
Supplementary information

**Electrophotocatalytic oxygenation of
multiple adjacent C–H bonds**

In the format provided by the
authors and unedited

Supporting Information for

**Electrophotocatalytic Oxygenation of
Multiple Adjacent C–H Bonds**

Tao Shen¹⁻³, Yi-Lun Li³, Ke-Yin Ye,^{3*} and Tristan H. Lambert^{1*}

¹Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
14850

²Frontiers Science Center for Transformative Molecules, School of Chemistry and
Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

³ Key Laboratory of Molecule Synthesis and Function Discovery (Fujian Province
University), College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China.

*Correspondence to: Tristan.lambert@cornell.edu

1. General Information	S2
1.1 Analytic methods	S2
1.2 Reagents	S2
2. Experimental Section	S3
2.1 Reaction set up and experimental procedures	S3-9
2.2 Troubleshooting: Frequently asked questions	S10-11
2.3 Preparation of new starting materials	S12-17
2.4 Optimization of the reaction conditions	S18-19
2.5 Mechanistic studies	S19-36
2.6 Unsuccessful and challenging substrates	S37
2.7 Attempted use of traditional oxidants	S38-41
2.8 Characterization of new compounds	S42-81
3. NMR Spectra	S82-353
4. X-ray Data Analysis	S354-357
5. References	S358

1. General Information

1.1 Analytic methods

^1H NMR, ^{13}C NMR data were obtained on AVANCE III Bruker 400 MHz or JEOL 500 MHz nuclear resonance spectrometers unless otherwise noted. ^1H NMR chemical shifts (in ppm) were referenced to CHCl_3 ($\delta = 7.26$ ppm) in CDCl_3 , DMSO ($\delta = 2.50$ ppm) in DMSO-d_6 , MeOH ($\delta = 3.31$ ppm) in CD_3OD , or as an internal standard. The data of ^1H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constant (J values) in Hz and integration. ^{13}C -NMR spectra were obtained by the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.16$ ppm), DMSO-d_6 ($\delta = 39.52$ ppm), CD_3OD (49.00 ppm). Flash chromatography was performed using 300-400 mesh silica gel with the indicated eluent according to standard techniques. Thin-layer chromatography (TLC) was conducted with silica gel 60 F₂₅₄ pre-coated plates (0.25 mm) and visualized with UV and phosphomolybdic acid unless otherwise noted. Analysis of crude reaction mixtures was performed on a SHIMADZU GC-MS-QP2010 SE system.

The mass spectral (MS) data were obtained on a Thermo Fisher Scientific™ Exactive™ Plus (EMR) Orbitrap LCMS.

1.2 Reagents

All commercially available compounds were purchased from Energy Chemical, Innochem, TCI, Adamas, Alfa-Aesar. All the solvents and all the other reagents were directly used from purchased without any further purification unless otherwise specified.

2. Experimental Section

2.1 Graphical depiction of the electrophotocatalytic oxygenation of multiple contiguous C–H bonds

Materials used for set-up:

Woods clamp lamp light with aluminum reflector (12 inch). Compact fluorescent light bulb (5000K daylight, 23W).

Anode set-up: A carbon cloth (CeTech WOS1002, 15 mm × 15 mm × 0.3 mm) connected with PT-3 electrode clamp purchased from Gaoss Union.

Cathode set-up: A platinum plate (99.99%, 15 mm × 15 mm × 0.3 mm) was connected with PT-1 electrode clamp purchased from Gaoss Union.



Fig. S1 Step 1: Materials used for undivided cell set-up.

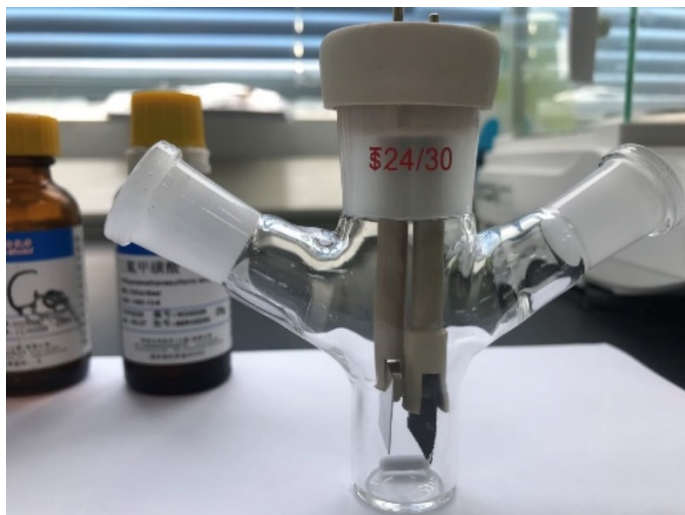


Fig. S2 Step 2: Set-up for the undivided cell.



Fig. S3 Step 3: $\text{TAC}^+\text{ClO}_4^-$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (113.0 mg, 0.52 mmol, 0.1 M), *n*-butylbenzene **S8** (40.2 mg, 0.3 mmol), added to the cell.

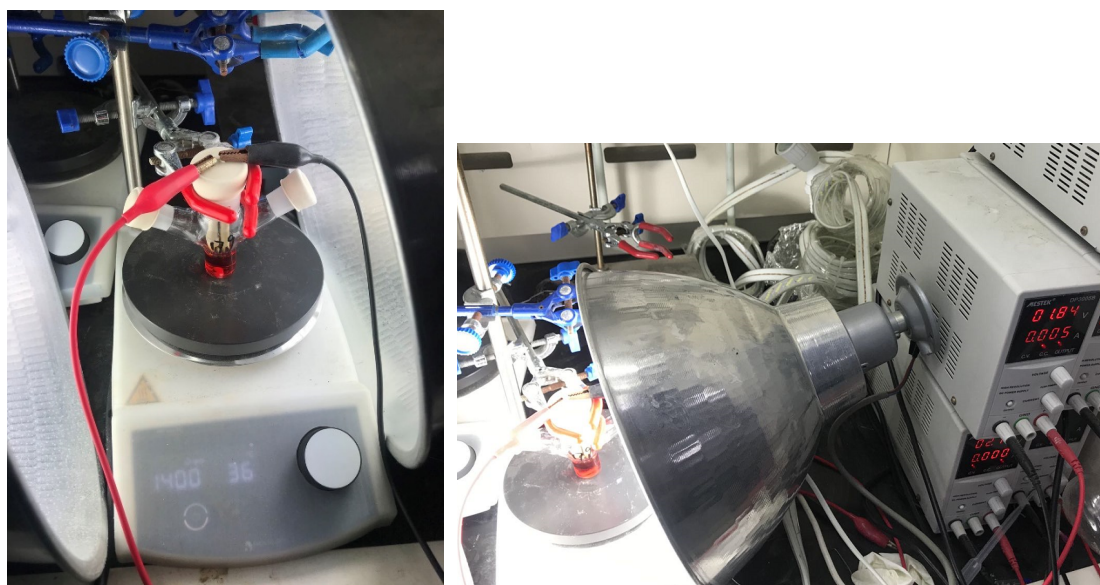


Fig. S4 Step 4: Electrolysis experiments were performed using MESTEK DC power supply. Set up the cell with constant current of 5 mA for 10 hours.

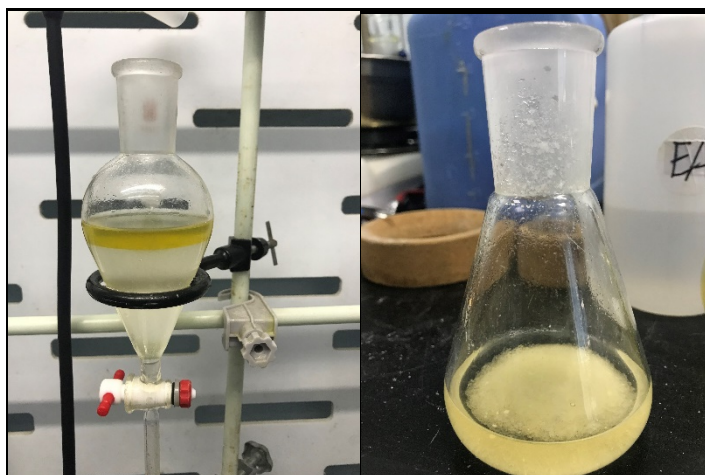


Fig. S5 Step 5: Left: dilute with EtOAc (20 mL) and washed with sat. Na_2CO_3 (aq). Right: dried over Na_2SO_4 and filtered.

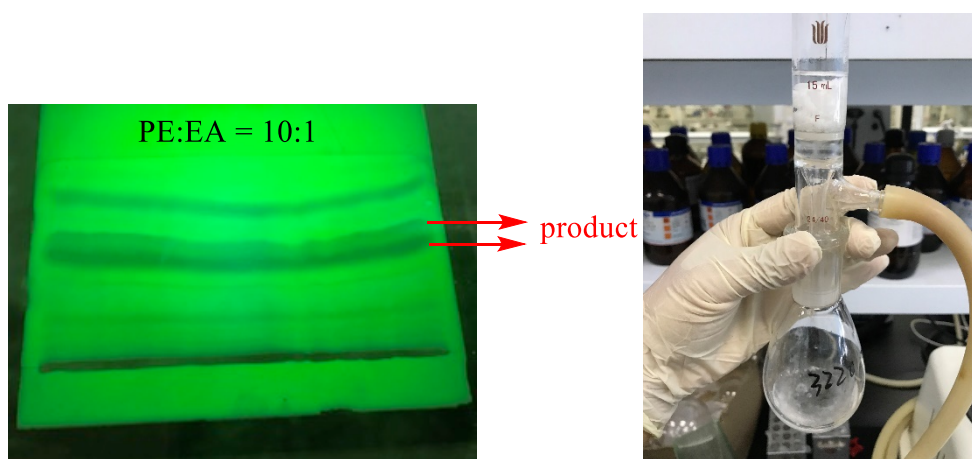


Fig. S6 Step 6: Purified by preparative thin-layer chromatography (PTLC) (eluent: petroleum ether:ethyl acetate = 10:1), note that both bands should be collected.



Fig. S7 Weight of product **8'** (55.5 mg, 74% yield). Pure product is a colorless oil.

Direct synthesis of vicinal diols after hydrolysis:

Diols were obtained followed by hydrolysis of crude mixture using saturated Na_2CO_3 (aq.) (10 mL) and MeOH (10 mL) at RT for 10 h.

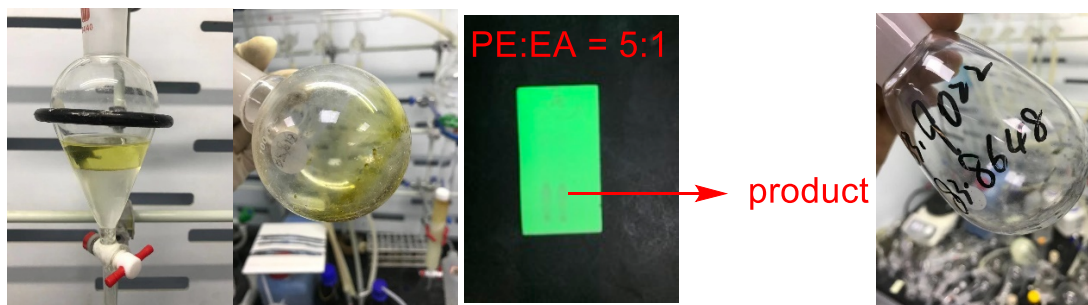
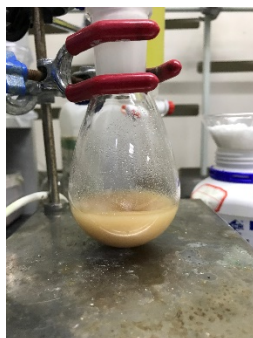
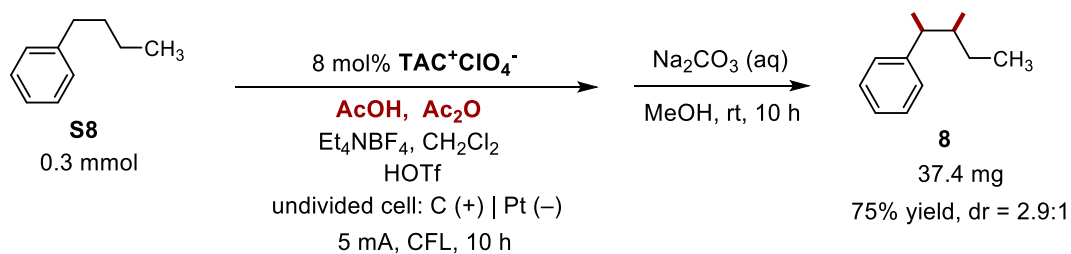


Fig. S8 Hydrolysis after *EPC* reaction with Na_2CO_3 (aq.)/MeOH

For gram scale reaction (e.g. 10 mmol for Celestolide):

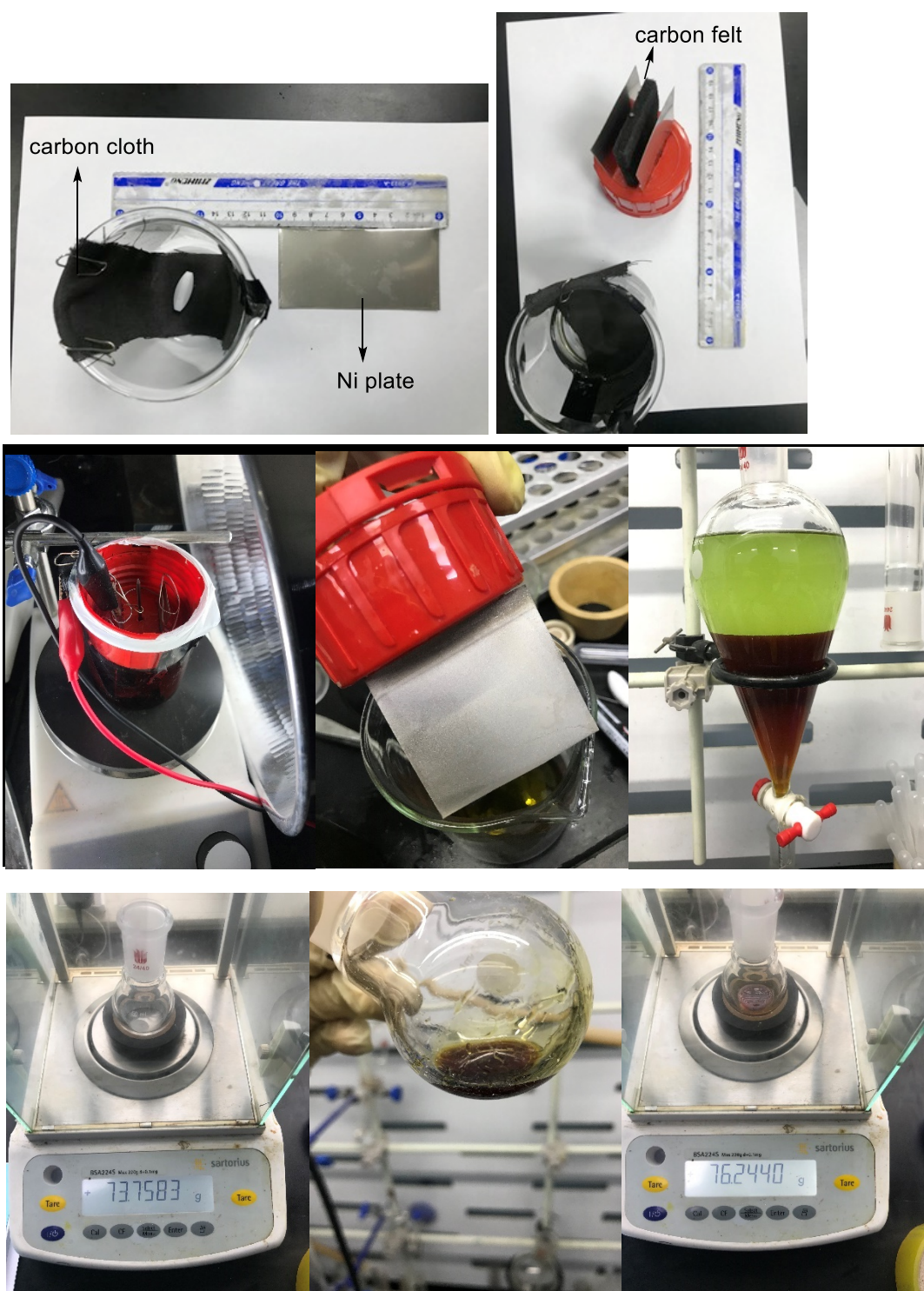


Fig. S9 Gram scale reaction set up

Experimental procedures

Typical procedure for dioxygenation products:

Condition A: For primary alkylbenzenes, an oven-dried undivided cell as described above was equipped with a stir bar. To the cell was added $\text{TAC}^+\text{ClO}_4^-$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (113.0 mg, 0.52 mmol, 0.1 M), HOAc (3.5 mL), Ac_2O (0.5 mL), *n*-butylbenzene **S8** (40.2 mg, 0.3 mmol), and DCM (1.0 mL). The mixture was stirred for 1 min, and then HOTf (200 μL) was carefully added. The cell was sealed using a rubber septum and parafilm and was backfilled with N_2 atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for the specified amount of time, the highest E_{cell} was set at 3.0 V. The system was cooled by a fan throughout the duration of the reaction. After completion of the reaction as monitored by GC-MS (usually 10-15 h), the reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3 $\times$ 5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3 $\times$ 15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . Following concentration in vacuo, the crude product was purified by preparative thin-layer chromatography (PTLC) (eluent: petroleum ether:ethyl acetate = 10:1) to afford 55.5 mg (74% yield) of **8'** as a colorless oil. In some cases, diols were obtained by subjecting the crude residue to a mixture of saturated Na_2CO_3 (aq.) (10 mL) and MeOH (10 mL) at RT for 10 h.

Condition B: For secondary alkylbenzenes, an oven-dried undivided cell as described above was equipped with a stir bar. To the cell was added $\text{TAC}^+\text{ClO}_4^-$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (113 mg, 0.53 mmol, 0.1 M), HOAc (3.5 mL), Ac_2O (0.5 mL), cumene **S31** (36.0 mg, 0.3 mmol), DCM (1.0 mL), and TFA (300 μL). The cell was sealed using a rubber septum and parafilm and was backfilled with N_2 atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for 36 h, the highest E_{cell} was set at 3.5 V. The system was cooled by a fan throughout the duration of the reaction. After completion of the reaction as monitored by GC-MS (usually 36 h), the reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3 $\times$ 5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3 $\times$ 15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . Following concentration in vacuo, the crude product was purified by preparative thin-layer chromatography (PTLC) (eluent: petroleum ether:ethyl acetate = 10:1) to afford 51.0 mg (72% yield) of **31** as a colorless oil. In some cases, diols were obtained by subjecting the crude residue to a mixture of saturated Na_2CO_3 (aq.) (10 mL) and MeOH (10 mL) at RT for 10 h.

Typical procedure for trioxygenation products:

Condition A: An oven-dried undivided cell as described above was equipped with a stir bar. To the cell was added $\text{TAC}^+\text{ClO}_4^-$ (11.3 mg, 0.024 mmol), Et_4NBF_4 (113.0 mg, 0.52 mmol, 0.1 M), HOAc (3.5 mL), Ac_2O (0.5 mL), cumene **S31** (40.2 mg, 0.3 mmol), and DCM (1.0 mL). The mixture was stirred for 1 min, and then HOTf (200 μL) was carefully added. The cell was sealed using a rubber septum and parafilm and was backfilled with N_2 atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for the

specified amount of time, the highest E_{cell} was set at 3.0 V. The system was cooled by a fan throughout the duration of the reaction. After completion of the reaction as monitored by GC-MS (usually 12-15 h), the reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3×5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3×15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . Following concentration in vacuo, the crude product was purified by preparative thin-layer chromatography (PTLC) (eluent: petroleum ether:ethyl acetate = 5:1) to afford 53.8 mg (61% yield) of **50** as a colorless oil. In some case, triols were obtained followed by subjecting the crude residue to a mixture of saturated Na_2CO_3 (aq.) (10 mL) and MeOH (10 mL) at RT for 10 h.

Typical procedure for dioxygenation and trioxygenation of cyclic and linear amine derivatives:

Condition A: An oven-dried undivided cell as described above was equipped with a stir bar. To the cell was added $\text{TAC}^+\text{ClO}_4^-$ (14.1 mg, 0.03 mmol), Et_4NBF_4 (113.0 mg, 0.52 mmol, 0.1 M), HOAc (3.5 mL), Ac_2O (0.5 mL), 2,2,2-trifluoro-1-(4-methylpiperidin-1-yl)ethan-1-one **S80** (58.5 mg, 0.3 mmol), and DCM (1.0 mL). The mixture was stirred for 1 min, and then HOTf (200 μL) was carefully added. The cell was sealed using a rubber septum and parafilm and was backfilled with N_2 atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for the specified amount of time, the highest E_{cell} was set at 3.5 V. The system was cooled by a fan throughout the duration of the reaction. After completion of the reaction as monitored by GC-MS (usually 12-18 h), the reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3×5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3×15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . Following concentration in vacuo, the crude product was purified by preparative thin-layer chromatography (PTLC) (eluent: petroleum ether:ethyl acetate = 5:1) to afford 39.8 mg (36% yield) of **80** as a light yellow oil. Note: typically these products exist as a mixture of rotamers due restricted rotation about the amide bond, which complicates the ^1H NMR spectra.

Typical procedure for gram-scale reaction

Condition C: An oven-dried 250 mL baker as described above (see **Fig. S9**) was equipped with a stir bar. To the beaker was added Celestolide (2.44 g, 10 mmol), $\text{TAC}^+\text{ClO}_4^-$ (235 mg, 0.5 mmol), Et_4NBF_4 (3.8 g, 0.1 M), HOAc (120 mL), Ac_2O (12 mL), and DCM (40 mL). The mixture was stirred for 1 min, and then HOTf (6 mL) was carefully added. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 50 mA for 48 h. The system was cooled by a fan throughout the duration of the reaction. The reaction mixture was poured into 300 mL water, the carbon cloth anode was washed with DCM (3×10 mL). The aqueous layer was separated and extracted with DCM (3×100 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . Following concentration in vacuo, the crude product was purified by flash chromatography (eluent: petroleum ether:ethyl acetate = 5:1) to afford 2.5 g (69% yield) of **91** as a yellow-brown oil.

2.2 Troubleshooting: Frequently Asked Questions

Question 1:

Are there any precautions that need to be taken for performing this reaction?

Answer: All reagents were used without any special handling. The reactions were performed under an atmosphere of N₂. Usually, the final E_{cell} was approximately 2.5-2.7 V. After the reaction, care should be taken when removing the septum in case of pressure build up from H₂ gas generation. *Carbon felt did not work well in this reaction.* Finally, the reaction was kept cool using a fan.

Question 2:

Is this reaction sensitive to water?

Answer: This reaction has been found to be not very sensitive to water. Usually, commercial acetic acid and acetic anhydride were used directly without any purification. Anhydrous electrolyte was used. However, we found that HOTf was very hygroscopic, and thus it is necessary to keep it dry. If the yield is low, using HOTf, Et₄NBF₄, acetic acid and acetic anhydride from a newly opened container might be helpful.

Question 3:

Is this reaction sensitive to air?

Answer: This reaction has been found to not be sensitive to air, and thus no rigorous degassing is required. We tested the model reaction without degassing, and the yield was only slightly decreased. However, leaving the reaction open to air results in solvent evaporation, and in some cases the air may be too wet, which may reduce the yield. Thus, we recommend performing this reaction under an inert atmosphere.

Question 4:

Is stirring crucial for this reaction?

Answer: Yes, the dioxygenation reaction is heterogeneous, and thus stirring is critical. The preferred stirring rate is from 1000 to 1400 rpm.

Question 5:

What are the common byproducts of this reaction?

Answer: When monitored by GC-MS, substrates, ketone, benzylic ester, or α -ketal ester products could be observed in small amount as byproducts. In cases where the yield of product is low, degradation of substrates to unidentified materials may be involved.

Question 6:

How do I monitor the reaction?

Answer: In general, 12-15 h is enough for high conversion (>90%) for dioxygenation of unbranched benzenes on a 0.3 mmol scale. Reaction monitoring can be done by GC-MS or by TLC analysis with UV visualization (254 nm) of disappearance of the starting material for most substrates. *Note that the complete disappearance of substrates does not mean that the reaction has necessarily finished. In most case the full conversion of the substrates into a monobenzylic ester intermediate was completed quickly (4-6 h); however, at that time the dioxygenation product is typically present*

in significantly lower quantities. Stopping the reaction when most of the monobenzyllic ester intermediate has disappeared (as determined by GC-MS) is usually optimal.

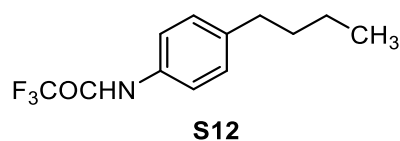
Question 7:

How can the electrodes be cleaned after the reaction?

Answer: The carbon cloth anode should be replaced for each reaction. The Pt cathode was washed with water, immersed in concentrated sulfuric acid for 1 h (particularly if it has turned black), washed again with deionized water, and dried in the oven.

2.3 Preparation and characterization of newly reported starting

materials

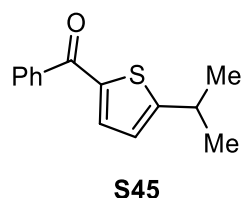


N-(4-butylphenyl)-2,2,2-trifluoroacetamide: To a 100 mL round-bottom flask charged with DCM (50 mL) and cooled to 0 °C was added 4-butylaniline (1.49 g, 10.0 mmol, 1.0 equiv.) and Et₃N (2.02 g, 20 mmol, 2.0 equiv.). Trifluoroacetic anhydride (2.52 g, 12 mmol, 1.2 equiv.) was then added dropwise. The mixture was stirred at room temperature for 4 h, partitioned between water (50 mL) and CH₂Cl₂ (50 mL), and then quenched with a saturated solution of sodium carbonate (10 mL). The organic layer was isolated, and the aqueous layer was extracted with CH₂Cl₂ (3x50 mL). The organic layers were combined, dried over MgSO₄, and concentrated via rotary evaporation. The crude material was purified by flash chromatography (10% EtOAc/Hex) to afford the product **S12** as a light yellow solid (2.20 g, 9.0 mmol, 90% yield).

¹H NMR (CDCl₃, 500 MHz): 7.97 (brs, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 1.61-1.55 (m, 2H), 1.36-1.32 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz): 155.0 (q, *J* = 36.8 Hz), 141.5, 132.8, 129.3, 120.7, 115.9 (q, *J* = 286.8 Hz), 35.2, 33.6, 22.4, 14.0.

HRMS: calc. for C₁₂H₁₄F₃NNaO⁺ (*M*+Na)⁺, 268.0920, found, 268.0923.

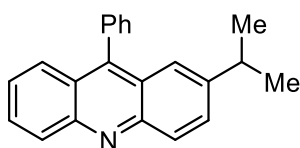


(5-isopropylthiophen-2-yl)(phenyl)methanone: Following a modified procedure from literature⁴⁴, a dry 10-mL Schlenk tube containing a magnetic stirbar was charged with Pd(PPh₃)₄ (10 mol%, 119 mg, 0.2 mmol), DPPP (14 mol%, 112 mg, 0.28 mmol) and dry PhCF₃ (5.0 mL). After stirring at room temperature for 10 minutes, phenyl(thiophen-2-yl)methanone (376 mg, 1 equiv, 2.0 mmol), Cs₂CO₃ (2 equiv, 1.0 mmol, 326 mg) and 2-iodopropane (1 equiv, 340 mg, 2 mmol) were added sequentially. The tube was capped tightly and the mixture was vigorously stirred in a pre-warmed 110 °C oil bath. After 72 h, the reaction mixture was concentrated via rotary evaporation. The crude material was purified by flash chromatography (5% EtOAc/Hex) to afford the product **S45** as a light yellow solid (128.8 mg, 28% yield).

¹H NMR (CDCl₃, 500 MHz): 7.83 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.55-7.46 (m, 3H), 6.87 (d, *J* = 4.0 Hz, 1H), 3.26-3.20 (m, 1H), 1.38 (d, *J* = 7.0 Hz, 6H).

¹³C NMR (CDCl₃, 125 MHz): 188.2, 163.9, 140.6, 138.4, 135.5, 132.0, 129.2, 128.4, 123.7, 30.8, 24.6.

HRMS: calc. for C₁₄H₁₅OS⁺ (*M*+H)⁺, 231.0838, found, 231.0833.



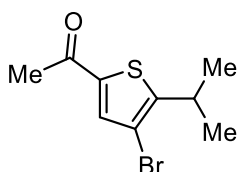
S49

2-isopropyl-9-phenylacridine: This substrate was prepared from (2-aminophenyl)(phenyl)methanone and 4-isopropylcyclohexan-1-one following the procedure of literature.⁴⁵

¹H NMR (CDCl₃, 500 MHz): 8.27-8.23 (m, 2H), 7.74-7.66 (m, 3H), 7.62-7.57 (m, 3H), 7.46-7.43 (m, 3H), 7.40-7.37 (m, 1H), 3.02-2.96 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 6H)

¹³C NMR (CDCl₃, 125 MHz): 148.4, 148.2, 146.4, 146.0, 136.2, 130.5, 130.2, 129.7, 129.6, 129.5, 128.5, 128.3, 126.8, 125.5, 125.4, 125.2, 122.3, 34.4, 23.6.

HRMS: calc. for C₂₂H₂₀N⁺ (M+H)⁺, 298.1590, found, 298.1586.



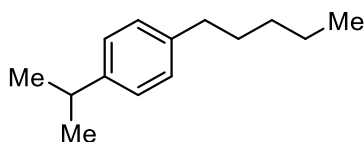
S73

1-(4-bromo-5-isopropylthiophen-2-yl)ethan-1-one: To a 100 mL round-bottom flask charged with DCM (50 mL) and cooled to -20 °C was added 1-(5-isopropylthiophen-2-yl)ethan-1-one (168 mg, 1.0 mmol, 1.0 equiv.) which was prepared from 2-isopropylthiophene and acetic anhydride. Br₂ (192 mg, 1.2 mmol, 1.2 equiv.) was then added dropwise. The mixture was stirred at 0 °C for 2 h, partitioned between water (10 mL) and CH₂Cl₂ (10 mL), and then quenched with a saturated solution of sodium thiosulfate (10 mL). The organic layer was isolated, and the aqueous layer was extracted with CH₂Cl₂ (3x10 mL). The organic layers were combined, dried over MgSO₄, and concentrated via rotary evaporation. The crude material was purified by flash chromatography (5% EtOAc/Hex) to afford the product **S73** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.51 (s, 1H), 3.36-3.31 (m, 1H), 2.51 (s, 3H), 1.32 (d, *J* = 6.5 Hz, 6H).

¹³C NMR (CDCl₃, 125 MHz): 189.8, 157.3, 140.4, 135.2, 108.1, 30.6, 26.4, 23.6;

HRMS: calc. for C₉H₁₂BrOS⁺ (M+H)⁺, 246.9787, found, 246.9783.



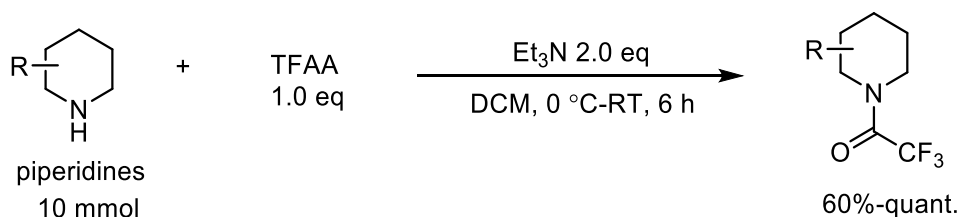
S99

1-isopropyl-4-pentylbenzene: This substrate was prepared from 1-(4-pentylphenyl)ethan-1-one by Wittig reaction followed by reduction with hydrogen catalyzed by Pd/C.

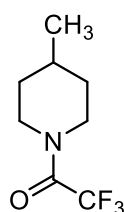
¹H NMR (CDCl₃, 500 MHz): 7.14-7.08 (m, 4H), 2.89-2.83 (m, 1H), 2.56 (t, *J* = 8.0 Hz, 2H), 1.63-1.57 (m, 2H), 1.36-1.32 (m, 4H), 1.24-1.22 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz): 146.2, 140.4, 128.4, 126.3, 35.7, 33.9, 31.8, 31.4, 24.3, 22.7, 14.2.

HRMS: calc. for $C_{14}H_{23}^+$ ($M+H$) $^+$, 191.1794, found, 191.1791.



The piperidines substrates are synthesized following the same procedure for synthesis of *N*-(4-butylphenyl)-2,2,2-trifluoroacetamide **S12**.



S80

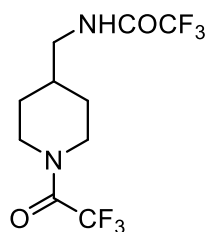
2,2,2-trifluoro-1-(4-methylpiperidin-1-yl)ethan-1-one

1H NMR ($CDCl_3$, 500 MHz): 4.44-4.42 (m, 1H), 3.93-3.90 (m, 1H), 3.06 (t, J = 12.5 Hz, 1H), 2.70 (t, J = 13.0 Hz, 1H), 1.73-1.62 (m, 3H), 1.19-1.11 (m, 2H), 1.09-0.91 (m, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 155.3 (q, J = 35.1 Hz), 116.7 (q, J = 286.1 Hz), 46.1 (q, J = 3.5 Hz), 44.0, 34.4, 33.5, 30.8, 21.4.

^{19}F NMR ($CDCl_3$, 471 MHz): -68.9.

HRMS: calc. for $C_8H_{13}F_3NO^+$ ($M+H$) $^+$, 196.0944, found, 196.0940.



S81

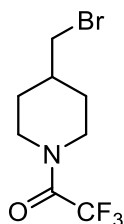
2,2,2-trifluoro-*N*-((1-(2,2,2-trifluoroacetyl)piperidin-4-yl)methyl)acetamide

1H NMR ($CDCl_3$, 500 MHz): 7.51 (brs, 1H), 4.49-4.47 (m, 1H), 4.01-3.98 (m, 1H), 3.31-3.18 (m, 2H), 3.10 (t, J = 12.0 Hz, 1H), 2.74 (t, J = 12.5 Hz, 1H), 1.95-1.88 (m, 1H), 1.83-1.80 (m, 2H), 1.23-1.88 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): 157.9 (q, J = 36.4 Hz), 155.6 (q, J = 36.0 Hz), 116.6 (q, J = 286.0 Hz), 116.0 (q, J = 285.8 Hz), 45.6, 44.7, 43.4, 35.6, 30.0, 29.1.

^{19}F NMR ($CDCl_3$, 471 MHz): -68.9, -75.8.

HRMS: calc. for $C_{10}H_{13}F_6N_2O_2^+$ ($M+H$) $^+$, 307.0876, found, 307.0880.



S82

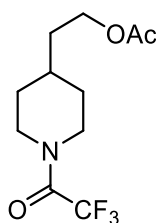
1-(4-(bromomethyl)piperidin-1-yl)-2,2,2-trifluoroethan-1-one

^1H NMR (CDCl_3 , 500 MHz): 4.54-4.50 (m, 1H), 4.01-3.97 (m, 1H), 3.29-3.24 (m, 2H), 3.11-3.06 (m, 1H), 2.72 (t, $J = 12.5$ Hz, 1H), 1.98-1.87 (m, 3H), 1.31-1.21 (m, 2H).

^{13}C NMR (CDCl_3 , 125 MHz): 155.3 (q, $J = 35.2$ Hz), 116.6 (q, $J = 286.4$ Hz), 45.5, 43.3, 38.1, 37.8, 31.2, 30.3.

^{19}F NMR (CDCl_3 , 471 MHz): -68.9.

HRMS: calc. for $\text{C}_8\text{H}_{12}\text{BrF}_3\text{NO}^+$ ($\text{M}+\text{H}$) $^+$, 274.0049, found, 274.0046.



S83

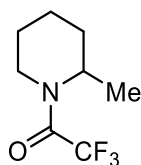
(1-(2,2,2-trifluoroacetyl)piperidin-4-yl)methyl acetate

^1H NMR (CDCl_3 , 500 MHz): 4.52-4.48 (m, 1H), 4.10 (t, $J = 6.5$ Hz, 2H), 3.99-3.96 (m, 1H), 3.12-3.06 (m, 1H), 2.76-2.70 (m, 1H), 2.03 (s, 3H), 1.83-1.80 (m, 2H), 1.71-1.65 (m, 1H), 1.61-1.57 (m, 2H), 1.24-1.18 (m, 2H).

^{13}C NMR (CDCl_3 , 125 MHz): 171.2, 155.4 (q, $J = 35.2$ Hz), 116.7 (q, $J = 286.2$ Hz), 61.9, 46.0 (q, $J = 3.6$ Hz), 43.8, 34.8, 32.9, 32.5, 31.5, 21.0.

^{19}F NMR (CDCl_3 , 471 MHz): -68.8.

HRMS: calc. for $\text{C}_{11}\text{H}_{17}\text{F}_3\text{NO}_3^+$ ($\text{M}+\text{H}$) $^+$, 268.1155, found, 268.1151.



S84

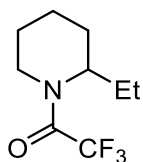
2,2,2-trifluoro-1-(2-methylpiperidin-1-yl)ethan-1-one

^1H NMR (CDCl_3 , 500 MHz): 4.79-4.35 (m, 1H), 4.26-3.73 (m, 1H), 3.22-2.83 (m, 1H), 1.74-1.57 (m, 5H), 1.49-1.39 (m, 1H), 1.30-1.19 (m, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 155.6 (q, $J = 34.5$ Hz), 155.5 (q, $J = 34.5$ Hz), 117.0 (q, $J = 287.1$ Hz), 116.8 (q, $J = 285.9$ Hz), 49.0, 46.2, 40.9, 38.0, 30.7, 29.6, 26.0, 25.4, 18.5, 16.8, 15.4.

^{19}F NMR (CDCl_3 , 471 MHz): -68.8, -69.0.

HRMS: calc. for $\text{C}_8\text{H}_{13}\text{F}_3\text{NO}^+$ ($\text{M}+\text{H}$) $^+$, 196.0944, found, 196.0939.



S85

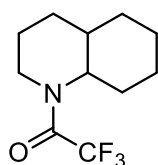
1-(2-ethylpiperidin-1-yl)-2,2,2-trifluoroethan-1-one

¹H NMR (CDCl₃, 500 MHz): 4.53-4.29 (m, 1H), 3.86-3.68 (m, 1H), 3.10-2.72 (m, 1H), 1.73-1.35 (m, 8H), 0.82-0.77 (m, 3H).

¹³C NMR (CDCl₃, 125 MHz): 155.9 (q, *J* = 39.7 Hz), 116.9 (q, *J* = 286.2 Hz), 116.8 (q, *J* = 286.4 Hz), 51.8, 41.0, 40.9, 38.3, 28.3, 27.7, 26.0, 25.2, 22.8, 22.1, 19.1, 18.5, 10.1.

¹⁹F NMR (CDCl₃, 471 MHz): -68.2, -68.8, -72.6.

HRMS: calc. for C₉H₁₅F₃NO⁺ (M+H)⁺, 210.1100, found, 210.1098.



S86

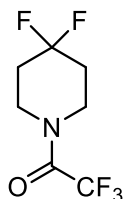
2,2,2-trifluoro-1-(octahydroquinolin-1(2H)-yl)ethan-1-one

¹H NMR (CDCl₃, 500 MHz): 3.56 (s, 1H), 3.37-3.29 (m, 2H), 2.11-2.08 (m, 1H), 1.81-1.53 (m, 7H), 1.41-1.18 (m, 3H), 1.14-0.98 (m, 2H).

¹³C NMR (CDCl₃, 125 MHz): 156.2 (q, *J* = 34.8 Hz), 116.5 (q, *J* = 286.4 Hz), 62.8, 39.7, 37.6, 32.7, 29.4, 25.9, 25.6, 25.3, 23.0.

¹⁹F NMR (CDCl₃, 471 MHz): -69.6.

HRMS: calc. for C₁₁H₁₇F₃NO⁺ (M+H)⁺, 236.1257, found, 236.1250.



S87

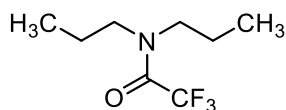
1-(4,4-difluoropiperidin-1-yl)-2,2,2-trifluoroethan-1-one

¹H NMR (CDCl₃, 500 MHz): 3.74-3.67 (m, 2H), 3.66-3.65 (m, 2H), 2.06-1.98 (m, 4H).

¹³C NMR (CDCl₃, 125 MHz): 155.6 (q, *J* = 35.9 Hz), 120.8 (t, *J* = 241.0 Hz), 116.4 (q, *J* = 286.8 Hz), 42.5, 40.5 (t, *J* = 5.5 Hz), 34.5 (t, *J* = 24.0 Hz), 33.5 (t, *J* = 24.0 Hz).

¹⁹F NMR (CDCl₃, 471 MHz): -69.1, -98.4.

HRMS: calc. for C₇H₉F₅NO⁺ (M+H)⁺, 218.0599, found, 218.0594.



S90

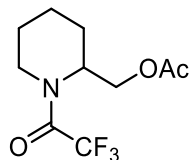
2,2,2-trifluoro-N,N-dipropylacetamide

¹H NMR (CDCl₃, 500 MHz): 3.31-3.25 (m, 4H), 1.63-1.54 (m, 4H), 0.88-0.85 (m, 6H).

¹³C NMR (CDCl₃, 125 MHz): 156.7 (q, *J* = 35.5 Hz), 116.7 (q, *J* = 286.1 Hz), 49.1 (q, *J* = 3.6 Hz), 48.5, 21.9, 20.1, 11.1, 10.8.

¹⁹F NMR (CDCl₃, 471 MHz): -68.9, -68.8.

HRMS: calc. for C₈H₁₅F₃NO⁺ (M+H)⁺, 198.1100, found, 198.1096.



104

(1-(2,2,2-trifluoroacetyl)piperidin-2-yl)methyl acetate

¹H NMR (CDCl₃, 500 MHz): 4.95-3.82 (m, 4H), 3.28-2.86 (m, 1H), 2.03-2.02 (m, 3H), 1.78-1.52 (m, 6H).

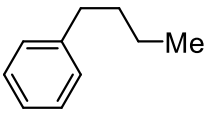
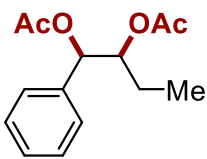
¹³C NMR (CDCl₃, 125 MHz): 170.7, 170.5, 156.5 (q, *J* = 34.4 Hz), 116.7 (q, *J* = 286.2 Hz), 116.6 (q, *J* = 286.1 Hz), 61.0, 60.8, 52.0, 48.9, 41.6, 38.7, 26.4, 25.5, 25.2, 25.0, 20.6, 19.2, 19.1.

¹⁹F NMR (CDCl₃, 471 MHz): -68.0, -68.9.

HRMS: calc. for C₁₀H₁₅F₃NO₃⁺ (M+H)⁺, 254.0999, found, 254.0994.

2.4 Optimization of the reaction conditions

Table S1. Optimization of reaction conditions with *n*-butylbenzene.^a

 S8 0.3 mmol 8 mol% TAC⁺ClO₄⁻ AcOH, Ac₂O Et₄NBF₄, CH₂Cl₂, HOTf divided cell: C (+) Pt (-) 5 mA, CFL, N₂, RT, 10 h  8' 74%, dr = 3.3:1	
Deviations	yield of 8'
none	78% (74%) ^b
TFA instead of HOTf	0% (87%) ^c
MeSO ₃ H instead of HOTf	11% (73%) ^c
without HOTf	0%
without Ac ₂ O	49%
LiClO ₄ instead of Et ₄ NBF ₄	54%
TBAPF ₆ instead of Et ₄ NBF ₄	58%
C felt as anode	33%
C cloth as cathode	46%
Fe as cathode	<5%
Ni as cathode	44%
Ni as cathode for 18 h	66%
under air	68%
without TAC	33%
without light	38%
without electricity	0%

^aReaction conditions: **S8** (0.3 mmol), TAC⁺ (0.024 mmol), Et₄NBF₄ (0.1 M), (HOAc:Ac₂O:DCM:HOTf = 3.5 mL:0.5 mL:1.0 mL:0.2 mL), carbon cloth anode, Pt cathode, under N₂, at RT, in an undivided cell with constant current of 5 mA for 10 h. Yields determined on NMR yield using CH₂Br₂ as internal standard.

^bIsolated yield. ^c Yield of benzylic monoester. TFA = trifluoroacetic acid, HOTf = trifluoromethanesulfonic acid.

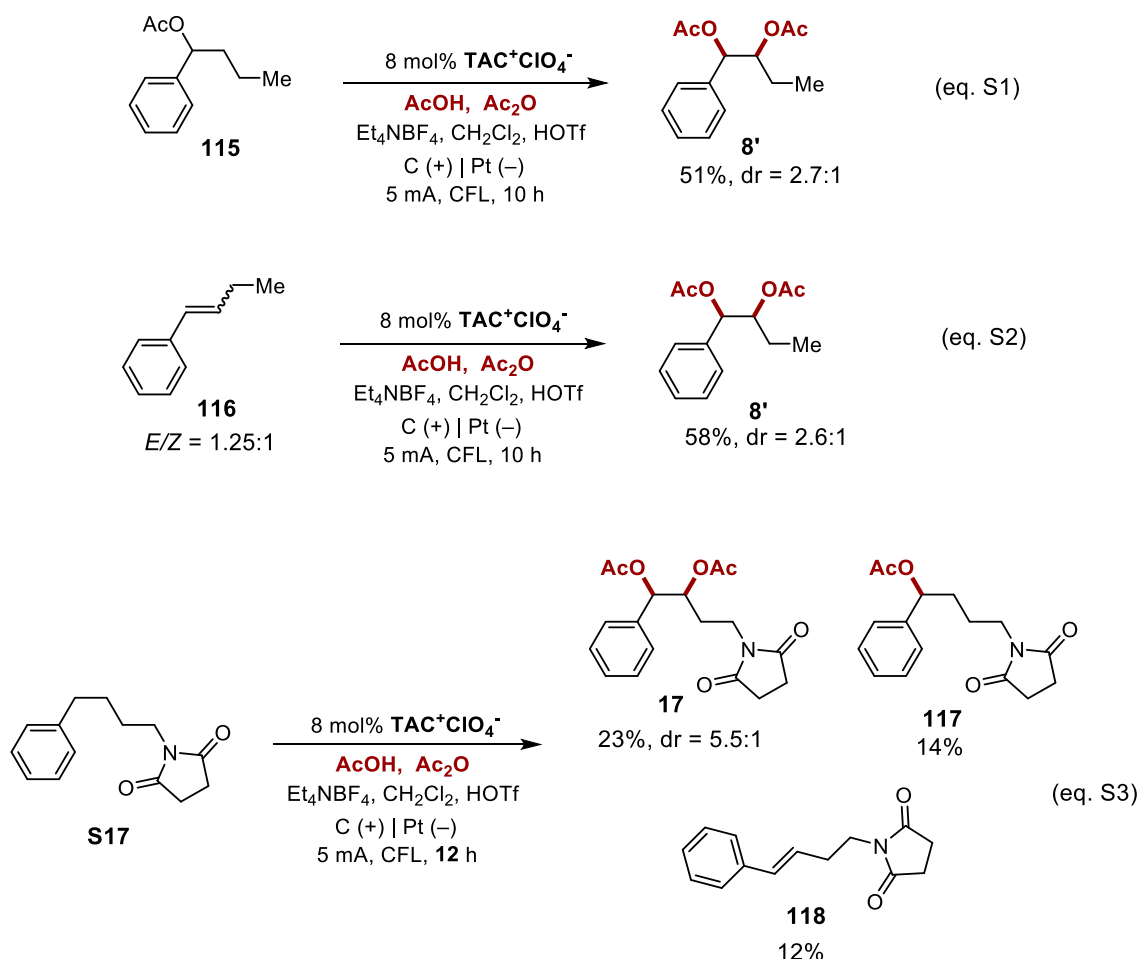
Typical reaction procedure as **Condition A**: an oven-dried undivided cell as described above was equipped with a stir bar. To the cell was added TAC⁺ClO₄⁻ (11.3 mg, 0.024 mmol), Et₄NBF₄ (113.0 mg, 0.52 mmol, 0.1 M), HOAc (3.5 mL), Ac₂O (0.5 mL), *n*-butylbenzene **S8** (40.2 mg, 0.3 mmol), and DCM (1.0 mL). The

mixture was stirred for 1 min, and then HOTf (200 μ L) was carefully added. The cell was sealed using a rubber septum and parafilm and was backfilled with N₂ atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for 10 h. The system was cooled by a fan throughout the duration of the reaction. The reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3 $\times$ 5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3 $\times$ 15 mL), and the combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. Following concentration in vacuo, the crude product was mixed with CH₂Br₂ (52.2 mg, 21.0 μ L) as an internal standard and CDCl₃ (1 mL) for the ¹H NMR experiment.

2.5 Mechanistic studies

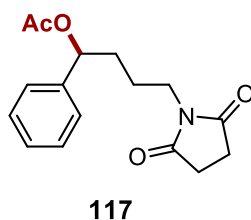
2.5.1 Verification of possible intermediates for dioxygenation of primary alkylbenzene.

Some possible intermediates were tested under the standard conditions.



Eq. S3: An oven-dried H-type cell was prepared as described above and equipped with a stir bar. To the anodic chamber were added 1-(4-phenylbutyl)pyrrolidine-2,5-dione (69.3 mg, 0.3 mmol) **S17**, TAC⁺ClO₄⁻ (11.3 mg, 0.024 mmol), Et₄NBF₄ (113.0 mg, 0.52 mmol, 0.1 M), HOAc (3.5 mL), Ac₂O (0.5 mL), DCM

(1.0 mL), and HOTf (200 μ L). The cell was sealed using a rubber septum and parafilm and was backfilled with N₂ atmosphere. The solution was then stirred at room temperature under irradiation, and electrolysis was initiated at a controlled current of 5 mA for 12 h. The system was cooled by a fan throughout the duration of the reaction. Then the reaction mixture was poured into a saturated sodium carbonate solution (ca. 20 mL). The carbon cloth anode was washed with EtOAc (3 $\times$ 5 mL) and these washes were added to the reaction mixture. The aqueous layer was separated and extracted with EtOAc (3 $\times$ 10 mL), and the combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. Following concentration in vacuo, the crude product was purified by PTLC (eluent: petroleum ether:ethyl acetate = 3:1) to afford 23.9 mg (23% yield) of **21** and 12.1 mg (14% yield) of 4-(2,5-dioxopyrrolidin-1-yl)-1-phenylbutyl acetate **117** and 8.2 mg (12% yield) of (*E*)-1-(4-phenylbut-3-en-1-yl)pyrrolidine-2,5-dione **118**.

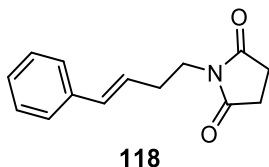


117: yellow oil;

¹H NMR (CDCl₃, 500 MHz): 7.35-7.28 (m, 5H), 5.73 (dd, *J* = 8.0 Hz, *J* = 6.0 Hz, 1H), 4.56-4.47 (m, 2H), 2.68 (s, 4H), 2.07 (s, 3H), 1.94-1.86 (m, 1H), 1.80-1.73 (m, 1H), 1.64-1.51 (m, 2H).

¹³C NMR (CDCl₃, 500 MHz): 177.4, 170.5, 140.3, 128.6, 128.2, 126.5, 75.4, 38.5, 33.7, 28.3, 23.9, 21.4.

HRMS: calc. for C₁₆H₂₀NO₄⁺ (*M*+H)⁺, 290.1387, found, 290.1390.



118: white solid;

¹H NMR (CDCl₃, 500 MHz): 7.33-7.19 (m, 5H), 6.40 (d, *J* = 15.5 Hz, 1H), 6.13-6.07 (m, 1H), 3.69-3.66 (m, 2H), 2.67 (s, 4H), 2.52-2.49 (m, 2H).

¹³C NMR (CDCl₃, 500 MHz): 177.4, 137.3, 132.7, 128.7, 127.5, 126.3, 126.1, 38.4, 31.4, 28.2.

HRMS: calc. for C₁₄H₁₆NO₂⁺ (*M*+H)⁺, 230.1176, found, 230.1176.

2.5.2 In situ NMR analysis for dioxygenation of alkylbenzene S8

This reaction proceeded without Ac_2O , albeit in lower yield (49%, see Table S1). In situ NMR analysis was performed using HOAc-d_4 as solvent.

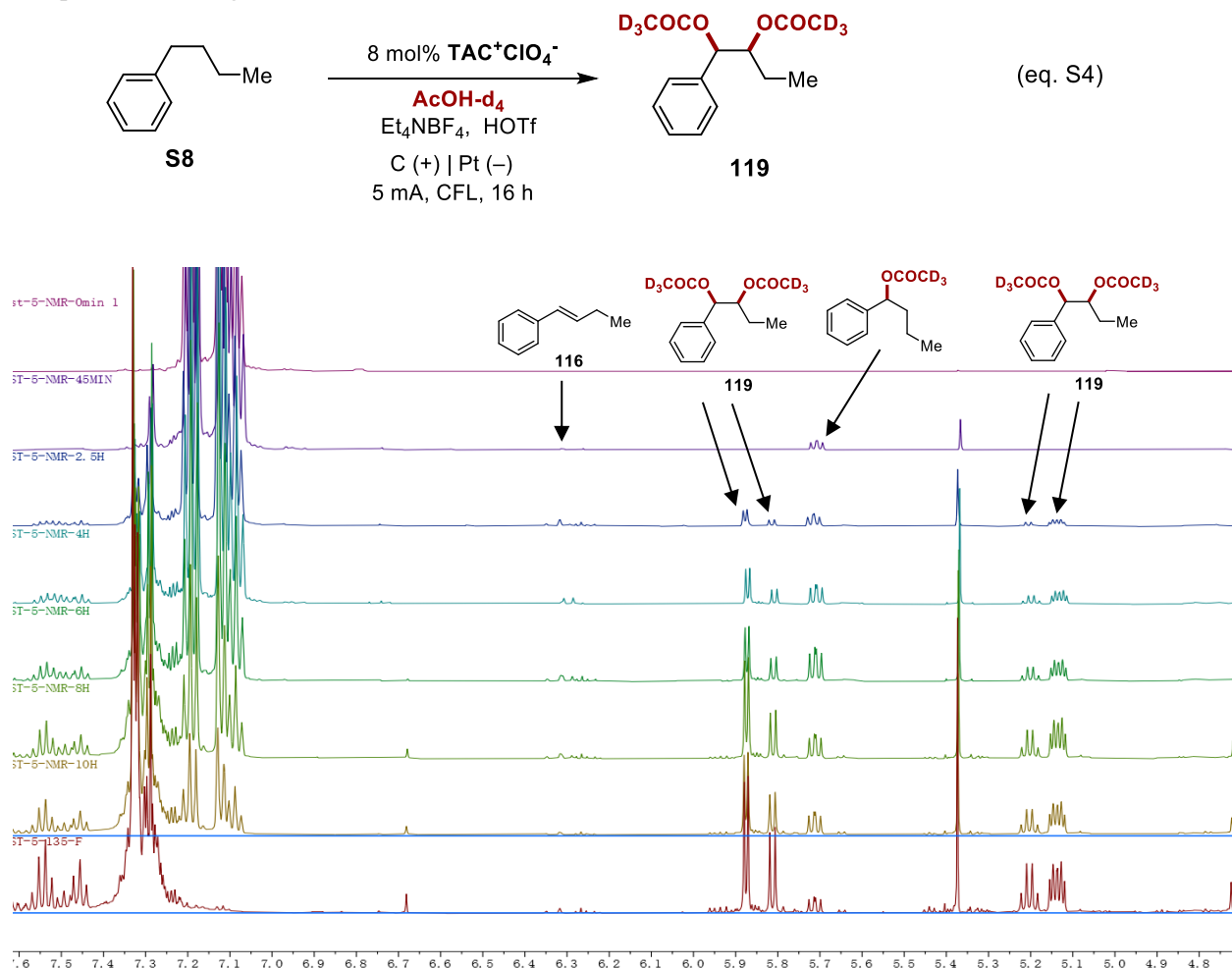


Fig. S10 In situ NMR analysis for eq. S4

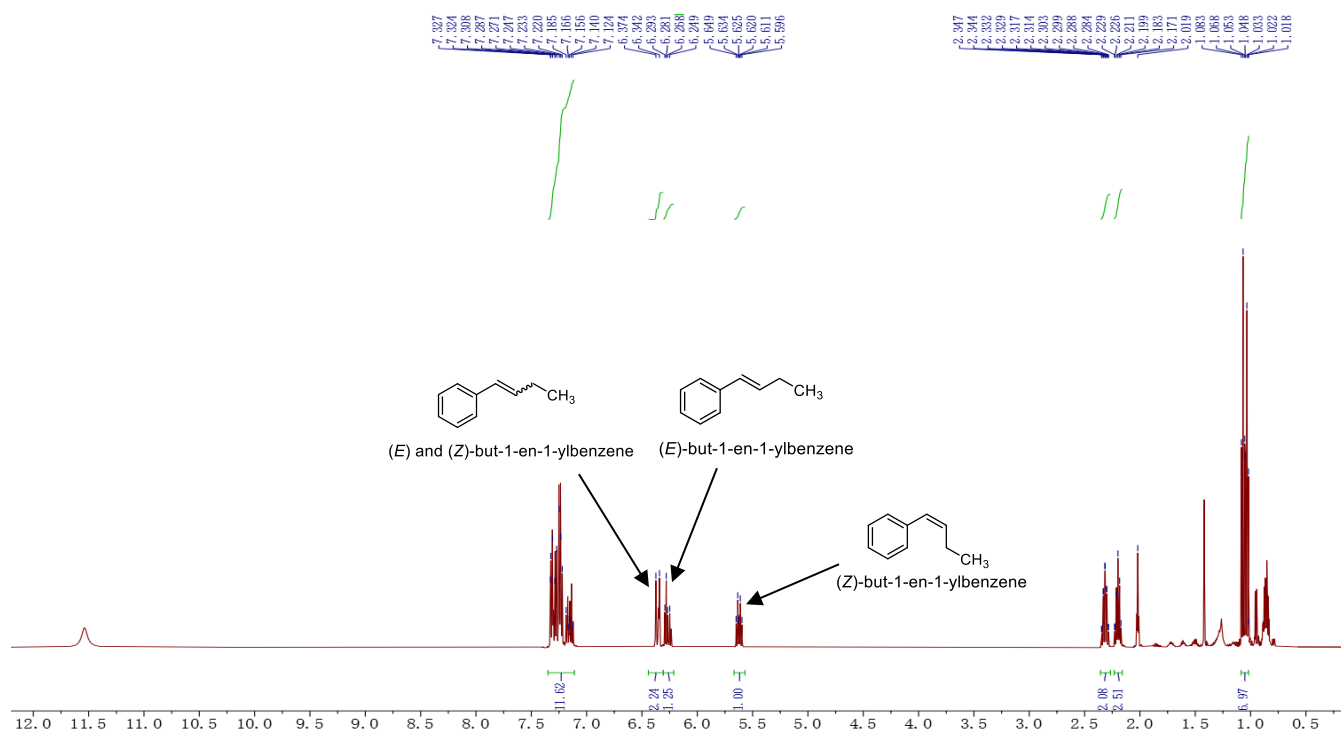


Fig. S11 ^1H NMR of but-1-en-1-ylbenzene **116** ($E:Z=1.25:1$, mixture) in HOAc-d_4

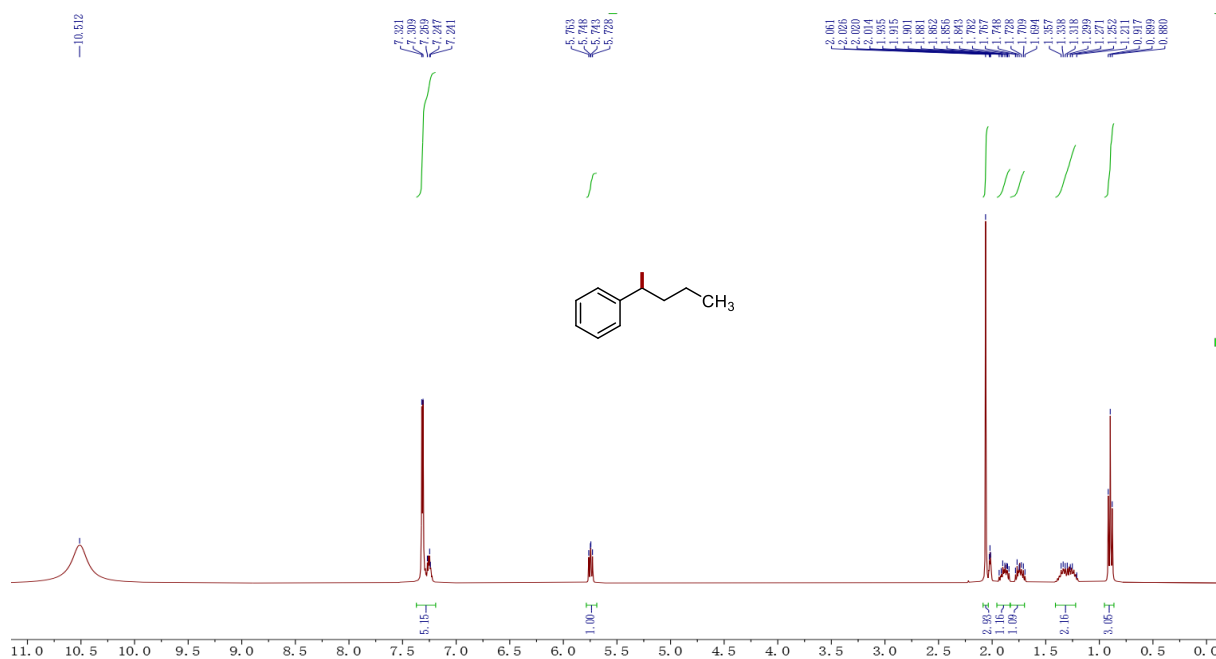


Fig. S12 ^1H NMR of 1-phenylbutyl acetate **115** in HOAc-d_4 (400 MHz)

*In addition, 1-phenylbutyl acetate **115** and (E)-but-1-en-1-ylbenzene **116** were detected under the standard conditions by GC-MS, albeit in only trace amounts. See “2.5.4 Side products studies”*

2.5.3 Mechanistic studies for dioxygenation, trioxxygenation and tetraoxygenation of branched alkylbenzene.

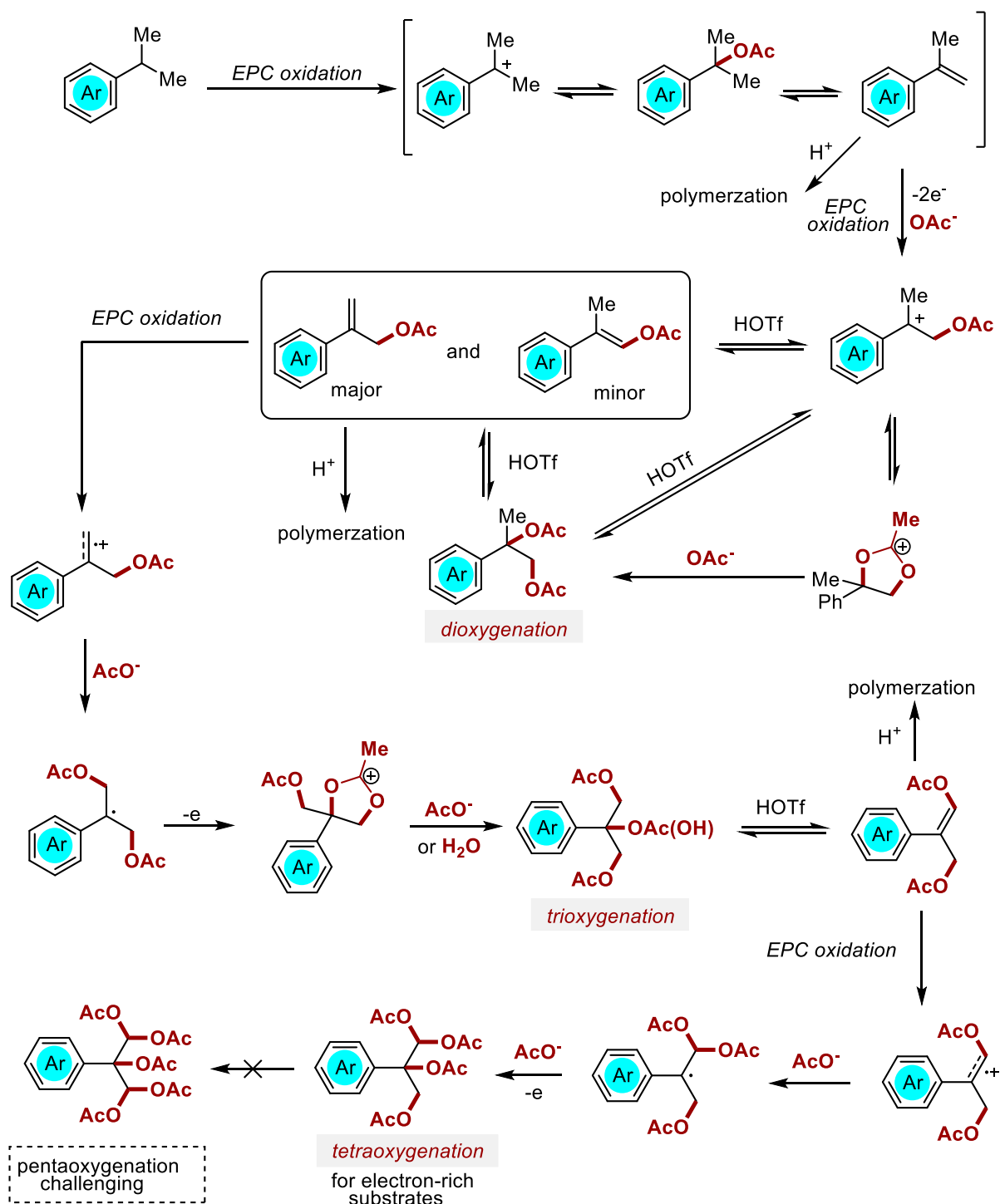


Fig. S13 Possible mechanism for dioxygenation, trioxxygenation, and tetraoxygenation of branched alkylbenzenes.

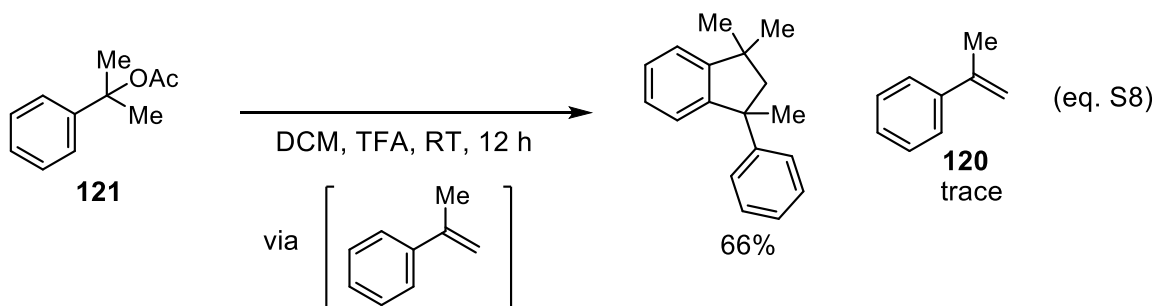
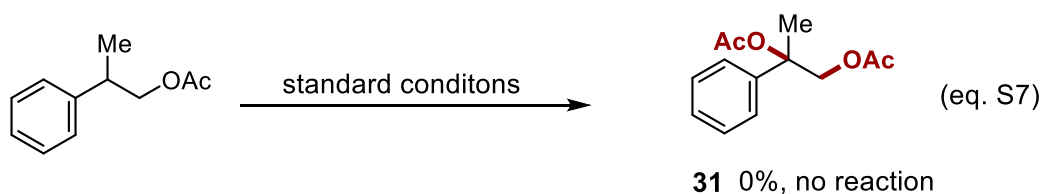
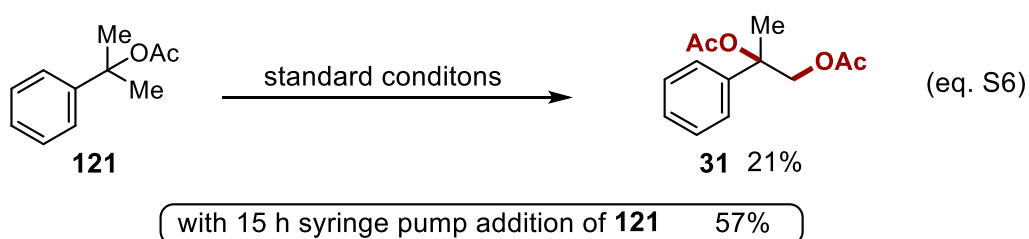
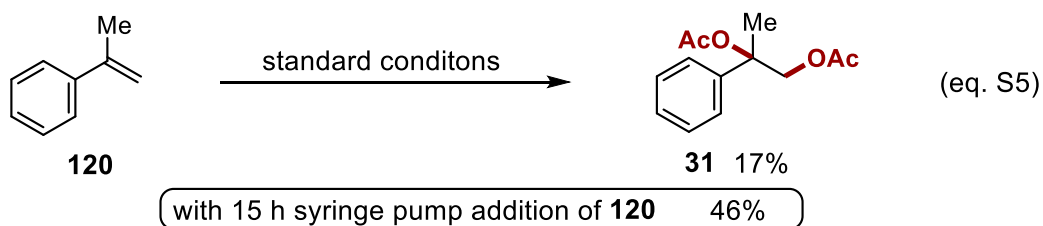
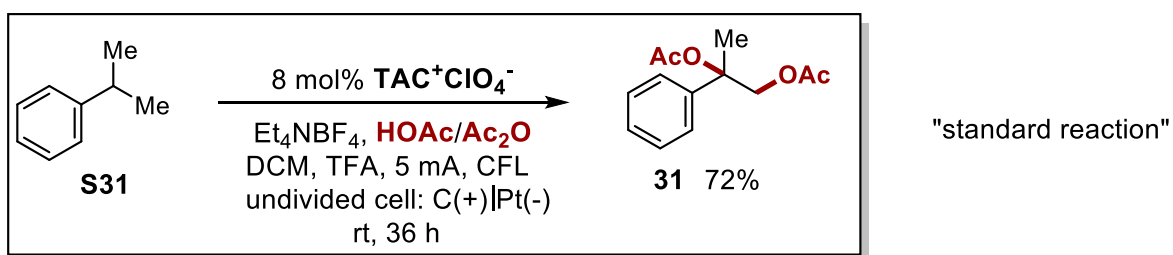


Fig. S14 Verification of possible intermediates for dioxxygenation of cumene.

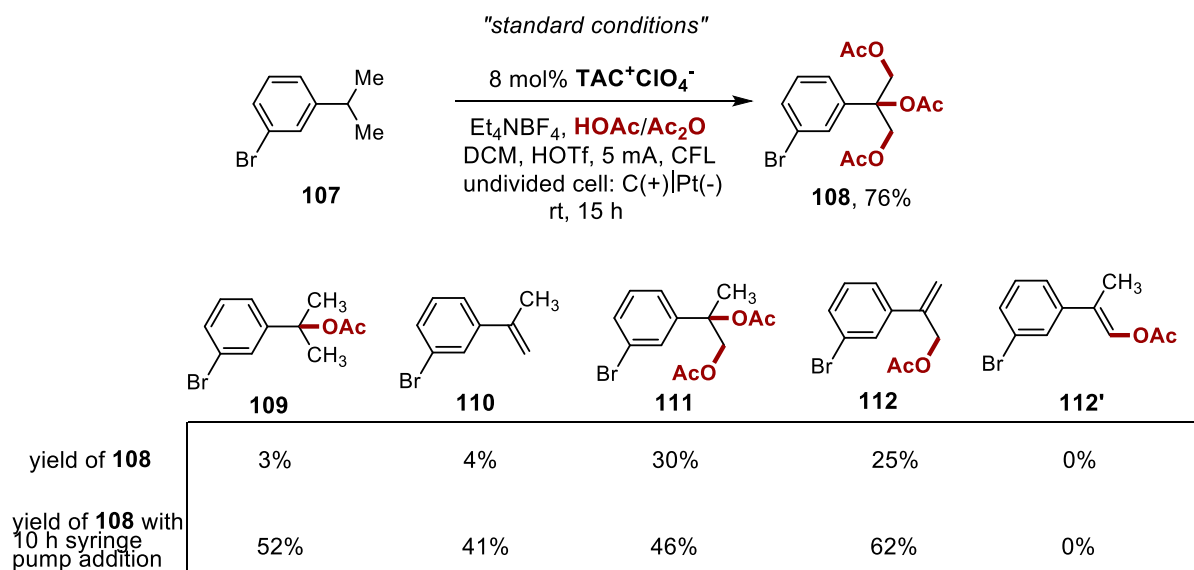


Fig. S15 Verification of possible intermediates for trioxygenation of **107**.

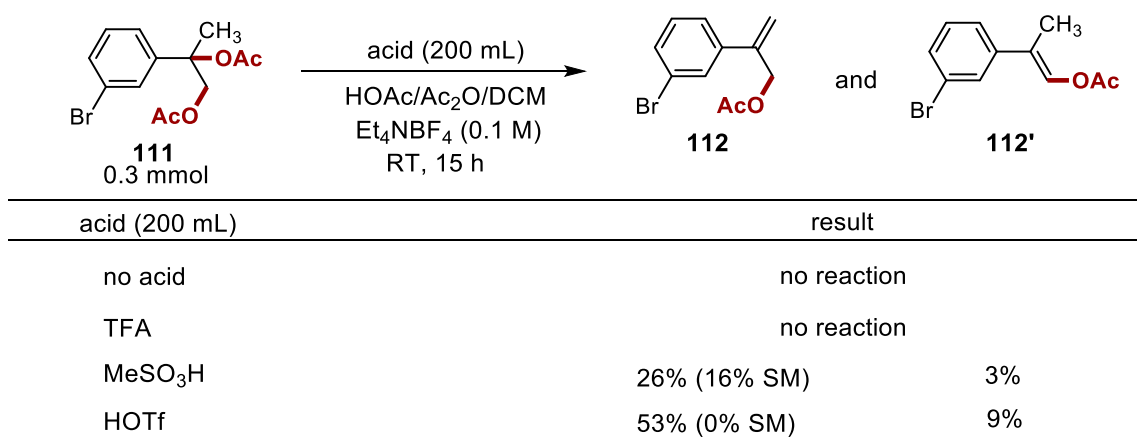
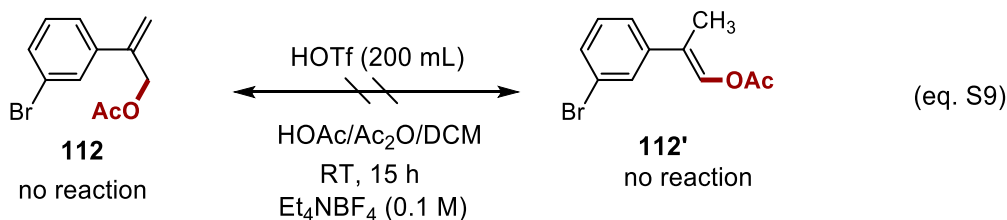
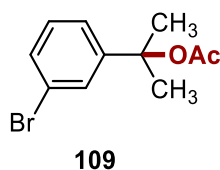


Fig. S16 Verification of the key role of HOTf in elimination of dioxygenation product **111**.



Related intermediates were prepared as follows:



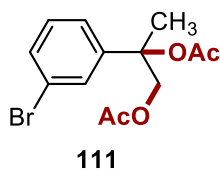
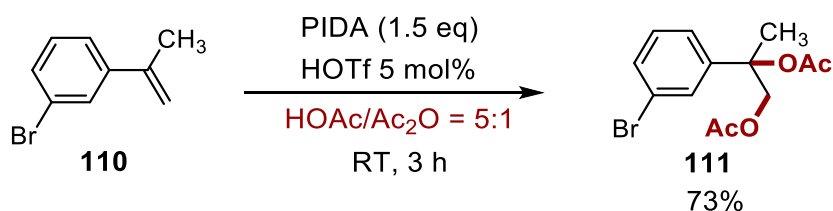
2-(3-bromophenyl)propan-2-yl acetate (109)

The product was prepared from 2-(3-bromophenyl)propan-2-ol (0.5 M) with DMAP (5 mol%) in mixed solvent (DCM/Ac₂O = 1:1) at room temperature for 12 h.

¹H NMR (CDCl₃, 400 MHz): 7.52 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 2.07 (s, 3H), 1.78 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): 169.8, 148.4, 130.2, 130.0, 127.8, 123.1, 122.7, 80.9, 28.7, 22.3.

HRMS: calc. for C₁₁H₁₃BrNaO₂⁺ (M+Na)⁺, 278.9991, found, 278.9987.



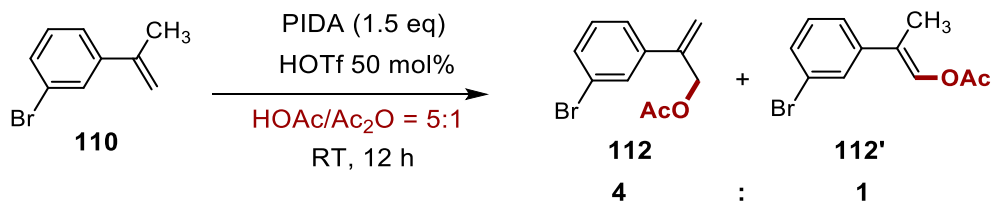
2-(3-bromophenyl)propane-1,2-diyl diacetate (111)

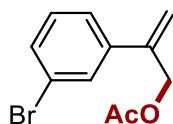
The product was prepared following references⁴⁶ from 1-bromo-3-(prop-1-en-2-yl)benzene (0.5 M) with 5 mol% HOTf stirring in mixed solvent (HOAc/Ac₂O = 5:1).

¹H NMR (CDCl₃, 500 MHz): 7.45 (t, *J* = 8.5 Hz, 2H), 7.41-7.39 (m, 1H), 7.25-7.19 (m, 2H), 4.33 (d, *J* = 11.5 Hz, 1H), 4.27 (d, *J* = 11.5 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 1.85 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 170.5, 169.4, 143.8, 131.0, 130.1, 128.4, 123.7, 122.8, 81.0, 69.6, 22.1, 21.9, 20.9.

HRMS: calc. for C₁₃H₁₅BrNaO₄⁺ (M+Na)⁺, 337.0046, found, 337.0041.





112

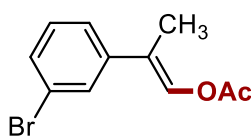
2-(3-bromophenyl)allyl acetate (112)

The product was prepared following modified procedure from references⁴⁶ from 1-bromo-3-(prop-1-en-2-yl)benzene (0.5 M) with 50 mol% HOTf stirring in mixed solvent (HOAc/Ac₂O = 5:1) for 12 h.

¹H NMR (CDCl₃, 500 MHz): 7.57 (t, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 5.55 (s, 1H), 5.40 (s, 1H), 4.93 (s, 2H), 2.08 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): 170.8, 141.5, 140.4, 131.1, 130.1, 129.3, 124.7, 122.8, 116.7, 65.6, 21.0.

HRMS: calc. for C₁₁H₁₁BrNaO₂⁺ (M+Na)⁺, 276.9835, found, 276.9831.



112'

(*E*)-2-(3-bromophenyl)prop-1-en-1-yl acetate (112')

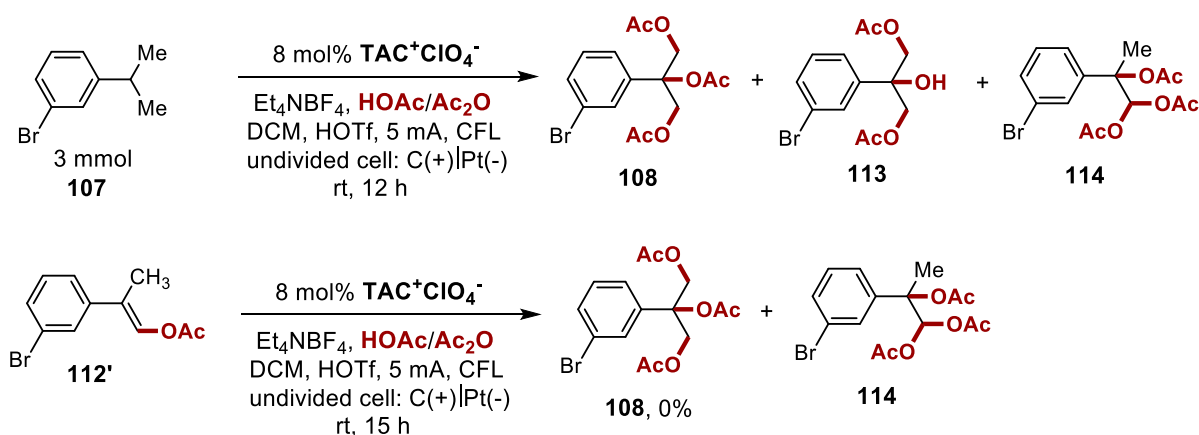
The product was prepared following modified procedure from references⁴⁶ from 1-bromo-3-(prop-1-en-2-yl)benzene (0.5 M) with 50 mol% HOTf stirring in mixed solvent (HOAc/Ac₂O = 5:1) for 12 h.

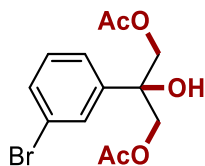
¹H NMR (CDCl₃, 500 MHz): 7.52-7.51 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 2.22 (s, 3H), 2.06 (d, *J* = 1.5 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz): 168.0, 141.4, 133.4, 130.3, 130.1, 129.0, 124.5, 122.8, 120.5, 20.9, 13.6.

HRMS: calc. for C₁₁H₁₁BrNaO₂⁺ (M+Na)⁺, 276.9835, found, 276.9831.

108, **113**, and **114** were prepared from **107** under standard conditions for 12 h, side product **114** could also be prepared from another elimination product **112'** under standard conditions.



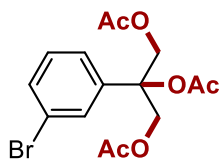


113

2-(3-bromophenyl)-2-hydroxypropane-1,3-diyl diacetate (113)

^1H NMR (CDCl_3 , 500 MHz): 7.68 (t, $J = 2.0$ Hz, 1H), 7.47-7.45 (m, 1H), 7.40-7.38 (m, 1H), 7.25 (t, $J = 8.0$ Hz, 1H), 4.37 (d, $J = 11.5$ Hz, 2H), 4.31 (d, $J = 11.5$ Hz, 2H), 3.16 (s, 1H), 2.06 (s, 6H).

HRMS: calc. for $\text{C}_{13}\text{H}_{15}\text{BrNaO}_5^+$ ($\text{M}+\text{Na}$) $^+$, 352.9995, found, 352.9989.



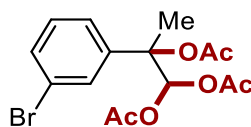
108

2-(3-bromophenyl)propane-1,2,3-triyl triacetate: (108)

^1H NMR (CDCl_3 , 500 MHz): 7.48-7.45 (m, 2H), 7.27-7.24 (m, 2H), 4.65 (s, 4H), 2.12 (s, 3H), 2.05 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): 170.2, 169.2, 140.5, 131.6, 130.2, 128.4, 123.8, 122.9, 80.9, 64.5, 21.8, 20.8.

HRMS: calc. for $\text{C}_{15}\text{H}_{17}\text{BrNaO}_6^+$ ($\text{M}+\text{Na}$) $^+$, 395.0101, found, 395.0091.



114

2-(3-bromophenyl)propane-1,1,2-triyl triacetate: (114)

^1H NMR (CDCl_3 , 500 MHz): 7.48 (t, $J = 2.0$ Hz, 1H), 7.43-7.41 (m, 1H), 7.30-7.28 (m, 1H), 7.21 (t, $J = 8.0$ Hz, 1H), 6.93 (s, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H).

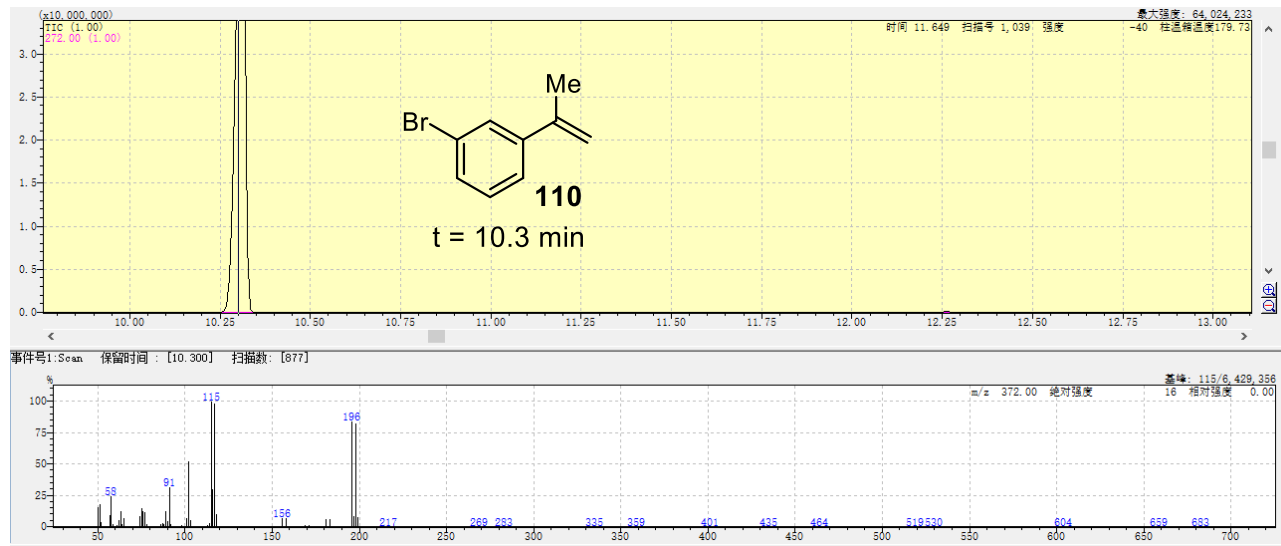
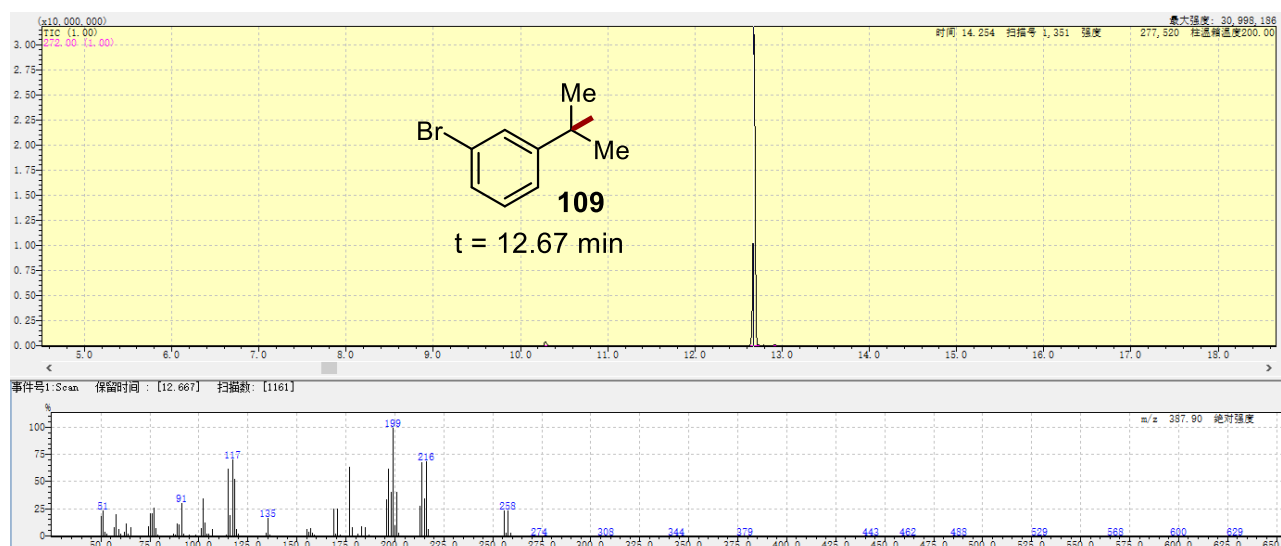
^{13}C NMR (CDCl_3 , 125 MHz): 168.8, 168.4, 168.0, 141.3, 131.4, 129.9, 129.4, 124.7, 122.6, 89.8, 81.9, 22.0, 20.8, 20.3, 18.1.

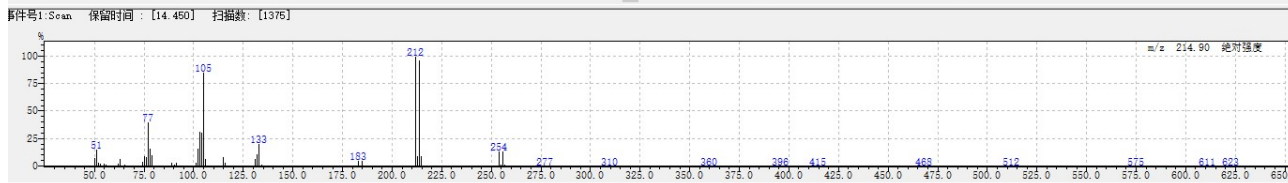
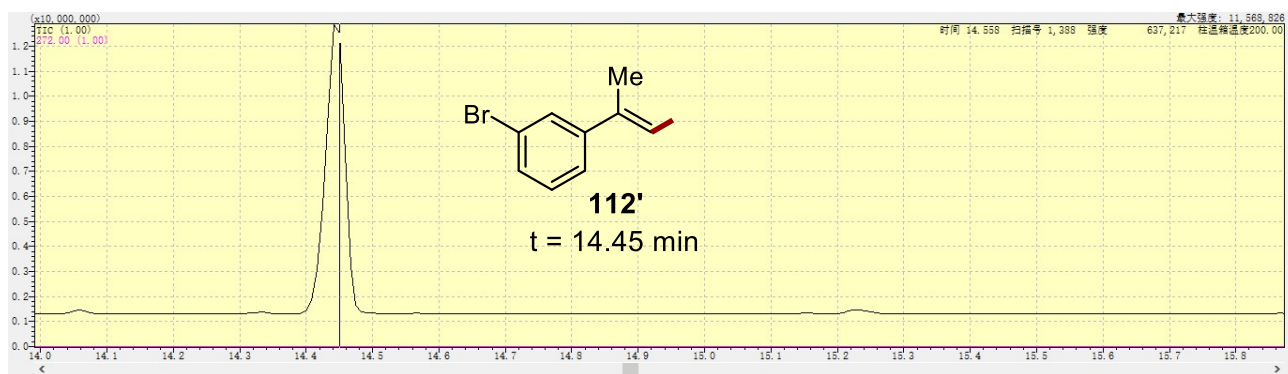
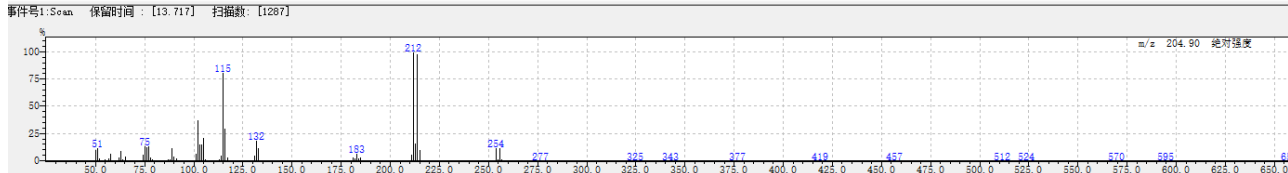
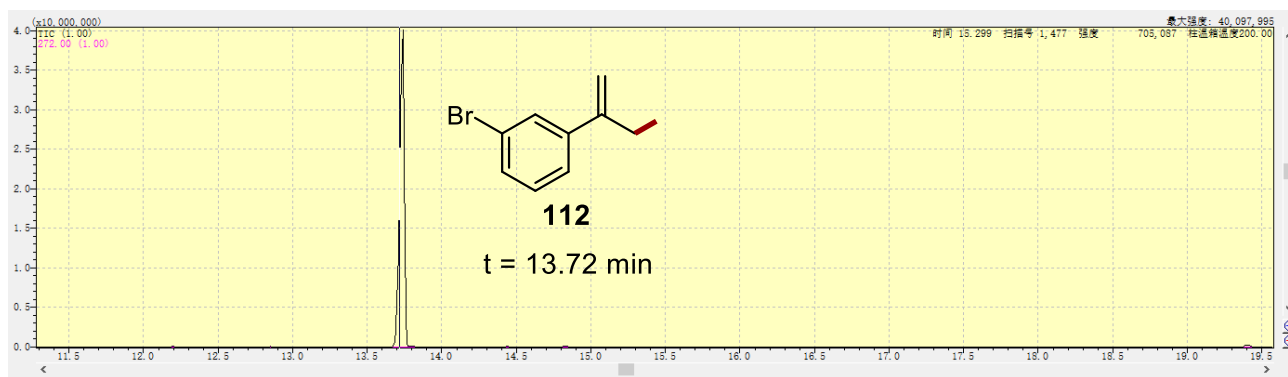
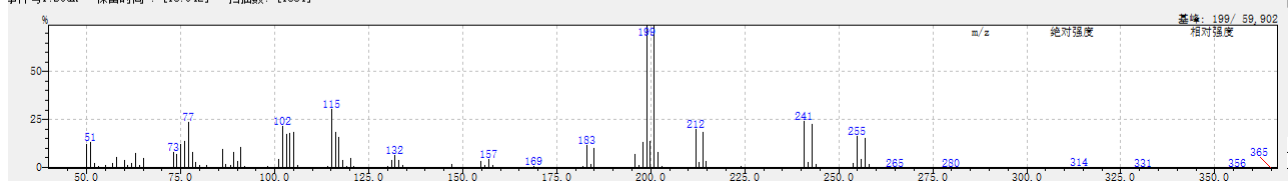
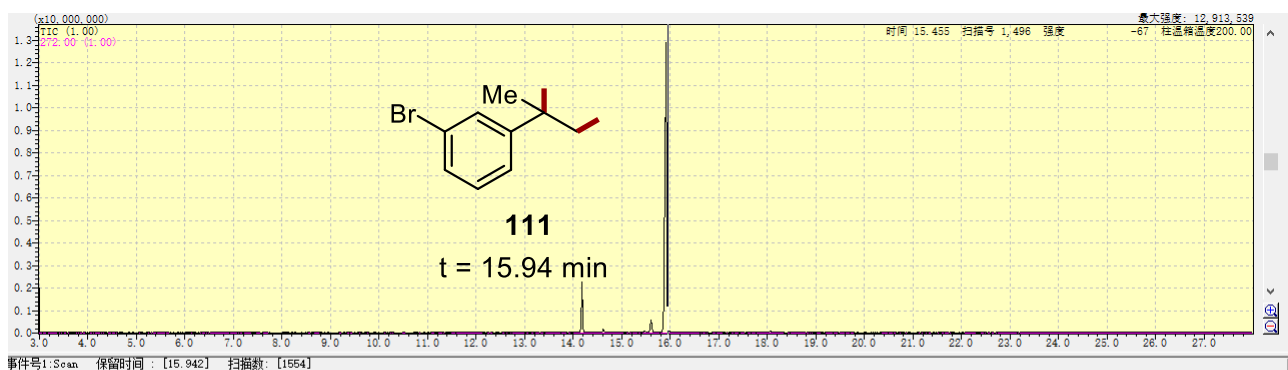
HRMS: calc. for $\text{C}_{15}\text{H}_{17}\text{BrNaO}_6^+$ ($\text{M}+\text{Na}$) $^+$, 395.0101, found, 395.0095.

2.5.4 In situ GC-MS analysis for trioxygenation of branched alkylbenene

107

With possible intermediates and products in hand, we further confirmed the retention time of every compound on GC-MS.





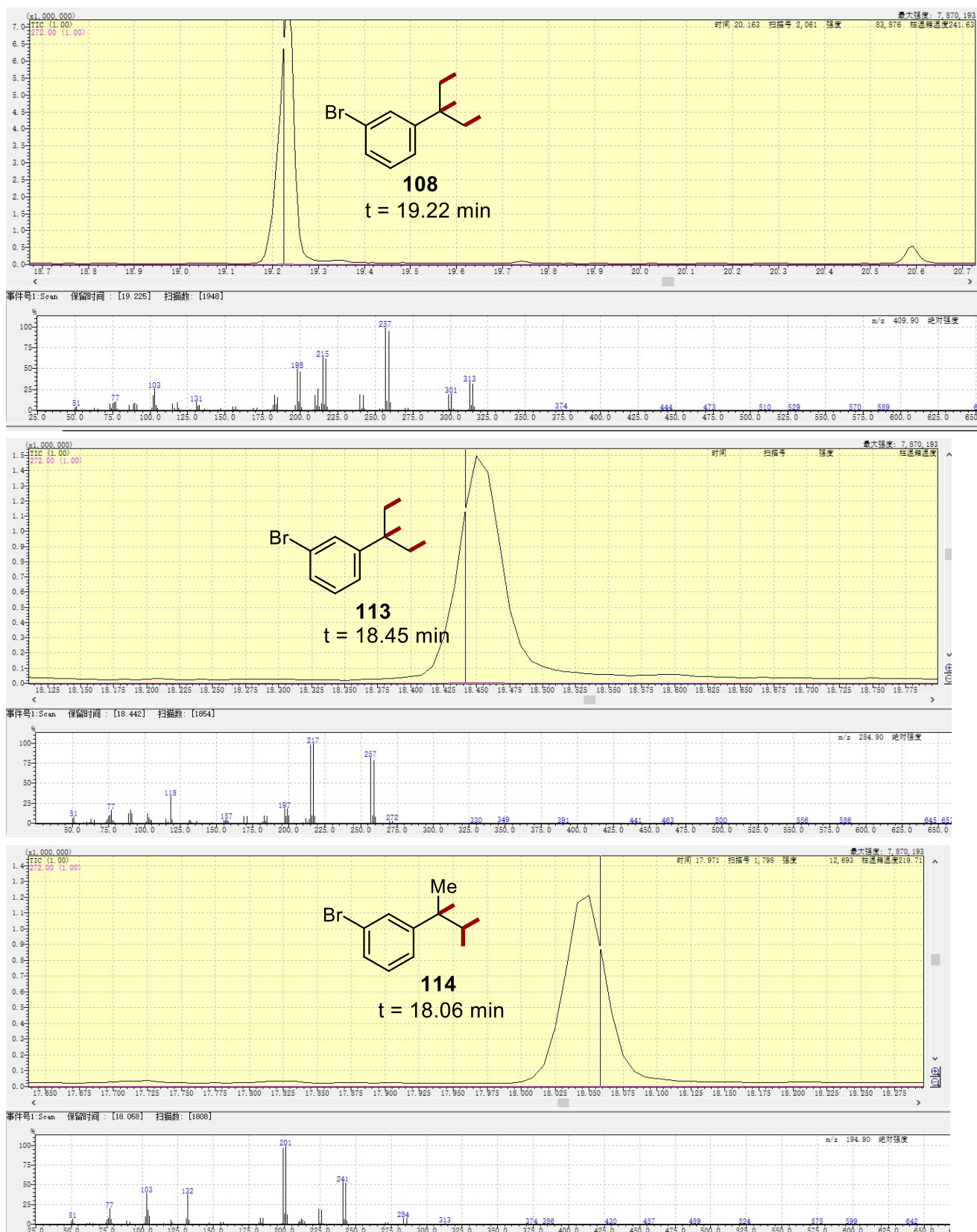
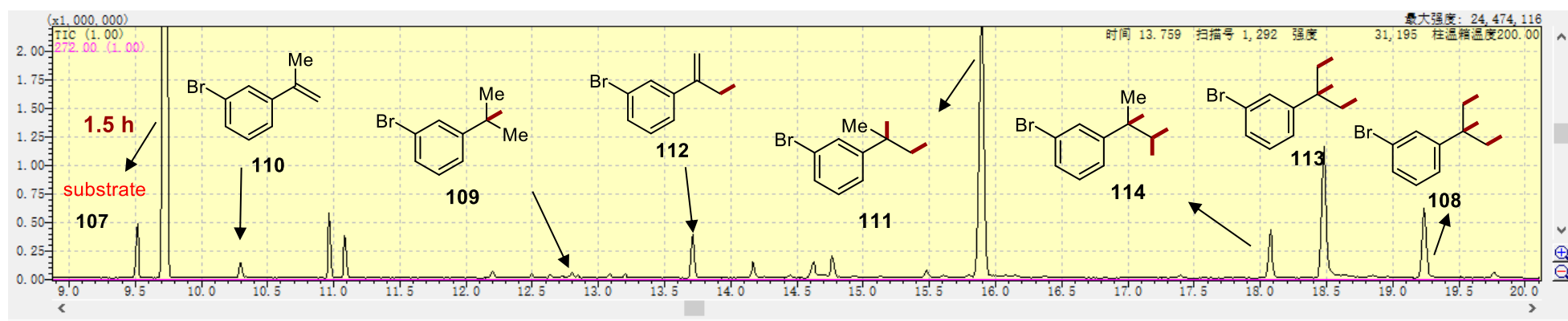
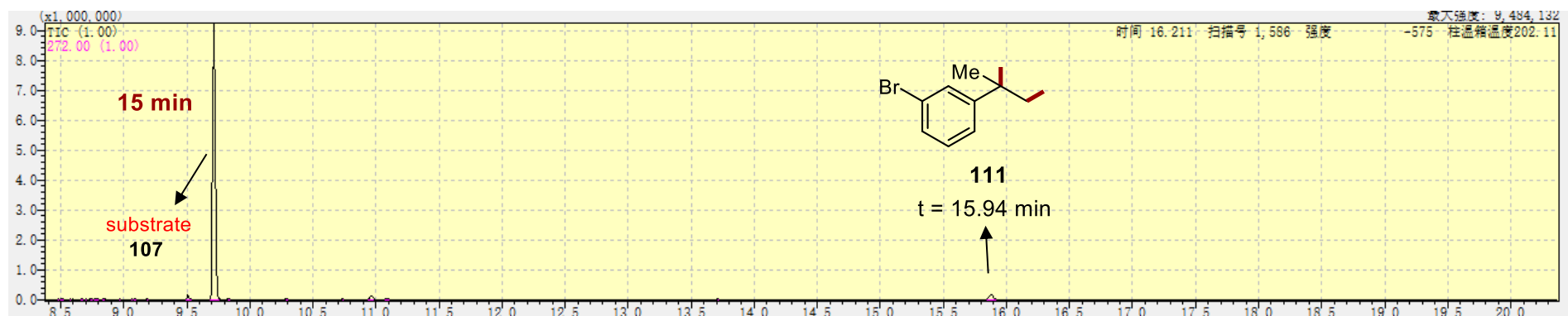
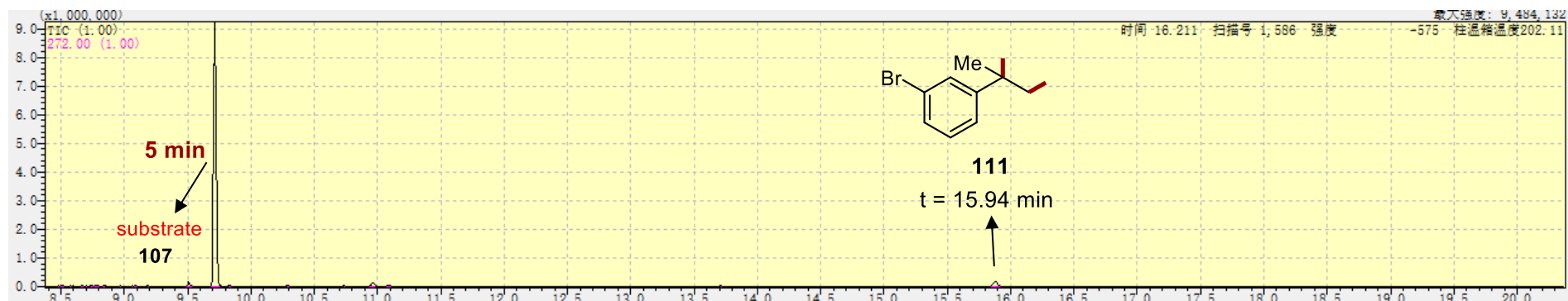
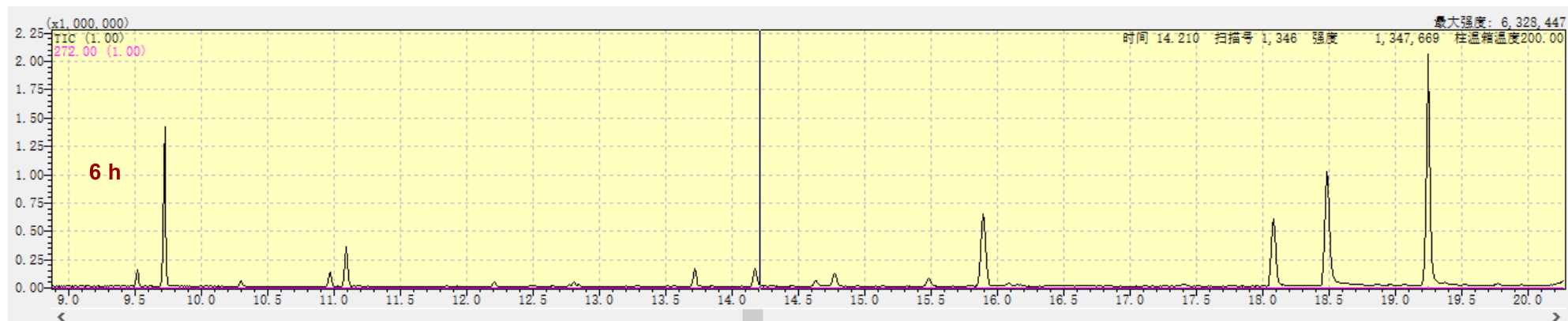
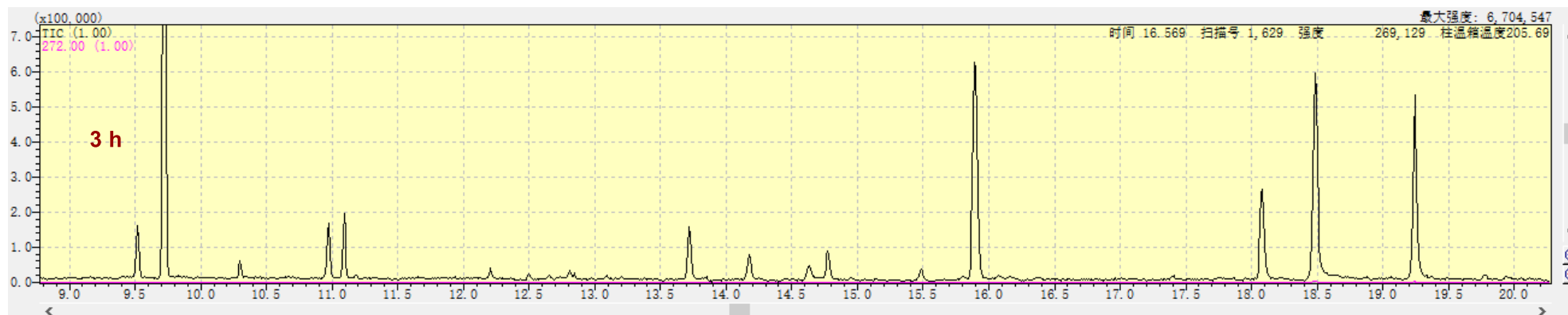


Fig. S17 Verification of some intermediates and products of trioxygenation of **107** on GC-MS.





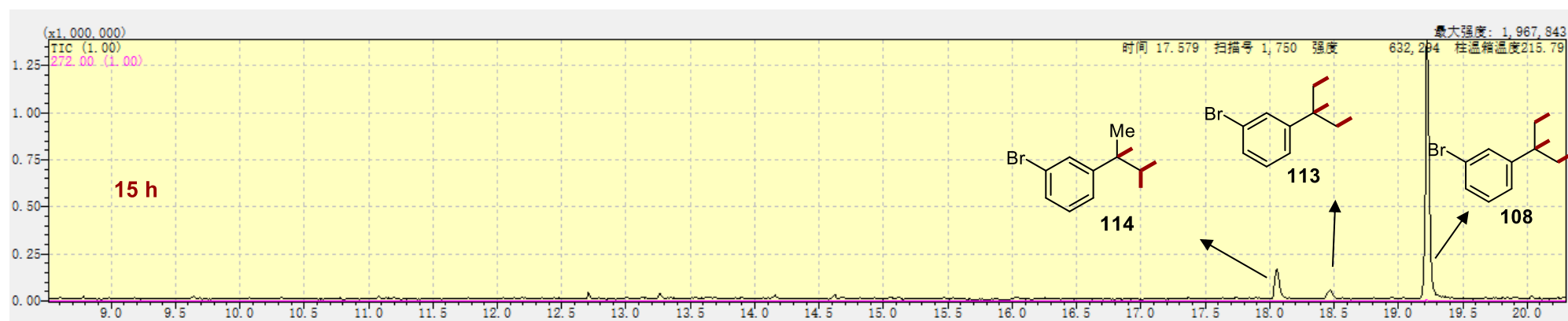
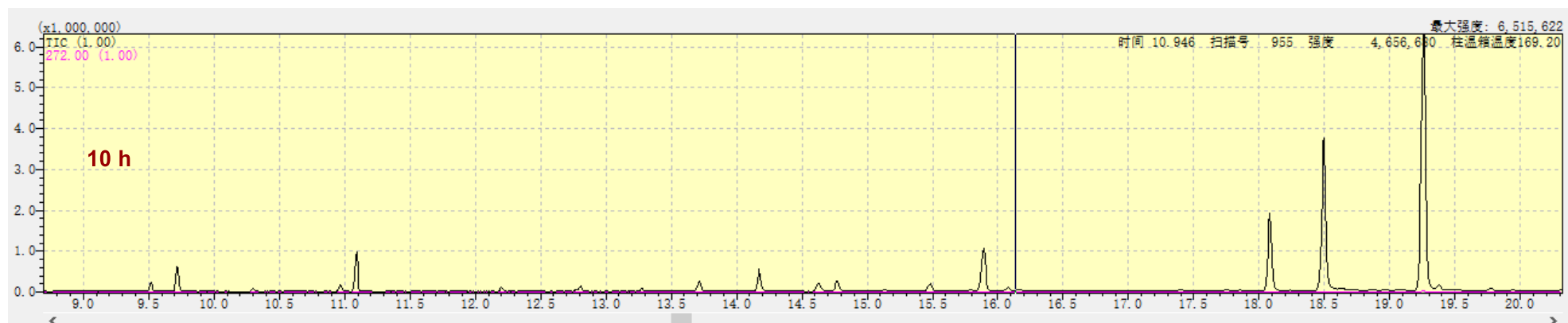


Fig. S18 In situ GC-MS analysis for trioxxygenation of **107**

2.5.5 Side products studies

We have studied the dioxygenation reaction of *n*-butylbenzene **S8** to determine the mass balance for a representative reaction. The reaction was run under the standard conditions, and after 10 h the reaction mixture was analyzed by GC-MS. The peak time of each compound was referenced with standard samples.

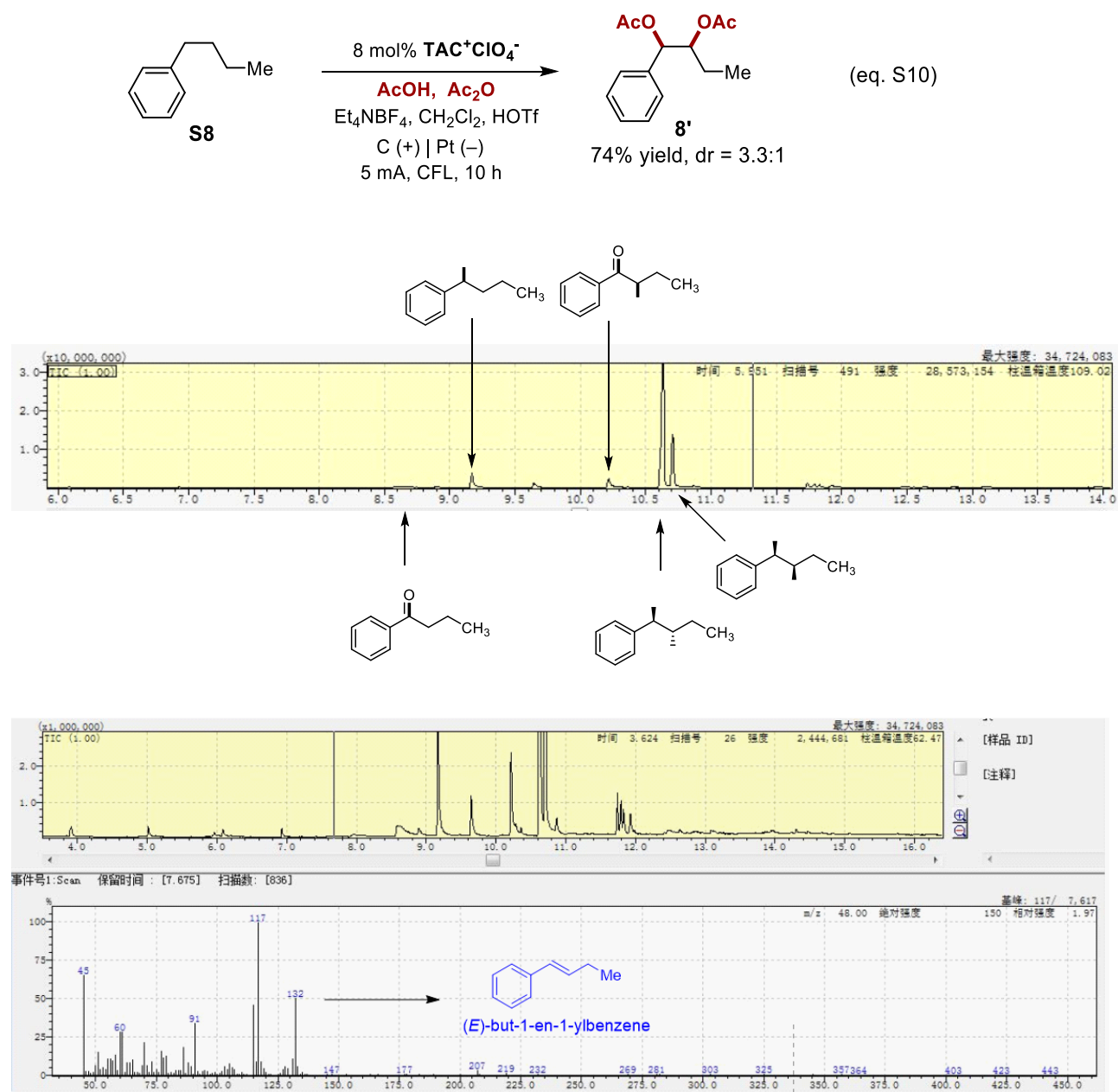


Fig. S19 GC-MS for dioxygenation reaction of *n*-butylbenzene.

In addition, (*E*)-but-1-en-1-ylbenzene **116** was detected under the standard conditions by GC-MS, albeit in only trace amounts.

The conversion of substrates is usually 100%. In cases where yields are moderate, the following factors may contribute to the diminished efficiency:

- 1) In some cases, ketones were detected as side products in less than 5% yield.
- 2) Benzylic ester (monooxygenation) products could sometimes be detected (~5%). In some electron-deficient substrates, benzylic monooxygenation products were much more prevalent, and even sometimes the main products, see “2.6. *Unsuccessful and Challenging Substrates.*”
- 3) α -Ketal ester products could sometimes be detected (~5%). Although present in only small amounts, they tend to have similar R_f values as the dioxygenation products, rendering isolation by chromatography difficult. In such cases, the reaction mixture was treated with Na_2CO_3 (aq.)/MeOH to obtain the pure diols instead of the diacetate ester products.
- 4) In trioxygenation reaction, 2-phenylpropane-1,1,2-triyl triacetate could be obtained in ~5% yield as another kind of trioxygenation product. This side product was generated from another elimination intermediate-(*E*)-2-phenylprop-1-en-1-yl acetate, which was a minor elimination product of dioxygenation intermediate. See “2.5.4 *In situ GC-MS analysis for trioxygenation of secondary alkylbenzene*”
- 5) In some cases, especially for some very electron-rich substrates, substrate decomposition was competitive.

2.6. Unsuccessful and Challenging Substrates

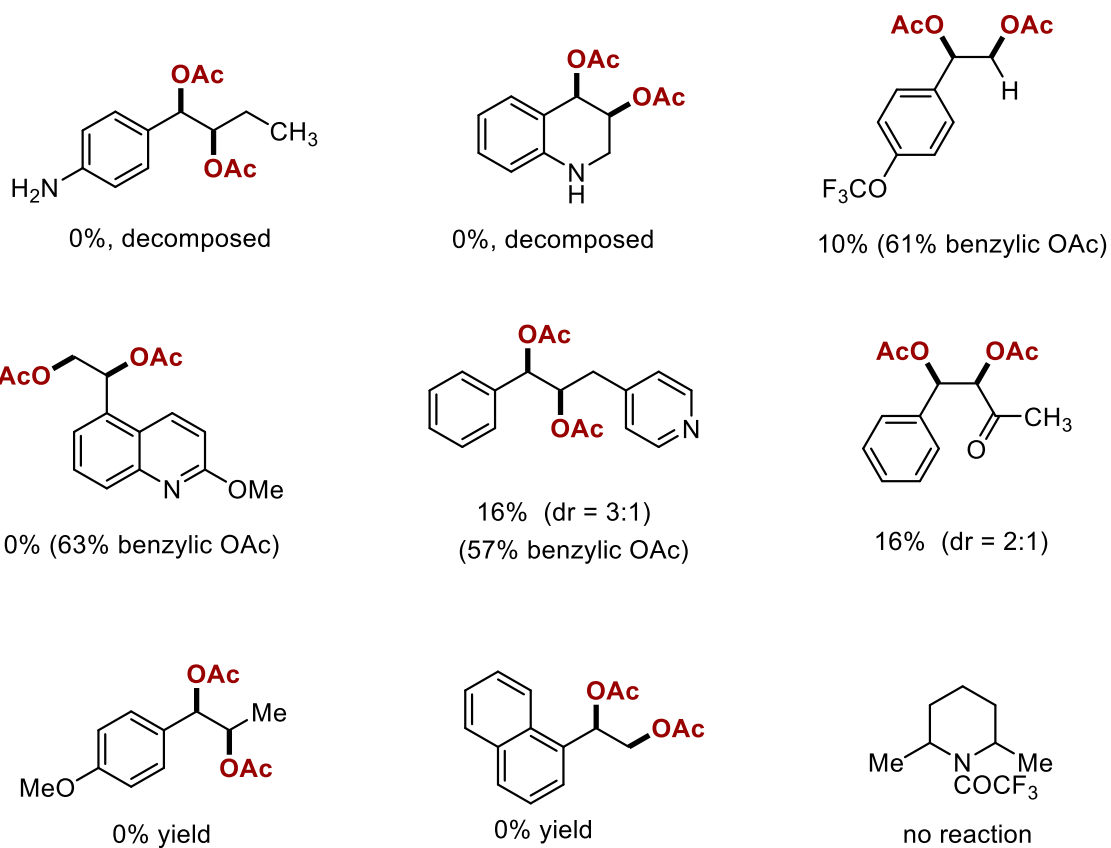
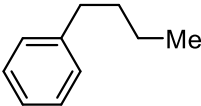
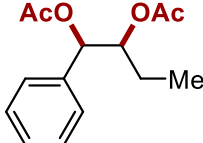


Fig. S20 Unsuccessful and challenging substrates

2.7 Comparison with other chemical oxidants

2.7.1 Table. S2 Comparison with common chemical oxidants for synthesis of dioxygenation product 8'

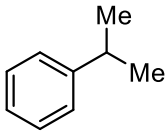
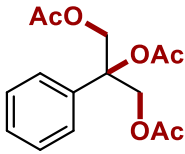
 S8 oxidant (4.0 eq) AcOH, Ac₂O Et₄NBF₄ (0.1 M), CH₂Cl₂, HOTf RT, 10 h  8'		
Entry	oxidant	8' (%)
1	Pb(OAc) ₄	0
2	oxone	0
3	TBHP	0
4	TEMPO	0
5	MnO ₂	0
6	DDQ	0
7	PIDA	0
8	NFSI	0
9	NaIO ₄	0
10	O ₂ (balloon)	0

2.7.2 Table. S3 Comparison with common chemical oxidants for synthesis of dioxygenation product 31.

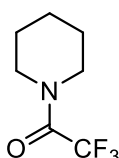
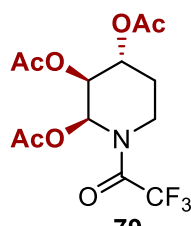
CC(C)c1ccccc1 (S31) $\xrightarrow[\text{Et}_4\text{NBF}_4 (0.1 \text{ M}), \text{CH}_2\text{Cl}_2, \text{TFA}, \text{RT}, 36 \text{ h}]{\text{oxidant (4.0 eq)}, \text{AcOH}, \text{Ac}_2\text{O}}$ CC(O)(O)c1ccccc1 (31)

Entry	oxidant	31 (%)
1	Pb(OAc) ₄	0
2	oxone	0
3	TBHP	0
4	TEMPO	0
5	MnO ₂	0
6	DDQ	2%
7	PIDA	0
8	NFSI	0
9	NaIO ₄	0
10	O ₂ (ballon)	0

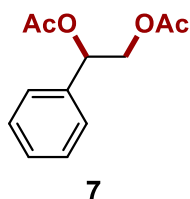
2.7.1 Table. S4 Comparison with common chemical oxidants for synthesis of trioxygenation product 50

 S31 oxidant (4.0 eq) AcOH, Ac₂O Et₄NBF₄ (0.1 M), CH₂Cl₂, HOTf RT, 15 h  50		
Entry	oxidant	50 (%)
1	Pb(OAc) ₄	0
2	oxone	0
3	TBHP	0
4	TEMPO	0
5	MnO ₂	0
6	DDQ	0
7	PIDA	0
8	NFSI	0
9	NaIO ₄	0
10	O ₂ (balloon)	0

2.7.1 Table. S5 Comparison with common chemical oxidants for synthesis of trioxygenation product 79 from piperidine amide 78.

 78 oxidant (6.0 eq) AcOH, Ac₂O Et₄NBF₄ (0.1 M), CH₂Cl₂, HOTf RT, 15 h  79		
Entry	oxidant	79 (%)
1	Pb(OAc) ₄	0
2	K ₂ S ₂ O ₈	0
3	TBHP	0
4	TEMPO	0
5	MnO ₂	0
6	DDQ	0
7	PIFA	0
8	NFSI	0
9	NaIO ₄	0
10	O ₂ (balloon)	0

2.8 Characterization of products

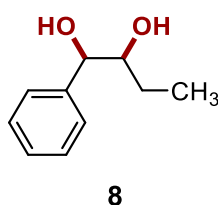


1-phenylethane-1,2-diyl diacetate (**7**)⁴⁷

Following **Condition A** with a reaction time of 15 h, the reaction of ethylbenzene (31.8 mg, 0.3 mmol) afforded 38.6 mg (58% yield) of **7** as a colorless oil.

¹H NMR (CDCl₃, 500 MHz): 7.37-7.33 (m, 5H), 6.01 (dd, *J* = 8.0 Hz, *J* = 4.0 Hz, 1H), 4.35-4.27 (m, 2H), 2.12 (s, 3H), 2.06 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 170.8, 170.2, 136.6, 128.8, 128.7, 126.8, 73.5, 66.2, 21.2, 20.9.



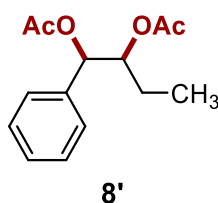
1-phenylbutane-1,2-diol (**8**)⁴⁸

Following **Condition A** with a reaction time of 10 h, then hydrolysis with Na₂CO₃ (aq.)/MeOH, the reaction of *n*-butylbenzene (40.2 mg, 0.3 mmol) afforded 37.4 mg (75% yield, *anti:syn* = 2.9:1) of **8** as a colorless oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.34-7.28 (m, 7H), 4.66 (d, *J* = 4.5 Hz, 1H), 4.40 (d, *J* = 7.0 Hz, 0.35H), 3.73-3.69 (m, 1H), 3.60-3.56 (m, 0.4H), 2.89 (brs, 2H), 2.34 (brs, 1H), 1.44-1.26 (m, 2.8H), 0.94-0.90 (m, 4.3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 141.4, 140.5, 128.6, 128.4, 128.1, 127.9, 127.0, 126.9, 77.4, 76.9, 76.8, 25.7, 24.6, 10.4, 10.1.

HRMS: calc. for C₁₀H₁₅O₂⁺ (M+H)⁺, 167.1067, found, 167.1067.



1-phenylbutane-1,2-diyl diacetate (**8'**)

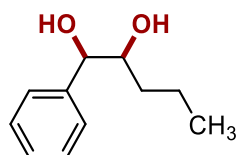
Following **Condition A** with a reaction time of 10 h, the reaction of *n*-butylbenzene (40.2 mg, 0.3 mmol) afforded 55.5 mg (74% yield, *anti:syn* = 3.3:1) of **8'** as a colorless oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.35-7.29 (m, 6.8H), 5.91 (d, *J* = 4.5 Hz, 1H), 5.81 (d, *J* = 7.0 Hz, 0.3H), 5.23-5.19 (m, 0.3H), 5.16-5.12 (m, 1H), 2.11 (s, 3H), 2.07 (s, 1H), 2.04 (s, 1H), 2.01 (s, 3H), 1.62-1.44 (m, 2.67H), 0.87 (t, *J* = 7.5 Hz, 4.15H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 170.7, 170.6, 170.1, 170.0, 137.1, 136.6, 128.6, 128.4, 128.3, 127.4, 127.2, 76.4, 76.1, 75.9, 75.6, 23.7, 22.4, 21.15, 21.10, 20.98, 20.95, 9.91,

9.53.

HRMS: calc. for $C_{14}H_{18}NaO_4^+$ ($M+Na$) $^+$, 273.1097, found, 273.1094.



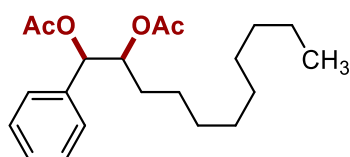
9

1-phenylpentane-1,2-diol (9)³⁷

Following **Condition A** with HOAc (9.0 mL), Ac₂O (1.0 mL), DCM (2.0 mL), HOTf (0.5 mL), with a reaction time of 18 h, the reaction of pentylbenzene (148.0 mg, 1.0 mmol) afforded a mixture, which was hydrolyzed with saturated Na₂CO₃ (aq.) (20 mL) and MeOH (20 mL) at RT for 10 h to afford **9** 122.4 mg (68%, *anti:syn* = 2.3:1) as a yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.33-7.25 (m, 7.5H), 4.61 (d, *J* = 4.0 Hz, 1H), 4.33 (d, *J* = 7.0 Hz, 0.43H), 3.78-3.75 (m, 1H), 3.63-3.60 (m, 0.5H), 3.48-3.28 (m, 1.3H), 2.68-2.64 (m, 1.7H), 1.50-1.41 (m, 1.4H), 1.30-1.91 (m, 4.8H), 0.85-0.79 (m, 4.4H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 141.4, 140.5, 128.5, 128.3, 128.0, 127.7, 127.0, 126.9, 78.1, 77.0, 75.8, 75.0, 34.8, 33.4, 19.1, 18.9, 14.0, 13.9.



10

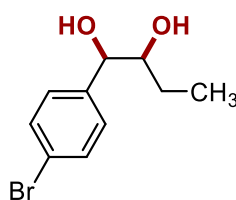
1-phenyldodecane-1,2-diyl diacetate (10)

Following **Condition A** with a reaction time of 10 h, the reaction of *n*-dodecylbenzene (73.8 mg, 0.3 mmol) afforded 84.9 mg (78% yield, *anti:syn* = 4:1) of **10** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.35-7.29 (m, 6.6H), 5.91 (d, *J* = 4.0 Hz, 1H), 5.78 (d, *J* = 7.0 Hz, 0.26H), 5.29-5.25 (m, 0.24H), 5.22-5.18 (m, 1H), 2.11 (s, 3H), 2.07 (s, 0.83H), 2.02 (s, 0.88H), 2.01 (s, 3H), 1.52-1.48 (m, 2H), 1.32-1.21 (m, 21H), 0.89-0.86 (m, 4H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 170.6, 170.5, 170.0, 137.2, 136.6, 128.6, 128.4, 128.3, 127.4, 127.2, 76.6, 75.8, 74.9, 74.7, 32.0, 30.6, 29.63, 29.59, 29.56, 29.51, 29.44, 29.39, 29.35, 29.2, 25.5, 25.1, 22.8, 21.2, 21.1, 21.0, 20.9, 14.2.

HRMS: calc. for $C_{22}H_{34}NaO_4^+$ ($M+Na$) $^+$, 385.2349, found, 385.2348.



11

1-(4-bromophenyl)butane-1,2-diol (11)

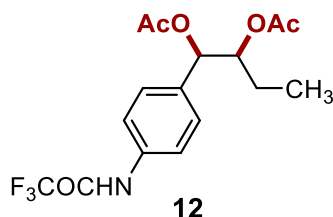
Following **Condition A** with a reaction time of 12 h, followed by hydrolysis with Na₂CO₃ (aq.)/MeOH, the reaction of 1-bromo-4-butylbenzene (63.9 mg, 0.3 mmol) afforded 56.6 mg (77%

yield, *anti:syn* = 3.7:1) of **11** as a light yellow solid.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.48-7.45 (m, 2.56H), 7.24-7.21 (m, 2.60H), 4.65 (d, *J* = 4.5 Hz, 1H), 4.41 (d, *J* = 7.0 Hz, 0.27H), 3.74-3.70 (m, 1H), 3.56-3.52 (m, 0.27H), 2.92 (brs, 0.2H), 2.65 (brs, 0.9H), 2.46 (brs, 0.29H), 2.02 (brs, 1H), 1.43-0.94 (m, 2.66H), 0.95-0.92 (m, 3.8H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 140.4, 139.5, 131.7, 131.5, 128.7, 122.0, 121.8, 77.0, 76.6, 76.3, 25.7, 24.5, 10.4, 10.1.

HRMS: calc. for C₁₀H₁₃BrNaO₂⁺ (M+Na)⁺, 266.9991, found, 266.9993.



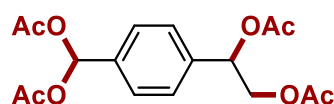
1-(4-(2,2,2-trifluoroacetamido)phenyl)butane-1,2-diyl diacetate (**12**)

Following **Condition A** with HOTf (100 μL) with a reaction time of 12 h, the reaction of *N*-(4-butylphenyl)-2,2,2-trifluoroacetamide (73.5 mg, 0.3 mmol) afforded 69.3 mg (64% yield, *anti:syn* = 1:1.2) of **12** as a yellow solid.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 8.60-8.58 (m, 2H), 7.58-7.56 (m, 4.4H), 7.34-7.32 (m, 4.4H), 5.86 (d, *J* = 5.0 Hz, 1H), 5.76 (d, *J* = 7.0 Hz, 1.2H), 5.20-5.16 (m, 1.1H), 5.12-5.09 (m, 1H), 2.13 (s, 3H), 2.09 (s, 3.3H), 2.05 (s, 3.3H), 2.02 (s, 3H), 1.59-1.53 (m, 2H), 1.51-1.44 (m, 2.5H), 0.89-0.85 (m, 6.8H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 171.0, 170.8, 170.4, 170.2, 155.1 (q, *J* = 29.6 Hz), 135.8, 135.5, 135.0, 134.6, 128.2, 128.1, 120.7, 120.5, 115.8 (q, *J* = 285.0 Hz), 76.1, 75.9, 75.7, 75.2, 23.7, 22.5, 21.1, 21.0, 20.98, 20.95, 9.84, 9.53.

HRMS: calc. for C₁₆H₁₉F₃NO₅⁺ (M+H)⁺, 362.1210, found, 362.1211.



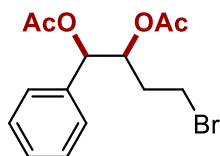
(4-(1,2-diacetoxyethyl)phenyl)methylene diacetate (**13**)

Following **Condition A** with a reaction time of 12 h, the reaction of 1-ethyl-4-methylbenzene (36.0 mg, 0.3 mmol) afforded 46.5 mg (44% yield) of **13** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.63 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.01 (dd, *J* = 8.0 Hz, *J* = 3.5 Hz, 1H), 4.34-4.25 (m, 2H), 2.13-2.12 (m, 9H), 2.07 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 170.5, 170.1, 168.9, 138.3, 135.9, 127.2, 127.1, 89.4, 73.1, 66.0, 21.2, 21.0, 20.9.

HRMS: calc. for C₁₇H₂₀O₈Na⁺ (M+Na)⁺, 375.1050, found, 375.1049.



14

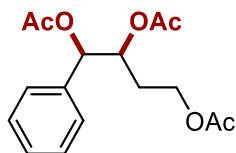
4-bromo-1-phenylbutane-1,2-diyl diacetate (14)

Following **Condition A** with a reaction time of 15 h, the reaction of (4-bromobutyl)benzene (64.0 mg, 0.3 mmol) afforded 57.2 mg (58% yield, *anti:syn* = 5.6:1) of **14** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.38-7.29 (m, 6H), 6.04 (d, *J* = 4.0 Hz, 1H), 5.82 (d, *J* = 6.5 Hz, 0.18H), 5.44-5.40 (m, 0.18H), 5.32-5.28 (m, 1H), 3.37-3.23 (m, 2.43H), 2.20-2.15 (m, 4.18H), 2.09-2.02 (m, 5.9H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 170.4, 170.2, 169.9, 136.3, 136.0, 128.8, 128.6, 128.5, 128.4, 127.3, 126.7, 76.0, 75.1, 73.6, 73.0, 34.1, 32.0, 28.5, 28.0, 21.2, 21.1, 20.95, 20.88.

HRMS: calc. for C₁₄H₁₇BrNaO₄⁺ (M+Na)⁺, 351.0202, found, 351.0207.



15

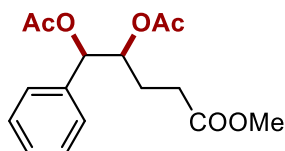
1-phenylbutane-1,2,4-triyl triacetate (15)

Following **Condition A** with a reaction time of 12 h, the reaction of 4-phenylbutyl acetate (57.6 mg, 0.3 mmol) afforded 61.0 mg (66% yield, *anti:syn* = 1.8:1) of **15** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.37-7.31 (m, 8H), 5.99 (d, *J* = 4.5 Hz, 1H), 5.83 (d, *J* = 7.0 Hz, 0.55H), 5.41-5.37 (m, 0.55H), 5.31-5.27 (m, 1H), 4.10-4.00 (m, 3.4H), 2.14 (s, 3H), 2.09-2.08 (m, 3H), 2.02-2.01 (m, 5H), 1.99 (s, 3H), 1.91-1.86 (m, 2.2H), 1.81-1.77 (m, 1.1H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 171.0, 170.9, 136.6, 136.2, 128.8, 128.7, 128.6, 128.5, 127.4, 127.0, 76.4, 75.4, 71.9, 71.6, 60.5, 60.4, 29.8, 28.1, 21.14, 21.09, 20.96, 20.91, 20.9.

HRMS: calc. for C₁₆H₂₀NaO₆⁺ (M+Na)⁺, 331.1152, found, 331.1153.



16

5-methoxy-5-oxo-1-phenylpentane-1,2-diyl diacetate (16)

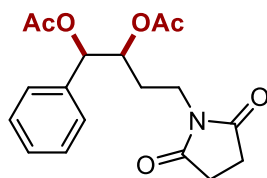
Following **Condition A** with a reaction time of 15 h, the reaction of methyl 5-phenylpentanoate (57.6 mg, 0.3 mmol) afforded 50.8 mg (55% yield, *anti:syn* = 1:3.5) of **16** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.34-7.29 (m, 6.8H), 5.95 (d, *J* = 4.5 Hz, 0.3H), 5.78 (d, *J* = 7.0 Hz, 1H), 5.32-5.28 (m, 1H), 5.20-5.16 (m, 0.25H), 3.69 (s, 0.84H), 3.63 (s,

3H), 2.32-2.27 (m, 2.7H), 2.13 (s, 1H), 2.07 (s, 3H), 2.02 (s, 3H), 1.99 (s, 1H), 1.93-1.79 (m, 0.56H), 1.76-1.73 (m, 2H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 173.3, 173.1, 170.5, 170.4, 170.0, 136.6, 136.3, 128.85, 128.76, 128.5, 128.4, 127.4, 127.0, 76.4, 75.4, 74.2, 73.7, 51.8, 30.2, 29.9, 24.2, 21.2, 21.1, 20.93, 20.88.

HRMS: calc. for C₁₆H₂₀NaO₆⁺ (M+Na)⁺, 331.1152, found, 331.1151.



17

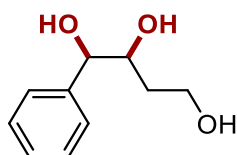
4-(2,5-dioxopyrrolidin-1-yl)-1-phenylbutane-1,2-diyl diacetate (**17**)

Following **Condition A** with a reaction time of 18 h, the reaction of 1-(4-phenylbutyl)pyrrolidine-2,5-dione (69.3 mg, 0.3 mmol) afforded 38.7 mg (89% purity, contains 4.3 mg, 4.8% yield of 4-(2,5-dioxopyrrolidin-1-yl)-1-oxo-1-phenylbutan-2-yl acetate that could not be further separated, *anti:syn* = 5.6:1), 33% yield of **17** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.36-7.30 (m, 6.5H), 5.92 (d, *J* = 4.5 Hz, 1H), 5.80 (d, *J* = 6.0 Hz, 0.18H), 5.18-5.14 (m, 0.17H), 5.12-5.08 (m, 1H), 3.59-3.44 (m, 2.4H), 2.69-2.67 (m, 0.78H), 2.65 (s, 4H), 2.12 (s, 3H), 2.07 (s, 0.57H), 2.04 (s, 3H), 2.02 (s, 0.57H), 1.95-1.78 (m, 2.4H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 177.2, 170.6, 169.9, 136.1, 128.62, 128.55, 128.52, 128.1, 127.3, 127.0, 75.8, 75.4, 72.3, 72.1, 35.2, 35.1, 28.24, 28.2, 26.9, 21.1, 21.0.

HRMS: calc. for C₁₈H₂₁NNaO₆ (M+Na)⁺, 370.1261, found, 370.1257.



18

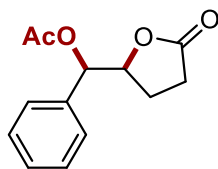
1-phenylbutane-1,2,4-triol (**18**)

Following **Condition A** with a reaction time of 12 h, then hydrolysis with Na₂CO₃ (aq.)/MeOH, the reaction of 4-phenylbutan-1-ol (45.0 mg, 0.3 mmol) afforded 27.3 mg (50% yield, *anti:syn* = 3.5:1) of **18** as a colorless oil after hydrolysis.

¹H NMR (DMSO-d₆, 500 MHz, mixture of regioisomers): 7.33-7.27 (m, 4H), 7.22-7.18 (m, 1H), 5.17 (d, *J* = 4.5 Hz, 1H), 4.53-4.25 (m, 3H), 3.65-3.61 (m, 1H), 3.52-3.42 (m, 2H), 1.62-1.56 (m, 1H), 1.42-1.37 (m, 1H).

¹³C NMR (DMSO-d₆, 125 MHz, mixture of regioisomers): 143.5, 143.2, 127.7, 127.6, 127.2, 127.1, 126.9, 126.6, 76.6, 76.5, 72.1, 58.4, 58.3, 35.7, 34.9. (one carbon overlapped).

HRMS: calc. for C₁₀H₁₄NaO₃⁺ (M+Na)⁺, 205.0835, found, 205.0836.



19

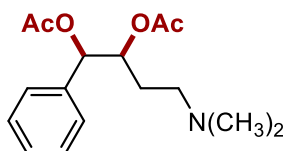
5-oxotetrahydrofuran-2-yl(phenyl)methyl acetate (19)⁴⁹

Following **Condition A** with a reaction time of 15 h, the reaction of 5-phenylpentanoic acid (53.4 mg, 0.3 mmol) afforded 30.9 mg (44% yield, *anti:syn* = 1:1) of **19** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.39-7.34 (m, 10H), 5.97 (d, *J* = 4.0 Hz, 1H), 5.80 (d, *J* = 6.5 Hz, 1H), 4.82-4.76 (m, 2H), 2.46-2.27 (m, 4H), 2.20-2.17 (m, 2H), 2.15 (s, 3H), 2.12 (s, 3H), 2.09-1.96 (m, 2H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 176.8, 176.6, 169.9, 169.8, 135.6, 135.0, 129.1, 129.0, 128.9, 128.6, 127.5, 127.1, 80.73, 80.7, 76.7, 75.8, 28.2, 27.9, 24.3, 22.5, 21.2, 21.1.

HRMS: calc. for C₁₃H₁₄NaO₄⁺ (M+Na)⁺, 257.0784, found, 257.0783.



20

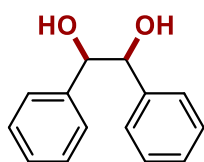
4-(dimethylamino)-1-phenylbutane-1,2-diyl diacetate (20)

Following **Condition A** with a reaction time of 15 h, the reaction of *N,N*-dimethyl-4-phenylbutan-1-amine (53.1 mg, 0.3 mmol) afforded 25.1 mg (77% purity, contains 5.8 mg, 7.7% yield of 4-(dimethylamino)-1-oxo-1-phenylbutan-2-yl acetate that could not be further separated, *anti:syn* = 6:1), 22% yield of **20** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.35-7.27 (m, 6H), 5.95 (d, *J* = 4.5 Hz, 1H), 5.82 (d, *J* = 6.5 Hz, 0.16H), 5.33-5.29 (m, 0.16H), 5.23-5.20 (m, 1H), 2.61 (t, *J* = 8.0 Hz, 0.7H), 2.40 (t, *J* = 8.0 Hz, 2H), 2.28 (s, 6H), 2.16 (s, 0.5H), 2.14 (s, 3H), 2.02-2.01 (m, 3.7H), 1.81-1.76 (m, 2.33H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 170.6, 170.4, 170.2, 170.0, 136.5, 136.2, 128.8, 128.6, 128.5, 127.3, 127.0, 121.6, 76.2, 75.4, 74.3, 73.3, 58.2, 55.4, 44.7, 44.2, 26.4, 21.2, 21.1, 21.0.

HRMS: calc. for C₁₆H₂₄NO₄⁺ (M+H)⁺, 294.1700, found, 294.1697.



21

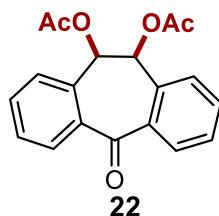
1,2-diphenylethane-1,2-diol (21)⁵⁰

Following **Condition A** with HOTf (100 μL) and a reaction time of 24 h, followed by hydrolysis with Na₂CO₃ (aq.)/MeOH, the reaction of 1,2-diphenylethane (54.6 mg, 0.3 mmol) afforded 23.1

mg (36% yield, *anti:syn* = 1:3) of **21** as a white solid.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.34-7.23 (m, 10H), 7.13-7.11 (m, 4H), 4.83 (s, 0.65H), 4.71 (s, 2H), 2.89 (s, 2H), 2.24 (s, 0.63H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 139.9, 139.8, 128.4, 128.3, 128.1, 127.2, 127.1, 79.2, 78.2.



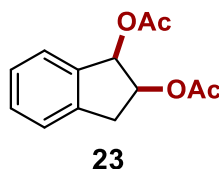
5-oxo-10,11-dihydro-5H-dibenzo[a,d][7]annulene-10,11-diyl diacetate (22)

Following **Condition A** with a reaction time of 18 h, the reaction of 10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (62.4 mg, 0.3 mmol) afforded 36.9 mg (38% yield, *anti:syn* = 1:4.2) of **22** as a light yellow solid.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.99 (d, *J* = 9.5 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 0.5H), 7.56-7.44 (m, 6.8H), 7.38 (d, *J* = 6.0 Hz, 2H), 6.39 (s, 0.5H), 6.30 (s, 2H), 2.08 (s, 1.73H), 1.88 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 194.5, 170.3, 169.7, 138.6, 134.1, 133.9, 132.7, 131.3, 130.4, 130.1, 129.5, 129.1, 74.8, 73.4, 21.1, 20.9.

HRMS: calc. for C₁₉H₁₇O₅⁺ (*M*+H)⁺, 325.1071, found, 325.1068.

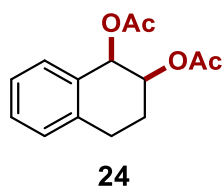


2,3-dihydro-1H-indene-1,2-diyl diacetate (23)⁴⁷

Following **Condition A** with a reaction time of 18 h, the reaction of 2,3-dihydro-1H-indene (35.4 mg, 0.3 mmol) afforded 34.4 mg (49% yield, *anti:syn* = 4:1) of **23** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.40-7.24 (m, 5.5H), 6.25 (d, *J* = 3.5 Hz, 1H), 6.22 (d, *J* = 5.5 Hz, 0.25H), 5.56-5.53 (m, 0.25H), 5.47-5.44 (m, 1H), 3.52 (dd, *J* = 17.0 Hz, *J* = 7.0 Hz, 1H), 3.24 (dd, *J* = 16.0 Hz, *J* = 6.5 Hz, 0.25H), 3.13 (dd, *J* = 16.0 Hz, *J* = 6.0 Hz, 0.25H), 2.90 (dd, *J* = 17.0 Hz, *J* = 4.5 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 0.8H), 2.08 (s, 3H), 2.07 (s, 0.8H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 170.80, 170.76, 170.6, 140.7, 140.3, 138.4, 138.2, 129.8, 129.7, 127.58, 127.57, 125.9, 125.8, 125.14, 125.08, 80.9, 78.9, 75.2, 73.4, 37.0, 36.0, 21.23, 21.20, 21.0, 20.9.

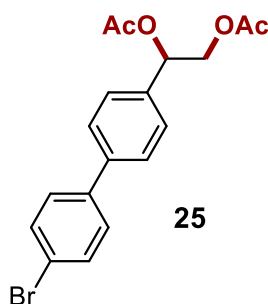


1,2,3,4-tetrahydronaphthalene-1,2-diyl diacetate (24)⁴⁷

Following **Condition A** with a reaction time of 18 h, the reaction of 1,2,3,4-tetrahydronaphthalene (39.6 mg, 0.3 mmol) afforded 53.6 mg (72% yield, *anti:syn* = 1:1) of **24** as a light yellow oil.

¹H NMR (CDCl₃, 400 MHz, mixture of regioisomers): 7.28-7.14 (m, 8H), 6.18 (d, *J* = 3.6 Hz, 1H), 6.06 (d, *J* = 5.6 Hz, 1H), 5.27-5.22 (m, 1H), 5.20-5.16 (m, 1H), 3.08-2.87 (m, 4H), 2.29-2.16 (m, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.05-2.04 (m, 6H), 2.02-1.95 (m, 1H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 170.7, 170.5, 170.4, 136.7, 136.5, 132.79, 132.77, 130.1, 129.2, 128.9, 128.8, 128.7, 128.4, 126.6, 126.5, 71.5, 71.0, 70.2, 69.4, 27.2, 25.8, 25.0, 23.4, 21.3, 21.23, 21.18.

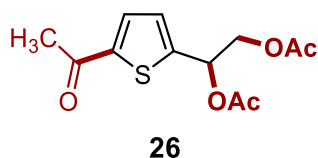
**1-(4'-bromo-[1,1'-biphenyl]-4-yl)ethane-1,2-diyl diacetate (25)**

Following **Condition A** with a reaction time of 15 h, the reaction of 4-bromo-4'-ethyl-1,1'-biphenyl (78.6 mg, 0.3 mmol) afforded 41.8 mg (37% yield) of **25** as a yellow solid.

¹H NMR (CDCl₃, 500 MHz): 7.55 (dd, *J* = 8.0 Hz, *J* = 6.0 Hz, 4H), 7.44 (dd, *J* = 8.5 Hz, *J* = 3.5 Hz, 4H), 6.04 (dd, *J* = 8.0 Hz, *J* = 4.0 Hz, 1H), 4.39-4.30 (m, 2H), 2.14 (s, 3H), 2.08 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 170.8, 170.2, 140.5, 139.5, 136.0, 132.1, 128.8, 127.4, 127.3, 122.0, 73.2, 66.1, 21.2, 21.0.

HRMS: calc. for C₁₈H₁₇BrNaO₄⁺ (*M*+Na)⁺, 399.0202, found, 399.0202.

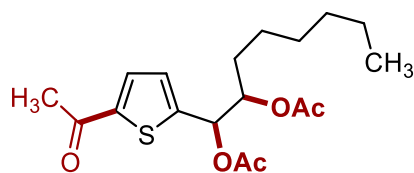
**1-(5-acetylthiophen-2-yl)ethane-1,2-diyl diacetate (26)**

Following **Condition A** with a reaction time of 18 h, the reaction of 2-ethylthiophene (33.6 mg, 0.3 mmol) afforded 41.3 mg (51% yield) of **26** as a yellow solid.

¹H NMR (CDCl₃, 500 MHz): 7.56 (d, *J* = 3.5 Hz, 1H), 7.08 (d, *J* = 4.5 Hz, 1H), 6.22 (dd, *J* = 7.0 Hz, *J* = 4.0 Hz, 1H), 4.22 (dd, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 4.30 (dd, *J* = 12.0 Hz, *J* = 7.0 Hz, 1H), 2.52 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 190.7, 170.5, 169.8, 147.7, 144.6, 132.2, 127.1, 69.6, 65.4, 26.7, 21.0, 20.8.

HRMS: calc. for C₁₂H₁₅O₅S⁺ (*M*+H)⁺, 271.0635, found, 271.0634.



27

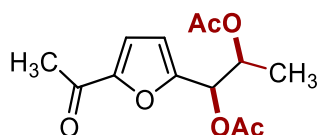
1-(5-acetylthiophen-2-yl)octane-1,2-diyl diacetate (27)

Following **Condition A** with a reaction time of 12 h, the reaction of 2-octylthiophene (58.8 mg, 0.3 mmol) afforded 68.0 mg (64% yield, *anti:syn* = 1.4:1) of **27** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.56-7.54 (m, 1.8H), 7.06-7.04 (m, 1.8H), 6.09 (d, *J* = 3.5 Hz, 1H), 6.06 (d, *J* = 5.0 Hz, 0.72H), 5.26-5.18 (m, 1.76H), 2.53 (s, 3H), 2.51 (s, 2.3H), 2.09 (s, 5.6H), 2.07 (s, 3H), 2.05 (s, 2.3H), 1.52-1.46 (m, 3.6H), 1.26-1.20 (m, 14H), 0.85-0.82 (m, 5.6H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 190.8, 190.7, 170.5, 170.3, 169.8, 169.7, 148.4, 147.2, 144.8, 144.5, 132.2, 131.9, 127.8, 127.2, 74.1, 73.7, 72.2, 71.8, 31.7, 30.5, 29.9, 29.03, 29.0, 26.7, 25.3, 25.1, 22.6, 21.1, 21.0, 20.9, 20.88, 14.1.

HRMS: calc. for C₁₈H₂₇O₅S⁺ (M+H)⁺, 355.1574, found, 355.1574.



28

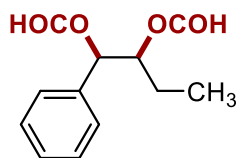
1-(5-acetylfuran-2-yl)propane-1,2-diyl diacetate (28)

Following **Condition A** with HOTf (150 μL) for 18 h, the reaction of 1-(5-propylfuran-2-yl)ethan-1-one (45.6 mg, 0.3 mmol) afforded 26.5 mg (33% yield) of **28** as a yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 7.32 (d, *J* = 3.5 Hz, 0.35H), 7.23 (d, *J* = 3.5 Hz, 0.35H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.50 (d, *J* = 4.0 Hz, 1H), 6.28 (d, *J* = 6.0 Hz, 0.2H), 5.90 (d, *J* = 6.5 Hz, 1H), 5.80-5.75 (m, 0.3H), 5.44-5.39 (m, 1H), 2.57 (s, 1H), 2.47 (s, 3H), 2.17 (s, 1H), 2.12 (s, 3.4H), 2.06 (s, 3H), 1.57 (d, *J* = 7.0 Hz, 1.1H), 1.20 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 186.8, 186.5, 170.5, 170.2, 169.8, 154.1, 153.9, 152.9, 151.2, 119.0, 117.6, 117.2, 111.9, 71.7, 70.2, 70.0, 69.4, 26.5, 26.2, 21.1, 20.8, 20.7, 16.7, 16.4.

HRMS: calc. for C₁₃H₁₆NaO₆⁺ (M+Na)⁺, 291.0839, found, 291.0833.



29

((1-phenylbutane-1,2-diyl)bis(oxy))bis((λ²-methanol) (29)

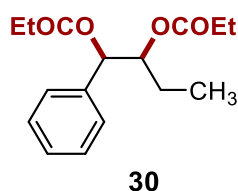
Following **Condition A** with a reaction time of 16 h, the reaction of *n*-butylbenzene (40.2 mg, 0.3 mmol) with formic acid afforded 34.0 mg (51% yield, *anti:syn* = 1:2.3) of **29** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 8.13-8.07 (m, 2.7H), 7.40-7.32 (m, 7.6H),

6.05 (d, $J = 4.5$ Hz, 0.43H), 5.93 (d, $J = 6.5$ Hz, 1H), 5.39-5.35 (m, 1H), 5.32-5.28 (m, 0.45H), 1.64-1.58 (m, 0.84H), 1.52-1.46 (m, 2H), 0.88 (t, $J = 7.5$ Hz, 4.5H).

^{13}C NMR (CDCl_3 , 125 MHz, mixture of regioisomers): 160.6, 160.5, 160.0, 159.9, 136.1, 135.5, 129.1, 128.9, 128.8, 128.6, 127.5, 127.4, 75.9, 75.7, 75.4, 75.1, 23.7, 22.4, 9.8, 9.4.

HRMS: calc. for $\text{C}_{12}\text{H}_{14}\text{NaO}_4^+$ ($\text{M}+\text{Na}$) $^+$, 245.0784, found, 245.0783.



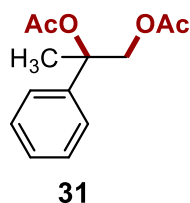
1-phenylbutane-1,2-diyl dipropionate (**30**)

Following **Condition A** with a reaction time of 12 h, the reaction of *n*-butylbenzene (40.2 mg, 0.3 mmol) with propionic acid and propionic anhydride afforded 55.0 mg (66% yield, *anti:syn* = 4.6:1) of **30** as a light yellow oil.

^1H NMR (CDCl_3 , 500 MHz, mixture of regioisomers): 7.37-7.27 (m, 6.4H), 5.92 (d, $J = 5.0$ Hz, 1H), 5.81 (d, $J = 7.0$ Hz, 0.22H), 5.26-5.22 (m, 0.22H), 5.18-5.15 (m, 1H), 2.44-2.23 (m, 5H), 1.63-1.42 (m, 2.63H), 1.17-1.06 (m, 7.5H), 0.89-0.83 (m, 4H).

^{13}C NMR (CDCl_3 , 125 MHz, mixture of regioisomers): 174.1, 174.0, 173.5, 173.3, 137.3, 136.9, 128.63, 128.58, 128.4, 128.2, 127.4, 127.3, 76.3, 75.9, 75.6, 75.5, 27.84, 27.82, 27.8, 28.7, 23.8, 22.6, 9.9, 9.5, 9.4, 9.22, 9.16.

HRMS: calc. for $\text{C}_{16}\text{H}_{23}\text{O}_4^+$ ($\text{M}+\text{H}$) $^+$, 279.1591, found, 279.1590.

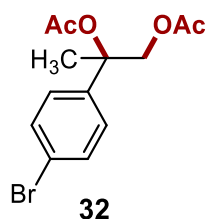


2-phenylpropane-1,2-diyl diacetate (**31**)⁴⁶

Following **Condition B**, the reaction of cumene (36.0 mg, 0.3 mmol) afforded 51.0 mg (72% yield) of **31** as a light yellow oil.

^1H NMR (CDCl_3 , 500 MHz): 7.37-7.29 (m, 5H), 4.38 (d, $J = 11.5$ Hz, 1H), 4.29 (d, $J = 11.5$ Hz, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 170.7, 169.6, 141.3, 128.5, 127.9, 125.0, 81.7, 70.1, 22.2, 21.9, 21.0.



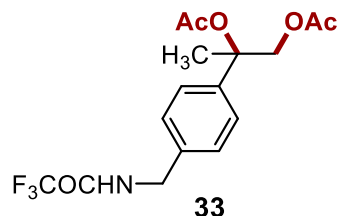
2-(4-bromophenyl)propane-1,2-diyl diacetate (**32**)

Following **Condition B**, the reaction of 1-bromo-4-isopropylbenzene (59.7 mg, 0.3 mmol) afforded 86.9 mg (92% yield) of **32** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.47 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.33 (d, *J* = 11.5 Hz, 1H), 4.28 (d, *J* = 11.5 Hz, 1H), 2.07 (s, 3H), 2.04 (s, 3H), 1.86 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 170.5, 169.5, 140.5, 131.7, 126.9, 121.9, 81.2, 69.6, 22.1, 21.9, 20.9.

HRMS: calc. for C₁₃H₁₅BrNaO₄⁺ (*M*+Na)⁺, 337.0046, found, 337.0044.



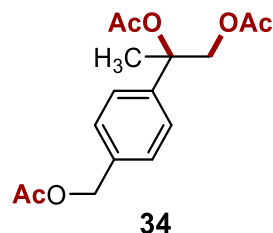
2-(4-((2,2,2-trifluoroacetamido)methyl)phenyl)propane-1,2-diyl diacetate (**33**)

Following **Condition B**, the reaction of 2,2,2-trifluoro-*N*-(4-isopropylbenzyl)acetamide (73.5 mg, 0.3 mmol) afforded 81.2 mg (75% yield) of **33** as a yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.32 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.95 (brs, 1H), 4.47 (d, *J* = 6.0 Hz, 2H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.26 (d, *J* = 11.5 Hz, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 1.87 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 170.7, 169.7, 157.4 (q, *J* = 37.2 Hz), 141.5, 135.5, 128.2, 125.7, 116.0 (q, *J* = 286.1 Hz), 81.4, 69.9, 43.5, 22.1, 21.9, 20.9.

HRMS: calc. for C₁₆H₁₈F₃NNaO₅⁺ (*M*+Na)⁺, 384.1029, found, 384.1028.



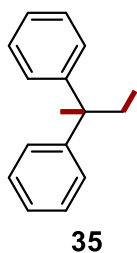
2-(4-(acetoxymethyl)phenyl)propane-1,2-diyl diacetate (**34**)

(4-Isopropylphenyl)methanol (45.0 mg, 0.3 mmol) was stirred with Ac₂O (0.5 mL) for 1 h in the undivided cell, then followed **Condition B** to afford 61.0 mg (66% yield) of **34** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.35-7.30 (m, 4H), 5.07 (s, 2H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.27 (d, *J* = 11.5 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.87 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 170.9, 170.5, 169.5, 141.4, 135.4, 128.4, 125.2, 81.4, 69.8, 65.8, 22.1, 21.9, 21.0, 20.8.

HRMS: calc. for C₁₆H₂₀NaO₆⁺ (*M*+Na)⁺, 331.1152, found, 331.1152.



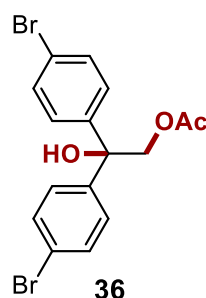
1,1-diphenylethane-1,2-diyl diacetate (**35**)

Following **Condition B**, the reaction of ethane-1,1-diylidibenzen (54.6 mg, 0.3 mmol) afforded 43.8

mg (49% yield) of **35** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.38-7.25 (m, 10H), 5.24 (s, 2H), 2.15 (s, 3H), 1.89 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 170.3, 169.4, 141.9, 128.2, 127.8, 126.5, 84.5, 66.4, 22.2, 20.8.



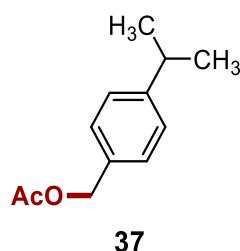
2,2-bis(4-bromophenyl)-2-hydroxyethyl acetate (**36**)

Following **Condition B** without Ac₂O, the reaction of 4,4'-(ethane-1,1-diyl)bis(bromobenzene) (102.0 mg, 0.3 mmol) afforded 83.2 mg (67% yield) of **36** as a light yellow solid.

¹H NMR (CDCl₃, 500 MHz): 7.41-7.25 (m, 8H), 4.68 (s, 2H), 3.02 (brs, 1H), 2.02 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 171.0, 143.6, 128.5, 127.7, 126.4, 77.6, 70.0, 21.0.

HRMS: calc. for C₁₆H₁₄Br₂NaO₃⁺ (M+Na)⁺, 434.9202, found, 434.9205.



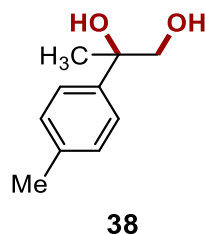
4-isopropylbenzyl acetate (**37**)

Following **Condition B** without Ac₂O, the reaction of *p*-cymene (40.2 mg, 0.3 mmol) afforded 12.7 mg (22% yield) of **37** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.28 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 5.07 (s, 2H), 2.94-2.88 (m, 1H), 2.08 (s, 3H), 1.24 (d, *J* = 7.5 Hz, 6H).

¹³C NMR (CDCl₃, 125 MHz): 171.1, 149.2, 133.4, 128.6, 126.8, 66.4, 34.0, 24.0, 21.1.

HRMS: calc. for C₁₂H₁₇O₂⁺ (M+H)⁺, 193.1223, found, 193.1223.



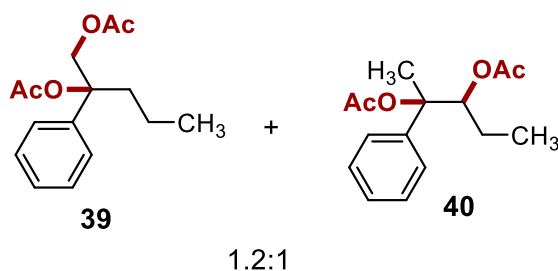
2-hydroxy-2-(*p*-tolyl)propyl acetate (**38**)⁵¹

Following **Condition B** without Ac₂O, the reaction of *p*-cymene (40.2 mg, 0.3 mmol) afforded 13.9 mg (28% yield) of **38** as a light yellow solid after hydrolysis.

