Supporting Information for

Copper-Catalyzed, Stereoconvergent, *cis*-Diastereoselective Borylative Cyclization of *ω*-Mesylate-*α,β*-Unsaturated Esters and Ketones

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1. Instrumentation and Chemicals

1.1 Instrumentation

Unless indicated otherwise, all reactions were conducted under an atmosphere of argon using standard vacuum-line techniques. NMR spectra were recorded on Advance Bruker Avance III 500 M (^{1}H: 500 MHz; ^{13}C: 126 MHz) spectrometer. Tetramethylsilane (^{1}H) and $CDCl_3$ (^{13}C) were employed as internal standards. *J* values are given in Hertz. High-resolution mass spectra (ESI-HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometers. Gas chromatographic analyses were conducted on a Shimadzu GC-2014C equipped with a flame ionization detector. Silica gel (Qingdao Haiyang Chemical Co., Ltd ZCX-3, spherical, neutral, 50–60 μm) and aluminum oxide (Aladdin, activated, neutral,200-300 mesh) were used for column chromatography.

1.2 Chemicals

Materials were obtained from commercial suppliers and purified by the standard procedure unless otherwise noted. CuCl was purchased from Acros and used as received. (±)-Binap and PCy_3 were purchased from Wu Han hsenbruy Chemical Co., Ltd.. Bis(pinacolato)diboron (B_2Pin_2, purchased from Dalian Ally-Chem Co., Ltd.) was recrystallized from *n*-pentane. SIPr·HCl was prepared according to the reported procedures. ^{t}BuOK was purchased from Acros and purified by sublimation. THF, dioxane, toluene, and DMF were purchased from Sinopharm Chemical Reagent Co, Ltd. (SCRC), distilled from sodium metal and degassed via three freeze–pump–thaw cycles before use.

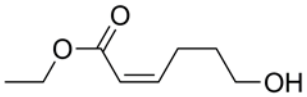
Other chemicals were purchased from the following Supplies:

Ethyl bromoacetate (Adamas Reagent, Ltd), γ-butyrolactone and α-Methyl-γ-Butyrolactone (Shanghai TitanChem), DIBAL-H (Energy Chemical, Shanghai), DMAP (Adamas Reagent, Ltd), Methanesulfonyl chloride (Beijing Ouhe Technology Co., Ltd.), Phosphorus trichloride (Alfa Aesar), 2-tert-Butylphenol (J&K Scientific Ltd.), Methyl 2-bromopropionate (Energy Chemical), Cinnamyl alcohol (J&K Scientific Ltd.), Anisic aldehyde (Beijing Ouhe Technology Co., Ltd.), 4-Chlorophenethylalcohol (J&K Scientific Ltd.), Benzyl alcohol (Aladdin Industrial Inc.), *N*-Benzylethanolamine (TCI Shanghai), ethyl 4-bromocrotonate (Energy Chemical), Lithium aluminium hydride (Alfa Aesar).

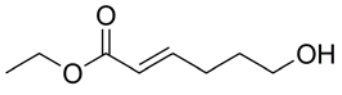
1.3 Synthesis of Substrate Alcohol Precursors

The alcohol precursors for the synthesis of substrates were prepared according to the reported procedures:

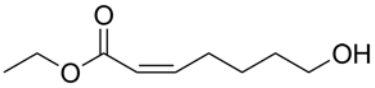
(*Z*)-ethyl 6-hydroxyhex-2-enoate (**S1**),[1] (*E*)-ethyl 6-hydroxyhex-2-enoate (**S2**),[1] (*Z*)-ethyl 7-hydroxyhept-2-enoate (**S3**),[1] (*E*)-ethyl 6-hydroxyhept-2-enoate (**S4**),[1] (*E*)-ethyl 7-hydroxyhept-2-enoate (**S5**),[2] (*E*)-methyl 6-hydroxy-2-methylhex-2-enoate (**S6**),[2] (*E*)-methyl 7-hydroxy-2-methylhept-2-enoate (**S7**),[2] (*Z*)-benzyl 6-hydroxyhex-2-enoate (**S8**),[3] (*E*)-4-methoxybenzyl 6-hydroxyhex-2-enoate (**S9**),[3] (*E*)-cinnamyl 6-hydroxyhex-2-enoate (**S10**),[3] (*E*)-4-chlorophenethyl 6-hydroxyhex-2-enoate (**S11**),[3] (*E*)-7-hydroxyhept-3-en-2-one (**S12**),[1] (*E*)-ethyl 5-hydroxypent-2-enoate (**S13**).[2]



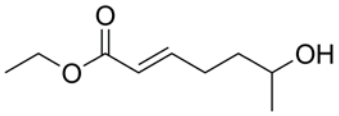
(*Z*)-ethyl 6-hydroxyhex-2-enoate (**S1**)



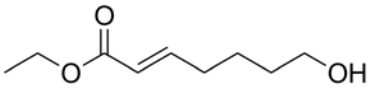
(*E*)-ethyl 6-hydroxyhex-2-enoate (**S2**)



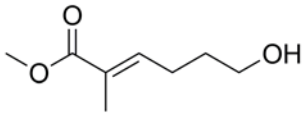
(*Z*)-ethyl 7-hydroxyhept-2-enoate (**S3**)



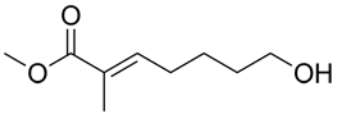
(*E*)-ethyl 6-hydroxyhept-2-enoate (**S4**)



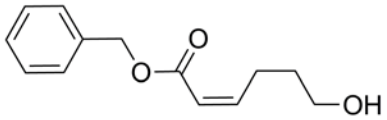
(*E*)-ethyl 7-hydroxyhept-2-enoate (**S5**)



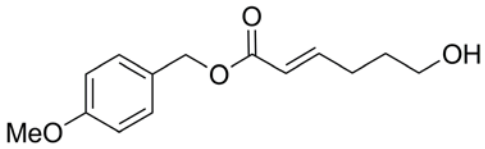
(*E*)-methyl 6-hydroxy-2-methylhex-2-enoate (**S6**)



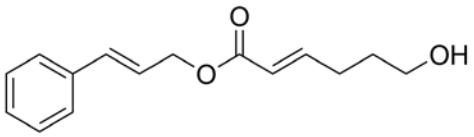
(*E*)-methyl 7-hydroxy-2-methylhept-2-enoate (**S7**)



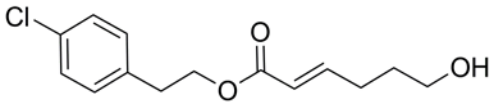
(*Z*)-benzyl 6-hydroxyhex-2-enoate (**S8**)



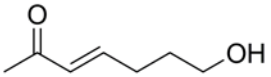
(*E*)-4-methoxybenzyl 6-hydroxyhex-2-enoate (**S9**)



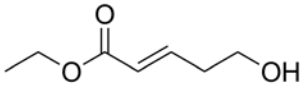
(*E*)-cinnamyl 6-hydroxyhex-2-enoate (**S10**)



(*E*)-4-chlorophenethyl 6-hydroxyhex-2-enoate (**S11**)



(*E*)-7-hydroxyhept-3-en-2-one (**S12**)



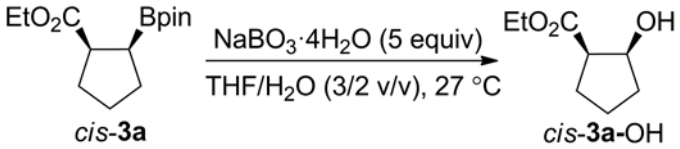
(*E*)-ethyl 5-hydroxypent-2-enoate (**S13**)

2. General Procedure for the Copper-Catalyzed Reaction

In air, $B_2(Pin)_2$ (152 mg, 0.6 mmol) was placed in a 20 mL screw-capped reaction vial. The vial was moved into a glove box. Then, CuCl (5.0 mg, 0.05 mmol), dppe (20.0 mg, 0.05 mmol), KO^{t}Bu (56.0 mg, 0.5 mmol), degassed anhydrous DMF (1.0 mL) and a stirring bar were added in turn. The vial was moved out of the glove box and connected to an argon line through a needle. After the mixture was stirred for 10 min at 25 °C, the alkene substrate (0.5 mmol) was added dropwise. The mixture was stirred for 16 h at 25 °C. Then the reaction mixture was diluted with ethyl acetate and then passed through a Florisil short column (eluent ethyl acetate). After evaporation under reduced pressure, the residue was subjected to aluminum oxide column chromatography to obtain the desired product.

3. Structure Determination for *cis*-3a

The *cis*-structure of *cis*-**3a** was determined by derivatized it to alcohol (*cis*-**3a**-OH), which is a known compound.[4,5]

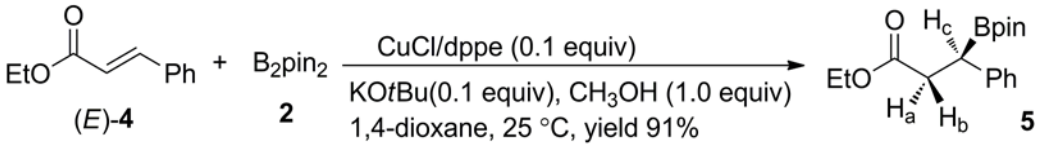


Cis-**3a** (53.6 mg, 0.2 mmol), $NaBO_3 \cdot 4H_2O$ (307 mg, 2 mmol), THF (0.3 mL) and H_2O (0.2 mL) were added into a reaction tube and the mixture was stirred at 27 °C (monitored by TLC analysis). When the reaction finished, water was added and the cis-3a-OH was extracted with CH_2Cl_2. After drying and evaporation, the crude product was purified by silica gel chromatography (yield 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.44 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.09 (b, 1H), 2.68 (ddd, *J* = 10.2, 8.7, 4.4 Hz, 1H), 2.13–1.55 (m, 6H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 73.9, 60.8, 49.6, 34.2, 26.6, 22.2, 14.3.

4. Copper-Catalyzed Hydroboration of (*E*/*Z*)-Ethyl Cinnamate [(*E*/*Z*)-**4**]

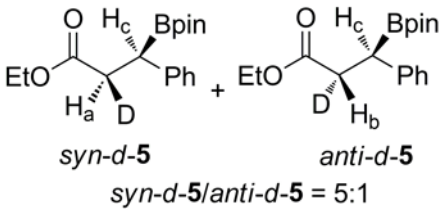
The reactions were carried out using the following general procedure: In air, $B_2(Pin)_2$ (0.6 mmol, 152 mg) and dppe (0.05 mmol, 20 mg) were placed in a screw-capped reaction vial. The vial was moved into a glove box. Then, CuCl (0.05 mmol, 5 mg), KO*t*Bu (0.05 mmol, 5.6 mg), and 1,4-dioxane (2.0 mL) were added. The vial was moved out of the glove box and connected to an argon line through a needle. After the mixture was stirred for 20 min at 65 °C (became black color), the temperature was cooled to 27 °C, then the substrate [(*E*)-ethyl cinnamate, (*Z*)-ethyl cinnamate, or a 1:1 mixture of them) and methnol (21 μL, 1.0 equiv) were added dropwise in turn. The mixture was stirred for a specified period of time. The reaction mixture was diluted with 20% ethyl acetate/80% hexane and then passed through a Florisil short column (ethyl acetate:hexane = 20:80). After evaporation under reduced pressure, the residue was subjected to silica gel column chromatography (ethyl acetate:hexane = 5:95).

Ethyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (5)



Wite solid. Known compound.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ7.28 – 7.18 (m, 4H), 7.17 – 7.12 (m, 1H), 4.17 – 4.05 (m, 2H), δ 2.88 (dd, *J* = 16.3, 10.1 Hz, 1H), 2.74 (dd, *J* = 10.0, 6.1 Hz, 1H), 2.65 (dd, *J* = 16.3, 6.0 Hz, 1H), 1.22 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 141.4, 128.5, 128.2, 125.7, 83.6, 60.4, 37.4, 24.6, 24.5, 14.3.

Ethyl 2-D-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn-d*-5 and *anti-d*-5)



^{1}H NMR (500 MHz, $CDCl_3$) for *syn-d*-**5** δ 7.28 – 7.20 (m, 4H), 7.17 – 7.12 (m, 1H), 4.17 – 4.05 (m, 2H), 2.86 (d, *J* = 10.3 Hz, 1H), 2.73 (d, *J* = 10.3 Hz, 1H), 2.63 (d, *J* = 6.0 Hz, 1H), 1.22 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) for *syn-d*-**5** δ 173.5, 141.5, 128.6, 128.3, 125.8, 83.6, 60.4, 24.7, 24.6, 14.4.

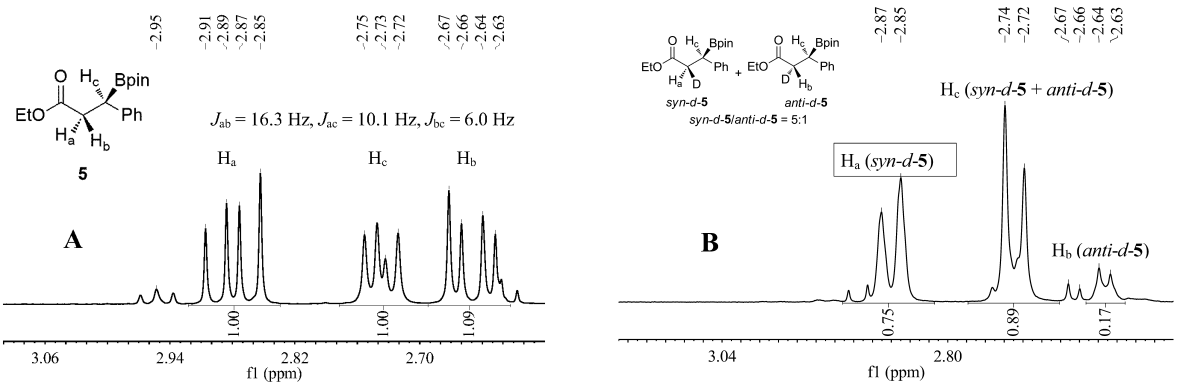


Figure S1. ^{1}H NMR spectra of **5** (**A**) and the mixture of *syn-d*-**5** and *anti-d*-**5** (5:1) (**B**).

5. Variation of the (*E*)-4 and (*Z*)-4 conversions with time in the copper-catalyzed hydroboration reactions.

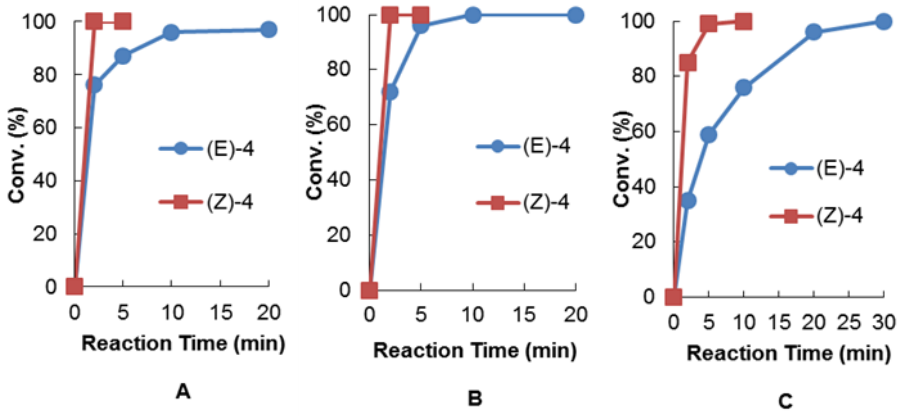
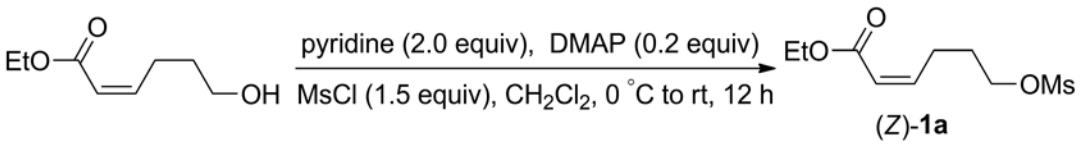


Figure S2. A: The reaction was conducted using (*E*)-4 and (*Z*)-4. B: Competitive hydroboration of a 1:1 mixture of (*E*)-4 and (*Z*)-4. C: Competitive deuteroboration of a 1:1 mixture of (*E*)-4 and (*Z*)-4.

6. Synthesis and Structure Data of the Substrates

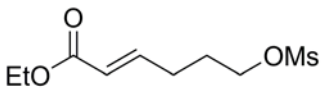
(*Z*)-ethyl 6-[(methylsulfonyl)oxy]hex-2-enoate [(*Z*)-1a]



In a 25 mL dry two-neck flask equipped with a magnetic bar was added DMAP (2.0 mmol, 0.20 equiv, 244 mg). The flask was then evacuated and back-filled with argon three times. Dry CH_2Cl_2 (10 mL), pyridine (20 mmol, 2.0 equiv, 1.6 mL) and (Z)-ethyl 6-hydroxyhex-2-enoate (10 mmol, 1.0 equiv) were added in turn to the flask. The reaction mixture was cooled to 0 °C and then methanesulfonyl chloride (15 mmol, 1.5 equiv) was added dropwise. After the reaction was slowly warmed to room temperature through 1 d with stirring, it was quenched with 5% HCl (10 mL) at 0 °C. The organic layer was separated and the water layer was extracted with ether (3 × 15 mL). The combined organic layer was then washed with water (30 mL)

and dried with Na_2SO_4. The solution was concentrated in vacuo, which afforded an oil that was purified by silica gel column chromatography (eluent ethyl acetate : hexane = 10–30:90–70) to give (*Z*)-**1a** (yield 84%) as a pale yellow oil. New compound. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.20 (dt, *J* = 11.5, 7.7 Hz, 1H), 5.84 (dt, *J* = 11.4, 1.3 Hz, 1H), 4.26 (t, *J* = 6.5 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.01 (s, 3H), 2.79 (qd, *J* = 7.7, 1.4 Hz, 2H), 1.93 (quint, *J* = 7.0 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.27, 147.63, 121.37, 69.39, 60.12, 37.51, 28.57, 25.05, 14.36. HRMS (ESI) m/z calcd for $C_9H_{17}O_5S^+$ $(M+H)^+$ 237.07912, found 237.07904.

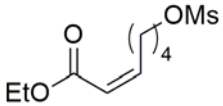
(*E*)-ethyl 6-[(methylsulfonyl)oxy]hex-2-enoate [(*E*)-1a]



(*E*)-**1a**

Colorless oil, yield 84%, new compound. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.87 (dt, *J* = 15.6, 1.4 Hz, 1H), 4.25 (t, *J* = 6.3 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.02 (s, 3H), 2.39 – 2.32 (m, 2H), 1.97– 1.89 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 146.6, 122.7, 68.8, 60.4, 37.5, 28.1, 27.6, 14.3. HRMS (ESI) m/z calcd for $C_9H_{17}O_5S^+$ $(M+H)^+$ 237.07912, found 237.07904.6

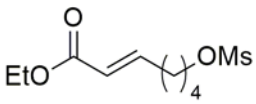
(*Z*)-ethyl 7-[(methylsulfonyl)oxy]hept-2-enoate [(*Z*)-1b]



(*Z*)-**1b**

Colorless oil, known compound. [7] Yield 75%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.18 (dt, *J* = 11.5, 7.6 Hz, 1H), 5.80 (dt, *J* = 11.5, 1.6 Hz, 1H), 4.25 (t, *J* = 6.4 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.00 (s, 3H), 2.70 (qd, *J* = 7.6, 1.6 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.62 –1.54 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.44, 149.09, 120.69, 69.85, 60.02, 37.46, 28.71, 28.13, 24.88, 14.38. HRMS (ESI) m/z calcd for $C_{10}H_{19}O_5S^+$ $(M+H)^+$ 251.09477, found 251.09477.

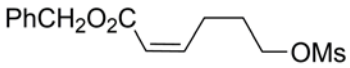
(*E*)-ethyl 7-[(methylsulfonyl)oxy]hept-2-enoate [(*E*)-1b]



(*E*)-**1b**

Colorless oil, known compound. [7] Yield 84%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.84 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.24 (t, *J* = 6.3 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.01 (s, 3H), 2.26 (qd, *J* = 7.3, 1.4 Hz, 2H), 1.83–1.75 (m, 2H), 1.65–1.55 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.64 , 147.92, 122.28, 69.52, 60.42, 37.59, 31.53, 28.71, 24.12, 14.41. HRMS (ESI) m/z calcd for $C_{10}H_{19}O_5S^+$ $(M+H)^+$ 251.09477, found 251.09477.

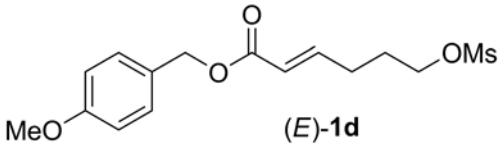
(*Z*)-benzyl 6-[(methylsulfonyl)oxy]hex-2-enoate [(*Z*)-1c]



(*Z*)-**1c**

Colorless oil, new compound. Yield 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 5H), 6.25 (dt, *J* = 11.5, 7.7 Hz, 1H), 5.90 (dt, *J* = 11.4, 1.5 Hz, 1H), 5.16 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 2H), 2.98 (s, 3H), 2.80 (qd, *J* = 7.7, 1.5 Hz, 2H), 1.98 – 1.87 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.99, 148.41, 136.09, 128.74, 128.39, 121.39, 121.06, 69.31, 66.05, 37.52, 28.56, 25.17. HRMS (ESI) m/z calcd for $C_{14}H_{19}O_5S^+$ $(M+H)^+$ 299.09477, found 299.09479.

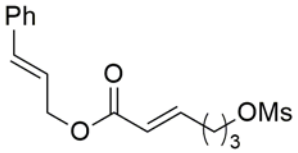
(*E*)-4-methoxybenzyl 6-[(methylsulfonyl)oxy]hex-2-enoate [(*E*)-1d]



(*E*)-**1d**

Colorless oil, new compound. Yield 75%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.95 (dt, *J* = 15.5, 6.9 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.89 (d, *J* = 15.7 Hz, 1H), 5.11 (s, 2H), 4.35 (td, *J* = 7.1, 1.0 Hz, 2H), 3.81 (s, 3H), 3.00 (s, 3H), 2.35 (q, *J* = 7.0 Hz, 2H), 1.97 – 1.87 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.29, 149.46, 130.23, 129.81, 122.52, 121.99, 114.05, 68.64, 66.15, 37.5, 27.90, 22.27. HRMS (ESI) m/z calcd for $C_{15}H_{21}O_6S^+$ $(M+H)^+$ 329.10534, found 329.10541.

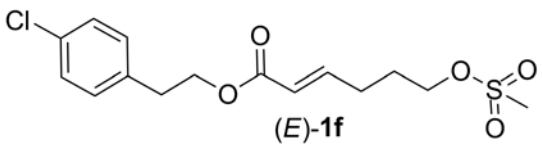
(*E*)-cinnamyl 6-[(methylsulfonyl)oxy]hex-2-enoate [(*E*)-1e]



(*E*)-**1e**

Colorless oil, new compound. Yield 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.35 –7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 6.98 (dt, *J* = 15.6, 6.9 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.92 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.80 (dd, *J* = 6.4, 1.2 Hz, 2H), 4.25 (t, *J* = 6.3 Hz, 2H), 3.01 (s, 3H), 2.41 – 2.33 (m, 2H), 1.99 – 1.89 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.12, 147.23, 136.31, 134.38, 128.73, 128.21, 126.74, 123.30, 122.50, 68.78, 65.13, 37.58, 28.21, 27.69. HRMS (ESI) m/z calcd for $C_{16}H_{21}O_5S^+$ $(M+H)^+$ 325.11042, found 325.11044.

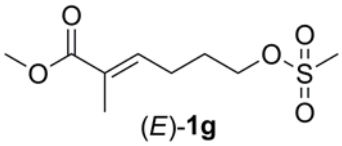
(*E*)-4-chlorophenethyl 6-[(methylsulfonyl)oxy]hex-2-enoate [(*E*)-1f]



(*E*)-**1f**

Colorless oil, new compound. Yield 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.18 – 7.14 (m, 2H), 6.91 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.85 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.33 (t, *J* = 6.9 Hz, 2H), 4.24 (t, *J* = 6.3 Hz, 2H), 3.01 (s, 3H), 2.94 (t, *J* = 6.9 Hz, 2H), 2.39 – 232 (m, 2H), 1.96 – 1.88 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.20, 147.13, 136.47, 132.52, 130.38, 128.75, 122.46, 68.76, 64.65, 37.58, 34.60, 28.17, 27.69. HRMS (ESI) m/z calcd for $C_{15}H_{20}ClO_5S^+$ $(M+H)^+$ 347.07145, found 347.07150.

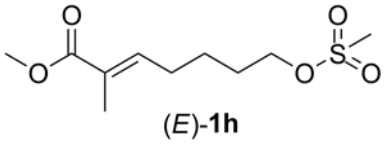
(*E*)-methyl 2-methyl-6-[(methylsulfonyl)oxy]hex-2-enoate [(*E*)-1g]



(*E*)-**1g**

Colorless oil, new compound. Yield 84%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72 (td, *J* = 7.5, 1.4 Hz, 1H), 4.25 (t, *J* = 6.3 Hz, 2H), 3.75 (s, 3H), 3.02 (s, 3H), 2.34 (q, *J* = 7.4 Hz, 2H), 1.96 – 1.89 (m, 3H), 1.86 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.48, 139.87, 129.25, 69.09, 51.96, 37.55, 28.24, 24.69, 12.59. HRMS (ESI) m/z calcd for $C_9H_{17}O_5S^+$ $(M+H)^+$ 237.07912, found 237.07903.

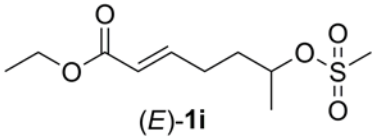
(*E*)-methyl 2-methyl-7-[(methylsulfonyl)oxy]hept-2-enoate [(*E*)-1h]



(*E*)-**1h**

Colorless oil, new compound. Yield 84%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (td, *J* = 7.4, 1.4 Hz, 1H), 4.24 (t, *J* = 6.4 Hz, 2H), 3.74 (s, 3H), 3.01 (s, 3H), 2.23 (q, *J* = 7.4 Hz, 2H), 1.84 (d, *J* = 1.2 Hz, 3H), 1.82 –1.75 (m, 2H), 1.63 – 1.55 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.60, 141.25, 128.45, 69.65, 51.86, 37.51, 28.84, 27.99, 24.62, 12.55. HRMS (ESI) m/z calcd for $C_{10}H_{19}O_5S^+$ $(M+H)^+$ 251.09477, found 251.09477.

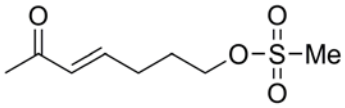
(*E*)-ethyl 6-[(methylsulfonyl)oxy]hept-2-enoate [(*E*)-1i]



(*E*)-**1i**

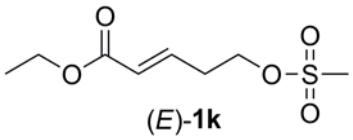
Colorless oil, new compound. Yield 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.87 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.88 – 4.79 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.01 (s, 3H), 2.42 – 2.25 (m, 2H), 1.93 – 1.83 (m, 1H), 1.83 – 1.73 (m, 1H), 1.45 (d, *J* = 6.3 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.46, 147.02, 122.41, 78.89, 60.39, 38.84, 35.00, 27.86, 21.27, 14.34. HRMS (ESI) m/z calcd for $C_{10}H_{19}O_5S^+$ $(M+H)^+$ 251.09477, found 251.09477.

(*E*)-6-oxohept-4-en-1-yl methanesulfonate [(*E*)-1j]



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (dt, *J* = 15.4, 6.8 Hz, 1H), 6.13 (dd, *J* = 15.9, 1.4 Hz, 1H), 4.28 – 4.23 (m, 2H), 3.02 (d, *J* = 0.8 Hz, 3H), 2.38 (q, *J* = 7.2 Hz, 2H), 2.26 (d, *J* = 1.2 Hz, 3H), 1.99 – 1.91 (m, 2H).

(*E*)-ethyl 5-[(methylsulfonyl)oxy]pent-2-enoate [(*E*)-1k]

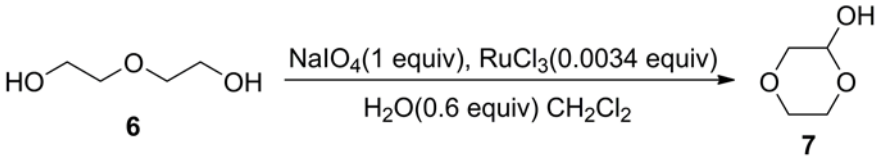


(*E*)-**1k**

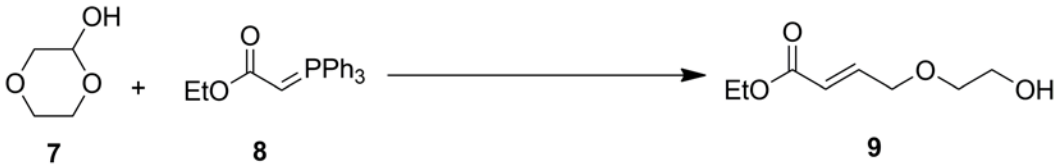
Colorless oil (yield 80%), known compound.[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (dt, *J* = 15.7, 6.9 Hz, 1H), 5.95 (dt, *J* = 15.7, 1.5 Hz, 1H), 4.34 (t, *J* = 6.4 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.03 (s, 3H), 2.67 (qd, *J* = 6.5, 1.5 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.97, 142.13, 124.77, 77.16, 67.34, 60.60, 37.69, 31.91, 14.31.

7. The Synthesis of (*Z*)-1l, (*E*)-1l and (*E*)-1m

The synthesis of (*E*)-ethyl 4-(2-((methylsulfonyl)oxy)ethoxy)but-2-enoate [(*E*)-1l]



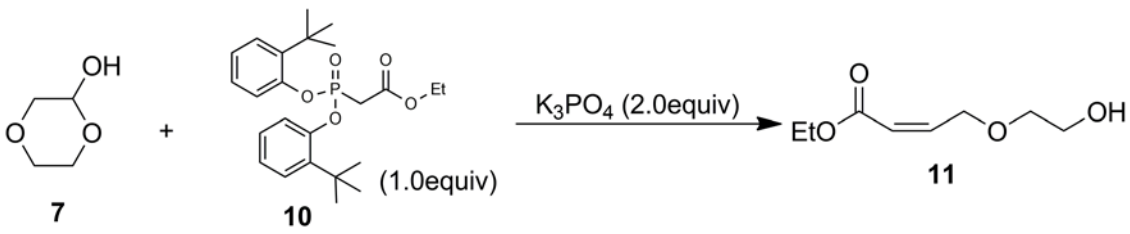
In a 250 mL two neck flask were added $NaIO_4$ (10.65 g, 50 mmol), $RuCl_3 \cdot H_2O$ (35 mg, 0.17 mmol). The flask was evacuated and re-filled argon three times. CH_2Cl_2 (75 mL) and **6** (5.30 g, 50 mmol) were added in turn. The solution was stirred at 40 °C for 10 min. Water (0.54 g, 30 mmol) was added and stirred 120 min. After the reaction, the reaction mixture was filtered through a celite and washed with CH_2Cl_2. The filtrate was concentrated and **7** was obtained (4.94 g, 95%).



7 (0.83 g, 10 mmol),**8** (3.84 g, 10 mmol) and CH_2Cl_2 (10 mL) were added to a 25 mL two neck flask. The solution was stirred at 28 °C in the atmosphere of argon for 48 h. The reaction mixture was transferred to 100 mL flask with the aid of CH_2Cl_2 and silica gel was added. After evaporation of the solvent, the silica adsorbed product was purified by silica gel column chromatography (EtOAc: Hexane = 30 : 70). **9** is a colorless oil (1.28 g, 74%).

(*E*)-**1l** was prepared by the method described for (*Z*)-**1a** (78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 15.8, 4.4 Hz, 1H), 6.07 (dt, *J* = 15.8, 2.0 Hz, 1H), 4.43 – 4.37 (m, 2H), 4.25 – 4.18 (m, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.79 – 3.73 (m, 2H), 3.07 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.16, 143.31, 121.95, 69.94, 68.84, 68.69, 60.63, 37.79, 14.34. HRMS (ESI) m/z calcd for $C_9H_{17}O_6S^+$ $(M+H)^+$ 253.07404, found 253.07404.

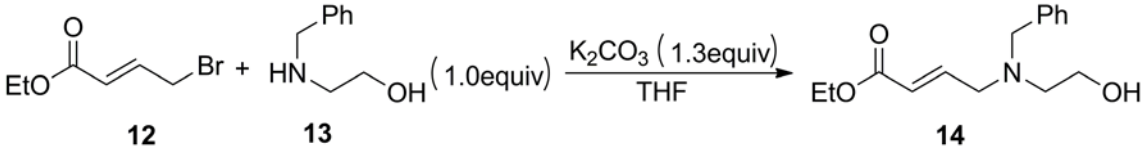
The synthesis of (*Z*)-ethyl 4-(2-((methylsulfonyl)oxy)ethoxy)but-2-enoate [(*Z*)-1l]



In a 25 mL two neck flask was added anhydrous K_3PO_4 (4.25 g, 20 mmol) and a stirrer bar. After the flask was evaporated and re-filled argon three times, **10** (4.32 g, 10 mmol) and 10 mL anhydrous CH_3CN were added and the mixture was stirred for 5 min. The flask was cooled to 0 °C and **7** (1.04 g, 10 mmol) was added dropwise. The reaction mixture was stirred for 48 h while the reaction temperature gradually increased from 0 °C to 28 °C. After filtration, the filtrate was concentrated and the crude product was purified by silica gel column chromatography (EtOAc : Hexane = 0–30 : 100–70). 1.39 g 11 was obtained (yield 80%).

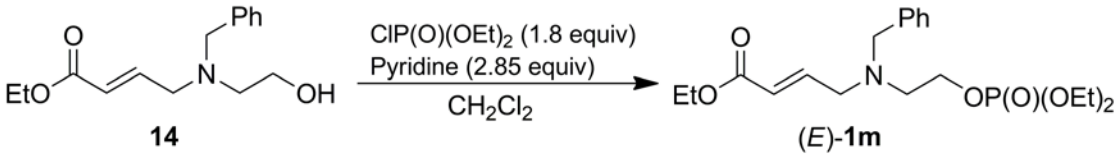
(*Z*)-**1l** was prepared by the method described for (*Z*)-**1a** (colorless iol, yield 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.37–6.31 (m, 1H), 5.87–5.82 (m, 1H), 4.66–4.62 (m, 2H), 4.41 – 4.36 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.78–3.73 (m, 2H), 3.06 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.00, 147.03, 120.31, 69.1 , 68.48, 60.42, 52.66, 37.75, 14.29. HRMS (ESI) m/z calcd for $C_9H_{17}O_6S^+$ $(M+H)^+$ 253.07404, found253.07404.

The Synthesis of (*E*)-ethyl 4-(benzyl(2-((diethoxyphosphoryl)oxy)ethyl)amino)but-2-enoate [(*E*)-1m]



12 **13** **14**

In a two neck flask was added K_2CO_3 (0.898 g, 6.5 mmol, 1.3 equiv.). The flask was evacuated and re-filled argon three times. **13** (0.756 g, 5.0 mmol, 1.0 equiv) and 7 mL THF were added. **12** (0.965 g, 5.0 mmol) in 4 mL THF was added dropwise with stirring. The mixture was stirred at 28 °C for 12 h. The mixture was passed through a short silica gel column with the aid of ethyl acetate. After concentration, the crude product was purified by silica gel column chromatography (EtOAc : Hexane = 0–40 : 100–60). **14** was obtained in a yield of 80%.

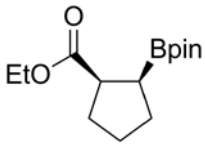


14 (*E*)-**1m**

In a two neck flask were added **14** (1.30 g, 5.0 mmol), pyridine (1.4 mL, 14.1 mmol) and 5 mL CH_2Cl_2. The solution was cooled to 0 °C and $ClP(O)(OEt)_2$ (9.0 mmol) was added dropwise. The mixture was stirred from 0–25 °C for 14 h. Water (10 mL) was added and organics were extracted with CH_2Cl_2 (30 mL×3). The combined organic layer was then washed with saturated $CuSO_4$ aqu. solution and brine, respectively, and dried with Na_2SO_4. The solution was concentrated in vacuo, which afforded an oil that was purified by silica gel column chromatography (eluent ethyl acetate : hexane = 0–40:100–60) to give (*E*)-**1m** (yield 75%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H), 7.00–6.92 (m, 1H), 6.05 (d, *J* = 15.7 Hz, 1H), 4.25–4.18 (m, 2H), 4.16–4.07 (m, 6H), 3.70 (s, 2H), 3.32 (d, *J* = 5.8 Hz, 2H), 2.82 (t, *J* = 6.0 Hz, 2H), 1.38–1.28 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.36, 145.88, 138.75, 128.80, 128.47, 127.34, 123.18, 65.55 (d, *J* = 6.2 Hz), 63.90 (d, *J* = 5.9 Hz), 60.48, 59.01, 55.18, 53.41 (d, *J* = 7.6 Hz), 16.26 (d, *J* = 6.7 Hz), 14.37. HRMS (ESI) m/z calcd for $C_{19}H_{30}NO_6P^+$ $(M+H)^+$ 400.18835, found 400.18839.

8. Structure Data of the Products

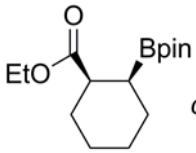
Ethyl 2-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (*cis*-3a)



cis-**3a**

Colorless oil. Yield 86%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.09 (q, *J* = 7.1 Hz, 2H), 2.99 (td, *J* = 8.4, 5.4 Hz, 1H), 1.98 – 1.88 (m, 1H), 1.87 – 1.69 (m, 4H), 1.61 – 1.48 (m, 1H), 1.44 – 1.34 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.25 (s, 6H), 1.23 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.1, 83.1 (2C), 60.3, 46.5, 31.3, 27.8, 25.9 25.1 (2C), 24.9 (2C), 14.4. HRMS (ESI) m/z calcd for $C_{14}H_{26}BO_4$ $(M+H)^+$ 269.19187, found 269.19229.

