS (ESI⁺): calculated for C₁₈H₂₇NO₄SNa[M+Na]⁺: 376.1553, found 376.1555.

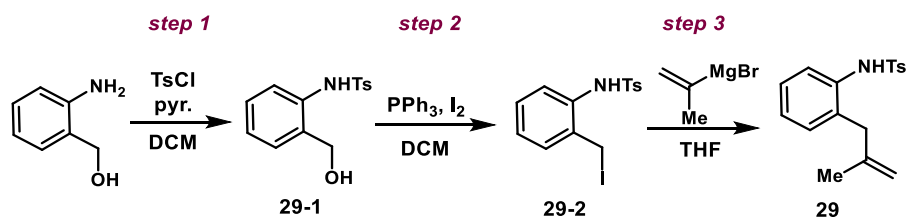
Step 2: To a solution of **28-1** (1.41 g, 4.0 mmol, 1.0 equiv.) in methanol (20 mL) was added K₂CO₃ (2.76 g, 20.0 mmol, 5.0 equiv.). After refluxing for 5 h, water (50 mL) was introduced and the aqueous layer was extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated to give **28** (0.99 g, 98%) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.69 (s, 1H), 4.61 (s, 1H), 4.52 – 4.42 (m, 1H), 3.00 – 2.90 (m, 2H), 2.43 (s, 3H), 1.99 (t, *J* = 7.5 Hz, 2H), 1.65 (s, 3H), 1.64 – 1.56 (m, 3H) ppm

¹³C NMR (151 MHz, CDCl₃) δ 144.6, 143.5, 137.2, 129.8, 127.2, 110.9, 43.0, 34.8, 27.6, 22.3, 21.7 ppm

HRMS (ESI⁺): calculated for C₁₃H₂₀NO₂S[M+H]⁺: 254.1209, found 254.1210.

4-Methyl-*N*-(2-(2-methylallyl)phenyl)benzenesulfonamide (**29**)



Step 1: The above compounds **29-1** was prepared by following reported procedures.¹³ To a solution of anilines (15.0 mmol, 1.0 equiv.) in anhydrous DCM (30 mL) was added *p*-toluenesulfonyl chloride (16.5 mmol, 1.1 equiv.) and pyridine (45.0 mmol, 3.0 equiv.). Then the mixture was stirred at 23 °C overnight. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with 40 mL H₂O and extracted with Et₂O (3 × 50 mL). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash chromatography (hexanes/EtOAc = 30:1-10:1) to afford the desired sulfonamide.

Step 2: To a solution of triphenylphosphine (10.3 mmol, 1.03 equiv.) in dry dichloromethane (30 mL) was added iodine (10.3 mmol, 1.03 equiv.). After stirring for 5 min, alcohol (10 mmol, 1.0 equiv.) was added to the above mixture. After complete conversion of the alcohol (monitored by TLC), the reaction was quenched with an aqueous solution of sodium thiosulfate (20 mL). The organic layers were removed and the aqueous solution extracted with EtOAc (50 mL). The combined organic layers were dried using sodium sulfate, filtered and concentrated. The residue was purified by column chromatography (hexanes/EtOAc = 10:1) to get the desired iodide product.

Step 3: To a solution of *N*-(2-(iodomethyl)phenyl)-4-methylbenzenesulfonamide (2.0 mmol, 1.0 equiv.) in anhydrous THF (10.0 mL) at 0 °C was added prop-1-en-2-ylmagnesium bromide (6.0 mmol, 3.0 equiv.) dropwise. Then the reaction mixture was allowed to warm up to 23 °C and stirred for 12 h. After completion of the reaction (monitored by TLC), the reaction was quenched with saturated NH₄Cl aqueous solution and diluted with 40 mL H₂O and extracted with EtOAc (3 × 50 mL). The combined organic layers

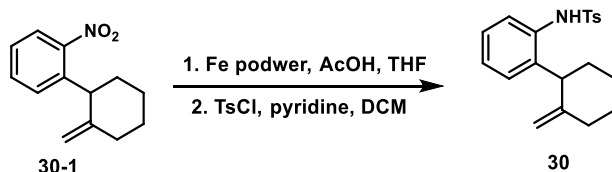
were washed with brine, dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash chromatography (hexanes/EtOAc = 30:1-10:1) to afford the desired sulfonamide at high yield.

^1H NMR (400 MHz, CDCl_3): δ 7.66 – 7.54 (m, 2H), 7.46 (dd, J = 8.0, 0.9 Hz, 1H), 7.20 (dd, J = 9.6, 4.8 Hz, 3H), 7.09 (td, J = 7.4, 1.2 Hz, 1H), 7.03 (dd, J = 7.5, 1.4 Hz, 1H), 6.72 (s, 1H), 4.88 (s, 1H), 4.61 (s, 1H), 2.92 (s, 2H), 2.38 (s, 3H), 1.57 (s, 3H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 143.9, 143.7, 137.0, 135.6, 131.4, 131.1, 129.7, 127.9, 127.2, 126.1, 124.2, 113.0, 77.5, 77.2, 76.8, 41.0, 22.2, 21.7 ppm

HRMS (ESI $^+$): calculated for $\text{C}_{17}\text{H}_{20}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 301.1209, found 302.1212.

4-Methyl-*N*-(2-(2-methylenecyclohexyl)phenyl)benzenesulfonamide (30)



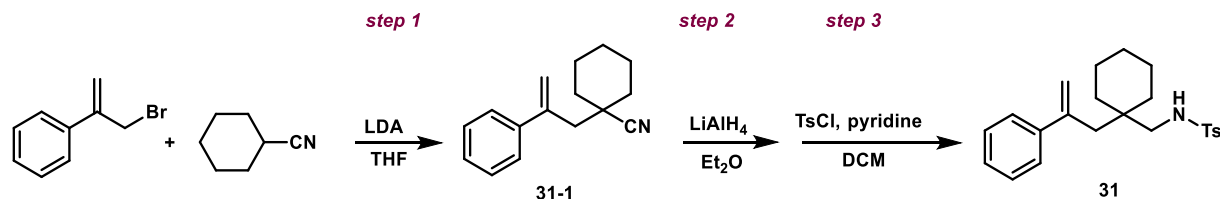
The compound **30a-1** was prepared by following reported procedures.¹⁷ The spectroscopic data was in accordance with those reported in literature. And the procedure of sulfonation of amines was the same with the procedure of synthesis of **29-1**.

^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, J = 8.3 Hz, 2H), 7.48 (dd, J = 7.7, 1.6 Hz, 1H), 7.28 – 7.15 (m, 4H), 7.09 (dd, J = 7.5, 1.7 Hz, 1H), 6.34 (s, 1H), 4.63 (d, J = 1.4 Hz, 1H), 3.86 (d, J = 1.3 Hz, 1H), 2.50 (dd, J = 12.0, 3.2 Hz, 1H), 2.39 (s, 4H), 2.00 (td, J = 13.1, 4.0 Hz, 1H), 1.90 – 1.75 (m, 2H), 1.58 (qd, J = 12.3, 3.4 Hz, 1H), 1.52 – 1.42 (m, 1H), 1.31 (qt, J = 13.1, 3.8 Hz, 1H), 1.21 – 1.10 (m, 1H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 151.2, 144.0, 137.3, 137.0, 134.7, 129.9, 127.7, 127.6, 127.3, 127.0, 126.3, 108.6, 44.7, 36.9, 33.0, 28.6, 26.8, 21.8 ppm

HRMS (ESI $^+$): calculated for $\text{C}_{20}\text{H}_{24}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 342.1522, found 342.1525.

4-methyl-*N*-((1-(2-phenylallyl)cyclohexyl)methyl)benzenesulfonamide (31)



Step 1: Compound **31-1** was prepared following a reported procedure.¹⁸ To a freshly prepared LDA (from 21.0 mmol *n*-BuLi and 24.0 mmol diisopropyl amine at 0 °C for 30 min) in THF (40 mL) was added nitrile (20.0 mmol, 1.0 equiv.) dropwise at -78 °C. The resulting mixture was stirred at the same temperature for 30 min. Allyl bromide (28.0 mmol, 1.4 equiv.) was added to the reaction mixture dropwise before allowing the reaction mixture to warm up to 23 °C. After stirring for 12 h, the reaction mixture was quenched with

water at 0 °C and extracted with EtOAc. The combined extracts were washed with brine, dried over MgSO₄, and concentrated. The crude product was used in the next step directly without further purification.

Step 2: To a suspension of LiAlH₄ (36 mmol, 2.0 equiv.) in anhydrous Et₂O (30 mL) was added alkene-substituted acetonitrile (18 mmol, 1.0 equiv.) in anhydrous Et₂O (10 mL) dropwise at 0 °C. Then the reaction mixture was allowed to warm to 23 °C slowly and stirred for 16 h. After completion of the reaction (monitored by TLC), the reaction was quenched by the sequential addition of H₂O (1.5 mL), 15 % NaOH aqueous solution (3.0 mL), and H₂O (1.5 mL) and stirred for another 30 min. The resulting white precipitate was filtered through a pad of celite and washed with Et₂O. The filtrate was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used in the next step directly without further purification.

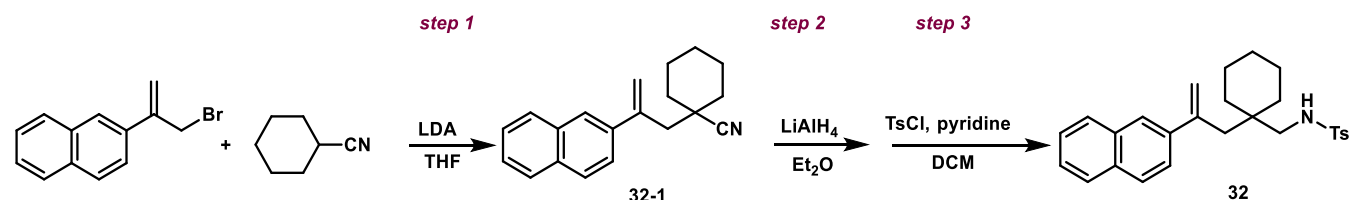
Step 3: The above compound was prepared by following a reported procedure.¹³ To a solution of amines (15.0 mmol, 1.0 equiv.) in anhydrous DCM (30 mL) was added *p*-toluenesulfonyl chloride (16.5 mmol, 1.1 equiv.) and pyridine (45.0 mmol, 3.0 equiv.). Then the mixture was stirred at 23 °C overnight. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with 40 mL H₂O and extracted with Et₂O (3 × 50 mL). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash chromatography (hexanes:EtOAc = 30:1-10:1) to afford the desired sulfonamide at high yield.

¹H NMR (600 MHz, CDCl₃): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 5.5 Hz, 5H), 7.22 (d, *J* = 7.6 Hz, 2H), 5.17 (s, 1H), 5.03 (s, 1H), 3.95 (t, *J* = 7.0 Hz, 1H), 2.55 – 2.45 (m, 4H), 2.41 (s, 3H), 1.50 – 1.22 (m, 10H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 146.0, 143.8, 143.1, 136.9, 129.6, 128.9, 127.7, 127.0, 126.5, 118.0, 48.7, 37.6, 26.1, 21.7, 21.5 ppm

HRMS (ESI⁺): calculated for C₂₃H₂₉NO₂S[M+H]⁺: 384.1992, found 384.1995.

4-Methyl-N-((1-(2-(naphthalen-2-yl)allyl)cyclohexyl)methyl)benzenesulfonamide (32)



The procedure analogous to that used to synthesize **31**.

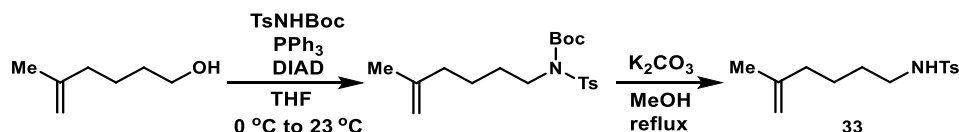
¹H NMR (400 MHz, CDCl₃): δ 7.86 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.79 (dd, *J* = 9.5, 6.1 Hz, 2H), 7.69 (d, *J* = 1.1 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.0

Hz, 2H), 5.31 (d, $J = 1.7$ Hz, 1H), 5.13 (d, $J = 1.4$ Hz, 1H), 3.91 (t, $J = 7.3$ Hz, 1H), 2.59 (s, 2H), 2.47 (d, $J = 7.4$ Hz, 2H), 2.30 (s, 3H), 1.47 – 1.26 (m, 10H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 145.8, 142.8, 141.1, 136.5, 133.6, 132.9, 129.4, 128.6, 128.2, 127.8, 126.7, 126.5, 126.3, 124.9, 124.7, 118.7, 48.7, 42.2, 37.6, 33.9, 26.1, 21.5 ppm

HRMS (ESI⁺): calculated for $\text{C}_{27}\text{H}_{32}\text{NO}_2\text{S}[\text{M}+\text{H}]^+$: 434.2148, found 434.2152.

4-Methyl-N-(5-methylhex-5-en-1-yl)benzenesulfonamide (33)



The procedure analogous to that used to synthesize **29**.

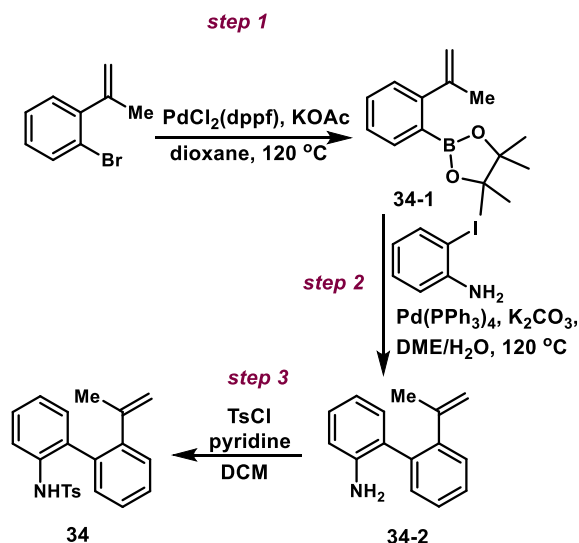
Compound **33** (1.02g, 95%) was obtained as a brown oil.

^1H NMR (600 MHz, CDCl_3): δ 7.75 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 4.67 (s, 1H), 4.59 (s, 1H), 4.54 (t, $J = 5.8$ Hz, 1H), 2.94 (q, $J = 6.6$ Hz, 2H), 2.43 (s, 3H), 1.94 (t, $J = 7.3$ Hz, 2H), 1.65 (s, 3H), 1.50 – 1.42 (m, 2H), 1.42 – 1.32 (m, 2H) ppm

^{13}C NMR (151 MHz, CDCl_3): δ 145.3, 143.5, 137.1, 129.8, 127.2, 110.3, 43.2, 37.2, 29.2, 24.5, 22.3, 21.6 ppm

HRMS (ESI⁺): calculated for $\text{C}_{14}\text{H}_{22}\text{NO}_2\text{S} [\text{M}+\text{H}]^+$: 268.1366, found 268.1367.

4-Methyl-N-(2'-(prop-1-en-2-yl)-[1,1'-biphenyl]-2-yl)benzenesulfonamide (34)



Step 1: The above compound **34-1** was prepared by following reported procedures.²³ To a mixture of 1-bromo-2-(prop-1-en-2-yl)benzene (12.0 mmol, 1 equiv.), bis(pinacolato)diboron (13.2 mmol, 1.1 equiv.), KOAc (24.0 mmol, 2 equiv.) in H_2O (3mL) and 1,4-dioxane (35 mL) under argon was added $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.6 mmol, 0.05 equiv.) and the suspension was degassed for 2 min while stirring vigorously. And the mixture was stirred at 120 °C for 18 h under reflux. After completion of the reaction (monitored by TLC),

the reaction mixture was diluted with 20 mL H₂O and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash chromatography (hexanes:EtOAc = 30:1-10:1) to afford the desired product.

Step 2: To a solution of 2-iodoaniline (5 mmol, 1.0 equiv.) and 4,4,5,5-tetramethyl-2-(2-(prop-1-en-2-yl)phenyl)-1,3,2-dioxaborolane (5 mmol, 1.0 equiv.) in DME (25 mL) and distilled water (25 mL) under argon was added Pd(PPh₃)₄ (0.25 mmol, 0.05 equiv.) and K₂CO₃ (20 mmol, 4 equiv.). And then the mixture was warmed to reflux under 120 °C for 16 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with 20 mL H₂O and extracted with EtOAc (3 × 30 mL). The combined organic layers were dried using sodium sulfate, filtered and concentrated. The residue was purified by column chromatography (hexanes:EtOAc = 10:1) to get the desired product.

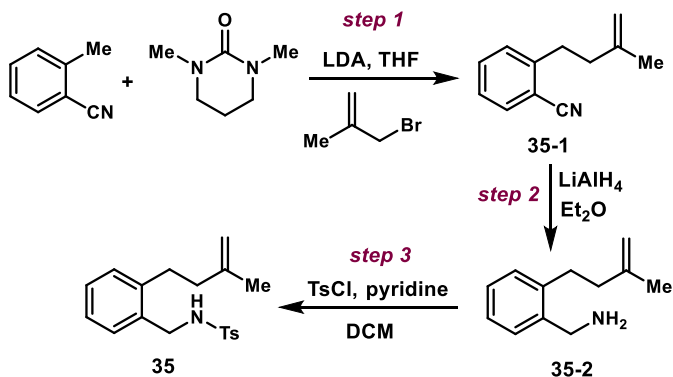
Step 3: The procedure analogous to that used to synthesize **29-1**.

¹H NMR (600 MHz, CDCl₃): δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.32 (q, *J* = 7.8 Hz, 3H), 7.20 – 7.09 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 6.44 (d, *J* = 7.5 Hz, 1H), 5.03 (s, 1H), 4.93 (s, 1H), 2.39 (s, 3H), 1.57 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 146.0, 144.0, 143.7, 136.7, 134.8, 134.2, 134.0, 130.9, 130.8, 129.9, 129.4, 128.9, 128.8, 127.8, 127.5, 125.1, 121.7, 117.4, 23.5, 21.9 ppm

HRMS (ESI⁺): calculated for C₂₂H₂₂NO₂S[M+H]⁺: 364.1366, found 364.1368.

4-Methyl-N-(2-(3-methylbut-3-en-1-yl)benzyl)benzenesulfonamide (**35**)



Step 1: The above nitrile intermediate **35-1** was prepared following reported procedures. The spectroscopic data was in accordance with those reported in literature.²³

Step 2: The procedure analogous to that used to synthesize **31-2**.

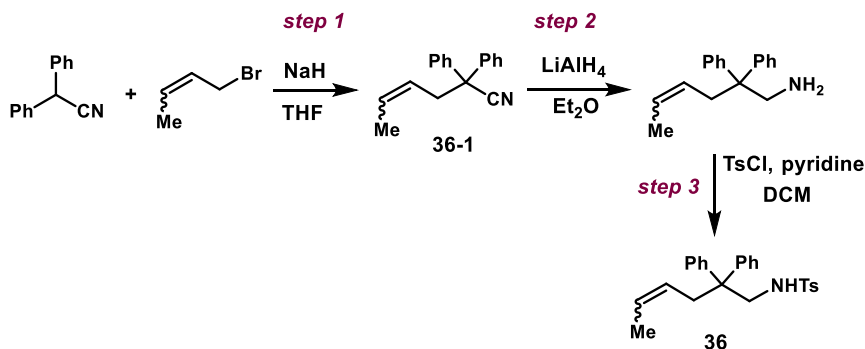
Step 3: The procedure analogous to that used to synthesize **29-1**.

¹H NMR (400 MHz, CDCl₃): δ 7.82 – 7.73 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.08 (m, 3H), 4.73 (s, 1H), 4.63 (d, *J* = 0.9 Hz, 1H), 4.41 (s, 1H), 4.11 (d, *J* = 5.9 Hz, 2H), 2.72 – 2.62 (m, 2H), 2.44 (s, 3H), 2.24 – 2.11 (m, 2H), 1.72 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 145.1, 143.8, 141.0, 136.6, 133.5, 130.0, 129.7, 129.6, 128.6, 127.4, 126.6, 110.7, 45.0, 39.4, 30.8, 22.7, 21.7 ppm

HRMS (ESI⁺): calculated for C₁₉H₂₄NO₂S[M+H]⁺: 330.1522, found 330.1524.

***N*-(2,2-diphenylhex-4-en-1-yl)-4-methylbenzenesulfonamide (36)**



Step 1: The above alkene-substituted nitrile **36-1** was prepared by following a reported procedure.¹² To a suspension of NaH (26 mmol, 1.3 equiv.) in anhydrous THF (20 mL) was added nitrile (20 mmol, 1.0 equiv.) in anhydrous THF (10 mL) dropwise at 0 °C. The reaction mixture was allowed to stir for 1 h at 0 °C and then allyl bromide (26 mmol, 1.3 equiv.) was slowly added. The reaction mixture was warmed to 23 °C and allowed to stir at that temperature (monitored by TLC). After completion of the reaction, the reaction mixture was extracted with EtOAc (3 × 50 mL) and the combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was used in the next step directly without further purification.

Step 2: The procedure analogous to that used to synthesize **31-2**.

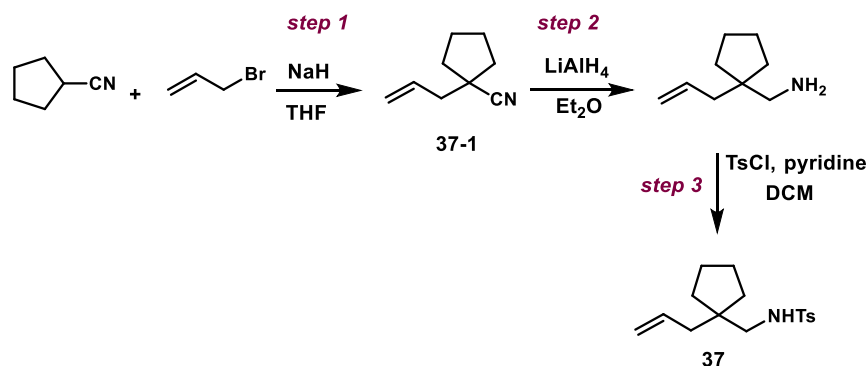
Step 3: The procedure analogous to that used to synthesize **29-1**.

¹H NMR (400 MHz, CDCl₃): δ 7.58 (t, *J* = 10.0 Hz, 2H), 7.32 – 7.14 (m, 8H), 7.10 – 6.97 (m, 4H), 5.53 – 5.18 (m, 1H), 5.09 – 4.73 (m, 1H), 3.92 – 3.69 (m, 1H), 3.50 (d, *J* = 6.4 Hz, 2H), 2.84 (dd, *J* = 36.4, 7.1 Hz, 2H), 2.50 – 2.36 (m, 3H), 1.45 (ddd, *J* = 8.3, 6.6, 1.3 Hz, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 144.9, 143.5, 136.3, 129.8, 129.8, 128.5, 127.9, 127.3, 126.7, 125.3, 49.6, 49.2, 40.1, 21.7, 18.2 ppm

HRMS (ESI⁺): calculated for C₂₅H₂₈NO₂S[M+H]⁺: 406.1835, found 406.1838.

***N*-((1-allylcyclohexyl)methyl)-4-methylbenzenesulfonamide (37)**



The procedure analogous to that used to synthesize **2-1**.

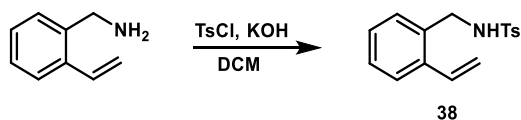
¹H NMR (600 MHz, CDCl₃): δ 7.73 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.69 (ddt, J = 17.3, 10.0, 7.4 Hz, 1H), 5.05 – 4.94 (m, 2H), 4.76 (t, J = 6.6 Hz, 1H), 2.73 (d, J = 6.7 Hz, 2H), 2.42 (s, 3H), 2.06 (d, J = 7.4 Hz, 2H), 1.63 – 1.50 (m, 4H), 1.43 – 1.30 (m, 4H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 143.4, 137.0, 135.1, 129.8, 127.2, 117.8, 50.2, 45.7, 42.1, 35.3, 24.8, 21.6 ppm

HRMS (ESI⁺): calculated for C₁₆H₂₄NO₂S[M+H]⁺: 294.1520, found 294.1522.

The analytical data was consistent with the literature.²⁶

4-Methyl-*N*-(2-vinylbenzyl)benzenesulfonamide (**38**)



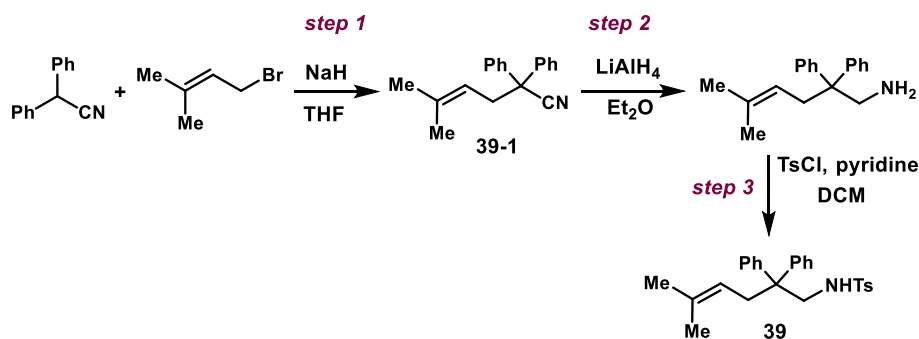
The procedure of literature about synthesis of substrate **38** was followed.²⁴

¹H NMR (600 MHz, CDCl₃): δ 7.75 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.17 (dd, J = 7.4, 1.0 Hz, 1H), 7.12 (d, J = 7.0 Hz, 1H), 6.77 (dd, J = 17.3, 10.9 Hz, 1H), 5.61 (dd, J = 17.3, 1.1 Hz, 1H), 5.28 (dd, J = 10.9, 1.1 Hz, 1H), 4.48 (s, 1H), 4.16 (d, J = 5.9 Hz, 2H), 2.44 (s, 3H), 1.58 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 143.7, 137.2, 136.7, 133.4, 132.8, 129.9, 129.6, 128.7, 128.2, 127.4, 126.4, 117.4, 77.4, 77.2, 77.0, 45.4, 21.7 ppm

HRMS (ESI⁺): calculated for C₁₆H₁₈NO₂S[M+H]⁺: 288.1054, found 288.1054.

4-Methyl-*N*-(5-methyl-2,2-diphenylhex-4-en-1-yl)benzenesulfonamide (**39**)



Step 1: The procedure analogous to that used to synthesize **36-1**.

Step 2: The procedure analogous to that used to synthesize **31-2**.

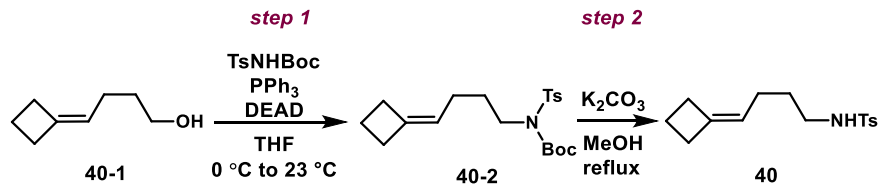
Step 3: The procedure analogous to that used to synthesize **29-1**.

^1H NMR (400 MHz, CDCl_3): δ 7.56 (d, J = 8.3 Hz, 2H), 7.23 (ddt, J = 11.8, 6.7, 4.0 Hz, 9H), 7.07 – 7.03 (m, 4H), 4.71 (ddd, J = 7.2, 5.9, 1.3 Hz, 1H), 3.86 (t, J = 6.2 Hz, 1H), 3.49 (d, J = 6.3 Hz, 2H), 2.80 (d, J = 7.2 Hz, 2H), 2.42 (s, 3H), 1.55 (d, J = 0.5 Hz, 3H), 1.37 (s, 3H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 144.9, 143.5, 136.2, 135.7, 129.8, 128.4, 128.0, 127.3, 126.8, 118.6, 50.3, 49.8, 35.7, 26.1, 21.7, 18.0 ppm

HRMS (ESI $^+$): calculated for $\text{C}_{26}\text{H}_{30}\text{NO}_2\text{S}[\text{M}+\text{H}]^+$: 420.1992, found 420.1995.

***N*-(4-cyclobutylidenebutyl)-4-methylbenzenesulfonamide (40)**



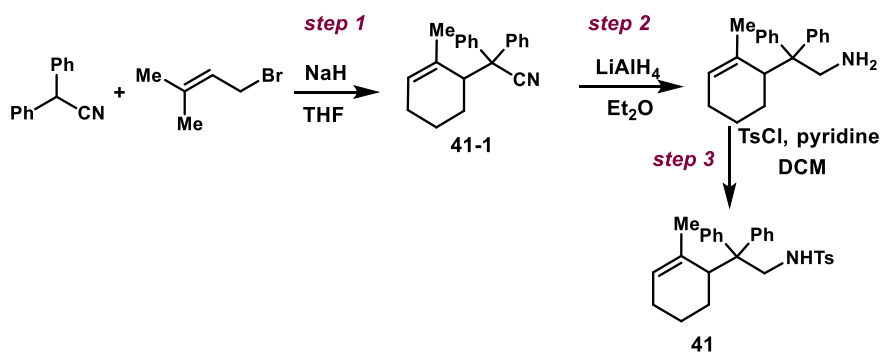
The procedure of the synthesis of **28** was followed, alcohol **40-1** was used as starting material.

^1H NMR (400 MHz, CDCl_3): δ 7.81 – 7.70 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.99 – 4.83 (m, 1H), 4.73 (t, J = 6.1 Hz, 1H), 2.91 (dd, J = 13.3, 6.9 Hz, 2H), 2.66 – 2.47 (m, 4H), 2.42 (s, 3H), 2.00 – 1.73 (m, 4H), 1.47 (p, J = 7.1 Hz, 2H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 143.4, 141.4, 137.1, 129.8, 127.2, 118.8, 43.0, 31.0, 29.4, 29.3, 25.1, 21.6, 17.1 ppm

HRMS (ESI $^+$): calculated for $\text{C}_{15}\text{H}_{22}\text{NO}_2\text{S}[\text{M}+\text{H}]^+$: 280.1366, found 280.1368.

4-Methyl-*N*-(2-(2-methylcyclohex-2-en-1-yl)-2,2-diphenylethyl)benzenesulfonamide (41)



Step 1: The procedure analogous to that used to synthesize 36-1.

Step 2: The procedure analogous to that used to synthesize 31-2.

Step 3: The procedure analogous to that used to synthesize 29-1.

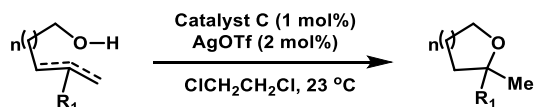
^1H NMR (400 MHz, CDCl_3): δ 7.51 (d, J = 8.2 Hz, 2H), 7.32 – 7.26 (m, 7H), 7.23 – 7.09 (m, 5H), 5.47 (s, 1H), 4.03 (dd, J = 11.4, 8.5 Hz, 1H), 3.71 (dd, J = 8.4, 3.1 Hz, 1H), 3.16 (dd, J = 11.5, 3.3 Hz, 1H), 3.05 (s, 1H), 2.45 (s, 3H), 1.79 – 1.61 (m, 2H), 1.51 – 1.38 (m, 1H), 1.38 – 1.27 (m, 1H), 1.26 (d, J = 10.3 Hz, 3H), 1.17 – 1.03 (m, 1H), 0.90 (ddd, J = 16.8, 8.5, 4.6 Hz, 1H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 144.1, 143.5, 139.4, 135.9, 134.5, 130.2, 130.0, 129.8, 128.5, 127.7, 127.4, 127.2, 126.8, 54.5, 51.8, 47.2, 27.2, 25.9, 25.1, 21.7, 20.4 ppm

HRMS (ESI $^+$): calculated for $\text{C}_{28}\text{H}_{31}\text{NO}_2\text{S}[\text{M}+\text{H}]^+$: 446.2070, found 446.2152.

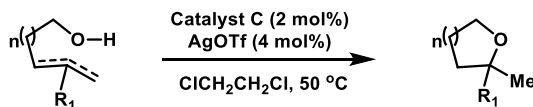
5. Substrate Scope

5.1 Intramolecular Hydroalkoxylation Catalyzed by the Catalyst C



General Procedure I

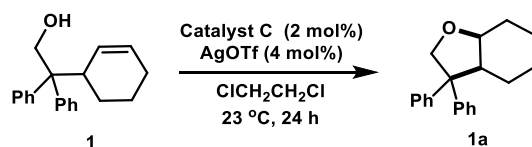
In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst C (1.6 mg, 1 mol%), silver trifluoromethanesulfonate (0.5 mg, 2 mol%), the substrate (0.1 mmol, 1.0 equiv.), and $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at room temperature (23 °C) for 24 h. The reaction mixture was diluted with CH_2Cl_2 , filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography (hexane/ethyl acetate = 40:1) to give the product.



General Procedure II

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst **C** (3.2 mg, 2 mol%), silver trifluoromethanesulfonate (1.0 mg, 4 mol%), the substrate (0.1 mmol, 1.0 equiv.), and $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at room temperature (23 °C) or 50 °C for 24 to 48 h. The reaction mixture was cooled to room temperature (23 °C), diluted with CH_2Cl_2 , filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography (hexane/ethyl acetate = 40:1) to give the product.

(3a*S*,7a*S*)-3,3-Diphenyloctahydrobenzofuran (**1a**)



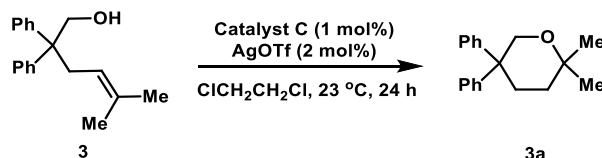
The general procedure II was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **1a** (25.1 mg, 90% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl_3): δ 7.44 – 7.42 (m, 2H), 7.24 – 7.22 (m, 4H), 7.16 – 7.13 (m, 4H), 4.78 (d, J = 8.6 Hz, 1H), 4.65 (d, J = 8.6 Hz, 1H), 4.20 – 4.19 (m, 1H), 2.77 (dt, J = 10.1, 5.1 Hz, 1H), 1.97 (d, J = 13.5 Hz, 1H), 1.71 – 1.63 (m, 2H), 1.49 – 1.38 (m, 3H), 1.19 – 1.12 (m, 1H), 1.00 – 0.91 (m, 1H) ppm

¹³C NMR (101 MHz, CDCl_3): δ 146.5, 143.6, 128.6, 128.3, 126.9, 126.2, 126.1, 76.4, 74.6, 59.7, 44.6, 29.0, 25.8, 24.6, 20.3 ppm

The analytical data was consistent with the literature.²

2,2-Dimethyl-5,5-diphenyltetrahydro-2*H*-pyran (**3a**)



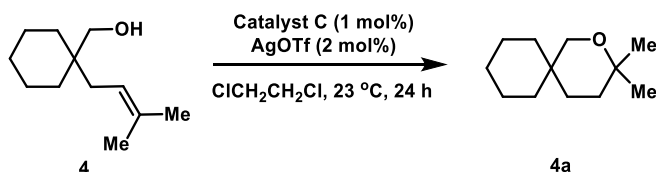
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **3a** (24.0 mg, 90% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl_3): δ 7.32 – 7.28 (m, 4H), 7.28 – 7.25 (m, 4H), 7.19 – 7.16 (m, 2H), 4.05 (s, 2H), 2.44 – 2.41 (m, 2H), 1.41 – 1.39 (m, 2H), 1.23 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl_3): δ 146.5, 128.2, 128.0, 126.1, 71.4, 69.1, 46.0, 32.6, 30.9, 26.5 ppm

The analytical data was consistent with the literature.²

3,3-Dimethyl-2-oxaspiro[5.5]undecane (**4a**)



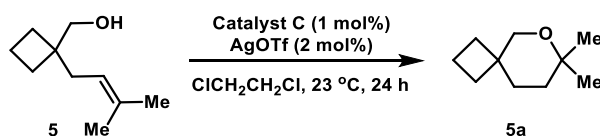
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **4a** (14.6 mg, 80% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 3.35 (s, 2H), 1.41 – 1.25 (m, 4H), 1.15 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 71.5, 70.1, 34.0, 32.1, 31.9, 26.9, 26.4, 21.6 ppm

HRMS (ESI⁺): calc'd for C₁₂H₂₃O [M+H]⁺: 183.1743, found 183.1743.

7,7-Dimethyl-6-oxaspiro[3.5]nonane (5a)



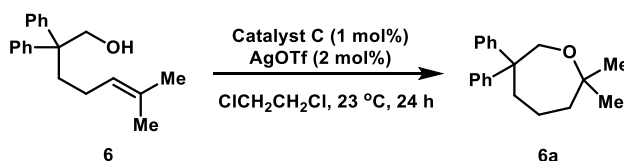
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **5a** (13.1 mg, 85% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 3.48 (s, 2H), 1.87 – 1.73 (m, 4H), 1.69 – 1.60 (m, 2H), 1.58 (dd, *J* = 7.5, 4.9 Hz, 2H), 1.37 (dd, *J* = 7.5, 4.9 Hz, 2H), 1.14 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 70.9, 70.2, 37.9, 33.1, 32.3, 29.8, 26.2, 15.4 ppm

HRMS (ESI⁺): calc'd for C₁₀H₁₉O [M+H]⁺: 155.1430, found 155.1430.

2,2-Dimethyl-6,6-diphenyloxepane (6a)



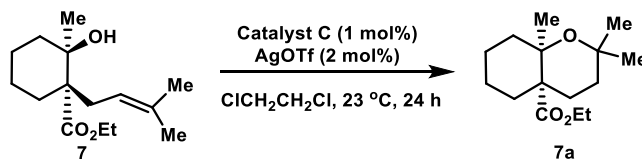
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **6a** (26.7 mg, 95% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.28 – 7.21 (m, 8H), 7.15 (d, *J* = 6.9 Hz, 2H), 4.17 (s, 2H), 2.30 – 2.27 (m, 2H), 1.75 – 1.70 (m, 4H), 1.12 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 147.3, 128.2, 128.0, 125.8, 75.8, 69.6, 52.0, 42.3, 41.8, 28.0, 20.7 ppm

HRMS (ESI⁺): calc'd for C₂₀H₂₅O [M+H]⁺: 281.1900, found 281.1901.

Ethyl (4a*S*,8a*R*)-2,2,8a-trimethylhexahydro-2*H*-chromene-4a(5*H*)-carboxylate (7a)



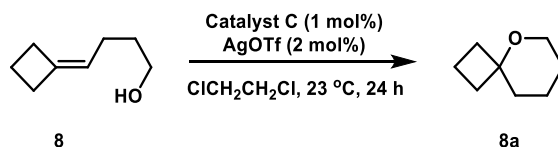
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **7a** (20.4 mg, 80% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 4.12 (qd, *J* = 7.1, 1.0 Hz, 2H), 2.25 (td, *J* = 14.1, 4.7 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.91 – 1.83 (m, 1H), 1.75 (td, *J* = 13.9, 4.8 Hz, 1H), 1.68 – 1.51 (m, 5H), 1.45 – 1.40 (m, 3H), 1.28 – 1.24 (m, 9H), 1.22 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 176.0, 73.3, 71.0, 60.3, 46.6, 38.5, 33.6, 31.9, 29.3, 28.9, 26.8, 25.3, 22.5, 21.5, 14.3 ppm

HRMS (ESI⁺): calc'd for C₁₅H₂₇O₃ [M+H]⁺: 255.1955, found 255.1953.

5-Oxaspiro[3.5]nonane (**8a**)



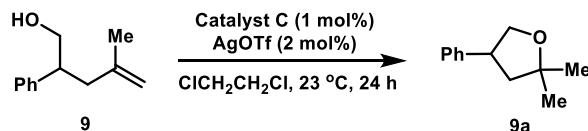
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **8a** (6.3 mg, 50% yield) as a colorless oil. When the reaction was conducted with an internal standard, the yield was determined to be 92% yield by ¹H NMR.

¹H NMR (400 MHz, CDCl₃): δ 3.56 – 3.52 (m, 2H), 2.00 – 1.90 (m, 4H), 1.79 – 1.71 (m, 1H), 1.60 – 1.52 (m, 5H), 1.47 (dt, *J* = 8.2, 4.4 Hz, 2H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 76.7, 62.9, 34.0, 32.9, 25.9, 20.3, 12.7 ppm

HRMS (ESI⁺): calc'd for C₈H₁₅O [M+H]⁺: 127.1117, found 127.118.

2,2-Dimethyl-4-phenyltetrahydrofuran (**9a**)



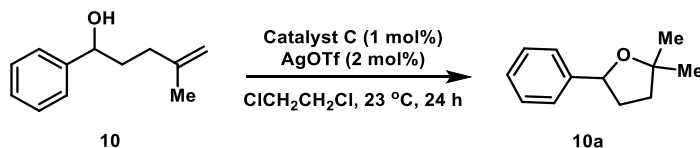
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **9a** (16.7 mg, 95% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃): δ 7.24 – 7.22 (m, 2H), 7.17 – 7.13 (m, 3H), 4.14 (t, *J* = 8.1 Hz, 1H), 3.71 (t, *J* = 8.9 Hz, 1H), 3.47 (dt, *J* = 17.6, 8.1 Hz, 1H), 2.14 (dd, *J* = 12.3, 8.0 Hz, 1H), 1.80 (dd, *J* = 12.1, 10.9 Hz, 1H), 1.31 (s, 3H), 1.24 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 141.9, 128.6, 127.4, 126.6, 81.5, 73.7, 47.1, 45.6, 28.9, 28.5 ppm

The analytical data was consistent with the literature²⁷.

2,2-Dimethyl-5-phenyltetrahydrofuran (10a)



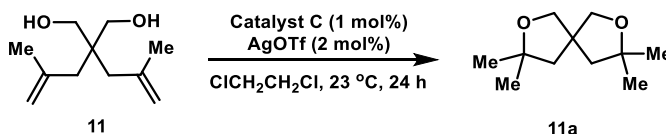
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **10a** (16.7 mg, 95% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.29 – 7.22 (m, 4H), 7.18 – 7.14 (m, 1H), 4.92 – 4.88 (m, 1H), 2.29 – 2.20 (m, 1H), 1.87 – 1.77 (m, 3H), 1.31 (s, 3H), 1.28 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 143.7, 128.4, 127.2, 125.9, 81.4, 80.6, 39.2, 35.8, 29.2, 28.5 ppm

The analytical data was consistent with the literature.⁵

3,3,8,8-Tetramethyl-2,7-dioxaspiro[4.4]nonane (11a)



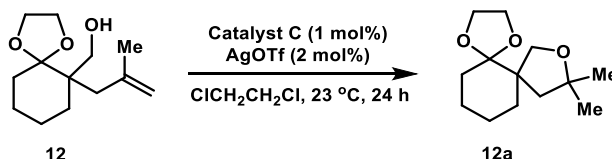
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **11a** (16.9 mg, 92% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 3.79 (d, *J* = 8.5 Hz, 2H), 3.60 (d, *J* = 8.5 Hz, 2H), 1.78 (s, 4H), 1.19 (d, *J* = 9.5 Hz, 12H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 80.3, 76.6, 52.9, 49.5, 29.0, 28.5 ppm

The analytical data was consistent with the literature².

9,9-Dimethyl-1,4,8-trioxadispiro[4.0.46.45]tetradecane (12a)



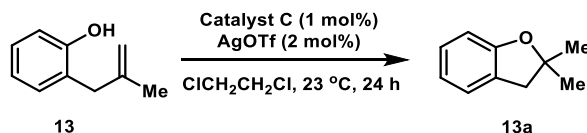
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **12a** (19.6 mg, 87% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 3.98 – 3.95 (m, 4H), 3.90 (d, *J* = 8.9 Hz, 1H), 3.57 (d, *J* = 8.9 Hz, 1H), 1.93 (d, *J* = 12.7 Hz, 1H), 1.78 – 1.68 (m 3H), 1.54 – 1.41 (m, 6H), 1.28 (s, 3H), 1.25 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 111.2, 81.1, 72.4, 65.0, 64.7, 53.1, 46.1, 36.2, 32.6, 29.7, 27.8, 23.2, 22.2 ppm

HRMS (ESI⁺): calc'd for C₁₃H₂₃O₃ [M+H]⁺: 227.1642, found 227.1640.

2,2-Dimethyl-2,3-dihydrobenzofuran (13a)



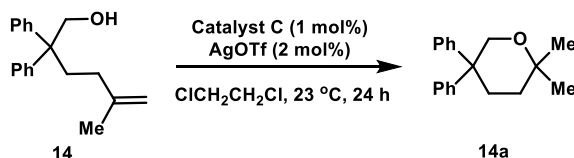
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **13a** (12.7 mg, 86% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.14 – 7.09 (m, 2H), 6.84 – 6.80 (m, 1H), 6.73 (d, J = 8.0 Hz, 1H), 3.01 (s, 2H), 1.48 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 159.0, 128.1, 127.2, 125.3, 120.1, 109.7, 86.6, 43.0, 28.3 ppm

The analytical data was consistent with the literature.⁶

2,2-Dimethyl-5,5-diphenyltetrahydro-2H-pyran (14a)



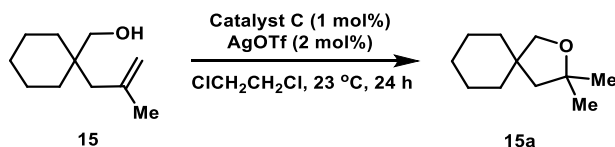
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **14a** (18.6 mg, 70% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.33 – 7.23 (m, 8H), 7.19 – 7.14 (m, 2H), 4.05 (s, 2H), 2.44 – 2.41 (m, 2H), 1.41 – 1.38 (m, 2H), 1.22 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 146.5, 128.2, 128.0, 126.1, 71.3, 69.1, 46.0, 32.7, 30.9, 26.7 ppm

The analytical data was consistent with the literature.²

3,3-Dimethyl-2-oxaspiro[4.5]decane (15a)



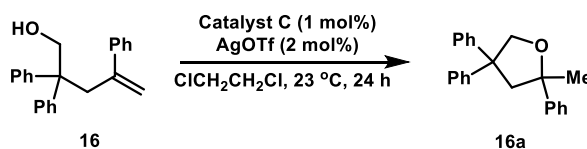
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **15a** (10.1 mg, 60% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 3.57 (s, 2H), 1.55 (s, 2H), 1.47 – 1.36 (m, 10H), 1.22 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 80.5, 44.9, 37.0, 29.3, 26.1, 23.9 ppm

HRMS (ESI⁺): calc'd for C₁₁H₂₁O [M+H]⁺: 169.1587, found 169.1586.

2-Methyl-2,4,4-triphenyltetrahydrofuran (16a)



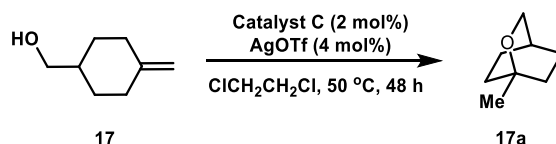
The general procedure I was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **16a** (18.8 mg, 60% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.35 – 7.30 (m, 4H), 7.24 – 7.16 (m, 4H), 7.13 – 7.07 (m, 4H), 7.04 – 6.99 (m, 3H), 4.77 (dd, *J* = 9.2, 1.0 Hz, 1H), 4.13 (d, *J* = 9.2 Hz, 1H), 3.04 (d, *J* = 12.7 Hz, 1H), 2.91 (dd, *J* = 12.6, 1.0 Hz, 1H), 1.28 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 149.6, 146.9, 146.0, 128.5, 128.4, 128.3, 127.3, 127.2, 126.4, 126.3, 124.4, 85.0, 76.1, 57.0, 52.7, 31.3 ppm

The analytical data was consistent with the literature²⁹.

(1s,4s)-1-methyl-2-oxabicyclo[2.2.2]octane (17a)



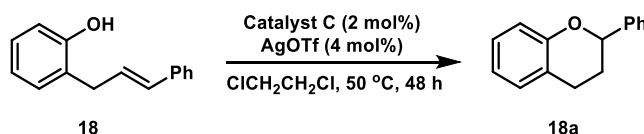
The general procedure II was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **17a** (6.3 mg, 50% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 3.89 (q, *J* = 1.4 Hz, 2H), 1.82 – 1.75 (m, 4H), 1.64 – 1.55 (m, 5H), 1.04 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 70.2, 68.3, 33.0, 27.1, 25.8, 25.0 ppm

HRMS (ESI⁺): calc'd for C₈H₁₅O [M+H]⁺: 127.1117, found 127.1118.

2-Phenylchromane (18a)



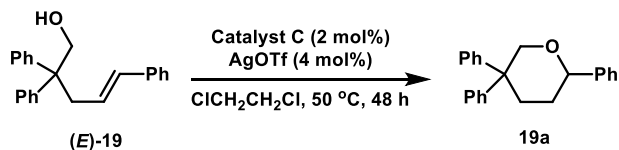
The general procedure II was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **18a** (16.8 mg, 80% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.48 – 7.41 (m, 4H), 7.37 – 7.36 (m, 1H), 7.19 – 7.12 (m, 2H), 6.97 – 6.90 (m, 2H), 5.10 (dd, *J* = 10.1, 2.4 Hz, 1H), 3.03 (ddd, *J* = 17.0, 11.3, 6.0 Hz, 1H), 2.83 (dt, *J* = 16.5, 4.9 Hz, 1H), 2.25 (ddt, *J* = 13.6, 5.9, 3.0 Hz, 1H), 2.18 – 2.08 (m, 1H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 155.2, 141.9, 129.7, 128.6, 128.0, 127.5, 126.1, 122.0, 120.4, 117.1, 77.9, 30.1, 25.2 ppm

The analytical data was consistent with the literature.¹⁰

2,5,5-Triphenyltetrahydro-2H-pyran (19a)



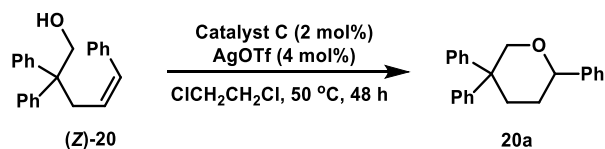
The general procedure II was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **19a** (26.7 mg, 85% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.46 – 7.44 (m, 2H), 7.27 – 7.11 (m, 13H), 4.72 (dd, J = 12.1, 2.5 Hz, 1H), 4.39 (dd, J = 11.4, 2.5 Hz, 1H), 3.63 (d, J = 12.1 Hz, 1H), 2.57 – 2.46 (m, 2H), 1.69 (dq, J = 13.7, 3.3 Hz, 1H), 1.53 – 1.43 (m, 1H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 146.7, 145.9, 142.8, 129.1, 128.5, 128.2, 127.6, 127.2, 126.5, 126.2, 125.9, 80.5, 75.5, 46.0, 35.2, 30.4 ppm

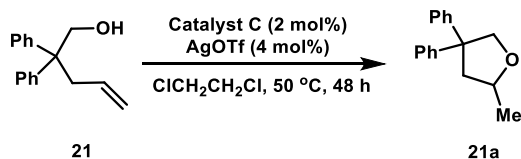
The analytical data was consistent with the literature.¹⁰

2,5,5-Triphenyltetrahydro-2H-pyran (20a)



The general procedure II was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **20a** (21.0 mg, 67% yield) as a colorless oil. The analytical data was consistent with **13a**.

2-Methyl-4,4-diphenyltetrahydrofuran (21a)



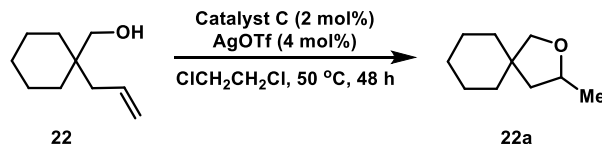
The general procedure II was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **21a** (19.0 mg, 80% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.32 – 7.28 (m, 6H), 7.23 – 7.17 (m, 4H), 4.61 – 4.58 (m, 1H), 4.22 – 4.13 (m, 2H), 2.64 (ddd, J = 12.1, 5.7, 0.9 Hz, 1H), 2.27 (dd, J = 12.1, 9.5 Hz, 1H), 1.59 (s, 1H), 1.30 (d, J = 6.1 Hz, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 146.5, 146.3, 128.5, 128.4, 127.3, 126.5, 126.3, 77.0, 74.9, 56.5, 46.7, 21.5 ppm

The analytical data was consistent with the literature.¹¹

3-Methyl-2-oxaspiro[4.5]decane (22a)



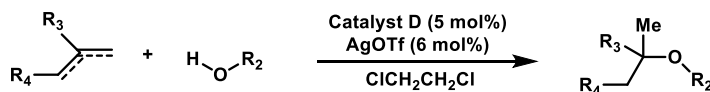
The general procedure II was followed. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **22a** (10.8 mg, 70% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 4.06 – 3.98 (m, 1H), 3.63 (d, J = 8.5 Hz, 1H), 3.47 (d, J = 8.5 Hz, 1H), 1.86 (dd, J = 12.3, 6.3 Hz, 1H), 1.44 – 1.40 (m, 10H), 1.23 (d, J = 6.1 Hz, 3H), 1.20 (d, J = 9.1 Hz, 1H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 74.9, 44.3, 37.5, 36.0, 26.1, 24.1, 23.8, 21.58 ppm

The analytical data was consistent with the literature.²

5.2 Intermolecular Hydroalkoxylation Catalyzed by the Catalyst D



General Procedure I

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst **D** (13.7 mg, 5 mol%), silver trifluoromethanesulfonate (3.1 mg, 6 mol%), alkenes (0.2 mmol, 1.0 equiv.), alcohols (0.3 mmol, 1.5 equiv.) and ClCH₂CH₂Cl (1 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at 50 °C for 16 h. Then the reaction mixture was cooled to room temperature (23 °C) and diluted with CH₂Cl₂, filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography (hexane/ethyl acetate = 40:1) to give the product.

General Procedure II

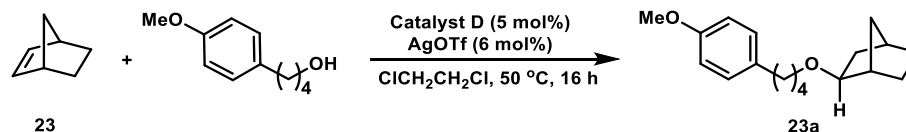
In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added catalyst **D** (13.7 mg, 5 mol%), silver trifluoromethanesulfonate (3.1 mg, 6 mol%), alkenes (0.2 mmol, 1.0 equiv.), alcohols (1.4 mmol, 7.0 equiv.) and ClCH₂CH₂Cl (1 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at room temperature (23 °C) or 50 °C for 24 h. The reaction mixture was diluted with CH₂Cl₂, filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography (hexane/ethyl acetate = 40:1) to give the product.

General Procedure III

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added catalyst **D** (5.5 mg, 2 mol%), silver trifluoromethanesulfonate (1.5 mg, 3 mol%), alkenes (0.2 mmol, 1.0 equiv.), alcohols (0.3 mmol, 1.5 equiv.) and ClCH₂CH₂Cl (1 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at room temperature (23 °C). The reaction mixture diluted with CH₂Cl₂,

filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography (hexane/ethyl acetate = 40:1) to give the product.

(1R,2R,4S)-2-(4-(4-methoxyphenyl)butoxy)bicyclo[2.2.1]heptane (23a)



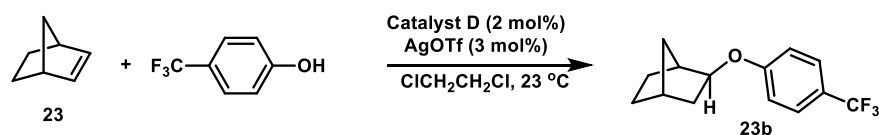
The general procedure I was followed and the reaction mixture was stirred at 50 °C for 16 h. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **23a** (40.0 mg, 73% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.09 (d, *J* = 7.3 Hz, 2H), 6.82 (d, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 1.6 Hz, 3H), 3.43 – 3.29 (m, 3H), 2.57 (t, *J* = 7.1 Hz, 2H), 2.25 (d, *J* = 30.0 Hz, 2H), 1.62 – 1.26 (m, 9H), 1.08 – 0.96 (m, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 157.8, 134.8, 129.4, 113.8, 82.6, 68.2, 55.4, 40.5, 39.7, 35.3, 34.9, 29.8, 28.7, 28.6, 24.8 ppm

HRMS (ESI⁺): calc'd for C₁₈H₂₇O₂ [M+H]⁺: 275.2006, found 275.2005.

(1S,2S,4R)-2-(4-(trifluoromethyl)phenoxy)bicyclo[2.2.1]heptane (23b)



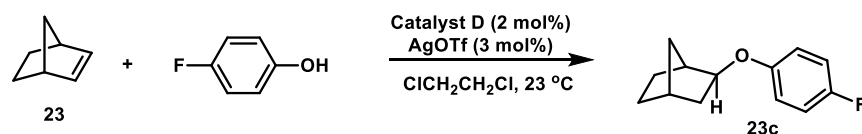
The general procedure III was followed and the reaction mixture was stirred at 23 °C for 24 h. The crude residue was purified by column chromatography (hexane) to yield **23b** (48 mg, 94% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.20 (d, *J* = 6.6 Hz, 1H), 2.47 (d, *J* = 4.4 Hz, 1H), 2.33 – 2.34 (m, 1H), 1.78 (ddd, *J* = 13.2, 6.7, 2.4 Hz, 1H), 1.70 – 1.65 (m, 1H), 1.61 – 1.50 (m, 3H), 1.21 (ddd, *J* = 9.9, 2.4, 1.3 Hz, 1H), 1.18 – 1.15 (m, 2H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 160.5, 126.9 (q, *J* = 3.9 Hz), 124.7 (q, *J* = 271.2 Hz), 122.4 (q, *J* = 32.5 Hz), 115.5, 80.6, 41.3, 40.1, 35.6, 35.4, 28.5, 24.4 ppm

¹⁹F NMR (376 MHz, CDCl₃): δ – 61.4 ppm

(1S,2S,4R)-2-(4-fluorophenoxy)bicyclo[2.2.1]heptane (23c)



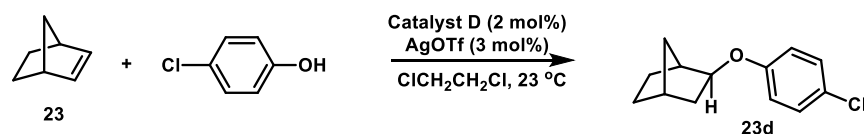
The general procedure III was followed and the reaction mixture was stirred at 23 °C for 24 h. The crude residue was purified by column chromatography (hexane) to yield **23c** (29 mg, 71% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.98 – 6.90 (m, 2H), 6.82 – 6.73 (m, 2H), 4.10 (d, *J* = 6.7 Hz, 1H), 2.43 (d, *J* = 4.4 Hz, 1H), 2.31 – 2.32 (m, 1H), 1.73 (ddd, *J* = 13.1, 6.7, 2.4 Hz, 1H), 1.69 – 1.63 (m, 1H), 1.57 – 1.45 (m, 3H), 1.18 (ddd, *J* = 9.8, 2.4, 1.4 Hz, 1H), 1.14 – 1.12 (m, 2H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 157.1 (d, *J* = 237.5 Hz), 154.0 (d, *J* = 1.8 Hz), 116.5 (d, *J* = 7.9 Hz), 115.8 (d, *J* = 23.0 Hz), 80.8, 41.2, 40.1, 35.6, 35.28, 28.6, 24.4 ppm

¹⁹F NMR (376 MHz, CDCl₃): δ -124.8 ppm

(1S,2S,4R)-2-(4-chlorophenoxy)bicyclo[2.2.1]heptane (23d)

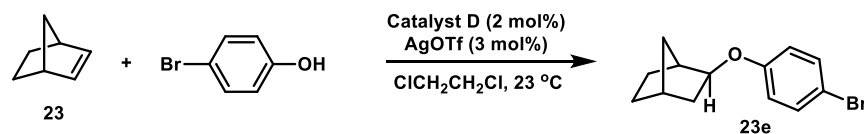


The general procedure III was followed and the reaction mixture was stirred at 23 °C for 24 h. The crude residue was purified by column chromatography (hexane) to yield **23d** (41 mg, 93% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.20 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 4.11 (d, *J* = 6.6 Hz, 1H), 2.43 (d, *J* = 4.4 Hz, 1H), 2.31 – 2.32 (m, 1H), 1.74 (ddd, *J* = 13.1, 6.7, 2.4 Hz, 1H), 1.68 – 1.63 (m, 1H), 1.58 – 1.46 (m, 3H), 1.19 (ddd, *J* = 9.8, 2.4, 1.3 Hz, 1H), 1.15 – 1.13 (m, 2H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 156.5, 129.3, 125.1, 116.8, 80.5, 41.2, 40.0, 35.6, 35.3, 28.6, 24.4 ppm

(1S,2S,4R)-2-(4-bromophenoxy)bicyclo[2.2.1]heptane (23e)

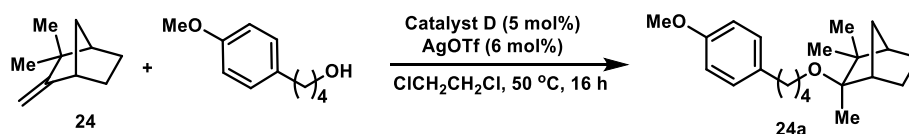


The general procedure III was followed and the reaction mixture was stirred at 23 °C for 24 h. The crude residue was purified by column chromatography (hexane) to yield **23e** (48 mg, 90% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.34 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 4.11 (d, *J* = 6.6 Hz, 1H), 2.43 (d, *J* = 4.4 Hz, 1H), 2.31 – 2.32 (m, 1H), 1.74 (ddd, *J* = 13.1, 6.7, 2.4 Hz, 1H), 1.68 – 1.63 (m, 1H), 1.60 – 1.49 (m, 3H), 1.19 (ddd, *J* = 9.9, 2.4, 1.3 Hz, 1H), 1.15 – 1.12 (m, 2H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 157.0, 132.3, 117.4, 112.4, 80.5, 77.5, 77.2, 76.8, 41.2, 40.2, 35.6, 35.3, 28.5, 24.4 ppm

(1S,4S,5R)-5-(4-(4-methoxyphenyl)butoxy)-2,2-dimethylbicyclo[2.2.1]heptane (24a)



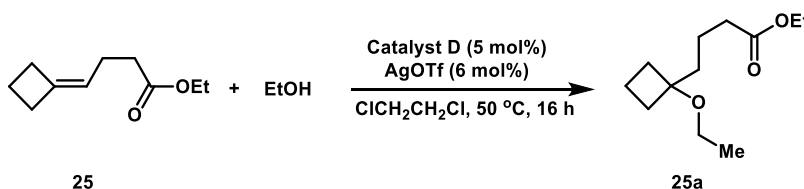
The general procedure I was followed and the reaction mixture was stirred at 50 °C for 16 h. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **21a** (58.2 mg, 92% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.41 (dt, *J* = 9.1, 6.2 Hz, 1H), 3.26 (dt, *J* = 9.1, 6.1 Hz, 1H), 3.15 (dd, *J* = 7.5, 3.4 Hz, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.75 – 1.45 (m, 1H), 1.00 – 0.98 (m, 4H), 0.88 (s, 3H), 0.80 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 157.7, 135.0, 129.4, 113.8, 87.1, 69.0, 55.4, 49.3, 46.5, 45.2, 38.8, 34.9, 34.7, 29.8, 28.6, 27.5, 20.4, 20.4, 12.4 ppm

HRMS (ESI⁺): calc'd for C₂₁H₃₃O₂ [M+H]⁺: 339.2295, found 339.2296.

Ethyl 4-(1-ethoxycyclobutyl)butanoate (**25a**)



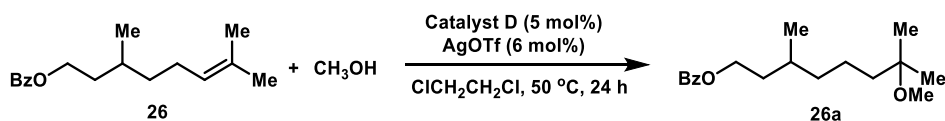
The general procedure I was followed and the reaction mixture was stirred at 50 °C for 16 h. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **25a** (34.2 mg, 80% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 4.12 (q, *J* = 7.1 Hz, 2H), 3.27 (q, *J* = 7.0 Hz, 2H), 2.33 – 2.30 (m, 2H), 2.09 – 2.01 (m, 2H), 1.88 – 1.82 (m, 2H), 1.77 – 1.63 (m, 5H), 1.56 – 1.49 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 173.8, 78.7, 60.3, 56.7, 34.6, 34.5, 32.2, 18.8, 16.0, 14.4, 12.8 ppm

HRMS (ESI⁺): calc'd for C₁₂H₂₃O₃ [M+H]⁺: 215.1642, found 215.1641.

7-Methoxy-3,7-dimethyloctyl benzoate (**26a**)



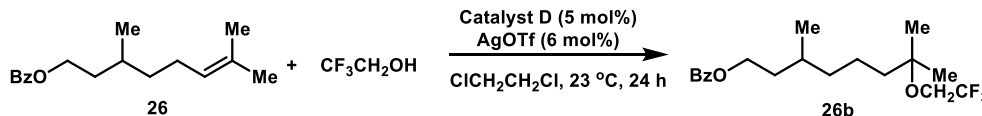
The general procedure II was followed and the reaction mixture was stirred at 50 °C for 24 h. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **26a** (39.7 mg, 68% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 8.05 – 8.02 (m, 2H), 7.57 – 7.53 (m, 1H), 7.45 – 7.41 (m, 2H), 4.41 – 4.31 (m, 2H), 3.17 (s, 3H), 1.86 – 1.78 (m, 1H), 1.63 – 1.53 (m, 1H), 1.46 – 1.18 (m, 7H), 1.13 (s, 6H), 0.97 (d, *J* = 6.5 Hz, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 166.8, 132.9, 130.6, 129.7, 128.5, 74.7, 63.7, 49.2, 40.2, 37.6, 35.7, 30.1, 25.1, 21.3, 19.7 ppm

HRMS (ESI⁺): calc'd for C₁₈H₂₉O₃ [M+H]⁺: 293.2111, found 293.2110.

3,7-Dimethyl-7-(2,2,2-trifluoroethoxy)octyl benzoate (26b)



The general procedure II was followed and the reaction mixture was stirred at 23 °C for 24 h. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **26b** (47.5 mg, 66% yield) as a colorless oil.

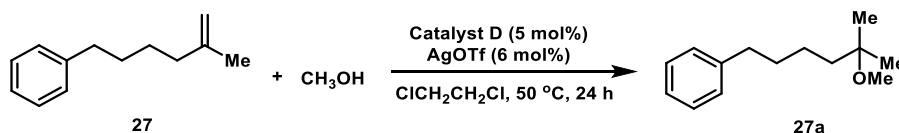
¹H NMR (400 MHz, CDCl₃): δ 8.05 – 8.03 (m, 2H), 7.58 – 7.53 (m, 1H), 7.46 – 7.42 (m, 2H), 4.41 – 4.31 (m, 2H), 3.69 (q, *J* = 8.7 Hz, 2H), 1.84 – 1.77 (m, 1H), 1.62 – 1.54 (m, 1H), 1.47 – 1.21 (m, 7H), 1.18 (s, 6H), 0.97 (d, *J* = 6.5 Hz, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 166.8, 132.9, 130.6, 129.7, 128.5, 124.3 (q, *J* = 281.1 Hz), 76.9, 63.6, 60.5 (q, *J* = 34.2 Hz), 40.5, 37.4, 35.7, 30.0, 25.2, 21.1, 19.6 ppm

¹⁹F NMR (565 MHz, CDCl₃): δ -74.5 (t, *J* = 8.5 Hz) ppm

HRMS (ESI⁺): calc'd for C₁₉H₂₈F₃O₃ [M+H]⁺: 383.1805, found 383.1802.

(5-Methoxy-5-methylhexyl)benzene (27a)



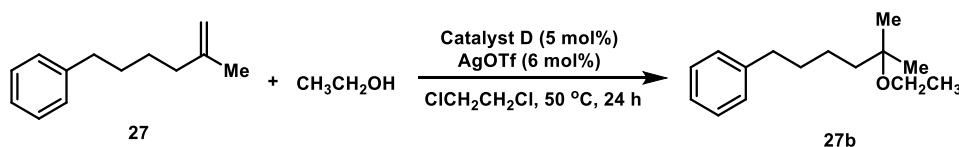
The general procedure II was followed and the reaction mixture was stirred at 50 °C for 24 h. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **27a** (27.6 mg, 67% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.29 – 7.25 (m, 2H), 7.19 – 7.17 (m, 3H), 3.17 (s, 3H), 2.62 (t, *J* = 8.0 Hz, 2H), 1.65 – 1.58 (m, 2H), 1.51 – 1.47 (m, 2H), 1.40 – 1.32 (m, 2H), 1.13 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 142.9, 128.5, 128.4, 125.7, 74.7, 49.2, 39.9, 36.1, 32.3, 25.1, 23.8 ppm

HRMS (ESI⁺): calc'd for C₁₄H₂₂ONa [M+Na]⁺: 229.1563, found 229.1568.

(5-Ethoxy-5-methylhexyl)benzene (27b)



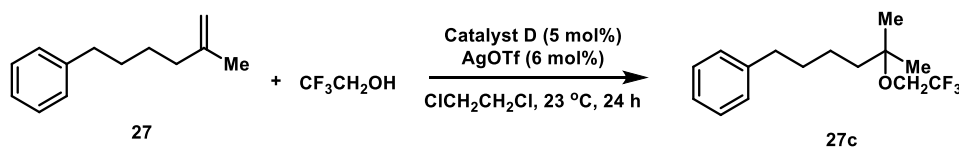
The general procedure II was followed and the reaction mixture was stirred at 50 °C for 24 h. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **27b** (13.6 mg, 31% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.29 – 7.25 (m, 2H), 7.19 – 7.15 (m, 3H), 3.35 (q, *J* = 7.0 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 1.65 – 1.57 (m, 2H), 1.51 – 1.47 (m, 2H), 1.41–1.33 (m, 2H), 1.16 – 1.12 (m, 9H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 142.9, 128.5, 128.4, 125.7, 74.5, 56.4, 40.1, 36.1, 32.3, 25.8, 23.8, 20.2, 16.3 ppm

HRMS (ESI⁺): calc'd for C₁₅H₂₄ONa [M+Na]⁺: 243.1719, found 243.1716.

(5-Methyl-5-(2,2,2-trifluoroethoxy)hexyl)benzene (27c)



The general procedure II was followed and the reaction mixture was stirred at 23 °C for 24 h. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **27c** (29.0 mg, 53% yield) as a colorless oil.

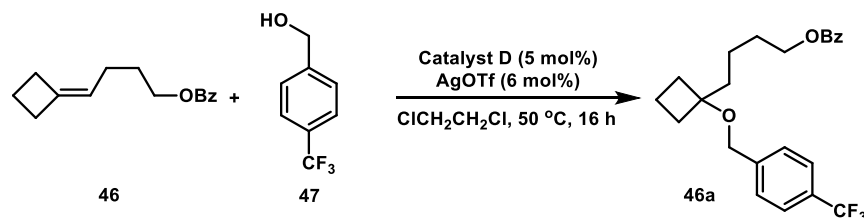
¹H NMR (600 MHz, CDCl₃): δ 7.30 – 7.26 (m, 2H), 7.19 – 7.18 (m, 3H), 3.70 (q, *J* = 8.7 Hz, 2H), 2.63 (t, *J* = 5.2 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.53 – 1.51 (m, 2H), 1.43 – 1.38 (m, 2H), 1.19 (s, 6H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 142.7, 128.5, 128.4, 125.8, 124.5 (q, *J* = 277.8 Hz), 76.9, 60.5 (q, *J* = 34.2 Hz), 40.3, 36.0, 32.0, 25.2, 23.6 ppm

¹⁹F NMR (565 MHz, CDCl₃): δ -74.5 (t, *J* = 8.1 Hz) ppm

HRMS (ESI⁺): calc'd for C₁₅H₂₁F₃ONa [M+Na]⁺: 297.1437, found 297.1437.

4-(1-((4-(trifluoromethyl)benzyl)oxy)cyclobutyl)butyl benzoate (46a)



The general procedure I was followed and the reaction mixture was stirred at 50 °C for 16 h. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **46a** (73 mg, 90% yield) as a pale yellow oil.

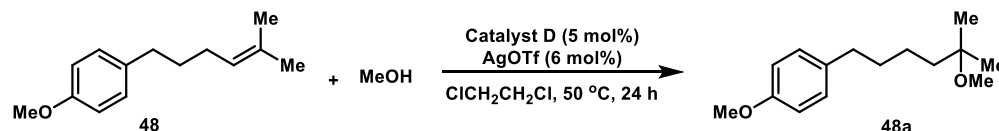
¹H NMR (400 MHz, CDCl₃): δ 8.03 – 8.02 (m, 2H), 7.59 – 7.51 (m, 3H), 7.46 – 7.38 (m, 4H), 4.41 – 4.35 (m, 4H), 2.23 – 2.15 (m, 2H), 2.01 – 1.91 (m, 2H), 1.87 – 1.79 (m, 5H), 1.65 – 1.51 (m, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 166.7, 143.5, 133.0, 130.5, 129.6, 129.5 (q, *J* = 32.2 Hz), 128.5, 127.4, 125.32 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 272.9 Hz), 79.0, 64.9, 63.4, 35.1, 32.1, 29.1, 19.7, 12.9 ppm

¹⁹F NMR (376 MHz, CDCl₃): δ -62.4 ppm

HRMS (ESI⁺): calc'd for C₂₃H₂₅F₃O₃Na [M+Na]⁺: 429.1648, found 429.1648.

1-methoxy-4-(5-methoxy-5-methylhexyl)benzene (48a)



The general procedure II was followed and the reaction mixture was stirred at 50 °C for 24 hours. The crude residue was purified by column chromatography (hexane/ethyl acetate = 40:1) to yield **48a** (26.4 mg, 56% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.17 (s, 3H), 2.56 (t, *J* = 8.0 Hz, 2H), 1.62 – 1.54 (m, 2H), 1.50 – 1.46 (m, 2H), 1.39 – 1.33 (m, 2H), 1.13 (s, 6H) ppm

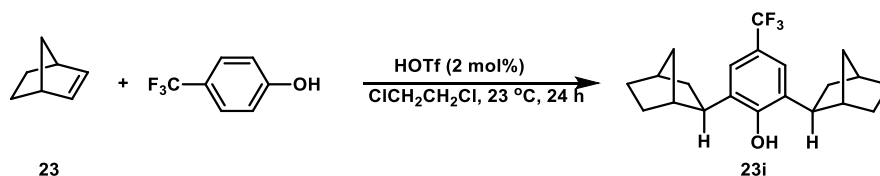
¹³C NMR (101 MHz, CDCl₃): δ 157.7, 135.0, 129.4, 113.8, 74.8, 55.4, 49.2, 39.9, 35.2, 32.5, 25.1, 23.7 ppm

HRMS (ESI⁺): calc'd for C₁₅H₂₄O₂Na [M+Na]⁺: 259.1669, found 259.1663.

5.3 HOTf-catalyzed Hydroarylation of Norbornene with Phenol

General Procedure

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added HOTf (0.6 mg, 2 mol%), alkenes (0.2 mmol, 1.0 equiv.), alcohols (0.3 mmol, 1.5 equiv.) and ClCH₂CH₂Cl (1 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at room temperature (23 °C) for 24 h. The reaction mixture diluted with CH₂Cl₂, filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography (hexane/ethyl acetate = 20:1) to give the product.



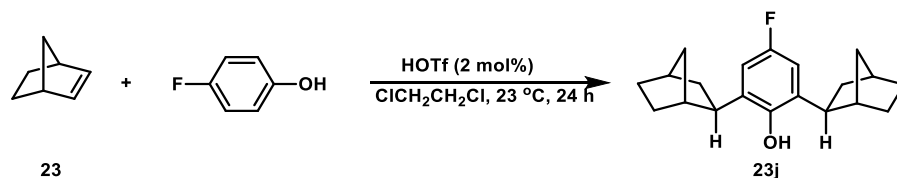
The crude residue was purified by column chromatography (hexane/ethyl acetate = 20:1) to yield **23i** (19 mg, 54% yield, 1:1 dr) as a white solid.

¹H NMR (600 MHz, CDCl₃, 2 isomers): δ 7.29 (s, 2H), 5.10 (s, 1H), 2.84 – 2.81 (m, 2H), 2.45 (s, 2H), 2.39 (s, 2H), 1.87 – 1.83 (m, 2H), 1.70 – 1.65 (m, 2H), 1.64 – 1.59 (m, 2H), 1.54 – 1.49 (m, 4H), 1.42 – 1.38 (m, 2H), 1.35 – 1.30 (m, 2H), 1.28 – 1.27 (m, 2H) ppm

¹³C NMR (150 MHz, CDCl₃, 2 isomers): δ [154.05, 154.03], [133.00, 132.98], 125.08 (d, *J* = 271.4 Hz), [121.85 (d, *J* = 31.6 Hz), 121.83 (d, *J* = 23.8 Hz)], 125.56 – 125.51 (m), [41.02, 41.96], [40.86, 40.85], [38.32, 38.23], [37.05, 37.03], [36.37, 36.32], [30.36, 30.34], [29.17, 29.16] ppm

¹⁹F NMR (564 MHz, CDCl₃, 2 isomers): δ -61.03 ppm

HRMS (ESI): calc'd for C₂₁H₂₄F₃O [M-H]⁻: 349.1779, found 349.1783.



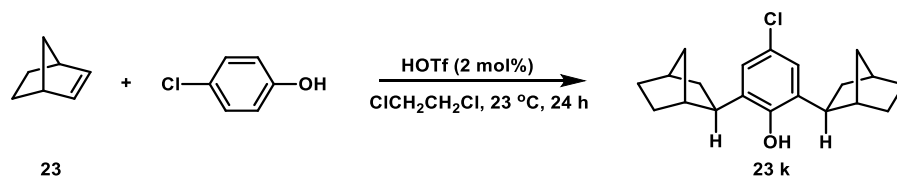
The crude residue was purified by column chromatography (hexane/ethyl acetate = 20:1) to yield **23j** (21 mg, 67% yield, 1:1 dr) as a white solid.

¹H NMR (600 MHz, CDCl₃, 2 isomers): δ 6.76 (s, 1H), 6.74 (s, 1H), 4.55 (s, 1H), 2.81 – 2.79 (m, 2H), 2.38 – 2.37 (m, 4H), 1.85 – 1.80 (m, 2H), 1.68 – 1.56 (m, 4H), 1.52 – 1.47 (m, 4H), 1.40 – 1.36 (m, 2H), 1.33 – 1.28 (m, 2H), 1.26 – 1.23 (m, 2H) ppm

¹³C NMR (150 MHz, CDCl₃, 2 isomers): δ 157.00 (d, *J* = 235.7 Hz), [147.01, 146.99], [134.38, 134.34], [109.81 (d, *J* = 23.8 Hz), 109.78 (d, *J* = 23.8 Hz)], [41.23, 41.15], 41.06, [38.50, 38.40], [36.98, 36.96], [36.34, 36.29], [30.37, 30.25], [29.16, 29.14] ppm

¹⁹F NMR (564 MHz, CDCl₃, 2 isomers): δ -123.69, -123.72 ppm

HRMS (ESI): calc'd for C₂₀H₂₄FO [M-H]⁻: 299.1811, found 299.1818.

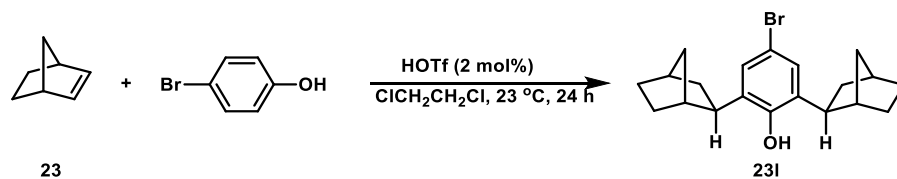


The crude residue was purified by column chromatography (hexane/ethyl acetate = 20:1) to yield **23k** (22 mg, 71% yield, 1:1 dr) as a white solid.

¹H NMR (400 MHz, CDCl₃, 2 isomers): δ 6.99 (s, 2H), 4.71 (s, 1H), 2.80 – 2.76 (m, 2H), 2.43 – 2.33 (m, 4H), 1.86 – 1.76 (m, 2H), 1.65 – 1.58 (m, 4H), 1.53 – 1.47 (m, 4H), 1.41 – 1.20 (m, 8H) ppm

¹³C NMR (101 MHz, CDCl₃, 2 isomers): δ [149.85, 149.83], [134.47, 134.45], 125.0, [123.31, 123.28], [41.11, 41.04], [40.98, 40.96], [38.42, 38.32], [37.01, 36.99], [36.37, 36.32], [30.38, 30.36], [29.17, 29.15] ppm

HRMS (ESI): calc'd for C₂₀H₂₄ClO [M-H]⁻: 315.1516, found 315.1522.



The crude residue was purified by column chromatography (hexane/ethyl acetate = 20:1) to yield **23I** (52 mg, 75% yield, 1:1 dr) as a white solid.

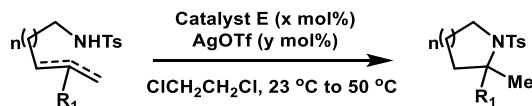
¹H NMR (600 MHz, CDCl₃, 2 isomers): δ 7.13 (s, 2H), 4.73 (s, 1H), 2.79 – 2.76 (m, 2H), 2.39 – 2.37 (m, 4H), 1.85 – 1.78 (m, 2H), 1.65 – 1.55 (m, 4H), 1.51 – 1.48 (m, 4H), 1.37 – 1.23 (m, 8H) ppm

¹³C NMR (150 MHz, CDCl₃, 2 isomers): δ [150.39, 150.37], [134.95, 134.93], [126.22, 126.19], 112.70, [41.08, 41.02], [40.95, 40.93], [38.41, 38.31], [37.01, 36.98], [36.36, 36.32], [30.37, 30.35], [29.15, 29.14] ppm

HRMS (ESI): calc'd for C₂₀H₂₄BrO [M-H]⁺: 359.1011, found 359.1016.

Norbornene and para-substituted phenols (CF₃, F, Cl, Br) underwent hydroalkoxylation catalyzed by complex **D**/AgOTf at either room temperature (23 °C) and 50 °C. However, hydroarylation products were formed when triflic acid replaced catalyst **D**. These results indicated our catalytic system was different from triflic acid.

5.4 Intramolecular Hydroamination by the Catalyst E

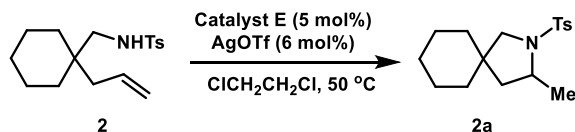


General Procedure I: To a 4 mL vial equipped with a magnetic stir bar were added the catalyst **E** (0.001mmol, 1 mol%), silver trifluoromethanesulfonate (0.6 mg, 0.002 mmol, 2 mol%) and ClCH₂CH₂Cl (1.0 mL) in a nitrogen filled glovebox. The mixture was stirred at 23 °C for 1 h. Then to the mixture was added a solution of **37** (30.7 mg, 0.1 mmol, 1.0 equiv) in ClCH₂CH₂Cl (0.5 mL). The vial was taken outside of the glovebox and the resulting mixture was stirred at 23 °C for 24 h. When the reaction was finished (monitored by TLC), the mixture was diluted with CH₂Cl₂ and concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc/hexane = 1/20) to afford the desired product.

General Procedure II: To a 4 mL vial equipped with a magnetic stir bar were added the catalyst **E** (0.005mmol, 5 mol%), silver trifluoromethanesulfonate (1.5 mg, 0.006 mmol, 6 mol%) and ClCH₂CH₂Cl (1.0 mL) in a nitrogen filled glovebox. The mixture was stirred at 23 °C for 1 h. Then to the mixture was added a solution of **37** (30.7 mg, 0.1 mmol, 1.0 equiv) in ClCH₂CH₂Cl (0.5 mL). The vial was taken outside of the glovebox and the resulting mixture was stirred at 50 °C for 48 h. When the reaction was finished (monitored by TLC), the mixture was diluted with CH₂Cl₂ and concentrated under reduced

pressure. The residue was purified by flash chromatography (EtOAc/hexane = 1/20) to afford the desired product.

3-Methyl-2-tosyl-2-azaspiro[4.5]decane (2a)



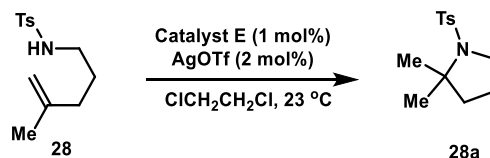
The general procedure II was followed. White solid (19.0 mg, 62% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 3.56 (dp, J = 8.6, 6.2 Hz, 1H), 3.24 (d, J = 10.7 Hz, 1H), 3.14 (d, J = 10.7 Hz, 1H), 2.42 (s, 3H), 1.80 (dd, J = 12.6, 7.2 Hz, 1H), 1.49 – 1.06 (m, 13H), 0.89 – 0.62 (m, 2H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 143.2, 135.2, 129.6, 127.6, 58.9, 55.3, 47.2, 41.1, 36.7, 34.4, 26.0, 23.8, 23.0, 22.9, 21.6 ppm

HRMS (ESI⁺): calculated for C₁₇H₂₆NO₂S[M+H]⁺: 308.1679, found 308.1678.

2,2-Dimethyl-1-tosylpyrrolidine (28a)



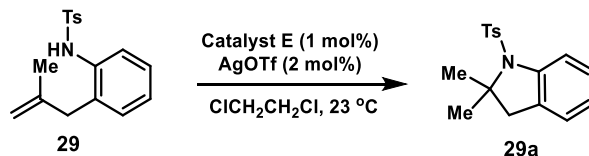
The general procedure I was followed. White solid (21.2 mg, 84% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 3.39 (t, J = 6.4 Hz, 2H), 2.41 (s, 3H), 1.87 – 1.71 (m, 4H), 1.44 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 142.6, 138.8, 129.5, 127.2, 65.2, 49.5, 43.0, 28.4, 22.6, 21.6 ppm

HRMS (ESI⁺): calculated for C₁₃H₂₀NO₂S[M+H]⁺: 254.1209, found 254.1206.

2,2-Dimethyl-1-tosylindoline (29a)



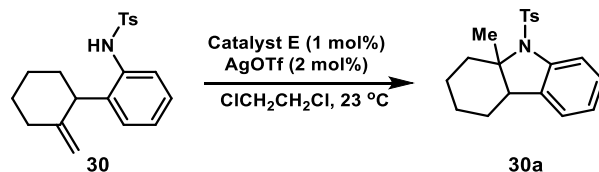
The general procedure I was followed. White solid (25.6 mg, 85% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.84 – 7.75 (m, 2H), 7.47 (d, J = 8.2 Hz, 1H), 7.24 (t, J = 6.9 Hz, 2H), 7.16 – 7.11 (m, 1H), 7.10 (dd, J = 5.9, 5.3 Hz, 1H), 6.93 (td, J = 7.4, 0.8 Hz, 1H), 2.97 (s, 2H), 2.37 (s, 3H), 1.66 (s, 7H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 143.5, 142.1, 139.4, 129.7, 128.4, 127.8, 126.8, 125.1, 122.8, 114.2, 77.5, 76.9, 70.1, 46.2, 28.7, 21.6 ppm

HRMS (ESI⁺): calculated for C₁₇H₂₀NO₂S[M+H]⁺: 302.1209, found 302.1205.

9a-Methyl-9-tosyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (30a)



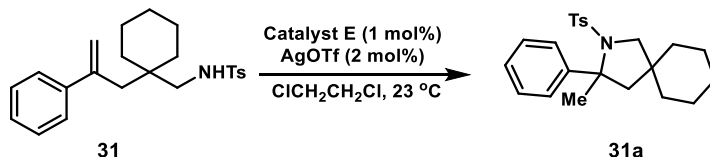
The general procedure I was followed. White solid (21.5 mg, 63% yield).

¹H NMR (600 MHz, CDCl₃): δ 7.82 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 6.99 (t, J = 7.4 Hz, 1H), 2.95 (s, 1H), 2.38 (s, 3H), 2.11 – 1.98 (m, 2H), 1.82 (t, J = 12.6 Hz, 1H), 1.74 (s, 4H), 1.52 – 1.43 (m, 2H), 1.37 – 1.18 (m, 2H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 143.4, 142.2, 139.6, 133.0, 129.6, 127.6, 126.7, 122.9, 122.78, 114.8, 73.8, 48.1, 34.9, 24.3, 23.9, 21.7, 21.5, 20.8 ppm

HRMS (ESI⁺): calculated for C₂₀H₂₄NO₂S[M+H]⁺: 342.1522, found 342.1520.

3-Methyl-3-phenyl-2-tosyl-2-azaspiro[4.5]decane (31a)



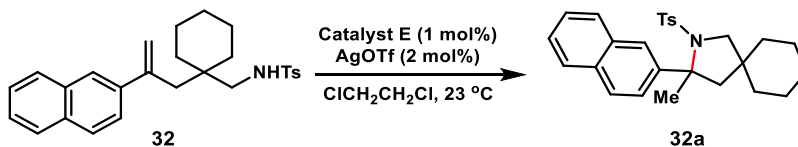
The general procedure I was followed. White solid (36.9 mg, 96% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, J = 8.3 Hz, 2H), 7.40 (dd, J = 8.2, 0.9 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 7.22 – 7.17 (m, 3H), 3.48 (d, J = 9.8 Hz, 1H), 3.40 (d, J = 9.8 Hz, 1H), 2.40 (s, 3H), 2.19 (d, J = 13.3 Hz, 1H), 1.97 (d, J = 13.3 Hz, 1H), 1.90 (s, 3H), 1.44 – 1.24 (m, 10H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 144.7, 142.6, 138.0, 133.1, 132.3, 129.2, 128.5, 127.9, 127.3, 126.0, 124.7, 124.5, 77.5, 76.8, 69.8, 40.7, 37.2, 28.2, 25.8, 23.5, 21.6 ppm

HRMS (ESI⁺): calculated for C₂₃H₃₀NO₂S[M+H]⁺: 384.1992, found 384.1987.

3-Methyl-3-(naphthalen-2-yl)-2-tosyl-2-azaspiro[4.5]decane 32a



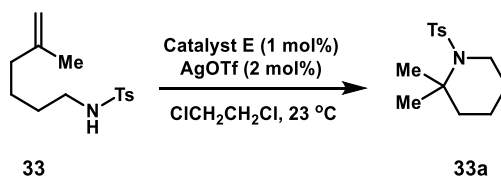
The general procedure I was followed. White solid (40.8 mg, 94% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, J = 1.7 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.67 (d, J = 8.7 Hz, 1H), 7.57 – 7.37 (m, 5H), 7.08 (d, J = 8.0 Hz, 2H), 3.60 (d, J = 9.8 Hz, 1H), 3.48 (d, J = 9.8 Hz, 1H), 2.36 (s, 3H), 2.28 (d, J = 13.4 Hz, 1H), 2.12 – 1.95 (m, 4H), 1.52 – 1.24 (m, 10H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 144.7, 142.6, 138.0, 133.1, 132.3, 129.2, 128.5, 127.9, 127.3, 126.0, 124.7, 124.5, 77.5, 76.8, 69.8, 40.7, 37.2, 28.2, 25.8, 23.5, 21.6 ppm

HRMS (ESI⁺): calculated for C₂₇H₃₂NO₂S[M+H]⁺: 434.2148, found 434.2145.

2,2-Dimethyl-1-tosylpiperidine (33a)



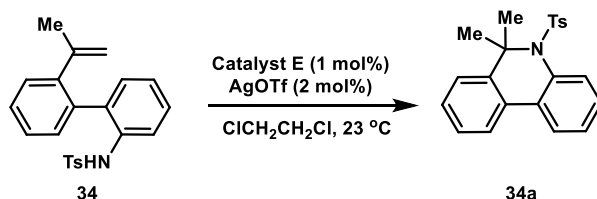
The general procedure I was followed. White solid (23.5 mg, 88% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.11 (m, 2H), 3.52 – 3.32 (m, 2H), 2.34 (s, 3H), 1.64 – 1.45 (m, 5H), 1.45 – 1.35 (m, 2H), 1.21 (s, 7H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 142.7, 140.5, 129.5, 127.1, 77.5, 76.8, 58.0, 43.8, 41.5, 26.3, 21.6, 20.6 ppm

HRMS (ESI⁺): calculated for C₁₄H₂₃NO₂S[M+H]⁺: 268.1366, found 268.1362.

6,6-Dimethyl-5-tosyl-5,6-dihydrophenanthridine (34a)



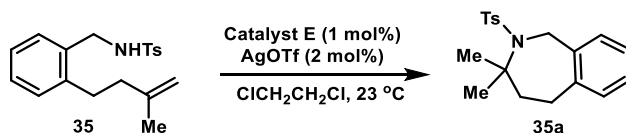
The general procedure I was followed. White solid (28.6 mg, 79% yield).

¹H NMR (600 MHz, CDCl₃): δ 7.73 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.55 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.38 (dtd, *J* = 19.5, 7.4, 1.4 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.08 (m, 3H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 2H), 2.17 (s, 6H), 1.25 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 142.6, 140.2, 136.9, 135.2, 131.8, 131.1, 130.7, 128.3, 128.2, 127.7, 127.4, 127.0, 123.7, 123.3, 77.4, 77.0, 60.5, 29.8, 21.4 ppm

HRMS (ESI⁺): calculated for C₂₂H₂₃NO₂S[M+H]⁺: 364.1366, found 364.1360.

3,3-Dimethyl-2-tosyl-2,3,4,5-tetrahydro-1H-benzo[*c*]azepine (35a)



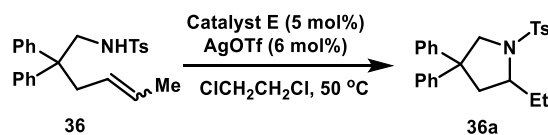
The general procedure I was followed. White solid (25.6 mg, 78% yield).

¹H NMR (600 MHz, CDCl₃): δ 7.29 – 7.23 (m, 2H), 7.18 (dd, *J* = 15.1, 6.3 Hz, 3H), 7.08 (d, *J* = 7.1 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 4.84 (s, 2H), 2.80 (d, *J* = 10.8 Hz, 2H), 2.32 (s, 3H), 1.94 – 1.86 (m, 2H), 1.41 (s, 6H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 142.4, 141.3, 139.4, 137.3, 129.7, 129.2, 128.9, 127.5, 126.8, 126.2, 77.4, 77.0, 61.2, 48.0, 42.1, 30.0, 26.6, 21.5 ppm

HRMS (ESI⁺): calculated for C₁₉H₂₄NO₂S[M+H]⁺: 330.1552, found 330.1518.

2-Ethyl-4,4-diphenyl-1-tosylpyrrolidine (36a)



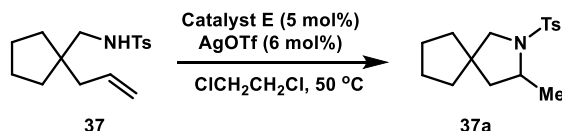
The general procedure II was followed. White solid (25.1 mg, 62% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, J = 8.2 Hz, 2H), 7.32 – 7.17 (m, 5H), 7.17 – 7.04 (m, 7H), 4.14 (d, J = 10.4 Hz, 1H), 4.04 (dd, J = 10.5, 0.9 Hz, 1H), 3.63 (d, J = 6.8 Hz, 1H), 2.84 – 2.69 (m, 1H), 2.38 (d, J = 6.6 Hz, 3H), 2.30 (dd, J = 12.8, 7.3 Hz, 1H), 2.04 (ddd, J = 11.9, 7.6, 3.3 Hz, 1H), 1.37 – 1.23 (m, 2H), 0.82 (t, J = 7.5 Hz, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 145.9, 144.9, 143.0, 135.8, 129.6, 128.6, 127.2, 126.7, 126.6, 126.6, 126.3, 77.48 (s), 76.8, 61.3, 58.8, 52.5, 42.6, 28.3, 21.6, 10.2 ppm

HRMS (ESI⁺): calculated for C₂₅H₂₈NO₂S[M+H]⁺: 406.1835, found 406.1829.

3-Methyl-2-tosyl-2-azaspiro[4.4]nonane (37a)



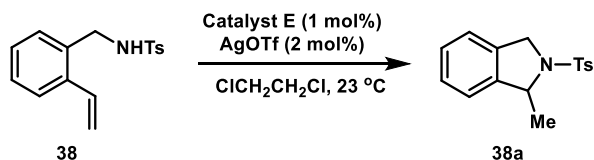
The general procedure II was followed. Colorless oil (28.4 mg, 97% yield)

¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 3.71 – 3.51 (m, 1H), 3.25 (d, J = 10.2 Hz, 1H), 3.07 (d, J = 10.2 Hz, 1H), 2.42 (s, 3H), 1.81 (dd, J = 12.1, 7.7 Hz, 1H), 1.65 – 1.42 (m, 7H), 1.40 (d, J = 6.2 Hz, 3H), 1.01 (dt, J = 14.7, 7.4 Hz, 1H), 0.96 – 0.83 (m, 1H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 143.2, 135.3, 129.6, 127.6, 60.1, 56.3, 48.6, 46.9, 36.8, 36.7, 24.6, 24.4, 22.9, 21.6 ppm

HRMS (ESI⁺): calculated for C₁₆H₂₄NO₂S[M+H]⁺: 294.1520, found 294.1522.

1-Methyl-2-tosylisoindoline (38a)



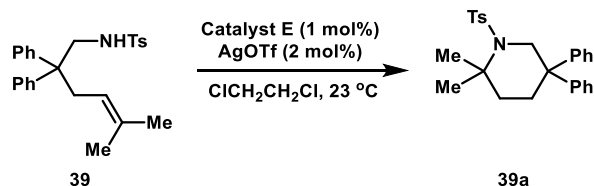
The general procedure I was followed. White solid (26.7 mg, 93% yield).

¹H NMR (600 MHz, CDCl₃): δ 7.75 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.22 (dd, J = 13.1, 6.9 Hz, 2H), 7.14 (d, J = 7.0 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 4.92 (d, J = 6.3 Hz, 1H), 4.73 (d, J = 13.8 Hz, 1H), 4.56 (d, J = 13.7 Hz, 1H), 2.38 (s, 3H), 1.67 (d, J = 6.4 Hz, 3H) ppm

^{13}C NMR (151 MHz, CDCl_3): δ 143.6, 141.8, 135.1, 134.8, 129.9, 127.9, 127.67 (s), 122.5, 77.4, 77.0, 62.0, 53.9, 23.9, 21.6 ppm

HRMS (ESI+): calculated for $\text{C}_{16}\text{H}_{18}\text{NO}_2\text{S}[\text{M}+\text{H}]^+$: 288.1053, found 288.1049.

2,2-Dimethyl-5,5-diphenyl-1-tosylpiperidine (39a)



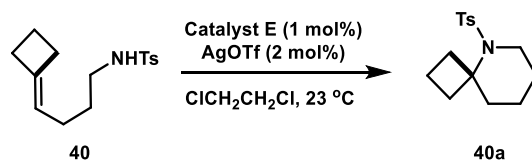
The general procedure I was followed. White solid (39.0 mg, 93% yield).

^1H NMR (600 MHz, CDCl_3): δ 7.40 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 7.9 Hz, 4H), 7.20 (t, J = 7.6 Hz, 4H), 7.10 (dd, J = 17.8, 7.6 Hz, 4H), 4.03 (s, 2H), 2.36 – 2.28 (m, 5H), 1.50 – 1.36 (m, 2H), 1.17 (s, 6H) ppm

^{13}C NMR (151 MHz, CDCl_3): δ 145.9, 143.0, 139.6, 129.5, 128.6, 127.6, 127.4, 126.3, 77.37 (s), 77.0, 57.5, 51.2, 46.6, 38.3, 31.1, 25.9, 21.6 ppm

HRMS (ESI+): calculated for $\text{C}_{26}\text{H}_{30}\text{NO}_2\text{S}[\text{M}+\text{H}]^+$: 420.1992, found 420.1987.

5-Tosyl-5-azaspiro[3.5]nonane (40a)



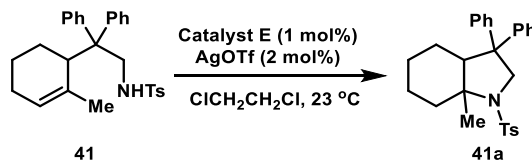
The general procedure I was followed. White solid (26.7 mg, 96% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, J = 8.3 Hz, 2H), 7.36 – 7.13 (m, 2H), 3.47 – 3.31 (m, 2H), 2.42 (s, 3H), 2.32 – 2.16 (m, 2H), 2.05 – 1.90 (m, 2H), 1.83 – 1.74 (m, 2H), 1.72 – 1.63 (m, 2H), 1.63 – 1.51 (m, 4H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 142.6, 141.3, 129.6, 126.7, 77.5, 76.8, 61.0, 44.5, 34.1, 31.8, 25.5, 21.6, 21.1, 14.6 ppm

HRMS (ESI+): calculated for $\text{C}_{15}\text{H}_{22}\text{NO}_2\text{S}[\text{M}+\text{H}]^+$: 280.1366, found 280.1363.

7a-Methyl-3,3-diphenyl-1-tosyloctahydro-1H-indole (41a)



The general procedure II was followed. White solid (40.6 mg, 91% yield).

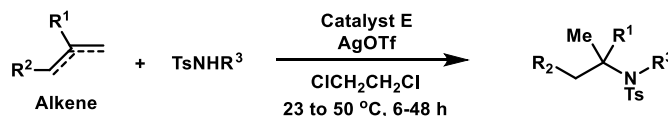
^1H NMR (600 MHz, CDCl_3): δ 7.59 (d, J = 8.1 Hz, 2H), 7.19 – 6.96 (m, 12H), 6.89 (d, J = 7.6 Hz, 2H), 4.29 (t, J = 19.9 Hz, 1H), 3.02 (d, J = 10.0 Hz, 1H), 2.56 (d, J = 6.5 Hz, 1H), 2.23 (d, J = 10.1 Hz, 3H),

2.19 (d, $J = 18.8$ Hz, 1H), 2.10 (t, $J = 17.7$ Hz, 1H), 1.90 (t, $J = 25.2$ Hz, 1H), 1.67 – 1.57 (m, 1H), 1.55 – 1.39 (m, 2H), 1.30 (s, 3H), 1.12 (dd, $J = 25.9, 21.1$ Hz, 2H), 0.89 (ddd, $J = 20.7, 7.4, 3.8$ Hz, 2H), 0.19 – -0.10 (m, 1H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 147.4, 144.8, 142.9, 137.8, 129.6, 128.5, 127.7, 127.2, 126.6, 77.5, 76.8, 67.2, 59.3, 53.8, 53.6, 49.7, 36.3, 26.7, 23.4, 21.6, 21.3, 20.6 ppm

HRMS (ESI⁺): calculated for $\text{C}_{28}\text{H}_{32}\text{NO}_2\text{S}[\text{M}+\text{H}]^+$: 446.2148, found 446.2143.

5.5 Intermolecular Hydroamination Catalyzed by the Catalyst E



General Procedure I

In a nitrogen filled glovebox, to a 4 mL vial with a magnetic stir bar were added catalyst **E** (3.0 mg, 0.002 mmol, 2 mol%), silver trifluoromethanesulfonate (1.0 mg, 0.004 mmol, 4 mol%), alkenes (0.1 mmol, 1.0 equiv.), sulfonamide (0.15 mmol, 1.5 equiv.) and $\text{ClCH}_2\text{CH}_2\text{Cl}$ (0.7 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at 23 °C or 50 °C for 8 to 24 h (unless otherwise stated: see experimental details). The reaction mixture was diluted with CH_2Cl_2 , filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography ($\text{EtOAc}/\text{hexane} = 1/20$ to 1/3) to give the product.

General Procedure II

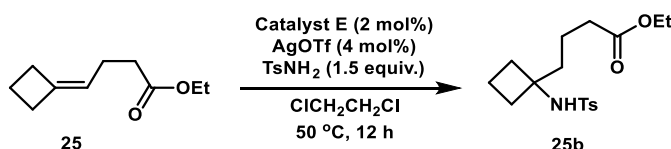
In a nitrogen filled glovebox, to a 5 mL vial with a magnetic stir bar were added catalyst **E** (3.0 mg, 0.002 mmol, 2 mol%), silver trifluoromethanesulfonate (1.0 mg, 0.004 mmol, 4 mol%), alkenes (0.5 mmol, 5.0 equiv.), sulfonamide (0.1 mmol, 1.0 equiv.) and $\text{ClCH}_2\text{CH}_2\text{Cl}$ (0.7 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at 23 °C or 50 °C for 6 to 8 h (unless otherwise stated: see experimental details). The reaction mixture was diluted with CH_2Cl_2 , filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography ($\text{EtOAc}/\text{hexane} = 1/20$ to 1/3) to give the product.

General procedure III

In a nitrogen filled glovebox, to a 4 mL vial with a magnetic stir bar were added catalyst **E** (7.6 mg, 0.005 mmol, 5 mol%), silver trifluoromethanesulfonate (1.5 mg, 0.006 mmol, 6 mol%), alkenes (0.1 mmol, 1.0 equiv.), sulfonamide (0.15 mmol, 1.5 equiv.) and $\text{ClCH}_2\text{CH}_2\text{Cl}$ (0.7 mL). Then the vial was taken outside of the glovebox and the resulting mixture was stirred at 50 °C for 48 h (unless otherwise stated: see experimental details). The reaction mixture was diluted with CH_2Cl_2 , filtered through a pad of celite and concentrated. The residue was purified with silica gel chromatography ($\text{EtOAc}/\text{hexane} = 1/20$ to 1/3) to

give the product.

Ehyl 4-(1-((4-methylphenyl)sulfonamido)cyclobutyl)butanoate (25b)



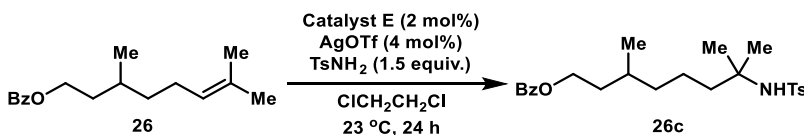
The general procedure I was followed and the reaction mixture was stirred at 50 °C for 12 h. The crude residue was purified by column chromatography (EtOAc/hexane= 1/20 to 1/3) to yield **25b** (26.1 mg, 77% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.94 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 2.19 – 2.04 (m, 4H), 1.94 – 1.81 (m, 2H), 1.79 – 1.59 (m, 4H), 1.58 – 1.42 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 173.6, 143.2, 140.1, 129.7, 127.1, 60.4, 59.6, 37.2, 34.0, 33.6, 21.6, 19.1, 14.9, 14.4 ppm

HRMS (ESI⁺): calc'd for C₁₇H₂₆NO₄S [M+H]⁺: 340.1583, found 340.1573.

3,7-Dimethyl-7-((4-methylphenyl)sulfonamido)octyl benzoate (26c)



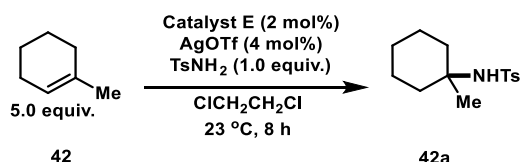
The general procedure I was followed and the reaction mixture was stirred at 23 °C for 24 h. The crude residue was purified by column chromatography (EtOAc/hexane= 1/20 to 1/3) to yield **26c** (39.7 mg, 92% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ 8.04 (dd, J = 8.3, 1.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.63 – 7.49 (m, 1H), 7.49 – 7.40 (m, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.60 (s, 1H), 4.46 – 4.22 (m, 2H), 2.40 (s, 3H), 1.83 – 1.68 (m, 1H), 1.54 (dd, J = 11.5, 5.4 Hz, 2H), 1.47 – 1.39 (m, 2H), 1.33 – 1.19 (m, 4H), 1.16 (d, J = 2.5 Hz, 6H), 1.13 – 1.02 (m, 1H), 0.91 (d, J = 6.4 Hz, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 166.8, 142.9, 140.7, 133.0, 130.6, 129.7, 129.6, 128.5, 127.1, 63.5, 57.2, 43.2, 37.2, 35.6, 30.0, 27.9, 27.8, 21.6, 21.3, 19.6 ppm

HRMS (ESI⁺): calc'd for C₂₄H₃₄NO₄S [M+H]⁺: 432.2209, found 432.2201.

4-Methyl-N-(1-methylcyclohexyl)benzenesulfonamide (42a)



The general procedure II was followed and the reaction mixture was stirred at 23 °C for 8 h. The crude

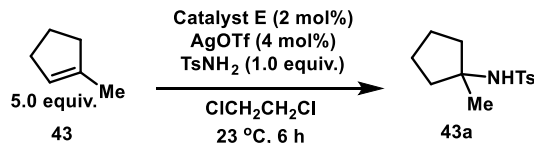
residue was purified by column chromatography (hexane: EtOAc = 20:1 to 3:1) to yield **42a** (23.0 mg, 86% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 4.70 (s, 1H), 2.41 (s, 3H), 1.76 – 1.63 (m, 2H), 1.38 (d, J = 8.9 Hz, 8H), 1.17 (s, 3H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 142.8, 141.0, 129.6, 127.0, 57.0, 38.5, 26.9, 25.3, 21.9, 21.6 ppm

HRMS (ESI⁺): calc'd for C₁₄H₂₁NO₂SNa [M+Na]⁺: 290.1191, found 290.1182.

4-Methyl-N-(1-methylcyclopentyl)benzenesulfonamide (**43a**)



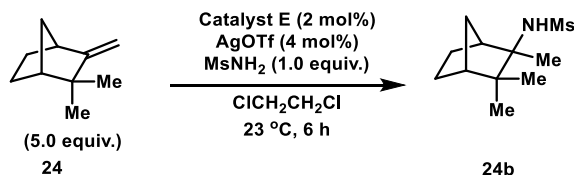
The general procedure II was followed and the reaction mixture was stirred at 23 °C for 6 h. The crude residue was purified by column chromatography (hexane: EtOAc = 20:1 to 3:1) to yield **43a** (24.0 mg, 95% yield) as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.78 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 4.79 (s, 1H), 2.42 (s, 3H), 1.86 – 1.74 (m, 2H), 1.61 – 1.51 (m, 4H), 1.50 – 1.46 (m, 2H), 1.28 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 142.9, 140.5, 129.6, 127.0, 64.8, 40.2, 26.7, 23.0, 21.6 ppm

HRMS (ESI⁺): calc'd for C₁₃H₁₉NO₂SNa [M+Na]⁺: 276.1034, found 276.1025.

N-((1S,2R,4R)-2,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)methanesulfonamide (**24b**)



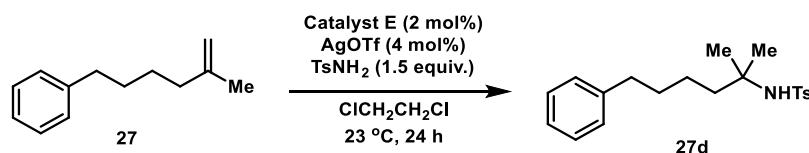
The general procedure II was followed and the reaction mixture was stirred at 23 °C for 6 h. The crude residue was purified by column chromatography (EtOAc/hexane = 1/20 to 1/3) to yield **24b** (22.6 mg, 98% yield) as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 4.50 (d, J = 8.9 Hz, 1H), 3.28 (td, J = 8.9, 4.2 Hz, 1H), 2.92 (s, 3H), 1.93 – 1.85 (m, 1H), 1.76 – 1.66 (m, 3H), 1.60 (td, J = 12.1, 4.2 Hz, 1H), 1.21 – 1.15 (m, 1H), 1.14 – 1.08 (m, 1H), 0.92 (s, 3H), 0.88 (s, 3H), 0.83 (s, 3H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 61.6, 48.7, 47.1, 45.1, 41.3, 40.6, 36.4, 27.0, 20.4, 20.3, 12.5 ppm

HRMS (ESI⁺): calc'd for C₁₁H₂₁NO₂SNa [M+Na]⁺: 254.1191, found 254.1181.

4-Methyl-N-(2-methyl-6-phenylhexan-2-yl)benzenesulfonamide (**27d**)



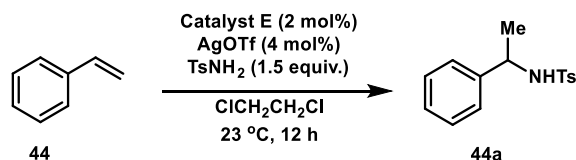
The general procedure I was followed and the reaction mixture was stirred at 23 °C for 24 h. The crude residue was purified by column chromatography (EtOAc/hexane= 1/20 to 1/3) to yield **27d** (29.7 mg, 86% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, J = 8.3 Hz, 1H), 7.22 – 7.18 (m, 4H), 7.14 – 7.07 (m, 1H), 7.06 (d, J = 8.3 Hz, 2H), 4.61 (s, 1H), 2.46 (t, J = 8.1 Hz, 1H), 2.33 (s, 3H), 1.48 – 1.33 (m, 4H), 1.27 – 1.14 (m, 2H), 1.08 (s, 6H) ppm

¹³C NMR (101 MHz, CDCl₃): δ 142.9, 142.6, 140.7, 129.6, 128.45, 128.4, 127.1, 125.8, 57.2, 42.8, 35.9, 31.7, 27.8, 23.7, 21.6 ppm

HRMS (ESI⁺): calc'd for C₂₀H₂₇NO₂SNa [M+Na]⁺: 368.1660, found 368.1650.

4-Methyl-N-(1-phenylethyl)benzenesulfonamide (**44a**)



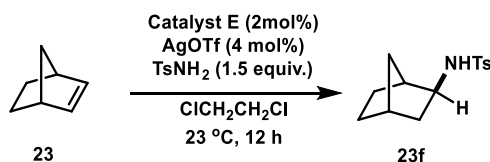
The general procedure I was followed and the reaction mixture was stirred at 23 °C for 12 h. The crude residue was purified by column chromatography (EtOAc/hexane= 1/20 to 1/3) to yield **44a** (26.7 mg, 97% yield) as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.62 (d, J = 7.7 Hz, 2H), 7.18 (t, J = 7.3 Hz, 5H), 7.10 (d, J = 7.2 Hz, 2H), 5.00 (d, J = 6.8 Hz, 1H), 4.46 (p, J = 6.8 Hz, 1H), 2.38 (s, 3H), 1.42 (d, J = 6.8 Hz, 3H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 143.2, 142.2, 137.8, 129.6, 128.7, 127.6, 127.2, 126.2, 53.8, 23.7, 21.6 ppm

HRMS (ESI⁺): calc'd for C₁₅H₁₇NO₂SNa [M+Na]⁺: 298.0878, found 298.0870.

N-((1S,2S,4R)-bicyclo[2.2.1]heptan-2-yl)-4-methylbenzenesulfonamide (**23f**)



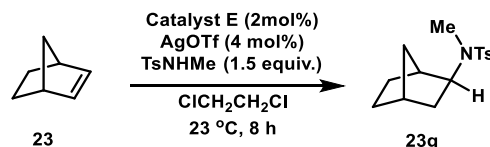
The general procedure I was followed and the reaction mixture was stirred at 23 °C for 12 h. The crude residue was purified by column chromatography (EtOAc/hexane= 1/20 to 1/5) to yield **23f** (26.1 mg, 98% yield) as a white solid.

¹H NMR (600 MHz, CDCl₃): δ 7.75 (d, J = 7.7 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 4.51 (d, J = 6.2 Hz,

1H), 3.12 (s, 1H), 2.43 (s, 3H), 2.19 (s, 1H), 2.10 (s, 1H), 1.58 (d, $J = 9.4$ Hz, 1H), 1.48 – 1.34 (m, 2H), 1.31 (d, $J = 10.1$ Hz, 1H), 1.15 (d, $J = 13.2$ Hz, 1H), 1.11 (d, $J = 10.1$ Hz, 1H), 1.08 – 0.96 (m, 2H) ppm
 ^{13}C NMR (151 MHz, CDCl_3): δ 143.4, 138.1, 129.8, 127.2, 56.8, 42.6, 41.0, 35.7, 35.3, 28.1, 26.5, 21.7 ppm

HRMS (ESI⁺): calc'd for $\text{C}_{14}\text{H}_{20}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 266.1215, found 266.1205.

***N*-((1*S*,2*S*,4*R*)-bicyclo[2.2.1]heptan-2-yl)-*N*,4-dimethylbenzenesulfonamide (23g)**



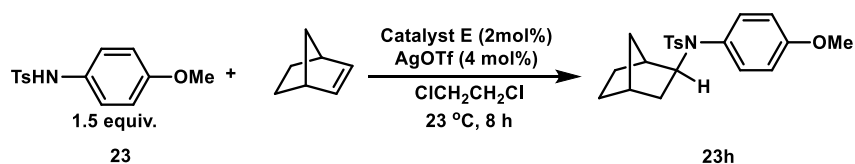
The general procedure I was followed and the reaction mixture was stirred at 23 °C for 8 h. The crude residue was purified by column chromatography (EtOAc/hexane= 1/20 to 1/5) to yield **23g** (25.1 mg, 90% yield) as a white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.3$ Hz, 2H), 3.83 (dd, $J = 8.5, 5.9$ Hz, 1H), 2.71 (s, 3H), 2.42 (s, 3H), 2.20 (s, 1H), 1.87 (s, 1H), 1.55 (ddd, $J = 12.8, 8.5, 2.2$ Hz, 1H), 1.45 – 1.32 (m, 4H), 1.21 – 1.11 (m, 1H), 1.12 – 1.00 (m, 2H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 143.1, 136.4, 129.7, 127.4, 60.0, 39.24, 36.9, 36.8, 35.9, 30.0, 29.3, 27.4, 21.6 ppm

HRMS (ESI⁺): calc'd for $\text{C}_{15}\text{H}_{22}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 280.1371, found 280.1362.

***N*-((1*S*,2*S*,4*R*)-bicyclo[2.2.1]heptan-2-yl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (23h)**



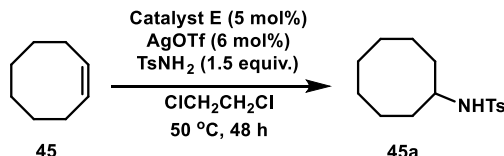
The general procedure I was followed and the reaction mixture was stirred at 23 °C for 8 h. The crude residue was purified by column chromatography (EtOAc/hexane= 1/25 to 1/7) to yield **23h** (35.9 mg, 97% yield) as a white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.58 (d, $J = 8.3$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 2H), 6.92 – 6.85 (m, 2H), 6.83 – 6.75 (m, 2H), 4.11 (dd, $J = 8.1, 5.3$ Hz, 1H), 3.79 (s, 3H), 2.42 (s, 3H), 2.21 (d, $J = 3.0$ Hz, 1H), 2.03 (s, 1H), 1.70 (ddd, $J = 12.8, 8.4, 2.1$ Hz, 1H), 1.53 (ddd, $J = 8.0, 4.6, 2.5$ Hz, 1H), 1.40 (ddd, $J = 10.1, 8.0, 3.8$ Hz, 1H), 1.29 – 1.17 (m, 1H), 1.17 – 1.02 (m, 1H), 0.79 (dd, $J = 9.9, 0.8$ Hz, 1H), 0.73 – 0.59 (m, 1H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 159.5, 143.1, 137.8, 133.5, 129.5, 127.8, 114.0, 62.3, 55.5, 42.0, 38.8, 35.7, 28.8, 28.1, 21.7 ppm

HRMS (ESI⁺): calc'd for $\text{C}_{21}\text{H}_{26}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 372.1628, found 372.1627.

N-cyclooctyl-4-methylbenzenesulfonamide (**45a**)



The general procedure III was followed and the reaction mixture was stirred at 50 °C for 48 h. The crude residue was purified by column chromatography (EtOAc/hexane= 1/20 to 1/5) to yield **45a** (18.3 mg, 65% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 4.31 (d, J = 7.7 Hz, 1H), 3.37 (dq, J = 12.5, 4.3 Hz, 1H), 2.43 (s, 3H), 1.80 – 1.63 (m, 2H), 1.63 – 1.33 (m, 12H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 143.3, 138.4, 129.8, 127.1, 54.0, 32.9, 27.3, 25.4, 23.3, 21.7 ppm

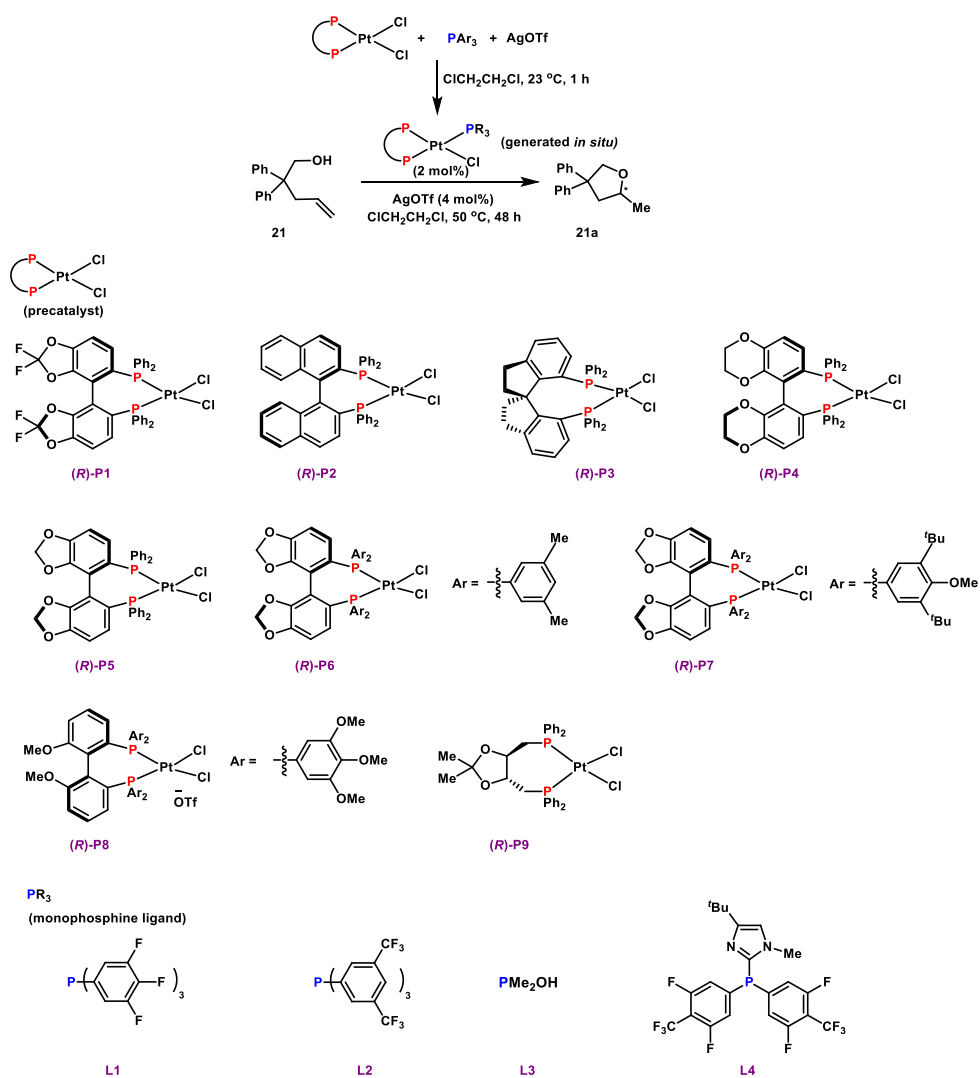
The spectroscopic data were in accordance with those reported in literature.²⁵

6. Catalytic Enantioselective Hydrofunctionalization

6.1 General Procedure for Chiral Catalyst Screening by Hydroalkoxylation of **21**

2,2-Diphenylpent-4-en-1-ol **21** was selected as model substrate and the screening was performed in an argon filled-glovebox. 9 Chiral precatalysts and 4 monophosphine ligands were investigated.

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the precatalyst (0.002mmol, 2 mol%), silver trifluoromethanesulfonate (1.5 mg, 0.006 mmol, 6 mol%), ClCH₂CH₂Cl (200 μ L). The mixture was stirred at room temperature (23 °C) for 1 h. And monophosphine ligand (0.002mmol, 2 mol%) dissolved in ClCH₂CH₂Cl (100 μ L) was added to the above mixture. The resulting solution was stirred for 5 min and **21** (24 mg, 0.1 mmol, 1.0 equiv) was added. The mixture was stirred at 50 °C for 48 h. The reaction mixture was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using hexane/ ethyl acetate (20/1) to provide the product **21a**.



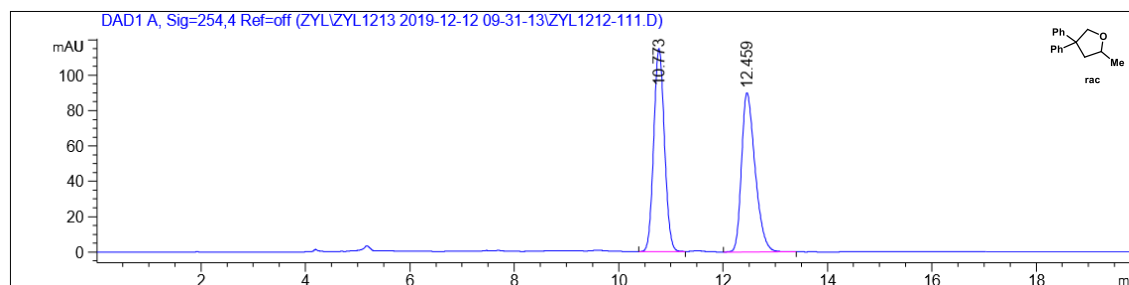
Supplementary Figure 2. Chiral Pre-catalyst and Monodentate Phosphine Ligand

Supplementary Table 5: Chiral Catalysts Screening by Hydroalkoxylation of 21

Entry	Precatalyst	Monophosphine Ligand	Yield (%)	ee (%)
1	P1	L1	20	0
2	P2	L1	36	0
3	P3	L1	40	0
4	P4	L1	trace (21) ^b	-- (0) ^b
5	P5	L1	38	0
6	P6	L1	15	0
7	P7	L1	trace (20) ^b	-- (0) ^b
8	P8	L1	25	0
9	P9	L1	N.R.	--
10	P1	L2	18	0
11	P2	L2	24	0
12	P9	L3	N.R.	--
13	P1	L4	35 ^b	35 ^b
14	P2	L4	44 ^b	35 ^b
15	P2	--	trace	--

^a Yields of isolated products are given. ^b 5 mol% catalyst was generated in situ (Precatalyst (5 mol%), L (5 mol%), AgOTf (12 mol%)), $\text{ClCH}_2\text{CH}_2\text{Cl}$, 50 °C, 48 h.

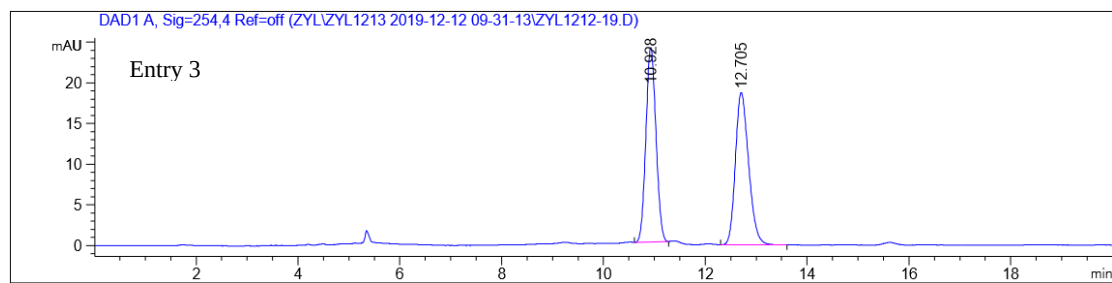
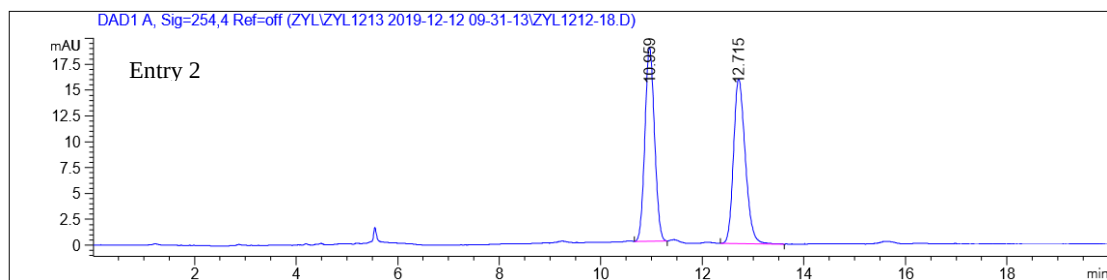
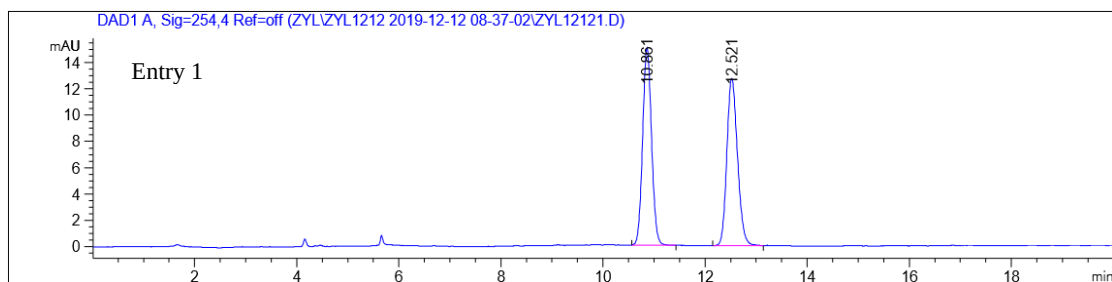
HPLC (AD-H, 0.46*25 cm, 5 μm , hexane / isopropylalcohol = 99/1, flow 0.7 mL/min, detection at 254 nm)

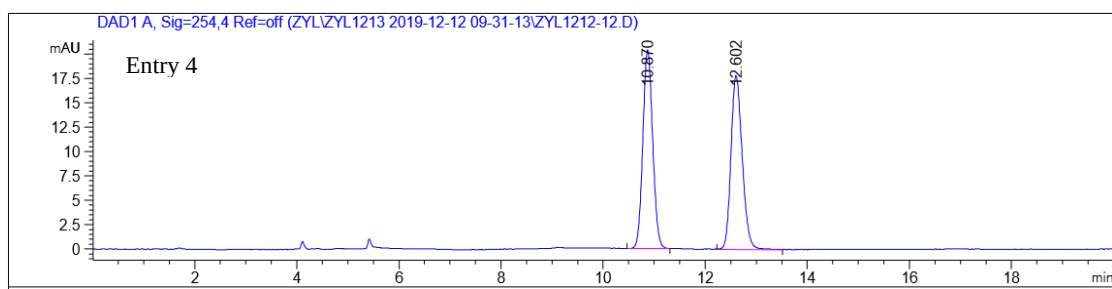


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.773	BB	0.2221	1634.30518	114.82312	50.1018
2	12.459	BB	0.2750	1627.66626	90.00819	49.8982

Totals : 3261.97144 204.83131

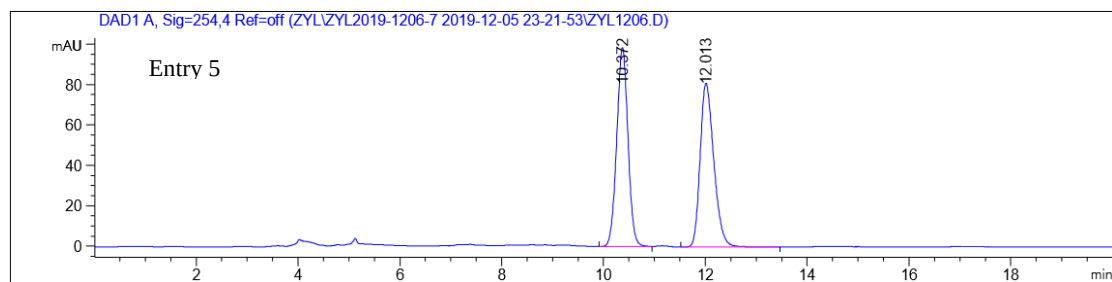




Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.870	BB	0.2103	273.16055	20.38731	50.0295
2	12.602	BB	0.2364	272.83859	17.84177	49.9705

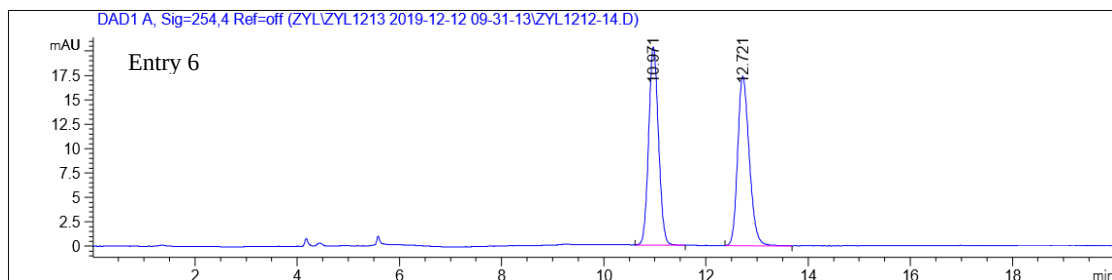
Totals : 545.99915 38.22907



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.372	BB	0.2371	1509.30530	98.34425	50.0029
2	12.013	BB	0.2852	1509.12976	81.04923	49.9971

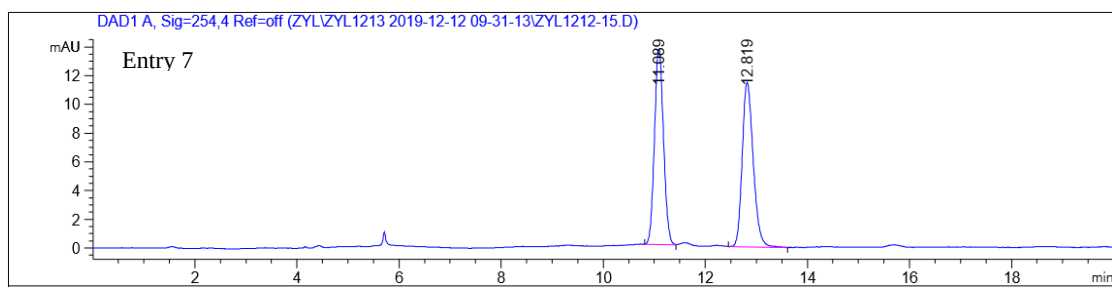
Totals : 3018.43506 179.39349



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.971	BB	0.2079	271.35812	20.30522	49.8231
2	12.721	BB	0.2436	273.28510	17.36303	50.1769

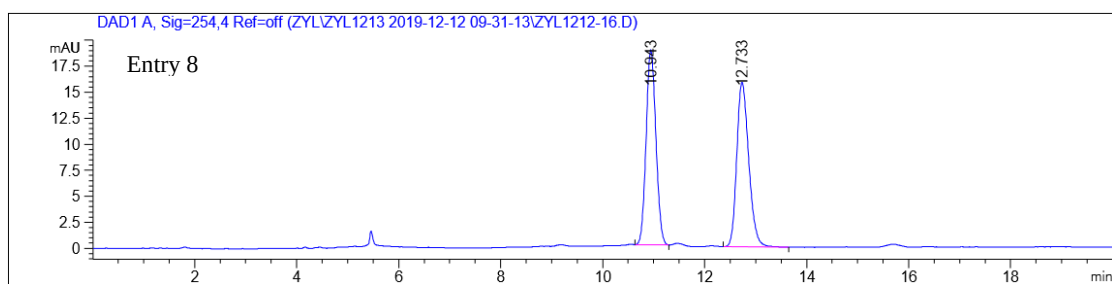
Totals : 544.64322 37.66825



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.089	BB	0.1908	166.52278	13.60602	49.2429
2	12.819	BB	0.2308	171.64363	11.45737	50.7571

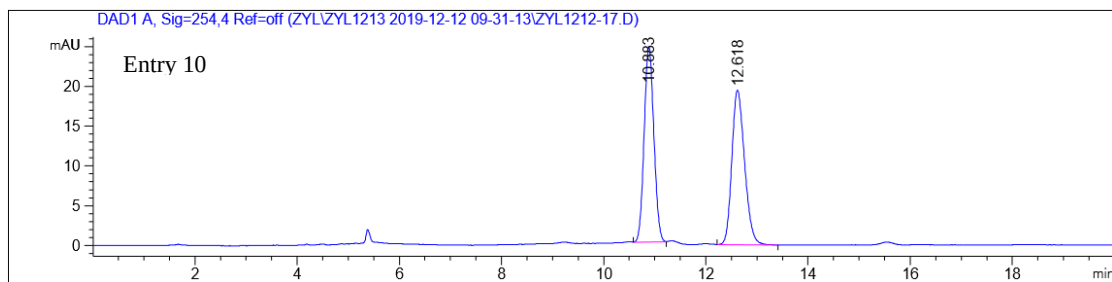
Totals : 338.16641 25.06338



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.943	BB	0.2073	249.58208	18.74781	49.1462
2	12.733	BB	0.2525	258.25430	15.81542	50.8538

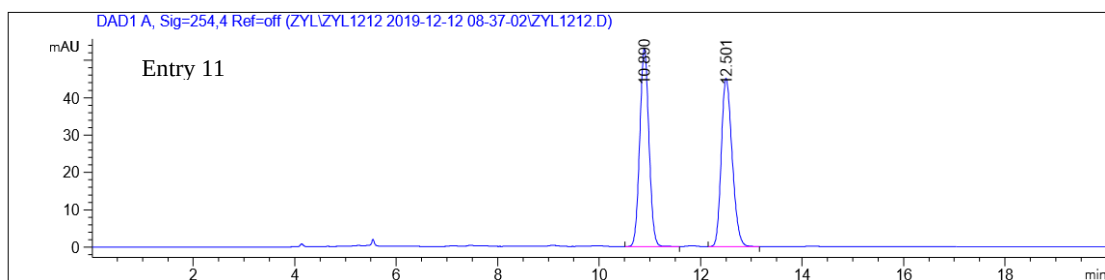
Totals : 507.83638 34.56324



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.883	BB	0.2082	324.20340	24.52976	49.0294
2	12.618	BB	0.2685	337.03900	19.42263	50.9706

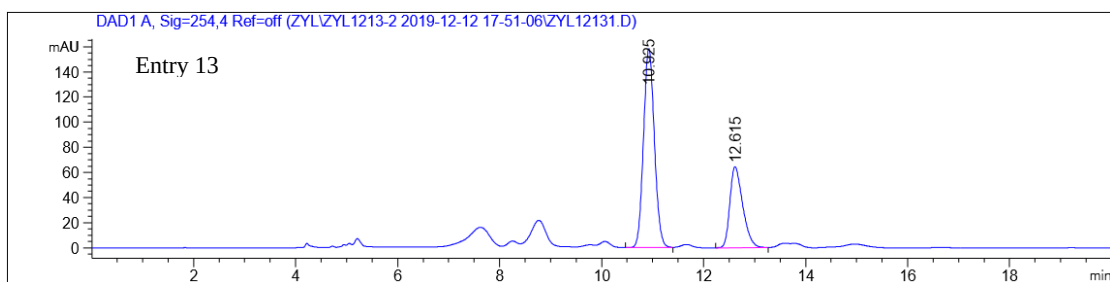
Totals : 661.24240 43.95240



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.890	BB	0.1954	670.22284	53.04930	49.9197
2	12.501	BB	0.2319	672.37891	45.11346	50.0803

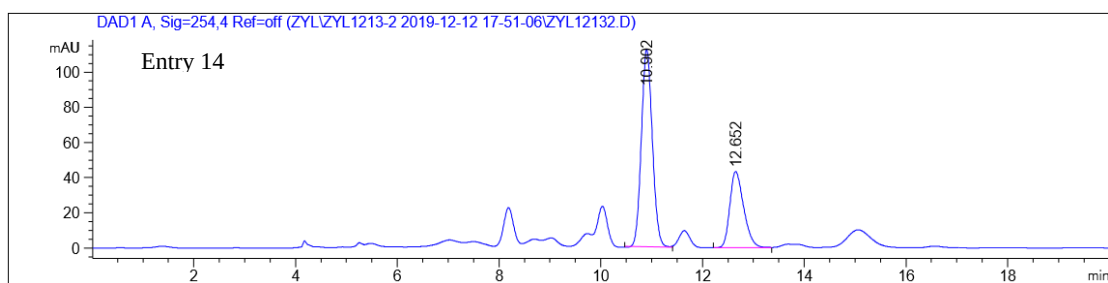
Totals : 1342.60175 98.16276



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.925	BB	0.2304	2338.62427	158.22594	67.5249
2	12.615	BB	0.2654	1124.72827	64.50167	32.4751

Totals : 3463.35254 222.72761



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.902	MM	0.2505	1686.37671	112.20116	67.3360
2	12.652	BB	0.2882	818.04419	43.35111	32.6640

Totals : 2504.42090 155.55228

6.2 Control Experiments

Procedure: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the precatalyst (0.002mmol, 5 mol%), silver trifluoromethanesulfonate (0.01 mmol, 10 mol%), $\text{ClCH}_2\text{CH}_2\text{Cl}$ (200 μL). The resulting mixture was stirred at room temperature (23 $^\circ\text{C}$) for 1 h. And monophosphine ligand **L4**,

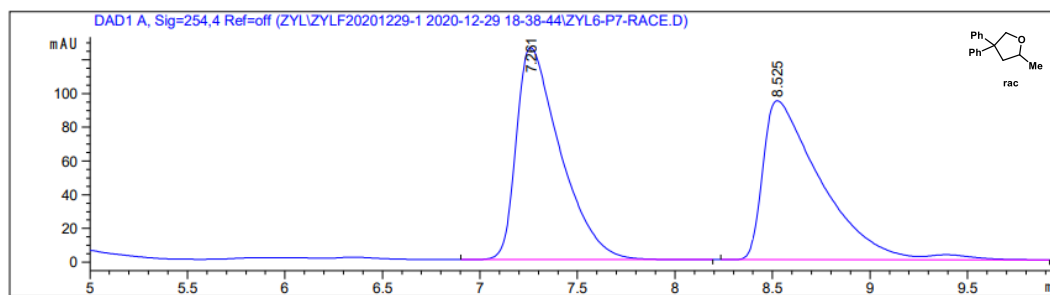
HOTf, **1** (24 mg, 0.1 mmol, 1.0 equiv) and 4,4'-di-*tert*-butyl-1,1'-biphenyl (0.5 equiv.) used as an internal standard were added into the above mixture. The mixture was stirred at 50 °C for 48 h. The reaction mixture was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using hexane/ ethyl acetate (20/1) to provide the product **21a**. The yield of **1a** was determined by crude ¹H NMR analysis.

Supplementary Table 6: The Effect of HOTf on Catalytic Activity and Enantioselectivity

L4

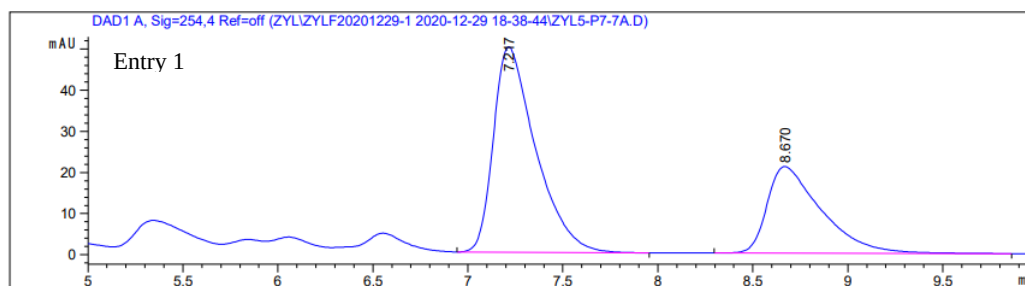
Entry	catalyst	additive	HOTf(x mol%)	Yield (%) ^a	ee (%)
1	(BINAP)PtCl ₂	L4	0	27	30
2	(BINAP)PtCl ₂	L4	5	50	13
3	BINAP	L4	0	0	--
4	BINAP	L4	5	91	0
5	(BINAP)PtCl ₂	--	0	<5	--

HPLC (AD-H, 0.46*25 cm, 5μm, hexane / isopropylalcohol = 99/1, flow 0.7 mL/min, detection at 254 nm)



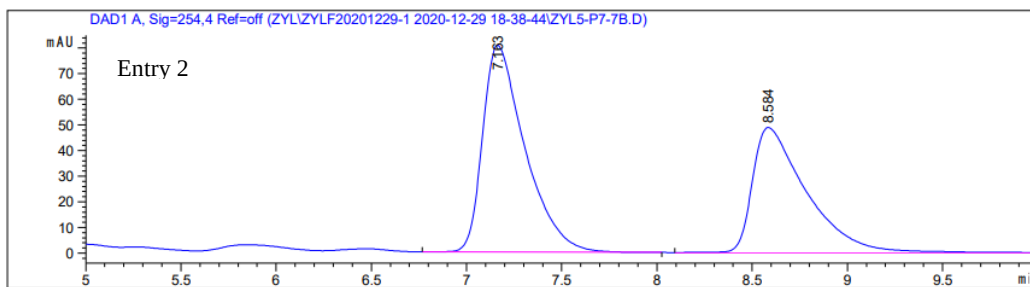
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.261	BB	0.2310	1972.47388	125.76474	50.1004
2	8.525	BV R	0.2924	1964.56946	94.24731	49.8996



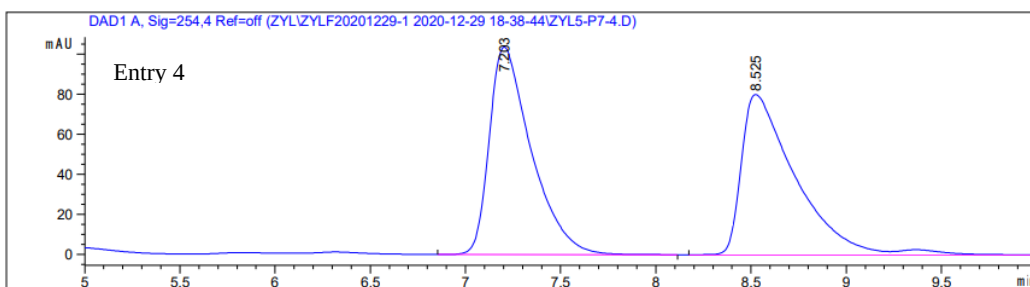
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.217	BB	0.2283	770.54462	49.86490	64.8991
2	8.670	BB	0.2849	416.75110	21.05275	35.1009



Signal 1: DAD1 A, Sig=254,4 Ref=off

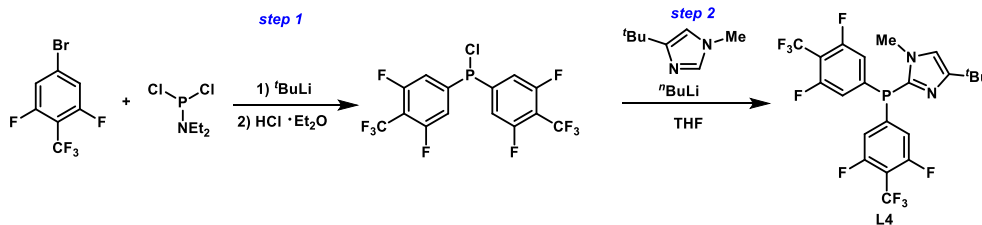
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.163	BB	0.2286	1248.29028	80.65449	56.6351
2	8.584	BB	0.2825	955.80389	48.79872	43.3649



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.203	BB	0.2268	1584.15149	103.35302	50.0544
2	8.525	BV R	0.2803	1580.70898	79.84180	49.9456

6.3 Synthesis of the Chiral Catalysts M and N



Step 1: Chlorobis(3,5-difluoro-4-(trifluoromethyl)phenyl)phosphane was prepared according to literature²¹. To a suspension of 5-bromo-1,3-difluoro-2-(trifluoromethyl)benzene (6.26 g, 24 mmol) in Et_2O (20 mL) at -78°C under argon was added dropwise $t\text{-BuLi}$ (18.5 mL, 1.3 M in hexanes, 24 mmol).

The reaction was stirred at -78 °C for 1 h. The solution of 1,1-dichloro-*N,N*-diethylphosphanamine (1.91 g, 11 mmol) dissolved in Et₂O was added dropwise. The mixture was stirred at room temperature (23 °C) for 12 h. The reaction was quenched with aqueous NH₄Cl (50 mL) and extracted with ether (2 x 60 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under vacuum. The crude product was dissolved in Hexane at -10 °C. A solution of HCl in Et₂O (3 equiv., 1.45 M in Et₂O) was added. The mixture was stirred -10 °C for 2 h. The solution was filtered through a pad of celite and concentrated. The crude product used in the next step without further purification.

Step 2: Monophosphine ligand **L4** was prepared according to literature²². To a suspension of 4-(*tert*-butyl)-1-methyl-1*H*-imidazole in Et₂O (20 mL) at -78 °C under argon was added dropwise *n*-BuLi (4.2 mL, 2.4 M in hexanes, 10 mmol). The reaction was stirred at -78 °C for 1 h. The solution of chlorobis(3,5-difluoro-4-(trifluoromethyl)phenyl)phosphane (2.57 g, 6 mmol) dissolved in THF was added dropwise. The mixture was stirred at 23 °C for 2 h. The reaction was quenched with aqueous NH₄Cl (50 mL) and extracted with ether (2 x 60 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under vacuum. The crude product was purified by silica gel column chromatography using hexane/ ethyl acetate (20/1) to provide the product **L4** 2-(bis(3,5-difluoro-4-(trifluoromethyl)phenyl)phosphanyl)-4-(*tert*-butyl)-1-methyl-1*H*-imidazole (2.50 g, 79%) as a pale yellow solid.

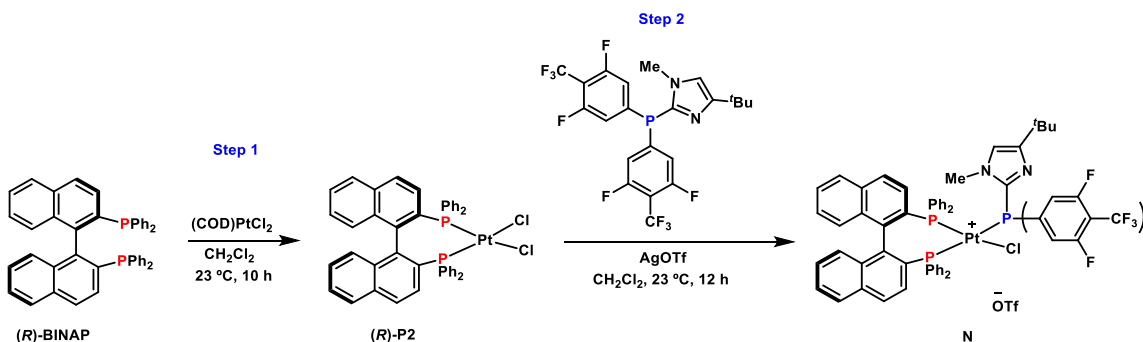
¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.32 (m, 4H), 6.84 (d, *J* = 3.6 Hz, 1H), 3.84 (s, 3H), 1.30 (s, 9H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 159.60 (dd, *J* = 263.7, 9.1 Hz), 156.1 (d, *J* = 3.0 Hz), 143.9 (dd, *J* = 18.3, 8.0 Hz), 139.2 (d, *J* = 6.8 Hz), 121.6 (q, *J* = 274.3 Hz), 119.1 (d, *J* = 1.6 Hz), 117.8 – 117.5 (m), 108.9 – 108.2 (m), 34.0, 32.3, 30.2 ppm

³¹P NMR (162 MHz, CDCl₃): δ -37.5 ppm

¹⁹F NMR (376 MHz, CDCl₃): δ -56.5 (t, *J* = 22.1 Hz), -109.7 (q, *J* = 22.0 Hz) ppm

HRMS (ESI⁺): calc'd for C₂₂H₁₈F₁₀N₂P [M+H]⁺: 531.1042, found 531.1037.



Step 1: In an argonfilled glovebox, to a 20 mL scintillation vial with a magnetic stir bar were added (R)-BINAP(200 mg, 0.32 mmol), (COD)PtCl₂ (120 mg, 0.32 mmol) and 3 mL CH₂Cl₂, then the vial was taken outside of the dry box and the resulting mixture was stirred at room temperature (23 °C) for 10 h. The yellow solution was filtered and then evaporated to provide yellow solid, which was recrystallized through 1 mL CH₂Cl₂ and 1 mL hexane to give yellow precipitate. The solid was collected and dried in *vacuo* to yield **(R)-P2** (257 mg, 91% yield).

Step 2: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added **(R)-P2** (100 mg, 0.11 mmol), silver trifluoromethanesulfonate (29 mg, 0.11 mmol), 2-(bis(3,5-difluoro-4-(trifluoromethyl)phenyl)phosphanyl)-4-(*tert*-butyl)-1-methyl-1H-imidazole (65 mg, 0.12 mmol) and 2 mL CH₂Cl₂. Then the vial was taken outside of the glovebox and the resulting mixture was stirred at room 23 °C for 12 h. The orange solution was filtered and CH₂Cl₂ was evaporated to provide pale yellow solid, which was recrystallized through CH₂Cl₂ and hexane to give white precipitate. The solid was collected and dried in *vacuo* to yield catalyst **N** (168 mg, 98% yield).