¹H NMR (CDCl₃, 500 MHz): 7.34 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.78 (d, *J* = 11.0

Hz, 1H), 3.62 (d, $J = 11.0$ Hz, 1H), 2.55 (brs, 1H), 2.34 (s, 3H), 1.82 (brs, 1H), 1.52 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 142.1, 137.0, 129.3, 125.1, 74.9, 71.3, 26.2, 21.1.



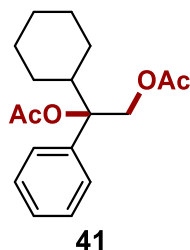
2-phenylpentane-1,2-diyl diacetate (**39**) and 2-phenylpentane-2,3-diyl diacetate (**40**)

Following **Condition B** for 48 h, the reaction of pentan-2-ylbenzene (44.4 mg, 0.3 mmol) afforded 42.0 mg mixture of **39** (29% yield) and **40** (24% yield, *anti:syn* = 3.6:1) as a light yellow oil.

^1H NMR (CDCl_3 , 500 MHz, mixture of regioisomers): 7.36-7.27 (m, 10.5H), 5.14 (dd, $J = 10.5$ Hz, $J = 2.5$ Hz, 0.65H), 5.03 (dd, $J = 10.5$ Hz, $J = 2.5$ Hz, 0.18H), 4.76 (d, $J = 11.5$ Hz, 1H), 4.64 (d, $J = 12.0$ Hz, 1H), 2.30-2.24 (m, 1H), 2.12 (s, 3H), 2.08 (s, 2.6H), 1.98 (s, 2.2H), 1.92 (s, 3H), 1.74-1.70 (m, 0.23H), 1.52-1.36 (m, 1H), 1.30-1.10 (m, 3.6H), 0.87 (t, $J = 7.5$ Hz, 3H), 0.76 (t, $J = 7.5$ Hz, 2H).

^{13}C NMR (CDCl_3 , 125 MHz, mixture of regioisomers): 170.7, 170.6, 169.7, 169.3, 141.3, 141.1, 128.4, 128.1, 127.7, 127.5, 125.7, 125.6, 125.1, 84.7, 84.4, 83.9, 80.1, 80.0, 66.6, 38.2, 22.3, 22.2, 22.1, 22.0, 21.1, 20.9, 20.8, 20.2, 18.3, 16.5, 14.3, 10.6, 10.5.

HRMS: calc. for $\text{C}_{15}\text{H}_{20}\text{NaO}_4^+$ ($\text{M}+\text{Na}$) $^+$, 287.1254, found, 287.1253.



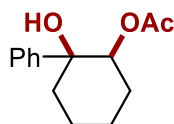
1-cyclohexyl-1-phenylethane-1,2-diyl diacetate (**41**)

Following **Condition B**, the reaction of (1-cyclohexylethyl)benzene (56.4 mg, 0.3 mmol) afforded 54.7 mg (60% yield) of **41** as a light yellow solid.

^1H NMR (CDCl_3 , 500 MHz): 7.32 (t, $J = 7.5$ Hz, 2H), 7.28-7.25 (m, 1H), 7.19 (t, $J = 7.0$ Hz, 2H), 5.05 (d, $J = 12.0$ Hz, 1H), 4.97 (d, $J = 12.0$ Hz, 1H), 2.14 (s, 3H), 2.06 (s, 3H), 1.79-1.57 (m, 6H), 1.22-1.13 (m, 2H), 0.99-0.74 (m, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 170.8, 169.8, 138.9, 127.9, 127.4, 125.6, 86.5, 63.9, 44.6, 27.7, 26.8, 26.6, 26.4, 26.3, 22.1, 21.0.

HRMS: calc. for $\text{C}_{18}\text{H}_{24}\text{NaO}_4^+$ ($\text{M}+\text{Na}$) $^+$, 327.1567, found, 327.1567.



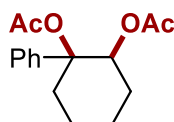
cis-42

2-hydroxy-2-phenylcyclohexyl acetate (42)⁴⁷

Following **Condition B**, the reaction of cyclohexylbenzene (48.0 mg, 0.3 mmol) afforded 7.7 mg (11% yield) of **42** as a white solid. This product was isolated as a single diastereomer (*cis*).

¹H NMR (CDCl₃, 500 MHz): 7.46-7.44 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 5.29 (dd, *J* = 10.8 Hz, *J* = 5.2 Hz, 1H), 2.26 (brs, 1H), 2.25-1.84 (m, 4H), 1.81 (s, 3H), 1.77-1.63 (m, 3H), 1.48-1.40 (m, 1H).

¹³C NMR (CDCl₃, 125 MHz): 169.9, 146.1, 128.4, 127.1, 124.8, 76.4, 75.4, 39.8, 27.3, 24.3, 21.2, 21.0.



cis-43

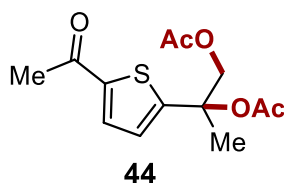
1-phenylcyclohexane-1,2-diyl diacetate (43)⁴⁷

Following **Condition B**, the reaction of cyclohexylbenzene (48.0 mg, 0.3 mmol) afforded 20.7 mg (25% yield) of **43** as a white solid. This product was isolated as a single diastereomer (*cis*).

¹H NMR (CDCl₃, 500 MHz): 7.31-7.23 (m, 5H), 4.75 (dd, *J* = 11.5 Hz, *J* = 4.0 Hz, 1H), 3.02-2.99 (m, 1H), 2.19 (s, 3H), 2.13-2.08 (m, 1H), 1.98-1.90 (m, 1H), 1.88-1.79 (m, 2H), 1.85 (s, 3H), 1.72-1.68 (m, 1H), 1.53-1.38 (m, 2H).

¹³C NMR (CDCl₃, 125 MHz): 169.9, 169.5, 140.6, 128.1, 127.5, 125.5, 83.9, 77.4, 31.3, 27.7, 24.1, 22.1, 21.0, 20.9.

HRMS: calc. for C₁₂H₁₅O₄⁺ (M+H)⁺, 223.0965, found, 223.0965.



44

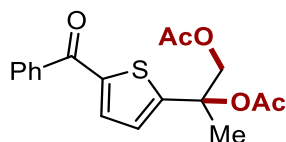
2-(5-acetylthiophen-2-yl)propane-1,2-diyl diacetate (44)

Following **Condition B** for 24 h, the highest *E*_{cell} was set at 2.8 V, the reaction of 1-(5-isopropylthiophen-2-yl)ethan-1-one (50.4 mg, 0.3 mmol) afforded 45.2 mg (53% yield) of **44** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.53 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 4.0 Hz, 1H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 2.51 (s, 3H), 2.06-2.05 (m, 6H), 1.92 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): 190.8, 170.3, 169.4, 154.1, 143.8, 132.2, 125.2, 79.8, 69.2, 26.6, 22.9, 22.0, 20.8.

HRMS: calc. for C₁₃H₁₆NaO₅S⁺ (M+Na)⁺, 307.0611, found, 307.0604.



45

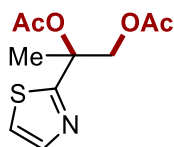
2-(5-benzoylthiophen-2-yl)propane-1,2-diyl diacetate (45)

Following **Condition B** for 24 h, the highest E_{cell} was set at 2.8 V, the reaction of (5-isopropylthiophen-2-yl)(phenyl)methanone (69.0 mg, 0.3 mmol) afforded 59.2 mg (57% yield) of **45** as a light yellow oil.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): 7.84-7.82 (m, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.50-7.47 (m, 3H), 7.03 (d, $J = 4.0$ Hz, 1H), 4.47 (d, $J = 11.0$ Hz, 1H), 4.45 (d, $J = 11.5$ Hz, 1H), 2.09-2.08 (m, 6H), 1.97 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 188.3, 170.4, 169.5, 154.5, 143.0, 137.9, 134.6, 132.4, 129.2, 128.6, 125.1, 79.9, 69.2, 23.0, 22.1, 20.9.

HRMS: calc. for $\text{C}_{18}\text{H}_{18}\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$, 369.0767, found, 369.0760.



46

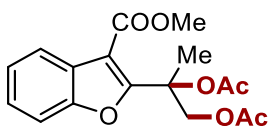
2-(thiazol-2-yl)propane-1,2-diyl diacetate (46)

Following **Condition C** for 24 h, the reaction of 2-isopropylthiazole (38.1 mg, 0.3 mmol) afforded 32.1 mg (44% yield) of **46** as a light yellow oil.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): 7.75 (d, $J = 3.0$ Hz, 1H), 7.33 (d, $J = 3.0$ Hz, 1H), 4.67 (d, $J = 11.5$ Hz, 1H), 4.57 (d, $J = 11.5$ Hz, 1H), 2.11 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 171.0, 170.4, 169.5, 142.5, 119.7, 81.5, 68.3, 22.6, 22.0, 20.8.

HRMS: calc. for $\text{C}_{10}\text{H}_{13}\text{NNaO}_4\text{S}^+$ ($\text{M}+\text{Na}$) $^+$, 266.0457, found, 266.0460.



47

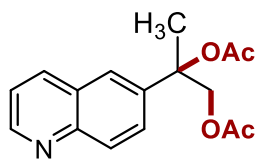
2-(3-(methoxycarbonyl)benzofuran-2-yl)propane-1,2-diyl diacetate (47)

Following **Condition A** with HOTf (150 μL) for 16 h, the highest E_{cell} was set at 1.8 V, the reaction of methyl 2-isopropylbenzofuran-3-carboxylate (65.4 mg, 0.3 mmol) afforded 23.0 mg (23% yield) of **47** as a yellow oil.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): 7.96-7.95 (m, 1H), 7.50 (dd, $J = 7.0$ Hz, $J = 1.5$ Hz, 1H), 7.36-7.29 (m, 2H), 4.73 (d, $J = 11.0$ Hz, 1H), 4.66 (d, $J = 11.0$ Hz, 1H), 3.95 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 170.5, 169.6, 163.7, 160.8, 152.9, 126.4, 125.4, 124.2, 122.6, 111.5, 109.9, 77.9, 66.9, 51.8, 21.3, 20.9, 20.8.

HRMS: calc. for $\text{C}_{17}\text{H}_{18}\text{NaO}_7^+$ ($\text{M}+\text{Na}$) $^+$, 357.0945, found, 357.0937.



48

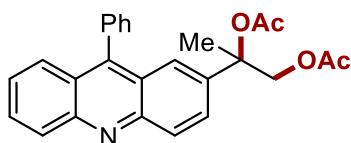
2-(quinolin-6-yl)propane-1,2-diyl diacetate (48)

Following **Condition A** with HOTf (250 μ L) for 24 h, the reaction of 6-isopropylquinoline (51.3 mg, 0.3 mmol) afforded 24.1 mg (28% yield) of **48** as a yellow oil.

^1H NMR (CDCl_3 , 500 MHz): 8.91 (dd, $J = 4.0$ Hz, $J = 2.0$ Hz, 1H), 8.15 (dd, $J = 8.5$ Hz, $J = 2.0$ Hz, 1H), 8.10 (d, $J = 9.0$ Hz, 1H), 7.77 (d, $J = 2.0$ Hz, 1H), 7.72 (dd, $J = 9.0$ Hz, $J = 2.0$ Hz, 1H), 7.42 (dd, $J = 8.0$ Hz, $J = 4.0$ Hz, 1H), 4.50 (d, $J = 11.5$ Hz, 1H), 4.42 (d, $J = 11.5$ Hz, 1H), 2.13 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 170.5, 169.6, 150.8, 147.7, 139.7, 136.5, 129.8, 127.9, 126.7, 124.1, 121.6, 81.5, 69.7, 22.1, 20.9 (one carbon overlapped).

HRMS: calc. for $\text{C}_{16}\text{H}_{18}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$, 288.1230, found, 288.1224.



49

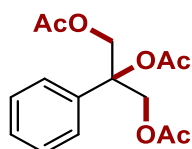
2-(9-phenylacridin-2-yl)propane-1,2-diyl diacetate (49)

Following **Condition A** for 18 h, the highest E_{cell} was set at 2.8 V, the reaction of 2-isopropyl-9-phenylacridine (59.4 mg, 0.2 mmol) afforded 25.6 mg (31% yield) of **49** as a yellow oil.

^1H NMR (CDCl_3 , 500 MHz): 8.27 (d, $J = 9.0$ Hz, 2H), 7.79-7.71 (m, 3H), 7.63-7.57 (m, 4H), 7.48-7.41 (m, 3H), 4.36-4.31 (m, 2H), 2.03 (s, 3H), 1.98 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 170.5, 169.5, 149.0, 148.0, 147.7, 138.4, 135.8, 130.6, 130.5, 130.3, 129.5, 128.6, 128.5, 127.5, 127.0, 126.0, 125.4, 124.7, 123.0, 81.8, 69.7, 22.8, 22.0, 20.8.

HRMS: calc. for $\text{C}_{26}\text{H}_{24}\text{NO}_4^+$ ($\text{M}+\text{H}$) $^+$, 414.1700, found, 414.1692.



50

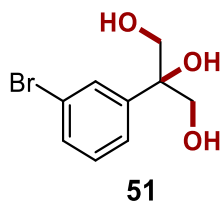
2-phenylpropane-1,2,3-triyl triacetate (50)

Following **Condition A** with a reaction time of 15 h, the reaction of cumene (36.0 mg, 0.3 mmol) afforded 53.8 mg (61% yield) of **50** as a light yellow oil.

^1H NMR (CDCl_3 , 500 MHz): 7.38-7.31 (m, 5H), 4.68 (dd, $J = 18.0$ Hz, $J = 12.0$ Hz, 4H), 2.11 (s, 3H), 2.04 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): 170.3, 169.2, 138.1, 128.7, 128.4, 125.1, 81.6, 64.8, 21.8, 20.8.

HRMS: calc. for $\text{C}_{15}\text{H}_{18}\text{NaO}_6^+$ ($\text{M}+\text{Na}$) $^+$, 317.0996, found, 317.0998.



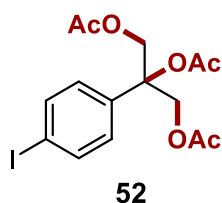
2-(3-bromophenyl)propane-1,2,3-triol (51)

Following **Condition A** with a reaction time of 18 h, the reaction of 1-bromo-3-isopropylbenzene (59.7 mg, 0.3 mmol) afforded 56.3 mg (76% yield) of **51** as a light yellow oil after hydrolysis.

¹H NMR (DMSO-d₆, 500 MHz): 7.65 (s, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 4.93 (s, 1H), 4.65 (t, *J* = 6.0 Hz, 2H), 3.59-3.50 (m, 4H).

¹³C NMR (DMSO-d₆, 125 MHz): 147.6, 129.6, 129.2, 129.0, 125.4, 121.1, 76.2, 66.1.

HRMS: calc. for C₉H₁₁BrNaO₃⁺ (M+Na)⁺, 268.9784, found, 268.9785.



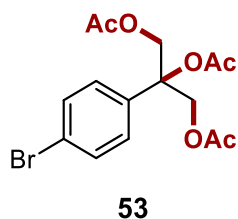
2-(4-iodophenyl)propane-1,2,3-triyl triacetate (52)

Following **Condition A** with a reaction time of 15 h, the reaction of 1-iodo-4-isopropylbenzene (73.8 mg, 0.3 mmol) afforded 40.3 mg (32% yield) of **52** as a yellow solid.

¹H NMR (CDCl₃, 400 MHz): 7.69 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 4.64 (s, 4H), 2.10 (s, 3H), 2.04 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): 170.2, 169.2, 138.0, 137.8, 127.1, 94.3, 81.3, 64.4, 21.8, 20.8.

HRMS: calc. for C₁₅H₁₇INaO₆⁺ (M+Na)⁺, 442.9962, found, 442.9963.



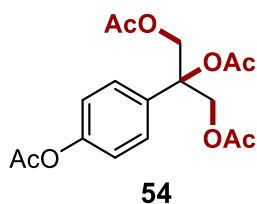
2-(4-bromophenyl)propane-1,2,3-triyl triacetate (53)

Following **Condition A** with a reaction time of 15 h, the reaction of 1-bromo-4-isopropylbenzene (59.7 mg, 0.3 mmol) afforded 70.5 mg (63% yield) of **53** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.49 (d, *J* = 9.0 Hz, 2H), 7.22 (d, *J* = 9.0 Hz, 2H), 4.65 (dd, *J* = 13.5 Hz, *J* = 12.0 Hz, 4H), 2.10 (s, 3H), 2.04 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): 170.2, 169.1, 137.3, 131.8, 126.9, 122.6, 81.2, 64.4, 21.7, 20.8.

HRMS: calc. for C₁₅H₁₇BrNaO₆⁺ (M+Na)⁺, 395.0101, found, 395.0103.



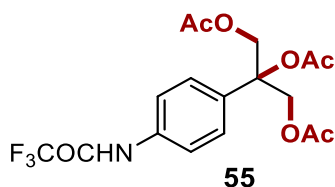
2-(4-acetoxyphenyl)propane-1,2,3-triyl triacetate (54)

Following **Condition A** with a reaction time of 12 h, the reaction of 4-isopropylphenyl acetate (53.4 mg, 0.3 mmol) afforded 38.0 mg (36% yield) of **54** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.36 (d, *J* = 9.0 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 2H), 4.67 (dd, *J* = 15.0 Hz, *J* = 11.5 Hz, 4H), 2.30 (s, 3H), 2.10 (s, 3H), 2.05 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): 170.3, 169.3, 169.2, 150.6, 135.6, 126.4, 121.8, 81.4, 64.7, 21.8, 21.3, 20.8.

HRMS: calc. for C₁₇H₂₀NaO₈⁺ (M+Na)⁺, 375.1050, found, 375.1048.



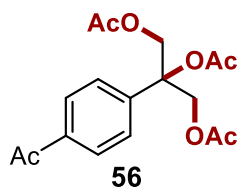
2-(4-(2,2,2-trifluoroacetamido)phenyl)propane-1,1,2,3-tetraol tetraacetate (55)

Following **Condition A** with a reaction time of 12 h, the reaction of 2,2,2-trifluoro-*N*-(4-isopropylphenyl)acetamide (69.3 mg, 0.3 mmol) afforded 55.9 mg (46% yield) of **55** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 8.84 (brs, 1H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.31 (d, *J* = 9.0 Hz, 2H), 4.70-4.64 (m, 4H), 2.12 (s, 3H), 2.05 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): 170.4, 169.6, 155.1 (q, *J* = 37.8 Hz), 135.7, 135.6, 126.0, 120.6, 115.8 (q, *J* = 286.8 Hz), 81.2, 64.5, 21.7, 20.7.

HRMS: calc. for C₁₇H₁₈F₃NNaO₇⁺ (M+Na)⁺, 428.0928, found, 428.0927.



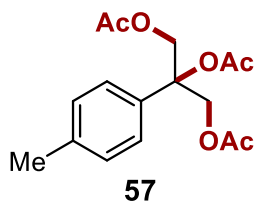
2-(4-acetylphenyl)propane-1,2,3-triyl triacetate (56)

Following **Condition A** with a reaction time of 18 h, the reaction of 1-(4-isopropylphenyl)ethan-1-one (48.6 mg, 0.3 mmol) afforded 39.3 mg (39% yield, 95% pure, containing 2 mg, 2% yield of 2-(4-acetylphenyl)-2-hydroxypropane-1,3-diyl diacetate), 37% yield of **56** as a yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.96 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), 4.69 (dd, *J* = 14.5 Hz, *J* = 11.5 Hz, 4H), 2.60 (s, 3H), 2.13 (s, 3H), 2.05 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): 197.5, 170.2, 169.2, 143.3, 136.9, 128.7, 125.5, 81.2, 64.4, 26.7, 21.8, 20.8.

HRMS: calc. for C₁₇H₂₀NaO₇⁺ (M+Na)⁺, 359.1101, found, 359.1101



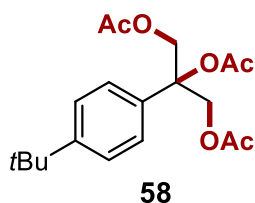
2-(*p*-tolyl)propane-1,2,3-triyl triacetate (**57**)

Following **Condition A** with a reaction time of 12 h, the reaction of *p*-cymene (40.2 mg, 0.3 mmol) afforded 47.1 mg (51% yield) of **57** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.22 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 4.67 (dd, *J* = 15.0 Hz, *J* = 11.5 Hz, 4H), 2.33 (s, 3H), 2.10 (s, 3H), 2.04 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): 170.4, 169.3, 138.2, 135.1, 129.4, 125.0, 81.5, 64.9, 21.9, 21.2, 20.9.

HRMS: calc. for C₁₆H₂₀NaO₆⁺ (M+Na)⁺, 331.1152, found, 331.1153.



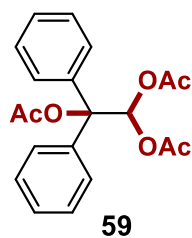
2-(4-(*tert*-butyl)phenyl)propane-1,2,3-triyl triacetate (**58**)

Following **Condition A** with a reaction time of 12 h, the reaction of 1-(*tert*-butyl)-4-isopropylbenzene (52.8 mg, 0.3 mmol) afforded 38.9 mg (37% yield) of **58** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz): 7.37 (d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 4.67 (dd, *J* = 20.0 Hz, *J* = 11.5 Hz, 4H), 2.10 (s, 3H), 2.05 (s, 6H), 1.30 (s, 9H).

¹³C NMR (CDCl₃, 125 MHz): 170.4, 169.3, 151.3, 134.9, 125.6, 124.8, 81.6, 65.0, 34.6, 31.4, 21.9, 20.9.

HRMS: calc. for C₁₉H₂₆NaO₆⁺ (M+Na)⁺, 373.1622, found, 373.1620.



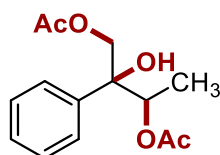
2,2-diphenylethane-1,1,2-triyl triacetate (**59**)

Following **Condition A** with a reaction time of 12 h, the reaction of ethane-1,1-diylidibenzene (54.6 mg, 0.3 mmol) afforded 38.4 mg (36% yield) of **59** as a light yellow solid.

¹H NMR (CDCl₃, 500 MHz): 8.13 (s, 1H), 7.53-7.31 (m, 10H), 2.04 (s, 3H), 2.02 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): 168.4, 168.3, 139.1, 128.7, 128.2, 127.6, 87.3, 85.4, 22.0, 20.9.

HRMS: calc. for C₂₀H₂₀NaO₆⁺ (M+Na)⁺, 379.1152, found, 379.1161.



60

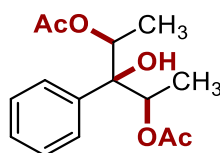
2-hydroxy-2-phenylbutane-1,3-diyl diacetate (**60**)

Following **Condition A** with a reaction time of 18 h, the reaction of *sec*-butylbenzene (40.2 mg, 0.3 mmol) afforded 47.9 mg (60% yield, *anti:syn* = 1:1) of **60** as a colorless oil.

¹H NMR (CDCl₃, 400 MHz, mixture of regioisomers): 7.52-7.45 (m, 4H), 7.39-7.27 (m, 6H), 5.32 (q, *J* = 6.4 Hz, 1H), 5.25 (q, *J* = 6.4 Hz, 1H), 4.55-4.31 (m, 4H), 2.86-2.85 (m, 2H), 2.11 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.11 (d, *J* = 6.4 Hz, 3H), 1.03 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 171.3, 170.4, 170.1, 140.1, 139.6, 128.5, 128.3, 127.9, 127.8, 126.3, 125.6, 77.0, 76.9, 73.9, 72.9, 69.1, 67.9, 21.4, 21.3, 20.93, 20.91, 14.7, 14.2. (one carbon overlapped).

HRMS: calc. for C₁₄H₁₈NaO₅⁺ (*M*+Na)⁺, 289.1046, found, 289.1047.



61

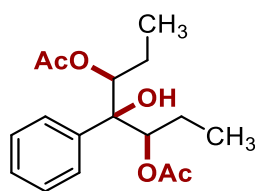
3-hydroxy-3-phenylpentane-2,4-diyl diacetate (**61**)

Following **Condition A** with a reaction time of 12 h, the reaction of pentan-3-ylbenzene (44.4 mg, 0.3 mmol) afforded 44.5 mg (53% yield, *anti:syn* = 14:1) of **61** as a light yellow solid.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.42-7.29 (m, 5.4H), 5.45 (q, *J* = 6.5 Hz, 2H), 5.37 (q, *J* = 6.0 Hz, 0.14H), 2.86 (s, 1H), 2.49 (s, 0.06H), 2.10 (s, 6H), 1.91 (s, 0.44H), 1.14 (d, *J* = 6.5 Hz, 0.45H), 1.03 (d, *J* = 6.5 Hz, 6H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 170.8, 138.6, 128.1, 127.6, 126.5, 79.3, 74.1, 21.4, 15.4.

HRMS: calc. for C₁₅H₂₁O₅⁺ (*M*+H)⁺, 281.1384, found, 281.1385.



62

4-hydroxy-4-phenylheptane-3,5-diyl diacetate (**62**)

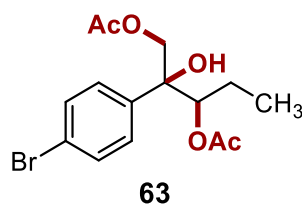
Following **Condition A** with a reaction time of 20 h, the reaction of heptan-4-ylbenzene (52.8 mg, 0.3 mmol) afforded 35.1 mg (38% yield, *anti:syn* = 10:1) of **62** as a light yellow solid.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.41-7.29 (m, 5.9H), 5.31 (dd, *J* = 11.0 Hz, *J* = 2.0 Hz, 2H), 5.03 (dd, *J* = 10.0 Hz, *J* = 2.5 Hz, 0.2H), 2.75 (brs, 1H), 2.15-2.13 (m, 6.9H), 1.55-1.48 (m, 2.3H), 1.43-1.37 (m, 2.2H), 0.76 (t, *J* = 7.5 Hz, 6H), 0.70 (t, *J* = 7.5 Hz, 0.65H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 171.8, 138.6, 128.0, 127.6, 126.7, 80.1,

78.6, 22.9, 21.1, 10.6.

HRMS: calc. for $C_{17}H_{24}NaO_5^+$ ($M+Na$) $^+$, 331.1516, found, 331.1520.



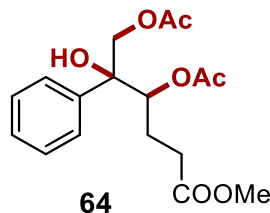
2-(4-bromophenyl)pentane-1,2,3-triol (**63**)

Following **Condition A** with a reaction time of 18 h, the reaction of 1-bromo-4-(pentan-2-yl)benzene (68.1 mg, 0.3 mmol) afforded 53.8 mg (50% yield, *anti:syn* = 1.8:1) of **63** as a light yellow solid.

1H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.51-7.35 (m, 6.6H), 5.22 (dd, J = 11.0 Hz, J = 3.0 Hz, 1H), 5.17 (dd, J = 11.0 Hz, J = 3.0 Hz, 0.56H), 4.49 (d, J = 11.5 Hz, 0.54H), 4.38 (d, J = 11.5 Hz, 1H), 4.26 (d, J = 12.0 Hz, 1H), 4.24 (d, J = 12.5 Hz, 0.54H), 3.03 (s, 0.54H), 2.97 (s, 1H), 2.14 (s, 3H), 2.06 (s, 1.7H), 2.04 (s, 0.7H), 1.98 (s, 3H), 1.66-1.62 (m, 0.57H), 1.57-1.52 (m, 1H), 1.33-1.28 (m, 1H), 1.24-1.19 (m, 0.57H), 0.81 (t, J = 7.5 Hz, 1.7H), 0.75 (t, J = 7.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 171.2, 170.9, 170.4, 139.5, 139.0, 131.6, 131.3, 128.1, 127.6, 122.1, 121.9, 78.1, 77.2, 77.1, 68.8, 67.9, 22.6, 21.7, 21.1, 21.0, 20.9, 20.8, 10.5, 10.2.

HRMS: calc. for $C_{15}H_{19}BrNaO_5^+$ ($M+Na$) $^+$, 381.0308, found, 381.0308.



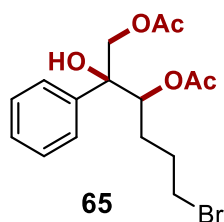
2-hydroxy-6-methoxy-6-oxo-2-phenylhexane-1,3-diyl diacetate (**64**)

Following **Condition A** with a reaction time of 24 h, the reaction of methyl 5-phenylhexanoate (61.8 mg, 0.3 mmol) afforded 37.5 mg (37% yield, *anti:syn* = 2.6:1) of **64** as a light yellow oil.

1H NMR ($CDCl_3$, 500 MHz, mixture of regioisomers): 7.53 (d, J = 8.0 Hz, 0.9H), 7.47 (d, J = 8.0 Hz, 2H), 7.40-7.35 (m, 3H), 7.33-7.29 (m, 1.5H), 5.38 (dd, J = 10.0 Hz, J = 3.0 Hz, 1H), 5.27 (dd, J = 10.0 Hz, J = 2.5 Hz, 0.38H), 4.56 (d, J = 11.5 Hz, 0.4H), 4.39 (d, J = 11.5 Hz, 1H), 4.29 (d, J = 11.5 Hz, 1H), 4.22 (d, J = 11.5 Hz, 0.4H), 3.64 (s, 1.36H), 3.61 (s, 3H), 3.11 (brs, 0.35H), 2.98 (s, 1H), 2.30-2.23 (m, 1.3H), 2.22-2.16 (m, 2H), 2.14 (s, 3H), 2.045-2.041 (m, 2.6H), 1.98 (s, 3H), 1.95 (s, 3H), 1.92-1.85 (m, 1H), 1.71-1.64 (m, 1.6H).

^{13}C NMR ($CDCl_3$, 125 MHz, mixture of regioisomers): 173.6, 173.3, 171.2, 170.8, 170.4, 139.9, 139.4, 128.6, 128.3, 128.0, 127.9, 126.2, 125.6, 77.2, 77.0, 76.0, 75.0, 69.1, 68.1, 51.8, 51.7, 30.5, 30.2, 25.0, 24.0, 21.2, 21.0, 20.9, 20.8.

HRMS: calc. for $C_{17}H_{22}NaO_7^+$ ($M+Na$) $^+$, 361.1258, found, 361.1267.



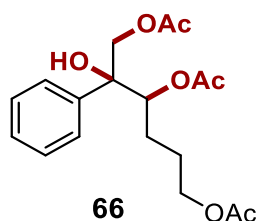
6-bromo-2-hydroxy-2-phenylhexane-1,3-diyl diacetate (**65**)

Following **Condition A** with a reaction time of 24 h, the reaction of (6-bromohexan-2-yl)benzene (72.0 mg, 0.3 mmol) afforded 40.3 mg (36% yield, *anti:syn* = 1:1.2) of **65** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.53-7.30 (m, 9H), 5.34 (dd, *J* = 10.0 Hz, *J* = 2.5 Hz, 0.87H), 5.25 (dd, *J* = 10.5 Hz, *J* = 2.5 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 11.5 Hz, 0.84H), 4.30 (d, *J* = 11.5 Hz, 0.84H), 4.25 (d, *J* = 11.5 Hz, 1H), 3.34-3.24 (m, 4H), 2.92-2.90 (m, 2H), 2.15 (s, 2.6H), 2.05 (s, 6H), 1.98 (s, 2.6H), 1.83-1.69 (m, 6H), 1.49-1.46 (m, 1H), 1.40-1.35 (m, 1H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 171.3, 171.2, 170.8, 170.4, 139.9, 139.4, 128.6, 128.3, 128.0, 127.9, 126.2, 125.4, 77.2, 77.0, 76.1, 74.9, 69.1, 68.0, 33.2, 32.9, 29.1, 28.9, 28.2, 27.4, 21.1, 20.9, 20.8.

HRMS: calc. for C₁₆H₂₁BrNaO₅⁺ (M+Na)⁺, 395.0465, found, 395.0465.



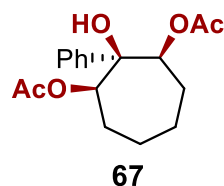
2-hydroxy-2-phenylhexane-1,3,6-triyl triacetate (**66**)

Following **Condition A** with a reaction time of 24 h, the reaction of 5-phenylhexan-1-ol (53.4 mg, 0.3 mmol) afforded 42.2 mg (40% yield, *anti:syn* = 1.8:1) of **66** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.52-7.30 (m, 8.5H), 5.35 (dd, *J* = 10.5 Hz, *J* = 2.5 Hz, 1H), 5.27 (dd, *J* = 10.5 Hz, *J* = 2.5 Hz, 0.5H), 4.54 (d, *J* = 12.0 Hz, 0.5H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 11.5 Hz, 0.5H), 4.03-3.90 (m, 3H), 3.00 (brs, 0.5H), 2.97 (brs, 1H), 2.15 (s, 3H), 2.06 (s, 1.6H), 2.04 (s, 1.6H), 2.00 (s, 1.6H), 1.97 (s, 3H), 1.95 (s, 3H), 1.70-1.63 (m, 2H), 1.58-1.52 (m, 2H), 1.46-1.24 (m, 2H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 171.3, 171.1, 170.8, 170.4, 140.1, 139.5, 128.6, 128.3, 128.0, 127.9, 126.2, 125.6, 77.3, 77.1, 76.5, 75.3, 69.1, 68.0, 64.0, 63.8, 26.0, 25.2, 25.1, 24.8, 21.1, 21.04, 20.97, 20.91, 20.8.

HRMS: calc. for C₁₈H₂₅O₇⁺ (M+H)⁺, 353.1595, found, 353.1594.



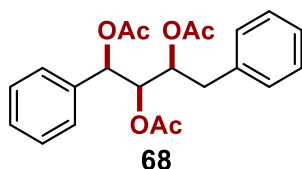
2-hydroxy-2-phenylcycloheptane-1,3-diyl diacetate (**67**)

Following **Condition A** with a reaction time of 12 h, the reaction of phenylcycloheptane (52.2 mg, 0.3 mmol) afforded 40.4 mg (44% yield, *cis*, dr>20:1) of **67** as a white solid.

¹H NMR (CDCl₃, 500 MHz): 7.38 (d, *J* = 8.0 Hz, 2H), 7.31-7.28 (m, 2H), 7.20 (t, *J* = 8.5 Hz, 1H), 5.21 (dd, *J* = 10.5 Hz, *J* = 2.5 Hz, 2H), 2.78 (s, 1H), 2.33-2.25 (m, 2H), 1.84-1.75 (m, 4H), 1.70-1.66 (m, 2H), 1.65 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): 169.5, 143.3, 128.1, 127.2, 125.0, 80.1, 77.7, 27.1, 21.9, 20.7.

HRMS: calc. for C₁₇H₂₂NaO₅⁺ (M+Na)⁺, 329.1359, found, 329.1360.



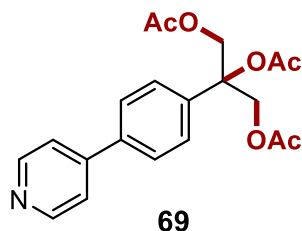
1,4-diphenylbutane-1,2,3-triyl triacetate (**68**)

Following **Condition A** for 18 h, the reaction of 1,4-diphenylbutane (63.0 mg, 0.3 mmol) afforded 38.0 mg (33% yield, dr = 2:1:1) of **68** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 7.37-7.26 (m, 5H), 7.25-7.03 (m, 5H), 6.32-6.00 (m, 1H), 5.47-5.18 (m, 1H), 4.62-4.21 (m, 1H), 2.98-2.45 (m, 1H), 2.40-2.26 (m, 1H), 2.16-2.12 (m, 3H), 2.09-2.02 (m, 6H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 170.8, 170.6, 170.4, 170.2, 169.8, 169.2, 145.8, 145.2, 142.2, 139.9, 138.8, 136.9, 133.3, 132.7, 130.1, 130.0, 128.8, 128.6, 128.3, 127.0, 126.8, 126.6, 71.1, 70.9, 70.1, 69.7, 69.6, 69.5, 69.4, 67.6, 67.5, 34.5, 33.5, 33.4, 33.36, 21.4, 21.3, 21.18, 21.14, 21.0, 20.9.

HRMS: calc. for C₂₂H₂₄NaO₆⁺ (M+Na)⁺, 407.1465, found, 407.1457.



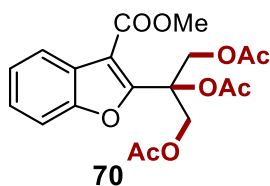
2-(4-(pyridin-4-yl)phenyl)propane-1,2,3-triyl triacetate (**69**)

Following **Condition A** for 18 h, the reaction of 4-(4-isopropylphenyl)pyridine (59.1 mg, 0.3 mmol) afforded 40.1 mg (36% yield) of **69** as a yellow oil.

¹H NMR (CDCl₃, 500 MHz): 8.65 (d, *J* = 6.0 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.52-7.51 (m, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 4.75-4.69 (m, 4H), 2.14 (s, 3H), 2.07 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): 170.2, 169.2, 150.3, 150.0, 147.8, 139.2, 127.3, 126.0, 121.7, 81.3, 64.6, 21.7, 20.8.

HRMS: calc. for C₂₀H₂₂NO₆⁺ (M+H)⁺, 372.1442, found, 372.1435.



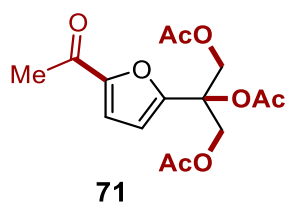
2-(3-(methoxycarbonyl)benzofuran-2-yl)propane-1,2,3-triyl triacetate (70)

Following **Condition A** with HOTf (150 μ L) for 16 h, the highest E_{cell} was set at 1.8 V, the reaction of methyl 2-isopropylbenzofuran-3-carboxylate (65.4 mg, 0.3 mmol) afforded 41.2 mg (35% yield) of **70** as a light yellow oil.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): 7.99-7.97 (m, 1H), 7.52-7.50 (m, 1H), 7.38-7.32 (m, 2H), 4.95 (d, J = 11.5 Hz, 2H), 4.92 (d, J = 11.5 Hz, 2H), 3.96 (s, 3H), 2.08 (s, 3H), 2.03 (s, 6H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 170.3, 169.2, 163.5, 158.4, 153.3, 125.9, 125.8, 124.4, 122.8, 111.6, 110.9, 77.8, 62.2, 52.0, 21.0, 20.8.

HRMS: calc. for $\text{C}_{19}\text{H}_{20}\text{NaO}_9^+$ ($\text{M}+\text{Na}$) $^+$, 415.1000, found, 415.0991.



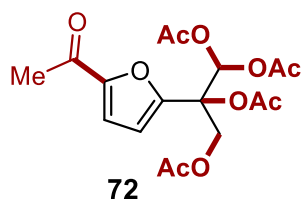
2-(5-acetylfuran-2-yl)propane-1,2,3-triyl triacetate (71)

Following **Condition A** with HOTf (150 μ L) for 15 h, the highest E_{cell} was set at 2.0 V, the reaction of 2-isopropylfuran (33.0 mg, 0.3 mmol) afforded 36.2 mg (37% yield) of **71** as a yellow oil.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): 7.13 (d, J = 3.5 Hz, 1H), 6.15 (d, J = 3.5 Hz, 1H), 4.74 (d, J = 11.5 Hz, 2H), 4.67 (d, J = 11.5 Hz, 2H), 2.45 (s, 3H), 2.08 (s, 3H), 2.06 (s, 6H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 186.6, 170.1, 169.2, 153.9, 152.4, 117.8, 110.9, 78.0, 62.3, 26.2, 21.6, 20.8.

HRMS: calc. for $\text{C}_{15}\text{H}_{18}\text{NaO}_8^+$ ($\text{M}+\text{Na}$) $^+$, 349.0894, found, 349.0885.



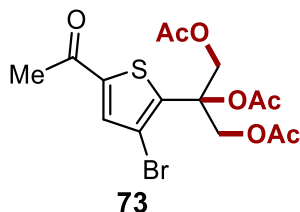
2-(5-acetylfuran-2-yl)propane-1,1,2,3-tetrayl tetraacetate (72)

Following **Condition A** with HOTf (150 μ L) for 15 h, the highest E_{cell} was set at 2.0 V, the reaction of 2-isopropylfuran (33.0 mg, 0.3 mmol) afforded 34.6 mg (30% yield) of **72** as a yellow oil.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): 7.34 (s, 1H), 7.15 (d, J = 3.5 Hz, 1H), 6.54 (d, J = 3.5 Hz, 1H), 4.99 (d, J = 12.0 Hz, 1H), 4.88 (d, J = 12.0 Hz, 1H), 2.45 (s, 3H), 2.11 (s, 3H), 2.10 (s, 6H), 2.08 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 186.5, 170.3, 168.9, 168.0, 152.7, 152.0, 117.6, 111.5, 86.5, 78.7, 61.1, 26.2, 21.4, 20.7.

HRMS: calc. for $\text{C}_{17}\text{H}_{20}\text{NaO}_{10}^+$ ($\text{M}+\text{Na}$) $^+$, 407.0949, found, 407.0940.



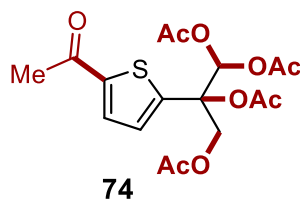
2-(5-acetyl-3-bromothiophen-2-yl)propane-1,2,3-triyl triacetate (**73**)

Following **Condition A** with HOTf (150 μ L) for 15 h, the highest E_{cell} was set at 2.0 V, the reaction of 1-(4-bromo-5-isopropylthiophen-2-yl)ethan-1-one (49.4 mg, 0.2 mmol) afforded 33.7 mg (40% yield) of **73** as a yellow oil.

^1H NMR (CDCl_3 , 500 MHz): 7.51 (s, 1H), 4.82 (d, J = 11.5 Hz, 2H), 4.79 (d, J = 11.5 Hz, 2H), 2.53 (s, 3H), 2.15 (s, 3H), 2.06 (s, 6H).

^{13}C NMR (CDCl_3 , 125 MHz): 189.7, 170.0, 168.8, 142.9, 142.6, 136.2, 107.8, 80.3, 62.5, 26.5, 21.2, 20.8.

HRMS: calc. for $\text{C}_{15}\text{H}_{17}\text{BrNaO}_7\text{S}^+$ ($\text{M}+\text{Na}$) $^+$, 442.9771, found, 442.9763.



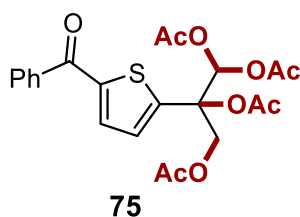
2-(5-acetylthiophen-2-yl)propane-1,1,2,3-tetrayl tetraacetate (**74**)

Following **Condition A** with HOTf (150 μ L) for 12 h, the highest E_{cell} was set at 2.0 V, the reaction of 2-isopropylthiophene (37.8 mg, 0.3 mmol) afforded 54.0 mg (45% yield) of **74** as a yellow oil.

^1H NMR (CDCl_3 , 500 MHz): 7.59 (d, J = 4.0 Hz, 1H), 7.31 (s, 1H), 7.09 (d, J = 4.0 Hz, 1H), 5.02 (d, J = 12.0 Hz, 1H), 4.97 (d, J = 12.0 Hz, 1H), 2.56 (s, 3H), 2.12 (s, 3H), 2.10 (s, 6H), 2.09 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 190.9, 170.3, 168.9, 168.1, 167.9, 146.6, 144.9, 131.9, 126.8, 86.3, 81.6, 62.5, 26.7, 21.7, 20.82, 20.80, 20.75.

HRMS: calc. for $\text{C}_{17}\text{H}_{20}\text{NaO}_9\text{S}^+$ ($\text{M}+\text{Na}$) $^+$, 423.0720, found, 423.0711.



2-(5-benzoylthiophen-2-yl)propane-1,1,2,3-tetrayl tetraacetate (**75**)

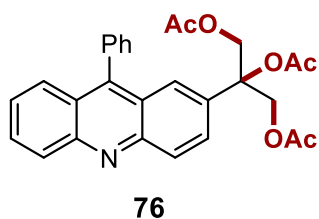
Following **Condition A** with HOTf (150 μ L) for 12 h, the highest E_{cell} was set at 2.0 V, the reaction of (5-isopropylthiophen-2-yl)(phenyl)methanone (69.0 mg, 0.3 mmol) afforded 70.7 mg (51% yield) of **75** as a light yellow oil.

^1H NMR (CDCl_3 , 500 MHz): 7.86-7.84 (m, 2H), 7.62-7.58 (m, 1H), 7.53-7.49 (m, 3H), 7.34 (s, 1H), 7.10 (d, J = 4.0 Hz, 1H), 5.04 (d, J = 12.0 Hz, 1H), 4.99 (d, J = 12.0 Hz, 1H), 2.14 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 188.2, 170.3, 168.9, 168.2, 168.0, 146.8, 144.1, 137.8, 134.2, 132.6,

129.3, 128.6, 126.4, 86.3, 81.6, 62.5, 21.7, 20.8, 20.7.

HRMS: calc. for $C_{22}H_{22}NaO_9S^+$ ($M+Na$)⁺, 485.0877, found, 485.0868.



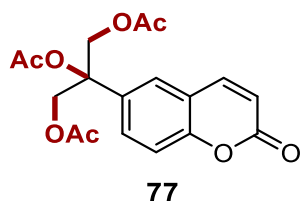
2-(9-phenylacridin-2-yl)propane-1,2,3-triyl triacetate (76)

Following **Condition A** for 18 h, the highest E_{cell} was set at 2.8 V, the reaction of 2-isopropyl-9-phenylacridine (59.4 mg, 0.2 mmol) afforded 26.4 mg (28% yield) of **76** as a yellow oil.

¹H NMR ($CDCl_3$, 500 MHz): 8.30-8.27 (m, 2H), 7.78-7.71 (m, 3H), 7.67-7.58 (m, 4H), 7.47-7.44 (m, 3H), 4.67 (d, $J = 11.5$ Hz, 2H), 4.61 (d, $J = 11.5$ Hz, 2H), 2.07 (s, 3H), 1.98 (s, 6H).

¹³C NMR ($CDCl_3$, 125 MHz): 170.2, 169.3, 149.2, 148.1, 147.8, 135.7, 135.3, 130.6, 130.5, 129.6, 128.7, 127.0, 126.1, 125.5, 124.6, 124.5, 123.7, 123.6, 123.5, 81.9, 64.9, 21.7, 20.8.

HRMS: calc. for $C_{28}H_{26}NO_6^+$ ($M+H$)⁺, 472.1755, found, 472.1746.



2-(2-oxo-2H-chromen-6-yl)propane-1,2,3-triyl triacetate (77)

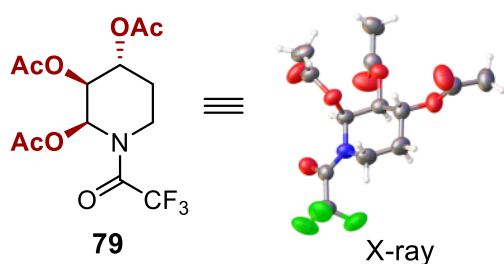
Following **Condition A** with HOTf (150 μ L) for 8 h, the highest E_{cell} was set at 2.5 V, the reaction of 6-isopropyl-2H-chromen-2-one (56.4 mg, 0.3 mmol) afforded 44.5 mg (41% yield) of **77** as a light yellow oil.

¹H NMR ($CDCl_3$, 500 MHz): 7.68 (d, $J = 9.5$ Hz, 1H), 7.50 (dd, $J = 9.0$ Hz, $J = 2.5$ Hz, 1H), 7.43 (d, $J = 2.5$ Hz, 1H), 7.31 (d, $J = 8.5$ Hz, 1H), 6.43 (d, $J = 9.5$ Hz, 1H), 4.68 (s, 4H), 2.10 (s, 3H), 2.02 (s, 6H).

¹³C NMR ($CDCl_3$, 125 MHz): 170.2, 169.2, 160.4, 153.7, 143.3, 134.7, 128.8, 124.7, 118.8, 117.6, 117.4, 80.9, 64.3, 21.8, 20.8.

HRMS: calc. for $C_{18}H_{18}NaO_8^+$ ($M+Na$)⁺, 385.0894, found, 385.0886.

Usually, the trioxygenation products of amides were obtained as rotamers from restricted rotation about the $COCF_3$ amide bond.



1-(2,2,2-trifluoroacetyl)piperidine-2,3,4-triyl triacetate (**79**)

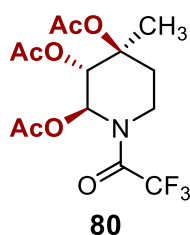
Following **Condition A** for 12 h, the reaction of 2,2,2-trifluoro-1-(piperidin-1-yl)ethan-1-one (90.5 mg, 0.5 mmol) afforded 99.4 mg (56% yield, dr = 10:1:0.6) of **79** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 7.23-6.42 (m, 1H), 5.28-5.23 (m, 1H), 4.98 (s, 1H), 4.56-3.22 (m, 2H), 2.31-2.27 (m, 1H), 2.14 (s, 3H), 2.11-2.07 (m, 1H), 2.05 (s, 3H), 2.02 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 170.2, 169.9, 169.8, 169.6, 169.4, 169.2, 168.4, 167.7, 156.2 (q, *J* = 34.5 Hz), 115.9 (q, *J* = 286.4 Hz), 115.8 (q, *J* = 286.4 Hz), 75.3, 74.8, 73.5, 70.9, 70.0, 67.8, 67.4, 66.5, 66.1, 39.5, 39.3, 37.7, 37.4, 29.4, 28.5, 25.5, 24.5, 20.8, 20.7, 20.4, 20.3.

¹⁹F NMR (CDCl₃, 471 MHz, mixture of isomers): -68.0, -69.1, -69.7.

HRMS: calc. for C₁₃H₁₆F₃NNaO₇⁺ (M+Na)⁺, 378.0771, found, 378.0773.



4-methyl-1-(2,2,2-trifluoroacetyl)piperidine-2,3,4-triyl triacetate (**80**)

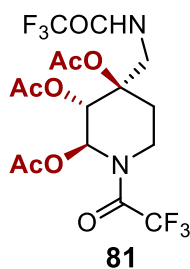
Following **Condition A** for 12 h, the reaction of 2,2,2-trifluoro-1-(4-methylpiperidin-1-yl)ethan-1-one (58.5 mg, 0.3 mmol) afforded 39.8 mg (36% yield, dr > 20:1) of **80** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 6.81-6.42 (m, 1H), 5.76-5.69 (m, 1H), 4.37-3.32 (m, 2H), 2.18-2.13 (m, 1H), 2.06 (s, 9H), 1.93-1.85 (m, 1H), 1.46 (d, *J* = 7.5 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 170.0, 168.9, 168.6, 167.9, 167.7, 156.86 (q, *J* = 36.6 Hz), 156.78 (q, *J* = 36.0 Hz), 116.1 (q, *J* = 286.1 Hz), 77.8, 77.6, 76.7, 74.4, 66.7, 66.4, 37.4 (q, *J* = 3.6 Hz), 35.2, 32.8, 31.4, 22.2, 22.1, 22.0, 20.7, 20.6, 20.54, 20.5, 20.4.

¹⁹F NMR (CDCl₃, 471 MHz, mixture of isomers): -68.3, -69.6.

HRMS: calc. for C₁₄H₁₈F₃NNaO₇⁺ (M+Na)⁺, 392.0928, found, 392.0924.



4-((2,2,2-trifluoroacetamido)methyl)-1-(2,2,2-trifluoroacetyl)piperidine-2,3,4-triyl triacetate (**81**)

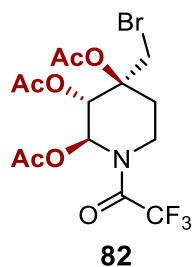
Following **Condition A** for 12 h, the reaction of 2,2,2-trifluoro-*N*-((1-(2,2,2-trifluoroacetyl)piperidin-4-yl)methyl)acetamide (91.8 mg, 0.3 mmol) afforded 86.4 mg (60% yield, dr = 10:1) of **81** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 7.32-7.22 (m, 1H), 7.13-6.82 (m, 1.2H), 4.97-4.96 (m, 0.1H), 1.74-4.71 (m, 1H), 4.44-4.35 (m, 0.5H), 3.84-3.19 (9m, 4H), 2.43-2.35 (m, 1H), 2.12-2.04 (m, 9H), 1.94-1.92 (m, 1.2H).

^{13}C NMR (CDCl_3 , 125 MHz, mixture of isomers): 170.8, 170.7, 170.6, 169.2, 168.9, 168.7, 167.9, 156.1 (q, $J = 37.0$ Hz), 115.9 (q, $J = 286.1$ Hz), 115.8 (q, $J = 286.0$ Hz), 79.0, 78.8, 74.7, 72.6, 71.6, 70.6, 40.9, 40.5, 34.7, 34.2, 27.2, 26.2, 20.5, 20.3.

^{19}F NMR (CDCl_3 , 471 MHz, mixture of isomers): -68.4, -69.1, -69.8, -69.9, -75.8, -75.9, -76.0, -76.1.

HRMS: calc. for $\text{C}_{16}\text{H}_{18}\text{F}_6\text{N}_2\text{NaO}_8^+$ ($\text{M}+\text{Na}$) $^+$, 503.0860, found, 503.0854.



4-(bromomethyl)-1-(2,2,2-trifluoroacetyl)piperidine-2,3,4-triyl triacetate (**82**)

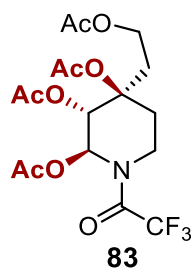
Following **Condition A** for 12 h, the reaction of 1-(4-(bromomethyl)piperidin-1-yl)-2,2,2-trifluoroethan-1-one (82.2 mg, 0.3 mmol) afforded 49.7 mg (37% yield, dr = 7:1) of **82** as a light yellow oil.

^1H NMR (CDCl_3 , 500 MHz, mixture of isomers): 6.86-6.49 (m, 1H), 5.71-5.61 (m, 1H), 4.45-3.31 (m, 4H), 2.56-2.46 (m, 1H), 2.14-2.08 (m, 9H), 1.86-0.79 (m, 1H).

^{13}C NMR (CDCl_3 , 125 MHz, mixture of isomers): 169.6, 168.4, 168.1, 167.6, 167.4, 156.7 (q, $J = 36.8$ Hz), 156.6 (q, $J = 37.2$ Hz), 116.0 (q, $J = 286.2$ Hz), 77.5, 77.3, 76.2, 73.8, 66.0, 65.7, 37.2, 35.0, 34.3, 34.1, 29.9, 28.4, 21.7, 20.7, 20.6, 20.5, 20.46, 20.42.

^{19}F NMR (CDCl_3 , 471 MHz, mixture of isomers): -68.2, -69.6.

HRMS: calc. for $\text{C}_{14}\text{H}_{17}\text{BrF}_3\text{NNaO}_7^+$ ($\text{M}+\text{Na}$) $^+$, 470.0033, found, 470.0026.



4-(2-acetoxyethyl)-1-(2,2,2-trifluoroacetyl)piperidine-2,3,4-triyl triacetate (**83**)

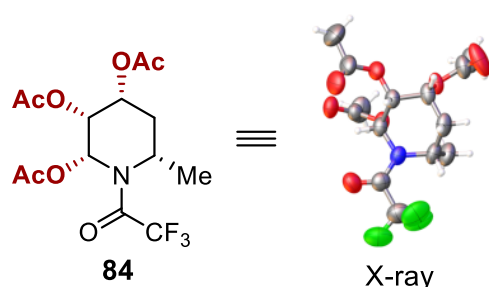
Following **Condition A** for 15 h, the reaction of 2-(1-(2,2,2-trifluoroacetyl)piperidin-4-yl)ethyl acetate (80.1 mg, 0.3 mmol) afforded 43.6 mg (33% yield, dr > 20:1) of **83** as a light yellow oil.

^1H NMR (CDCl_3 , 500 MHz, mixture of isomers): 6.84-6.47 (m, 1H), 5.71-5.63 (m, 1H), 4.40-4.38 (m, 0.5H), 4.11-4.07 (m, 2H), 3.81-3.30 (m, 1.7H), 2.40-2.30 (m, 2H), 2.10-2.02 (m, 13H), 1.93-1.83 (m, 1H).

^{13}C NMR (CDCl_3 , 125 MHz, mixture of isomers): 170.9, 169.8, 168.6, 168.4, 167.7, 167.5, 156.7 (q, $J = 35.8$ Hz), 116.0 (q, $J = 286.2$ Hz), 78.8, 78.6, 76.4, 74.1, 66.3, 65.9, 59.0, 37.1, 34.9, 32.1, 30.8, 29.5, 27.0, 22.0, 21.9, 21.0, 20.7, 20.6, 20.5, 20.4.

^{19}F NMR (CDCl_3 , 471 MHz, mixture of isomers): -68.3, -69.6.

HRMS: calc. for $\text{C}_{17}\text{H}_{22}\text{F}_3\text{NNaO}_9^+$ ($\text{M}+\text{Na}$) $^+$, 464.1139, found, 464.1134.



6-methyl-1-(2,2,2-trifluoroacetyl)piperidine-2,3,4-triyl triacetate (84**)**

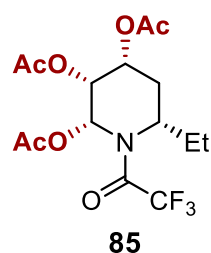
Following **Condition A** for 15 h, the reaction of 2,2,2-trifluoro-1-(2-methylpiperidin-1-yl)ethan-1-one (58.5 mg, 0.3 mmol) afforded 38.7 mg (35% yield, dr = 6:2:1) of **84** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 6.90-6.37 (m, 1H), 5.25-5.05 (m, 1H), 4.98-4.86 (m, 1H), 4.51-4.31 (m, 1H), 2.23-2.18 (m, 1H), 2.12-2.05 (m, 10H), 1.39-1.36 (m, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 170.3, 170.2, 169.8, 169.1, 168.9, 167.6, 156.7 (q, *J* = 36.8 Hz), 115.9 (q, *J* = 286.6 Hz), 115.7 (q, *J* = 286.2 Hz), 78.6, 74.2, 72.2, 71.2, 69.0, 68.4, 48.2, 47.6, 32.7, 29.6, 21.1, 20.9, 20.7, 20.5.

¹⁹F NMR (CDCl₃, 471 MHz, mixture of isomers): -68.1, -70.0.

HRMS: calc. for C₁₄H₁₈F₃NNaO₇⁺ (M+Na)⁺, 392.0928, found, 392.0923.



6-ethyl-1-(2,2,2-trifluoroacetyl)piperidine-2,3,4-triyl triacetate (85**)**

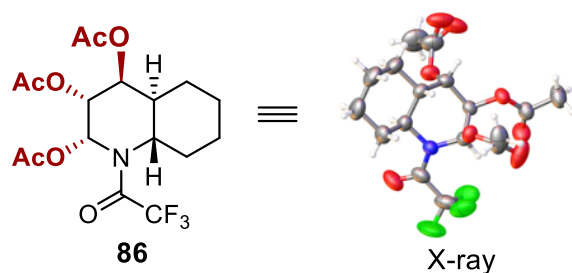
Following **Condition A** for 15 h, the reaction of 1-(2-ethylpiperidin-1-yl)-2,2,2-trifluoroethan-1-one (62.7 mg, 0.3 mmol) afforded 54.0 mg (47% yield, dr = 20:6.6:1) of **85** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 7.20-6.84 (m, 1H), 5.38-5.33 (m, 1H), 5.03 (s, 1H), 4.57-3.93 (m, 1H), 3.26-3.24 (m, 1H), 2.26-2.24 (m, 1H), 2.10-2.09 (m, 6H), 2.07-2.03 (m, 2H), 2.00-1.97 (m, 3H), 1.96-1.94 (m, 1H), 0.90 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 170.0, 169.8, 169.6, 169.2, 168.5, 167.6, 157.3 (q, *J* = 36.1 Hz), 116.0 (q, *J* = 286.4 Hz), 78.3, 74.6, 72.5, 71.8, 68.8, 67.8, 67.2, 66.1, 53.5, 50.8, 29.0, 28.0, 27.7, 27.0, 21.1, 21.0, 20.8, 20.7, 20.6, 20.5, 11.2, 10.5.

¹⁹F NMR (CDCl₃, 471 MHz, mixture of isomers): -67.9, -68.6.

HRMS: calc. for C₁₅H₂₀F₃NNaO₇⁺ (M+Na)⁺, 406.1084, found, 406.1076.



1-(2,2,2-trifluoroacetyl)decahydroquinoline-2,3,4-triyl triacetate (86)

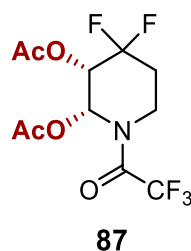
Following **Condition A** for 15 h, the reaction of 2,2,2-trifluoro-1-(octahydroquinolin-1(2H)-yl)ethan-1-one (70.5 mg, 0.3 mmol) afforded 54.0 mg (44% yield, dr = 16:1) of **86** as a light yellow solid.

¹H NMR (CDCl₃, 400 MHz, mixture of isomers): 6.83 (s, 1H), 6.39 (s, 0.07H), 5.05-5.03 (m, 0.09H), 4.99 (s, 1H), 4.90-4.88 (m, 1H), 4.76-4.71 (m, 0.09H), 3.75-3.69 (m, 1.1H), 3.43-3.36 (m, 0.1H), 2.47-2.41 (m, 2H), 2.15-2.14 (m, 3H), 2.07-2.05 (m, 3H), 1.82-1.75 (m, 3.3H), 1.43-1.24 (m, 4.4H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 170.1, 169.0, 168.3, 156.2 (q, *J* = 36.8 Hz), 115.8 (q, *J* = 286.2 Hz), 73.4, 72.8, 72.2, 54.7, 39.5, 31.6, 28.3, 25.7, 25.0, 20.8, 20.7, 20.4.

¹⁹F NMR (CDCl₃, 471 MHz, mixture of isomers): -68.2, -69.1.

HRMS: calc. for C₁₇H₂₂F₃NNaO₇⁺ (M+Na)⁺, 432.1241, found, 432.1236.



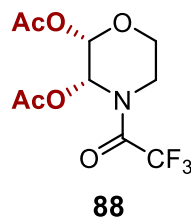
4,4-difluoro-1-(2,2,2-trifluoroacetyl)piperidine-2,3-diyl diacetate (87)

Following **Condition A** for 15 h, the reaction of 1-(4,4-difluoropiperidin-1-yl)-2,2,2-trifluoroethan-1-one (108.5 mg, 0.5 mmol) afforded 63.3 mg (38% yield, dr = 1.5:1) of **87** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 7.25-6.49 (m, 1H), 5.27-5.14 (m, 1H), 4.59-3.96 (m, 1H), 3.69-3.33 (m, 1H), 2.40-2.18 (m, 2H), 2.13-2.10 (m, 6H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 169.4, 168.7, 168.3, 168.0, 156.4 (q, *J* = 37.1 Hz), 118.7 (dd, *J* = 243.1 Hz, 14.9 Hz), 116.7 (dd, *J* = 241.9 Hz, 15.2 Hz), 115.9 (q, *J* = 286.2 Hz), 115.8 (q, *J* = 286.2 Hz), 74.5, 72.7, 68.1 (dt, *J* = 99.5 Hz, 19.8 Hz), 66.3 (ddd, *J* = 76.2 Hz, 36.8 Hz, 23.0 Hz), 37.2 (d, *J* = 255.5 Hz), 36.9 (d, *J* = 250.0 Hz), 33.0 (dt, *J* = 107.6 Hz, 25.0 Hz), 29.8 (dt, *J* = 134.0 Hz, 23.8 Hz), 20.3, 20.2, 20.1.

HRMS: calc. for C₁₁H₁₂F₅NNaO₅⁺ (M+Na)⁺, 356.0528, found, 356.0521.



4-(2,2,2-trifluoroacetyl)morpholine-2,3-diyl diacetate (**88**)

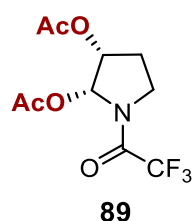
Following **Condition A** for 12 h, the reaction of 2,2,2-trifluoro-1-morpholinoethan-1-one (91.5 mg, 0.5 mmol) afforded 97.2 mg (65% yield, dr = 1.4:1) of **88** as a colorless oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 6.57-6.20 (m, 1H), 6.02-5.95 (m, 1H), 4.24-4.01 (m, 2H), 3.83-3.76 (m, 1.5H), 3.49-3.43 (m, 0.5H), 2.14 (s, 3H), 2.11 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 168.6, 168.5, 156.7 (q, *J* = 36.0 Hz), 115.9 (q, *J* = 286.1 Hz), 88.3, 87.5, 75.0, 72.2, 59.5, 40.9, 37.9, 20.8, 20.7, 20.6, 20.5.

¹⁹F NMR (CDCl₃, 471 MHz, mixture of isomers): -75.8, -75.9.

HRMS: calc. for C₁₀H₁₂F₃NNaO₆⁺ (M+Na)⁺, 322.0509, found, 322.0502.



1-(2,2,2-trifluoroacetyl)pyrrolidine-2,3-diyl diacetate (**89**)

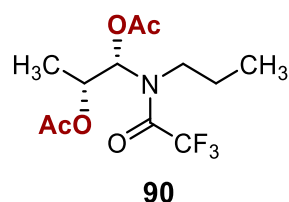
Following **Condition A** for 12 h, the reaction of 2,2,2-trifluoro-1-(pyrrolidin-1-yl)ethan-1-one (50.1 mg, 0.3 mmol) afforded 42.4 mg (50% yield, dr = 3:1) of **89** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 6.71-6.62 (m, 0.3H), 6.54-6.41 (m, 1H), 5.29-5.19 (m, 0.3H), 5.16-5.09 (m, 1H), 3.94-3.49 (m, 2.5H), 2.41-2.10 (m, 2.7H), 2.06-1.99 (m, 7.7H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 169.8, 169.7, 169.5, 169.4, 169.0, 168.6, 156.4 (q, *J* = 38.2 Hz), 156.3 (q, *J* = 37.8 Hz), 115.8 (q, *J* = 286.0 Hz), 115.7 (q, *J* = 285.6 Hz), 115.6 (q, *J* = 285.9 Hz), 84.5, 83.6 (q, *J* = 3.0 Hz), 78.9, 78.2 (q, *J* = 3.2 Hz), 76.3, 74.1, 71.1, 69.4, 45.9, 44.8 (q, *J* = 3.8 Hz), 43.9, 43.5 (q, *J* = 4.2 Hz), 29.2, 27.2, 26.3, 24.0, 20.9, 20.8, 20.6, 20.5, 20.4.

¹⁹F NMR (CDCl₃, 471 MHz, mixture of isomers): -71.6, -71.7, -73.0, -73.2.

HRMS: calc. for C₁₀H₁₂F₃NNaO₅⁺ (M+Na)⁺, 306.0560, found, 306.0551.



1-(2,2,2-trifluoro-N-propylacetamido)propane-1,2-diyl diacetate (**90**)

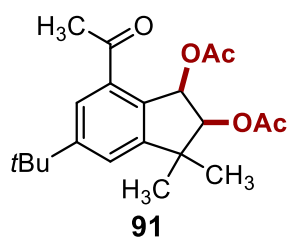
Following **Condition A** for 12 h, the reaction of 2,2,2-trifluoro-*N,N*-dipropylacetamide (59.1 mg, 0.3 mmol) afforded 40.4 mg (43% yield, dr = 2.3:1) of **90** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 6.59-6.38 (m, 1H), 5.41-5.14 (m, 1H), 3.46-3.16 (m, 2H), 2.10-2.07 (m, 3H), 2.03-2.00 (m, 3H), 1.63-1.53 (m, 2H), 1.25-1.20 (m, 3H), 0.92-0.87 (m, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 169.9, 169.7, 169.6, 169.0, 168.7, 168.2, 157.4 (q, *J* = 36.5 Hz), 157.3 (q, *J* = 36.4 Hz), 116.1 (q, *J* = 286.2 Hz), 80.4, 80.3, 68.6, 67.6, 67.2, 67.1, 66.8, 46.8, 46.3, 45.7, 45.3, 24.2, 24.0, 21.1, 20.9, 20.6, 20.3, 16.5, 16.4, 15.8, 15.6, 11.4, 11.2.

¹⁹F NMR (CDCl₃, 471 MHz, mixture of isomers): -67.3, -69.7.

HRMS: calc. for C₁₂H₁₈F₃NNaO₅⁺ (M+Na)⁺, 336.1029, found, 336.1023.



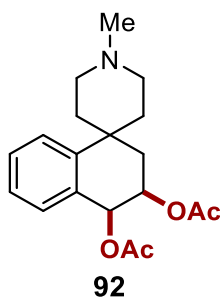
7-Acetyl-5-(tert-butyl)-3,3-dimethyl-2,3-dihydro-1H-indene-1,2-diyl diacetate (91)

Following **Condition A** with a reaction time of 12 h, the reaction of 1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one (73.2 mg, 0.3 mmol) afforded 88.6 mg (82% yield, *anti:syn* = 1:1.3) of **91** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.78 (d, *J* = 1.5 Hz, 0.74H), 7.72 (d, *J* = 1.5 Hz, 1H), 7.42 (d, *J* = 1.5 Hz, 0.75H), 7.36 (d, *J* = 1.5 Hz, 1H), 6.60 (d, *J* = 6.0 Hz, 0.73H), 6.49 (d, *J* = 3.5 Hz, 1H), 5.25-5.24 (m, 1.82), 2.57 (s, 2.4H), 2.56 (s, 3H), 2.08 (s, 6H), 2.05 (s, 2.4H), 2.02 (s, 3H), 1.36-1.35 (m, 18H), 1.34 (s, 2.2H), 1.26 (s, 2.4H), 1.21 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 199.2, 198.7, 170.5, 170.4, 170.1, 169.9, 154.2, 153.9, 152.8, 152.7, 135.0, 134.8, 132.9, 132.3, 126.4, 126.0, 123.7, 123.3, 85.2, 78.8, 78.6, 72.6, 45.5, 44.6, 35.2, 35.1, 31.44, 31.42, 28.5, 28.2, 28.1, 26.4, 25.9, 23.5, 21.1, 21.0, 20.82, 20.79.

HRMS: calc. for C₂₁H₂₈NaO₅⁺ (M+Na)⁺, 383.1829, found, 383.1833.



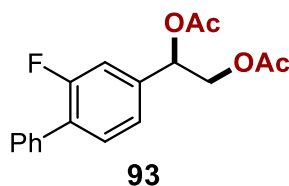
2-hydroxy-2-phenylhexane-1,3,6-triyl triacetate (92)

Following **Condition A** with a reaction time of 12 h, the reaction of 1'-methyl-3,4-dihydro-2H-spiro[naphthalene-1,4'-piperidine] (64.5 mg, 0.3 mmol) afforded 55.6 mg (56% yield, *anti:syn* = 1:1) of **92** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of regioisomers): 7.54-7.47 (m, 1H), 7.40-7.28 (m, 1H), 7.24-7.13 (m, 2H), 6.18-6.16 (m, 1H), 5.20-5.14 (m, 1H), 2.88-2.83 (m, 2H), 2.47-2.28 (m, 7H), 2.16-2.08 (m, 6H), 2.03-1.94 (m, 2H), 1.90-1.76 (m, 1H), 1.70-1.63 (m, 1H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 171.1, 170.7, 170.6, 144.6, 144.0, 133.0, 132.3, 131.0, 129.9, 128.7, 127.3, 127.0, 126.9, 126.8, 126.4, 72.7, 70.3, 69.8, 68.3, 52.0, 51.5, 51.3, 46.7, 46.3, 46.2, 39.8, 39.1, 37.6, 37.0, 36.9, 36.6, 33.1, 29.8, 21.3, 21.27, 21.2.

HRMS: calc. for C₁₉H₂₅NNaO₄⁺ (M+Na)⁺, 354.1676, found, 354.1678.



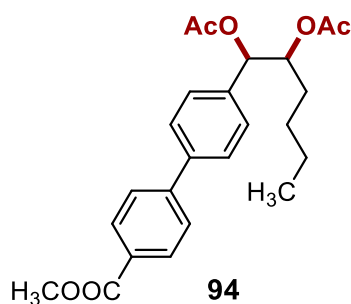
1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethane-1,2-diyl diacetate (93)

Following **Condition A** with HOTf (300 μ L) and a reaction time of 12 h, the reaction of 4-ethyl-2-fluoro-1,1'-biphenyl (60.0 mg, 0.3 mmol) afforded 33.2 mg (35% yield) of **93** as a light yellow oil.

^1H NMR (CDCl_3 , 400 MHz): 7.52 (d, $J = 7.2$ Hz, 2H), 7.46-7.37 (m, 4H), 7.26-7.16 (m, 2H), 6.02 (dd, $J = 8.0$ Hz, $J = 4.8$ Hz, 1H), 4.40-4.27 (m, 2H), 2.15 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (CDCl_3 , 125 MHz): 170.7, 170.1, 159.8 (d, $J = 247.1$ Hz), 138.0 (d, $J = 7.1$ Hz), 135.3, 131.4 (d, $J = 4.2$ Hz), 129.4 (d, $J = 13.8$ Hz), 129.1 (d, $J = 3.0$ Hz), 128.6, 128.0, 122.7 (d, $J = 3.6$ Hz), 114.6 (d, $J = 24.0$ Hz), 72.6, 65.9, 21.1, 20.8.

HRMS: calc. for $\text{C}_{18}\text{H}_{17}\text{FNaO}_4^+$ ($\text{M}+\text{Na}$) $^+$, 339.1003, found, 339.1001.



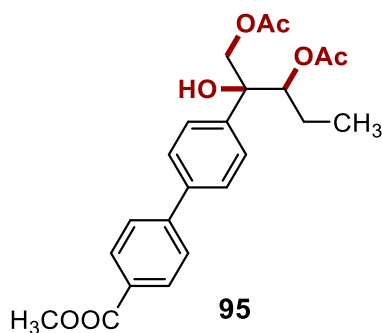
1-(4'-(Methoxycarbonyl)-[1,1'-biphenyl]-4-yl)hexane-1,2-diyl diacetate (94)

Following **Condition A** for 15 h, the reaction of methyl 4'-hexyl-[1,1'-biphenyl]-4-carboxylate (88.8 mg, 0.3 mmol) afforded 71.7 mg (58% yield, *anti:syn* = 1.8:1) of **94** as a light yellow oil.

^1H NMR (CDCl_3 , 500 MHz, mixture of regioisomers): 8.11-8.09 (m, 3H), 7.66-7.60 (m, 7H), 7.46-7.44 (m, 3H), 5.95 (d, $J = 4.5$ Hz, 1H), 5.83 (d, $J = 6.5$ Hz, 0.54H), 5.33-5.29 (m, 0.54H), 5.26-5.23 (m, 1H), 3.95 (s, 1.6H), 1.94 (s, 3H), 2.14 (s, 3H), 2.10 (s, 1.6H), 2.05 (s, 1.7H), 2.04 (s, 3H), 1.57-1.25 (m, 10H), 0.87-0.83 (m, 4.7H).

^{13}C NMR (CDCl_3 , 125 MHz, mixture of regioisomers): 170.6, 170.5, 170.1, 170.0, 167.0, 145.1, 145.0, 140.2, 139.9, 137.1, 136.6, 130.2, 129.1, 128.0, 127.9, 127.5, 127.2, 127.1, 127.0, 76.3, 75.6, 74.8, 74.5, 52.2, 30.3, 29.0, 27.6, 27.3, 22.5, 21.2, 21.1, 21.06, 21.0, 14.0, 13.9.

HRMS: calc. for $\text{C}_{24}\text{H}_{28}\text{NaO}_6^+$ ($\text{M}+\text{Na}$) $^+$, 435.1778, found, 435.1777.



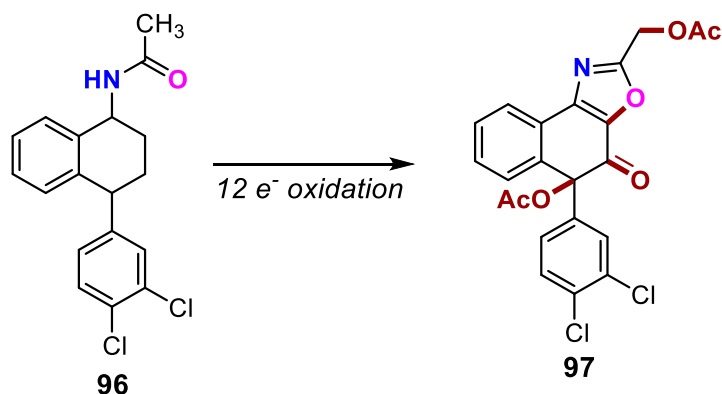
2-hydroxy-2-phenylhexane-1,3,6-triyl triacetate (**95**)

Following **Condition A** with a reaction time of 12 h, the reaction of methyl 4'-(pentan-2-yl)-[1,1'-biphenyl]-4-carboxylate (84.6 mg, 0.3 mmol) afforded 50.9 mg (41% yield, *anti:syn* = 1.8:1) of **95** as a light yellow oil.

¹H NMR (CDCl₃, 400 MHz, mixture of regioisomers): 8.11 (d, *J* = 8.4 Hz, 3.5H), 7.69-7.56 (m, 9.7H), 5.32 (d, *J* = 12.8 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 0.56H), 4.57 (d, *J* = 11.6 Hz, 0.55H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.34-4.28 (m, 1.54H), 3.95 (m, 5H), 3.07 (brs, 0.54H), 3.01 (brs, 1H), 2.16 (s, 3H), 2.09 (s, 1.6H), 2.05 (s, 1.6H), 1.99 (s, 3H), 1.72-1.56 (m, 2H), 1.43-1.32 (m, 1H), 1.85-1.81 (m, 1.8H), 0.78 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz, mixture of regioisomers): 171.3, 171.2, 171.0, 170.5, 167.1, 145.0, 144.9, 140.4, 140.0, 139.4, 139.2, 130.2, 129.1, 129.0, 127.3, 127.0, 126.9, 126.3, 78.3, 77.34, 77.30, 69.1, 68.0, 52.2, 22.7, 21.8, 21.1, 21.0, 20.9, 20.8, 10.5, 10.3.

HRMS: calc. for C₂₃H₂₆NaO₇⁺ (M+Na)⁺, 437.1571, found, 437.1571.



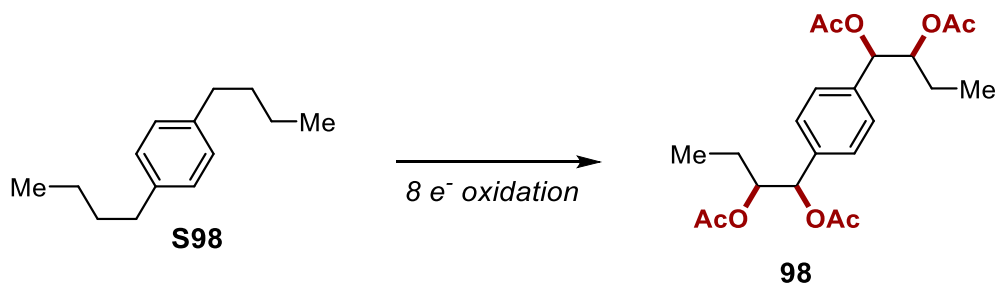
(5-acetoxy-5-(3,4-dichlorophenyl)-4-oxo-4,5-dihydronaphtho[1,2-d]oxazol-2-yl)methyl acetate (**97**)

Following **Condition A** with a reaction time of 20 h: The reaction of *N*-(4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide **96** (100.2 mg, 0.3 mmol) for 18 h afforded 64.7 mg (47% yield) of **97** as a white solid.

¹H NMR (CDCl₃, 500 MHz): 8.10-8.08 (m, 1H), 7.52 (td, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.46 (td, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.31-7.28 (m, 2H), 6.98 (dd, *J* = 8.5 Hz, *J* = 2.0 Hz, 1H), 5.30 (s, 2H), 2.25 (s, 3H), 2.20 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): 180.8, 170.0, 169.5, 165.3, 150.7, 141.9, 141.3, 137.1, 133.7, 133.2, 131.3, 130.7, 129.5, 128.7, 126.9, 125.9, 125.6, 124.8, 84.4, 57.9, 21.0, 20.6.

HRMS: calc. for C₂₂H₁₆Cl₂NO₆⁺ (M+H)⁺, 460.0349, found, 460.0342.



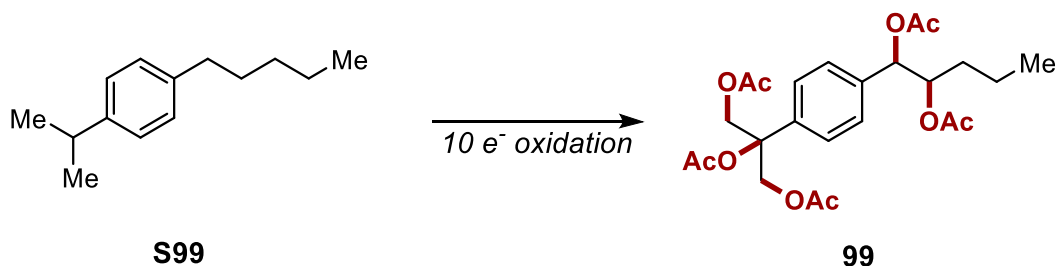
1,4-phenylenebis(butane-1,1,2-triyl) tetraacetate (**98**)

Following **Condition A** for 18 h, the reaction of 1,4-dibutylbenzene (57.0 mg, 0.3 mmol) afforded 44.3 mg (35% yield, dr = 1.9:1) of **98** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 7.33-7.32 (m, 6H), 5.93-5.88 (m, 2H), 5.82-5.78 (m, 1.1H), 5.20-5.17 (m, 1.1H), 5.13-5.09 (m, 2H), 2.13-1.99 (m, 19H), 1.59-1.42 (m, 6.5H), 0.89-0.83 (m, 9.9H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 170.7, 170.65, 170.62, 170.54, 170.5, 170.1, 170.0, 169.9, 137.1, 137.09, 137.05, 136.9, 136.7, 136.6, 127.6, 127.5, 127.47, 127.42, 127.26, 127.22, 127.19, 170.4, 169.3, 138.2, 135.1, 129.4, 125.0, 81.5, 64.9, 21.9, 21.2, 20.9, 76.1, 76.0, 75.9, 75.8, 75.3, 75.2, 23.7, 22.6, 22.4, 22.3, 21.14, 21.12, 20.9, 20.8, 9.95, 9.90, 9.87, 9.6, 9.5.

HRMS: calc. for C₂₂H₃₀NaO₈⁺ (M+Na)⁺, 445.1833, found, 445.1824.



2-(4-(1,2-diacetoxypentyl)phenyl)propane-1,2,3-triyl triacetate (**99**)

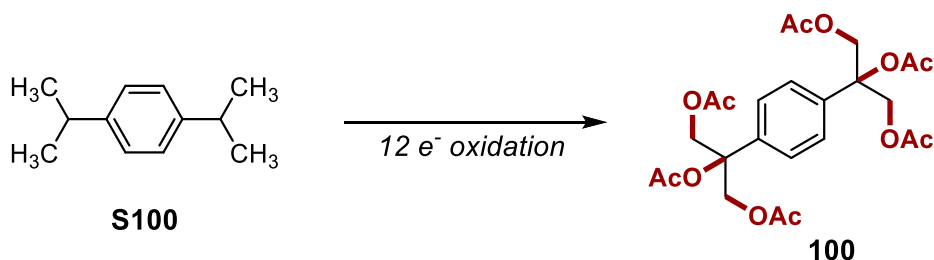
Following **Condition A** for 18 h, the reaction of 1-isopropyl-4-pentylbenzene (57.0 mg, 0.3 mmol) afforded 60.6 mg (42% yield, dr = 1.2:1) of **99** as a light yellow oil.

¹H NMR (CDCl₃, 500 MHz, mixture of isomers): 7.35-7.28 (m, 7.37H), 5.90 (d, *J* = 4.5 Hz, 1H), 5.79 (d, *J* = 6.5 Hz, 0.84H), 5.27-5.23 (m, 0.84H), 5.20-5.17 (m, 1H), 4.69-4.62 (m, 7.5H), 2.11-2.10 (m, 11H), 2.03-2.01 (m, 13H), 1.99-1.98 (m, 5H), 1.49-1.42 (m, 3H), 1.35-1.28 (m, 5H), 0.87-0.83 (m, 6H).

¹³C NMR (CDCl₃, 125 MHz, mixture of isomers): 170.7, 170.4, 170.3, 170.0, 169.9, 169.2, 138.4, 138.1, 137.2, 136.7, 127.6, 127.5, 125.4, 125.2, 81.5, 76.0, 75.4, 74.5, 74.3, 64.8, 64.7, 32.7, 31.2, 21.8, 21.2, 21.1, 21.0, 20.9, 20.8, 18.8, 18.5, 13.9, 13.8.

HRMS: calc. for C₂₄H₃₂NaO₁₀⁺ (M+Na)⁺, 503.1888, found, 503.1880.

Hexaoxidation of 1,4-diisopropylbenzene



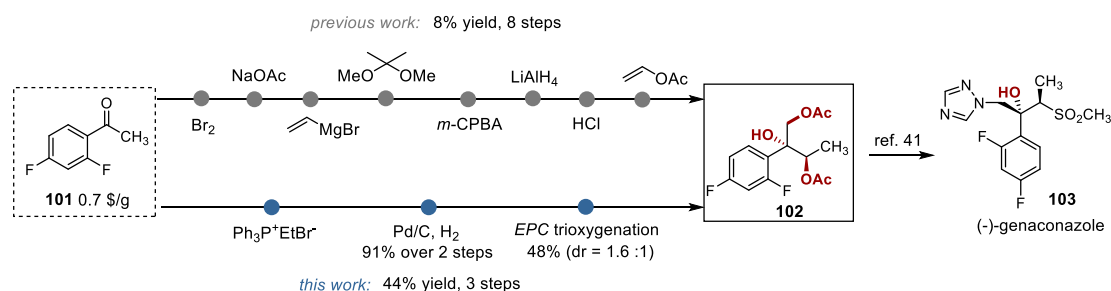
Following **Condition A** with a reaction time of 18 h: The reaction of 1,4-diisopropylbenzene **S100** (48.6 mg, 0.3 mmol) for 15 h afforded 68.9 mg (45% yield) of **100** as a yellow oil.

^1H NMR (CDCl_3 , 500 MHz): 7.34 (s, 4H), 4.67 (dd, $J = 20.0$ Hz, $J = 11.5$ Hz, 8H), 2.11 (s, 6H), 2.04 (s, 12H).

^{13}C NMR (CDCl_3 , 125 MHz): 170.3, 169.2, 138.2, 125.5, 81.4, 64.7, 21.8, 20.8.

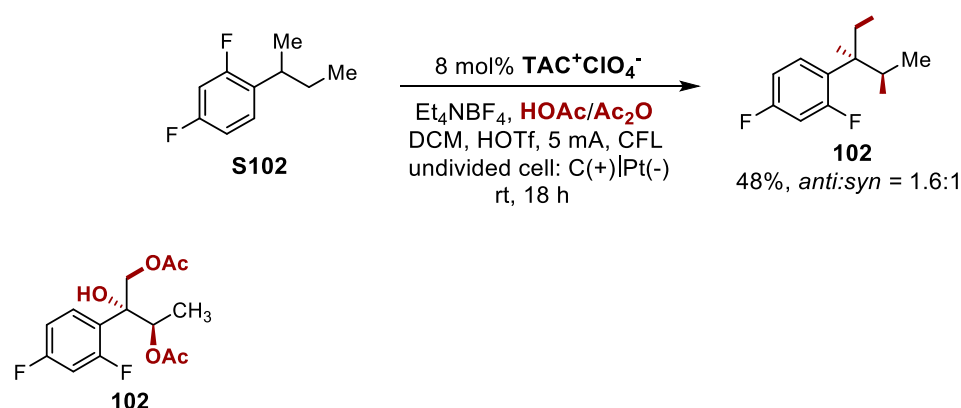
HRMS: calc. for $\text{C}_{24}\text{H}_{30}\text{NaO}_{12}^+$ ($\text{M}+\text{Na}$) $^+$, 533.1629, found, 533.1637.

Multiple contiguous C–H oxygenations facilitate rapid access to intermediate of genaonazole.



m-CPBA, meta-chloroperbenzoic acid; Ph, phenyl; Et, ethyl.

1-(*sec*-butyl)-2,4-difluorobenzene was synthesized from 1-(2,4-difluorophenyl)ethan-1-one via Wittig reaction and palladium-catalyzed hydrogenation in 91% yield in two steps.



2-(2,4-difluorophenyl)-2-hydroxybutane-1,3-diyl diacetate (**102**)

Following **Condition A** with a reaction time of 18 h: The reaction of 1-(*sec*-butyl)-2,4-difluorobenzene (51.0 mg, 0.3 mmol) for 18 h afforded 43.5 mg (48% yield, *anti:syn* = 1.6 : 1) of **102** as a yellow oil.⁴¹

^1H NMR (CDCl_3 , 500 MHz, mixture of regioisomers): 7.68–7.58 (m, 1.6H), 6.91–6.85 (m, 1.6H),

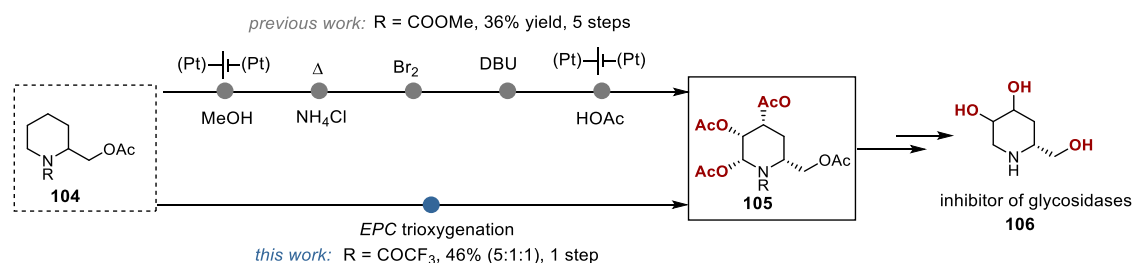
6.80-6.74 (m, 1.6H), 5.46 (qd, $J = 6.5$ Hz, $J = 2.0$ Hz, 1H), 5.34 (q, $J = 6.5$ Hz, 0.64H), 4.56-4.43 (m, 3.4H), 3.61 (s, 0.6H), 3.44 (s, 1H), 2.10 (s, 3H), 1.94 (s, 2H), 1.90 (s, 3H), 1.97 (s, 2H), 1.22 (d, $J = 6.5$ Hz, 2H), 1.01 (d, $J = 6.0$ Hz, 3H).

^{13}C NMR (CDCl_3 , 125 MHz, mixture of regioisomers): 171.93, 171.91, 170.2, 170.0, 162.8 (dd, $J = 248.0$ Hz, $J = 11.8$ Hz), 162.5 (dd, $J = 247.9$ Hz, $J = 11.4$ Hz), 159.6 (dd, $J = 247.5$ Hz, $J = 11.5$ Hz), 159.0 (dd, $J = 247.0$ Hz, $J = 11.9$ Hz), 130.6 (dd, $J = 9.4$ Hz, $J = 5.8$ Hz), 130.3 (dd, $J = 9.5$ Hz, $J = 5.8$ Hz), 123.0 (dd, $J = 12.8$ Hz, $J = 3.9$ Hz), 122.9 (dd, $J = 13.0$ Hz, $J = 3.8$ Hz), 111.5 (dd, $J = 20.6$ Hz, $J = 3.4$ Hz), 111.0 (dd, $J = 20.5$ Hz, $J = 3.5$ Hz), 104.3 (dd, $J = 28.2$ Hz, $J = 25.2$ Hz), 104.2 (dd, $J = 27.2$ Hz, $J = 25.1$ Hz), 77.0 (d, $J = 4.8$ Hz), 76.8 (d, $J = 4.8$ Hz), 72.6 (d, $J = 4.8$ Hz), 72.5 (d, $J = 4.8$ Hz), 68.9 (d, $J = 5.5$ Hz), 68.0 (d, $J = 5.5$ Hz), 21.2, 20.9, 20.7, 14.6, 14.5.

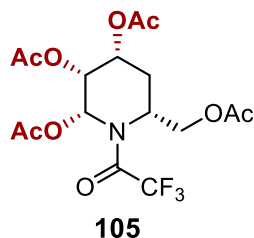
^{19}F NMR (CDCl_3 , 471 MHz): -107.1, -107.9, -110.7, -110.9.

MS (70 eV): m/z (%): 242 ($\text{M}^+ - 60$, 2), 173.1 (100).

Rapid access to an intermediate for synthesis of a glycosidase inhibitor.



DBU, 1,8-Diazabicyclo[5.4.0]undecane-7-ene.



(2*R*,3*R*,4*R*,6*R*)-6-(acetoxymethyl)-1-(2,2,2-trifluoroacetyl)piperidine-2,3,4-triyl triacetate (105)

Following **Condition A** for 15 h, the reaction of (*S*)-(1-(2,2,2-trifluoroacetyl)piperidin-2-yl)methyl acetate (75.9 mg, 0.3 mmol) afforded 58.9 mg (46% yield, dr = 5:1:1) of **105** as a light yellow oil.

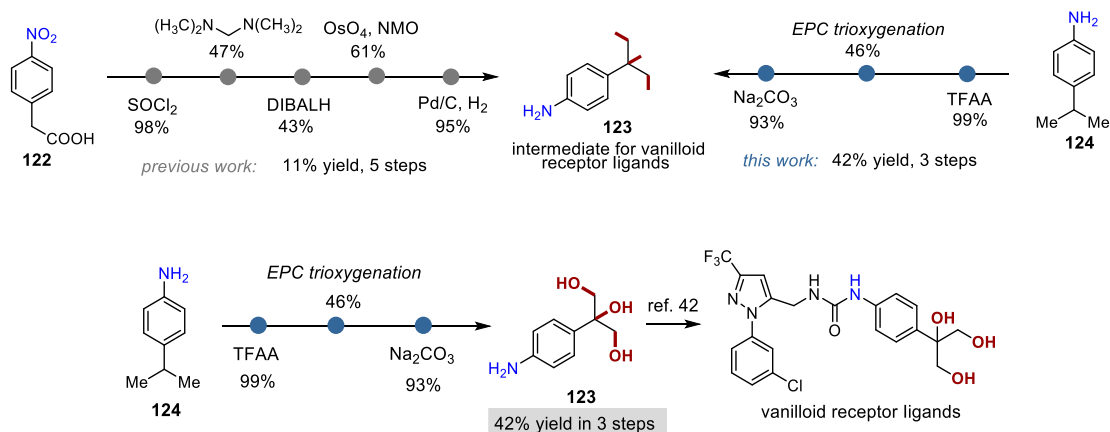
^1H NMR (CDCl_3 , 500 MHz, mixture of isomers): 7.17-6.45 (m, 1H), 5.39-4.81 (m, 3H), 4.55-4.28 (m, 2H), 2.27-2.18 (m, 1H), 2.12-2.00 (m, 13H).

^{13}C NMR (CDCl_3 , 125 MHz, mixture of isomers): 170.5, 169.7, 169.5, 169.3, 168.6, 168.3, 167.6, 157.4 (q, $J = 36.8$ Hz), 115.9 (q, $J = 286.6$ Hz), 74.2, 72.4, 68.0, 67.5, 66.3, 65.3, 64.3, 64.2, 49.7, 48.1, 47.0, 27.6, 24.5, 21.0, 20.9, 20.6, 20.4, 20.3.

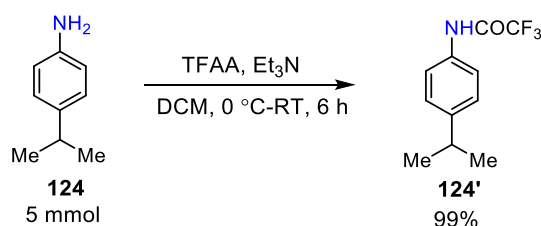
^{19}F NMR (CDCl_3 , 471 MHz, mixture of isomers): -68.2, -68.8.

HRMS: calc. for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{NNaO}_9^+$ ($\text{M} + \text{Na}$)⁺, 450.0982, found, 450.0977.

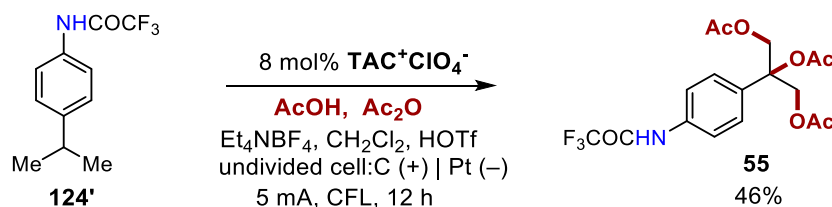
Rapid access to intermediate for vanilloid receptor ligands.



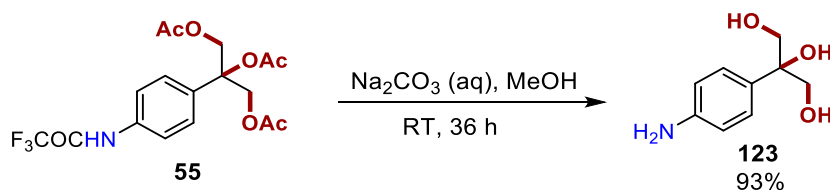
DIBAL-H, diisobutylaluminium hydride; NMO, *N*-methylmorpholine-*N*-oxide; TFAA, trifluoroacetic anhydride.



To a 100 mL round-bottom flask cooled to 0 °C were added 4-isopropylaniline **124** (675 mg, 5 mmol), Et_3N (1.01 g, 10 mmol, 2.0 equiv.) and DCM (20 mL). Trifluoroacetic anhydride (1.26 g, 6 mmol, 1.2 equiv.) was then added dropwise. The mixture was stirred at room temperature for 6 h, partitioned between water (50 mL) and CH_2Cl_2 (50 mL), and then quenched with a saturated solution of sodium carbonate (10 mL). The organic layer was isolated, and the aqueous layer was extracted with CH_2Cl_2 (3x50 mL). The organic layers were combined, washed twice with sodium carbonate (10 mL) and twice with HCl (aq) (10 mL), then dried over MgSO_4 and concentrated via rotary evaporation to furnish the product **124'** as a light yellow solid (1.14 g, 4.95 mmol, 99% yield), which was directly used in the next step.



Following **Condition A**, the reaction of 2,2,2-trifluoro-*N*-(4-isopropylphenyl)acetamide (69.3 mg, 0.3 mmol) for 12 h afforded 55.9 mg (46% yield) of **55** as a yellow oil.



2-(4-aminophenyl)propane-1,2,3-triol (**123**)

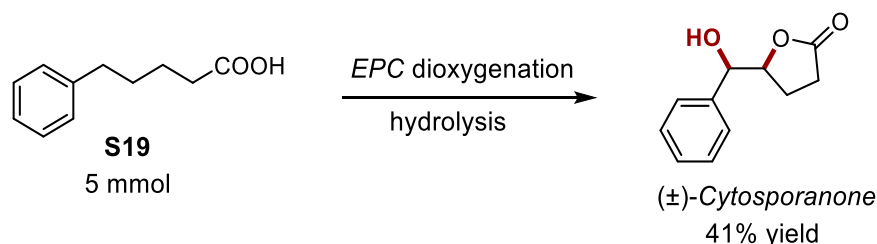
55 (55.9 mg) was added to a mixture of saturated solution of sodium carbonate (10 mL) and MeOH (10 mL), and the mixture was stirred at room temperature for 36 h. The mixture was concentrated in vacuo to remove MeOH and water, and the mixture was dissolved in MeOH (1.0 mL) and passed through a short silica gel column (5 cm) with EtOAc/MeOH=1:1 (50 mL). The eluent solution was concentrated in vacuo to afford 23.4 mg (93% yield) of **123** as a yellow oil.⁴³

¹H NMR (DMSO-d₆, 500 MHz): 7.11 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 2H), 4.86 (brs, 1H), 4.44-4.39 (m, 3H), 3.58 (s, 1H), 3.53-3.80 (m, 4H).

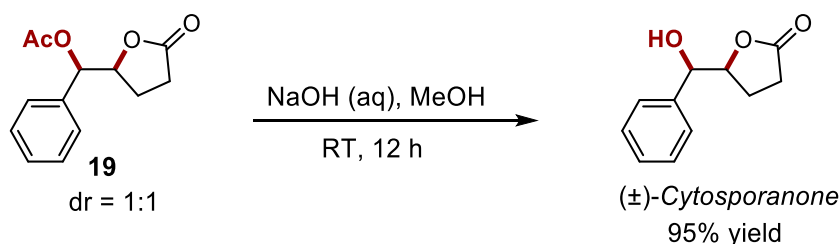
¹³C NMR (DMSO-d₆, 125 MHz): 147.4, 132.1, 127.1, 113.6, 76.0, 66.8.

HRMS: calc. for C₉H₁₃NNaO₃⁺ (M+Na)⁺, 206.0788, found, 206.0788.

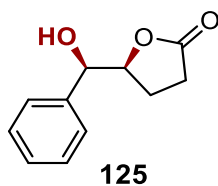
Rapid access to Cytosporanone



Following **Condition C** with Ni plate as cathode, the reaction of 5-phenylpentanoic acid **S19** (890 mg, 5 mmol) for 48 h afforded 503 mg (43% yield) of 5-oxotetrahydrofuran-2-yl(phenyl)methyl acetate **19** (dr = 1:1) as a yellow oil.

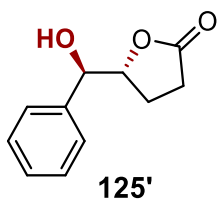


19 (503 mg) was added to a mixture of 3 M NaOH (aq) (50 mL) and MeOH (50.0 mL), and the mixture was stirred at room temperature for 12 h. The mixture was then poured into water and extracted with EtOAc (3×20 mL), and the combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. Following concentration in vacuo, the crude product was purified by chromatography (eluent: petroleum ether:ethyl acetate = 2:1) to afford 202 mg of *syn* regioisomer and 192 mg *anti* regioisomer as white solid.⁵²



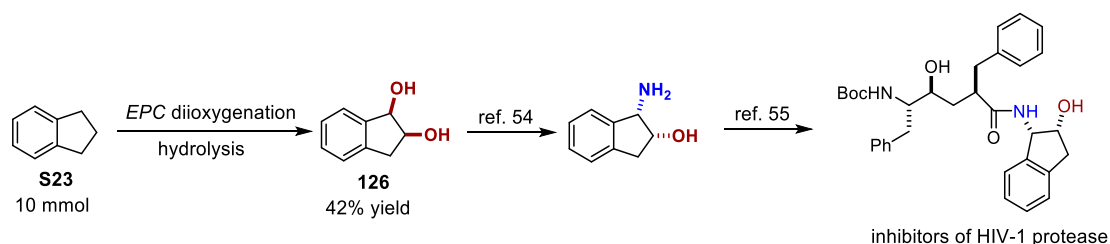
syn: $^1\text{H NMR}$ (CDCl_3 , 500 MHz): 7.41-7.30 (m, 5H), 5.11 (dd, $J = 15.0$ Hz, $J = 12.0$ Hz, 1H), 4.71-4.68 (m, 1H), 3.16 (brs, 1H), 2.59-2.52 (m, 1H), 2.46-2.40 (m, 1H), 2.39-2.24 (m, 1H), 1.95-1.88 (m, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 178.2, 138.7, 128.7, 128.1, 126.2, 83.6, 73.4, 28.7, 20.7.



anti: $^1\text{H NMR}$ (CDCl_3 , 500 MHz): 7.41-7.32 (m, 5H), 4.69-4.62 (m, 2H), 3.04 (brs, 1H), 2.46-2.42 (m, 2H), 2.04-1.99 (m, 2H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 177.2, 138.6, 128.8, 128.7, 127.1, 83.6, 76.4, 28.6, 24.1.

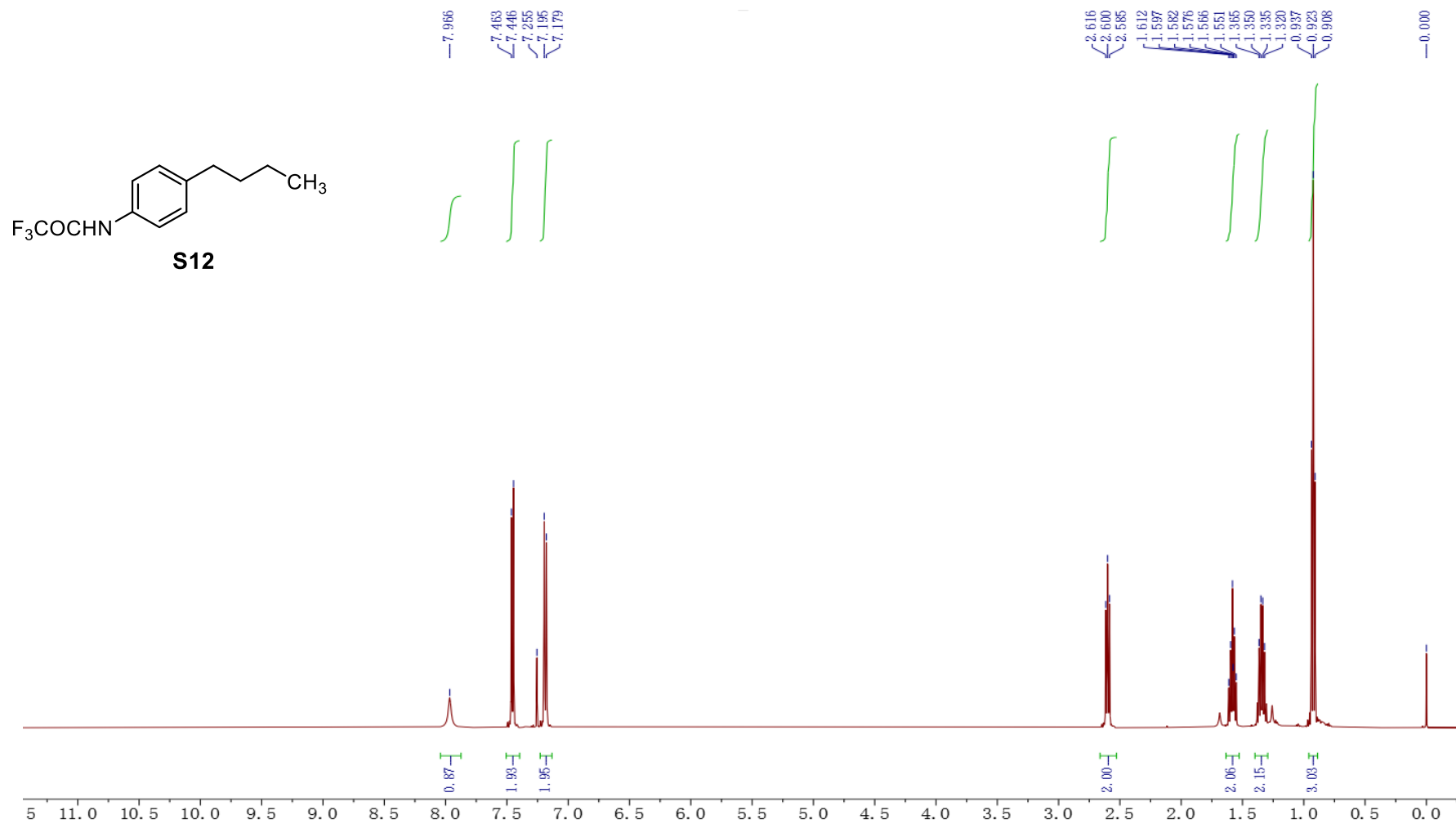


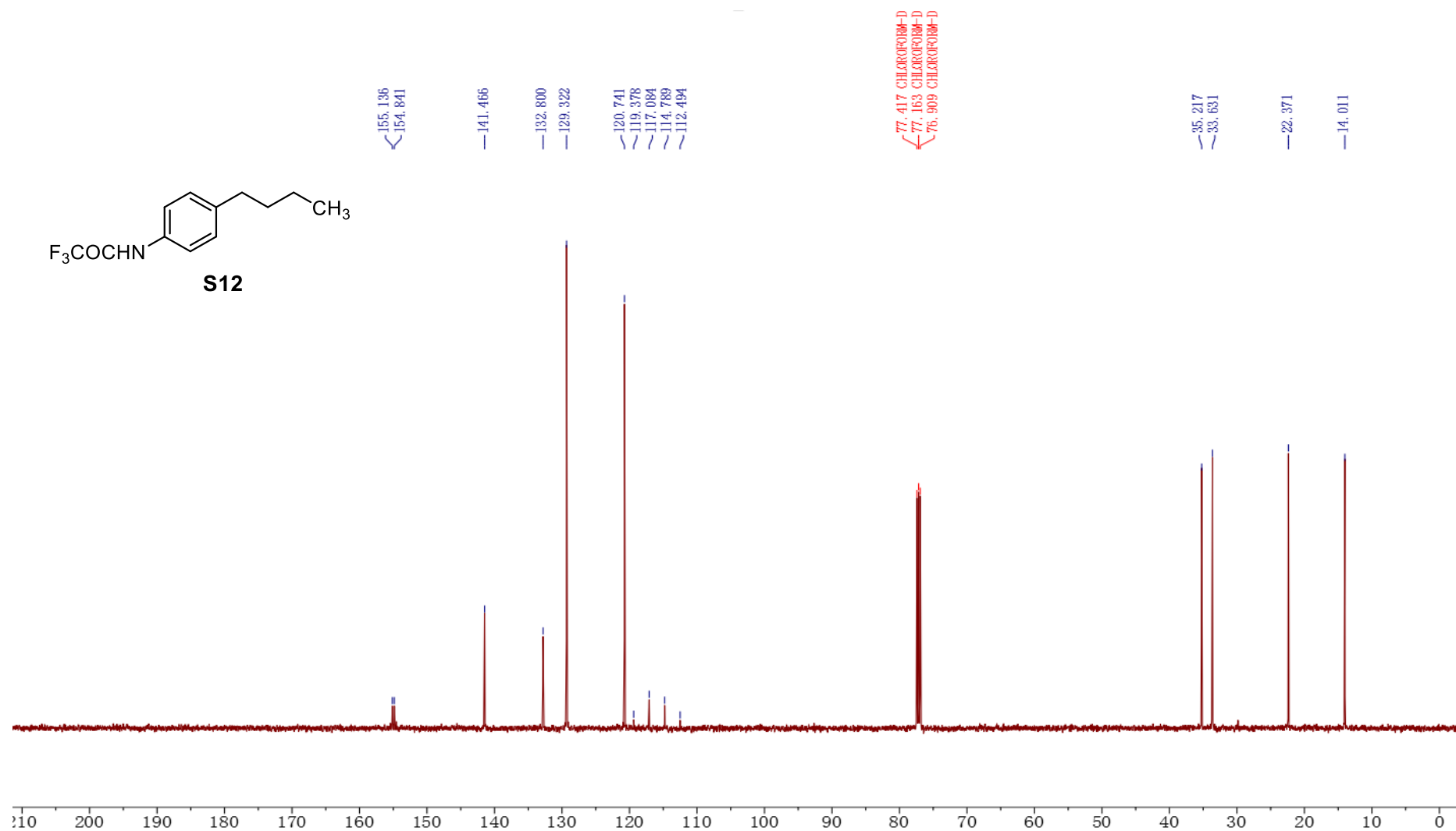
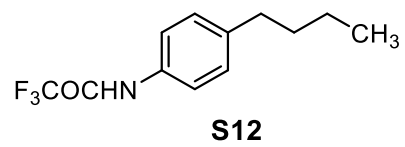
Following **Condition C** with a reaction time of 48 h and Ni plate as cathode, the reaction of 2,3-dihydro-1H-indene **S23** (1.18 g, 10.0 mmol) afforded 1.05 g (45% yield) of **23** as a light yellow oil. **23** (1.05 g) was added to a mixture of saturated solution of sodium carbonate (50 mL) and MeOH (50.0 mL), and the mixture was stirred at 60 °C for 12 h. The mixture was then poured into water and extracted with EtOAc (3×20 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . Following concentration in vacuo, the crude product was purified by chromatography (eluent: petroleum ether:ethyl acetate = 2:1) to afford 631 mg **126** (93%, *anti:syn* = 7:1) as a yellow solid.⁵³

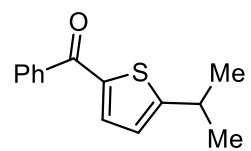
$^1\text{H NMR}$ (CD_3OD , 500 MHz, mixture of regioisomers): 7.38-7.33 (m, 1.12H), 7.23-7.17 (m, 3.4H), 4.89-4.86 (m, 1.12H), 4.04-4.37 (m, 0.15H), 4.27-4.23 (m, 1H), 3.21 (dd, $J = 16.0$ Hz, $J = 7.0$ Hz, 1H), 3.04 (dd, $J = 16.0$ Hz, $J = 6.0$ Hz, 0.15H), 2.92 (dd, $J = 16.0$ Hz, $J = 4.5$ Hz, 0.15H), 2.72 (dd, $J = 16.0$ Hz, $J = 7.0$ Hz, 1H).

$^{13}\text{C NMR}$ (CD_3OD , 125 MHz, mixture of regioisomers): 143.9, 141.6, 140.7, 129.4, 129.3, 128.0, 127.8, 126.1, 126.0, 125.8, 125.4, 82.5, 81.6, 76.8, 74.7, 39.1, 38.9. (one carbon overlapped)

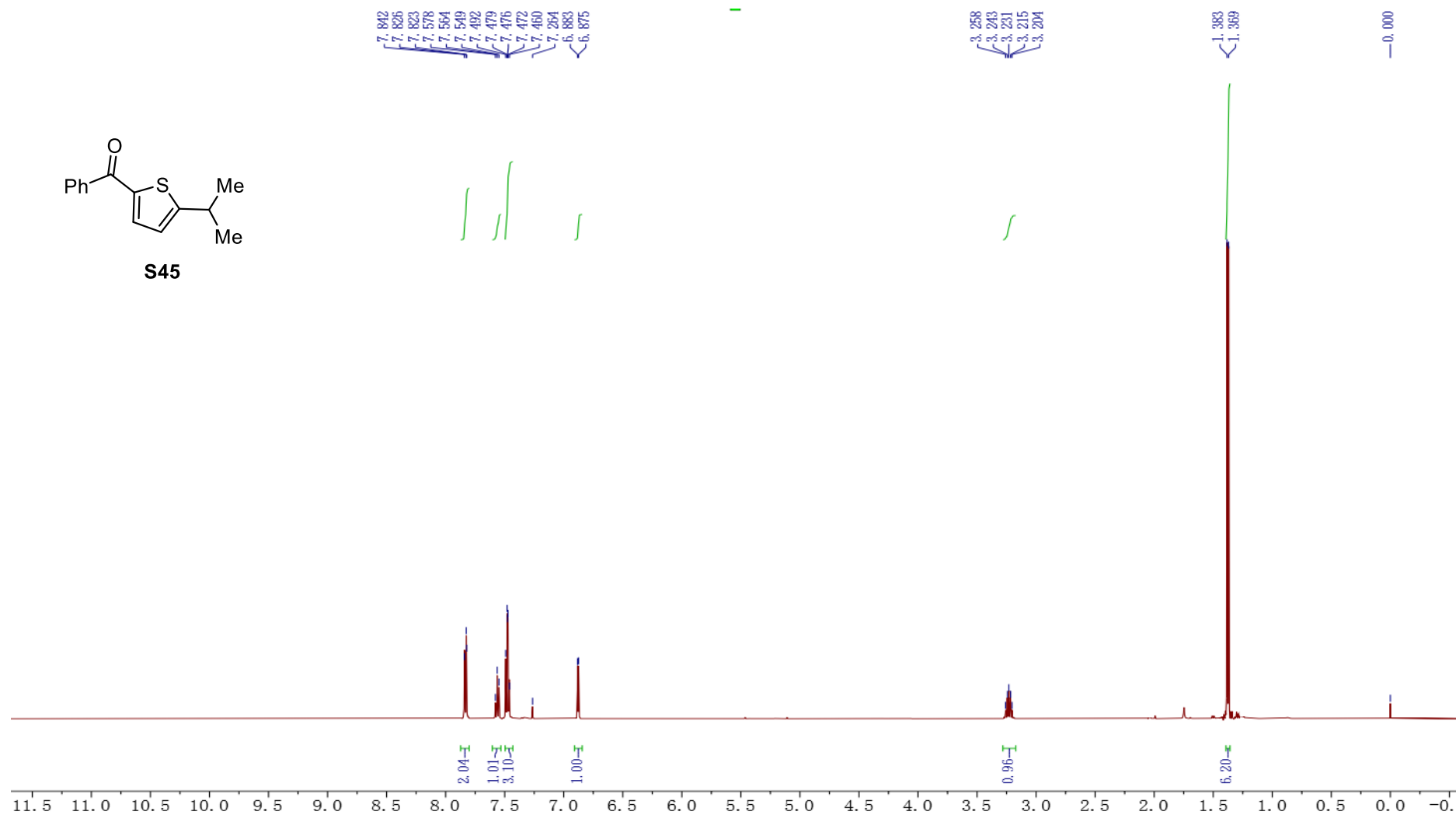
3. NMR Spectra

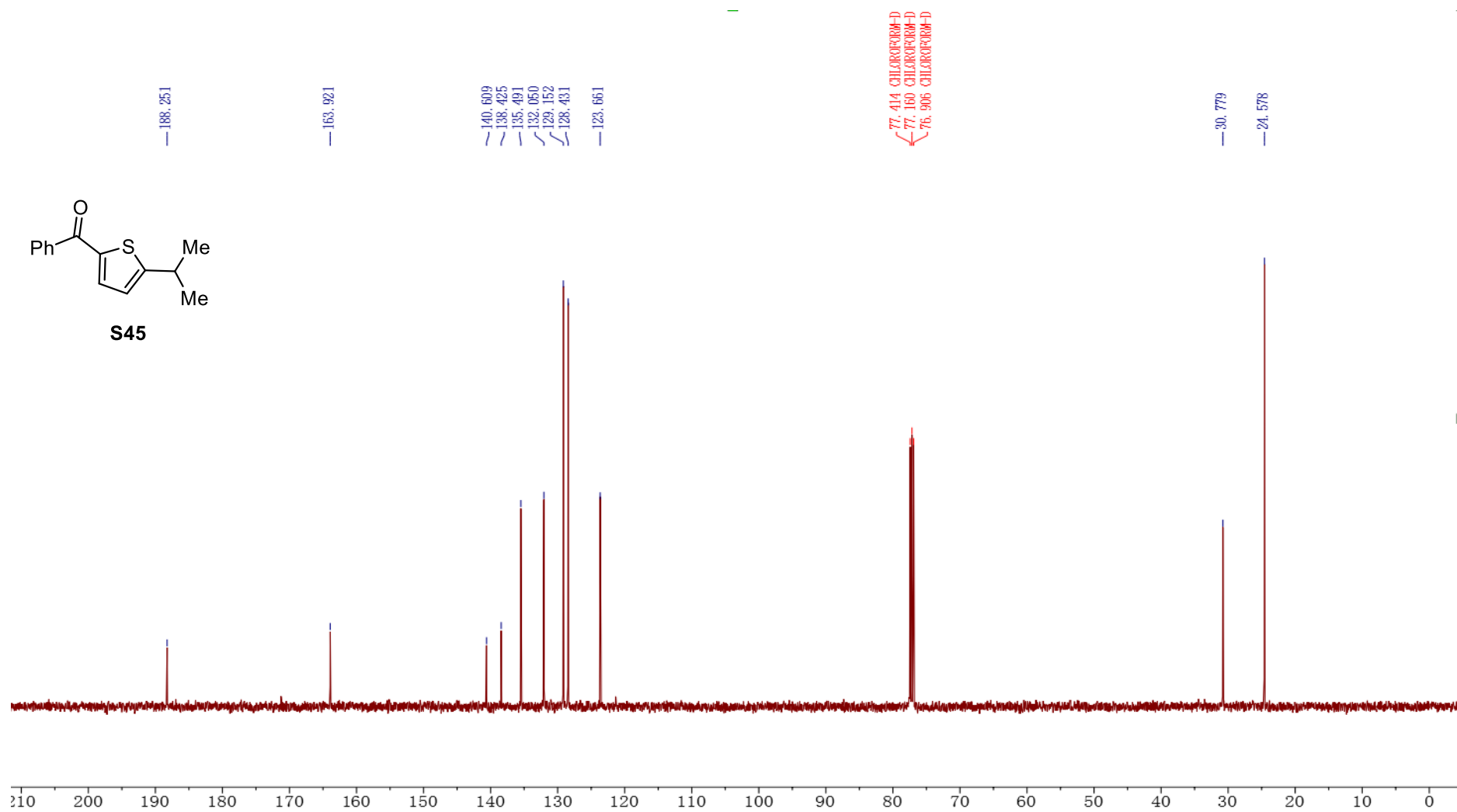


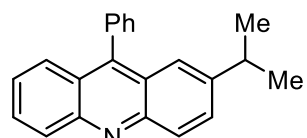




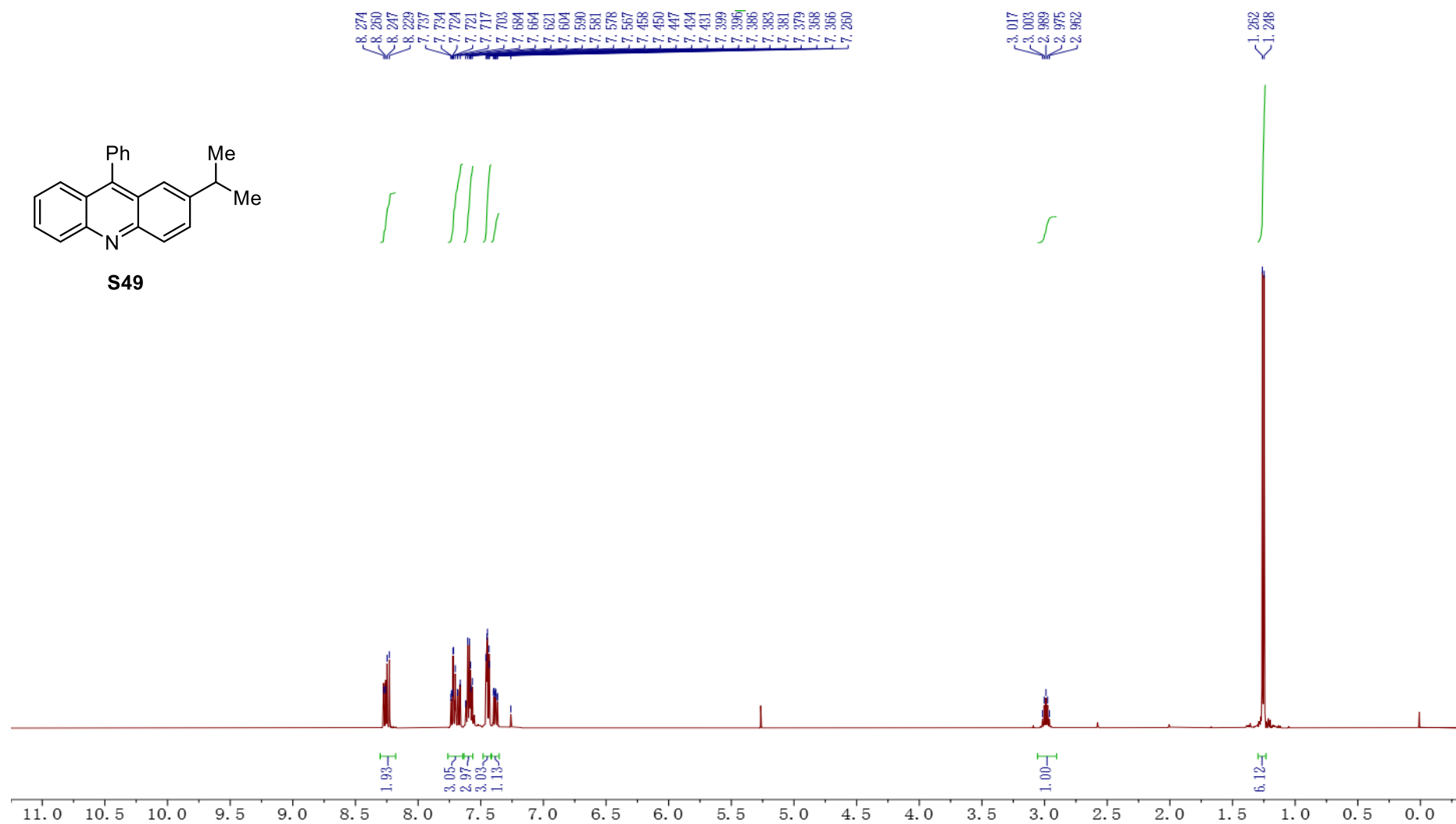
S45

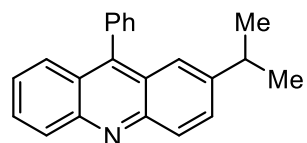




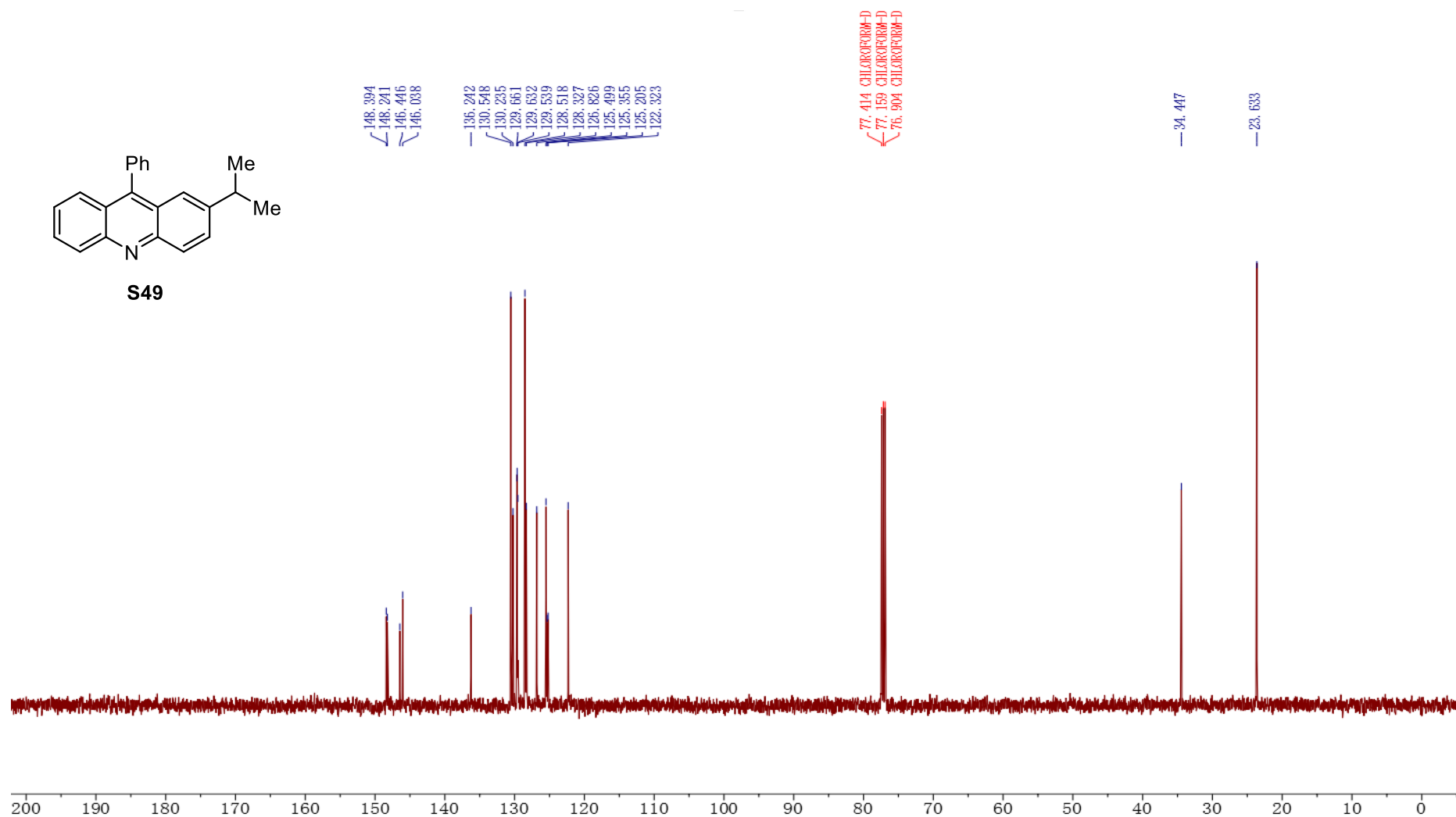


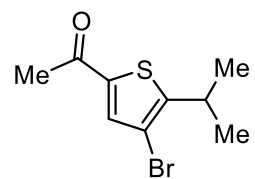
S49



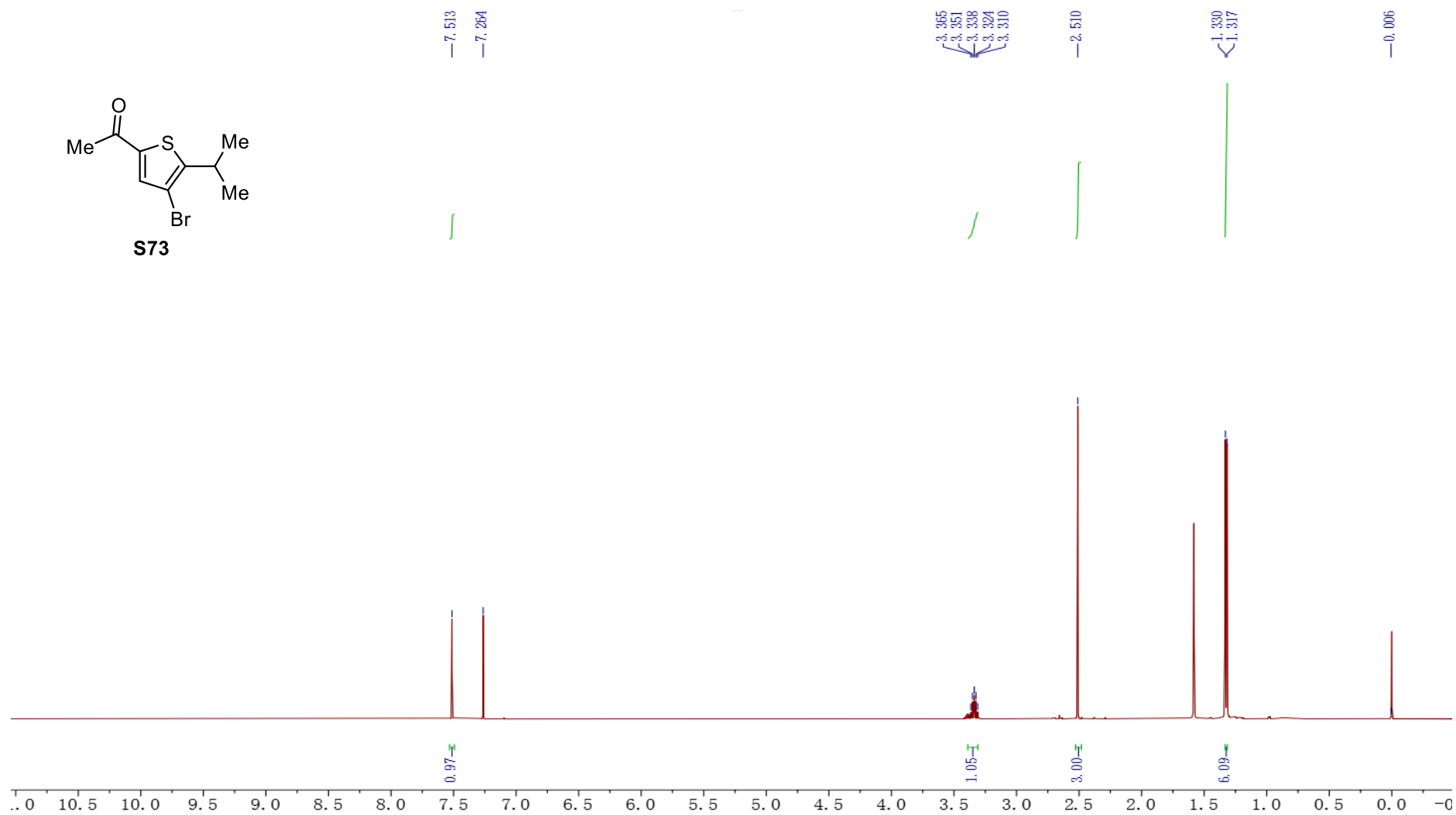


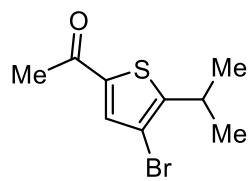
S49



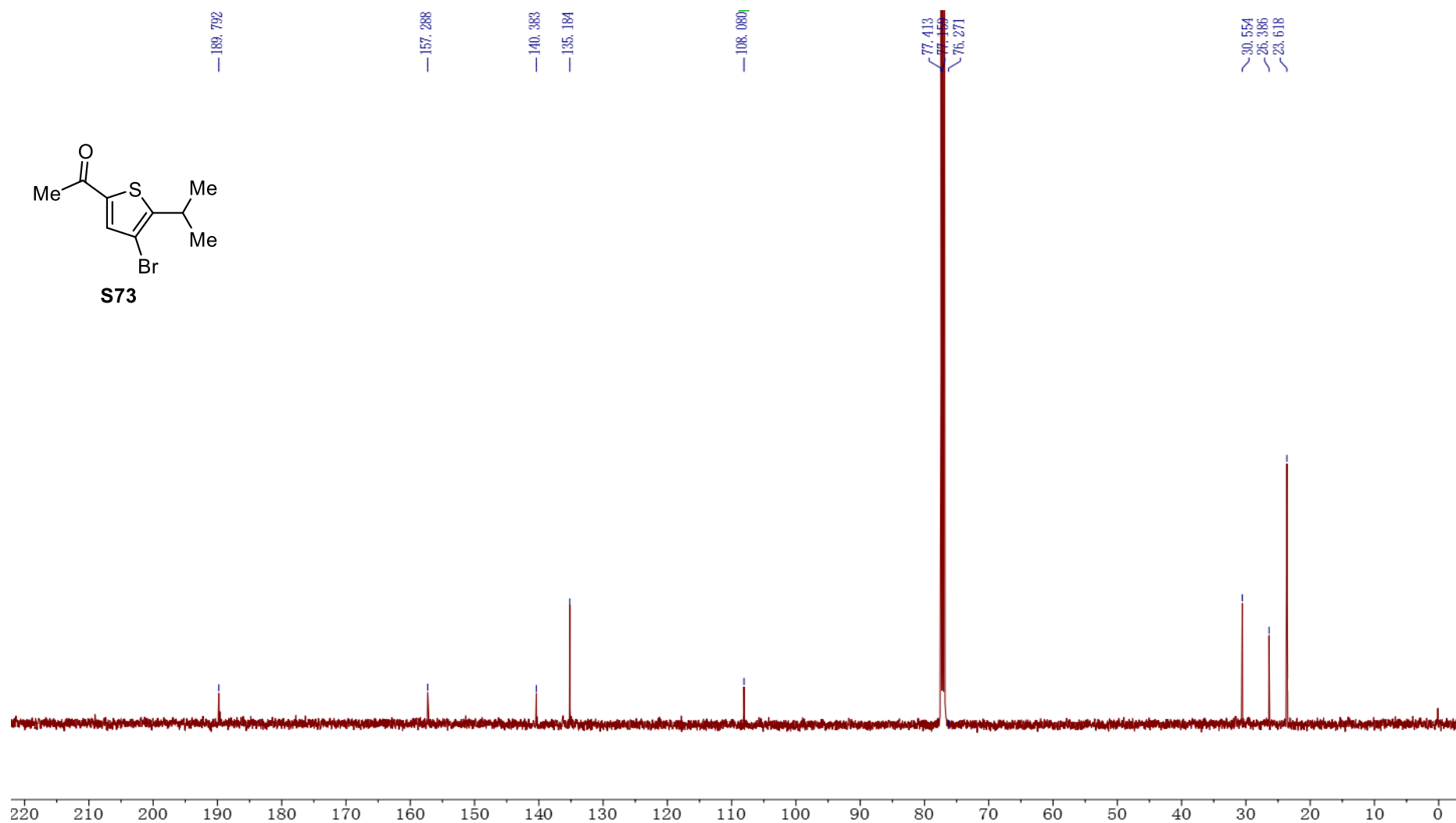


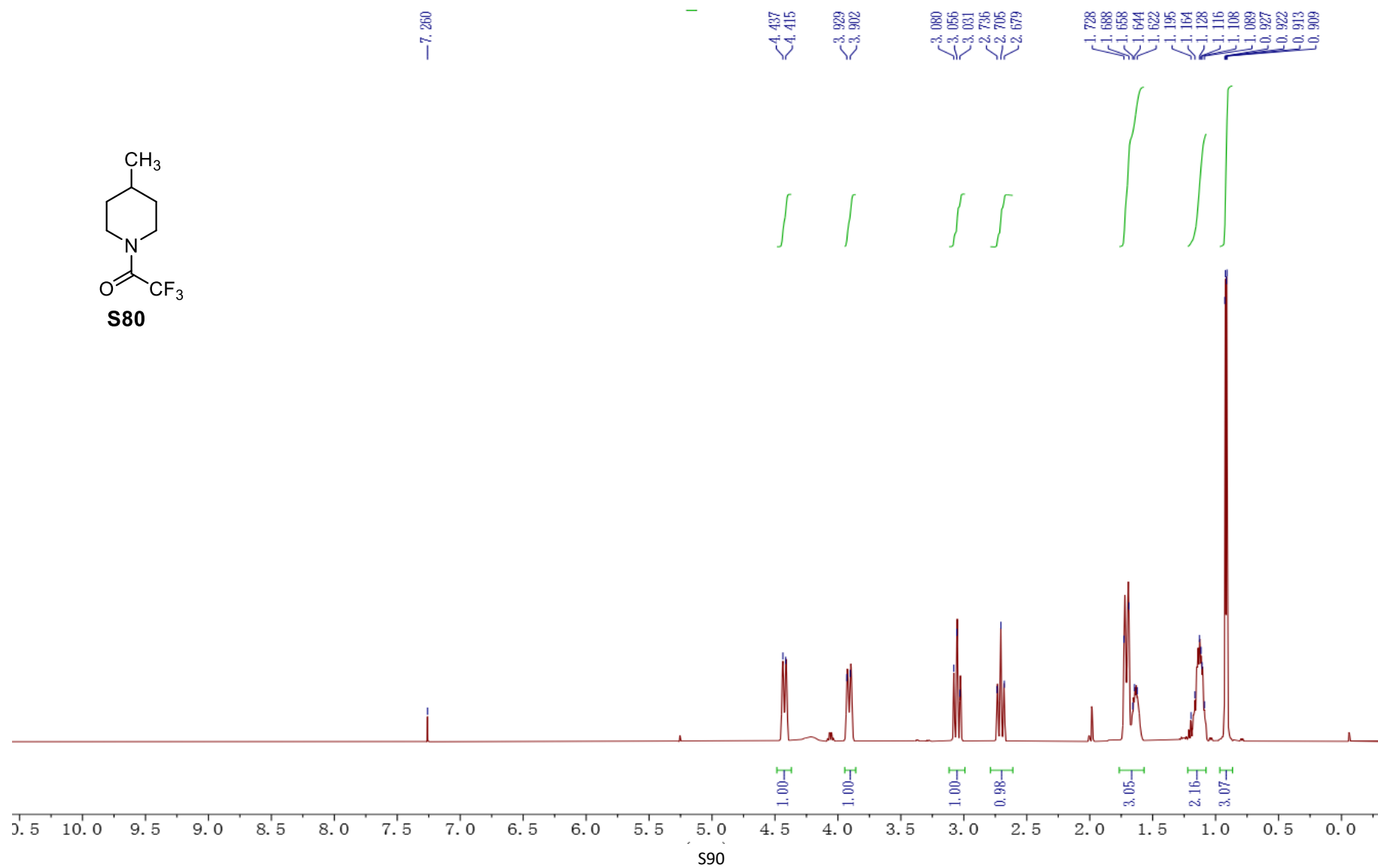
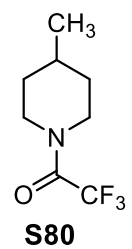
S73

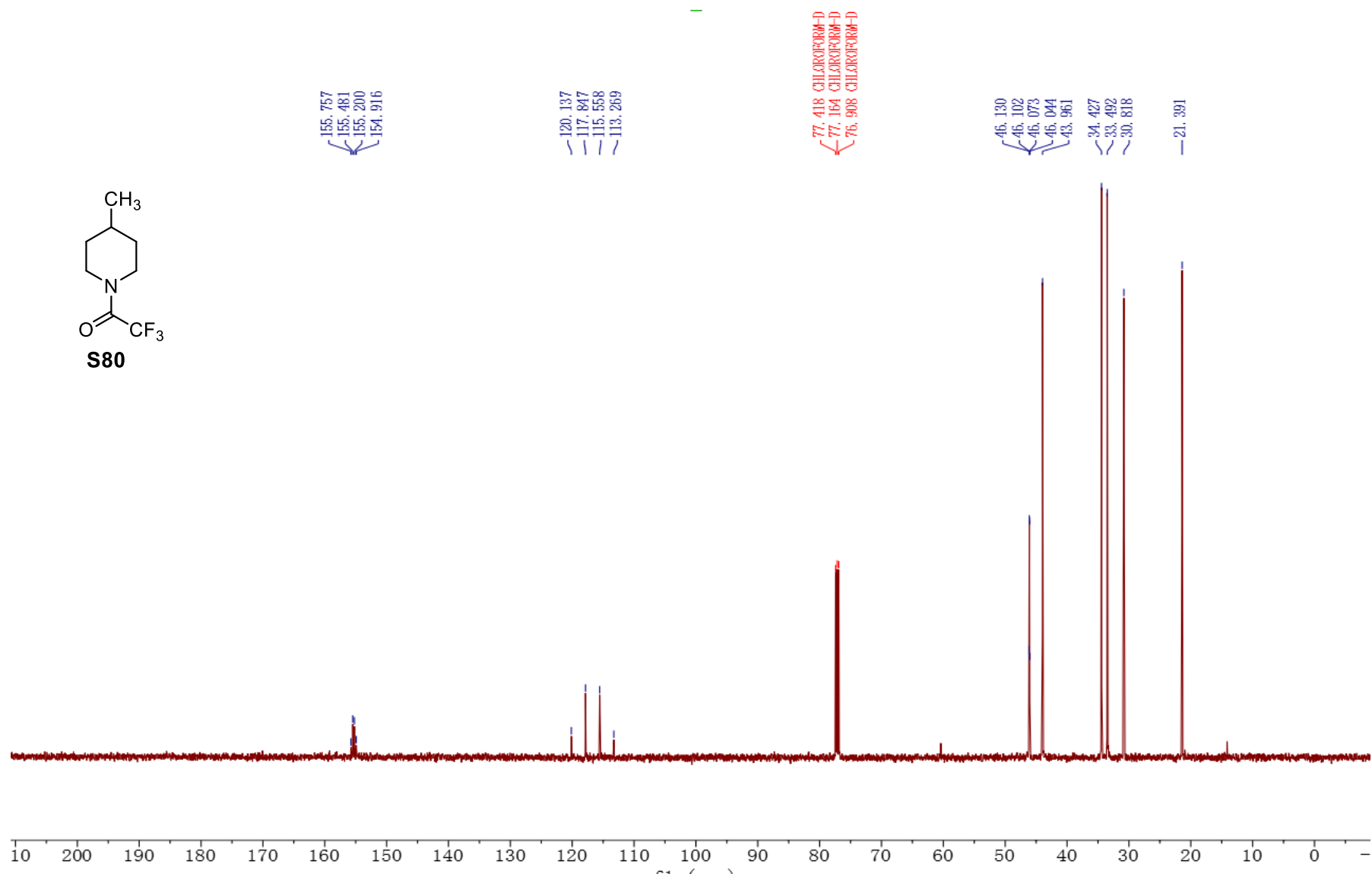
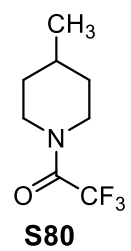


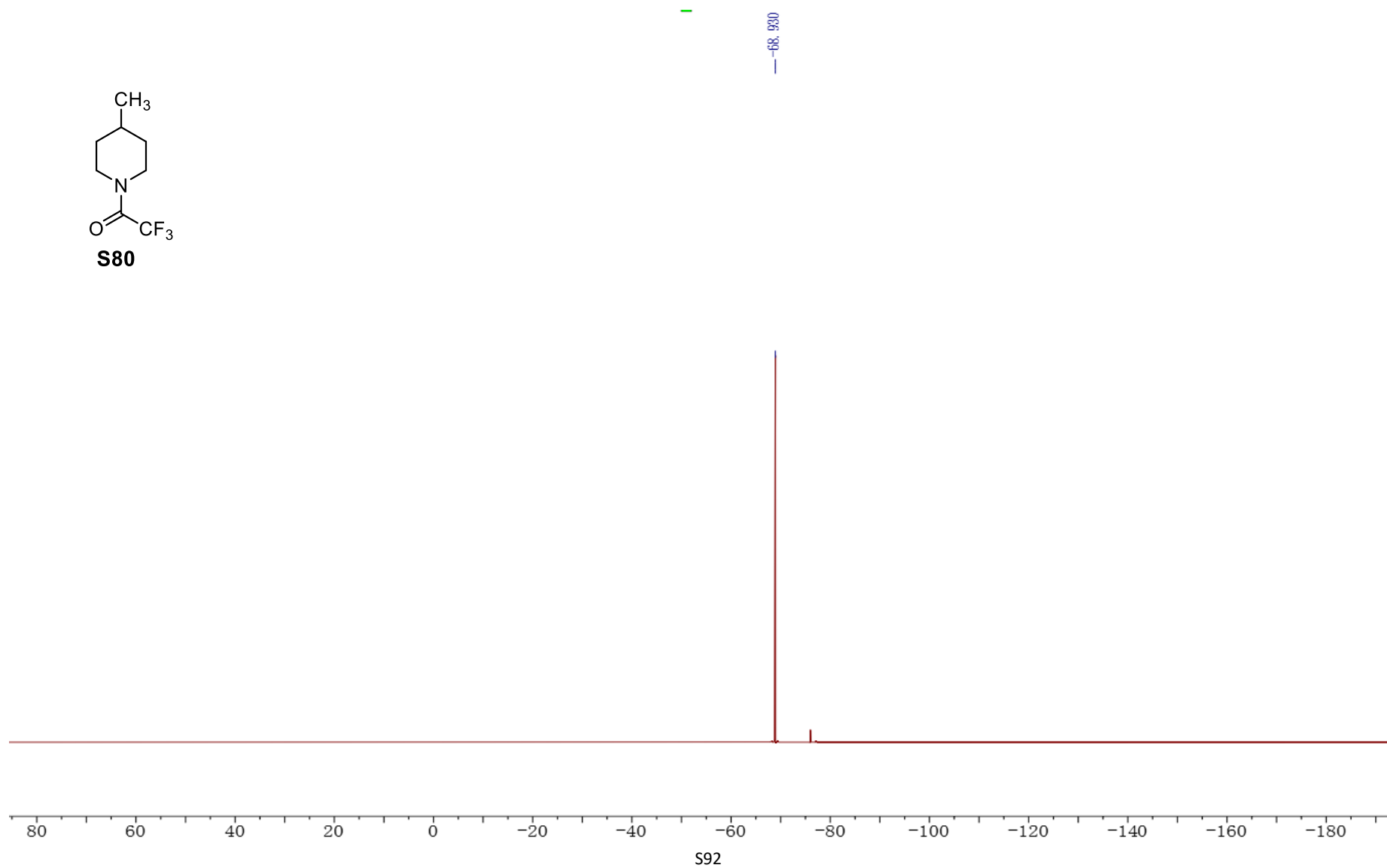
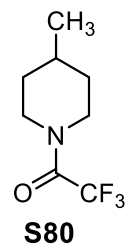


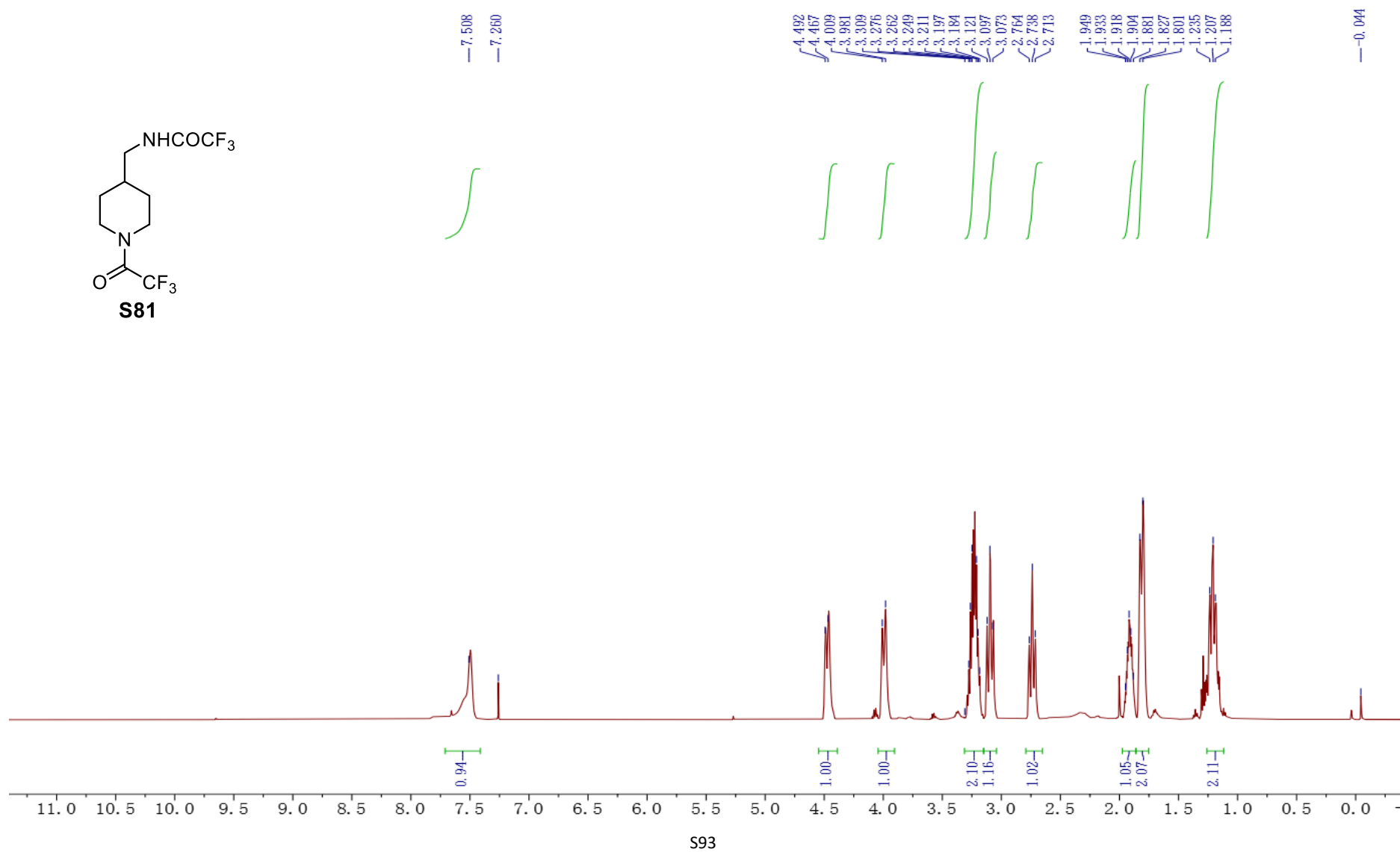
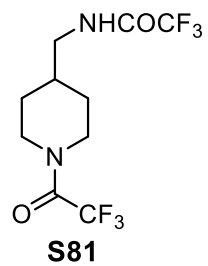
S73

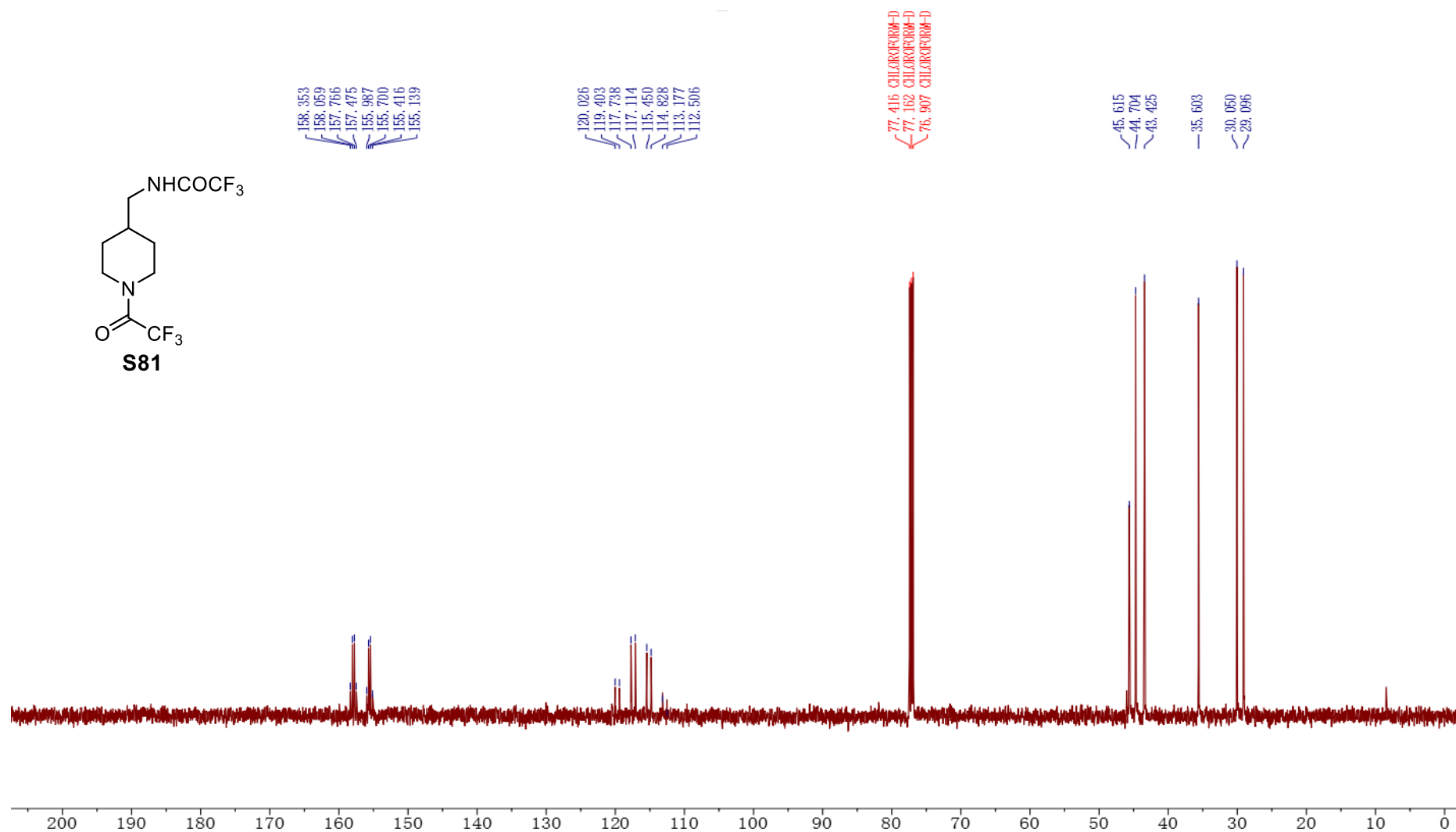
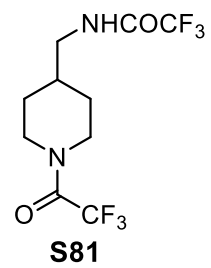


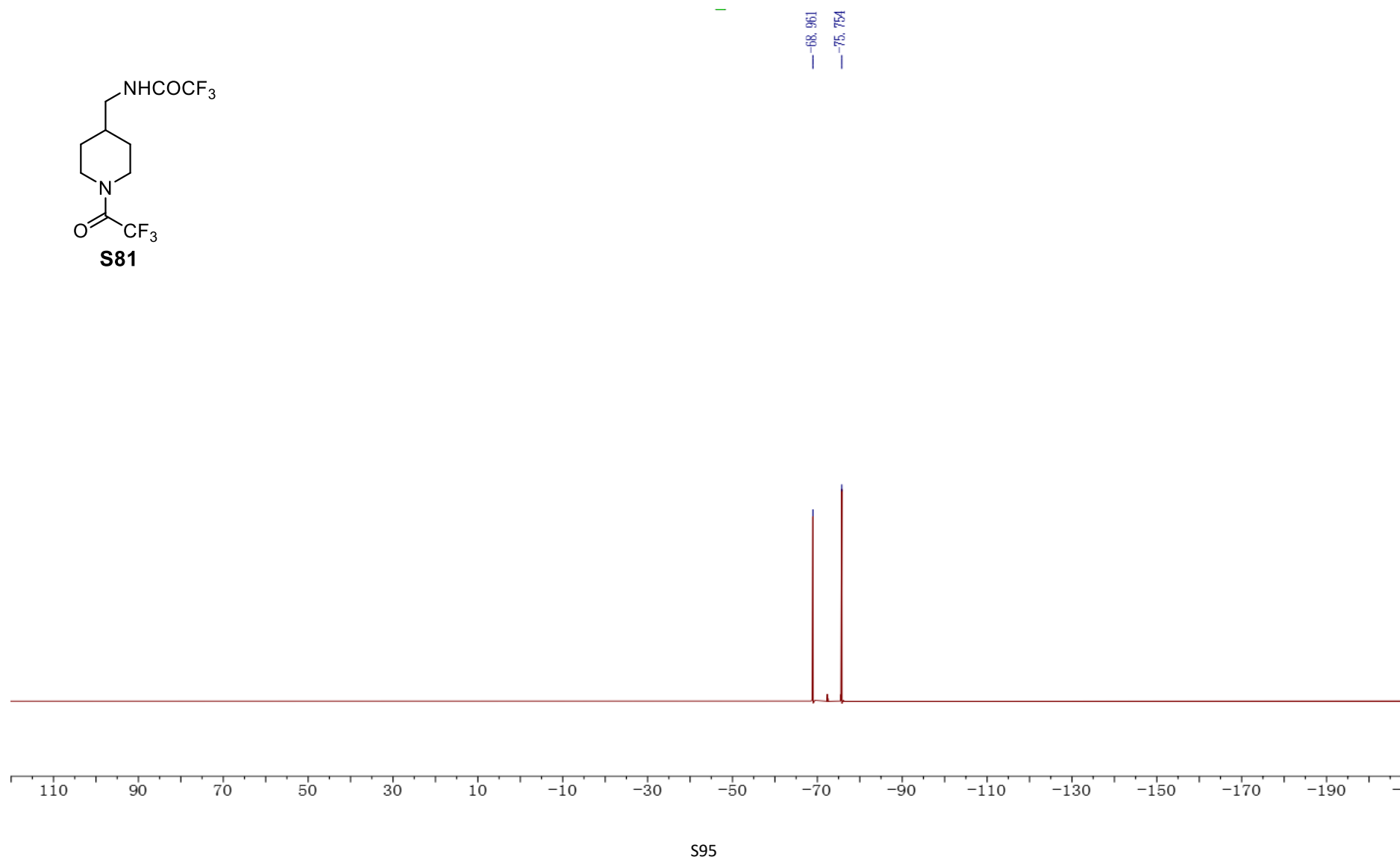
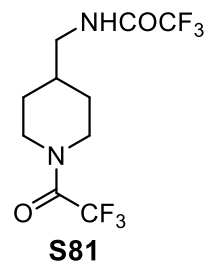


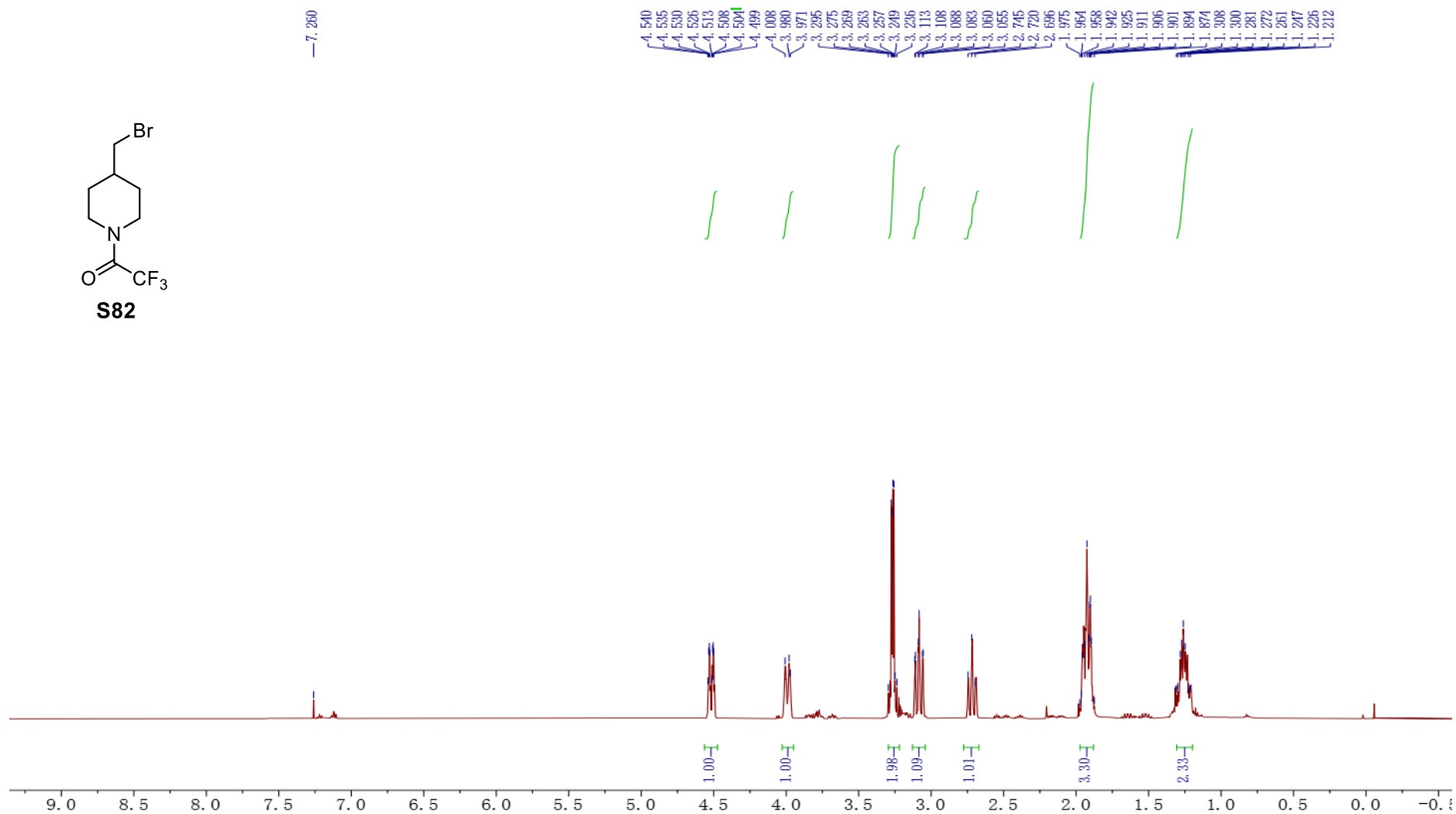
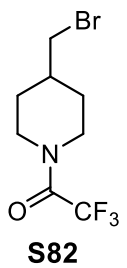


