

Supporting Information

Transition-Metal-Free Cross-Coupling Reaction of Iodocarboranes with Terminal Alkynes Enabled by UV Light: Synthesis of 1-Alkynyl-*o*-Carboranes and Carborane-Fused Cyclices

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1. General Procedures.

All reactions were carried out in flame-dried glassware under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox. ¹H NMR spectra were recorded on a Bruker DPX400 spectrometer at 400 MHz or a Bruker 500 spectrometer at 500 MHz. ¹⁹F NMR spectra were recorded on a Bruker DPX400 spectrometer at 376 MHz or a Bruker 500 spectrometer at 470 MHz. ¹³C NMR spectra were recorded on a Bruker DPX 400 spectrometer at 100 MHz or a Bruker 500 spectrometer at 126 MHz. ¹¹B NMR spectra were recorded on a Bruker DPX 400 spectrometer at 128 MHz or a Bruker 500 spectrometer at 160 MHz. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $\text{BF}_3\cdot\text{OEt}_2$ (0.00 ppm) for boron chemical shifts, and to external CFCl_3 (0.00 ppm) for fluorine chemical shifts. GC analyses were performed on Thermo Scientific Trace 1310. GC-MS analyses were performed on Agilent GC-MS 6890N. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. Compounds **1a**, **1aa-1ad**, **2Ab**, **4**, **6**, and **9** were prepared using literature methods.¹⁻³ All the other chemicals were purchased from commercial companies and used as received unless otherwise specified.

2. Preparation of Starting Materials

Synthesis of 1a, 1a-1b, 4, 6 and 9. These compounds were prepared using the reported procedures.^{1,2} *A typical procedure:* To a stirring solution of substituted *o*-carborane (5.0 mmol) in diethyl ether (40 mL) at 0 °C was added dropwise a solution of *n*-butyllithium in hexane (3.3 mL, 1.6 M, 5.3 mmol) under argon atmosphere. The suspension was stirred at room temperature for 1 h, then cooled to 0 °C, to which was added I₂ (1.300 g, 5.3 mmol) in a single portion. The resulting solution was stirred at room temperature for 1 h, and then quenched with 5% aqueous Na₂S₂O₃ solution (20 mL). The organic phase was separated, and the aqueous solution was extracted with diethyl ether (2 x 15 mL). The ether solutions were combined and dried over Na₂SO₄. The clear colorless solution was concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give the product **1, 4, 6 or 9**.

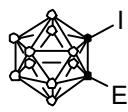
Synthesis of 1ac. To a stirring solution of *o*-carborane (0.720 g, 5.0 mmol) in diethyl ether (40 mL) at 0 °C in an ice-water bath was added dropwise a solution of *n*-butyllithium in hexane (3.1 mL, 1.6 M, 5.0 mmol) under argon atmosphere. The suspension was stirred at room temperature for 1 h, then cooled again to 0 °C, to which trimethyl chlorosilane (0.6 mL, 5.0 mmol) was added slowly. The resulting solution was stirred at room temperature for 1 h, then cooled to 0 °C, to which was added slowly a solution of *n*-butyllithium in hexane (3.1 mL, 1.6 M, 5.0 mmol) under argon atmosphere. The suspension was stirred at room temperature for 1 h, then cooled again to 0 °C, to which I₂ (1.300 g, 5.0 mmol) was added in a single portion. The resulting solution was stirred at room temperature for 1 h, then quenched with 5% aqueous Na₂S₂O₃ (20.0 mL). The organic phase was separated, and the aqueous solution was extracted with diethyl ether (2 x 15 mL). The ether solutions were combined and dried over Na₂SO₄. The clear colorless solution was concentrated to dryness in vacuo. The residue was dissolved in hexane and recrystallized to give **1ac**.

Synthesis of 1ad. 1-I-*o*-carborane was prepared using trimethylsilyl (TMS) as the protecting group through a one-pot reaction. To a stirring solution of *o*-carborane (0.720 g, 5.0 mmol) in diethyl ether (40 mL) at 0 °C in an ice-water bath was slowly added a solution of *n*-butyllithium in hexane (3.1 mL, 1.6 M, 5.0 mmol) under argon atmosphere. The suspension was stirred at room temperature for 1 h, then cooled to 0 °C, to which was slowly added trimethyl chlorosilane (0.6 mL, 5.0 mmol). The resulting solution was stirred at room temperature 1 h, then cooled again to 0 °C, to which was slowly added a solution of *n*-butyllithium in hexane (3.1 mL, 1.6 M, 5.0 mmol) under argon atmosphere. The suspension was stirred

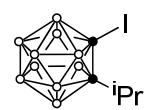
at room temperature for 1 h, then cooled again to 0 °C, to which was added I₂ (1.300 g, 5.0 mmol) in a single portion. The resulting solution was stirred at room temperature for 1 h, then quenched with 5% aqueous Na₂S₂O₃ (20 mL). The organic phase was dried over Na₂SO₄ and concentrated to dryness in vacuo. The residue was dissolved in acetone (20 mL) and K₂CO₃ (3.500 g, 25.0 mmol) was added. The suspension was stirred at room temperature for 2 h, filtered and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give **1ad**.



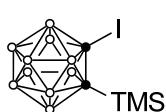
1a: White solid. Yield: 89%. ¹H NMR (400 MHz, CDCl₃): δ 2.17 (s, 3H) (CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -3.12 (1B), -5.30 (1B), -6.65 (2B), -7.08 (2B), -8.67 (2B), -9.92 (2B). These data are very similar to the reported ones.^{1,2}



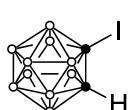
1aa: White solid. Yield: 87%. ¹H NMR (400 MHz, CDCl₃): δ 2.38 (q, *J* = 7.5 Hz, 2H) (CH₂), 1.20 (t, *J* = 7.5 Hz, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 80.22 (cage C), 34.43 (CH₂), 17.46 (cage C), 14.32 (CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -3.61 (1B), -4.47 (1B), -7.50 (4B), -8.78 (2B), -11.20 (2B). HRMS (EI): *m/z* calcd for C₄H₁₅B₁₀I [M]⁺: 298.1218. Found: 298.1221. These data are very similar to the reported ones.²



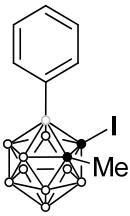
1ab: White solid. Yield: 64%. ¹H NMR (400 MHz, CDCl₃): δ 2.39 – 2.29 (m, 1H) (CH), 1.26 (d, *J* = 6.9 Hz, 6H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 85.03 (cage C), 37.57 (CH), 24.43 (CH₃), 20.42 (cage C). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -3.76 (2B), -7.59 (2B), -8.53 (4B), -12.07 (2B). HRMS (EI): *m/z* calcd for C₅H₁₇B₁₀I [M]⁺: 312.1373. Found: 312.1378.



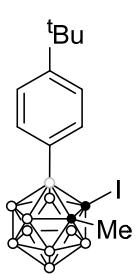
1ac: White solid. Yield: 69%. ¹H NMR (400 MHz, CDCl₃): δ 0.49 – 0.34 (m, 9H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 73.64, 8.28 (cage C), 0.20 (CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ 0.63 (1B), -2.41 (1B), -5.63 (2B), -7.23 (2B), -8.53 (2B), -10.36 (2B). HRMS (EI): *m/z* calcd for C₅H₁₉B₁₀ISi [M-H+CH₃OH]⁻: 373.1498. Found: 373.1496.



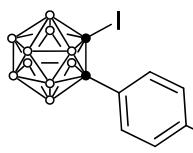
1ad: White solid. Yield: 71%. ¹H NMR (400 MHz, CDCl₃): δ 3.78 (s, 1H) (cage H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 66.12, 1.17 (cage C). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -1.29 (1B), -4.56 (1B), -8.62 (4B), -9.51 (2B), -12.27 (2B). HRMS (EI): *m/z* calcd for C₂H₁₁B₁₀I [M]⁺: 270.0904. Found: 270.0900. These data are very similar to the reported ones.²



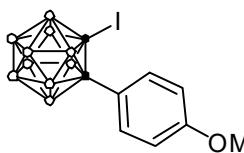
4: White solid. Yield: 93%. ^1H NMR (400 MHz, CDCl_3): δ 7.71 – 7.62 (m, 2H), 7.50 – 7.40 (m, 3H) (aromatic *H*), 1.99 (s, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 134.76, 129.94, 128.13 (aromatic *C*), 74.61 (cage *C*), 26.92 (CH_3), 22.77 (cage *C*). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -3.40 (3B), -4.79 (1B), -8.37 (3B), -11.29 (3B). HRMS (EI): *m/z* calcd for $\text{C}_9\text{H}_{17}\text{B}_{10}\text{I} [\text{M}]^+$: 360.1373. Found: 360.1376.



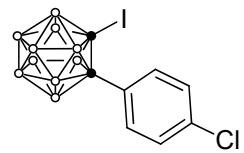
6: White solid. Yield: 65%. ^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, $J = 8.3$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H) (aromatic *H*), 1.99 (s, 3H), 1.35 (s, 9H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.92, 134.56, 125.09 (aromatic *C*, carbon signal adjacent to B was not observed), 74.58 (cage *C*), 34.87 ((CH_3)*C*), 31.36 ((CH_3)*C*), 26.96 (CH_3), 22.96 (cage *C*). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -3.50 (3B), -4.96 (1B), -8.40 (3B), -11.48 (3B). HRMS (EI): *m/z* calcd for $\text{C}_{13}\text{H}_{25}\text{B}_{10}\text{I} [\text{M}+\text{Cl}]^-$: 451.1708. Found: 451.1702.



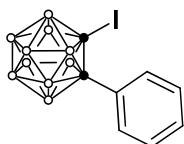
9a: White solid. Yield: 81%. ^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, $J = 8.6$ Hz, 2H), 7.42 (d, $J = 8.6$ Hz, 2H) (aromatic *H*), 1.34 (s, 9H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 154.65, 131.16, 130.35, 125.84 (aromatic *C*), 84.70 (cage *C*), 34.96 ((CH_3)*C*), 31.23 ((CH_3)*C*), 20.72 (cage *C*). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -3.05 (2B), -7.63 (2B), -9.30 (6B). HRMS (EI): *m/z* calcd for $\text{C}_{12}\text{H}_{28}\text{B}_{10}\text{I} [\text{M}]^+$: 402.1848. Found: 402.1847.



9b: White solid. Yield: 83%. ^1H NMR (400 MHz, CDCl_3): δ 7.56 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H) (aromatic *H*), 3.86 (s, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 161.73, 133.00, 125.62, 114.06 (aromatic *C*), 85.09 (cage *C*), 55.61 (CH_3), 21.86 (cage *C*). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -2.70 (1B), -3.79 (1B), -7.41 (2B), -9.14 (6B). HRMS (EI): *m/z* calcd for $\text{C}_9\text{H}_{17}\text{B}_{10}\text{IO} [\text{M}]^+$: 376.1326. Found: 376.1326.

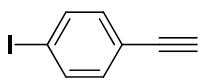


9c: White solid. Yield: 76%. ^1H NMR (400 MHz, CDCl_3): δ 7.58 (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H) (aromatic *H*). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 137.83, 132.72, 131.82, 129.18 (aromatic *C*), 83.33, 19.72 (cage *C*). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -2.59 (2B), -7.12 (2B), -8.76 (4B), -9.67 (2B). HRMS (APCI): *m/z* calcd for $\text{C}_8\text{H}_{14}\text{B}_{10}\text{ClII} [\text{M}+\text{Cl}]^-$: 416.0498. Found: 416.0495.



9d: White solid. Yield: 85%. ^1H NMR (400 MHz, CDCl_3): δ 7.65 (d, $J = 7.4$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.4$ Hz, 2H) (aromatic H). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -2.64 (2B), -7.16 (2B), -8.78 (4B), -9.64 (2B). These data are very similar to the reported ones.^{1,2}

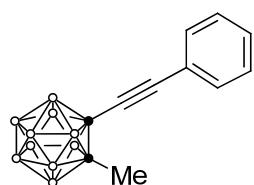
Synthesis of 2Ab. This compound was prepared using the reported procedures.³ To a stirring solution of [(4-iodophenyl)ethynyl]trimethylsilane (300.0 mg, 1.0 mmol) in chloroform (10 mL), was added methanol (10 mL) and potassium carbonate (276.0 mg, 2.0 mmol). The mixture was stirred at room temperature for 4 h, and then water (15 mL) was added. The organic phase was separated, and the aqueous solution was extracted with diethyl ether (2 x 15 mL). The organic phases were combined and dried over Na_2SO_4 . After removal of Na_2SO_4 , the clear colorless solution was concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give the product **2Ab**.



2Ab: White solid. Yield: 83%. ^1H NMR (400 MHz, CDCl_3): δ 7.69 – 7.65 (m, 2H), 7.23 – 7.19 (m, 2H) (aromatic H), 3.13 (s, 1H) (alkynyl H). These data are very similar to the reported ones.³

3. Preparation of 1-Alkynyl-*o*-Carboranes (3Aa-3Be).

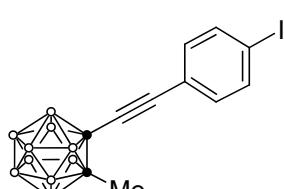
Iodocarborane **1** (0.1 mmol), alkyne (0.25 mmol) and NaHCO₃ (10.1 mg, 0.12 mmol) were mixed in CH₂Cl₂ (1 mL) in a 10 mL quartz-Schlenk flask equipped with a magnetic stirring bar. Under an atmosphere of argon, the reaction mixture was irradiated under 125 W UV (365 nm) lamp for 36-48 h with stirring (the lamp was placed 10 cm away from the flask with an exhaust fan to cool the reaction inside a fume hood at room temperature). Then, the reaction was stopped, and the resulting mixture was examined by GC-MS analysis. The reaction was quenched with water (10 mL) and extracted with diethyl ether (15 mL×3). The ether solutions were combined and dried over Na₂SO₄. After removal of Na₂SO₄, the clear colorless solution was concentrated to dryness in vacuo. Then, the residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give the desired product **3**.



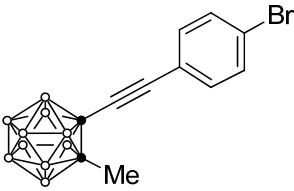
3Aa: White solid. Yield: 76%. ¹H NMR (400 MHz, acetone-d₆): δ 7.61 – 7.57 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H) (aromatic H), 2.33 (s, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, acetone-d₆): δ 133.21, 131.35, 129.69, 120.42 (aromatic C), 83.92, 81.93 (alkynyl C), 78.69, 67.89 (cage C), 24.20 (CH₃). ¹¹B{¹H} NMR (128 MHz, acetone-d₆): δ -3.49 (1B), -6.89 (1B), -8.25 (2B), -10.47 (6B). HRMS (EI): *m/z* calcd for C₁₁H₁₈B₁₀ [M]⁺: 258.2406. Found: 258.2406.

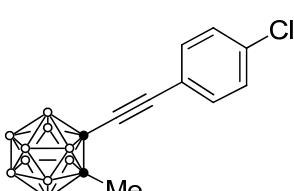


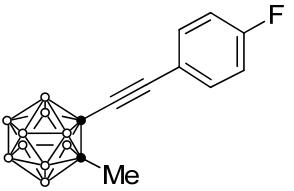
Figure S1. Molecular structure of **3Aa**

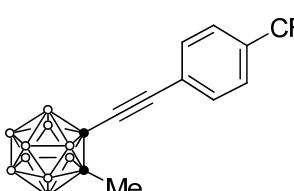


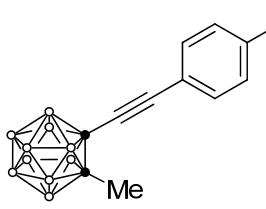
3Ab: White solid. Yield: 65%. ¹H NMR (500 MHz, acetone-d₆): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H) (aromatic H), 2.32 (s, 3H) (CH₃). ¹³C{¹H} NMR (126 MHz, acetone-d₆): δ 138.95, 134.77, 120.02, 97.47 (aromatic C), 83.14, 82.96 (alkynyl C), 78.73, 67.65 (cage C), 24.21 (CH₃). ¹¹B{¹H} NMR (160 MHz, acetone-d₆): δ -2.10 (1B), -5.60 (1B), -7.06 (2B), -9.17 (6B). HRMS (EI): *m/z* calcd for C₁₁H₁₇B₁₀I [M]⁻: 384.1389. Found: 384.1386.

 **3Ac:** White solid. Yield: 76%. ^1H NMR (400 MHz, acetone-d₆) δ 7.65 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H) (aromatic H), 2.32 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 134.98, 132.95, 125.36, 119.62 (aromatic C), 82.96, 82.74 (alkynyl C), 78.73, 67.58 (cage C), 24.21 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -2.30 (1B), -5.83 (1B), -7.26 (2B), -9.39 (6B). HRMS (EI): *m/z* calcd for C₁₁H₁₇B₁₀Br [M]⁺: 337.1503. Found: 337.1504.

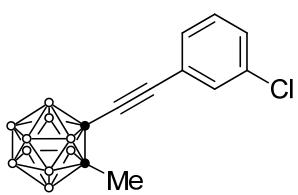
 **3Ad:** White solid. Yield: 80%. ^1H NMR (400 MHz, acetone-d₆): δ 7.62 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H) (aromatic H), 2.32 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 137.02, 134.88, 129.99, 119.22 (aromatic C), 82.84, 82.67 (alkynyl C), 78.75, 67.61 (cage C), 24.21 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -2.33 (1B), -5.83 (1B), -7.25 (2B), -9.40 (6B). HRMS (EI): *m/z* calcd for C₁₁H₁₇B₁₀Cl [M]⁺: 292.2016. Found: 292.2015.

 **3Ae:** White solid. Yield: 78%. ^1H NMR (400 MHz, acetone-d₆): δ 7.69 – 7.66 (m, 2H), 7.26 – 7.21 (m, 2H) (aromatic H), 2.32 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 164.54 (d, $^1J_{\text{C-F}} = 250.8$ Hz), 135.80 (d, $^3J_{\text{C-F}} = 8.9$ Hz), 117.00 (d, $^2J_{\text{C-F}} = 22.6$ Hz), 116.80 (d, $^4J_{\text{C-F}} = 3.5$ Hz) (aromatic C), 82.89, 81.77 (alkynyl C), 78.72, 67.79 (cage C), 24.21 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.44 (1B), -6.90 (1B), -8.29 (2B), -10.47 (6B). $^{19}\text{F}\{\text{H}\}$ NMR (377 MHz, acetone-d₆): δ -108.87. HRMS (EI): *m/z* calcd for C₁₁H₁₇B₁₀F [M]⁺: 276.2312. Found: 276.2315.

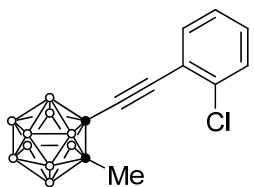
 **3Af:** White solid. Yield: 70%. ^1H NMR (400 MHz, acetone-d₆): δ 7.84 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H) (aromatic H), 2.35 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 134.03, 132.15 (d, $^2J_{\text{C-F}} = 32.7$ Hz), 126.57 (q, $^3J_{\text{C-F}} = 3.8$ Hz) (aromatic C), 124.77 (d, $^1J_{\text{C-F}} = 272.7$ Hz) (CF₃), 124.64 (aromatic C), 83.98, 82.08 (alkynyl C), 78.77, 67.18 (cage C), 24.24 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -1.97 (1B), -5.66 (1B), -7.11 (2B), -9.19 (6B). $^{19}\text{F}\{\text{H}\}$ NMR (377 MHz, acetone-d₆): δ -63.63. HRMS (EI): *m/z* calcd for C₁₂H₁₇B₁₀F₃ [M]⁺: 326.2280. Found: 326.2283.



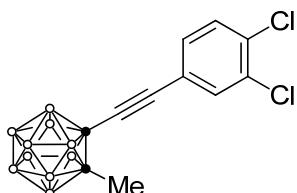
3Ag: White solid. Yield: 62%. ^1H NMR (400 MHz, acetone-d₆): δ 8.04 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H) (aromatic H), 3.90 (s, 3H) (COOCH₃), 2.34 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, acetone-d₆): δ 166.27 (COOCH₃), 133.42, 132.48, 130.38, 124.88 (aromatic C), 84.21, 82.72 (alkynyl C), 78.72, 67.35 (cage C), 52.70 (COOCH₃), 24.23 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (160 MHz, acetone-d₆): δ -2.60 (1B), -6.25 (1B), -7.66 (2B), -9.77 (6B). HRMS (ESI): *m/z* calcd for C₁₃H₂₀B₁₀O₂ [M-H]⁻: 315.2400. Found: 315.2392.



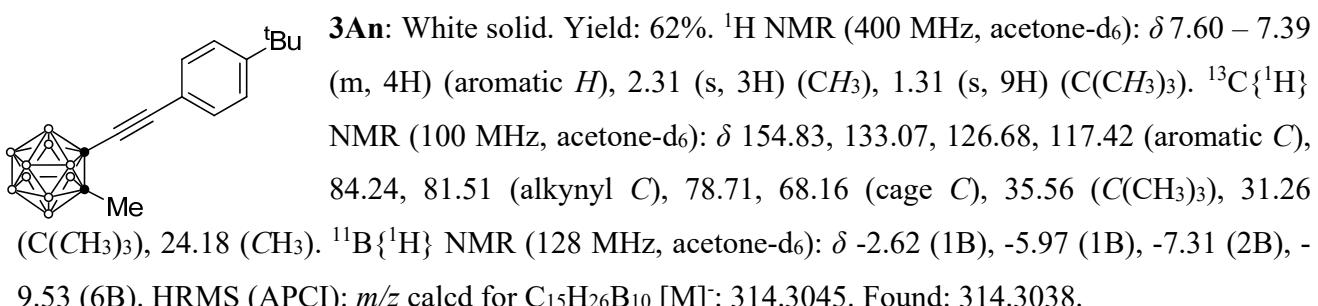
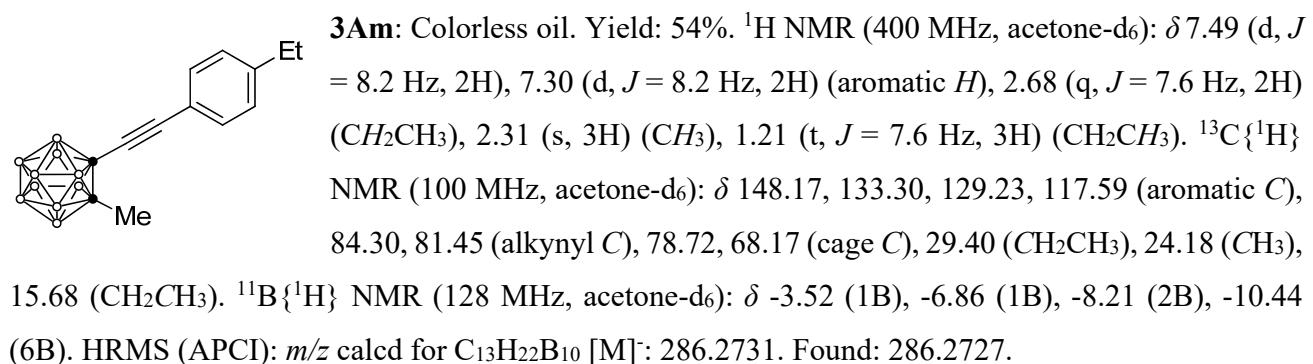
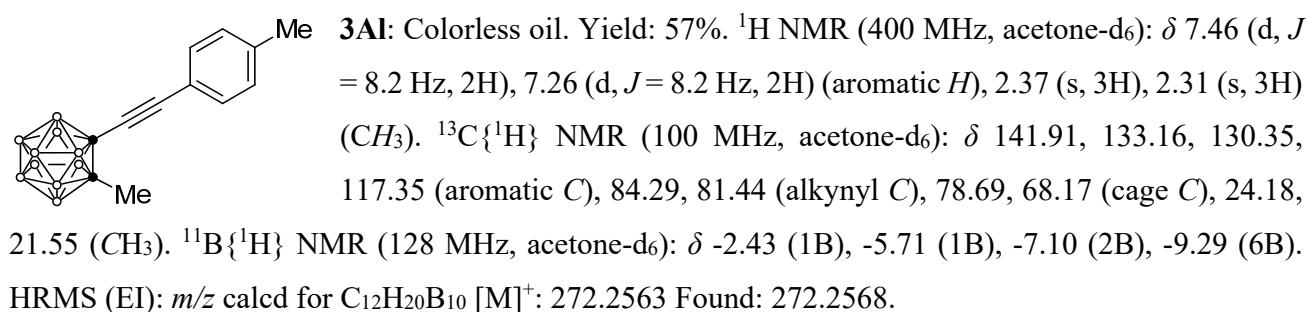
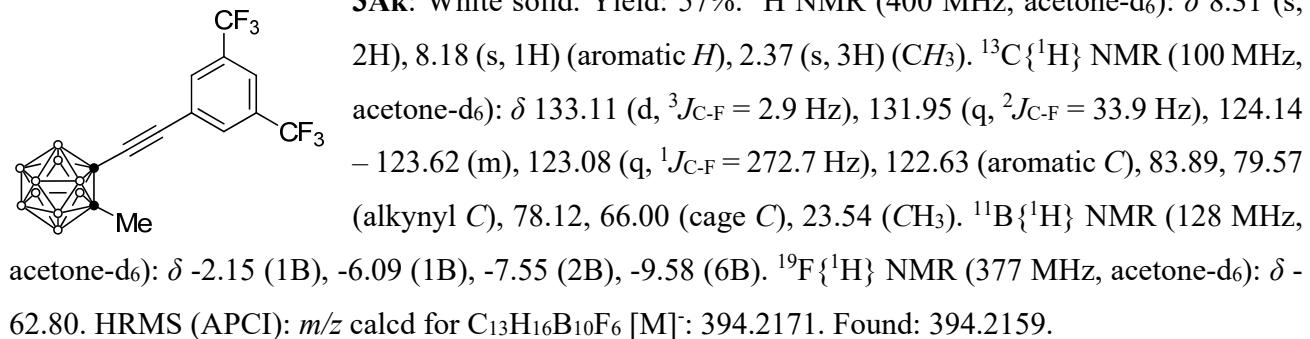
3Ah: White solid. Yield: 74%. ^1H NMR (400 MHz, acetone-d₆): δ 7.65 (s, 1H), 7.57 – 7.55 (m, 2H), 7.48 (t, $J = 8.8$ Hz, 1H) (aromatic H), 2.34 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 134.98, 132.79, 131.78, 131.54, 131.44, 122.38 (aromatic C), 82.96, 82.13 (alkynyl C), 78.79, 67.39 (cage C), 24.25 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.23 (1B), -6.86 (1B), -8.26 (2B), -10.41 (6B). HRMS (EI): *m/z* calcd for C₁₁H₁₇B₁₀Cl [M]⁺: 292.2016. Found: 292.2013.

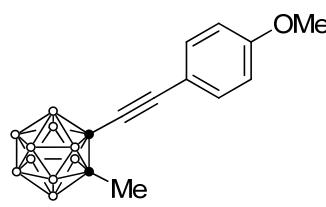


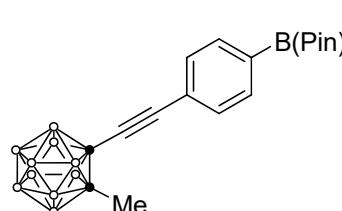
3Ai: White solid. Yield: 63%. ^1H NMR (400 MHz, acetone-d₆): δ 7.69 (dd, $J = 7.7$, 1.1 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.42 (td, $J = 7.6$, 1.4 Hz, 1H) (aromatic H), 2.35 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 137.19, 135.12, 132.82, 130.48, 128.23, 120.44 (aromatic C), 86.78, 80.33 (alkynyl C), 78.74, 67.48 (cage C), 24.33 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.21 (1B), -6.86 (1B), -8.27 (2B), -10.38 (6B). HRMS (APCI): *m/z* calcd for C₁₁H₁₇B₁₀Cl [M]: 292.2031. Found: 292.2028.

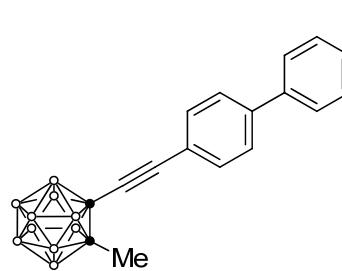


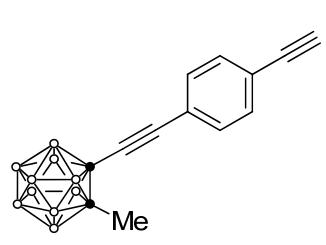
3Aj: White solid. Yield: 75%. ^1H NMR (400 MHz, acetone-d₆): δ 7.83 (d, $J = 1.4$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.57 (dd, $J = 8.3$, 1.4 Hz, 1H) (aromatic H), 2.33 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 135.25, 134.86, 133.27, 133.03, 131.94, 120.84 (aromatic C), 83.64, 81.19 (alkynyl C), 78.77, 67.19 (cage C), 24.24 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.09 (1B), -6.82 (1B), -8.28 (2B), -10.35 (6B). HRMS (APCI): *m/z* calcd for C₁₁H₁₆B₁₀Cl₂ [M]⁻: 326.1644. Found: 326.1636.

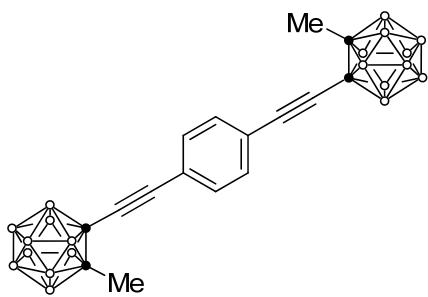



3Ao: Colorless oil. Yield: 57%. ^1H NMR (400 MHz, acetone-d₆): δ 7.53 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H) (aromatic *H*), 3.85 (s, 3H) (OCH₃), 2.30 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 162.30, 134.96, 115.29, 112.03 (aromatic *C*), 84.45, 80.86 (alkynyl *C*), 78.69, 68.46 (cage *C*), 55.87 (OCH₃), 24.15 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -2.60 (1B), -5.80 (1B), -7.14 (2B), -9.37 (6B). HRMS (EI): *m/z* calcd for C₁₂H₂₀B₁₀O [M]⁺: 288.2512. Found: 288.2512.


3Ap: White solid. Yield: 67%. ^1H NMR (400 MHz, acetone-d₆): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H) (aromatic *H*), 2.33 (s, 3H), 1.34 (s, 12H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 135.55, 132.38, 122.99 (aromatic *C*), 84.99 (OC), 83.75, 83.02 (alkynyl *C*), 78.72, 67.75 (cage *C*), 25.16, 24.21 (CH₃) (carbon signal adjacent to B was not observed). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ 30.69 (1B), -3.38 (1B), -6.87 (1B), -8.27 (2B), -10.41 (6B). HRMS (APCI): *m/z* calcd for C₁₇H₂₉B₁₁O₂ [M]⁻: 384.3268. Found: 384.3269.


3Aq: White solid. Yield: 65%. ^1H NMR (400 MHz, acetone-d₆): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.70 – 7.66 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H) (aromatic *H*), 2.34 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 143.77, 140.34, 133.82, 129.90, 129.05, 128.05, 127.80, 119.22 (aromatic *C*), 83.88, 82.54 (alkynyl *C*), 78.75, 67.98 (cage *C*), 24.21 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -2.46 (1B), -5.87 (1B), -7.22 (2B), -9.40 (6B). HRMS (APCI): *m/z* calcd for C₁₇H₂₂B₁₀ [M]⁻: 334.2739. Found: 334.2727.


3Ar: Colorless oil. Yield: 53%. ^1H NMR (400 MHz, acetone-d₆): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H) (aromatic *H*), 3.90 (s, 1H) (alkynyl *H*), 2.33 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 133.38, 133.08, 125.23, 120.76 (aromatic *C*), 83.57, 83.20, 83.10, 82.29 (alkynyl *C*), 78.75, 67.63 (cage *C*), 24.22 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.34 (1B), -6.89 (1B), -8.30 (2B), -10.42 (6B). HRMS (APCI): *m/z* calcd for C₁₃H₁₈B₁₀ [M]⁻: 282.2424. Found: 282.2414.



3As: White solid. Yield: 13%. ^1H NMR (400 MHz, acetone-d₆): δ 7.67 (s, 4H) (aromatic H), 2.33 (s, 6H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 133.56, 122.36 (aromatic C), 84.32, 82.71 (alkynyl C), 78.76, 67.41 (cage C), 24.22 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -2.11 (1B), -5.81 (1B), -7.20 (2B), -9.28 (6B). HRMS (APCI): *m/z* calcd for C₁₆H₃₀B₂₀ [M]⁻: 438.4369. Found: 438.4357.

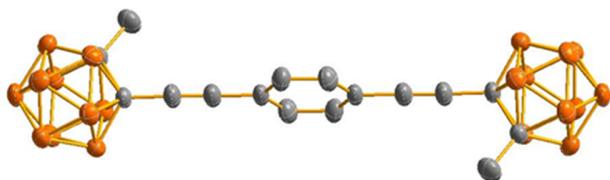
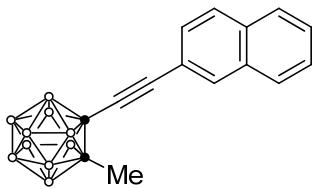


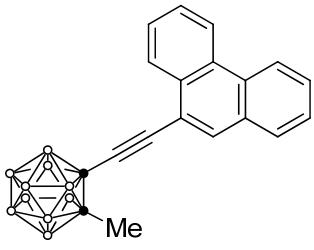
Figure S2. Molecular structure of **3As**



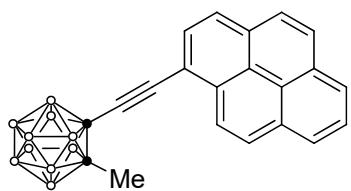
3At: White solid. Yield: 58%. ^1H NMR (400 MHz, acetone-d₆): δ 8.23 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 3H), 7.70 – 7.50 (m, 3H) (aromatic H), 2.37 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 134.60, 134.15, 133.66, 129.49, 128.90, 128.83, 128.76, 128.72, 128.08, 117.62 (aromatic C), 84.34, 82.12 (alkynyl C), 78.81, 68.03 (cage C), 24.25 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -2.53 (1B), -5.95 (1B), -7.31 (2B), -9.48 (6B). HRMS (APCI): *m/z* calcd for C₁₅H₂₀B₁₀ [M]⁻: 308.2576. Found: 308.2569.



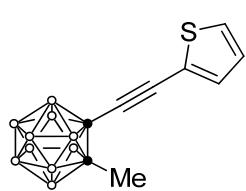
Figure S3. Molecular structure of **3At**



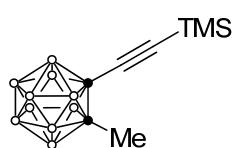
3Au: White solid. Yield: 43%. ^1H NMR (400 MHz, acetone-d₆): δ 8.87 – 8.84 (m, 1H), 8.81 (d, J = 8.3 Hz, 1H), 8.27 (s, 1H), 8.26 – 8.23 (m, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.82 – 7.76 (m, 3H), 7.70 (t, J = 7.4 Hz, 1H) (aromatic H), 2.43 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 135.47, 131.74, 131.47, 131.26, 130.92, 129.90, 129.80, 128.73, 128.67, 128.38, 126.66, 124.23, 123.75, 116.58 (aromatic C), 86.29, 82.48 (alkynyl C), 78.82, 68.08 (cage C), 24.40 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.35 (1B), -6.77 (1B), -8.15 (2B), -10.32 (6B). HRMS (APCI): m/z calcd for C₁₉H₂₂B₁₀ [M]⁺: 358.2734. Found: 358.2731.



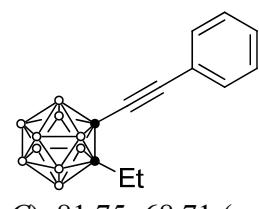
3Av: Pale yellow solid. Yield: 39%. ^1H NMR (400 MHz, acetone-d₆): δ 8.42 – 8.39 (m, 4H), 8.31 – 8.25 (m, 3H), 8.21 (d, J = 9.0 Hz, 1H), 8.16 (t, J = 7.7 Hz, 1H) (aromatic H), 2.48 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 133.75, 133.68, 132.04, 131.69, 131.40, 130.68, 130.34, 128.06, 127.82, 127.49, 127.45, 125.65, 124.97, 124.87, 124.57, 114.15 (aromatic C), 87.46, 83.33 (alkynyl C), 24.44 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.28 (1B), -6.74 (1B), -8.03 (2B), -10.27 (6B). HRMS (APCI): m/z calcd for C₂₁H₂₂B₁₀ [M+H+CH₃OH]⁺: 415.3060. Found: 415.3059.



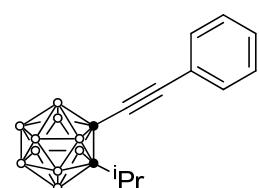
3Aw: Colorless oil. Yield: 23%. ^1H NMR (400 MHz, acetone-d₆): δ 7.71 (dd, J = 5.1, 1.1 Hz, 1H), 7.54 (dd, J = 3.7, 1.1 Hz, 1H), 7.14 (dd, J = 5.1, 3.7 Hz, 1H) (aromatic H), 2.29 (s, 3H) (CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 136.65, 131.72, 128.65, 119.64 (aromatic C), 85.57, 78.86 (alkynyl C), 77.60, 67.93 (cage C), 24.16 (CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -2.19 (1B), -5.76 (1B), -7.25 (2B), -9.34 (6B). HRMS (APCI): m/z calcd for C₉H₁₆B₁₀S [M]⁺: 264.1981. Found: 264.1980.



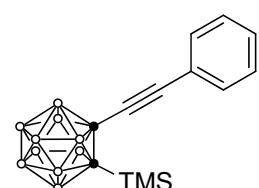
3Ax: Colorless oil. Yield: 40%. ^1H NMR (400 MHz, acetone-d₆): δ 2.24 (s, 3H) (CH₃), 0.22 (s, 9H) (TMS H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 96.81, 90.78 (alkynyl C), 78.36, 67.44 (cage C), 24.02 (CH₃), -0.75 (TMS C). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -2.26 (1B), -5.72 (1B), -7.18 (2B), -9.30 (6B). HRMS (APCI): m/z calcd for C₈H₂₂B₁₀Si [M]⁺: 254.2505. Found: 254.2498.



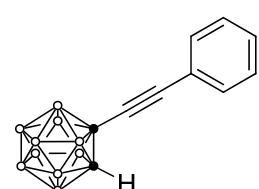
3Aaa: Colorless oil. Yield: 75%. ^1H NMR (400 MHz, acetone-d₆): δ 7.59 – 7.56 (m, 2H), 7.55 – 7.49 (m, 1H), 7.47 – 7.42 (m, 2H) (aromatic H), 2.62 (q, J = 7.5 Hz, 2H) (CH₂CH₃), 1.24 (t, J = 7.5 Hz, 3H) (CH₂CH₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 133.19, 131.33, 129.69, 120.41 (aromatic C), 84.32, 83.95 (alkynyl C), 81.75, 68.71 (cage C), 30.39 (CH₂CH₃), 14.30 (CH₂CH₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.76 (1B), -6.12 (1B), -9.12 (2B), -10.45 (4B), -11.88 (2B). HRMS (APCI): m/z calcd for C₁₂H₂₀B₁₀ [M]⁺: 272.2574. Found: 272.2572.



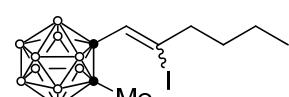
3Aab: Colorless oil. Yield: 44%. ^1H NMR (400 MHz, acetone-d₆): δ 7.59 – 7.55 (m, 2H), 7.54 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H) (aromatic H), 2.92 – 2.76 (m, 1H) (CH(CH₃)₂), 1.32 (d, J = 6.9 Hz, 6H) (CH(CH₃)₂). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 133.20, 131.36, 129.72, 120.42 (aromatic C), 89.47, 84.20 (alkynyl C), 81.68, 69.87 (cage C), 33.95 (CH(CH₃)₂), 24.31 (CH(CH₃)₂). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.06 (1B), -4.34 (1B), -9.32 (6B), -11.69 (2B). HRMS (APCI): m/z calcd for C₁₃H₂₂B₁₀ [M]⁺: 286.2731. Found: 286.2727.



3Aac: White solid. Yield: 55%. ^1H NMR (400 MHz, acetone-d₆): δ 7.44 – 7.54 (m, 5H) (aromatic H), 0.44 (s, 9H) (Si(CH₃)₃). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, acetone-d₆): δ 132.91, 131.35, 129.85, 120.40 (aromatic C), 84.30, 81.60 (alkynyl C), 76.15, 66.10 (cage C), -0.26 (Si(CH₃)₃). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -1.16 (1B), -2.42 (1B), -8.49 (4B), -9.54 (2B), -11.30 (2B). HRMS (APCI): m/z calcd for C₁₃H₂₄B₁₀Si [M]⁺: 316.2658. Found: 316.2651.



3Aad: Colorless oil. Yield: 49%. ^1H NMR (400 MHz, acetone-d₆): δ 7.40 – 7.51 (m, 5H) (aromatic H), 5.17 (s, 1H) (cage H). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, acetone-d₆): δ -3.28 (1B), -4.63 (1B), -9.84 (2B), -10.77 (4B), -13.47 (2B). This is a known compound.⁶



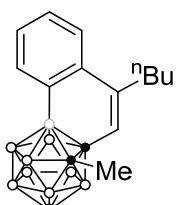
3Ba: Yield: 70%. cis: trans = 3.4: 1. The structures of stereoisomers were determined by ^1H , ^1H -NOESY. For **3Ba-cis**: Colorless oil. ^1H NMR (500 MHz, CDCl₃): δ 5.96 (s, 1H) (olefinic H), 2.65 (t, J = 7.3 Hz, 2H) (CH₂), 1.94 (s, 3H) (CH₃), 1.65 – 1.45 (m, 2H), 1.57 – 1.51 (m, 2H) (CH₂), 0.92 (t, J = 7.3 Hz, 3H) (CH₃) (the signals of

cage carbon atoms were not observed). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, CDCl_3): δ 125.29, 116.38 (olefinic *C*), 49.25, 31.65, 23.73, 21.36, 13.91 (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (160 MHz, CDCl_3): δ -2.91 (1B), -6.53 (1B), -10.83 (8B). HRMS (APCI): m/z calcd for $\text{C}_9\text{H}_{23}\text{B}_{10}\text{I} [\text{M}]^+$: 366.1858. Found: 366.1856.

For **3Ba-trans**: White solid. ^1H NMR (400 MHz, CDCl_3): δ 6.41 (s, 1H) (olefinic *H*), 2.77 – 2.66 (m, 2H) (CH_2), 1.99 (s, 3H) (CH_3), 1.63 – 1.48 (m, 2H), 1.47 – 1.32 (m, 2H) (CH_2), 0.96 (t, $J = 7.2$ Hz, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 130.94, 121.80 (olefinic *C*), 77.00, 76.46 (cage *C*), 39.28, 32.58, 23.77, 21.95, 14.08 (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -2.07 (1B), -4.70 (1B), -7.98 (2B), -9.50 (6B). HRMS (APCI): m/z calcd for $\text{C}_9\text{H}_{23}\text{B}_{10}\text{I} [\text{M}]^+$: 366.1858. Found: 366.1852.

4. Preparation of *o*-carborane-fused cycloids (**5**, **7** and **10**).

Iodocarborane **4** (0.3 mmol), alkyne (6.0 mmol) and 2,6-lutidine (42 μL , 0.36 mmol) were mixed in CH_2Cl_2 (3.0 mL) in a 10 mL quartz-Schlenk flask equipped with a magnetic stirring bar. Under an atmosphere of argon, the reaction mixture was irradiated with 36 W UV (365 nm) lamp for 48 h with stirring (the lamp was placed 10 cm away from the flask with an exhaust fan to cool the reaction inside a fume hood at room temperature). Then, the reaction was stopped, and the resulting mixture was examined by GC-MS analysis. The reaction was quenched with water (10 mL) and extracted with diethyl ether (15 mL \times 3). The ether solutions were combined and dried over Na_2SO_4 . After removal of Na_2SO_4 , the clear colorless solution was concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give the desired product **5**.



5Ba: White solid. Yield: 83%. ^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, $J = 7.2$ Hz, 1H), 7.65 (d, $J = 7.7$ Hz, 1H), 7.57 – 7.43 (m, 2H), 5.94 (s, 1H) (aromatic *H*), 2.64 (t, $J = 7.7$ Hz, 2H), 1.63 – 1.51 (m, 2H), 1.47 – 1.38 (m, 2H) (CH_2), 1.29 (s, 3H), 0.96 (t, $J = 7.3$ Hz, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.26, 135.23, 134.42, 129.96, 129.20, 126.26, 117.75 (aromatic *C*), 75.44, 69.36 (cage *C*), 34.34, 31.95, 22.87, 20.45, 14.04 (CH_2 & CH_3) (carbon signal adjacent to B was not observed). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -7.58 (3B), -10.54 (3B), -12.21 (1B), -13.54 (3B). HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{26}\text{B}_{10} [\text{M}]^+$: 314.3032. Found: 314.3032.

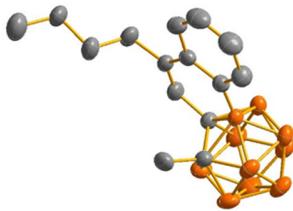
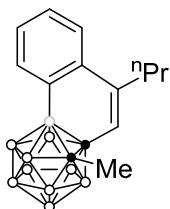
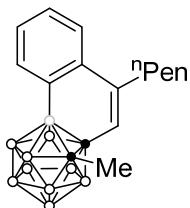


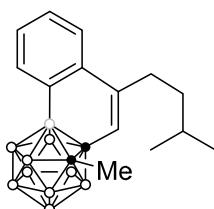
Figure S4. Molecular structure of **5Ba**



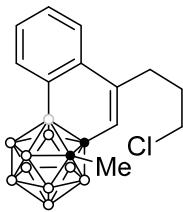
5Bb: White solid. Yield: 76%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (dd, $J = 7.1, 1.8$ Hz, 1H), 7.65 (d, $J = 7.7$ Hz, 1H), 7.56 – 7.31 (m, 2H) (aromatic H), 5.95 (s, vinyl H) (aromatic H), 2.63 (t, $J = 7.3$ Hz, 2H), 1.74 – 1.57 (m, 2H) (CH_2), 1.30 (s, 3H), 1.01 (t, $J = 7.3$ Hz, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 146.92, 135.24, 134.40, 129.96, 129.20, 126.26, 117.90 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 75.42, 69.34 (cage C), 36.56, 22.88, 20.47, 14.13 (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -7.28 (3B), -10.12 (3B), -11.84 (1B), -13.14 (3B). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{24}\text{B}_{10}^-$ [M]: 300.2894 Found: 300.2885.



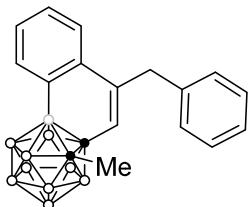
5Bc: Semisolid. Yield: 83%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (dd, $J = 7.1, 1.8$ Hz, 1H), 7.65 (d, $J = 7.7$ Hz, 1H), 7.60 – 7.41 (m, 2H) (aromatic H), 5.95 (s, 1H) (s, vinyl H), 2.64 (t, $J = 7.8$ Hz, 2H), 1.69 – 1.50 (m, 2H), 1.41 – 1.32 (m, 4H) (CH_2), 0.92 (t, $J = 7.0$ Hz, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.27, 135.23, 134.41, 129.96, 129.19, 126.24, 117.73 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 75.44, 69.36 (cage C), 34.57, 31.94, 29.51, 22.59, 20.45, 14.19 (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.89 (3B), -9.89 (3B), -11.55 (1B), -12.87 (3B). HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{28}\text{B}_{10}^-$ [M-H]: 327.3129. Found: 327.3131.



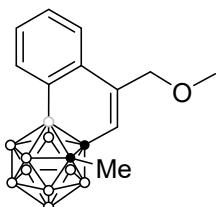
5Bd: White solid. Yield: 62%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 6.7$ Hz, 1H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.59 – 7.36 (m, 2H) (aromatic H), 5.95 (s, 1H) (vinyl H), 2.77 – 2.45 (m, 2H) (CH_2), 1.77 – 1.59 (m, 1H) (CH), 1.52 – 1.36 (m, 2H) (CH_2), 1.30 (s, 3H), 0.98 (d, $J = 6.6$ Hz, 6H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.66, 135.26, 134.40, 129.98, 129.21, 126.21, 117.66 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 75.44, 69.37 (cage C), 39.14, 32.57, 28.49, 22.66, 22.57, 20.43 (CH & CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.75 (3B), -9.86 (3B), -11.55 (1B), -12.83 (3B). HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{28}\text{B}_{10}^-$ [M-H]: 327.3129. Found: 327.3129.



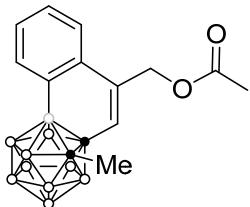
5Be: White solid. Yield: 79%. ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, $J = 6.4$ Hz, 1H), 7.67 (d, $J = 7.8$ Hz, 1H), 7.63 – 7.34 (m, 2H) (aromatic H), 6.02 (s, 1H) (vinyl H), 3.81 – 3.29 (m, 2H), 3.01 – 2.41 (m, 2H), 2.27 – 1.78 (m, 2H) (CH_2), 1.30 (s, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 145.56, 135.41, 133.84, 130.15, 129.50, 126.15, 118.75 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 74.99, 69.29 (cage C), 44.34, 32.17, 31.53, 20.48 (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.90 (3B), -9.98 (3B), -11.68 (1B), -12.95 (3B). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{23}\text{B}_{10}\text{Cl} [\text{M}-\text{H}]^-$: 333.2426. Found: 333.2429.



5Bf: White solid. Yield: 59%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 6.6$ Hz, 1H), 7.62 (d, $J = 7.9$ Hz, 1H), 7.49 – 7.37 (m, 2H), 7.35 – 7.27 (m, 2H), 7.24 (d, $J = 7.1$ Hz, 1H), 7.19 (d, $J = 7.3$ Hz, 2H) (aromatic H), 5.97 (s, 1H) (vinyl H), 4.53 – 3.82 (m, 2H) (CH_2), 1.38 (s, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 145.33, 138.43, 135.14, 134.37, 129.97, 129.36, 128.93, 128.44, 127.11, 126.89, 120.43 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 75.13, 69.47 (cage C), 40.62, 20.69 (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.88 (3B), -9.95 (3B), -11.60 (1B), -12.92 (3B). HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{24}\text{B}_{10} [\text{M}-\text{H}]^-$: 348.2817. Found: 348.2810.

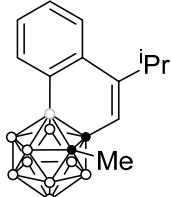


5Bg: White solid. Yield: 41%. ^1H NMR (400 MHz, CDCl_3): δ 8.17 – 7.84 (m, 1H), 7.63 – 7.55 (m, 1H), 7.57 – 7.43 (m, 2H) (aromatic H), 6.23 (s, 1H) (vinyl H), 4.54 – 4.44 (m, 2H) (CH_2), 3.46 (s, 3H), 1.32 (s, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 142.42, 135.14, 133.12, 130.04, 129.57, 125.74, 118.60 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 74.72 (cage C), 73.07 (CH_2), 69.44 (cage C), 58.73, 20.55 (CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -7.00 (3B), -10.12 (3B), -11.79 (1B), -12.97 (3B). HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{22}\text{B}_{10}\text{O} [\text{M}]^-$: 302.2689. Found: 302.2677.

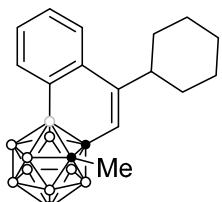


5Bh: White solid. Yield: 42%. ^1H NMR (400 MHz, CDCl_3): δ 8.36 – 7.76 (m, 1H), 7.66 – 7.38 (m, 3H) (aromatic H), 6.20 (s, 1H) (vinyl H), 5.37 – 4.55 (m, 2H) (CH_2), 2.14 (s, 3H), 1.32 (s, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.55 (CO), 140.67, 135.36, 132.64, 130.17, 129.87, 125.68, 119.84 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 74.17, 69.56

(cage C), 64.46 (CH_2), 21.09, 20.48 (CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.82 (3B), -9.97 (3B), -11.63 (1B), -12.89 (3B). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{22}\text{B}_{10}\text{O}_2$ [M-H] $^-$: 329.2557. Found: 329.2548.



5Bi: White solid. Yield: 63%. ^1H NMR (400 MHz, CDCl_3): δ 7.93 (dd, $J = 7.3, 1.7$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.64 – 7.38 (m, 2H) (aromatic H), 5.96 (s, 1H) (vinyl H), 3.30 (hept, $J = 6.7$ Hz, 1H) (CH), 1.54 – 0.45 (m, 9H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 153.06, 135.38, 134.16, 129.94, 129.05, 125.78, 114.88 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 75.42, 69.39 (cage C), 29.46, 23.46 (CH), 22.56, 20.32 (CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -7.03 (3B), -9.86 (3B), -11.60 (1B), -12.91 (3B). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{24}\text{B}_{10}$ [M] $^-$: 300.2894. Found: 300.2886.



5Bj: White solid. Yield: 62%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 6.9$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.52 (td, $J = 7.7, 1.7$ Hz, 1H), 7.46 (t, $J = 7.1$ Hz, 1H) (aromatic H), 5.92 (s, 1H) (vinyl H), 2.89 – 2.82 (m, 1H) (CH), 1.96 – 1.75 (m, 6H), 1.59 – 1.40 (m, 2H), 1.38 – 1.15 (m, 5H) (CH_3 & CH_2). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.06, 135.42, 134.11, 129.90, 129.01, 125.55, 115.40 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 75.56, 69.31 (cage C), 40.13, 34.48, 33.28, 27.10, 26.97, 26.46, 20.32 (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -7.13 (3B), -10.09 (3B), -11.70 (1B), -13.06 (3B). HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{28}\text{B}_{10}$ [M] $^-$: 340.3208. Found: 340.3203.

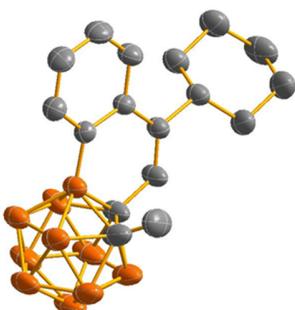
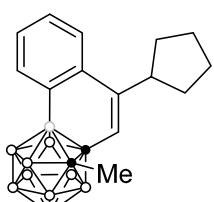
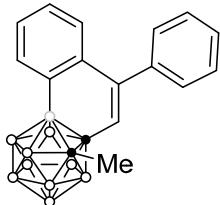


Figure S5. Molecular structure of **5Bj**

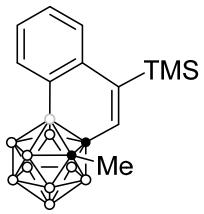


5Bk: White solid. Yield: 69%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (dd, $J = 7.1, 1.7$ Hz, 1H), 7.77 (d, $J = 7.9$ Hz, 1H), 7.69 – 7.41 (m, 2H) (aromatic H), 5.99 (s, 1H) (vinyl H), 3.30 (p, $J = 8.0$ Hz, 1H) (CH), 2.46 – 1.95 (m, 2H), 1.85 – 1.69 (m, 4H), 1.68 – 1.39 (m, 2H), (CH_2) 1.28 (s, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 150.28, 135.16, 135.00, 129.84, 129.02, 126.52, 114.47 (aromatic C, the signal of

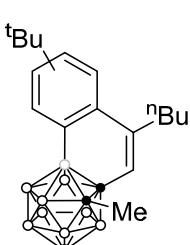
phenyl carbon atom adjacent to B was not observed), 75.55, 69.51 (cage C), 42.27, 33.42, 32.54, 24.94, 24.91, 20.38 (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -7.25 (3B), -10.05 (3B), -11.62 (1B), -13.06 (3B). HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{26}\text{B}_{10} [\text{M}]^-$: 326.3051. Found: 326.3045.



5Aa: White solid. Yield: 57%. ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, $J = 7.1$ Hz, 1H), 7.64 – 7.45 (m, 4H), 7.42 (t, $J = 7.7$ Hz, 1H), 7.36 – 7.15 (m, 3H) (aromatic H), 6.02 (s, 1H) (vinyl H), 1.50 (s, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 149.74, 139.27, 135.12, 134.86, 129.81, 129.56, 129.07, 128.61, 128.44, 119.85 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 74.86, 69.44 (cage C), 20.53 (CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.49 (3B), -9.64 (3B), -11.14 (1B), -12.58 (3B). HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{22}\text{B}_{10} [\text{M}]^-$: 334.2739. Found: 334.2729.



5Ax: White solid. Yield: 51%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (dd, $J = 6.7, 2.2$ Hz, 1H), 7.75 – 7.59 (m, 1H), 7.53 – 7.33 (m, 2H) (aromatic H), 6.23 (s, 1H) (vinyl H), 1.27 (s, 3H), 0.36 (s, 9H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 149.46, 136.02, 135.33, 130.42, 129.62, 129.07, 127.53 (aromatic C, the signal of phenyl carbon atom adjacent to B was not observed), 74.97, 69.03 (cage C), 20.40, 0.37 (CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.60 (3B), -9.63 (3B), -11.47 (1B), -12.71 (3B). HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{26}\text{B}_{10}\text{Si} [\text{M}]^-$: 330.2821. Found: 330.2813.



7Ba and **8Ba**. Yield: 79%. **7Ba:8Ba** = 14.3:1 by ^1H NMR spectra. Regioisomer **7Ba** was isolated as a pure product, whereas **8Ba** was obtained with the contamination of **7Ba**. For **7Ba**. White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 7.8$ Hz, 1H), 7.66 (d, $J = 1.8$ Hz, 1H), 7.51 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.26 (s, 1H) (aromatic H), 2.66 (t, $J = 7.7$ Hz, 2H), 1.72 – 1.50 (m, 2H), 1.49 – 1.39 (m, 2H) (CH_2), 1.36 (s, 9H), 1.29 (s, 3H), 0.97 (t, $J = 7.3$ Hz, 3H) (CH_3). For **8Ba**. ^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, $J = 2.2$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.53 (d, $J = 2.3$ Hz, 1H, half of the peak is overlapped with the major product), 5.93 (s, 1H) (aromatic H), 2.66 (t, $J = 7.7$ Hz, 2H), 1.72 – 1.50 (m, 2H), 1.49 – 1.39 (m, 2H) (CH_2), 1.39 (s, 9H), 1.29 (s, 3H), 0.97 (t, $J = 7.3$ Hz, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.79, 147.67, 134.93, 134.02, 126.39, 123.26, 117.64 (aromatic C), 75.46, 69.42 (cage C), 35.12, 34.44, 32.07, 31.39, 22.86, 20.53, 14.07. (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -7.28 (3B), -10.25 (3B), -11.74 (1B), -13.27 (3B). HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{34}\text{B}_{10} [\text{M}-\text{H}]^-$: 369.3600. Found: 369.3590.

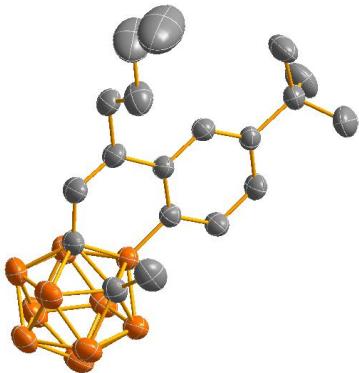
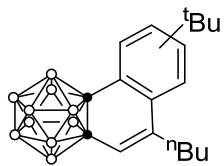


Figure S6. Molecular structure of **7Ba**



10Ba and 11Ba. Yield: 84%. **10Ba:11Ba = 1:1** by ^1H NMR spectra. Two regioisomers were separated by HPLC and their structures were confirmed by X-ray analyses. For **10Ba**. White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.61 (d, $J = 8.3$ Hz, 1H), 7.55 (s, 1H), 7.45 (d, $J = 8.2$ Hz, 1H), 6.20 (s, 1H) (aromatic H), 2.55 (d, $J = 7.6$ Hz, 2H), 1.55 – 1.51 (m, 2H), 1.45 – 1.35 (m, 2H) (CH_2), 1.34 (s, 9H) ($\text{C}(\text{CH}_3)_3$), 0.96 (t, $J = 7.3$ Hz, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.44, 136.06, 129.50, 127.95, 126.89, 126.58, 122.78, 122.21 (aromatic C), 72.77, 71.20 (cage C), 35.04, 32.83, 31.32, 30.85, 22.61, 14.06 (($\text{C}(\text{CH}_3)_3$) & CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.71 (1B), -7.88 (1B), -9.49 (2B), -11.62 (6B). HRMS (APCI): m/z calcd for $\text{C}_{18}\text{H}_{32}\text{B}_{10}$ [$\text{M}-\text{H}+\text{CH}_3\text{OH}$] $^-$: 387.3706. Found: 387.3695.

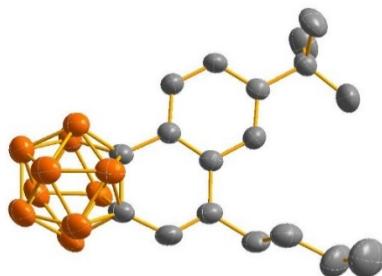


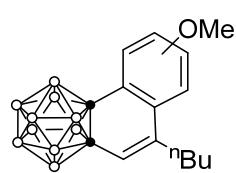
Figure S7. Molecular structure of **10Ba**

For **10Bb**. White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.70 (s, 1H), 7.48 (s, 2H), 6.16 (s, 1H) (aromatic H), 2.51 (t, $J = 7.6$ Hz, 2H), 1.56 – 1.50 (m, 2H), 1.44 – 1.38 (m, 2H) (CH_2), 1.36 (s, 9H) ($\text{C}(\text{CH}_3)_3$), 0.94 (t, $J = 7.3$ Hz, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.79, 135.91, 132.37, 126.55, 125.61, 125.43, 124.83, 121.37 (aromatic C), 73.18, 71.55 (cage C), 35.05, 32.74, 31.20, 30.81, 22.63, 14.03

((C(CH₃)₃ & CH₂ & CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -6.79 (1B), -8.04 (1B), -9.65 (2B), -11.78 (6B). HRMS (APCI): *m/z* calcd for C₁₈H₃₂B₁₀ [M-H+CH₃OH]⁺: 387.3706. Found: 387.3696.



Figure S8. Molecular structure of **10Bb**



10Bb and **11Bb**. Yield: 65%. **10Bb:11Bb** = 8.7:1 by ¹H NMR spectra. Regioisomer **10Bb** was isolated as a pure product, whereas **11Bb** was obtained with the contamination of **10Bb**. For **10Bb**. White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.96 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.23 (s, 1H) (aromatic *H*), 3.85 (s, 3H) (OCH₃), 2.50 (t, *J* = 7.6 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.43 – 1.34 (m, 2H) (CH₂), 0.95 (t, *J* = 7.3 Hz, 3H) (CH₃). For **11Bb**. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 3.2 Hz, 1H, half of the peak is overlapped with the major product), 7.00 (s, 1H, half of the peak is overlapped with the major product), 6.07 (s, 1H) (aromatic *H*), 3.88 (s, 3H) (OCH₃), 2.50 (t, *J* = 7.6 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.43 – 1.34 (m, 2H) (CH₂), 0.95 (t, *J* = 7.3 Hz, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 160.31, 135.93, 129.52, 128.99, 125.23, 122.92, 114.04, 112.02 (aromatic C), 72.72, 71.03 (cage C), 55.63, 32.74, 30.61, 22.59, 14.02 (CH₂ & CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -6.78 (1B), -7.76 (1B), -9.41 (2B), -11.52 (6B). HRMS (EI): *m/z* calcd for C₁₅H₂₆B₁₀O [M]⁺: 330.2989. Found: 330.2986.

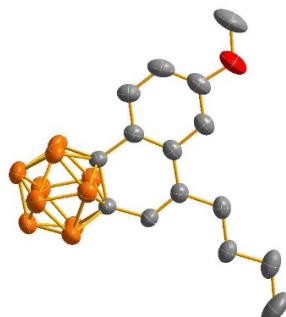
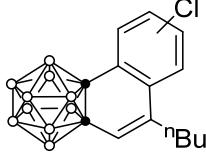


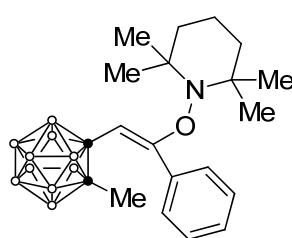
Figure S9. Molecular structure of **10Bb**



10Bc and **11Bc**. White solid. Yield: 47%. **10Bc:11Bc** = 3.6:1 by ^1H NMR spectra. These two regioisomers were inseparable. For **10Bc**. ^1H NMR (400 MHz, CDCl_3): δ 7.63 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 2.0 Hz, 1H), 7.40 (dd, J = 8.4, 2.0 Hz, 1H), 6.26 (s, 1H) (aromatic H), 2.50 (t, J = 15.2 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.44 – 1.36 (m, 2H) (CH_2), 0.96 (t, J = 7.3 Hz, 3H) (CH_3). For **11Bc**. ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, J = 2.0 Hz, 1H), 6.21 (s, 1H) (aromatic H, two aromatic hydrogens were unable to be identified), 2.50 (t, J = 15.2 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.44 – 1.36 (m, 2H) (CH_2), 0.96 (t, J = 7.3 Hz, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 135.92, 135.08, 131.07, 129.73, 129.65, 129.41, 129.37, 128.22, 127.09, 126.13, 125.93, 123.69, 122.55 (aromatic C), 71.82, 70.92, 66.01 (cage C), 32.50, 30.38, 22.54 (CH_2), 14.01 (CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -6.16 (1B), -7.47 (1B), -9.30 (2B), -11.50 (6B). HRMS (APCI): m/z calcd for $\text{C}_{14}\text{H}_{23}\text{B}_{10}\text{Cl} [\text{M}-\text{H}]$: 333.2421. Found: 333.2422.

5. Control experiments

5.1 Radical Trapping Experiments for Coupling Reaction of 1-I-2-Me-o-carborane (1a) with Phenylacetylene. Compound **1a** (28.4 mg, 0.1 mmol), phenylacetylene (27.4 μL , 0.25 mmol), radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 15.6 mg, 0.1 mmol) and NaHCO_3 (10.1 mg, 0.12 mmol) were dissolved in CH_2Cl_2 (1.0 mL) in a 10 mL quartz-Schlenk flask equipped with a magnetic stirring bar. Under an atmosphere of argon, the reaction mixture was irradiated with 125 UV (365 nm) for 36 h with stirring. Then the reaction was stopped and the resulting mixture was examined by GC-MS analyses. The reaction was quenched with water (10 mL) and extracted with diethyl ether (15 mL \times 3). The ether solutions were combined and dried over Na_2SO_4 . After removal of Na_2SO_4 , the clear colorless solution was concentrated to dryness in vacuo. Then, the residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give a TEMPO-trapped product **13Aa**.



13Aa: White solid. Yield: 14%. ^1H NMR (400 MHz, CDCl_3): δ 7.49 – 7.40 (m, 3H), 7.29 (d, J = 6.8 Hz, 2H) (aromatic H), 6.13 (s, 1H) (olefinic H), 1.93 (s, 3H), 1.59 (s, 6H), 1.16 (s, 6H), 1.10 (s, 6H) (CH_2 & CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 166.23, 133.19, 129.83, 129.56, 128.39, 98.65 (aromatic C & olefinic C), 79.01 (cage C, the signal of another cage carbon was

overlapped with CDCl_3), 60.83 (quaternary C), 39.78, 32.62, 23.67, 20.79, 16.98 (CH_2 & CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CDCl_3): δ -4.74 (1B), -6.47 (1B), -10.95 (8B). HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{37}\text{B}_{10}\text{NO} [\text{M}+\text{Na}]^+$: 438.3780. Found: 438.3766.

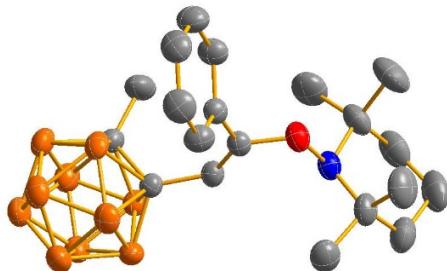
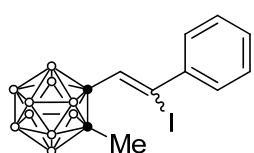


Figure S10. Molecular structure of **13Aa**

5.2 Isolation of byproduct 14Aa. Compound **1a** (28.4 mg, 0.1 mmol), phenylacetylene (27.4 μL , 0.25 mmol), and NaHCO_3 (10.1 mg, 0.12 mmol) were dissolved in CH_2Cl_2 (1.0 mL) in a 10 mL quartz-Schlenk flask equipped with a magnetic stirring bar. Under an atmosphere of argon, the reaction mixture was irradiated with 125 UV (365 nm) for 12 h with stirring. Then, the reaction was stopped and the resulting mixture was examined by GC-MS and ^1H NMR analysis. The reaction was quenched with water (10 mL) and extracted with diethyl ether (15 mL \times 3). The ether solutions were combined and dried over Na_2SO_4 . After removal of Na_2SO_4 , the clear colorless solution was concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give **3Aa** (13.7 mg, 53%) and **14Aa** (6.8 mg, 19%), respectively.

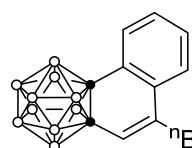


14Aa: Colorless oil. A mixture of inseparable *cis* and *trans* isomers was obtained in 19% yield. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.39 – 7.34 (m, 8H), 7.27 – 7.19 (m, 2H) (aromatic H), 6.71 (s, 1H), 6.23 (s, 1H) (olefinic H), 2.06 (s, 3H), 2.03 (s, 3H) (CH_3). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CD_2Cl_2): δ 144.64, 140.50, 131.74, 129.20, 128.83, 128.22, 128.05, 127.96, 127.93, 126.79, 110.70, 109.38 (aromatic C & olefinic C), 77.57, 76.81, 76.24 (cage C), 23.19 (CH_3). $^{11}\text{B}\{\text{H}\}$ NMR (128 MHz, CD_2Cl_2): δ -2.99 (1B), -6.67 (1B), -10.68 (8B). HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{19}\text{B}_{10}\text{I} [\text{M}-\text{H}]^-$: 385.1467. Found: 385.1466.

5.3 Isolation of a radical-coupling product 15Ba

Iodocarborene **9d** (103.8 mg, 0.3 mmol), 1-hexyne (689 μL , 6.0 mmol) and 2,6-lutidine (42 μL , 0.36 mmol) were mixed in CH_2Cl_2 (3.0 mL) in a 10 mL quartz-Schlenk flask equipped with a magnetic stirring

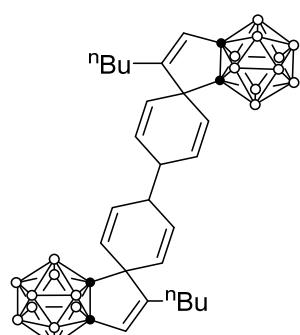
bar. Under an atmosphere of argon, the reaction mixture was irradiated with 36 W UV (365 nm) lamp for 48 h with stirring. Then, the reaction was stopped, and the resulting mixture was examined by GC-MS analyses. The reaction was quenched with water (10 mL) and extracted with diethyl ether (15 mL×3). The ether solutions were combined and dried over Na₂SO₄. After removal of Na₂SO₄, the clear colorless solution was concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give the desired product **10d** and byproduct **15Ba**.



10d. White solid. Yield: 40%. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.41 (m, 2H), 6.21 (s, 1H) (aromatic H), 2.53 (t, *J* = 8.0 Hz, 2H), 1.58 – 1.50 (m, 2H), 1.43 – 1.34 (m, 2H) (CH₂), 0.95 (t, *J* = 7.3 Hz, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 135.96, 132.70, 129.50, 129.36, 128.32, 127.55, 125.87, 122.31 (aromatic C), 72.61, 71.23 (cage C), 32.75, 30.70, 22.61 (CH₂), 14.03 (CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -6.42 (1B), -7.64 (1B), -9.30 (2B), -11.59 (6B). HRMS (EI): *m/z* calcd for C₁₄H₂₄B₁₀ [M]⁺: 300.2883. Found: 300.2878.



Figure S11. Molecular structure of **10d**



15Ba. White solid. Yield: 8%. ¹H NMR (400 MHz, CDCl₃): δ 5.98 (dd, *J* = 10.3, 2.7 Hz, 4H), 5.87 – 5.37 (m, 6H) (olefinic H), 2.98 (s, 2H) (CH), 2.10 – 1.66 (m, 4H), 1.38 – 1.29 (m, 4H), 1.28 – 1.21 (m, 4H) (CH₂), 0.91 – 0.75 (m, 6H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 162.06, 131.63, 128.28, 122.07 (olefinic C), 85.54, 83.98 (cage C), 56.40 (tertiary C), 39.75 (CH), 29.70, 28.24, 22.49 (CH₂), 14.00 (CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -5.28 (2B), -8.19 (4B), -10.28 (6B), -13.33 (2B), -14.64 (6B). HRMS (EI): *m/z* calcd for C₂₈H₅₀B₂₀ [M-H]⁻: 601.5862. Found: 601.5845.

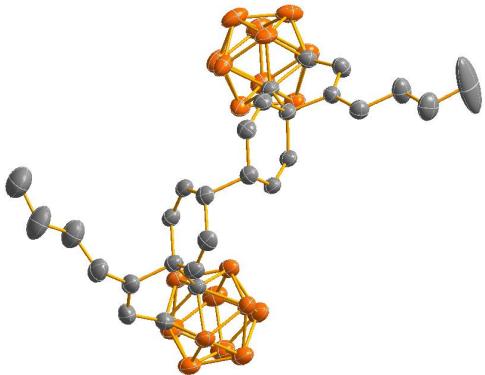


Figure S12. Molecular structure of **15Ba**

5.4 NMR study

A J Young valve NMR tube was charged with 1-I-2-Et-*o*-carborane (**1b**; 15 mg, 0.05 mmol), phenyl acetylene (13.8 μ L, 0.125 mmol), NaHCO₃ (5.0 mg, 0.06 mmol), CH₂Br₂ (3.4 μ L, 0.05 mmol; internal standard) and CD₂Cl₂ (0.5 mL). The NMR tube was placed 10 cm away from the UV light with exhaust fan to cool the reaction, and was irradiated under UV light (365 nm, 125 W) for 4 h at room temperature. The formation of iodoalkene was observed from the ¹H NMR spectrum (Figure S13b). Afterwards, the reaction was set in dark for 15 h. No more products were generated, and the starting material remained unchanged (Figure S13c). After the reaction was irradiated again under UV light for 7 h, more starting material was consumed, and the alkynylated product **3Aaa** was observed (Figure S 13d). The reaction was encumbered when setting in dark again for 15 h (Figure S13e). Irradiation was then resumed for 12 h, giving **3Aaa** as the main product at the expense of the starting material **1b** (Figure S13f). Based on these experimental results, it was clear that the reaction was initiated by UV light, and the reaction was stopped without UV irradiation. Thus, this reaction might not involve a radical chain mechanism.

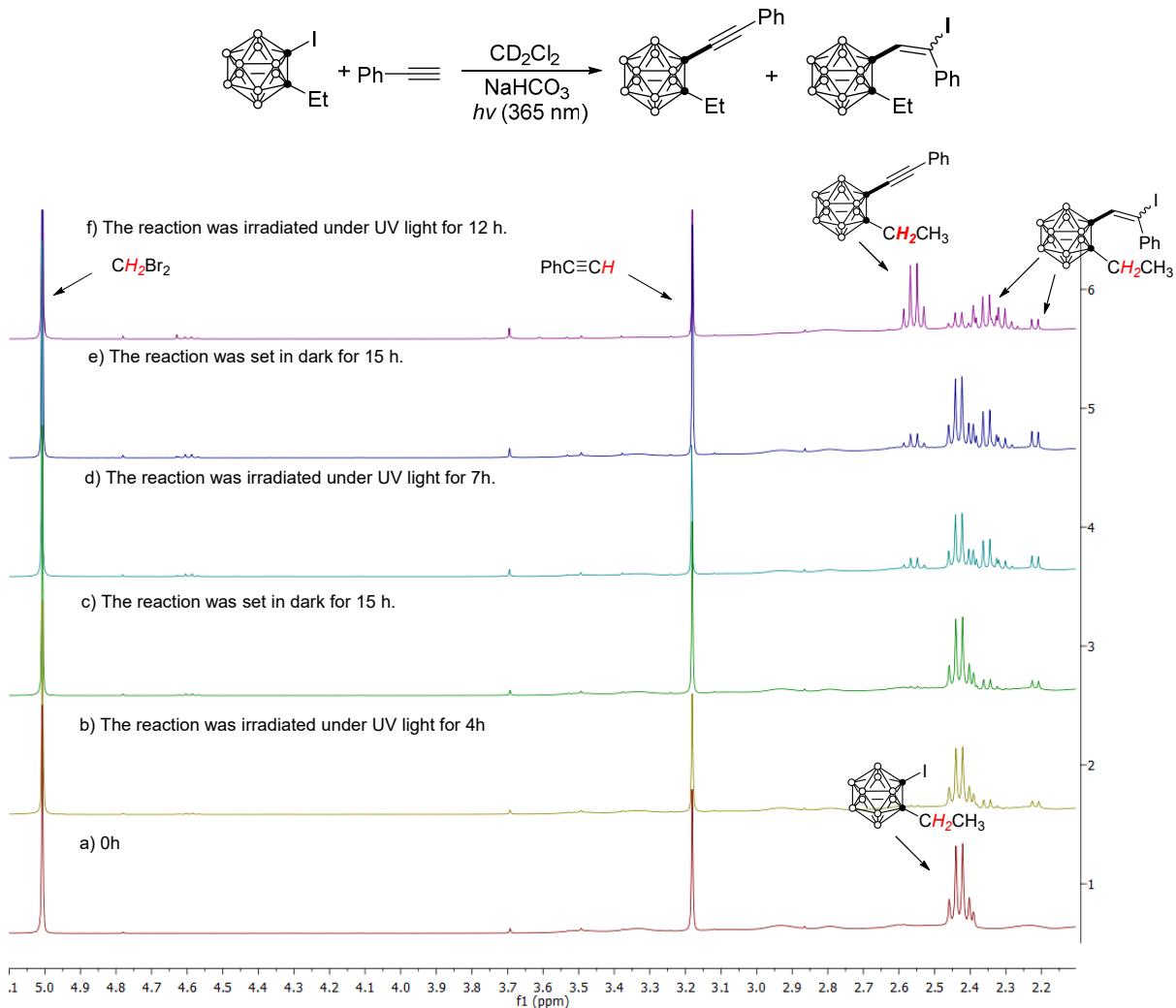


Figure S13. Time-dependent ¹H NMR spectra (400 MHz) of the control experiments (showing the portion $\delta = 2.1 - 5.1$ ppm for clarity): a) before UV irradiation, b) after UV irradiation for 4 h, c) under dark for 15 h, d) after UV irradiation for another 7 h, e) under dark for 15 h, f) after UV irradiation for additional 12 h.