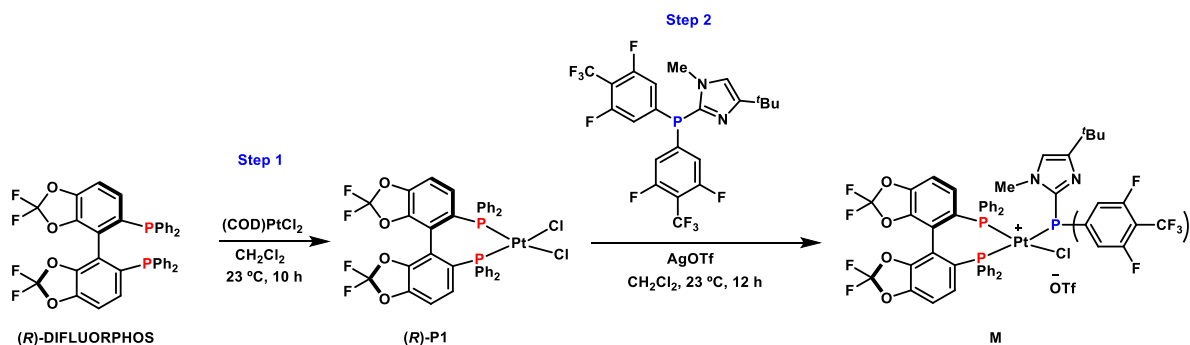
¹H NMR (600 MHz, CDCl₃): δ 8.30 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.54 – 7.49 (m, 2H), 7.47 – 7.28 (m, 17H), 7.13 – 7.09 (m, 1H), 7.09 – 7.05 (m, 1H), 6.98 – 6.90 (m, 3H), 6.85 – 6.84 (m, 3H), 6.57 (d, *J* = 8.6 Hz, 1H), 6.50 (d, *J* = 8.5 Hz, 1H), 6.44 (s, 1H), 3.83 (s, 3H), 1.51 (s, 9H) ppm

³¹C NMR (150 MHz, CDCl₃): δ 160.1 – 157.4 (m), 155.7 (d, *J* = 11.7 Hz), 140.6 – 140.5 (m), 138.7 – 138.6 (m), 136.2 – 136.0 (m), 135.2 (d, *J* = 10.1 Hz), 134.5 (d, *J* = 20.5 Hz), 134.1 – 134.0 (m), 133.2 – 132.6 (m), 132.1, 131.6 (d, *J* = 9.3 Hz), 130.9 (d, *J* = 10.6 Hz), 130.0 (d, *J* = 9.4 Hz), 129.5 (d, *J* = 11.1 Hz), 128.9 (d, *J* = 34.8 Hz), 128.5 (d, *J* = 34.1 Hz), 128.2 (d, *J* = 11.3 Hz), 127.8 (d, *J* = 10.5 Hz), 127.5 (d, *J* = 14.1 Hz), 127.3 (d, *J* = 7.2 Hz), 127.0 (d, *J* = 6.9 Hz), 126.6 (d, *J* = 5.6 Hz), 123.0, 121.0 (q, *J* = 319.5 Hz), 120.8 (q, *J* = 272.7 Hz), 120.0 – 119.5 (m), 118.7, 118.4 – 118.2 (m), 37.7, 32.4, 30.2 ppm

³¹P NMR (243 MHz, CDCl₃): δ 16.8 (d, ²*J*_{P-P} = 21 Hz, ¹*J*_{Pt-P} = 2760 Hz), 15.0 (d, ²*J*_{P-P} = 21 Hz, ¹*J*_{Pt-P} = 2762 Hz), 7.6 (t, ²*J*_{P-P} = 18 Hz, ¹*J*_{Pt-P} = 3554 Hz) ppm

¹⁹F NMR (565 MHz, CDCl₃): δ -56.7 – 57.0 (m), -77.9, -108.1 (d, *J* = 20.0 Hz) ppm

HRMS (ESI+): calc'd for C₆₆H₄₉ClF₁₀N₂P₃Pt [M-OTf]⁺: 1382.2280, found 1382.2275.



Step 1: In an argonfilled glovebox, to a 20 mL scintillation vial with a magnetic stir bar were added (R)-DIFLUORPHOS (100 mg, 0.15 mmol), (COD)PtCl₂ (55 mg, 0.15 mmol) and 1 mL CH₂Cl₂, then the vial was taken outside of the dry box and the resulting mixture was stirred at 23 °C for 10 h. The yellow solution was filtered and then evaporated to provide yellow solid, which was recrystallized through 1 mL CH₂Cl₂ and 1 mL hexane to give yellow precipitate. The solid was collected and dried in *vacuo* to yield **(R)-P1** (137 mg, 99% yield).

Step 2: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added **(R)-P1** (50 mg, 0.05 mmol), silver trifluoromethanesulfonate (14 mg, 0.05 mmol), 2-(bis(3,5-difluoro-4-(trifluoromethyl)phenyl)phosphanyl)-4-(*tert*-butyl)-1-methyl-1H-imidazole (31 mg, 0.06 mmol) and 1 mL CH₂Cl₂. Then the vial was taken outside of the glovebox and the resulting mixture was stirred at room 23 °C for 12 h. The orange solution was filtered and CH₂Cl₂ was evaporated to provide pale yellow solid, which was recrystallized through CH₂Cl₂ and Hexane to give white precipitate. The solid was collected and dried in *vacuo* to yield catalyst **M** (82 mg, 99% yield).

¹H NMR (400 MHz, CDCl₃): δ 8.61 (s, 1H), 7.66 – 7.35 (m, 21H), 7.22 (s, 2H), 7.09 – 7.02 (m, 4H), 6.85 (d, *J* = 8.3 Hz, 1H), 4.08 (s, 3H), 1.45 (s, 9H) ppm

¹³C NMR (151 MHz, CDCl₃): δ 160.5 – 157.2 (m), 155.8 (d, *J* = 3.4 Hz), 146.2 (d, *J* = 12.5 Hz), 142.3 (d, *J* = 14.4 Hz), 142.0 (d, *J* = 12.3 Hz), 137.4 (d, *J* = 20.5 Hz), 134.7, 133.5, 133.2, 132.6, 132.3 (d, *J* = 9.5 Hz), 131.3 – 130.9 (m), 130.4 – 129.6 (m), 129.3 (d, *J* = 8.9 Hz), 128.8 (d, *J* = 10.3 Hz), 125.80 (d, *J* = 70.1 Hz), 123.9 – 123.1 (m), 122.1, 121.8, 121.5, 121.3 (q, *J* = 321.0 Hz), 121.1, 120.9 (q, *J* = 274.8 Hz), 120.8 (q, *J* = 274.8 Hz), 118.6 – 118.4 (m), 117.6 (dd, *J* = 9.9, 2.6 Hz), 115.5 (d, *J* = 12.0 Hz), 111.8 (d, *J* = 12.1 Hz), 110.5 (d, *J* = 10.4 Hz), 38.2, 32.5, 30.2 ppm

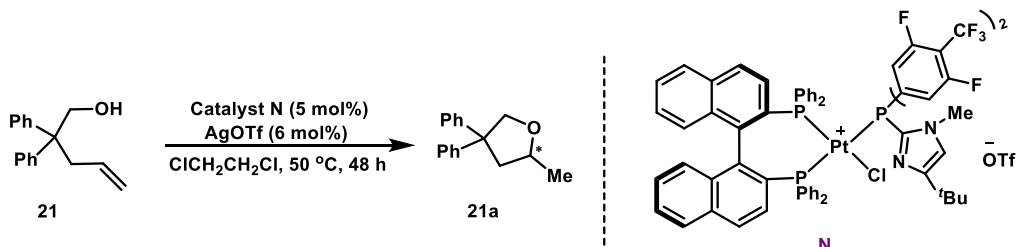
³¹P NMR (243 MHz, CDCl₃): δ 16.3 (d, ²*J*_{P-P} = 19 Hz, ¹*J*_{Pt-P} = 2714 Hz), 14.5 (d, ²*J*_{P-P} = 19 Hz, ¹*J*_{Pt-P} = 2701 Hz), 6.27 (d, ²*J*_{P-P} = 19 Hz, ¹*J*_{Pt-P} = 3052 Hz) ppm

¹⁹F NMR (376 MHz, CDCl₃): δ -46.8 (dd, *J* = 185.0, 89.2 Hz), -49.9 (dd, *J* = 247.2, 89.3 Hz), -56.8 – -57.0 (m), -78.0, -107.8 ppm

HRMS (ESI⁺): calc'd for C₆₀H₄₁ClF₁₄N₂O₄P₃Pt [M-OTf]⁺: 1442.1386, found 1442.1376.

6.4 General Procedure for Catalytic Enantioselective Hydroalkoxylation

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the chiral catalyst **M** or **N** (0.005mmol, 5 mol%), silver trifluoromethanesulfonate (0.006 mmol, 6 mol%), $\text{ClCH}_2\text{CH}_2\text{Cl}$. The mixture was stirred at room temperature (23 °C) for 1 h. And 2,2-diphenylpent-4-en-1-ol **21** (24 mg, 0.1 mmol, 1.0 equiv) was added. The resulting mixture was stirred at 50 °C for 48 h. The reaction mixture was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using hexane/ ethyl acetate (20/1) to provide the product **21a**.



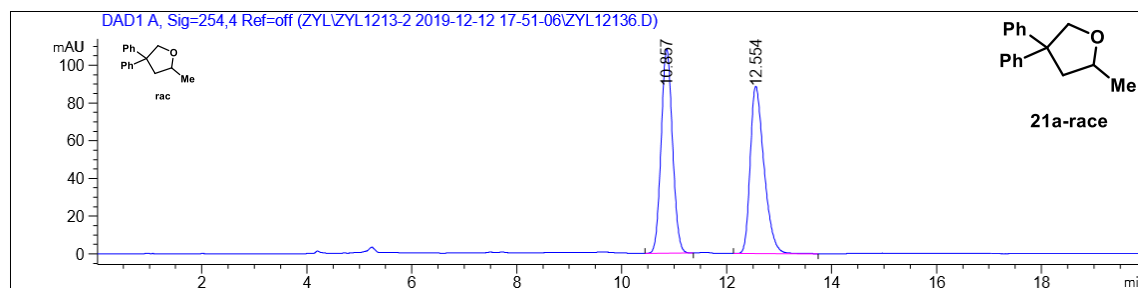
The desired product **21a** (10.0 mg, 42% yield, 36% ee) was obtained.

^1H NMR (400 MHz, CDCl_3): δ 7.32 – 7.28 (m, 6H), 7.23 – 7.17 (m, 4H), 4.61 – 4.58 (m, 1H), 4.22 – 4.13 (m, 2H), 2.64 (ddd, J = 12.1, 5.7, 0.9 Hz, 1H), 2.27 (dd, J = 12.1, 9.5 Hz, 1H), 1.59 (s, 1H), 1.30 (d, J = 6.1 Hz, 3H) ppm

^{13}C NMR (101 MHz, CDCl_3): δ 146.5, 146.3, 128.5, 128.4, 127.3, 126.5, 126.3, 77.0, 74.9, 56.5, 46.7, 21.5 ppm

The analytical data was consistent with the literature.¹¹

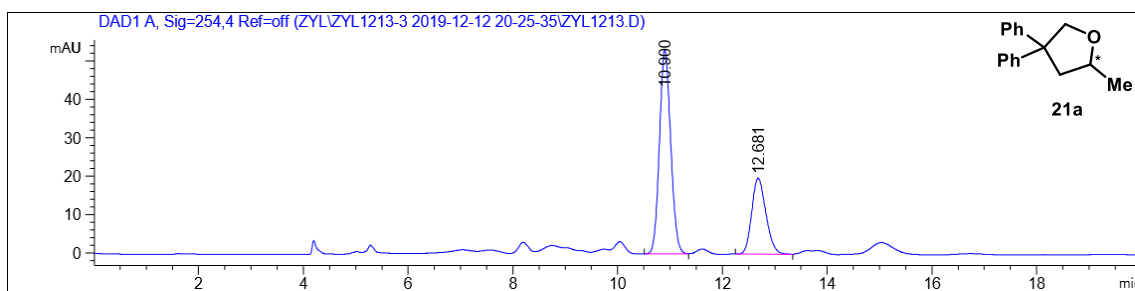
HPLC (AD-H, 0.46*25 cm, 5 μm , hexane / isopropyl alcohol = 99/1, flow 0.7 mL/min, detection at 254 nm) retention time = 10.900 min (major) and 12.681 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.857	BB	0.2351	1627.99878	108.46142	50.0790
2	12.554	BB	0.2772	1622.86401	88.81694	49.9210

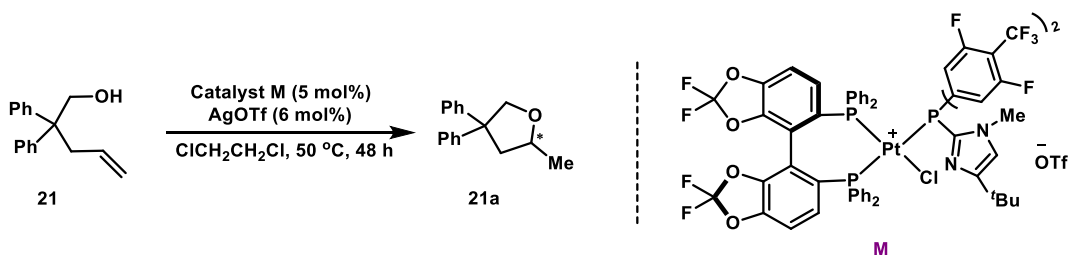
Totals : 3250.86279 197.27836



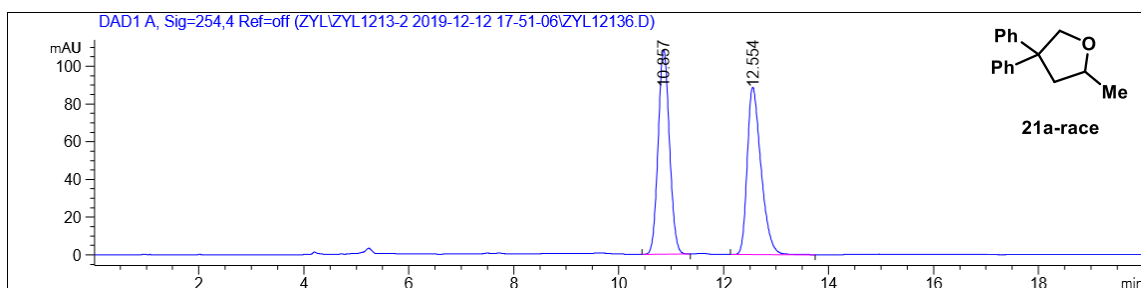
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.900	BB	0.2323	794.20441	53.15425	68.0628
2	12.681	BB	0.2919	372.66541	19.76850	31.9372

Totals : 1166.86981 72.92275



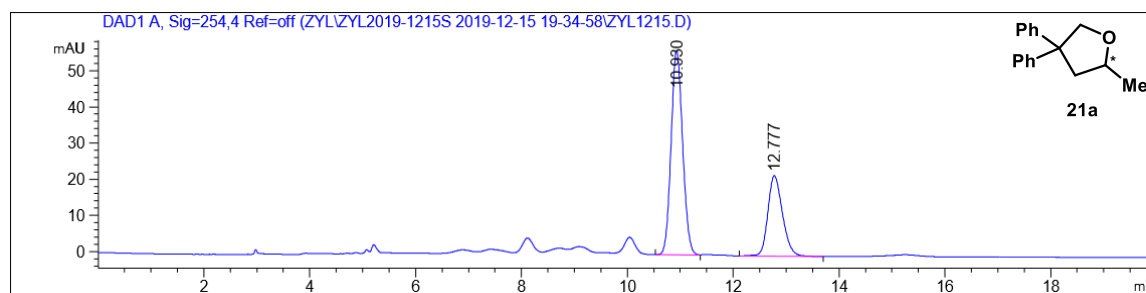
The desired product **21a** (7.9 mg, 33% yield, 33% ee) was obtained. HPLC (AD-H, 0.46*25 cm, 5 μm , hexane / isopropyl alcohol = 99/1, flow 0.7 mL/min, detection at 254 nm) retention time = 10.930 min (major) and 12.777 min (minor)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.857	BB	0.2351	1627.99878	108.46142	50.0790
2	12.554	BB	0.2772	1622.86401	88.81694	49.9210

Totals : 3250.86279 197.27836



Signal 1: DAD1 A, Sig=254,4 Ref=off

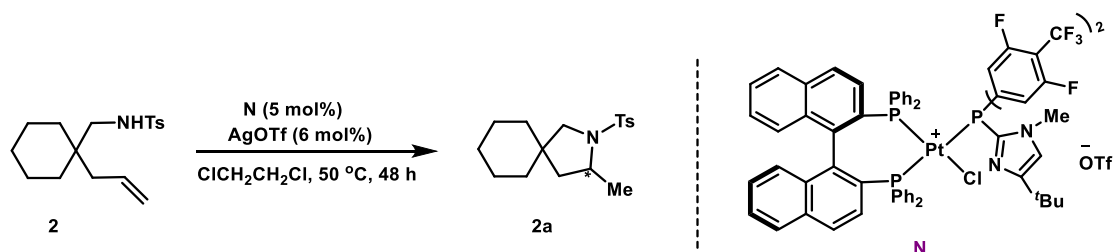
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.930	BB	0.2343	854.58081	56.55159	66.6114
2	12.777	BB	0.2946	428.35492	22.24724	33.3886

Totals : 1282.93573 78.79883

6.5 General Procedure for Catalytic Enantioselective Hydroamination

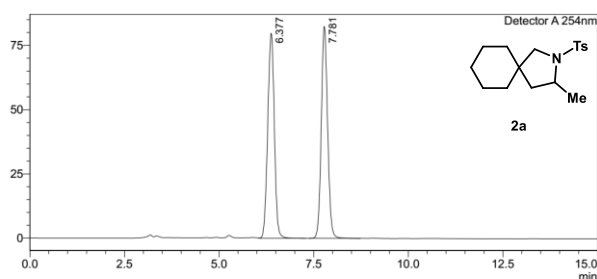
Catalyst **M** and catalyst **N** were generated *in situ*.

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the (**R**)-**P2** or (**R**)-**P1** (0.005mmol, 5 mol%), silver trifluoromethanesulfonate (0.012 mmol), $\text{ClCH}_2\text{CH}_2\text{Cl}$ (200 μL). The mixture was stirred at room temperature (23 $^\circ\text{C}$) for 1 h. And monophosphine ligand **L4** (0.002mmol, 5 mol%) dissolved in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (100 μL) was added into the above mixture. The resulting solution was stirred for 5 min and *N*-((1-allylcyclohexyl)methyl)-4-methylbenzenesulfonamide **2** (31 mg, 0.1 mmol, 1.0 equiv) was added. The mixture was stirred at 50 $^\circ\text{C}$ for 48 h. The reaction mixture was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using hexane/ ethyl acetate (20/1) to provide the product **2a**.



The desired product **2a** (15% yield, 58% ee) was obtained. HPLC (OJ-H, 0.46*25 cm, 5 μm , hexane / ethanol = 90/10, flow 1.0 mL/min, detection at 254 nm)retention time = 6.390 min (major) and 7.789 min (minor)

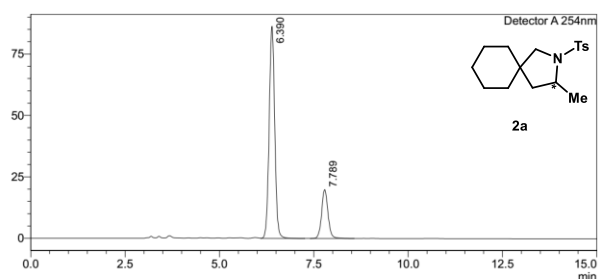
<Chromatogram>
mV



<Peak Table>

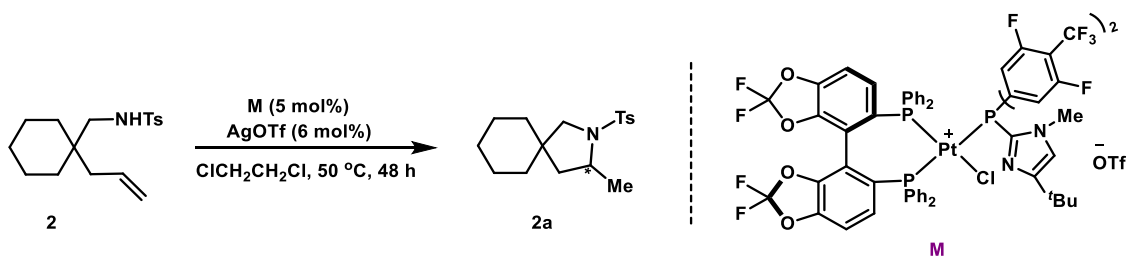
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.377	970636	79803	50.224		S	
2	7.781	961978	82513	49.776			
Total		1932614	162315				

<Chromatogram>
mV



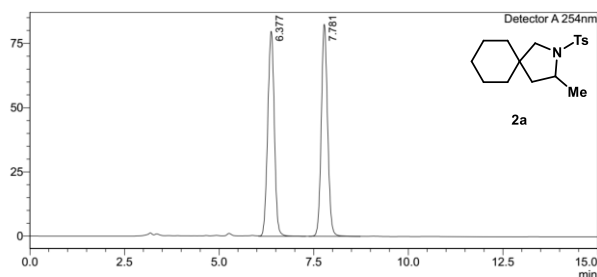
<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.390	885557	86312	79.105		S	
2	7.789	233919	19856	20.895			
Total		1119476	106168				



The desired product 2a (18% yield, 65% ee) was obtained. HPLC (OJ-H, 0.46*25 cm, 5μm, hexane / ethanol = 90/10, flow 1.0 mL/min, detection at 254 nm) retention time = 6.375 min (major) and 7.787 min (minor)

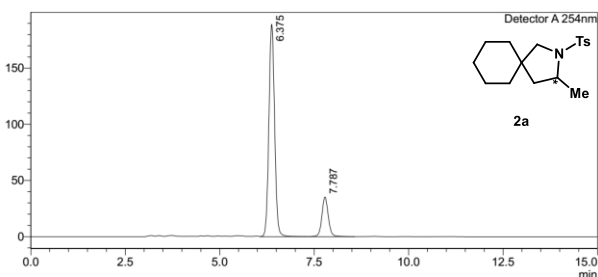
<Chromatogram>
mV



<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.377	970636	79803	50.224		S	
2	7.781	961978	82513	49.776			
Total		1932614	162315				

<Chromatogram>
mV



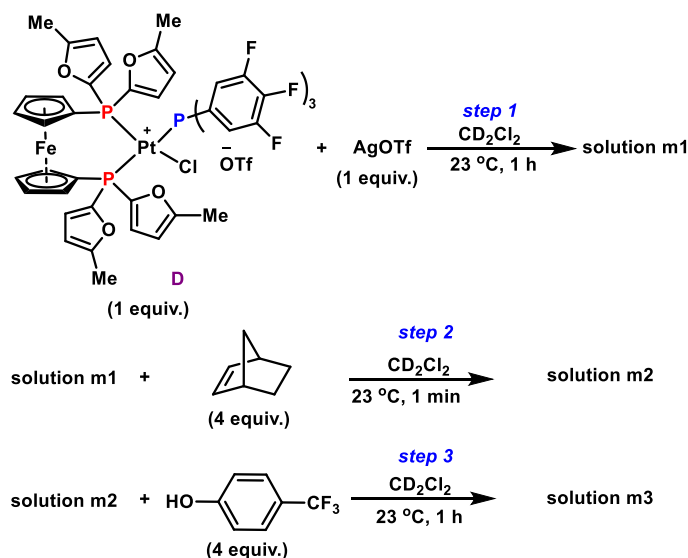
<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.375	1989577	189133	82.700		V	
2	7.787	416191	35288	17.300			
Total		2405768	224421				

7. NMR Monitoring of Hydroalkoxylation Reaction

7.1 NMR Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Catalyst D and Different Amounts of AgOTf

7.1.1 Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex D and 1 equiv. of AgOTf

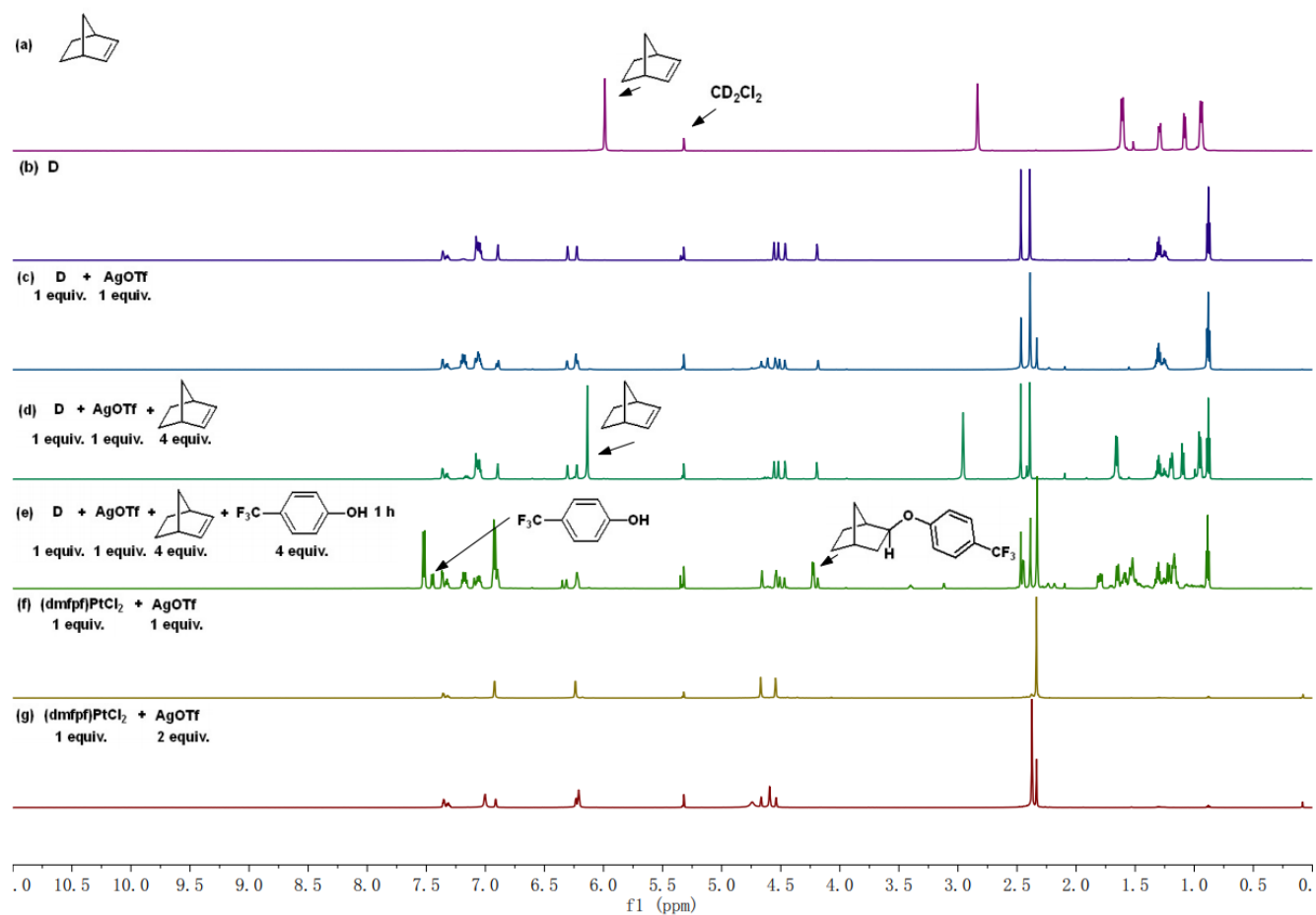


Procedure

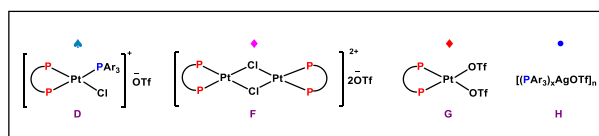
Step 1: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added **D** (28 mg, 0.02 mmol), AgOTf (5 mg, 0.02 mmol) and CD₂Cl₂ (500 μ L). The mixture was stirred at room temperature (23 °C) for 1 h to give solution m1. Solution m1 was recorded by ¹H NMR, ¹⁹F NMR and ³¹P NMR respectively. ³¹P NMR chemical shifts are referenced to an external PPh₃ standard in CD₂Cl₂ sealed in a capillary tube. Analysis of the ³¹P NMR showed that four new peaks at δ -33.5 ppm, -22.5 ppm, 12.5 ppm and 15.7 ppm were formed (Supplementary Figure 4b). Analysis of the ¹⁹F NMR showed new two peaks at -131.6 (d, J = 21.3 Hz) and -154.8 (t, J = 20.8 Hz) ppm were formed (Supplementary Figure 5b).

Step 2: Norbornene (7.5 mg, 0.08 mmol) dissolved in CD₂Cl₂ (100 μ L) was added into tube containing solution m1. The mixture was stirred for 30 min and the resulting-solution m2 was monitored by NMR techniques.

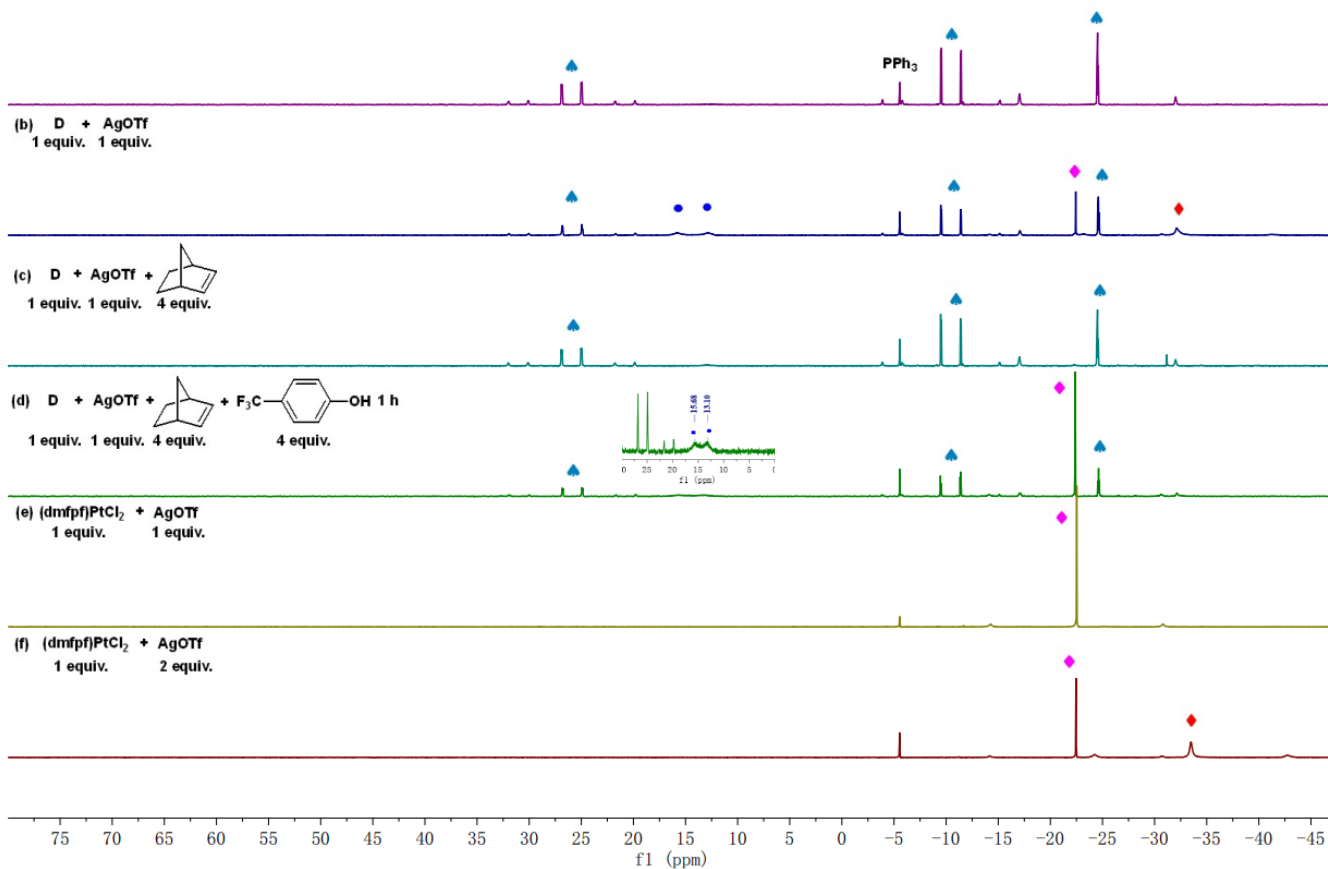
Step 3: 4-Trifluoromethylphenol (13 mg, 0.08 mmol) dissolved in CD₂Cl₂ (100 μ L) was added into tube containing solution m2. The mixture was stirred for 1 h and the resulting-solution was monitored by NMR techniques.



Supplementary Figure 3. ¹H NMR (600 MHz, CD₂Cl₂) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Catalyst **D** and 1 equiv. of AgOTf



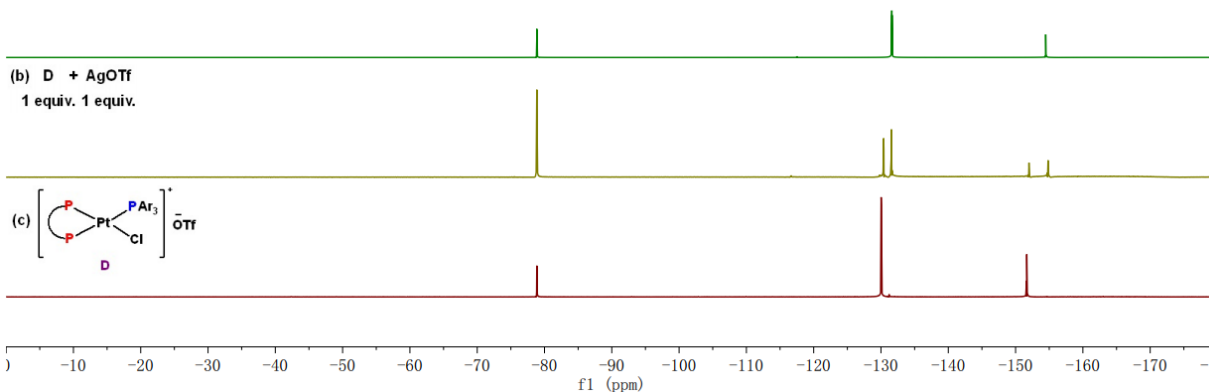
(a) **D**



Supplementary Figure 4. ³¹P NMR (243 MHz, CD₂Cl₂) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Catalyst **D** and 1 equiv. of AgOTf

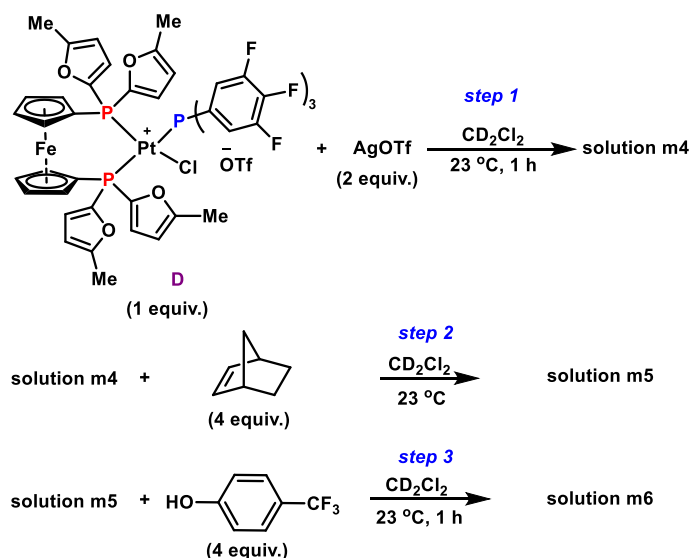
(a) [(PAr₃)₂AgOTf]_n

H



Supplementary Figure 5. ¹⁹F NMR (565 MHz, CD₂Cl₂) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Catalyst **D** and 1 equiv. of AgOTf

7.1.2 Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex **D** and 2 equiv. of AgOTf

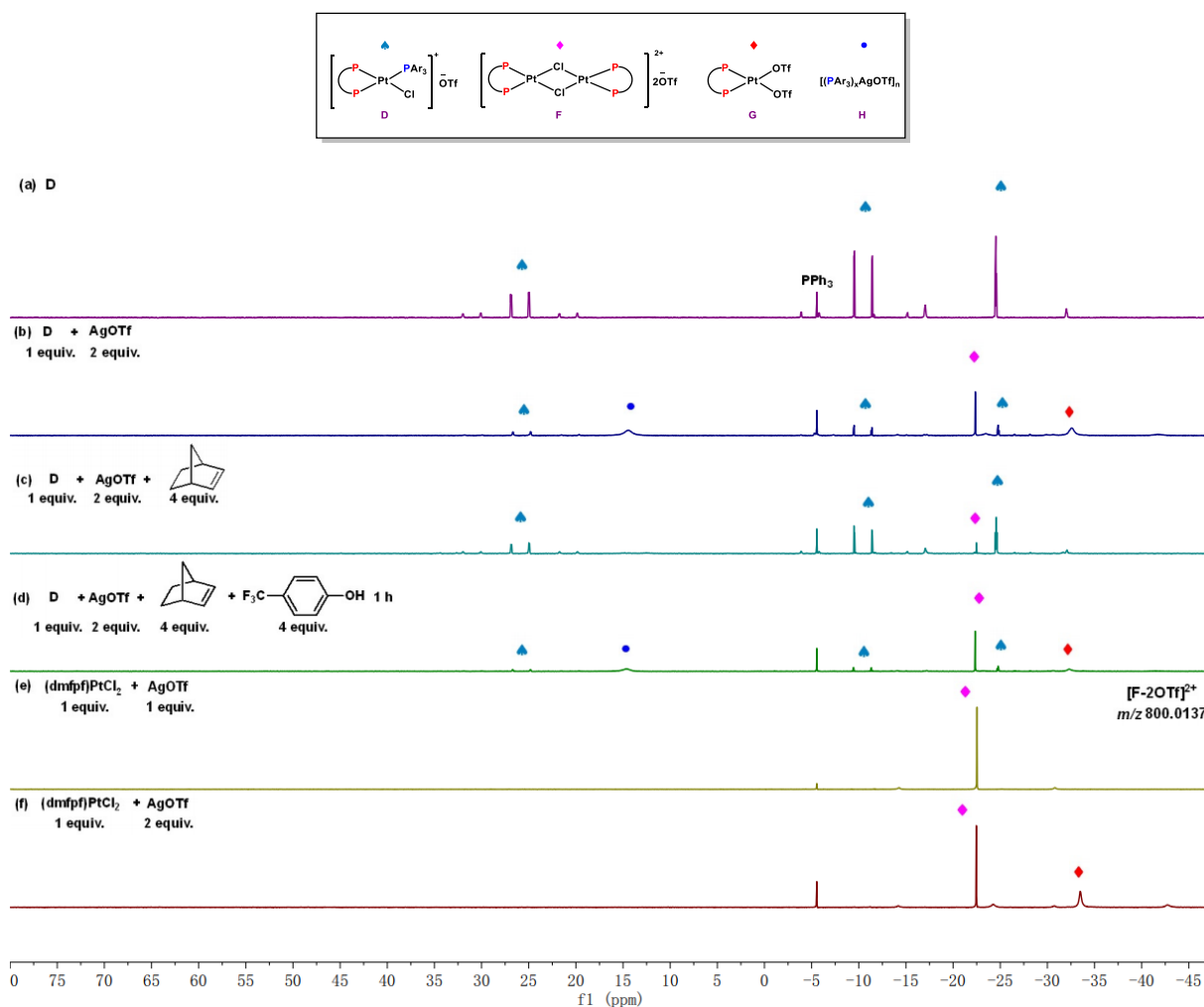


Procedure

Step 1: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added **D** (28 mg, 0.02 mmol), AgOTf (10mg, 0.04 mmol) and CD_2Cl_2 (500 μL). The mixture was stirred at room temperature (23 °C) for 1 h. The resulted solution was recorded by ^1H NMR and ^{31}P NMR respectively. ^{31}P NMR chemical shifts are referenced to an external PPh_3 standard in CD_2Cl_2 sealed in a capillary tube. Analysis of the ^{31}P NMR showed that three new peaks at δ -33.5 ppm, -22.5 ppm, 14.4 ppm were formed (Supplementary Figure 7b).

Step 2: Norbornene (7.5 mg, 0.08 mmol) dissolved in CD_2Cl_2 (100 μL) was added into tube containing solution m4. The mixture was stirred for 30 min and the resulting-solution m5 was monitored by NMR techniques. Analysis of the ^{31}P NMR showed that the new three groups of peaks [δ 33.6 (dd, $^2J_{\text{P-P}} = 410$, 22 Hz, $^1J_{\text{Pt-P}} = 3075$), -12.6 (dd, $^2J_{\text{P-P}} = 411$, 23 Hz, $^1J_{\text{Pt-P}} = 3463$), -17.2 (t, $^2J_{\text{P-P}} = 22$ Hz, $^1J_{\text{Pt-P}} = 1873$)] were formed (Supplementary Figure 8c).

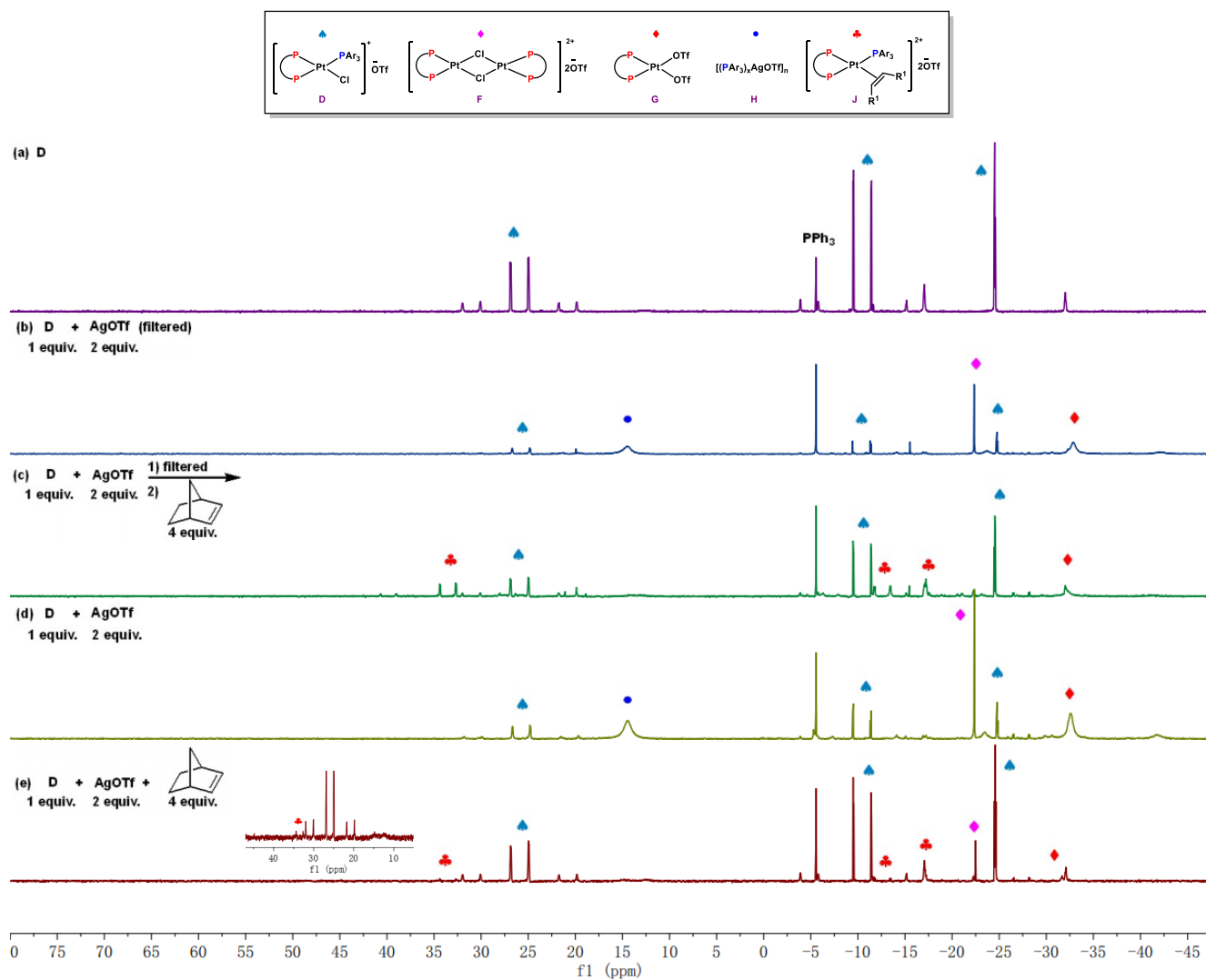
Step 3: 4-Trifluoromethylphenol (13 mg, 0.08 mmol) dissolved in CD_2Cl_2 (100 μL) was added into tube containing solution m5. The mixture was stirred for 1 h and the resulting-solution was monitored by NMR techniques.



Supplementary Figure 7. ^{31}P NMR (243 MHz, CD_2Cl_2) Monitoring of Hydroalkoxylation of

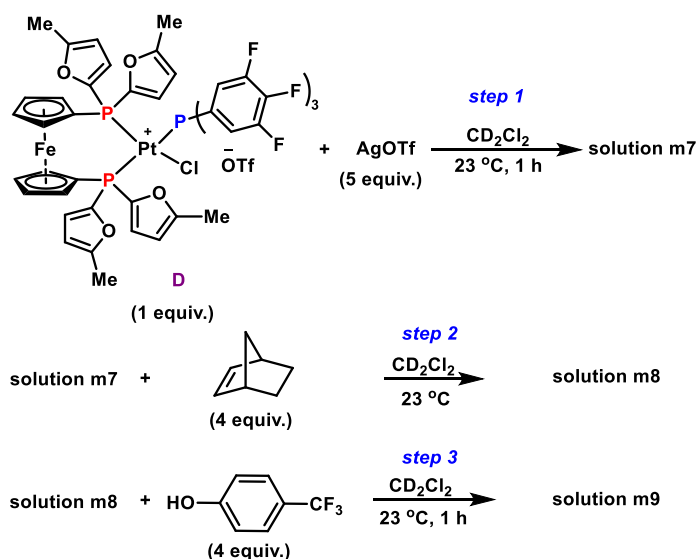
Norbornene and 4-Trifluoromethylphenol Catalyzed by Catalyst **D** and 2 equiv. of AgOTf

As shown below, the three new groups of peaks [δ 33.6 (dd, $^2J_{\text{P-P}} = 410$, 22 Hz, $^1J_{\text{Pt-P}} = 3075$), -12.6 (dd, $^2J_{\text{P-P}} = 411$, 23 Hz, $^1J_{\text{Pt-P}} = 3463$), -17.2 (t, $^2J_{\text{P-P}} = 22$ Hz, $^1J_{\text{Pt-P}} = 1873$)] were formed when adding norbornene to a mixture of complex **D** and AgOTf (Supplementary Figure 8e). To the filtrate of a mixture of complex **D** and 2 equiv. of AgOTf was added norbornene, the concentration of intermediate **J** increased (Supplementary Figure 8c).



Supplementary Figure 8. Comparison of ^{31}P NMR (243 MHz, CD_2Cl_2) of the Reaction of D + AgOTf + Norbornene and Reaction of the Filtrate of D and AgOTf + Norbornene (^{31}P NMR Chemical Shifts Are Referenced to An External PPh_3 Standard in CD_2Cl_2 Sealed in A Capillary Tube.)

7.1.3 Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex **D** and 5 equiv. of AgOTf

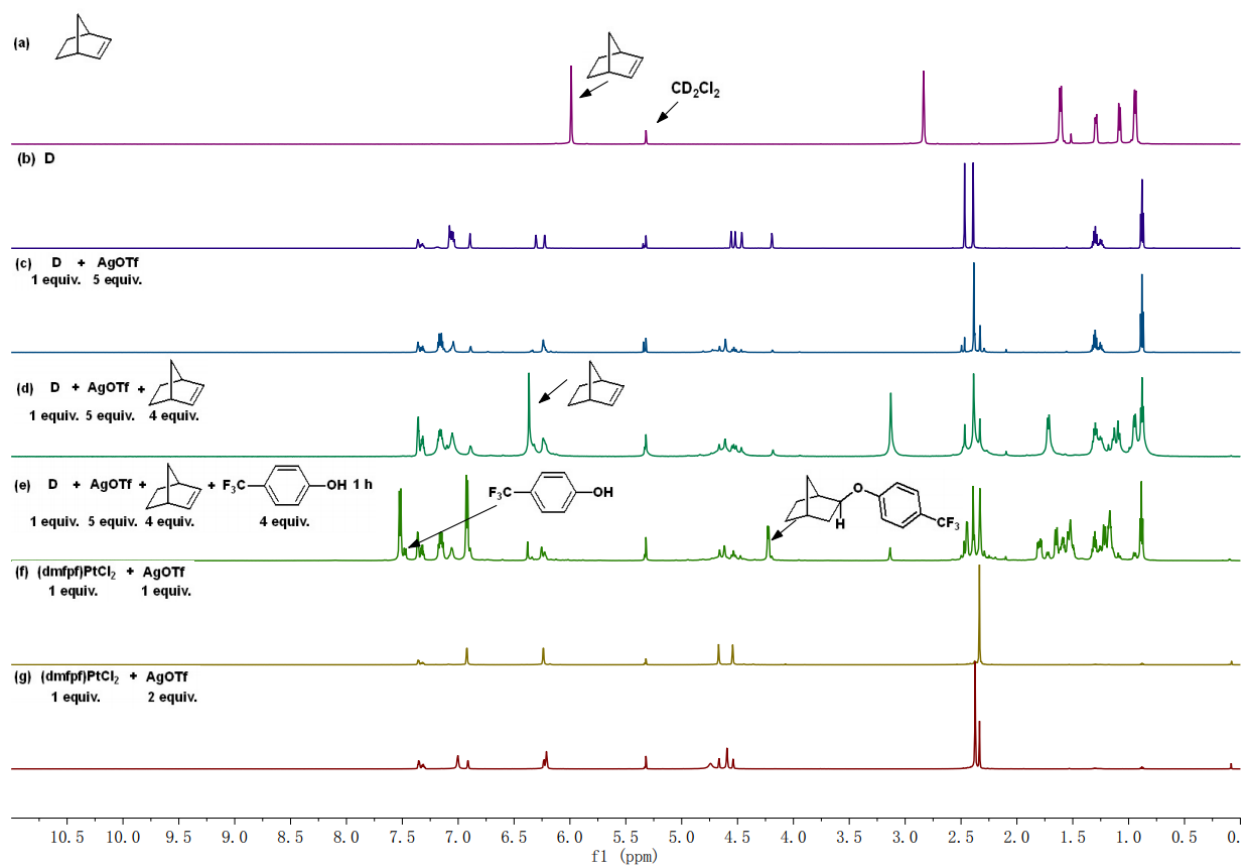


Procedure

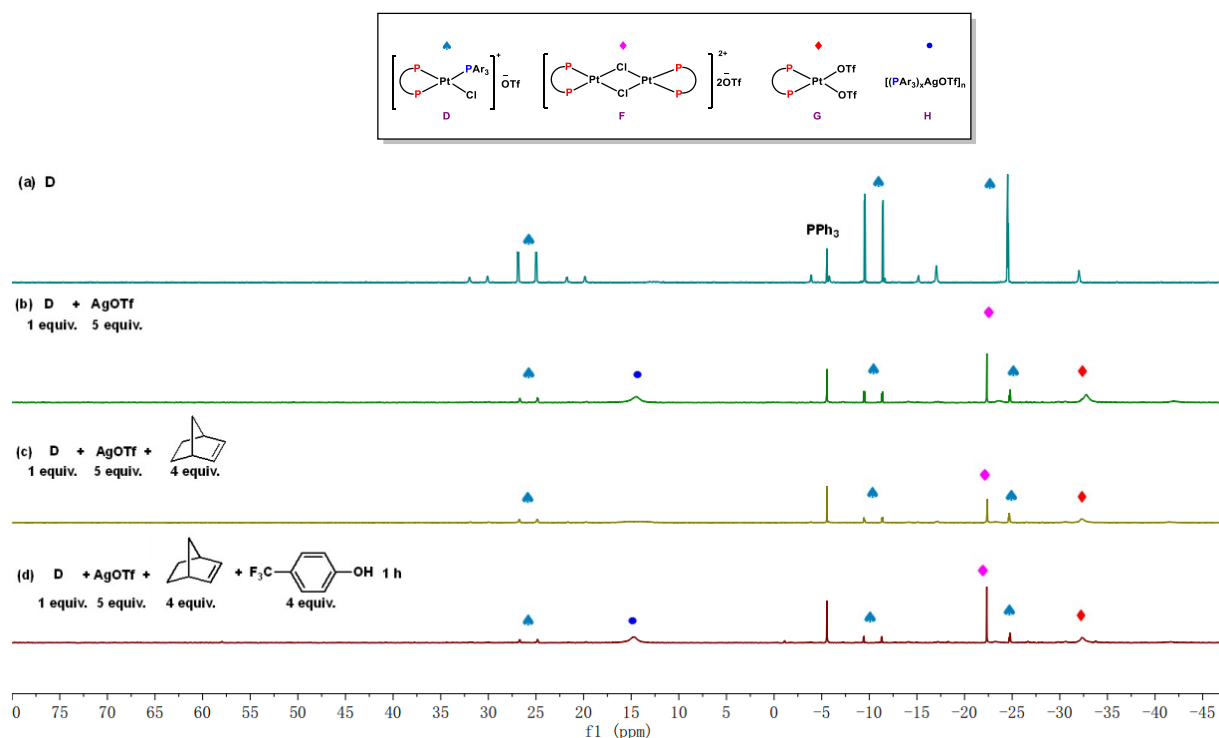
Step 1: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added **D** (28 mg, 0.02 mmol), AgOTf (26 mg, 0.1 mmol) and CD_2Cl_2 (500 μL). The mixture was stirred at room temperature (23 °C) for 1 h. The resulted solution was recorded by ^1H NMR and ^{31}P NMR respectively. ^{31}P NMR chemical shifts are referenced to an external PPh_3 standard in CD_2Cl_2 sealed in a capillary tube. Analysis of the ^{31}P NMR showed that three new peaks at δ -33.5 ppm, -22.4 ppm, 14.6 ppm were formed (Supplementary Figure10b).

Step 2: Norbornene (7.5 mg, 0.08 mmol) dissolved in CD_2Cl_2 (100 μL) was added into tube containing solution m7. The tube was stirred for 30 min and the resulting-solution was monitored by NMR techniques.

Step 3: 4-Trifluoromethylphenol (13 mg, 0.08 mmol) dissolved in CD_2Cl_2 (100 μL) was added into tube containing solution m8. The mixture was stirred for 1 h and the resulting-solution was monitored by NMR techniques.



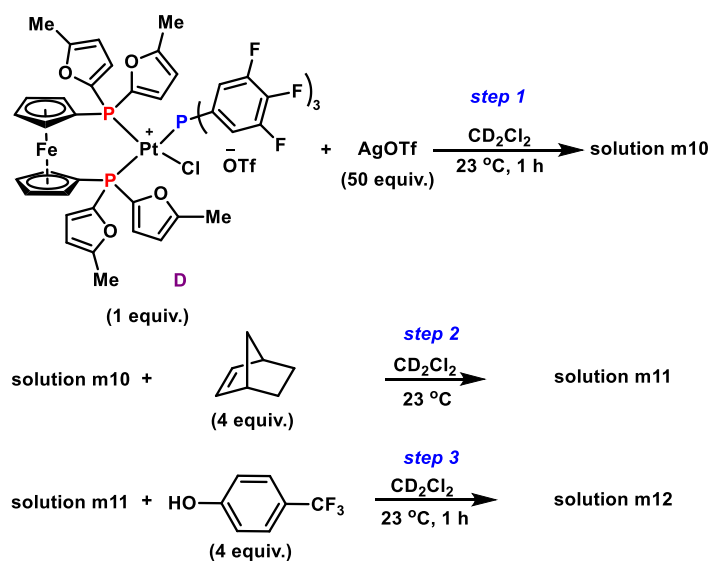
Supplementary Figure 9. ¹H NMR (600 MHz, CD₂Cl₂) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Catalyst **D** and 5 equiv. of AgOTf



Supplementary Figure 10. ^{31}P NMR (243 MHz, CD_2Cl_2) Monitoring of Hydroalkoxylation of

Norbornene and 4-Trifluoromethylphenol Catalyzed by Catalyst **D** and 5 equiv. of AgOTf

7.1.4 Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex **D** and 50 equiv. of AgOTf



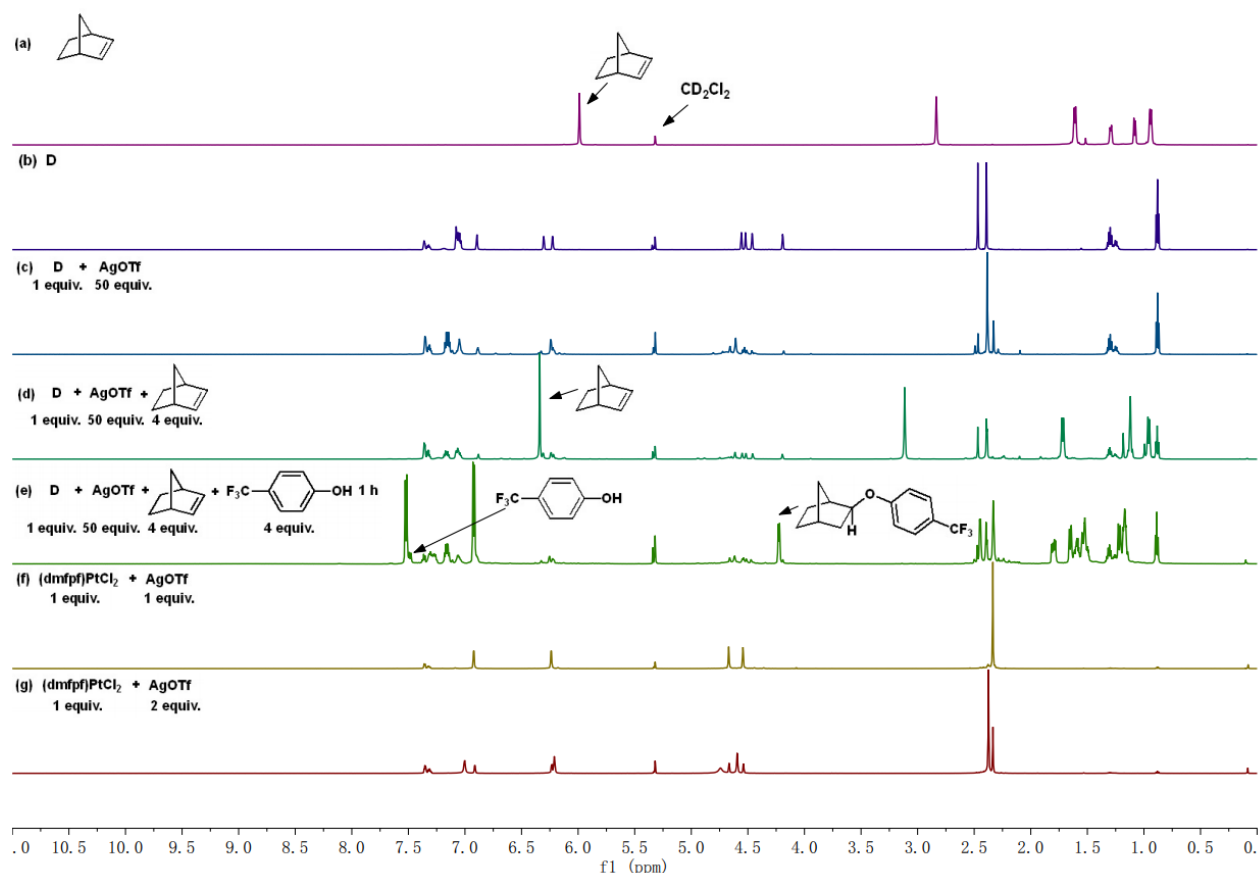
Procedure

Step 1: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added **D** (28 mg, 0.02 mmol), AgOTf (257mg, 1.0 mmol) and CD_2Cl_2 (500 μL). The mixture was stirred at room temperature (23 $^\circ\text{C}$) for 1 h. The resulted solution was recorded by ^1H NMR and ^{31}P NMR respectively. ^{31}P NMR chemical shifts are referenced to an external PPh_3 standard in CD_2Cl_2 sealed in a capillary tube. Analysis

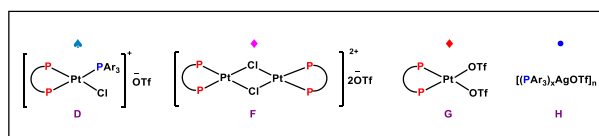
of the ^{31}P NMR showed that three new peaks at δ -33.5 ppm, -22.4 ppm, 14.6 ppm were formed (Supplementary Figure 12b).

Step 2: Norbornene (7.5 mg, 0.08 mmol) dissolved in CD_2Cl_2 (100 μL) was added into tube containing solution m10. The resulting mixture was stirred for 30 min and the resulting-solution was monitored by NMR techniques.

Step 3: 4-Trifluoromethylphenol (13 mg, 0.08 mmol) dissolved in CD_2Cl_2 (100 μL) was added into tube containing solution m11. The resulting mixture was stirred for 1 h and the resulting-solution was monitored by NMR techniques.



Supplementary Figure 11. ^1H NMR (600 MHz, CD_2Cl_2) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Catalyst D and 50 equiv. of AgOTf



(a) **D**



(b) **D** + AgOTf
1 equiv. 50 equiv.



(c) **D** + AgOTf + 
1 equiv. 50 equiv. 4 equiv.



(d) **D** + AgOTf +  + F₃C-C₆H₄-OH 1 h
1 equiv. 50 equiv. 4 equiv. 4 equiv.



(e) (dmfppf)PtCl₂ + AgOTf
1 equiv. 1 equiv.



(f) (dmfppf)PtCl₂ + AgOTf
1 equiv. 2 equiv.

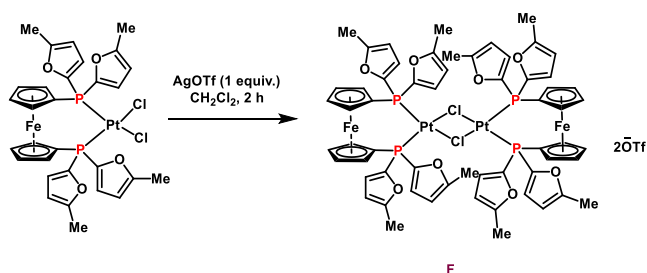


0 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

Supplementary Figure 12. ³¹P NMR (243 MHz, CD₂Cl₂) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Catalyst **D** and 50 equiv. of AgOTf

7.2 Synthesis of Complexes F, G, and H

7.2.1 Synthesis and Characterization of Complex F



Procedure: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added (dmfpf)PtCl₂ (100 mg, 0.12 mmol), silver trifluoromethanesulfonate (31 mg, 0.12 mmol, 1.0 equiv.) and 2 mL CH₂Cl₂. The mixture was stirred at room temperature (23 °C) for 2 h. The purple solution was filtered and CH₂Cl₂ was evaporated to provide purple solid, which was recrystallized through CH₂Cl₂ and hexane to give purple precipitate.

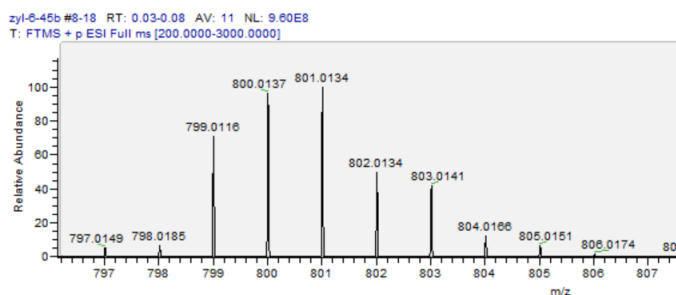
¹H NMR (600 MHz, CD₂Cl₂): δ 6.91 (d, J = 3.3 Hz, 8H), 6.23(d, J = 3.3 Hz, 8H), 4.66 (s, 8H), 4.53 (s, 8H), 2.32 (s, 24H) ppm

¹³C NMR (151 MHz, CD₂Cl₂): δ 161.9, 136.7 (d, J = 111 Hz), 127.8 – 127.6 (m), 109.2 (d, J = 3.7 Hz), 76.8 – 76.6 (m), 76.3 – 76.1 (m), 66.8 (d, J = 91.8 Hz), 14.3 ppm

³¹P NMR (243 MHz, CD₂Cl₂): δ -22.5 (d, $^1J_{\text{Pt-P}}$ = 4018 Hz) ppm

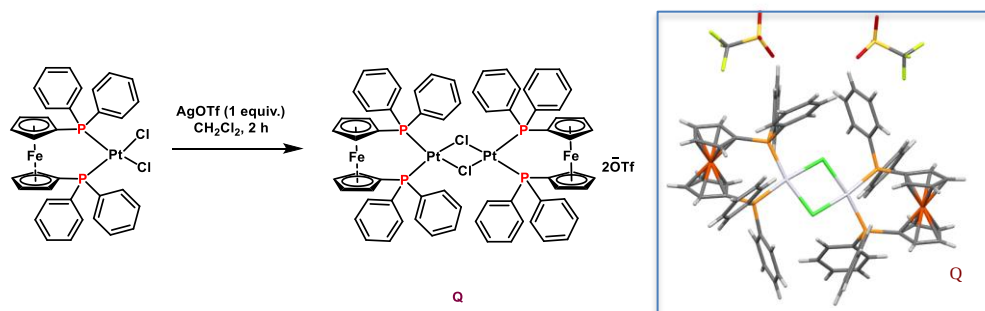
¹⁹F NMR (376 MHz, CD₂Cl₂): δ -78.5 (s) ppm

HRMS (ESI-): calculated for C₆₀H₅₆Cl₂Fe₂O₈P₄Pt₂ [M-2OTf]²⁺: m/z = 800.0149, found 800.0137.



Supplementary Figure 13. HRMS of Complex **F**

Attempts to form X-ray quality crystals of complex **F** failed. To check if complex **F** is a dinuclear species with a bridging Cl ligand, a test experiment used (dppf)PtCl₂ with 1 equiv. of AgOTf to generated a new complex **Q**. Complex **Q** was identified by X-ray crystallography as a dinuclear species with a bridging Cl ligand. So it assumed that complex **F** was like a dinuclear species with a bridging Cl ligand. Therefore the peak at δ -22.5 ppm was proposed to be the dinuclear complex **F**.



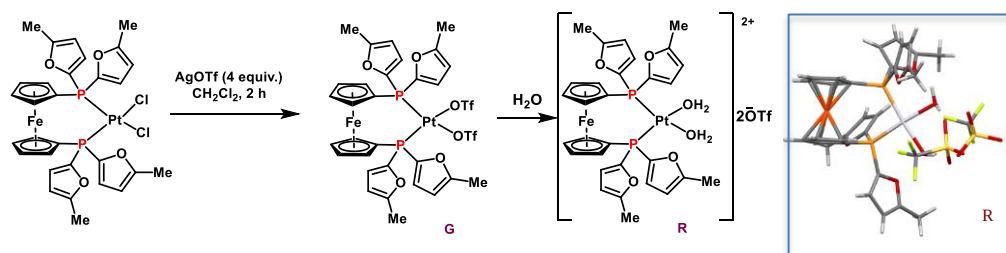
^1H NMR (400 MHz, CD_2Cl_2): δ 7.58 – 7.50 (m, 8H), 7.41 – 7.37(d, J = 3.3 Hz, 8H), 4.65 (s, 8H), 4.41 (s, 8H) ppm

^{13}C NMR (101 MHz, CD_2Cl_2): δ 134.4 – 134.3 (m), 133.7, 129.6 – 129.4 (m), 127.2 (d, J = 70.1 Hz), 77.7 – 77.5 (m), 76.4 – 76.3 (m), 68.11 (d, J = 79.7 Hz) ppm

^{31}P NMR (162 MHz, CD_2Cl_2): δ 18.3 (d, $^1J_{\text{Pt-P}}$ = 3983 Hz) ppm

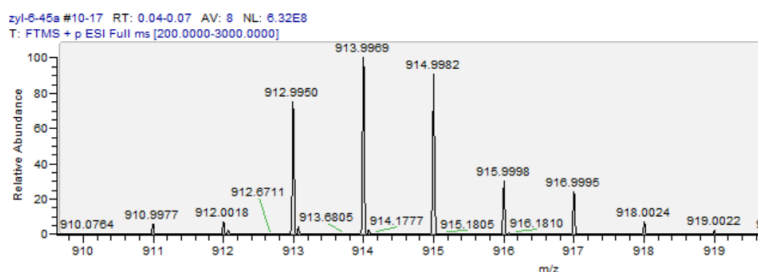
^{19}F NMR (376 MHz, CD_2Cl_2): δ -78.5 (s) ppm

7.2.2 Synthesis and Characterization of Complex G



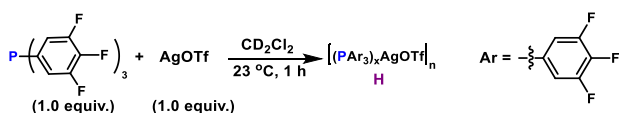
Procedure: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added (dmfpf)PtCl₂ (17 mg, 0.02 mmol), silver trifluoromethanesulfonate (20 mg, 0.08mmol, 4.0 equiv.) and 2 mL CH₂Cl₂. The mixture was stirred at room temperature (23 °C) for 2 h. We obtained a mixture of complex **F** and complex **G**. The major product was complex **G**. Complexes **G** was moisture-sensitive and readily formed complex **R**. Complex **G** was confirmed by HRMS at C₃₁H₂₈F₃FeO₇P₂S [M-OTf]⁺: 913.9975, found 913.9969. Therefore the peak at δ -33.5 ppm belonged to the complex **G**

^{31}P NMR (162 MHz, CD_2Cl_2): δ -33.5 (d, $^1J_{\text{Pt-P}}$ = 4511 Hz) ppm.



Supplementary Figure 14. HRMS of Complex G

7.2.3 Synthesis of Complex H

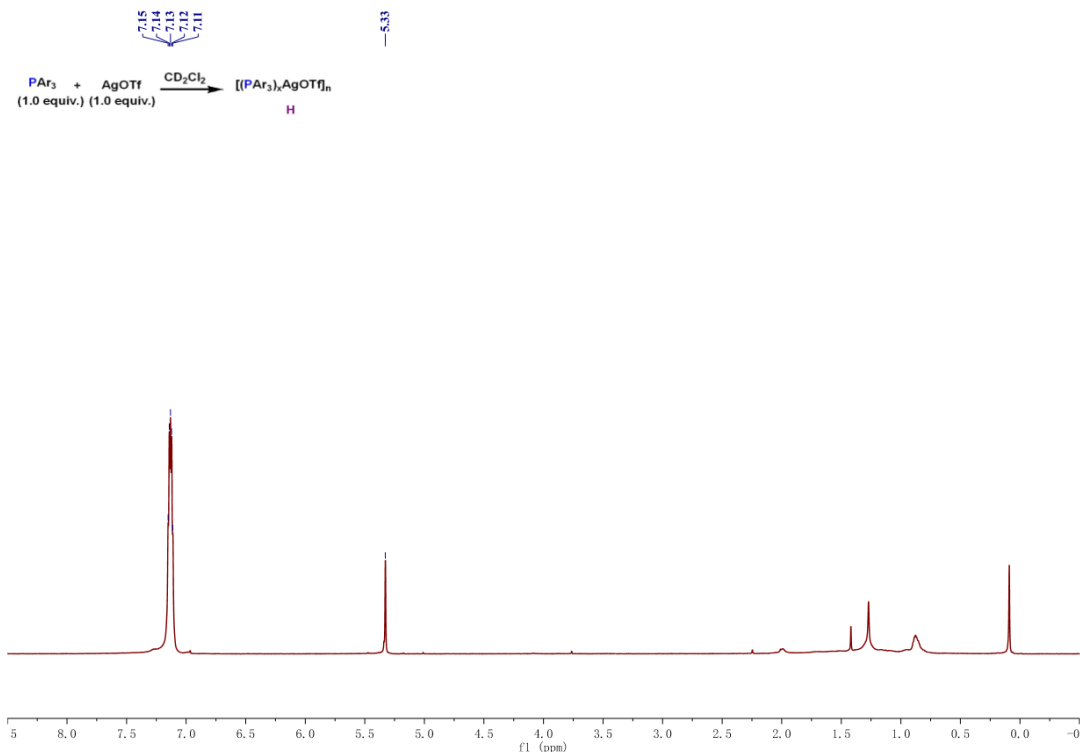


In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added tris(3,4,5-trifluorophenyl)phosphine (21 mg, 0.05 mmol), AgOTf (13 mg, 0.05 mmol) and CD₂Cl₂ (500 μL). The mixture was stirred at room temperature (23 °C) for 1 h. The resulting solution was recorded by ¹H NMR, ¹⁹F NMR and ³¹P NMR. Analysis of ³¹P NMR showed two peaks at δ 15.7 ppm and 12.5 ppm were formed (Supplementary Figure 15 to 17)¹⁹⁻²⁰.

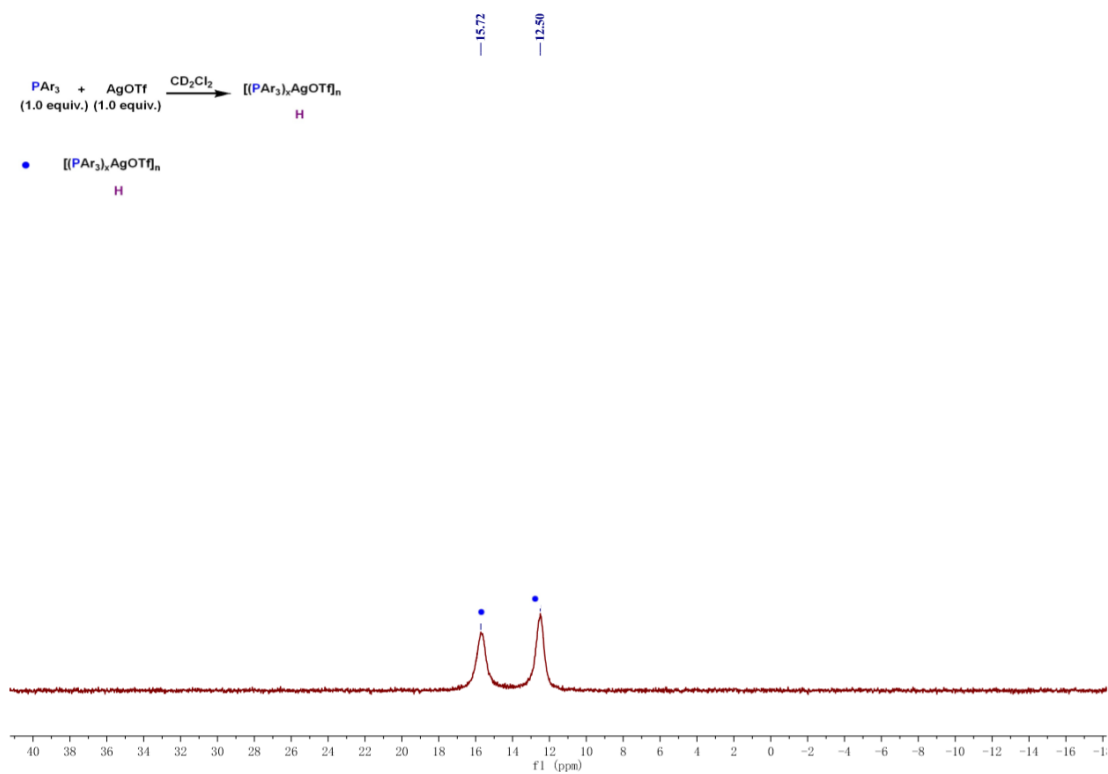
¹H NMR (600 MHz, CD₂Cl₂): δ 7.15 – 7.11(m, 6H) ppm

³¹P NMR (243 MHz, CD₂Cl₂): δ 15.7 (s), 12.5 (s) ppm

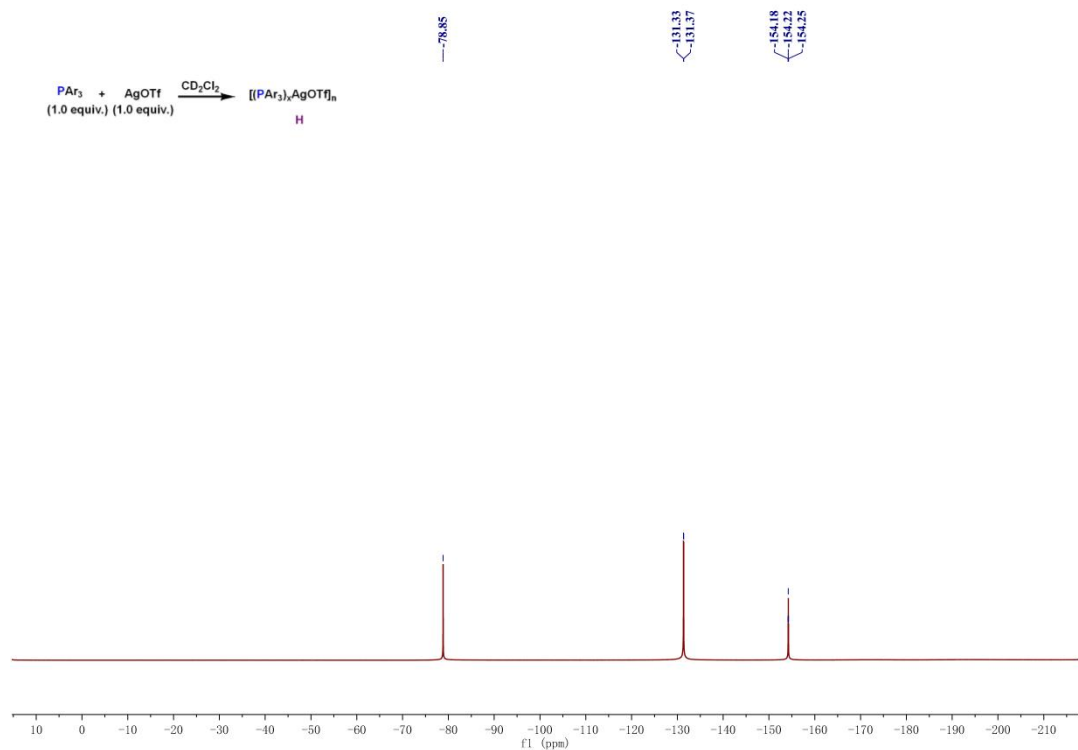
¹⁹F NMR (565 MHz, CD₂Cl₂): δ -78.9 (s), -131.6 (d, *J* = 21.3 Hz), -154.5 (t, *J* = 20.8 Hz) ppm



Supplementary Figure 15. ¹H NMR (600 MHz, CD₂Cl₂) of Complex **H**



Supplementary Figure 16. ^{31}P NMR (243 MHz, CD_2Cl_2) of Complex **H**



Supplementary Figure 17. ^{19}F NMR (565 MHz, CD_2Cl_2) of Complex **H**

7.3 Investigation of the Catalytic Activity of Complex F, G, and H

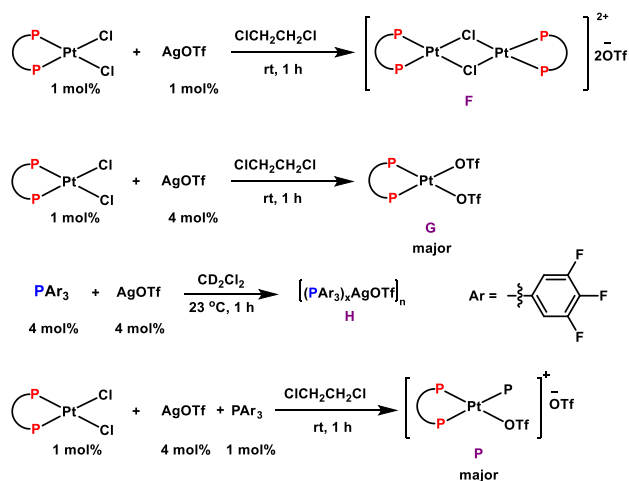
7.3.1 Comparison of the Catalytic Activity of Complex F, G and H

Complex **F** was generated from dmfpfPtCl₂ (1 mol%) and AgOTf (1 mol%) in ClCH₂CH₂Cl (Supplementary Table 7, entry 1).

Complex **G** was generated from dmfpfPtCl₂ (1 mol%) and AgOTf (4 mol%) in ClCH₂CH₂Cl (Supplementary Table 7, entry 2).

Complex **H** was generated from tris(3,4,5-trifluorophenyl)phosphine (1 mol%) and AgOTf (1 mol%) in ClCH₂CH₂Cl (Supplementary Table 7, entry 3).

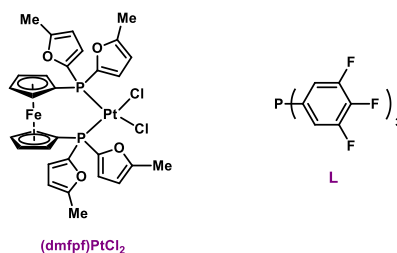
Complex **P** was generated from dmfpfPtCl₂ (1 mol%), AgOTf (4 mol%) and tris(3,4,5-trifluorophenyl)phosphine (1 mol%) in ClCH₂CH₂Cl (Supplementary Table 7, entry 4).



Supplementary Table 7: The Catalytic Activity of Complex F, G, and H

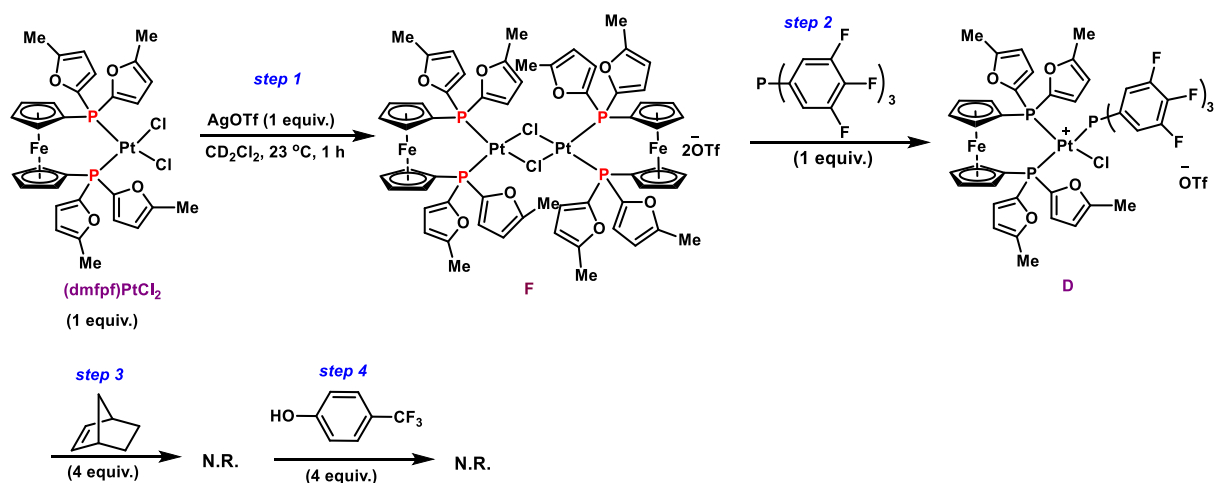
Entry	Catalyst	AgOTf (mol%)	L (mol%)	Yield (%) ^a
1	(dmfpf)PtCl ₂ (1 mol%)	1	--	0
2	(dmfpf)PtCl ₂ (1 mol%)	4	--	21
3	--	4	4	0
4	(dmfpf)PtCl ₂ (1 mol%)	4	1	49

^a Determined by ¹H NMR analysis using 4,4'-di-*tert*-butyl-1,1'-biphenyl as an internal standard



7.3.2 Investigation of the Catalytic Activity of Complex F

7.3.2.1 NMR Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex F and Tris(3,4,5-trifluorophenyl)phosphane

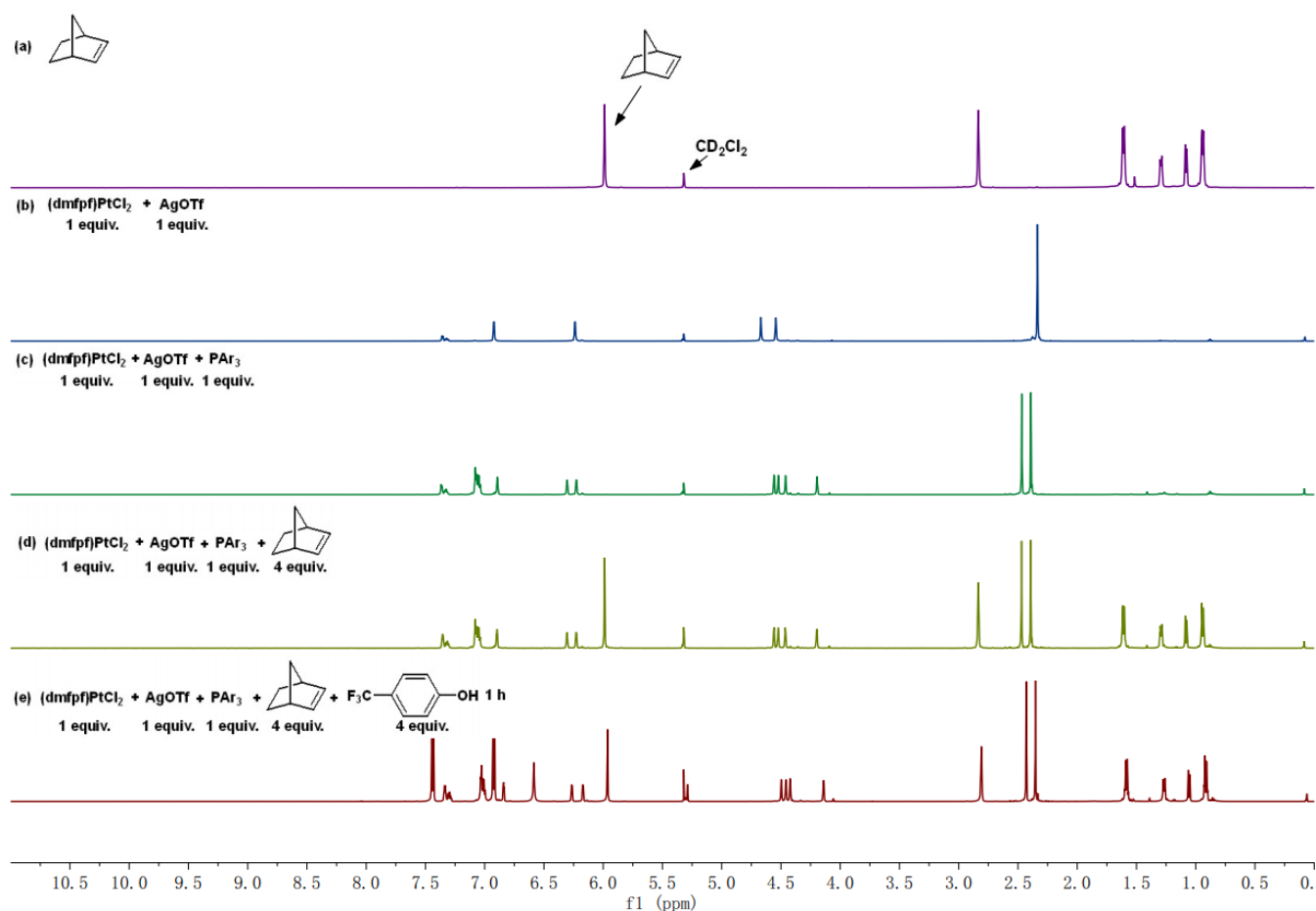


Step 1: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added (dmfpf)PtCl₂ (17 mg, 0.02 mmol), AgOTf (5 mg, 0.02 mmol) in CD₂Cl₂ (500 μ L). The mixture was stirred at room temperature (23 °C) for 1 h. The mixture was recorded by ¹H NMR and ³¹P NMR respectively. ³¹P NMR chemical shifts are referenced to an external PPh₃ standard in CD₂Cl₂ sealed in a capillary tube. Analysis of the ³¹P NMR showed that the new peaks at δ -22.5 ppm belonged to complex **F** (Supplementary Figure 19a).

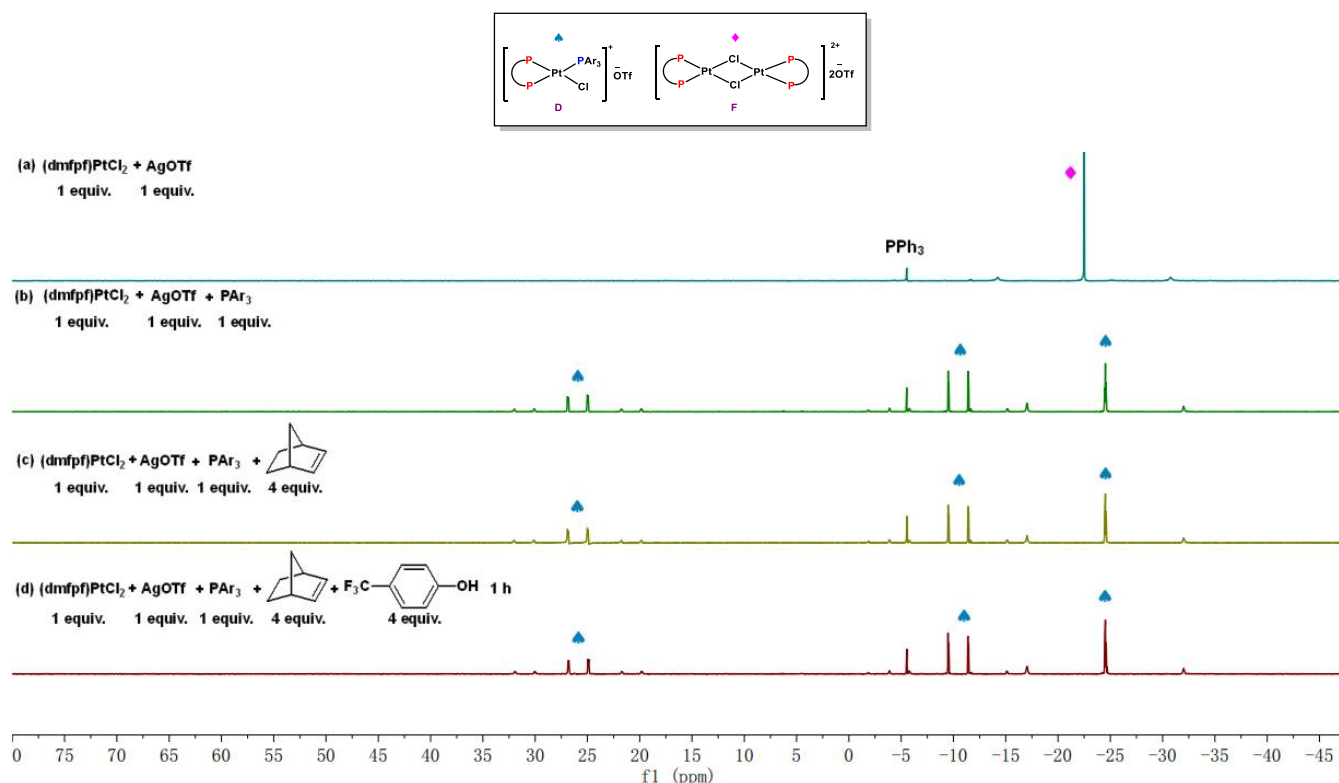
Step 2: To the above solution was added tris(3,4,5-trifluorophenyl)phosphane (8.5 mg, 0.02 mol, 1.0 equiv.). The resulted solution was recorded by ¹H NMR and ³¹P NMR respectively. The new three groups of peaks [δ 25.9 (dd, ²J_{P-P} = 461, 18 Hz, ¹J_{Pt-P} = 2484 Hz), -10.5 (dd, ²J_{P-P} = 461, 17 Hz, ¹J_{Pt-P} = 2735 Hz), -24.5 (t, ²J_{P-P} = 18 Hz, ¹J_{Pt-P} = 3641 Hz) ppm] were formed, which belonged to complex **D** (Supplementary Figure 19b).

Step 3: To the above solution was added norbornene (7.5 mg, 0.08 mmol, 4 equiv.), the resulted solution was recorded by ¹H NMR and ³¹P NMR respectively. Analysis of the ³¹P NMR showed there was no change (Supplementary Figure 18d and 19c).

Step 4: To the above solution was added 4-trifluoromethylphenol (13 mg, 0.08 mmol, 4 equiv.). No reaction occurred (Supplementary Figure 18e and 19d).

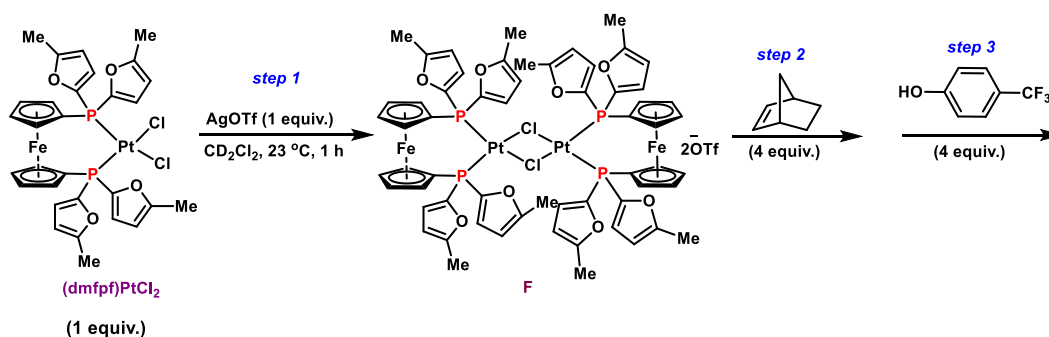


Supplementary Figure 18. ^1H NMR (600 MHz, CD_2Cl_2) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex **F** and Tris(3,4,5-trifluorophenyl)phosphane



Supplementary Figure 19. ^{31}P NMR (243 MHz, CD_2Cl_2) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex F and Tris(3,4,5-trifluorophenyl)phosphane

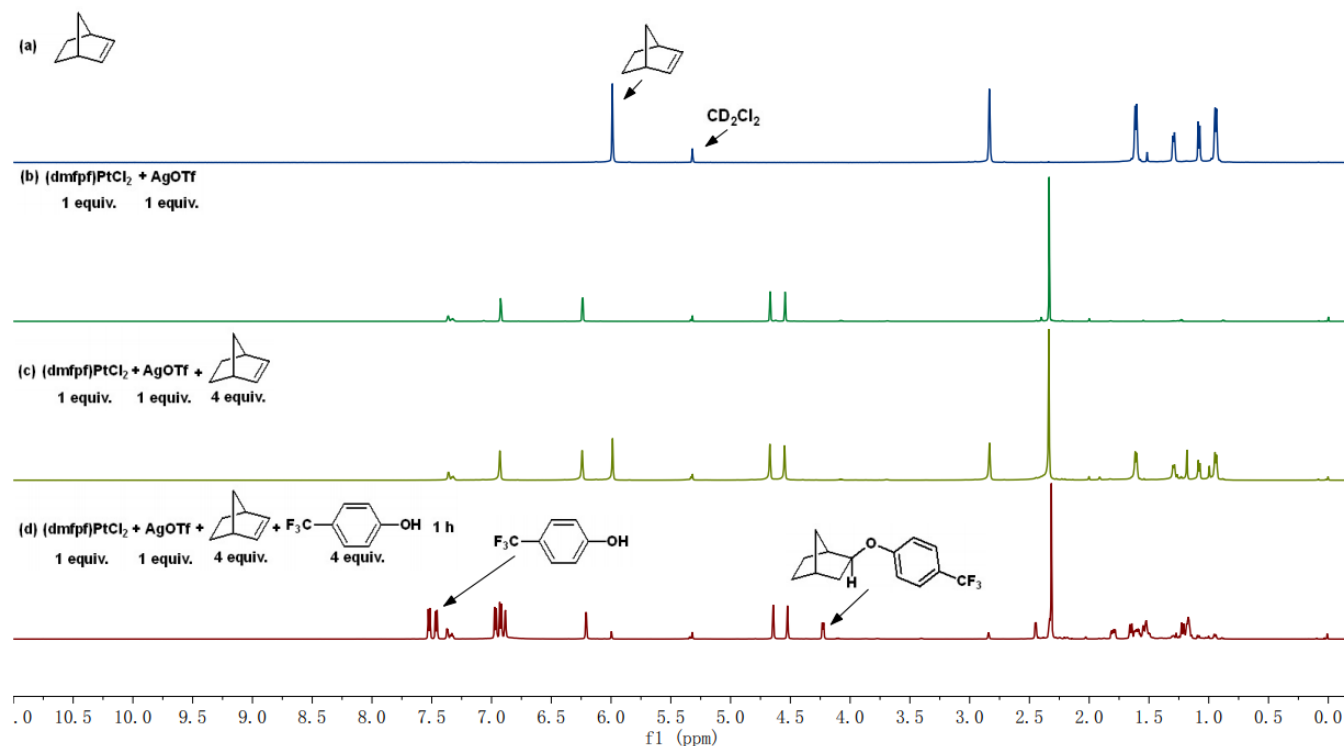
7.3.2.2 NMR Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex F



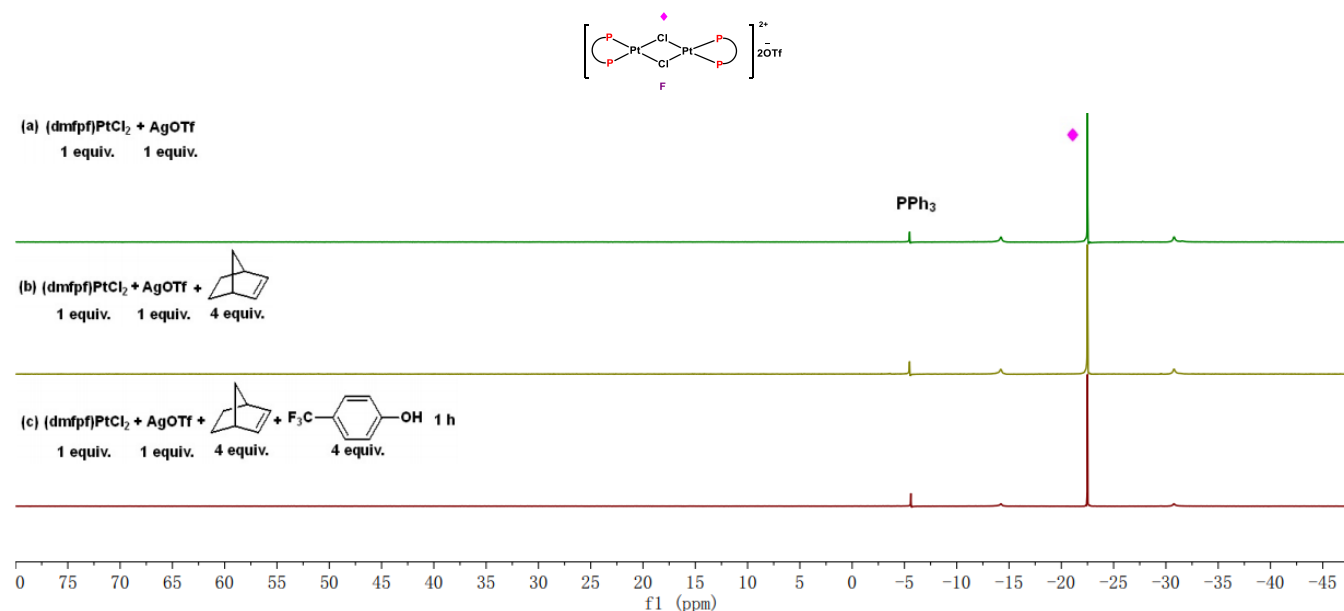
Step 1: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added $(\text{dmfppf})\text{PtCl}_2$ (17 mg, 0.02 mmol), AgOTf (5 mg, 0.02 mmol) in CD_2Cl_2 (500 μL). The mixture was stirred at room temperature (23°C) for 1 h. The mixture was recorded by ^1H NMR and ^{31}P NMR respectively. ^{31}P NMR chemical shifts are referenced to an external PPh_3 standard in CD_2Cl_2 sealed in a capillary tube.

Step 2: To the above solution was added norbornene (7.5 mg, 0.08 mmol, 4 equiv.), the resulted solution was recorded by ^1H NMR and ^{31}P NMR respectively. Analysis of the ^{31}P NMR showed there was no change (Supplementary Figure 20c and 21b).

Step 3: To the above solution was added 4-trifluoromethylphenol (13 mg, 0.08 mmol, 4 equiv.). hydroalkoxylation product **23b** was obtained in 50% yield after 1 h (Supplementary Figure 20d).



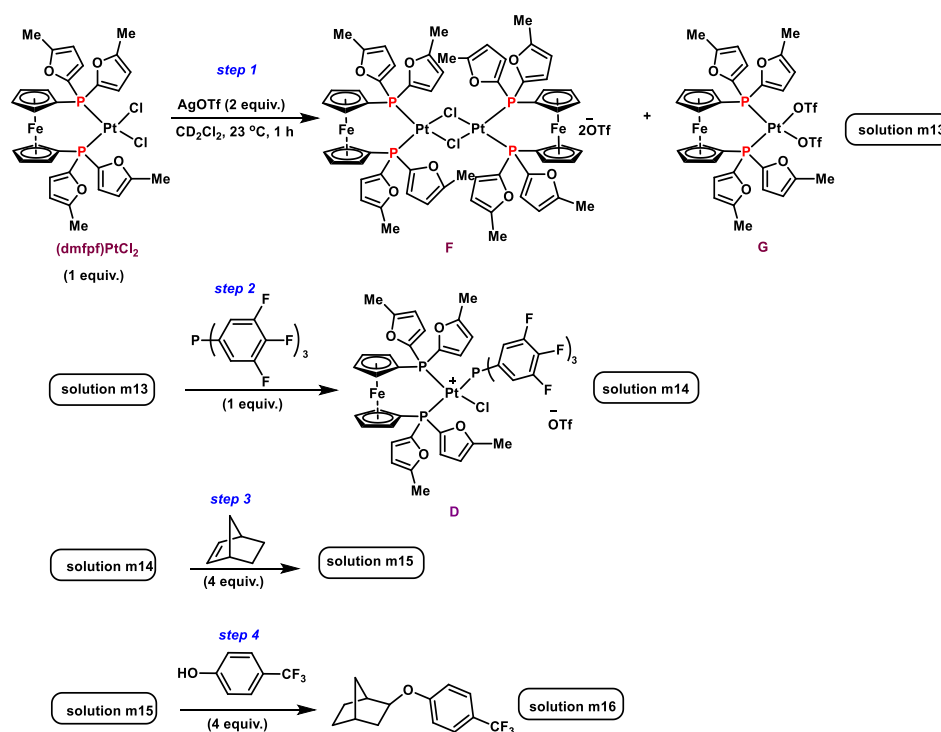
Supplementary Figure 20. ¹H NMR (600 MHz, CD₂Cl₂) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex **F**



Supplementary Figure 21. ³¹P NMR (243 MHz, CD₂Cl₂) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex **F**

7.3.3 Investigation of the Catalytic Activity of Complex **G**

7.3.3.1 NMR Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Unfiltered Complex G

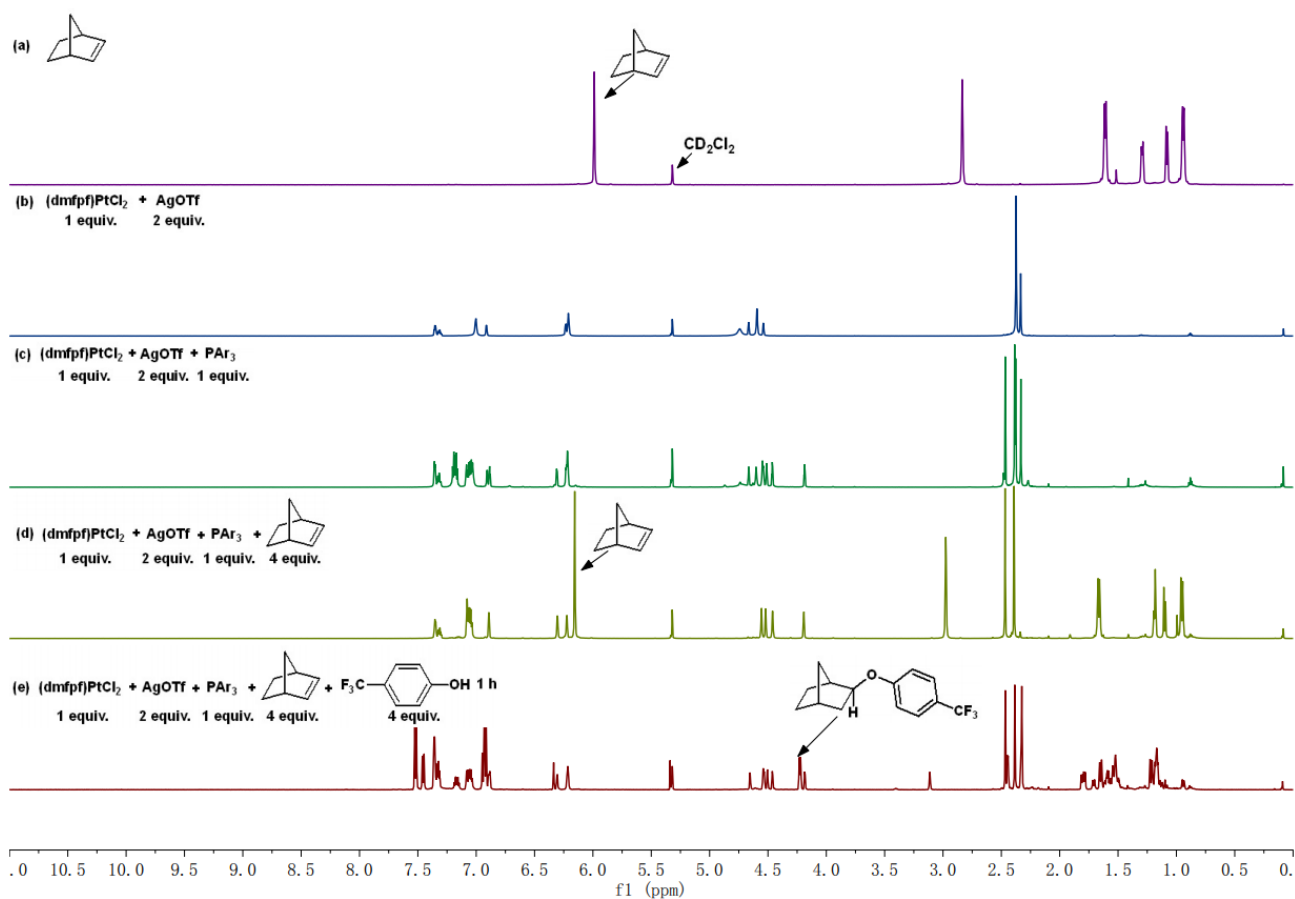


Step 1: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added (dmfpf)PtCl₂ (17 mg, 0.02 mmol), AgOTf (10 mg, 0.04 mmol) and CD₂Cl₂ (500 μ L). The mixture was stirred at room temperature (23 °C) for 1 h. The mixture was recorded by ¹H NMR and ³¹P NMR respectively. ³¹P NMR chemical shifts are referenced to an external PPh₃ standard in CD₂Cl₂ sealed in a capillary tube. Analysis of the ³¹P NMR showed that the new peaks at δ -22.5 ppm belonged to complex **F** and δ -33.5 ppm belonged to complex **G** (Supplementary Figure 23a).

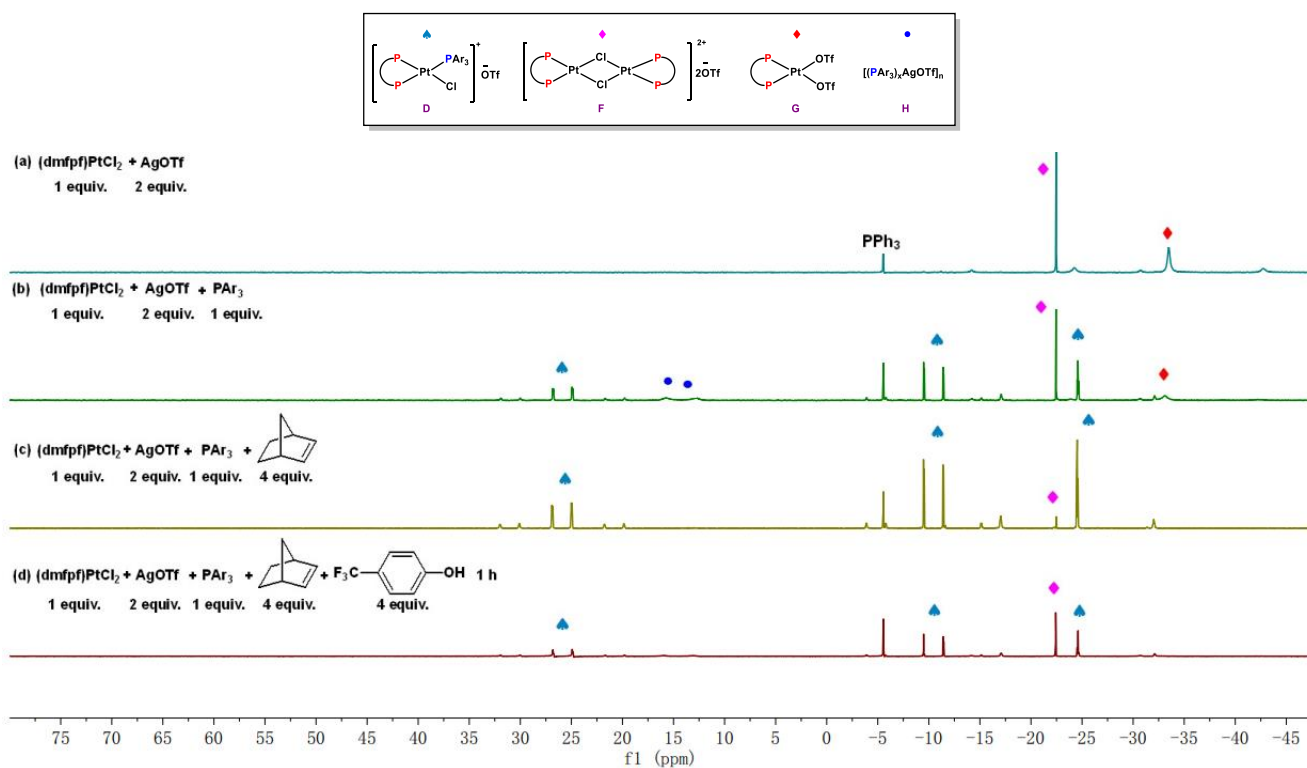
Step 2: To the above solution was added tris(3,4,5-trifluorophenyl)phosphane (8.5 mg, 0.02 mol, 1.0 equiv.). The resulted solution was recorded by ¹H NMR and ³¹P NMR respectively. The new three groups of peaks [δ 25.9 (dd, ²J_{P-P} = 461, 18 Hz, ¹J_{Pt-P} = 2484 Hz), -10.5 (dd, ²J_{P-P} = 461, 17 Hz, ¹J_{Pt-P} = 2735 Hz), -24.5 (t, ²J_{P-P} = 18 Hz, ¹J_{Pt-P} = 3641 Hz) ppm] were formed, which belonged to complex **D**. And the new peaks at δ 15.8 ppm and 12.8 ppm were formed, which belonged complex **H** (Supplementary Figure 23b).

Step 3: To the above solution m18 was added norbornene (7.5 mg, 0.08 mmol, 4 equiv.). The resulted solution was recorded by ¹H NMR and ³¹P NMR respectively. Analysis of the ³¹P NMR showed complex **G** and complex **F** disappeared. Analysis of the ¹H NMR showed the ¹H signal of the double bond moved downfield from 5.99 ppm to 6.14 ppm (Supplementary Figure 22d and S24).

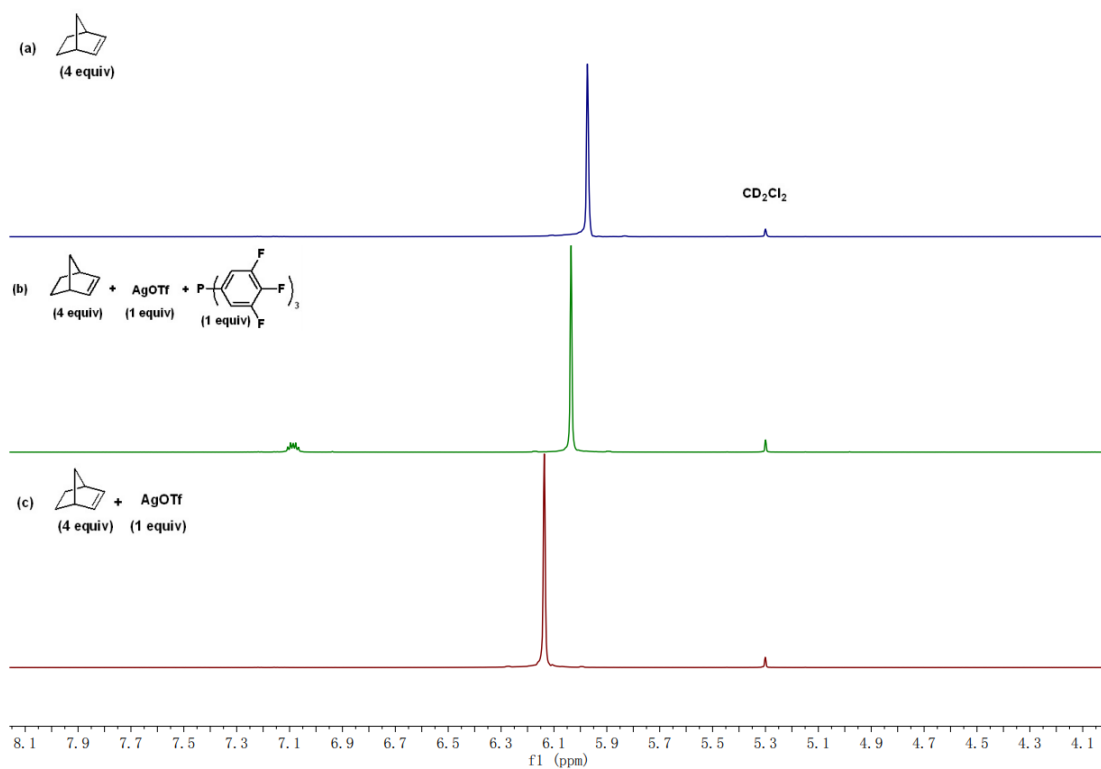
Step 4: To the above solution was added 4-trifluoromethylphenol (13 mg, 0.08 mmol, 4 equiv.). Analysis of the ^1H NMR showed that hydroalkoxylation product **23b** was obtained after 1 h (Supplementary Figure 23e).



Supplementary Figure 22. ^1H NMR (600 MHz, CD₂Cl₂) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex **G**

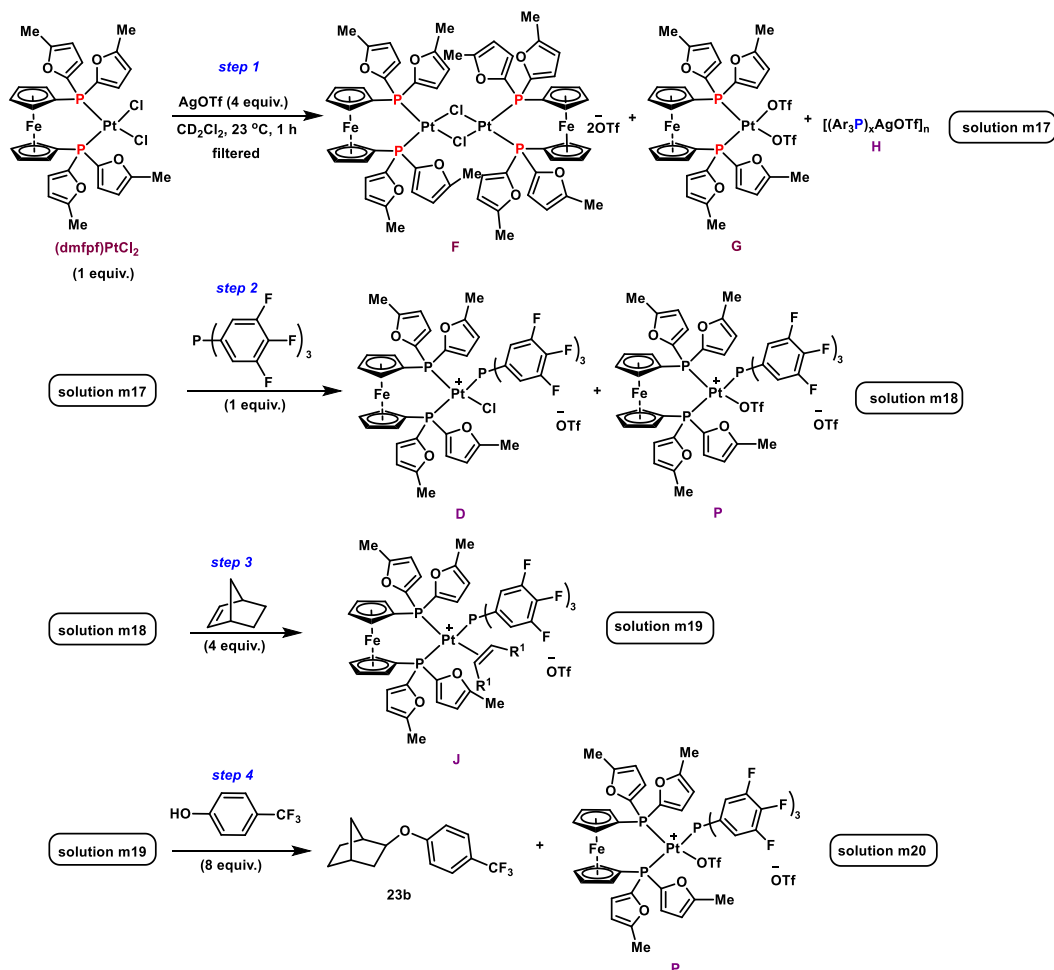


Supplementary Figure 23. ³¹P NMR (243 MHz, CD₂Cl₂) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Complex **G**



Supplementary Figure 24. Comparison of ¹H NMRs of Norbornene, AgOTf + Monodentate Phosphine + Norbornene and Norbornene + AgOTf

7.3.3.2 NMR Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Filtered Complex G



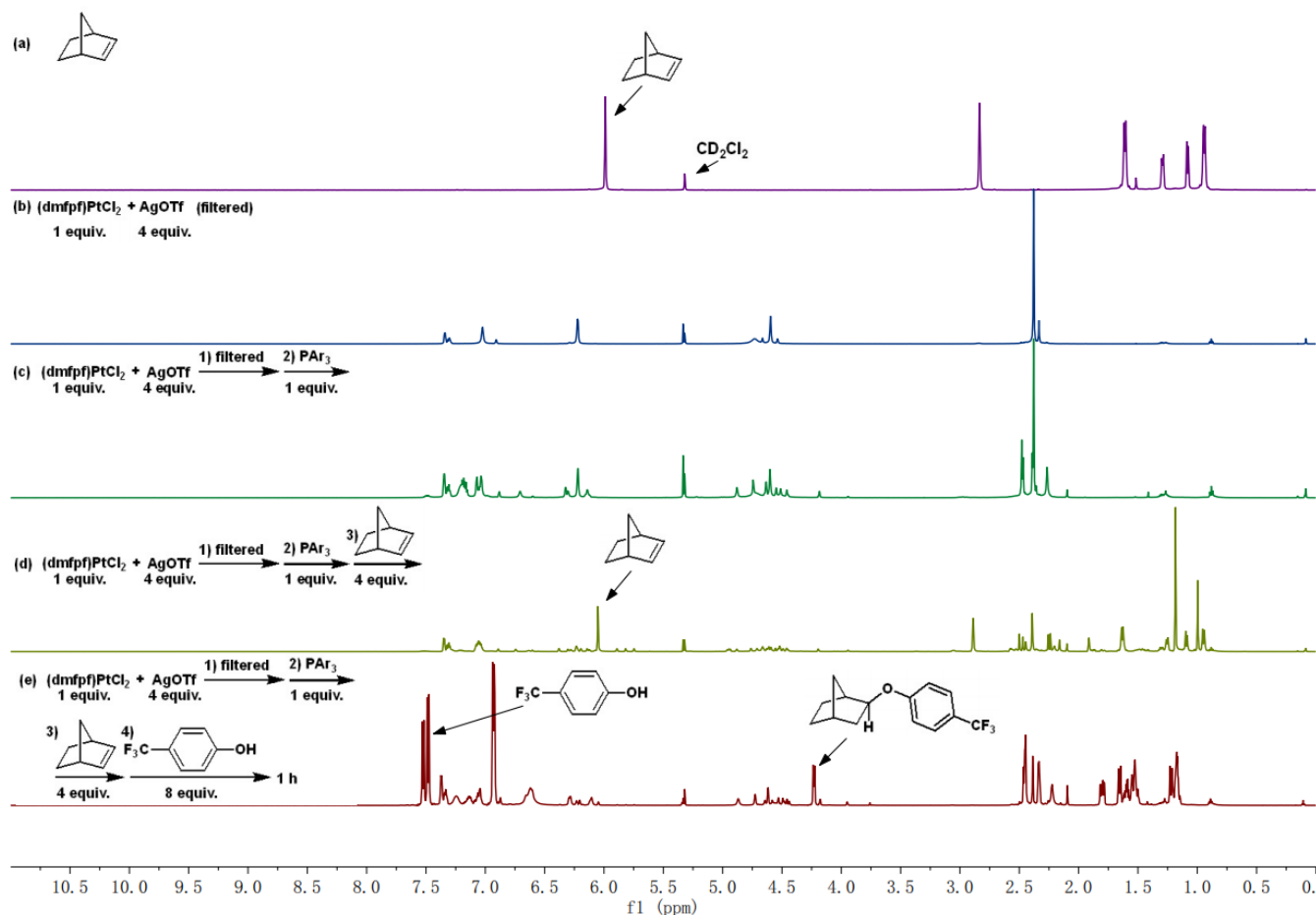
Step 1: In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added (dmfpf)PtCl₂ (17 mg, 0.02 mmol), AgOTf (20 mg, 0.08 mmol) and CD₂Cl₂ (500 μ L). The mixture was stirred at room temperature (23 °C) for 1 h. The mixture was filtered and filtrate was recorded by ¹H NMR and ³¹P NMR respectively. ³¹P NMR chemical shifts are referenced to an external PPh₃ standard in CD₂Cl₂ sealed in a capillary tube. Analysis of the ³¹P NMR showed that the new peaks at δ -22.4 ppm belonged to complex **F** and δ -33.2 ppm belonged to complex **G** (Supplementary Figure 26a).

Step 2: To the above solution was added monophosphine ligand tris(3,4,5-trifluorophenyl)phosphane (8.5 mg, 0.02 mol, 1.0 equiv.). The resulted solution was recorded by ¹H NMR and ³¹P NMR respectively. The new three groups of peaks [δ 25.9 (dd, ²J_{P-P} = 461, 18 Hz, ¹J_{Pt-P} = 2484 Hz), -10.5 (dd, ²J_{P-P} = 461, 17 Hz, ¹J_{Pt-P} = 2735 Hz), -24.5 (t, ²J_{P-P} = 18 Hz, ¹J_{Pt-P} = 3641 Hz) ppm] were formed, which belonged to complex **D**. And the new peaks at δ 16.0 ppm, 12.9 ppm were formed, which belonged complex **H**. Another new three groups of peaks [δ 25.8 (d, ²J_{P-P} = 411 Hz, ¹J_{Pt-P} = 2584 Hz), -6.2 (d, ²J_{P-P} = 411, ¹J_{Pt-P} = 2745 Hz),

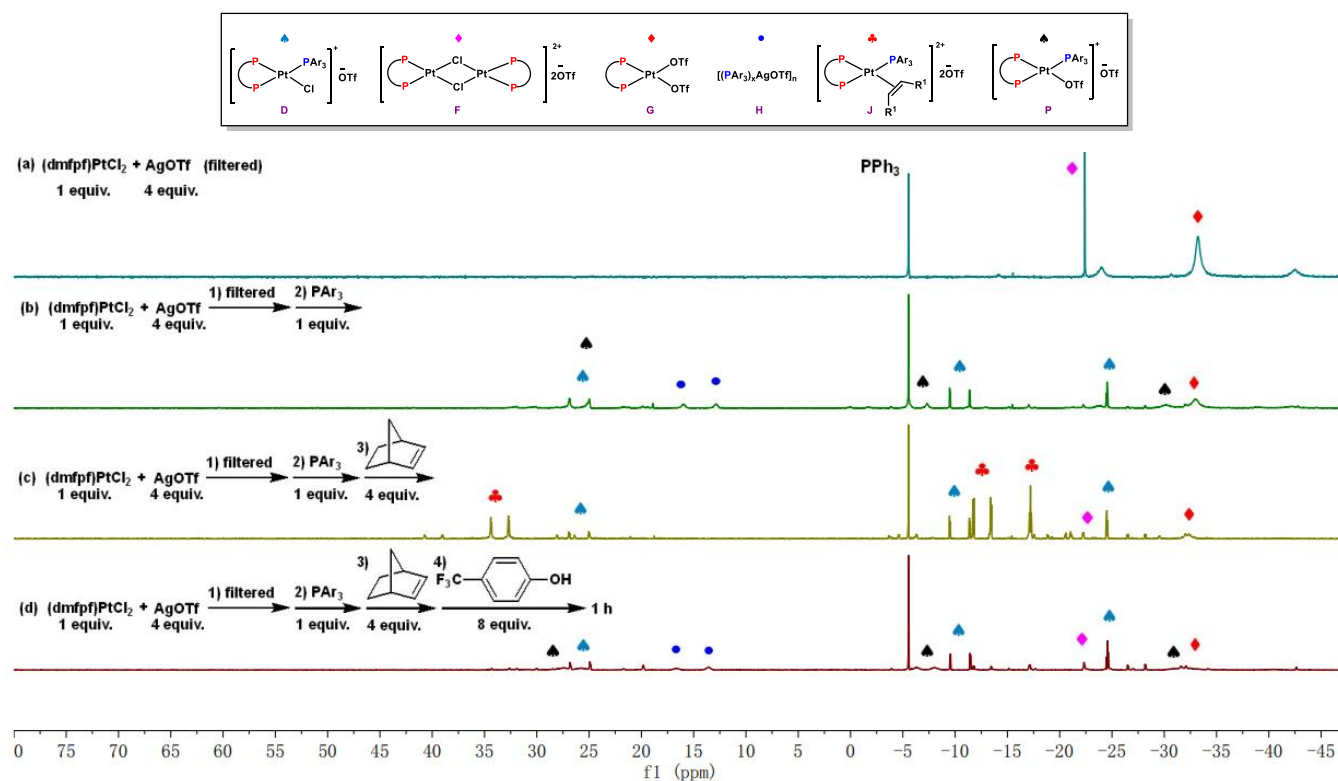
-29.9 (s, broad, $^1J_{\text{Pt-P}} = 4289$ Hz) ppm] were formed, which might belong to complex **P** (Supplementary Figure 26b).

Step 3: To the above solution was added norbornene (7.5 mg, 0.08 mmol, 4 equiv.), and the resulted solution was recorded by ^1H NMR and ^{31}P NMR respectively. The three new groups of peaks [δ 33.6 (dd, $^2J_{\text{P-P}} = 410$, 22 Hz, $^1J_{\text{Pt-P}} = 3075$), -12.6 (dd, $^2J_{\text{P-P}} = 411$, 23 Hz, $^1J_{\text{Pt-P}} = 3463$), -17.2 (t, $^2J_{\text{P-P}} = 22$ Hz, $^1J_{\text{Pt-P}} = 1873$)] were formed, which could belong to intermediate **J** (Supplementary Figure 26c).

Step 4: To the above solution was added 4-trifluoromethylphenol (26 mg, 0.16 mmol, 8 equiv.). Analysis of the ^1H NMR showed that the product **23b** was obtained after 1 h (Supplementary Figure 25e).

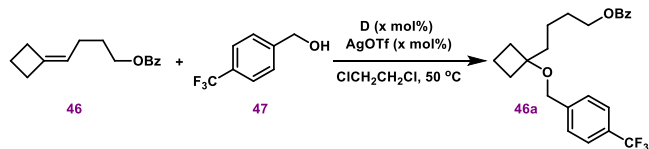


Supplementary Figure 25. ^1H NMR (600 MHz, CD_2Cl_2) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Filtered Complex **G**



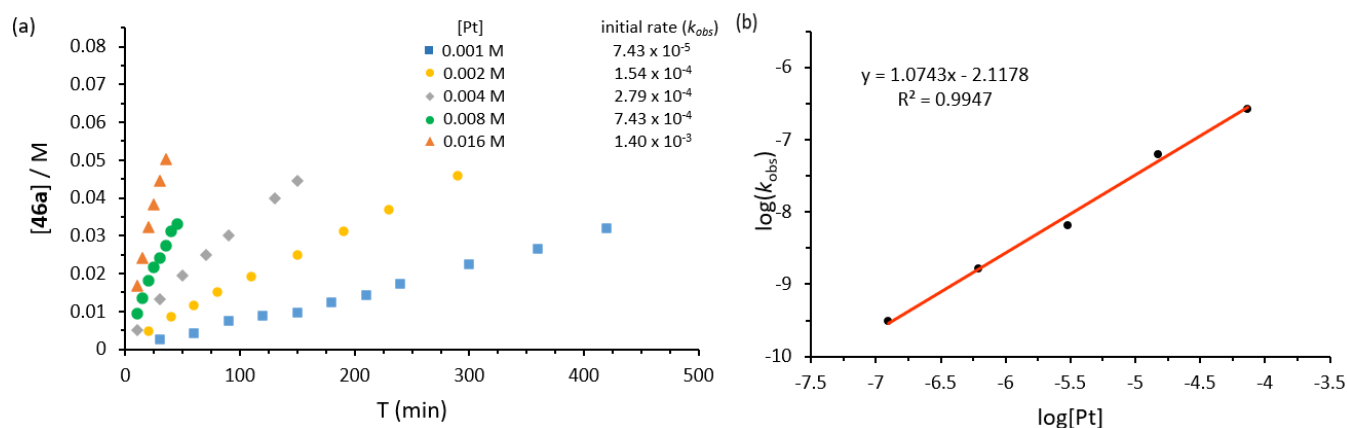
Supplementary Figure 26. ^{31}P NMR (243 MHz, CD_2Cl_2) Monitoring of Hydroalkoxylation of Norbornene and 4-Trifluoromethylphenol Catalyzed by Filtered Complex **G**

8. Kinetic Experiments



For catalyst concentration

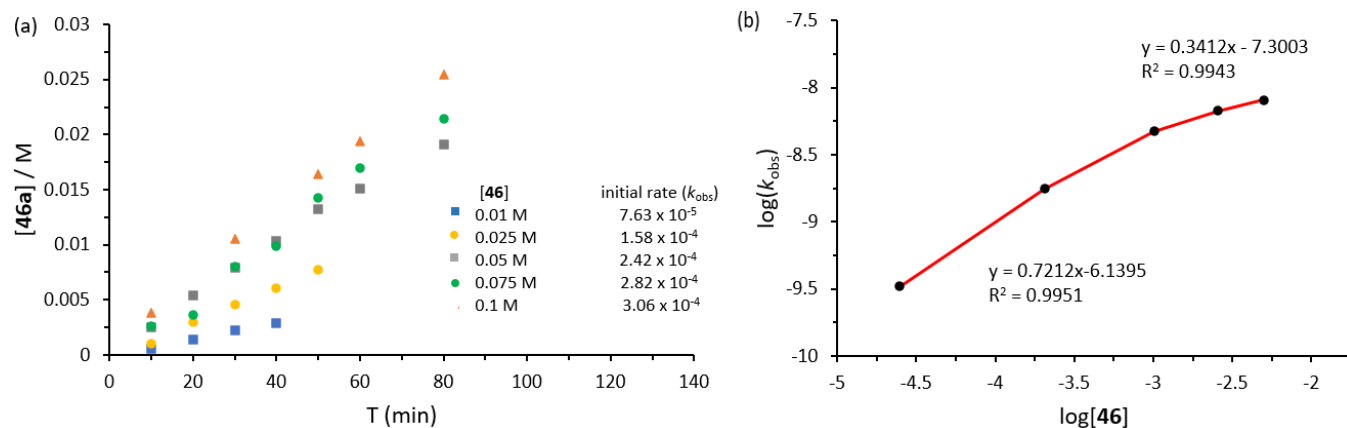
In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst **D** (1 μmol , 2 μmol , 4 μmol , 8 μmol , 16 μmol), AgOTf (1.0 equiv. relative to Pt), $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1.0 mL) and the mixture was stirred at room temperature (23°C) for 1 hour. A solution of 4-cyclobutylidenebutyl benzoate **46** (0.2 mmol, 46 mg), (4-(trifluoromethyl)phenyl)methanol **47** (0.2 mmol, 35 mg) and 4,4'-di-*tert*-butyl-1,1'-biphenyl (4 μmol) used as an internal standard in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1 mL) was added. The reaction was stirred at 50°C . Periodically, an aliquot was removed from the tube and analyzed by LCMS. The experimental results show that the reaction rates for the catalytic Hydroalkoxylation of olefin **46** is first-order in the Pt catalyst **D** (Supplementary Figure 27).



Supplementary Figure 27. Kinetic Analysis. **a** Plot of Initial Reaction Rates at Various Concentrations of Catalyst **D**. **b** Log-Log Plot of Initial Reaction Rates as A Function of Catalyst **D** Concentration.

For 4-cyclobutylidenebutyl benzoate concentration

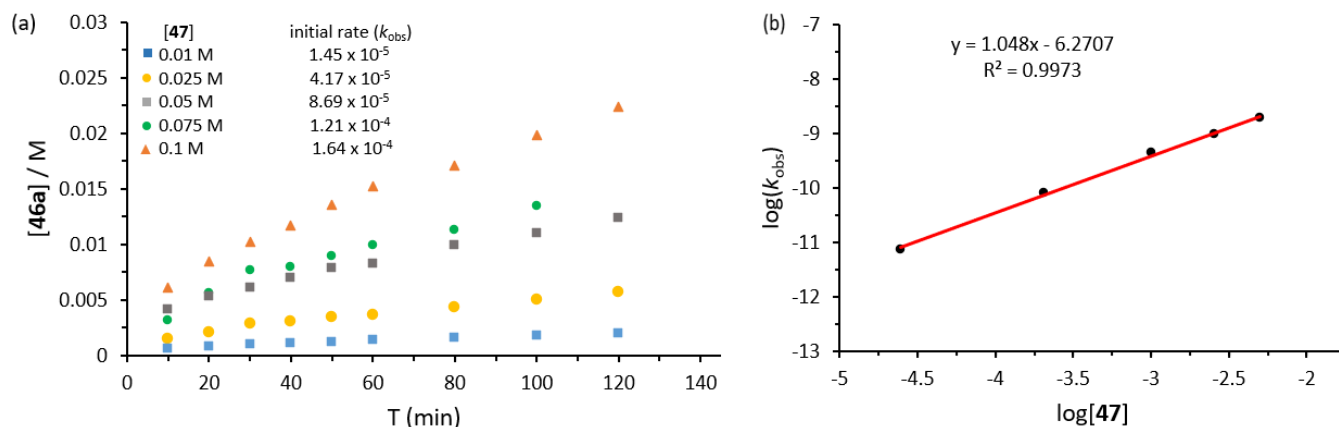
In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst **D** (8 μ mol, 11.0 mg), AgOTf (9.6 μ mol, 2.5 mg), $ClCH_2CH_2Cl$ (1.0 mL) in a 4 mL tube and the mixture was stirred at room temperature (23 $^{\circ}C$) for 1 hour. And then a solution of 4-cyclobutylidenebutyl benzoate **46** (0.02 mmol, 0.05 mmol, 0.1 mmol, 0.15 mmol, 0.2 mmol), (4-(trifluoromethyl)phenyl)methanol **47** (0.4 mmol, 70.5 mg) and 4,4'-di-*tert*-butyl-1,1'-biphenyl (2 mol% relative to **46**) in $ClCH_2CH_2Cl$ (1 mL) was added. The reaction was stirred at 50 $^{\circ}C$. Periodically, an aliquot was removed from the tube and analyzed by LCMS. Under low **[46]** concentration (0.01-0.05 M), a positive linear dependence on **[46]** (slope: 0.72) was observed. In the concentration range of 0.05-0.1 M, a positive linear with a lower slope (0.34) dependence on **[46]** was also obtained (Supplementary Figure 28).



Supplementary Figure 28. Kinetic Analysis. **a** Plot of Initial Reaction Rates at Various Concentrations of 4-Cyclobutylidenebutyl Benzoate. **b** Log-Log Plot of Initial Reaction Rates as A Function of 4-Cyclobutylidenebutyl Benzoate Concentration.

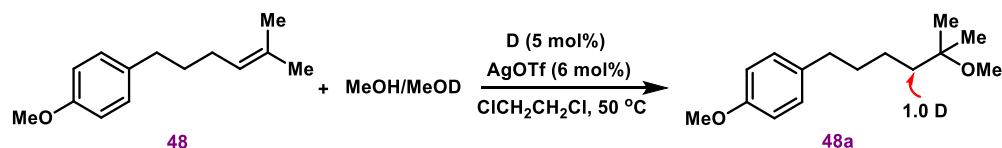
For (4-(trifluoromethyl)phenyl)methanol concentration

In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst **D** (8 μ mol, 11.0 mg), AgOTf (9.6 μ mol, 2.5 mg), ClCH₂CH₂Cl (1.0 mL) in a 4 mL tube and the mixture was stirred at room temperature (23 °C) for 1 hour. Then 4-cyclobutylidenebutyl benzoate **46** (0.4 mmol, 92.0 mg), (4-(trifluoromethyl)phenyl)methanol **47** (0.02 mmol, 0.05 mmol, 0.1 mmol, 0.15 mmol, 0.2 mmol), and 4,4'-di-*tert*-butyl-1,1'-biphenyl (2 mol% relative to **47**) used as an internal standard in ClCH₂CH₂Cl (1 mL) was added. The reaction was stirred at 50 °C. Periodically, an aliquot was removed from the tube and analyzed by LCMS. The experimental results show that the reaction rates for the catalytic Hydroalkoxylation of olefin **46** is first-order dependence on [**47**] (Supplementary Figure 29).

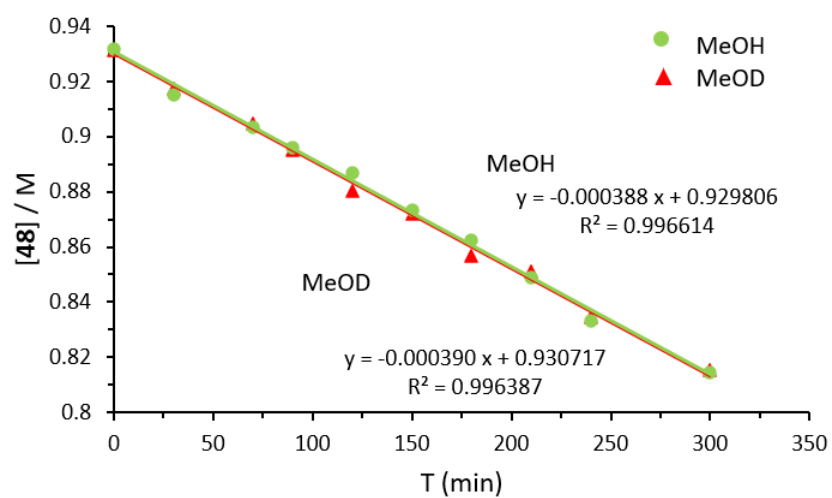


Supplementary Figure 29. Kinetic Analysis. **a** Plot of Initial Reaction Rates at Various Concentrations of (4-(Trifluoromethyl)Phenyl)Methanol. **b** Log-log Plot of Initial Reaction Rates as A Function of (4-(Trifluoromethyl)Phenyl)Methanol Concentration.

Kinetic Isotope Effects

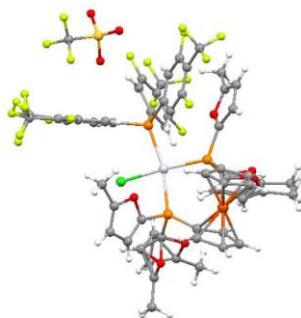


In an argon filled glovebox, to a 4 mL vial with a magnetic stir bar were added the catalyst **D** (10 μ mol, 13.7 mg), AgOTf (12 μ mol, 3.1 mg), ClCH₂CH₂Cl (1.0 mL) in a 4 mL tube and the mixture was stirred at room temperature (23 °C) for 1 hour. A solution of 1-methoxy-4-(5-methylhex-4-en-1-yl)benzene **48** (0.2 mmol, 41.0 mg), MeOH or MeOD (1.4 mmol) and 4,4'-di-*tert*-butyl-1,1'-biphenyl (0.5 equiv. relative to **48**) used as an internal standard in ClCH₂CH₂Cl (1 mL) was added. The reaction was stirred at 50 °C. Periodically, an aliquot was removed from the tube and analyzed by ¹H NMR (Supplementary Figure 30).



Supplementary Figure 30. KIE Measurements for Intermolecular Hydroalkoxylation $KIE = k_{MeOH}/k_{MeOD} = 0.99$

9. X-Ray Structure Determination

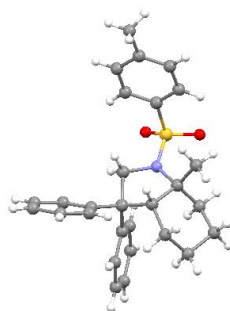


Supplementary Figure 31. Structure of **Catalyst E** with 50% Probability Anisotropic Displacement Ellipsoids

Supplementary Table 8: Crystal Data and Structure Refinement for Catalyst E

CCDC Number	1942024
Empirical formula	$\text{C}_{52}\text{H}_{34}\text{ClF}_{18}\text{FeO}_7\text{P}_3\text{PtS}$
Formula weight	1524.15
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	14.2361(9)
b/Å	15.0250(10)
c/Å	16.8881(11)
$\alpha/^\circ$	65.753(2)
$\beta/^\circ$	88.283(2)
$\gamma/^\circ$	66.531(2)
Volume/Å ³	2982.4(3)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.697
μ/mm^{-1}	2.850
F(000)	1492.0
Crystal size/mm ³	0.45 × 0.36 × 0.28
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	4.458 to 55.136

Index ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	41881
Independent reflections	13722 [R _{int} = 0.0441, R _{sigma} = 0.0480]
Data/restraints/parameters	13722/63/806
Goodness-of-fit on F ²	1.088
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0435, wR ₂ = 0.0909
Final R indexes [all data]	R ₁ = 0.0569, wR ₂ = 0.0993
Largest diff. peak/hole / e Å ⁻³	2.14/-2.36

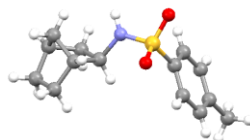


Supplementary Figure 32. Structure of **41a** with 50% Probability Anisotropic Displacement Ellipsoids

Supplementary Table 9: Crystal Data and Structure Refinement for **41a**

CCDC Number	1945616
Empirical formula	C _{28.5} H ₃₂ ClNO ₂ S
Formula weight	488.06
Temperature/K	100.03
Crystal system	orthorhombic
Space group	Pca2 ₁
a/Å	17.9334(10)
b/Å	14.9360(8)
c/Å	18.5885(9)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	4979.0(5)

Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.302
μ/mm^{-1}	0.264
F(000)	2072.0
Crystal size/ mm^3	$0.51 \times 0.48 \times 0.08$
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	4.17 to 55.154
Index ranges	$-23 \leq h \leq 23, -19 \leq k \leq 19, -24 \leq l \leq 24$
Reflections collected	74178
Independent reflections	11299 [$R_{\text{int}} = 0.0927, R_{\text{sigma}} = 0.0605$]
Data/restraints/parameters	11299/1/608
Goodness-of-fit on F^2	0.997
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0354, wR_2 = 0.0804$
Final R indexes [all data]	$R_1 = 0.0542, wR_2 = 0.0860$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.28/-0.35
Flack parameter	0.001(16)

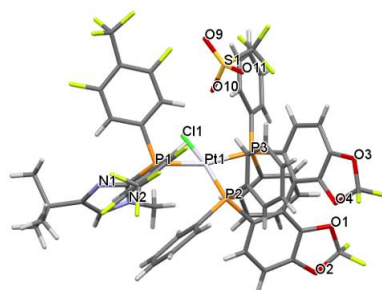


Supplementary Figure 33. Structure of **23f** with 50% Probability Anisotropic Displacement Ellipsoids

Supplementary Table 10: Crystal Data and Structure Refinement for **23f**

CCDC Number	1942471
Empirical formula	$\text{C}_{14.01}\text{H}_{19.01}\text{NO}_2\text{S}$
Formula weight	265.45
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/ $\text{\AA}$	19.0935(12)
b/ $\text{\AA}$	8.2000(5)

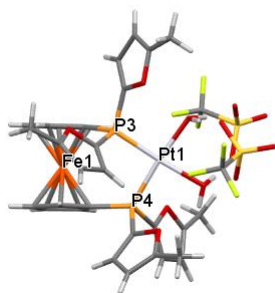
$c/\text{\AA}$	18.4861(11)
$\alpha/^\circ$	90
$\beta/^\circ$	112.539(2)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	2673.2(3)
Z	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.319
μ/mm^{-1}	0.236
$F(000)$	1136.0
Crystal size/ mm^3	$0.34 \times 0.32 \times 0.29$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.62 to 55.012
Index ranges	$-22 \leq h \leq 24, -10 \leq k \leq 10, -24 \leq l \leq 21$
Reflections collected	12215
Independent reflections	3073 [$R_{\text{int}} = 0.0453, R_{\text{sigma}} = 0.0376$]
Data/restraints/parameters	3073/734/294
Goodness-of-fit on F^2	1.044
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0483, wR_2 = 0.1244$
Final R indexes [all data]	$R_1 = 0.0649, wR_2 = 0.1374$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.40/-0.56



Supplementary Figure 34. Structure of Catalyst **M** with 50% Probability Anisotropic Displacement Ellipsoids

Supplementary Table 11: Crystal Data and Structure Refinement for Catalyst **M**

CCDC Number	2021353
Empirical formula	C ₆₁ H ₄₁ ClF ₁₇ N ₂ O ₇ P ₃ PtS
Formula weight	1591.09
Temperature/K	100
Crystal system	triclinic
Space group	P1
a/Å	13.6752(9)
b/Å	16.8453(11)
c/Å	18.9222(12)
$\alpha/^\circ$	70.156(2)
$\beta/^\circ$	89.890(2)
$\gamma/^\circ$	86.615(2)
Volume/Å ³	4092.2(5)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.479
μ/mm^{-1}	1.922
F(000)	1822.0
Crystal size/mm ³	0.32 × 0.29 × 0.16
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	4.578 to 59.264
Index ranges	-18 ≤ h ≤ 19, -23 ≤ k ≤ 23, -26 ≤ l ≤ 26
Reflections collected	111371
Independent reflections	45537 [R _{int} = 0.0415, R _{sigma} = 0.0568]
Data/restraints/parameters	45537/308/1990
Goodness-of-fit on F ²	1.033
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0429, wR ₂ = 0.1010
Final R indexes [all data]	R ₁ = 0.0505, wR ₂ = 0.1052
Largest diff. peak/hole / e Å ⁻³	1.71/-1.38
Flack parameter	-0.009(2)

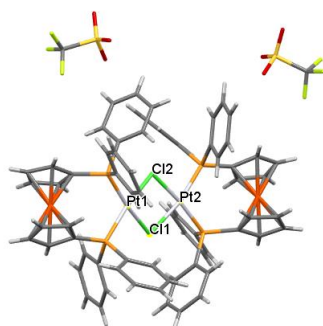


Supplementary Figure 35. Structure of Complex **R** with 50% Probability Anisotropic Displacement Ellipsoids

Supplementary Table 12: Crystal Data and Structure Refinement for Complex **R**

CCDC Number	2053041
Empirical formula	C ₃₀ H ₃₂ FeO ₆ P ₂ Pt
Formula weight	801.0671
Temperature/K	100
Crystal system	triclinic
Space group	P1
a/Å	10.3493(5)
b/Å	10.4314(5)
c/Å	20.0476(10)
$\alpha/^\circ$	91.063(2)
$\beta/^\circ$	99.470(2)
$\gamma/^\circ$	112.8780(10)
Volume/Å ³	1958.74(17)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.864
μ/mm^{-1}	4.213
F(000)	1080.0
Crystal size/mm ³	0.32 × 0.29 × 0.05
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	4.136 to 56.752
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -26 ≤ l ≤ 26
Reflections collected	38311

Independent reflections	9779 [$R_{\text{int}} = 0.0554$, $R_{\text{sigma}} = 0.0439$]
Data/restraints/parameters	9779/0/512
Goodness-of-fit on F^2	1.044
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0254$, $wR_2 = 0.0558$
Final R indexes [all data]	$R_1 = 0.0304$, $wR_2 = 0.0577$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.42/-1.45



Supplementary Figure 36. Structure of Catalyst **Q** with 50% Probability Anisotropic Displacement Ellipsoids

Supplementary Table 13: Crystal Data and Structure Refinement for Catalyst **Q**

CCDC Number	2053040
Empirical formula	$\text{C}_{70}\text{H}_{56}\text{Cl}_2\text{F}_6\text{Fe}_2\text{O}_6\text{P}_4\text{Pt}_2\text{S}_2$
Formula weight	1865.9744
Temperature/K	100
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	13.0484(3)
$b/\text{\AA}$	16.9540(4)
$c/\text{\AA}$	19.2928(5)
$\alpha/^\circ$	80.1960(10)
$\beta/^\circ$	76.9990(10)
$\gamma/^\circ$	76.8210(10)
Volume/ $\text{\AA}^3$	4017.10(17)
Z	2

$\rho_{\text{calc}}/\text{cm}^3$	1.808
μ/mm^{-1}	13.093
F(000)	2153.0
Crystal size/ mm^3	$0.31 \times 0.24 \times 0.22$
Radiation	$\text{MoK}\alpha$ ($\lambda = 1.54178$)
2Θ range for data collection/ $^\circ$	4.738 to 136.848
Index ranges	$-14 \leq h \leq 15, -20 \leq k \leq 20, -23 \leq l \leq 23$
Reflections collected	58377
Independent reflections	14714 [$R_{\text{int}} = 0.0617, R_{\text{sigma}} = 0.0502$]
Data/restraints/parameters	14714/199/1052
Goodness-of-fit on F^2	1.055
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0459, wR_2 = 0.1226$
Final R indexes [all data]	$R_1 = 0.0500, wR_2 = 0.1259$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	2.83/-1.85

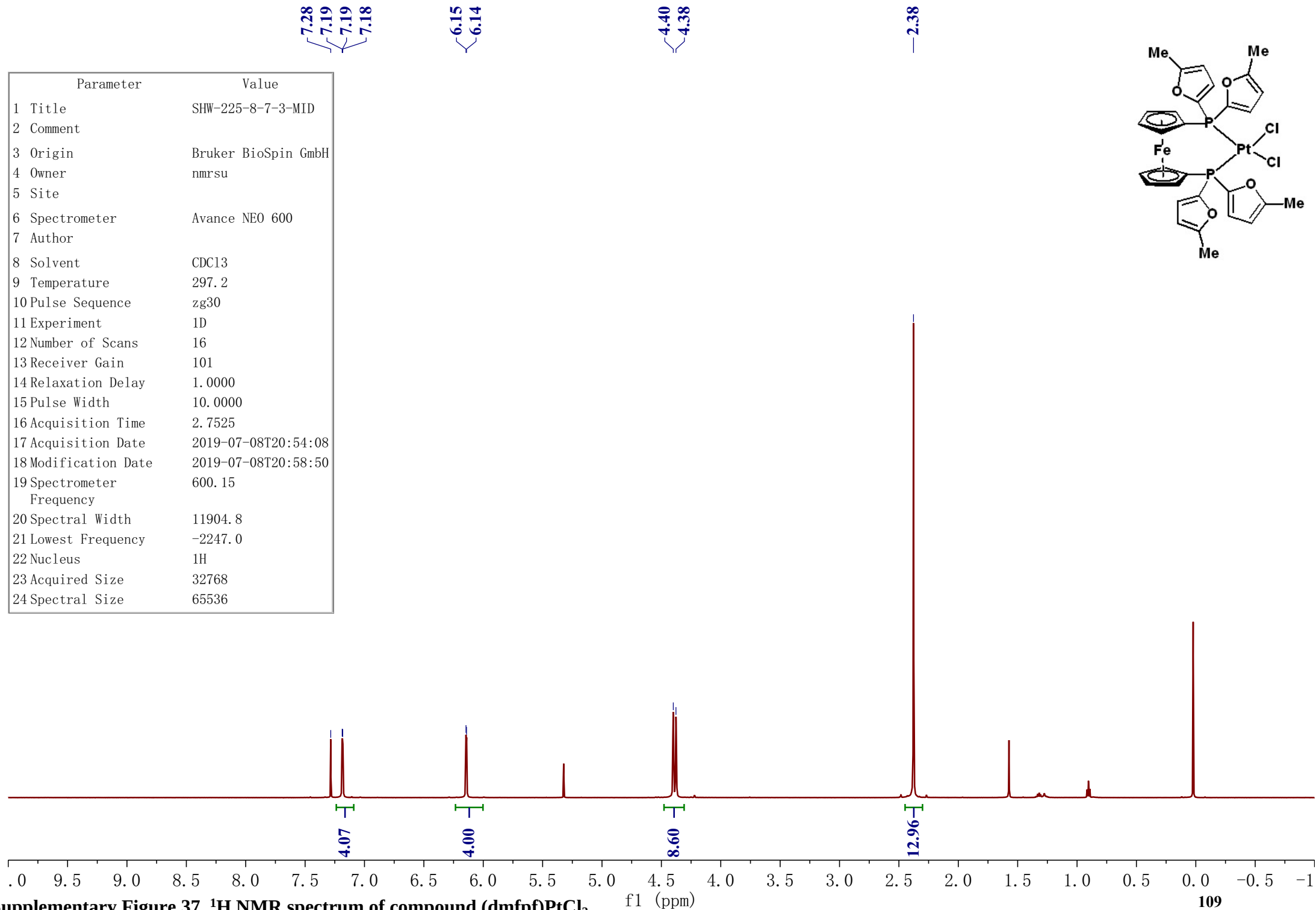
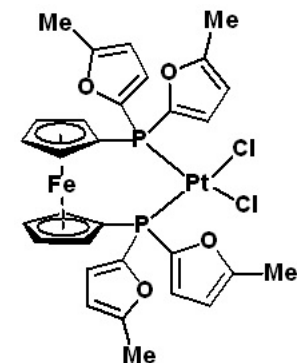
10. Supplementary References

1. Clarke, M. L. et al. The electron-poor phosphines $P\{C_6H_3(CF_3)_2-3,5\}_3$ and $P(C_6F_5)_3$ do not mimic phosphites as ligands for hydroformylation. A comparison of the coordination chemistry of $P\{C_6H_3(CF_3)_2-3,5\}_3$ and $P(C_6F_5)_3$ and the unexpectedly low hydroformylation activity of their rhodium complexes. *Dalton Trans.*, 1294-1300 (2005).
2. Qian, H., Han, X. & Widenhoefer, R. A. Platinum-catalyzed intramolecular hydroalkoxylation of γ - and δ -hydroxy olefins to form cyclic ethers. *J. Am. Chem. Soc.* **126**, 9536-9537 (2004).
3. Bloome, K. S. & Alexanian, E. J. Palladium-catalyzed carbonylative heck-type reactions of alkyl iodides. *J. Am. Chem. Soc.* **132**, 12823-12825 (2010).
4. Fujita, S., Abe, M., Shibuya, M. & Yamamoto, Y. Intramolecular hydroalkoxylation of unactivated alkenes using silane–iodine catalytic system. *Org. Lett.* **17**, 3822-3825 (2015).
5. Hartung, J. et al. (Schiff-base)vanadium(V) complex-catalyzed oxidations of substituted bis(homoallylic) alcohols–stereoselective synthesis of functionalized tetrahydrofurans. *Eur. J. Org. Chem.* 2388-2408 (2003).
6. Hoang, G. T., Walsh, D. J., McGarry, K. A., Anderson, C. B. & Douglas, C. J. Development and mechanistic study of quinoline-directed acyl C–O bond activation and alkene oxyacylation reactions. *J. Org. Chem.* **82**, 2972-2983 (2017).
7. Sparrow, K. J., Carley, S., Sohnel, T., Barker, D. & Brimble, M. A. Studies towards development of asymmetric double-Mannich reactions of chiral 2-oxocyclohexanecarboxylate derivatives with bis(aminol)ethers. *Tetrahedron* **71**, 2210-2221 (2015).
8. Chen, X., Merrett, J. T. & Chan, P. W. H. Gold-catalyzed formal [4 + 2] cycloaddition of 5-(ethynylamino)pent-2-yn-1-yl esters to 1,2,3,5-tetrahydrobenzo[*g*]quinolines. *Org. Lett.* **20**, 1542-1545 (2018).
9. Mihara, K., Okada, I., Chiba, K. & Kitano, Y. Facile synthesis of *N*-substituted amides from alkenes and amides by a brønsted acid mediated electrophilic addition reaction. *Synthesis* **46**, 1455-1462 (2014).
10. White, D. R., Hinds, E. M., Bornowski, E. C. & Wolfe, J. P. Pd-catalyzed alkene difunctionalization reactions of malonate nucleophiles: synthesis of substituted cyclopentanes via alkene aryl-alkylation and akenyl-alkylation. *Org. Lett.* **21**, 3813-3816 (2019).
11. Ferrand, L. et al. Niobium-catalyzed intramolecular addition of O–H and N–H bonds to alkenes: a tool for hydrofunctionalization. *Org. Lett.* **19**, 2062-2065 (2017).
12. Marion, F., Coulomb, J., Courillon, C., Fensterbank, L. & Malacria, M. Platinum dichloride-catalyzed cycloisomerization of ene-ynamides. *Org. Lett.* **6**, 1509-1511 (2004).
13. Kuznetsov, A., Makarov, A., Rubtsov, A. E., Butin, A. V. & Gevorgyan, V. Brønsted acid-catalyzed one-pot synthesis of indoles from *o*-aminobenzyl alcohols and furans. *J. Org. Chem.* **78**, 12144-12153 (2013).
14. Kapat, A., König, A., Montermini, F. & Renaud, P. A radical procedure for the anti-markovnikov hydroazidation of alkenes. *J. Am. Chem. Soc.* **133**, 13890-13893 (2011).
15. Ohmiya, H., Tsuji, T., Yorimitsu, H. & Oshima, K. Cobalt-catalyzed cross-coupling reactions of alkyl halides with allylic and benzylic grignard reagents and their application to tandem radical cyclization/cross-coupling reactions. *Chem. Eur. J.* **10**, 5640-5648 (2004).
16. Green, S. A., Vásquez-Céspedes, S. & Shenvi, R. A. Iron–nickel dual-catalysis: a new engine for olefin

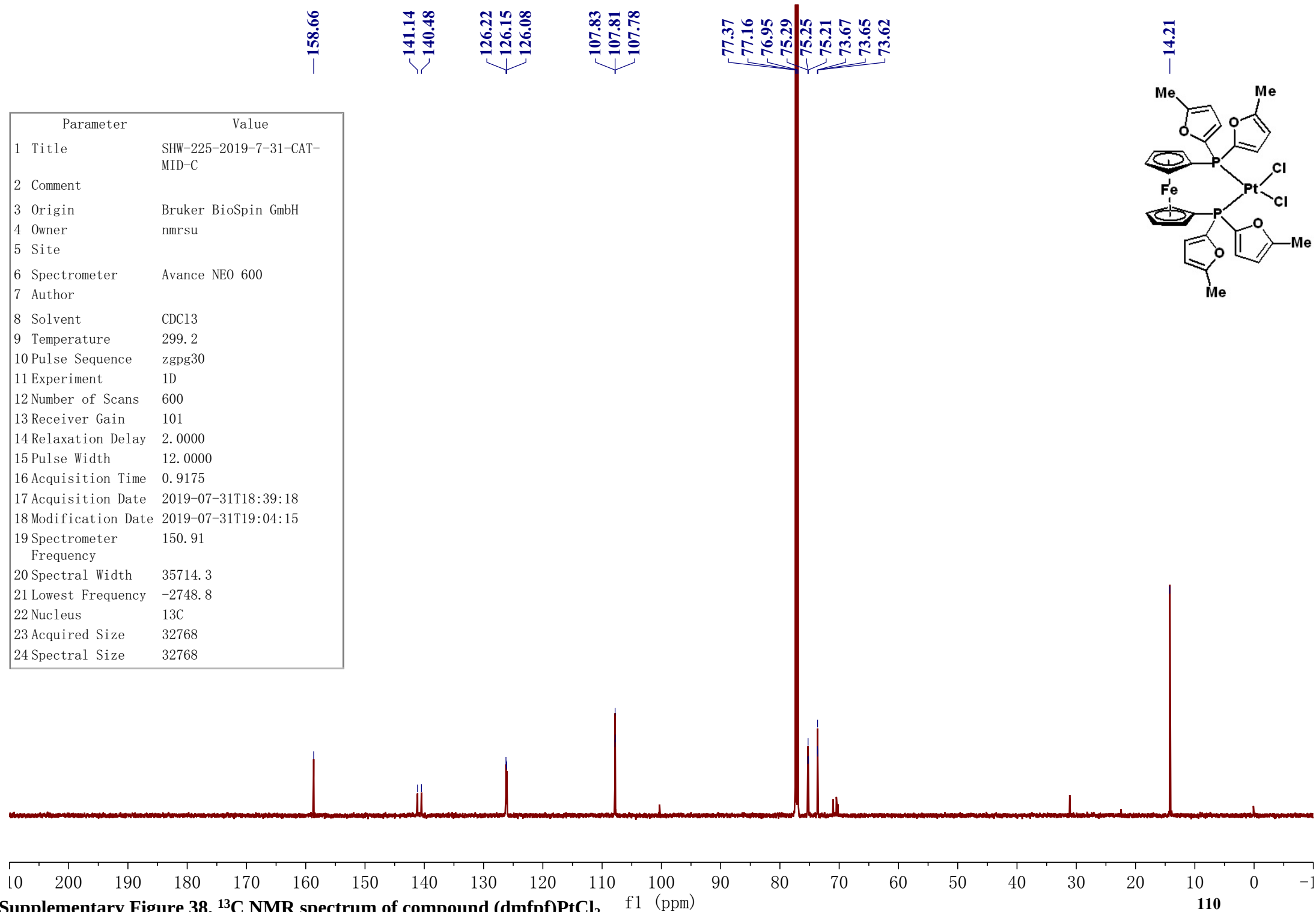
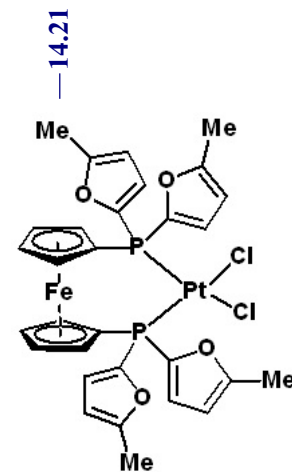
- functionalization and the formation of quaternary centers. *J. Am. Chem. Soc.* **140**, 11317-11324 (2018).
17. Ye, L., Lo, K.-Y., Gu, Q. & Yang, D. Pd-catalyzed intramolecular aminoalkylation of unactivated alkenes: access to diverse *N*-heterocycles. *Org. Lett.* **19**, 308-311 (2017).
 18. Zhu, X. & Chiba, S. TEMPO-mediated allylic C–H amination with hydrazones. *Org. Biomol. Chem.* **12**, 4567-4570 (2014).
 19. Driver, T. G. & Woerpel, K. A. Mechanism of silver-mediated di-*tert*-butylsilylene transfer from a silacyclopropane to an alkene. *J. Am. Chem. Soc.* **126**, 9993-10002 (2004).
 20. Lettko, L., Wood, J. S. & Rausch, M. D. Synthesis of (phosphine)silver(I) trifluoromethanesulfonate complexes and the molecular structure of di- μ -trifluoromethylsulfonate-(tetrakis-triphenylphosphine)disilver(I). *Inorganica Chimica Acta* **308**, 37-44 (2000).
 21. Clark, T. J. et al. Rhodium-catalyzed dehydrocoupling of fluorinated phosphine-borane adducts: synthesis, characterization, and properties of cyclic and polymeric phosphinoboranes with electron-withdrawing substituents at phosphorus. *Chem. Eur. J.* **11**, 4526-4534 (2005).
 22. Grotjahn, D. B. et al. Finding the proton in a key intermediate of anti-markovnikov alkyne hydration by a bifunctional catalyst. *J. Am. Chem. Soc.* **130**, 10860-10861 (2008).
 23. Watson, M. P. & Jacobsen, E. N. Asymmetric intramolecular arylcyanation of unactivated olefins via C–CN bond activation. *J. Am. Chem. Soc.* **130**, 12594-12595 (2008).
 24. Fustero, S. et al. Organocatalytic approach to benzofused nitrogen-containing heterocycles: enantioselective total synthesis of (+)-angustureine. *Chem. - Eur. J.* **14**, 9868-9872 (2008).
 25. Rosenfeld, D. C., Shekhar, S., Takemiya, A., Utsunomiya, M. & Hartwig, J. F. Hydroamination and hydroalkoxylation catalyzed by triflic acid. Parallels to reactions initiated with metal triflates. *Org. Lett.* **8**, 4179-4182 (2006).
 26. Zeng, W. & Chemler, S. R. Copper(II)-catalyzed enantioselective intramolecular carboamination of alkenes. *J. Am. Chem. Soc.* **129**, 12948-12949 (2007).
 27. Hazelden, I. R., Carmona, R. C., Langer, T., Pringle, P. G. & Bower, J. F. Pyrrolidines and piperidines by ligand-enabled aza-heck cyclizations and cascades of *N*-(pentafluorobenzoyloxy)carbamates. *Angew. Chem. Int. Ed.* **57**, 5124-5128 (2018).
 28. Escudero, J., Bellosta, V. & Cossy, J. Rhodium-catalyzed cyclization of *O,w*-unsaturated alkoxyamines: formation of oxygen-containing heterocycles. *Angew. Chem. Int. Ed.* **57**, 574-578 (2018).
 29. Rösner, C. & Hennecke, U. Homohalocyclization: electrophilic bromine-induced cyclizations of cyclopropanes. *Org. Lett.* **17**, 3226-3229 (2015).