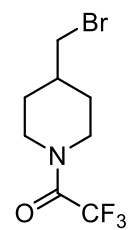




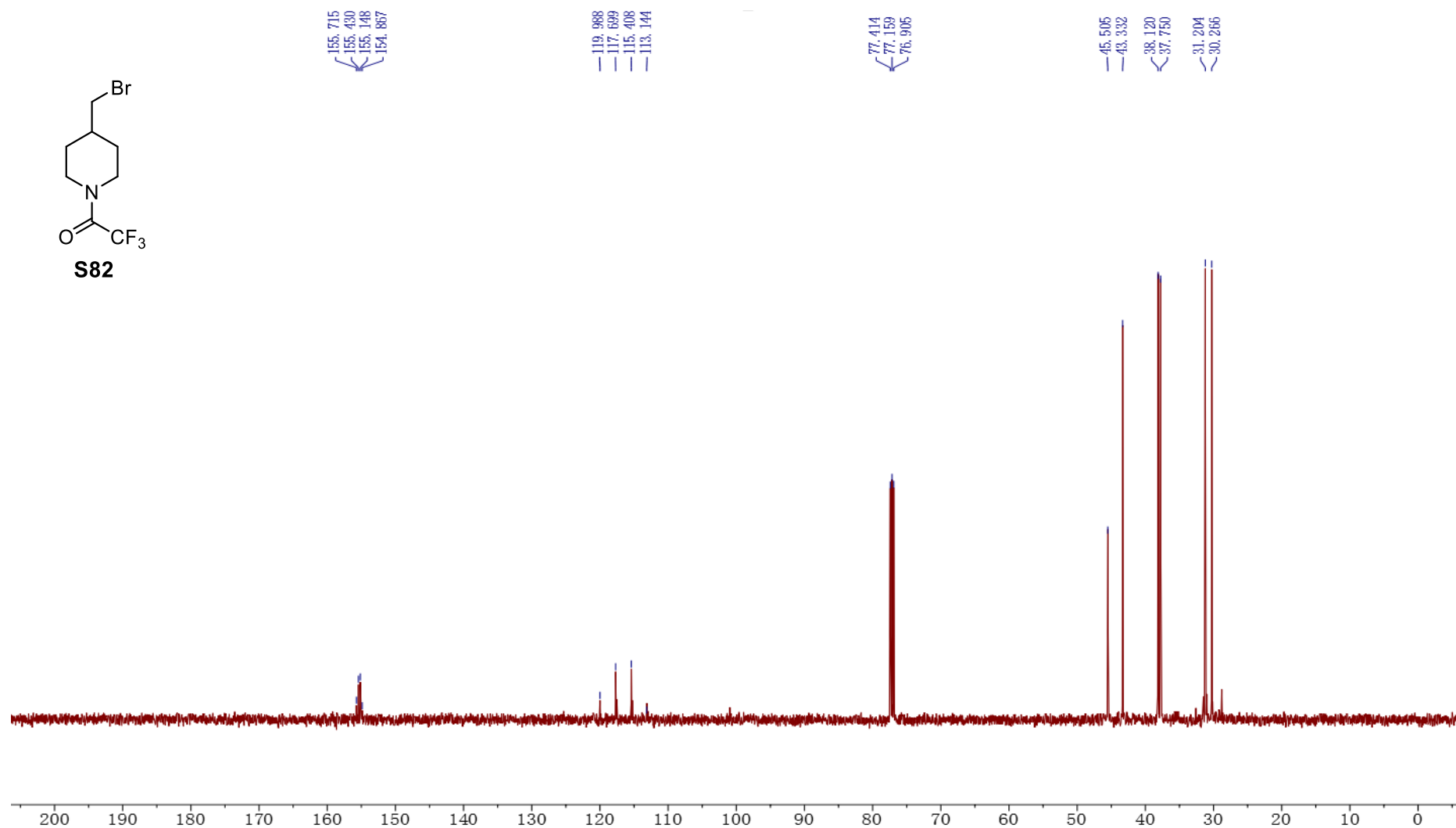


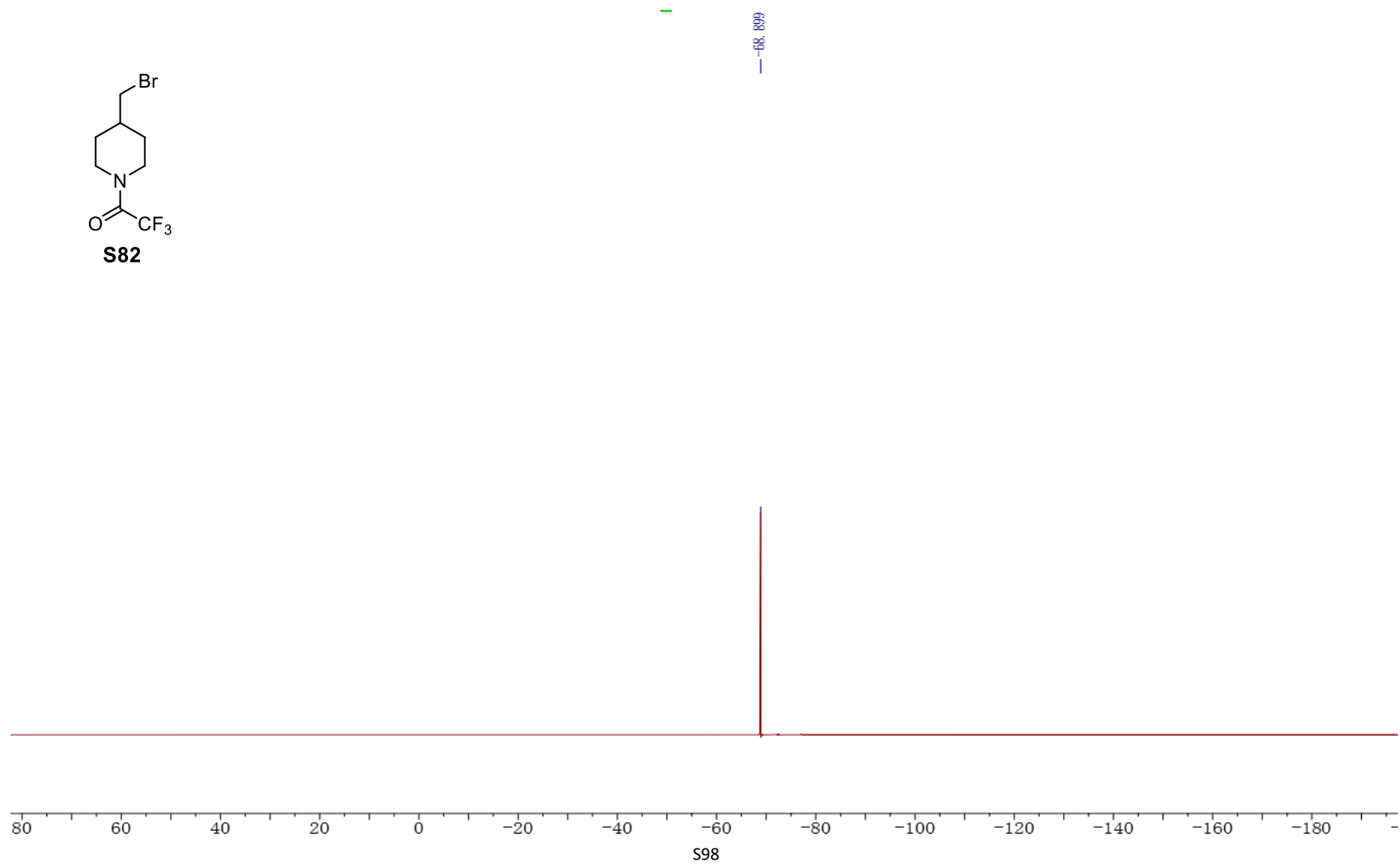
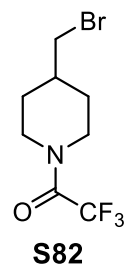


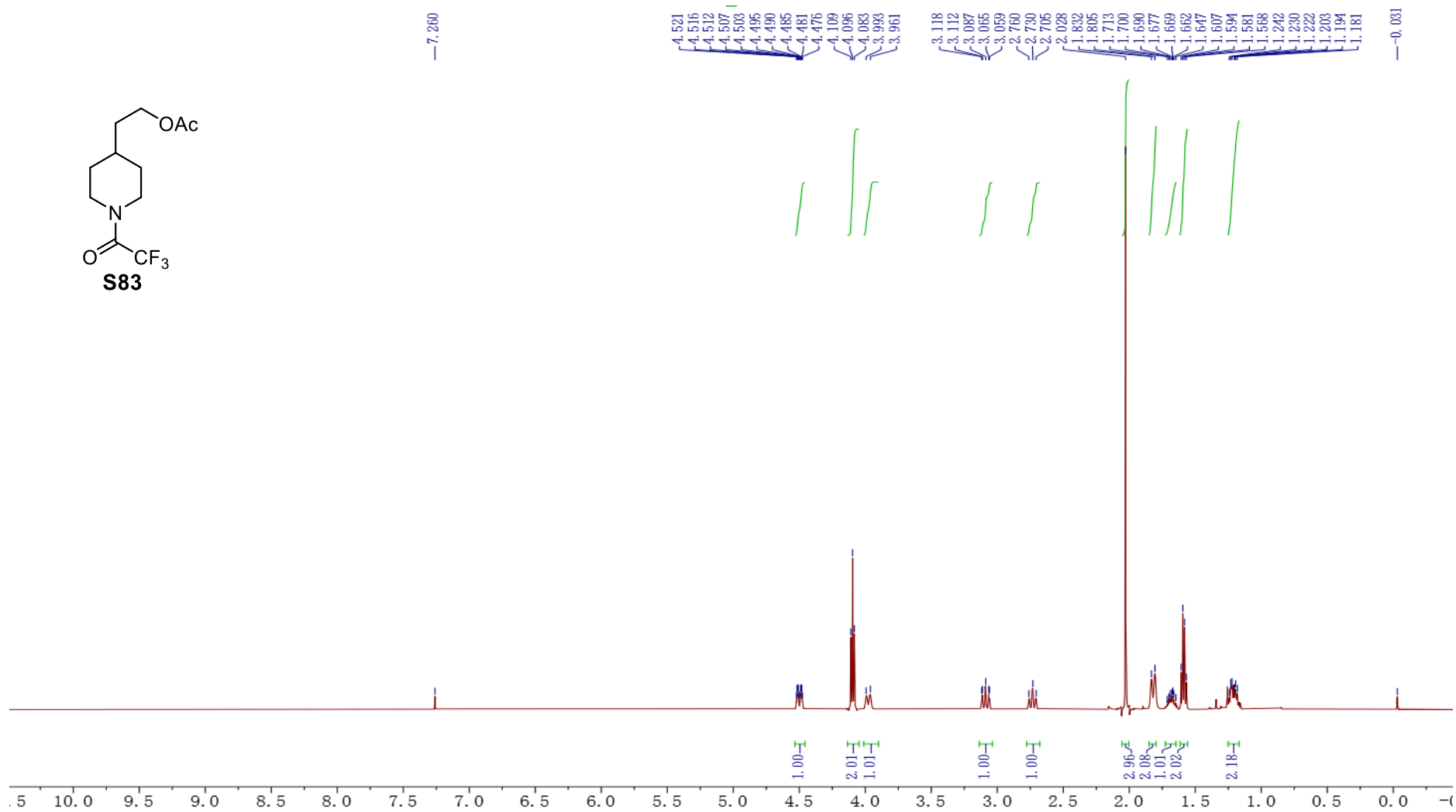
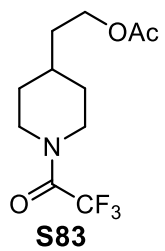


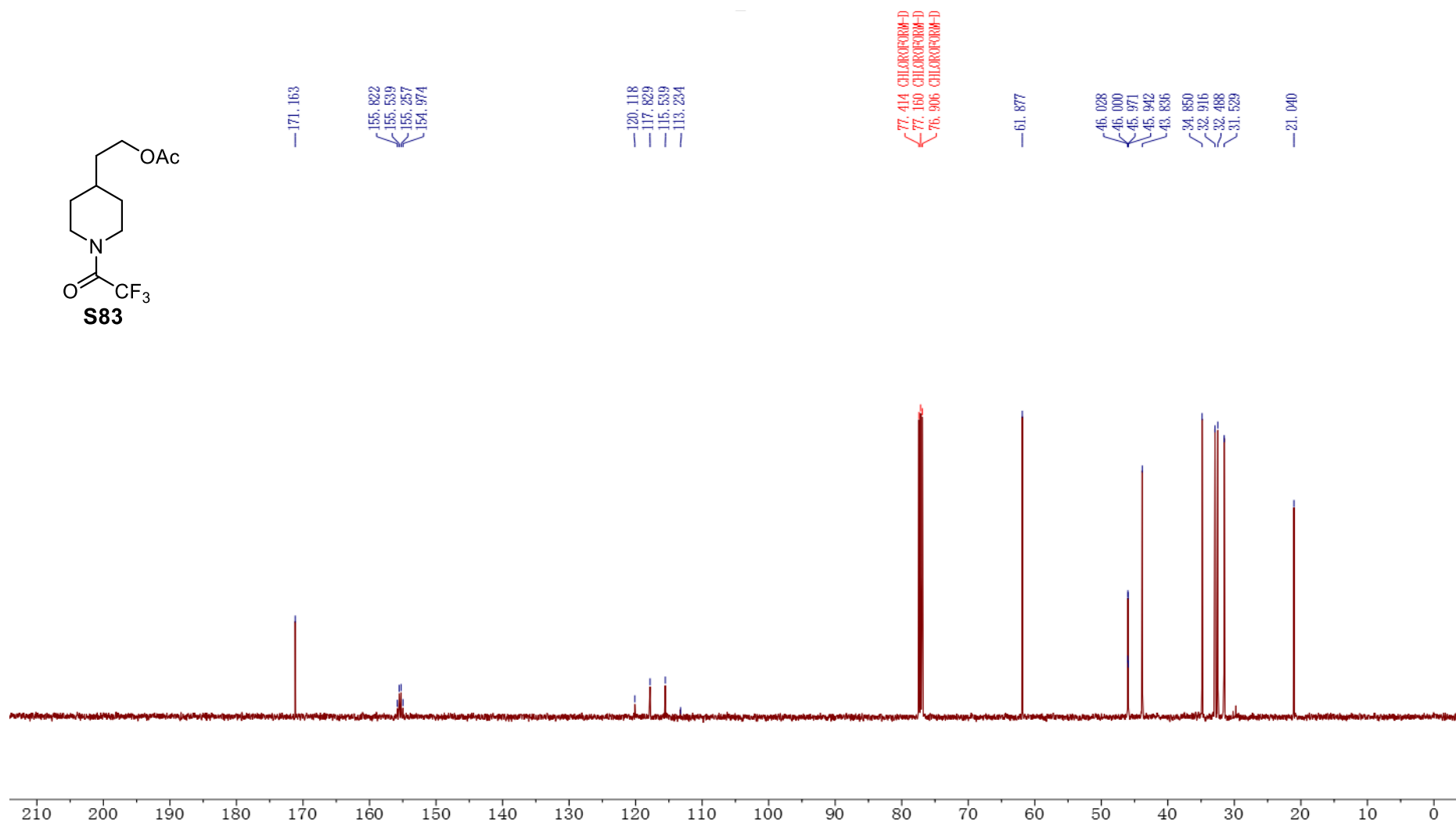
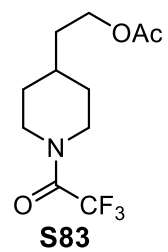


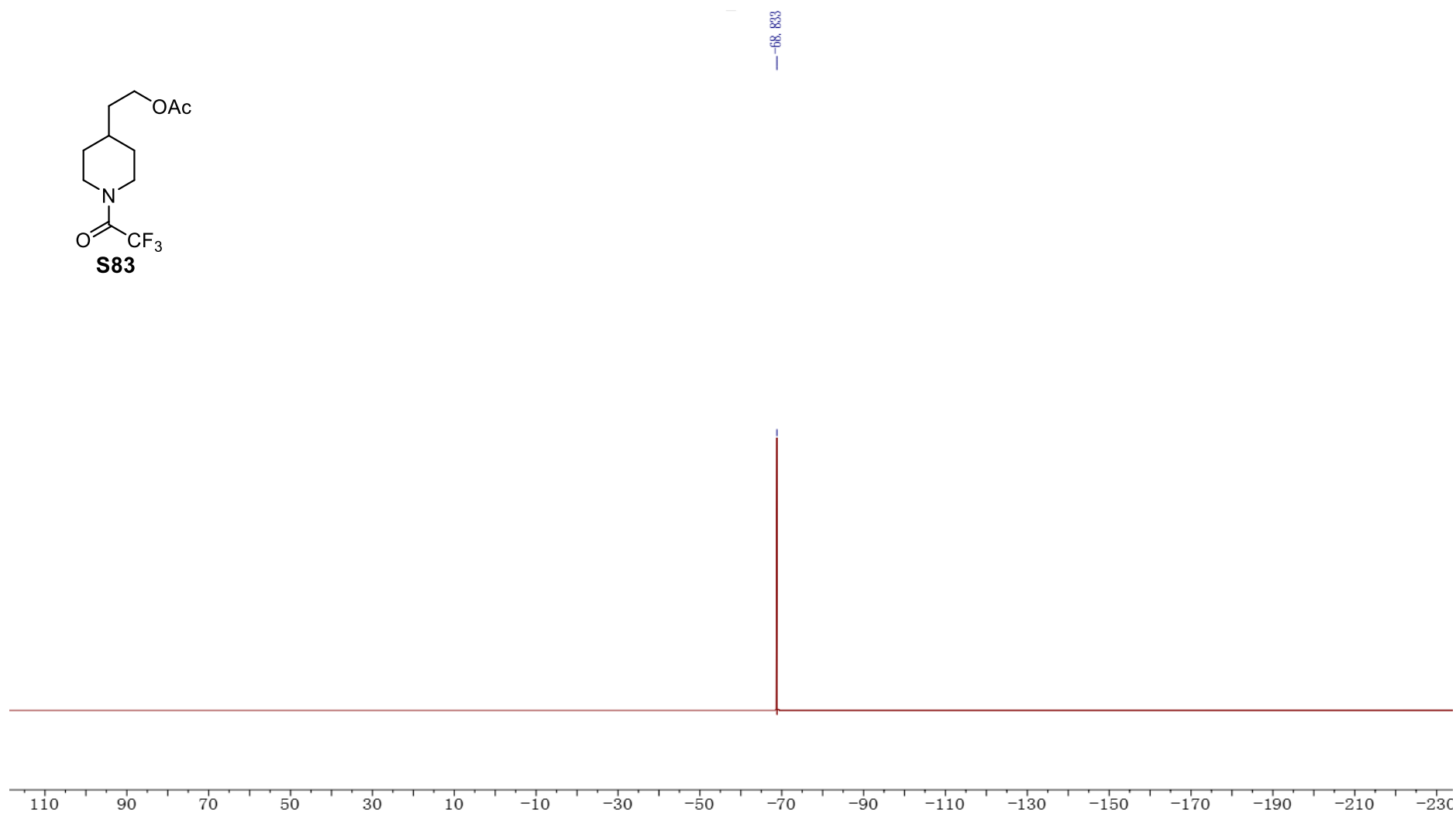
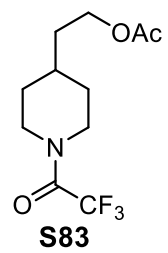
S82



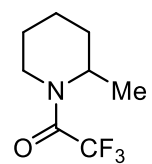




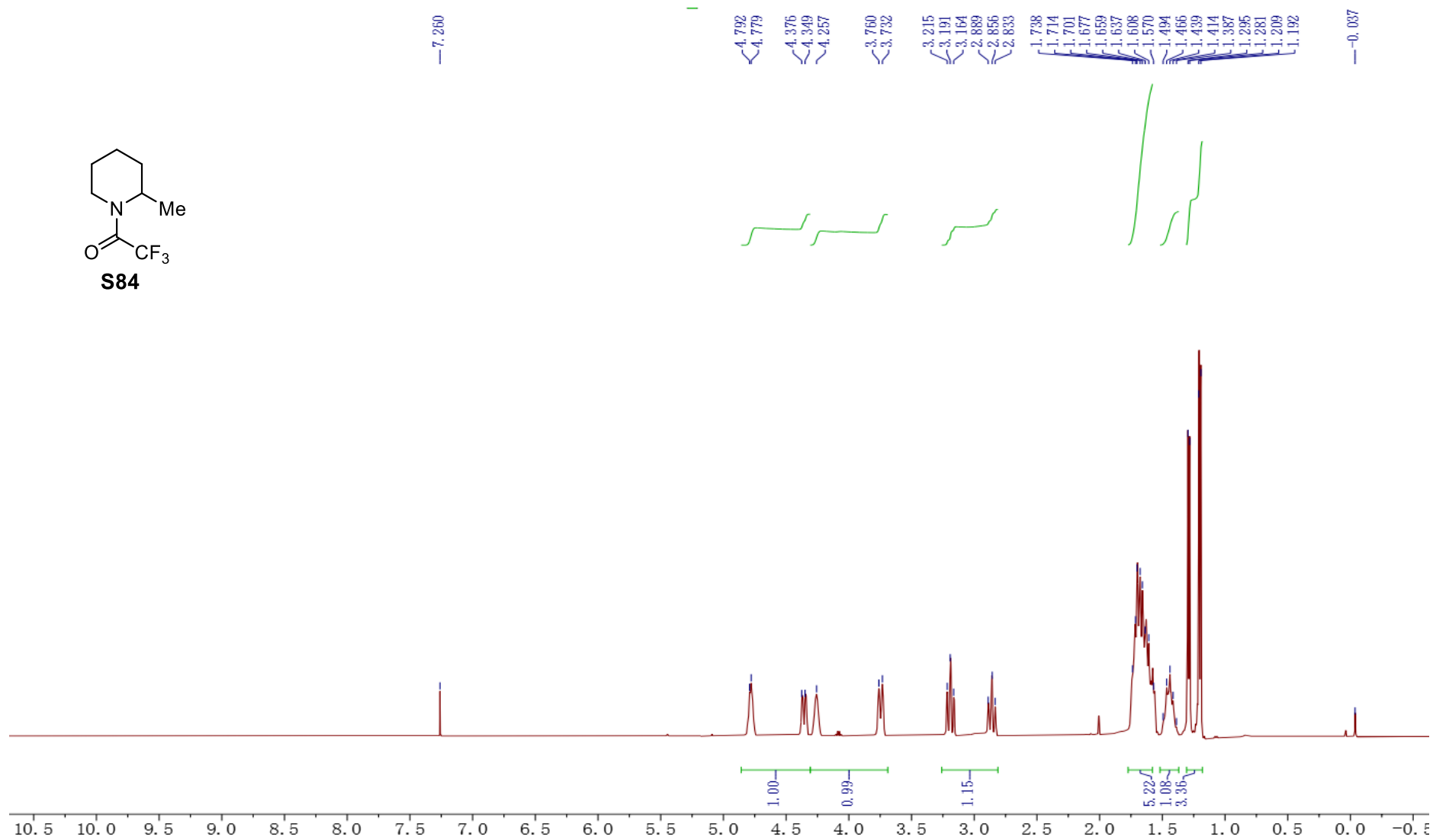


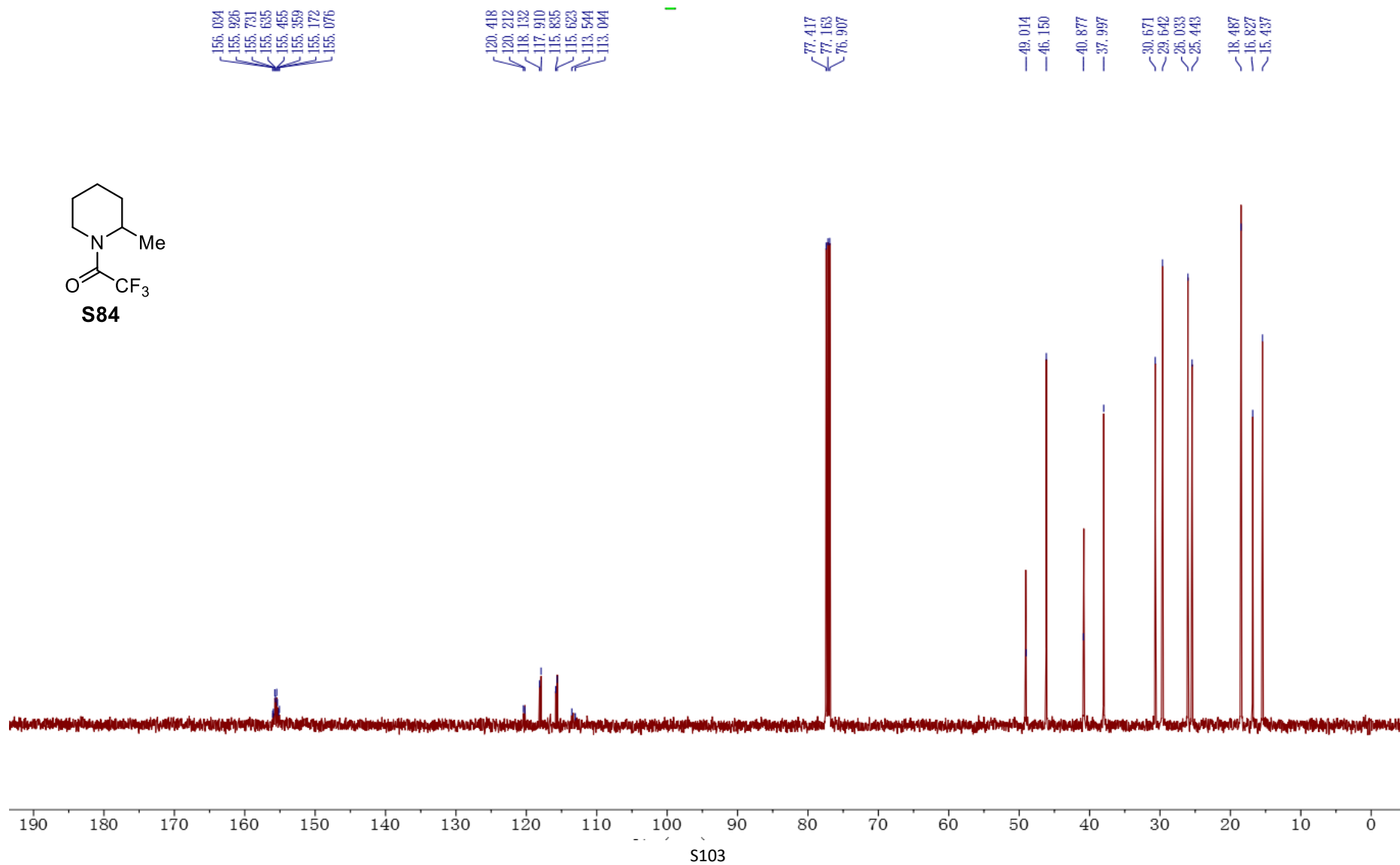
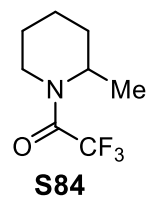


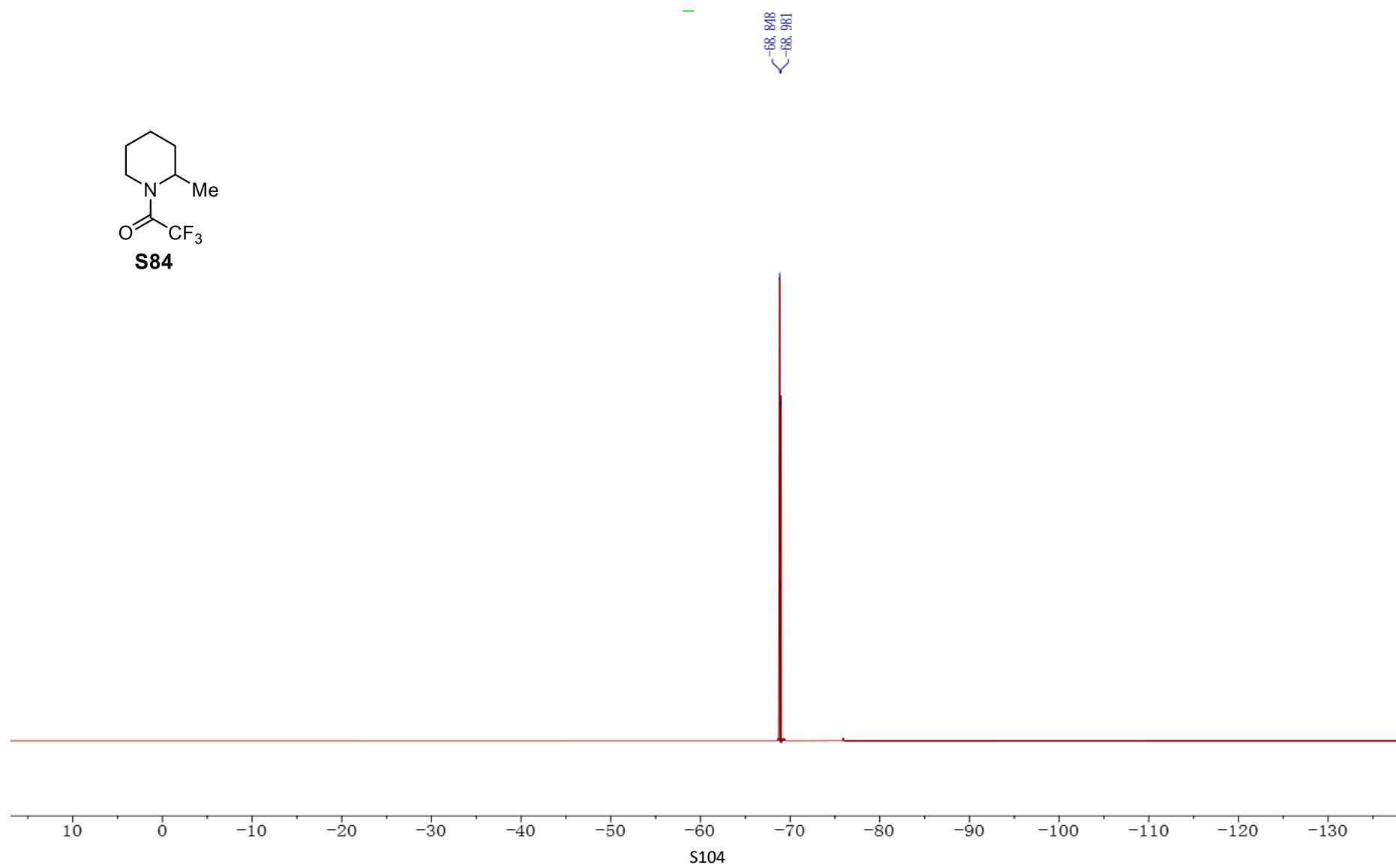
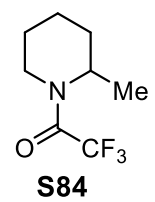
S101

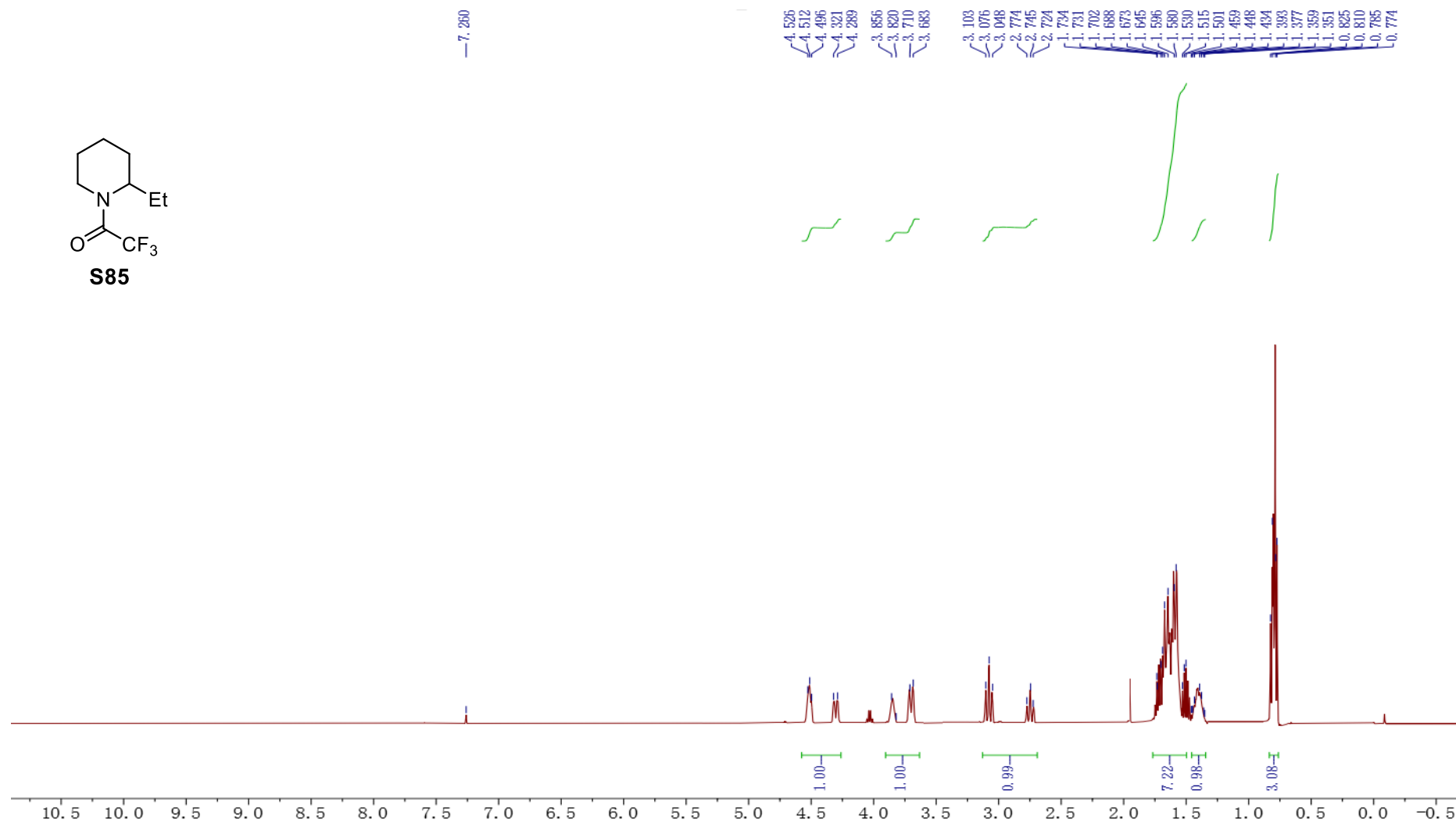
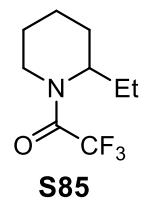


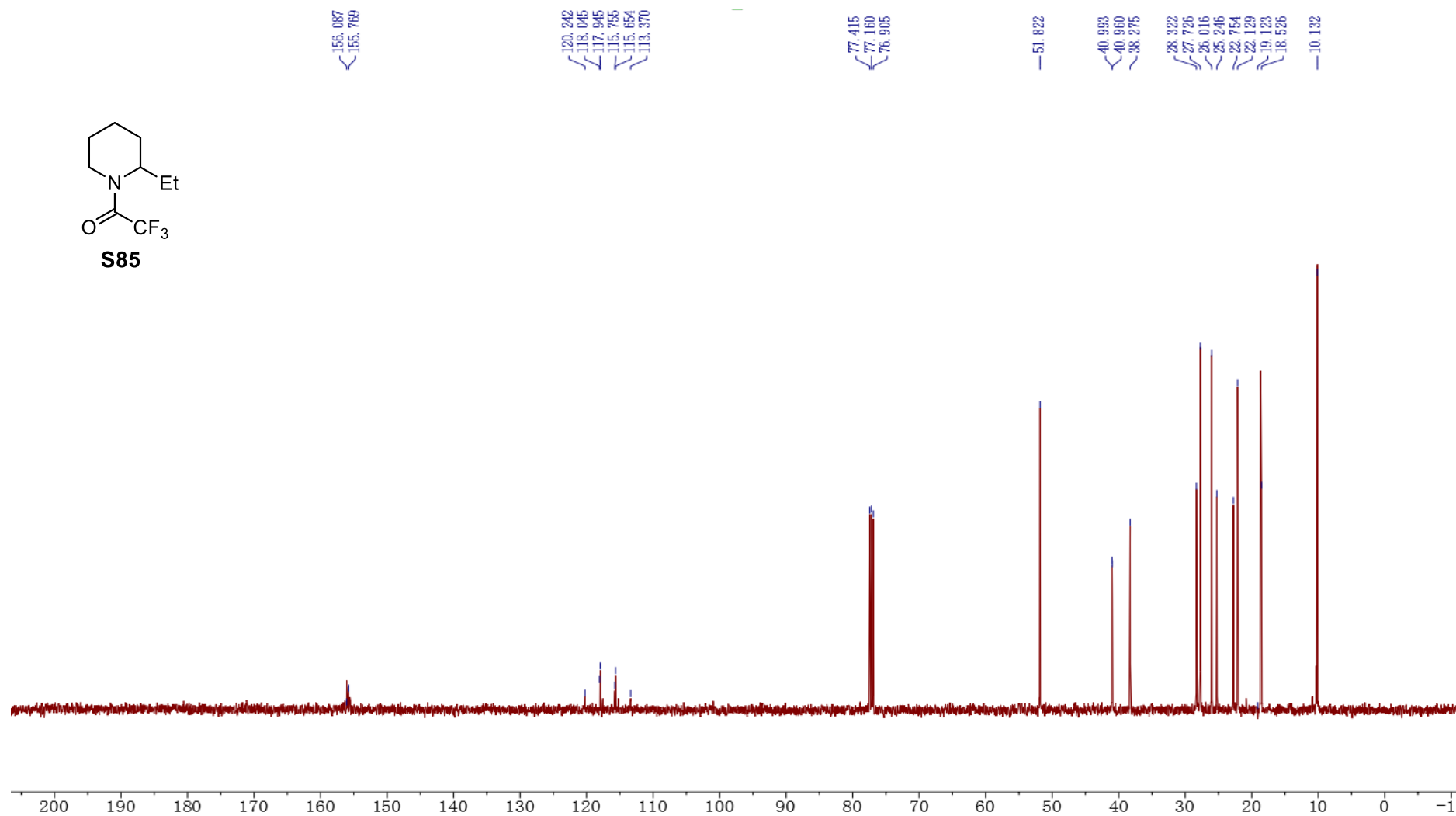
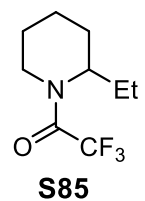
S84

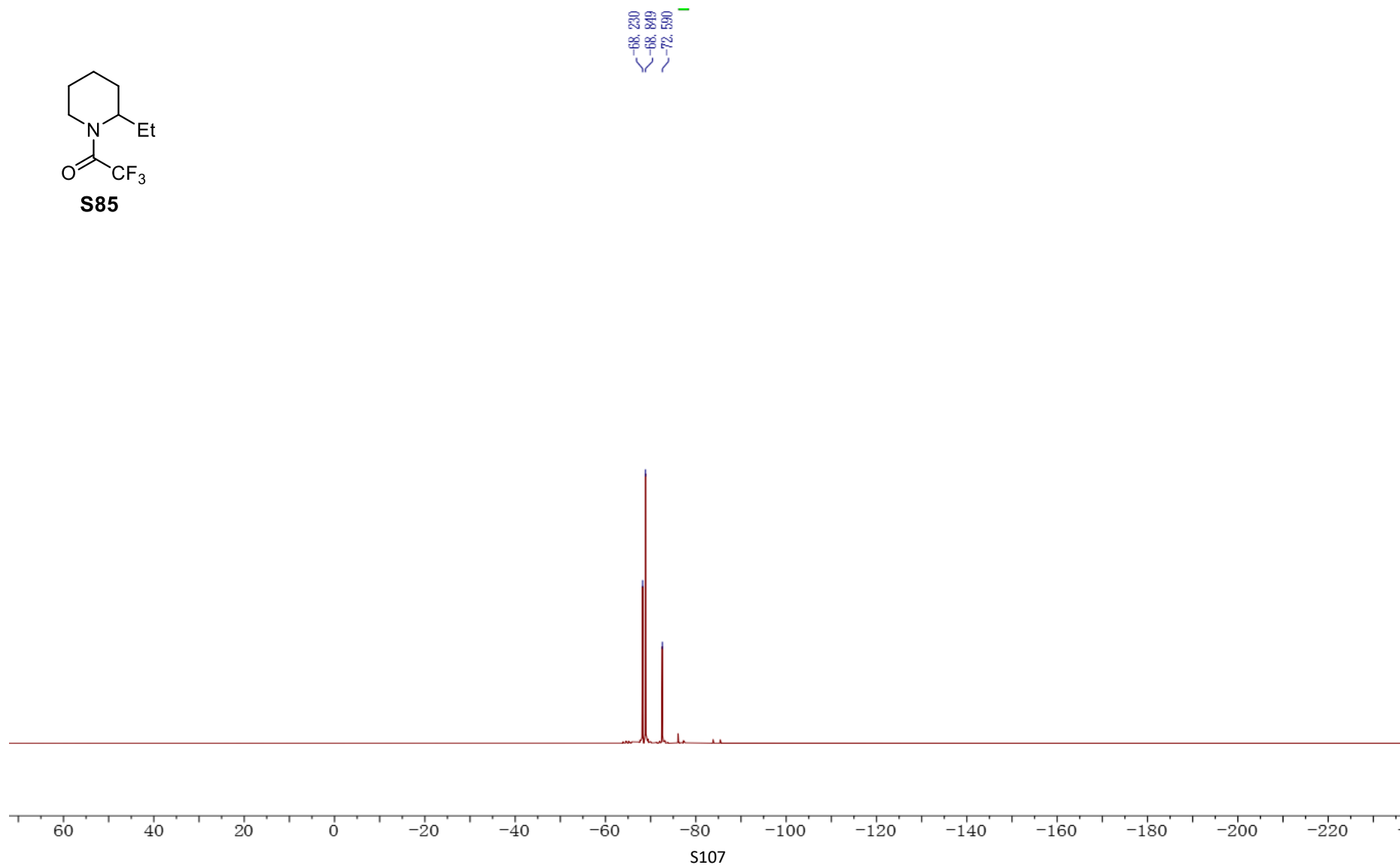
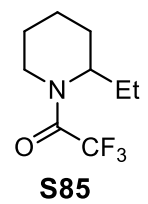


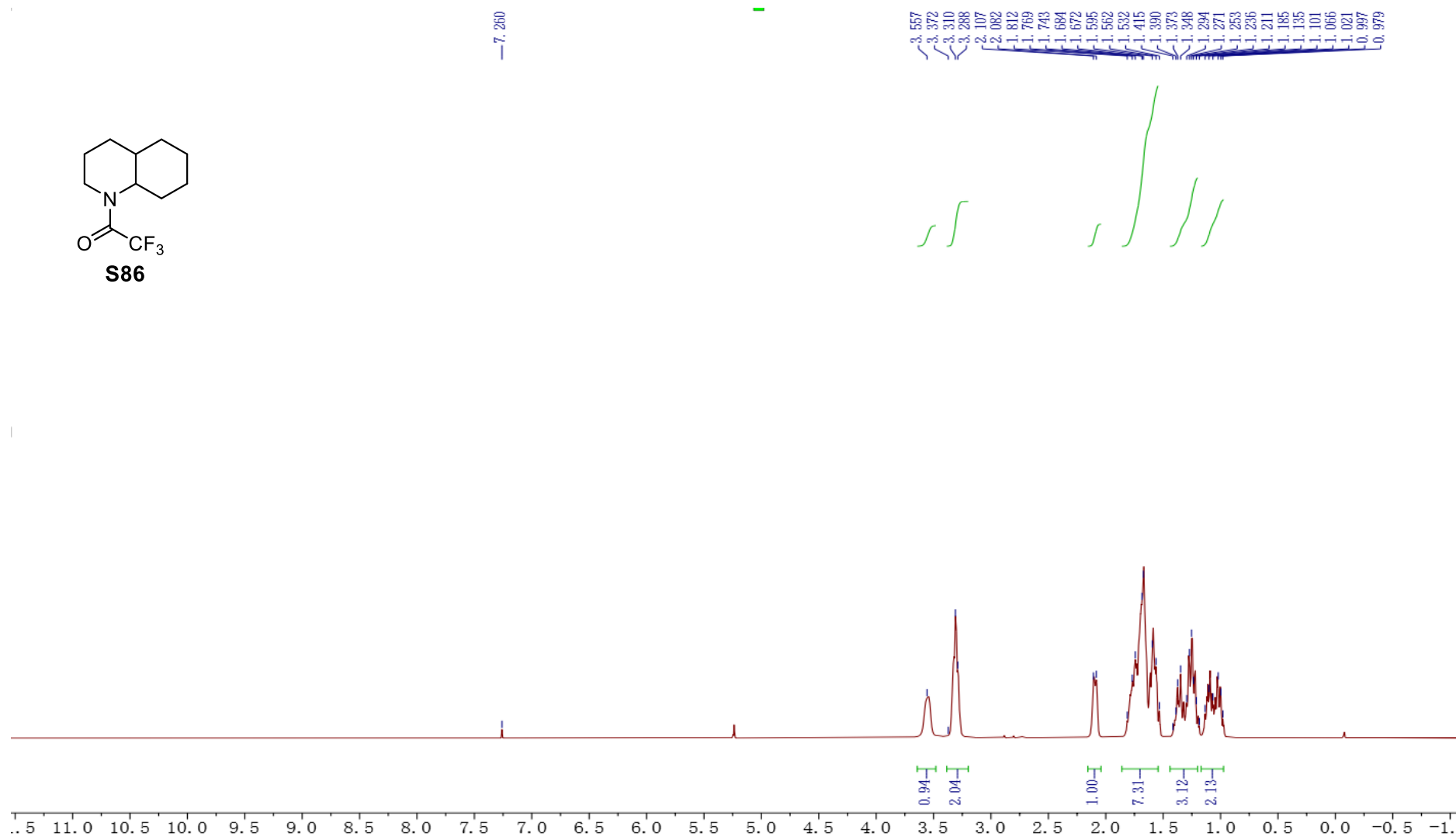
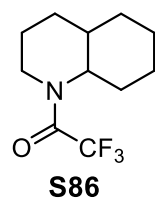




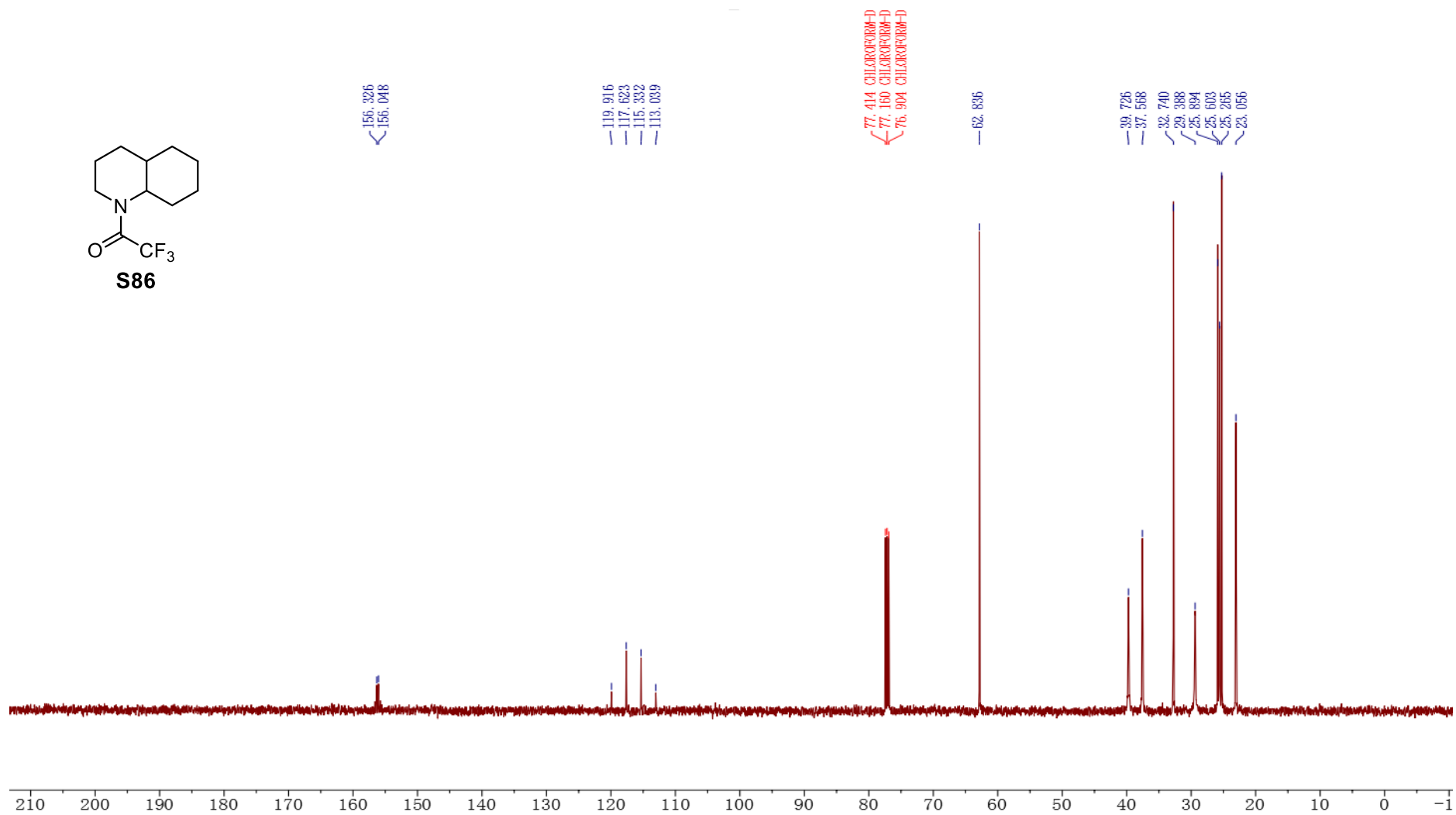
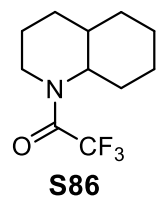


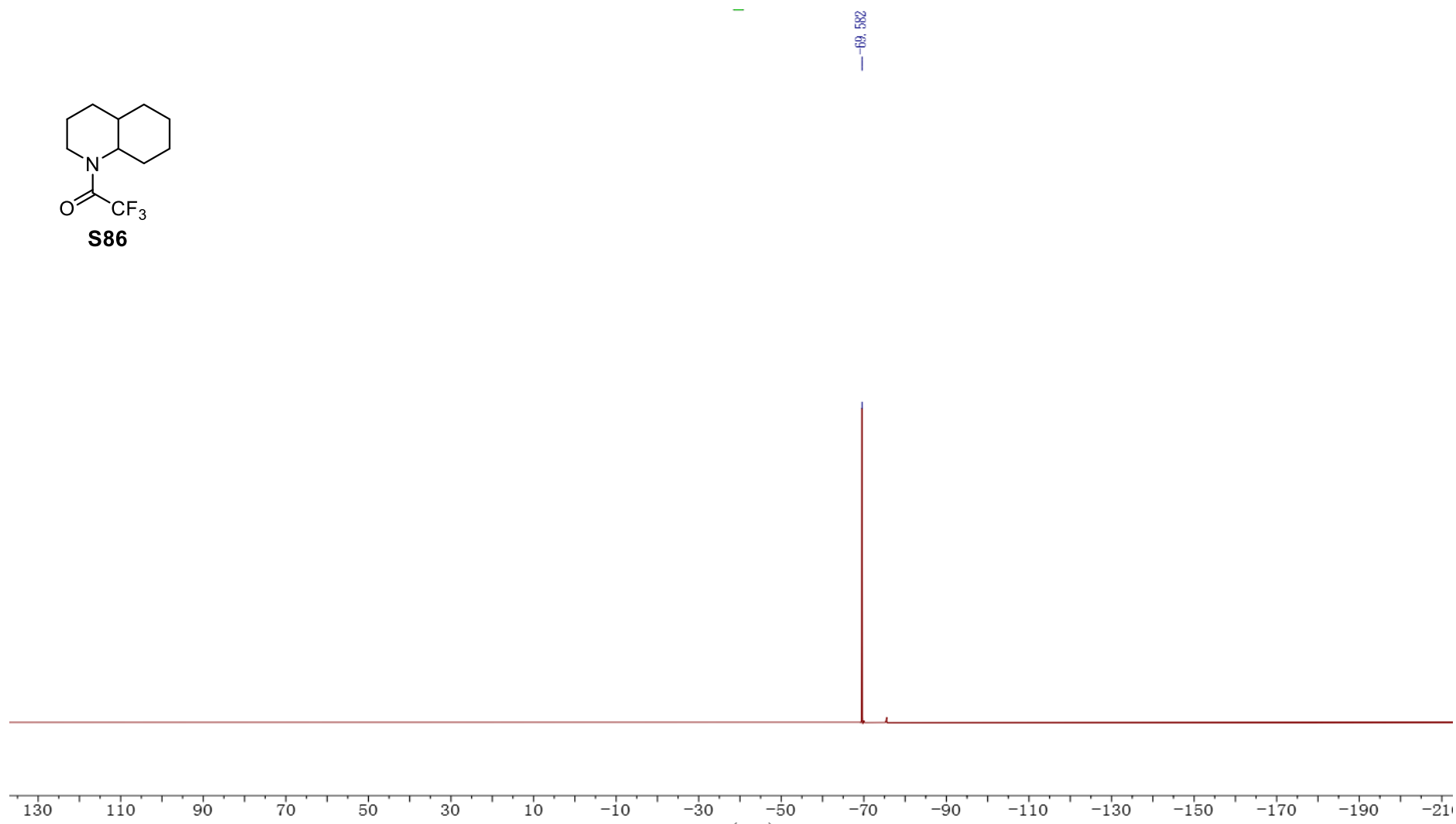
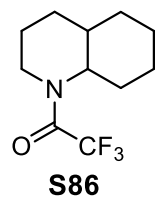




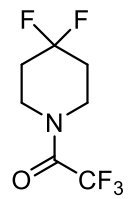


S108

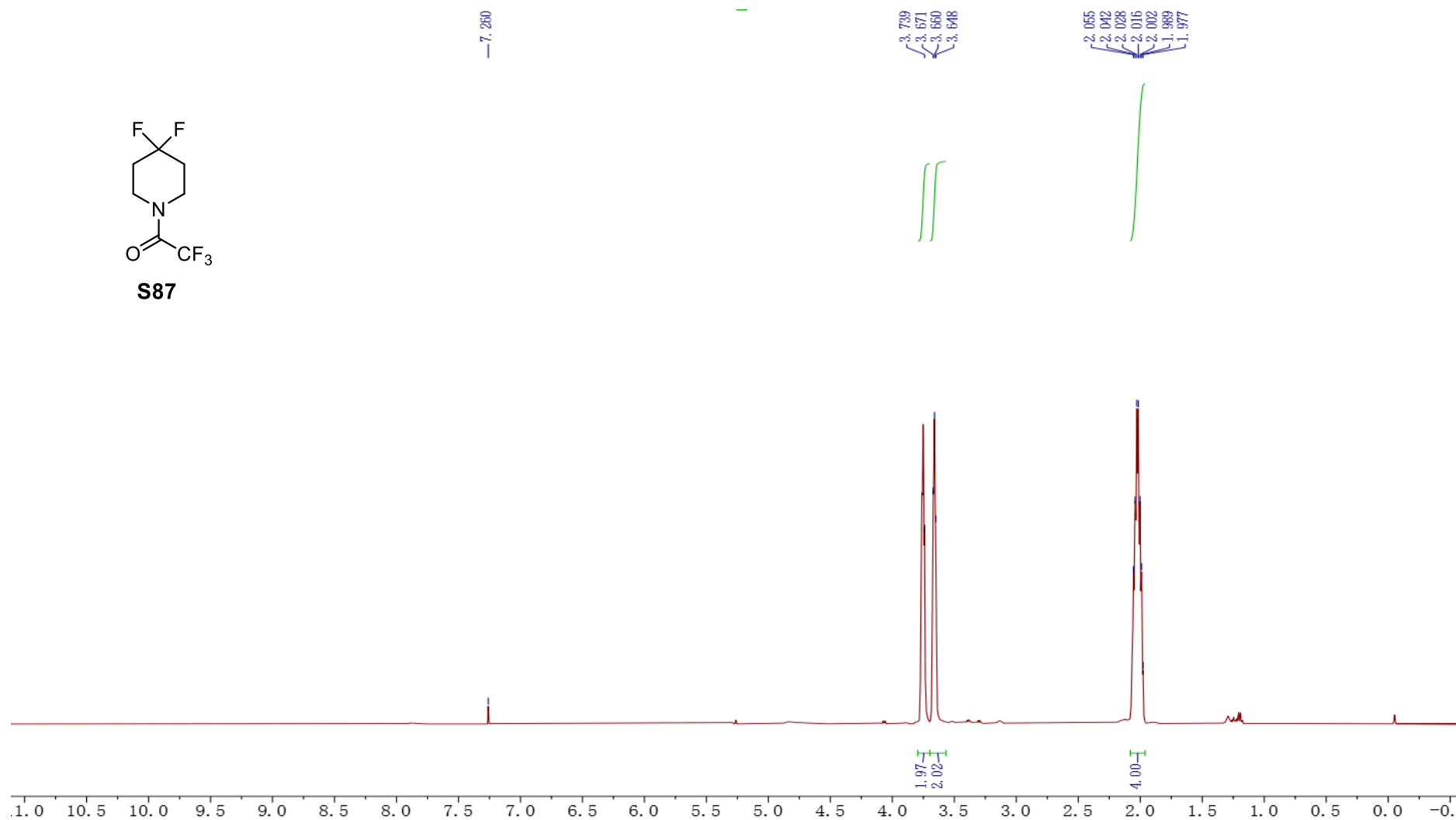


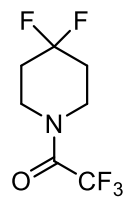


S110

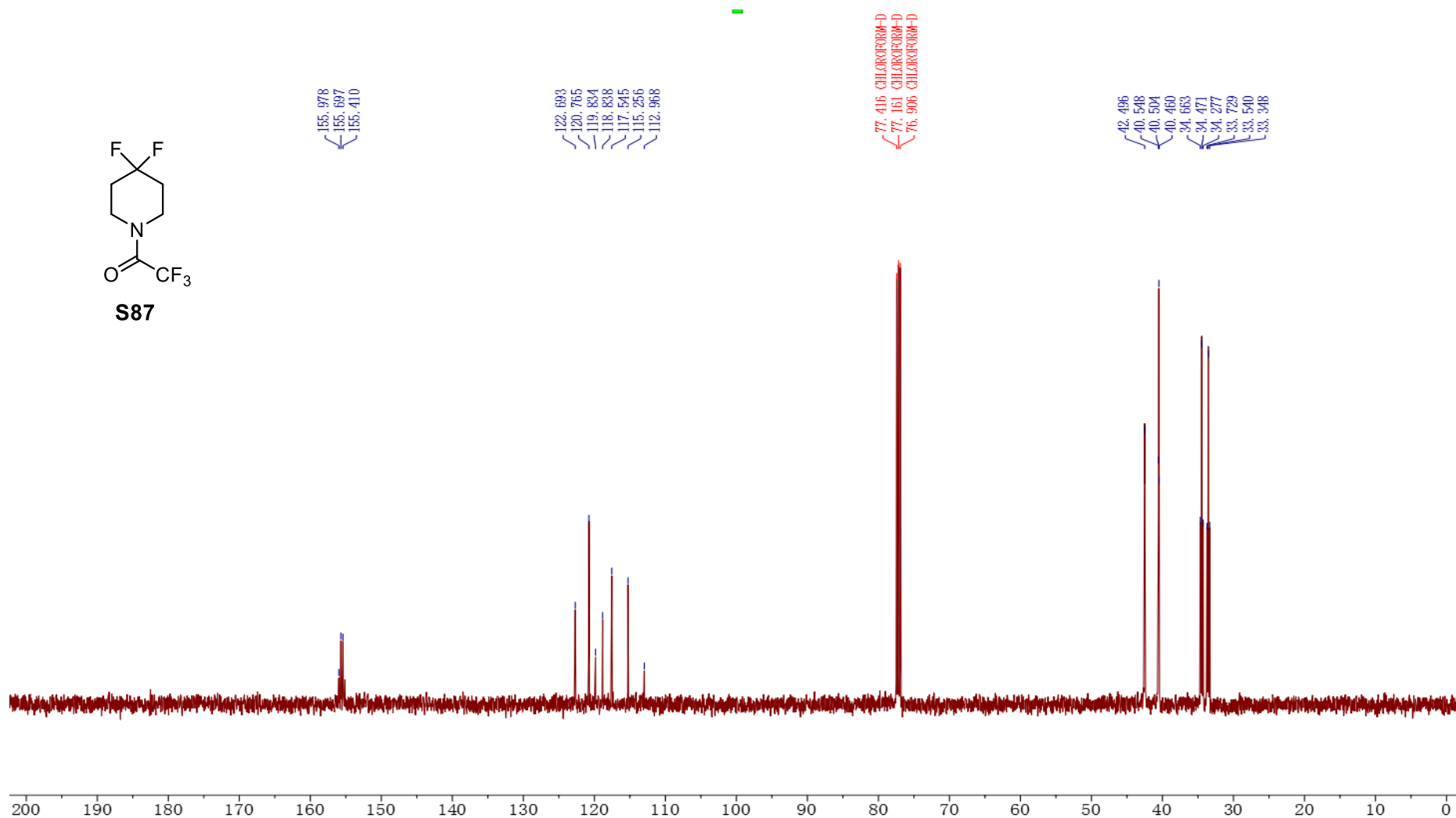


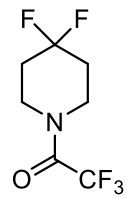
S87



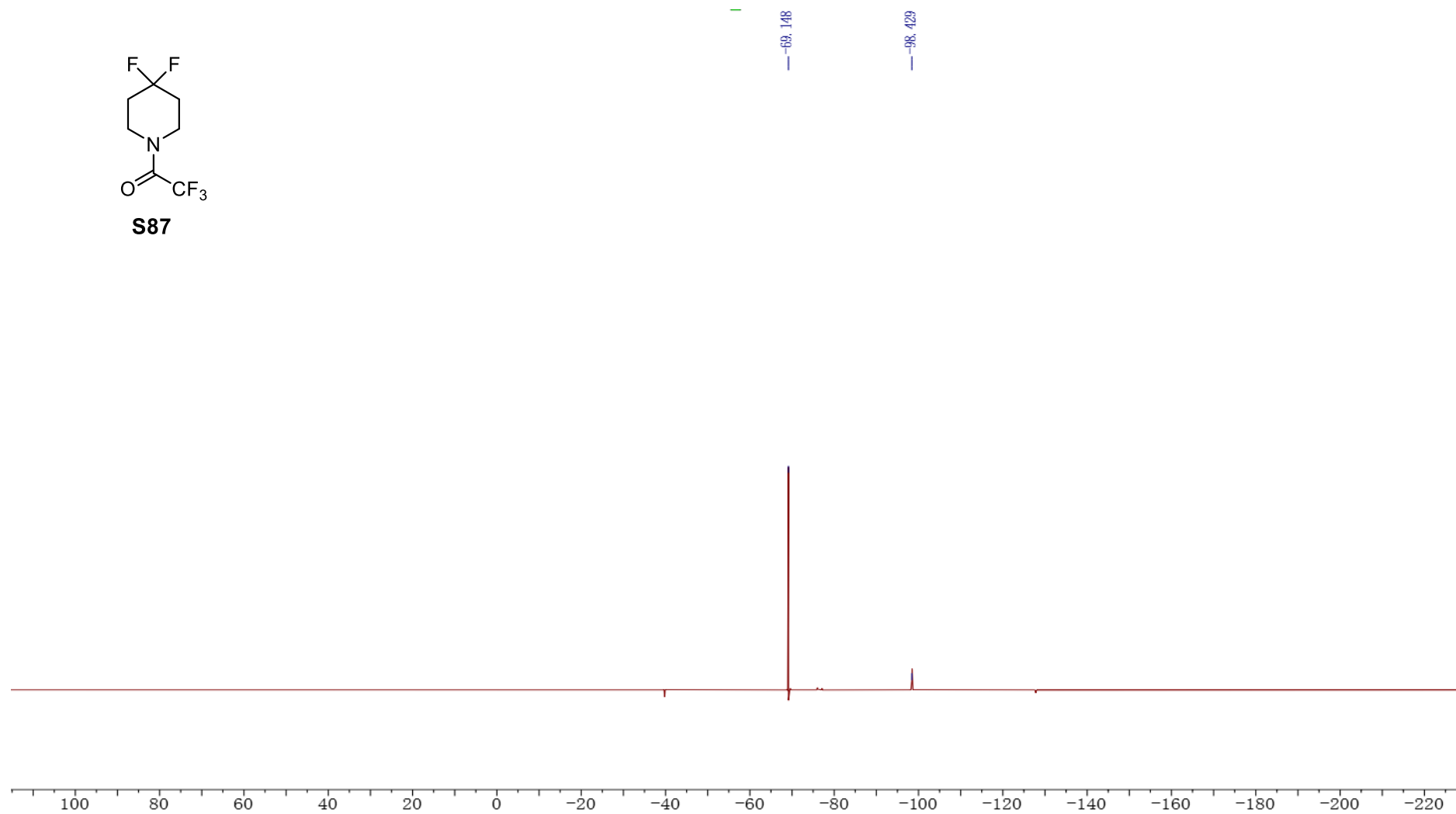


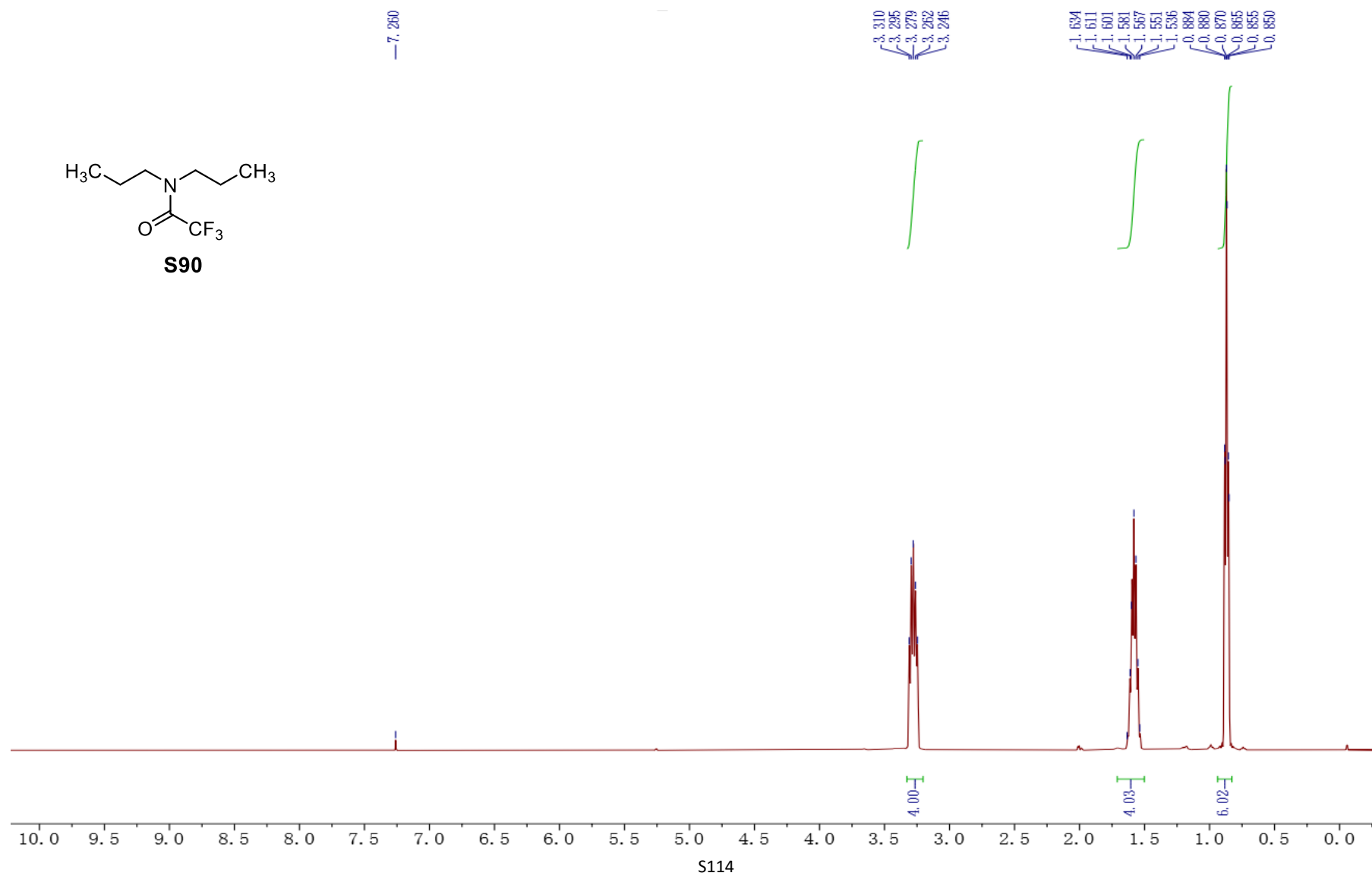
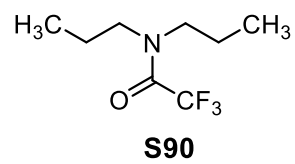
S87

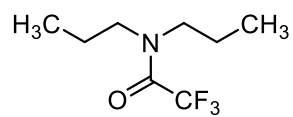




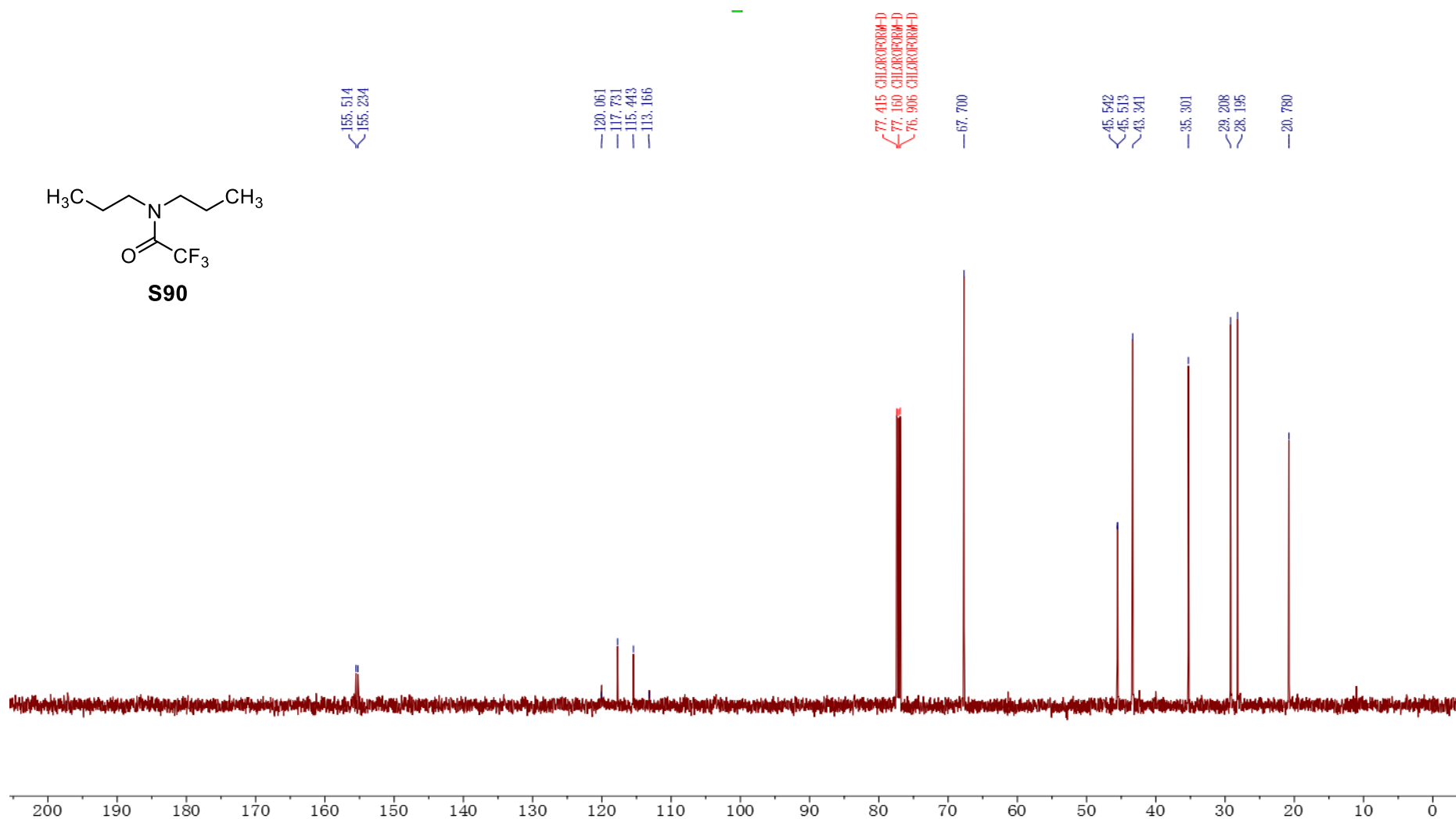
S87

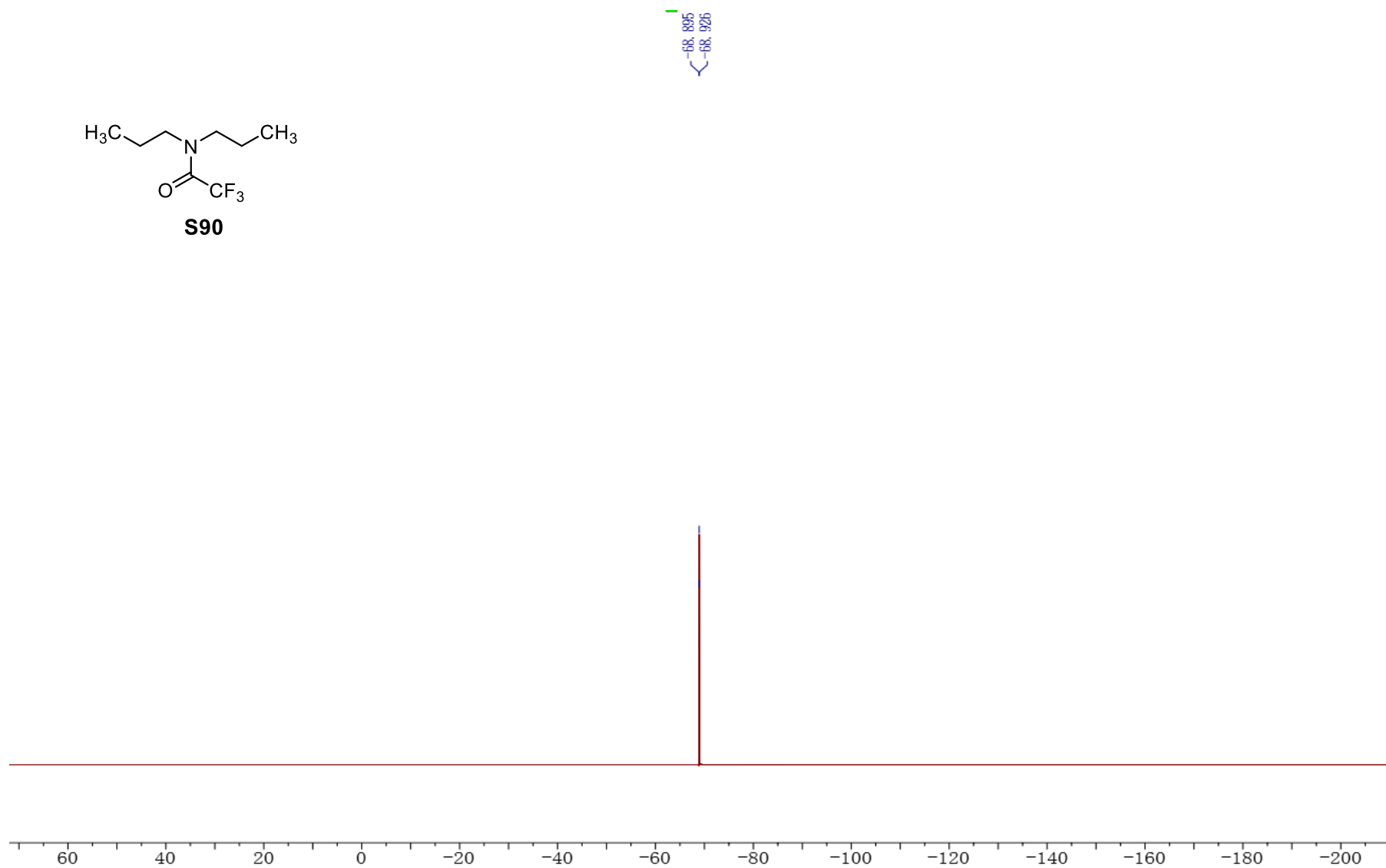
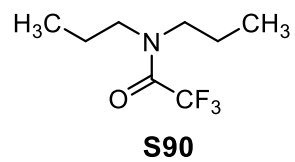


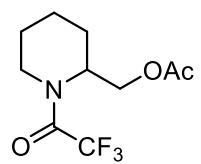




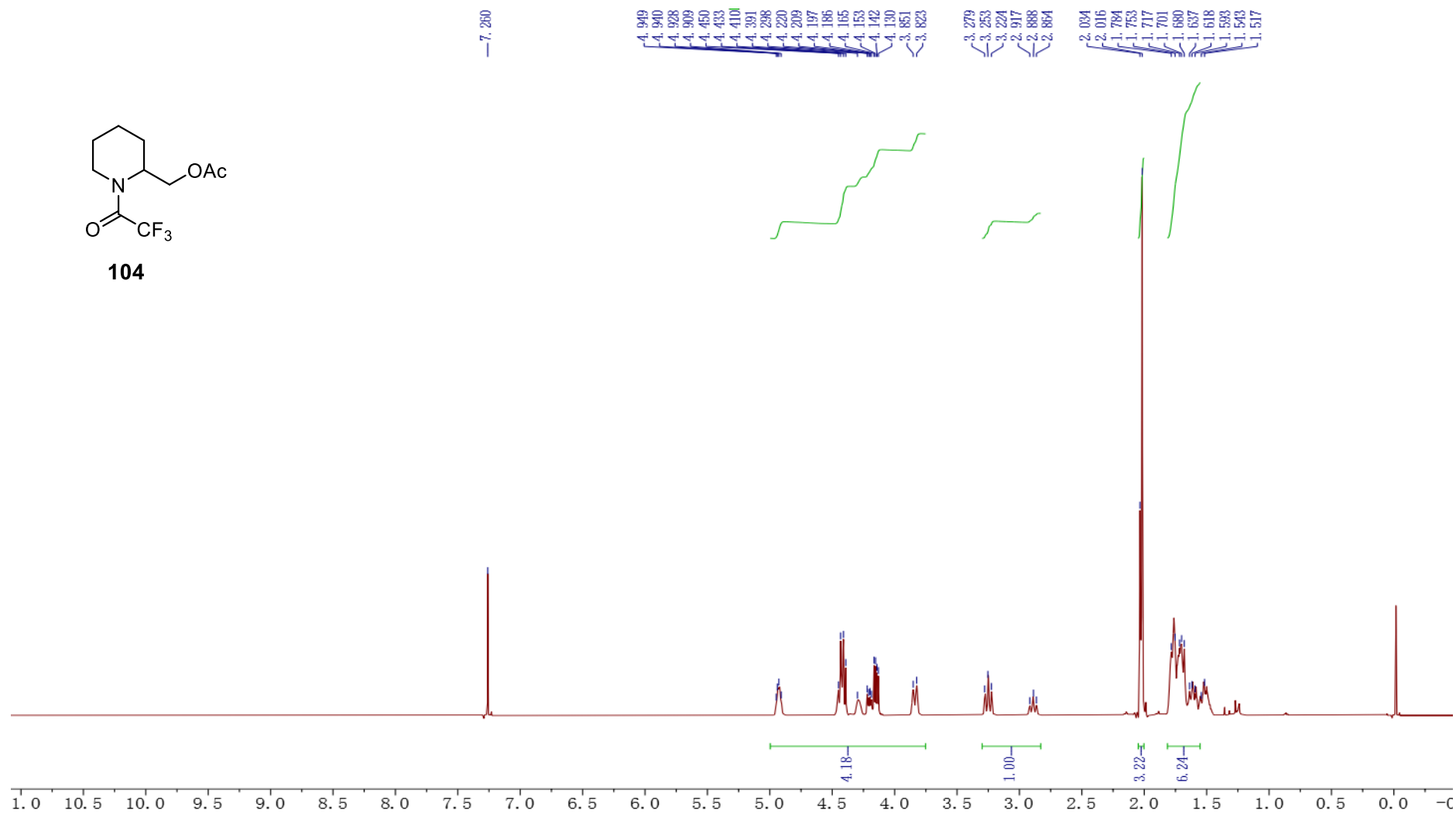
S90

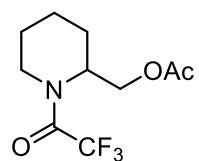




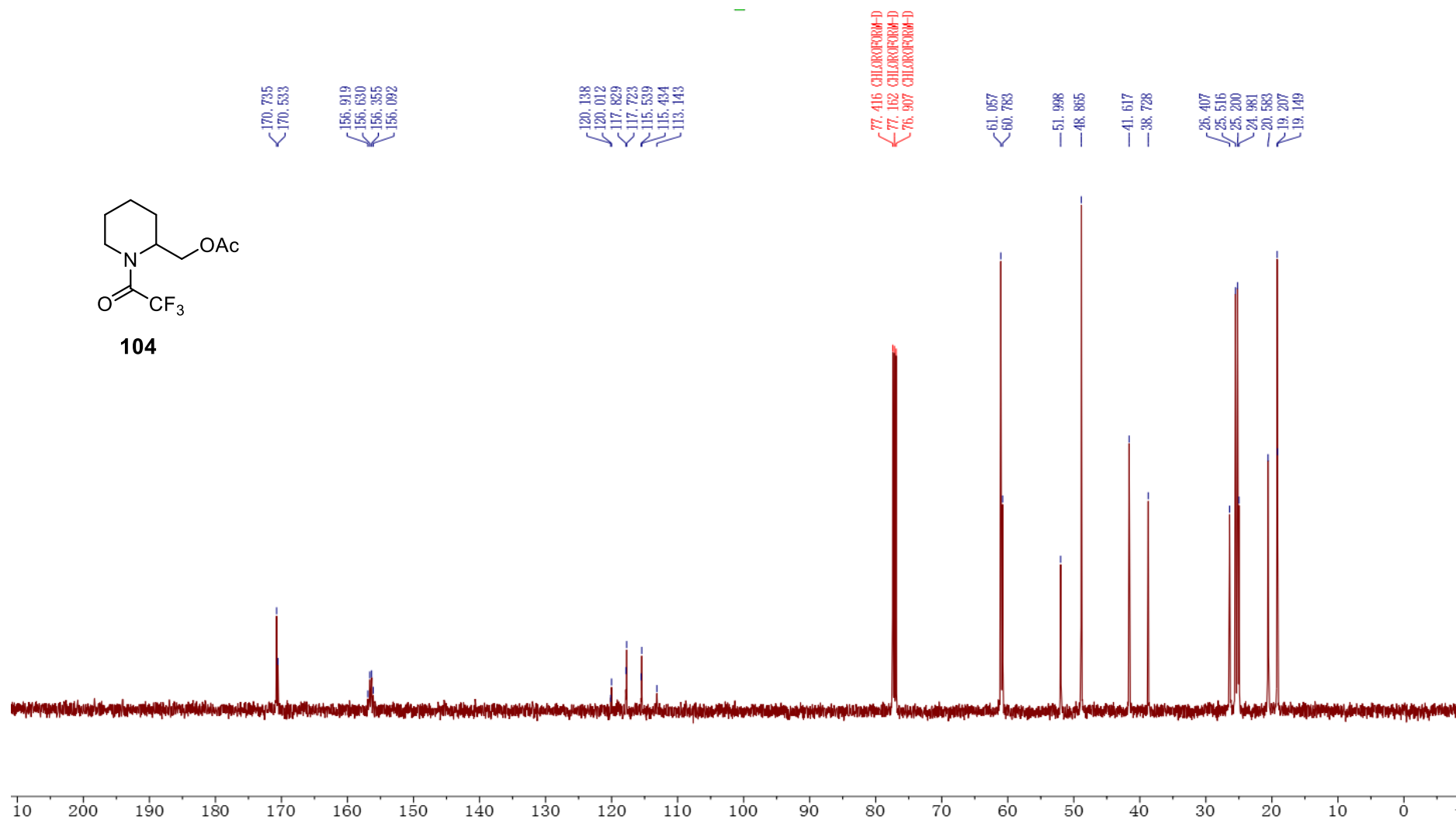


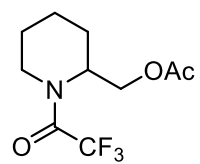
104



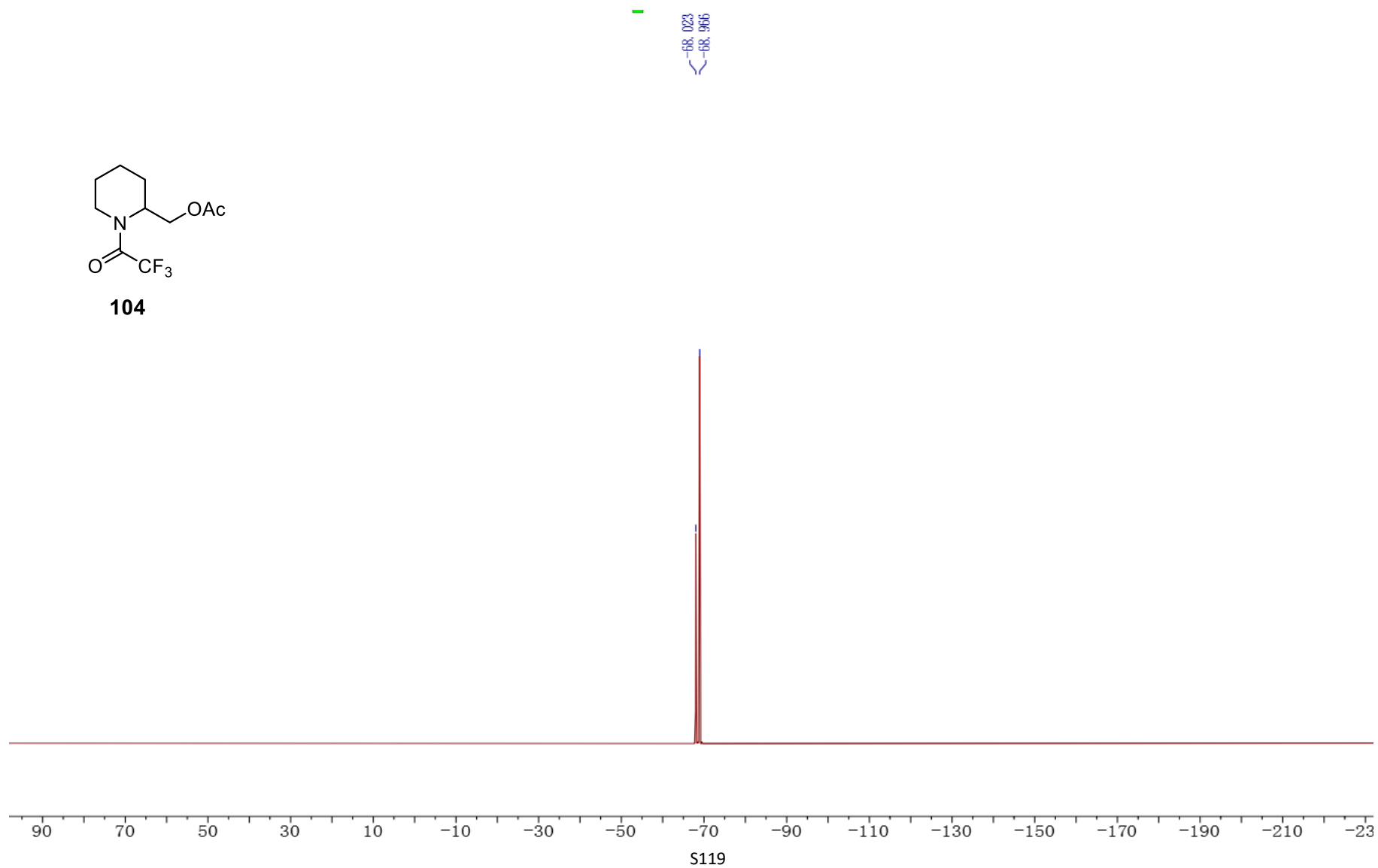


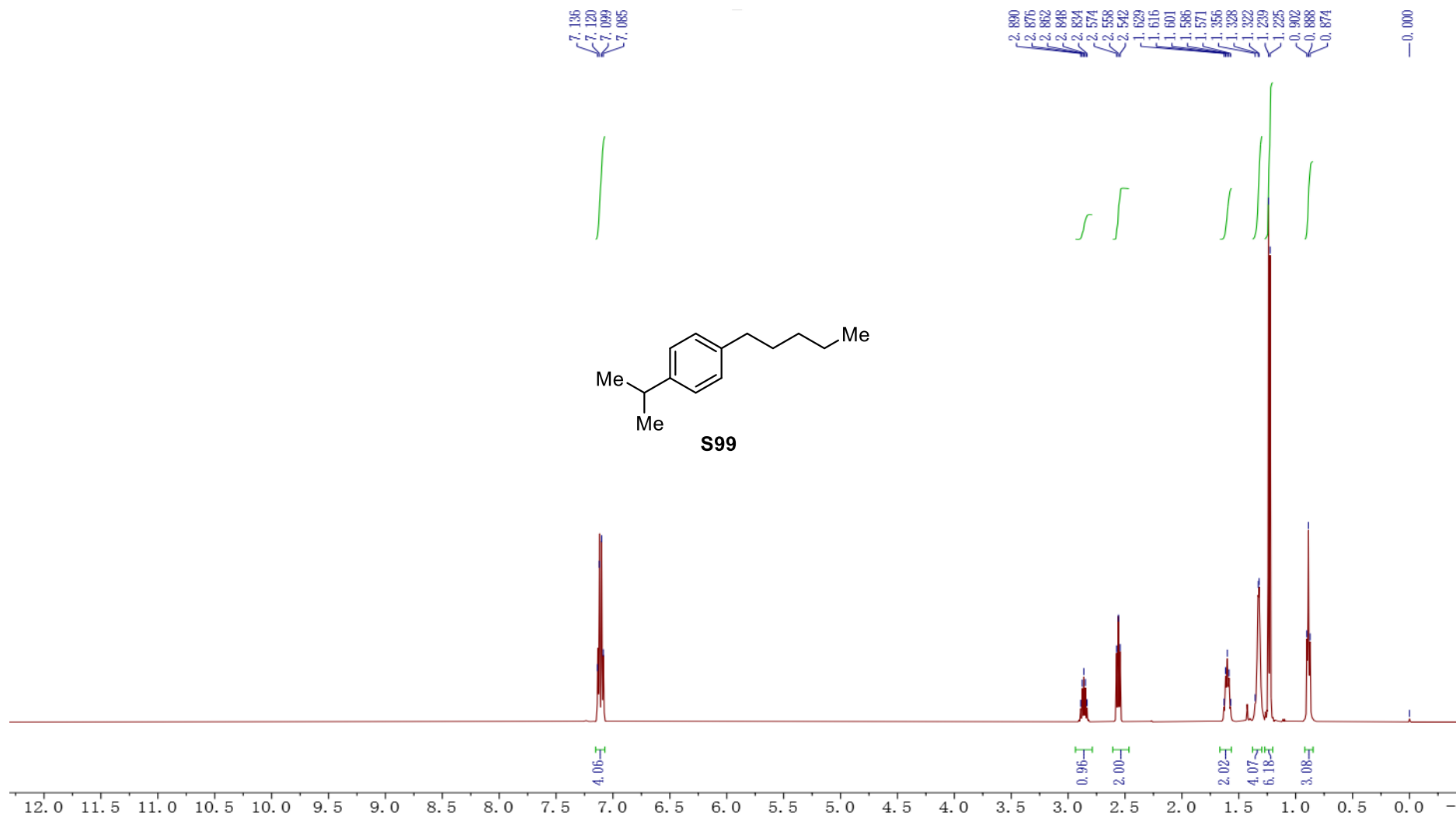
104



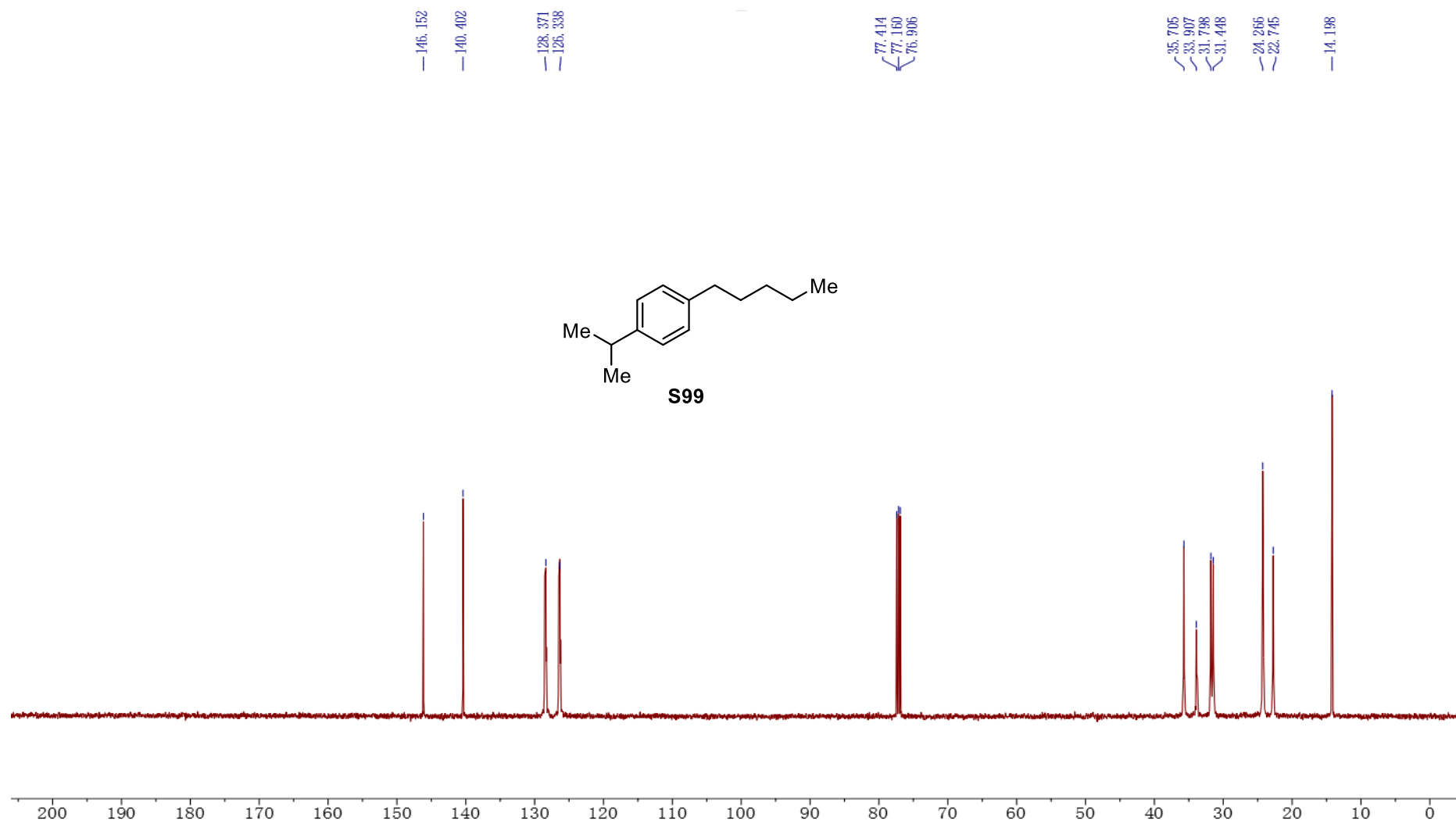


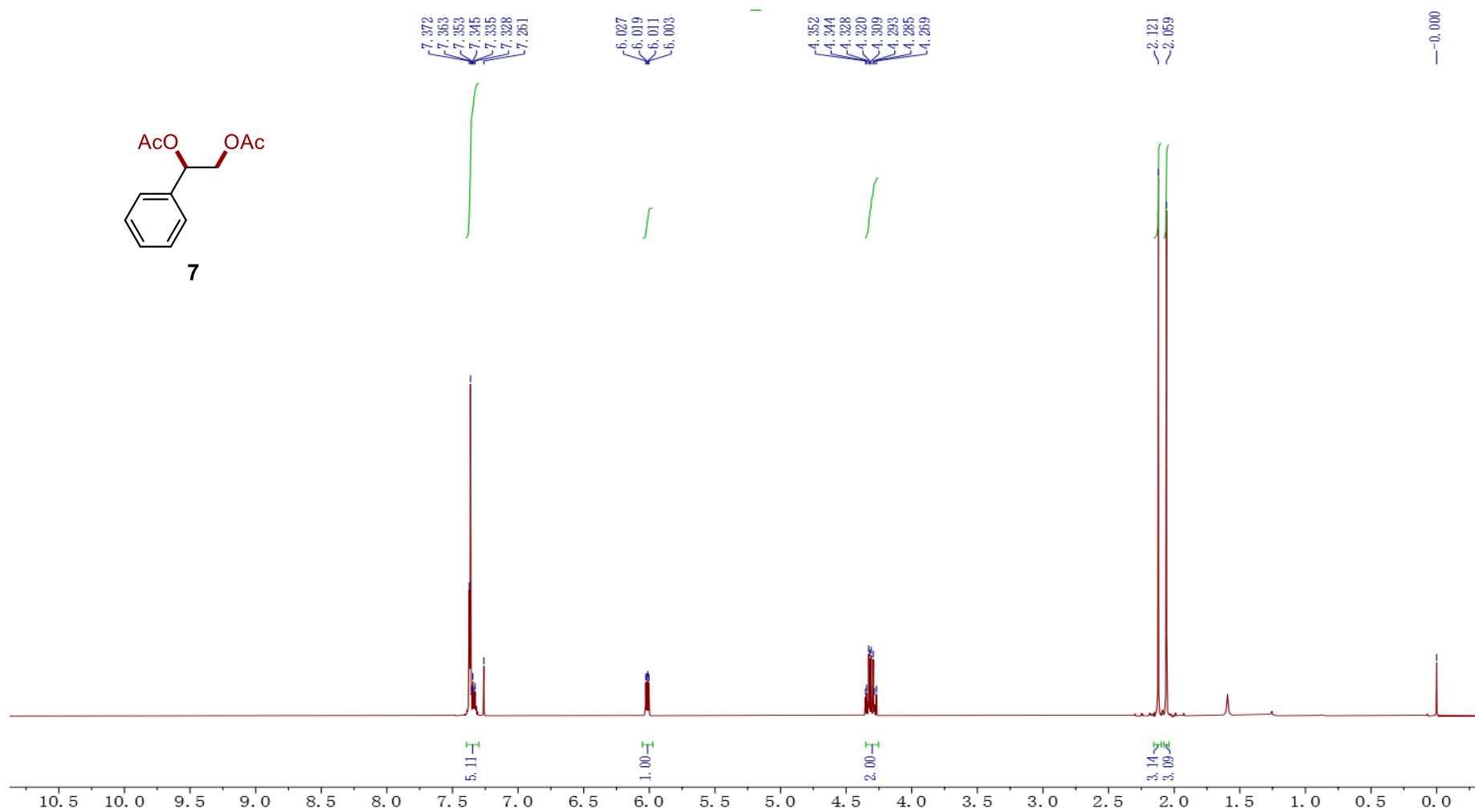
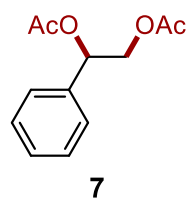
104

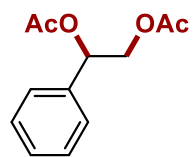




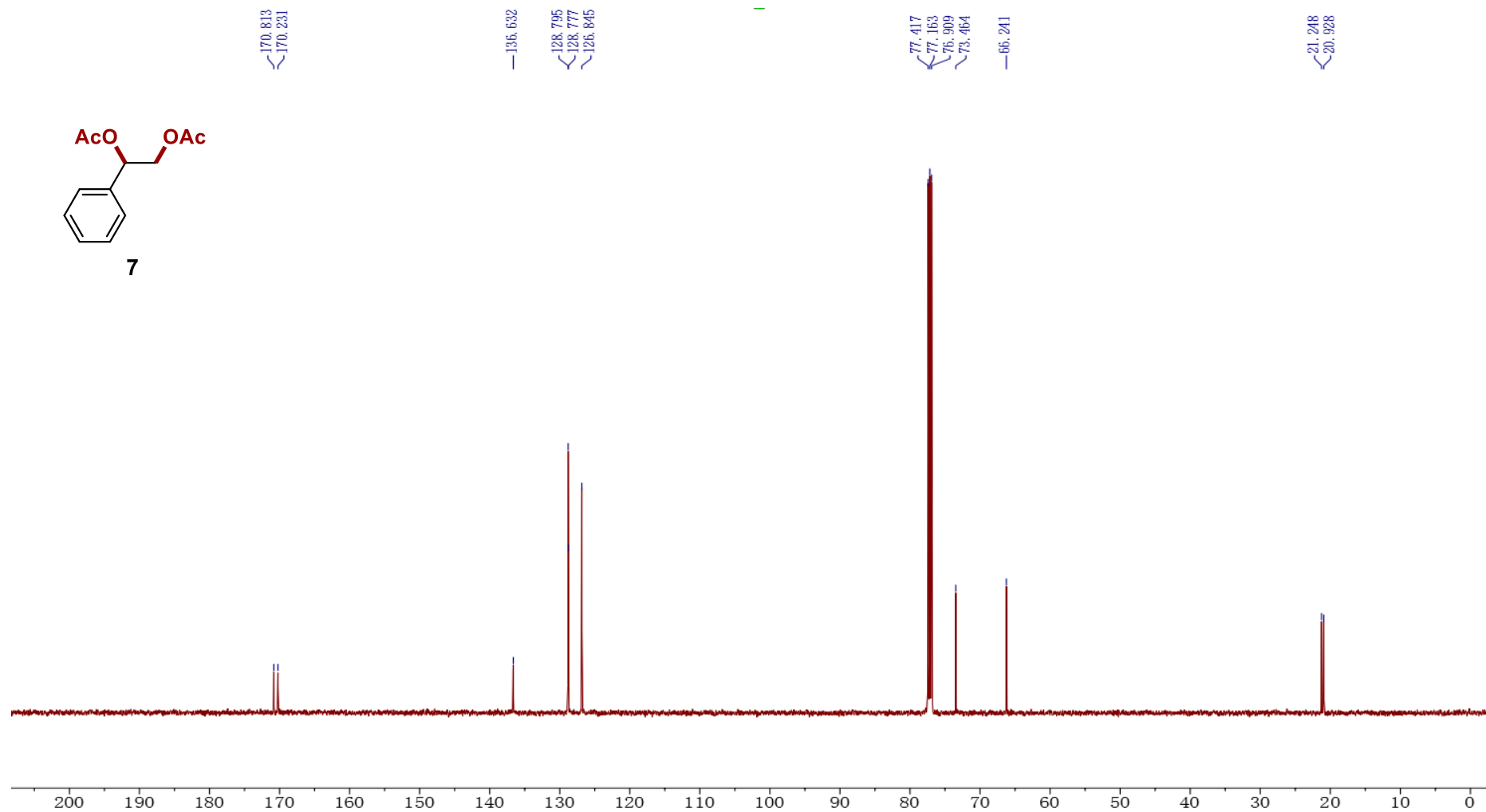
S120

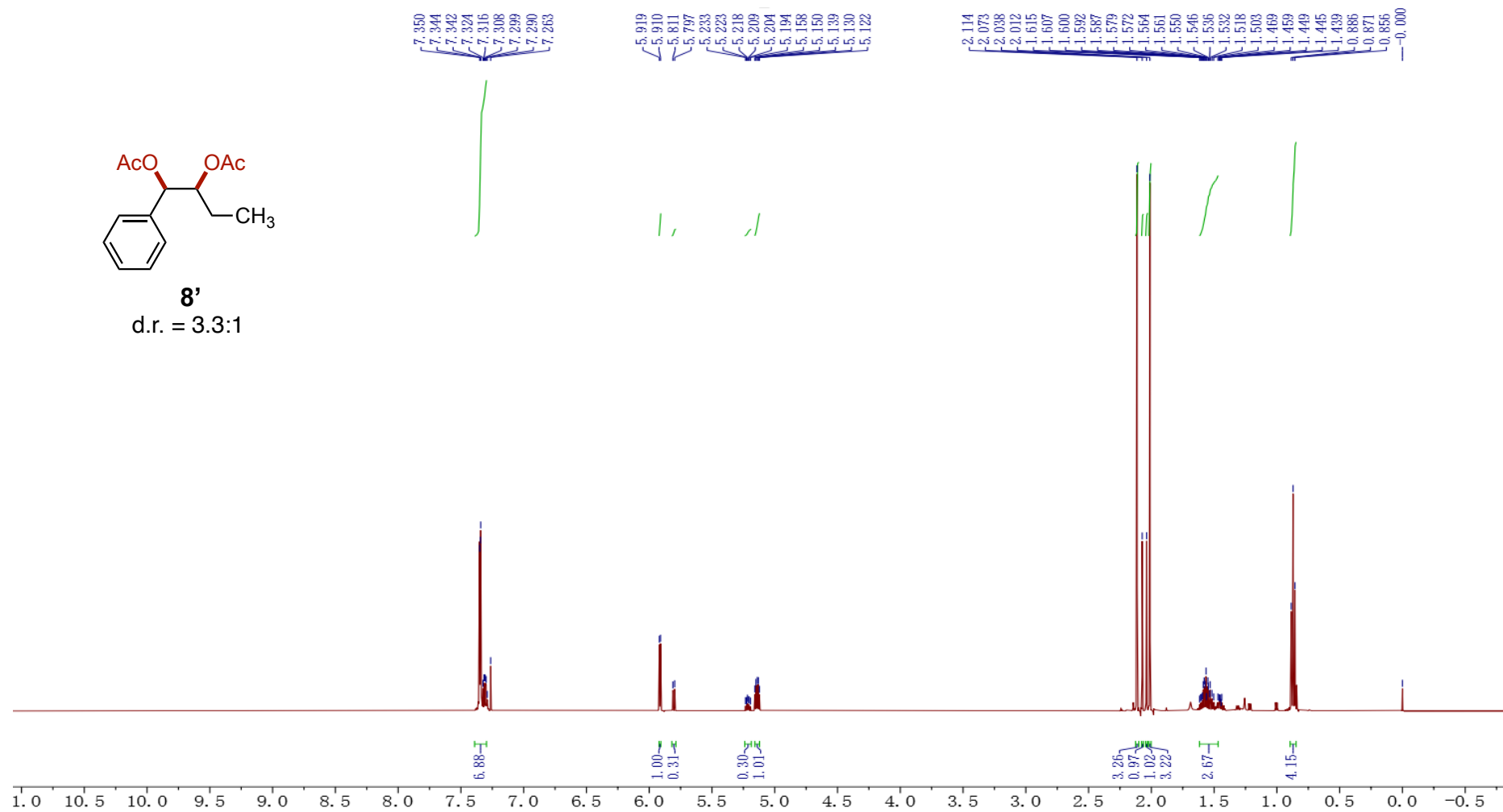
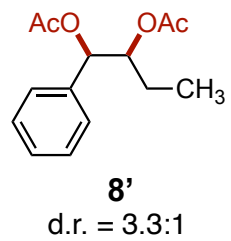


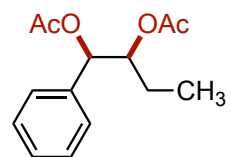




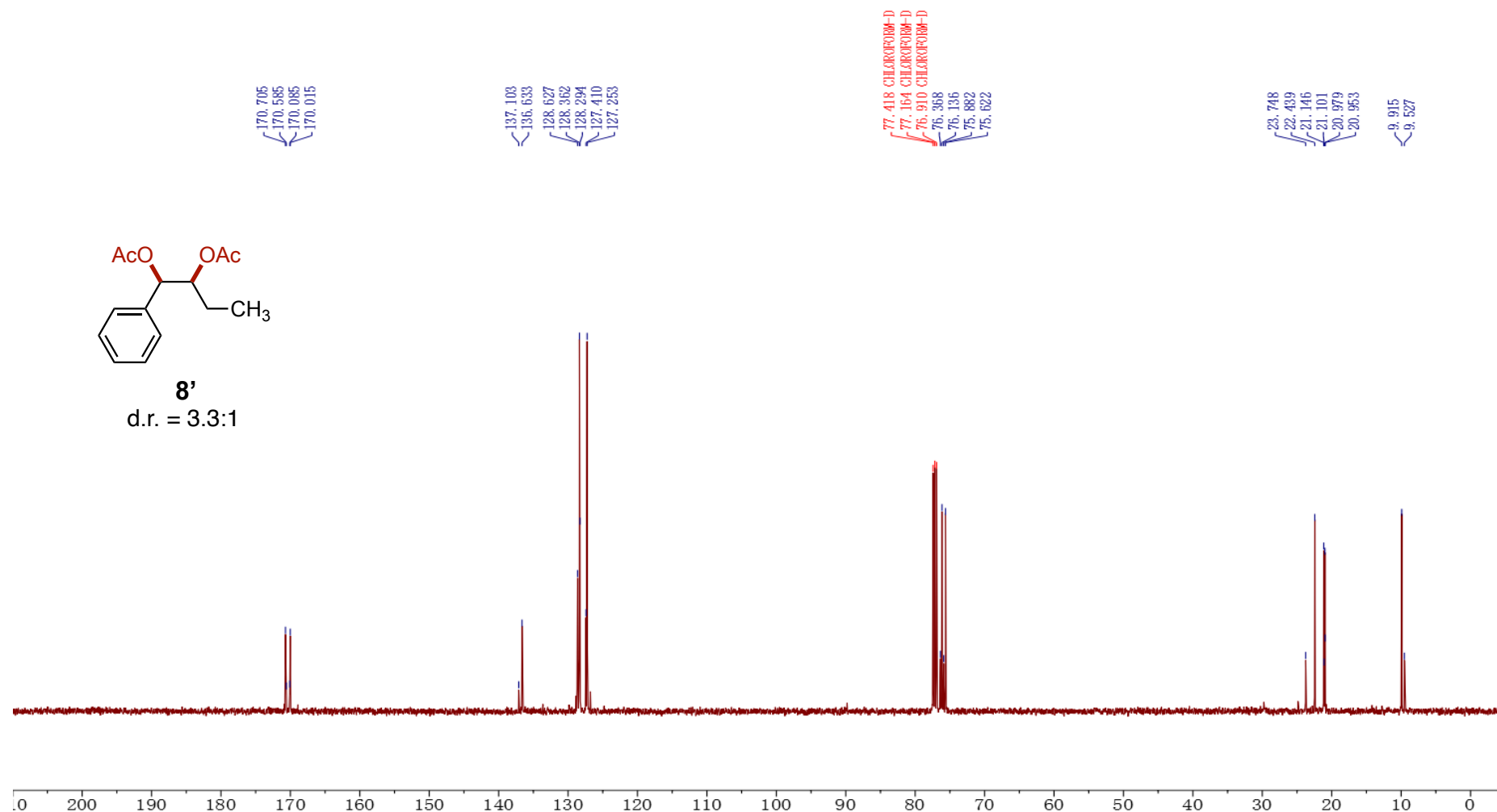
7

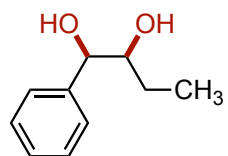






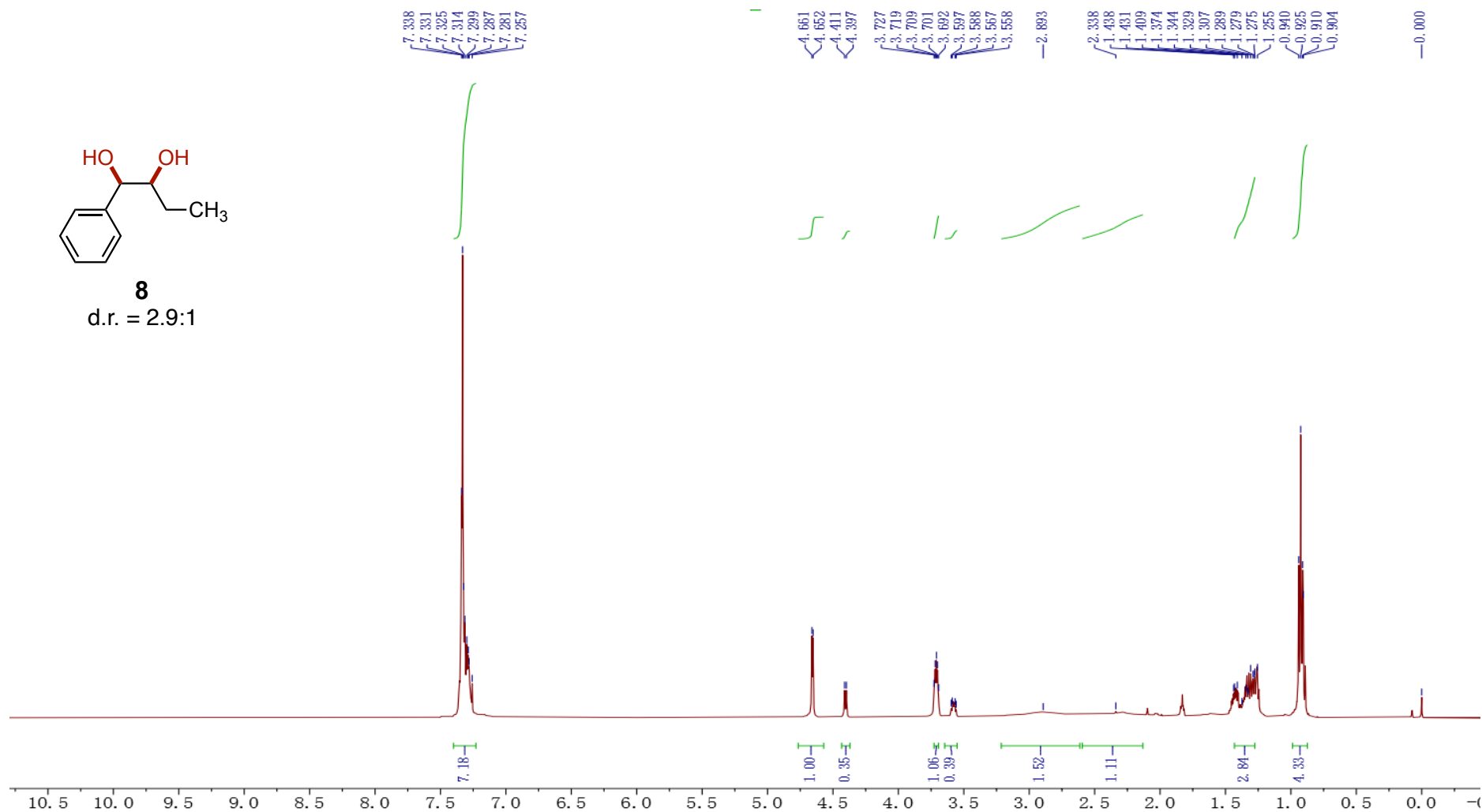
8'
d.r. = 3.3:1

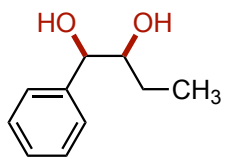




8

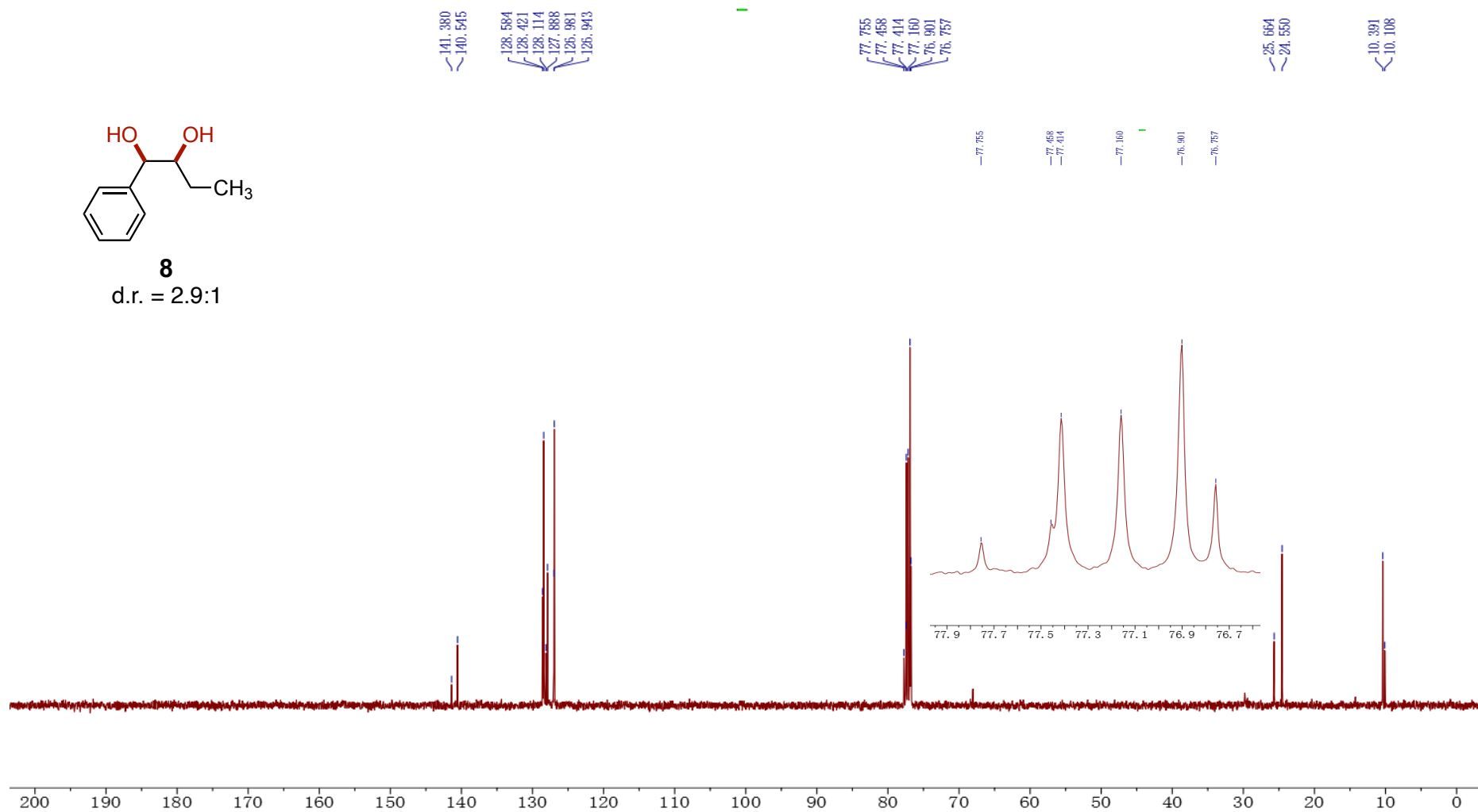
d.r. = 2.9:1

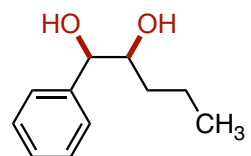




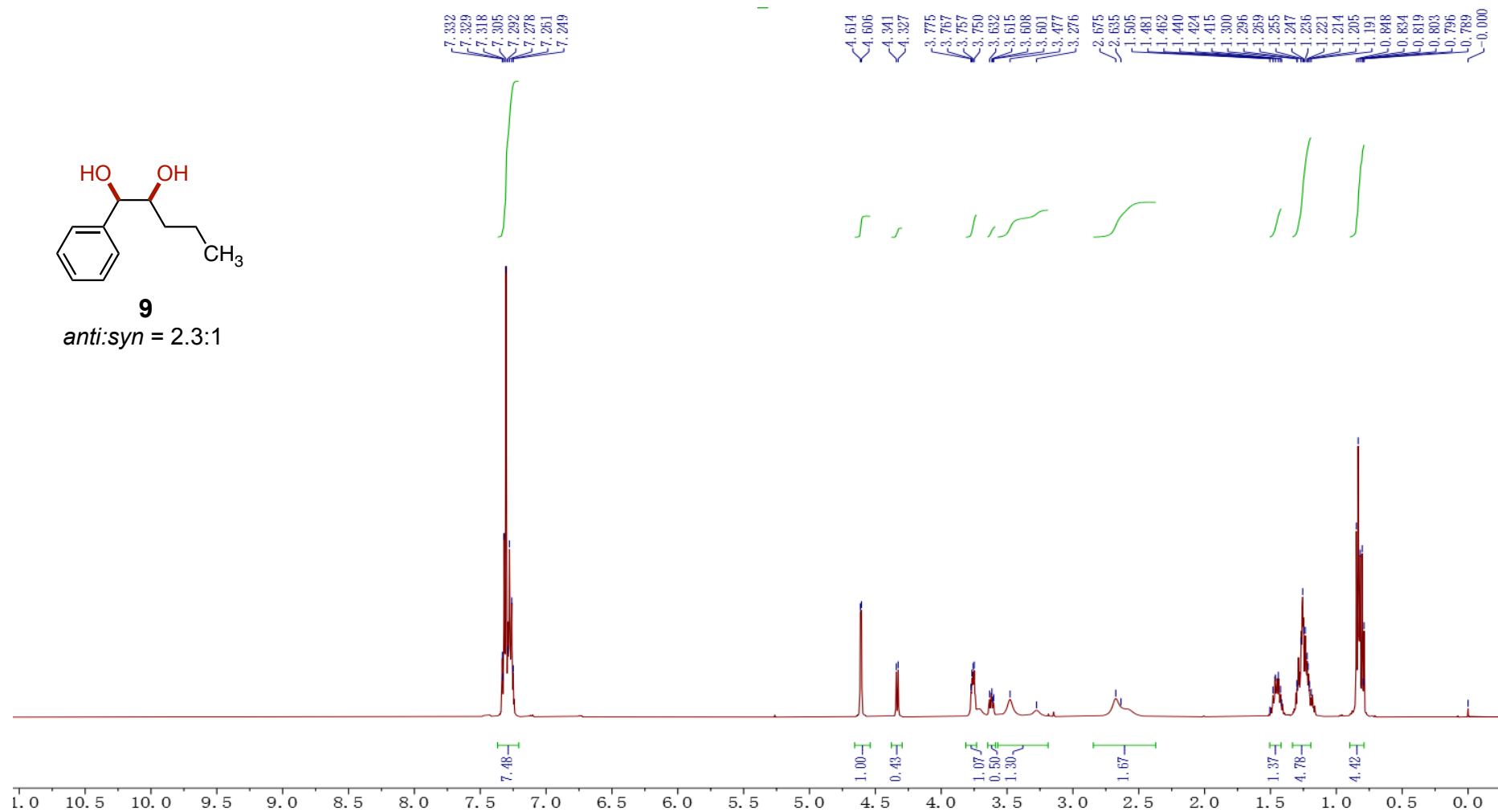
8

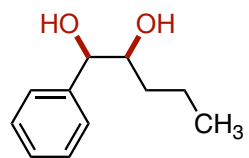
d.r. = 2.9:1





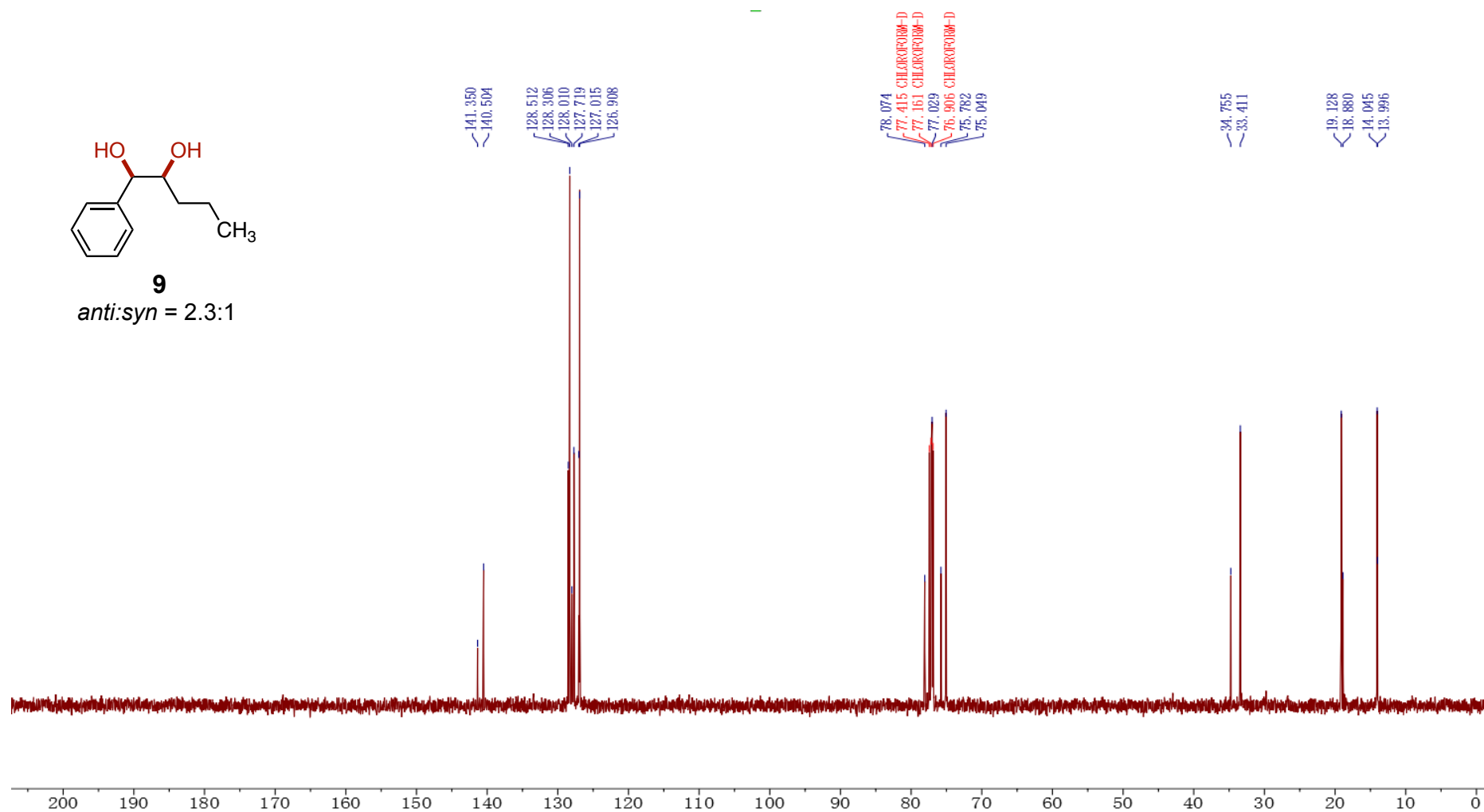
9
anti:syn = 2.3:1

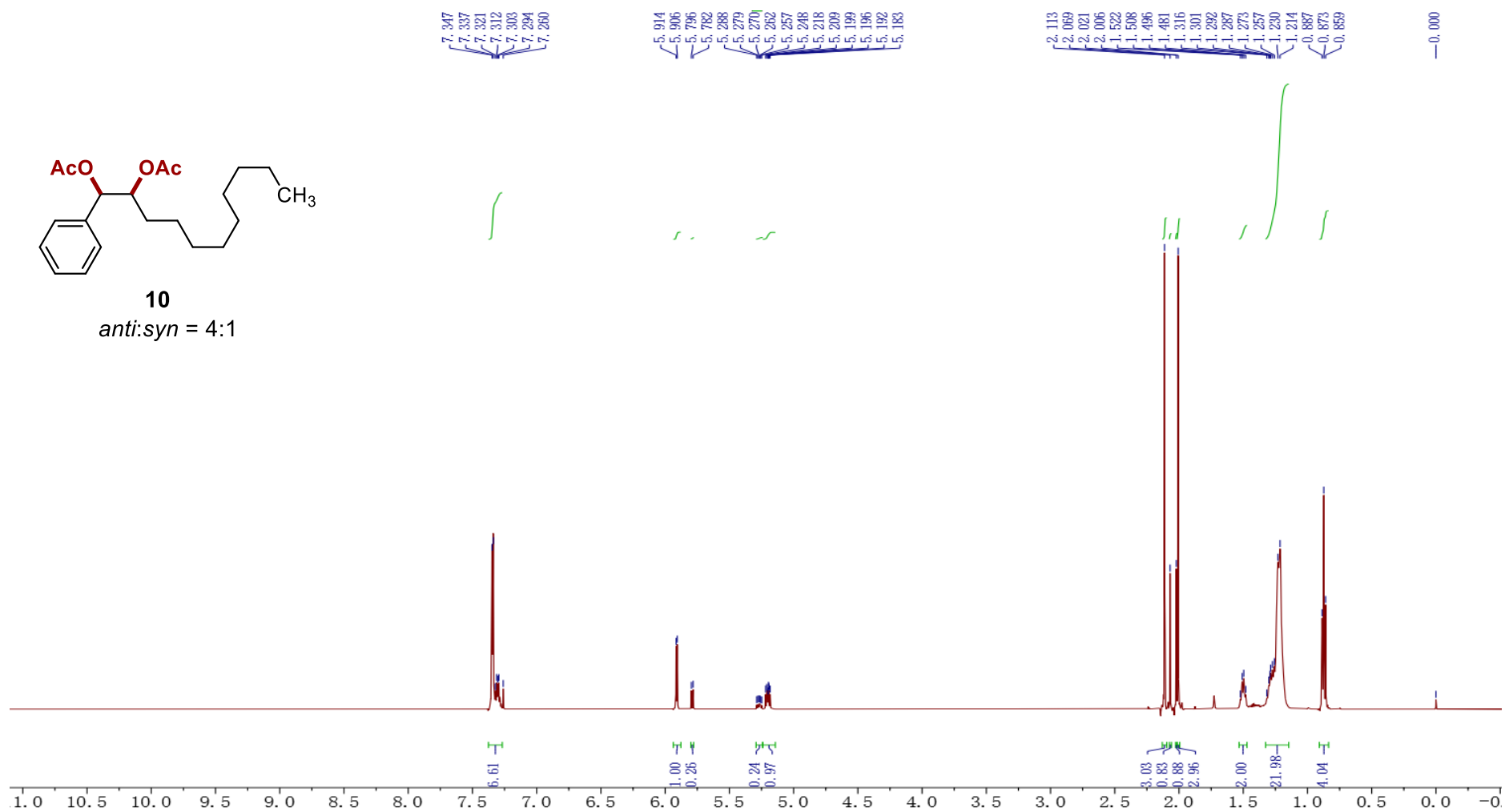


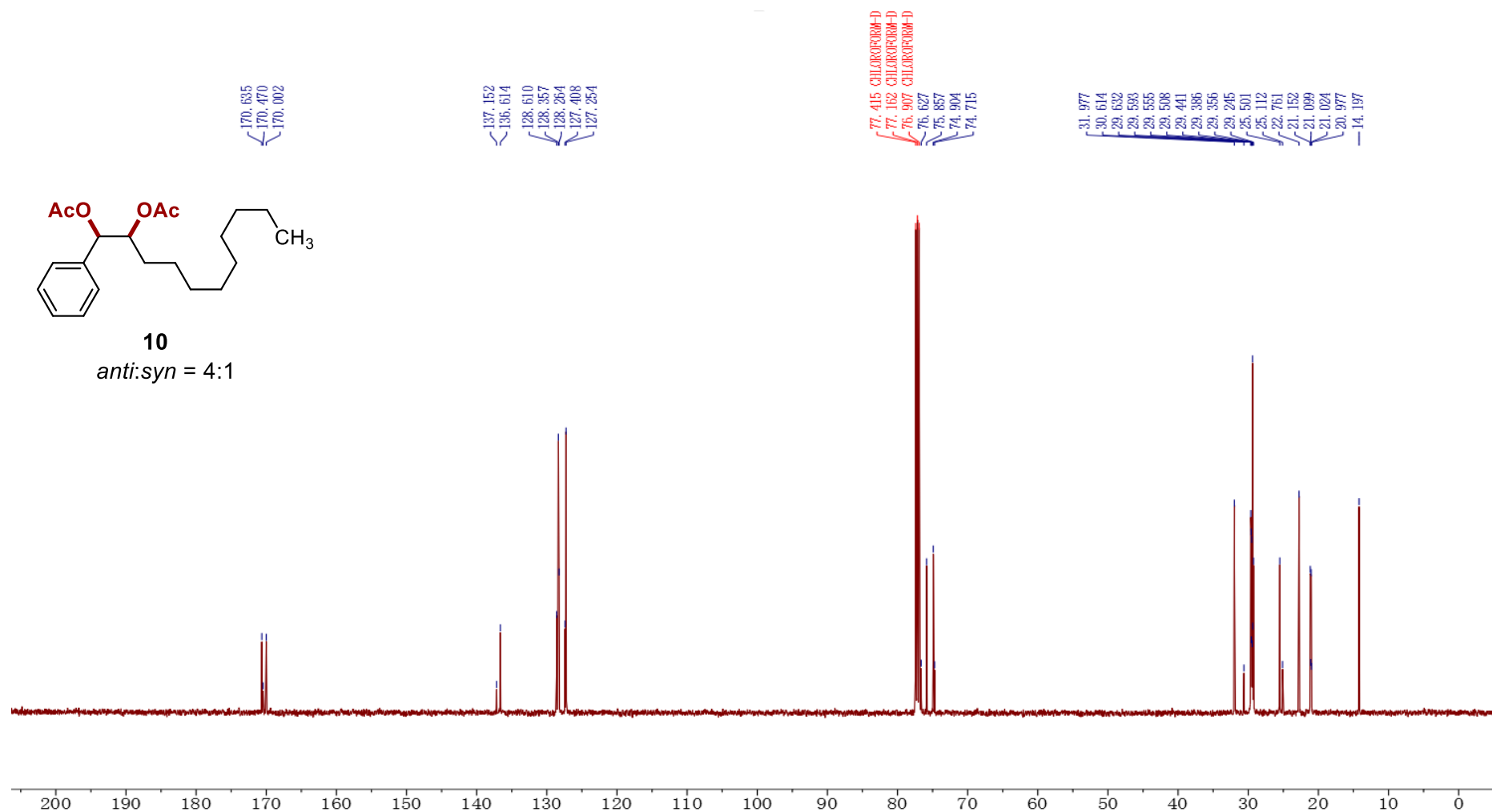


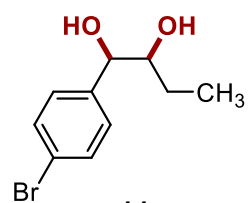
9

anti:syn = 2.3:1

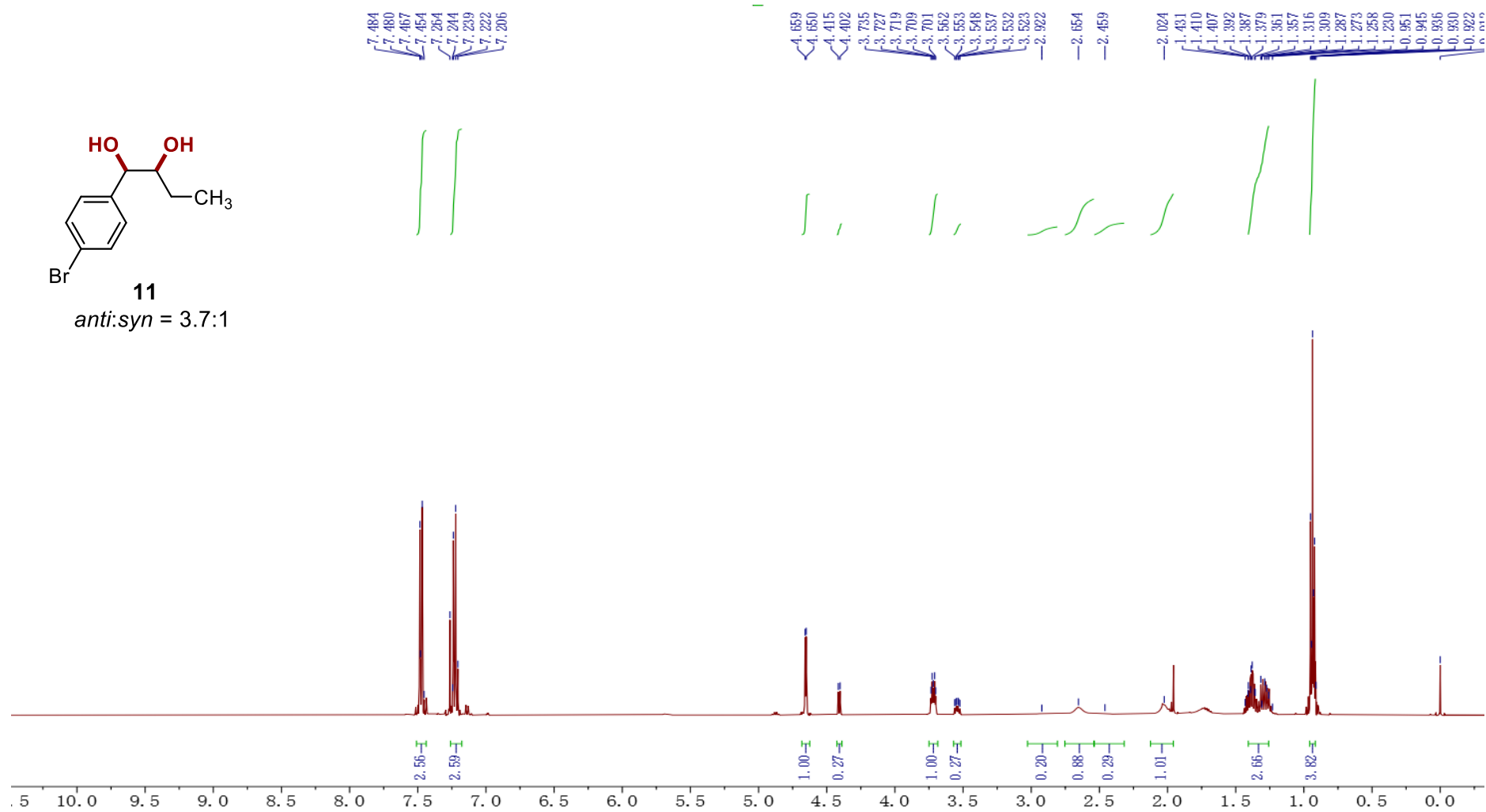


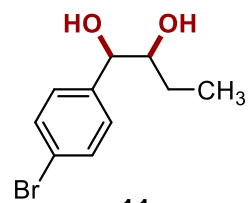




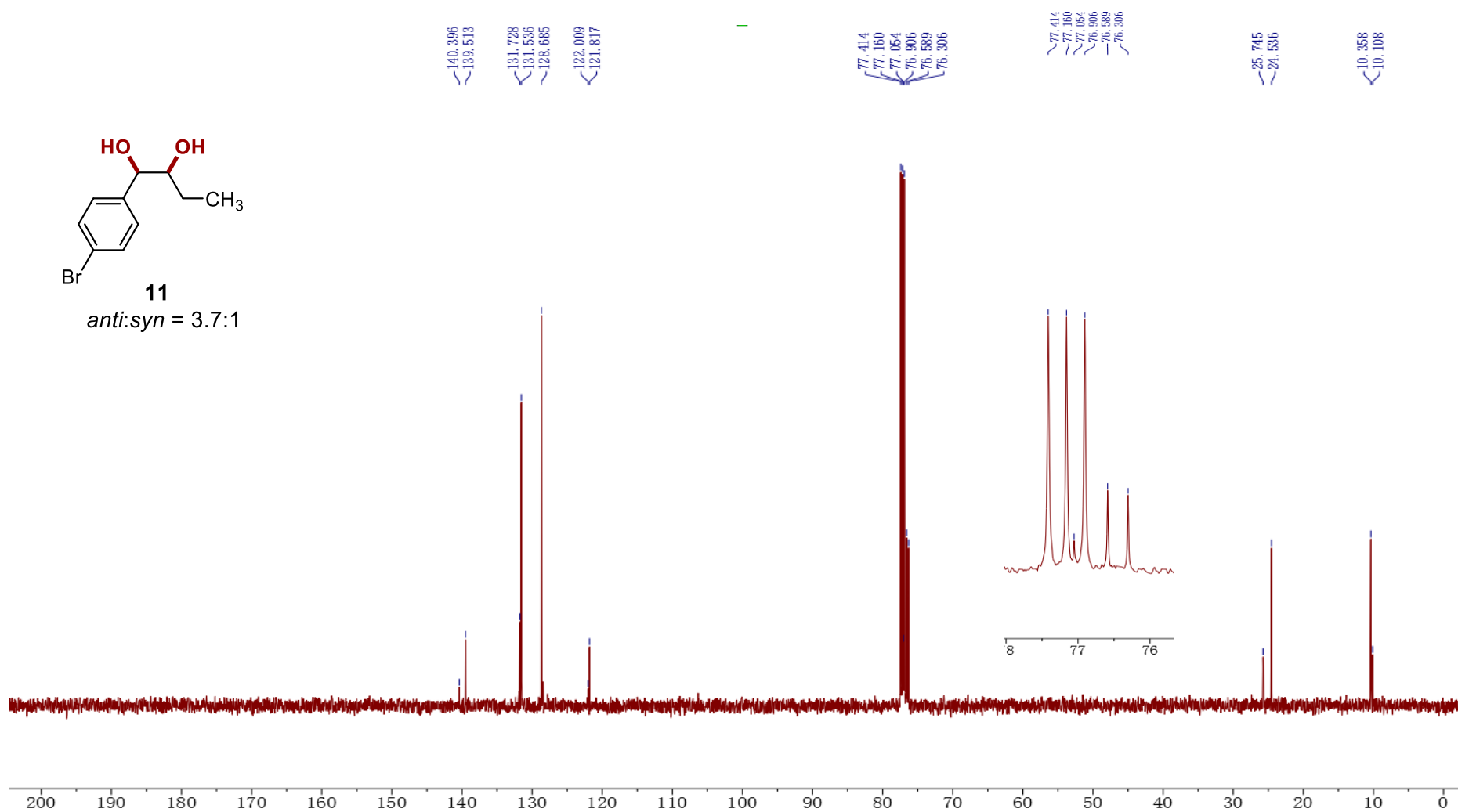


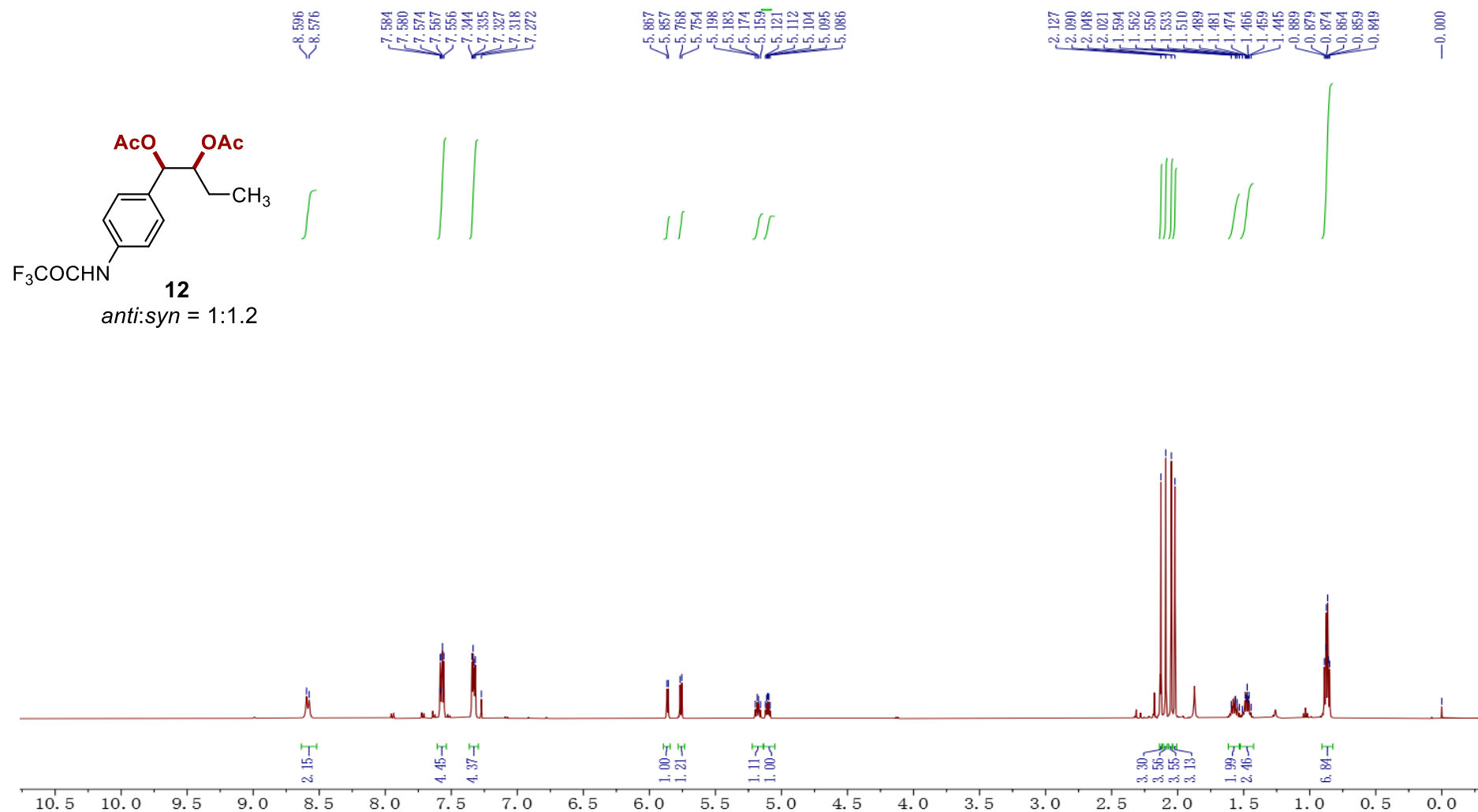
anti:syn = 3.7:1

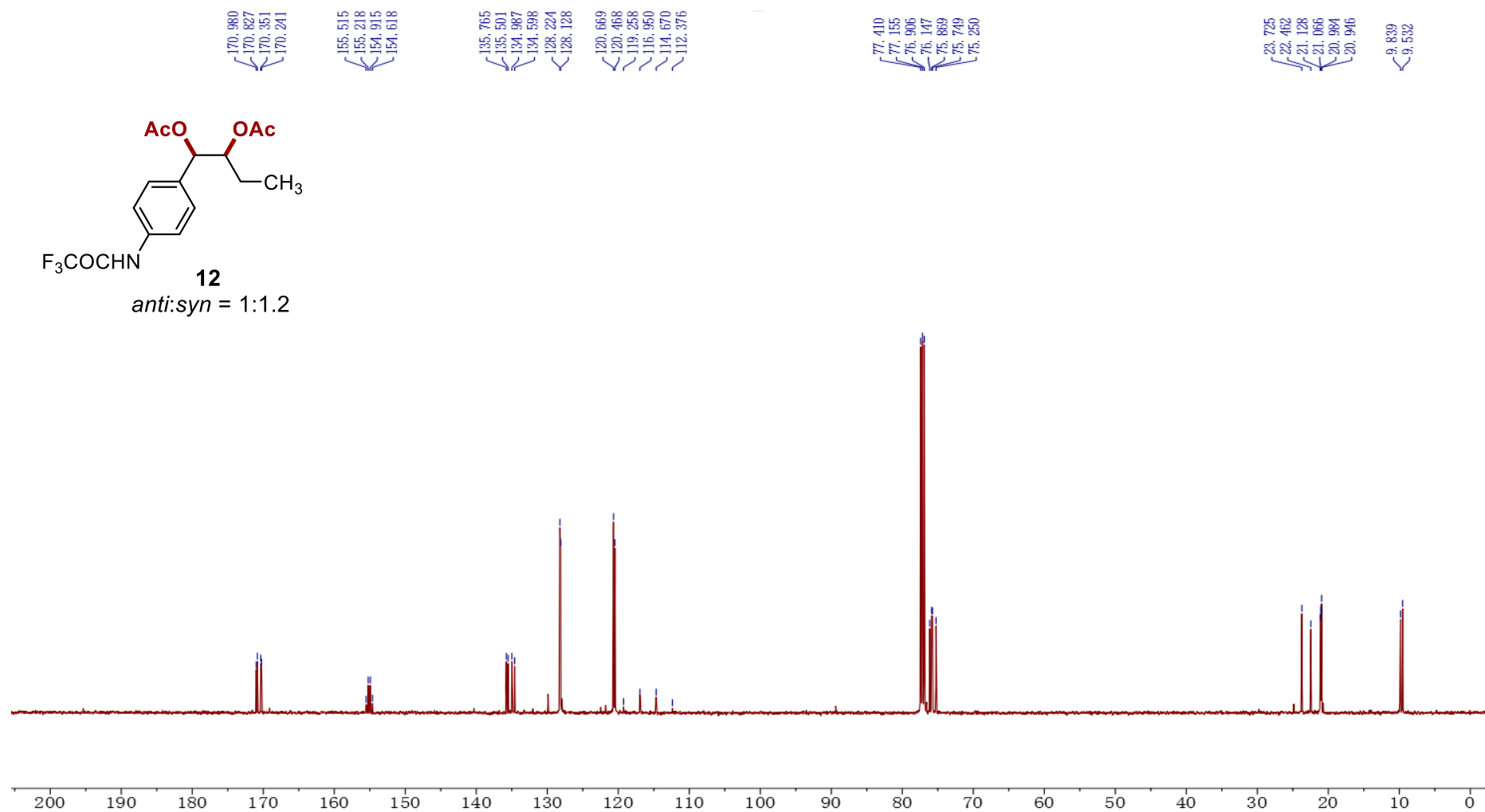


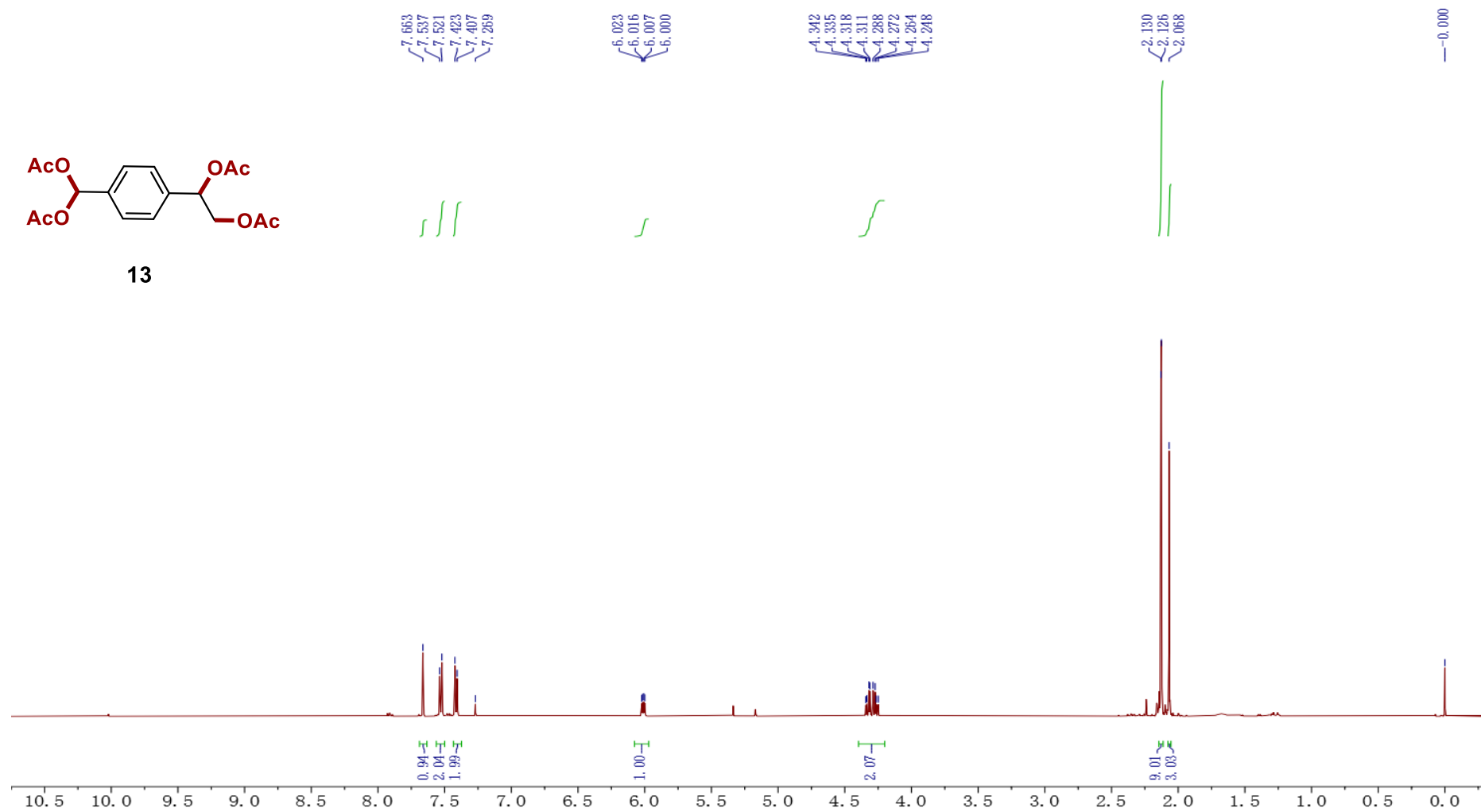


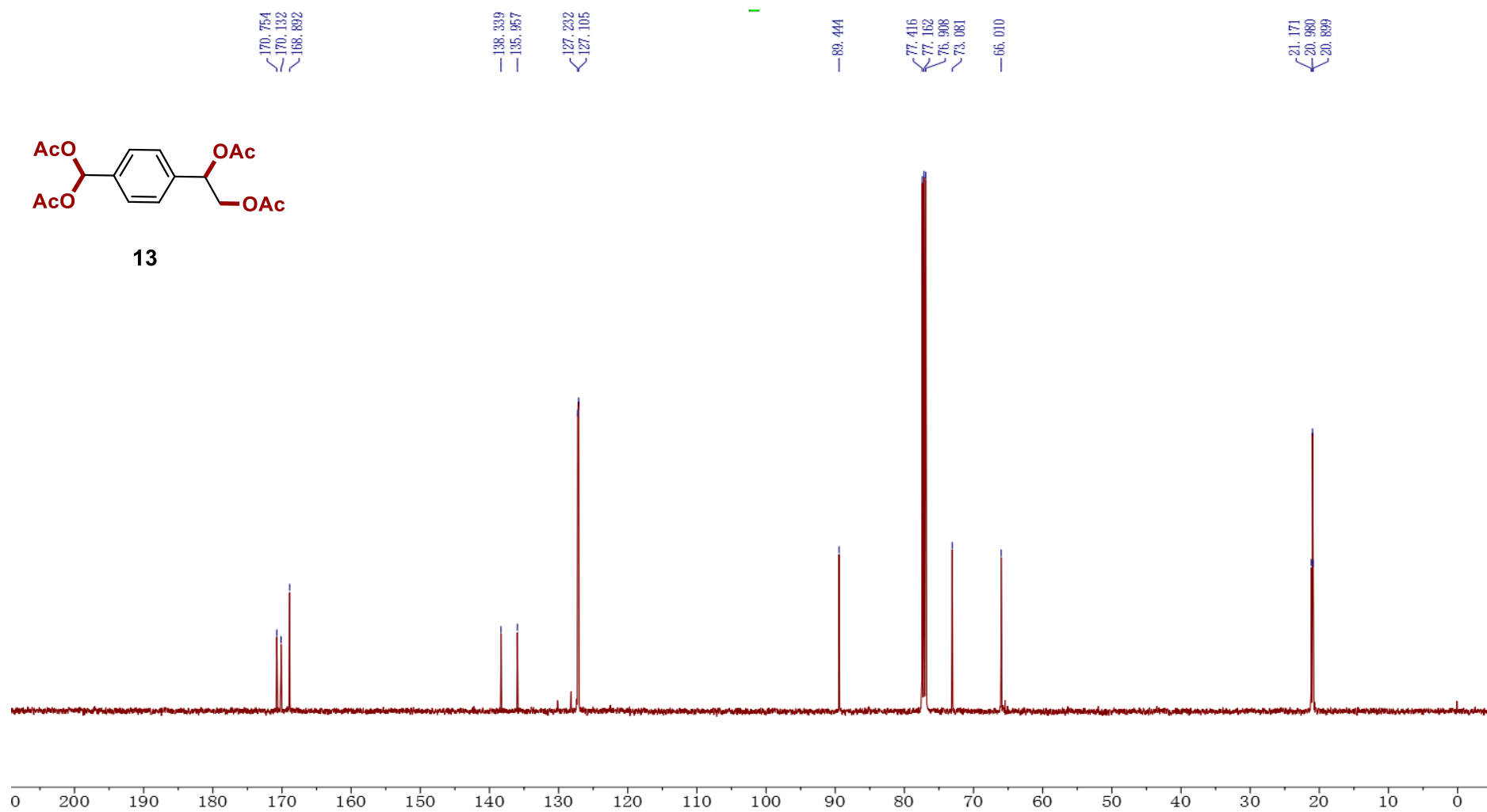
anti:syn = 3.7:1

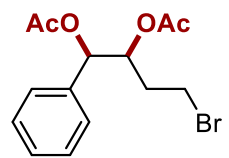






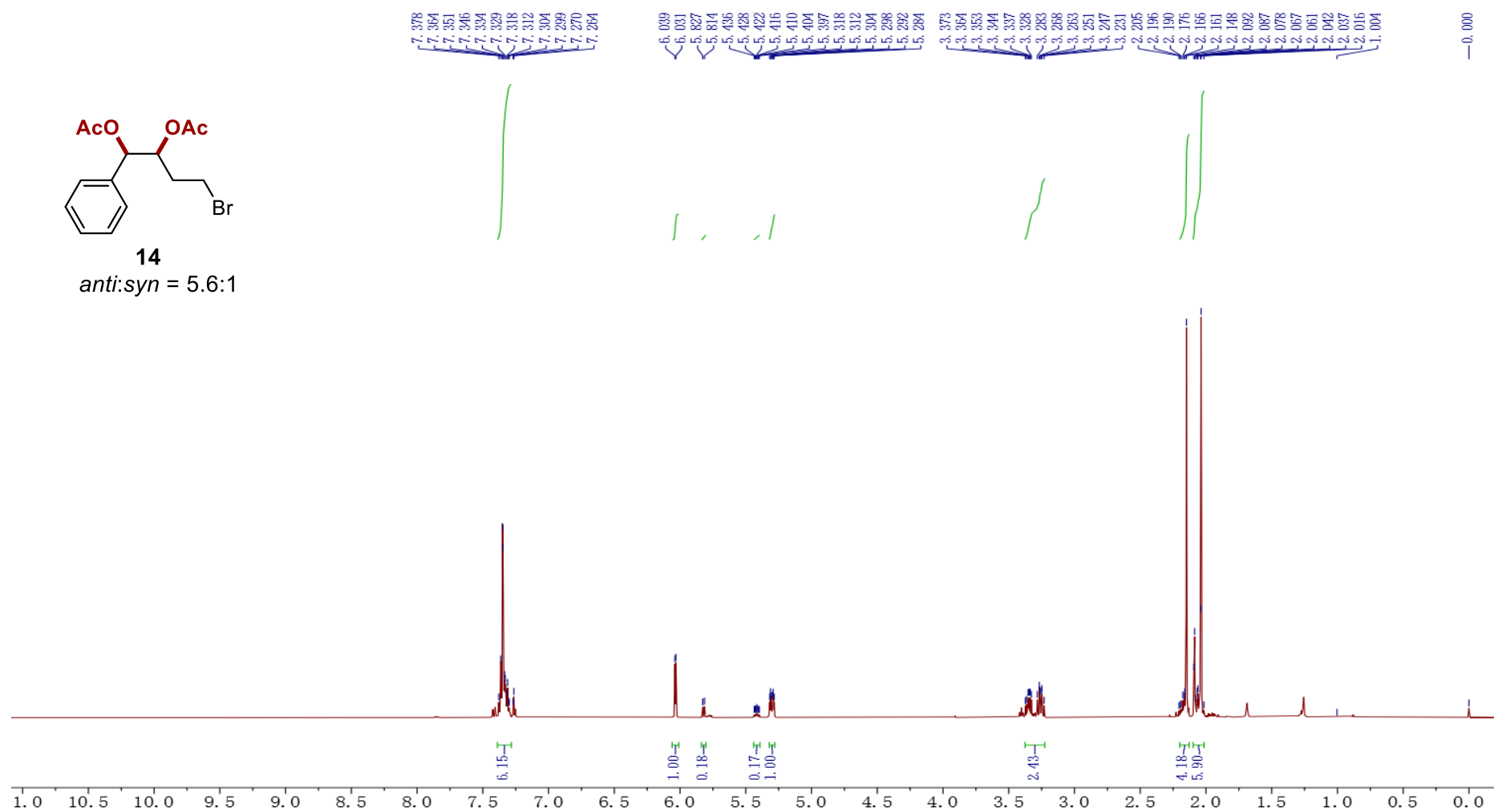


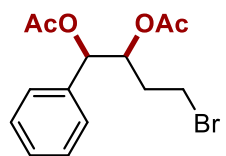




14

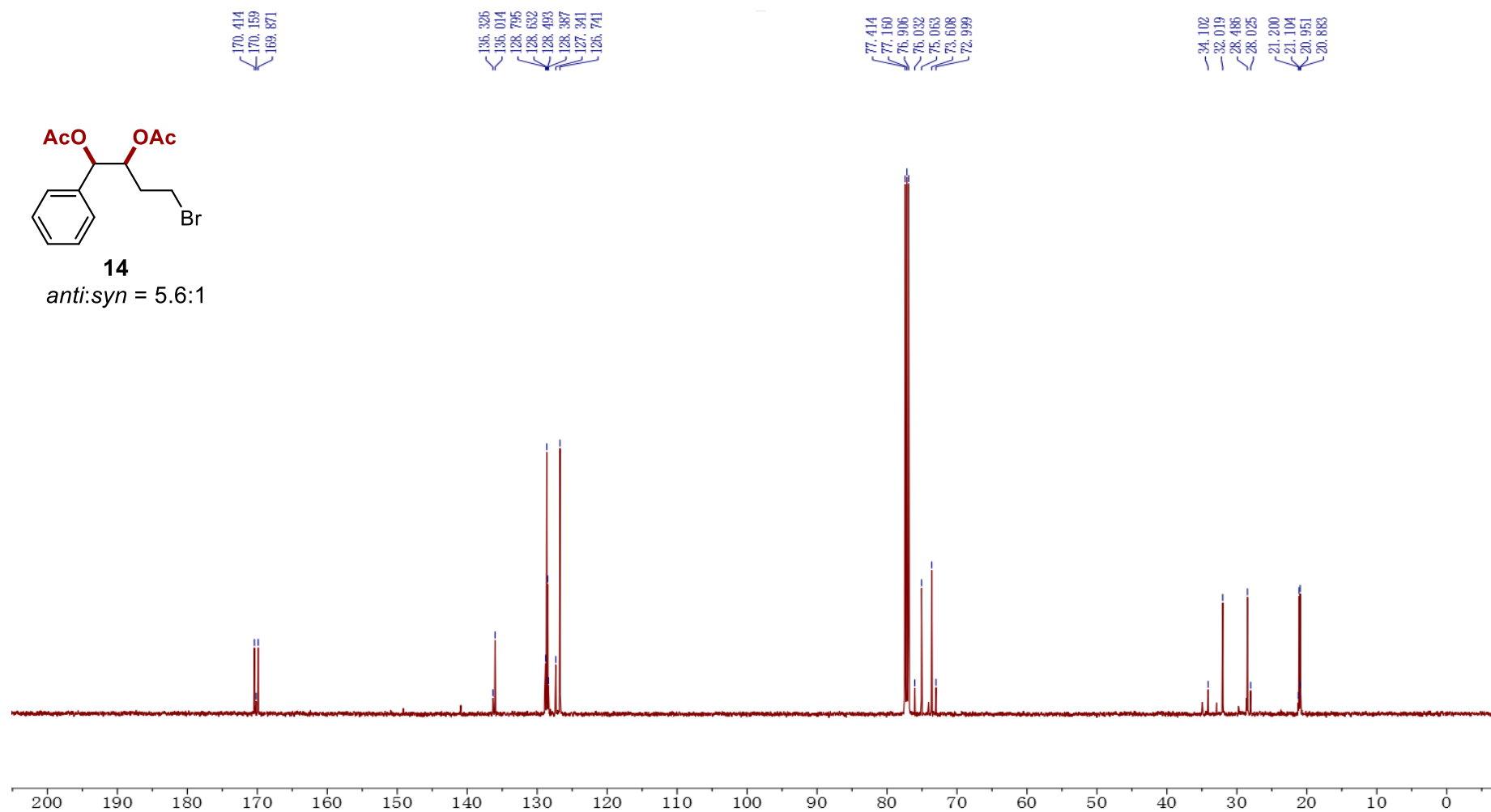
anti:syn = 5.6:1

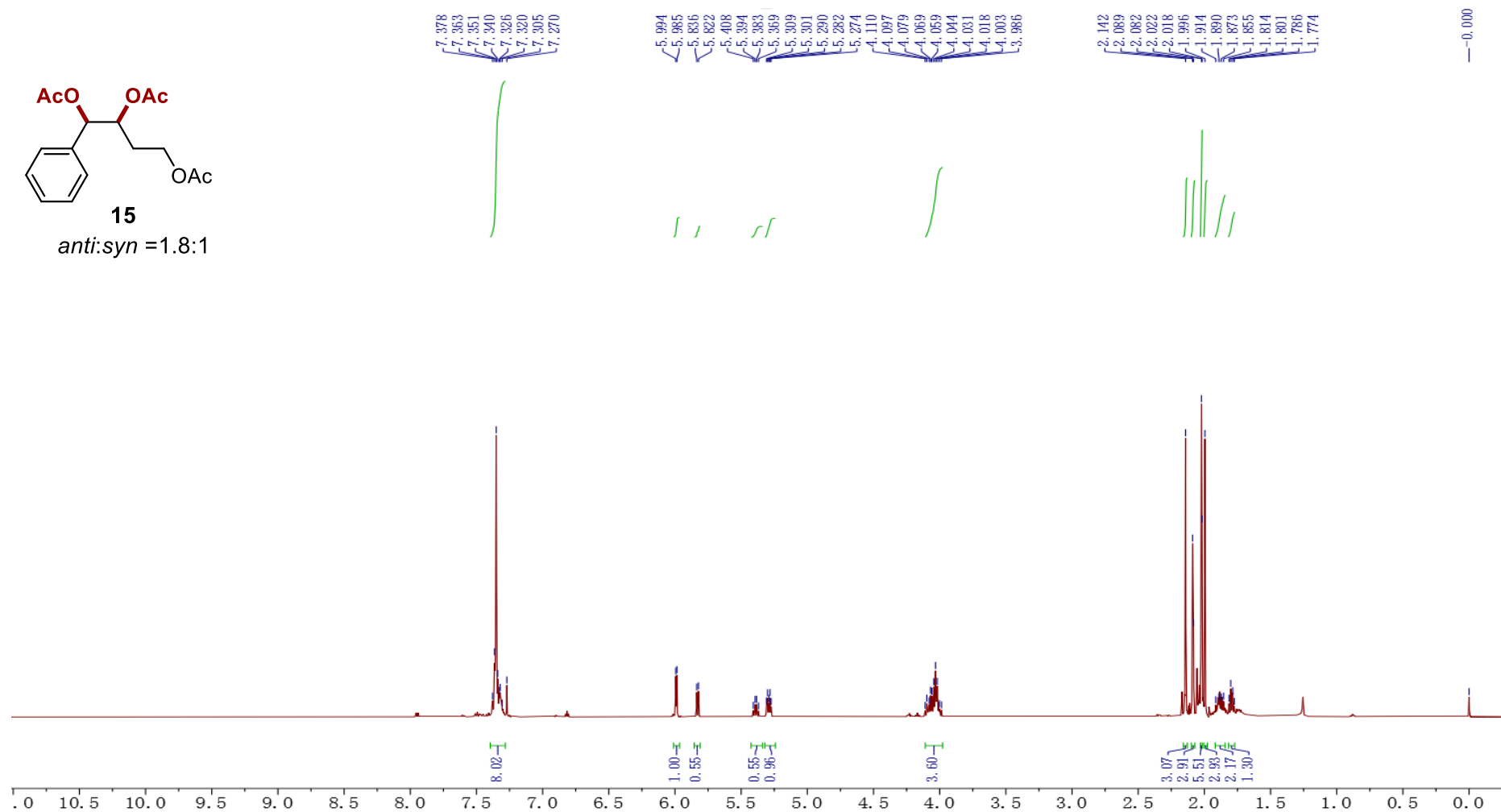
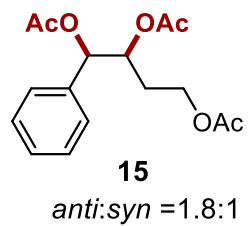