6. X-ray Structure Determination.

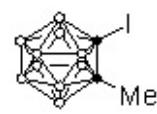
All data were collected at 296 K or 130K on a Bruker SMART 1000 CCD diffractometer or Bruker D8 venture diffractometer or a Bruker Kappa ApexII Duo diffractometer using Mo-K α radiation. An empirical absorption correction was applied using the SADABS program.⁴ All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F² using the SHELXTL program package.⁵ All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements were given in Tables S1 and S2.

Table S1. Crystal Data and Summary of Data Collection and Refinement.

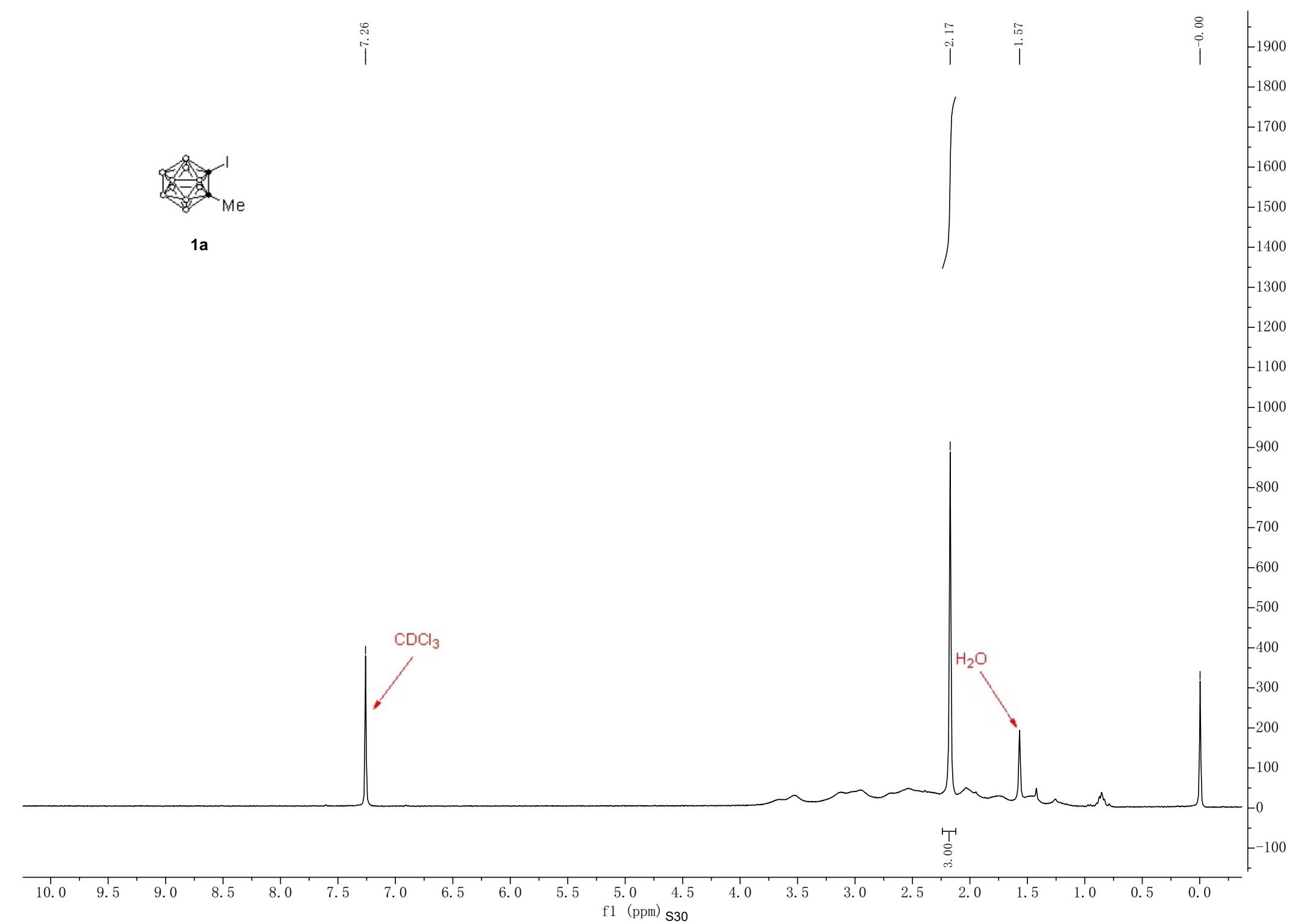
compound	3Aa	3As	3At	5Ba	5Bj	7Ba
formula	C ₁₁ H ₁₈ B ₁₀	C ₁₆ H ₃₀ B ₂₀	C ₁₅ H ₂₀ B ₁₀	C ₁₅ H ₂₆ B ₁₀	C ₁₇ H ₂₈ B ₁₀	C ₁₉ H ₃₄ B ₁₀
cryst size(mm ³)	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30			
fw	258.35	438.60	308.41	314.46	340.49	370.56
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
<i>a</i> , Å	11.030(2)	7.083(1)	15.046(1)	10.540(1)	7.818(1)	16.739(1)
<i>b</i> , Å	9.970(2)	24.866(1)	7.862(1)	14.201(1)	10.051(1)	12.549(1)
<i>c</i> , Å	15.231(2)	10.414(1)	15.308(1)	15.164(1)	13.067(2)	22.351(2)
α , deg	90	90	90	65.47(1)	95.65(1)	90
β , deg	107.56(1)	130.94(1)	95.32(1)	75.09(1)	91.48(1)	90
γ , deg	90	90	90	71.58(1)	94.65(1)	90
<i>V</i> , Å ³	156.9(3)	1385.5(1)	1803.1(1)	1938.1(2)	1017.9(2)	4695.5(4)
<i>Z</i>	4	2	4	4	2	8
<i>D</i> calcd, Mg/m ³	1.075	1.051	1.136	1.078	1.111	1.048
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
2 θ range, deg	4.04 to 50.49	3.27 to 50.49	3.63 to 50.49	2.98 to 50.49	4.09 to 50.49	4.38 to 55.88
μ , mm ⁻¹	0.051	0.048	0.056	0.053	0.055	0.052
<i>F</i> (000)	536	452	640	664	360	1584
no. of obsd reflns	2878	2515	3270	7009	3681	5630
no. of params refnd	190	163	226	489	253	262
goodness of fit	1.010	1.056	1.072	1.028	1.035	1.023
R1	0.066	0.0557	0.0503	0.0832	0.0809	0.0936
wR2	0.1595	0.1557	0.1416	0.2500	0.1212	0.2460

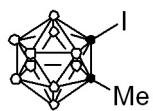
Table S2. Crystal Data and Summary of Data Collection and Refinement.

compound	10Ba	11Ba	10Bb	13Aa	10d	15Ba
formula	C ₁₈ H ₃₂ B ₁₀	C ₁₈ H ₃₂ B ₁₀	C ₁₅ H ₂₆ B ₁₀ O	C ₂₀ H ₃₇ B ₁₀ NO	C ₁₄ H ₂₄ B ₁₀	C ₂₈ H ₅₀ B ₂₀
cryst size(mm ³)	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20
fw	356.53	356.53	330.46	415.60	300.43	602.88
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
<i>a</i> , Å	15.086(1)	16.415(1)	14.316(1)	26.751(2)	10.768(2)	30.048(1)
<i>b</i> , Å	12.939(1)	12.582(1)	7.281(1)	8.554(1)	7.232(2)	10.831(1)
<i>c</i> , Å	11.593(1)	21.684(2)	19.028(1)	25.482(2)	23.173(5)	23.734(1)
<i>α</i> , deg	90	90	90	90	90	90
<i>β</i> , deg	102.26(1)	90	90	118.60(1)	90.91(1)	102.00(1)
<i>γ</i> , deg	90	90	90	90	90	90
<i>V</i> , Å ³	2211.4(2)	4478.5(4)	1983.4(2)	5119.3(4)	1804.4(7)	7555.8(6)
<i>Z</i>	4	8	4	8	4	8
<i>D_{calcd}</i> , Mg/m ³	1.071	1.058	1.107	1.078	1.106	1.060
radiation (<i>λ</i>), Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
2θ range, deg	4.78 to 50.49	4.49 to 50.49	3.56 to 50.50	5.07 to 50.49	4.20 to 50.50	4.25 to 50.50
μ, mm ⁻¹	0.053	0.052	0.058	0.058	0.054	0.051
<i>F</i> (000)	760	1520	696	1776	632	2544
no. of obsd reflns	3993	4046	1953	4628	3255	6821
no. of params refnd	280	254	145	289	217	433
goodness of fit	1.056	1.024	1.060	1.032	1.041	1.031
R1	0.0599	0.0625	0.0564	0.0717	0.0540	0.0657
wR2	0.1370	0.1652	0.1589	0.1876	0.1477	0.1756



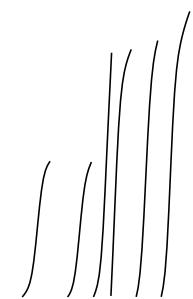
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1a

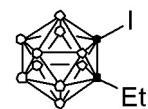
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f1 (ppm) S31

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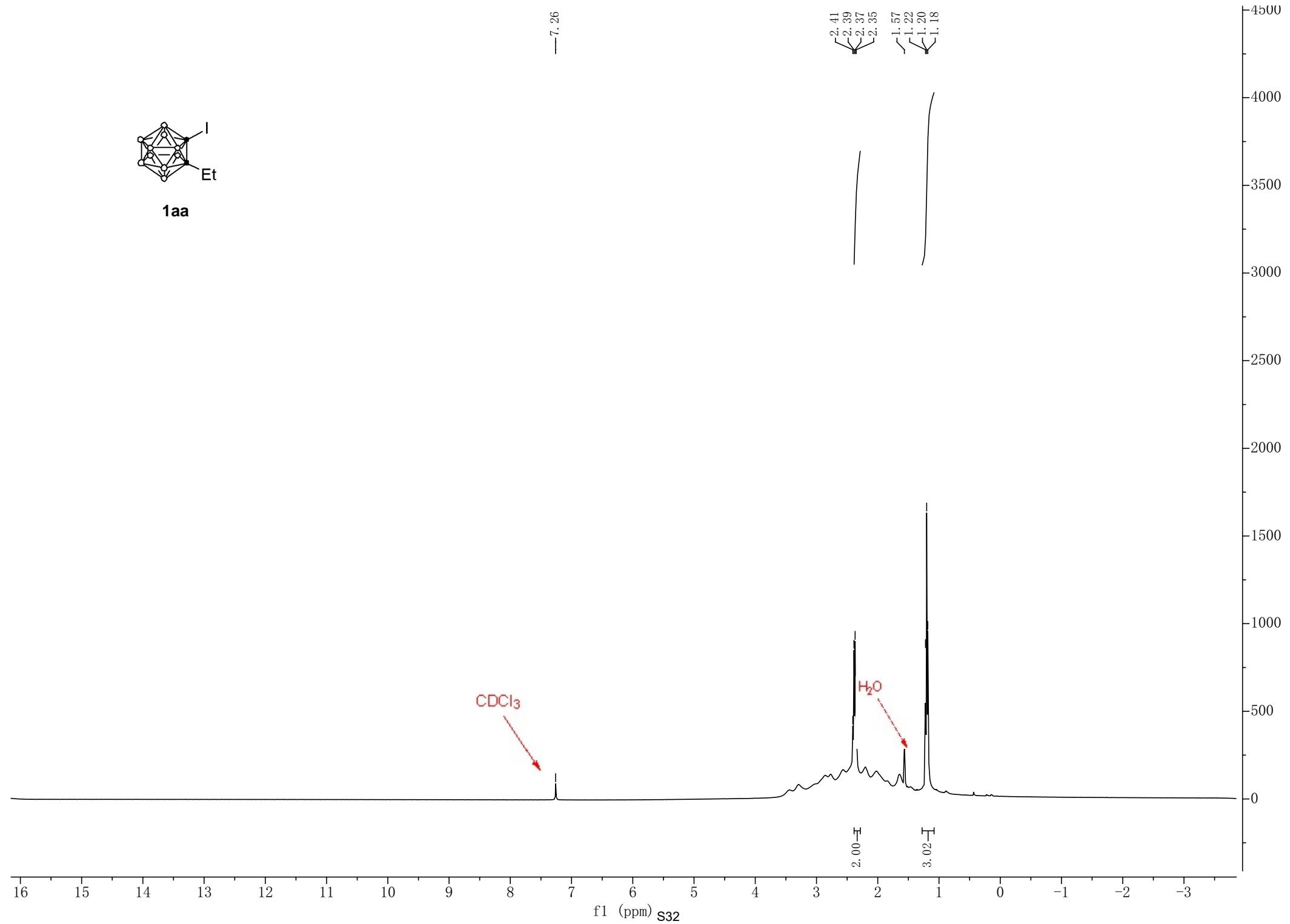
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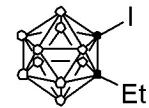
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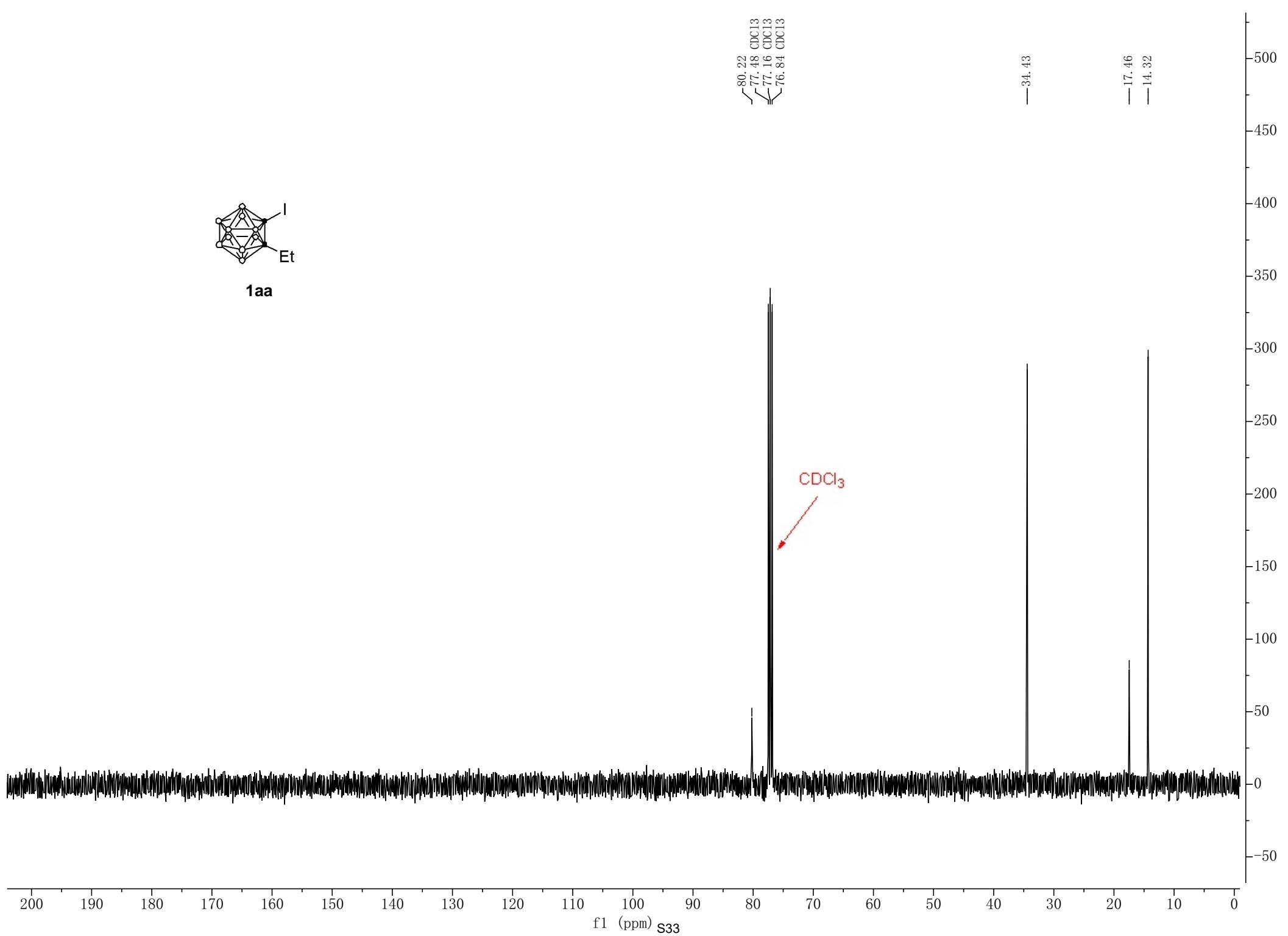
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3.02



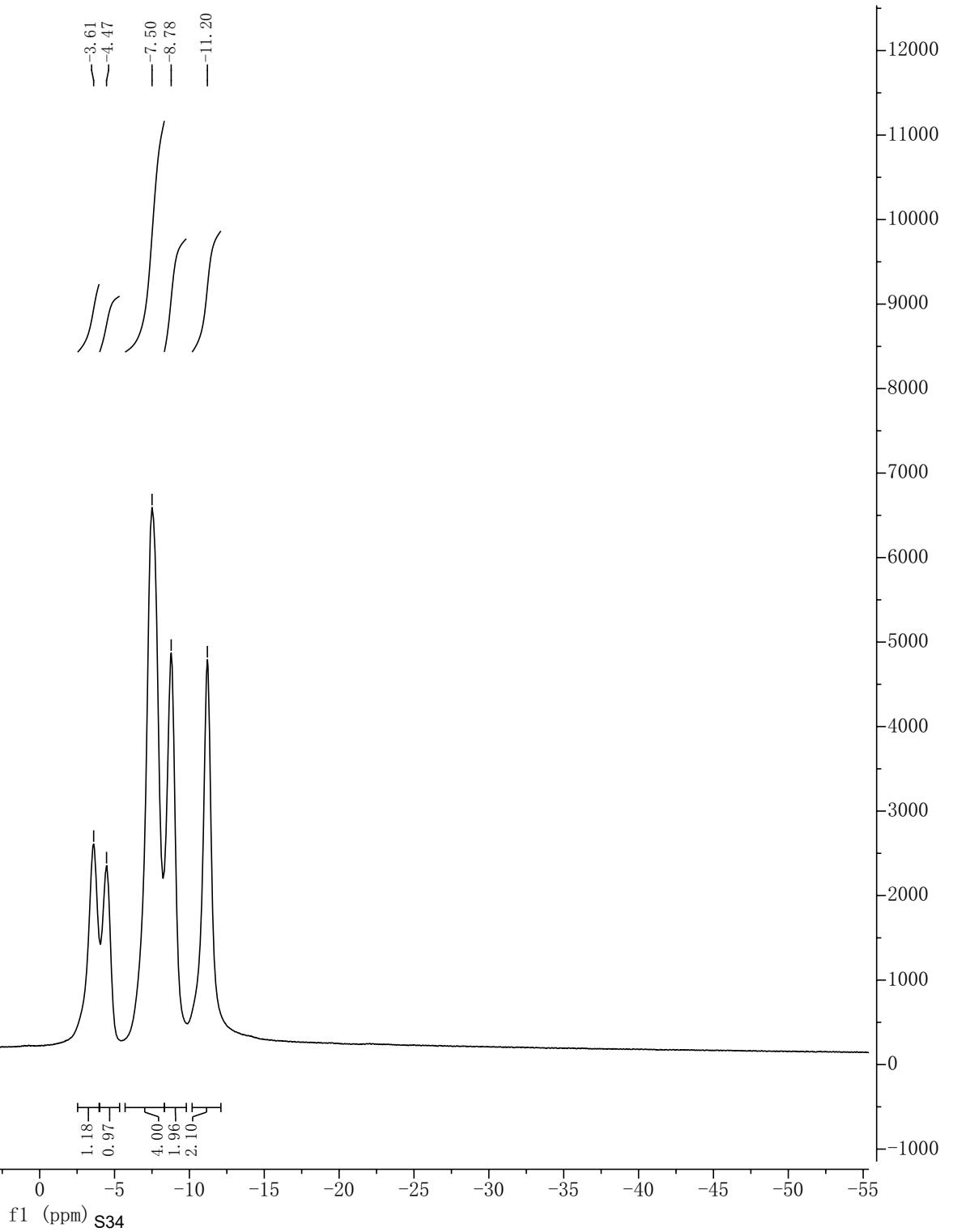


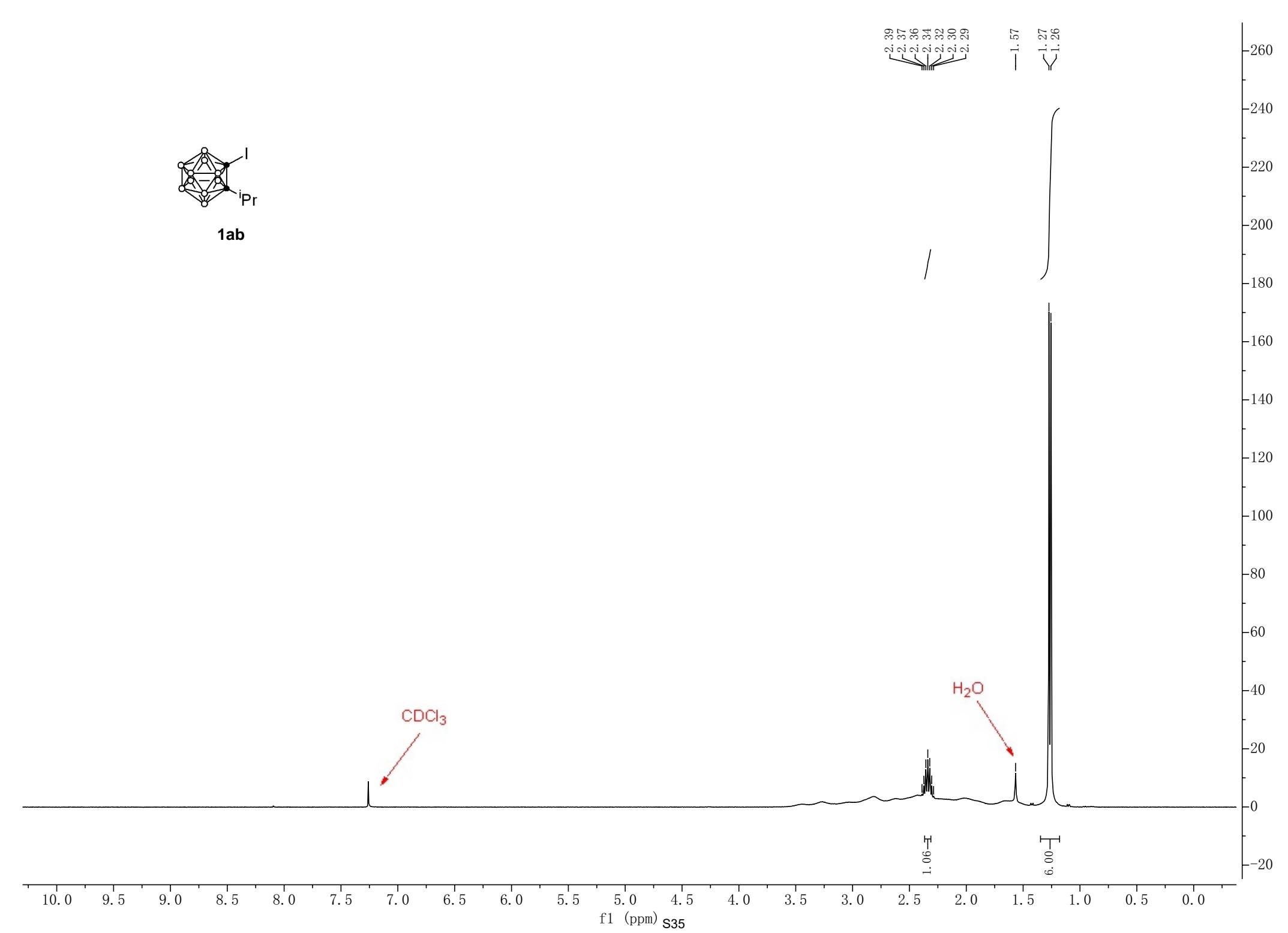
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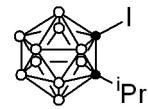




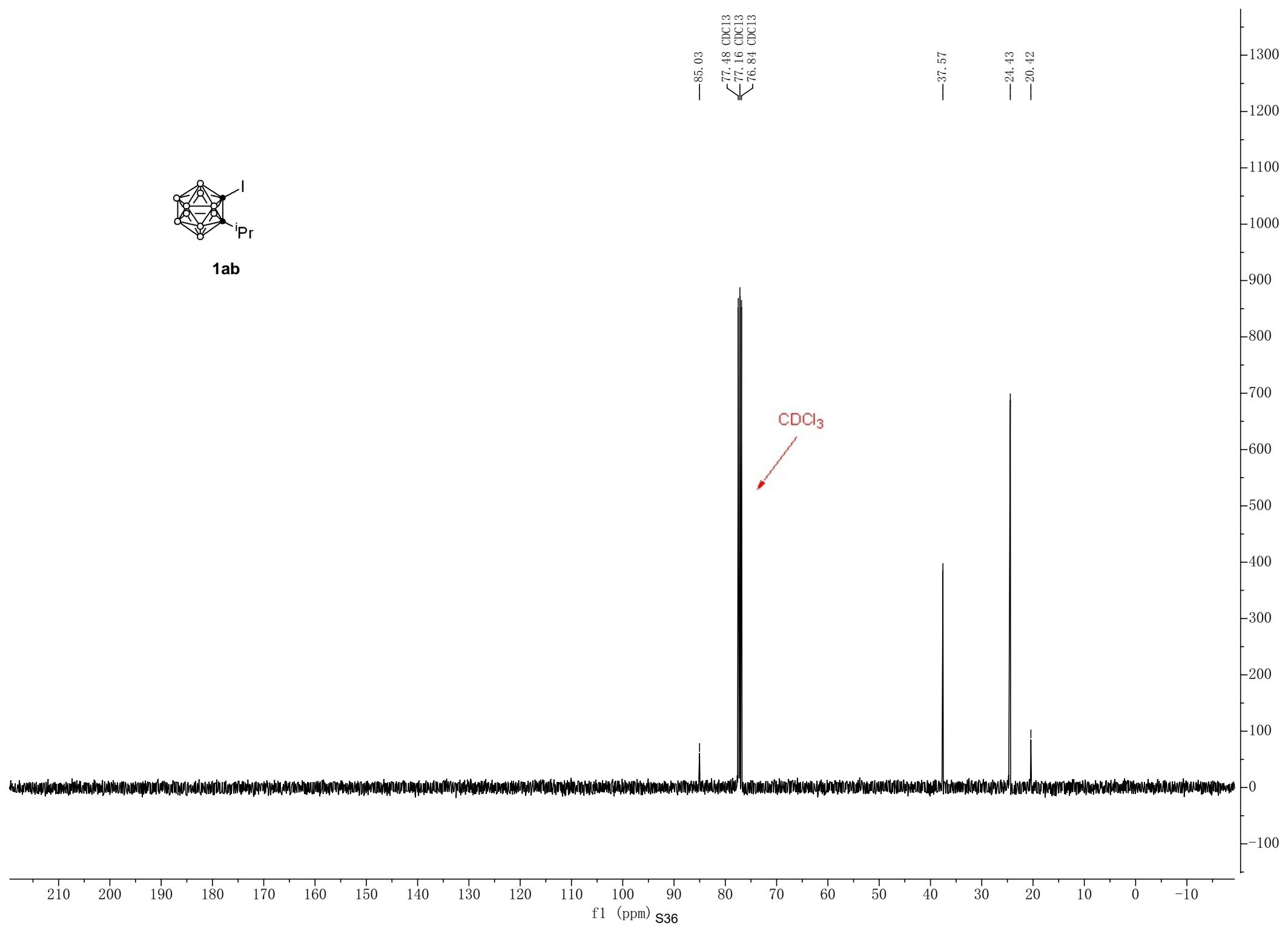
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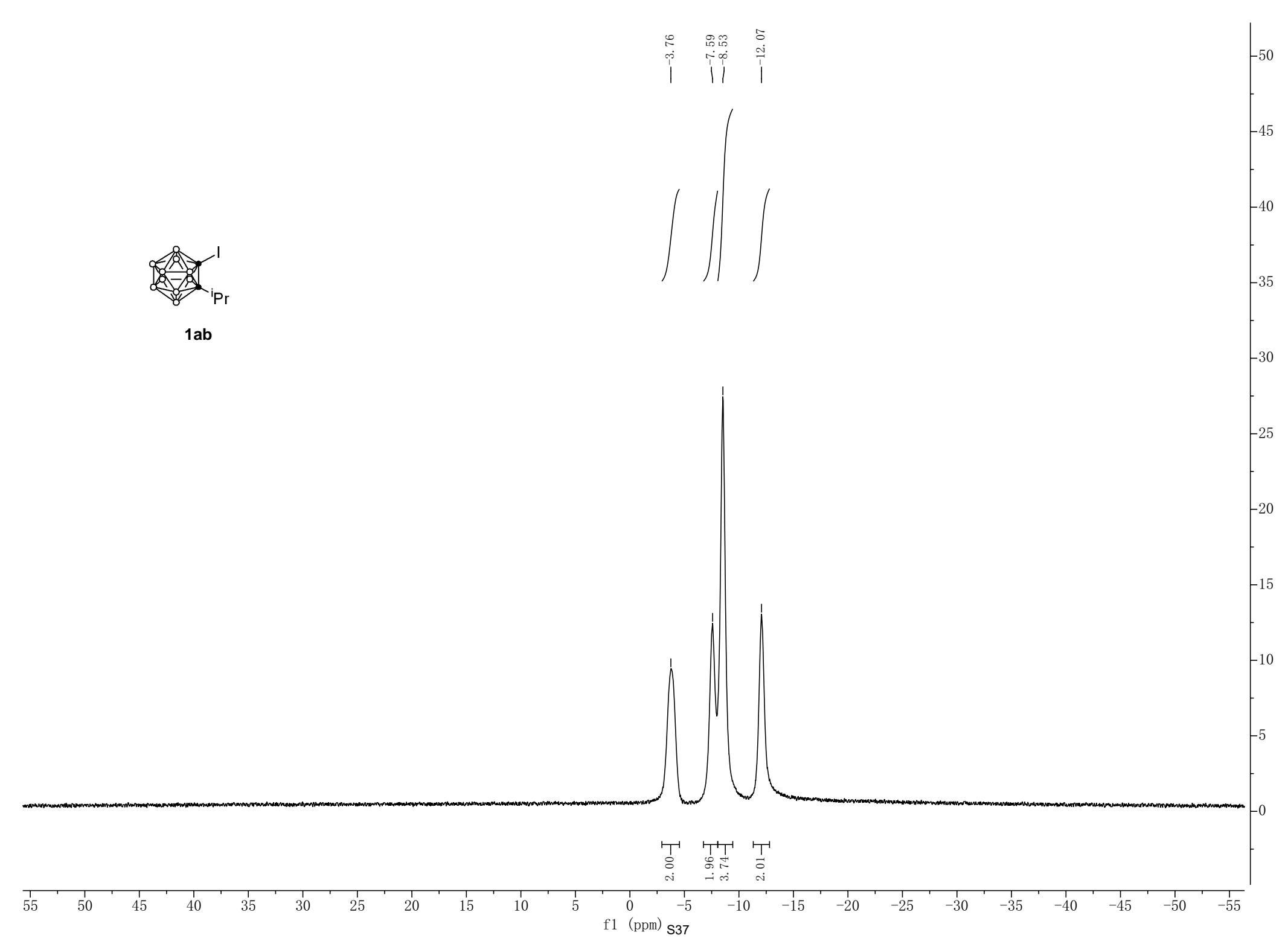


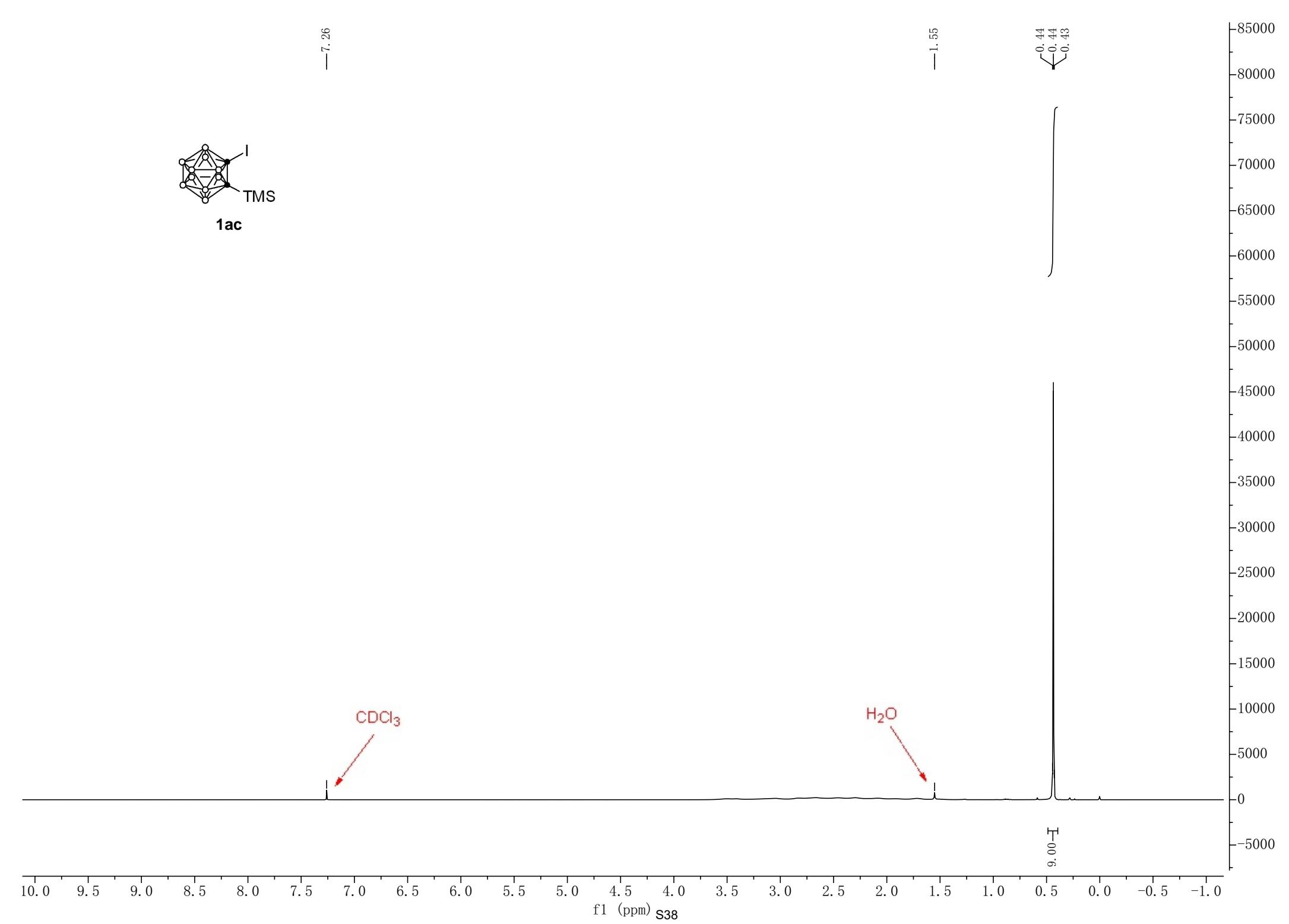


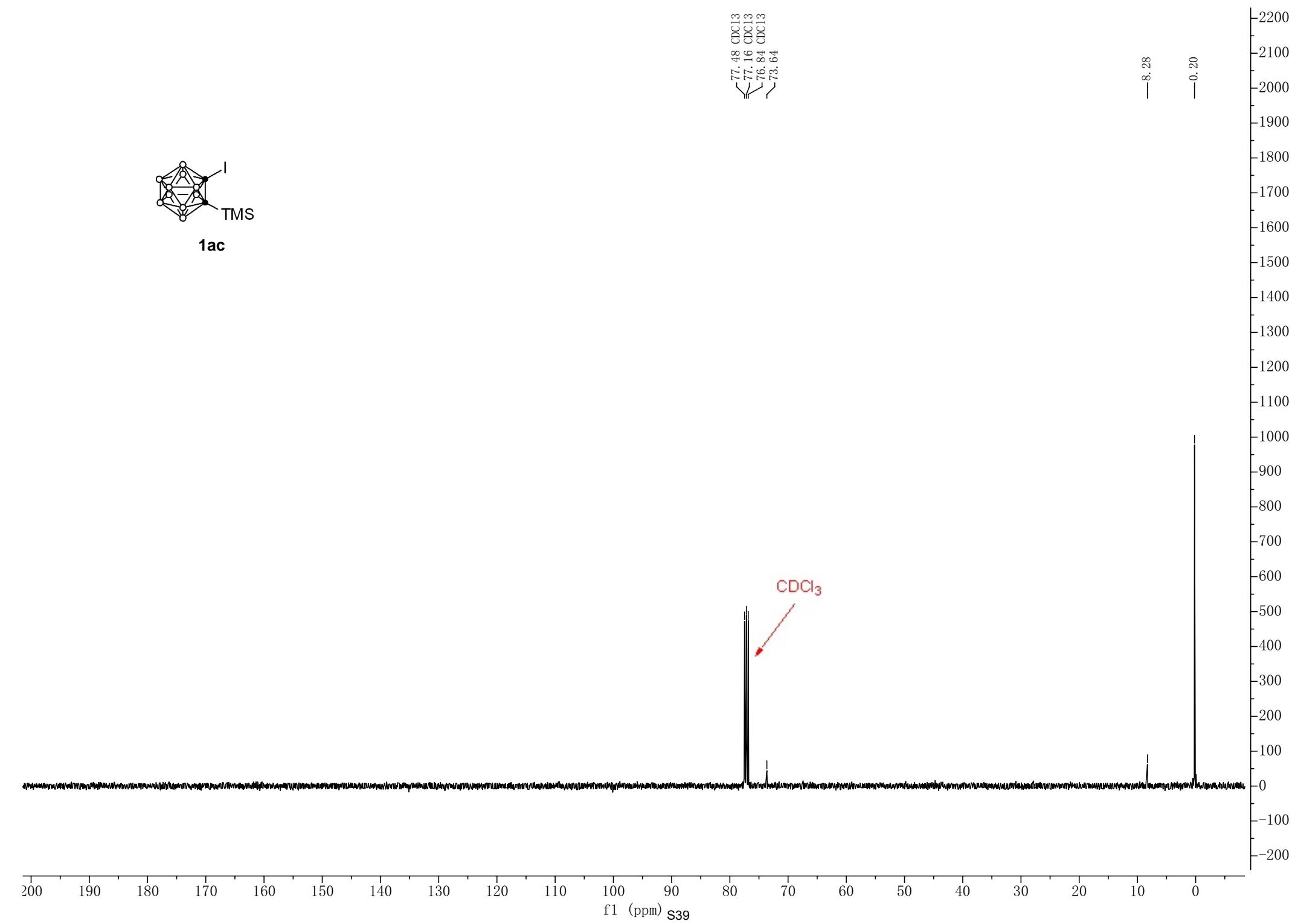


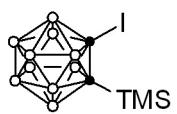
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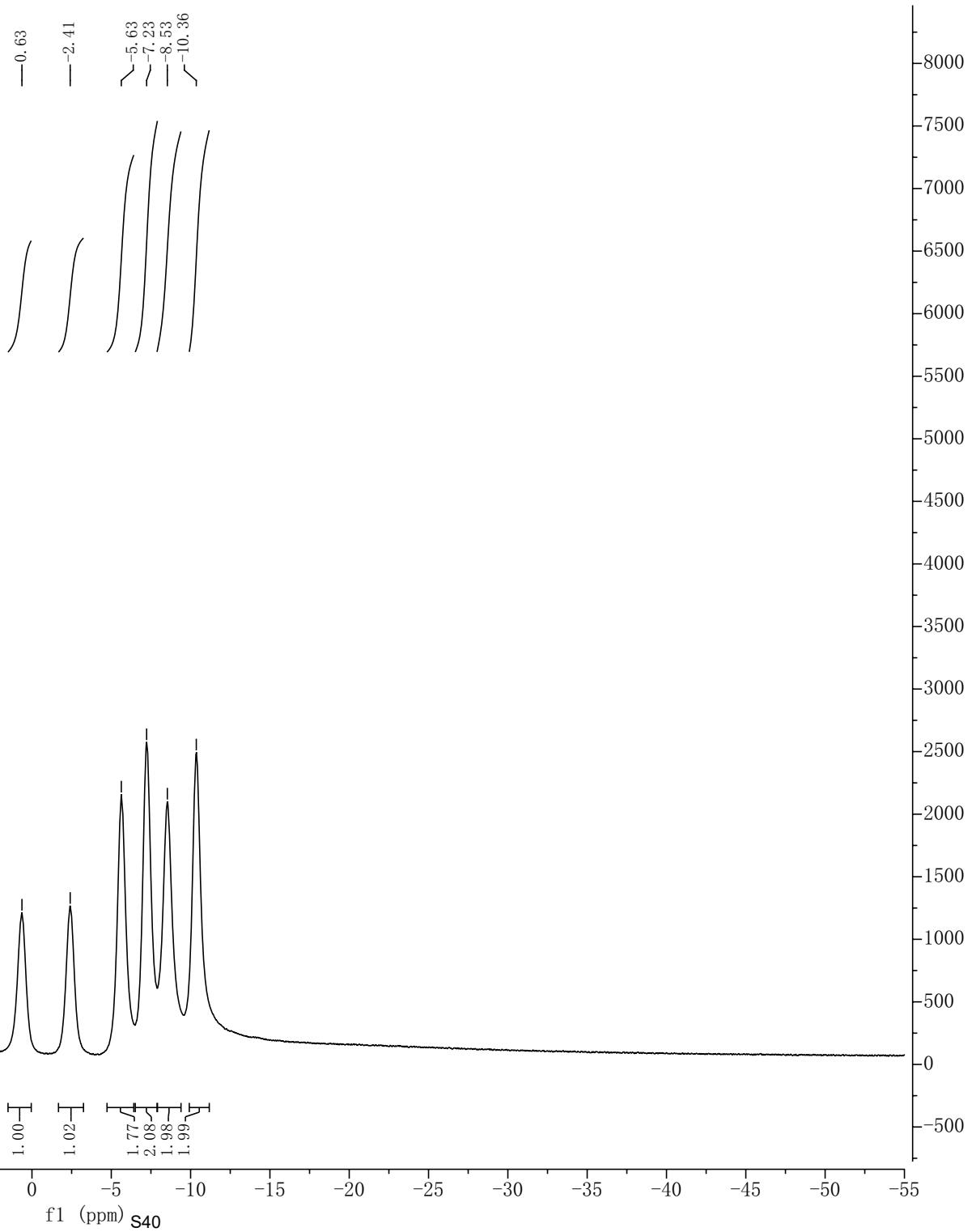


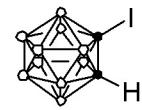




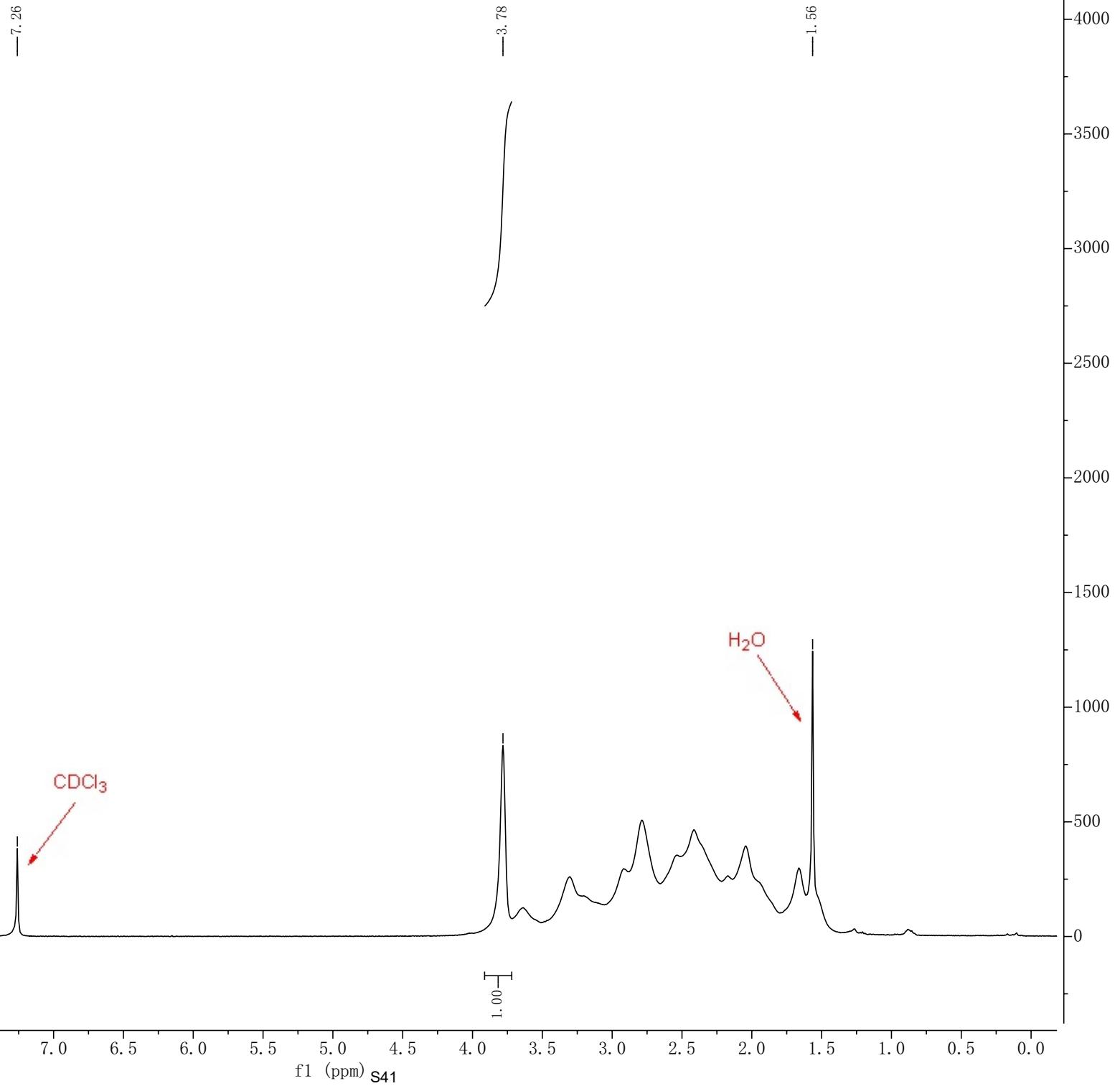


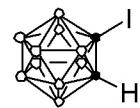
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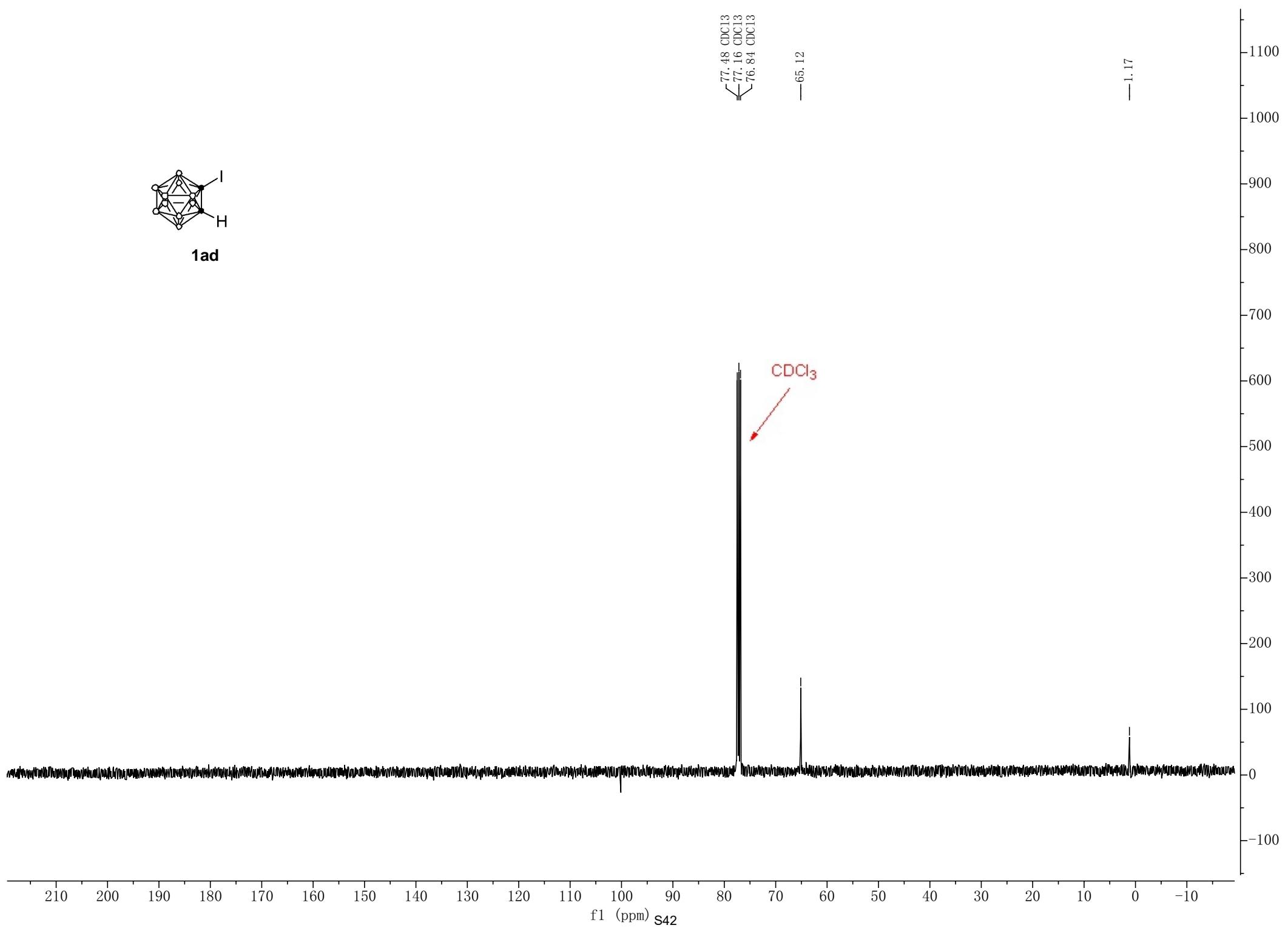


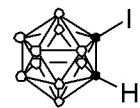
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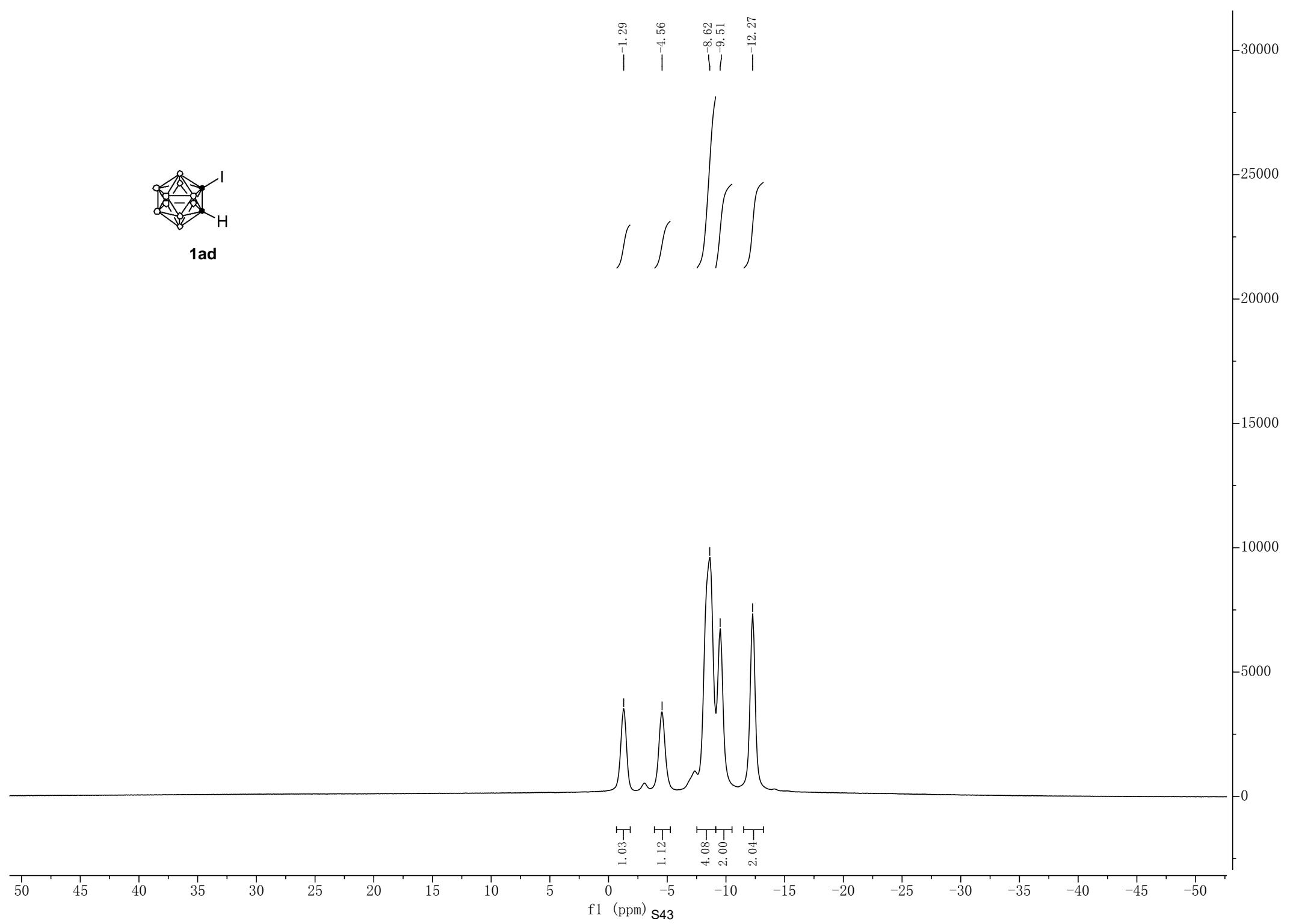


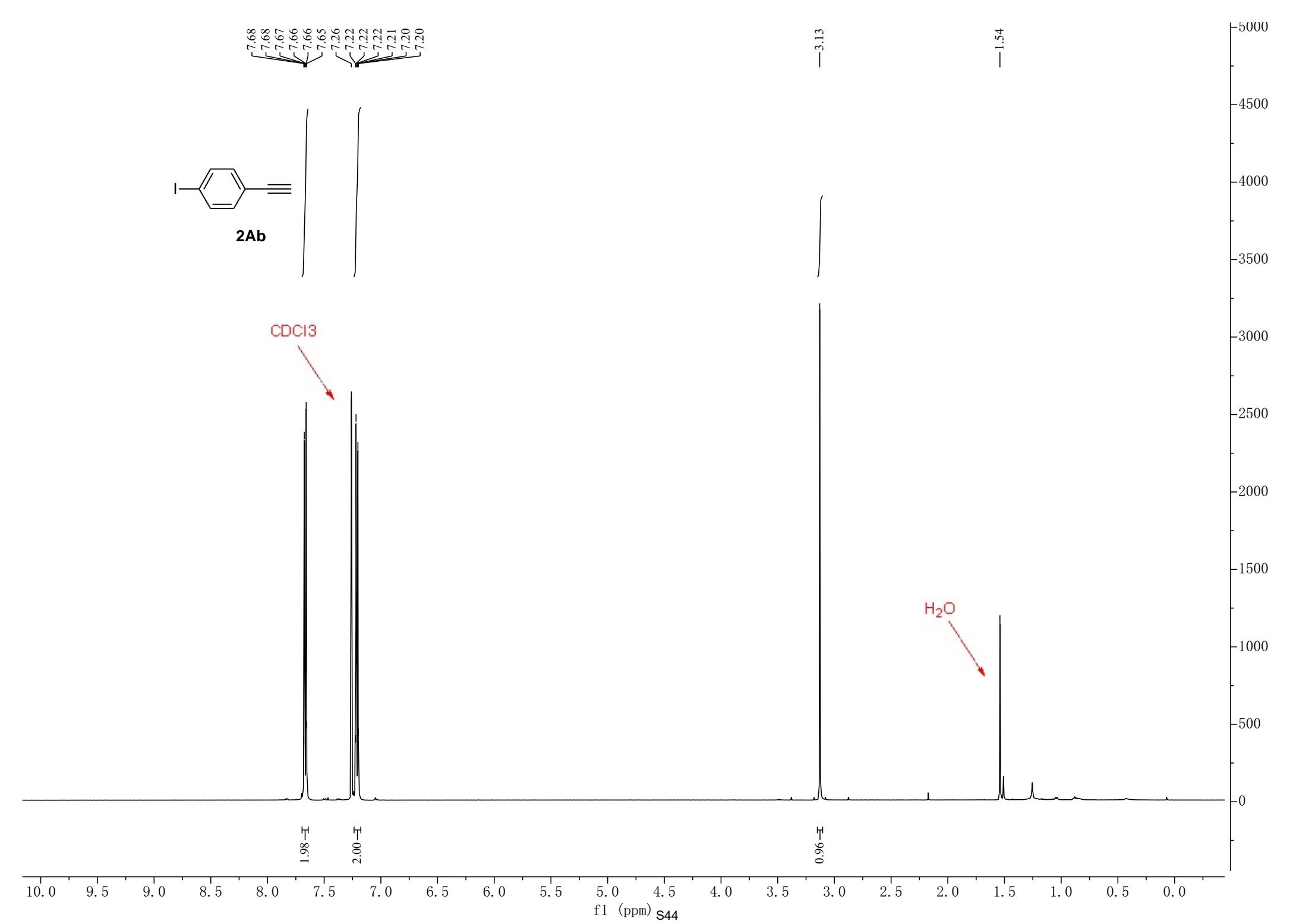
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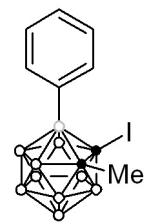




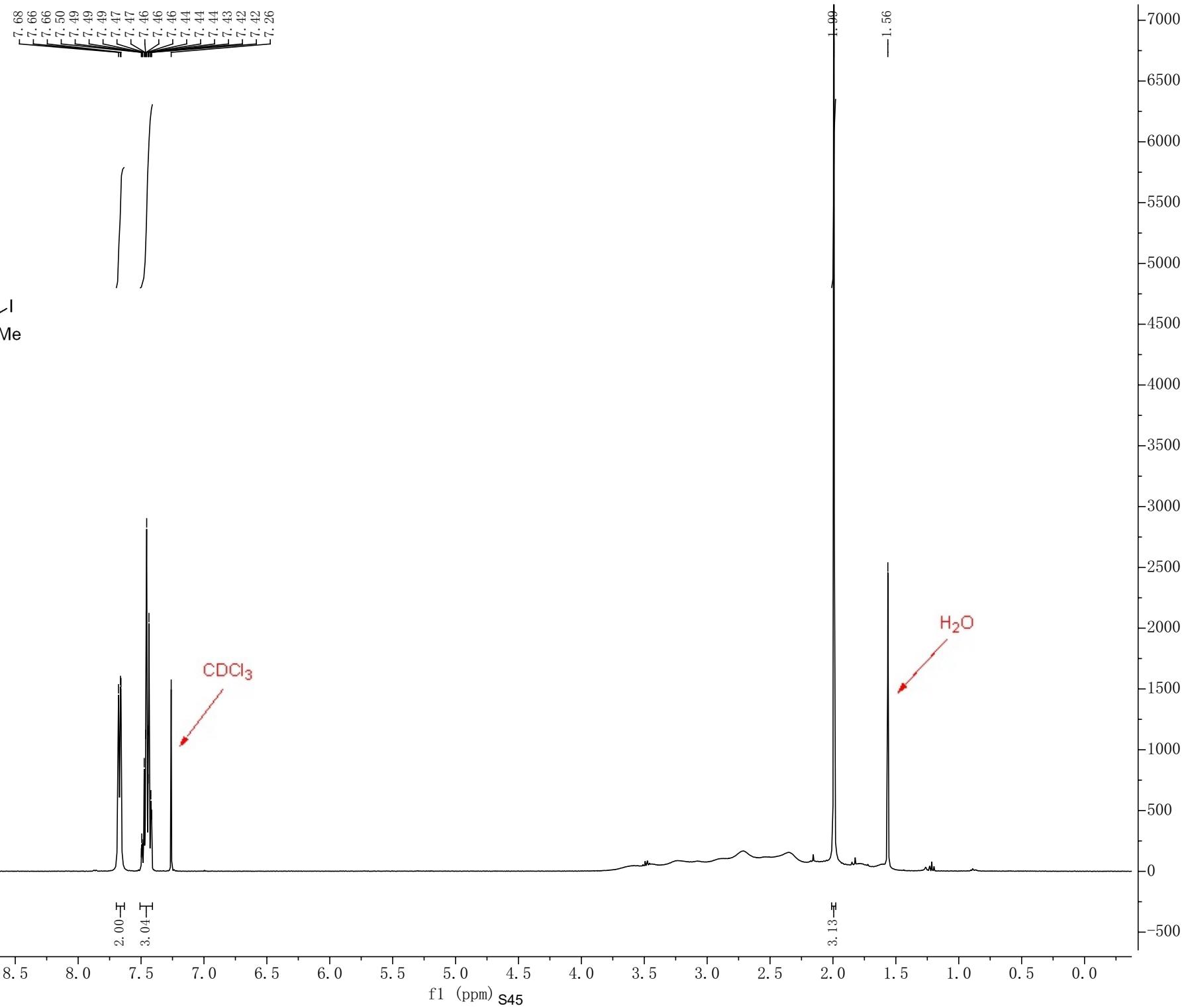
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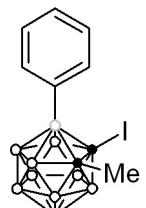




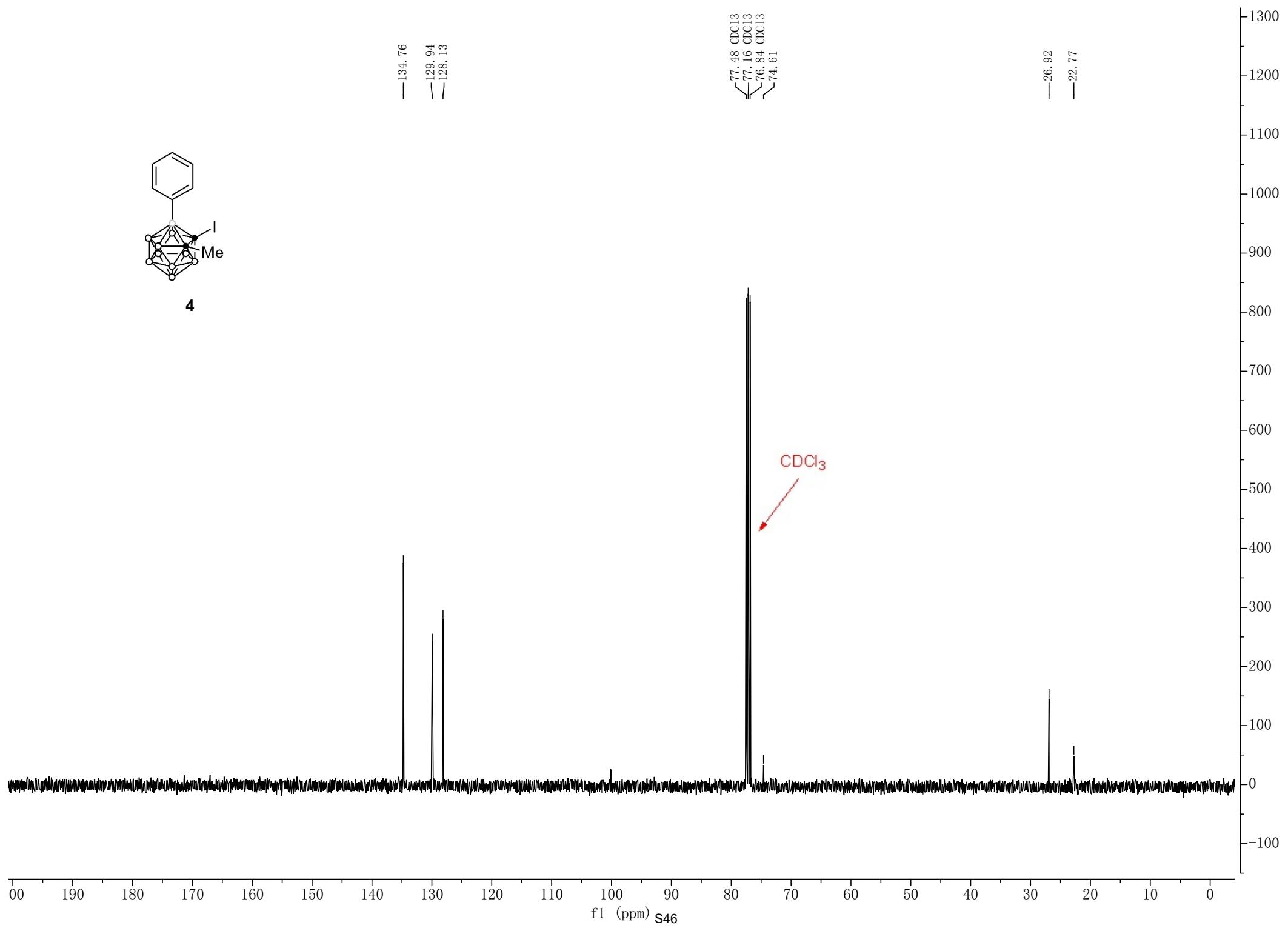


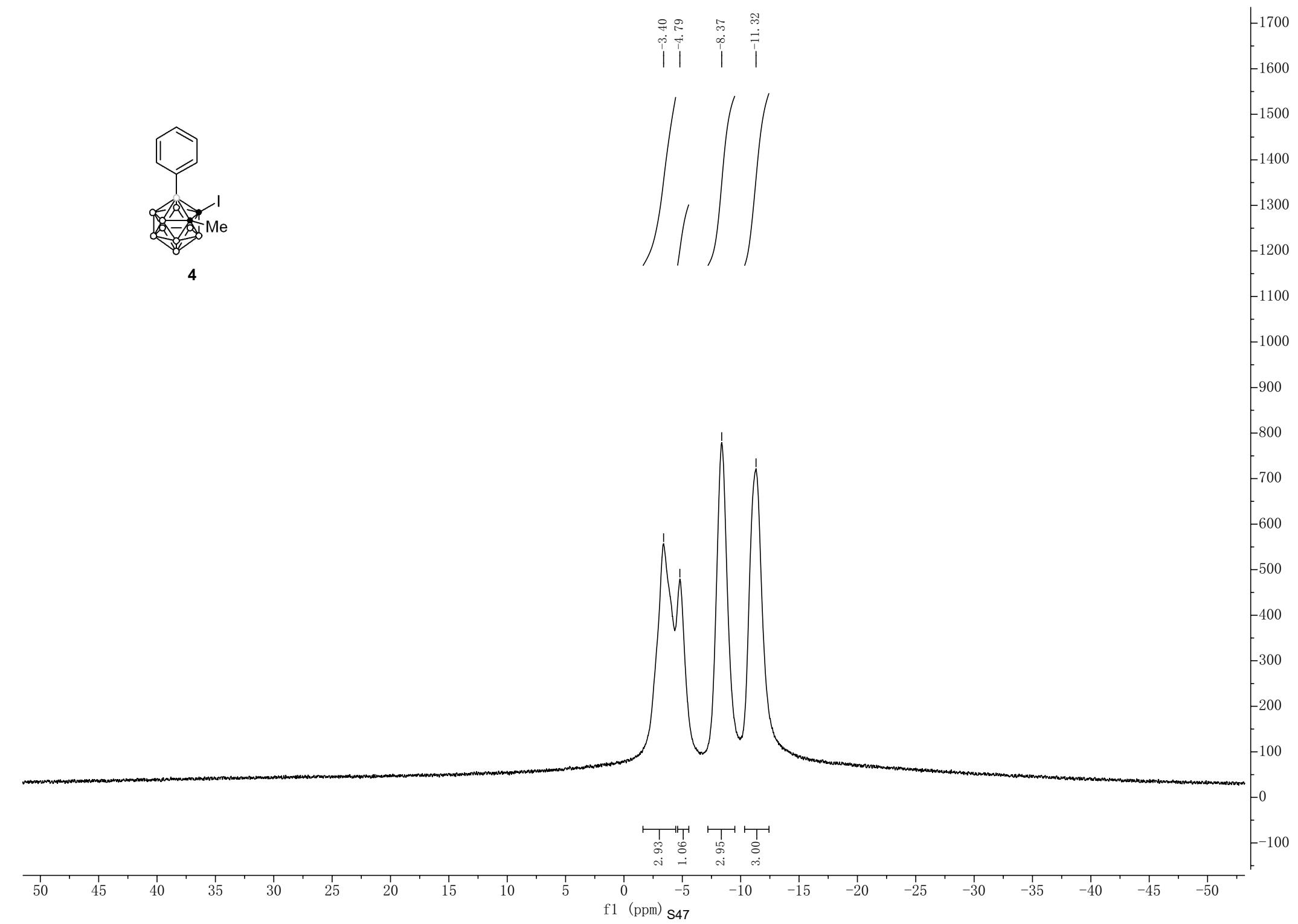
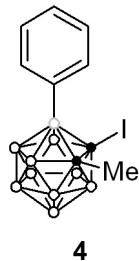
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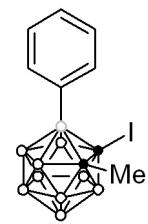




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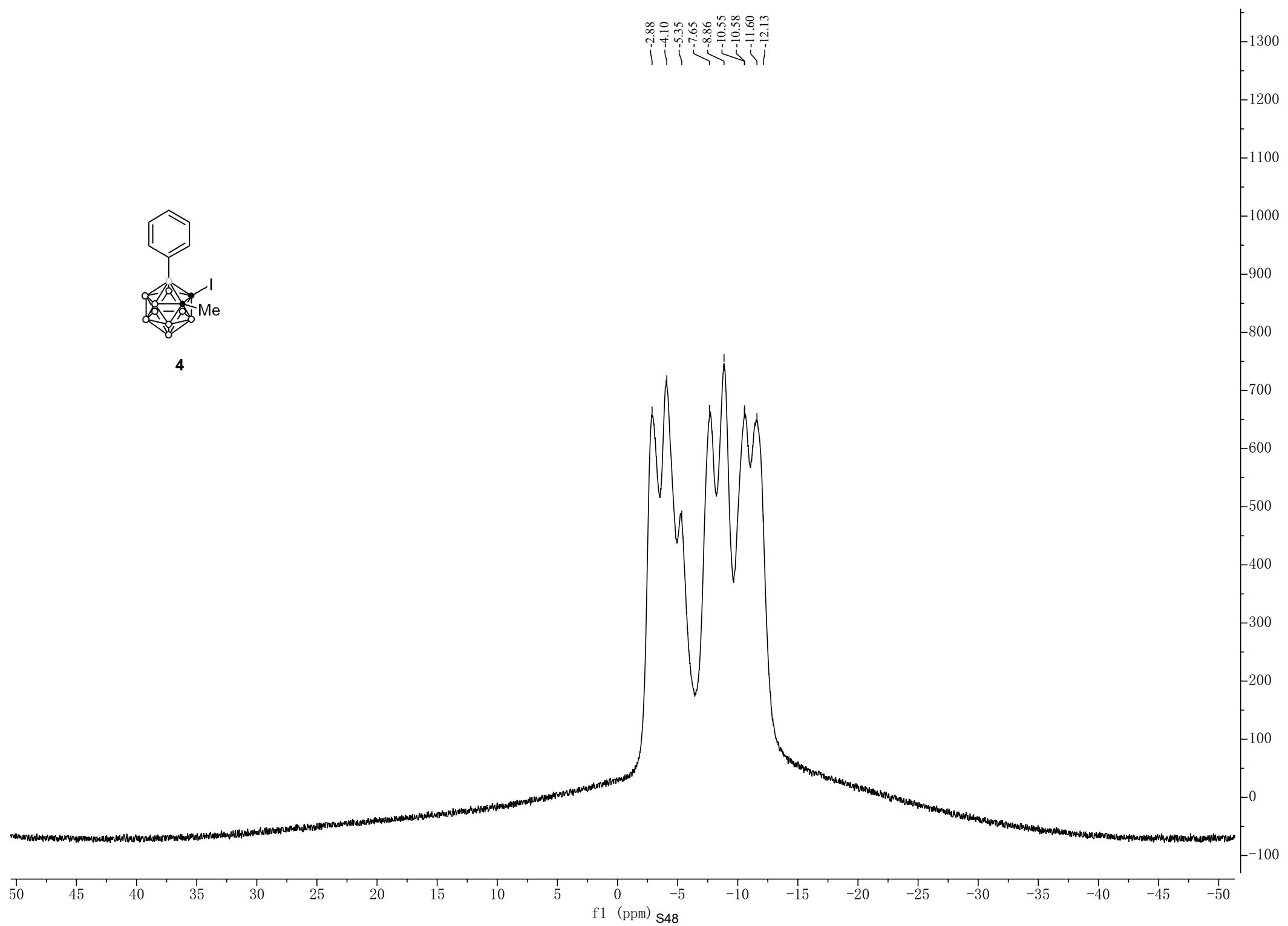


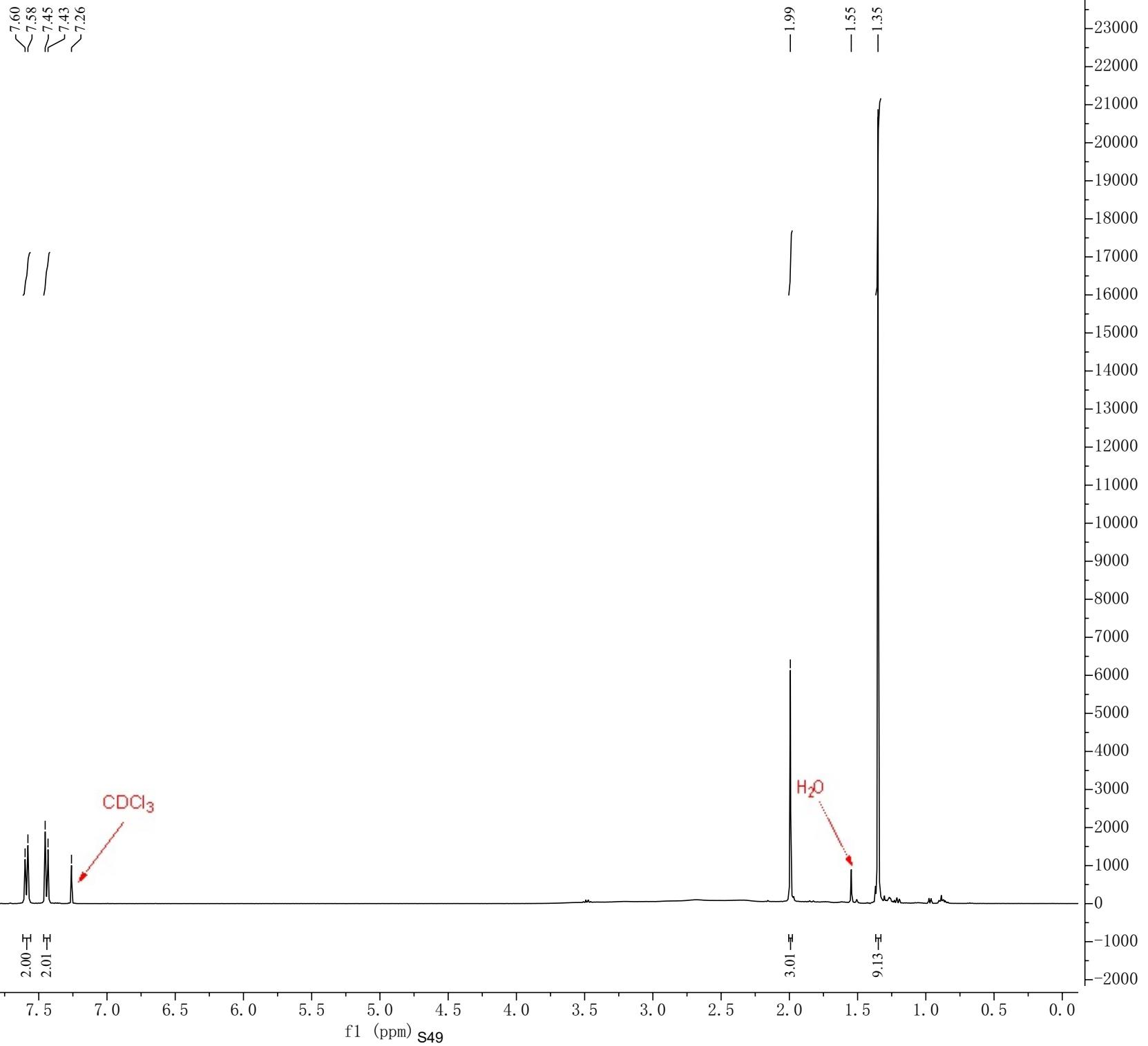
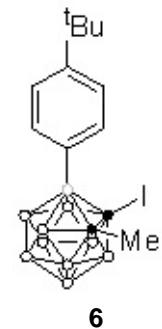