11. NMR Spectra

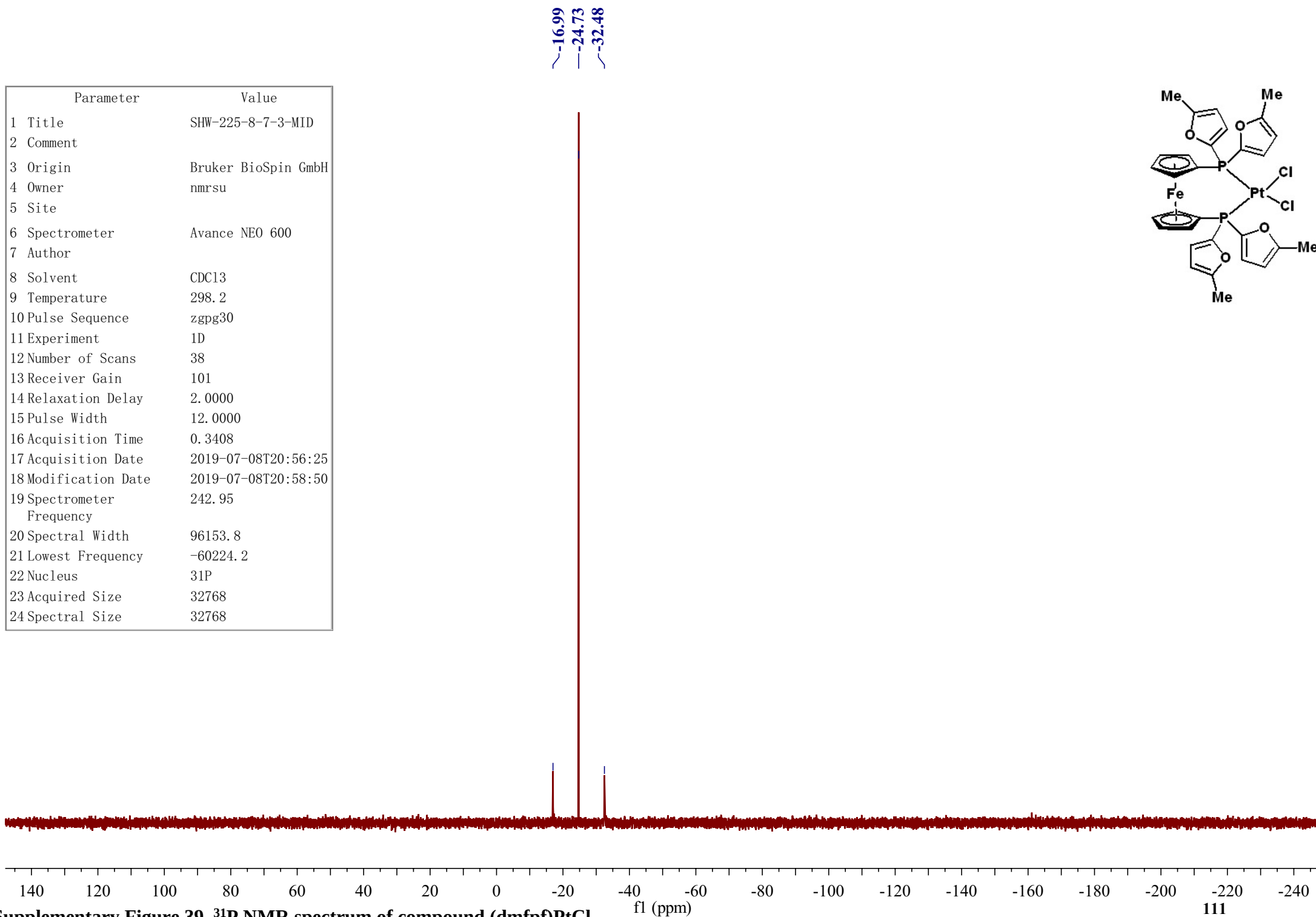
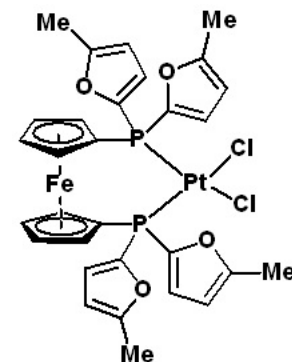
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2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2019-07-08T20:54:08
18 Modification Date	2019-07-08T20:58:50
19 Spectrometer	600.15
Frequency	
20 Spectral Width	11904.8
21 Lowest Frequency	-2247.0
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

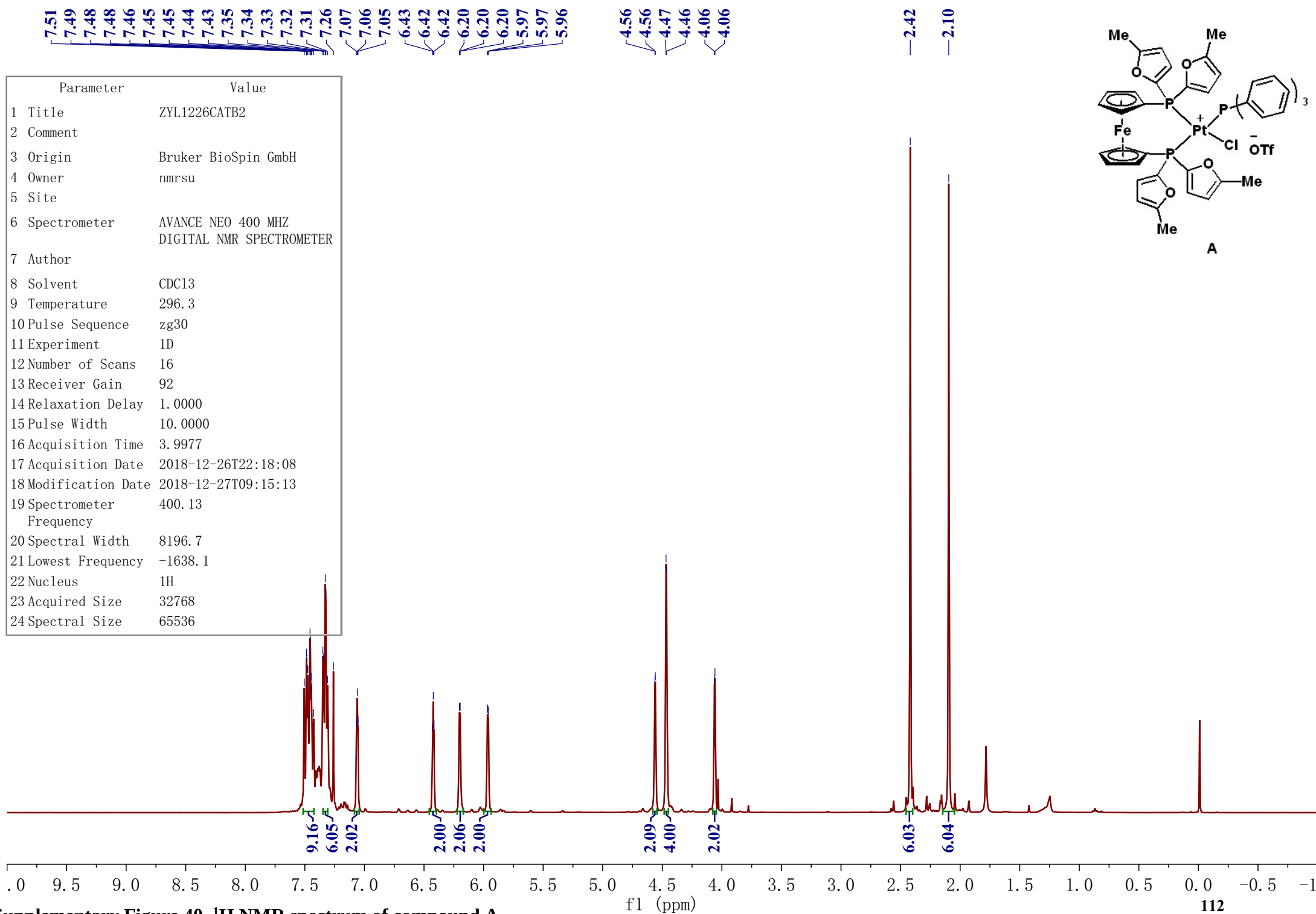


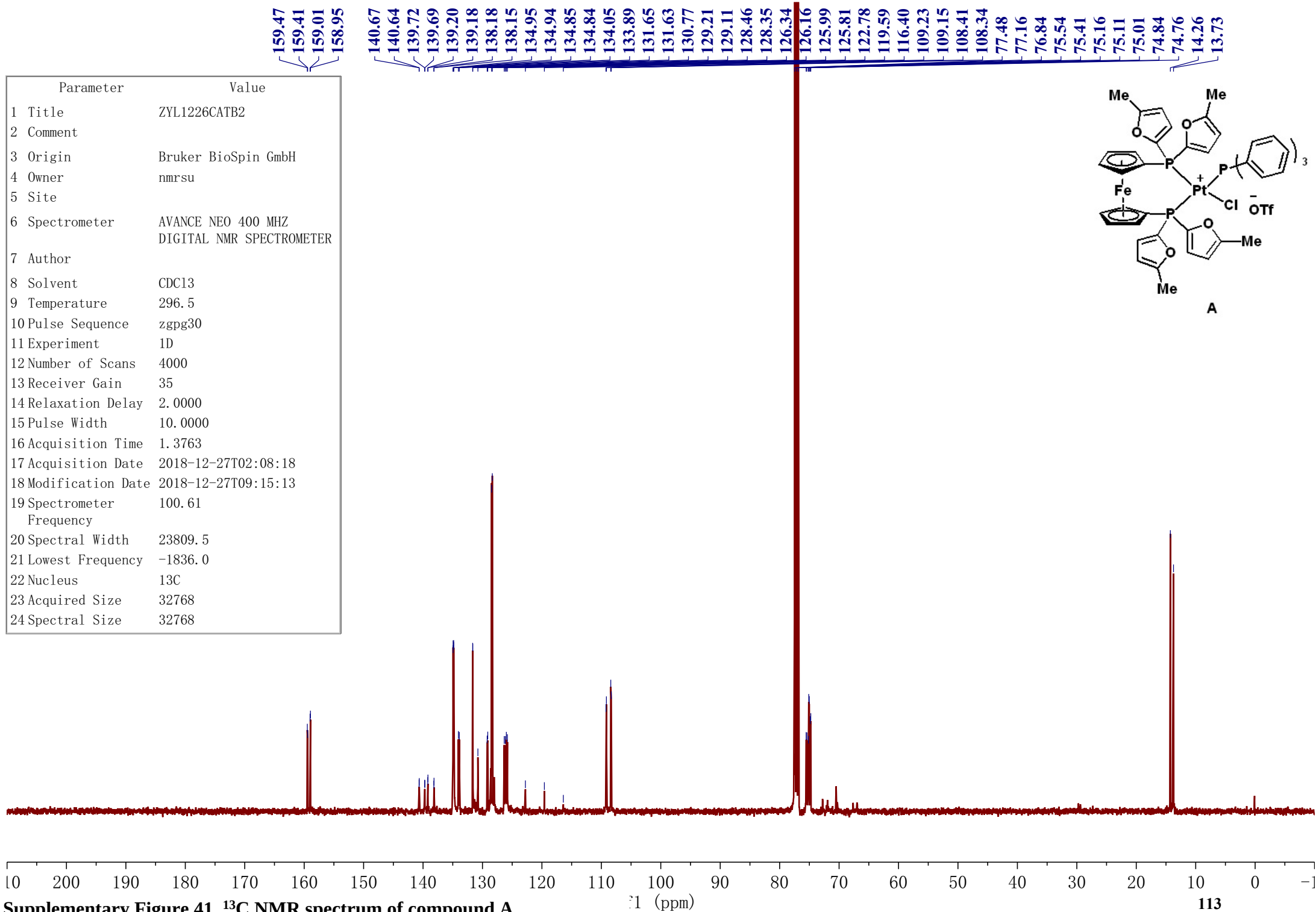
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2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	299.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	600
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-07-31T18:39:18
18 Modification Date	2019-07-31T19:04:15
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2748.8
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

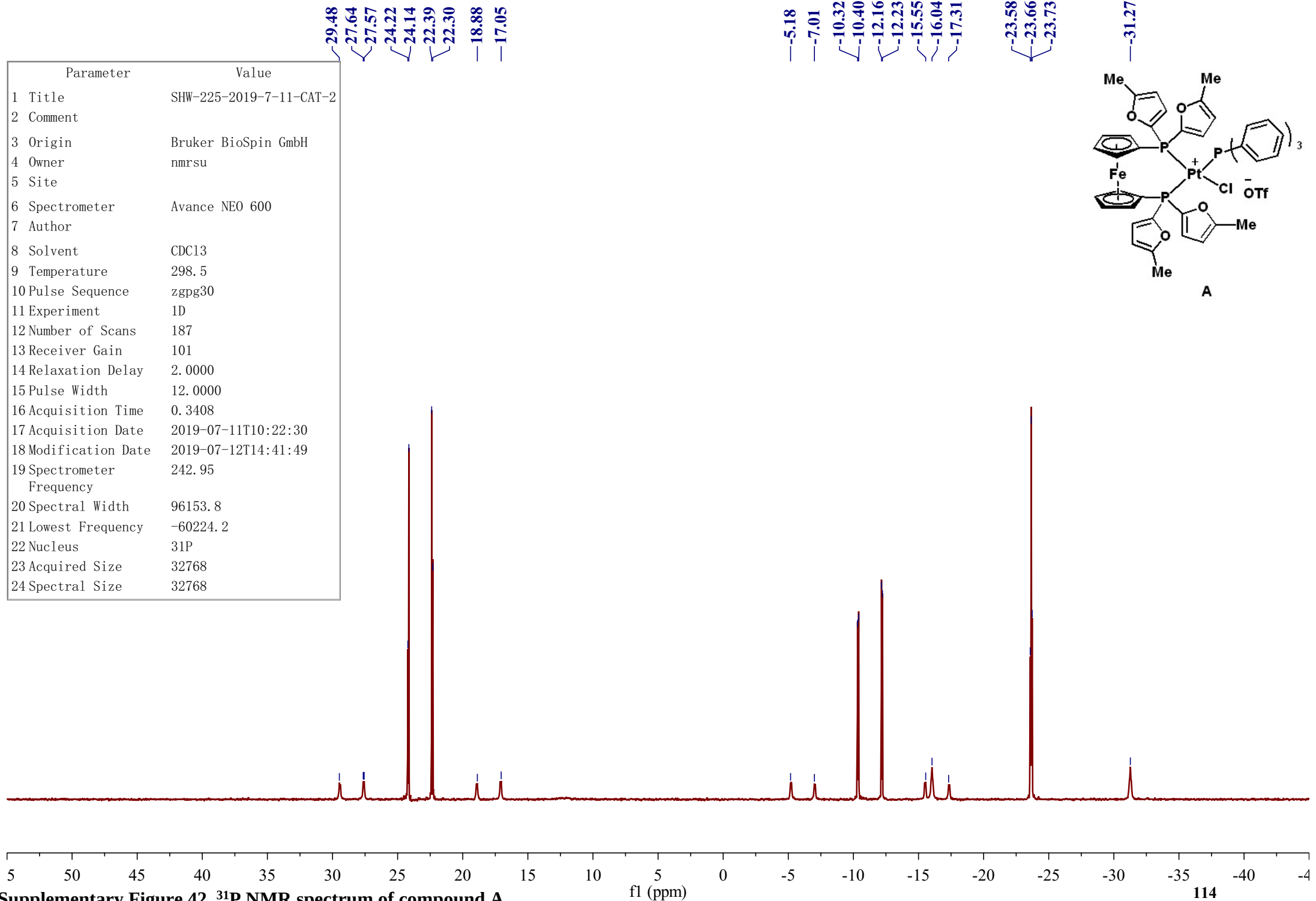


Parameter	Value
1 Title	SHW-225-8-7-3-MID
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	38
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.3408
17 Acquisition Date	2019-07-08T20:56:25
18 Modification Date	2019-07-08T20:58:50
19 Spectrometer Frequency	242.95
20 Spectral Width	96153.8
21 Lowest Frequency	-60224.2
22 Nucleus	31P
23 Acquired Size	32768
24 Spectral Size	32768



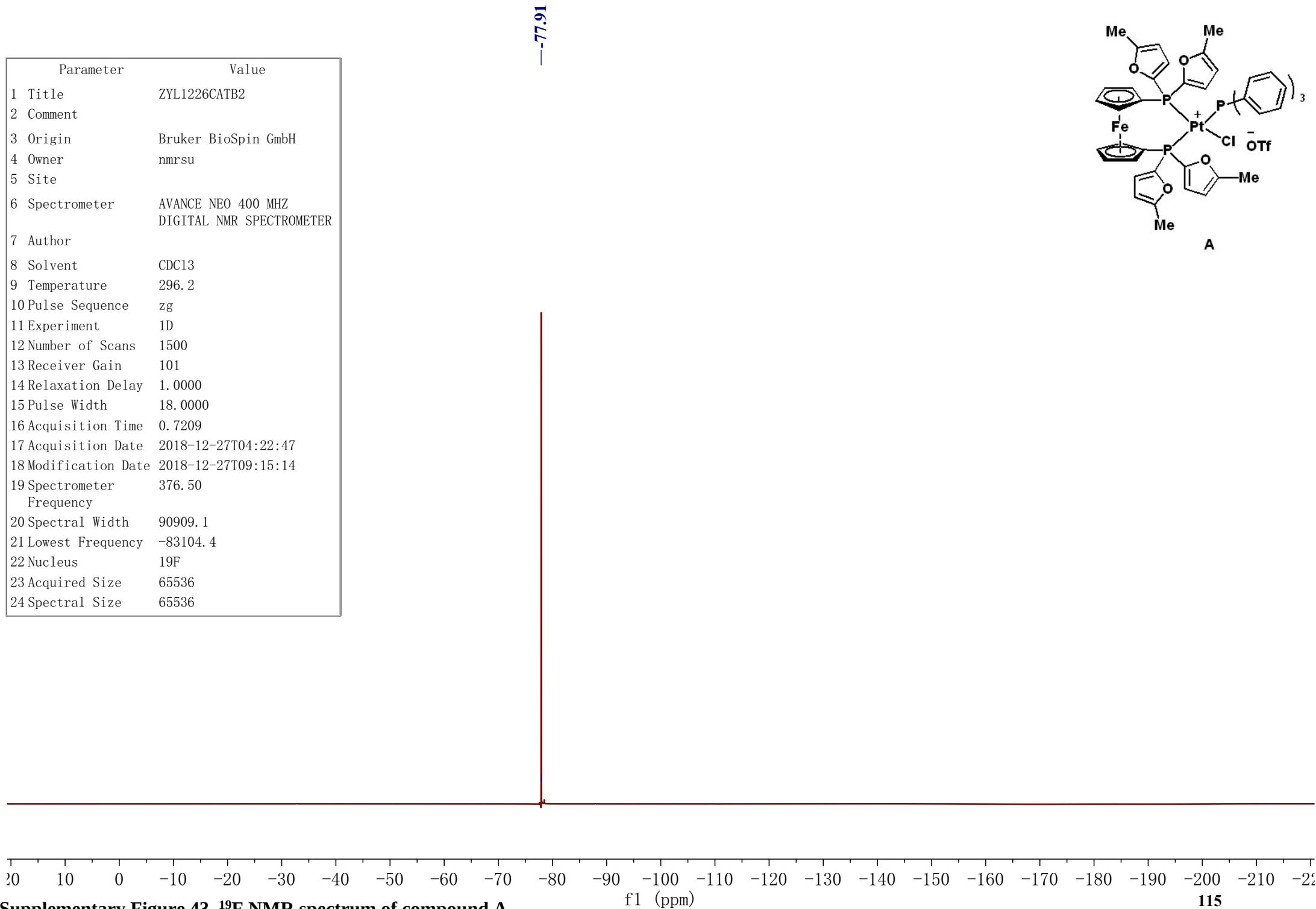




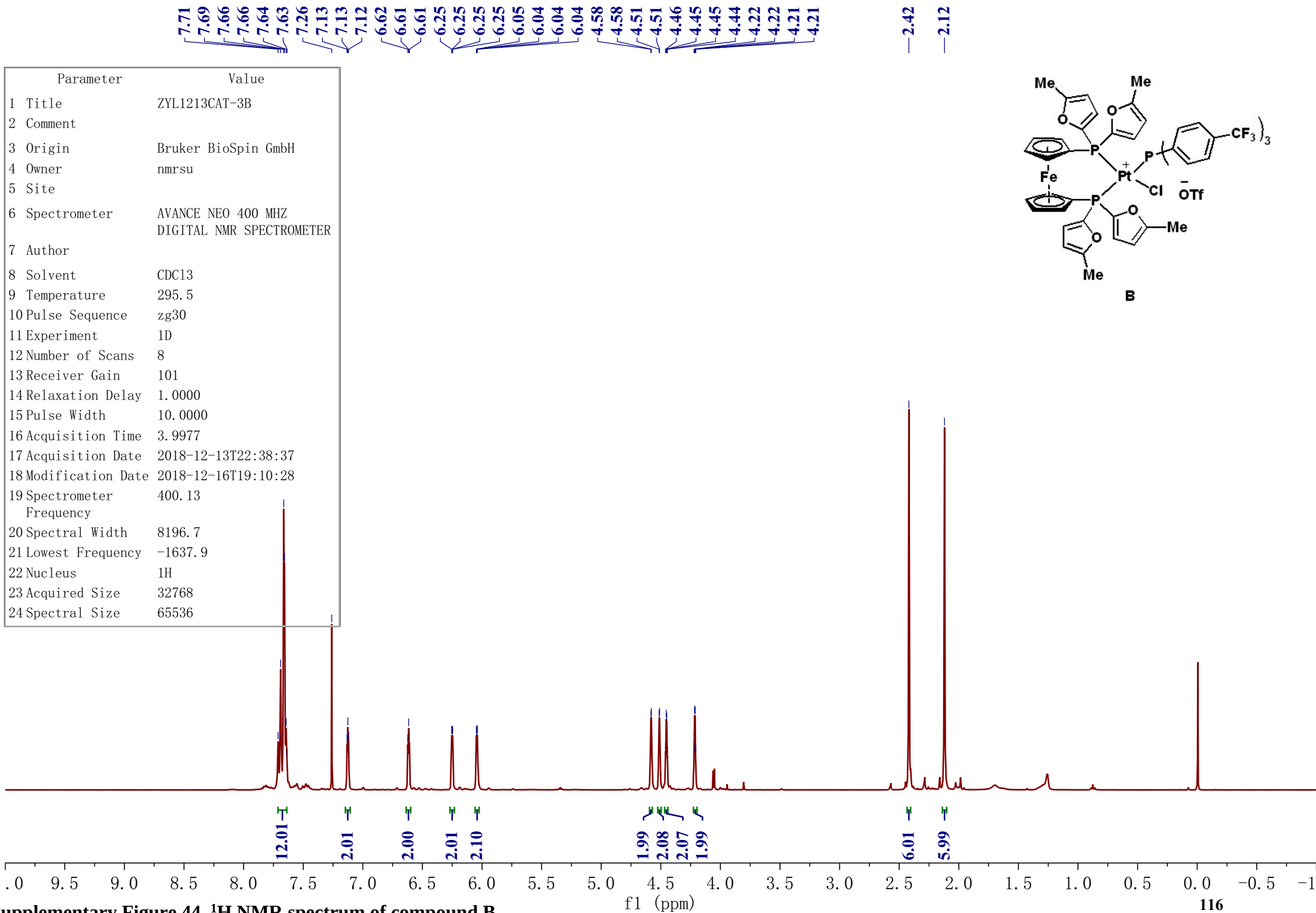


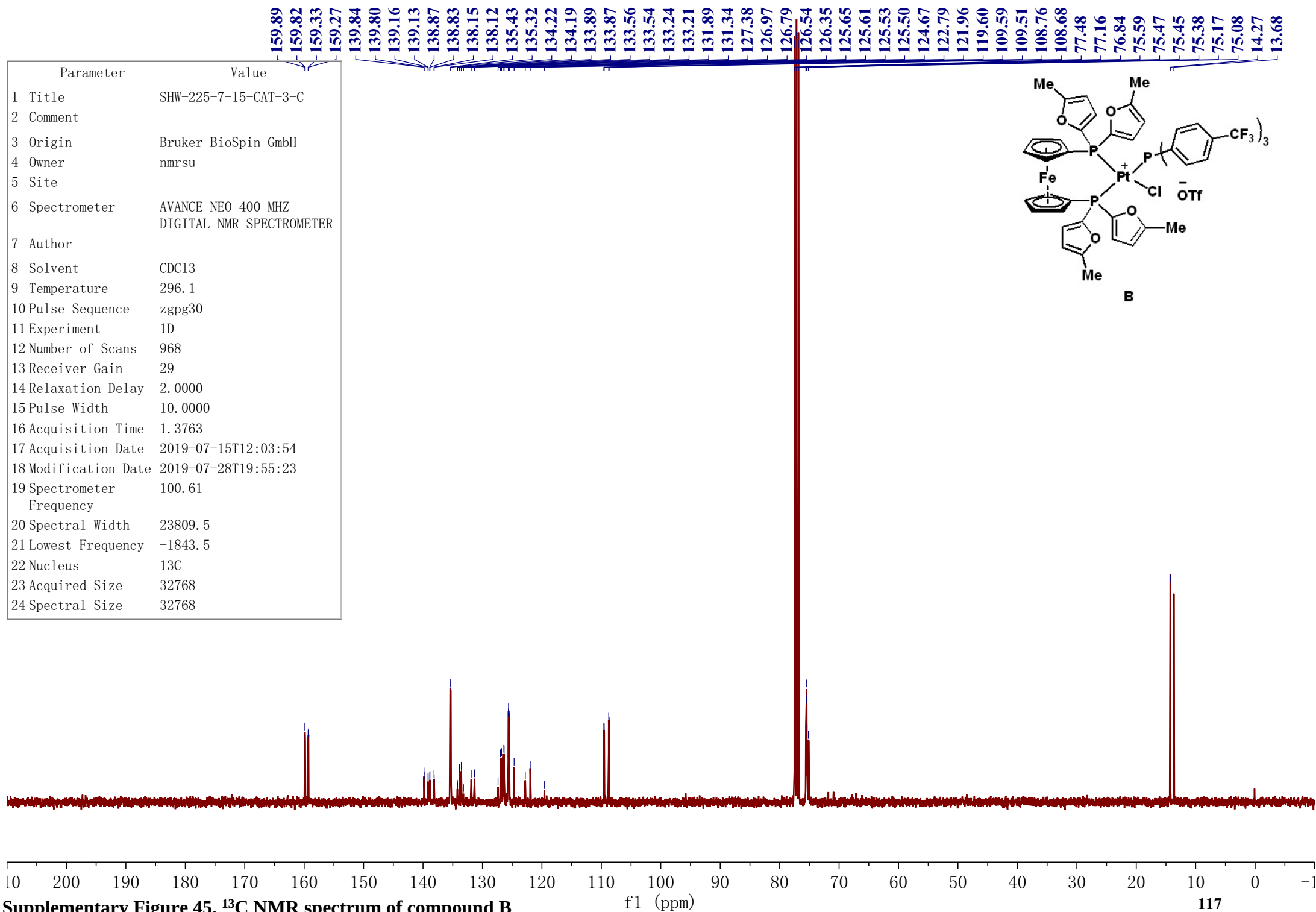
Supplementary Figure 42. ³¹P NMR spectrum of compound A

Parameter	Value
1 Title	ZYL1226CATB2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	296.2
10 Pulse Sequence	zg
11 Experiment	1D
12 Number of Scans	1500
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	18.0000
16 Acquisition Time	0.7209
17 Acquisition Date	2018-12-27T04:22:47
18 Modification Date	2018-12-27T09:15:14
19 Spectrometer Frequency	376.50
20 Spectral Width	90909.1
21 Lowest Frequency	-83104.4
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536

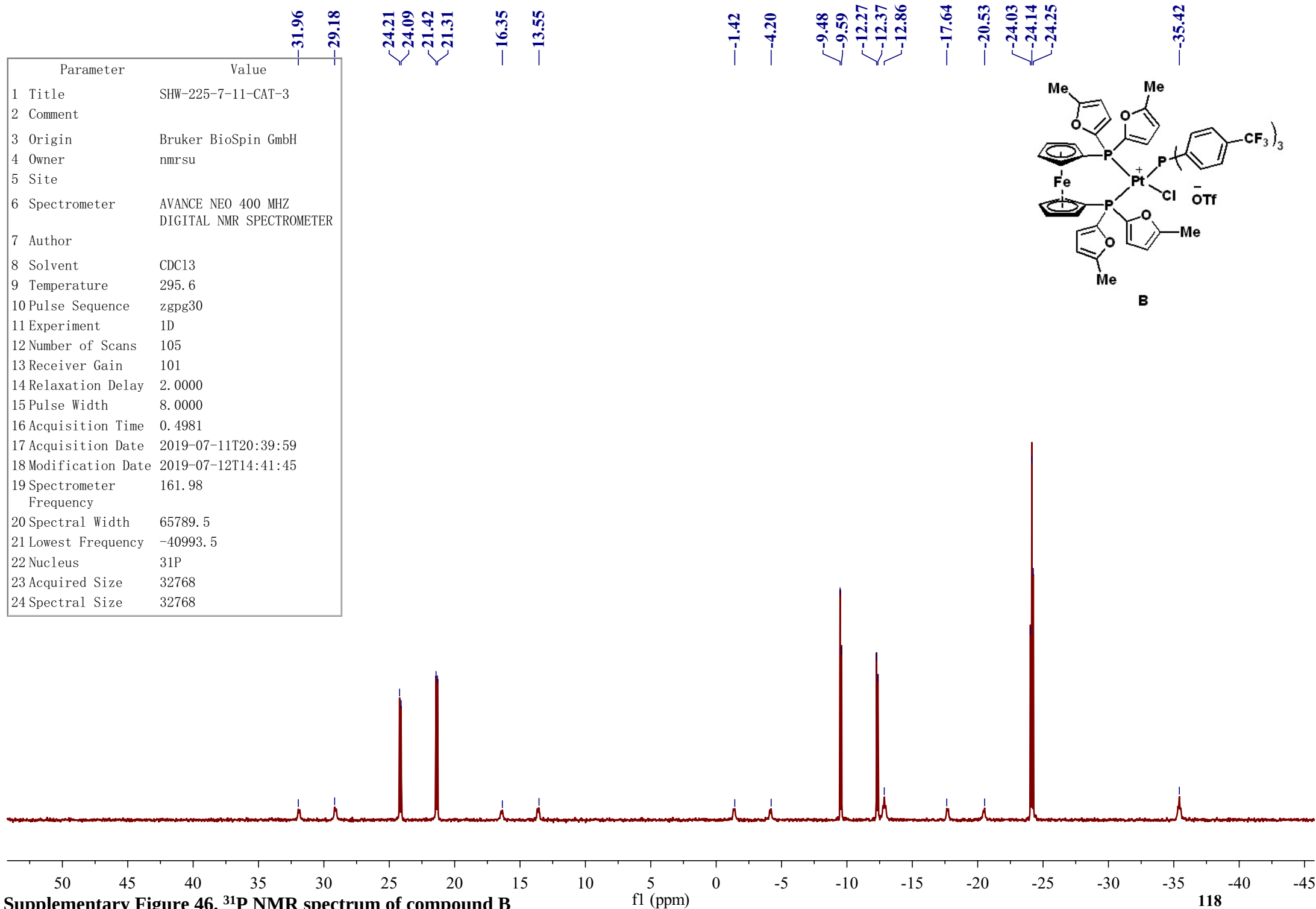


Supplementary Figure 43. ¹⁹F NMR spectrum of compound A



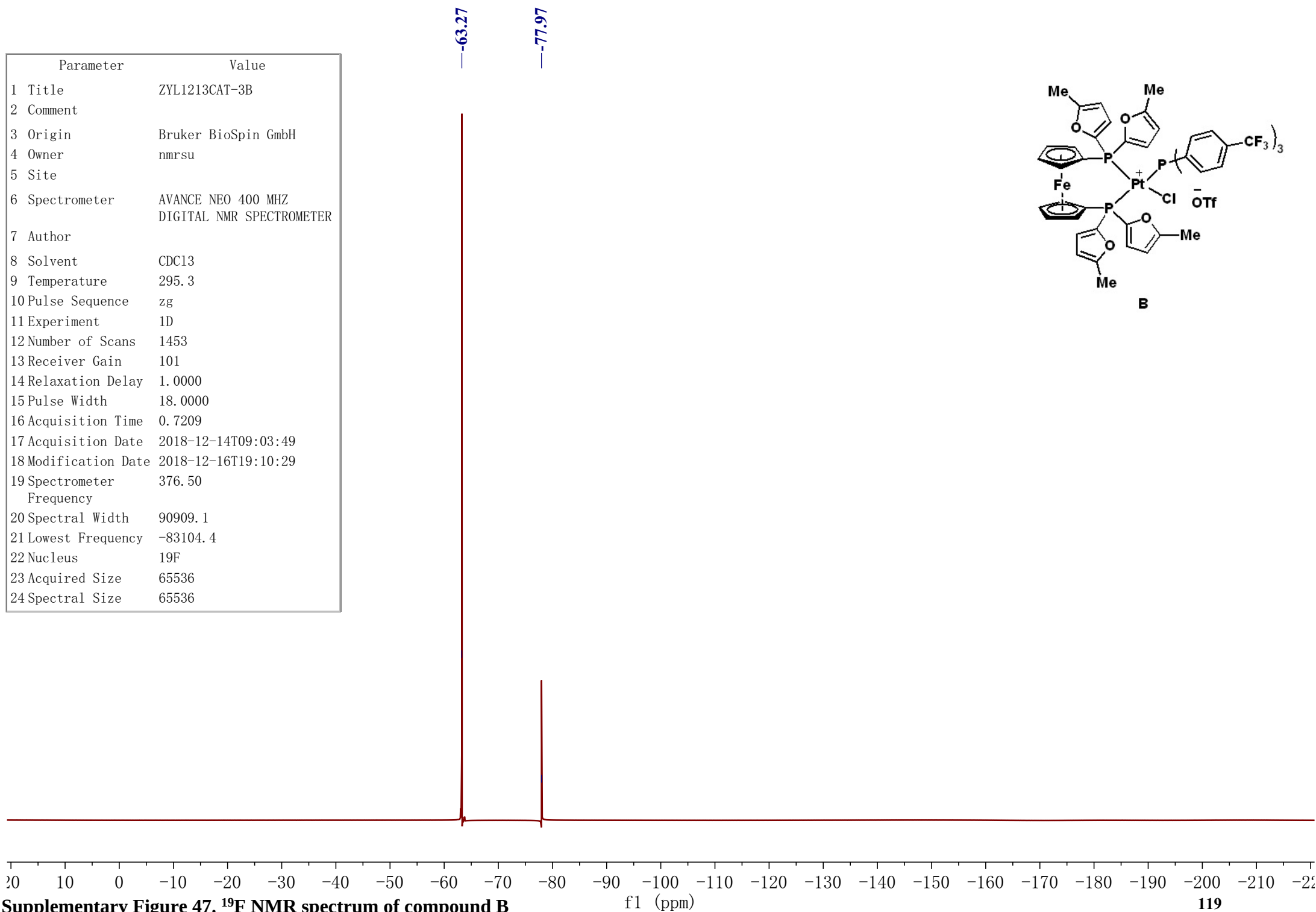


Supplementary Figure 45. ¹³C NMR spectrum of compound B

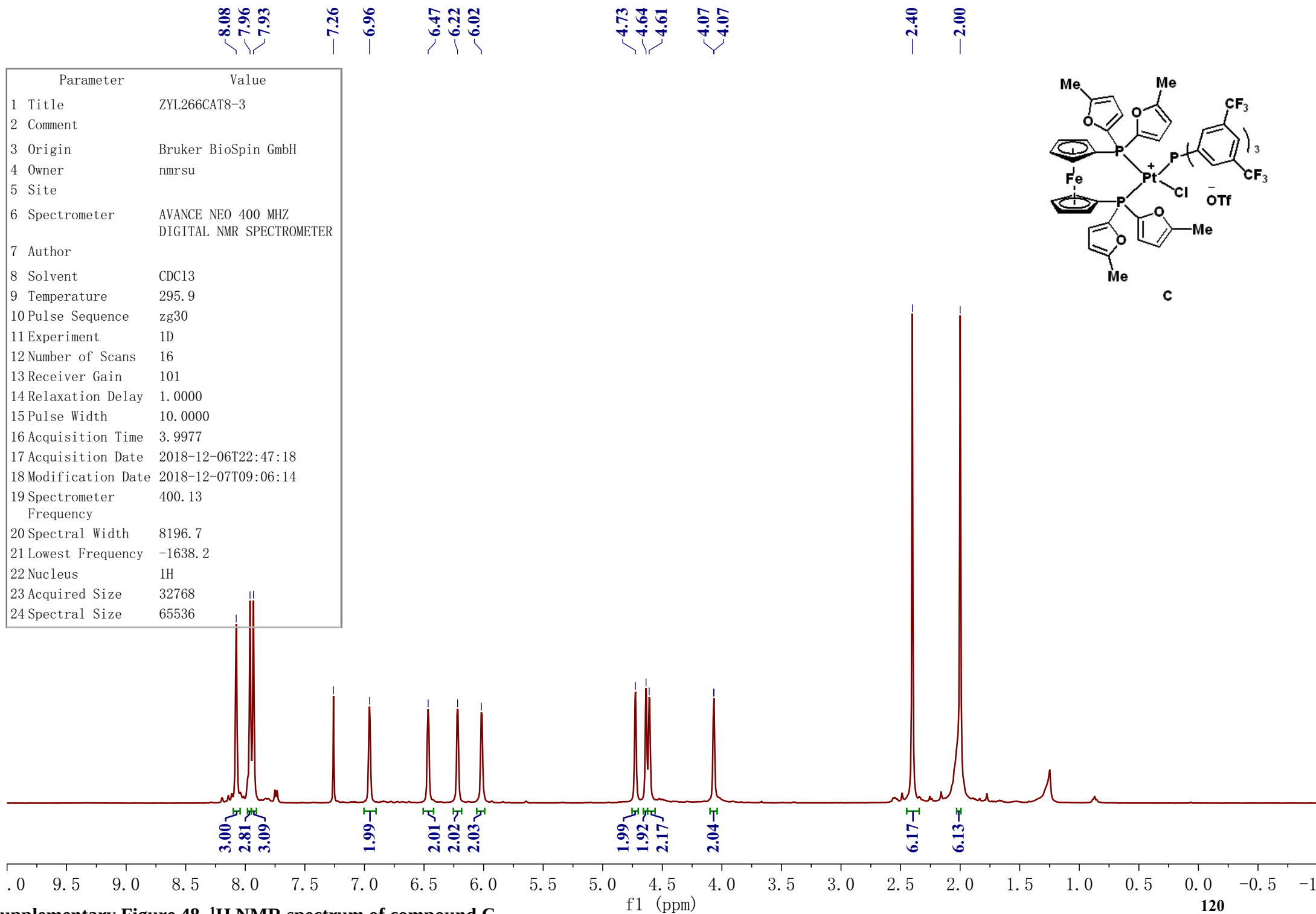


Supplementary Figure 46. ³¹P NMR spectrum of compound B

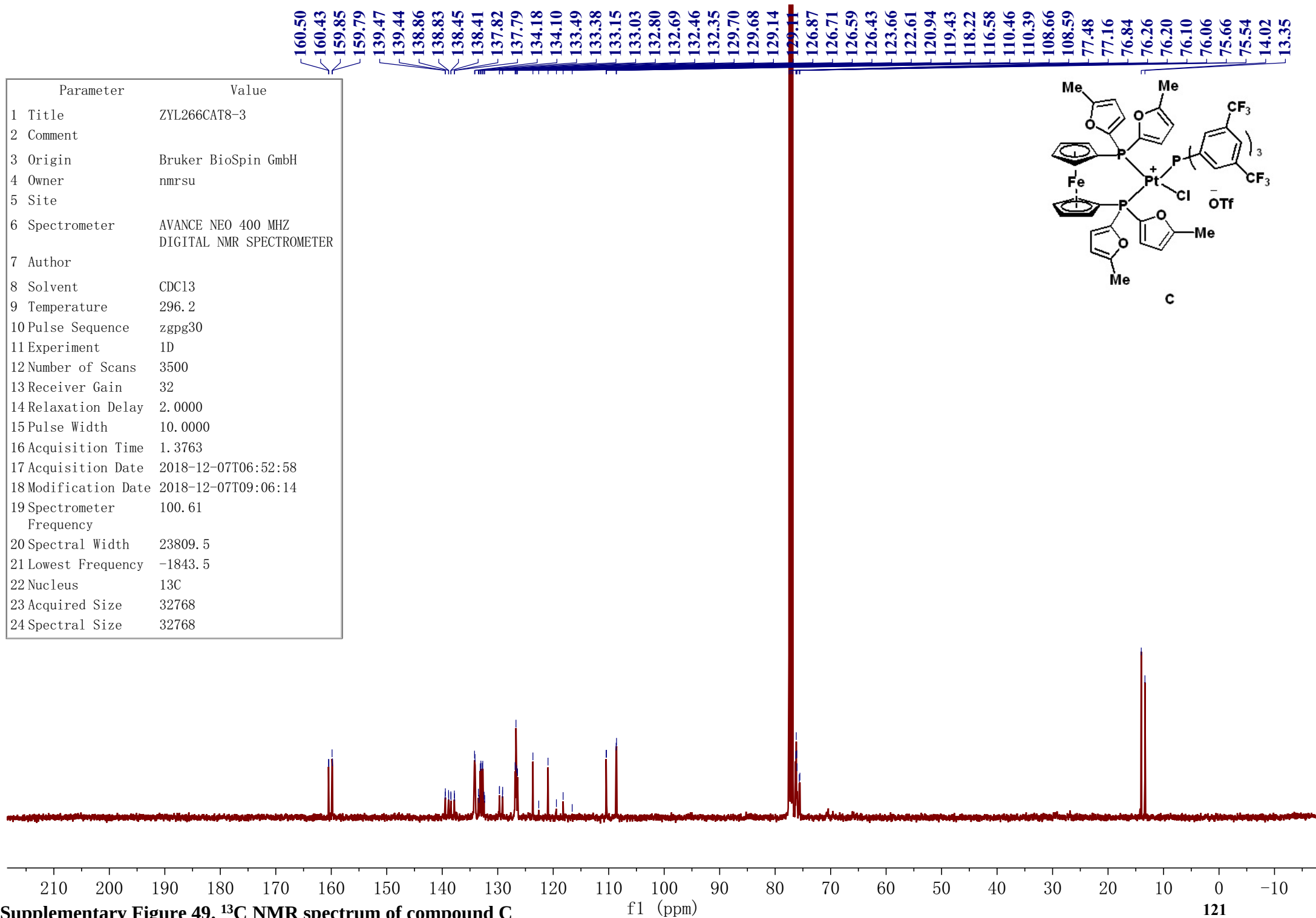
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2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.3
10 Pulse Sequence	zg
11 Experiment	1D
12 Number of Scans	1453
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	18.0000
16 Acquisition Time	0.7209
17 Acquisition Date	2018-12-14T09:03:49
18 Modification Date	2018-12-16T19:10:29
19 Spectrometer	376.50
Frequency	
20 Spectral Width	90909.1
21 Lowest Frequency	-83104.4
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536



Supplementary Figure 47. ¹⁹F NMR spectrum of compound B

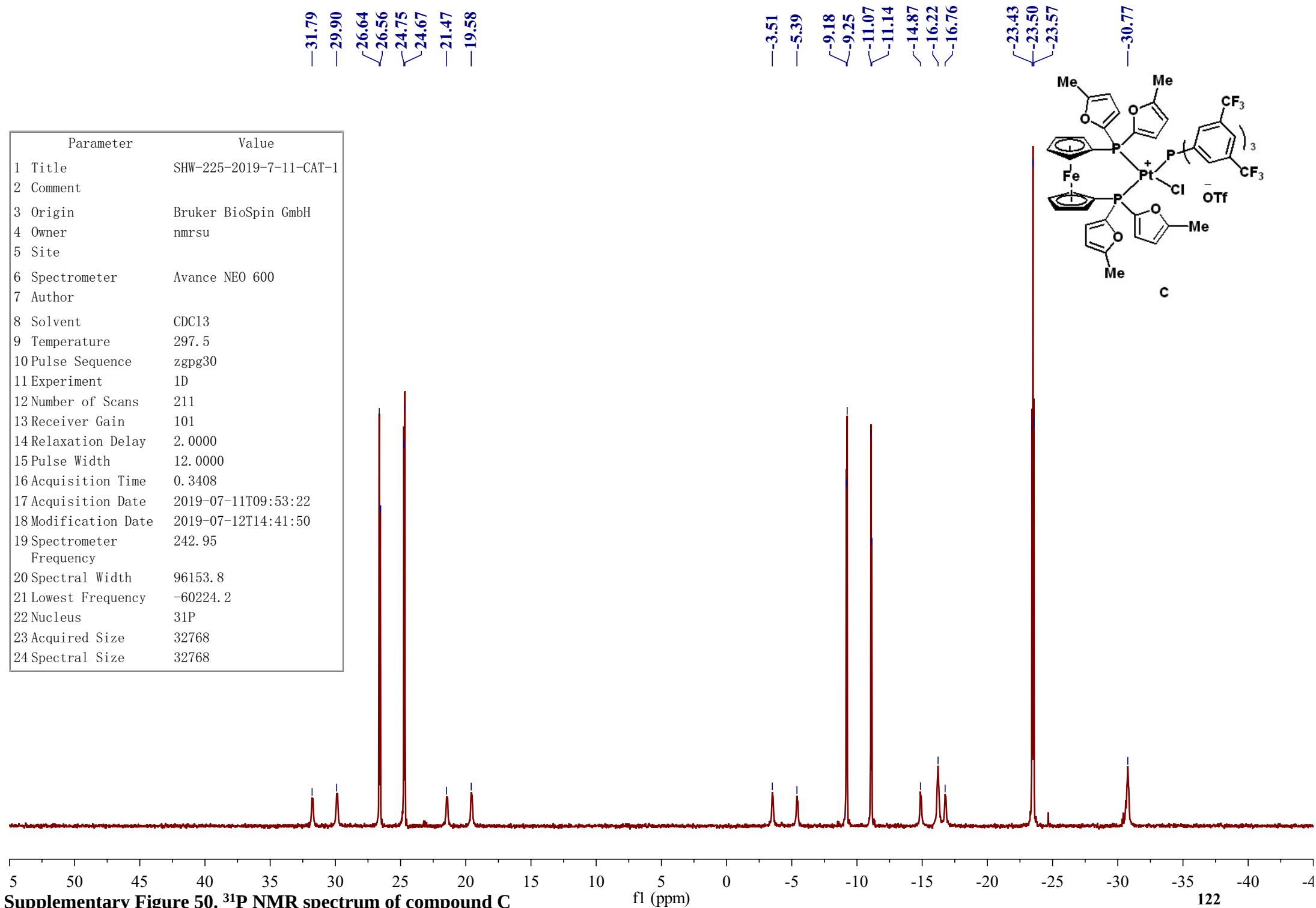


Parameter	Value
1 Title	ZYL266CAT8-3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	3500
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-07T06:52:58
18 Modification Date	2018-12-07T09:06:14
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1843.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



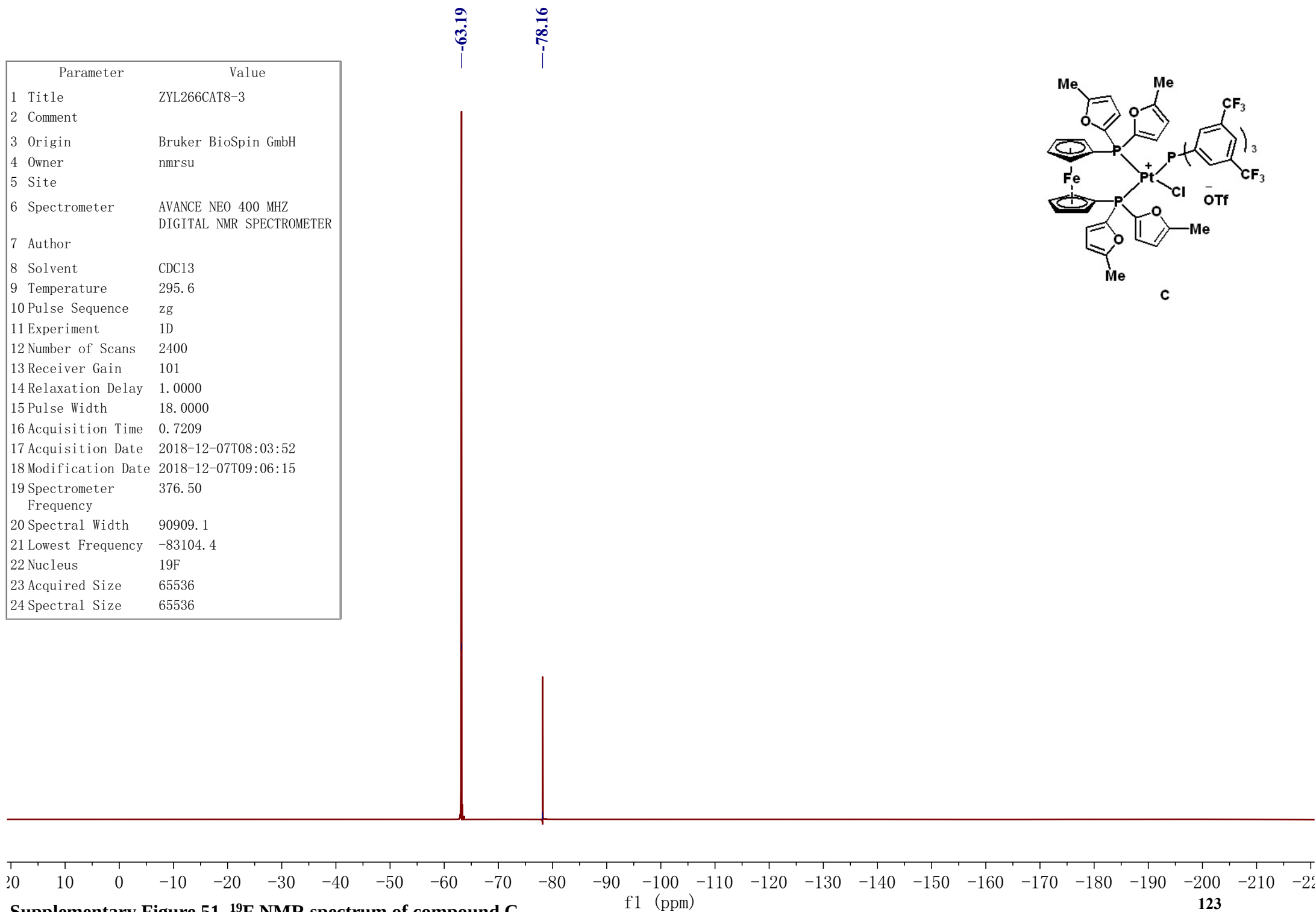
Supplementary Figure 49. ¹³C NMR spectrum of compound C

Parameter	Value
1 Title	SHW-225-2019-7-11-CAT-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	297.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	211
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.3408
17 Acquisition Date	2019-07-11T09:53:22
18 Modification Date	2019-07-12T14:41:50
19 Spectrometer	242.95
Frequency	
20 Spectral Width	96153.8
21 Lowest Frequency	-60224.2
22 Nucleus	31P
23 Acquired Size	32768
24 Spectral Size	32768

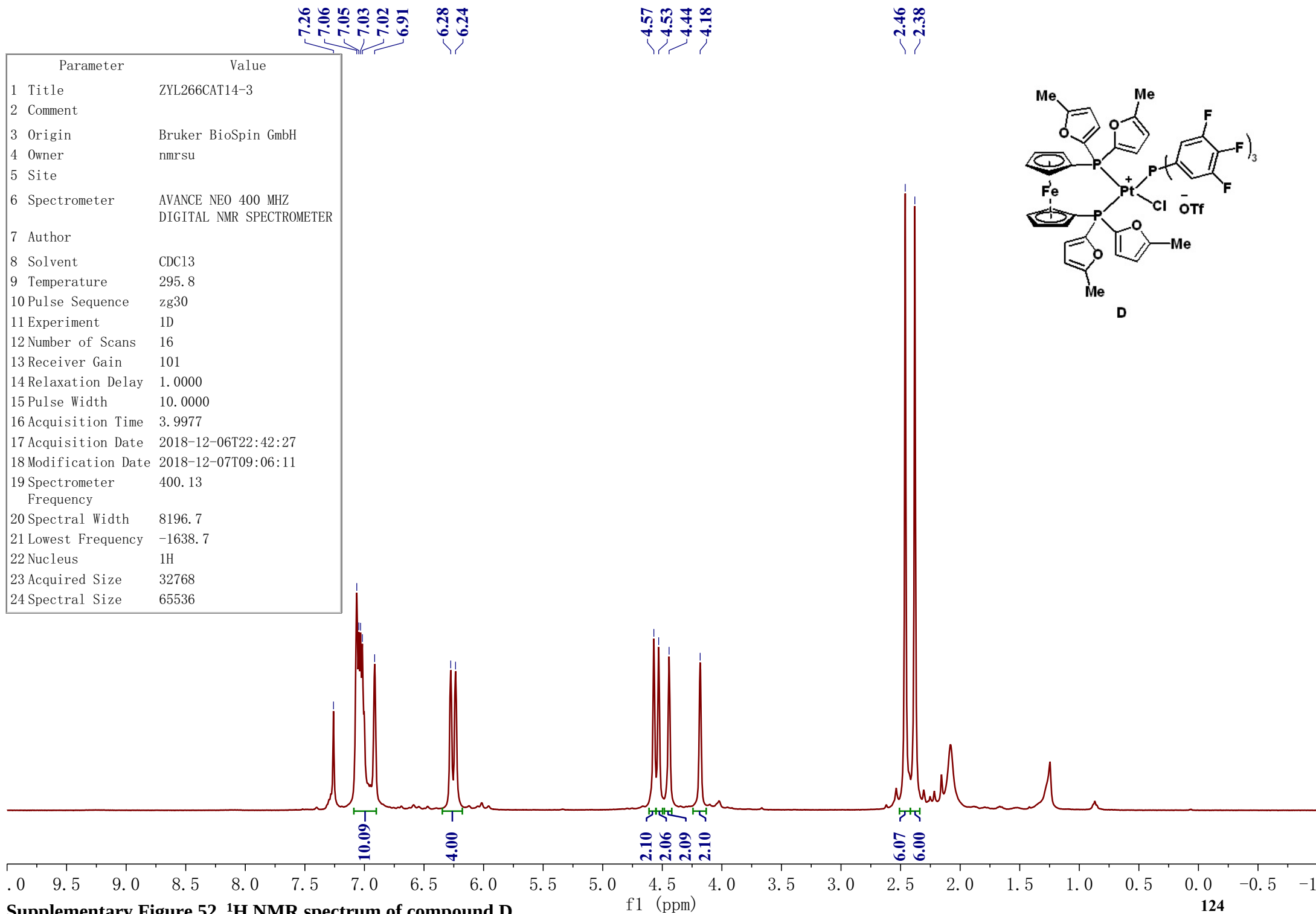


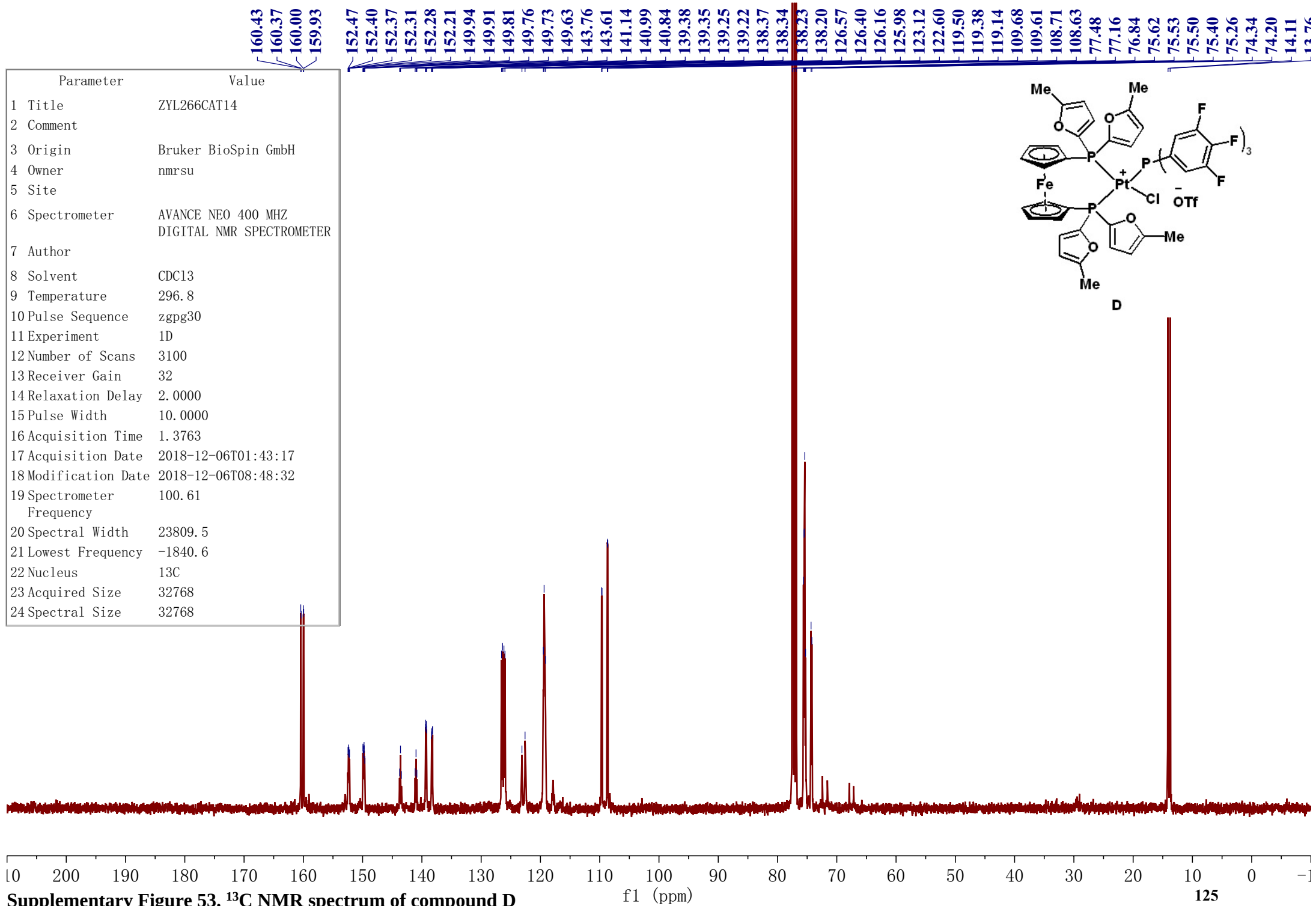
Supplementary Figure 50. ³¹P NMR spectrum of compound C

Parameter	Value
1 Title	ZYL266CAT8-3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	295.6
10 Pulse Sequence	zg
11 Experiment	1D
12 Number of Scans	2400
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	18.0000
16 Acquisition Time	0.7209
17 Acquisition Date	2018-12-07T08:03:52
18 Modification Date	2018-12-07T09:06:15
19 Spectrometer Frequency	376.50
20 Spectral Width	90909.1
21 Lowest Frequency	-83104.4
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536

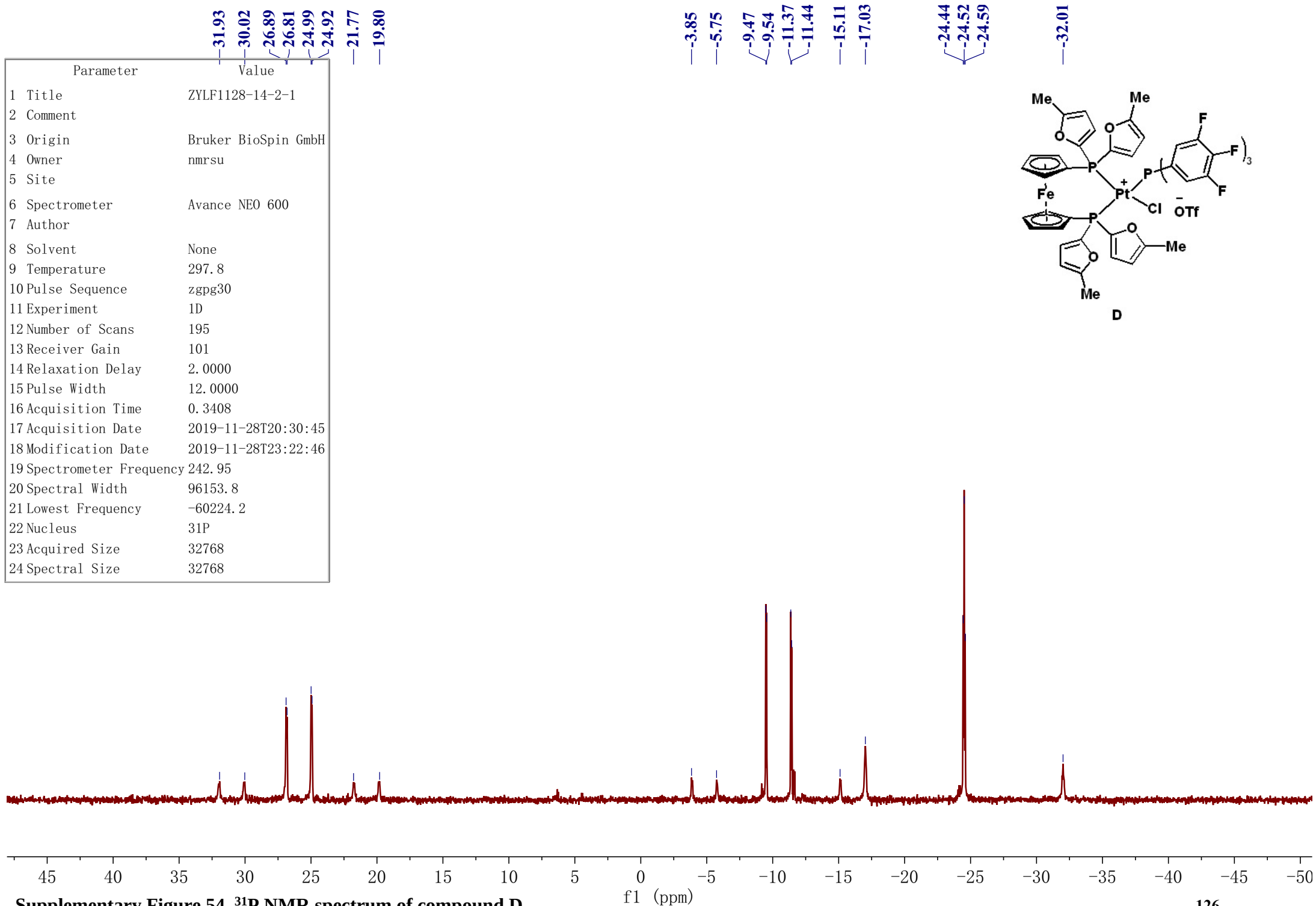


Supplementary Figure 51. ¹⁹F NMR spectrum of compound C



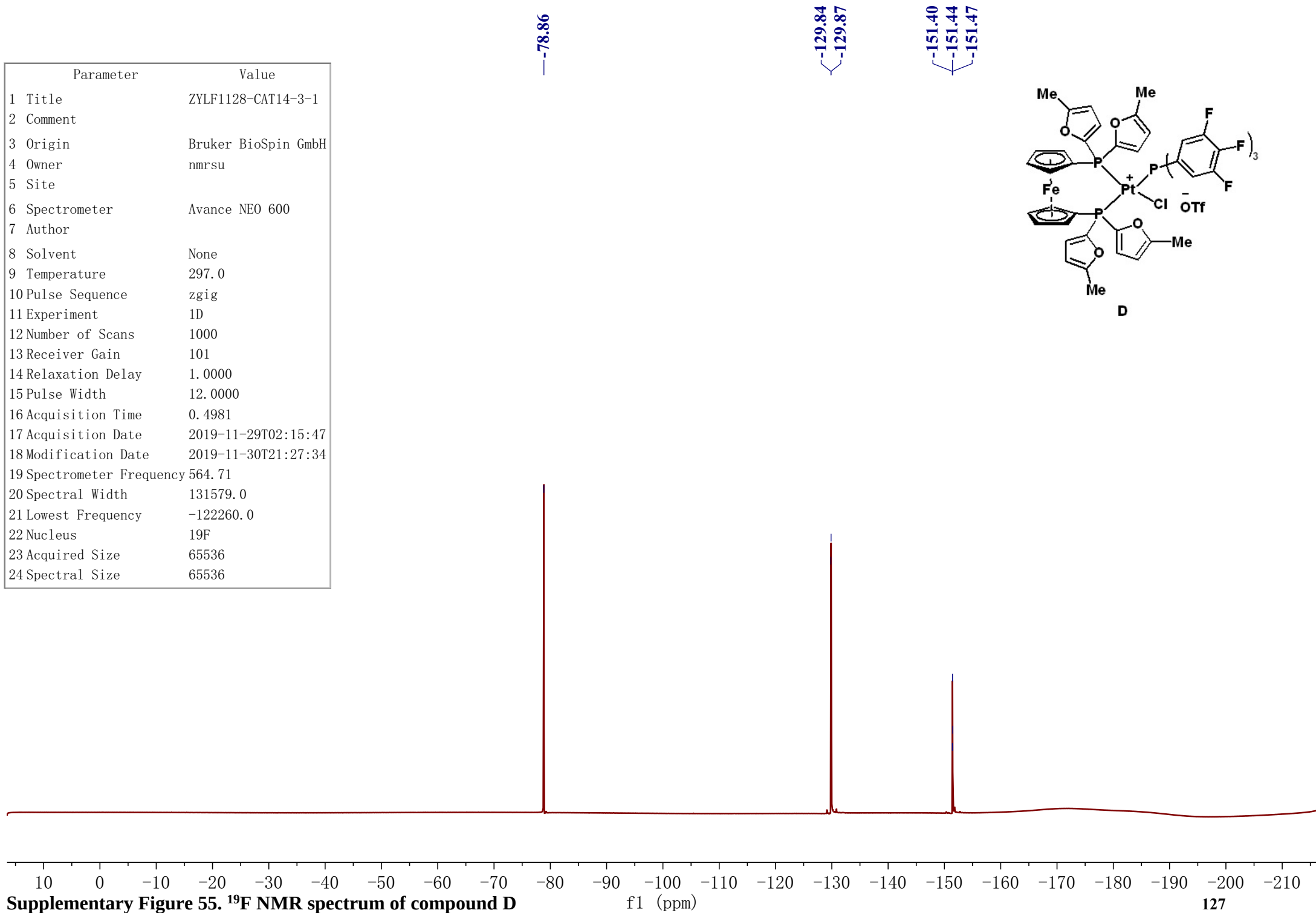


Parameter	Value
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2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	None
9 Temperature	297.8
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	195
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.3408
17 Acquisition Date	2019-11-28T20:30:45
18 Modification Date	2019-11-28T23:22:46
19 Spectrometer Frequency	242.95
20 Spectral Width	96153.8
21 Lowest Frequency	-60224.2
22 Nucleus	31P
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 54. ^{31}P NMR spectrum of compound D

Parameter	Value
1 Title	ZYLF1128-CAT14-3-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	None
9 Temperature	297.0
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	1000
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.4981
17 Acquisition Date	2019-11-29T02:15:47
18 Modification Date	2019-11-30T21:27:34
19 Spectrometer Frequency	564.71
20 Spectral Width	131579.0
21 Lowest Frequency	-122260.0
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536



Supplementary Figure S55. ¹⁹F NMR spectrum of compound D

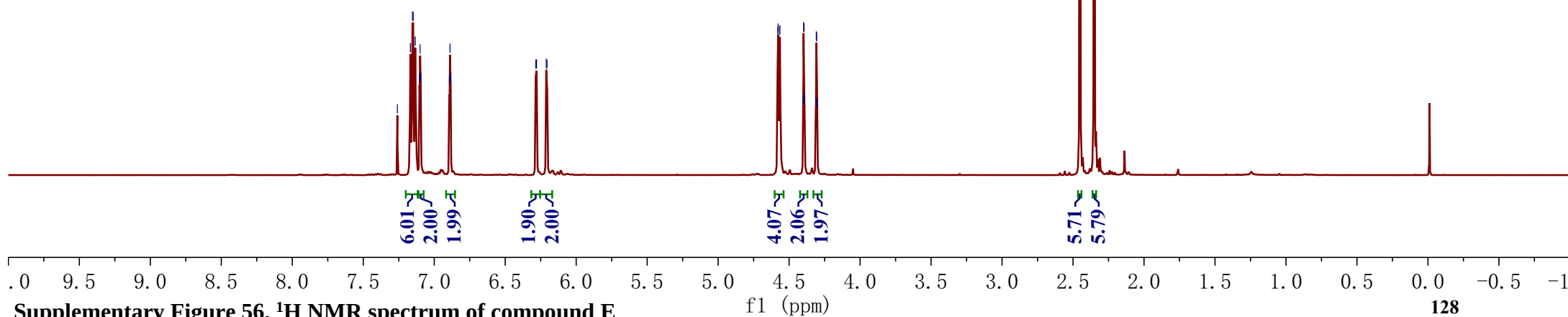
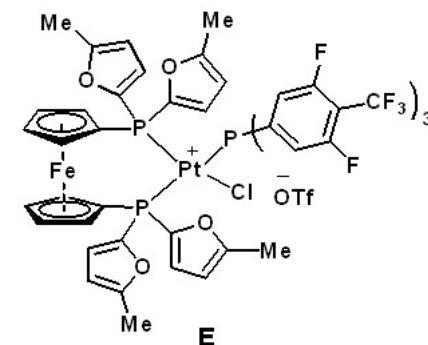
SHW-225-7-12-CAT-4

7.26
7.17
7.15
7.15
7.13
7.10
7.10
7.10
6.89
6.89
6.88
6.28
6.28
6.21
6.21

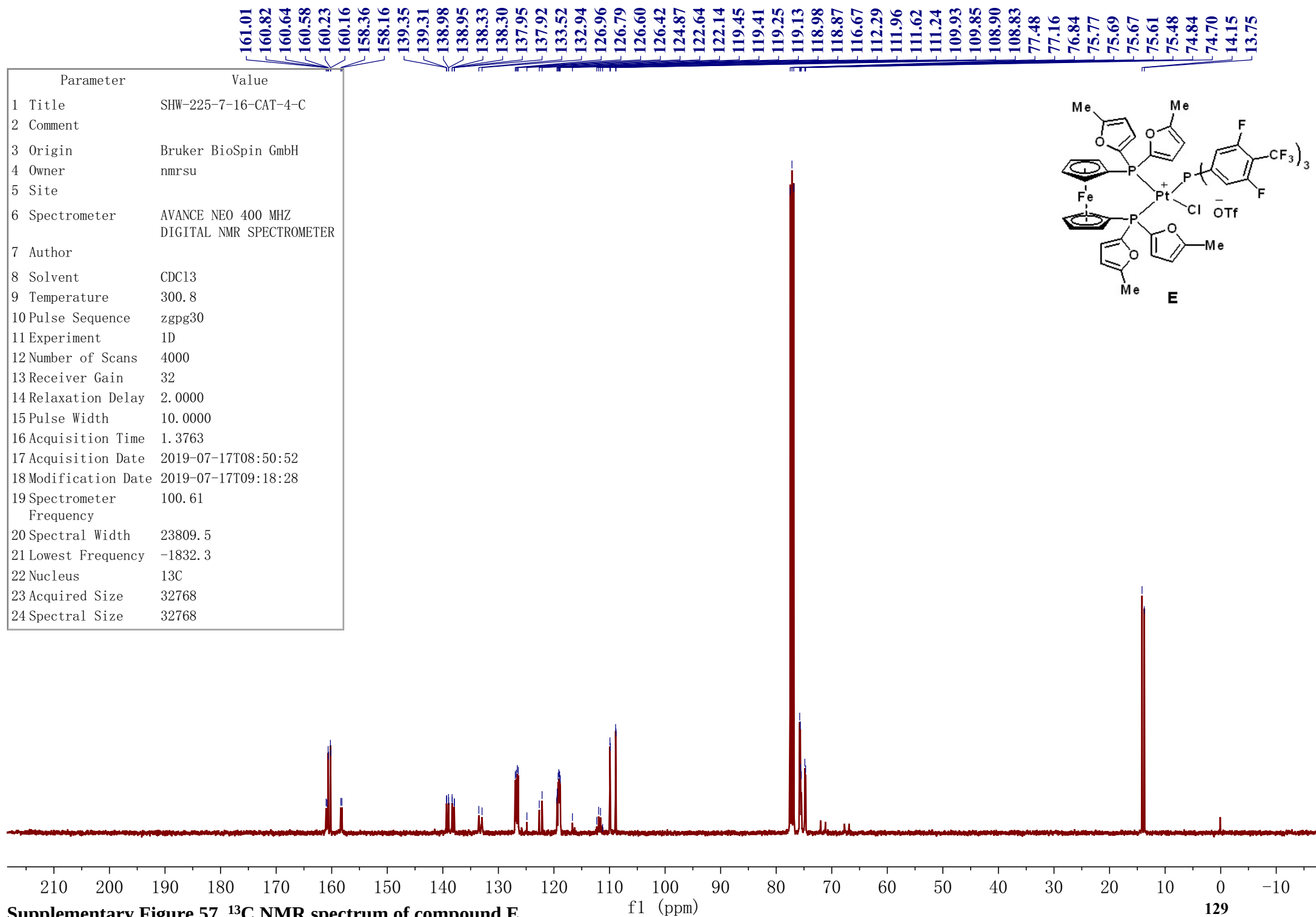
4.58
4.58
4.57
4.56
4.40
4.40
4.39
4.39
4.31
4.31
4.31
4.30

2.45
2.35

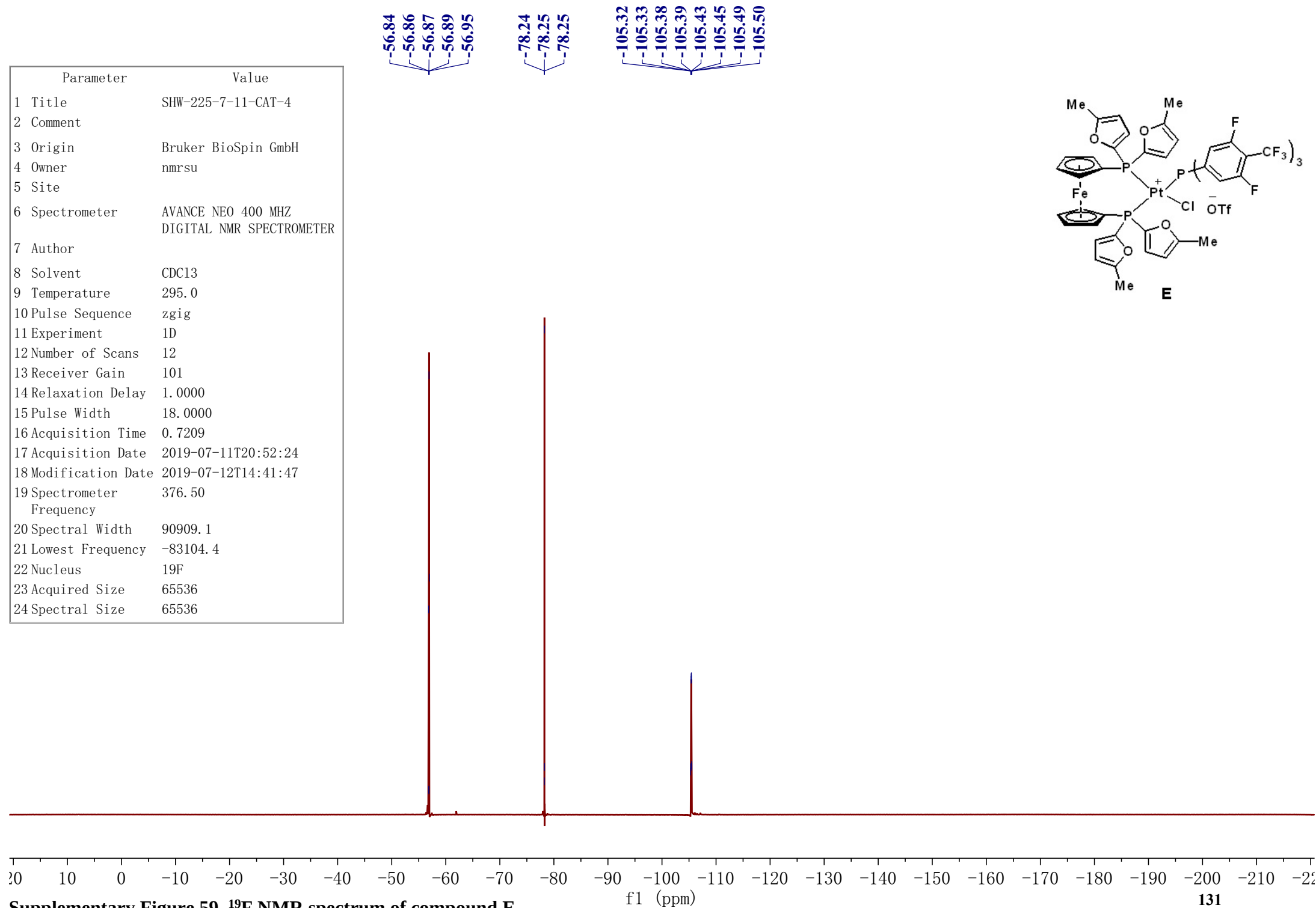
Parameter	Value
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2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	297.5
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	9
13 Receiver Gain	63
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2019-07-12T11:20:58
18 Modification Date	2019-07-28T19:31:07
19 Spectrometer	600.15
Frequency	
20 Spectral Width	11904.8
21 Lowest Frequency	-2254.9
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536



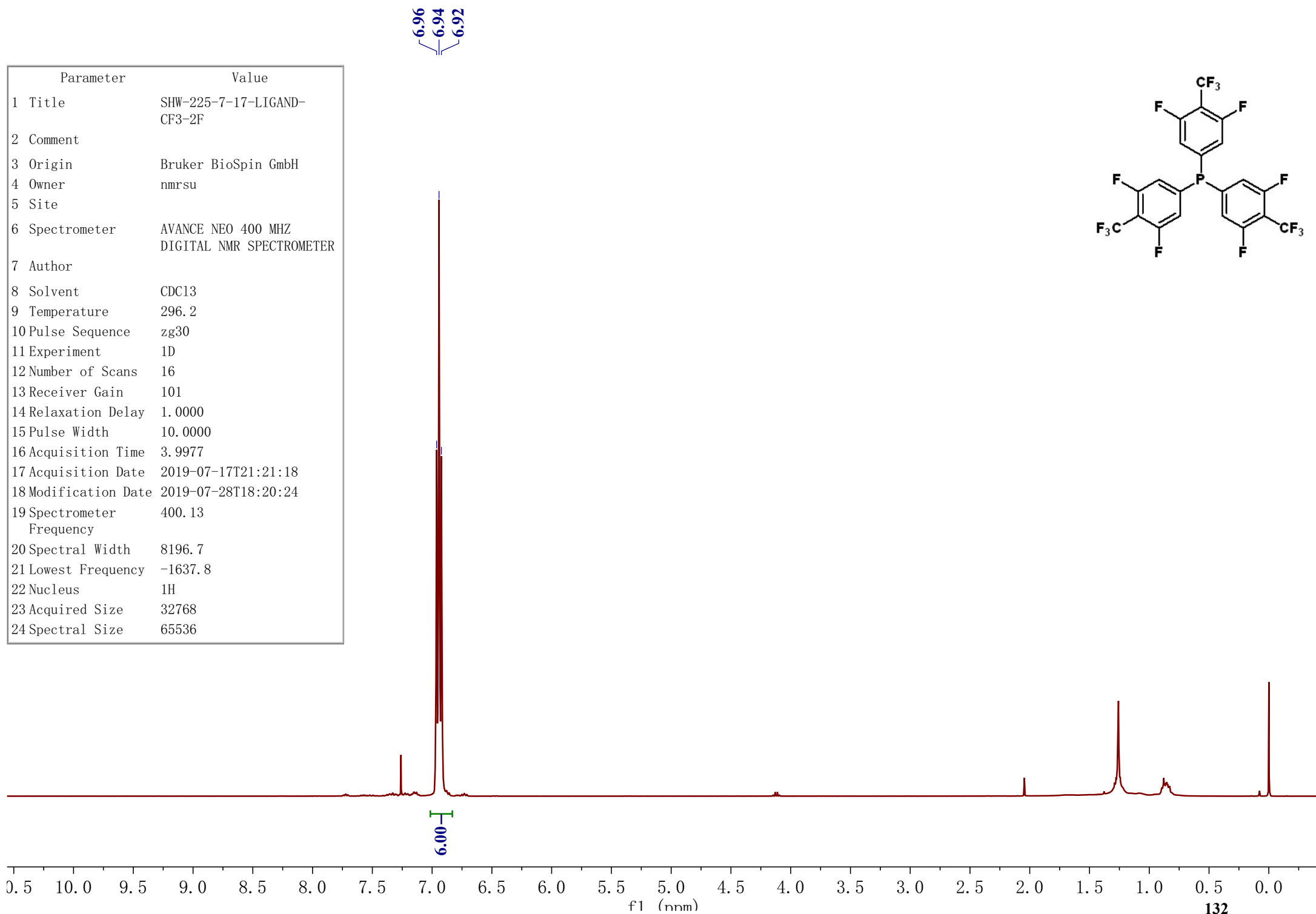
Supplementary Figure S6. ¹H NMR spectrum of compound E



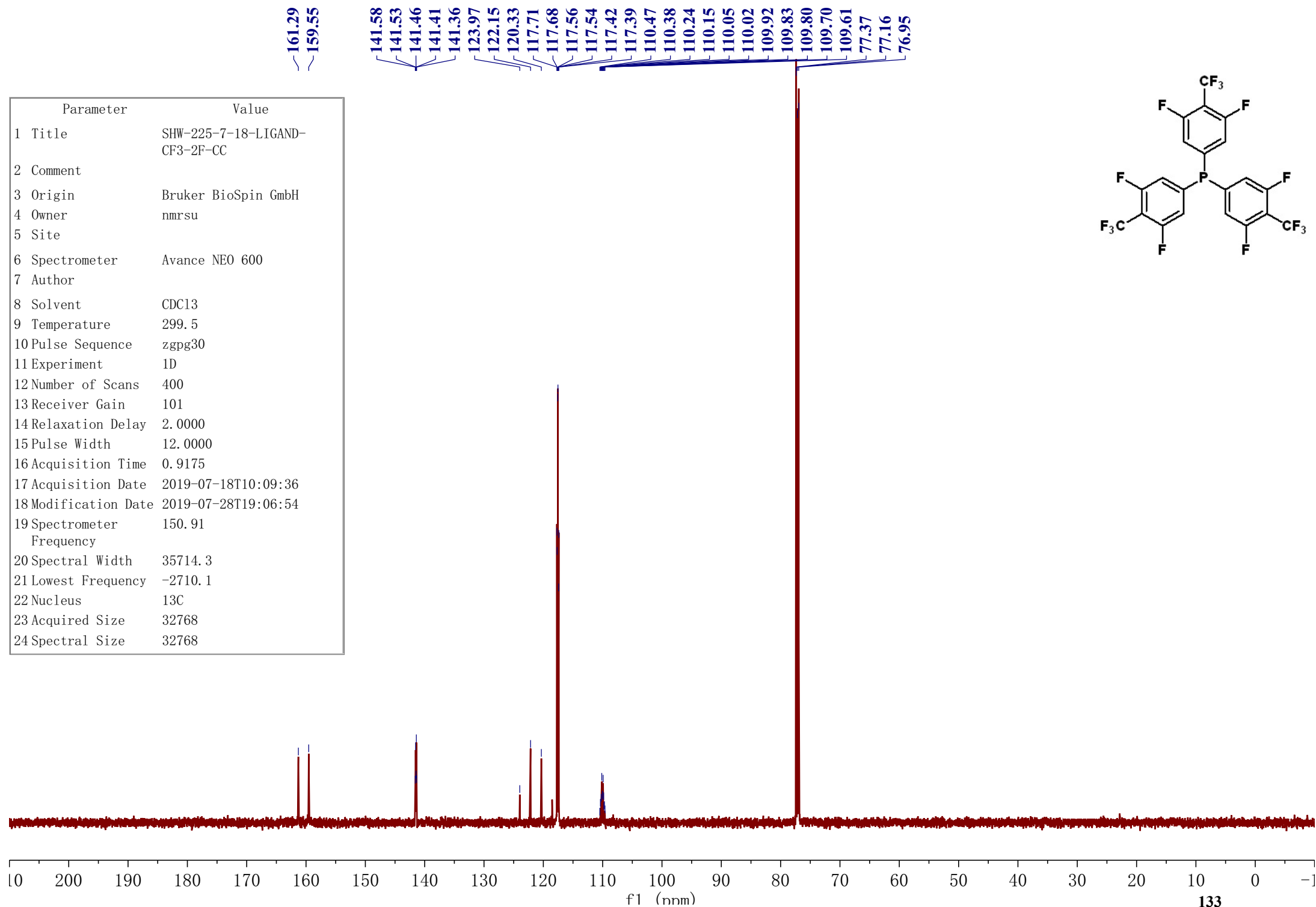
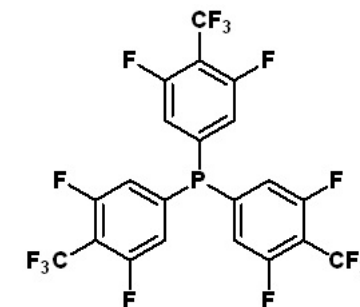
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4 Owner	nmrsl
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	295.0
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	12
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	18.0000
16 Acquisition Time	0.7209
17 Acquisition Date	2019-07-11T20:52:24
18 Modification Date	2019-07-12T14:41:47
19 Spectrometer	376.50
Frequency	
20 Spectral Width	90909.1
21 Lowest Frequency	-83104.4
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536



Supplementary Figure 59. ¹⁹F NMR spectrum of compound E

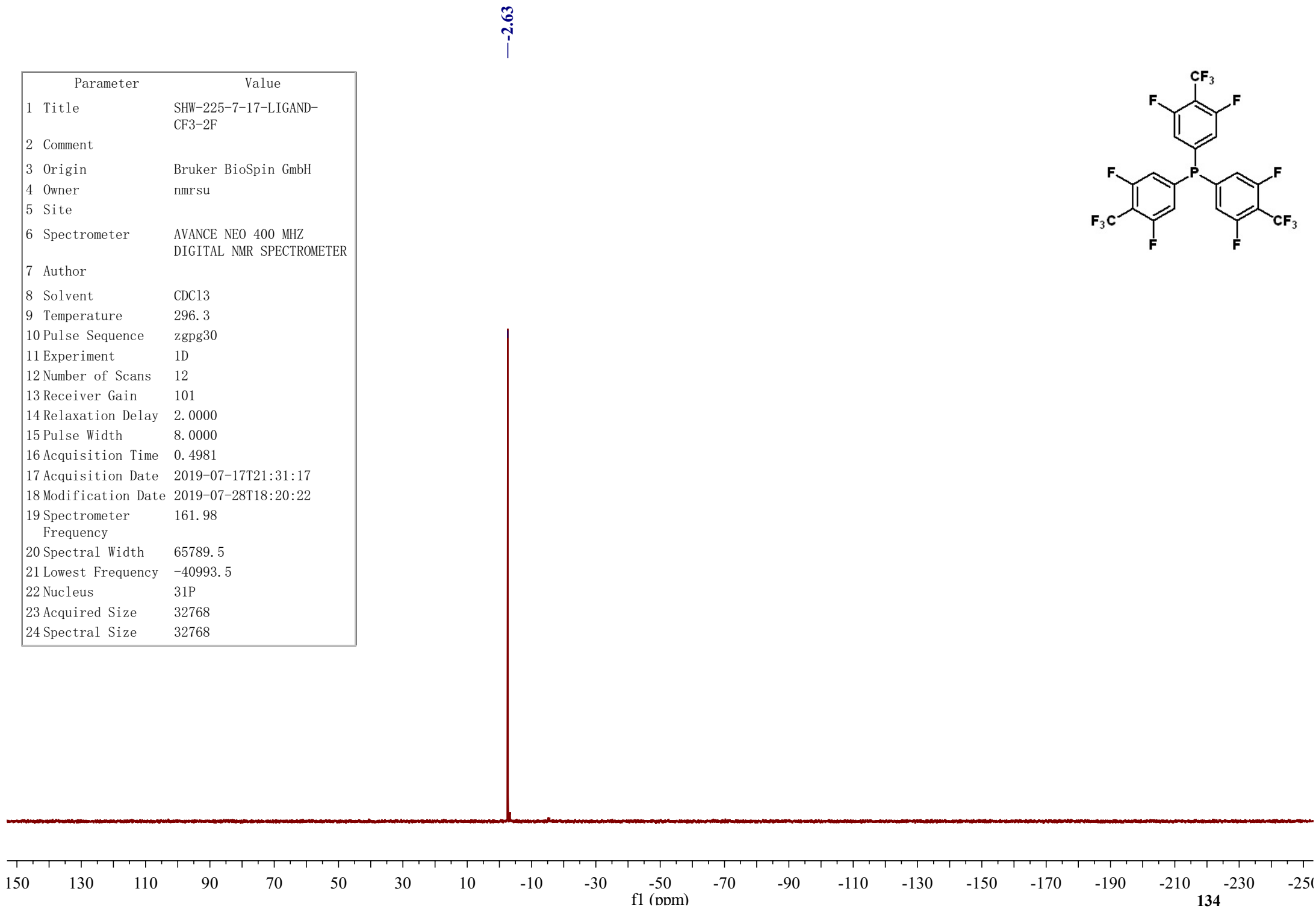
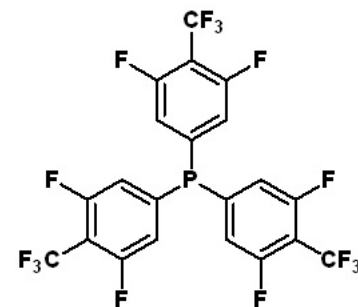


Parameter	Value
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2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	299.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	400
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-07-18T10:09:36
18 Modification Date	2019-07-28T19:06:54
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2710.1
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

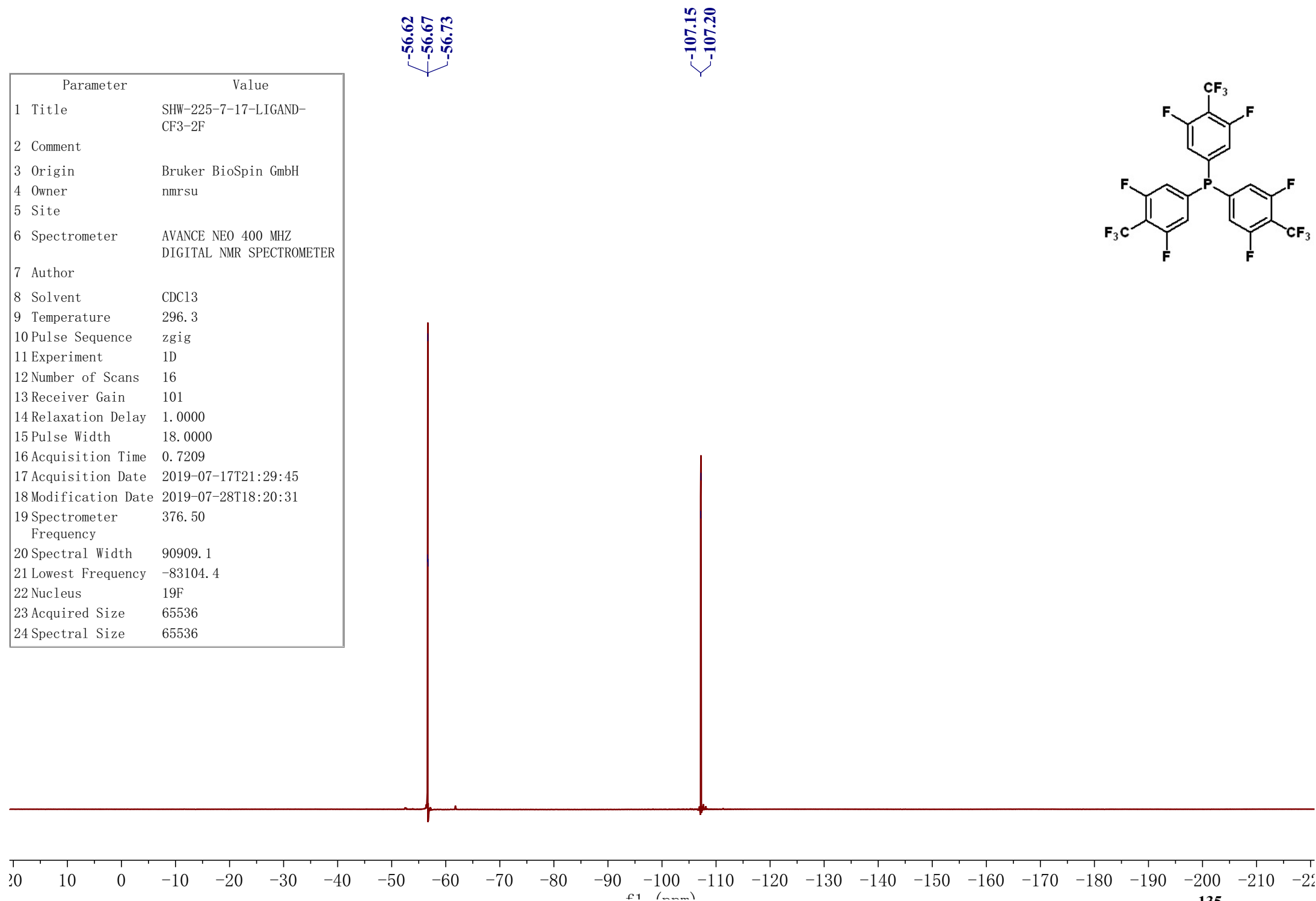
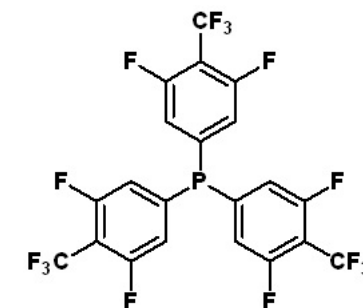


Supplementary Figure 61. ¹³C NMR spectrum of tris(3,5-difluoro-4-(trifluoromethyl)phenyl)phosphine

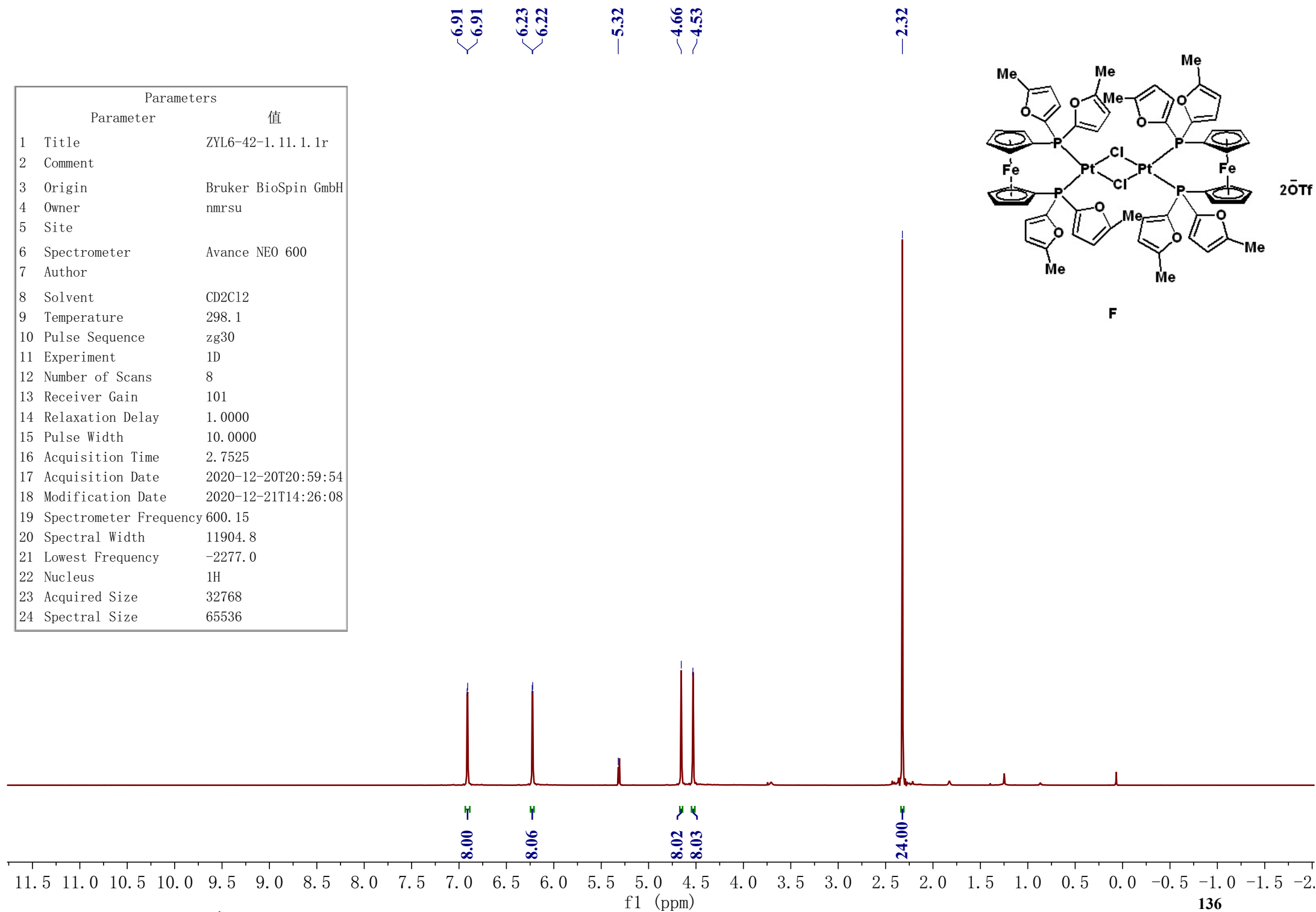
Parameter	Value
1 Title	SHW-225-7-17-LIGAND-CF3-2F
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	12
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	8.0000
16 Acquisition Time	0.4981
17 Acquisition Date	2019-07-17T21:31:17
18 Modification Date	2019-07-28T18:20:22
19 Spectrometer Frequency	161.98
20 Spectral Width	65789.5
21 Lowest Frequency	-40993.5
22 Nucleus	31P
23 Acquired Size	32768
24 Spectral Size	32768



Parameter	Value
1 Title	SHW-225-7-17-LIGAND- CF3-2F
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	296.3
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	18.0000
16 Acquisition Time	0.7209
17 Acquisition Date	2019-07-17T21:29:45
18 Modification Date	2019-07-28T18:20:31
19 Spectrometer	376.50
Frequency	
20 Spectral Width	90909.1
21 Lowest Frequency	-83104.4
22 Nucleus	19F
23 Acquired Size	65536
24 Spectral Size	65536

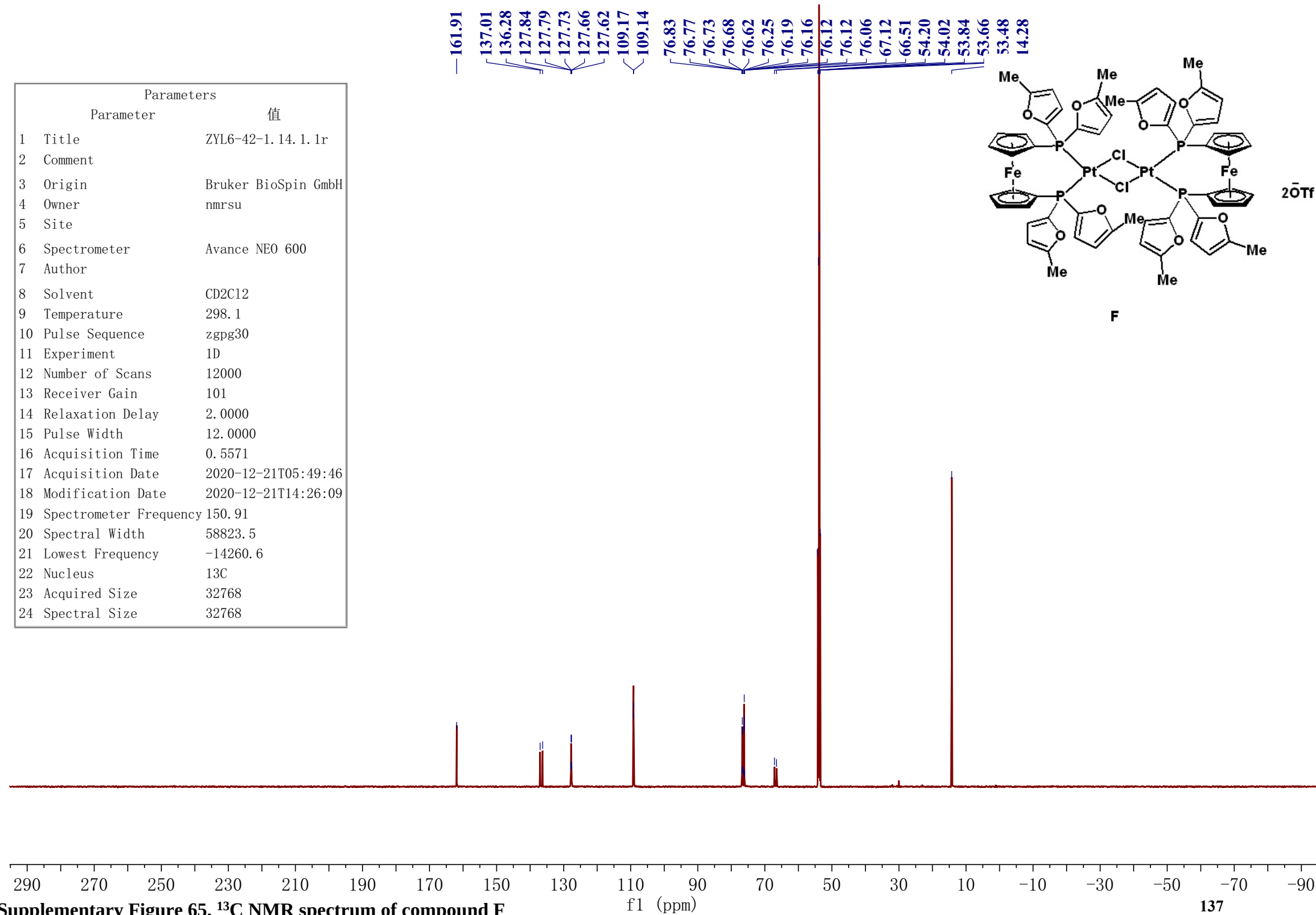


Parameters		
Parameter	值	
1 Title	ZYL6-42-1.11.1.1r	
2 Comment		
3 Origin	Bruker BioSpin GmbH	
4 Owner	nmrsu	
5 Site		
6 Spectrometer	Avance NEO 600	
7 Author		
8 Solvent	CD2C12	
9 Temperature	298.1	
10 Pulse Sequence	zg30	
11 Experiment	1D	
12 Number of Scans	8	
13 Receiver Gain	101	
14 Relaxation Delay	1.0000	
15 Pulse Width	10.0000	
16 Acquisition Time	2.7525	
17 Acquisition Date	2020-12-20T20:59:54	
18 Modification Date	2020-12-21T14:26:08	
19 Spectrometer Frequency	600.15	
20 Spectral Width	11904.8	
21 Lowest Frequency	-2277.0	
22 Nucleus	¹ H	
23 Acquired Size	32768	
24 Spectral Size	65536	



Supplementary Figure 64. ¹H NMR spectrum of compound F

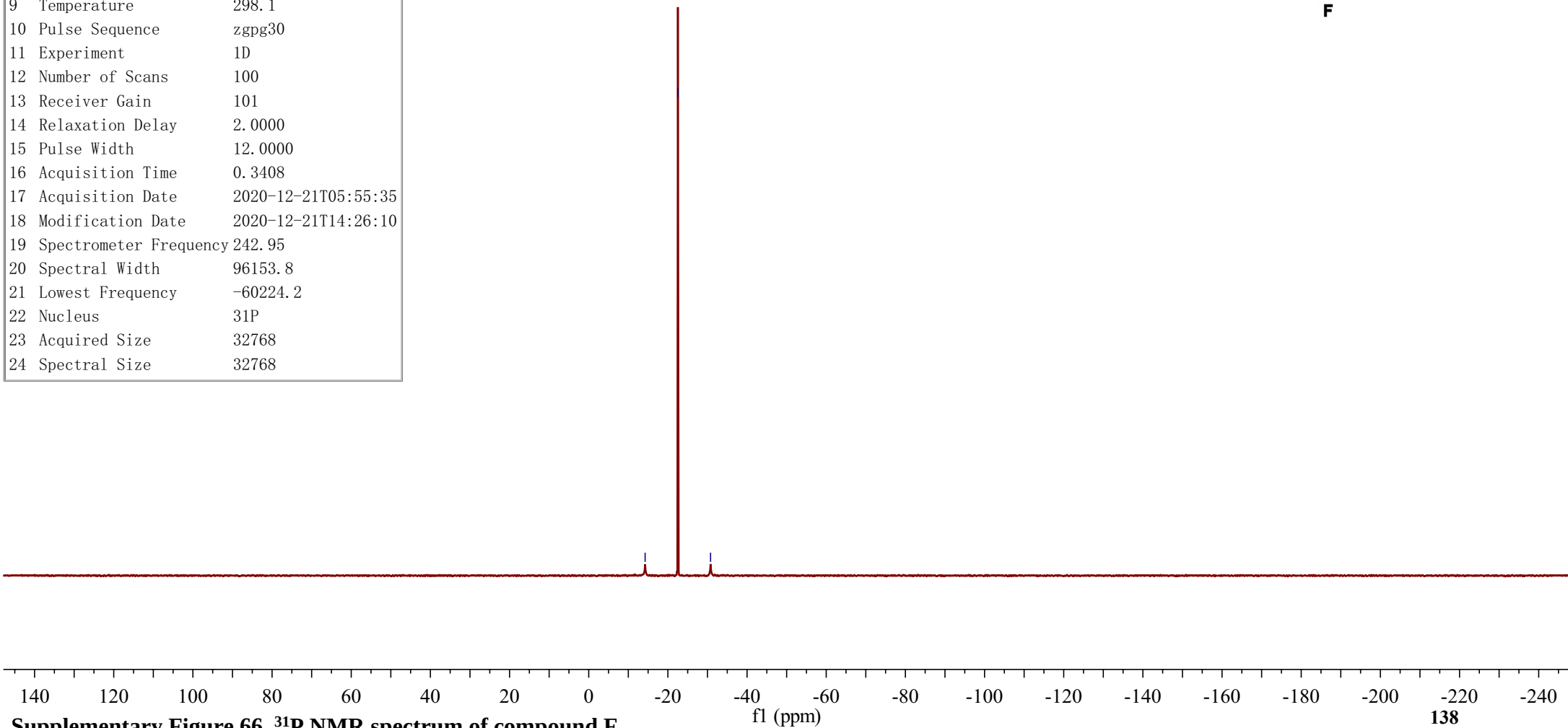
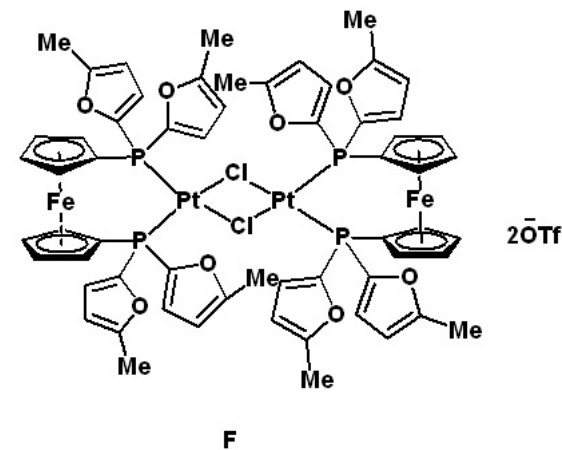
Parameters		
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1	Title	ZYL6-42-1.14.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Spectrometer	Avance NEO 600
7	Author	
8	Solvent	CD2Cl2
9	Temperature	298.1
10	Pulse Sequence	zgpg30
11	Experiment	1D
12	Number of Scans	12000
13	Receiver Gain	101
14	Relaxation Delay	2.0000
15	Pulse Width	12.0000
16	Acquisition Time	0.5571
17	Acquisition Date	2020-12-21T05:49:46
18	Modification Date	2020-12-21T14:26:09
19	Spectrometer Frequency	150.91
20	Spectral Width	58823.5
21	Lowest Frequency	-14260.6
22	Nucleus	¹³ C
23	Acquired Size	32768
24	Spectral Size	32768



Supplementary Figure 65. ¹³C NMR spectrum of compound F

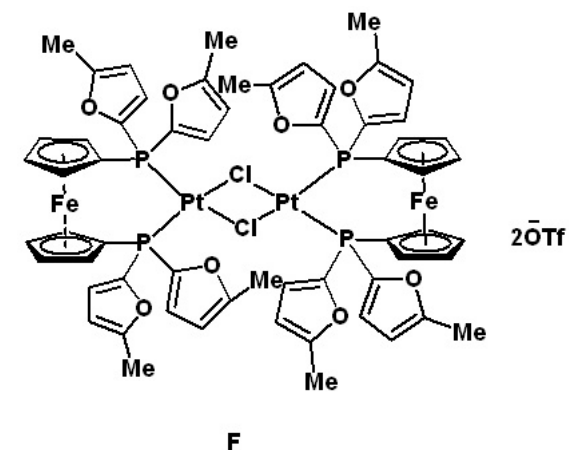
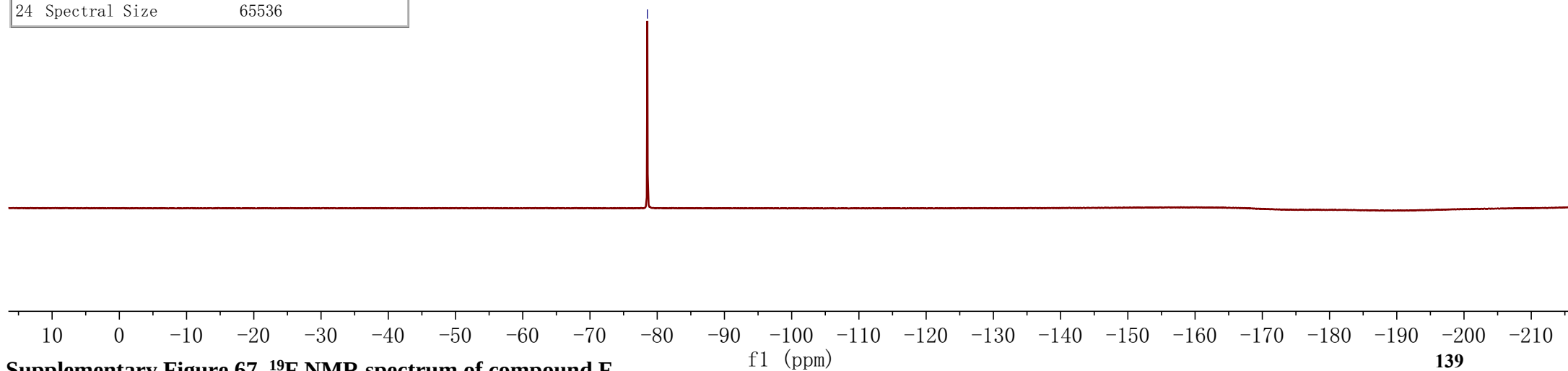
Parameters		
	Parameter	值
1	Title	ZYL6-42-1.15.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Spectrometer	Avance NEO 600
7	Author	
8	Solvent	CD2Cl2
9	Temperature	298.1
10	Pulse Sequence	zgpg30
11	Experiment	1D
12	Number of Scans	100
13	Receiver Gain	101
14	Relaxation Delay	2.0000
15	Pulse Width	12.0000
16	Acquisition Time	0.3408
17	Acquisition Date	2020-12-21T05:55:35
18	Modification Date	2020-12-21T14:26:10
19	Spectrometer Frequency	242.95
20	Spectral Width	96153.8
21	Lowest Frequency	-60224.2
22	Nucleus	31P
23	Acquired Size	32768
24	Spectral Size	32768

-14.25
 -22.52
 -30.78



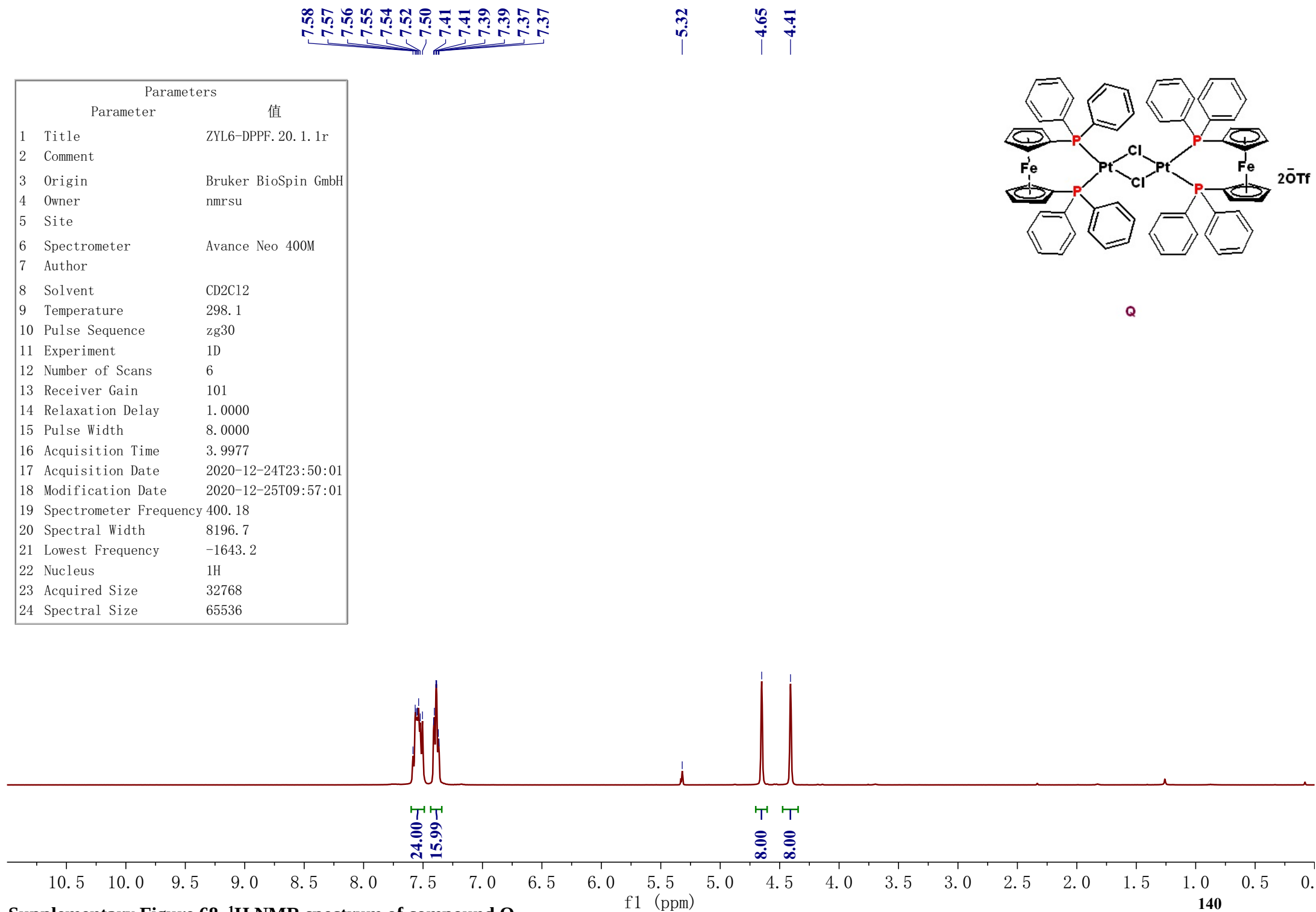
Supplementary Figure 66. ³¹P NMR spectrum of compound F

Parameters		
	Parameter	值
1	Title	ZYL6-42-1.16.1.1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Spectrometer	Avance NEO 600
7	Author	
8	Solvent	CD ₂ Cl ₂
9	Temperature	298.1
10	Pulse Sequence	zgig
11	Experiment	1D
12	Number of Scans	16
13	Receiver Gain	101
14	Relaxation Delay	1.0000
15	Pulse Width	12.0000
16	Acquisition Time	0.4981
17	Acquisition Date	2020-12-21T05:57:30
18	Modification Date	2020-12-21T14:26:10
19	Spectrometer Frequency	564.71
20	Spectral Width	131578.9
21	Lowest Frequency	-122260.0
22	Nucleus	¹⁹ F
23	Acquired Size	65536
24	Spectral Size	65536

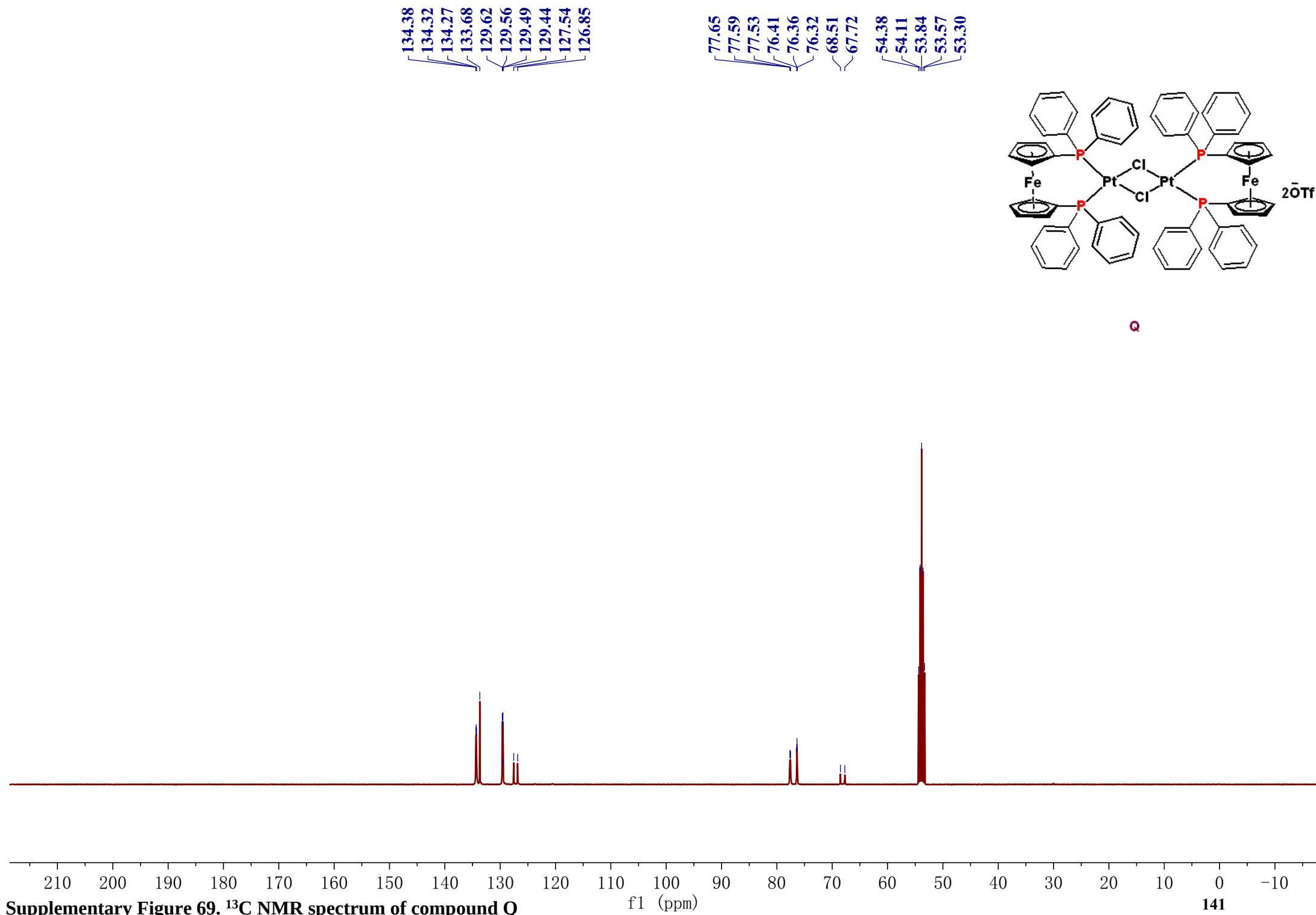


Supplementary Figure 67. ¹⁹F NMR spectrum of compound F

Parameters		
	Parameter	值
1	Title	ZYL6-DPPF. 20. 1. 1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Spectrometer	Avance Neo 400M
7	Author	
8	Solvent	CD2C12
9	Temperature	298. 1
10	Pulse Sequence	zg30
11	Experiment	1D
12	Number of Scans	6
13	Receiver Gain	101
14	Relaxation Delay	1. 0000
15	Pulse Width	8. 0000
16	Acquisition Time	3. 9977
17	Acquisition Date	2020-12-24T23:50:01
18	Modification Date	2020-12-25T09:57:01
19	Spectrometer Frequency	400. 18
20	Spectral Width	8196. 7
21	Lowest Frequency	-1643. 2
22	Nucleus	¹ H
23	Acquired Size	32768
24	Spectral Size	65536

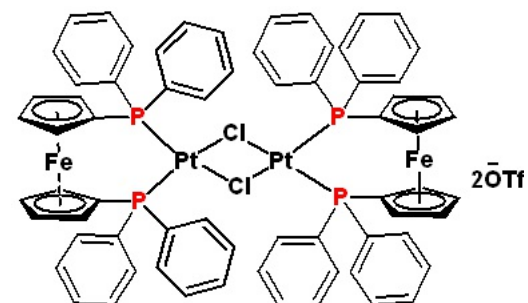


Supplementary Figure 68. ¹H NMR spectrum of compound Q

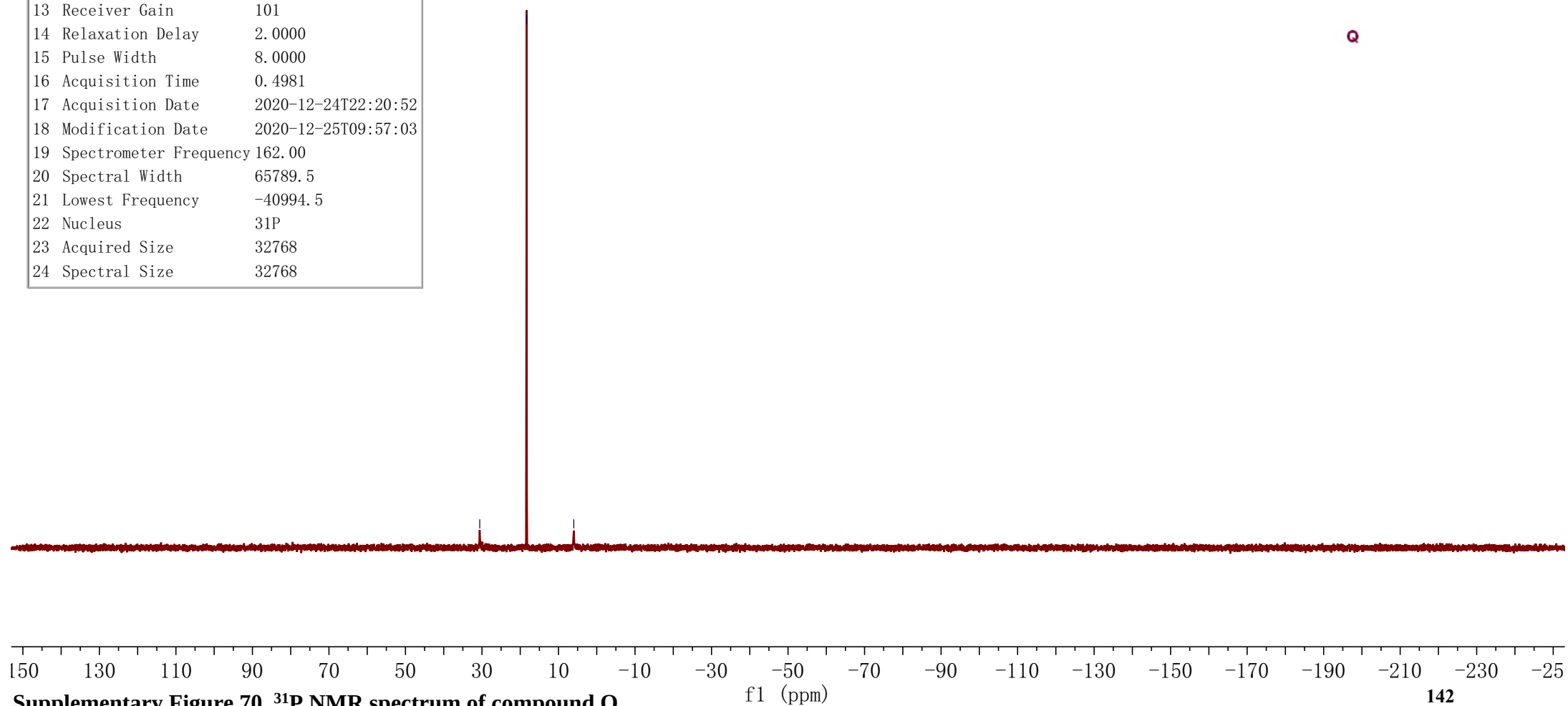


Parameters		
	Parameter	值
1	Title	ZYL6-DPPF. 24. 1. 1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Spectrometer	Avance Neo 400M
7	Author	
8	Solvent	CD ₂ Cl ₂
9	Temperature	298.2
10	Pulse Sequence	zgpg30
11	Experiment	1D
12	Number of Scans	16
13	Receiver Gain	101
14	Relaxation Delay	2.0000
15	Pulse Width	8.0000
16	Acquisition Time	0.4981
17	Acquisition Date	2020-12-24T22:20:52
18	Modification Date	2020-12-25T09:57:03
19	Spectrometer Frequency	162.00
20	Spectral Width	65789.5
21	Lowest Frequency	-40994.5
22	Nucleus	³¹ P
23	Acquired Size	32768
24	Spectral Size	32768

— 30.58
— 18.30
— 6.00

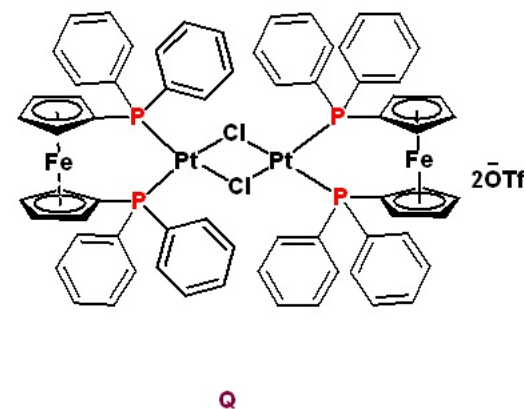
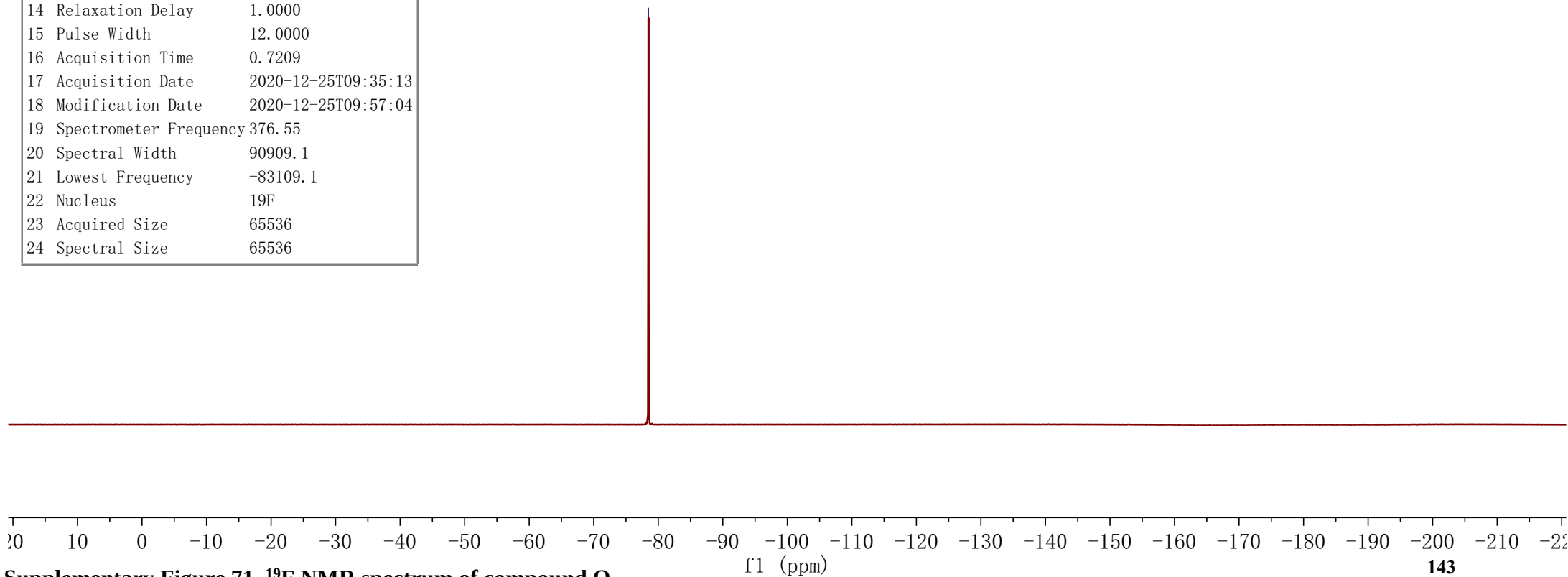


Q



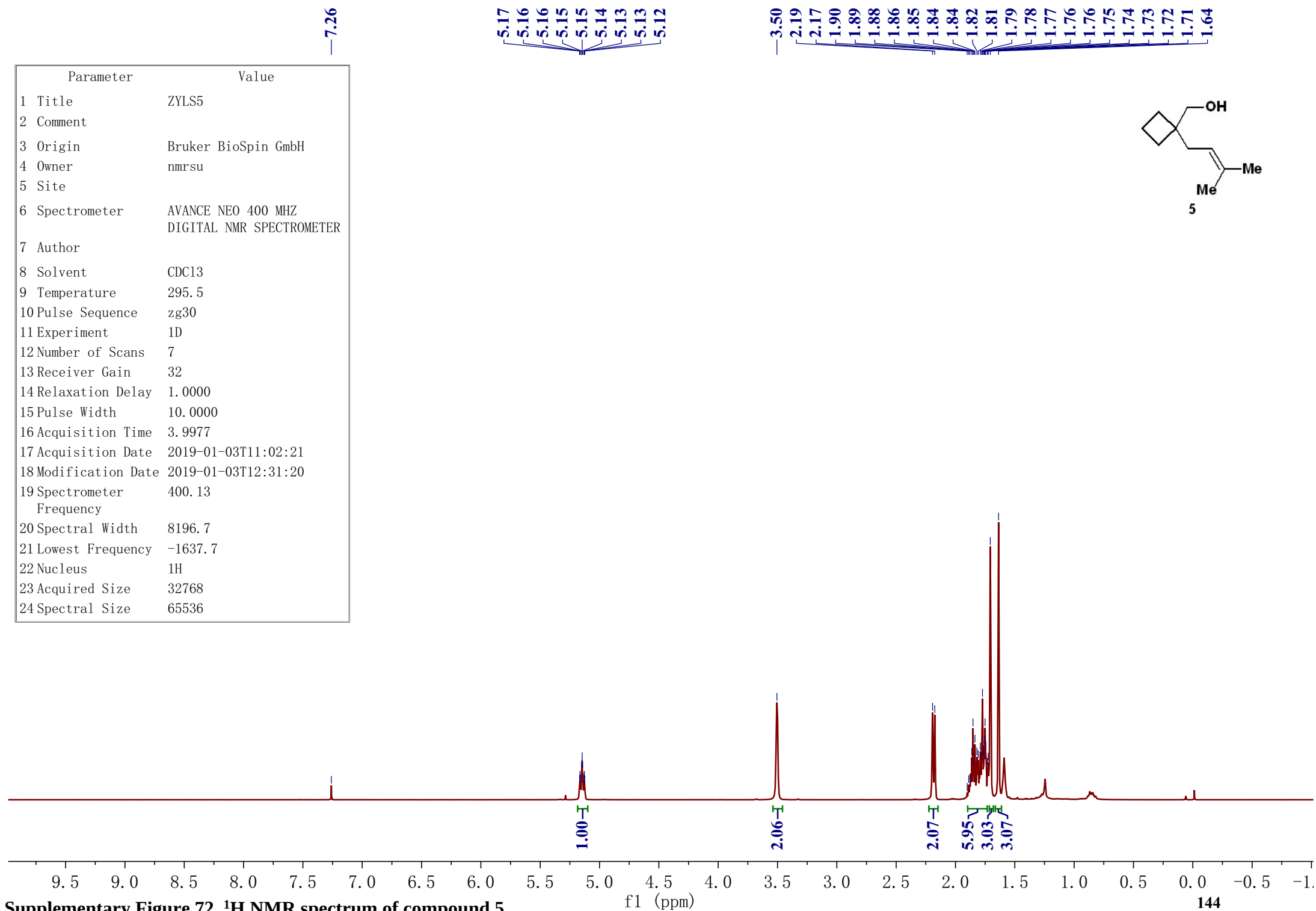
Supplementary Figure 70. ³¹P NMR spectrum of compound Q

Parameters		
	Parameter	值
1	Title	ZYL6-DPPF. 30. 1. 1r
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Spectrometer	Avance Neo 400M
7	Author	
8	Solvent	CD ₂ Cl ₂
9	Temperature	298.2
10	Pulse Sequence	zgig
11	Experiment	1D
12	Number of Scans	200
13	Receiver Gain	101
14	Relaxation Delay	1.0000
15	Pulse Width	12.0000
16	Acquisition Time	0.7209
17	Acquisition Date	2020-12-25T09:35:13
18	Modification Date	2020-12-25T09:57:04
19	Spectrometer Frequency	376.55
20	Spectral Width	90909.1
21	Lowest Frequency	-83109.1
22	Nucleus	¹⁹ F
23	Acquired Size	65536
24	Spectral Size	65536



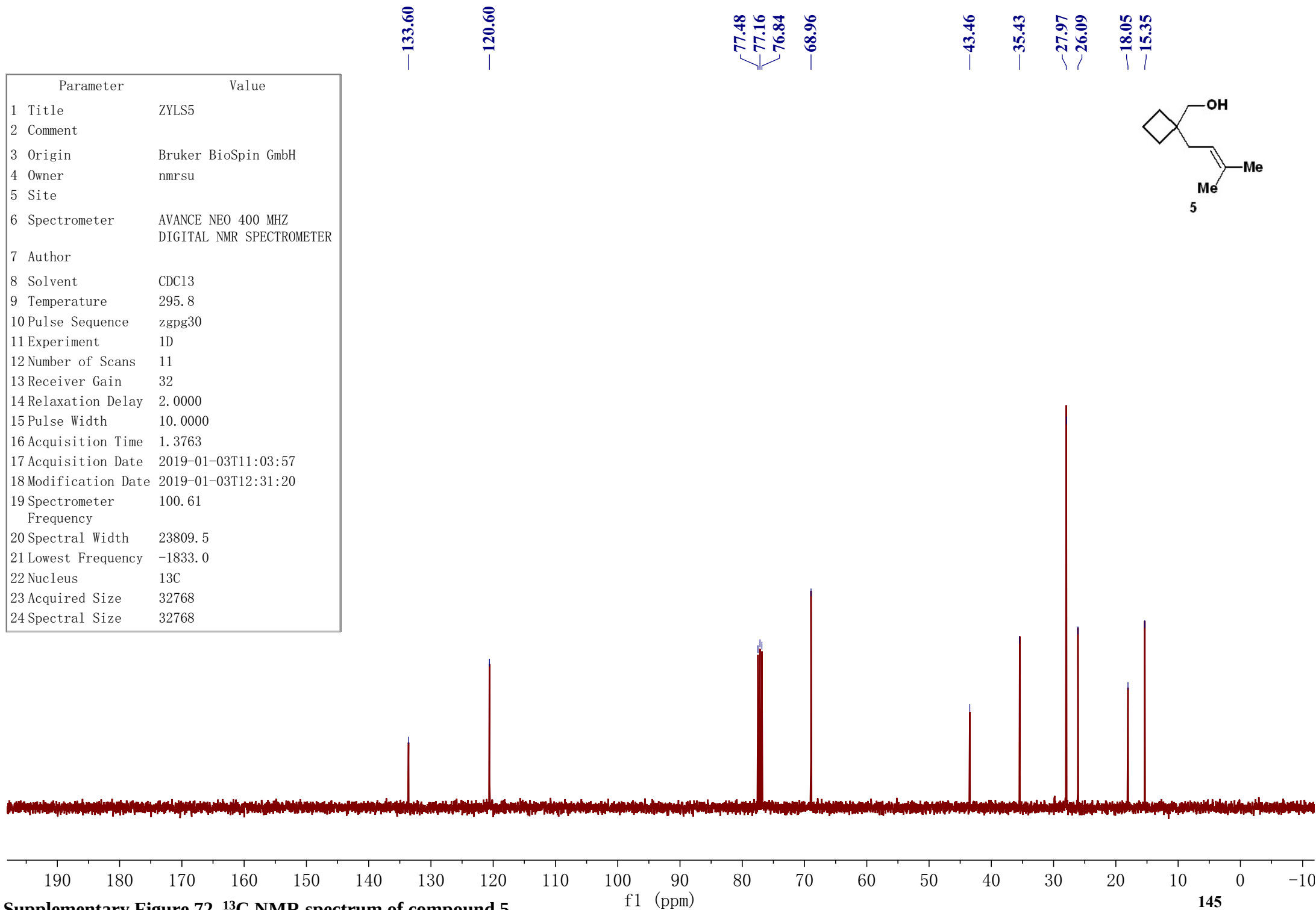
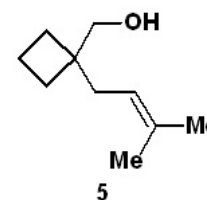
Supplementary Figure 71. ¹⁹F NMR spectrum of compound Q

Parameter	Value
1 Title	ZYLS5
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.5
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	7
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-01-03T11:02:21
18 Modification Date	2019-01-03T12:31:20
19 Spectrometer Frequency	400.13
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.7
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

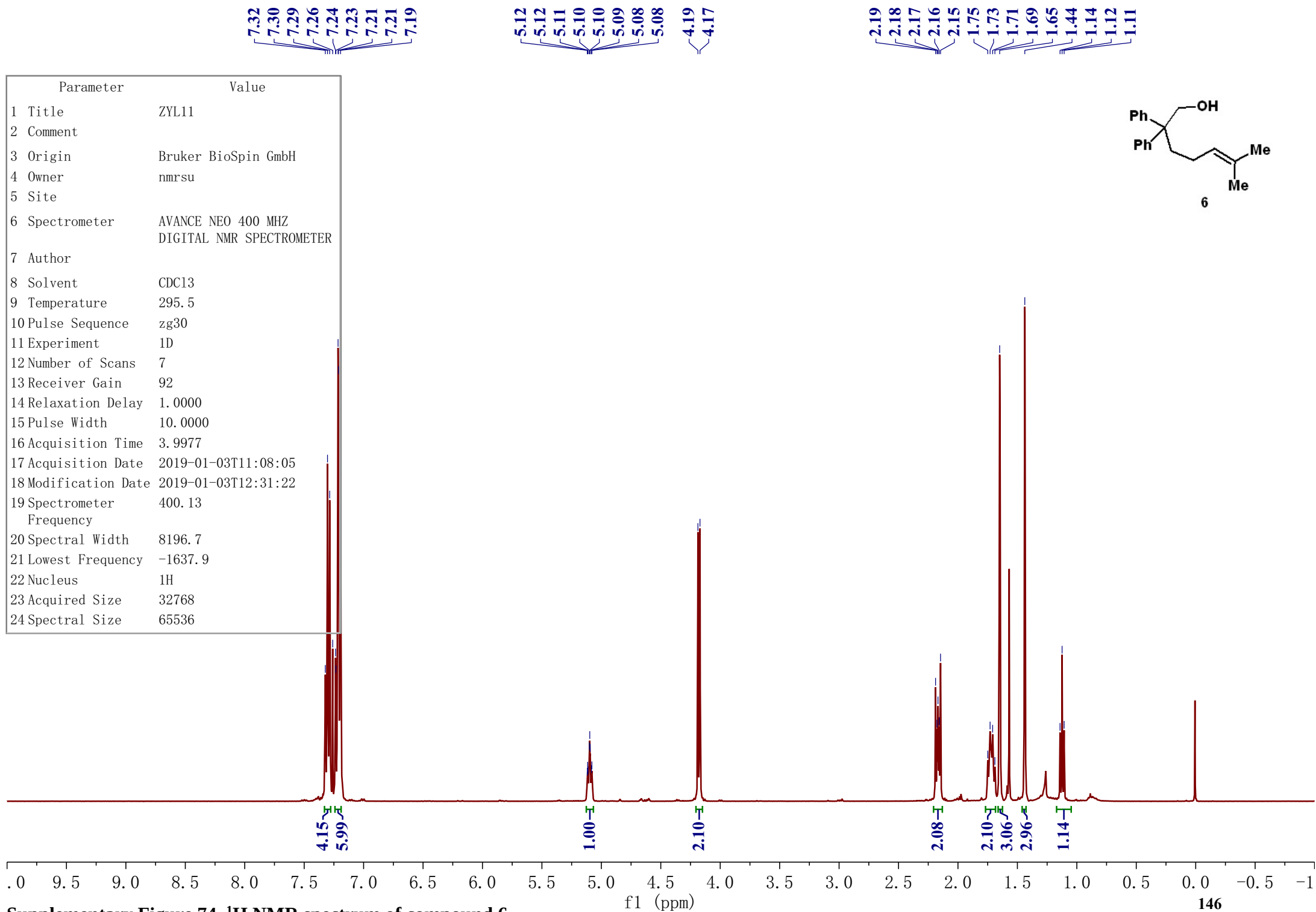


Supplementary Figure 72. ¹H NMR spectrum of compound 5

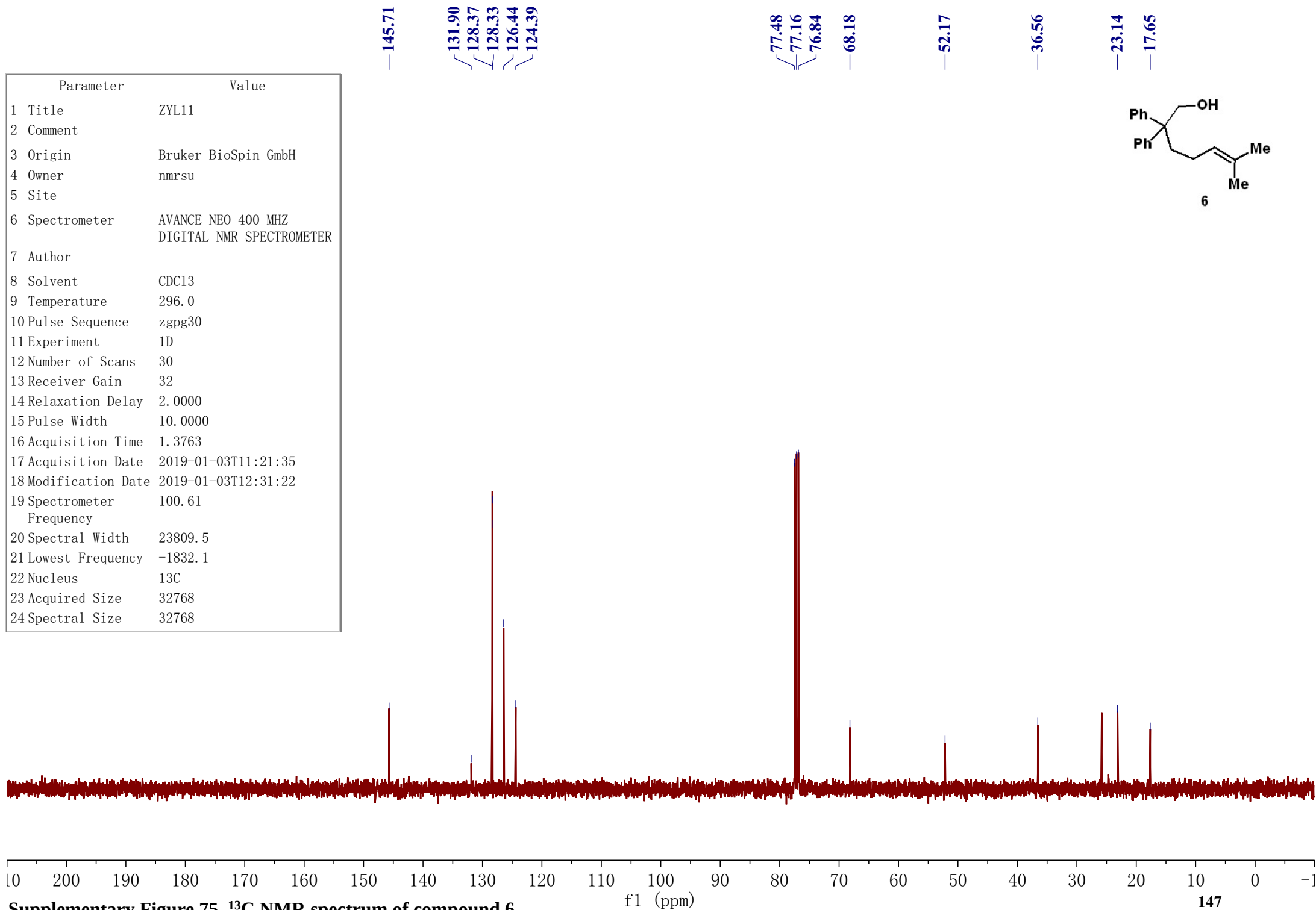
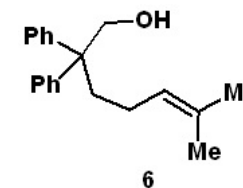
Parameter	Value
1 Title	ZYLS5
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.8
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	11
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-01-03T11:03:57
18 Modification Date	2019-01-03T12:31:20
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1833.0
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