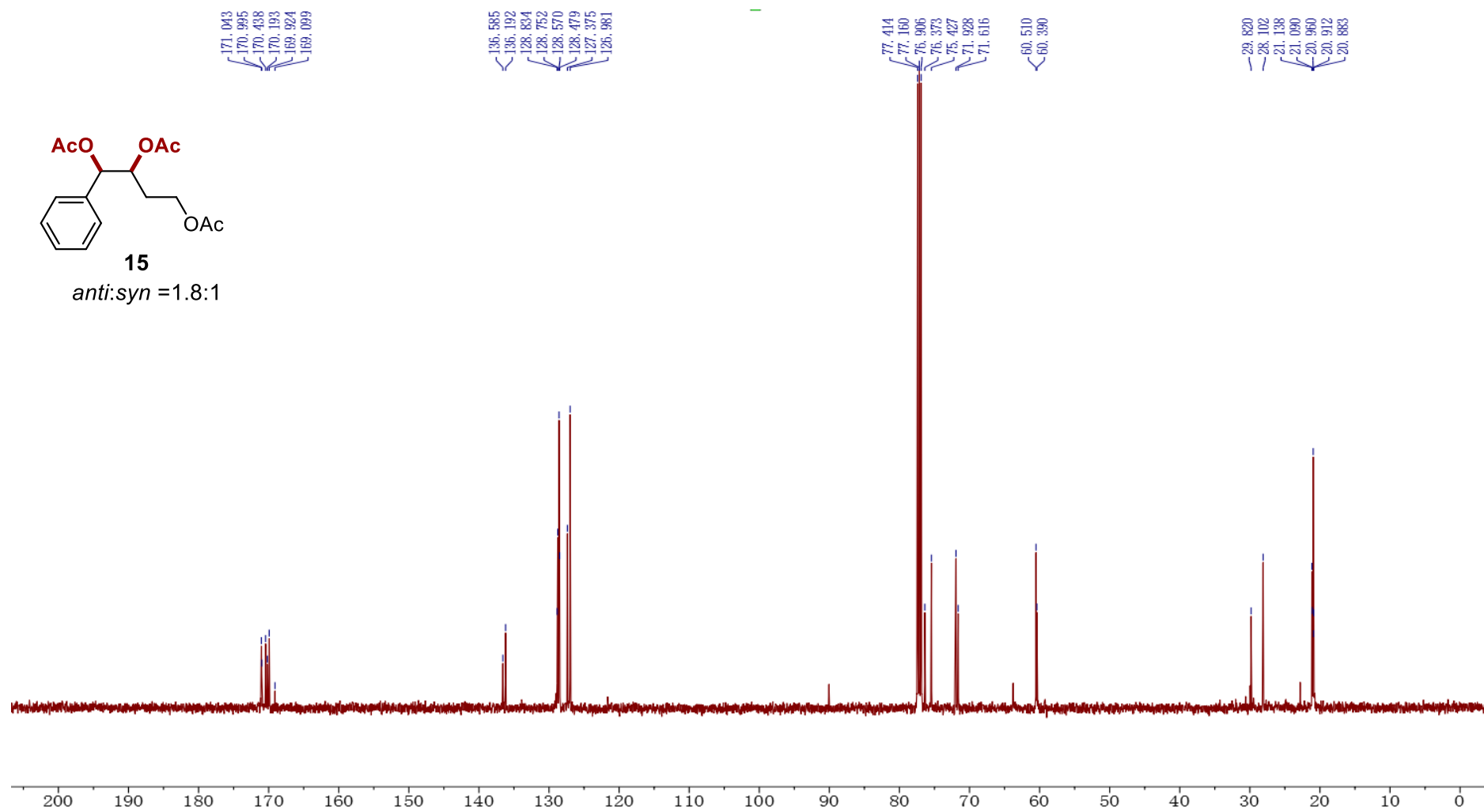


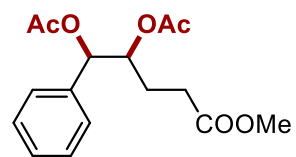
14

anti:syn = 5.6:1



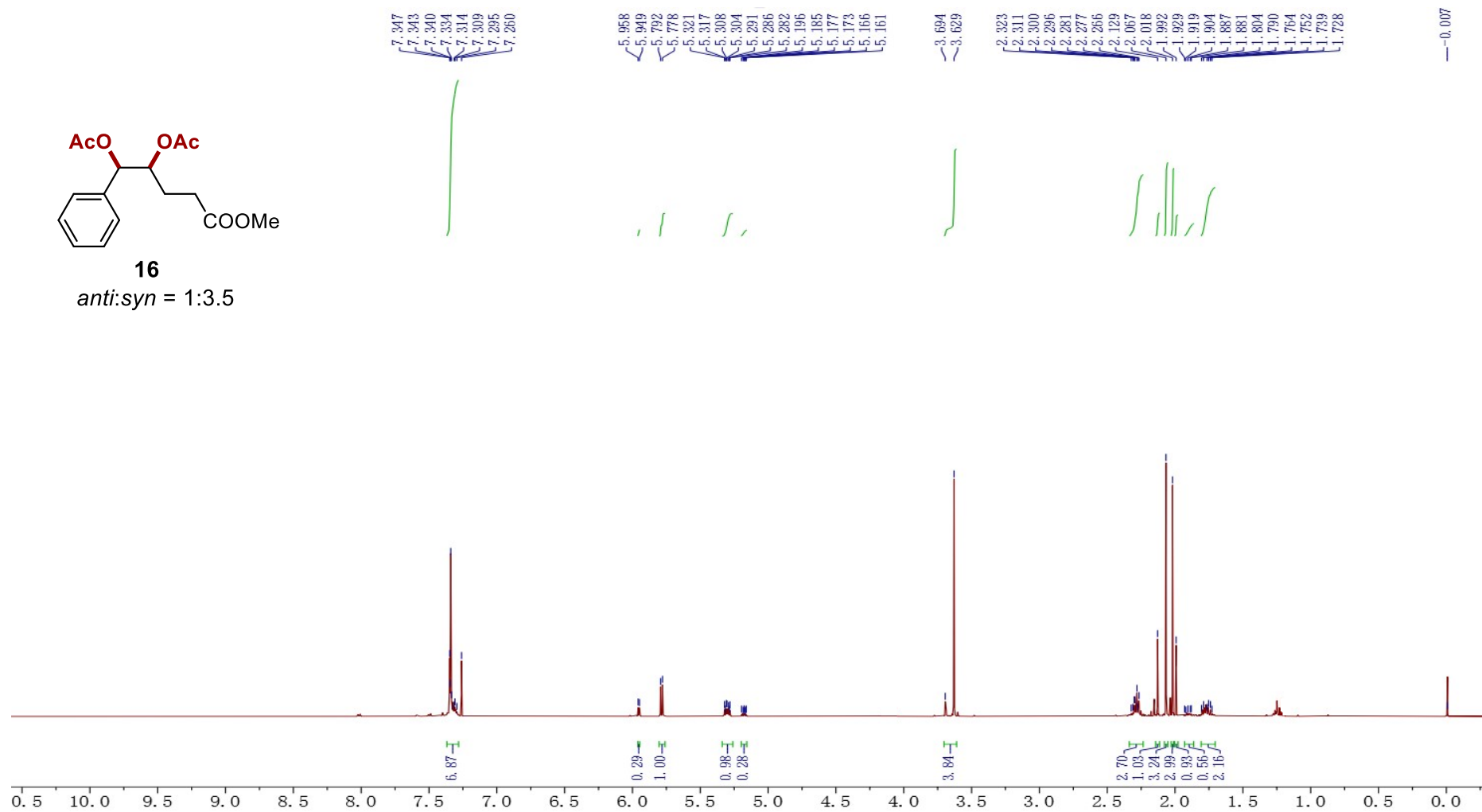


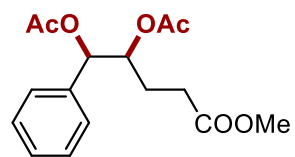




16

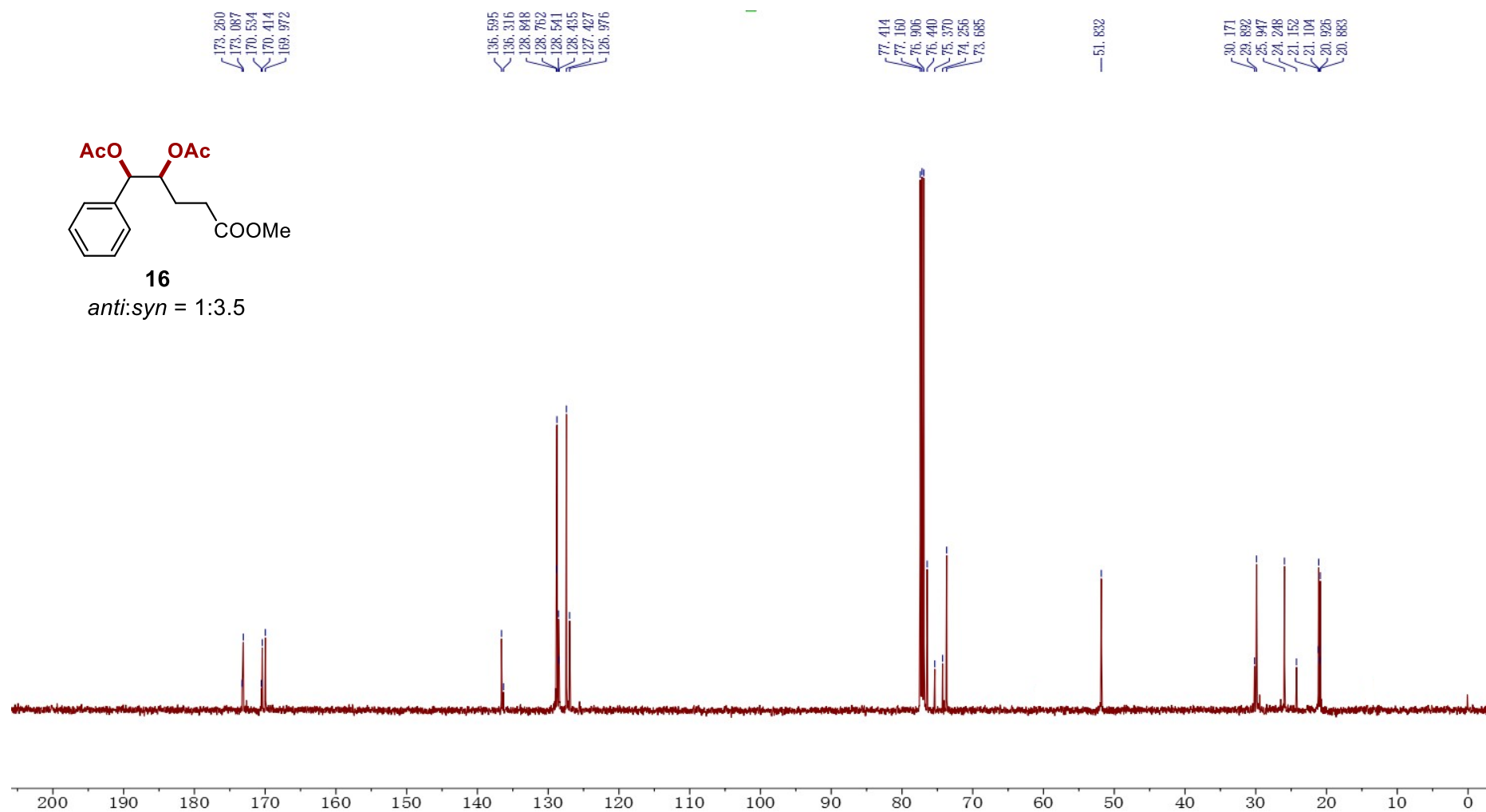
anti:syn = 1:3.5

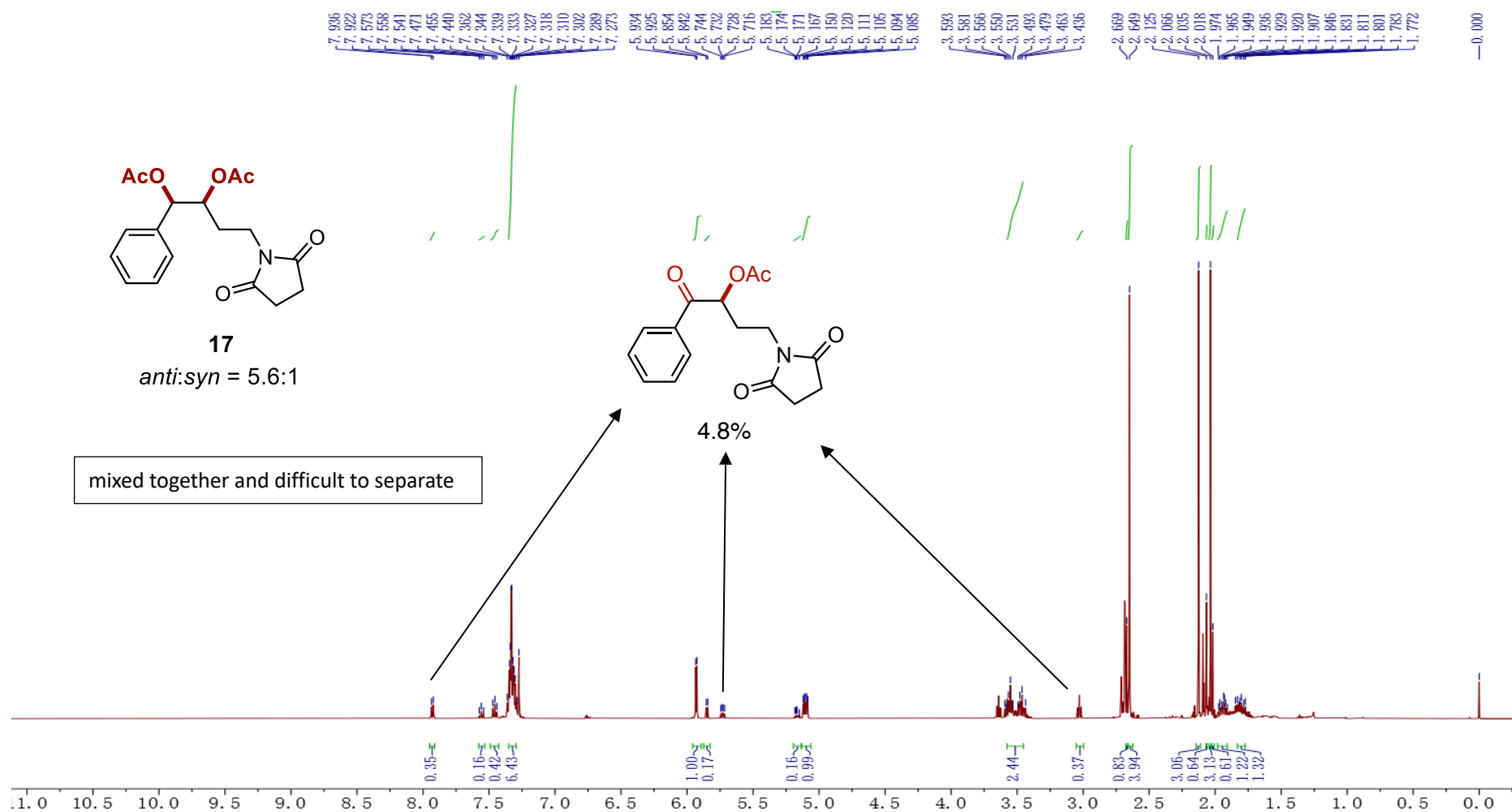


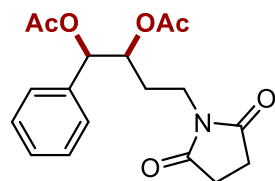


16

anti:syn = 1:3.5

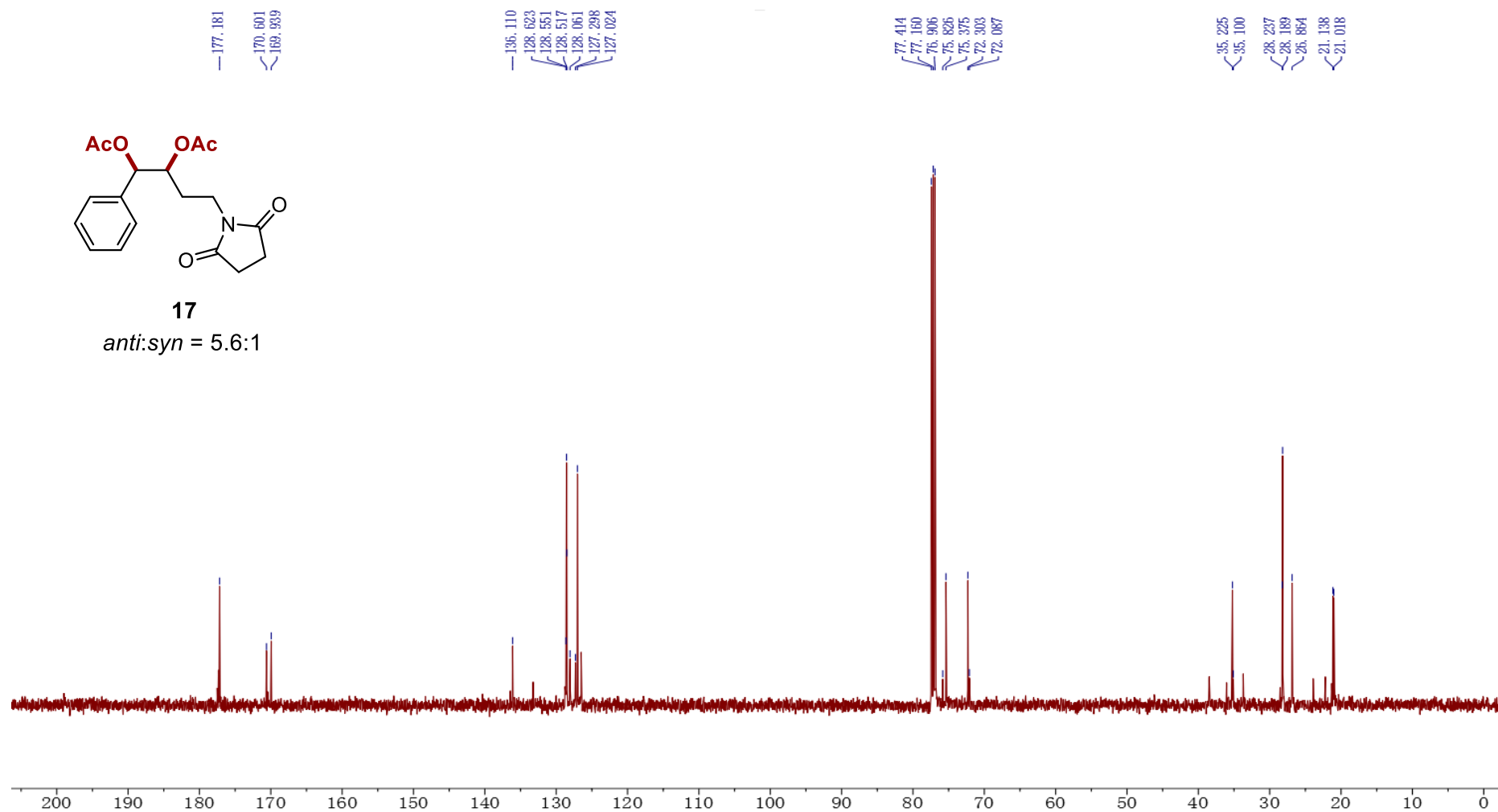


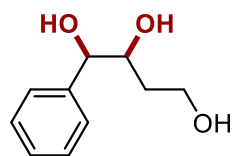




17

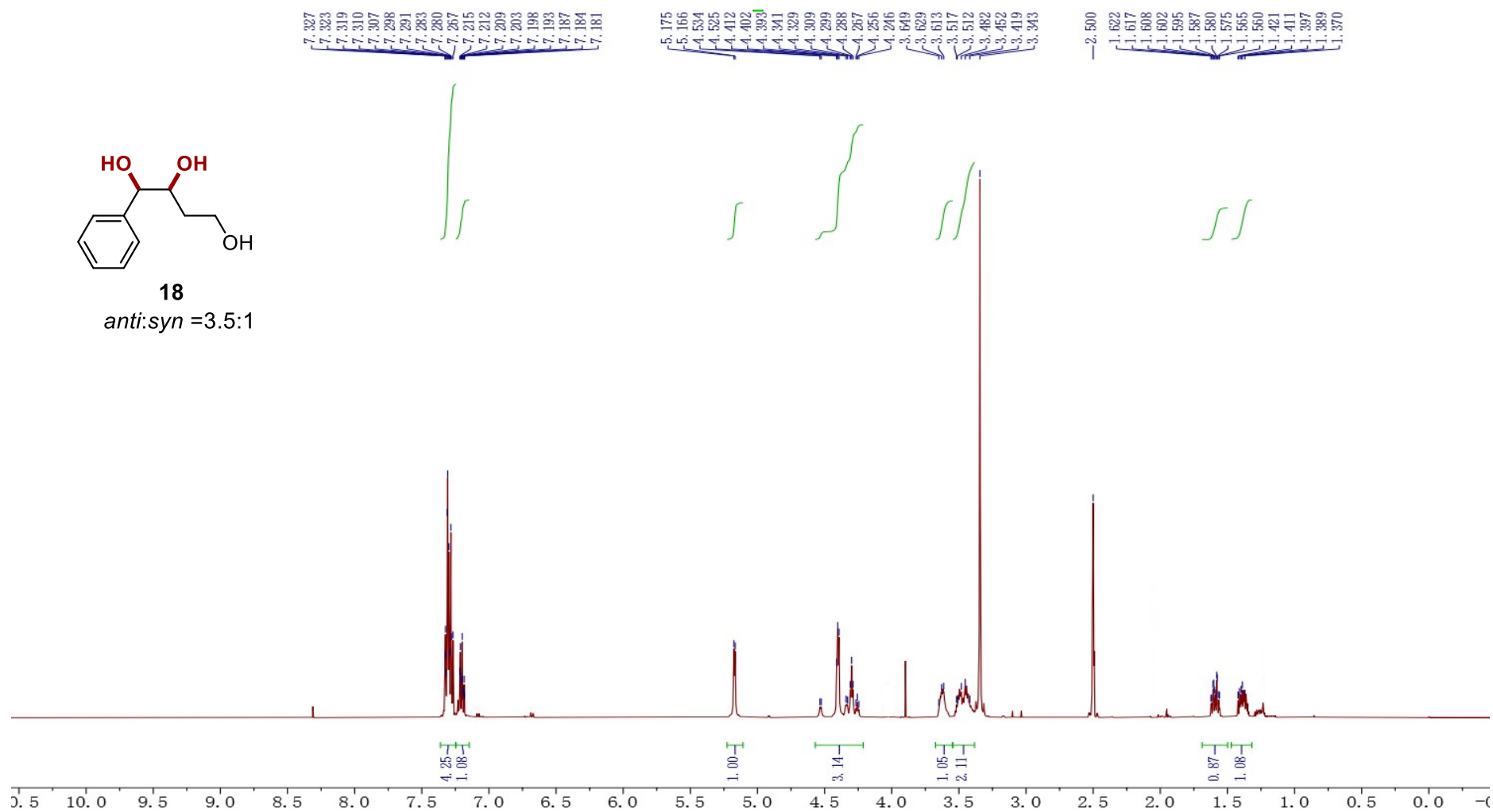
anti:syn = 5.6:1

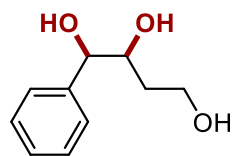




18

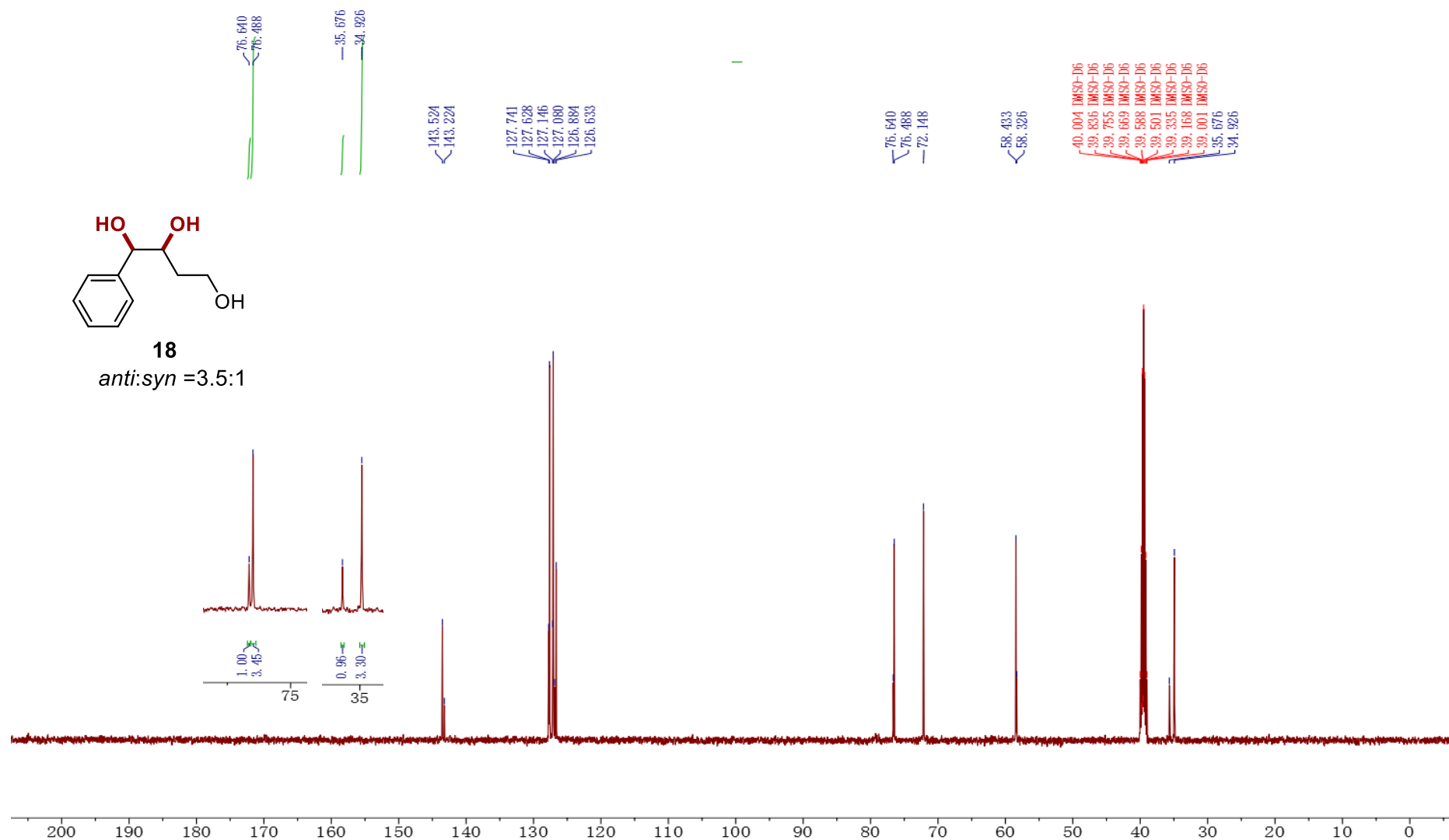
anti:syn = 3.5:1

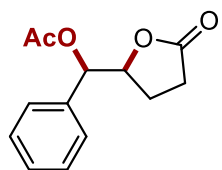




18

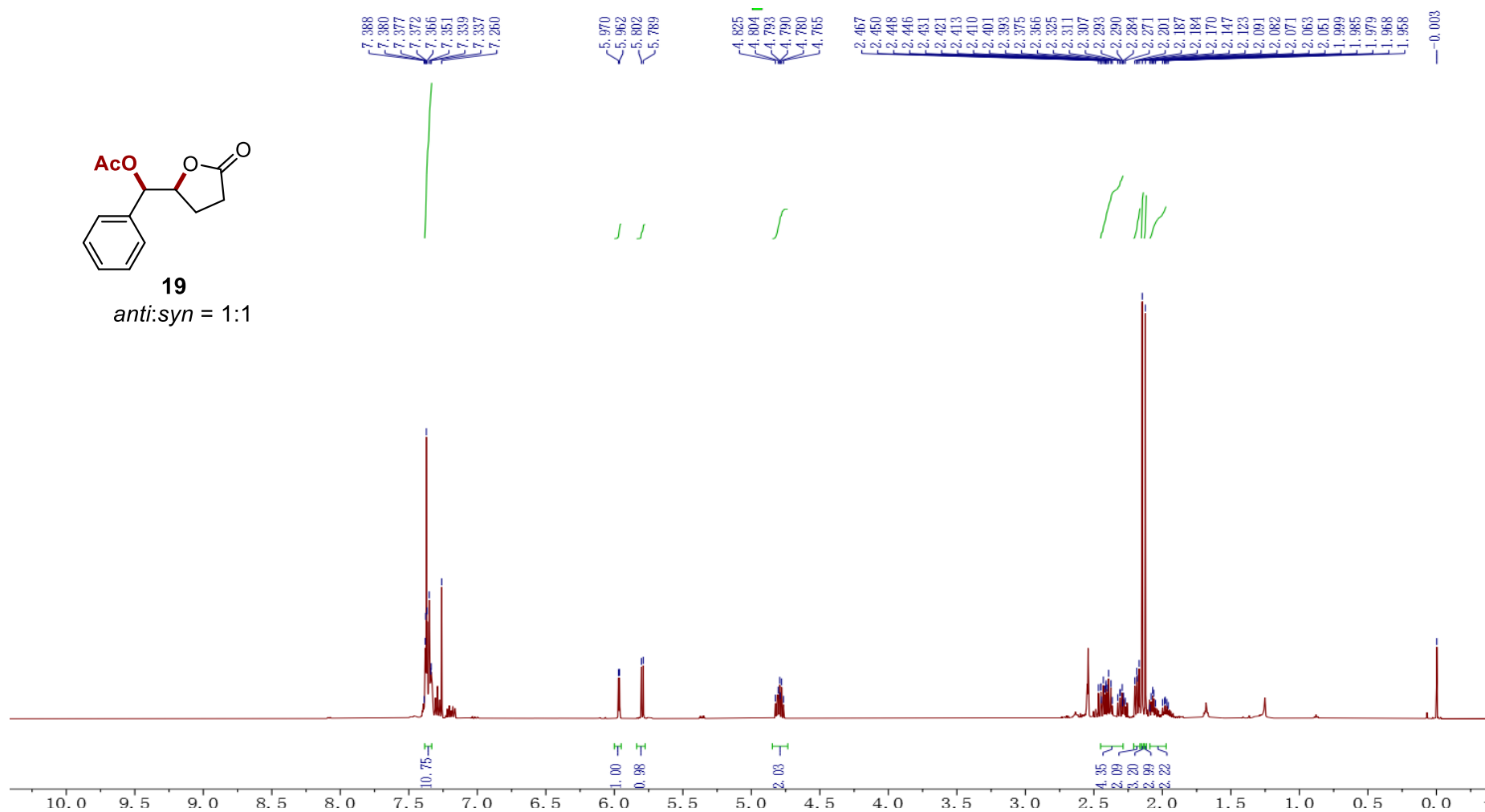
anti:syn = 3.5:1

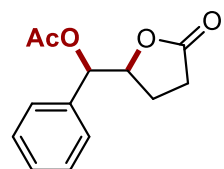




19

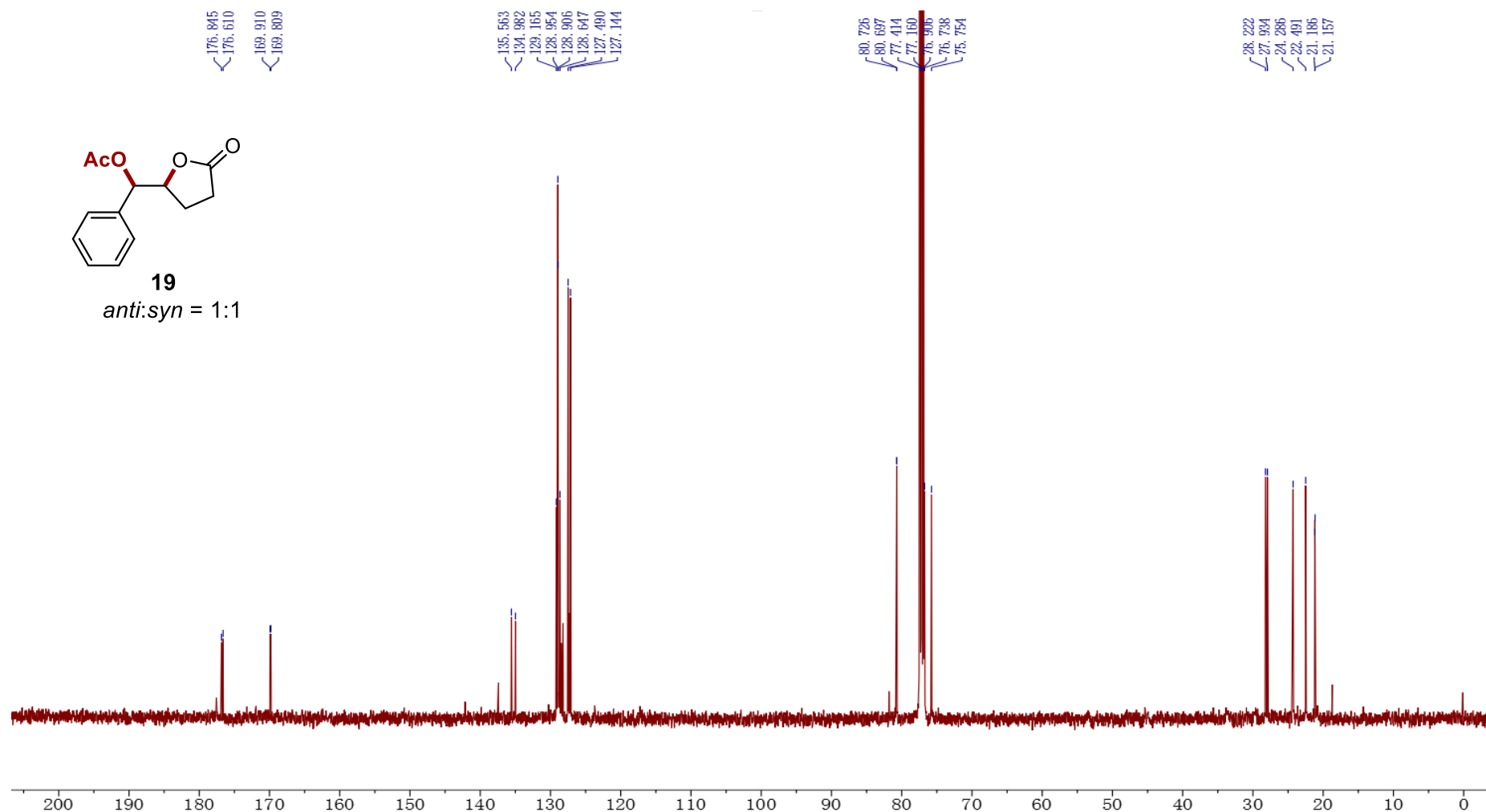
anti:syn = 1:1

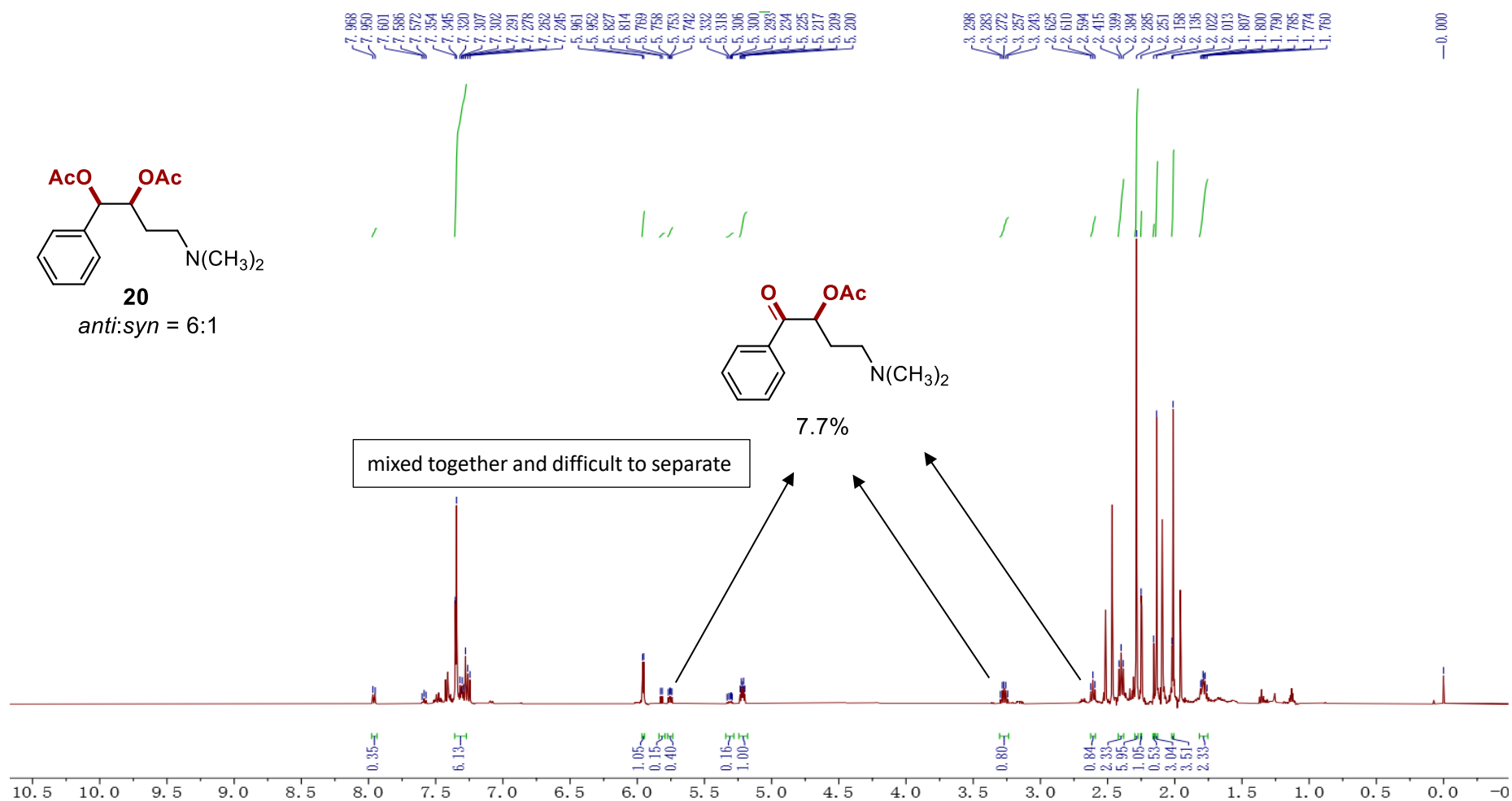


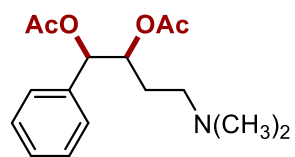


19

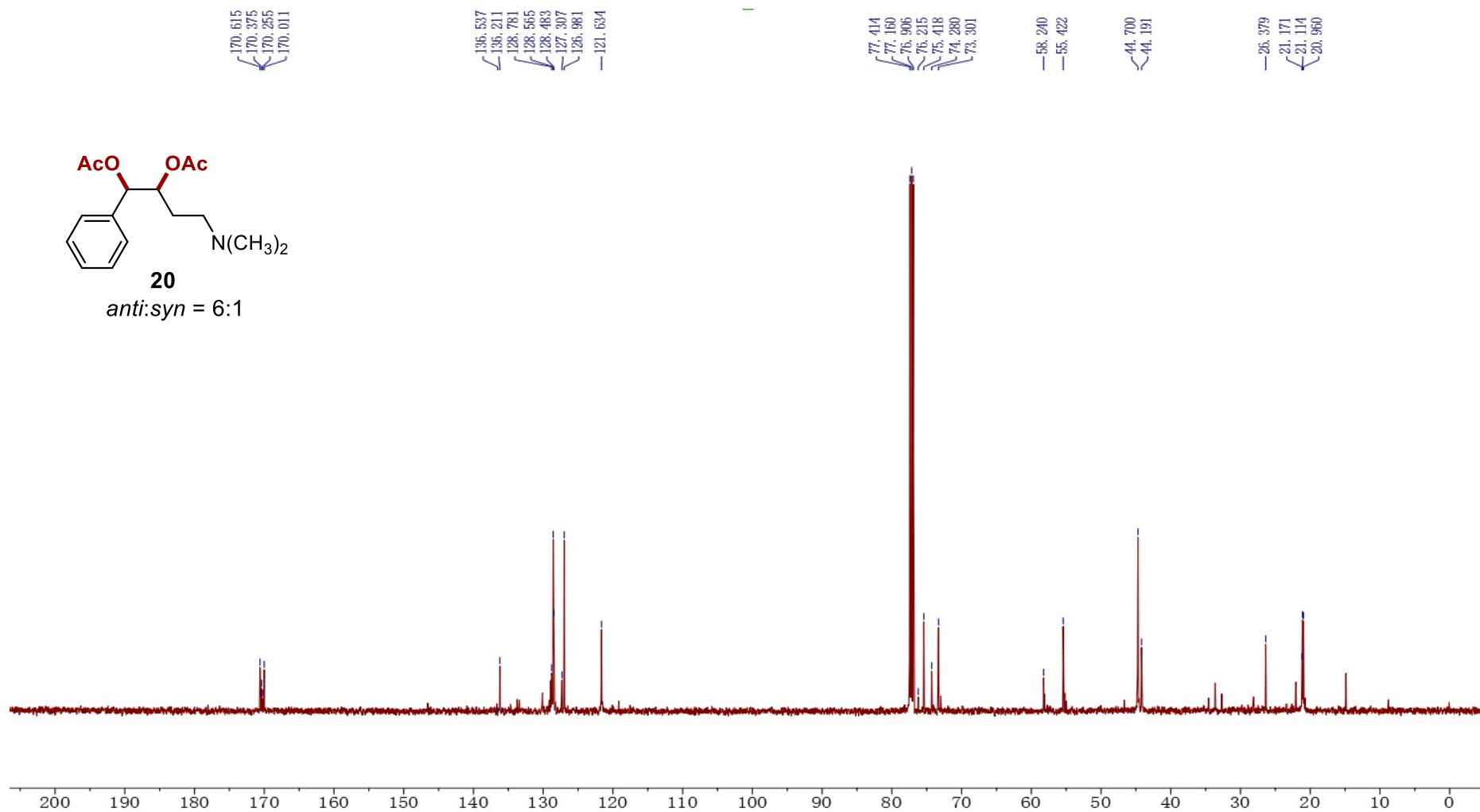
anti:syn = 1:1

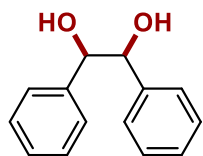






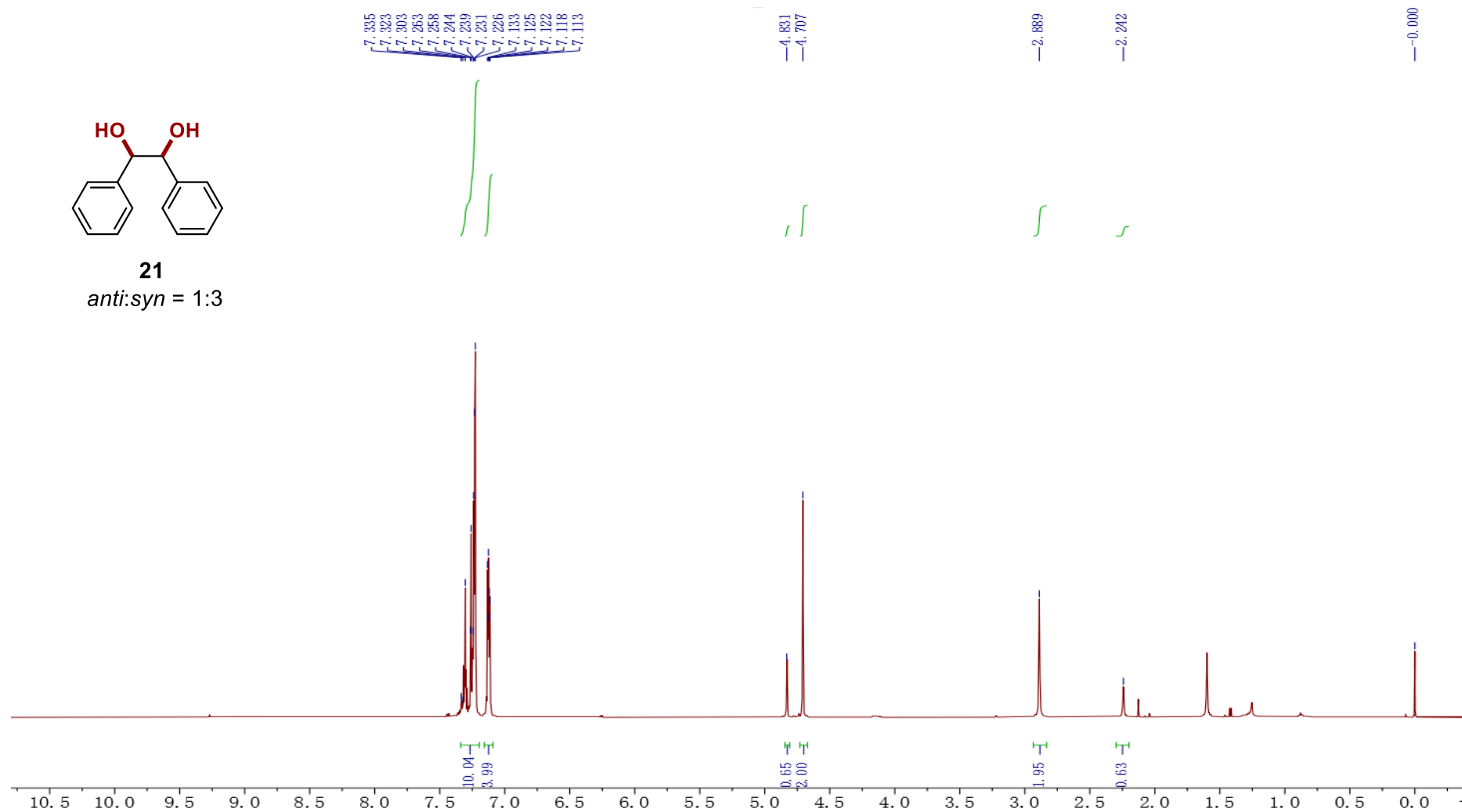
20
anti:syn = 6:1

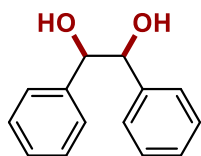




21

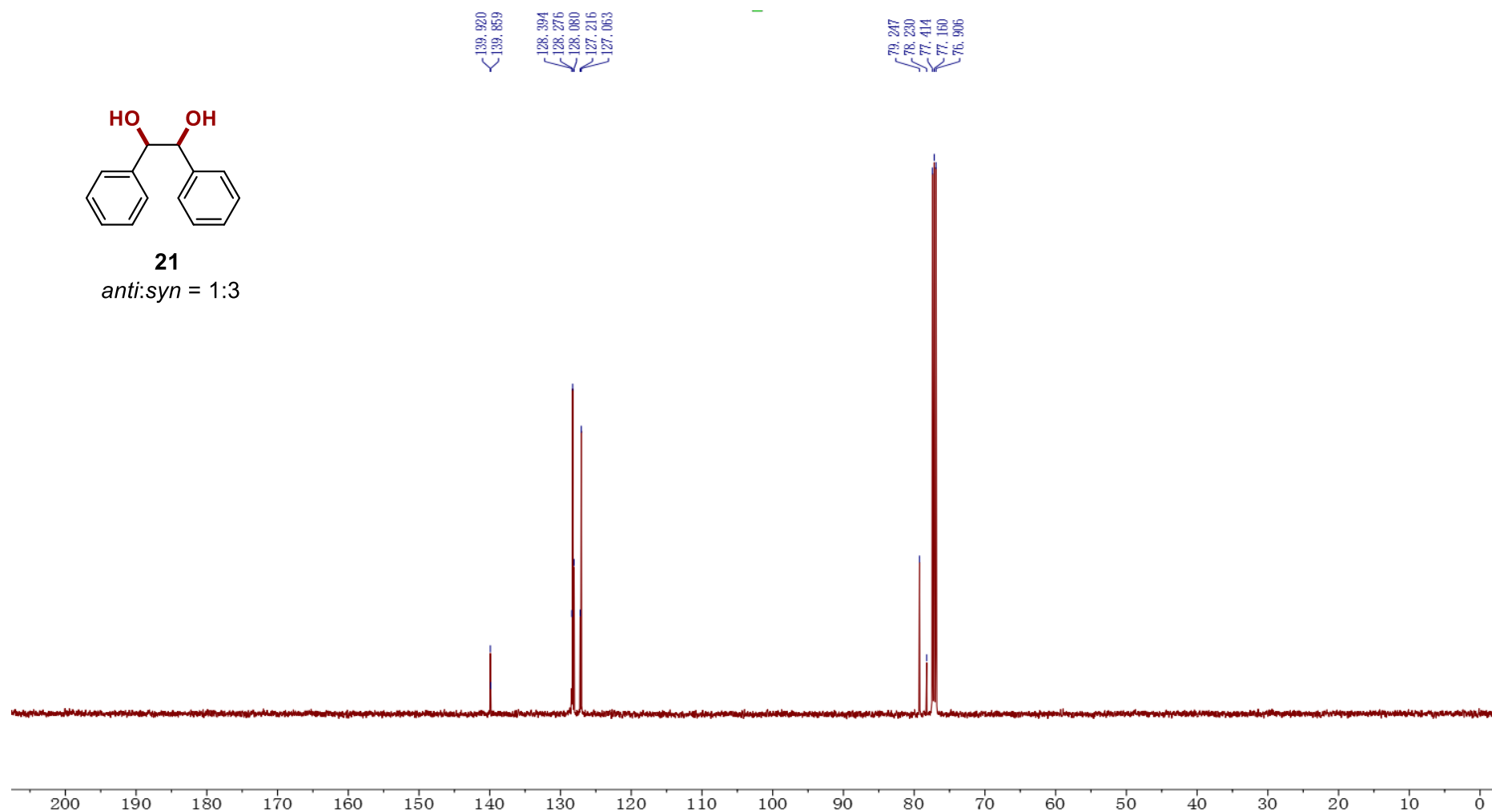
anti:syn = 1:3

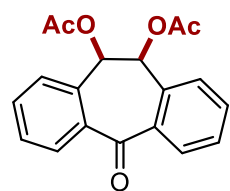




21

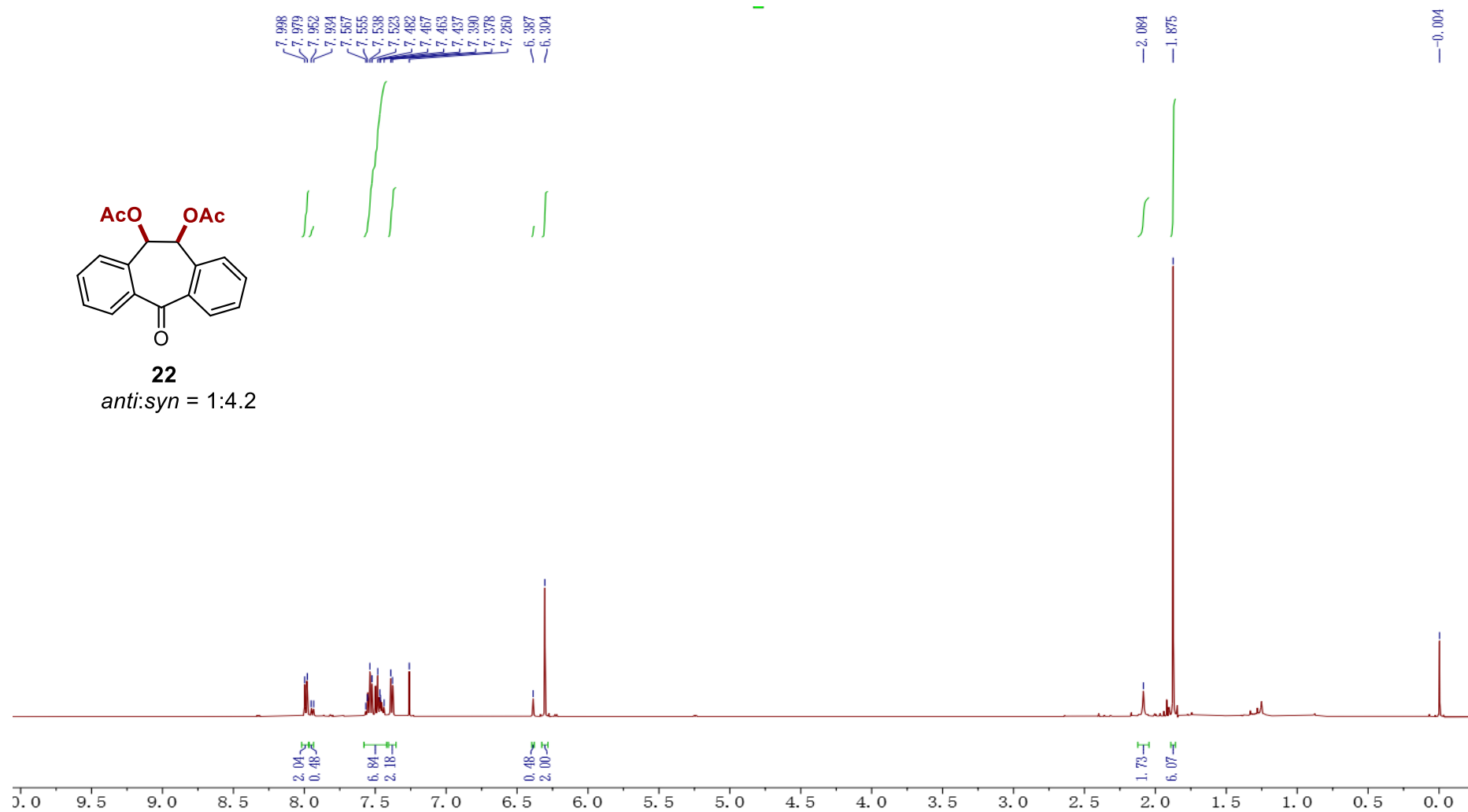
anti:syn = 1:3

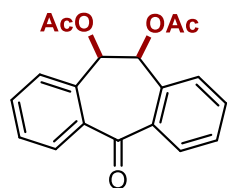




22

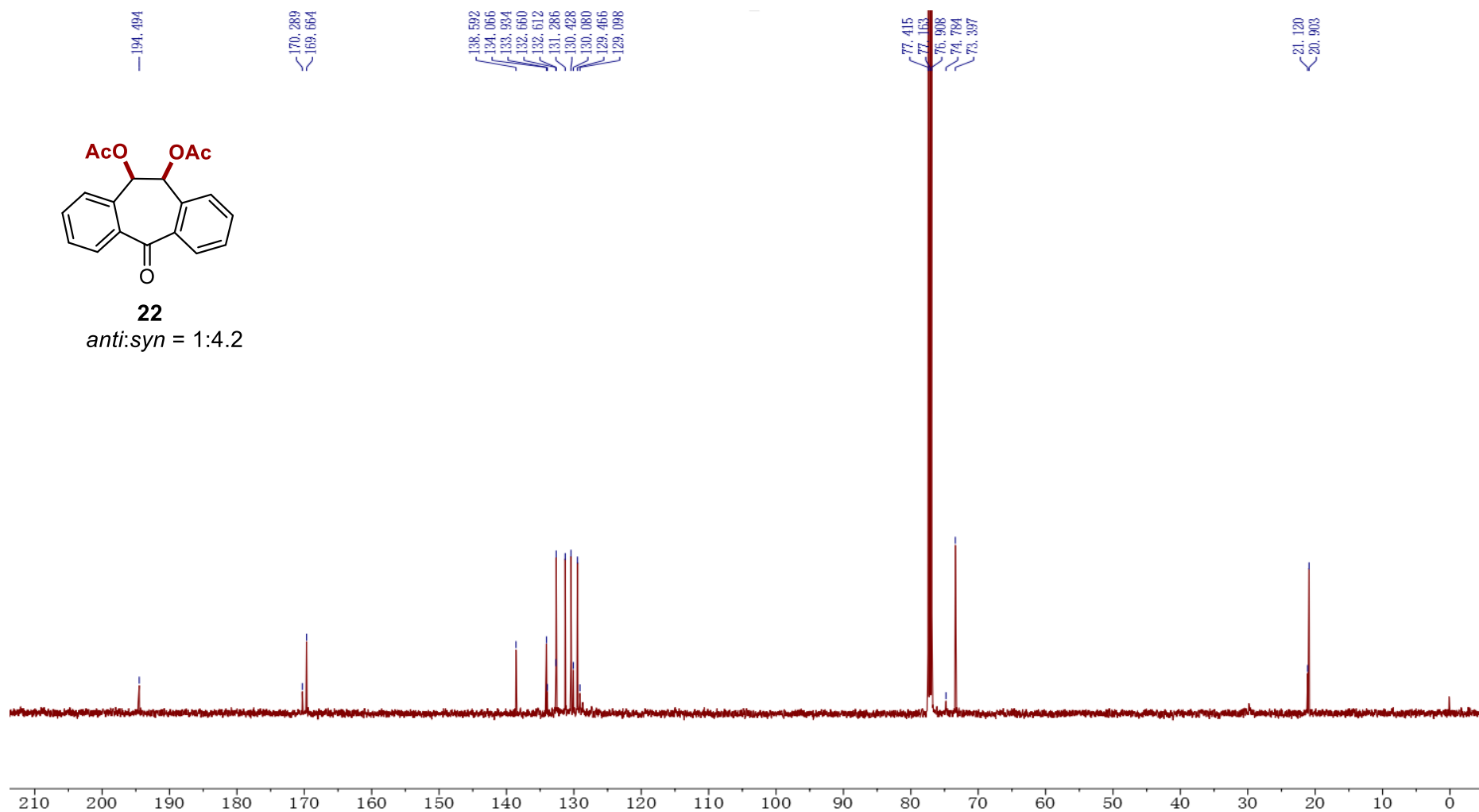
anti:syn = 1:4.2

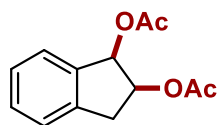




22

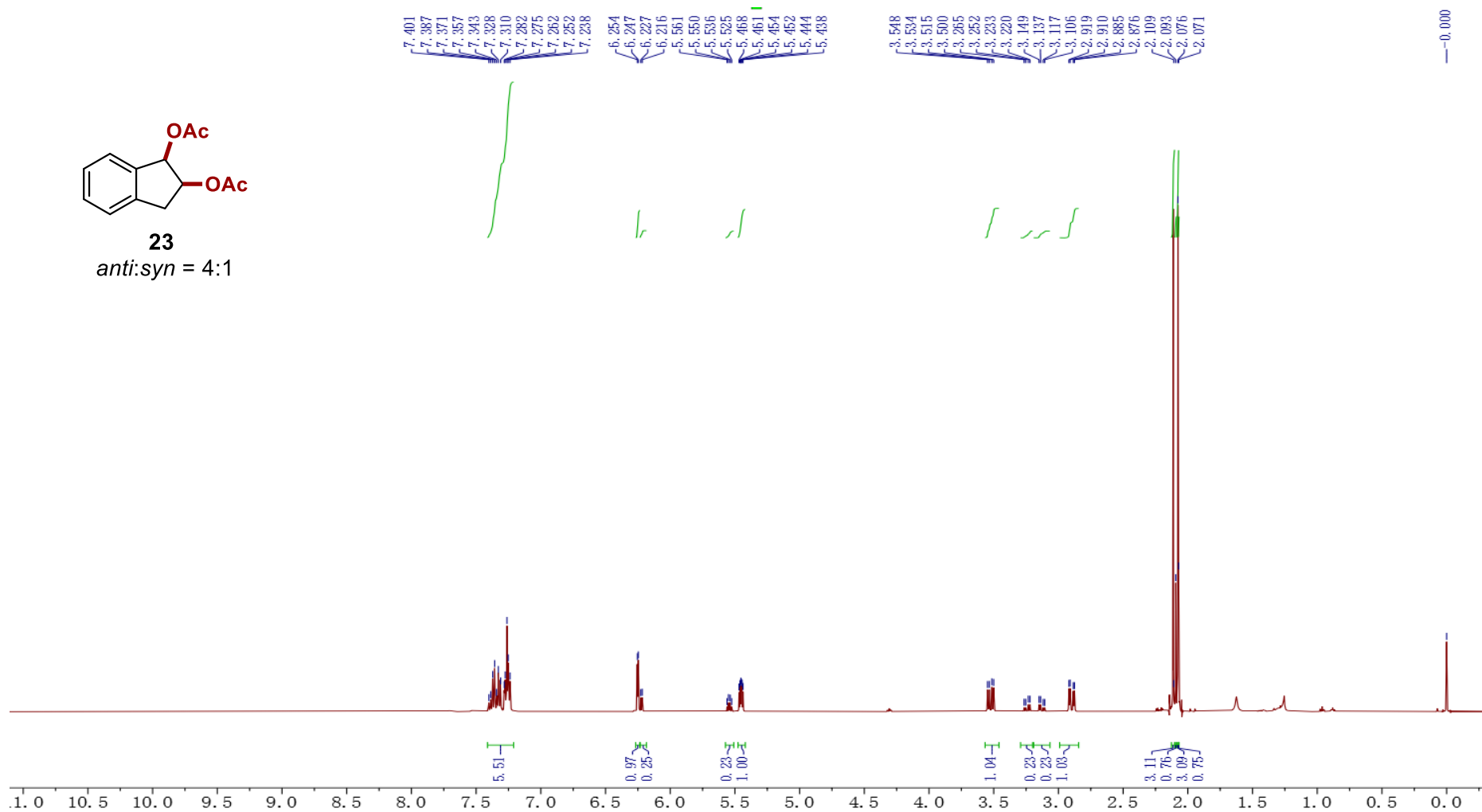
anti:syn = 1:4.2

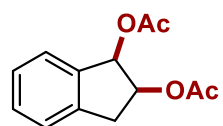




23

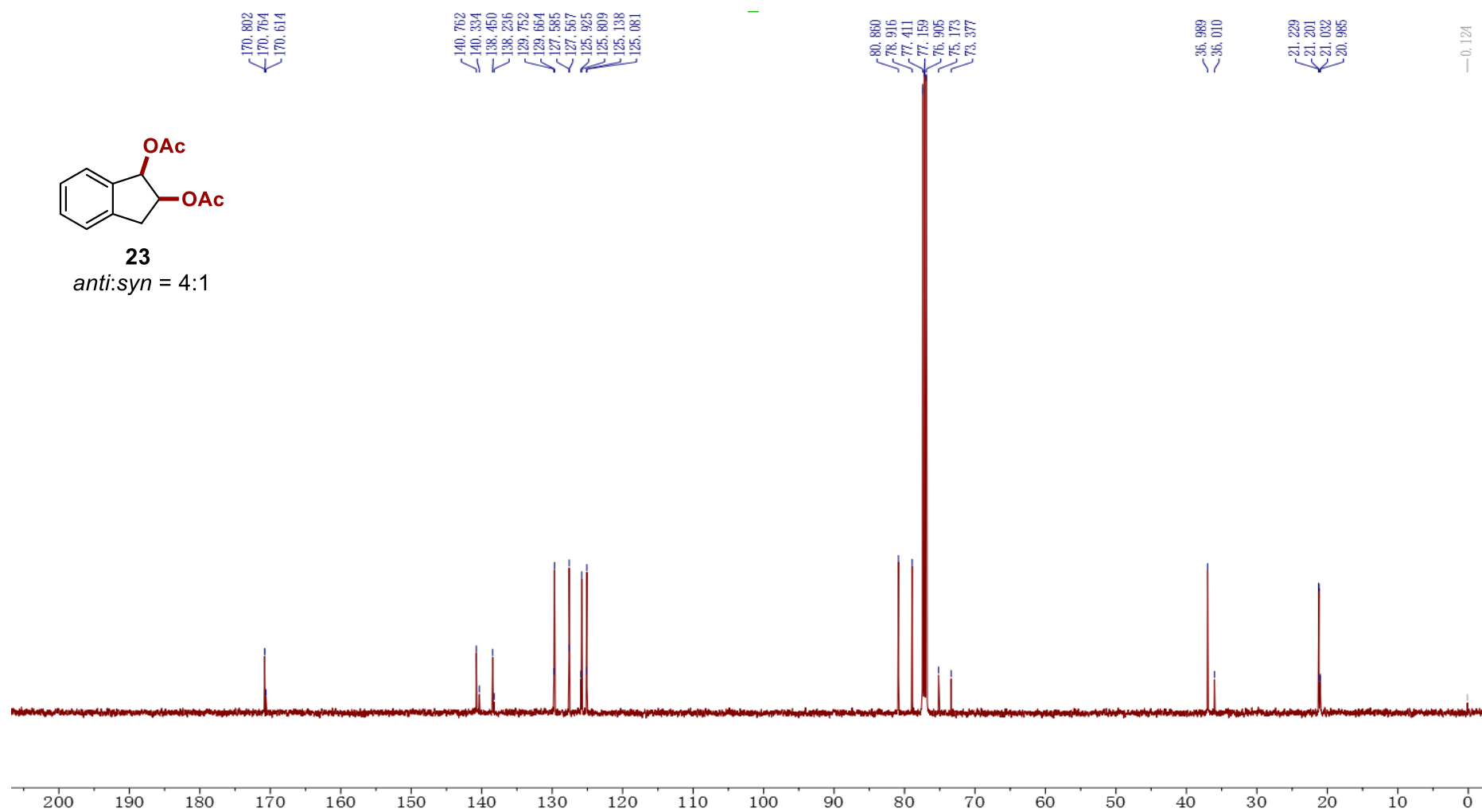
anti:syn = 4:1

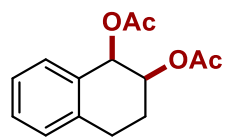




23

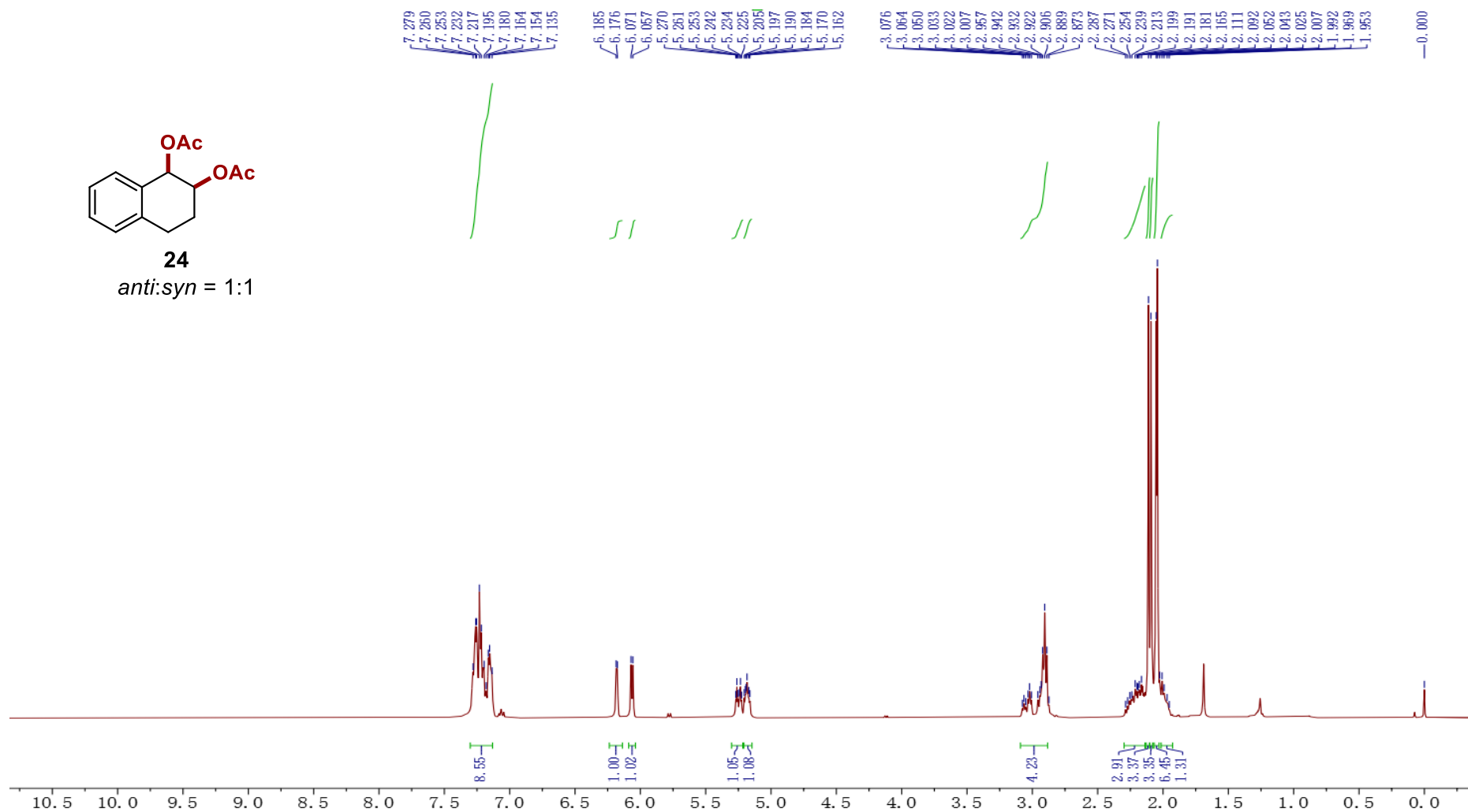
anti:syn = 4:1

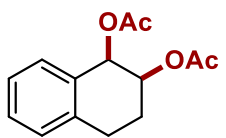




24

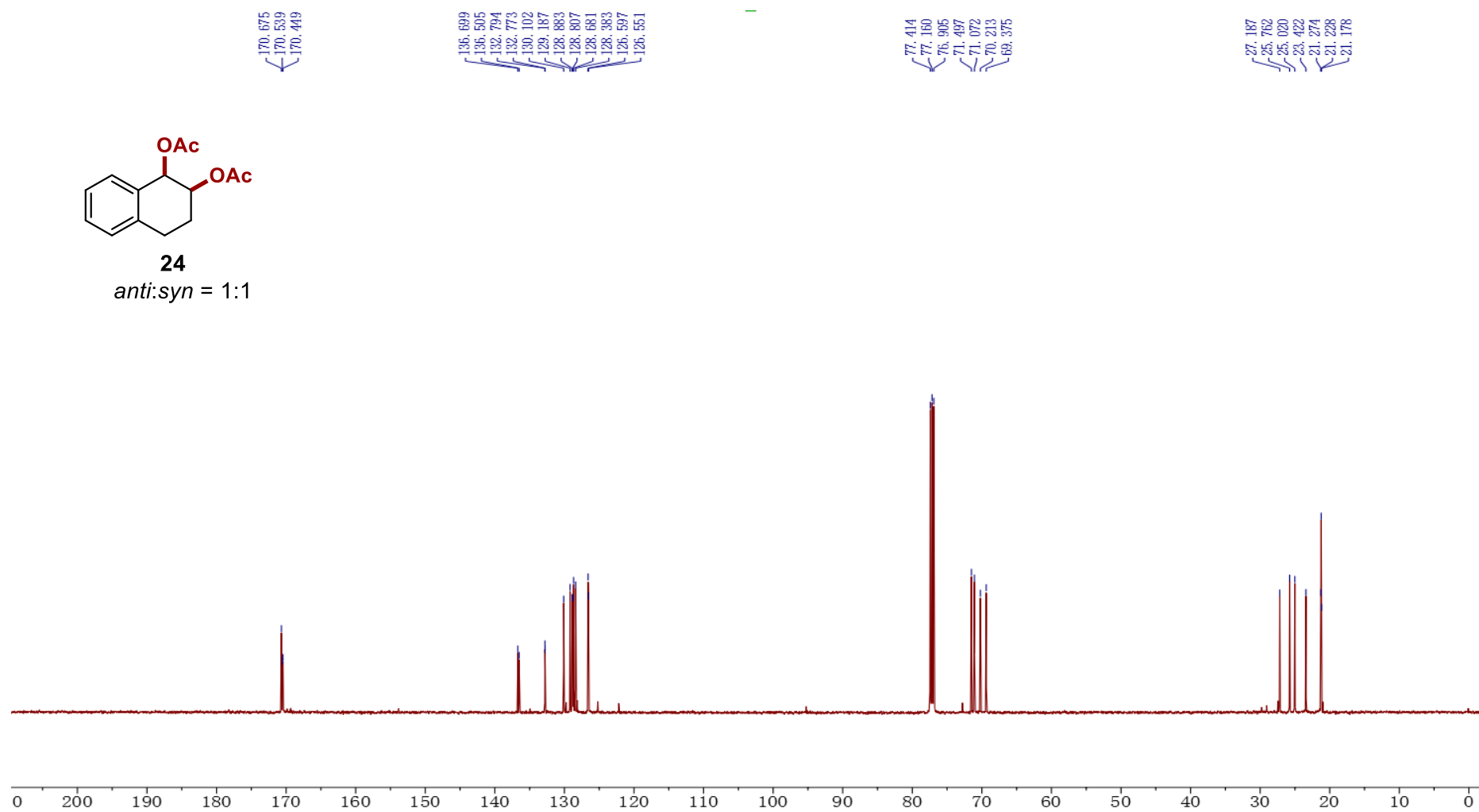
anti:syn = 1:1

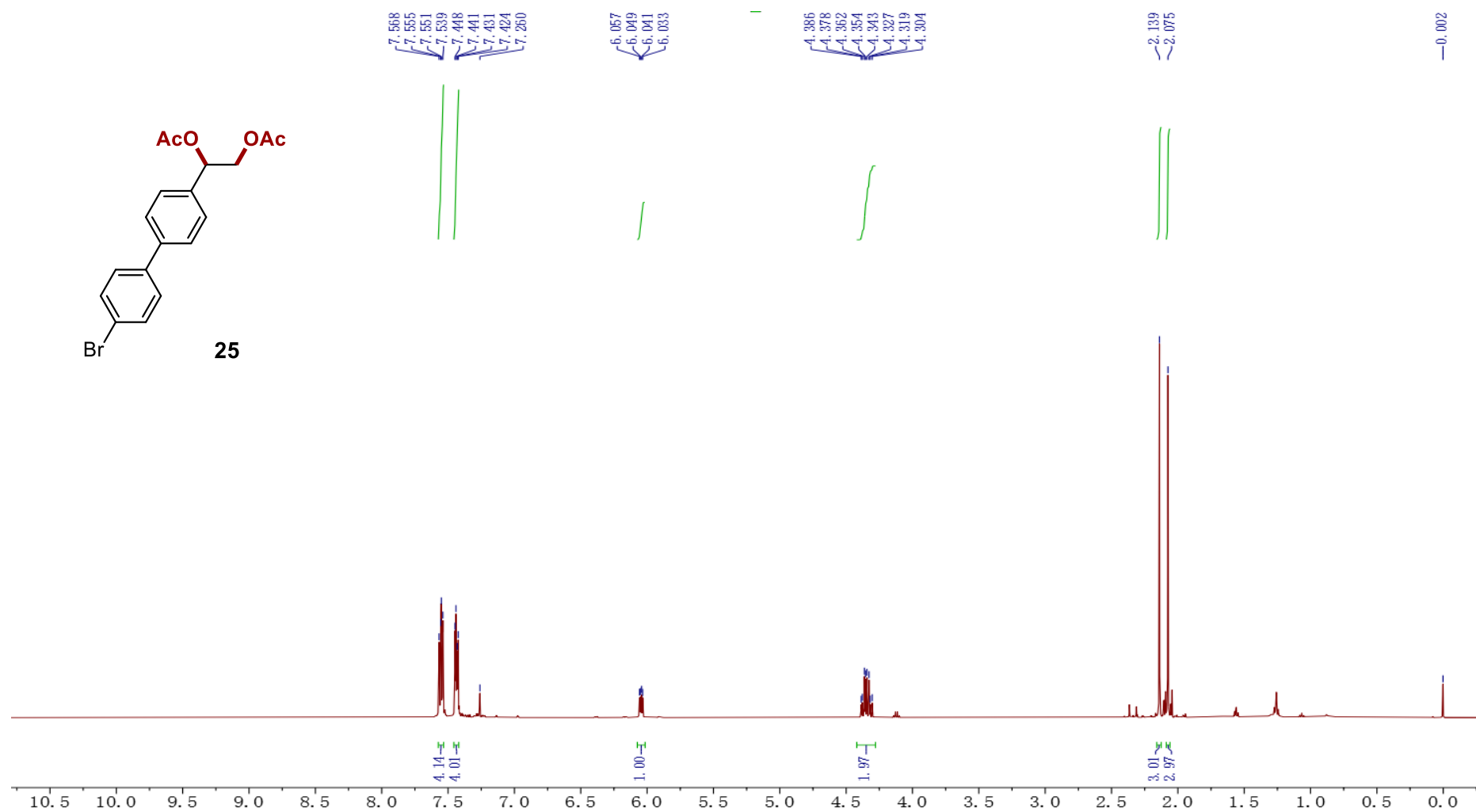
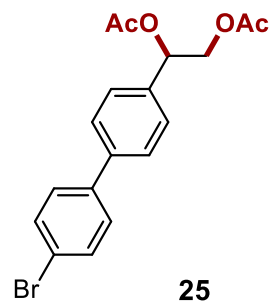


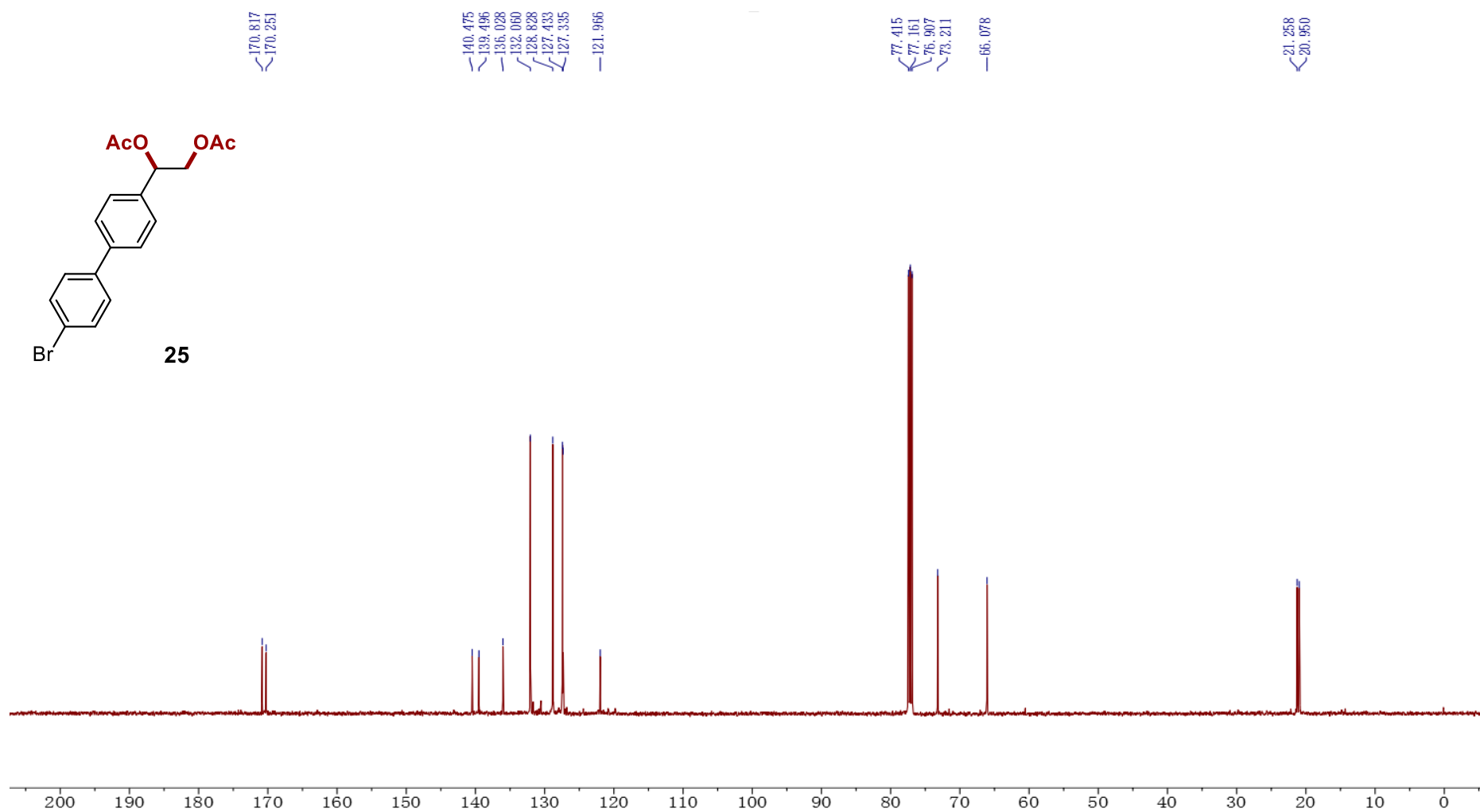


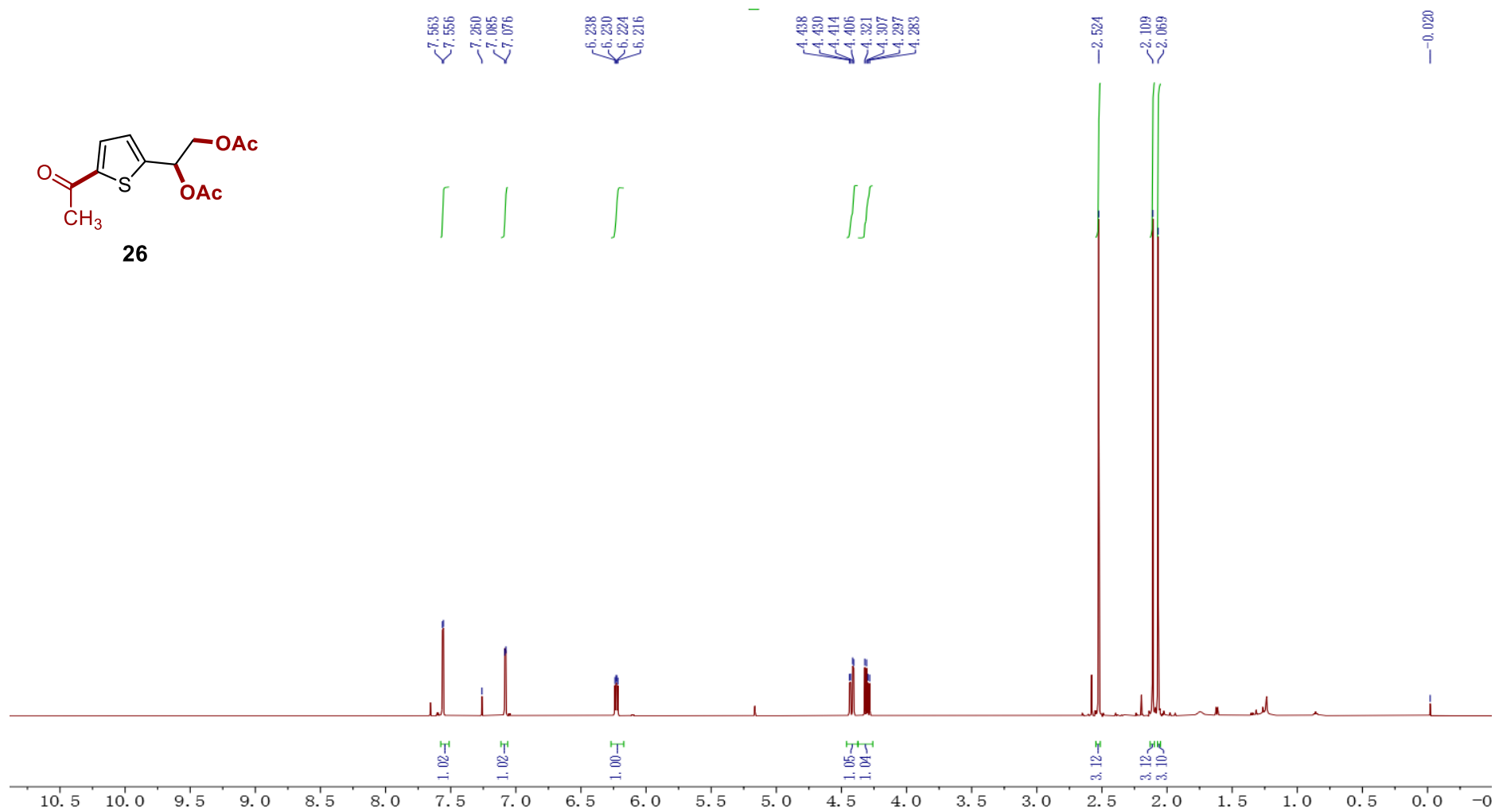
24

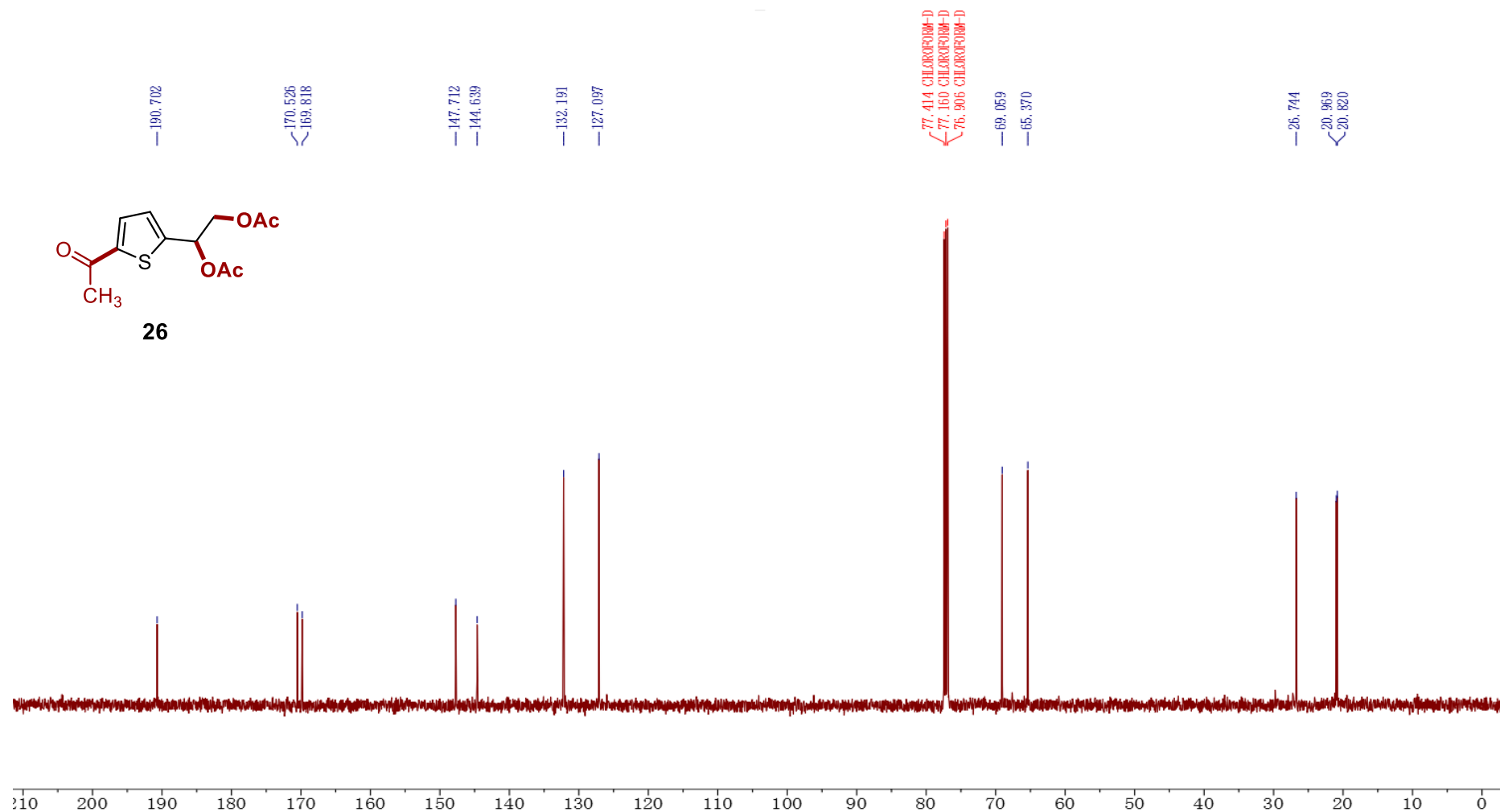
anti:syn = 1:1

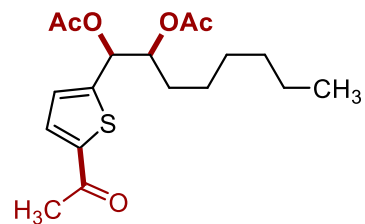






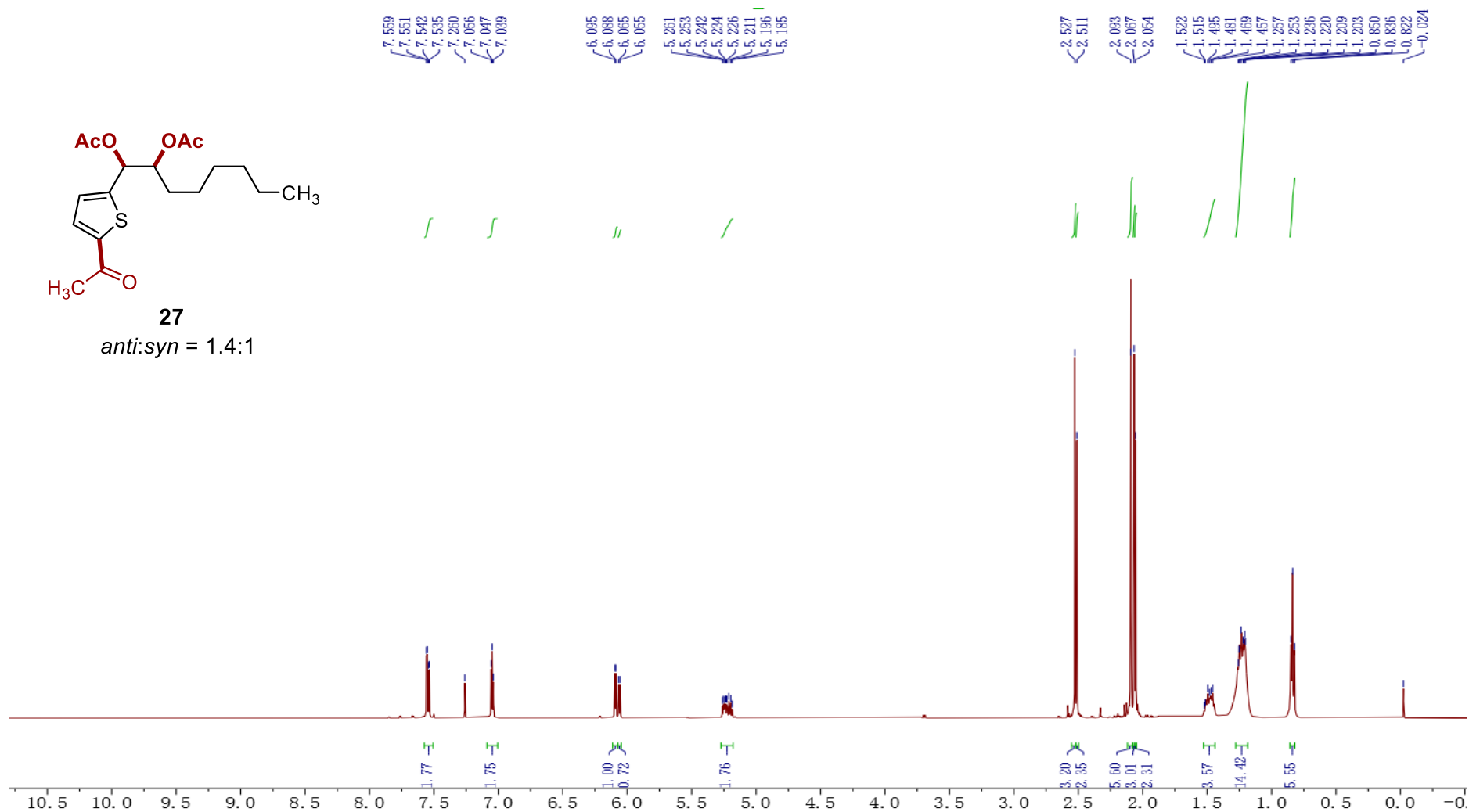


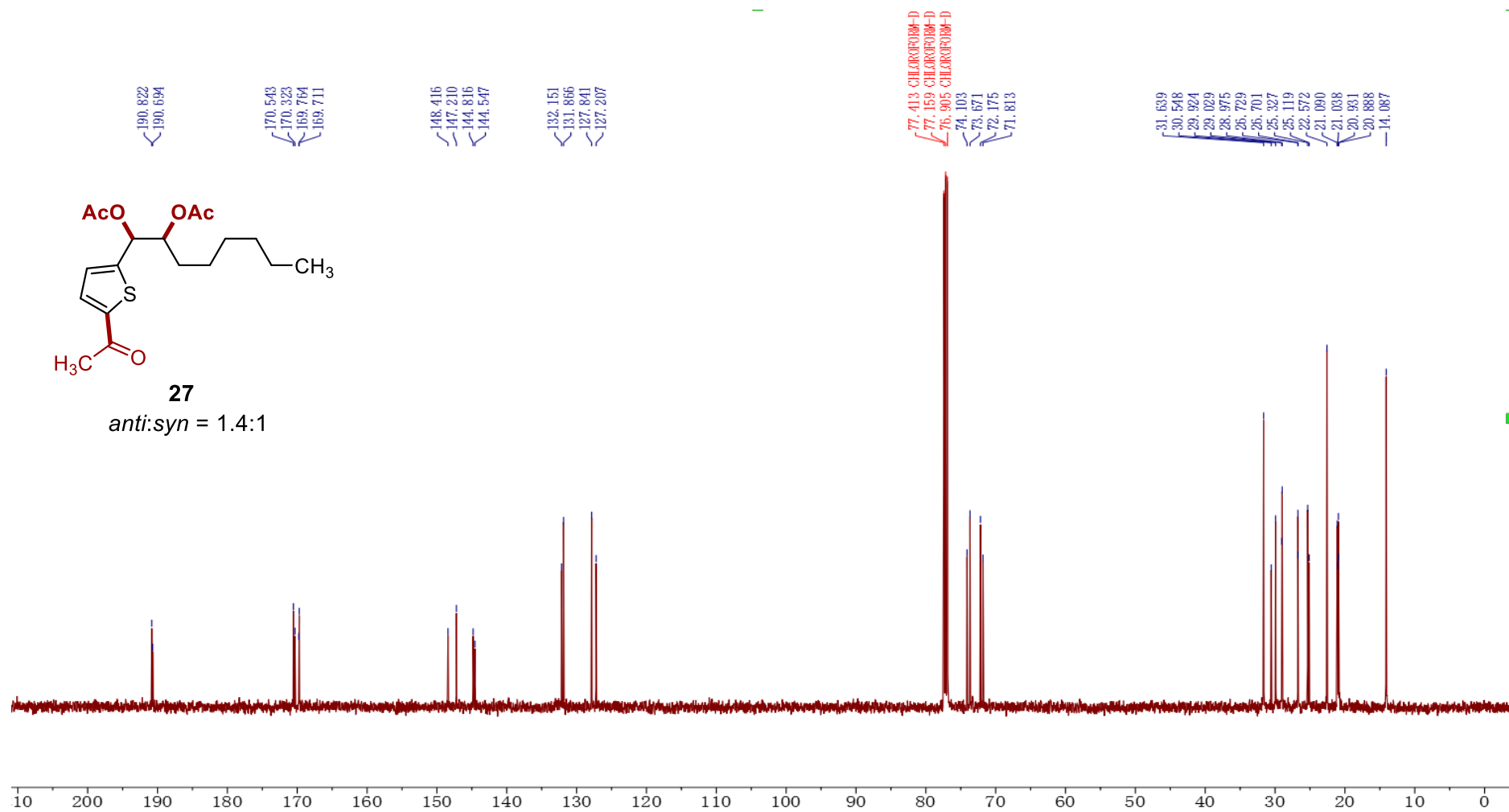


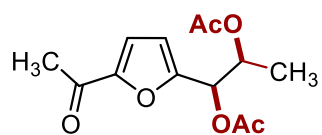


27

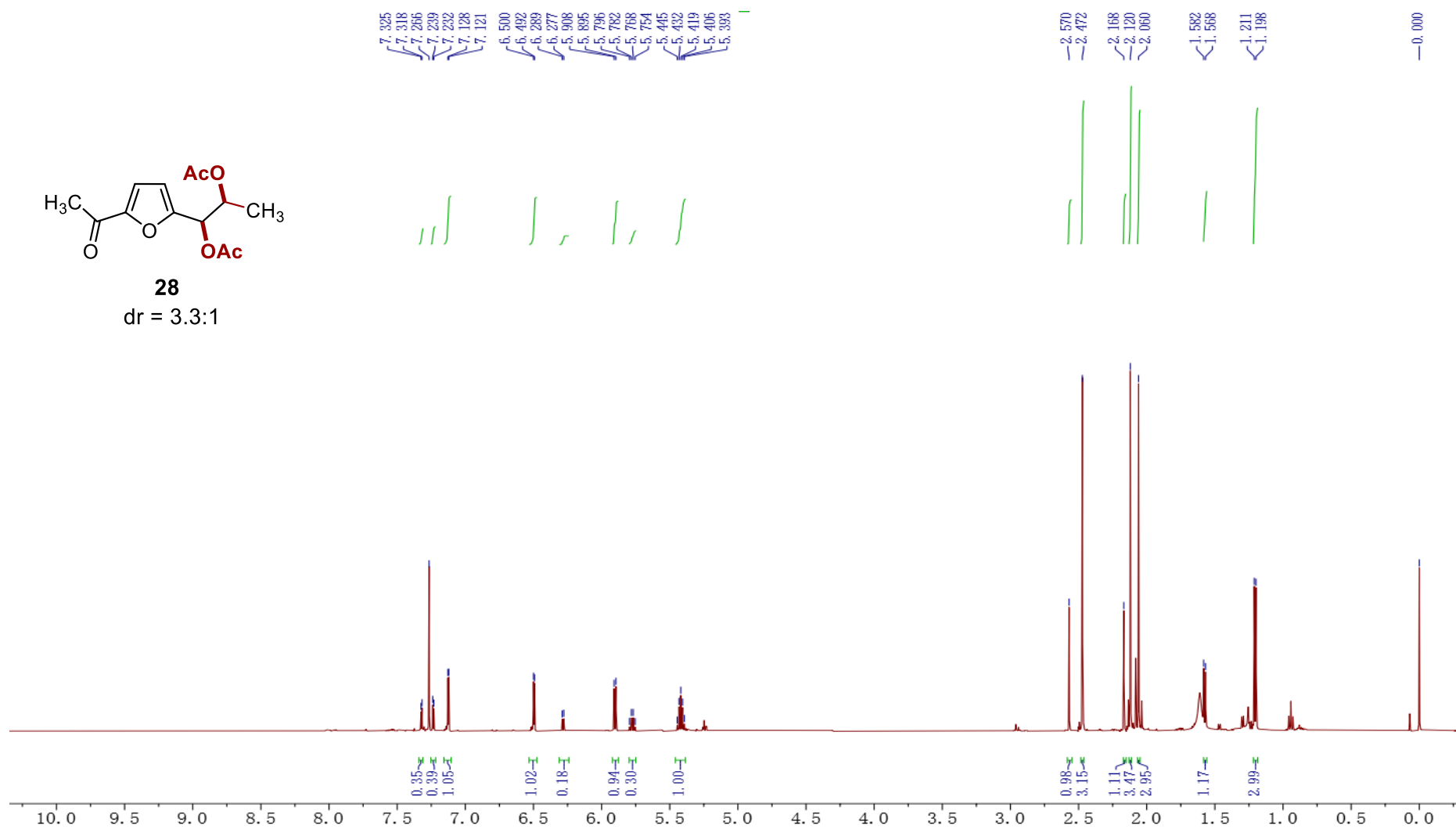
anti:syn = 1.4:1

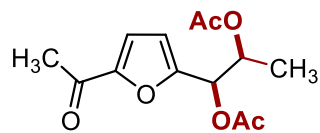




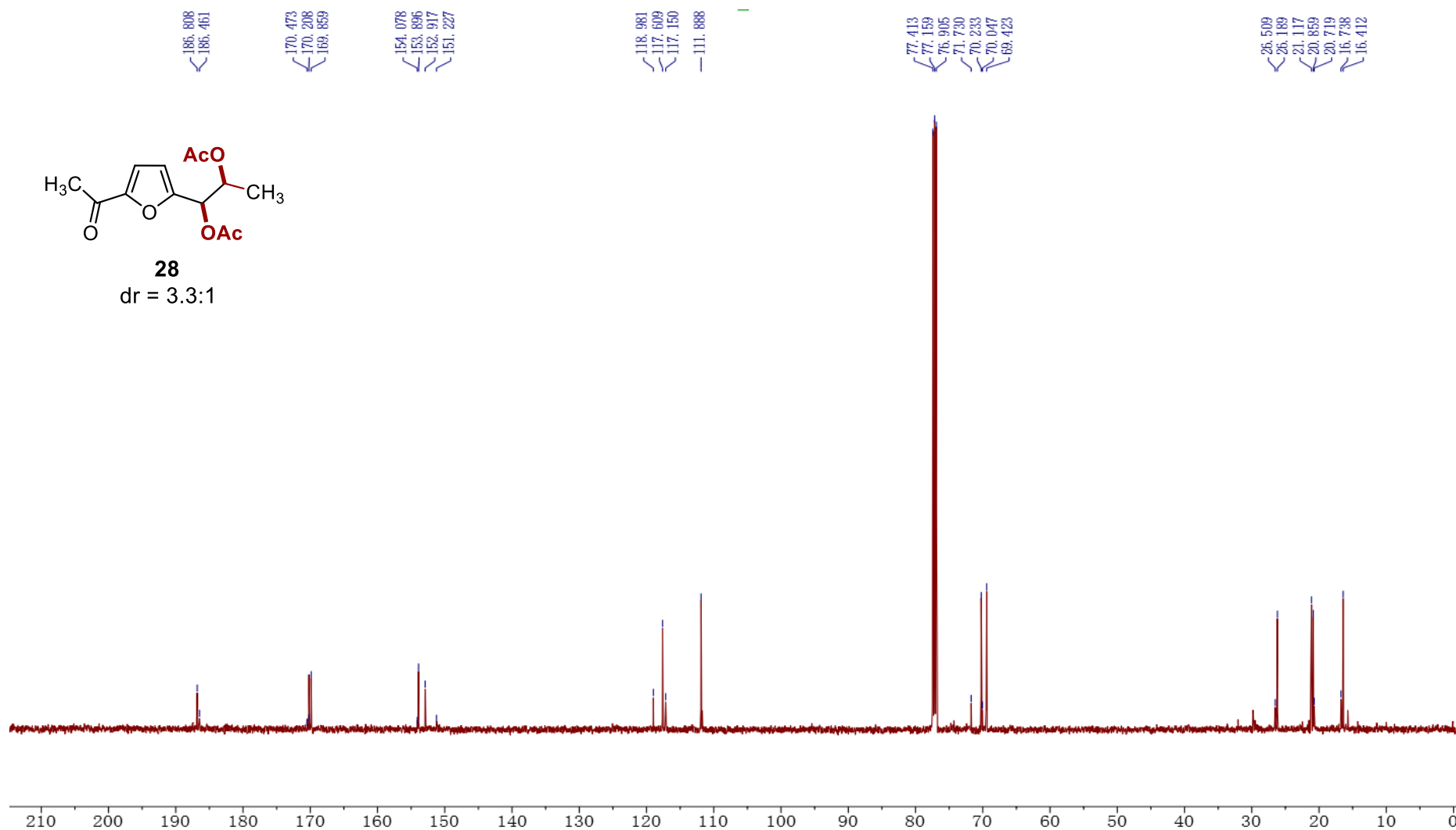


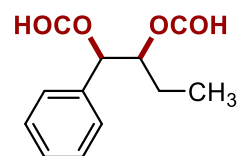
28
dr = 3.3:1





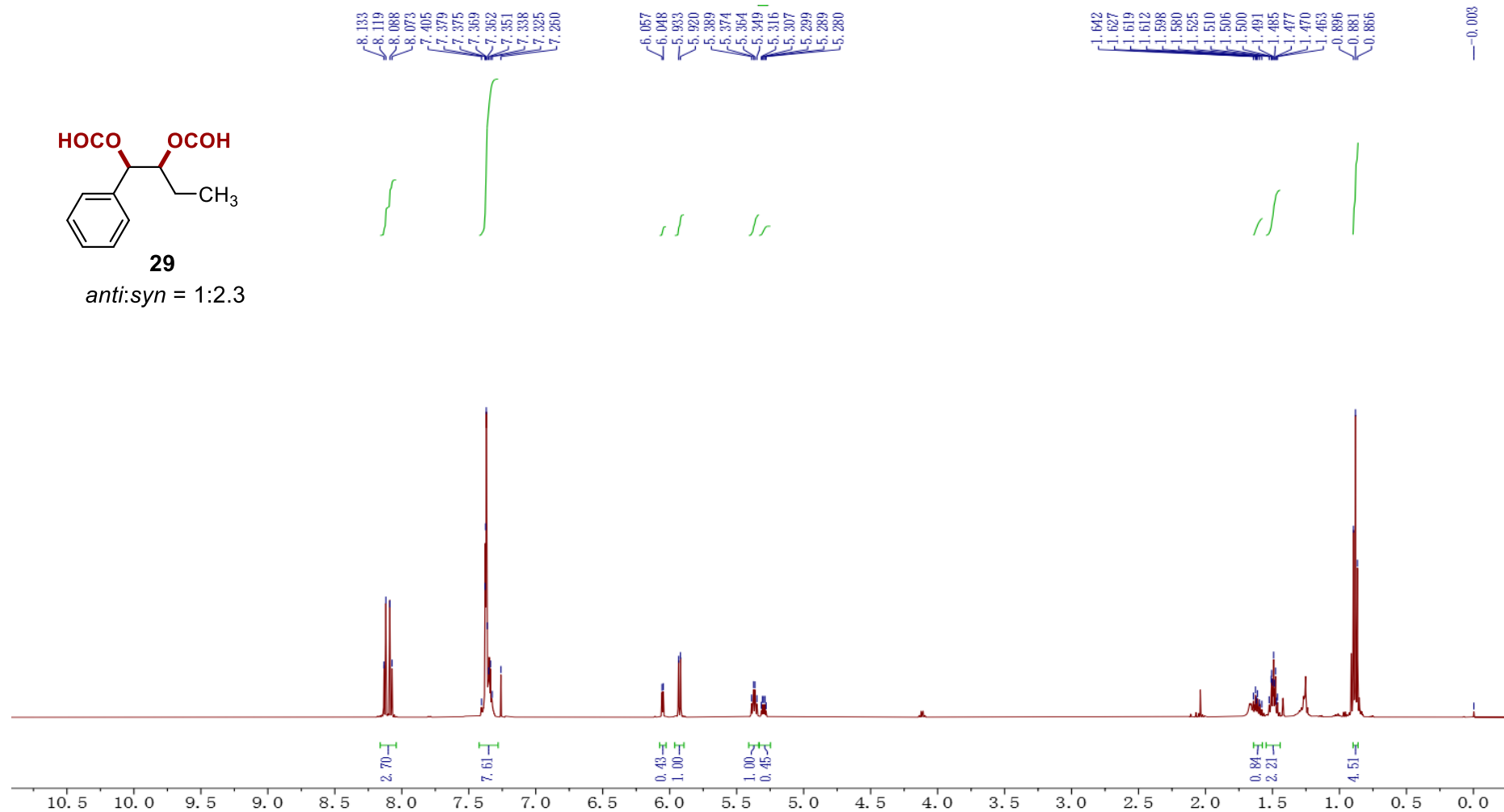
28
dr = 3.3:1



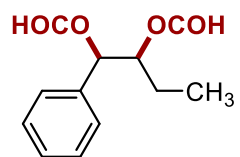


29

anti:syn = 1:2.3



S168



29

anti:syn = 1:2.3

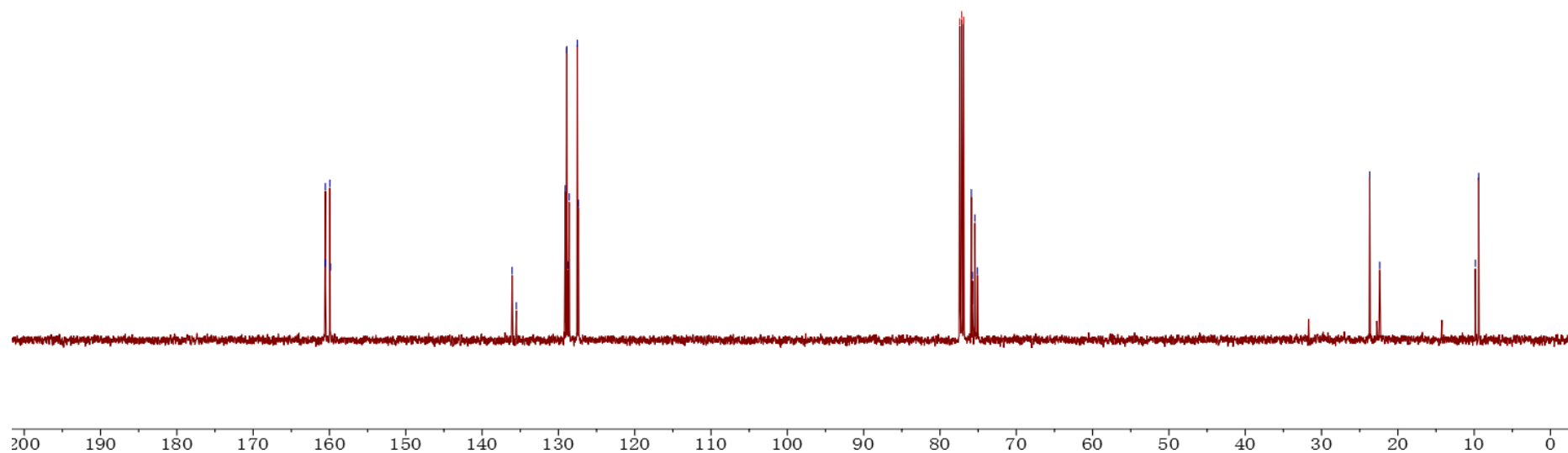
160.574
160.536
159.950
159.865

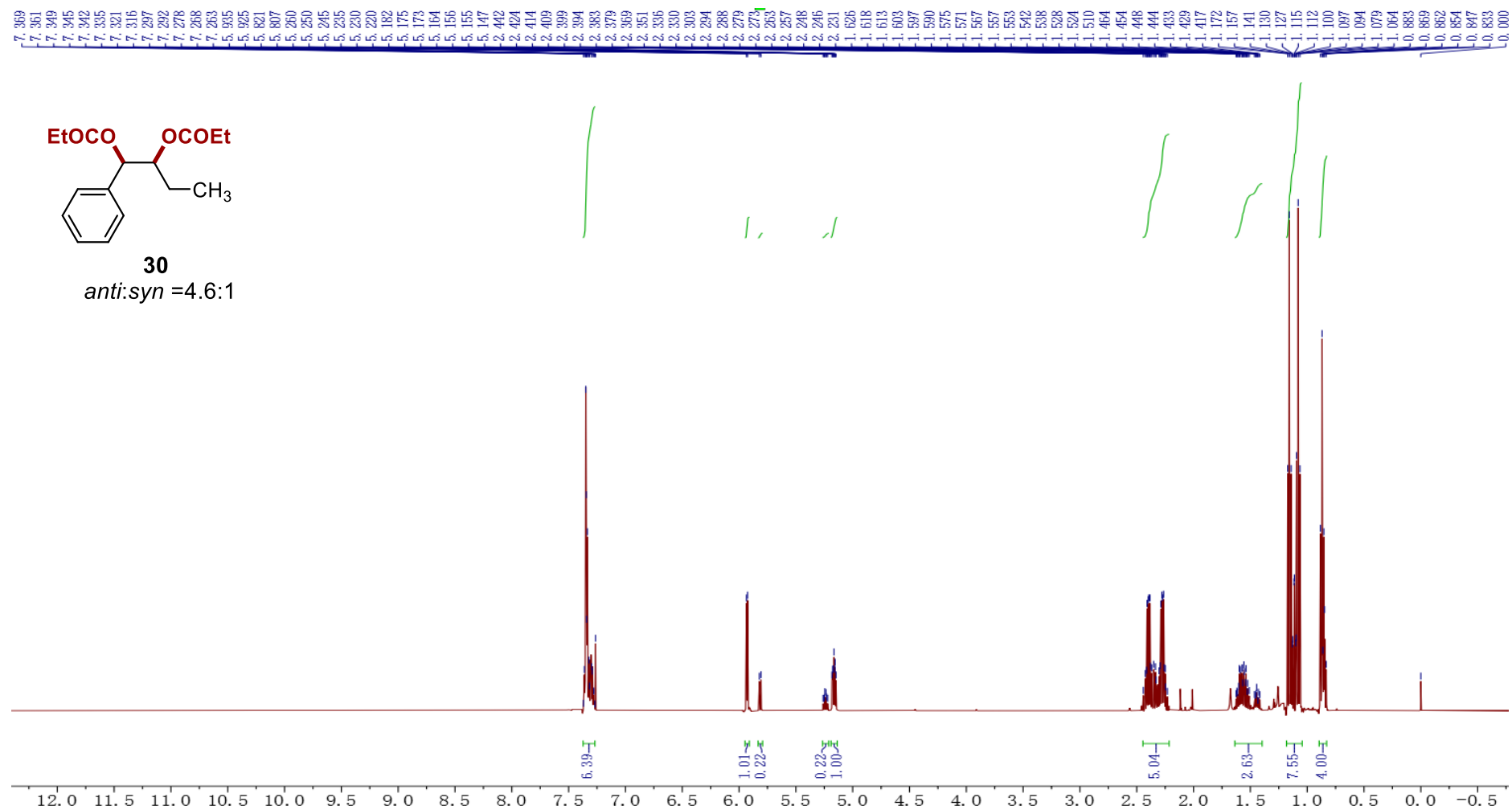
135.071
135.514
129.108
128.899
128.757
128.584
127.523
127.369

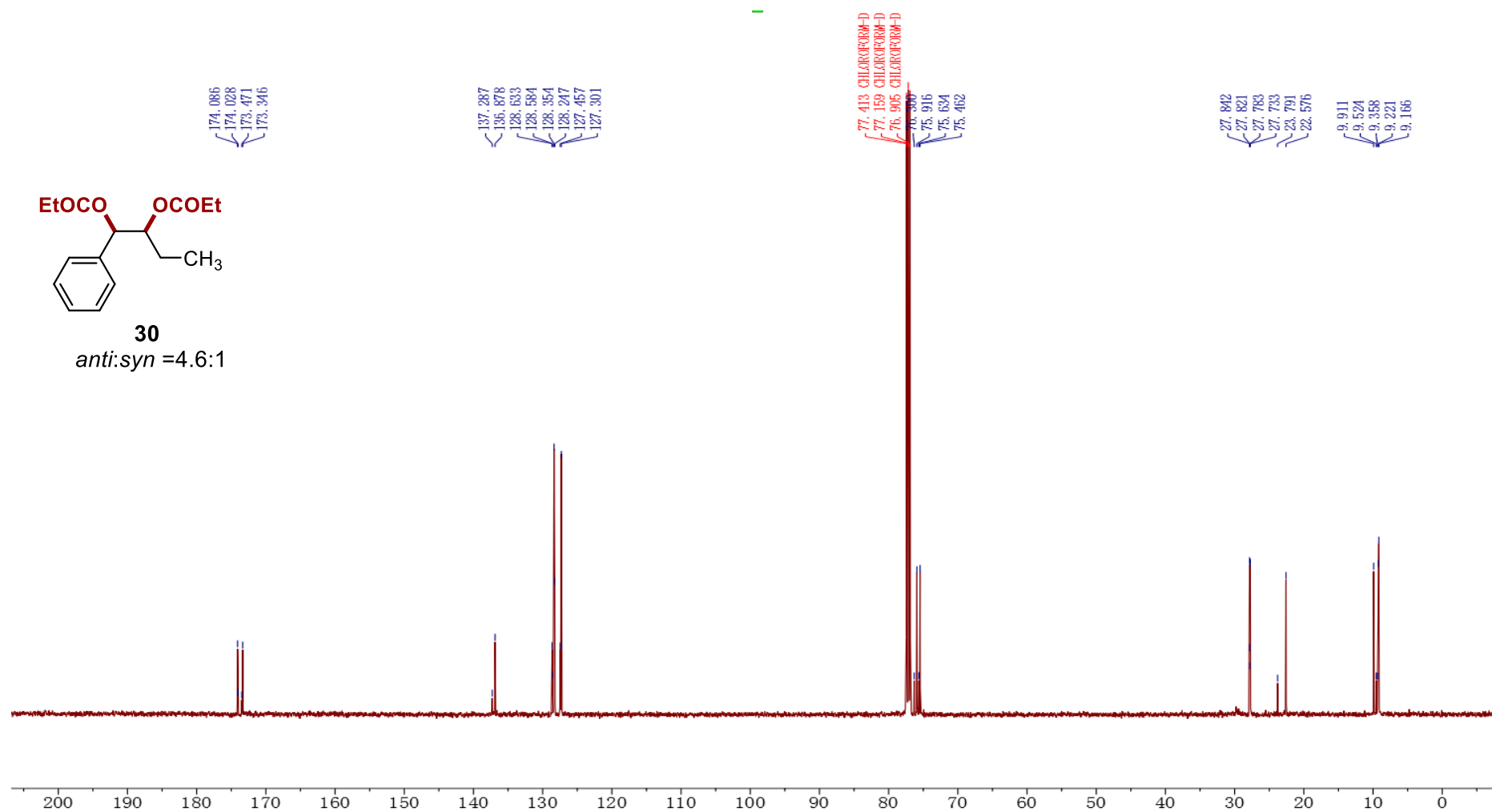
77.415 CHLOROFORM-D
77.160 CHLOROFORM-D
76.906 CHLOROFORM-D
75.880
75.739
75.427
75.095

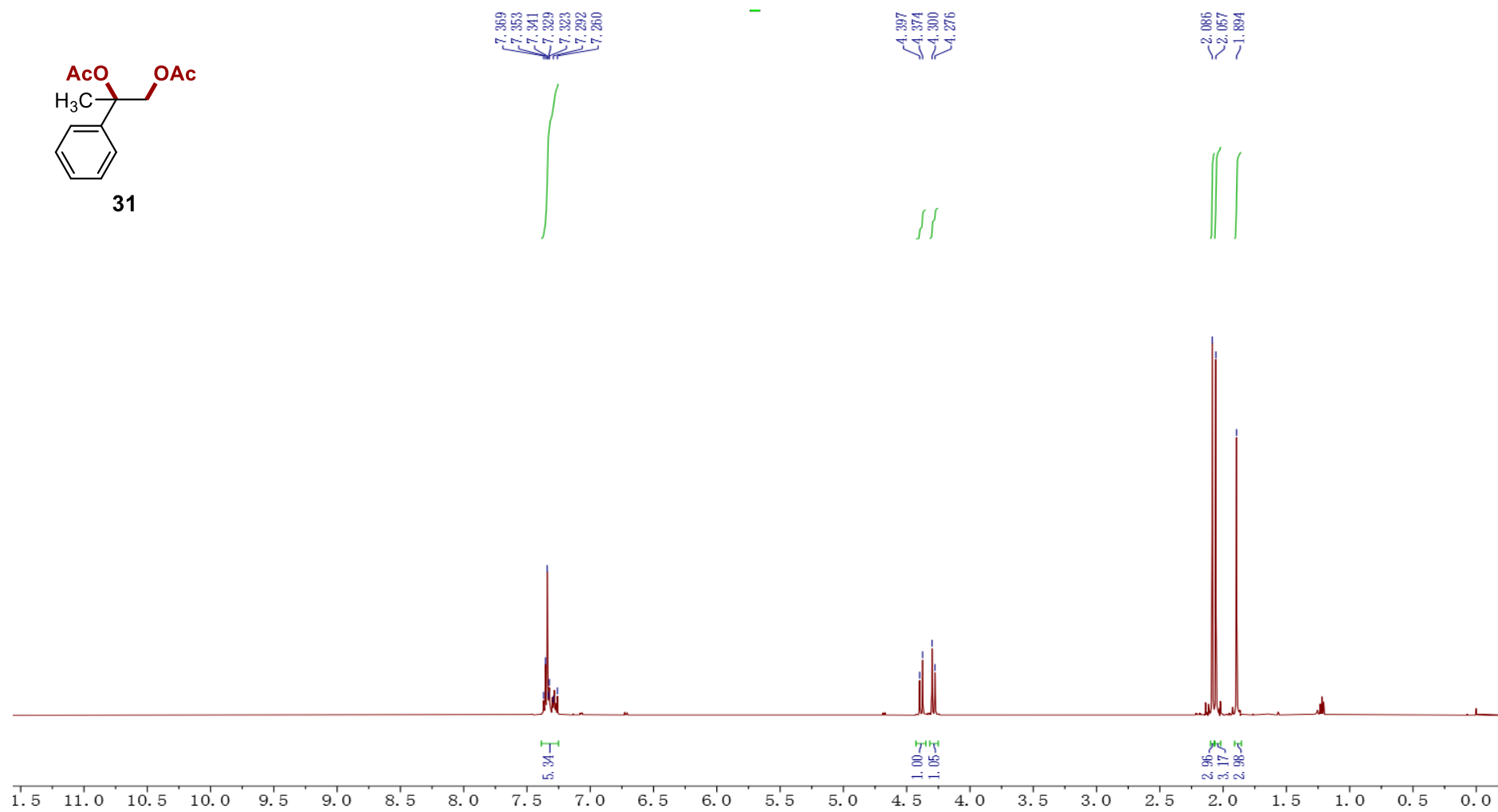
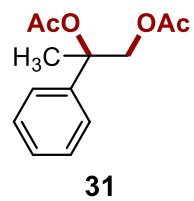
23.683
22.378

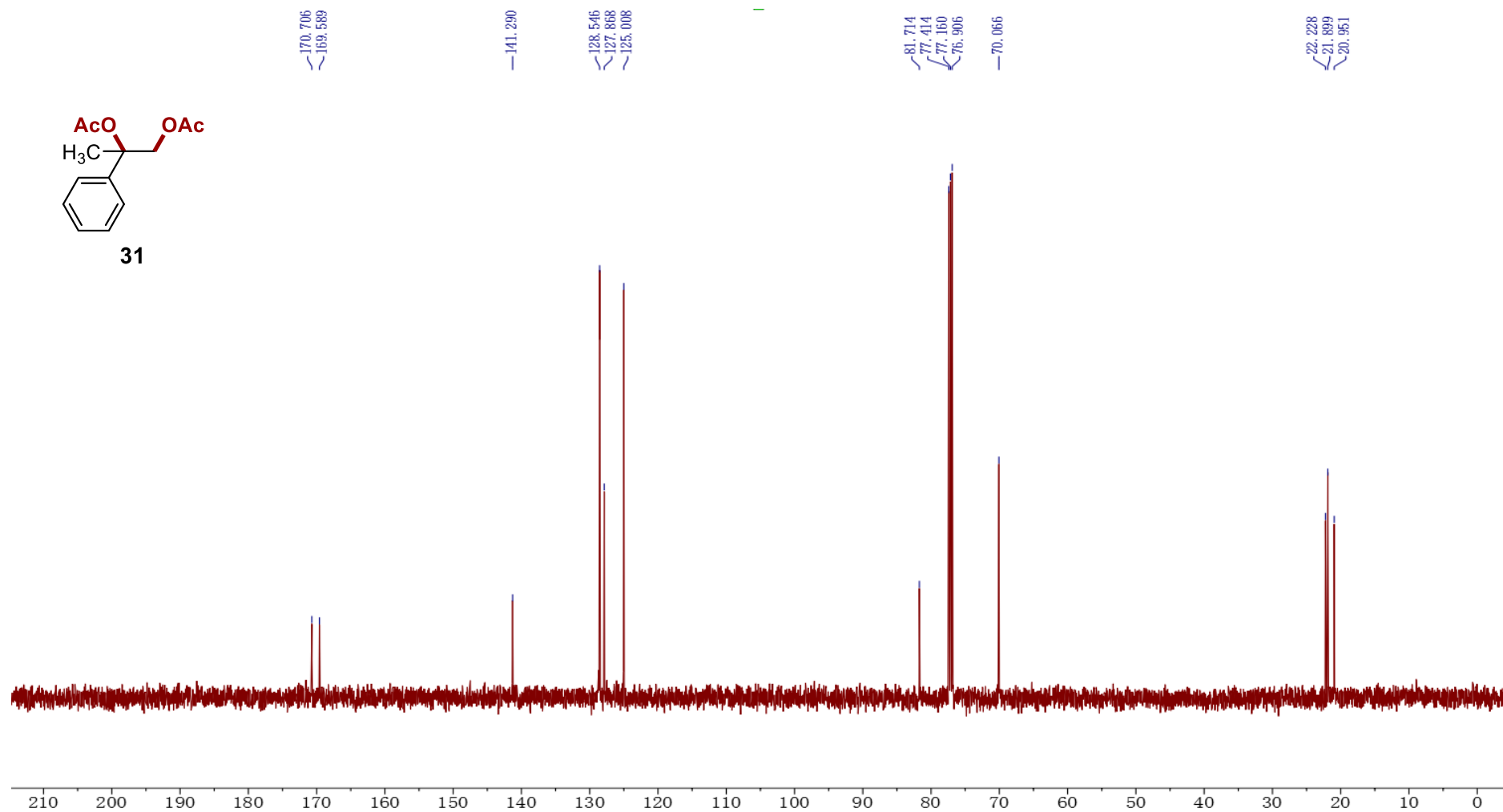
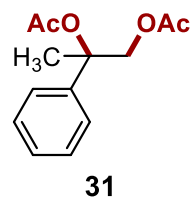
9.844
9.406

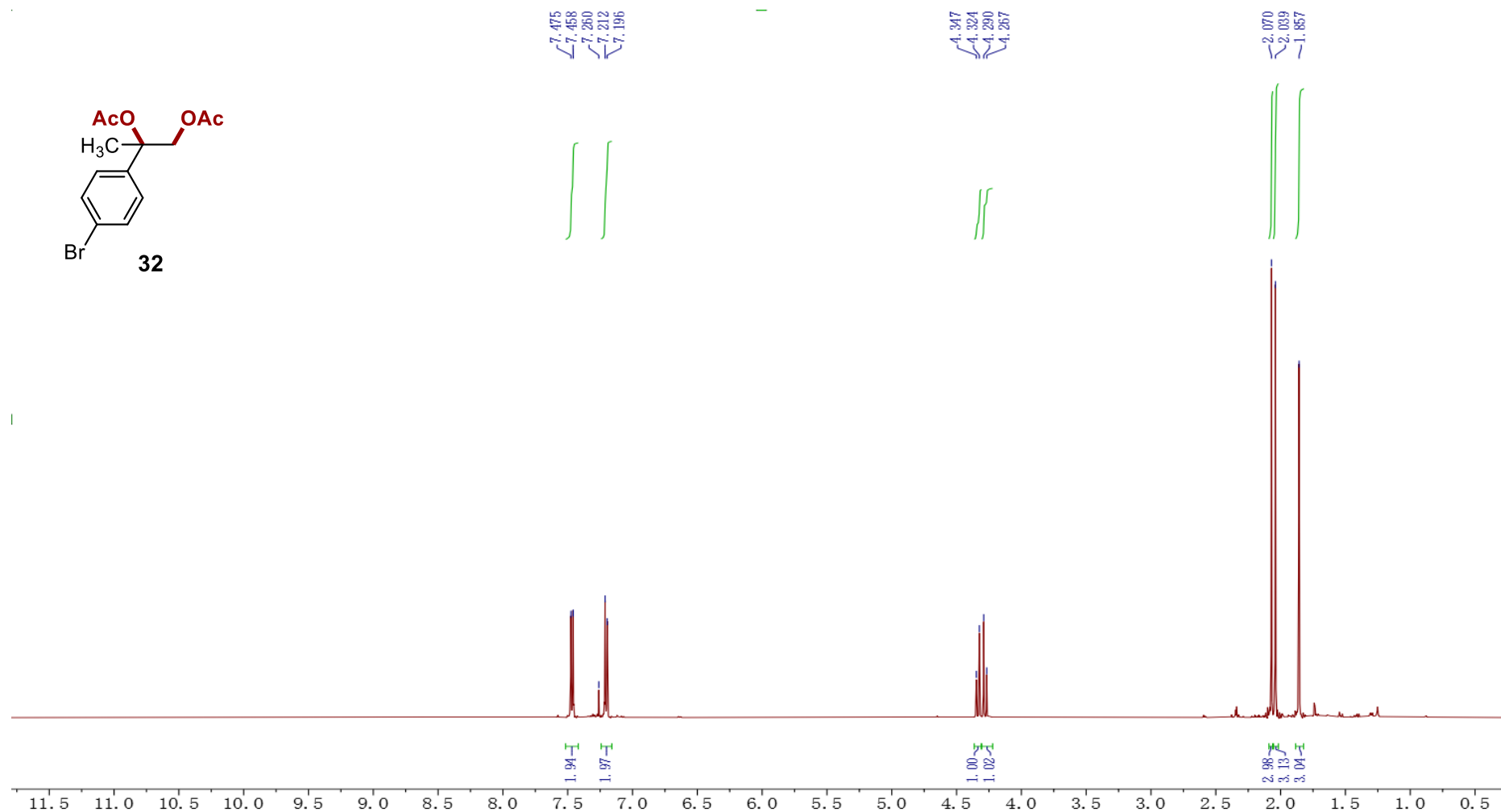
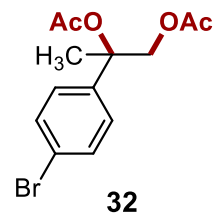


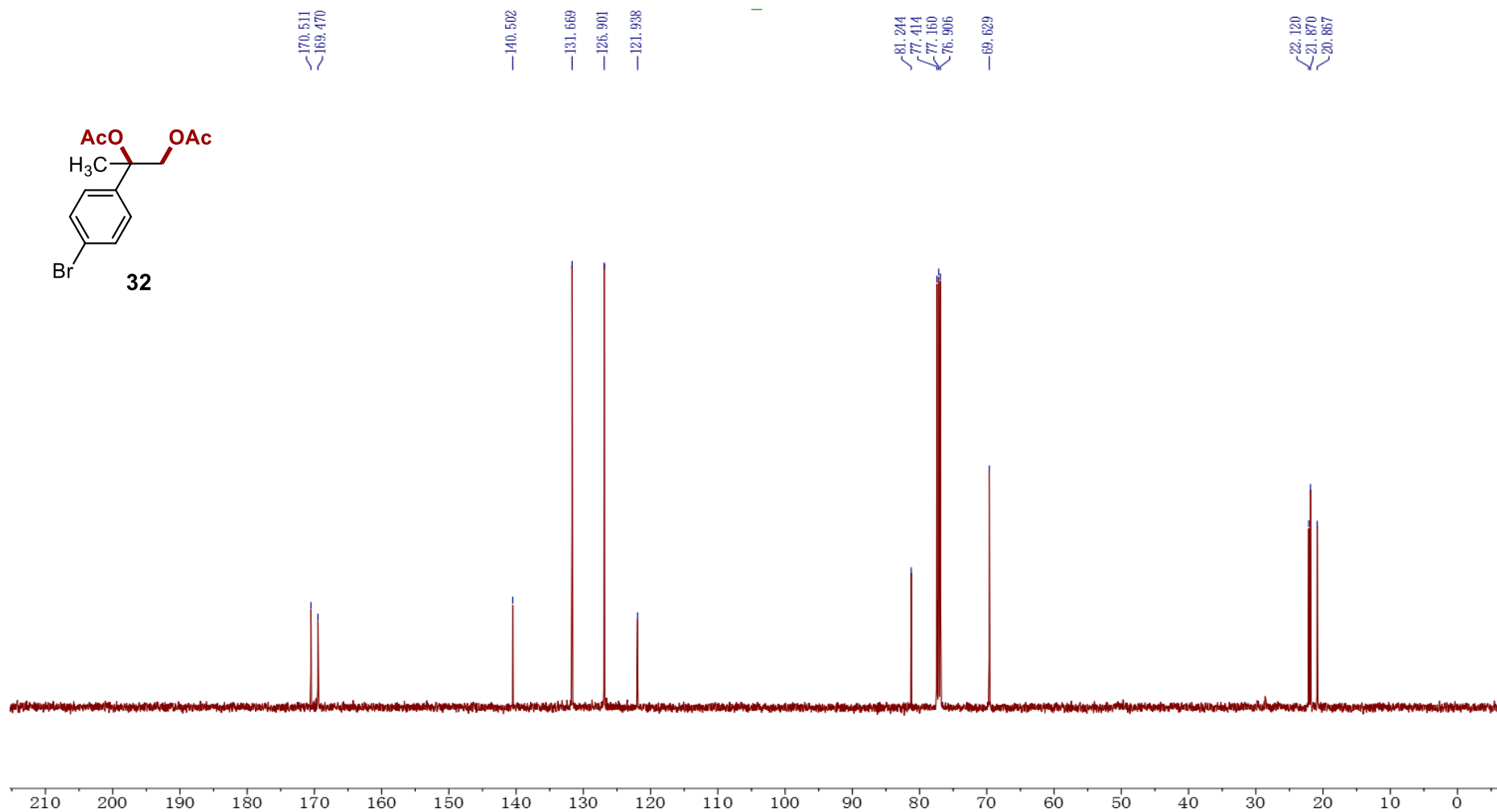
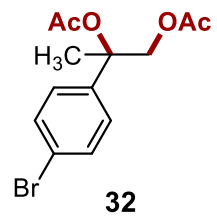


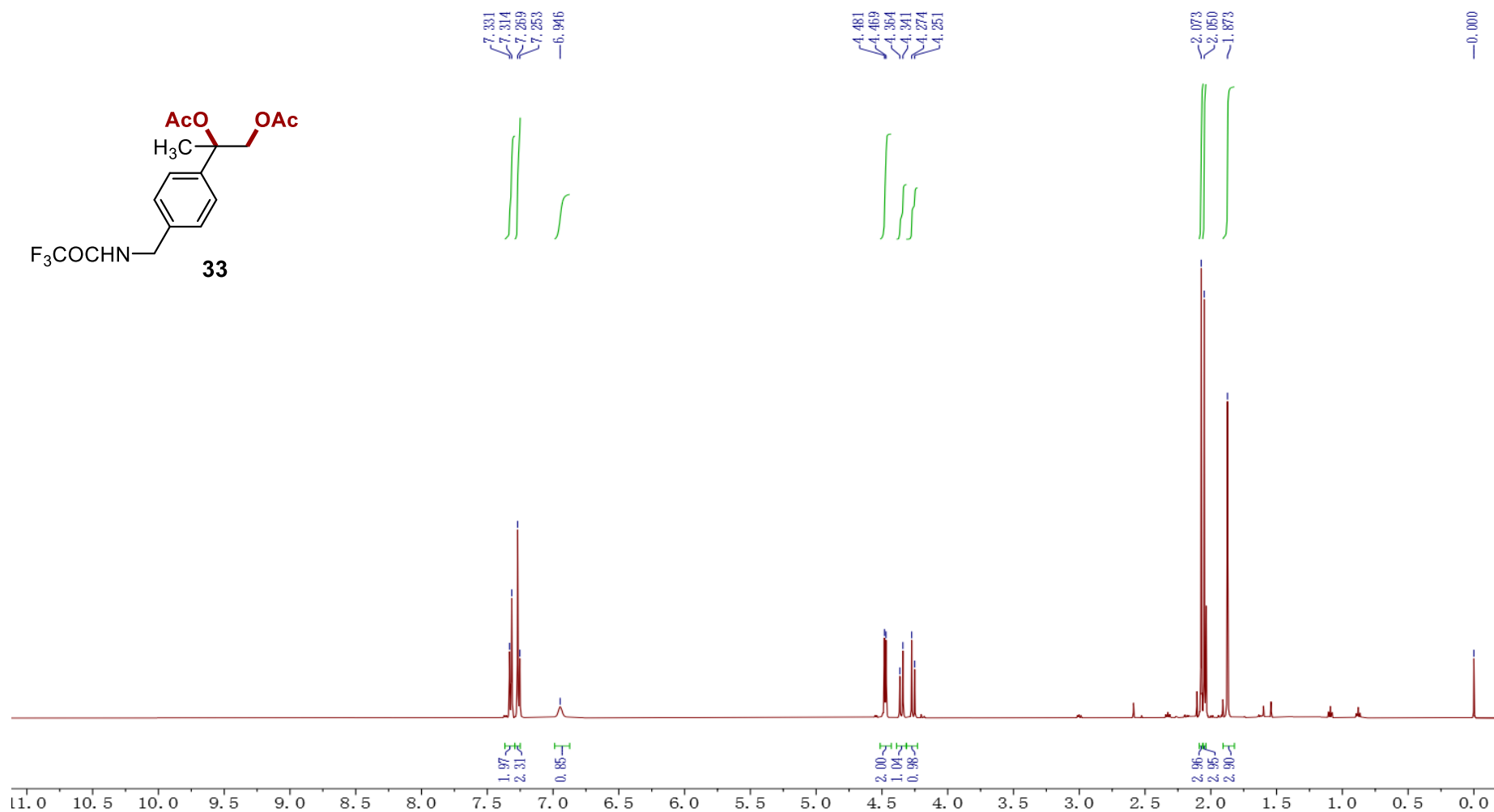


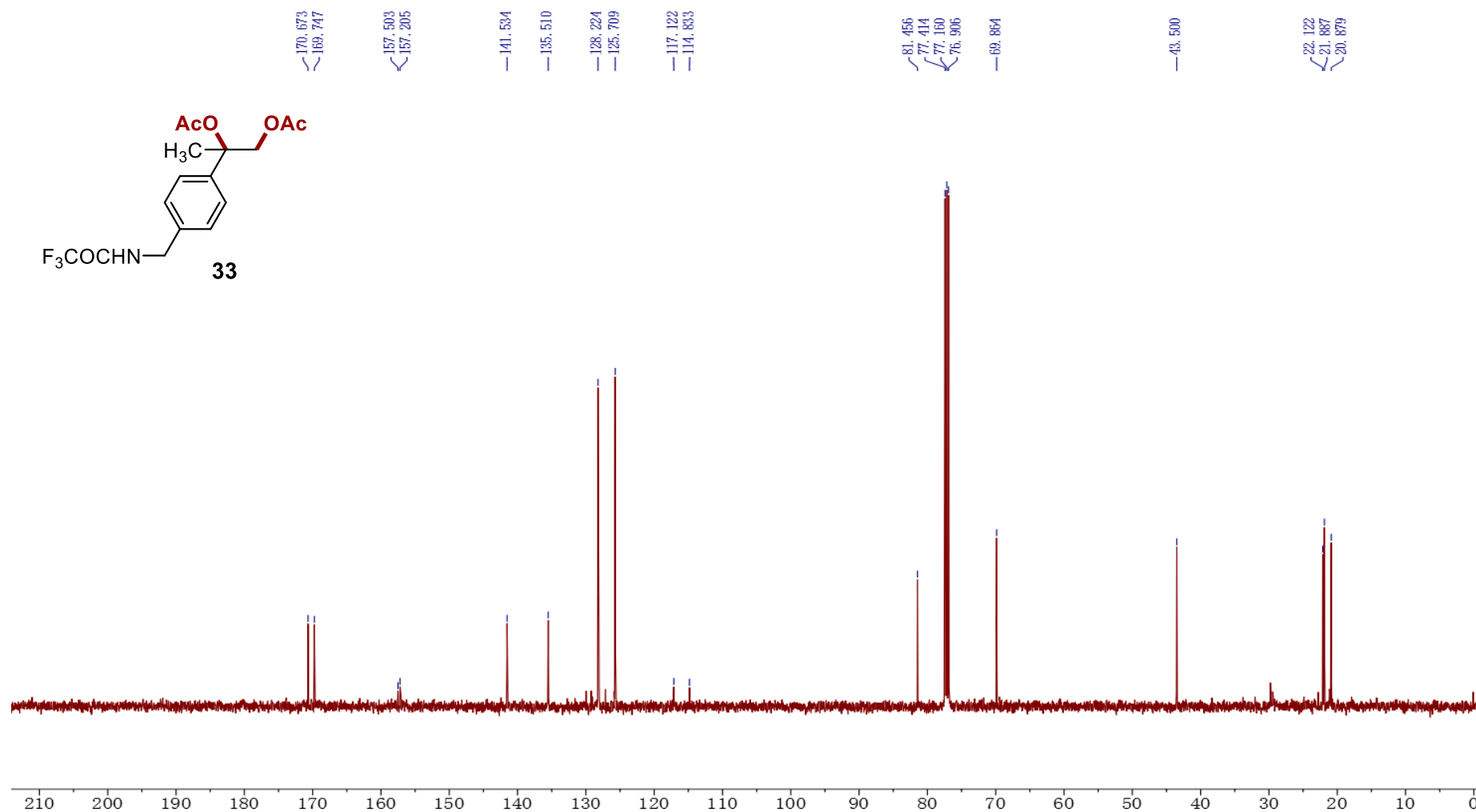


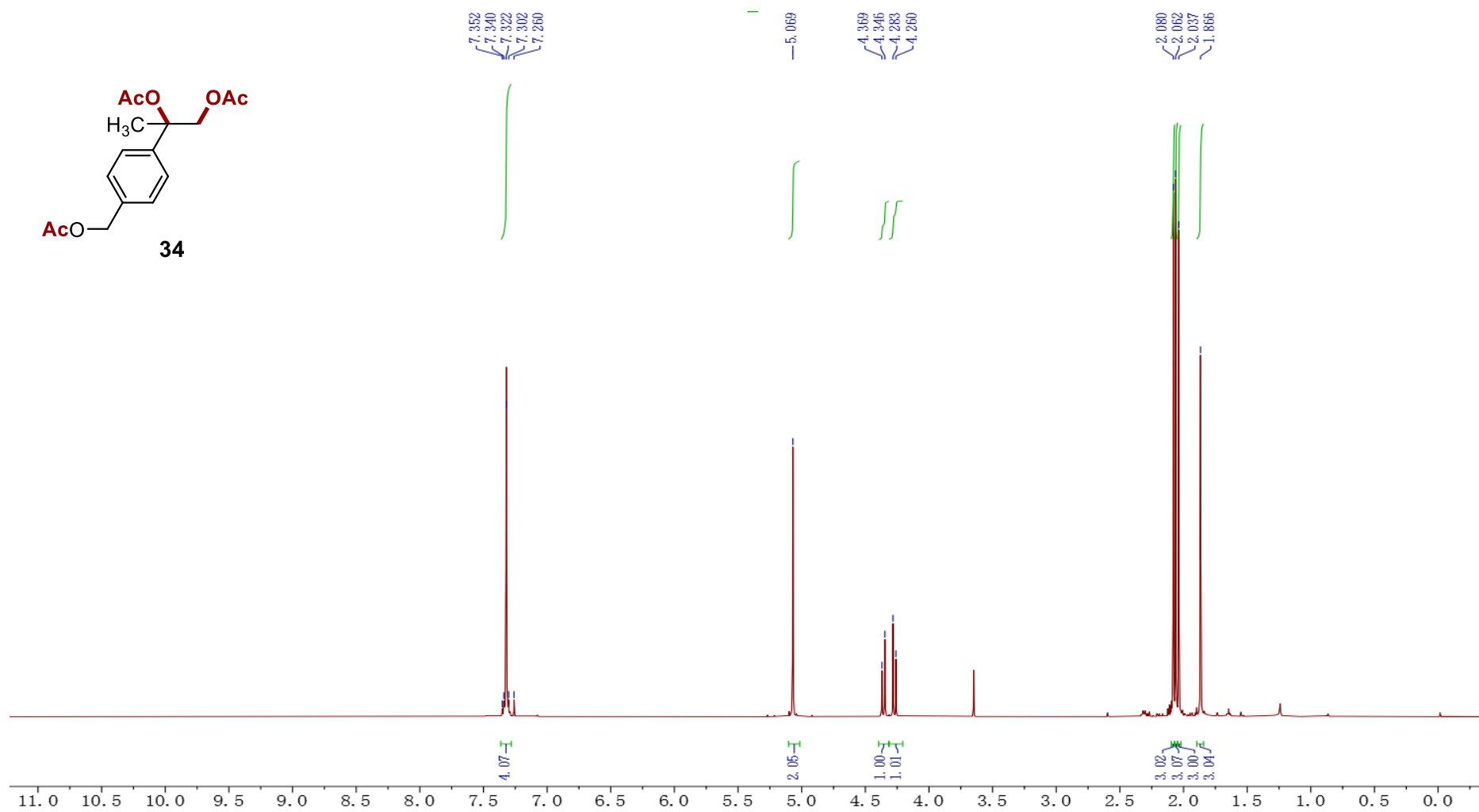


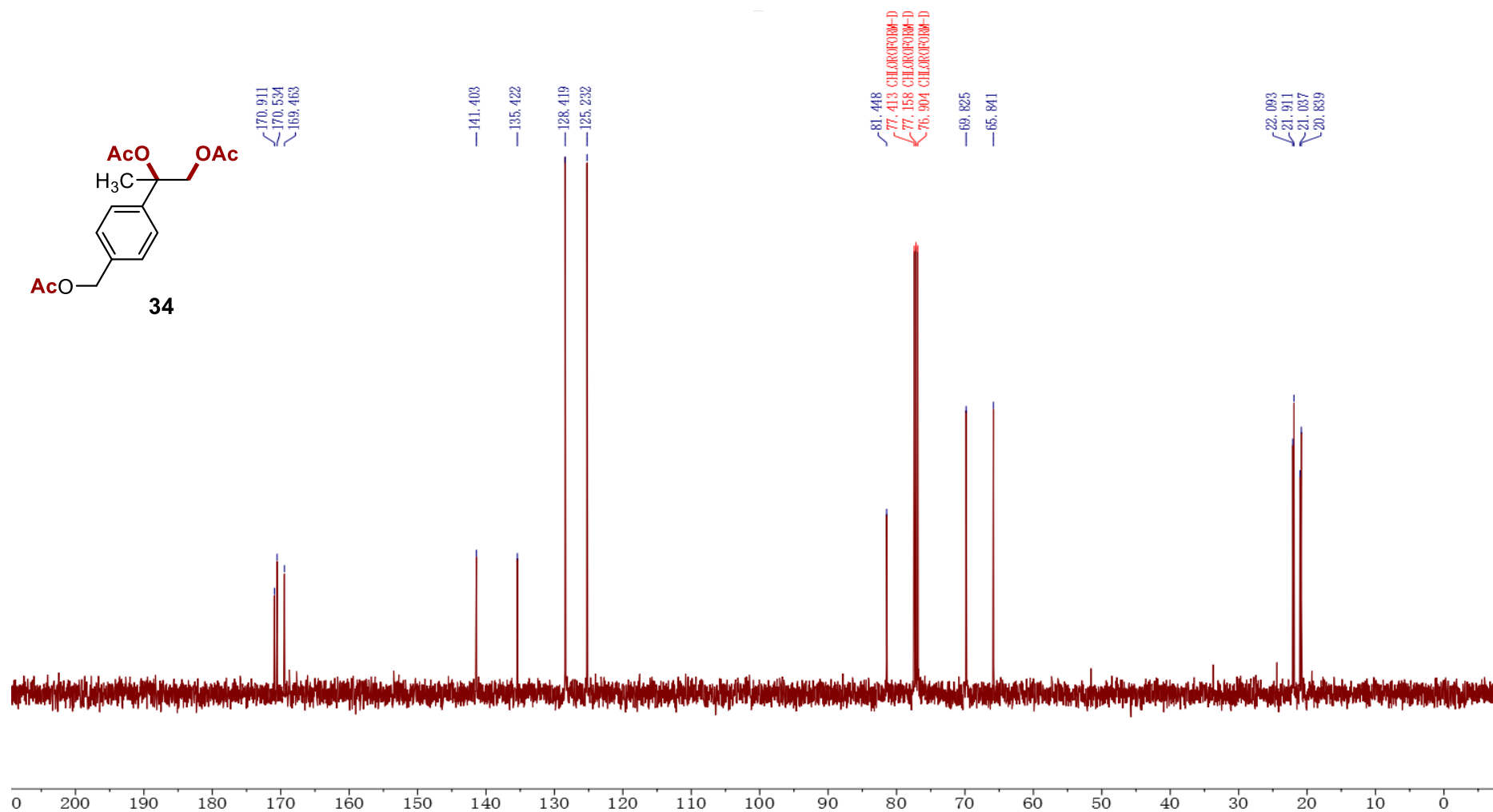


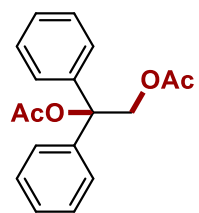




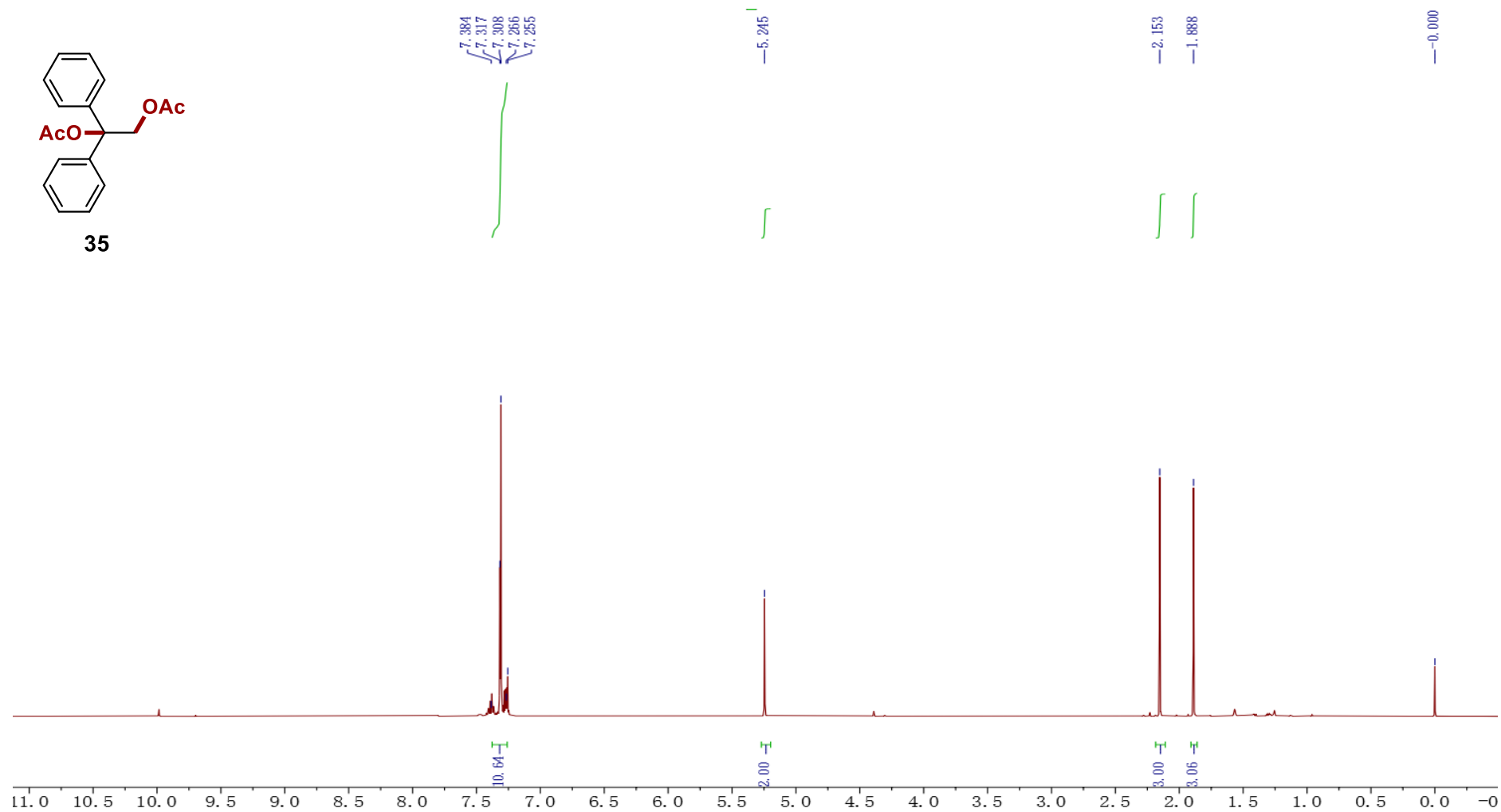


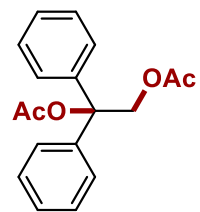




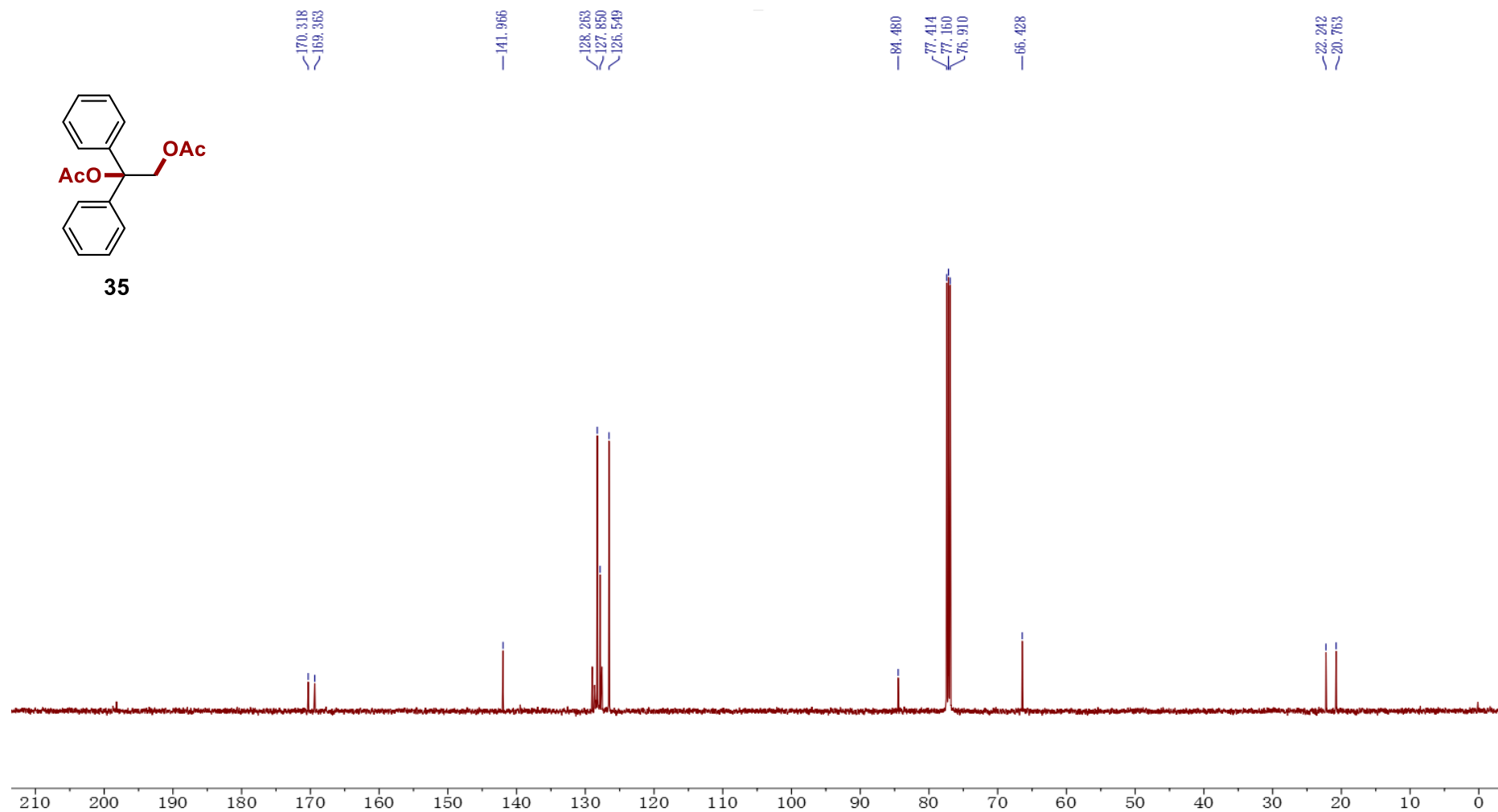


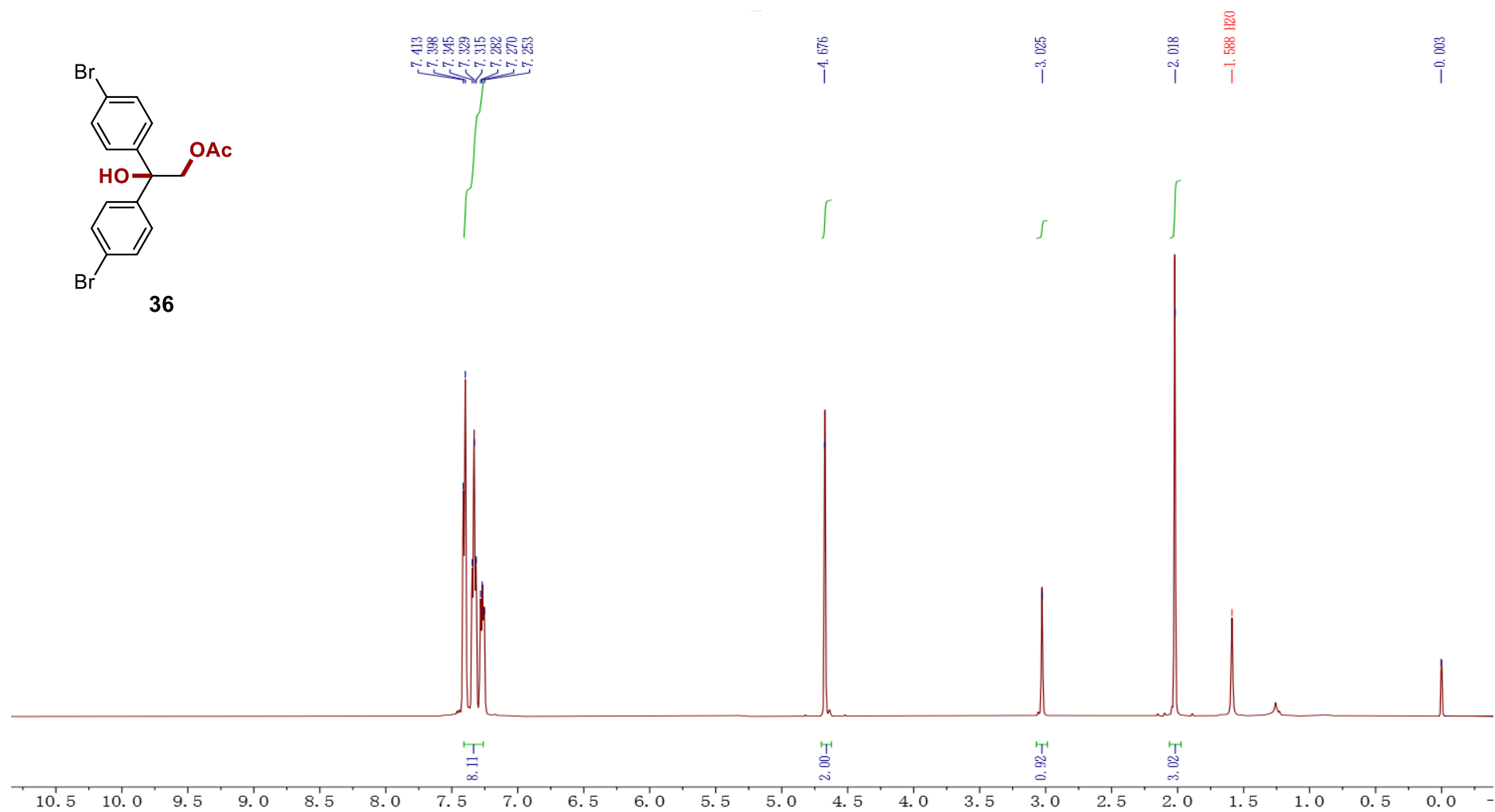
35

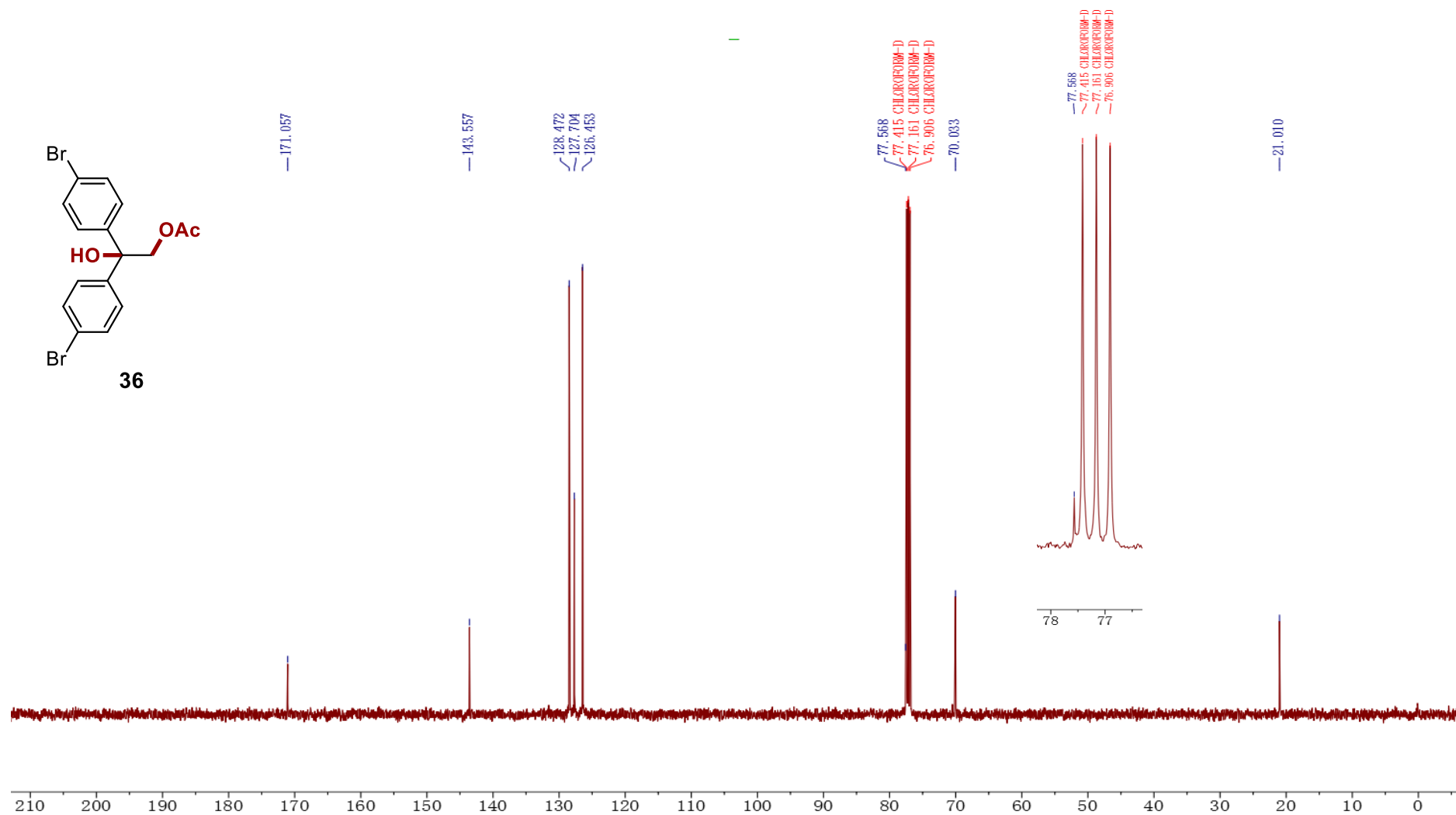


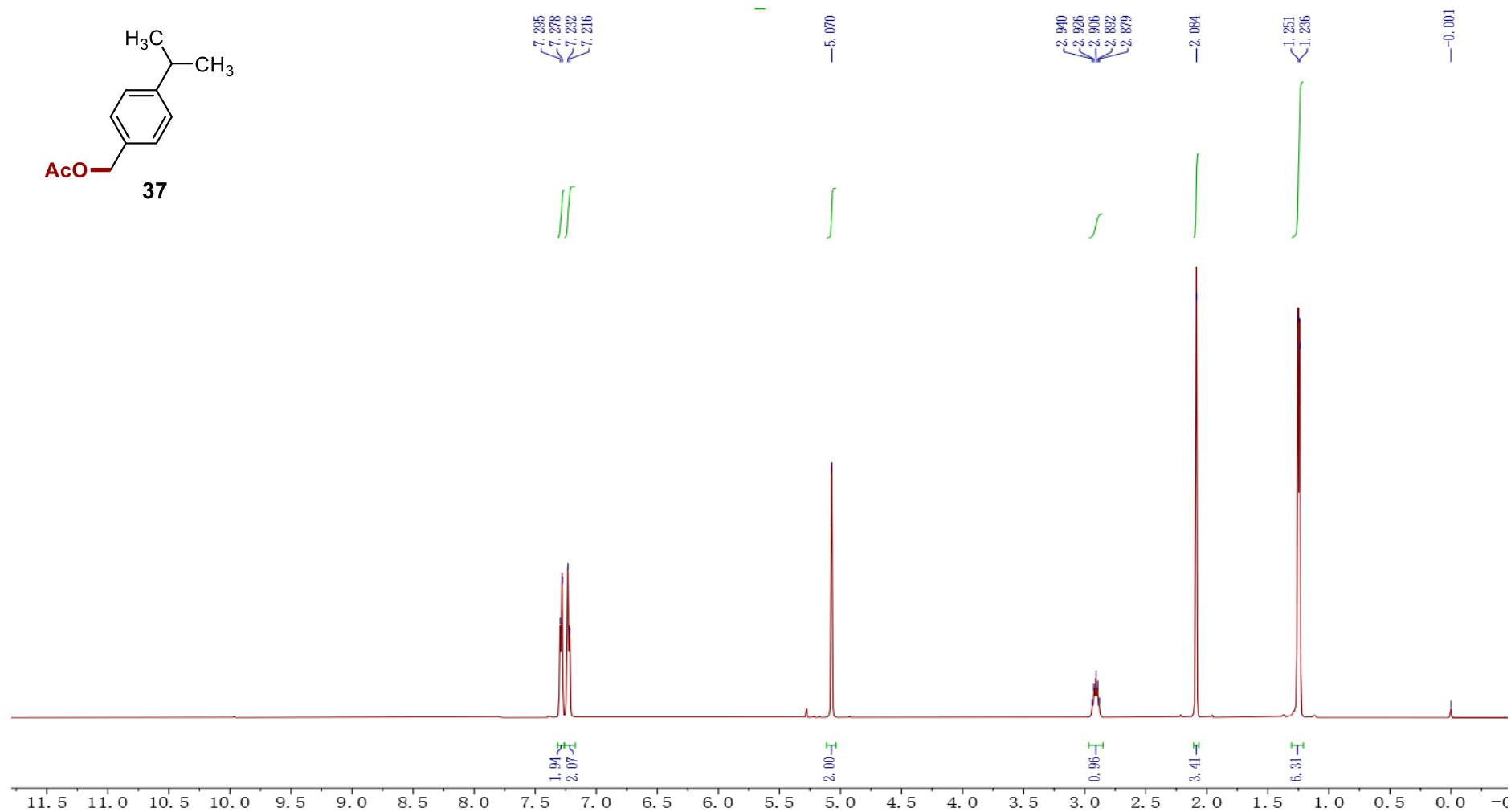
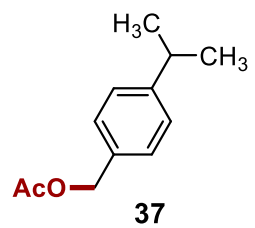