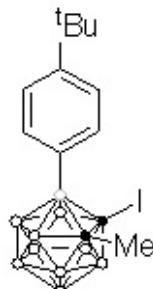


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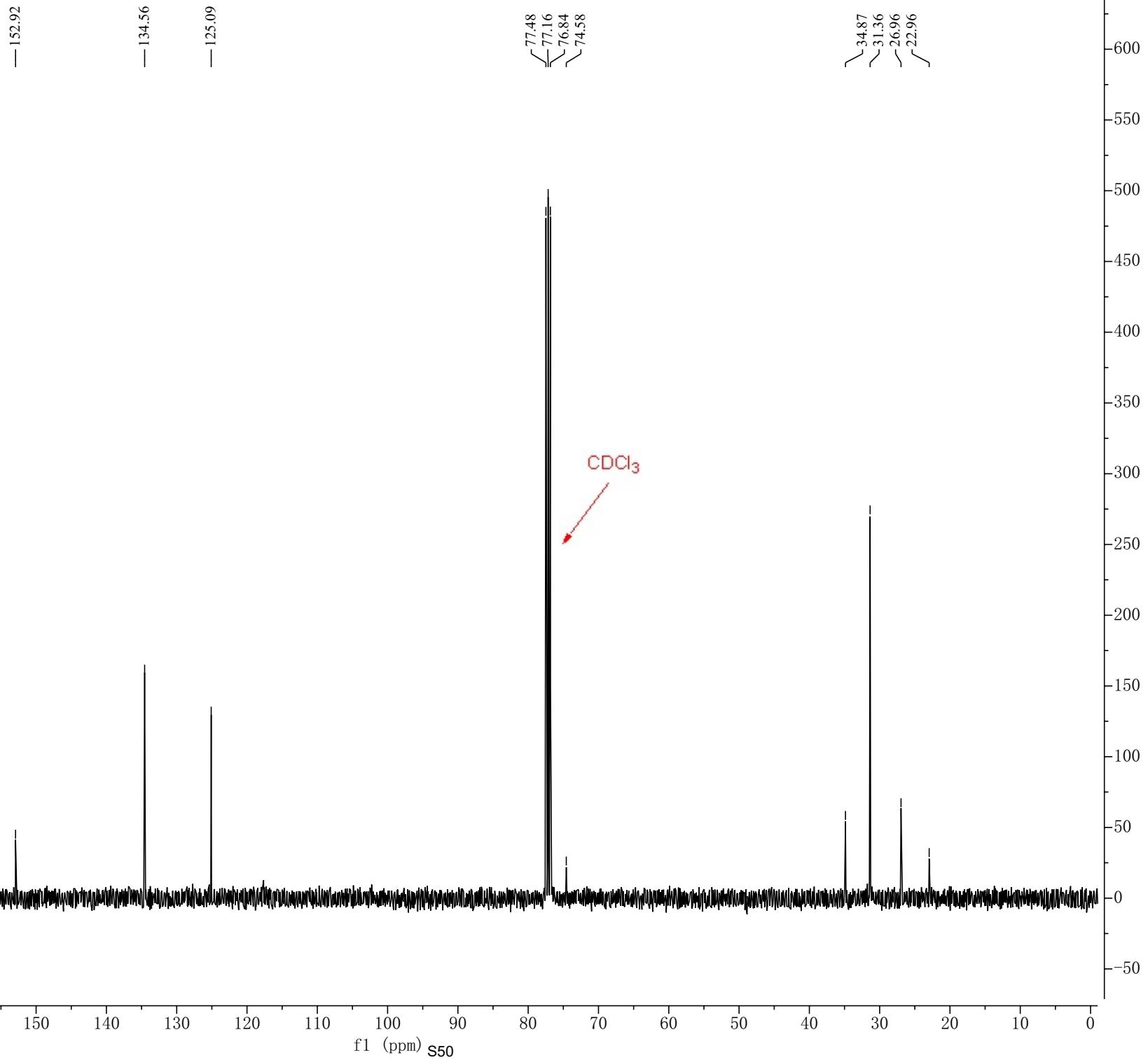
-2.88
-4.10
-5.35
-7.65
-8.86
-10.58
-11.60
-12.13

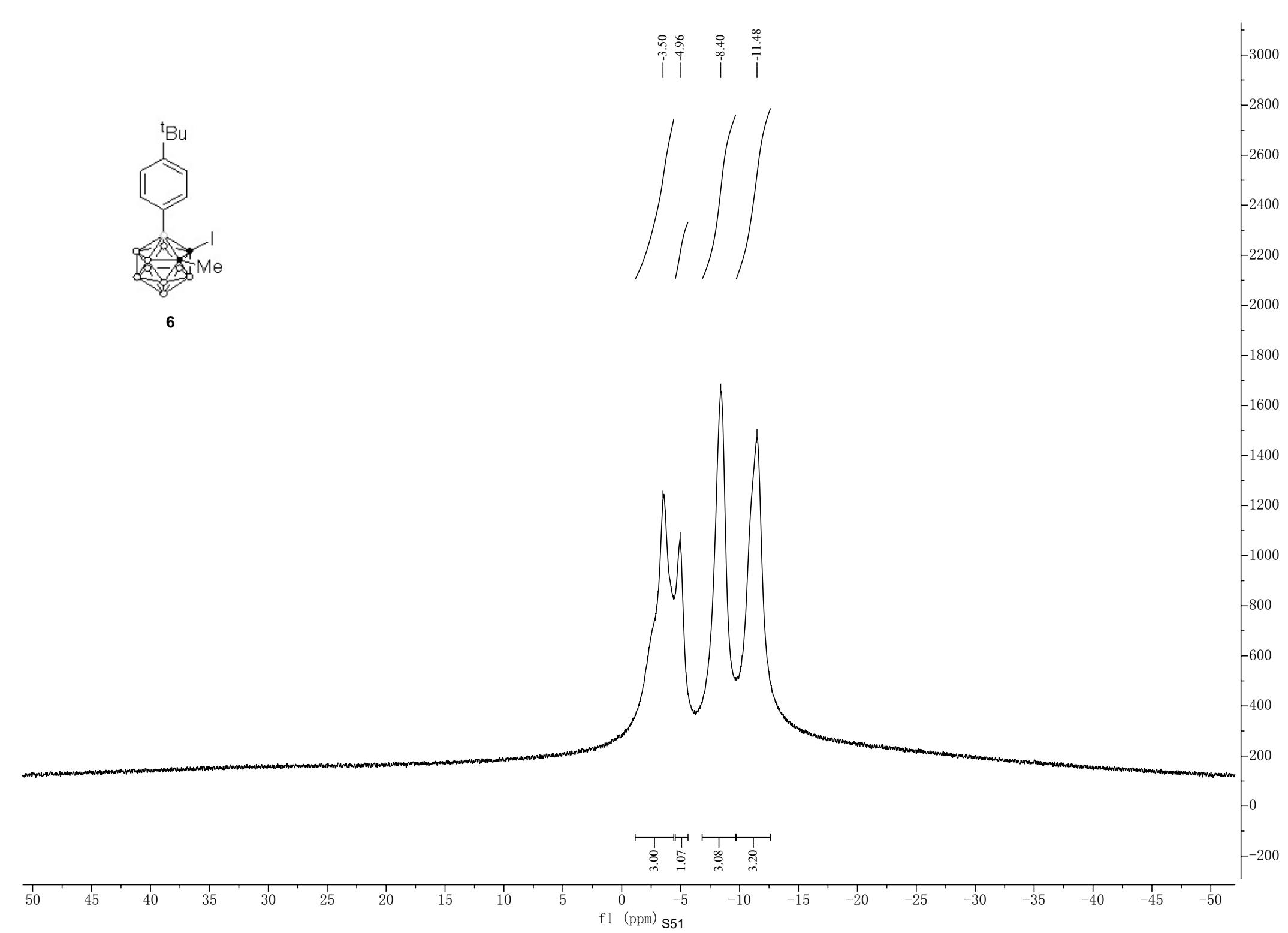
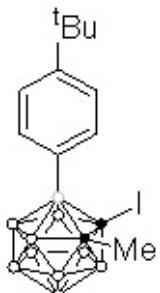


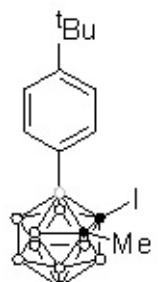




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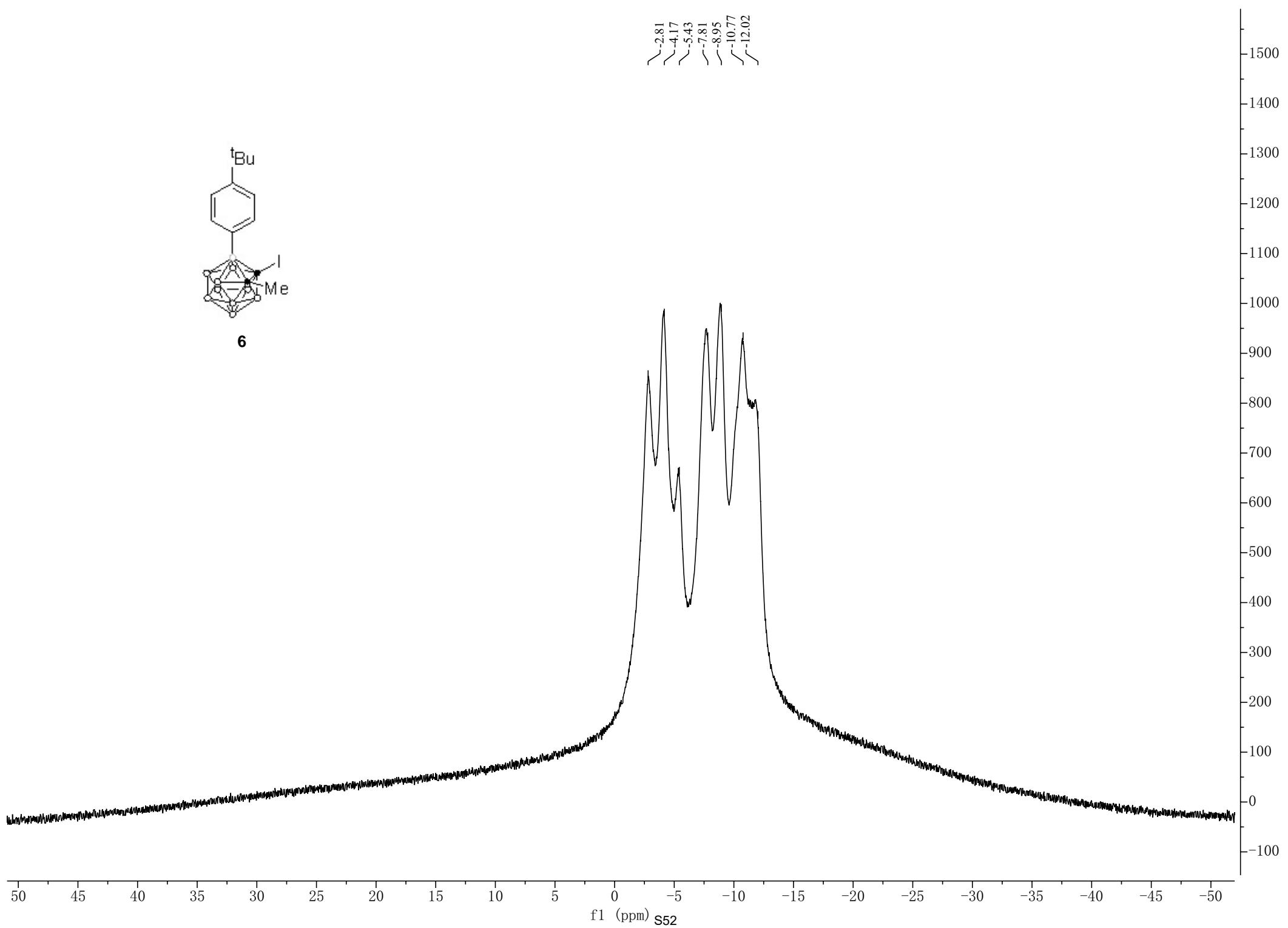


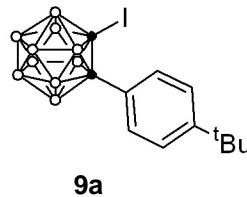




6

~ -2.81
~ -4.17
~ -5.43
~ -7.81
~ -8.95
~ -10.77
~ -12.02





7.56
7.54
7.43
7.41
7.41
7.26

—1.55
—1.34

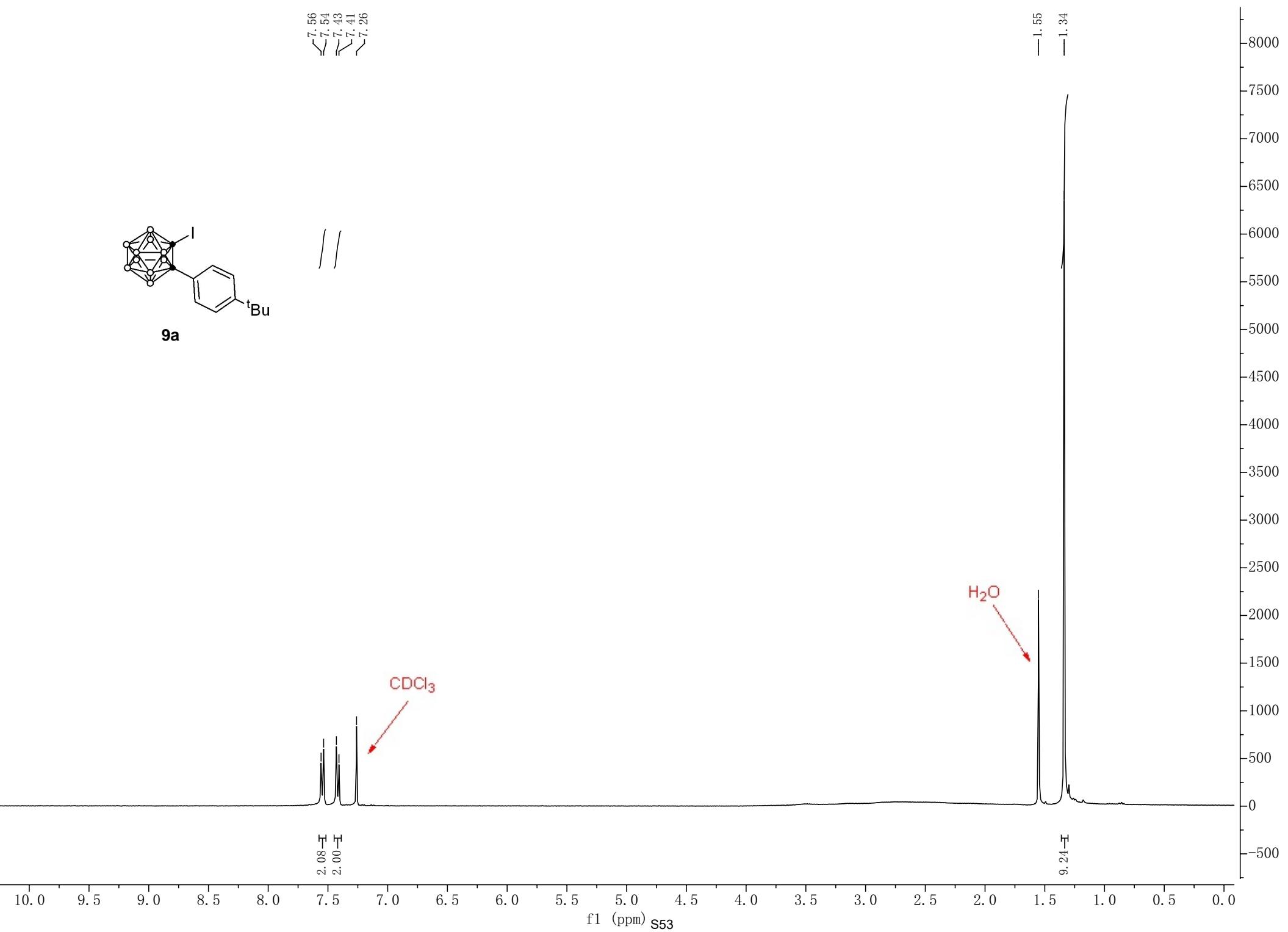
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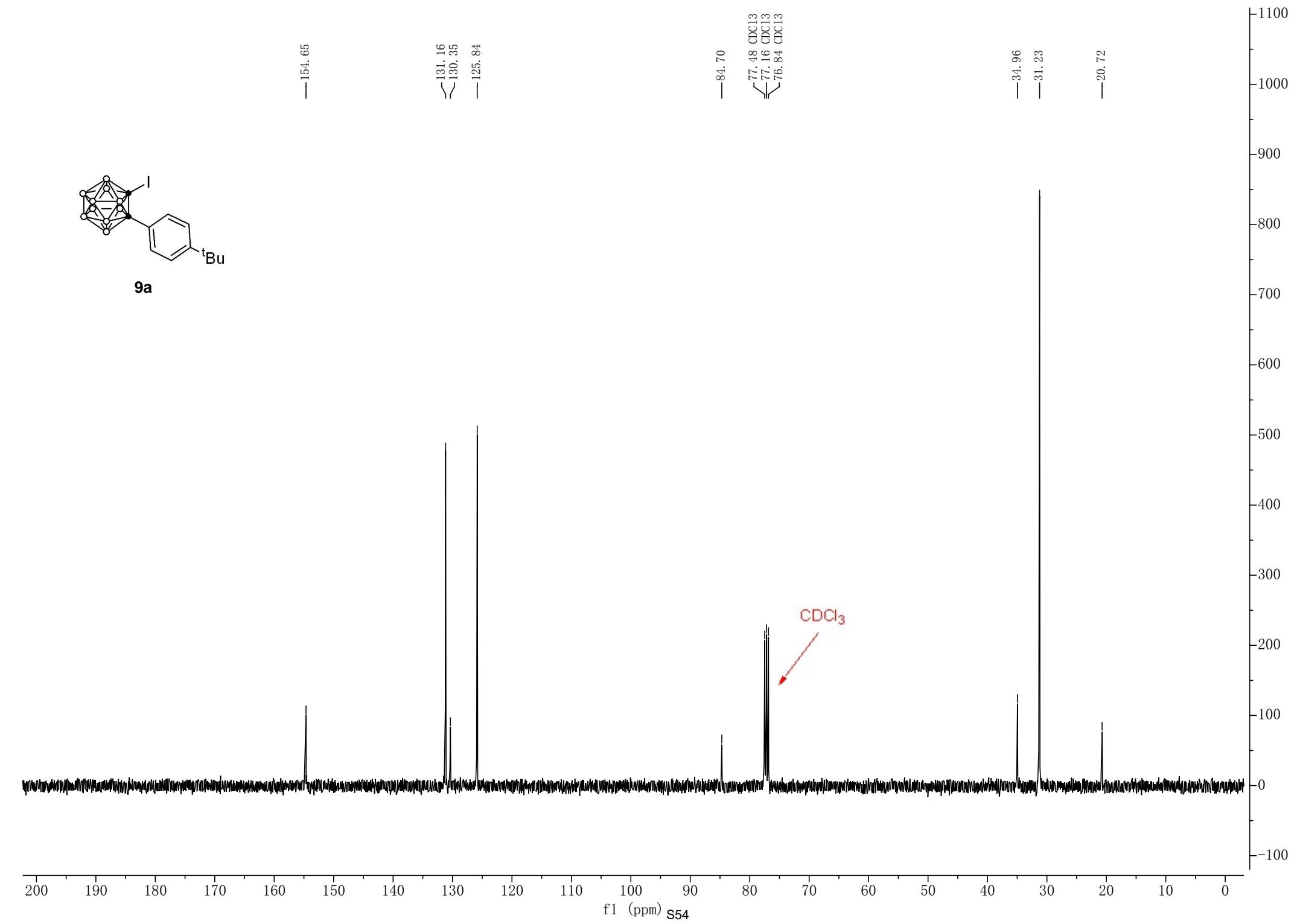
CDCl₃

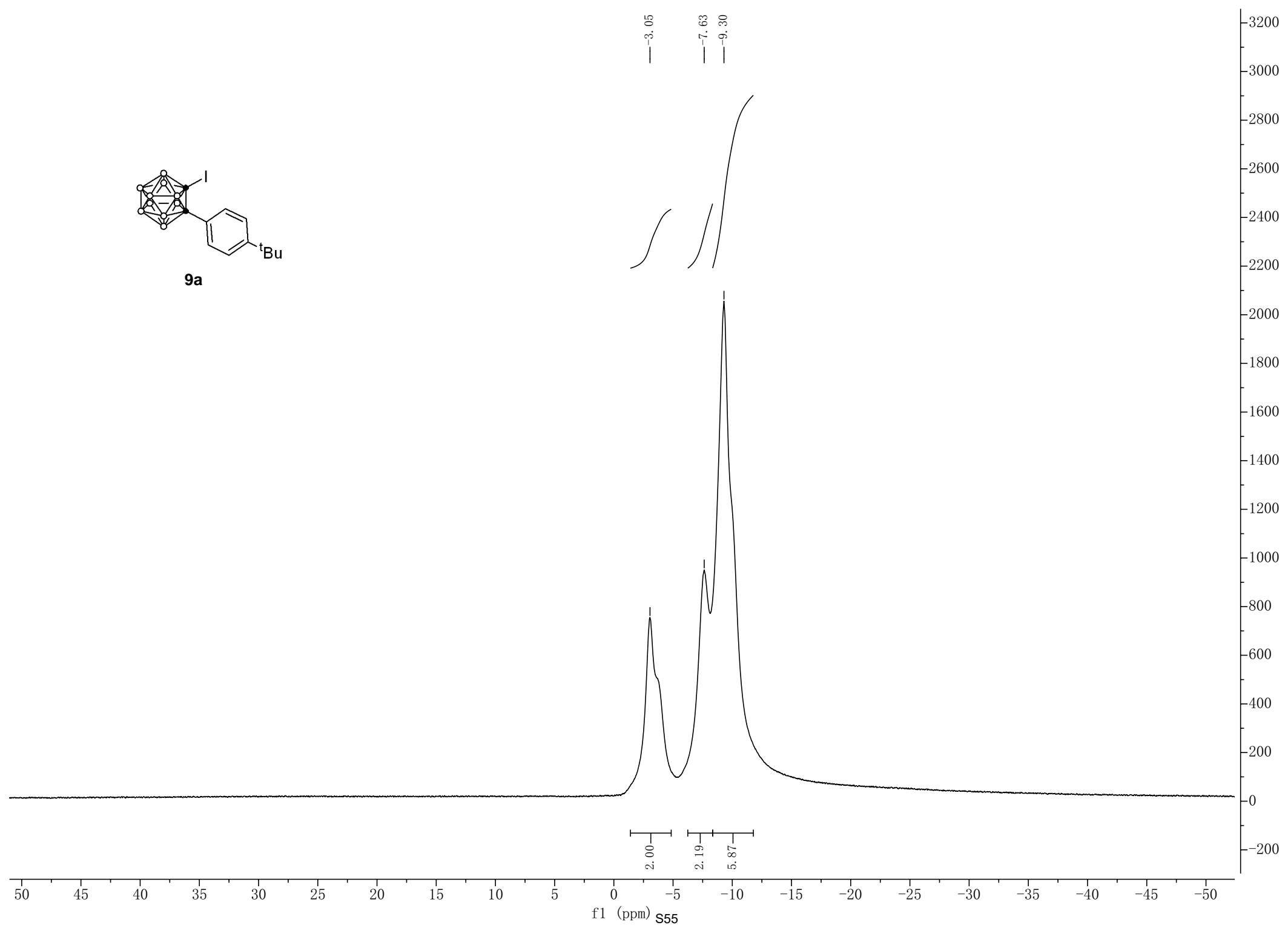
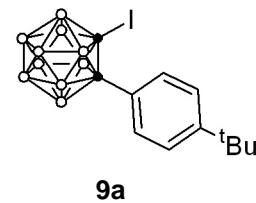
H₂O

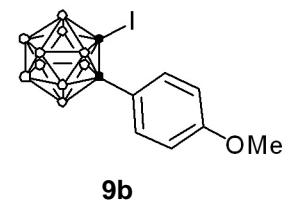
2.08-H
2.00-H
2.00-H

9.24-H









— 7.57
— 7.55
— 7.26
— 6.92
— 6.90

— 3.86
— 1.55

CDCl₃

H₂O

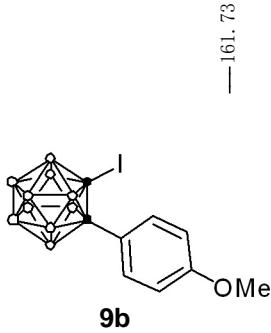
1.94 F
1.89 F

3.00 F

10.0 9.5 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) S56

6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500



—161.73

—133.00

—125.62

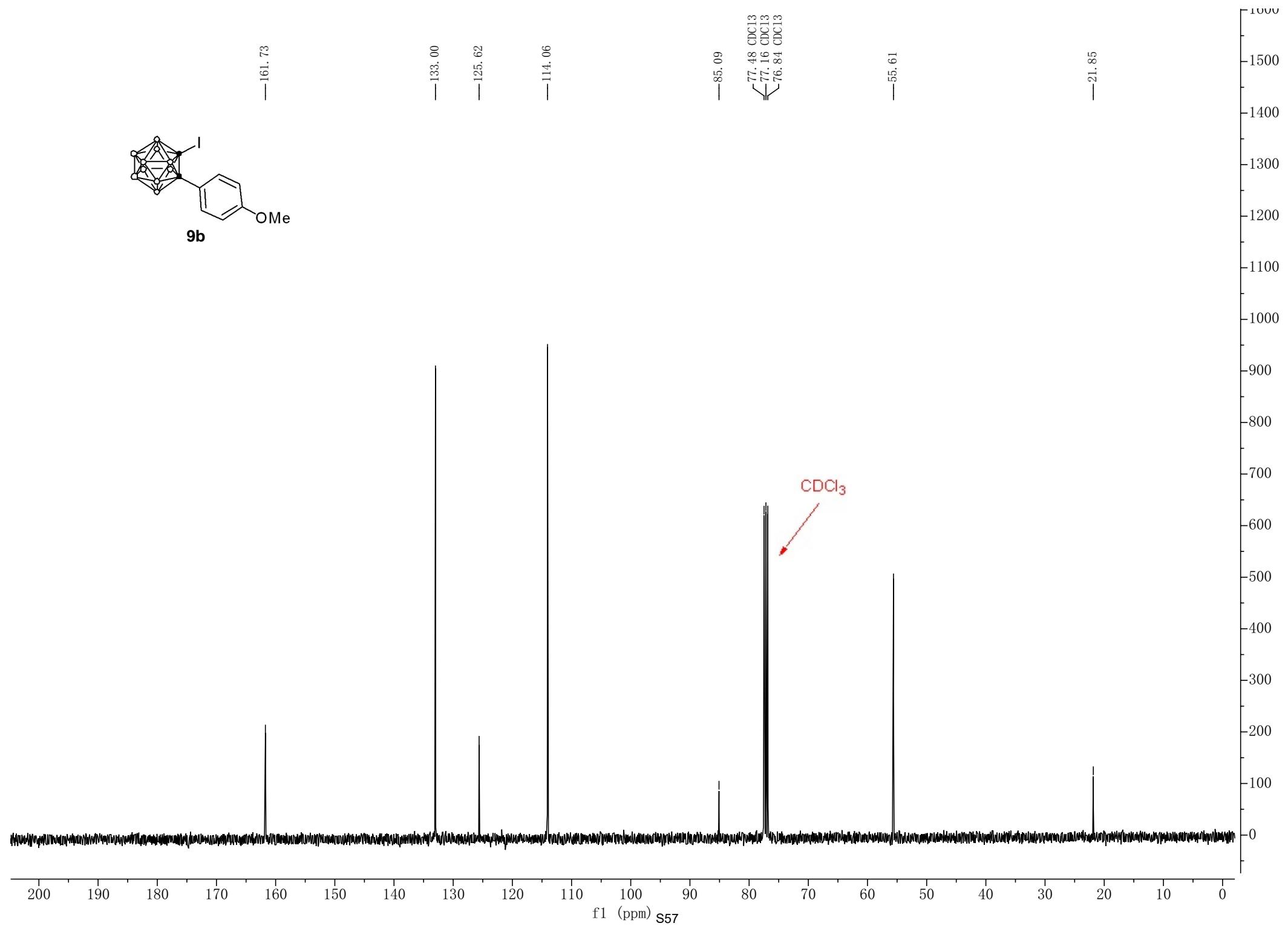
—114.06

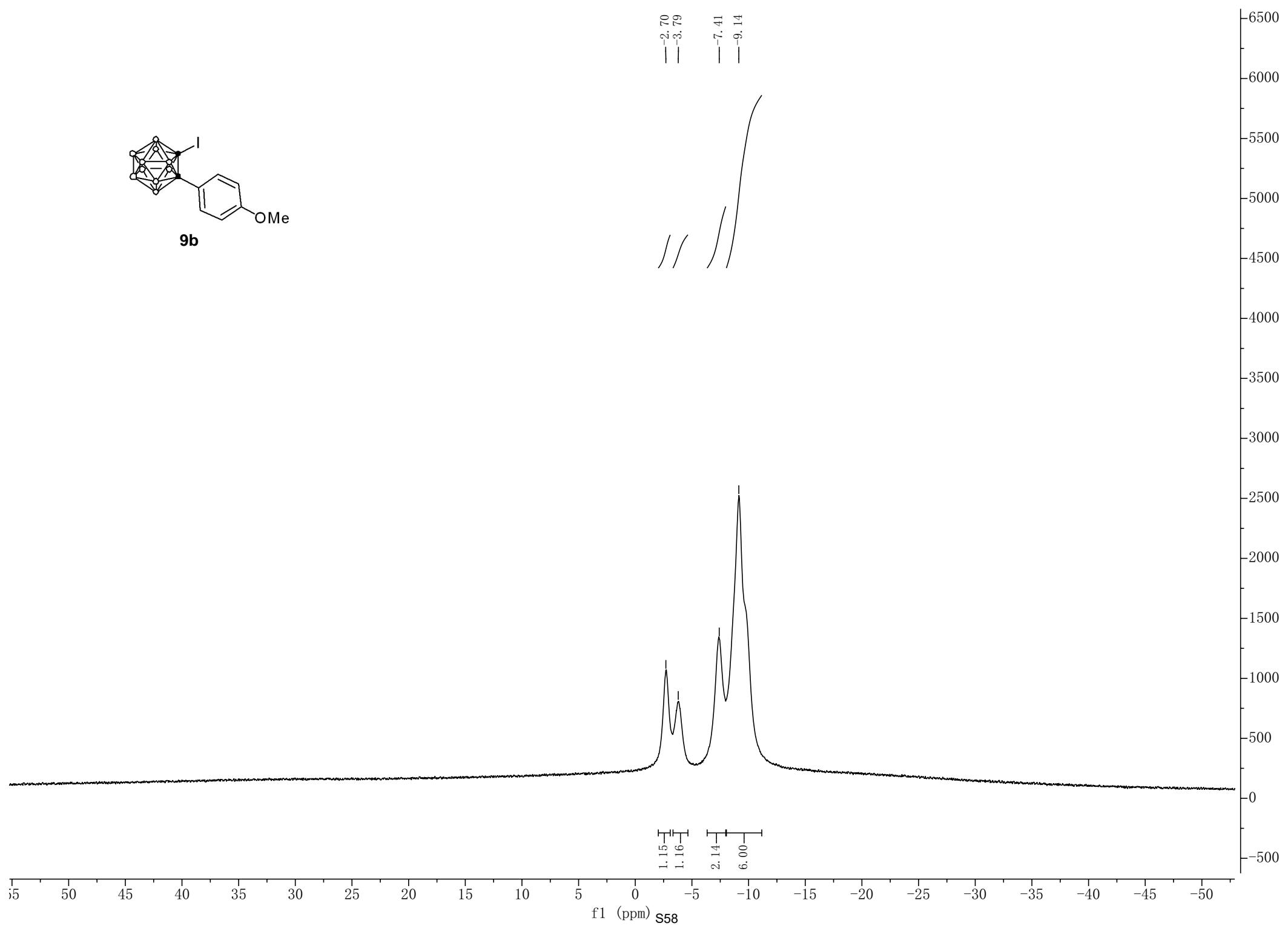
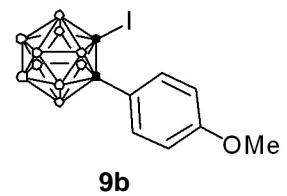
—85.09

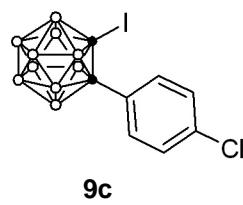
77.48 CDC13
77.16 CDC13
76.84 CDC13

—55.61

—21.85







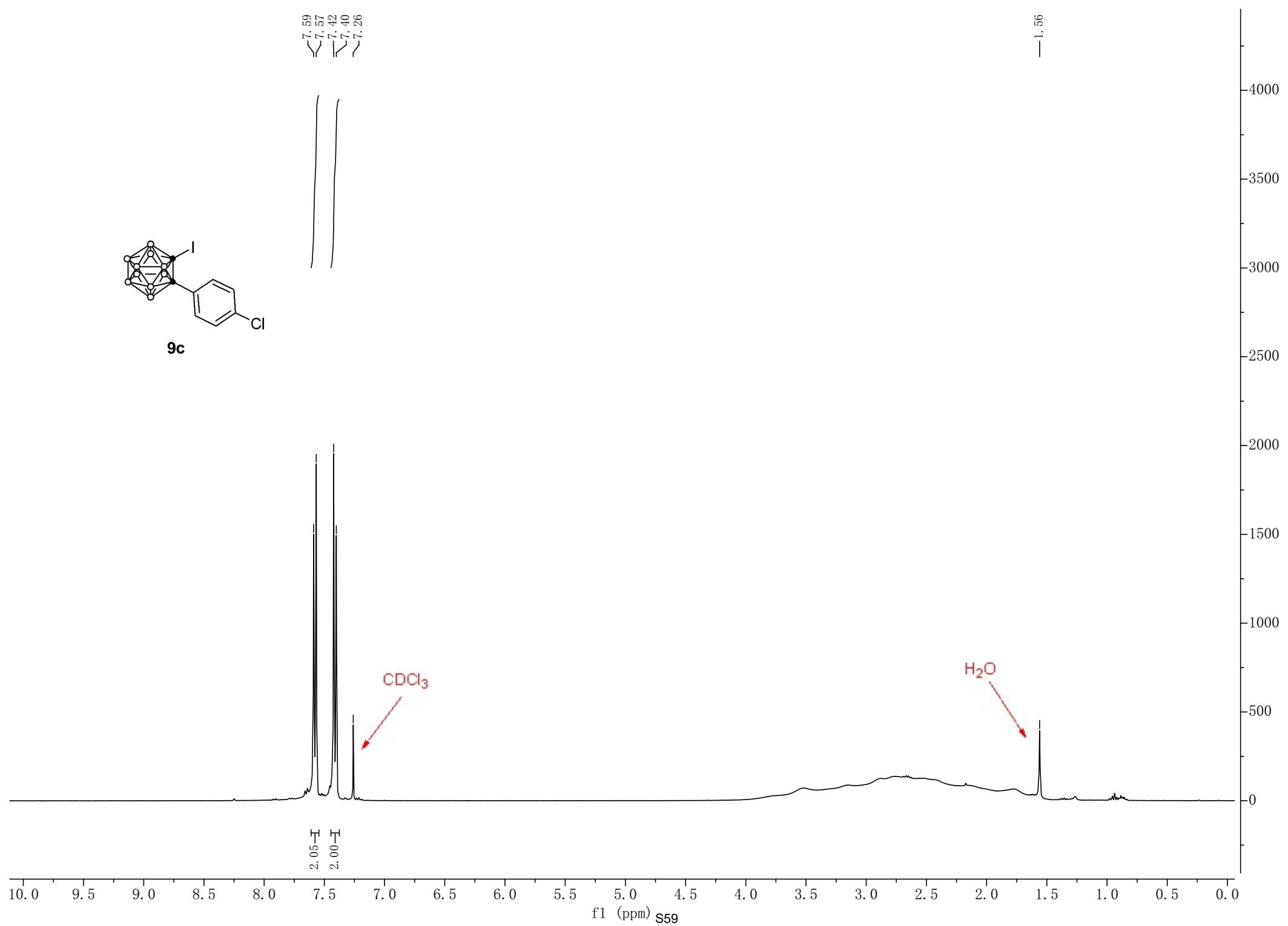
7.59
7.57
7.42
7.40
7.26

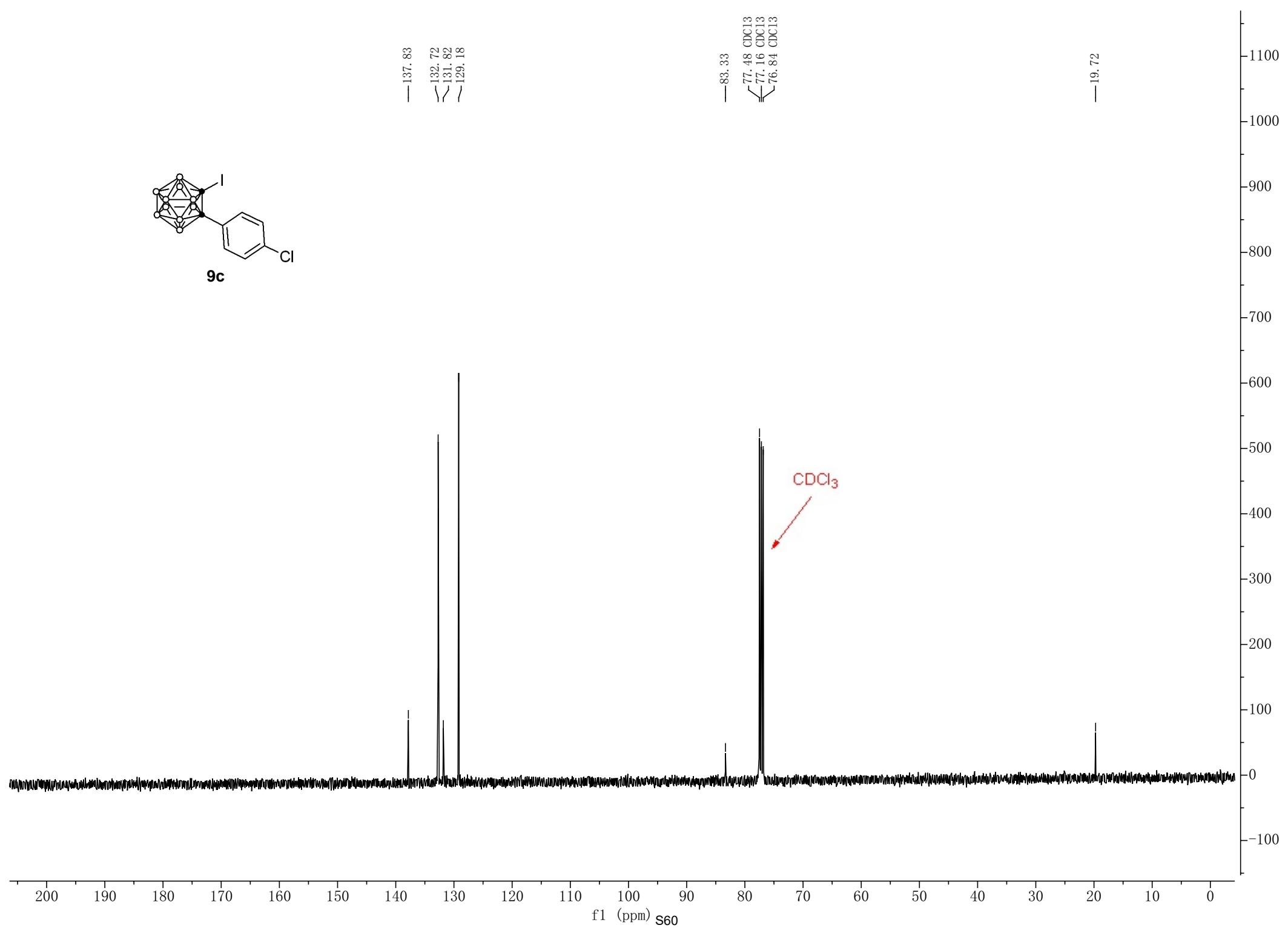
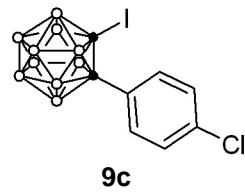
—1.56

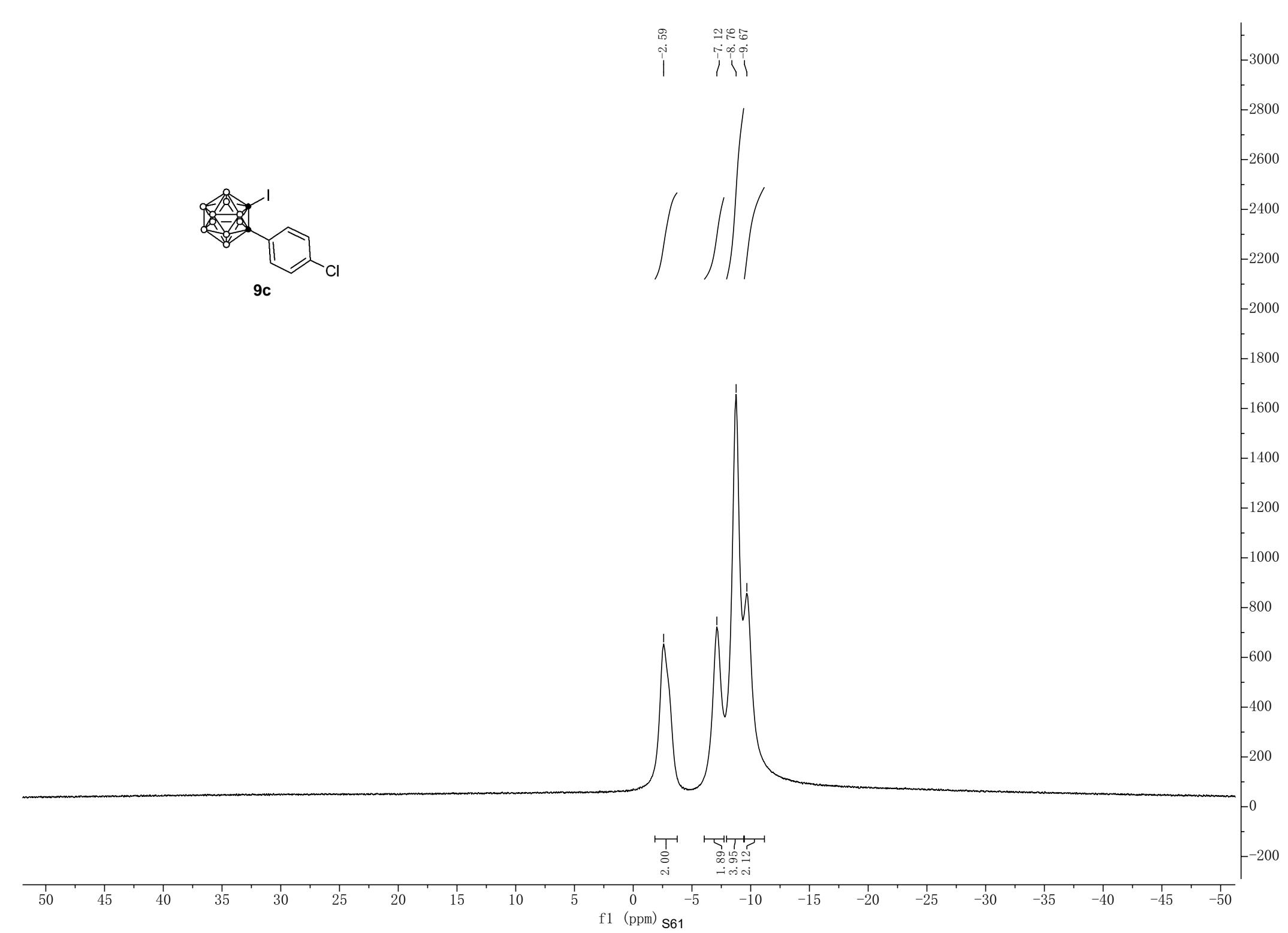
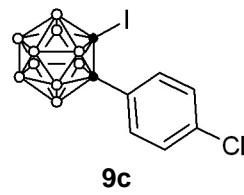
2.05 —T
2.00 —T

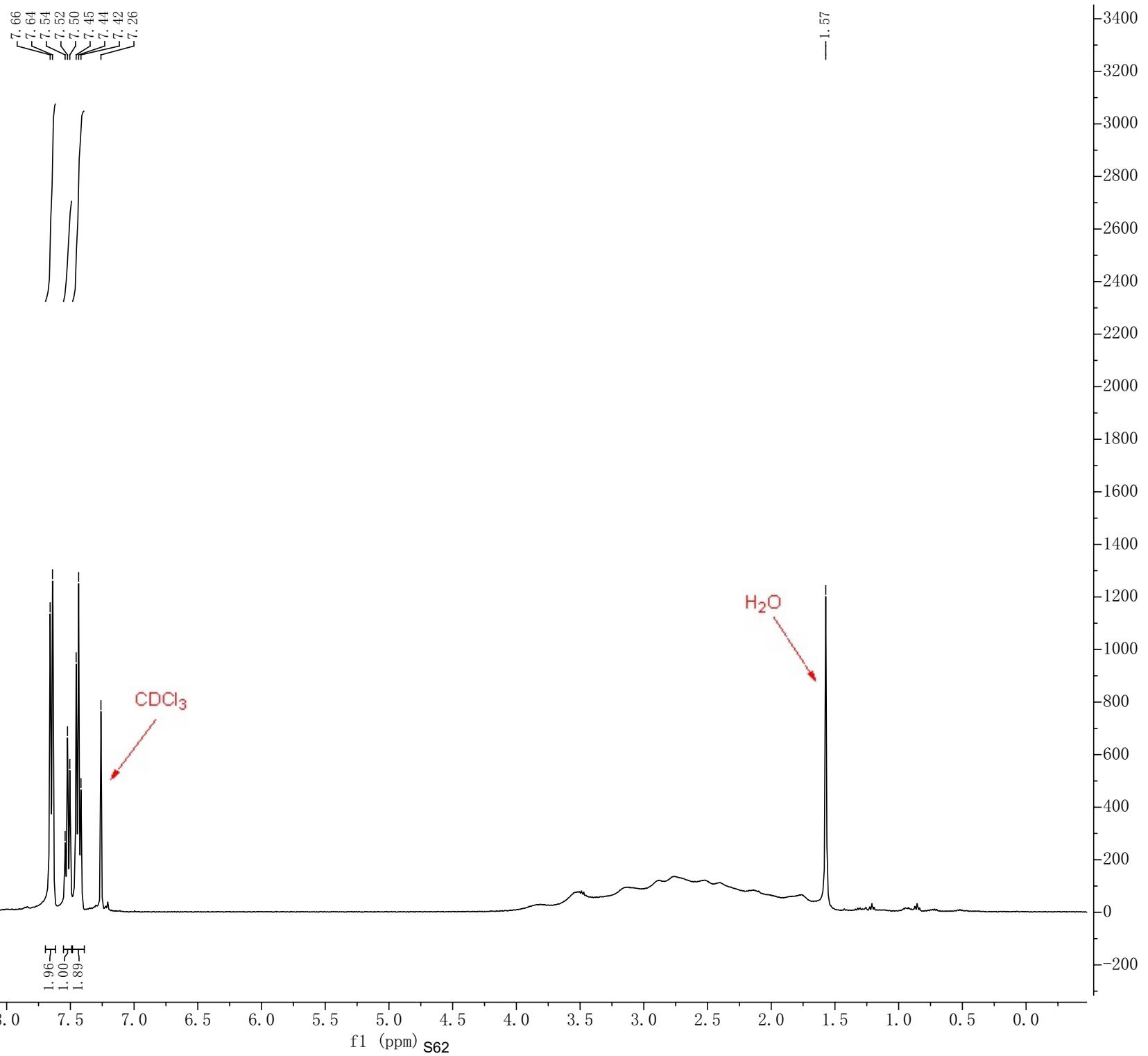
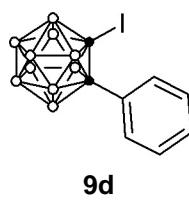
CDCl₃

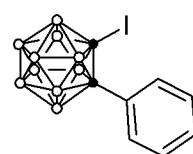
H₂O



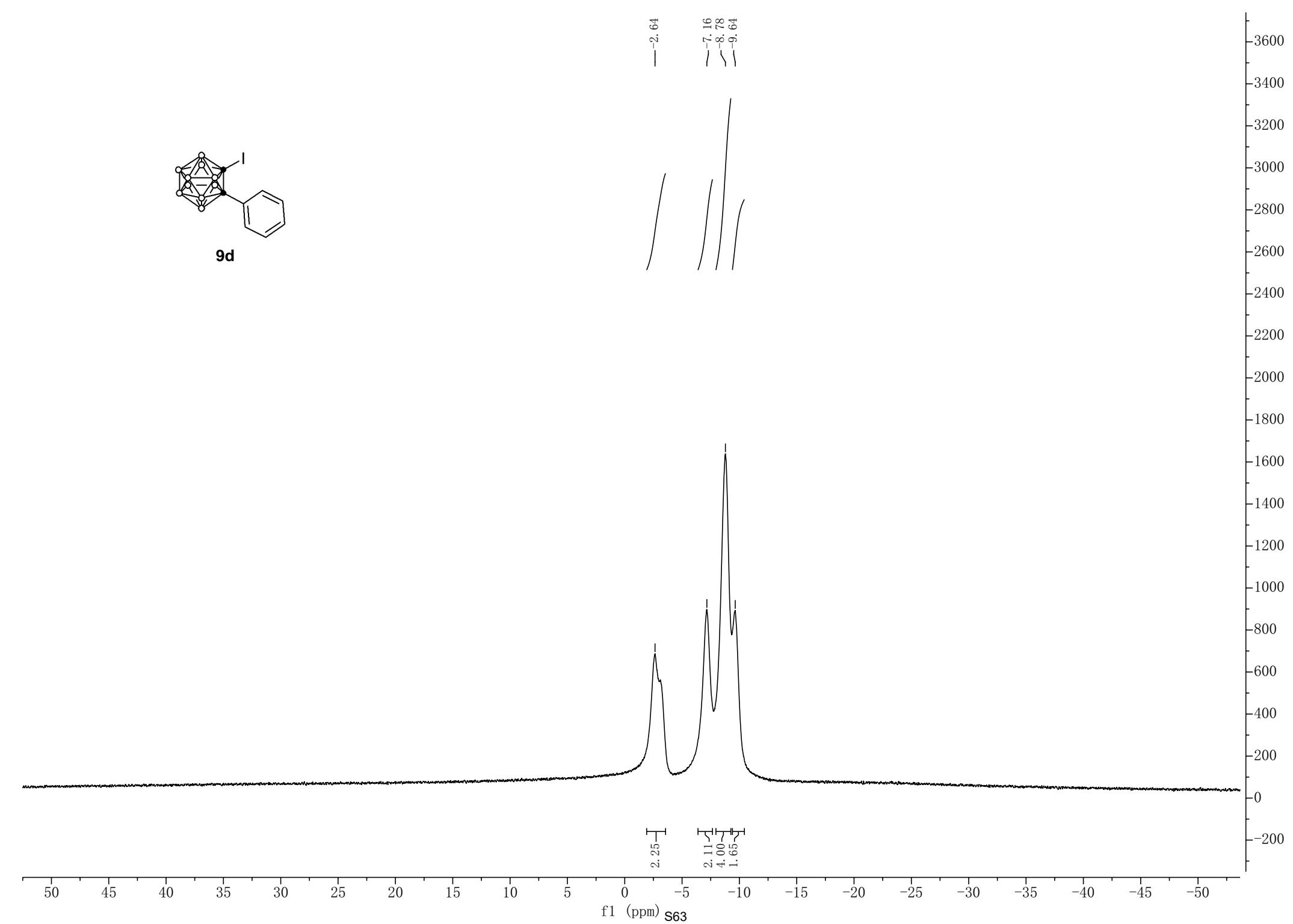


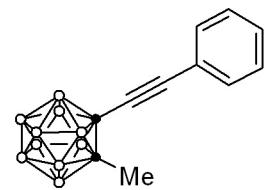




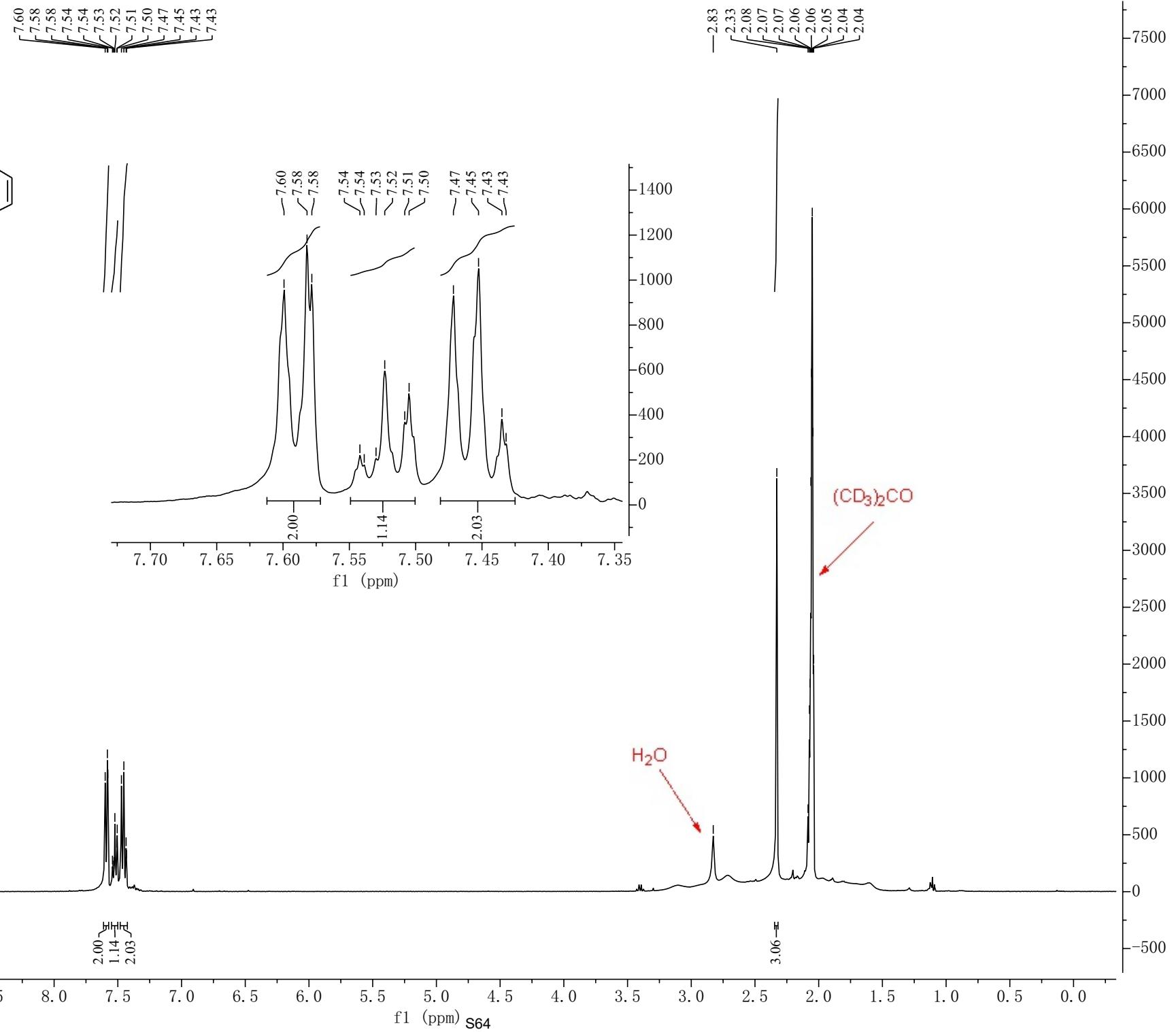


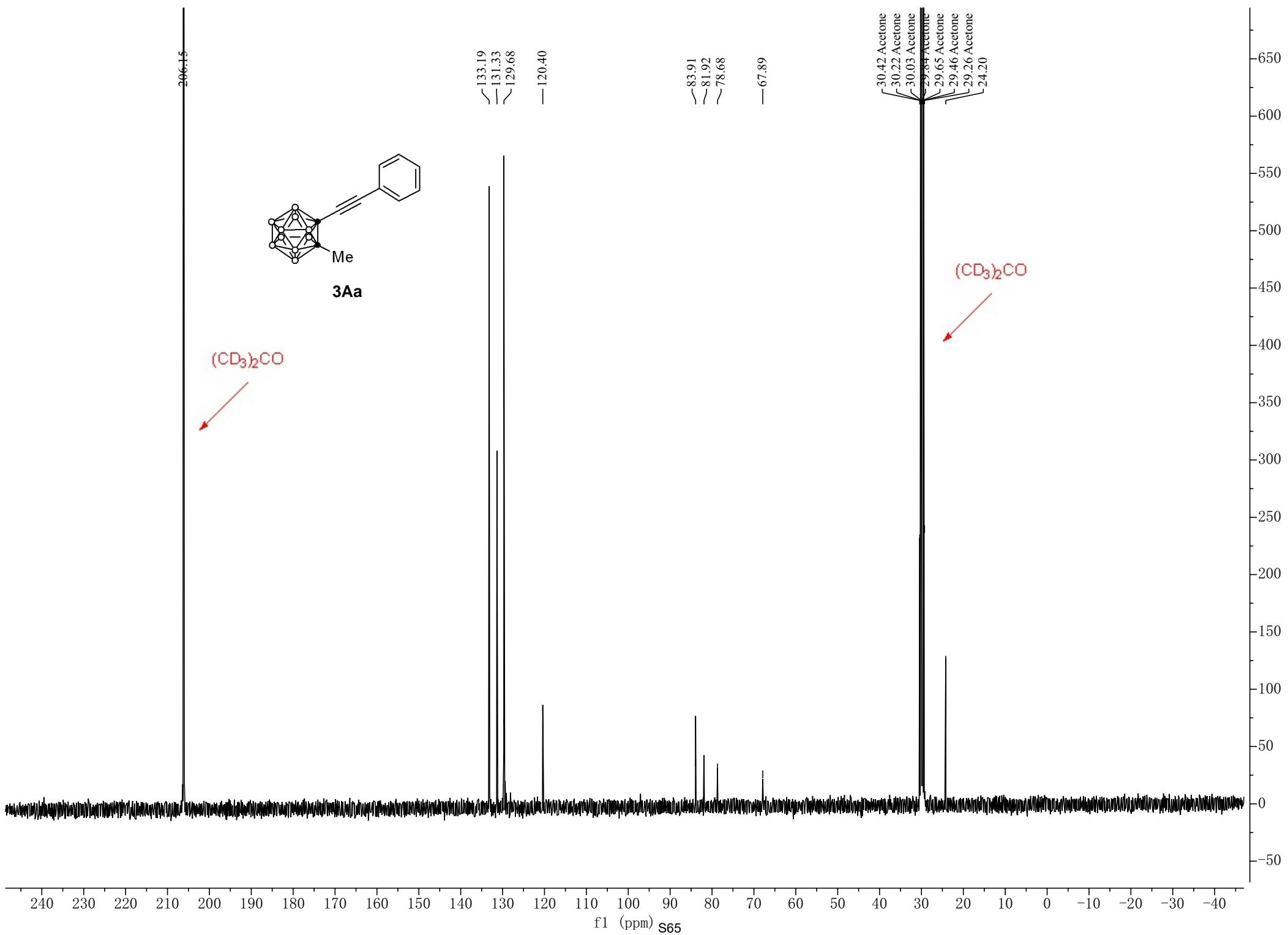
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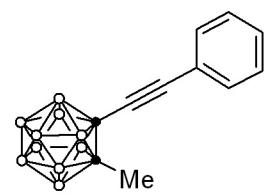




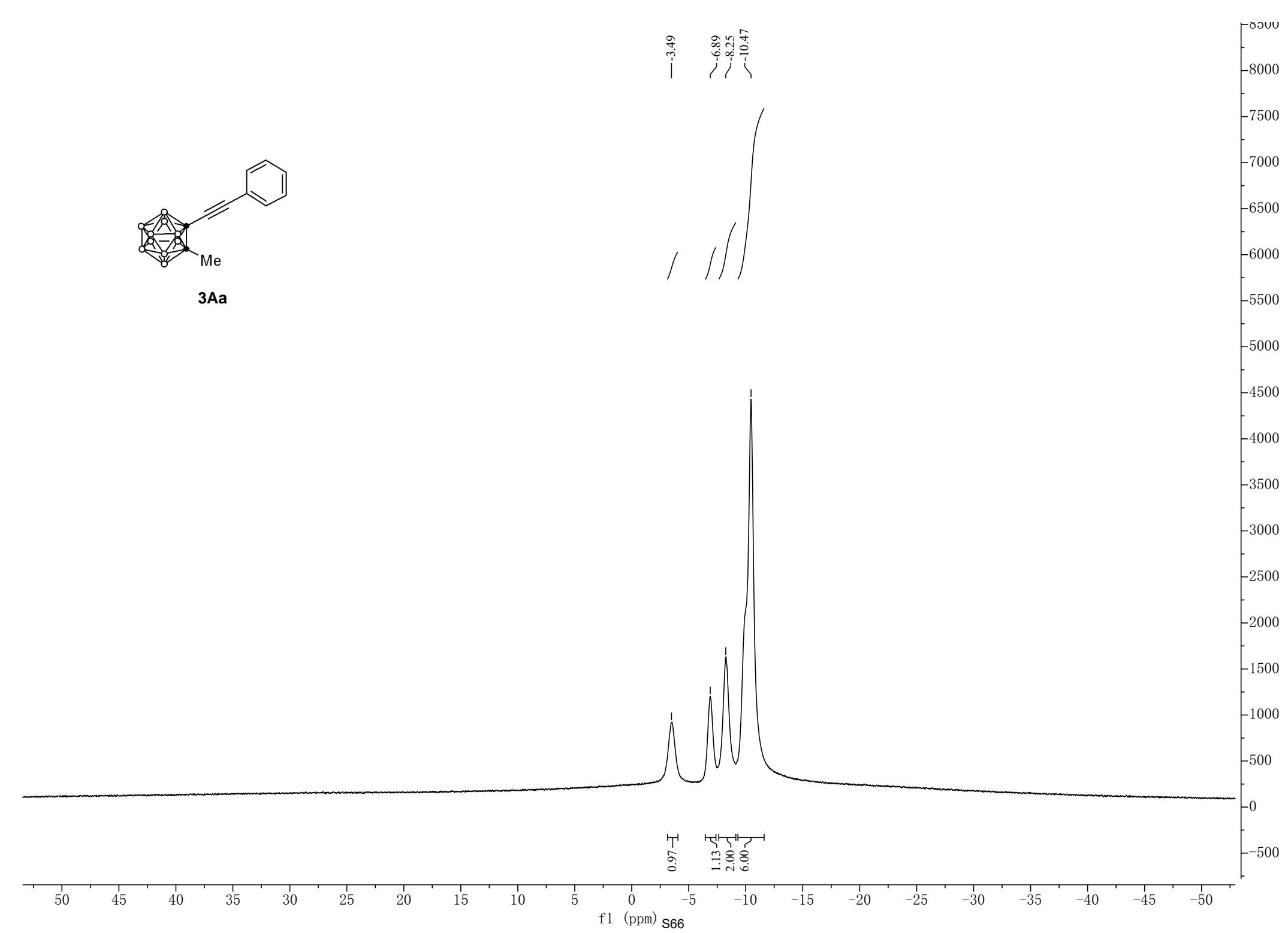
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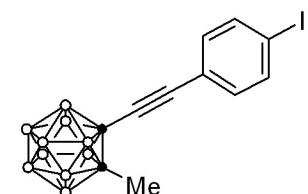






3Aa



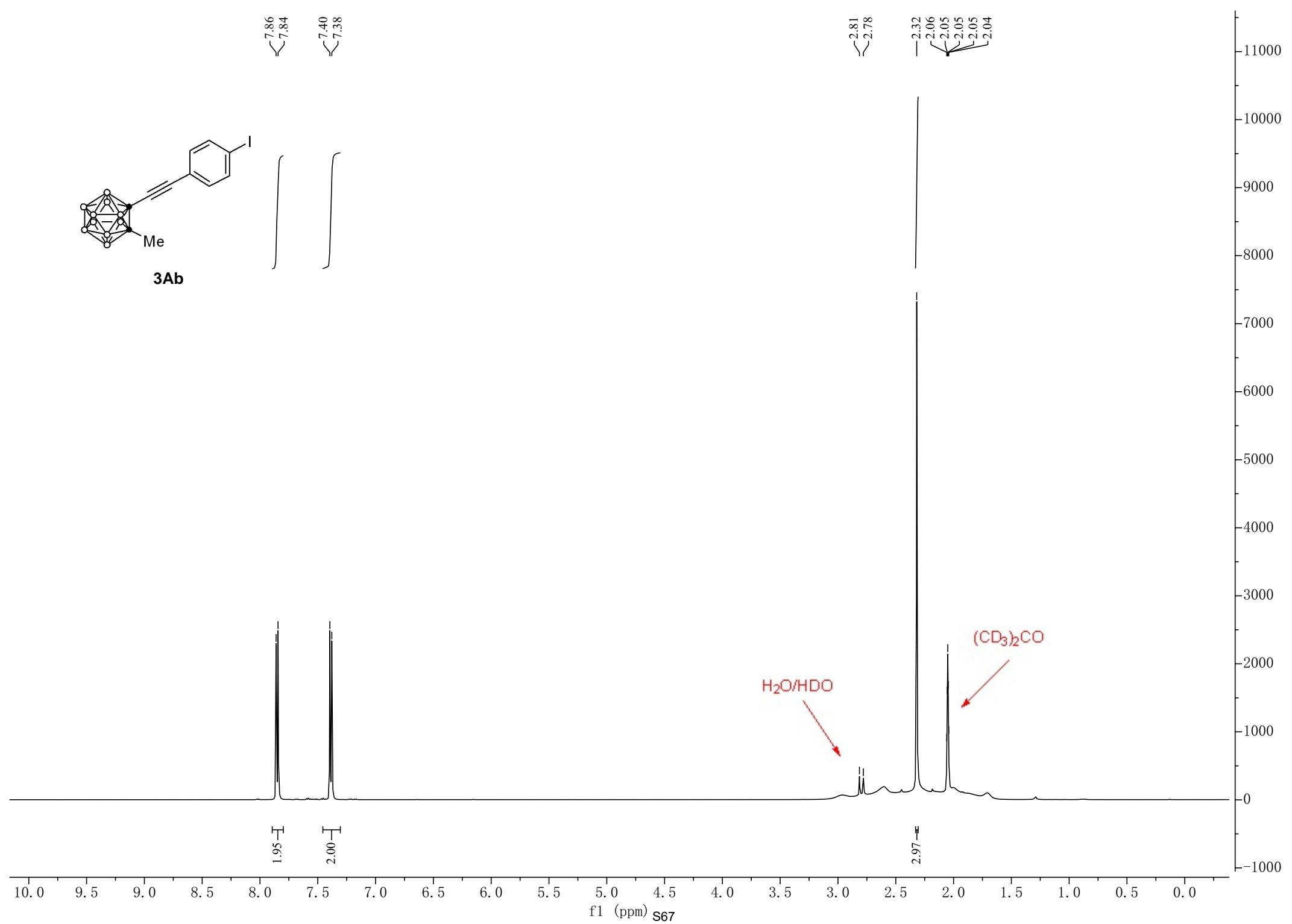


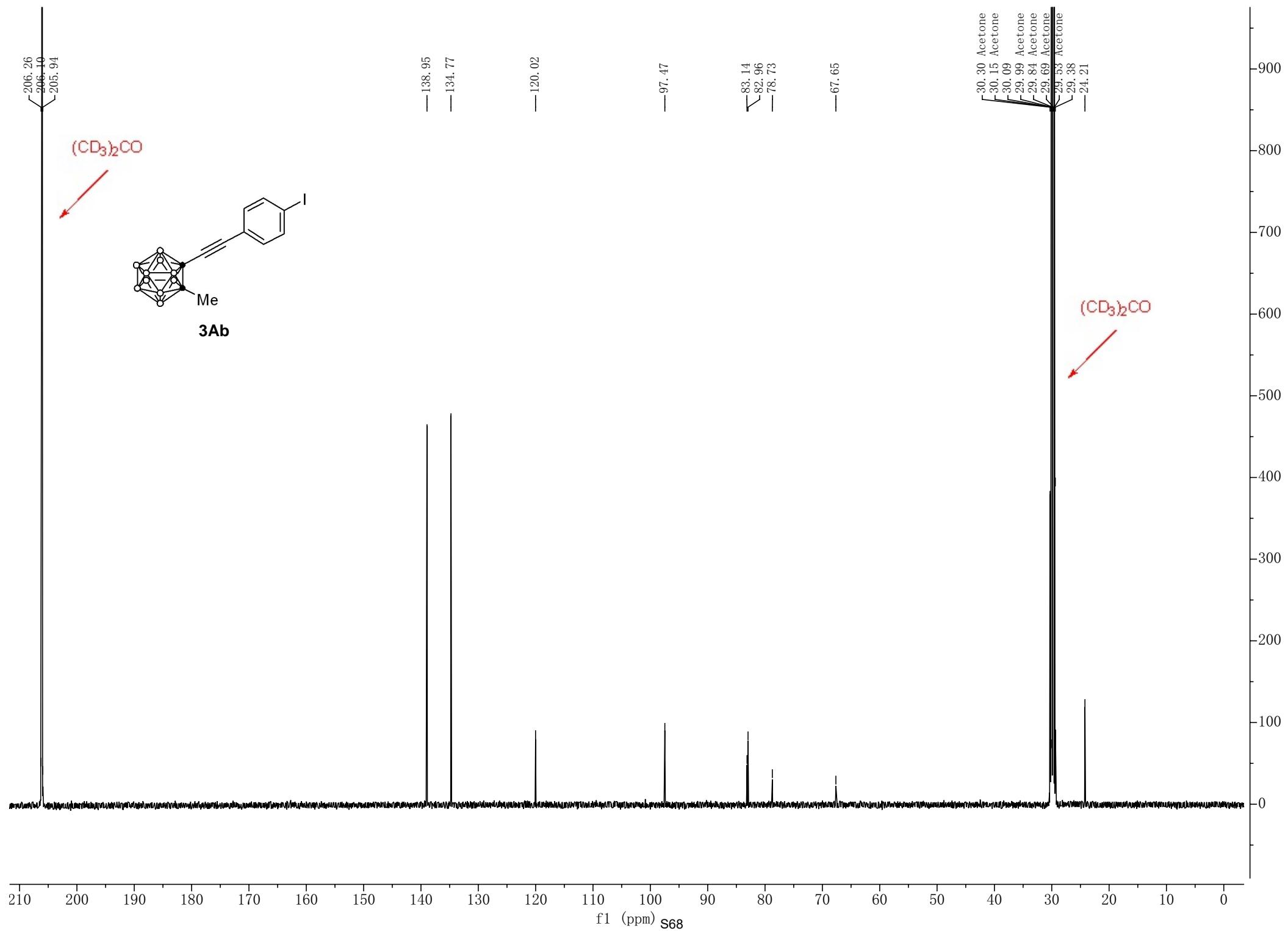
7.86
7.84

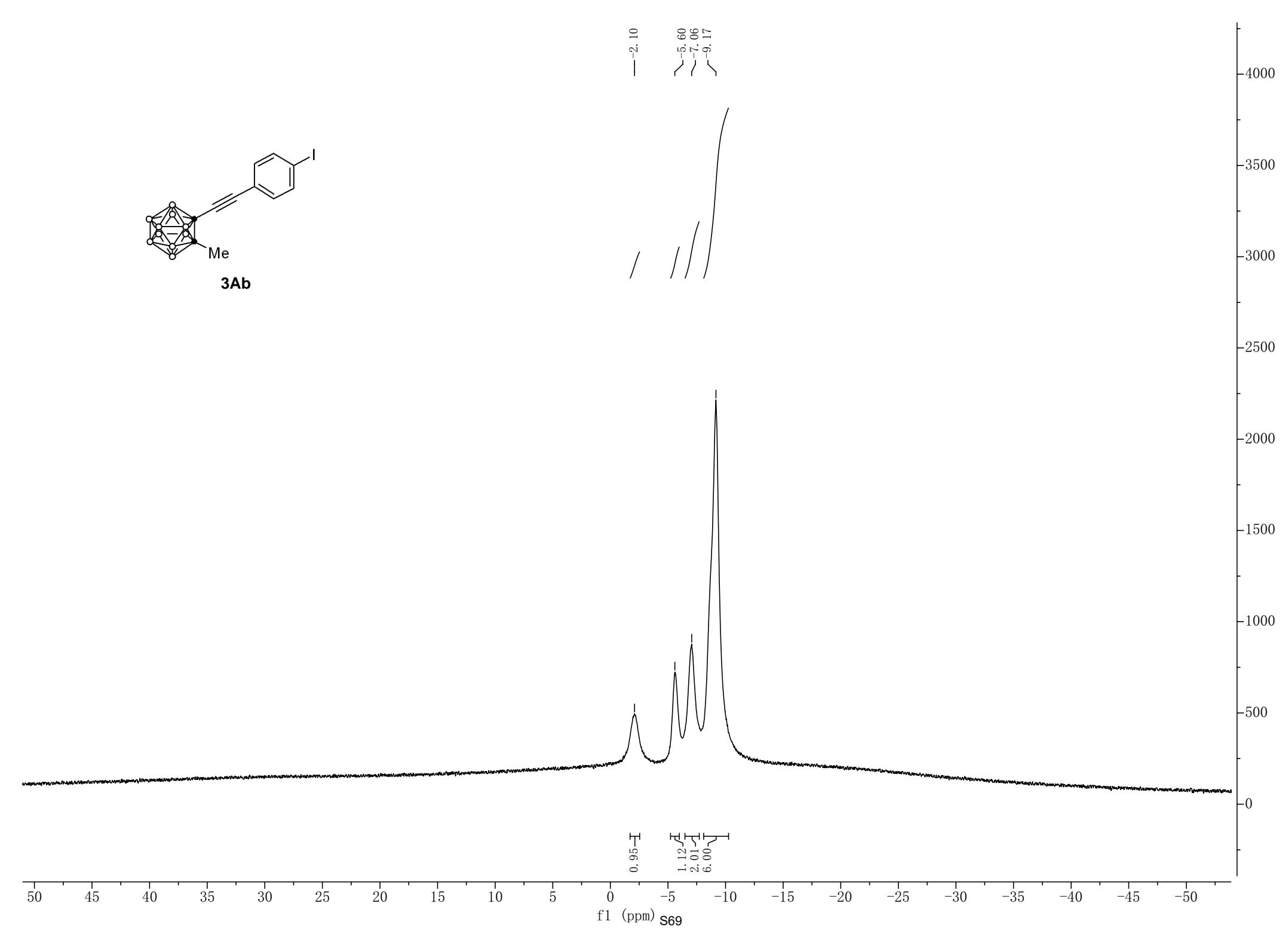
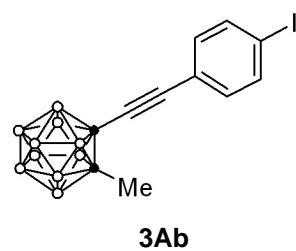
7.40
7.38