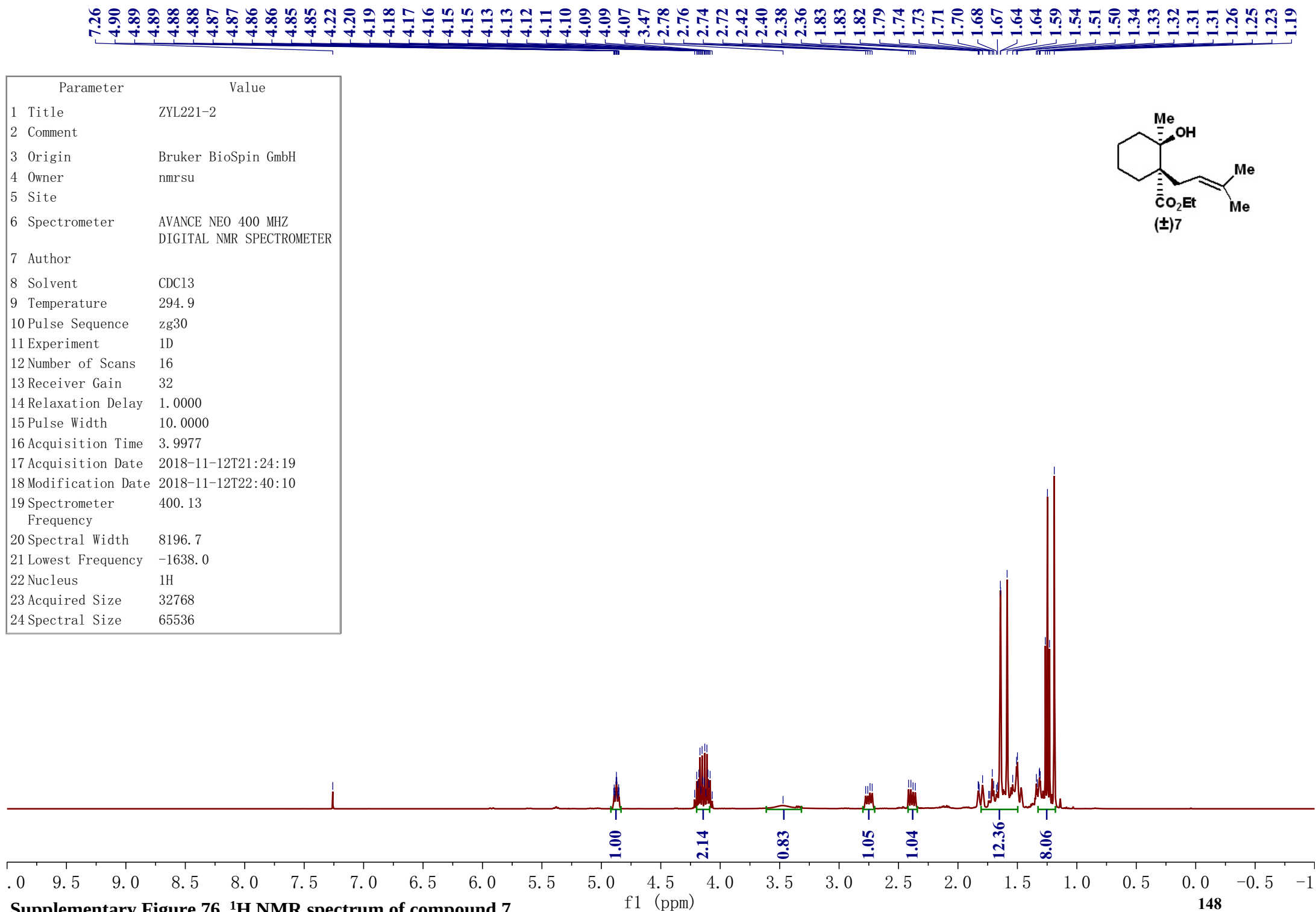
Supplementary Figure 72. ¹³C NMR spectrum of compound 5



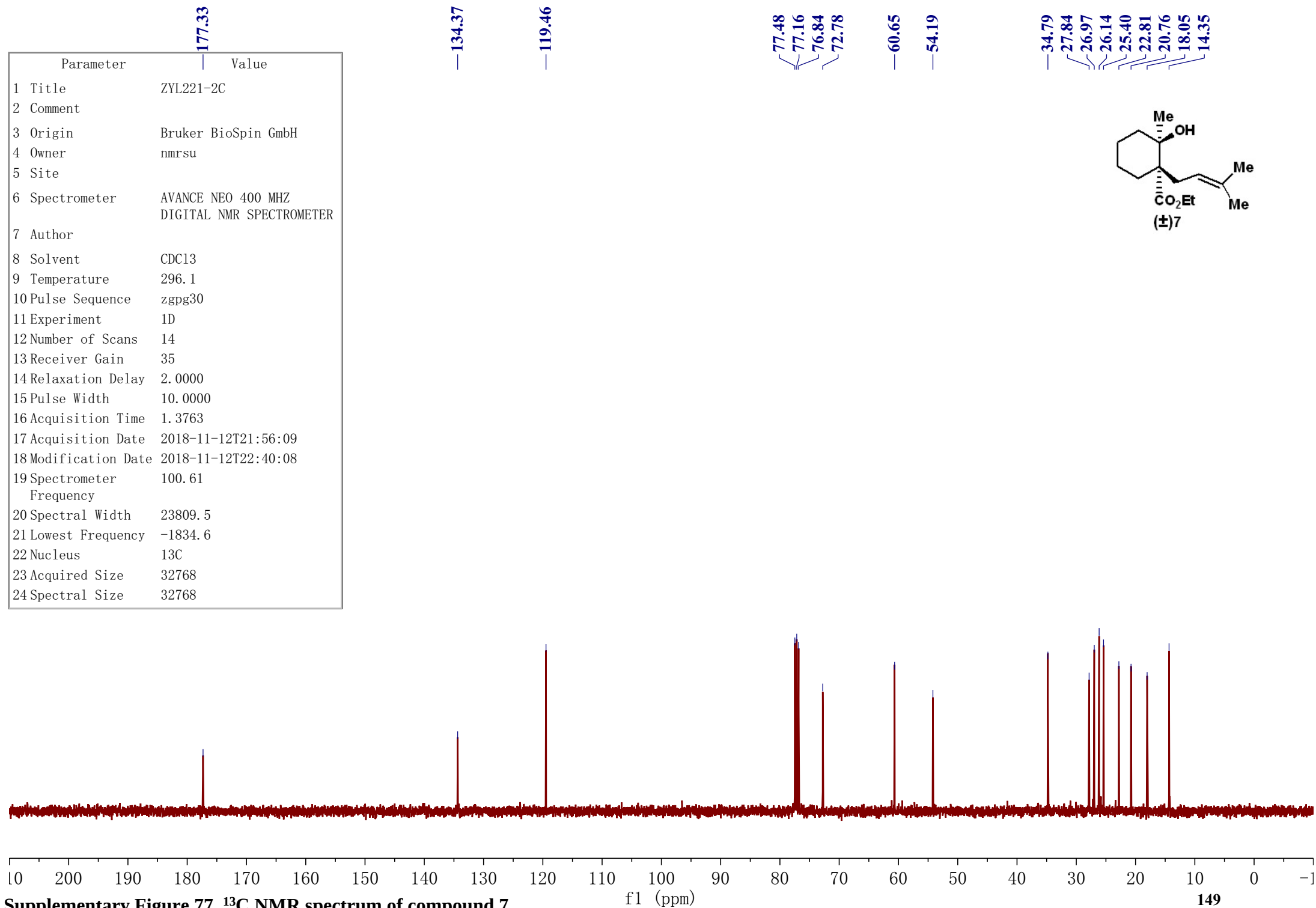
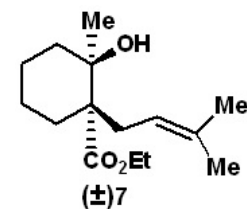
Parameter	Value
1 Title	ZYL11
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.0
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	30
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-01-03T11:21:35
18 Modification Date	2019-01-03T12:31:22
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1832.1
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 75. ¹³C NMR spectrum of compound 6

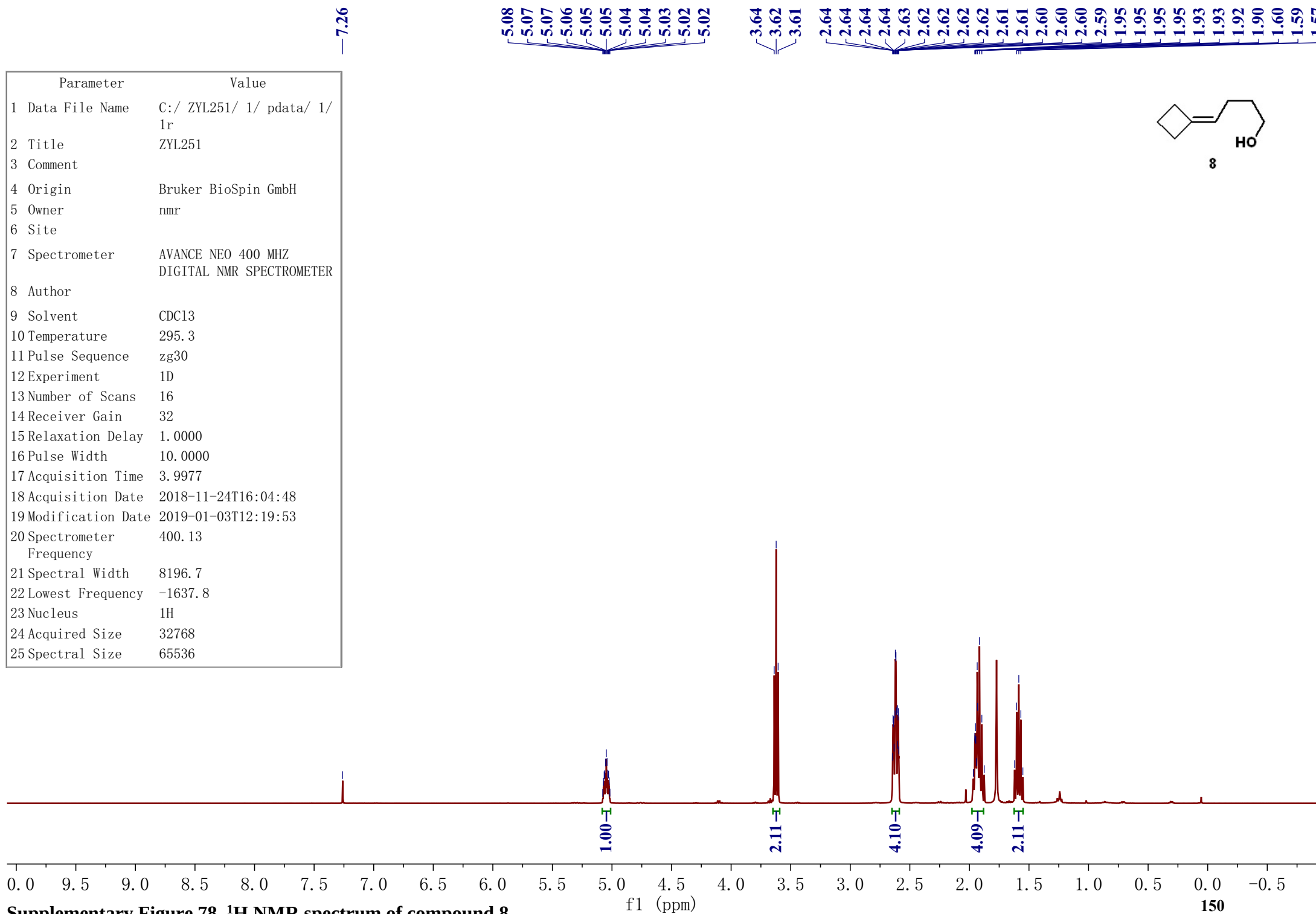
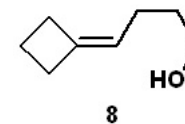


Parameter	Value
1 Title	ZYL221-2C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	14
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-11-12T21:56:09
18 Modification Date	2018-11-12T22:40:08
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1834.6
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



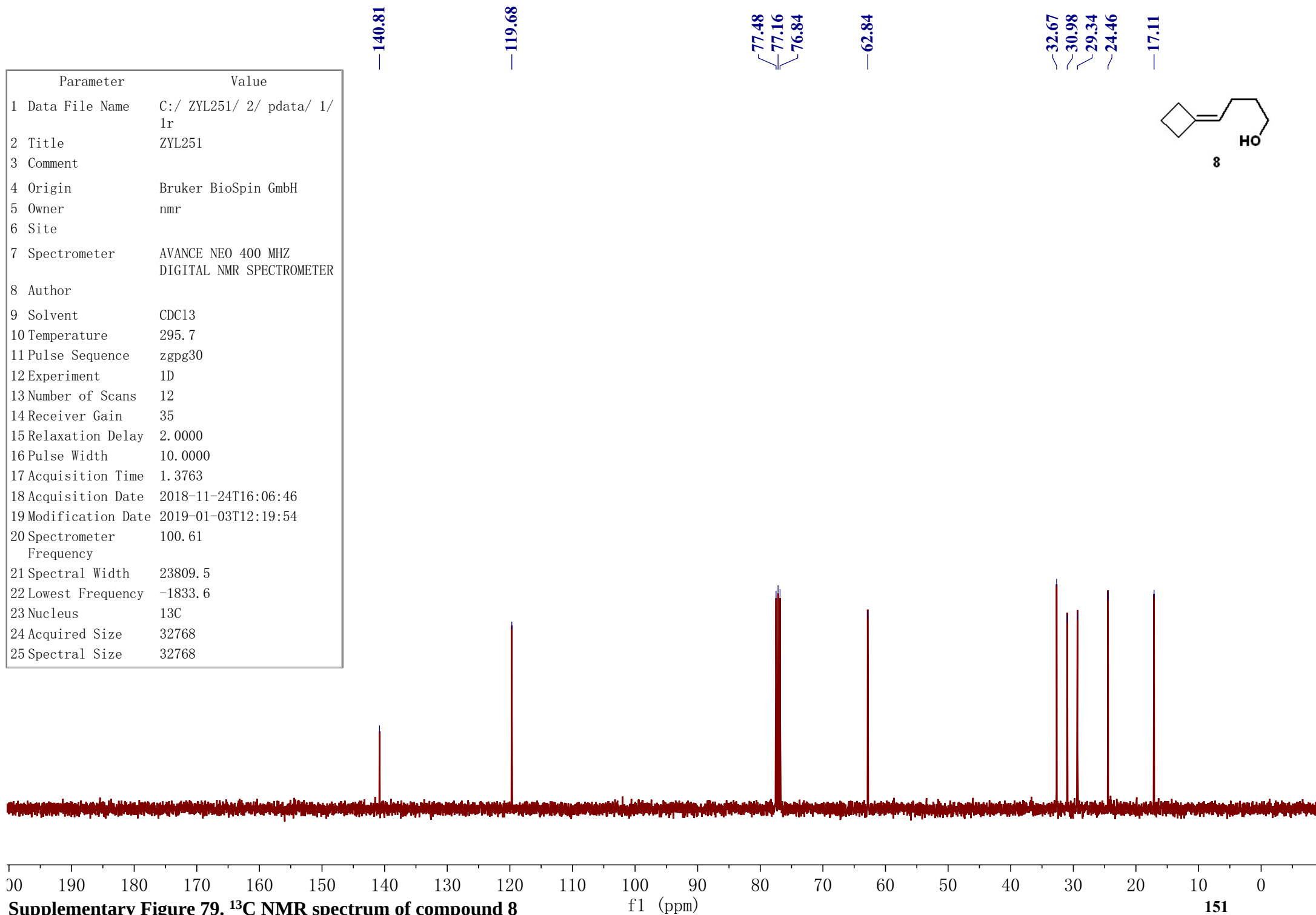
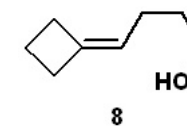
Supplementary Figure 77. ¹³C NMR spectrum of compound 7

Parameter	Value
1 Data File Name	C:/ ZYL251/ 1/ pdata/ 1/ 1r
2 Title	ZYL251
3 Comment	
4 Origin	Bruker BioSpin GmbH
5 Owner	nmr
6 Site	
7 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
8 Author	
9 Solvent	CDC13
10 Temperature	295.3
11 Pulse Sequence	zg30
12 Experiment	1D
13 Number of Scans	16
14 Receiver Gain	32
15 Relaxation Delay	1.0000
16 Pulse Width	10.0000
17 Acquisition Time	3.9977
18 Acquisition Date	2018-11-24T16:04:48
19 Modification Date	2019-01-03T12:19:53
20 Spectrometer	400.13
Frequency	
21 Spectral Width	8196.7
22 Lowest Frequency	-1637.8
23 Nucleus	¹ H
24 Acquired Size	32768
25 Spectral Size	65536



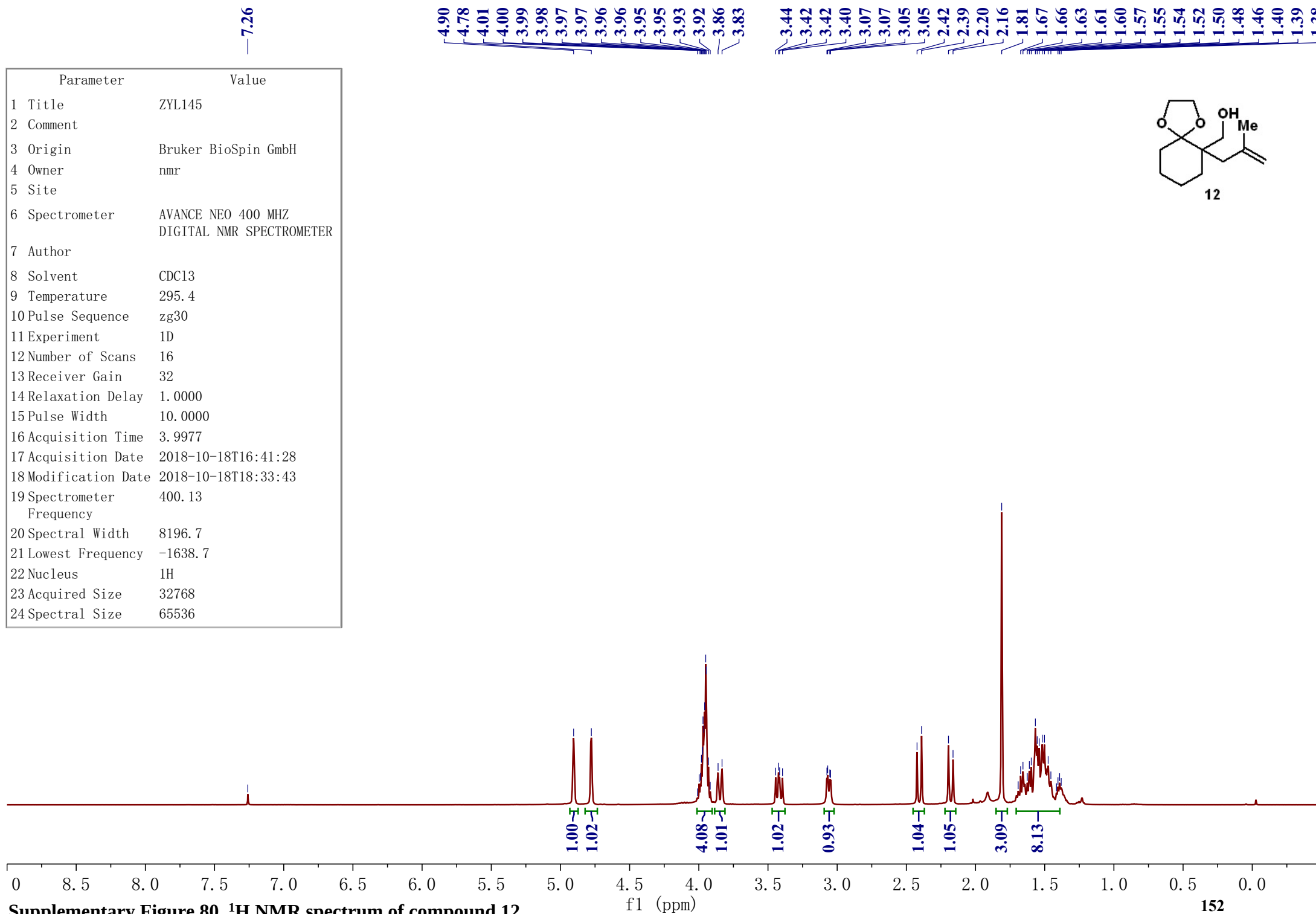
Supplementary Figure 78. ¹H NMR spectrum of compound 8

Parameter	Value
1 Data File Name	C:/ ZYL251/ 2/ pdata/ 1/ 1r
2 Title	ZYL251
3 Comment	
4 Origin	Bruker BioSpin GmbH
5 Owner	nmr
6 Site	
7 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
8 Author	
9 Solvent	CDC13
10 Temperature	295.7
11 Pulse Sequence	zgpg30
12 Experiment	1D
13 Number of Scans	12
14 Receiver Gain	35
15 Relaxation Delay	2.0000
16 Pulse Width	10.0000
17 Acquisition Time	1.3763
18 Acquisition Date	2018-11-24T16:06:46
19 Modification Date	2019-01-03T12:19:54
20 Spectrometer Frequency	100.61
21 Spectral Width	23809.5
22 Lowest Frequency	-1833.6
23 Nucleus	¹³ C
24 Acquired Size	32768
25 Spectral Size	32768



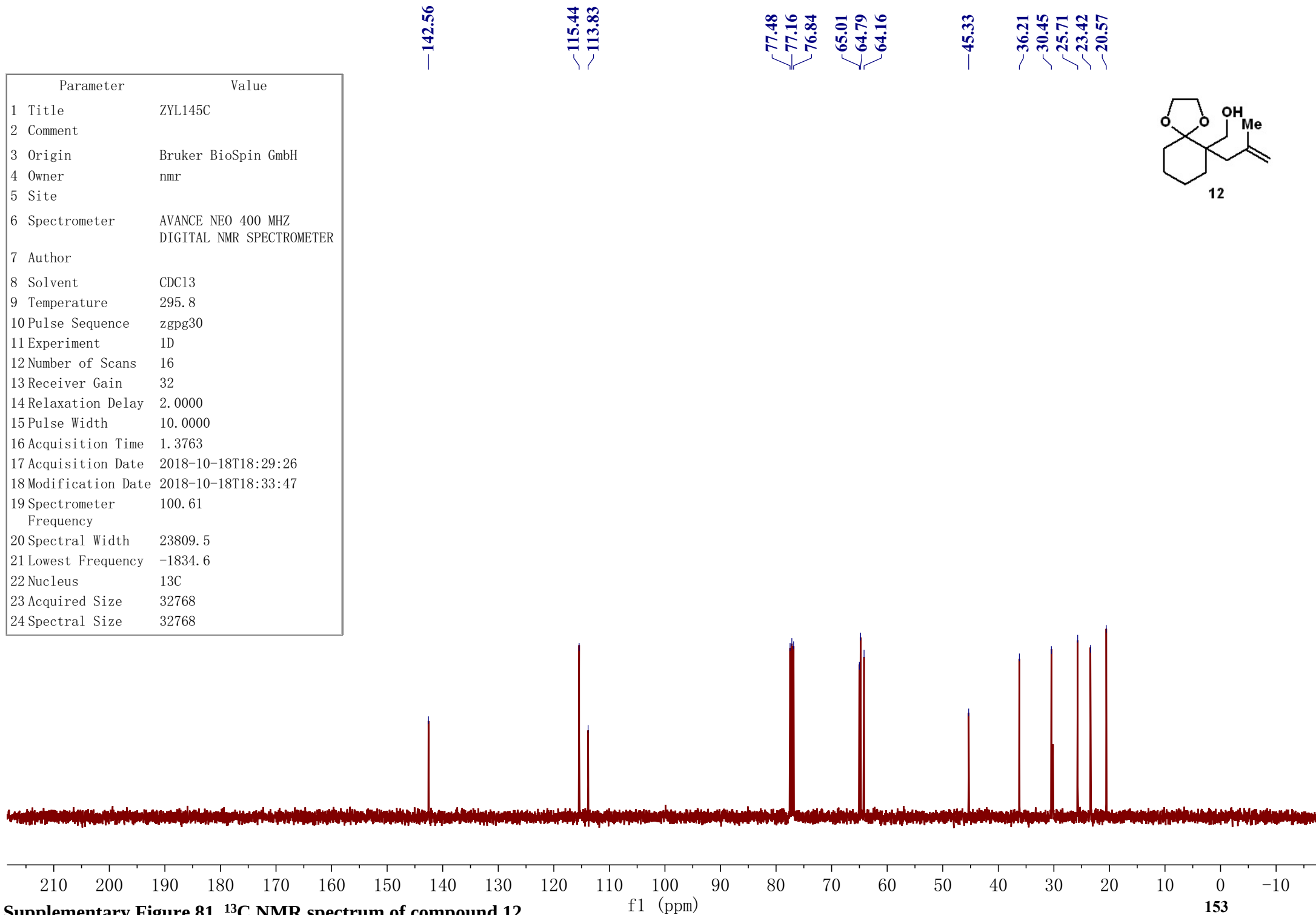
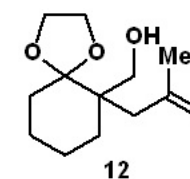
Supplementary Figure 79. ¹³C NMR spectrum of compound 8

Parameter	Value
1 Title	ZYL145
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.4
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-10-18T16:41:28
18 Modification Date	2018-10-18T18:33:43
19 Spectrometer Frequency	400.13
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.7
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

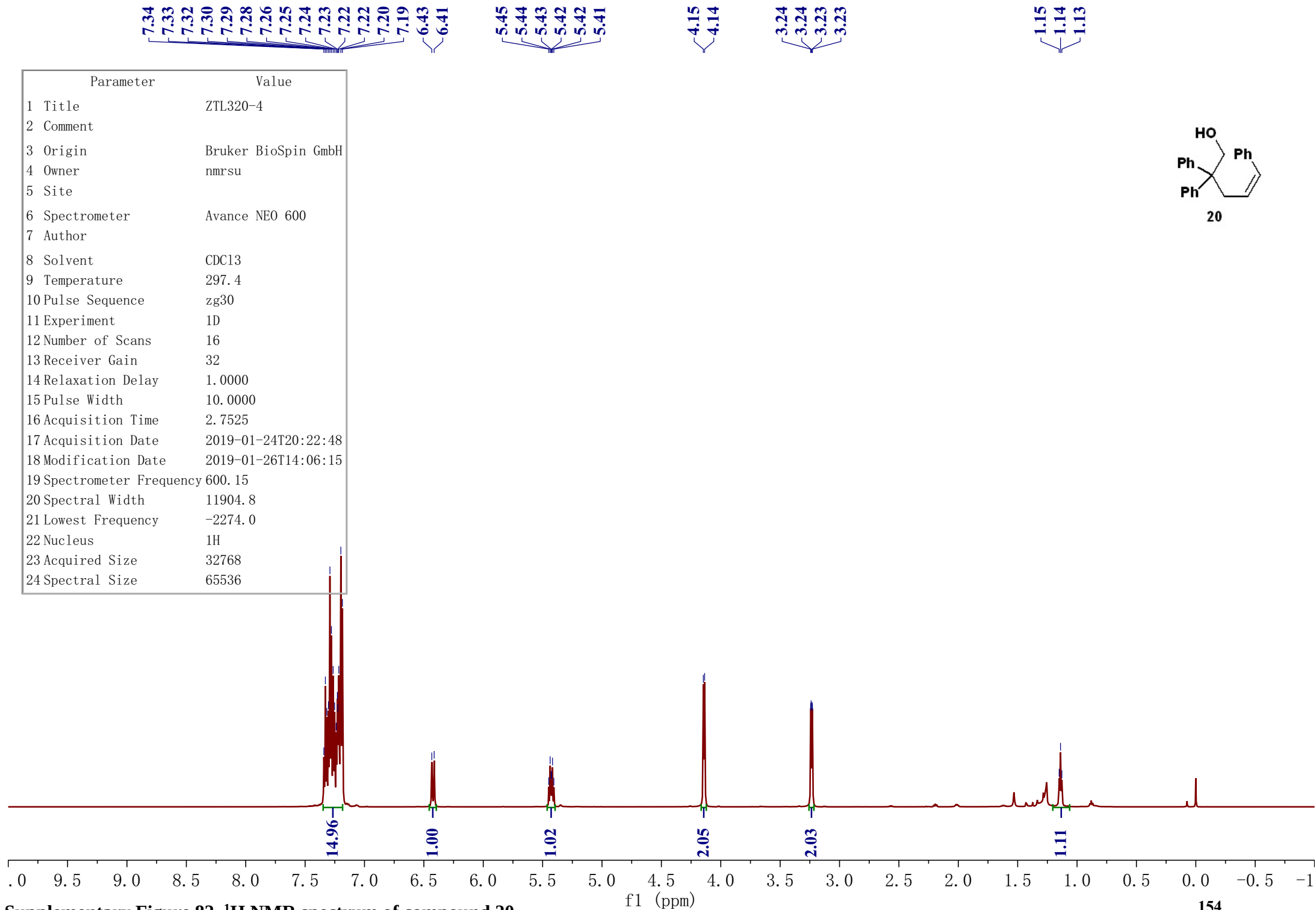


Supplementary Figure 80. ¹H NMR spectrum of compound 12

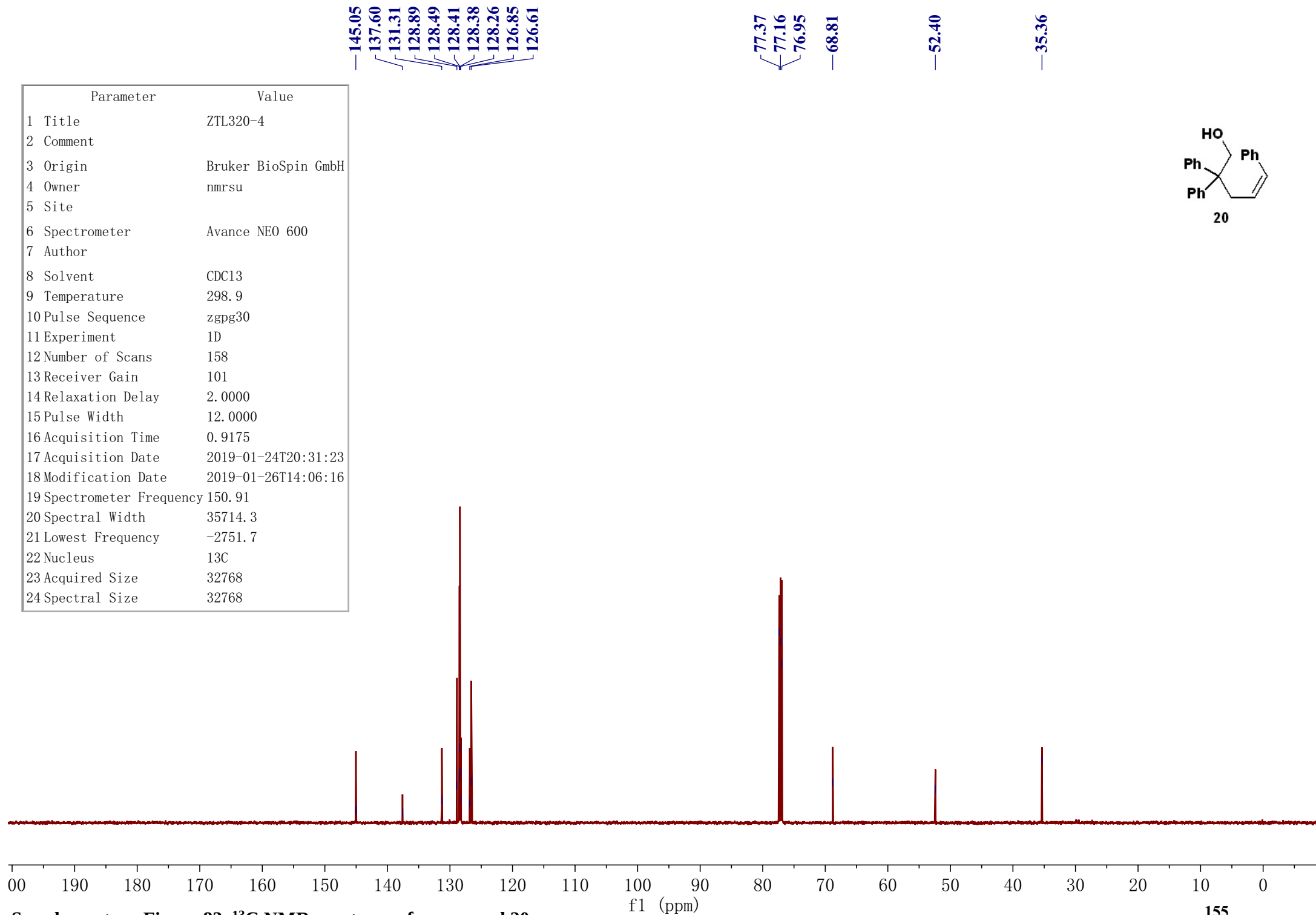
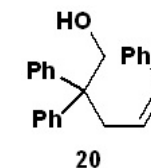
Parameter	Value
1 Title	ZYL145C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.8
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-10-18T18:29:26
18 Modification Date	2018-10-18T18:33:47
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1834.6
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 81. ¹³C NMR spectrum of compound 12

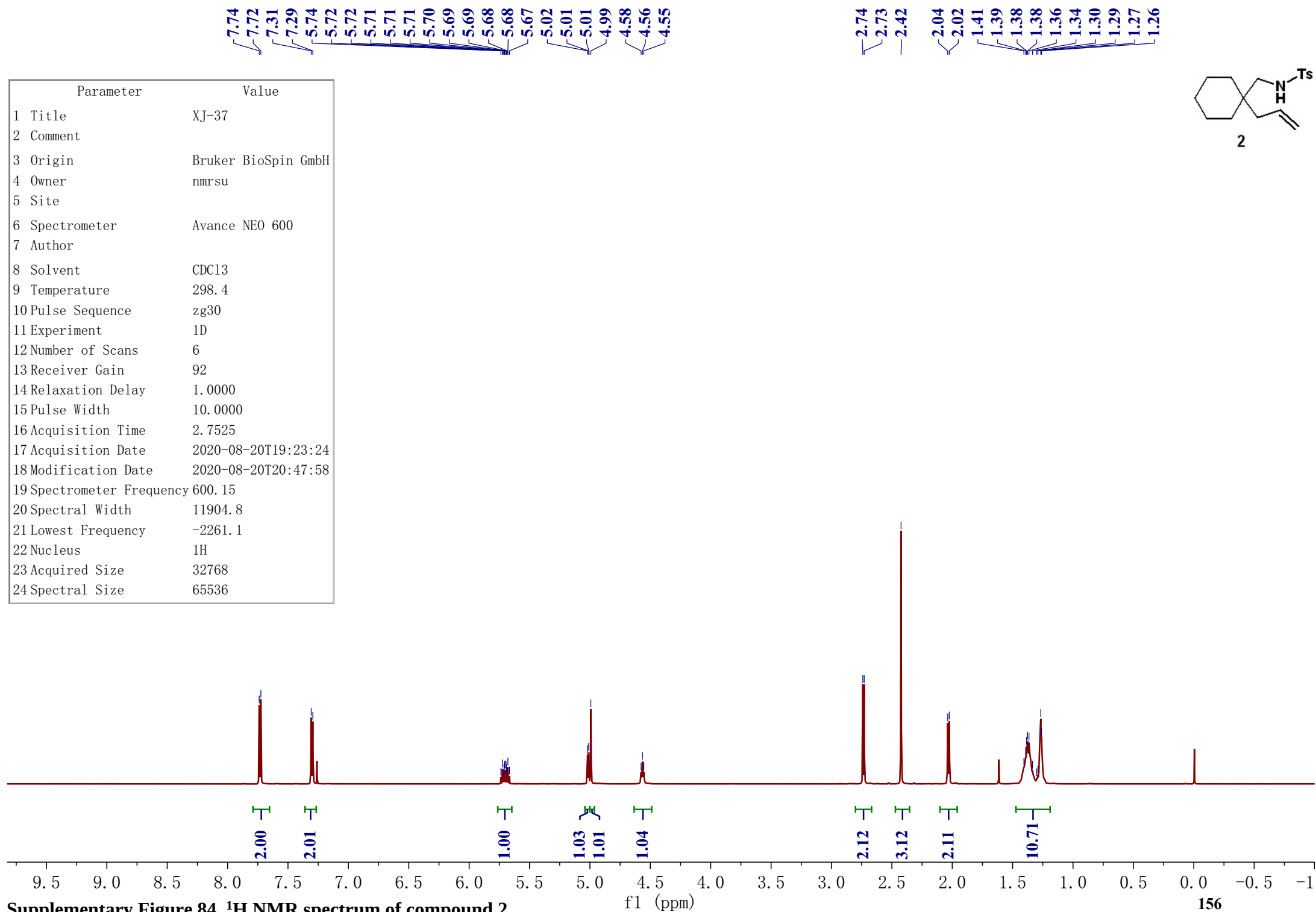
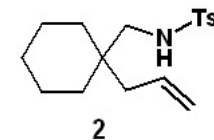


Parameter	Value
1 Title	ZTL320-4
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	298.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	158
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-01-24T20:31:23
18 Modification Date	2019-01-26T14:06:16
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2751.7
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



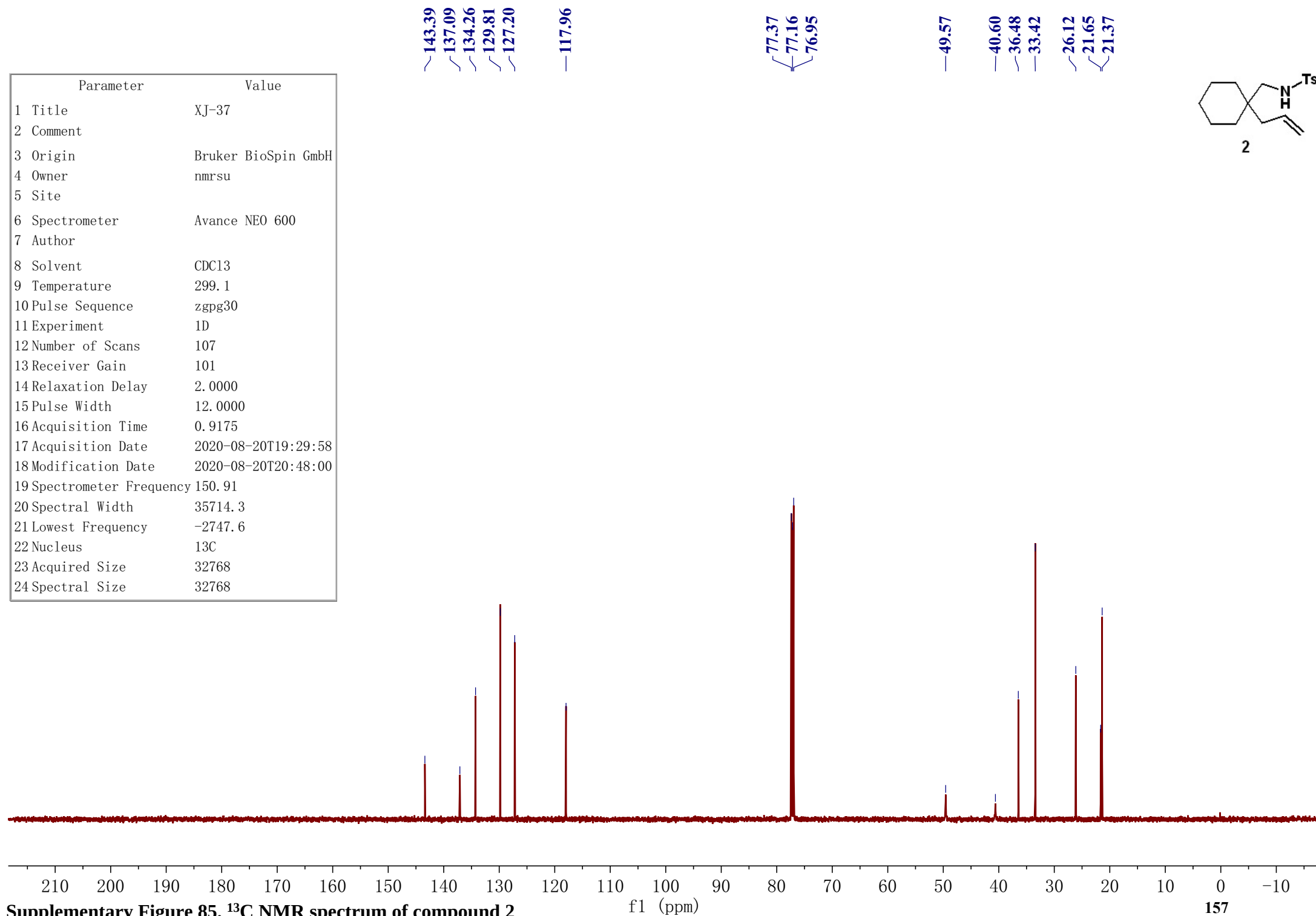
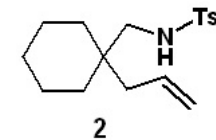
Supplementary Figure 83. ¹³C NMR spectrum of compound 20

Parameter	Value
1 Title	XJ-37
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.4
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	6
13 Receiver Gain	92
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2020-08-20T19:23:24
18 Modification Date	2020-08-20T20:47:58
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2261.1
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



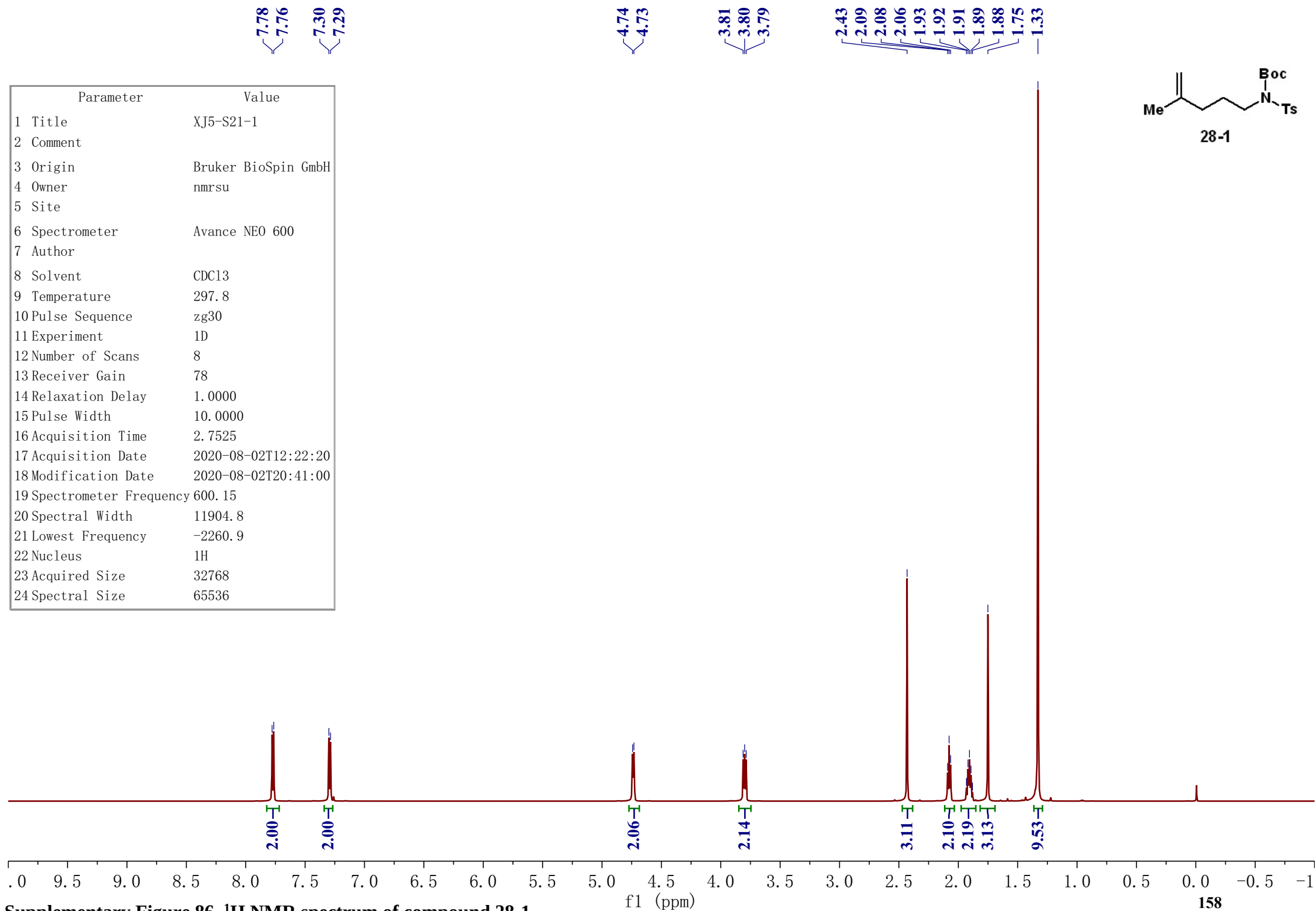
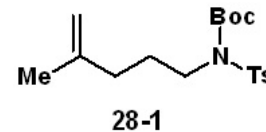
Supplementary Figure 84. ¹H NMR spectrum of compound 2

Parameter	Value
1 Title	XJ-37
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	299.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	107
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2020-08-20T19:29:58
18 Modification Date	2020-08-20T20:48:00
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2747.6
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768



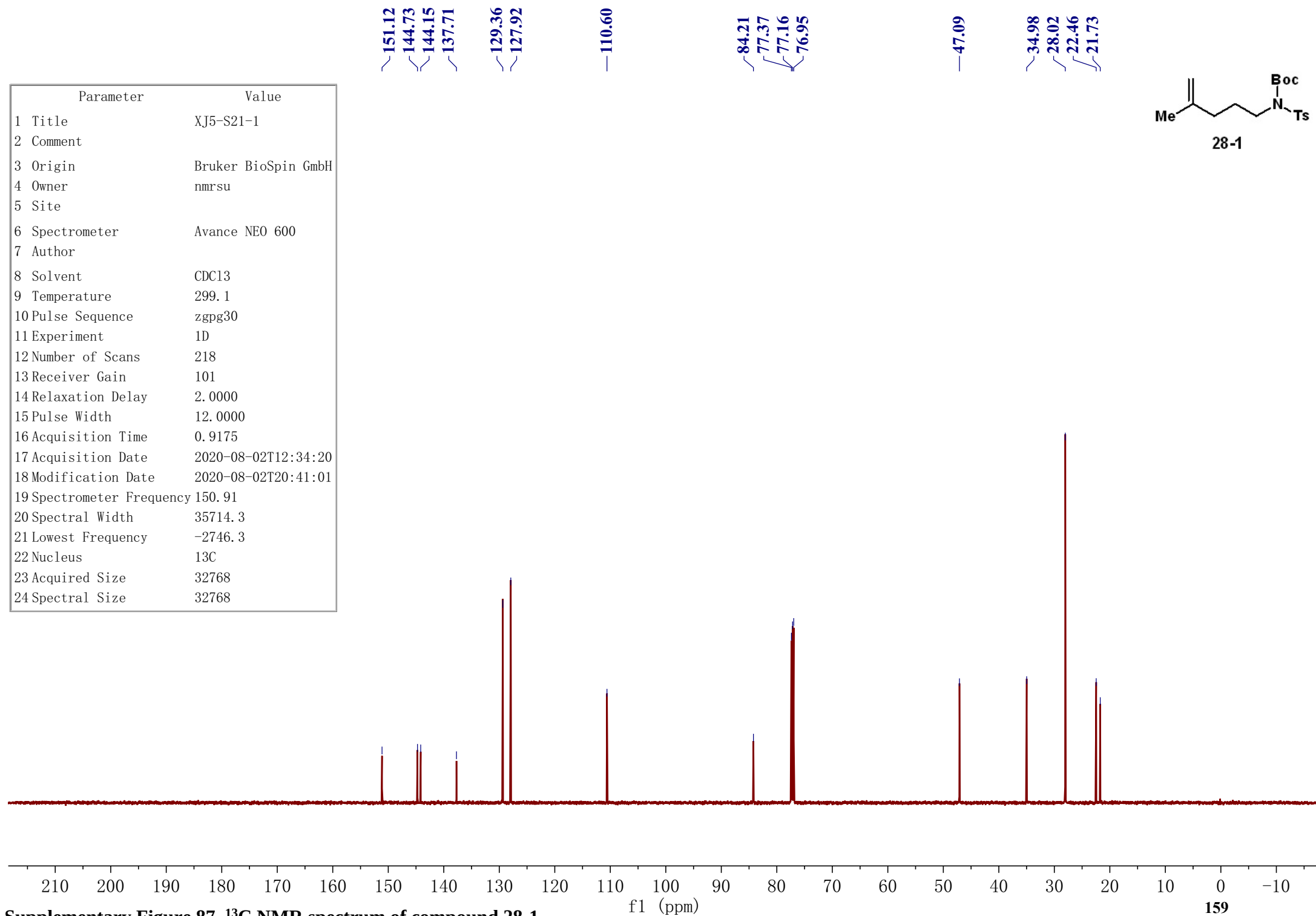
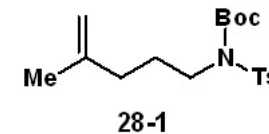
Supplementary Figure 85. ¹³C NMR spectrum of compound 2

Parameter	Value
1 Title	XJ5-S21-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	297.8
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	78
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2020-08-02T12:22:20
18 Modification Date	2020-08-02T20:41:00
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2260.9
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536

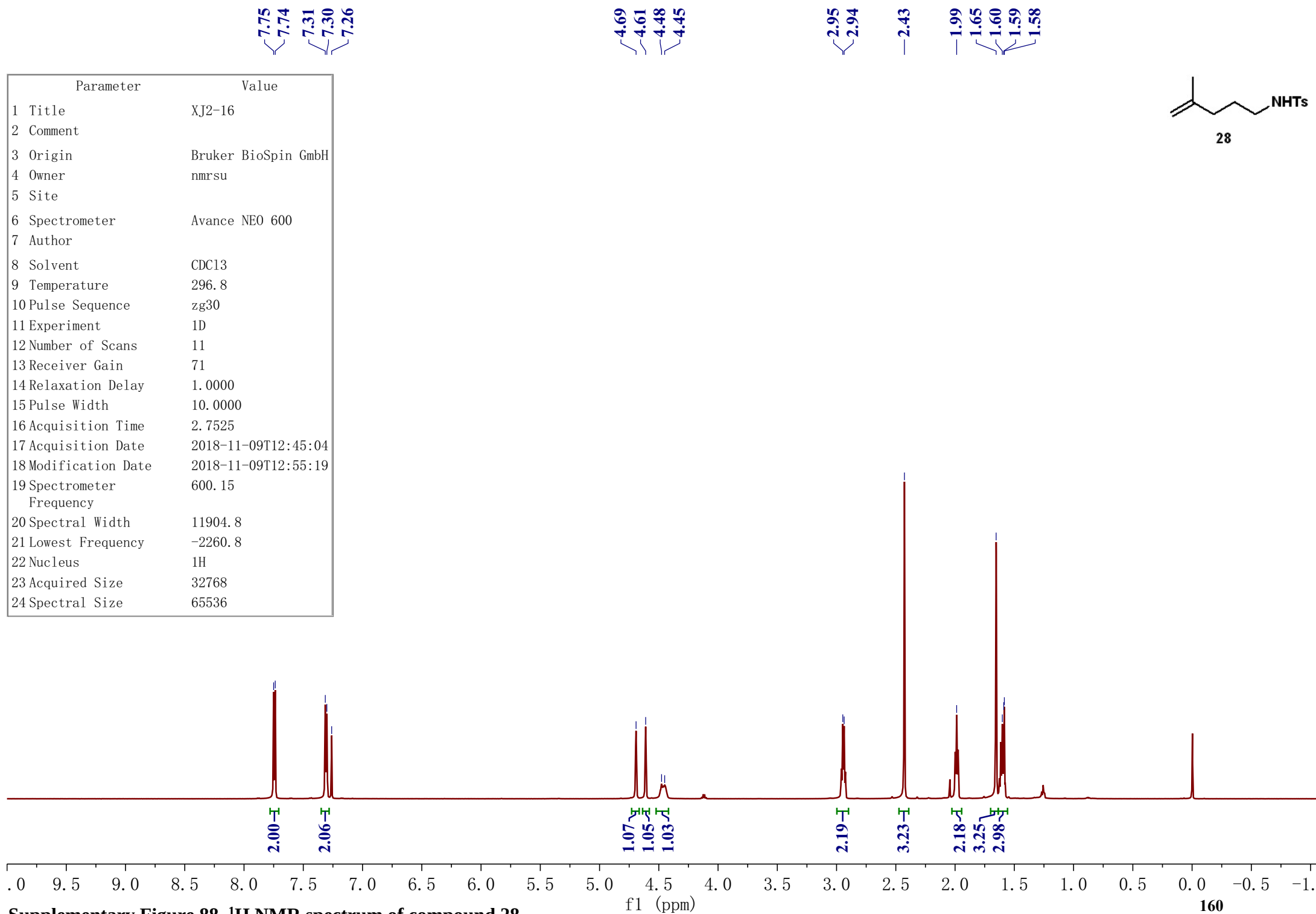
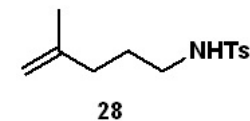


Supplementary Figure 86. ¹H NMR spectrum of compound 28-1

Parameter	Value
1 Title	XJ5-S21-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	299.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	218
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2020-08-02T12:34:20
18 Modification Date	2020-08-02T20:41:01
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2746.3
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

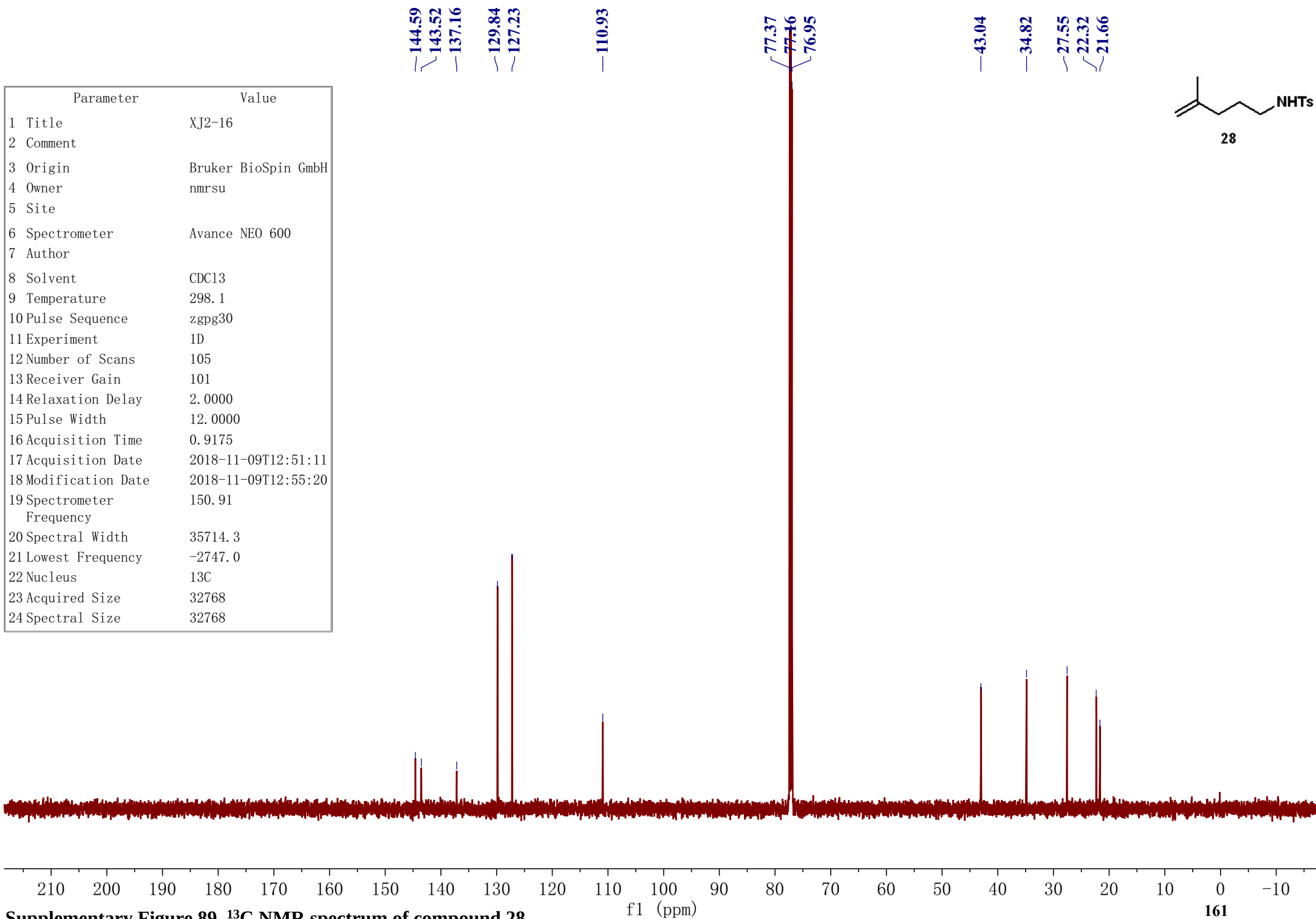
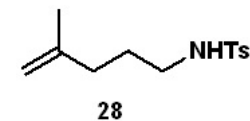


Parameter	Value
1 Title	XJ2-16
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	296.8
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	11
13 Receiver Gain	71
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2018-11-09T12:45:04
18 Modification Date	2018-11-09T12:55:19
19 Spectrometer	600.15
Frequency	
20 Spectral Width	11904.8
21 Lowest Frequency	-2260.8
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536

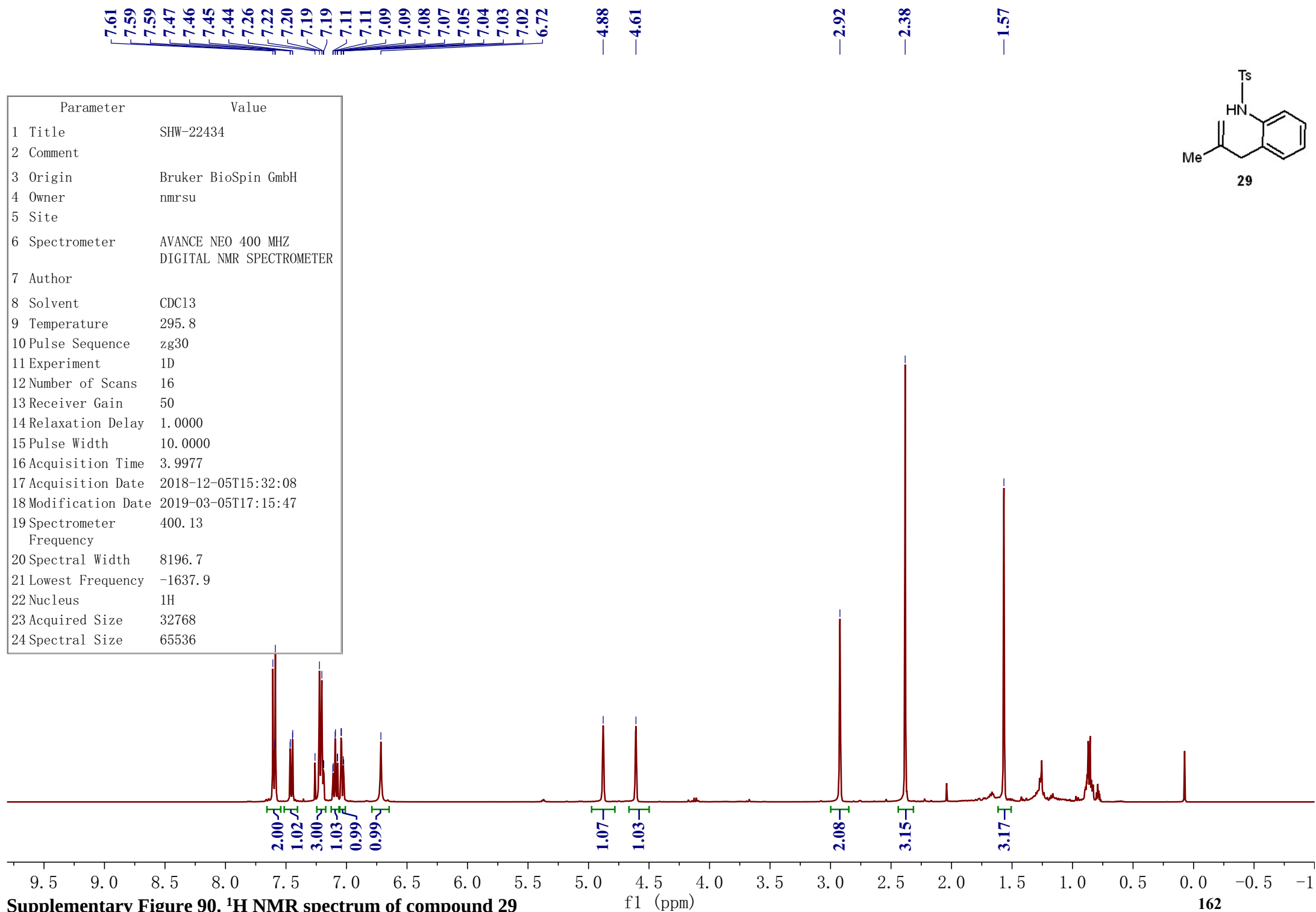


Supplementary Figure 88. ¹H NMR spectrum of compound 28

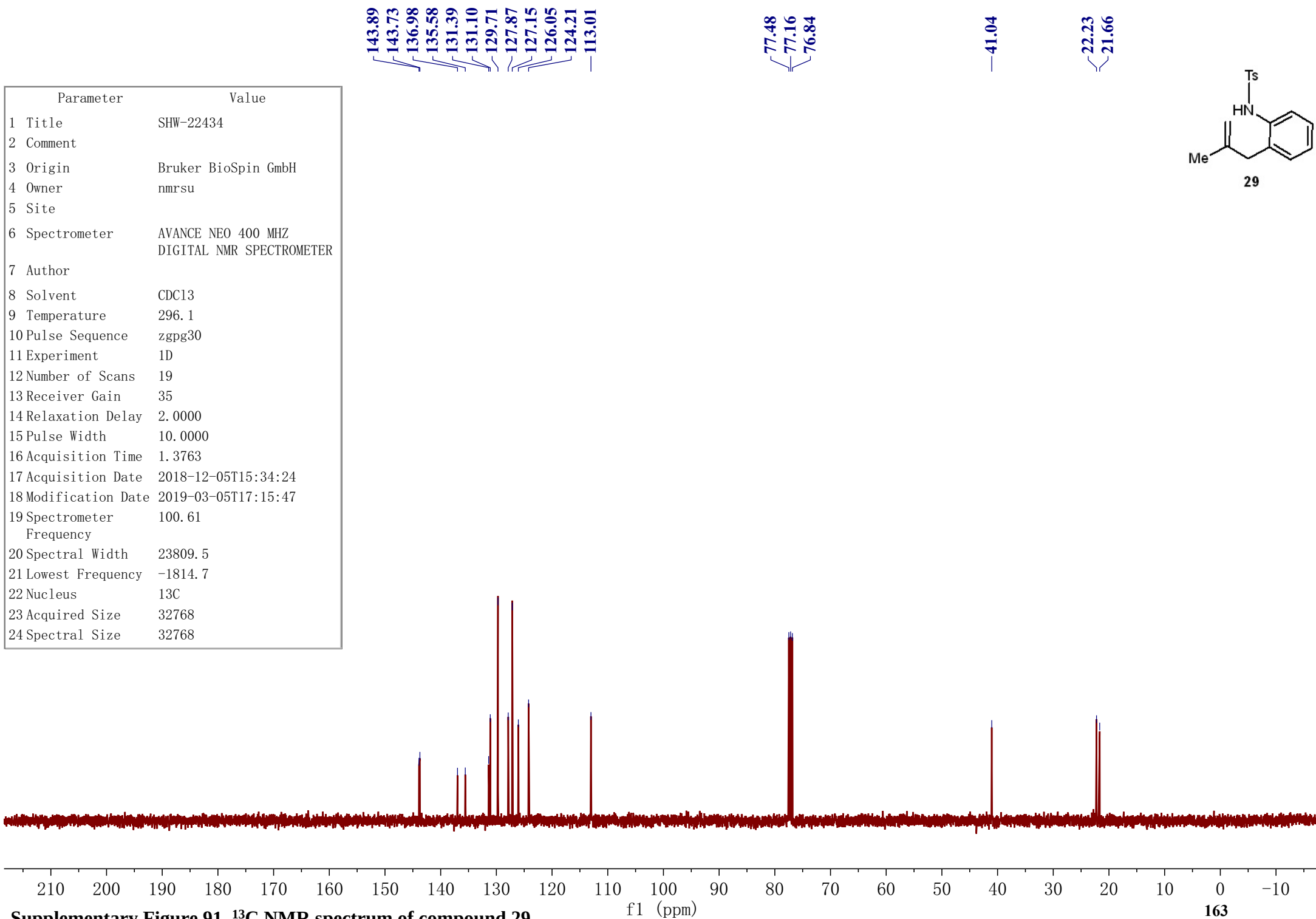
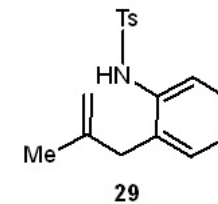
Parameter	Value
1 Title	XJ2-16
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	298.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	105
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2018-11-09T12:51:11
18 Modification Date	2018-11-09T12:55:20
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2747.0
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

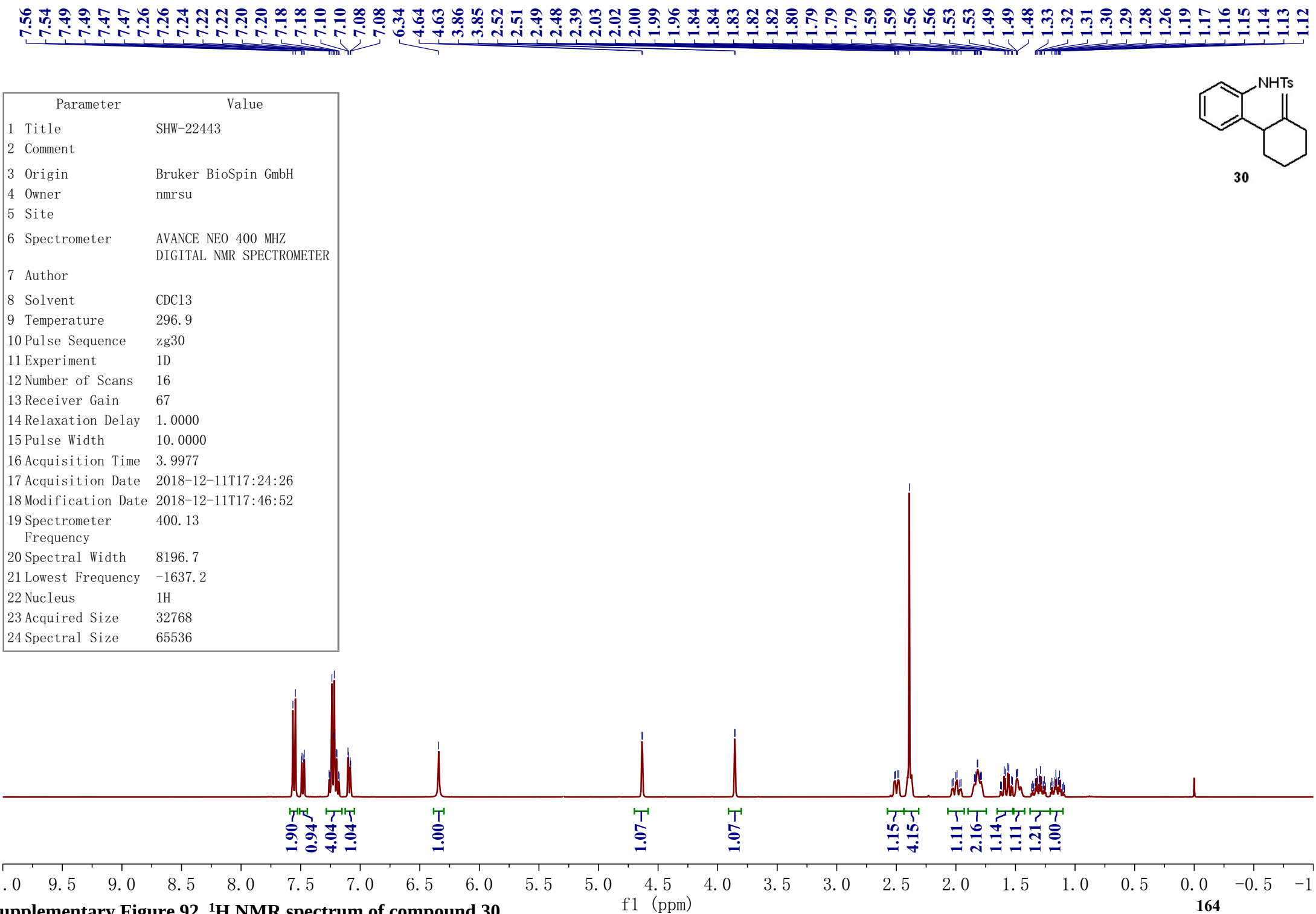


Supplementary Figure 89. ¹³C NMR spectrum of compound 28

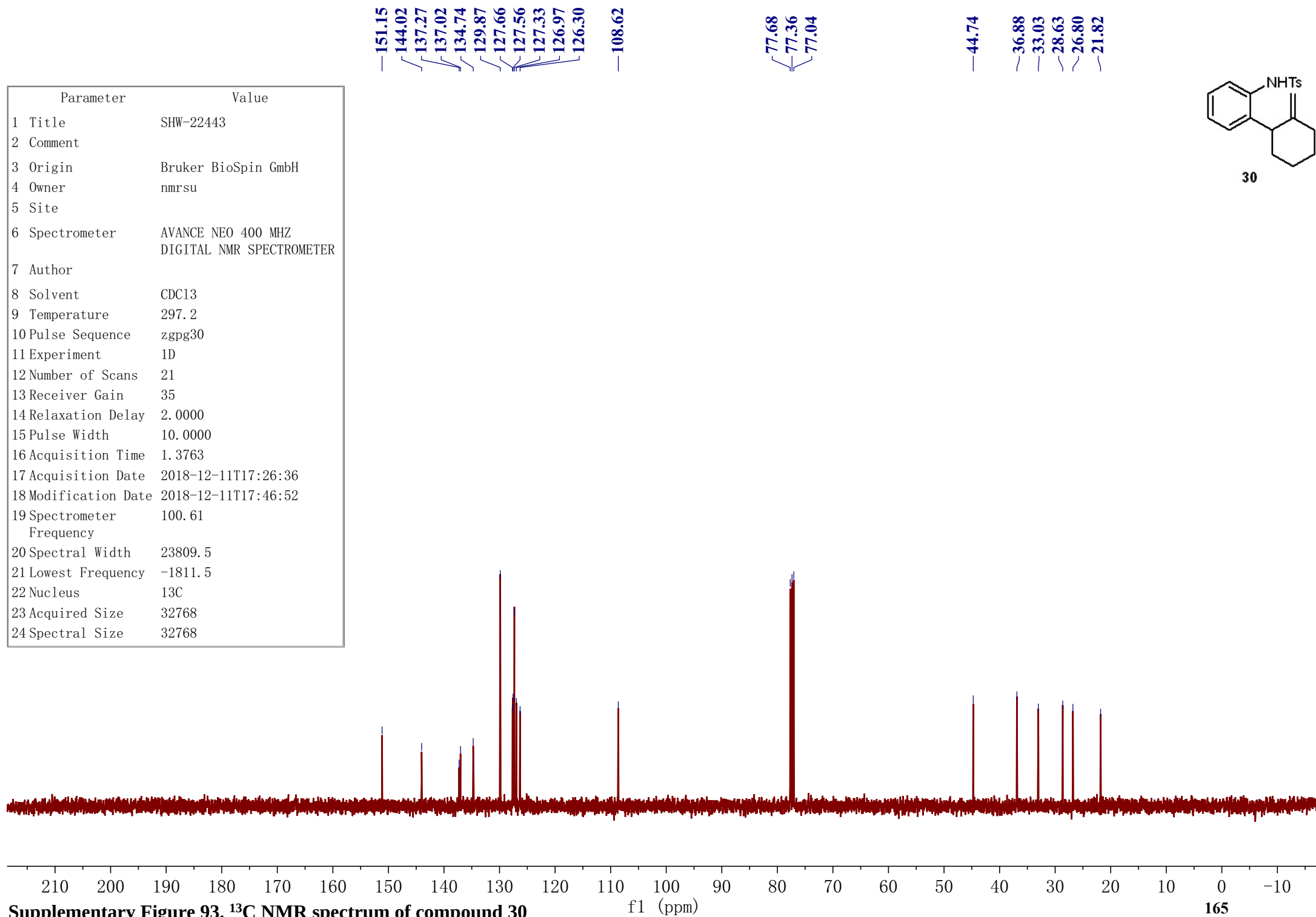
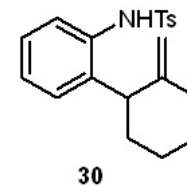


Parameter	Value
1 Title	SHW-22434
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	19
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-05T15:34:24
18 Modification Date	2019-03-05T17:15:47
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1814.7
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



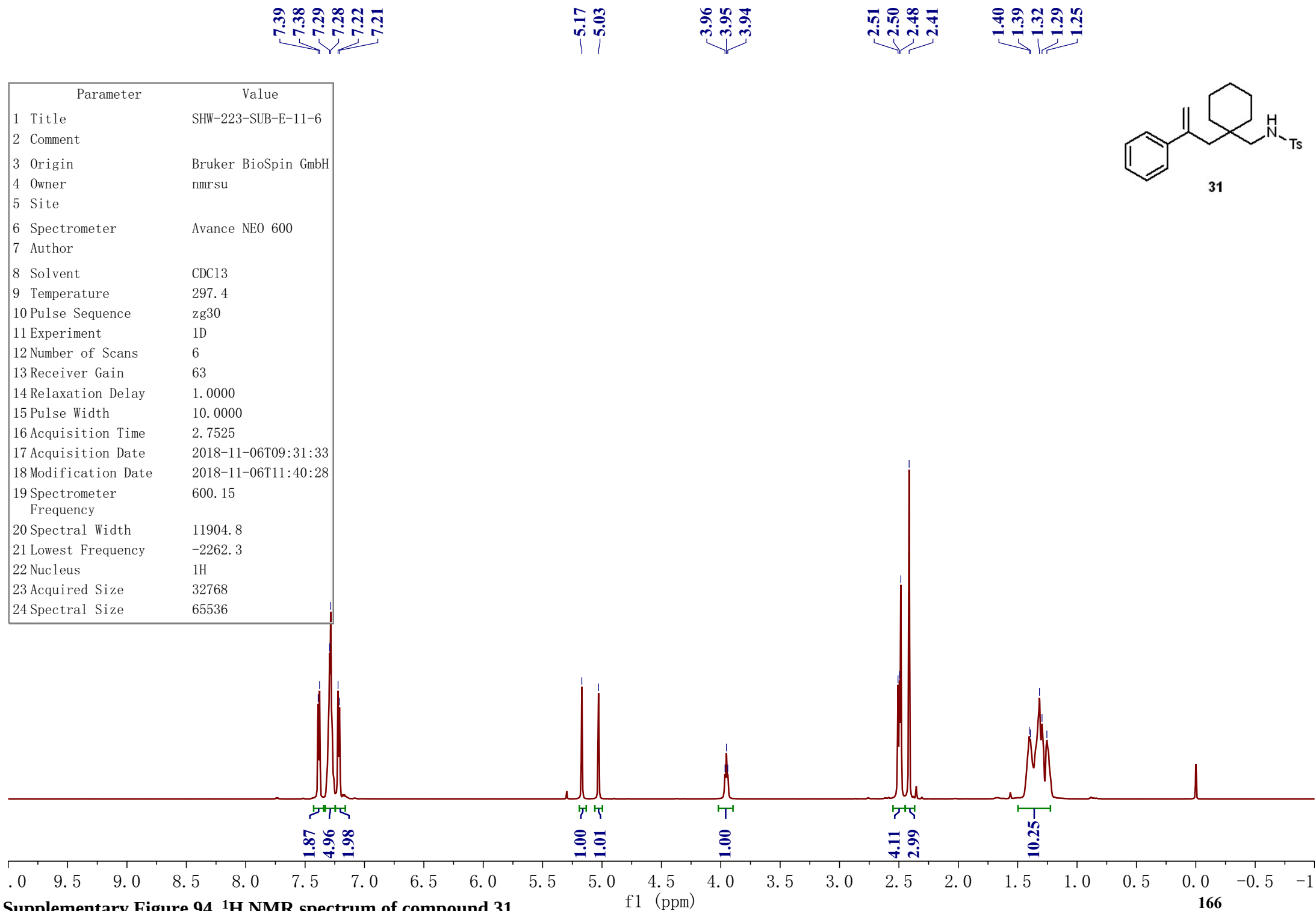
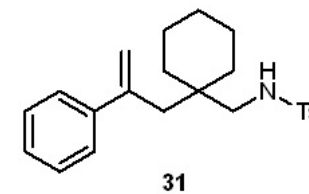


Parameter	Value
1 Title	SHW-22443
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	297.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	21
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-11T17:26:36
18 Modification Date	2018-12-11T17:46:52
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1811.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



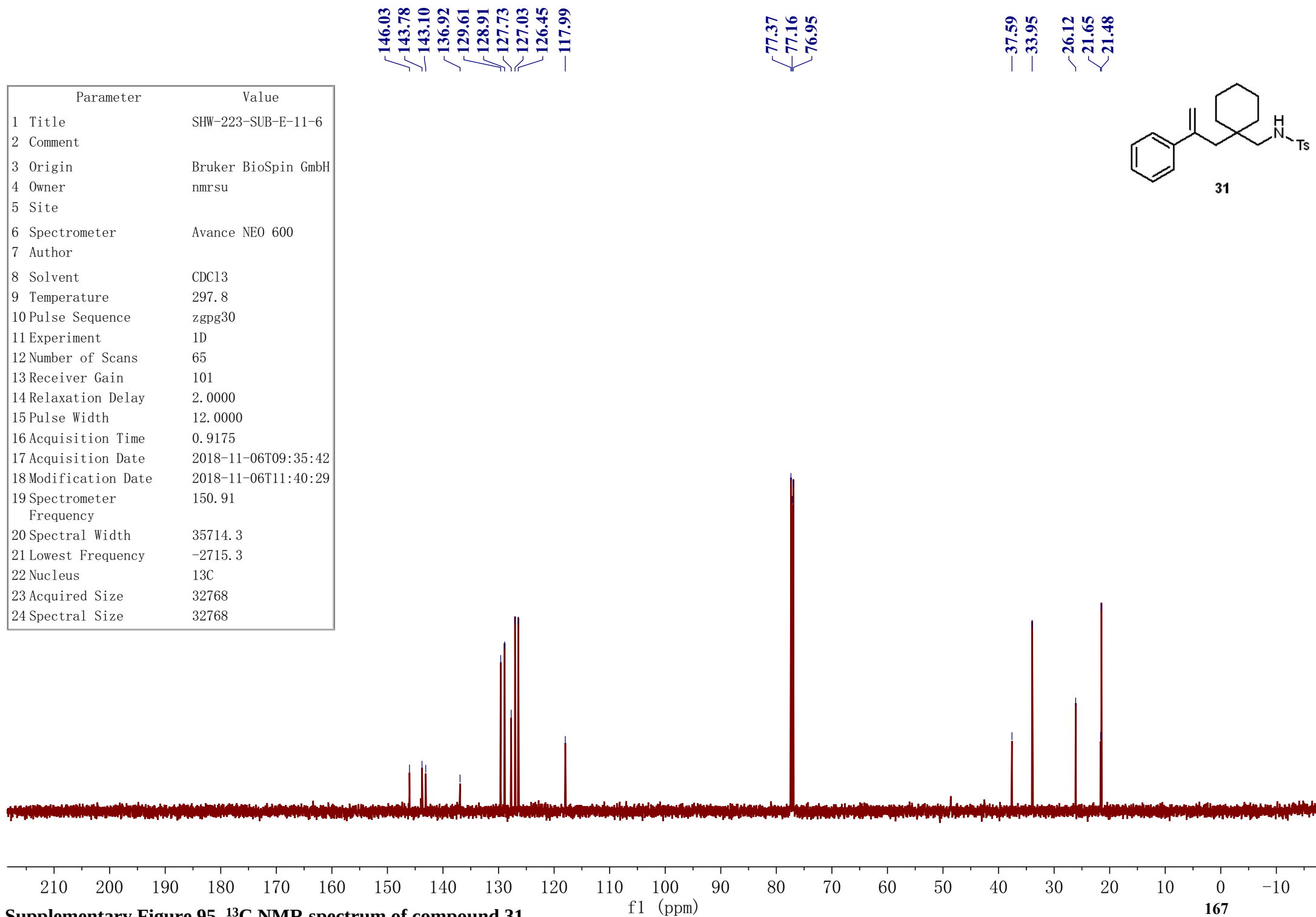
Supplementary Figure 93. ¹³C NMR spectrum of compound 30

Parameter	Value
1 Title	SHW-223-SUB-E-11-6
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	297.4
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	6
13 Receiver Gain	63
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2018-11-06T09:31:33
18 Modification Date	2018-11-06T11:40:28
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2262.3
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

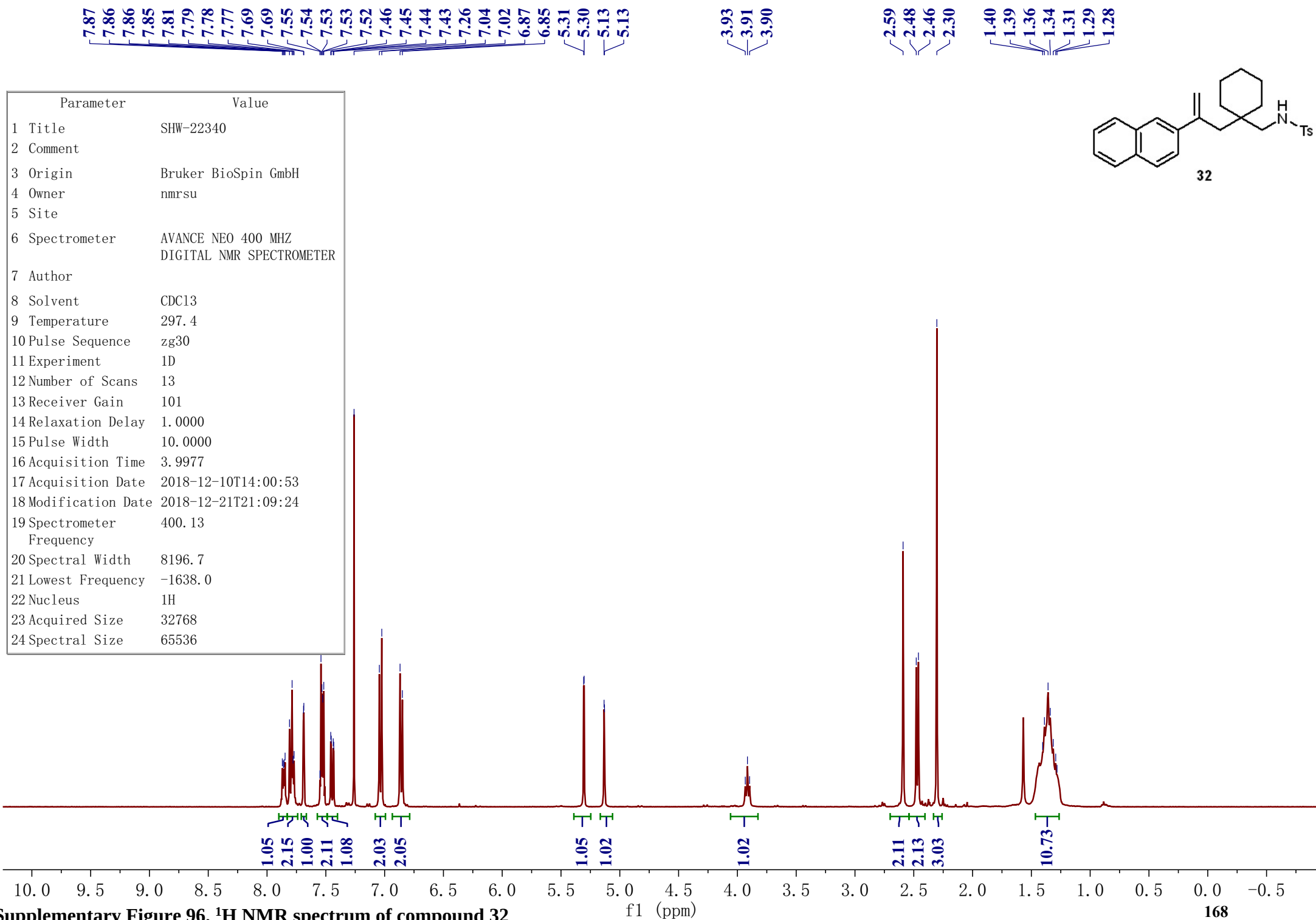


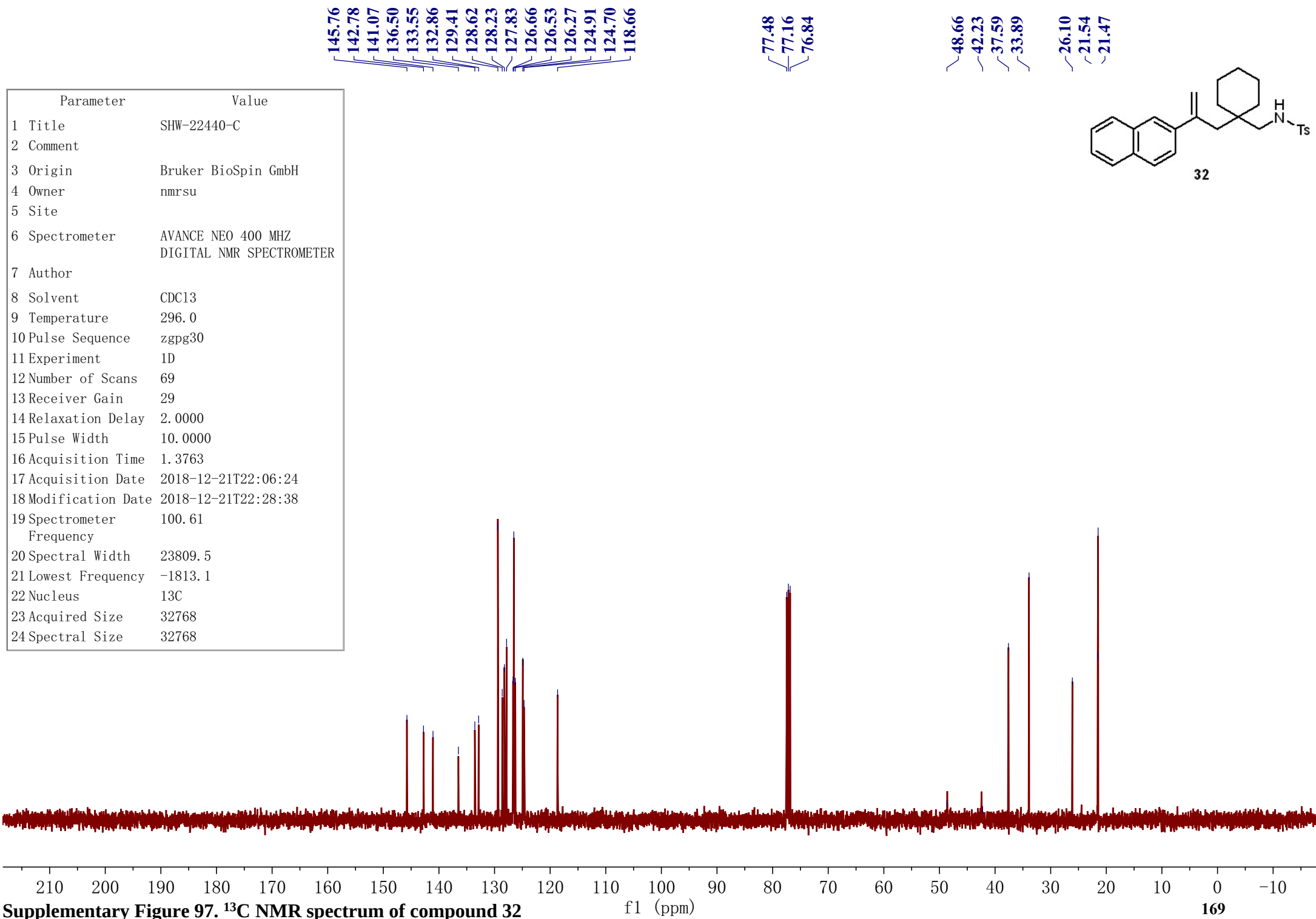
Supplementary Figure 94. ¹H NMR spectrum of compound 31

Parameter	Value
1 Title	SHW-223-SUB-E-11-6
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	297.8
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	65
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2018-11-06T09:35:42
18 Modification Date	2018-11-06T11:40:29
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2715.3
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

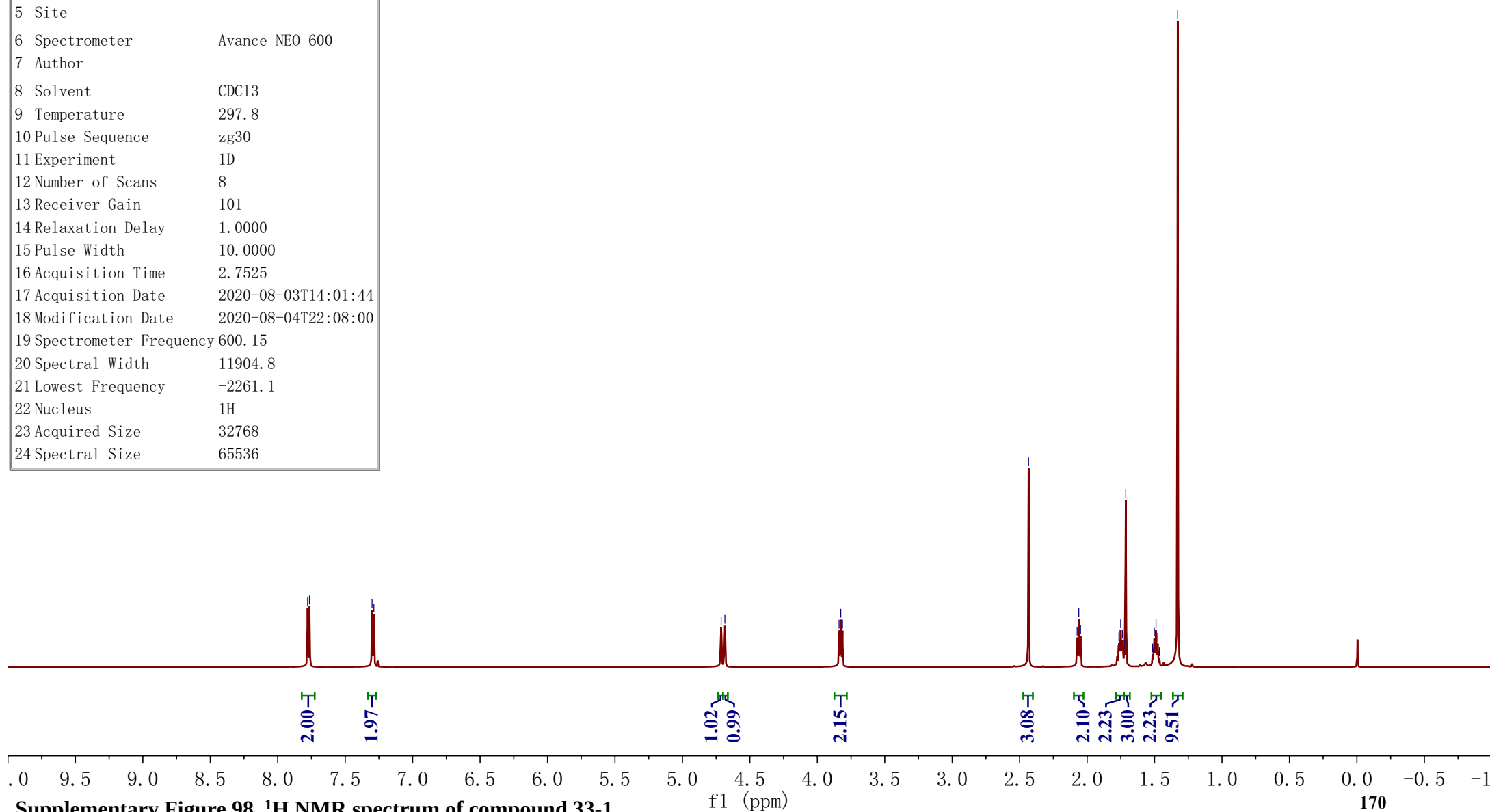
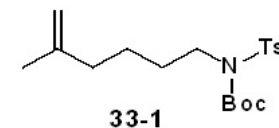


Supplementary Figure 95. ¹³C NMR spectrum of compound 31



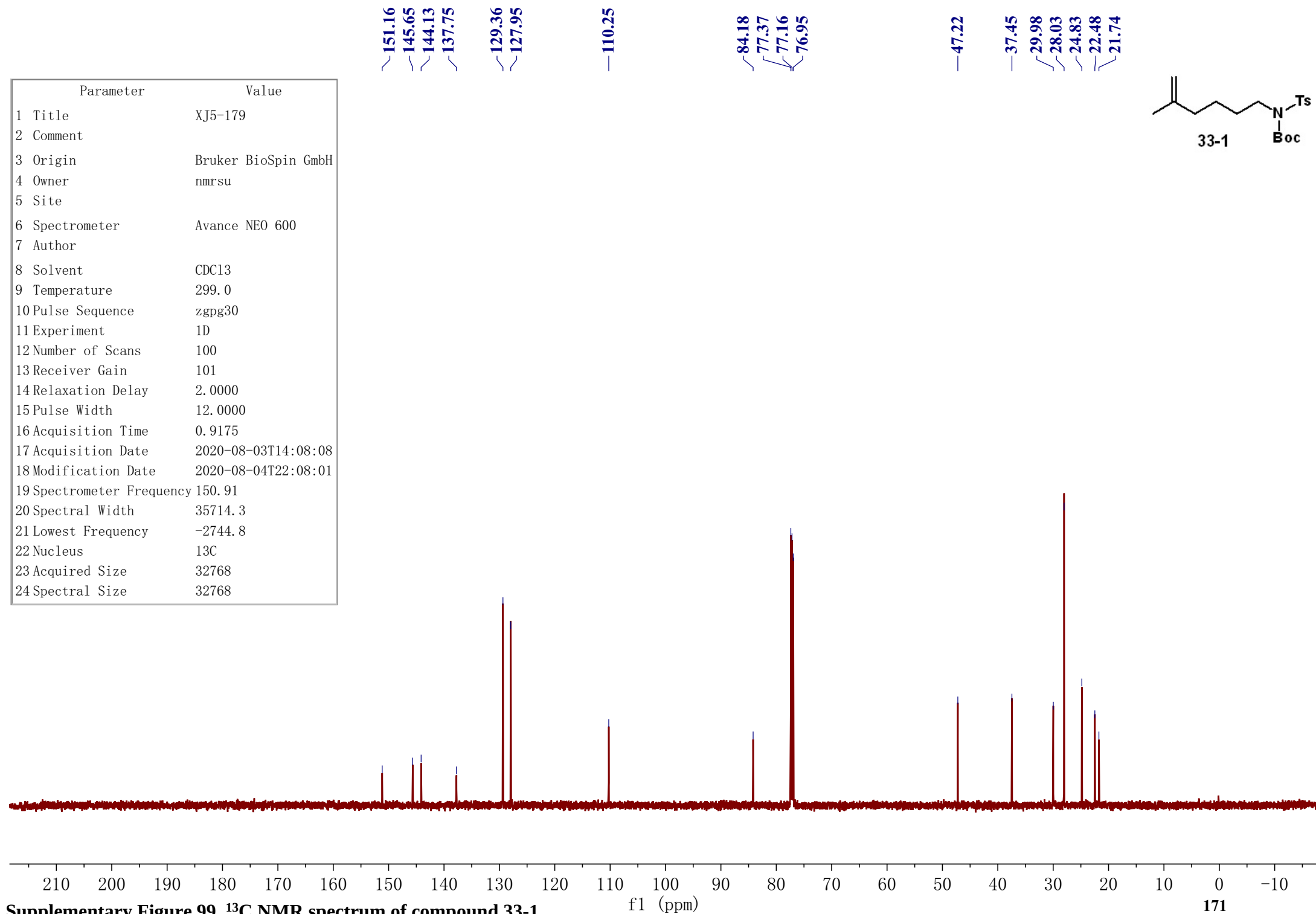
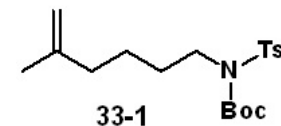


Parameter	Value
1 Title	XJ5-179
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	297.8
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2020-08-03T14:01:44
18 Modification Date	2020-08-04T22:08:00
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2261.1
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



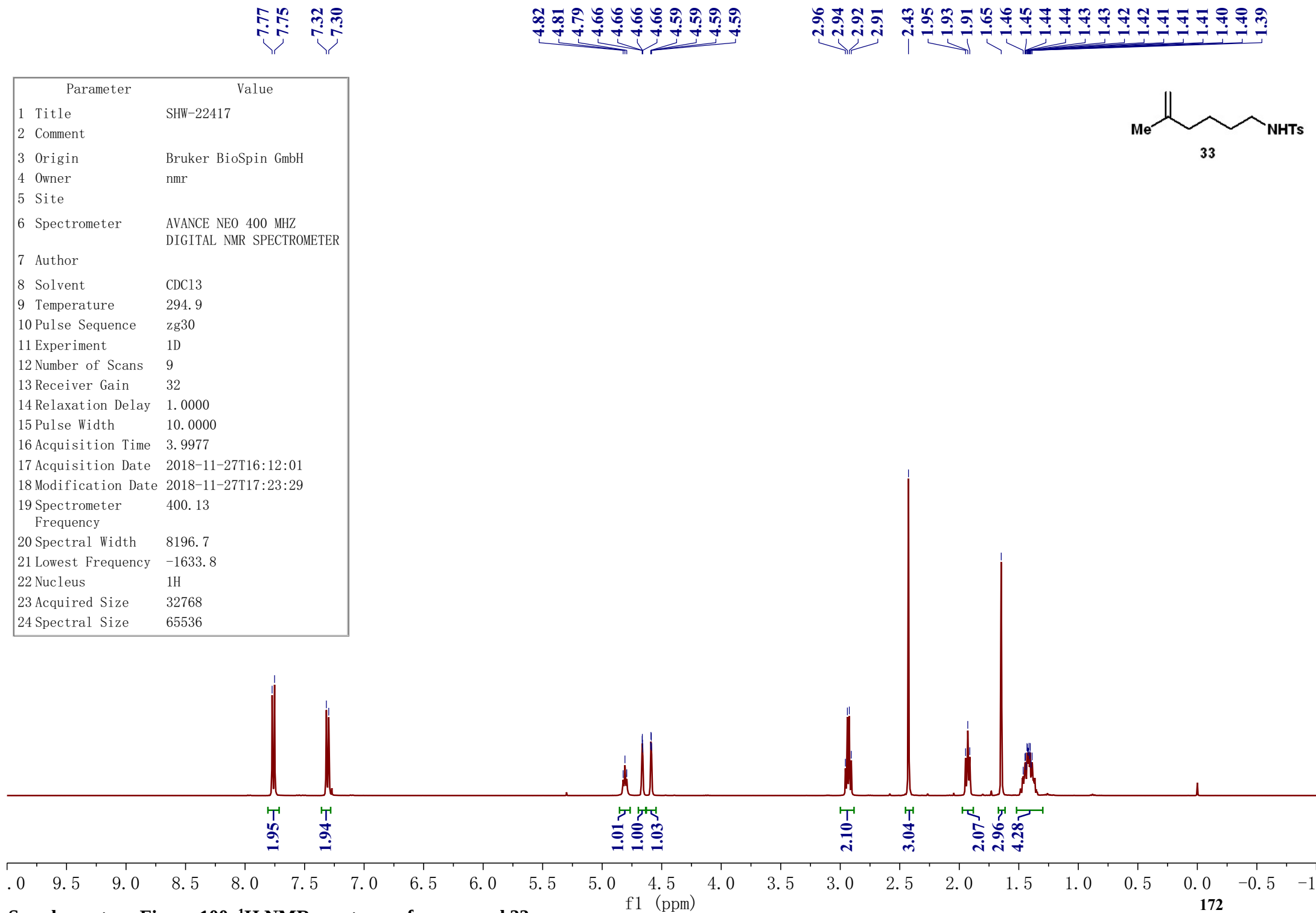
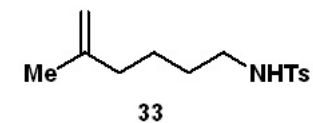
Supplementary Figure 98. ¹H NMR spectrum of compound 33-1

Parameter	Value
1 Title	XJ5-179
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	299.0
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	100
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2020-08-03T14:08:08
18 Modification Date	2020-08-04T22:08:01
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2744.8
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768



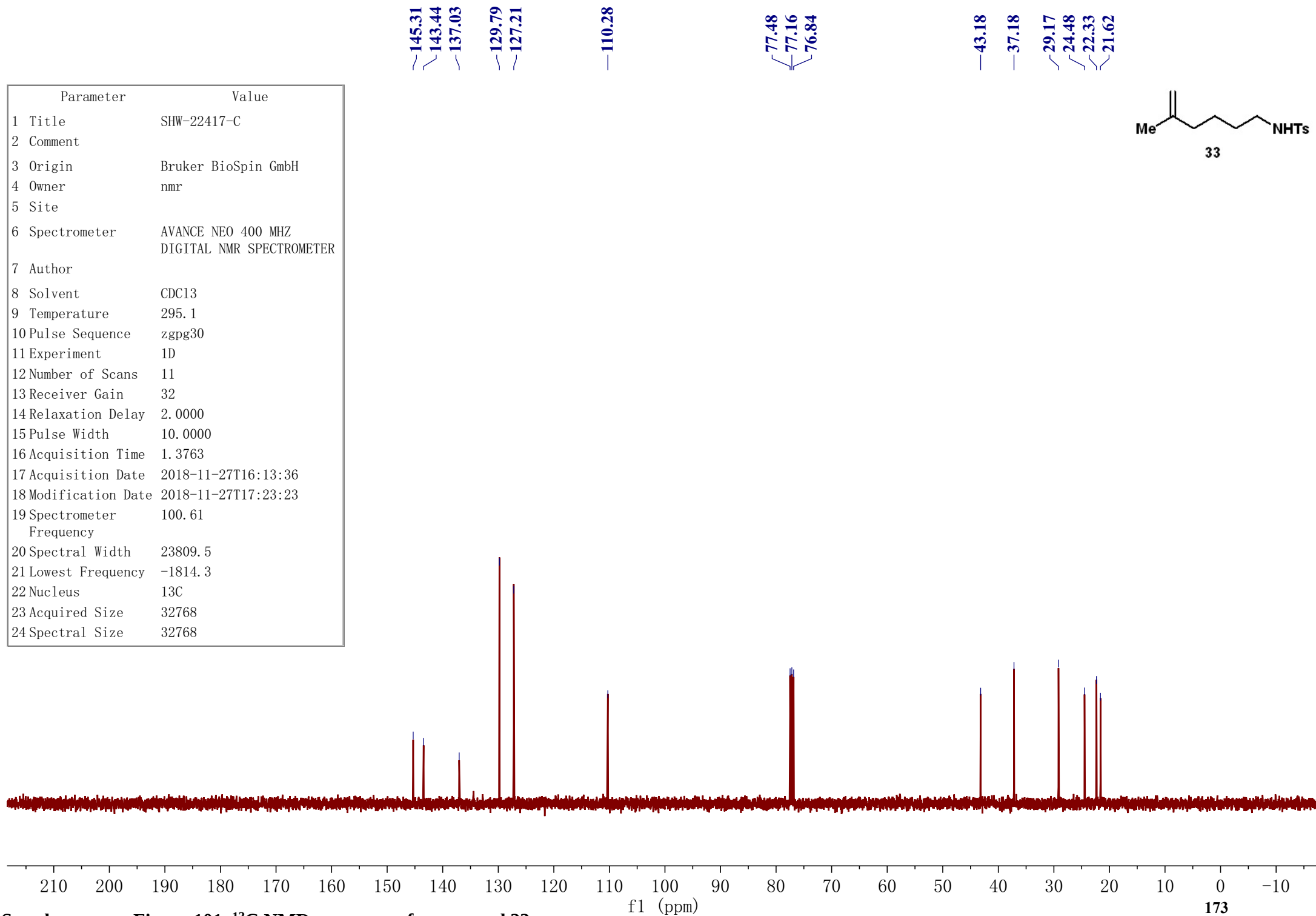
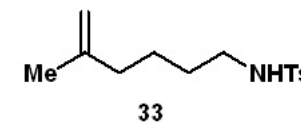
Supplementary Figure 99. ¹³C NMR spectrum of compound 33-1

Parameter	Value
1 Title	SHW-22417
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	294.9
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	9
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-11-27T16:12:01
18 Modification Date	2018-11-27T17:23:29
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1633.8
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



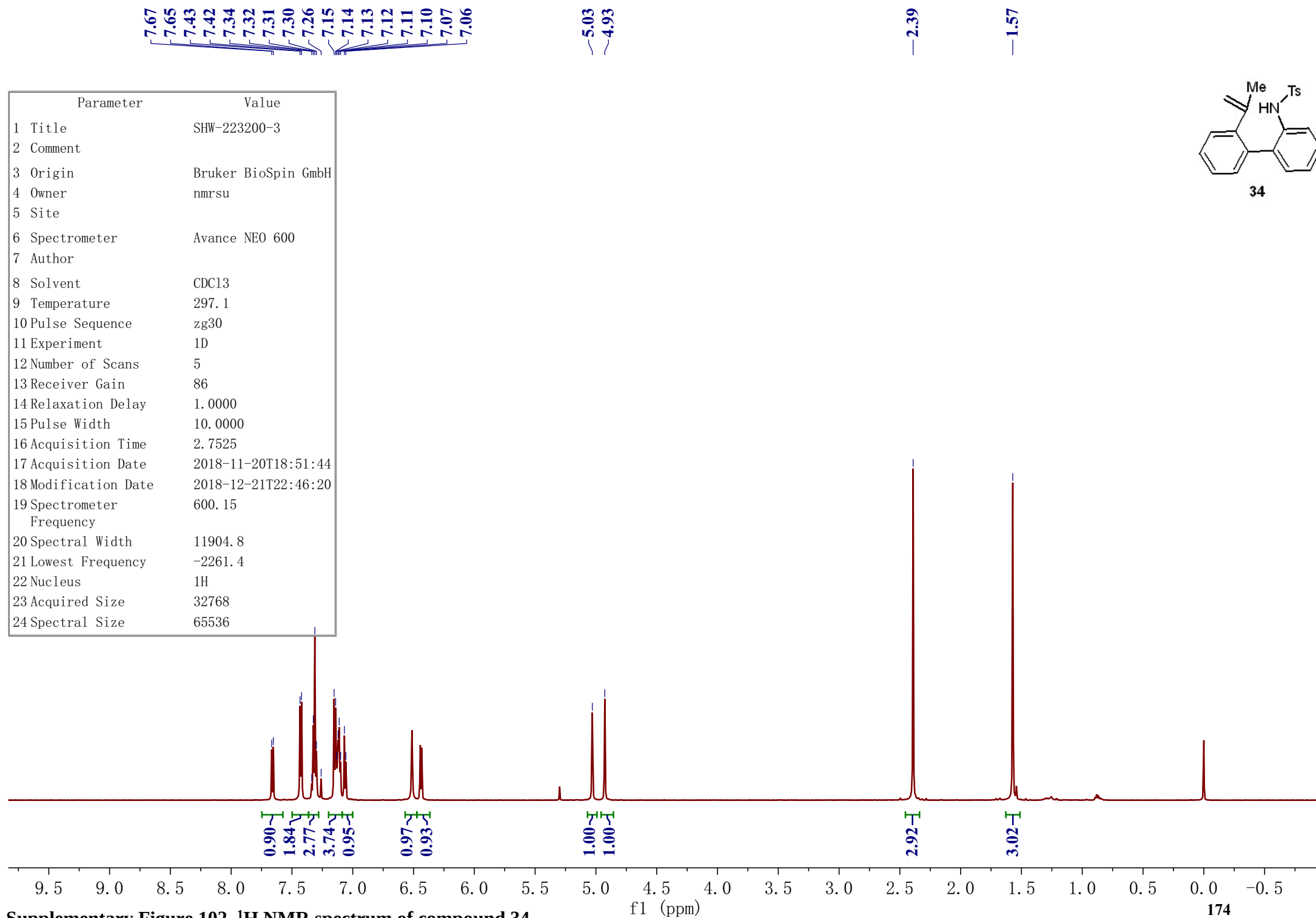
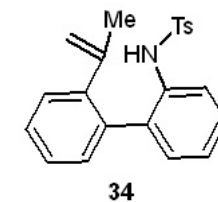
Supplementary Figure 100. ¹H NMR spectrum of compound 33

Parameter	Value
1 Title	SHW-22417-C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	295.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	11
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-11-27T16:13:36
18 Modification Date	2018-11-27T17:23:23
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1814.3
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



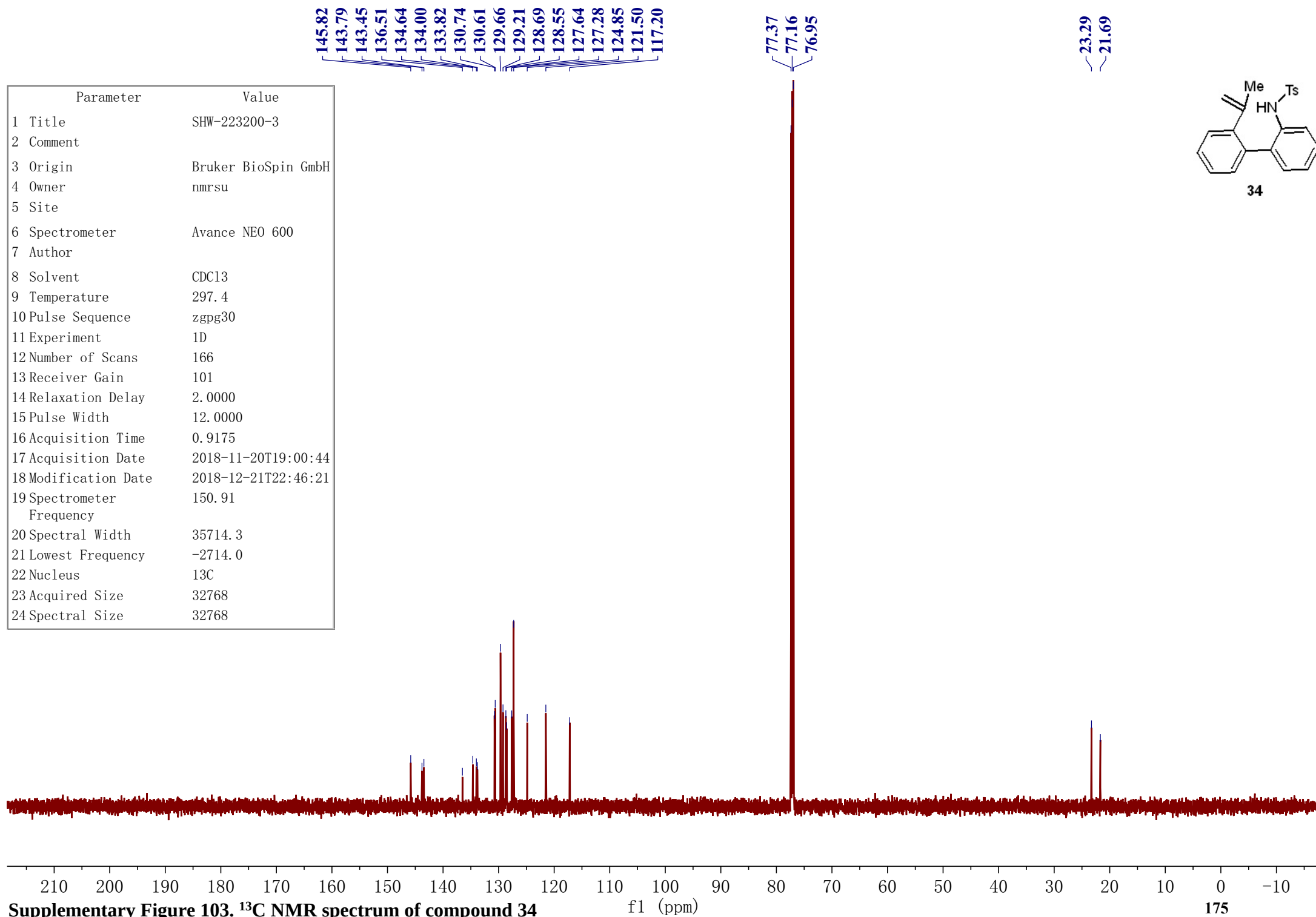
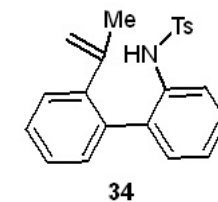
Supplementary Figure 101. ¹³C NMR spectrum of compound 33

Parameter	Value
1 Title	SHW-223200-3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	297.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	5
13 Receiver Gain	86
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2018-11-20T18:51:44
18 Modification Date	2018-12-21T22:46:20
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2261.4
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

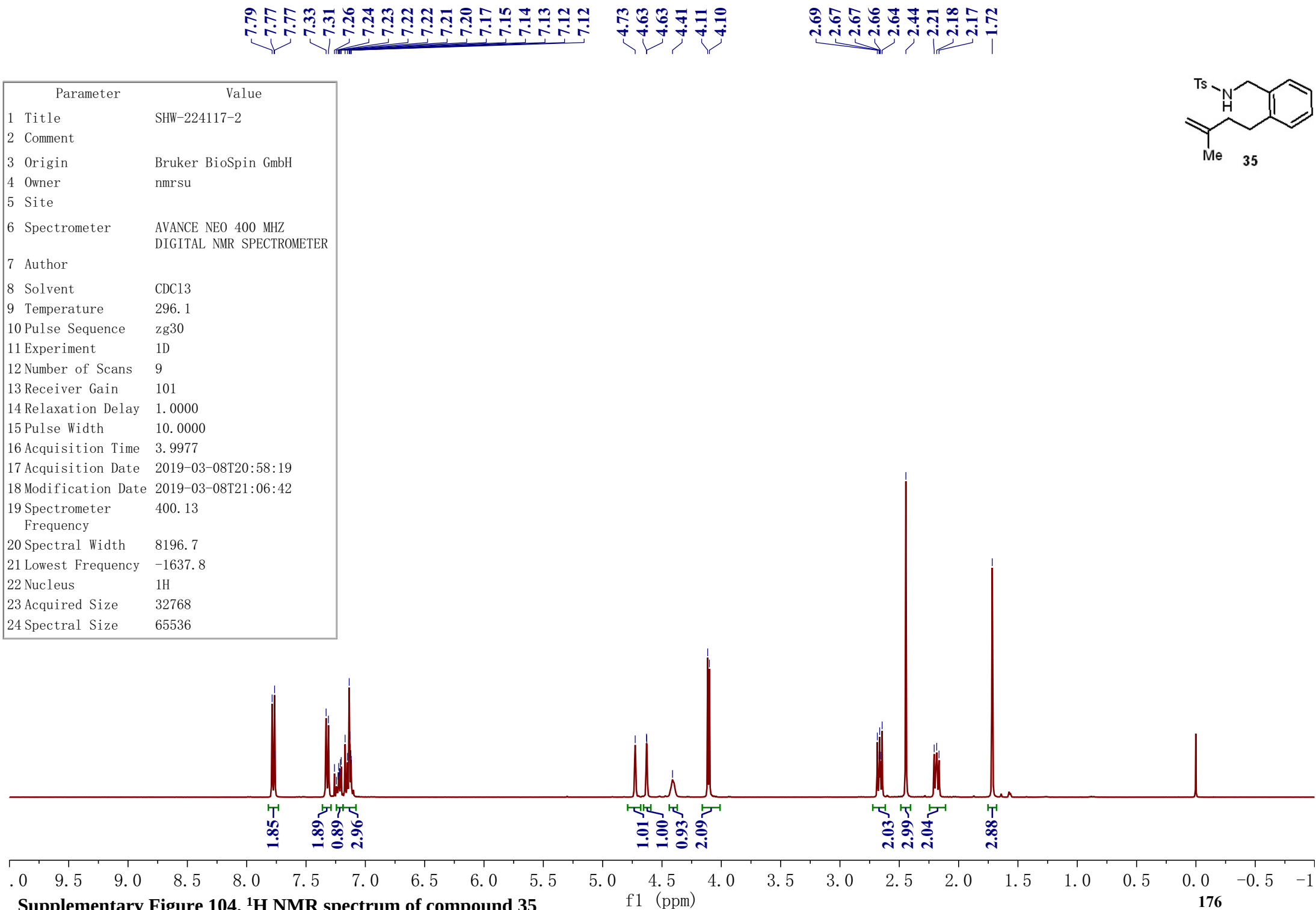


Supplementary Figure 102. ¹H NMR spectrum of compound 34

Parameter	Value
1 Title	SHW-223200-3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	297.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	166
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2018-11-20T19:00:44
18 Modification Date	2018-12-21T22:46:21
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2714.0
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

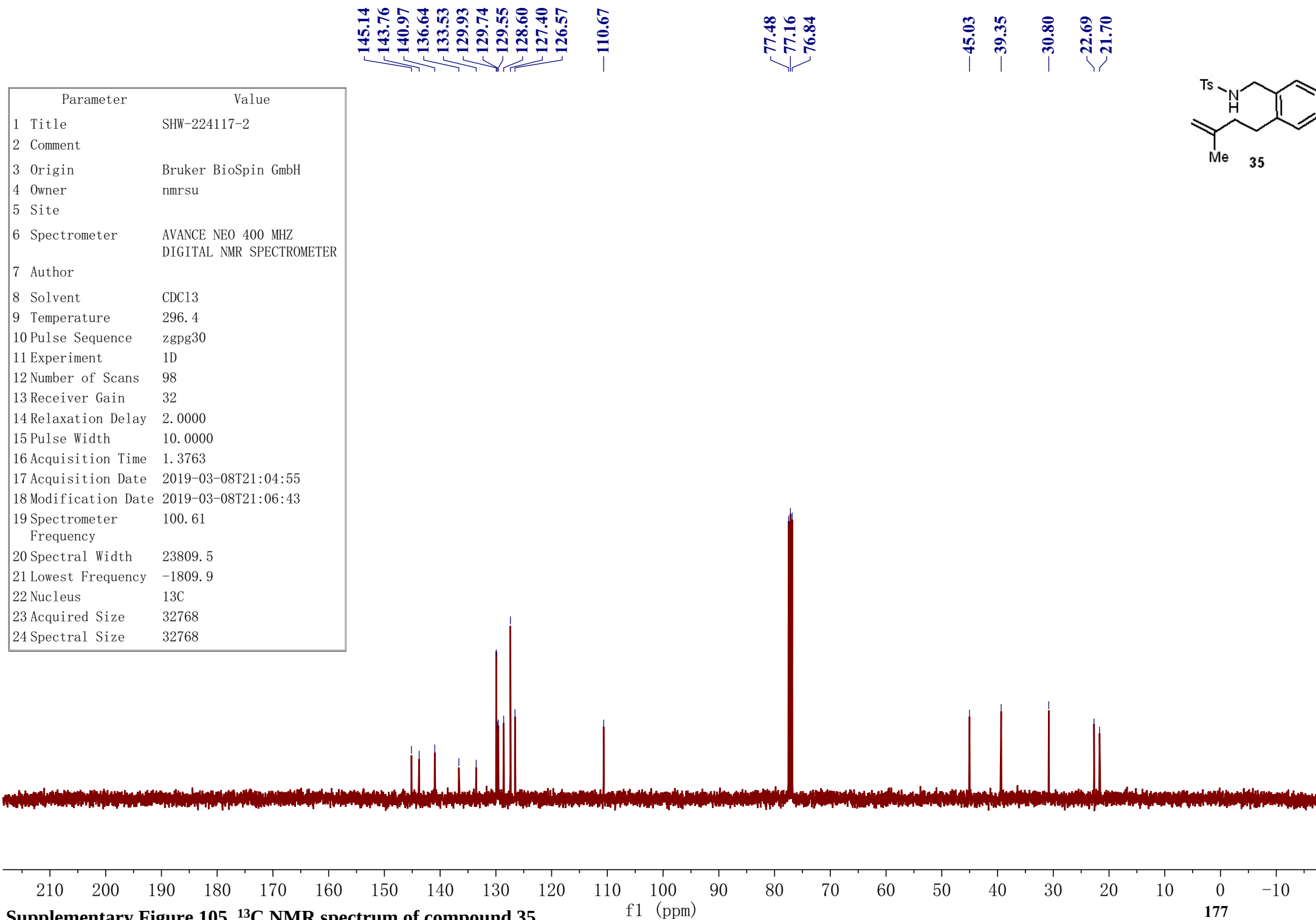


Parameter	Value
1 Title	SHW-224117-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	9
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-03-08T20:58:19
18 Modification Date	2019-03-08T21:06:42
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.8
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

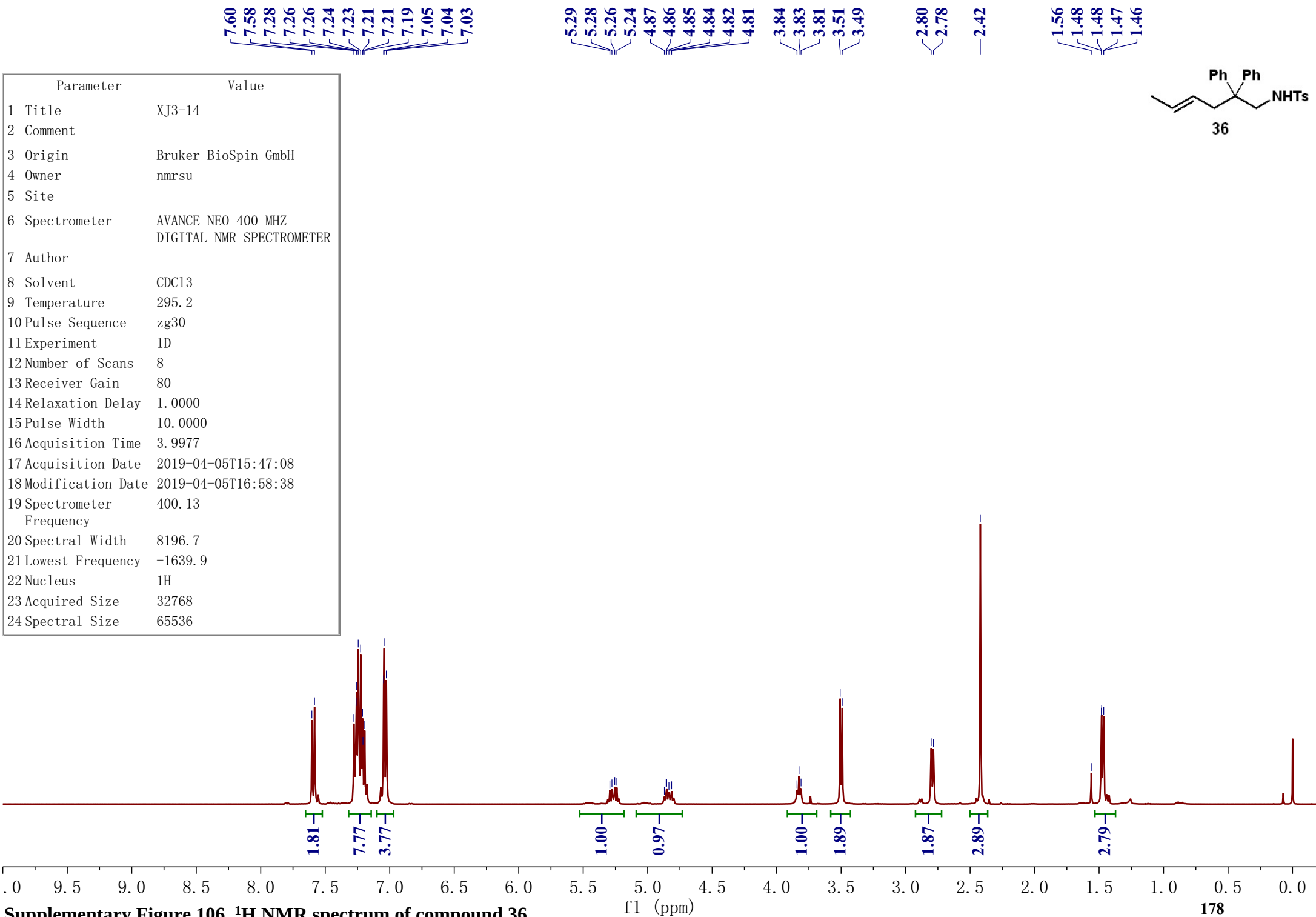


Supplementary Figure 104. ¹H NMR spectrum of compound 35

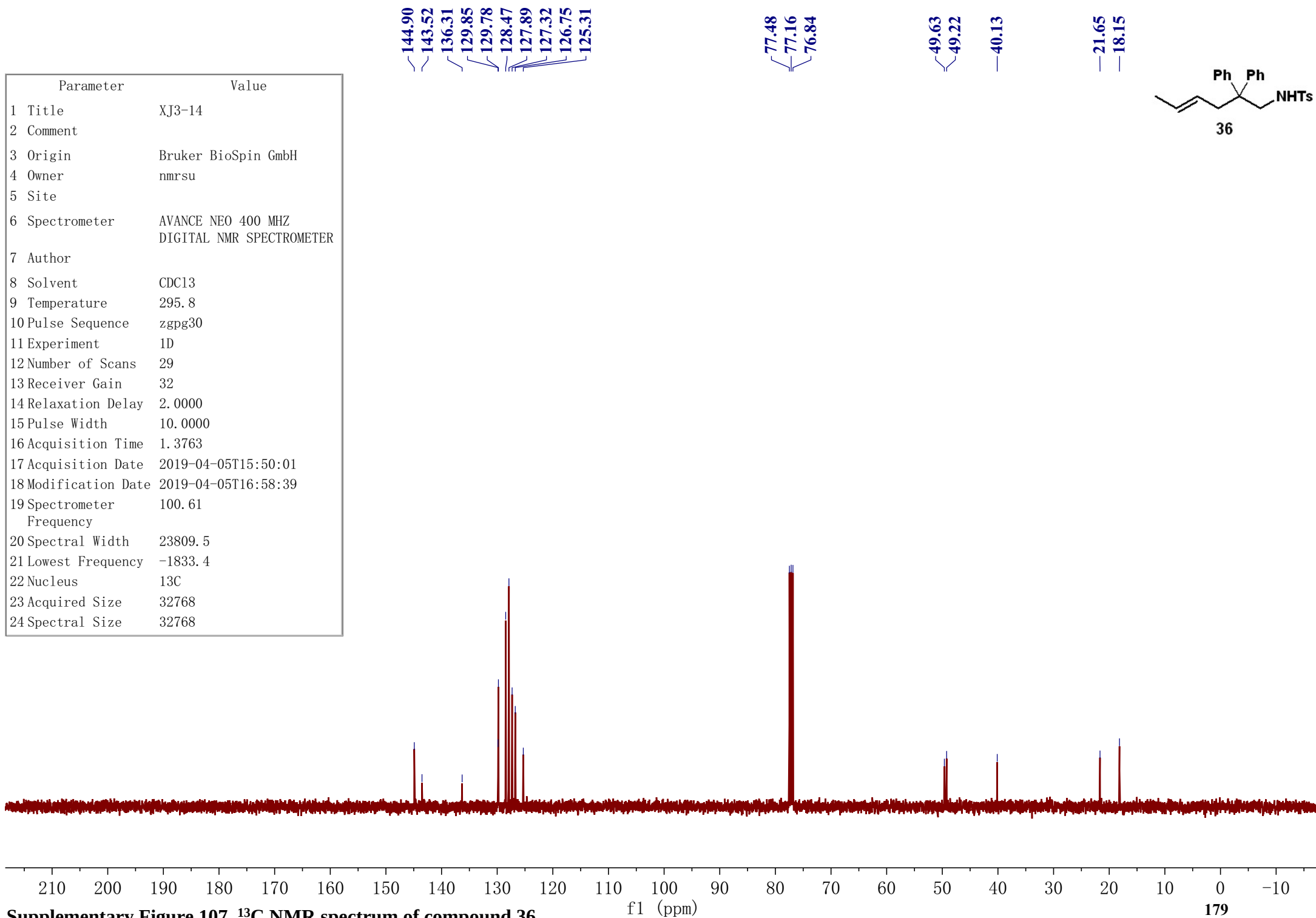
Parameter	Value
1 Title	SHW-224117-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	98
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-03-08T21:04:55
18 Modification Date	2019-03-08T21:06:43
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1809.9
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



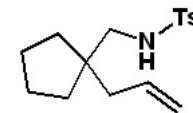
Supplementary Figure 105. ¹³C NMR spectrum of compound 35



Parameter	Value
1 Title	XJ3-14
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	295.8
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	29
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-04-05T15:50:01
18 Modification Date	2019-04-05T16:58:39
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1833.4
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 107. ¹³C NMR spectrum of compound 36



37

7.74
7.73

7.30
7.29

5.72
5.71
5.71
5.70
5.70
5.68
5.68
5.67
5.67
5.65
5.01
4.99
4.99
4.99
4.98
4.77
4.76
4.75

2.74
2.73

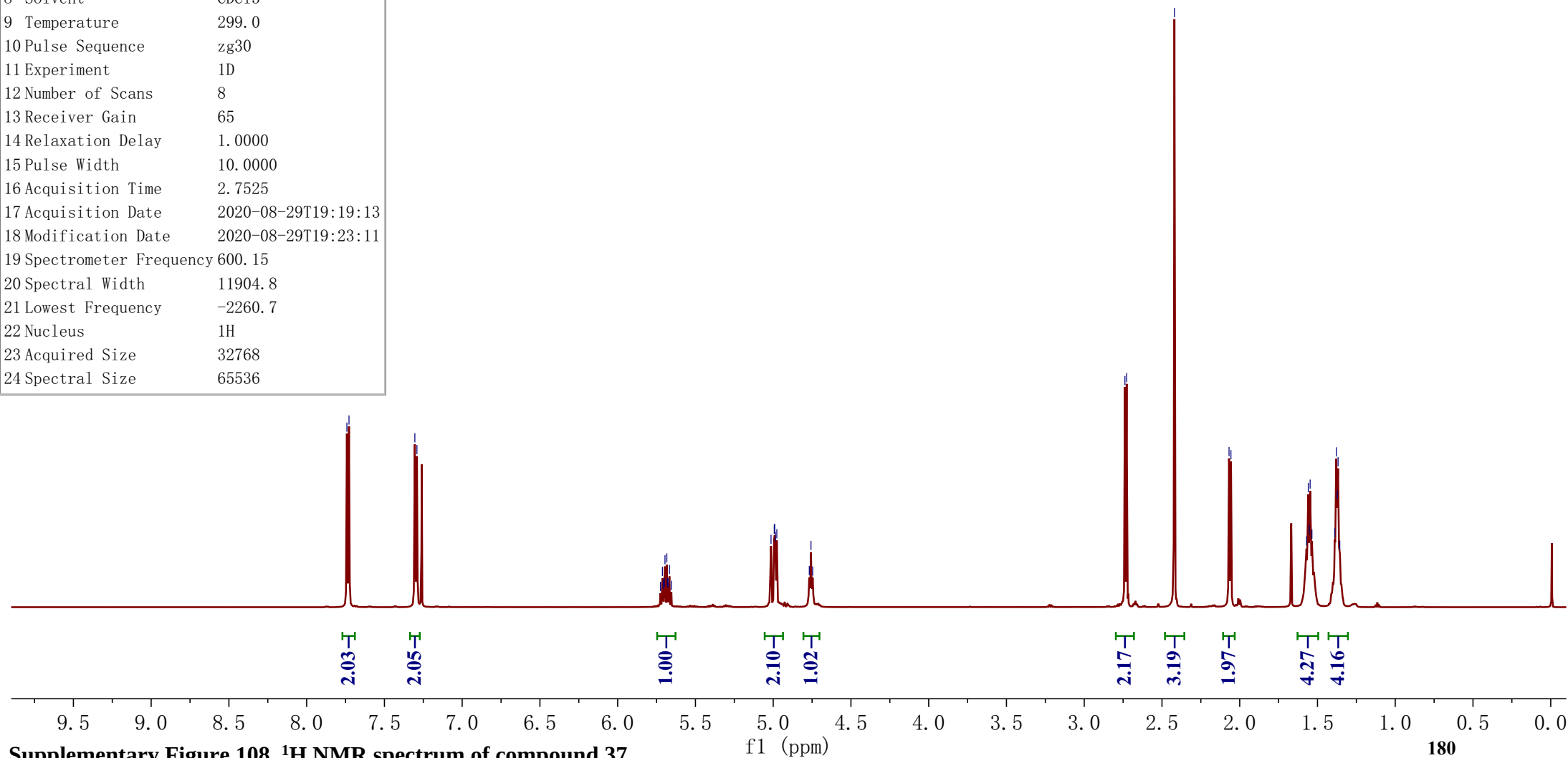
2.42

2.07
2.06

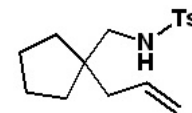
1.57
1.56
1.55
1.55

1.54
1.39
1.38
1.37
1.37
1.36

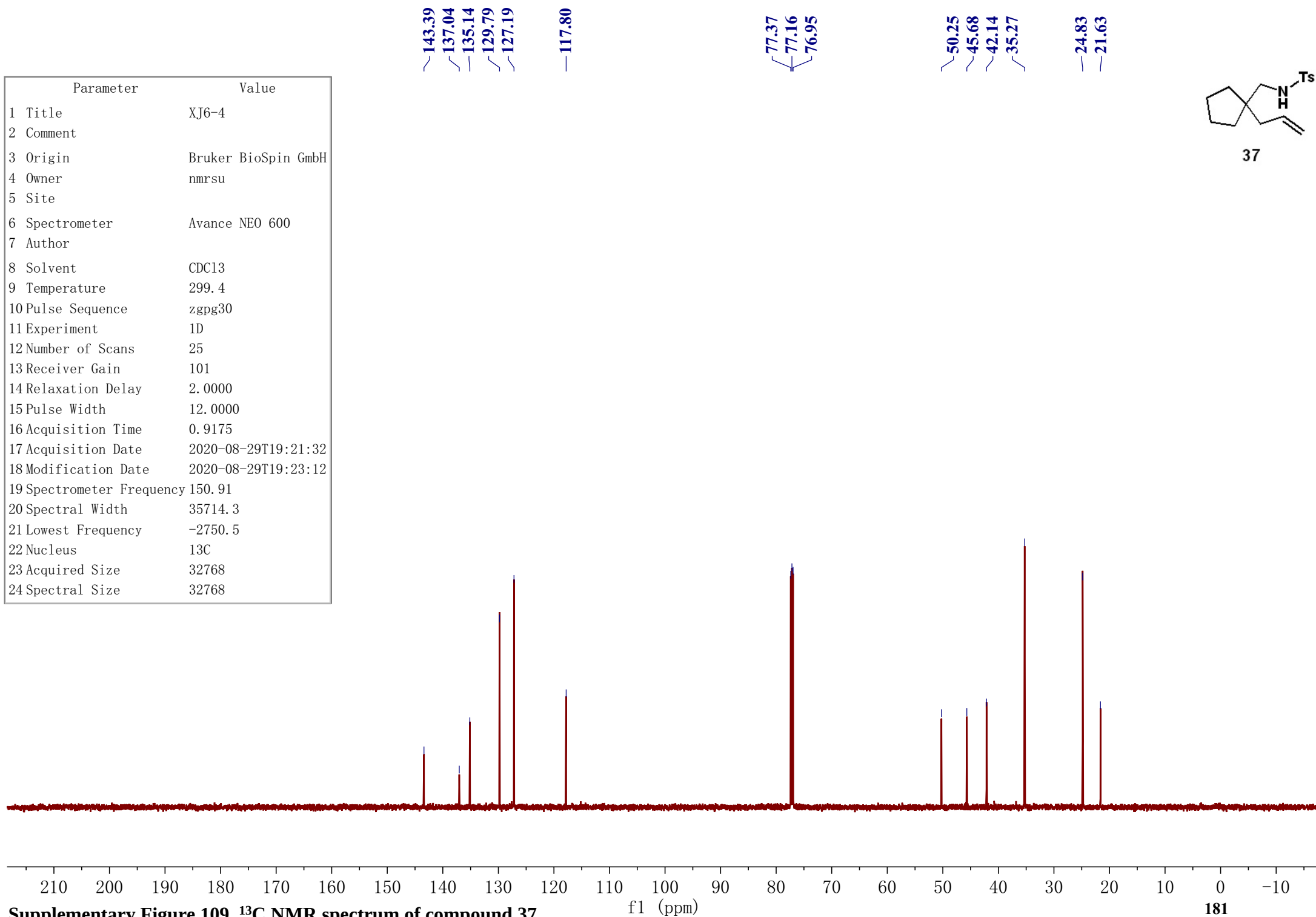
Parameter	Value
1 Title	XJ6-4
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	299.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	65
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2020-08-29T19:19:13
18 Modification Date	2020-08-29T19:23:11
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2260.7
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Parameter	Value
1 Title	XJ6-4
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	299.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	25
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2020-08-29T19:21:32
18 Modification Date	2020-08-29T19:23:12
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2750.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

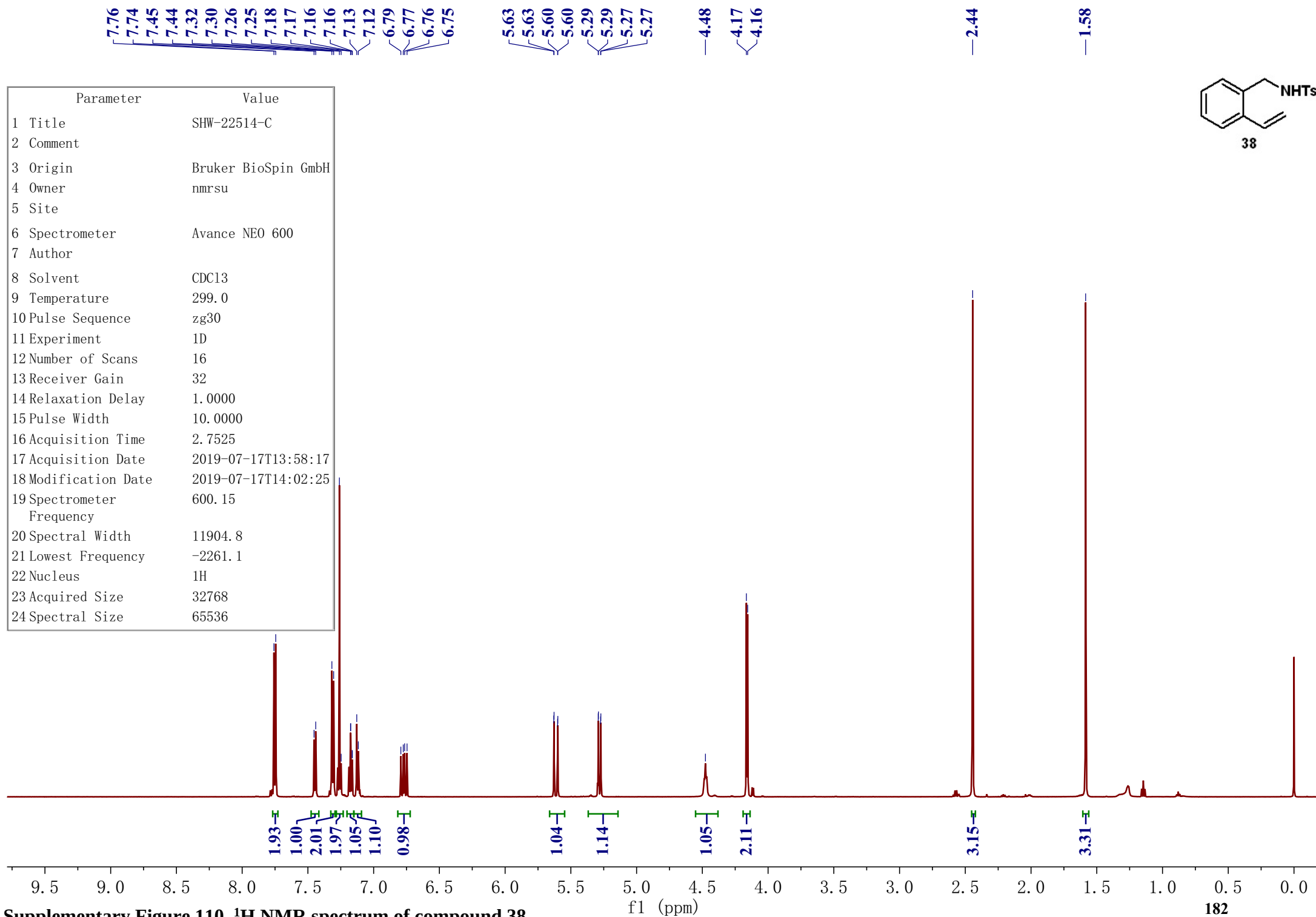
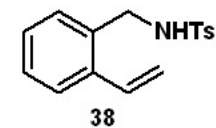


37

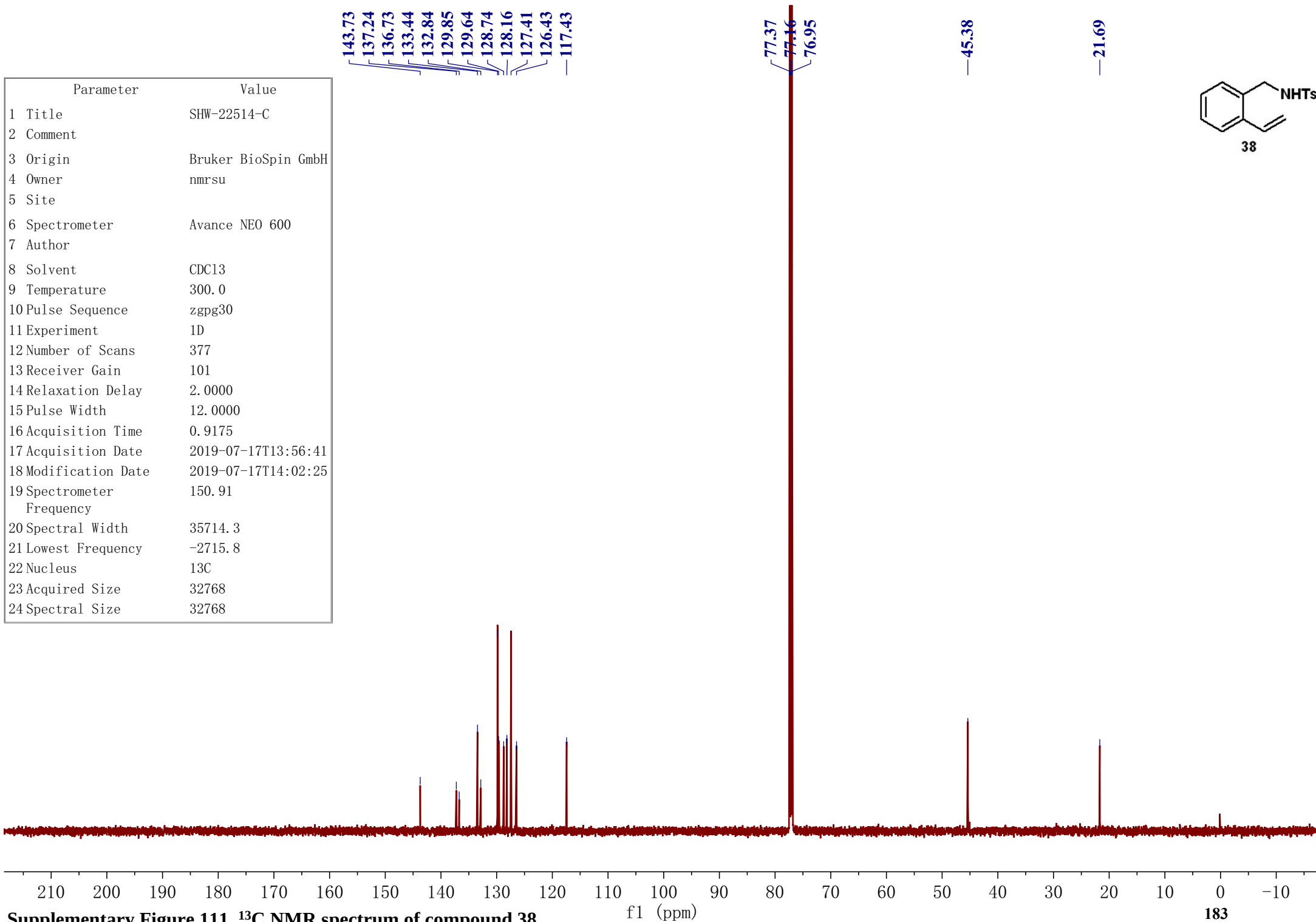
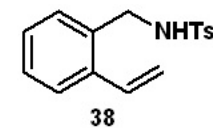


Supplementary Figure 109. ¹³C NMR spectrum of compound 37

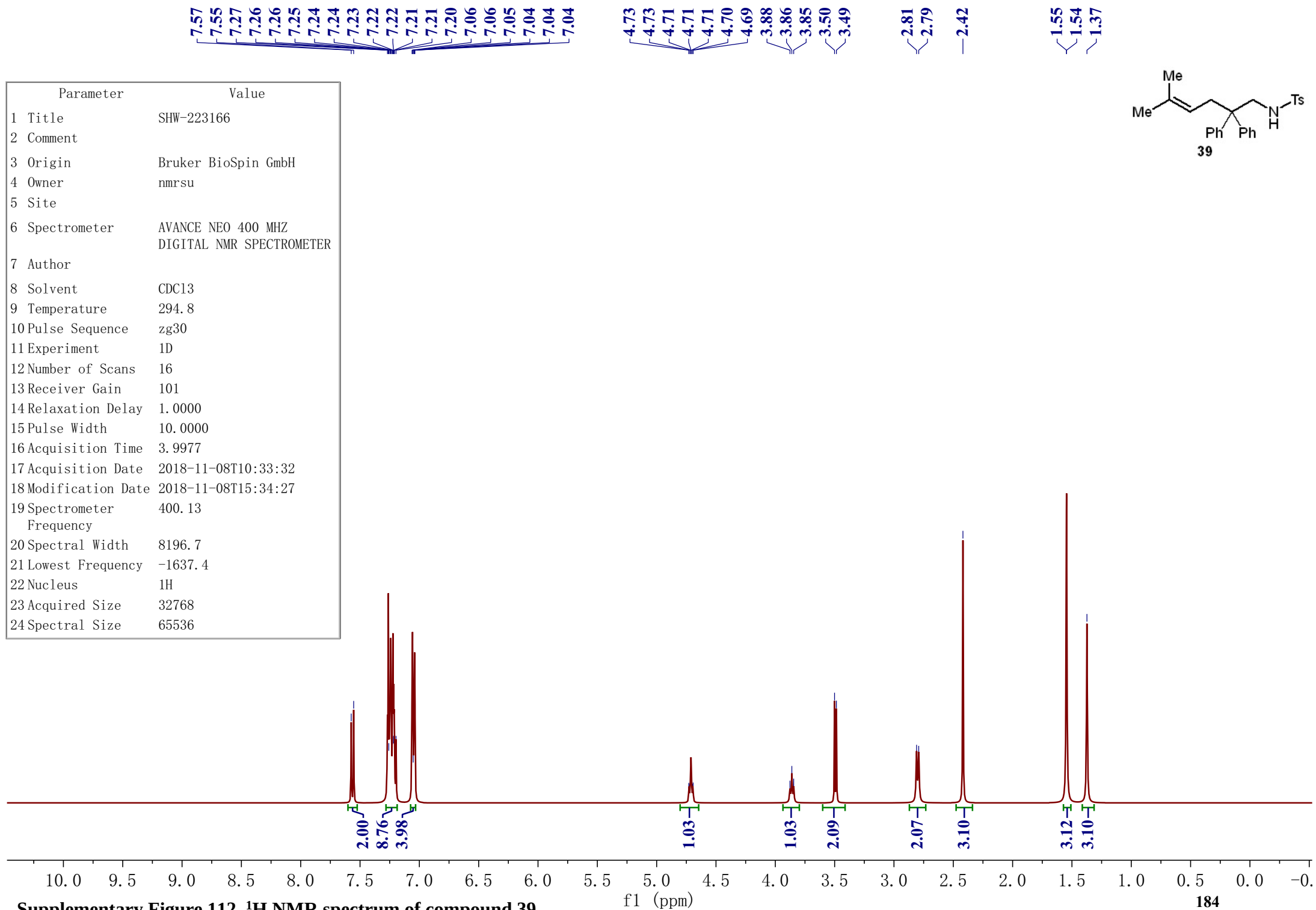
Parameter	Value
1 Title	SHW-22514-C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	299.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2019-07-17T13:58:17
18 Modification Date	2019-07-17T14:02:25
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2261.1
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Parameter	Value
1 Title	SHW-22514-C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	300.0
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	377
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-07-17T13:56:41
18 Modification Date	2019-07-17T14:02:25
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2715.8
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Parameter	Value
1 Title	SHW-223166
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	294.8
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-11-08T10:33:32
18 Modification Date	2018-11-08T15:34:27
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.4
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Supplementary Figure 112. ¹H NMR spectrum of compound 39

Parameter	Value
1 Title	SHW-223166-C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	71
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-21T22:14:19
18 Modification Date	2018-12-21T22:26:48
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1843.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

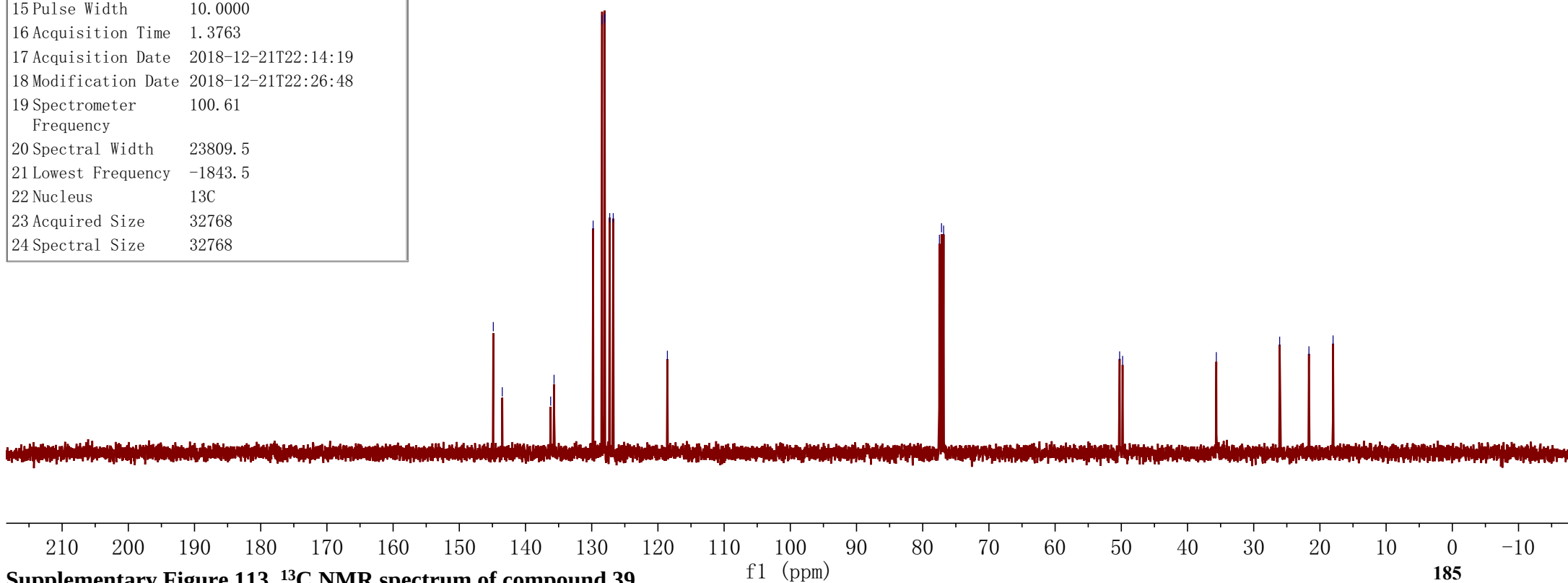
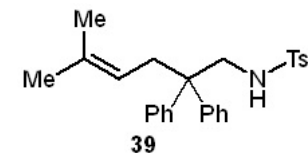
144.87
143.51
136.20
135.69
129.79
128.44
128.04
127.28
126.75
118.57