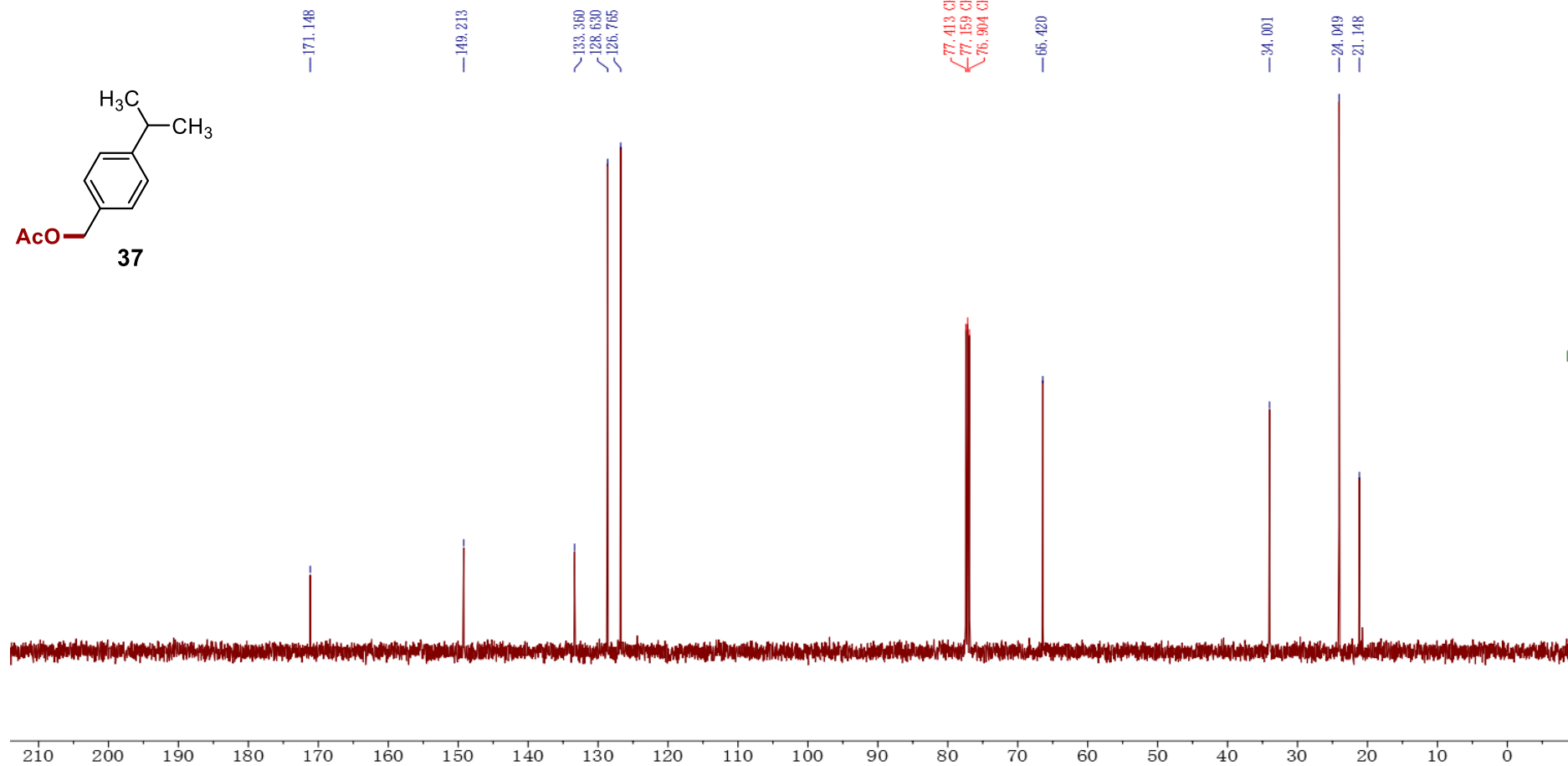
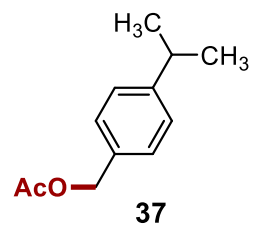
35

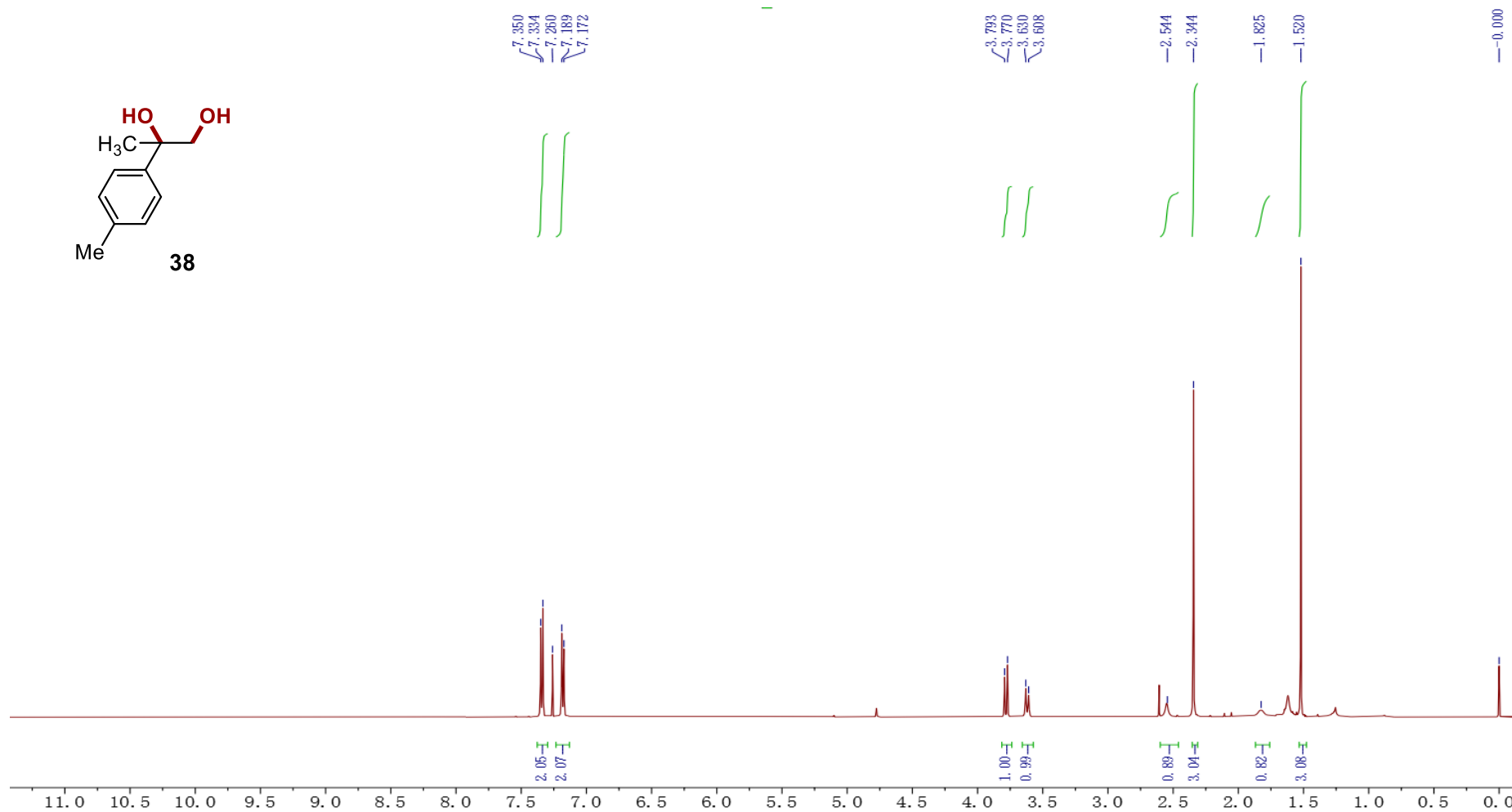
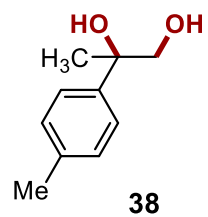


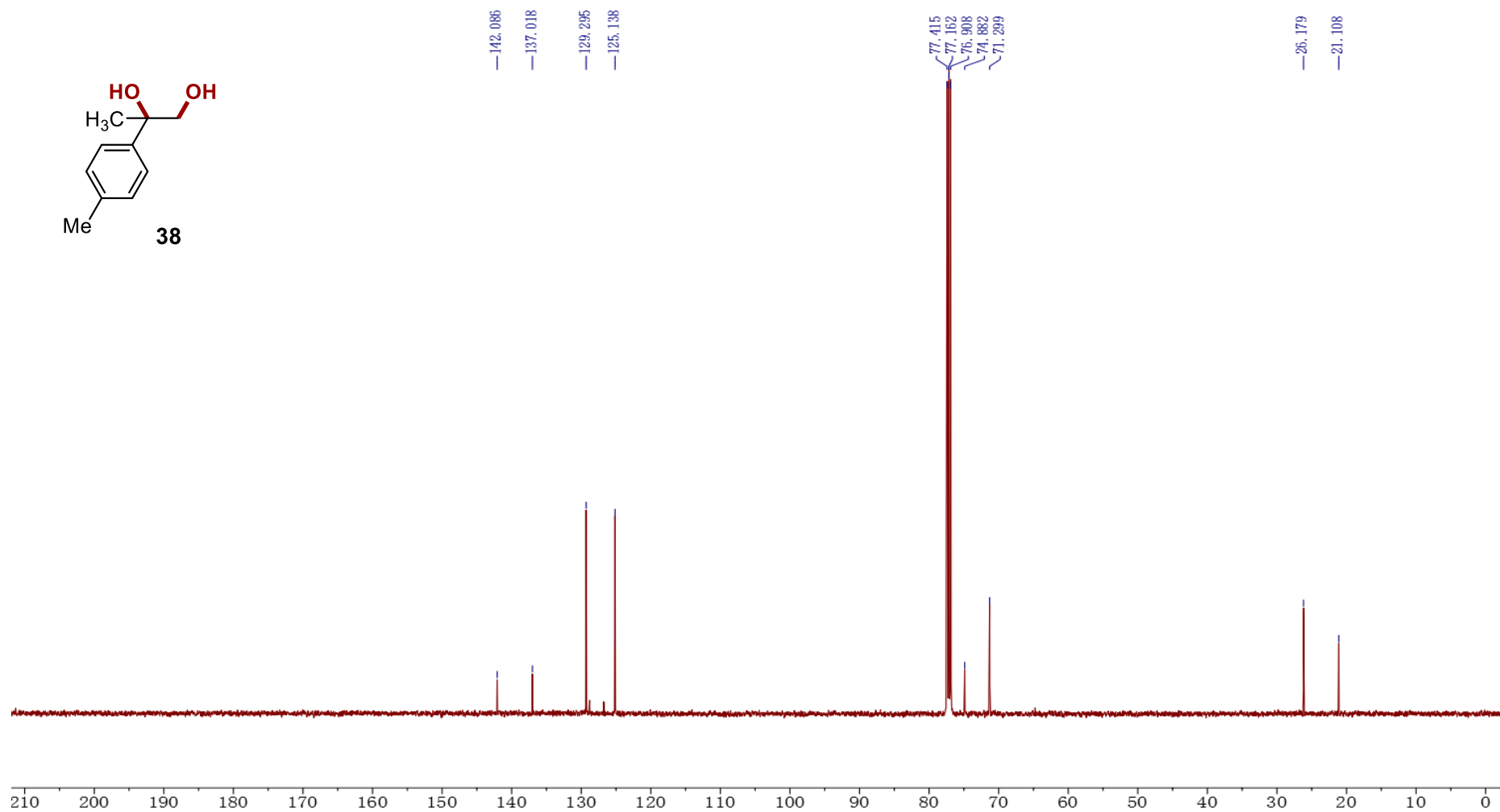
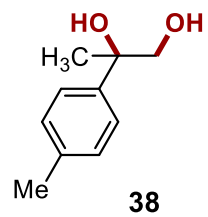


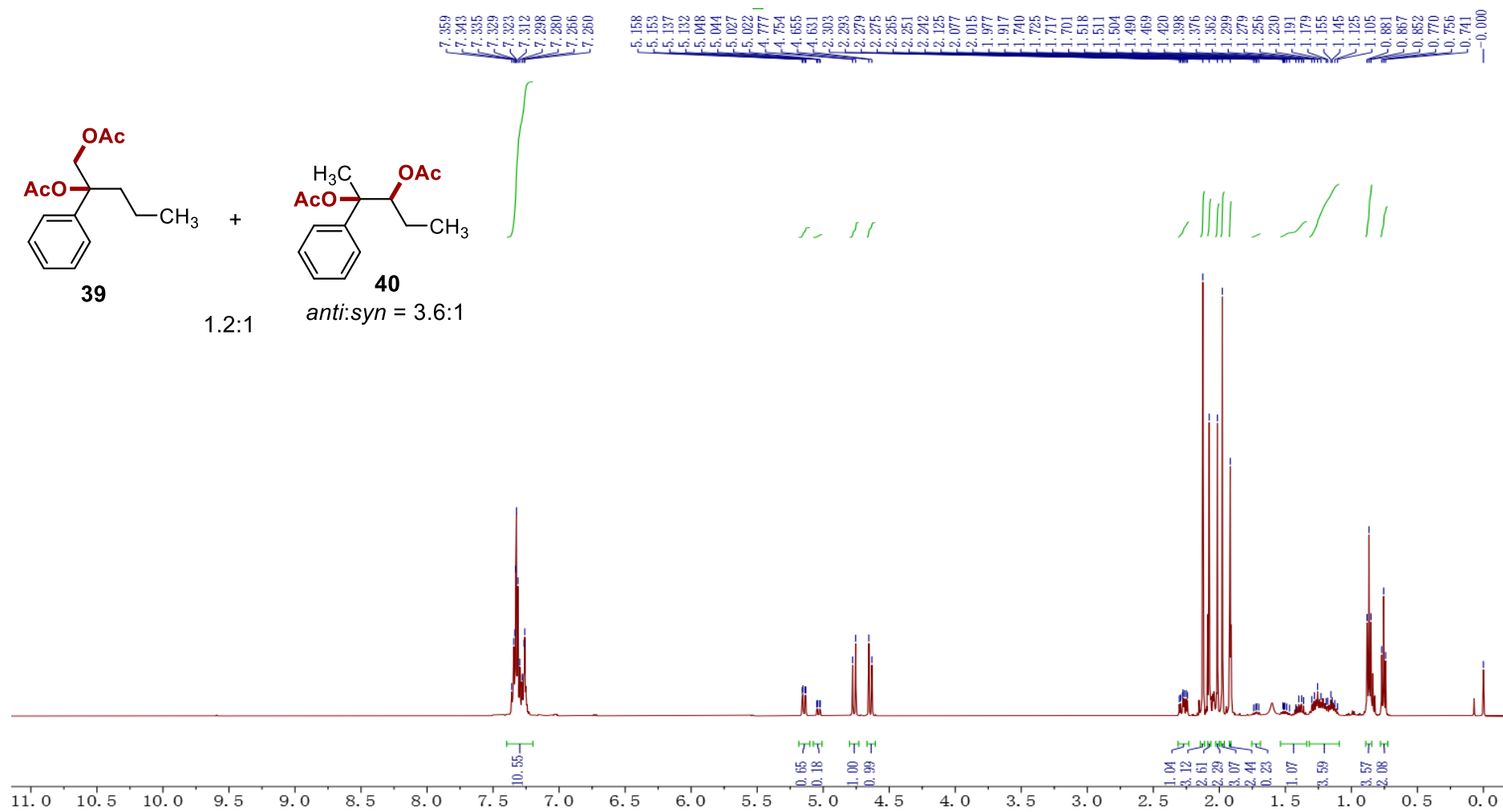


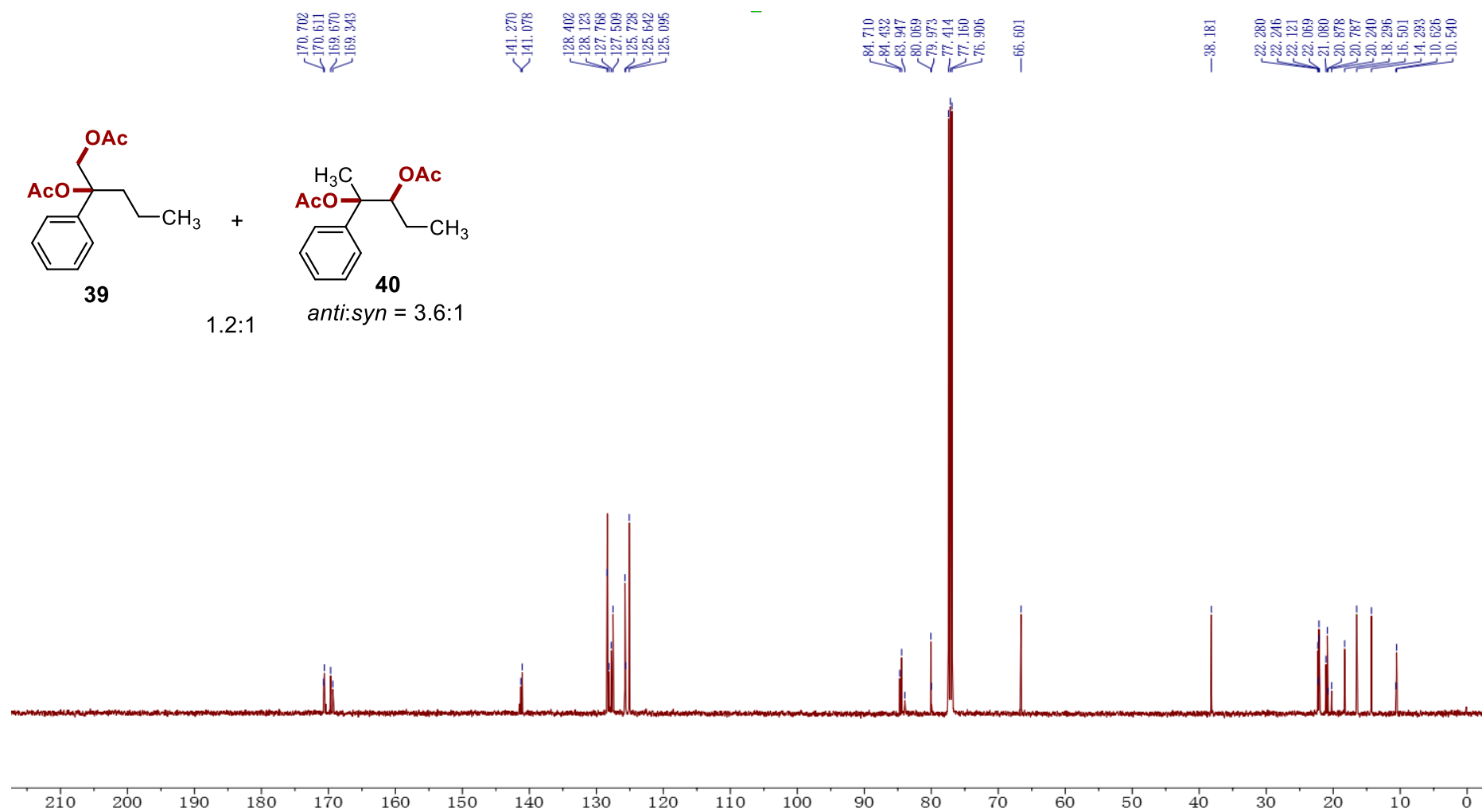


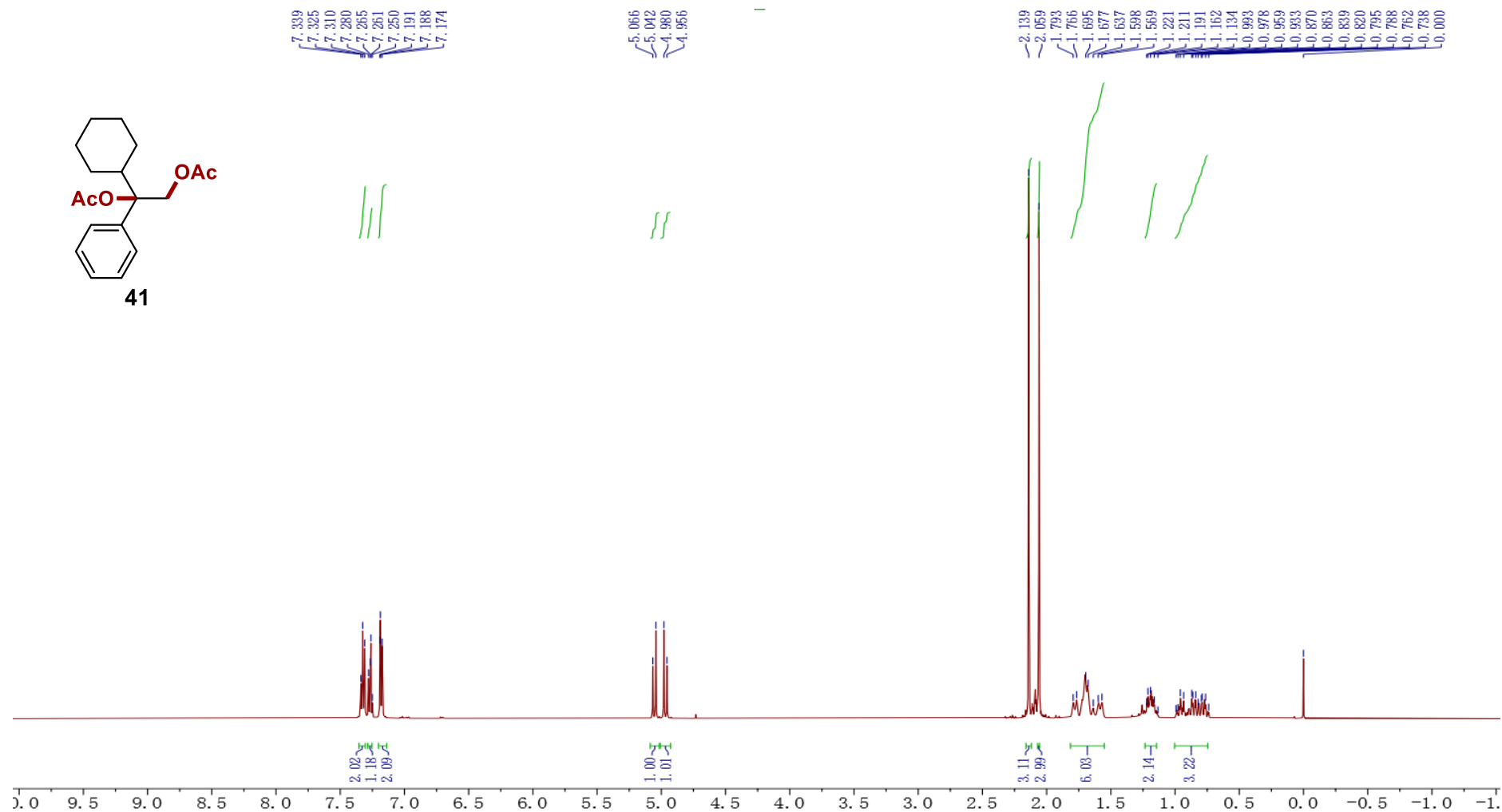
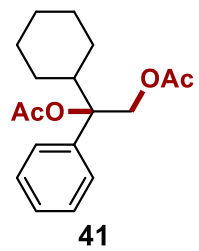


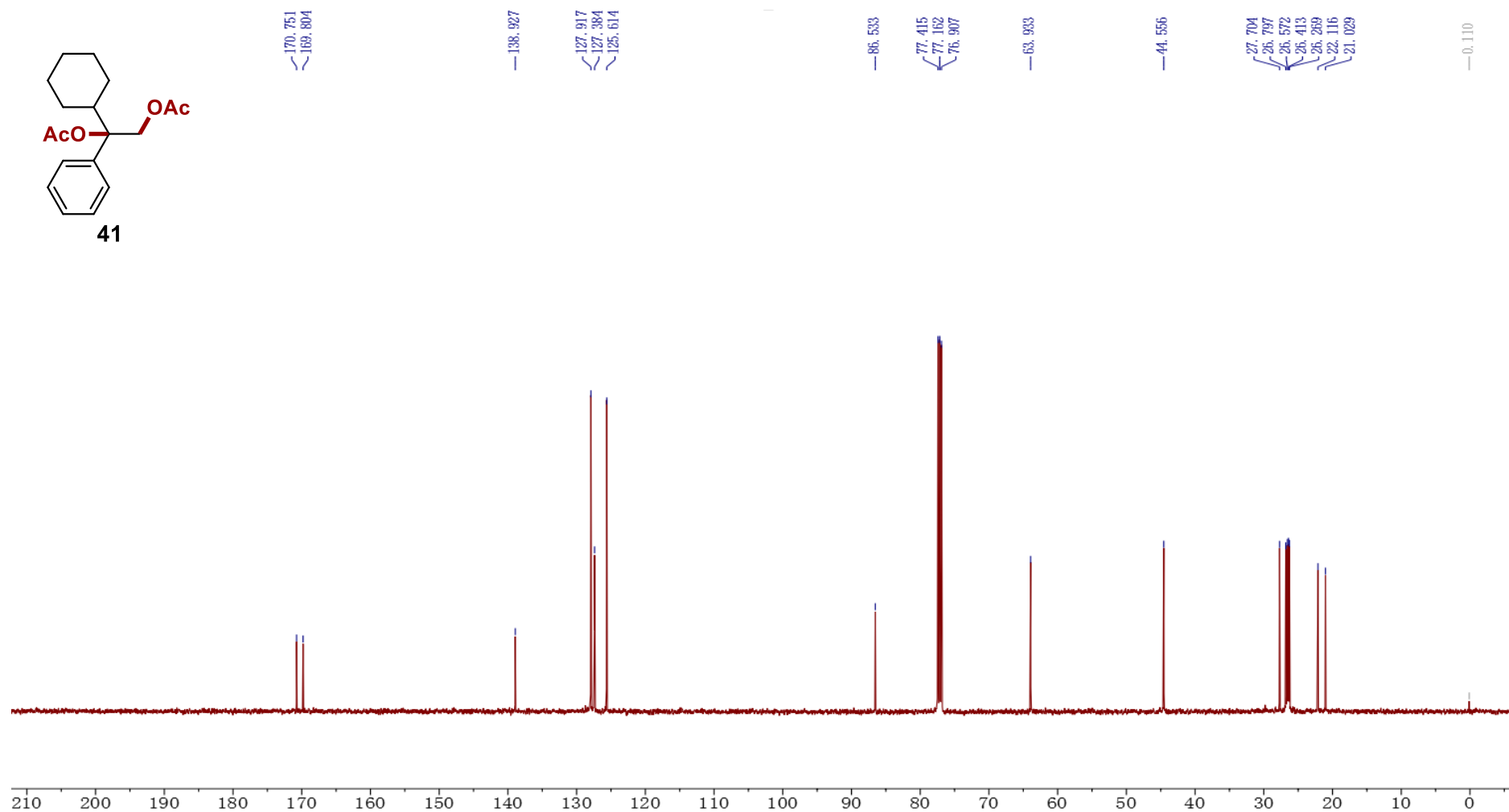
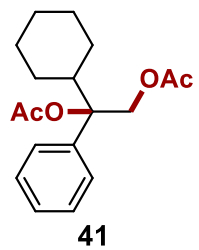


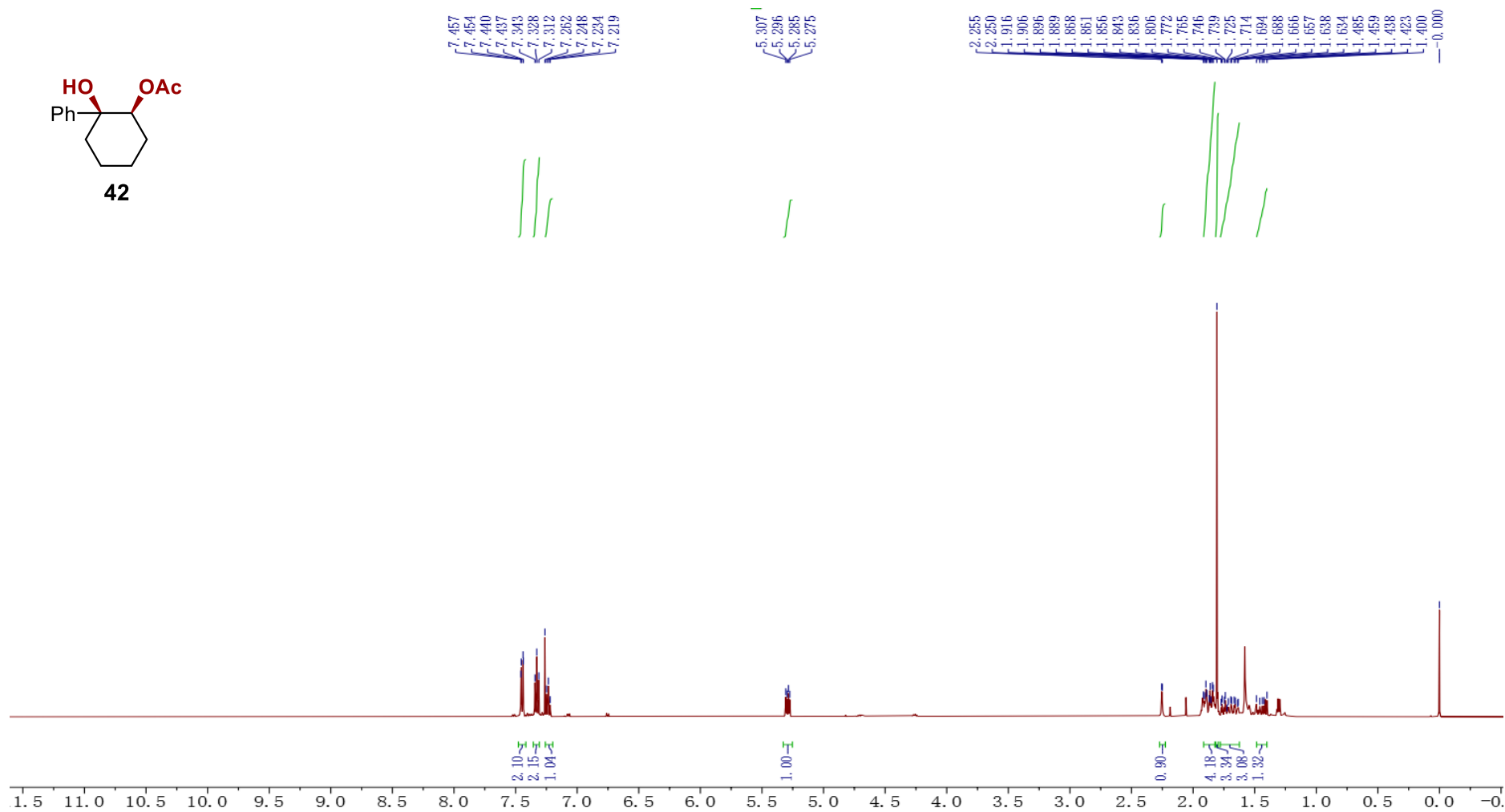
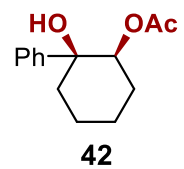


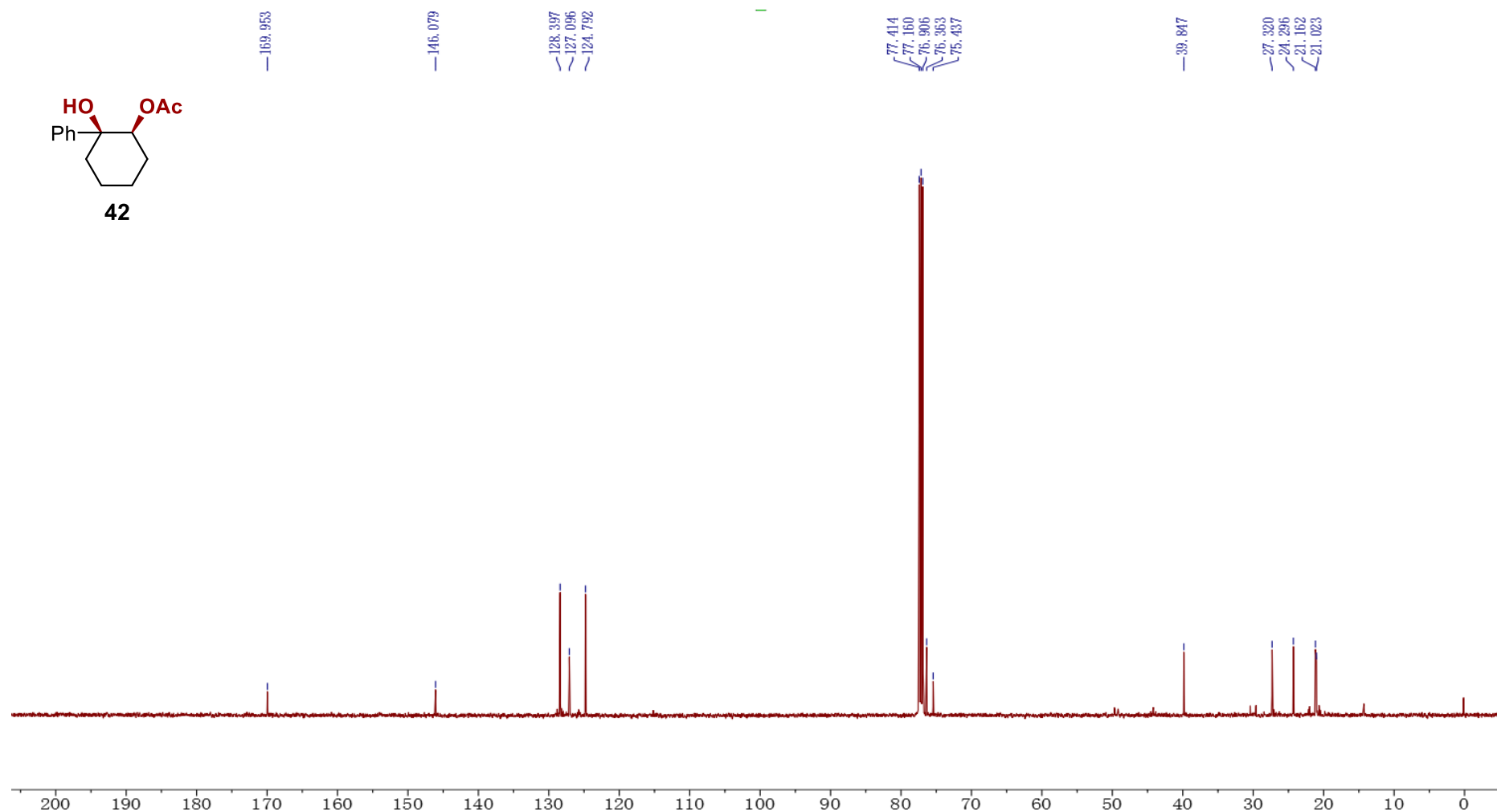
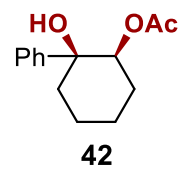


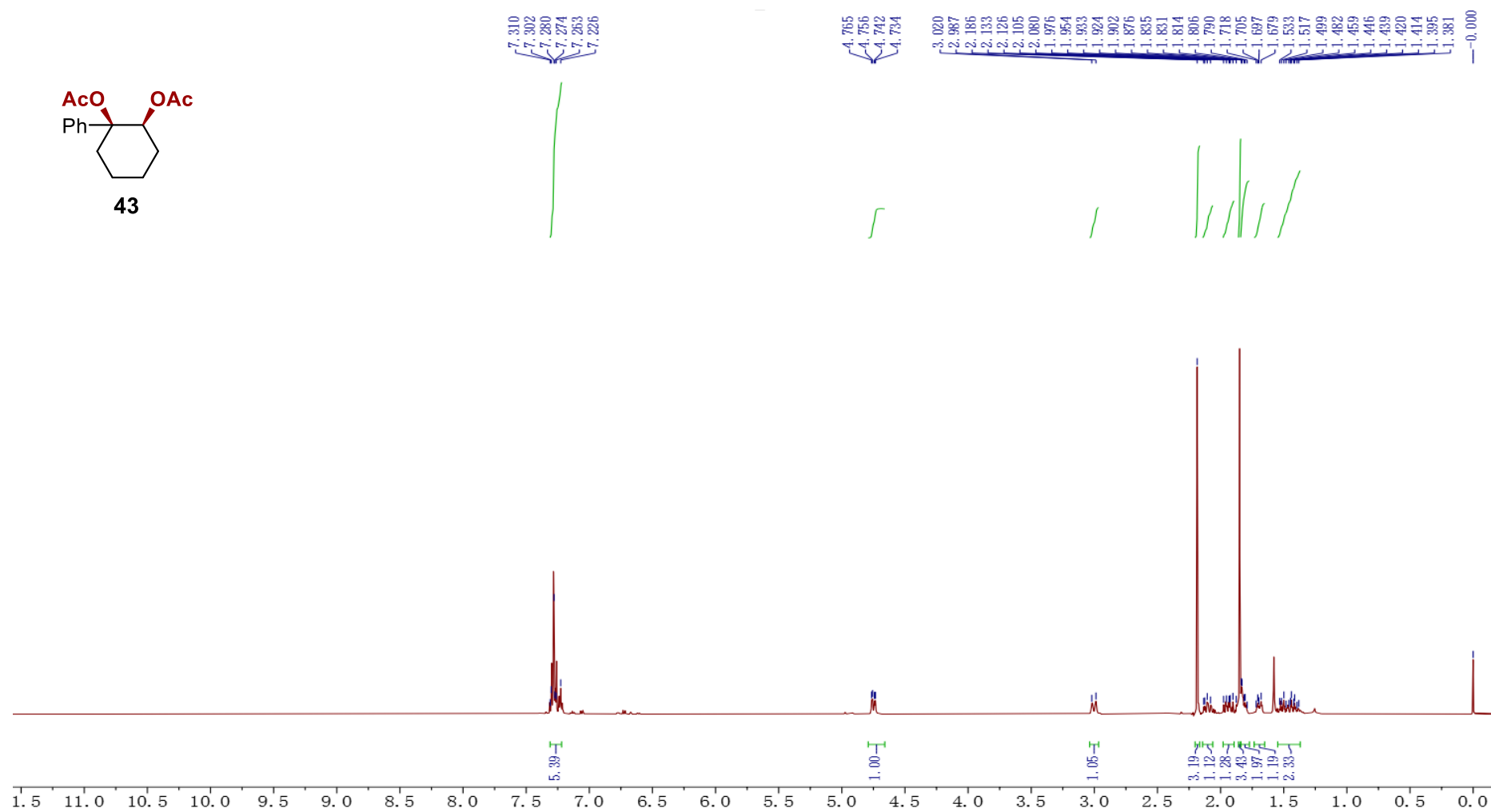
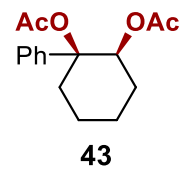


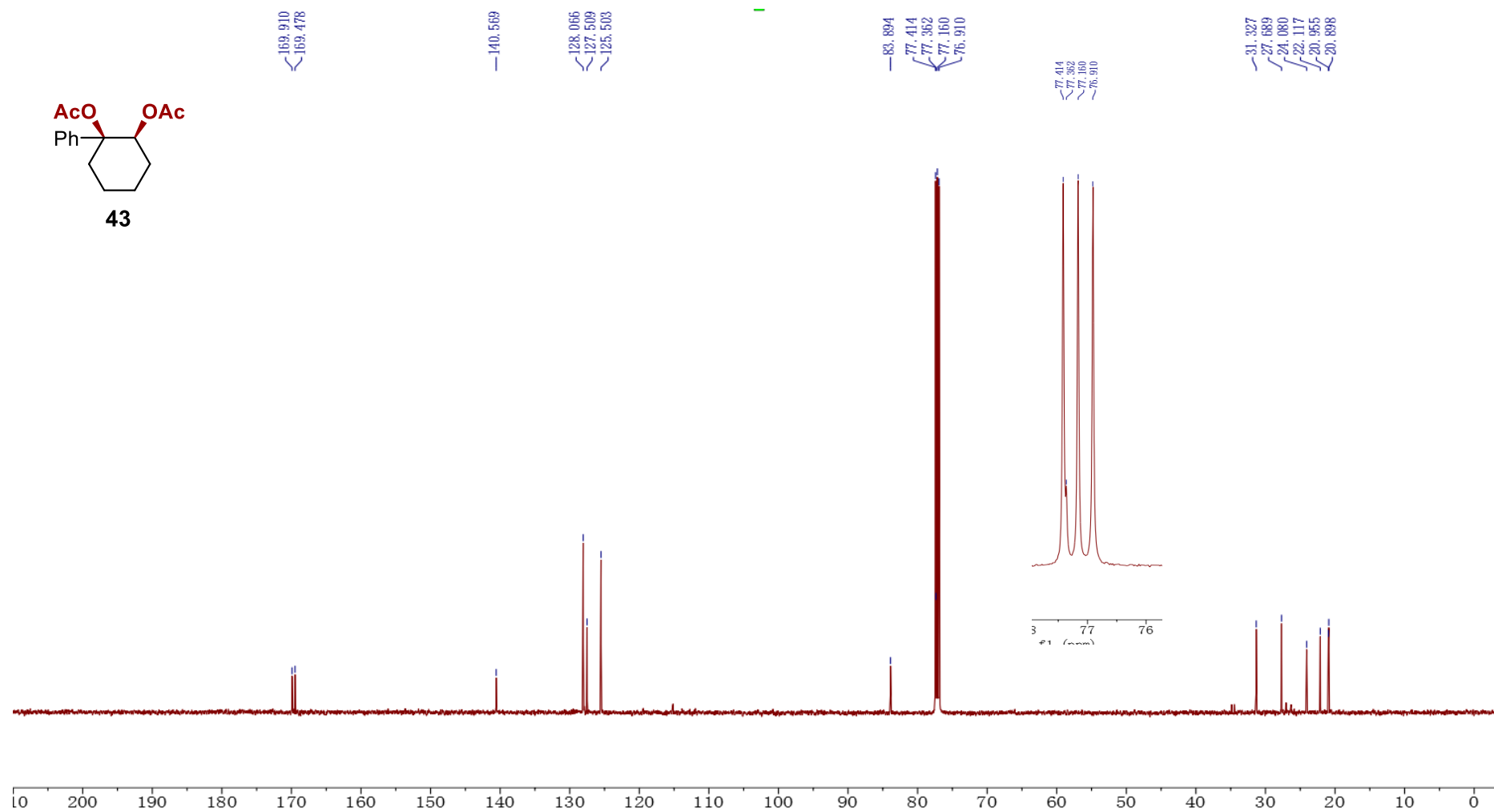


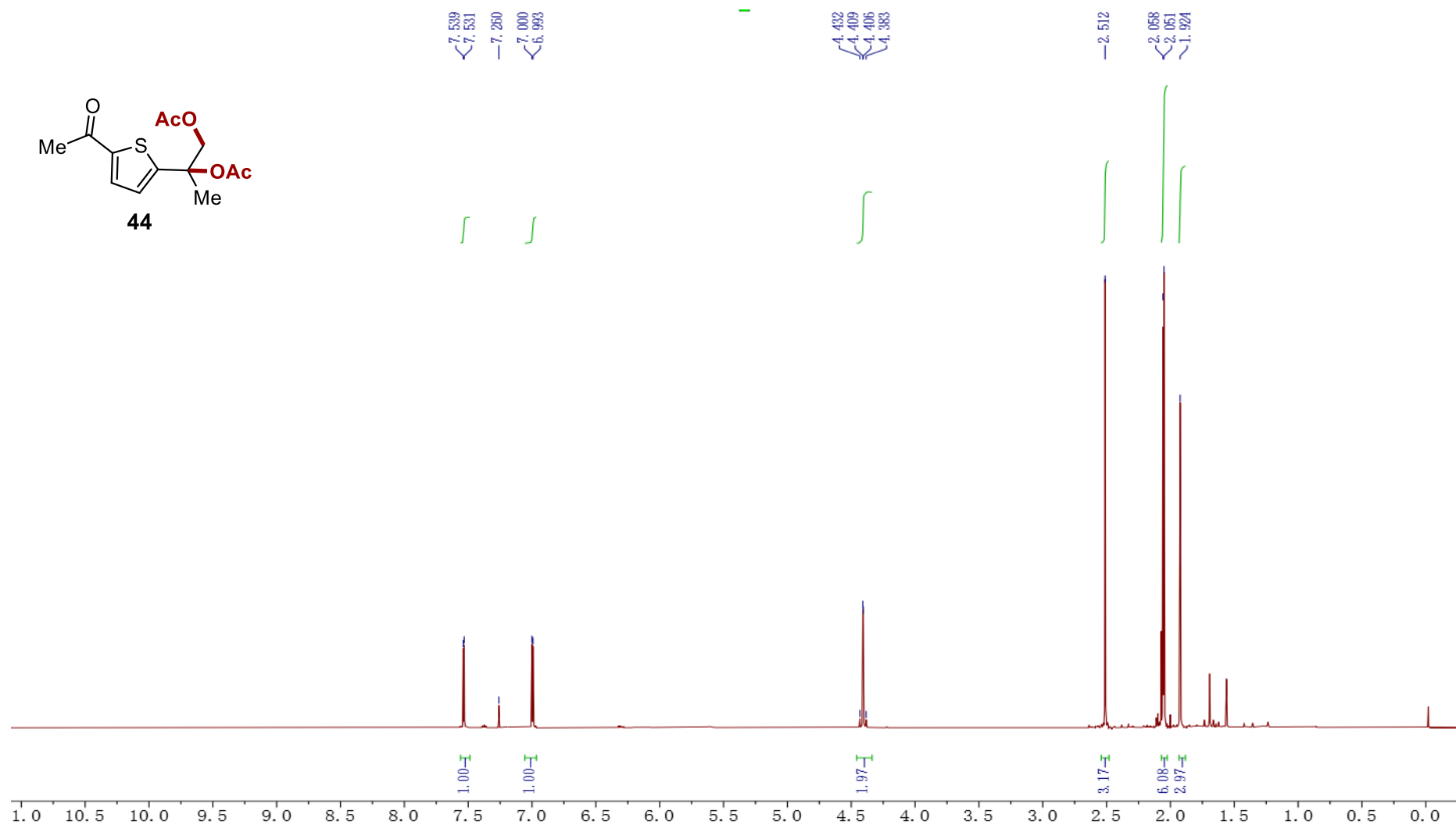


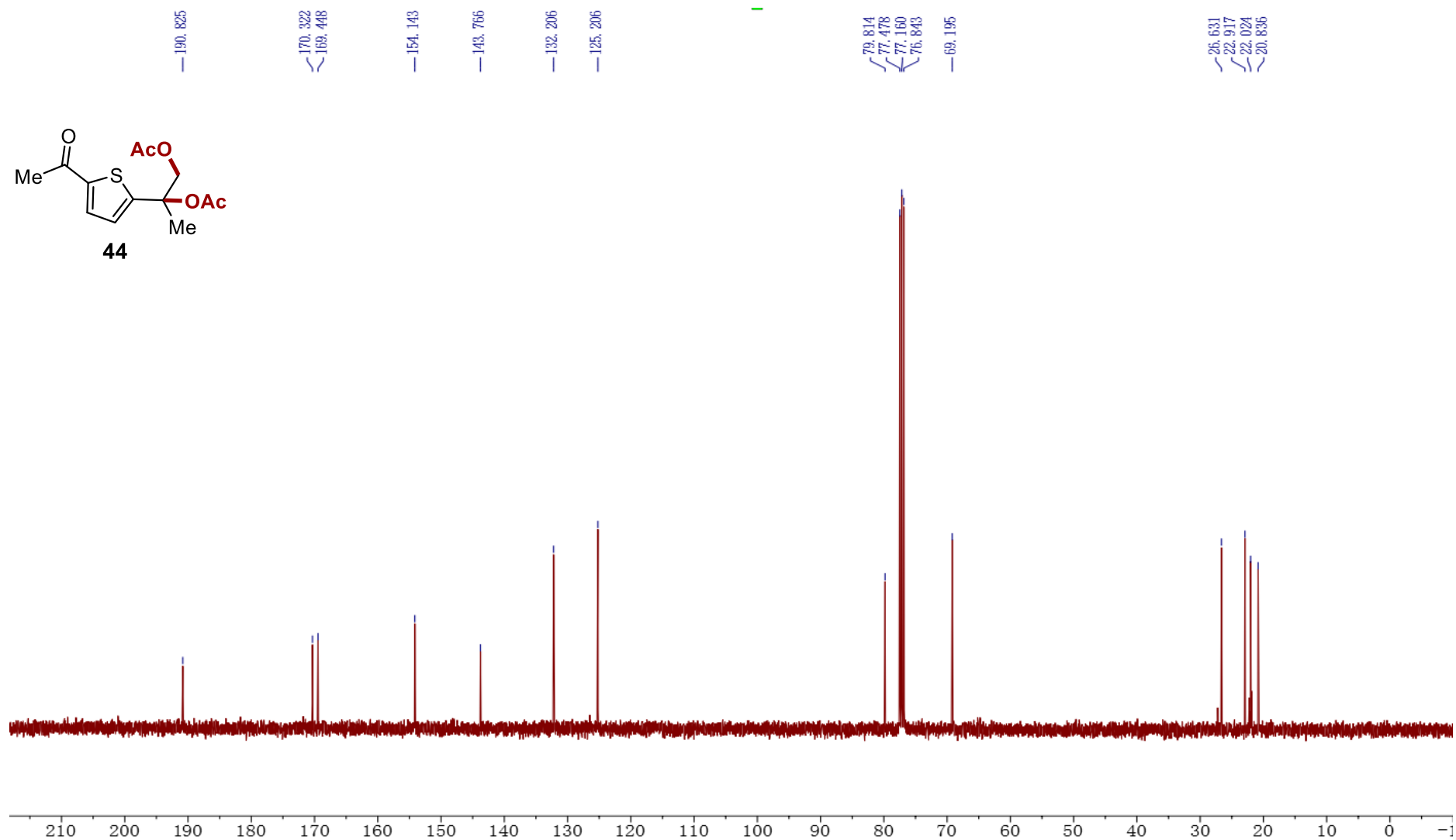
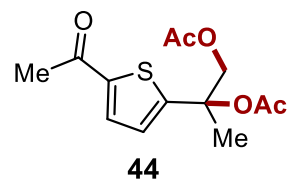


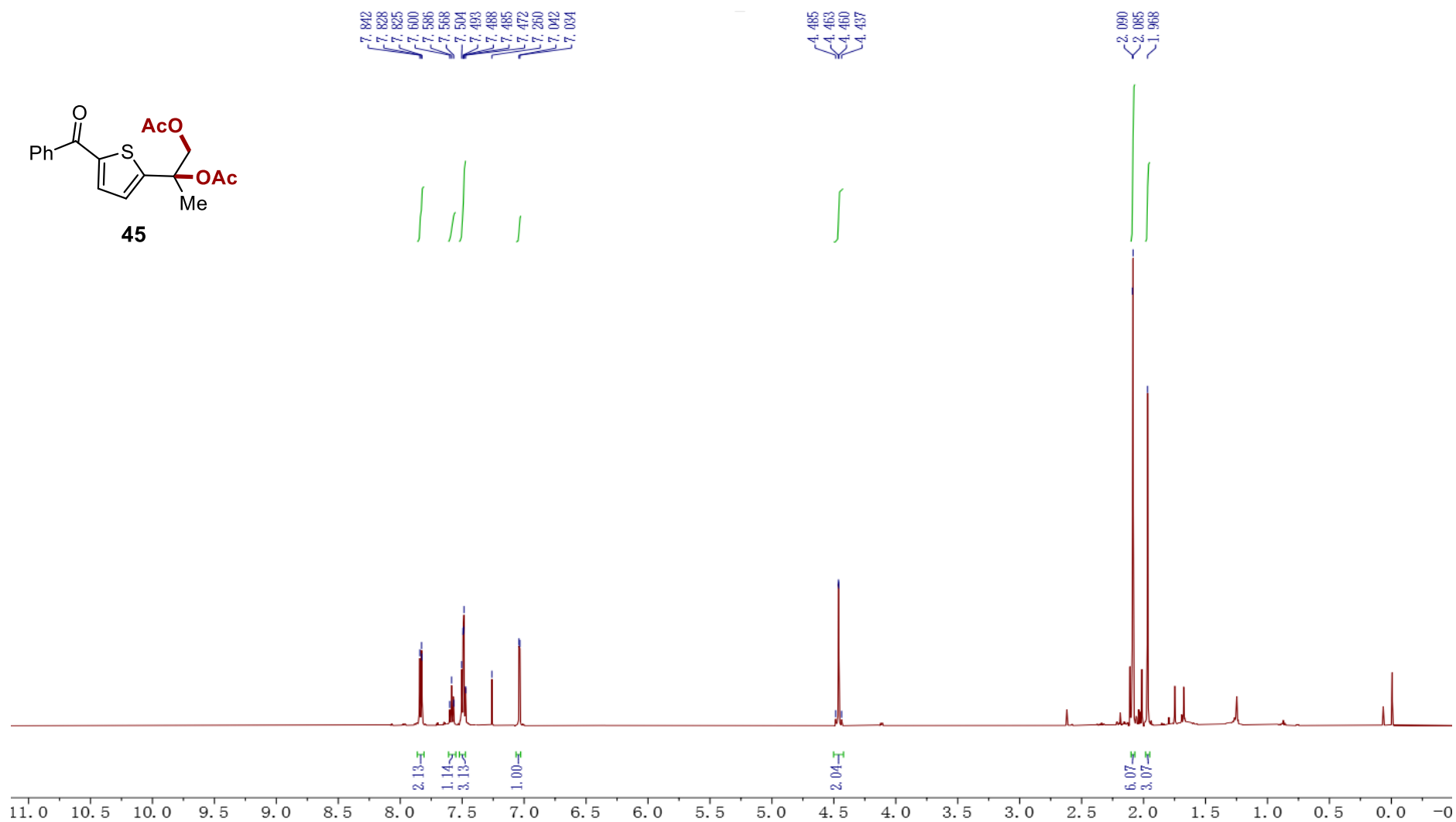


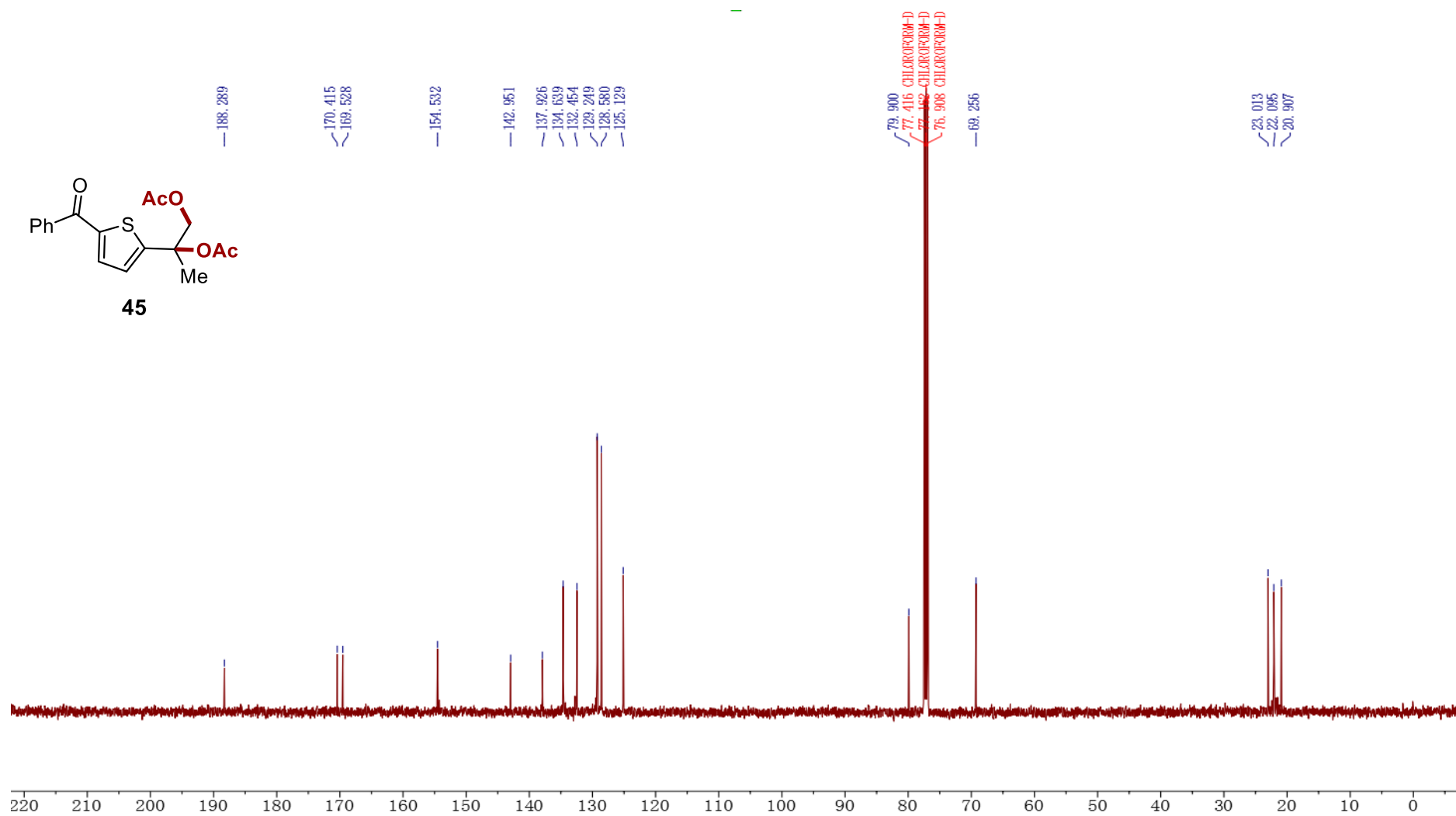


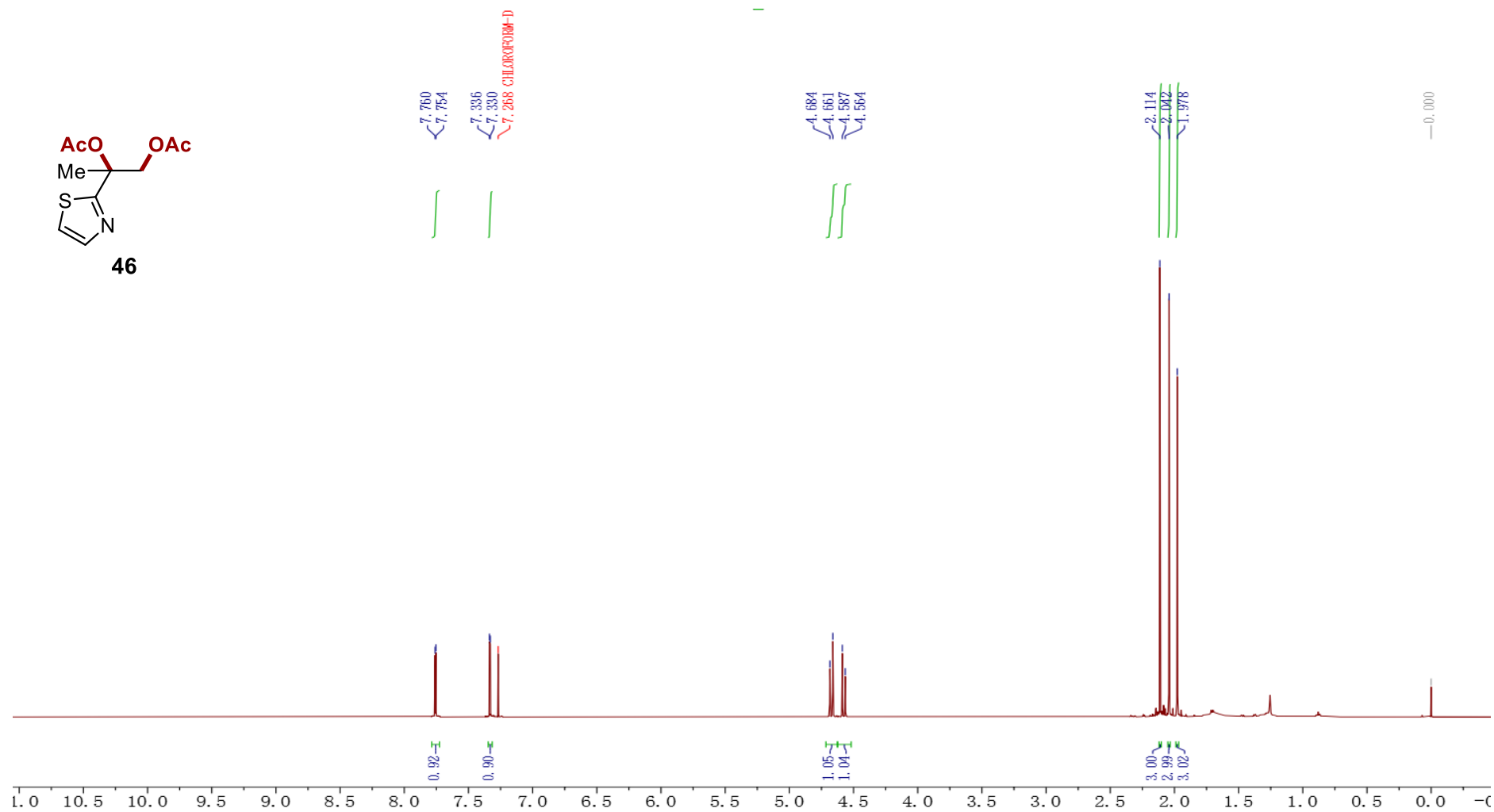
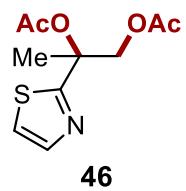


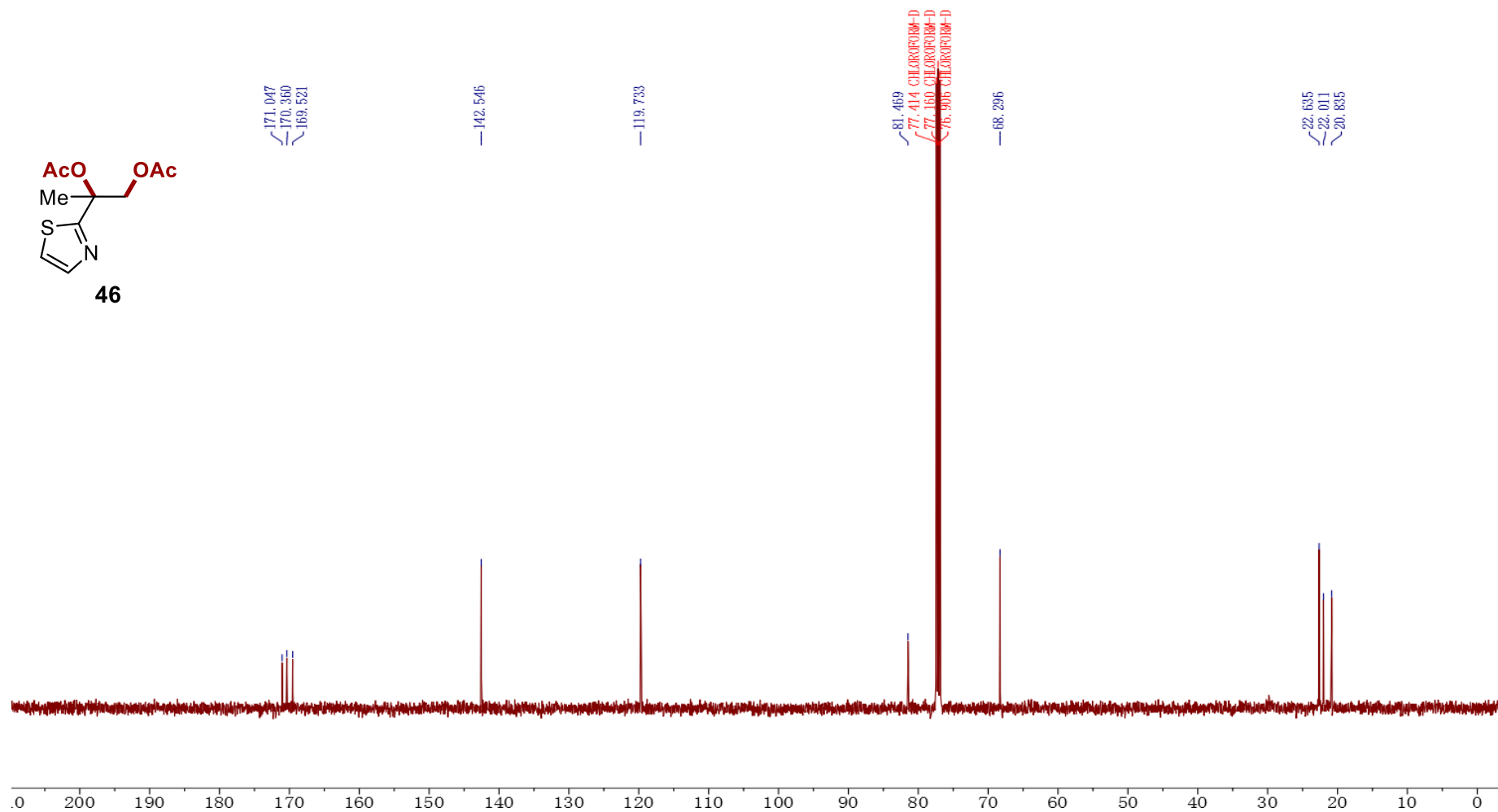


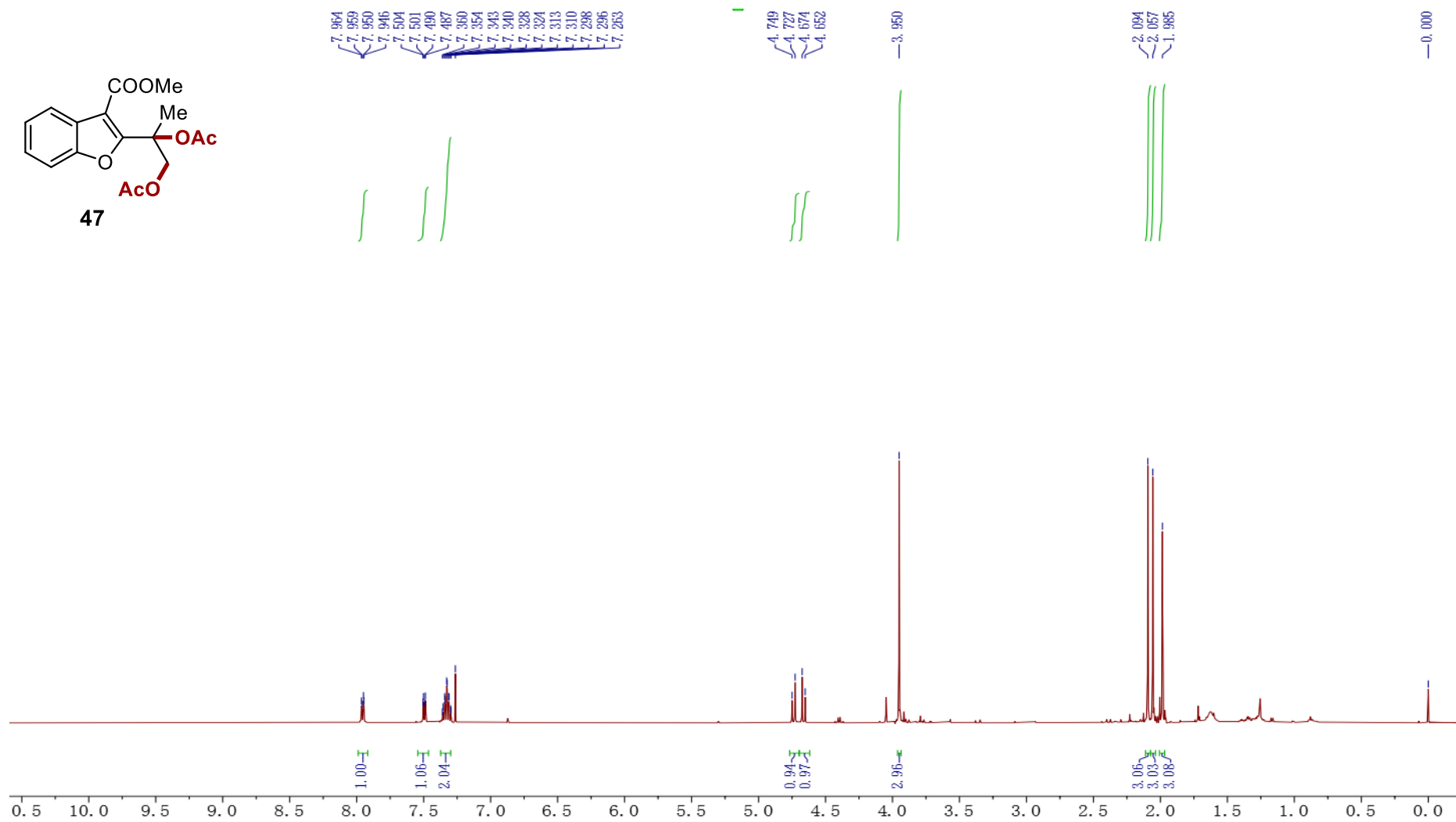


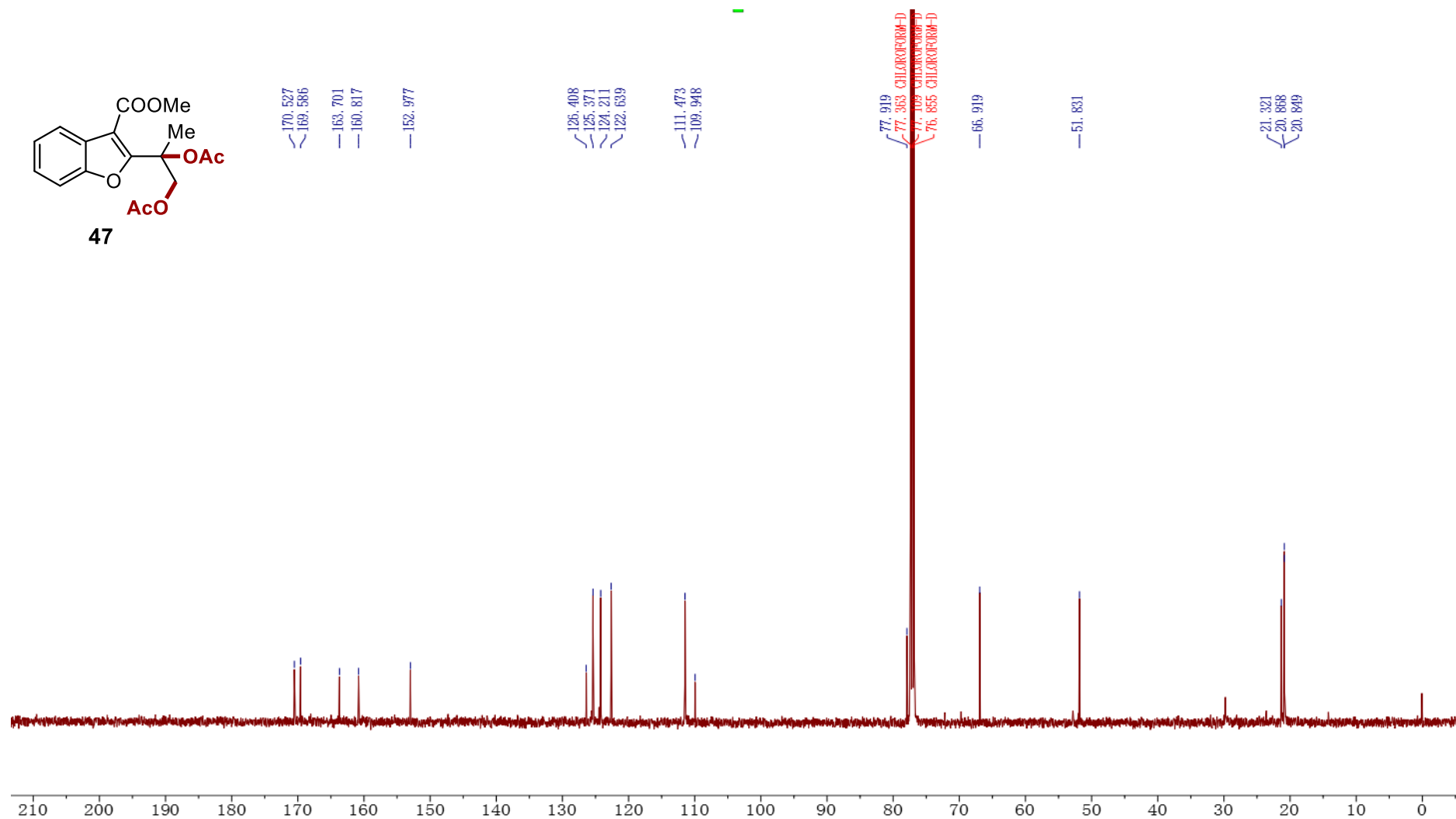
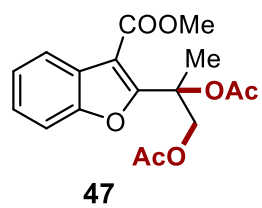


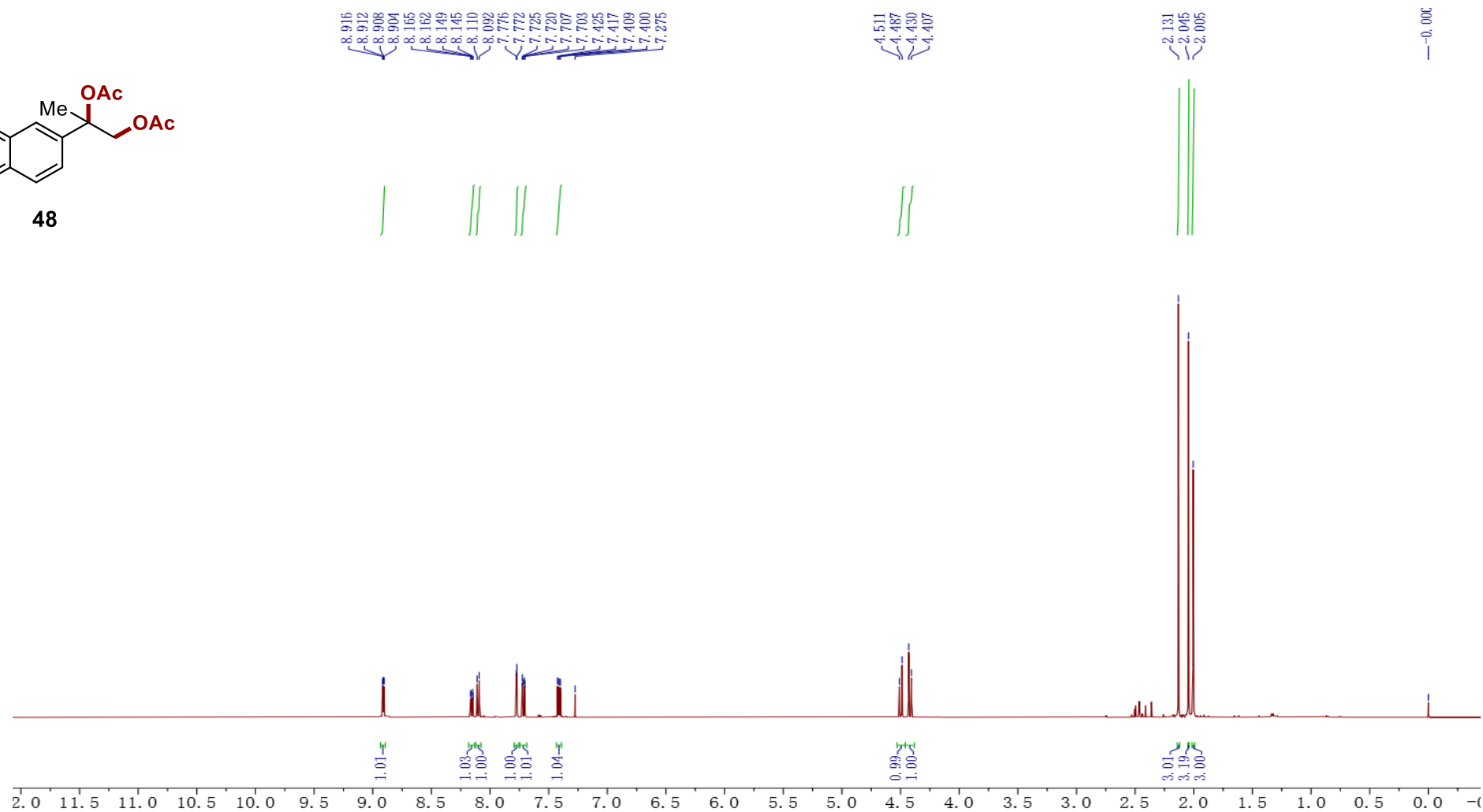
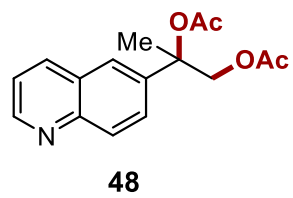


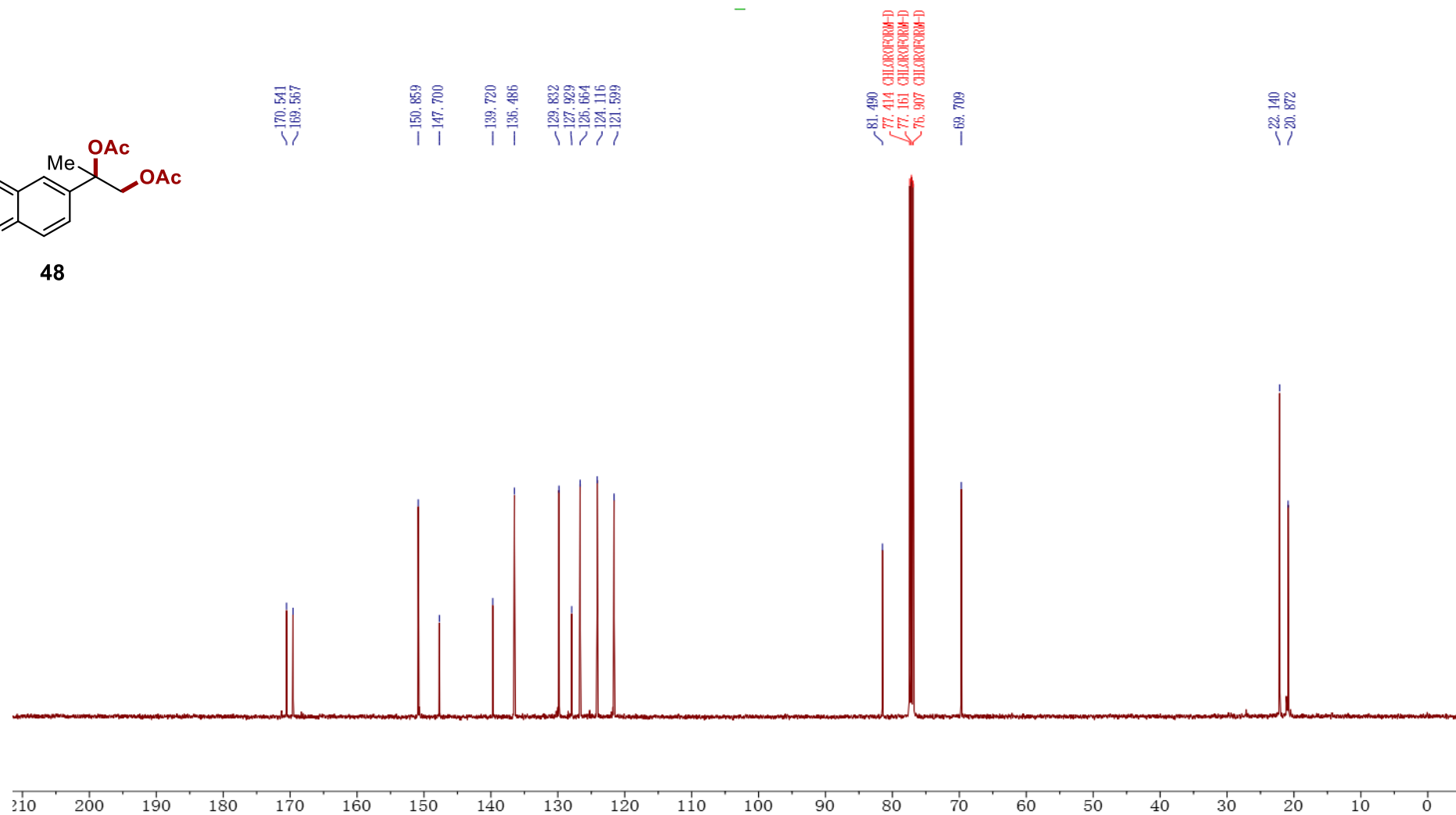
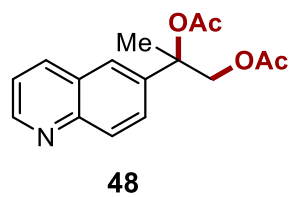


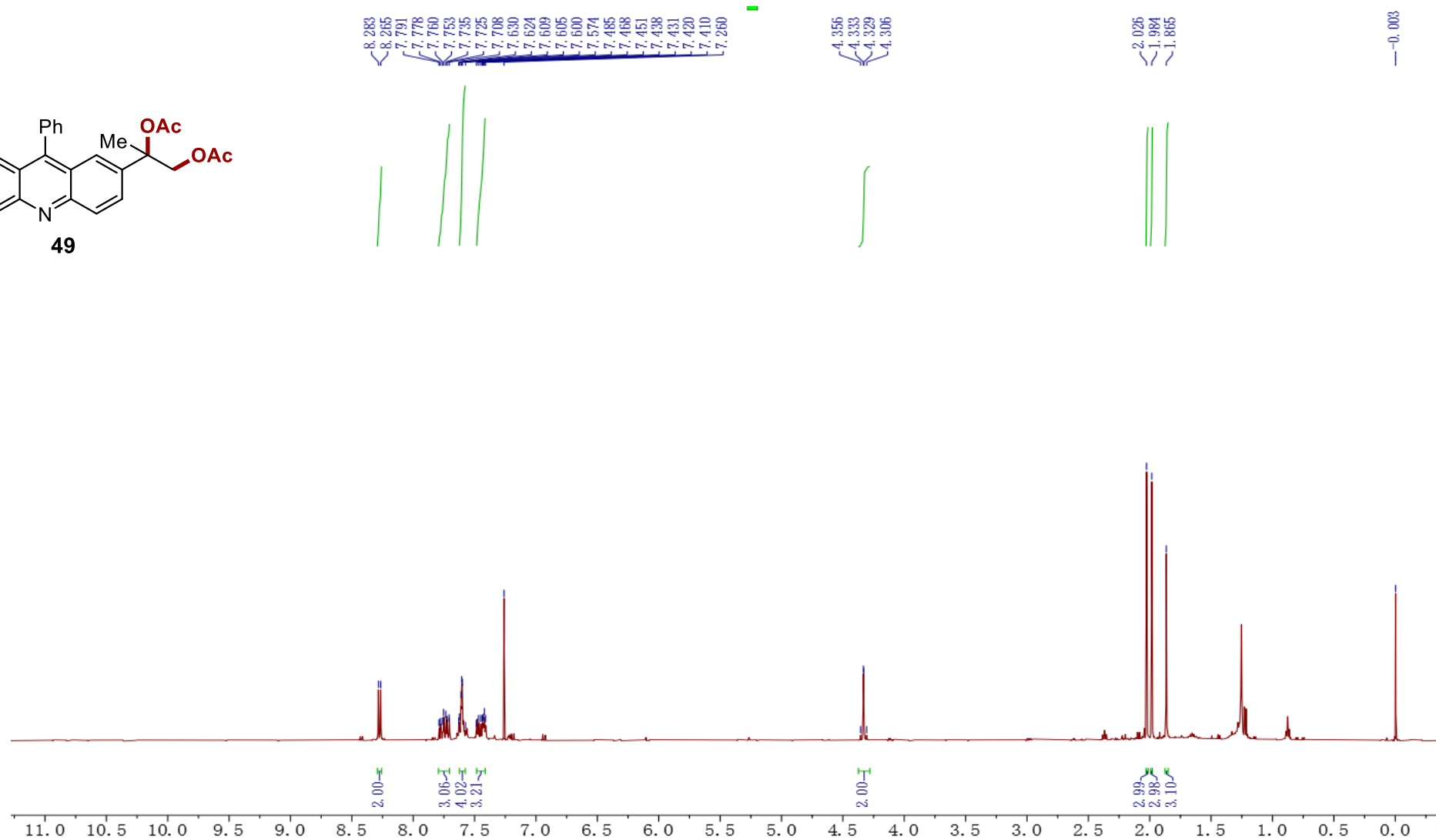
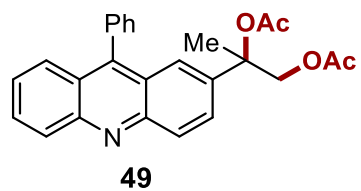


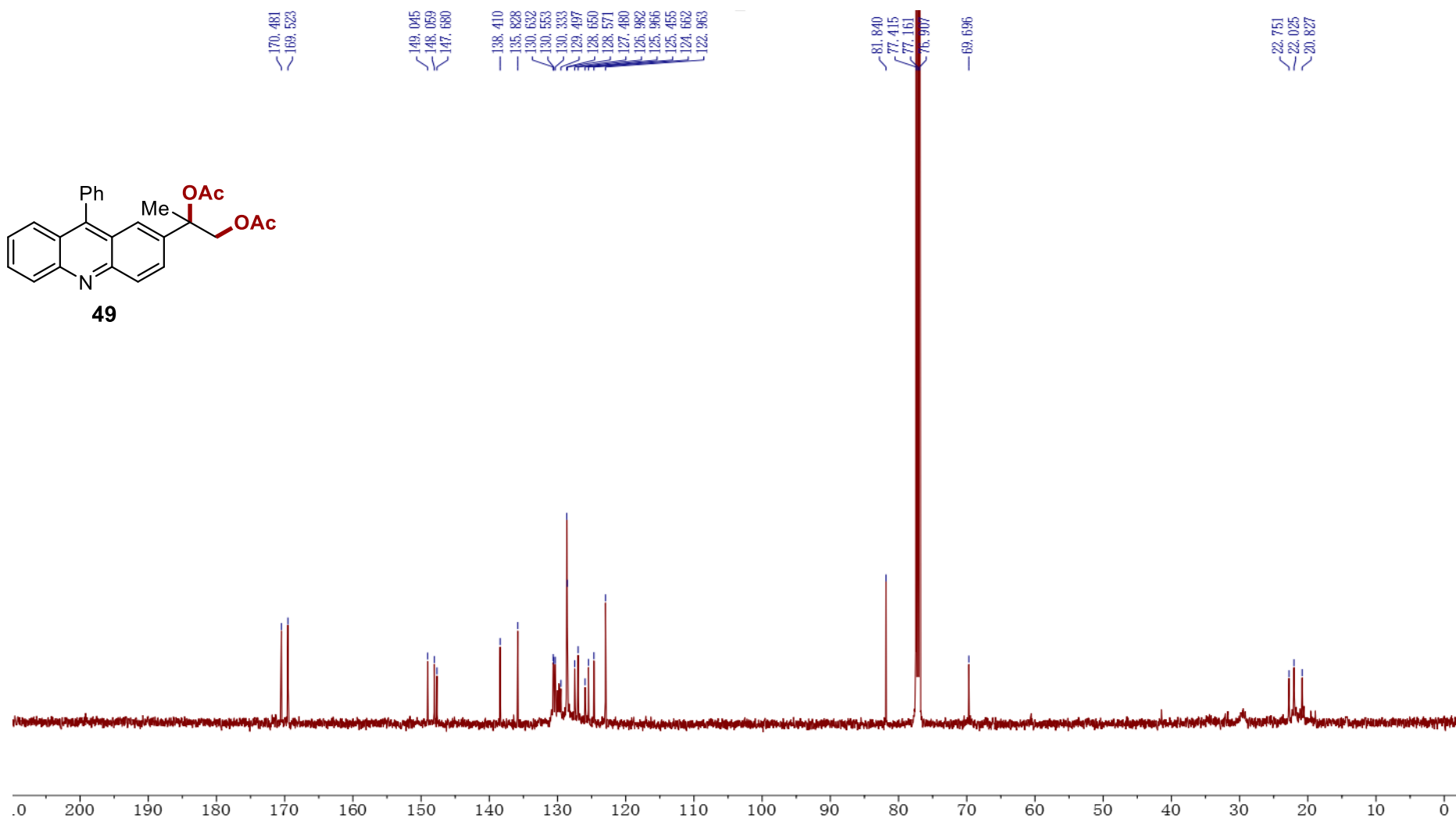
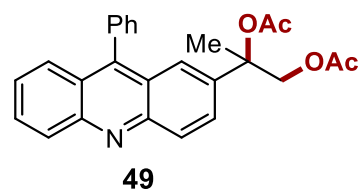


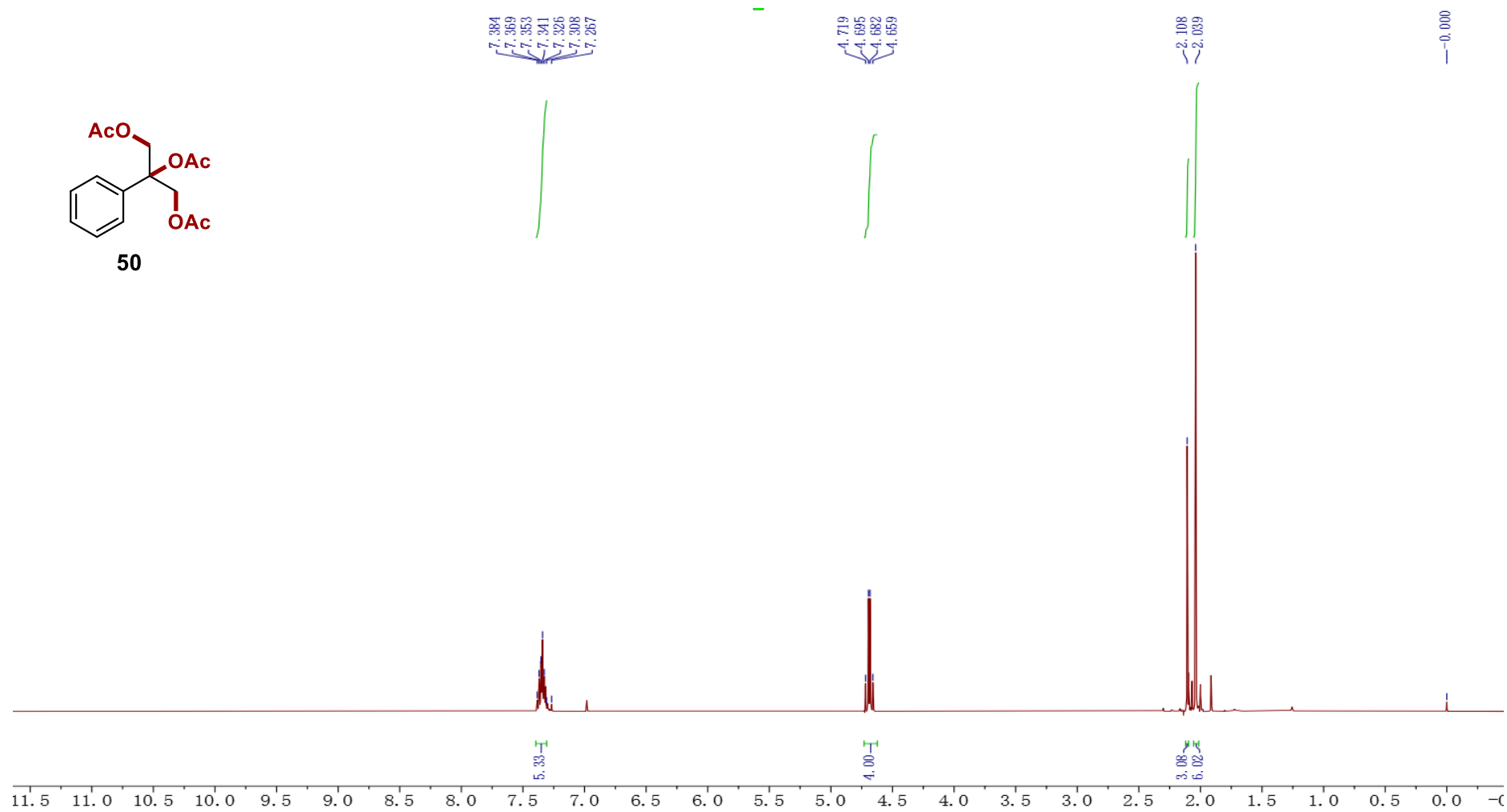


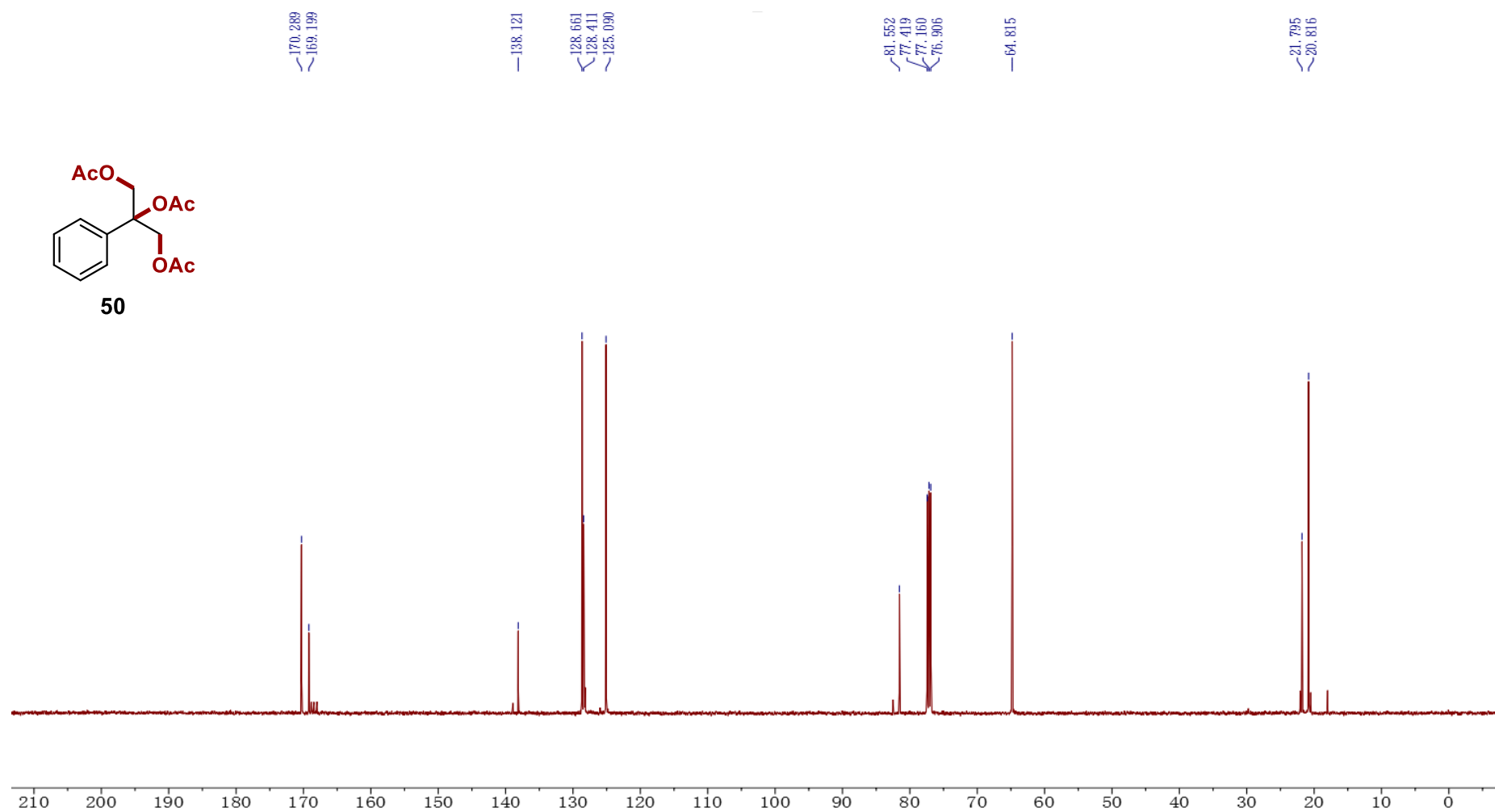


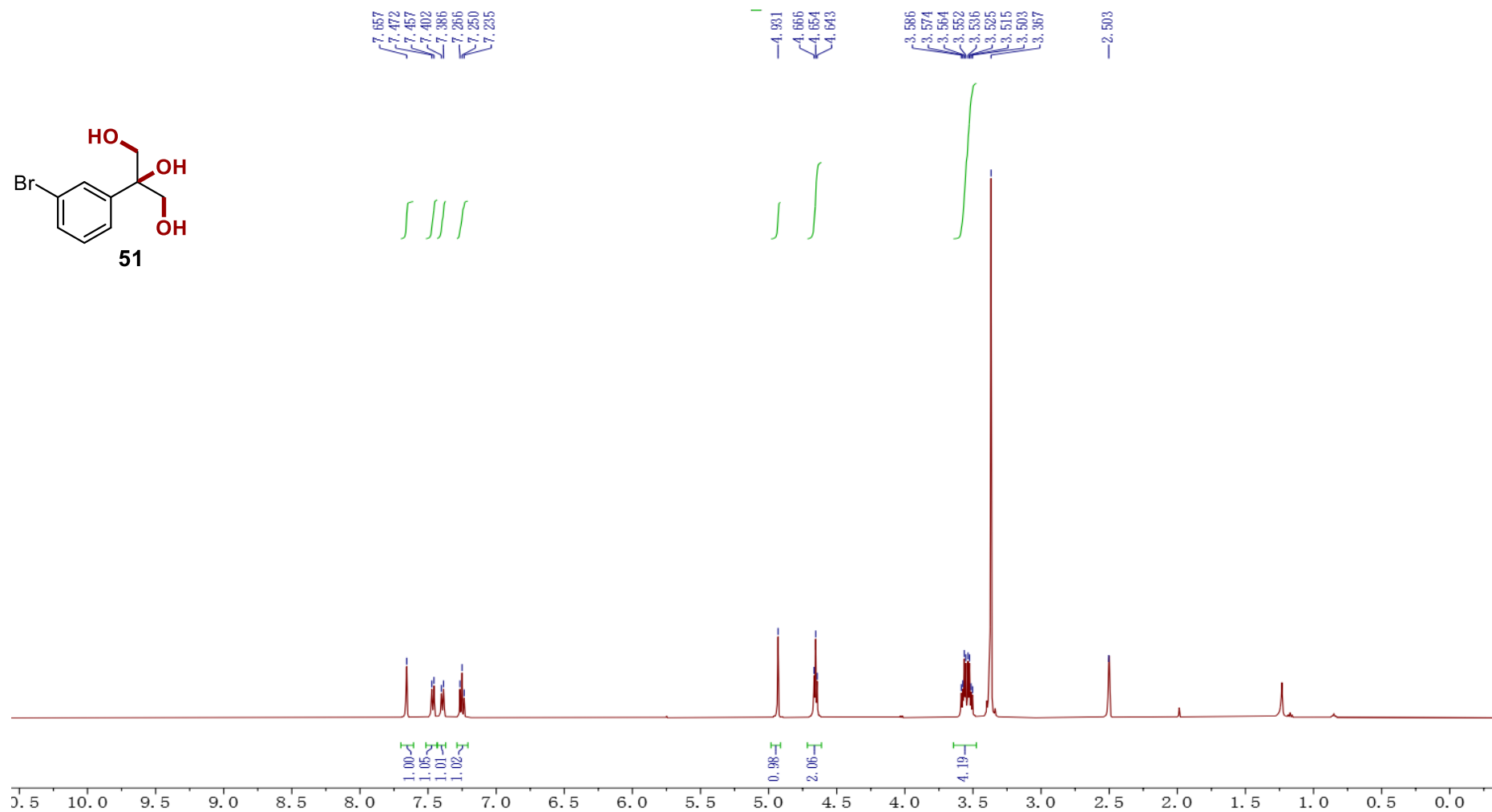


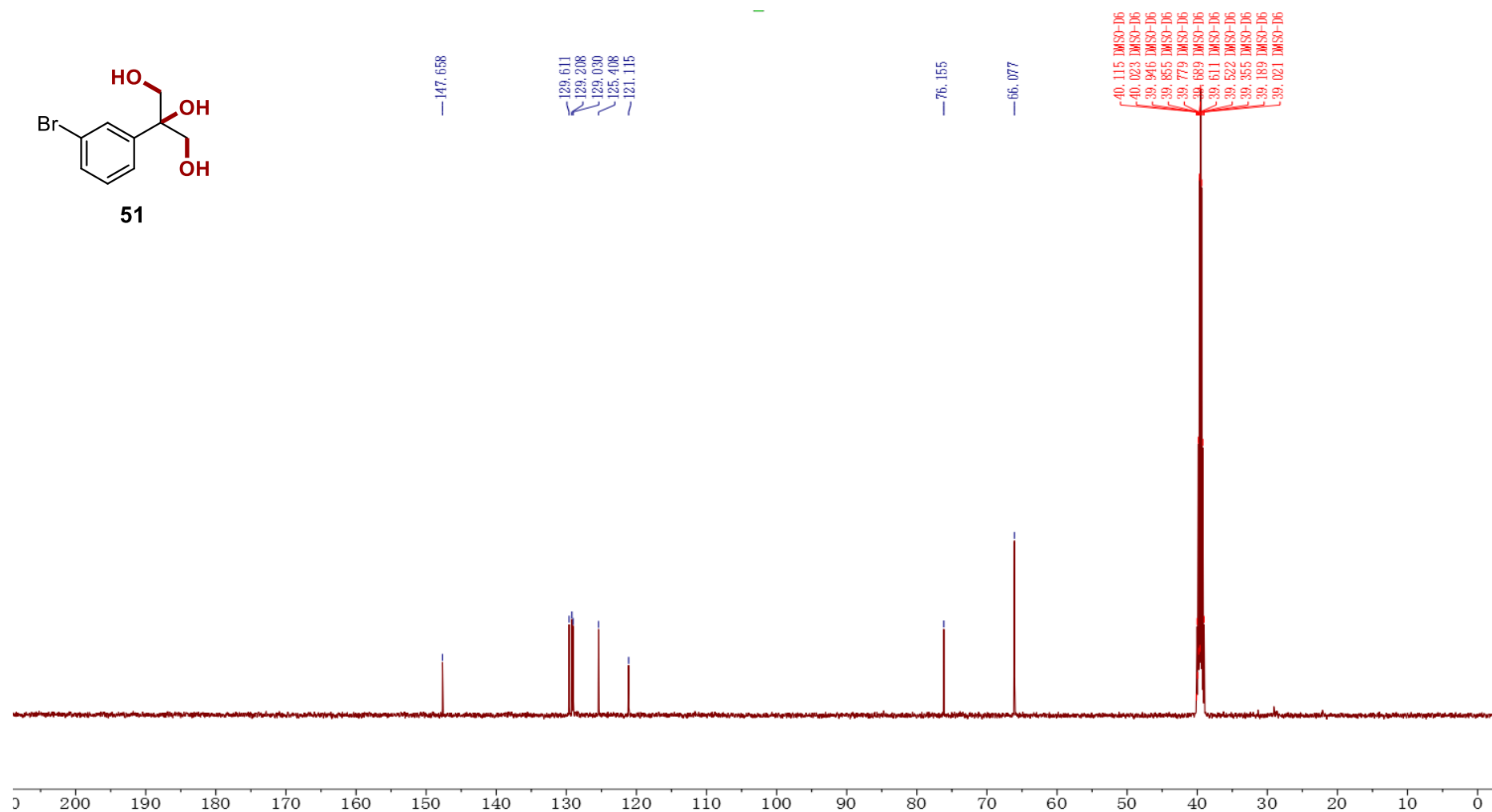


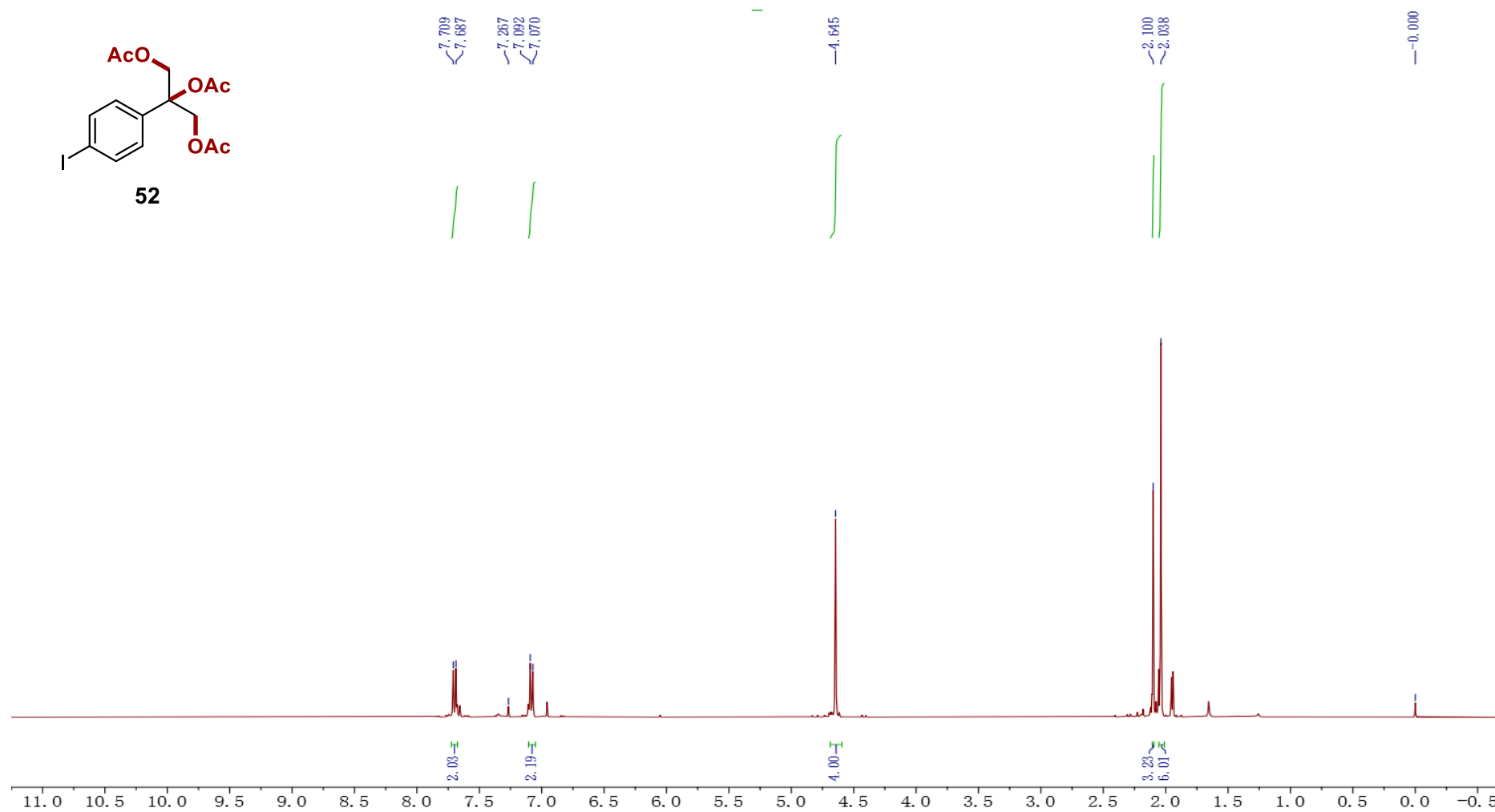


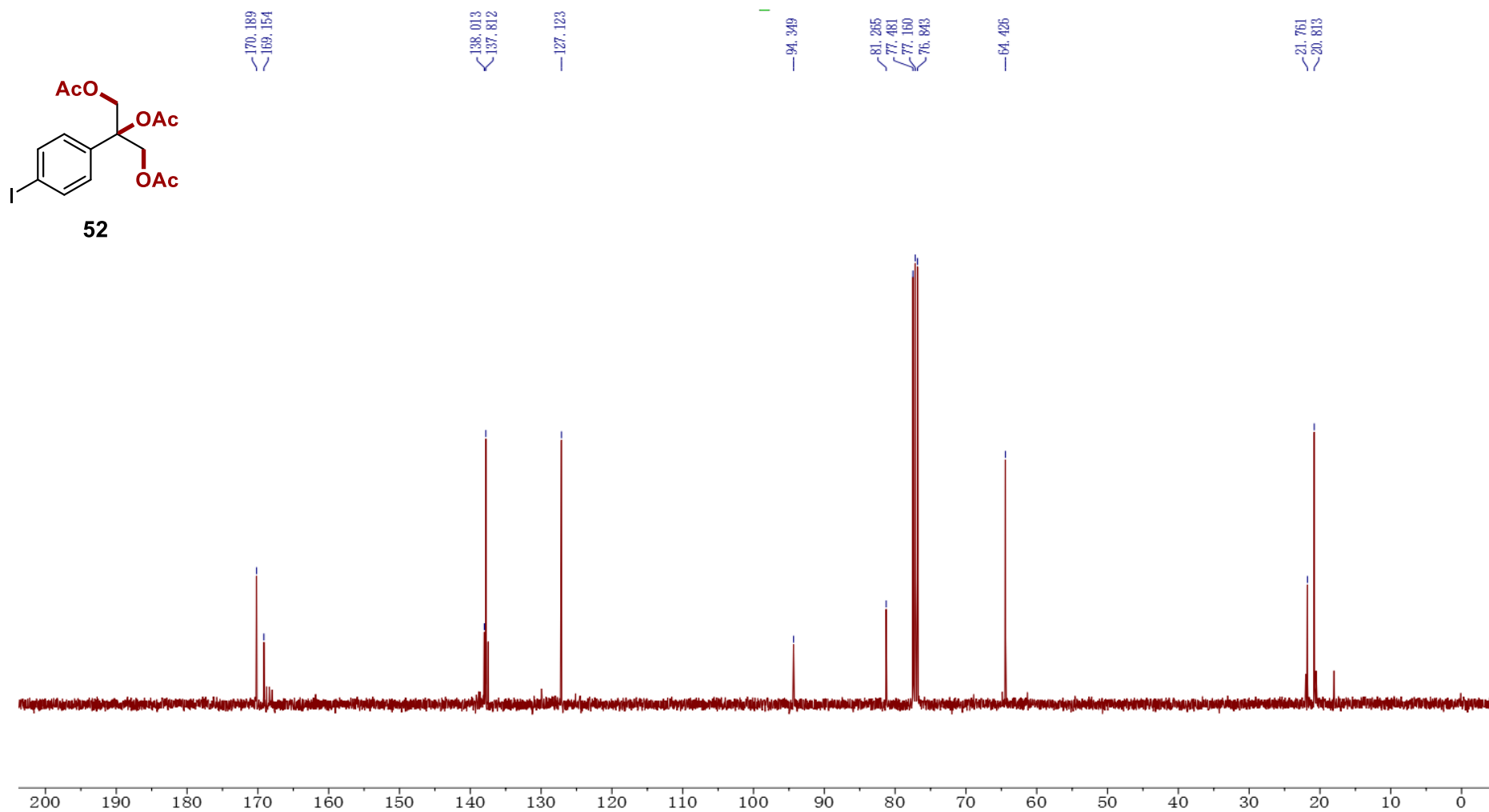


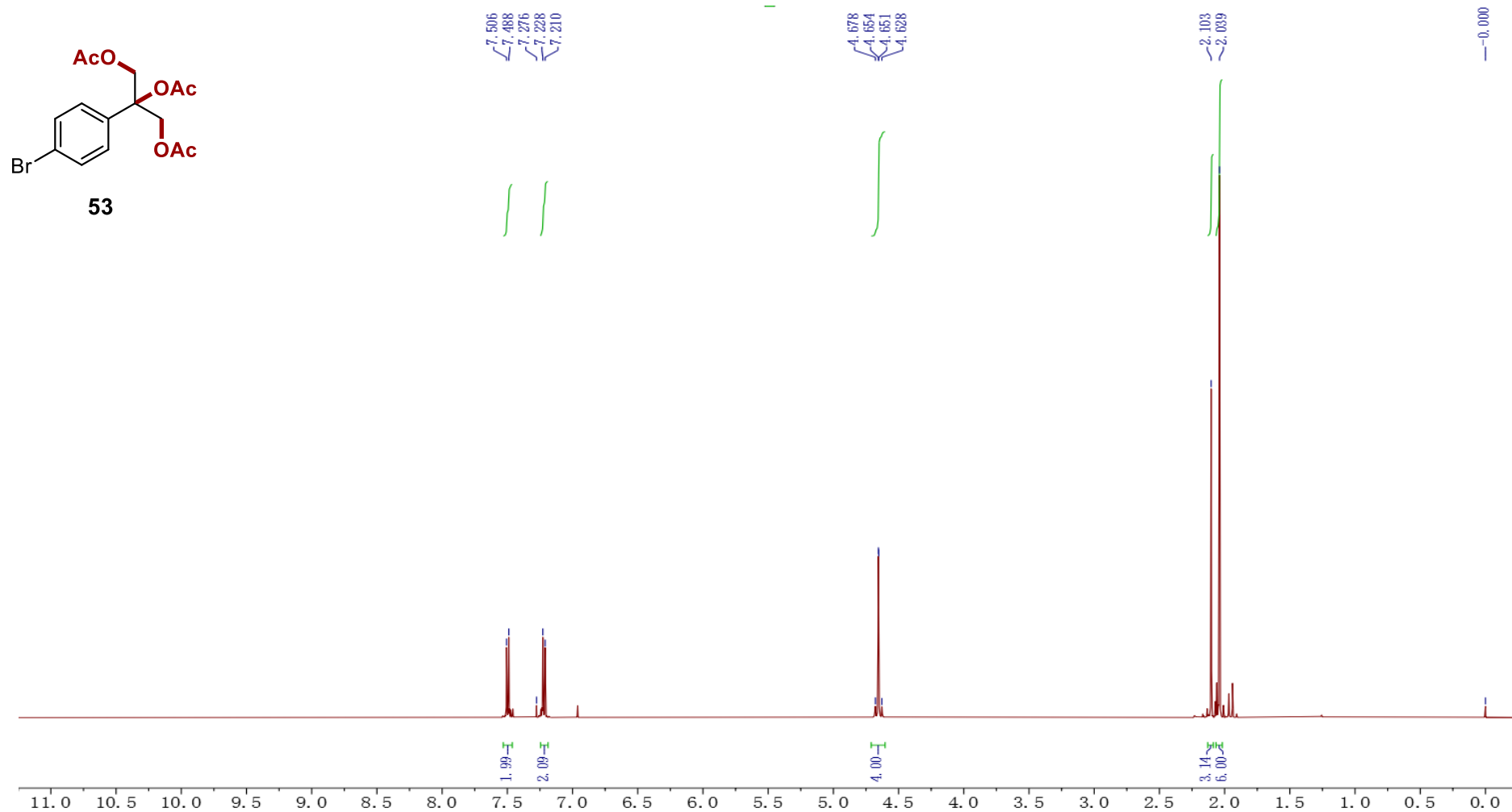


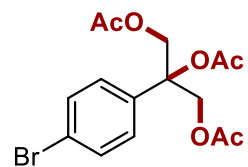




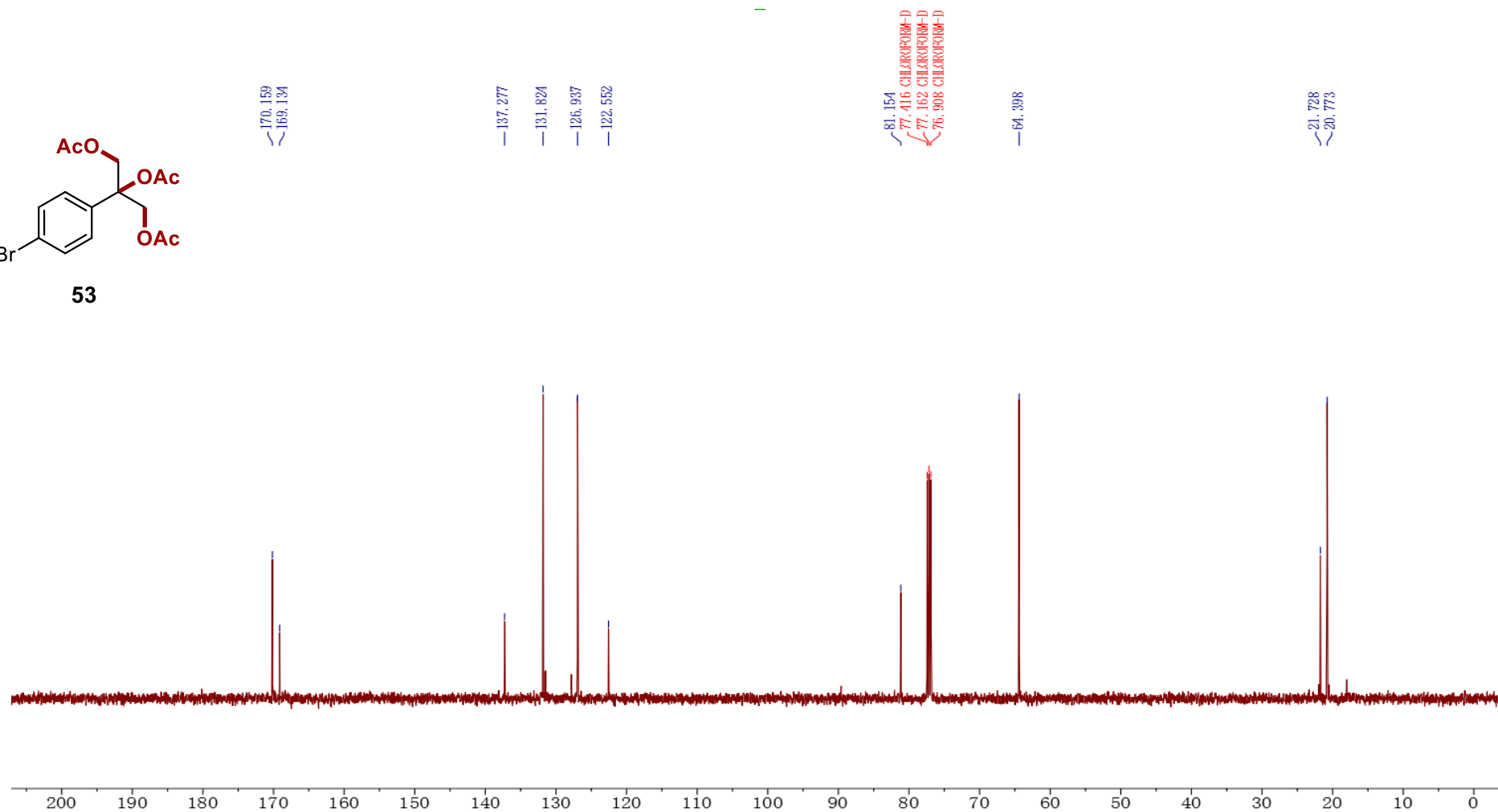


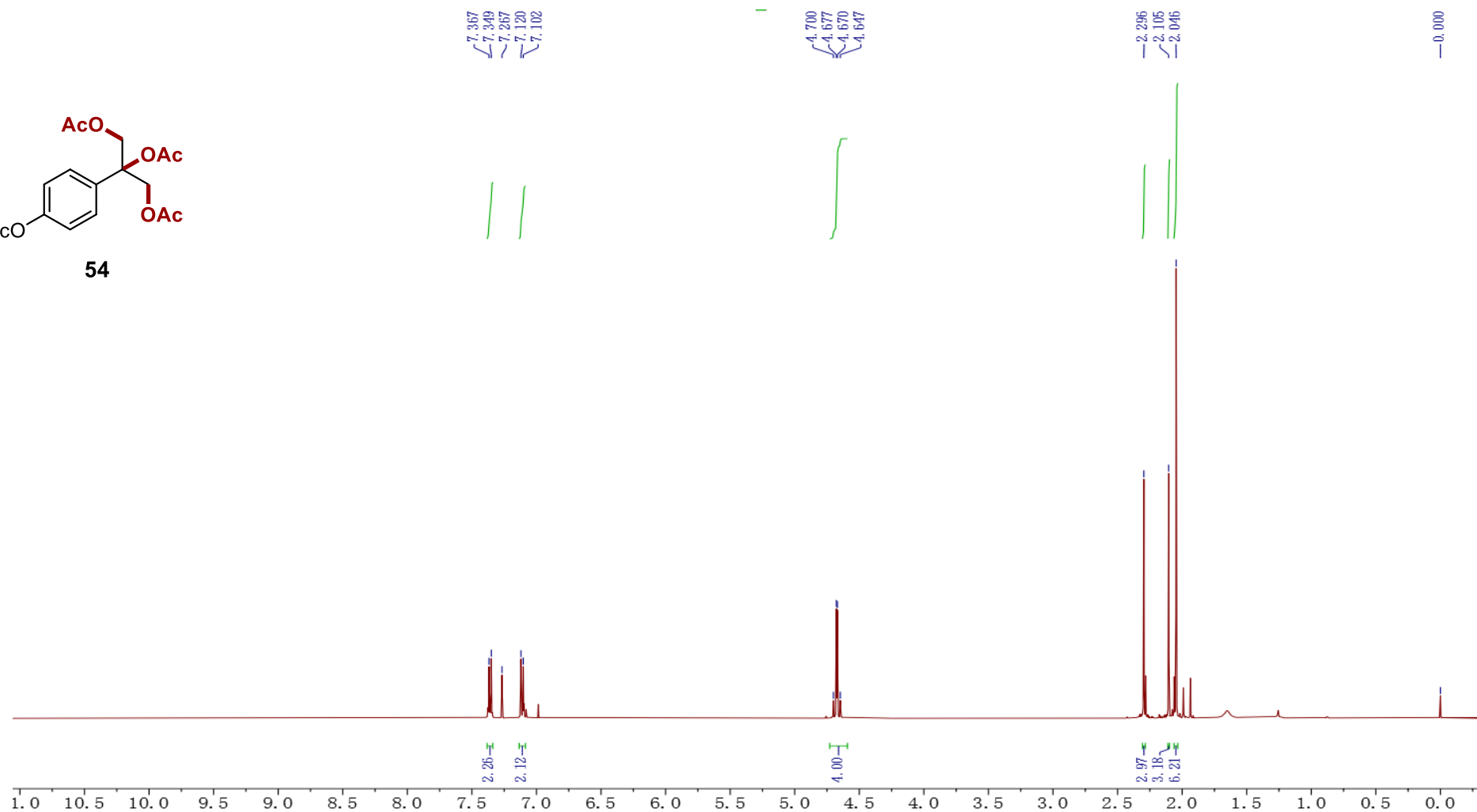
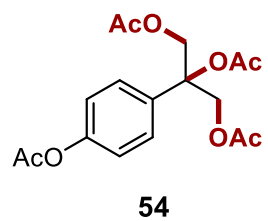


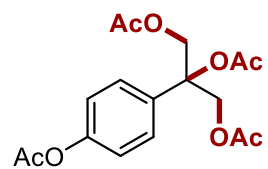




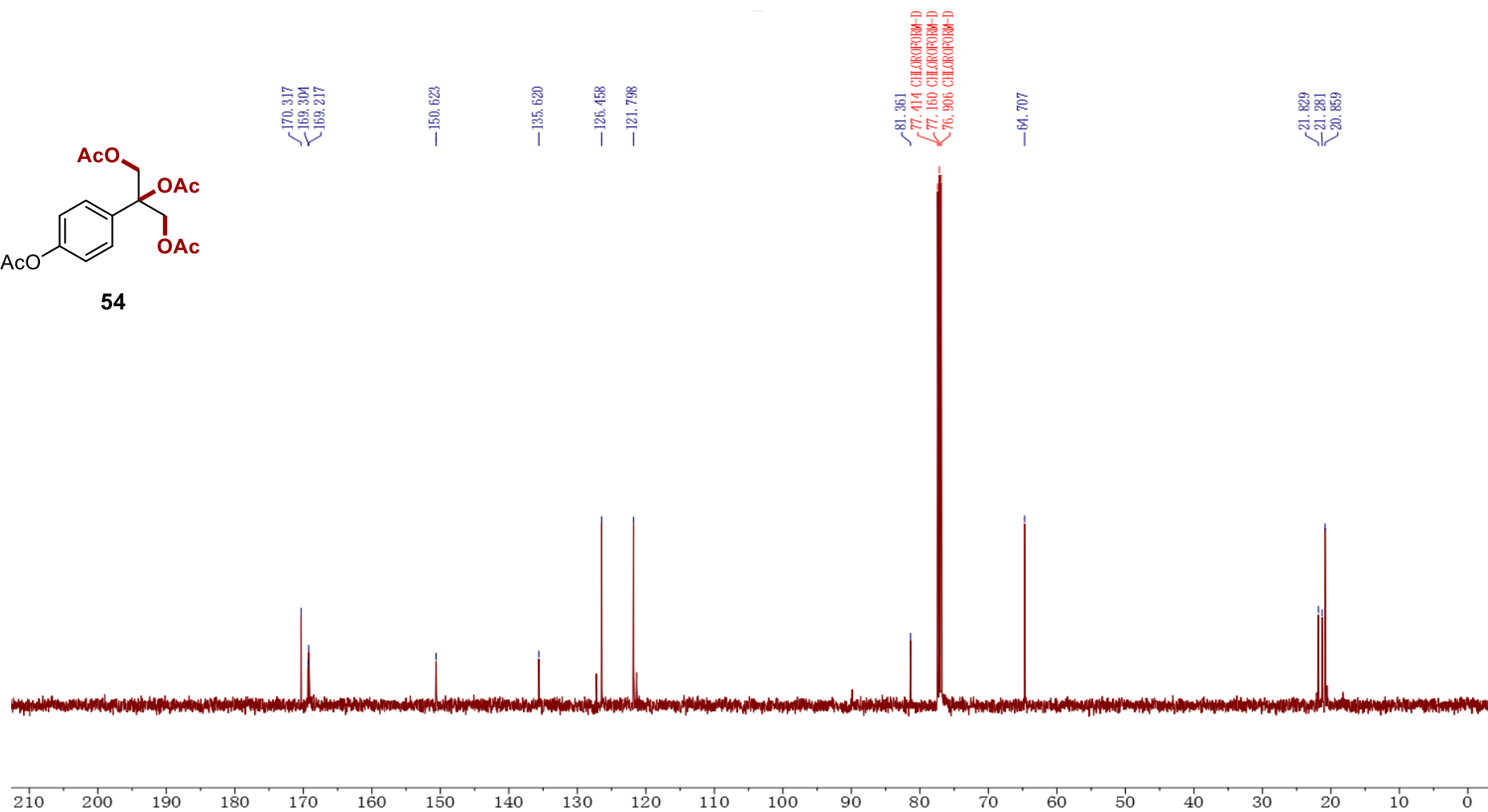
53

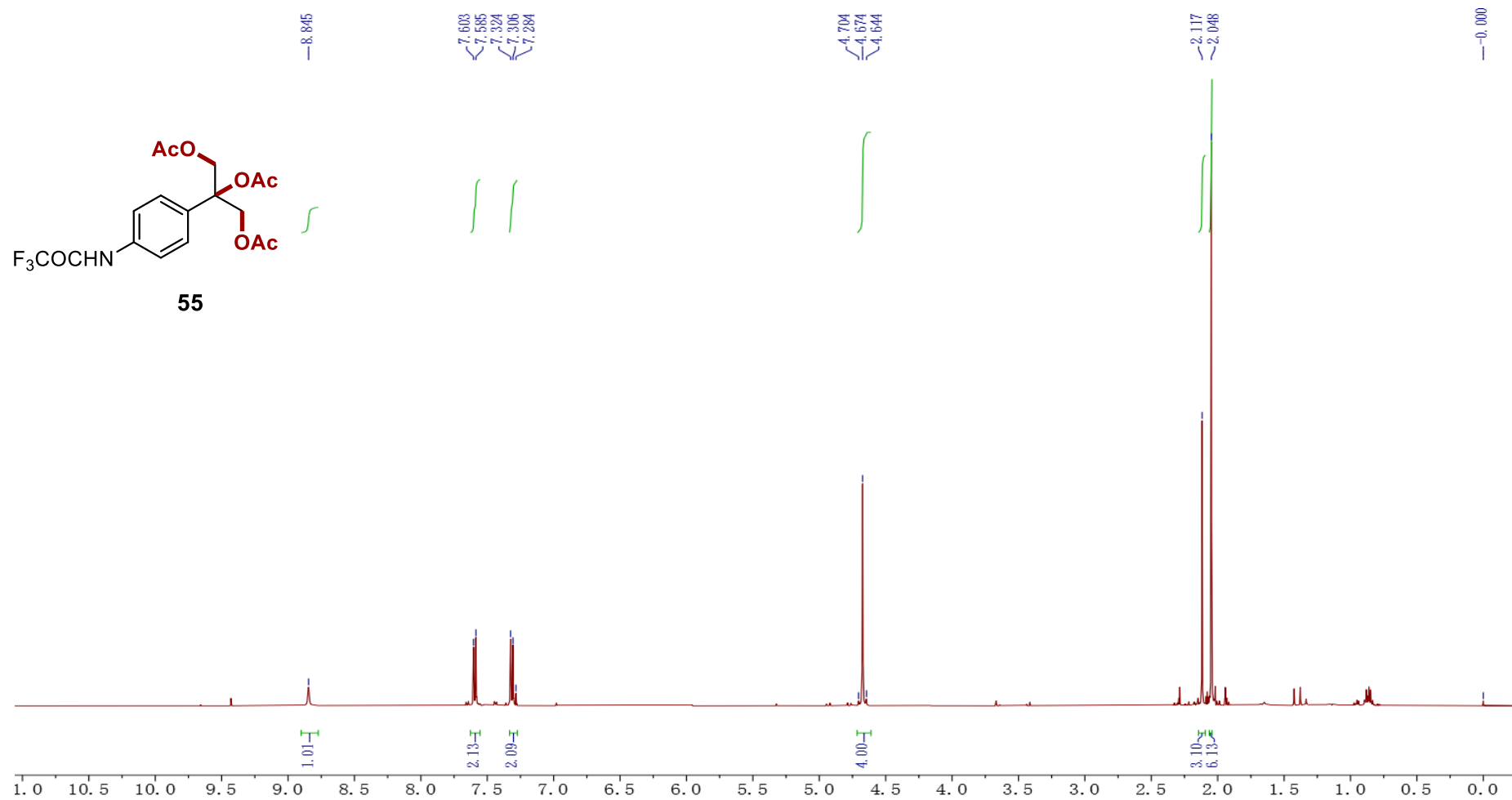


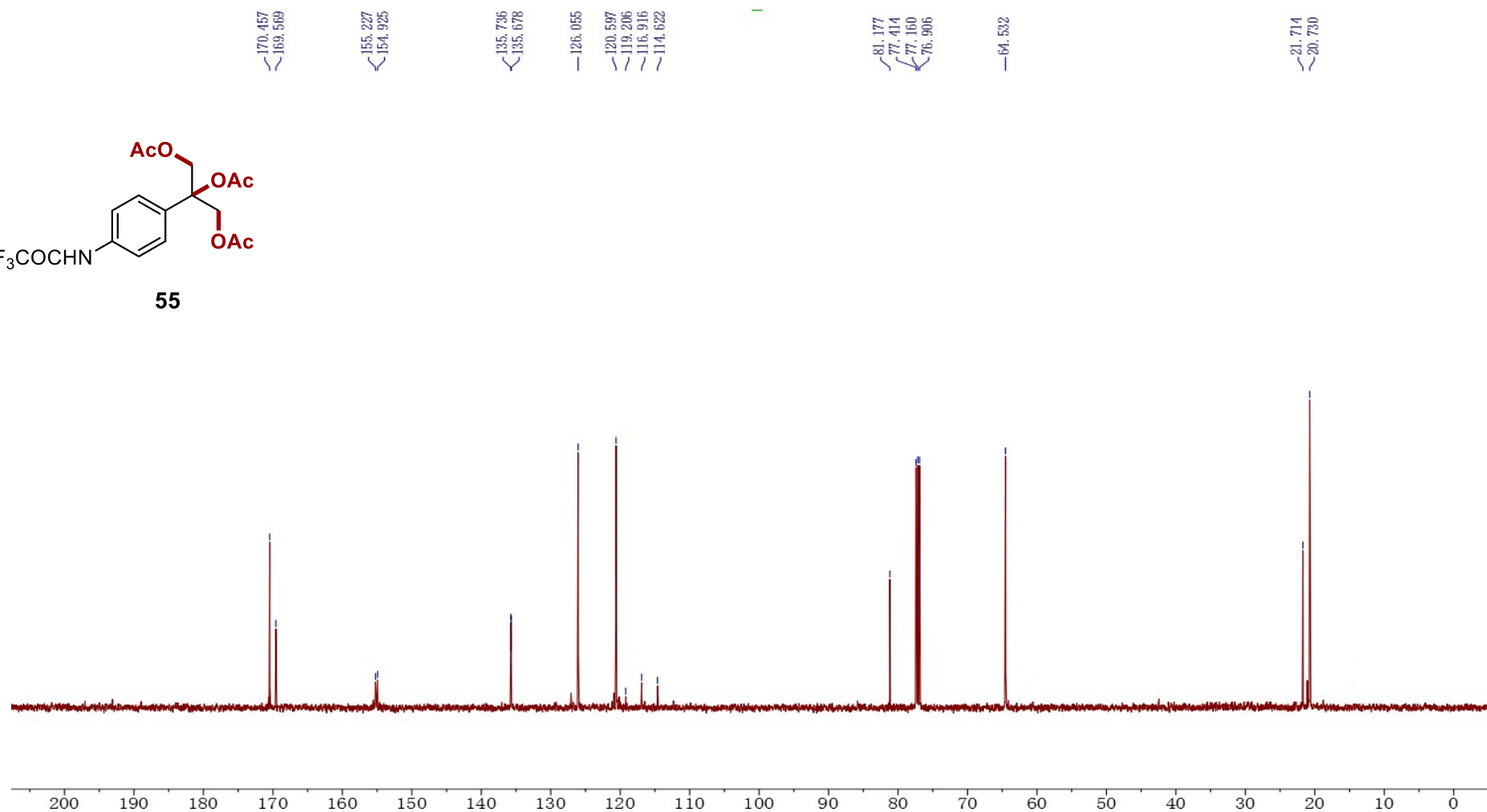
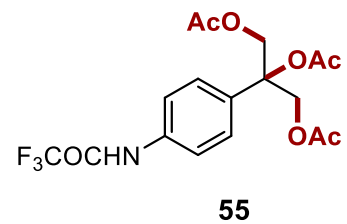


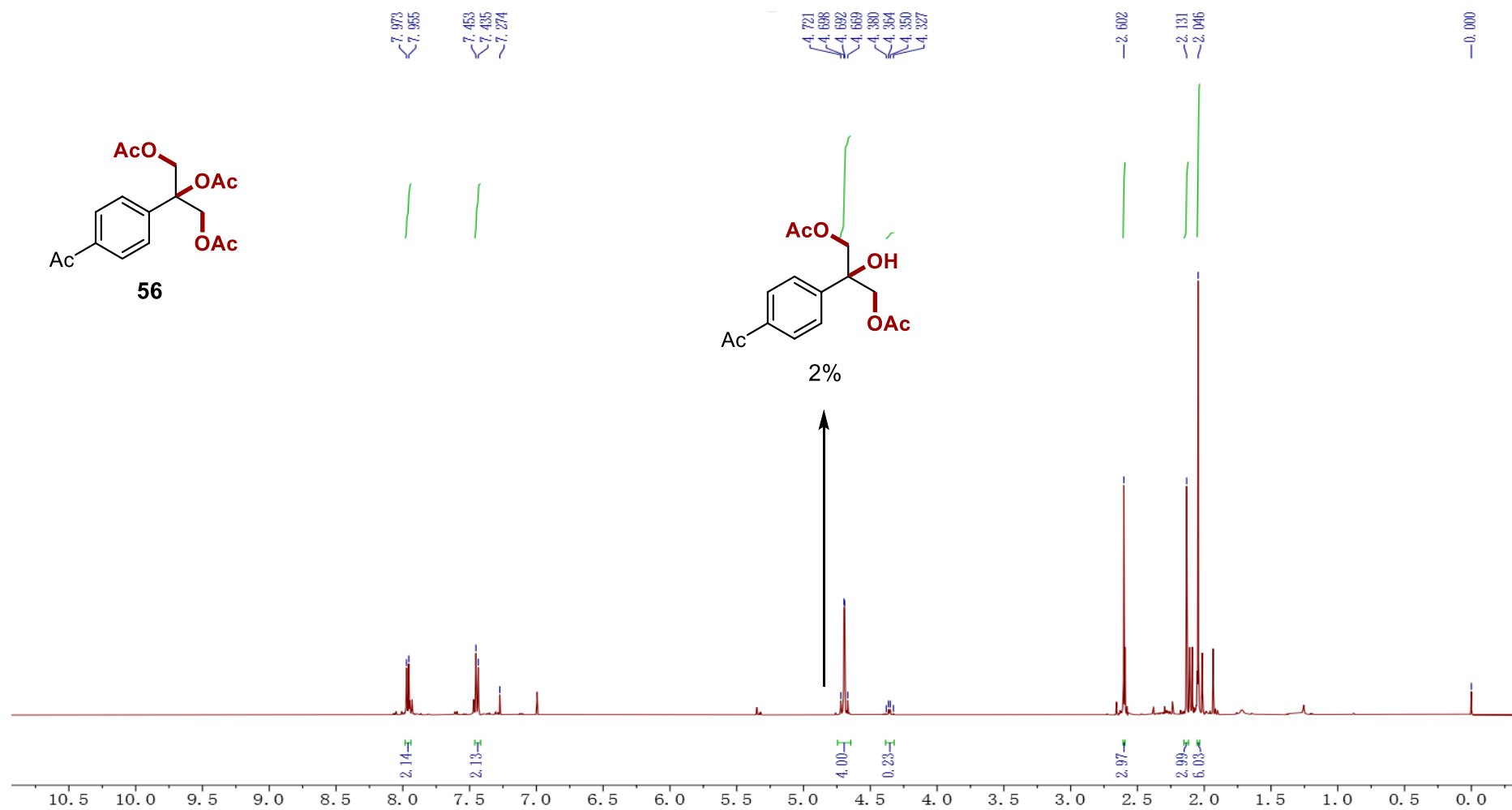


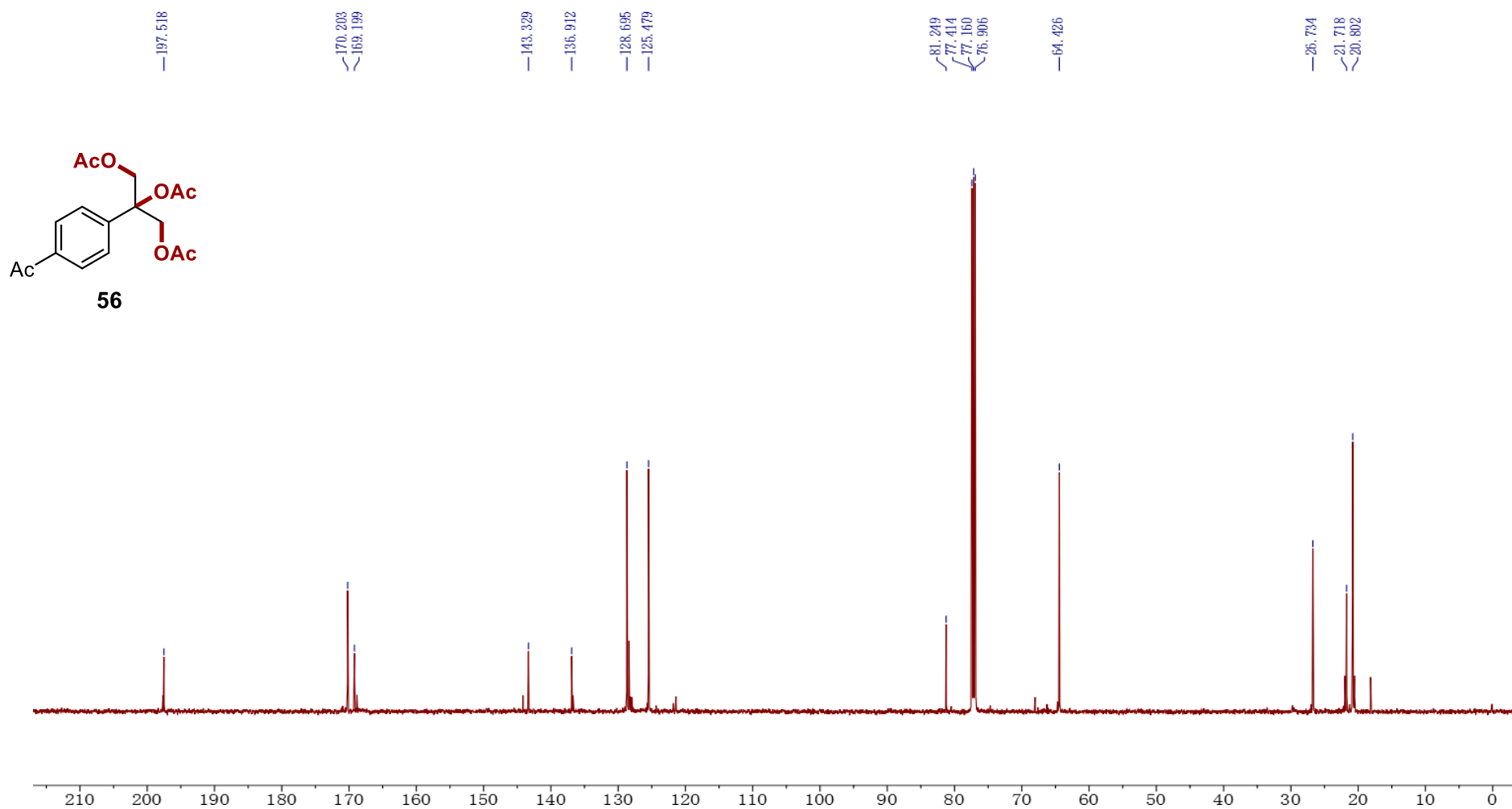
54

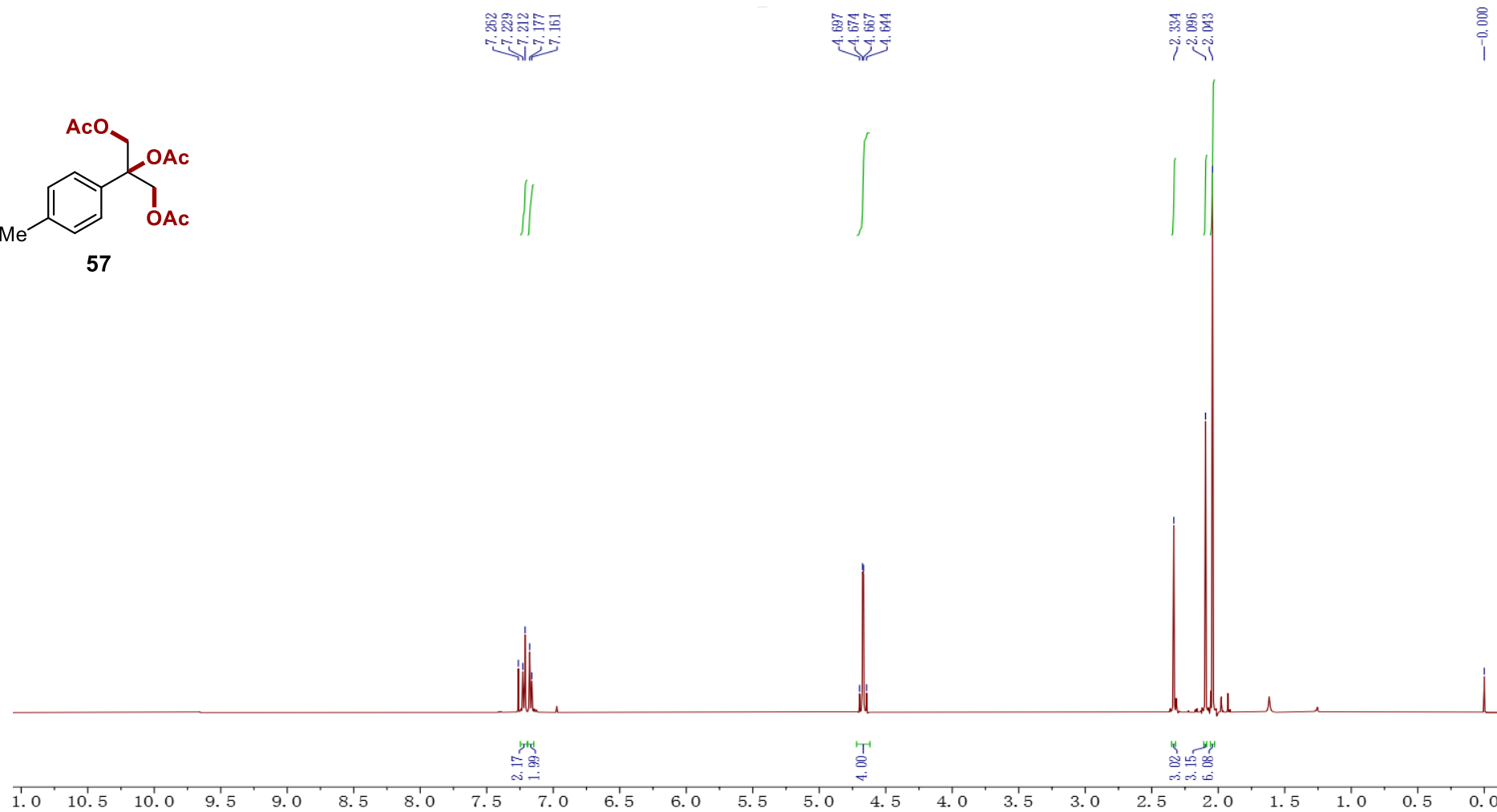
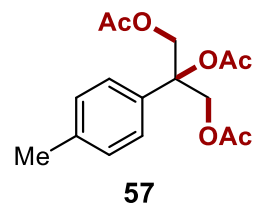


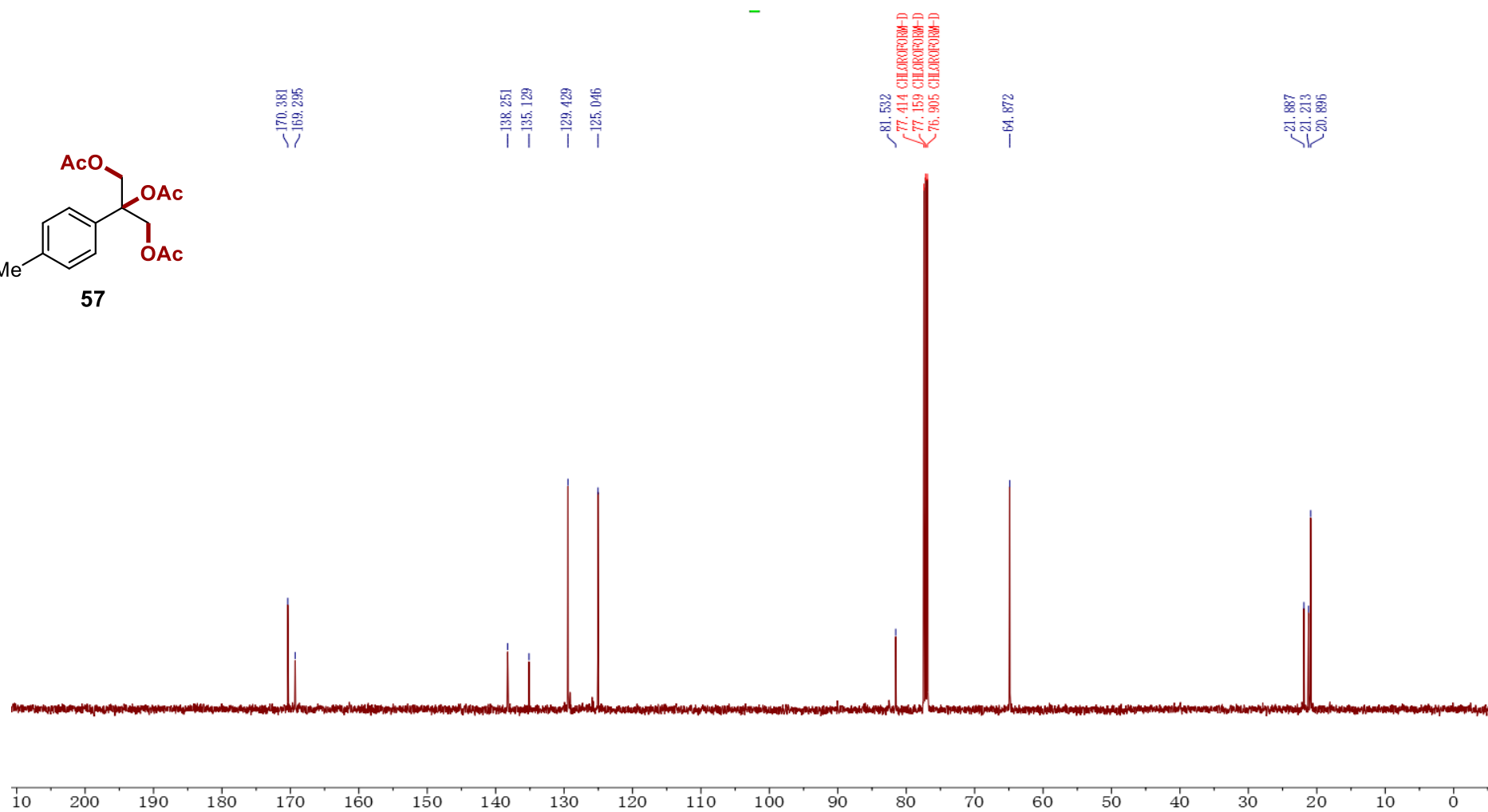
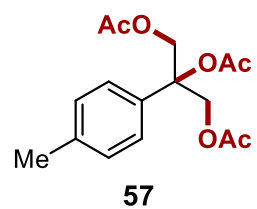