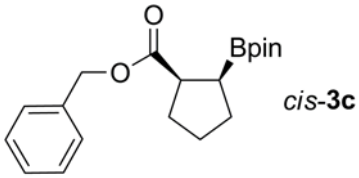
Ethyl 2-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexanecarboxylate (*cis*-3b)



cis-**3b**

Colorless oil. Yield 40% from (*E*)-**1b**, 44% from (*Z*)-**1b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.1 Hz, 2H), 2.67 – 2.59 (m, 1H), 1.97 – 1.87 (m, 1H), 1.78 – 1.65 (m, 2H), 1.61 – 1.53 (m, 1H), 1.52 – 1.42 (m, 2H), 1.42 – 1.32 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 6H), 1.23 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 83.0 (2C), 60.2, 43.21, 31.1, 27.9, 25.9, 25.7, 24.9 (2C), 24.9 (2C), 14.5. HRMS (ESI) m/z calcd for $C_{15}H_{28}BO_4$ $(M+H)^+$ 283.20752, found 283.20755.

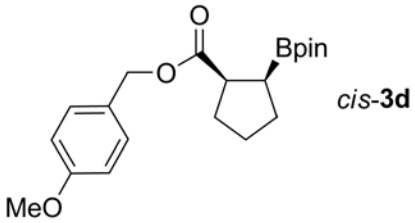
Benzyl 2-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (*cis*-3c)



cis-**3c**

Colorless oil. Yield 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.09 (s, 2H), 3.07 (td, *J* = 8.4, 5.5 Hz, 1H), 2.00 – 1.90 (m, 1H), 1.91 – 1.68 (m, 4H), 1.63 – 1.48 (m, 1H), 1.43 (q, *J* = 8.7 Hz, 1H), 1.23 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 136.6, 128.6, 128.1, 128.1, 83.2 (2C), 66.1, 46.5, 31.2, 27.8, 25.9, 25.1 (2C), 24.9 (2C). HRMS (ESI) m/z calcd for $C_{19}H_{28}BO_4$ $(M+H)^+$ 331.20752, found 331.20752.

4-Methoxybenzyl 2-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (*cis*-3d)

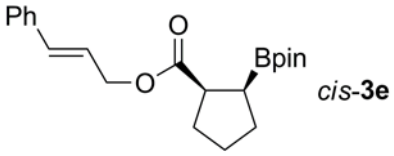


cis-**3d**

Colorless oil. Yield 40%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 6.91 – 6.84 (m, 2H), 5.02 (d, *J* = 3.1 Hz, 2H), 3.80 (s, 3H), 3.04 (td, *J* = 8.4, 5.4 Hz, 1H), 1.97 – 1.88 (m, 1H), 1.88 – 1.78 (m, 2H), 1.78 – 1.68 (m, 2H), 1.60 – 1.46 (m, 1H), 1.41 (q, *J* = 8.6 Hz, 1H), 1.24 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (126

MHz, $CDCl_3$) δ 176.9, 159.6, 129.9, 128.7, 114.0, 83.2 (2C), 65.9, 55.4, 46.5, 31.2, 27.8, 25. 9, 25.1 (2C), 24.9 (2C). HRMS (ESI) m/z calcd for $C_{20}H_{30}BO_5^+$ $(M+H)^+$ 361.21808, found 361.21851.

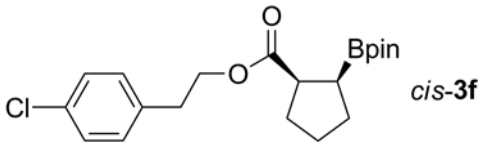
Cinnamyl 2-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (*cis*-3e)



cis-**3e**

Colorless oil. Yield 56%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 6.7 Hz, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.75 (ddd, *J* = 6.3, 2.4, 1.4 Hz, 2H), 3.11 (td, *J* = 8.4, 5.4 Hz, 1H), 2.05 – 1.97 (m, 1H), 1.96 – 1.89 (m, 1H), 1.89 – 1.75 (m, 3H), 1.66 – 1.55 (m, 1H), 1.47 (q, *J* = 8.6 Hz, 1H), 1.29 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 136.5, 133.8, 128.7, 128.1, 126.7, 123.8, 83.2 (2C), 65.0, 46.5, 31.2, 27.8, 25.9, 25.1 (2C), 24.9 (2C). HRMS (ESI) m/z calcd for $C_{21}H_{30}BO_4$ $(M+H)^+$ 357.22317, found 357.22324.

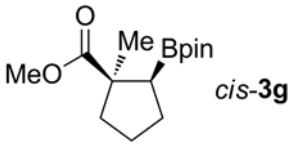
4-Chlorophenethyl 2-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (*cis*-3f)



cis-**3f**

Colorless oil. Yield 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.19 – 7.13 (m, 2H), 4.28 – 4.16 (m, 2H), 2.99 (td, *J* = 8.5, 5.1 Hz, 1H), 2.90 (t, *J* = 7.0 Hz, 2H), 1.94 – 1.86 (m, 1H), 1.85 – 1.65 (m, 4H), 1.58 – 1.46 (m, 1H), 1.39 (dd, *J* = 17.5, 8.6 Hz, 1H), 1.24 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 136.7, 132.4, 130.4, 128.7, 83.2 (2C), 64.6, 46.4, 34.6, 31.2, 27.7, 25.9, 25.1 (2C), 24.9 (2C). HRMS (ESI) m/z calcd for $C_{20}H_{29}BClO_4$ $(M+H)^+$ 379.18419, found 379.18419.

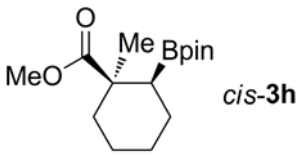
Methyl 1-methyl-2-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (*cis*-3g)



cis-**3g**

Colorless oil. Yield 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.63 (s, 3H), 2.14 – 2.06 (m, 1H), 1.91 – 1.82 (m, 1H), 1.82 – 1.72 (m, 1H), 1.72 – 1.58 (m, 2H), 1.55 – 1.45 (m, 1H), 1.37 (s, 3H), 1.24 (s, 6H), 1.22 (s, 6H), 1.06 (t, *J* = 9.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.2, 82.9 (2C), 53.1, 51.8, 40.0, 27.9, 25.6, 25.2 (2C), 24.9, 24.9 (2C). HRMS (ESI) m/z calcd for $C_{14}H_{26}BO_4$ $(M+H)^+$ 269.19187, found 269.19202.

Methyl 1-methyl-2-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexanecarboxylate (*cis*-3h)

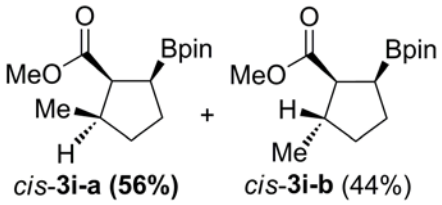


cis-**3h**

Colorless oil. Yield 76%. ^{1}H NMR (500 MHz, $CDCl_3$) δ3.65 (s, 3H), 2.10 – 2.01 (m, 1H), 1.77 – 1.67 (m, 1H), 1.62 – 1.50 (m, 3H), 1.50 – 1.38 (m, 1H), 1.30 (s, 3H), 1.34 – 1.18 (m, 2H), 1.24 (s, 6H), 1.22 (s, 3H), 0.92 – 0.84 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 82.7 (2C), 51.6, 45.3, 29.8, 27.1, 26.2, 25.4, 25.1 (2C), 24.8 (2C), 23.6. HRMS (ESI) m/z calcd for $C_{15}H_{28}BO_4$ $(M+H)^+$ 283.20752, found 283.20734.

Methyl 2-*cis*-methyl-5-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (*cis*-3i-a)

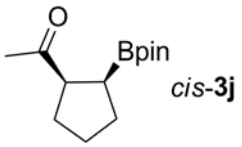
Methyl 2-*cis*-methyl-5-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanecarboxylate (*trans*-3i-b)



cis-**3i-a (56%)** *cis*-**3i-b** (44%)

Colorless oil. Yield 50%, *cis*-**3i**:*trans*-**3i** = 56:44. ^{1}H NMR (500 MHz, $CDCl_3$) δ *cis*-isomer: 4.10 (q, J = 7.0 Hz, 2H), 2.96 (dd, J_1= J_2 = 7.3 Hz, 1H), 2.26 – 2.14 (m, 1H), 2.08 – 2.00 (m, 1H), 1.86 –1.78 (m, 2H), 1.52 – 1.38 (m, 2H), 1.25 (t, J = 7.3 Hz, 3H), 1.24 (s, 6H), 1.20 (s, 6H), 0.98 (d, J = 6.9 Hz, 3H); *trans*-isomer: 4.10 (q, J = 7.0 Hz, 2H), 2.53 (dd, J = 9.3, 6.4 Hz, 1H), 2.26 – 2.14 (m, 1H), 1.95 – 1.88 (m, 1H), 1.86 –1.78 (m, 2H), 1.60 – 1.37 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H), 1.25 (s, 6H), 1.22 (s, 6H), 1.08 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ *cis*-isomer: 175.7, 83.2 (2C), 59.7, 51.8, 33.3, 25.9, 25.02 (2C), 24.85 (2C), 16.5, 14.6; *trans*-isomer: 176.9, 83.1 (2C), 60.2, 54.0, 40.0, 35.6, 27.7, 25.06 (2C), 24.92 (2C), 20.9, 14.4. HRMS (ESI) m/z calcd for $C_{14}H_{26}BO_4$ $(M+H)^+$ 268.19187, found 268.19183.

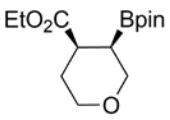
1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)ethanone (*cis*-3j)



cis-**3j**

Colorless oil. Yield 52%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.63 (s, 3H), 2.14–2.05 (m, 1H), 1.91–1.82 (m, 1H), 1.82–1.72 (m, 1H), 1.72–1.58 (m, 2H), 1.54–1.46 (m, 2H), 1.31–1.19 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.10–1.03 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.5, 82.8 (2C), 55.6, 30.4, 29.7, 28.1, 27.6, 26.1, 24.92 (2C), 24.82 (2C). HRMS (ESI) m/z calcd for $C_{13}H_{24}BO_3$ $(M+H)^+$ 239.18130, found 239.18129.

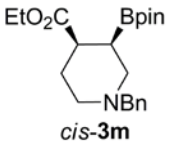
Ethyl 3-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2H-pyran-4-carboxylate (*cis*-3l)



cis-**3l**

Oil, NMR yield 65%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 (q, J = 7.1 Hz, 2H), 3.72–3.53 (m, 4H), 2.55 (dd, J = 16.8, 7.2 Hz, 1H), 2.48 (dd, J = 16.8, 6.2 Hz, 1H), 1.74–1.53 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.23 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 83.6, 71.8, 69.3, 68.5, 60.5, 37.8, 32.5, 24.9, 24.8, 14.4. HRMS (ESI) m/z calcd for $C_{14}H_{26}BO_5$ $(M+H)^+$ 285.18678, found 285.18680.

Ethyl 1-benzyl-3-*cis*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-4-carboxylate (*cis*-3m)



cis-**3m**

Oil, NMR yield 62%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.21 (m, 5H), 4.21–3.95 (m, 8H), 3.73 (d, *J* = 18.4 Hz, 1H), 3.58 (d, *J* = 13.7 Hz, 1H), 2.85–2.41 (m, 2H), 1.29–1.26 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 139.5, 129.1, 128.3, 127.0, 83.4, 75.2, 60.3, 59.1, 55.4, 33.5, 25.0, 25.0, 24.9, 24.7, 14.4. HRMS (ESI) m/z calcd for $C_{21}H_{33}BNO_4$ $(M+H)^+$ 374.24972, found 374.24966.

9. References

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5 Seebach, D.; Roggo, S.; Maetzke, T.; Braunschweiger, H.; Cercus, J.; Krieger, M. *Helv. Chim. Acta* **1987**, *70*, 1605.
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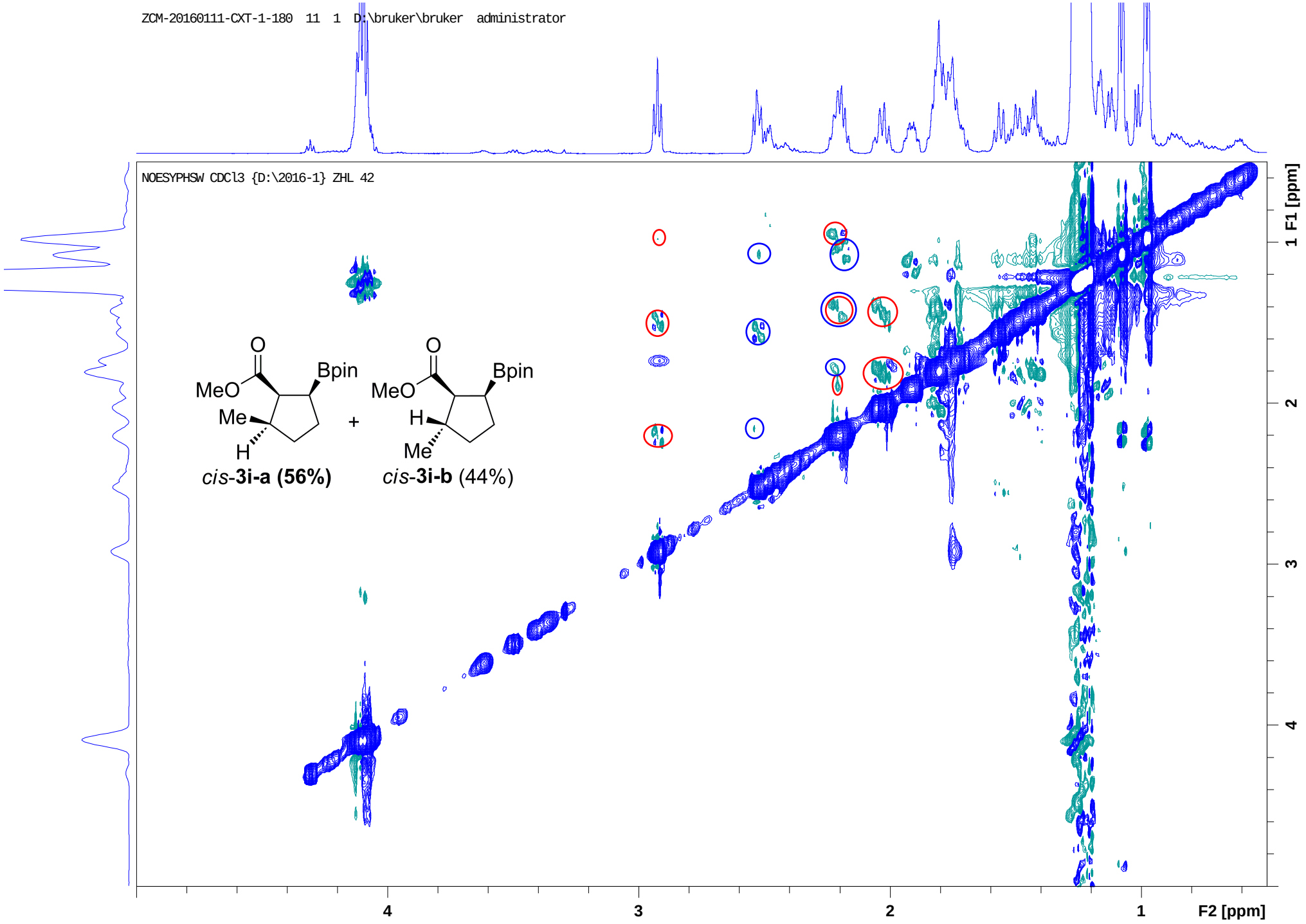
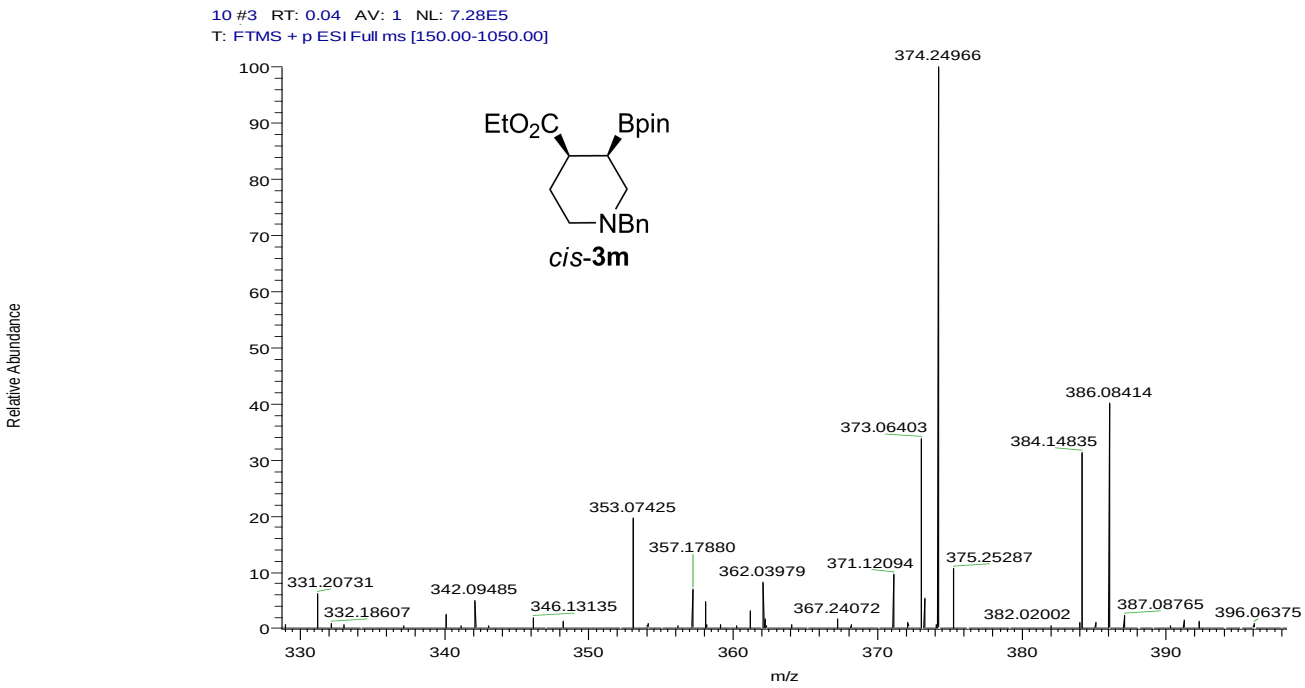
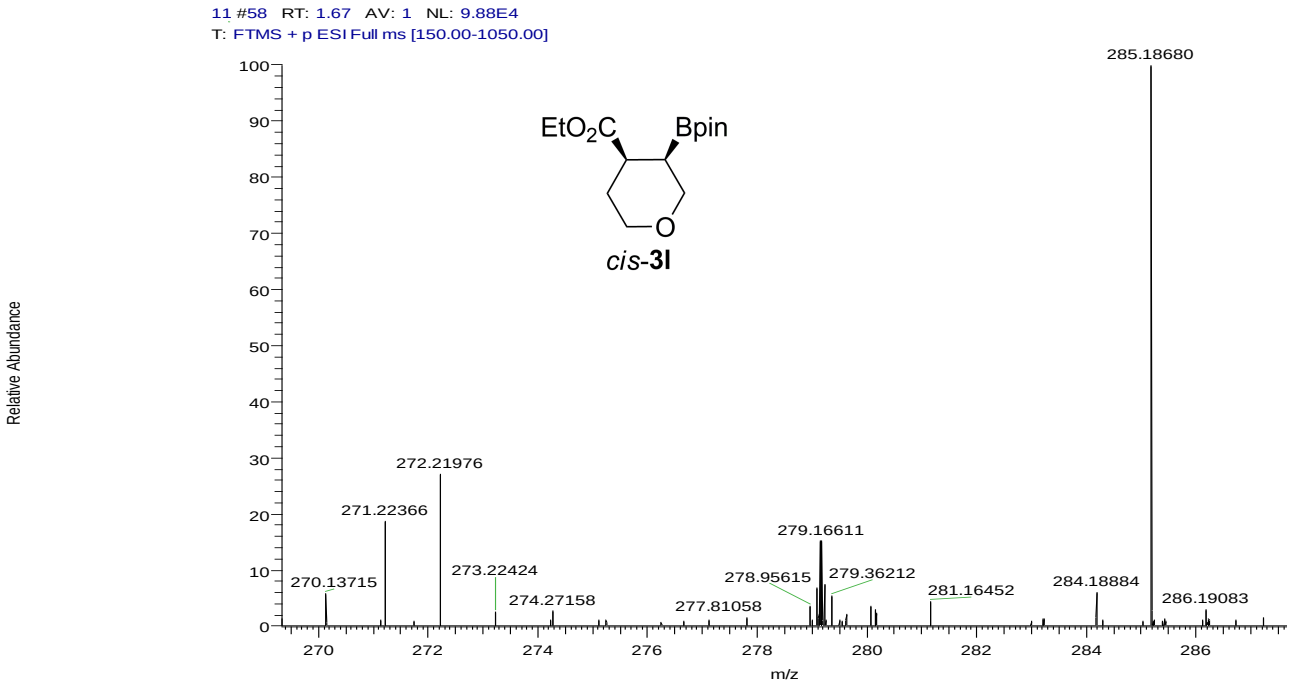

ZCM-20160111-CXT-1-180 11 1 D:\bruker\bruker administrator
NOESYPHSW CDCl3 {D:\2016-1} ZHL 42
MeO
Bpin
Me
H
cis-3i-a (56%)
+
MeO
Bpin
H
Me
cis-3i-b (44%)
F1 [ppm]
F2 [ppm]
1
2
3
4

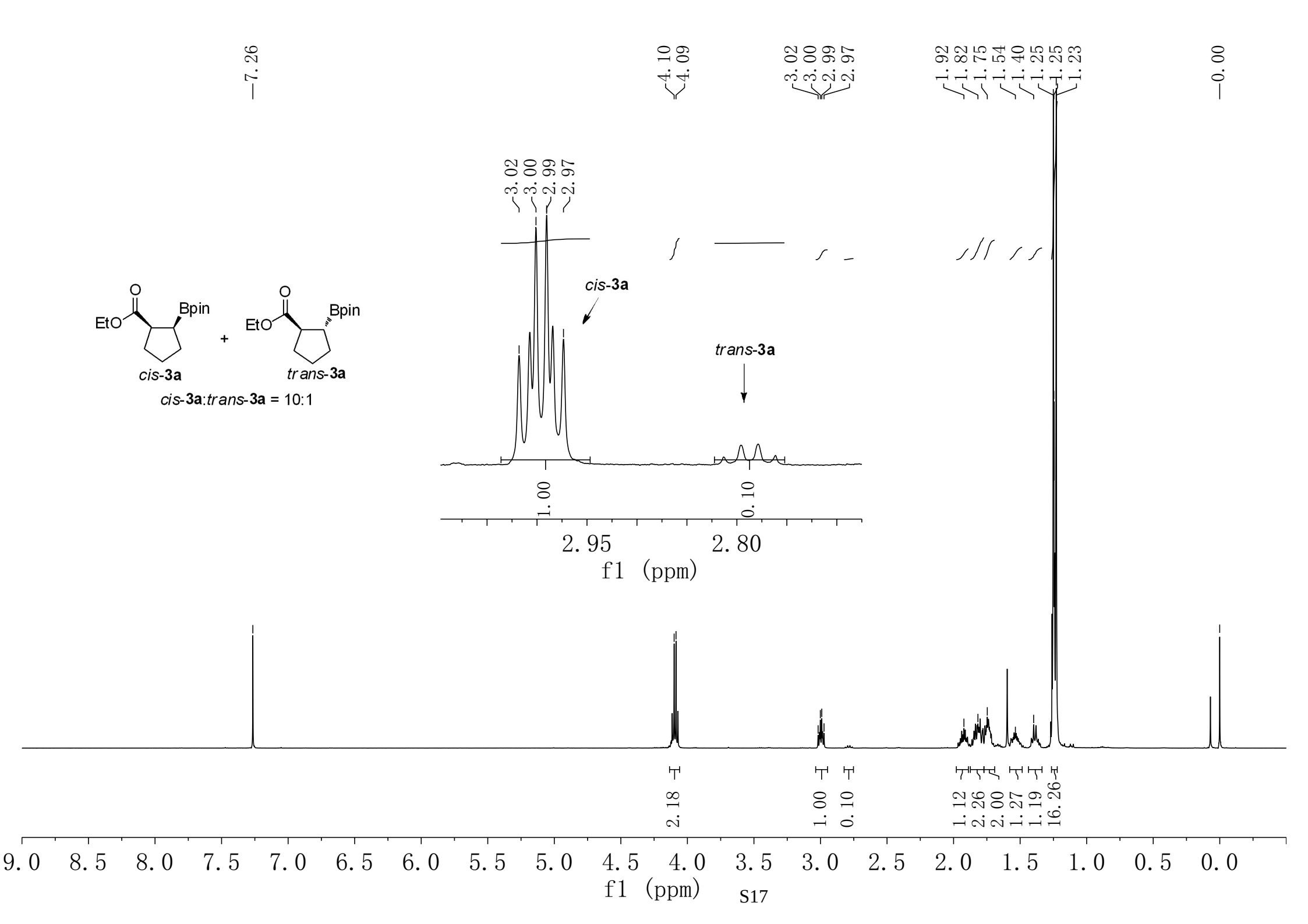
10. HRMS (ESI) m/z calcd for $C_{21}H_{33}BNO_4$ $(M+H)^+$ 374.24972, found 374.24966.

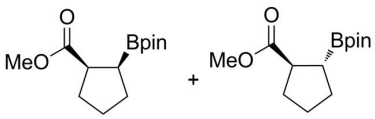


11. HRMS (ESI) m/z calcd for $C_{14}H_{26}BO_5$ $(M+H)^+$ 285.18678, found 285.18680.



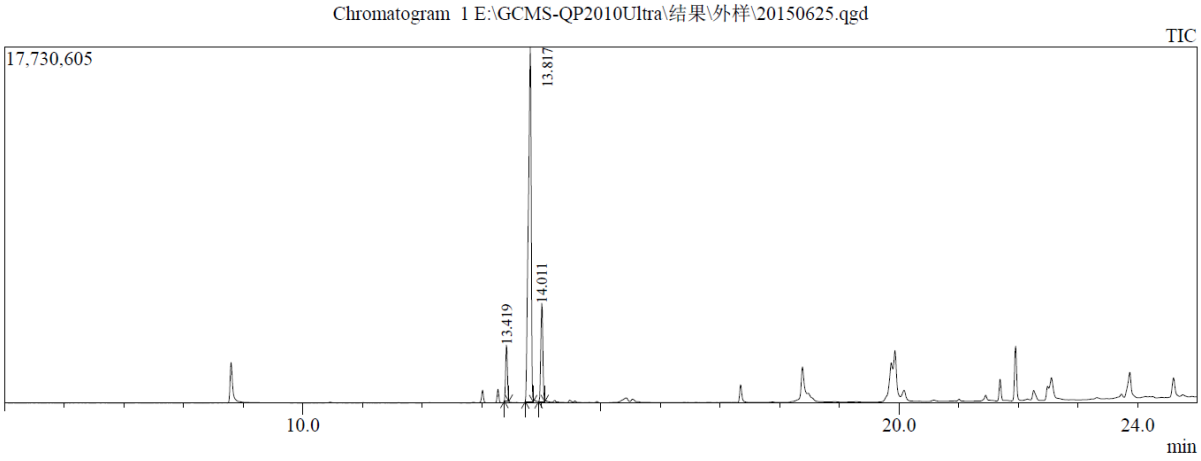
12. HRMS (ESI) m/z calcd for $C_{13}H_{24}BO_3$ $(M+H)^+$ 239.18130, found 239.18129.


7.26
4.10
4.09
3.02
3.00
2.99
2.97
1.92
1.82
1.75
1.54
1.40
1.25
1.23
0.00
cis-3a
trans-3a
cis-3a:trans-3a = 10:1
1.00
0.10
2.95
2.80
f1 (ppm)
2.18
1.00
0.10
1.12
2.26
2.00
1.27
1.19
16.26
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



cis-**3a** : *trans*-**3a** = 10:1

Chromatogram 1 E:\GCMS-QP2010Ultra\结果\外样\20150625.qgd



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	13.419	13.383	13.458	5795023	7.66	2802753	11.06	2.07	MI	
2	13.817	13.733	13.867	58707475	77.65	17657876	69.65	3.32	MI	
3	14.011	13.958	14.058	11103603	14.69	4891826	19.30	2.27	MI	
				75606101	100.00	25352455	100.00			

Library

<< Target >>

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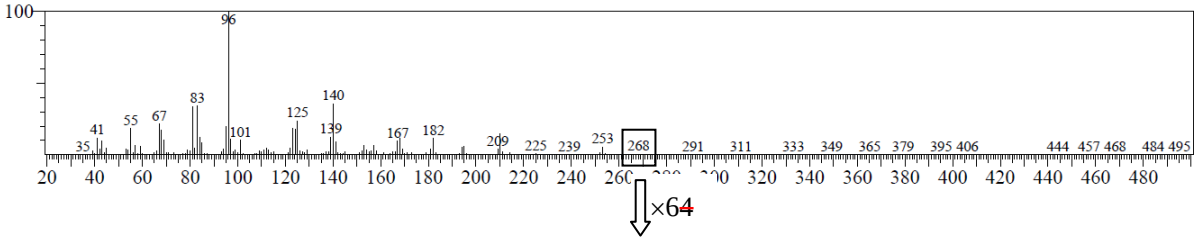
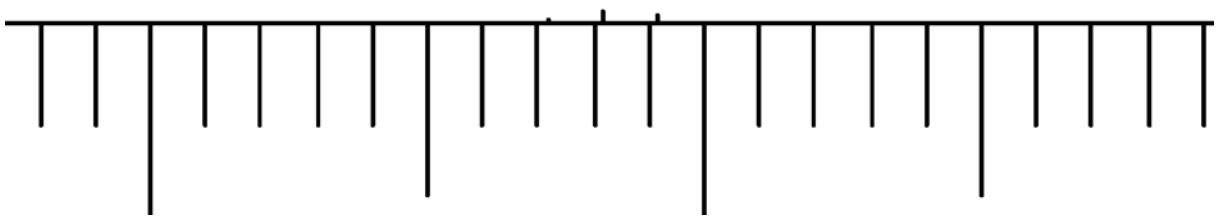
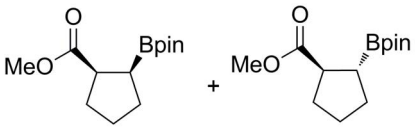


268





cis-**3a** : *trans*-**3a** = 10:1

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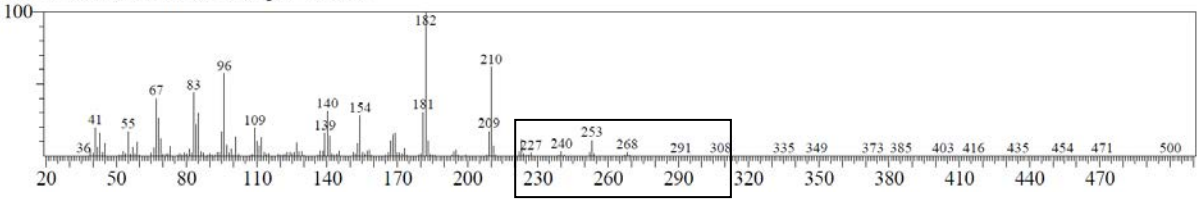

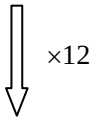

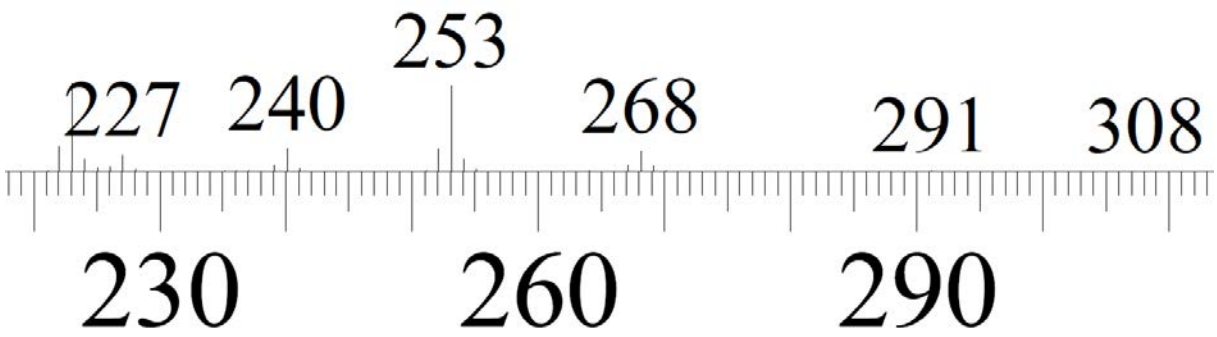

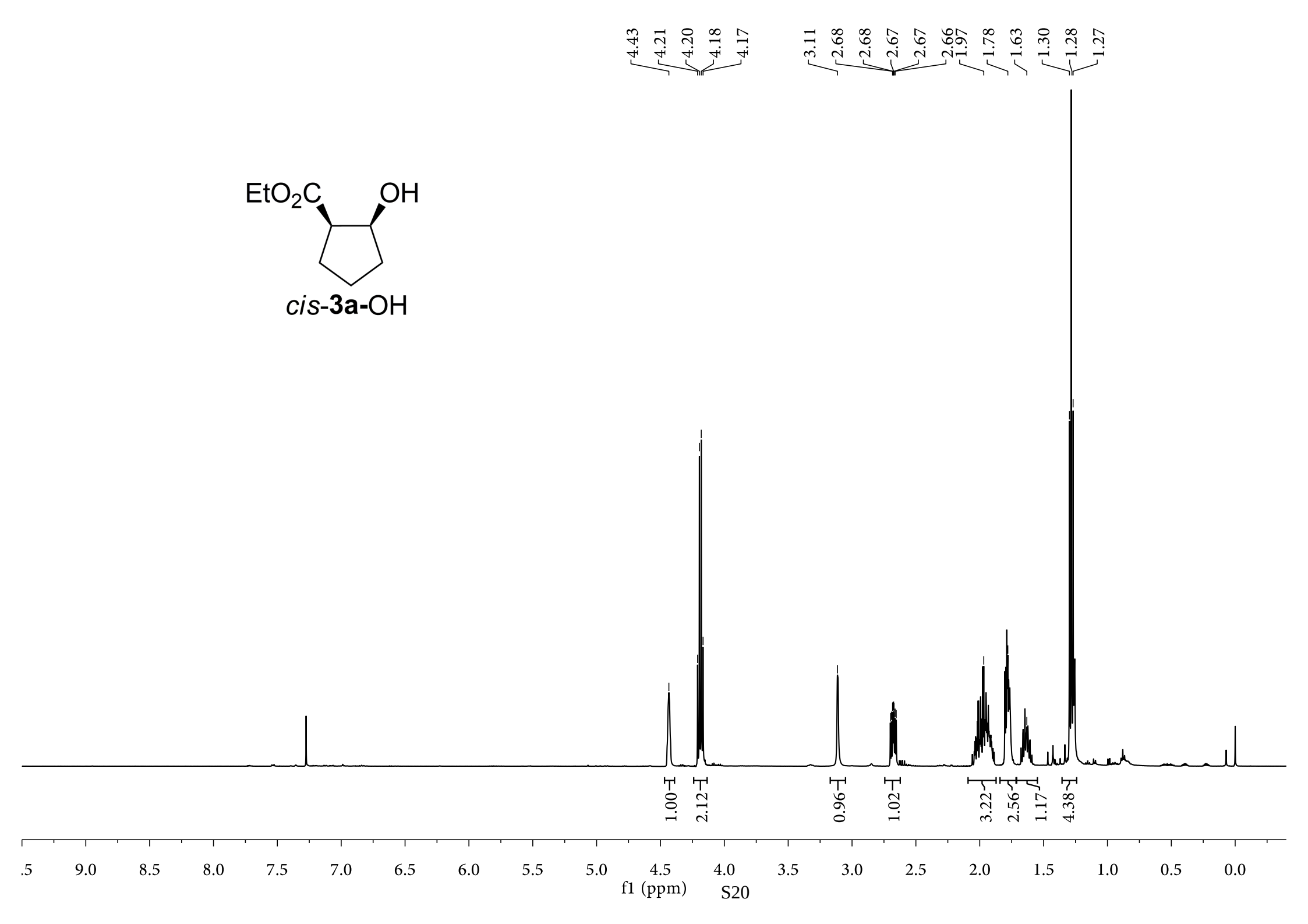
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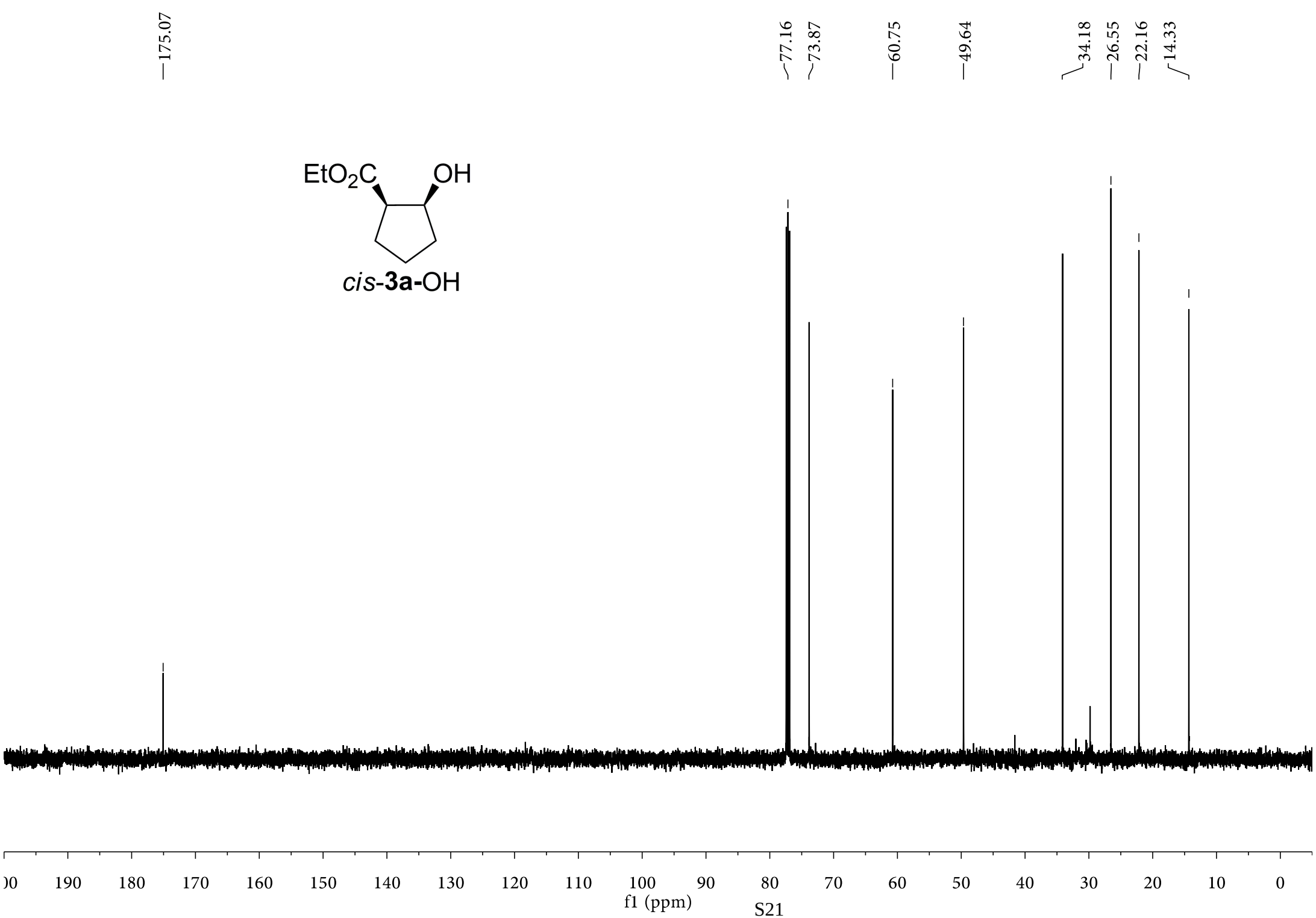
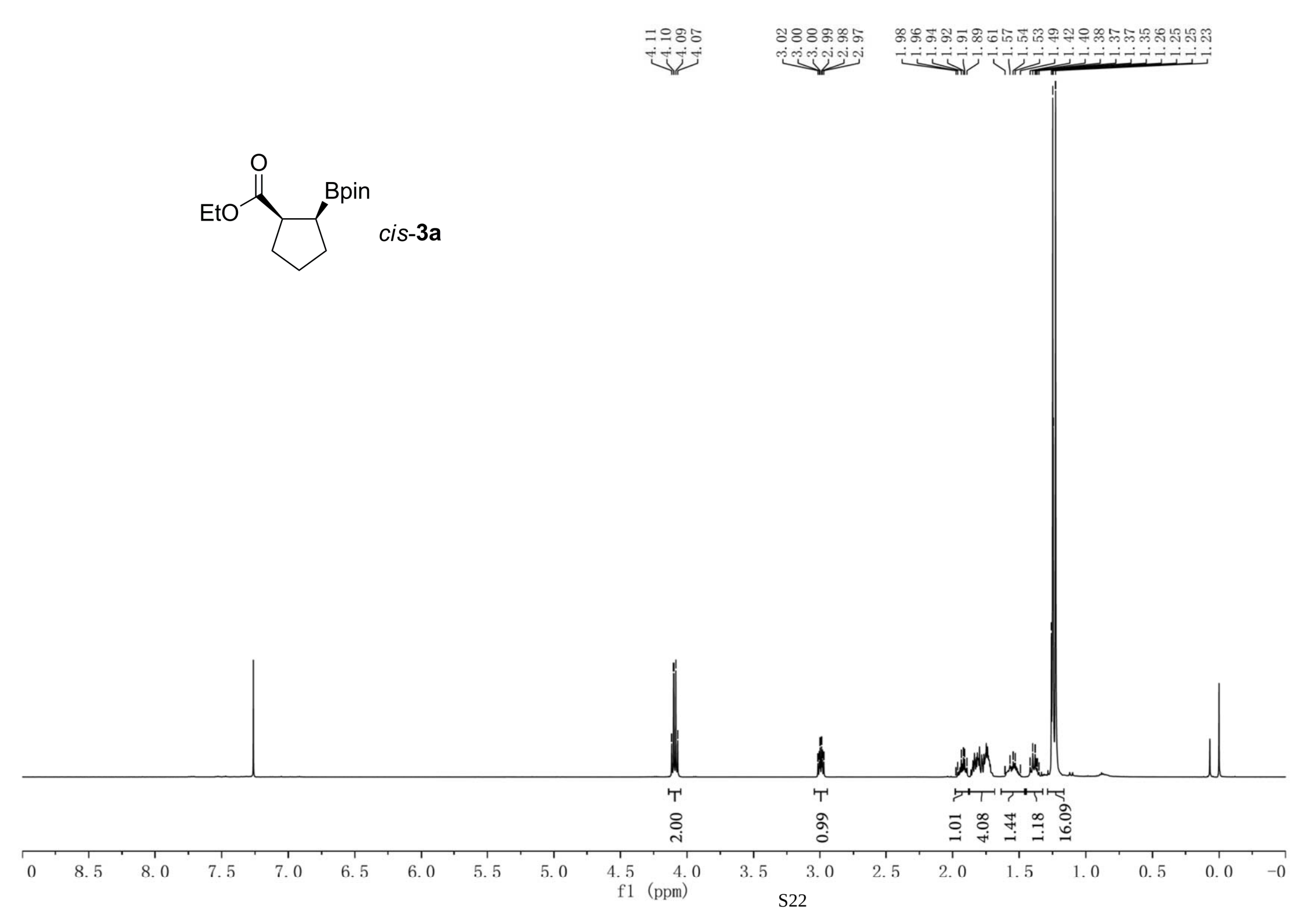
4.21
4.20
4.18
4.17
3.11
2.68
2.68
2.67
2.67
2.66
1.97
1.78
1.63
1.30
1.28
1.27
EtO2C
OH
cis-3a-OH
1.00
2.12
0.96
1.02
3.22
2.56
1.17
4.38
f1 (ppm)