77.48
77.16
76.84

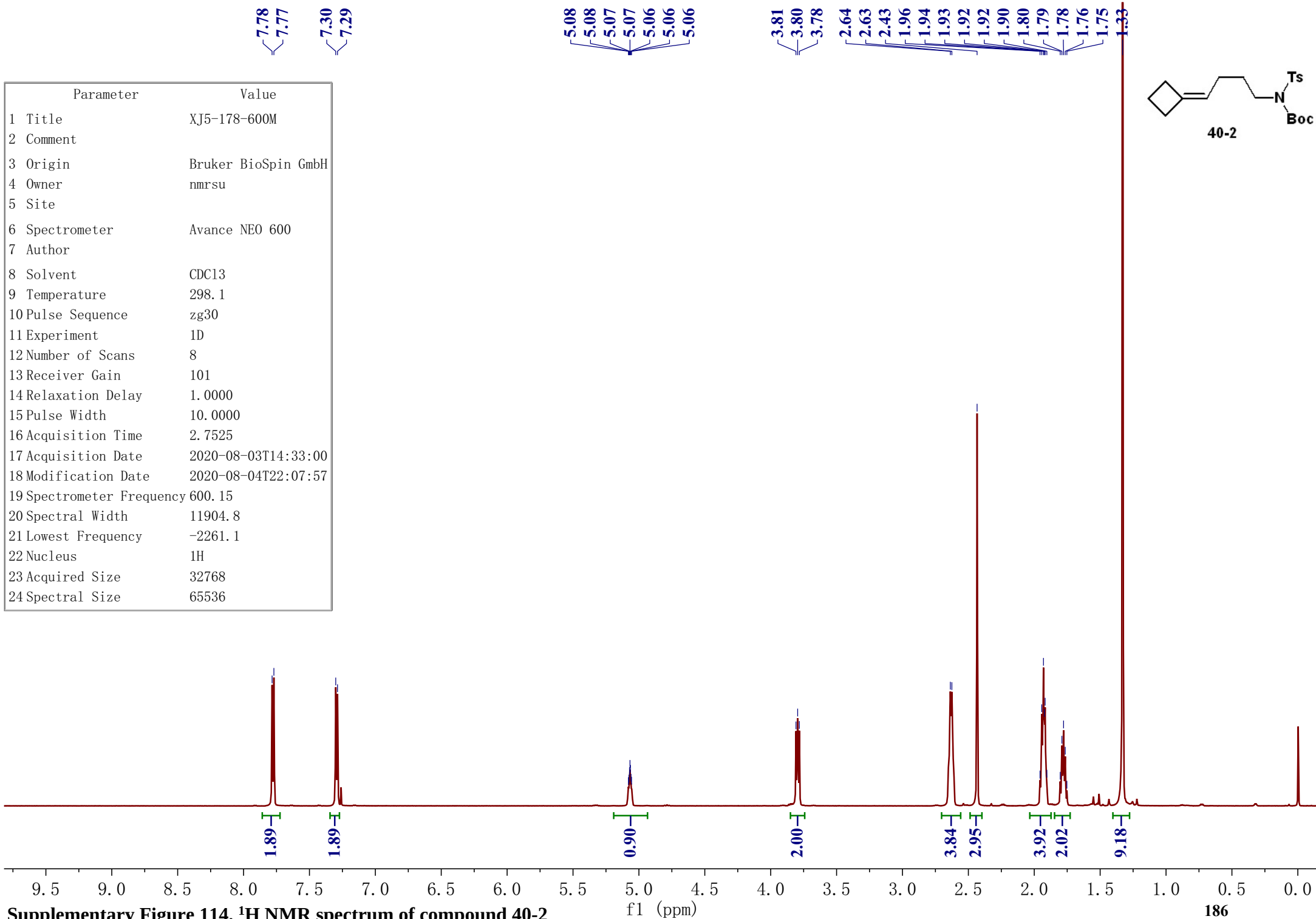
50.26
49.81

35.65

26.08
21.66
18.02

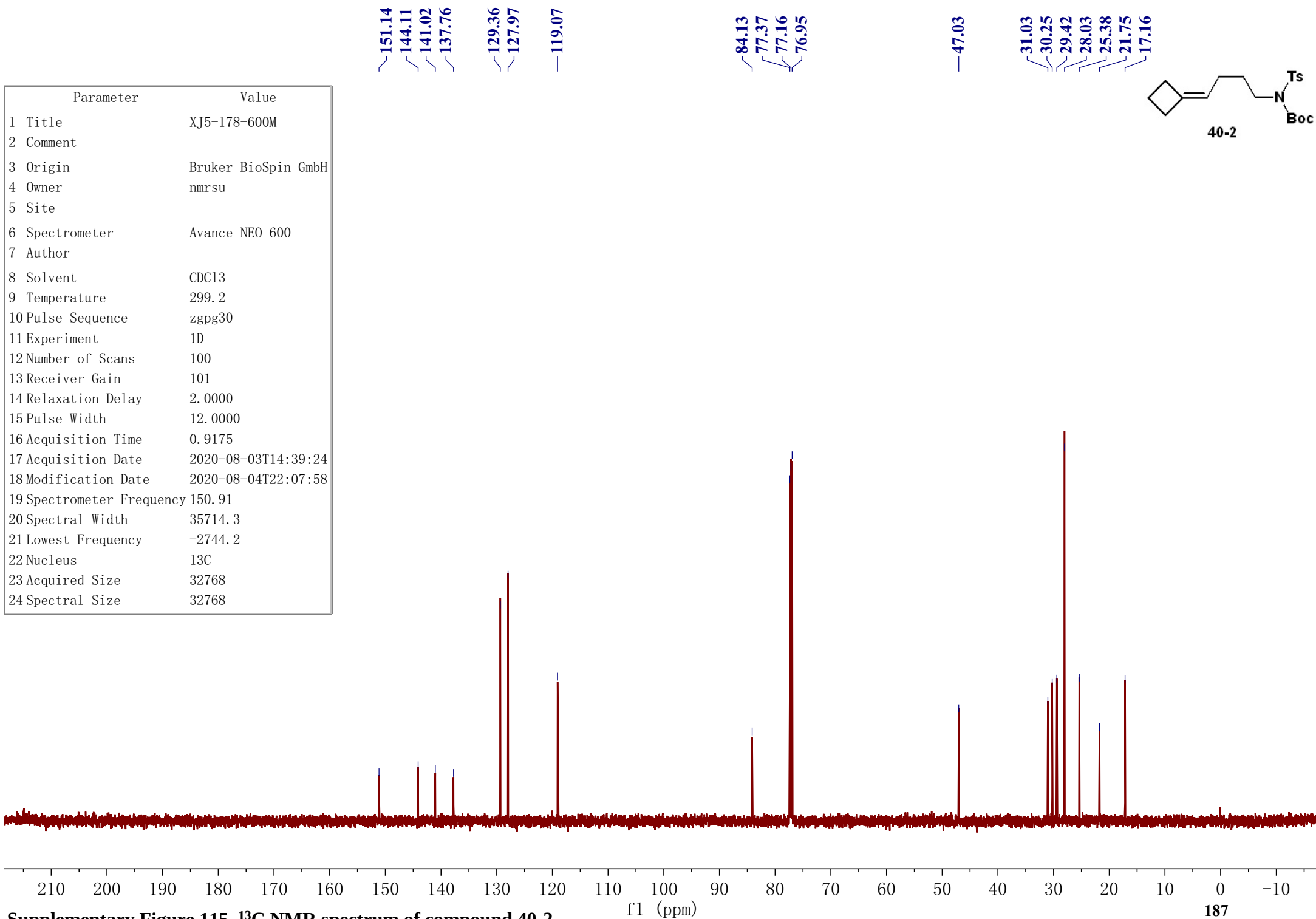


Parameter	Value
1 Title	XJ5-178-600M
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2020-08-03T14:33:00
18 Modification Date	2020-08-04T22:07:57
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2261.1
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



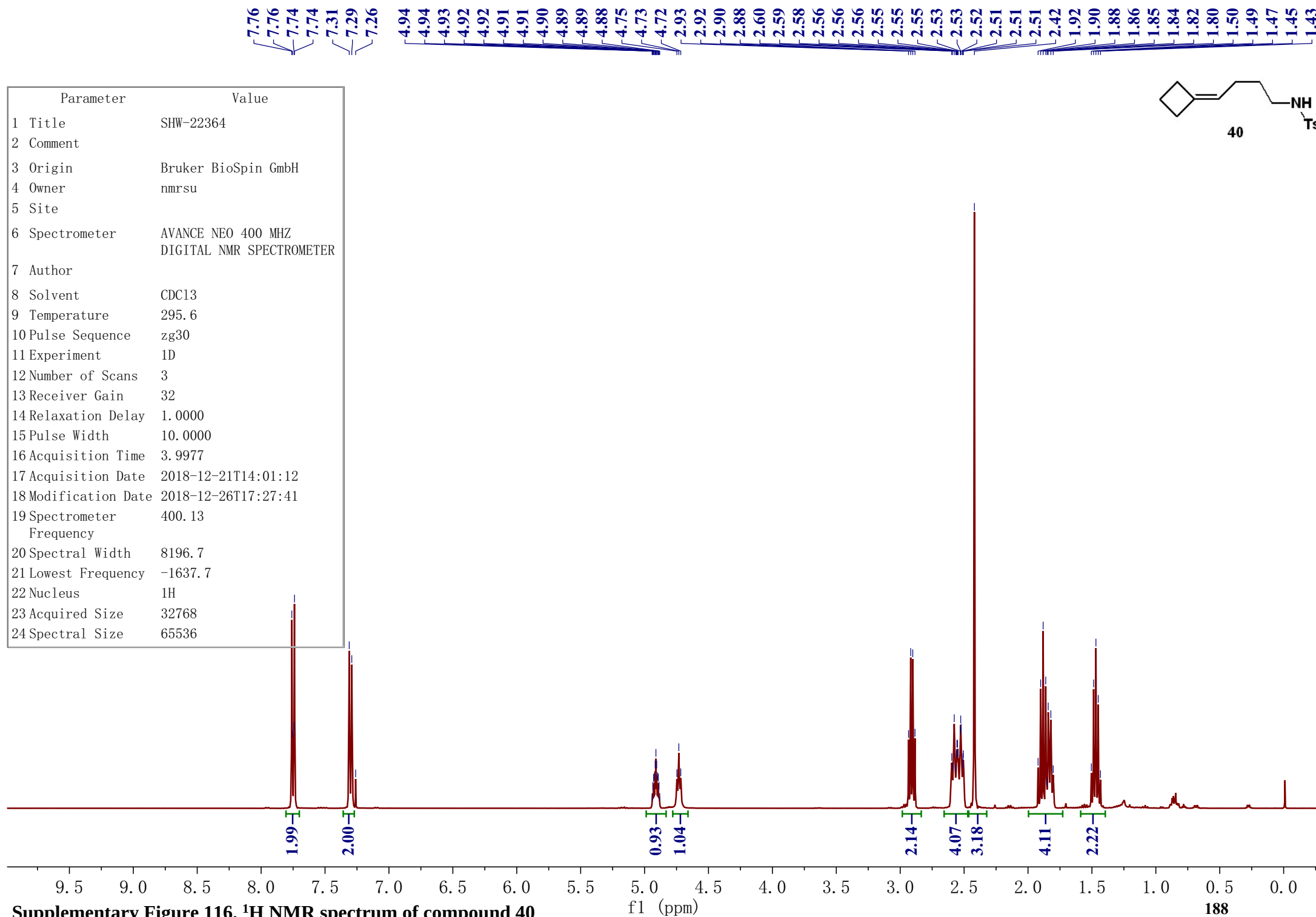
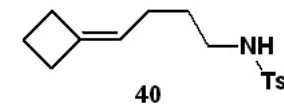
Supplementary Figure 114. ¹H NMR spectrum of compound 40-2

Parameter	Value
1 Title	XJ5-178-600M
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	299.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	100
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2020-08-03T14:39:24
18 Modification Date	2020-08-04T22:07:58
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2744.2
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768



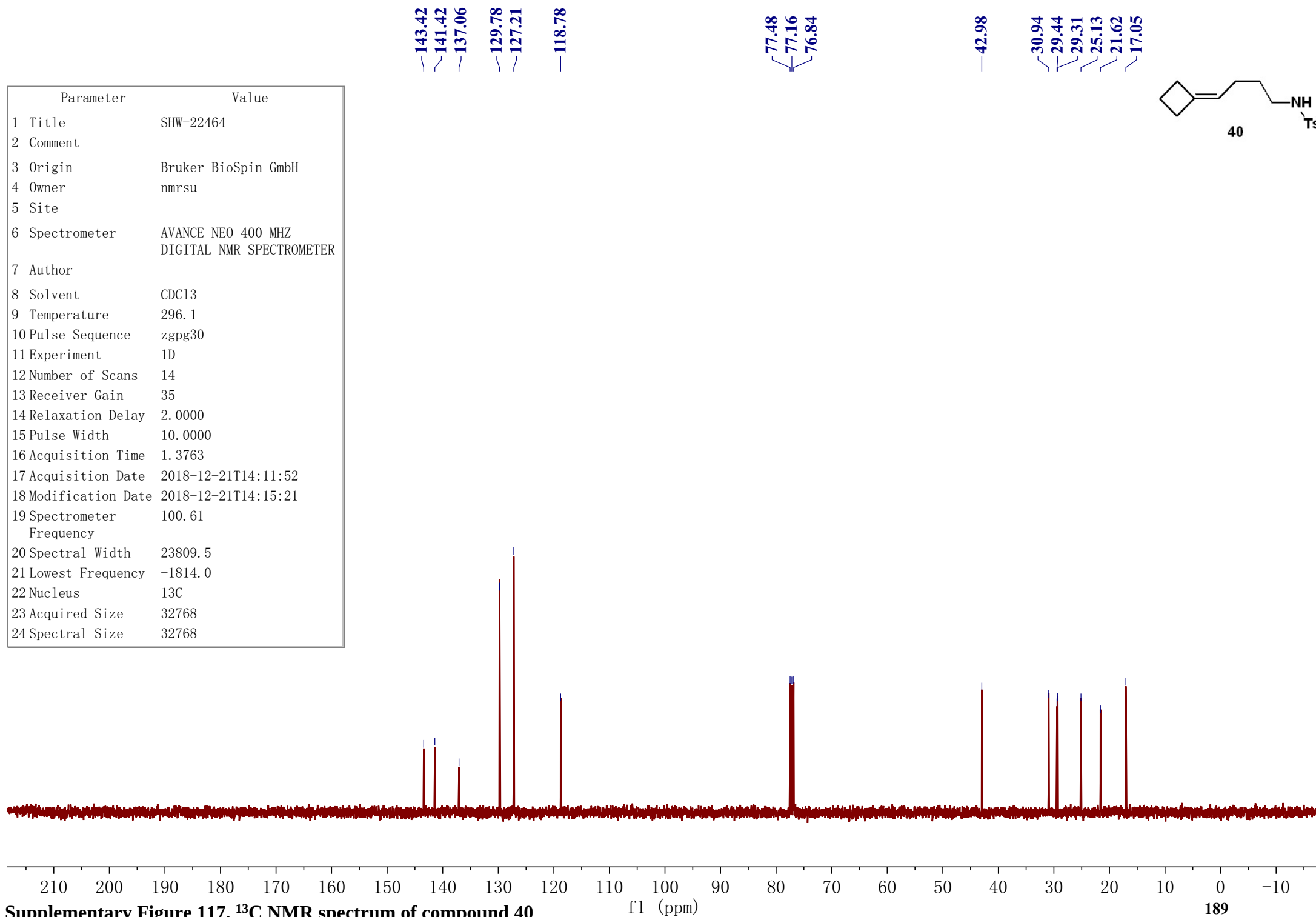
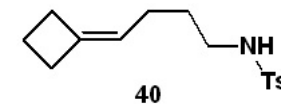
Supplementary Figure 115. ¹³C NMR spectrum of compound 40-2

Parameter	Value
1 Title	SHW-22364
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.6
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	3
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-12-21T14:01:12
18 Modification Date	2018-12-26T17:27:41
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.7
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

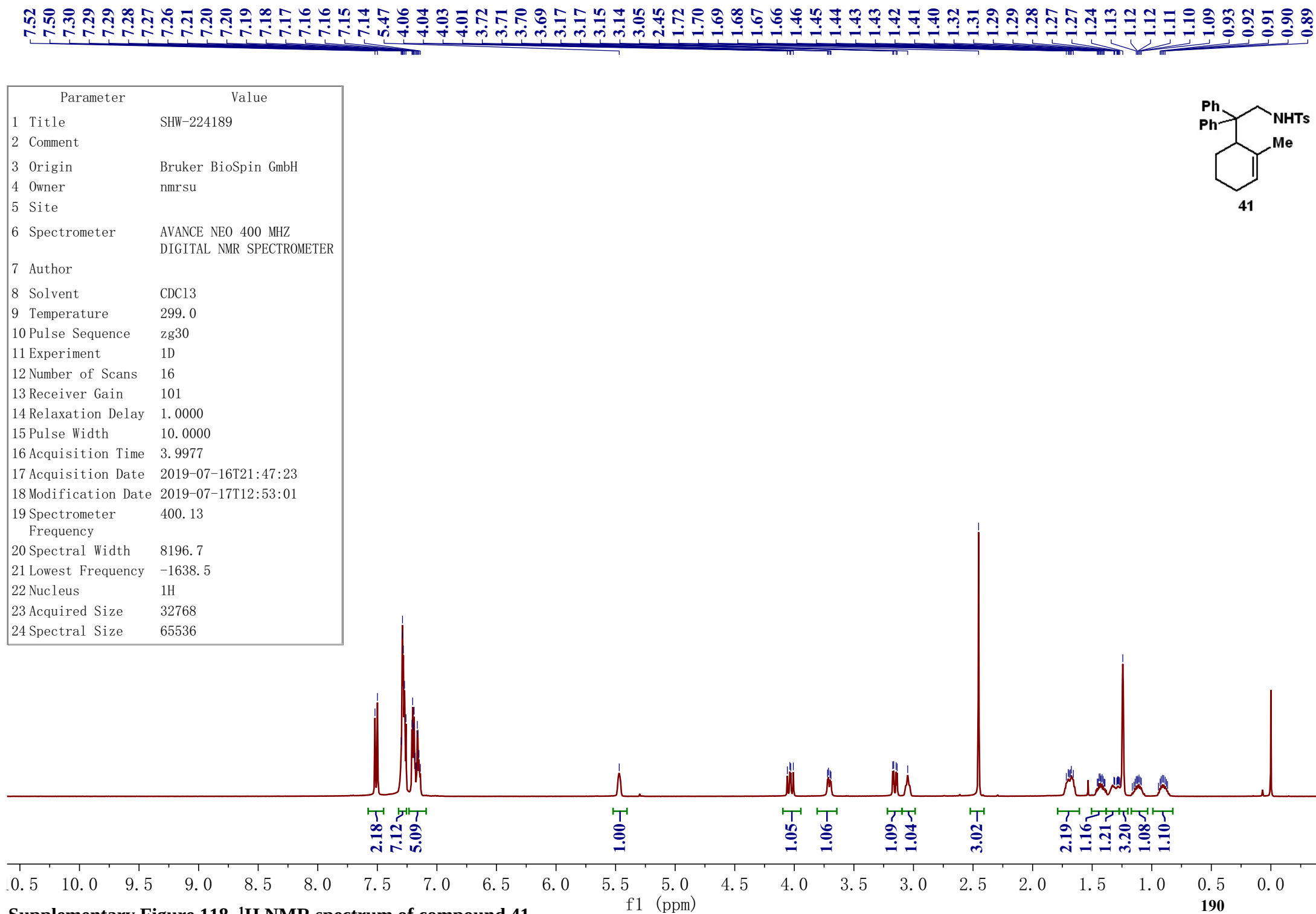


Supplementary Figure 116. ¹H NMR spectrum of compound 40

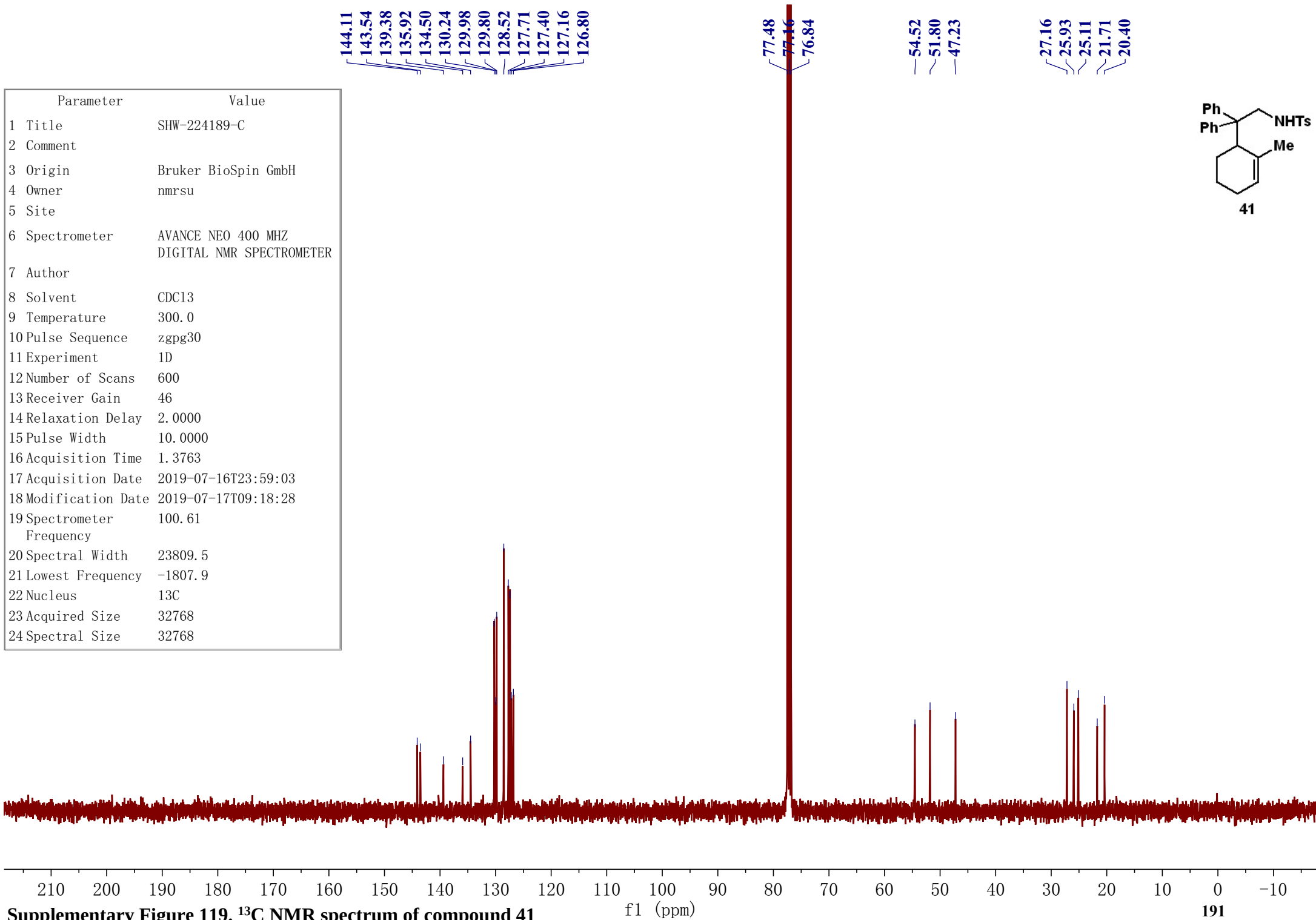
Parameter	Value
1 Title	SHW-22464
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	14
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-21T14:11:52
18 Modification Date	2018-12-21T14:15:21
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1814.0
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 117. ¹³C NMR spectrum of compound 40



Parameter	Value
1 Title	SHW-224189-C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	300.0
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	600
13 Receiver Gain	46
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-07-16T23:59:03
18 Modification Date	2019-07-17T09:18:28
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1807.9
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 119. ¹³C NMR spectrum of compound 41

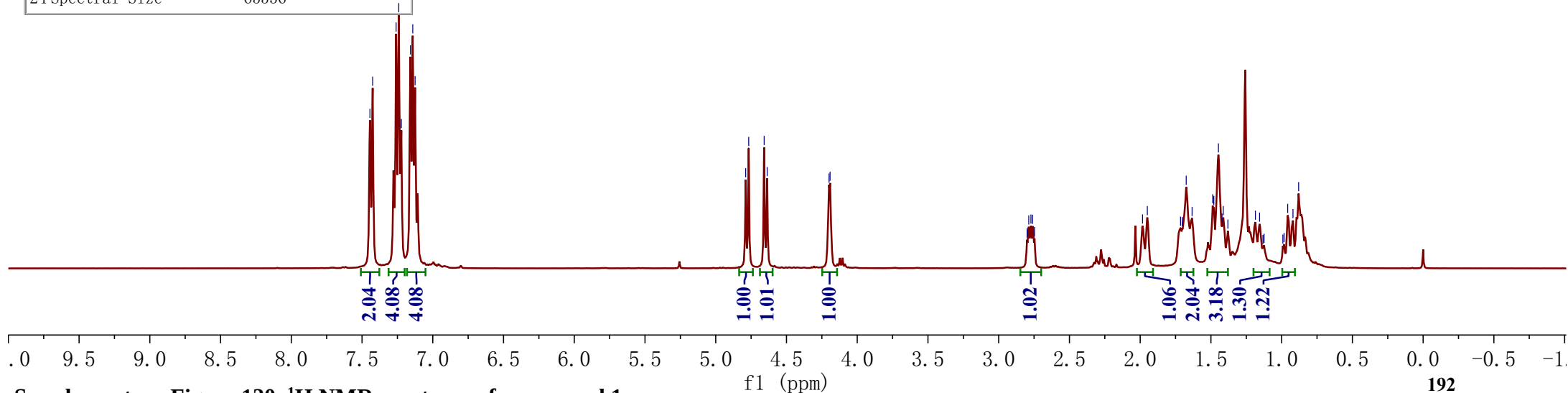
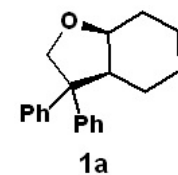
7.44
7.42
7.26
7.24
7.22
7.16
7.14
7.13

4.79
4.77
4.66
4.64
4.20
4.19

2.80
2.79
2.77
2.76
2.75

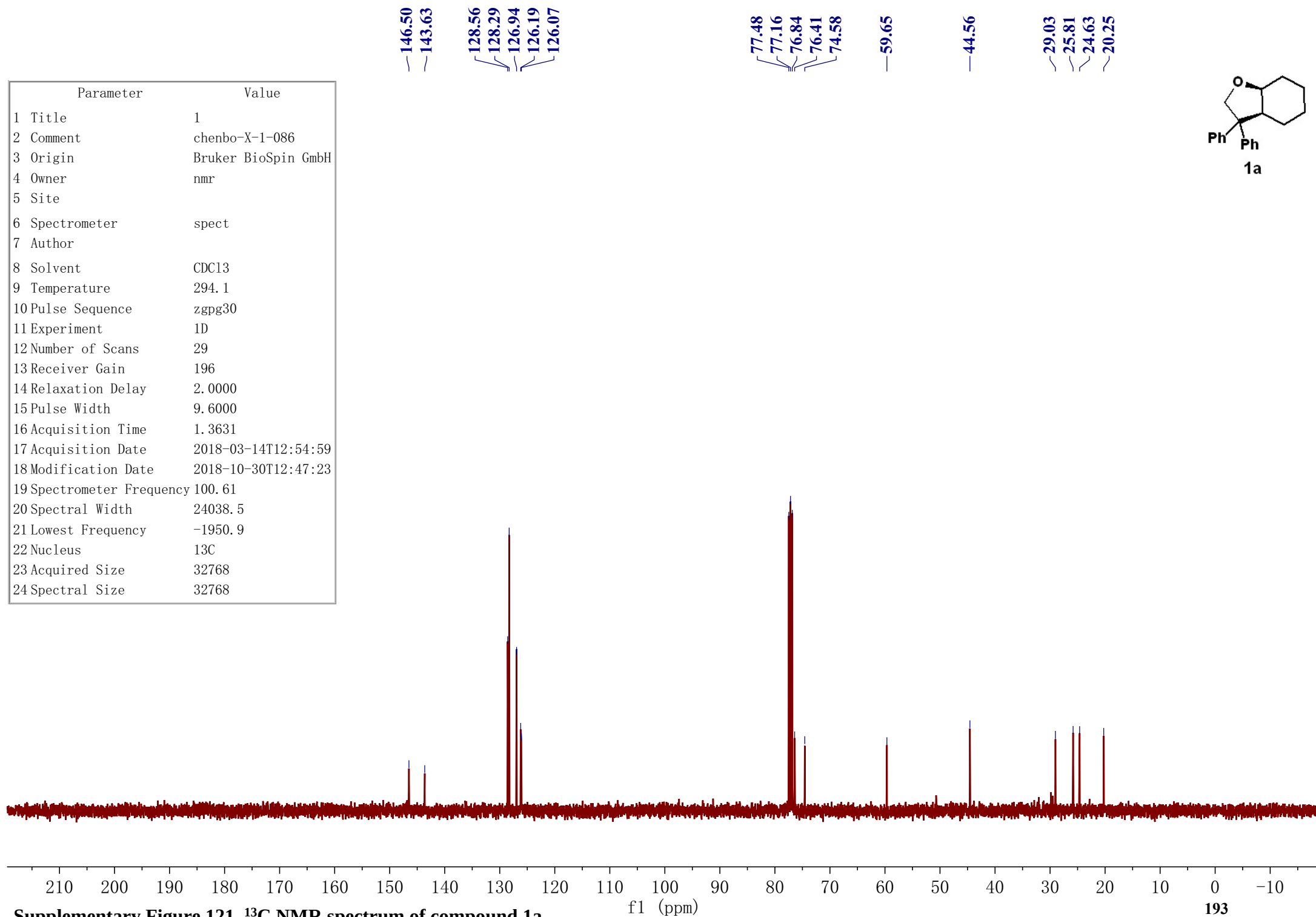
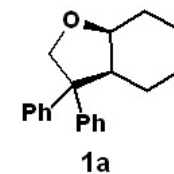
1.98
1.95
1.71
1.70
1.67
1.63
1.49
1.48
1.45
1.42
1.41
1.38
1.19
1.16
1.12
0.99
0.98
0.96
0.92
0.90

Parameter	Value
1 Title	1
2 Comment	chenbo-X-1-086
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	CDC13
9 Temperature	294.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	28
14 Relaxation Delay	1.0000
15 Pulse Width	8.7300
16 Acquisition Time	1.9999
17 Acquisition Date	2018-03-14T12:52:29
18 Modification Date	2018-10-30T12:47:22
19 Spectrometer Frequency	400.13
20 Spectral Width	8012.8
21 Lowest Frequency	-1555.9
22 Nucleus	1H
23 Acquired Size	16025
24 Spectral Size	65536



Supplementary Figure 120. ¹H NMR spectrum of compound 1a

Parameter	Value
1 Title	1
2 Comment	chenbo-X-1-086
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	CDC13
9 Temperature	294.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	29
13 Receiver Gain	196
14 Relaxation Delay	2.0000
15 Pulse Width	9.6000
16 Acquisition Time	1.3631
17 Acquisition Date	2018-03-14T12:54:59
18 Modification Date	2018-10-30T12:47:23
19 Spectrometer Frequency	100.61
20 Spectral Width	24038.5
21 Lowest Frequency	-1950.9
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 121. ¹³C NMR spectrum of compound **1a**

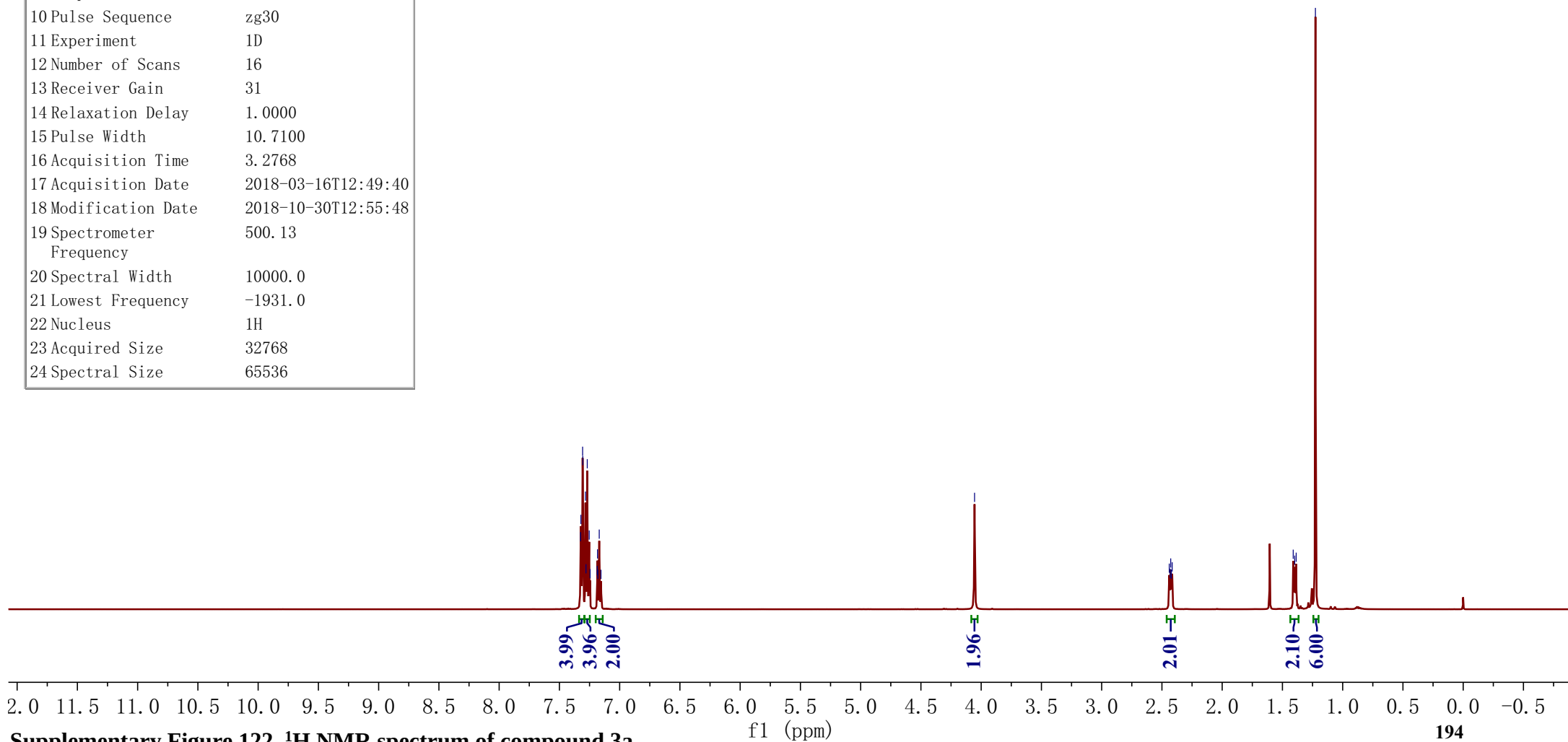
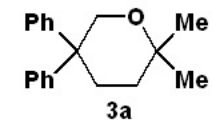
Parameter	Value
1 Title	2
2 Comment	chenbo-X-1-091-1
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	CDC13
9 Temperature	296.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	31
14 Relaxation Delay	1.0000
15 Pulse Width	10.7100
16 Acquisition Time	3.2768
17 Acquisition Date	2018-03-16T12:49:40
18 Modification Date	2018-10-30T12:55:48
19 Spectrometer	500.13
Frequency	
20 Spectral Width	10000.0
21 Lowest Frequency	-1931.0
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

7.32 7.32 7.31 7.31 7.28 7.28 7.27 7.25 7.25 7.19 7.18 7.18 7.17 7.16

4.05

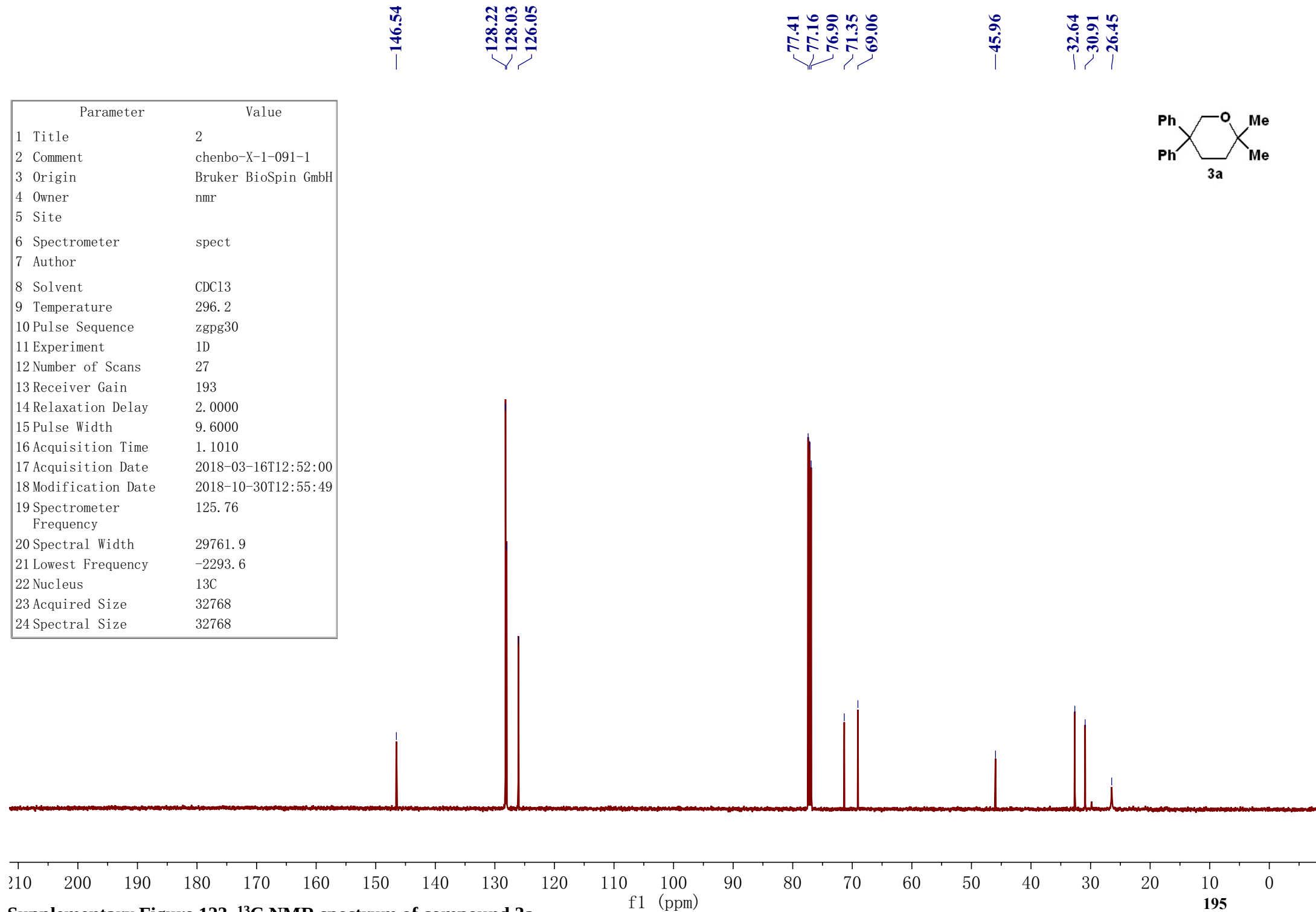
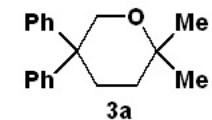
2.44 2.43 2.43 2.42 2.41

1.41 1.40 1.39 1.23



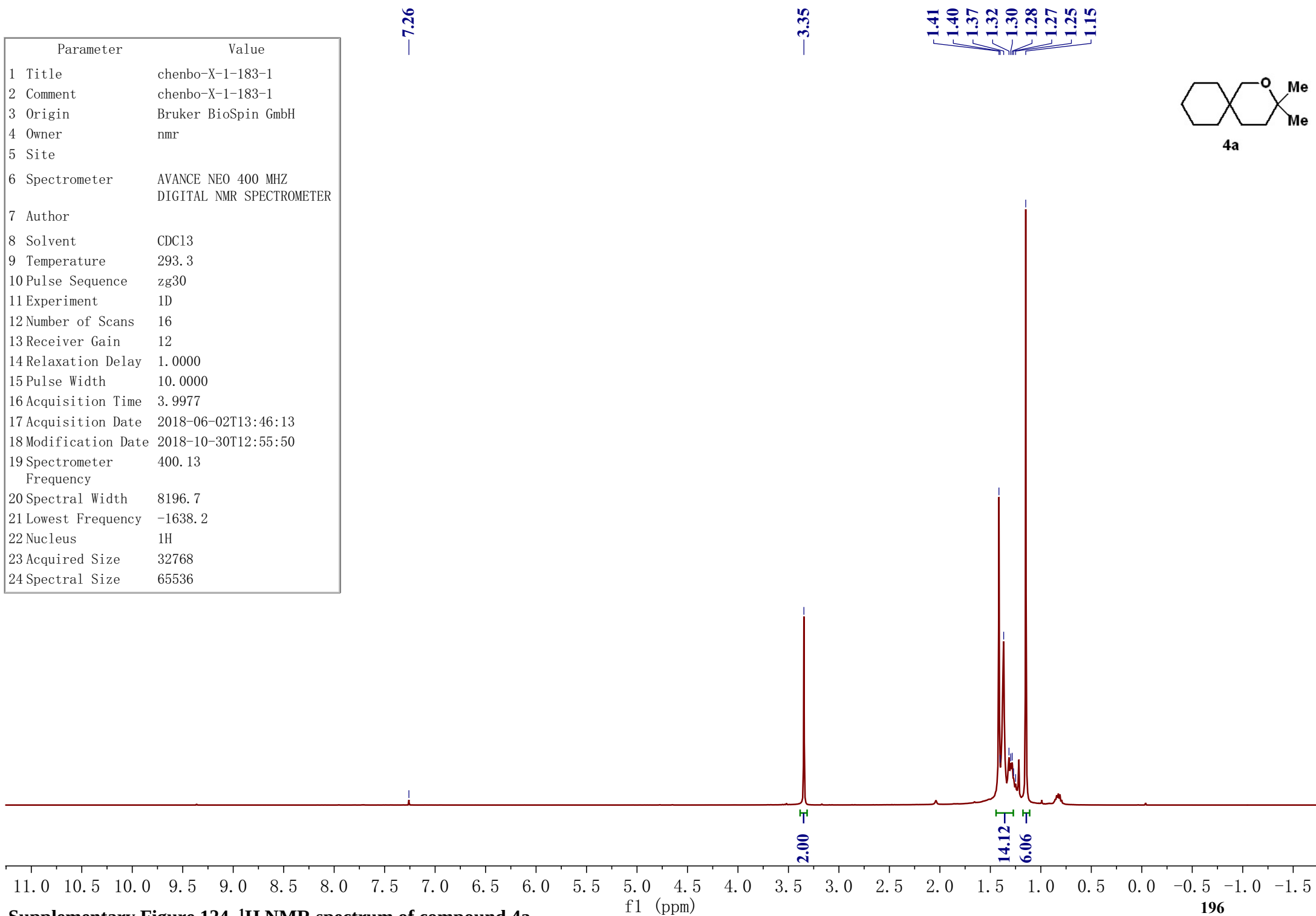
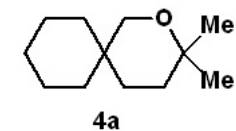
Supplementary Figure 122. ¹H NMR spectrum of compound 3a

Parameter	Value
1 Title	2
2 Comment	chenbo-X-1-091-1
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	CDC13
9 Temperature	296.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	27
13 Receiver Gain	193
14 Relaxation Delay	2.0000
15 Pulse Width	9.6000
16 Acquisition Time	1.1010
17 Acquisition Date	2018-03-16T12:52:00
18 Modification Date	2018-10-30T12:55:49
19 Spectrometer	125.76
Frequency	
20 Spectral Width	29761.9
21 Lowest Frequency	-2293.6
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768



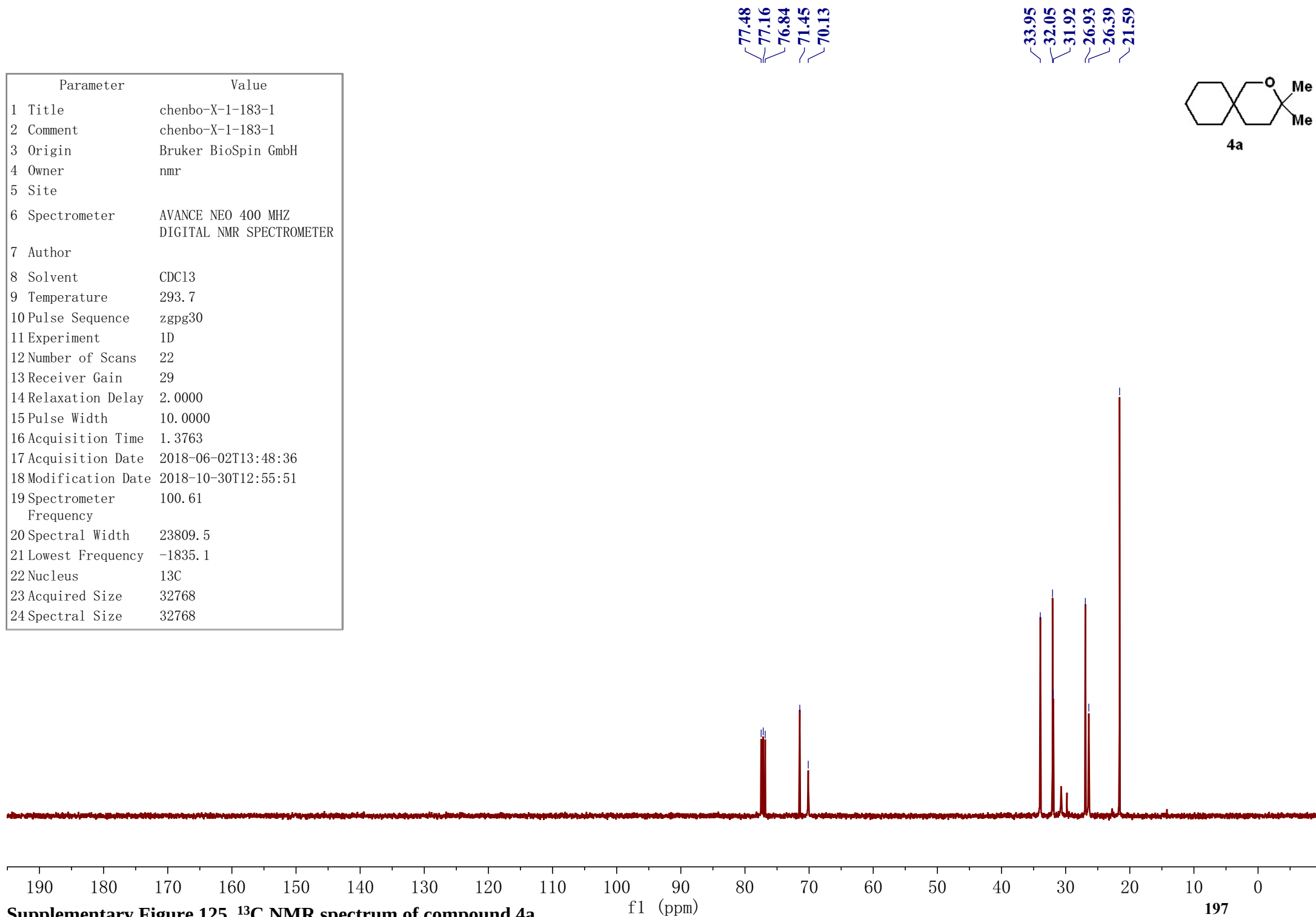
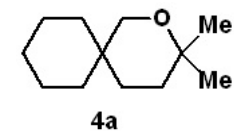
Supplementary Figure 123. ¹³C NMR spectrum of compound 3a

Parameter	Value
1 Title	chenbo-X-1-183-1
2 Comment	chenbo-X-1-183-1
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	293.3
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	12
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-06-02T13:46:13
18 Modification Date	2018-10-30T12:55:50
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.2
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536



Supplementary Figure 124. ¹H NMR spectrum of compound 4a

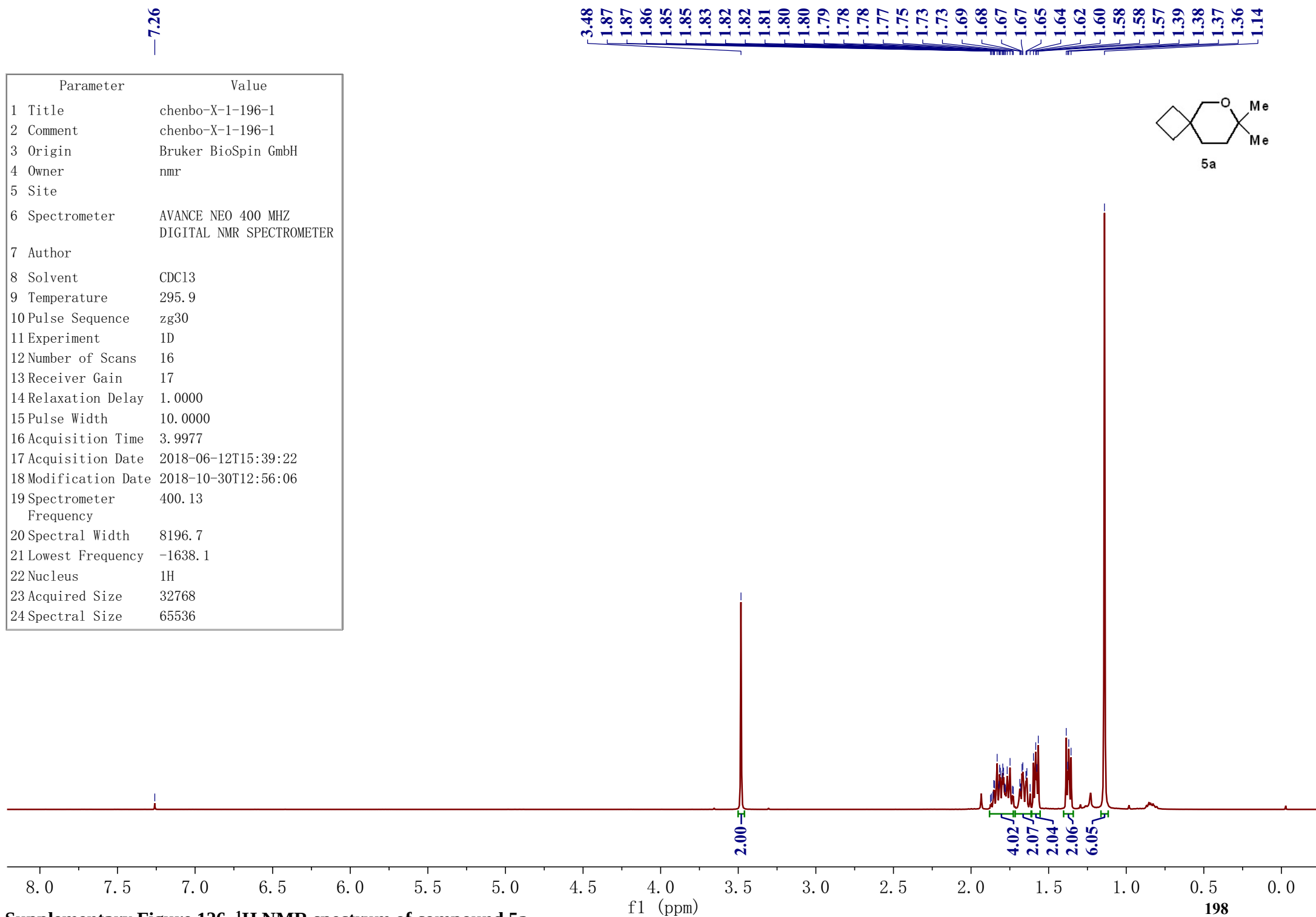
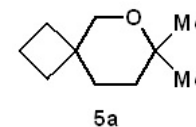
Parameter	Value
1 Title	chenbo-X-1-183-1
2 Comment	chenbo-X-1-183-1
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	293.7
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	22
13 Receiver Gain	29
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-06-02T13:48:36
18 Modification Date	2018-10-30T12:55:51
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1835.1
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



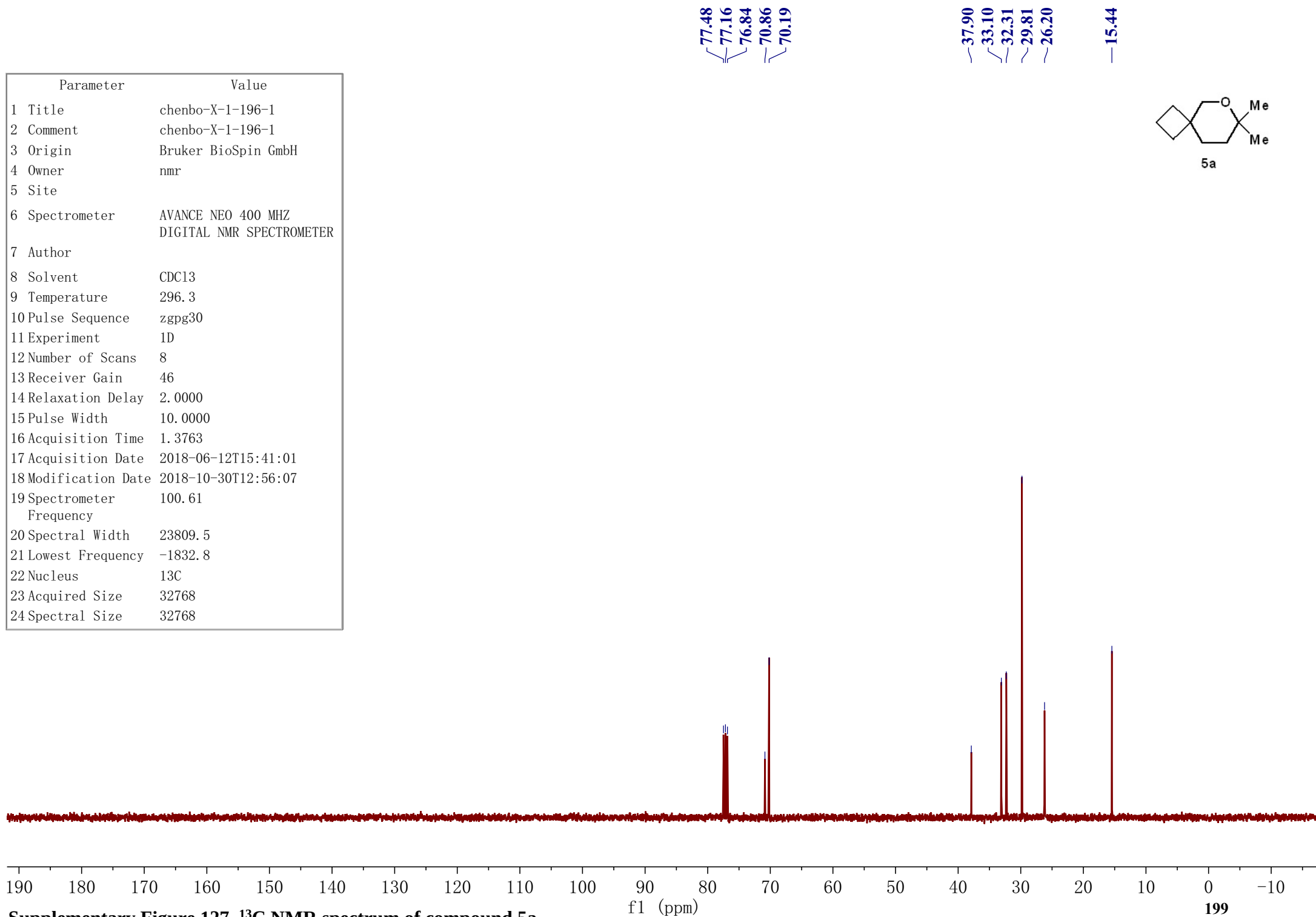
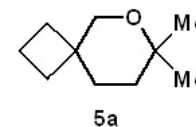
Supplementary Figure 125. ¹³C NMR spectrum of compound 4a

7.26

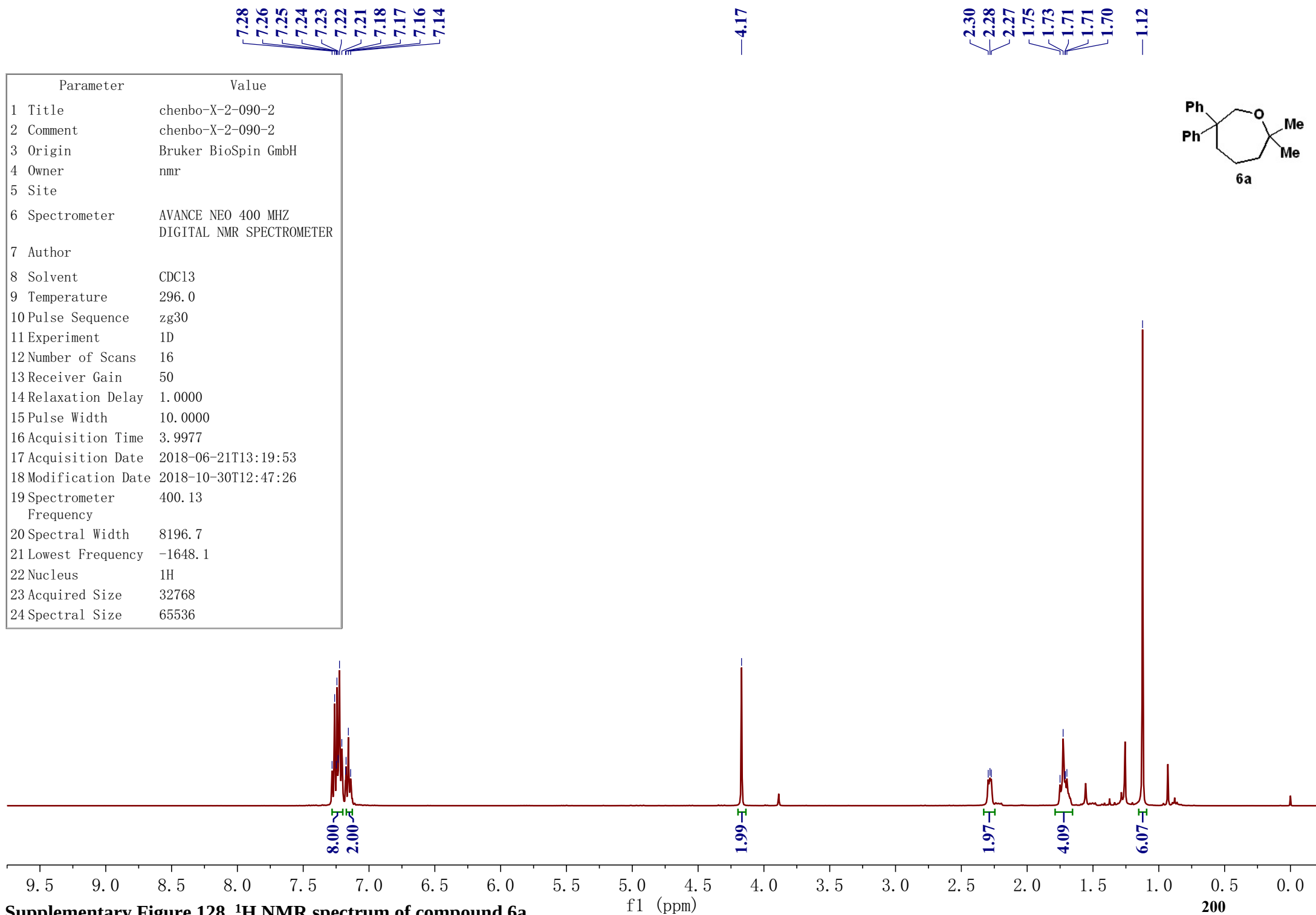
Parameter	Value
1 Title	chenbo-X-1-196-1
2 Comment	chenbo-X-1-196-1
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.9
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	17
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-06-12T15:39:22
18 Modification Date	2018-10-30T12:56:06
19 Spectrometer	400.13 Frequency
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.1
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

Supplementary Figure 126. ¹H NMR spectrum of compound 5a

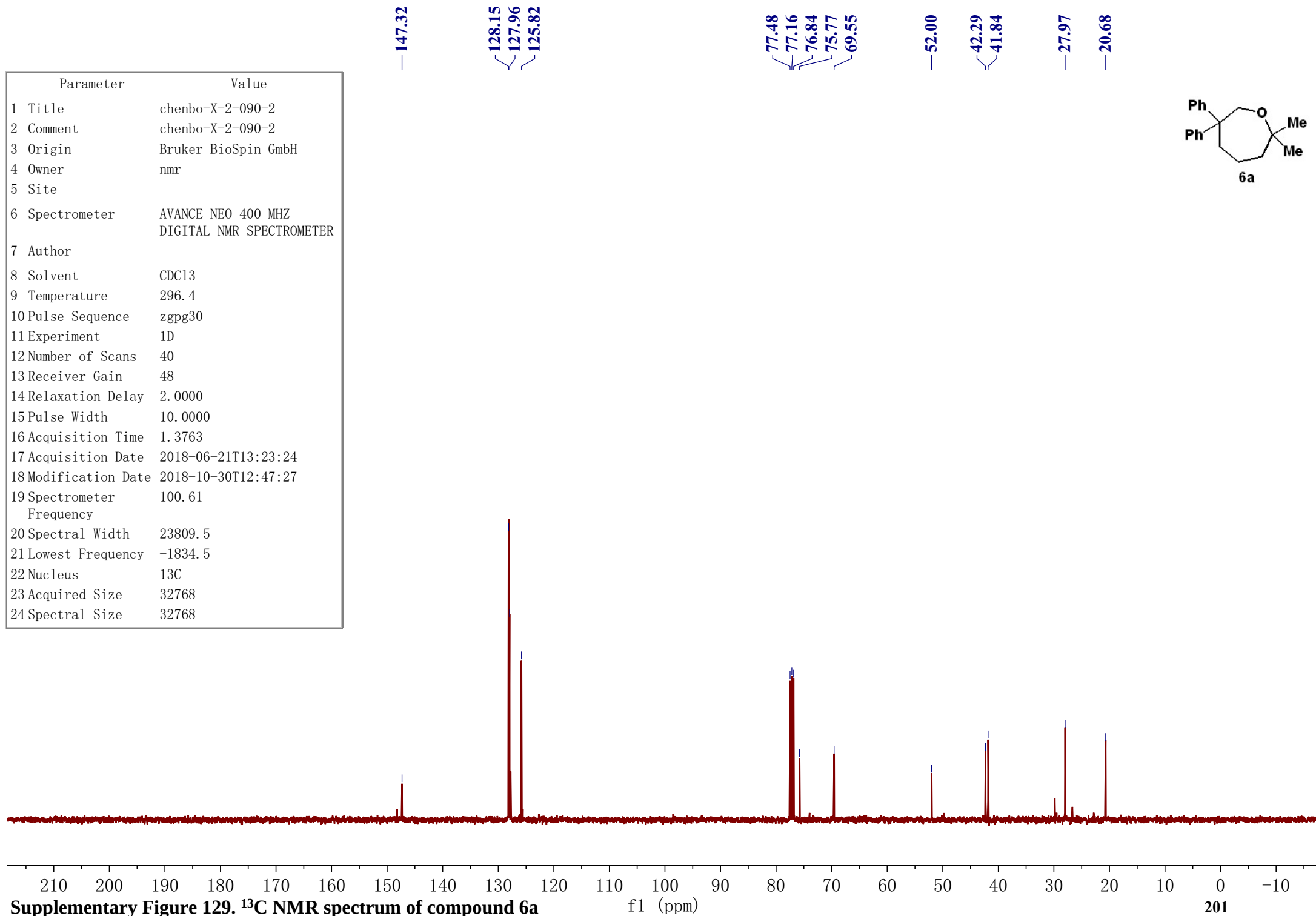
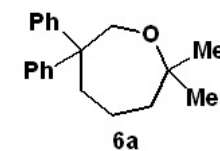
Parameter	Value
1 Title	chenbo-X-1-196-1
2 Comment	chenbo-X-1-196-1
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	46
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-06-12T15:41:01
18 Modification Date	2018-10-30T12:56:07
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1832.8
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

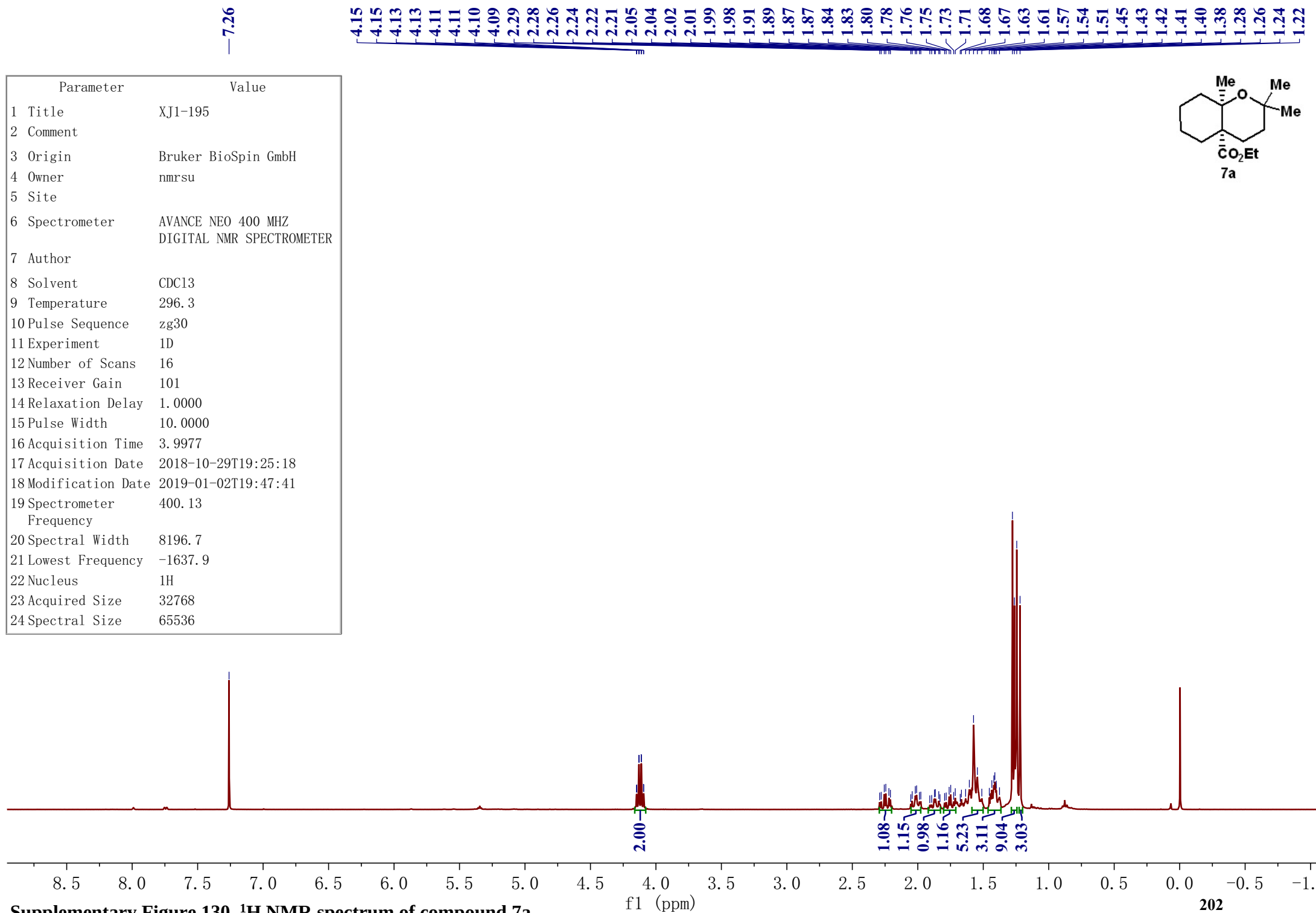


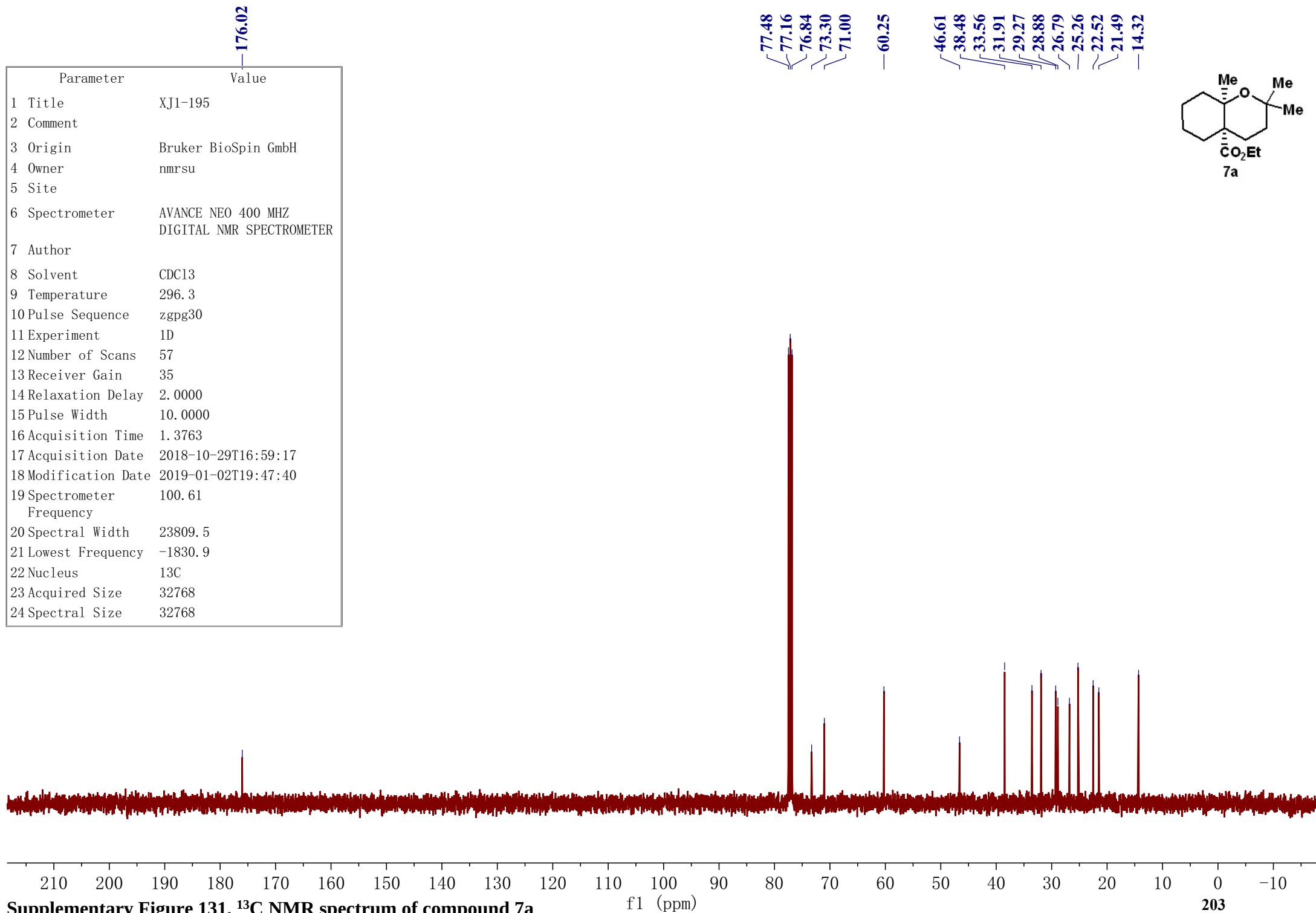
Supplementary Figure 127. ¹³C NMR spectrum of compound 5a



Parameter	Value
1 Title	chenbo-X-2-090-2
2 Comment	chenbo-X-2-090-2
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	40
13 Receiver Gain	48
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-06-21T13:23:24
18 Modification Date	2018-10-30T12:47:27
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1834.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

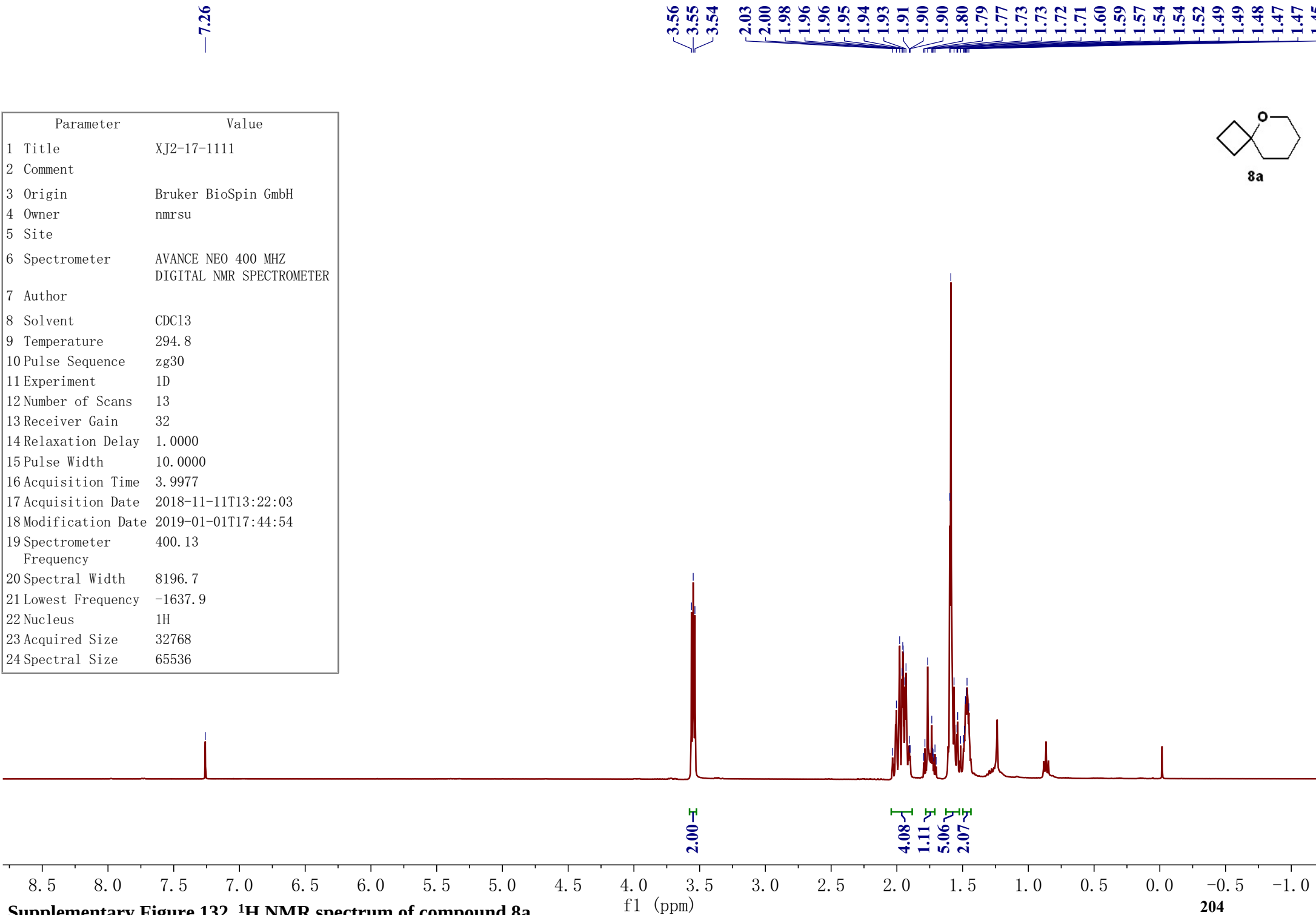






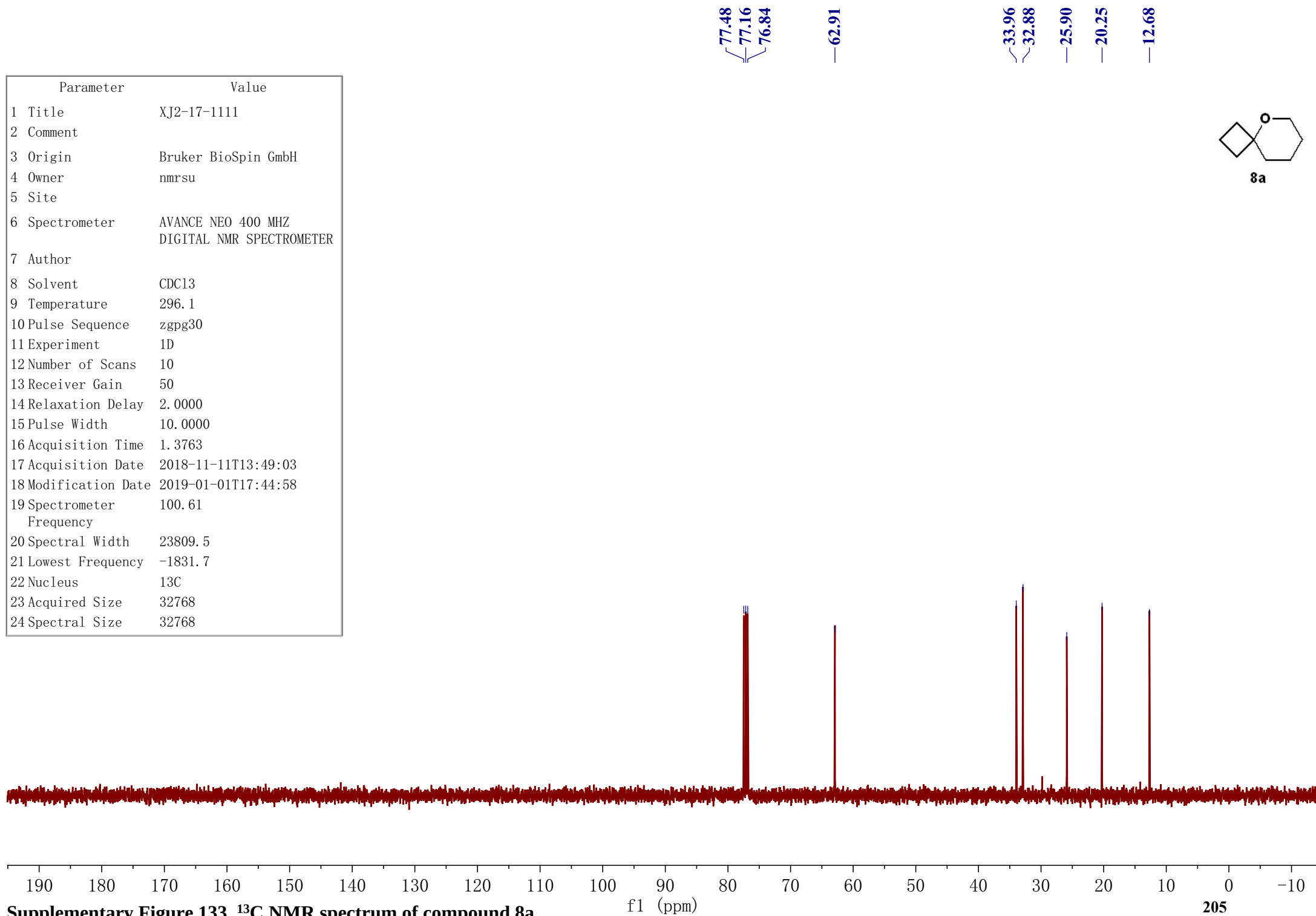
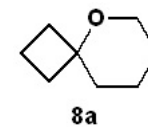
Supplementary Figure 131. ¹³C NMR spectrum of compound 7a

Parameter	Value
1 Title	XJ2-17-1111
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	294.8
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	13
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-11-11T13:22:03
18 Modification Date	2019-01-01T17:44:54
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.9
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Supplementary Figure 132. ¹H NMR spectrum of compound 8a

Parameter	Value
1 Title	XJ2-17-1111
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	10
13 Receiver Gain	50
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-11-11T13:49:03
18 Modification Date	2019-01-01T17:44:58
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1831.7
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

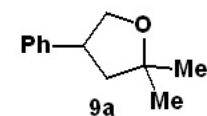


Supplementary Figure 133. ¹³C NMR spectrum of compound 8a

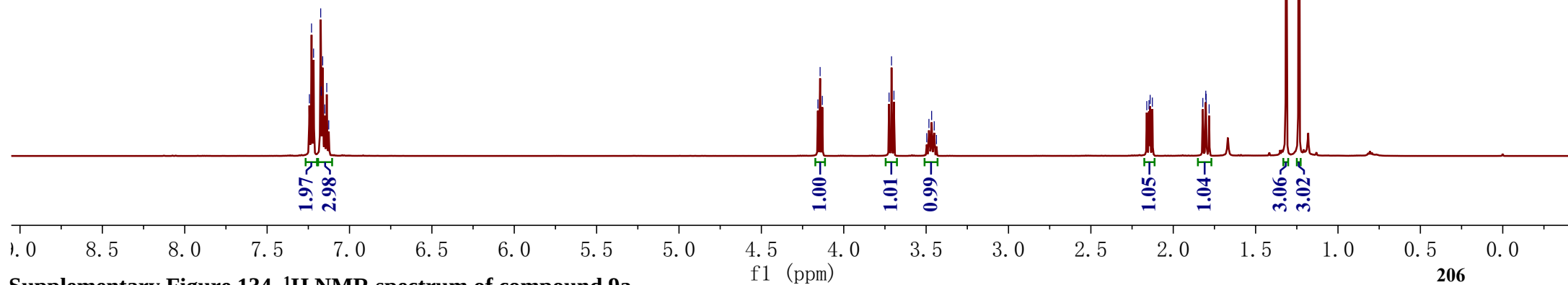
7.24
7.23
7.22
7.17
7.17
7.16
7.15
7.14
7.13

4.16
4.14
4.13
3.73
3.71
3.70
3.50
3.48
3.47
3.45
3.44

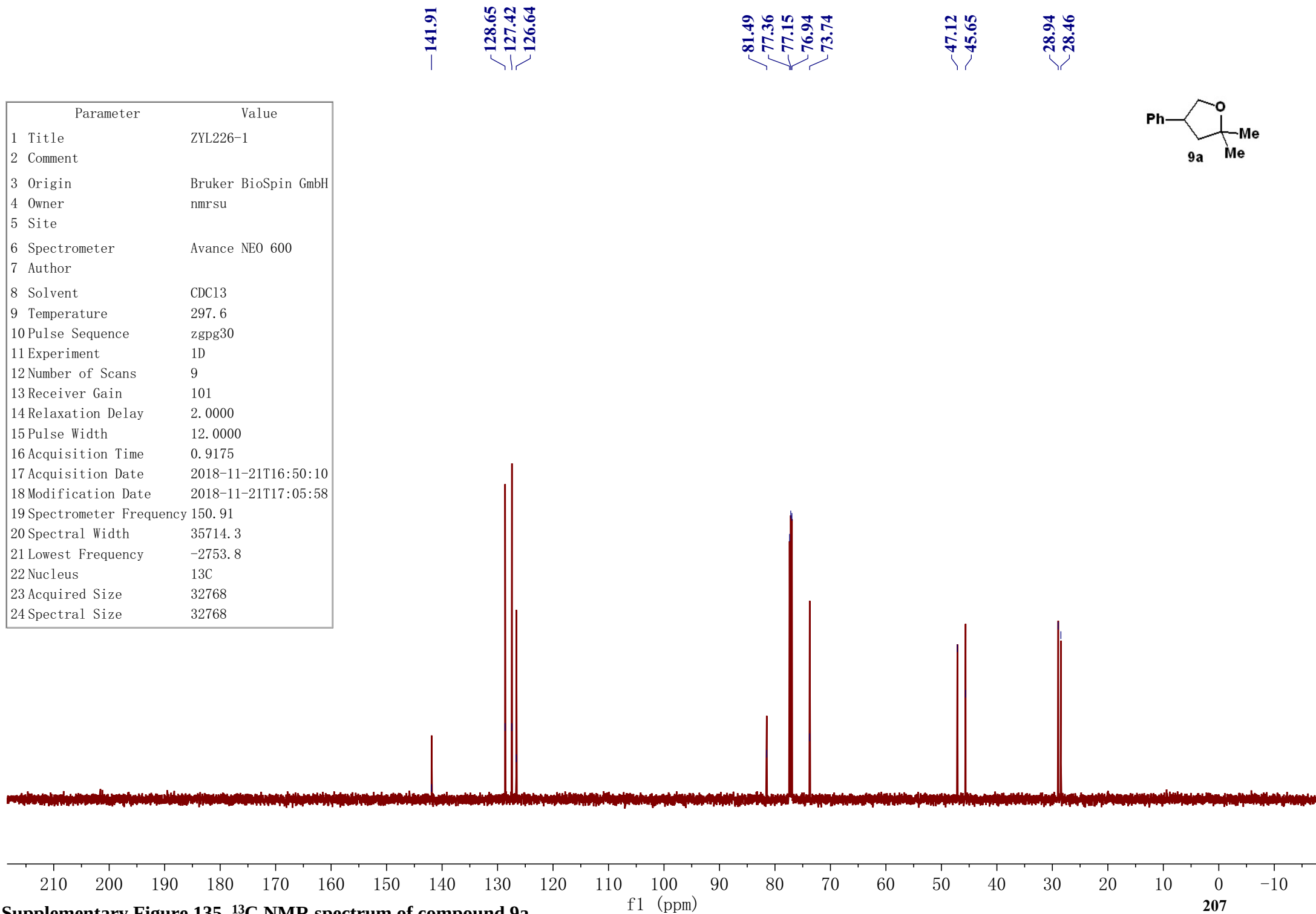
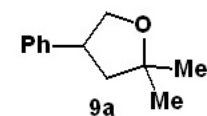
2.16
2.15
2.14
2.13
1.82
1.80
1.80
1.78
1.31
1.24



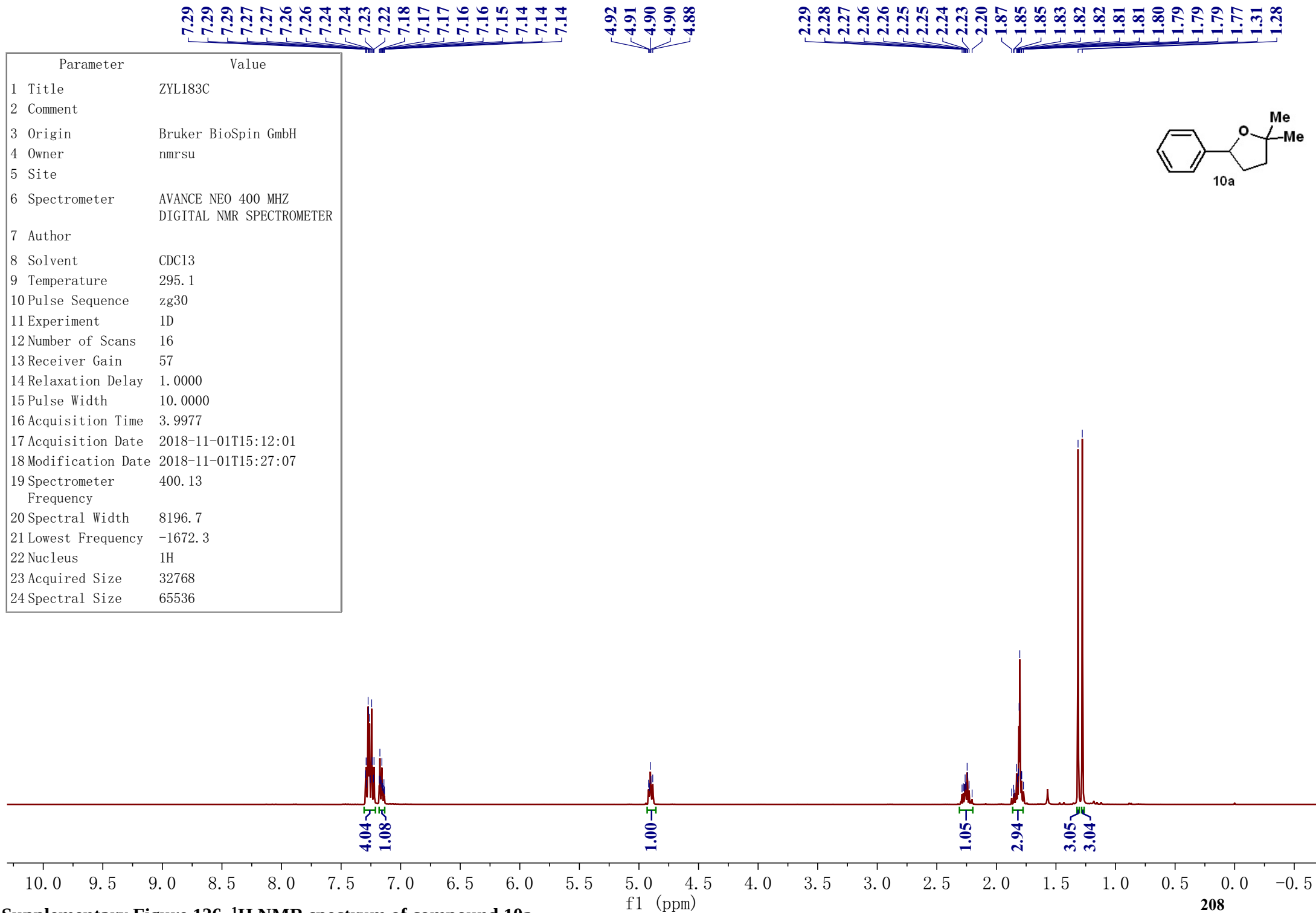
Parameter	Value
1 Title	ZYL226-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	297.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2018-11-21T16:48:59
18 Modification Date	2018-11-21T17:05:58
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2314.6
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Parameter	Value
1 Title	ZYL226-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	297.6
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	9
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2018-11-21T16:50:10
18 Modification Date	2018-11-21T17:05:58
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2753.8
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

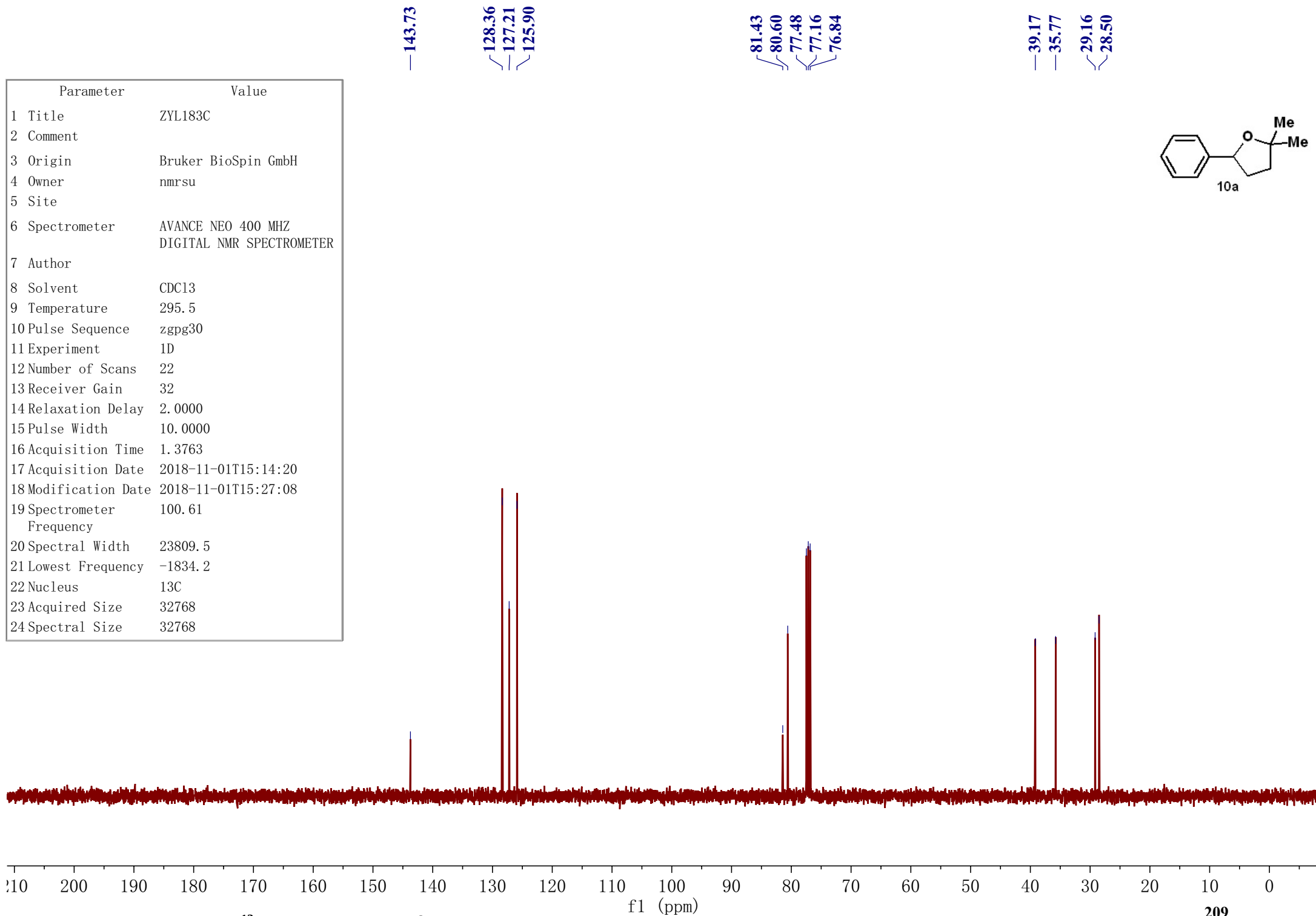
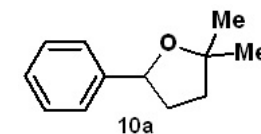


Supplementary Figure 135. ¹³C NMR spectrum of compound 9a

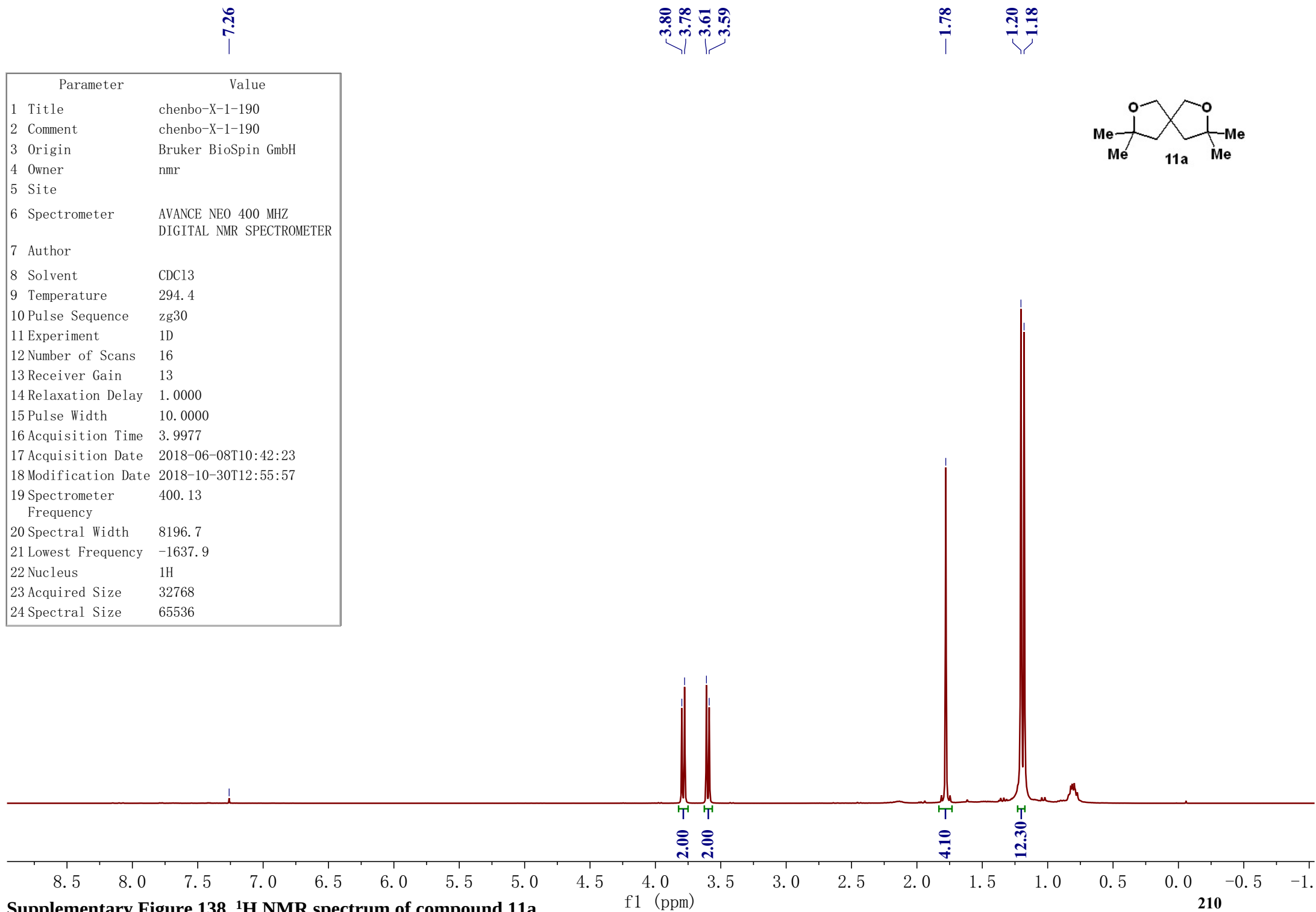


Supplementary Figure 136. ¹H NMR spectrum of compound 10a

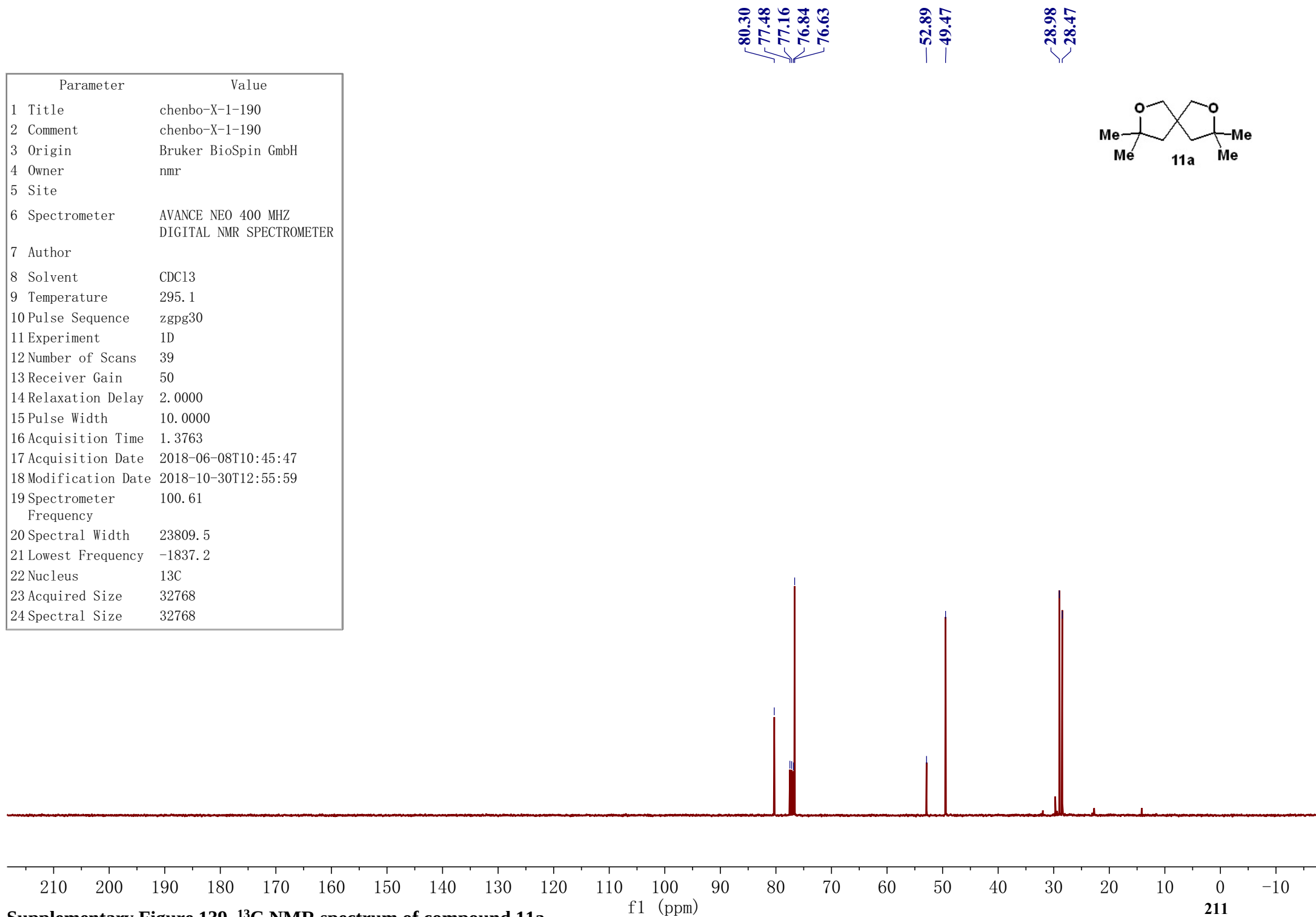
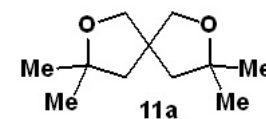
Parameter	Value
1 Title	ZYL183C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	22
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-11-01T15:14:20
18 Modification Date	2018-11-01T15:27:08
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1834.2
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 137. ¹³C NMR spectrum of compound 10a

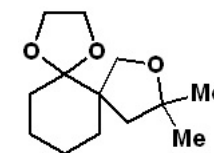


Parameter	Value
1 Title	chenbo-X-1-190
2 Comment	chenbo-X-1-190
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	39
13 Receiver Gain	50
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-06-08T10:45:47
18 Modification Date	2018-10-30T12:55:59
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1837.2
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

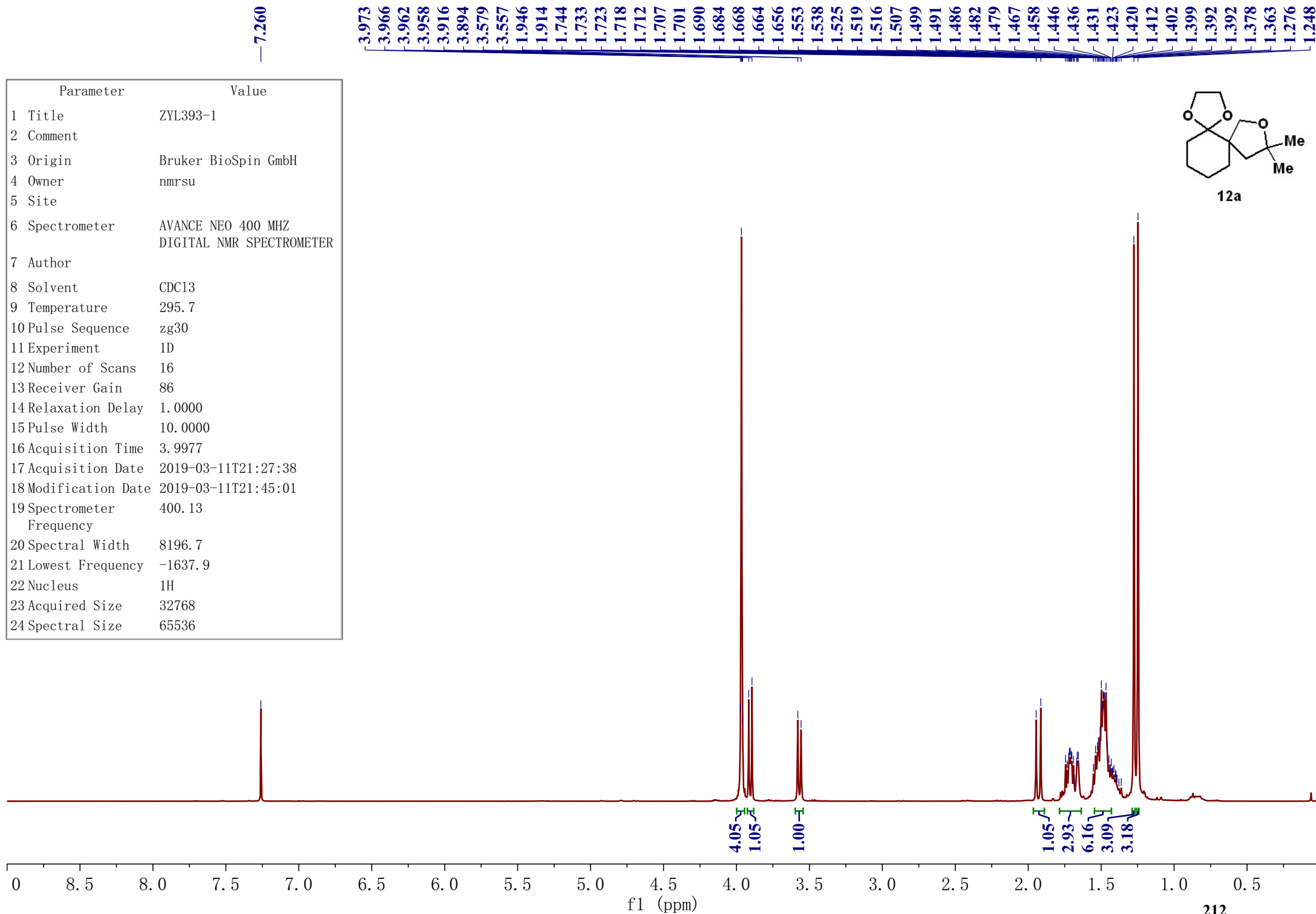


Supplementary Figure 139. ¹³C NMR spectrum of compound 11a

Parameter	Value
1 Title	ZYL393-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.7
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	86
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-03-11T21:27:38
18 Modification Date	2019-03-11T21:45:01
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.9
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

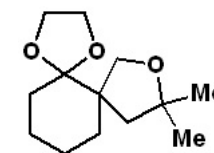


12a

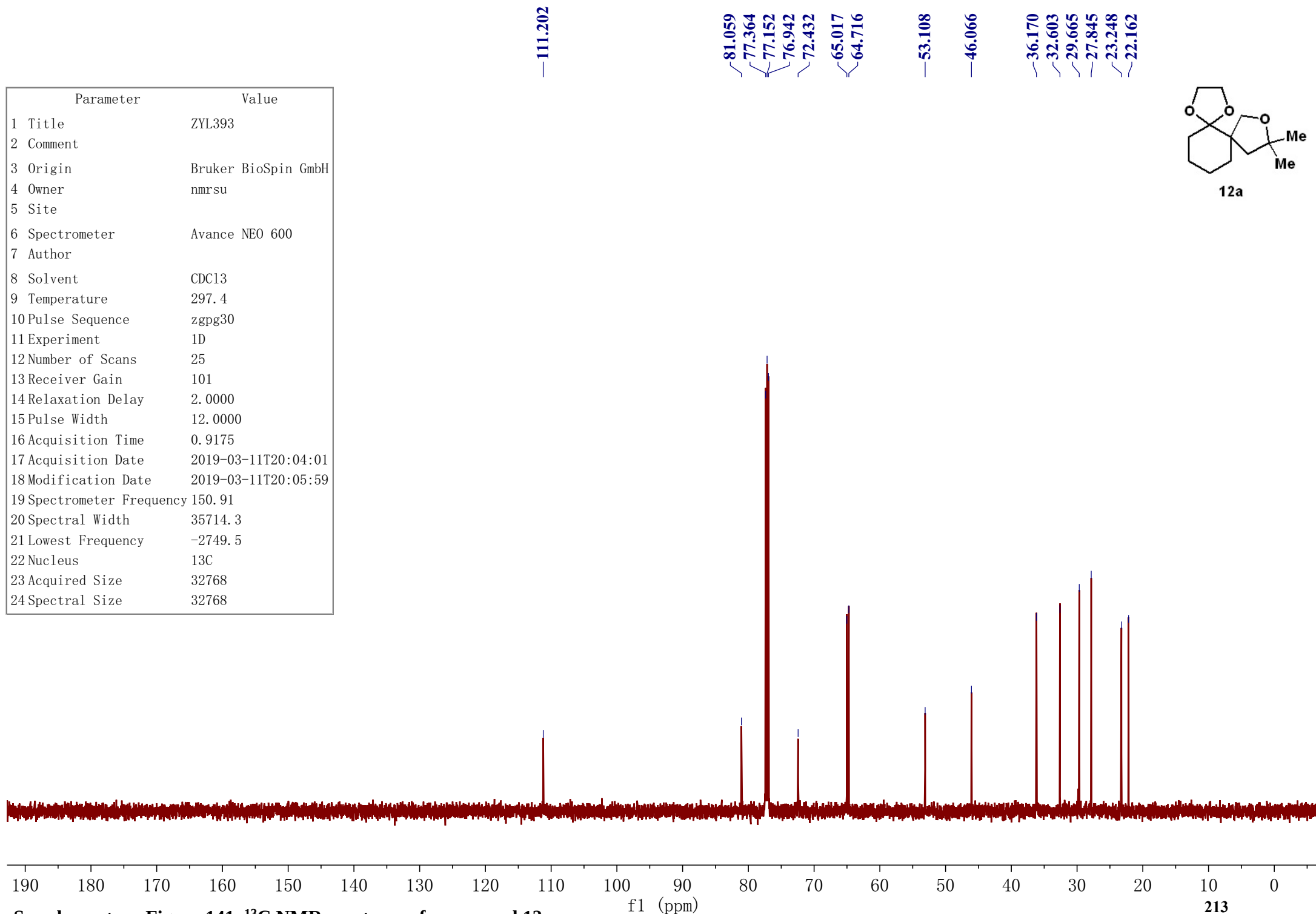


Supplementary Figure 140. ¹H NMR spectrum of compound 12a

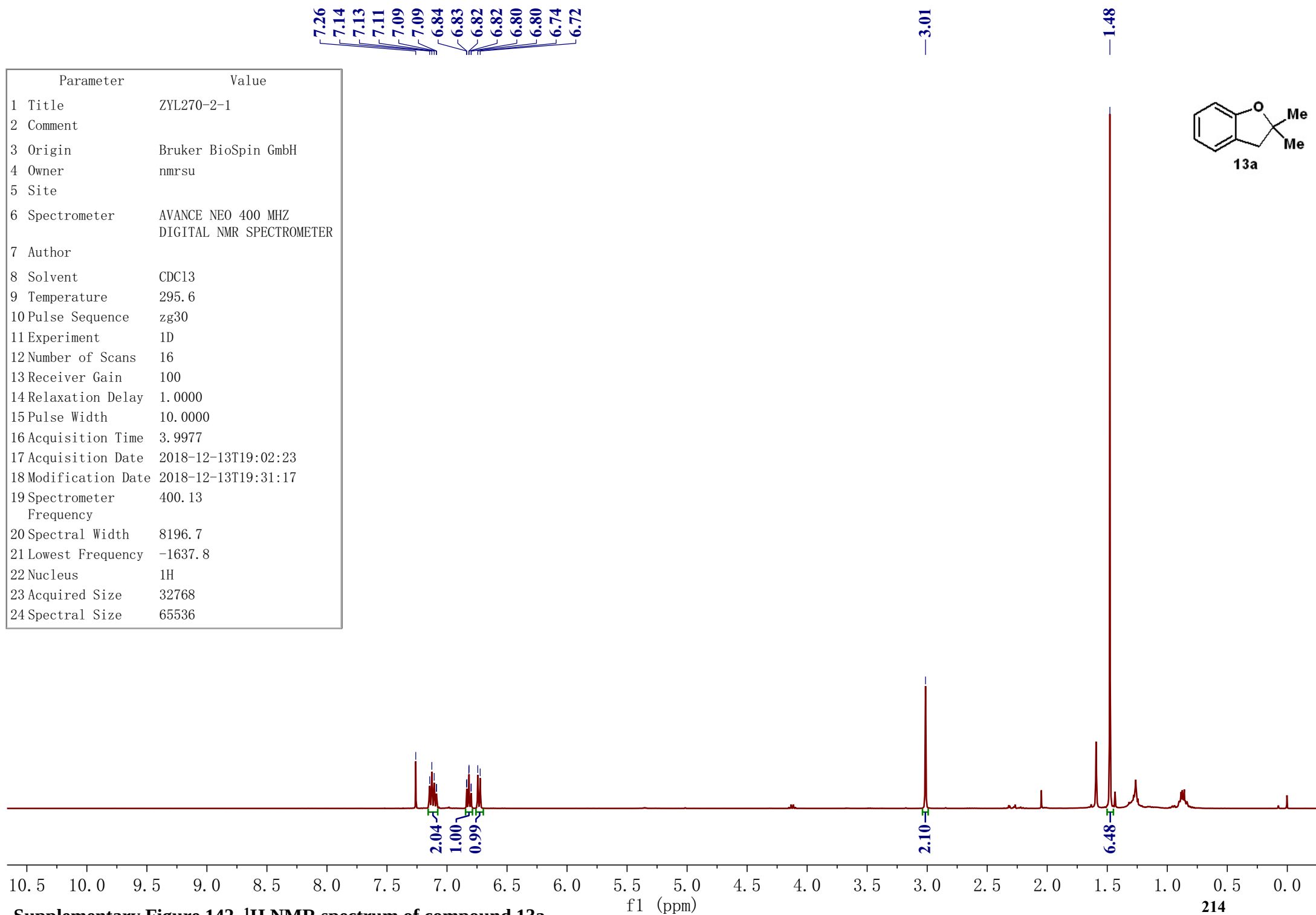
Parameter	Value
1 Title	ZYL393
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	25
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-03-11T20:04:01
18 Modification Date	2019-03-11T20:05:59
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2749.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



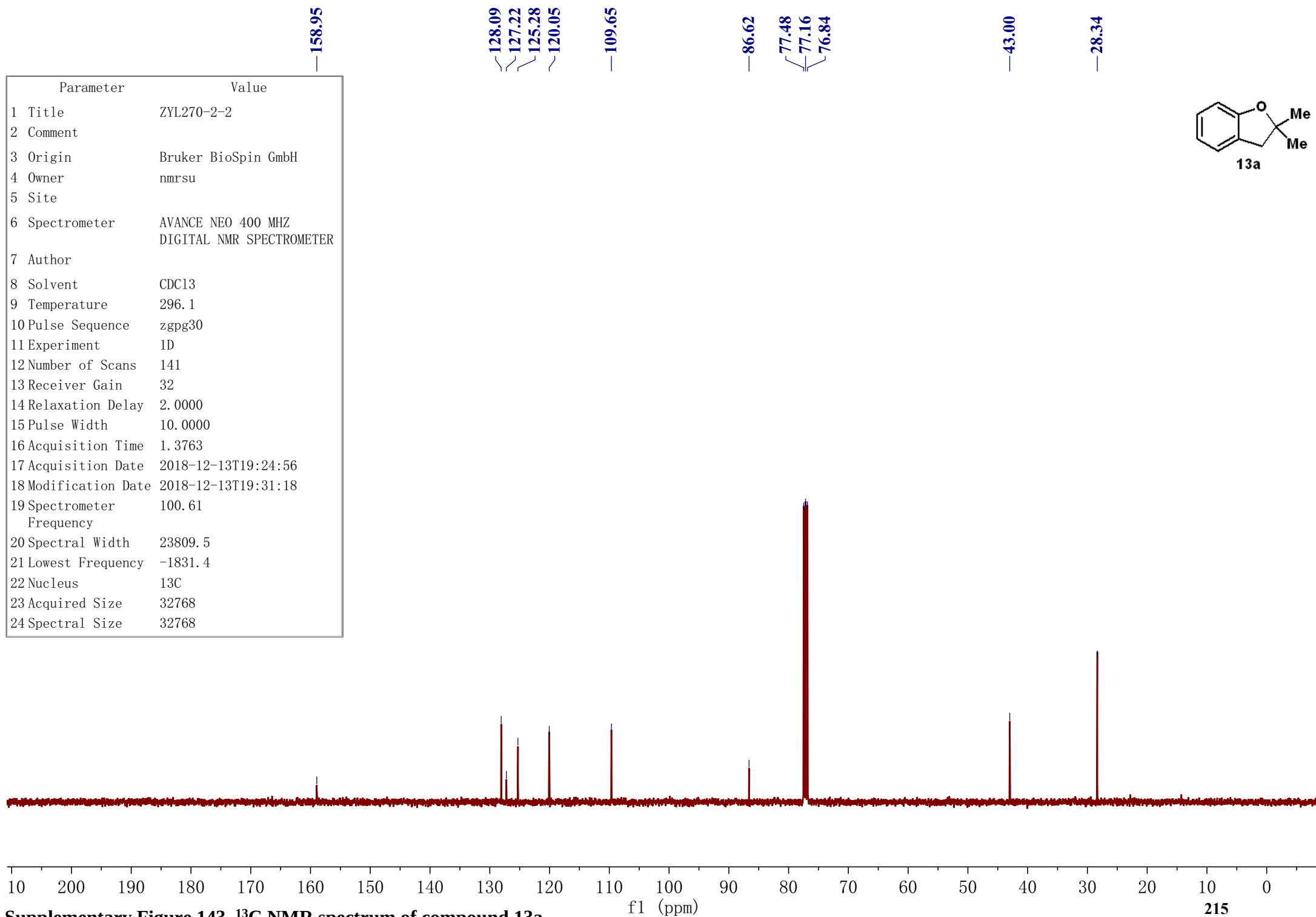
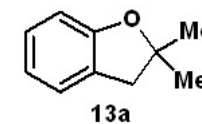
12a



Supplementary Figure 141. ¹³C NMR spectrum of compound 12a

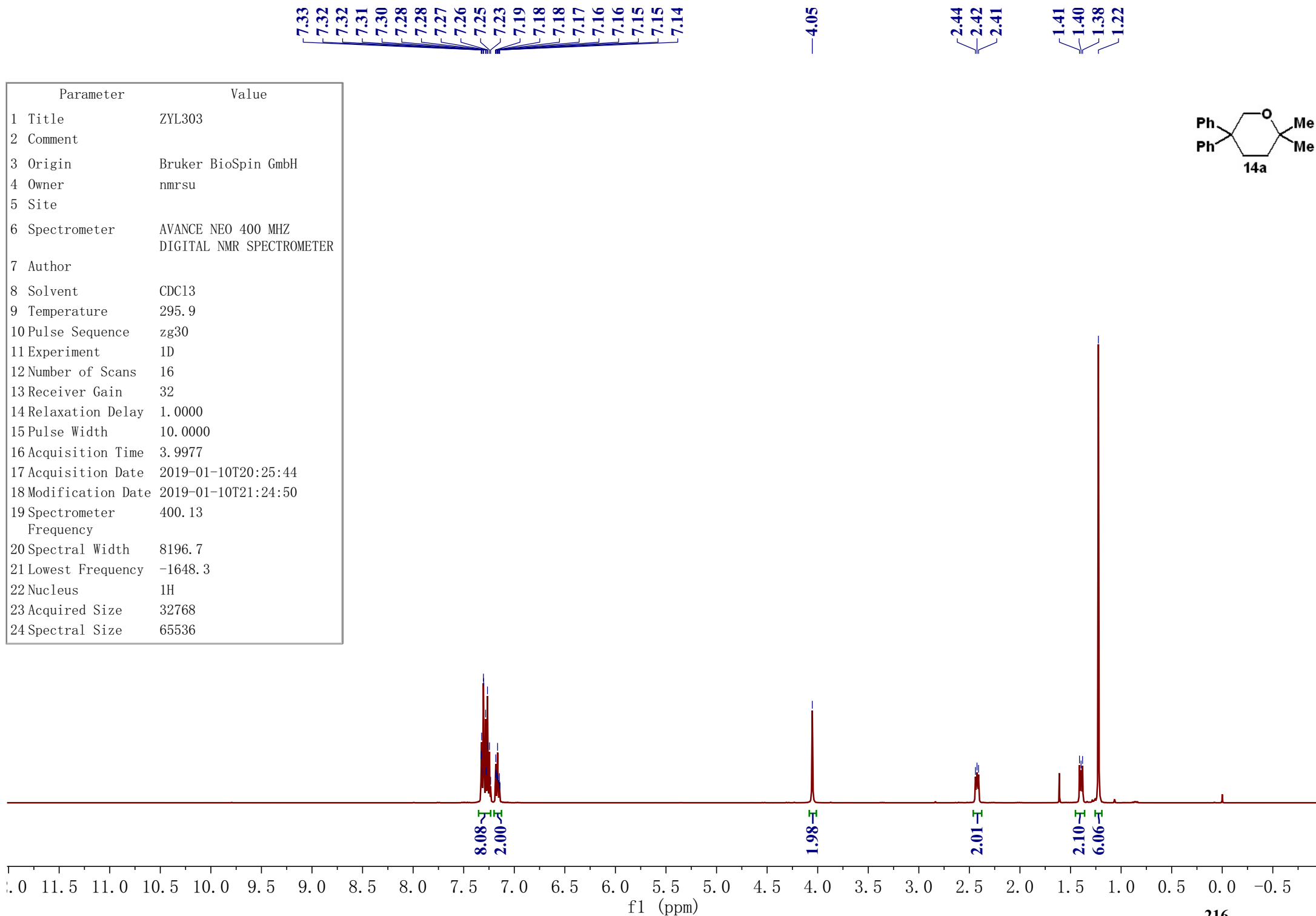
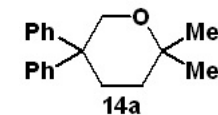


Parameter	Value
1 Title	ZYL270-2-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	141
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-13T19:24:56
18 Modification Date	2018-12-13T19:31:18
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1831.4
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



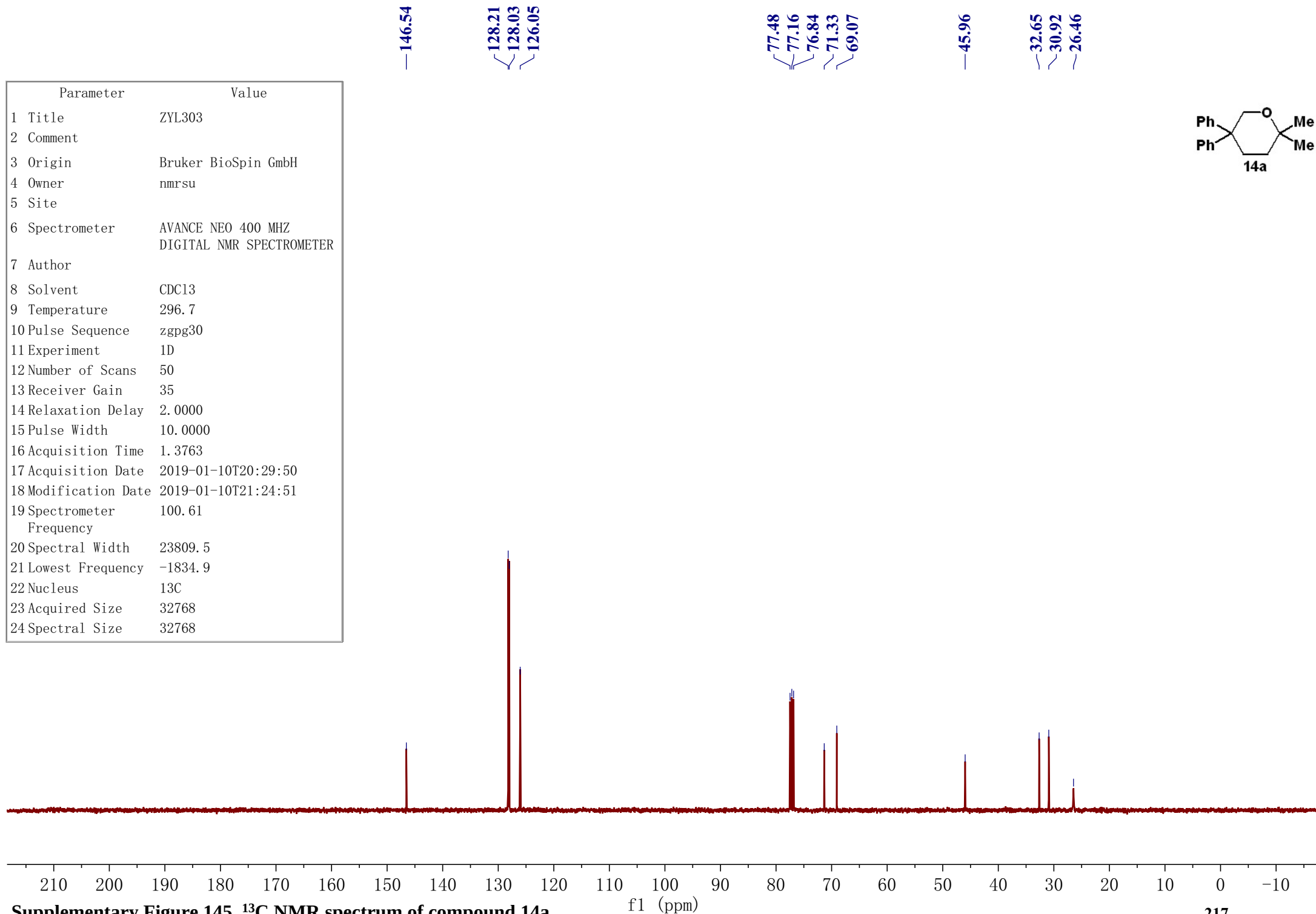
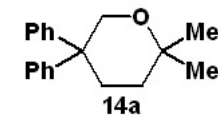
Supplementary Figure 143. ¹³C NMR spectrum of compound 13a

Parameter	Value
1 Title	ZYL303
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.9
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-01-10T20:25:44
18 Modification Date	2019-01-10T21:24:50
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1648.3
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Supplementary Figure 144. ¹H NMR spectrum of compound 14a

Parameter	Value
1 Title	ZYL303
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.7
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	50
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-01-10T20:29:50
18 Modification Date	2019-01-10T21:24:51
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1834.9
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

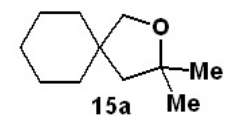


Supplementary Figure 145. ¹³C NMR spectrum of compound 14a

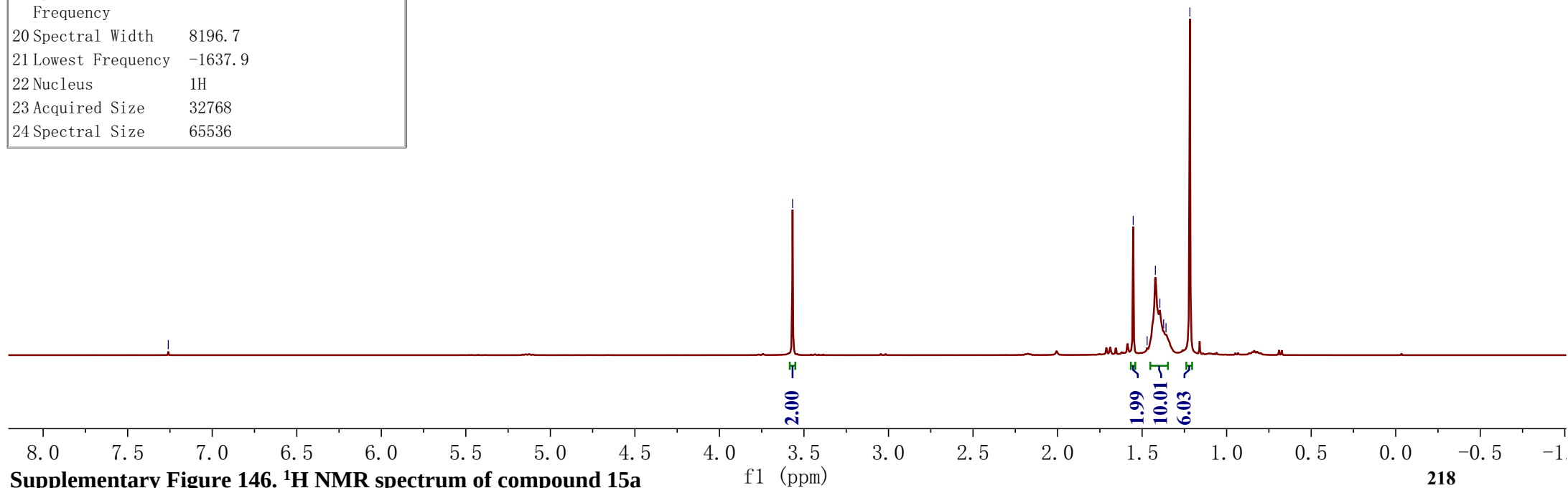
—7.26

—3.57

1.55
1.47
1.42
1.39
1.37
1.36
1.22

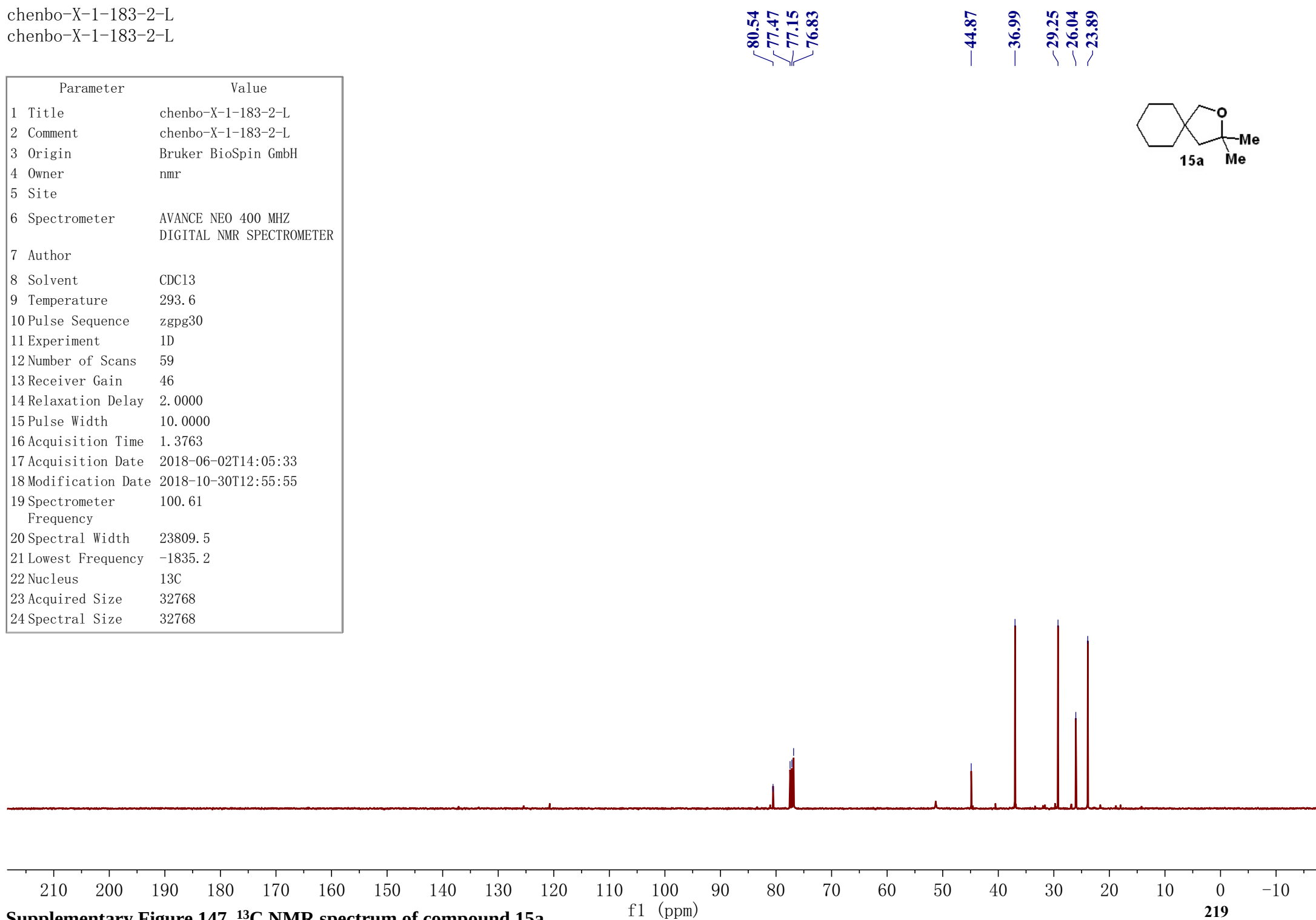
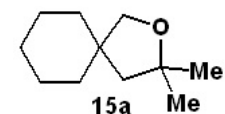


Parameter	Value
1 Title	chenbo-X-1-183-2-L
2 Comment	chenbo-X-1-183-2-L
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	293.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	15
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-06-02T14:00:58
18 Modification Date	2018-10-30T12:55:54
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.9
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

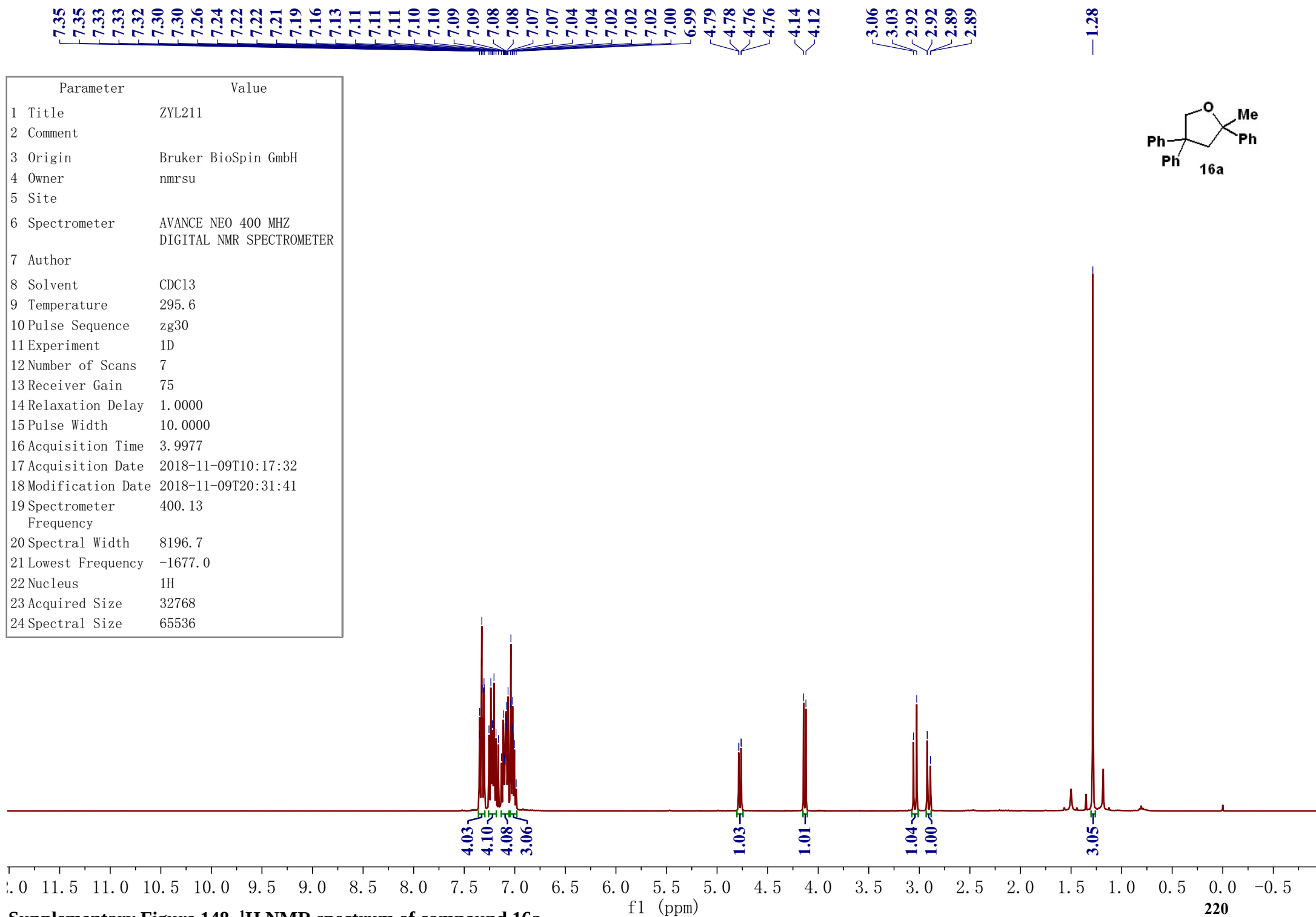


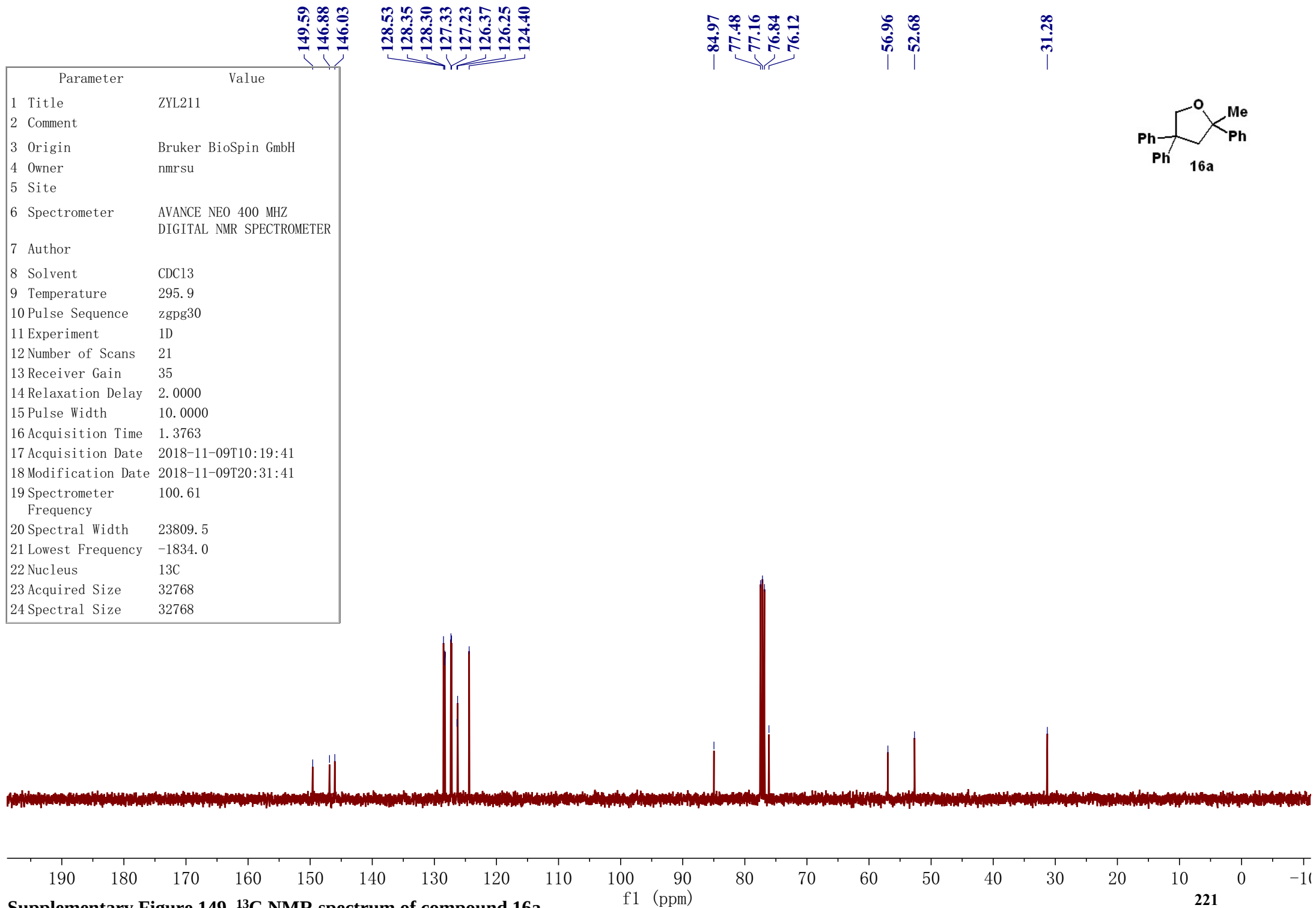
chenbo-X-1-183-2-L
chenbo-X-1-183-2-L

Parameter	Value
1 Title	chenbo-X-1-183-2-L
2 Comment	chenbo-X-1-183-2-L
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	293.6
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	59
13 Receiver Gain	46
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-06-02T14:05:33
18 Modification Date	2018-10-30T12:55:55
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1835.2
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



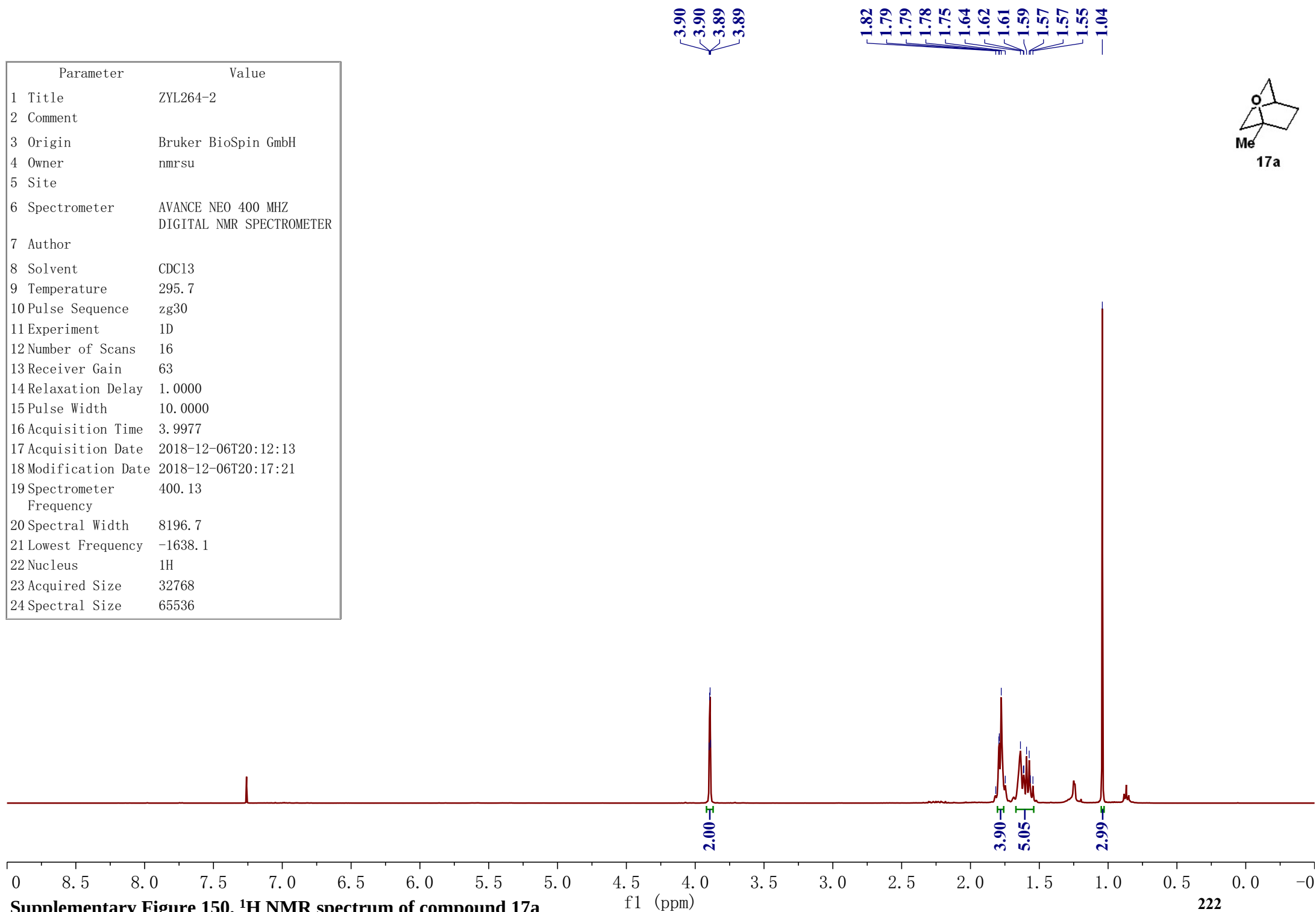
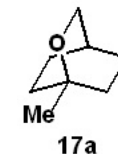
Supplementary Figure 147. ¹³C NMR spectrum of compound 15a





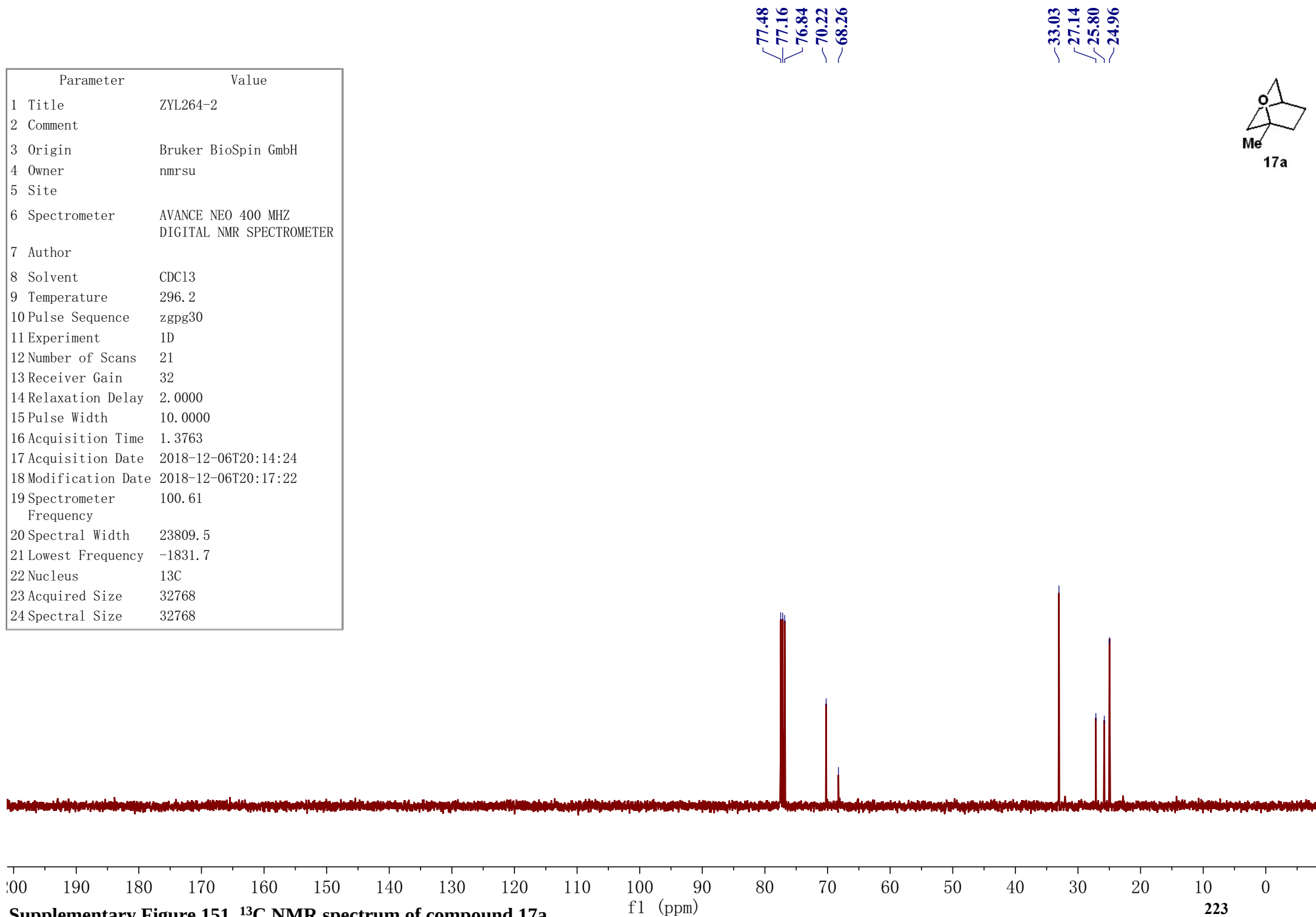
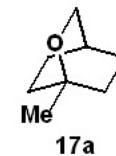
Supplementary Figure 149. ¹³C NMR spectrum of compound 16a

Parameter	Value
1 Title	ZYL264-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	295.7
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	63
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-12-06T20:12:13
18 Modification Date	2018-12-06T20:17:21
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.1
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536

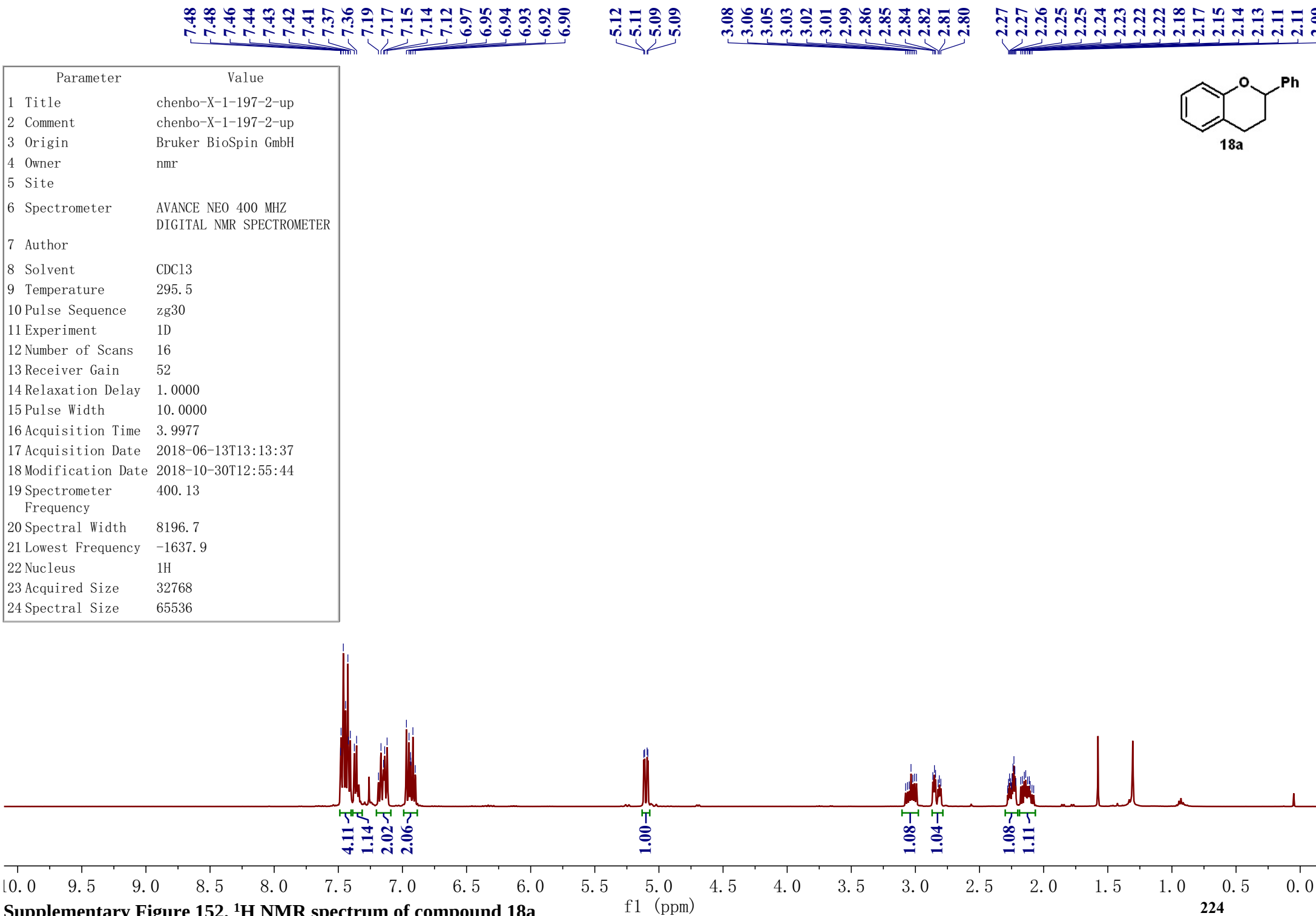


Supplementary Figure 150. ¹H NMR spectrum of compound 17a

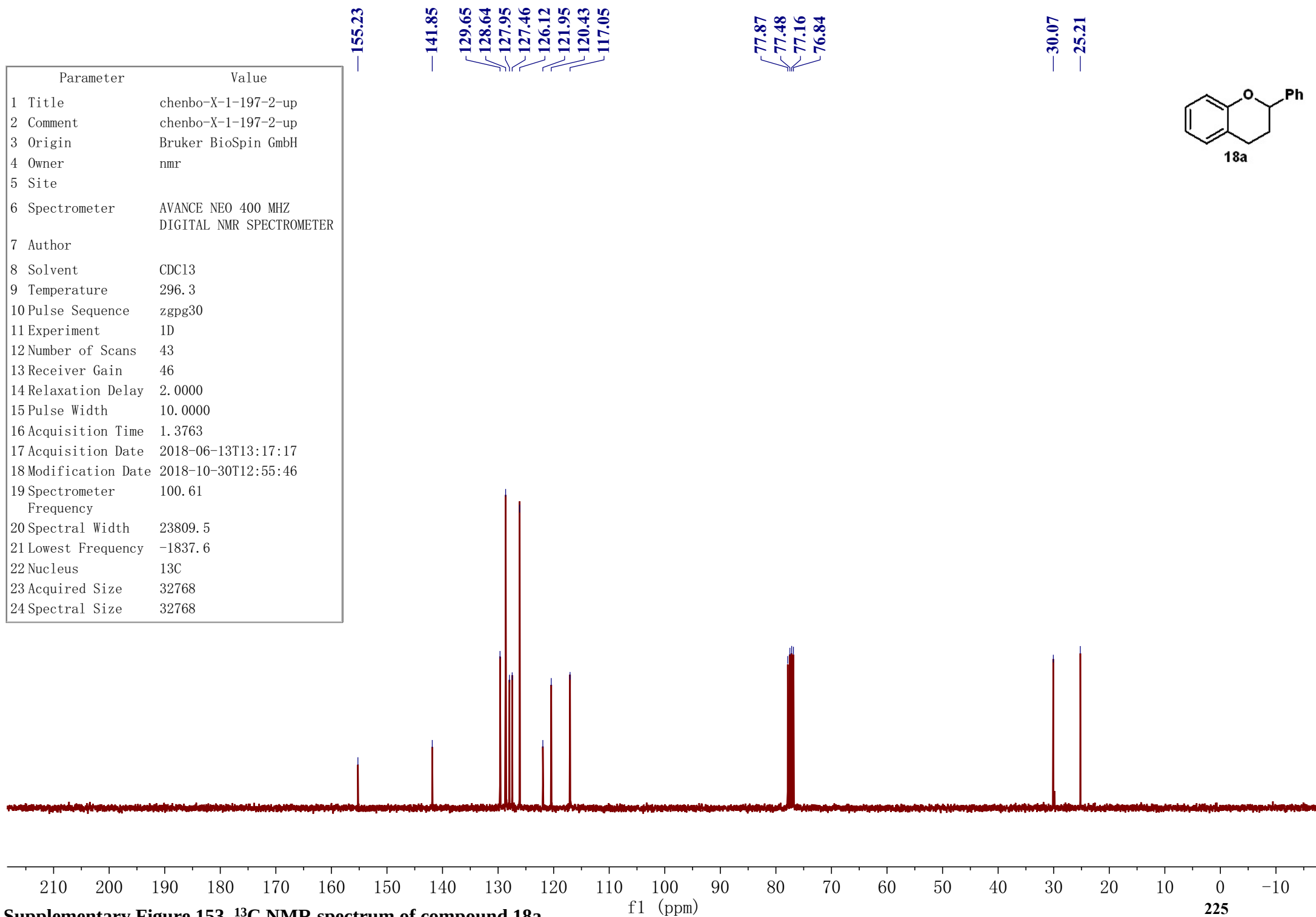
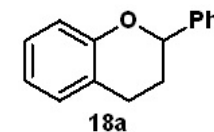
Parameter	Value
1 Title	ZYL264-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	21
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-06T20:14:24
18 Modification Date	2018-12-06T20:17:22
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1831.7
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