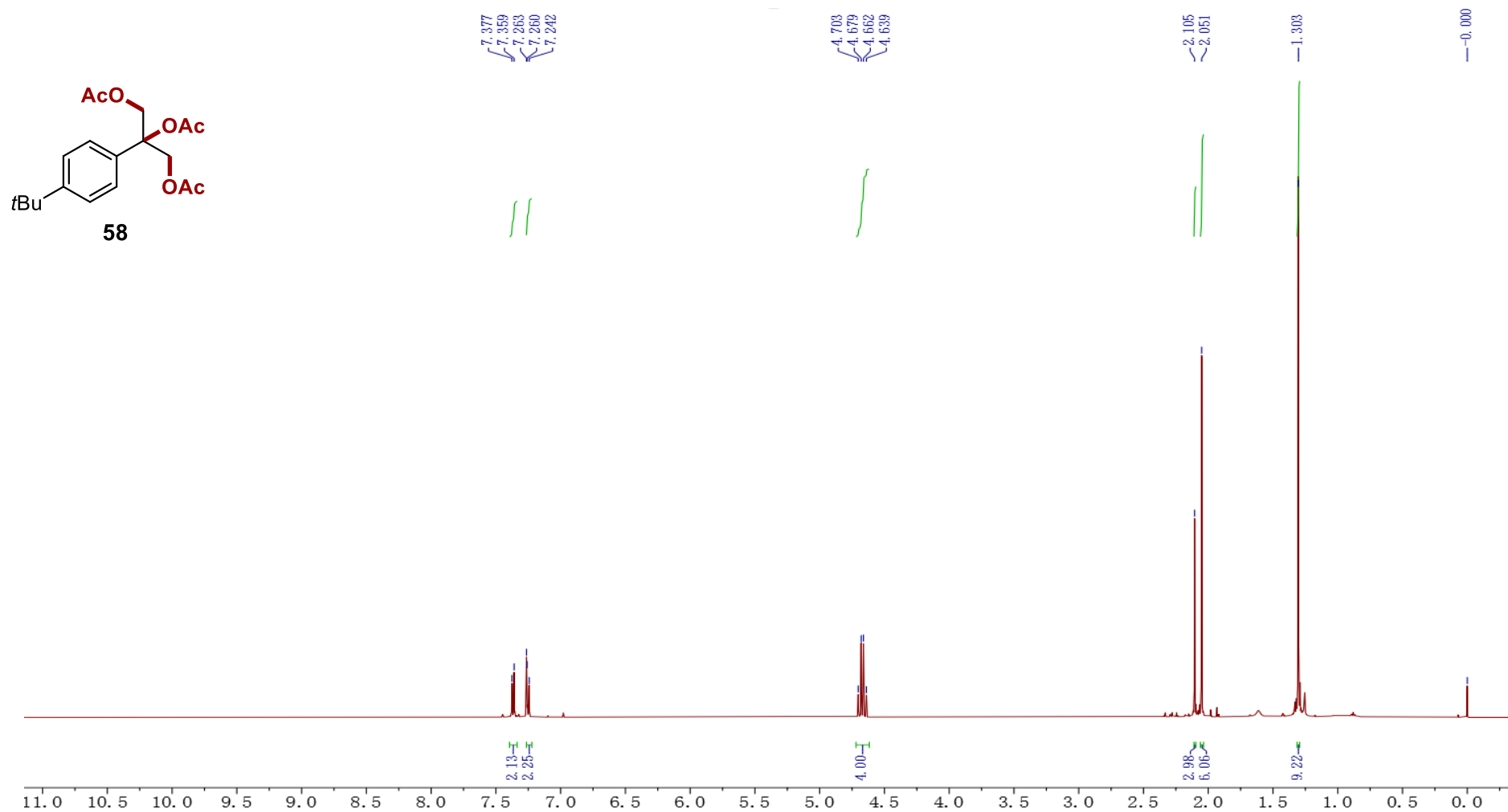


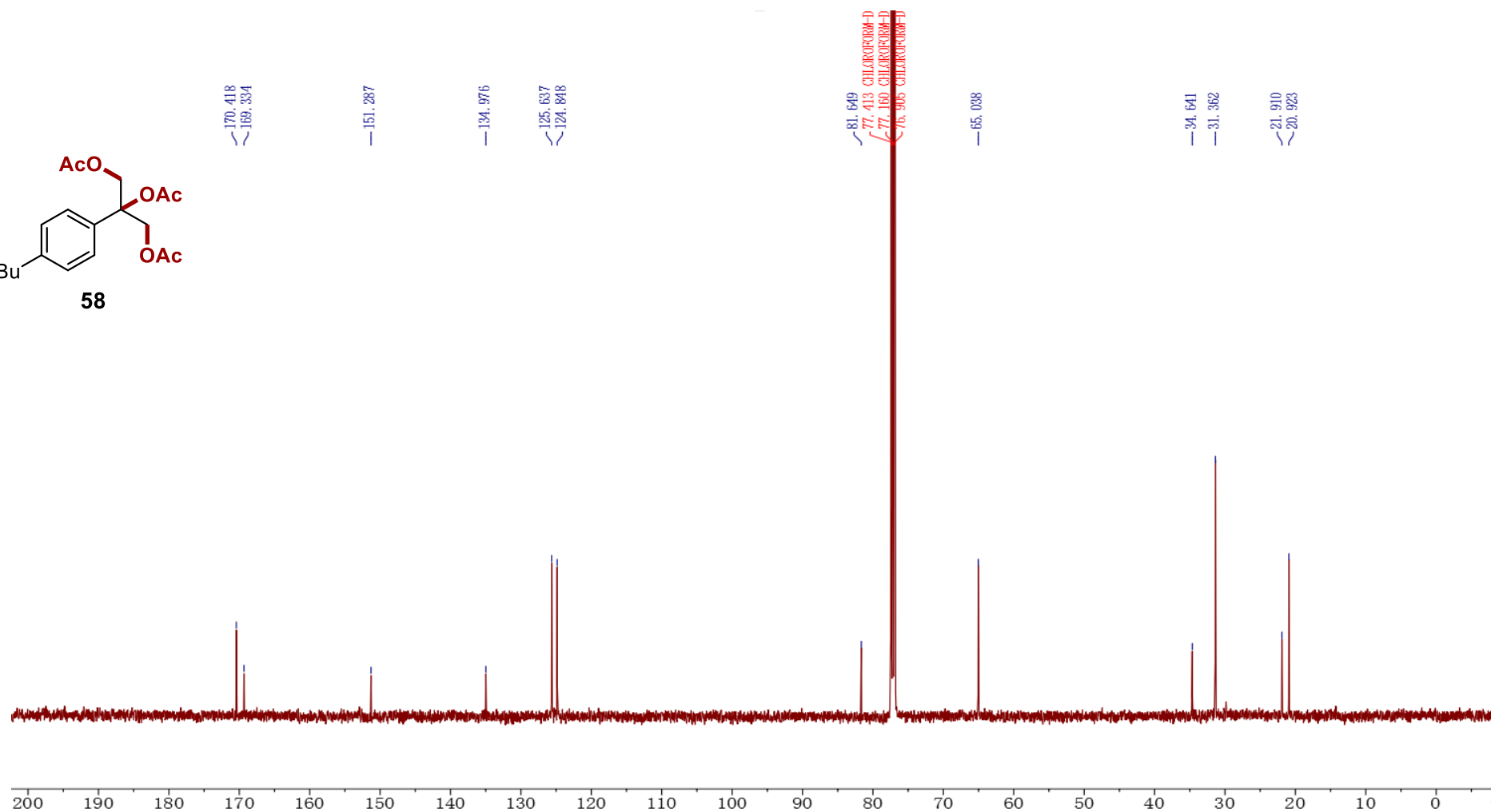
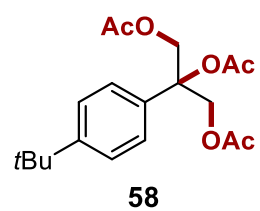


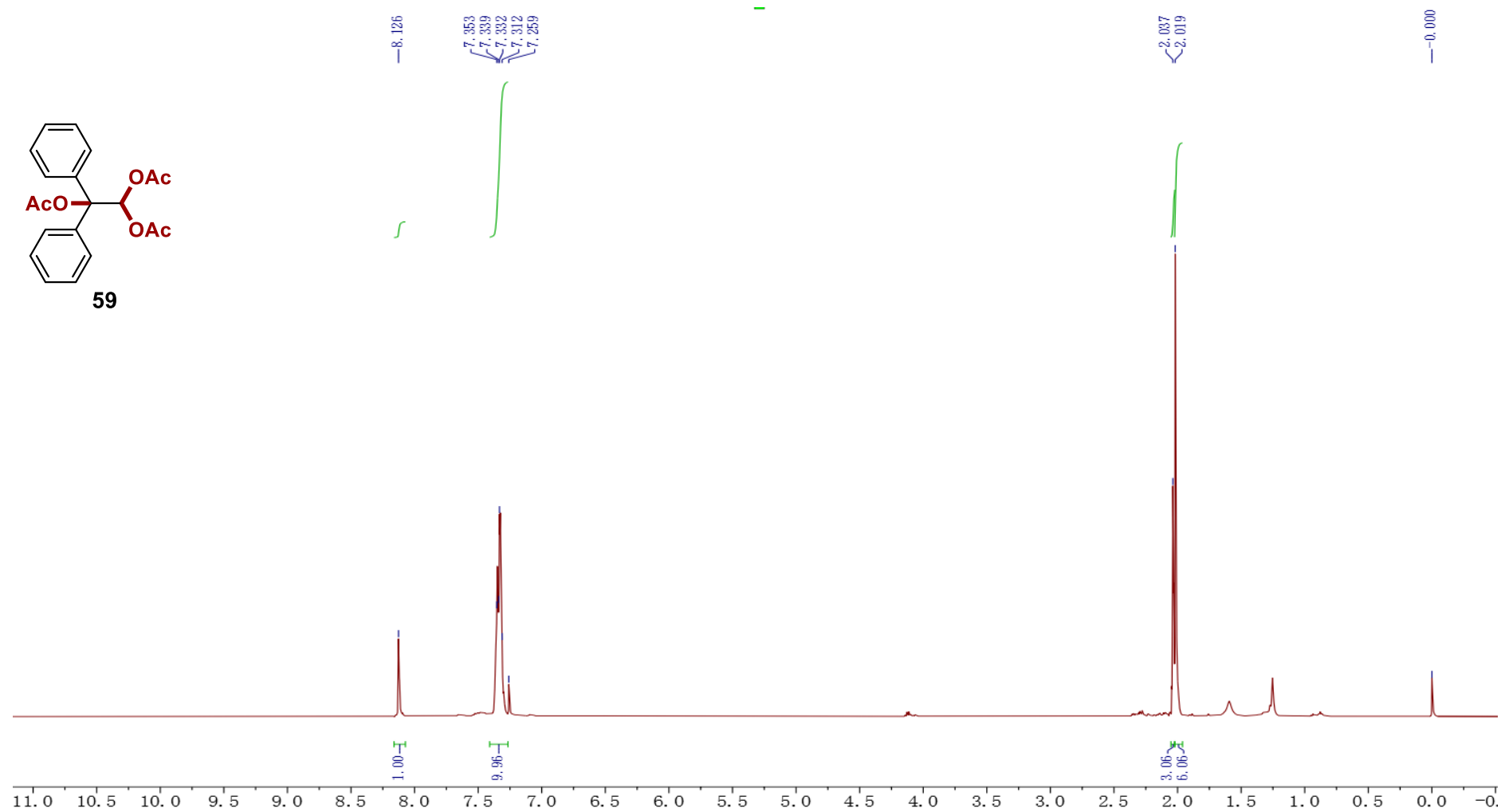


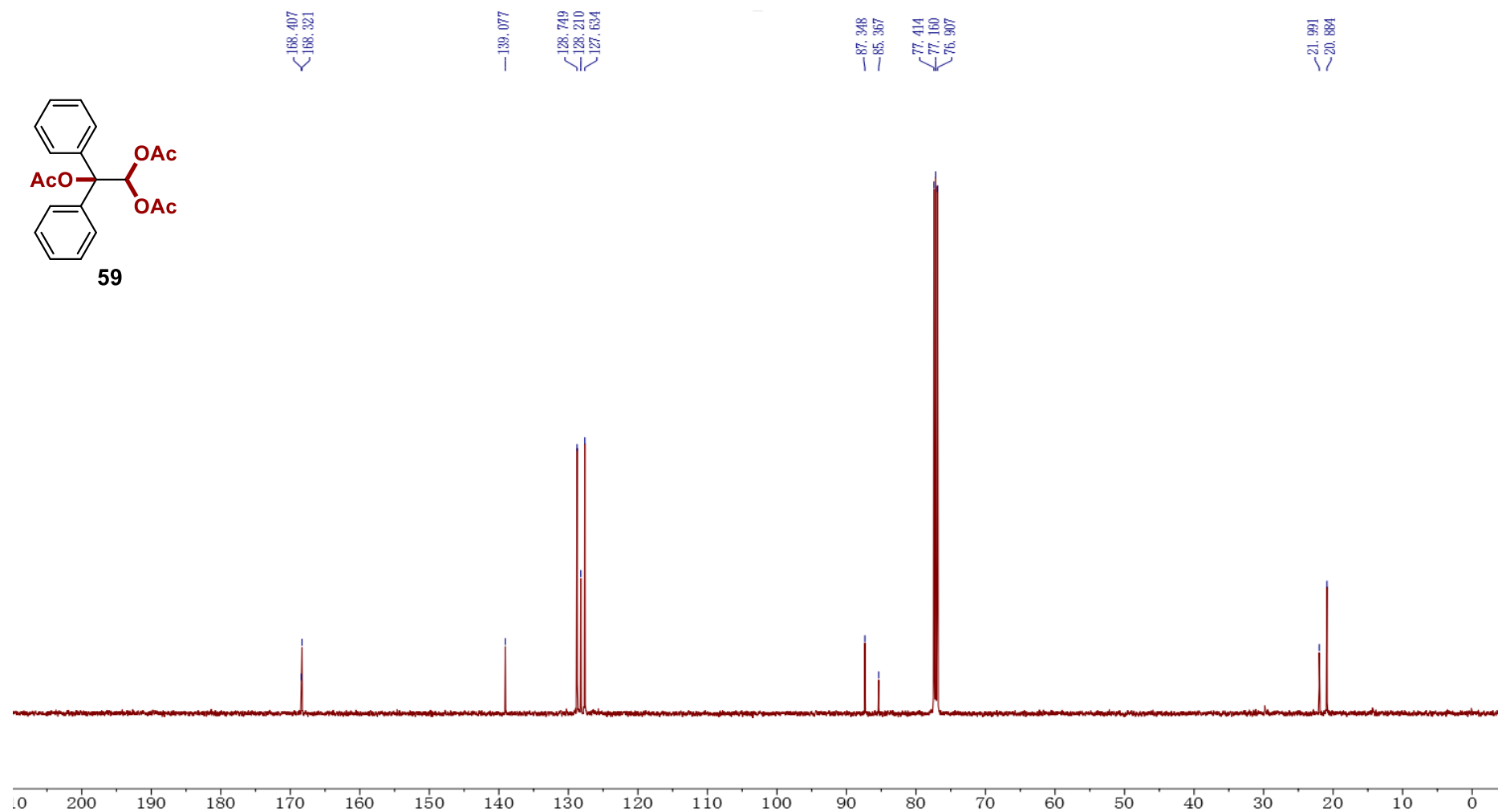


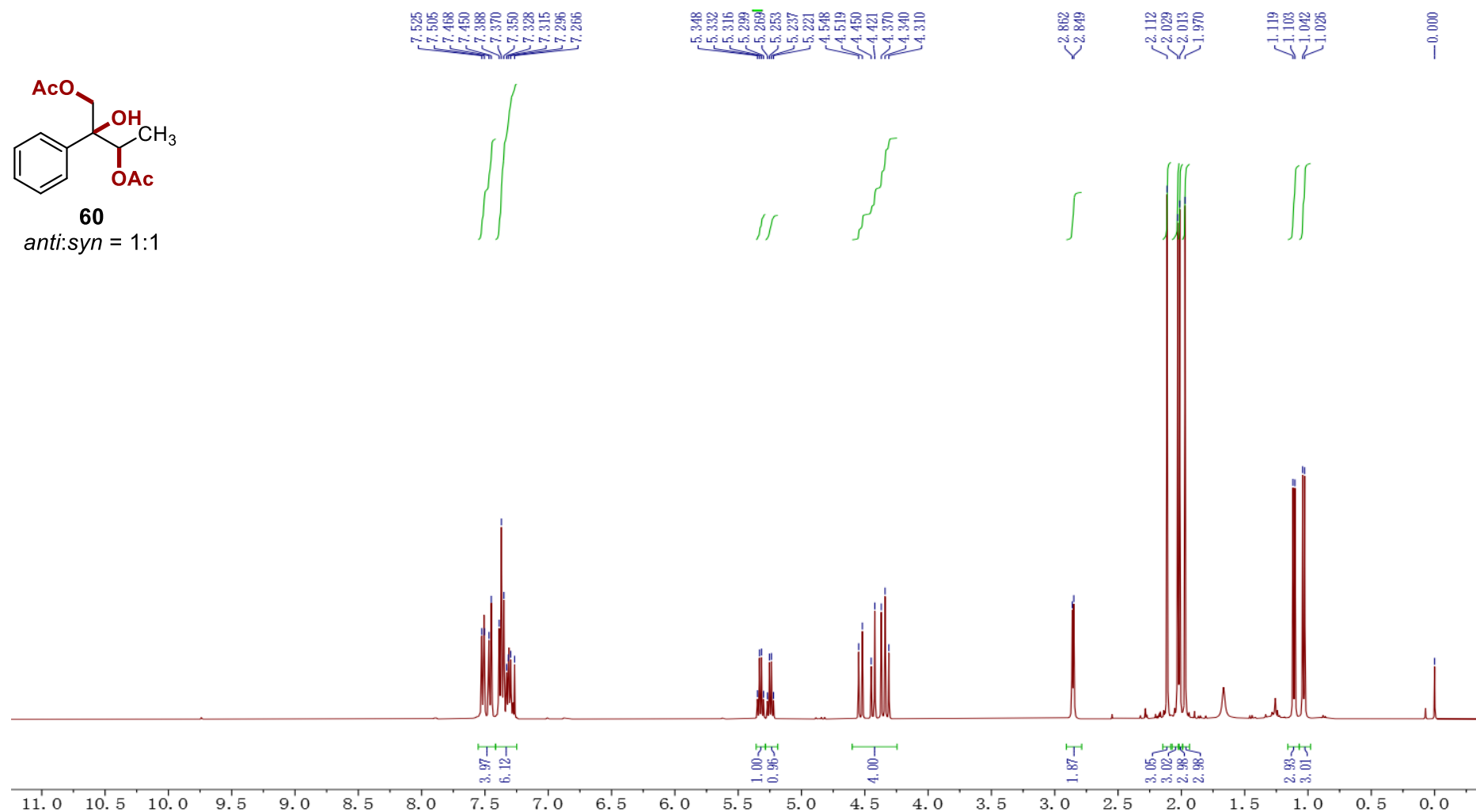
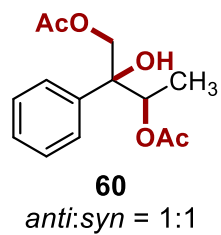


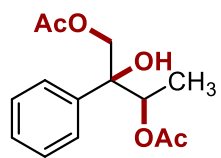






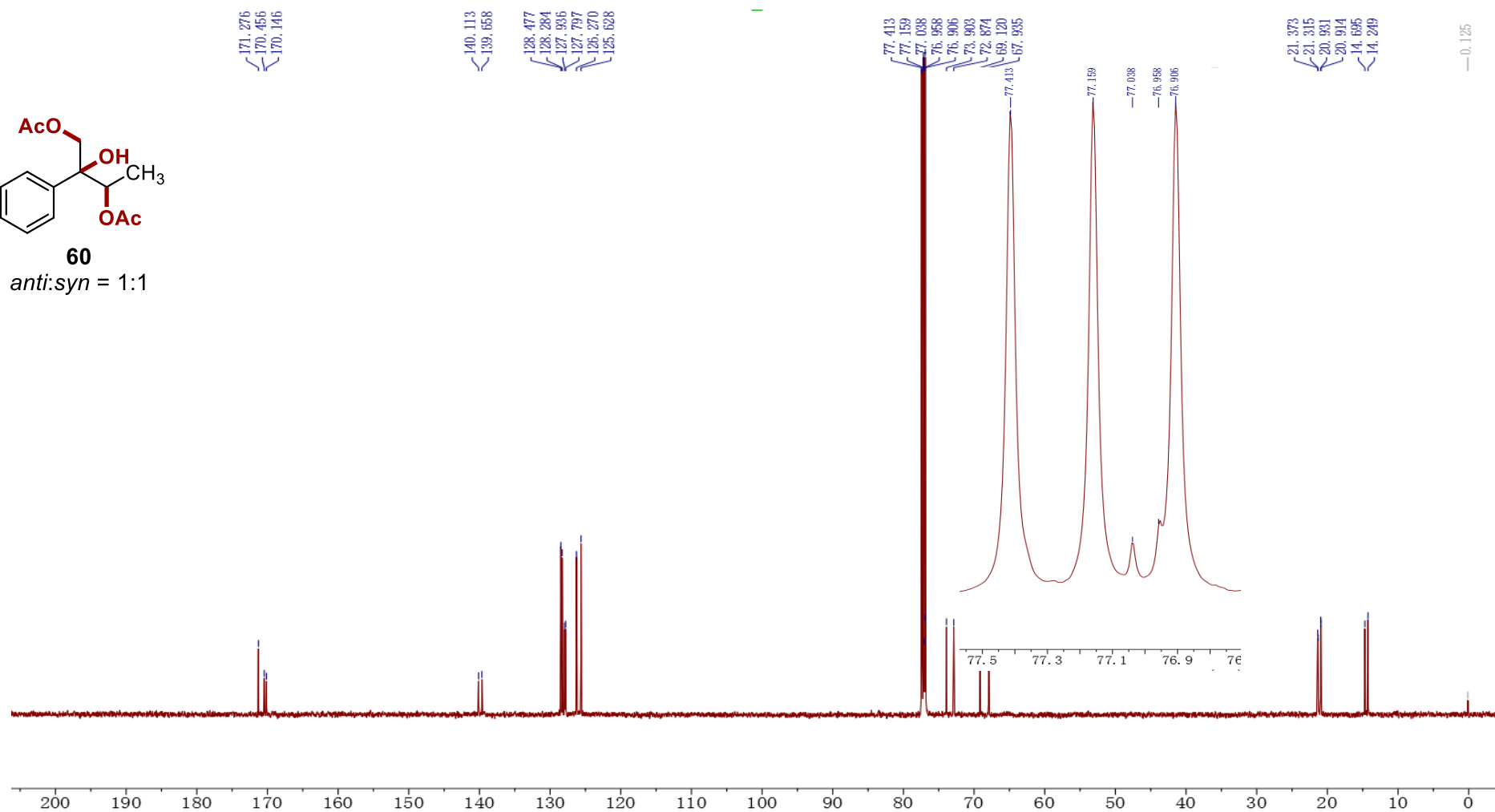


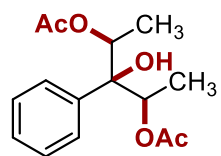




60

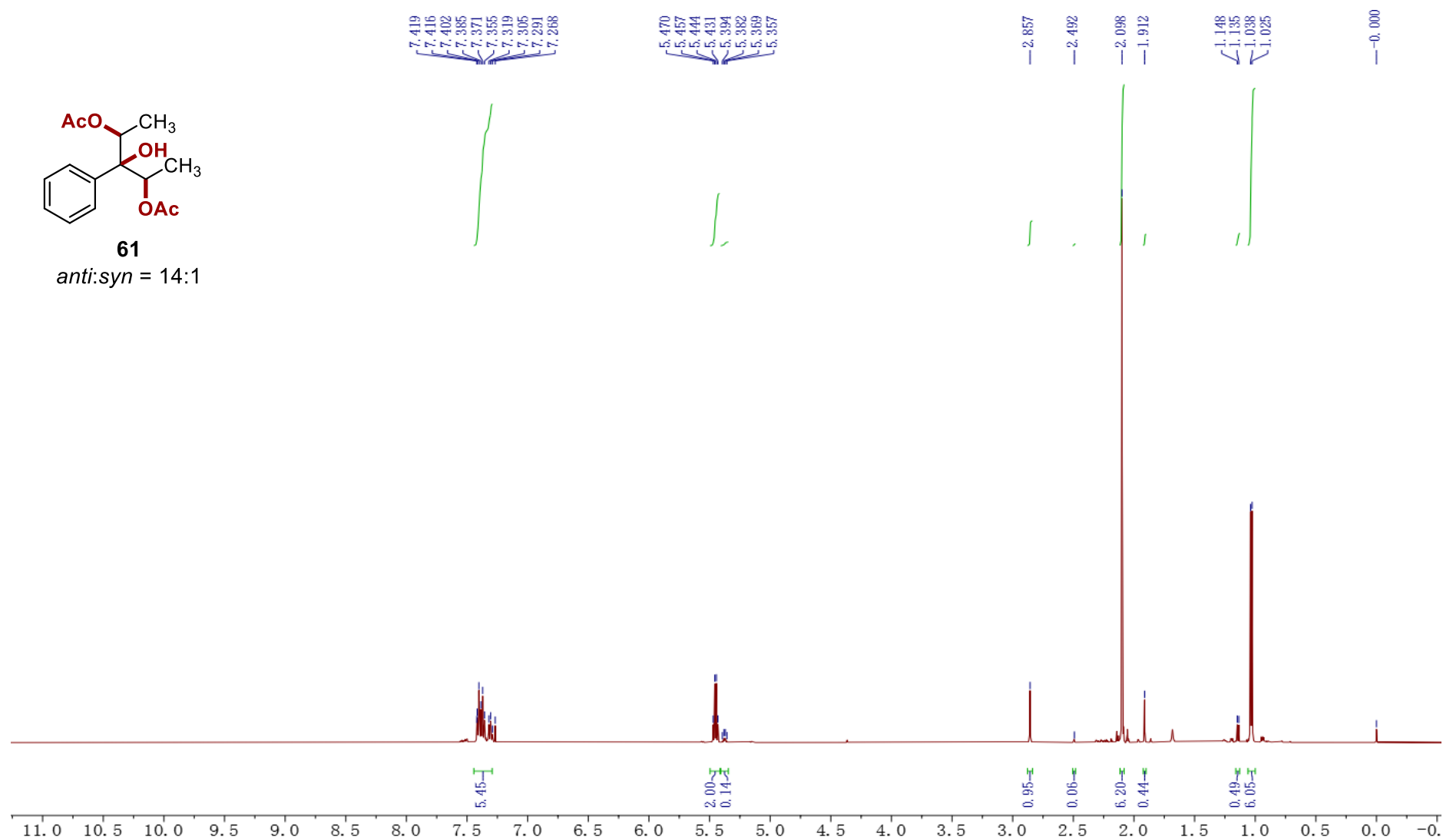
anti:syn = 1:1

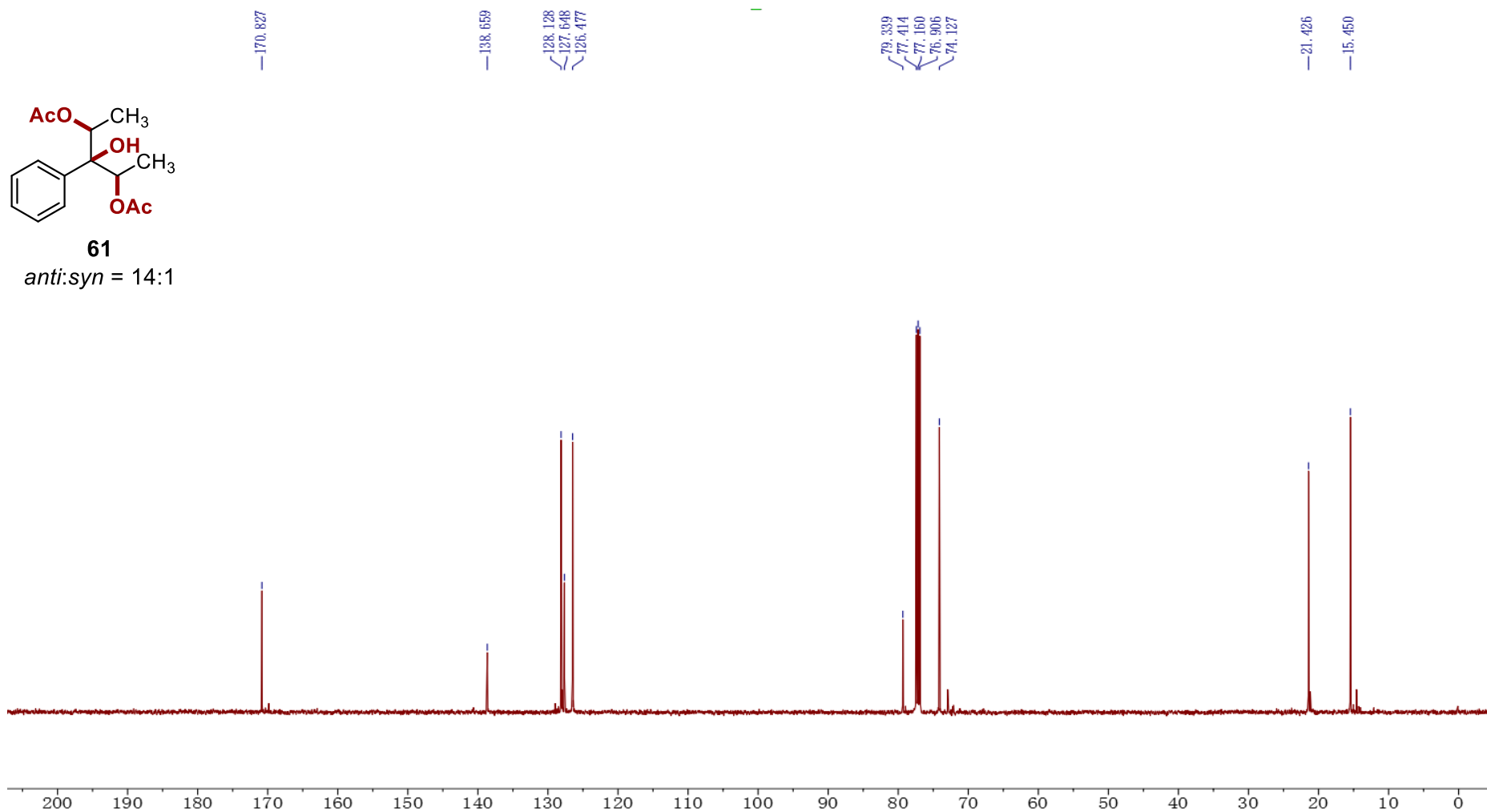


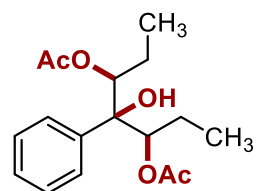


61

anti:syn = 14:1

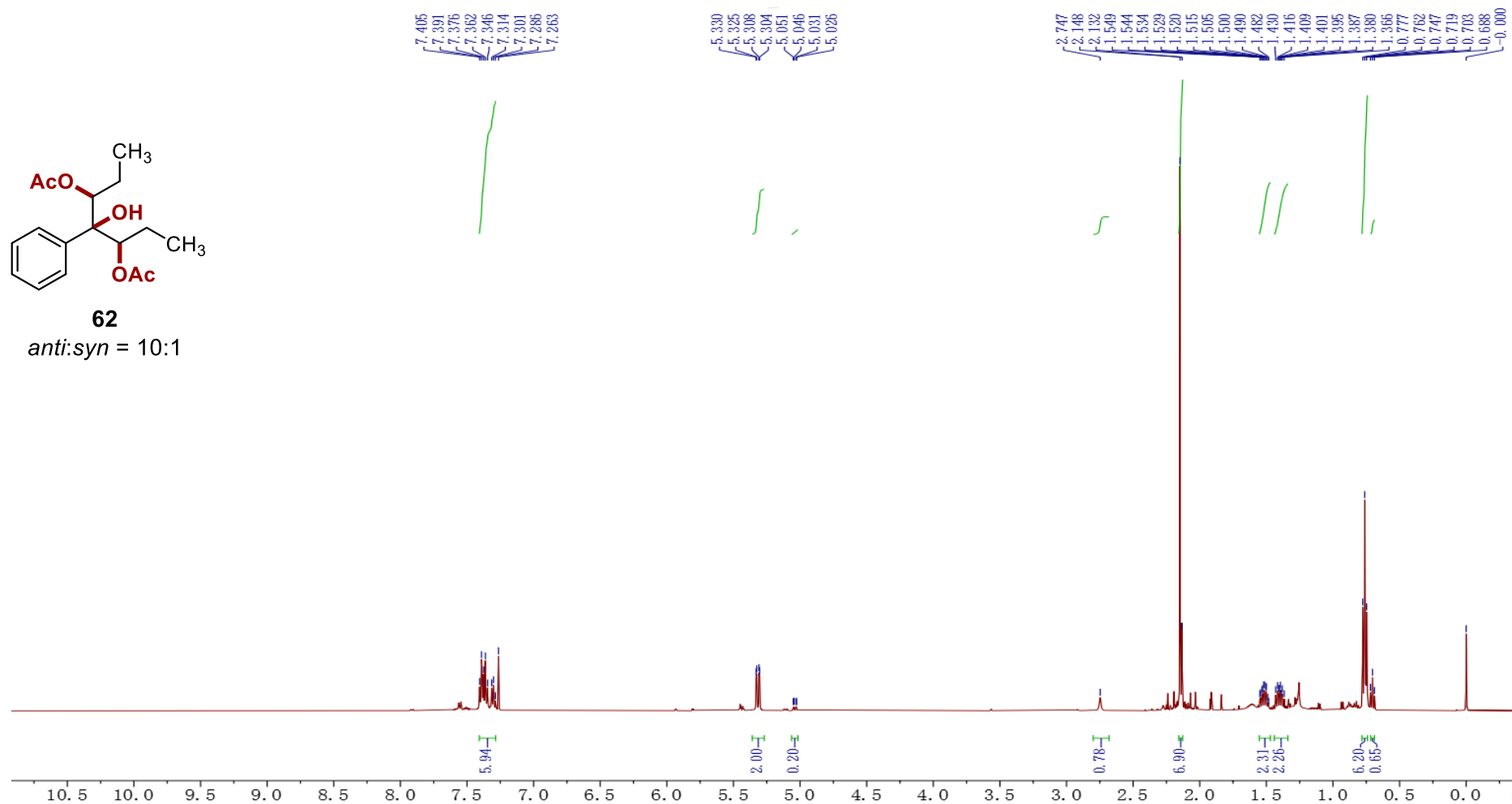


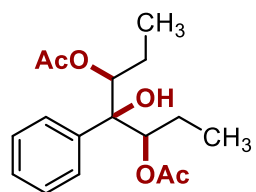




62

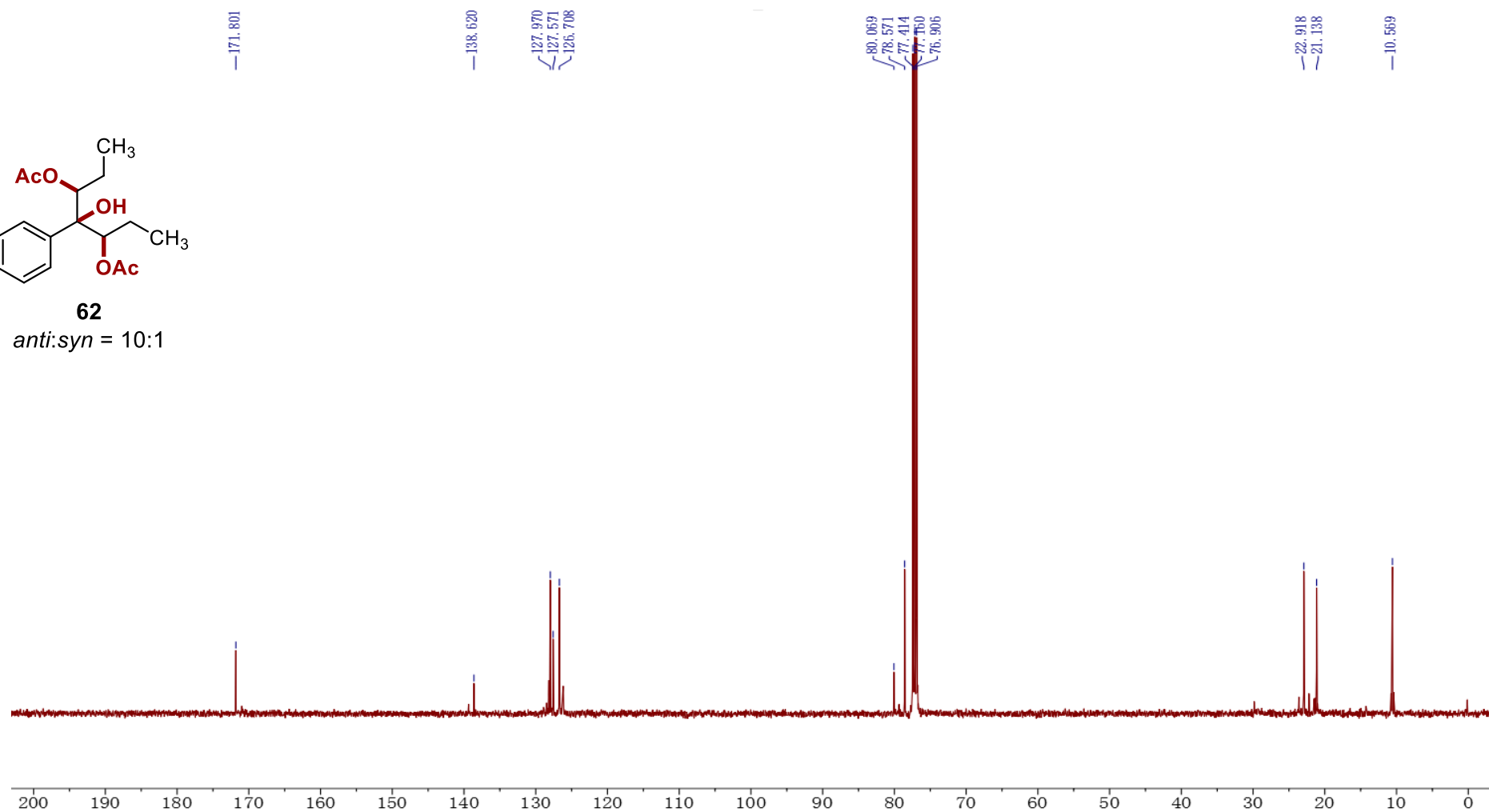
anti:syn = 10:1

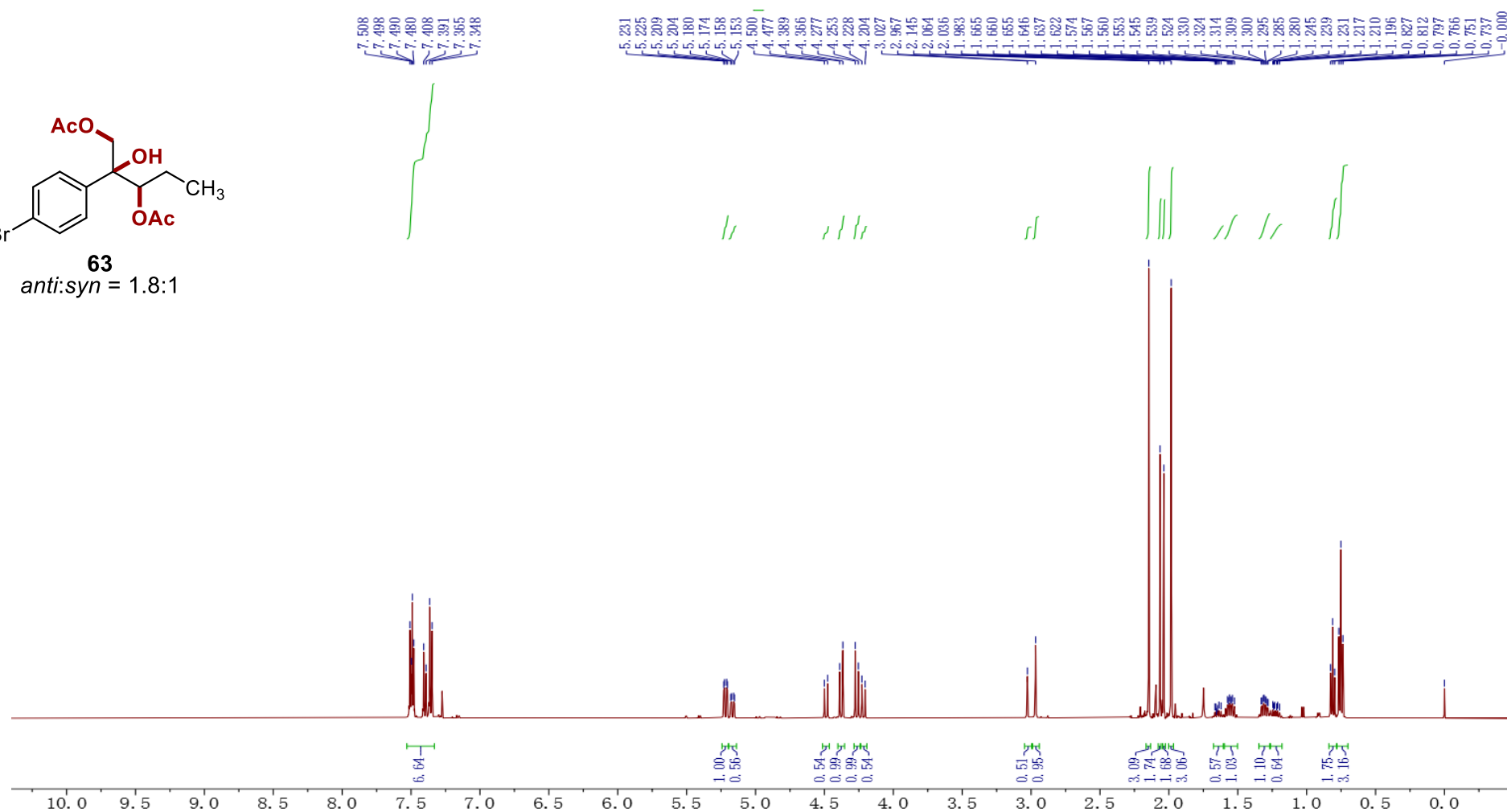
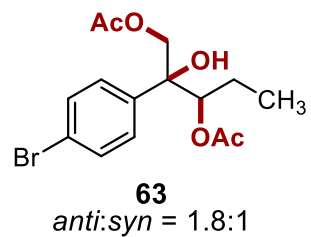


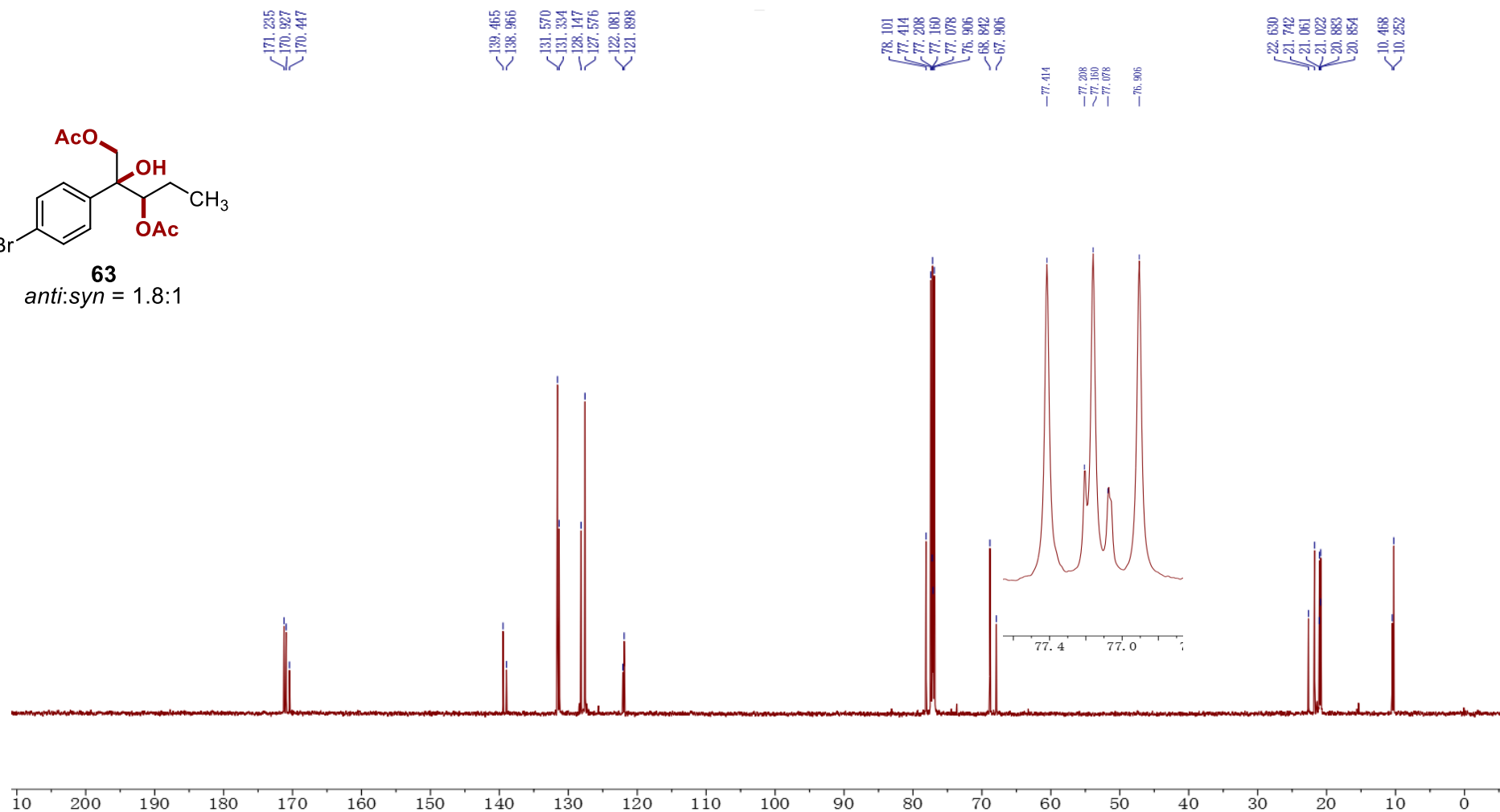
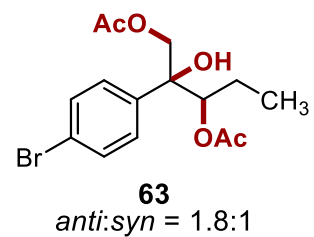


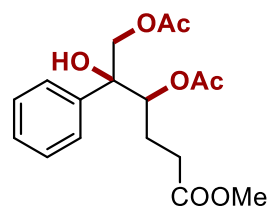
62

anti:syn = 10:1

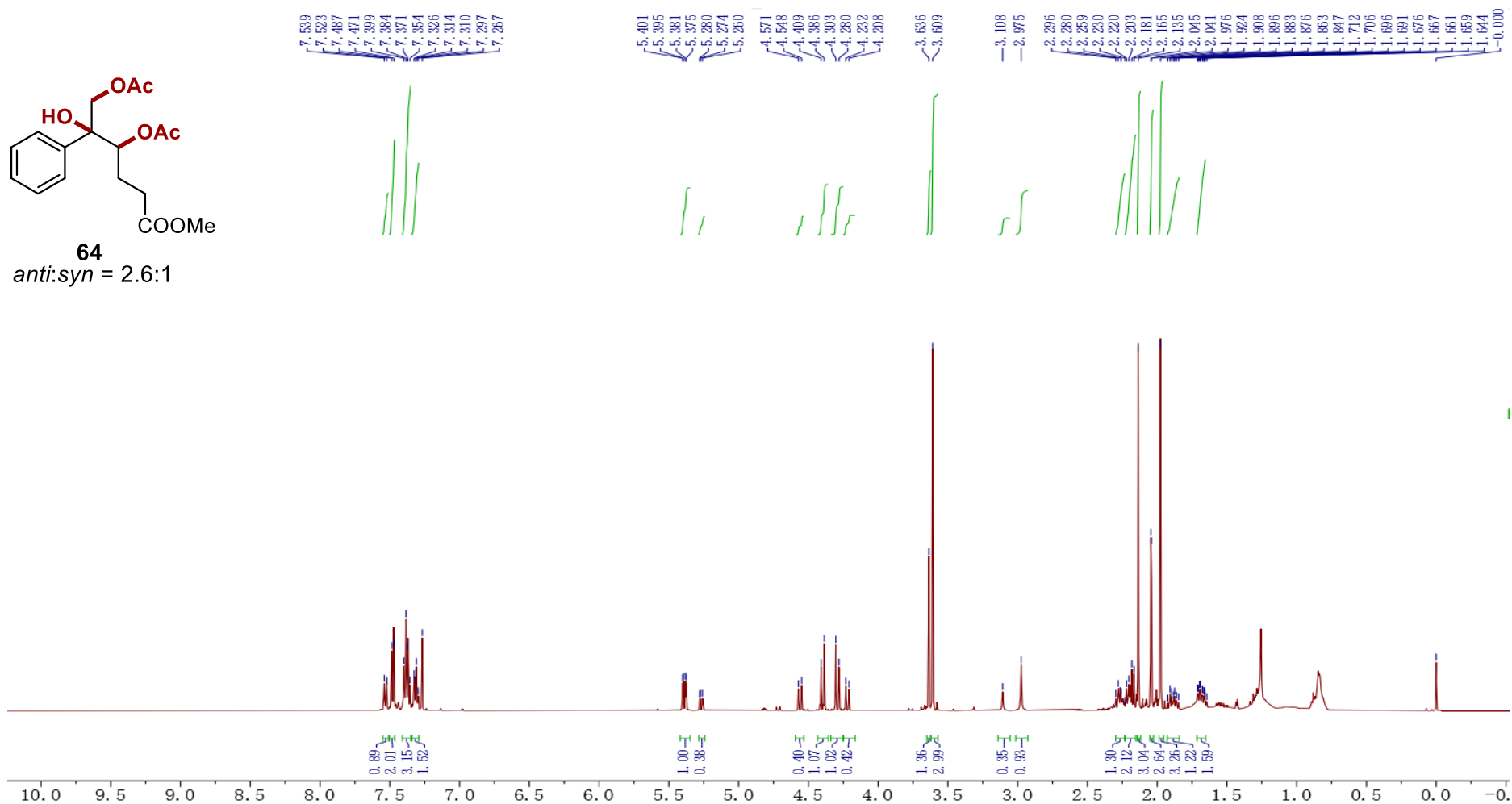


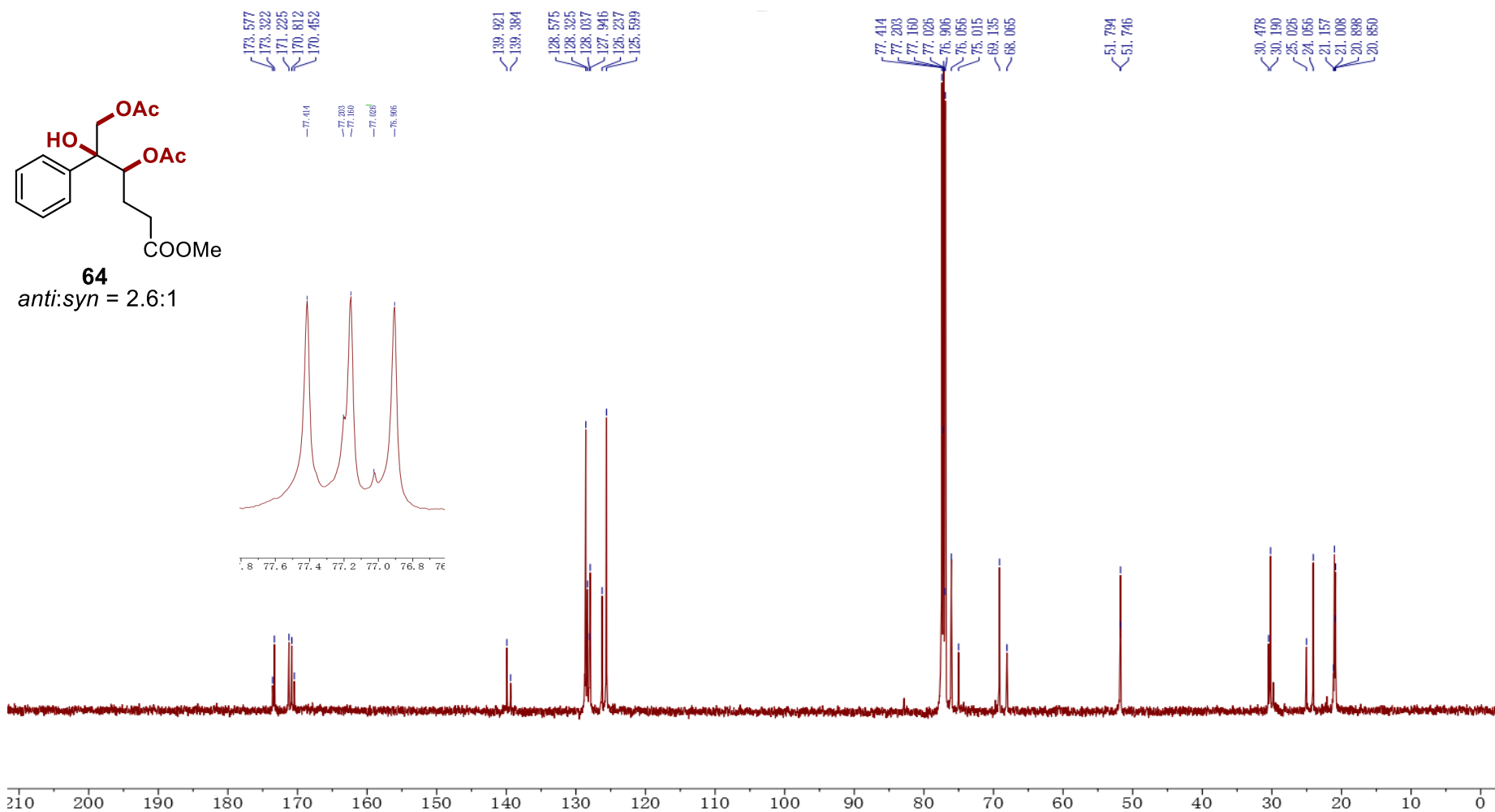


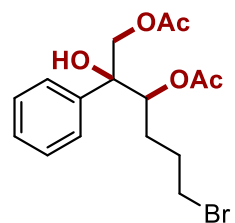




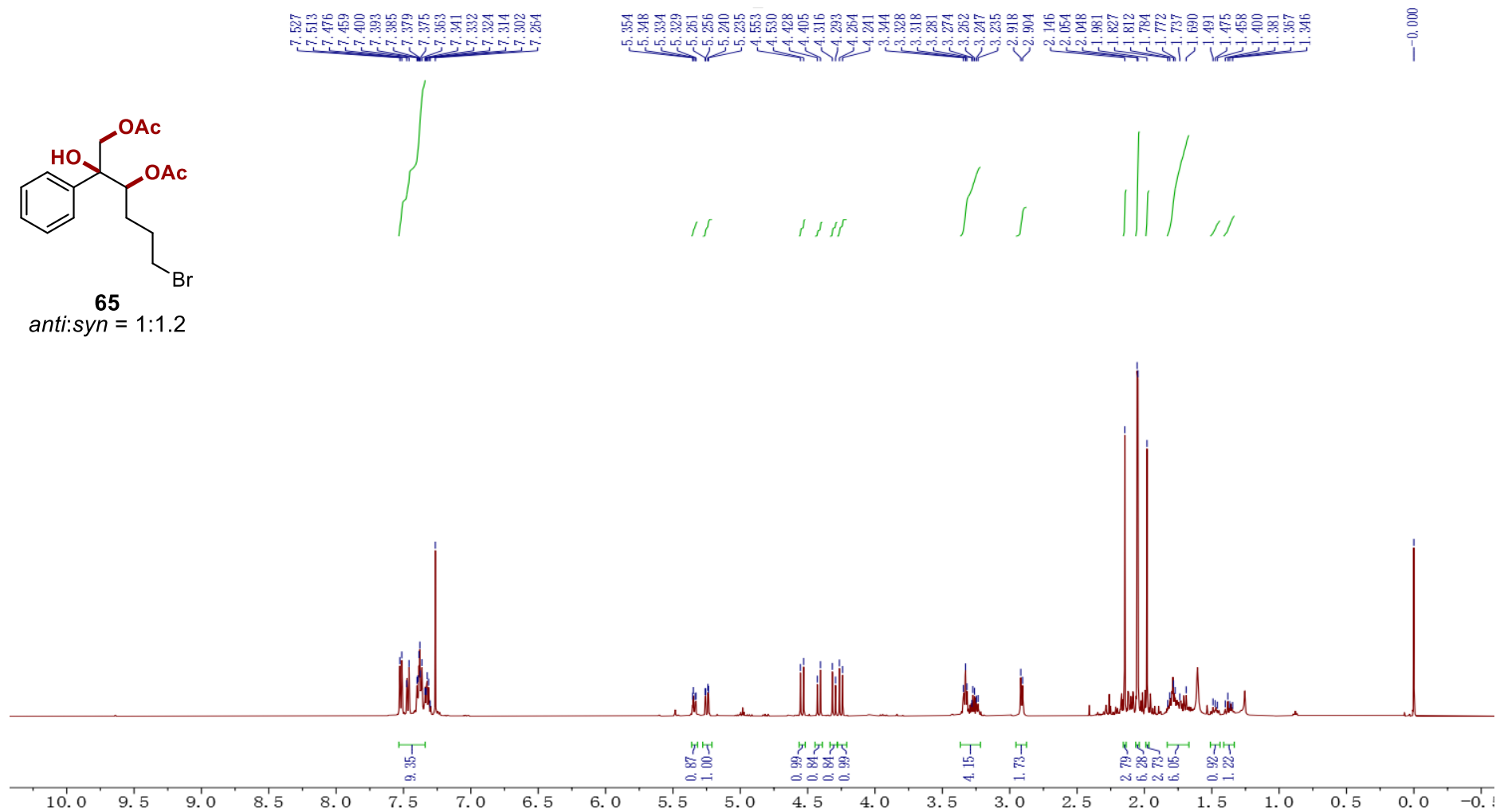
64
anti:syn = 2.6:1

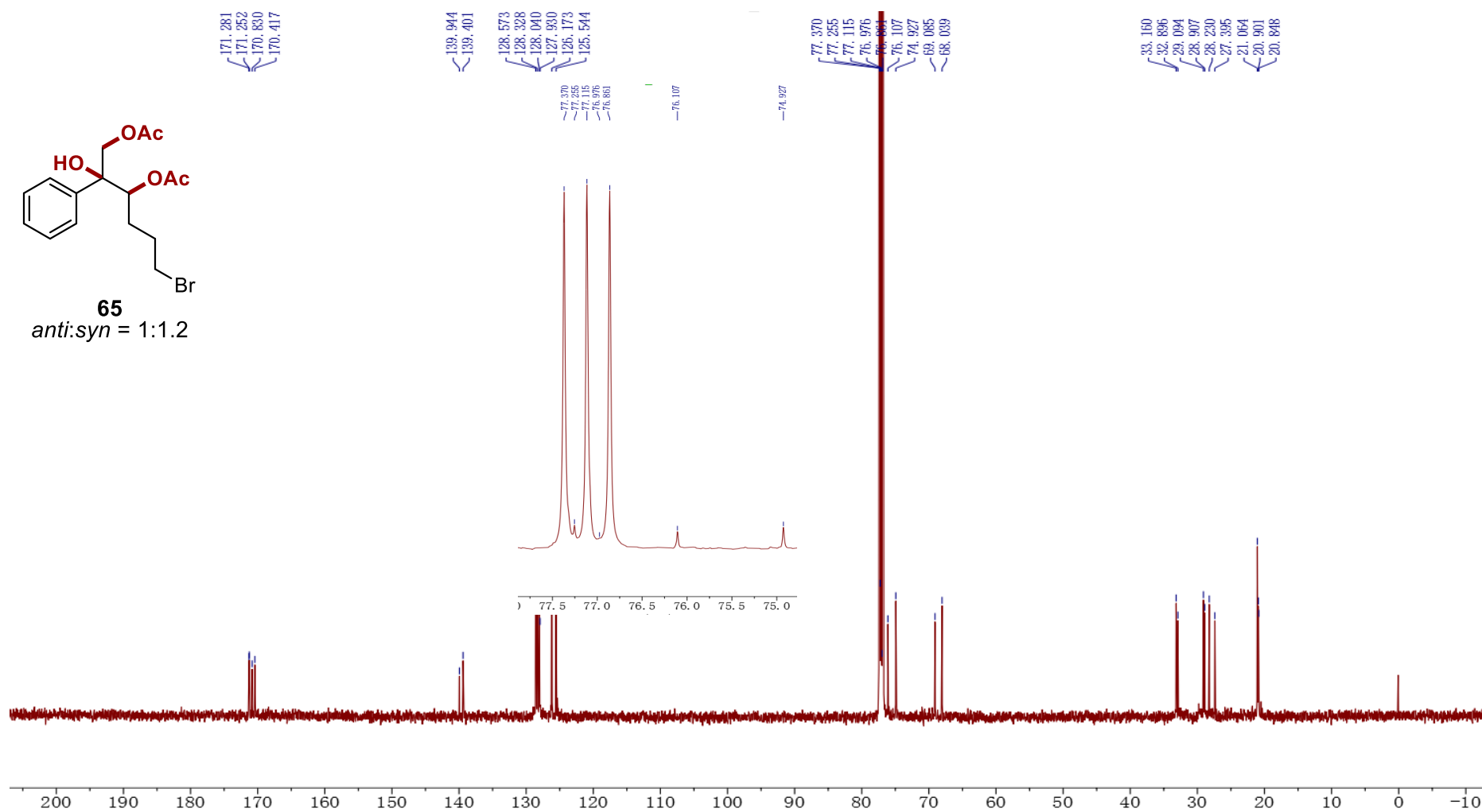


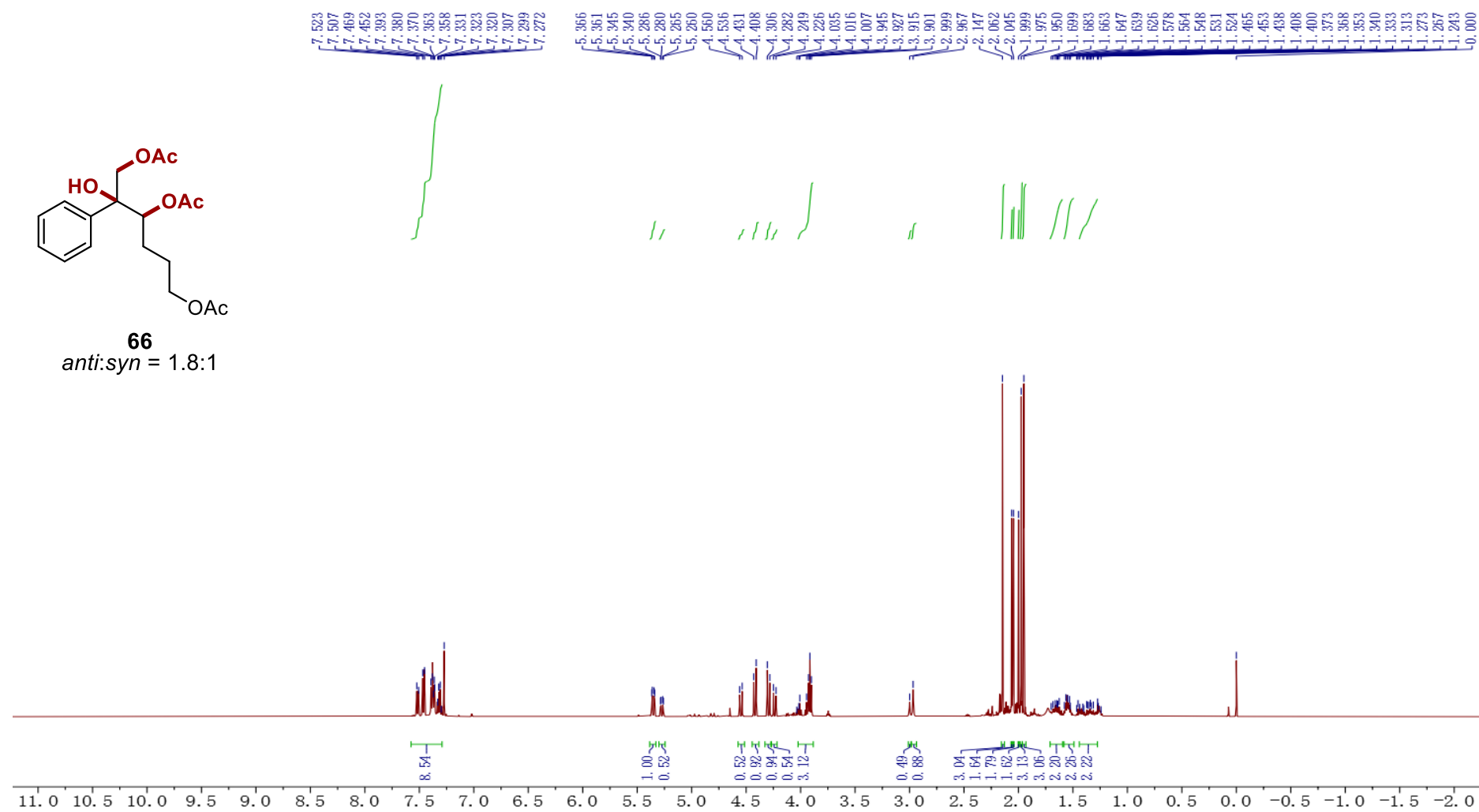


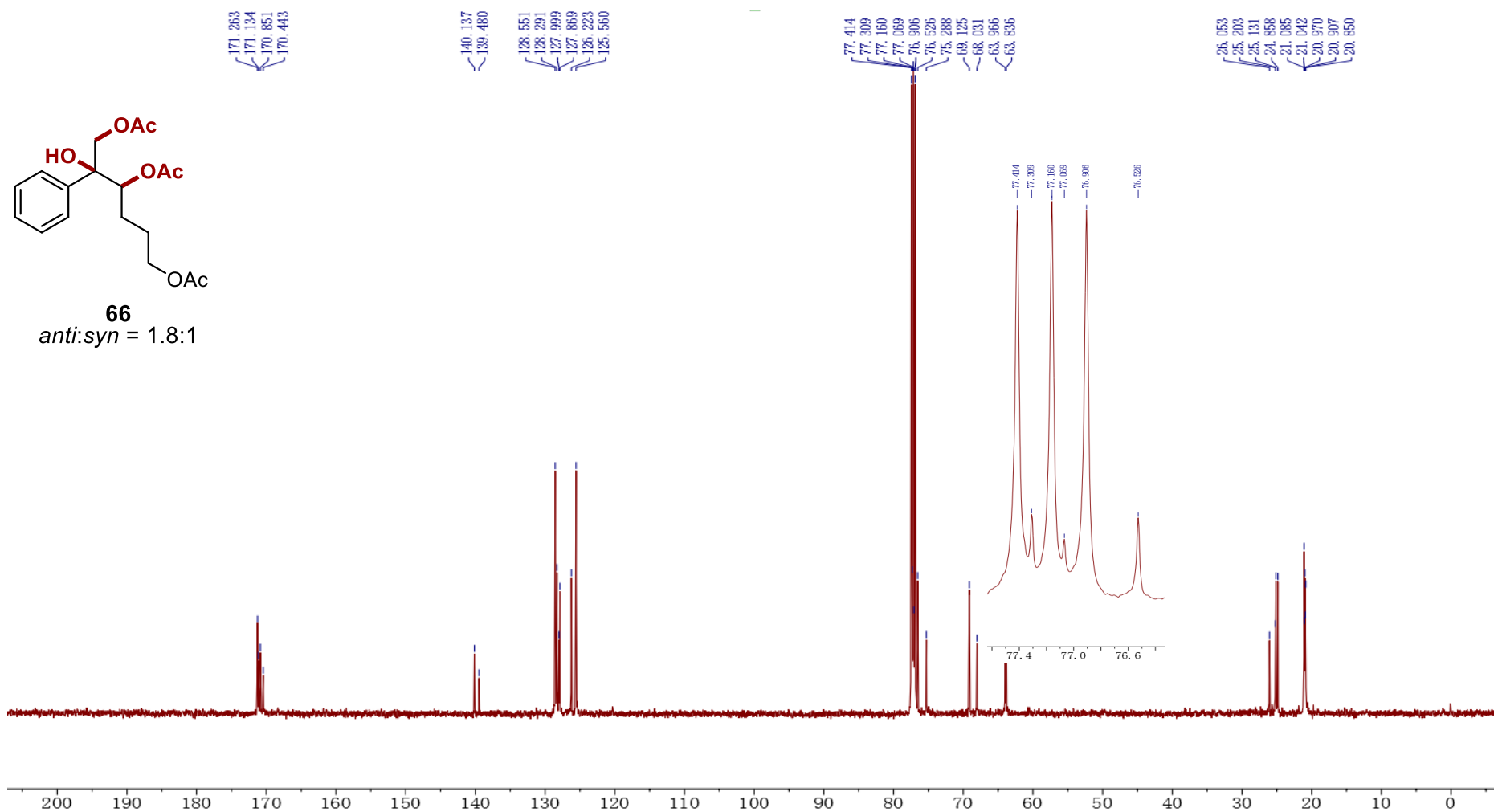


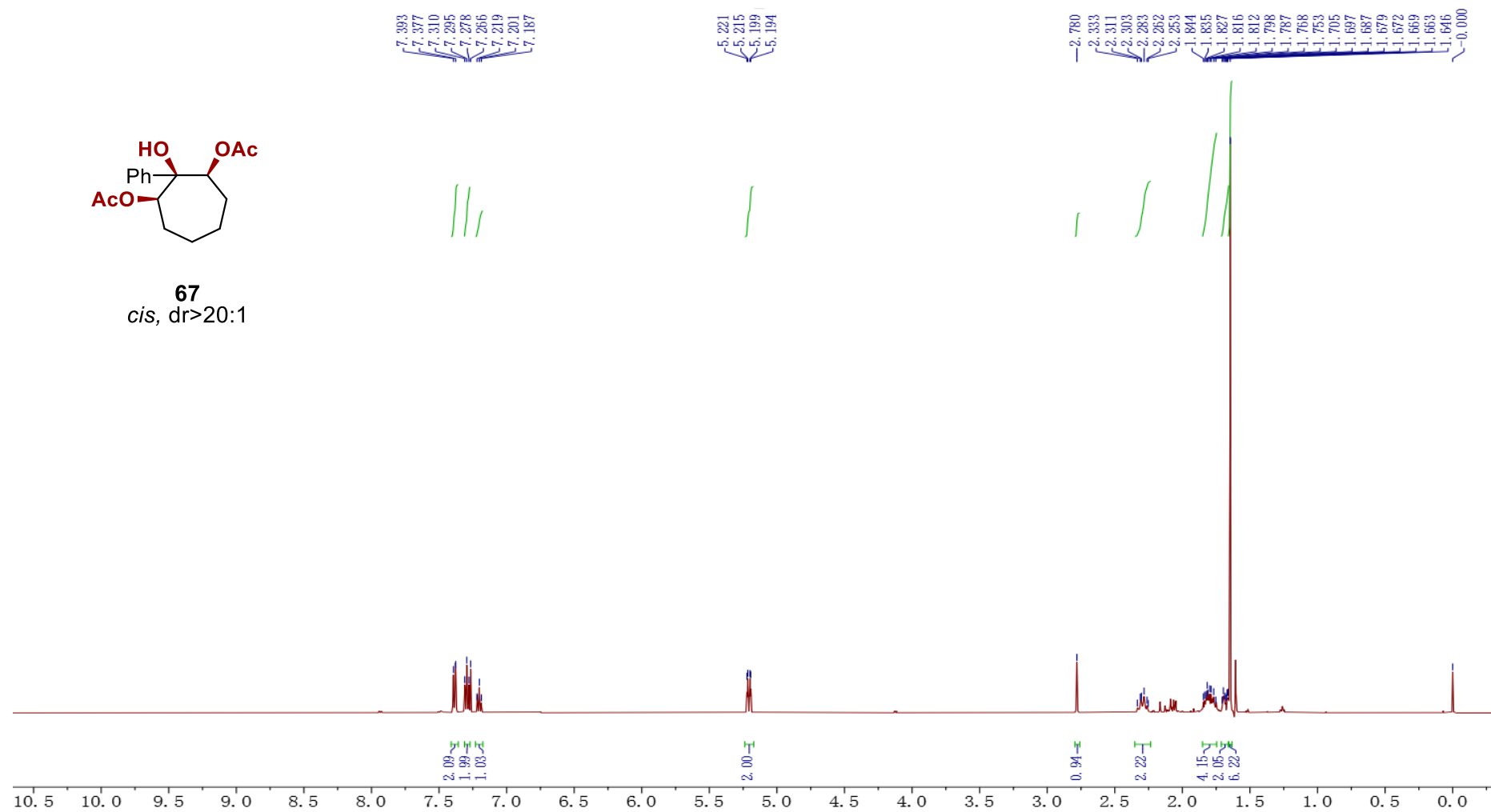
65
anti:syn = 1:1.2

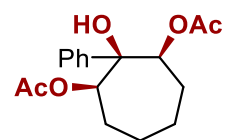




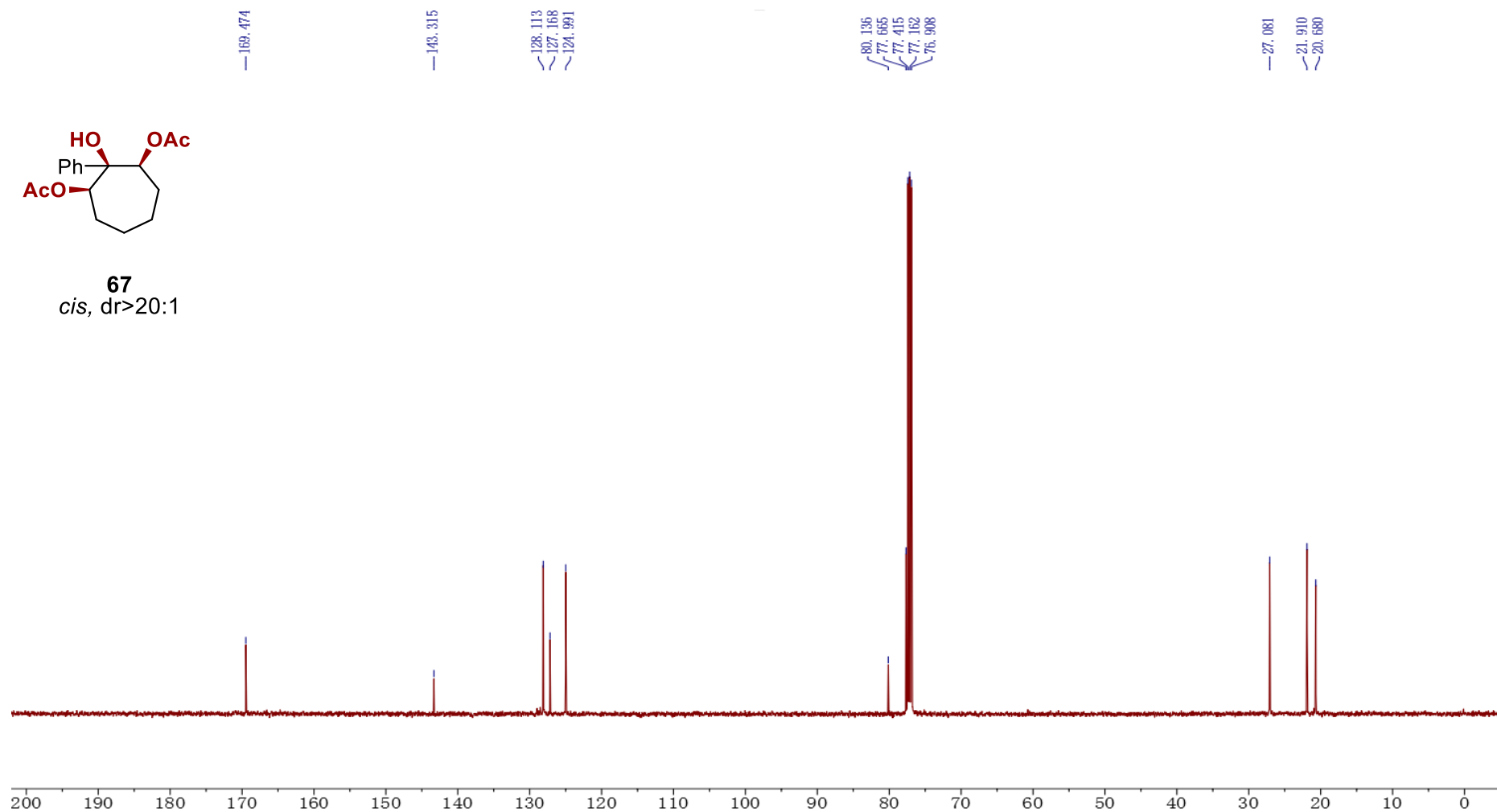


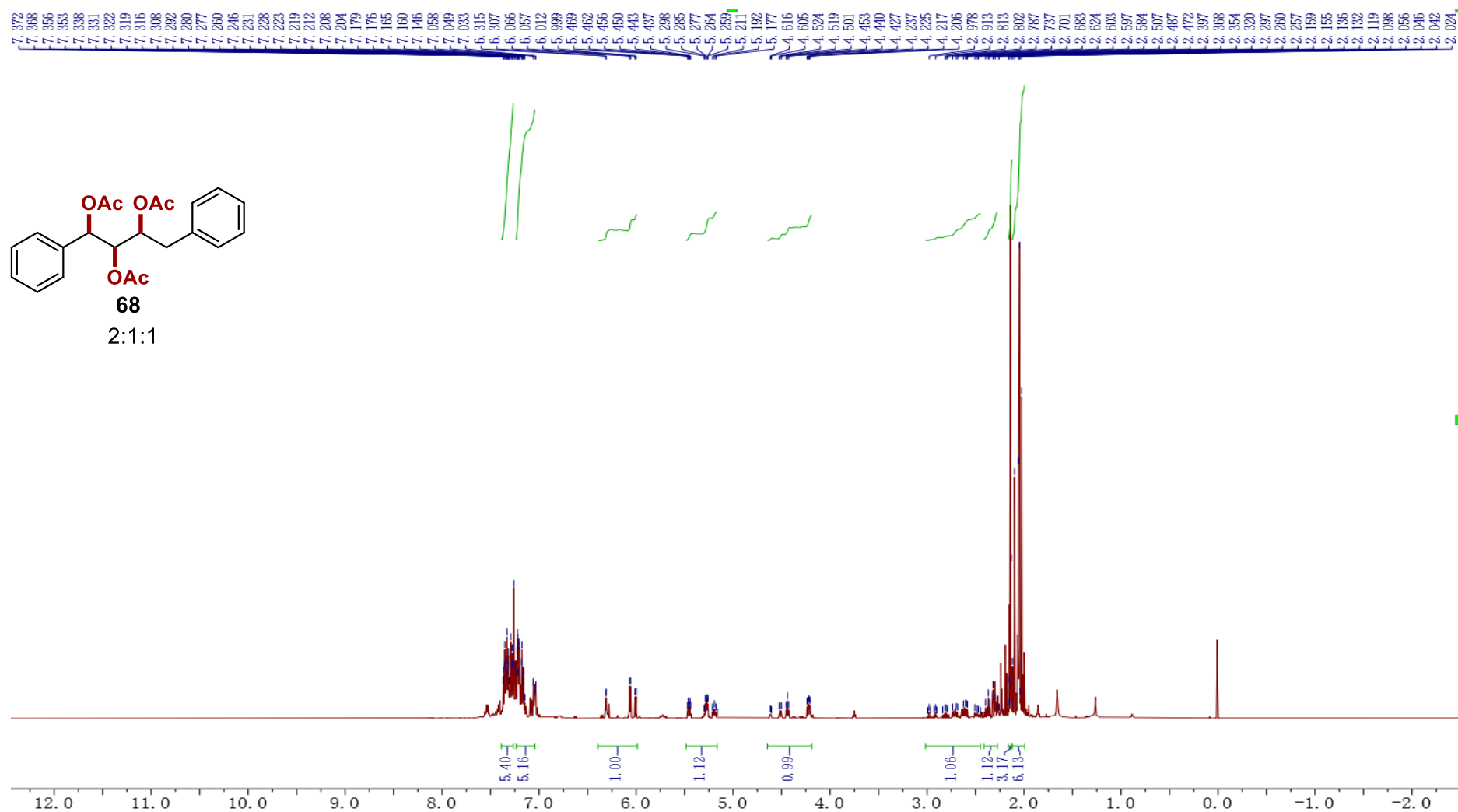


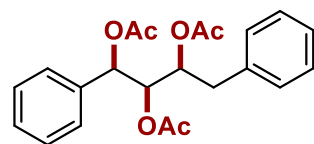




67
cis, dr>20:1

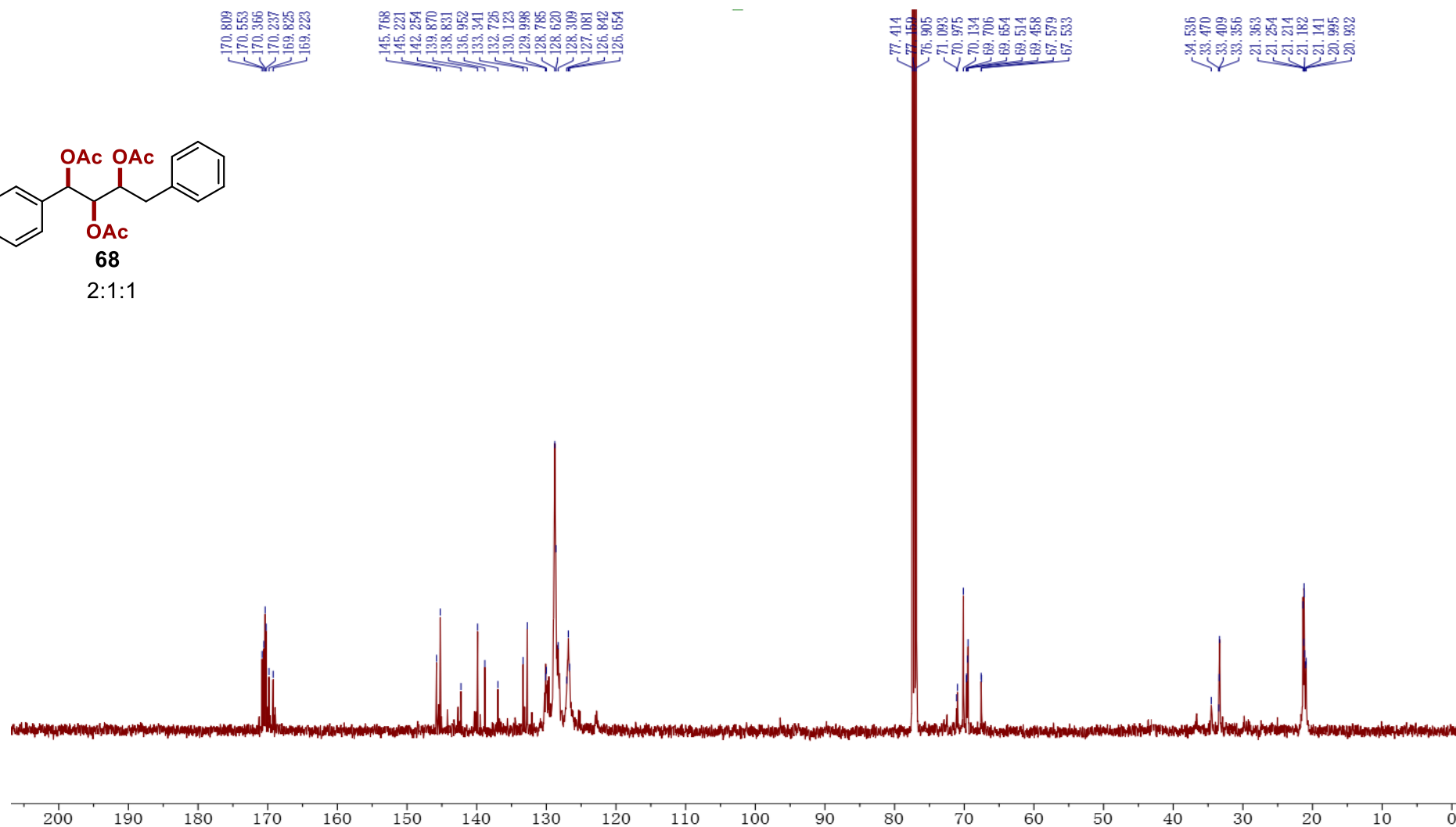


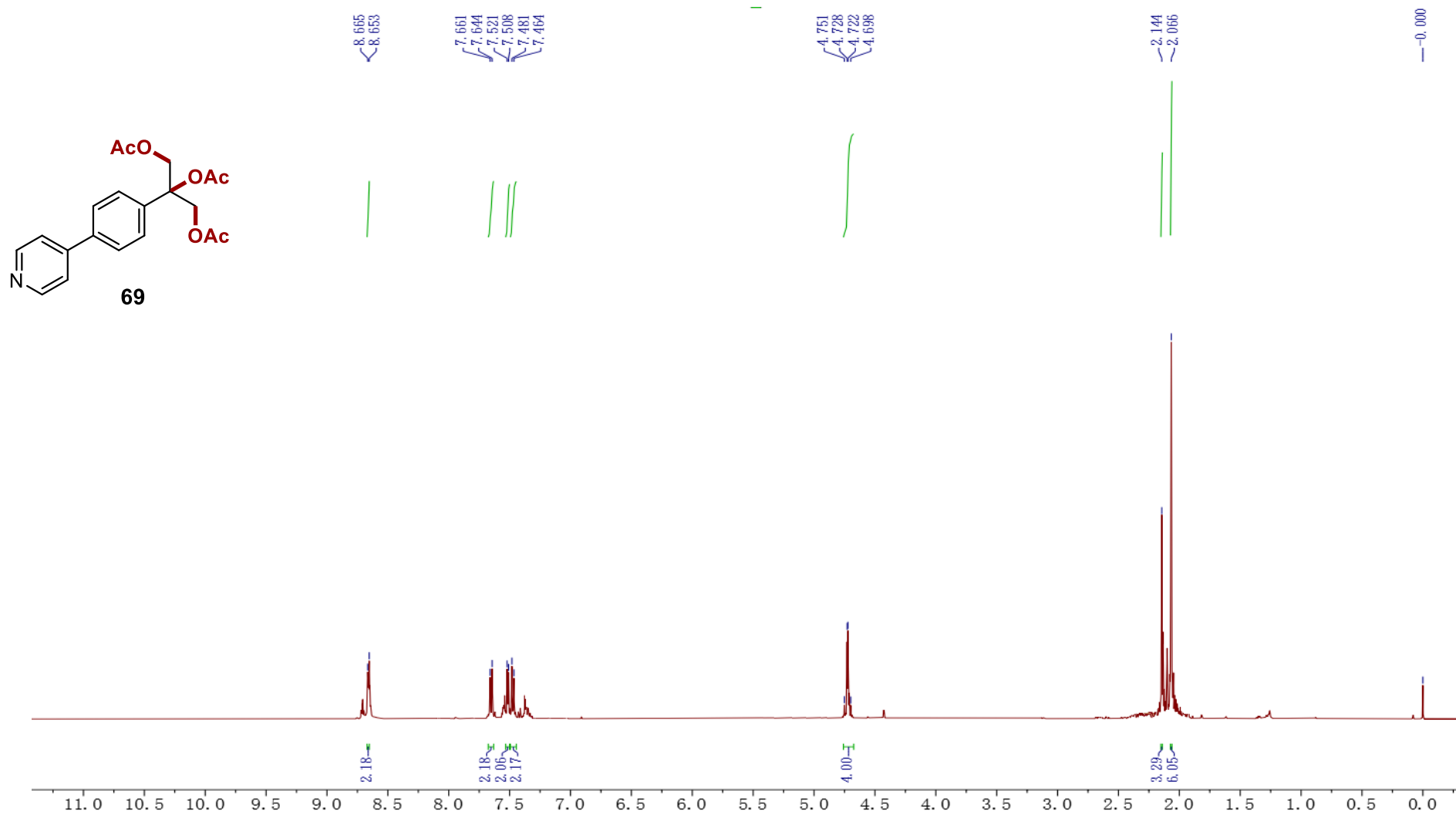


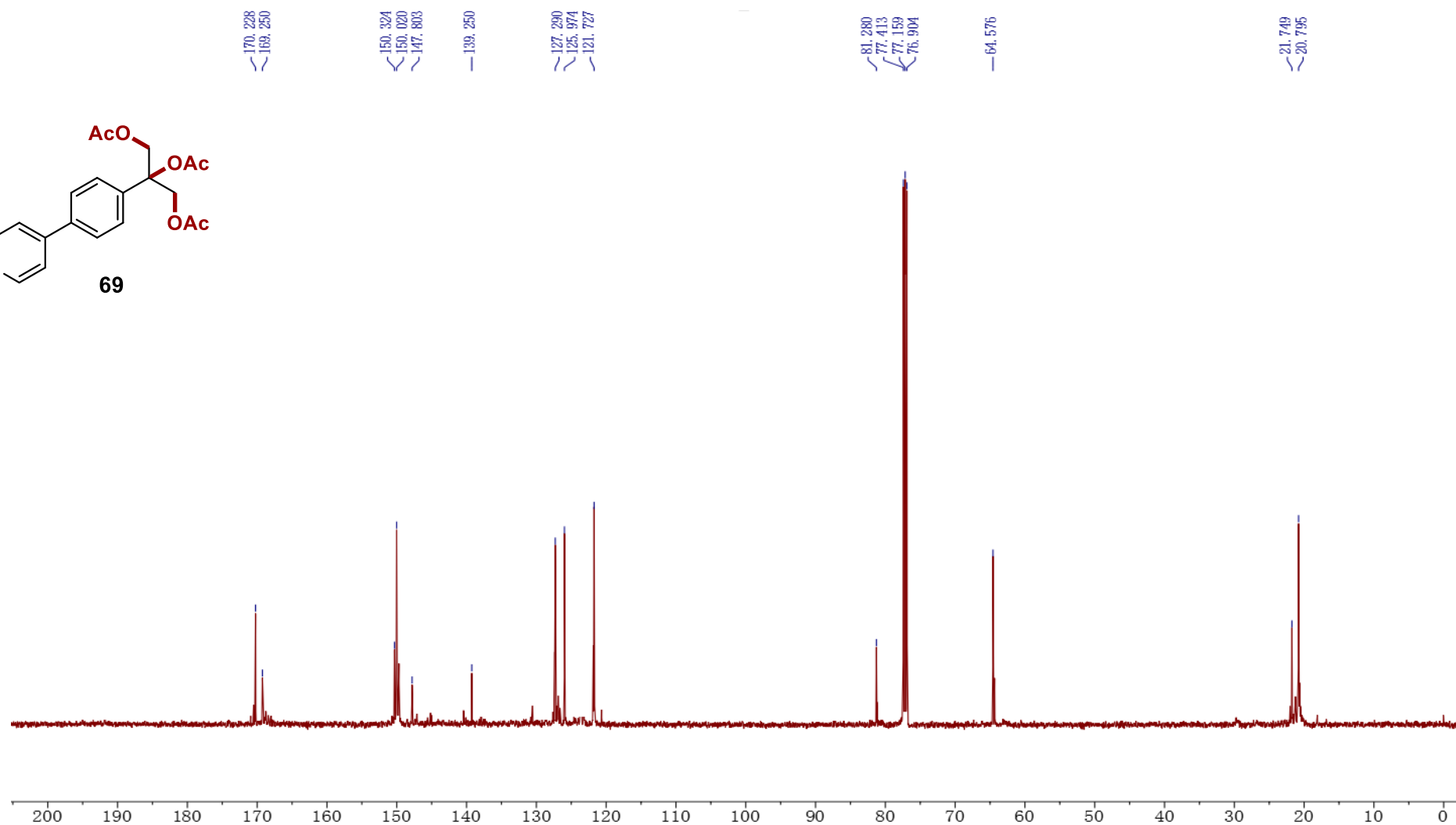
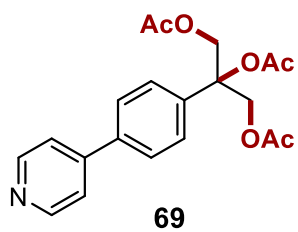


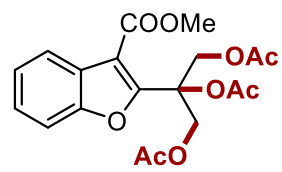
68

2:1:1

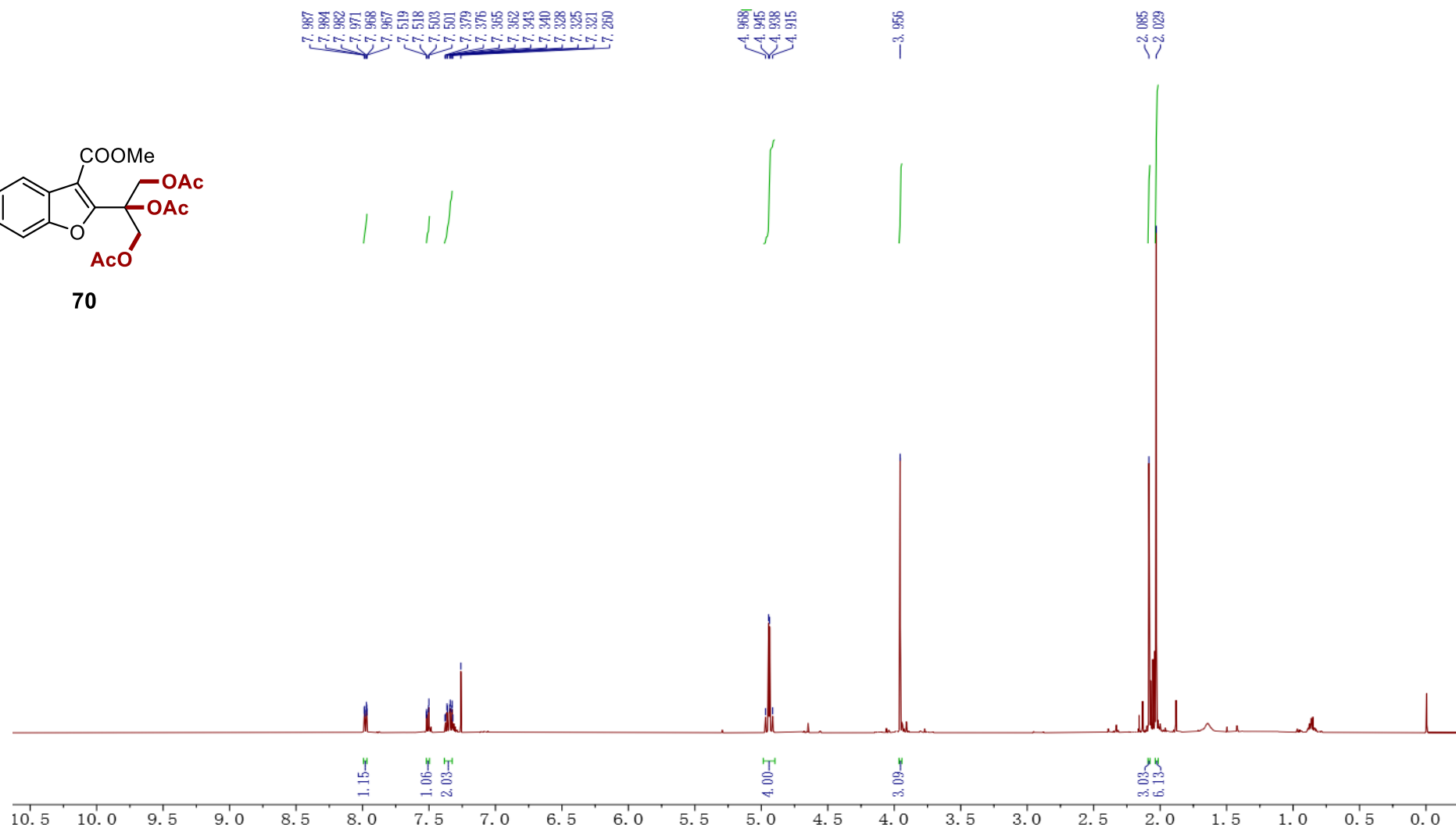


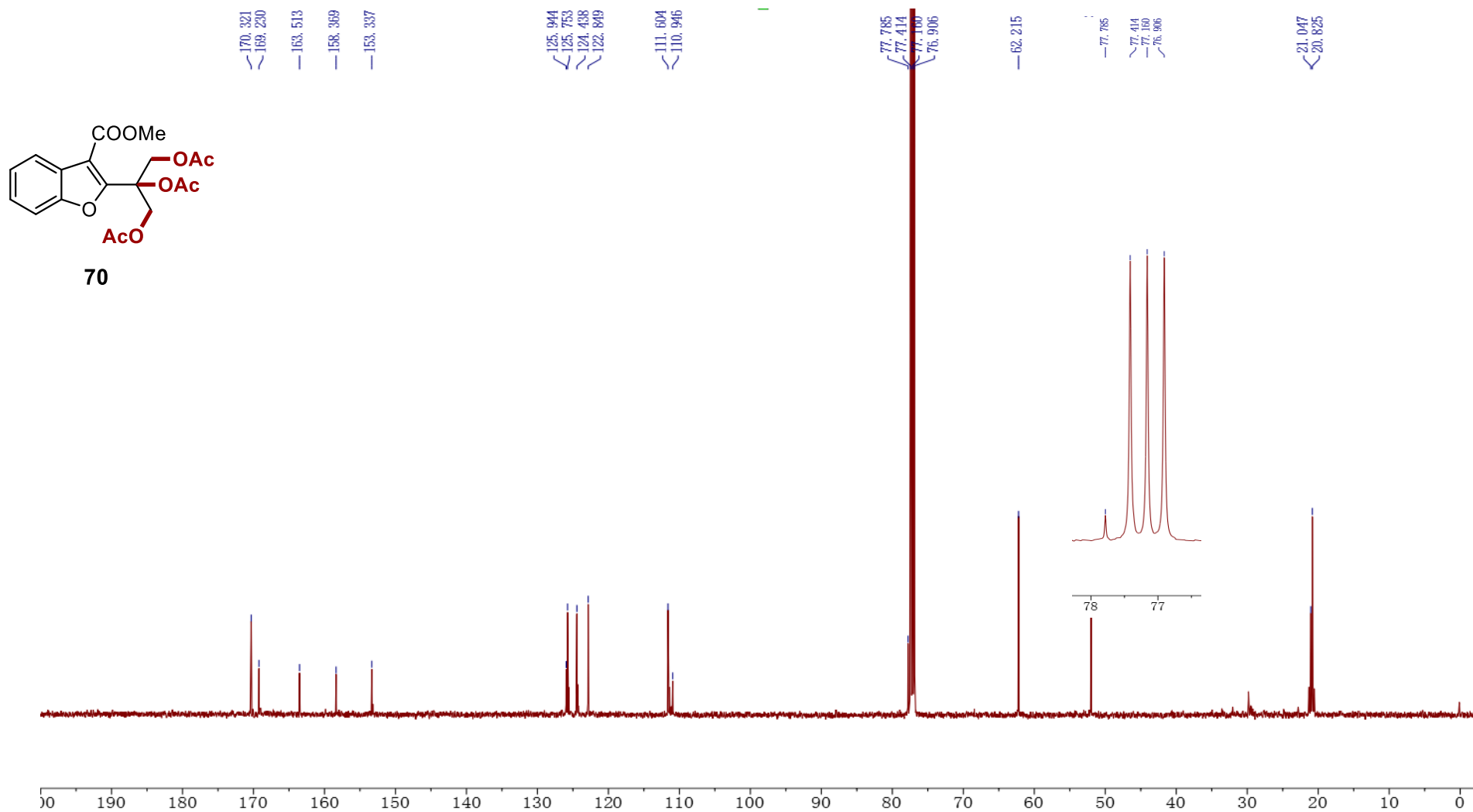


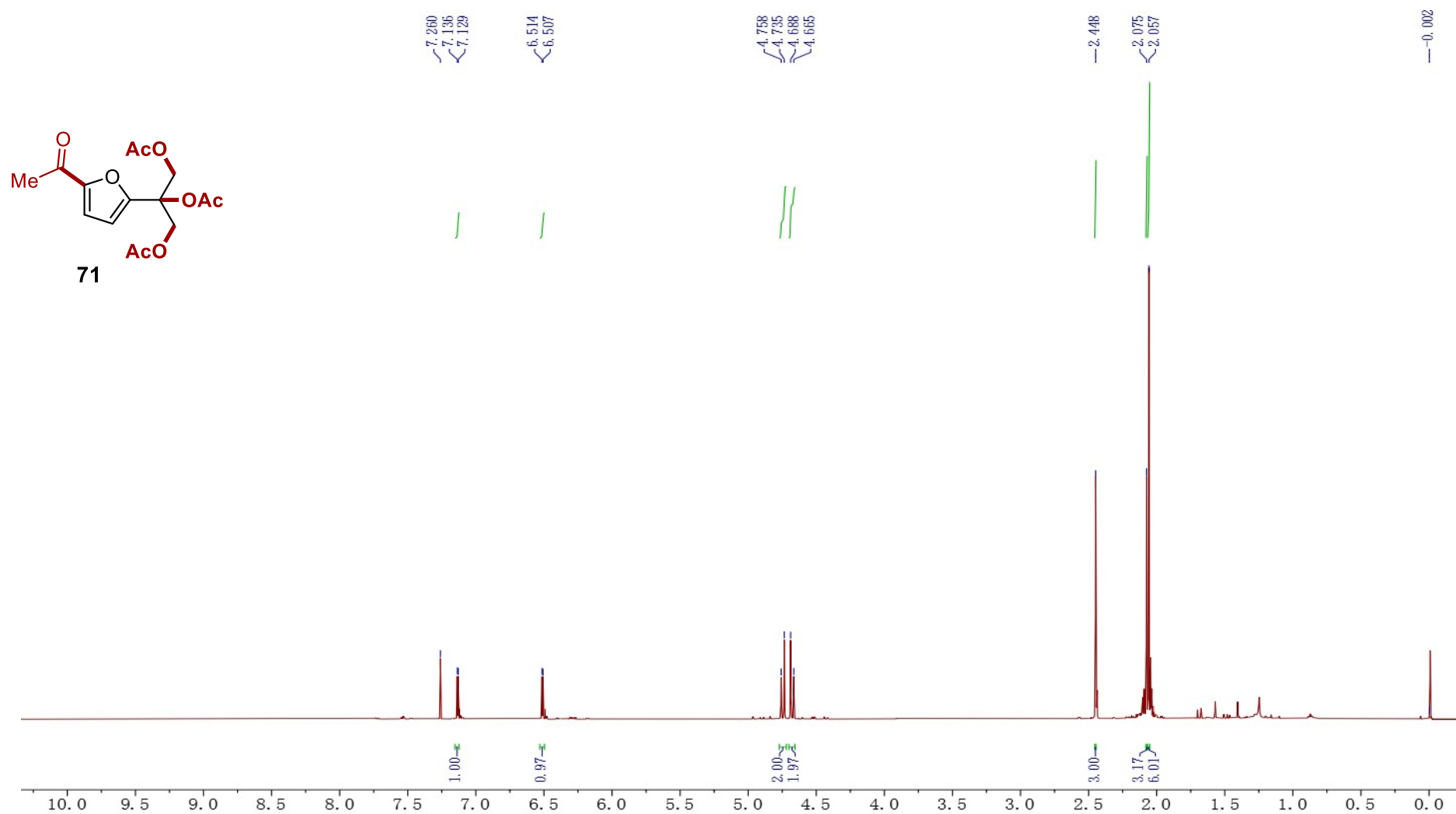


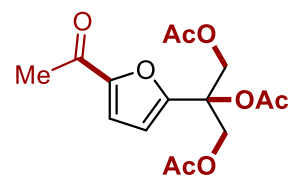


70

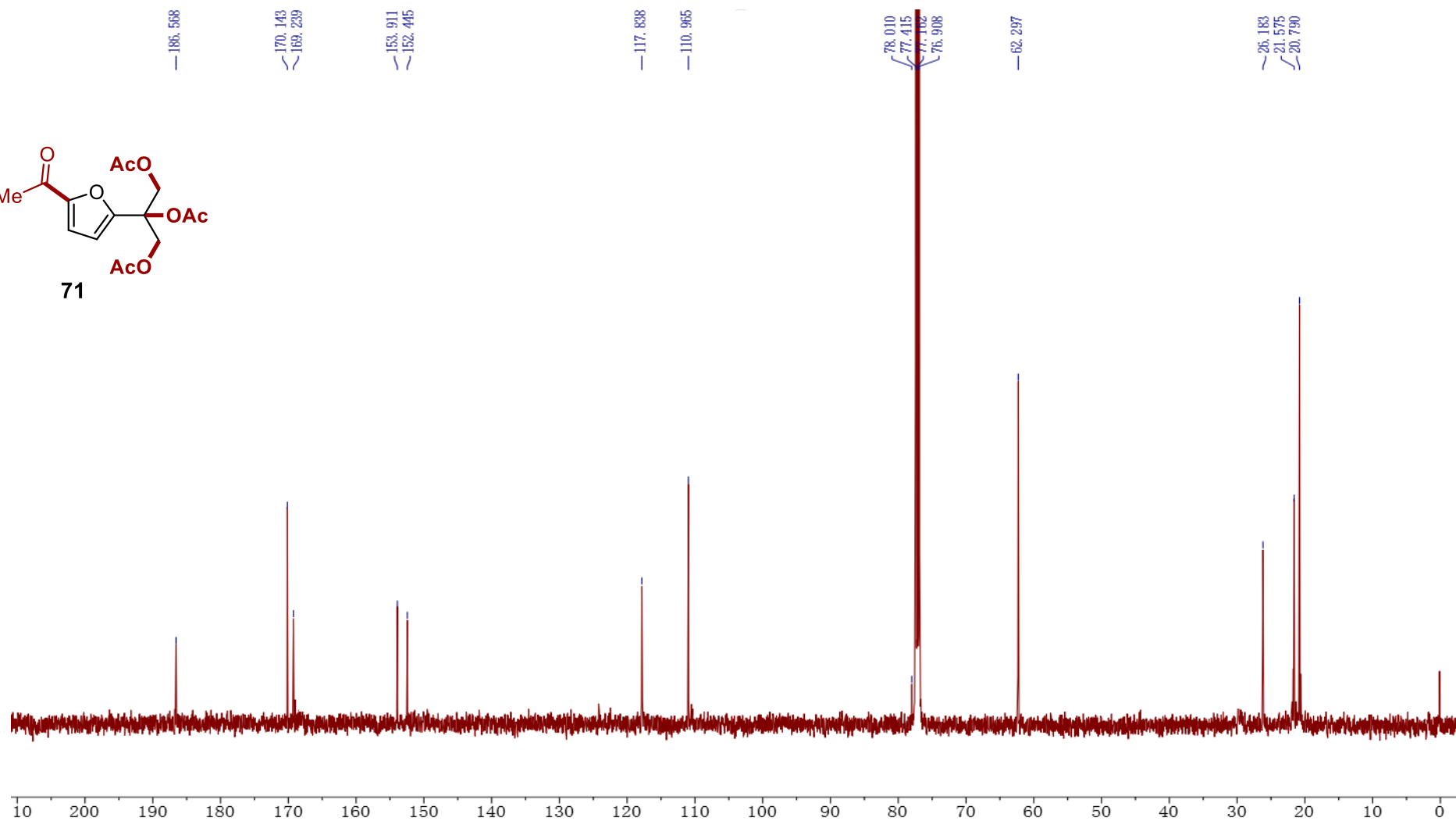


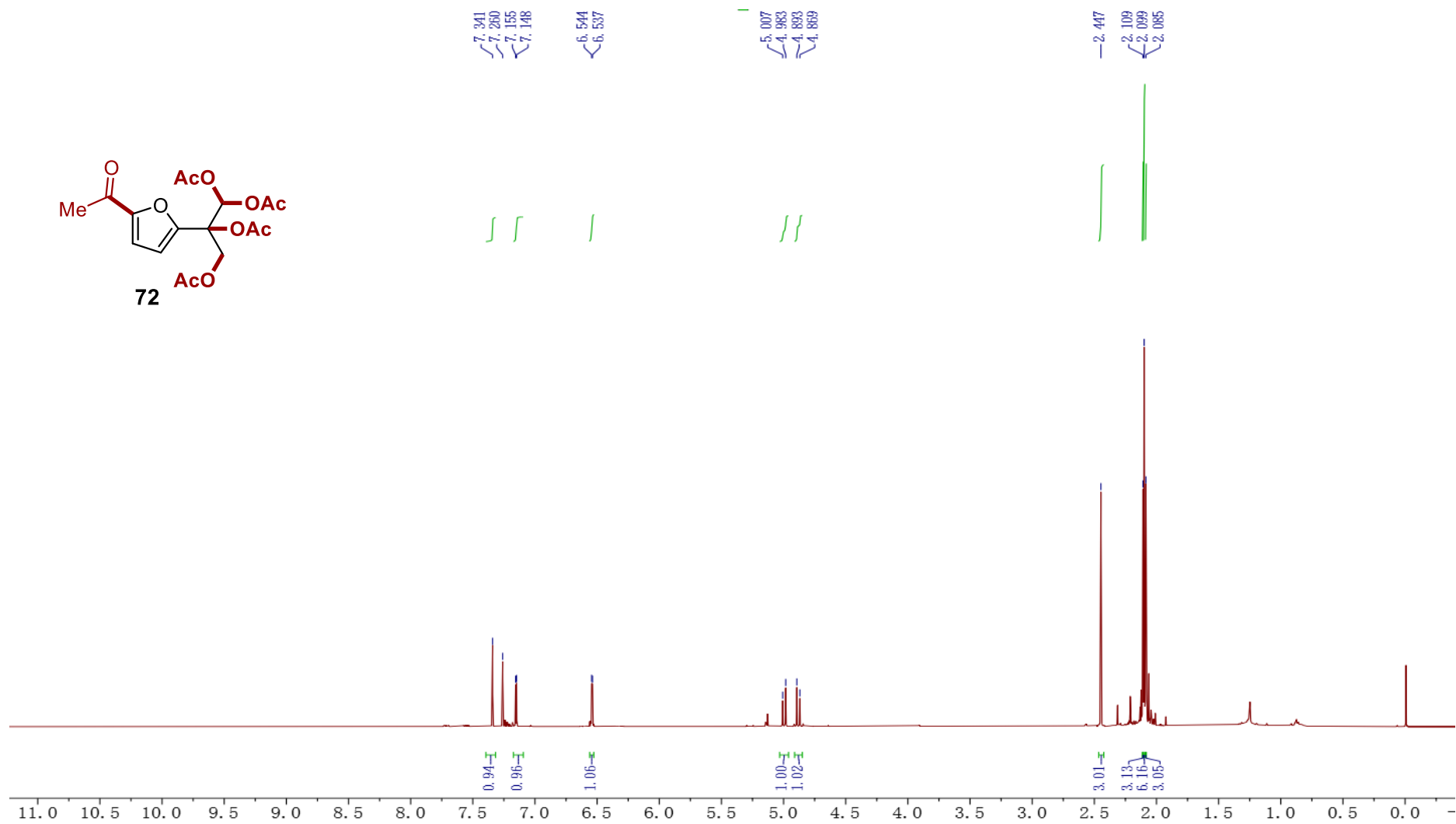
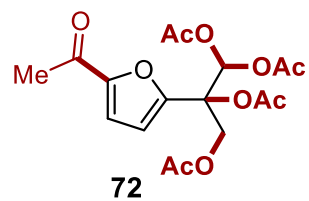


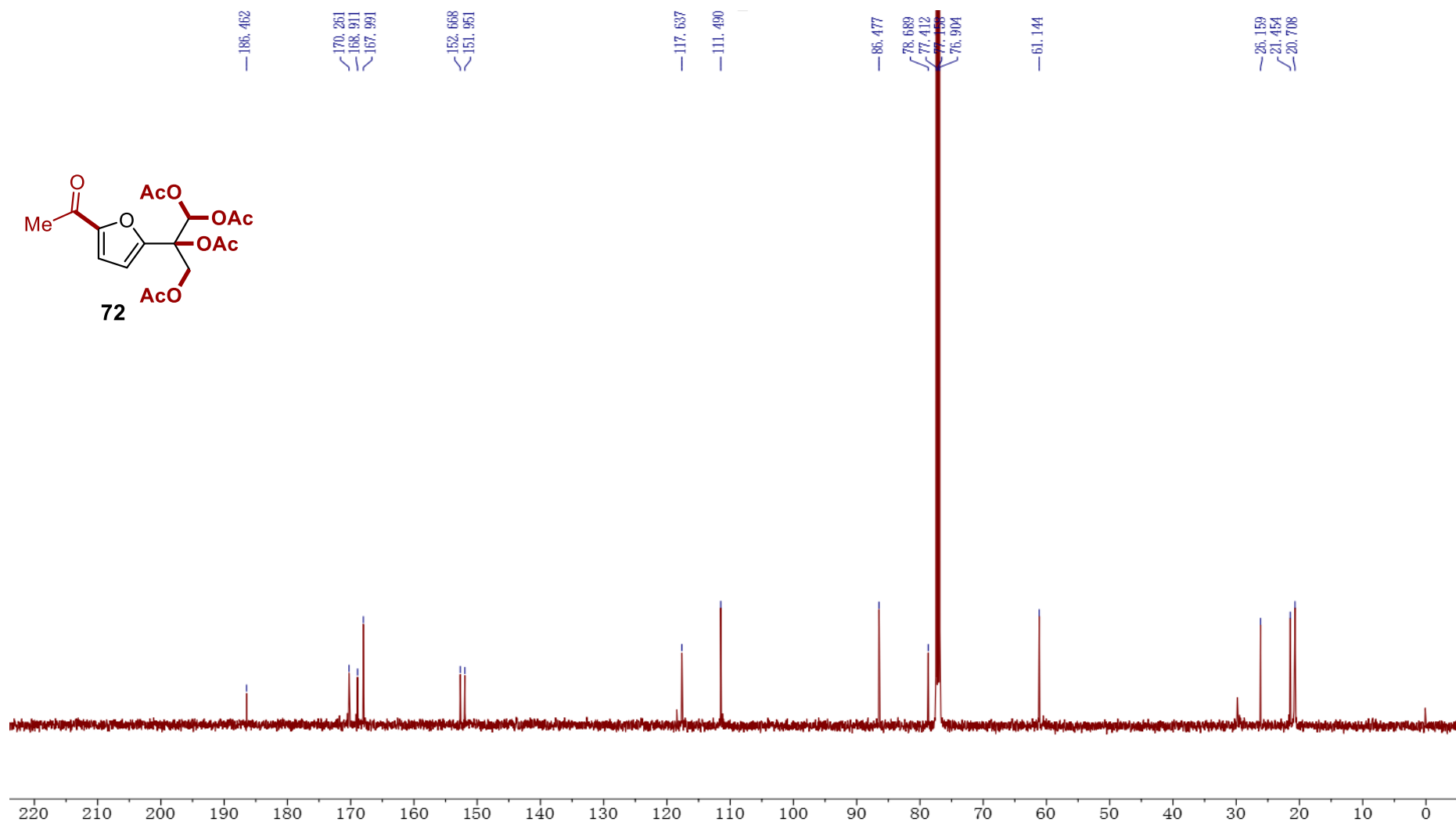


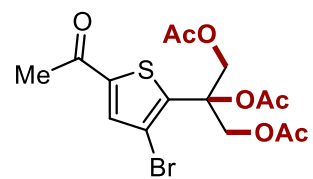


71

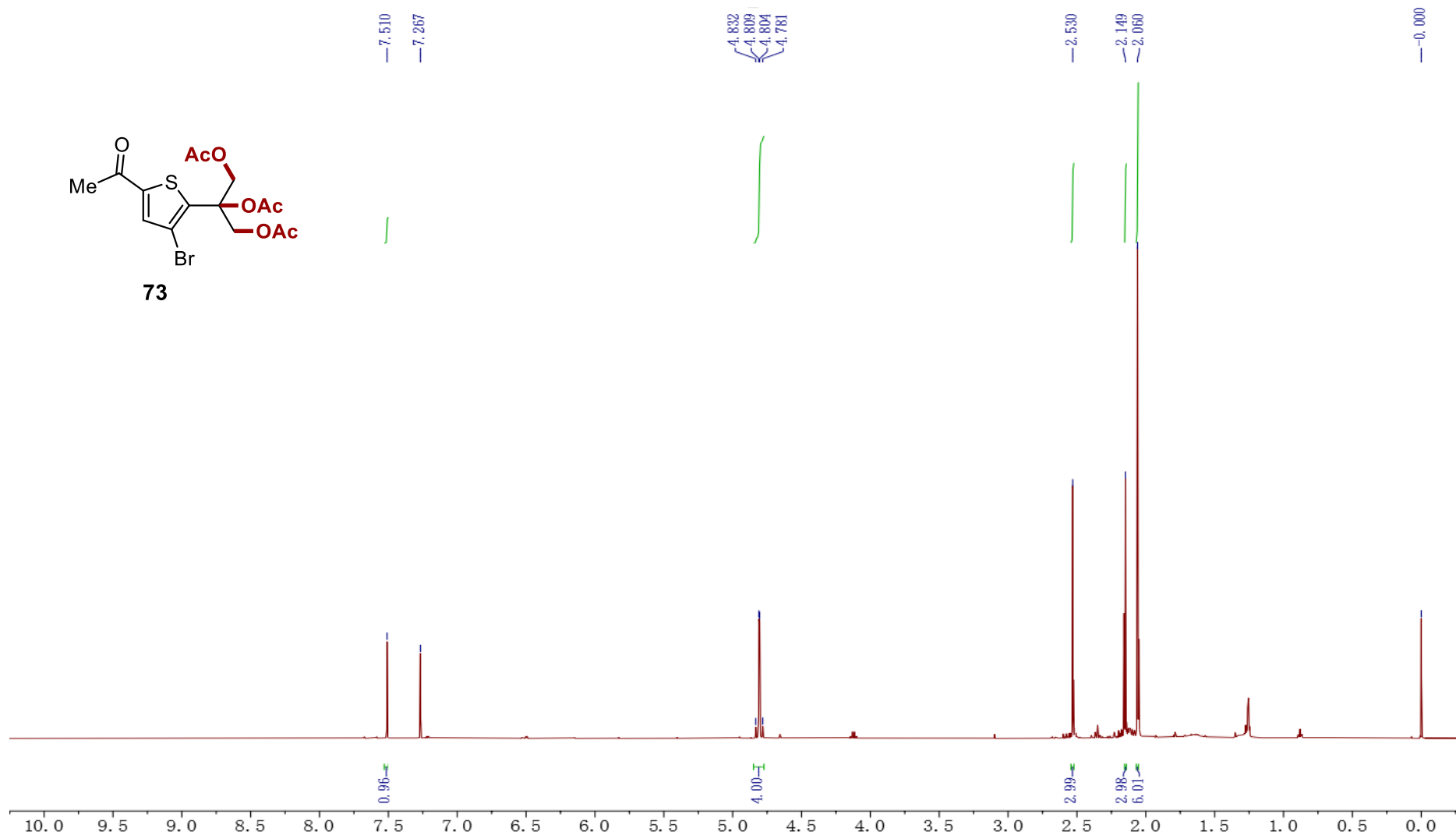


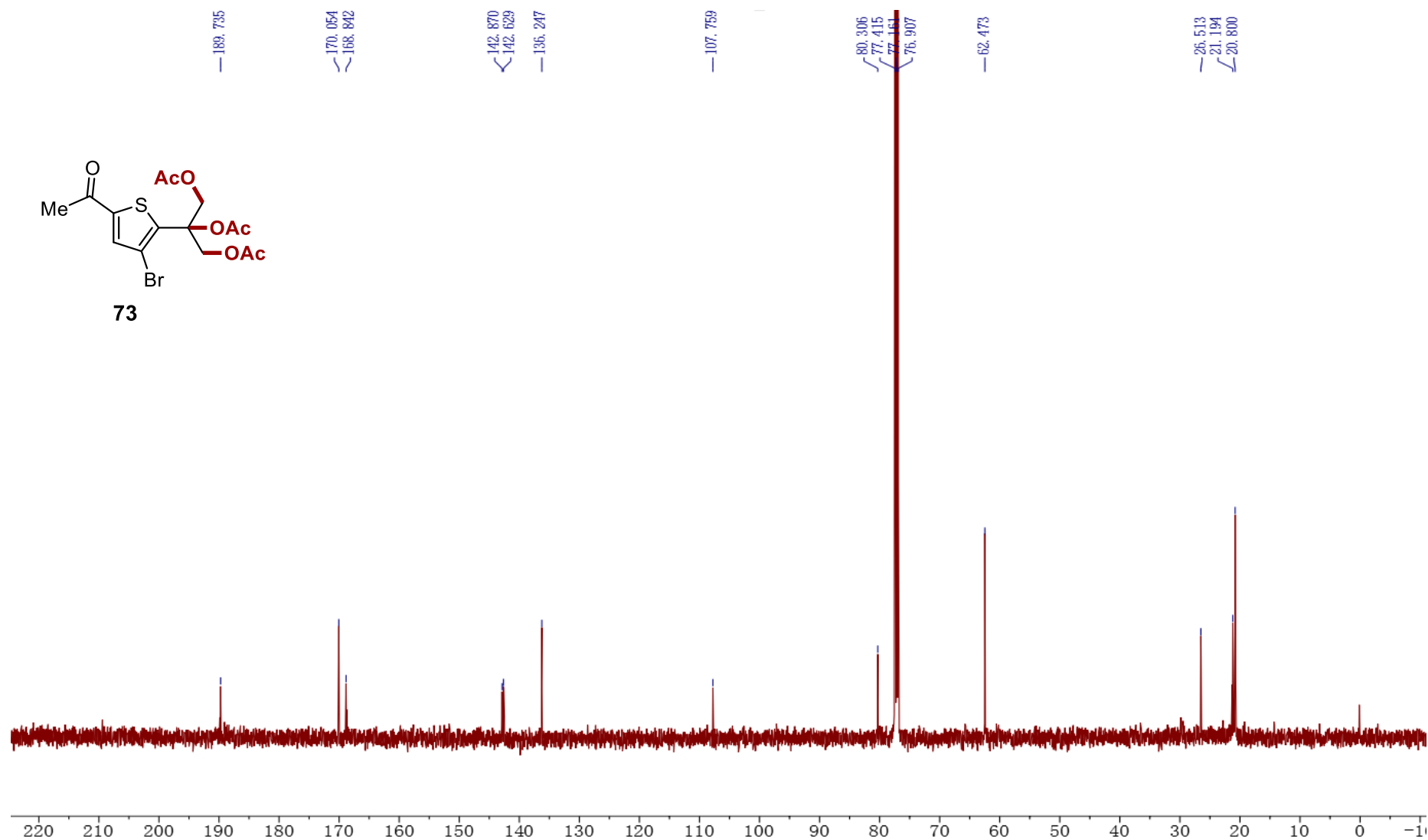
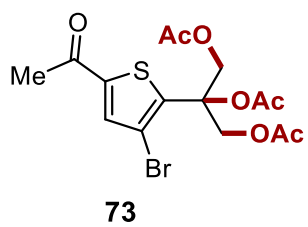


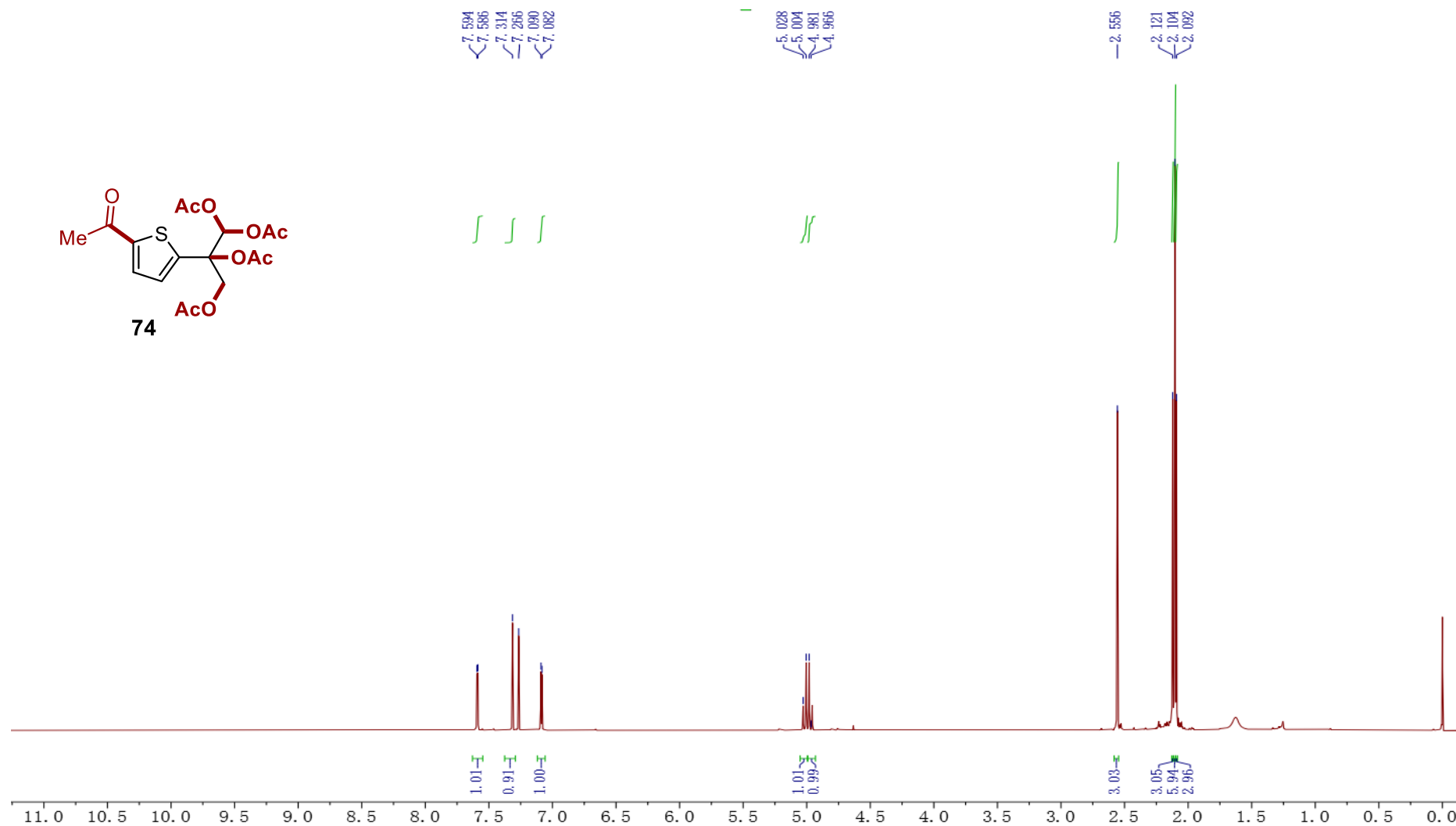
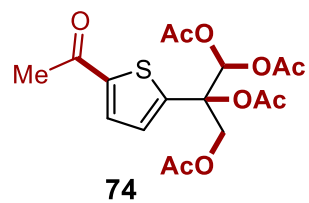


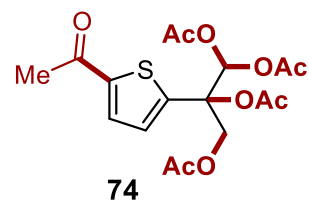


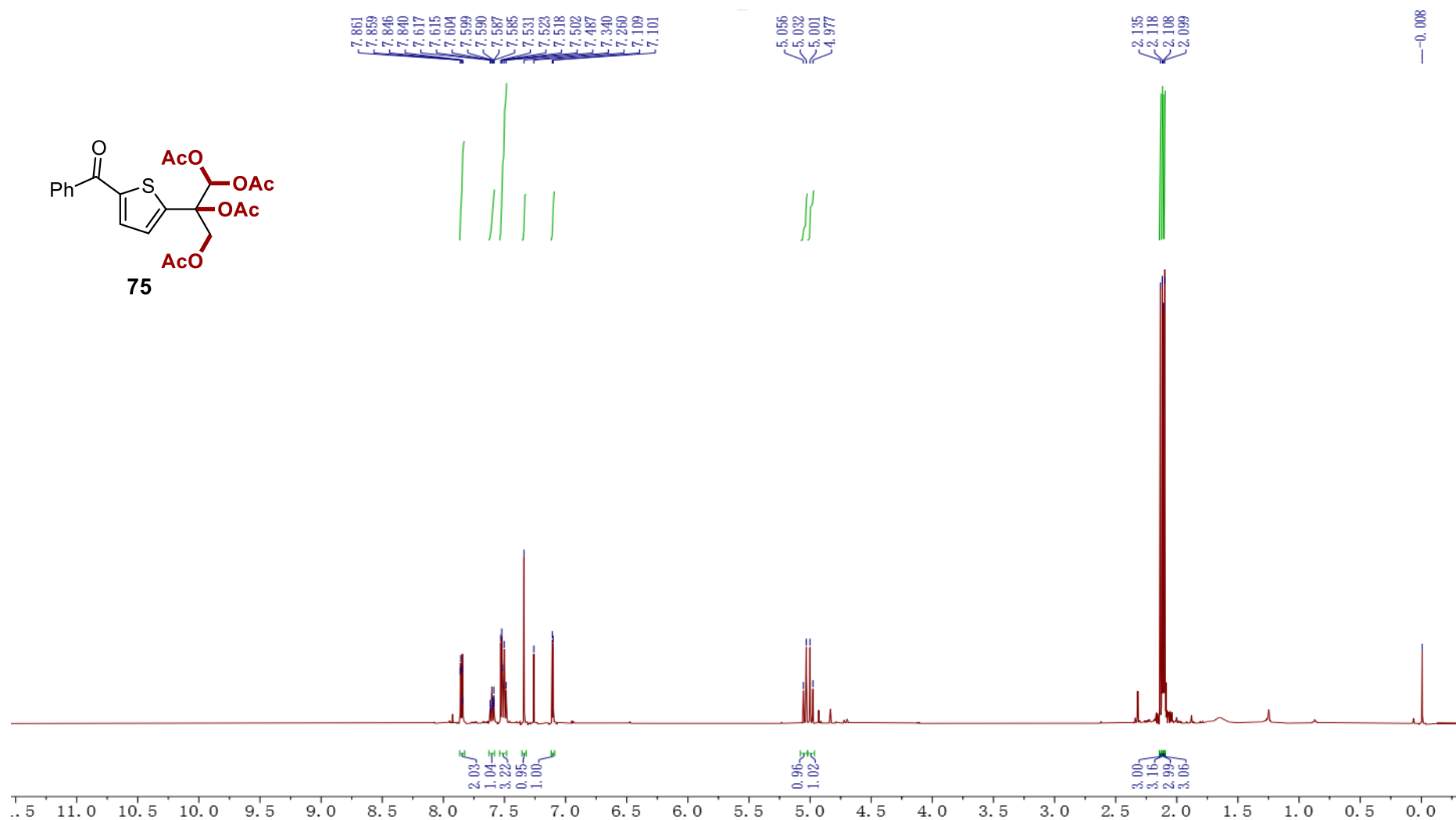
73

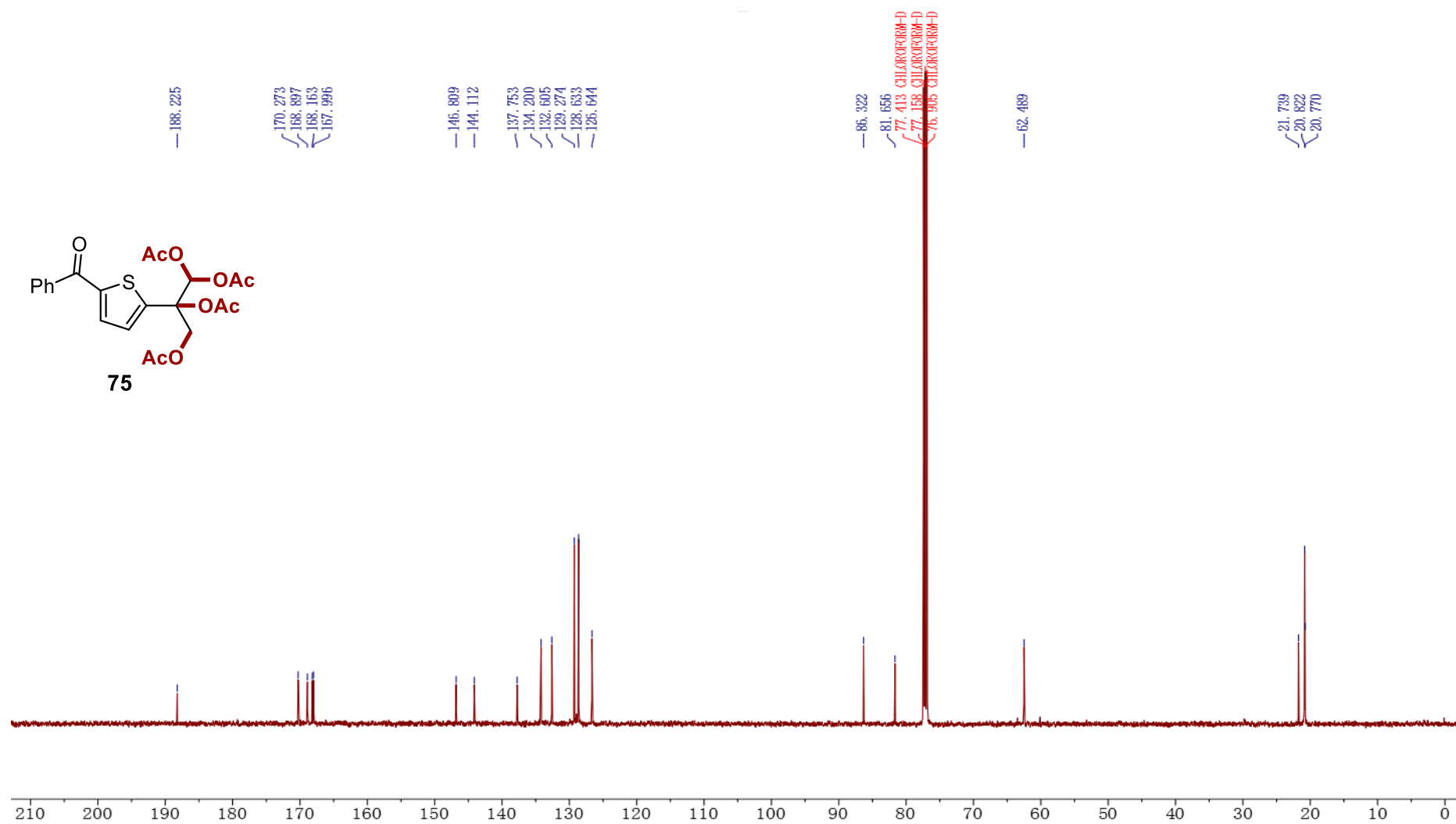


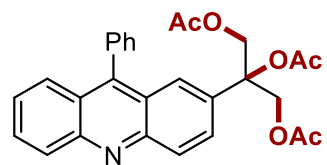




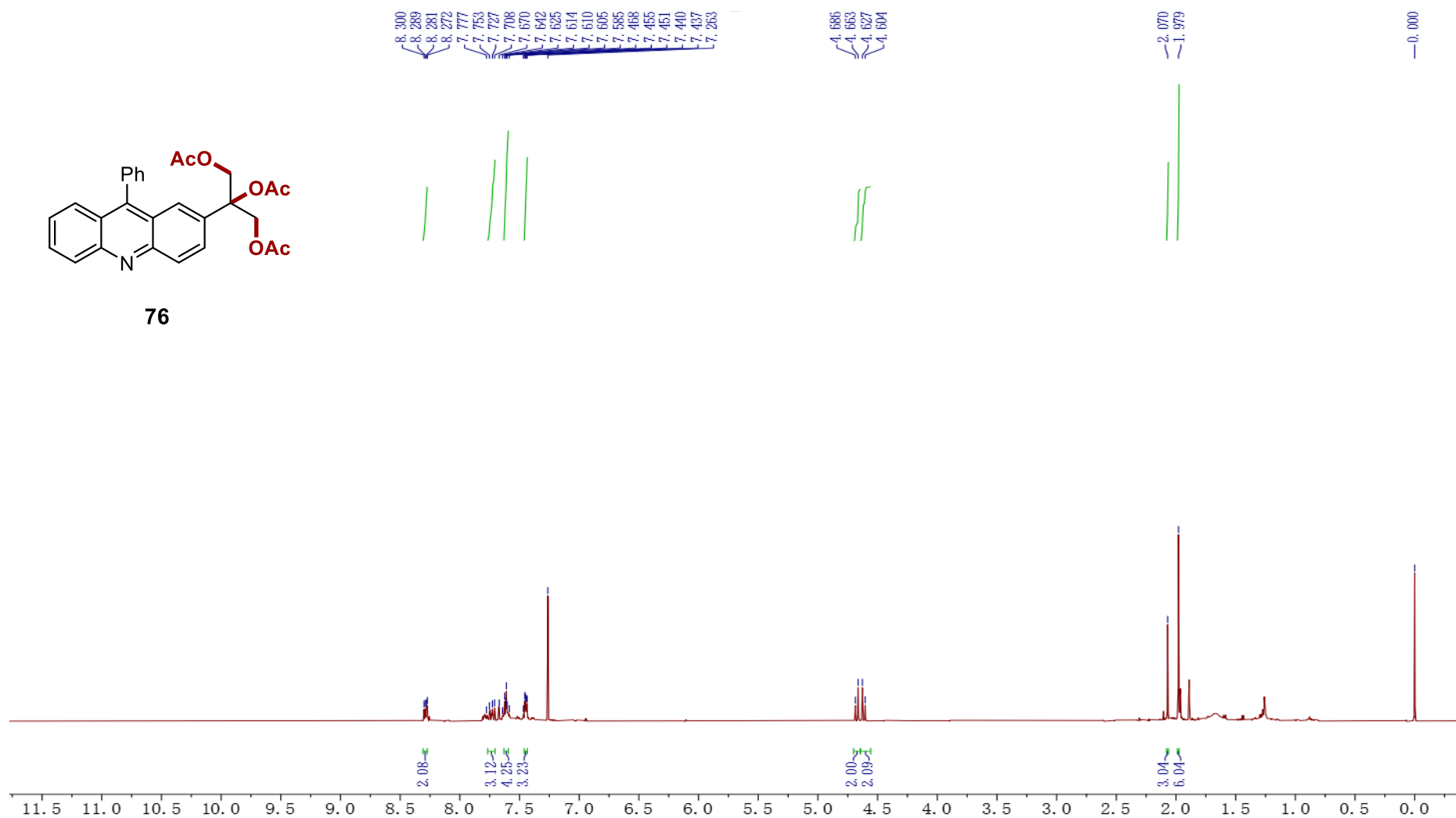


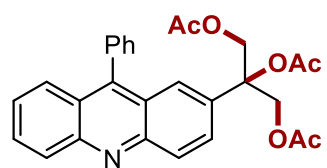




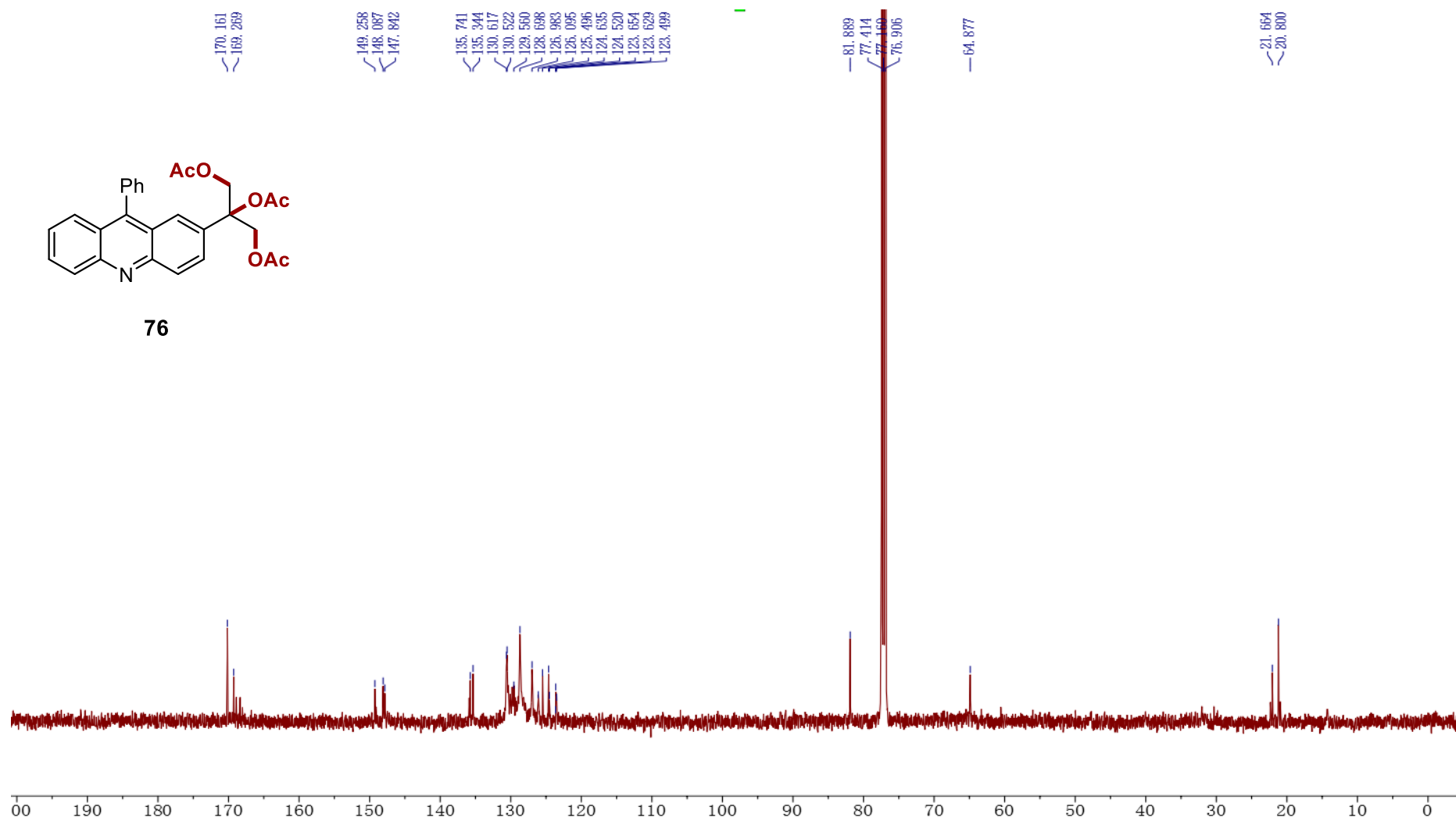


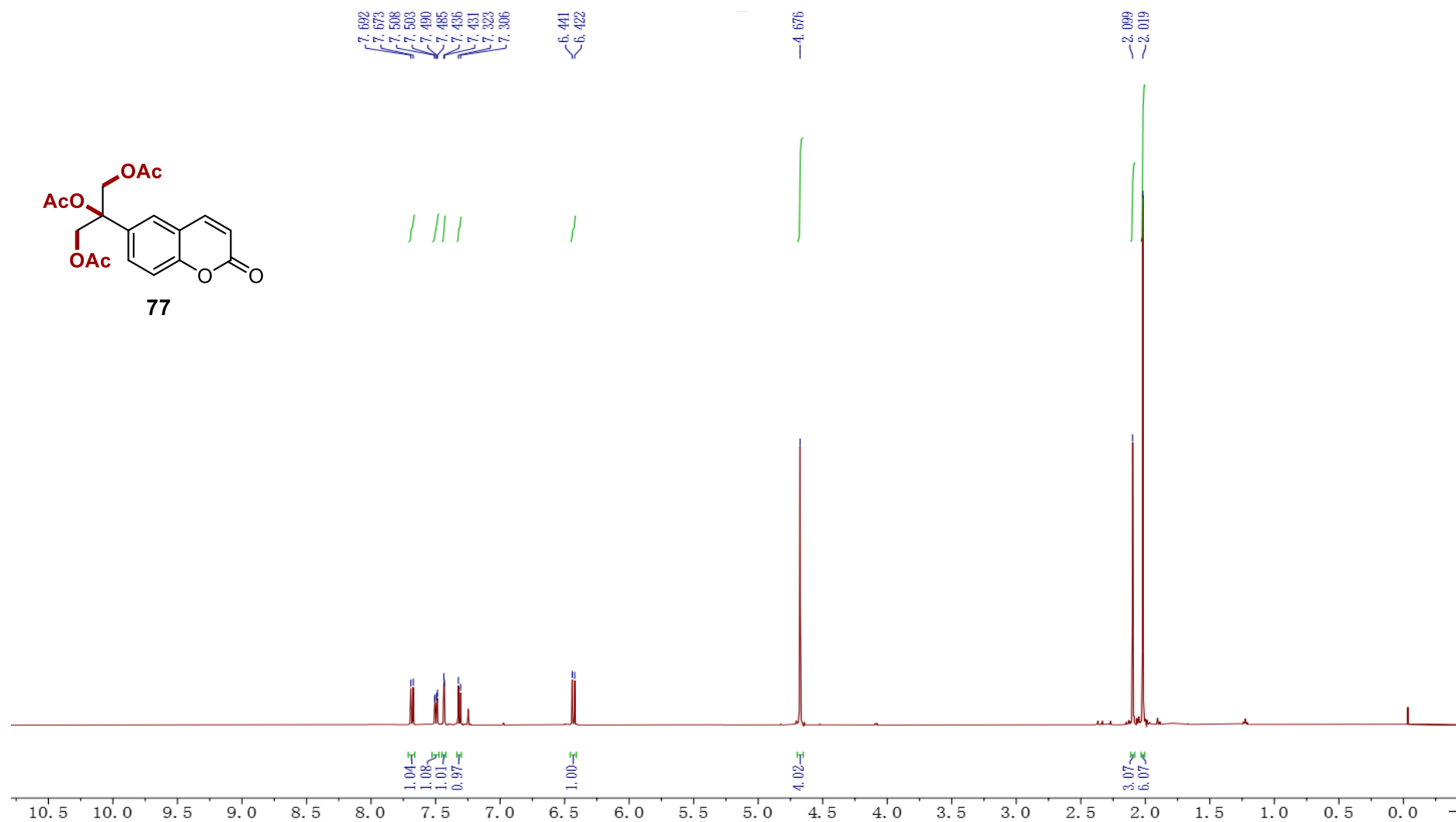
76

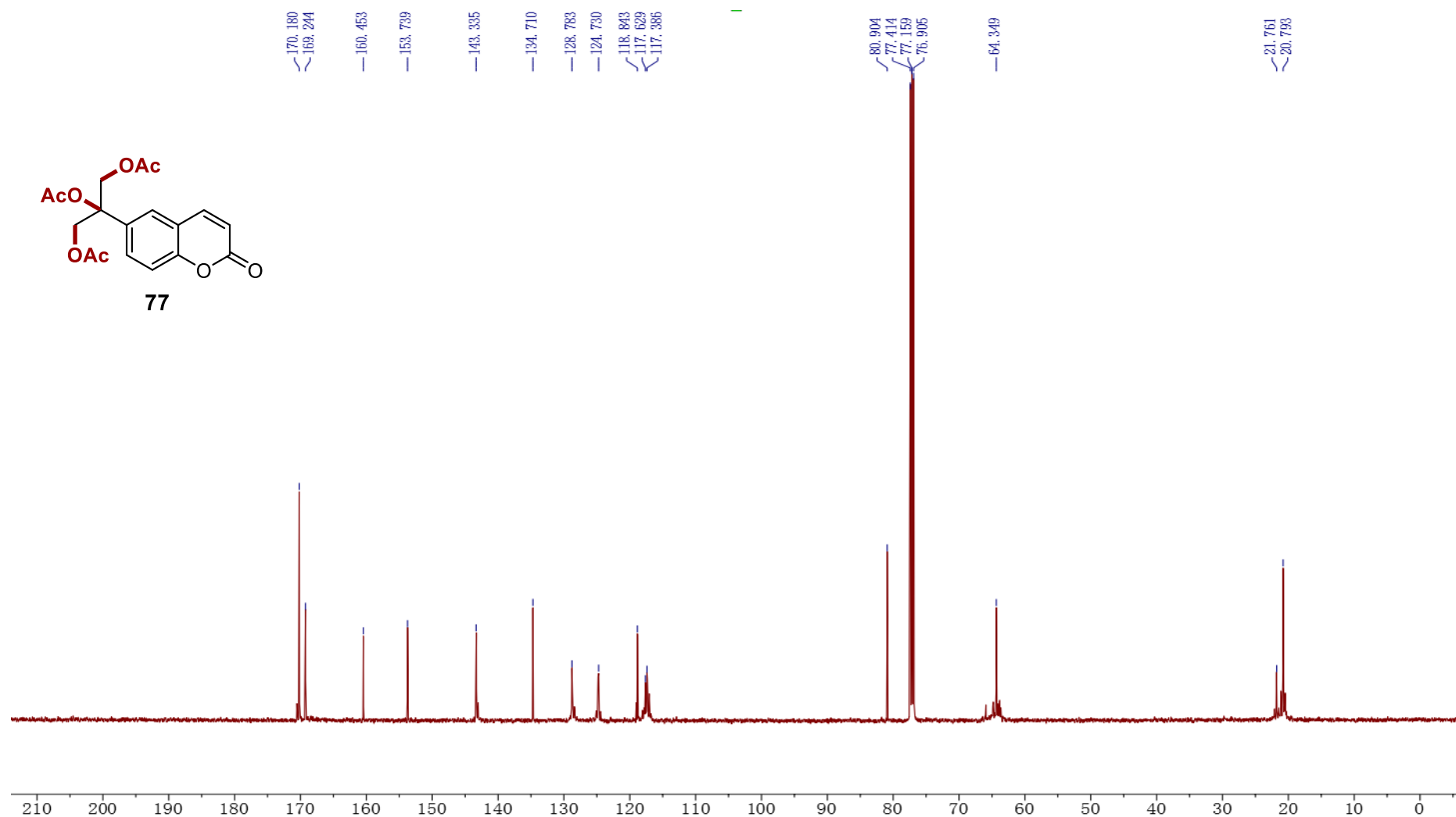


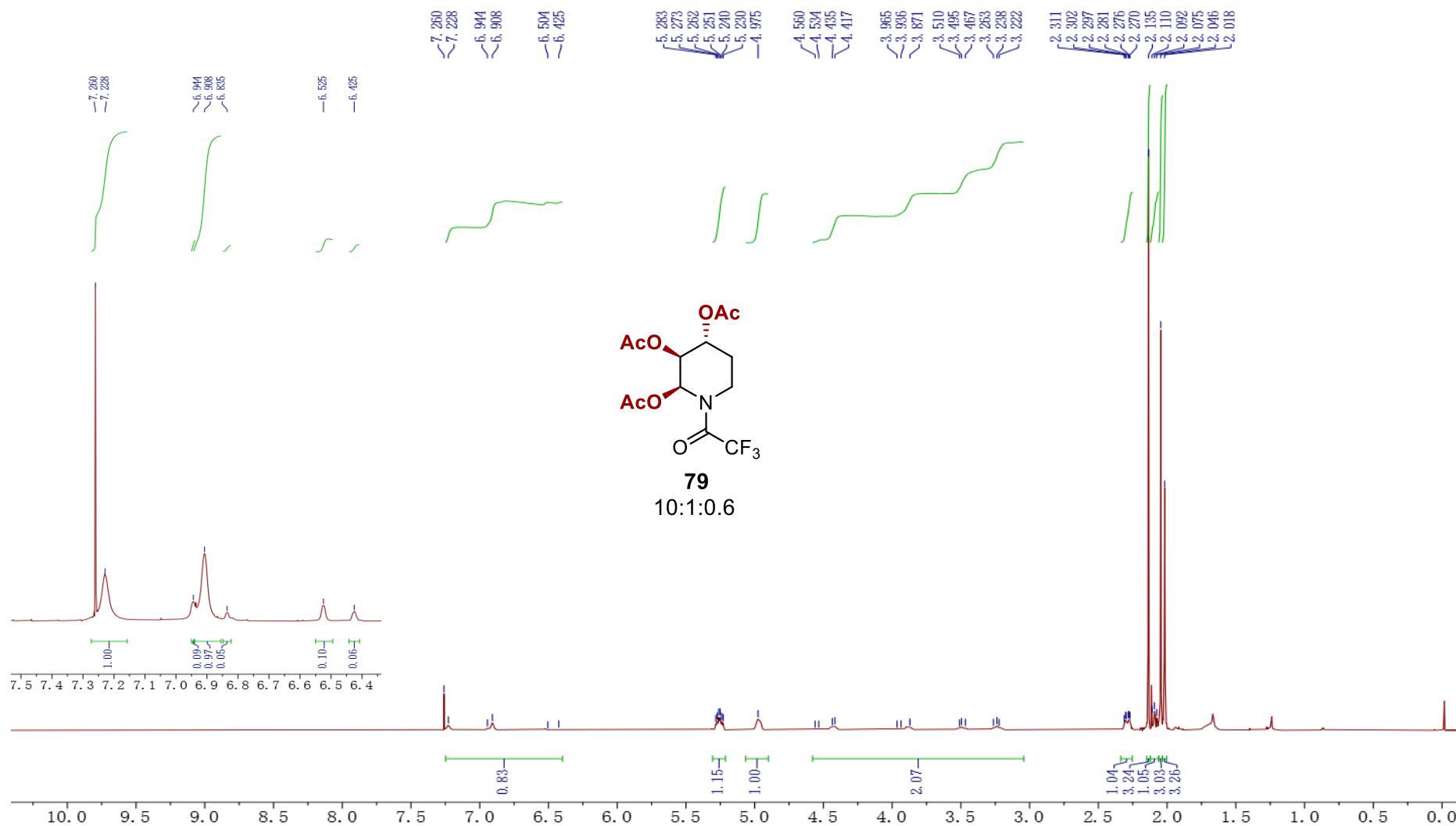


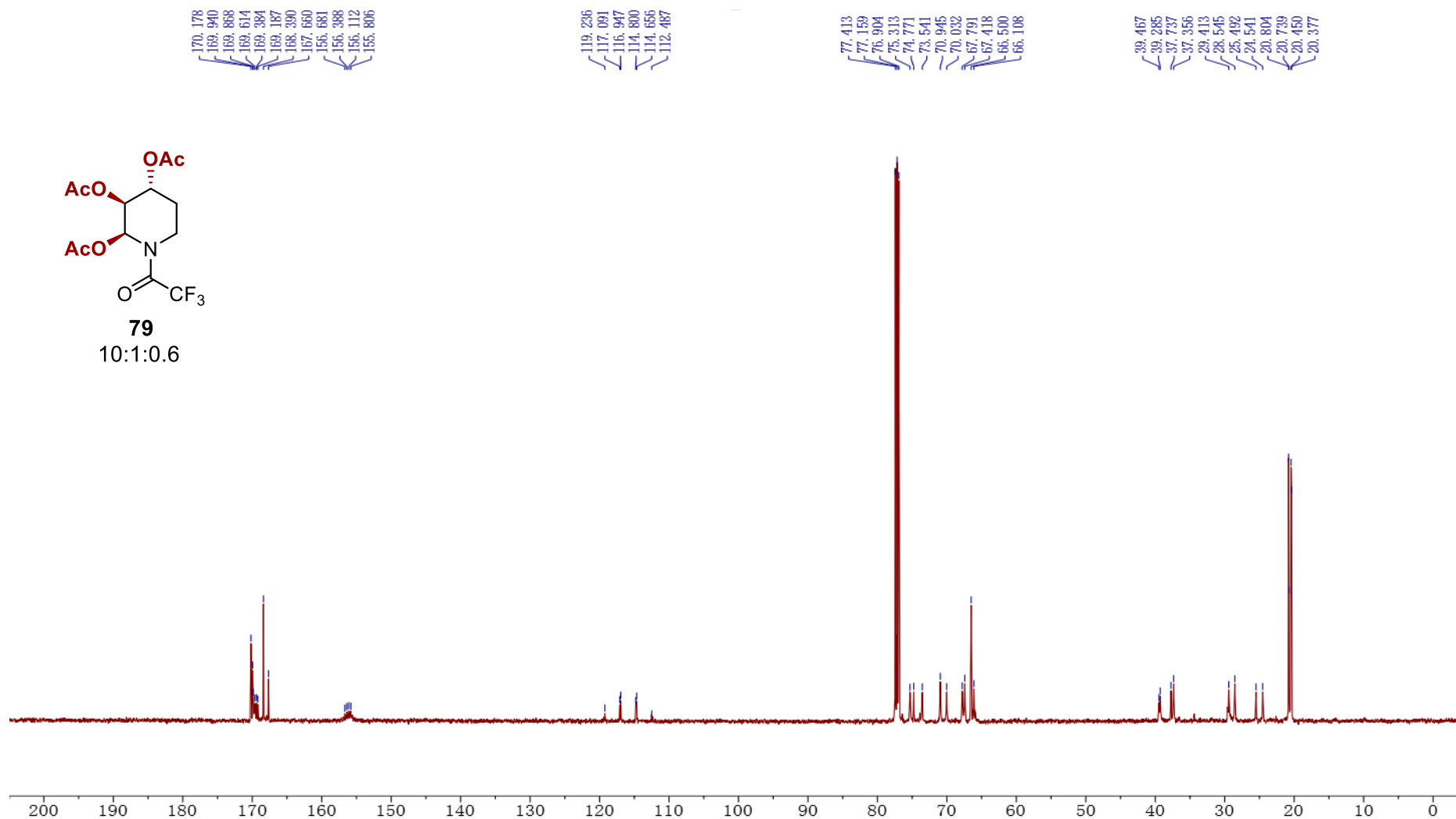
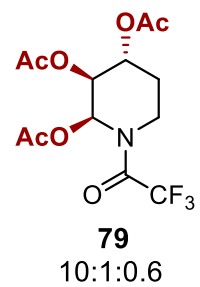
76

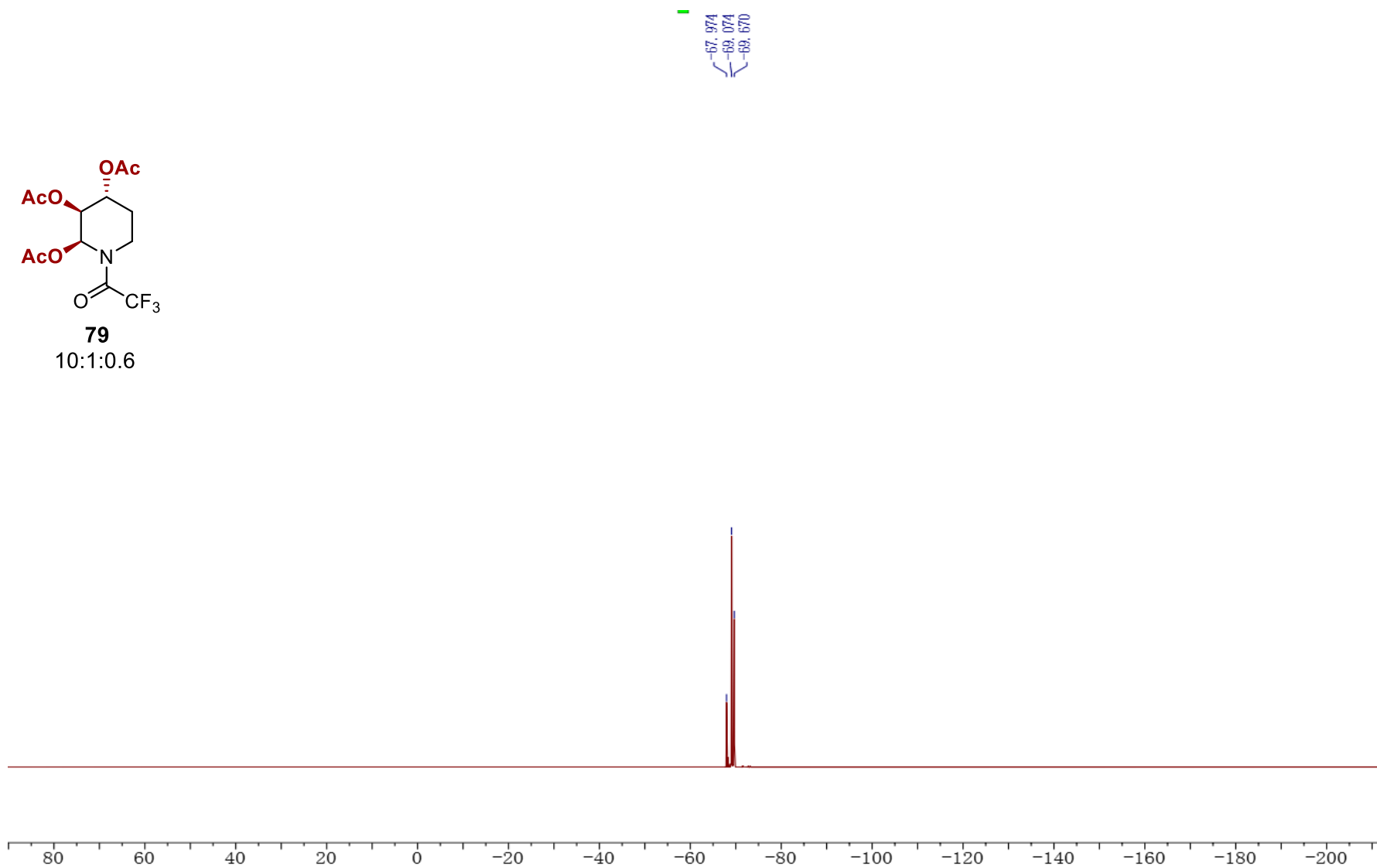
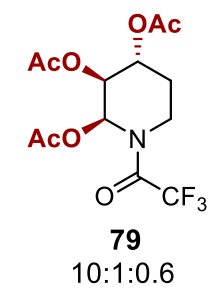