175.07
77.16
73.87
60.75
49.64
34.18
26.55
22.16
14.33
EtO2C
OH
cis-3a-OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.07
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3.00
3.00
2.99
2.98
2.97
1.98
1.96
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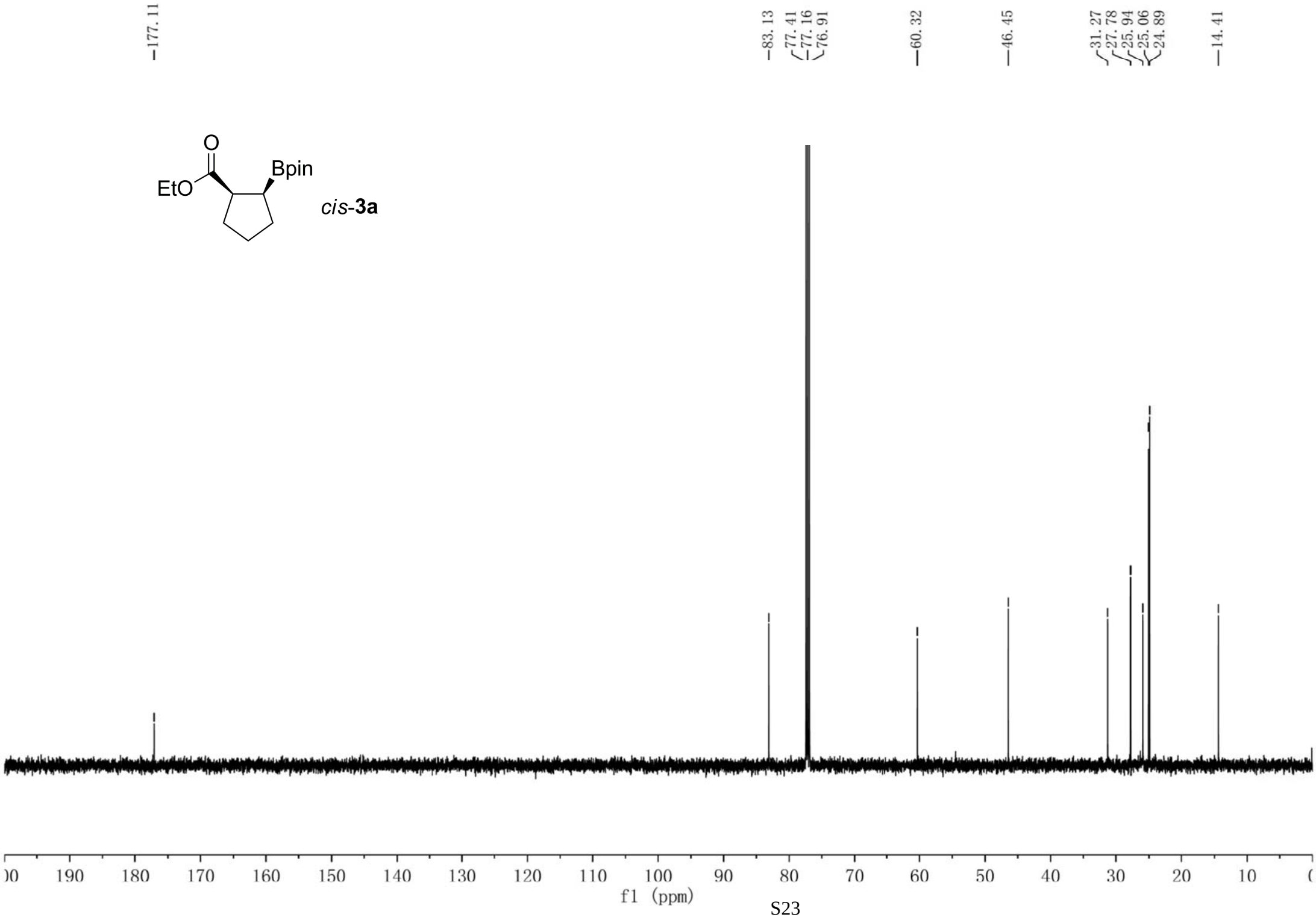
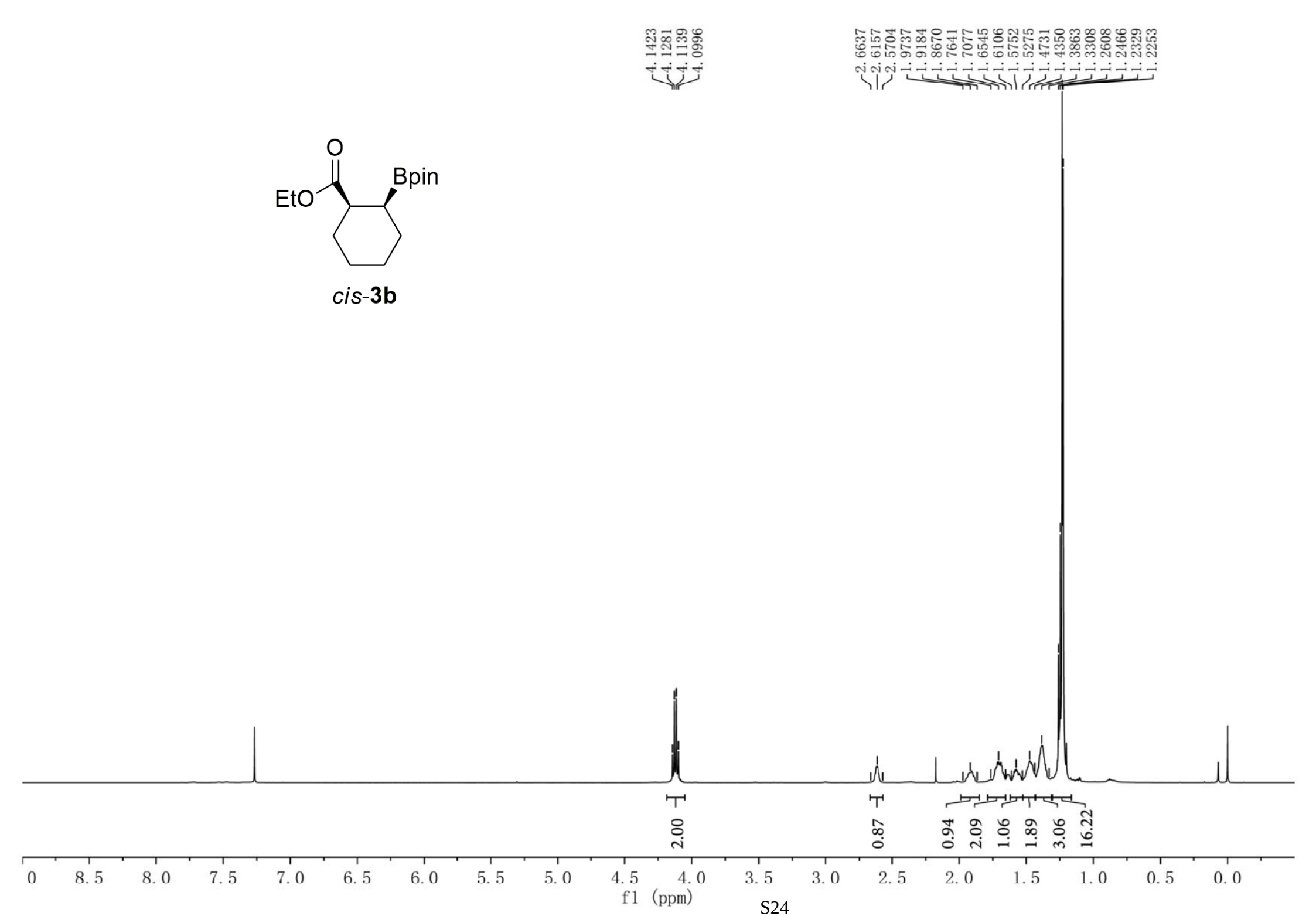
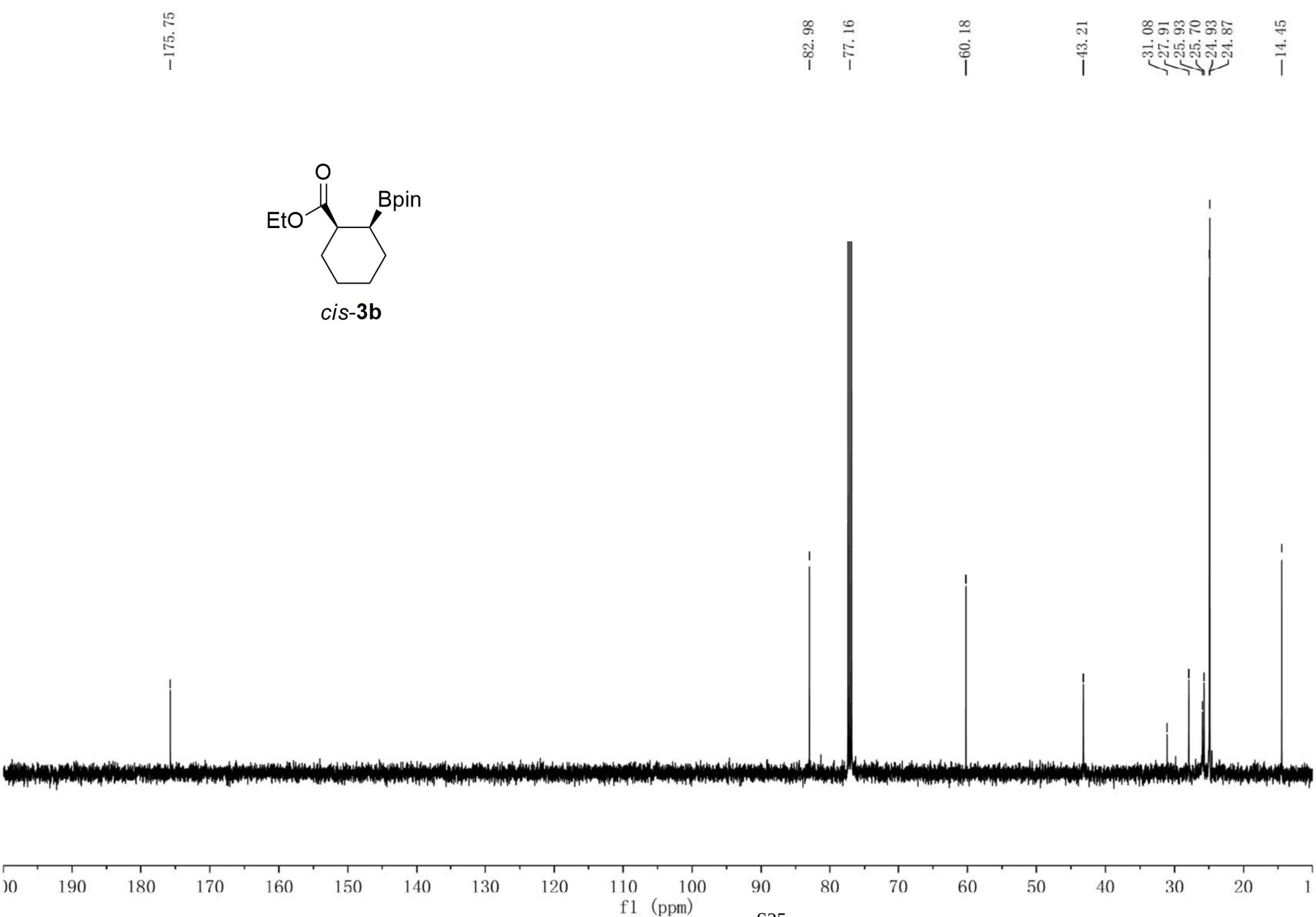
1.54
1.53
1.49
1.42
1.40
1.38
1.37
1.37
1.35
1.26
1.25
1.25
1.23
O
EtO
Bpin
2.00
0.99
1.01
4.08
1.44
1.18
16.09
f1 (ppm)

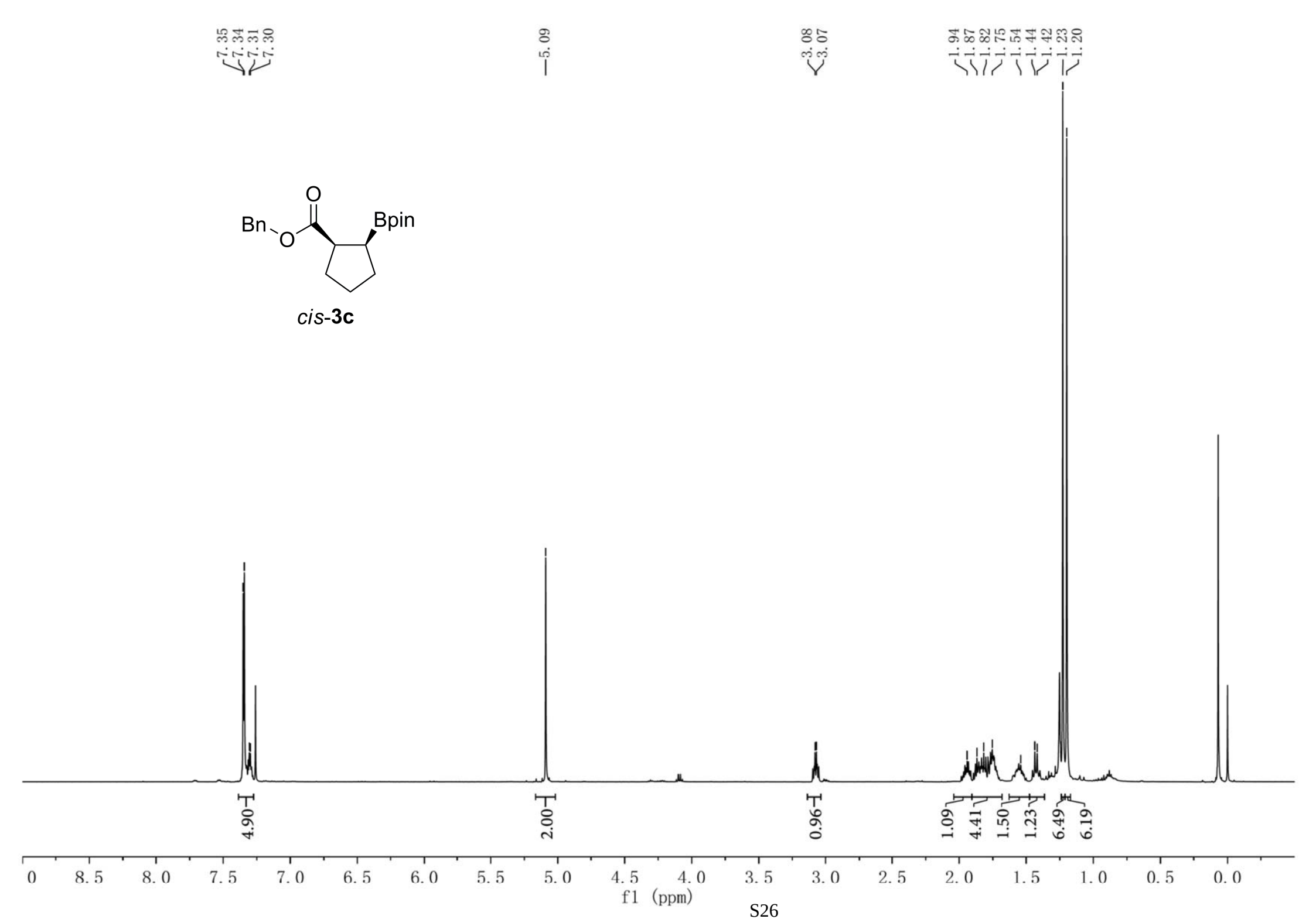
cis-**3a**

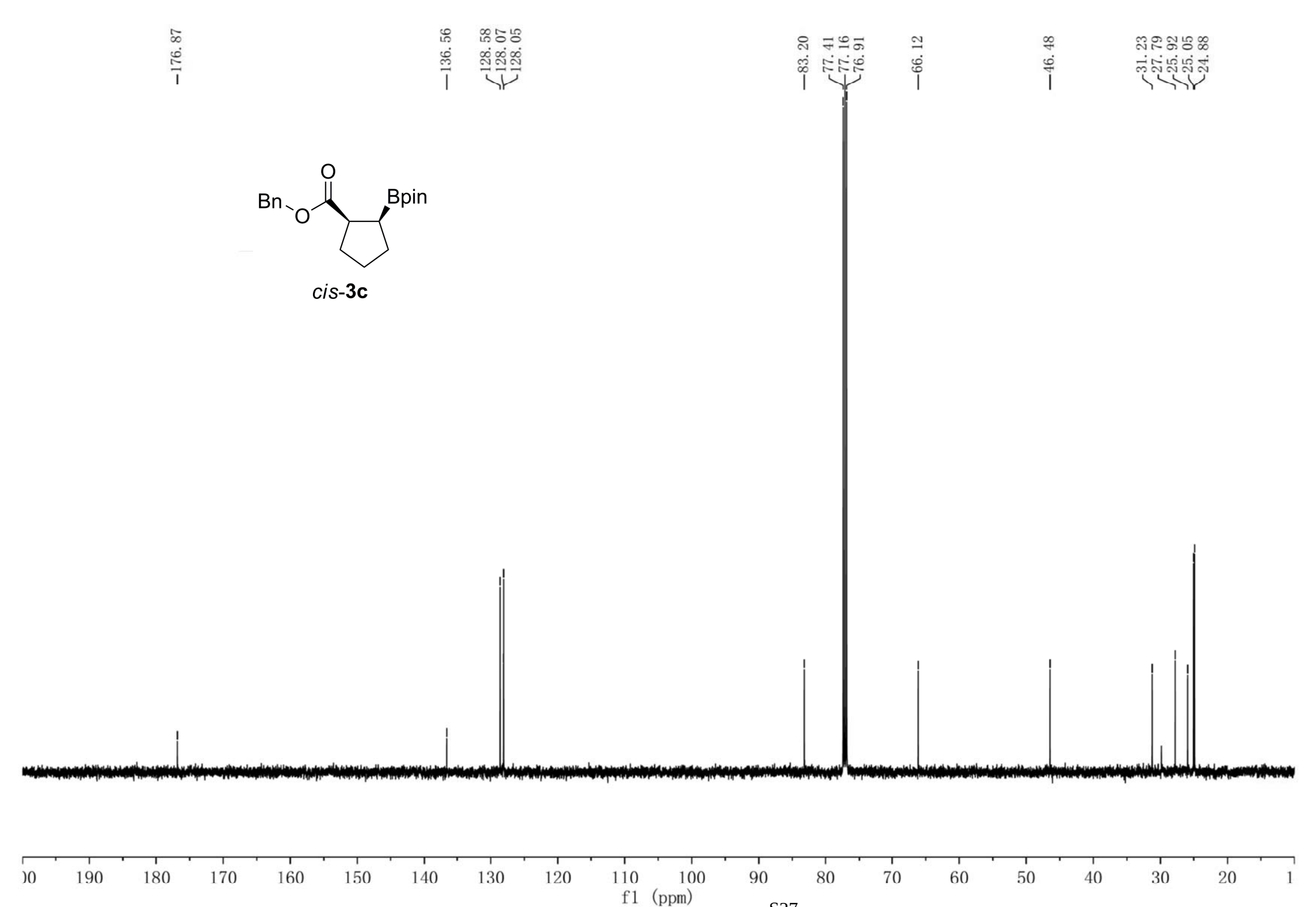

177.11
83.13
77.41
77.16
76.91
60.32
46.45
31.27
27.78
25.94
25.06
24.89
14.41
O
EtO
Bpin
cis-3a
f1 (ppm)

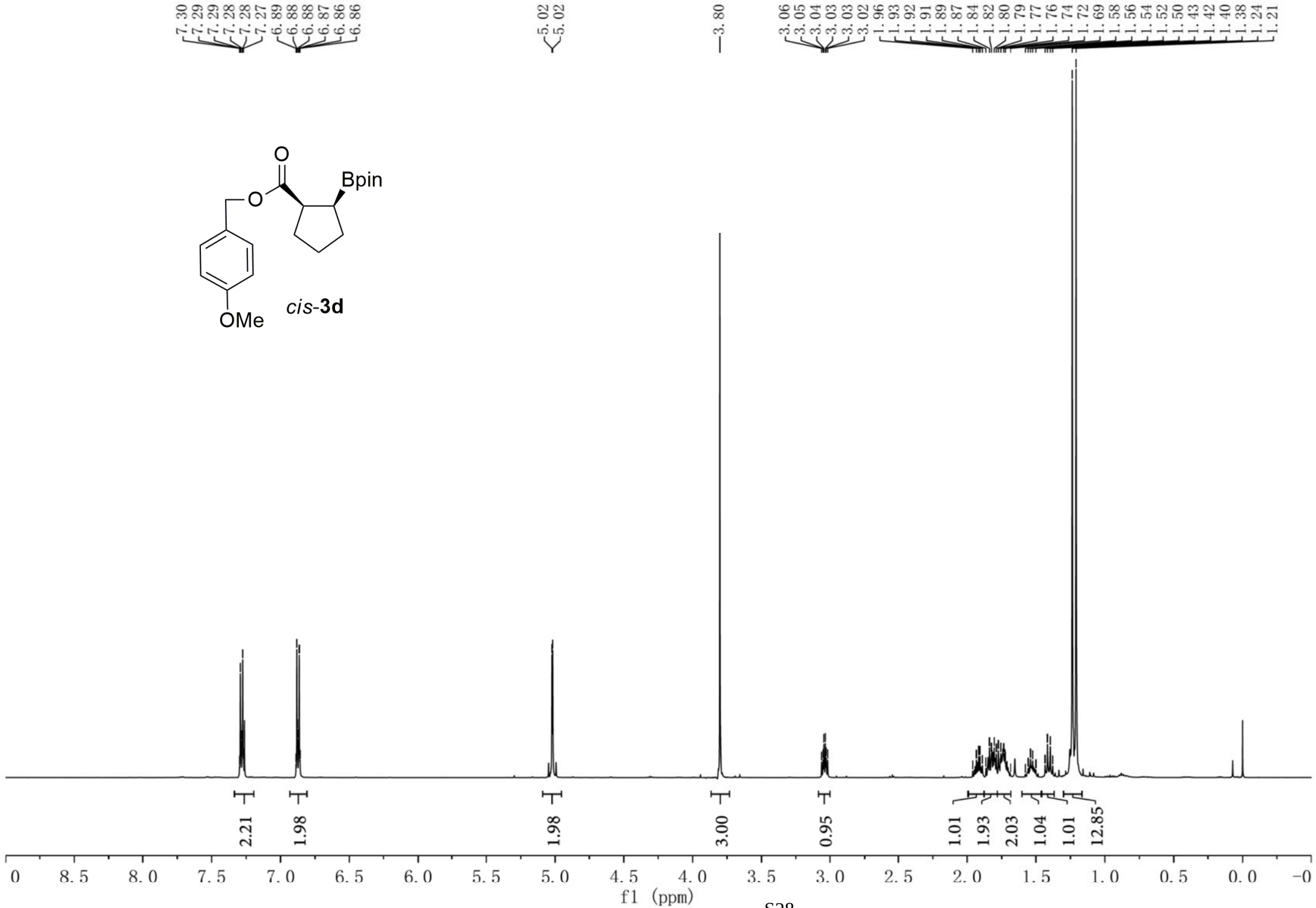

4.1423
4.1281
4.1139
4.0996
2.6637
2.6157
2.5704
1.9737
1.9184
1.8670
1.7641
1.7077
1.6545
1.6106
1.5752
1.5275
1.4731
1.4350
1.3863
1.3308
1.2608
1.2466
1.2329
1.2253
O
EtO
Bpin
2.00
0.87
0.94
2.09
1.06
1.89
3.06
16.22
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

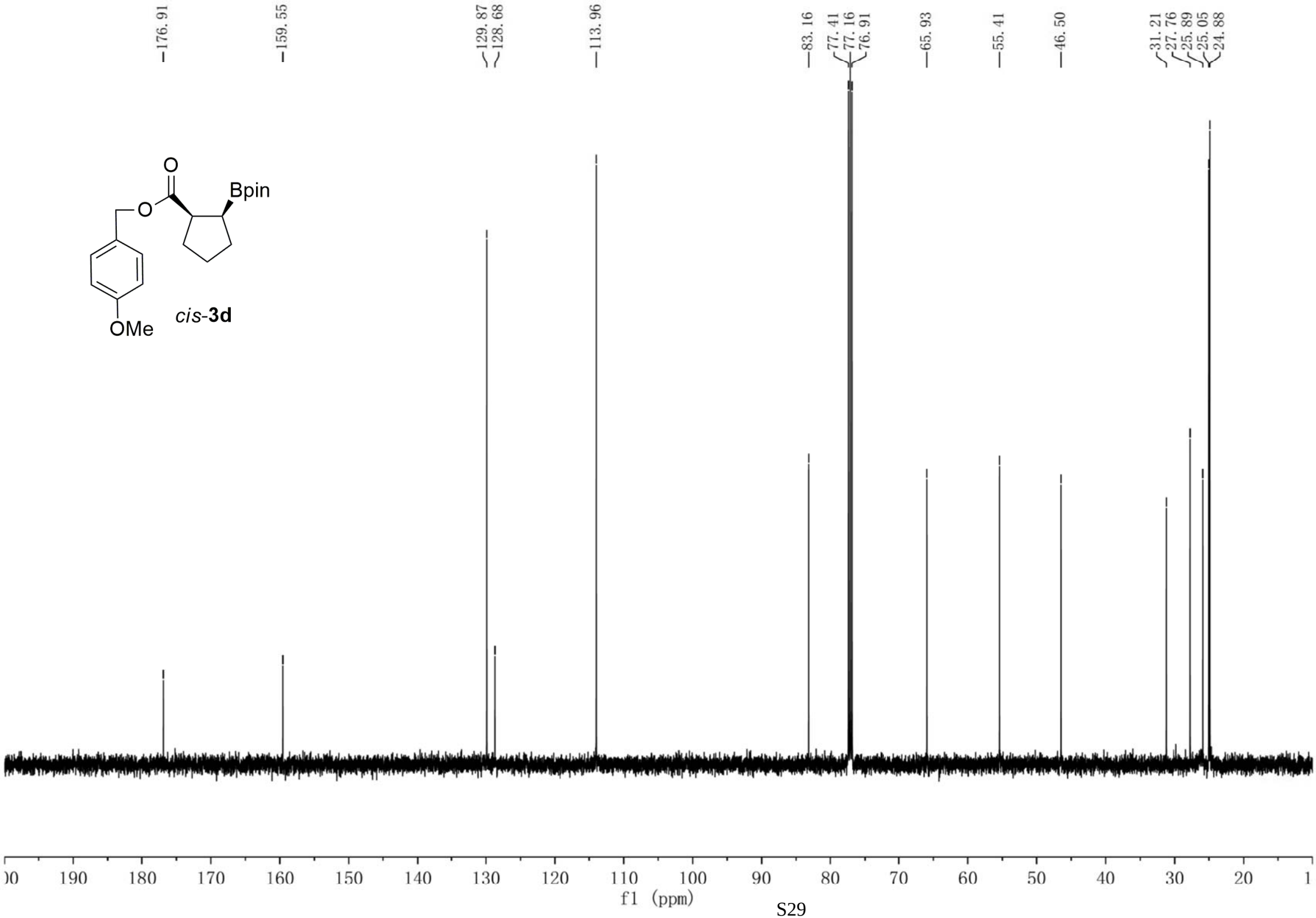
cis-**3b**

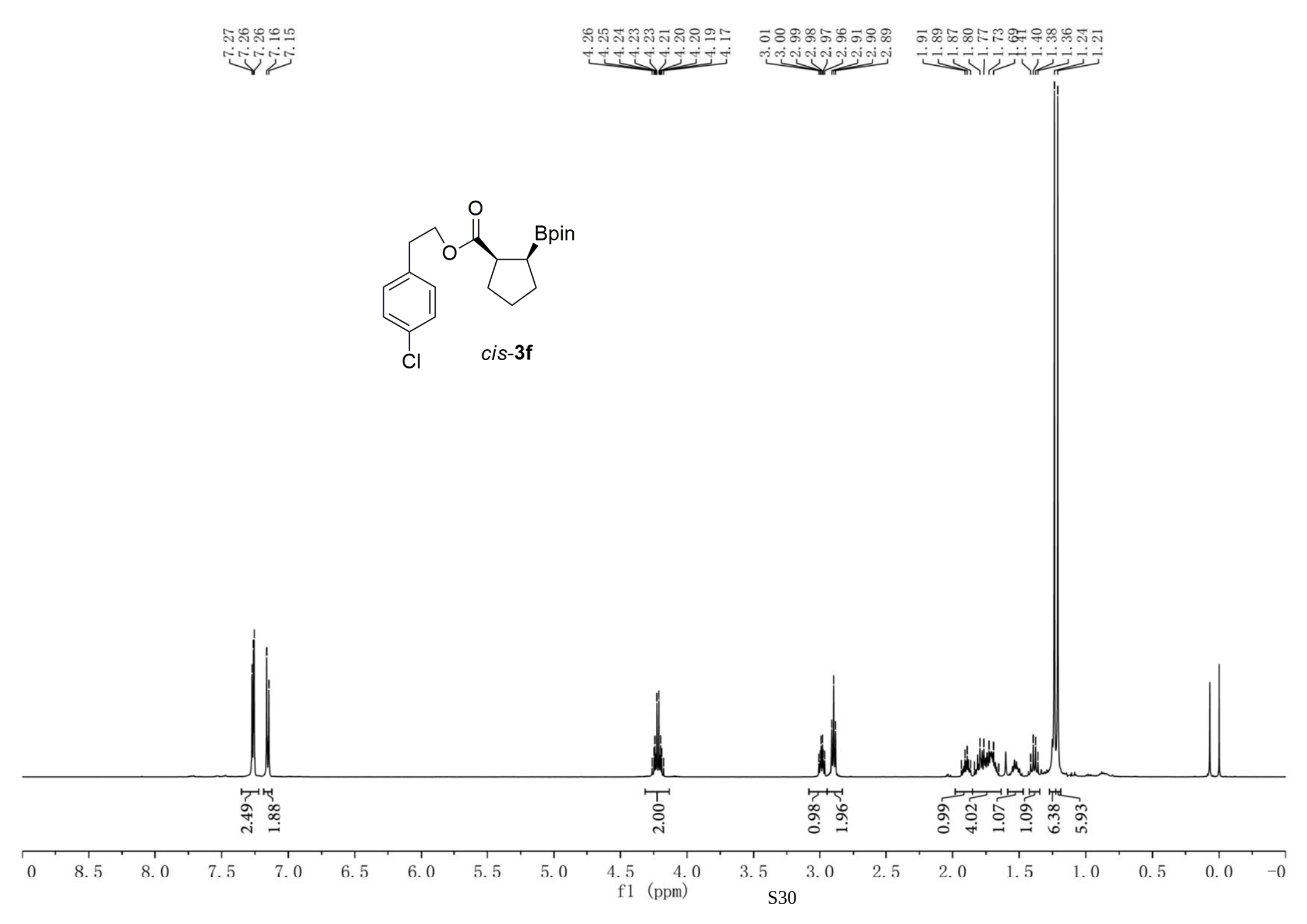

175.75
82.98
77.16
60.18
43.21
31.08
27.91
25.93
25.70
24.93
24.87
14.45
O
EtO
Bpin
cis-3b
f1 (ppm)