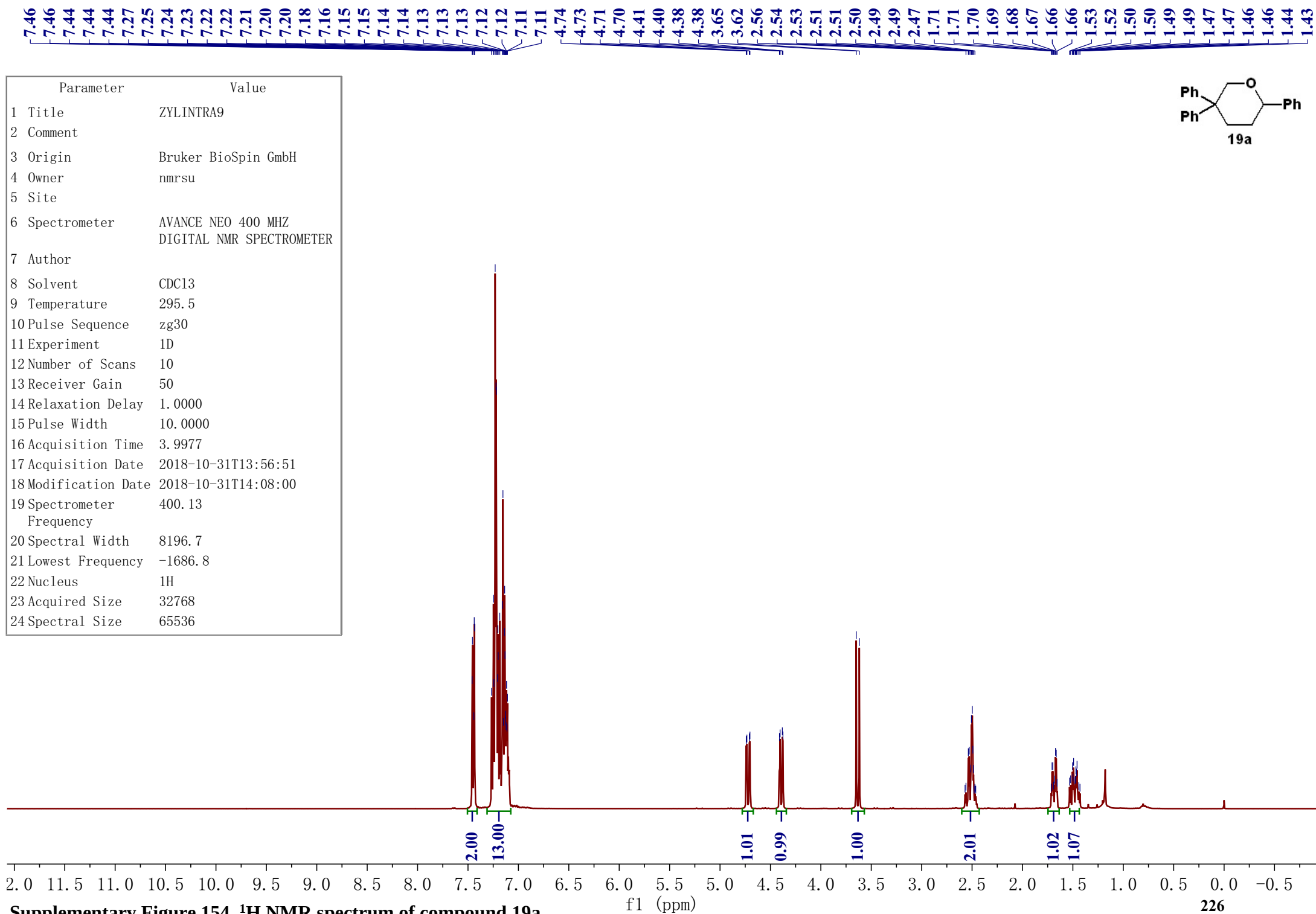
Supplementary Figure 151. ¹³C NMR spectrum of compound 17a



Parameter	Value
1 Title	chenbo-X-1-197-2-up
2 Comment	chenbo-X-1-197-2-up
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	296.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	43
13 Receiver Gain	46
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-06-13T13:17:17
18 Modification Date	2018-10-30T12:55:46
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1837.6
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 153. ¹³C NMR spectrum of compound 18a



Parameter	Value
1 Title	ZYLINTRA13
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	12
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-10-31T17:19:24
18 Modification Date	2018-10-31T17:49:02
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1838.0
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

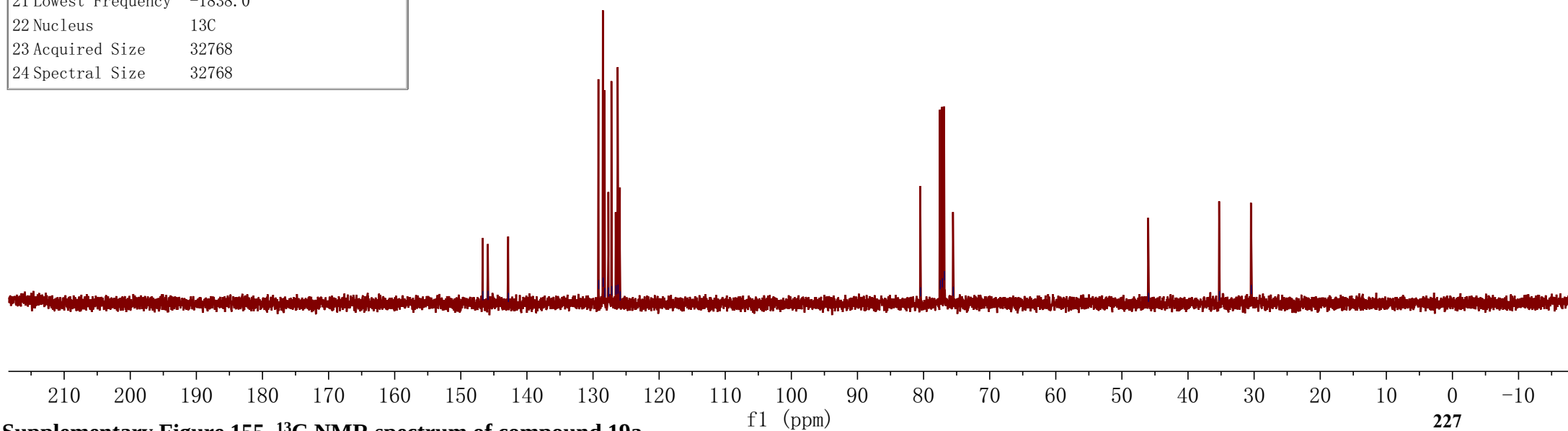
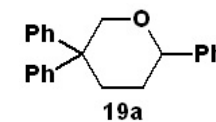
146.66
145.87
142.80
129.14
128.46
128.21
127.64
127.18
126.52
126.23
125.90

80.46
77.48
77.16
76.84
75.50

45.97

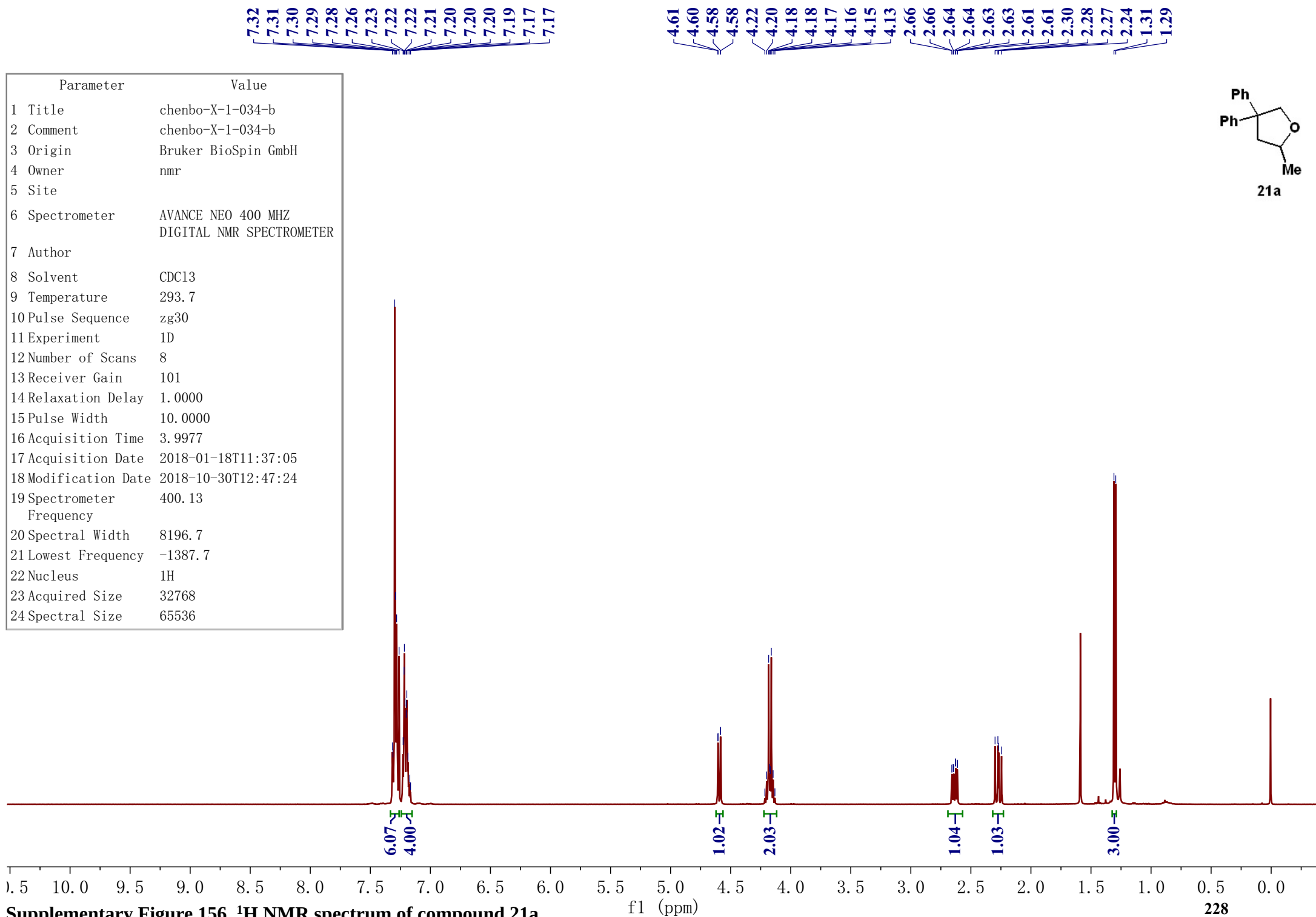
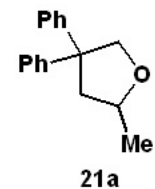
35.24

30.43



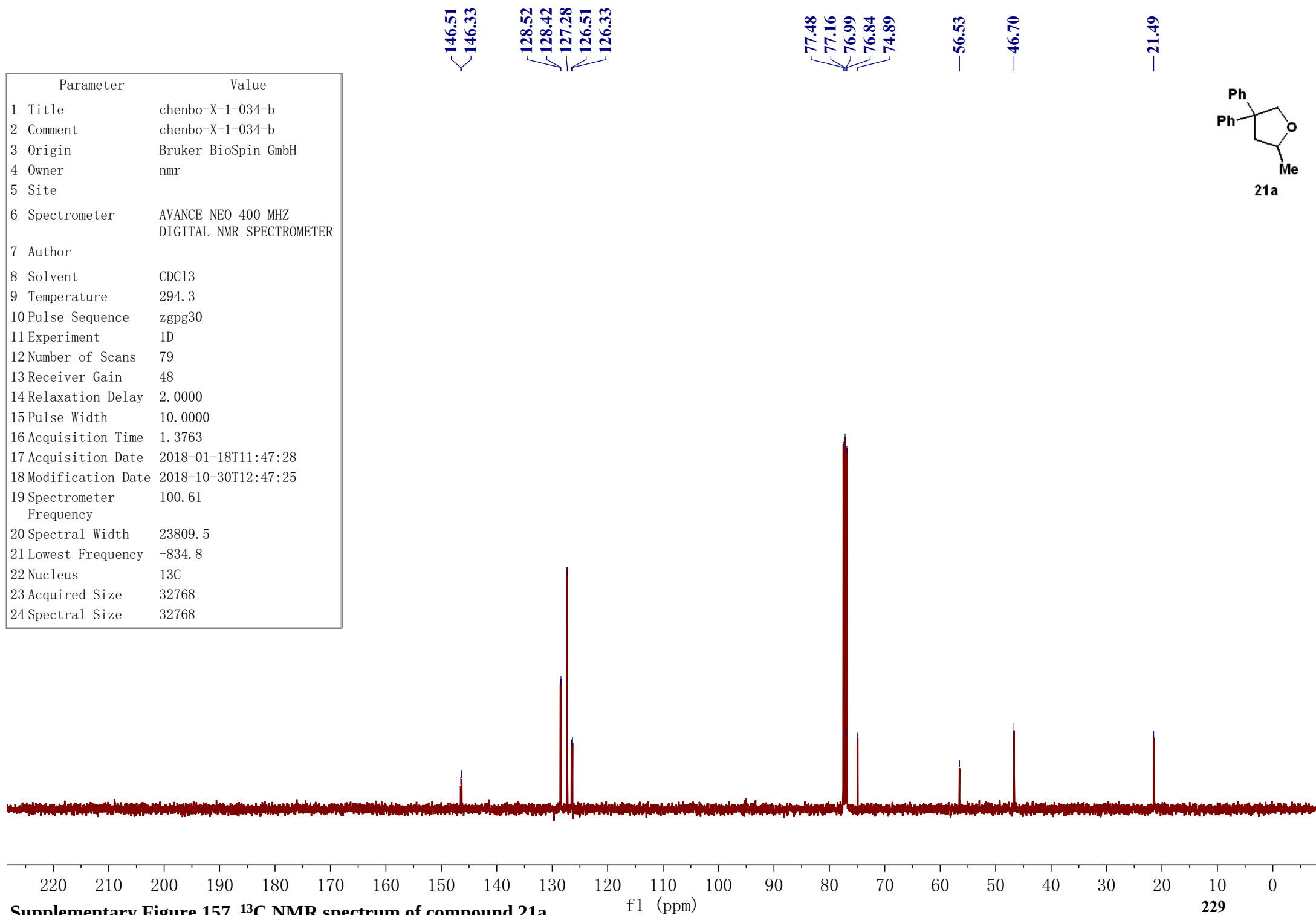
Supplementary Figure 155. ¹³C NMR spectrum of compound 19a

Parameter	Value
1 Title	chenbo-X-1-034-b
2 Comment	chenbo-X-1-034-b
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	293.7
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-01-18T11:37:05
18 Modification Date	2018-10-30T12:47:24
19 Spectrometer Frequency	400.13
20 Spectral Width	8196.7
21 Lowest Frequency	-1387.7
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

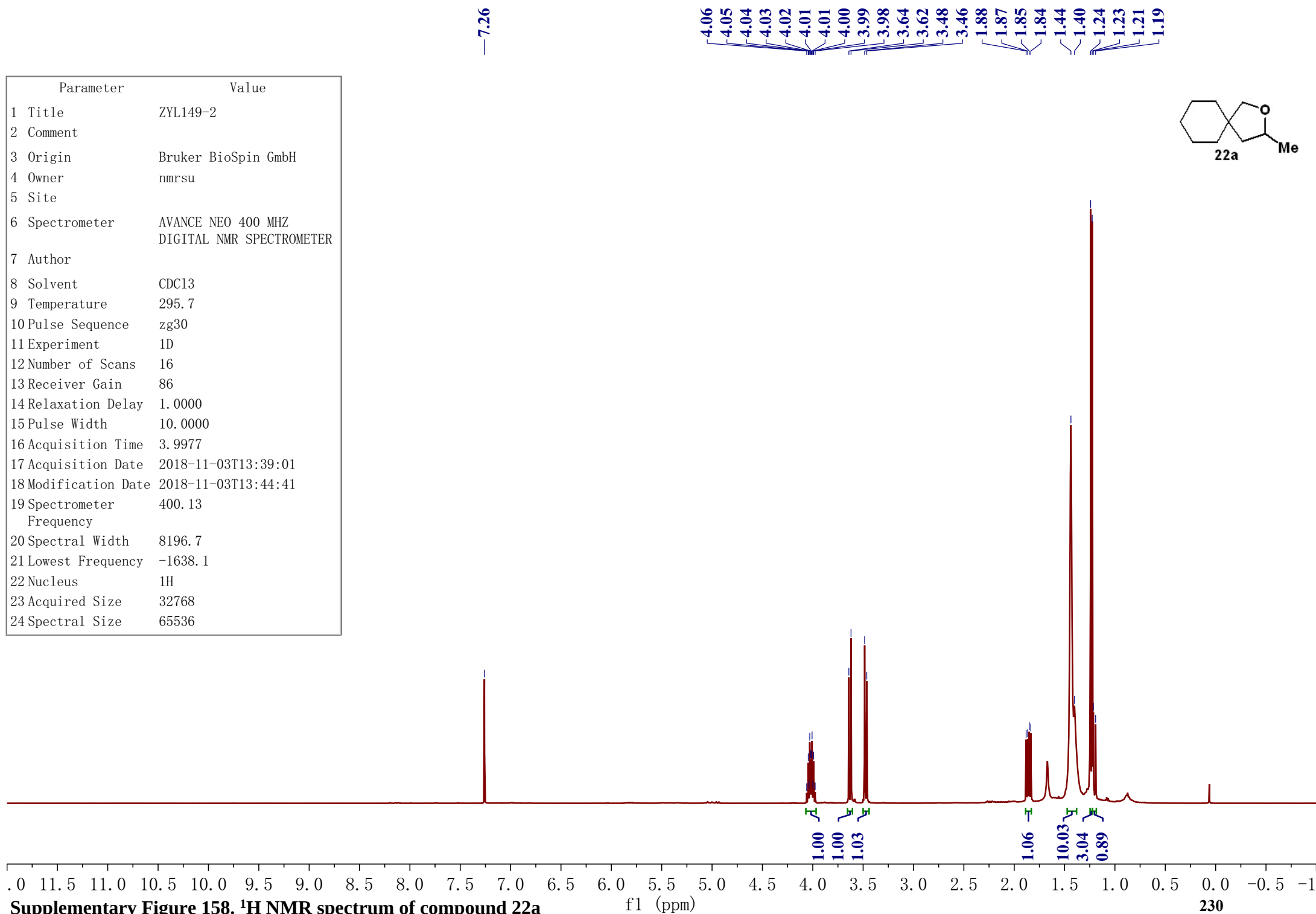
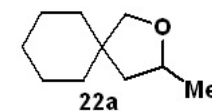


Supplementary Figure 156. ¹H NMR spectrum of compound 21a

Parameter	Value
1 Title	chenbo-X-1-034-b
2 Comment	chenbo-X-1-034-b
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	294.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	79
13 Receiver Gain	48
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-01-18T11:47:28
18 Modification Date	2018-10-30T12:47:25
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-834.8
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

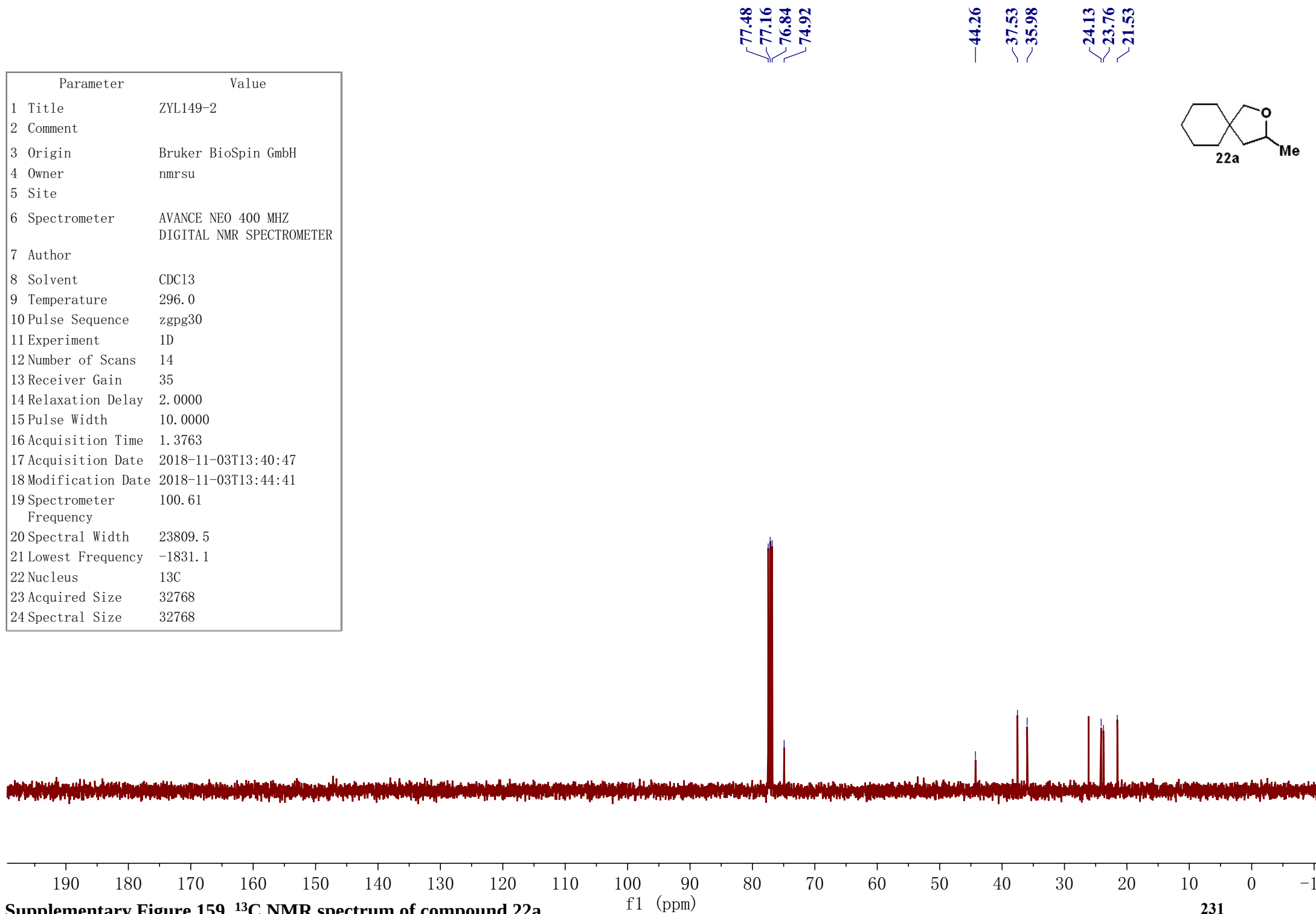
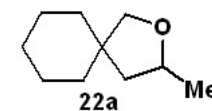


Parameter	Value
1 Title	ZYL149-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	295.7
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	86
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-11-03T13:39:01
18 Modification Date	2018-11-03T13:44:41
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.1
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



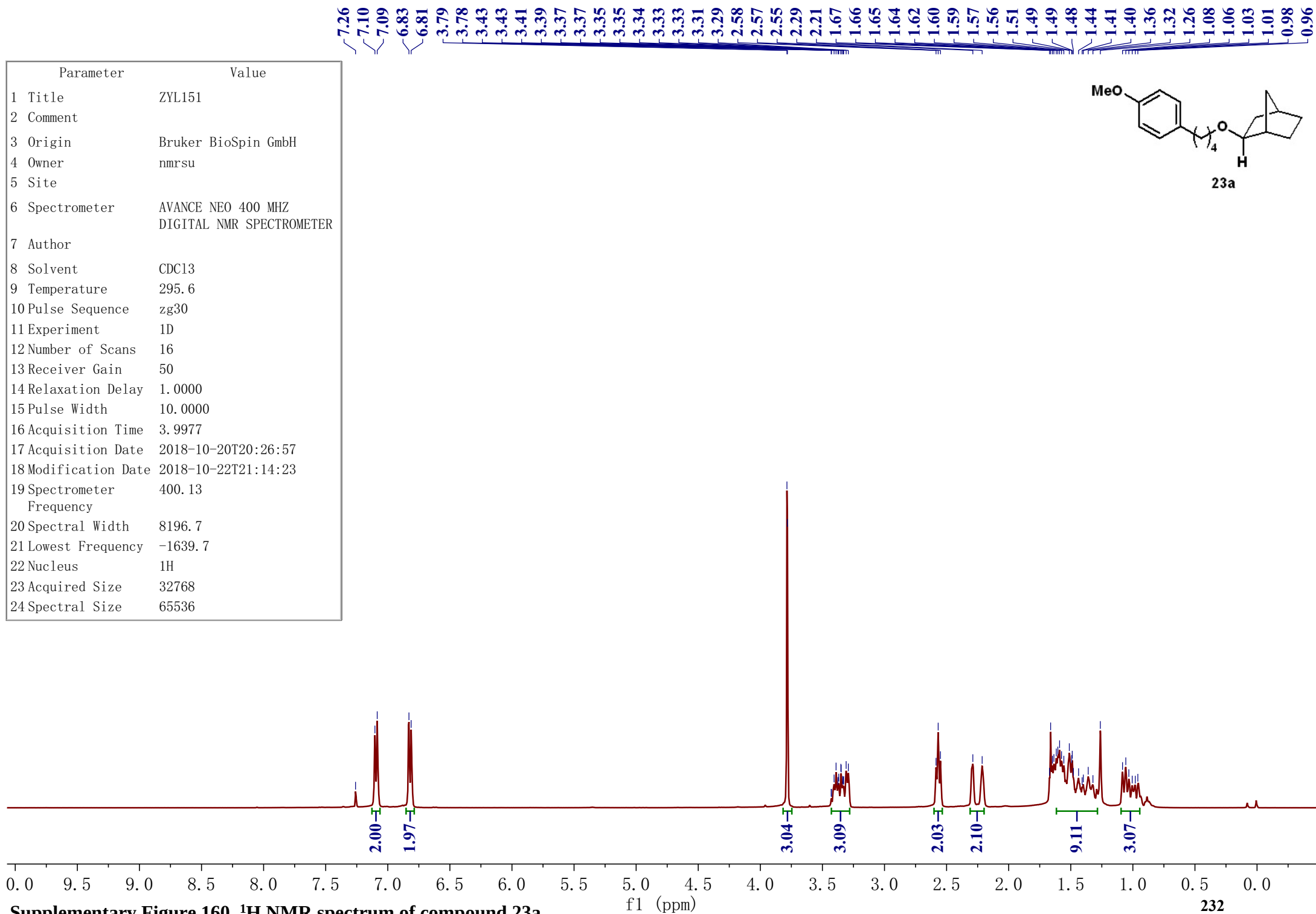
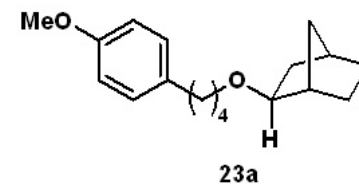
Supplementary Figure 158. ¹H NMR spectrum of compound 22a

Parameter	Value
1 Title	ZYL149-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.0
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	14
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-11-03T13:40:47
18 Modification Date	2018-11-03T13:44:41
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1831.1
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

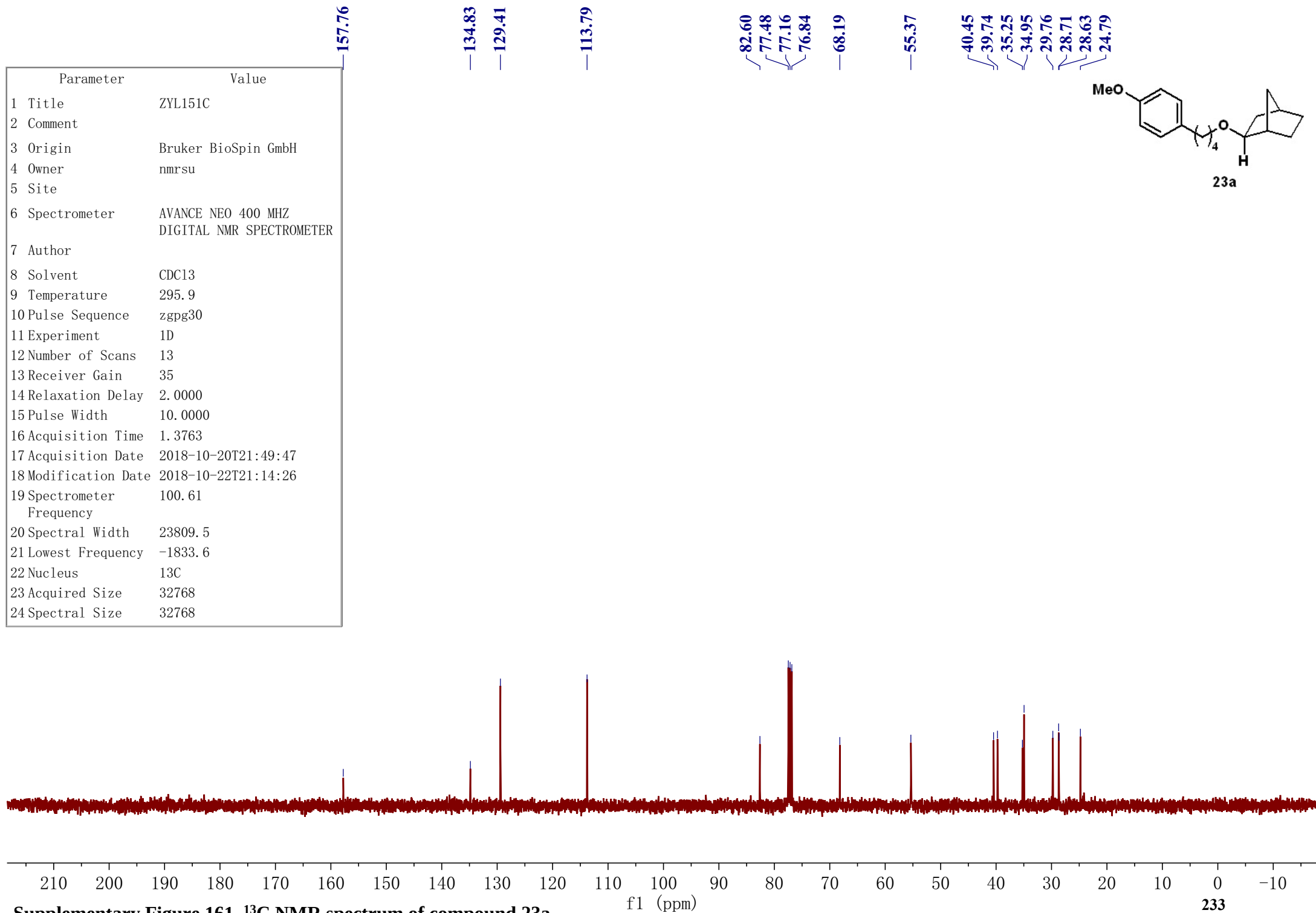


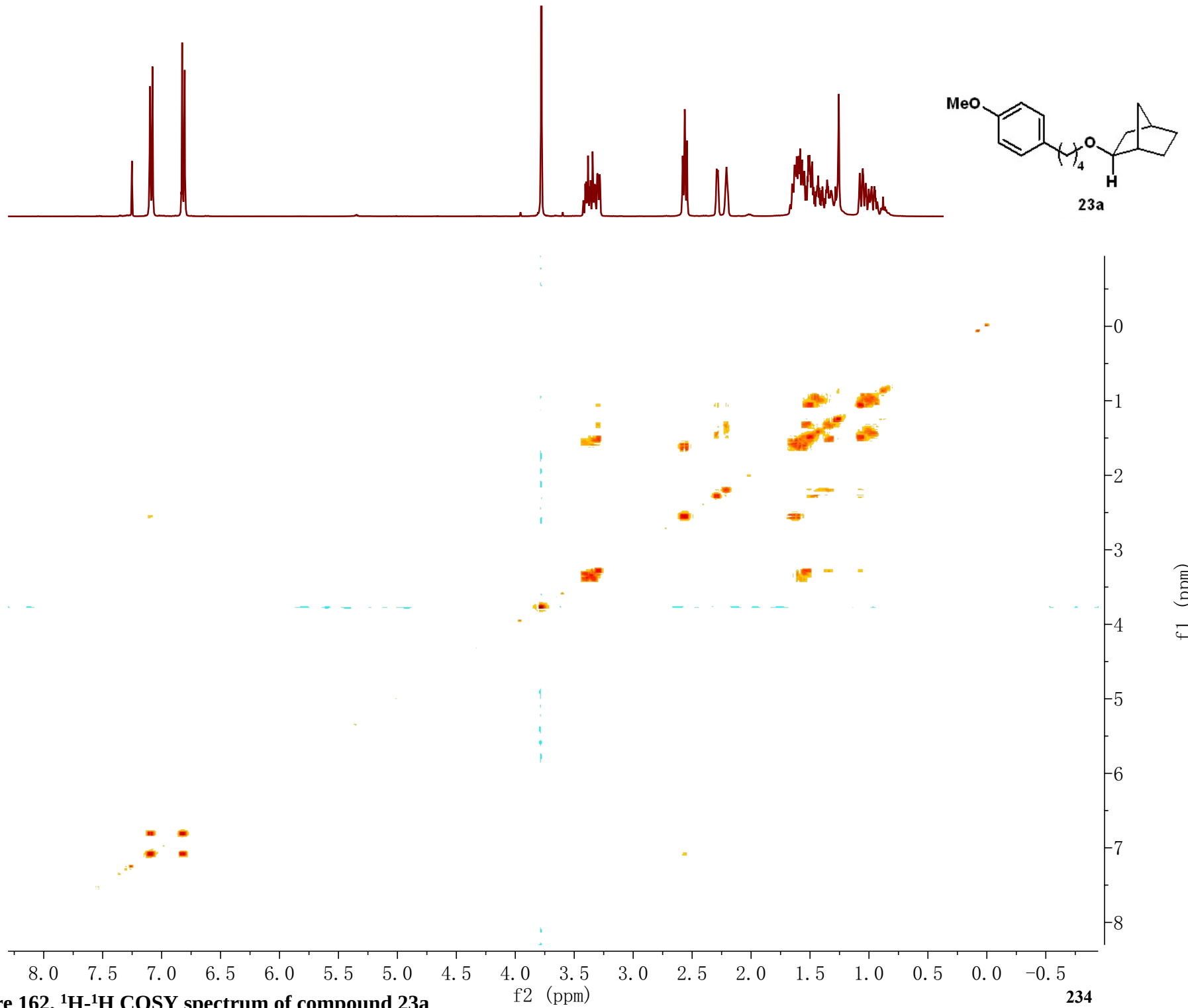
Supplementary Figure 159. ¹³C NMR spectrum of compound 22a

Parameter	Value
1 Title	ZYL151
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	295.6
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	50
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-10-20T20:26:57
18 Modification Date	2018-10-22T21:14:23
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1639.7
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536

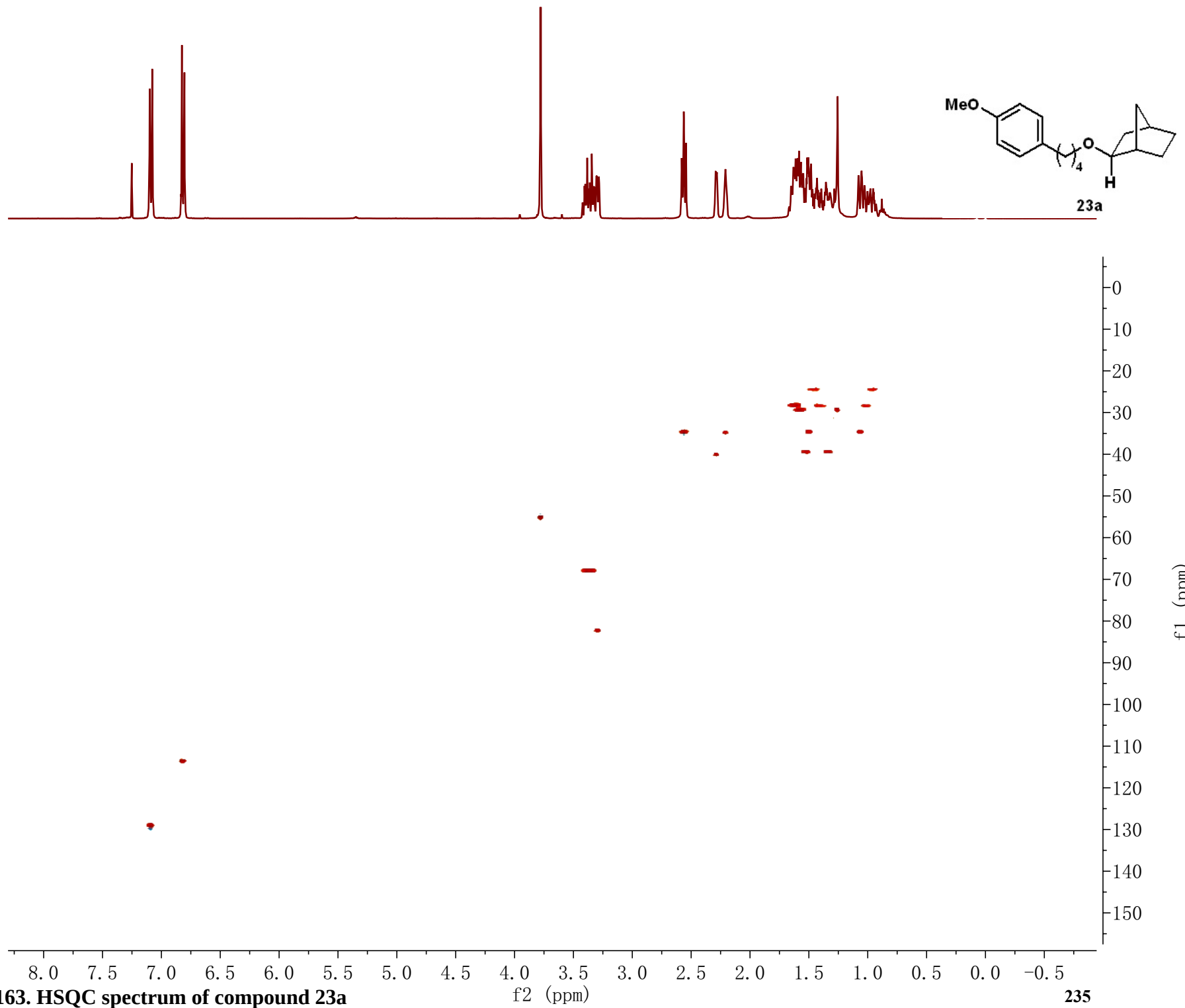


Supplementary Figure 160. ¹H NMR spectrum of compound 23a

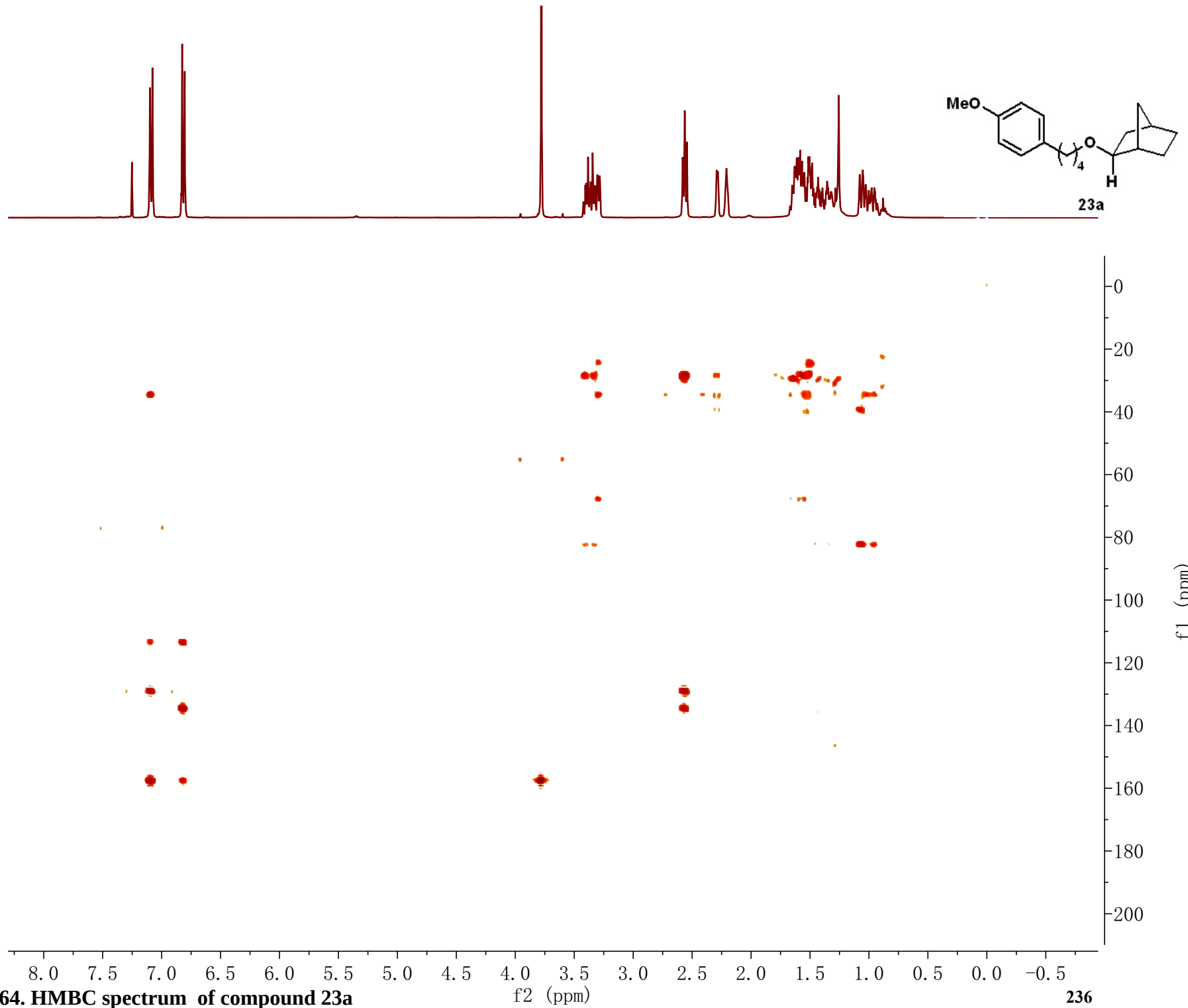




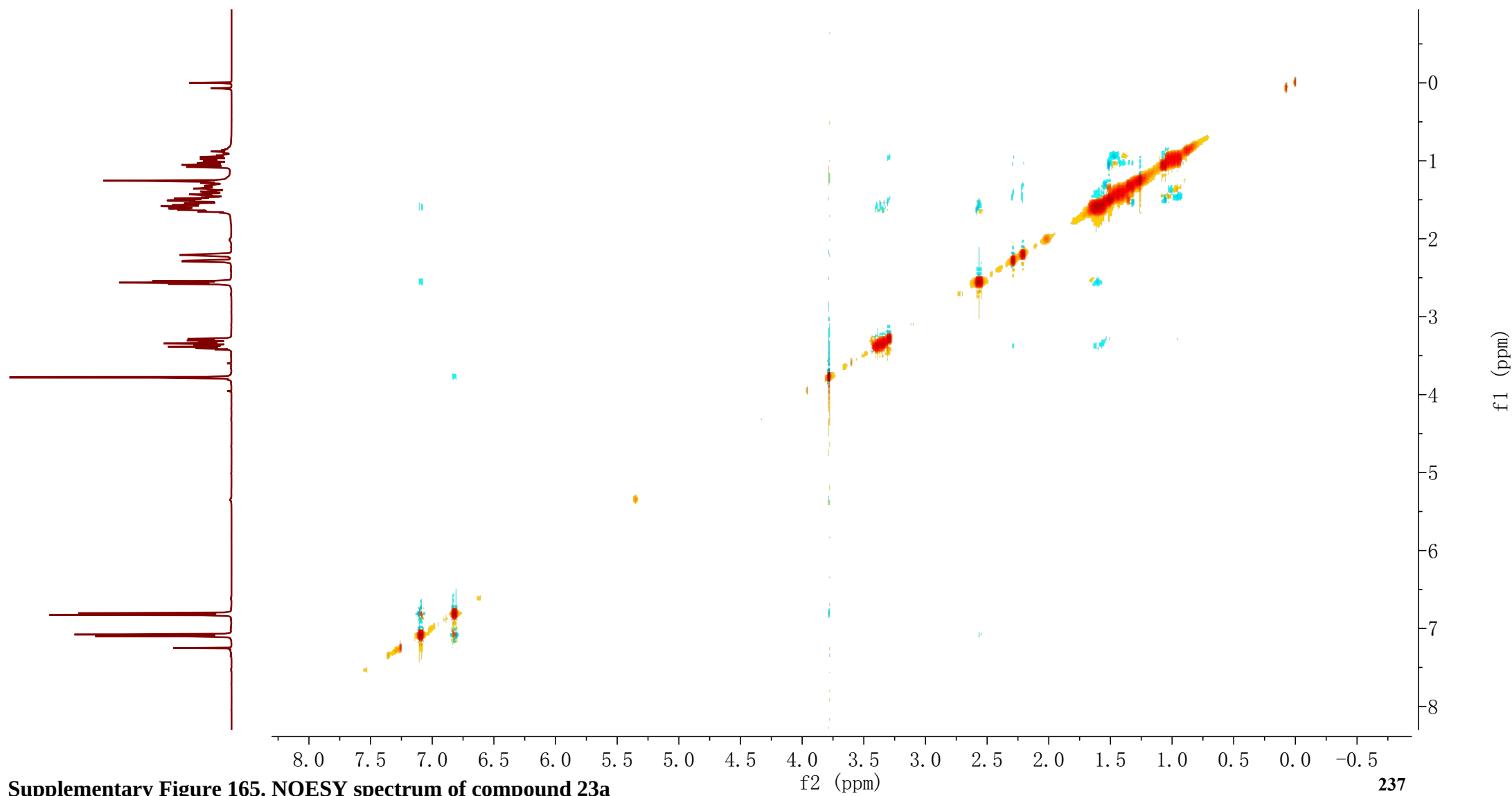
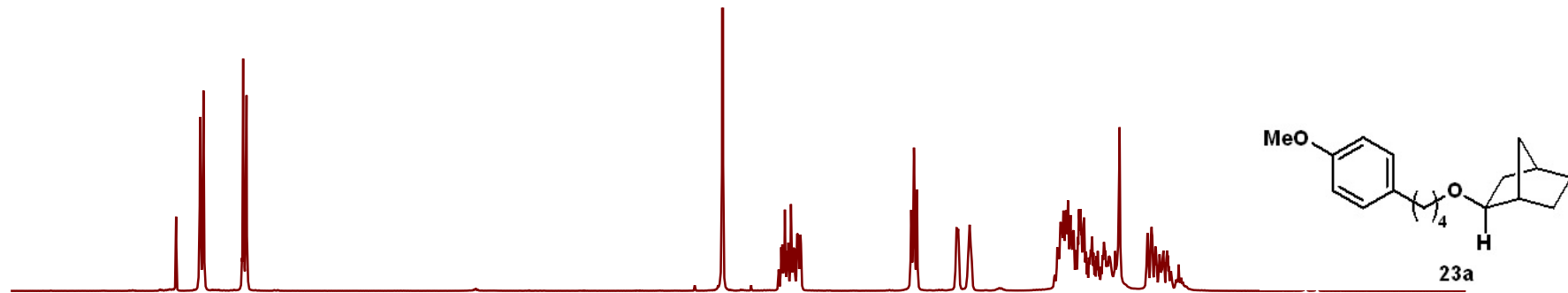
Supplementary Figure 162. ^1H - ^1H COSY spectrum of compound 23a



Supplementary Figure 163. HSQC spectrum of compound 23a

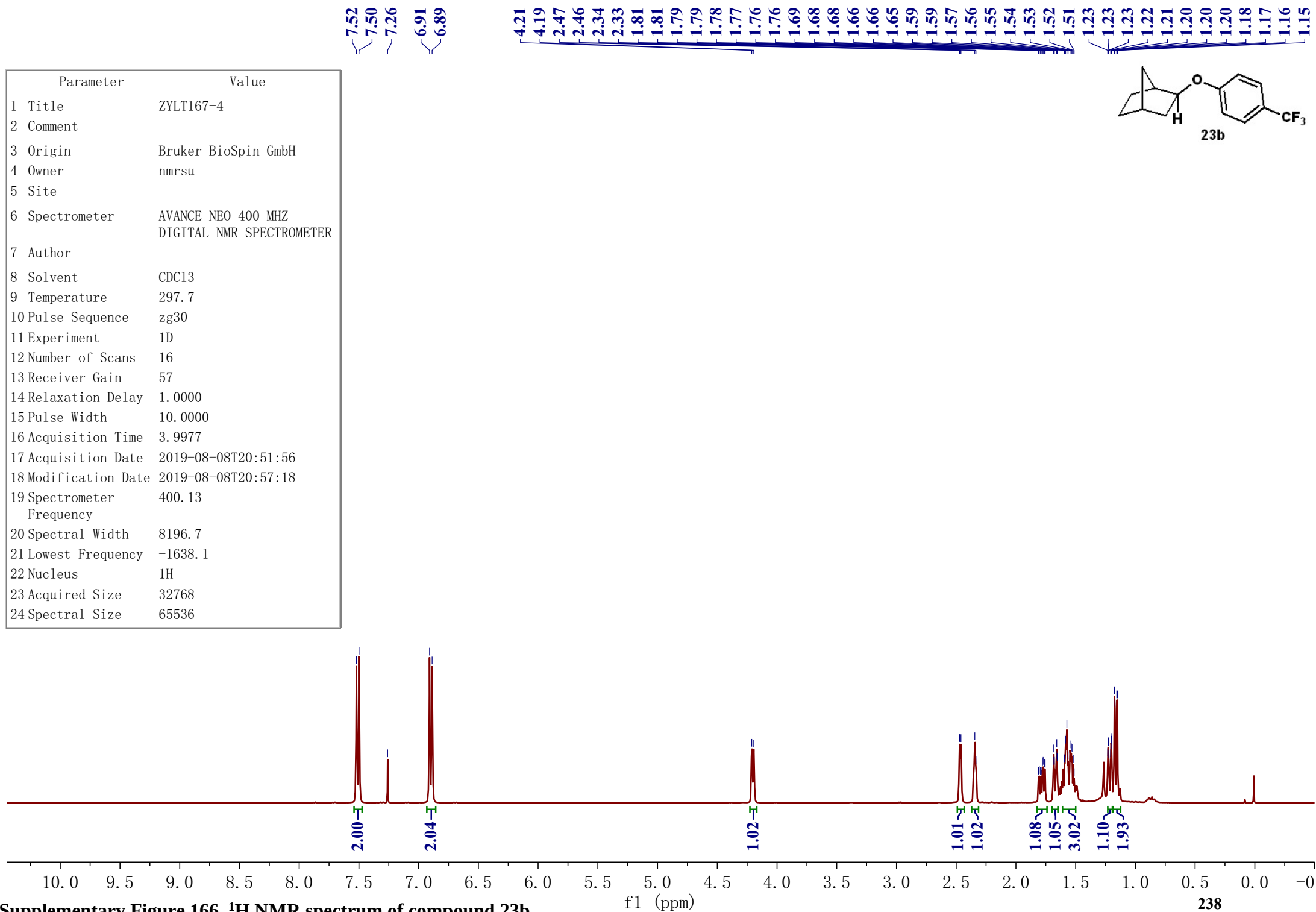
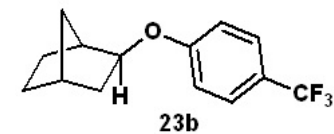


Supplementary Figure 164. HMBC spectrum of compound 23a



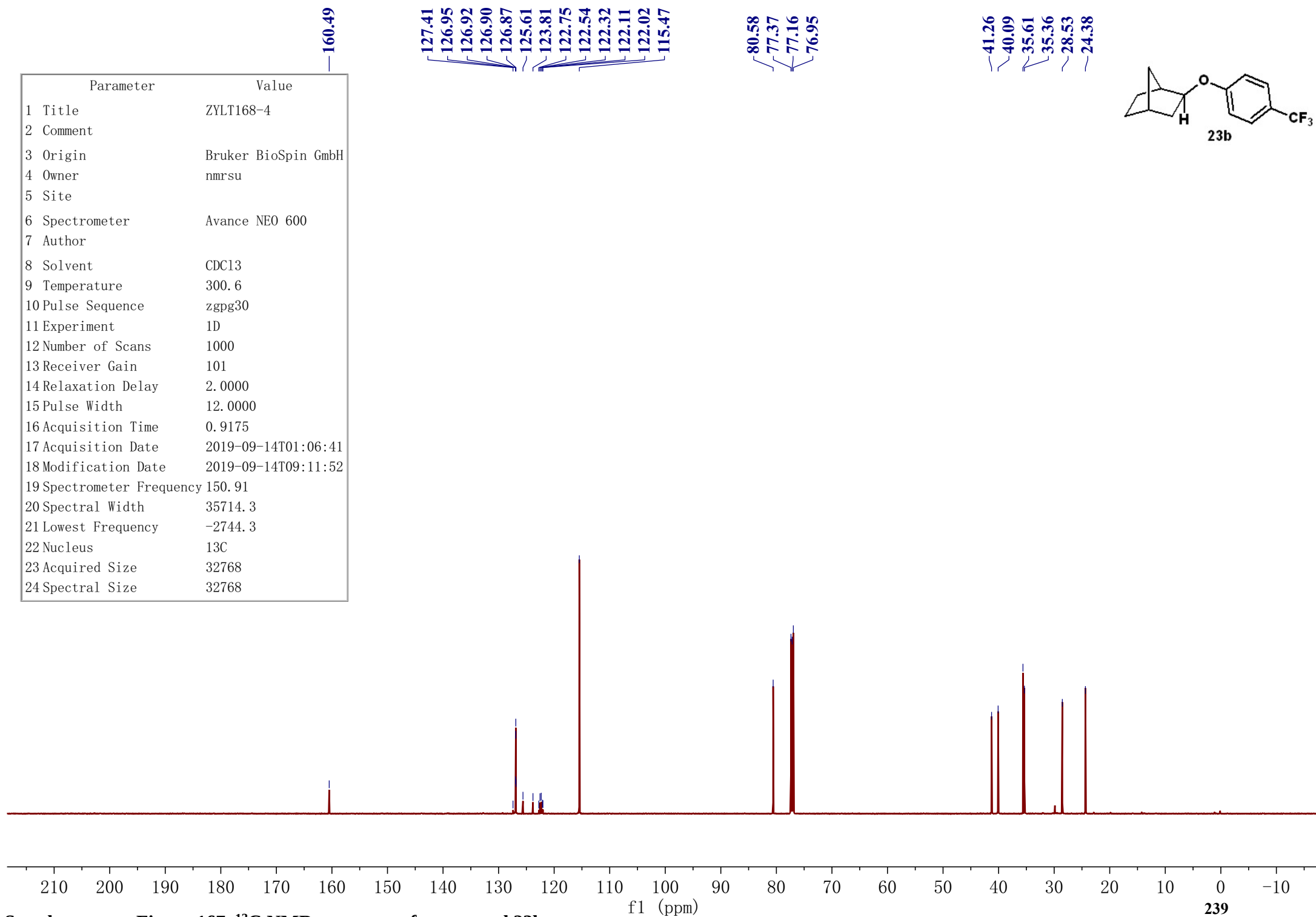
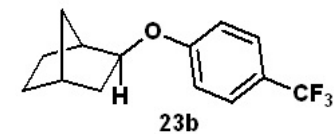
Supplementary Figure 165. NOESY spectrum of compound 23a

Parameter	Value
1 Title	ZYLT167-4
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	297.7
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	57
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-08-08T20:51:56
18 Modification Date	2019-08-08T20:57:18
19 Spectrometer	400.13 Frequency
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.1
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



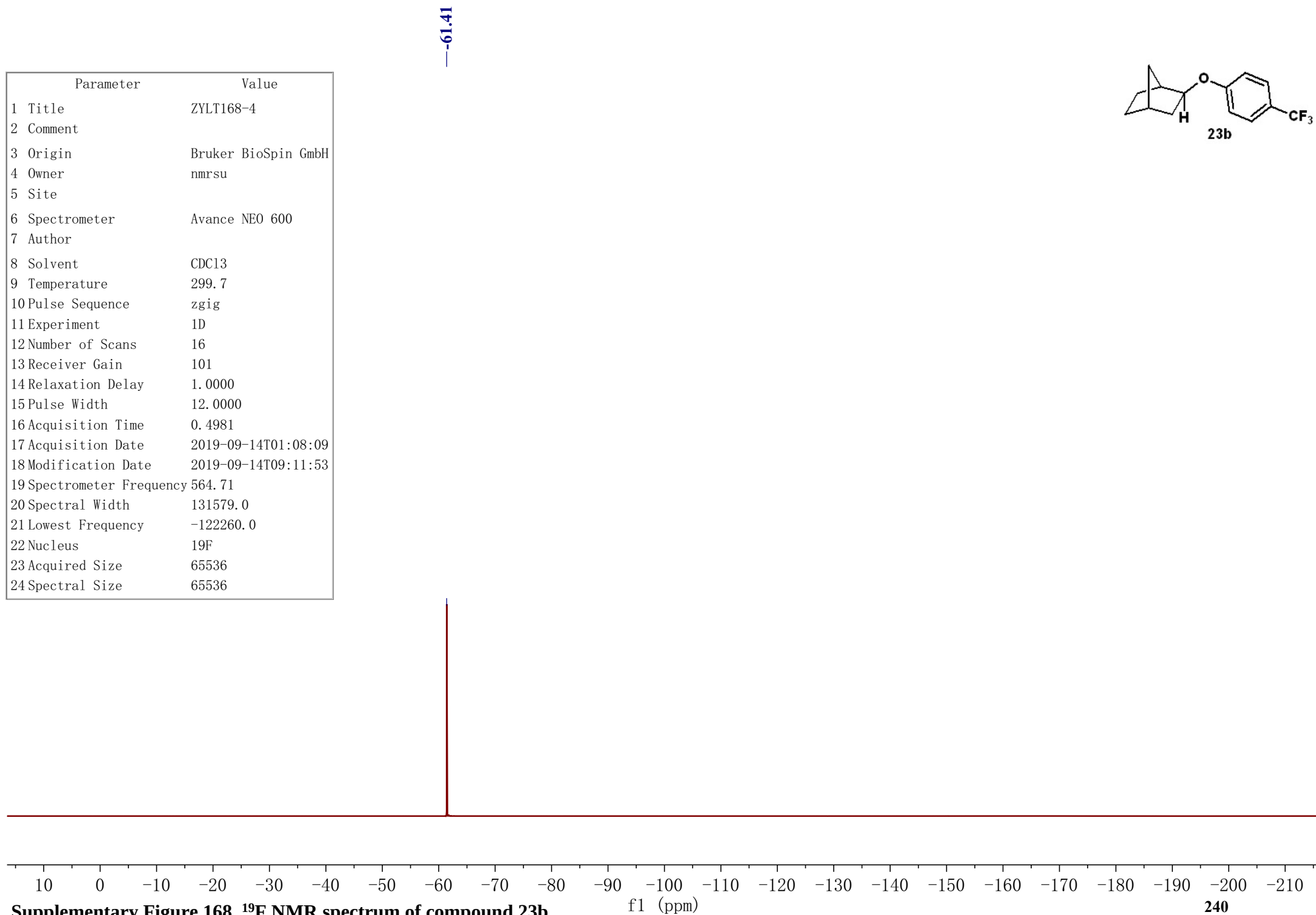
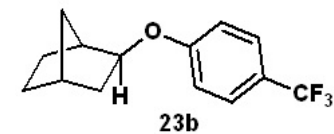
Supplementary Figure 166. ¹H NMR spectrum of compound 23b

Parameter	Value
1 Title	ZYLT168-4
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	300.6
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	1000
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-09-14T01:06:41
18 Modification Date	2019-09-14T09:11:52
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2744.3
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768

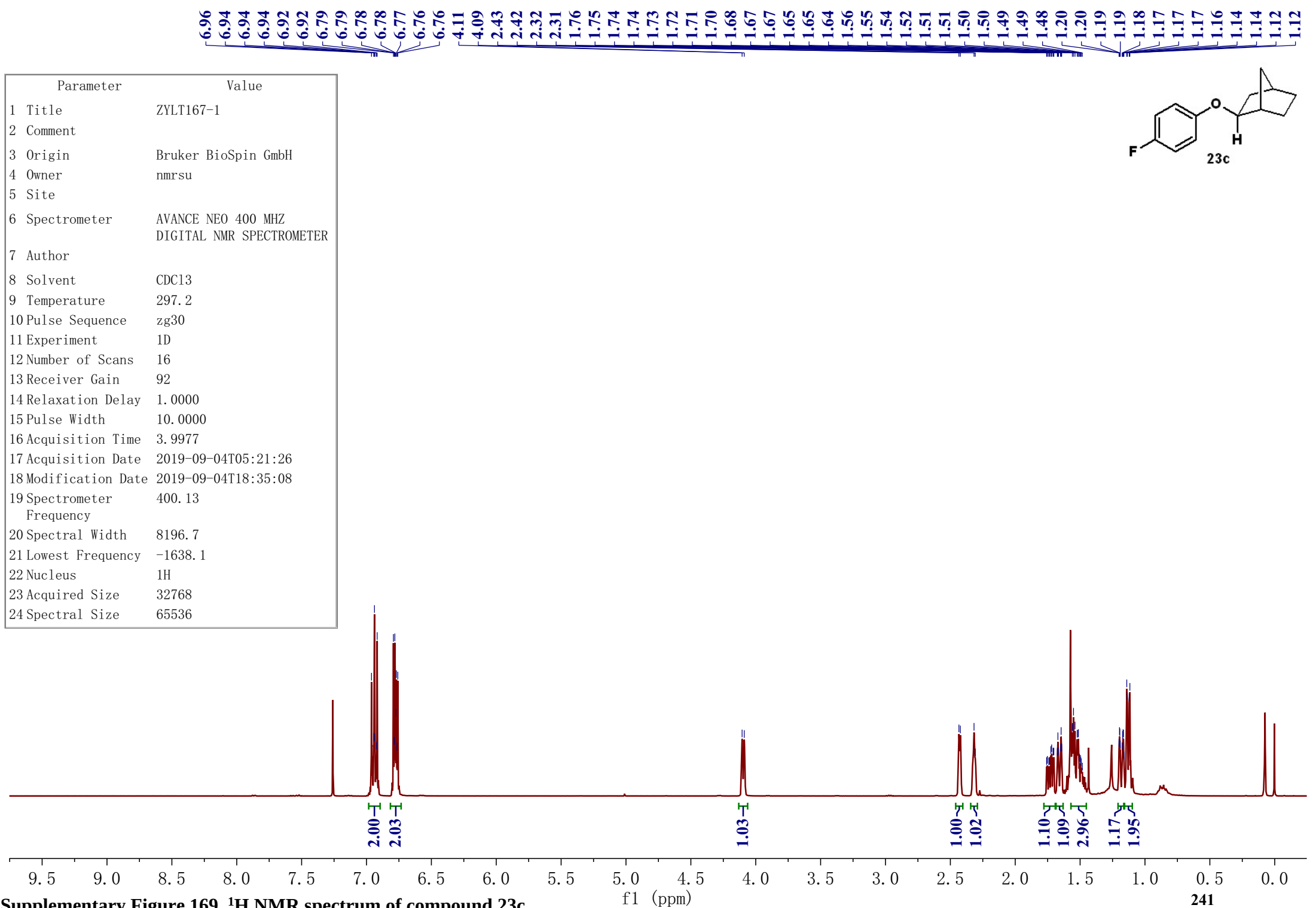
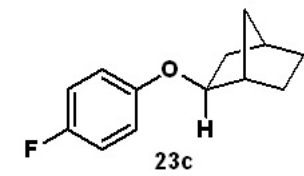


Supplementary Figure 167. ¹³C NMR spectrum of compound 23b

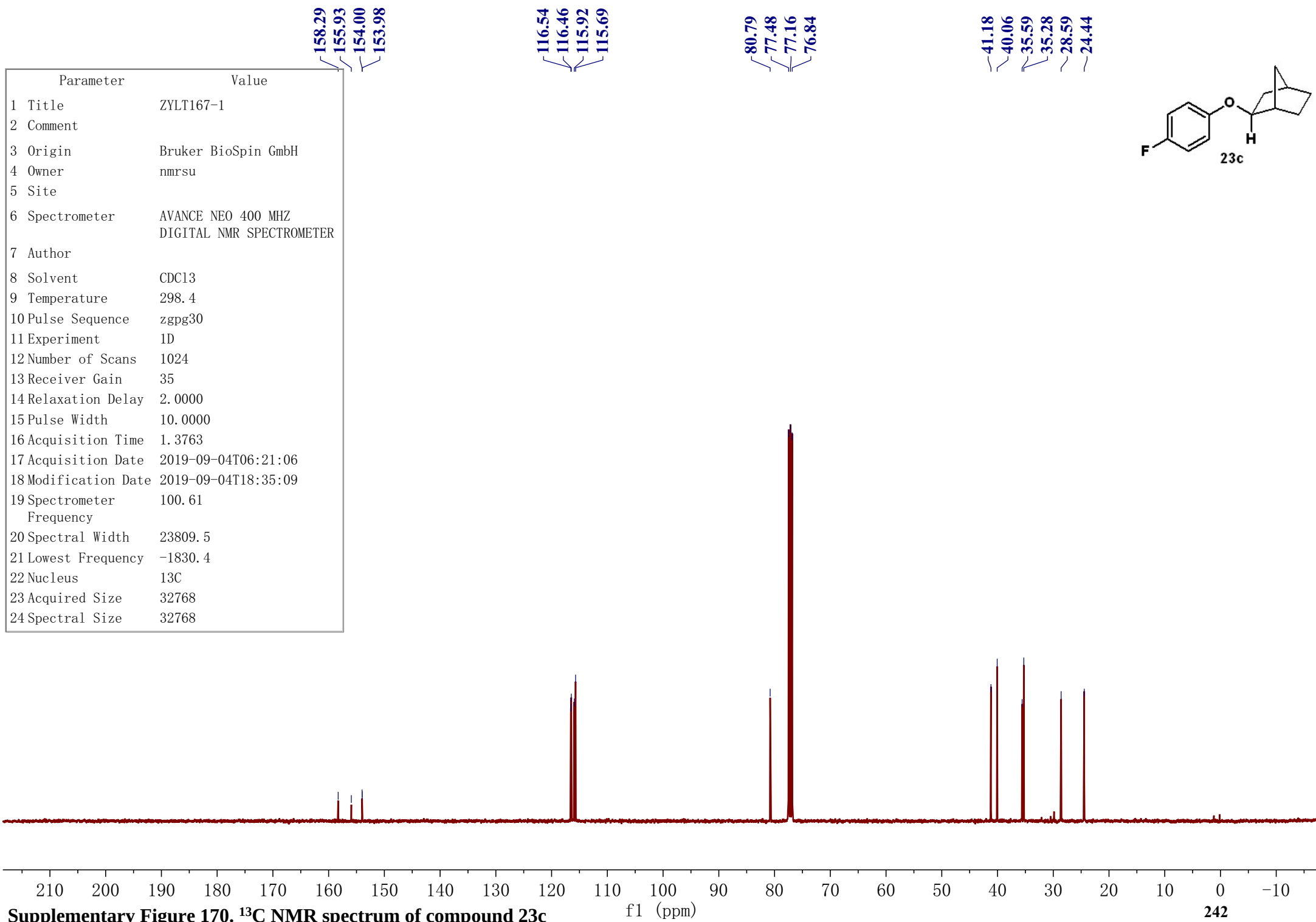
Parameter	Value
1 Title	ZYLT168-4
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	299.7
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.4981
17 Acquisition Date	2019-09-14T01:08:09
18 Modification Date	2019-09-14T09:11:53
19 Spectrometer Frequency	564.71
20 Spectral Width	131579.0
21 Lowest Frequency	-122260.0
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536



Parameter	Value
1 Title	ZYLT167-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	297.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	92
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-09-04T05:21:26
18 Modification Date	2019-09-04T18:35:08
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.1
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536

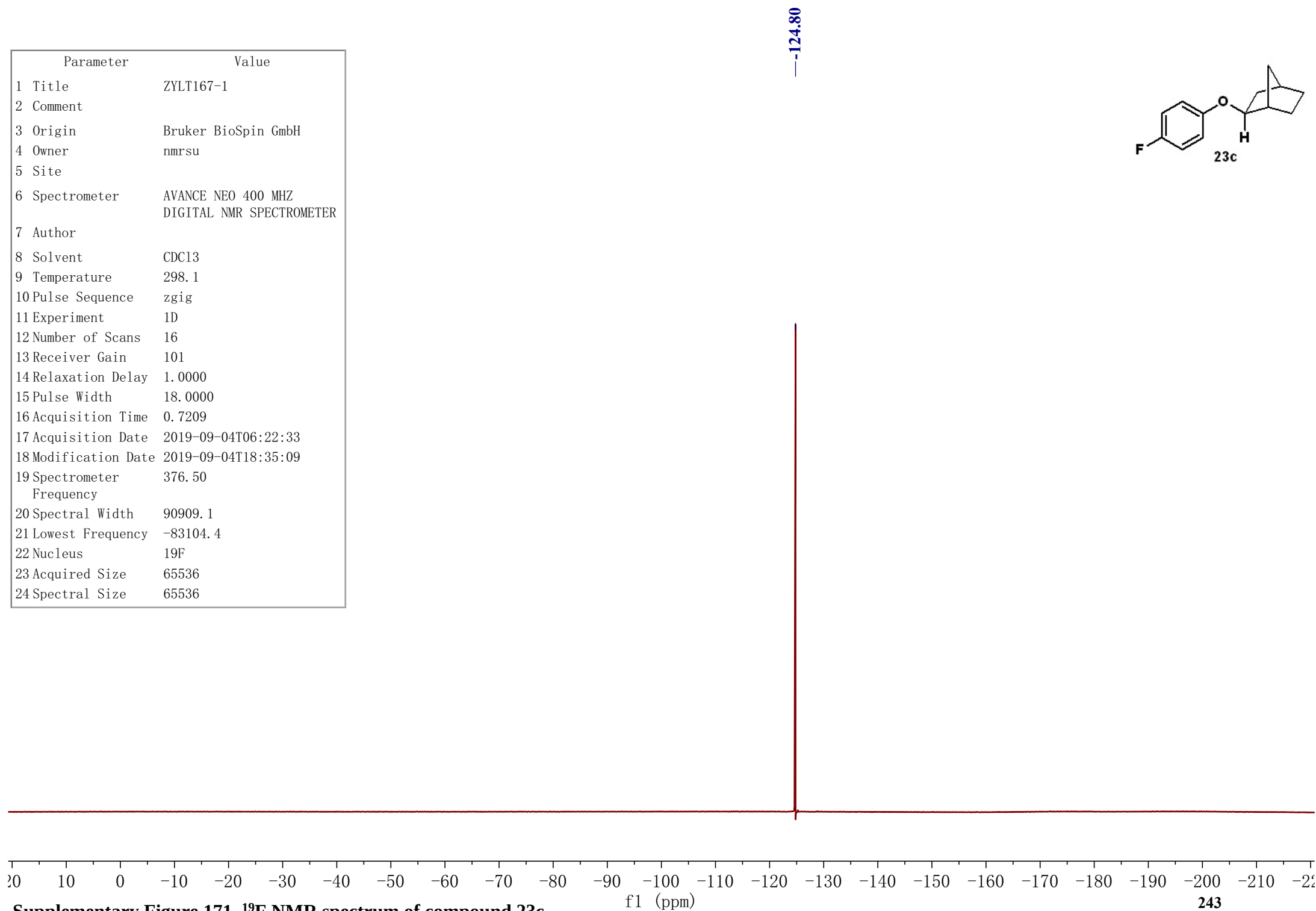
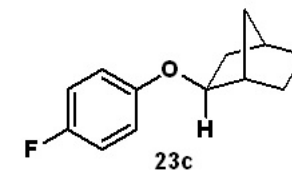


Supplementary Figure 169. ¹H NMR spectrum of compound 23c

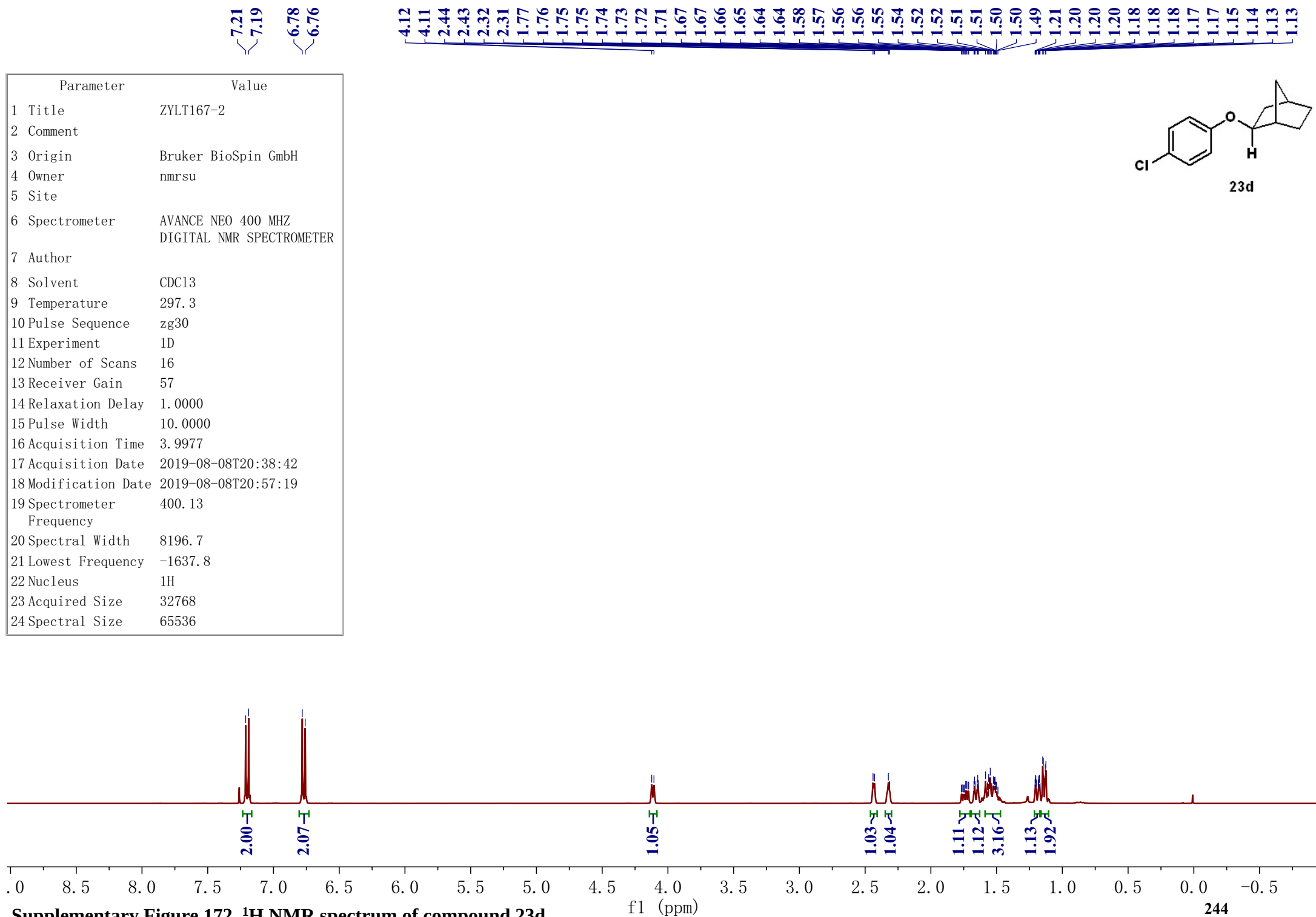
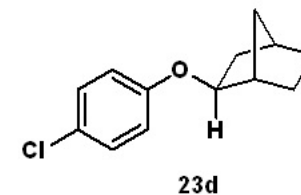


Supplementary Figure 170. ¹³C NMR spectrum of compound 23c

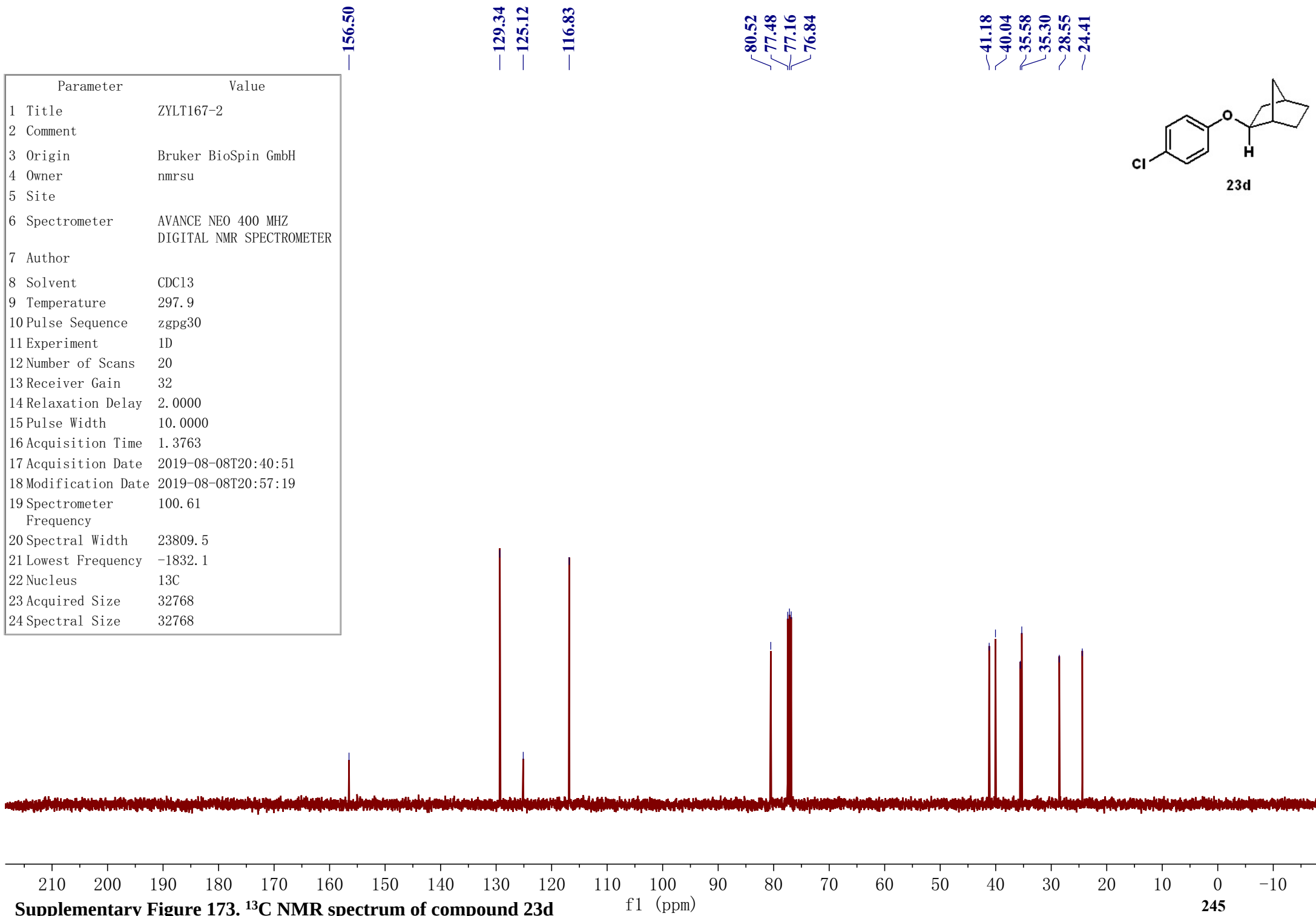
Parameter	Value
1 Title	ZYLT167-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	298.1
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	18.0000
16 Acquisition Time	0.7209
17 Acquisition Date	2019-09-04T06:22:33
18 Modification Date	2019-09-04T18:35:09
19 Spectrometer Frequency	376.50
20 Spectral Width	90909.1
21 Lowest Frequency	-83104.4
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536



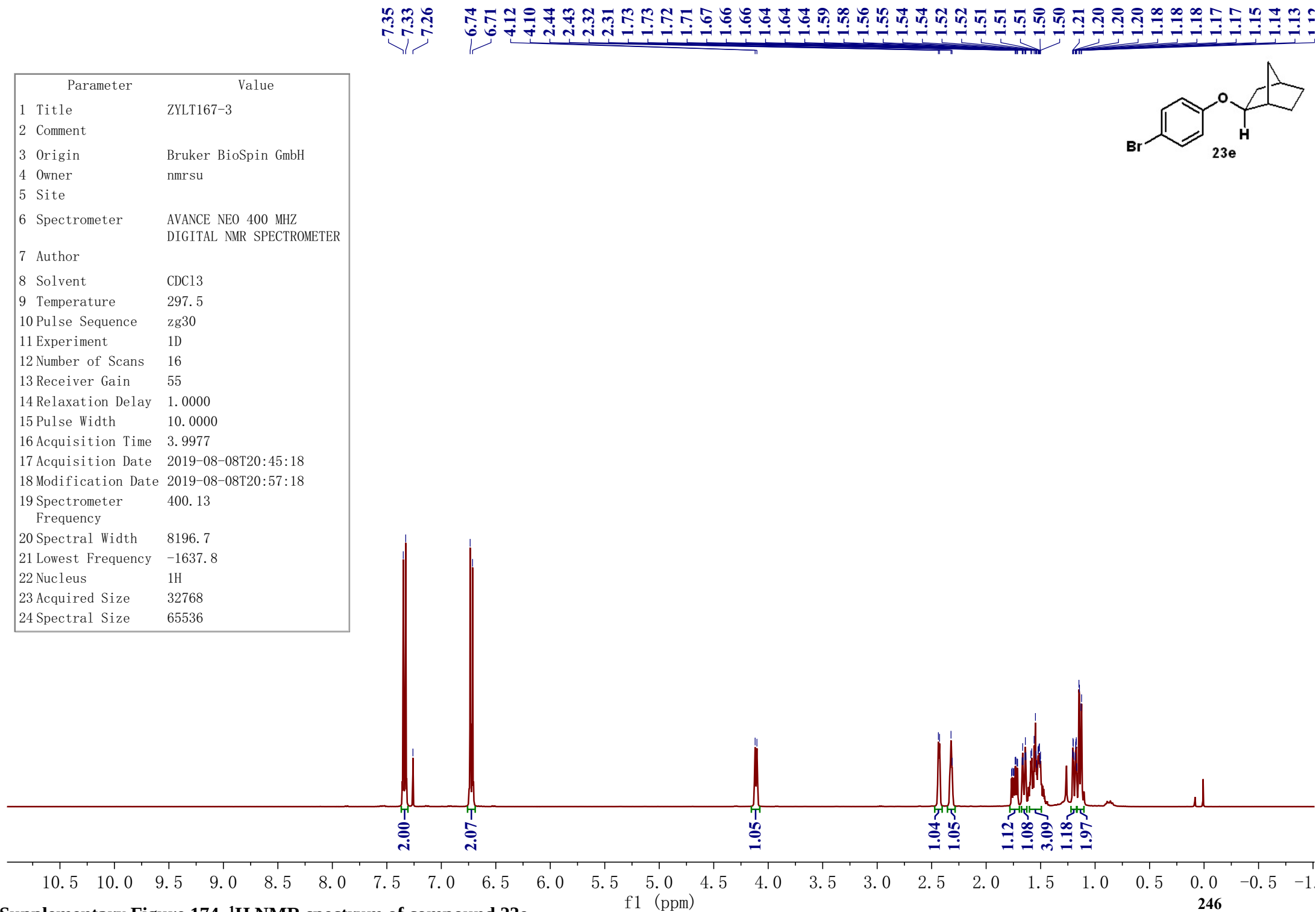
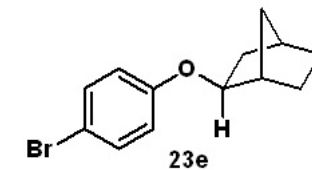
Parameter	Value
1 Title	ZYLT167-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.3
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	57
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-08-08T20:38:42
18 Modification Date	2019-08-08T20:57:19
19 Spectrometer Frequency	400.13
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.8
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Supplementary Figure 172. ¹H NMR spectrum of compound 23d

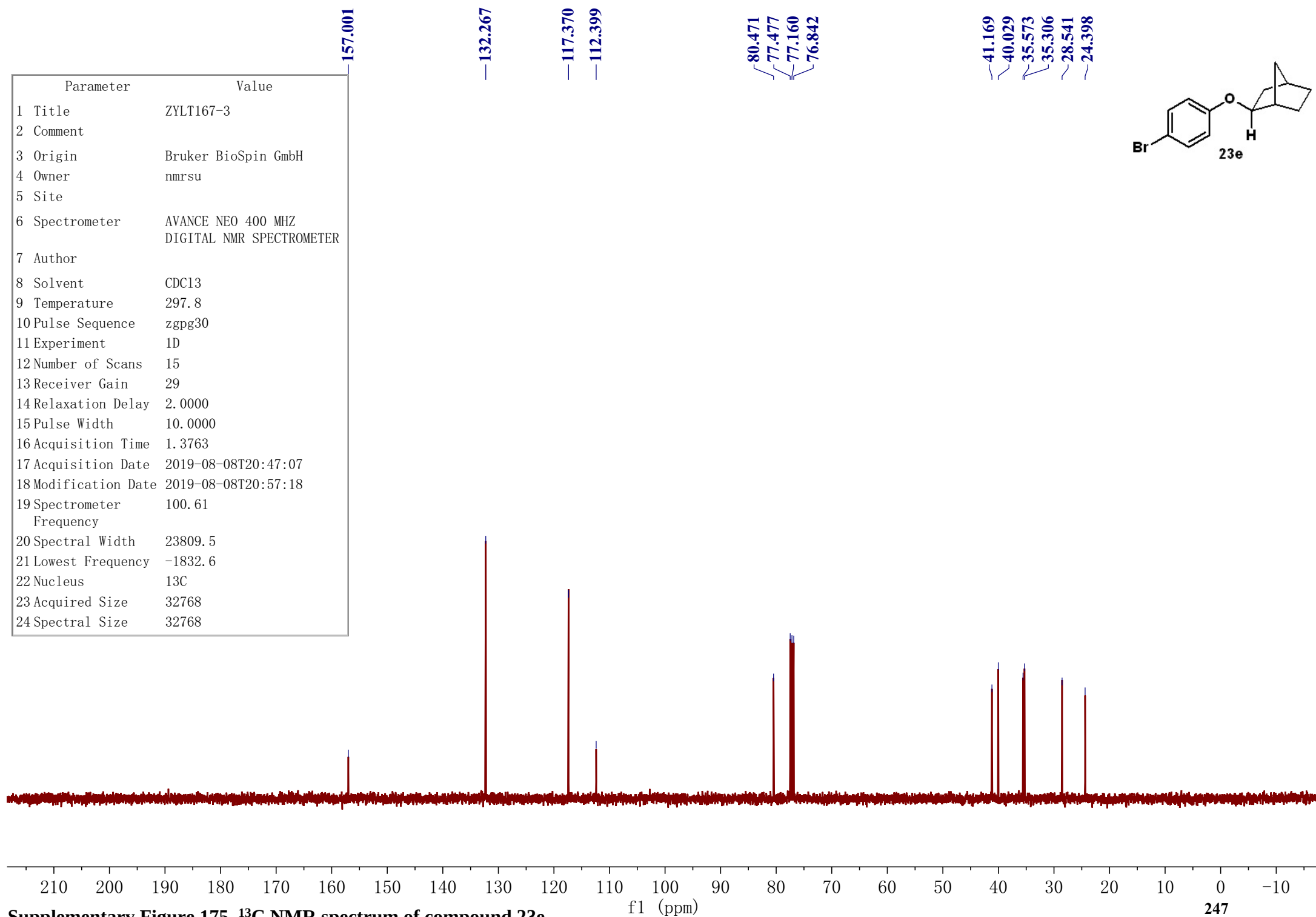
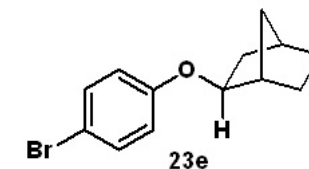


Parameter	Value
1 Title	ZYLT167-3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	297.5
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	55
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-08-08T20:45:18
18 Modification Date	2019-08-08T20:57:18
19 Spectrometer Frequency	400.13
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.8
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

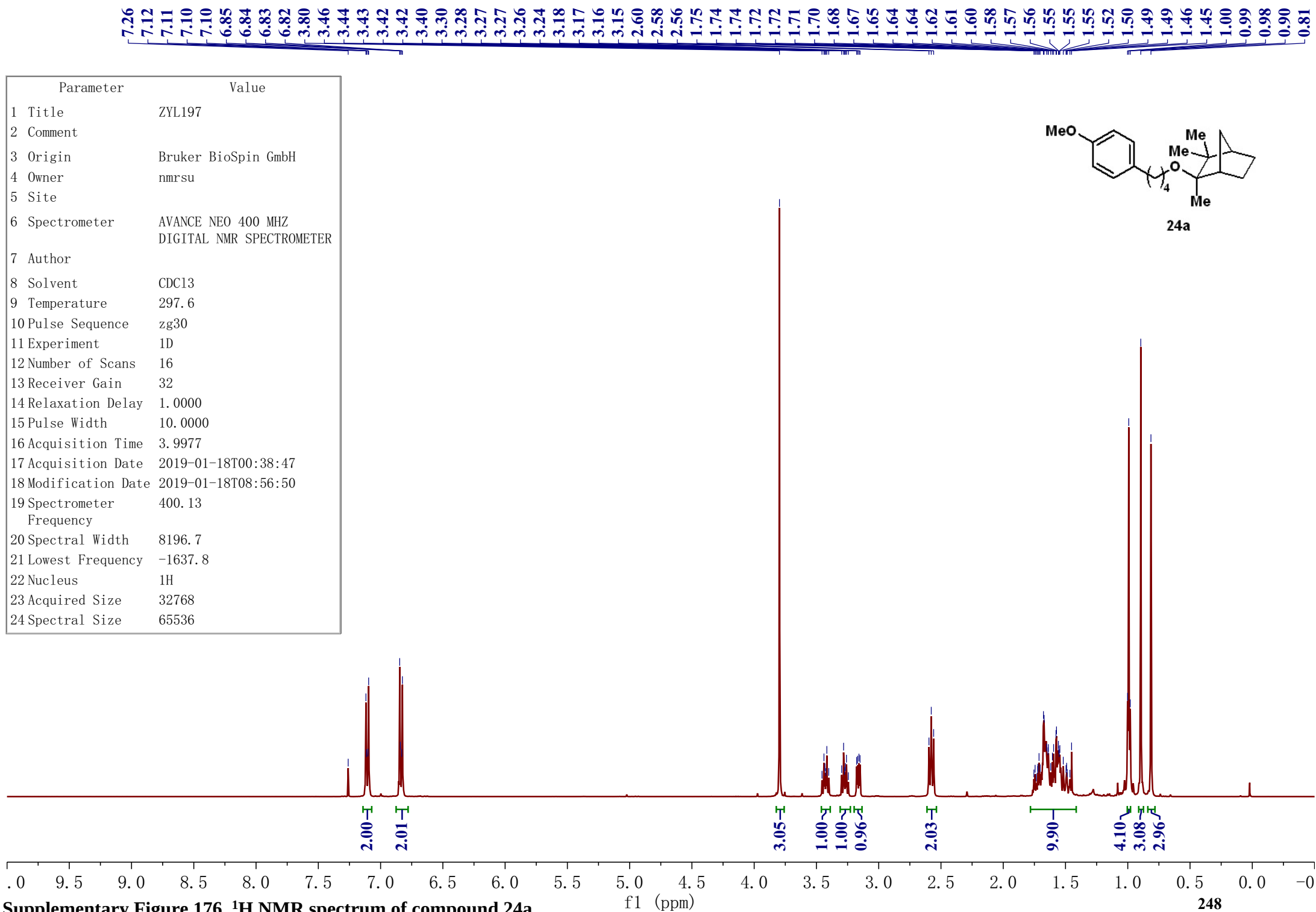


Supplementary Figure 174. ¹H NMR spectrum of compound 23e

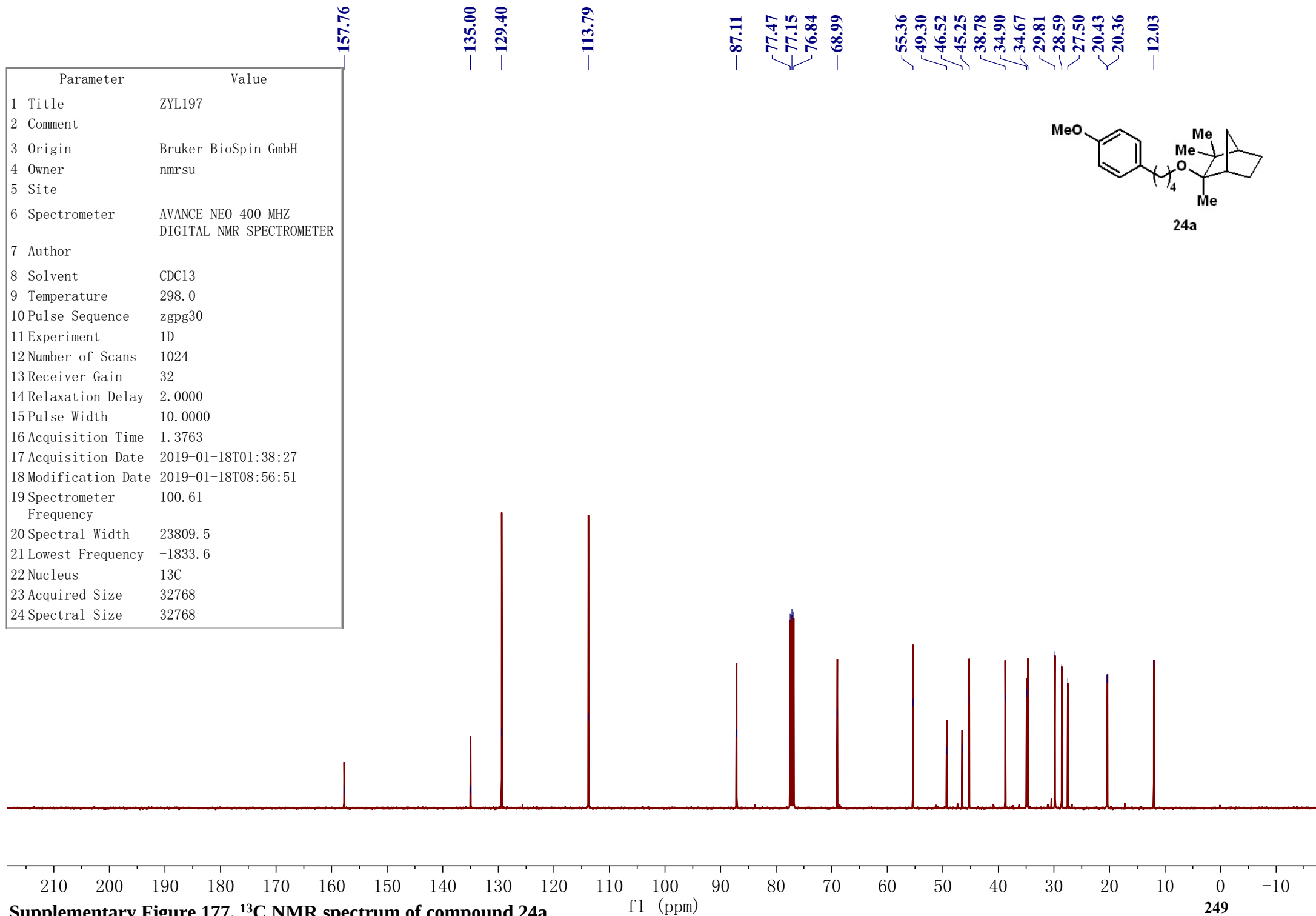
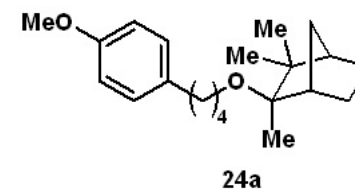
Parameter	Value
1 Title	ZYLT167-3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.8
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	15
13 Receiver Gain	29
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-08-08T20:47:07
18 Modification Date	2019-08-08T20:57:18
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1832.6
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



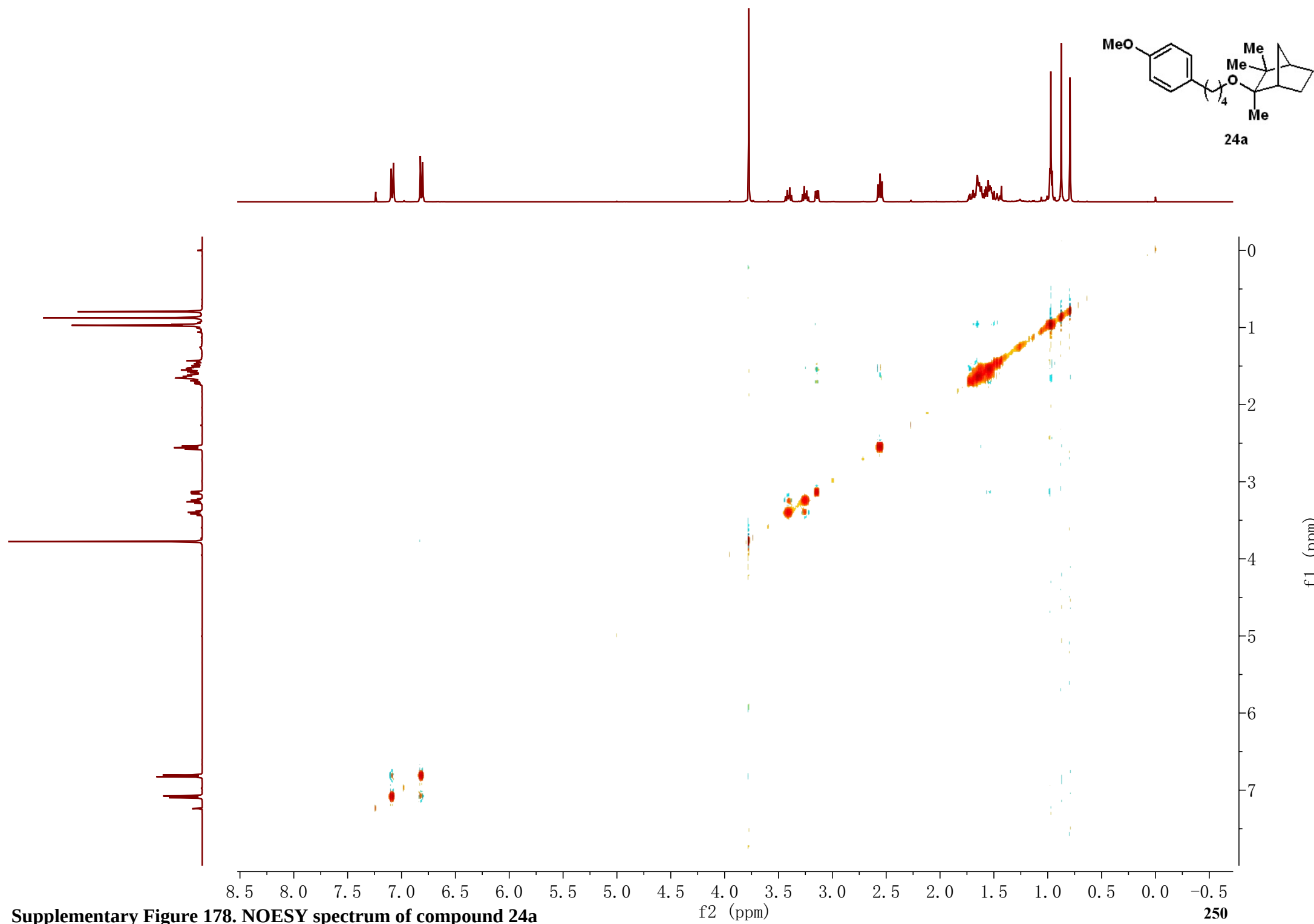
Supplementary Figure 175. ¹³C NMR spectrum of compound 23e

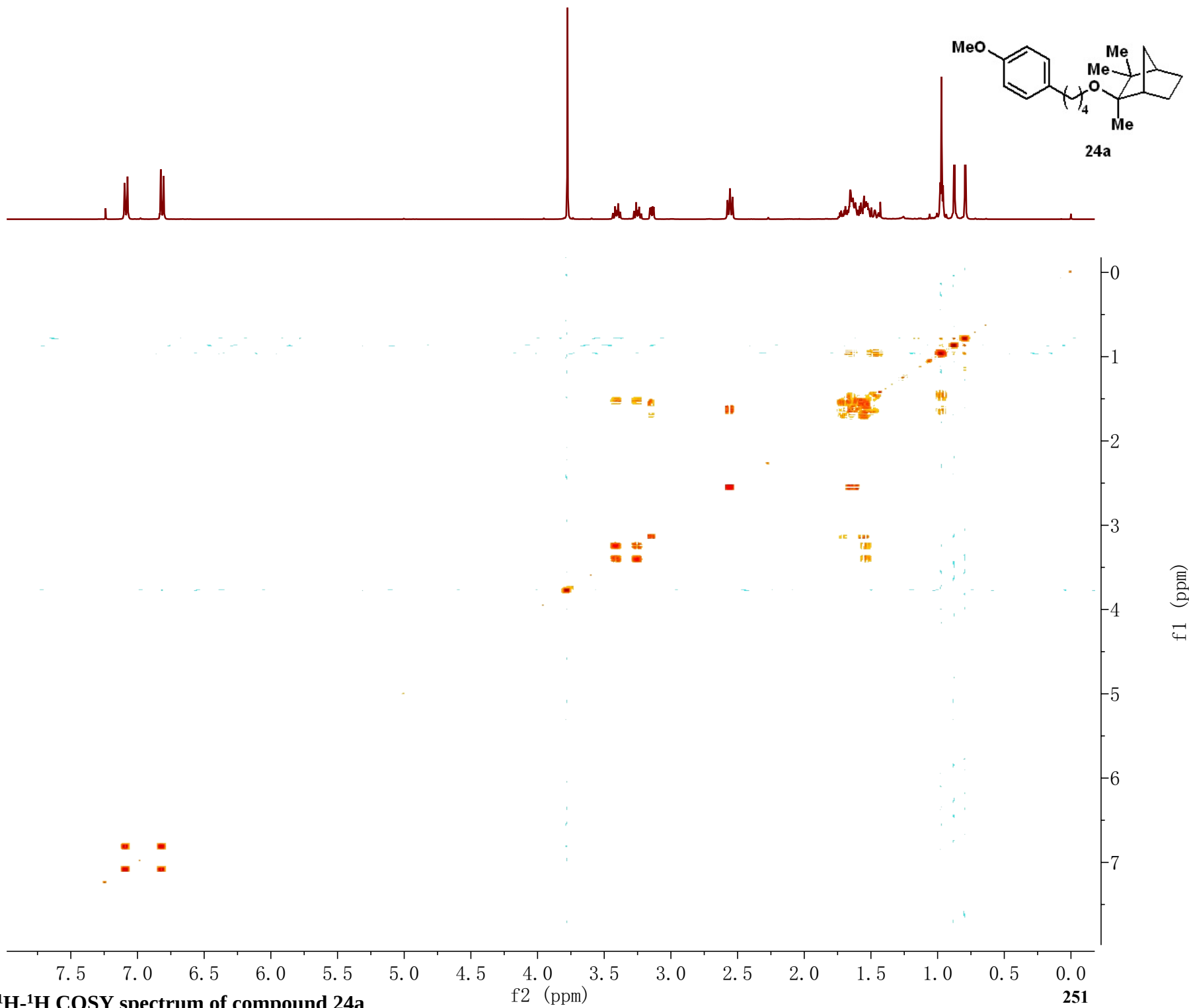
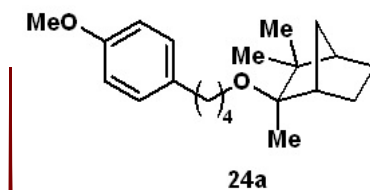


Parameter	Value
1 Title	ZYL197
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	298.0
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	1024
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-01-18T01:38:27
18 Modification Date	2019-01-18T08:56:51
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1833.6
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

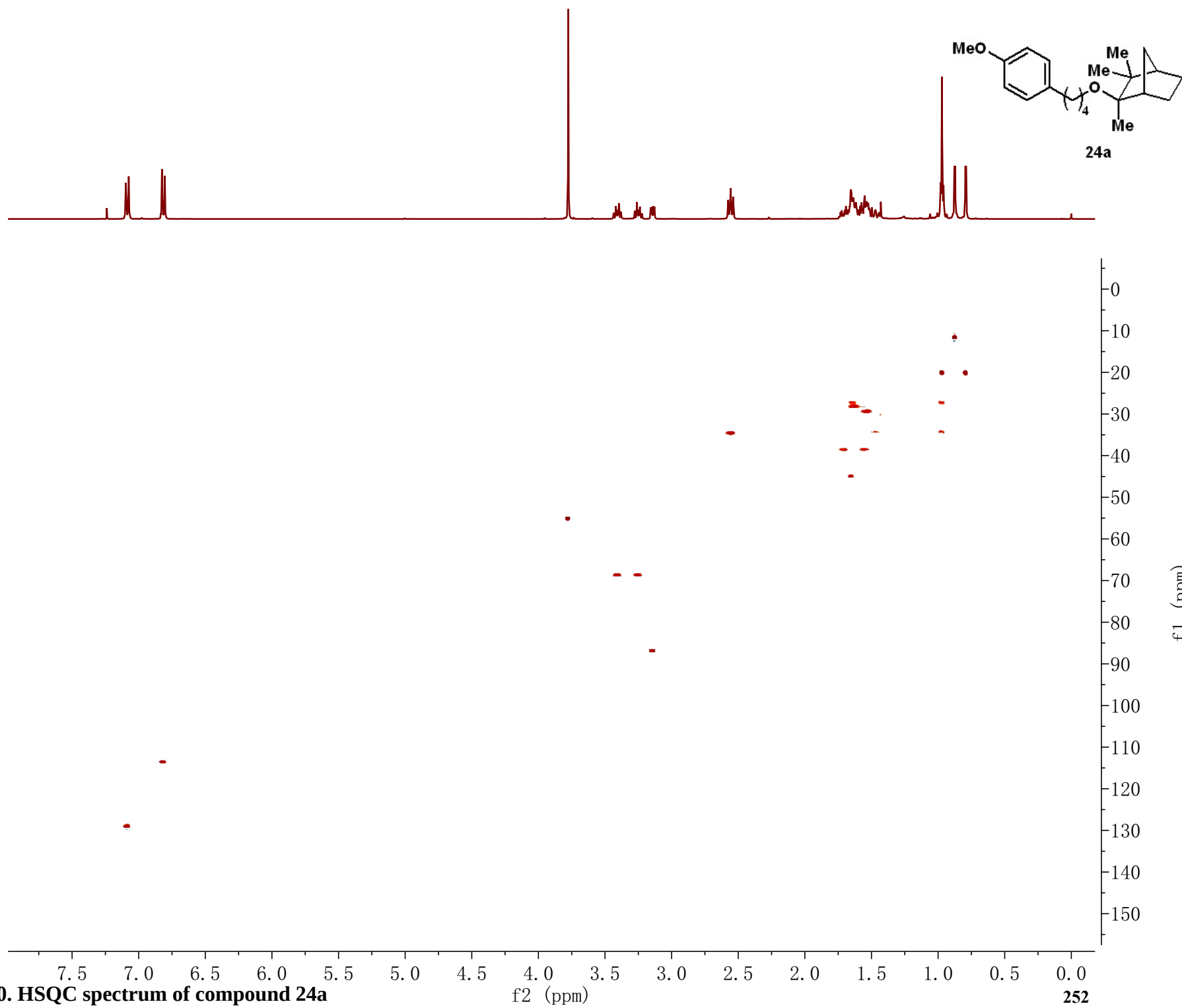


Supplementary Figure 177. ¹³C NMR spectrum of compound 24a

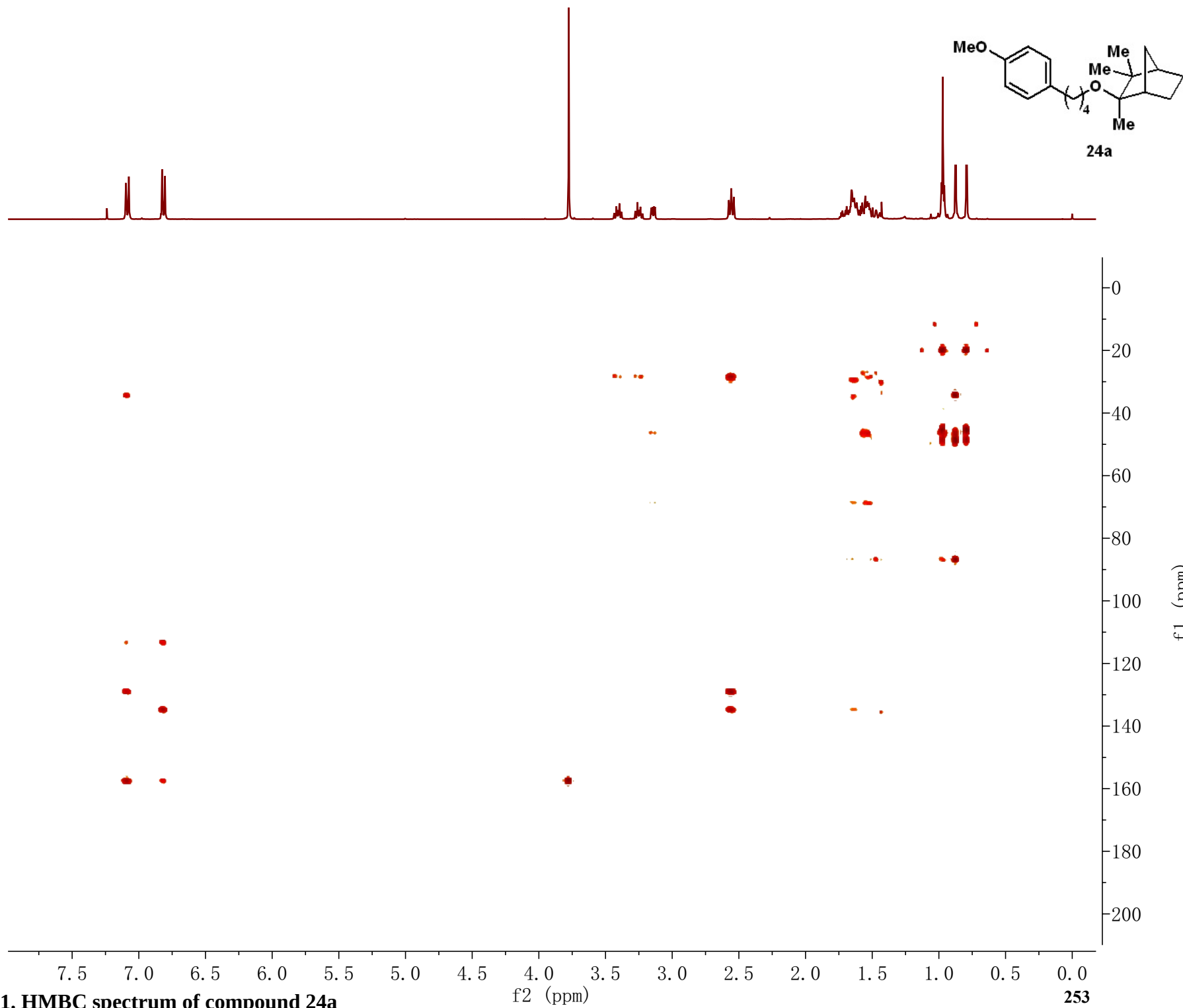




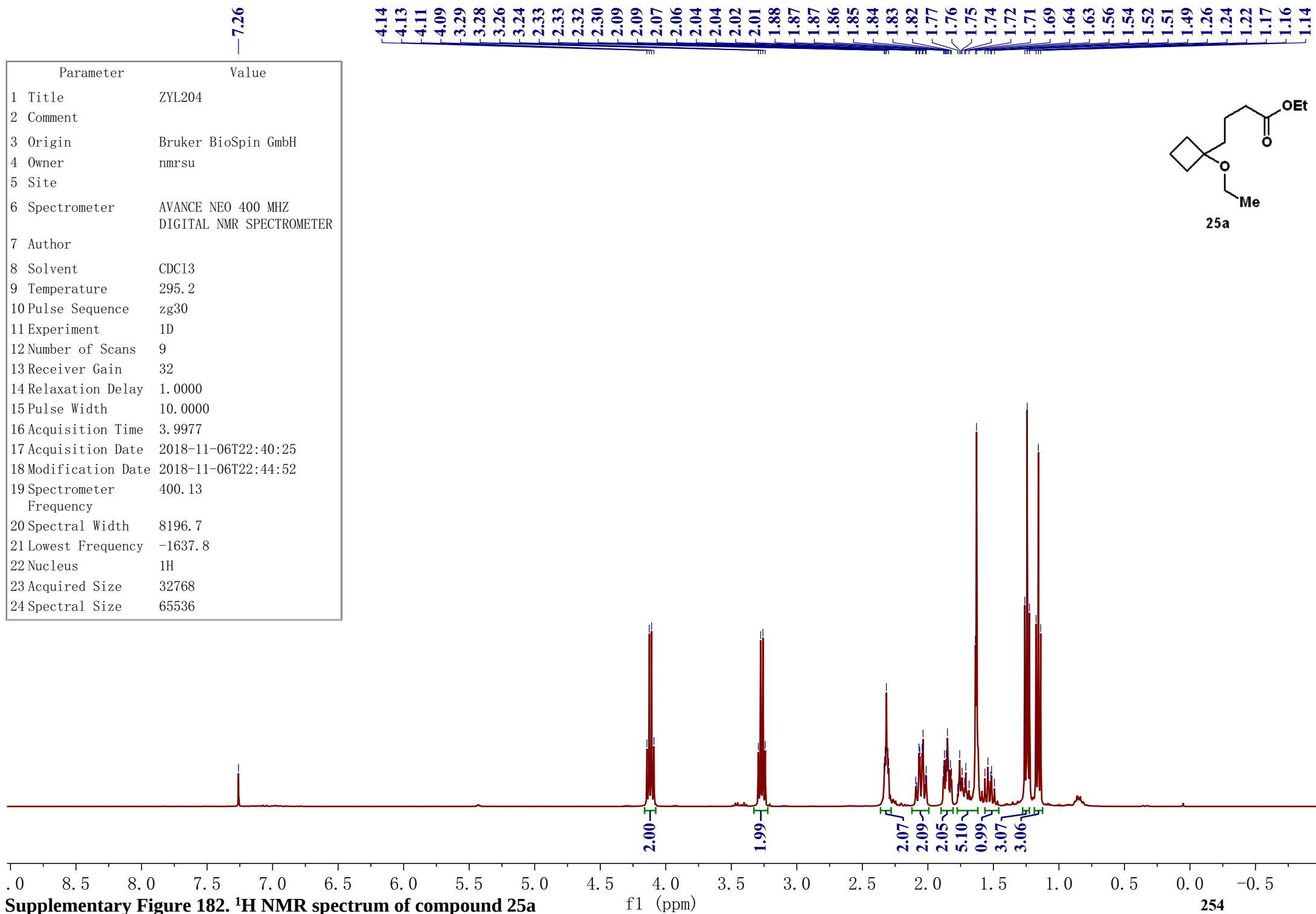
Supplementary Figure 179. ¹H-¹H COSY spectrum of compound 24a



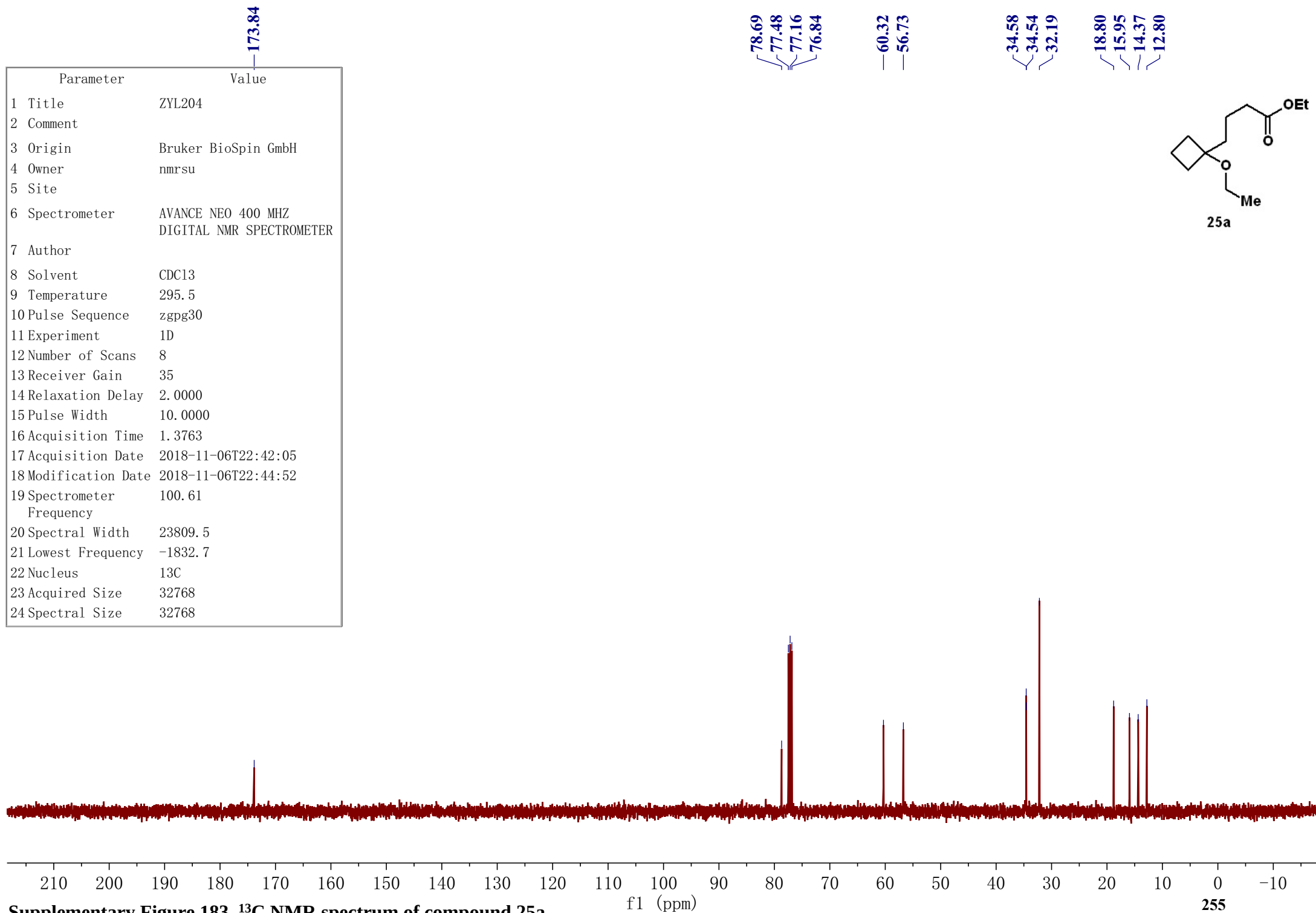
Supplementary Figure 180. HSQC spectrum of compound 24a



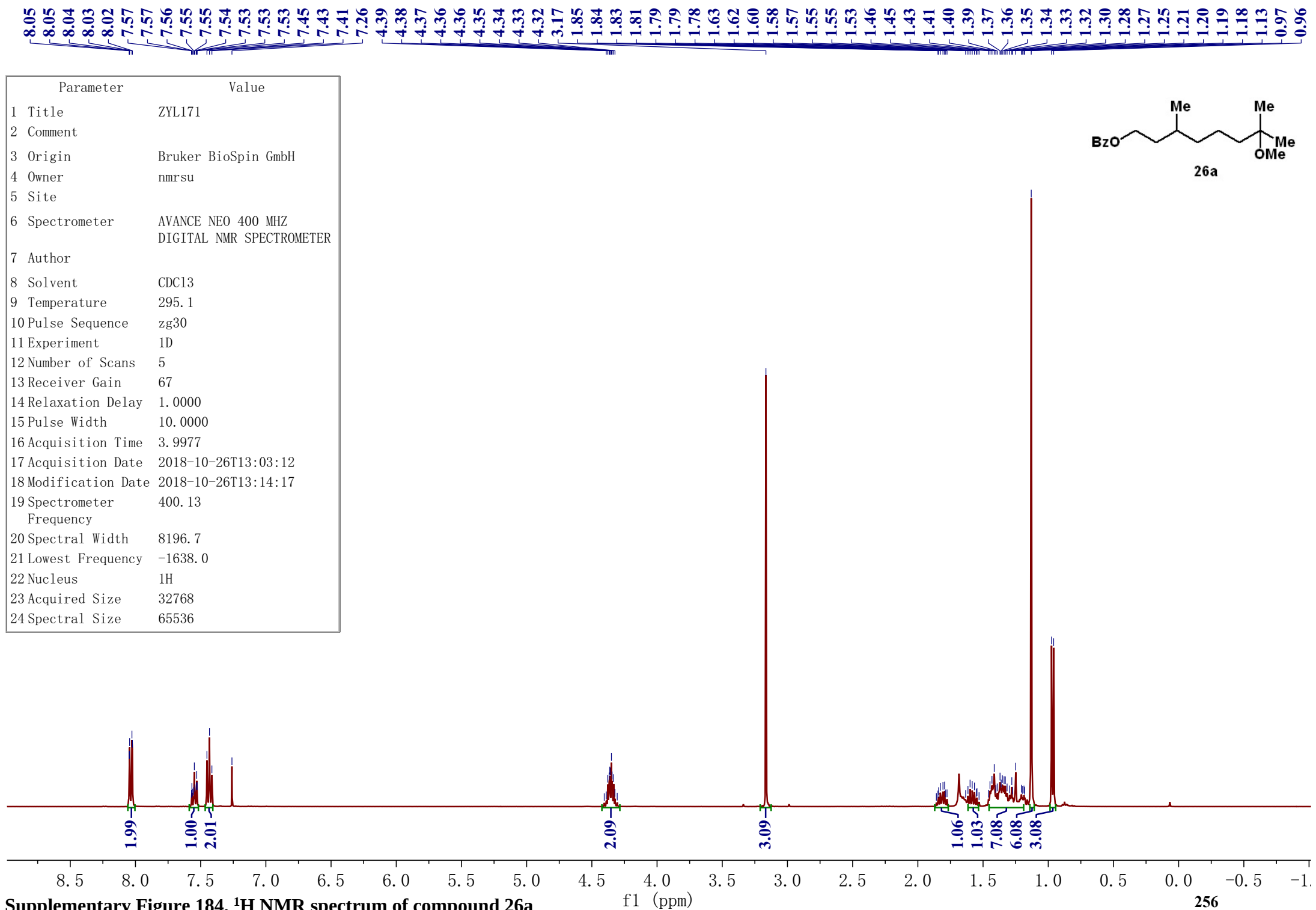
Parameter	Value
1 Title	ZYL204
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	295.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	9
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-11-06T22:40:25
18 Modification Date	2018-11-06T22:44:52
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.8
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536



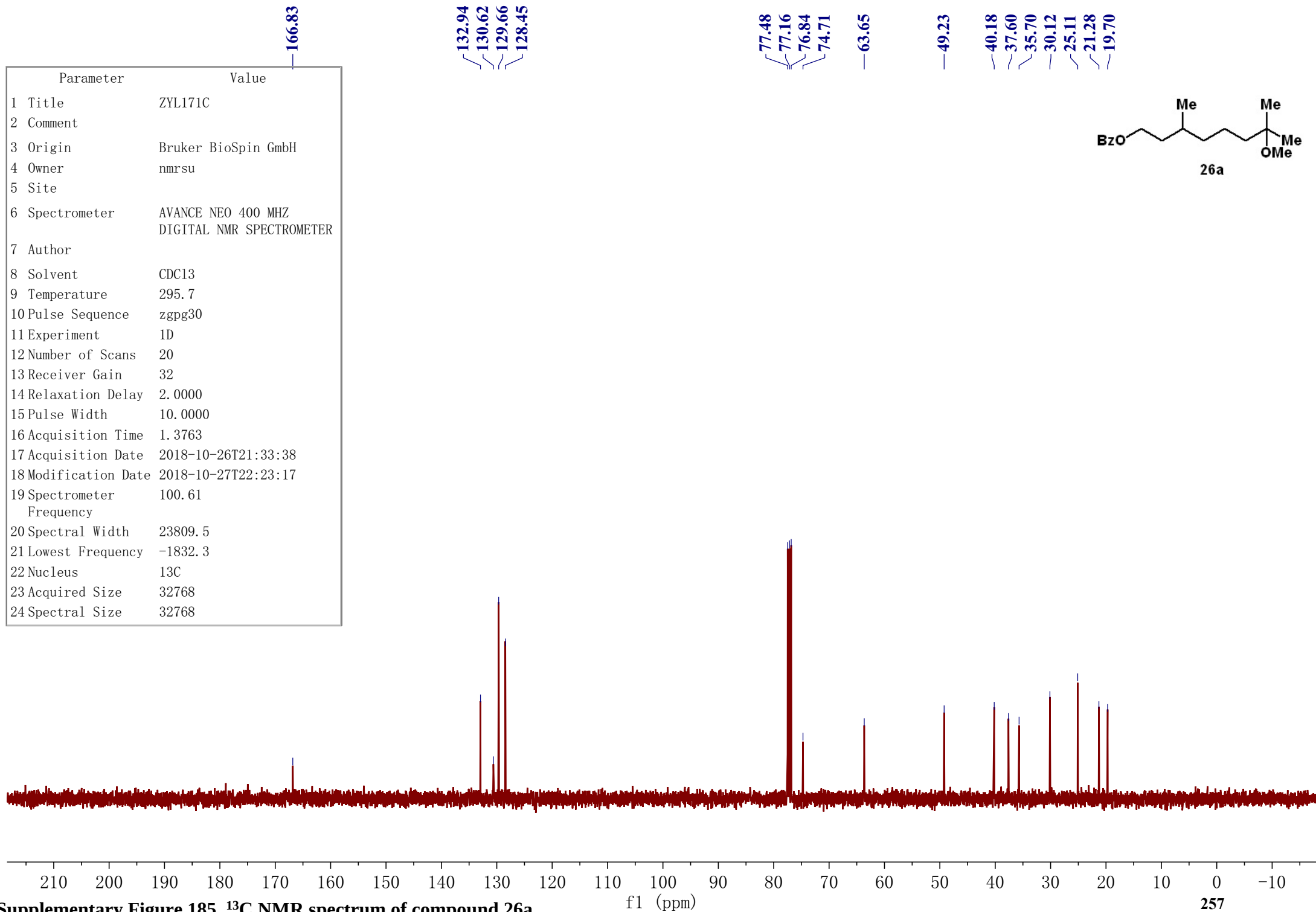
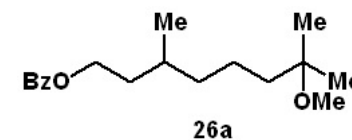
Parameter	Value
1 Title	ZYL204
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-11-06T22:42:05
18 Modification Date	2018-11-06T22:44:52
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1832.7
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 183. ¹³C NMR spectrum of compound 25a

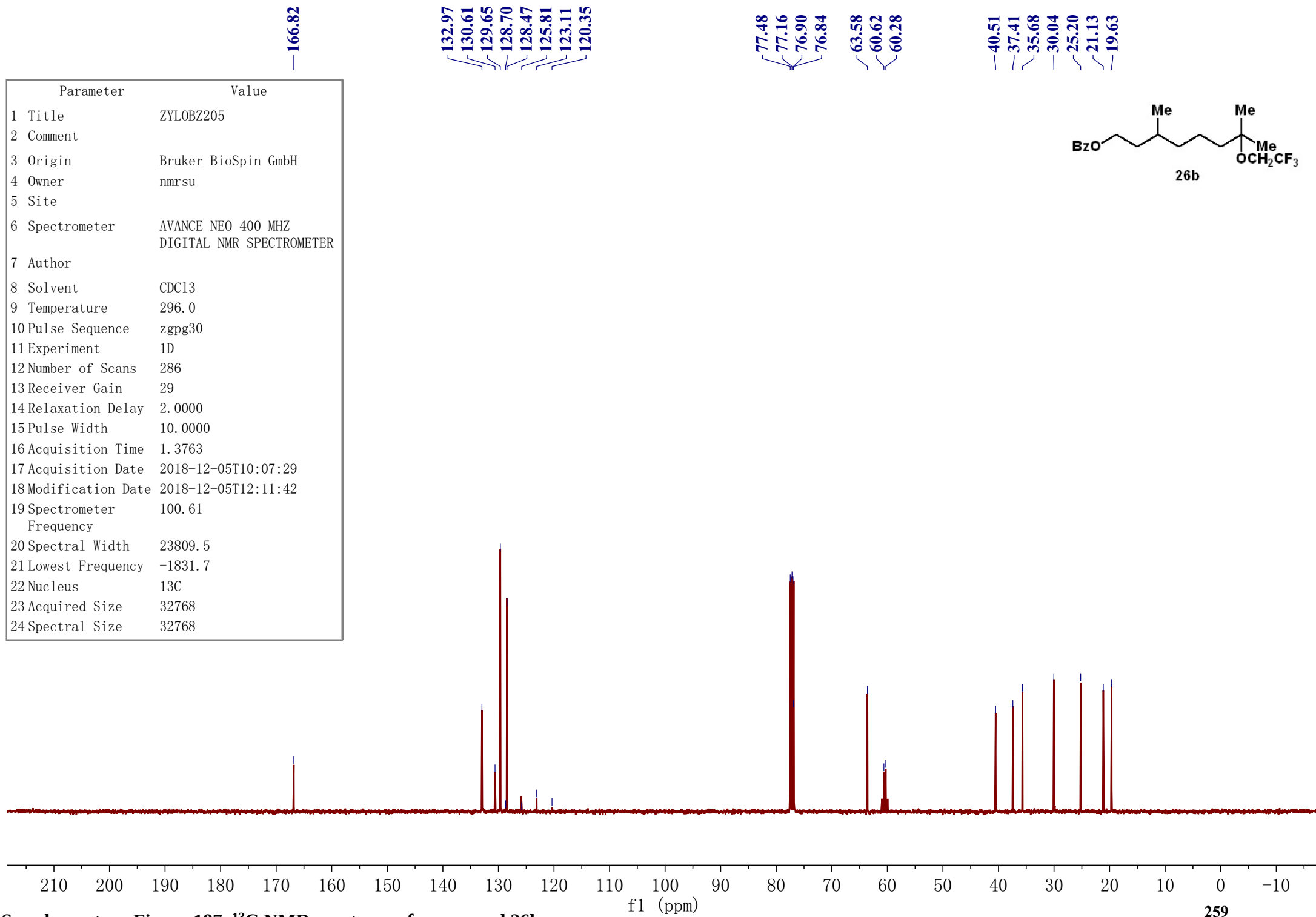
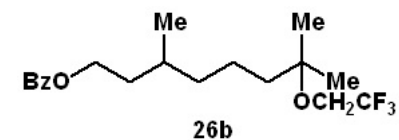


Parameter	Value
1 Title	ZYL171C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.7
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	20
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-10-26T21:33:38
18 Modification Date	2018-10-27T22:23:17
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1832.3
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 185. ¹³C NMR spectrum of compound 26a

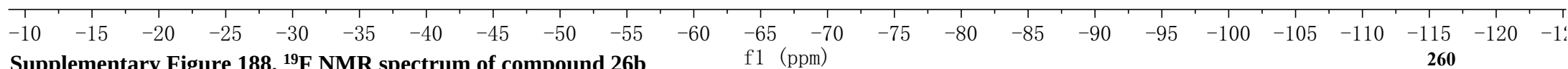
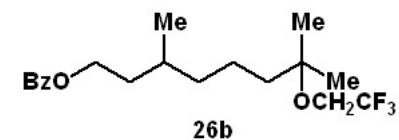
Parameter	Value
1 Title	ZYLOBZ205
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	296.0
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	286
13 Receiver Gain	29
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-05T10:07:29
18 Modification Date	2018-12-05T12:11:42
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1831.7
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



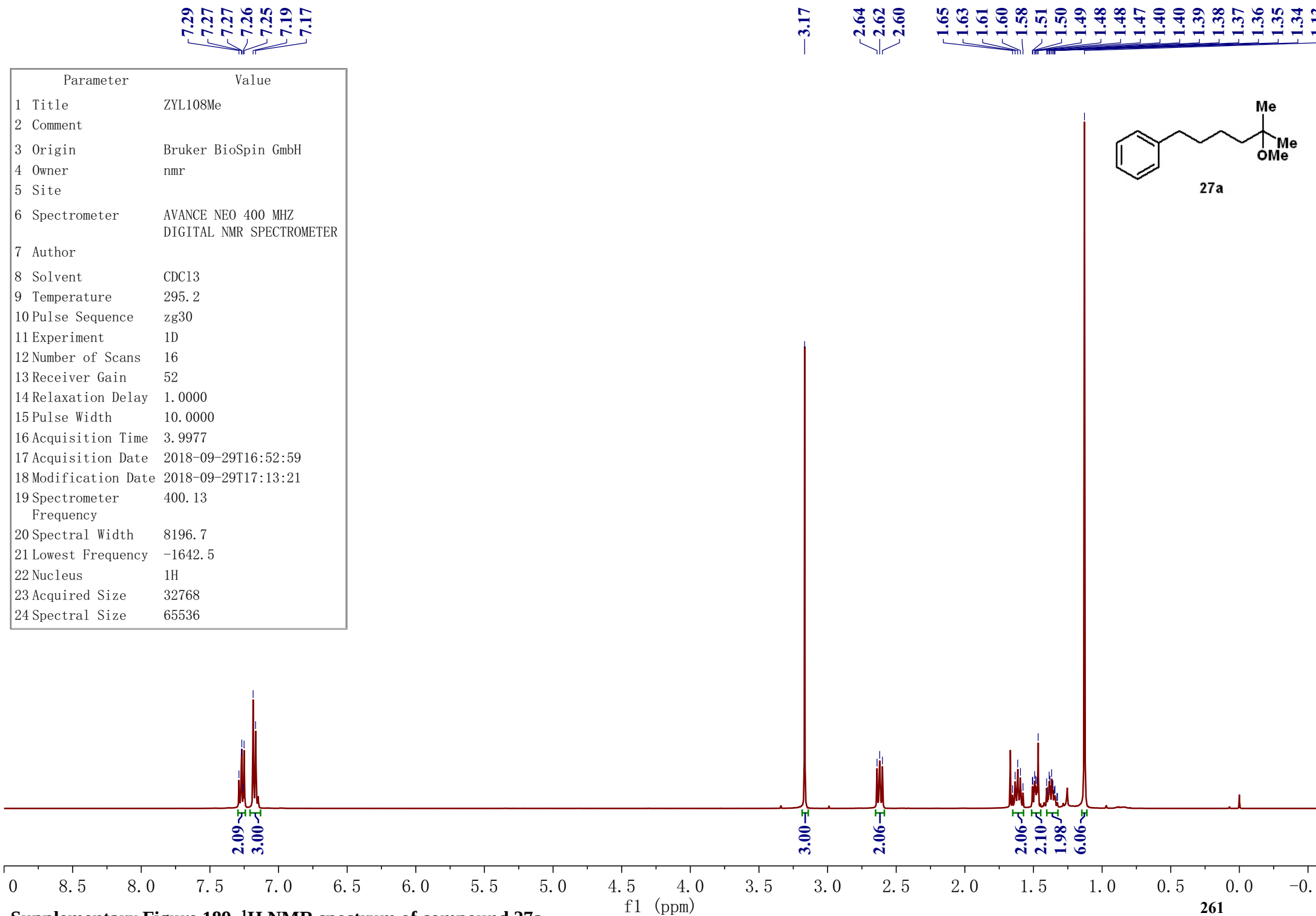
Supplementary Figure 187. ¹³C NMR spectrum of compound 26b

Parameter	Value
1 Data File Name	C:/ 2018工作/ 核磁/ 产物/ ZYL0BZ205/ ZYL12050BZ/ 10/ pdata/ 1/ 1r
2 Title	ZYL12050BZ
3 Comment	
4 Origin	Bruker BioSpin GmbH
5 Owner	nmrsu
6 Site	
7 Spectrometer	Avance NEO 600
8 Author	
9 Solvent	CDCl ₃
10 Temperature	297.3
11 Pulse Sequence	zg
12 Experiment	1D
13 Number of Scans	8
14 Receiver Gain	101
15 Relaxation Delay	1.0000
16 Pulse Width	12.0000
17 Acquisition Time	0.4981
18 Acquisition Date	2018-12-05T11:36:36
19 Modification Date	2018-12-05T17:08:32
20 Spectrometer Frequency	564.71
21 Spectral Width	131579.0
22 Lowest Frequency	-122260.0
23 Nucleus	¹⁹ F
24 Acquired Size	65536
25 Spectral Size	65536

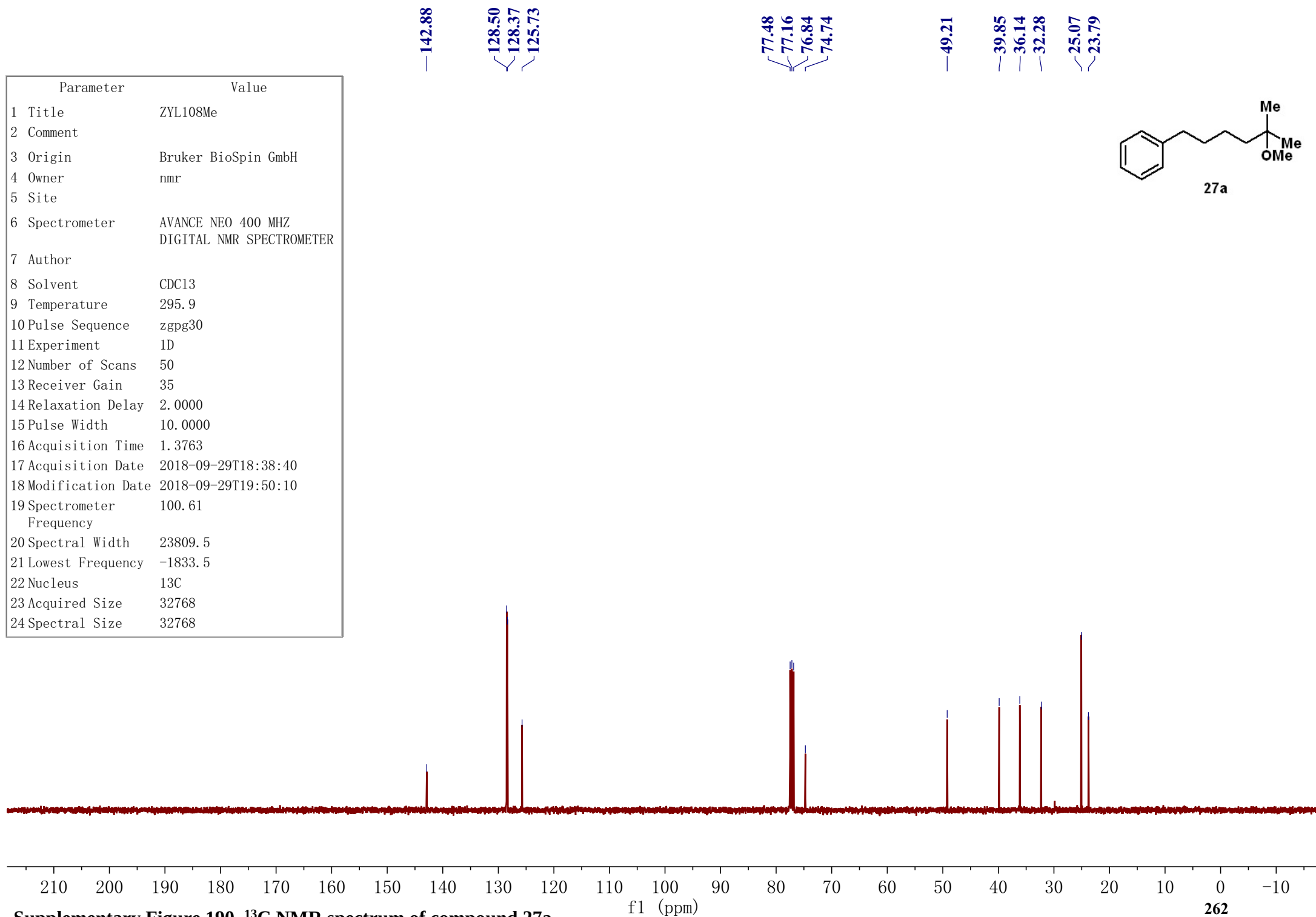
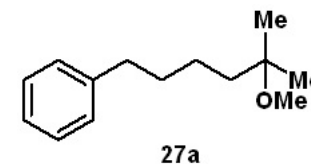
-74.49
-74.51
-74.52



Supplementary Figure 188. ¹⁹F NMR spectrum of compound 26b

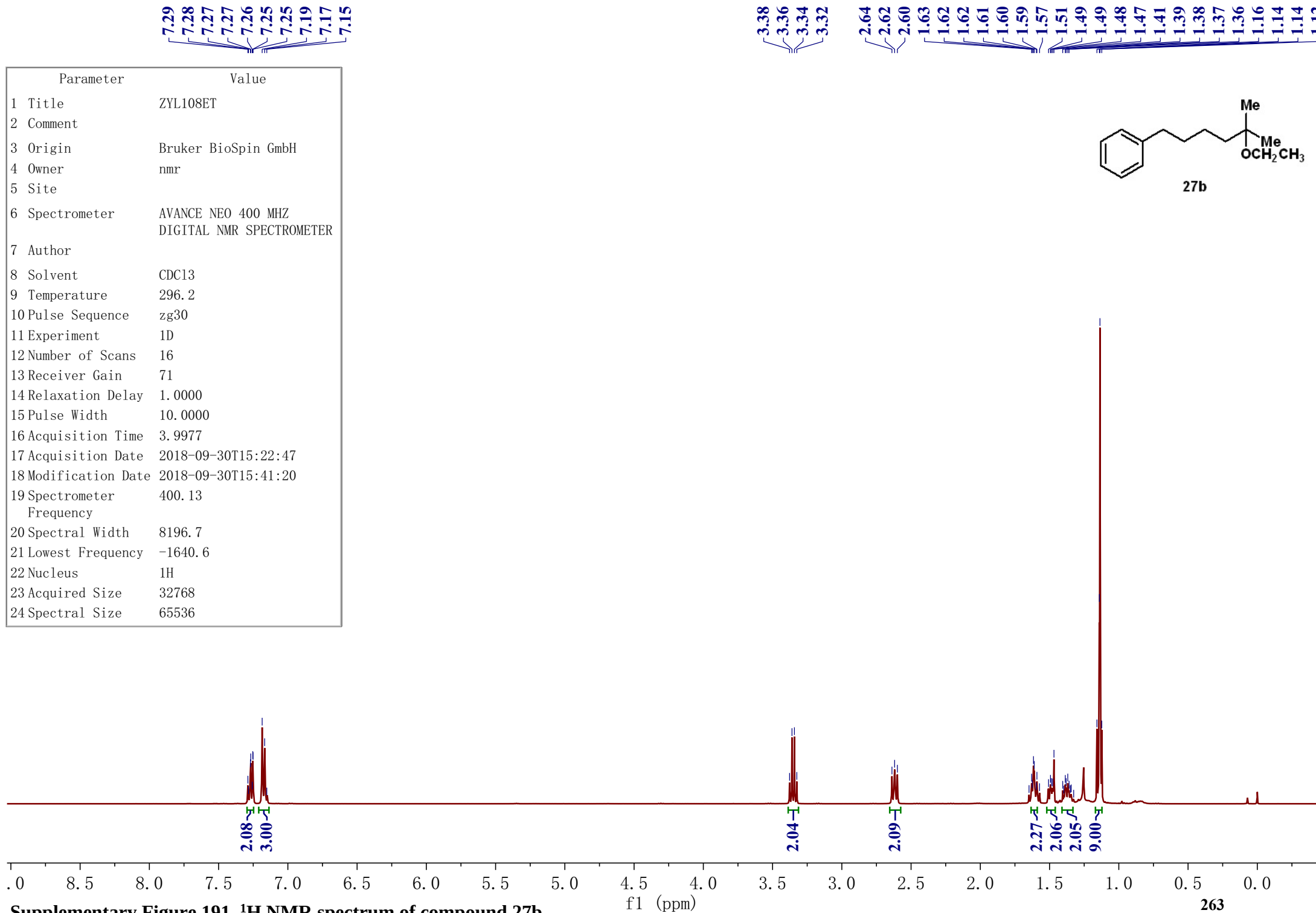


Parameter	Value
1 Title	ZYL108Me
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	295.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	50
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-09-29T18:38:40
18 Modification Date	2018-09-29T19:50:10
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1833.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



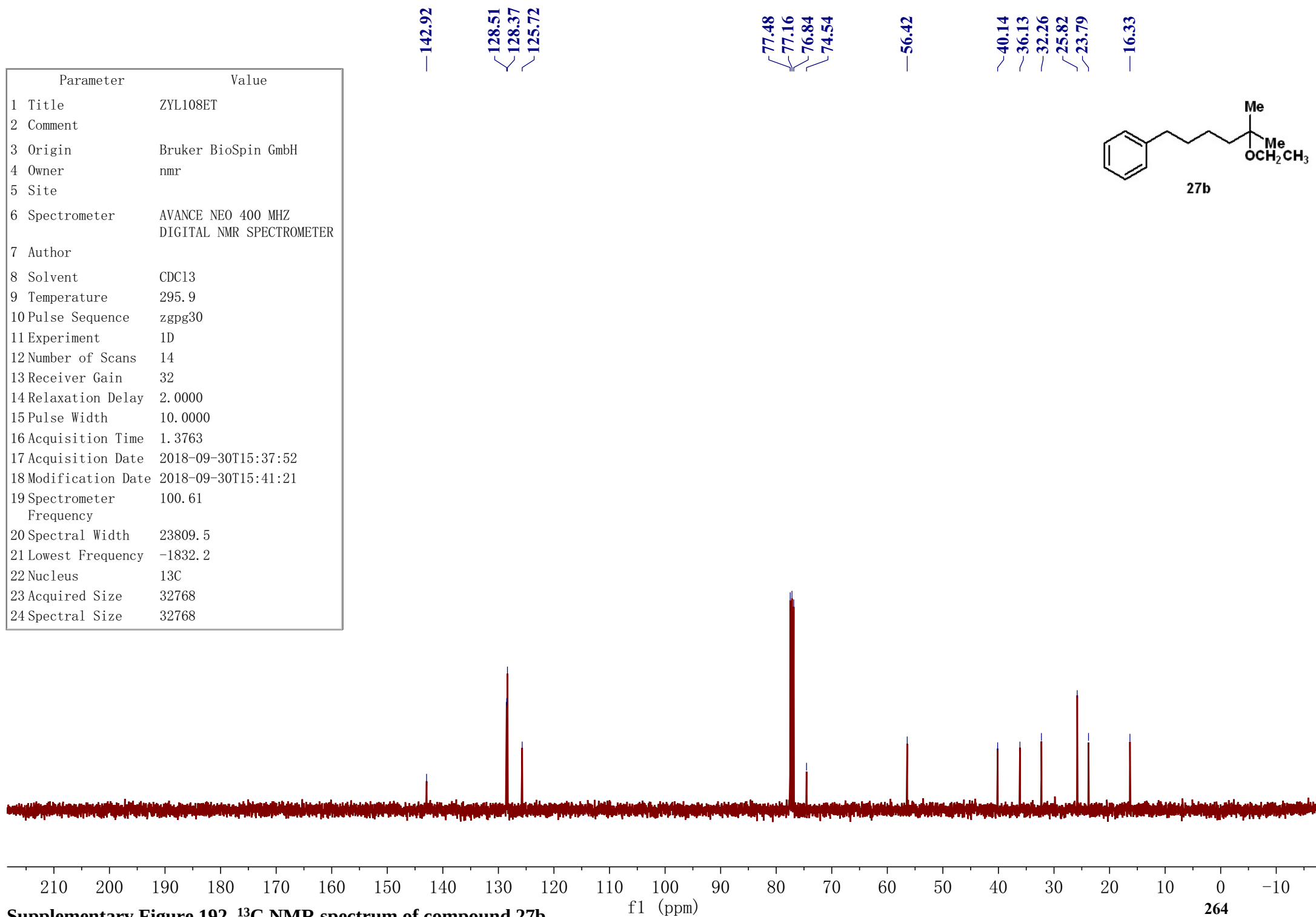
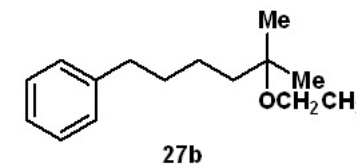
Supplementary Figure 190. ¹³C NMR spectrum of compound 27a

Parameter	Value
1 Title	ZYL108ET
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	71
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-09-30T15:22:47
18 Modification Date	2018-09-30T15:41:20
19 Spectrometer Frequency	400.13
20 Spectral Width	8196.7
21 Lowest Frequency	-1640.6
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Supplementary Figure 191. ¹H NMR spectrum of compound 27b

Parameter	Value
1 Title	ZYL108ET
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	14
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-09-30T15:37:52
18 Modification Date	2018-09-30T15:41:21
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1832.2
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

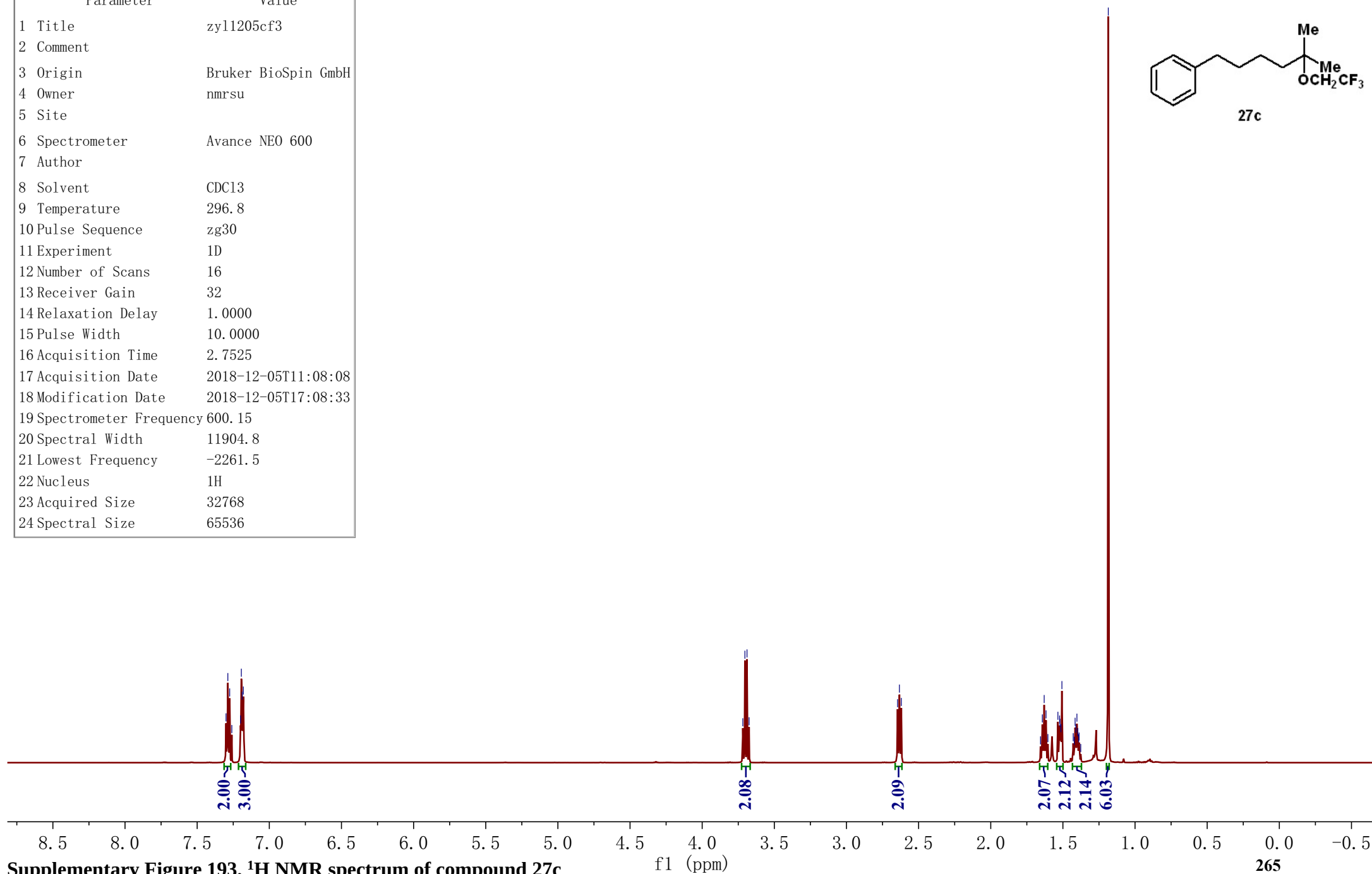
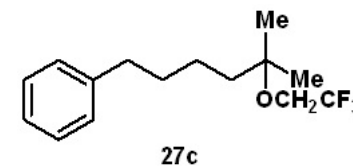


7.30
7.29
7.27
7.26
7.20
7.19
7.19
7.18

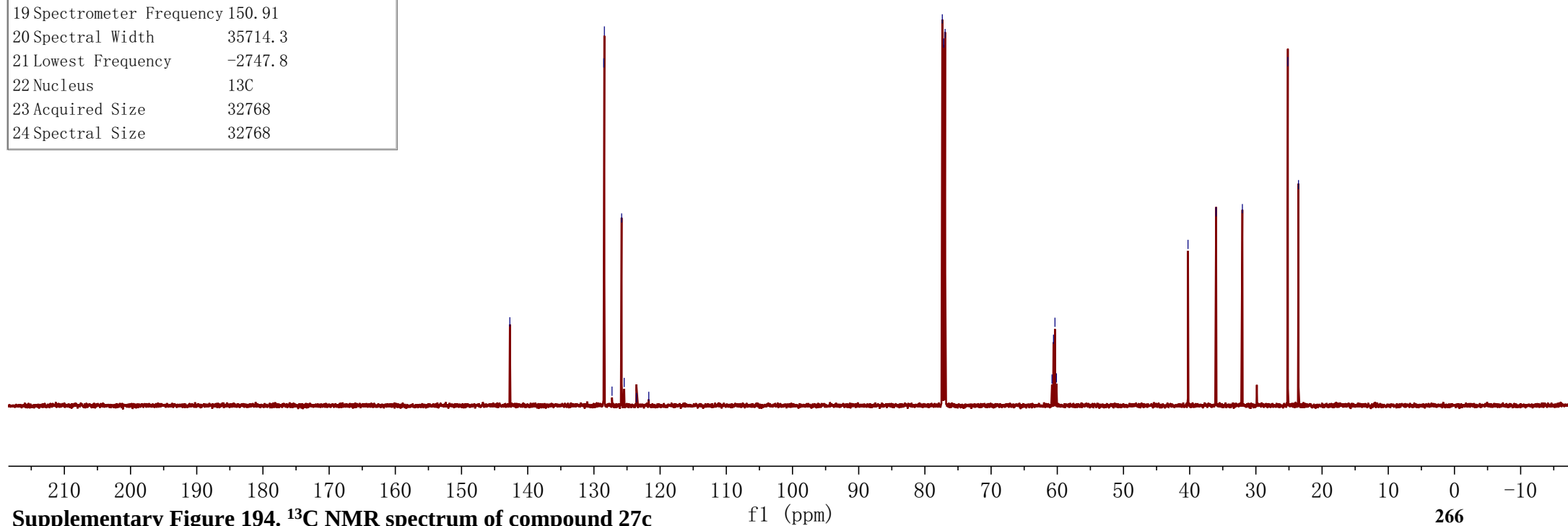
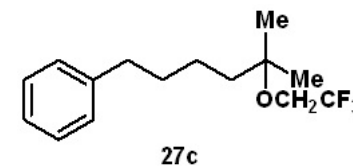
3.72
3.70
3.69
3.67