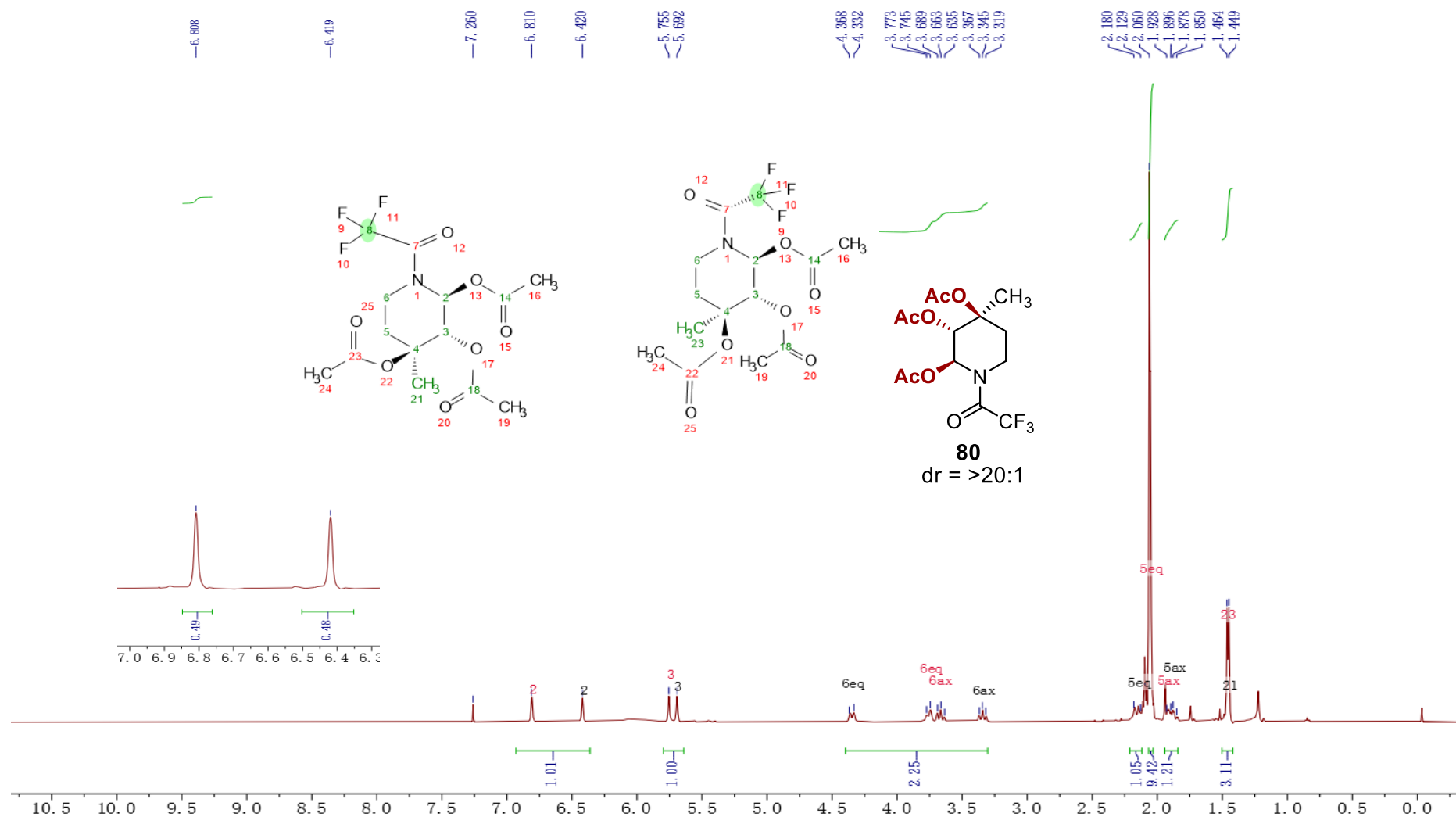


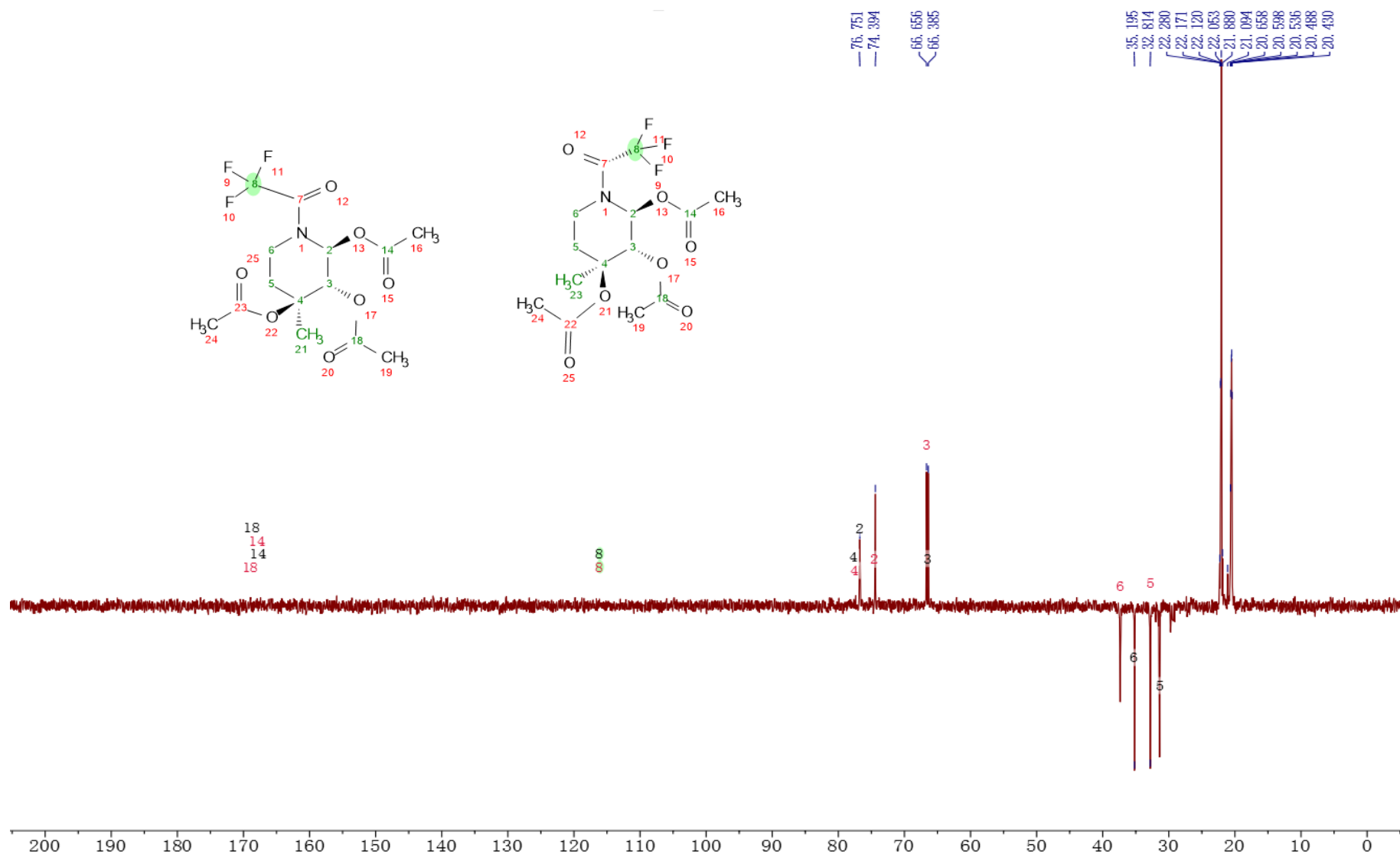




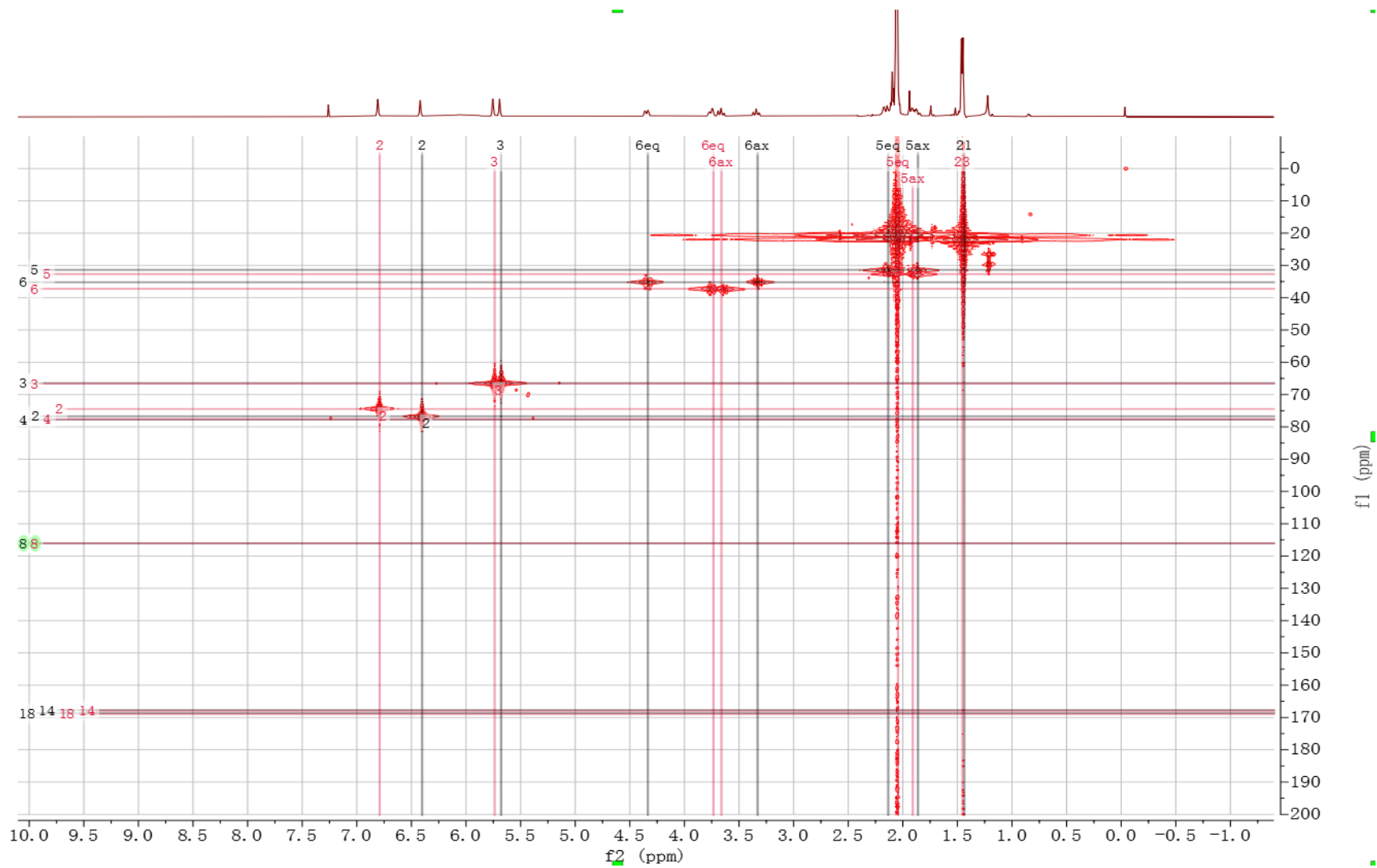


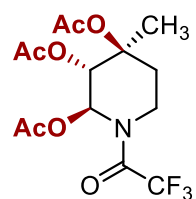






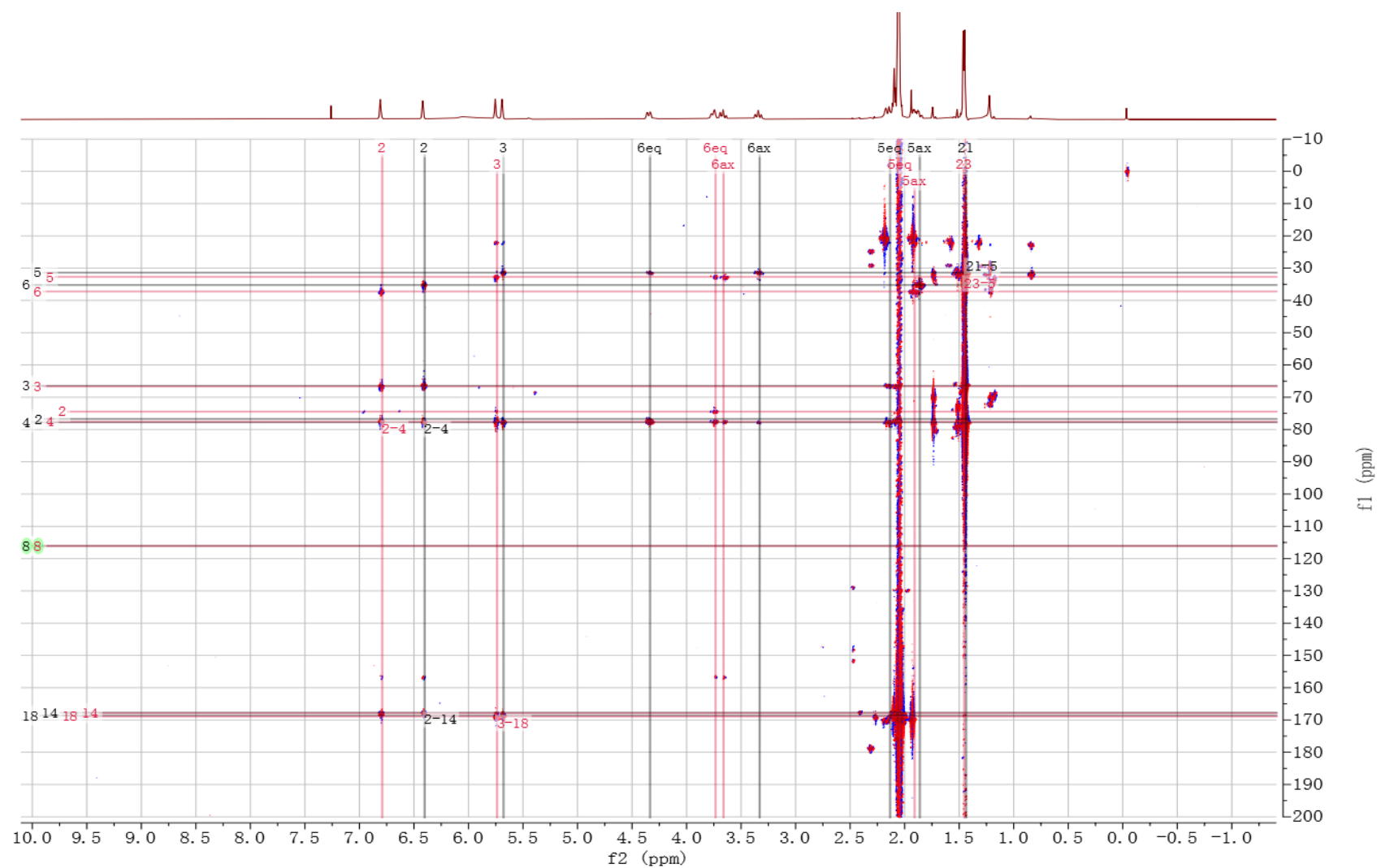


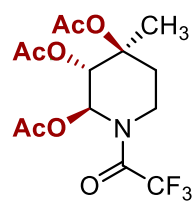




80

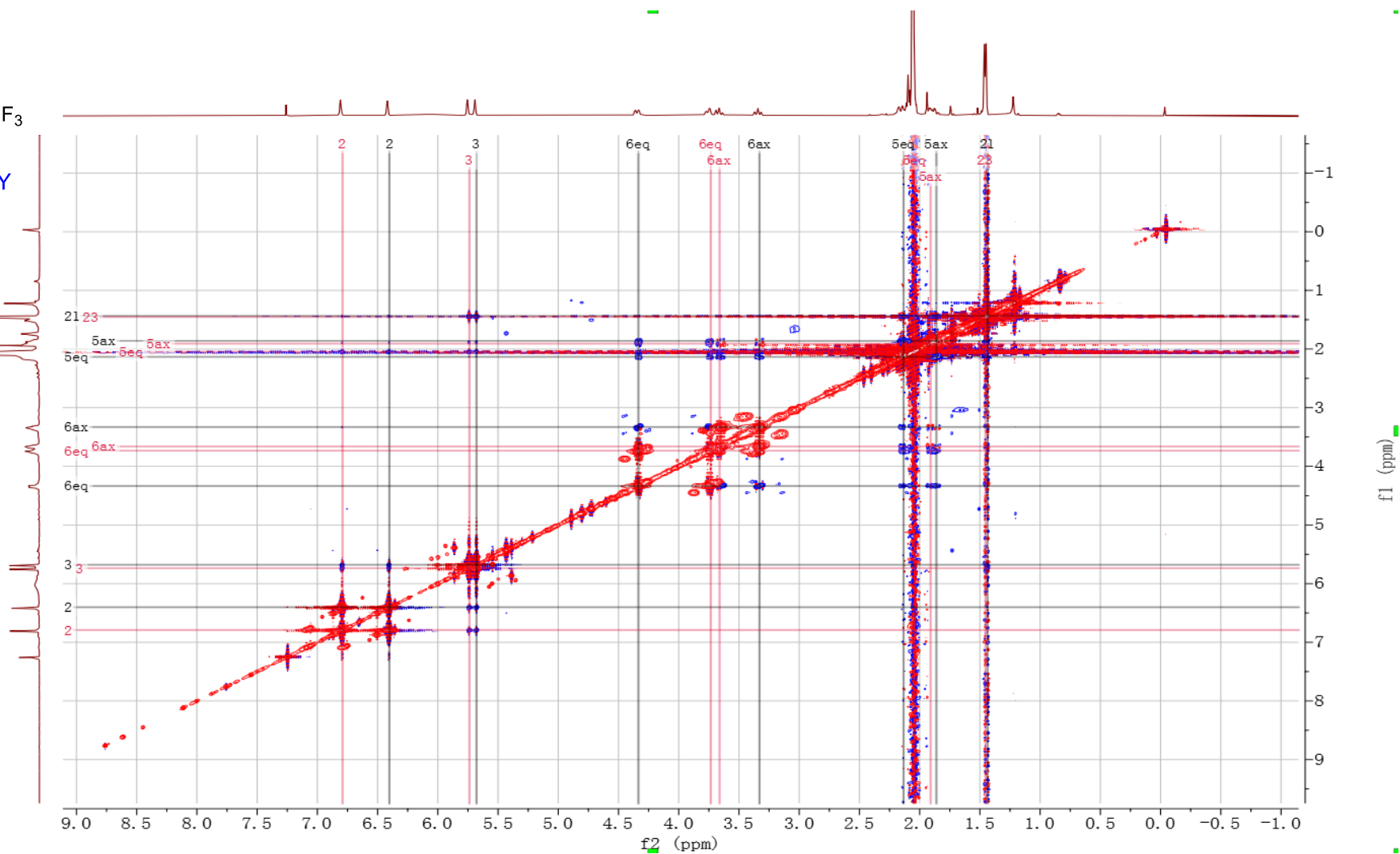
HMBC

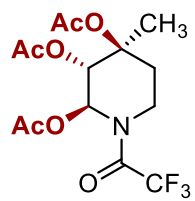




80

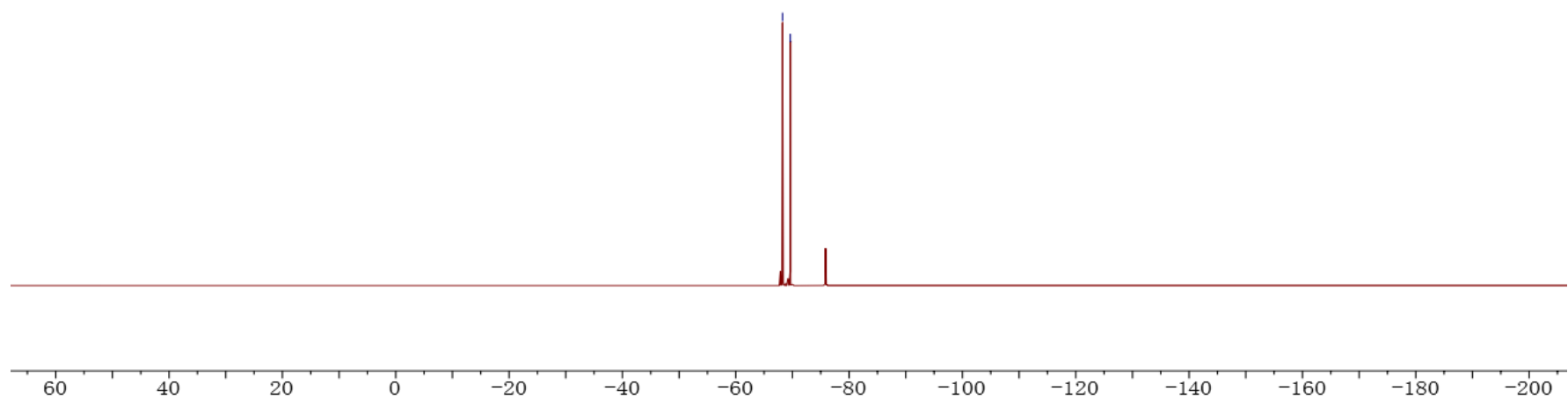
NOESY

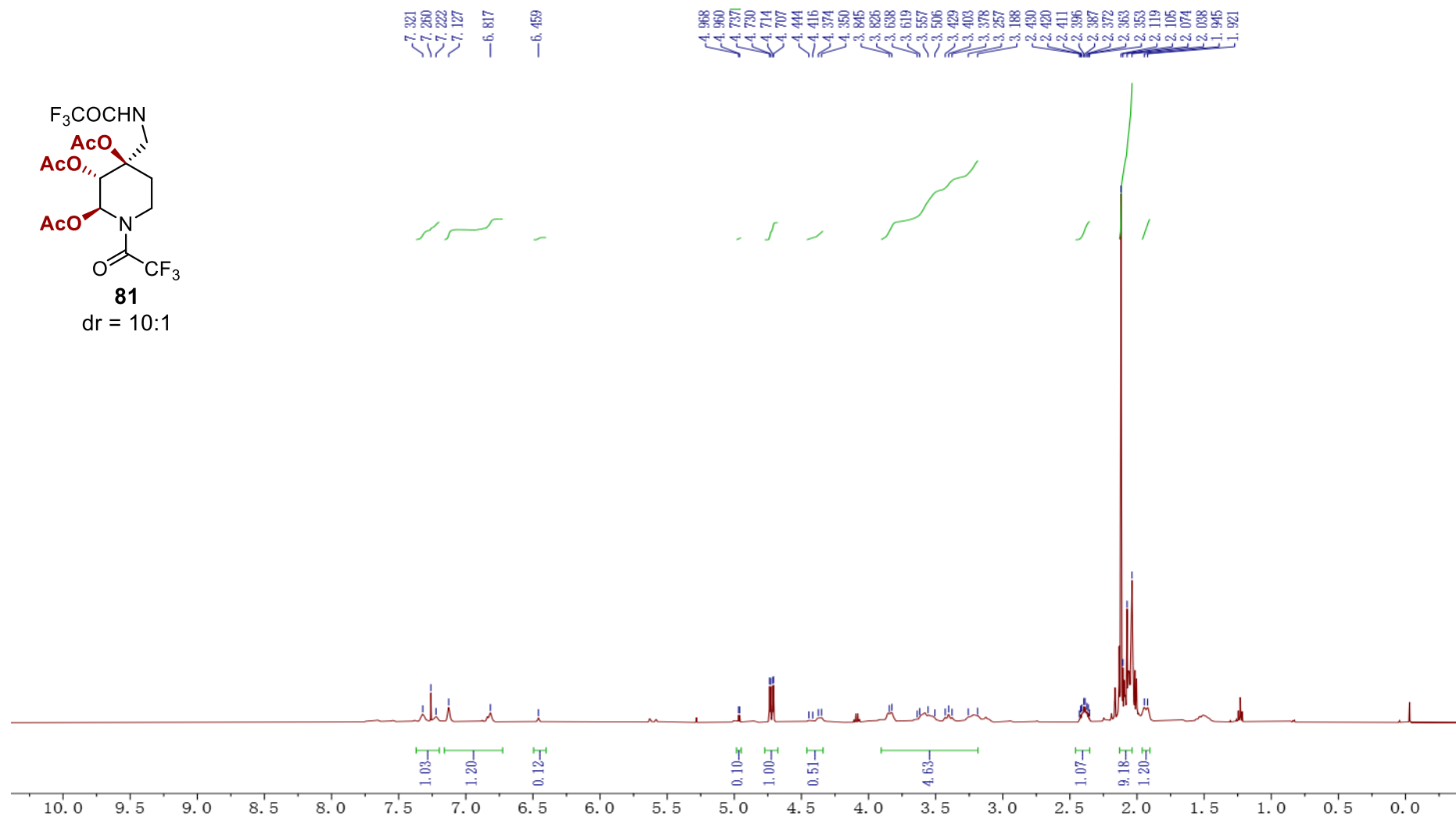


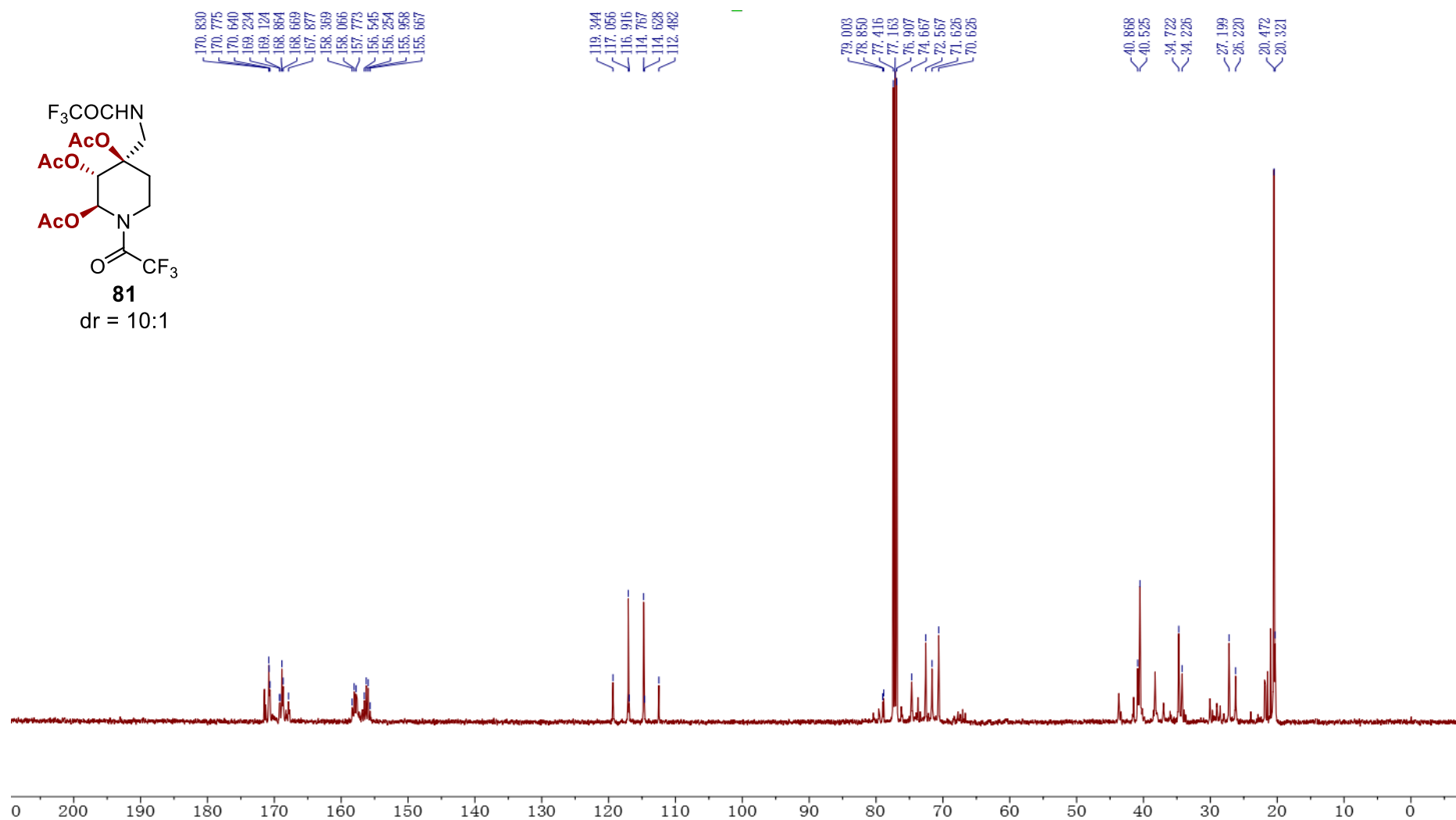


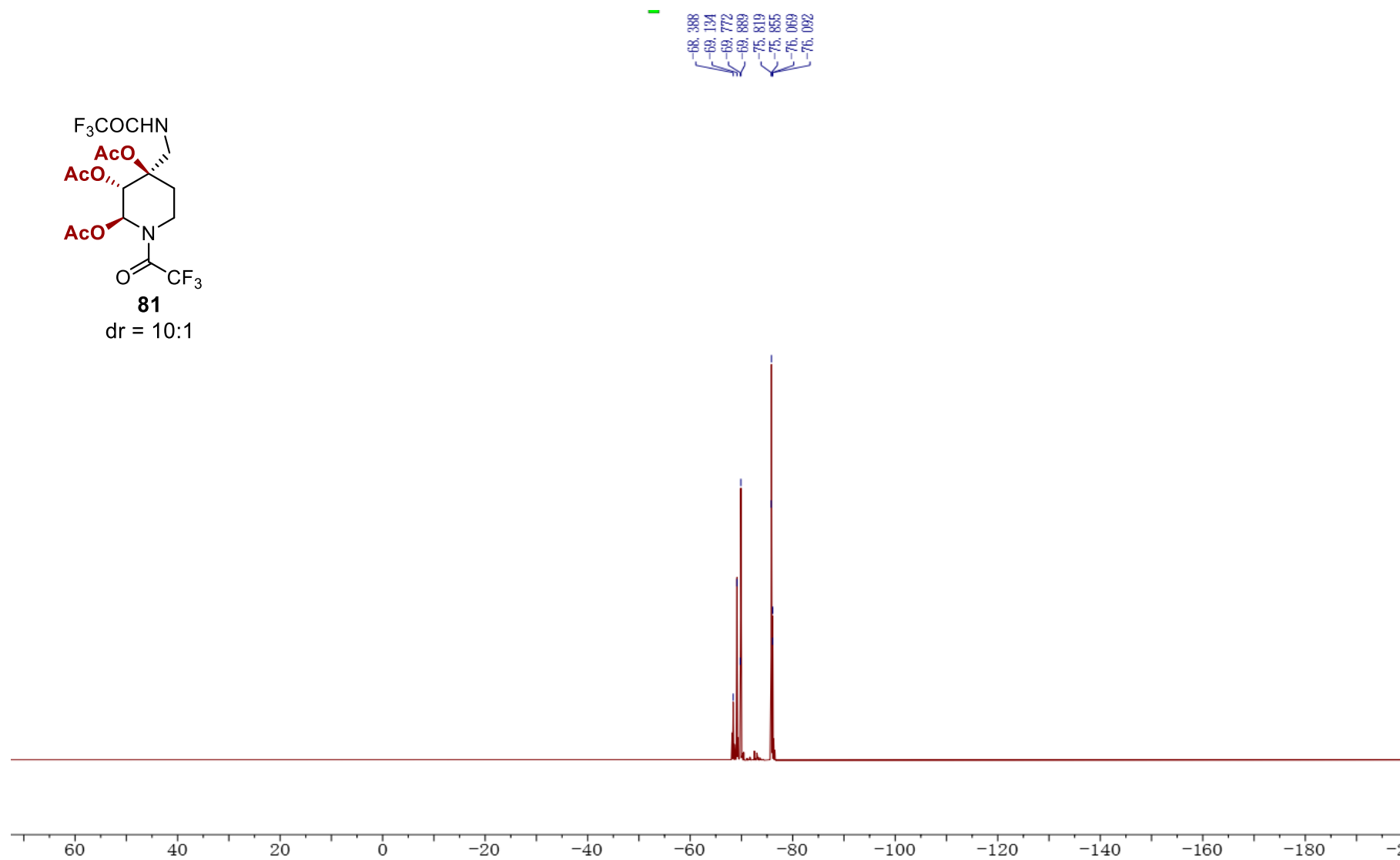
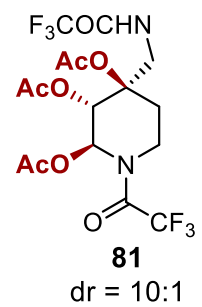
80
dr = >20:1

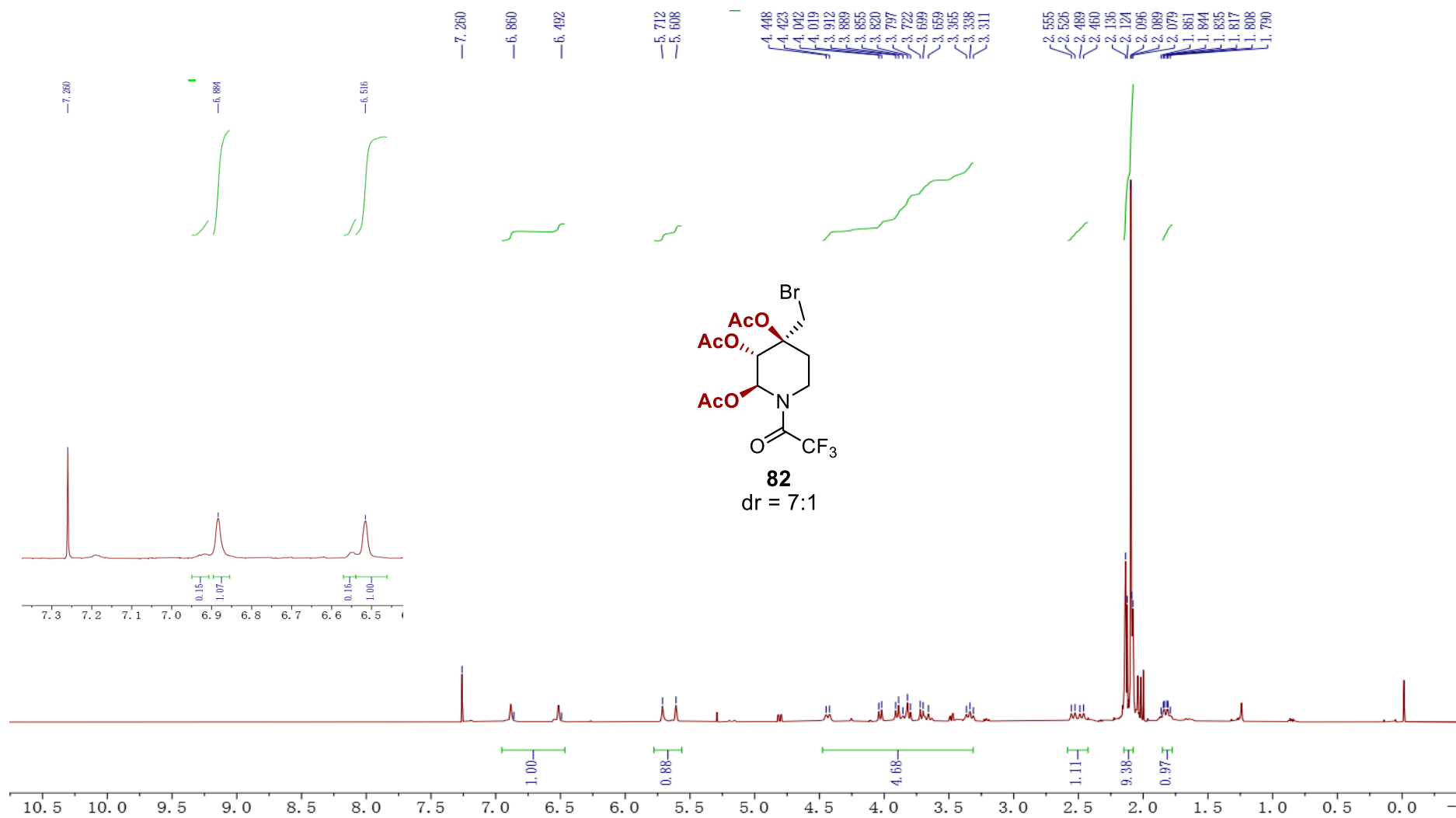
58, 260
69, 620

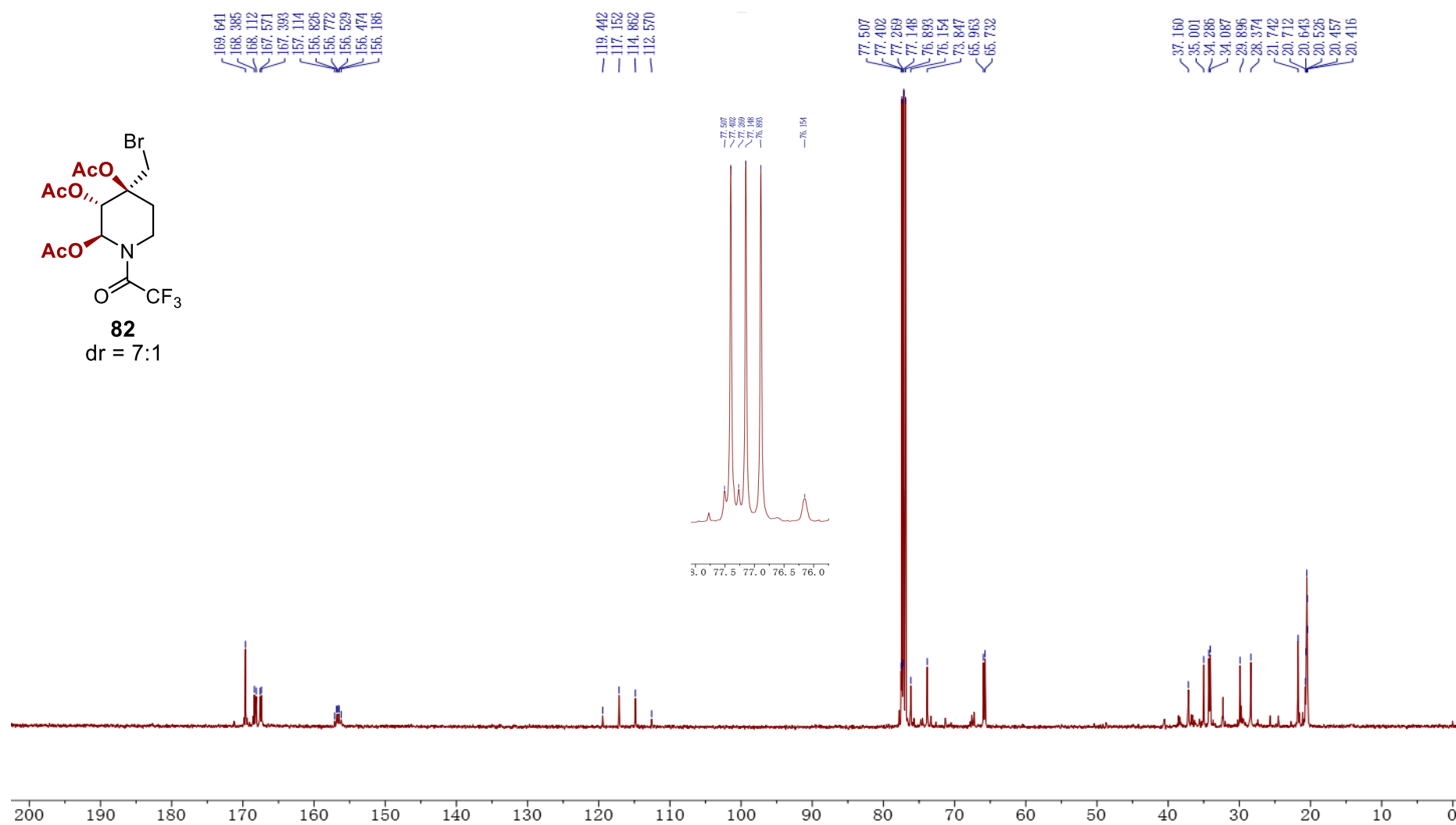


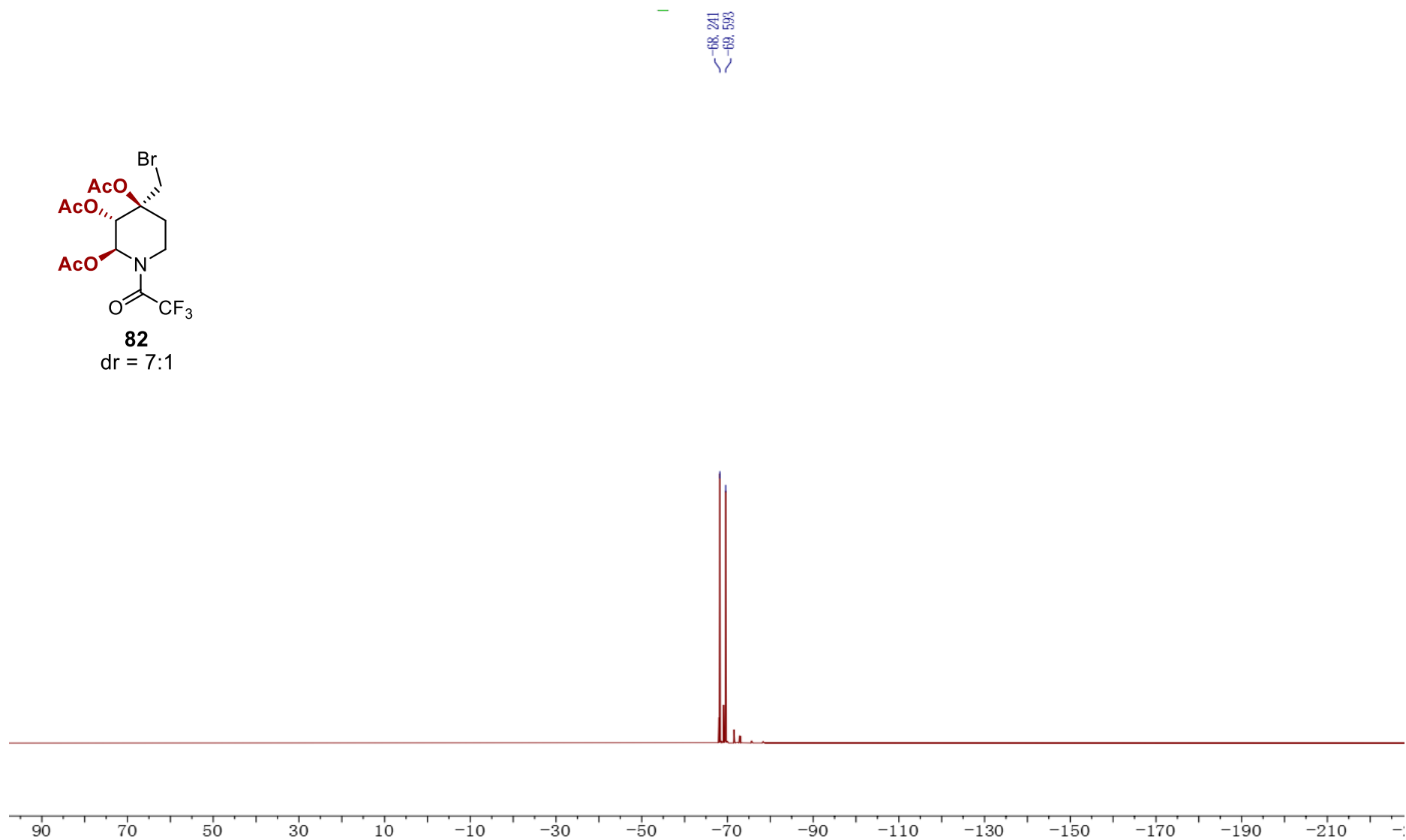
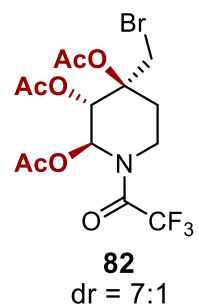


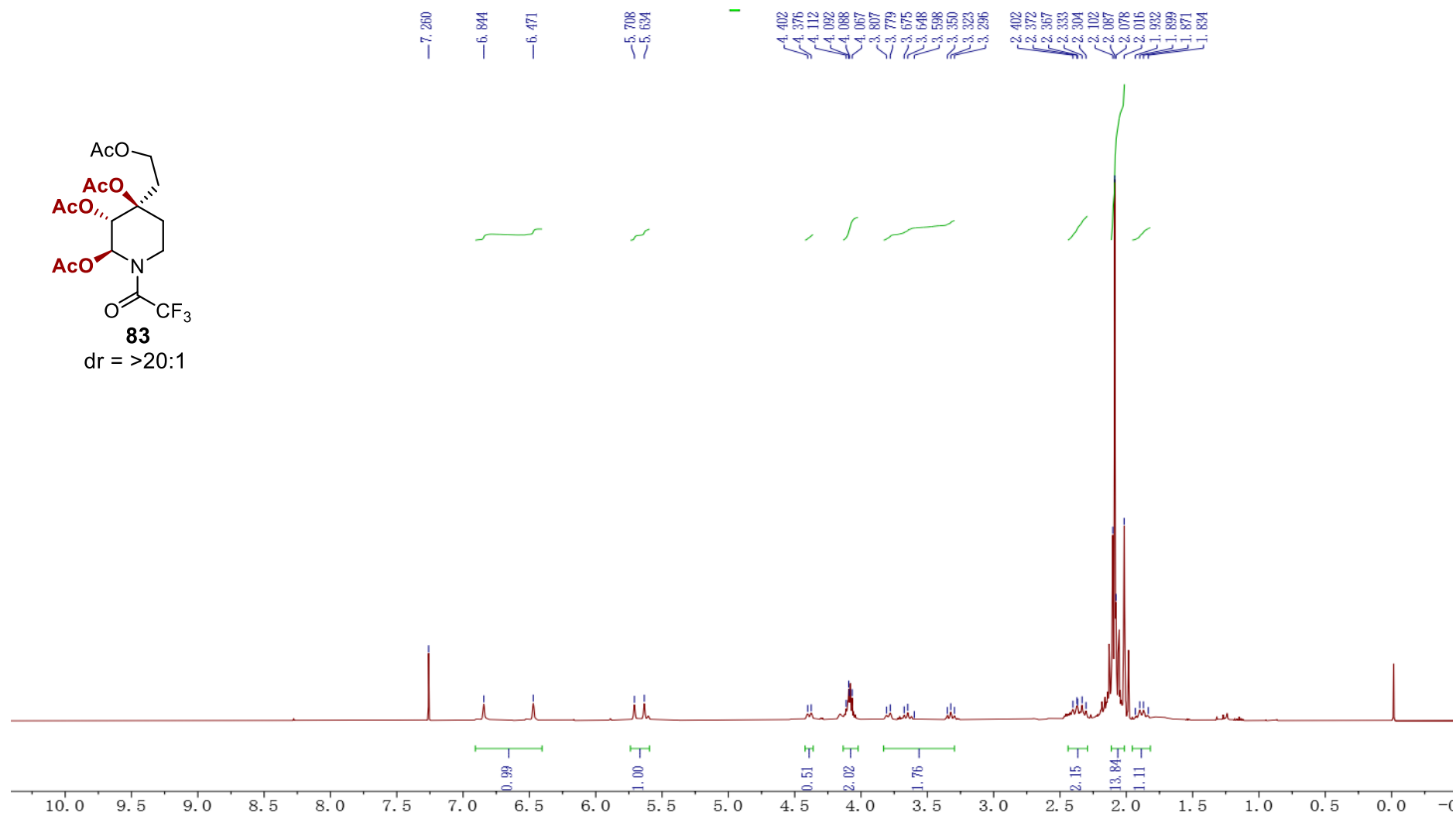


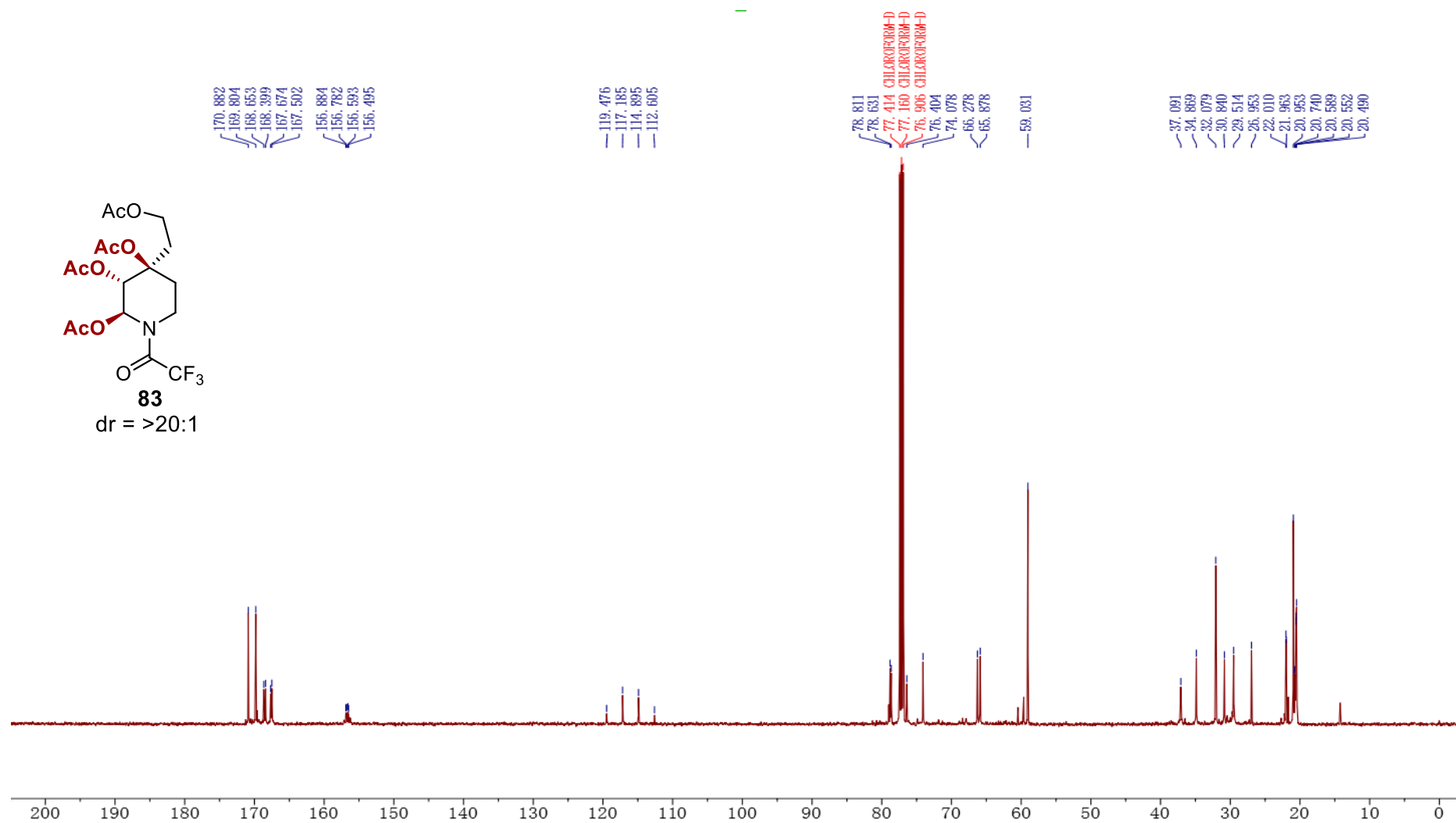


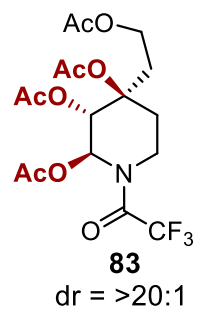




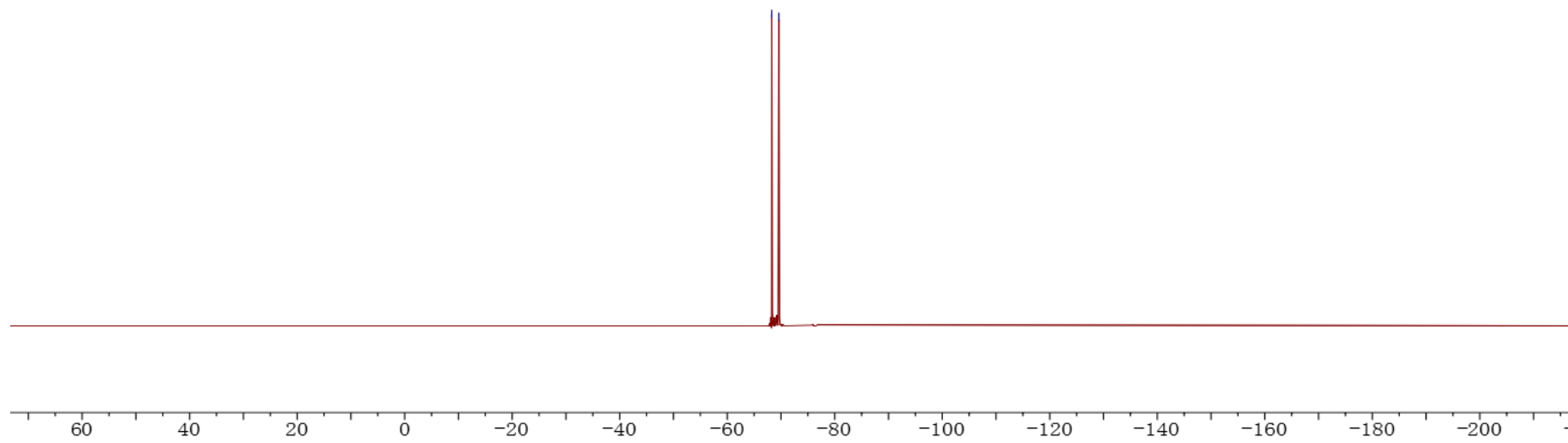




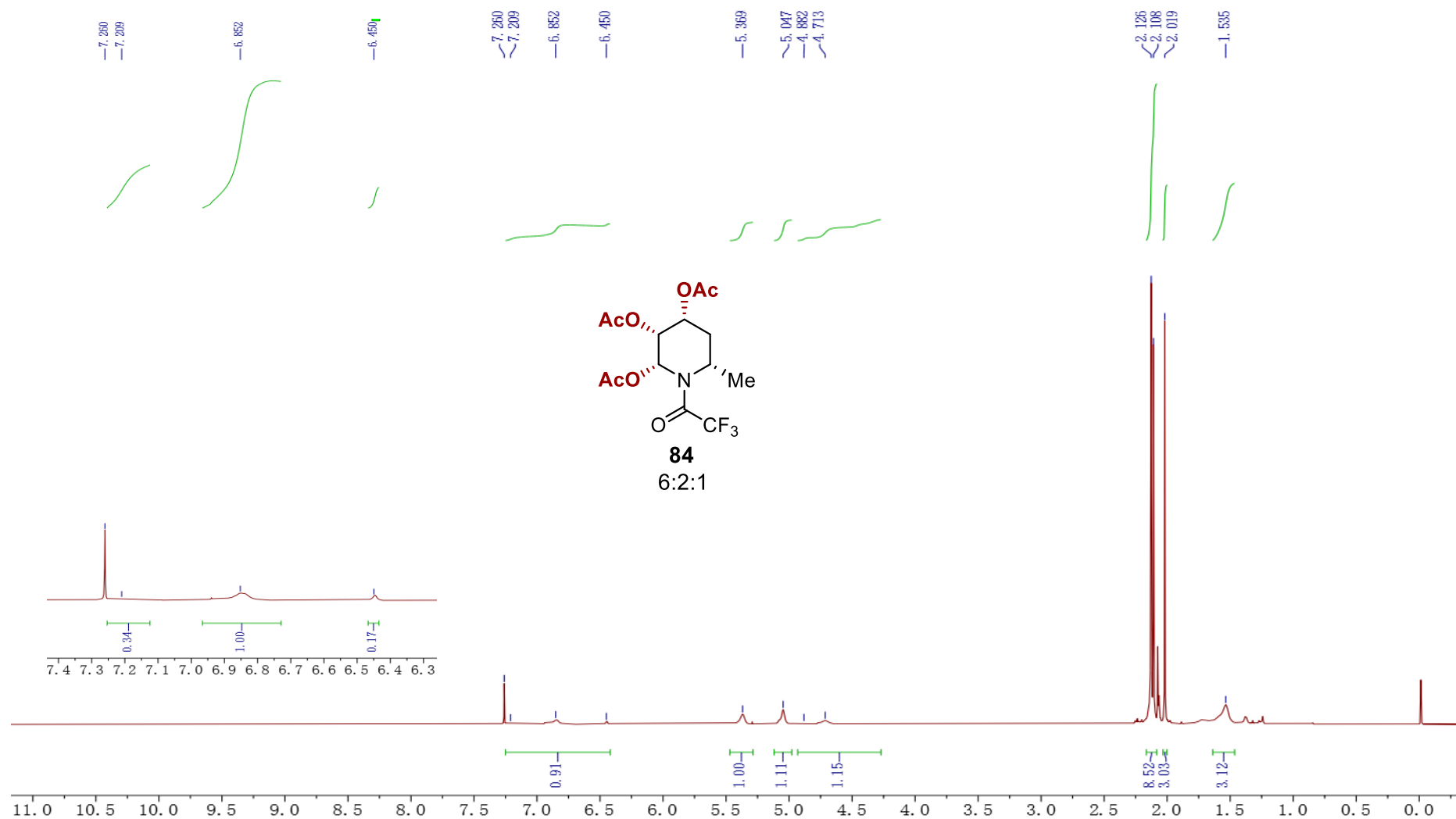


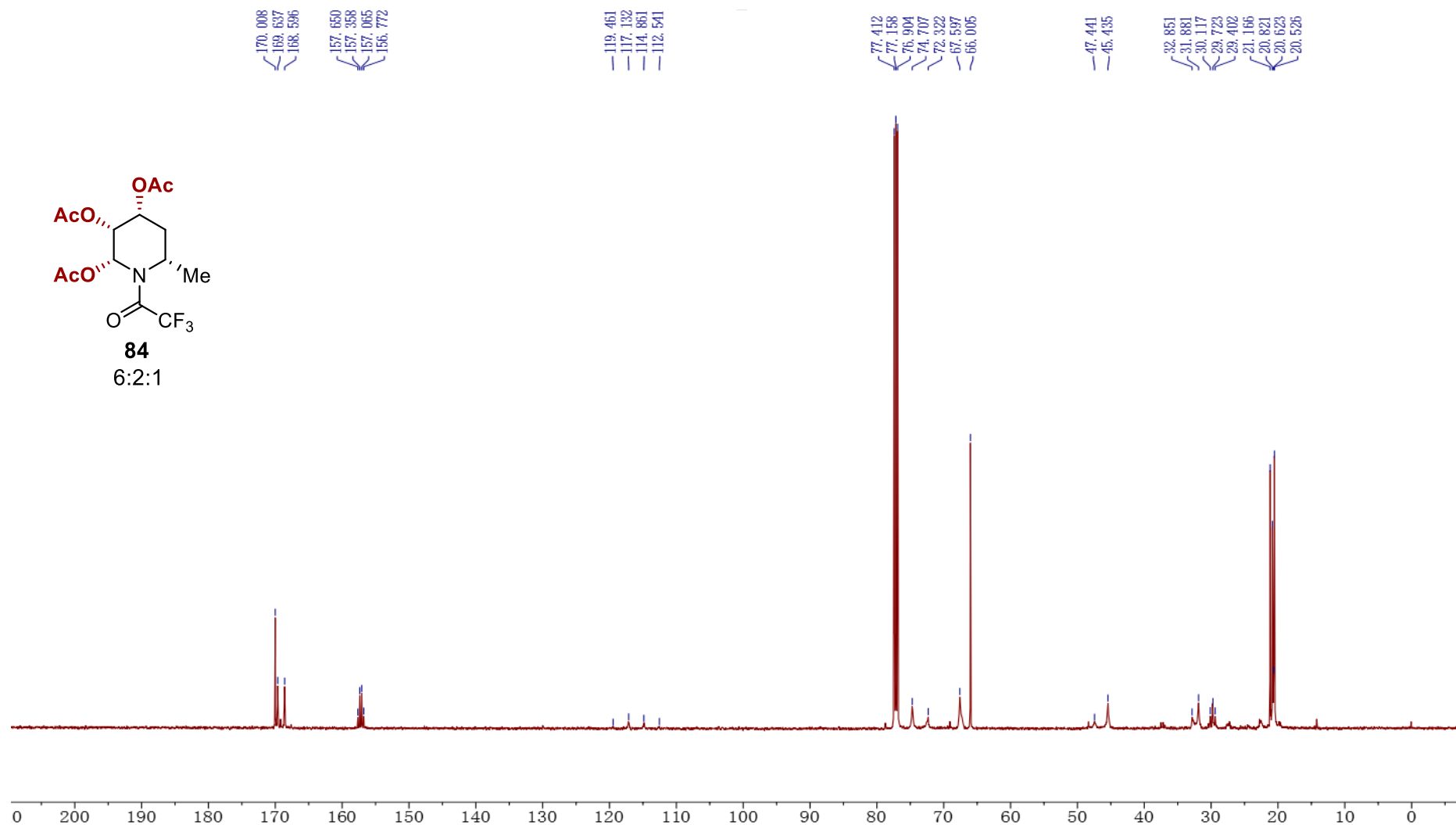


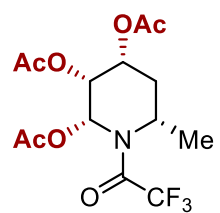
58.280
62.604



S283

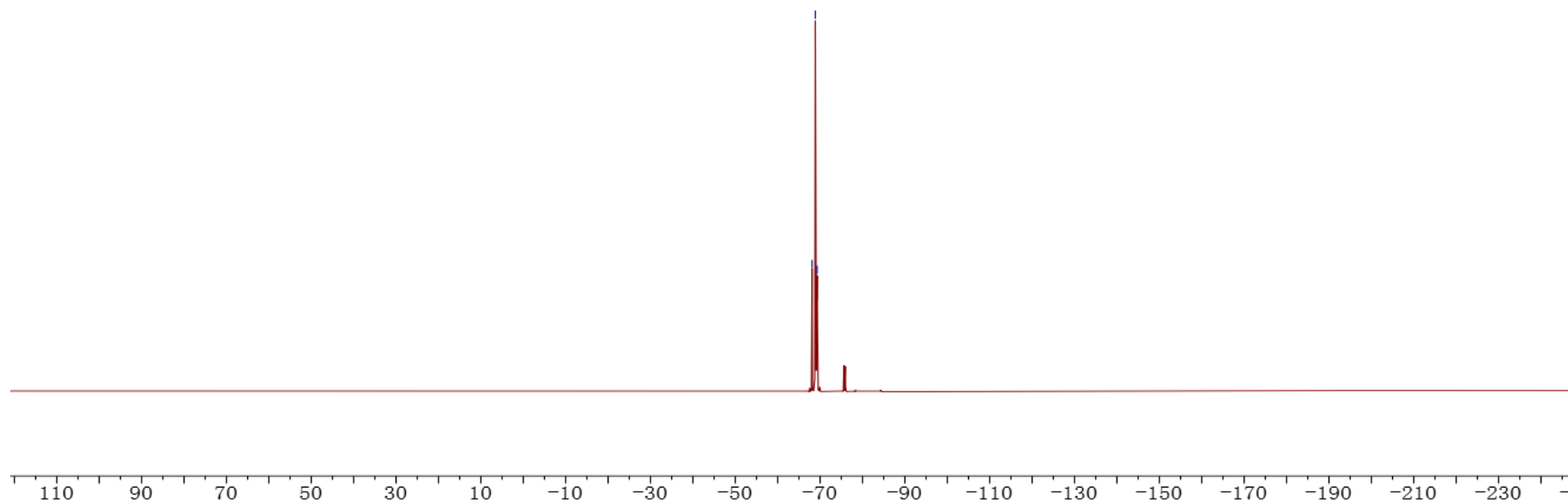




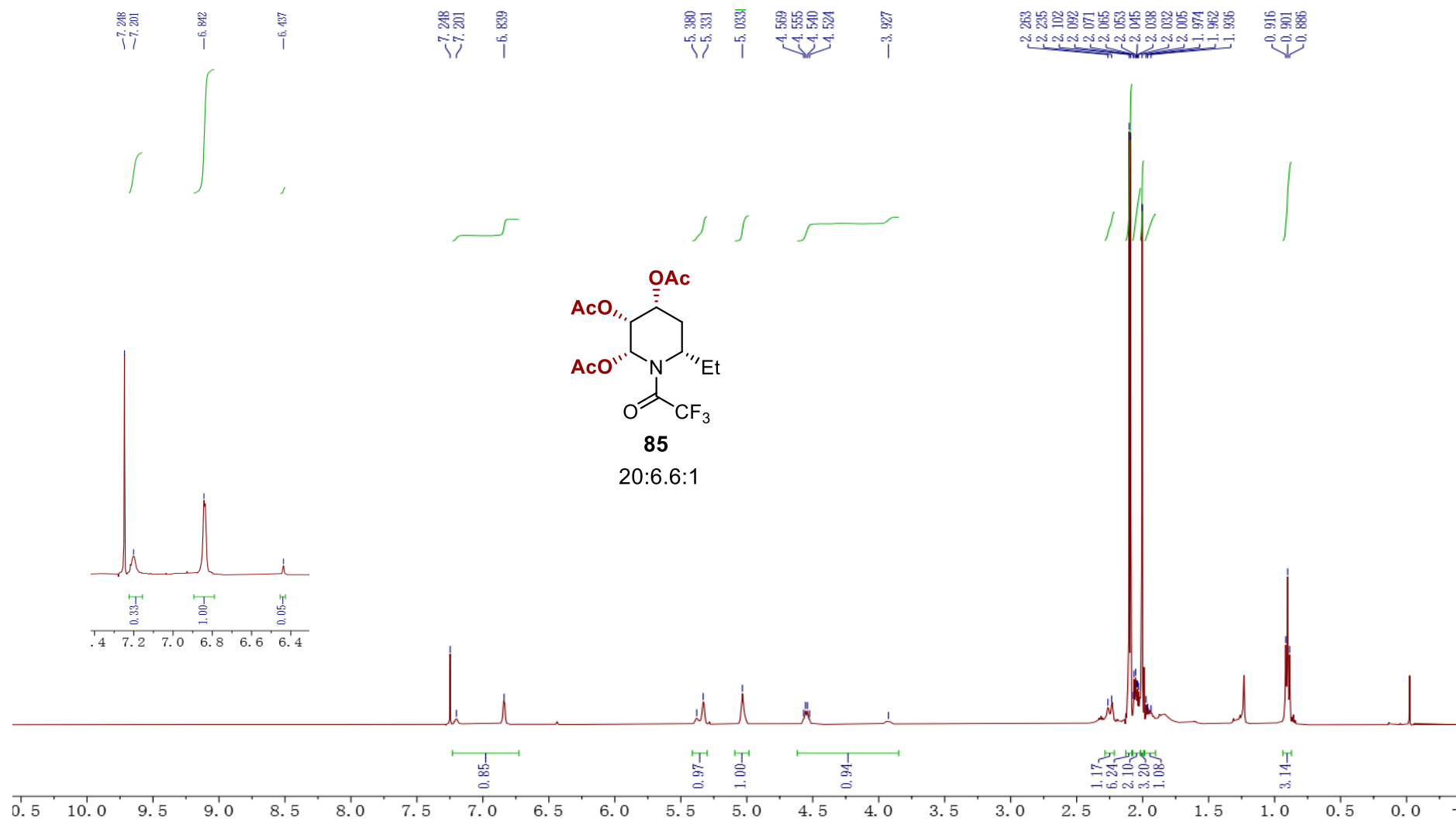


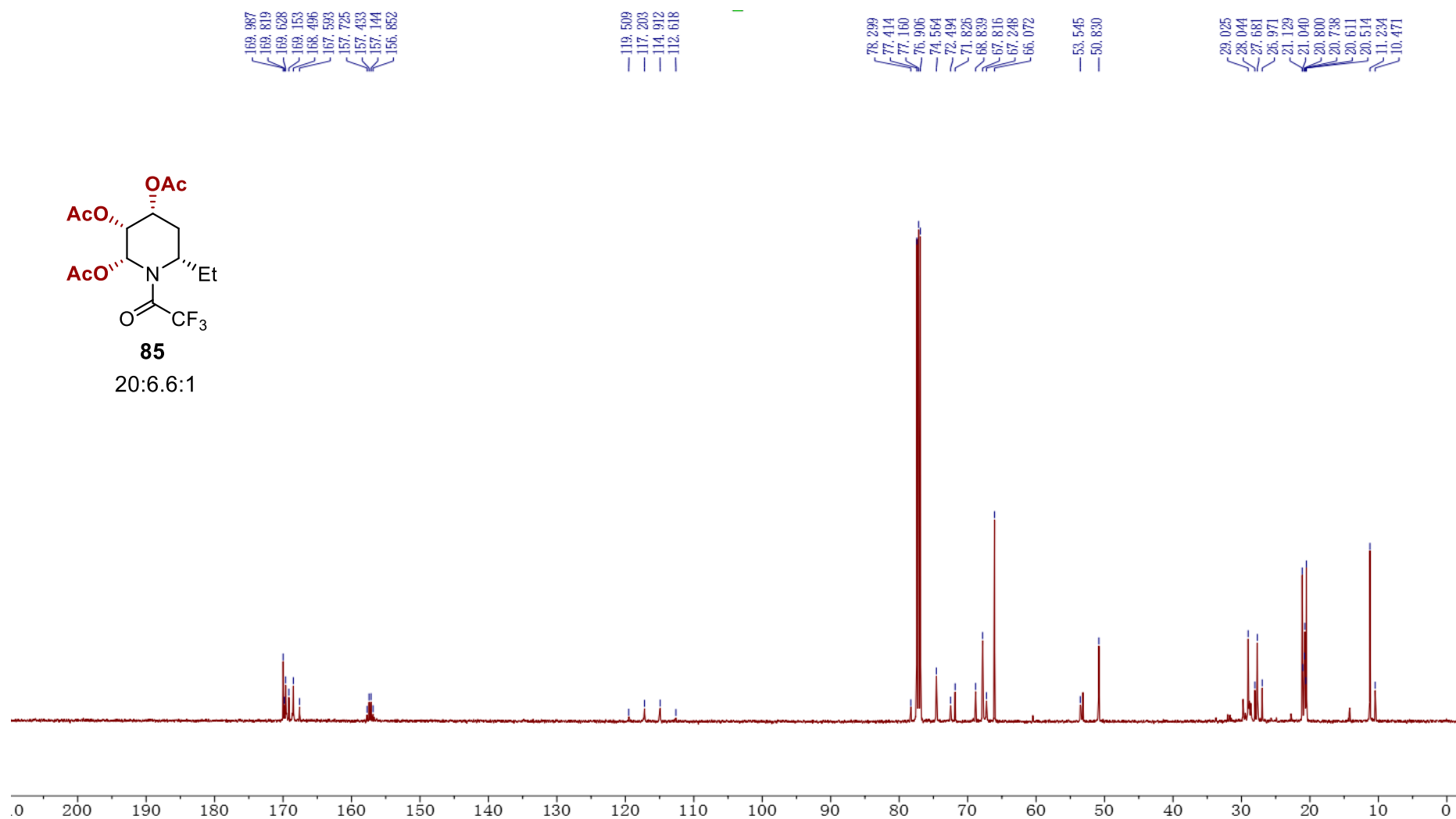
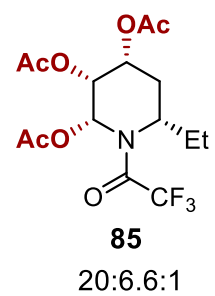
84
6:2:1

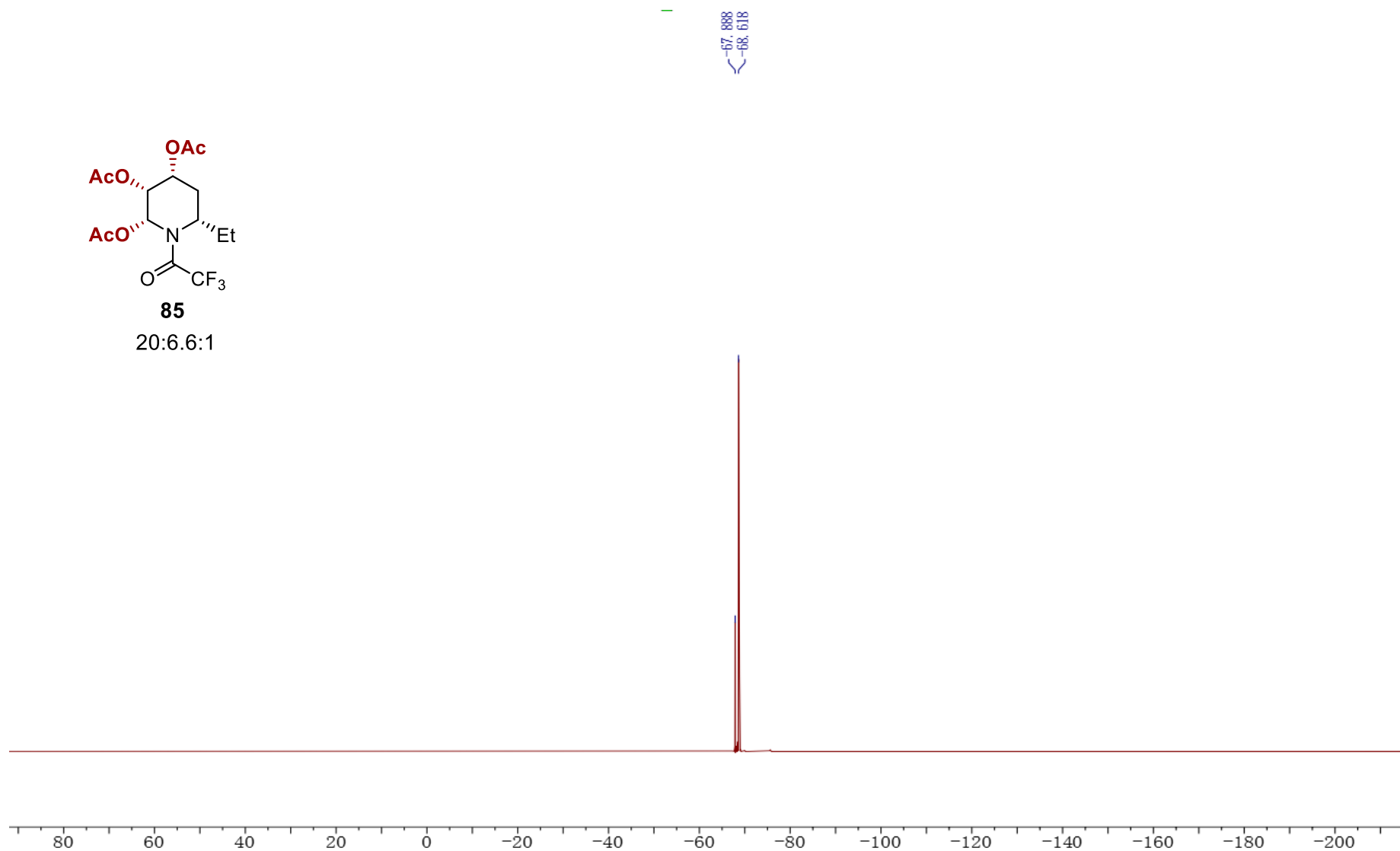
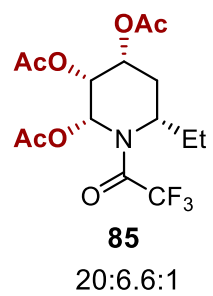
68.096
68.878
69.279

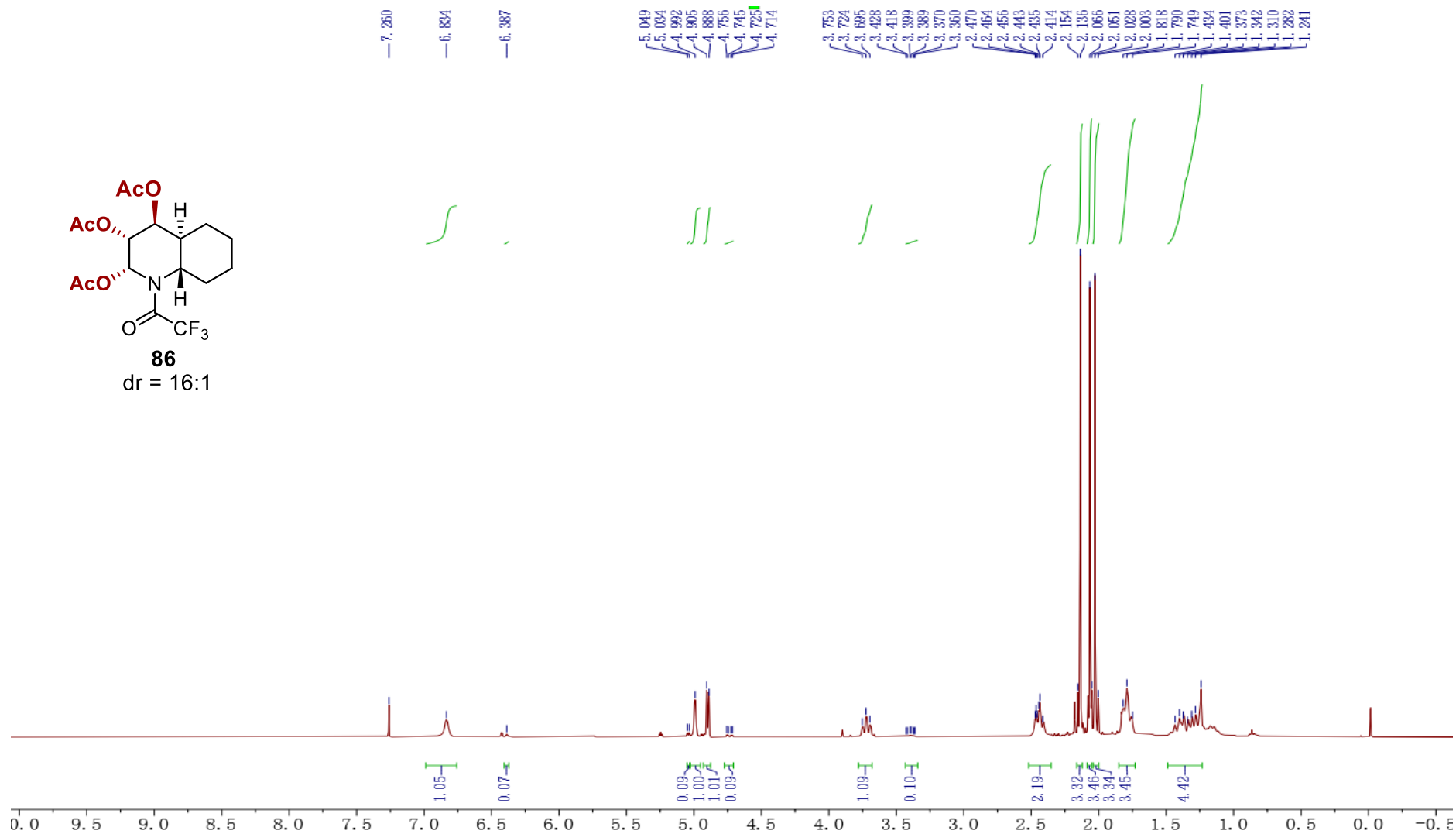
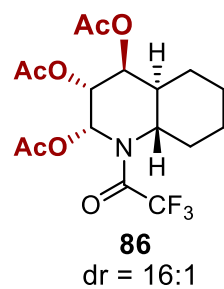


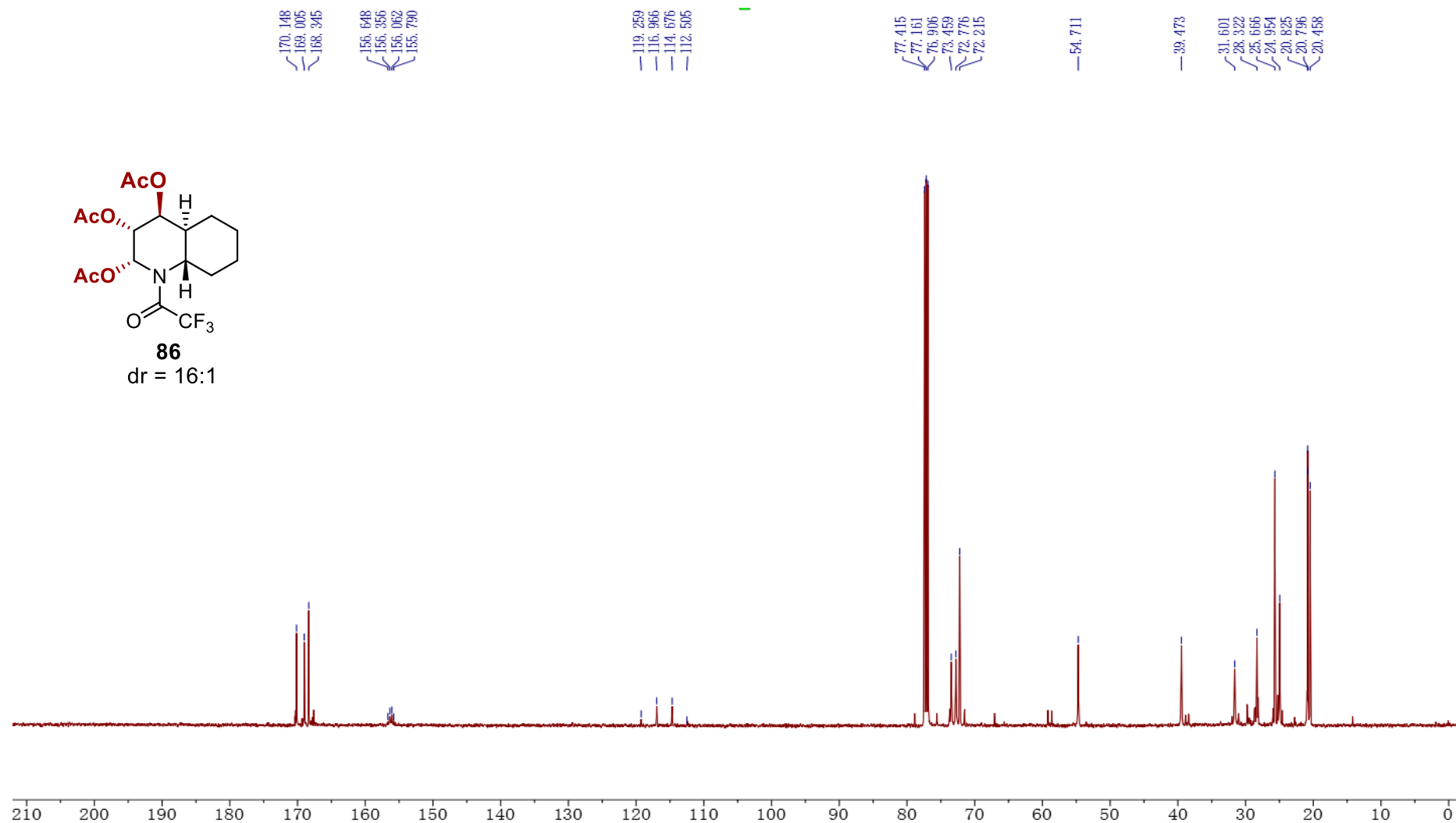
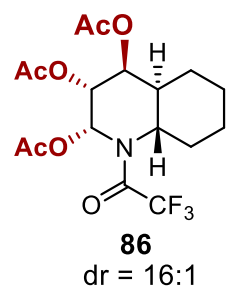
S286

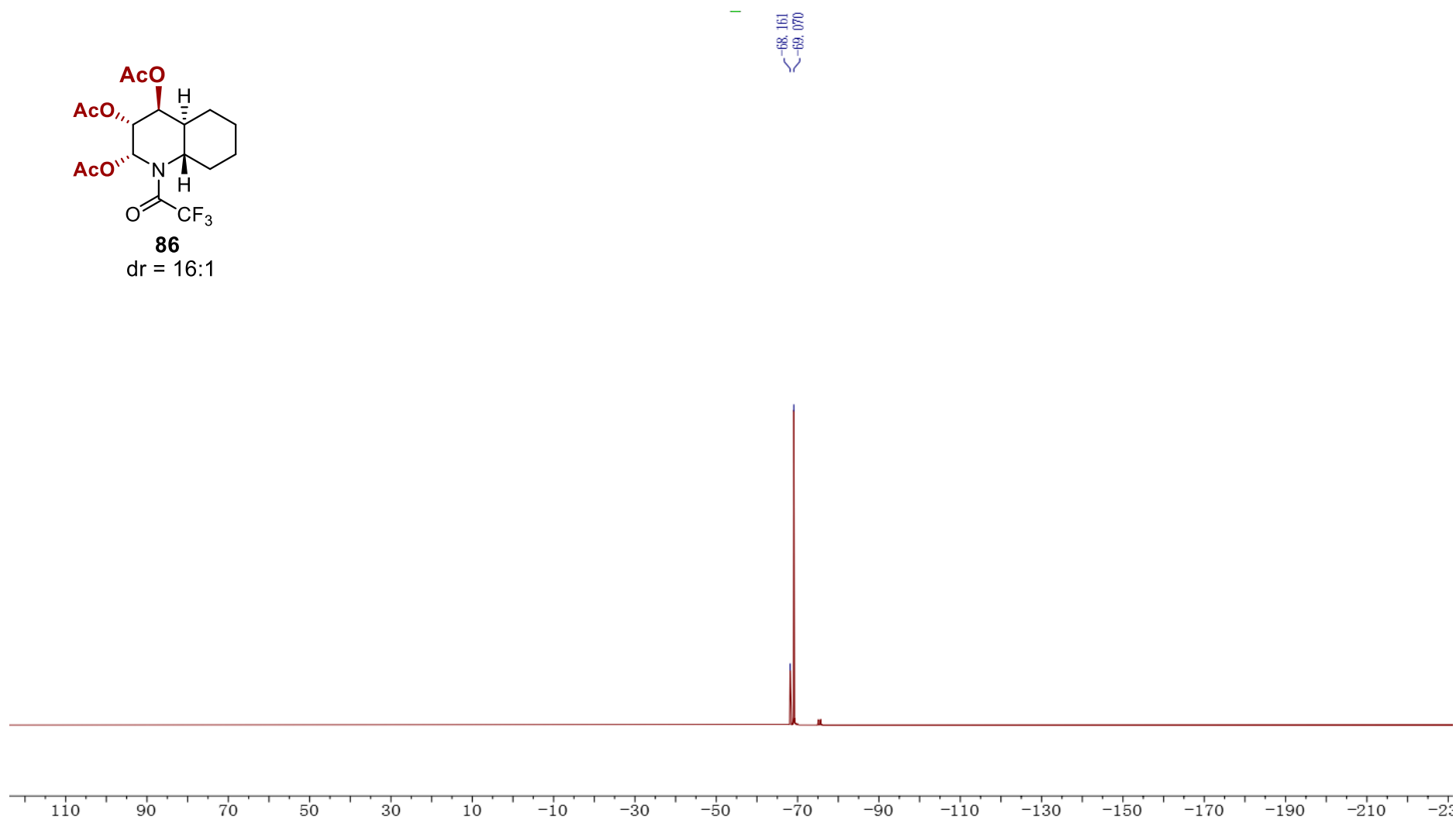
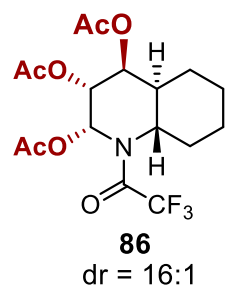


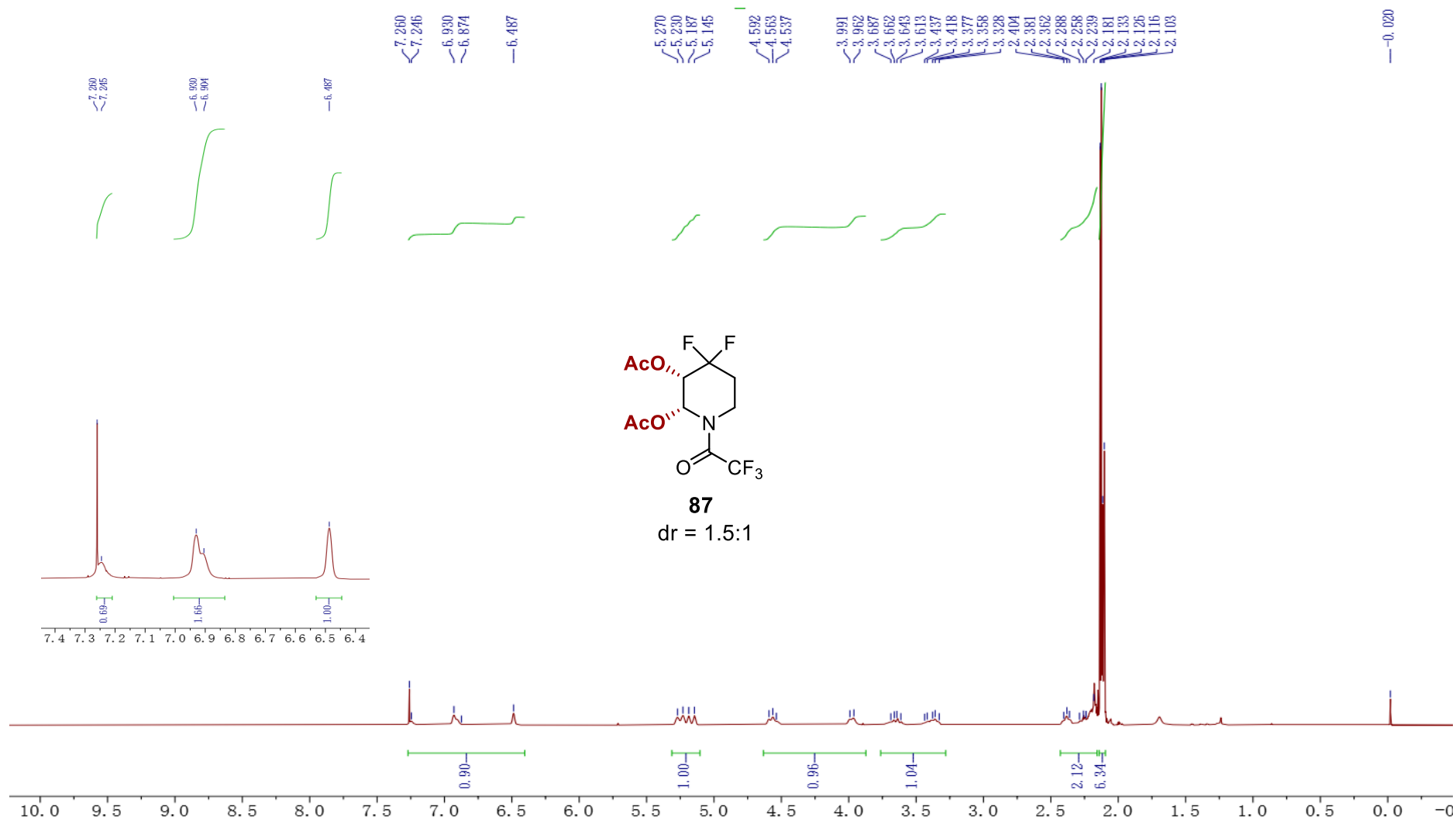


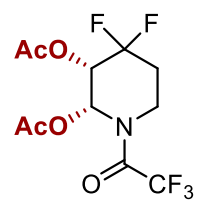




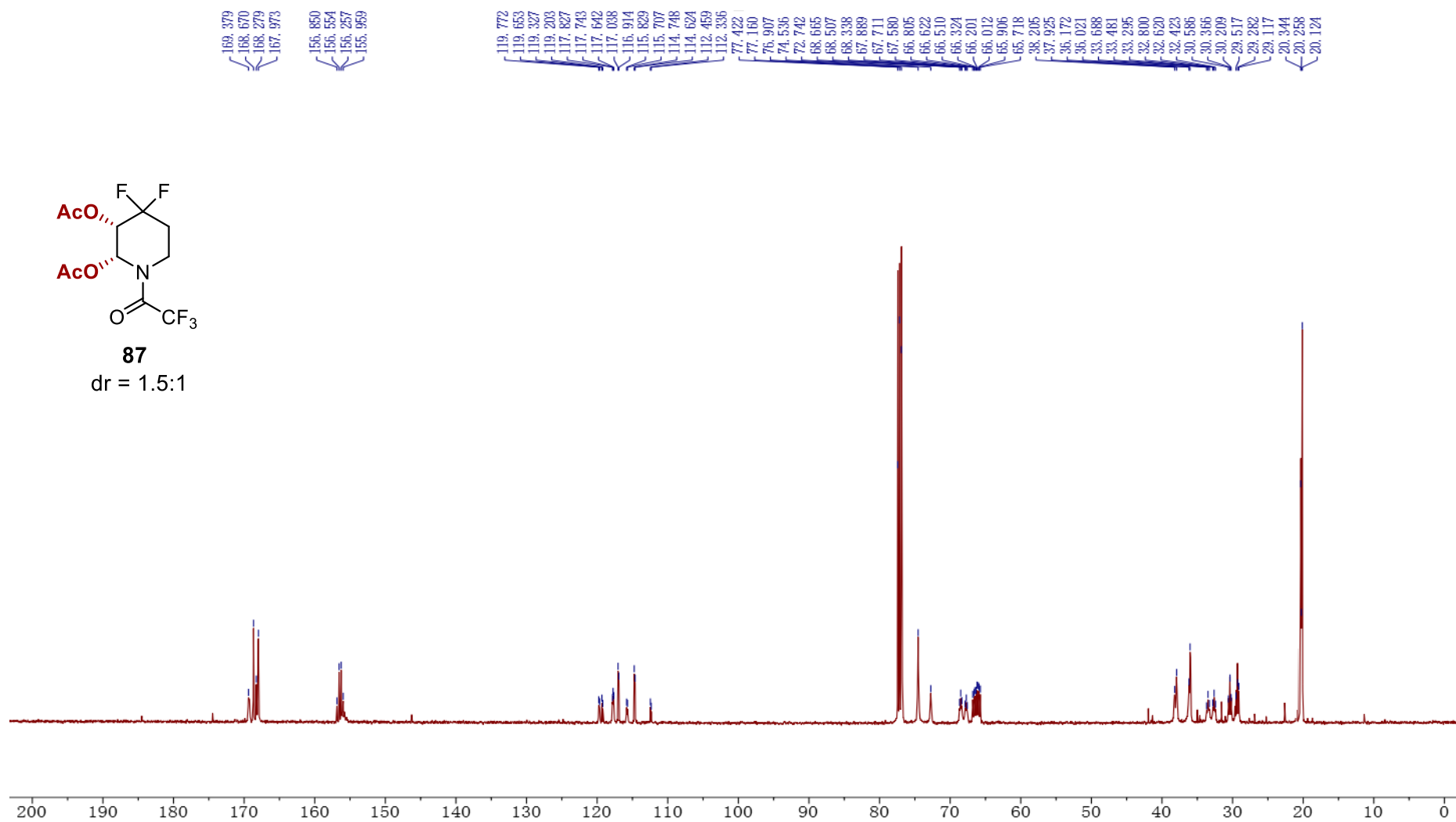


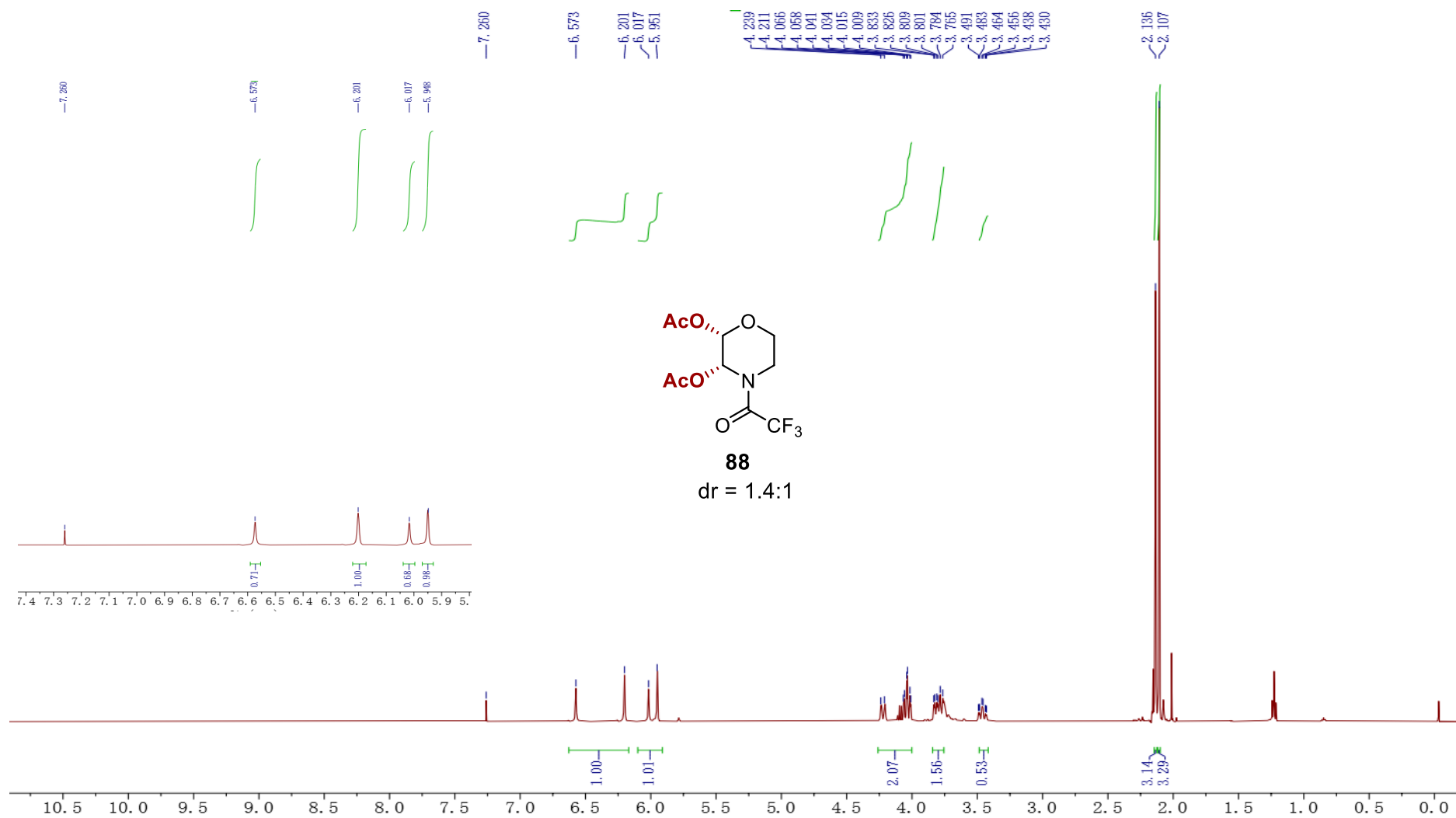


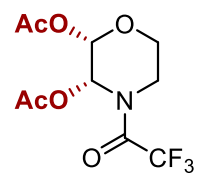




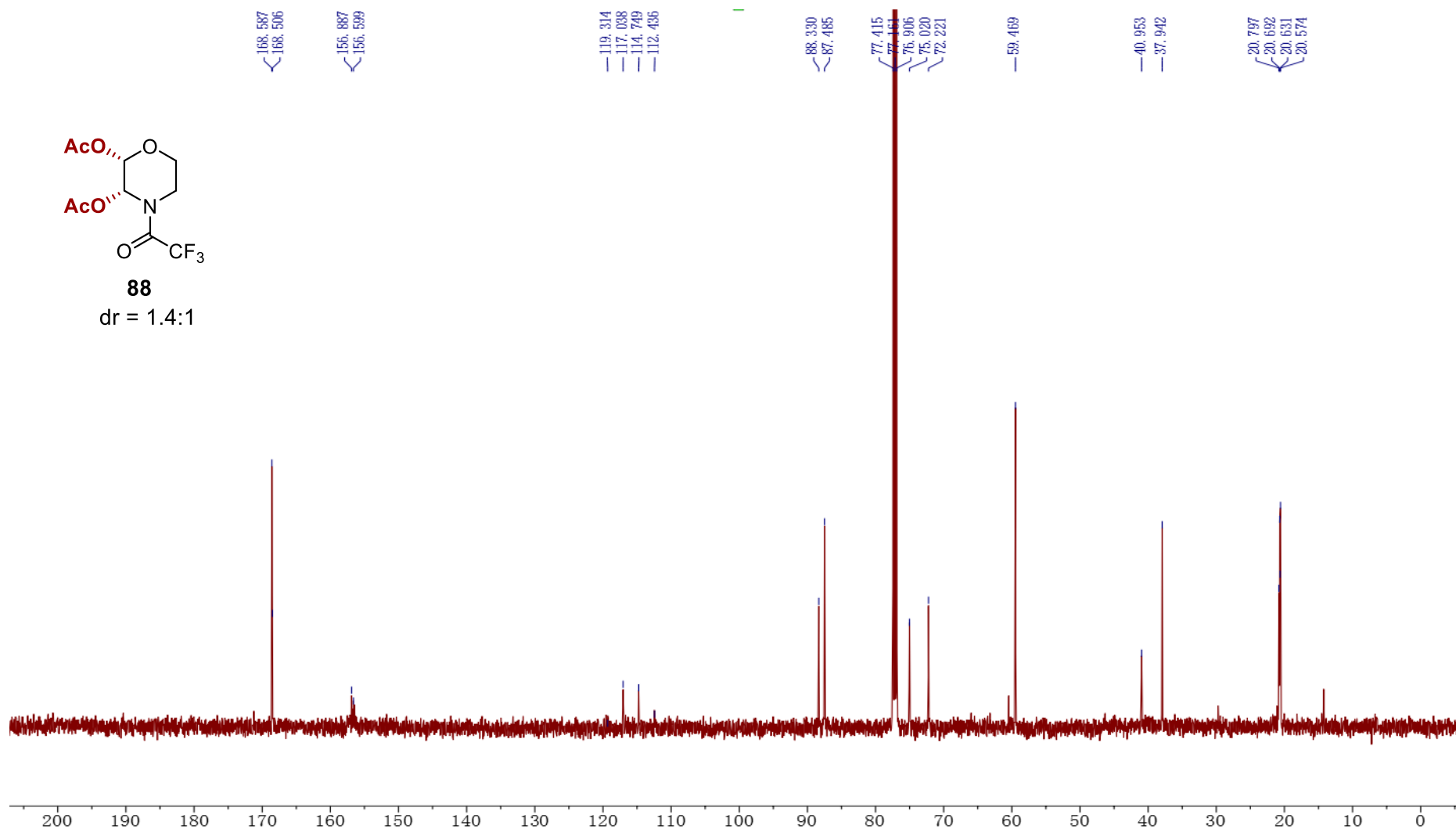
87
dr = 1.5:1

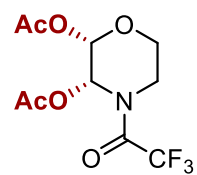






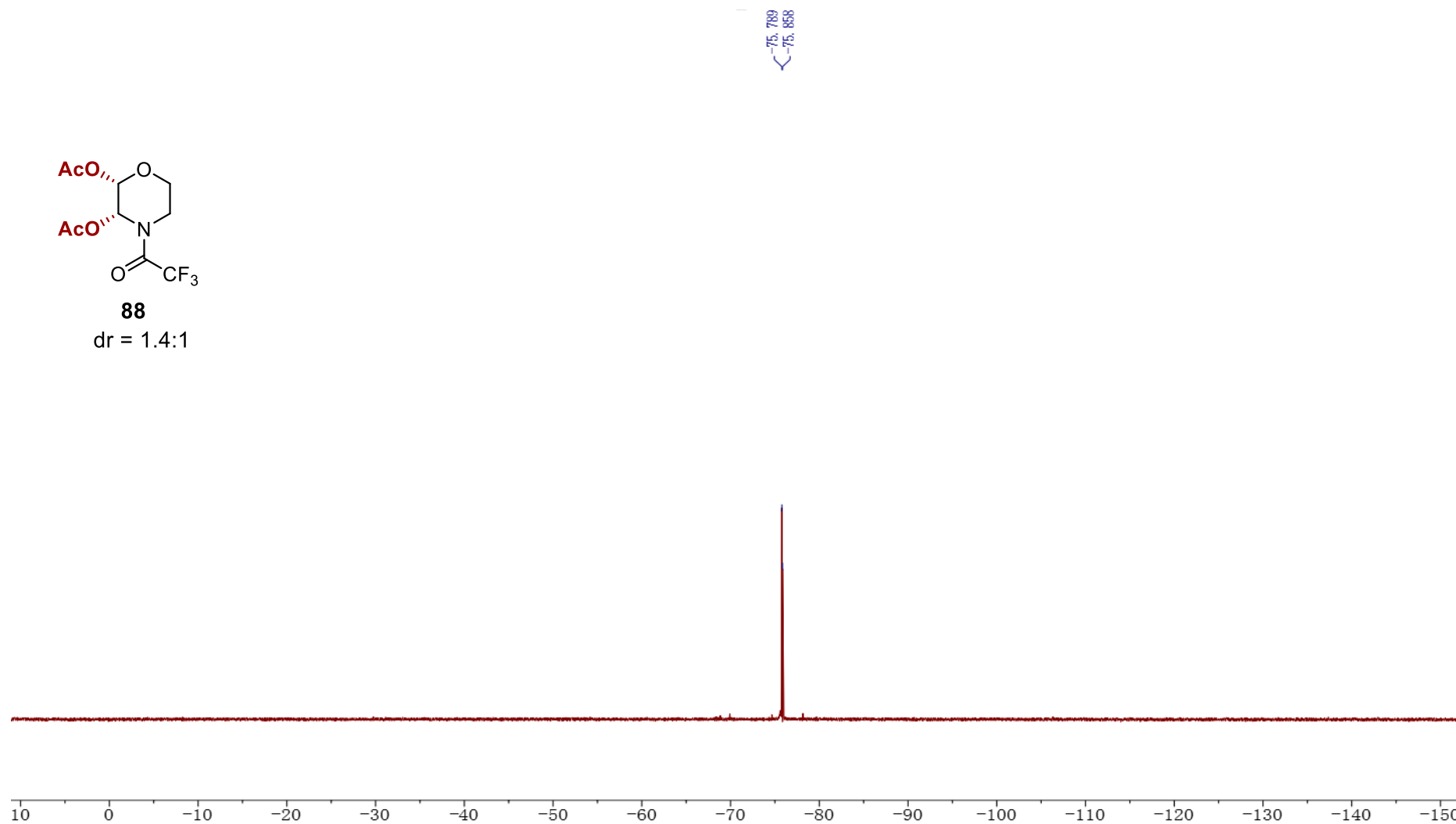
88
dr = 1.4:1

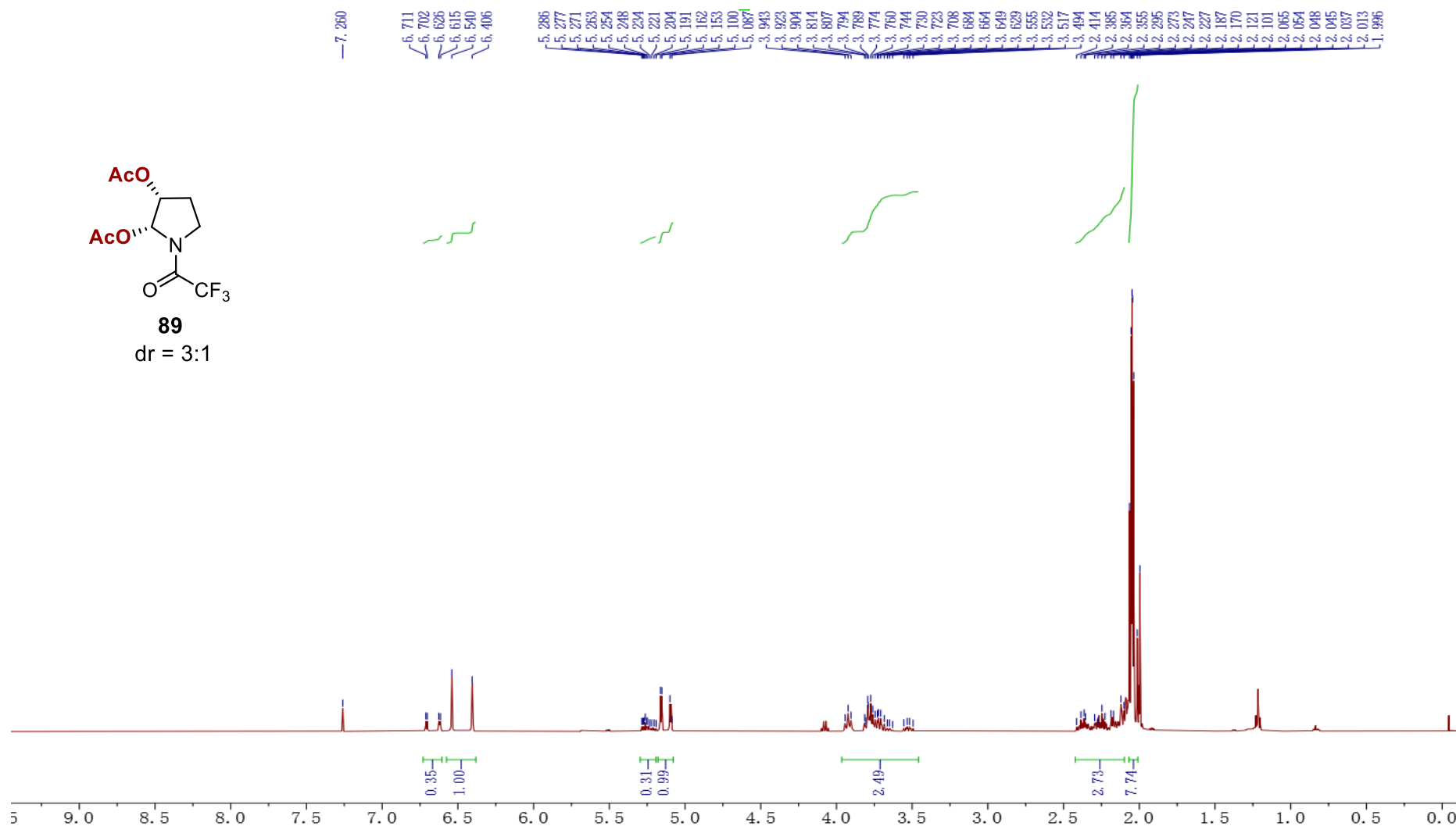
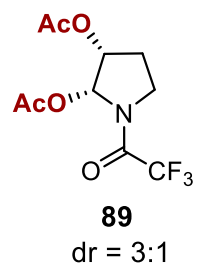


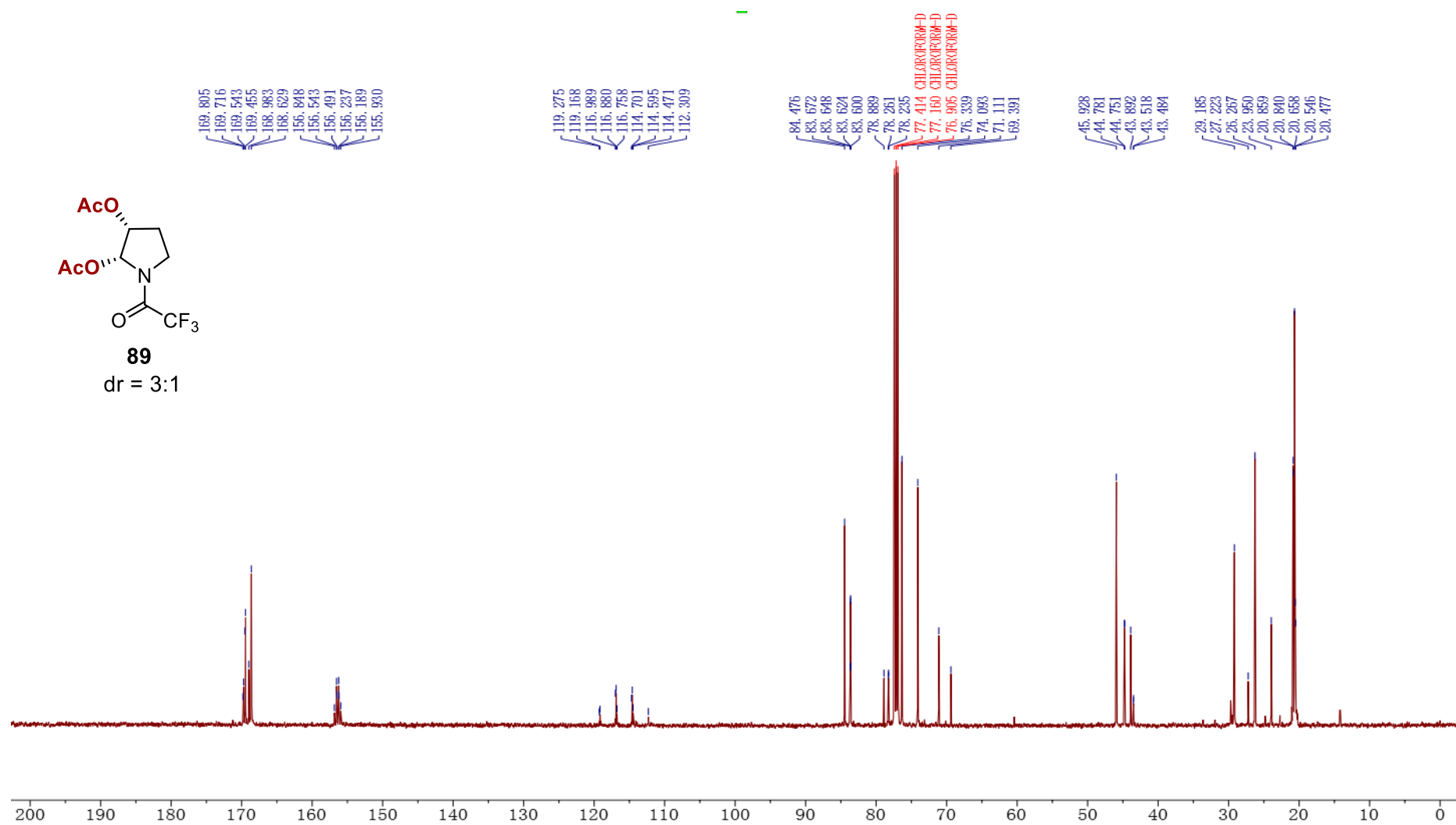


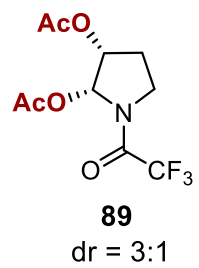
88

dr = 1.4:1

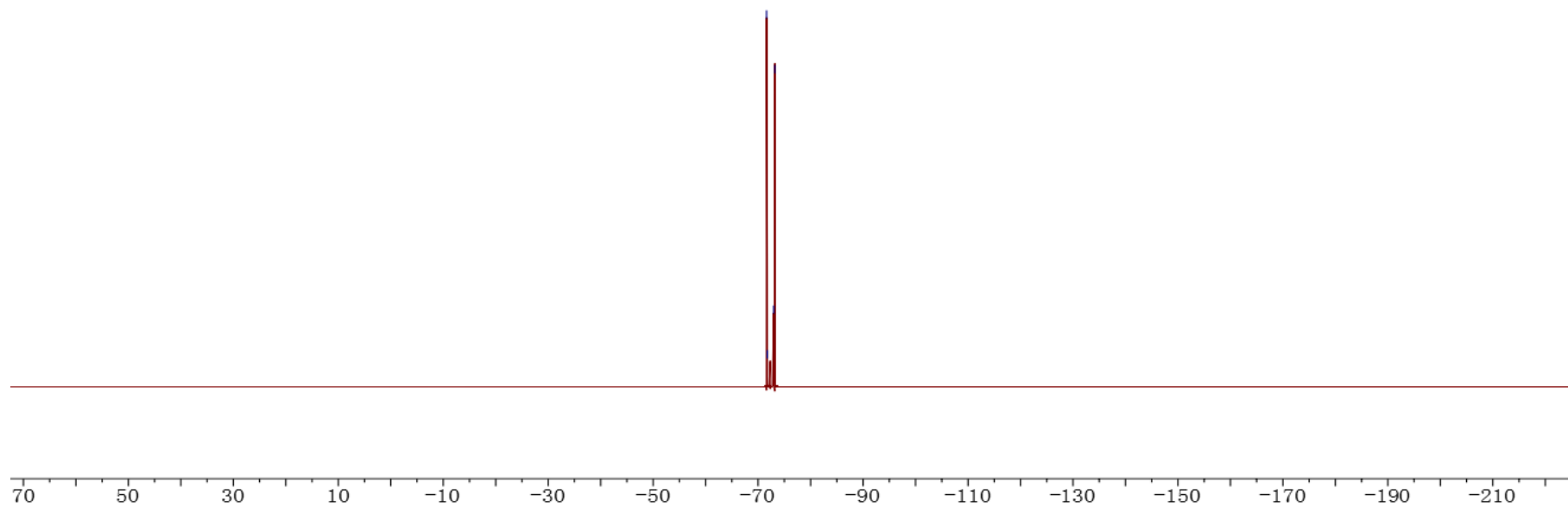




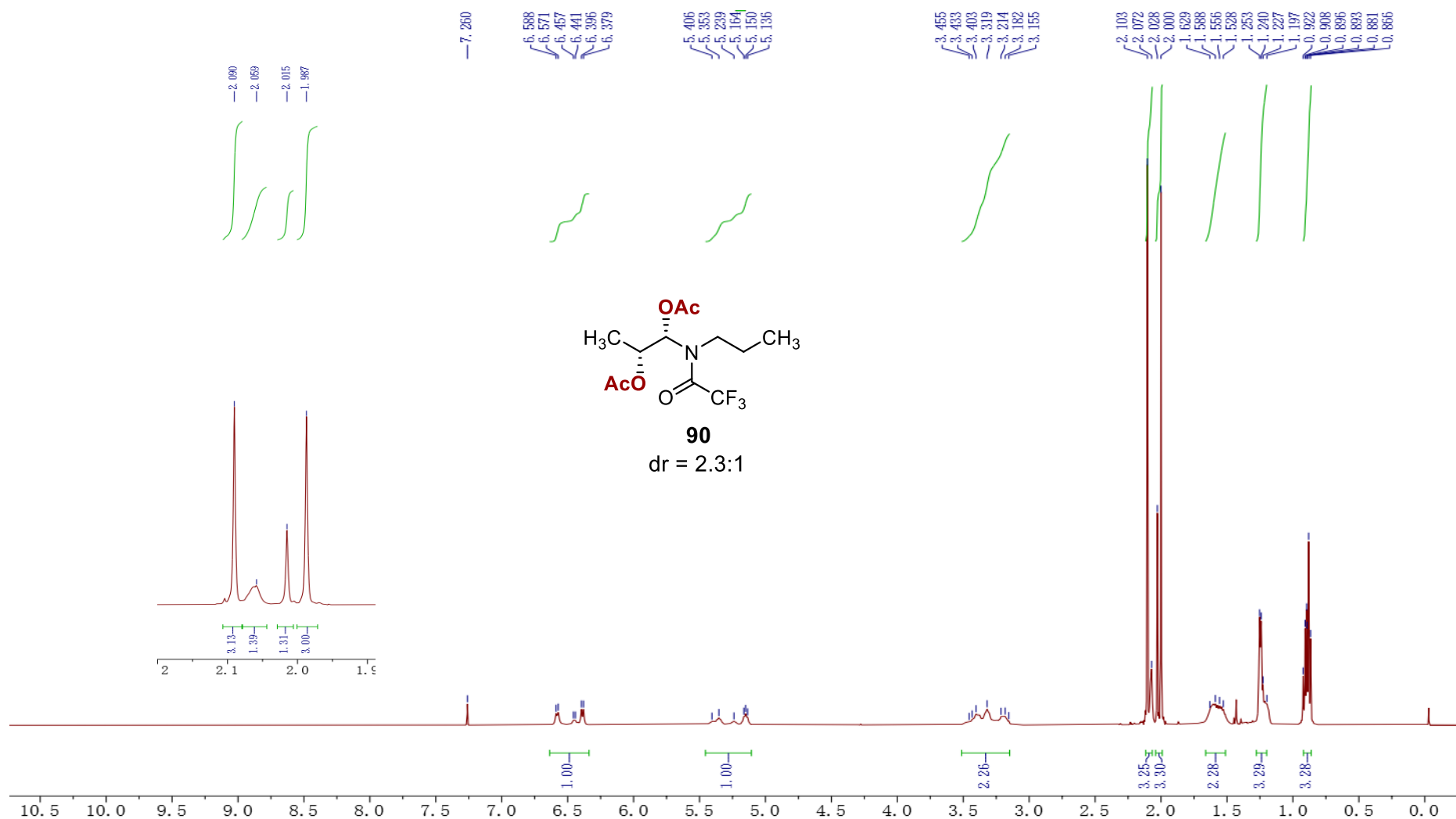


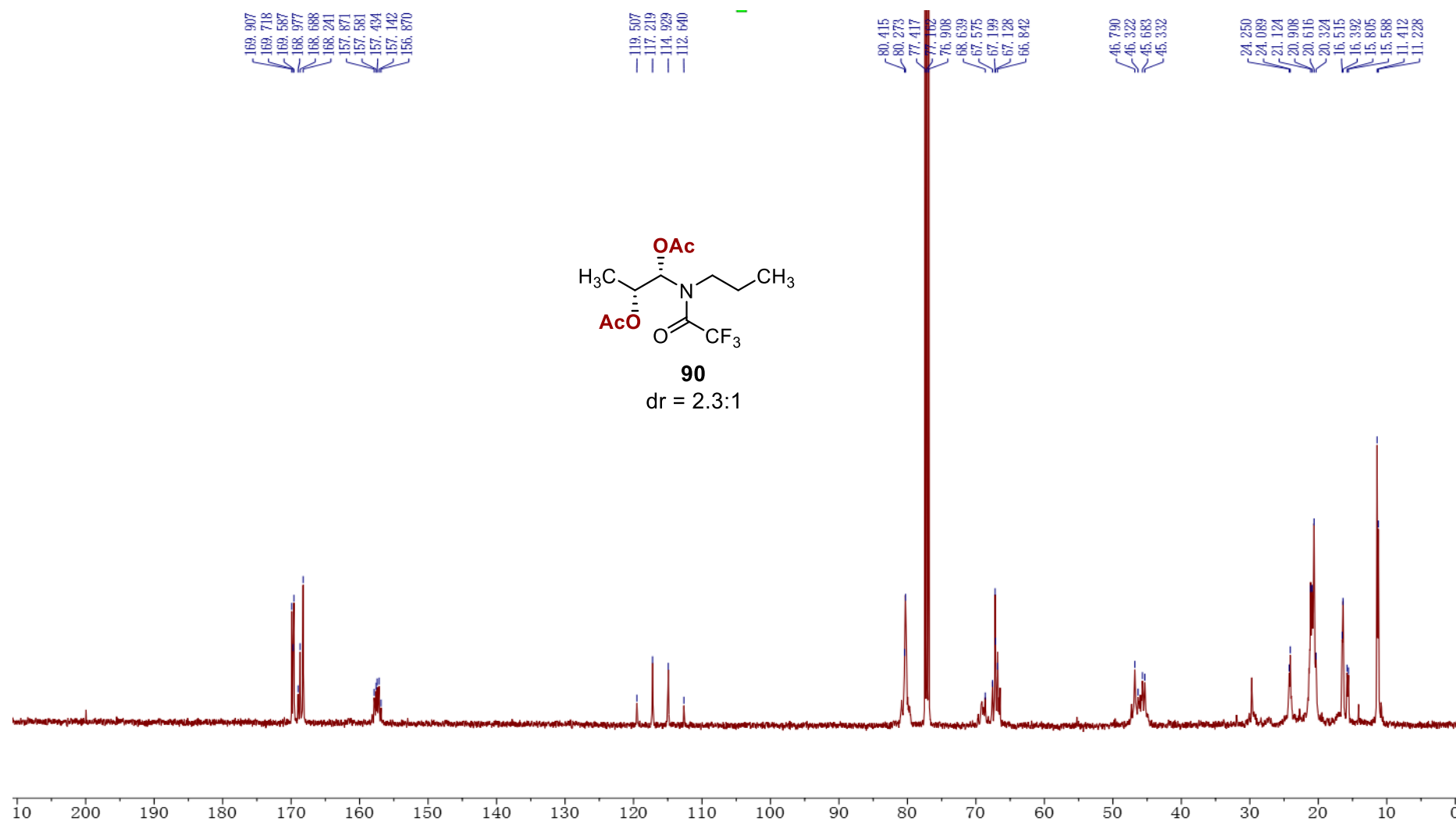


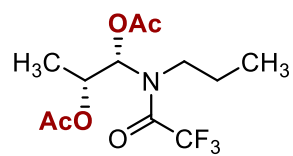
-71.603
-71.739
-72.967
-73.197



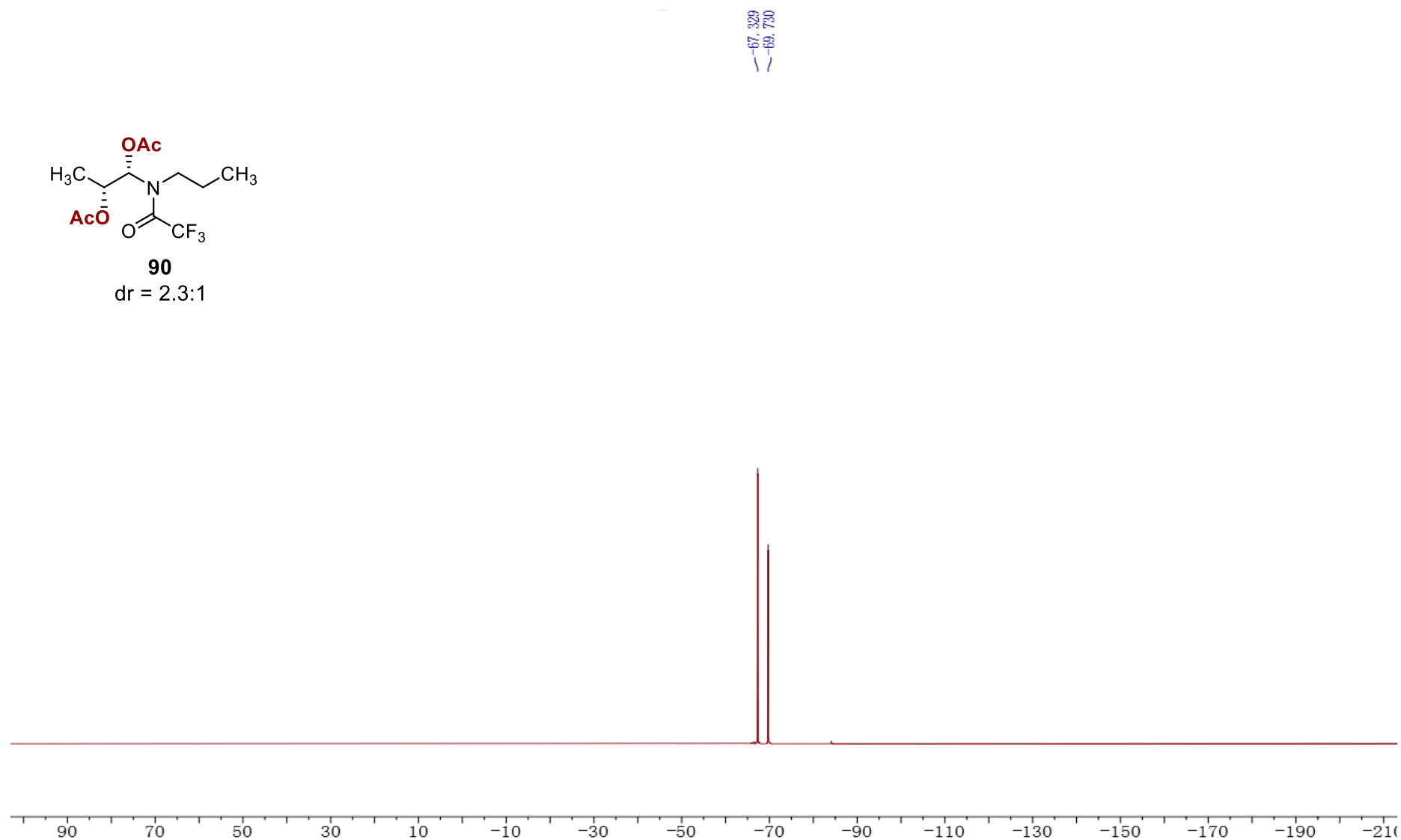
S300

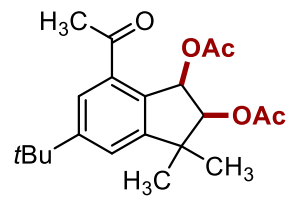




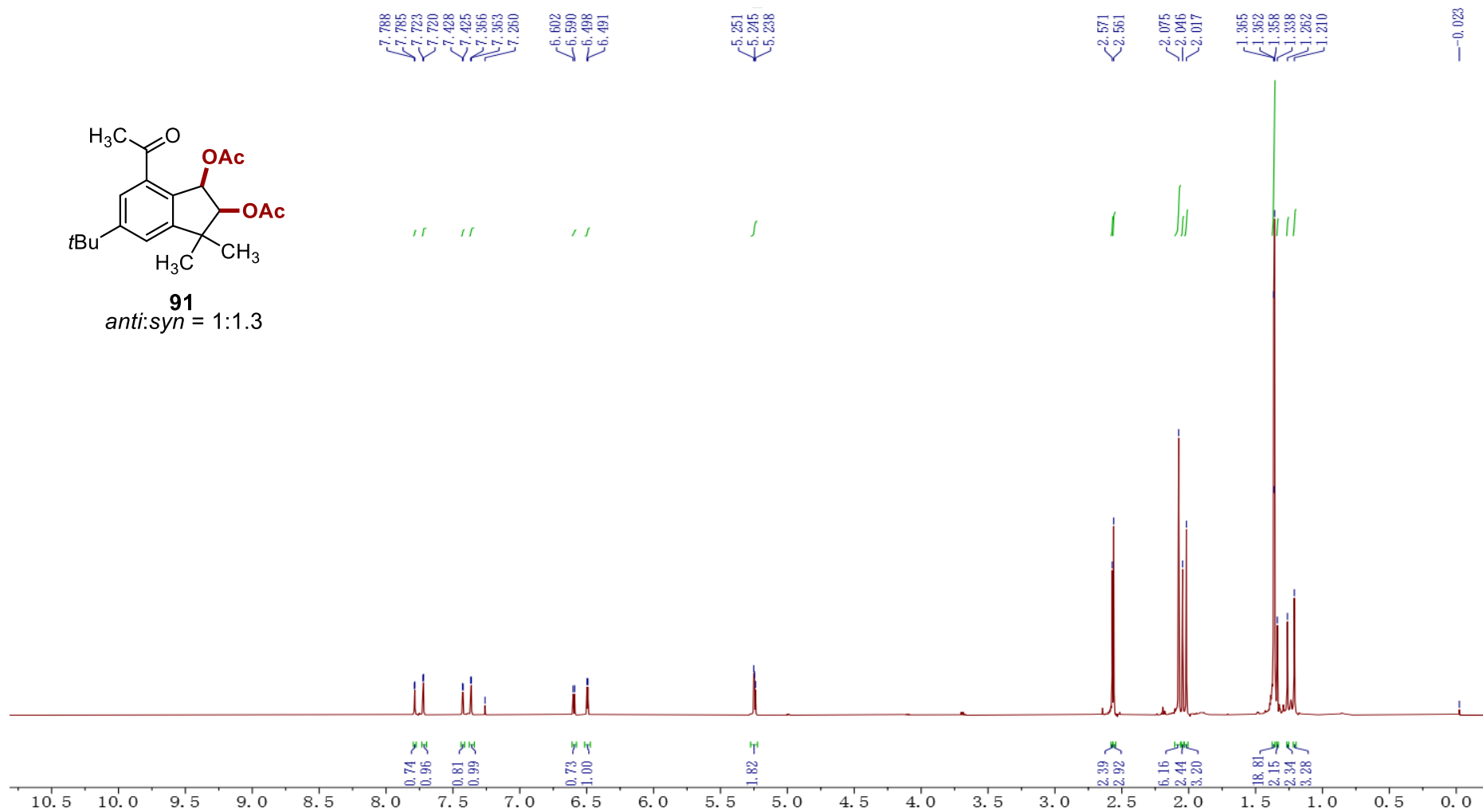


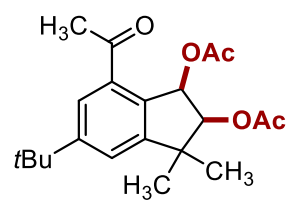
90
dr = 2.3:1



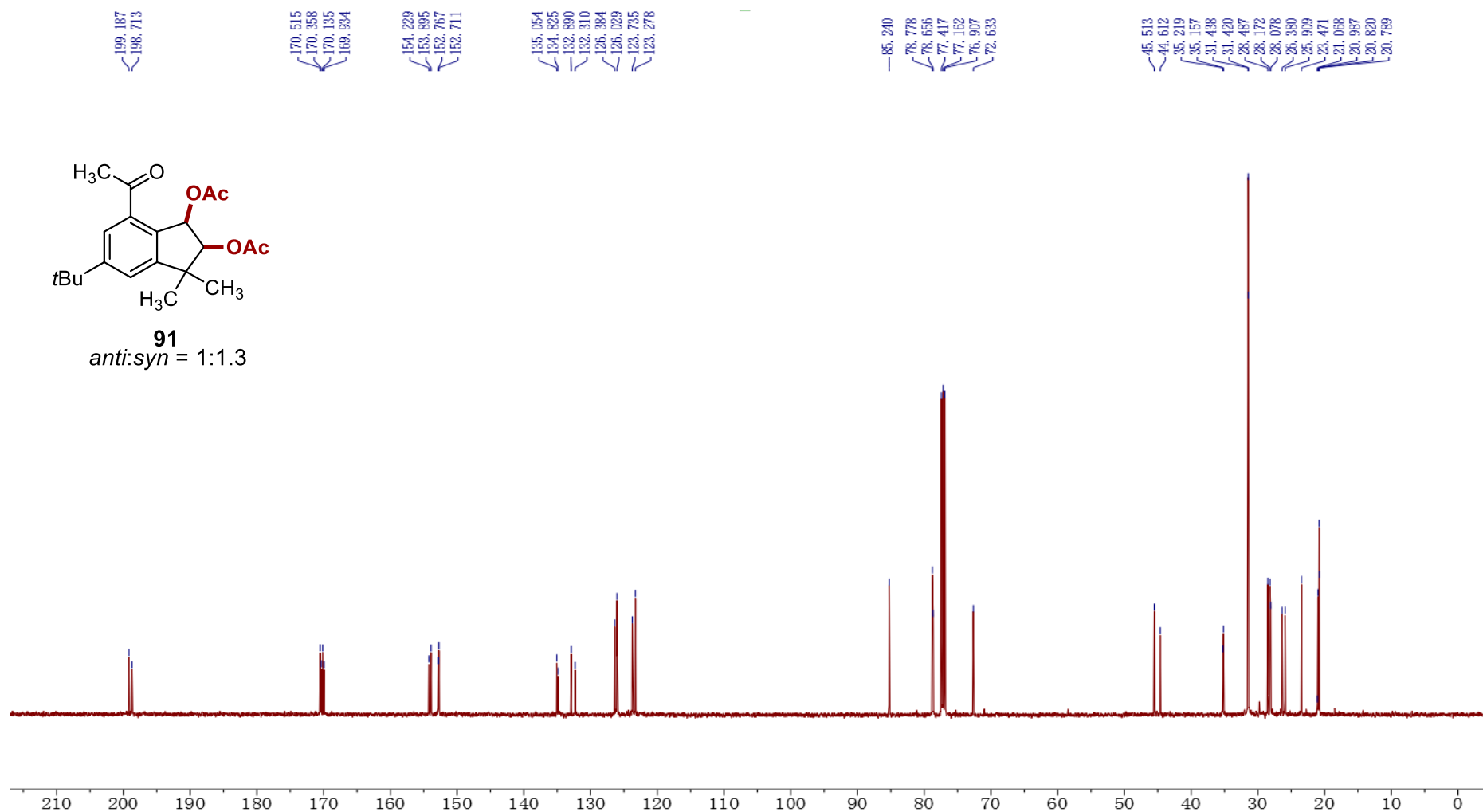


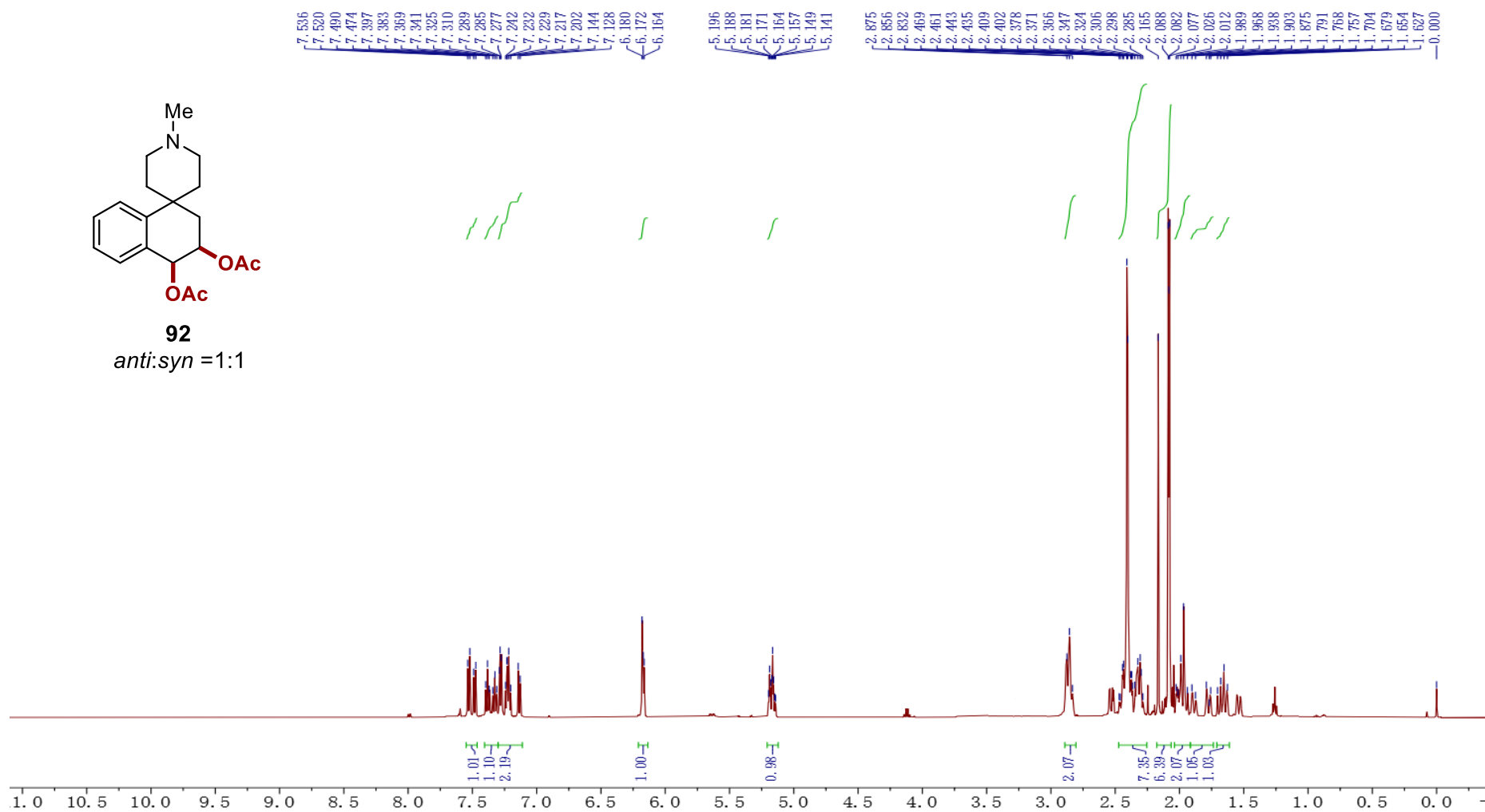
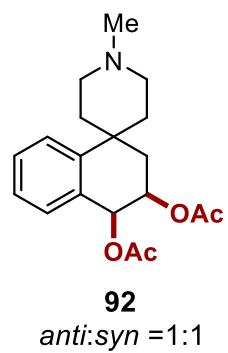
91
anti:syn = 1:1.3

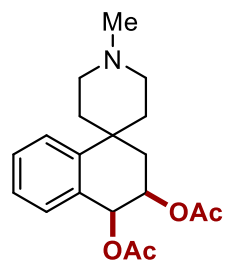




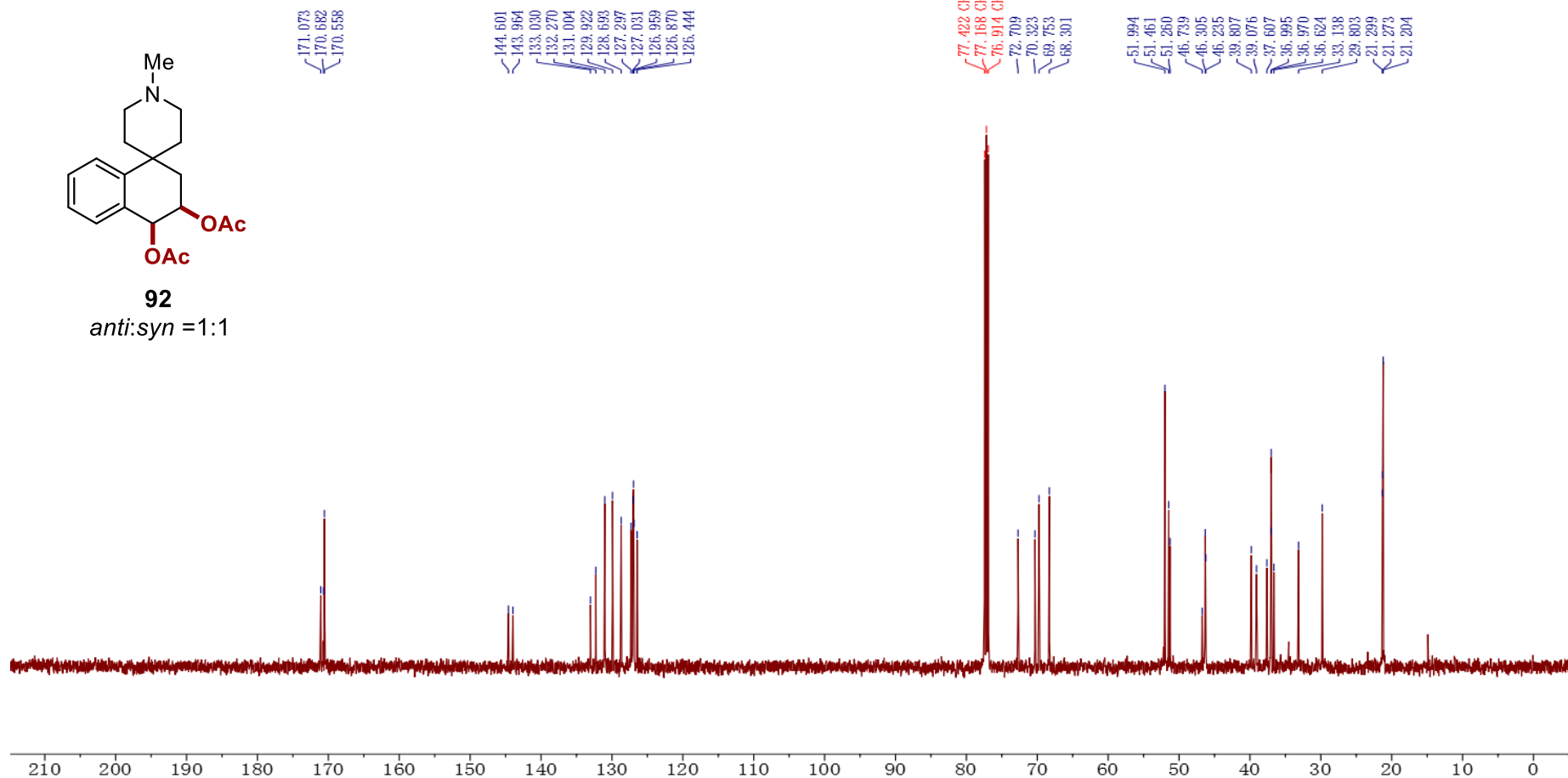
91
anti:syn = 1:1.3

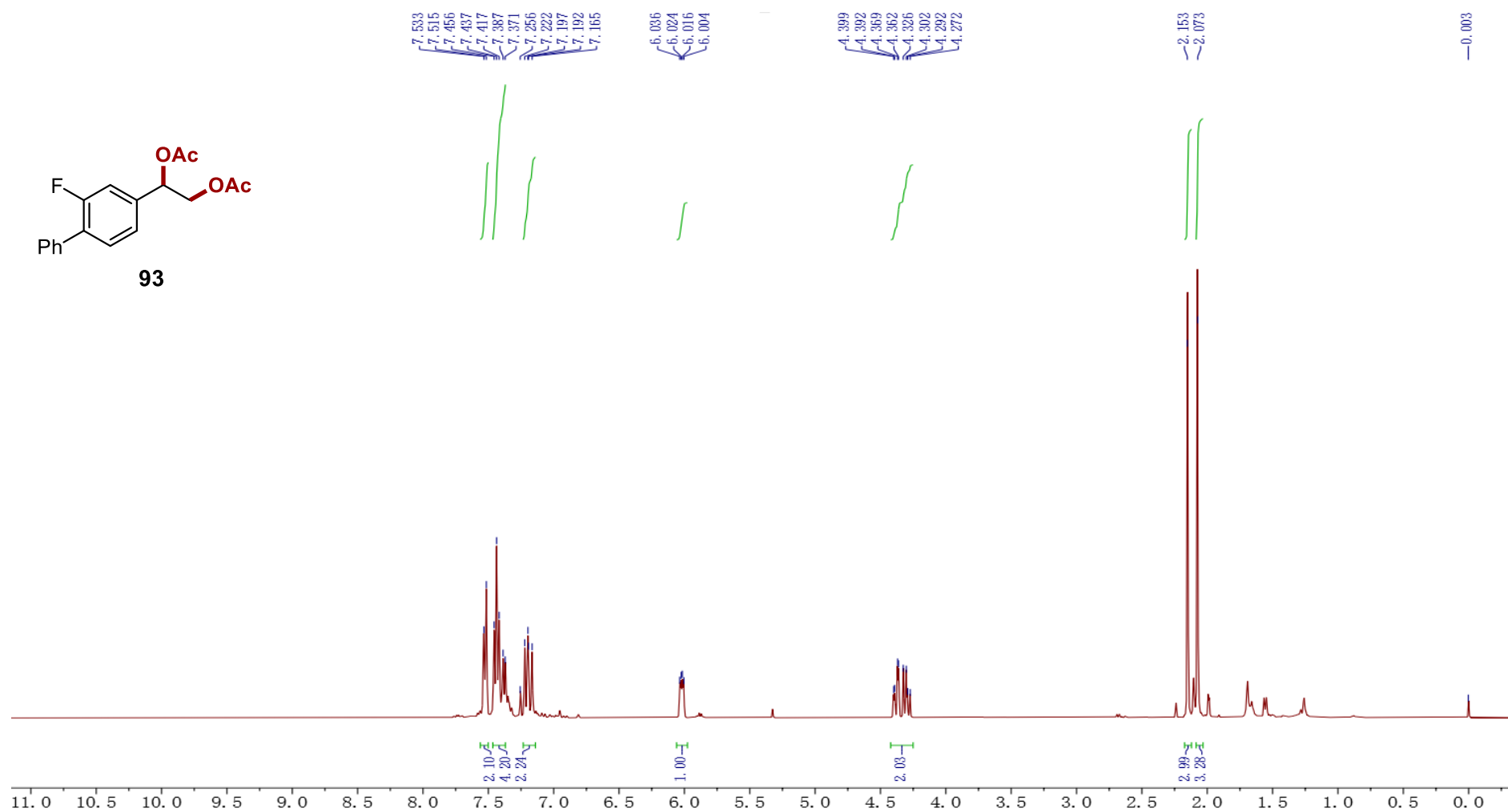


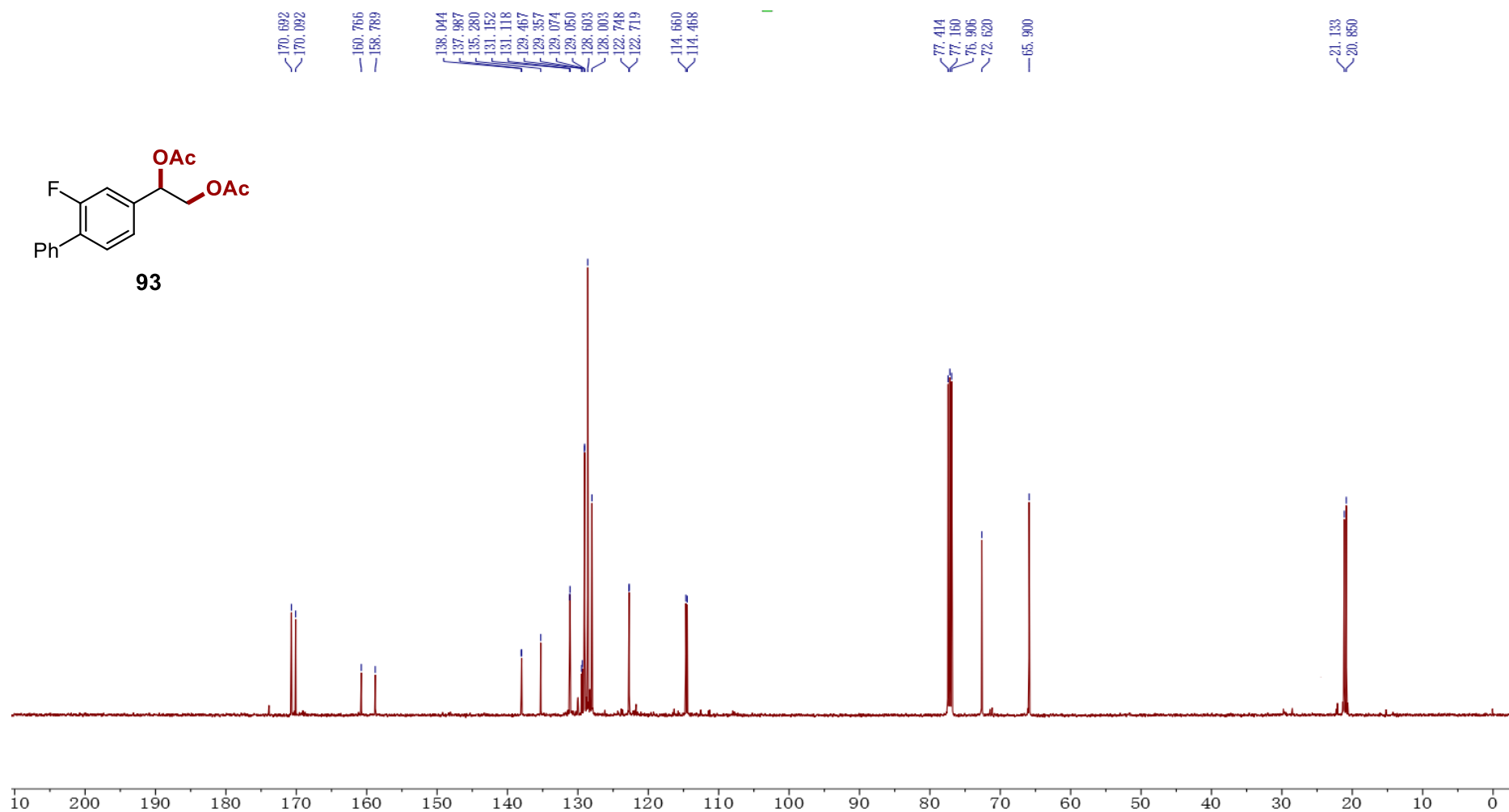


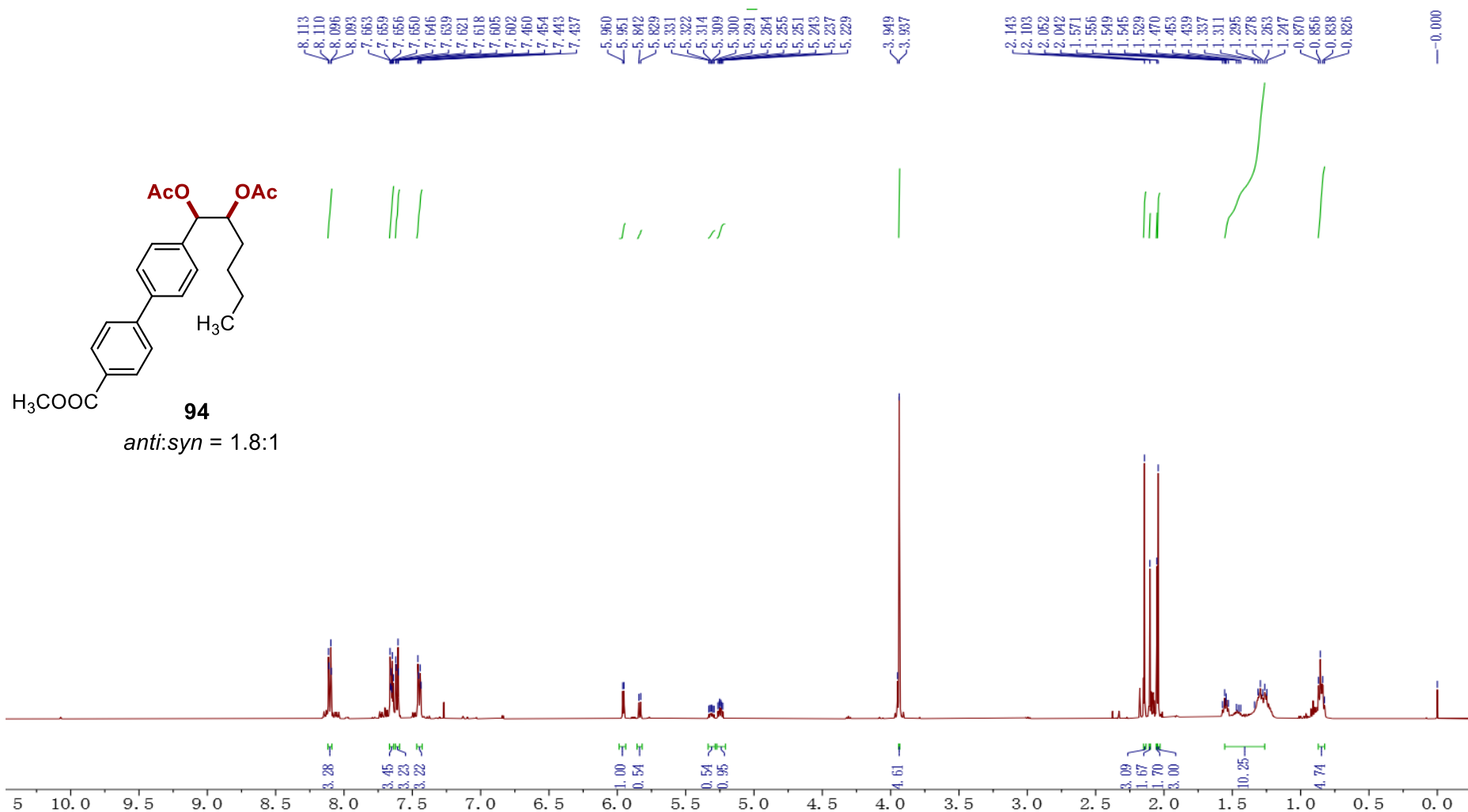


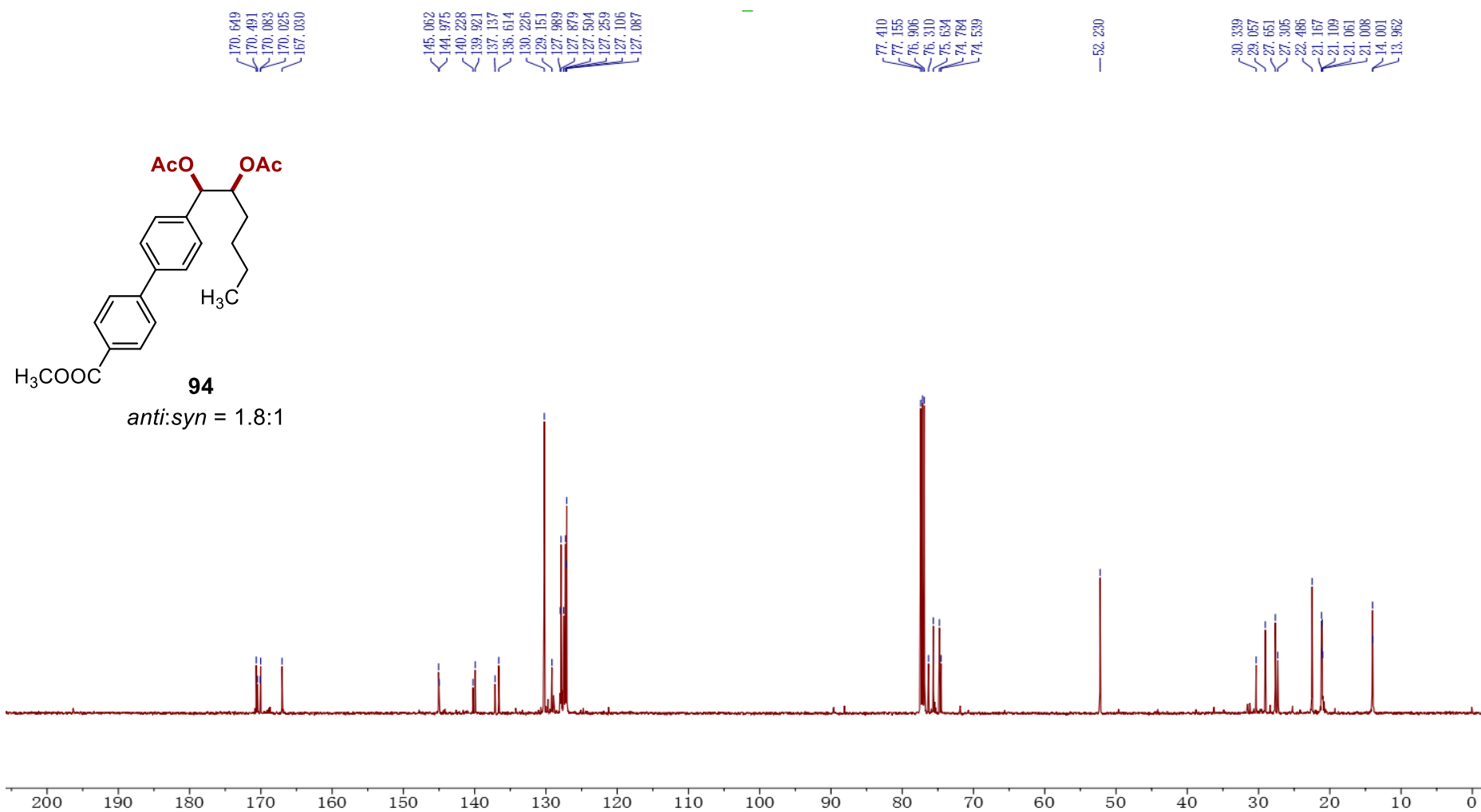
92
anti:syn = 1:1

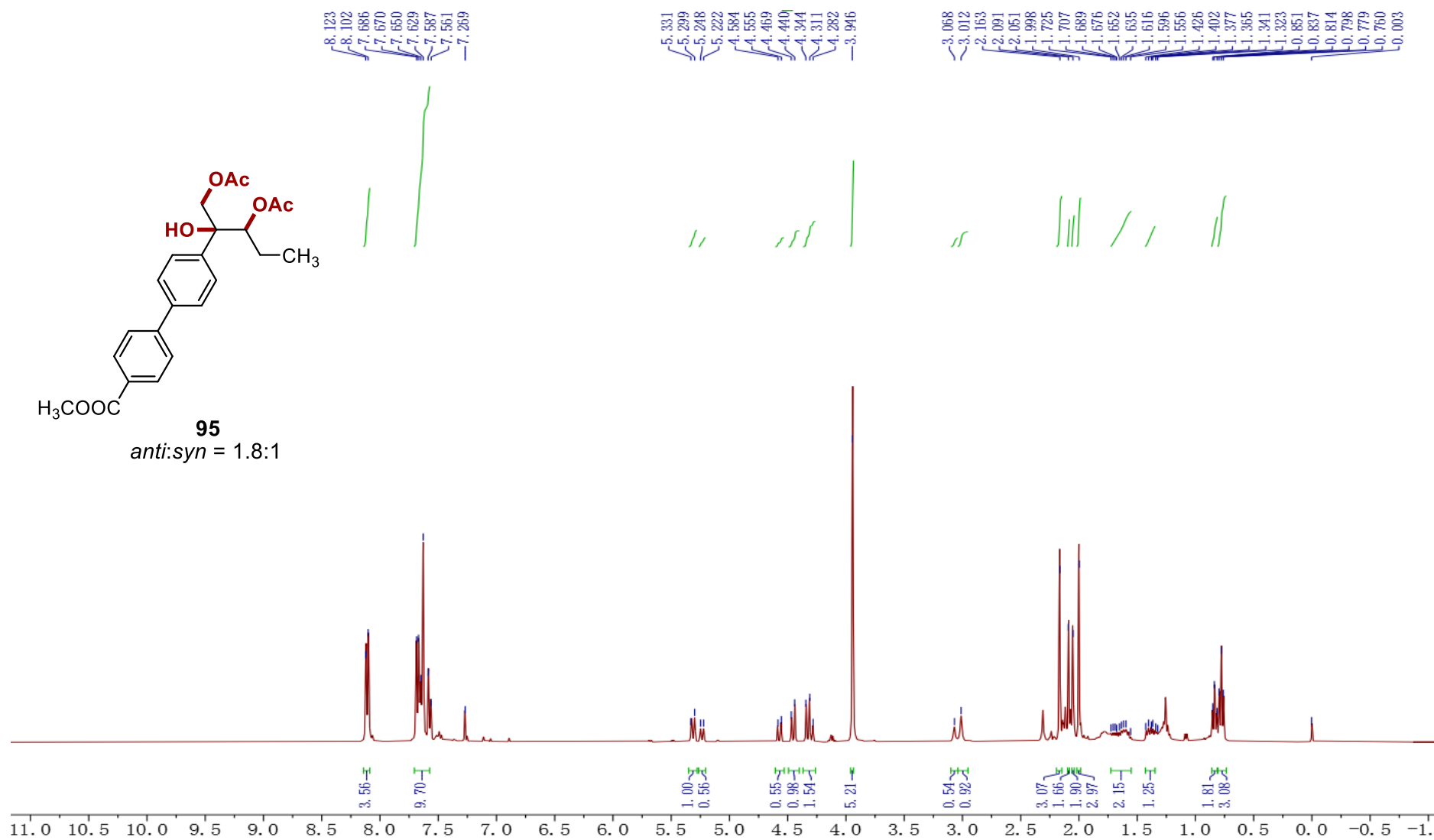


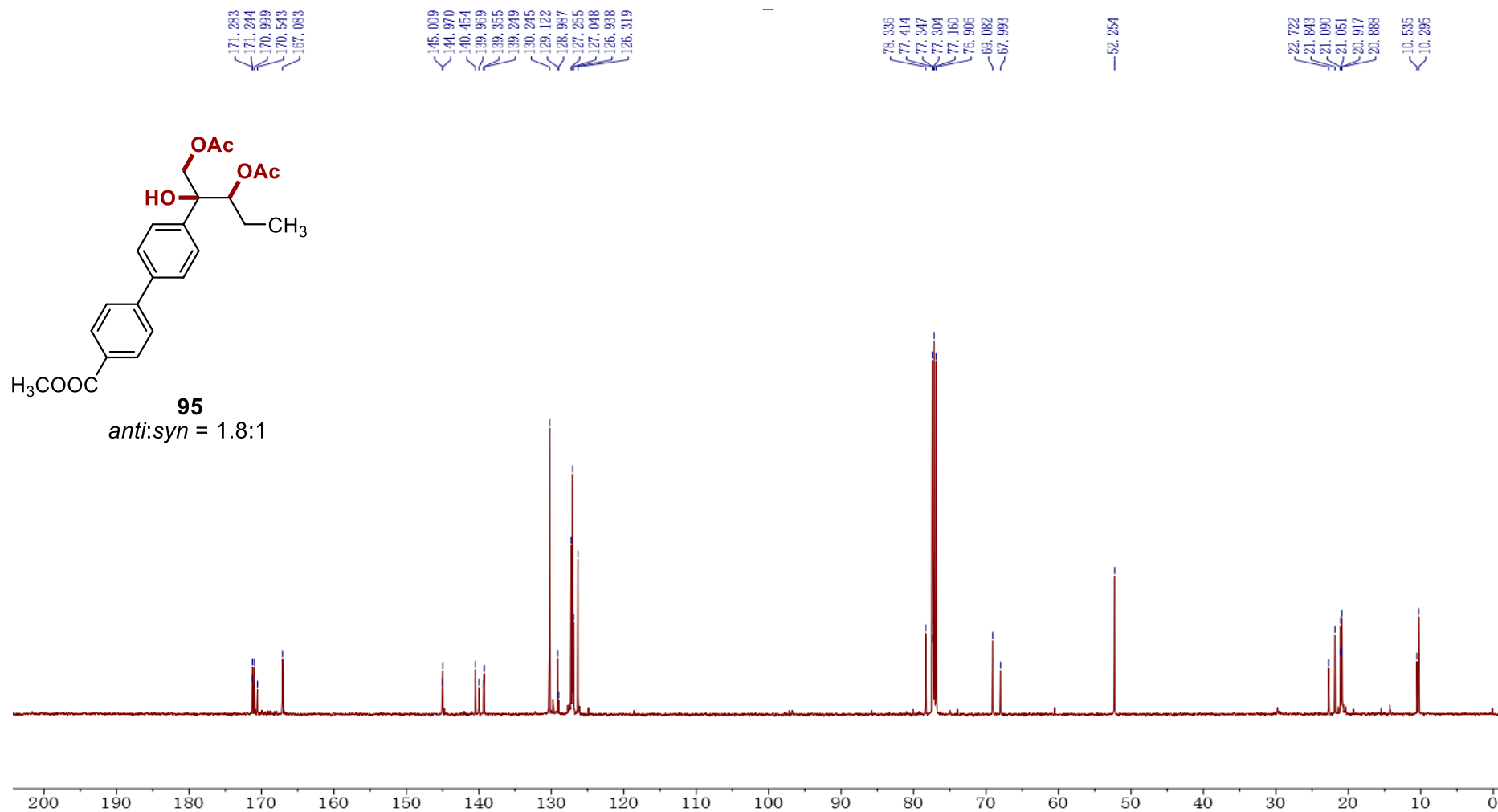


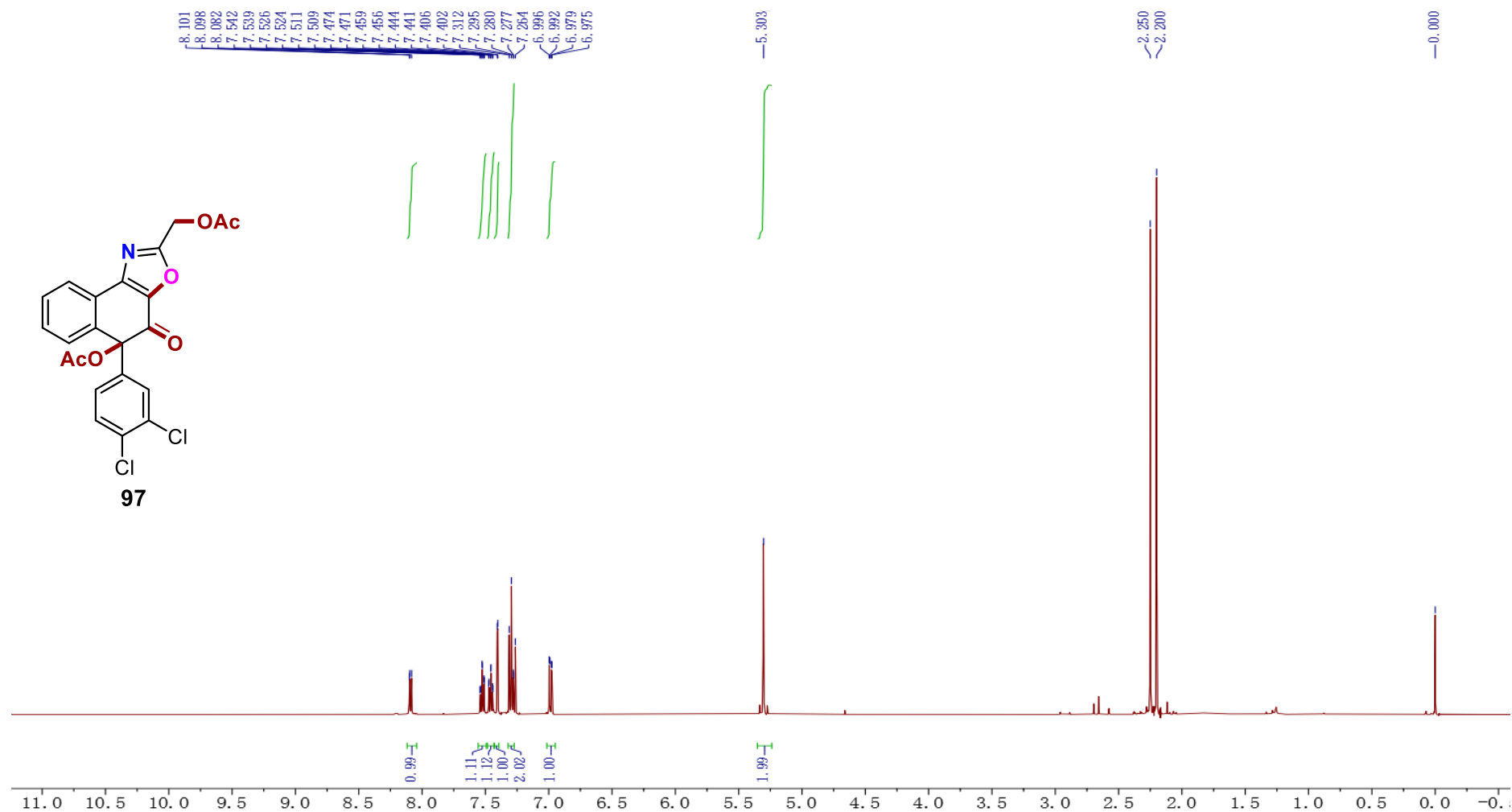


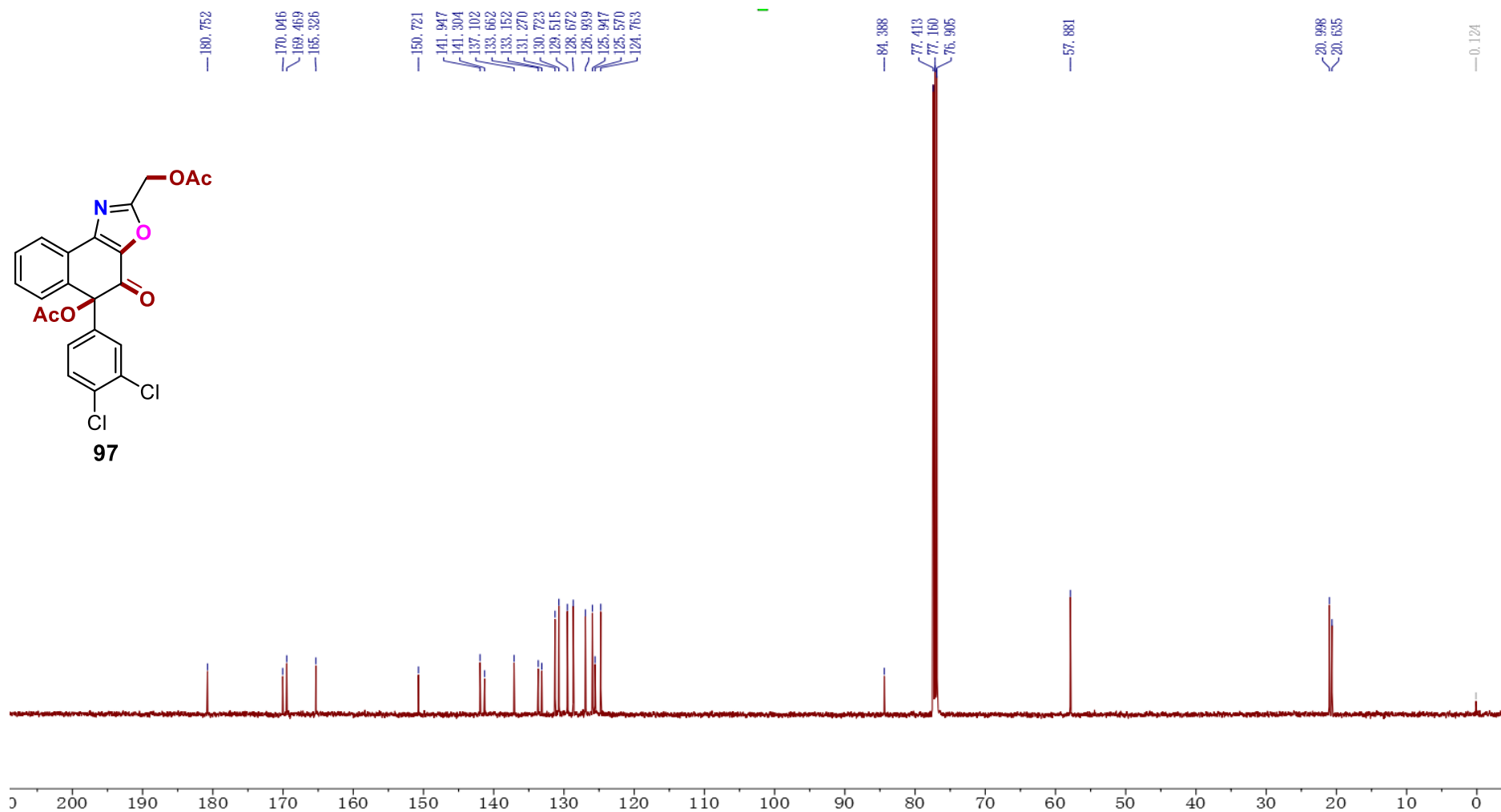


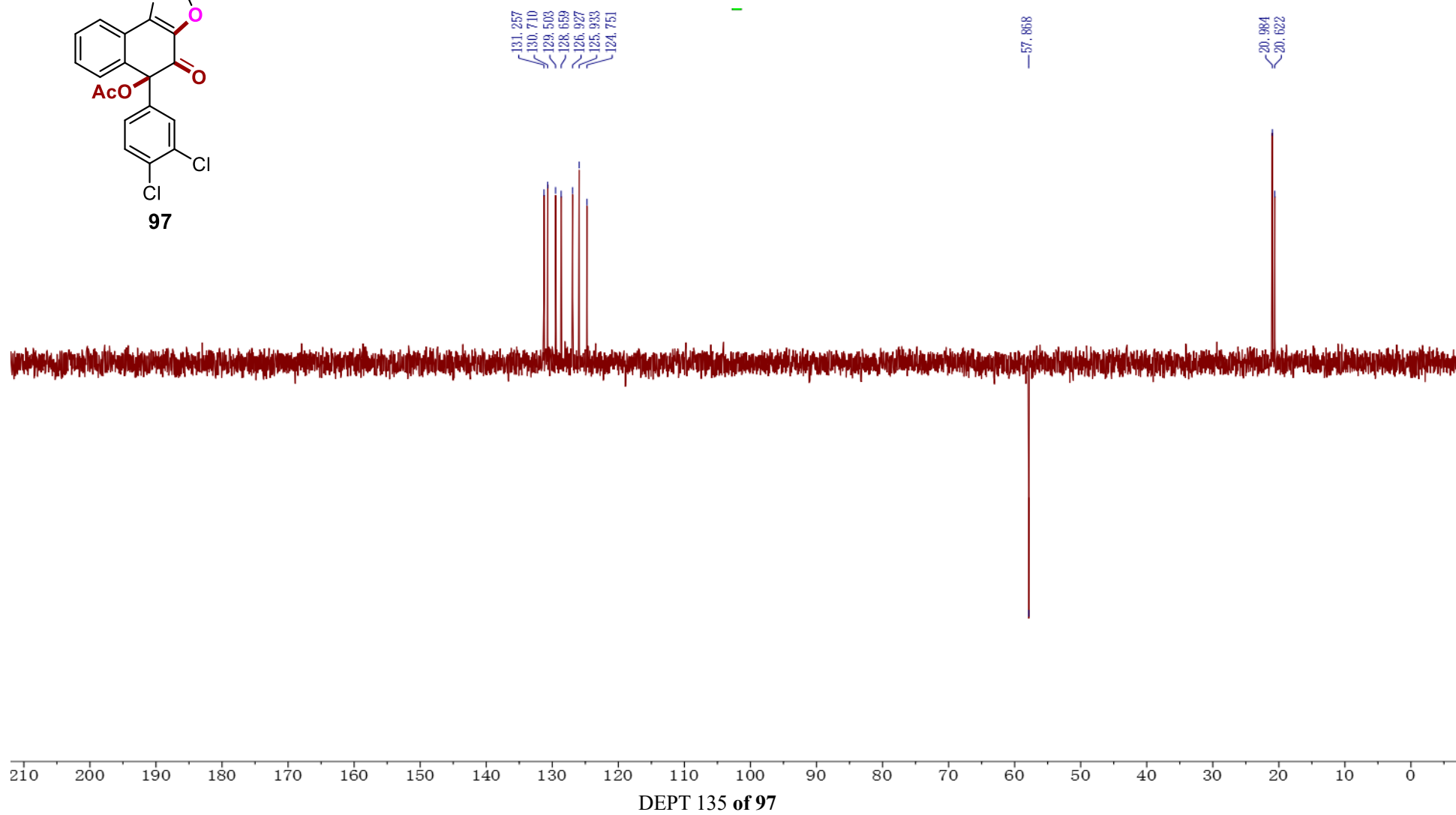
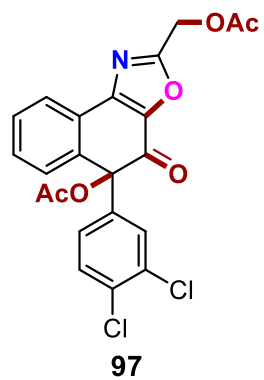