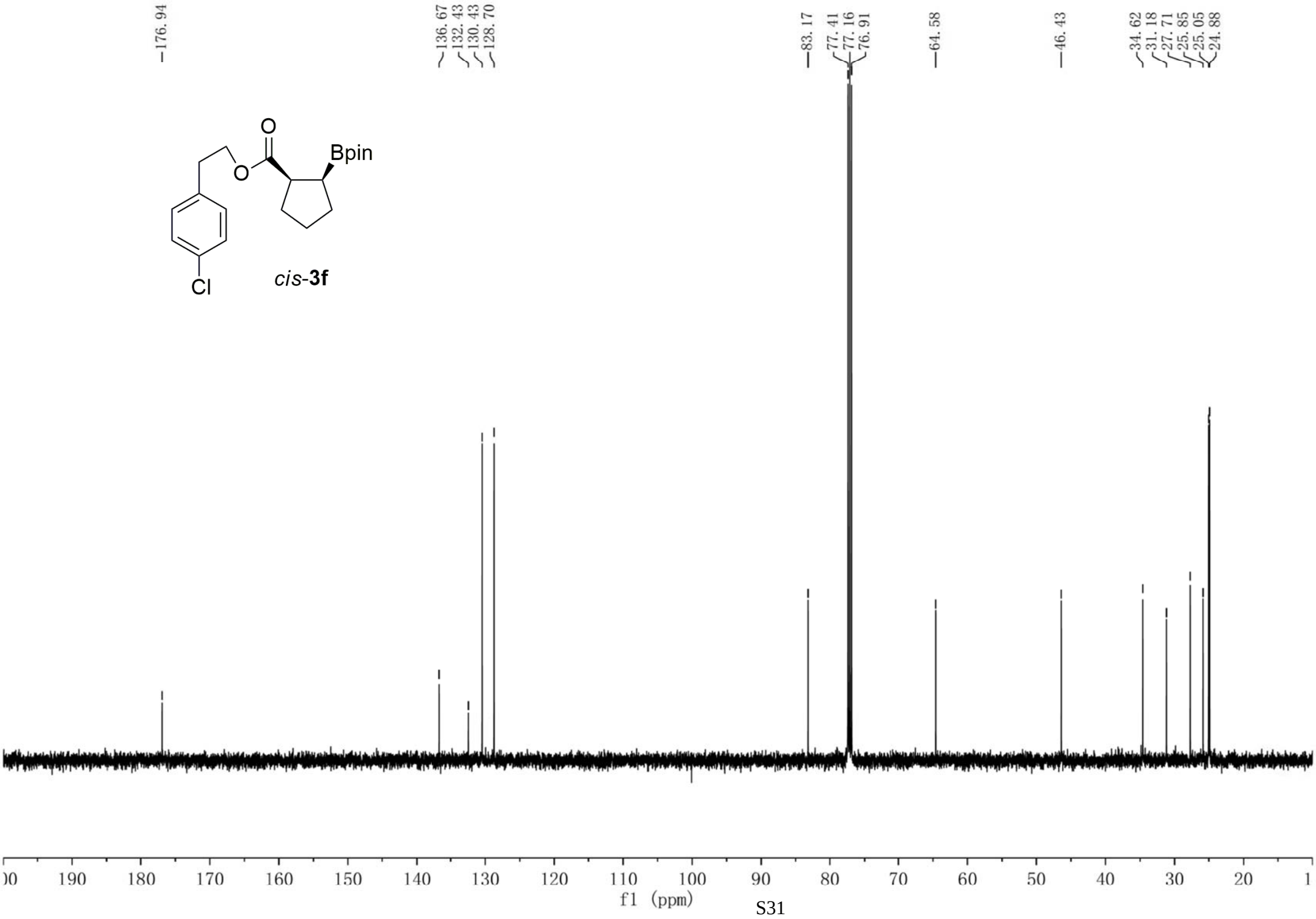

7.35
7.34
7.31
7.30
5.09
3.08
3.07
1.94
1.87
1.82
1.75
1.54
1.44
1.42
1.23
1.20
O
Bn
O
Bpin
cis-3c
4.90
2.00
0.96
1.09
4.41
1.50
1.23
6.49
6.19
f1 (ppm)

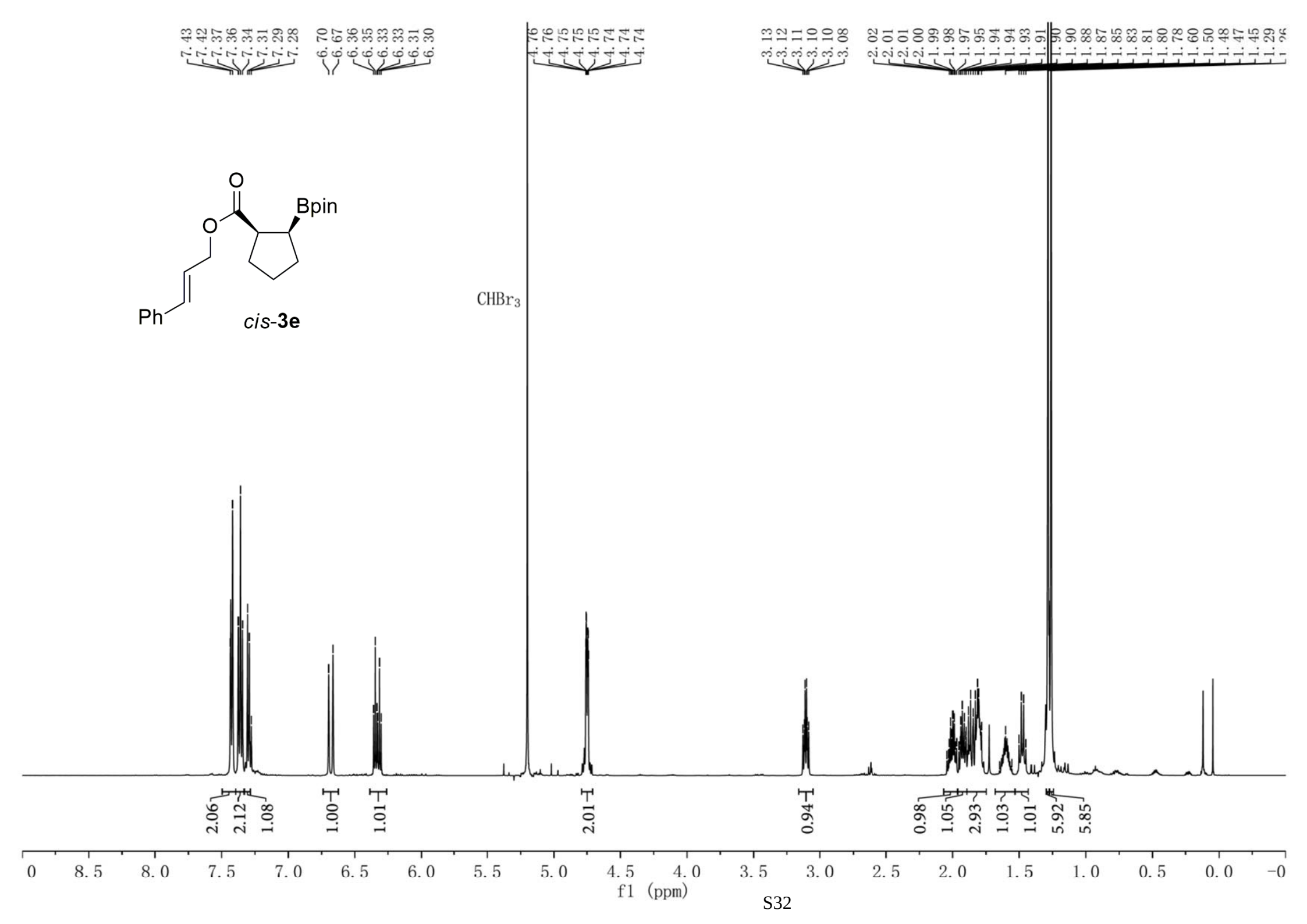

176.87
136.56
128.58
128.07
128.05
83.20
77.41
77.16
76.91
66.12
46.48
31.23
27.79
25.92
25.05
24.88
O
Bn
O
Bpin
cis-3c
f1 (ppm)

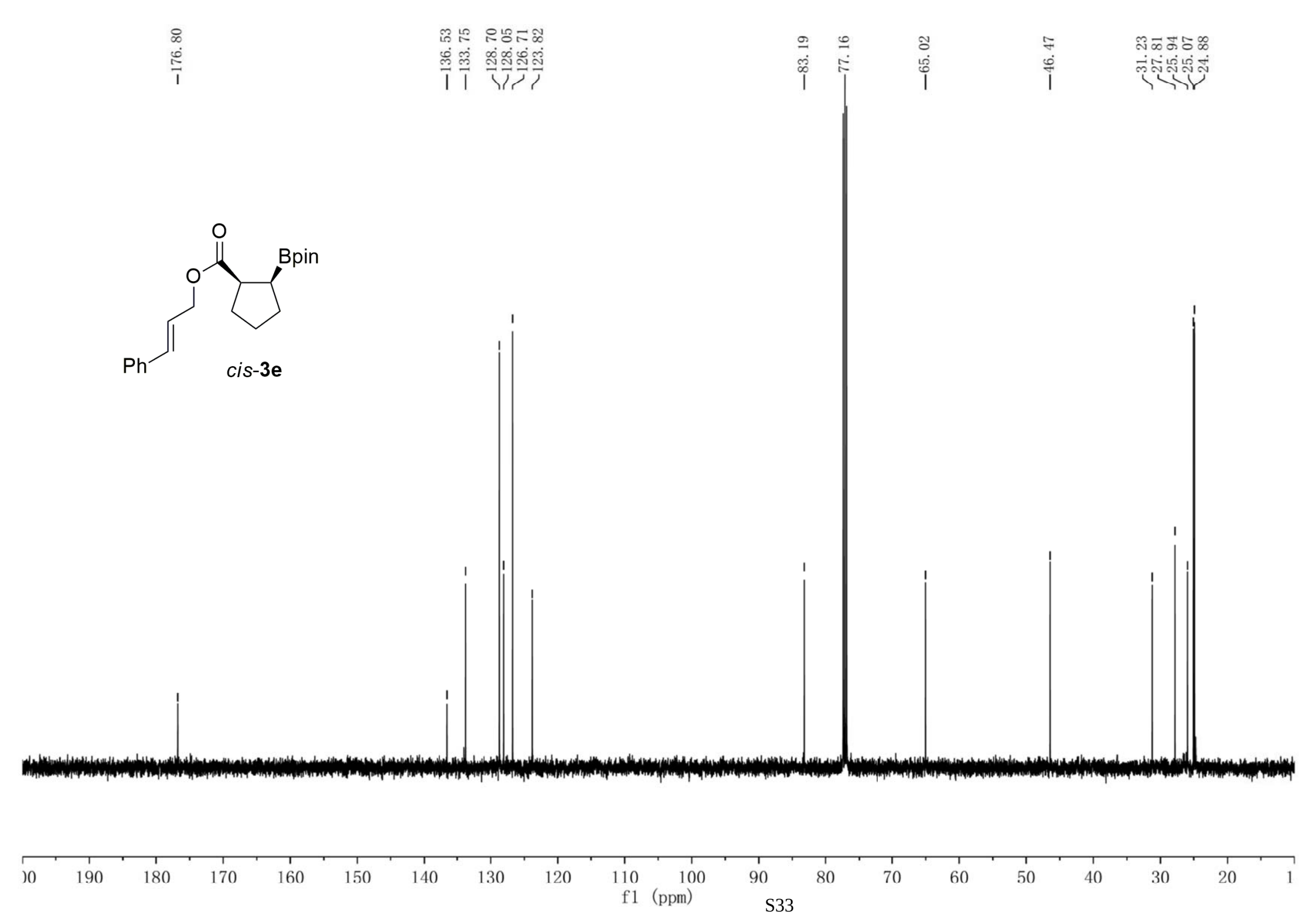

7.30
7.29
7.29
7.28
7.28
7.27
6.89
6.88
6.88
6.87
6.86
6.86
5.02
5.02
3.80
3.06
3.05
3.04
3.03
3.03
3.02
1.96
1.93
1.92
1.91
1.89
1.87
1.84
1.82
1.80
1.79
1.77
1.76
1.74
1.72
1.69
1.58
1.56
1.54
1.52
1.50
1.43
1.42
1.40
1.38
1.24
1.21
O
O
Bpin
OMe
cis-3d
2.21
1.98
1.98
3.00
0.95
1.01
1.93
2.03
1.04
1.01
12.85
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

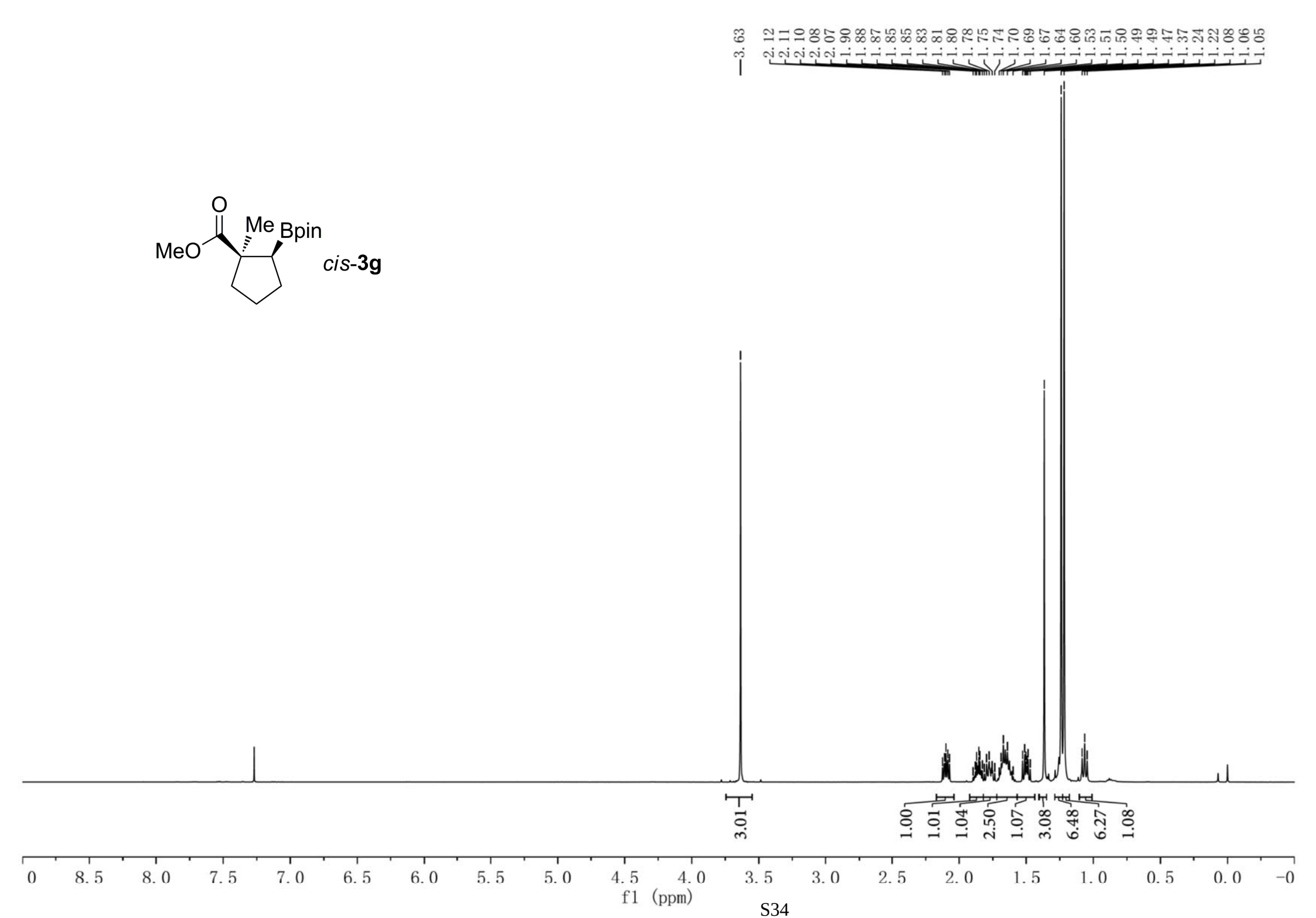

176.91
159.55
129.87
128.68
113.96
83.16
77.41
77.16
76.91
65.93
55.41
46.50
31.21
27.76
25.89
25.05
24.88
O
O
Bpin
OMe
cis-3d
f1 (ppm)

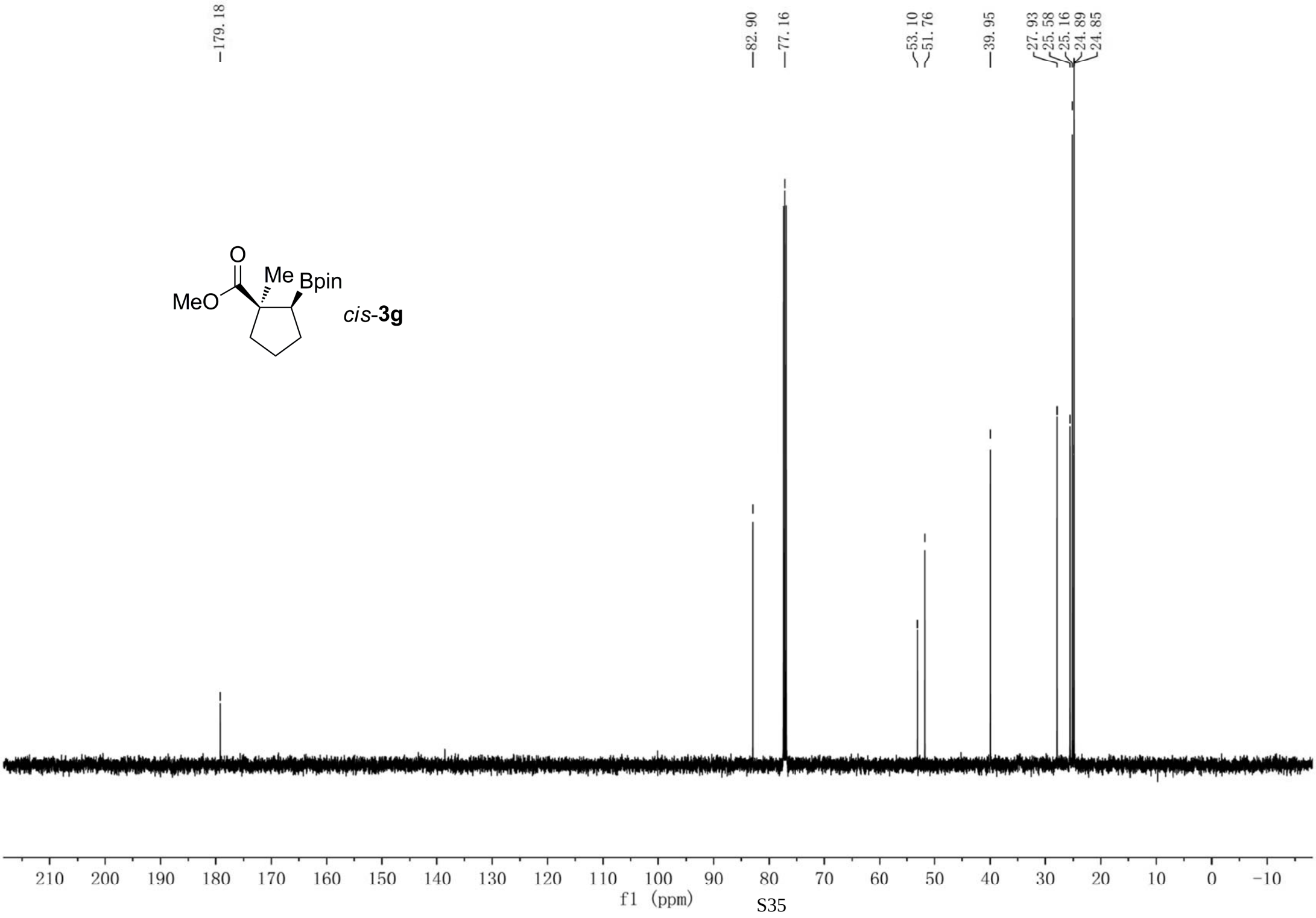

7.27
7.26
7.26
7.16
7.15
4.26
4.25
4.24
4.23
4.23
4.21
4.20
4.20
4.19
4.17
3.01
3.00
2.99
2.98
2.97
2.96
2.91
2.90
2.89
1.91
1.89
1.87
1.80
1.77
1.73
1.69
1.41
1.40
1.38
1.36
1.24
1.21
O
O
Bpin
Cl
cis-3f
2.49
1.88
2.00
0.98
1.96
0.99
4.02
1.07
1.09
6.38
5.93
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

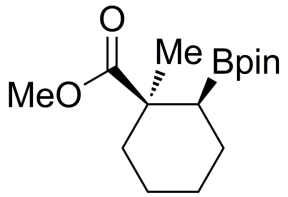

176.94
136.67
132.43
130.43
128.70
83.17
77.41
77.16
76.91
64.58
46.43
34.62
31.18
27.71
25.85
25.05
24.88
O
O
Bpin
Cl
cis-3f
f1 (ppm)


Bpin
Ph
cis-3e
CHBr3
f1 (ppm)

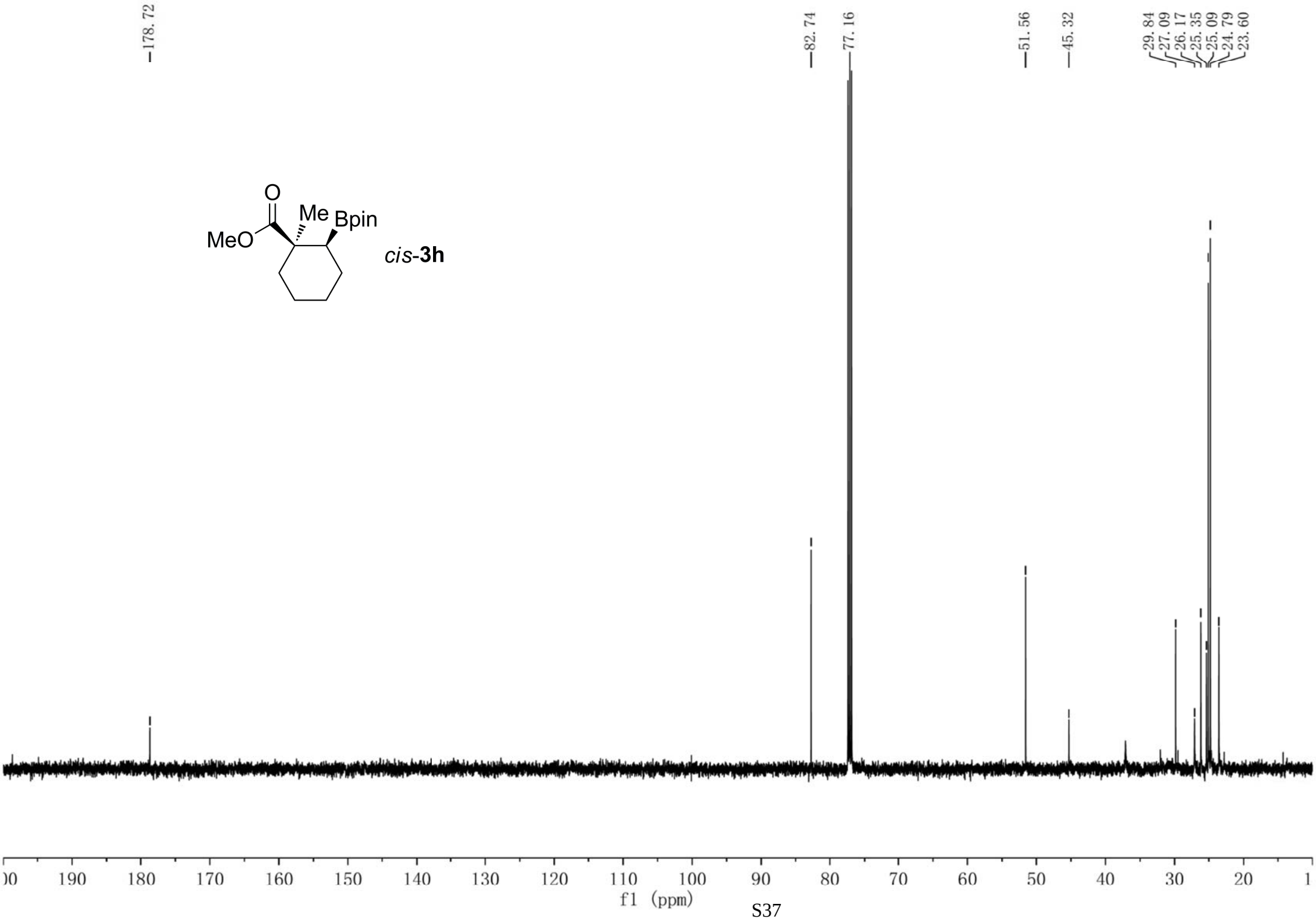

176.80
136.53
133.75
128.70
128.05
126.71
123.82
83.19
77.16
65.02
46.47
31.23
27.81
25.94
25.07
24.88
O
O
Bpin
Ph
cis-3e
f1 (ppm)

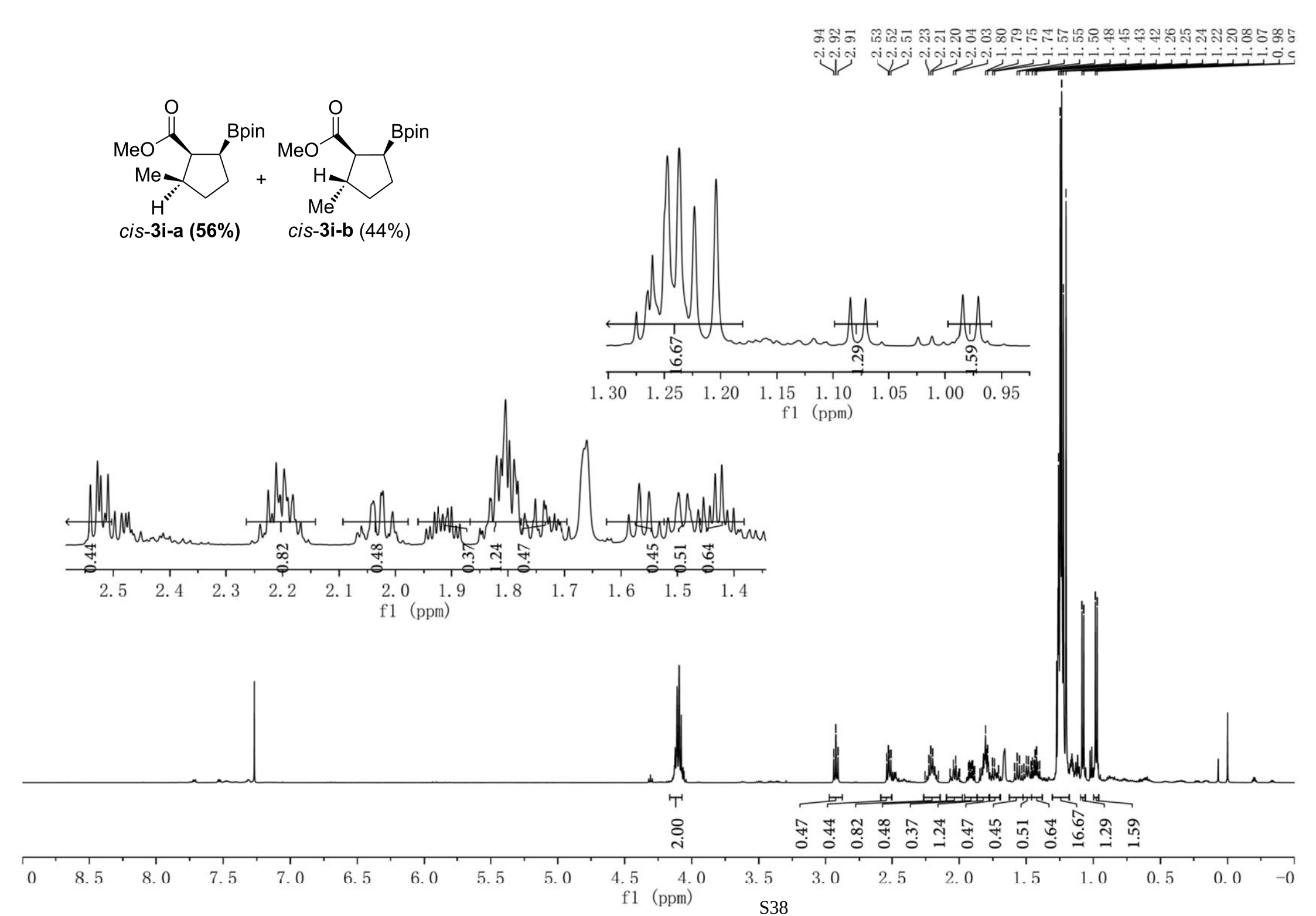

O
Me
Bpin
MeO
cis-3g
3.63
2.12
2.11
2.10
2.08
2.07
1.90
1.88
1.87
1.85
1.85
1.83
1.81
1.80
1.78
1.75
1.74
1.70
1.69
1.67
1.64
1.60
1.53
1.51
1.50
1.49
1.49
1.47
1.37
1.24
1.22
1.08
1.06
1.05
3.01
1.00
1.01
1.04
2.50
1.07
3.08
6.48
6.27
1.08
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

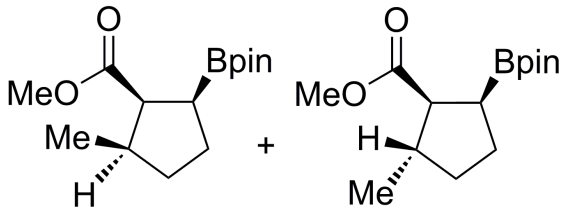

179.18
82.90
77.16
53.10
51.76
39.95
27.93
25.58
25.16
24.89
24.85
O
Me
Bpin
MeO
cis-3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



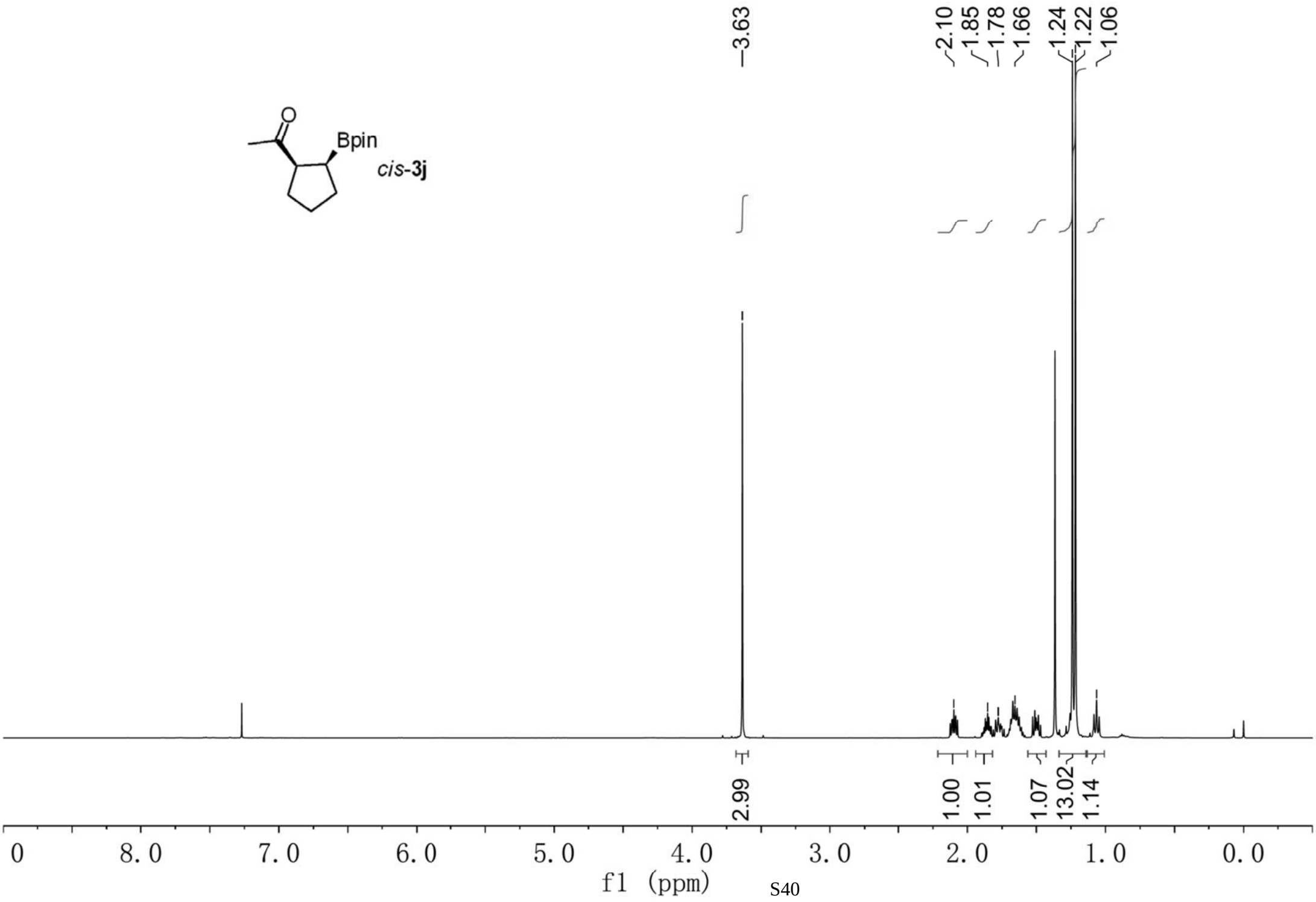
cis-**3h**

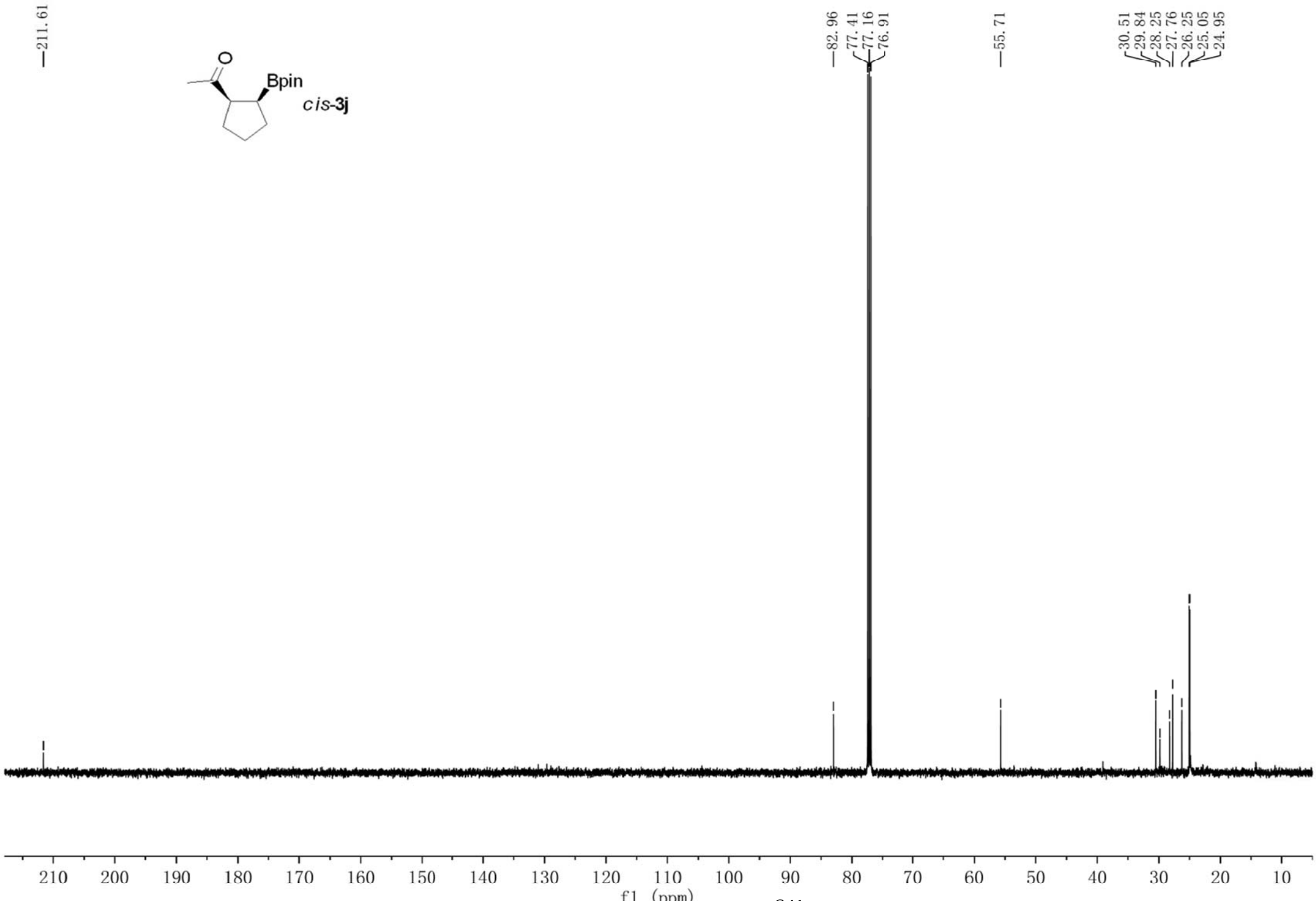

178.72
82.74
77.16
51.56
45.32
29.84
27.09
26.17
25.35
25.09
24.79
23.60
O
Me
Bpin
MeO
cis-3h
f1 (ppm)

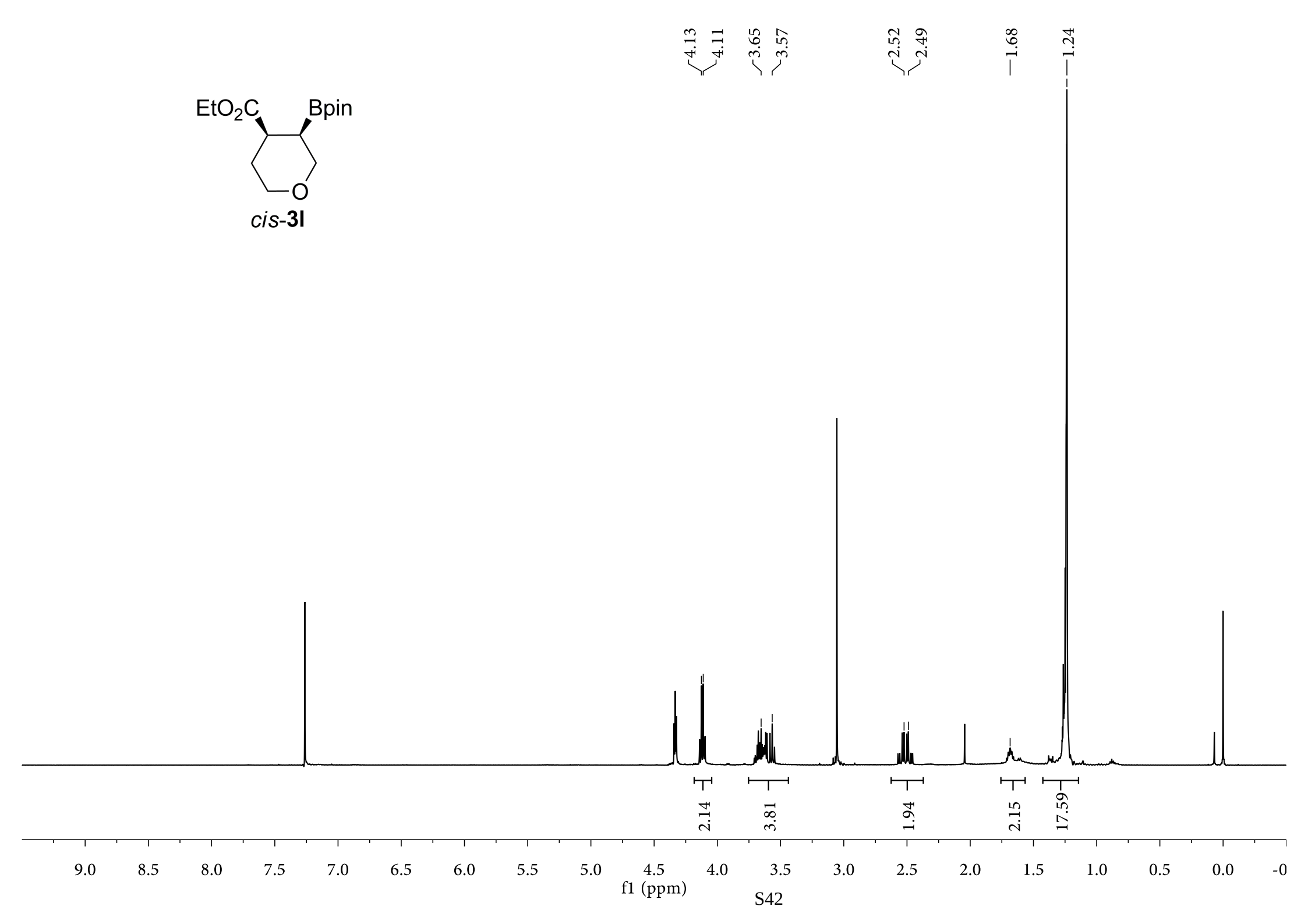

MeO
Bpin
Me
H
+
MeO
Bpin
H
Me
cis-3i-a (56%)
cis-3i-b (44%)
f1 (ppm)