2.65
2.63
2.62
1.66
1.64
1.63
1.62
1.60
1.53
1.52
1.52
1.51
1.51
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.39
1.38
1.19

Parameter	Value
1 Title	zyl1205cf3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	296.8
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2018-12-05T11:08:08
18 Modification Date	2018-12-05T17:08:33
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2261.5
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536

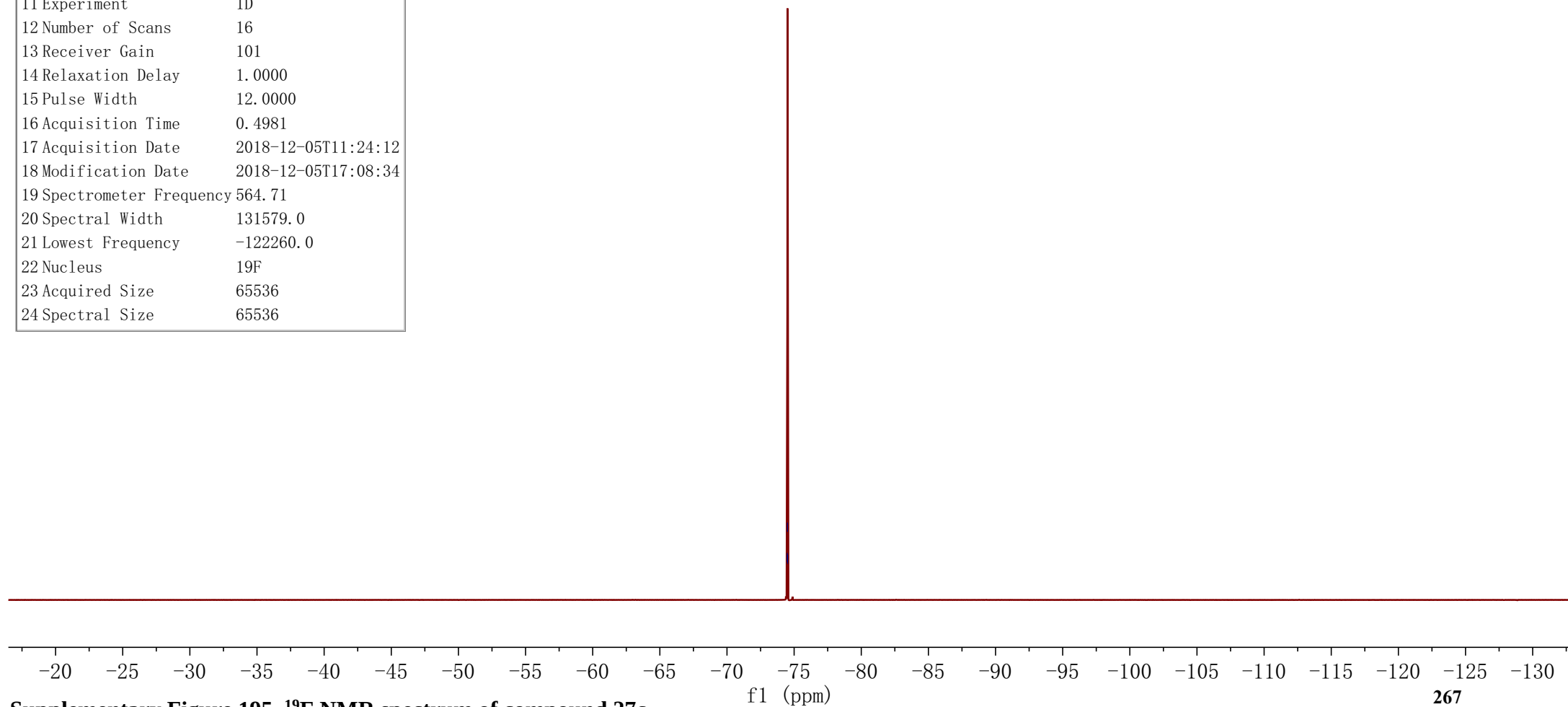
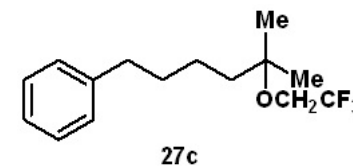


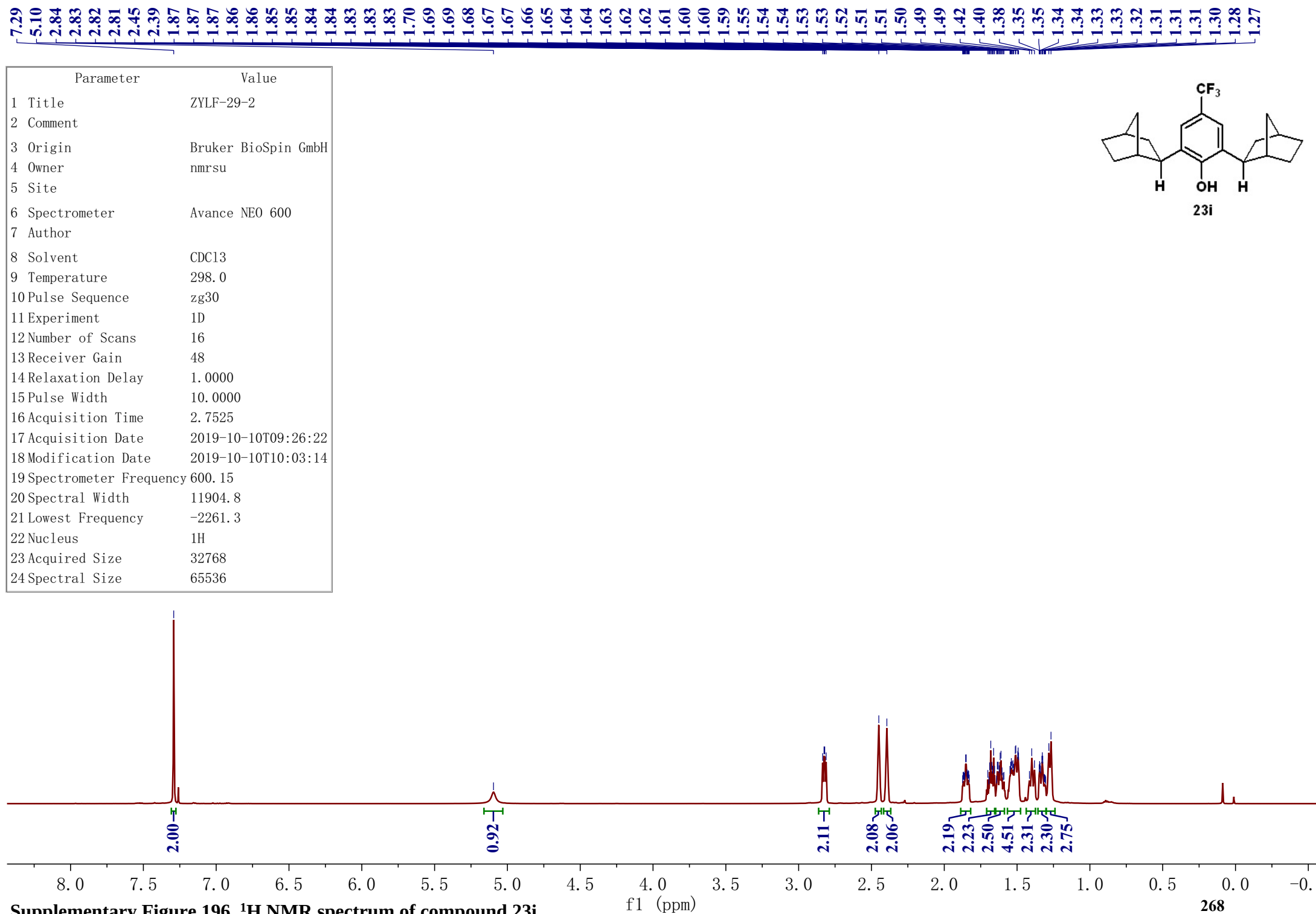
Parameter	Value
1 Title	zyl1205cf3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	199
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2018-12-05T11:22:54
18 Modification Date	2018-12-05T17:08:34
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2747.8
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



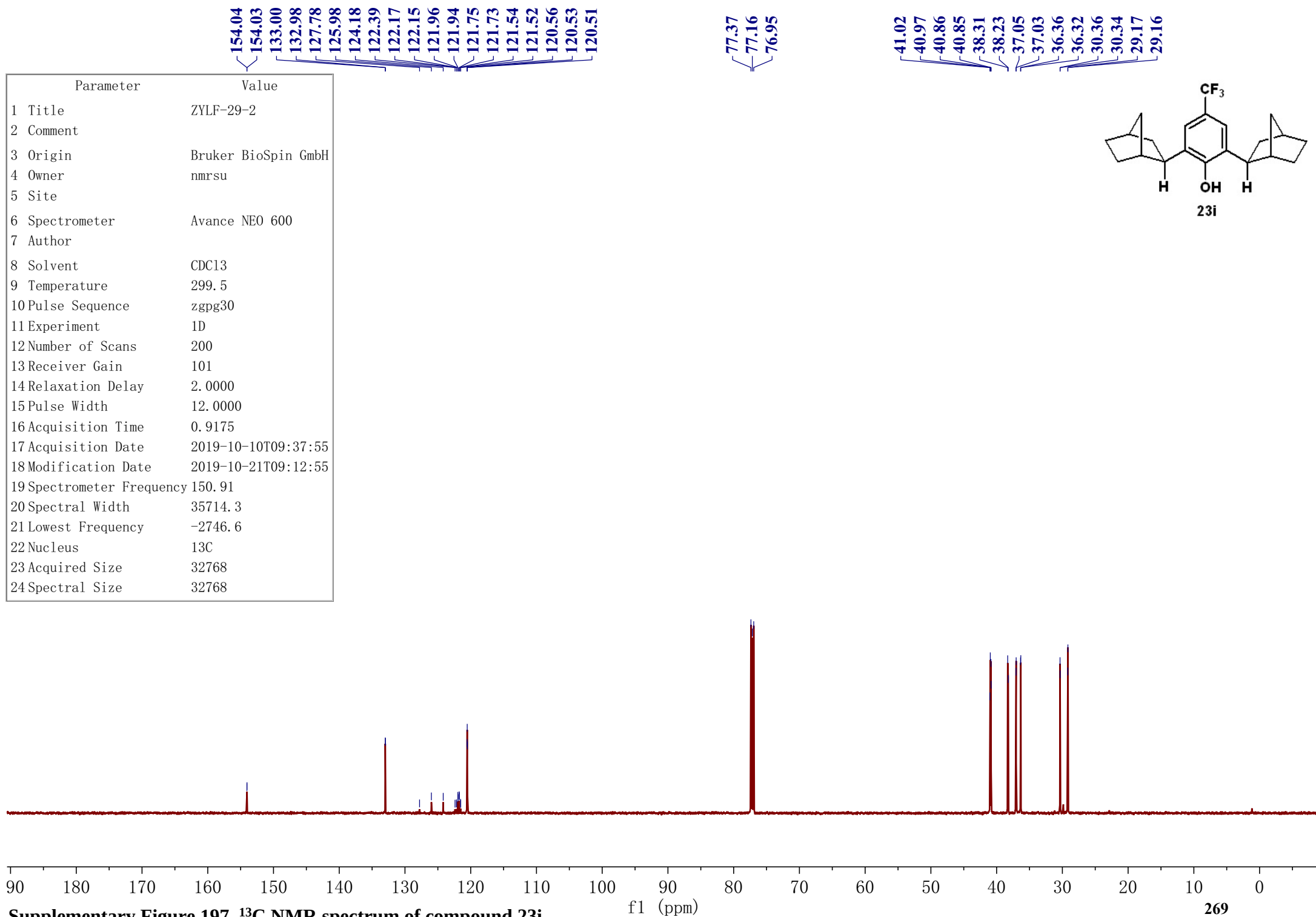
Parameter	Value
1 Title	zyl1205cf3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	297.7
10 Pulse Sequence	zg
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.4981
17 Acquisition Date	2018-12-05T11:24:12
18 Modification Date	2018-12-05T17:08:34
19 Spectrometer Frequency	564.71
20 Spectral Width	131579.0
21 Lowest Frequency	-122260.0
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536

-74.49
-74.50
-74.52



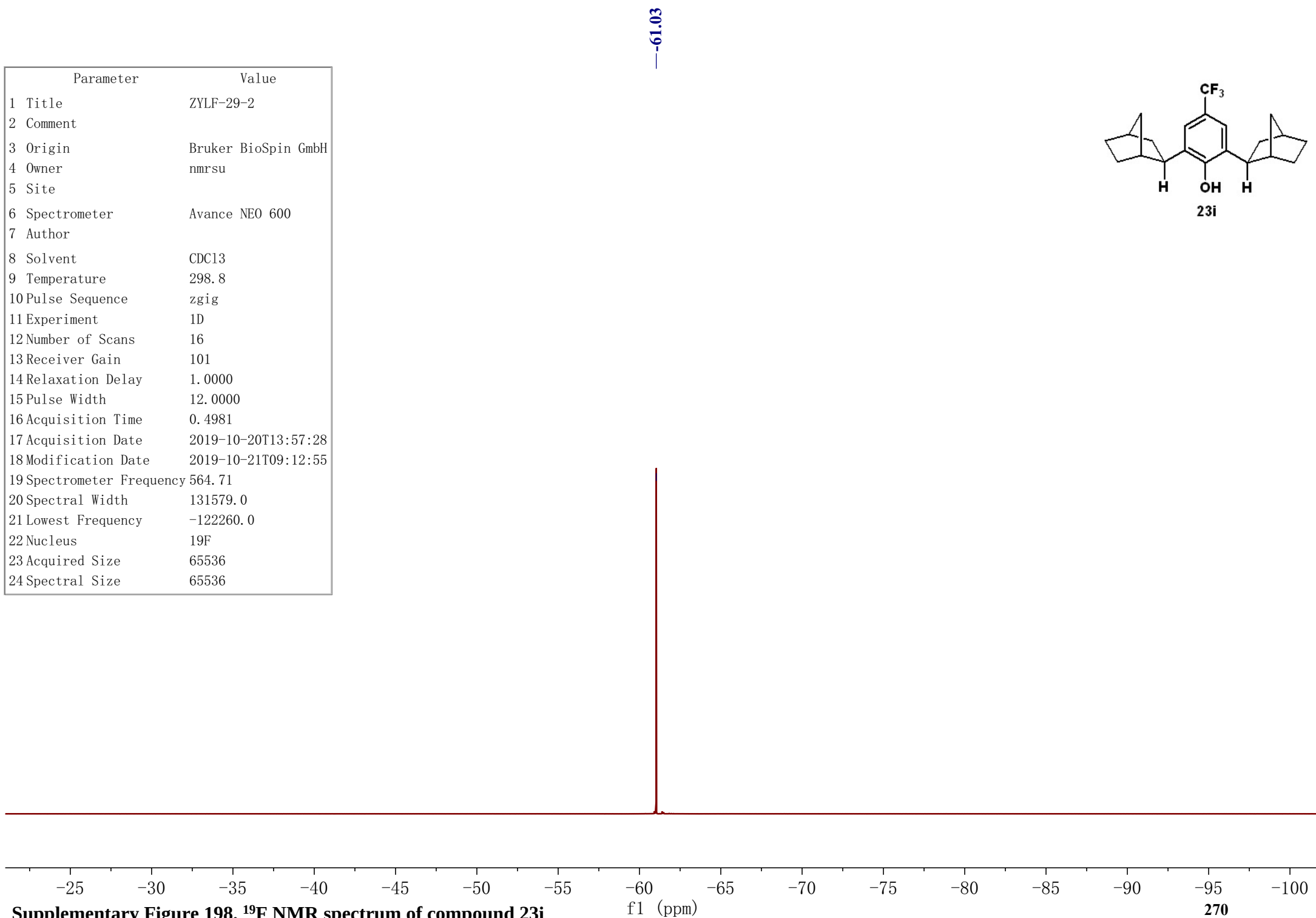
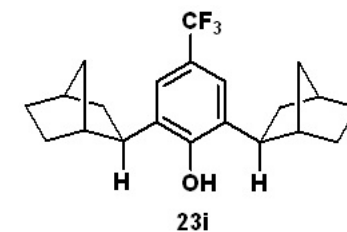


Supplementary Figure 196. ¹H NMR spectrum of compound 23i



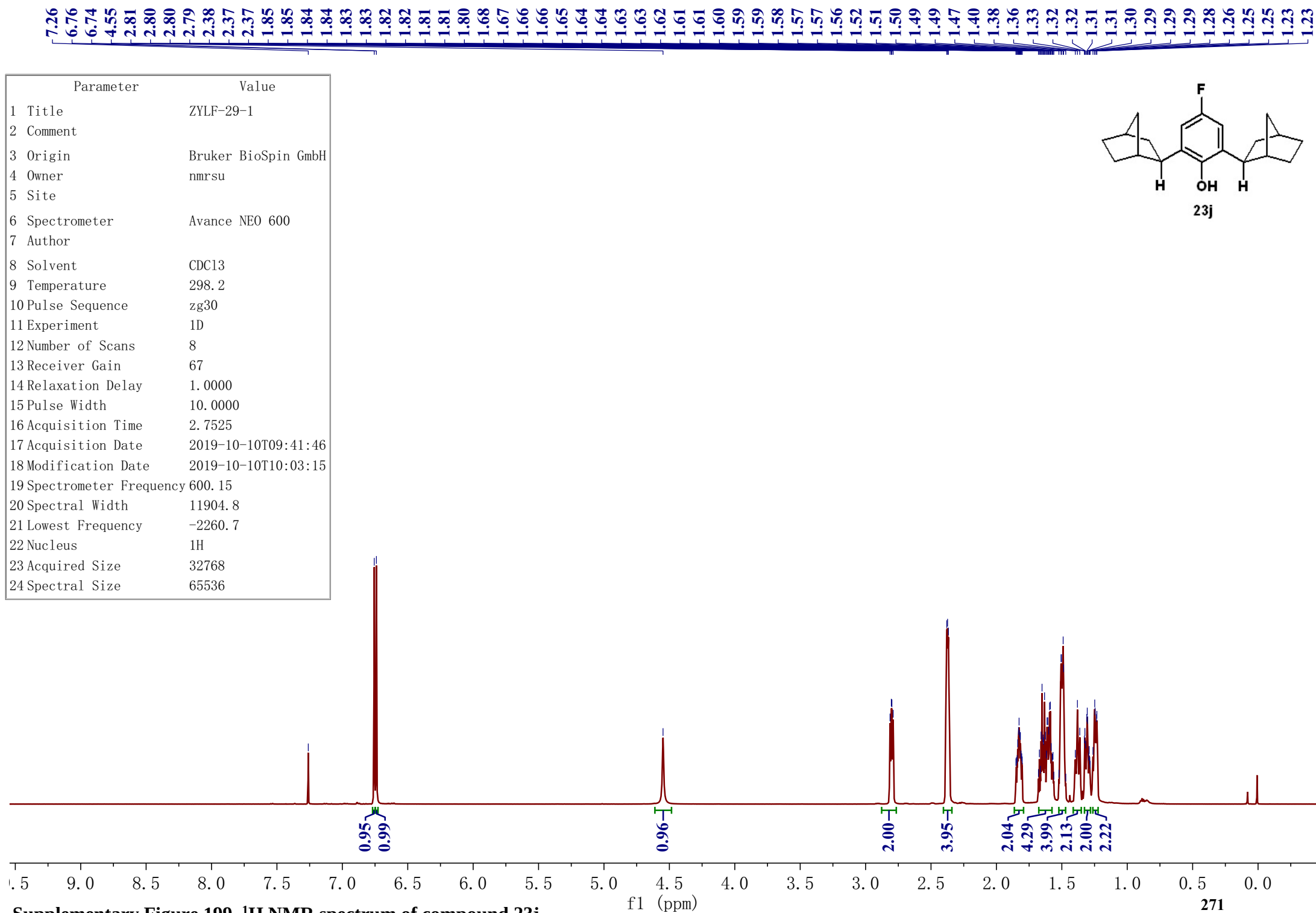
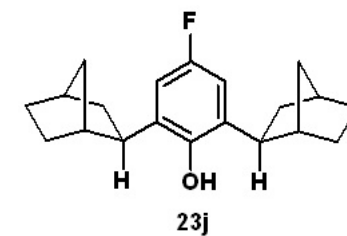
Supplementary Figure 197. ¹³C NMR spectrum of compound **23i**

Parameter	Value
1 Title	ZYLF-29-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	298.8
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.4981
17 Acquisition Date	2019-10-20T13:57:28
18 Modification Date	2019-10-21T09:12:55
19 Spectrometer Frequency	564.71
20 Spectral Width	131579.0
21 Lowest Frequency	-122260.0
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536



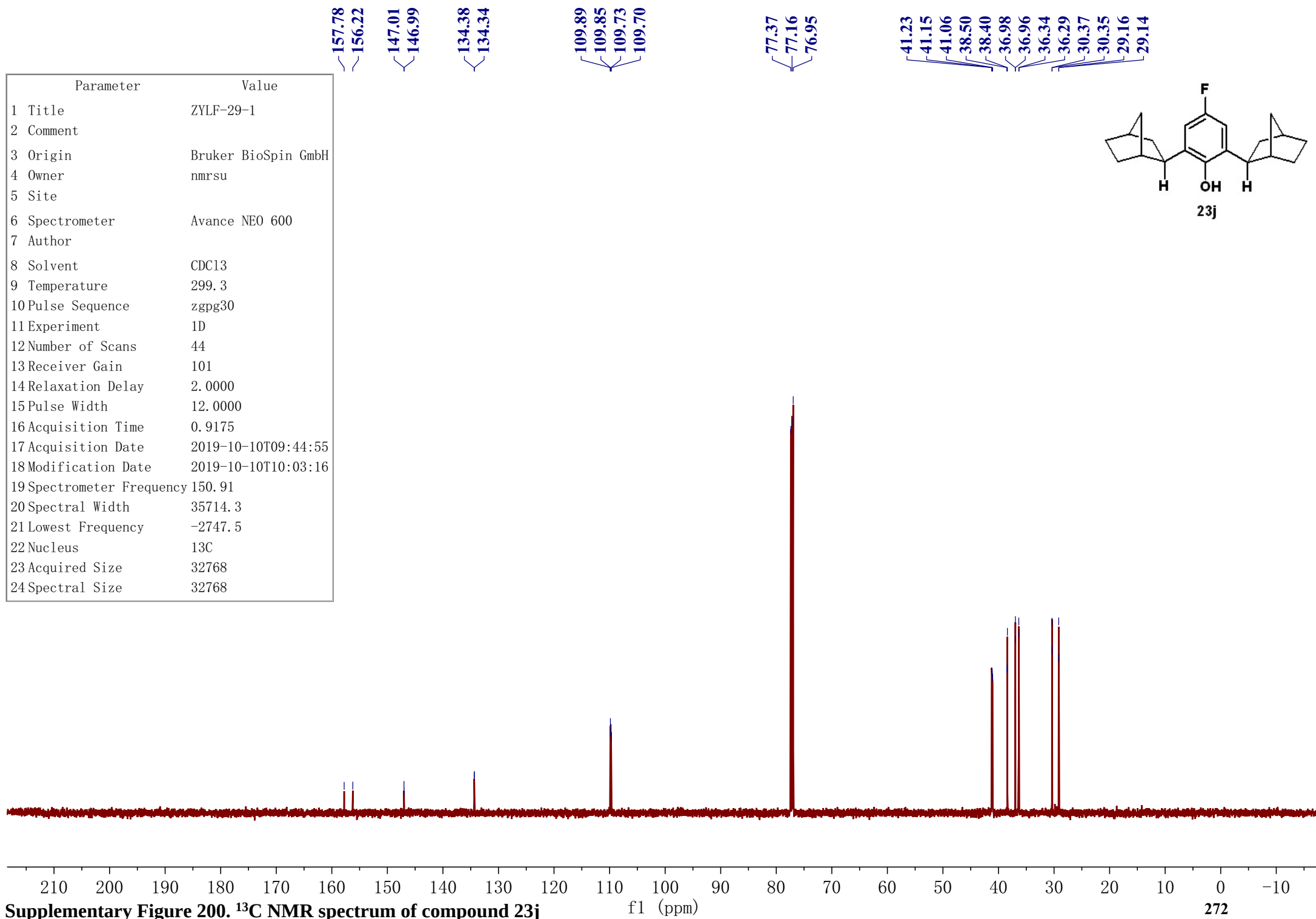
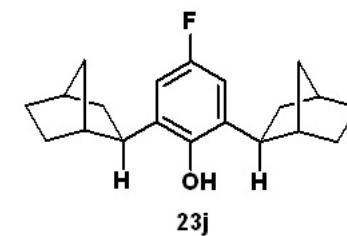
Supplementary Figure 198. ¹⁹F NMR spectrum of compound 23i

	Parameter	Value
1	Title	ZYLF-29-1
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmrsu
5	Site	
6	Spectrometer	Avance NEO 600
7	Author	
8	Solvent	CDC13
9	Temperature	298.2
10	Pulse Sequence	zg30
11	Experiment	1D
12	Number of Scans	8
13	Receiver Gain	67
14	Relaxation Delay	1.0000
15	Pulse Width	10.0000
16	Acquisition Time	2.7525
17	Acquisition Date	2019-10-10T09:41:46
18	Modification Date	2019-10-10T10:03:15
19	Spectrometer Frequency	600.15
20	Spectral Width	11904.8
21	Lowest Frequency	-2260.7
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536



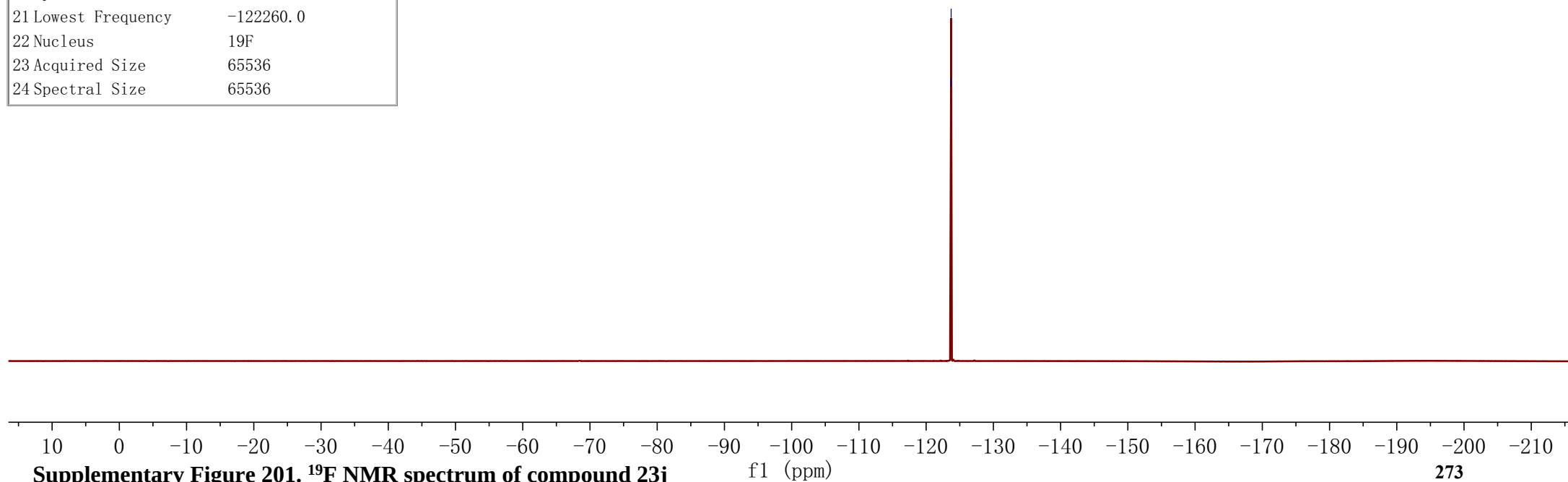
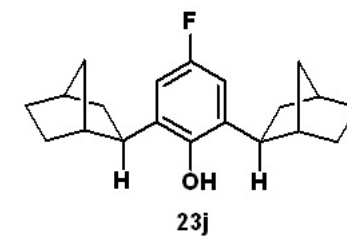
Supplementary Figure 199. ¹H NMR spectrum of compound 23j

Parameter	Value
1 Title	ZYLF-29-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	299.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	44
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-10-10T09:44:55
18 Modification Date	2019-10-10T10:03:16
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2747.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

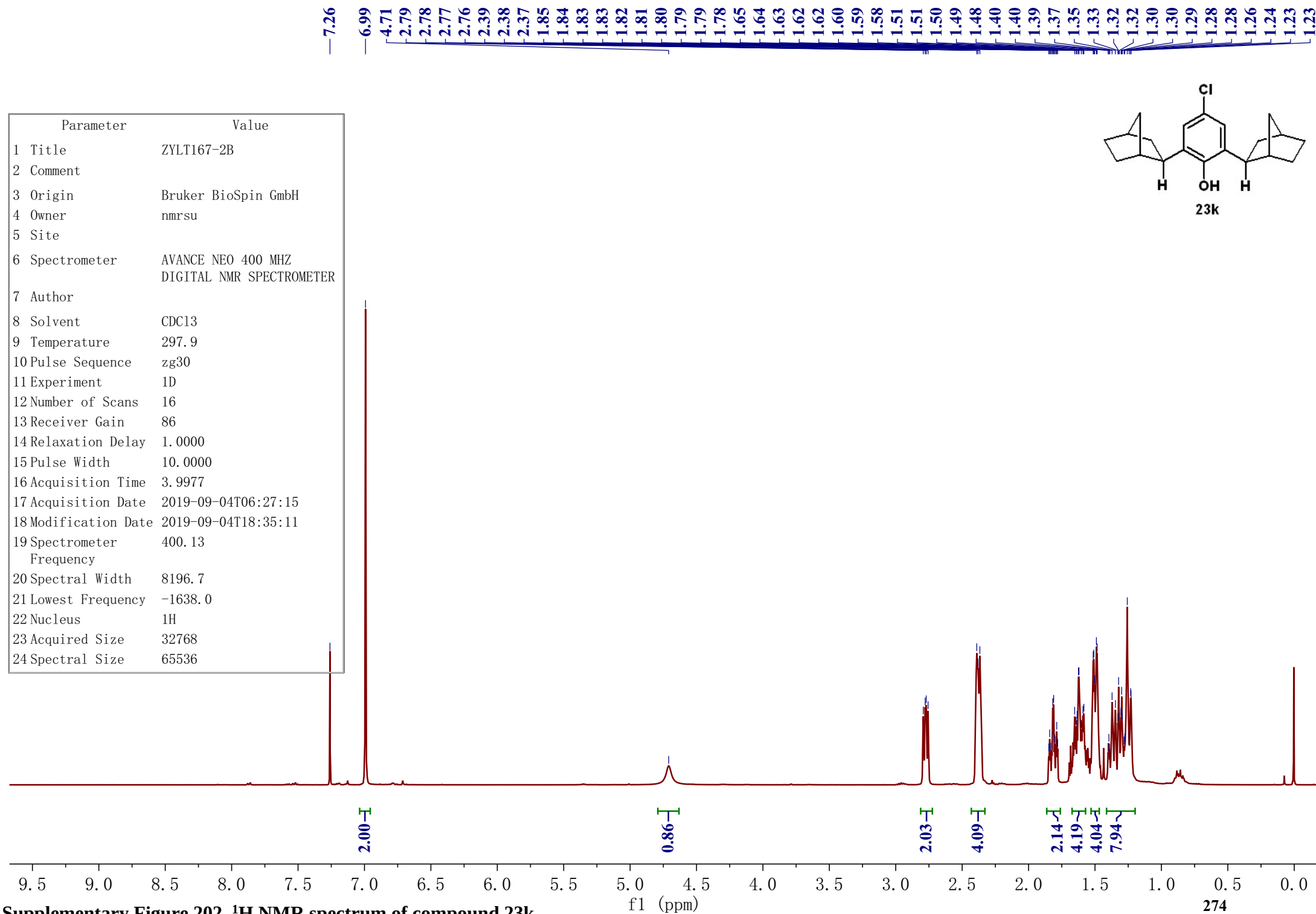
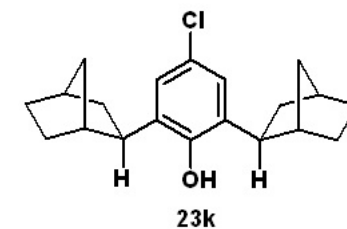


Parameter	Value
1 Title	ZYLF-29-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	298.8
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.4981
17 Acquisition Date	2019-10-20T13:53:28
18 Modification Date	2019-10-21T09:12:58
19 Spectrometer Frequency	564.71
20 Spectral Width	131579.0
21 Lowest Frequency	-122260.0
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536

-123.70
-123.72

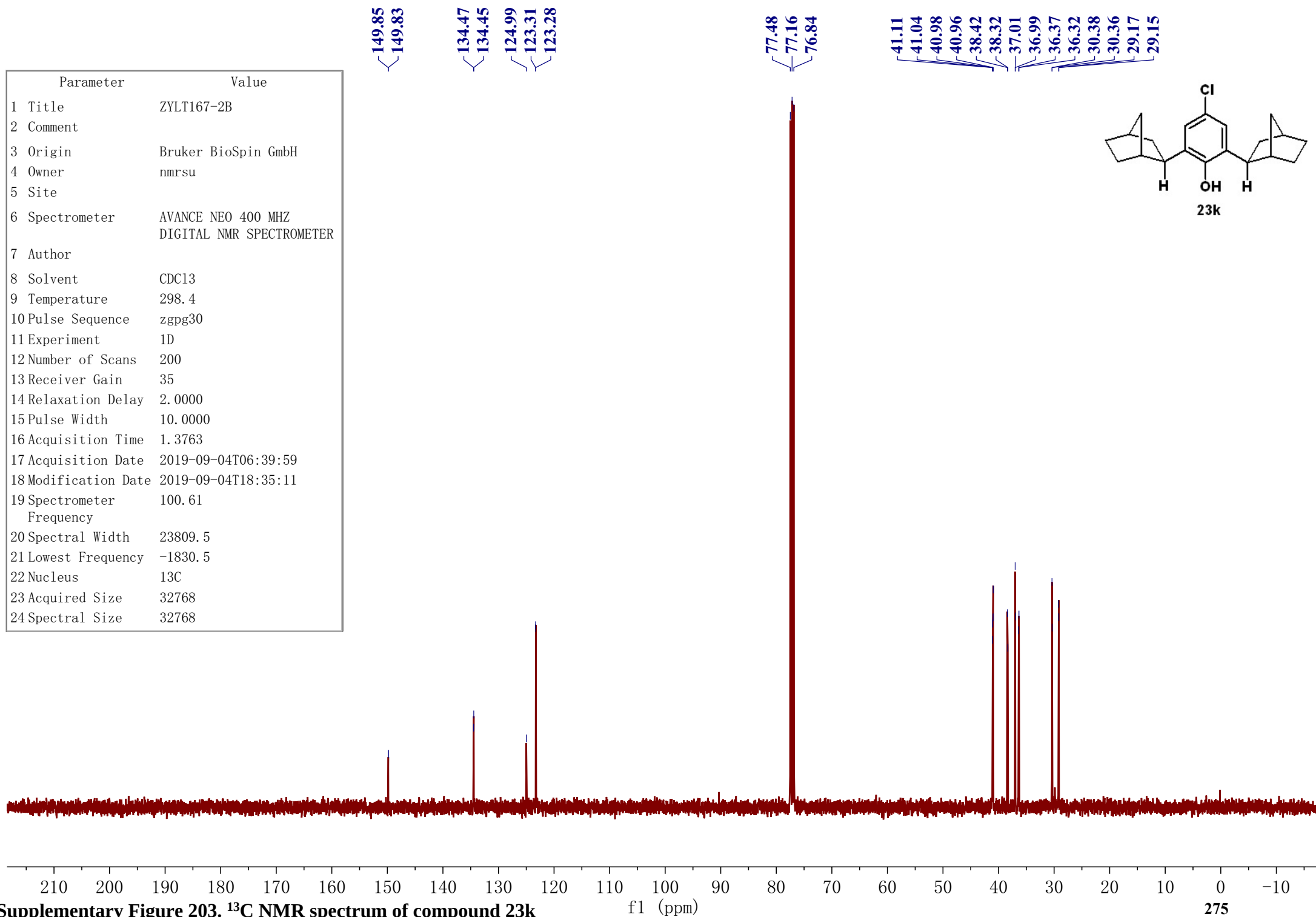
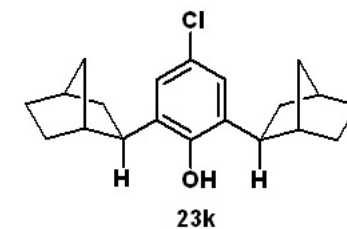


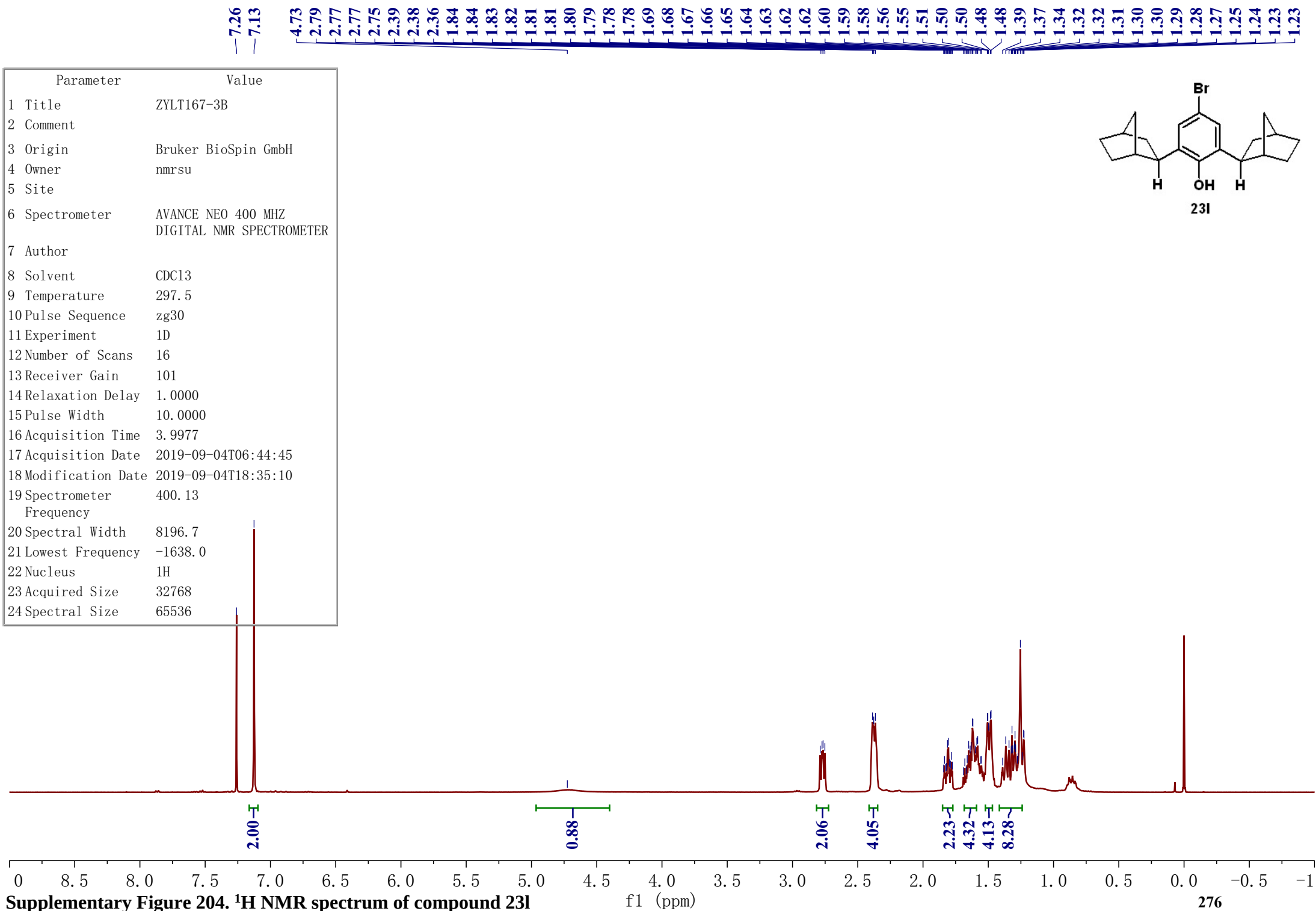
Parameter	Value
1 Title	ZYLT167-2B
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	297.9
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	86
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-09-04T06:27:15
18 Modification Date	2019-09-04T18:35:11
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.0
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



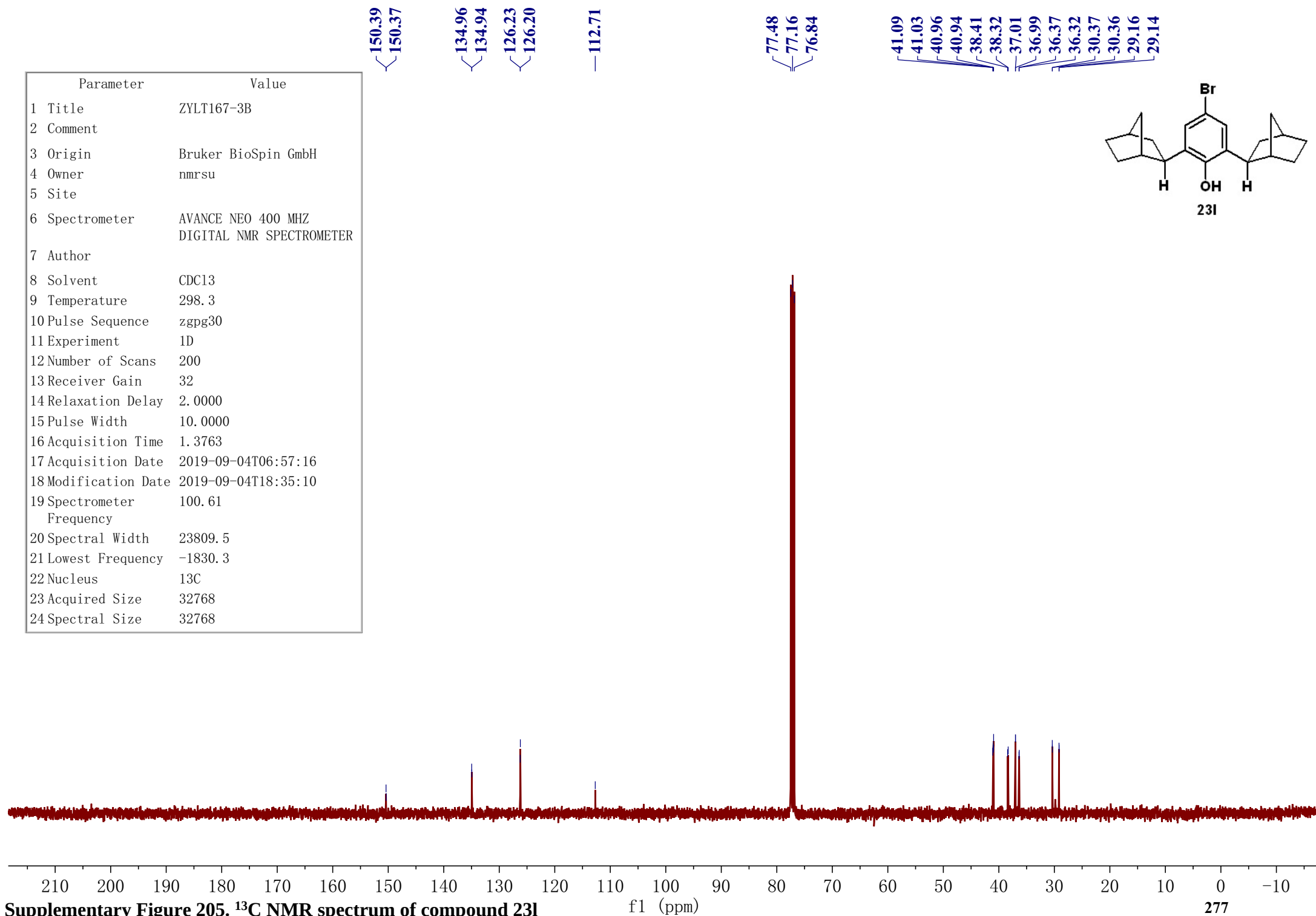
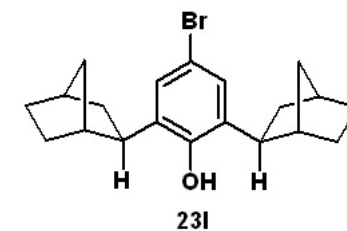
Supplementary Figure 202. ¹H NMR spectrum of compound 23k

Parameter	Value
1 Title	ZYLT167-2B
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	298.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	200
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-09-04T06:39:59
18 Modification Date	2019-09-04T18:35:11
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1830.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

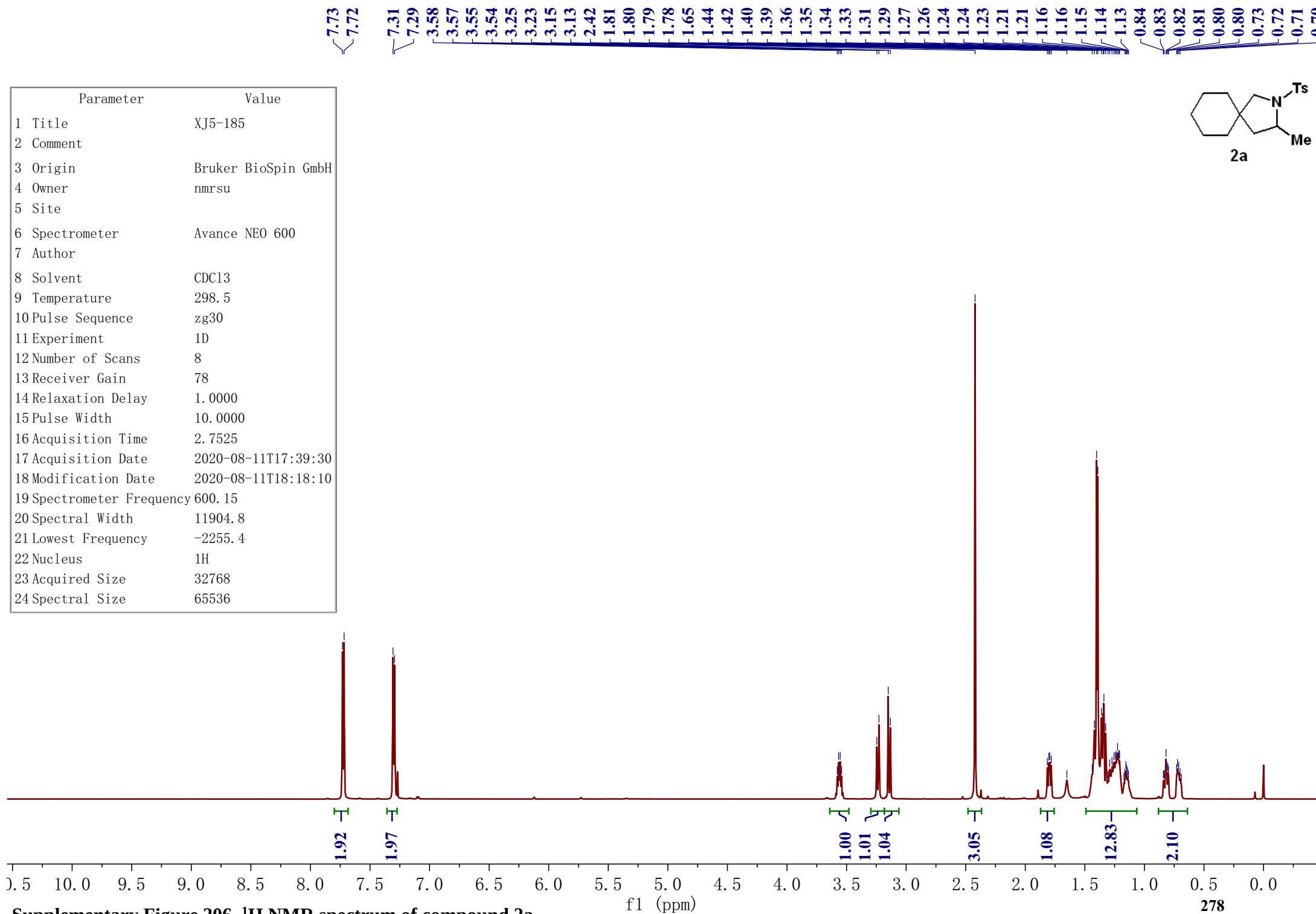
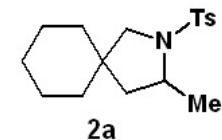




Parameter	Value
1 Title	ZYLT167-3B
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	298.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	200
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-09-04T06:57:16
18 Modification Date	2019-09-04T18:35:10
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1830.3
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

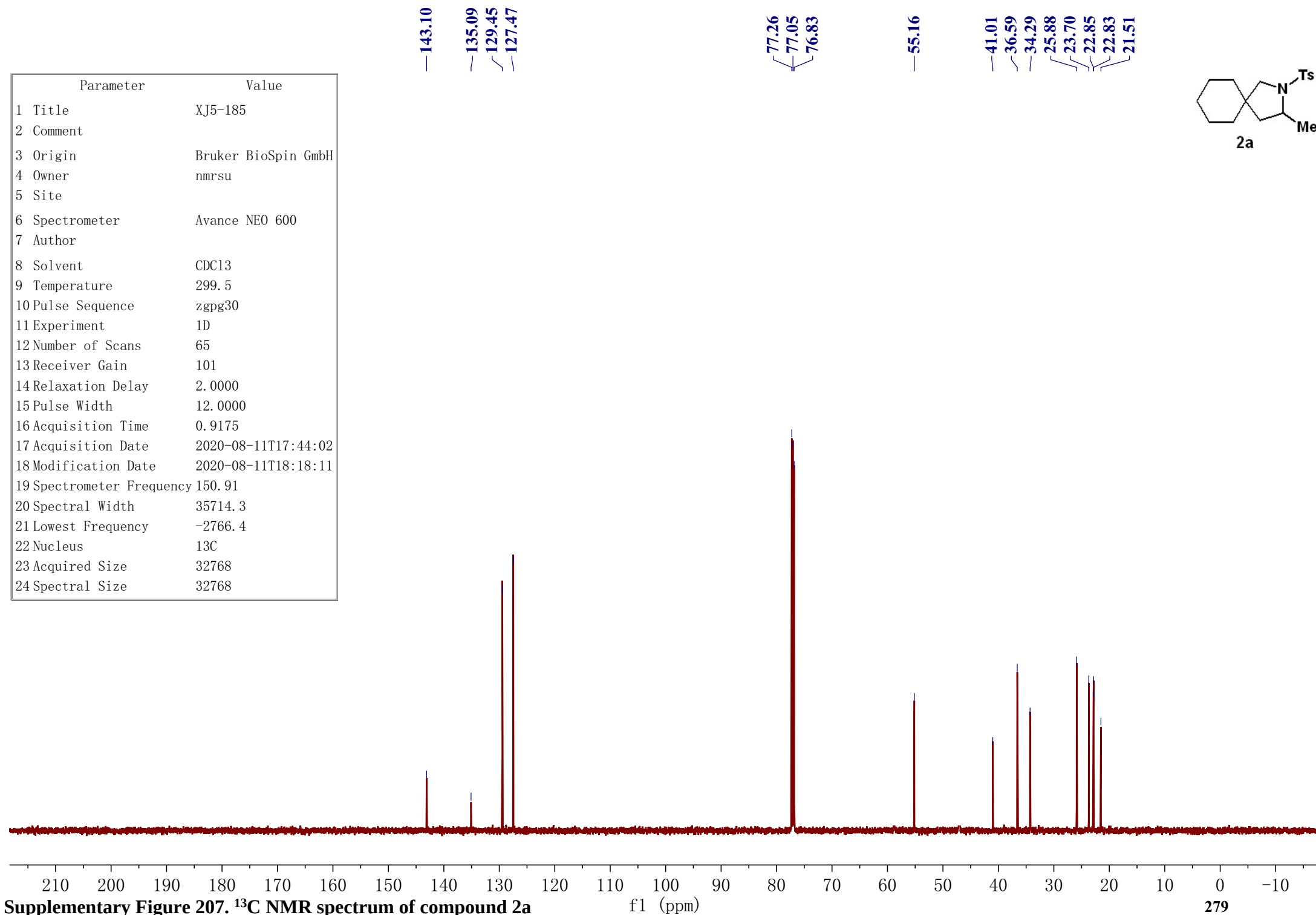
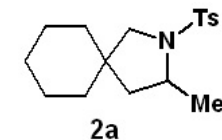


Parameter	Value
1 Title	XJ5-185
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	298.5
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	78
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2020-08-11T17:39:30
18 Modification Date	2020-08-11T18:18:10
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2255.4
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

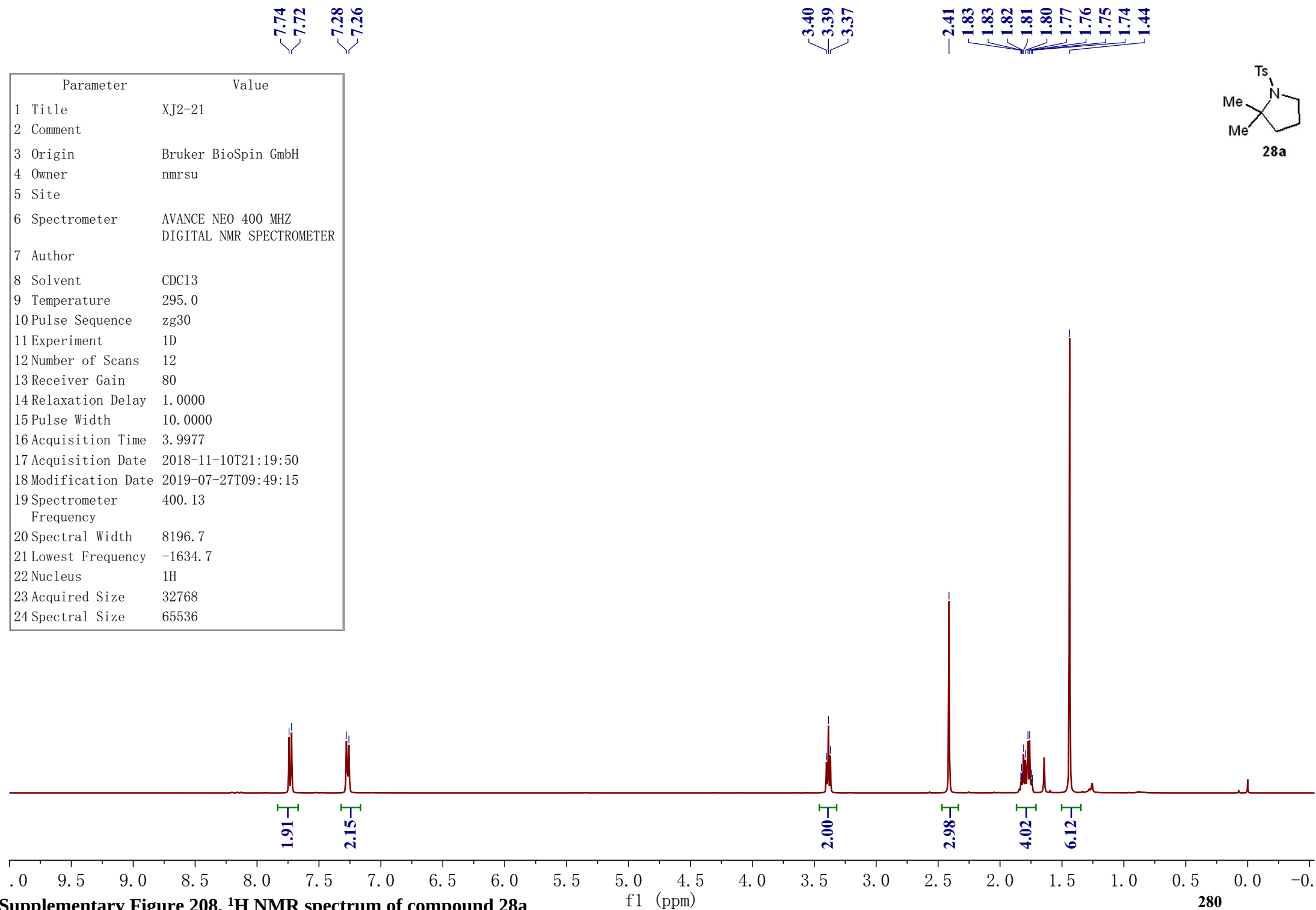
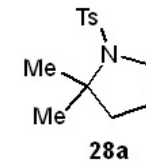


Supplementary Figure 206. ¹H NMR spectrum of compound 2a

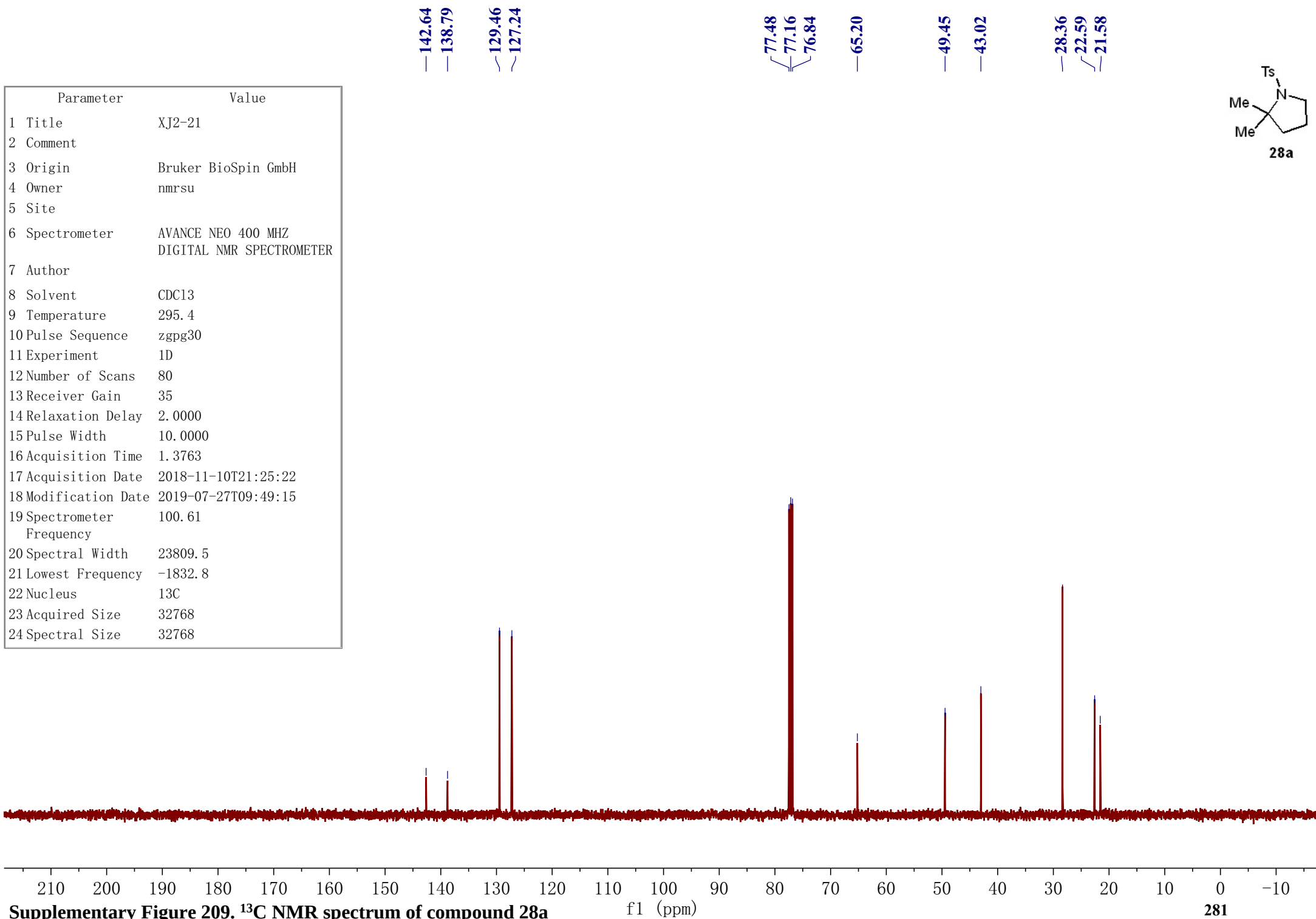
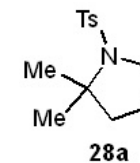
Parameter	Value
1 Title	XJ5-185
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	299.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	65
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2020-08-11T17:44:02
18 Modification Date	2020-08-11T18:18:11
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2766.4
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768



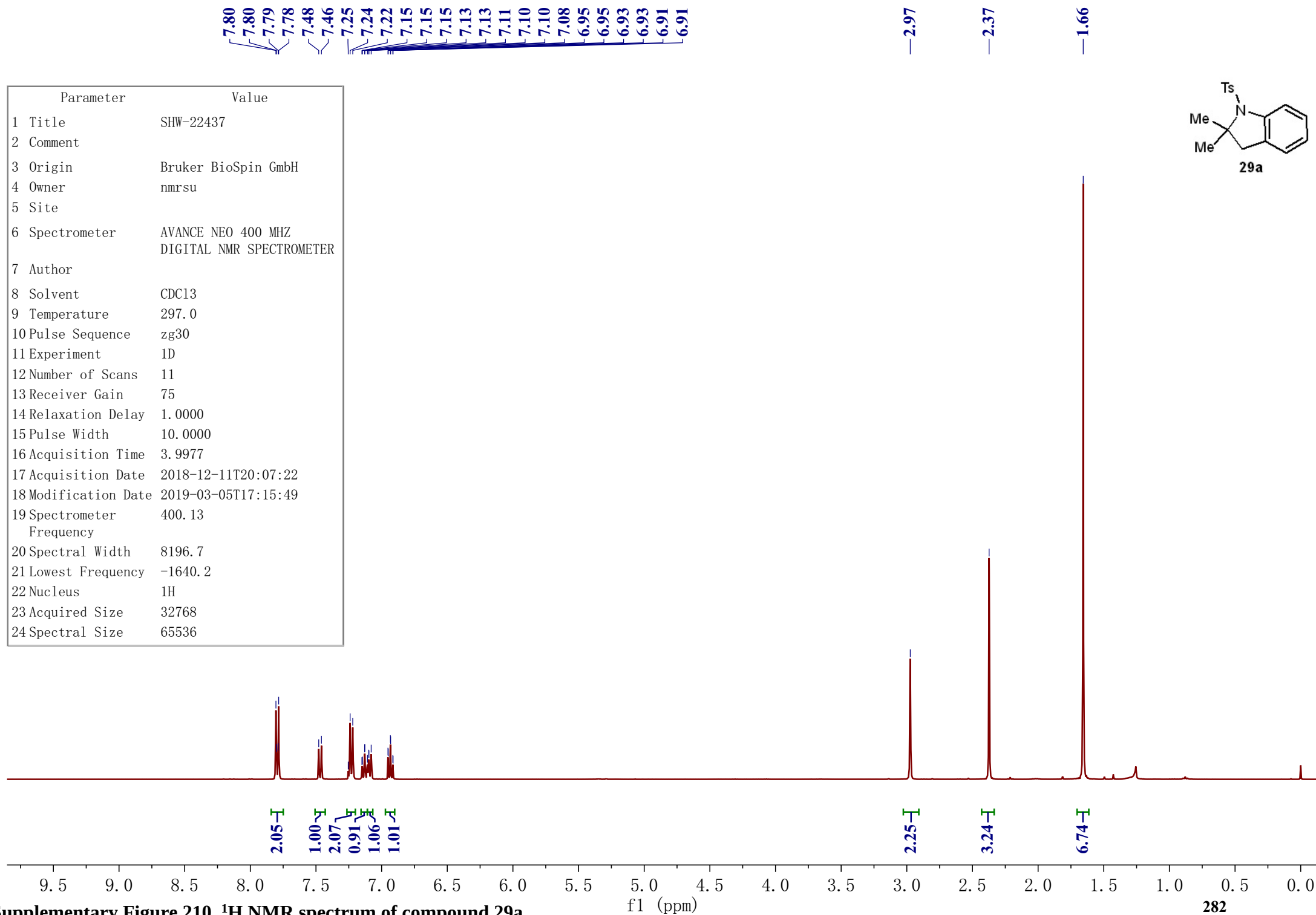
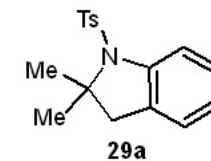
Parameter	Value
1 Title	XJ2-21
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	295.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	12
13 Receiver Gain	80
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-11-10T21:19:50
18 Modification Date	2019-07-27T09:49:15
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1634.7
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Parameter	Value
1 Title	XJ2-21
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	80
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-11-10T21:25:22
18 Modification Date	2019-07-27T09:49:15
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1832.8
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

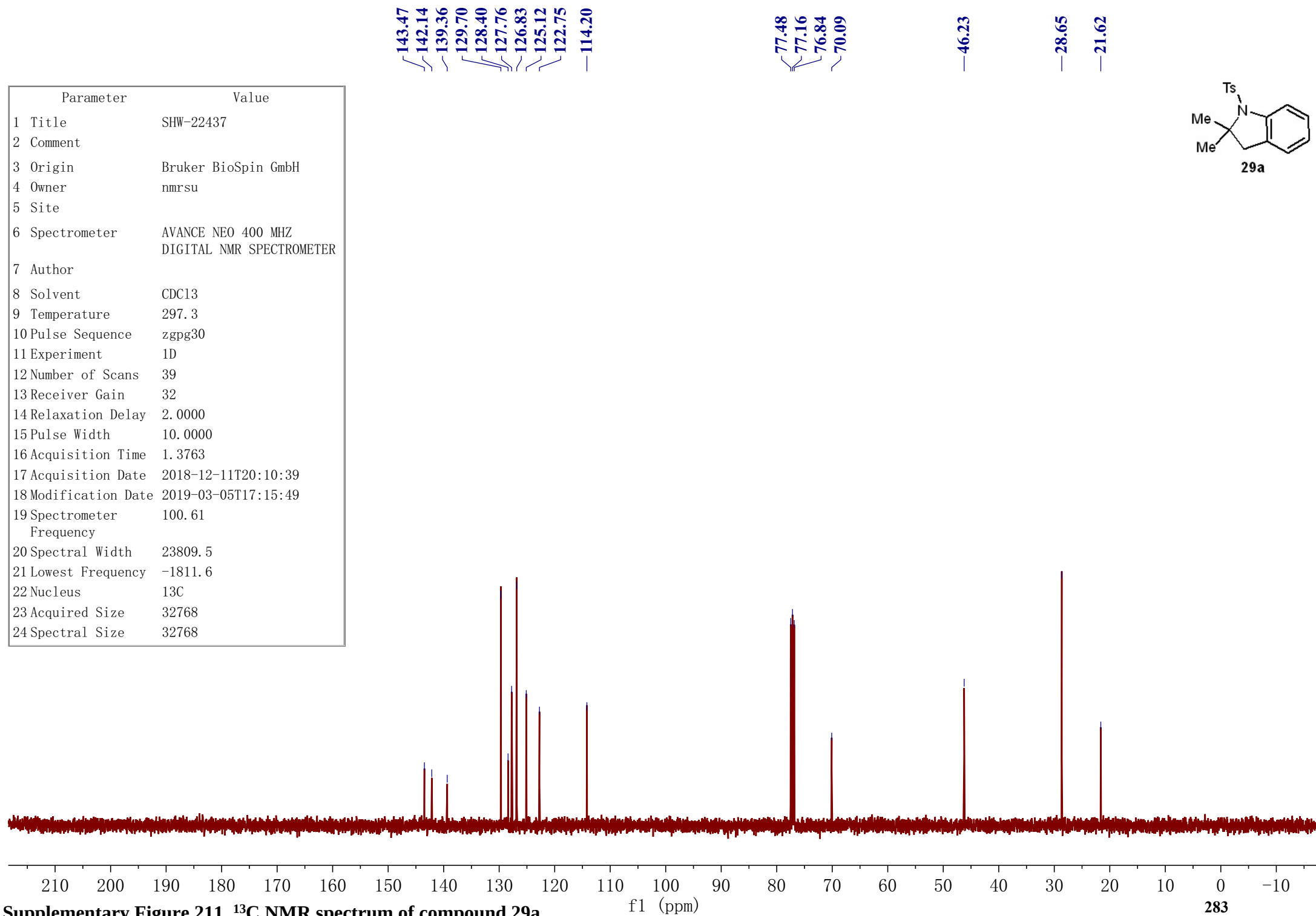
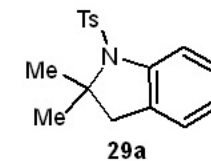


Parameter	Value
1 Title	SHW-22437
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	297.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	11
13 Receiver Gain	75
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-12-11T20:07:22
18 Modification Date	2019-03-05T17:15:49
19 Spectrometer Frequency	400.13
20 Spectral Width	8196.7
21 Lowest Frequency	-1640.2
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

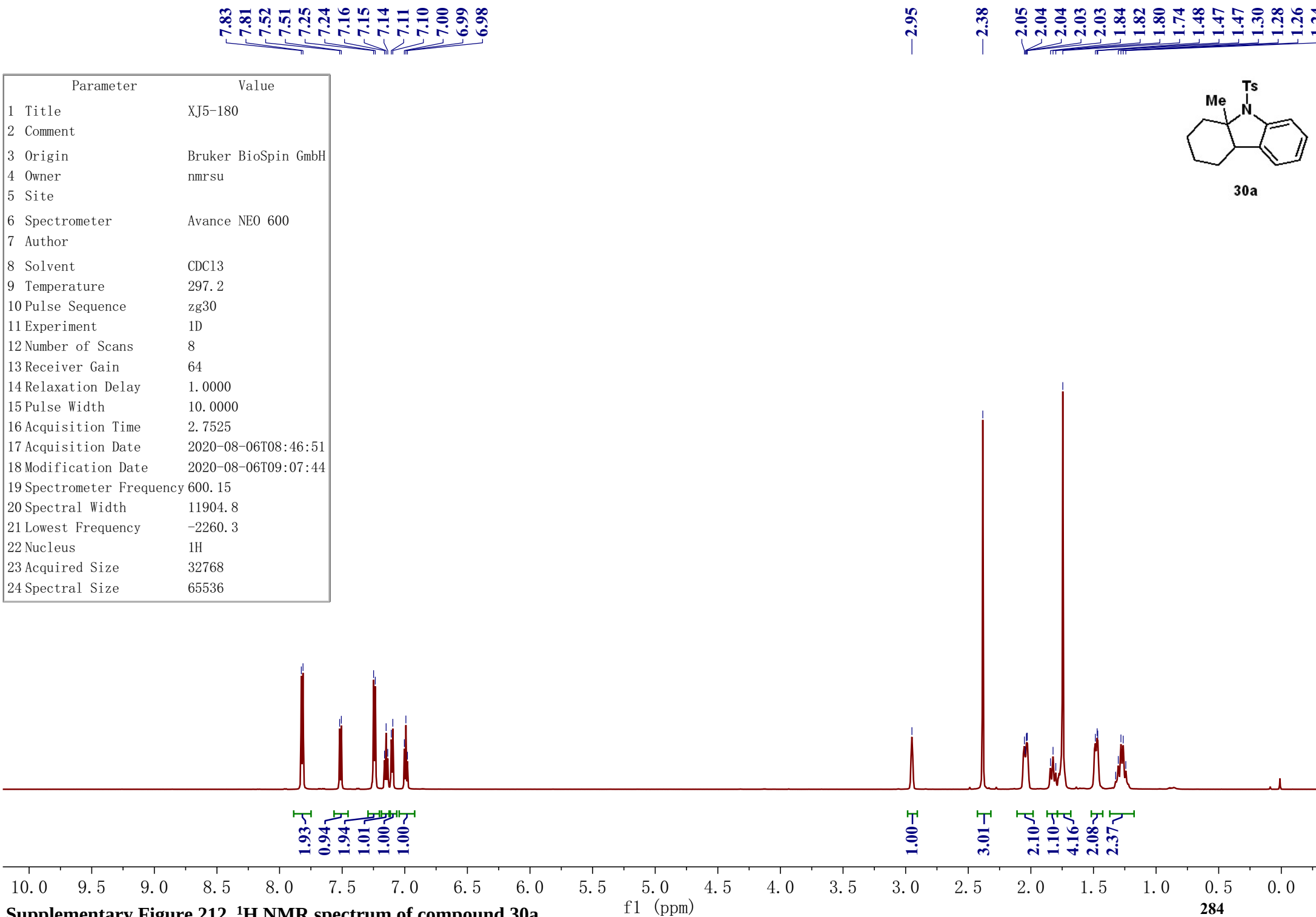


Supplementary Figure 210. ¹H NMR spectrum of compound 29a

Parameter	Value
1 Title	SHW-22437
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	297.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	39
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-11T20:10:39
18 Modification Date	2019-03-05T17:15:49
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1811.6
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

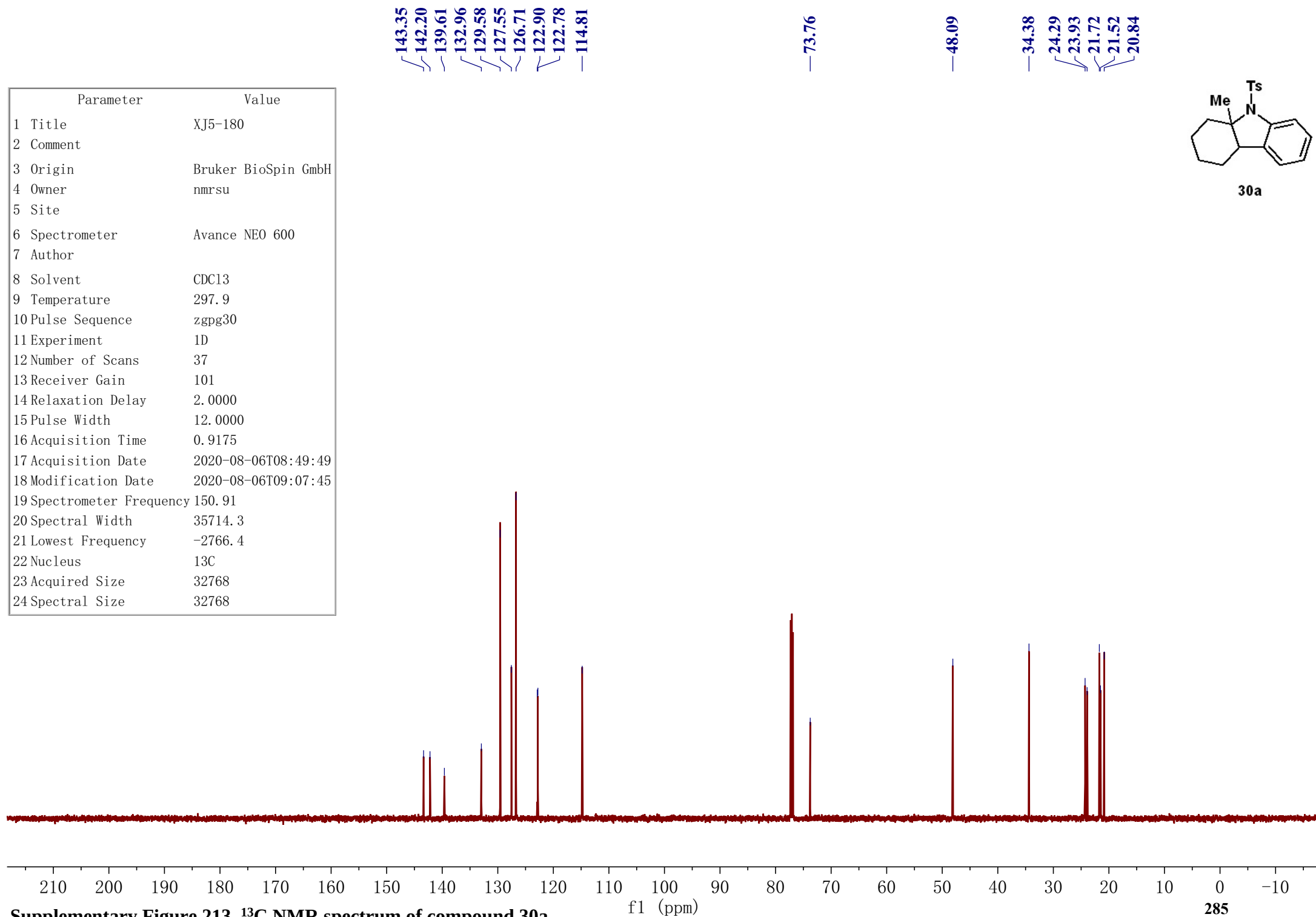
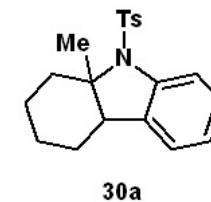


Parameter	Value
1 Title	XJ5-180
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	297.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	64
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2020-08-06T08:46:51
18 Modification Date	2020-08-06T09:07:44
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2260.3
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536



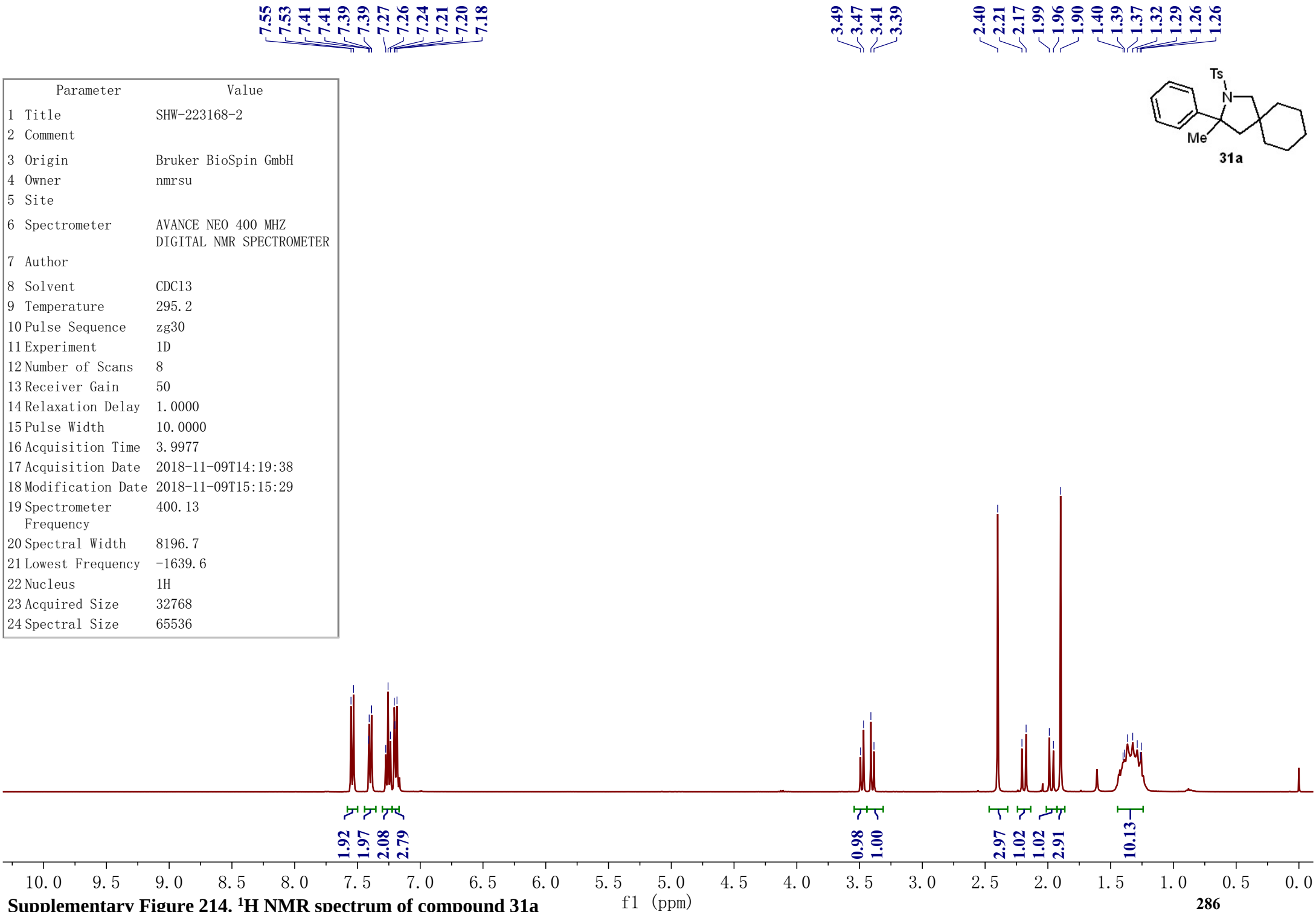
Supplementary Figure 212. ¹H NMR spectrum of compound 30a

Parameter	Value
1 Title	XJ5-180
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	37
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2020-08-06T08:49:49
18 Modification Date	2020-08-06T09:07:45
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2766.4
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 213. ¹³C NMR spectrum of compound 30a

Parameter	Value
1 Title	SHW-223168-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	295.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	50
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-11-09T14:19:38
18 Modification Date	2018-11-09T15:15:29
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1639.6
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536



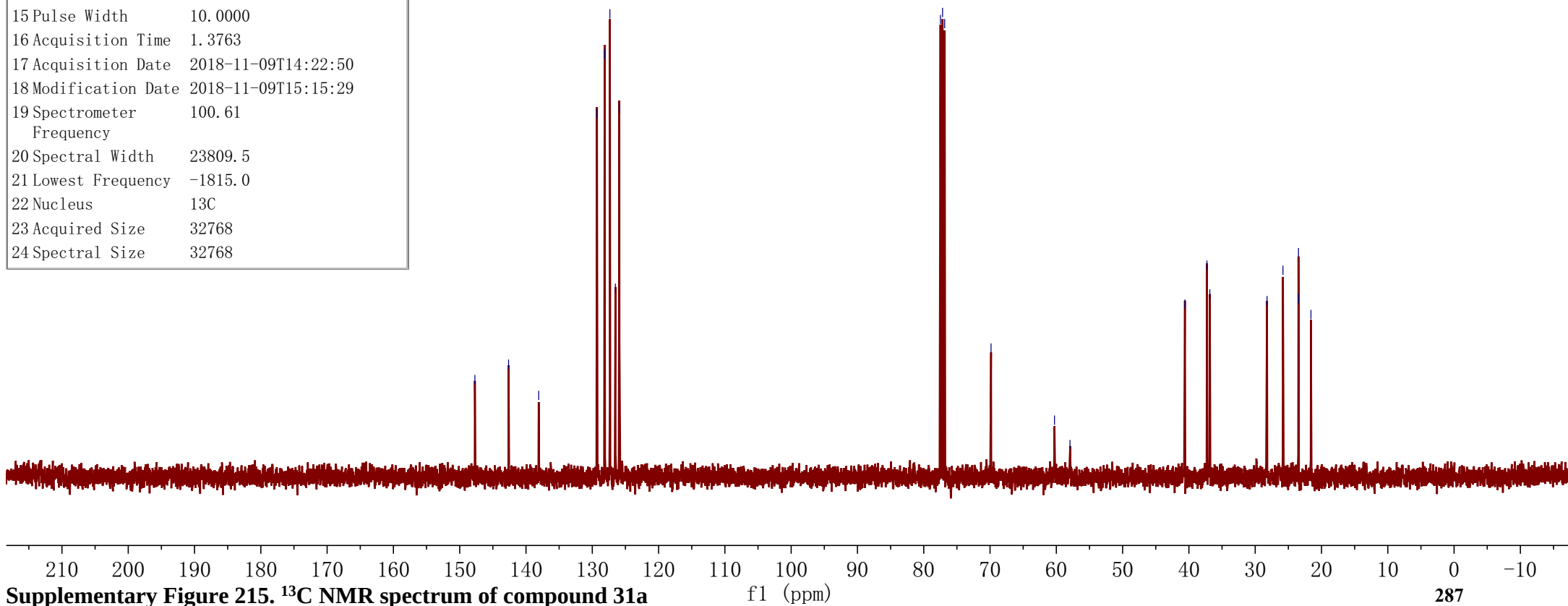
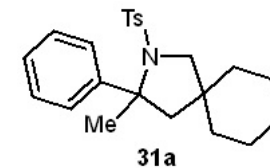
Supplementary Figure 214. ¹H NMR spectrum of compound 31a

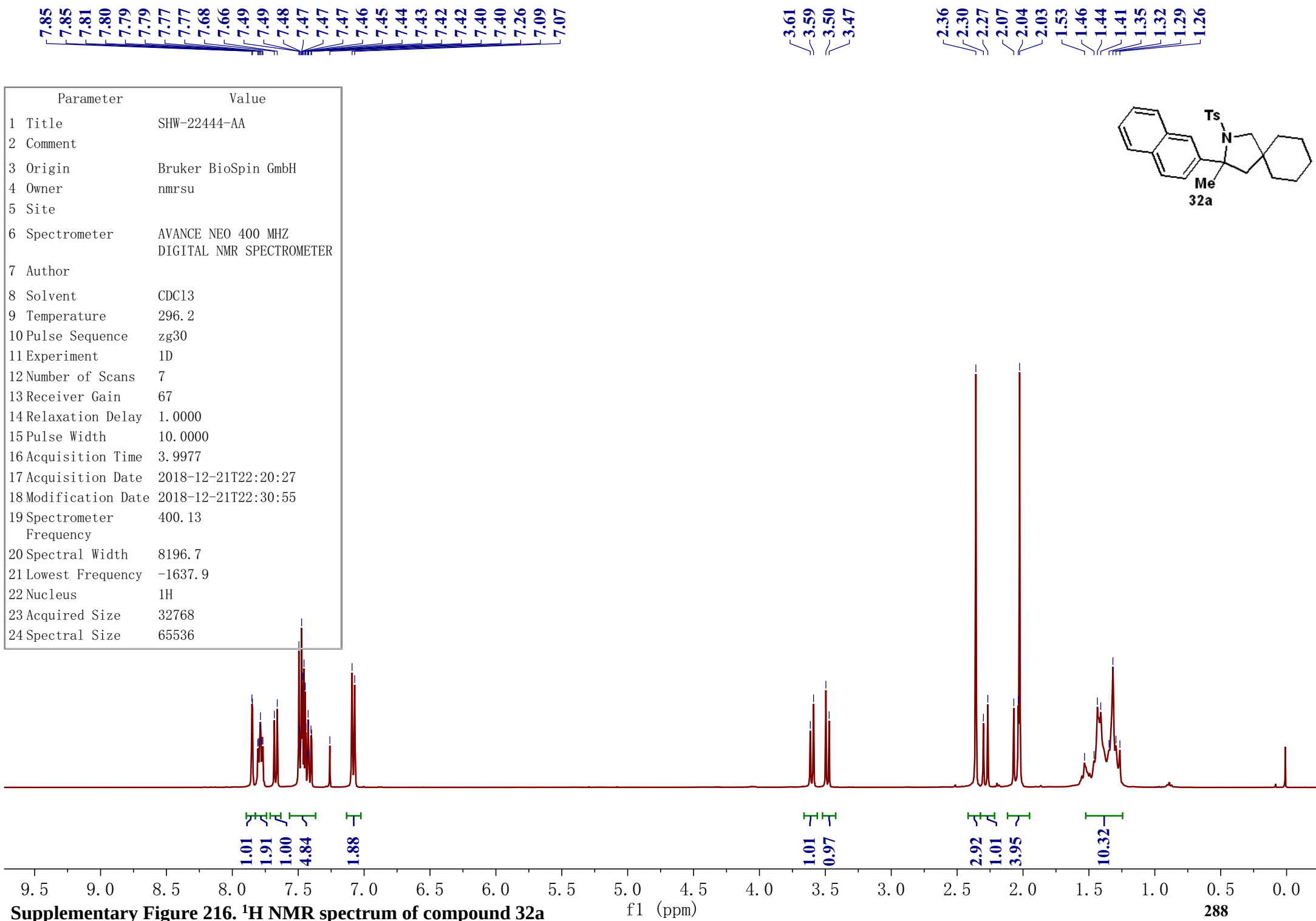
Parameter	Value
1 Title	SHW-223168-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	295.7
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	34
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-11-09T14:22:50
18 Modification Date	2018-11-09T15:15:29
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1815.0
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

147.71
142.63
138.08
129.29
128.13
127.35
126.51
125.91

77.48
77.16
76.84
69.85
60.28
57.94

40.61
37.28
36.84
28.22
25.81
23.47
23.45
21.59



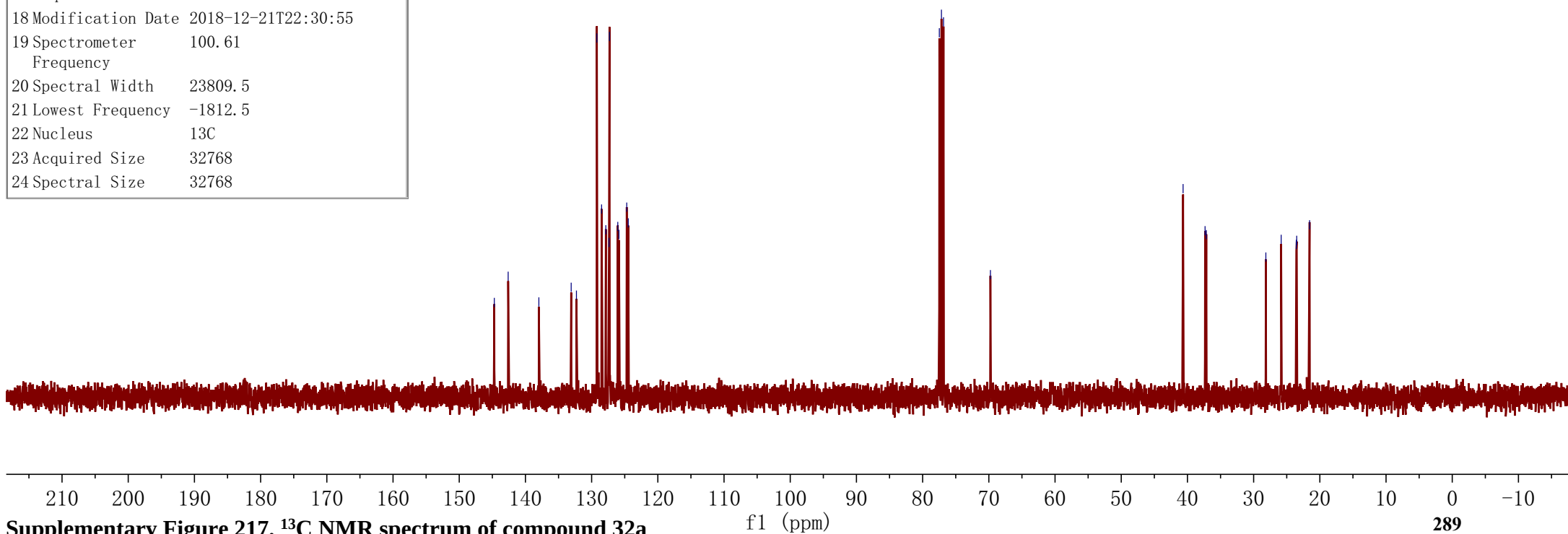
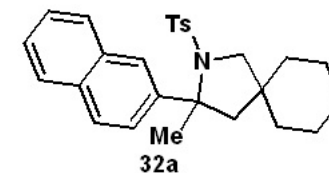


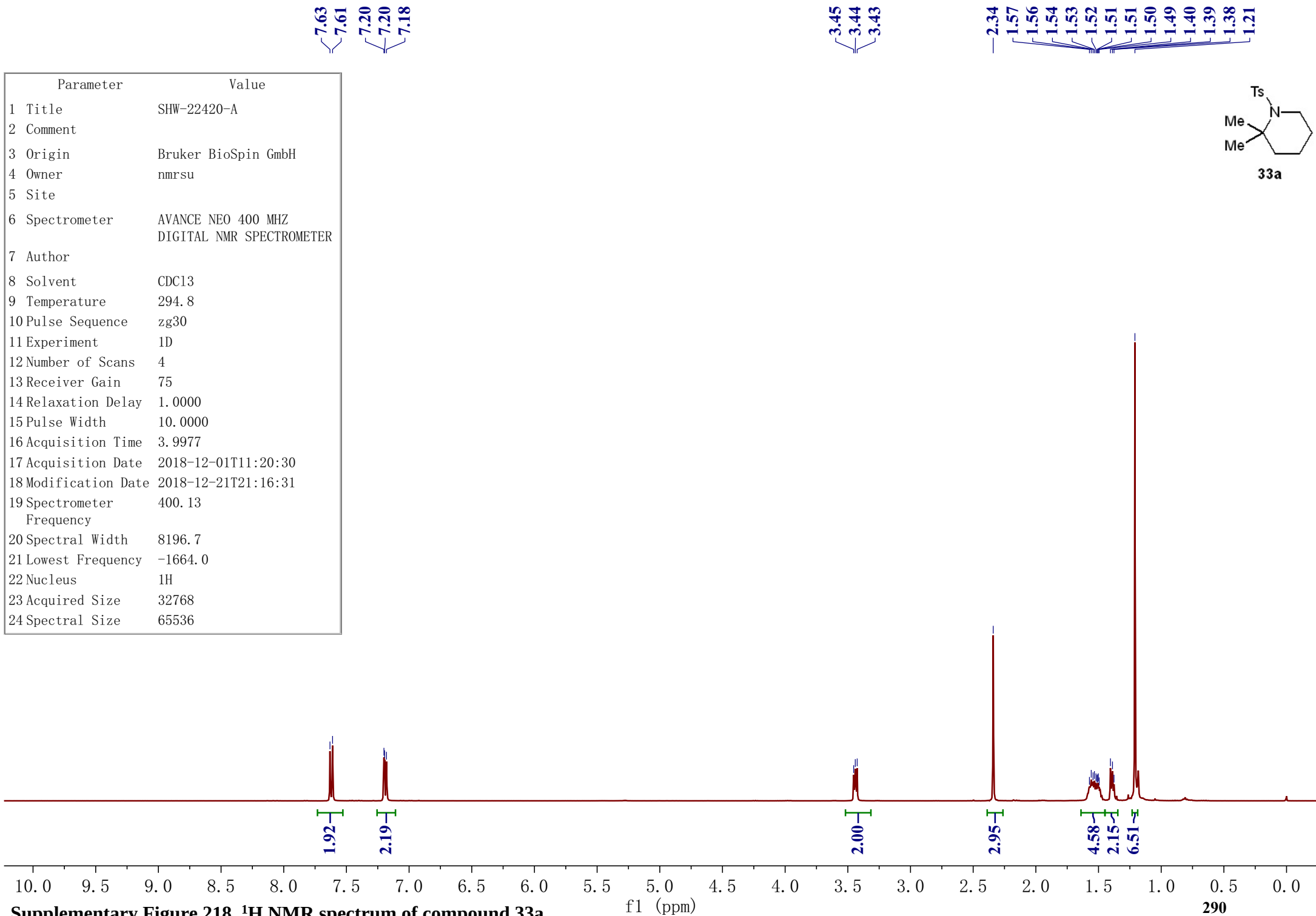
Parameter	Value
1 Title	SHW-22444-AA
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	296.7
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	43
13 Receiver Gain	50
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-21T22:23:57
18 Modification Date	2018-12-21T22:30:55
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1812.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

144.70
142.61
137.97
133.09
132.30
129.21
128.50
127.86
127.38
127.31
126.05
125.87
124.70
124.47

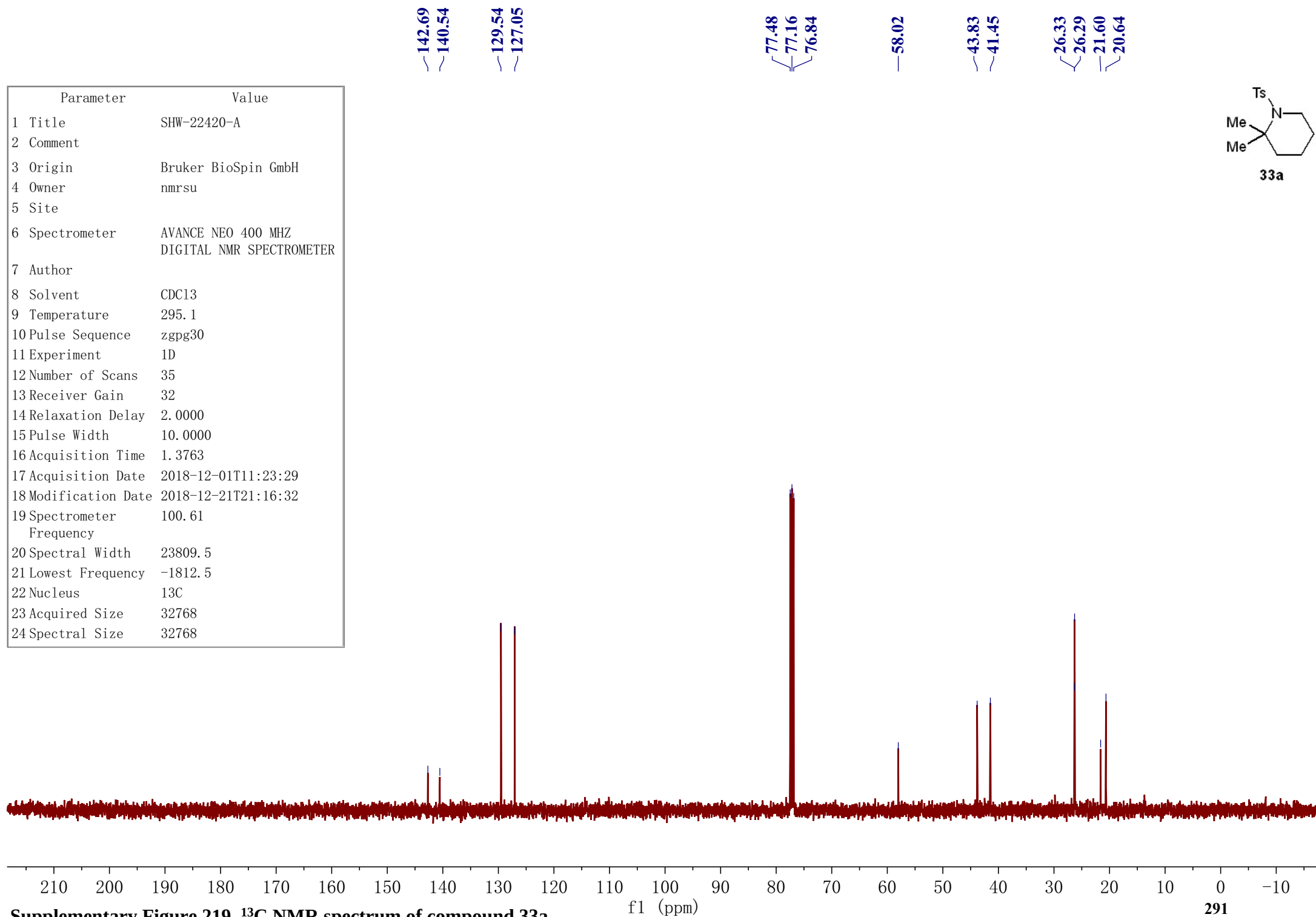
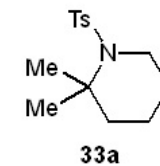
77.48
77.16
76.84
69.76

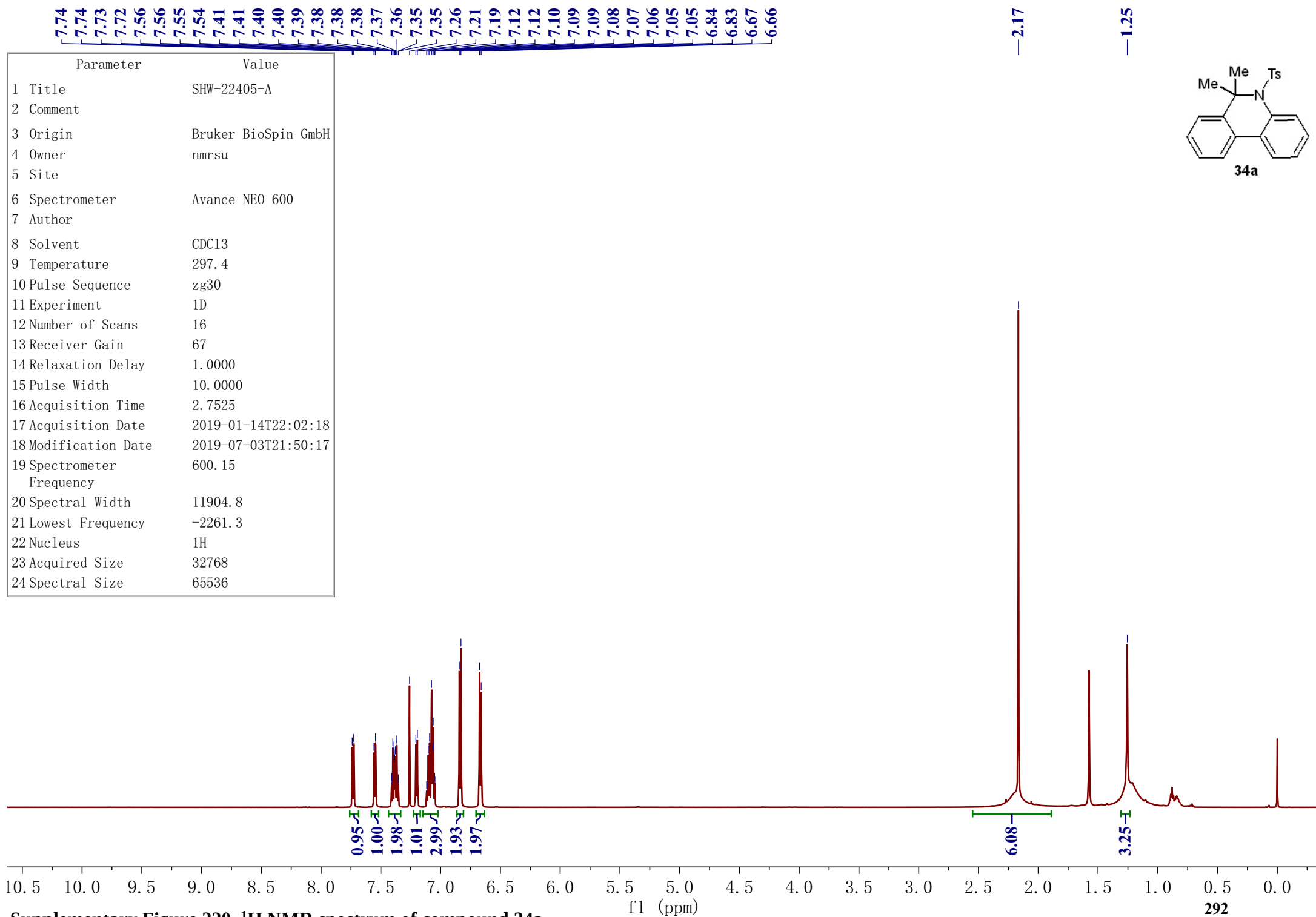
40.66
37.34
37.15
28.15
25.84
23.56
23.49
21.55



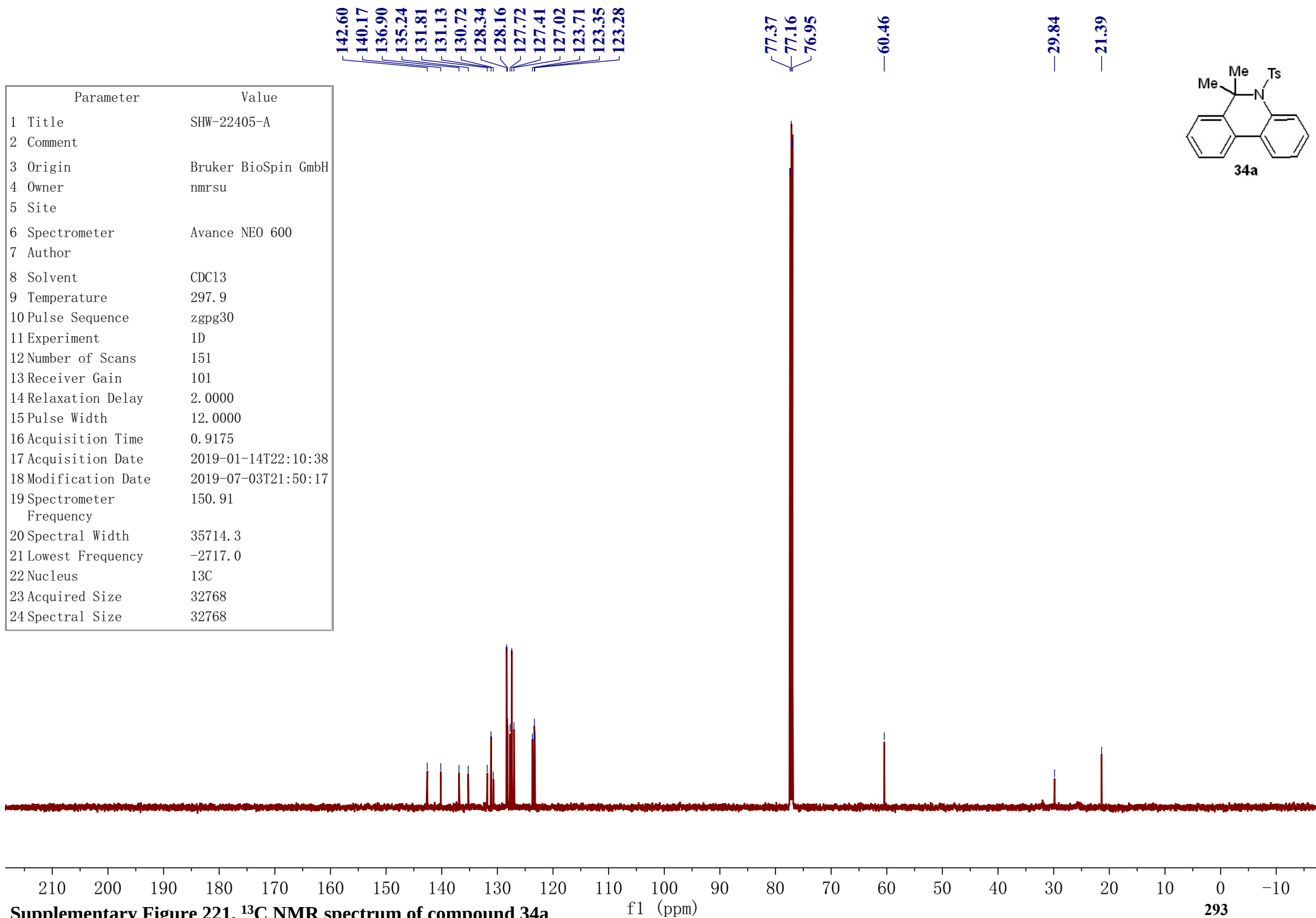


Parameter	Value
1 Title	SHW-22420-A
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	295.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	35
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-01T11:23:29
18 Modification Date	2018-12-21T21:16:32
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1812.5
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

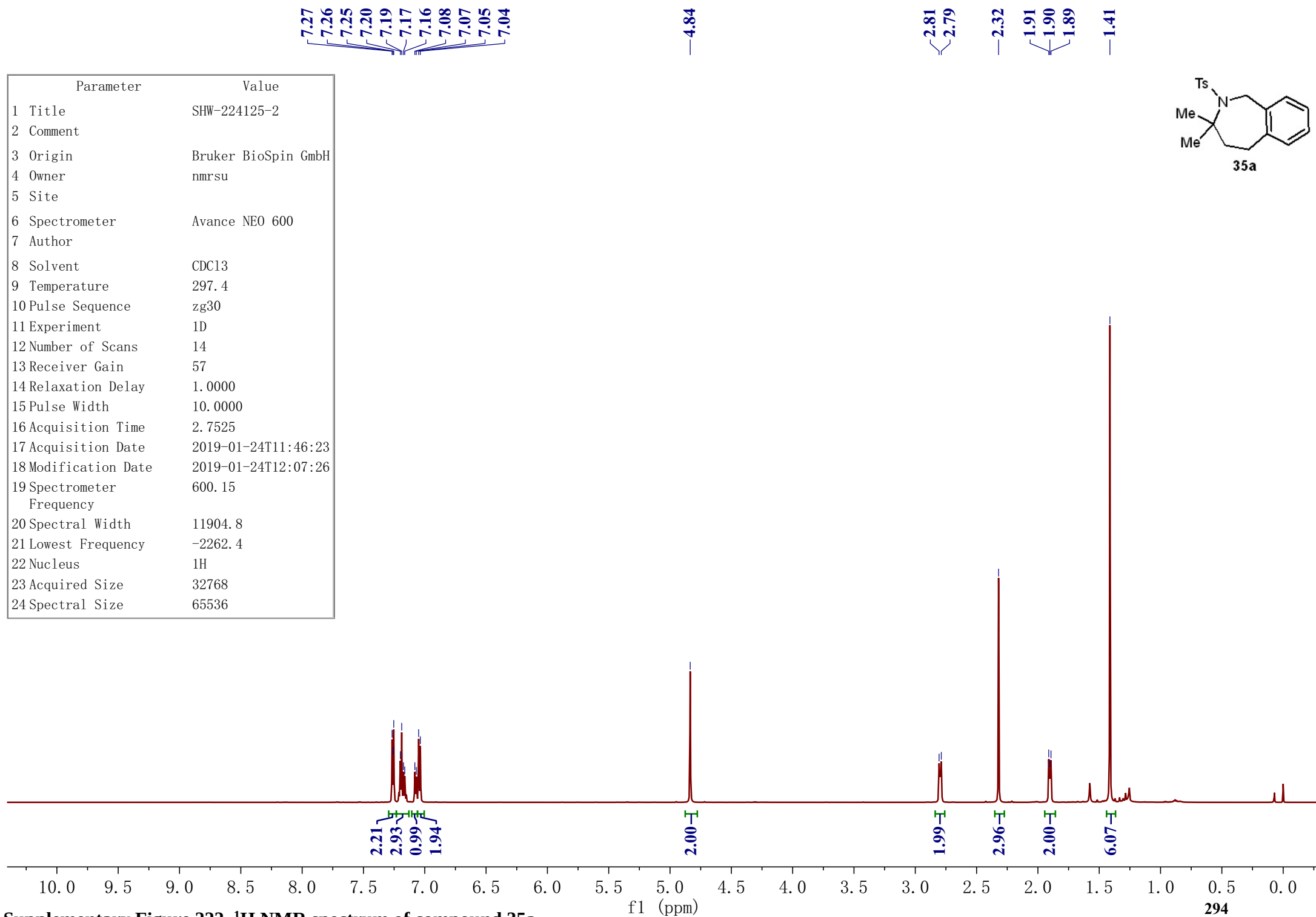




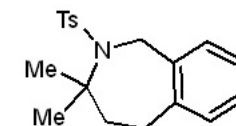
Parameter	Value
1 Title	SHW-22405-A
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	297.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	151
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-01-14T22:10:38
18 Modification Date	2019-07-03T21:50:17
19 Spectrometer	150.91
Frequency	
20 Spectral Width	35714.3
21 Lowest Frequency	-2717.0
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



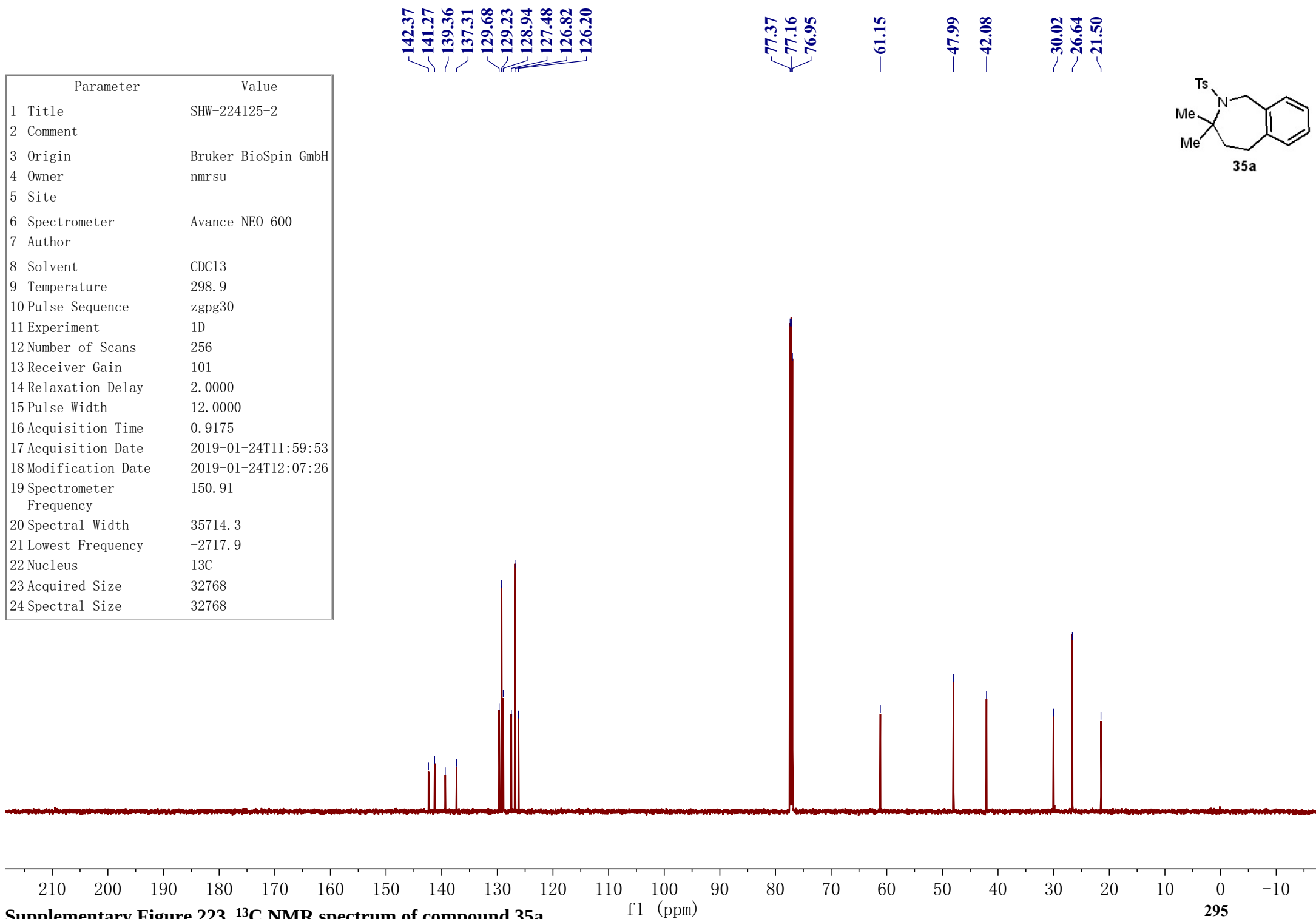
Supplementary Figure 221. ¹³C NMR spectrum of compound **34a**



Parameter	Value
1 Title	SHW-224125-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	298.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	256
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-01-24T11:59:53
18 Modification Date	2019-01-24T12:07:26
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2717.9
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



35a

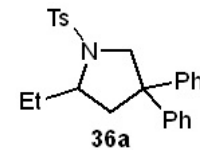


Supplementary Figure 223. ¹³C NMR spectrum of compound 35a

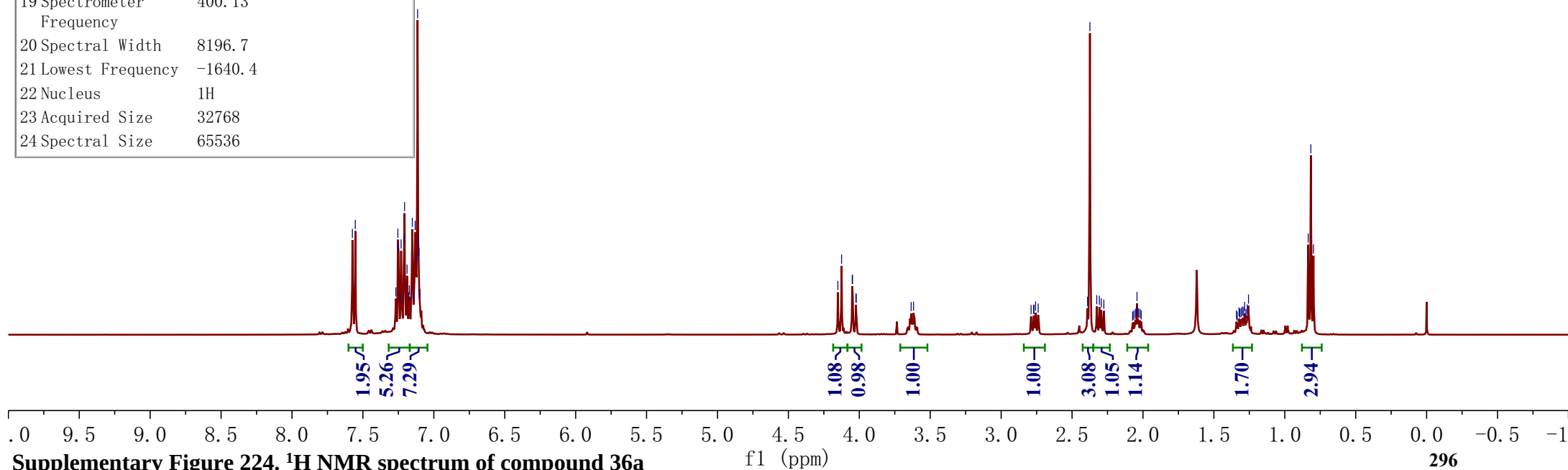
7.57
7.55
7.27
7.25
7.25
7.24
7.23
7.21
7.21
7.19
7.18
7.17
7.15
7.14
7.13
7.12
7.11
7.11
7.10

4.15
4.13
4.05
4.05
4.02
4.02
3.63
3.62
2.79
2.77
2.77
2.76
2.74

2.39
2.37
2.33
2.31
2.29
2.28
2.05
2.05
2.04
2.03
1.32
1.32
1.31
1.30
1.29
1.28
1.26
1.26
0.84
0.82
0.80

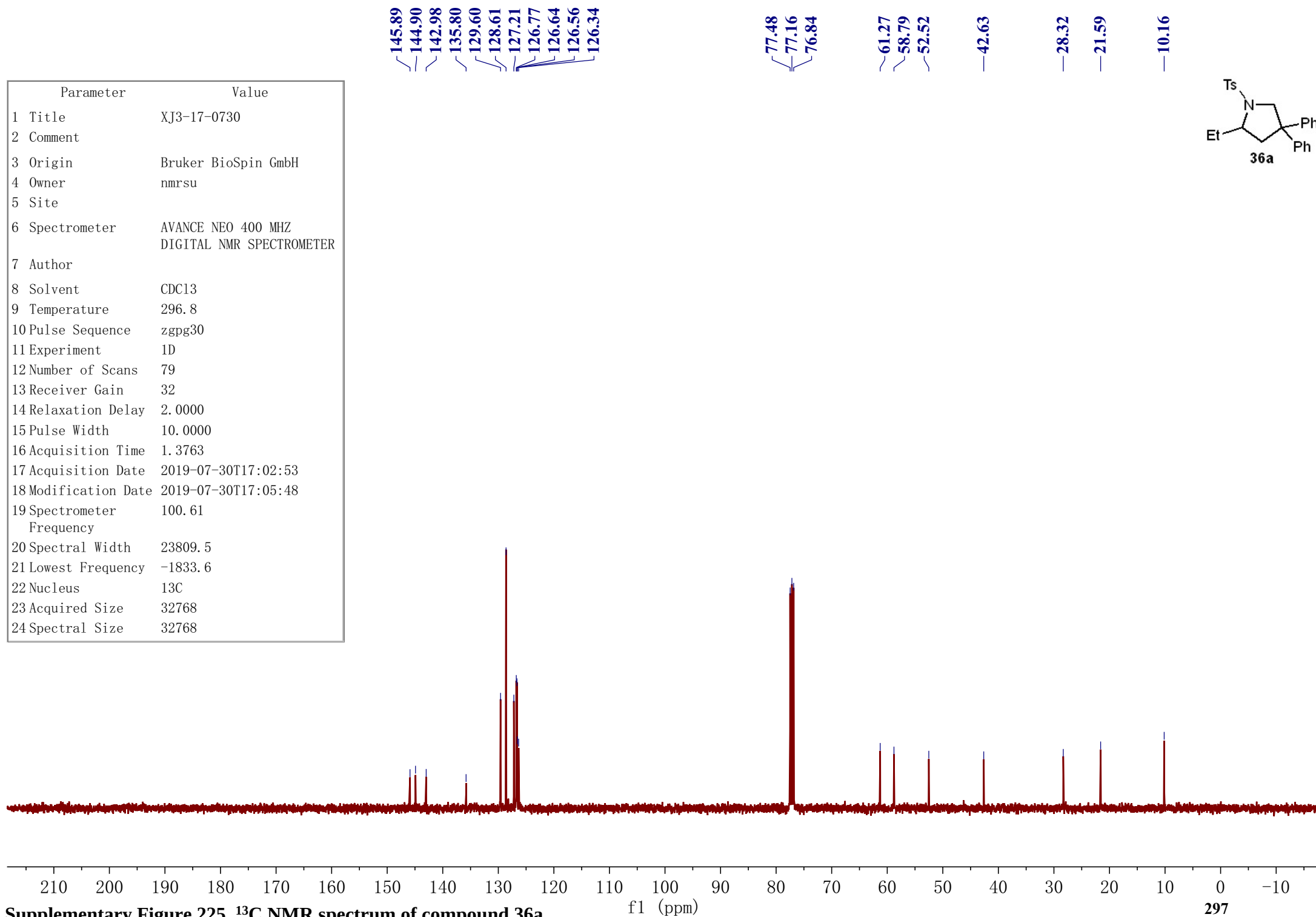


Parameter	Value
1 Title	XJ3-17-0730
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.7
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	6
13 Receiver Gain	75
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-07-30T16:57:08
18 Modification Date	2019-07-30T17:05:48
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1640.4
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



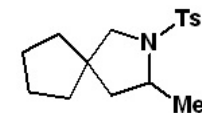
Supplementary Figure 224. ¹H NMR spectrum of compound 36a

Parameter	Value
1 Title	XJ3-17-0730
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr-su
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	296.8
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	79
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-07-30T17:02:53
18 Modification Date	2019-07-30T17:05:48
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1833.6
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

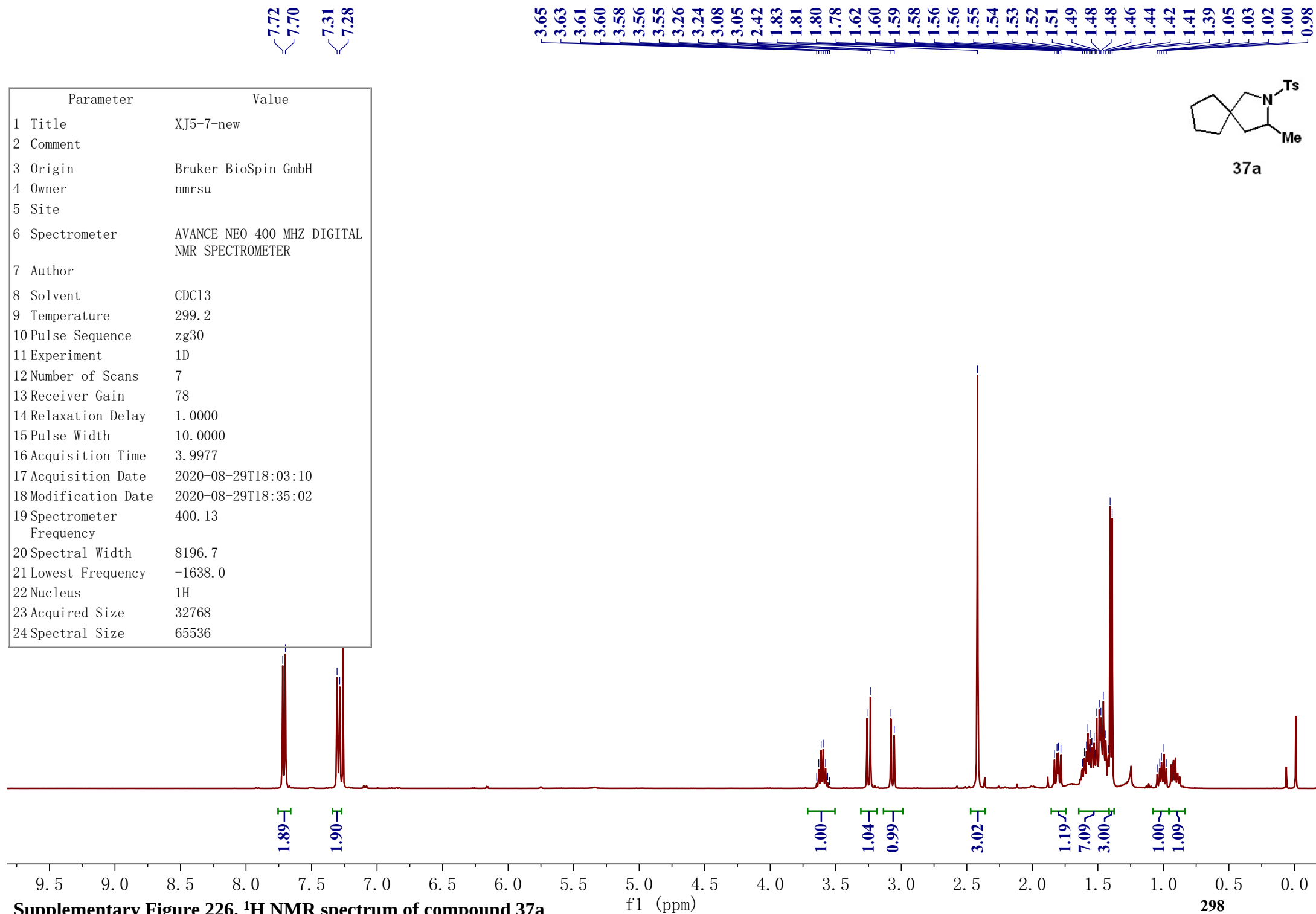


Supplementary Figure 225. ¹³C NMR spectrum of compound **36a**

Parameter	Value
1 Title	XJ5-7-new
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	299.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	7
13 Receiver Gain	78
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2020-08-29T18:03:10
18 Modification Date	2020-08-29T18:35:02
19 Spectrometer Frequency	400.13
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.0
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

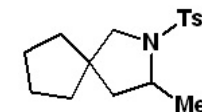


37a

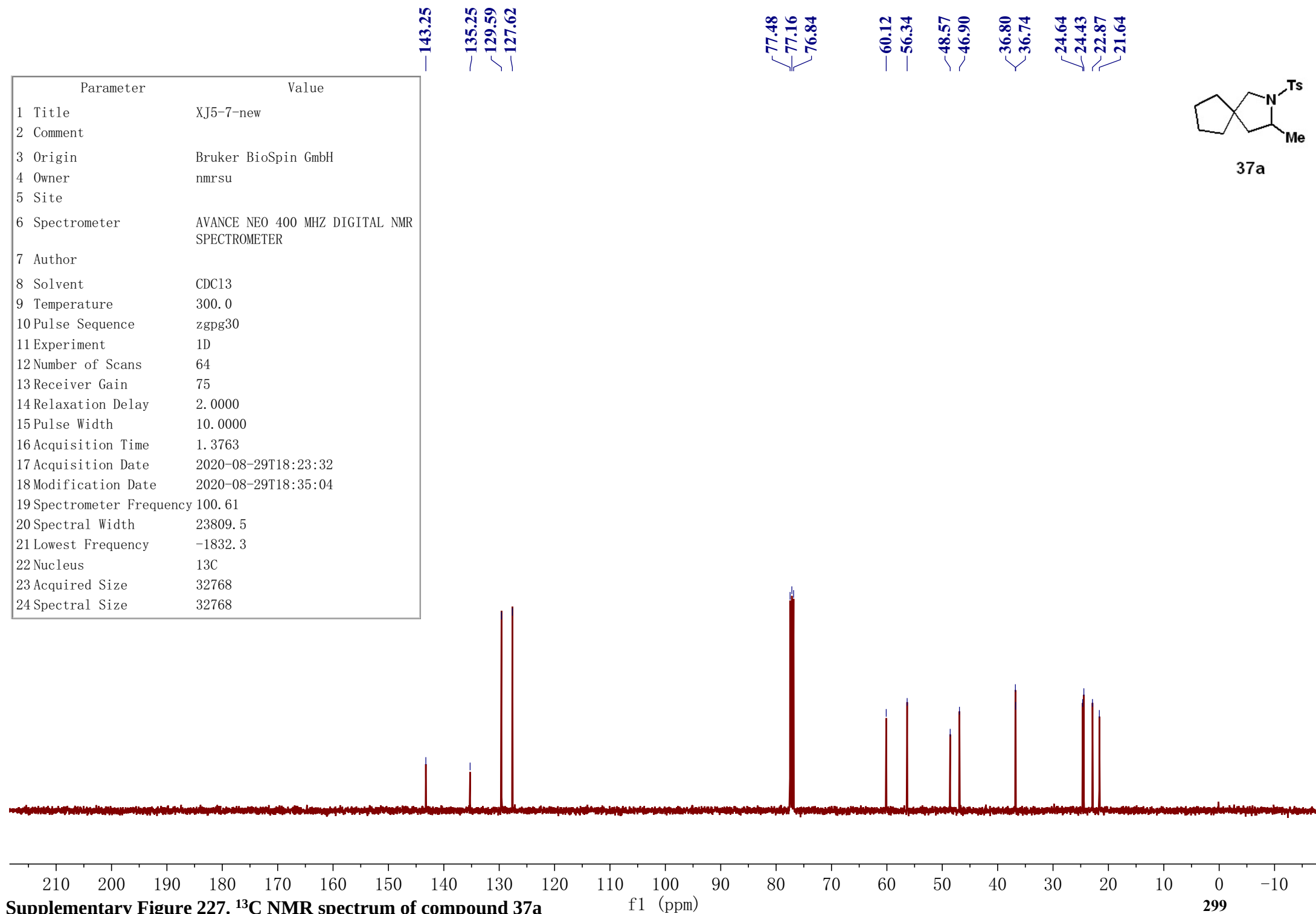


Supplementary Figure 226. ¹H NMR spectrum of compound 37a

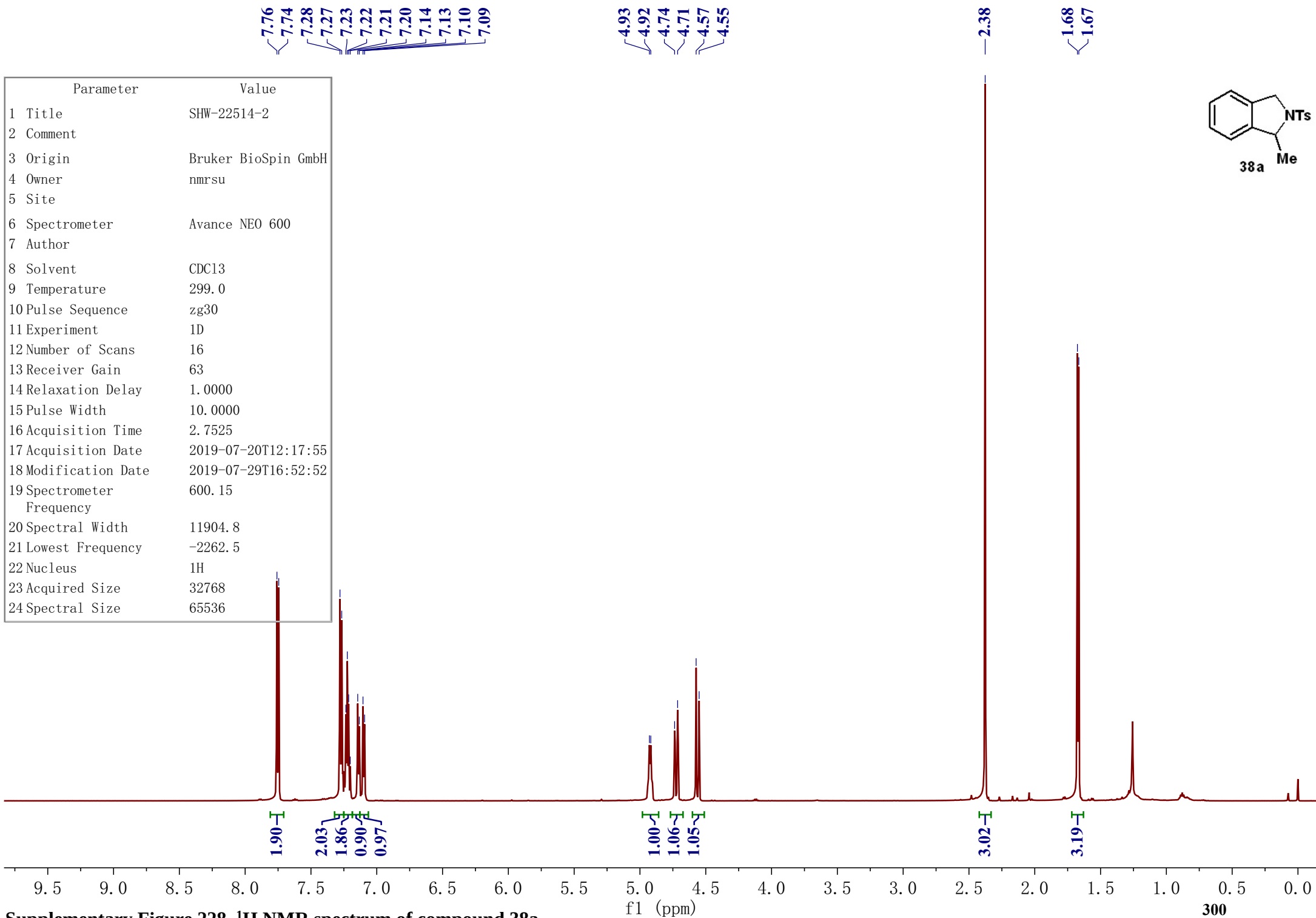
Parameter	Value
1 Title	XJ5-7-new
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	300.0
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	64
13 Receiver Gain	75
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2020-08-29T18:23:32
18 Modification Date	2020-08-29T18:35:04
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1832.3
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768



37a



Supplementary Figure 227. ¹³C NMR spectrum of compound 37a



Parameter	Value
1 Title	SHW-22514-2
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDC13
9 Temperature	299.6
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	62
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-07-20T12:21:45
18 Modification Date	2019-07-29T16:52:52
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2717.0
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

143.64
141.80
135.07
134.77
129.89
127.90
127.85
127.67
122.57
122.47

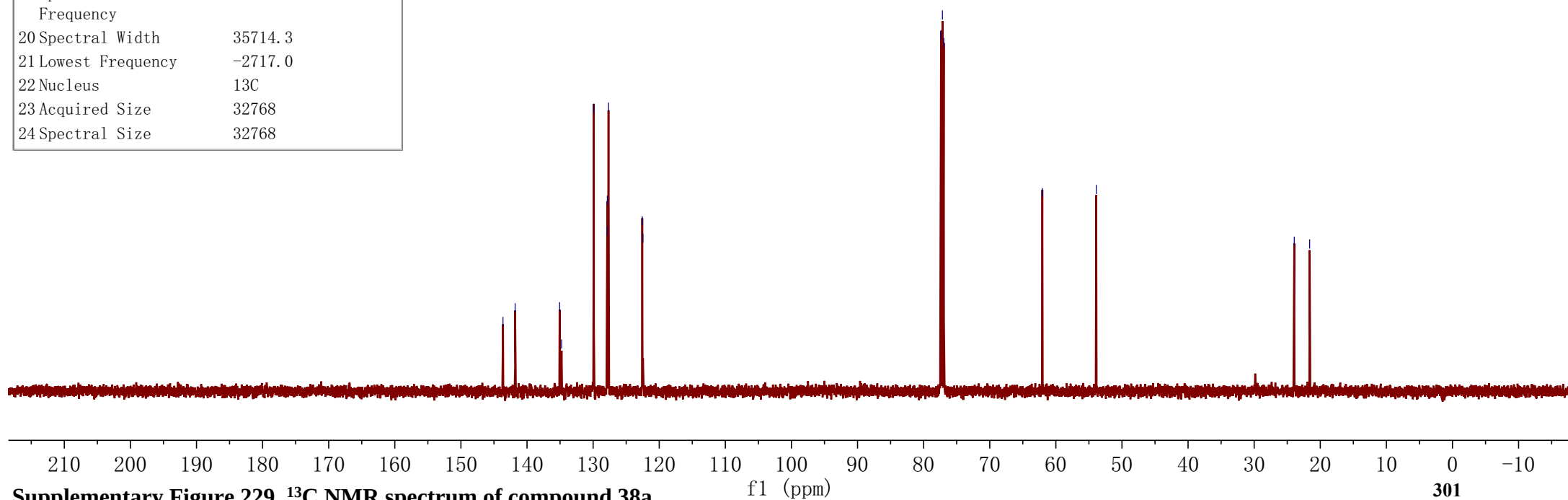
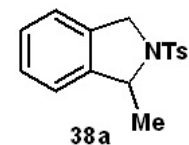
77.37
77.16
76.95

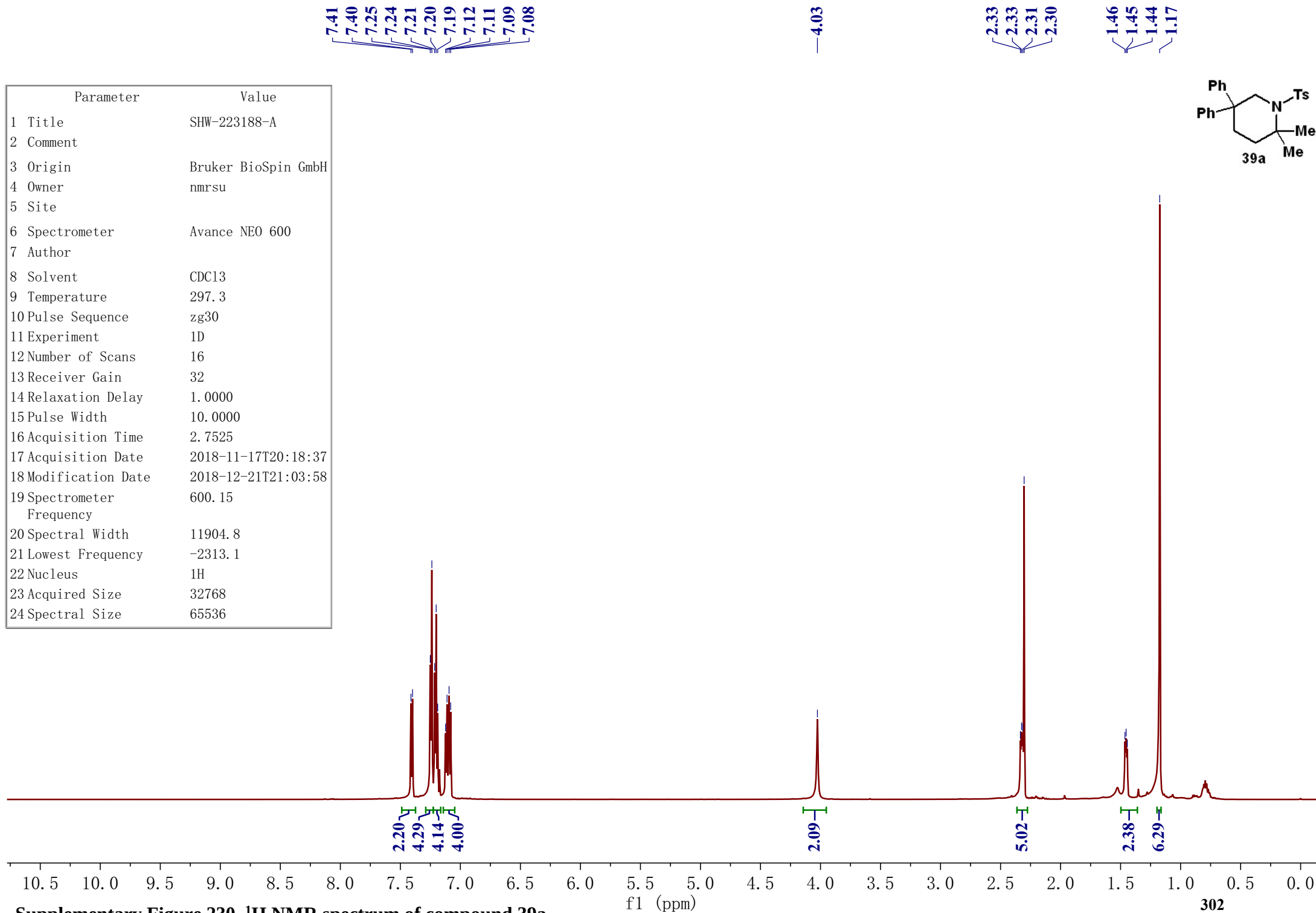
62.04

53.89

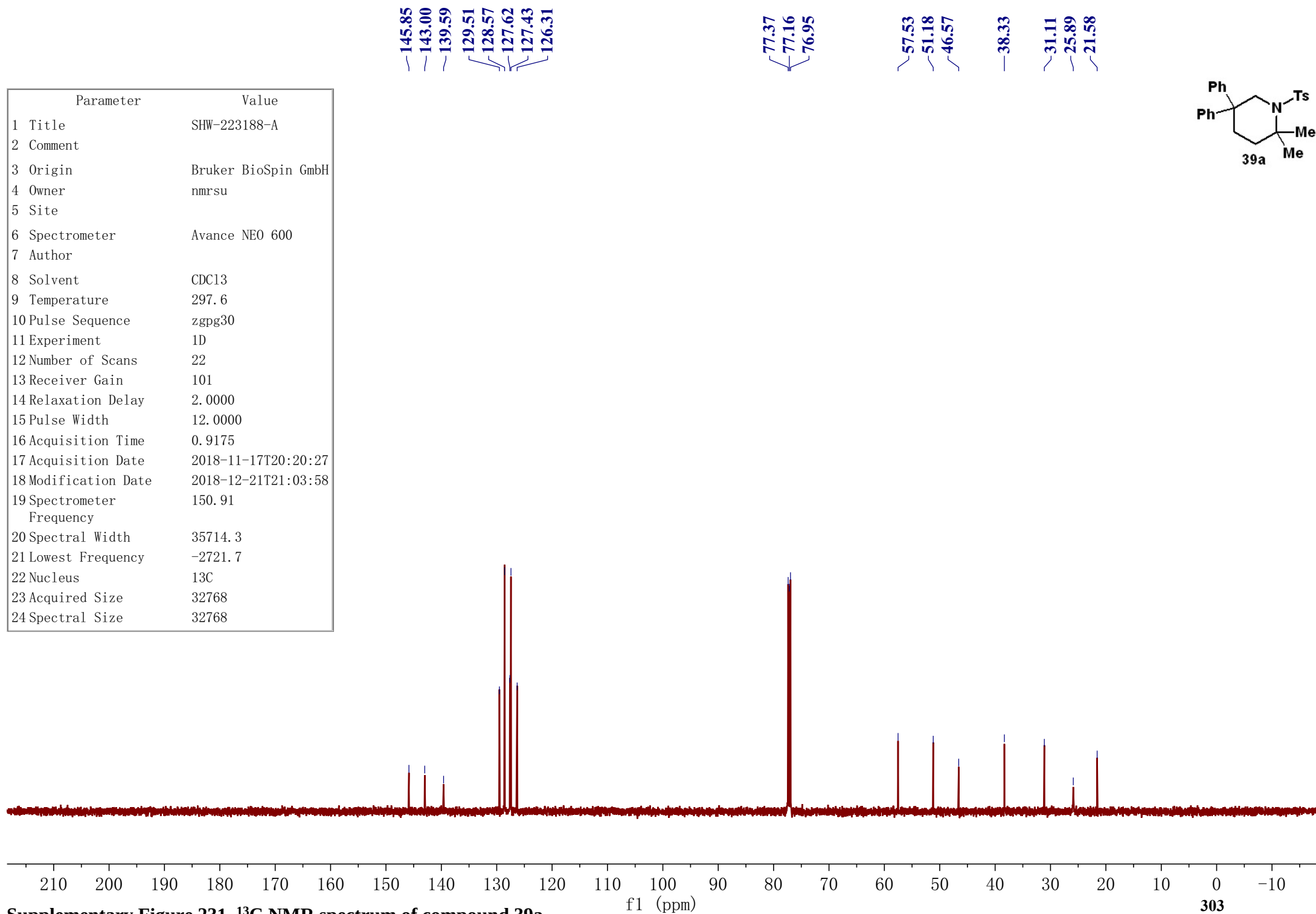
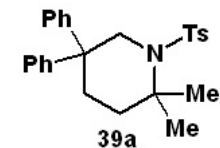
23.94

21.61



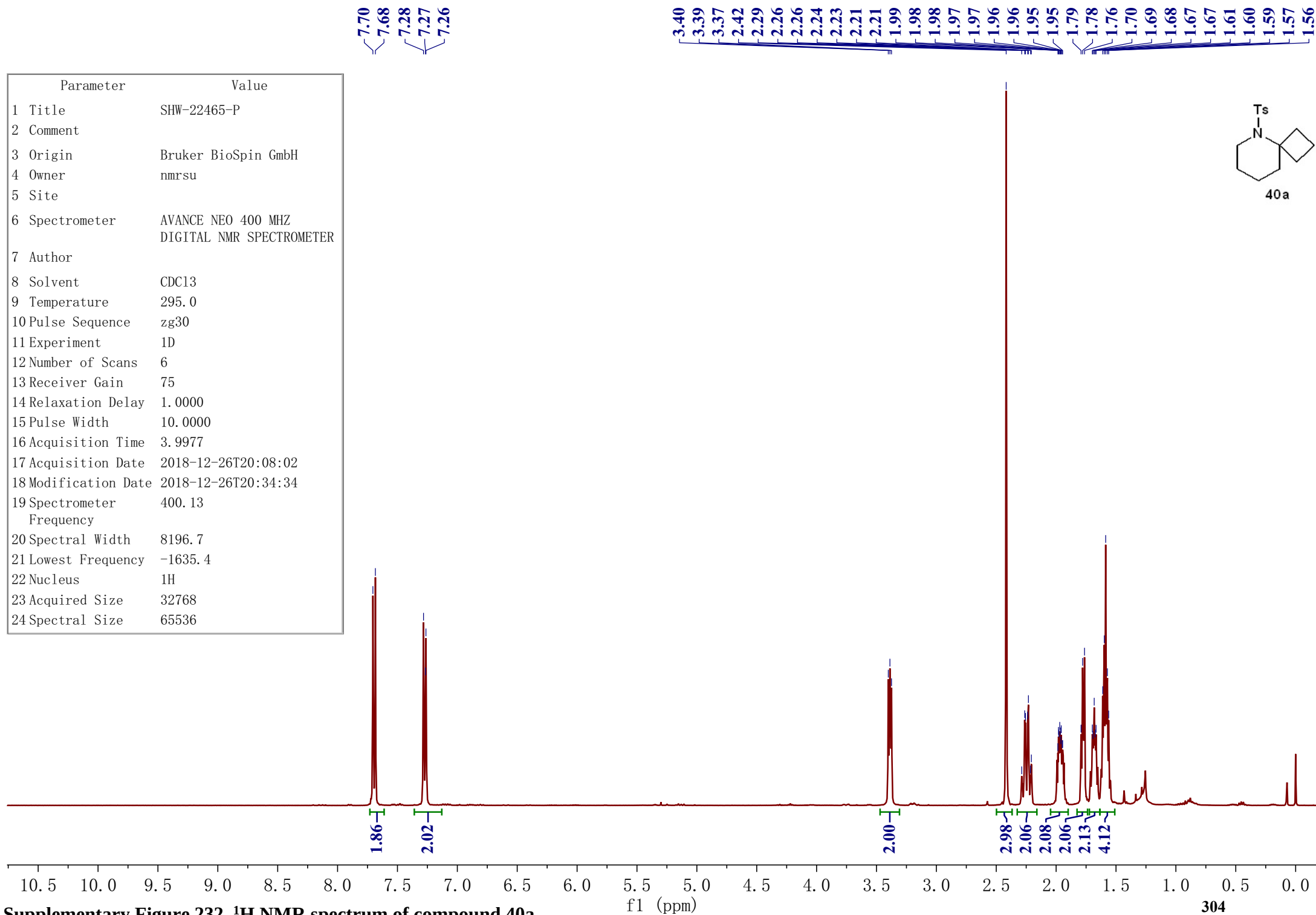


Parameter	Value
1 Title	SHW-223188-A
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	297.6
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	22
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2018-11-17T20:20:27
18 Modification Date	2018-12-21T21:03:58
19 Spectrometer	150.91
Frequency	
20 Spectral Width	35714.3
21 Lowest Frequency	-2721.7
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768



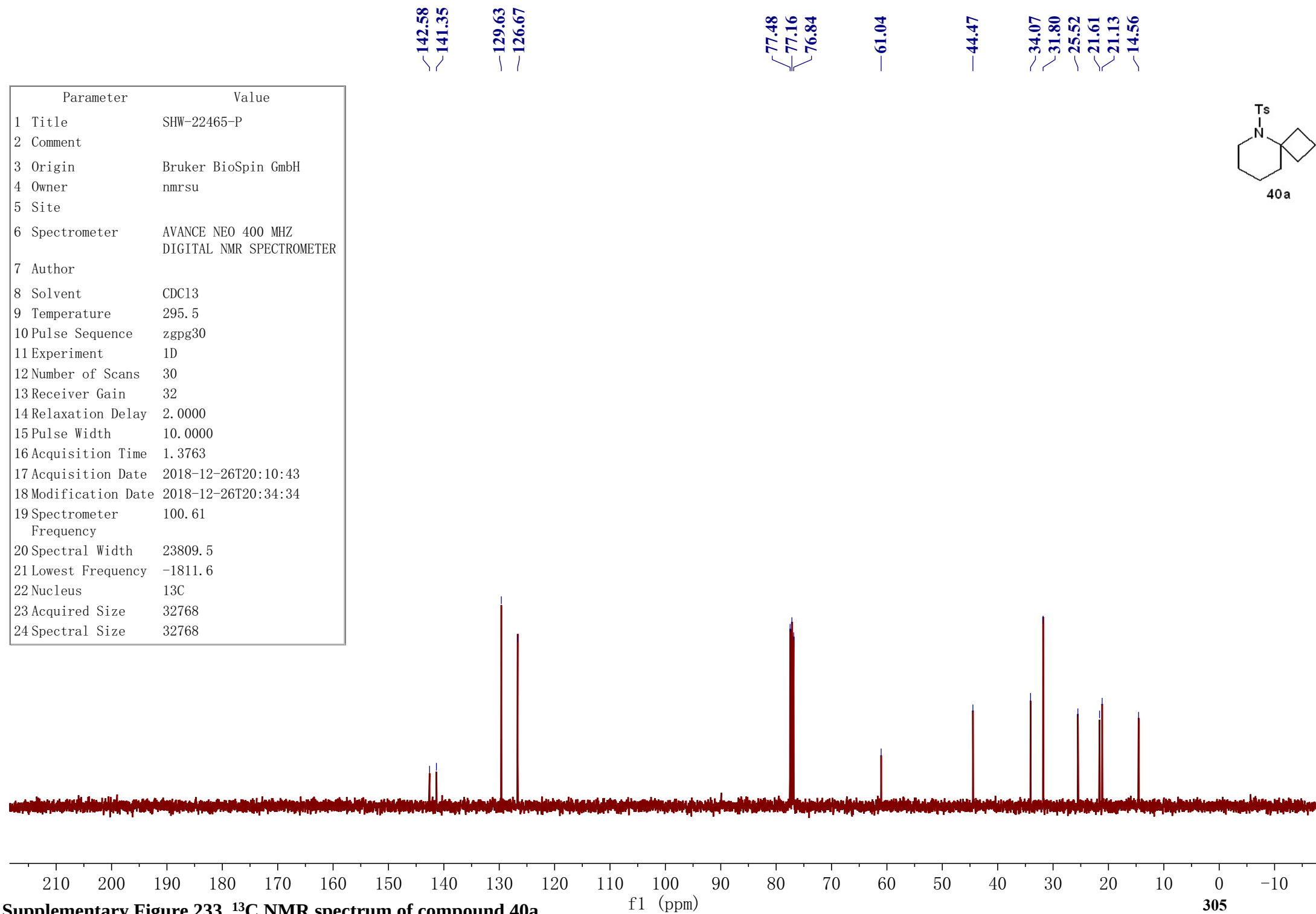
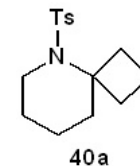
Supplementary Figure 231. ¹³C NMR spectrum of compound 39a

Parameter	Value
1 Title	SHW-22465-P
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	295.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	6
13 Receiver Gain	75
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-12-26T20:08:02
18 Modification Date	2018-12-26T20:34:34
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1635.4
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536



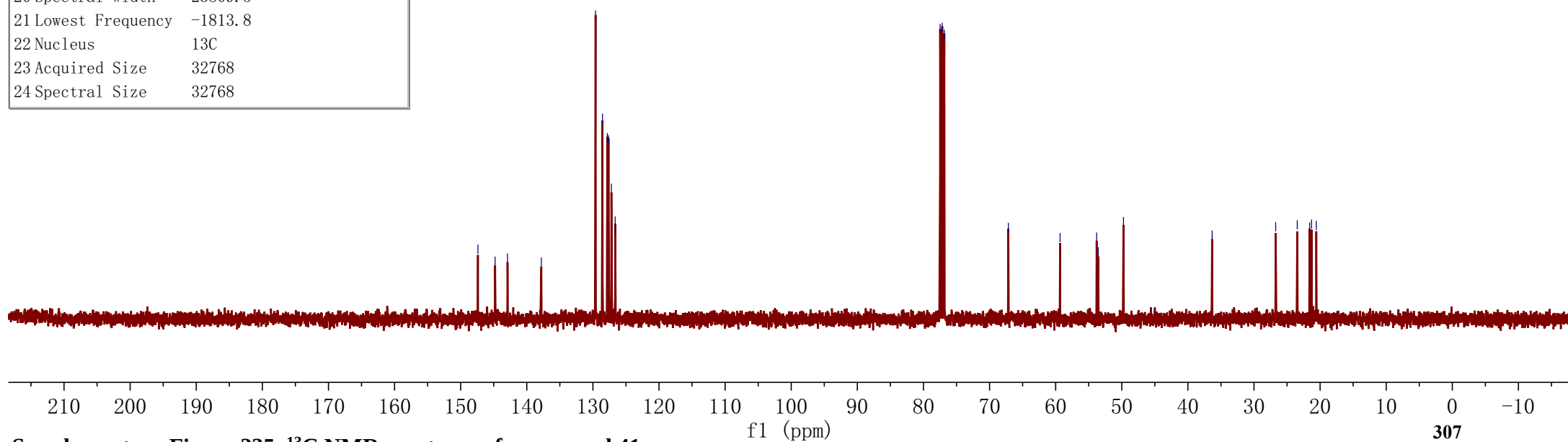
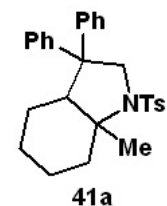
Supplementary Figure 232. ¹H NMR spectrum of compound 40a