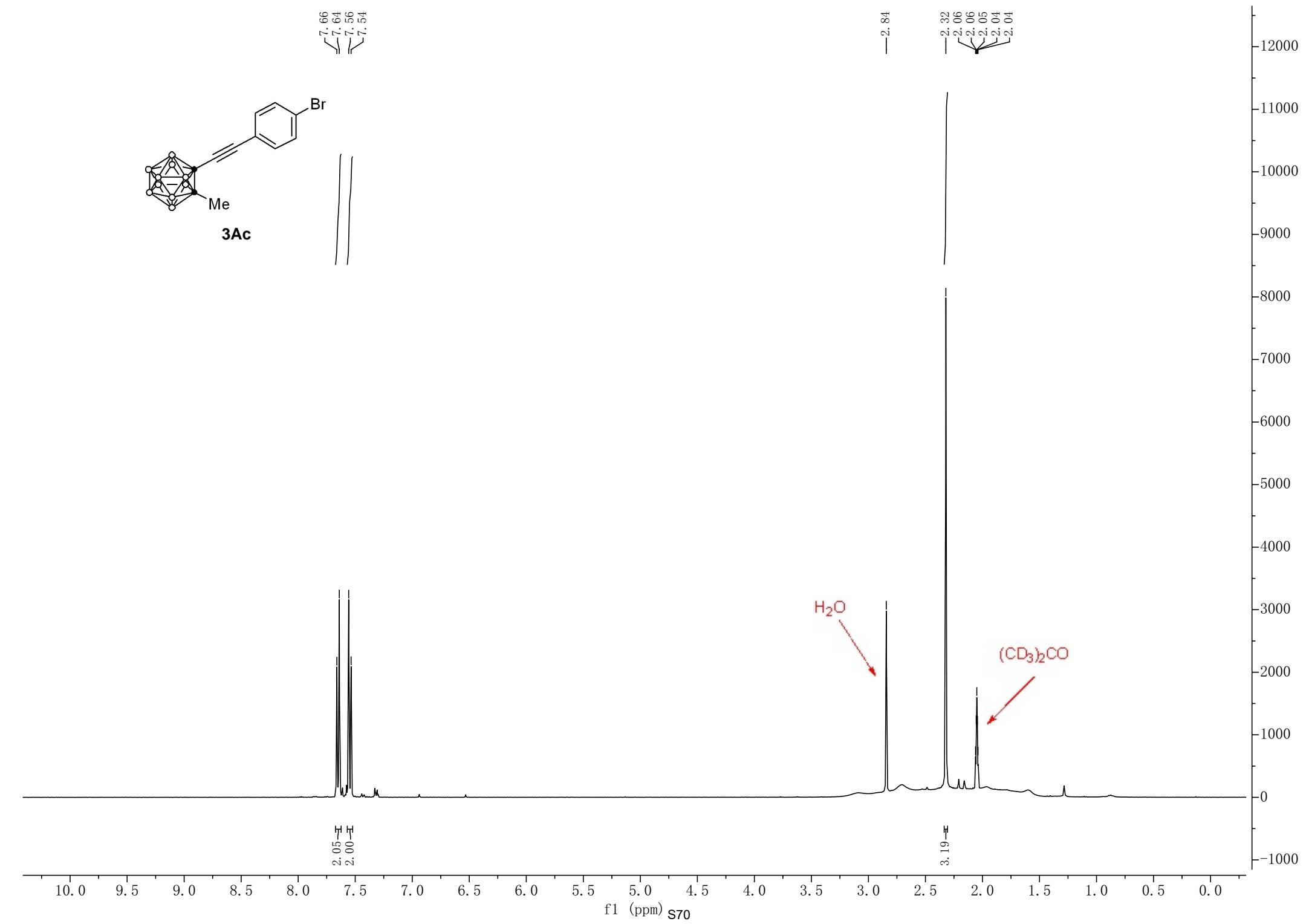
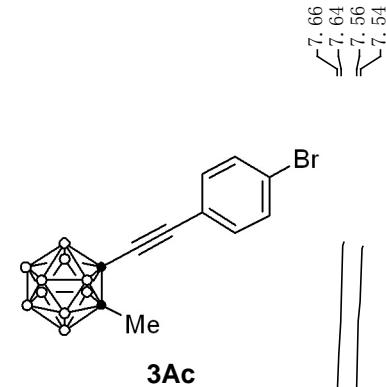
2.81
2.78

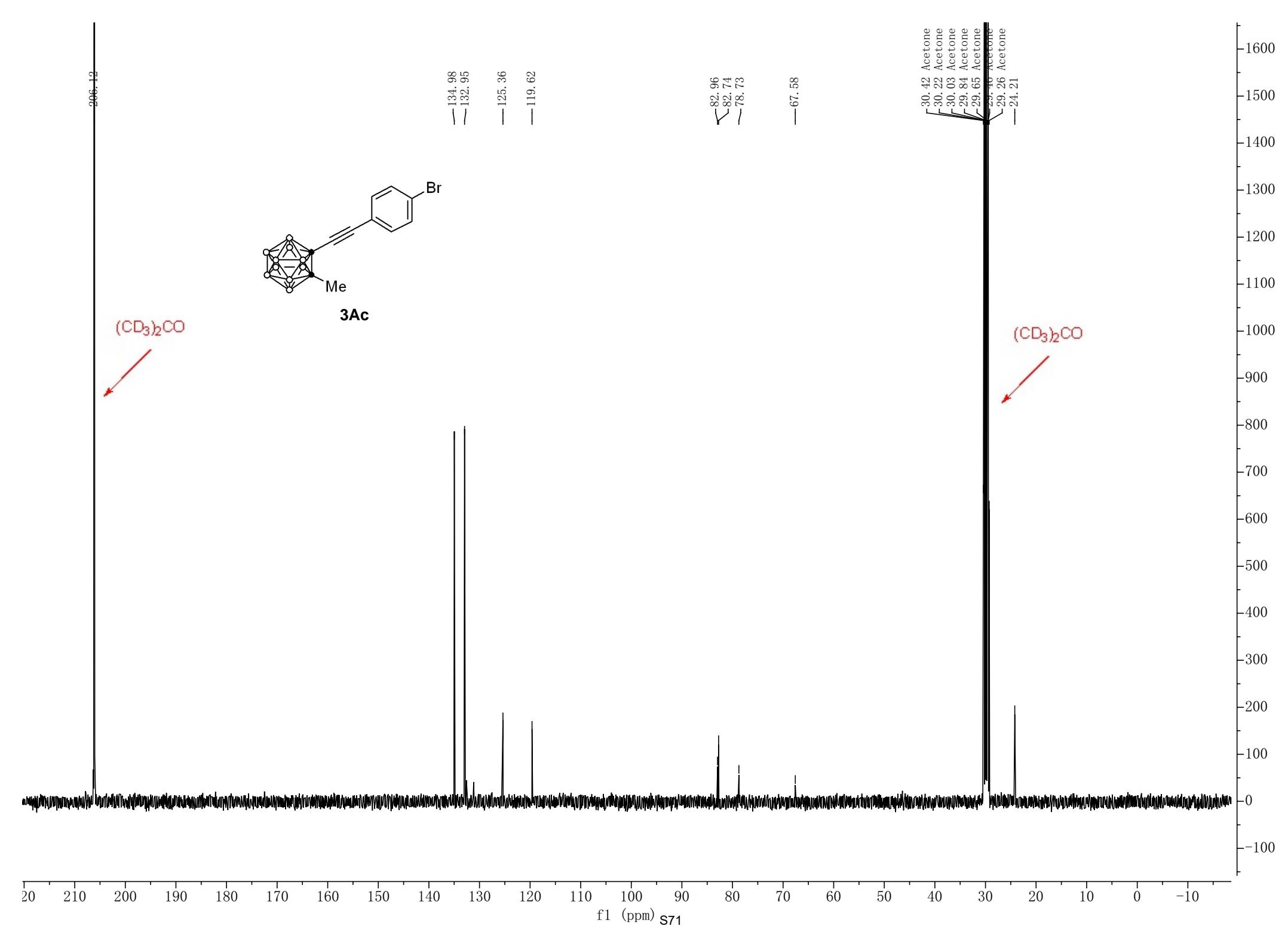
2.32
2.06
2.05
2.05
2.05
2.04

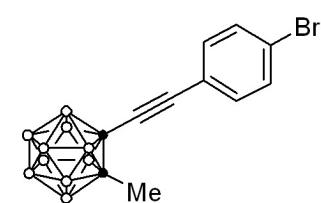




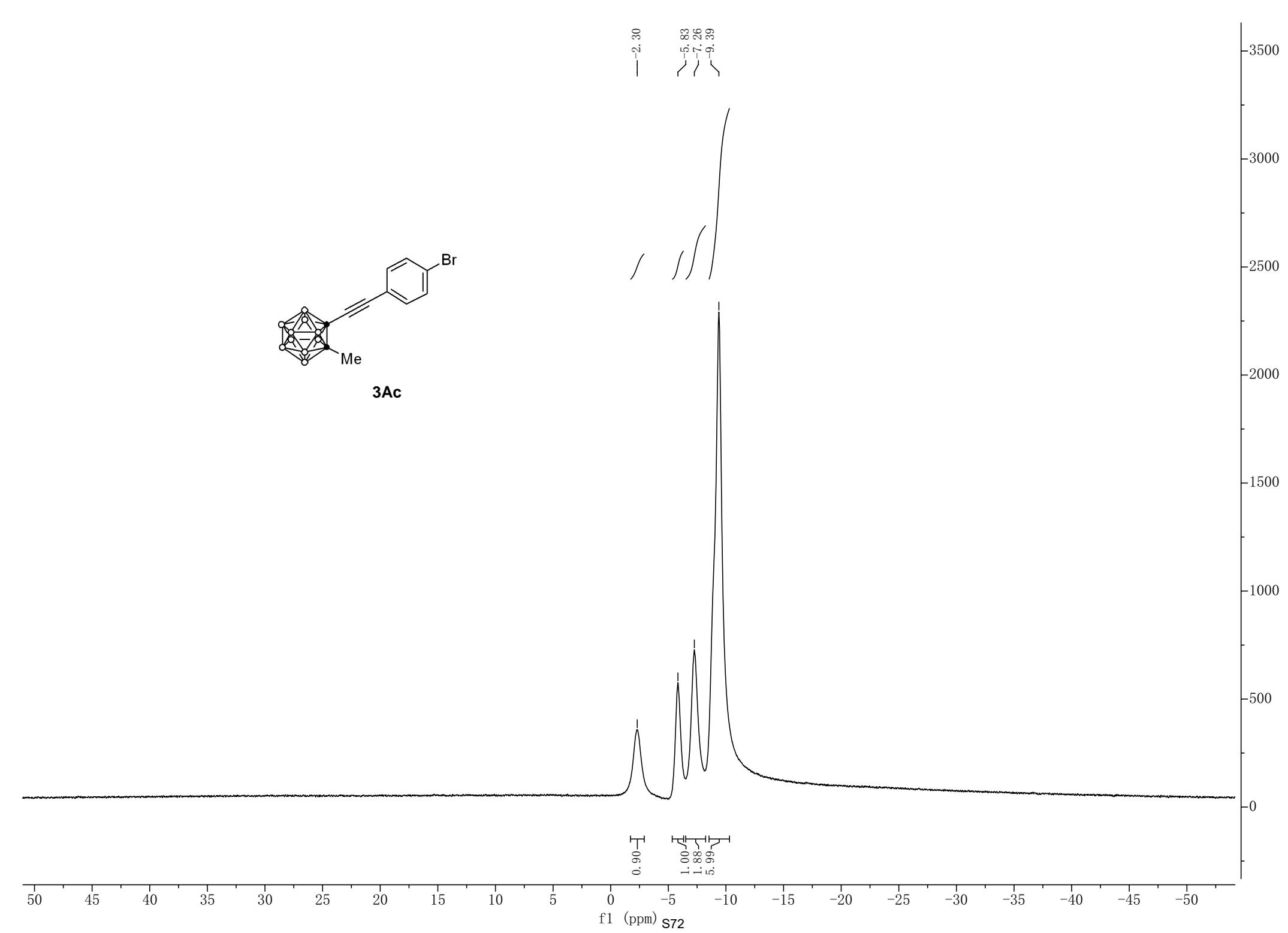


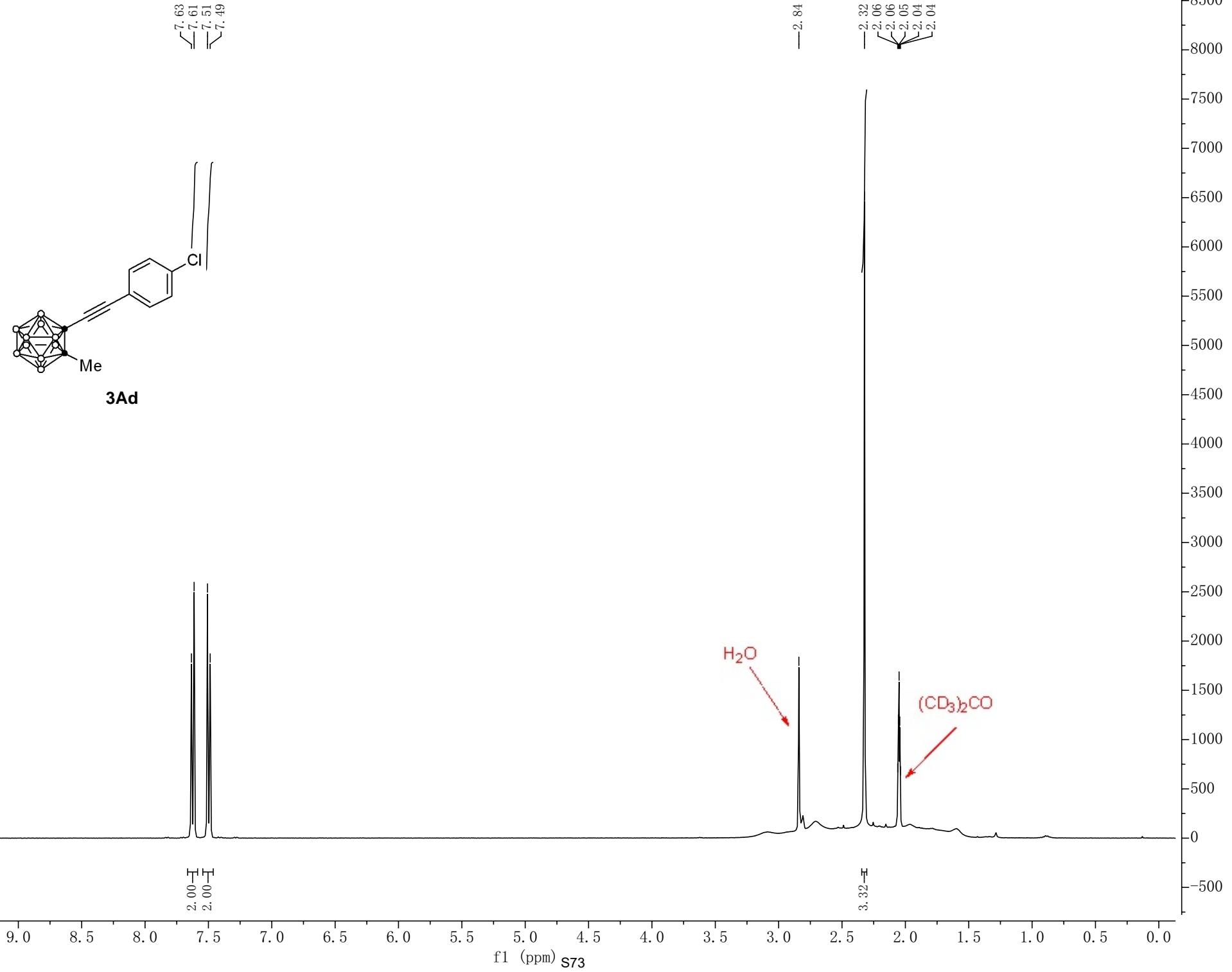


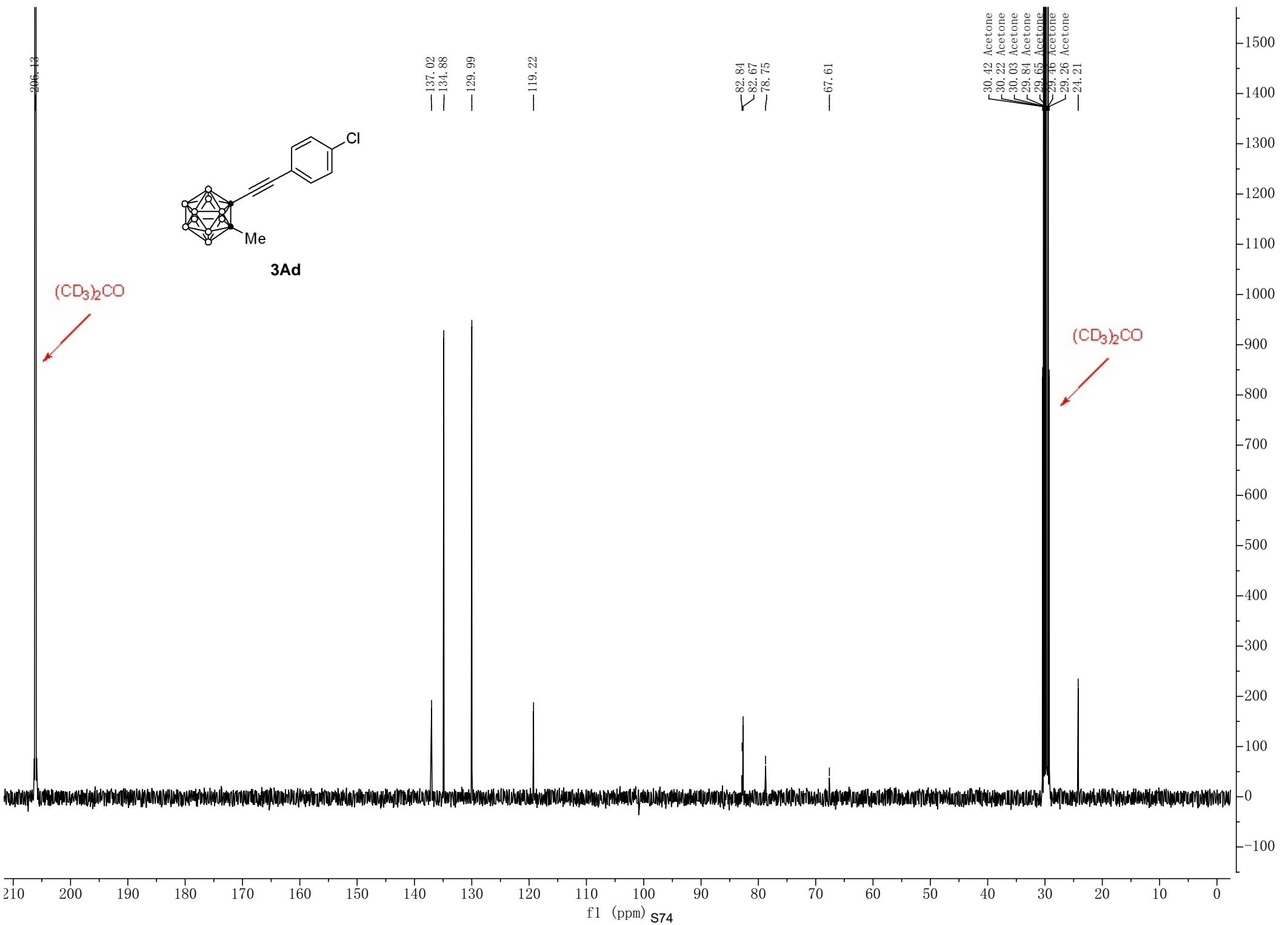


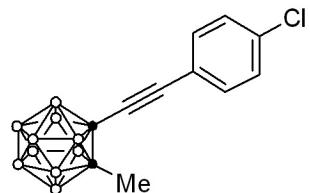


3Ac

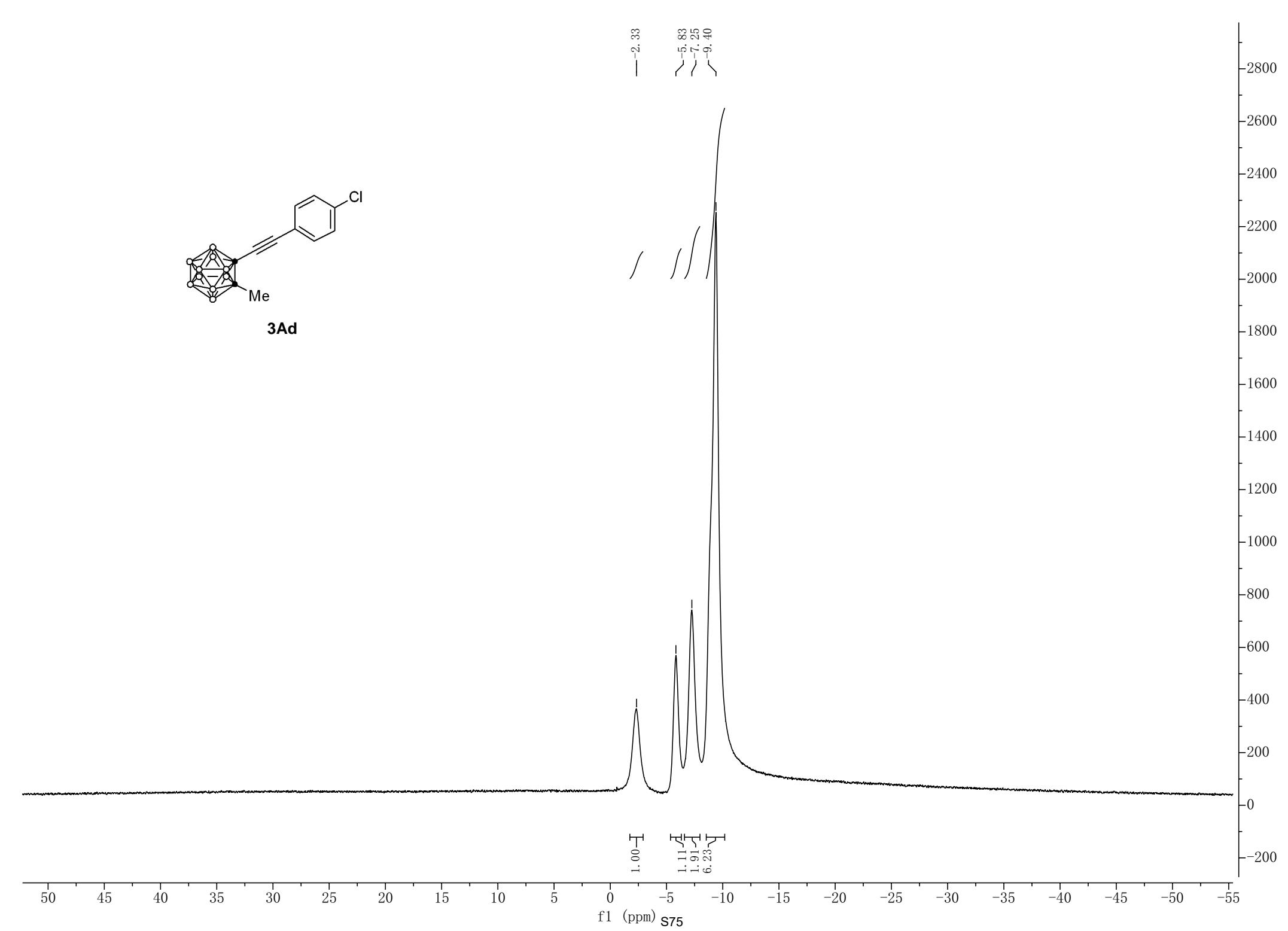


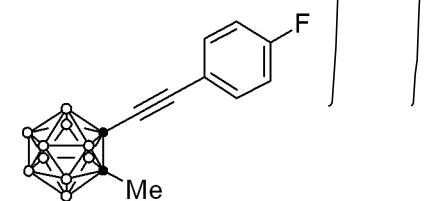




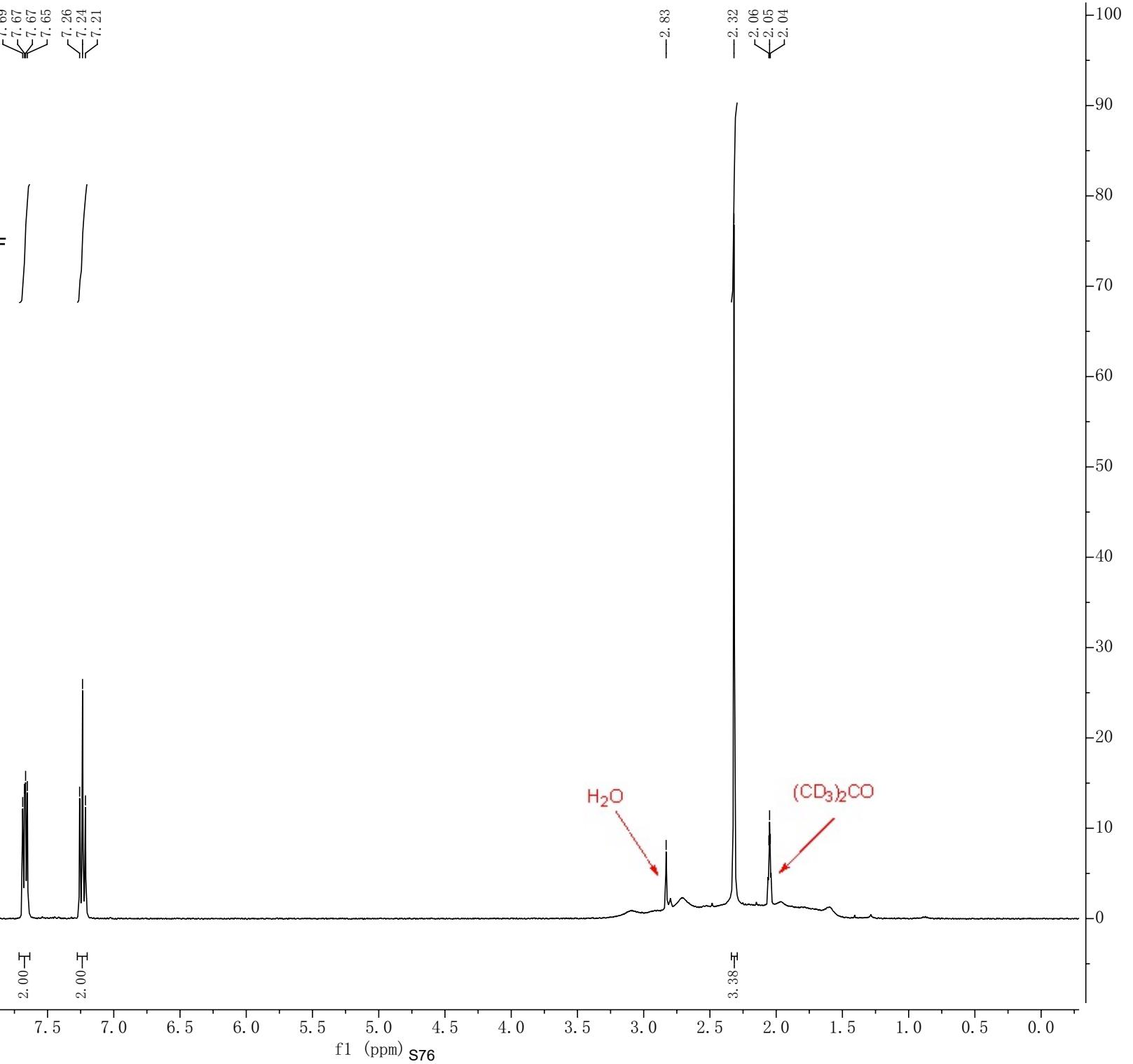


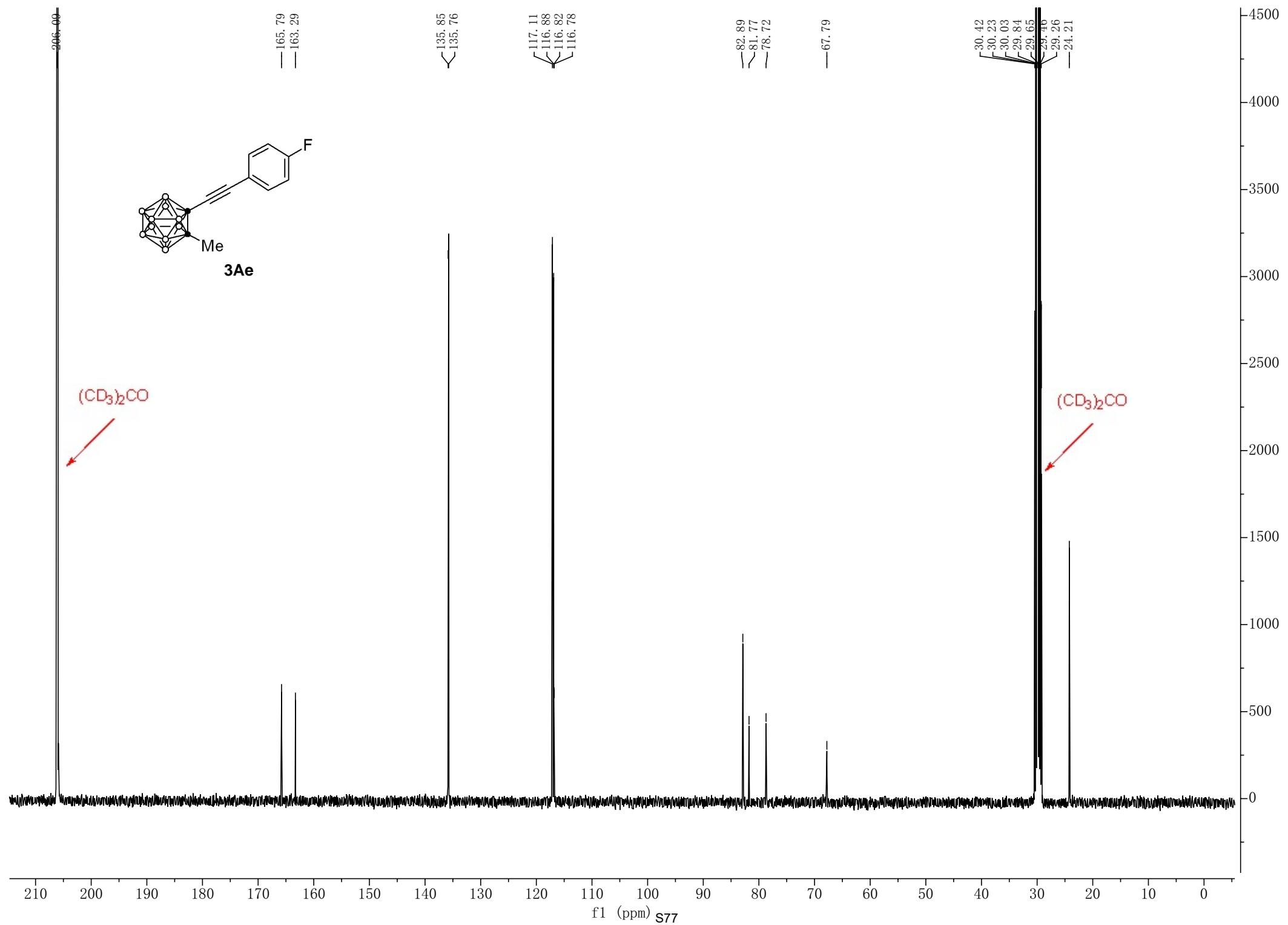
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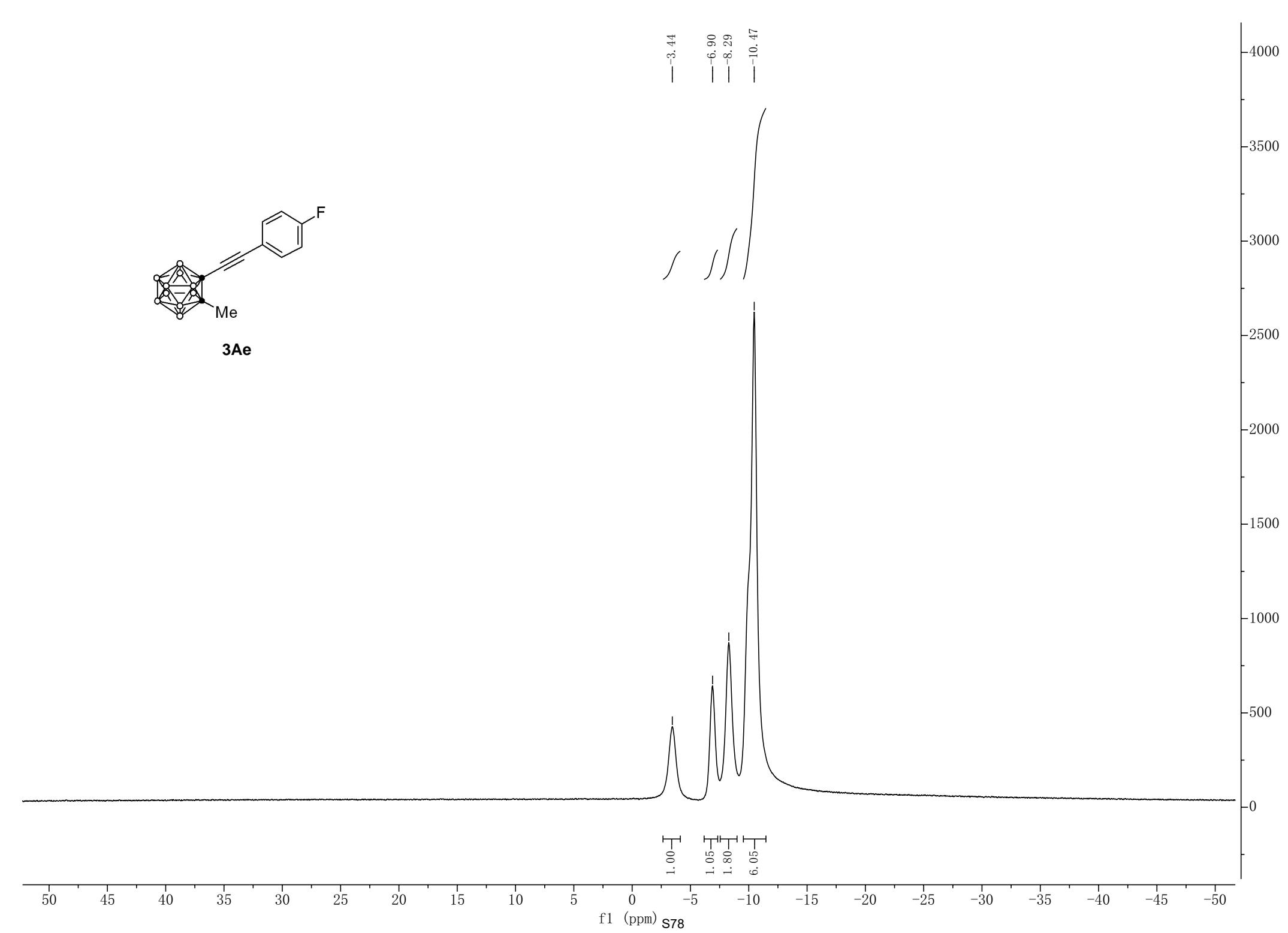
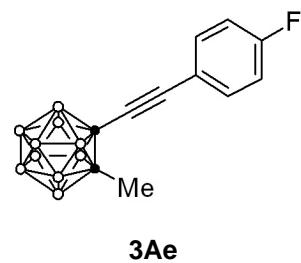


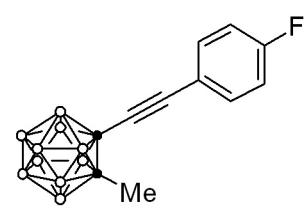


3Ae

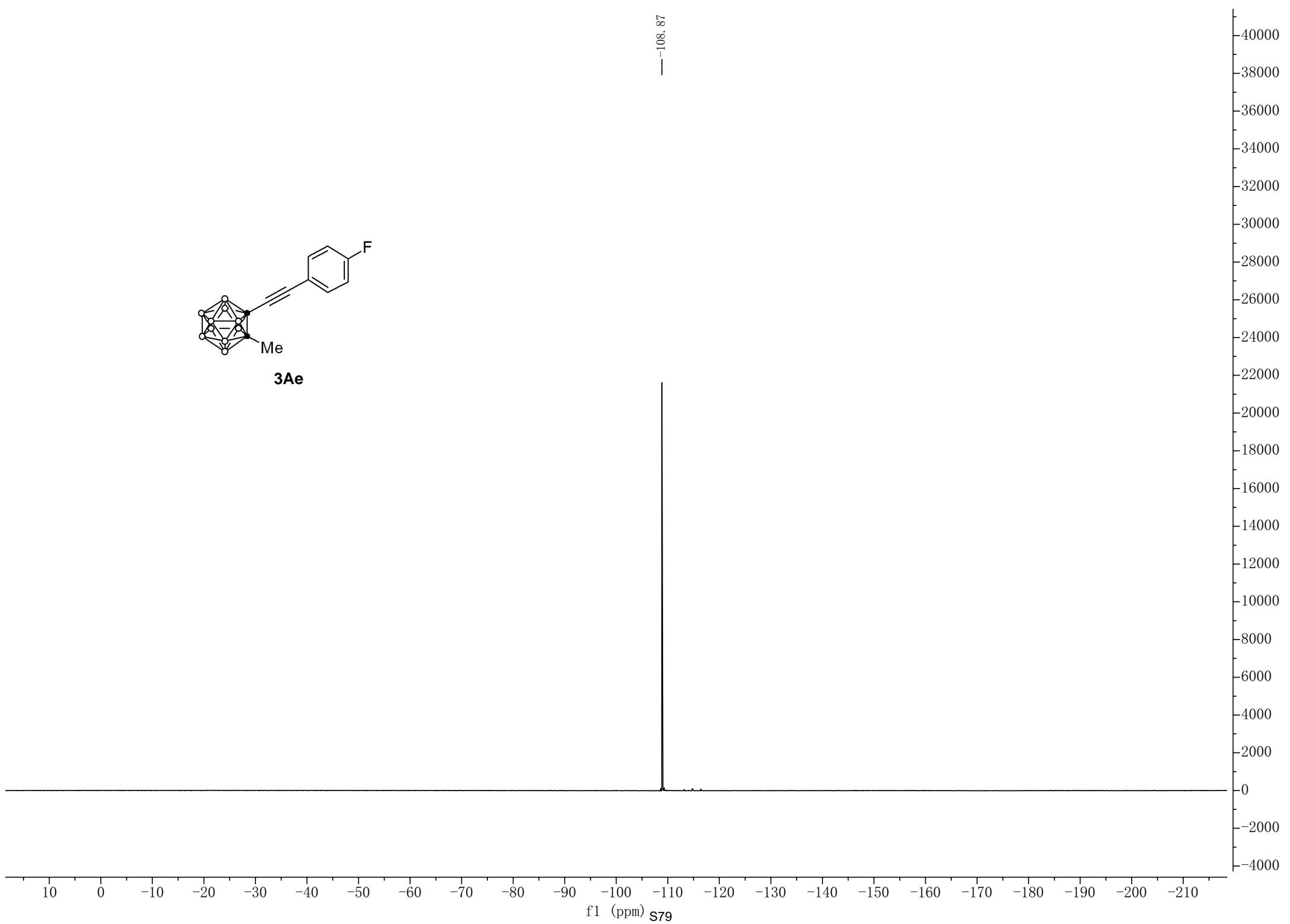


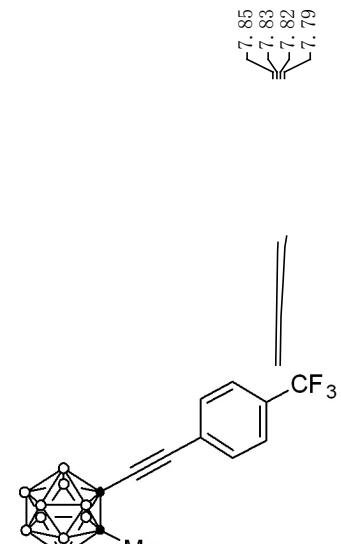




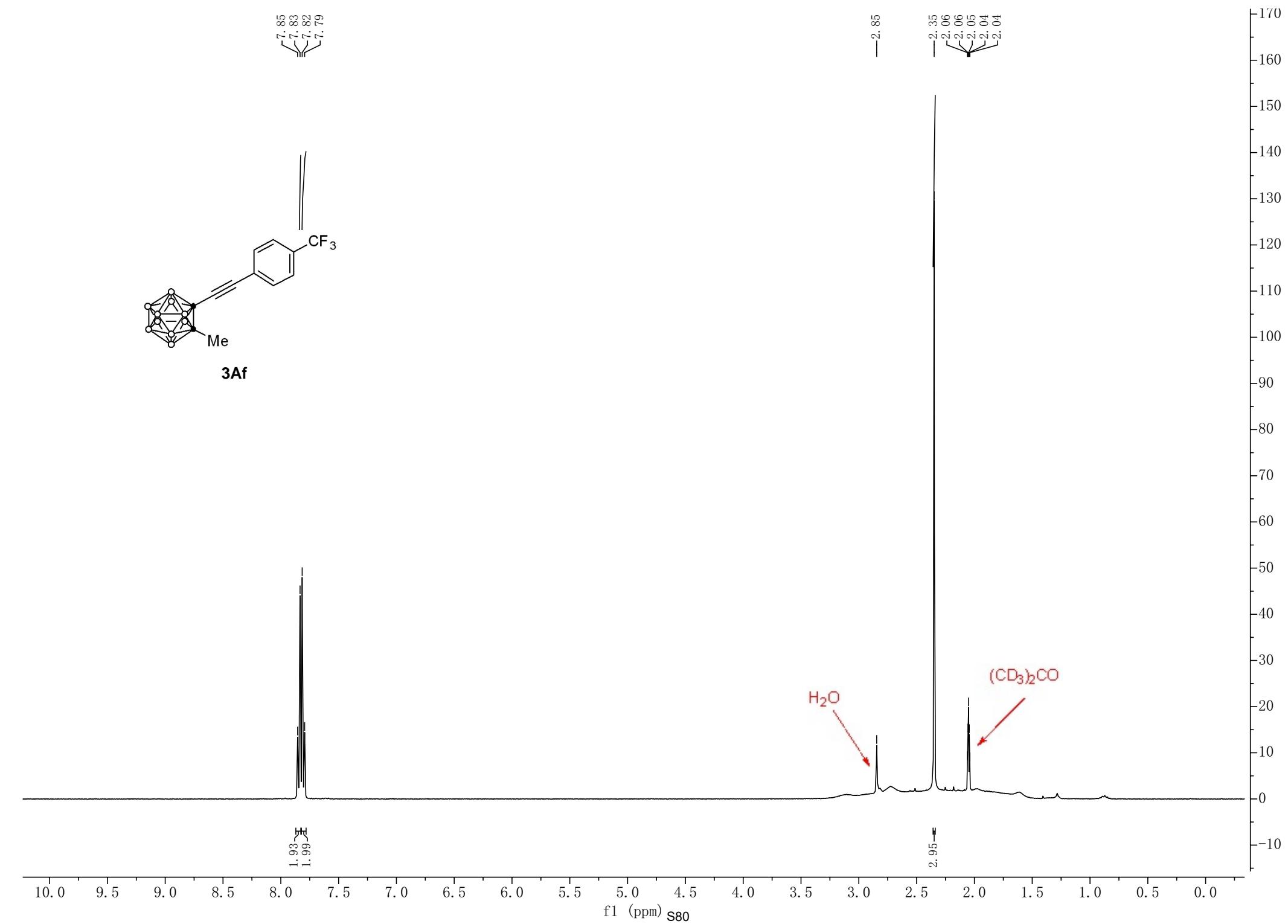


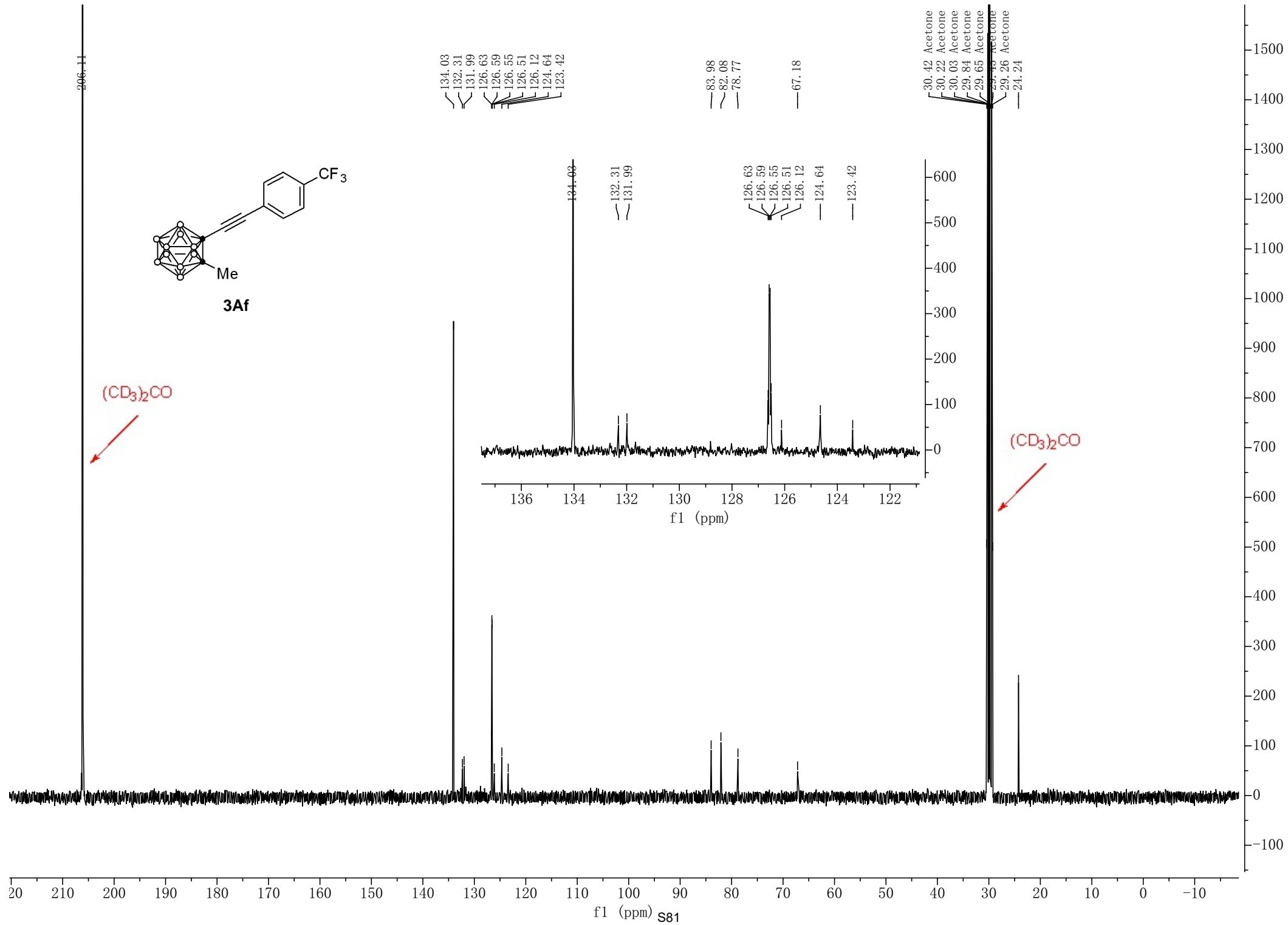
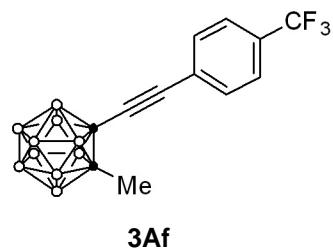
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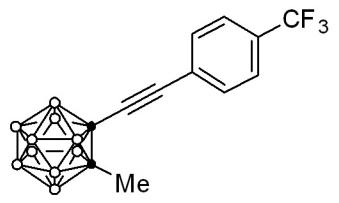




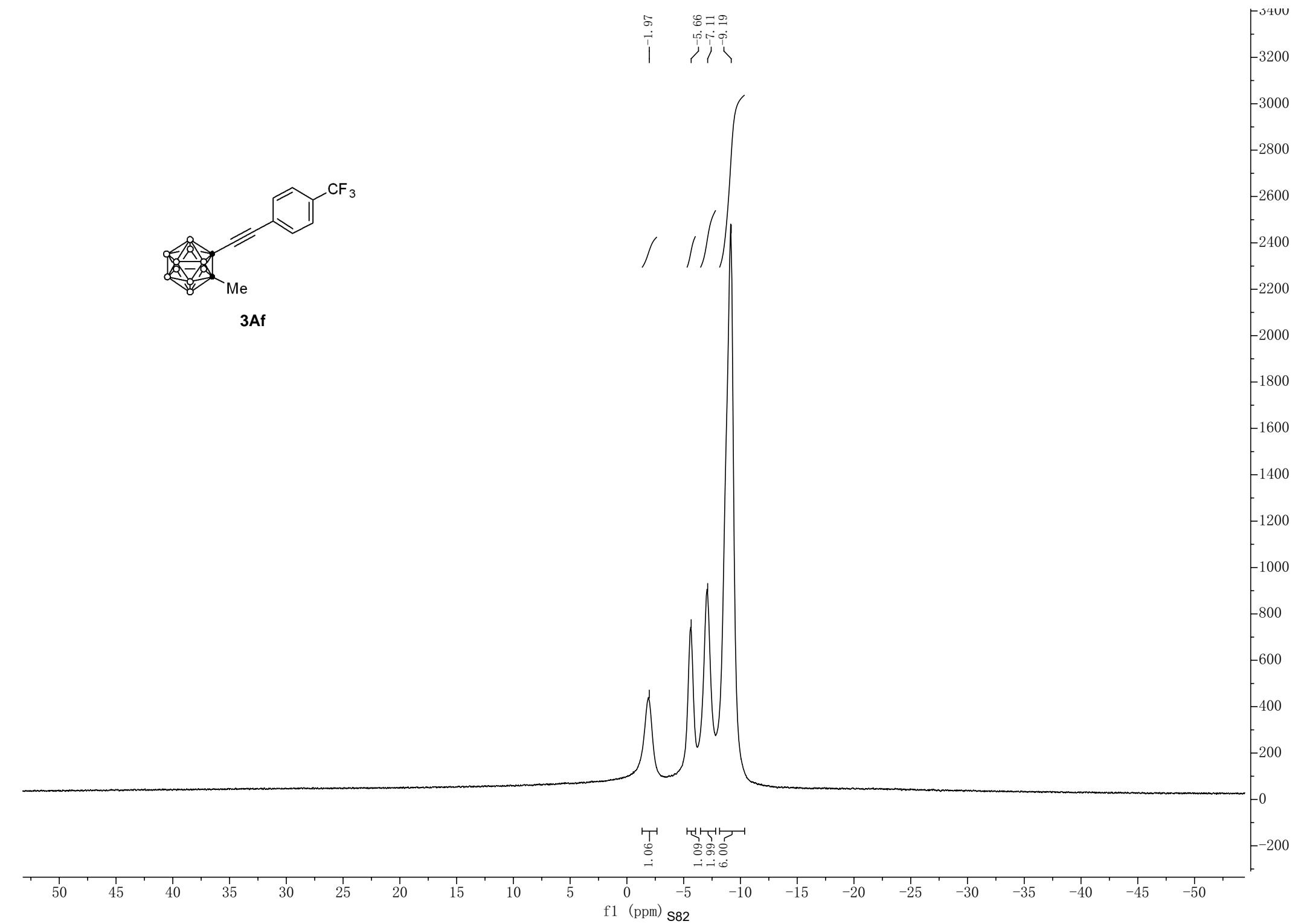
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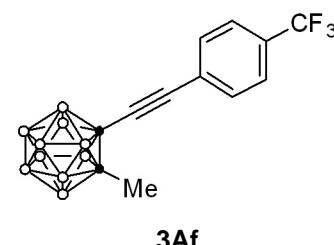






3Af

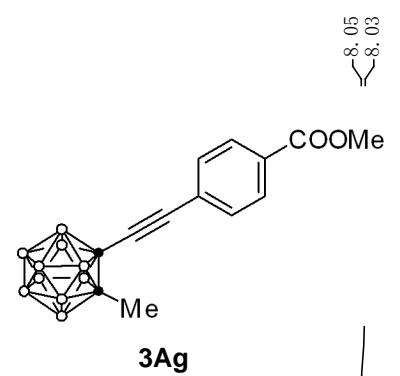




—63.63

10 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm) S83

85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

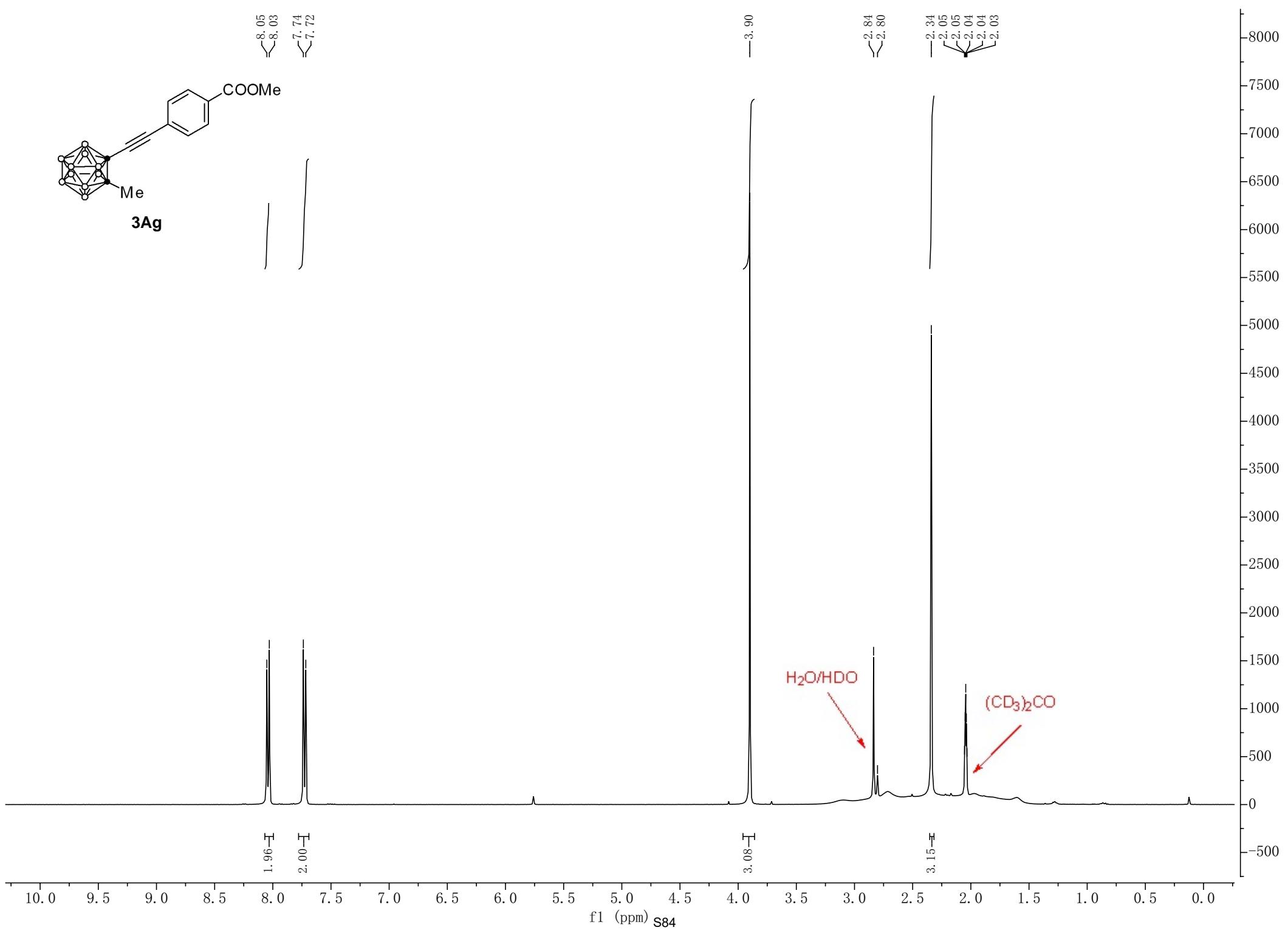


<8.05
<8.03
<7.74
<7.72

-3.90

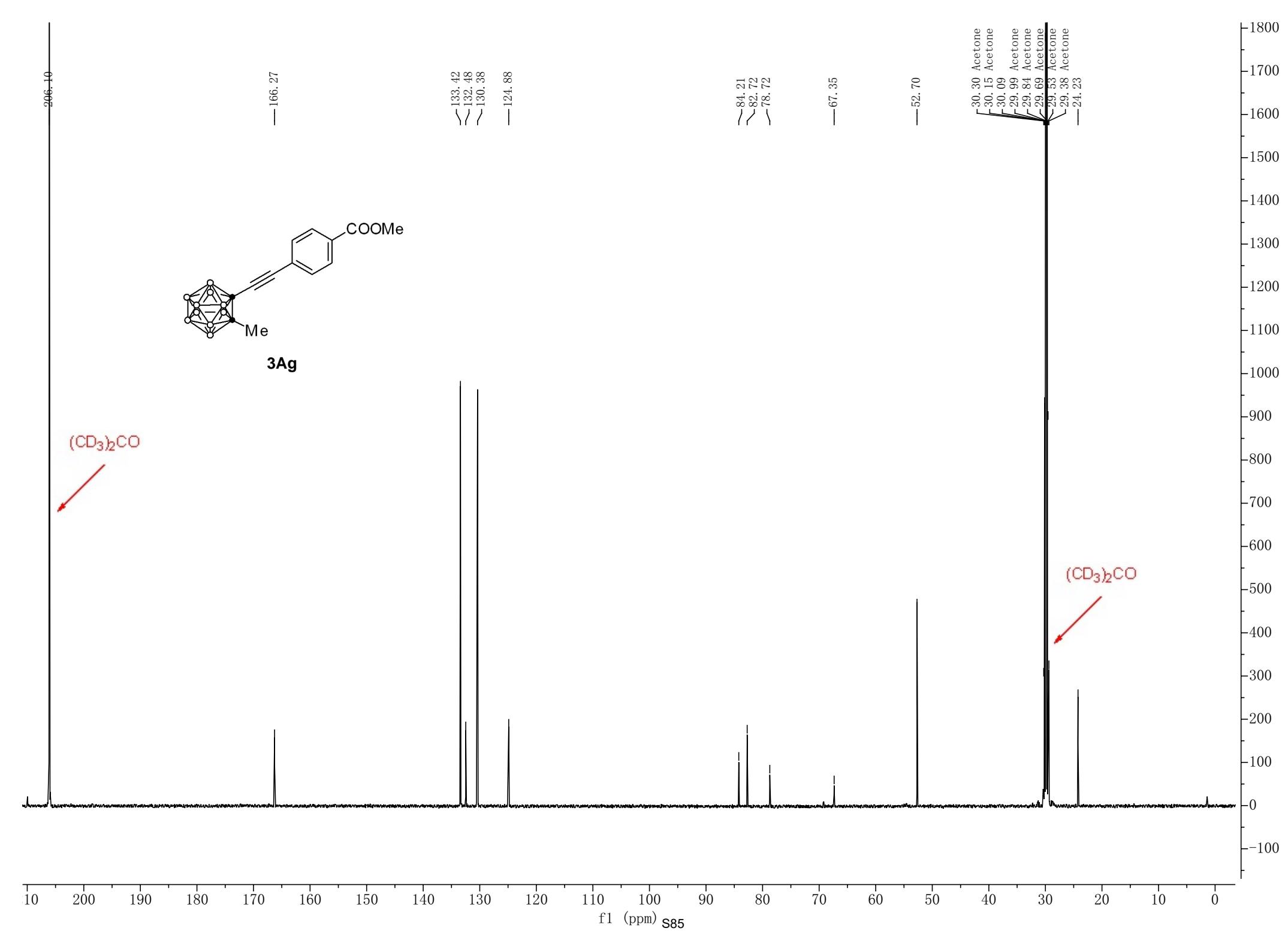
<2.84
<2.80

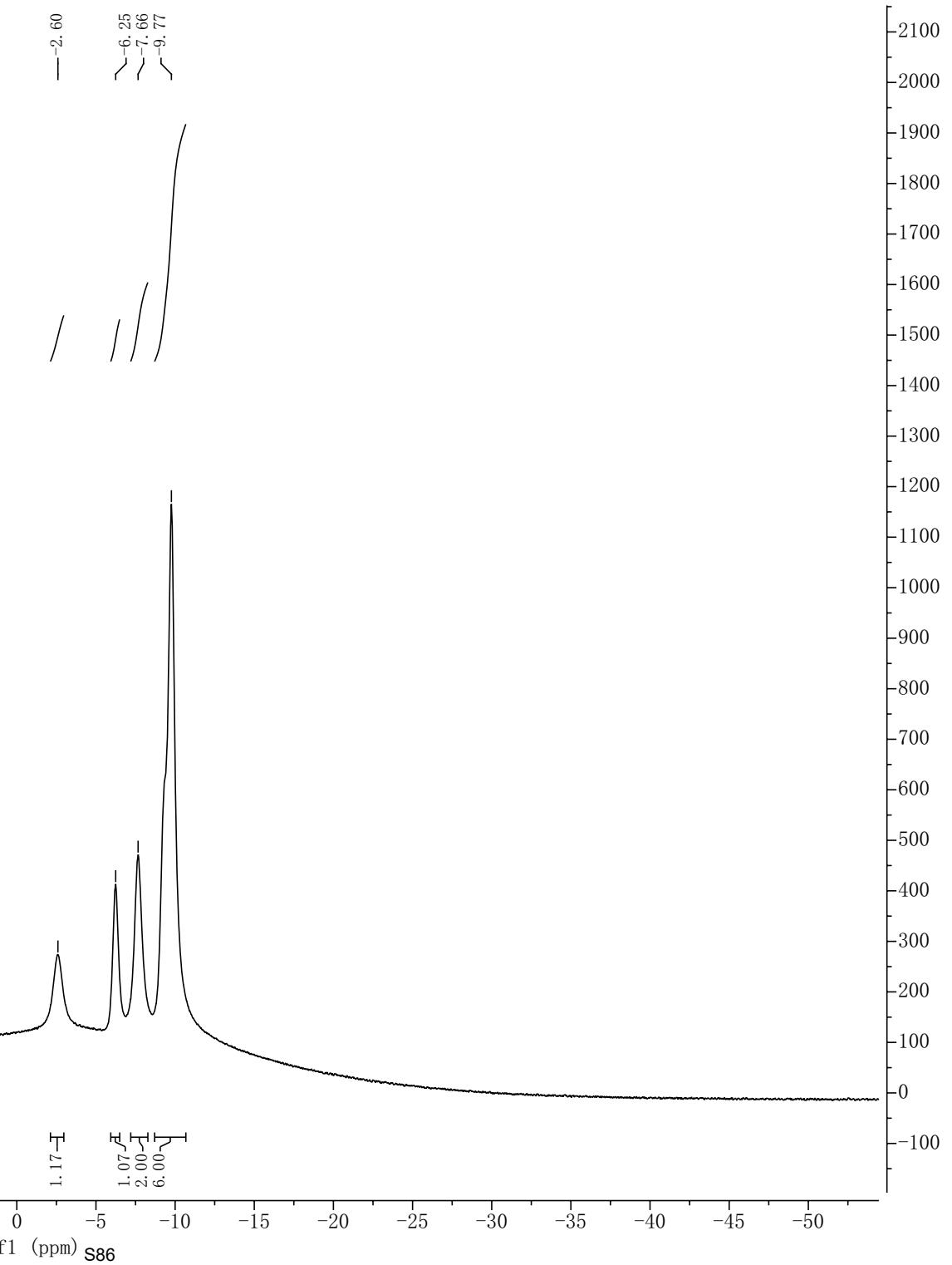
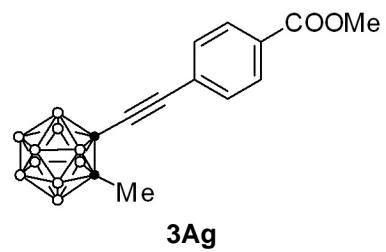
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<2.05
<2.04
<2.04
<2.03

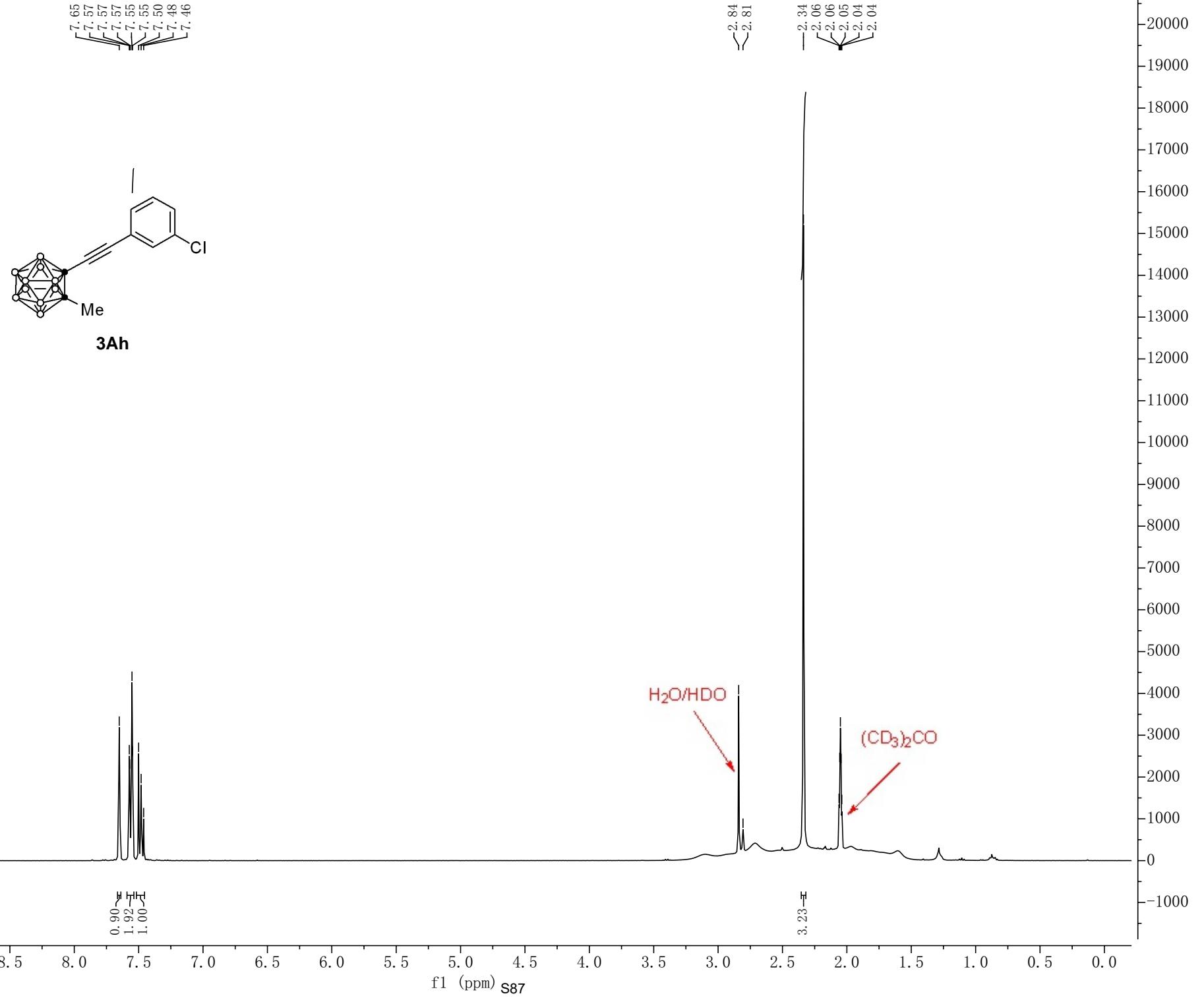


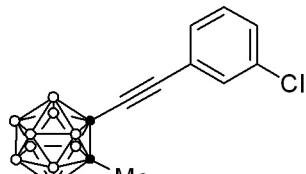
H₂O/HDO

(CD₃)₂CO







**3Ah** $(CD_3)_2CO$

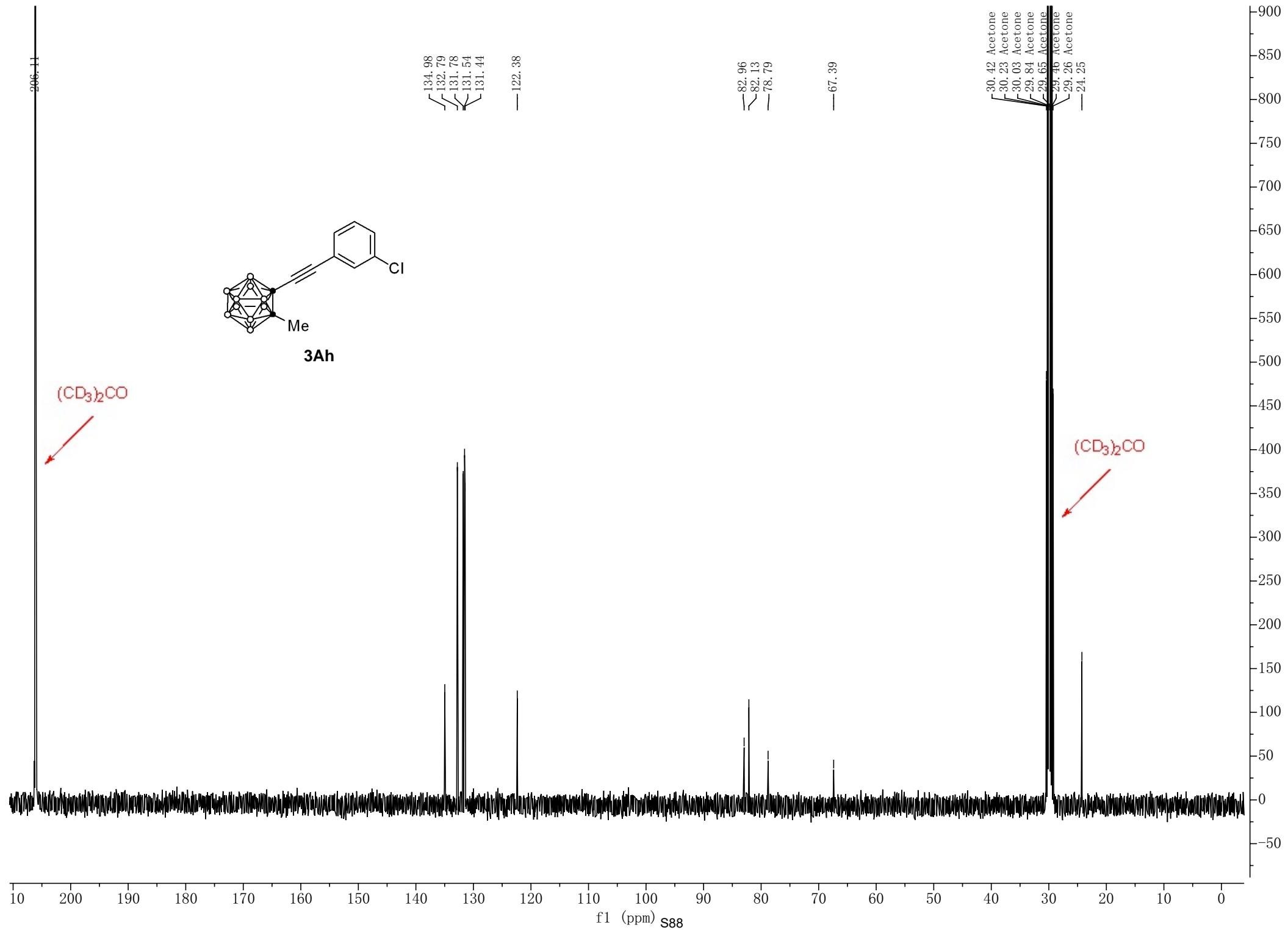
134.98
132.79
131.78
131.54
131.44

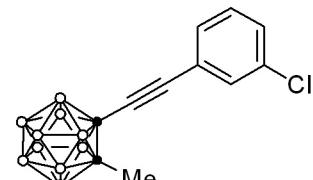
— 122.38

— 82.96
— 82.13
— 78.79

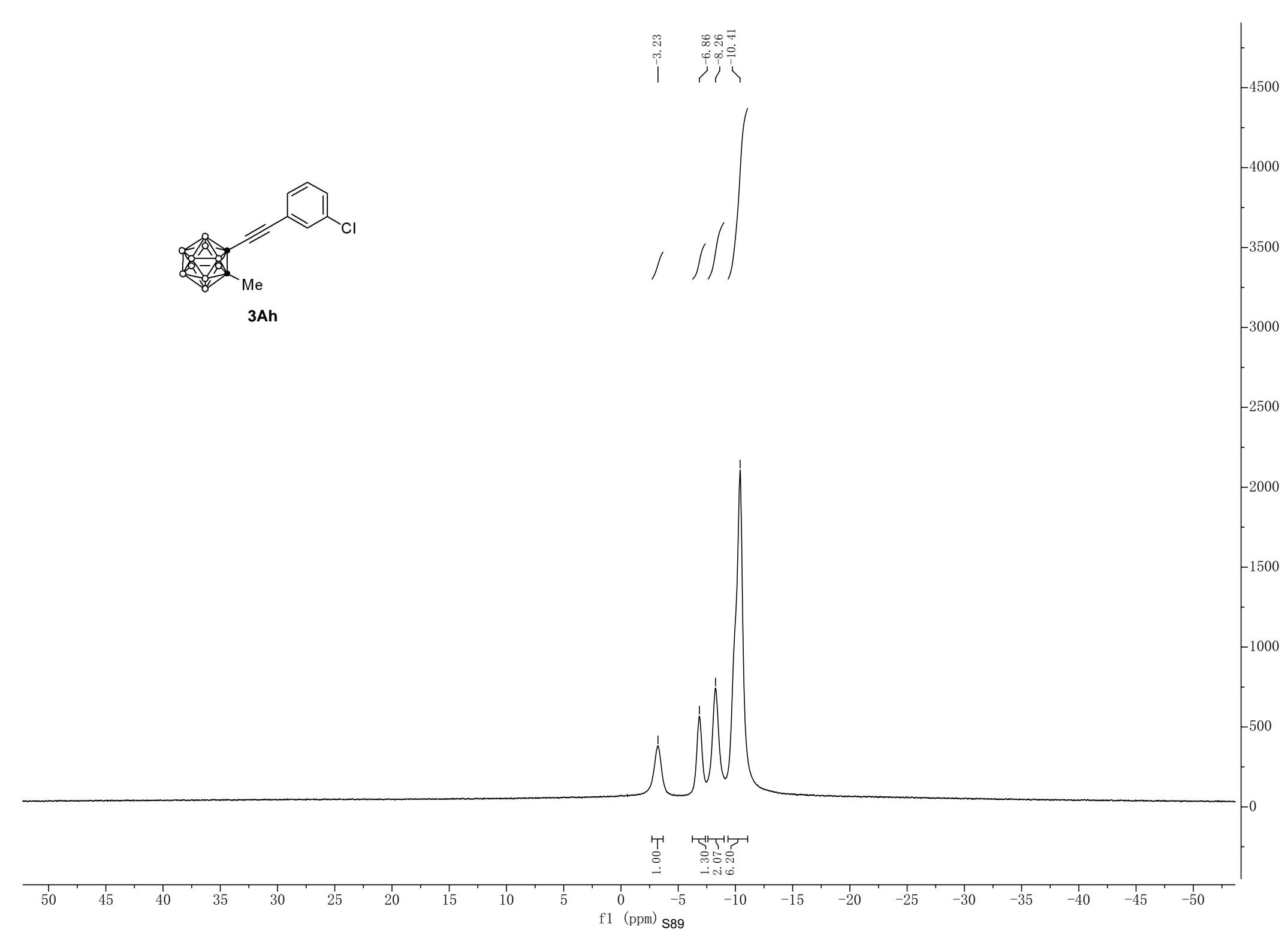
— 67.39

30.42 Acetone
30.23 Acetone
30.03 Acetone
29.84 Acetone
29.65 Acetone
29.46 Acetone
29.26 Acetone
— 24.25



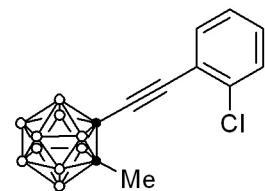


3Ah

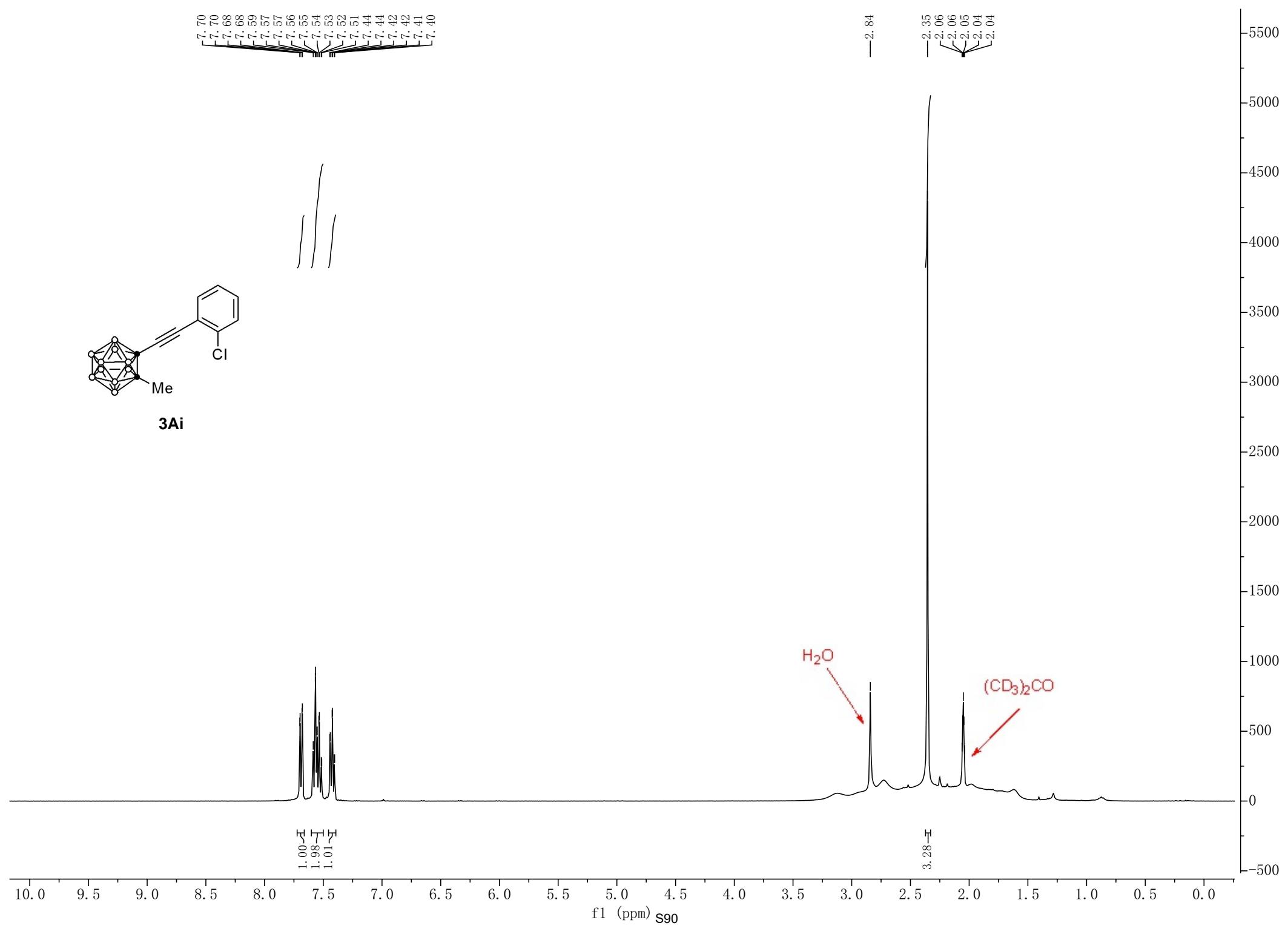


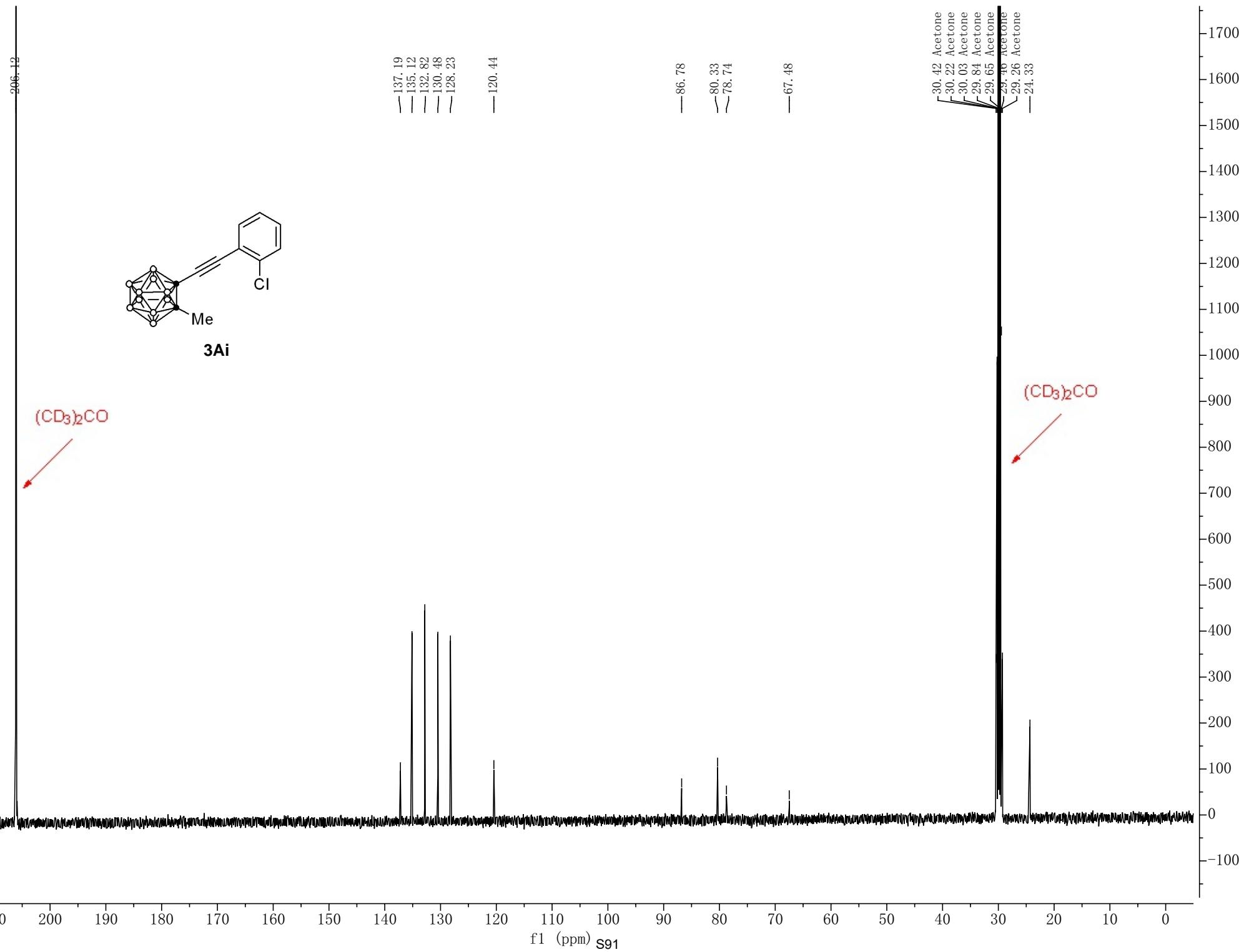
7.70
7.68
7.68
7.59
7.57
7.57
7.56
7.56
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7.53
7.52
7.51
7.44
7.44
7.42
7.41
7.40