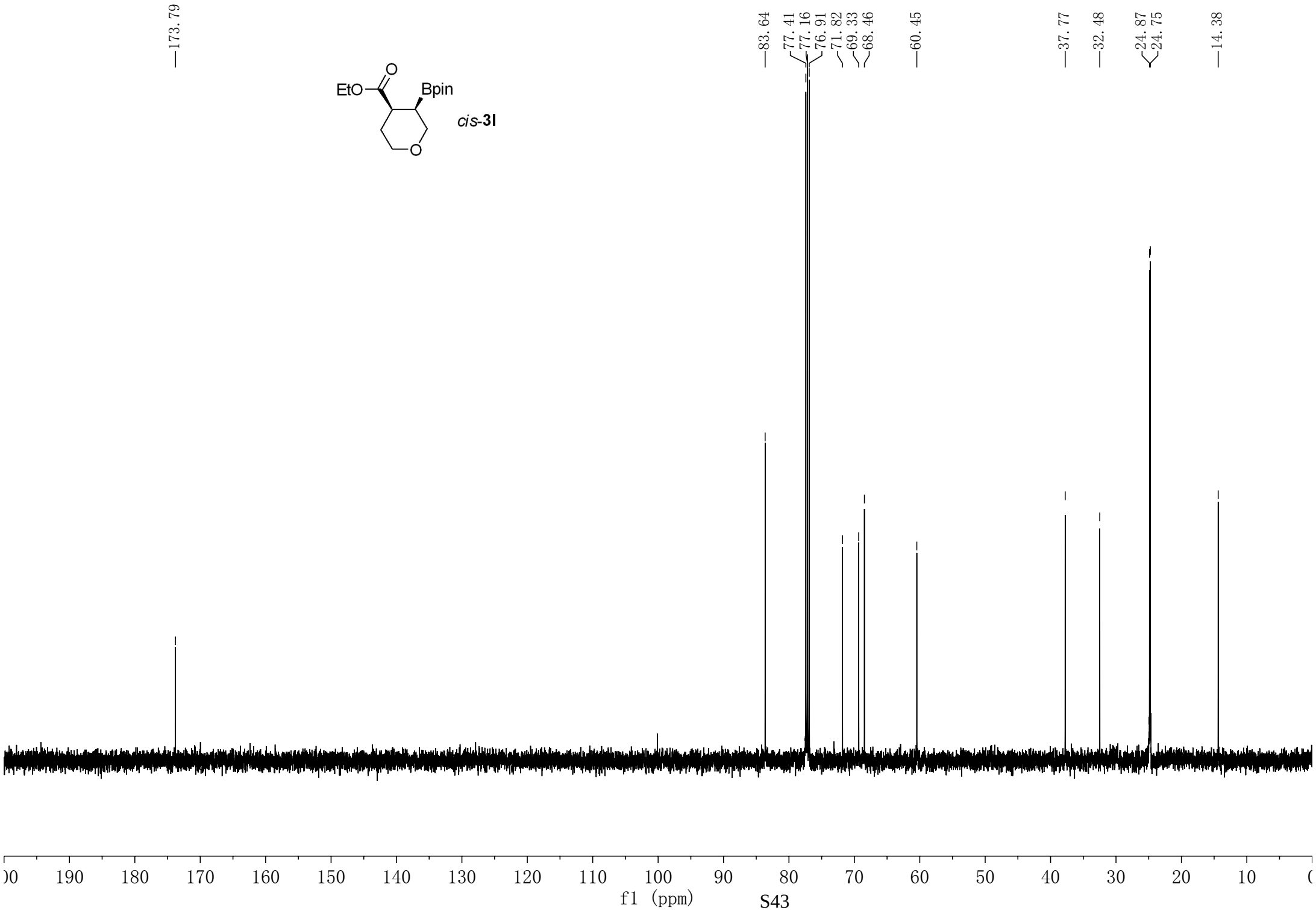


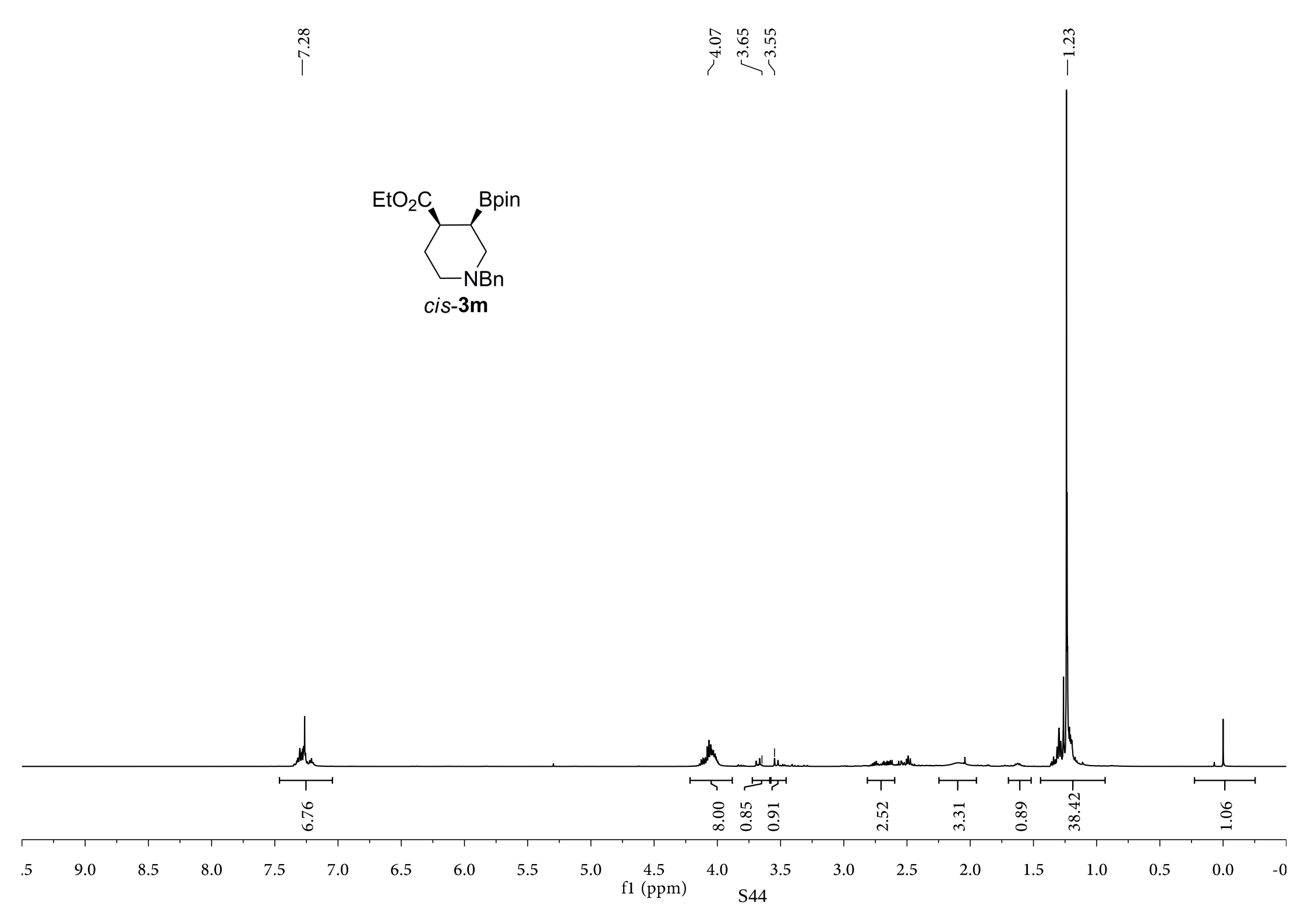
cis-**3i-a (56%)** *cis*-**3i-b** (44%)

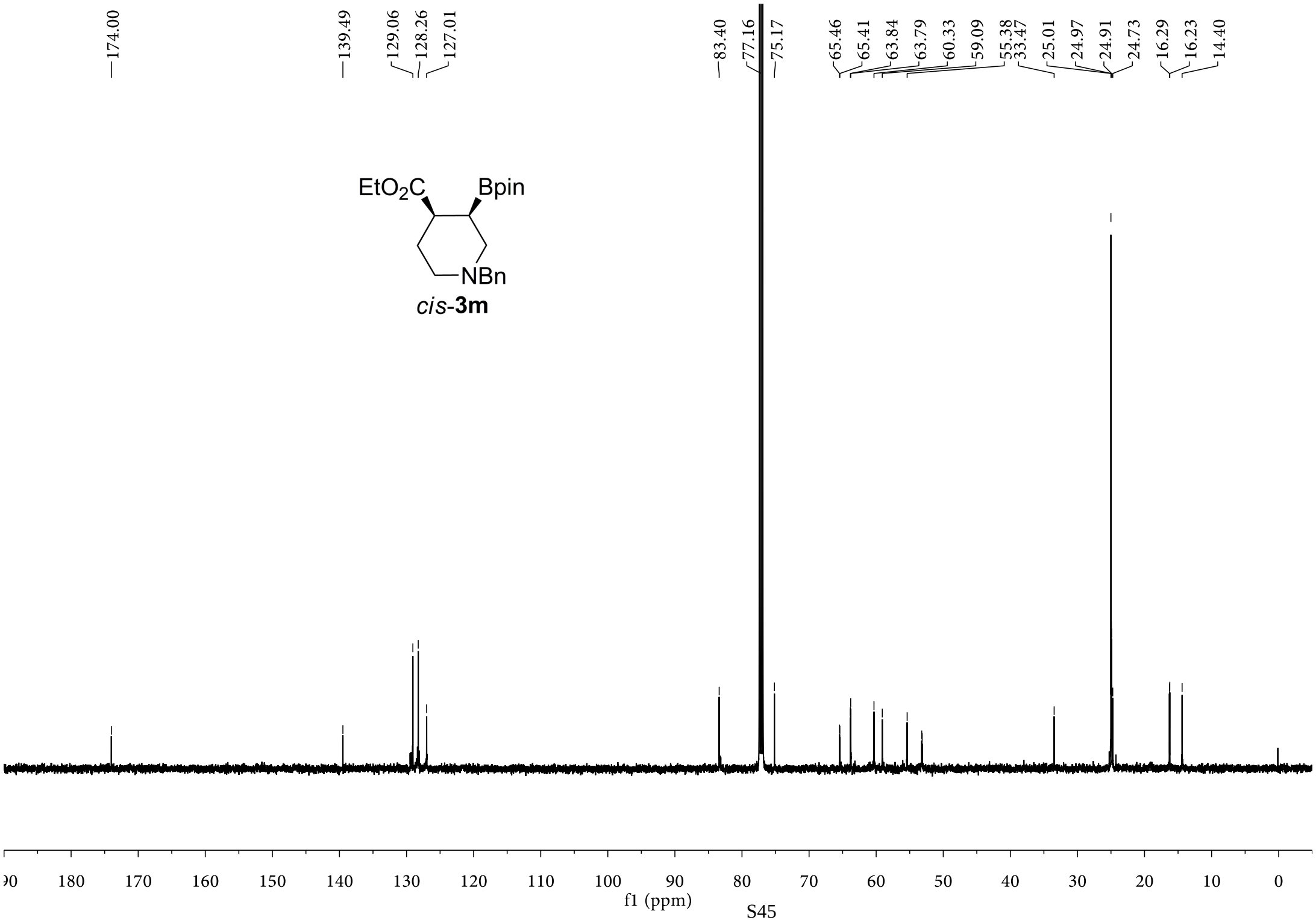

Bpin
cis-3j
3.63
2.10
1.85
1.78
1.66
1.24
1.22
1.06
2.99
1.00
1.01
1.07
13.02
1.14
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

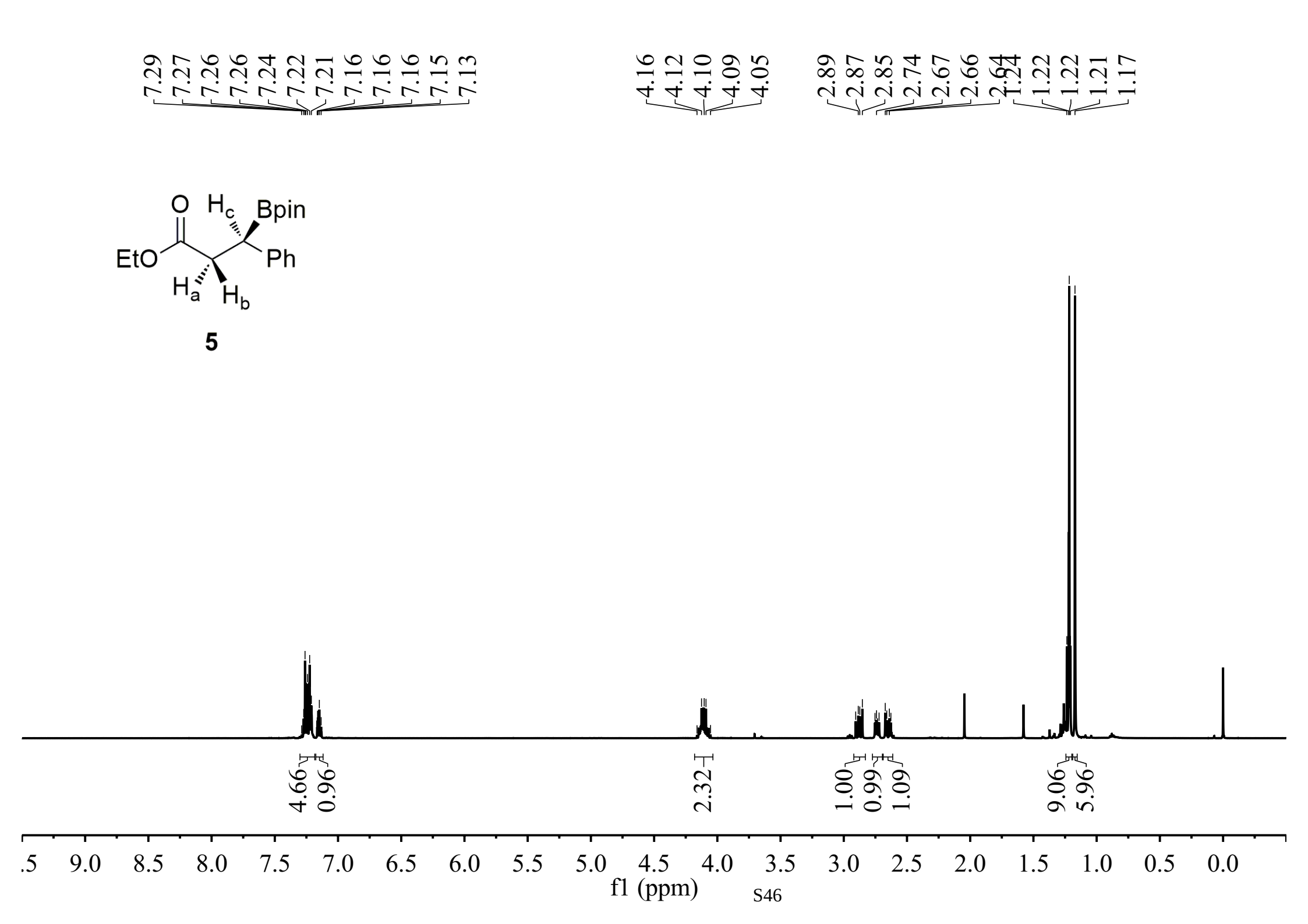

211.61
82.96
77.41
77.16
76.91
55.71
30.51
29.84
28.25
27.76
26.25
25.05
24.95
O
Bpin
cis-3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

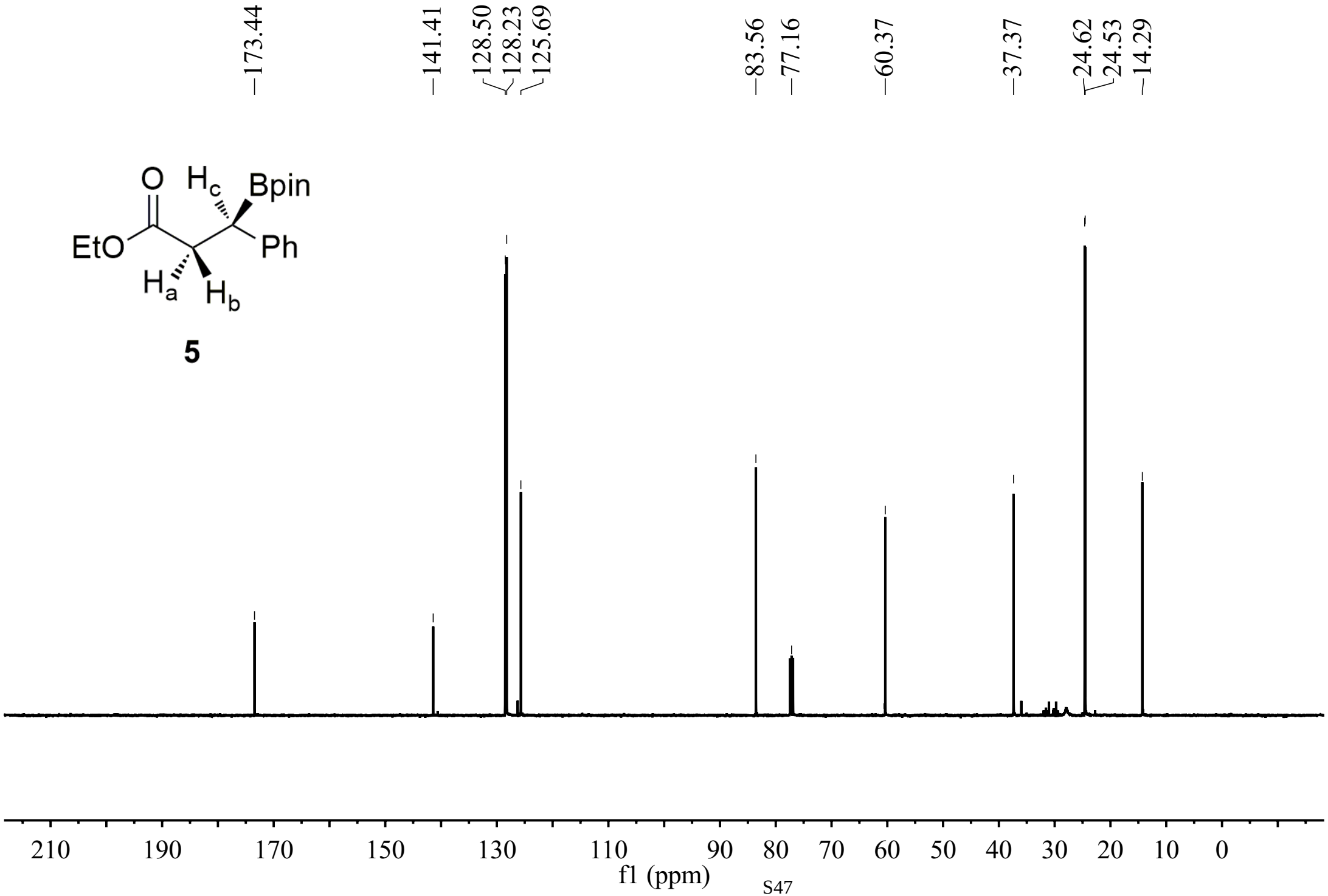

EtO2C
Bpin
O
cis-3l
4.13
4.11
3.65
3.57
2.52
2.49
1.68
1.24
2.14
3.81
1.94
2.15
17.59
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

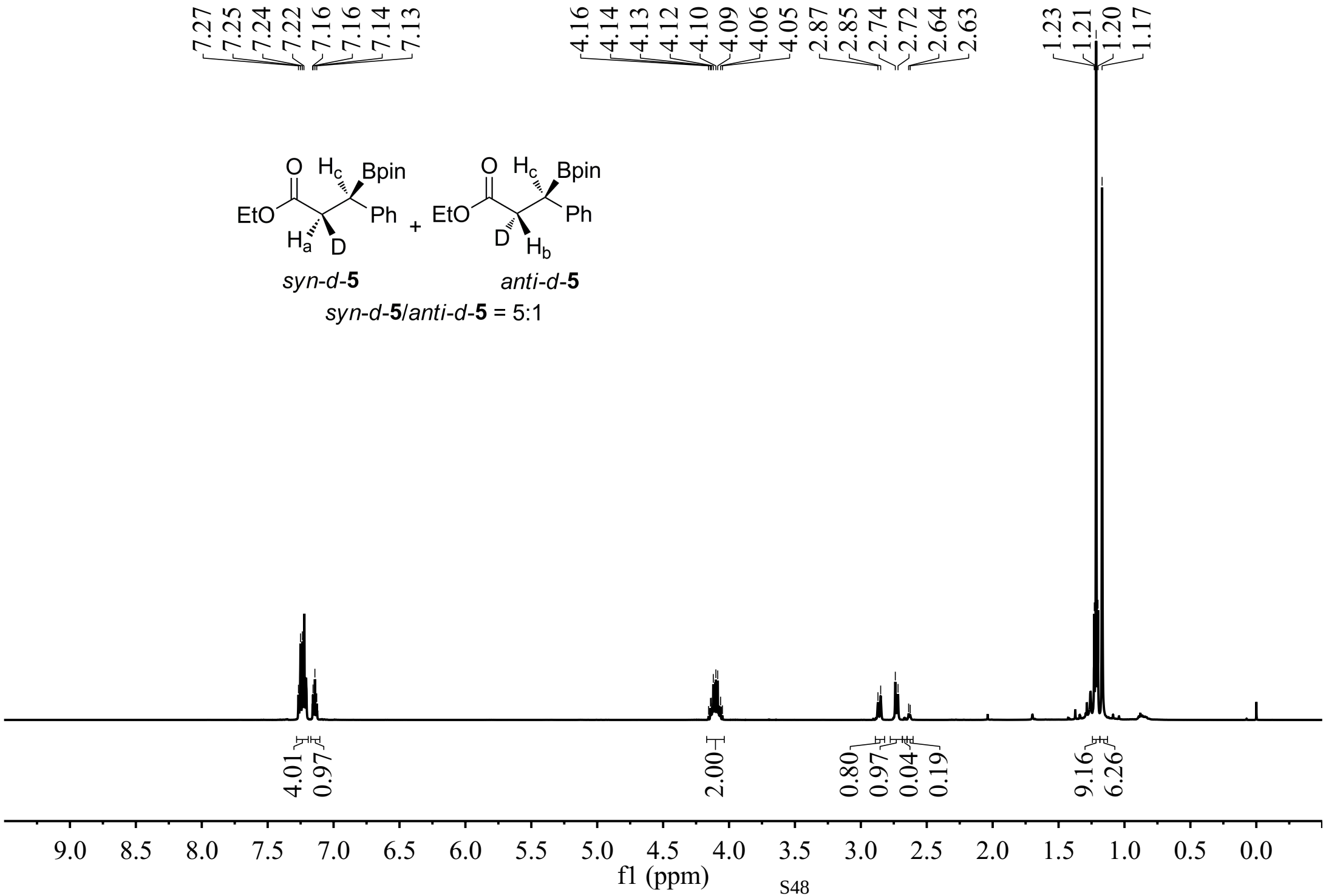

173.79
83.64
77.41
77.16
76.91
71.82
69.33
68.46
60.45
37.77
32.48
24.87
24.75
14.38
EtO
O
Bpin
O
cis-3l
f1 (ppm)

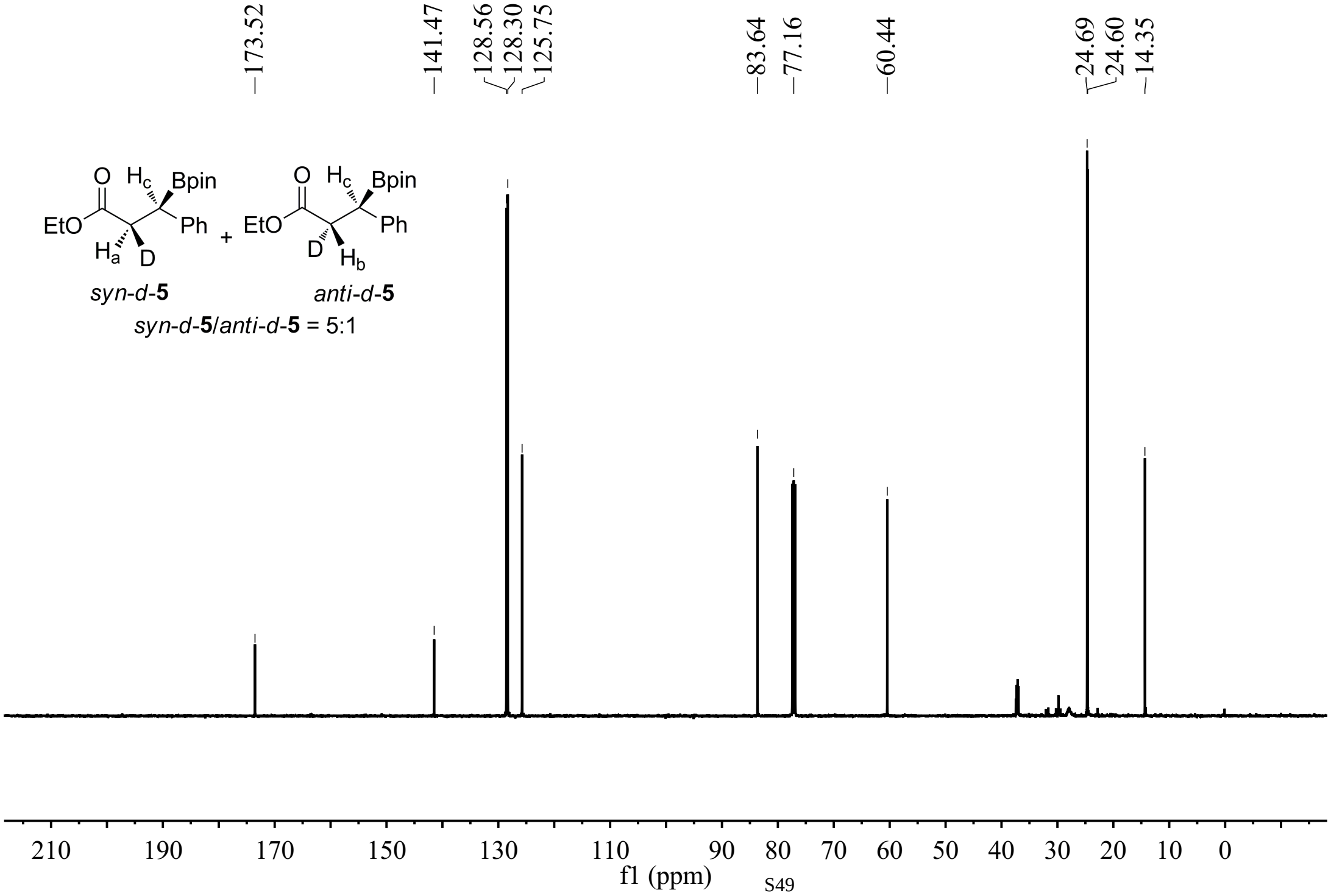

7.28
4.07
3.65
3.55
1.23
EtO2C
Bpin
NBn
cis-3m
6.76
8.00
0.85
0.91
2.52
3.31
0.89
38.42
1.06
f1 (ppm)

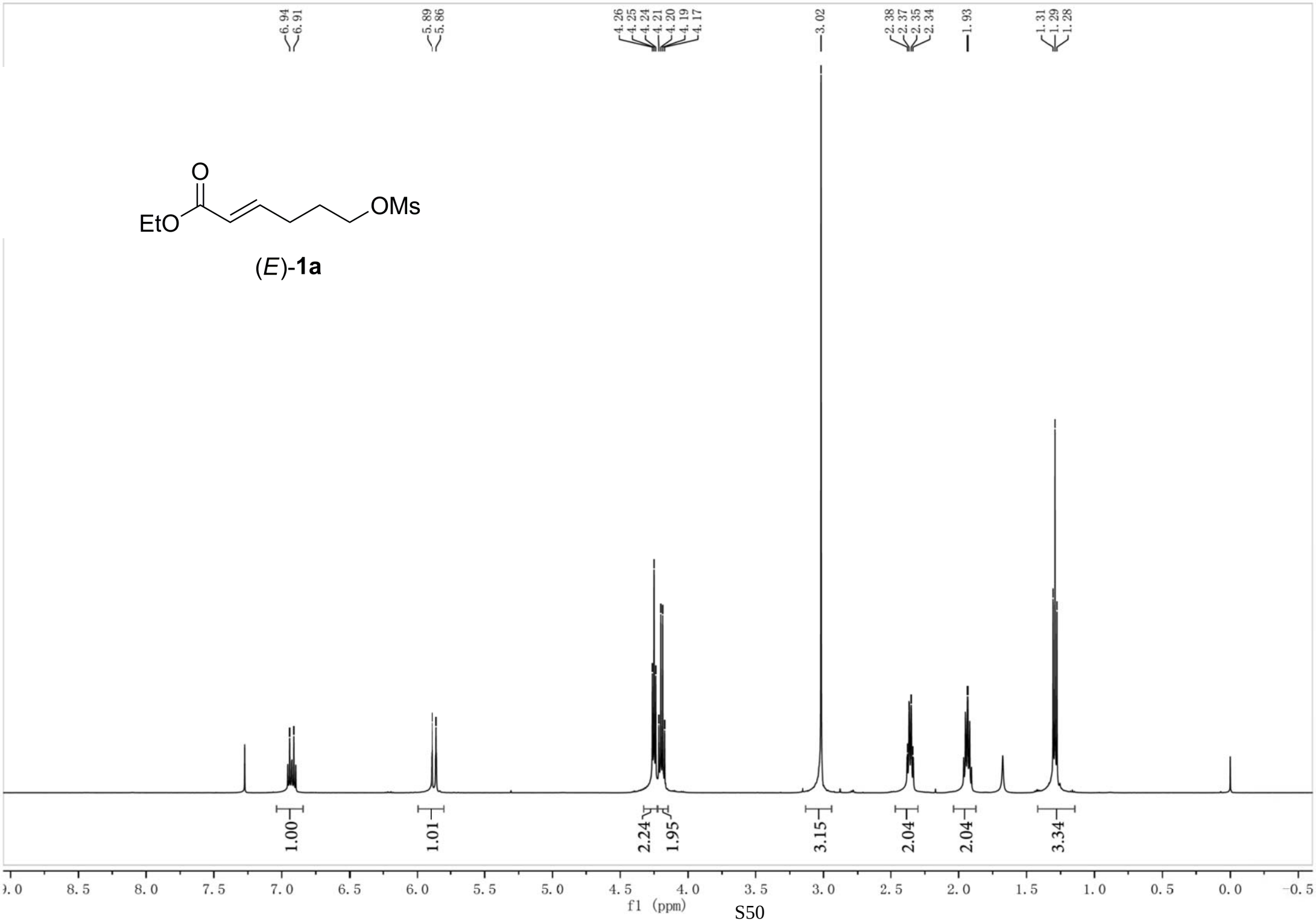

174.00
139.49
129.06
128.26
127.01
83.40
77.16
75.17
65.46
65.41
63.84
63.79
60.33
59.09
55.38
33.47
25.01
24.97
24.91
24.73
16.29
16.23
14.40
EtO2C
Bpin
NBn
cis-3m
f1 (ppm)

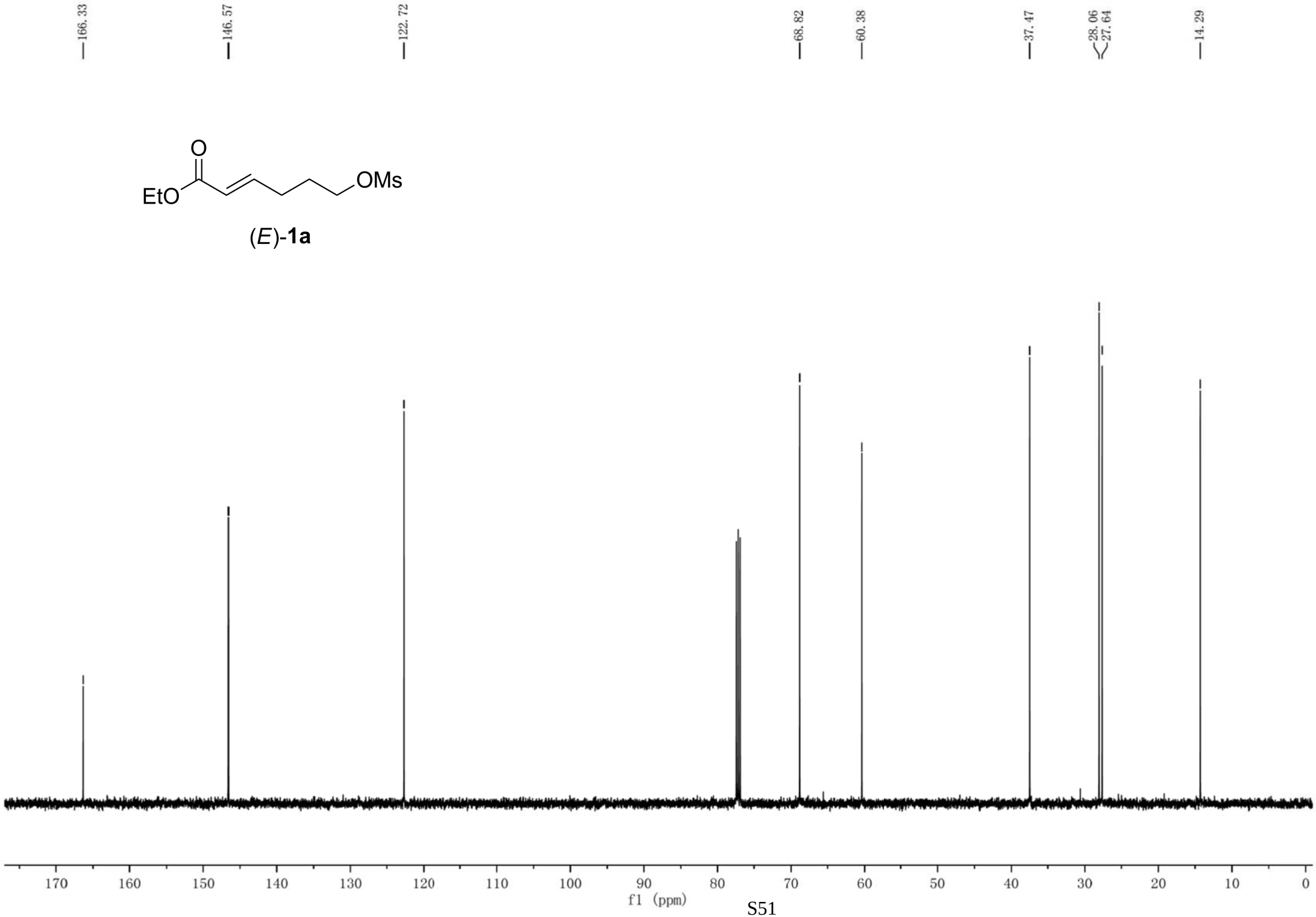

7.29
7.27
7.26
7.26
7.24
7.22
7.21
7.16
7.16
7.16
7.15
7.13
4.16
4.12
4.10
4.09
4.05
2.89
2.87
2.85
2.74
2.67
2.66
2.64
1.24
1.22
1.22
1.21
1.17
O
Hc
Bpin
EtO
Ph
Ha
Hb
5
4.66
0.96
2.32
1.00
0.99
1.09
9.06
5.96
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