Parameter	Value
1 Title	SHW-22465-P
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	30
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-26T20:10:43
18 Modification Date	2018-12-26T20:34:34
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1811.6
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

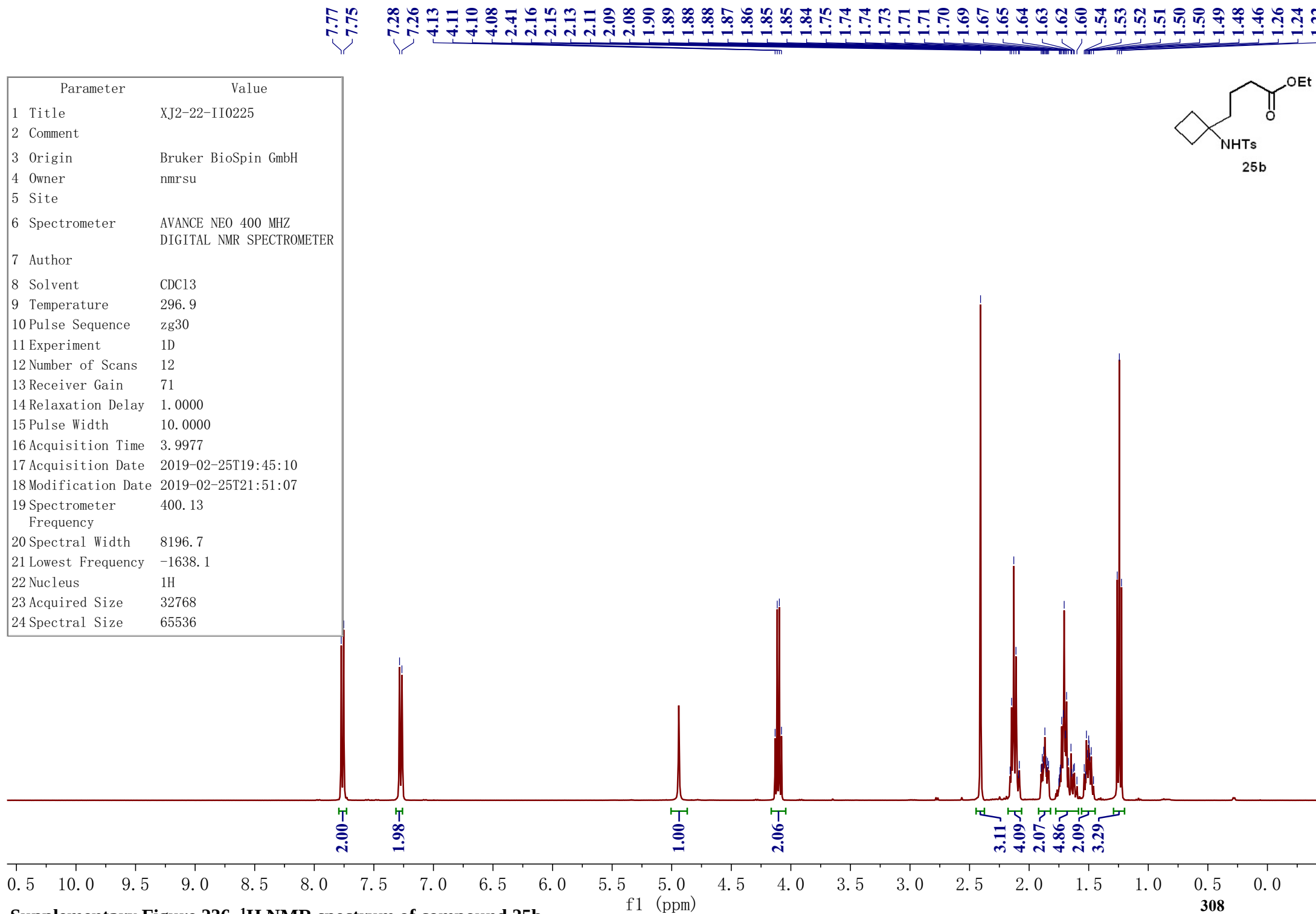
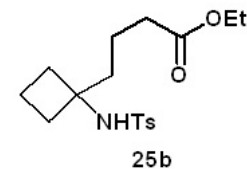


Parameter	Value
1 Title	SHW-224196-C
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr-su
5 Site	
6 Spectrometer	AVANCE NEO 400 MHz DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	33
13 Receiver Gain	35
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-07-29T19:07:21
18 Modification Date	2019-07-29T19:14:17
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1813.8
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

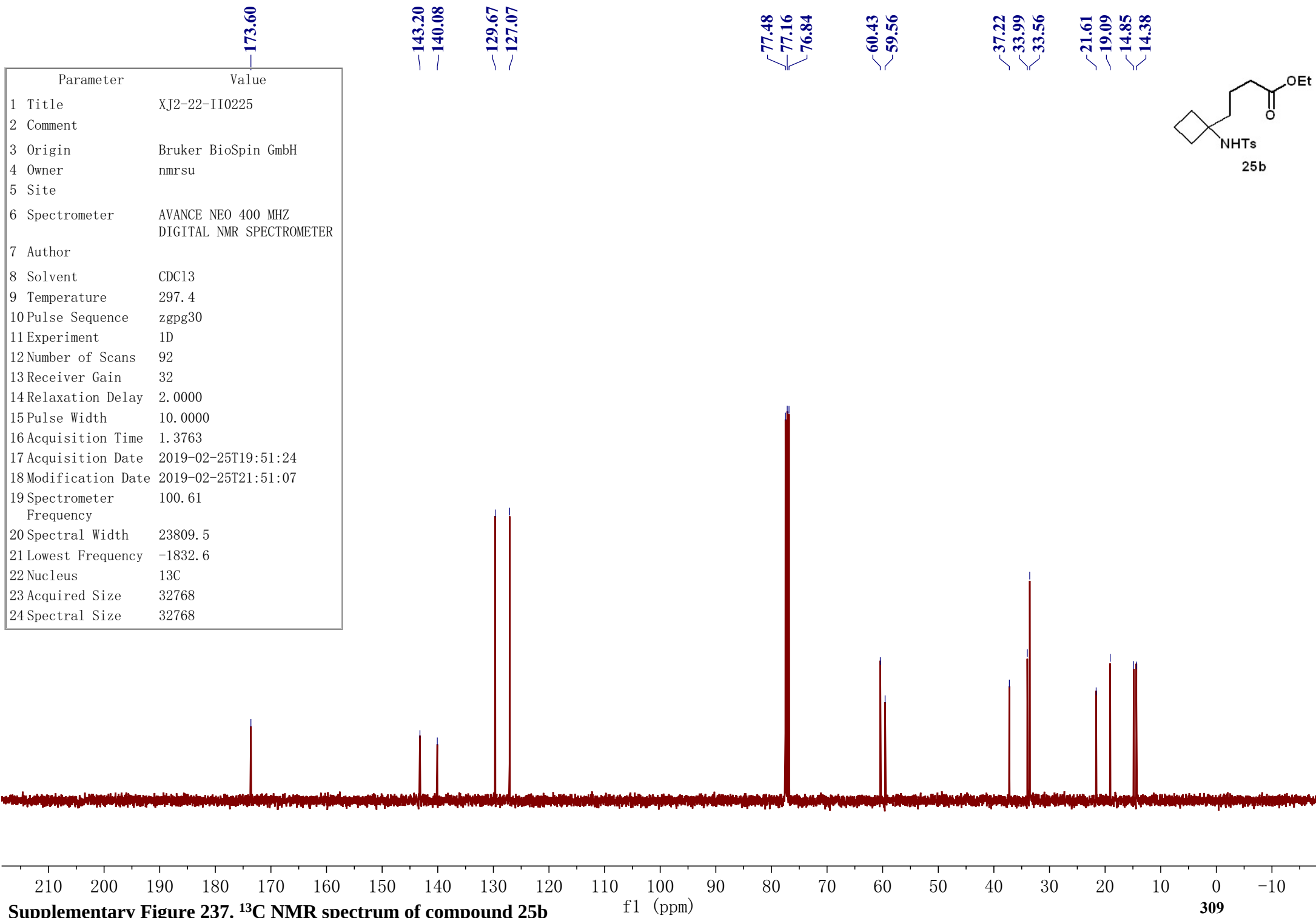
¹³C NMR chemical shifts (ppm):
 147.39, 144.79, 142.92, 137.80, 129.60, 128.54, 127.82, 127.64, 127.20, 126.63, 126.58,
 77.48, 77.16, 76.84, 67.16, 59.33, 53.80, 53.56, 49.74,
 36.33, 26.72, 23.46, 21.59, 21.29, 20.58

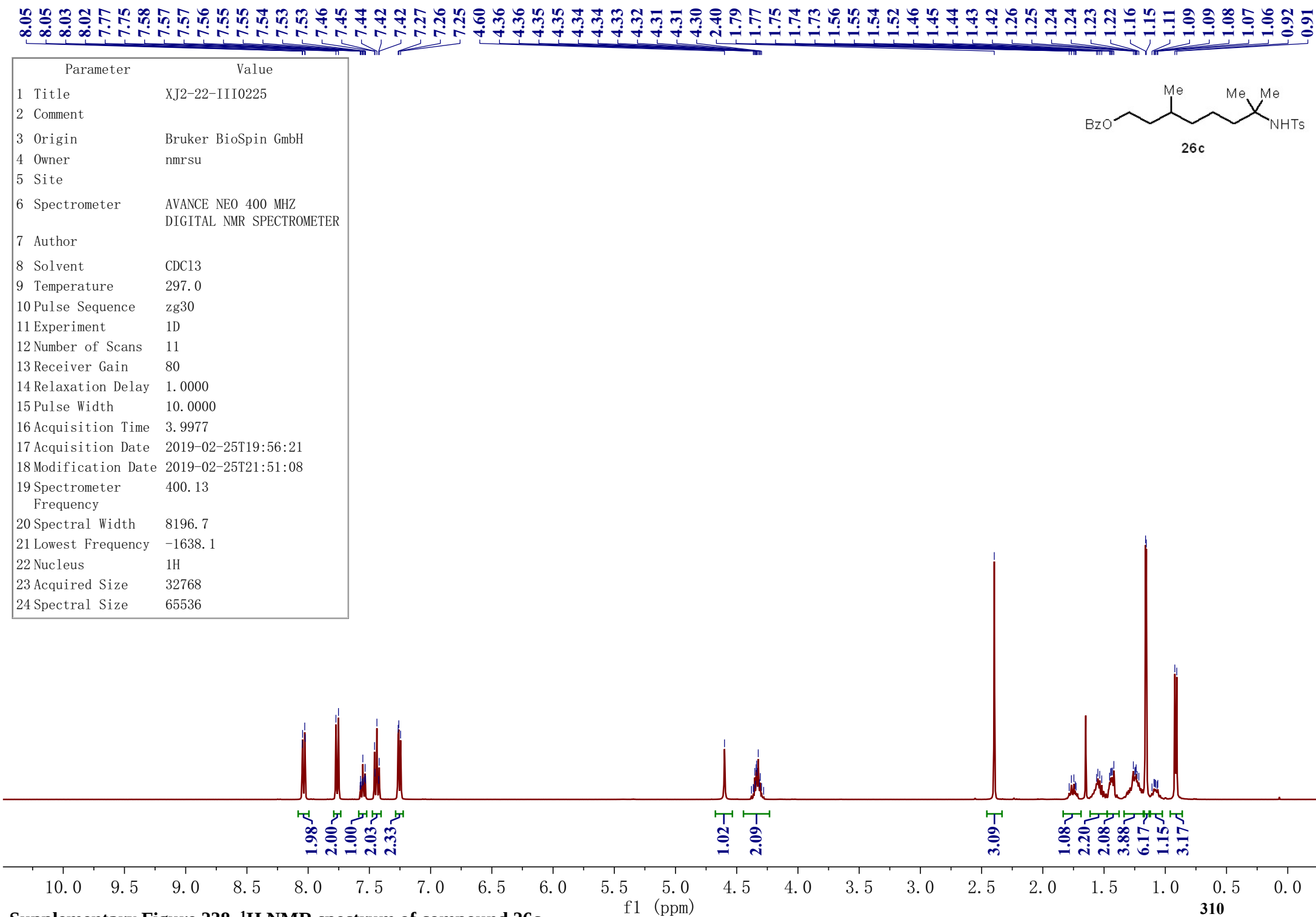


Parameter	Value
1 Title	XJ2-22-II0225
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.9
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	12
13 Receiver Gain	71
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-02-25T19:45:10
18 Modification Date	2019-02-25T21:51:07
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.1
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

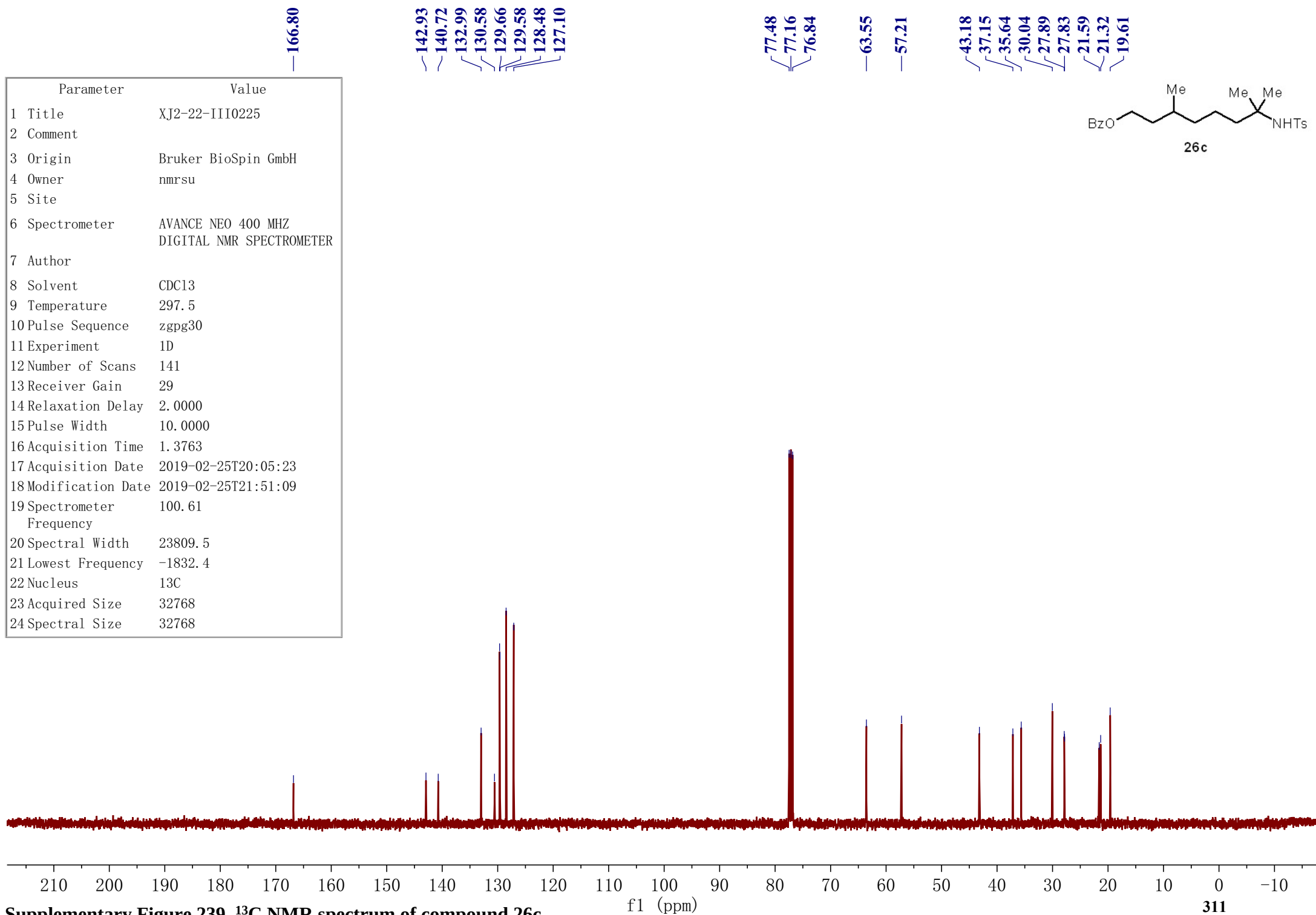
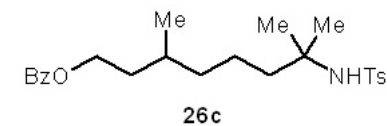


Supplementary Figure 236. ¹H NMR spectrum of compound 25b



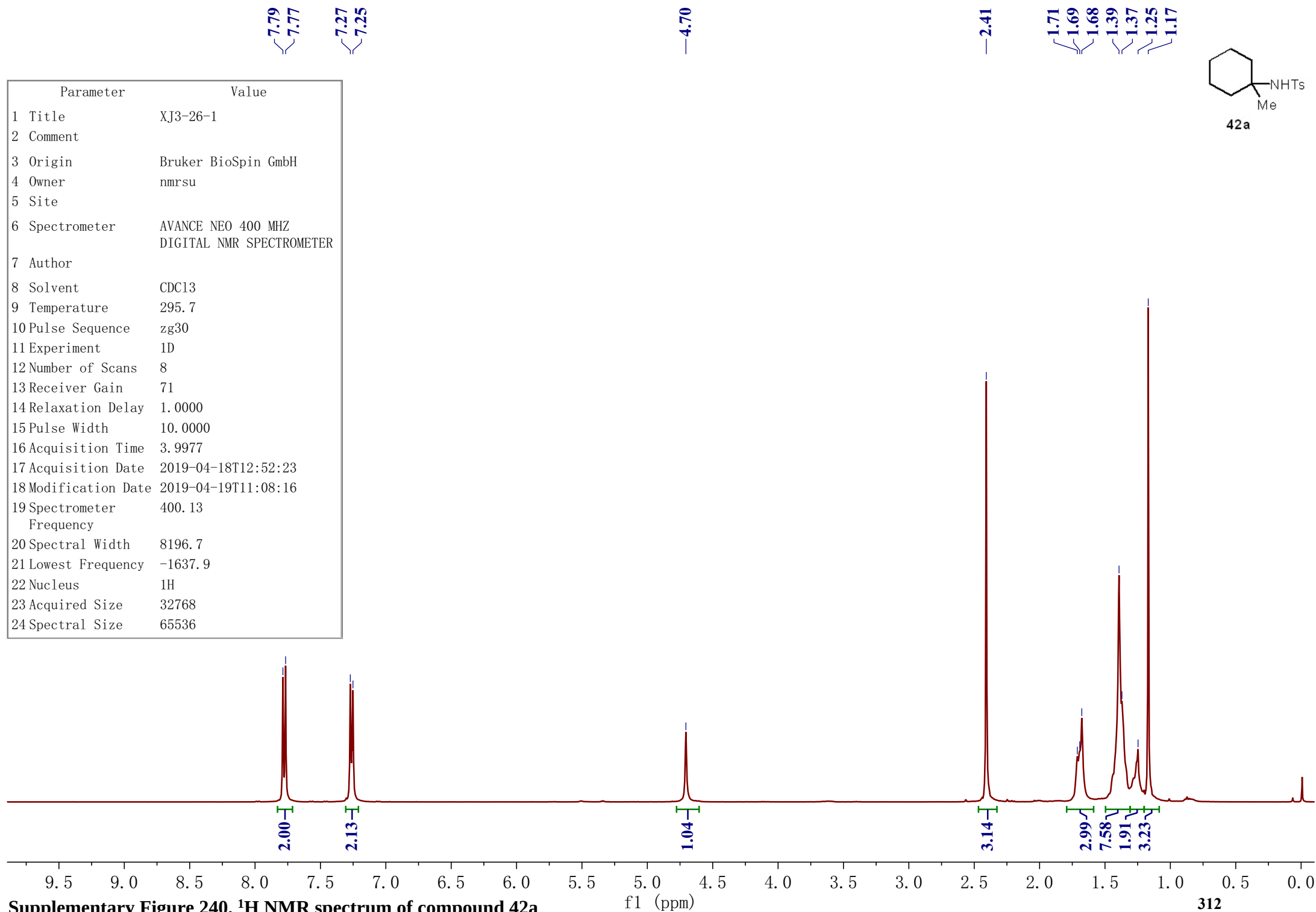
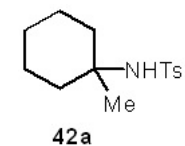


Parameter	Value
1 Title	XJ2-22-III0225
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	141
13 Receiver Gain	29
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-02-25T20:05:23
18 Modification Date	2019-02-25T21:51:09
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1832.4
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



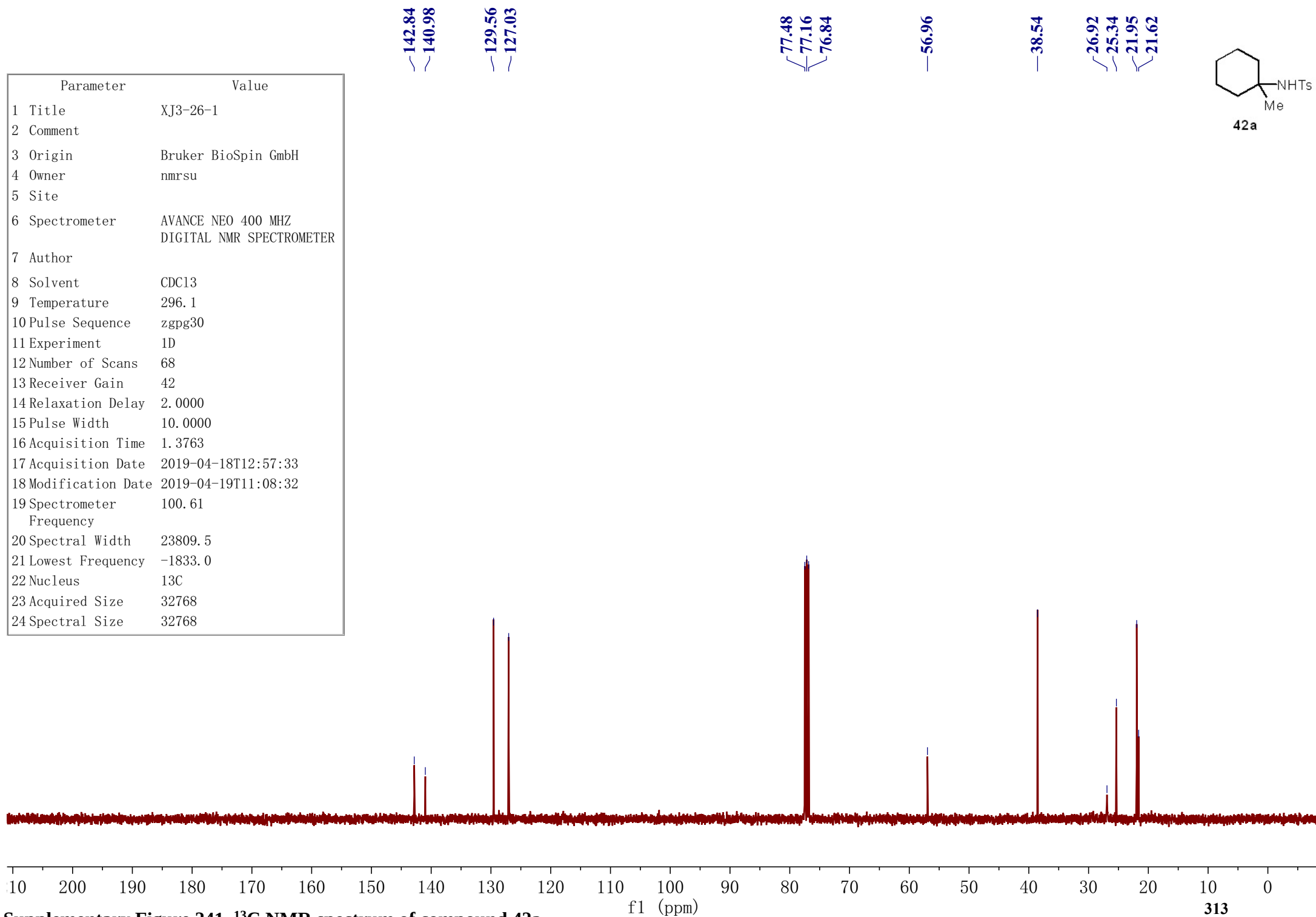
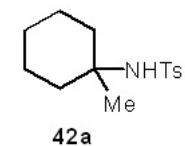
Supplementary Figure 239. ¹³C NMR spectrum of compound 26c

Parameter	Value
1 Title	XJ3-26-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	295.7
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	71
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-04-18T12:52:23
18 Modification Date	2019-04-19T11:08:16
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.9
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

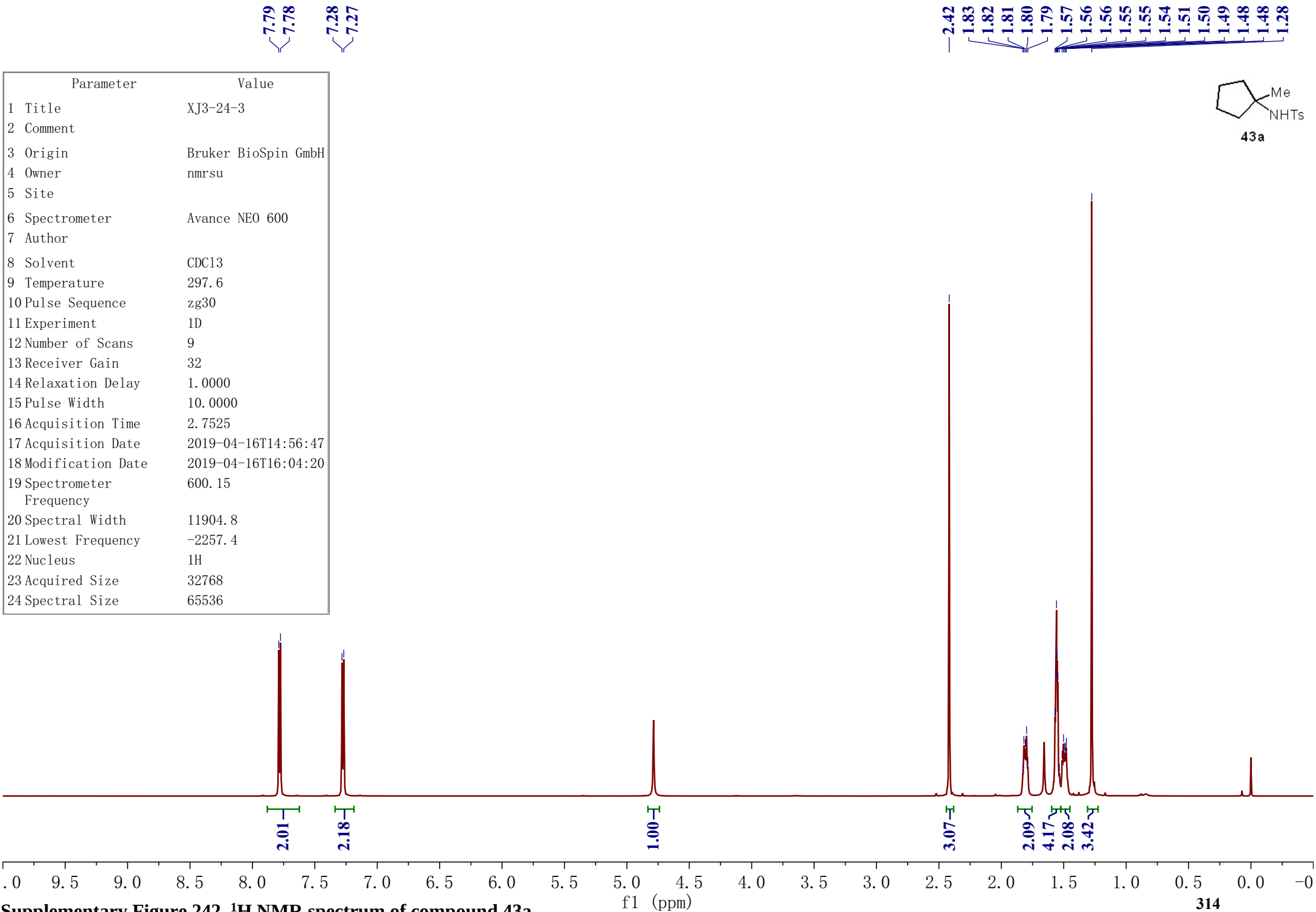


Supplementary Figure 240. ¹H NMR spectrum of compound 42a

Parameter	Value
1 Title	XJ3-26-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	296.1
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	68
13 Receiver Gain	42
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-04-18T12:57:33
18 Modification Date	2019-04-19T11:08:32
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1833.0
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

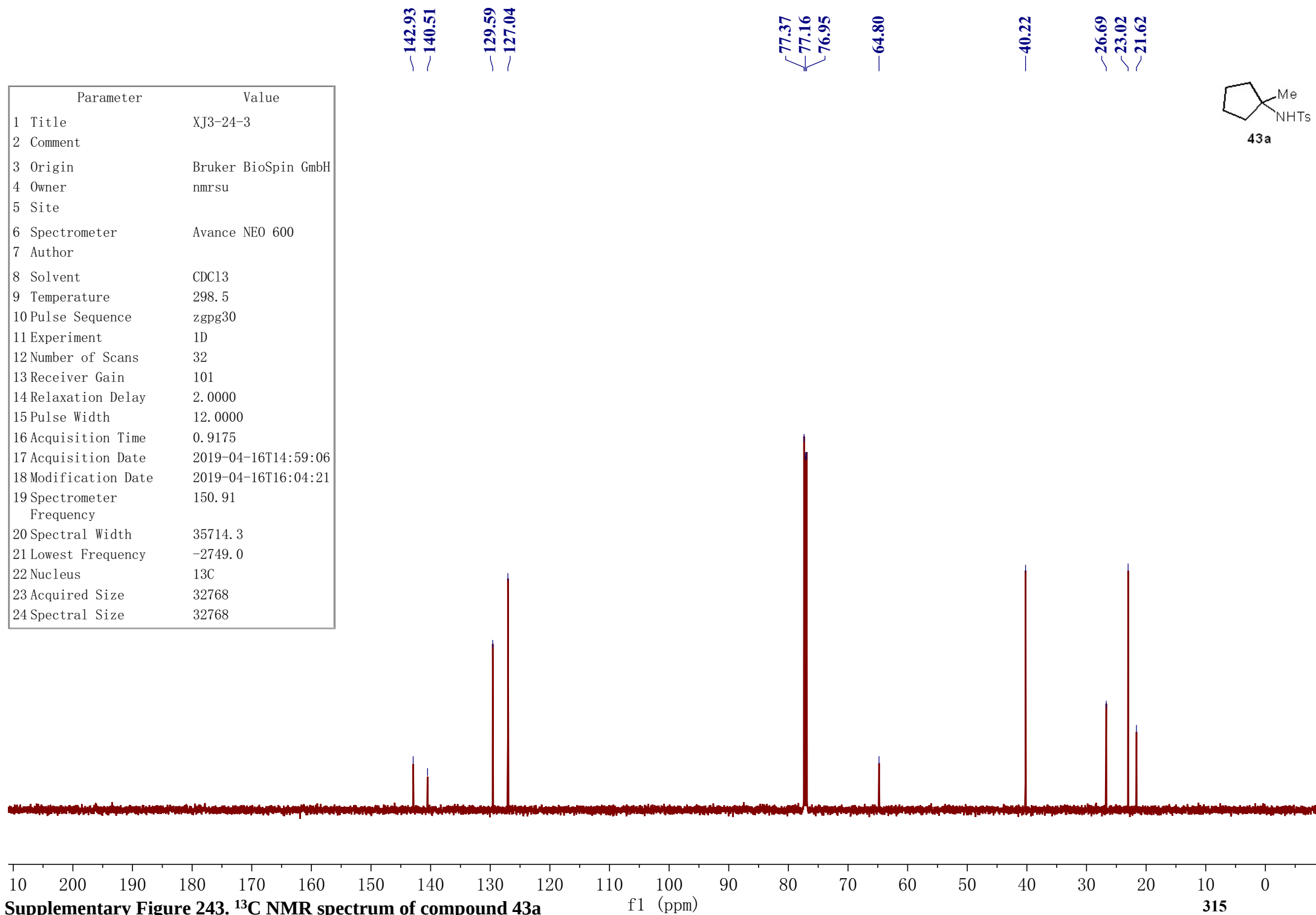
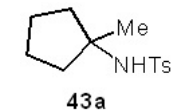


Supplementary Figure 241. ¹³C NMR spectrum of compound 42a

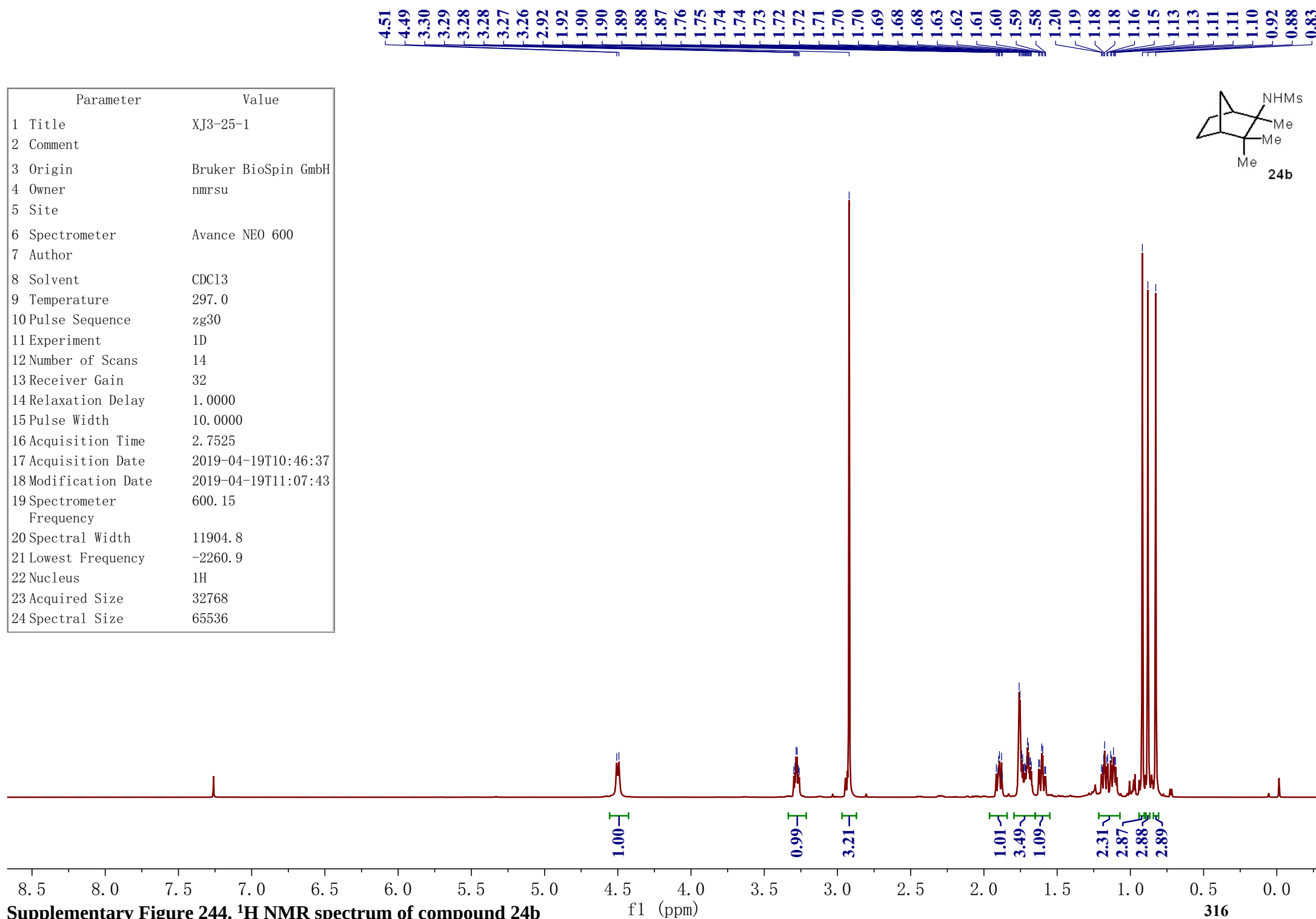
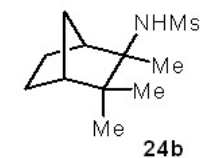


Supplementary Figure 242. ¹H NMR spectrum of compound 43a

Parameter	Value
1 Title	XJ3-24-3
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	32
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-04-16T14:59:06
18 Modification Date	2019-04-16T16:04:21
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2749.0
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768

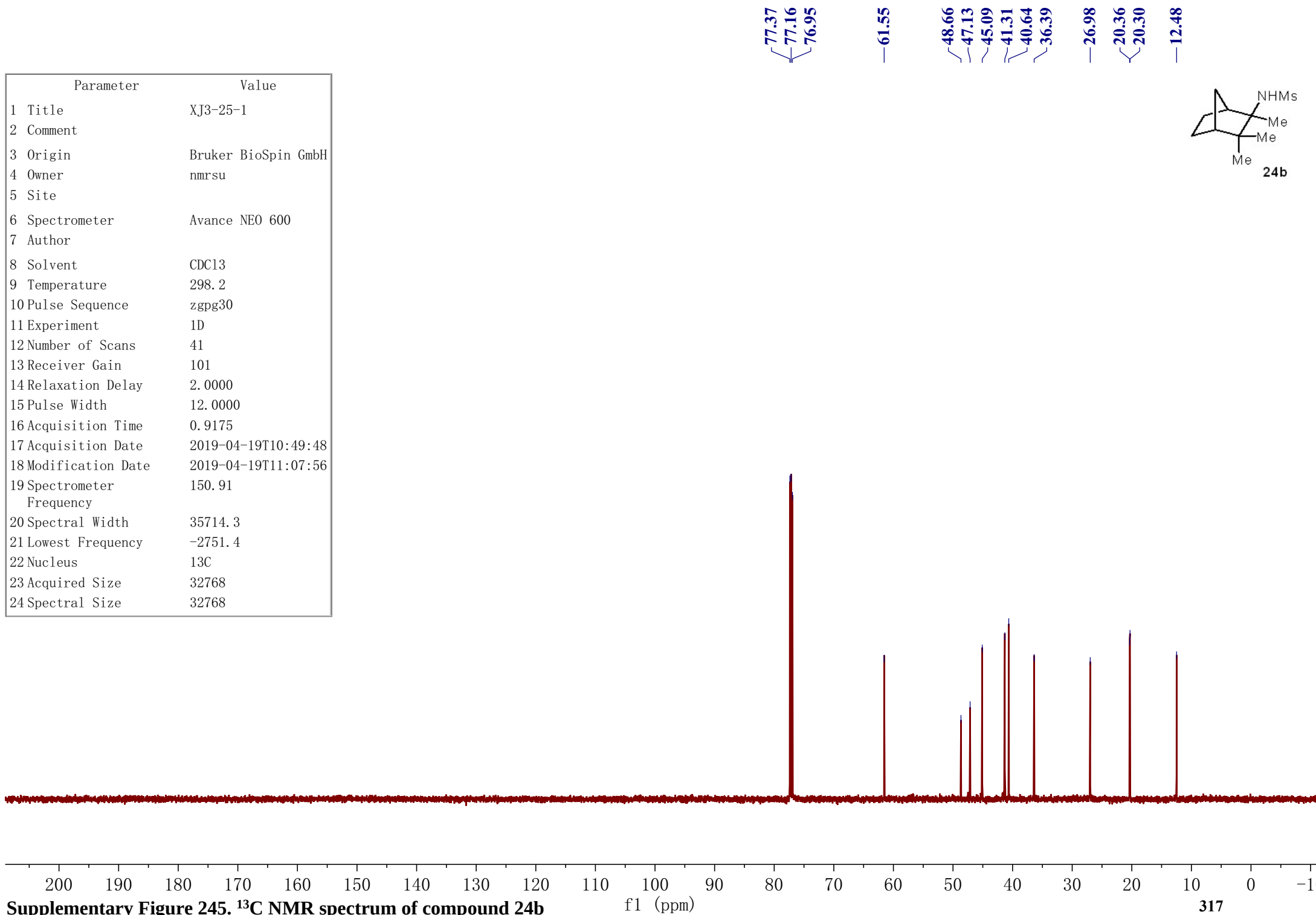
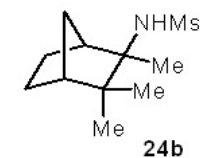


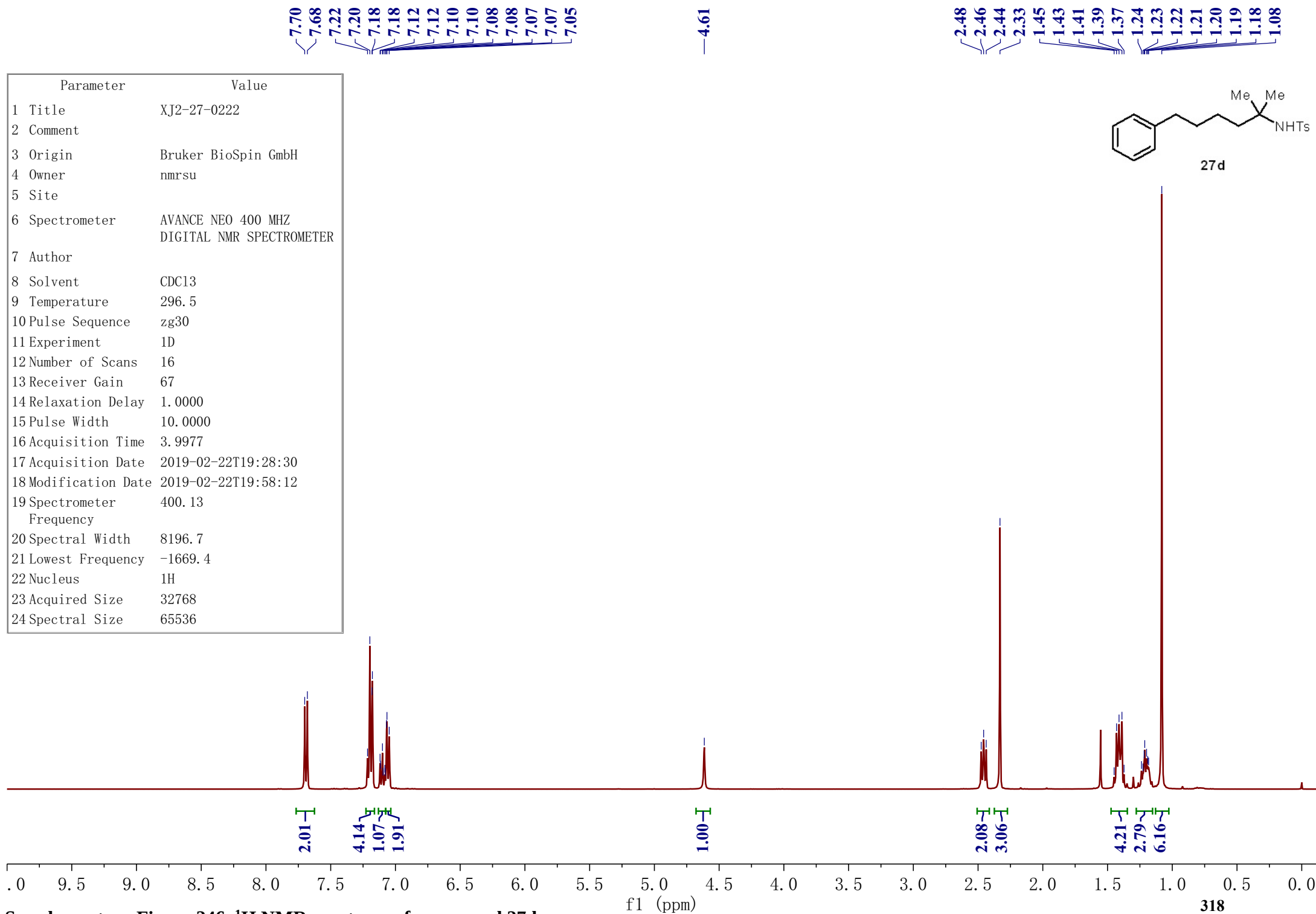
Parameter	Value
1 Title	XJ3-25-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	297.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	14
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	2.7525
17 Acquisition Date	2019-04-19T10:46:37
18 Modification Date	2019-04-19T11:07:43
19 Spectrometer Frequency	600.15
20 Spectral Width	11904.8
21 Lowest Frequency	-2260.9
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



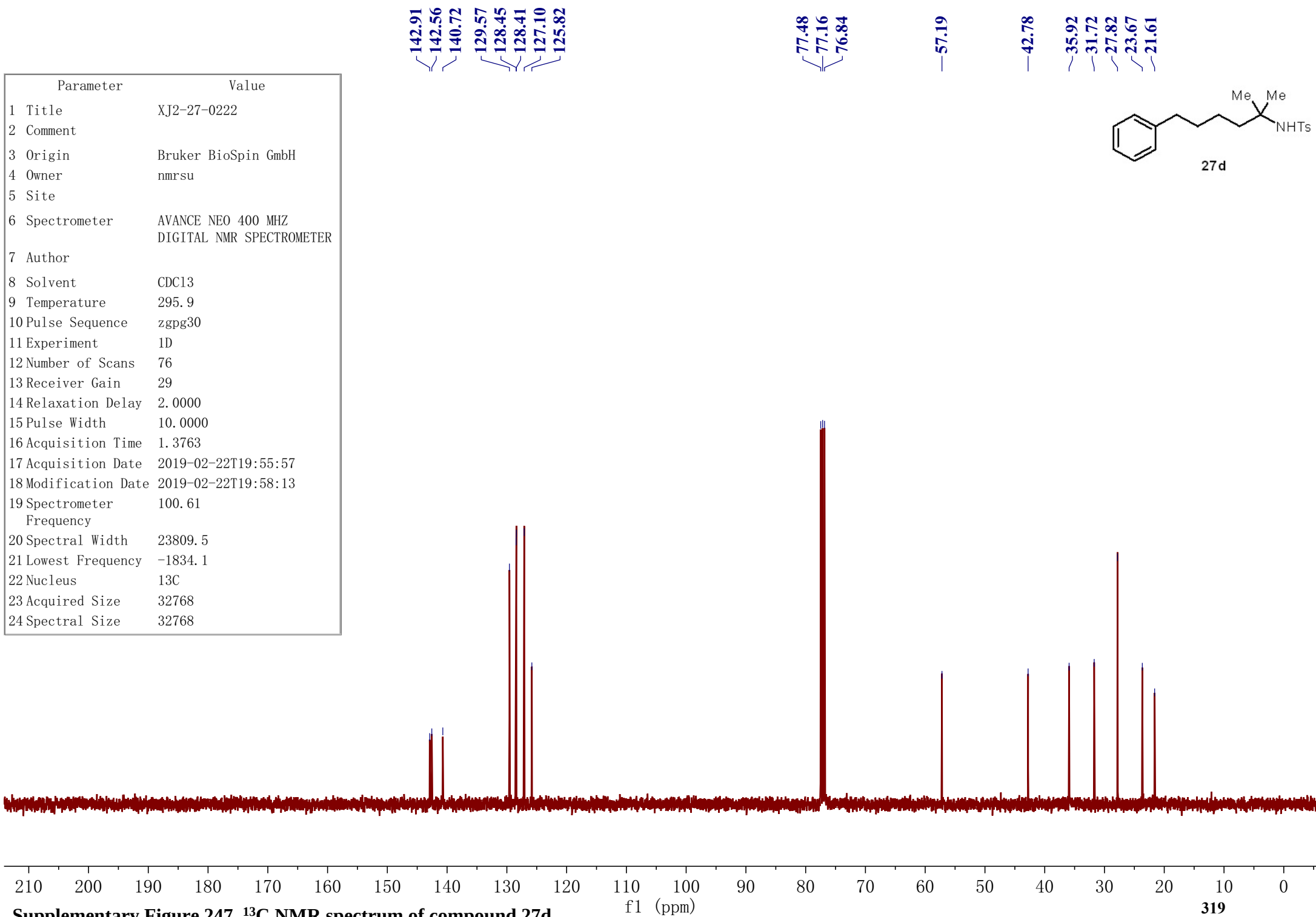
Supplementary Figure 244. ¹H NMR spectrum of compound 24b

Parameter	Value
1 Title	XJ3-25-1
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	41
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-04-19T10:49:48
18 Modification Date	2019-04-19T11:07:56
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2751.4
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	32768

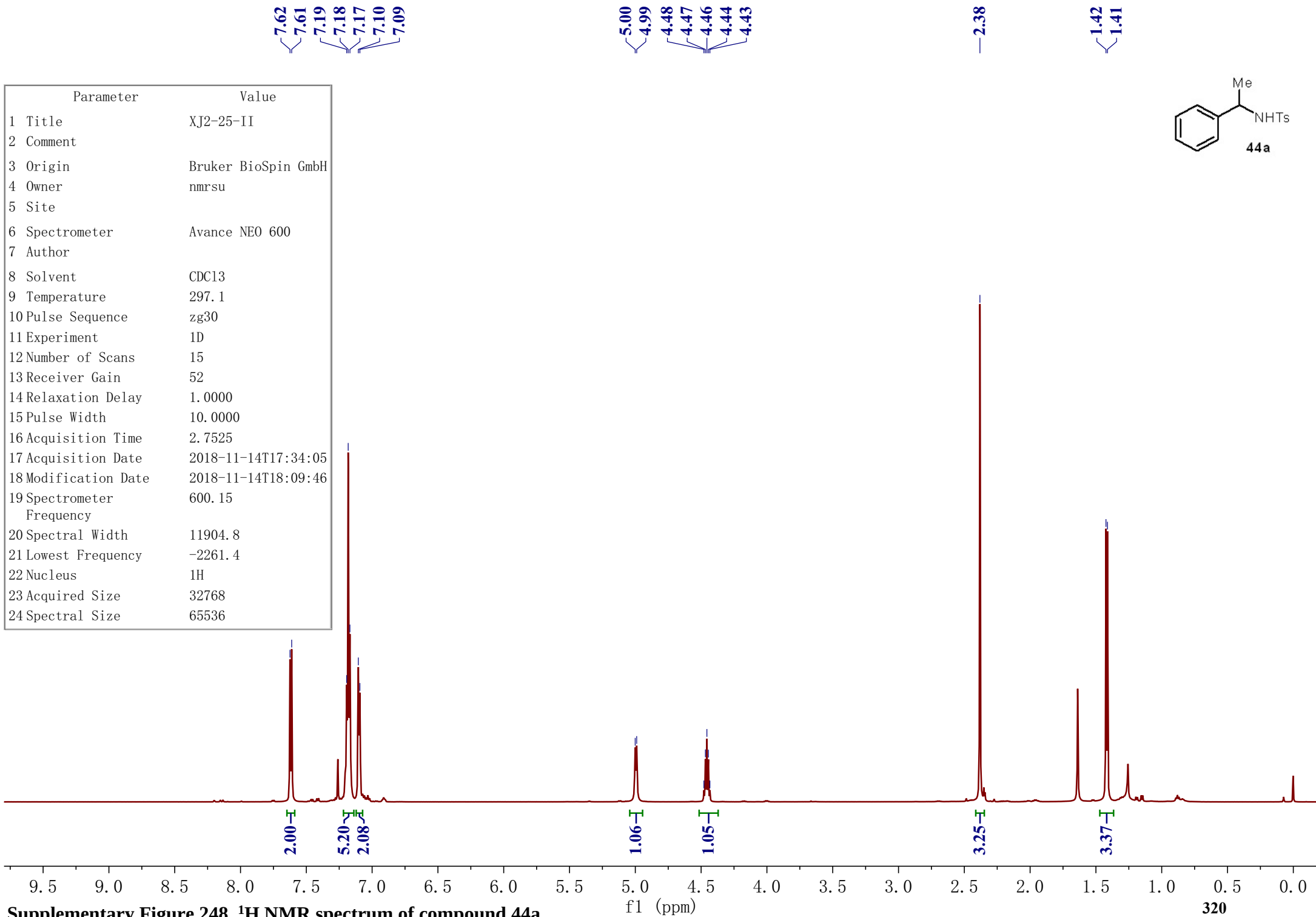




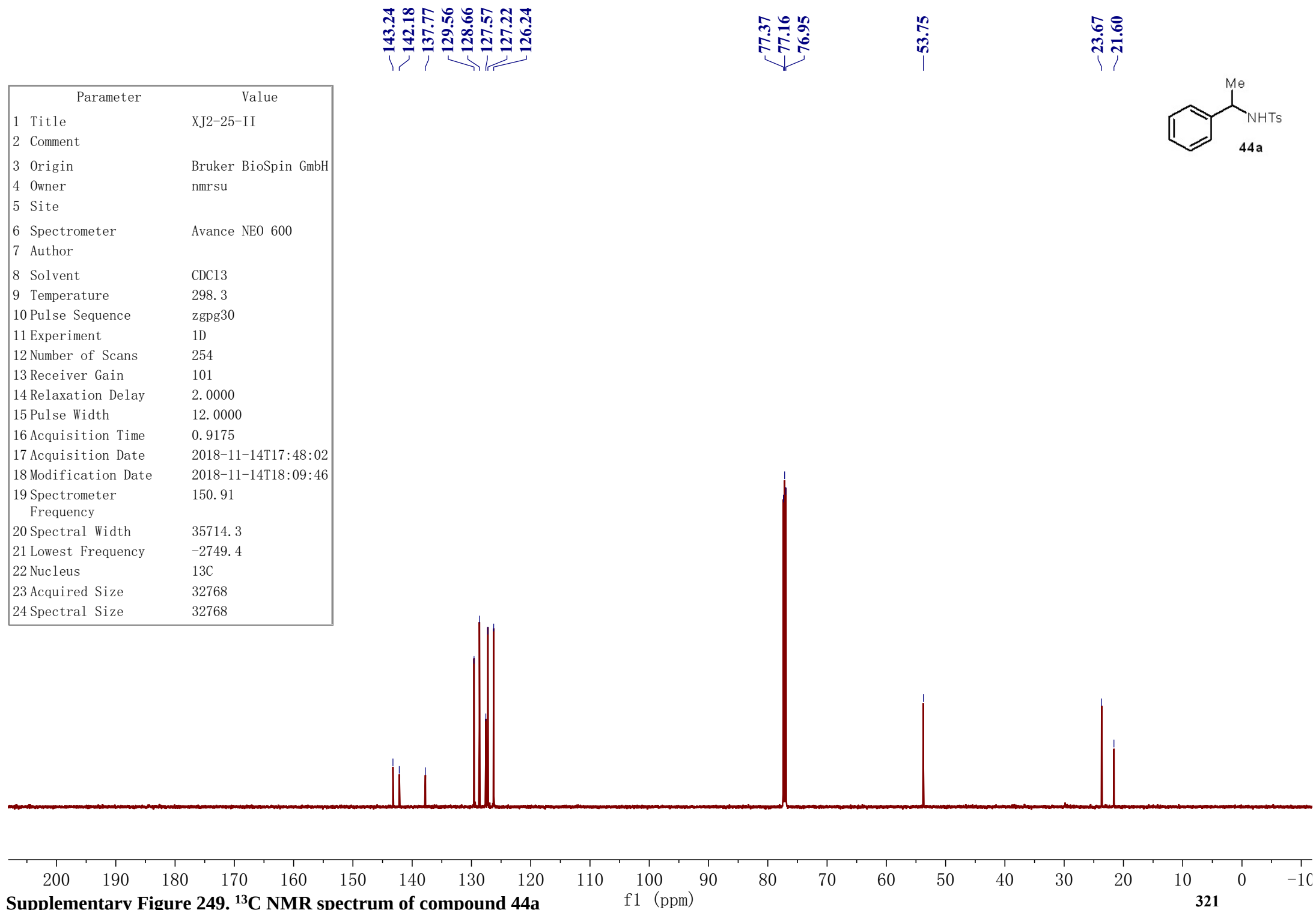
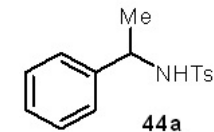
Parameter	Value
1 Title	XJ2-27-0222
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl ₃
9 Temperature	295.9
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	76
13 Receiver Gain	29
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2019-02-22T19:55:57
18 Modification Date	2019-02-22T19:58:13
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1834.1
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

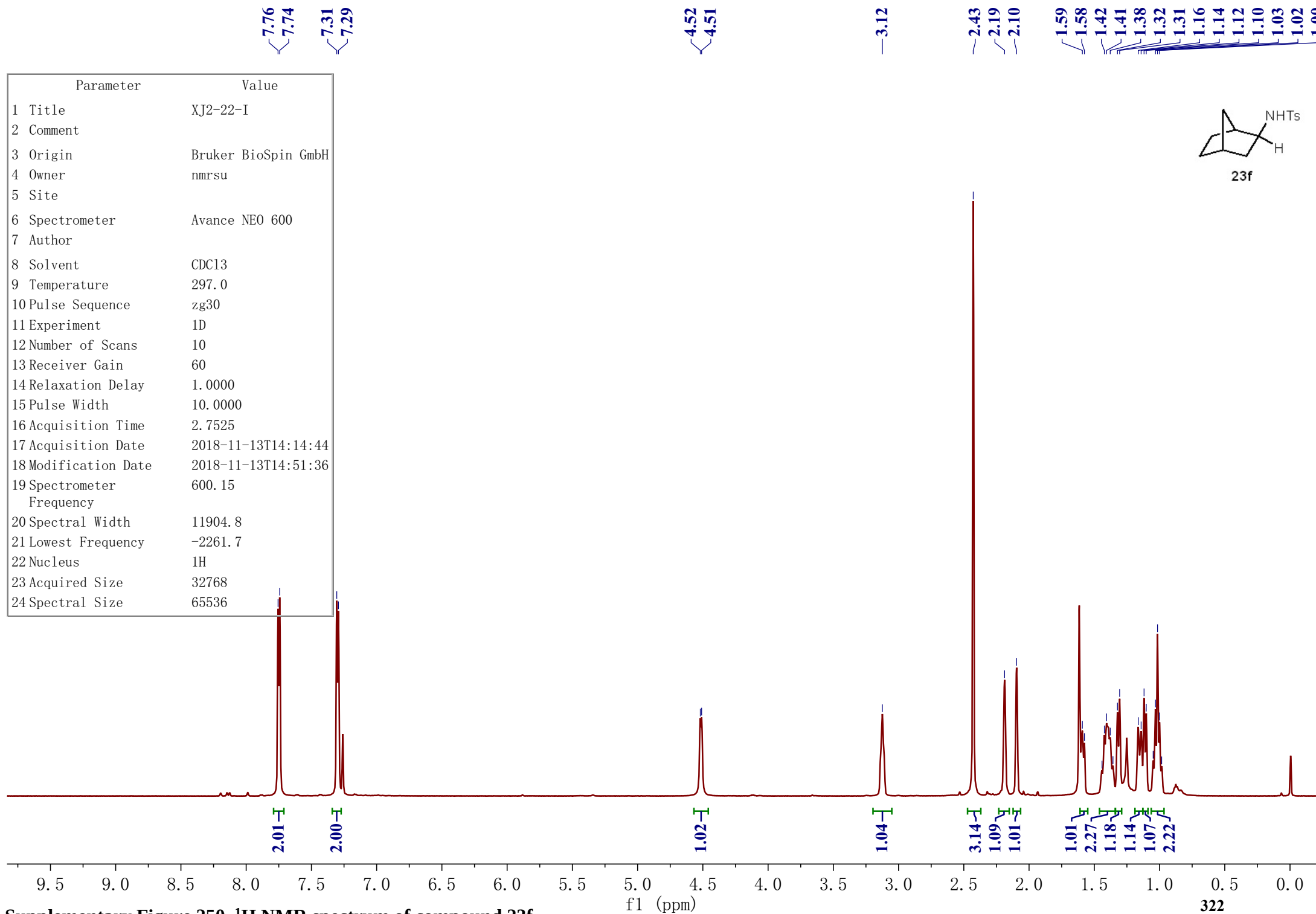


Supplementary Figure 247. ¹³C NMR spectrum of compound 27d



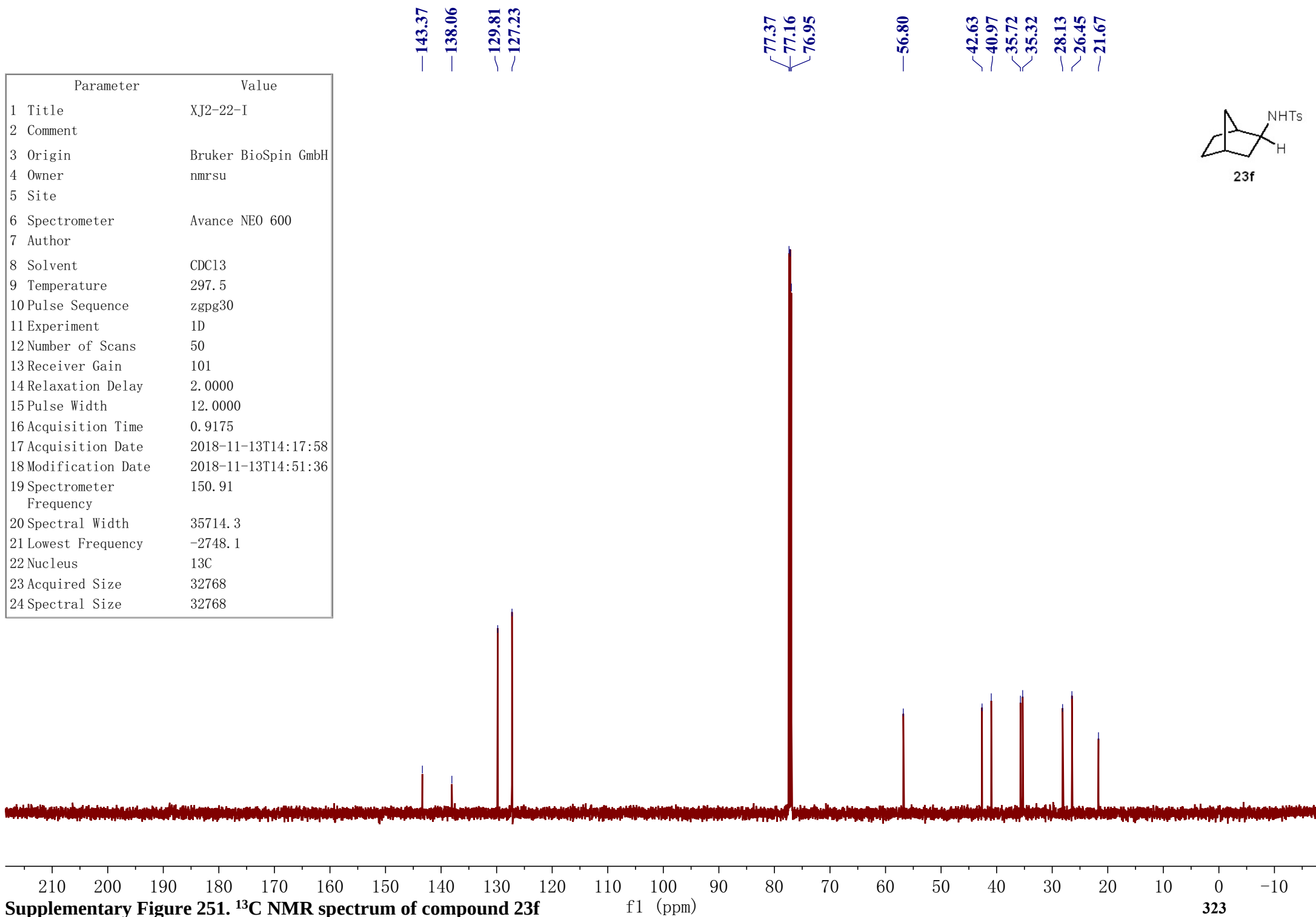
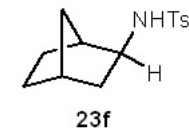
Parameter	Value
1 Title	XJ2-25-II
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl3
9 Temperature	298.3
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	254
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2018-11-14T17:48:02
18 Modification Date	2018-11-14T18:09:46
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2749.4
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

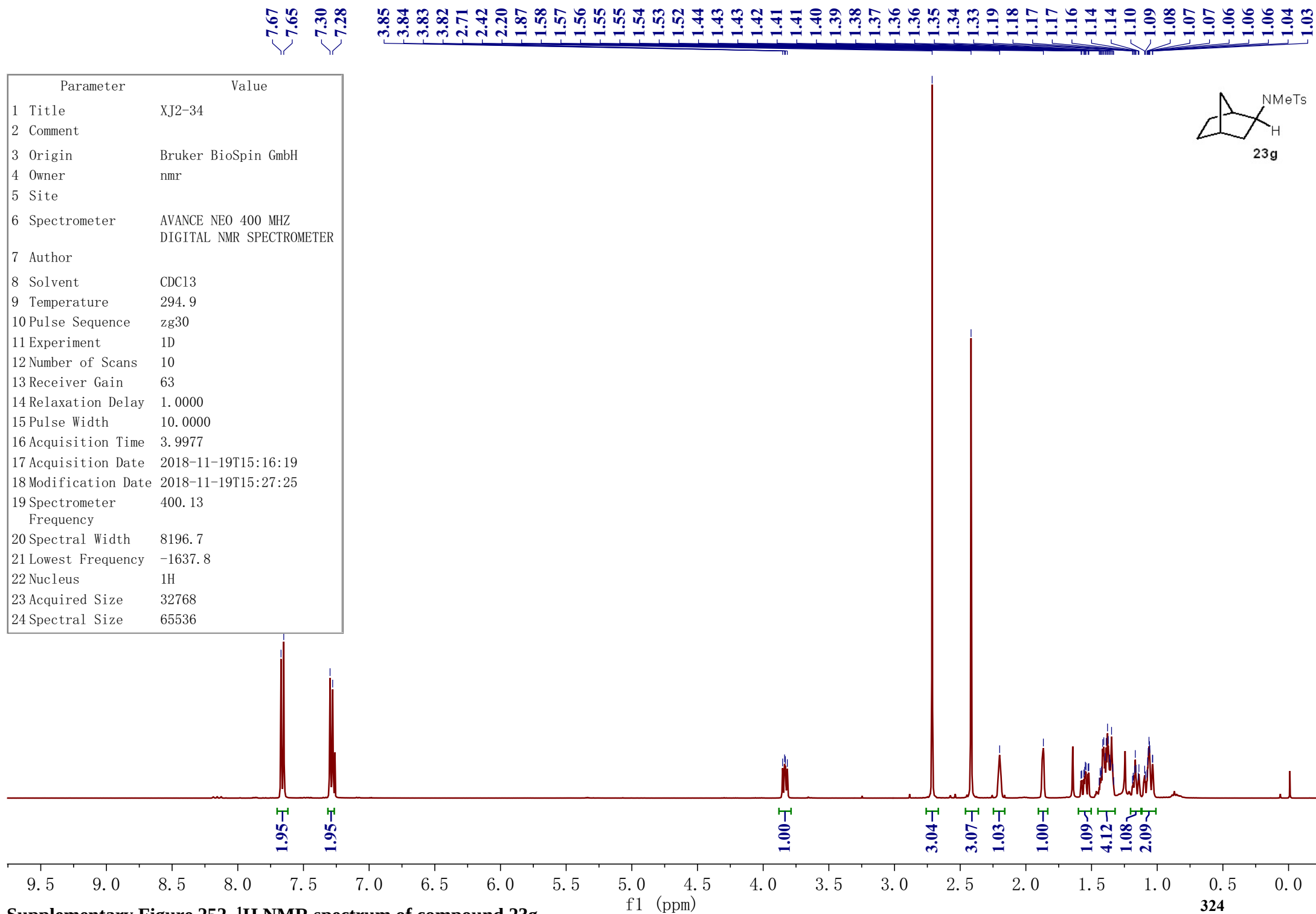




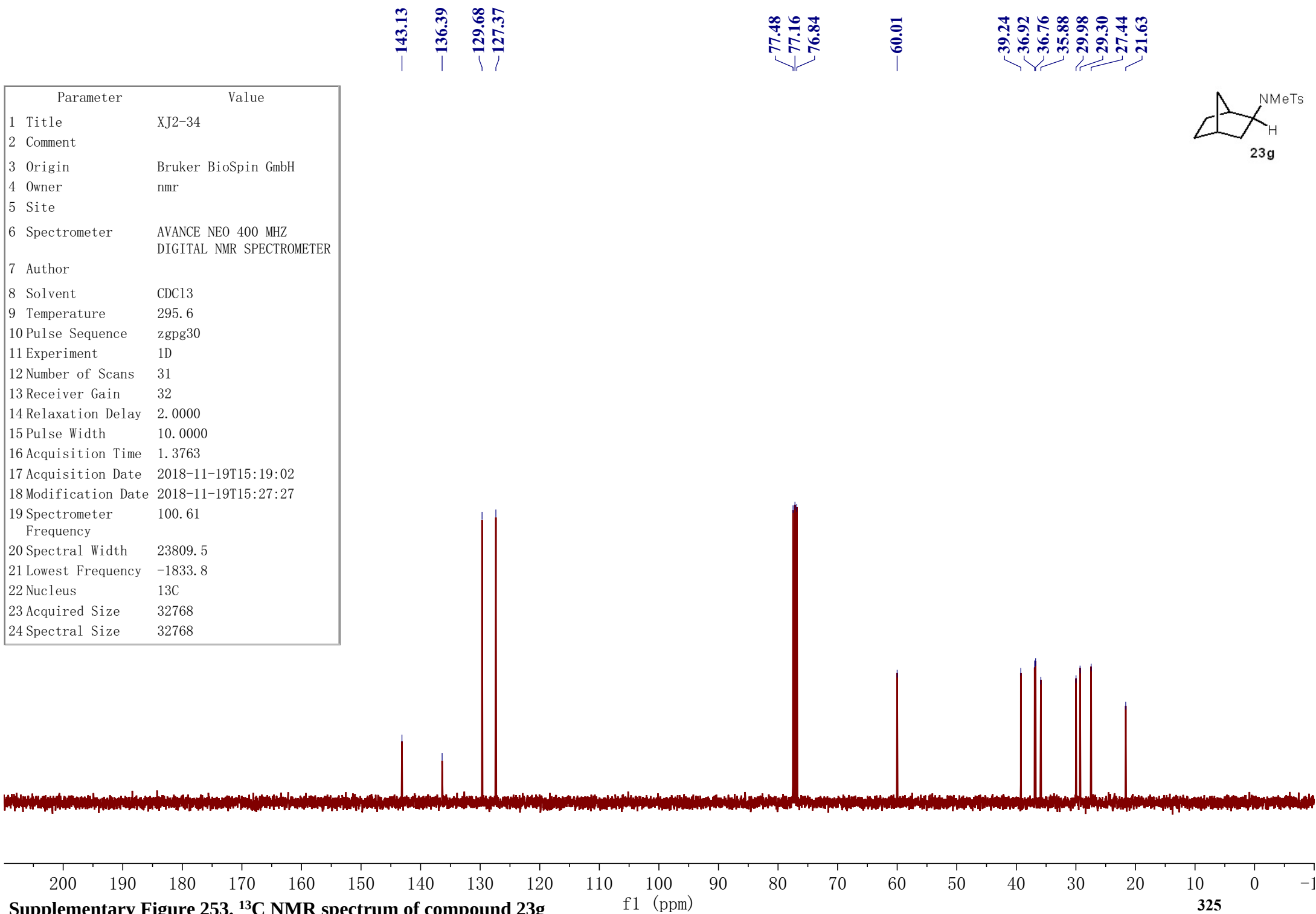
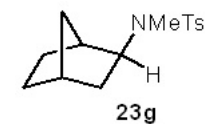
Supplementary Figure 250. ¹H NMR spectrum of compound 23f

Parameter	Value
1 Title	XJ2-22-I
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	50
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2018-11-13T14:17:58
18 Modification Date	2018-11-13T14:51:36
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2748.1
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

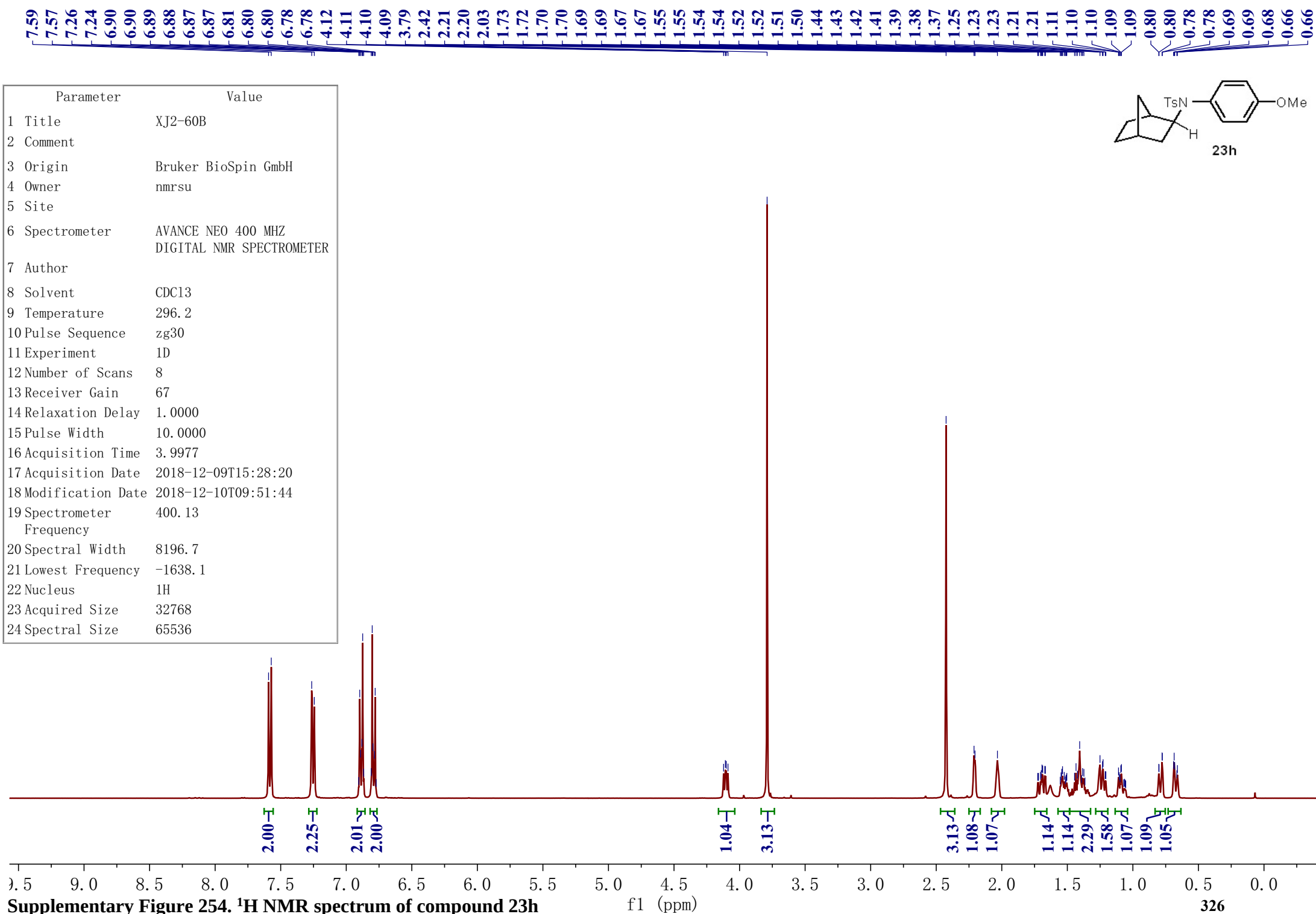
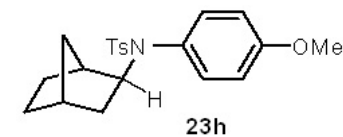




Parameter	Value
1 Title	XJ2-34
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	295.6
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	31
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-11-19T15:19:02
18 Modification Date	2018-11-19T15:27:27
19 Spectrometer Frequency	100.61
20 Spectral Width	23809.5
21 Lowest Frequency	-1833.8
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768

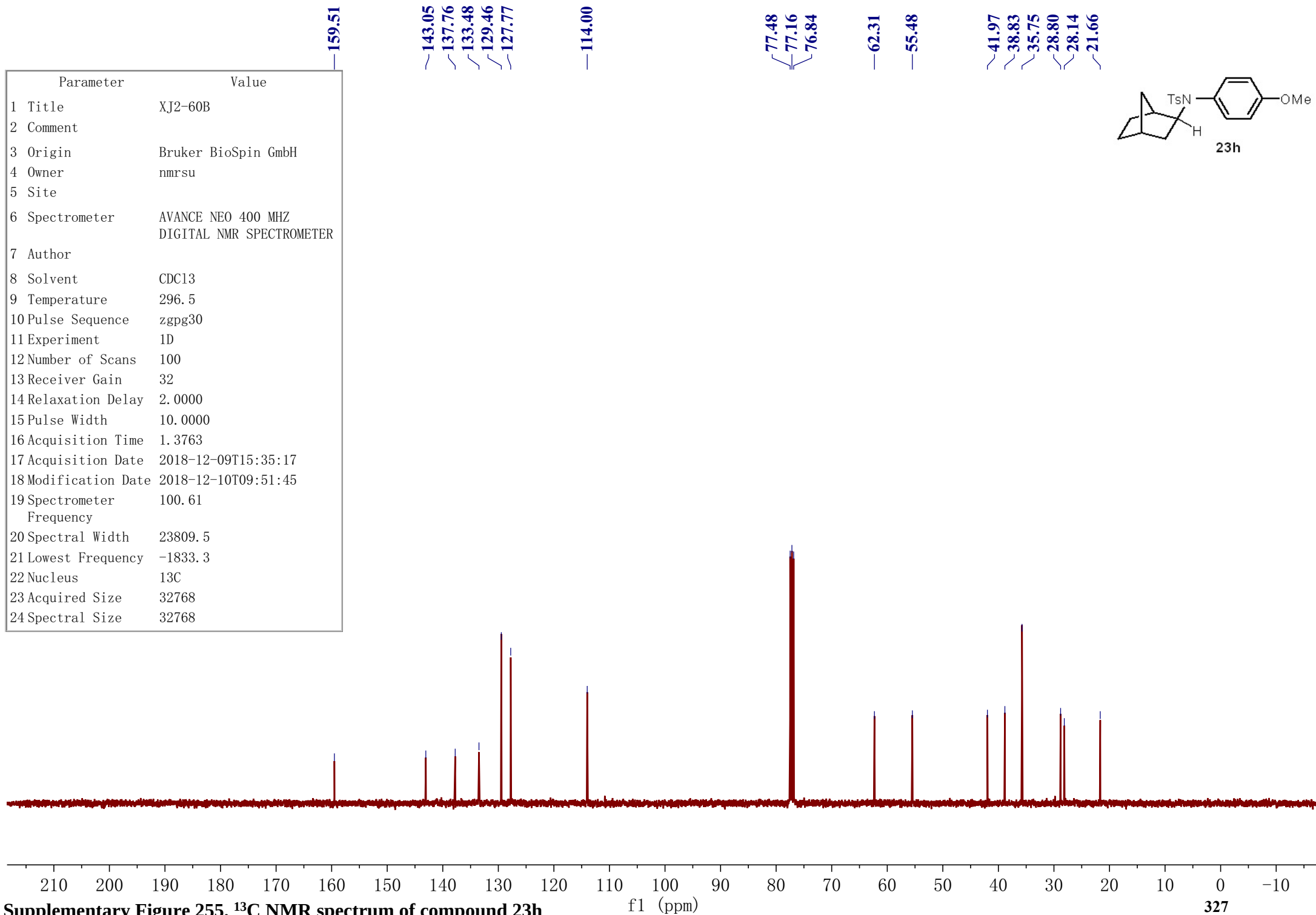
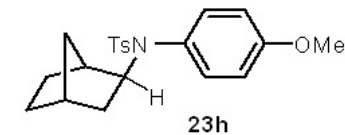


Parameter	Value
1 Title	XJ2-60B
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDCl3
9 Temperature	296.2
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	8
13 Receiver Gain	67
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-12-09T15:28:20
18 Modification Date	2018-12-10T09:51:44
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.1
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536



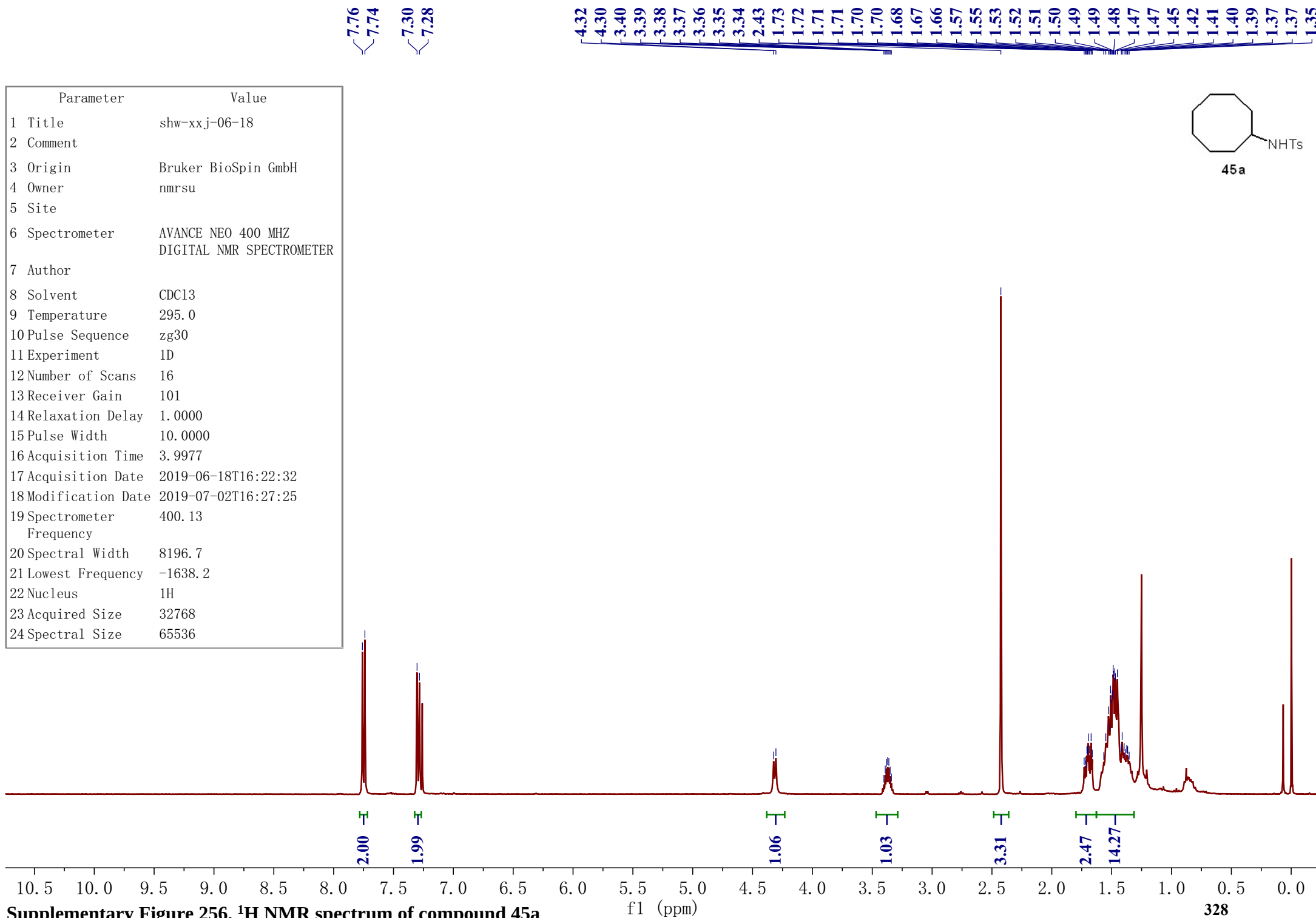
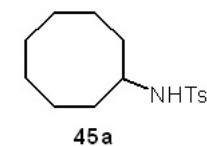
Supplementary Figure 254. ¹H NMR spectrum of compound 23h

Parameter	Value
1 Title	XJ2-60B
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.5
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	100
13 Receiver Gain	32
14 Relaxation Delay	2.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.3763
17 Acquisition Date	2018-12-09T15:35:17
18 Modification Date	2018-12-10T09:51:45
19 Spectrometer	100.61
Frequency	
20 Spectral Width	23809.5
21 Lowest Frequency	-1833.3
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



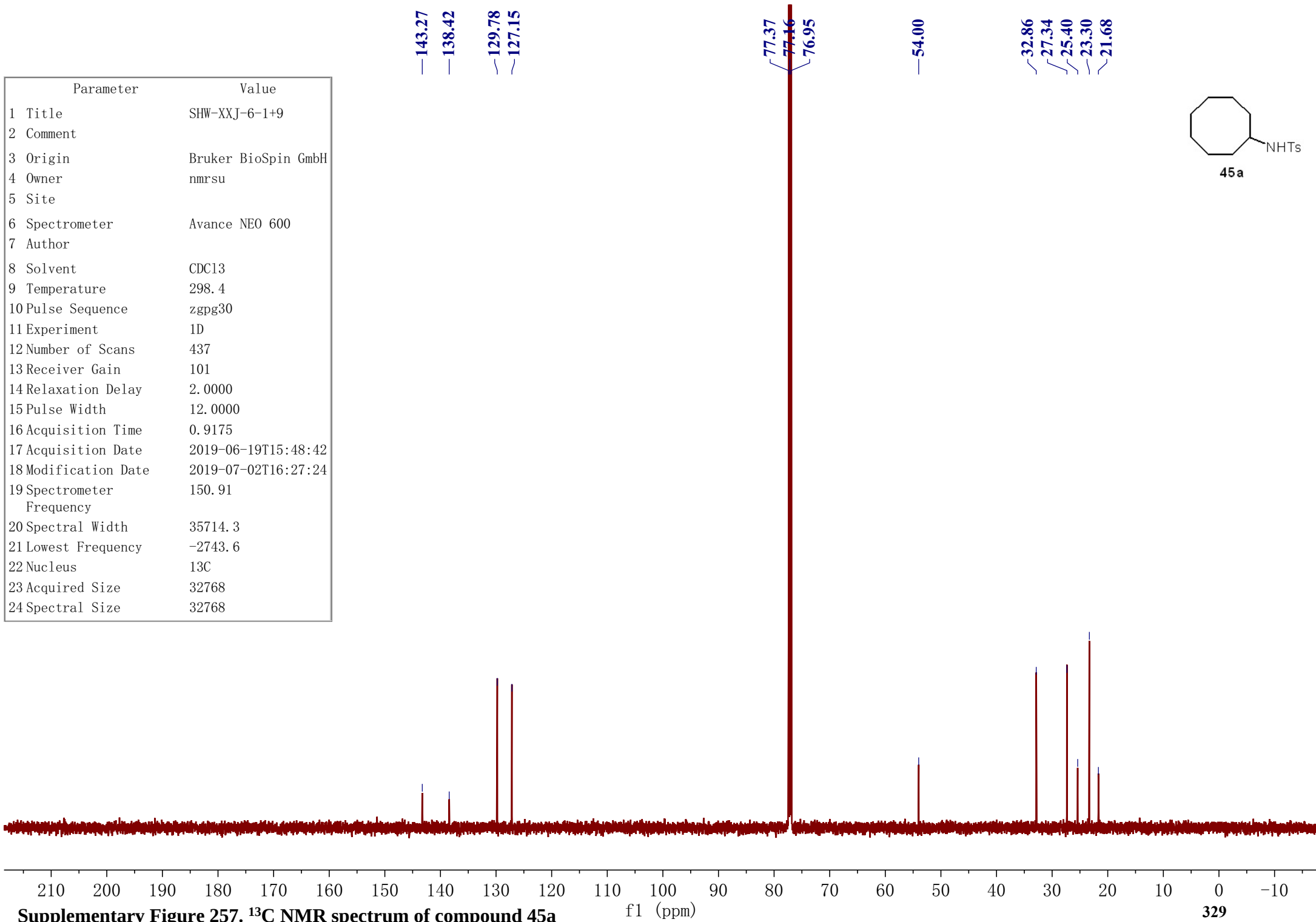
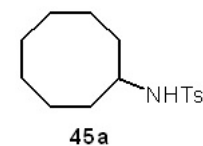
Supplementary Figure 255. ¹³C NMR spectrum of compound 23h

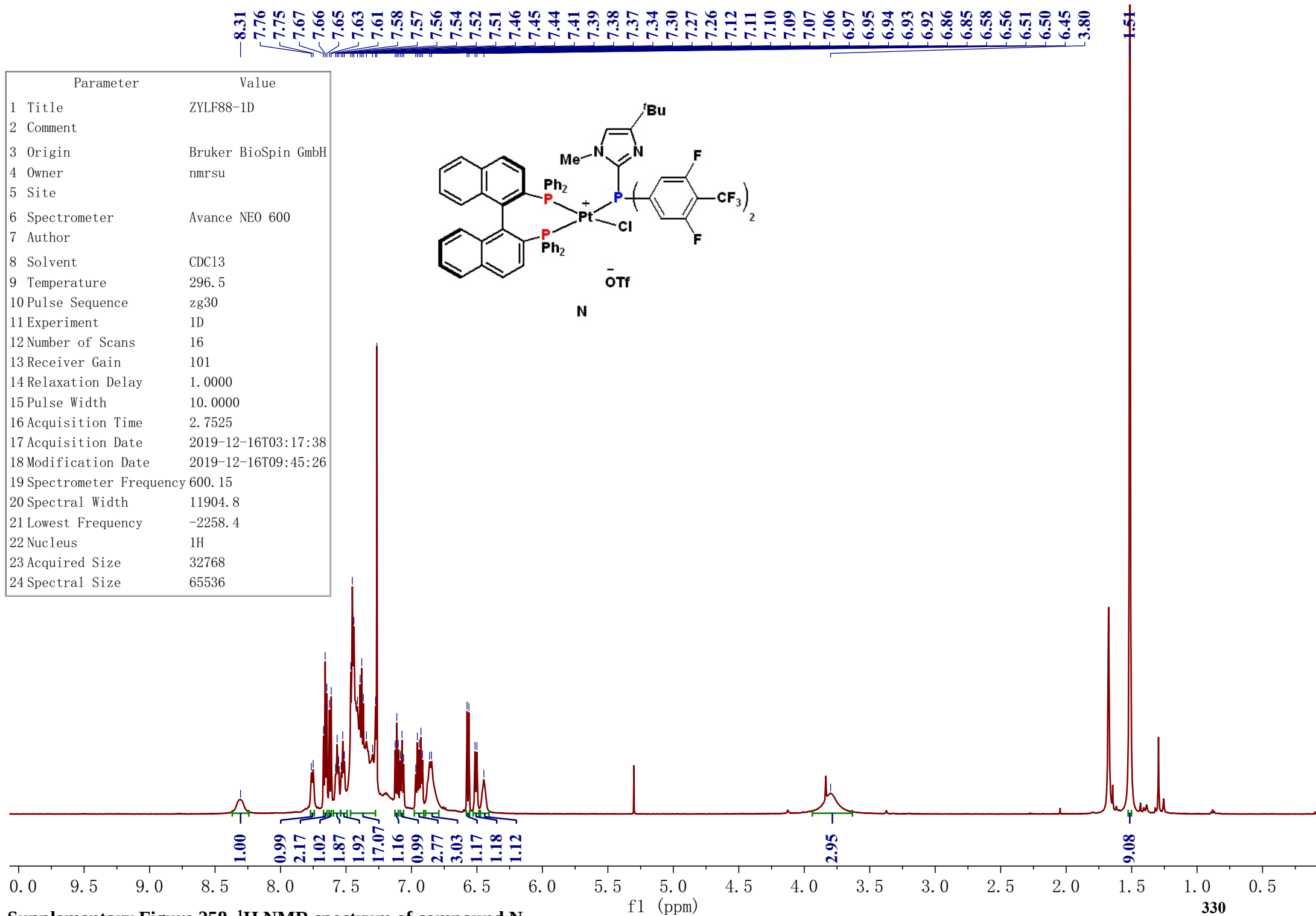
Parameter	Value
1 Title	shw-xxj-06-18
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-06-18T16:22:32
18 Modification Date	2019-07-02T16:27:25
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.2
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536

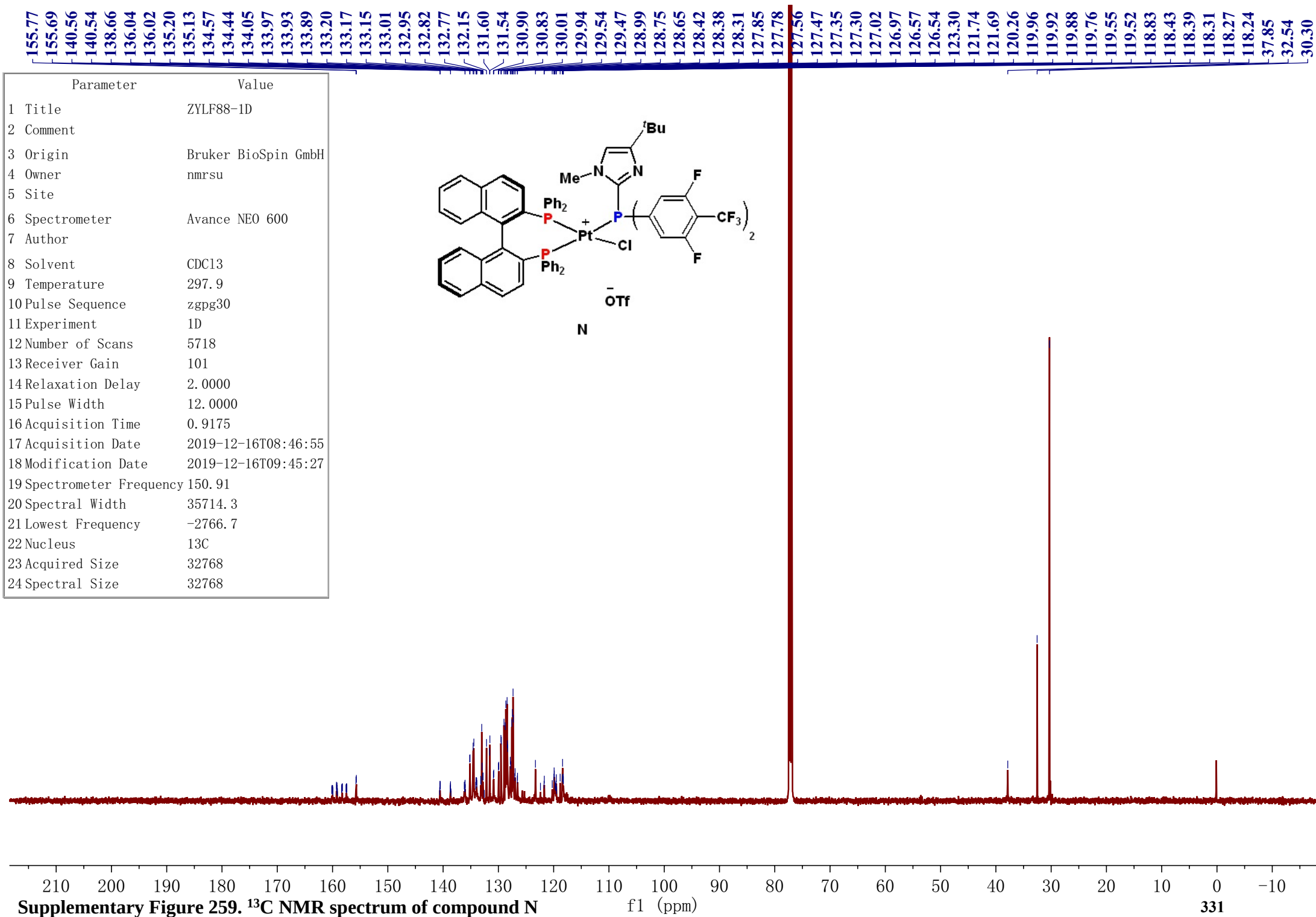


Supplementary Figure 256. ¹H NMR spectrum of compound 45a

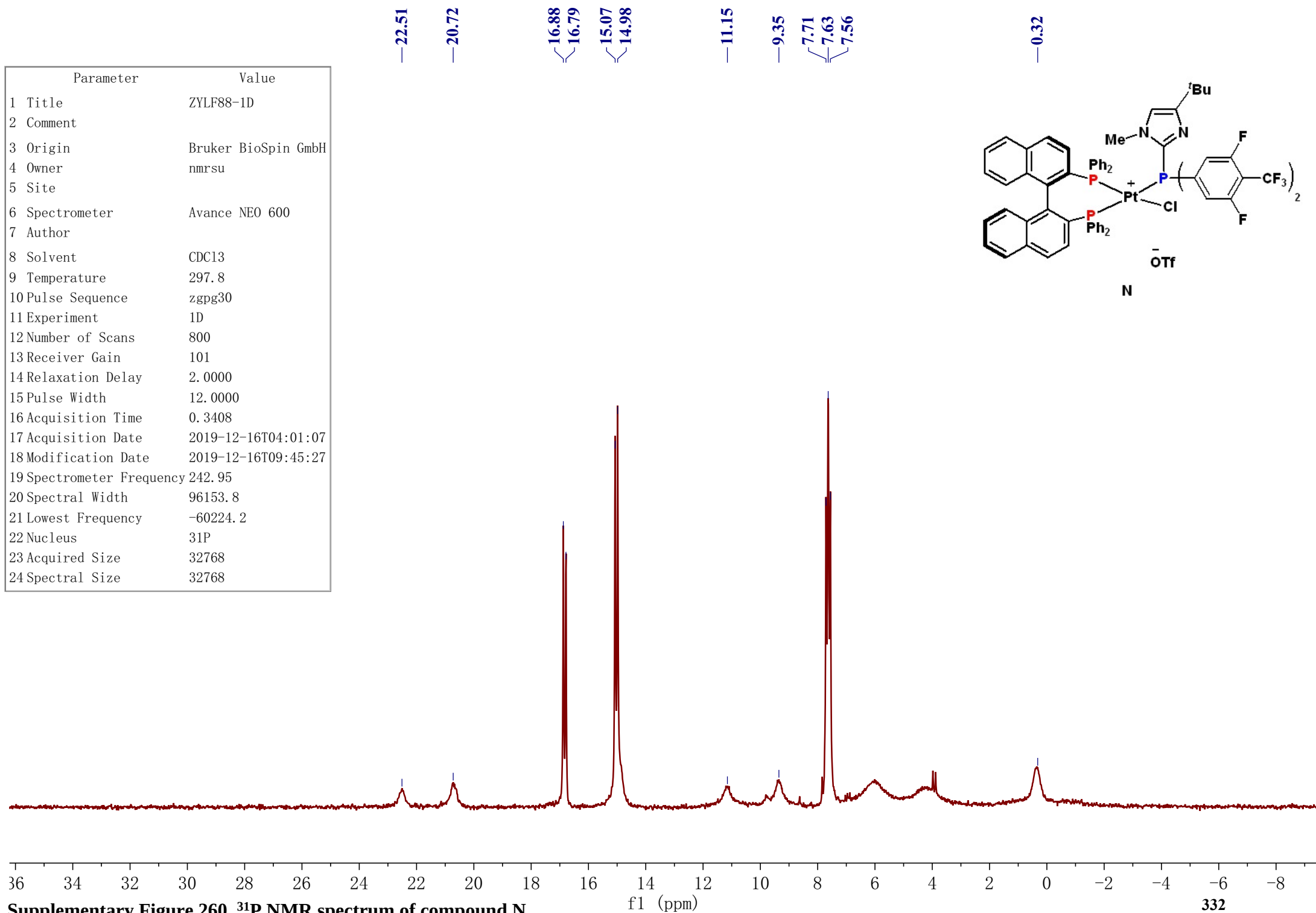
Parameter	Value
1 Title	SHW-XXJ-6-1+9
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	298.4
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	437
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-06-19T15:48:42
18 Modification Date	2019-07-02T16:27:24
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2743.6
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



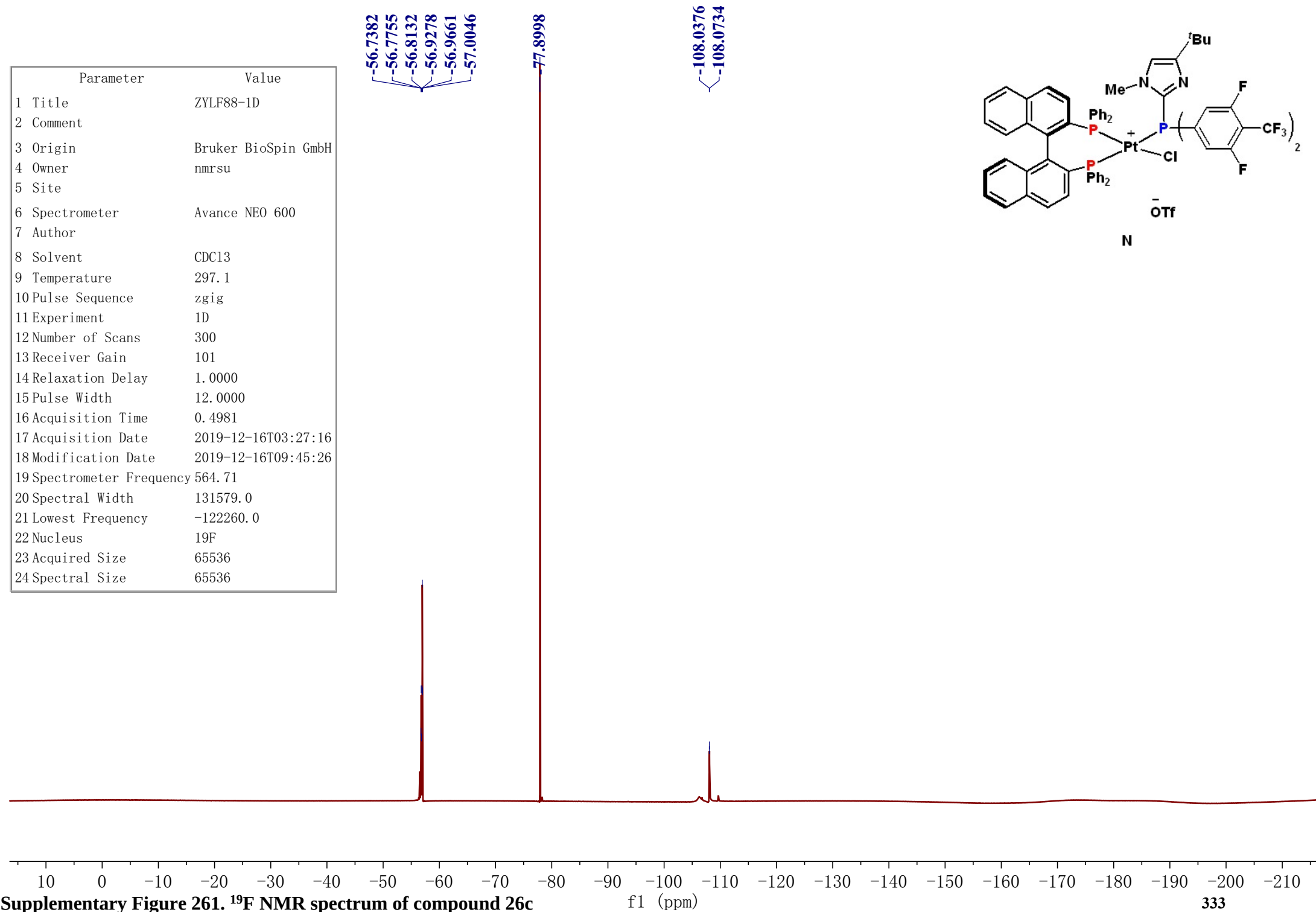




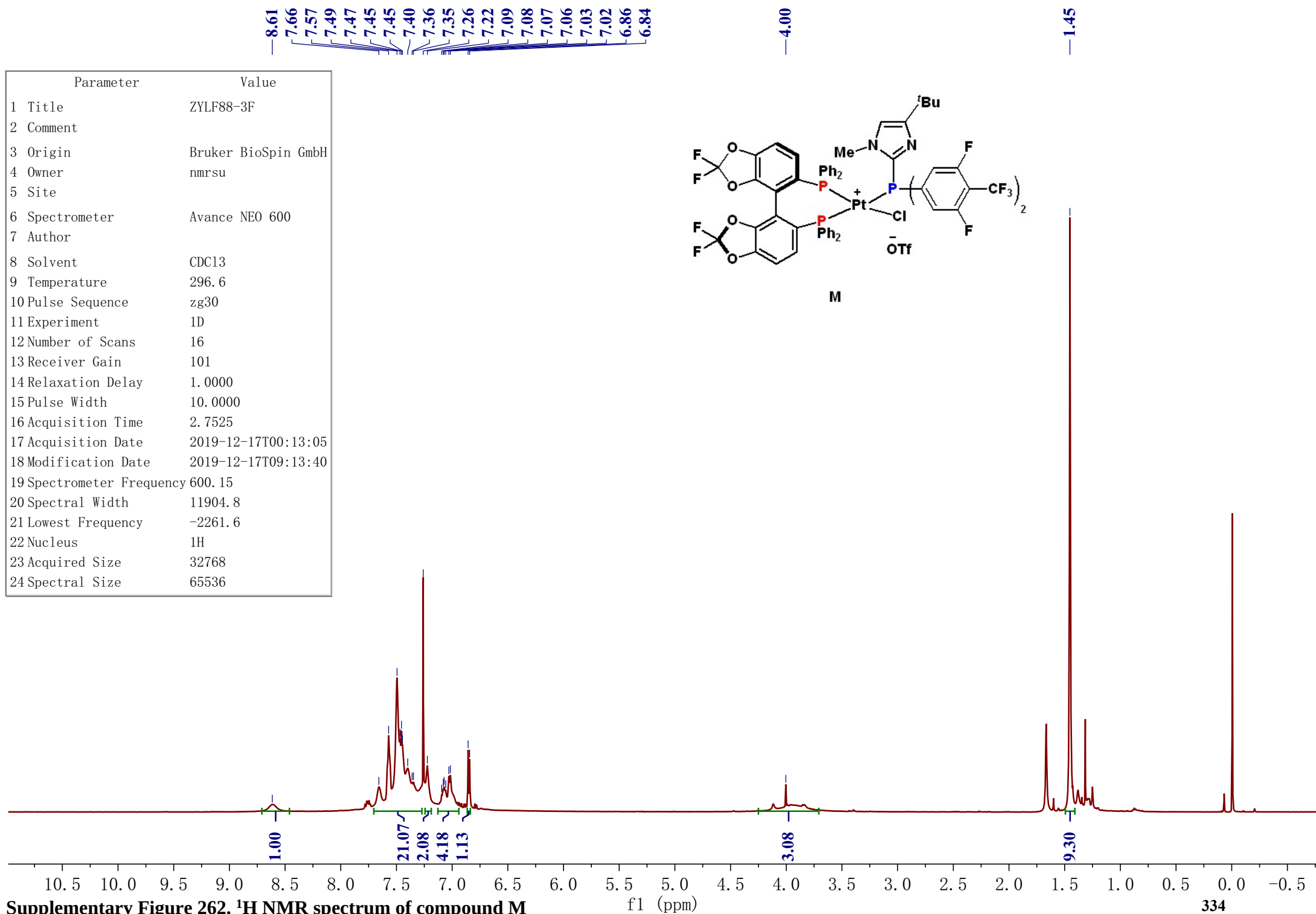
Parameter	Value
1 Title	ZYLF88-1D
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.8
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	800
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.3408
17 Acquisition Date	2019-12-16T04:01:07
18 Modification Date	2019-12-16T09:45:27
19 Spectrometer Frequency	242.95
20 Spectral Width	96153.8
21 Lowest Frequency	-60224.2
22 Nucleus	³¹ P
23 Acquired Size	32768
24 Spectral Size	32768



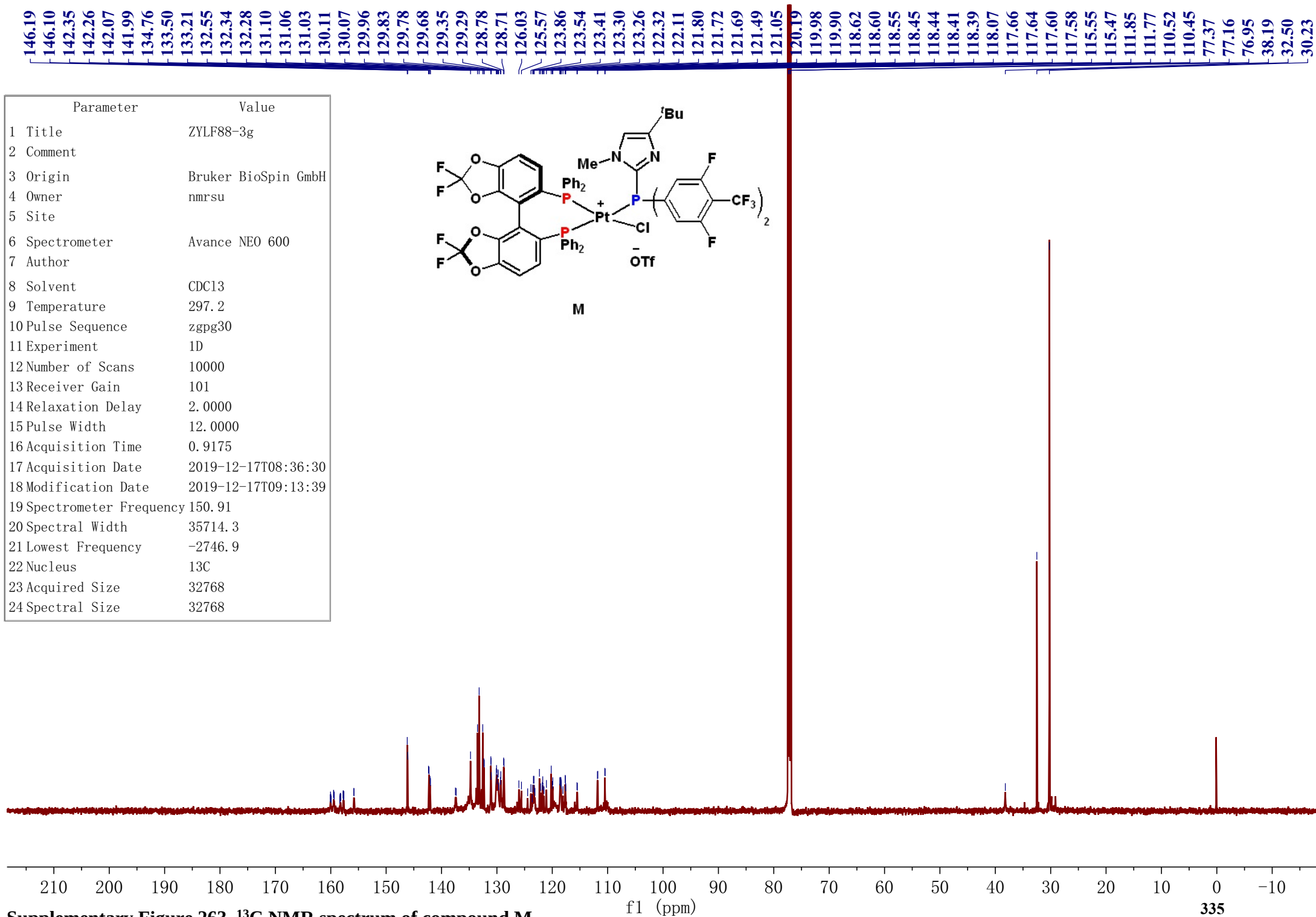
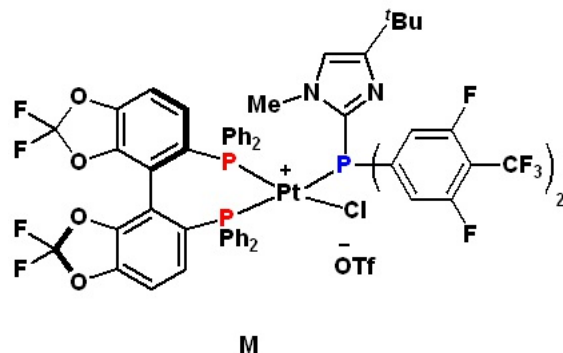
Parameter	Value
1 Title	ZYLF88-1D
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.1
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	300
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.4981
17 Acquisition Date	2019-12-16T03:27:16
18 Modification Date	2019-12-16T09:45:26
19 Spectrometer Frequency	564.71
20 Spectral Width	131579.0
21 Lowest Frequency	-122260.0
22 Nucleus	19F
23 Acquired Size	65536
24 Spectral Size	65536



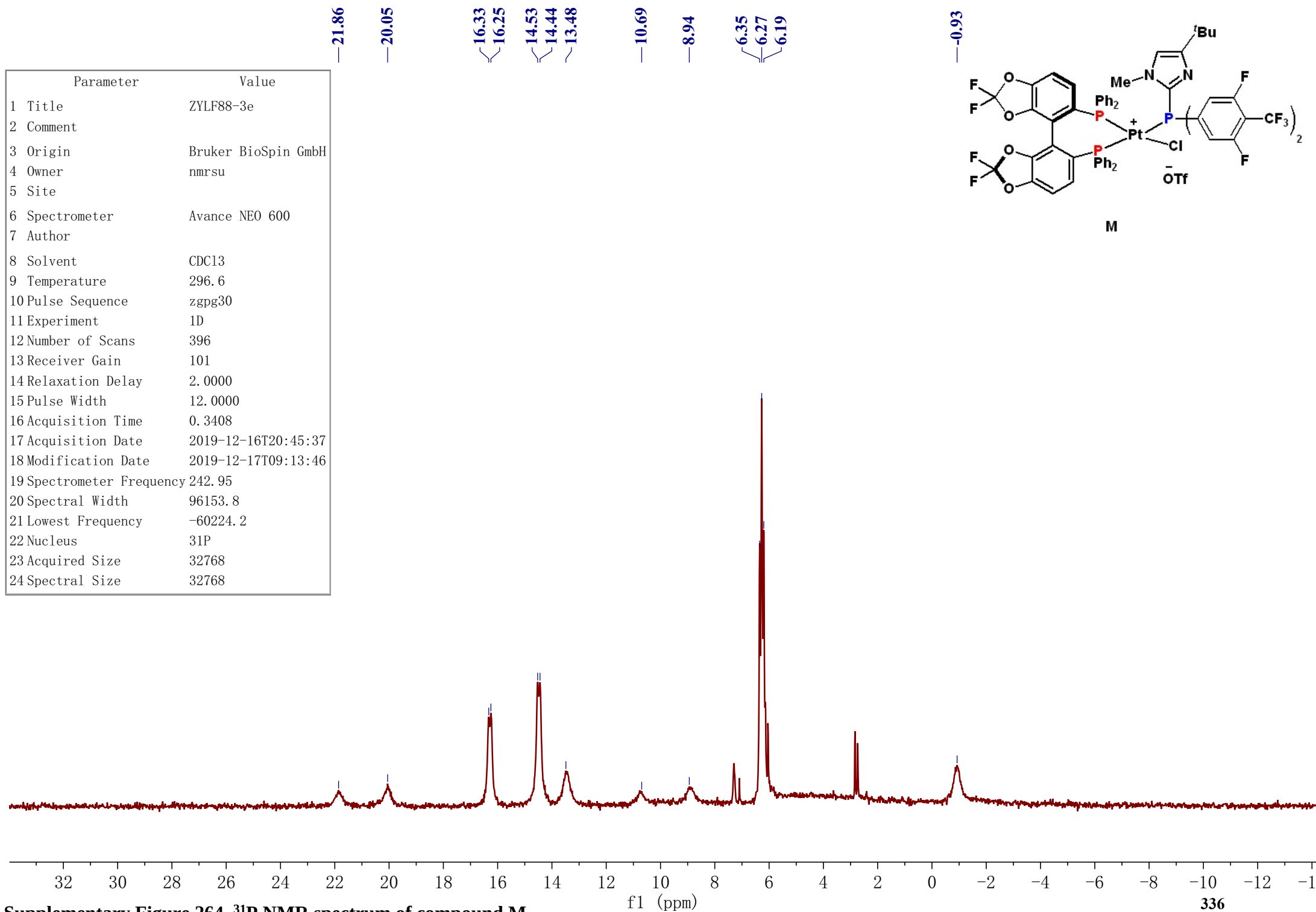
Supplementary Figure 261. ¹⁹F NMR spectrum of compound 26c



Parameter	Value
1 Title	ZYLF88-3g
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.2
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	10000
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.9175
17 Acquisition Date	2019-12-17T08:36:30
18 Modification Date	2019-12-17T09:13:39
19 Spectrometer Frequency	150.91
20 Spectral Width	35714.3
21 Lowest Frequency	-2746.9
22 Nucleus	¹³ C
23 Acquired Size	32768
24 Spectral Size	32768



Supplementary Figure 263. ¹³C NMR spectrum of compound M

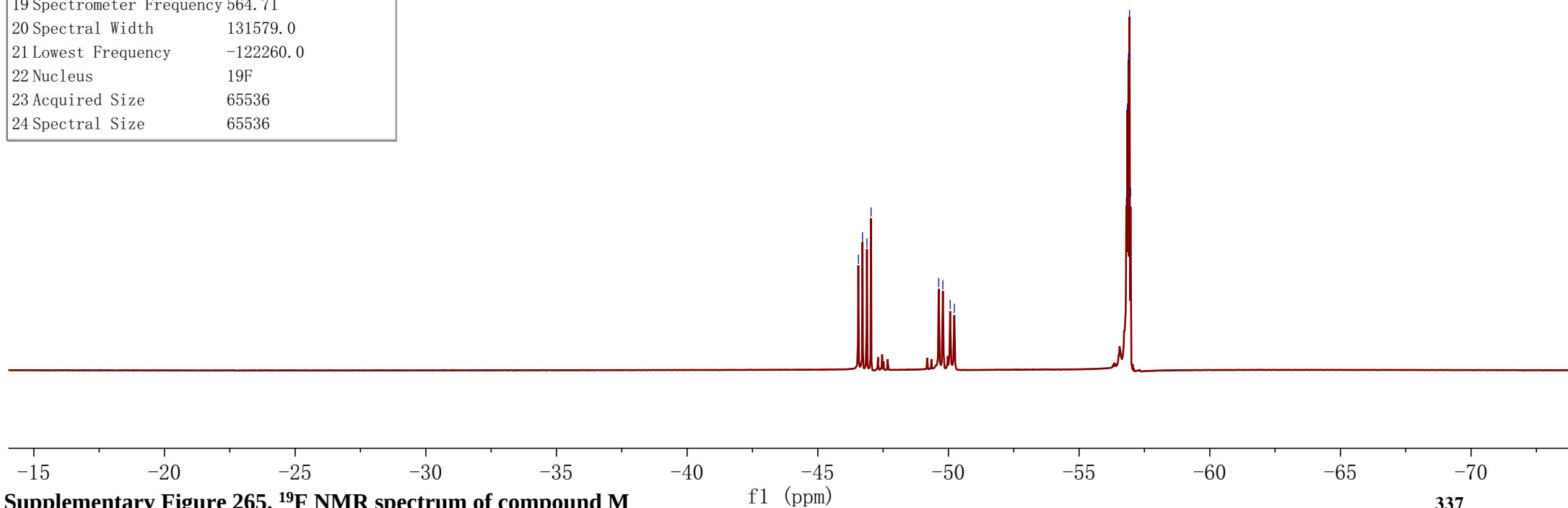
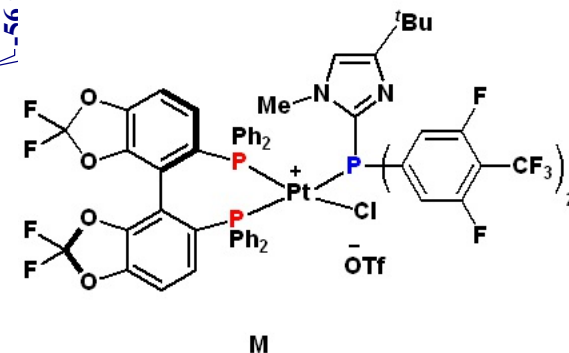


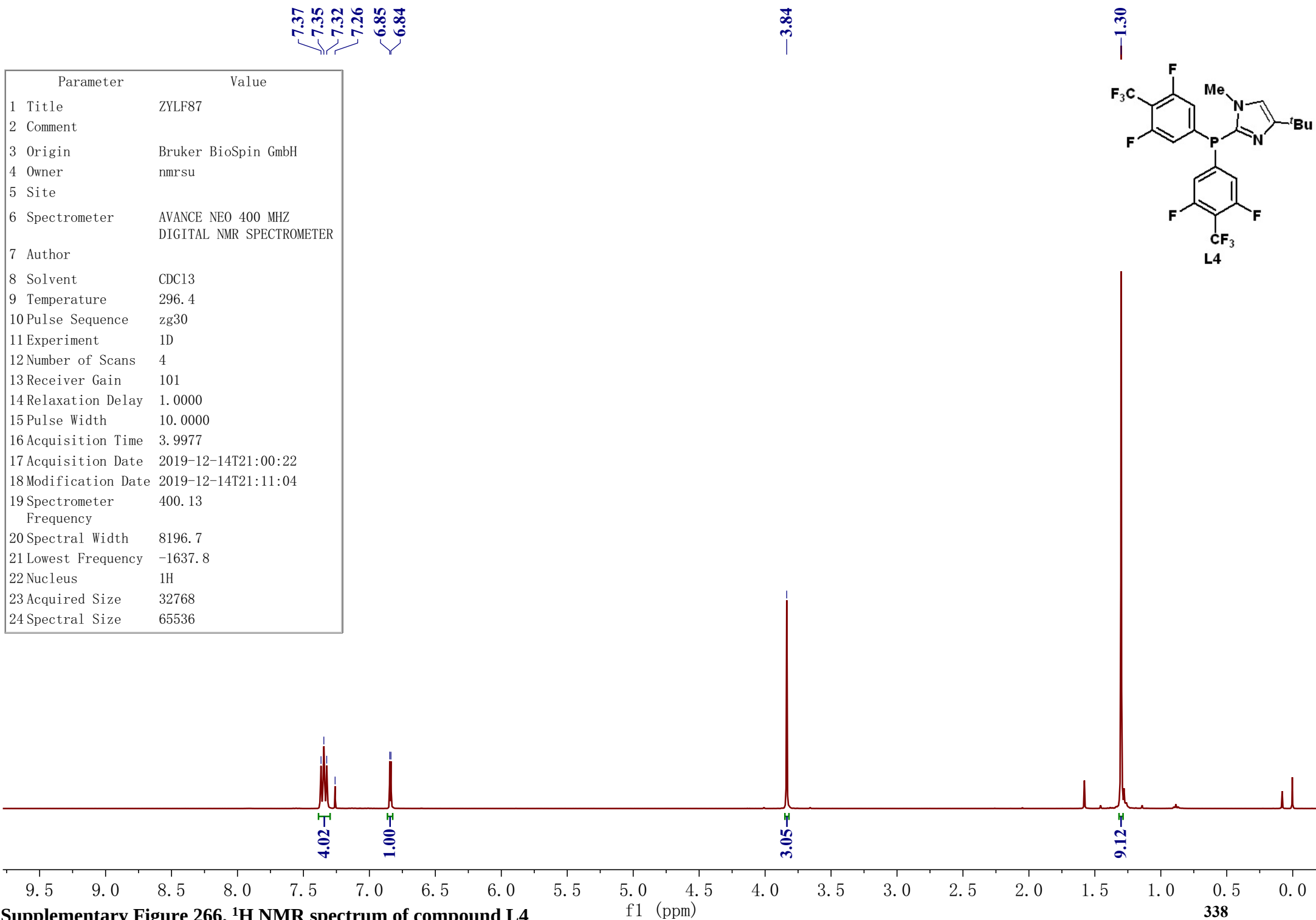
Supplementary Figure 264. ³¹P NMR spectrum of compound **M**

Parameter	Value
1 Title	ZYLF88-3F
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	Avance NEO 600
7 Author	
8 Solvent	CDCl ₃
9 Temperature	297.0
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	158
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	12.0000
16 Acquisition Time	0.4981
17 Acquisition Date	2019-12-17T00:18:27
18 Modification Date	2019-12-17T09:13:40
19 Spectrometer Frequency	564.71
20 Spectral Width	131579.0
21 Lowest Frequency	-122260.0
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536

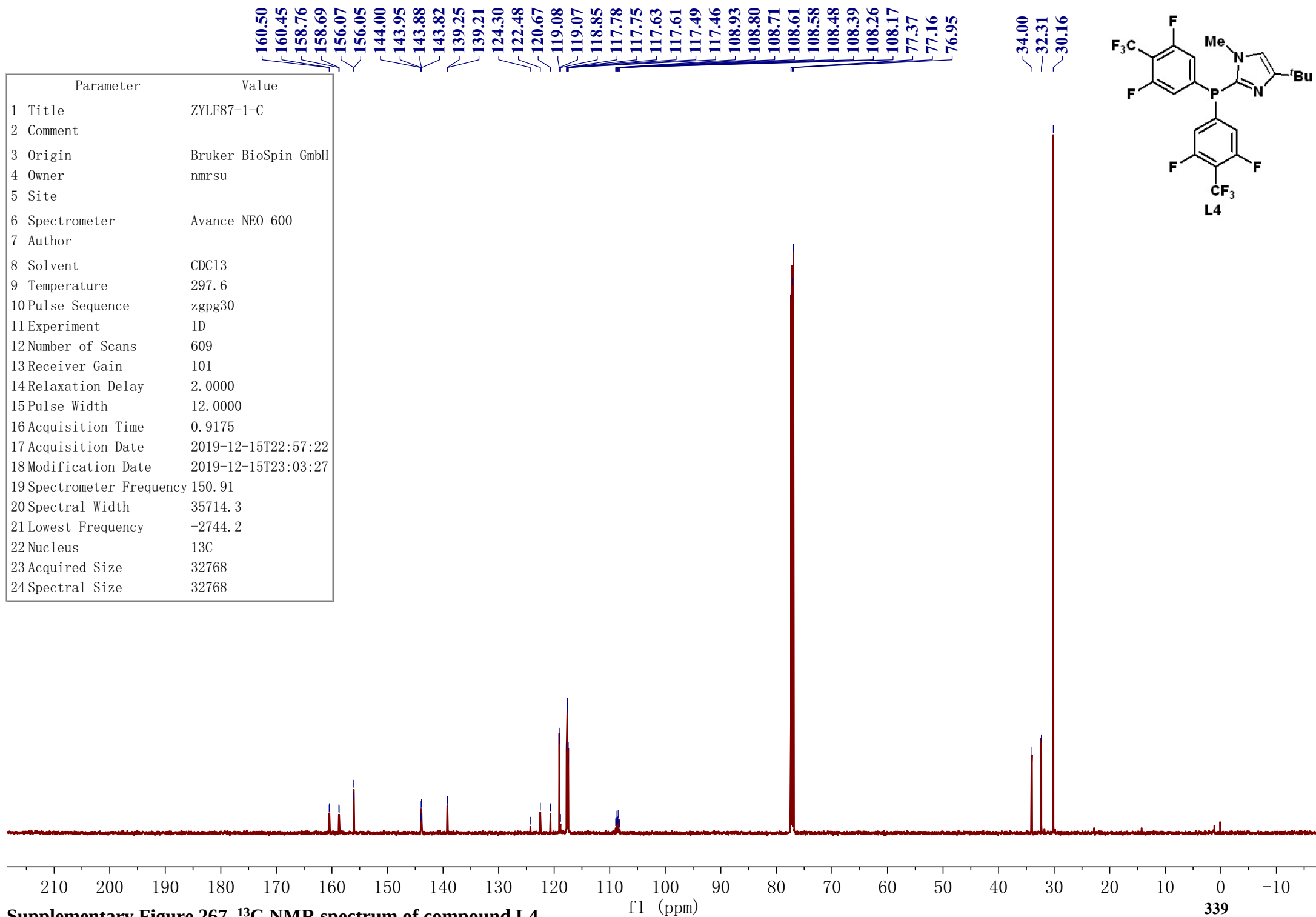
-46.55
-46.71
-46.88
-47.04
-49.63
-49.79
-50.07
-50.22

-56.81
-56.85
-56.89
-56.93
97

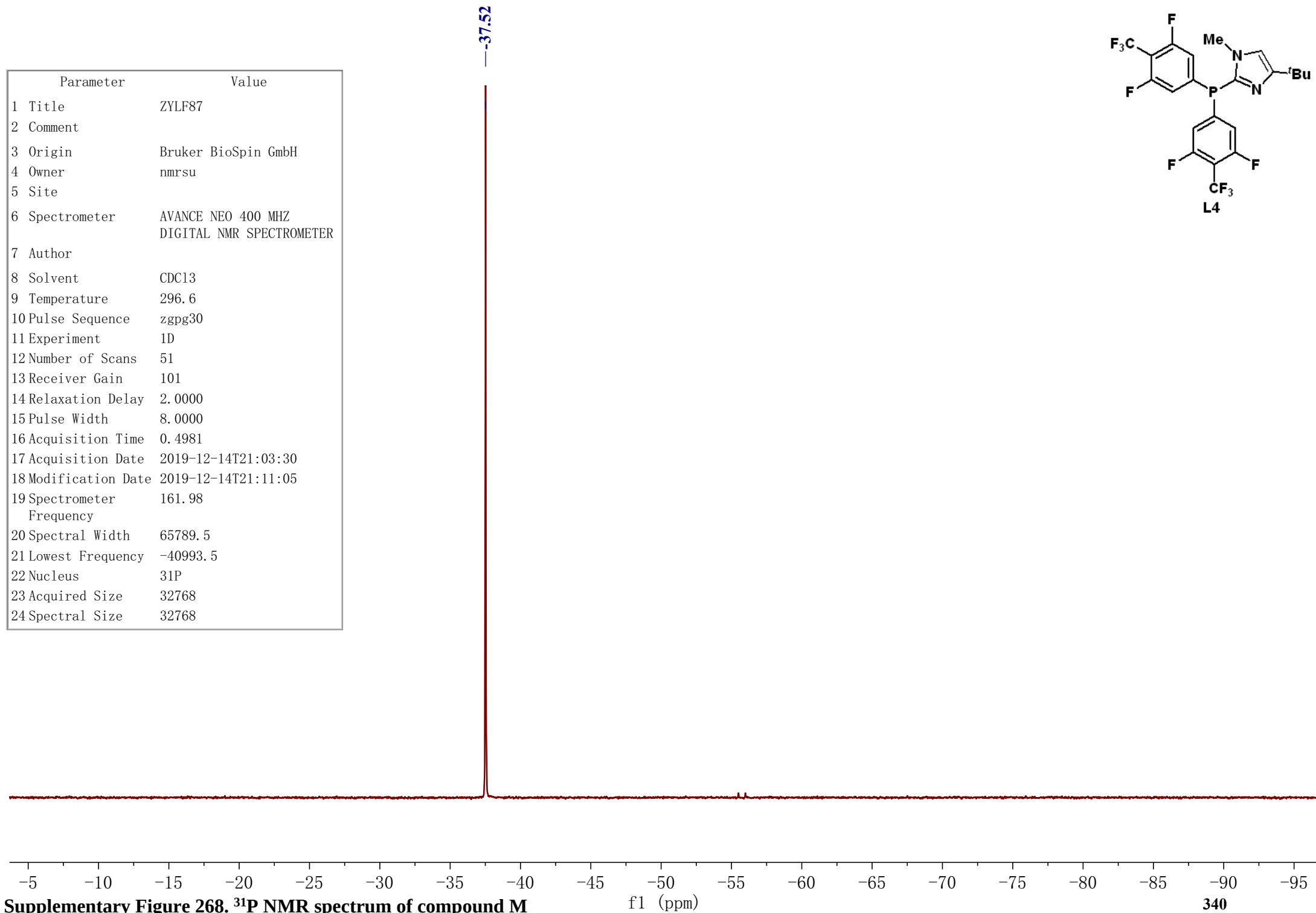
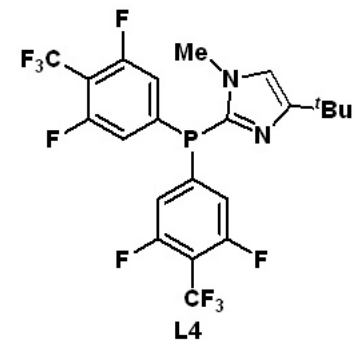




Supplementary Figure 266. ¹H NMR spectrum of compound L4

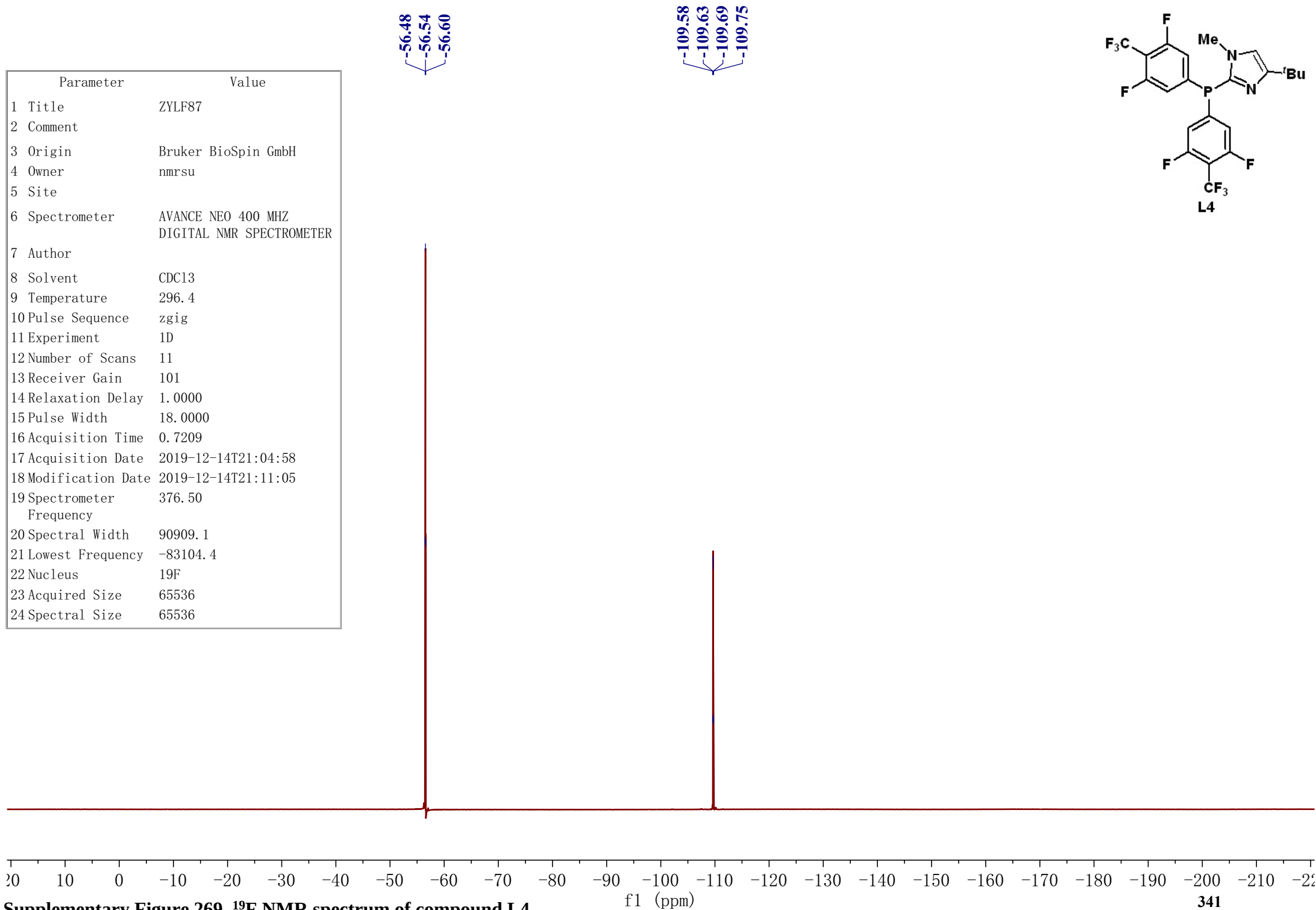


Parameter	Value
1 Title	ZYLF87
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.6
10 Pulse Sequence	zgpg30
11 Experiment	1D
12 Number of Scans	51
13 Receiver Gain	101
14 Relaxation Delay	2.0000
15 Pulse Width	8.0000
16 Acquisition Time	0.4981
17 Acquisition Date	2019-12-14T21:03:30
18 Modification Date	2019-12-14T21:11:05
19 Spectrometer Frequency	161.98
20 Spectral Width	65789.5
21 Lowest Frequency	-40993.5
22 Nucleus	³¹ P
23 Acquired Size	32768
24 Spectral Size	32768



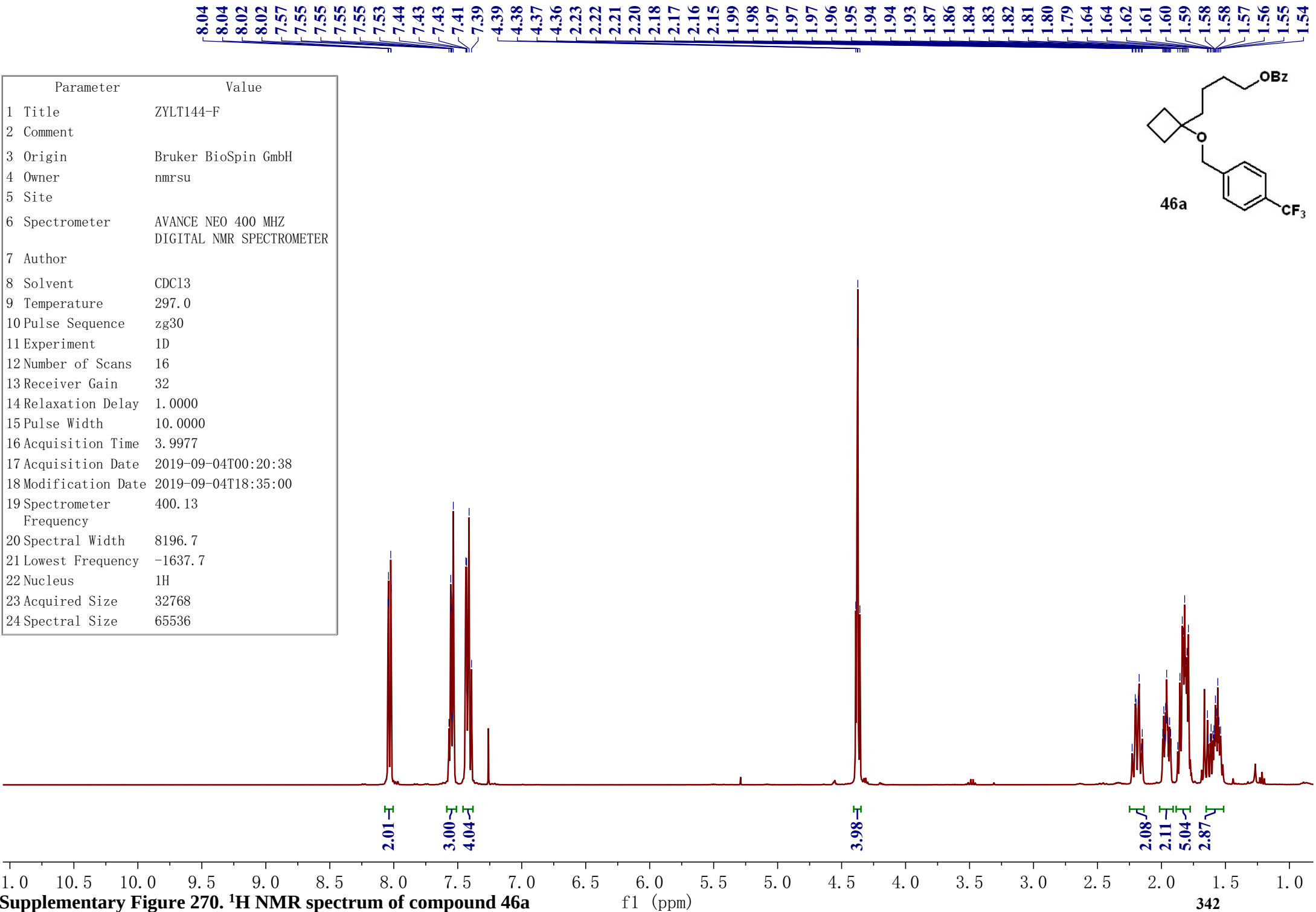
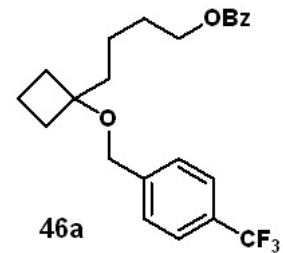
Supplementary Figure 268. ³¹P NMR spectrum of compound M

Parameter	Value
1 Title	ZYLF87
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	296.4
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	11
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	18.0000
16 Acquisition Time	0.7209
17 Acquisition Date	2019-12-14T21:04:58
18 Modification Date	2019-12-14T21:11:05
19 Spectrometer	376.50
Frequency	
20 Spectral Width	90909.1
21 Lowest Frequency	-83104.4
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536



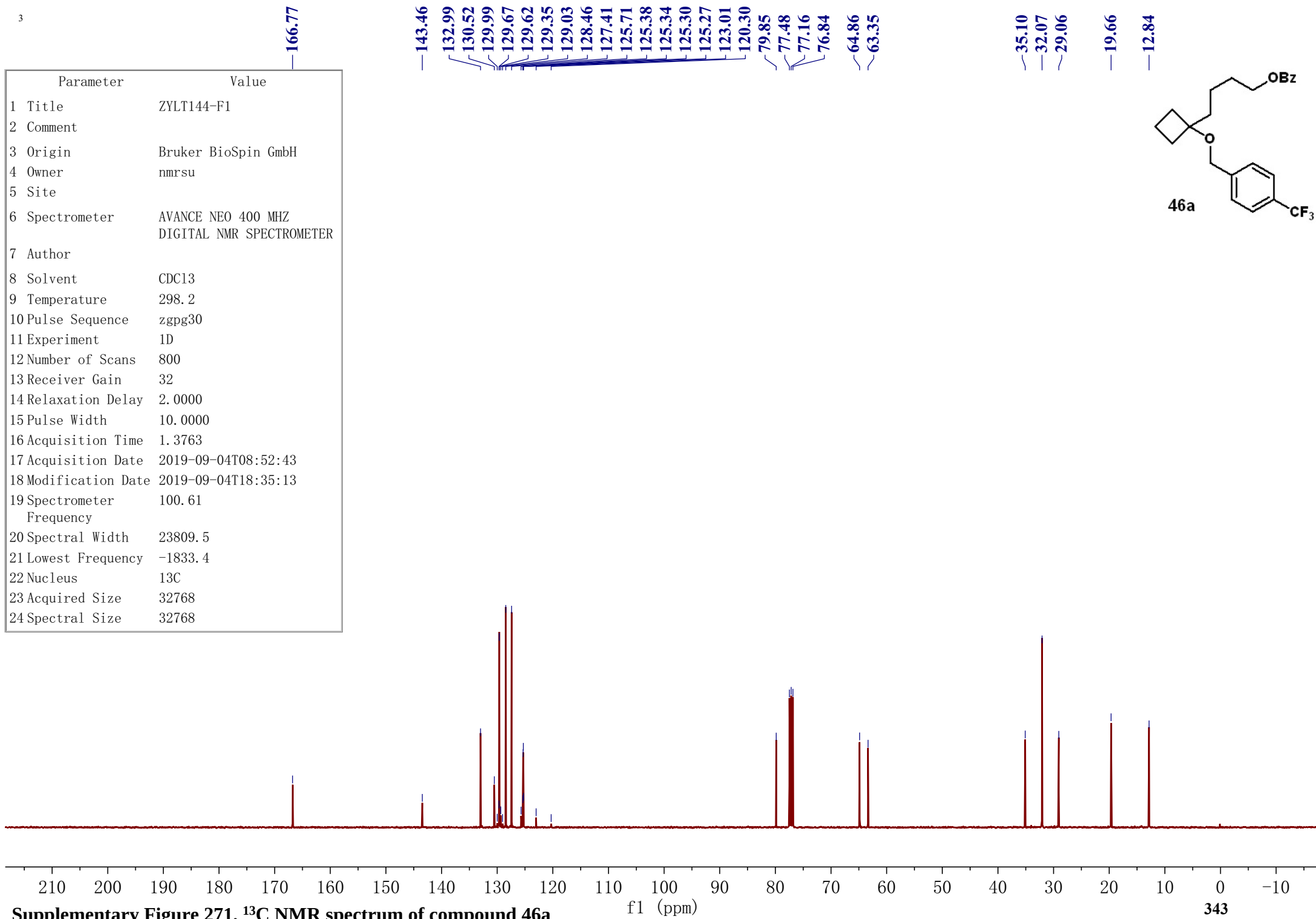
Supplementary Figure 269. ¹⁹F NMR spectrum of compound L4

Parameter	Value
1 Title	ZYLT144-F
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	297.0
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	32
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2019-09-04T00:20:38
18 Modification Date	2019-09-04T18:35:00
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1637.7
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536



Supplementary Figure 270. ¹H NMR spectrum of compound 46a

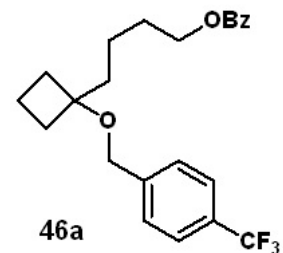
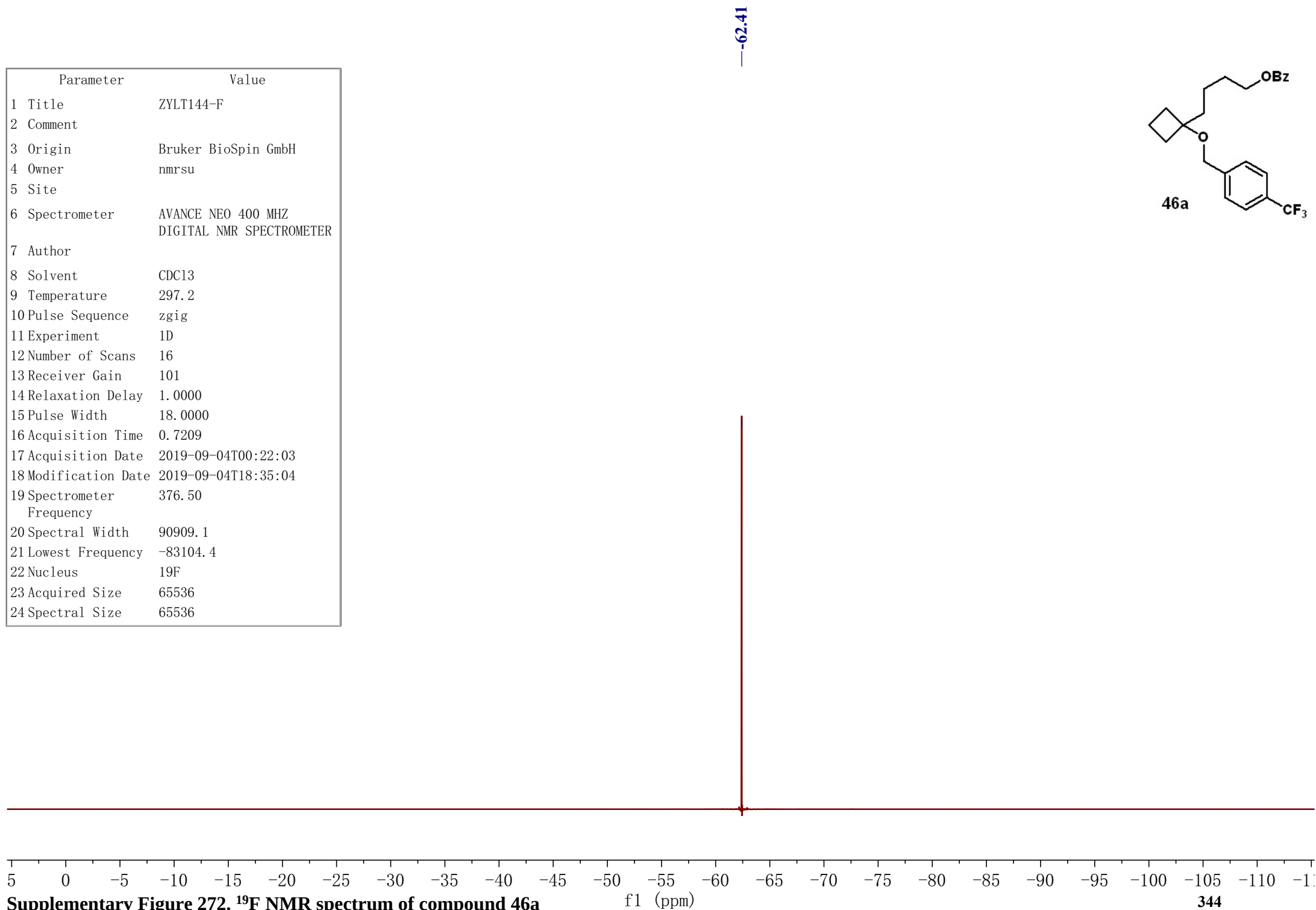
f1 (ppm)

Supplementary Figure 271. ¹³C NMR spectrum of compound 46a

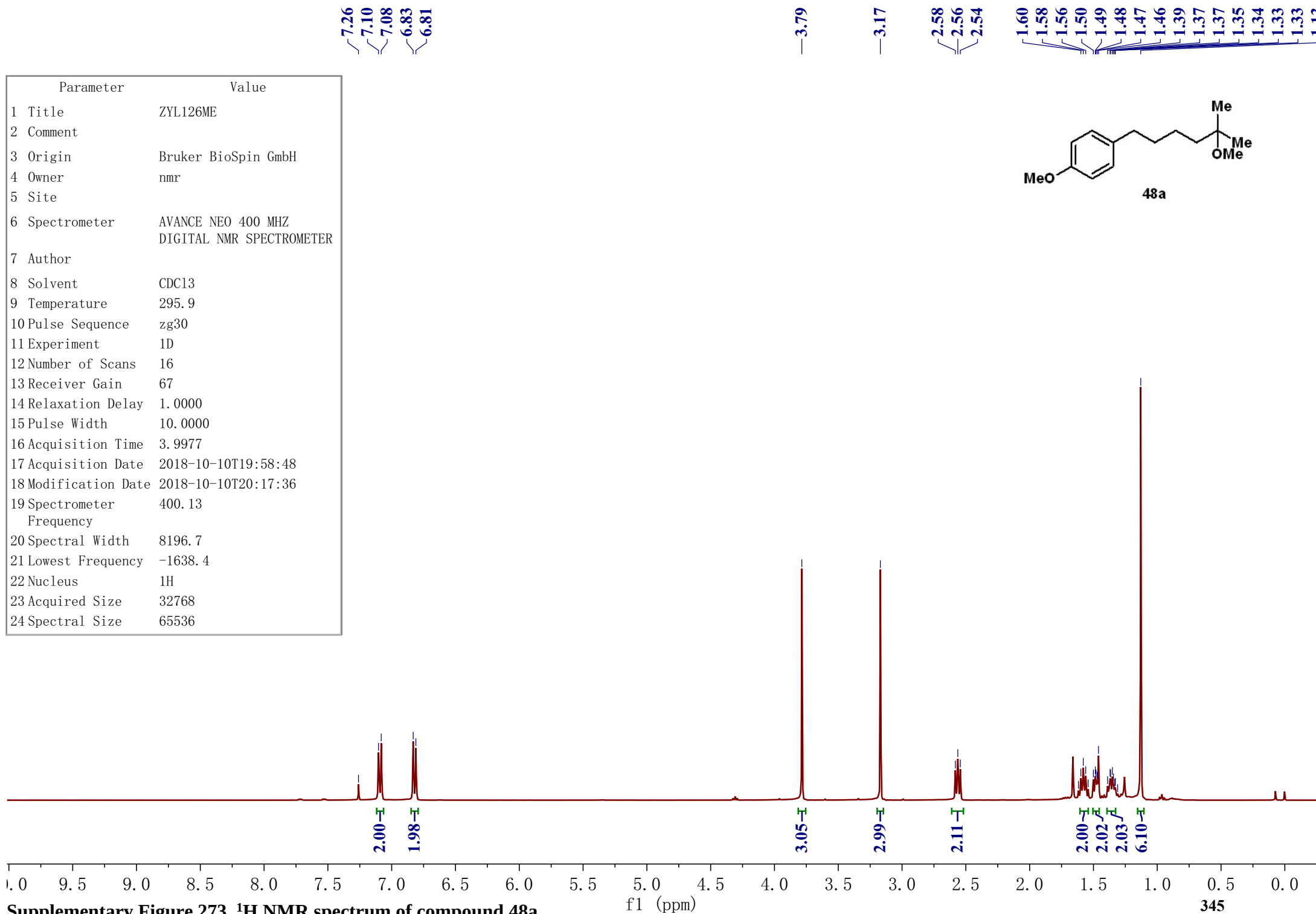
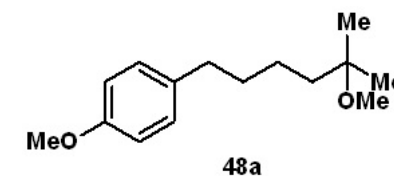
f1 (ppm)

343

Parameter	Value
1 Title	ZYLT144-F
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmrsu
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	297.2
10 Pulse Sequence	zgig
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	101
14 Relaxation Delay	1.0000
15 Pulse Width	18.0000
16 Acquisition Time	0.7209
17 Acquisition Date	2019-09-04T00:22:03
18 Modification Date	2019-09-04T18:35:04
19 Spectrometer Frequency	376.50
20 Spectral Width	90909.1
21 Lowest Frequency	-83104.4
22 Nucleus	¹⁹ F
23 Acquired Size	65536
24 Spectral Size	65536



Parameter	Value
1 Title	ZYL126ME
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	AVANCE NEO 400 MHZ DIGITAL NMR SPECTROMETER
7 Author	
8 Solvent	CDC13
9 Temperature	295.9
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	67
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	3.9977
17 Acquisition Date	2018-10-10T19:58:48
18 Modification Date	2018-10-10T20:17:36
19 Spectrometer	400.13
Frequency	
20 Spectral Width	8196.7
21 Lowest Frequency	-1638.4
22 Nucleus	¹ H
23 Acquired Size	32768
24 Spectral Size	65536



Supplementary Figure 273. ¹H NMR spectrum of compound 48a