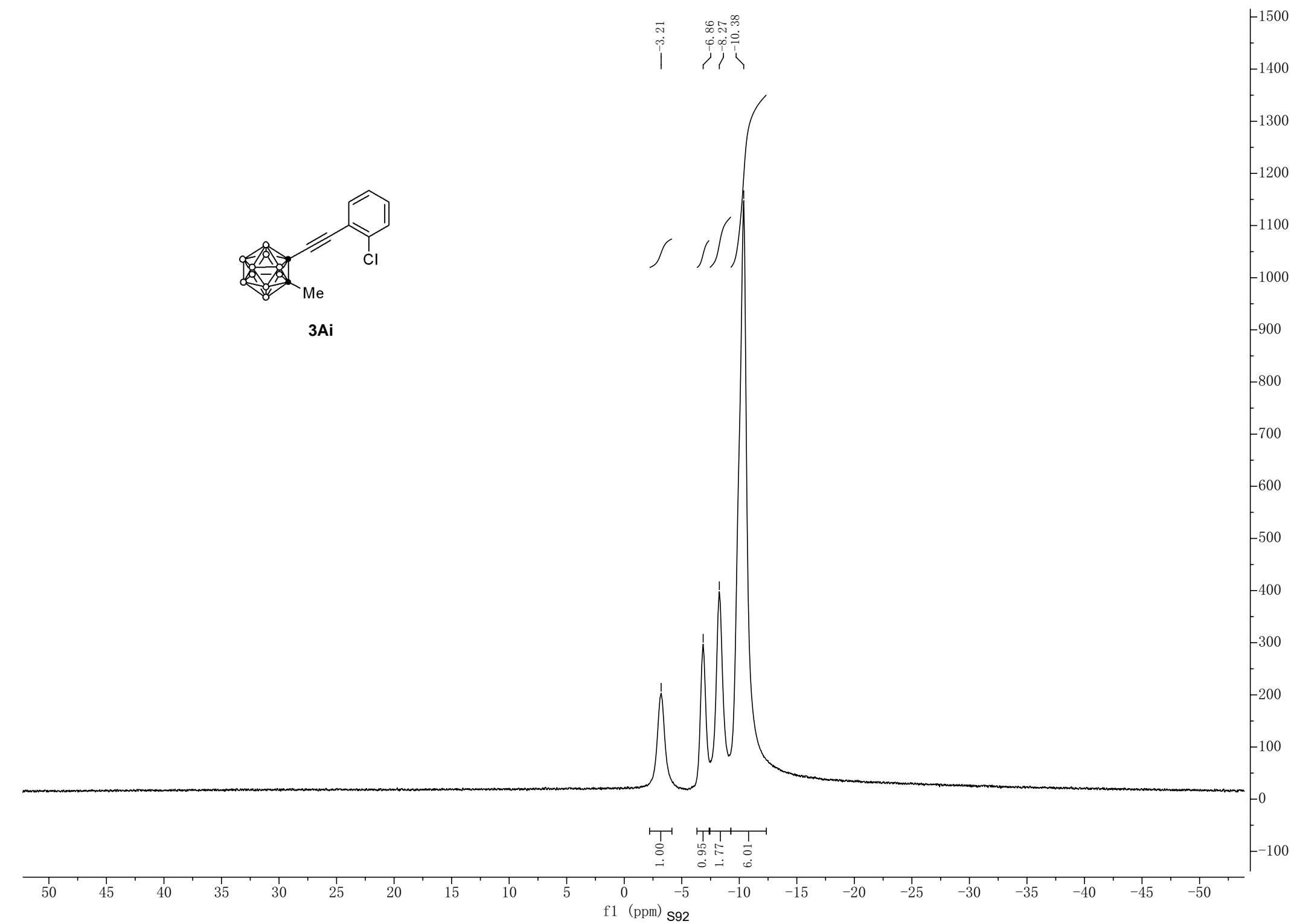
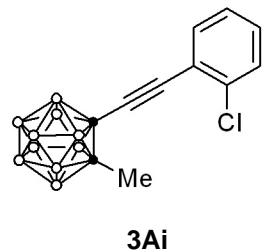
2.35
2.06
2.06
2.05
2.04
2.04

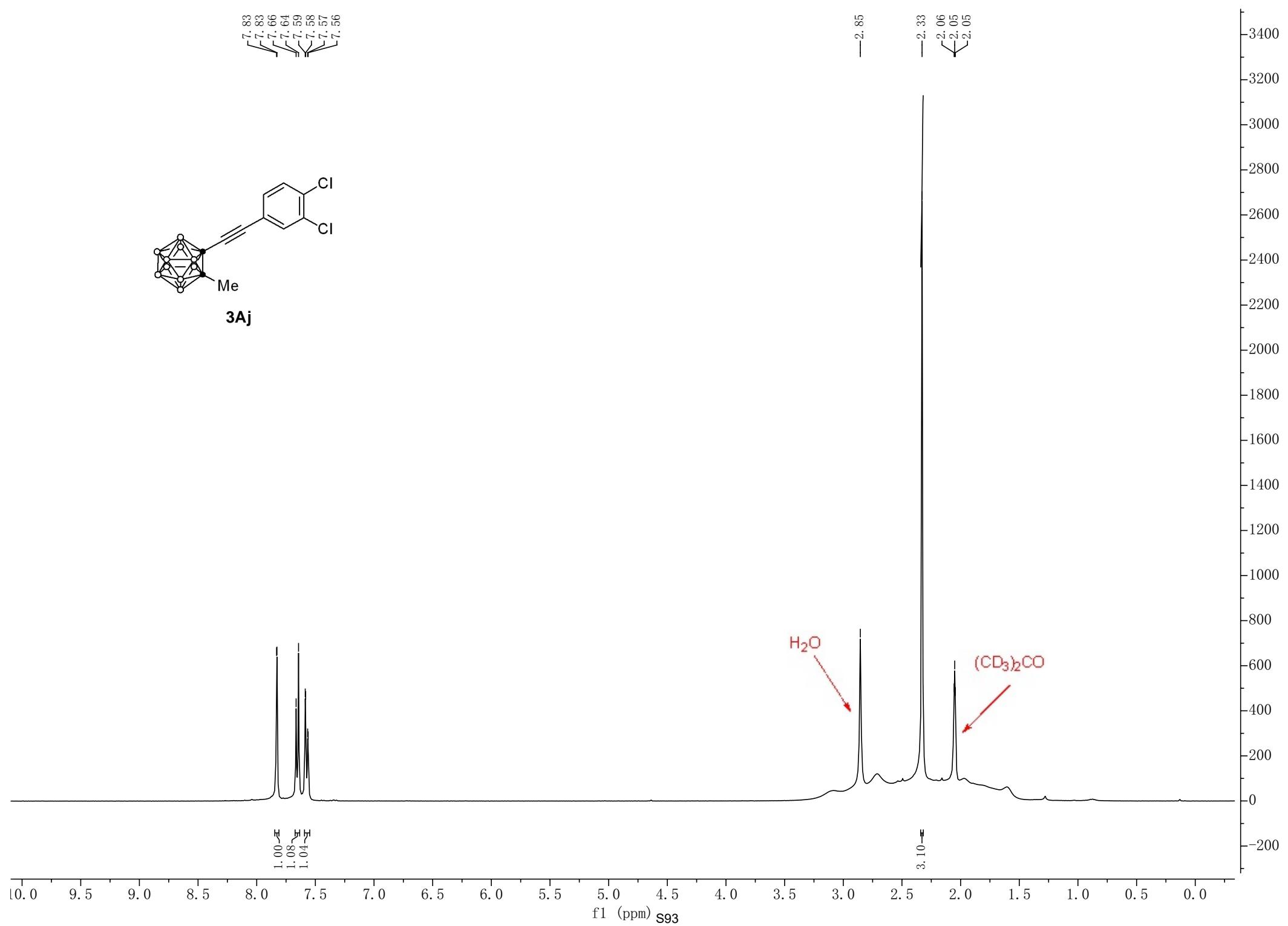
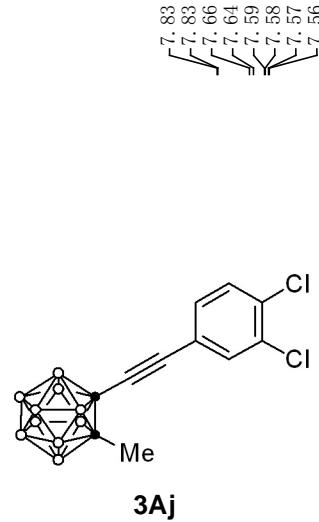


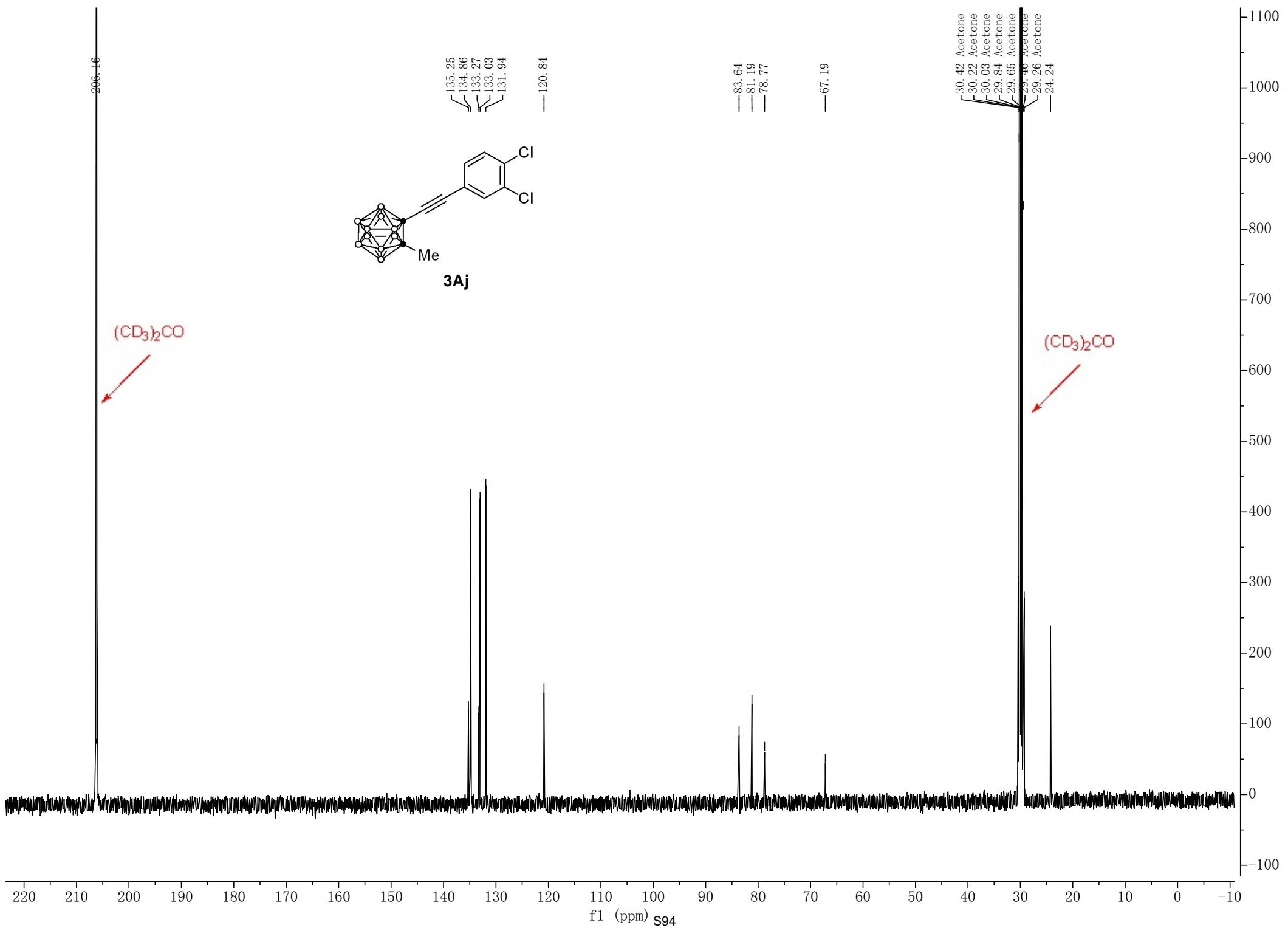
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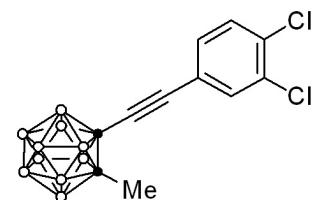




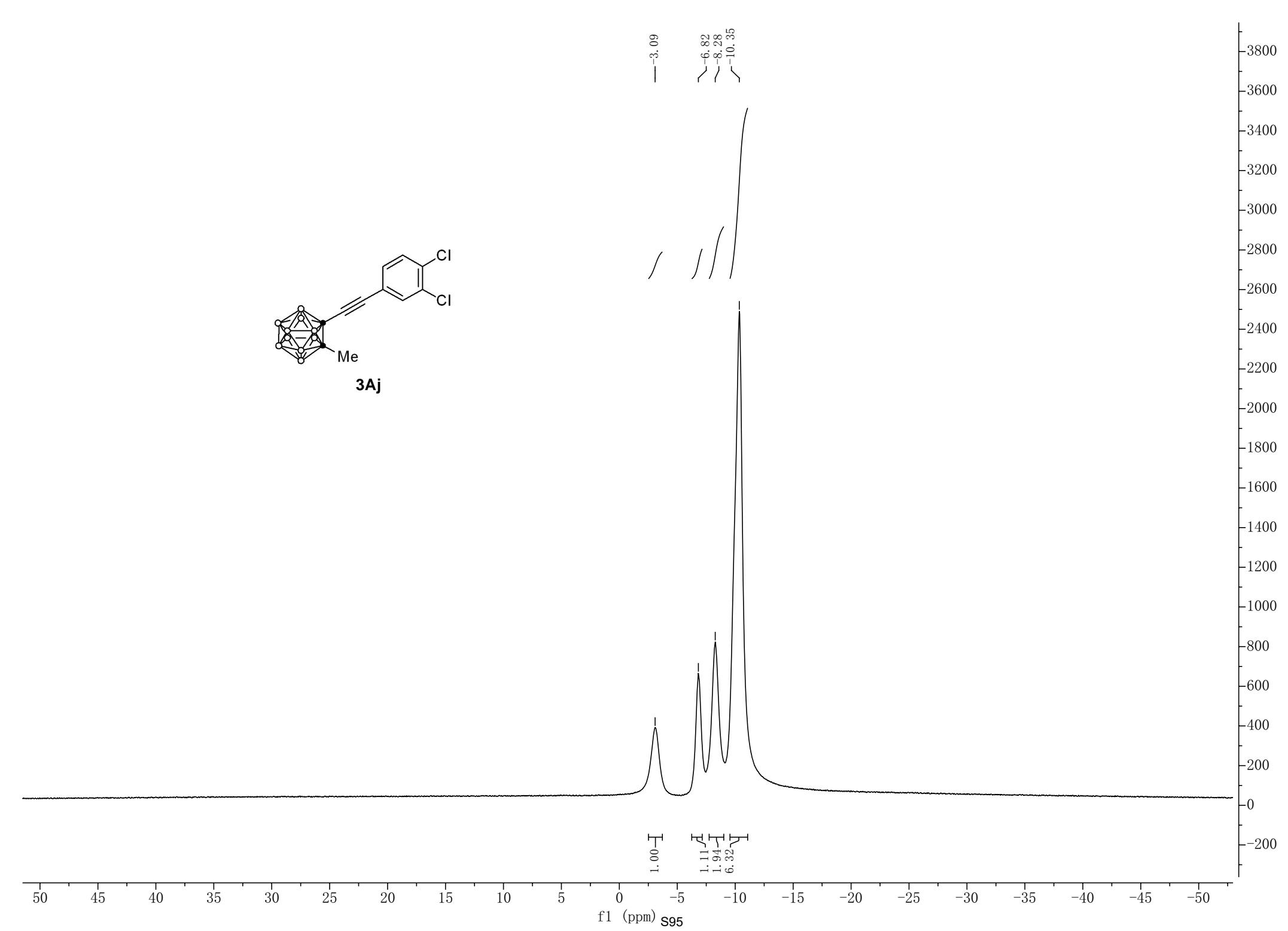


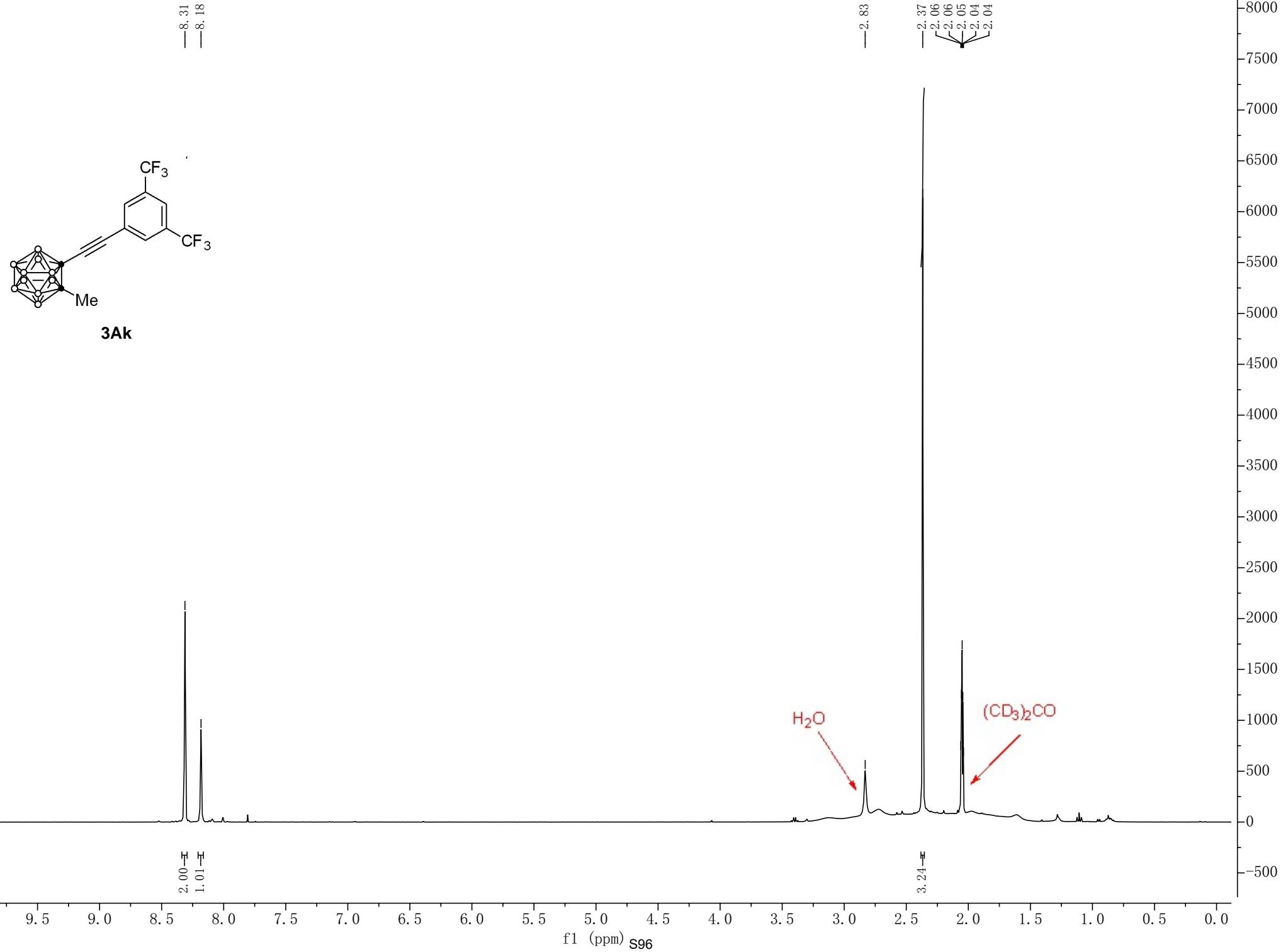


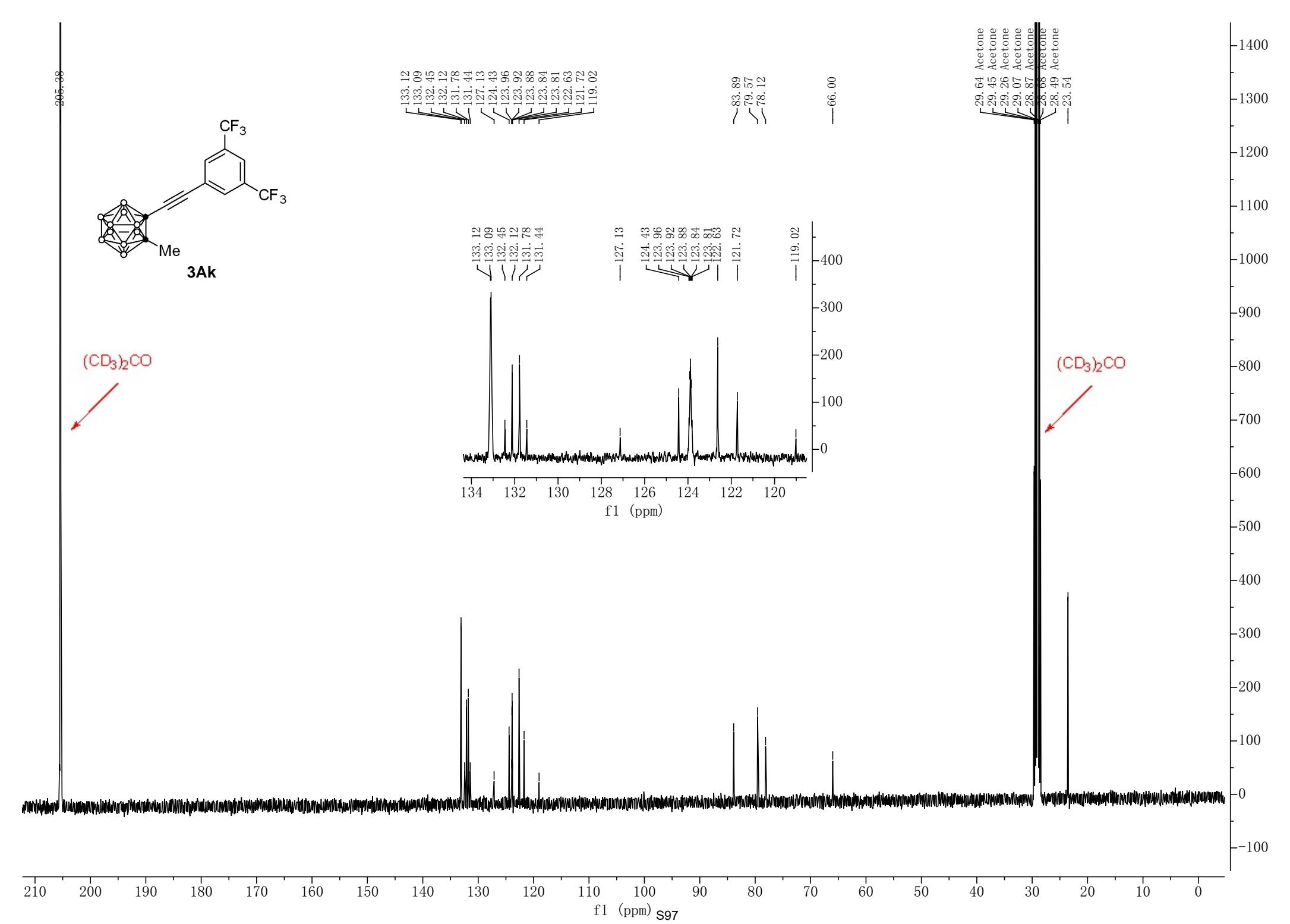


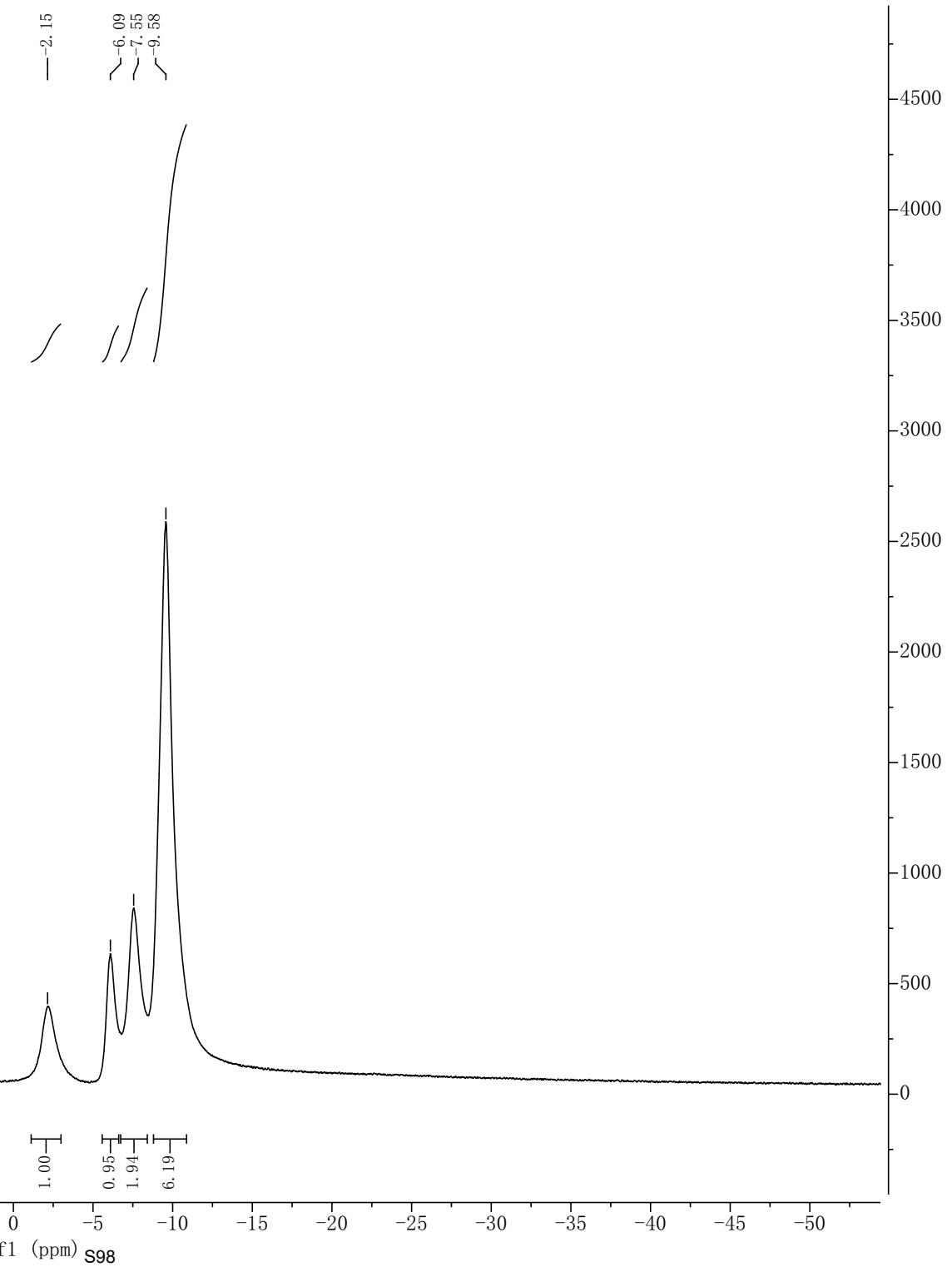
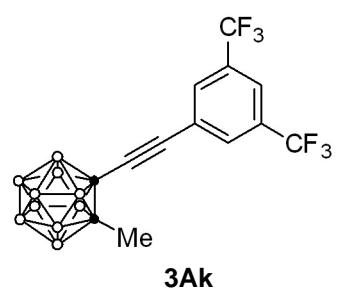


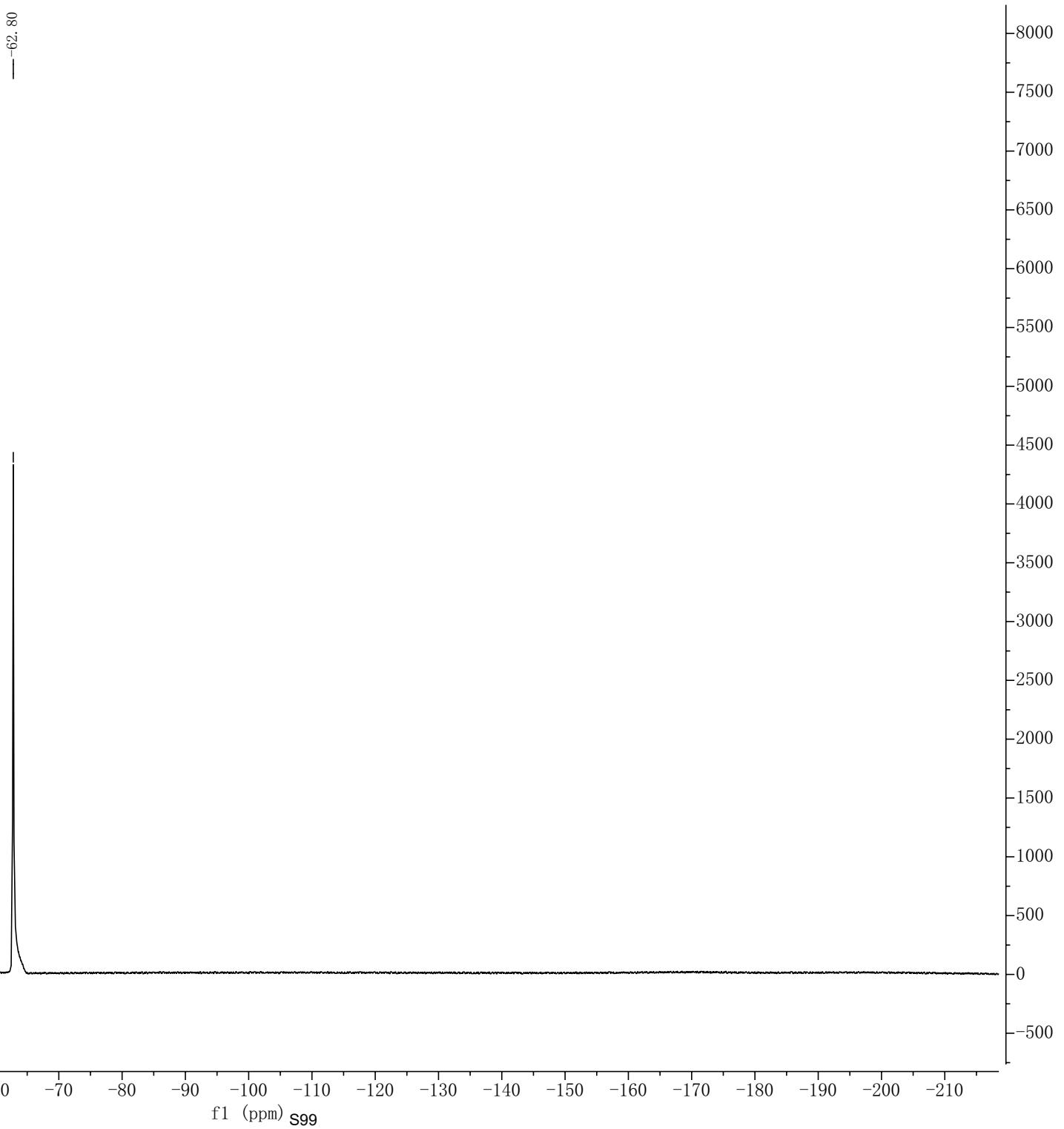
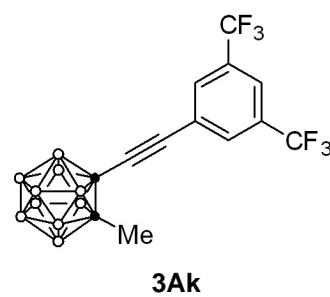
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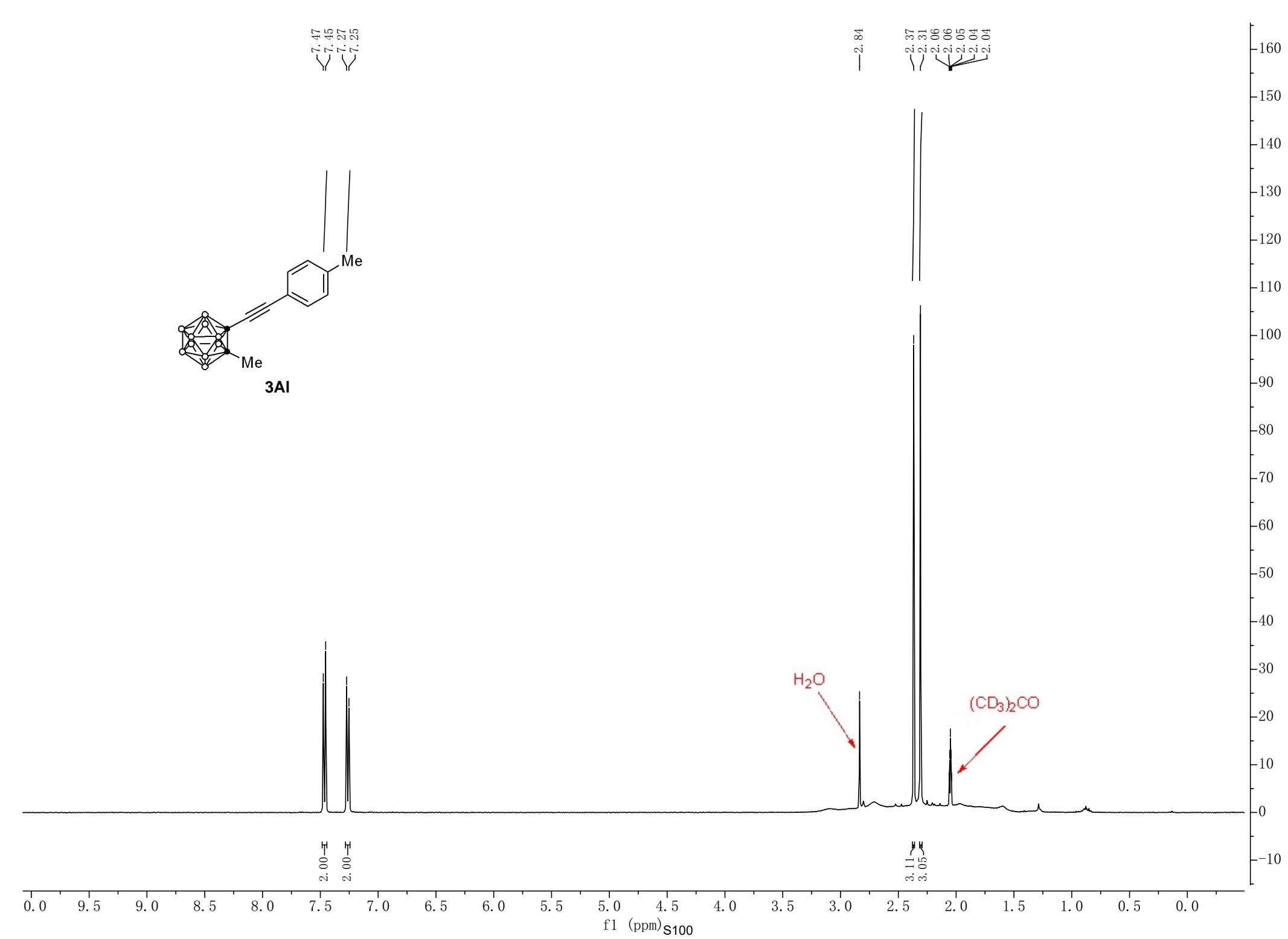
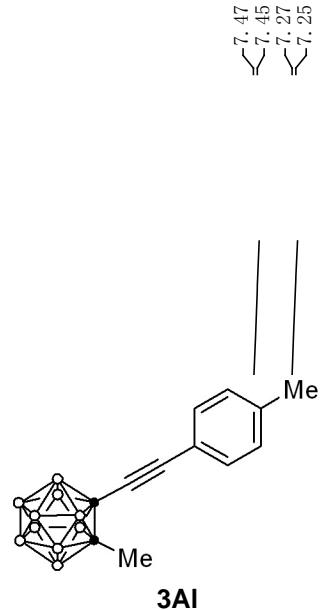


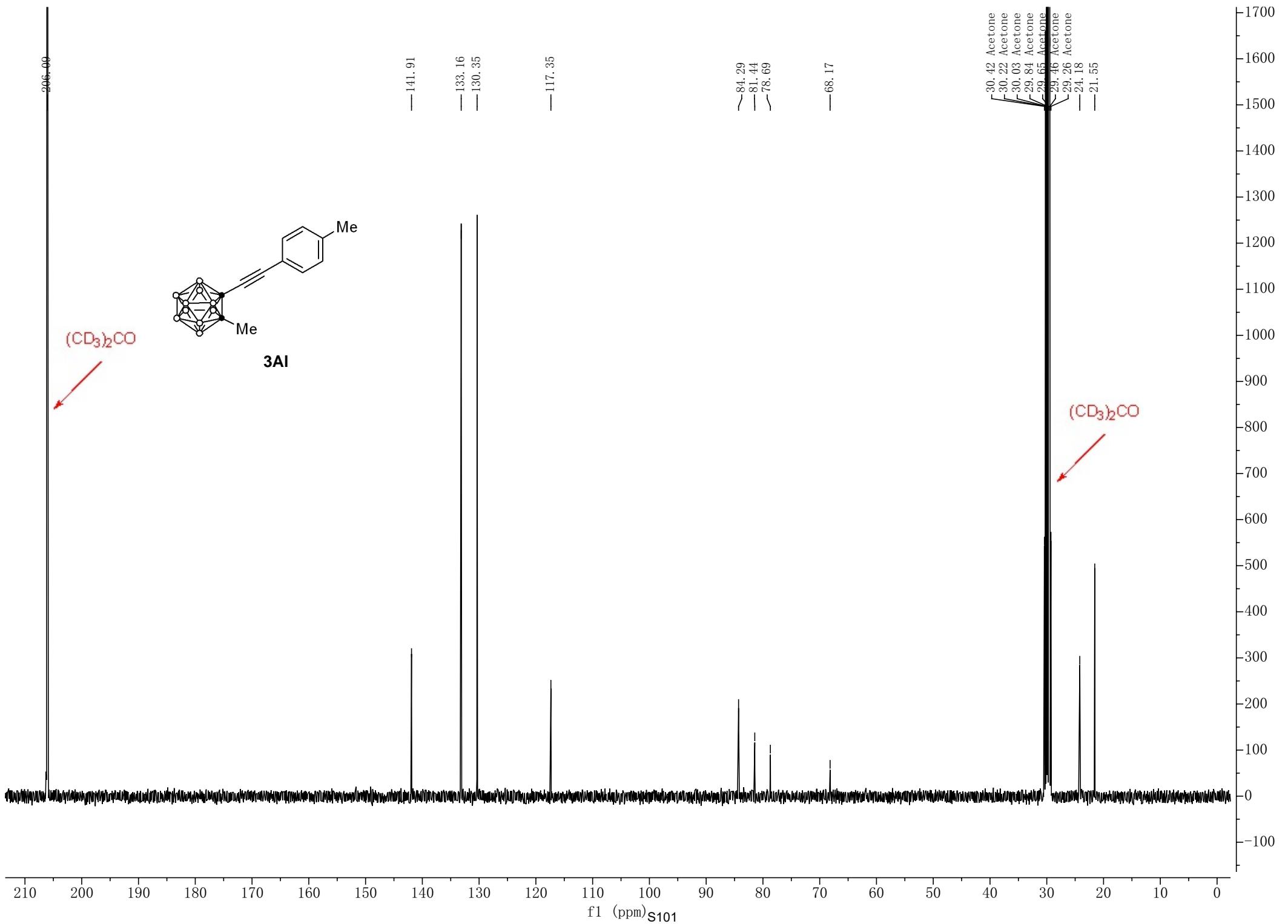


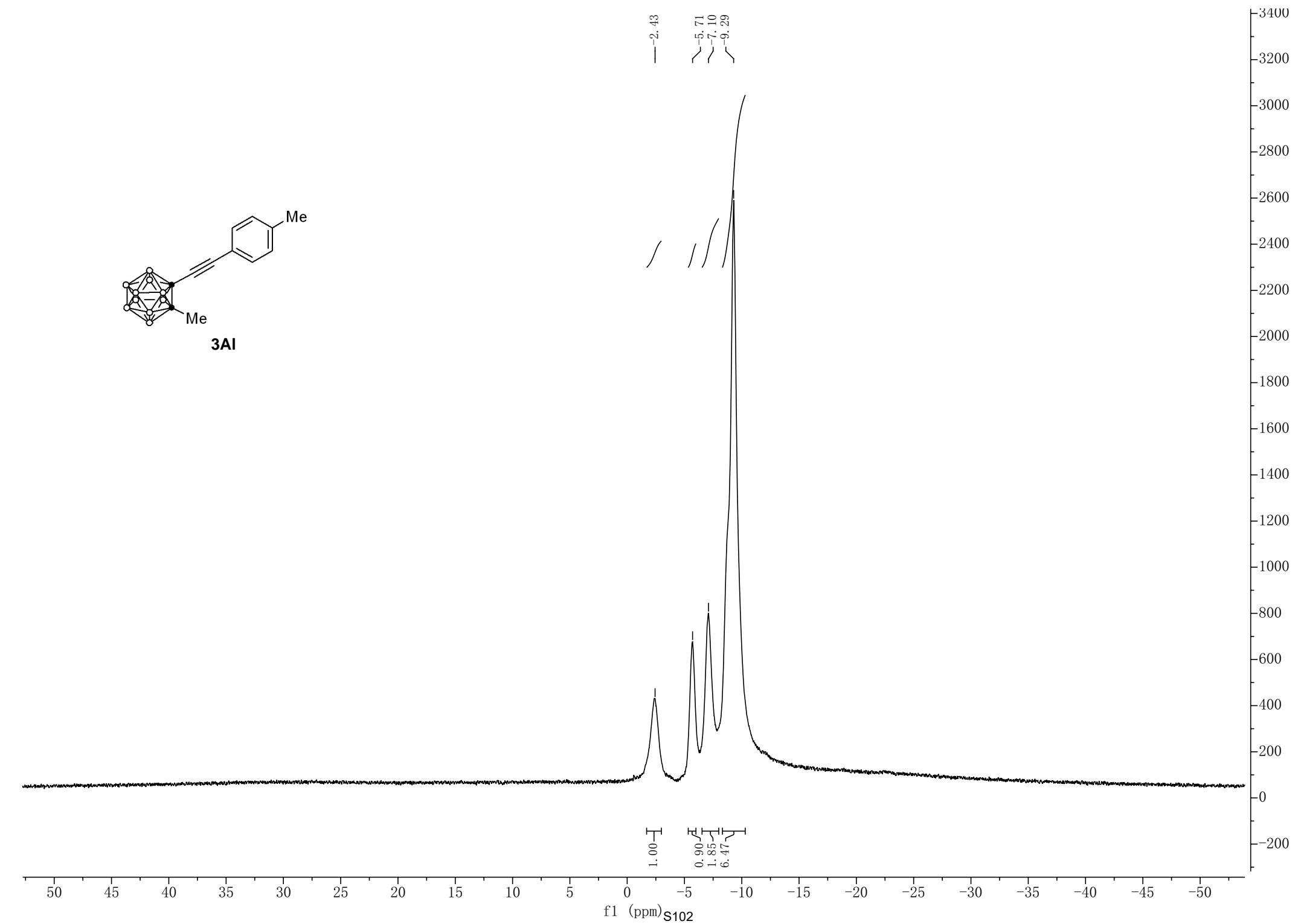
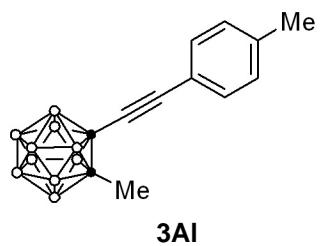


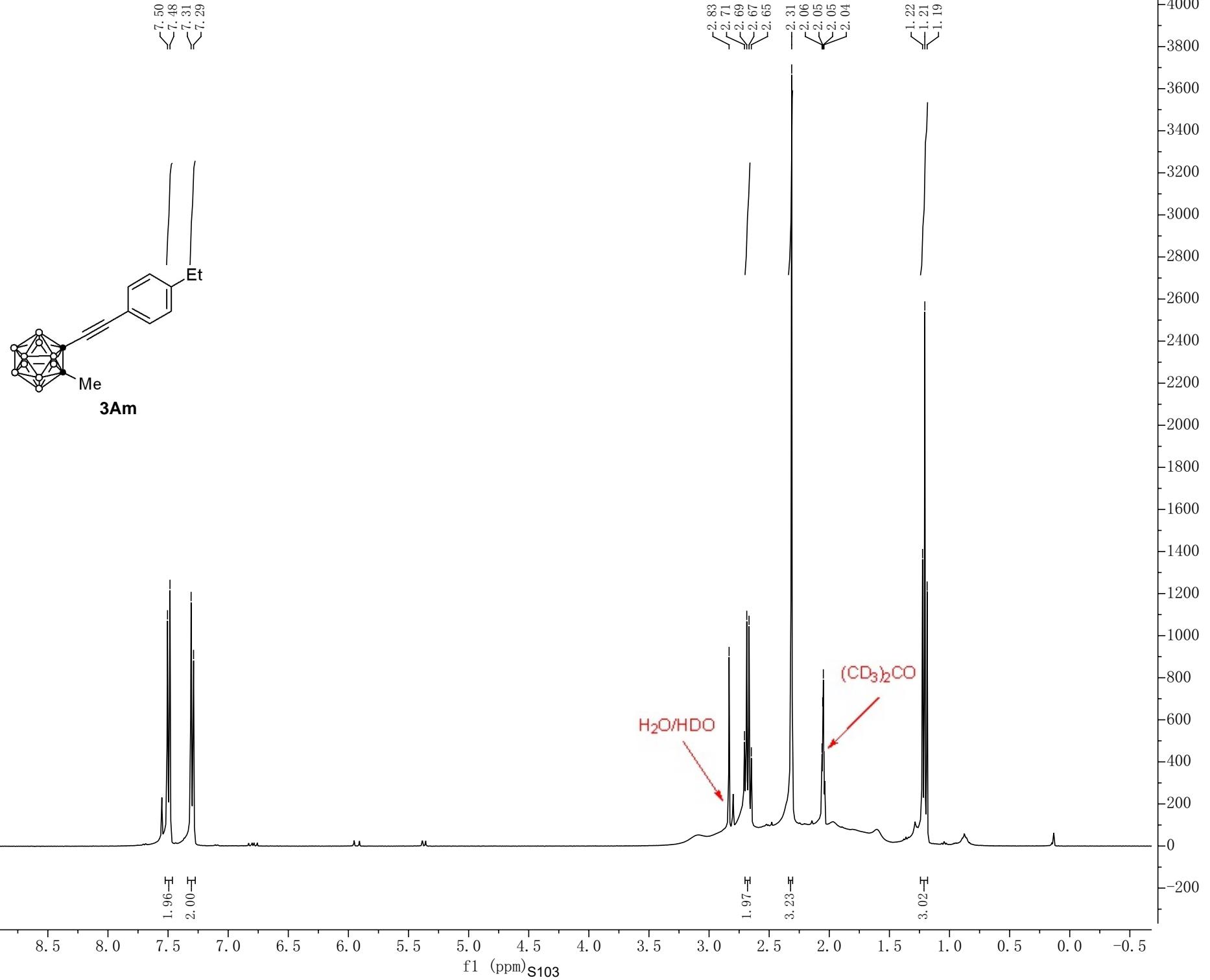


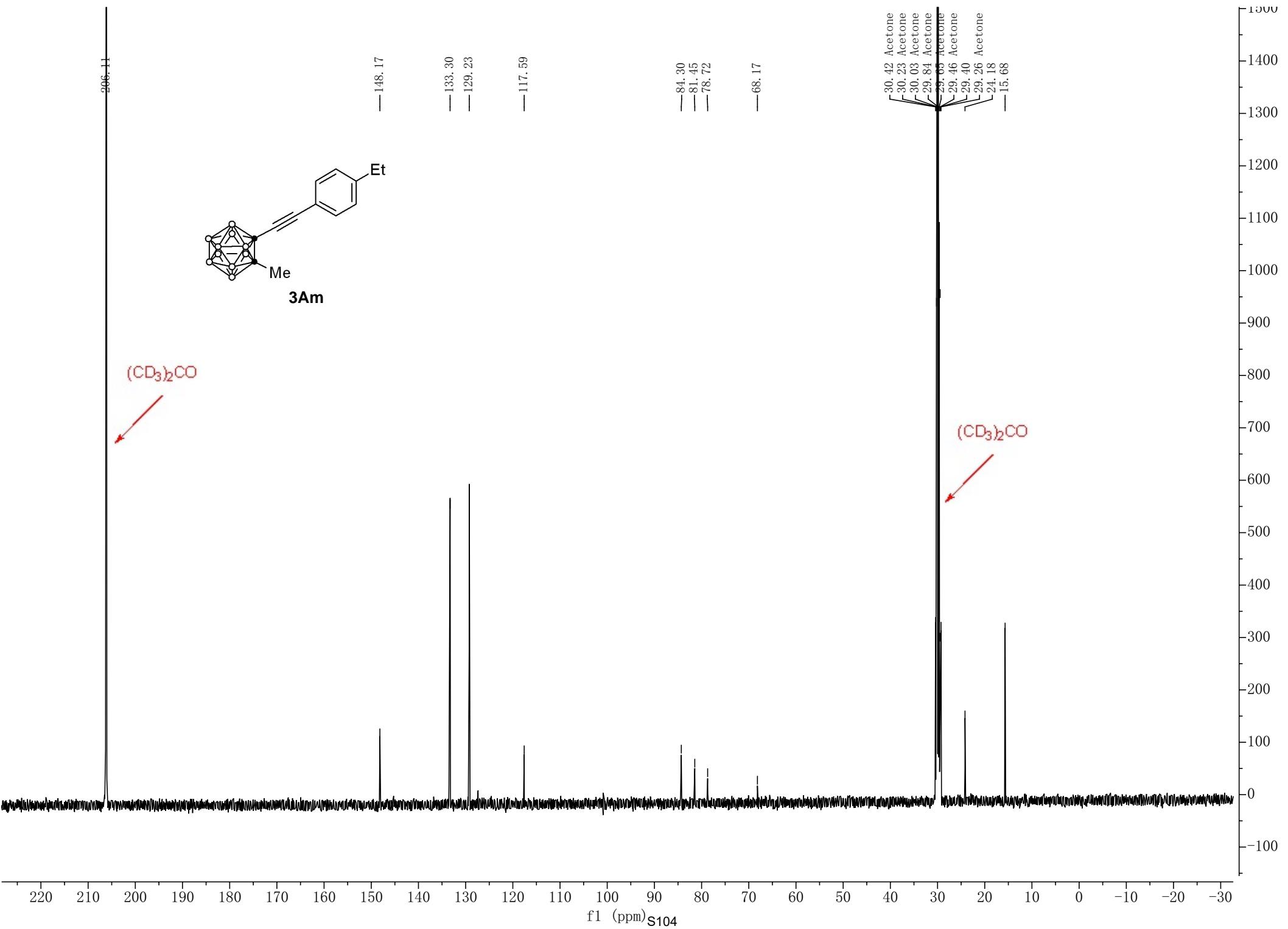


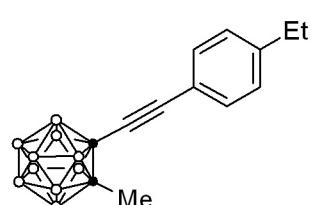




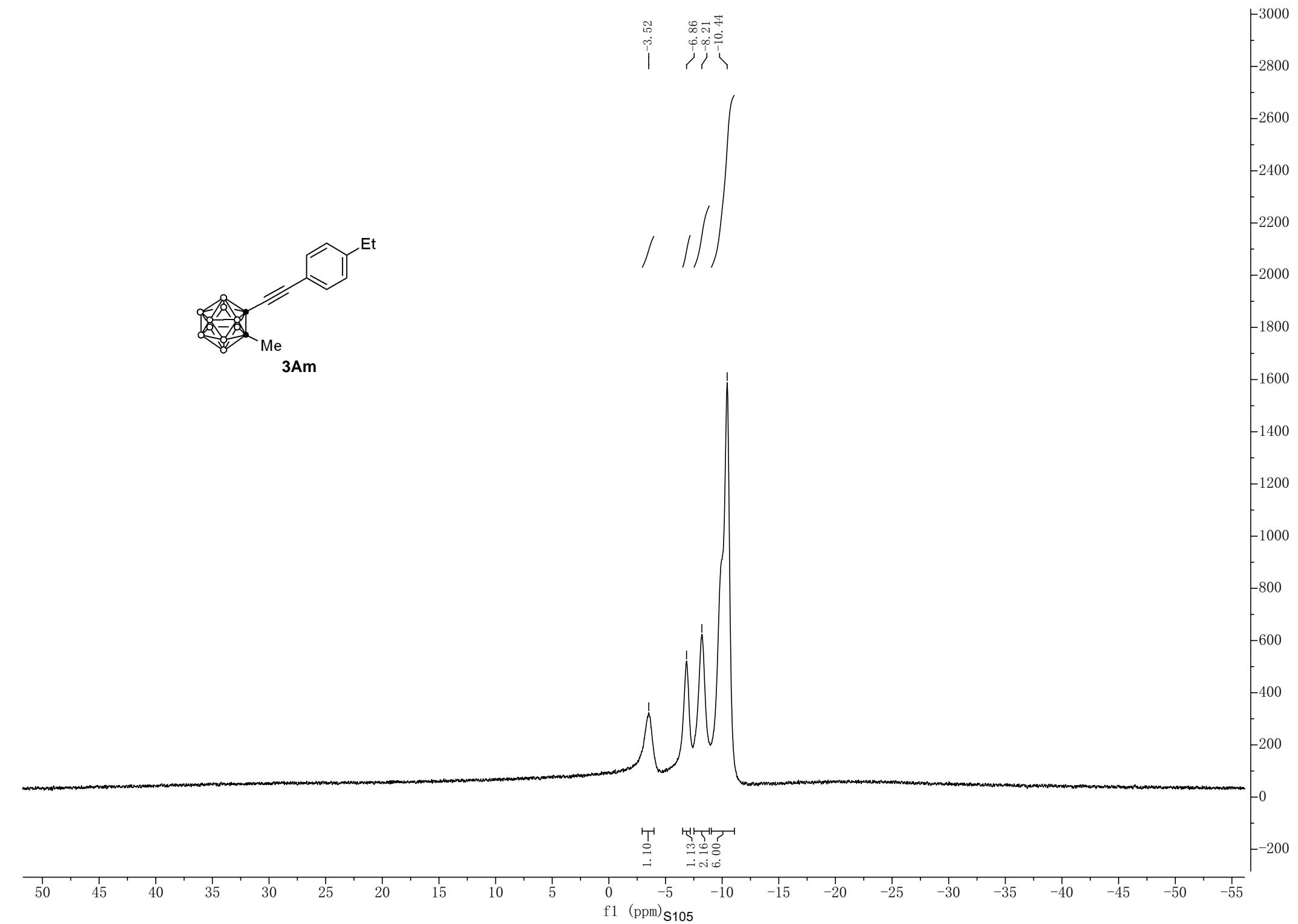


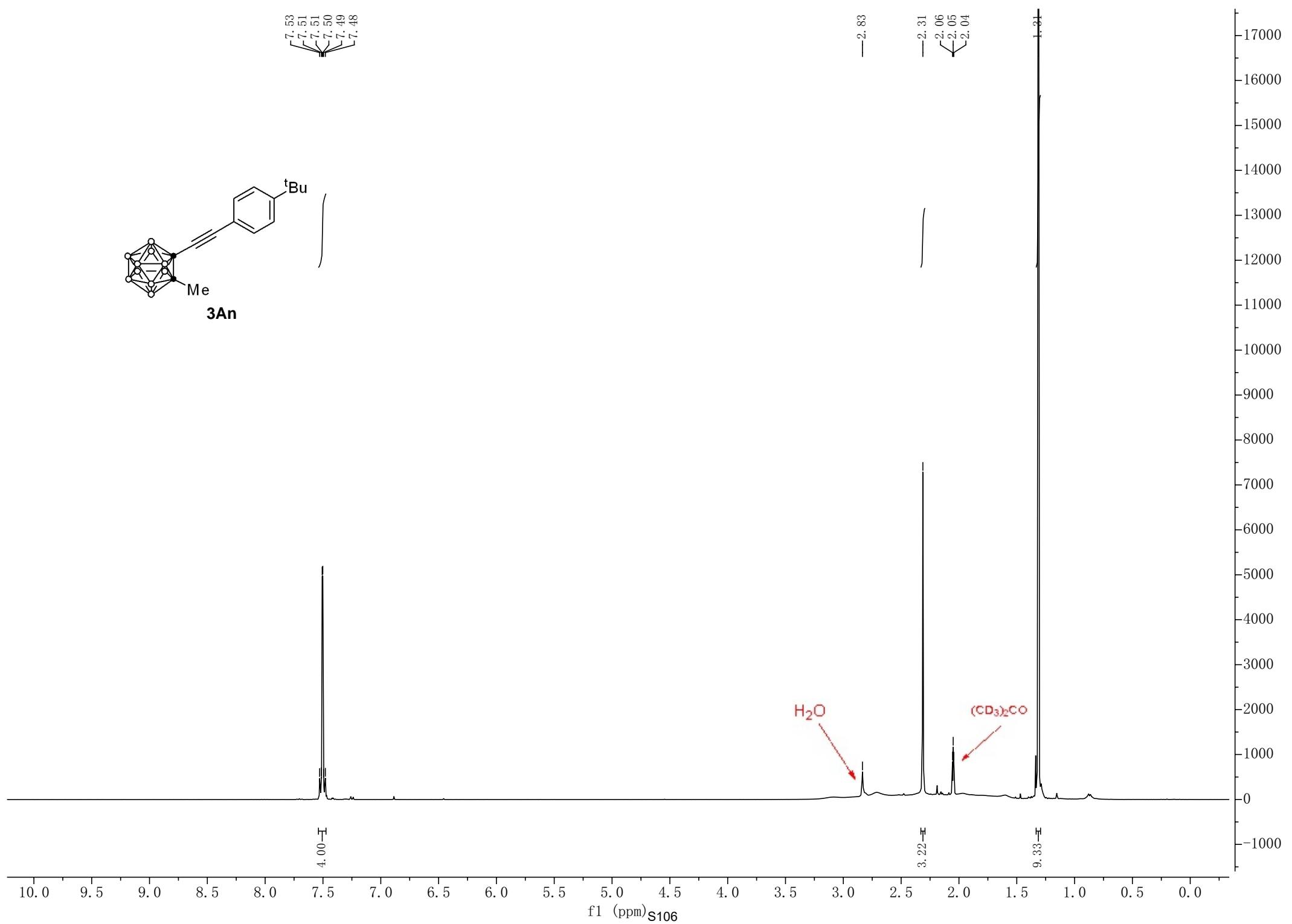
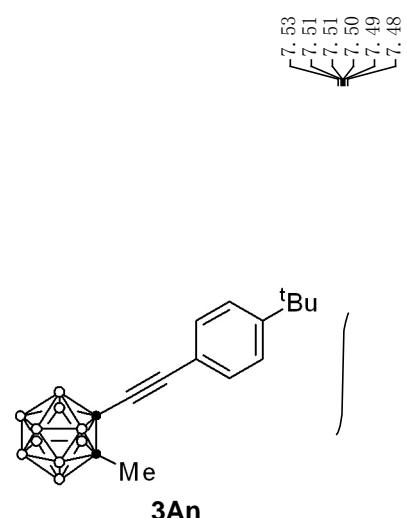


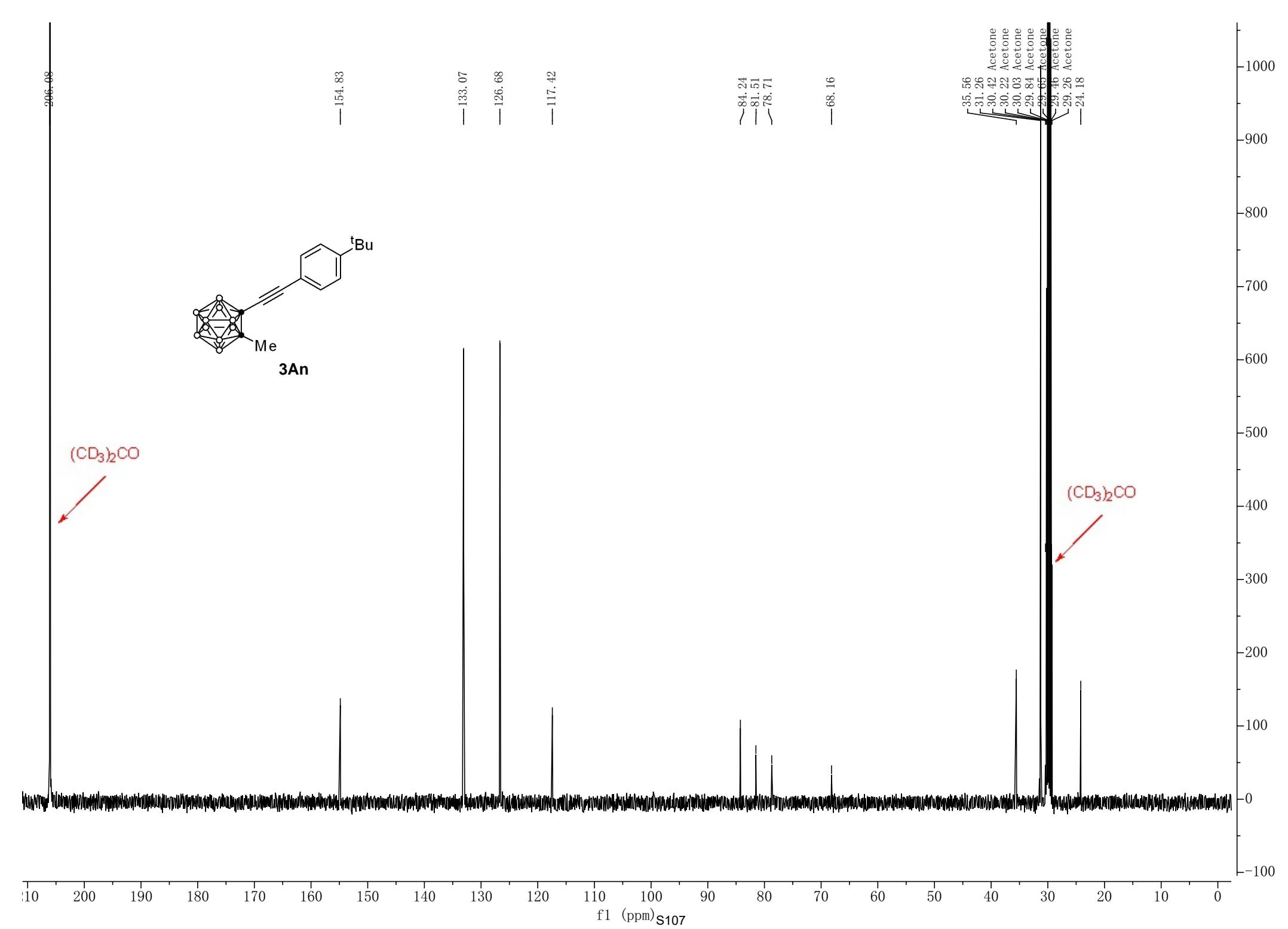


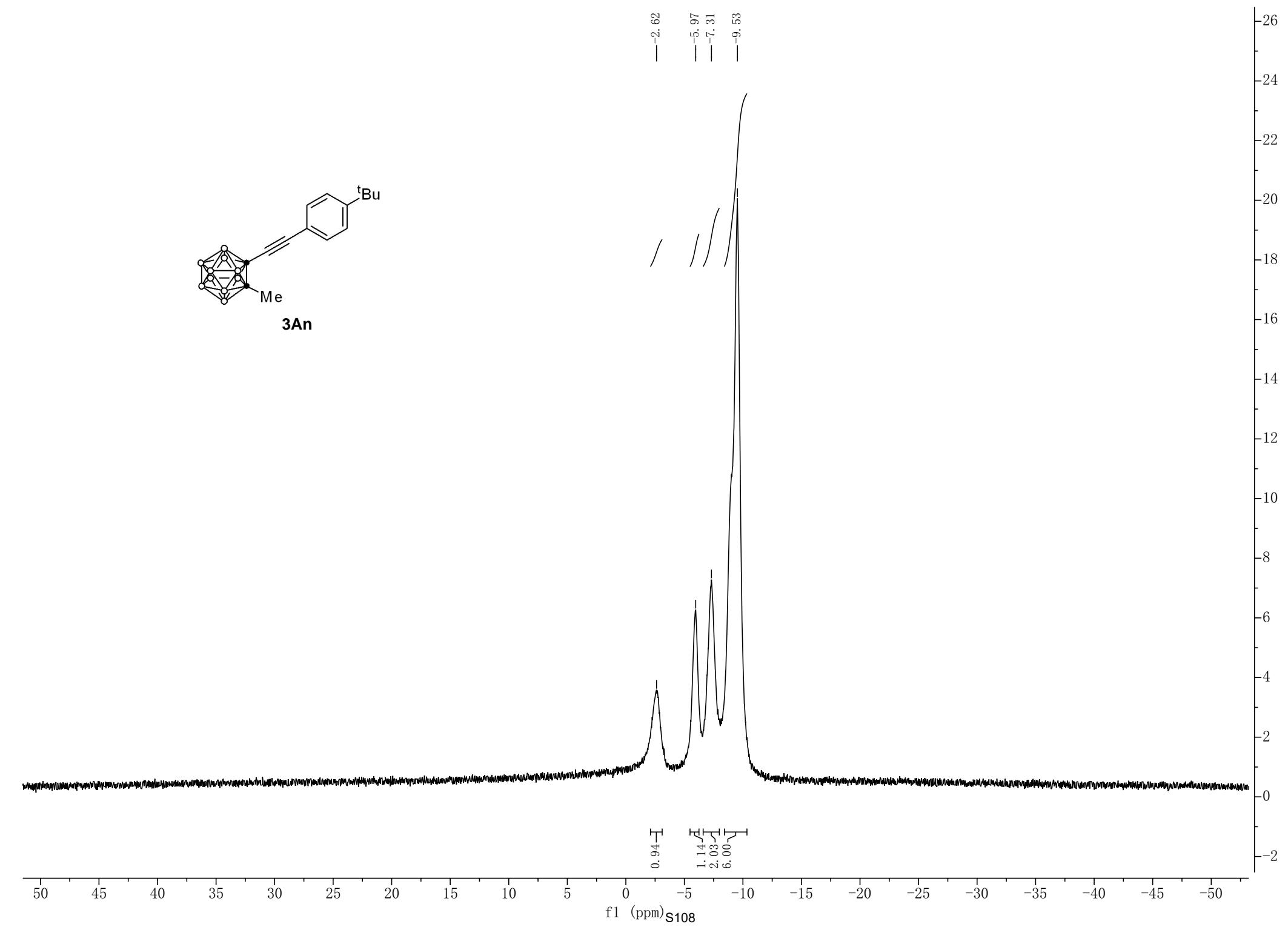
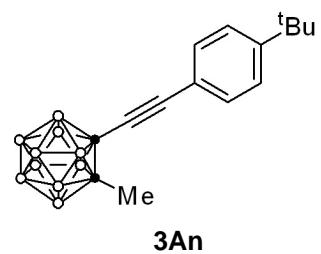


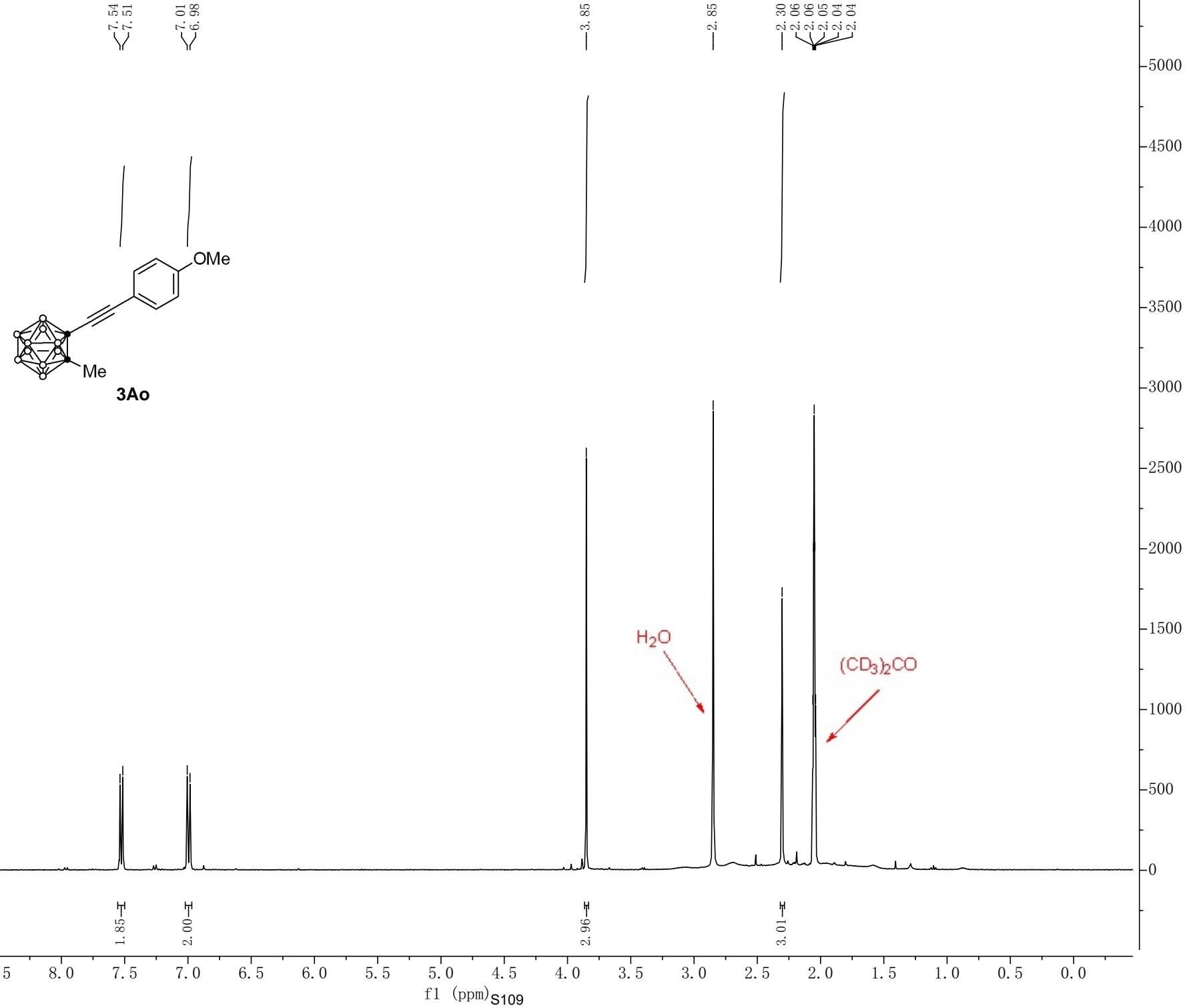
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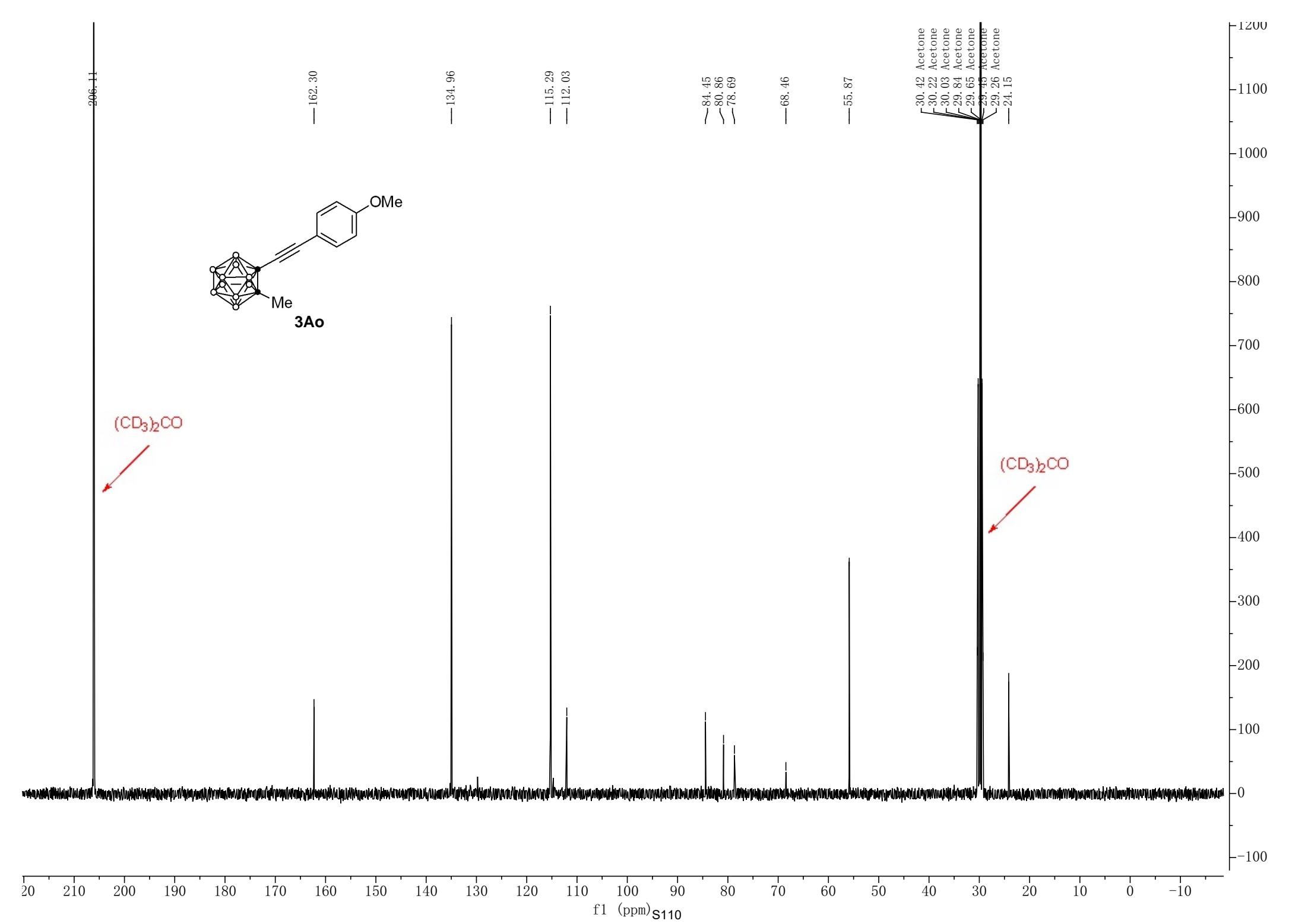