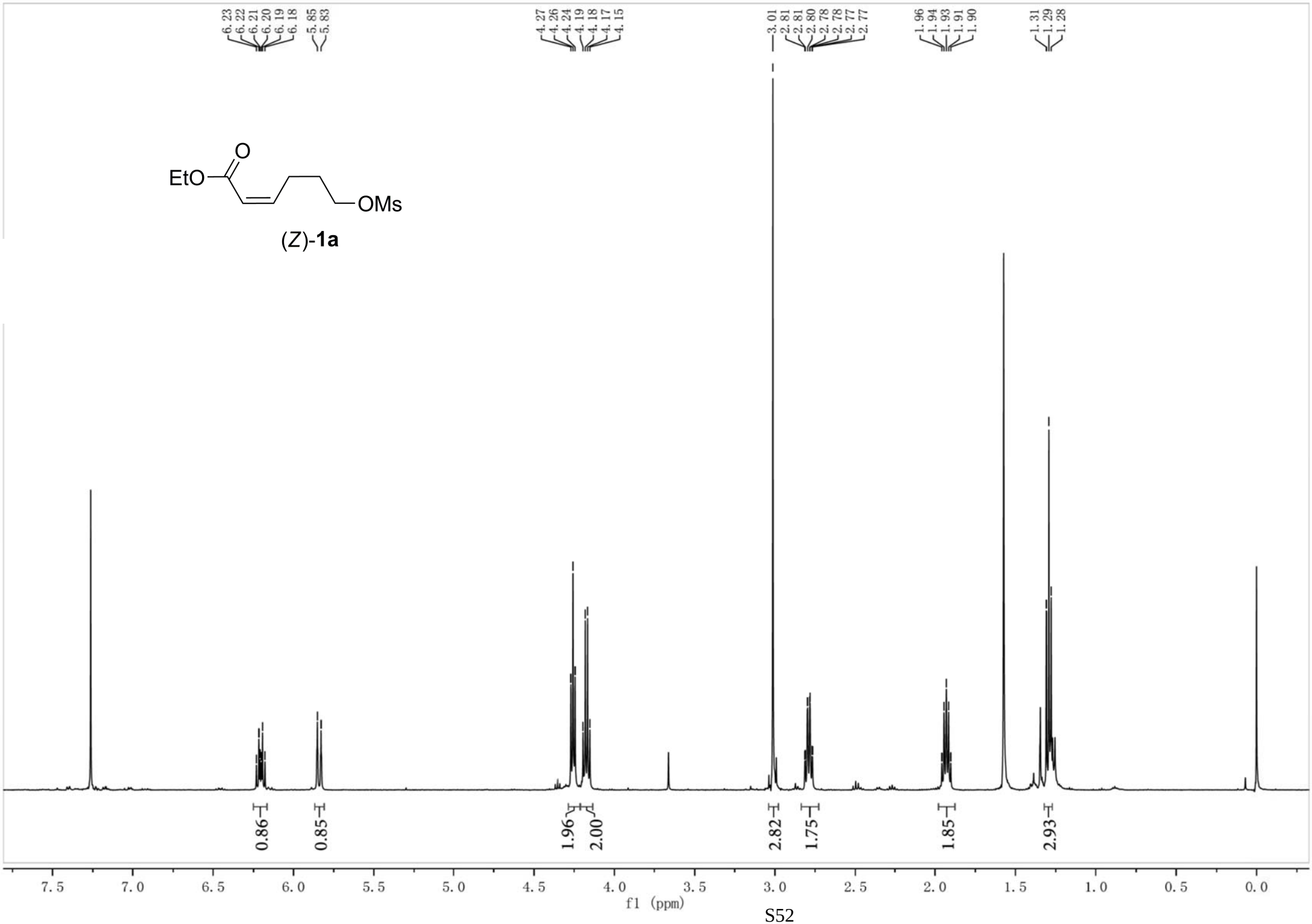

173.44
141.41
128.50
128.23
125.69
83.56
77.16
60.37
37.37
24.62
24.53
14.29
O
H_c
Bpin
EtO
Ph
H_a
H_b
5
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27
7.25
7.24
7.22
7.16
7.16
7.14
7.13
4.16
4.14
4.13
4.12
4.10
4.09
4.06
4.05
2.87
2.85
2.74
2.72
2.64
2.63
1.23
1.21
1.20
1.17
O
Hc
Bpin
EtO
Ph
Ha
D
+
O
Hc
Bpin
EtO
Ph
D
Hb
syn-d-5
anti-d-5
syn-d-5/anti-d-5 = 5:1
4.01
0.97
2.00
0.80
0.97
0.04
0.19
9.16
6.26
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.52
141.47
128.56
128.30
125.75
83.64
77.16
60.44
24.69
24.60
14.35
O
Hc
Bpin
EtO
Ph
Ha
D
+
O
Hc
Bpin
EtO
Ph
D
Hb
syn-d-5
anti-d-5
syn-d-5/anti-d-5 = 5:1
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.94
6.91
5.89
5.86
4.26
4.25
4.24
4.21
4.20
4.19
4.17
3.02
2.38
2.37
2.35
2.34
1.93
1.31
1.29
1.28
O
EtO
OMs
(E)-1a
1.00
1.01
2.24
1.95
3.15
2.04
2.04
3.34
f1 (ppm)


166.33
146.57
122.72
68.82
60.38
37.47
28.06
27.64
14.29
O
EtO
OMs
(E)-1a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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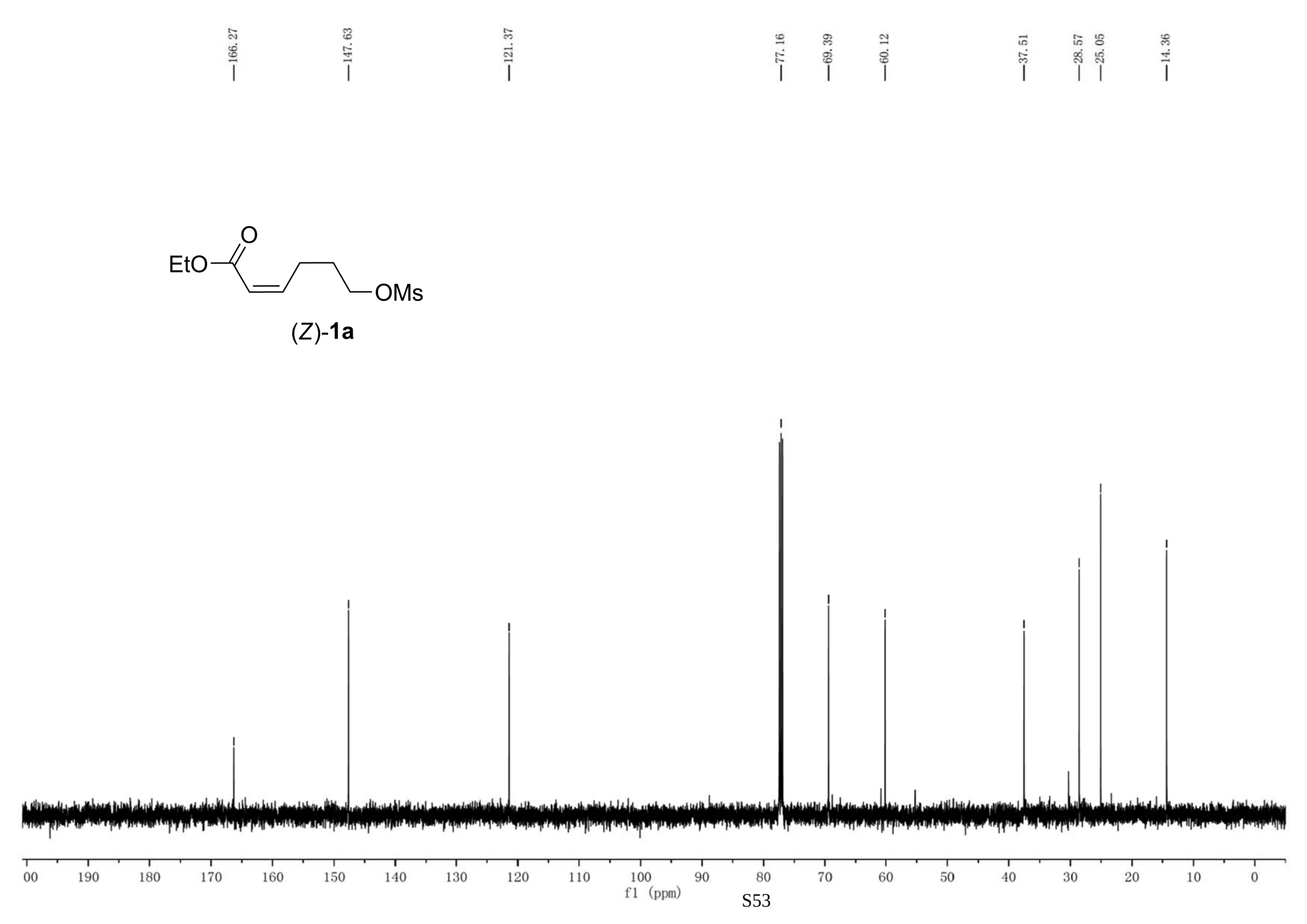
6.21
6.20
6.19
6.18
5.85
5.83
4.27
4.26
4.24
4.19
4.18
4.17
4.15
3.01
2.81
2.81
2.80
2.78
2.78
2.77
2.77
1.96
1.94
1.93
1.91
1.90
1.31
1.29
1.28
O
EtO
OMs
(Z)-1a
0.86
0.85
1.96
2.00
2.82
1.75
1.85
2.93
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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147.63
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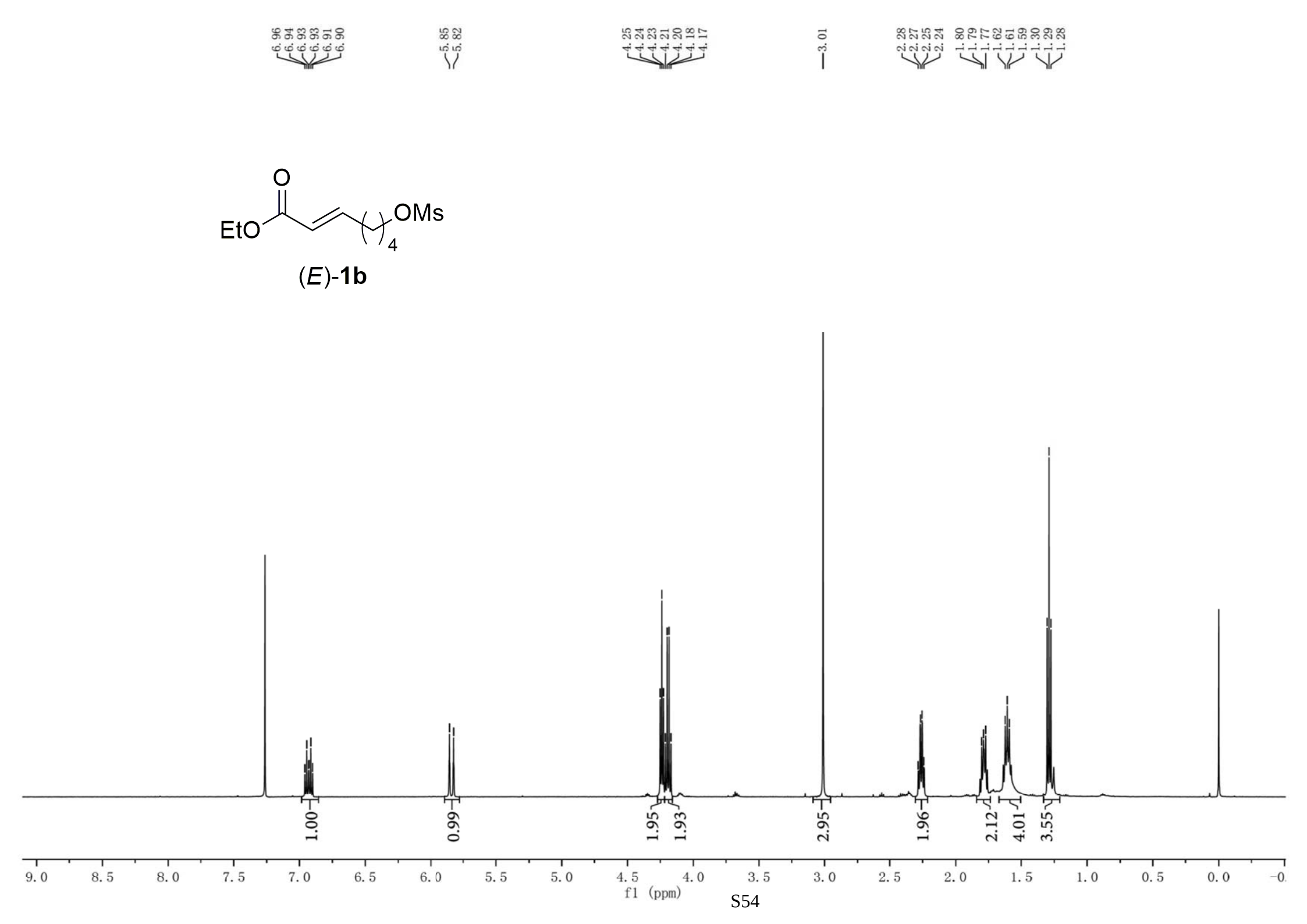
37.51
28.57
25.05
14.36
EtO
O
OMs
(Z)-1a
f1 (ppm)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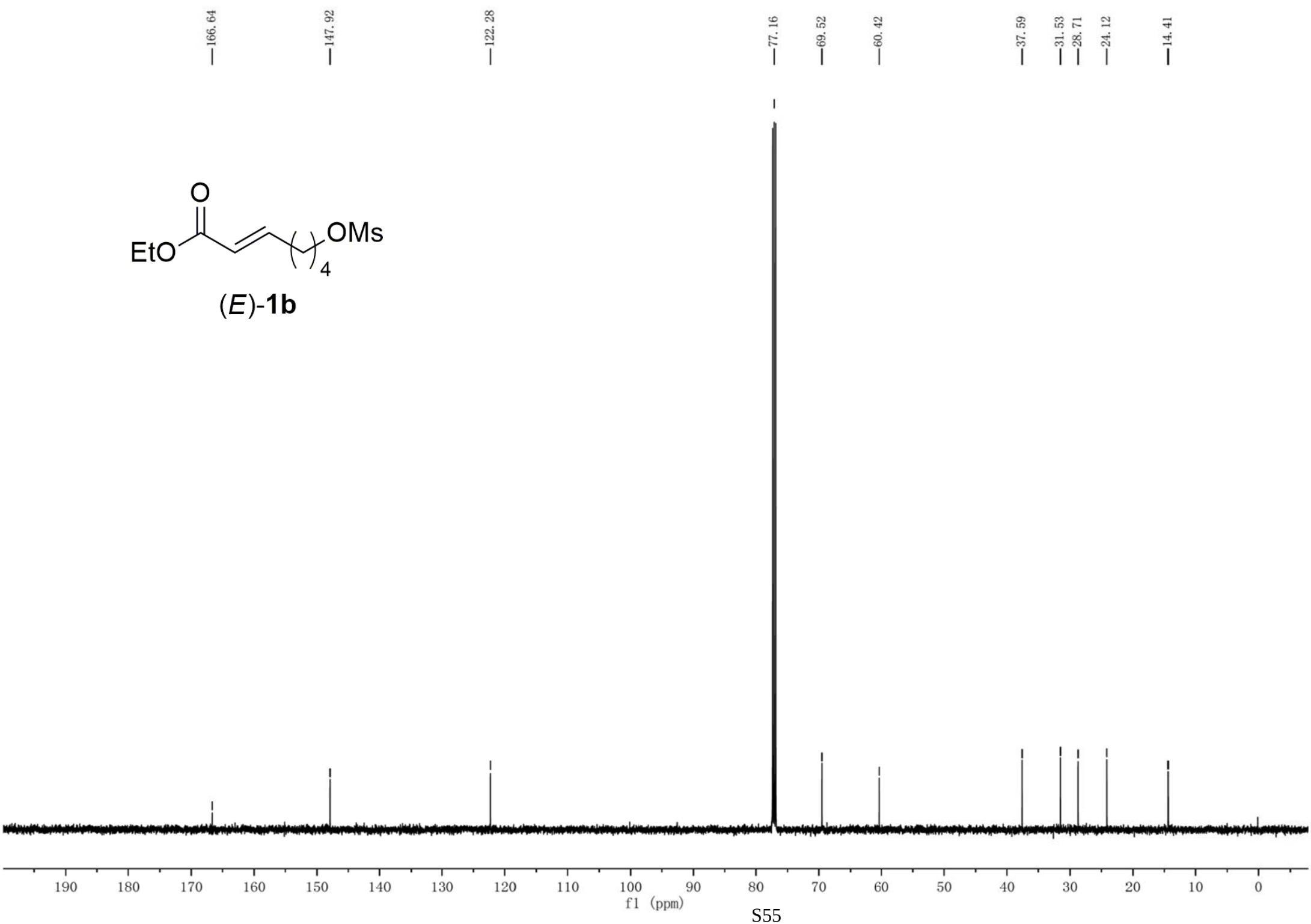
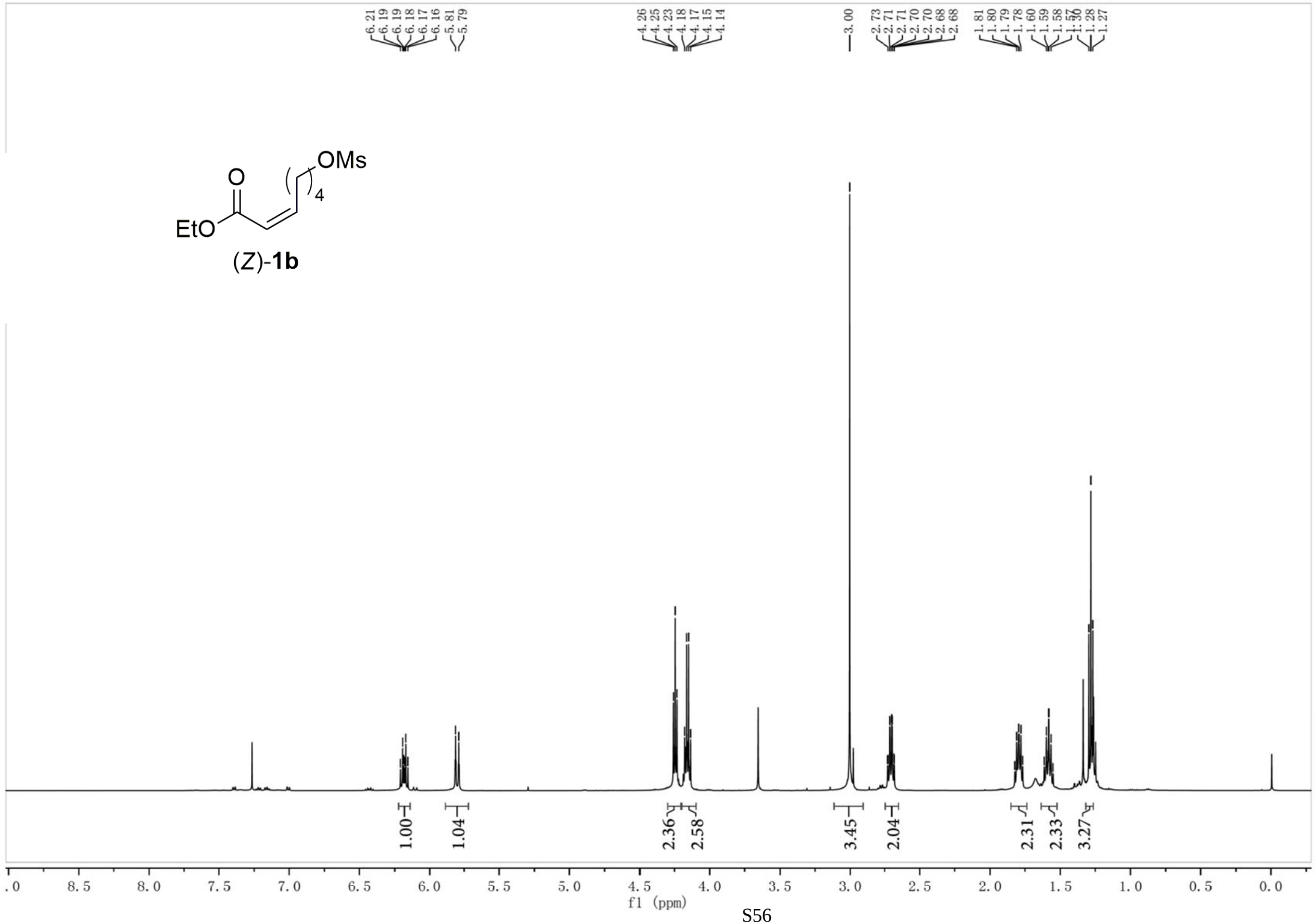
6.94
6.93
6.93
6.91
6.90
5.85
5.82
4.25
4.24
4.23
4.21
4.20
4.18
4.17
3.01
2.28
2.27
2.25
2.24
1.80
1.79
1.77
1.62
1.61
1.59
1.30
1.29
1.28
O
EtO
OMs
4
(E)-1b
1.00
0.99
1.95
1.93
2.95
1.96
2.12
4.01
3.55
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.64
147.92
122.28
77.16
69.52
60.42
37.59
31.53
28.71
24.12
14.41
O
EtO
OMs
4
(E)-1b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.21
6.19
6.19
6.18
6.17
6.16
5.81
5.79
4.26
4.25
4.23
4.18
4.17
4.15
4.14
3.00
2.73
2.71
2.71
2.70
2.70
2.68
2.68
1.81
1.80
1.79
1.78
1.60
1.59
1.58
1.30
1.28
1.27
OMs
O
4
EtO
(Z)-1b
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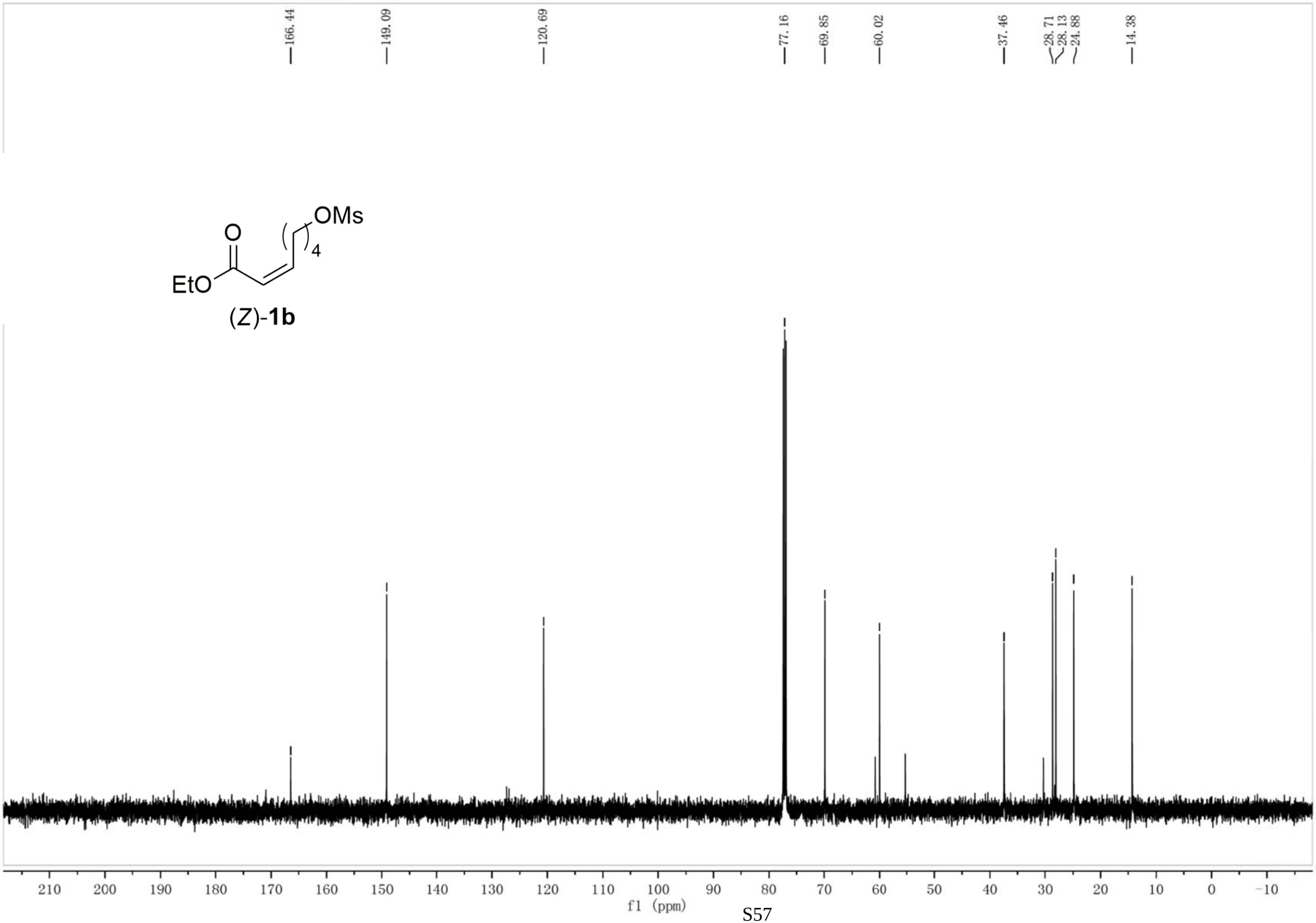
1.04
2.36
2.58
3.45
2.04
2.31
2.33
3.27
f1 (ppm)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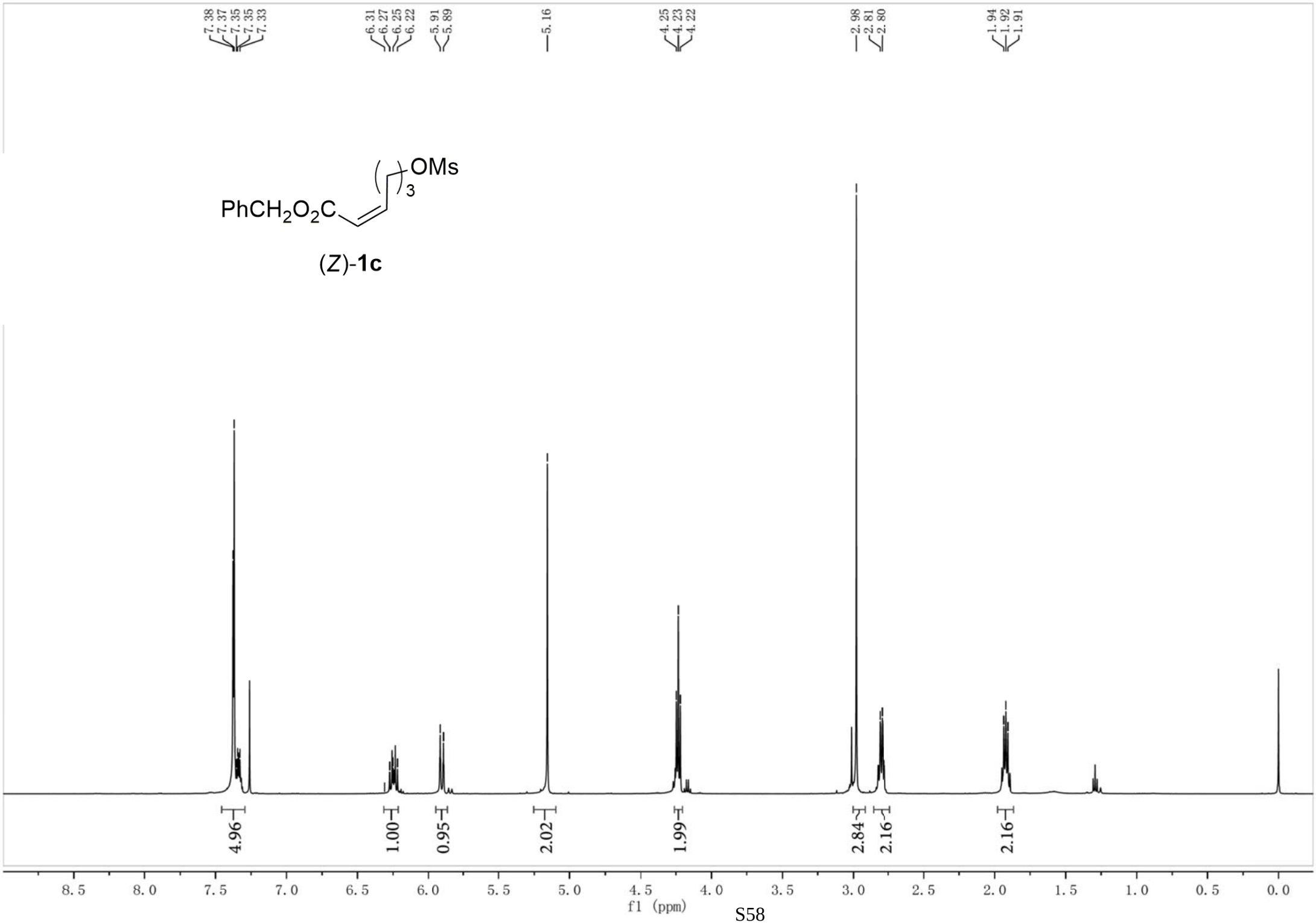
149.09
120.69
77.16
69.85
60.02
37.46
28.71
28.13
24.88
14.38
OMs
O
4
EtO
(Z)-1b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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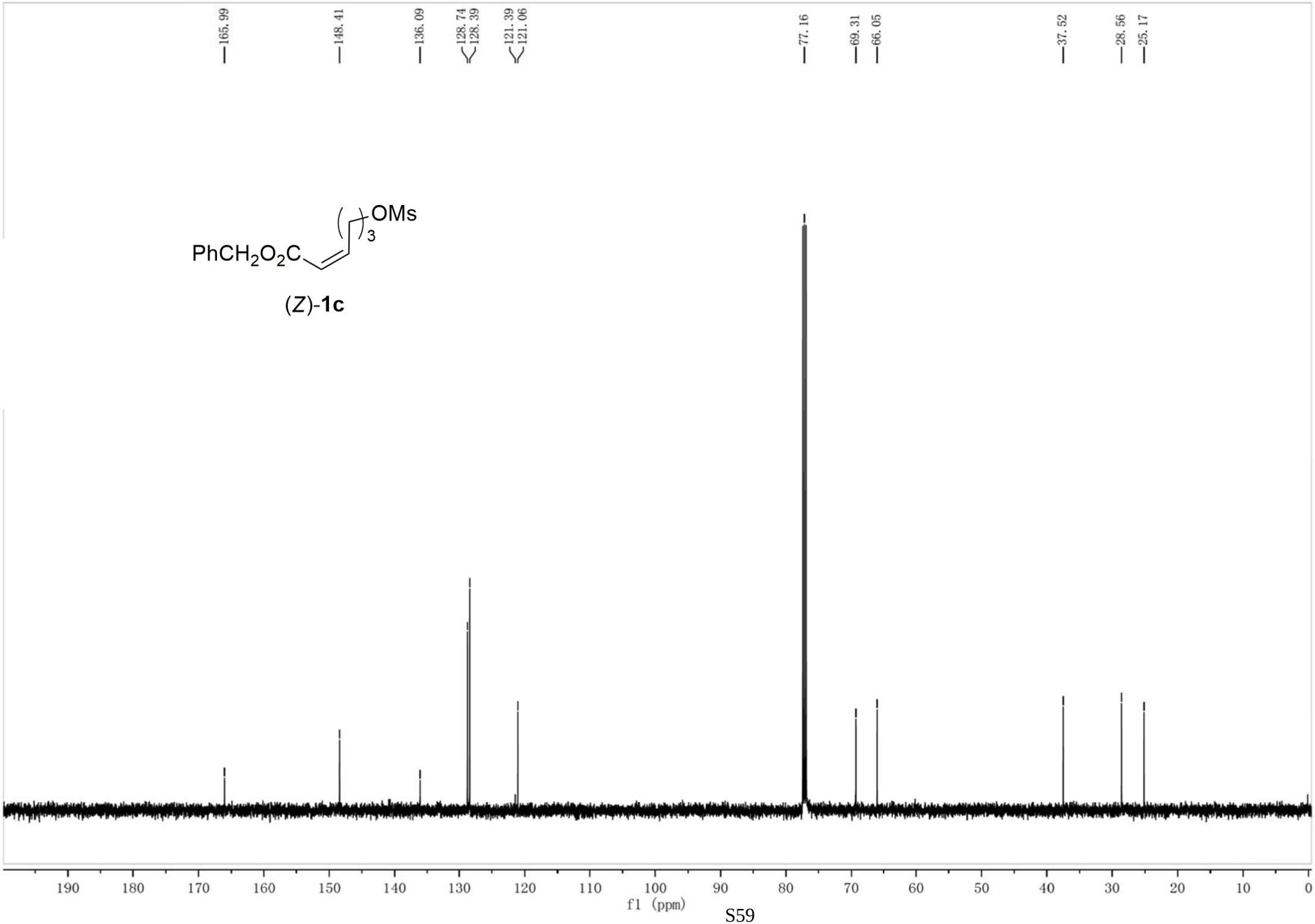
7.37
7.35
7.35
7.33
6.31
6.27
6.25
6.22
5.91
5.89
5.16
4.25
4.23
4.22
2.98
2.81
2.80
1.94
1.92
1.91
OMs
3
PhCH2O2C
(Z)-1c
4.96
1.00
0.95
2.02
1.99
2.84
2.16
2.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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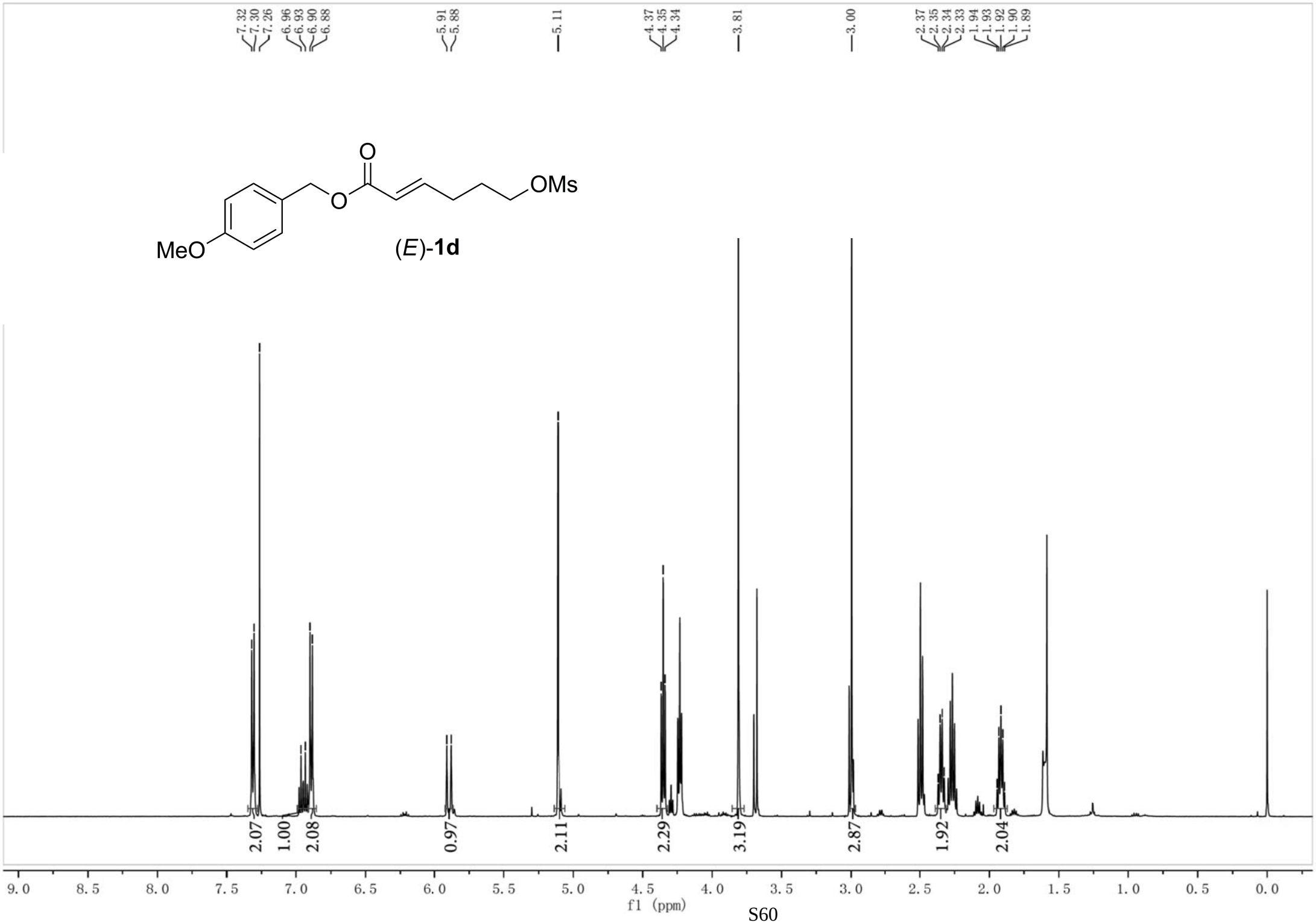
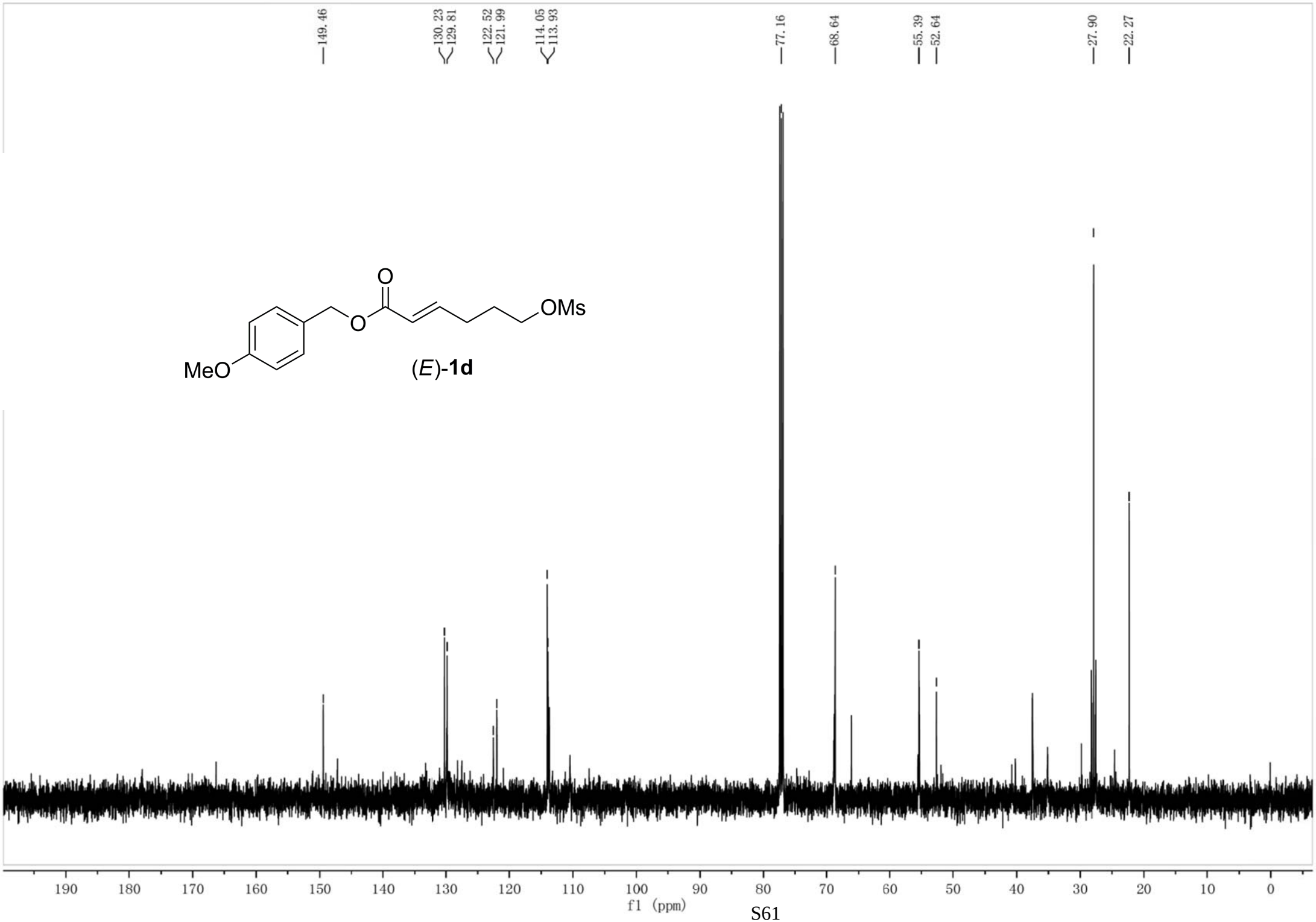
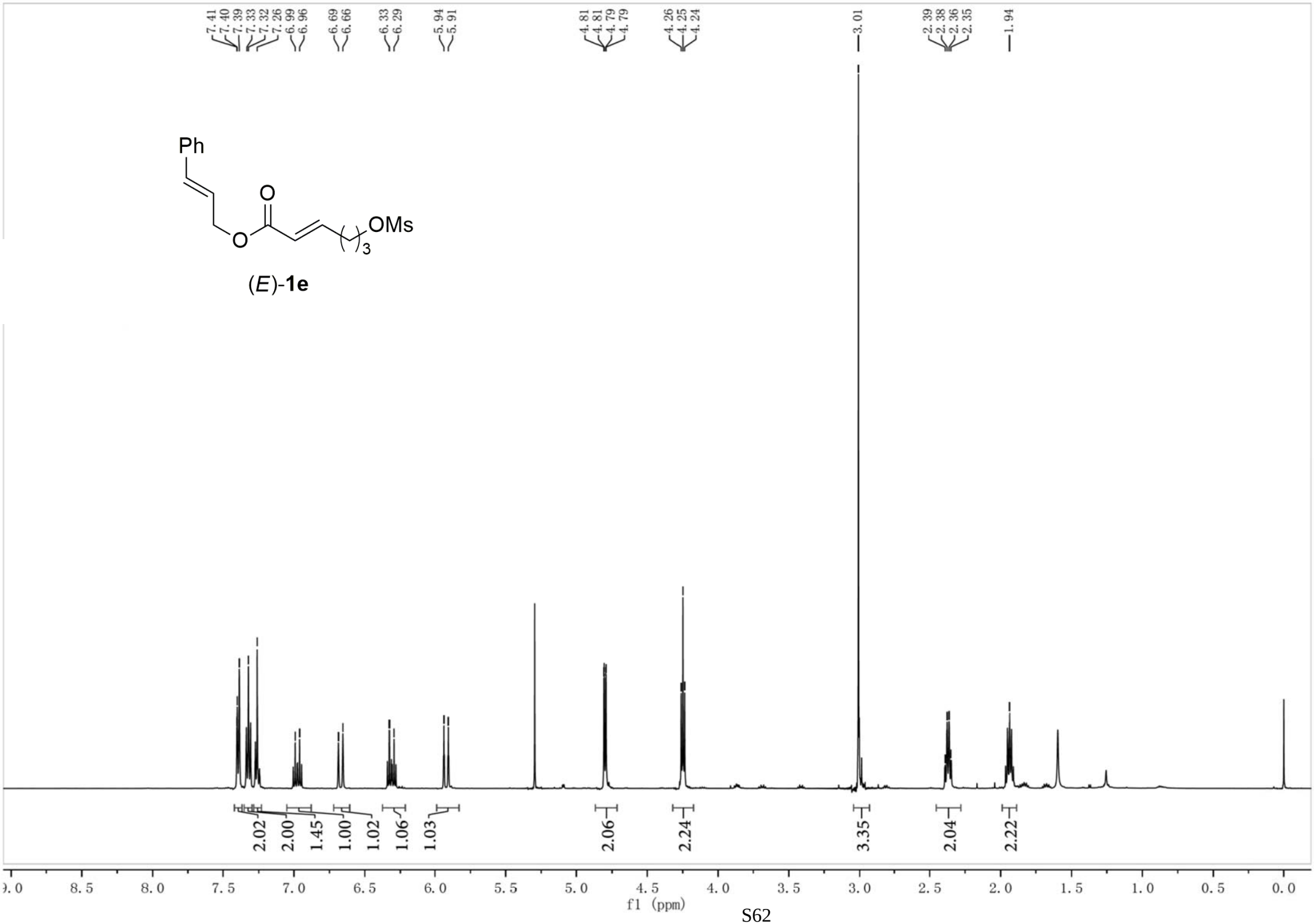
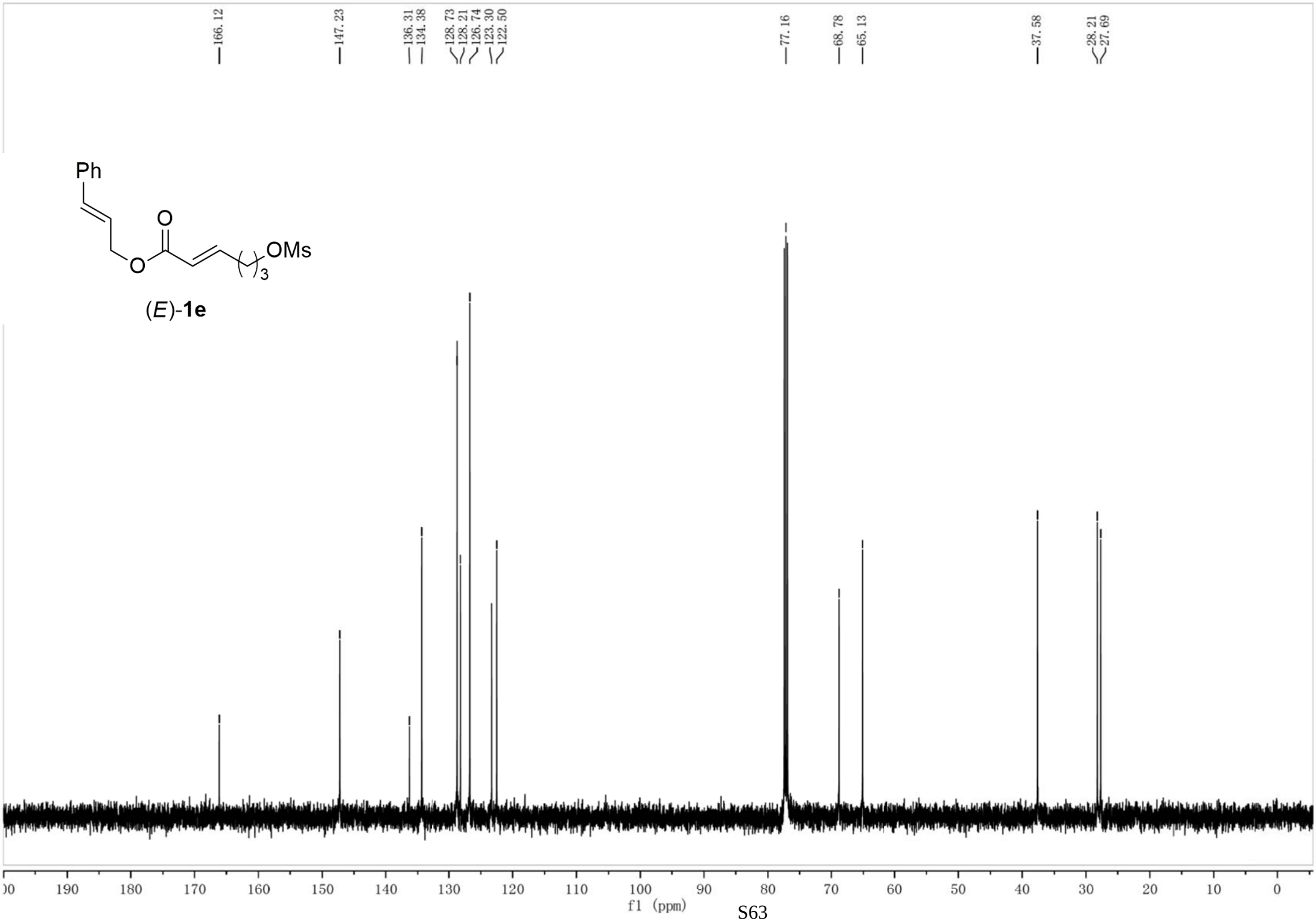
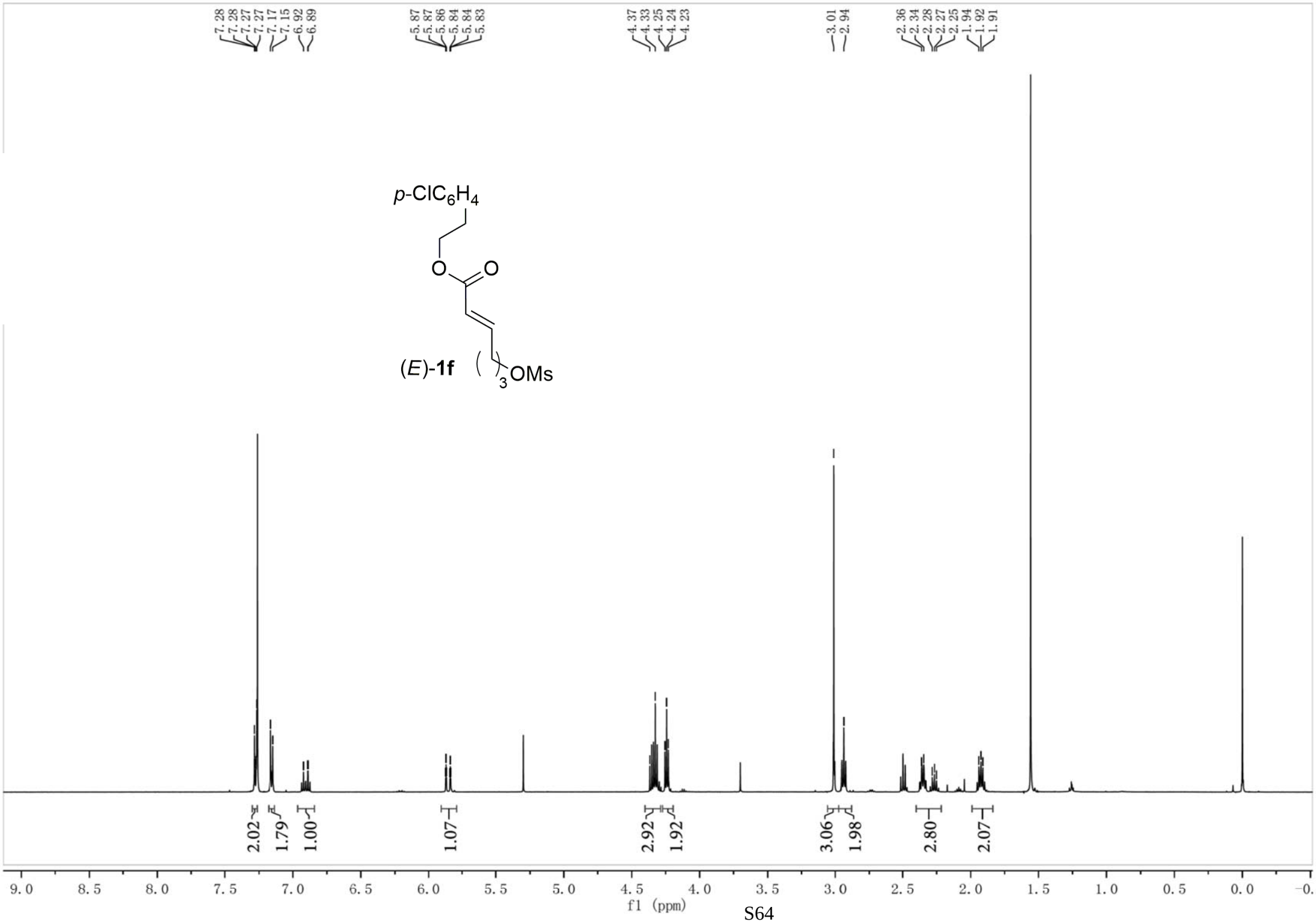
148.41
136.09
128.74
128.39
121.39
121.06
77.16
69.31
66.05
37.52
28.56
25.17
OMs
3
PhCH2O2C
(Z)-1c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.32
7.30
7.26
6.96
6.93
6.90
6.88
5.91
5.88
5.11
4.37
4.35
4.34
3.81
3.00
2.37
2.35
2.34
2.33
1.94
1.93
1.92
1.90
1.89
O
O
OMs
MeO
(E)-1d
2.07
1.00
2.08
0.97
2.11
2.29
3.19
2.87
1.92
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.46
130.23
129.81
122.52
121.99
114.05
113.93
77.16
68.64
55.39
52.64
27.90
22.27
O
O
OMs
MeO
(E)-1d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.41
7.40
7.39
7.33
7.32
7.26
6.99
6.96
6.69
6.66
6.33
6.29
5.94
5.91
4.81
4.81
4.79
4.79
4.26
4.25
4.24
3.01
2.39
2.38
2.36
2.35
1.94
Ph
O
O
OMs
3
(E)-1e
2.02
2.00
1.45
1.00
1.02
1.06
1.03
2.06
2.24
3.35
2.04
2.22
f1 (ppm)