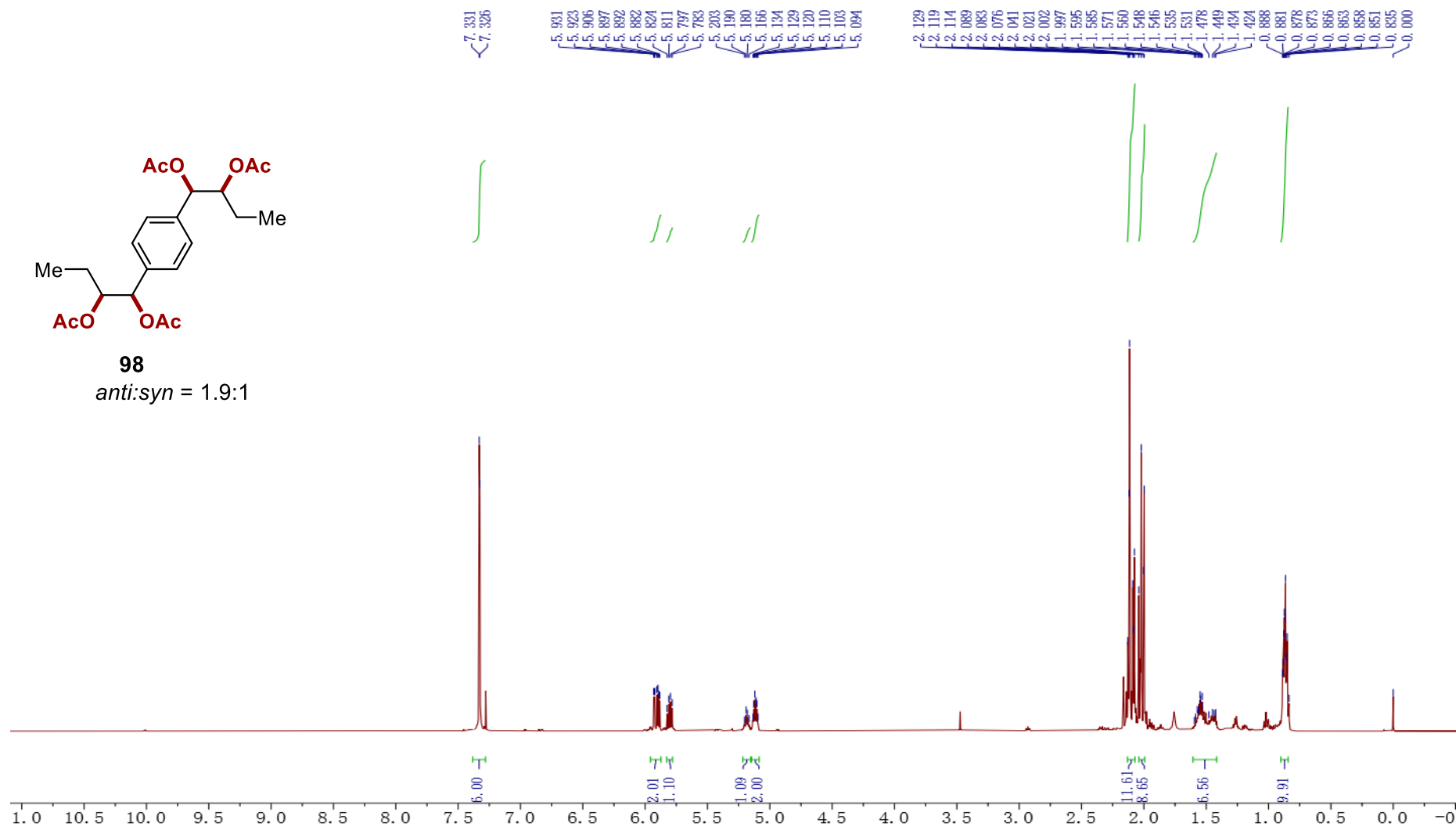


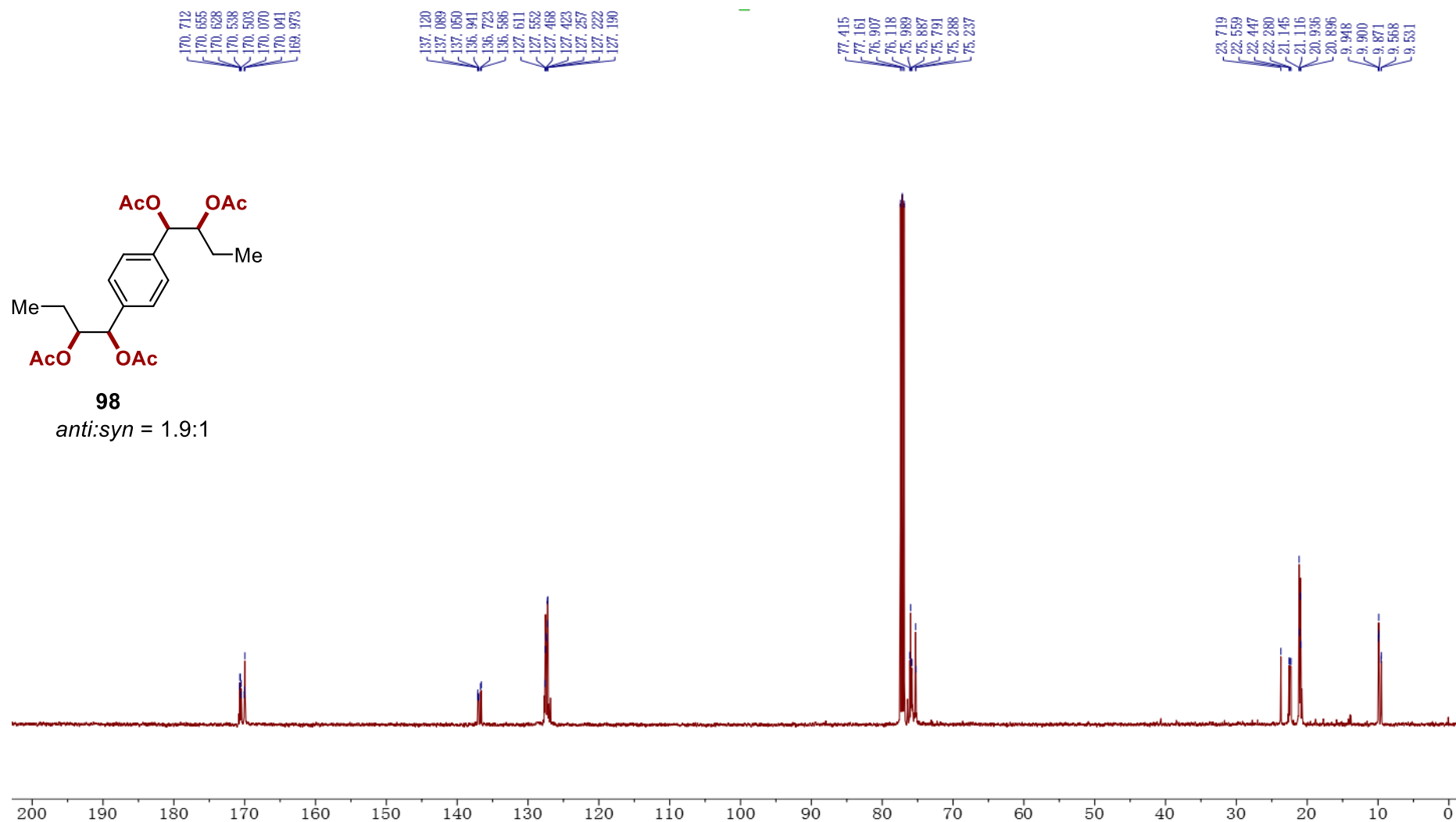


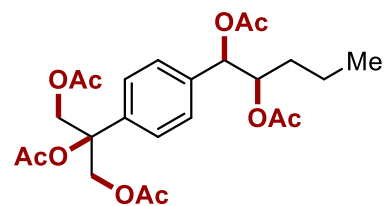






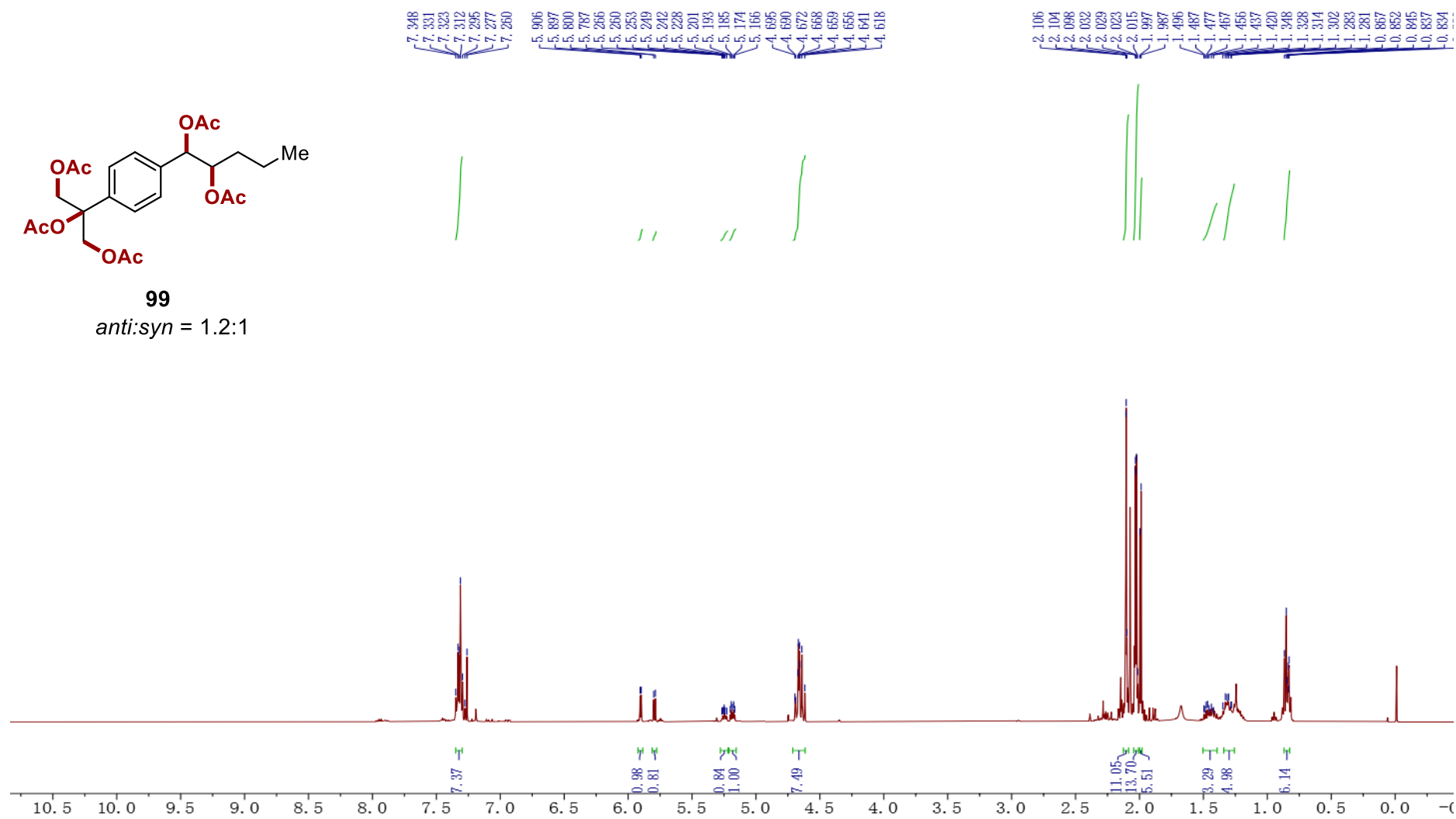


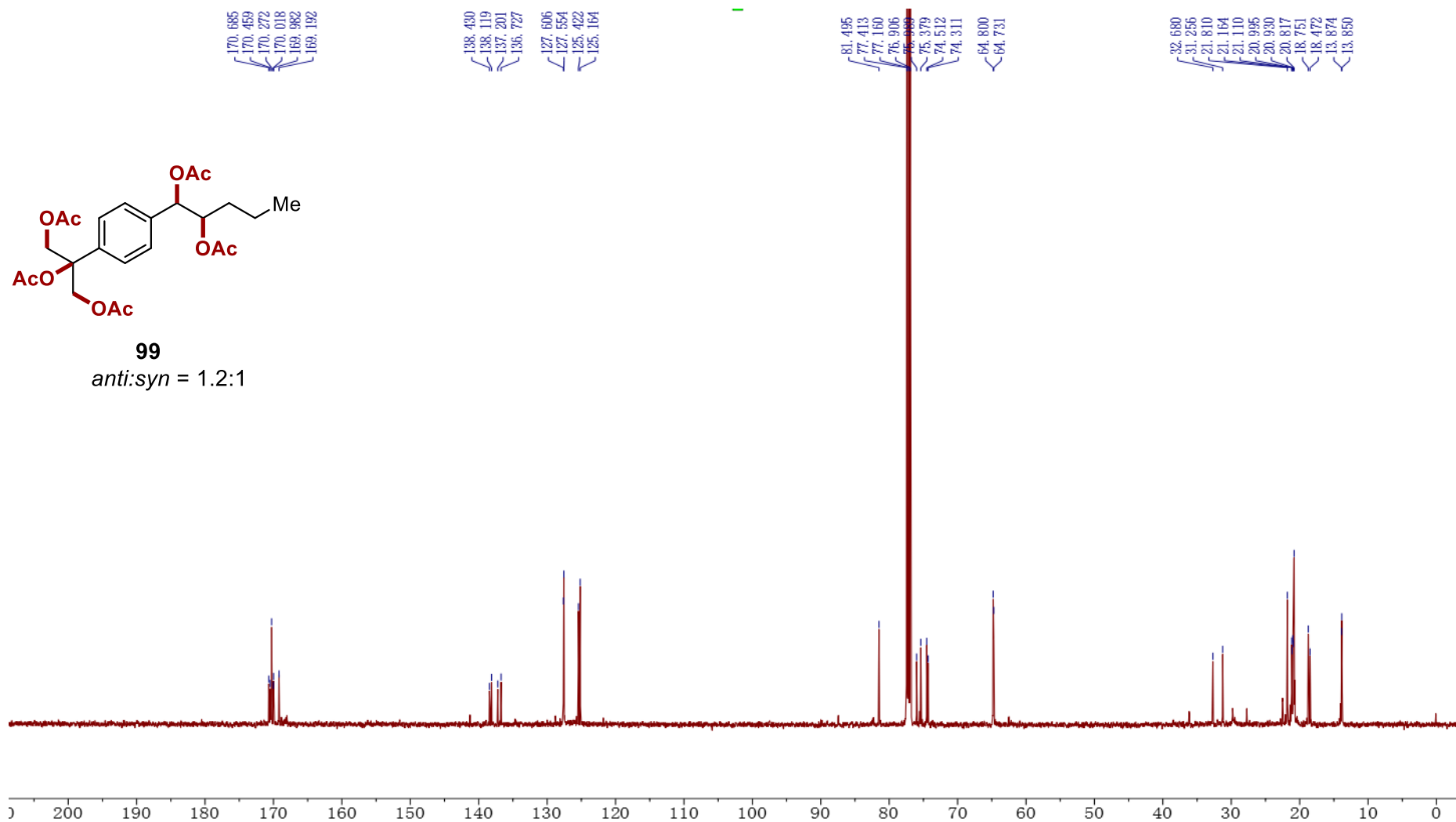


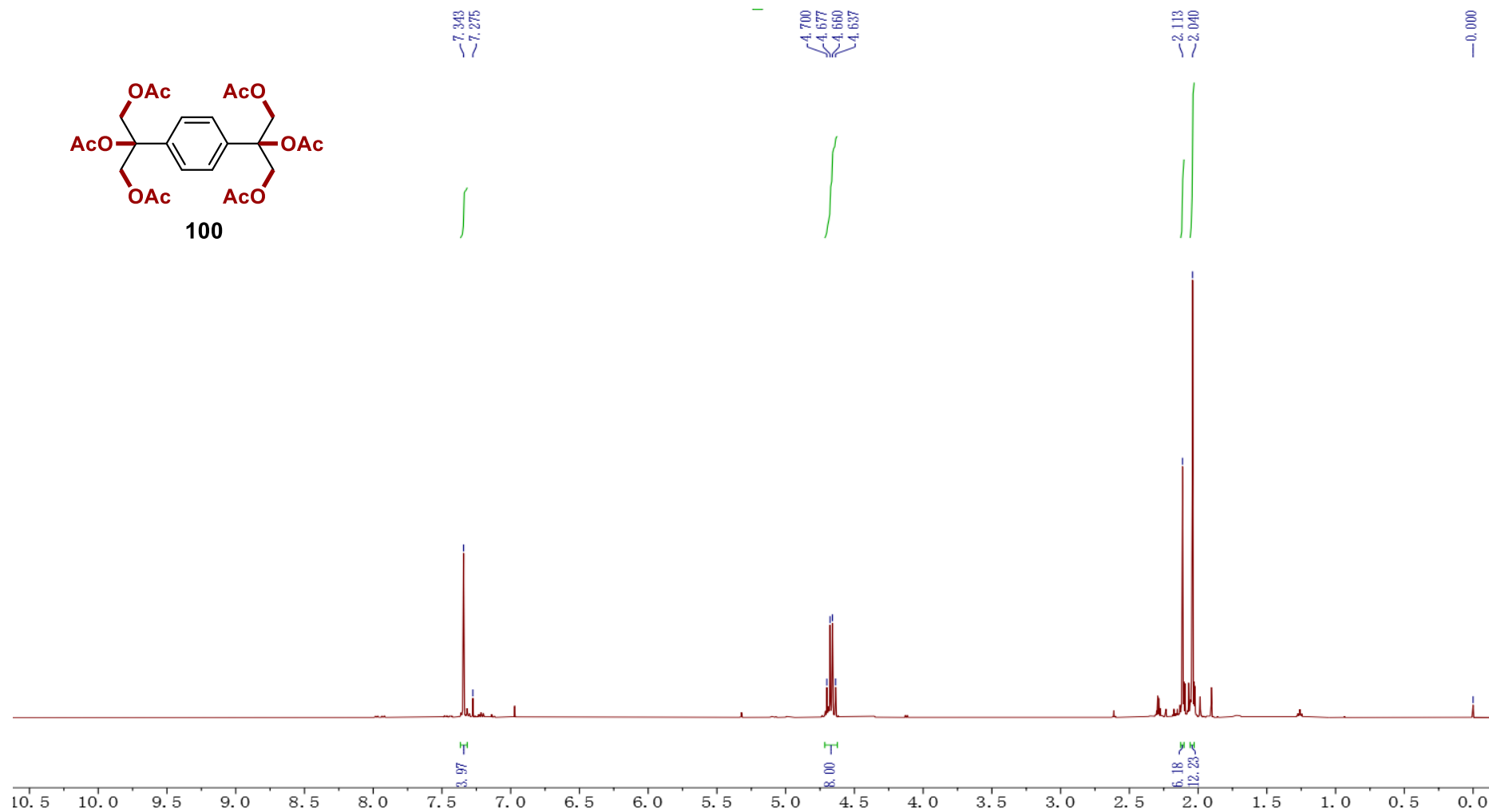
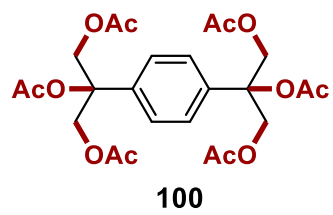


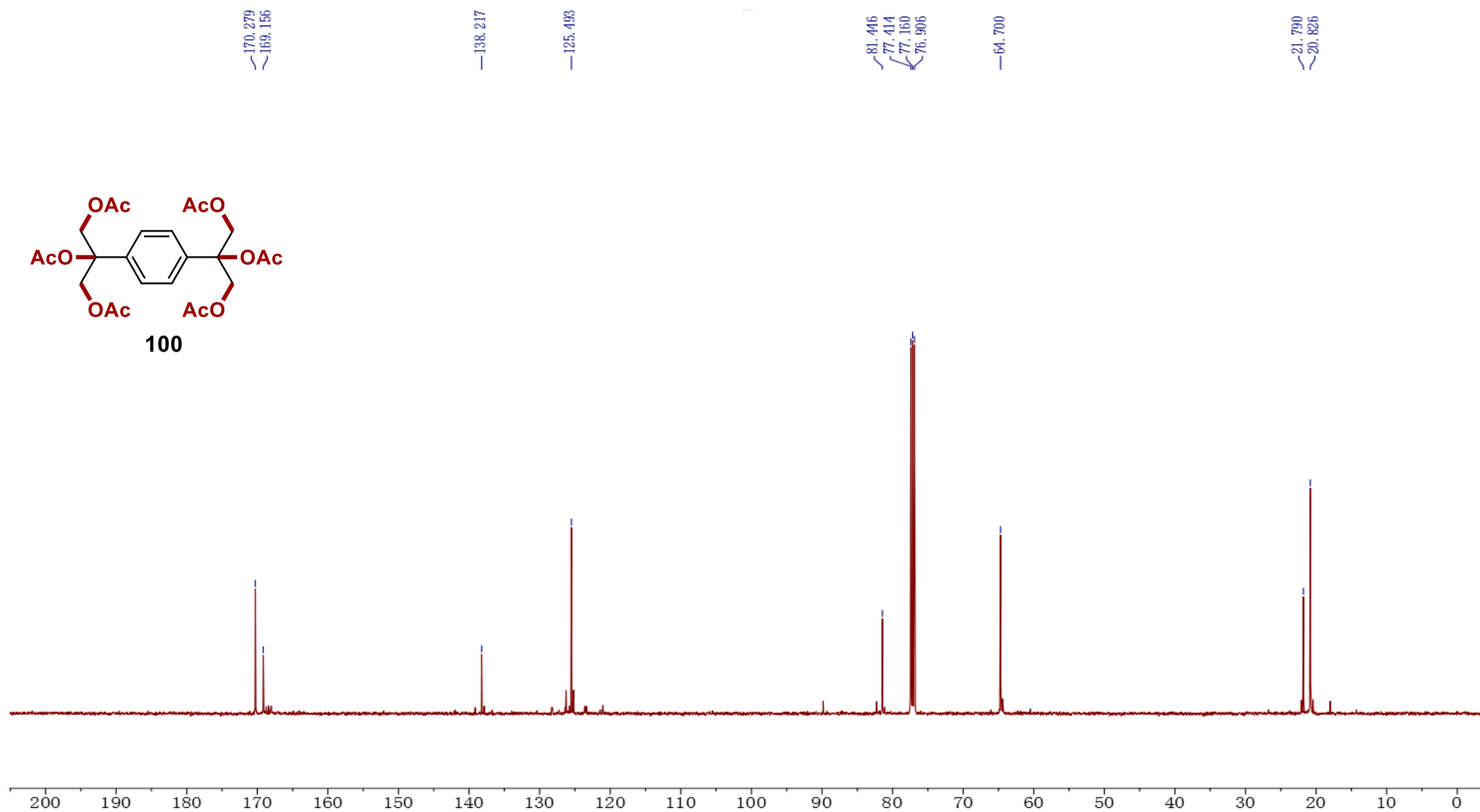
99

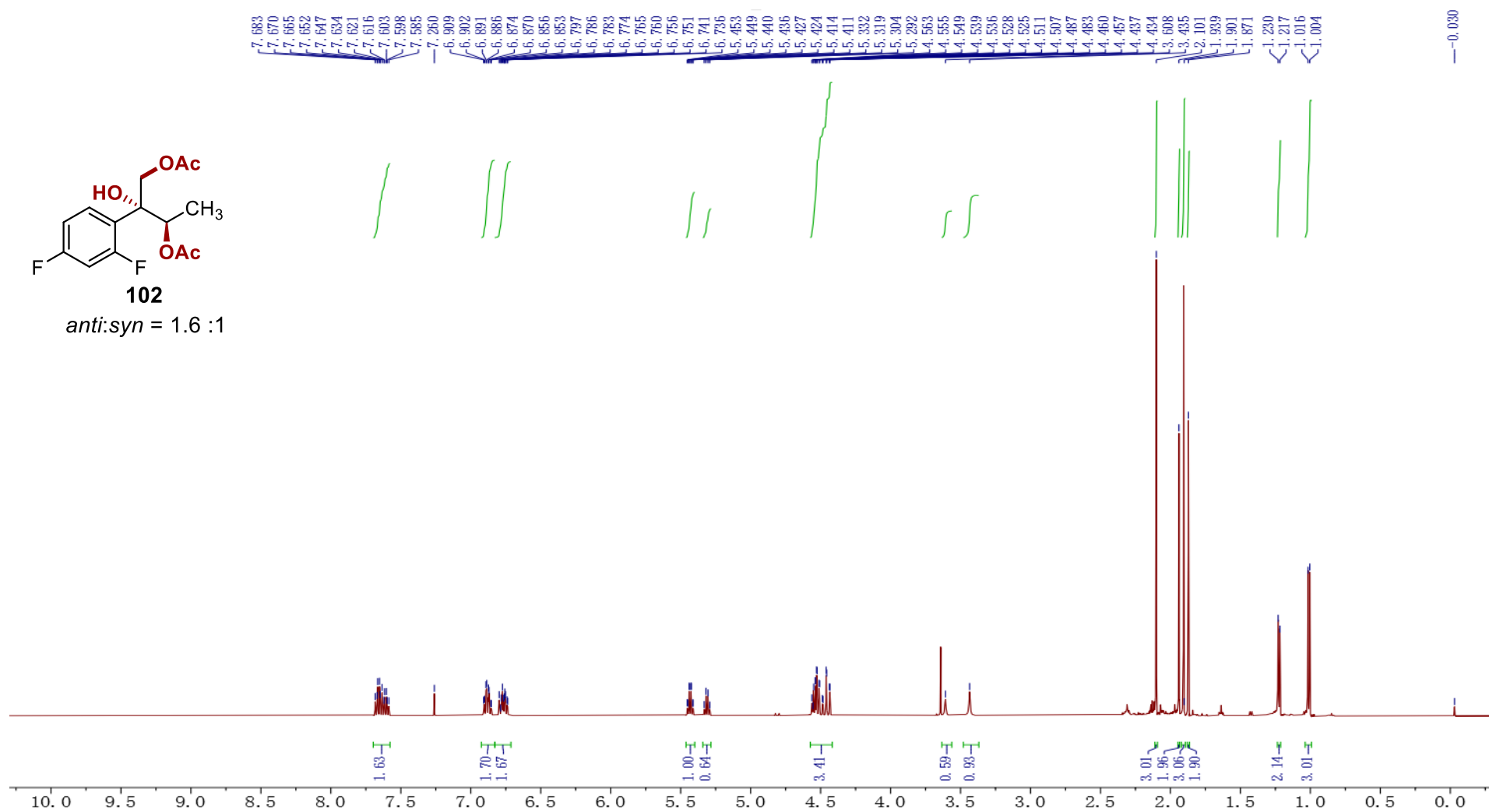
anti:syn = 1.2:1

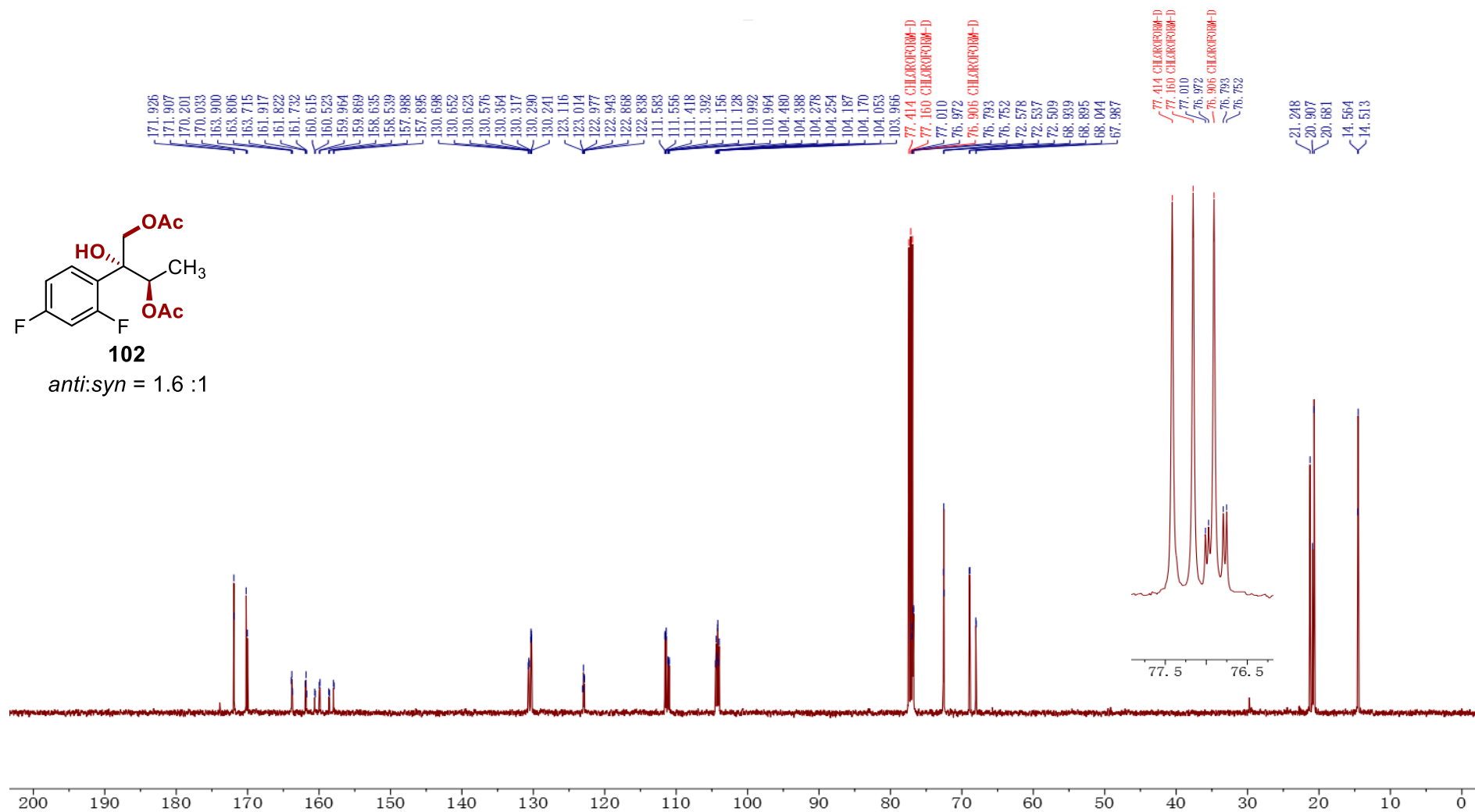
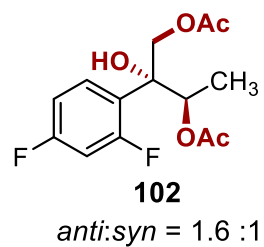


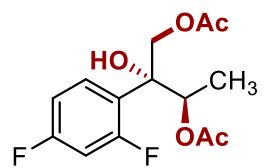






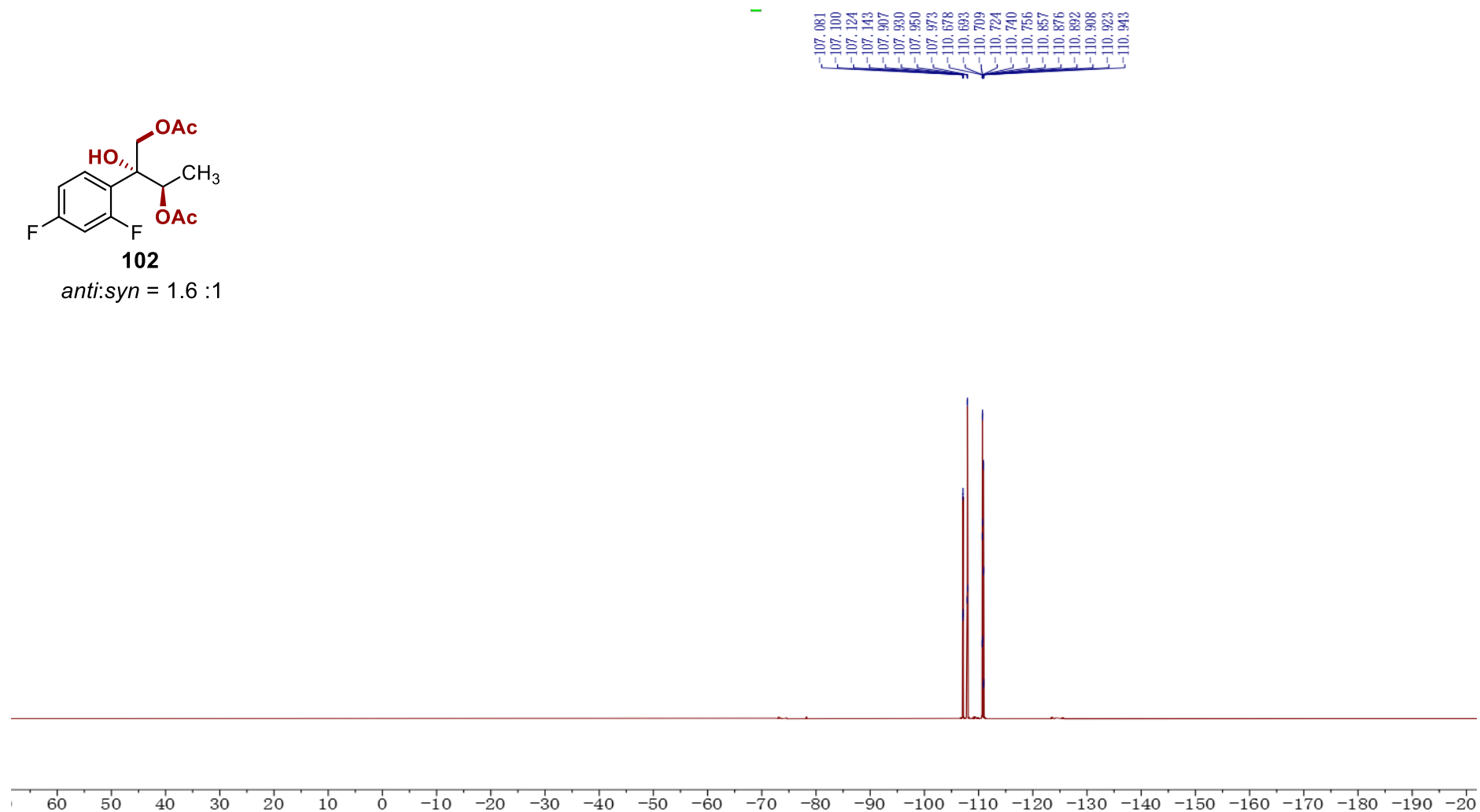


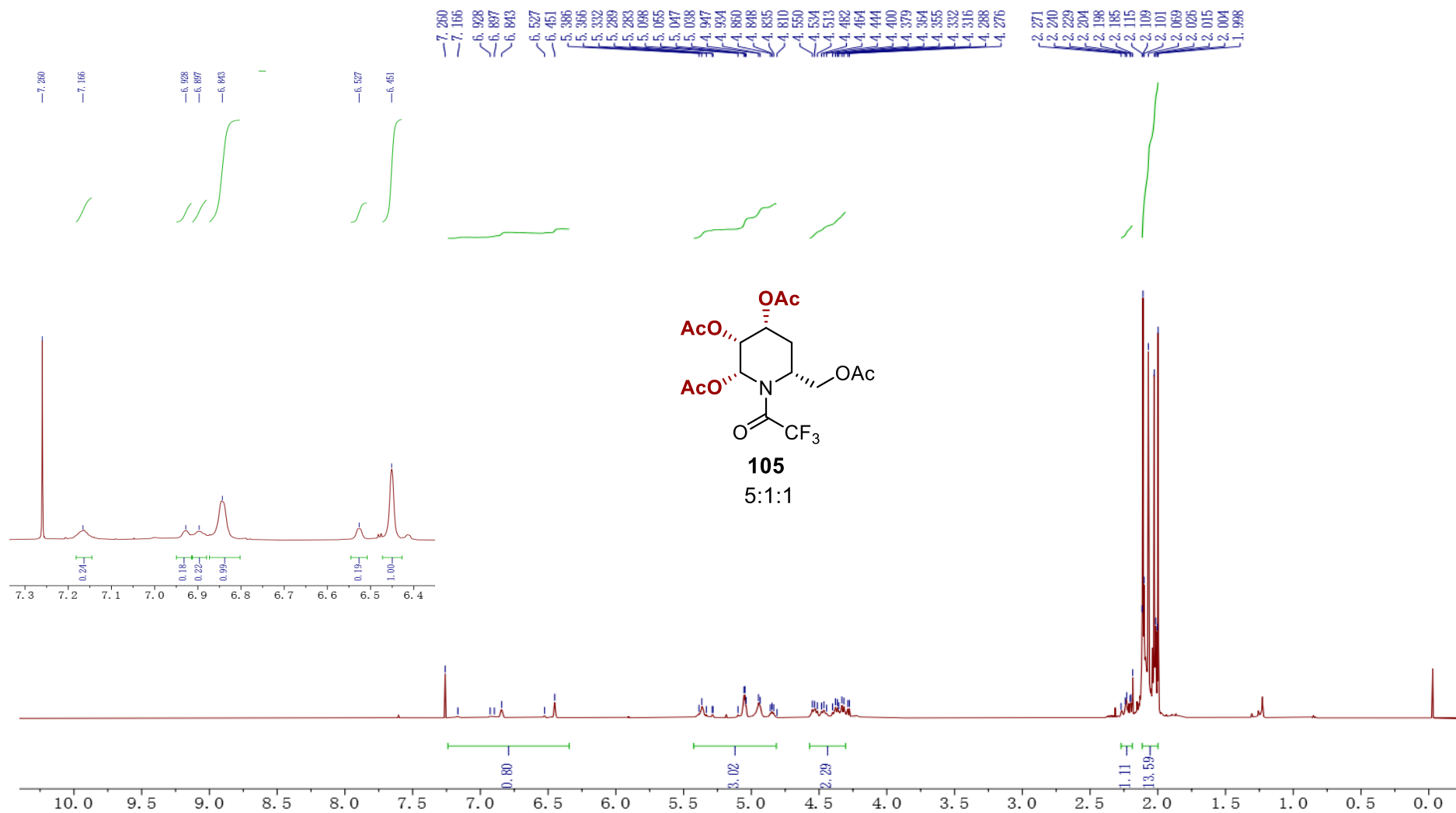


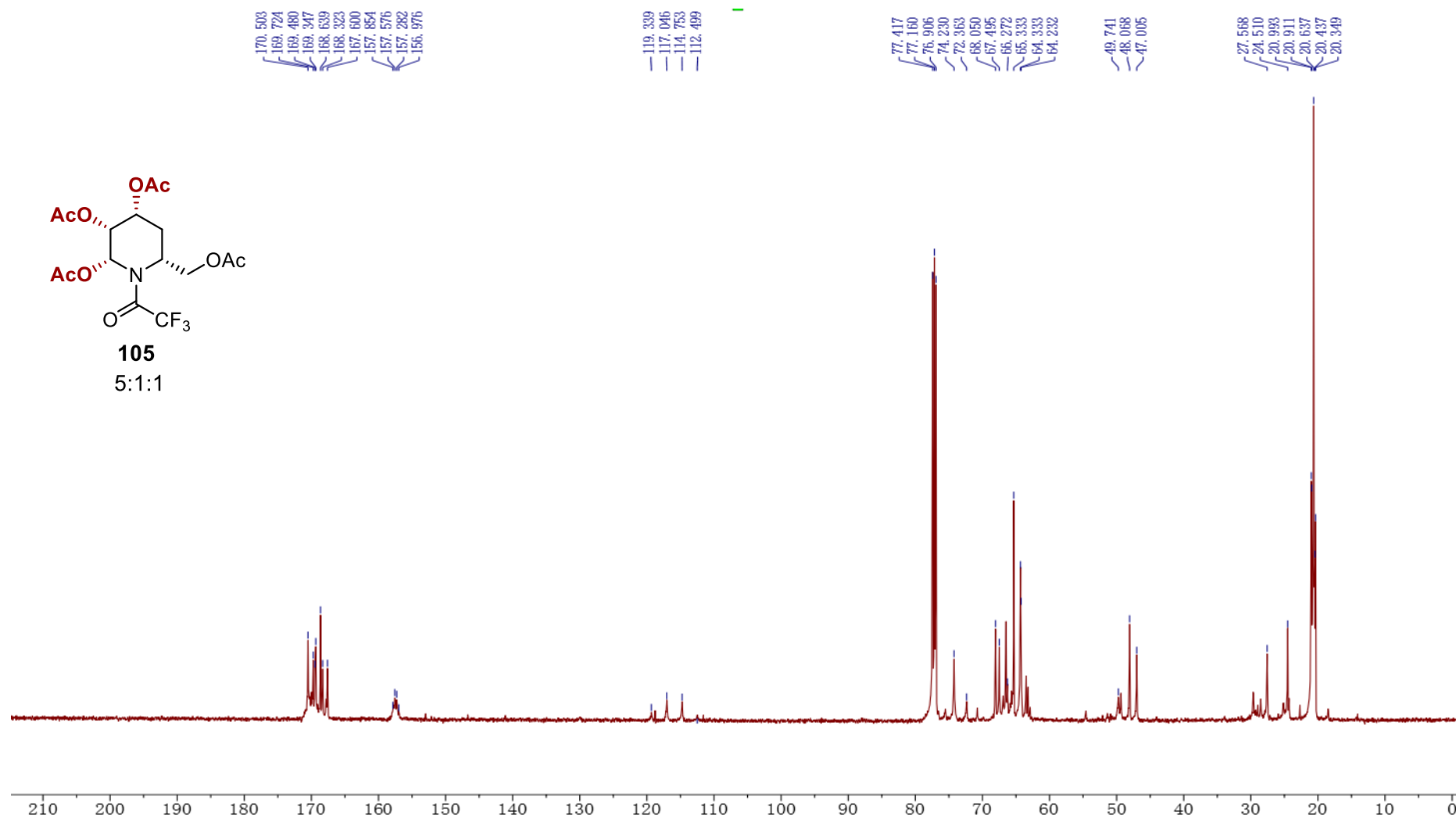


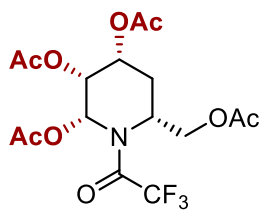
102

anti:syn = 1.6 :1



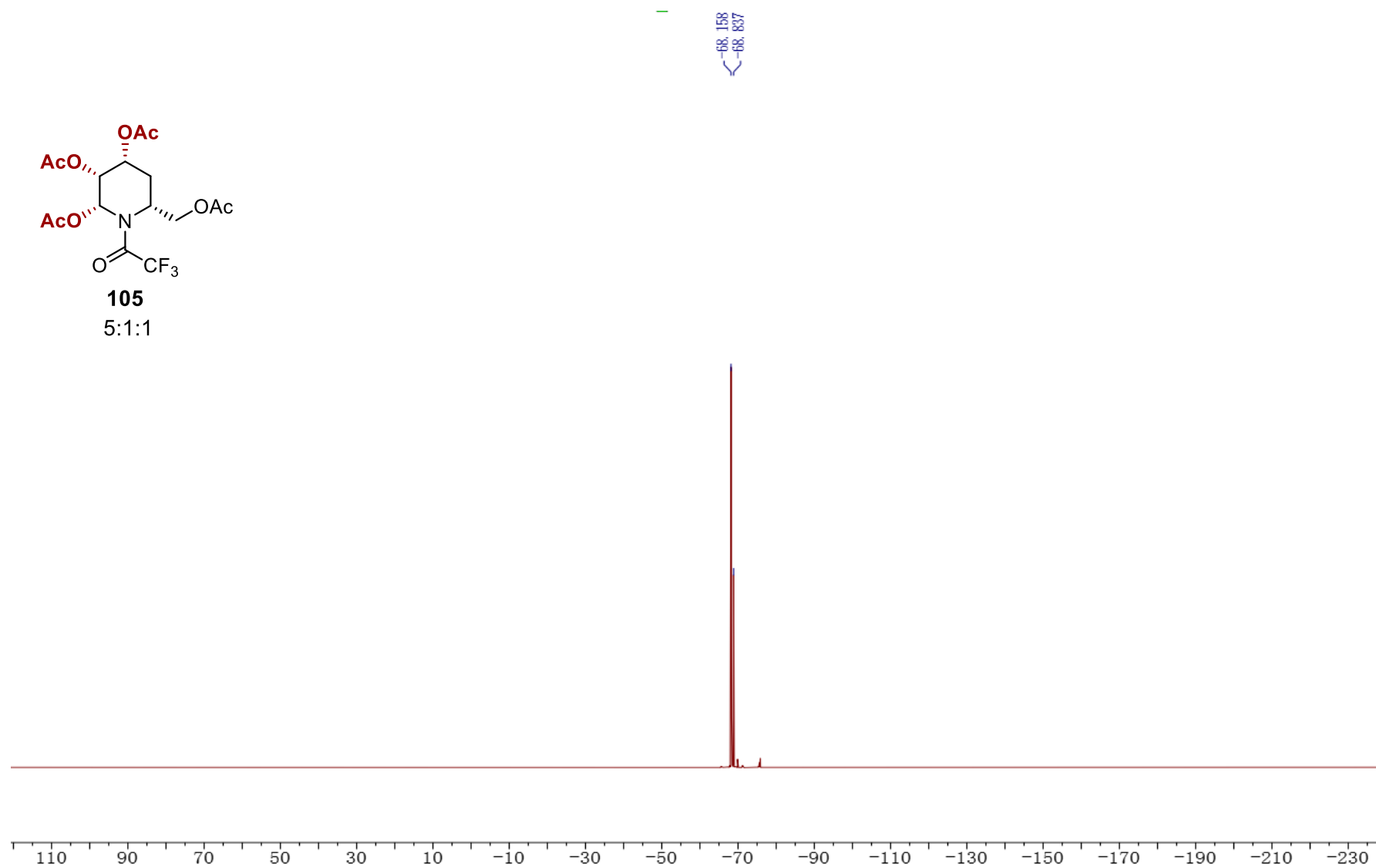




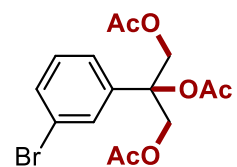


105

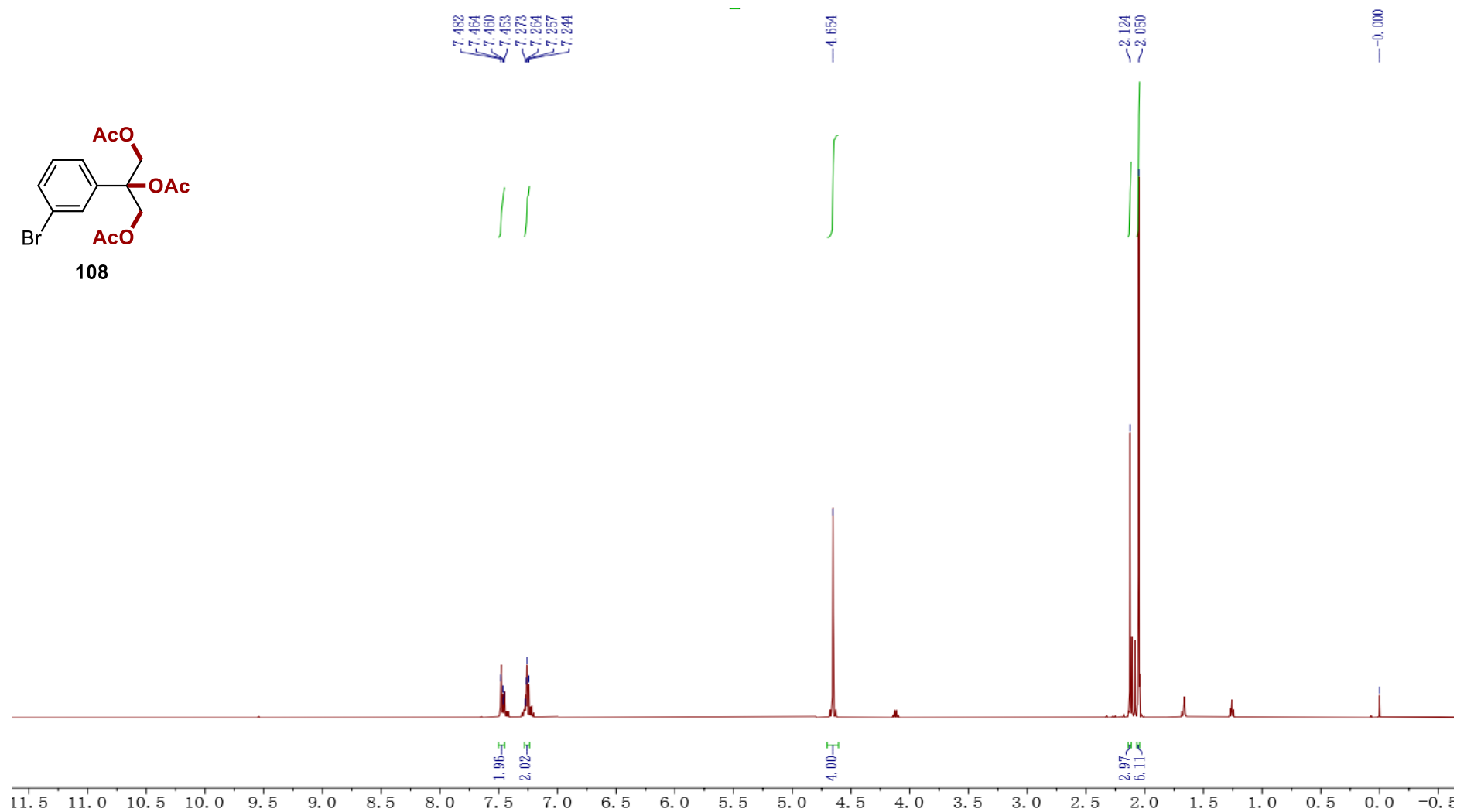
5:1:1

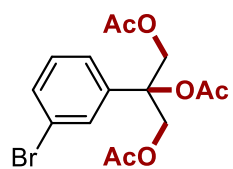


S328

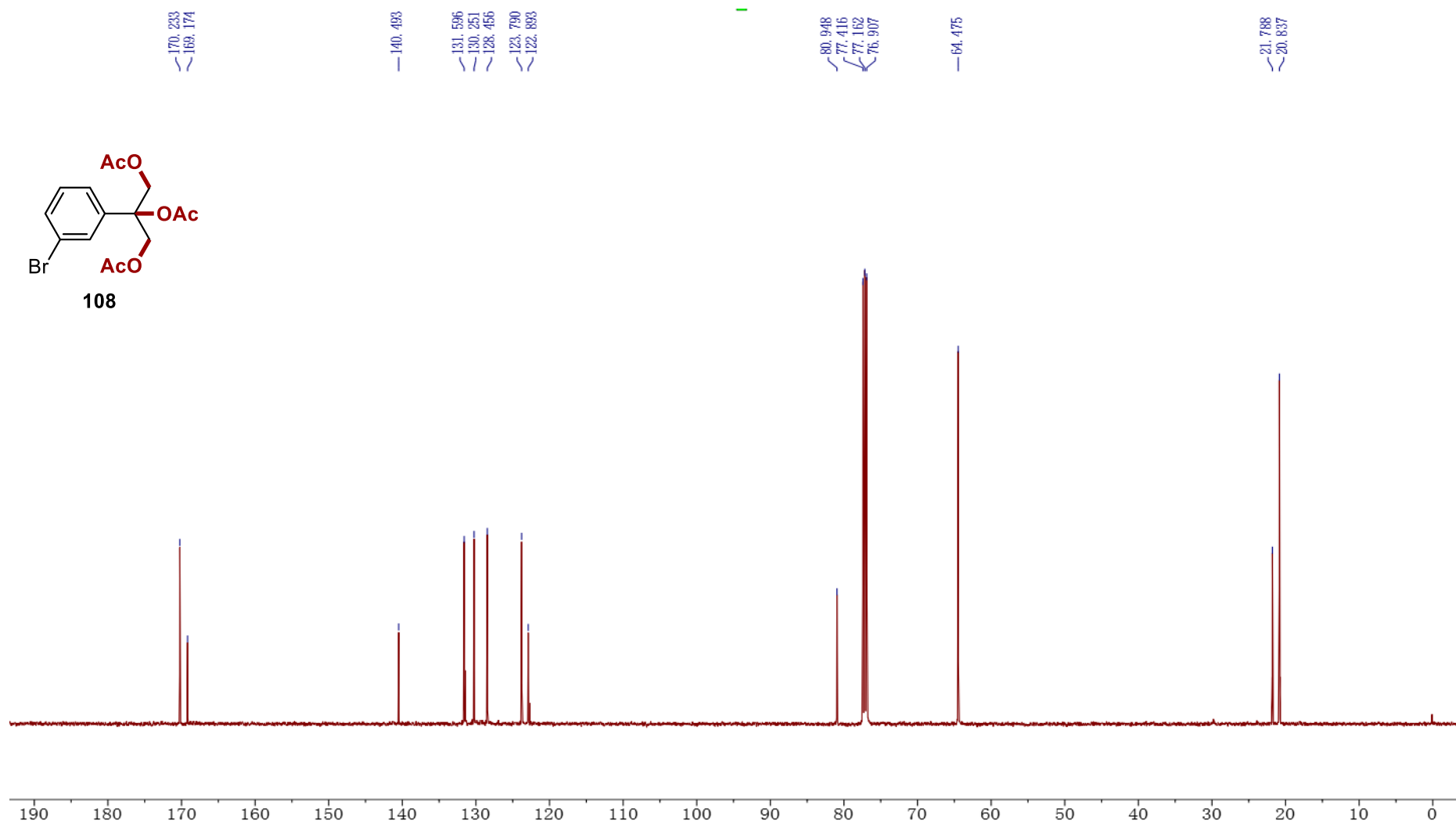


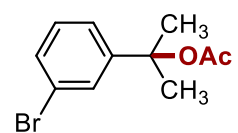
108



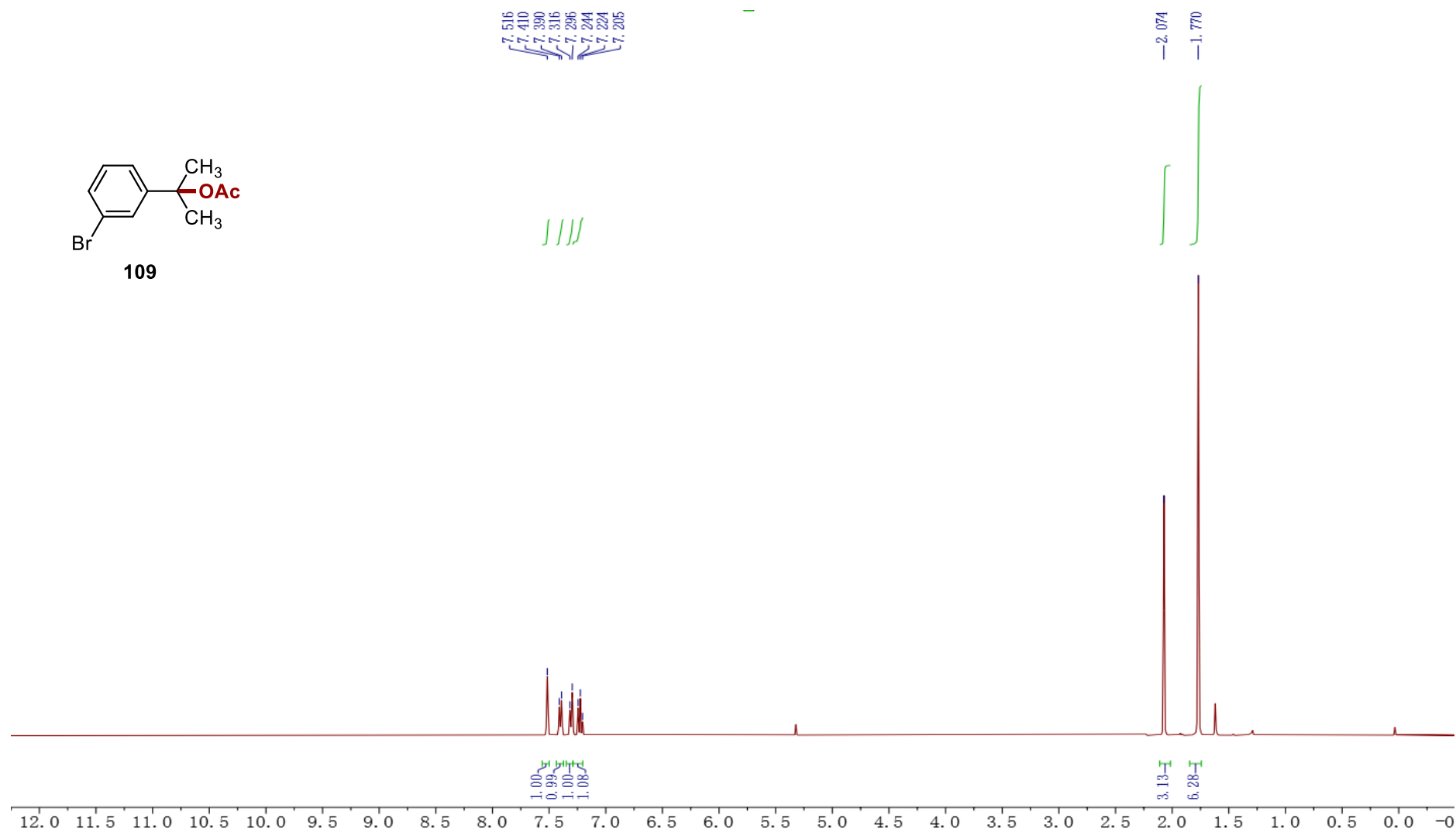


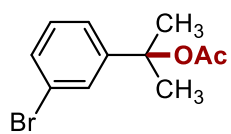
108



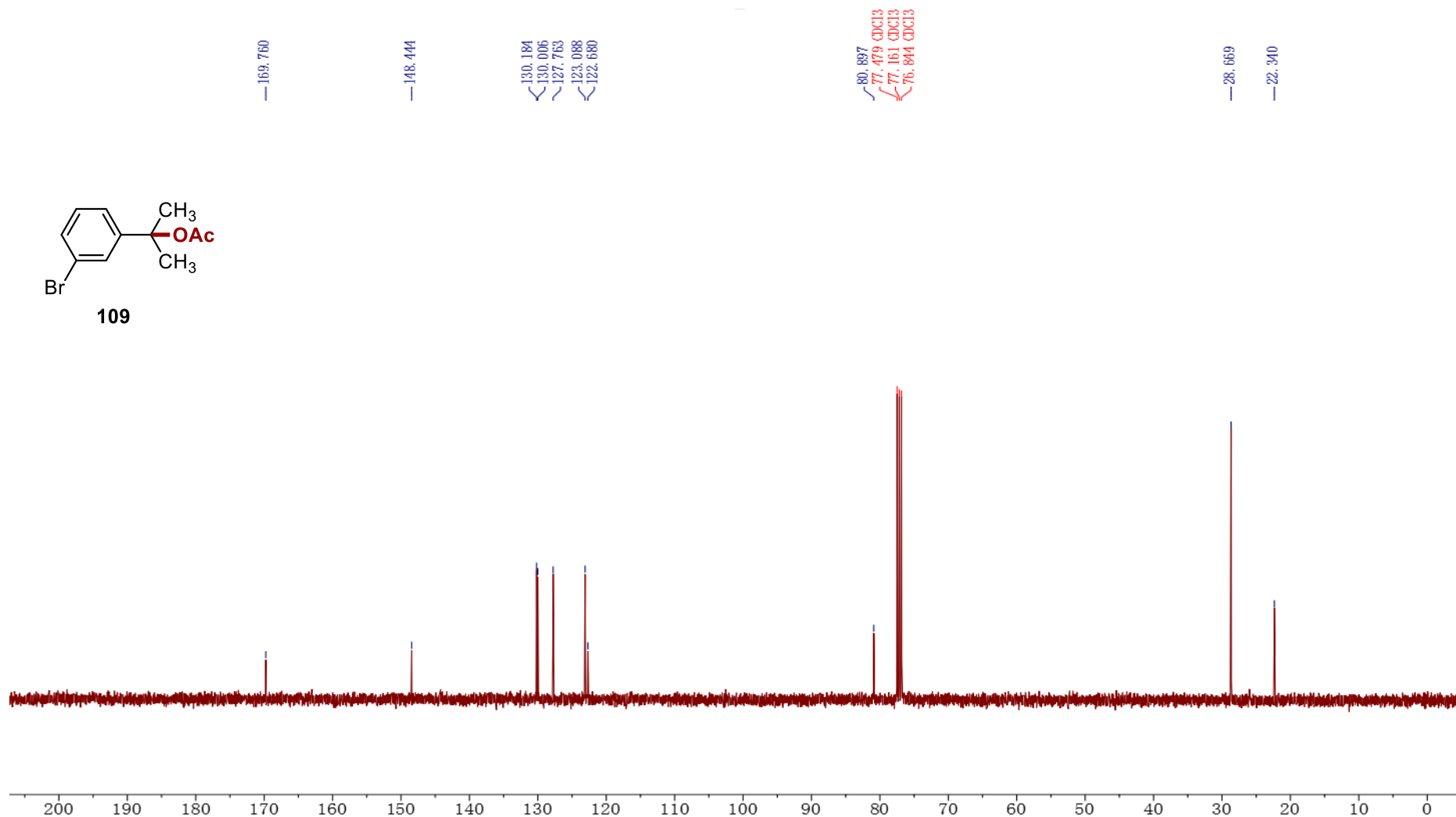


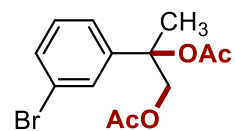
109





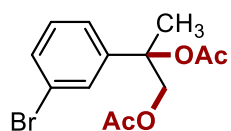
109



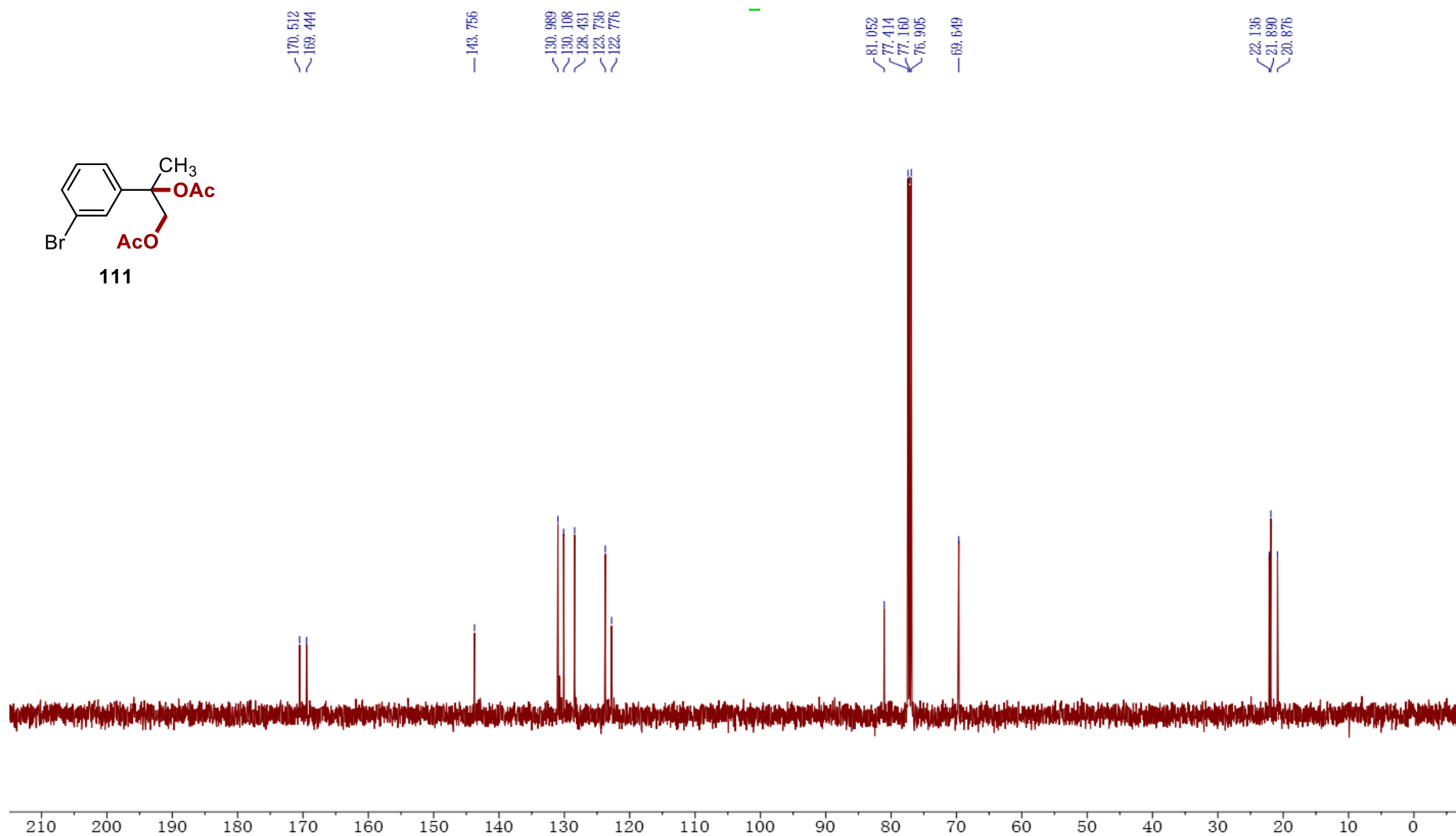


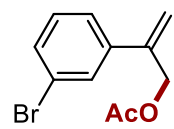
111



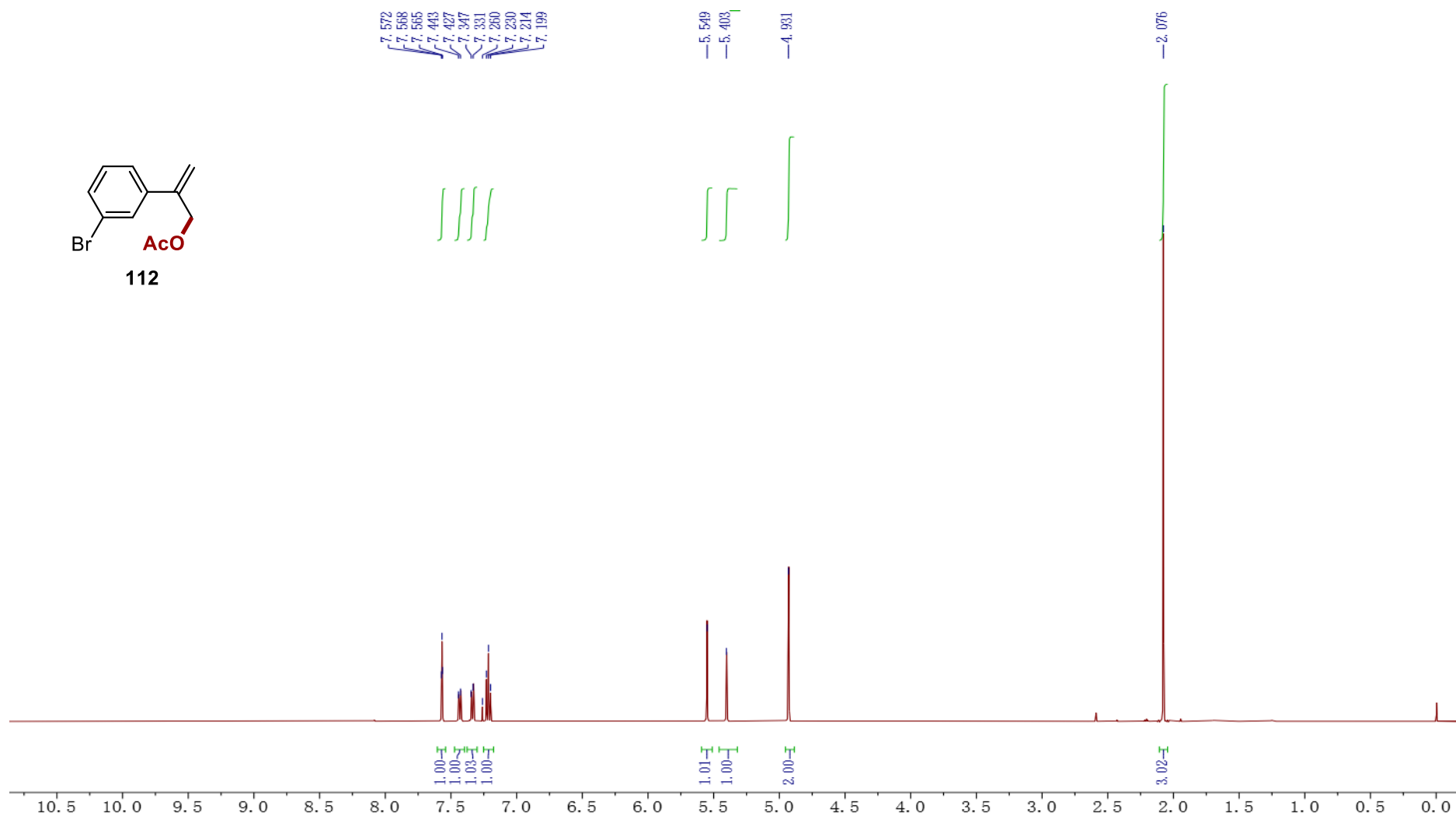


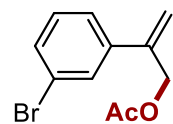
111



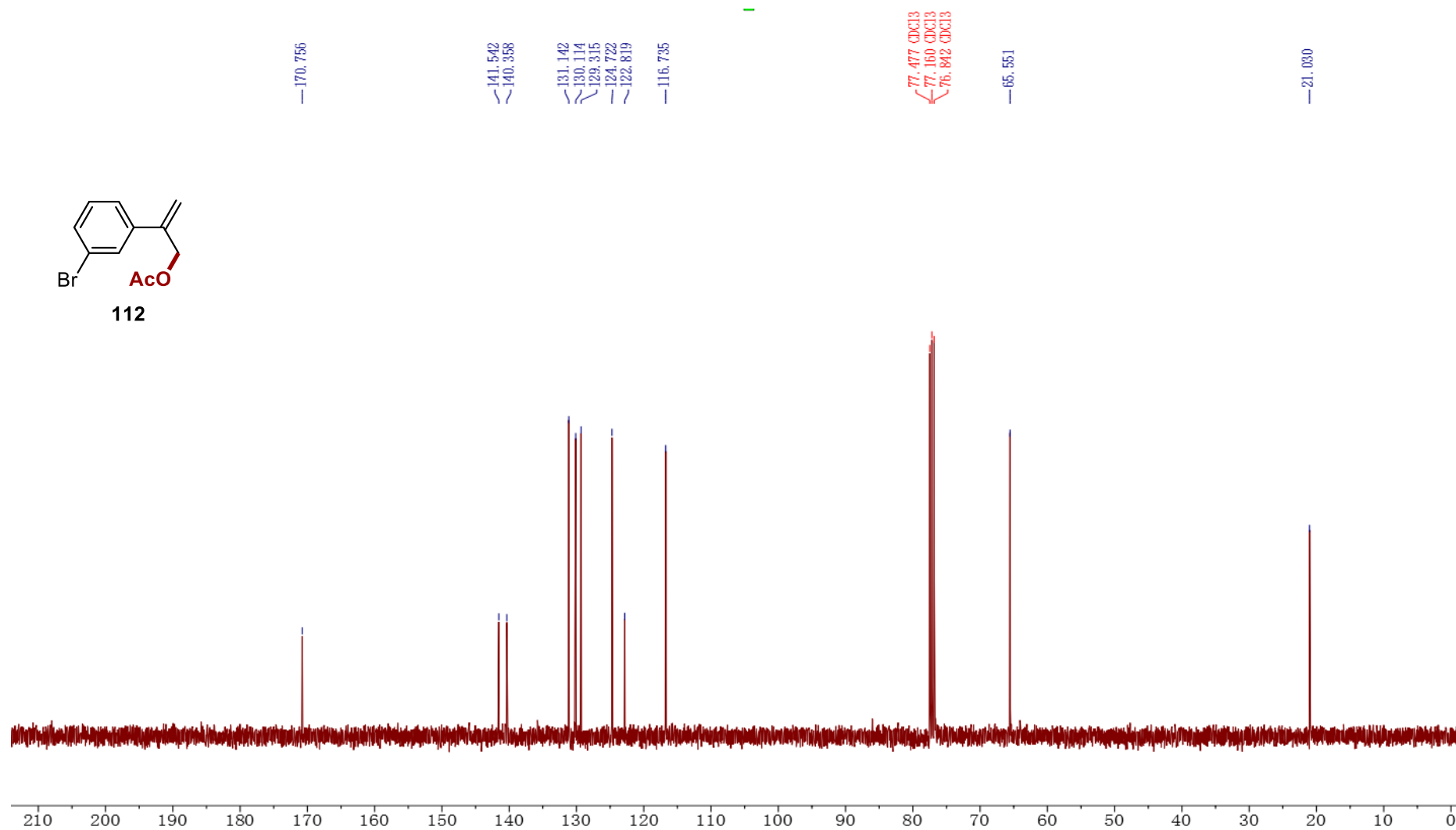


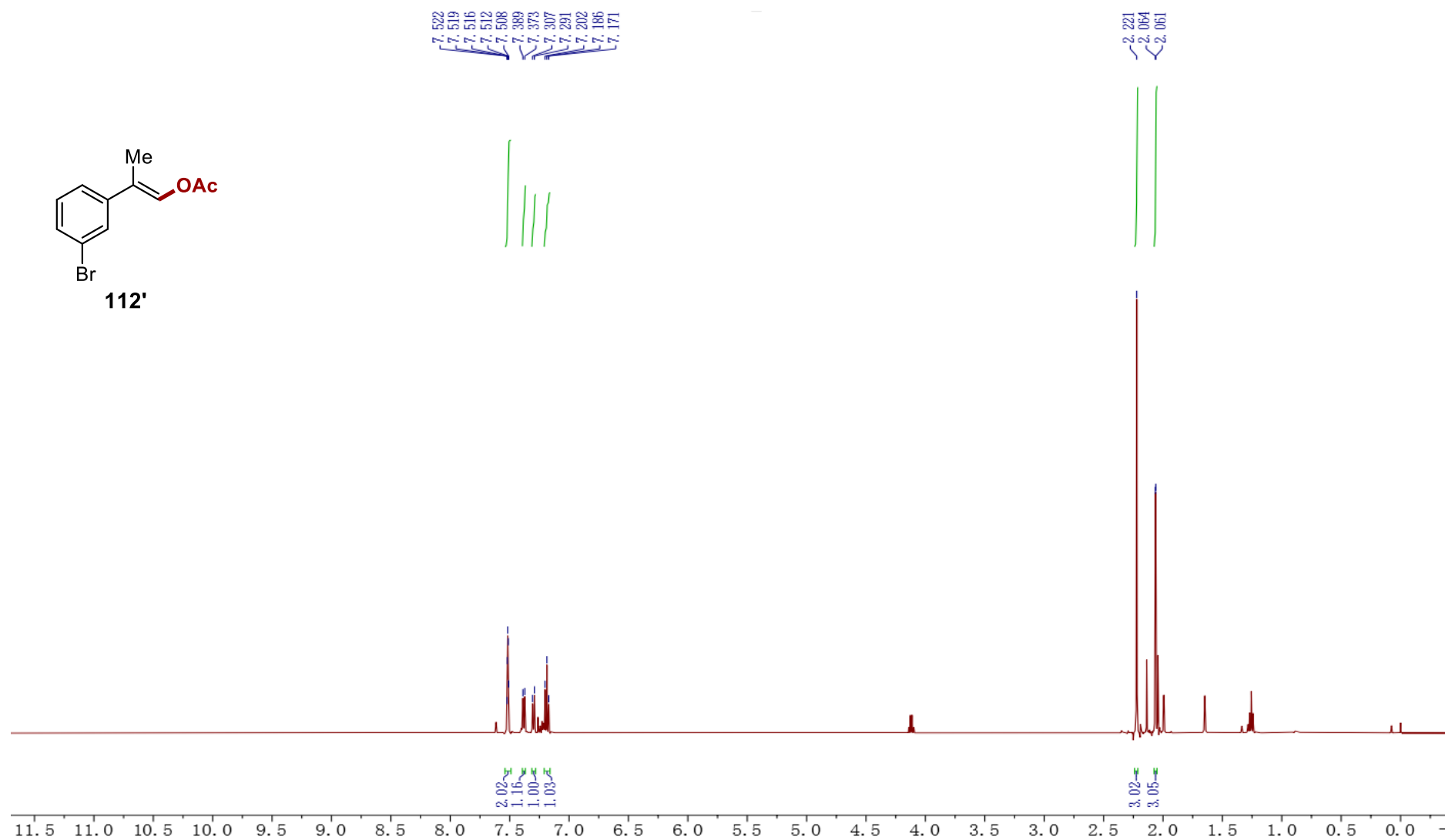
112

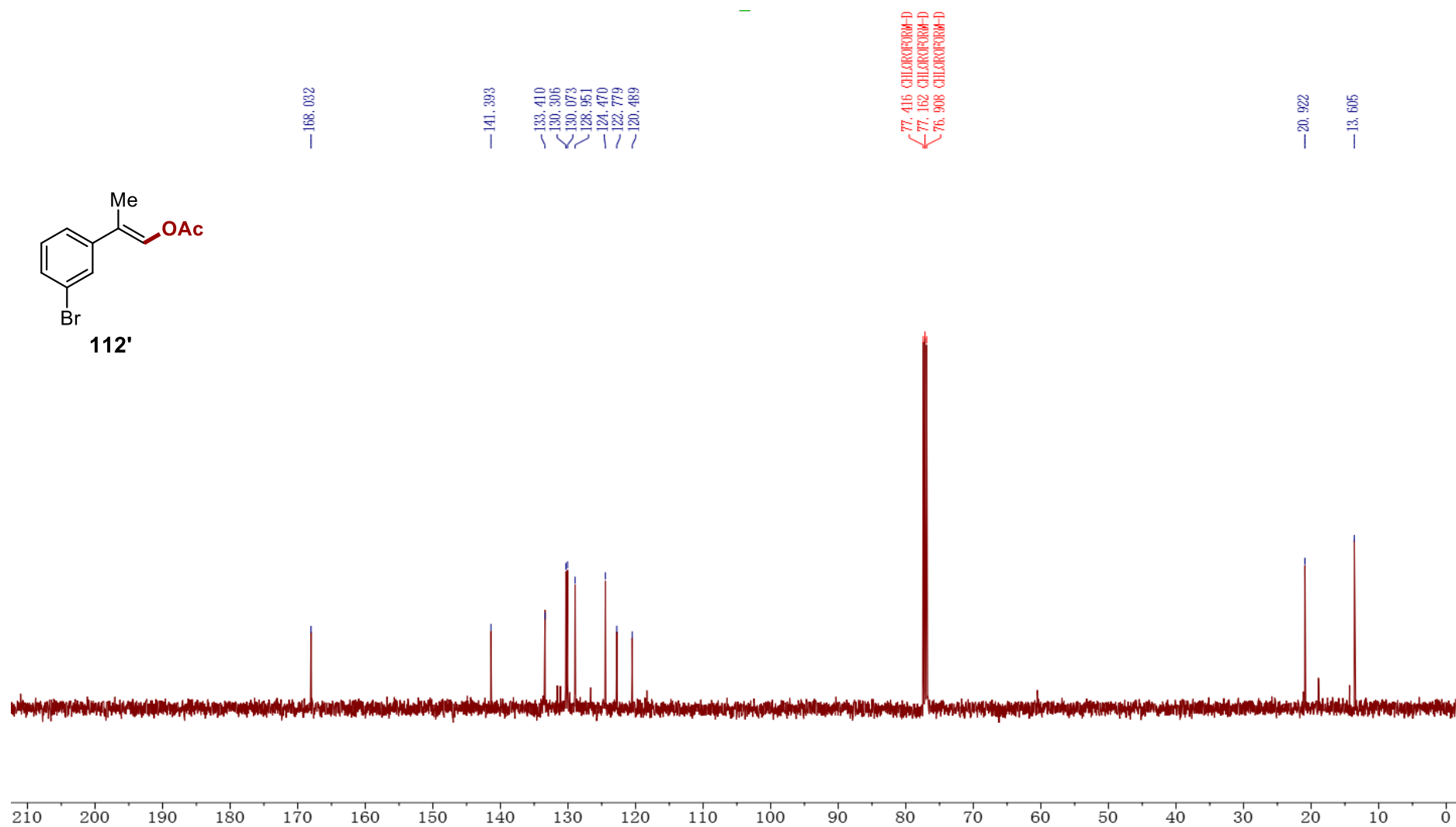


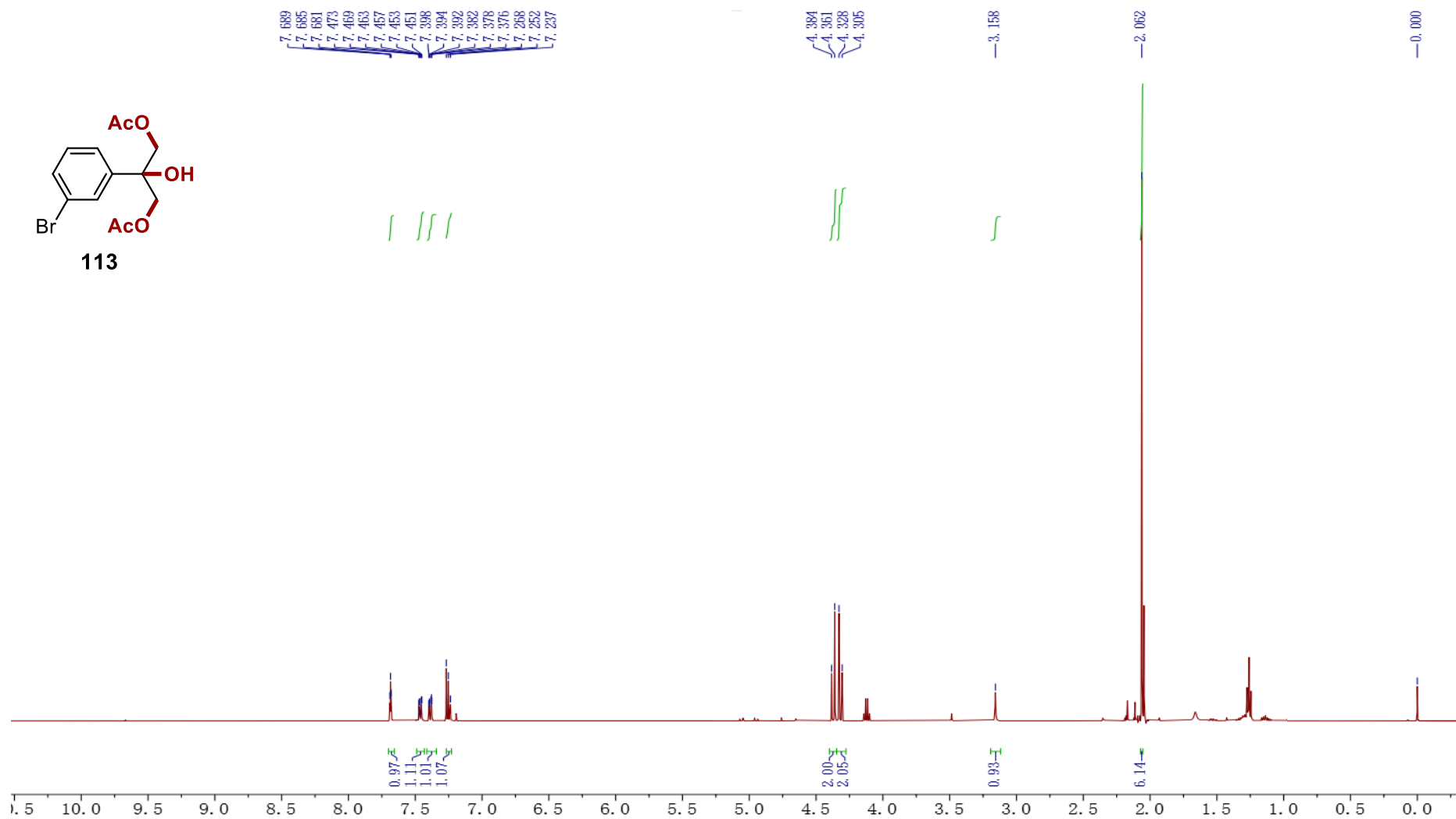


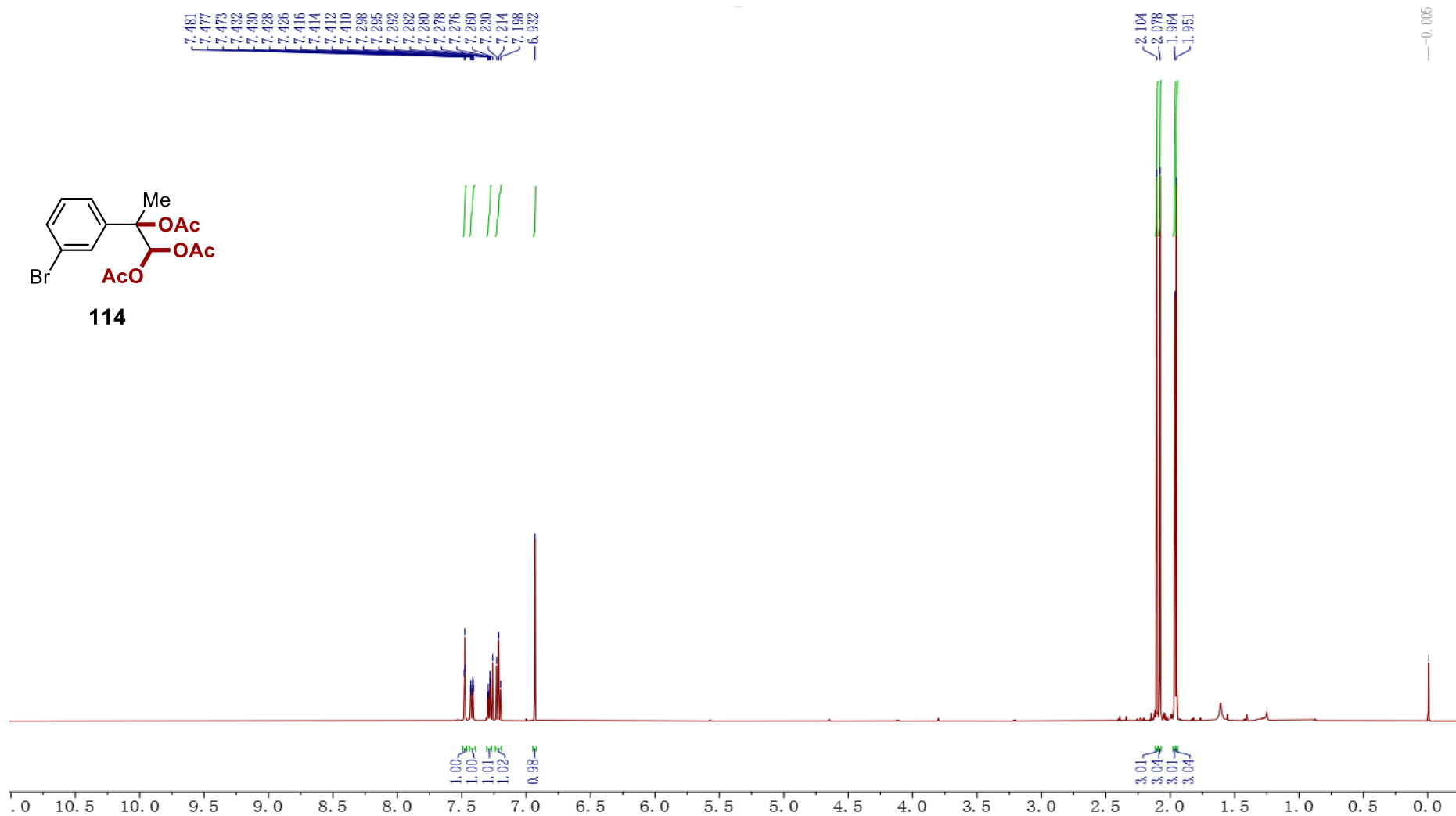
112

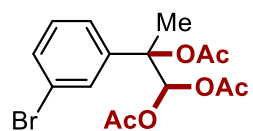




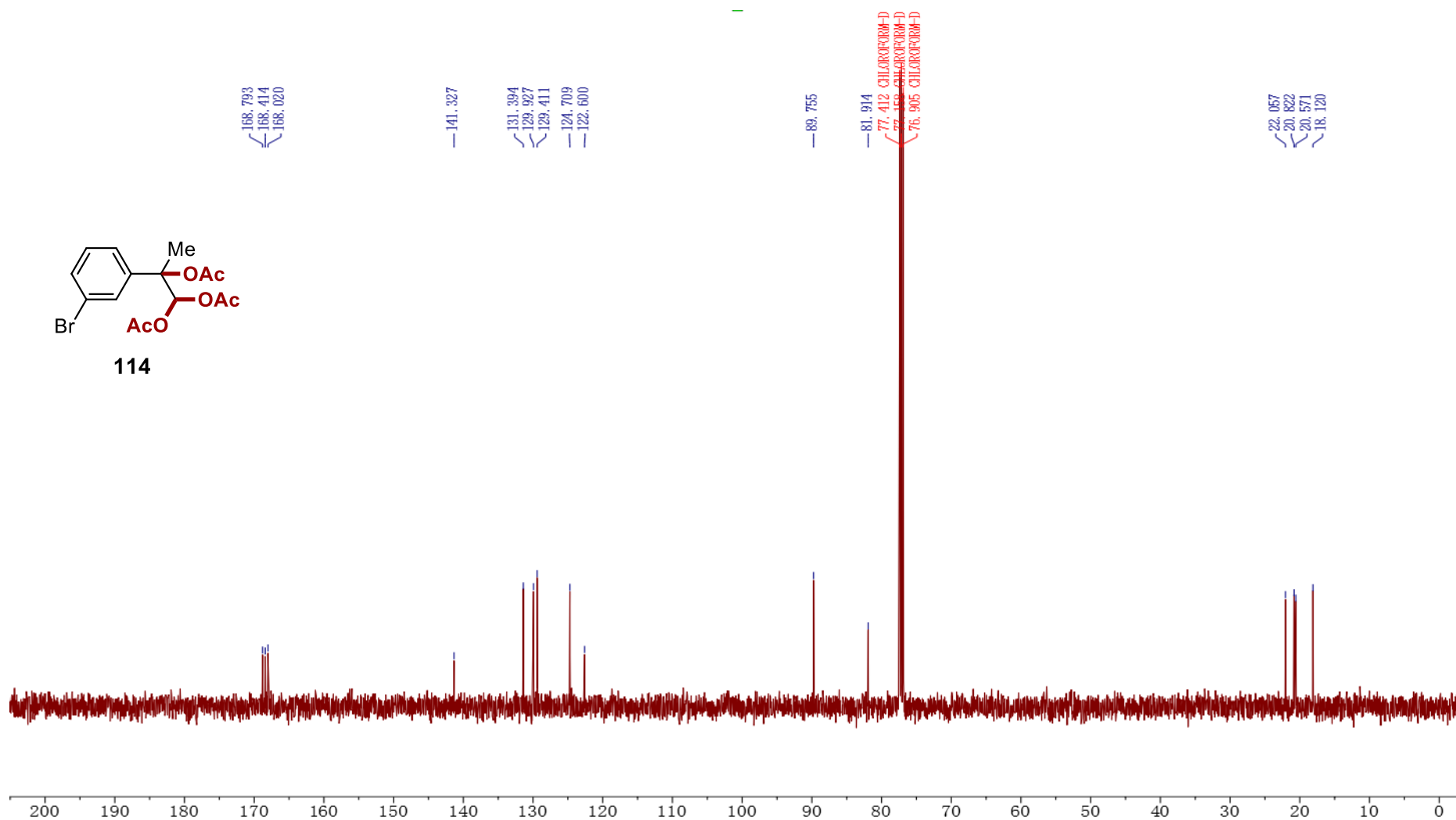


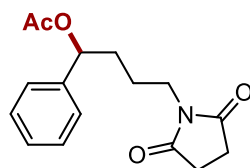




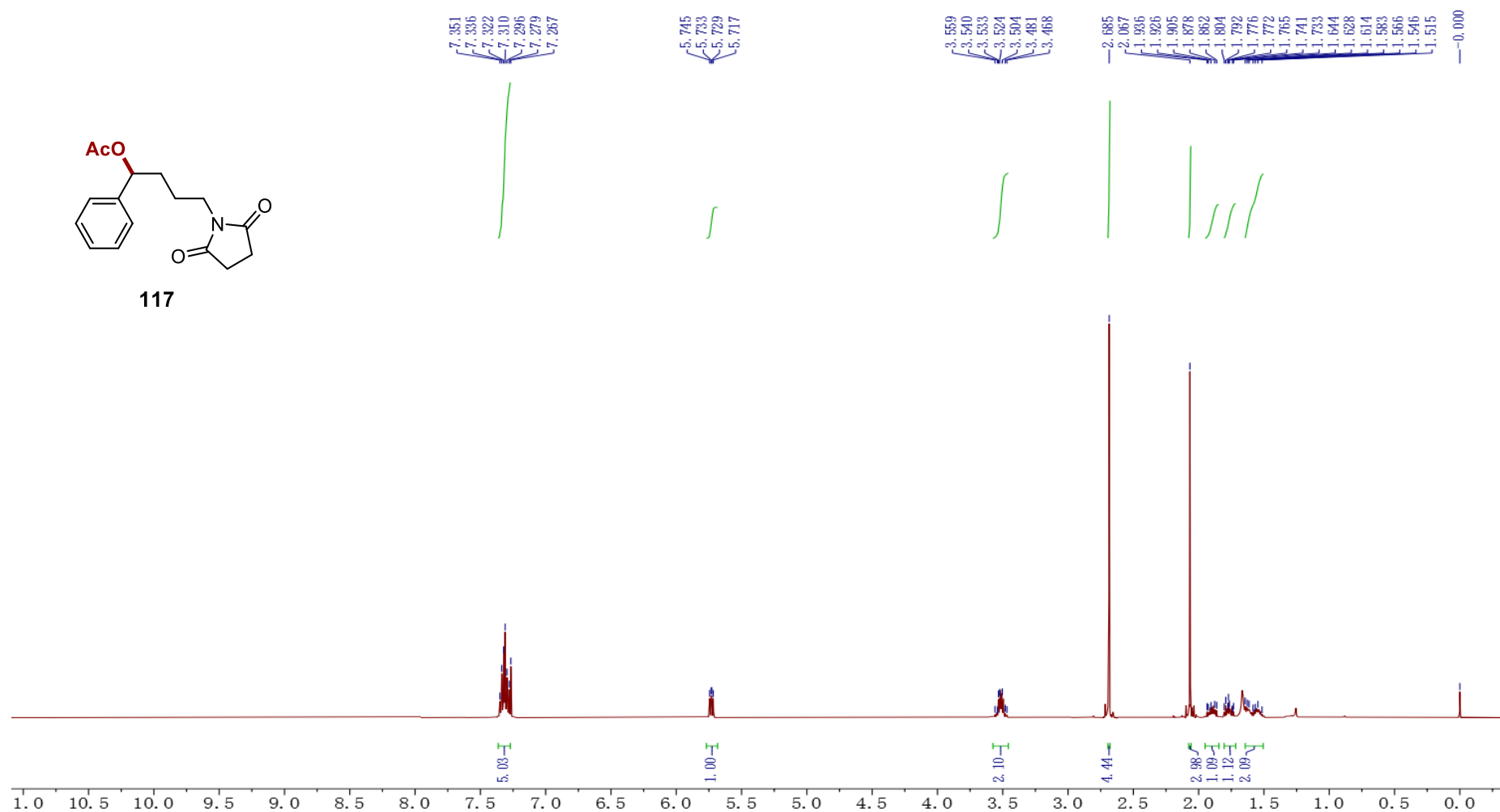


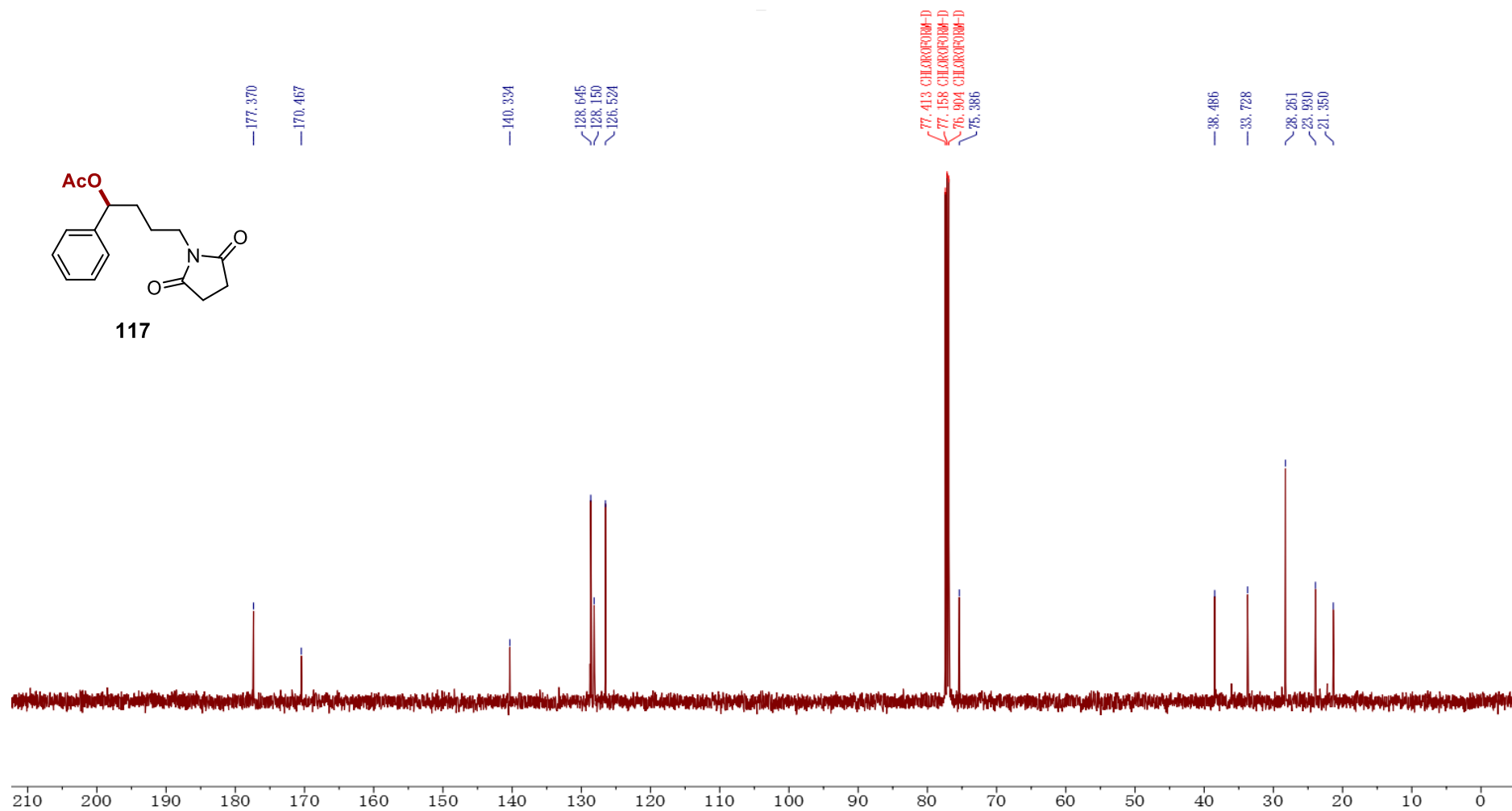
114

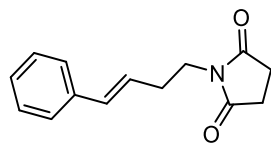




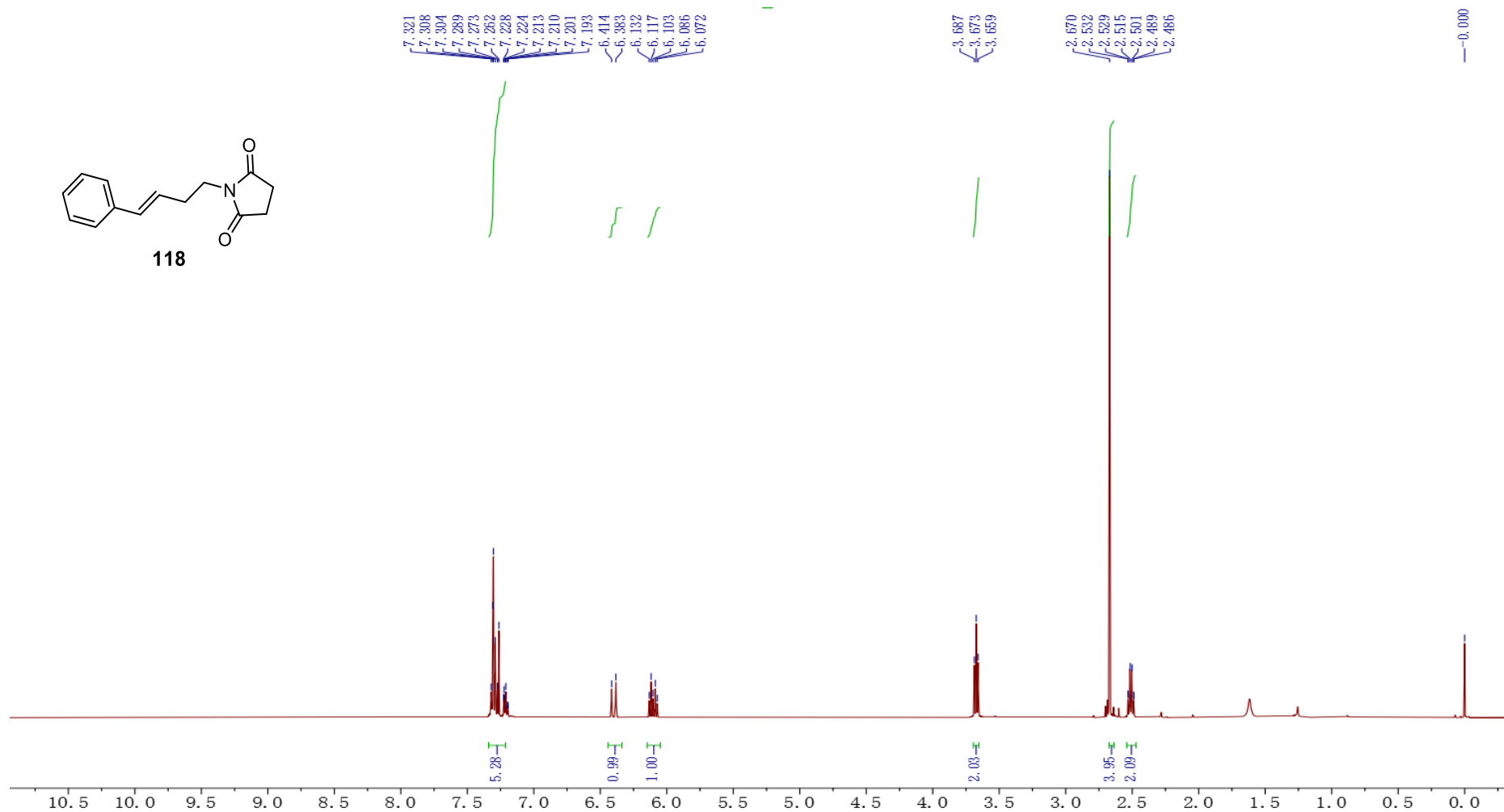
117

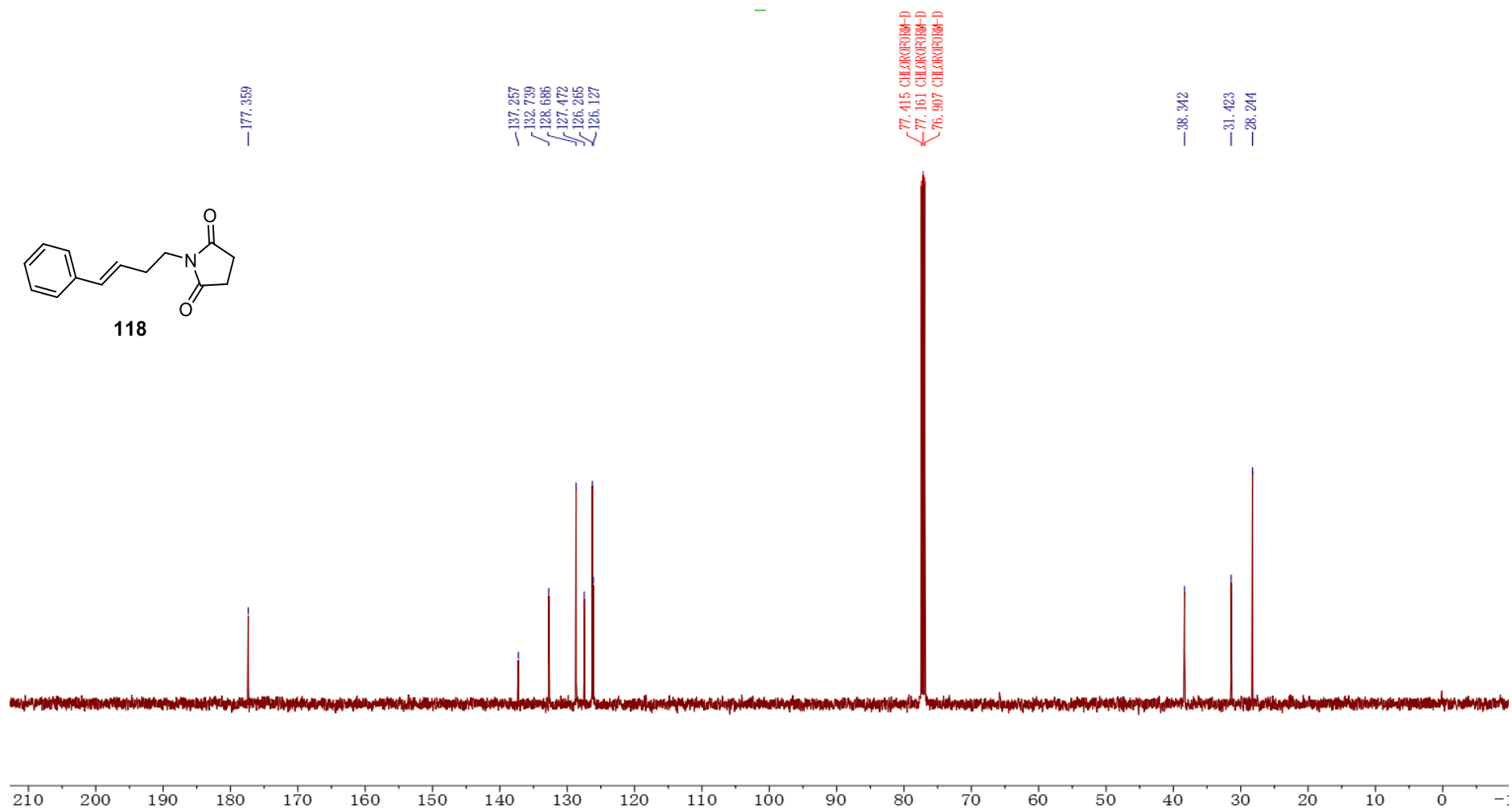


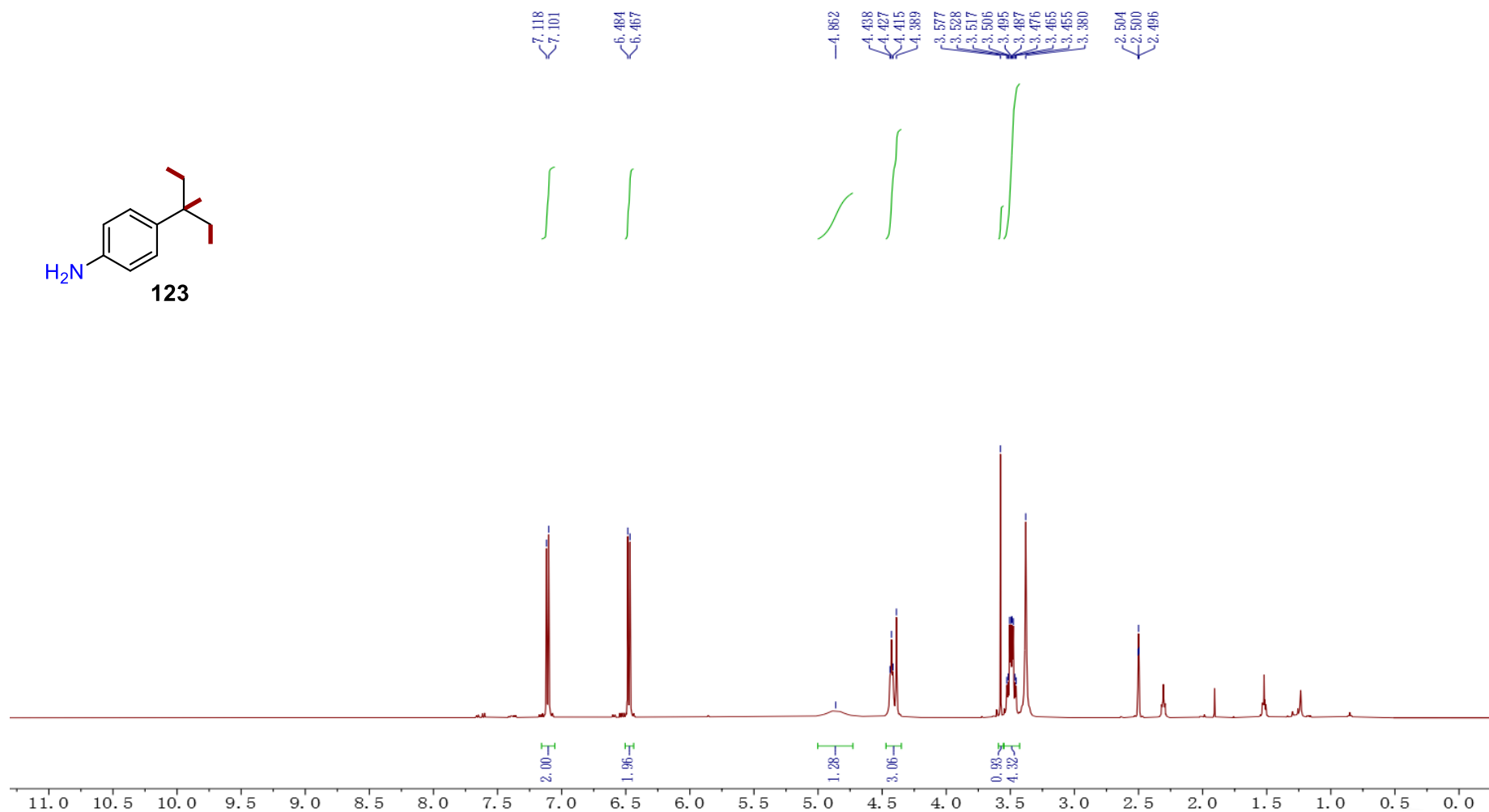
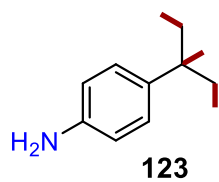


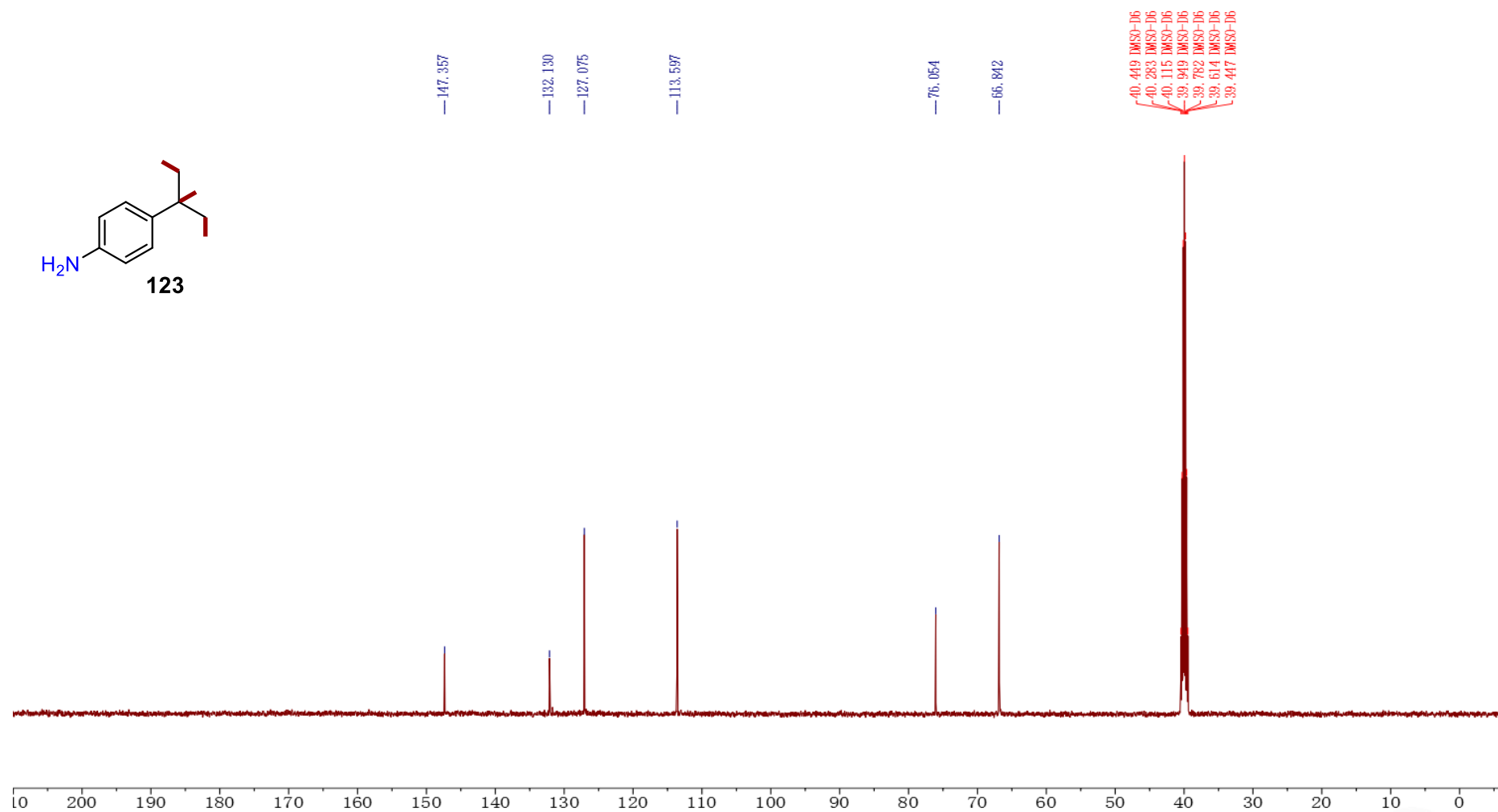
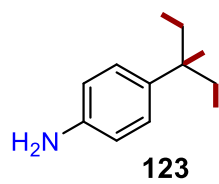


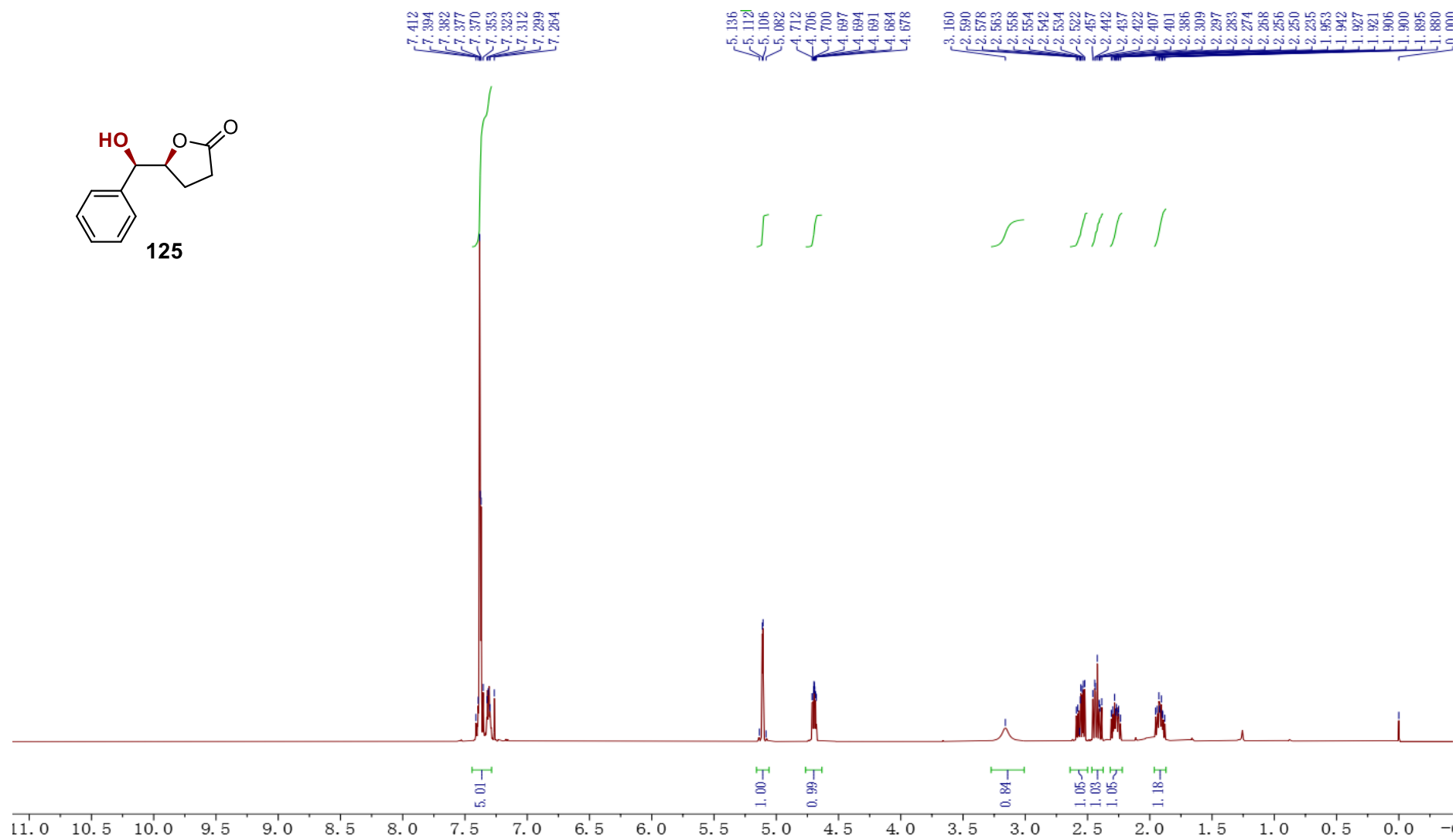
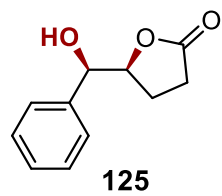
118

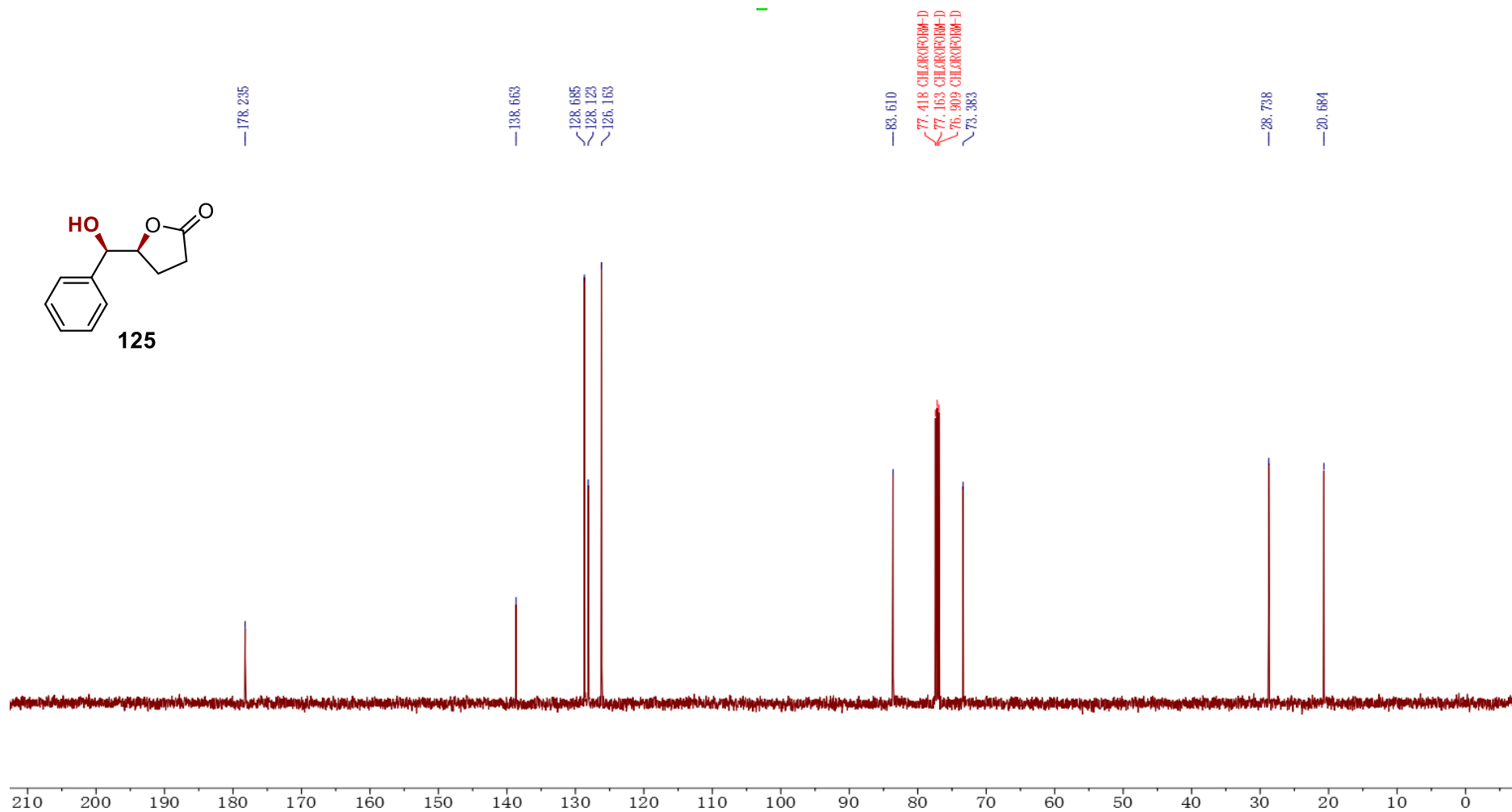
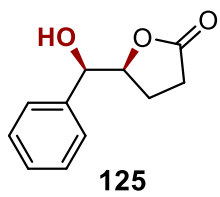


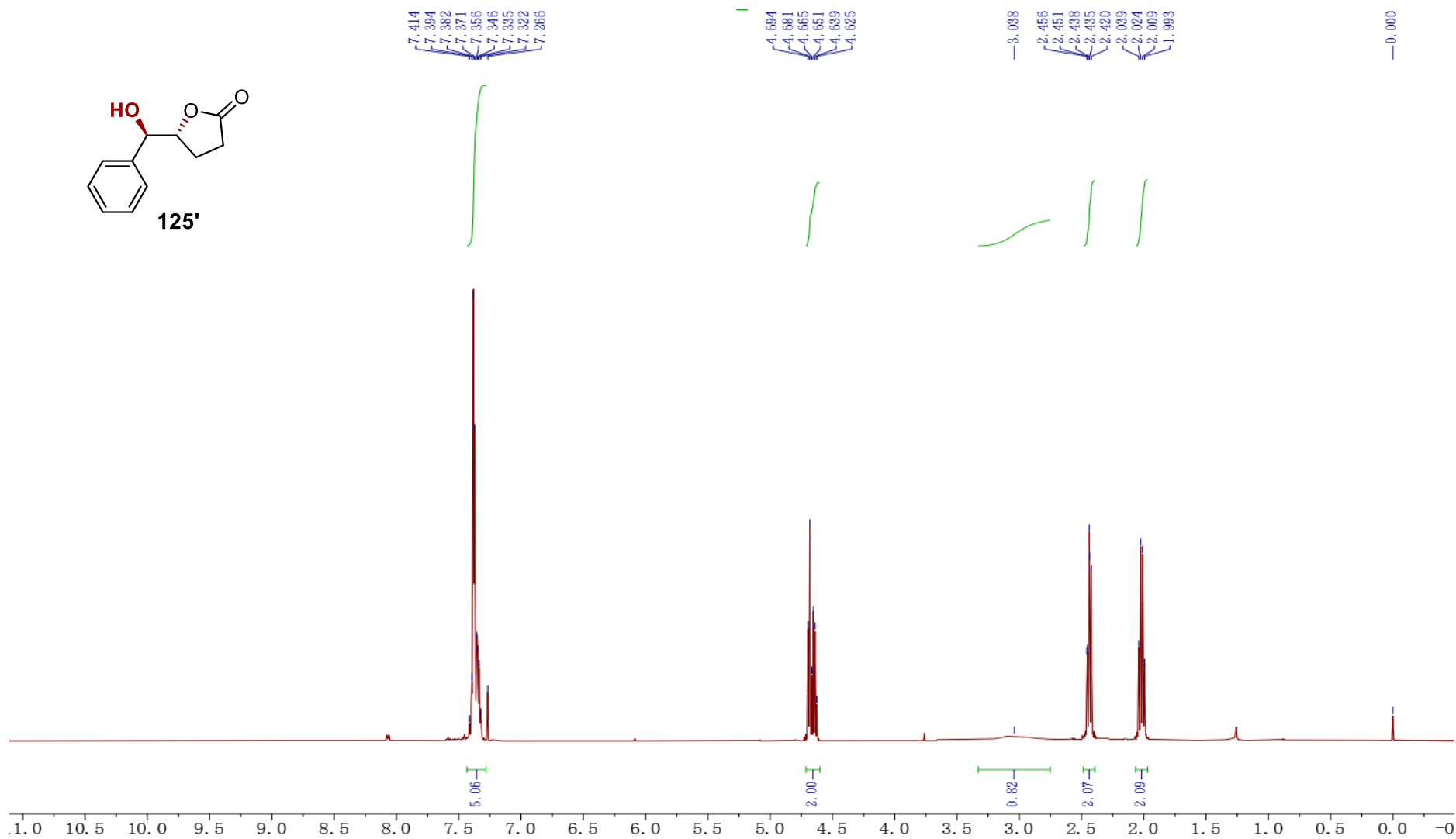
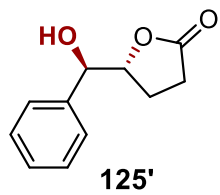


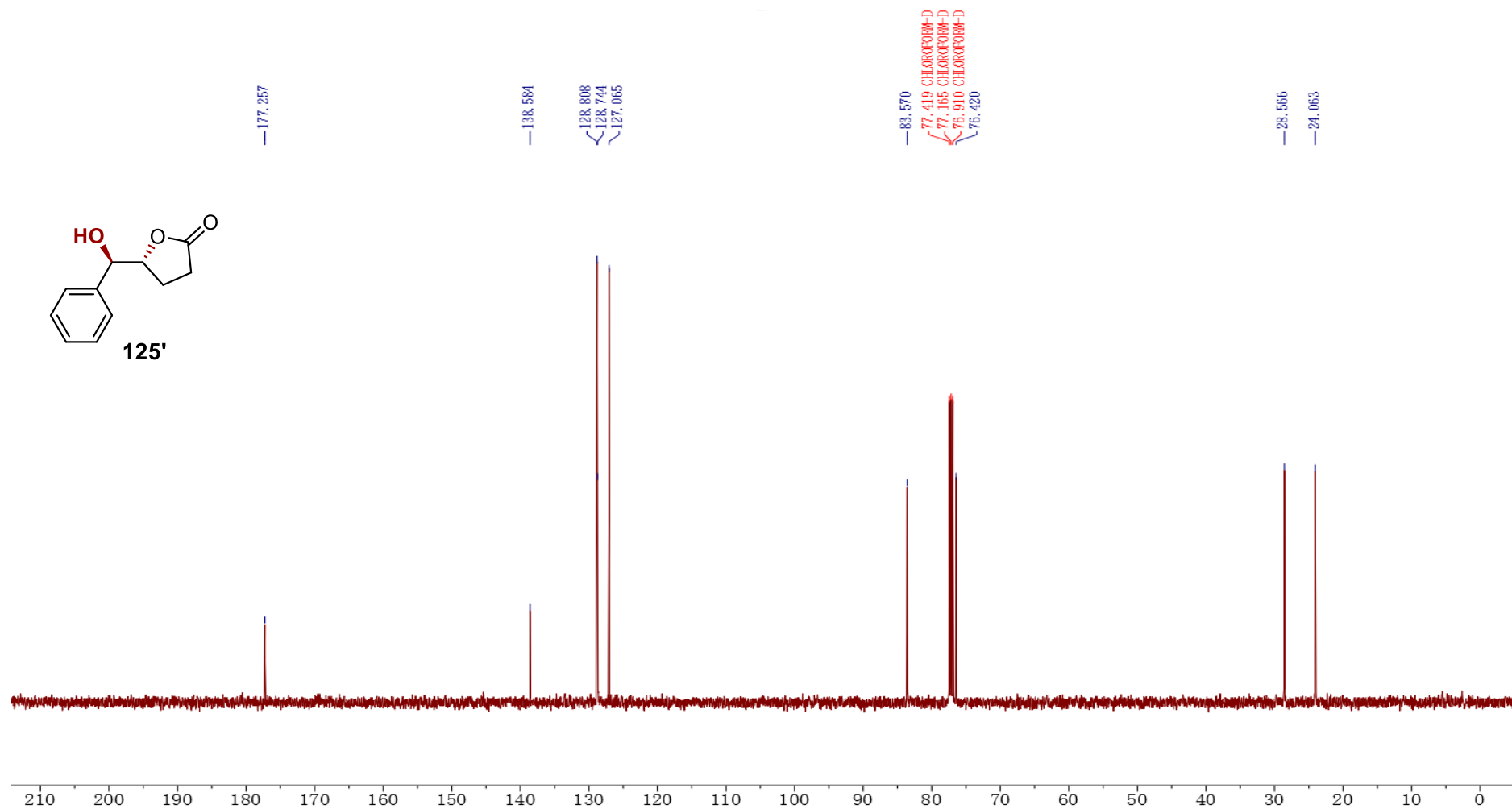


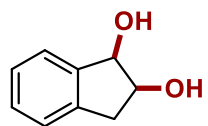




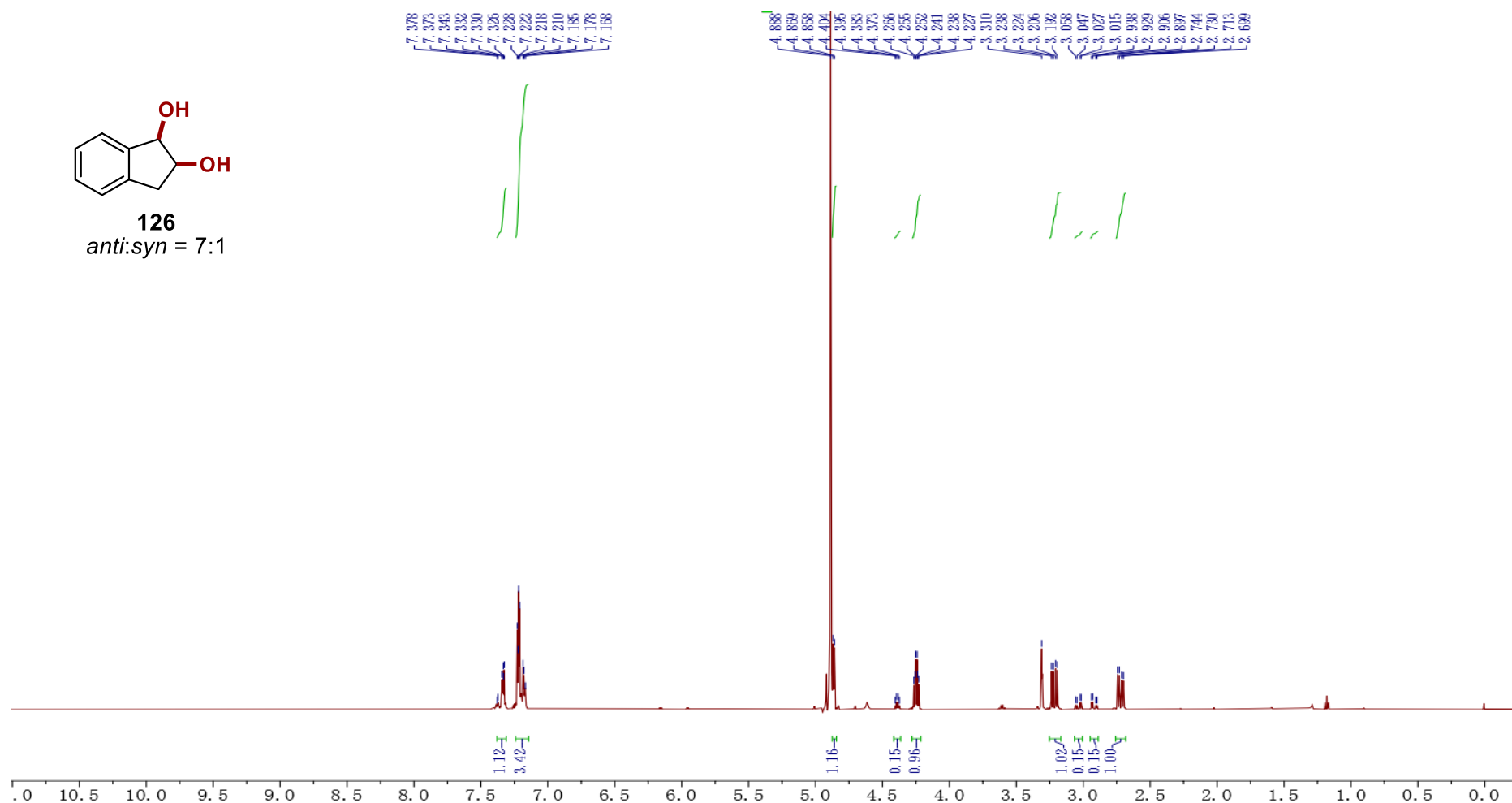


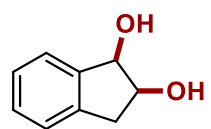




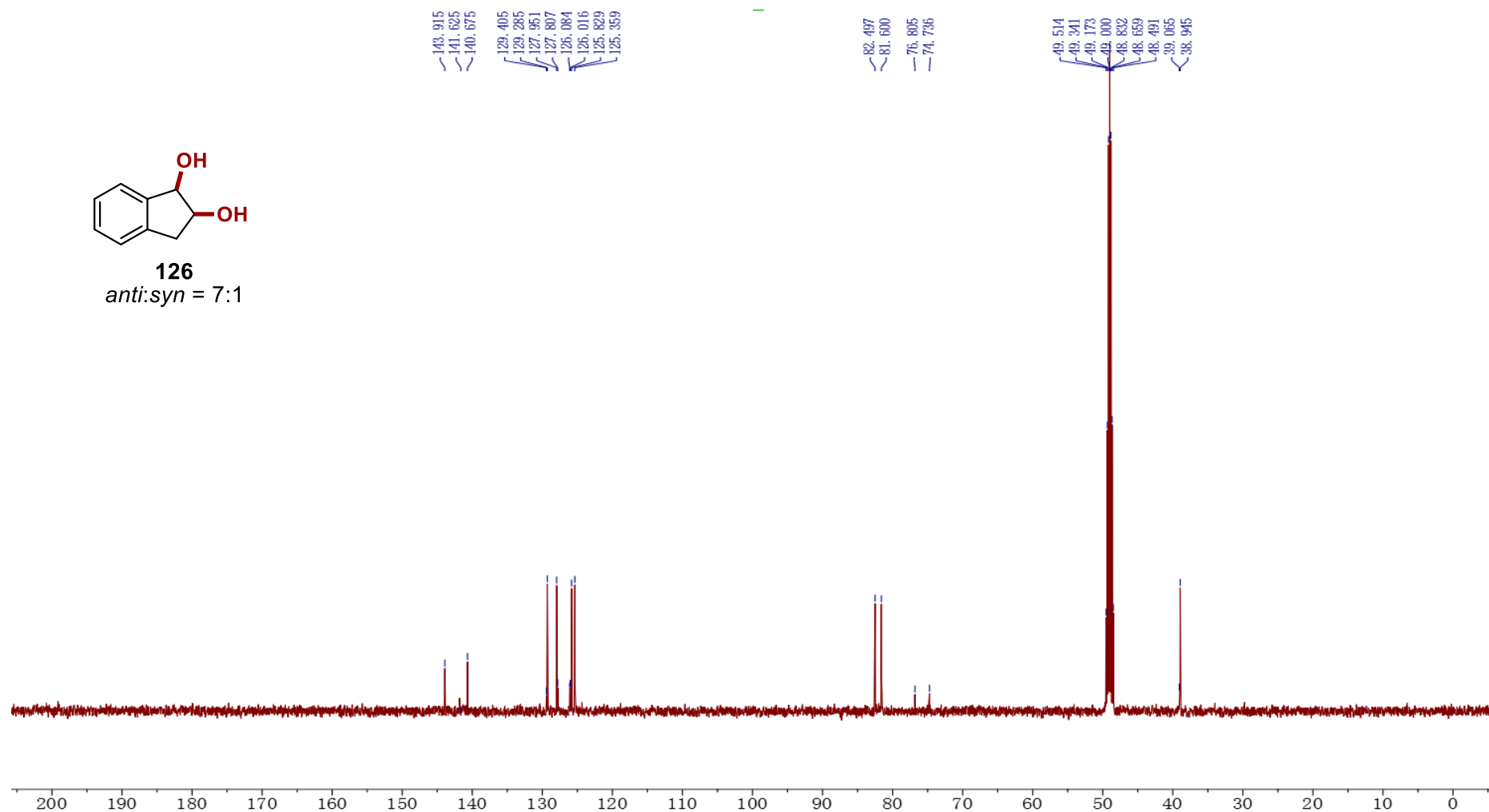


126
anti:syn = 7:1



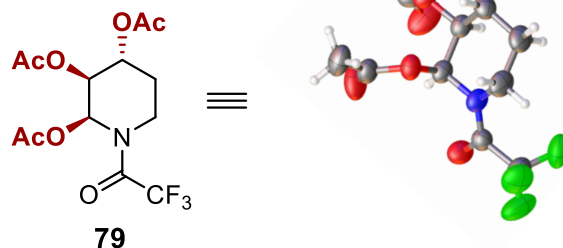


126
anti:syn = 7:1



3. X-ray Data Analysis

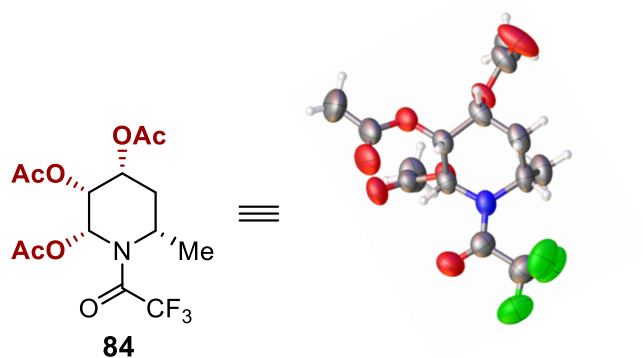
X-ray crystal structure of 79



Crystal data for 79

Bond precision:	C-C = 0.0033 Å	Wavelength=0.71073
Cell:	a=7.8954 (5) alpha=90	b=13.0762 (7) beta=103.939 (2) c=16.2277 (10) gamma=90
Temperature:	296 K	
Volume	Calculated 1626.04 (17)	Reported 1626.04 (17)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C13 H16 F3 N O7	C13 H16 F3 N O7
Sum formula	C13 H16 F3 N O7	C13 H16 F3 N O7
Mr	355.27	355.27
Dx, g cm ⁻³	1.451	1.451
Z	4	4
Mu (mm ⁻¹)	0.138	0.138
F000	736.0	736.0
F000'	736.61	
h,k,lmax	9,16,20	9,16,20
Nref	3342	3338
Tmin,Tmax	0.982,0.986	0.707,0.745
Tmin'	0.982	
Correction method=	# Reported T Limits: Tmin=0.707 Tmax=0.745	
AbsCorr =	MULTI-SCAN	
Data completeness=	0.999	Theta(max)= 26.438
R(reflections)=	0.0505 (2345)	wR2(reflections)= 0.1479 (3338)
S =	1.069	Npar= 220

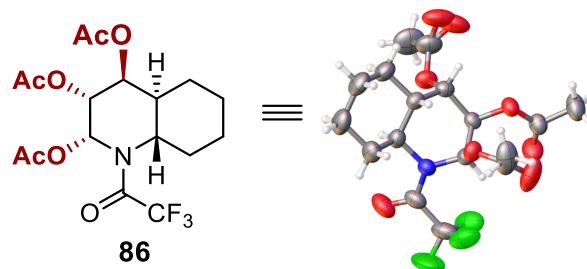
X-ray crystal structure of **84**



Crystal data for **84**

Bond precision:	C-C = 0.0048 Å		Wavelength=0.71073
Cell:	a=9.2059 (5)	b=9.7727 (6)	c=19.6698 (13)
	alpha=90	beta=90	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	1769.62 (19)	1769.62 (19)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C14 H18 F3 N O7	C14 H18 F3 N O7	
Sum formula	C14 H18 F3 N O7	C14 H18 F3 N O7	
Mr	369.29	369.29	
Dx, g cm-3	1.386	1.386	
Z	4	4	
Mu (mm-1)	0.130	0.130	
F000	768.0	768.0	
F000'	768.62		
h, k, lmax	11, 12, 24	11, 12, 24	
Nref	3468 [1999]	3467	
Tmin, Tmax	0.982, 0.987	0.705, 0.745	
Tmin'	0.982		
Correction method= # Reported T Limits: Tmin=0.705 Tmax=0.745			
AbsCorr = MULTI-SCAN			
Data completeness=	1.73/1.00	Theta (max)= 25.987	
R(reflections)=	0.0408 (2727)	wR2(reflections)=	
		0.1082 (3467)	
S =	1.016	Npar= 230	

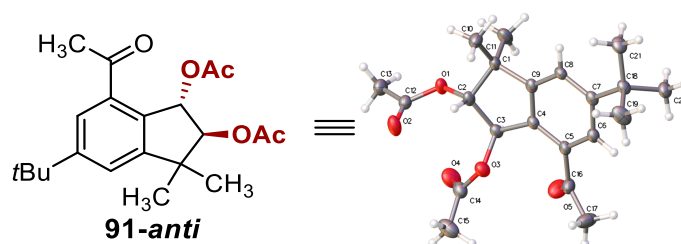
X-ray crystal structure of **86**



Crystal data for **86**

Bond precision:	C-C = 0.0031 Å	Wavelength=0.71073
Cell:	a=9.9714 (3) alpha=93.229 (2)	b=10.5375 (2) beta=92.248 (2)
Temperature:	296 K	
	Calculated	Reported
Volume	990.35 (4)	990.35 (4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C17 H22 F3 N O7	C17 H22 F3 N O7
Sum formula	C17 H22 F3 N O7	C17 H22 F3 N O7
Mr	409.36	409.35
Dx, g cm ⁻³	1.373	1.373
Z	2	2
Mu (mm ⁻¹)	0.123	0.123
F000	428.0	428.0
F000'	428.32	
h, k, lmax	12, 13, 13	12, 13, 13
Nref	4359	4121
Tmin, Tmax	0.985, 0.988	0.601, 1.000
Tmin'	0.976	
Correction method= # Reported T Limits: Tmin=0.601 Tmax=1.000		
AbsCorr = MULTI-SCAN		
Data completeness=	0.945	Theta(max)= 27.048
R(reflections)=	0.0469 (2812)	wR2(reflections)=
S =	1.091	0.1394 (4121)
	Npar= 267	

X-ray crystal structure of 91-*anti*



Crystal data for 91-*anti*:

Bond precision:	C-C = 0.0054 Å	Wavelength=1.54178
Cell:	a=24.4895(14) b=5.7695(3) c=17.9855(10)	
	alpha=90 beta=127.444(6) gamma=90	
Temperature: 296 K		
	Calculated	Reported
Volume	2017.6(3)	2017.6(2)
Space group	C c	C 1 c 1
Hall group	C -2yc	C -2yc
Moiety formula	C21 H28 O5	C21 H28 O5
Sum formula	C21 H28 O5	C21 H28 O5
Mr	360.43	360.43
Dx, g cm ⁻³	1.187	1.187
Z	4	4
Mu (mm ⁻¹)	0.679	0.679
F000	776.0	776.0
F000'	778.42	
h, k, lmax	30, 7, 22	30, 7, 22
Nref	4007[2005]	3968
Tmin, Tmax	0.850, 0.934	0.580, 0.754
Tmin'	0.816	
Correction method=	# Reported T Limits: Tmin=0.580 Tmax=0.754	
AbsCorr =	NONE	
Data completeness=	1.98/0.99	Theta(max)= 72.449
R(reflections)=	0.0500(3748)	wR2(reflections)= 0.1319(3968)
S =	1.048	Npar= 243

5. References

44. Wu, X. et al. A General Palladium-Catalyzed Method for Alkylation of Heteroarenes Using Secondary and Tertiary Alkyl Halides. *Angew. Chem. Int. Ed.* **53**, 13573-13577 (2014).
45. Senadi, G. C., Dhandabani, G. K., Hu, W.-P. & Wang, J.-J. Metal-free annulation/aerobic oxidative dehydrogenation of cyclohexanones with *o*-acylanilines: efficient syntheses of acridines. *Green Chem.* **18**, 6241-6245 (2016).
46. Kang, Y.-B. & Gade, L. H. The Nature of the Catalytically Active Species in Olefin Dioxygenation with $\text{PhI}(\text{OAc})_2$: Metal or Proton? *J. Am. Chem. Soc.* **133**, 3658–3667 (2011).
47. Zhong, W., Yang, J., Meng, X. & Li, Z. $\text{BF}_3 \cdot \text{OEt}_2$ -Promoted Diastereoselective Diacetoxylation of Alkenes by $\text{PhI}(\text{OAc})_2$. *J. Org. Chem.* **76**, 9997-10004 (2011).
48. Bellucci, G., Chmppe, C. & Cordoni, A. Enantioconvergent transformation of racemic cis- β -alkyl substituted styrene oxides to (R,R) threo diols by microsomal epoxide hydrolase catalysed hydrolysis. *Tetrahedron: Asymmetry* **7**, 197-202 (1996).
49. Li, Y., Song, D. & Dong, Vy M. Palladium-Catalyzed Olefin Dioxygenation. *J. Am. Chem. Soc.* **130**, 2962-2964 (2008).
50. Huang, J. & Corey, E. J. A Mechanistically Guided Design Leads to the Synthesis of an Efficient and Practical New Reagent for the Highly Enantioselective, Catalytic Dihydroxylation of Olefins. *Org. Lett.* **5**, 3455-3458 (2003).
51. Kim, J. H., Čorić, I., Palumbo, C. & List., B. Resolution of Diols via Catalytic Asymmetric Acetalization. *J. Am. Chem. Soc.* **137**, 1778-1781 (2015).
52. Zhang, S. et al. Electrocatalytic Dehydrogenative Esterification of Aliphatic Carboxylic Acids: Access to Bioactive Lactones. *Org. Lett.* **19**, 6622-6625 (2017).
53. Wang, Z., Cui, Y.-T., Xu, Z.-B. & Qu, J. Hot Water-Promoted Ring-Opening of Epoxides and Aziridines by Water and Other Nucleopliles. *J. Org. Chem.* **73**, 2270-2274 (2008).
54. Chartrain, M. M. et al. Quantitative conversion of indene to (1S,2R) indene oxide and (1S,2R)-indandiol by combination of haloperoxidase bioconversion and chemical steps. International patent no. WO9636724A1(1996).
55. Askin, D. et al. Highly diastereoselective alkylations of chiral amide enolates: new routes to hydroxyethylene dipeptide isostere inhibitors of HIV-1 protease. *J. Org. Chem.* **57**, 2771-2773 (1992).