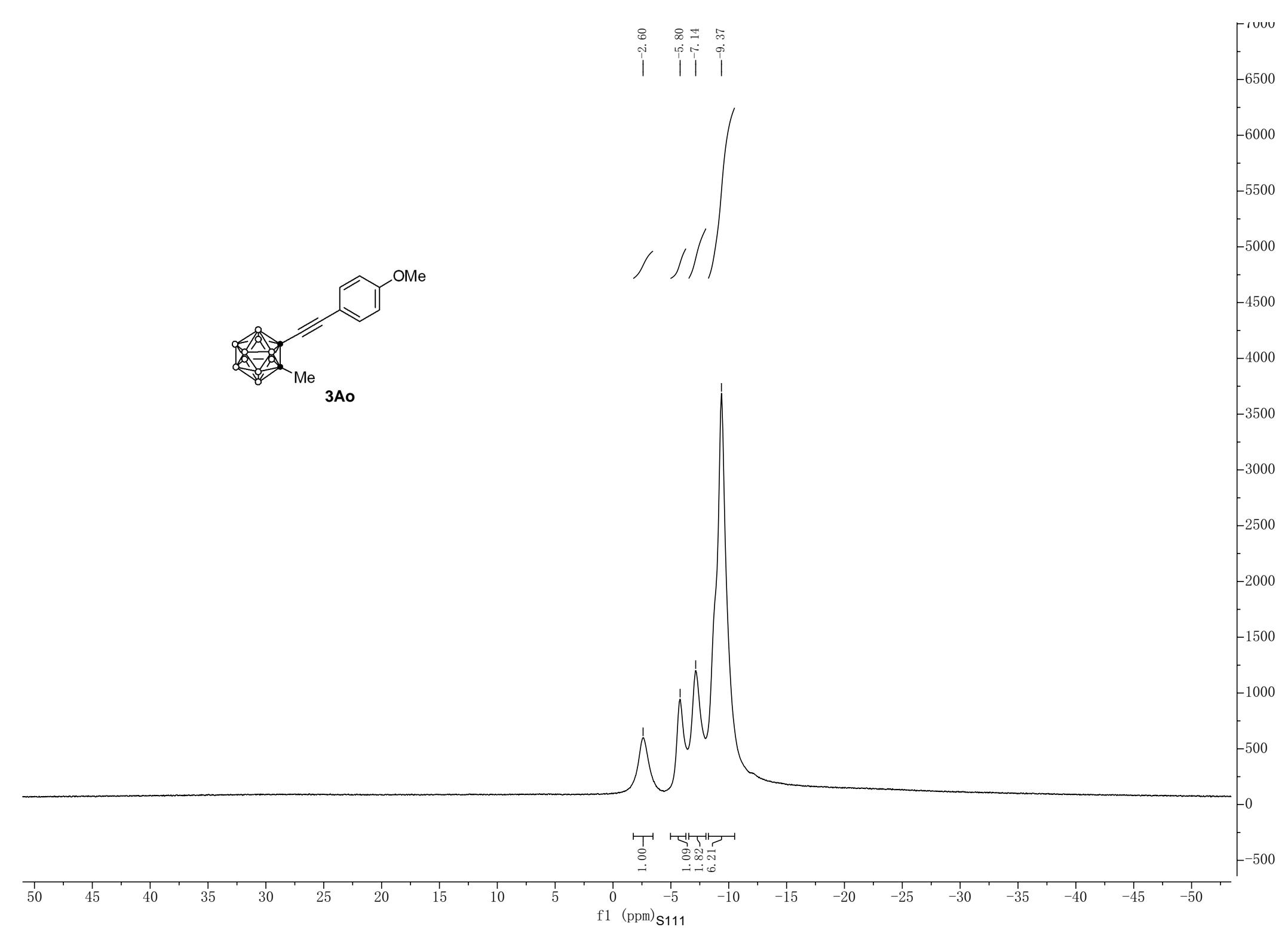
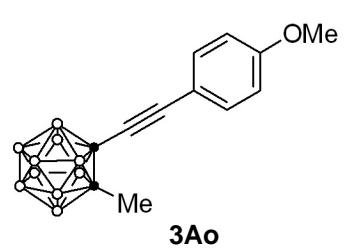


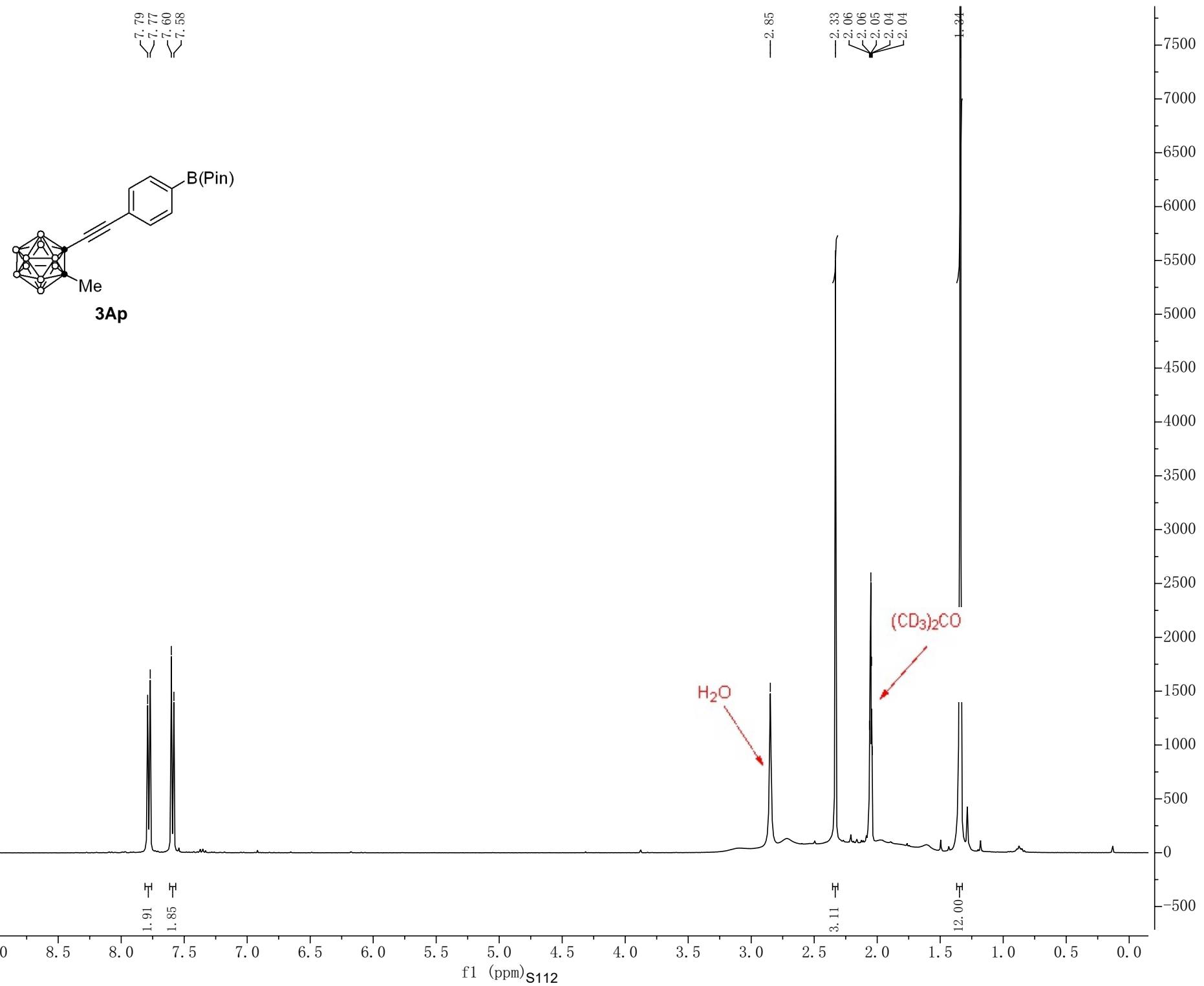


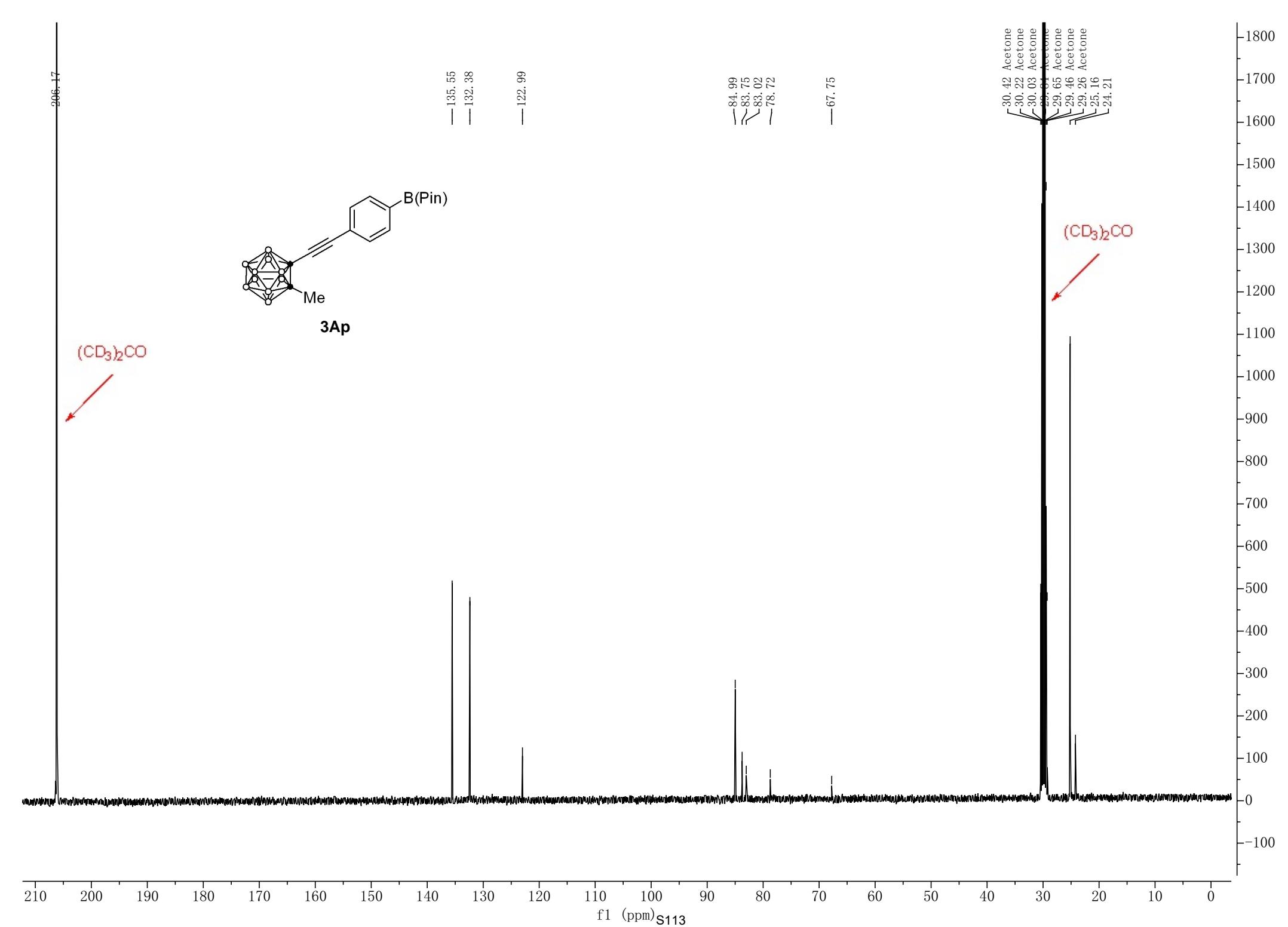


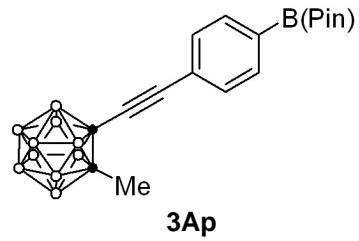








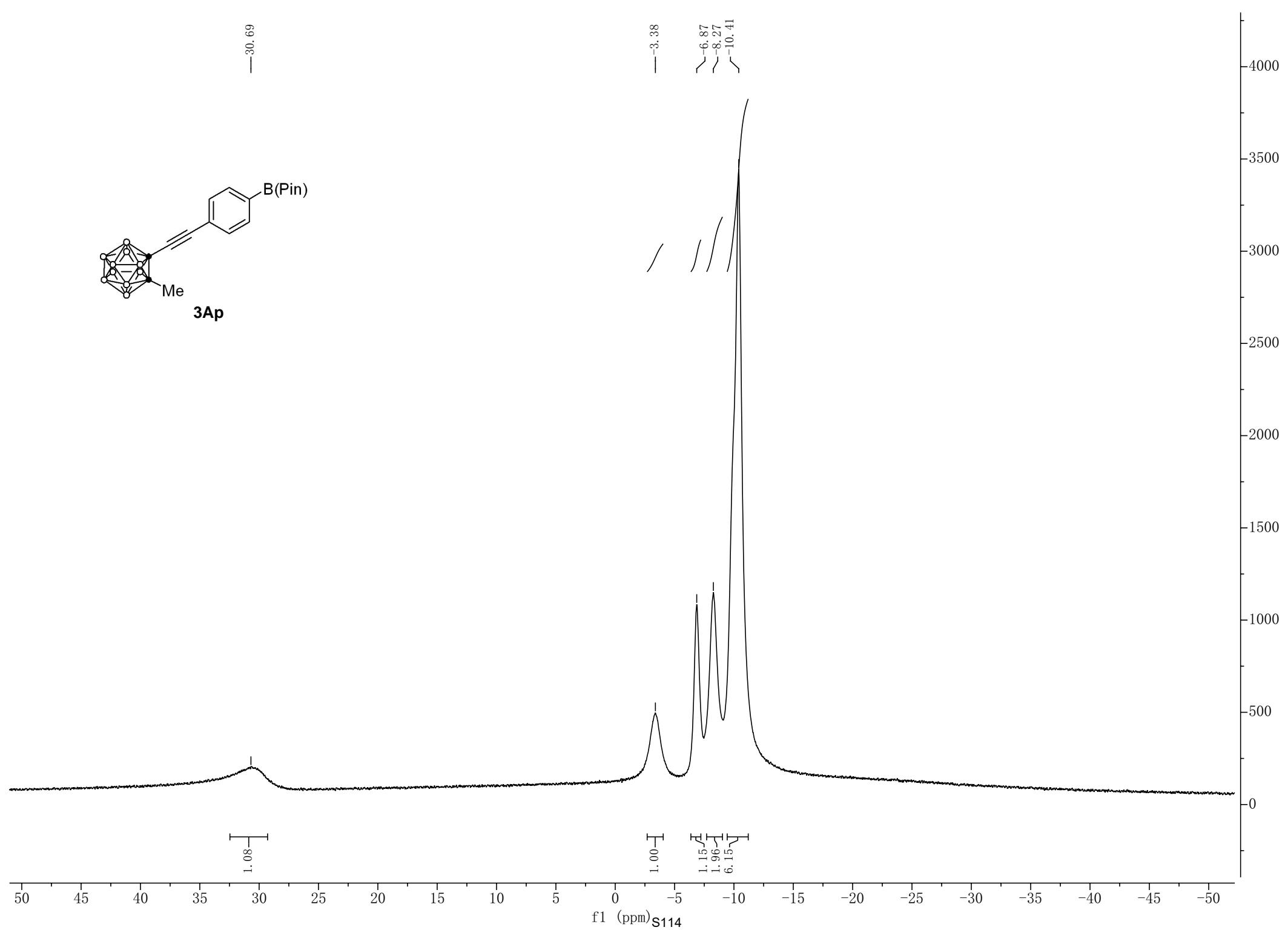




—30.69

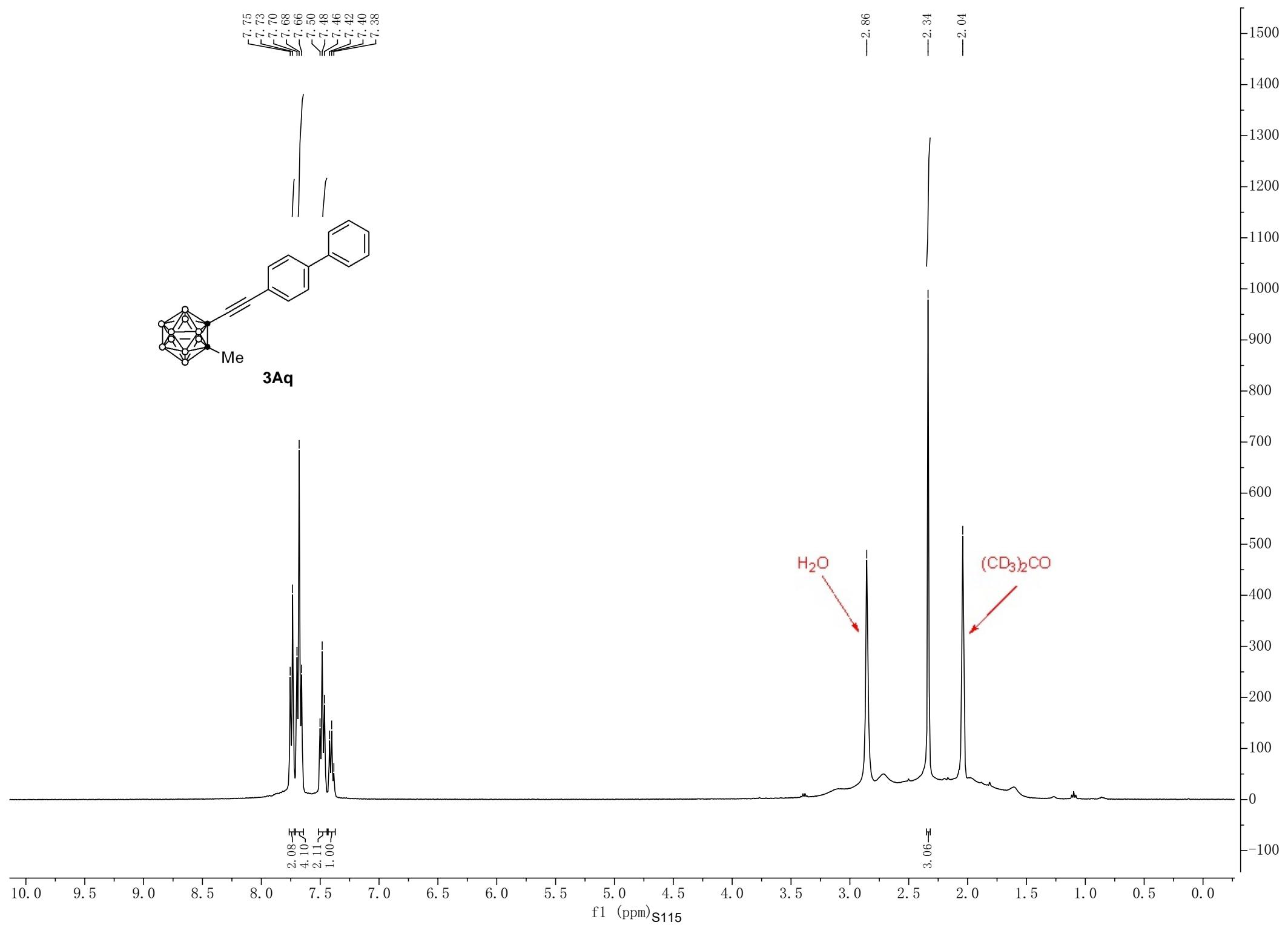
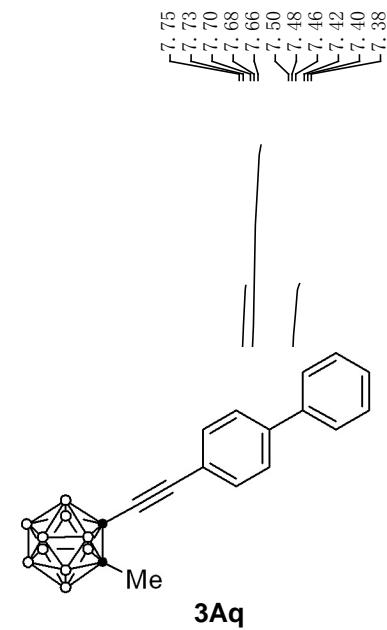
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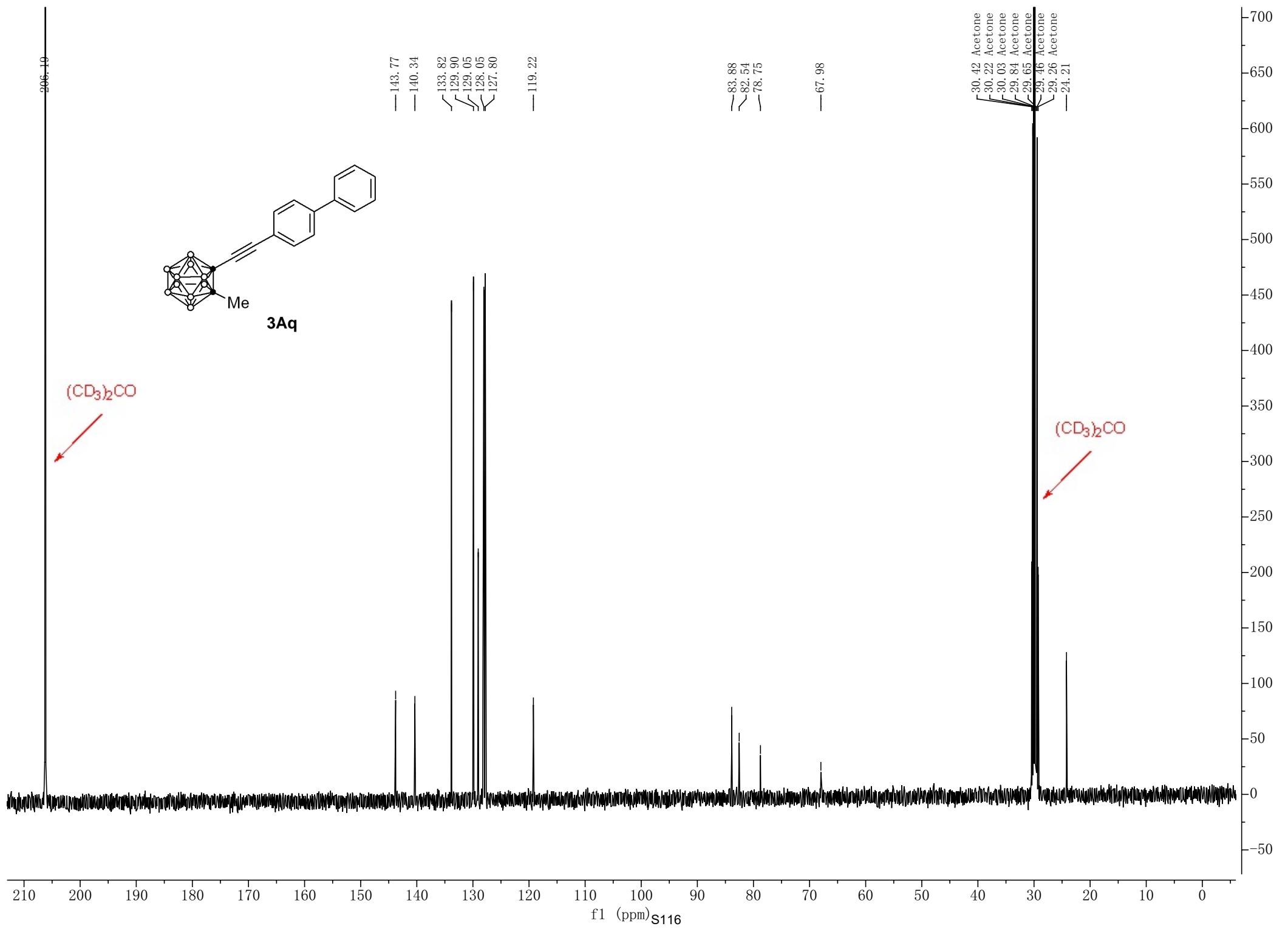
~
-6.87
~
-8.27
~
-10.41

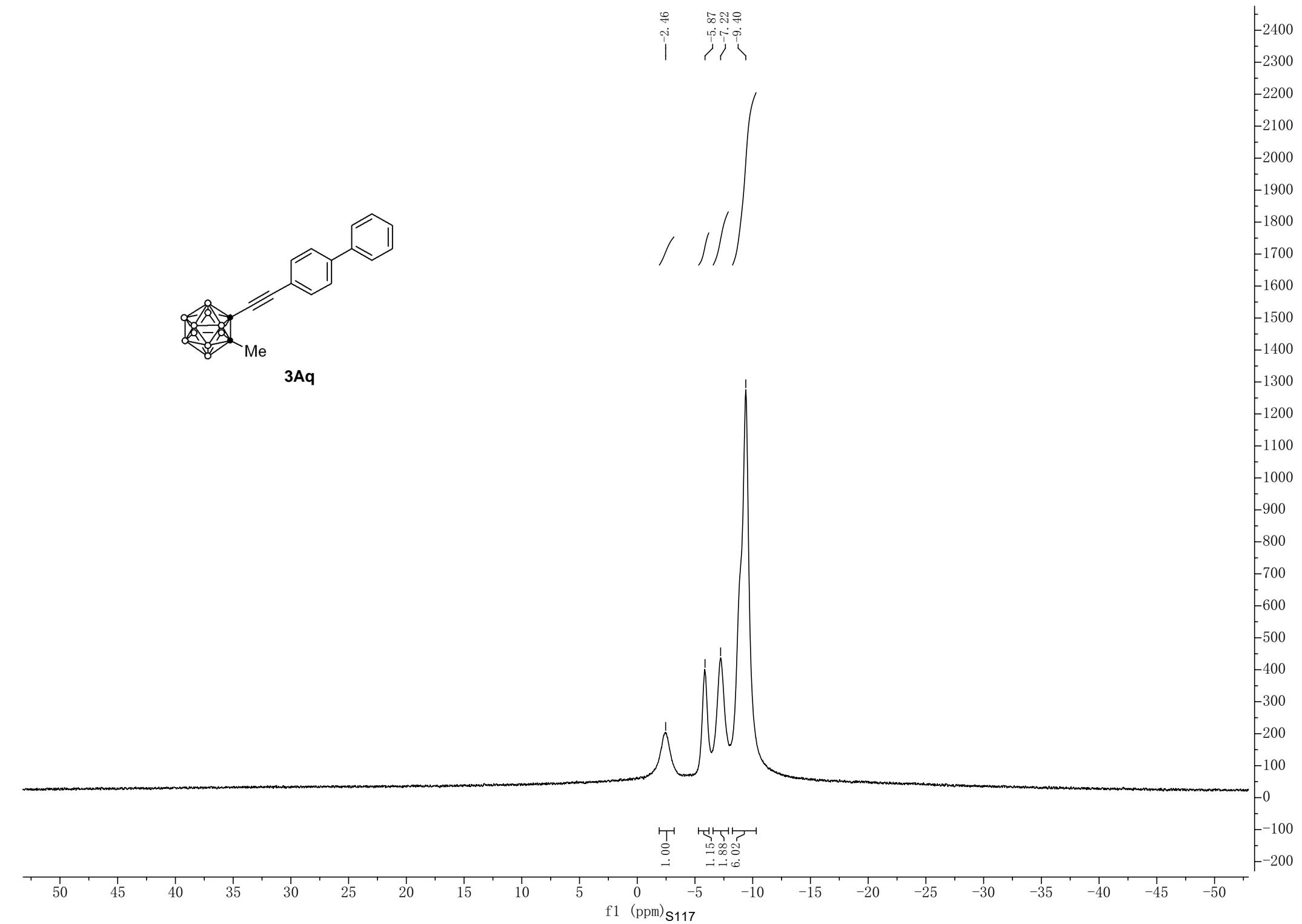
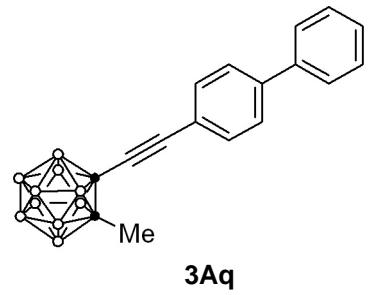


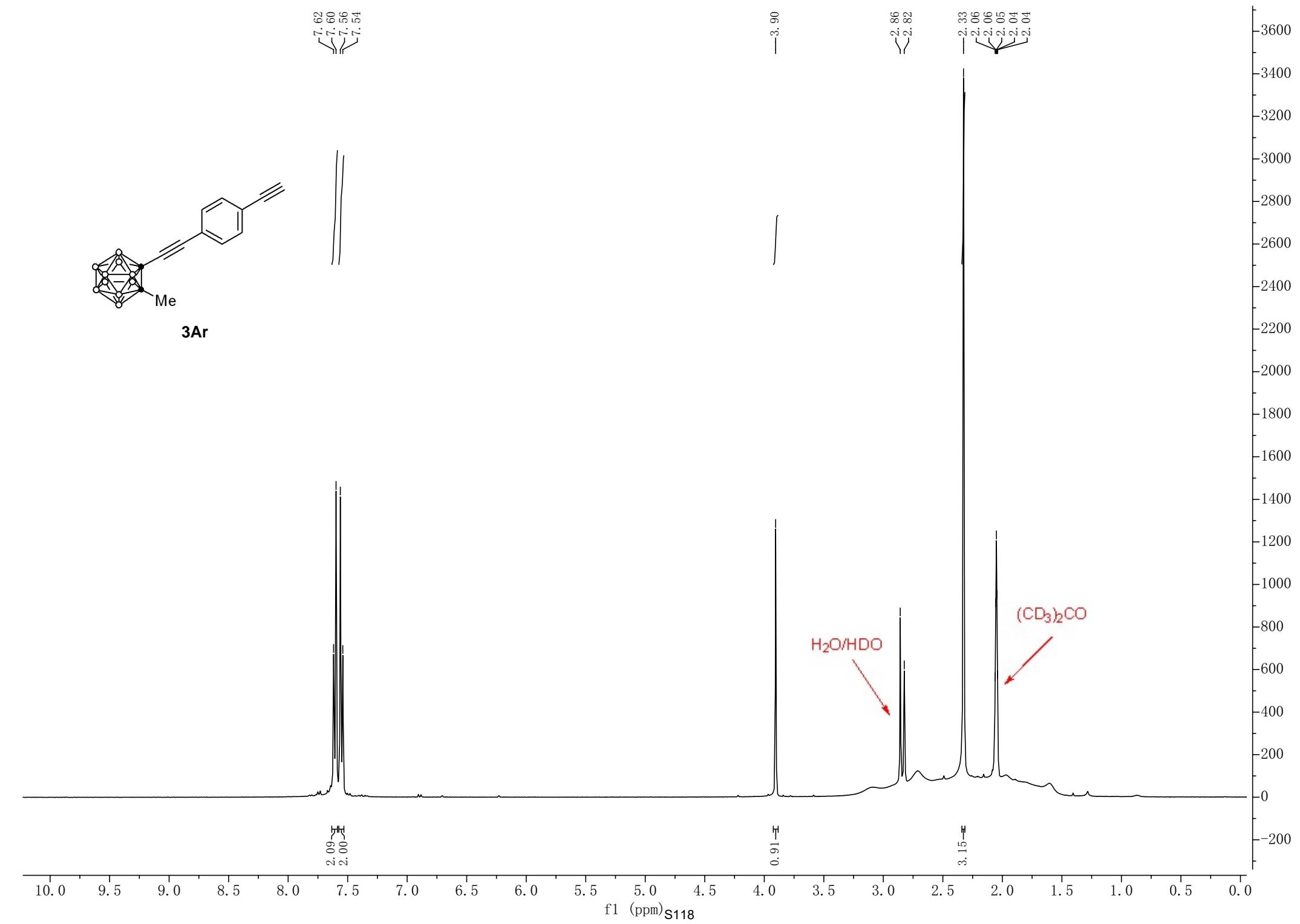
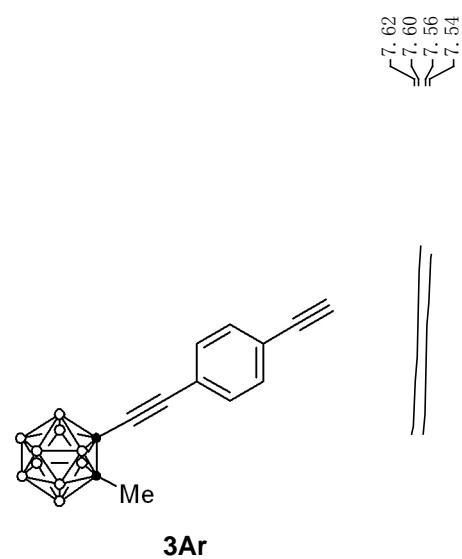
f1 (ppm)

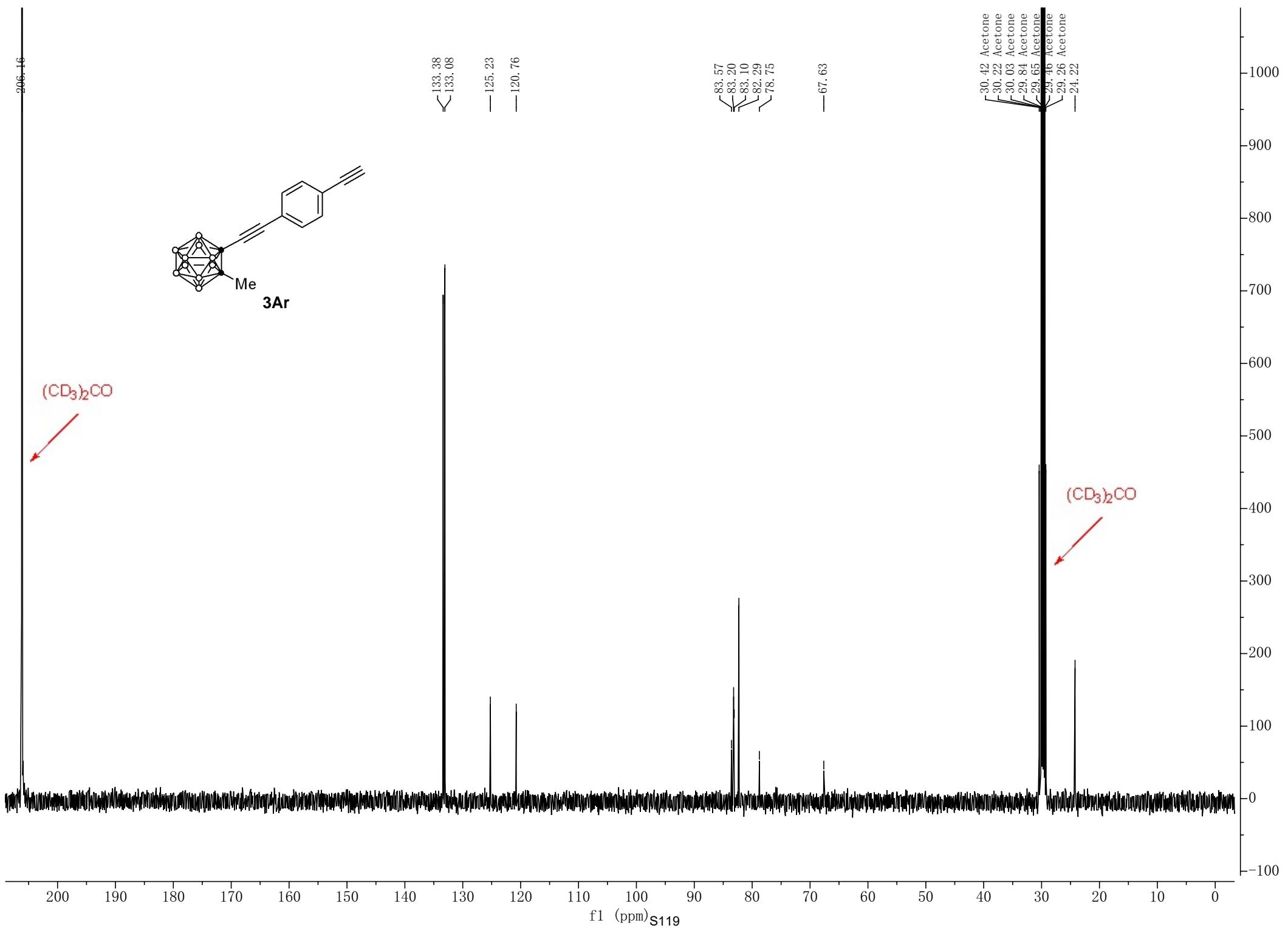
S114

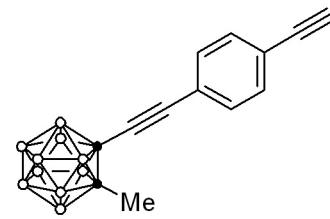




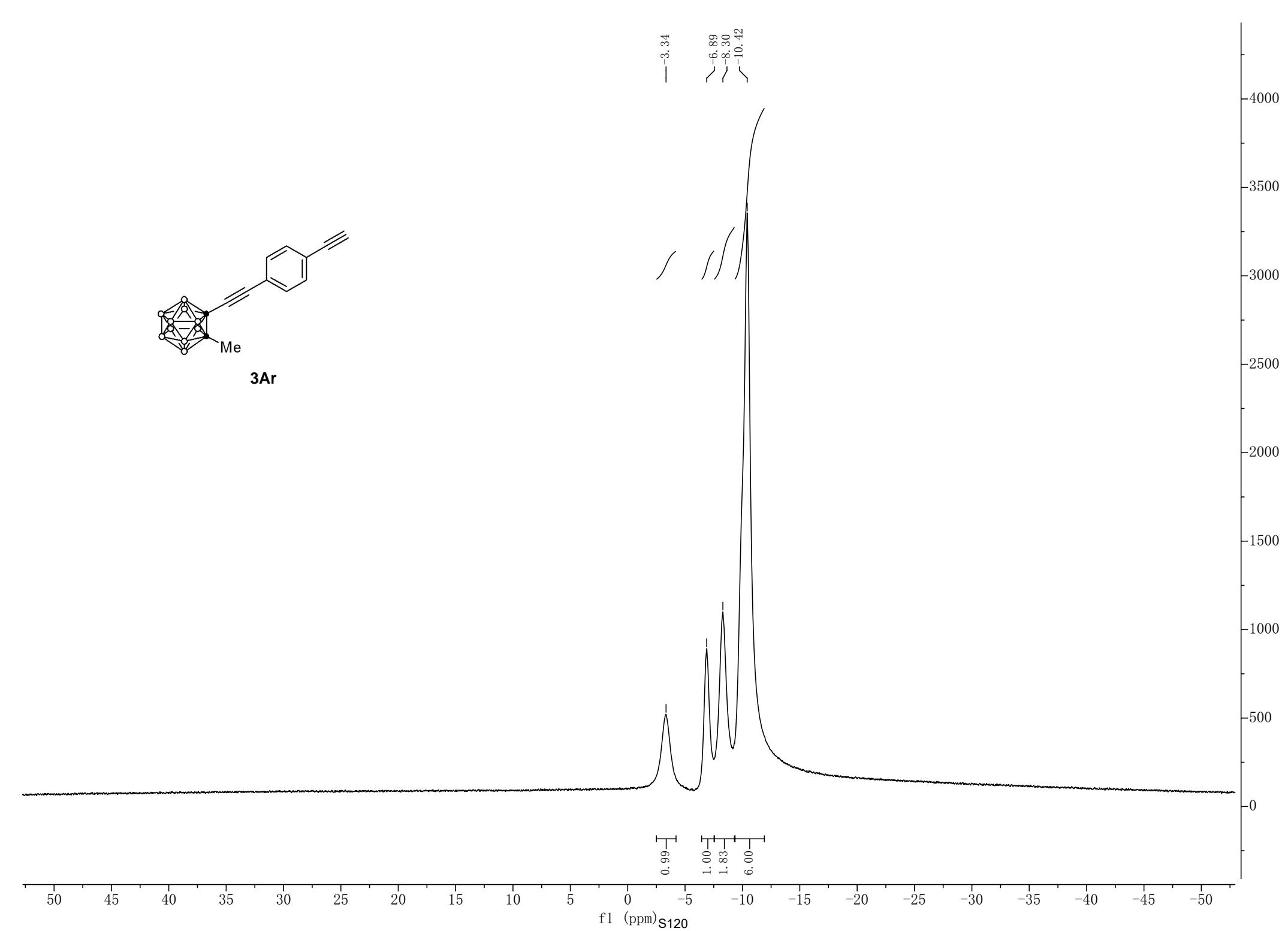


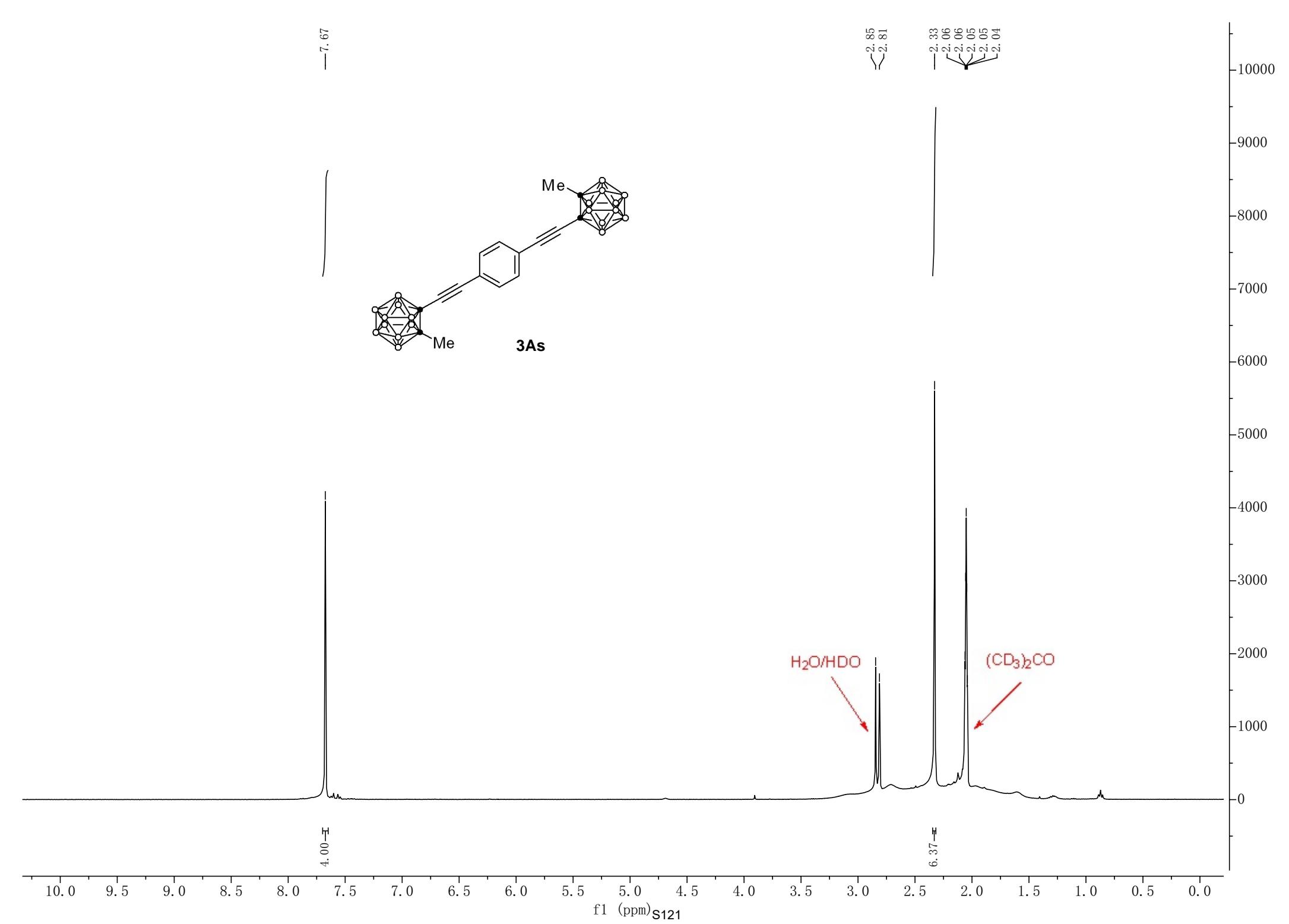


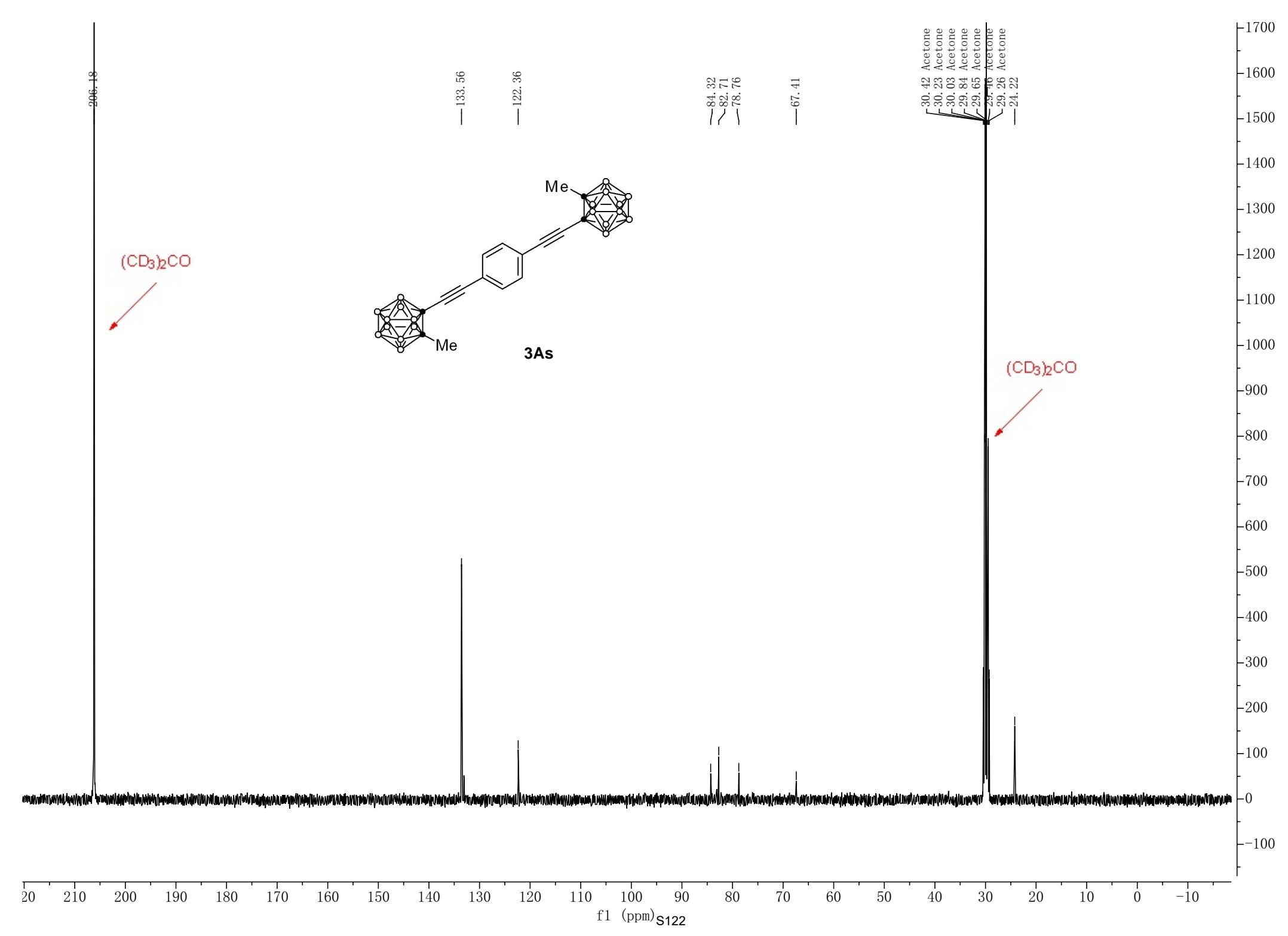


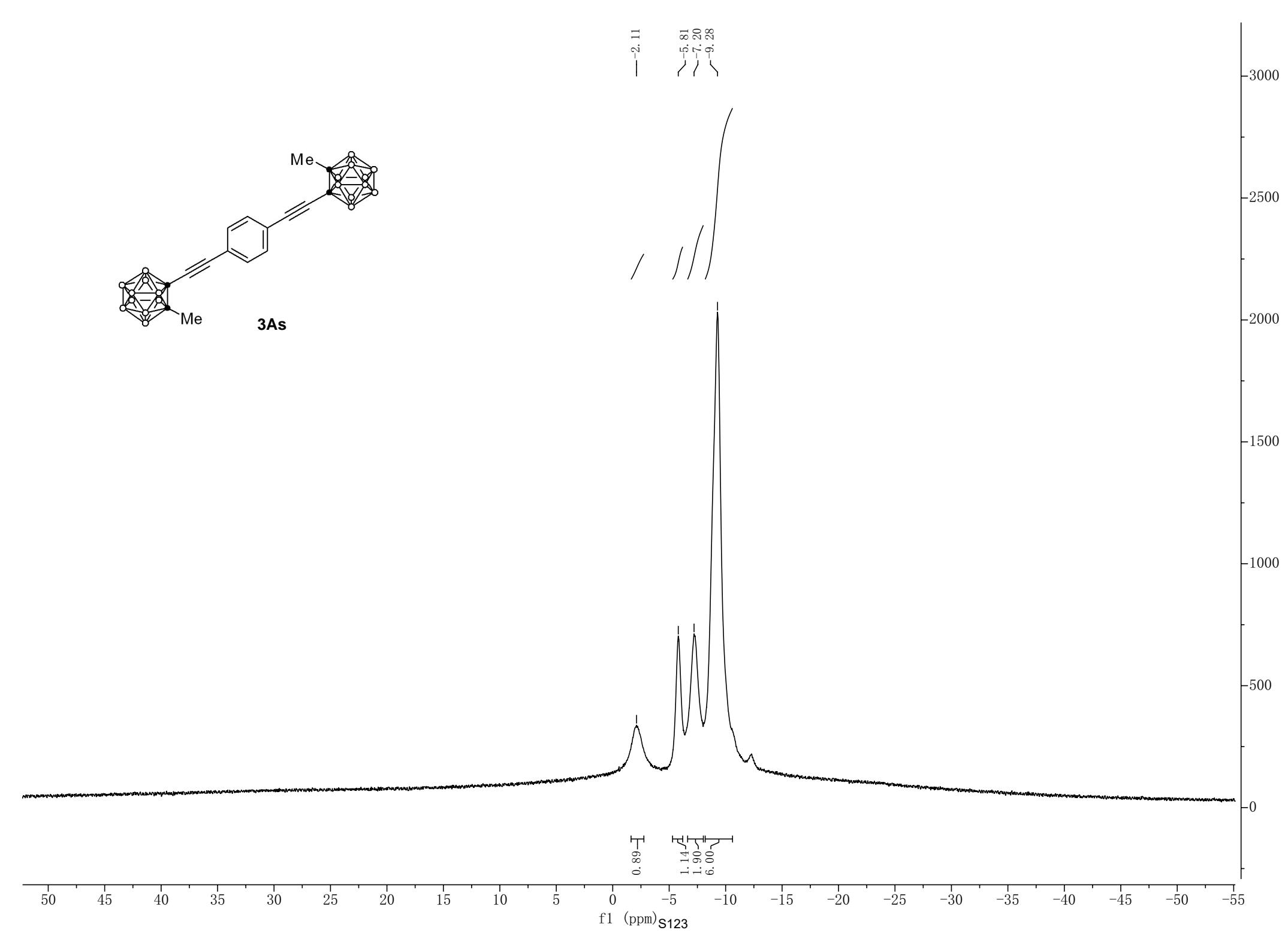
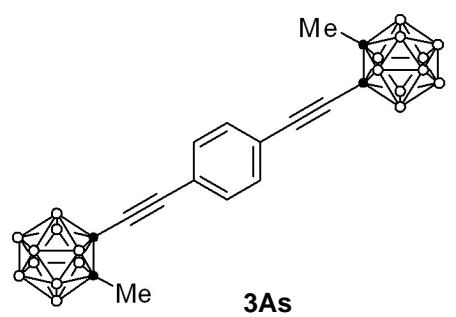


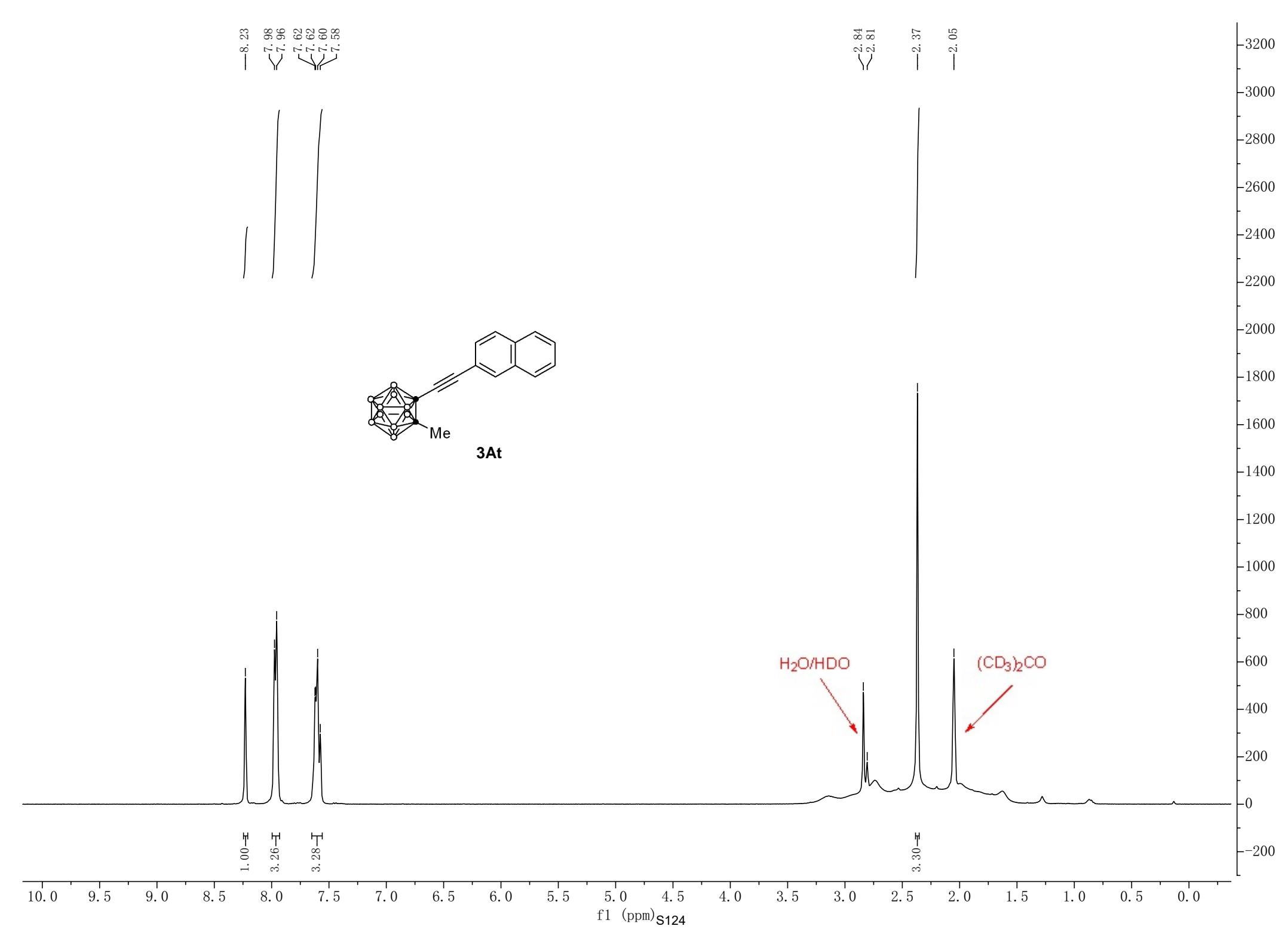
3Ar

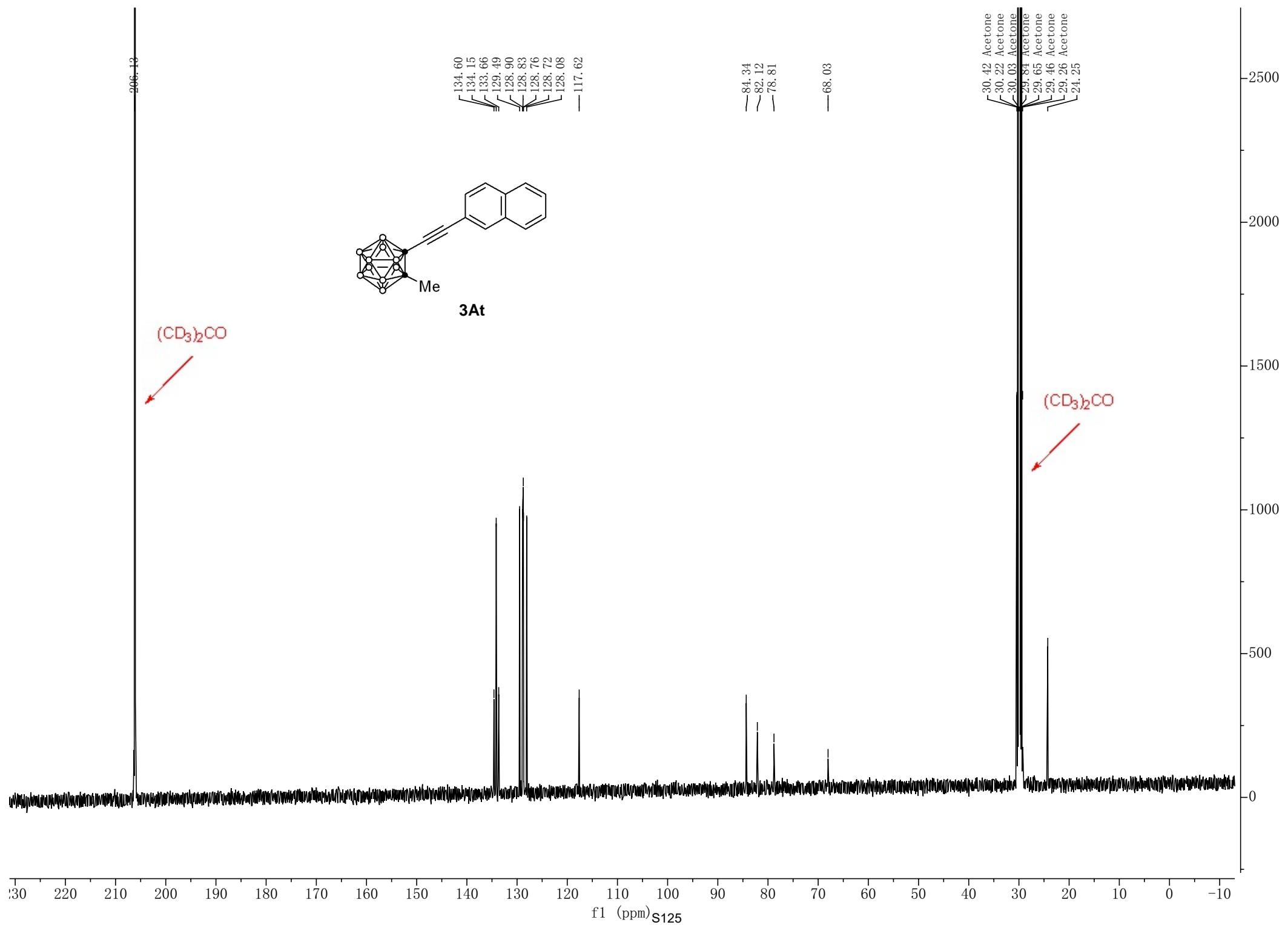


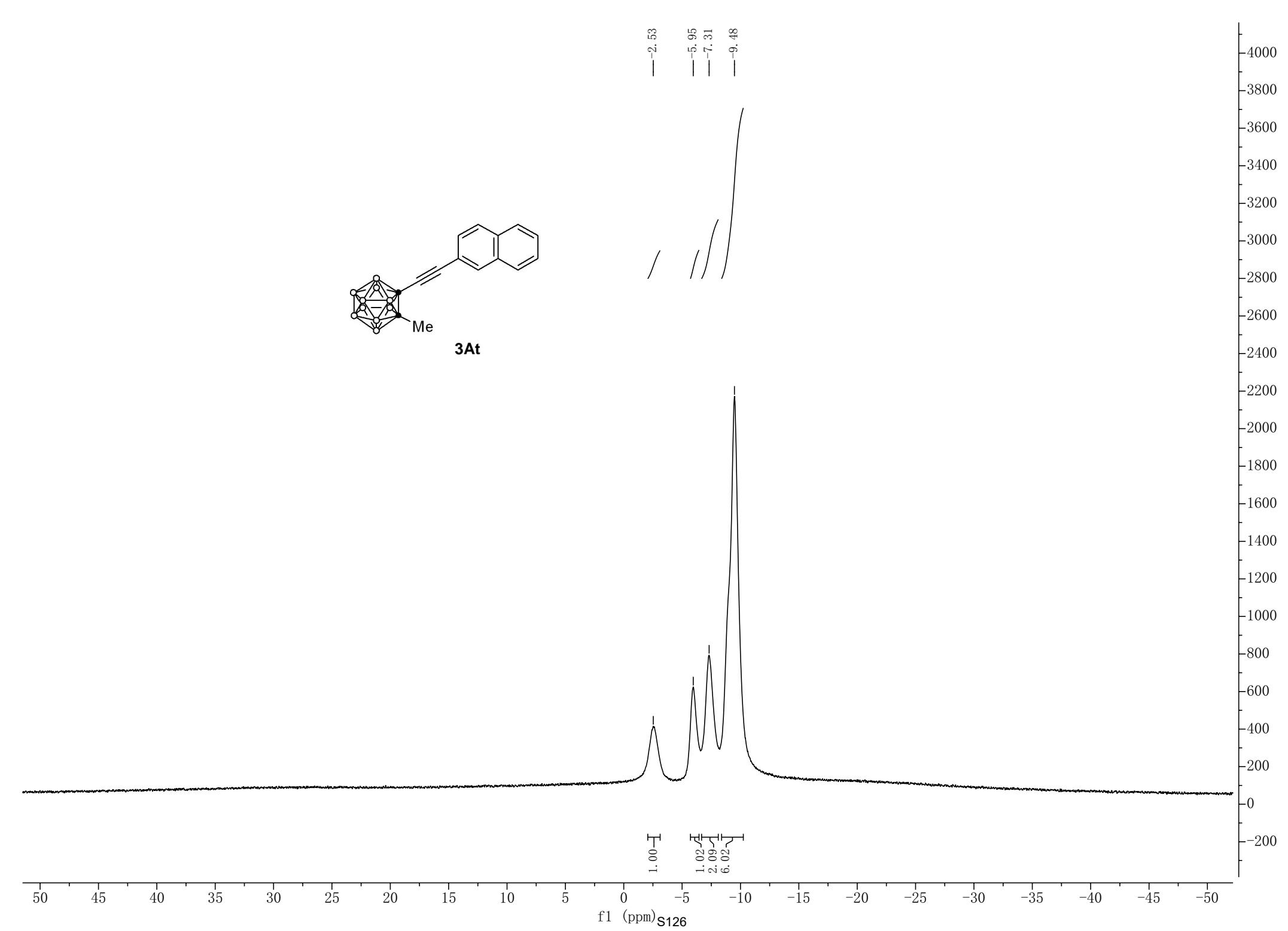
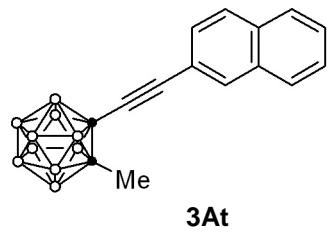


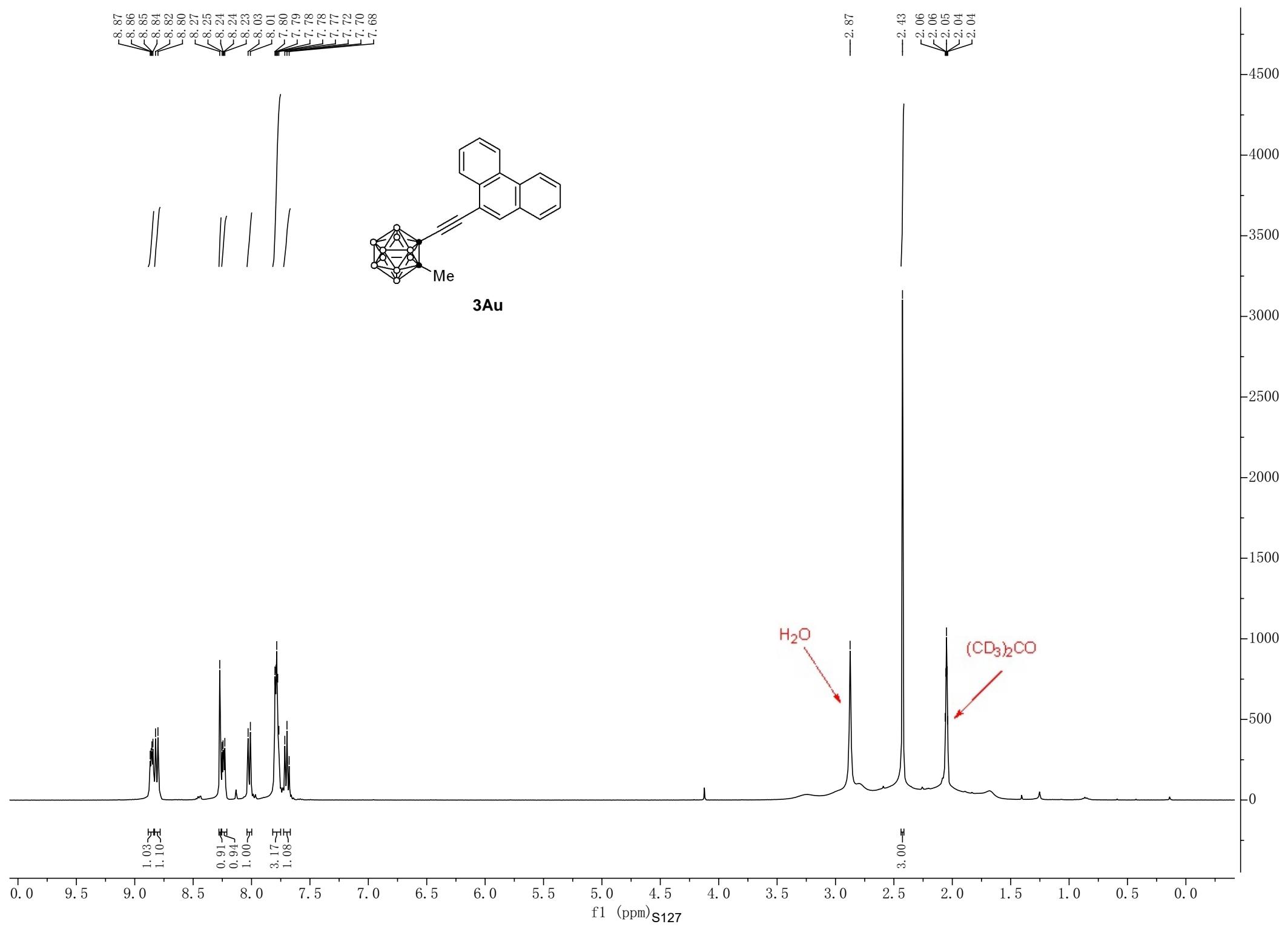




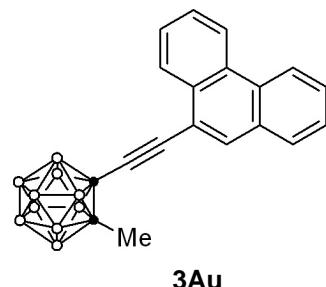








206.29



135.47
131.74
131.47
131.26
130.92
129.90
129.80
128.73
128.67
128.38
128.23
126.66
123.75
116.58

— 131.74
— 131.47
— 131.26
— 130.92

— 129.90
— 129.80
— 128.73
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— 128.38

— 123.75
— 122.48
— 78.82

— 126.66
— 124.23
— 123.75

— 68.08

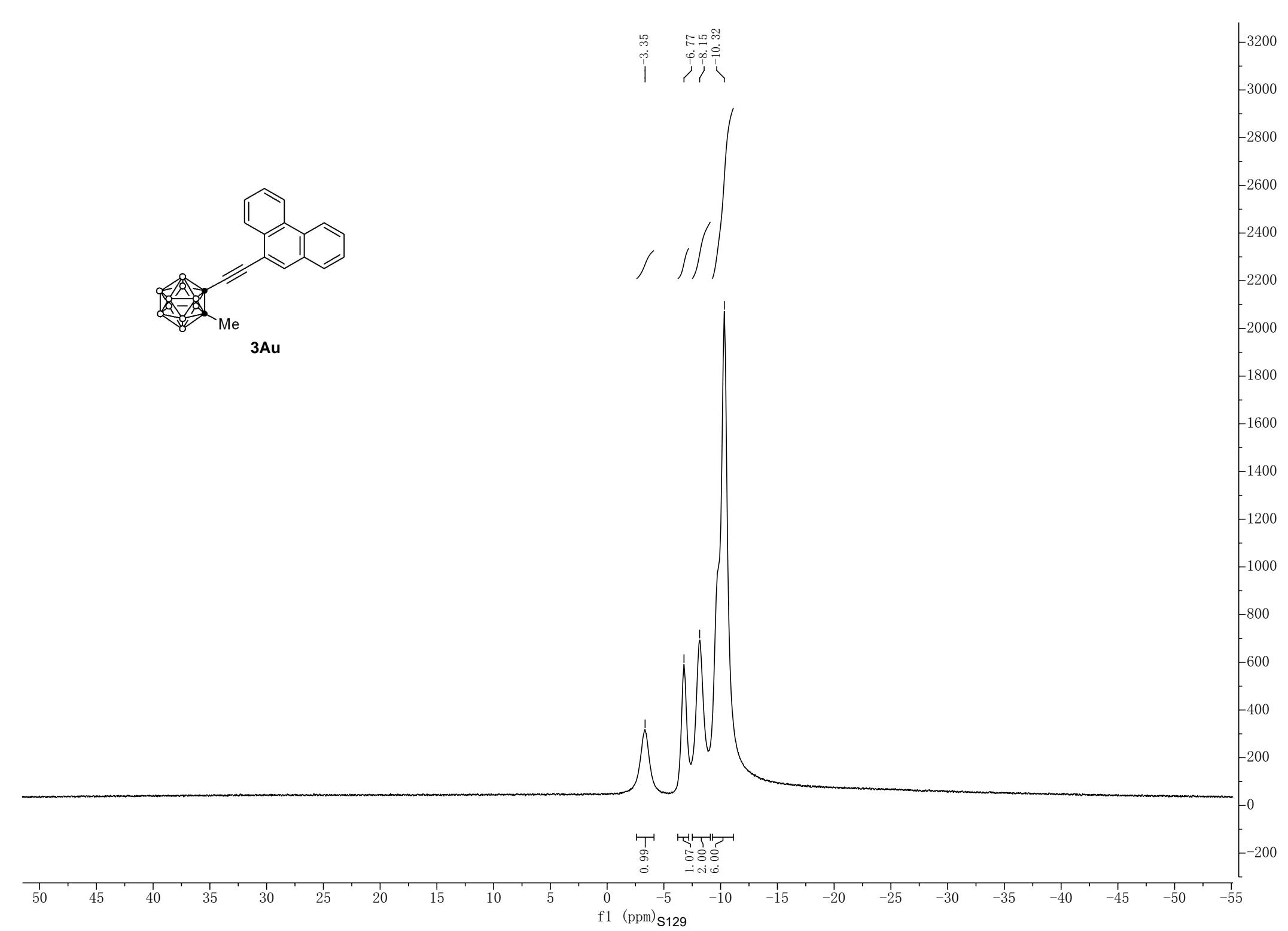
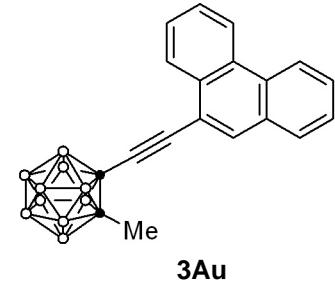
30.42 Acetone
30.22 Acetone
30.03 Acetone
29.84 Acetone
29.65 Acetone
29.46 Acetone
29.26 Acetone
24.40