166.12
147.23
136.31
134.38
128.73
128.21
126.74
123.30
122.50
77.16
68.78
65.13
37.58
28.21
27.69
Ph
O
O
OMs
3
(E)-1e
f1 (ppm)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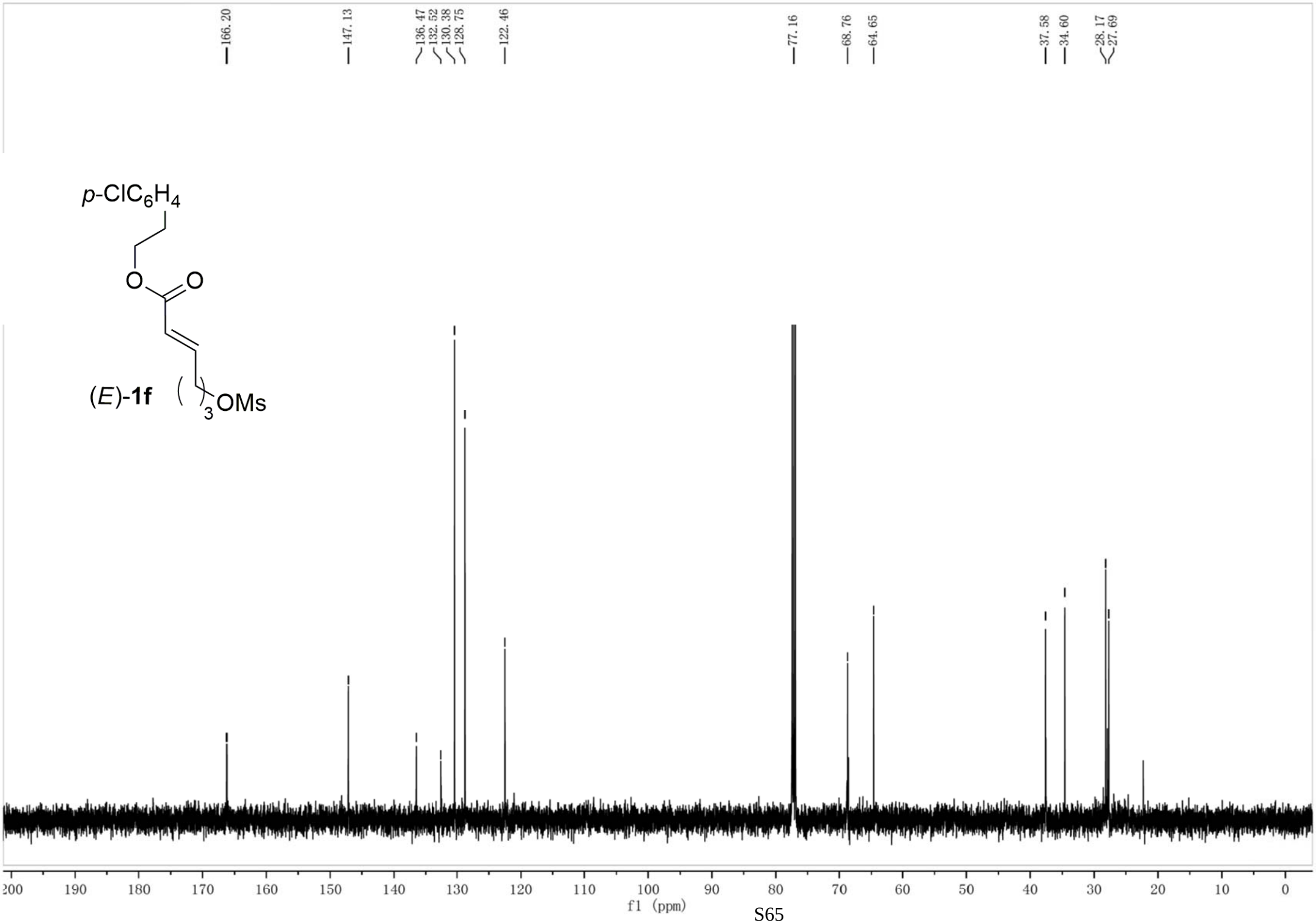
7.28
7.27
7.27
7.17
7.15
6.92
6.89
5.87
5.87
5.86
5.84
5.84
5.83
4.37
4.33
4.25
4.24
4.23
3.01
2.94
2.36
2.34
2.28
2.27
2.25
1.94
1.92
1.91
p-ClC6H4
O
O
(E)-1f
3
OMs
2.02
1.79
1.00
1.07
2.92
1.92
3.06
1.98
2.80
2.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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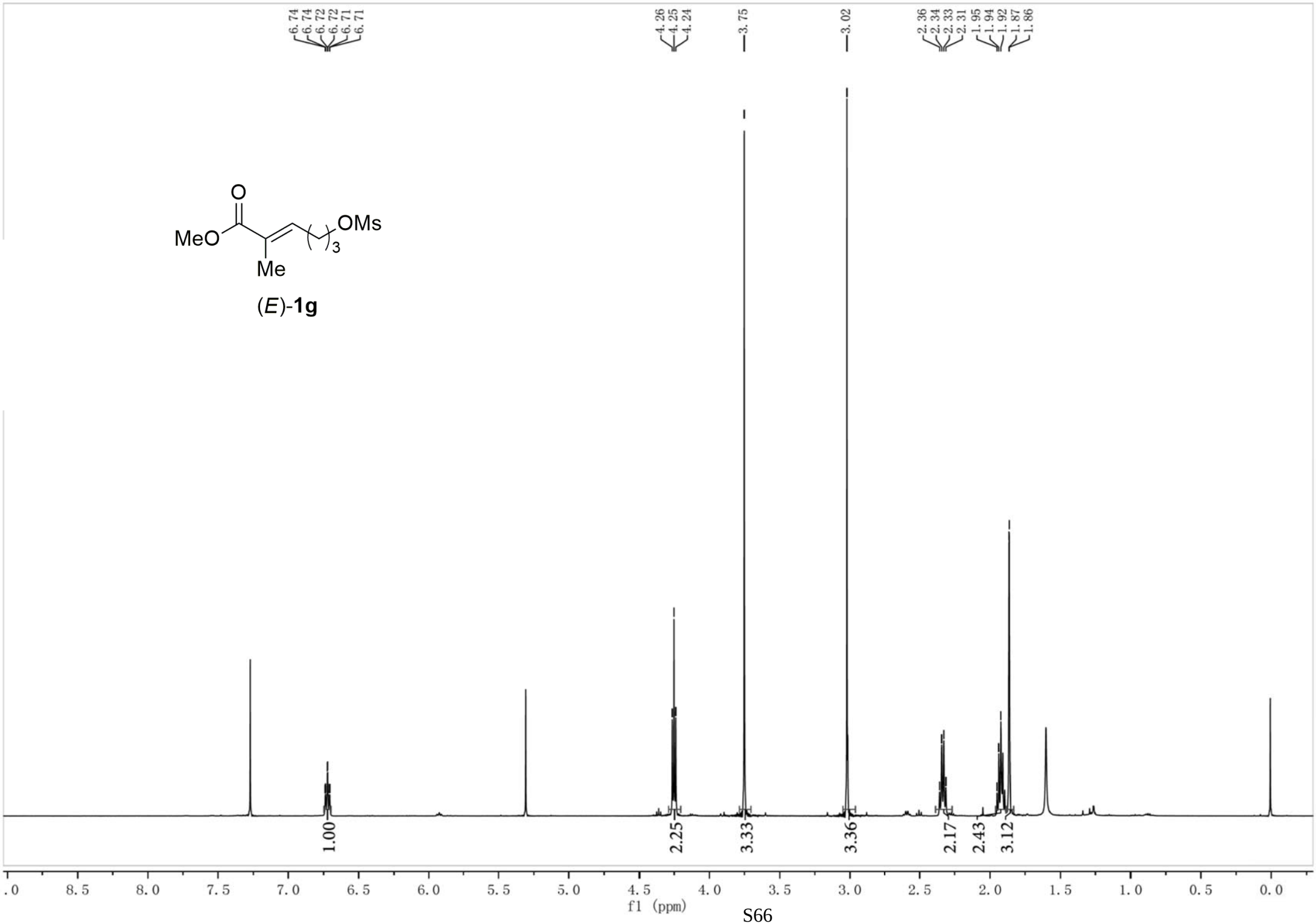
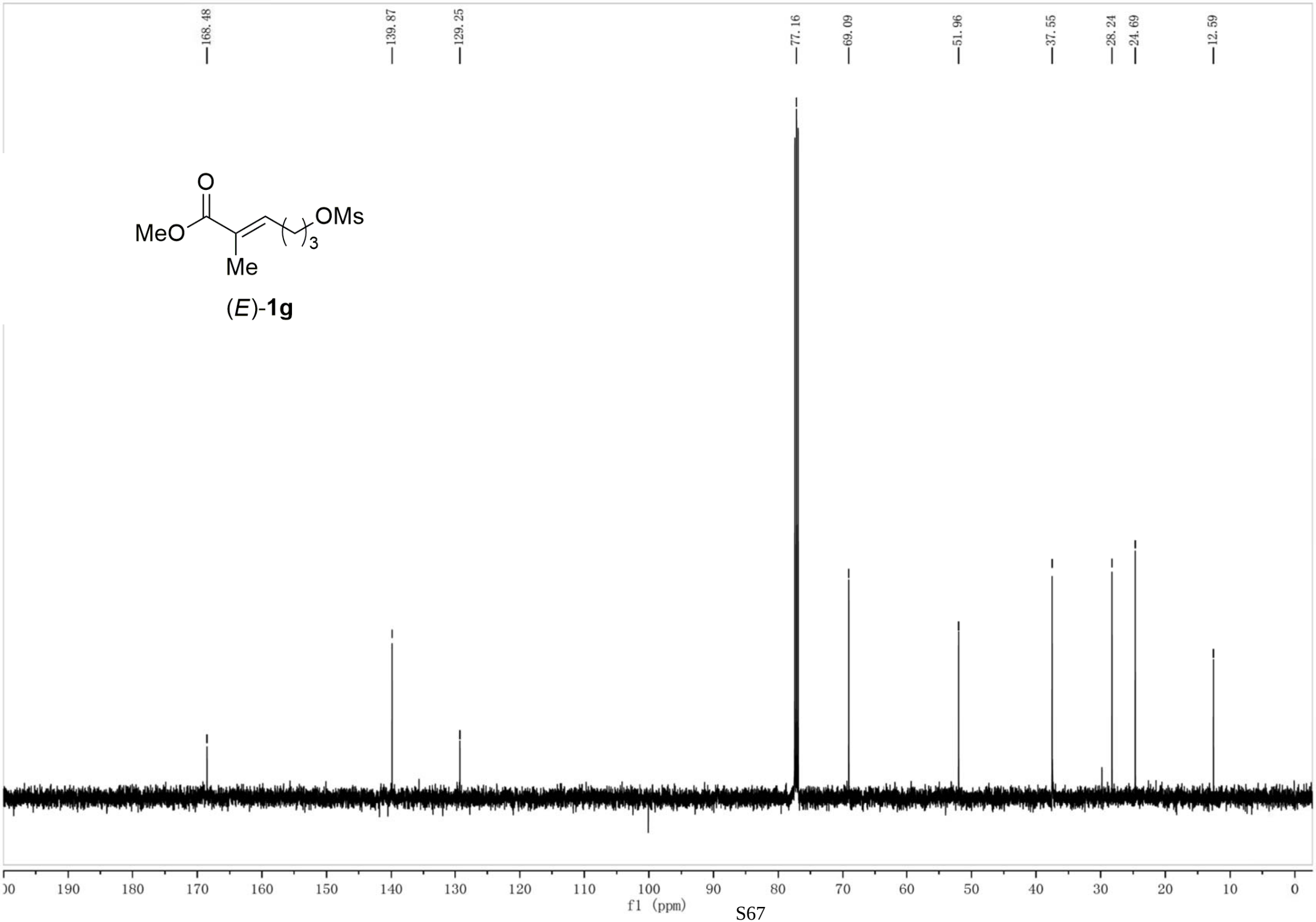
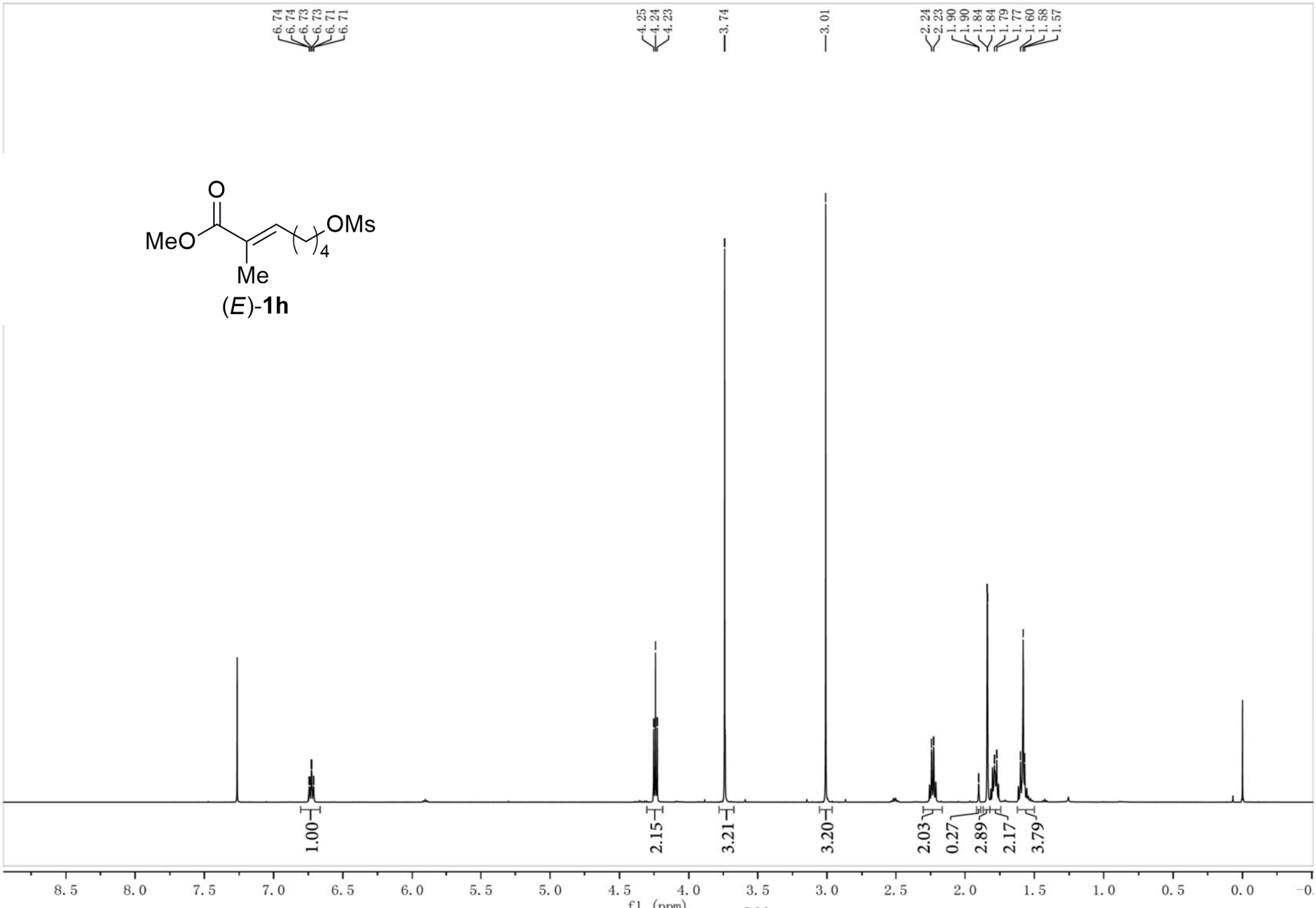
147.13
136.47
132.52
130.38
128.75
122.46
77.16
68.76
64.65
37.58
34.60
28.17
27.69
p-ClC6H4
O
O
(E)-1f
3
OMs
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.74
6.74
6.72
6.72
6.71
6.71
4.26
4.25
4.24
3.75
3.02
2.36
2.34
2.33
2.31
1.95
1.94
1.92
1.87
1.86
O
MeO
OMs
3
Me
(E)-1g
1.00
2.25
3.33
3.36
2.17
2.43
3.12
f1 (ppm)