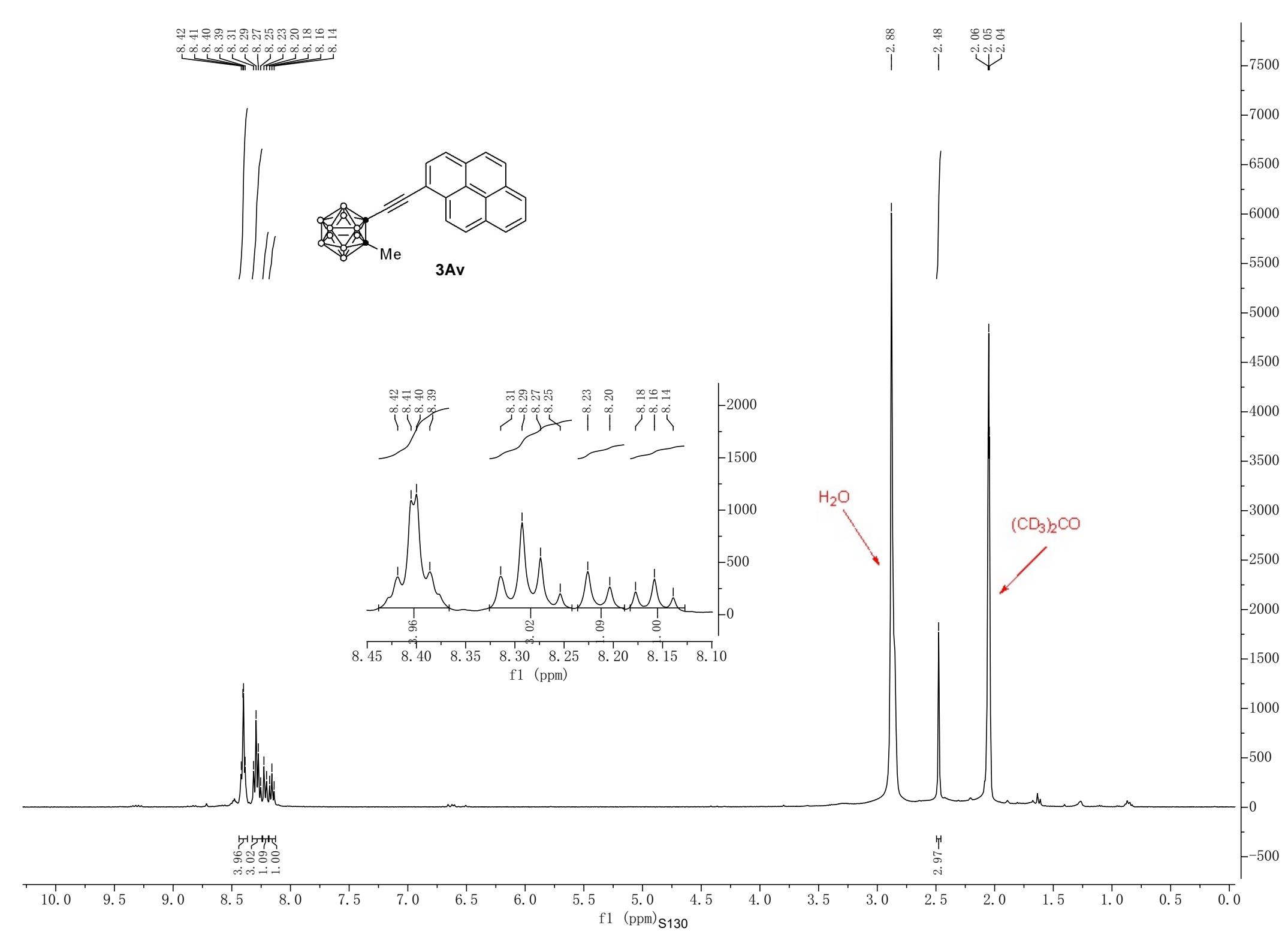
(CD₃)₂CO(CD₃)₂CO

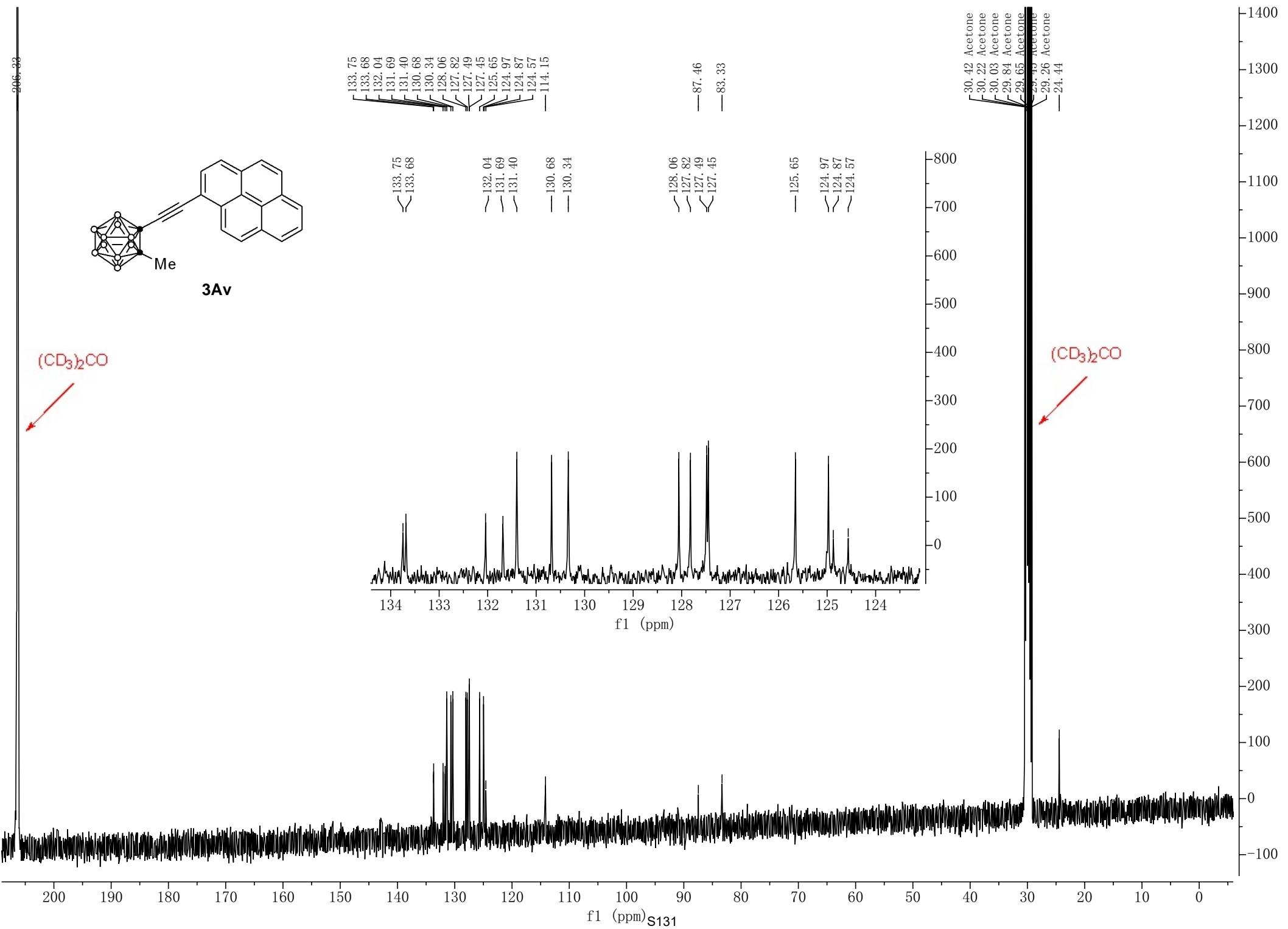
132 131 130 129 128 127 126 125 124 f1 (ppm)

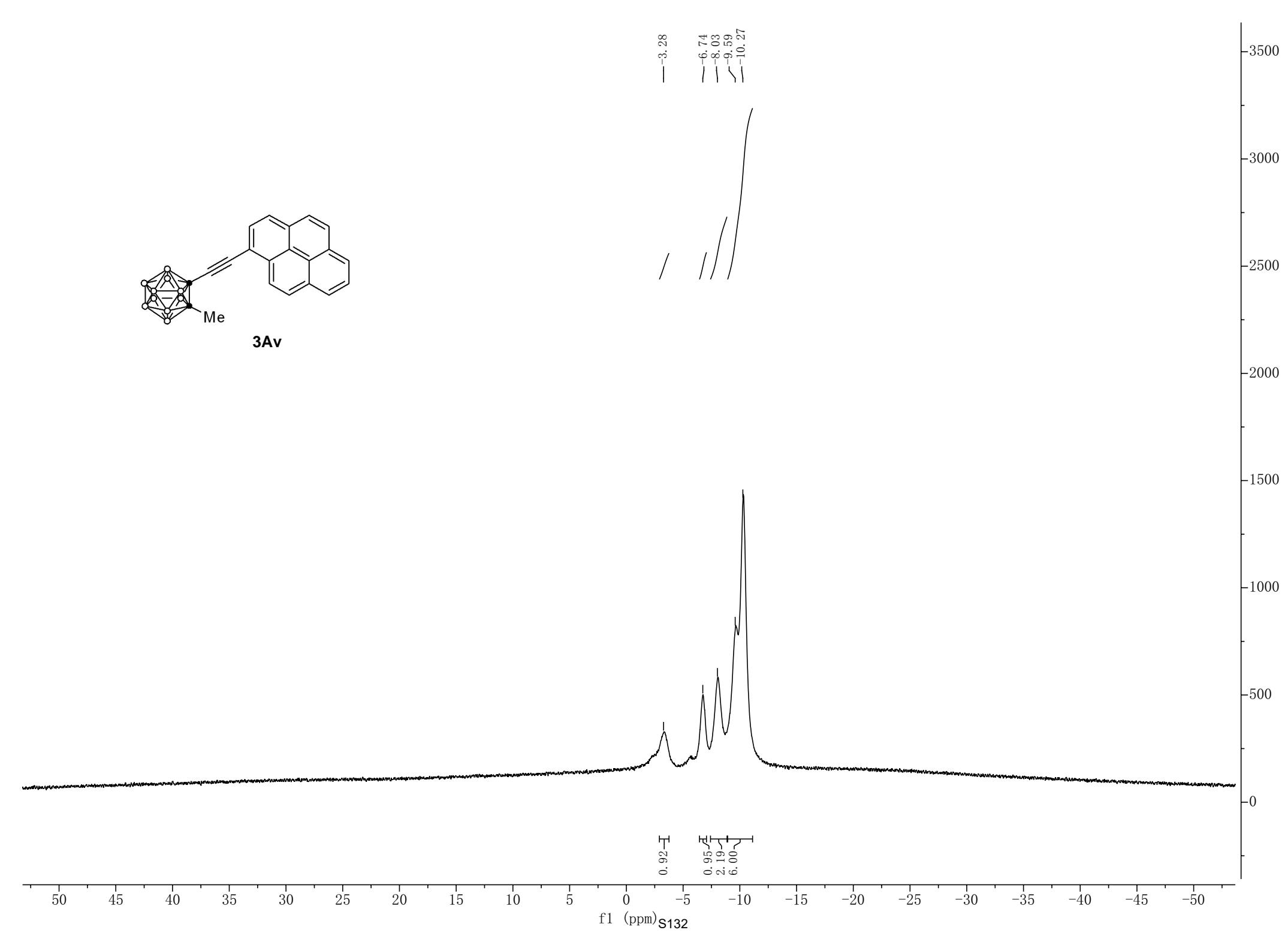
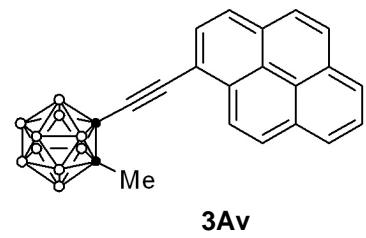
f1 (ppm) S₁₂₈

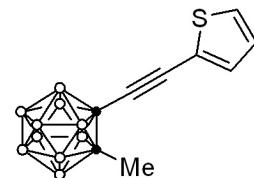
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



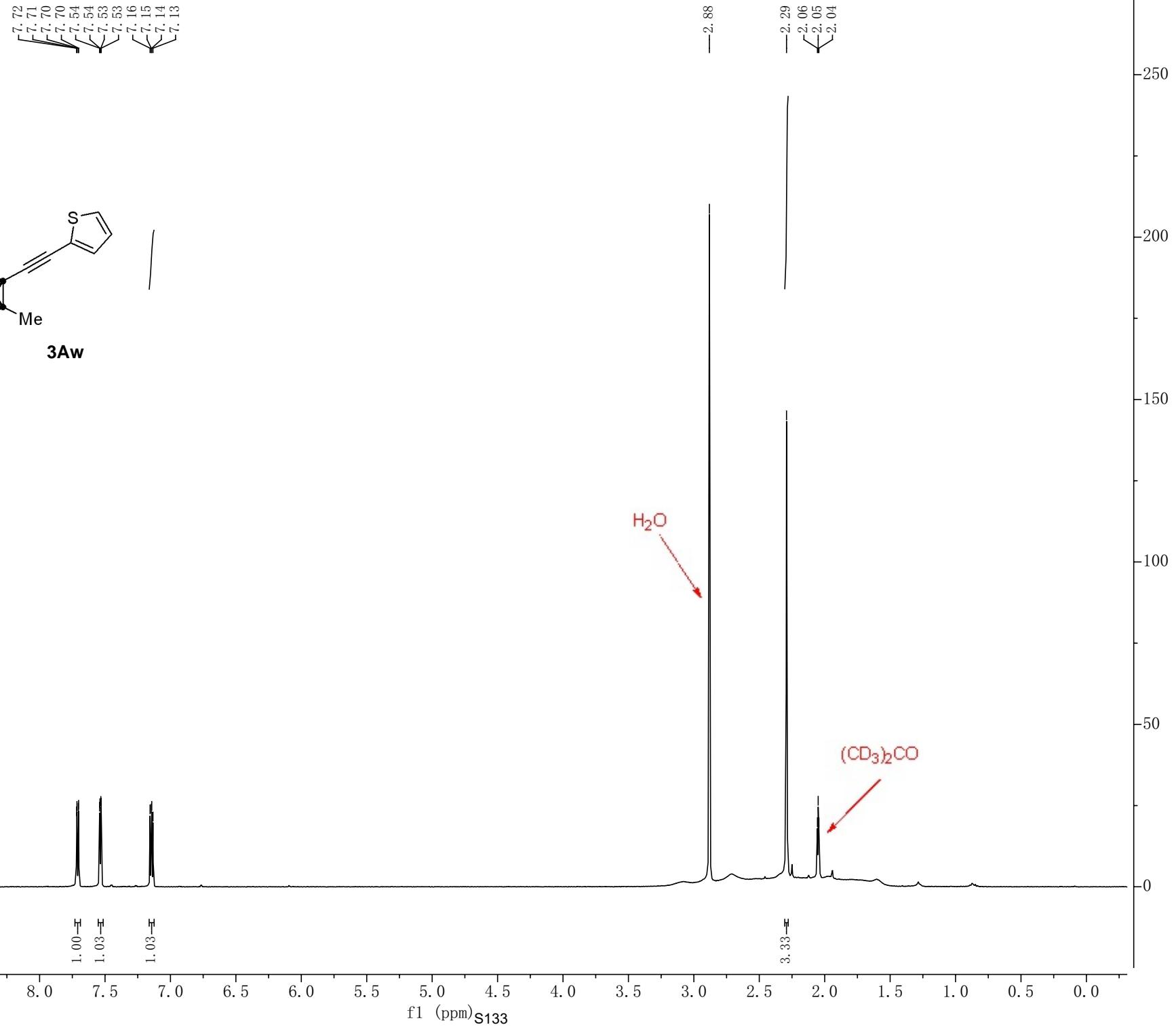




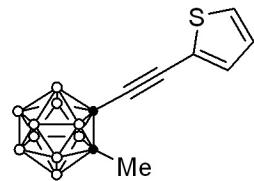




3Aw



206.20

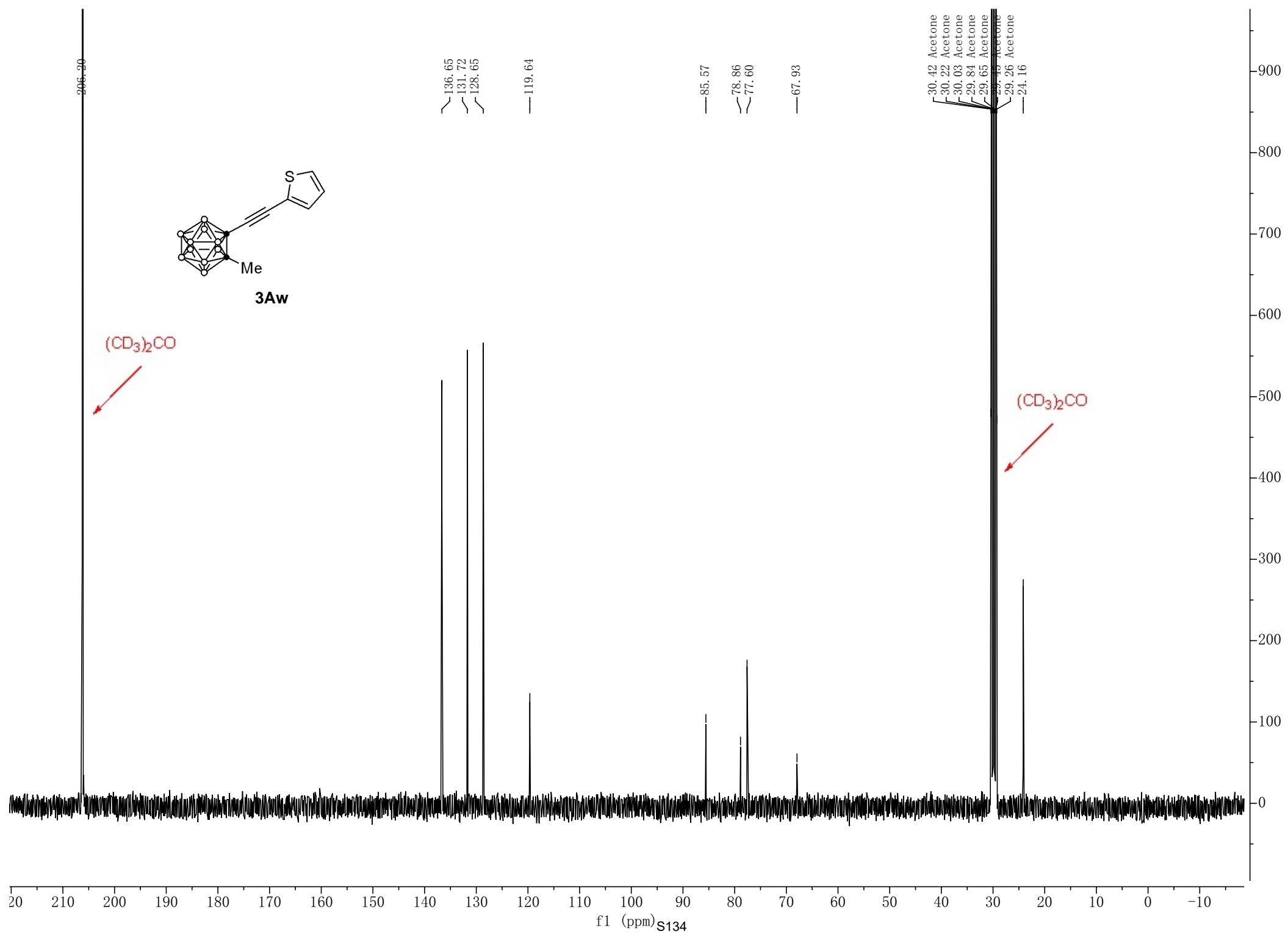
**3Aw** ~ 136.65
 ~ 131.72
 ~ 128.65

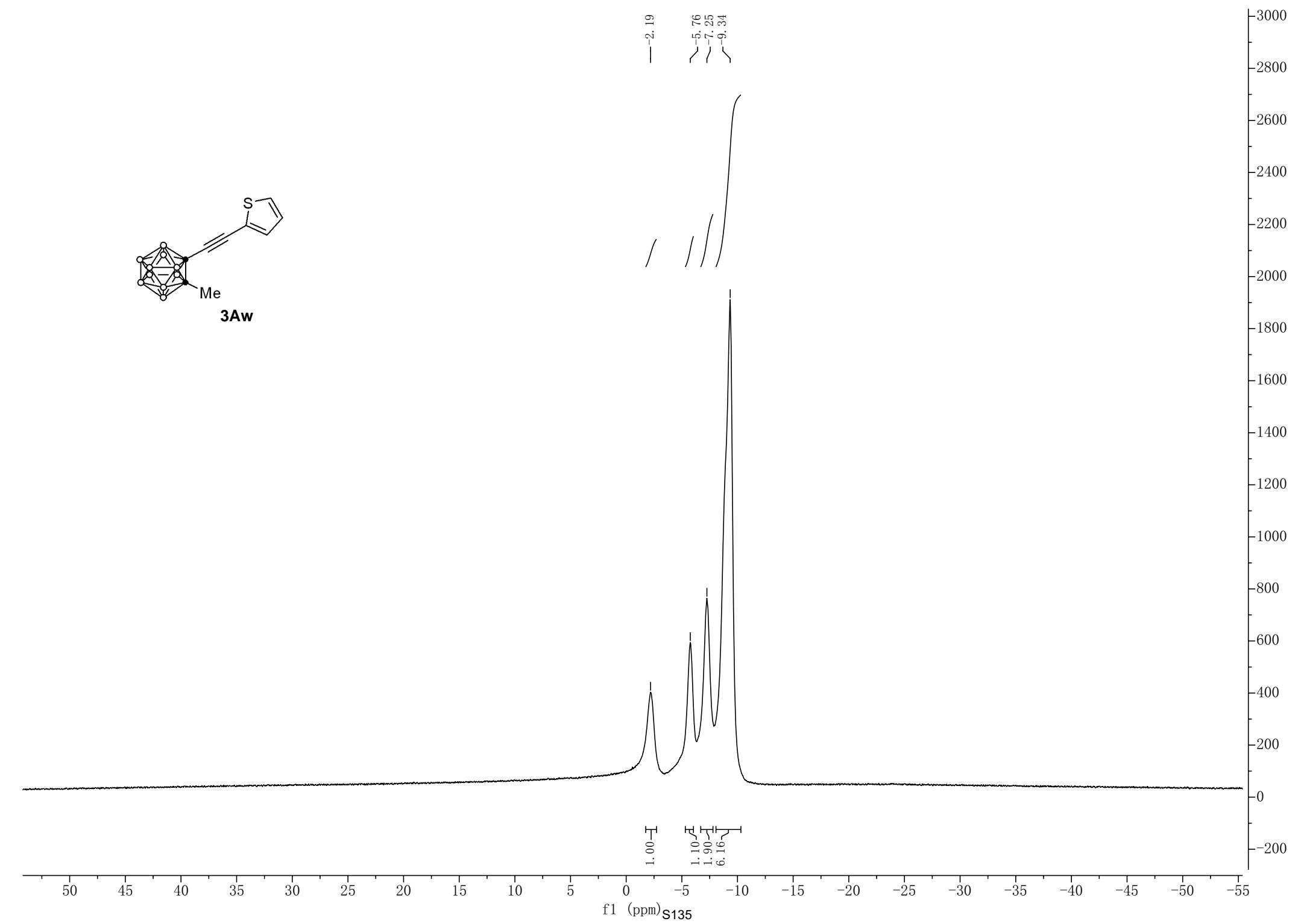
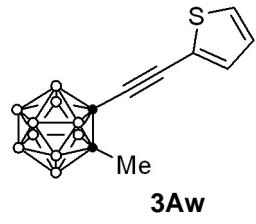
— 119.64

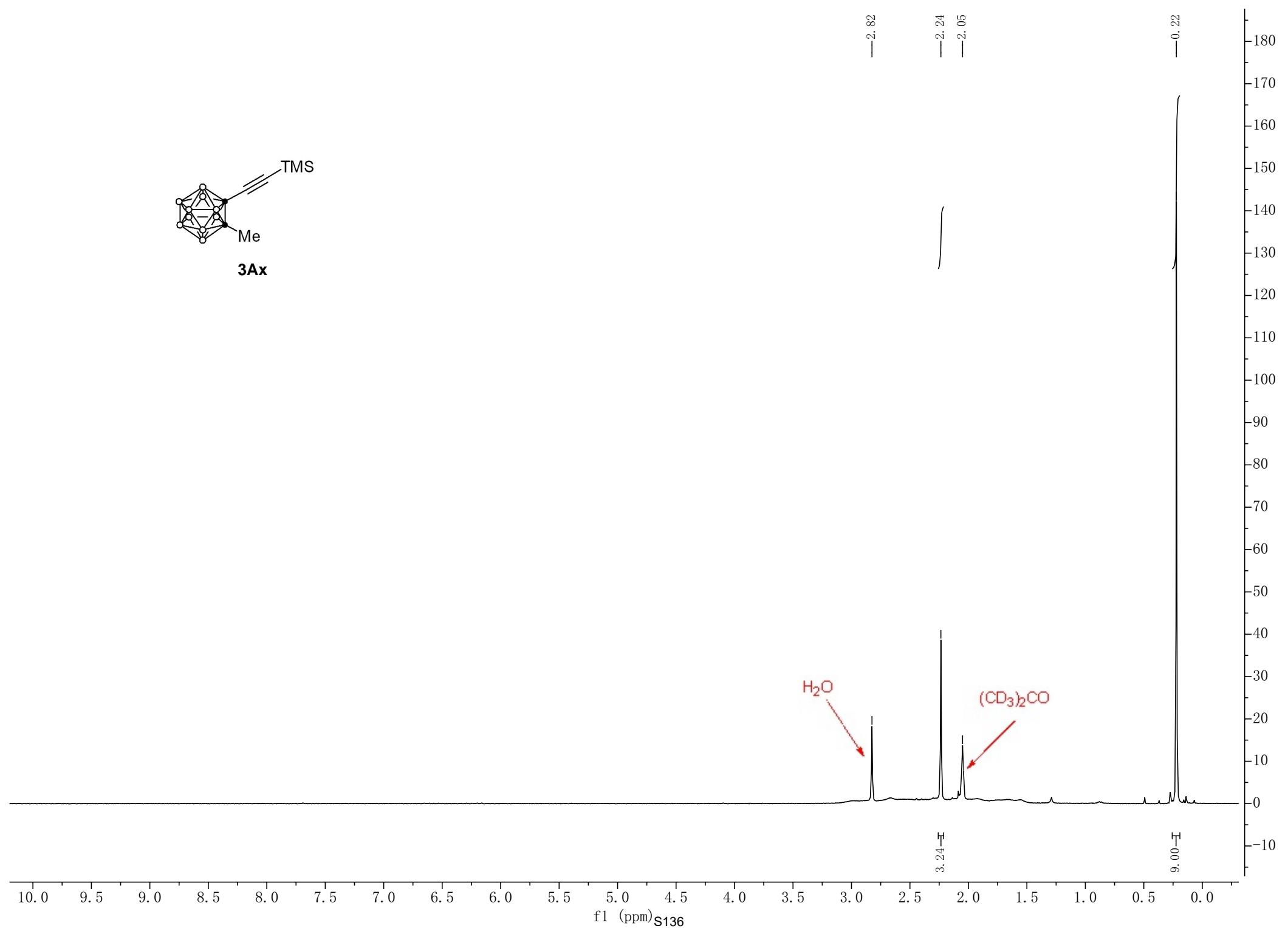
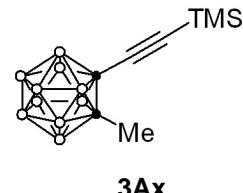
— 85.57

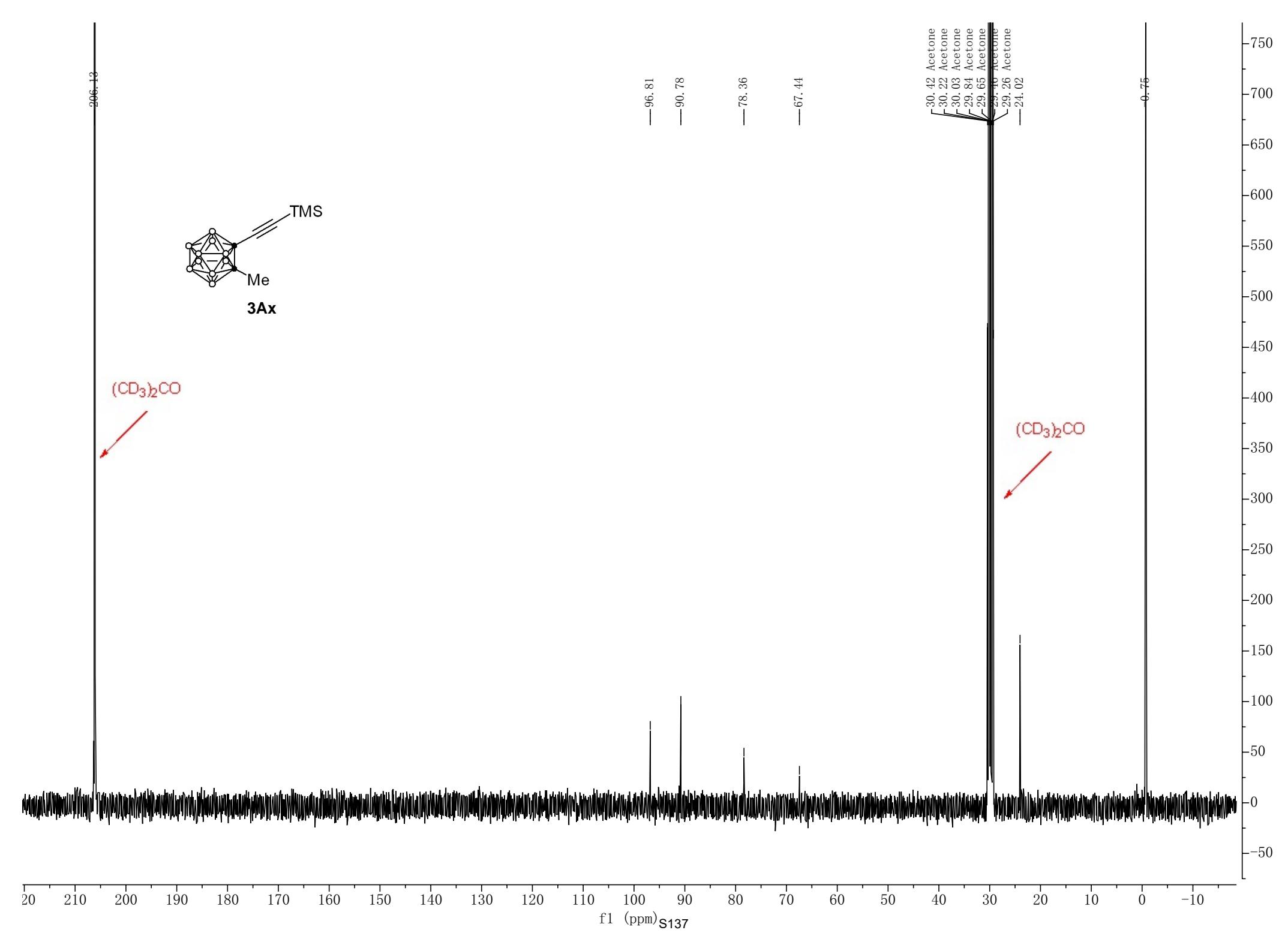
 ~ 78.86
 ~ 77.60

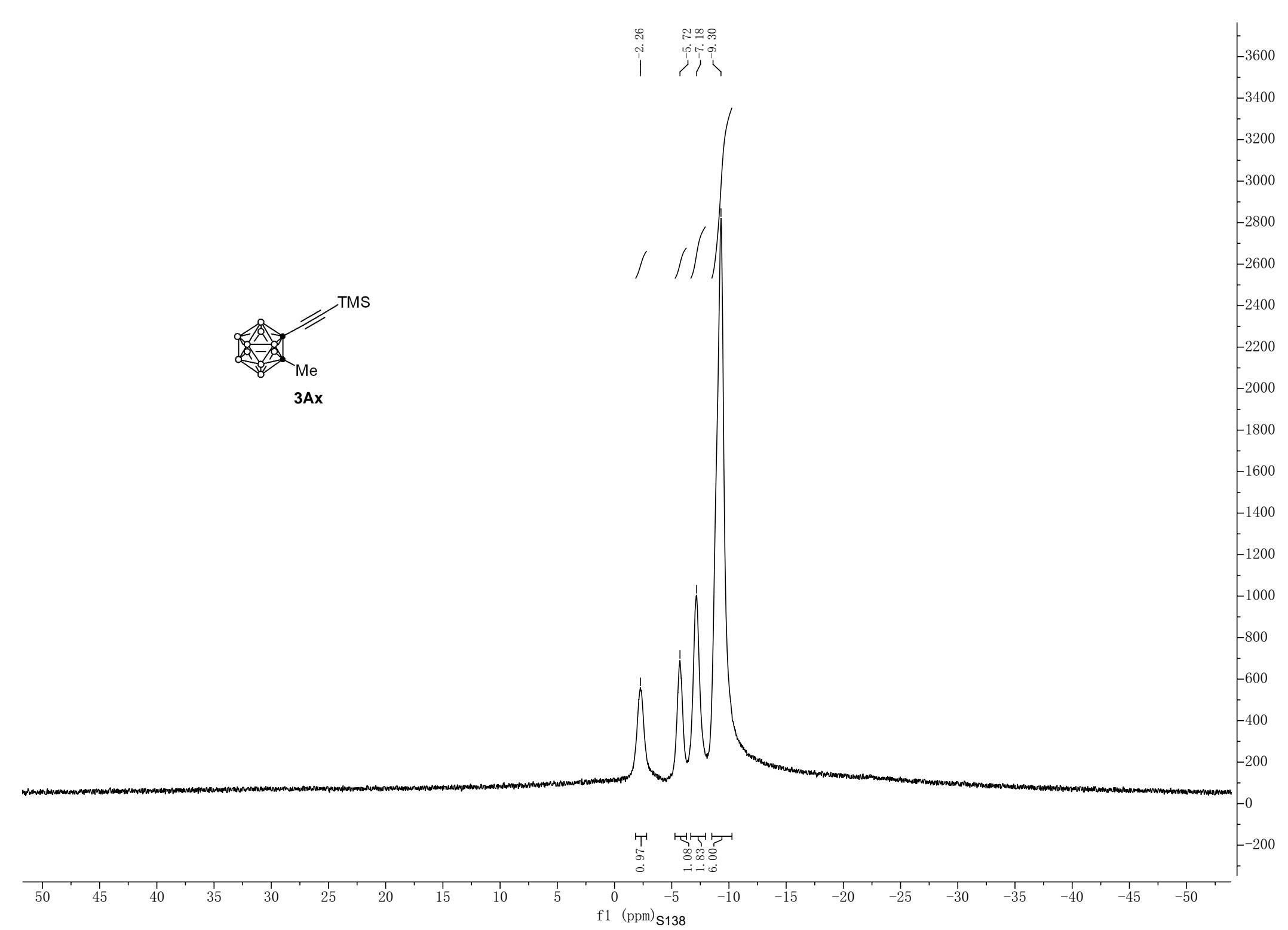
— 67.93

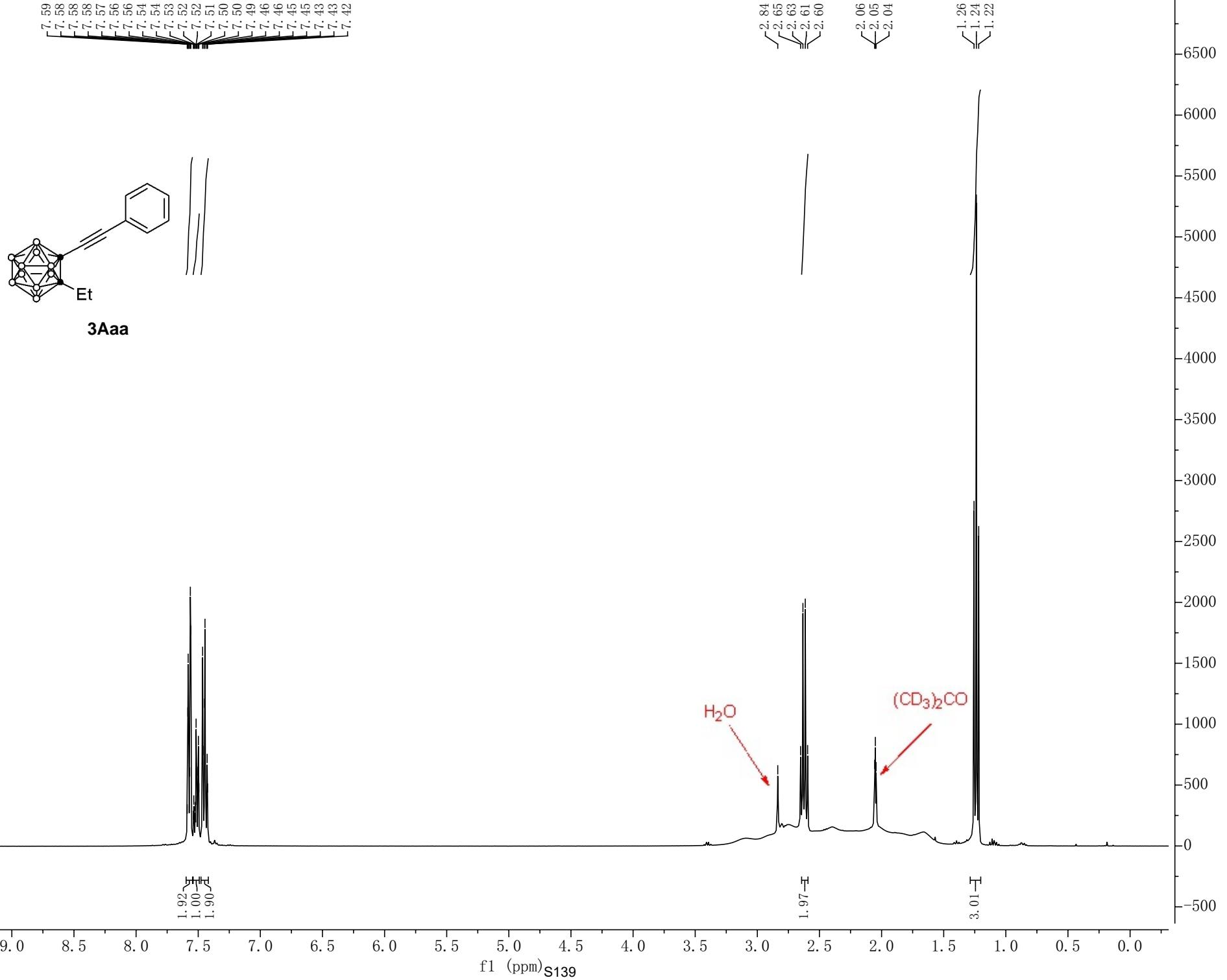
 $\begin{array}{ll} 30.42 & \text{Acetone} \\ 30.22 & \text{Acetone} \\ 30.03 & \text{Acetone} \\ 29.84 & \text{Acetone} \\ 29.65 & \text{Acetone} \\ 29.49 & \text{Acetone} \\ 29.26 & \text{Acetone} \\ 24.16 & \text{Acetone} \end{array}$ (CD₃)₂CO(CD₃)₂CO

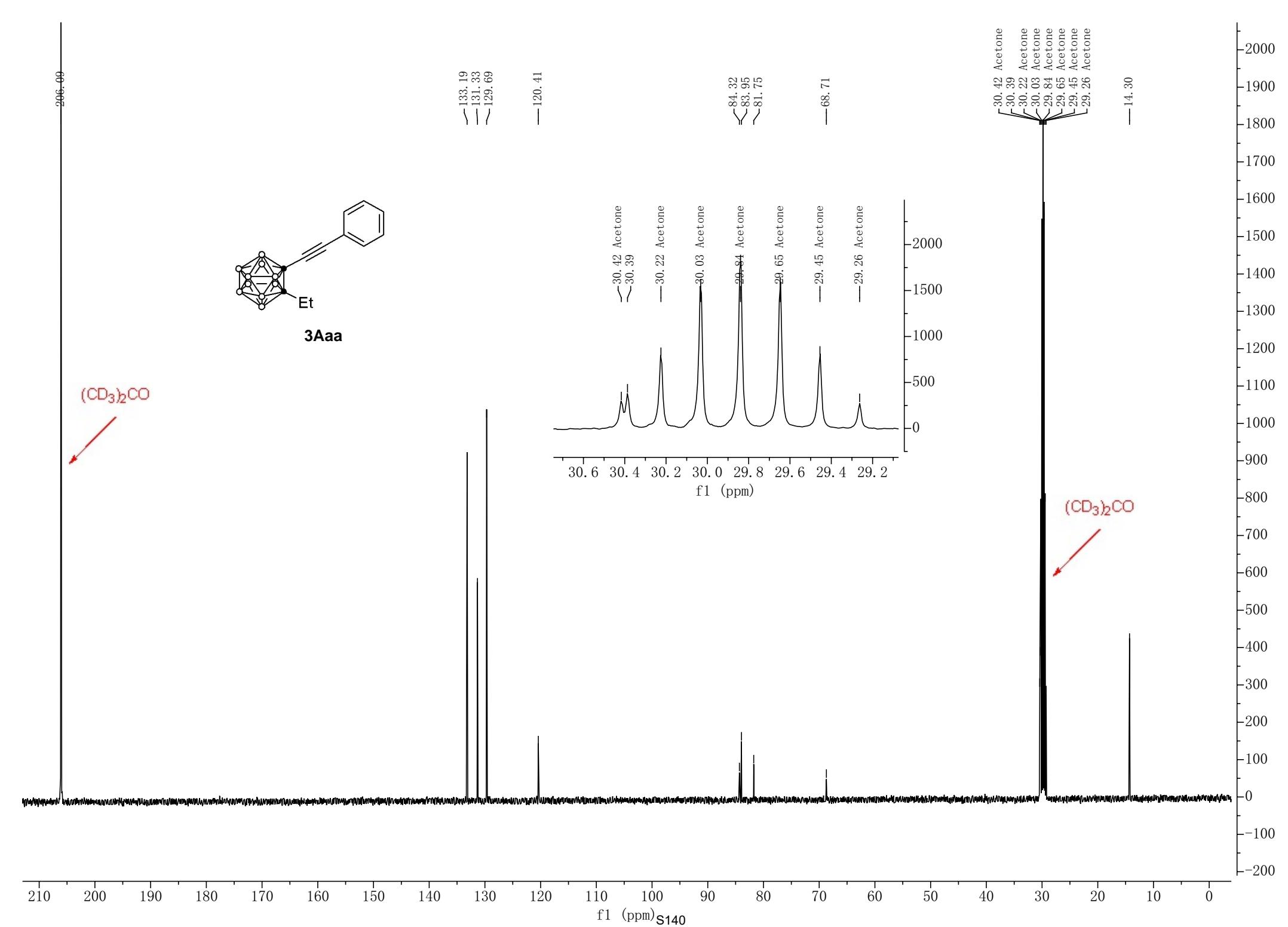


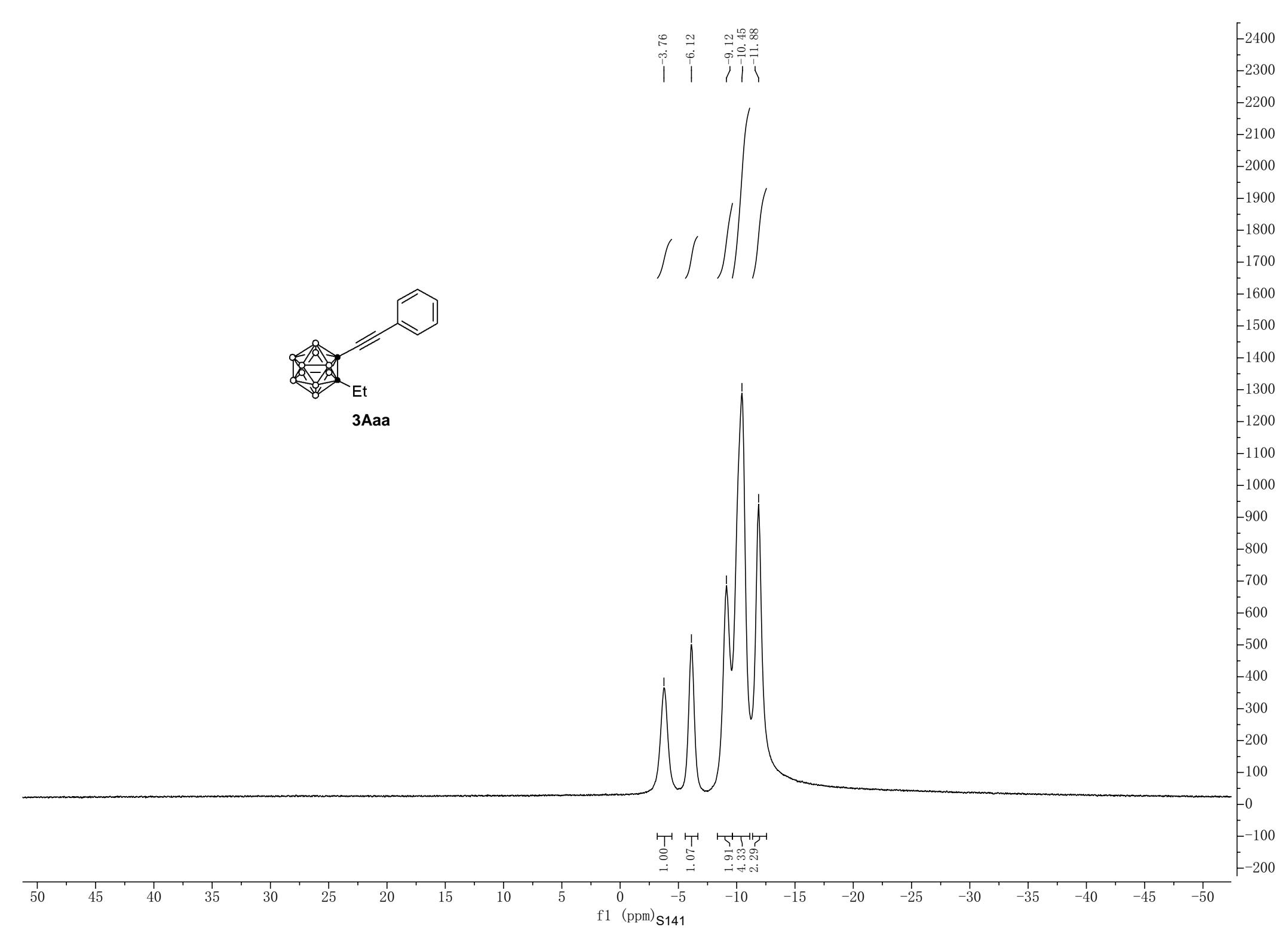


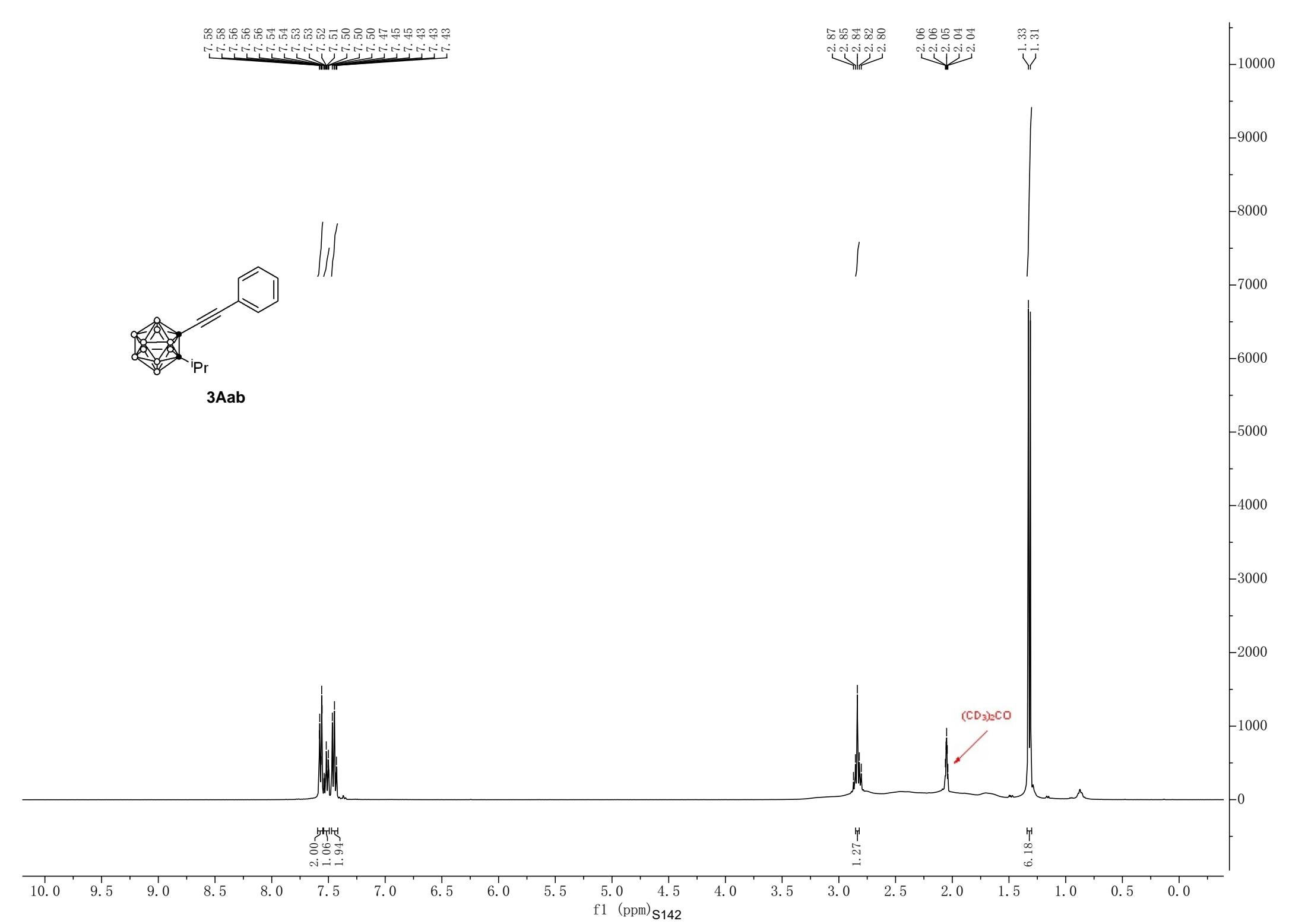


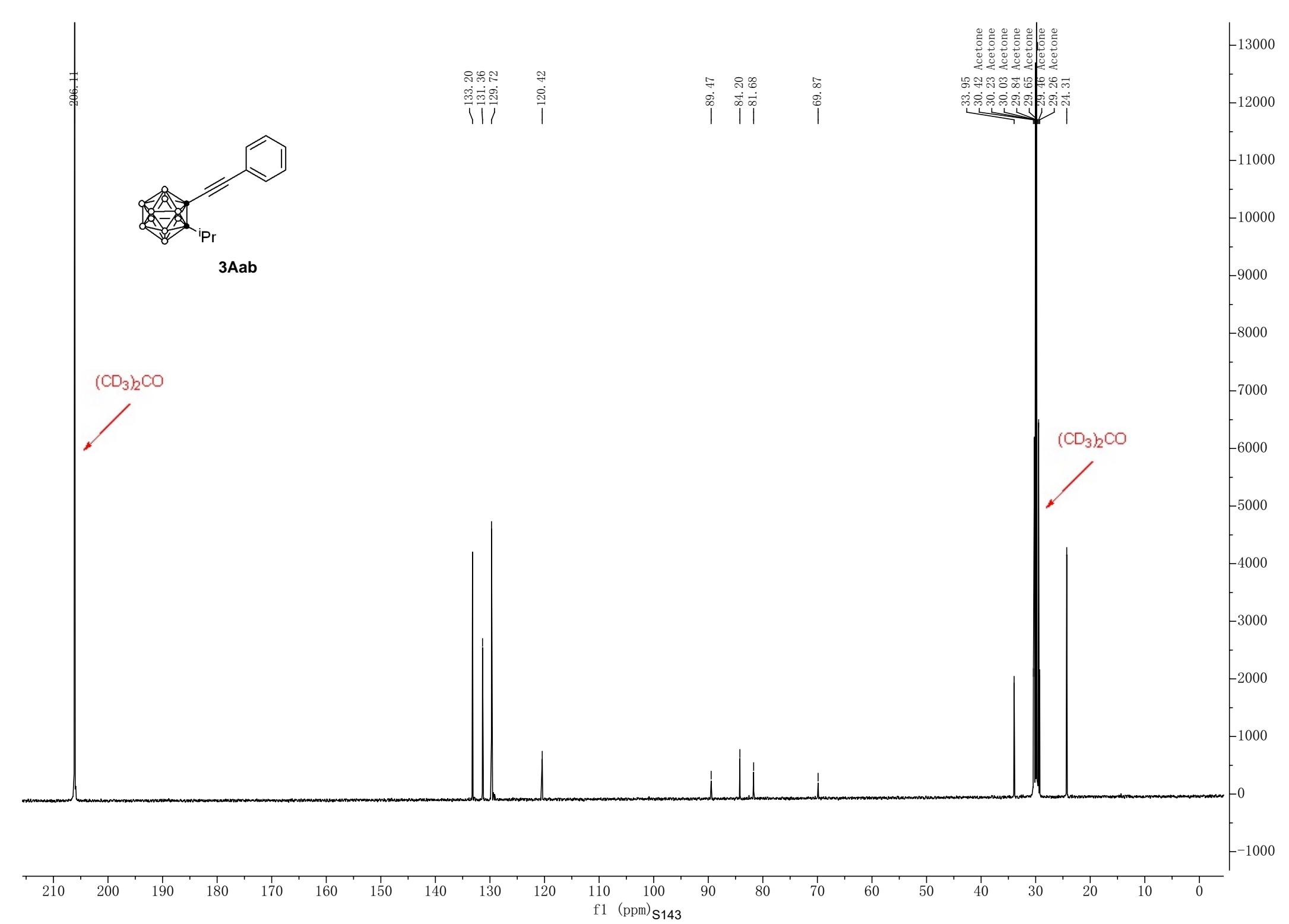


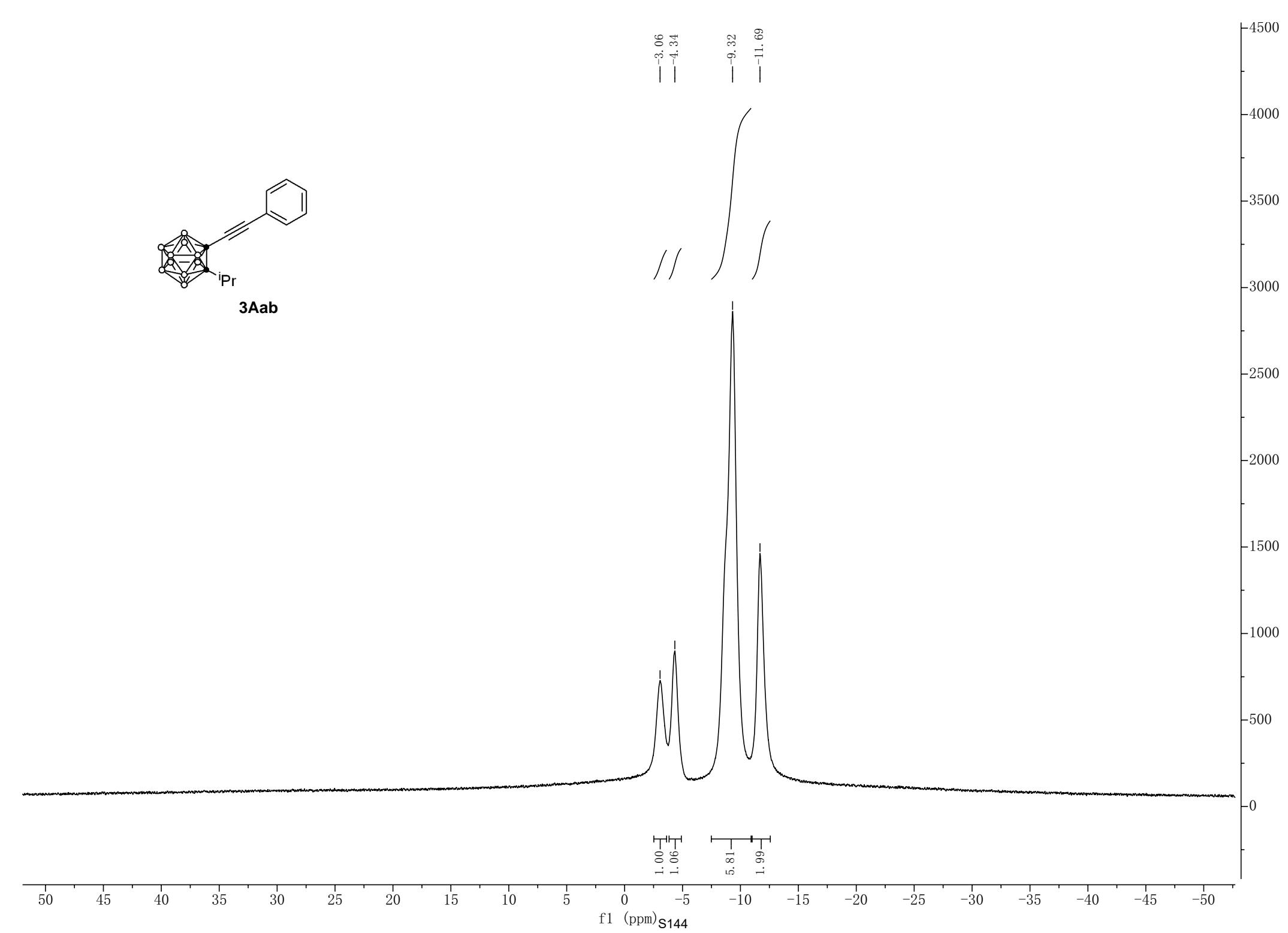
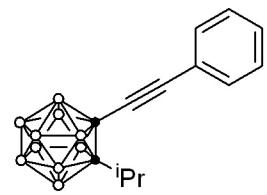


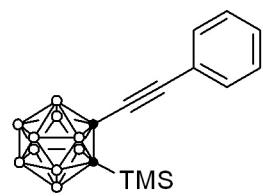












3Aac

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7.47
7.46
7.44

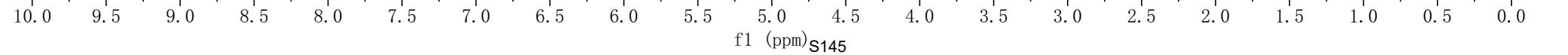
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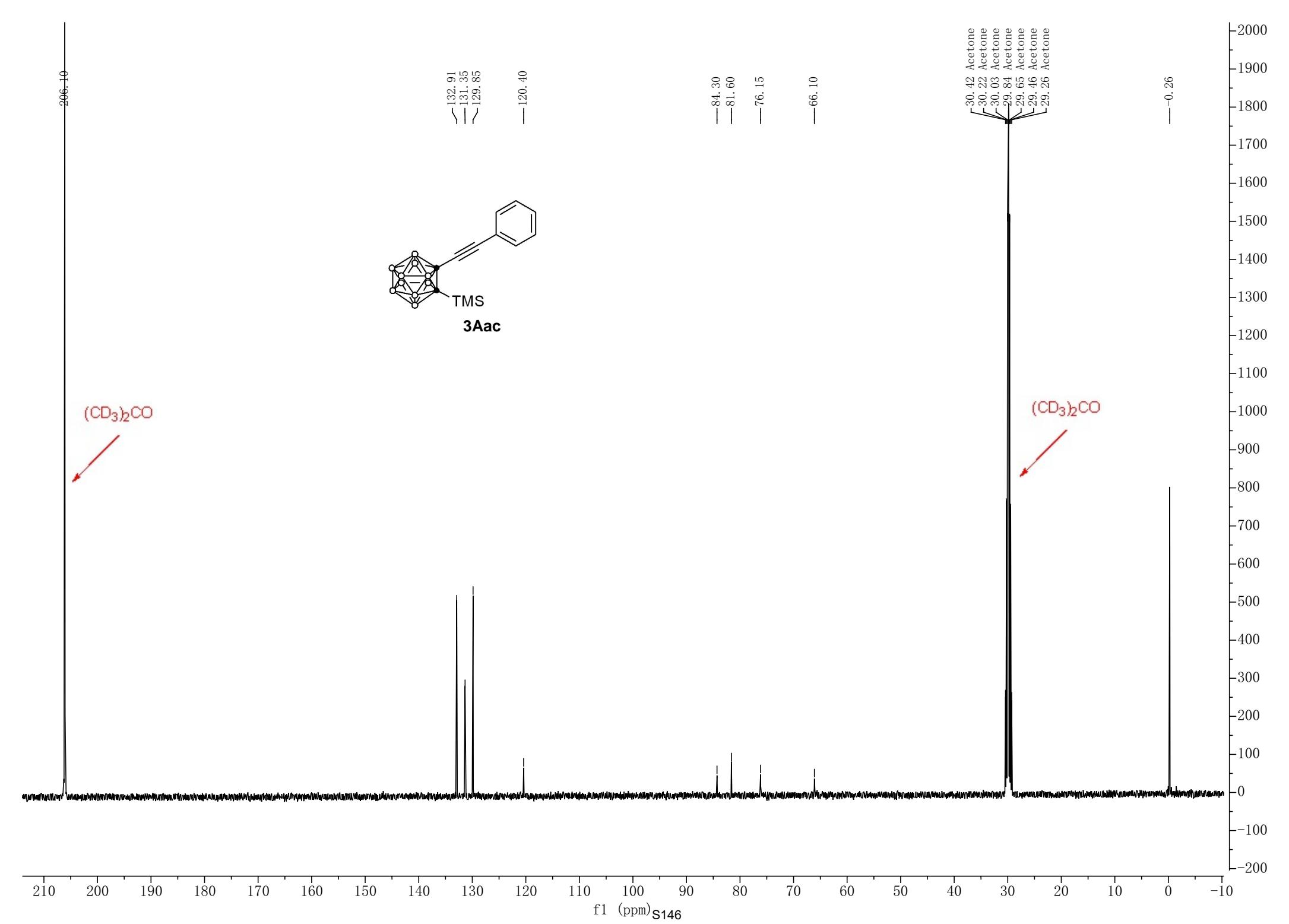
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2.05

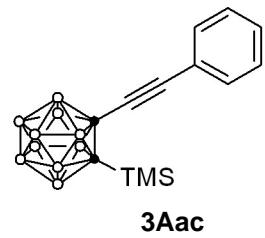
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5.02

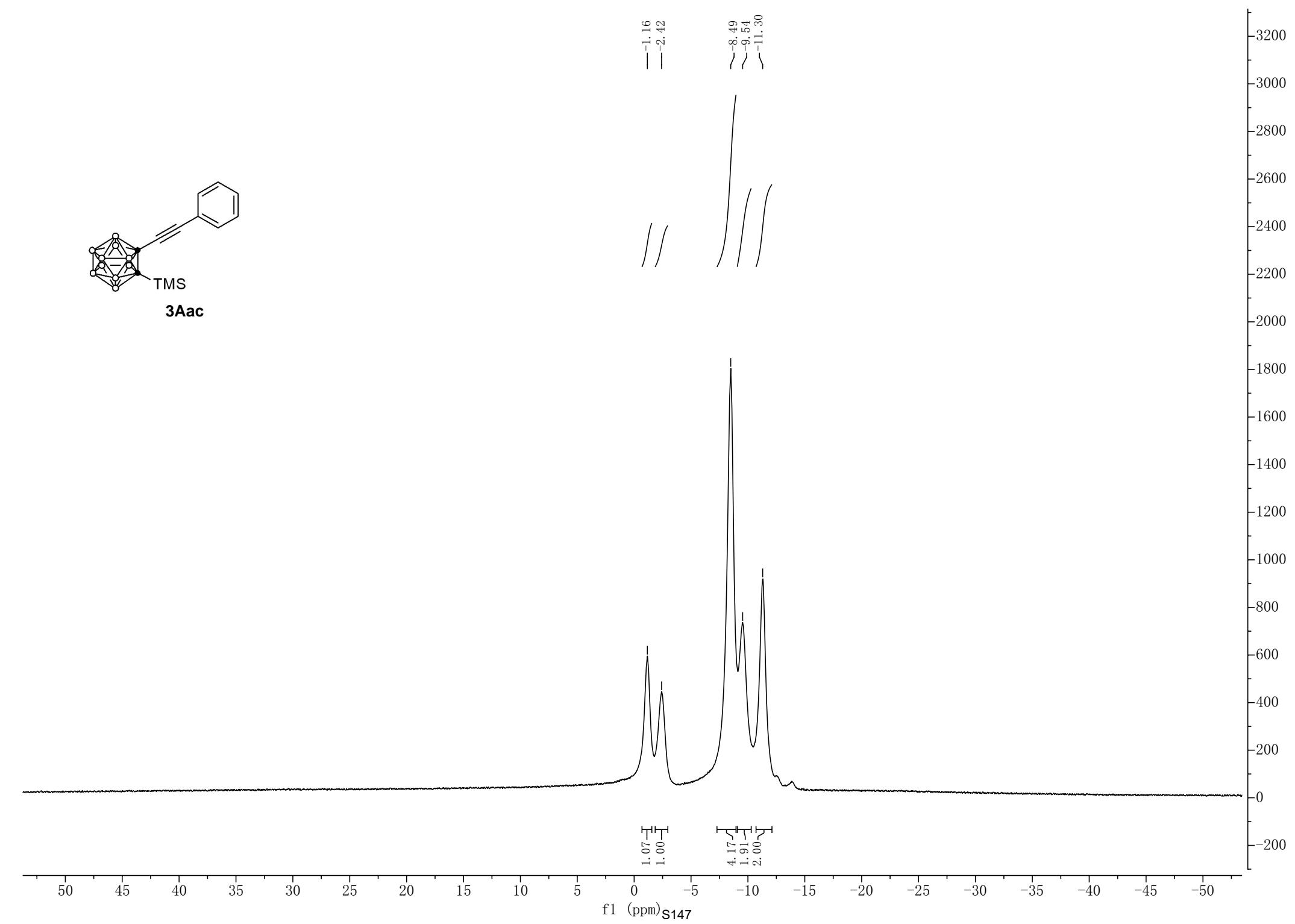
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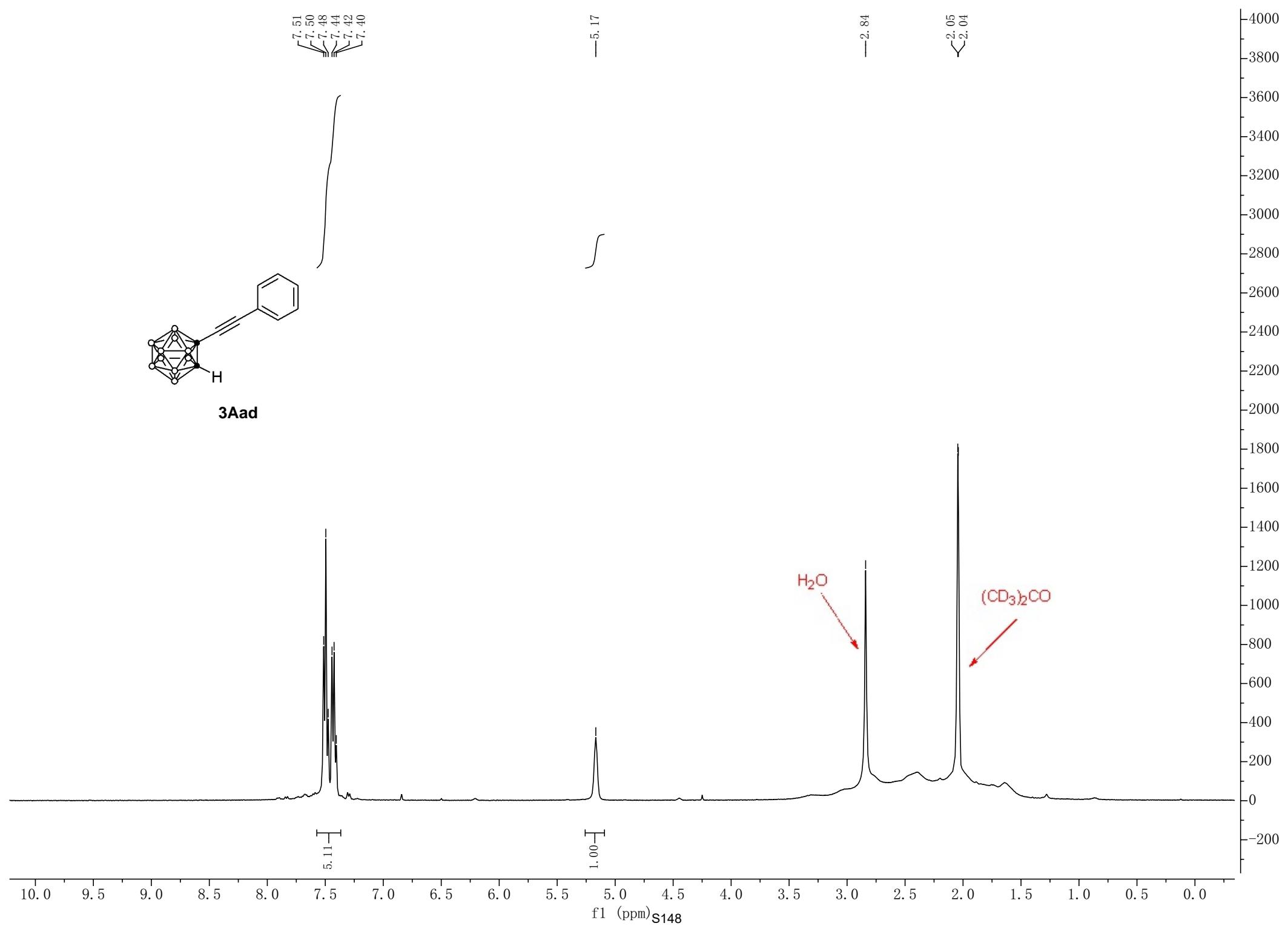
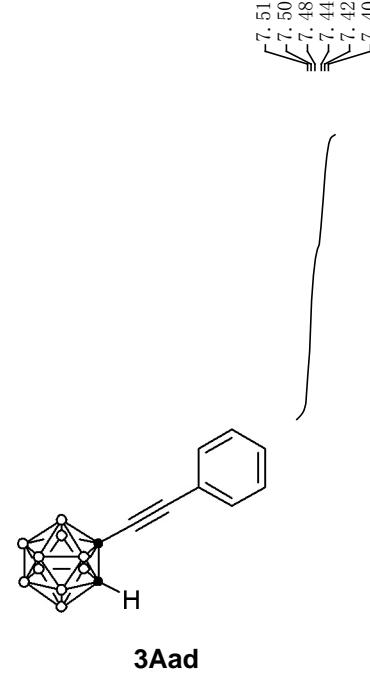


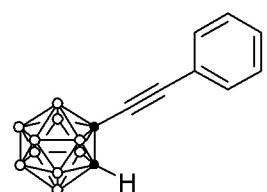




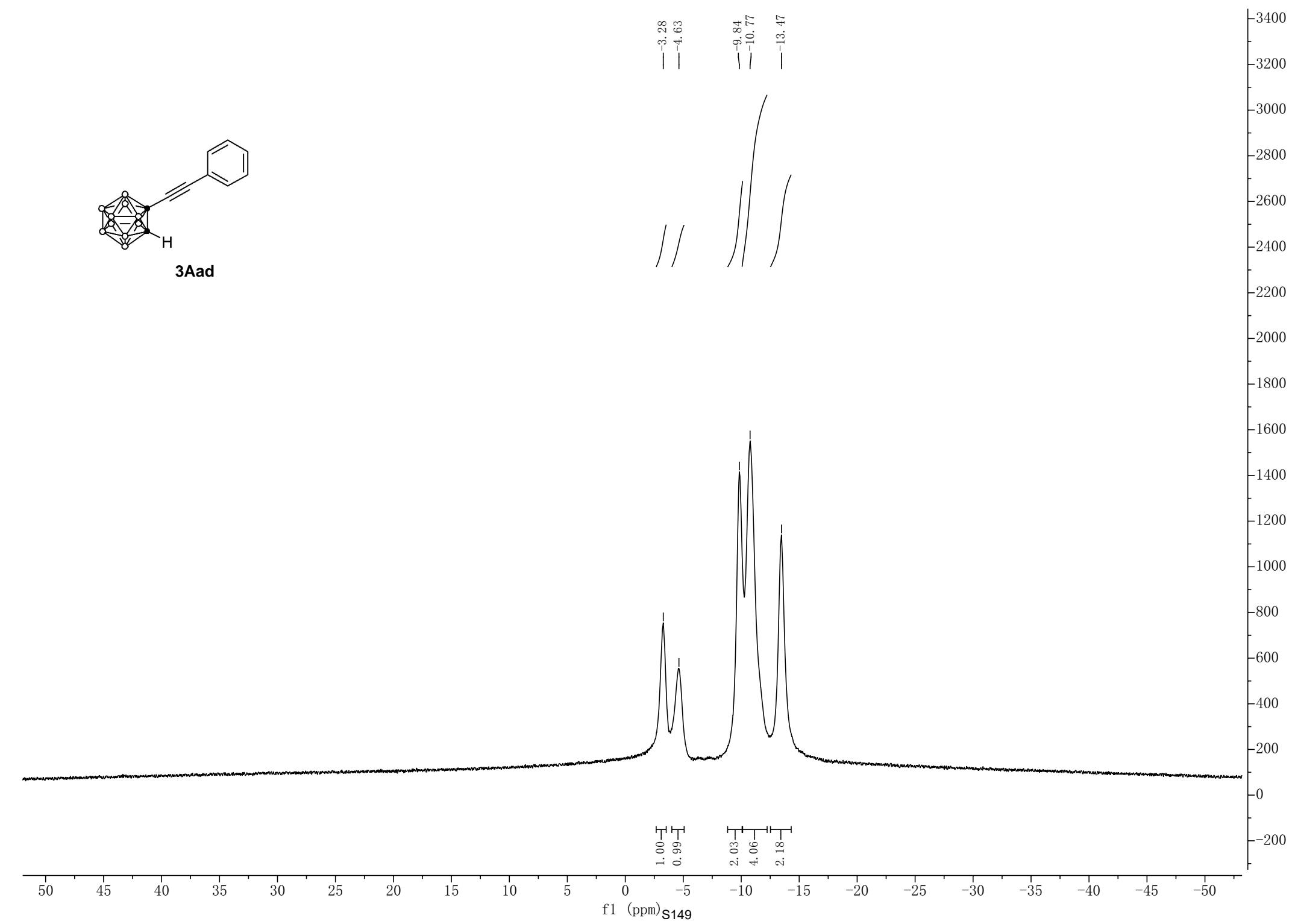
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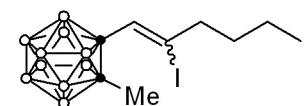




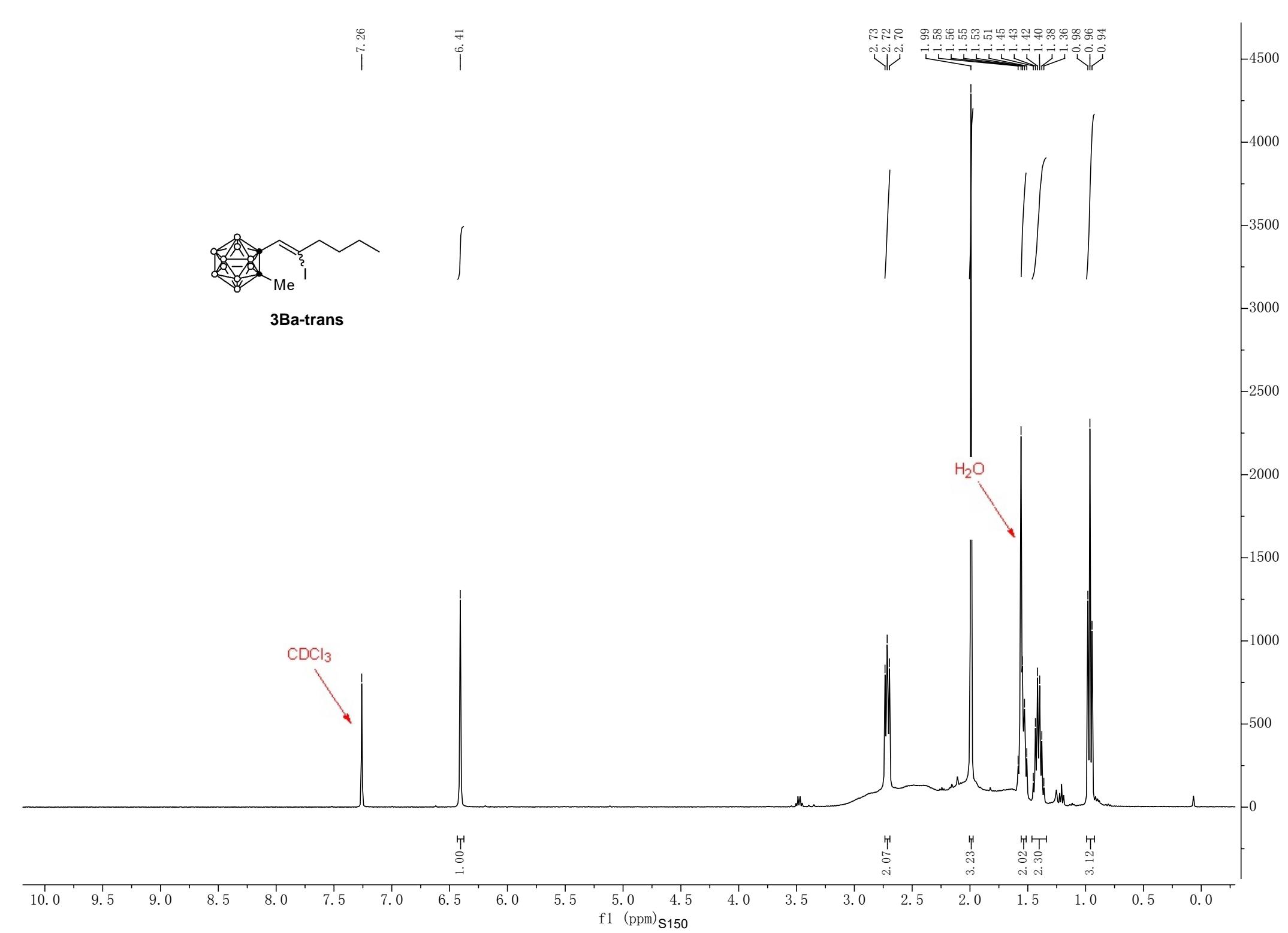


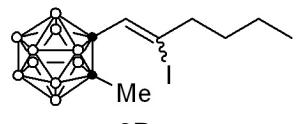
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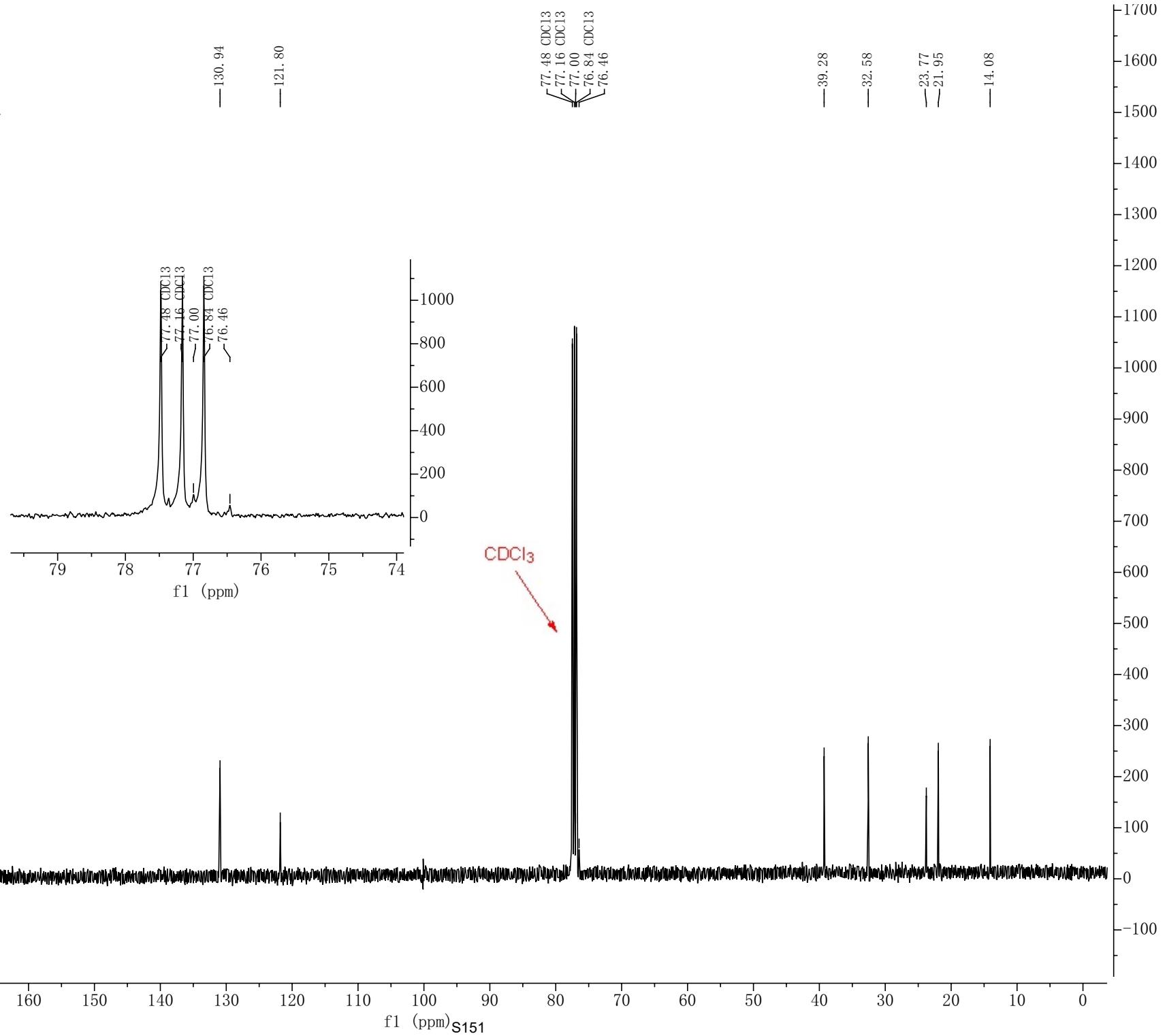