168.48
139.87
129.25
77.16
69.09
51.96
37.55
28.24
24.69
12.59
O
MeO
OMs
3
Me
(E)-1g
f1 (ppm)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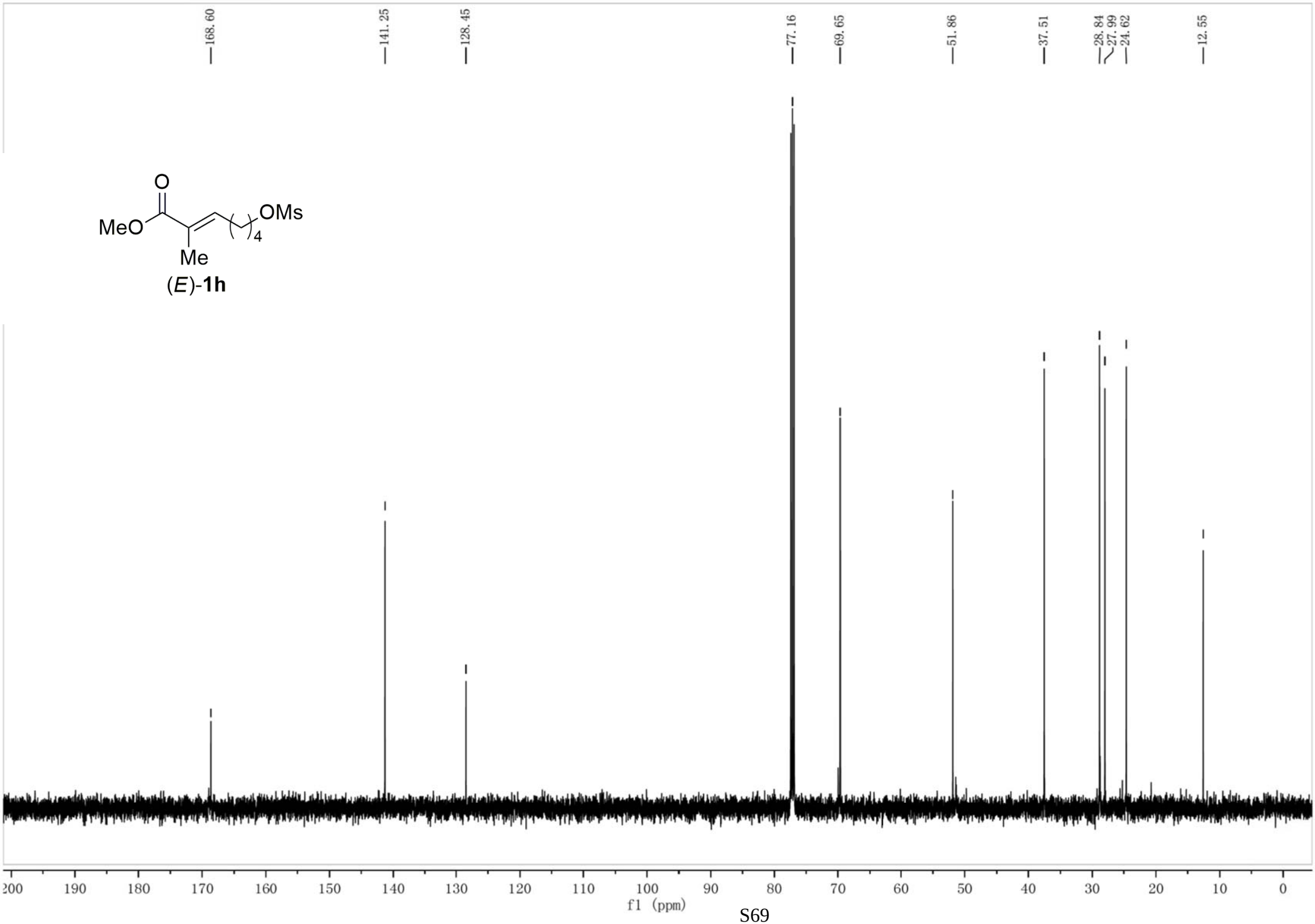
6.74
6.73
6.73
6.71
6.71
4.25
4.24
4.23
3.74
3.01
2.24
2.23
1.90
1.90
1.84
1.84
1.79
1.77
1.60
1.58
1.57
O
MeO
OMs
4
Me
(E)-1h
1.00
2.15
3.21
3.20
2.03
0.27
2.89
2.17
3.79
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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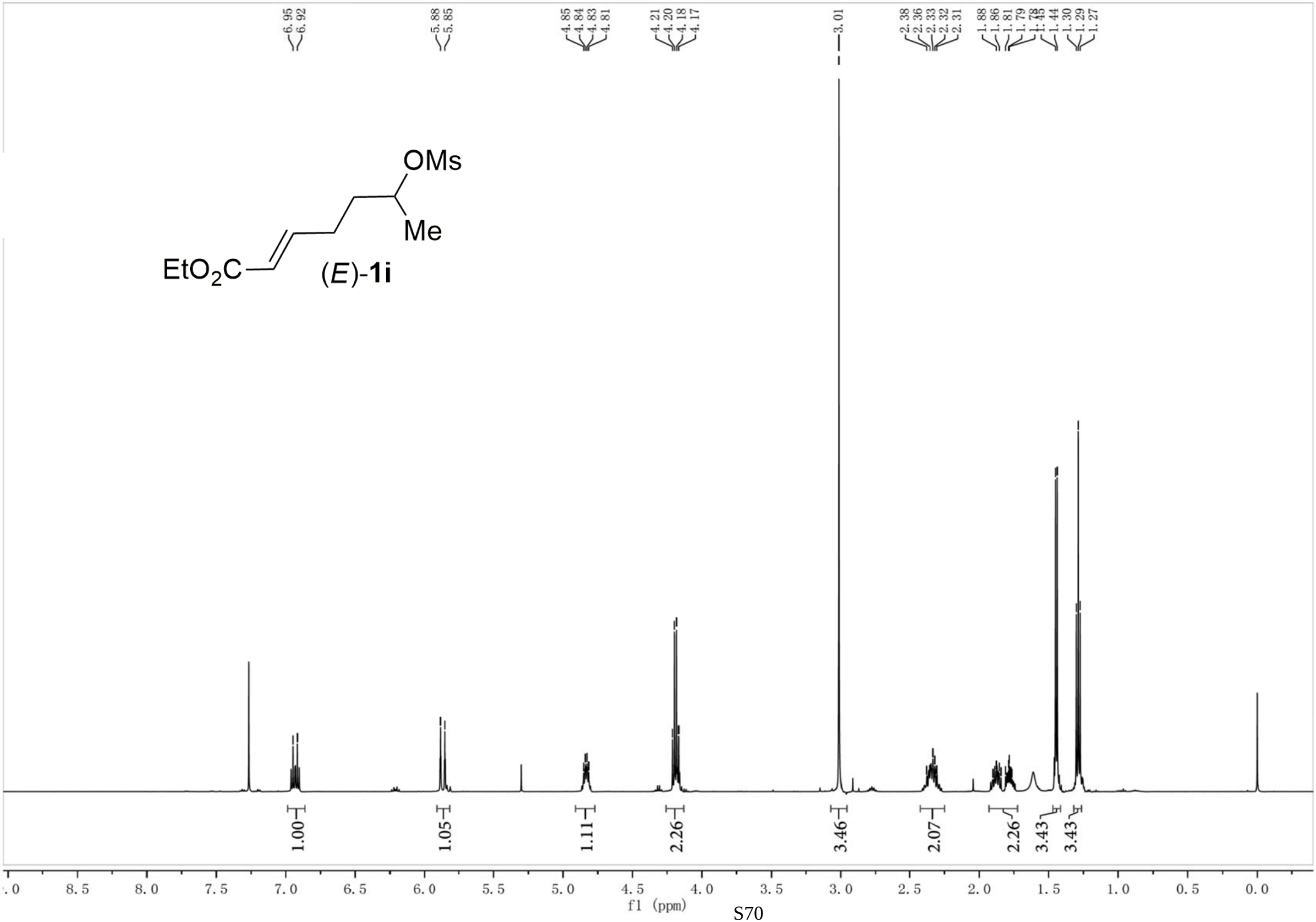
141.25
128.45
77.16
69.65
51.86
37.51
28.84
27.99
24.62
12.55
O
MeO
OMs
4
Me
(E)-1h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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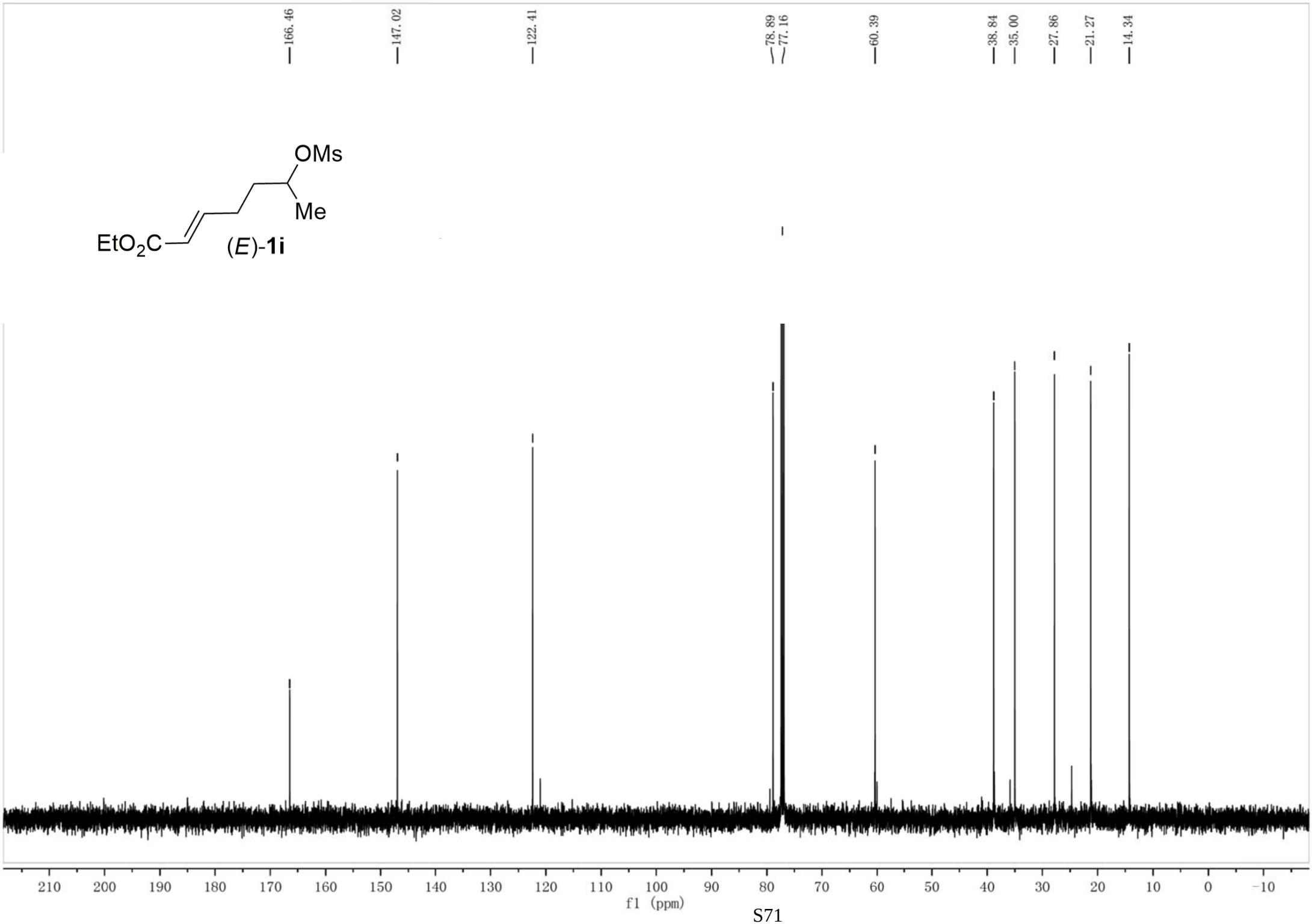
6.92
5.88
5.85
4.85
4.84
4.83
4.81
4.21
4.20
4.18
4.17
3.01
2.38
2.36
2.33
2.32
2.31
1.88
1.86
1.81
1.79
1.78
1.45
1.44
1.30
1.29
1.27
OMs
Me
EtO2C
(E)-1i
1.00
1.05
1.11
2.26
3.46
2.07
2.26
3.43
3.43
f1 (ppm)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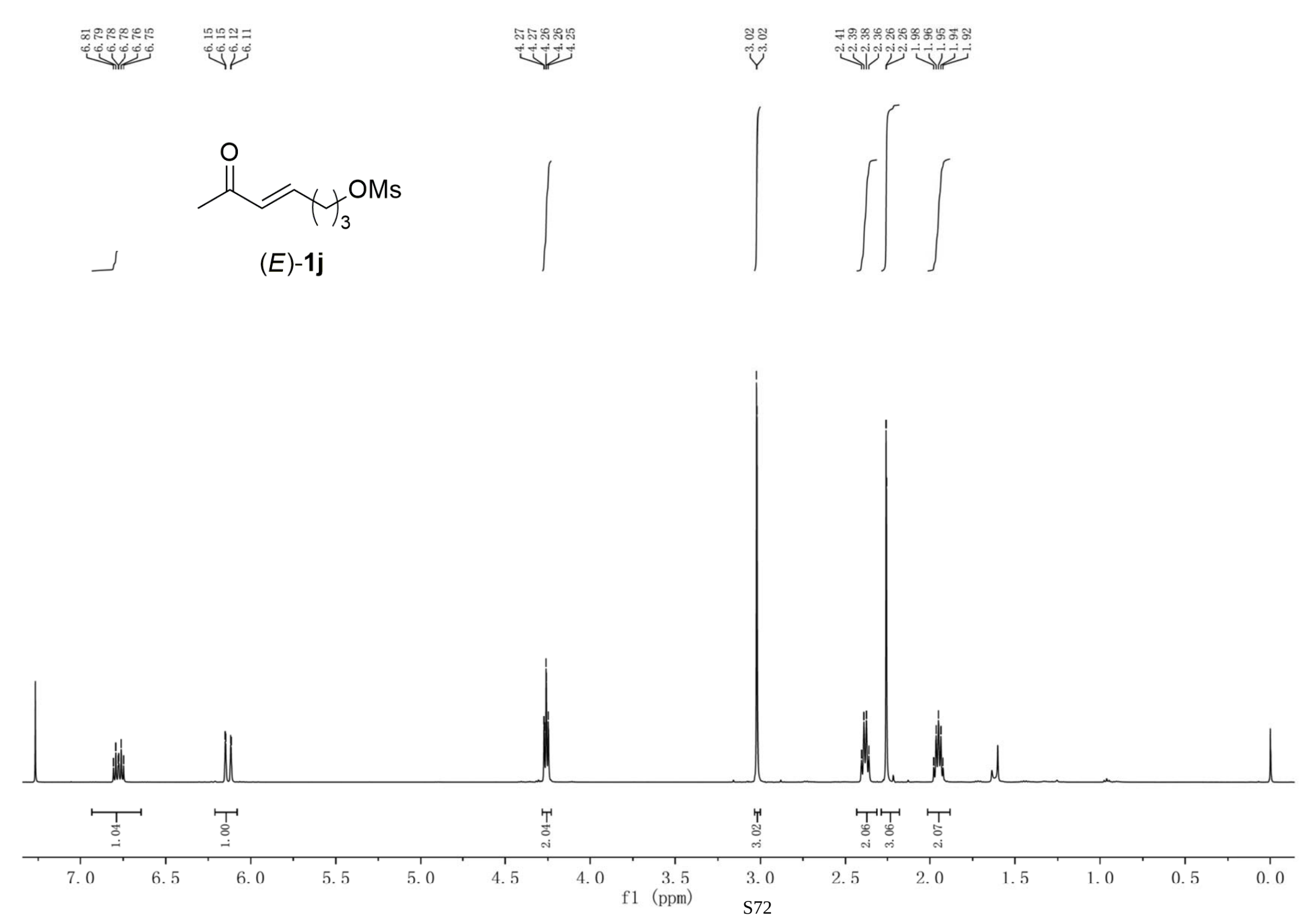
122.41
78.89
77.16
60.39
38.84
35.00
27.86
21.27
14.34
OMs
Me
EtO2C
(E)-1i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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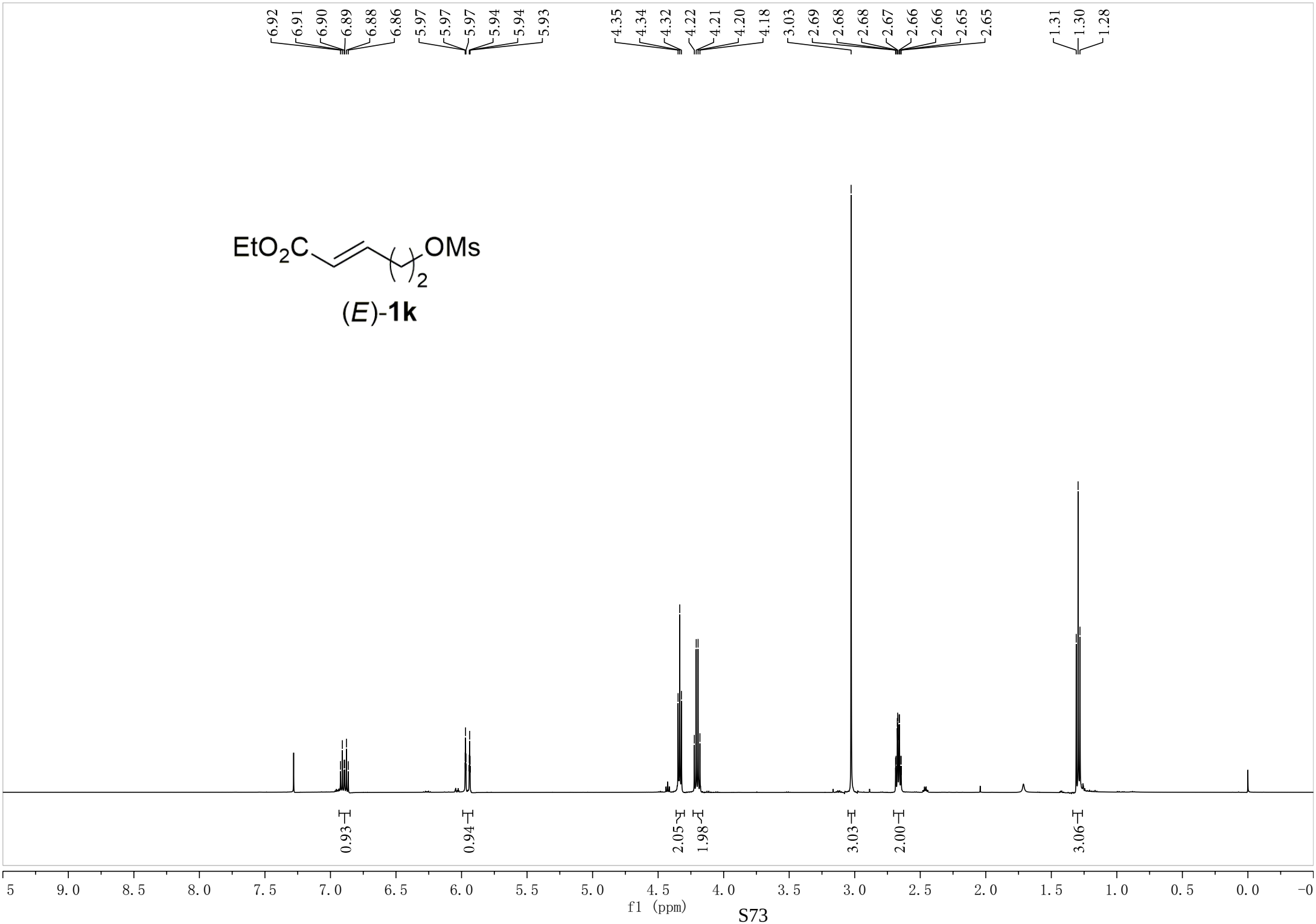
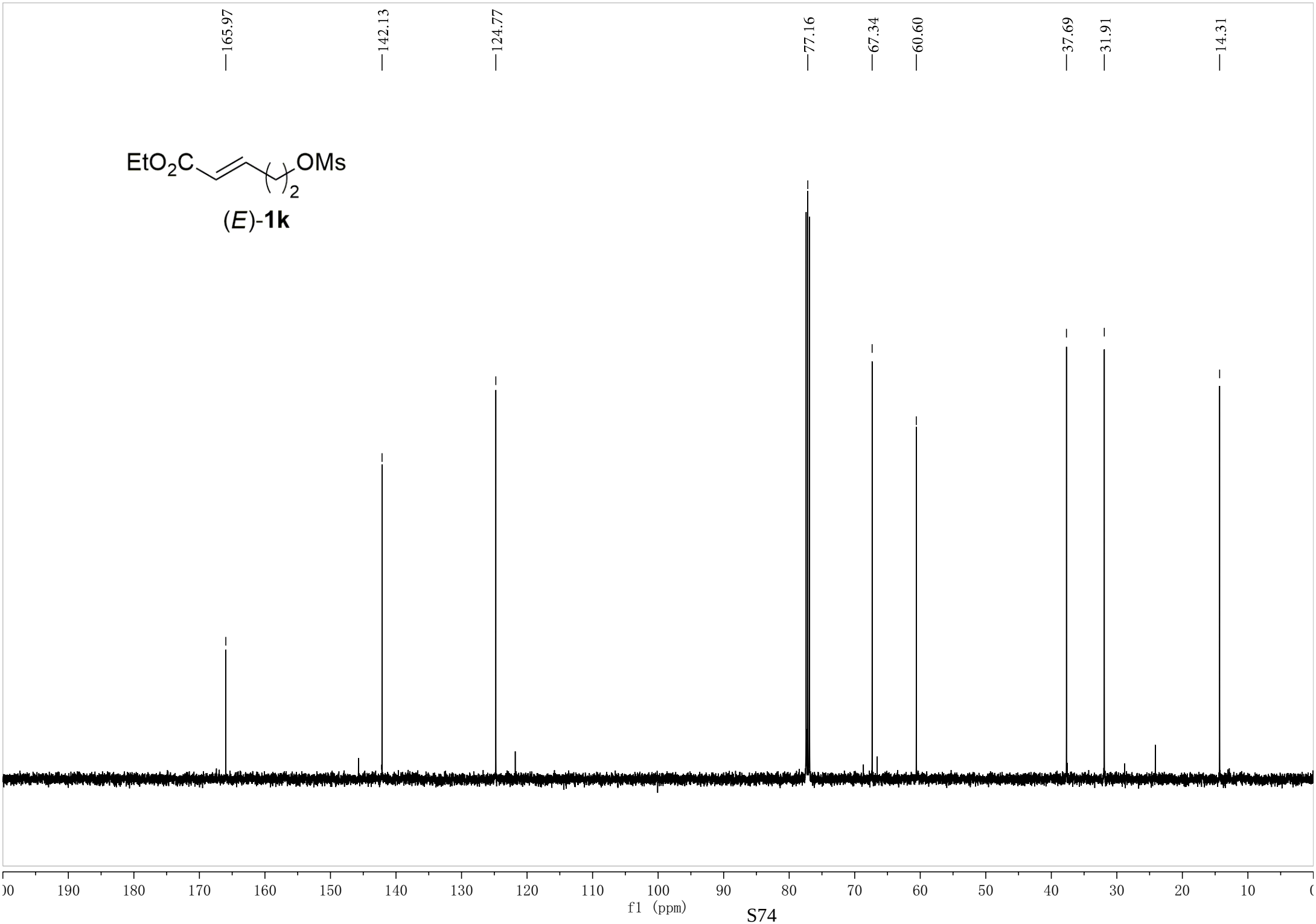
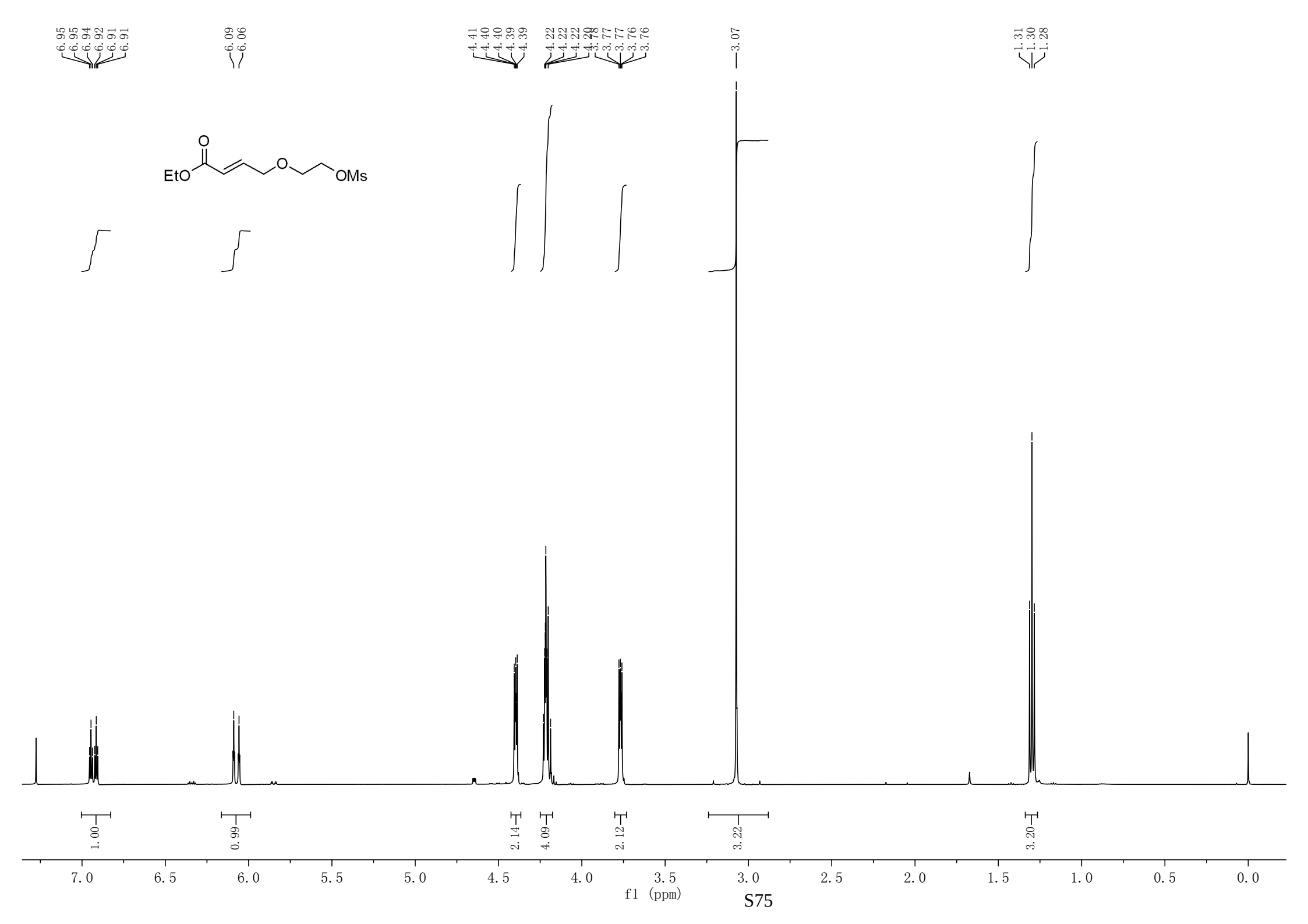
6.79
6.78
6.78
6.76
6.75
6.15
6.15
6.12
6.11
4.27
4.27
4.26
4.26
4.25
3.02
3.02
2.41
2.39
2.38
2.36
2.26
2.26
1.98
1.96
1.95
1.94
1.92
O
OMs
3
(E)-1j
1.04
1.00
2.04
3.02
2.06
3.06
2.07
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


6.92
6.91
6.90
6.89
6.88
6.86
5.97
5.97
5.97
5.94
5.94
5.93
4.35
4.34
4.32
4.22
4.21
4.20
4.18
3.03
2.69
2.68
2.68
2.67
2.66
2.66
2.65
2.65
1.31
1.30
1.28
EtO2C
OMs
2
(E)-1k
0.93
0.94
2.05
1.98
3.03
2.00
3.06
f1 (ppm)


165.97
142.13
124.77
77.16
67.34
60.60
37.69
31.91
14.31
EtO2C
OMs
2
(E)-1k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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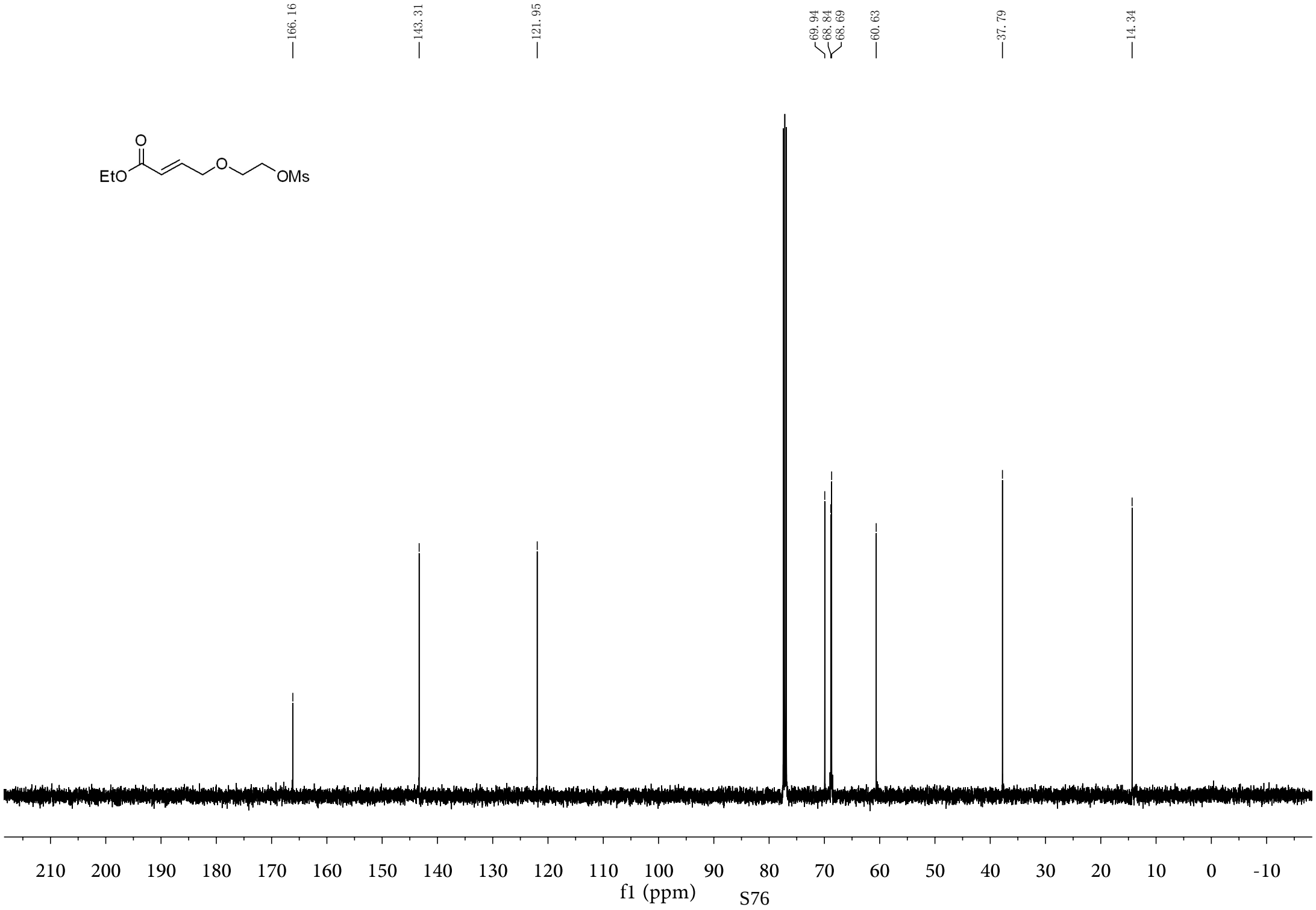
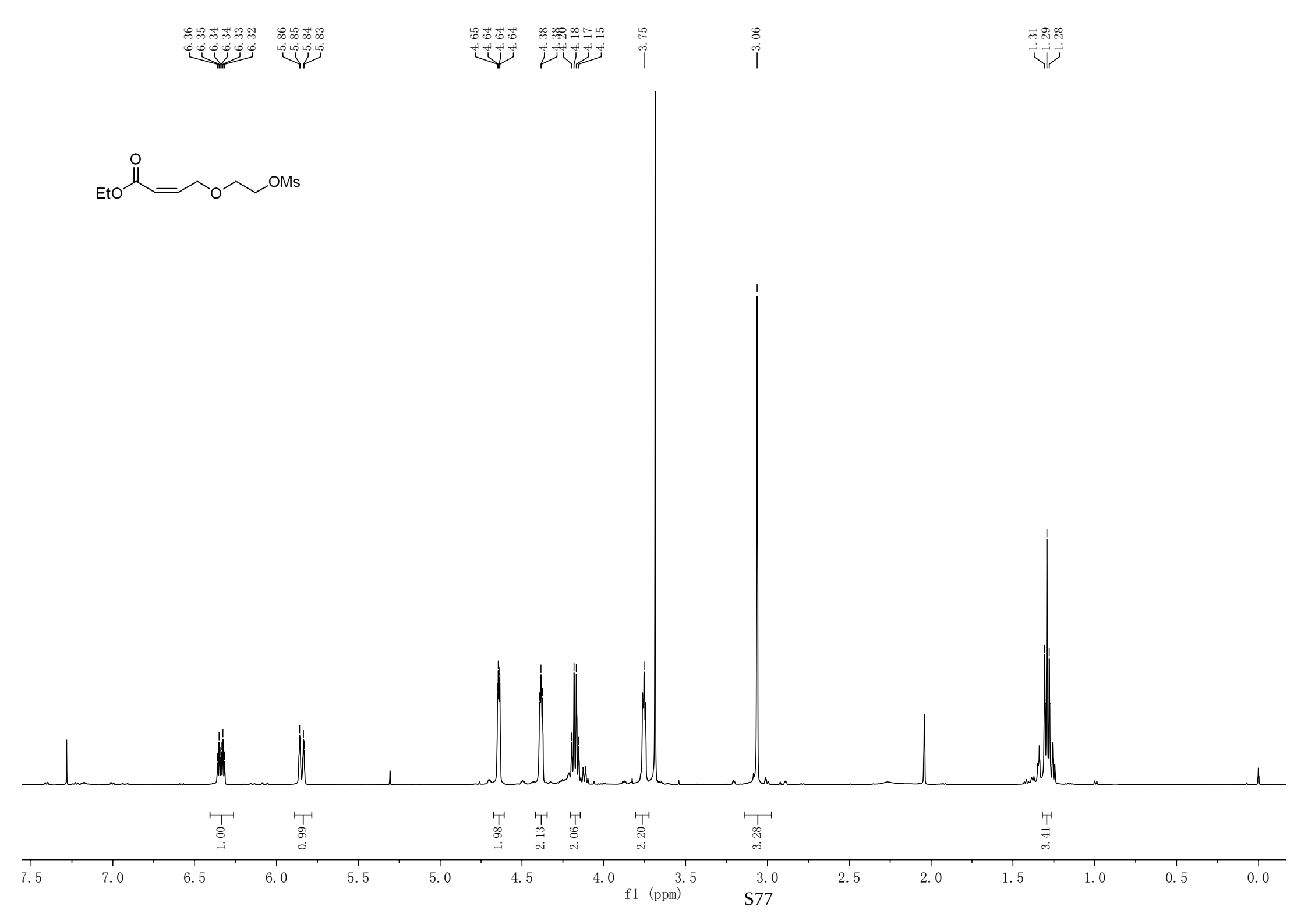
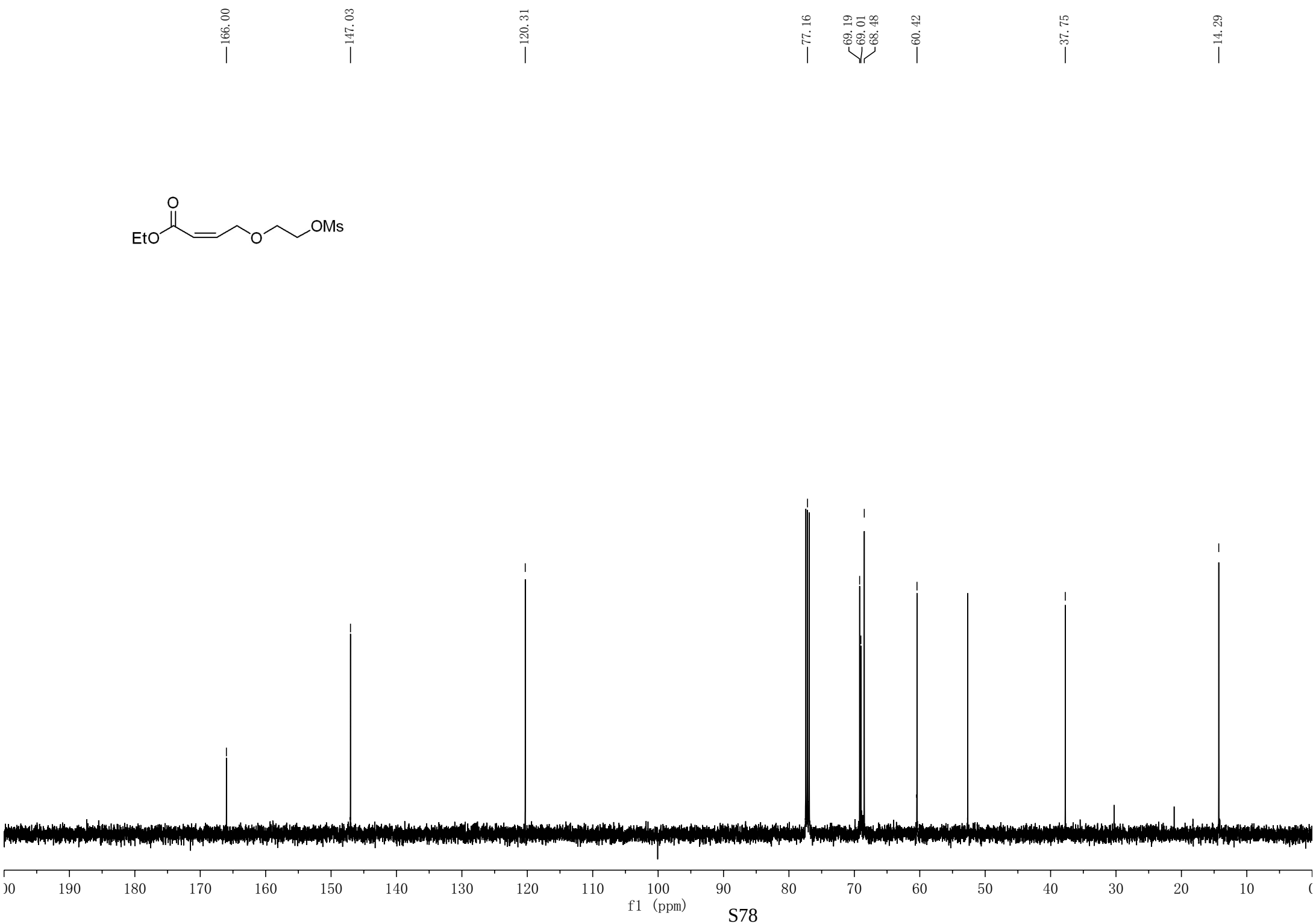
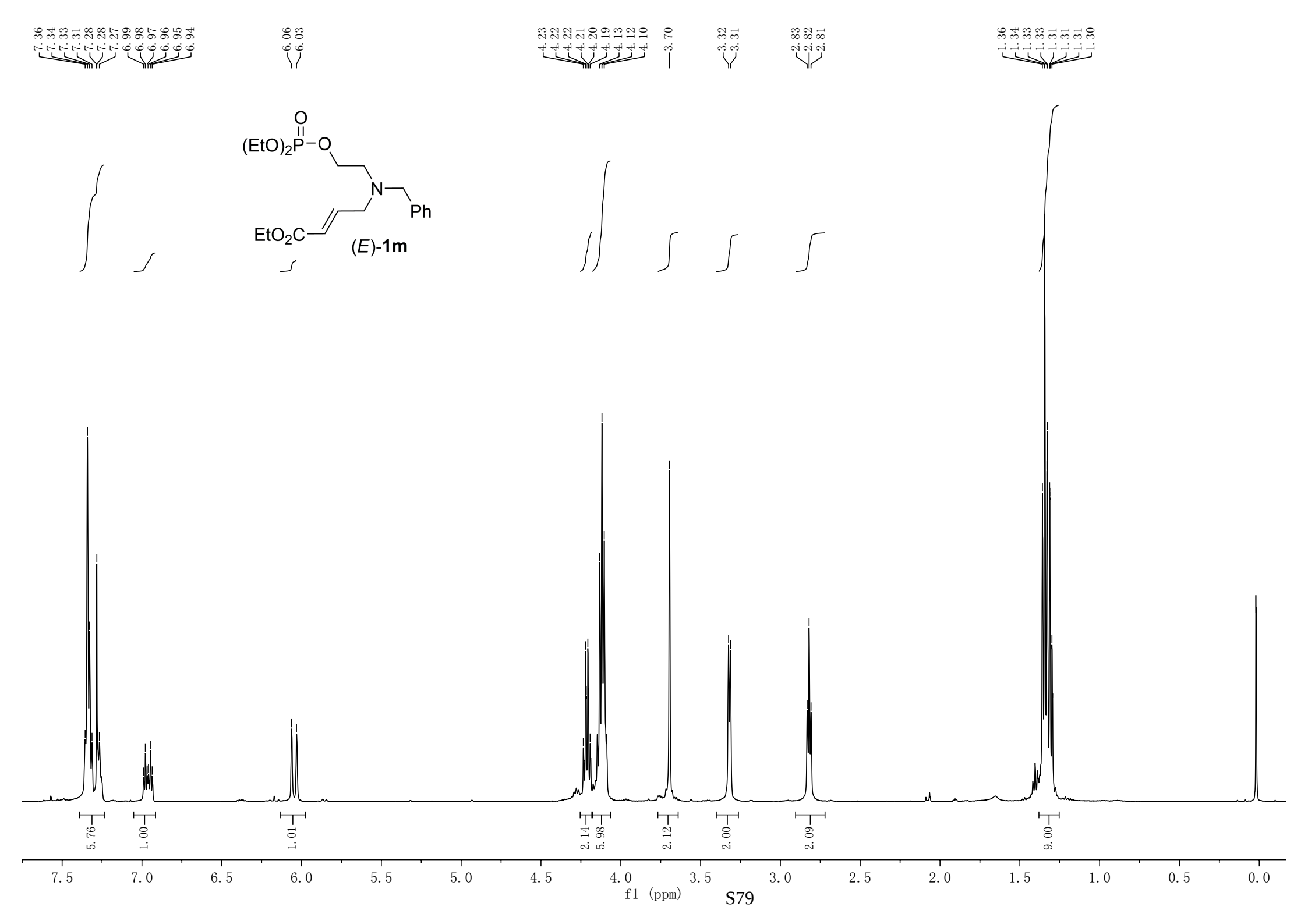
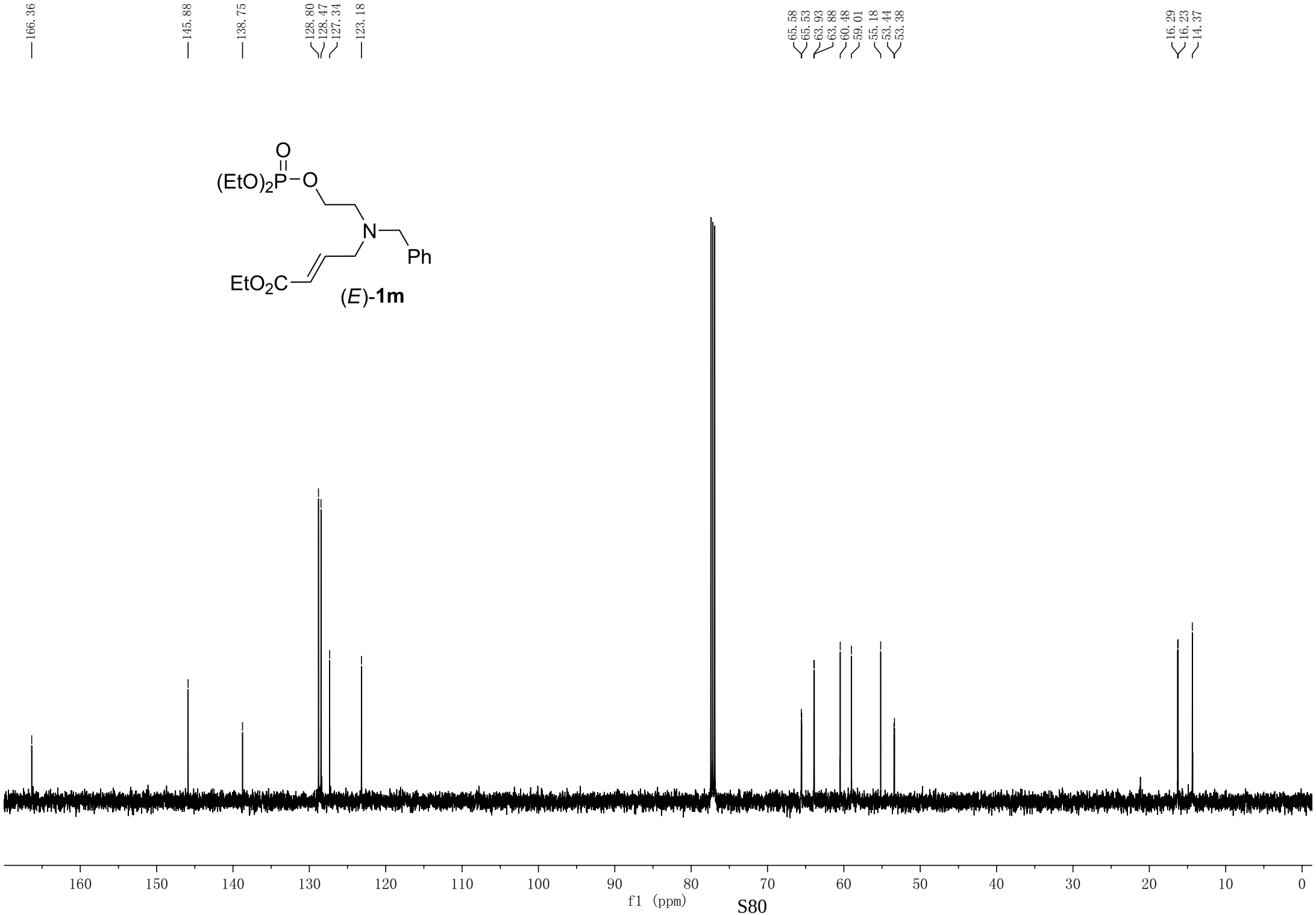
6.95
6.94
6.92
6.91
6.91
6.09
6.06
4.41
4.40
4.40
4.39
4.39
4.22
4.22
4.22
4.20
3.78
3.77
3.77
3.76
3.76
3.07
1.31
1.30
1.28
O
EtO
O
OMs
1.00
0.99
2.14
4.09
2.12
3.22
3.20
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.16
143.31
121.95
69.94
68.84
68.69
60.63
37.79
14.34
O
EtO
O
OMs
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


6.36
6.35
6.34
6.34
6.33
6.32
5.86
5.85
5.84
5.83
4.65
4.64
4.64
4.64
4.38
4.38
4.20
4.18
4.17
4.15
3.75
3.06
1.31
1.29
1.28
O
EtO
O
OMs
1.00
0.99
1.98
2.13
2.06
2.20
3.28
3.41
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.00
147.03
120.31
77.16
69.19
69.01
68.48
60.42
37.75
14.29
O
EtO
O
OMs
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.36
7.34
7.33
7.31
7.28
7.28
7.27
6.99
6.98
6.97
6.96
6.95
6.94
6.06
6.03
4.23
4.22
4.22
4.21
4.20
4.19
4.13
4.12
4.10
3.70
3.32
3.31
2.83
2.82
2.81
1.36
1.34
1.33
1.33
1.31
1.31
1.31
1.30
O
(EtO)2P−O
N
Ph
EtO2C
(E)-1m
5.76
1.00
1.01
2.14
5.98
2.12
2.00
2.09
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.36
145.88
138.75
128.80
128.47
127.34
123.18
65.58
65.53
63.93
63.88
60.48
59.01
55.18
53.44
53.38
16.29
16.23
14.37
O
(EtO)2P−O
N
Ph
EtO2C
(E)-1m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)