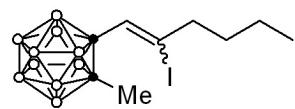
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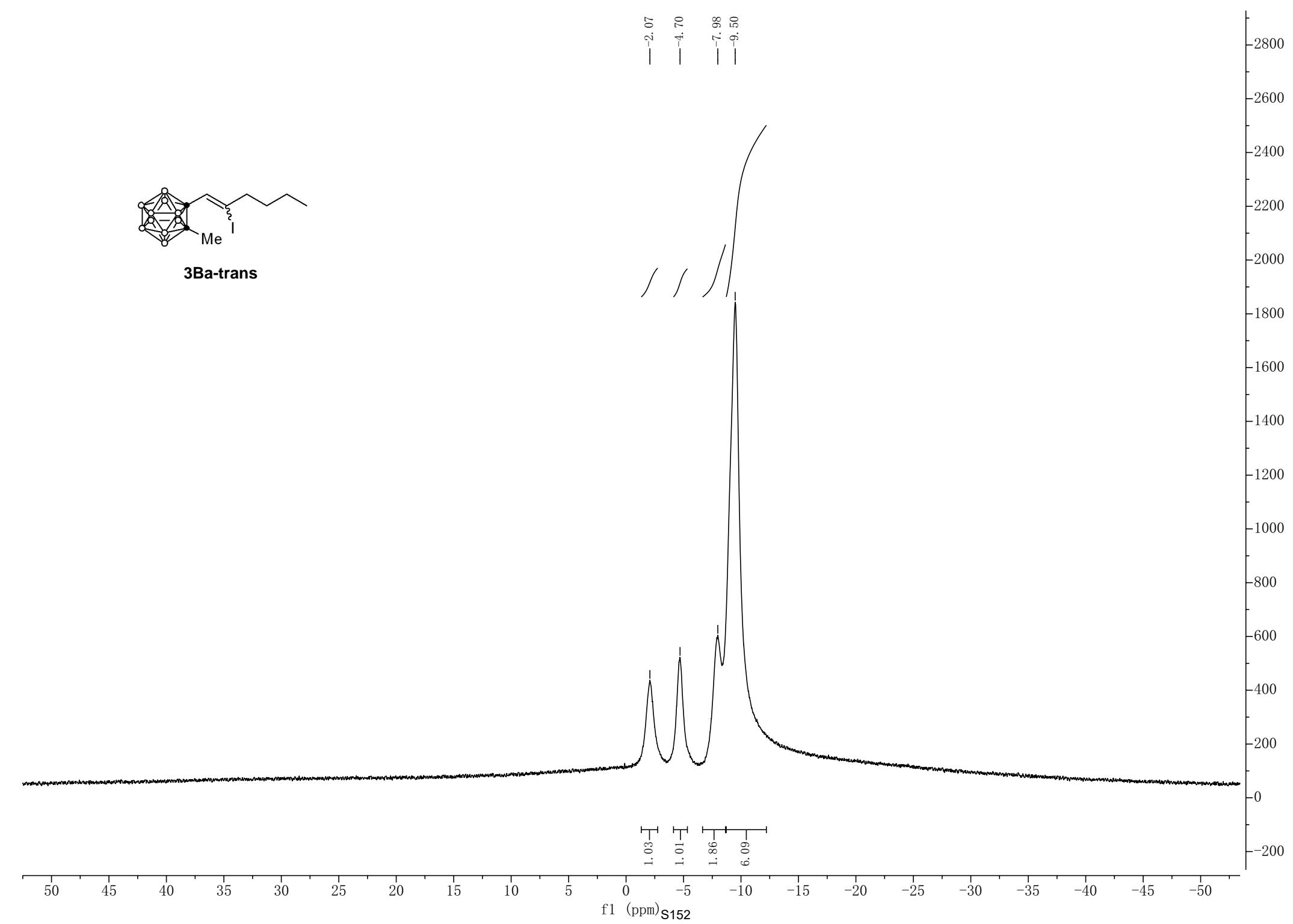


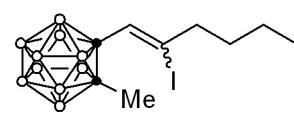
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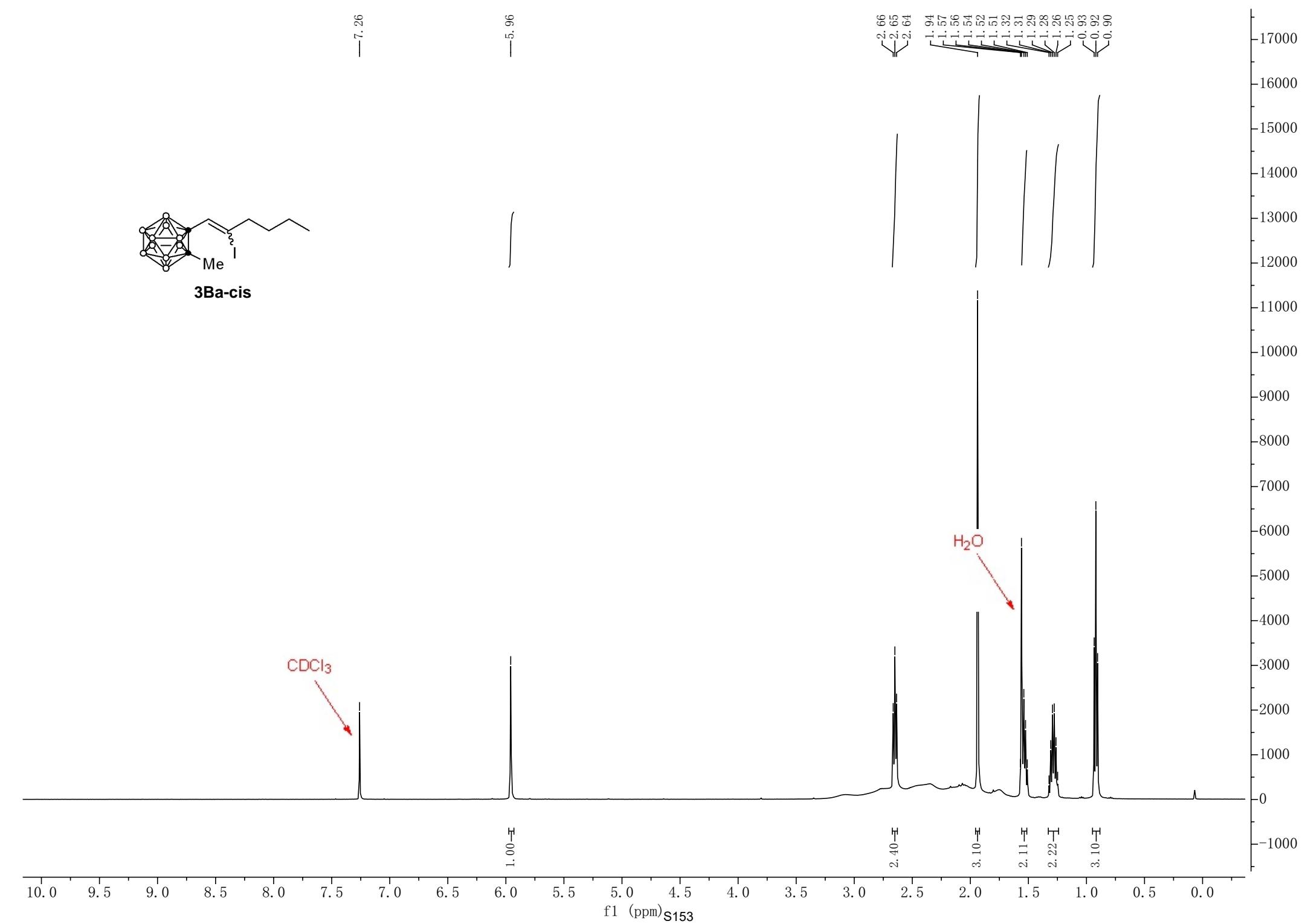


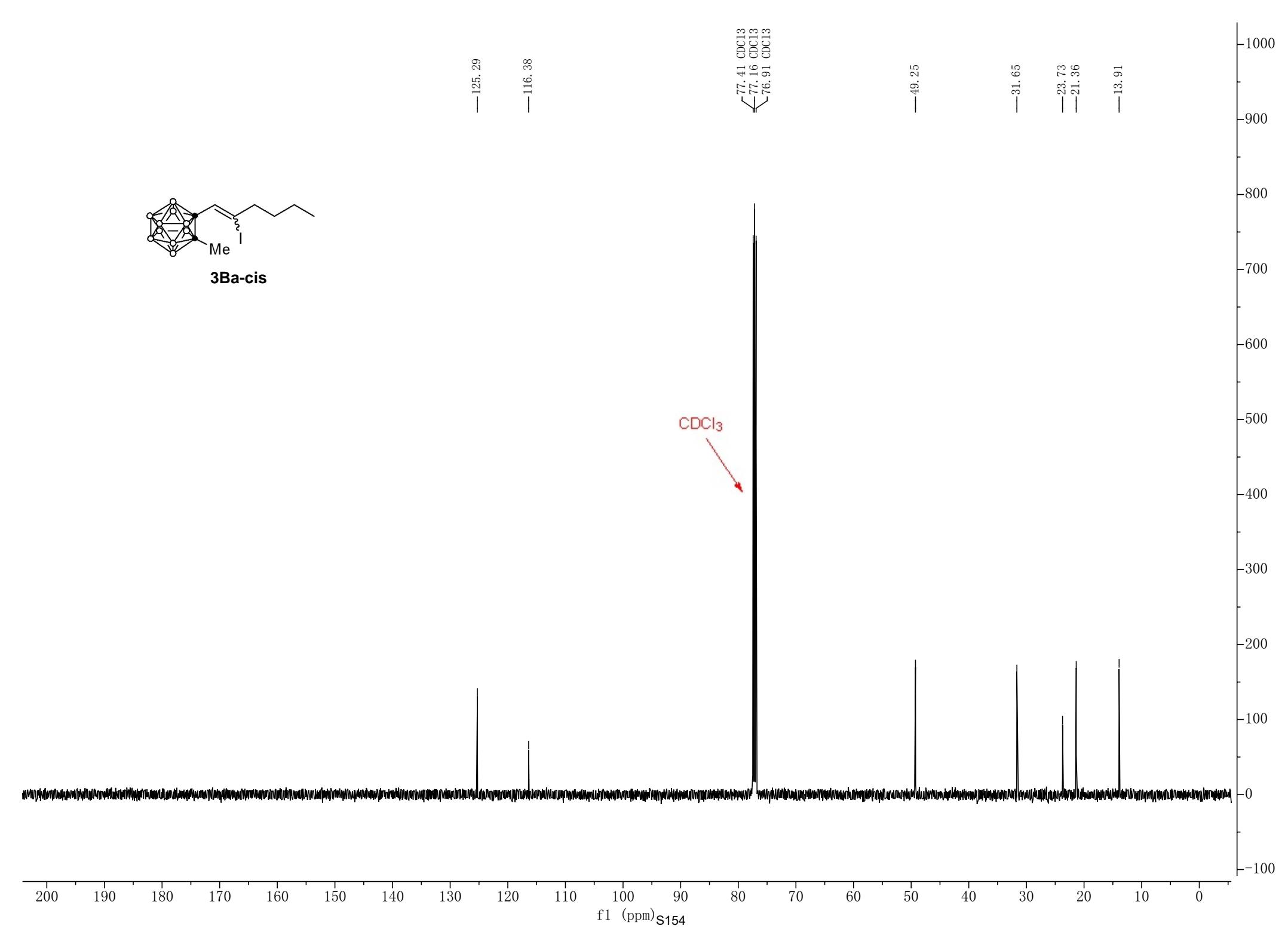
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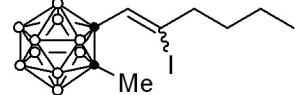




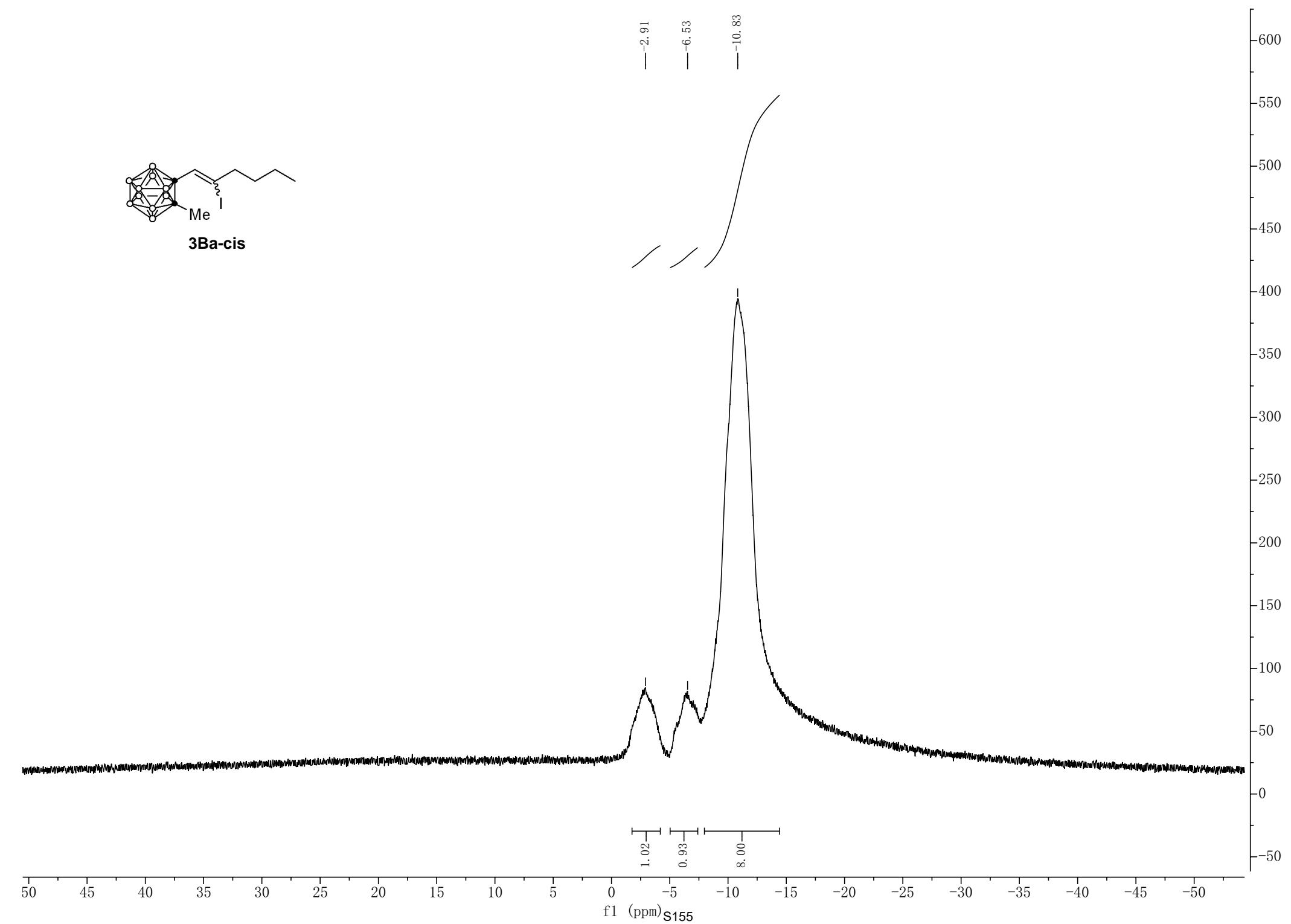
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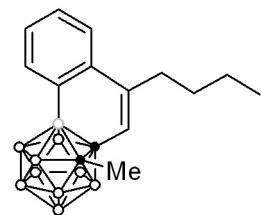




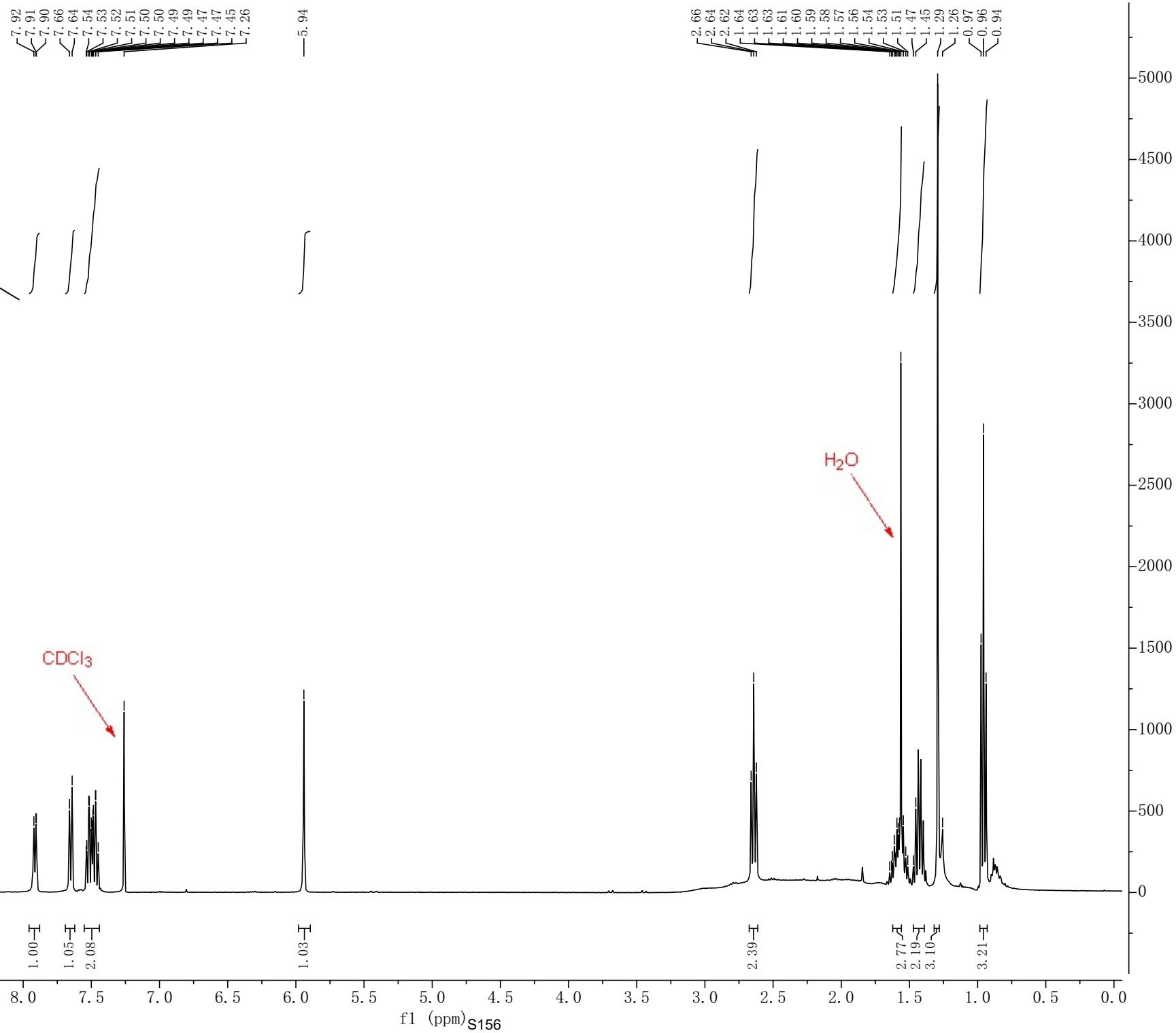


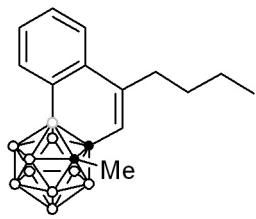
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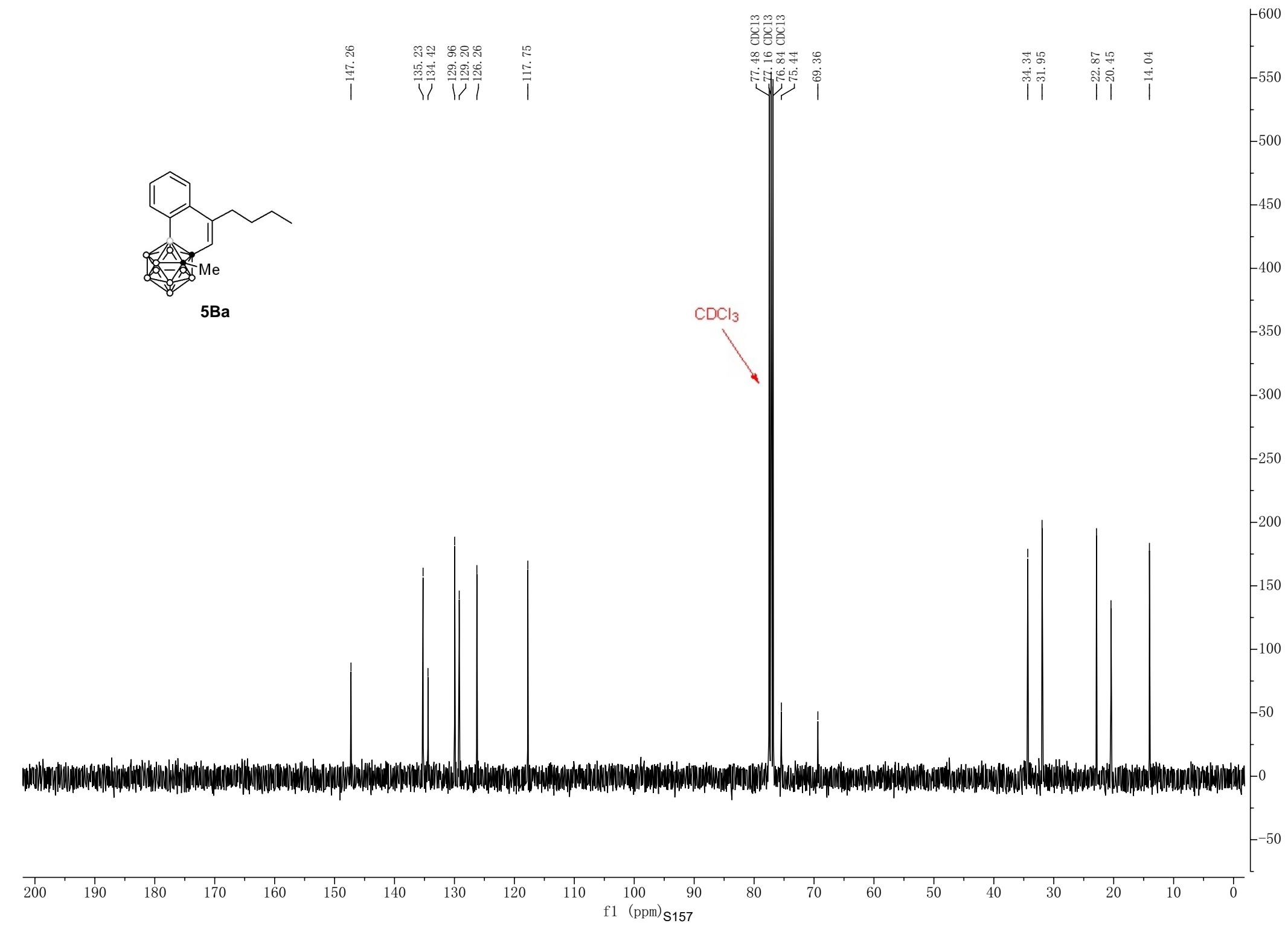


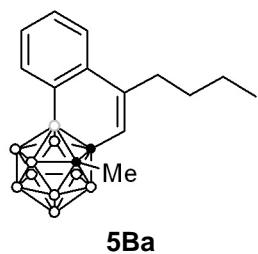
5Ba



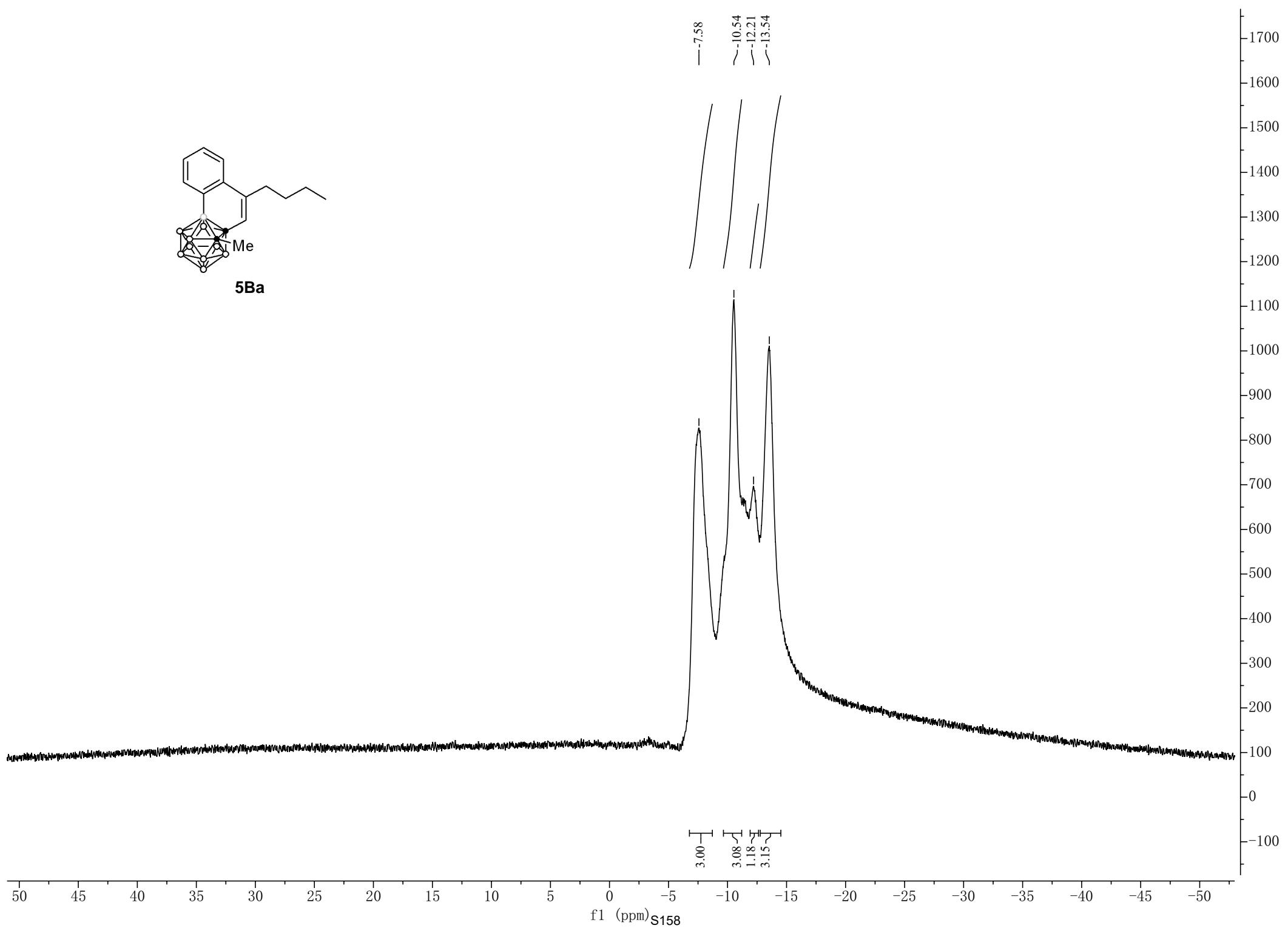


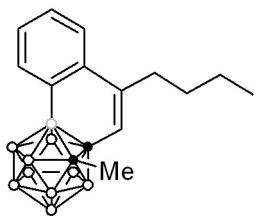
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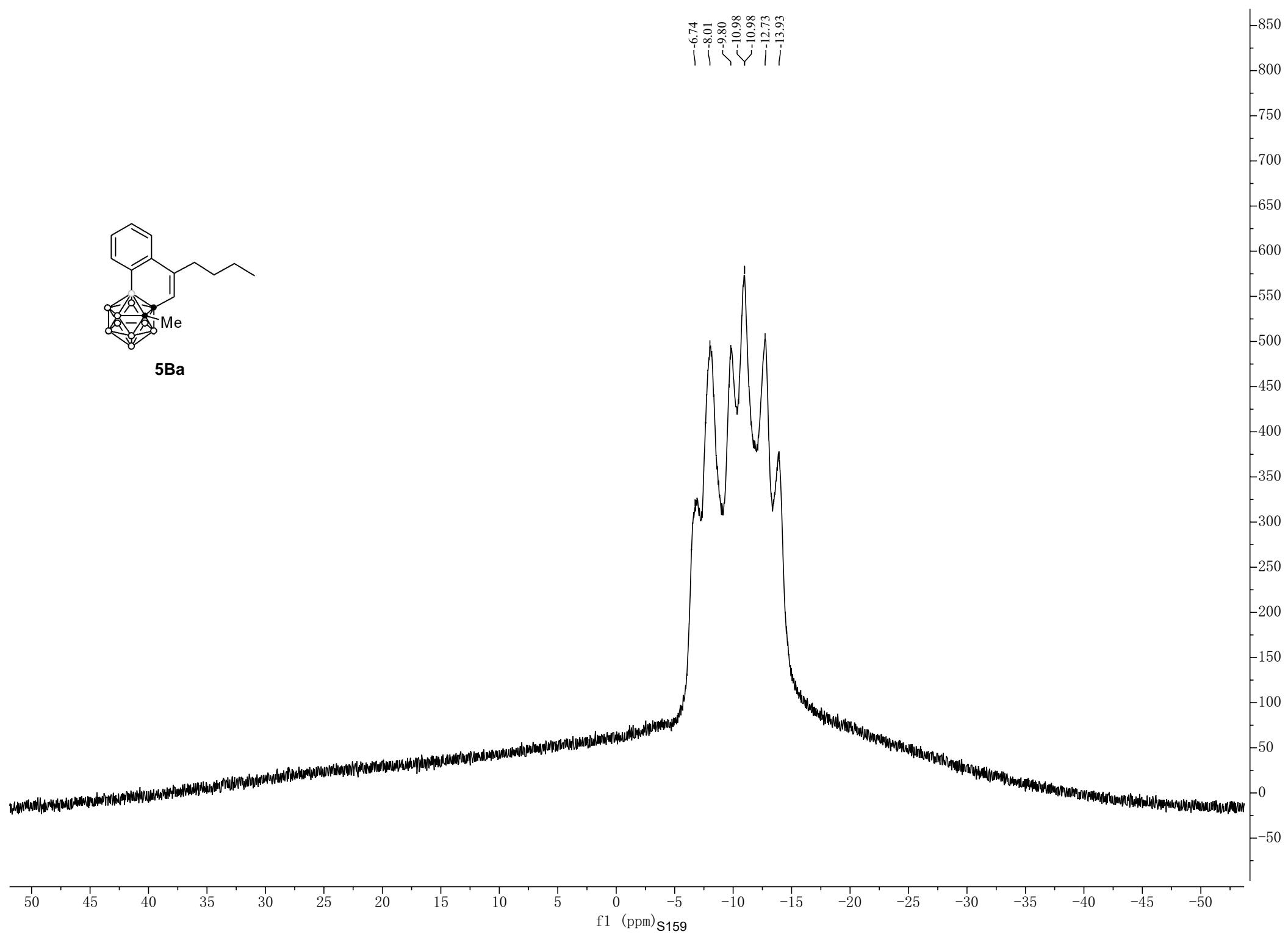


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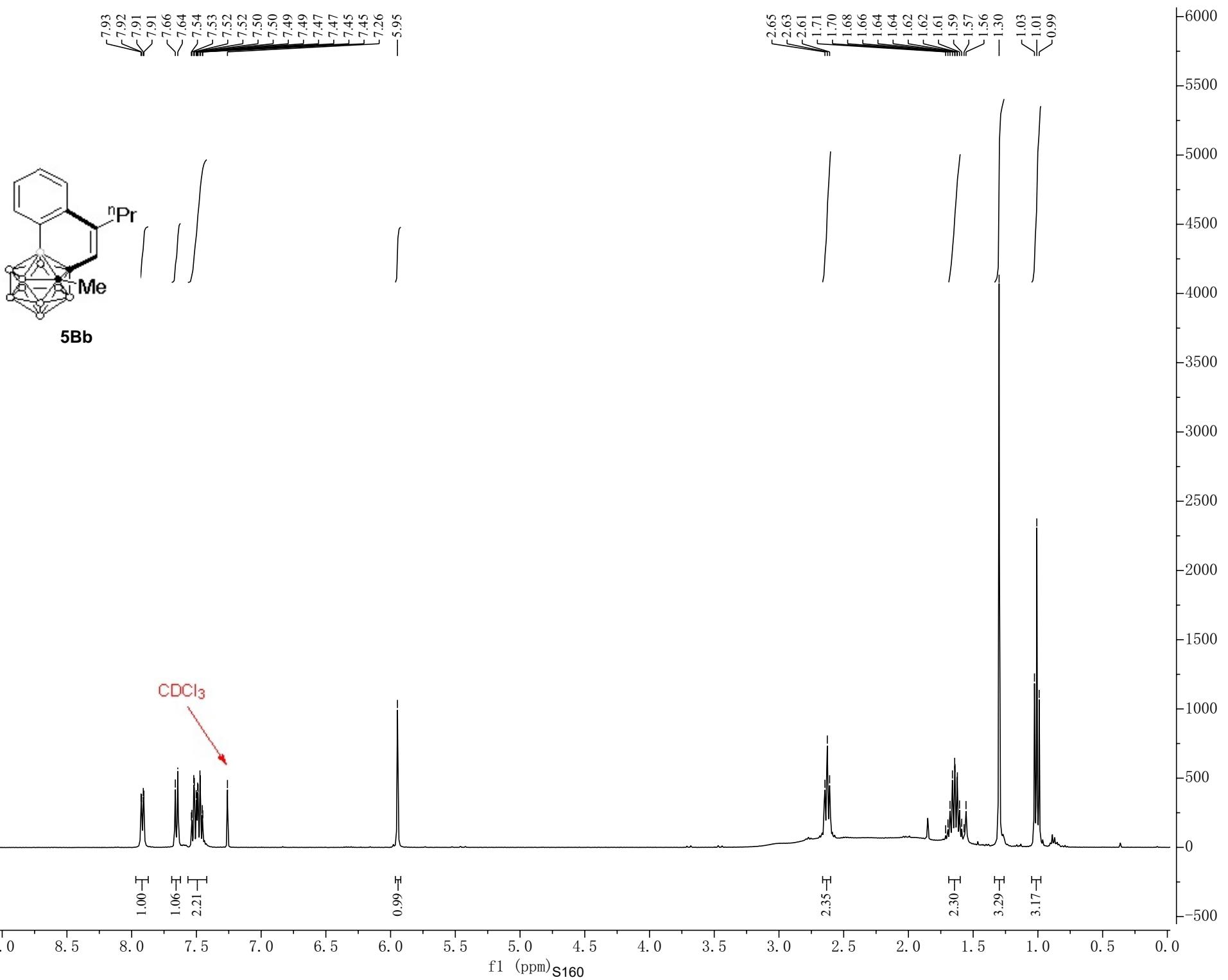


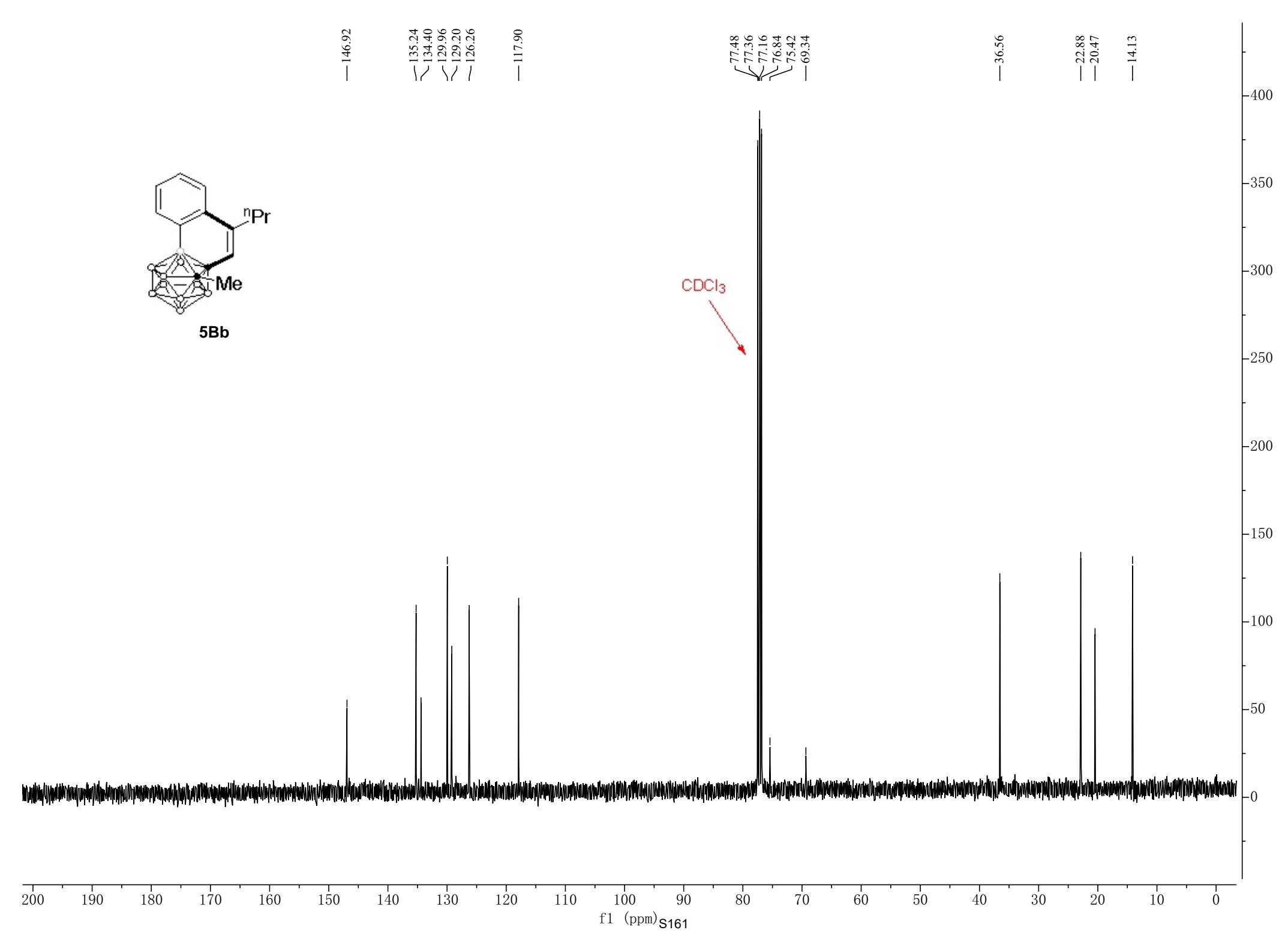


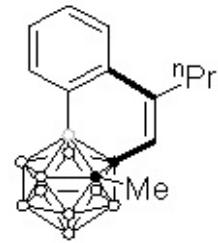
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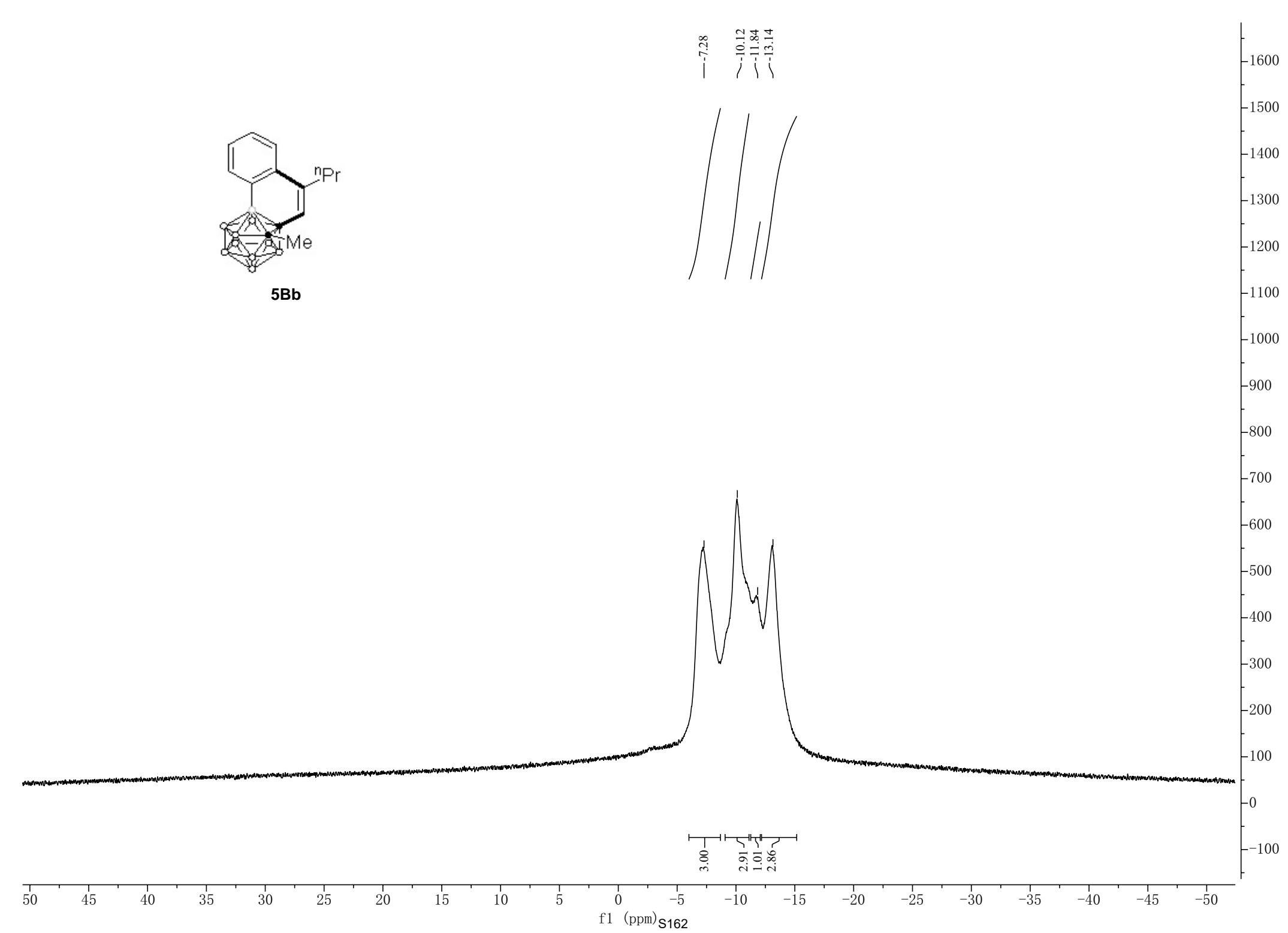
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-13.93

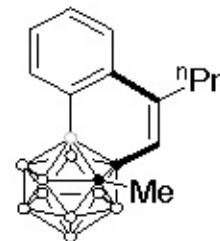






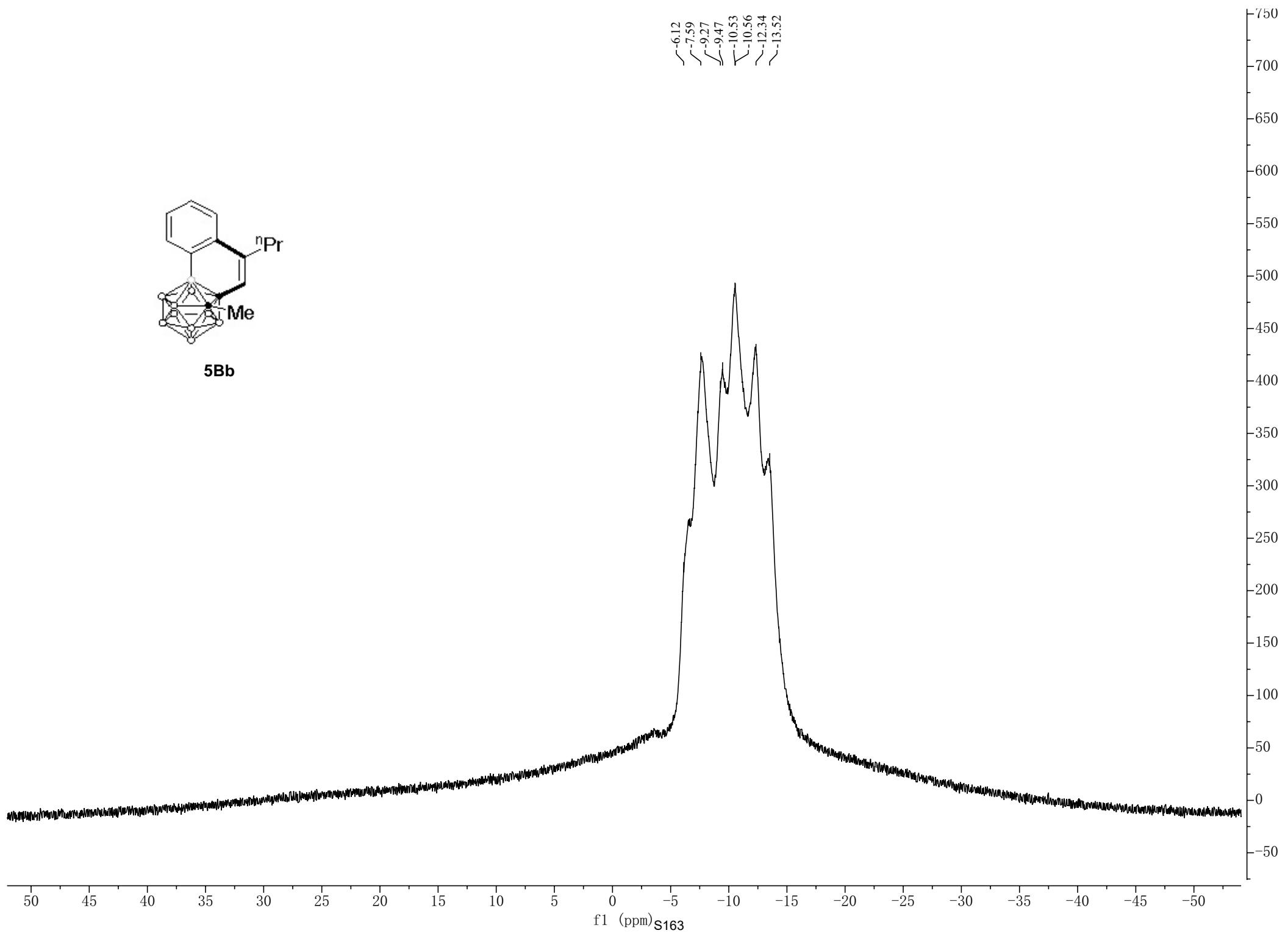
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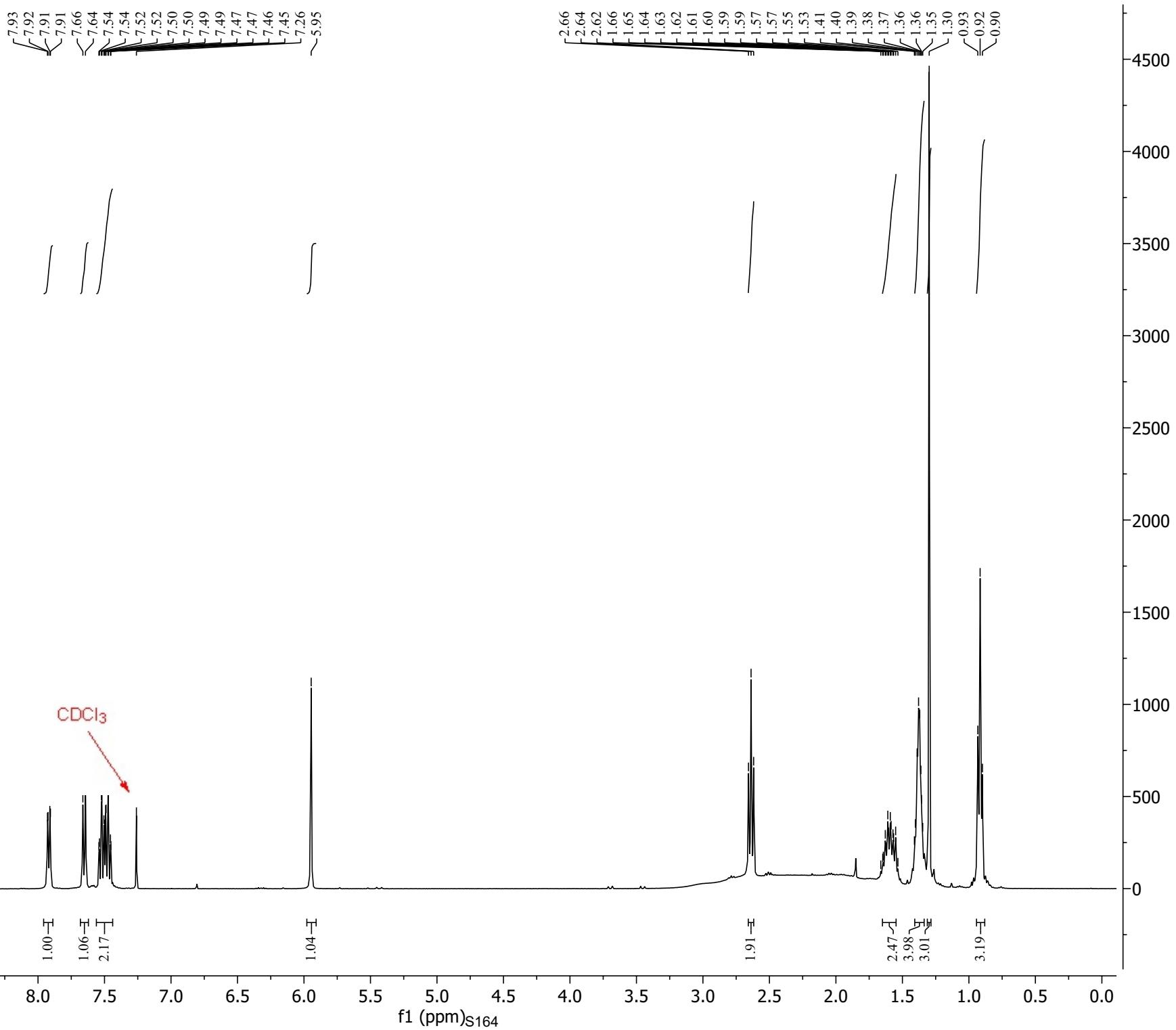
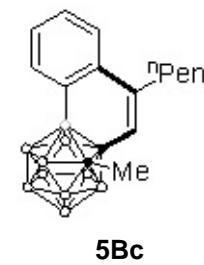


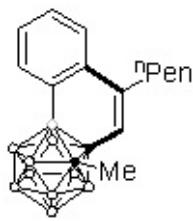


5Bb

✓ -6.12
✓ -7.59
✓ -9.27
✓ -9.47
✓ -10.53
✓ -10.56
✓ -12.34
✓ -13.52





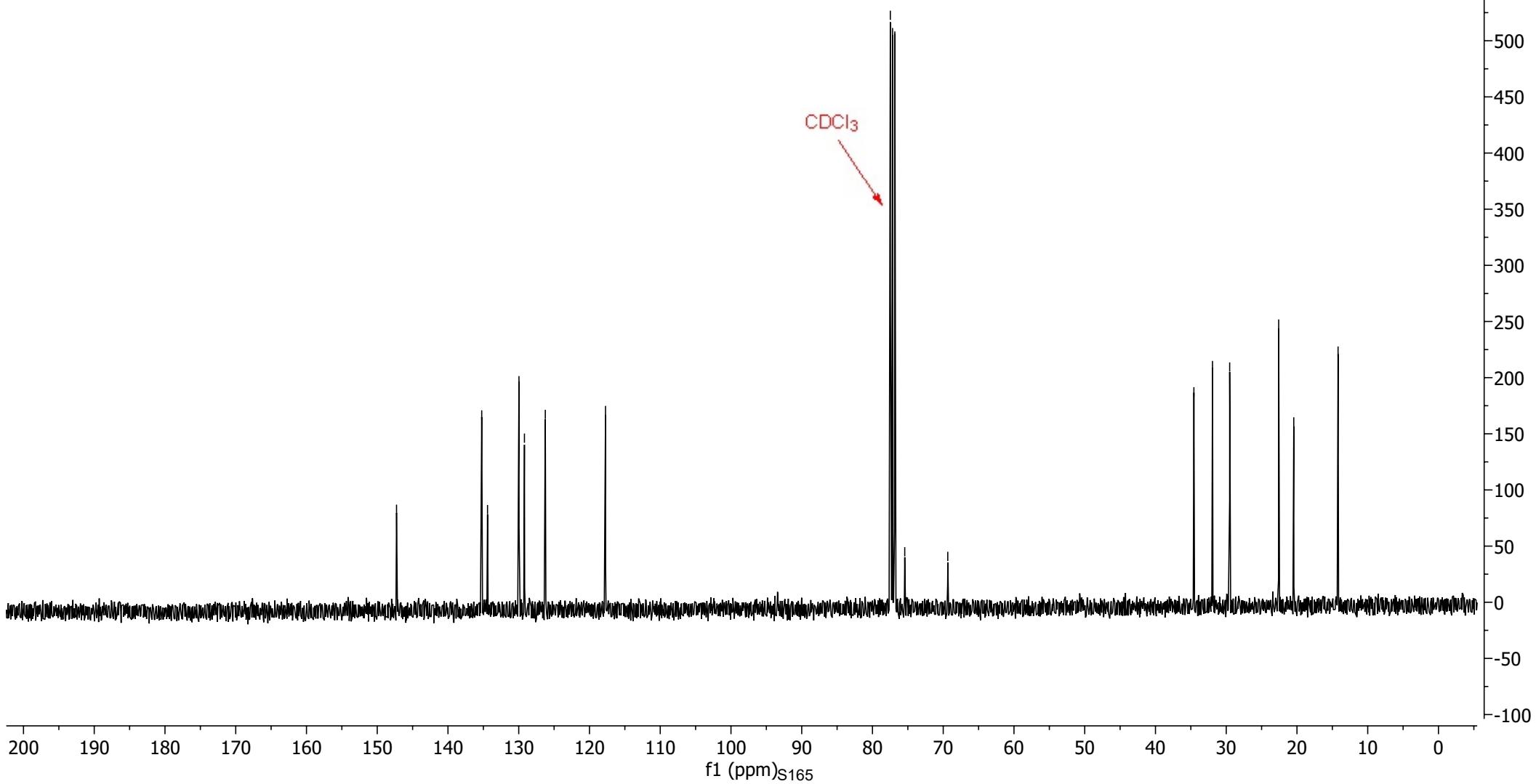


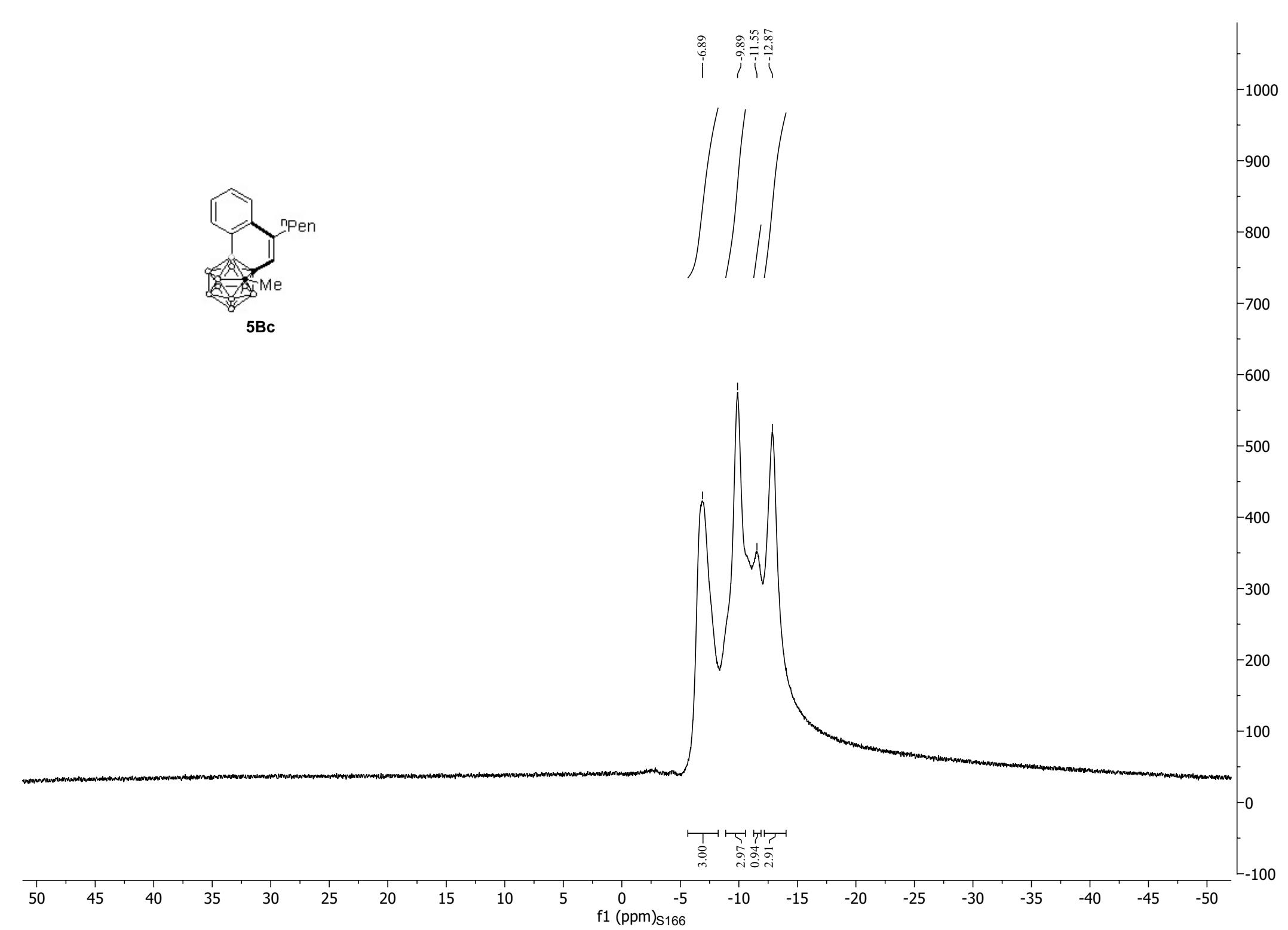
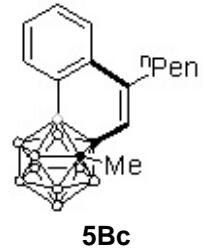
5Bc

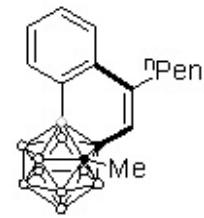
—147.27
—135.23
—134.41
—129.96
—129.19
—126.24
—117.73

—77.48
—77.16
—76.84
—75.44
—69.36

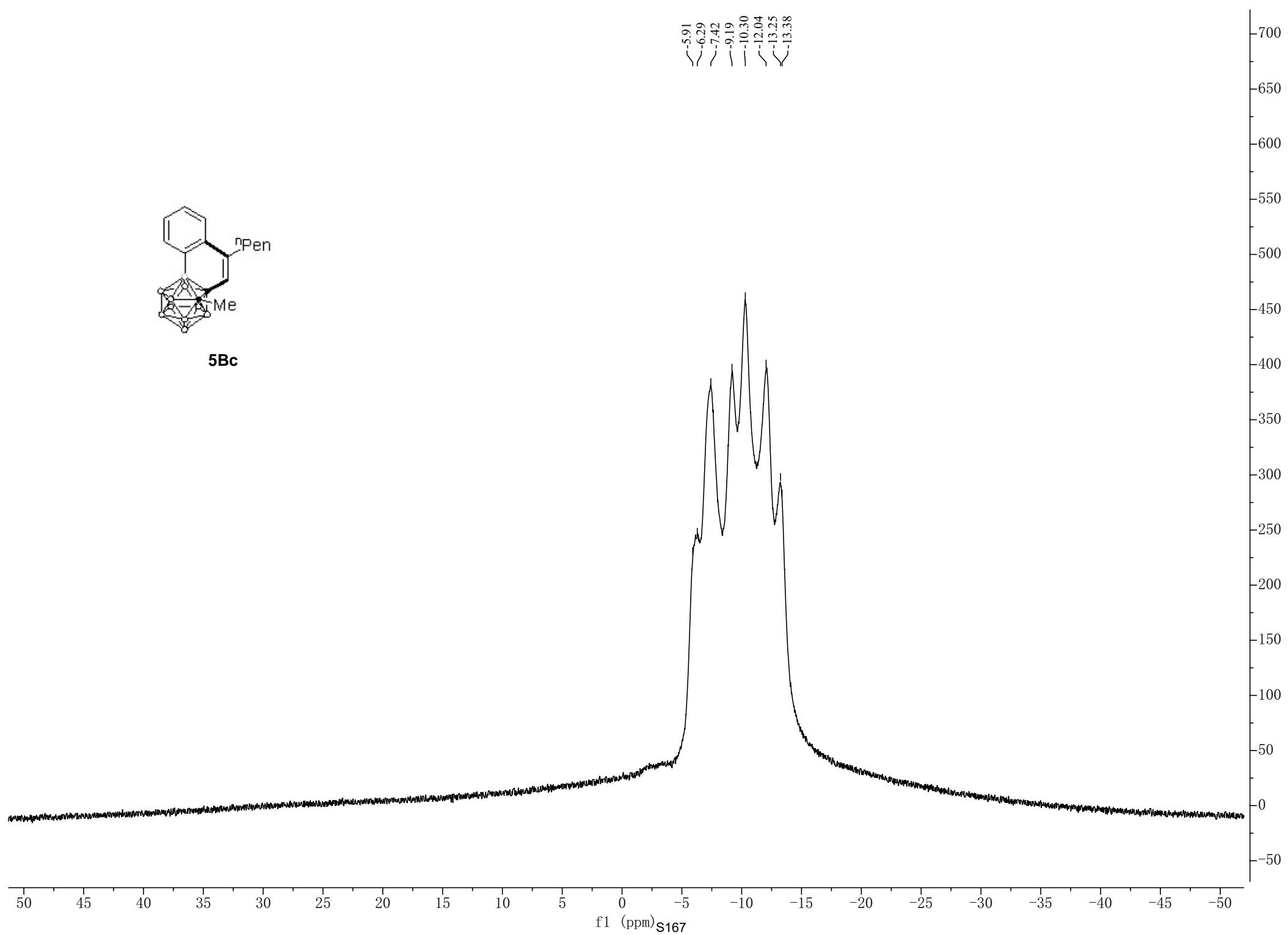
—34.57
—31.94
—29.51
—22.59
—20.45
—14.19

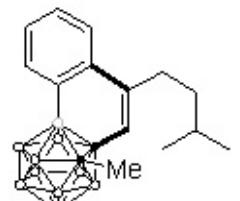




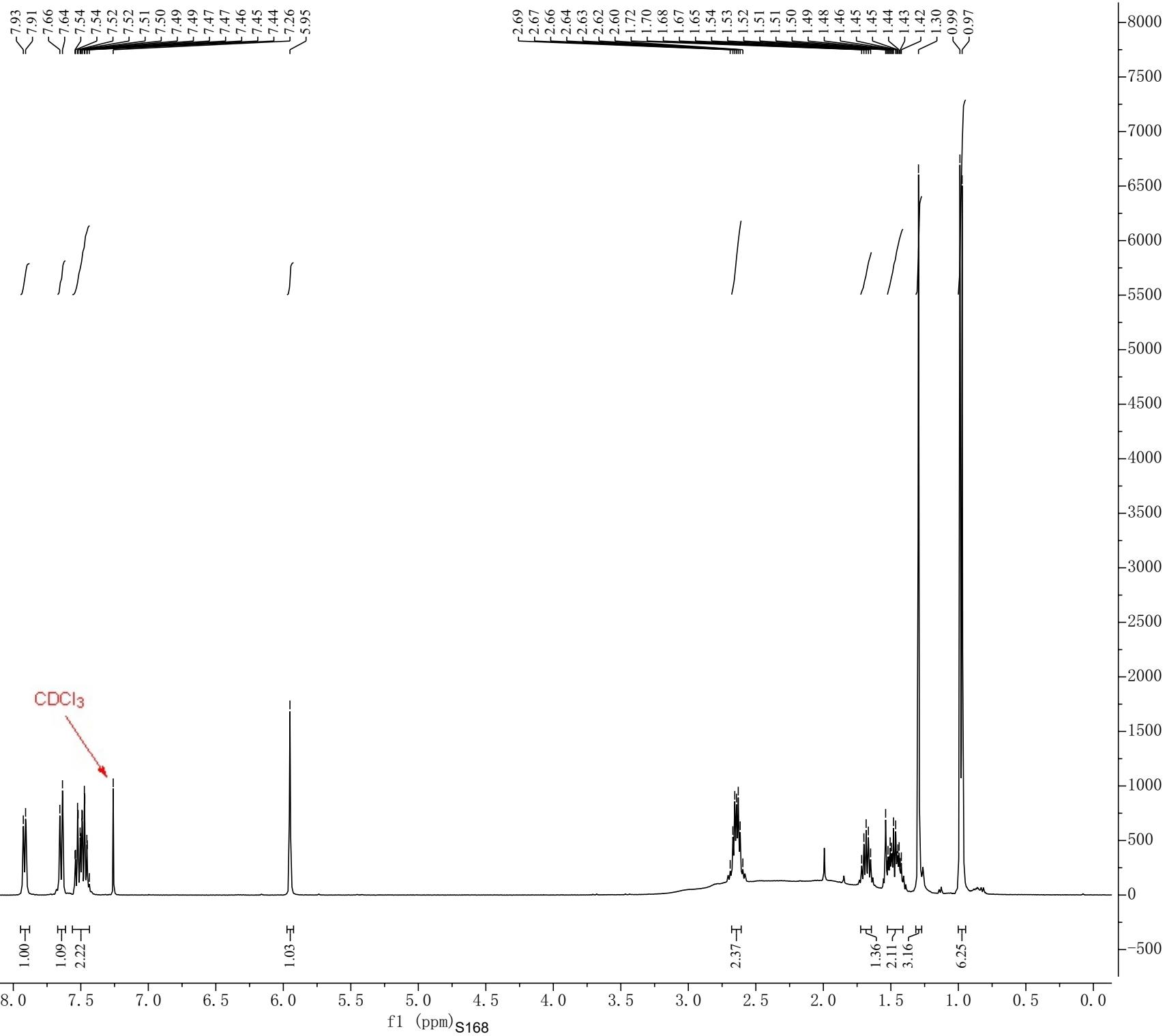


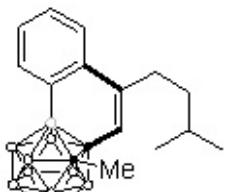
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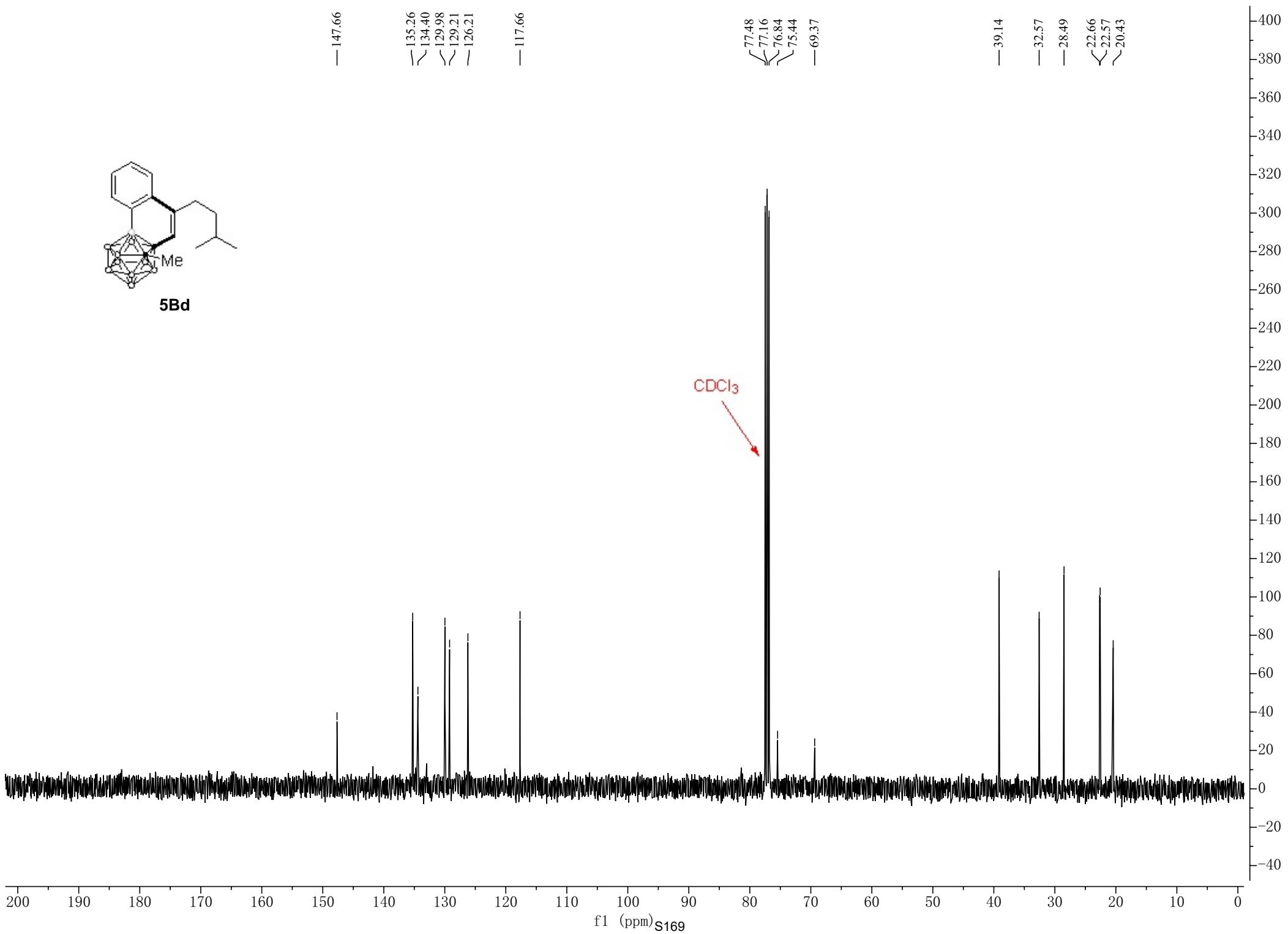


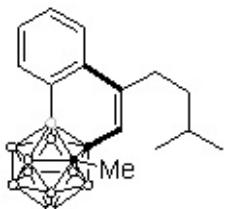
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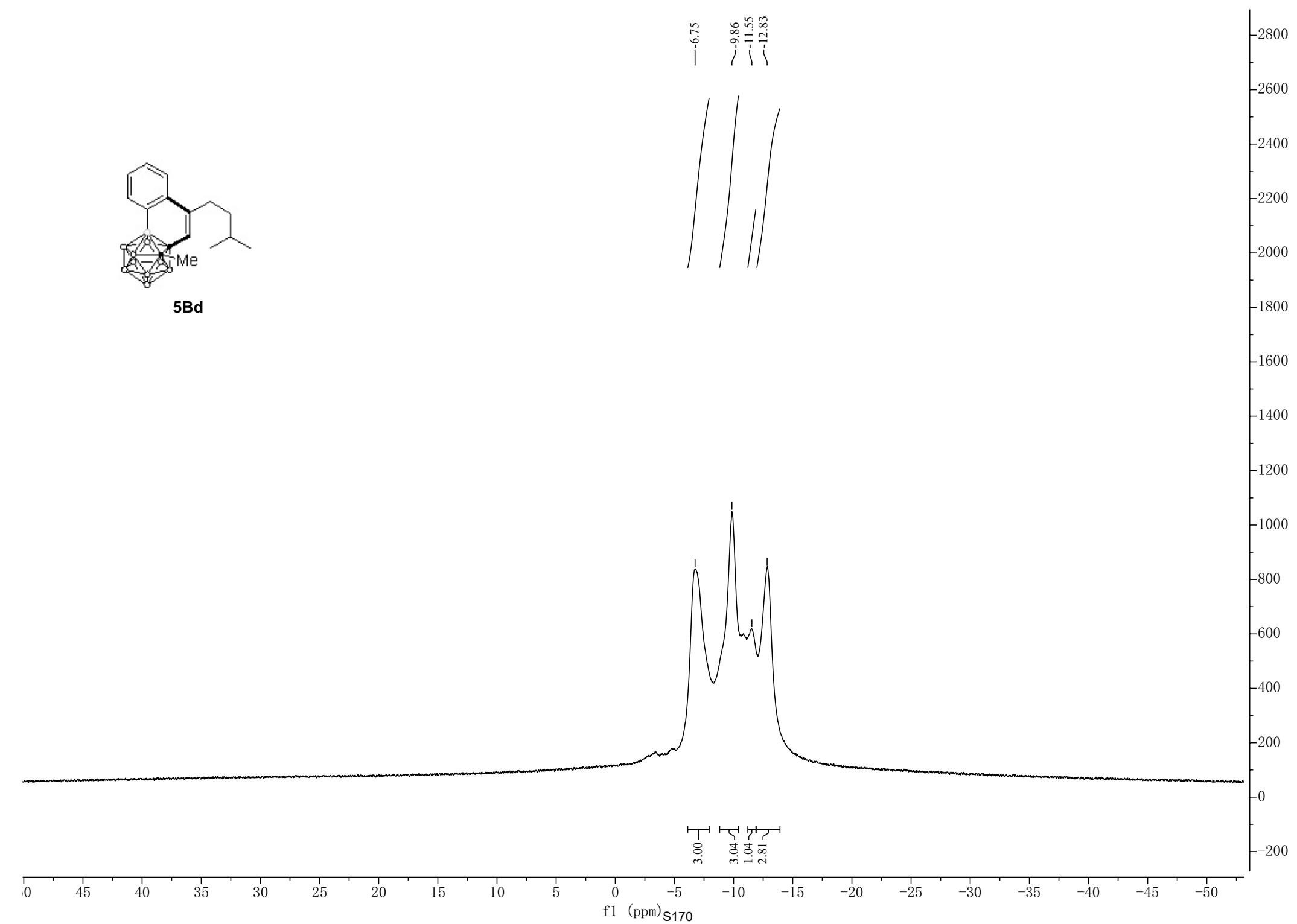


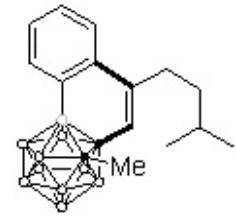
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— 135.26 —
— 134.40 —
— 129.98 —
— 129.21 —
— 126.21 —
— 117.66 —
— 77.48 —
— 77.16 —
— 76.84 —
— 75.44 —
— 69.37 —
— 39.14 —
— 32.57 —
— 28.49 —
— 22.66 —
— 22.57 —
— 20.43 —





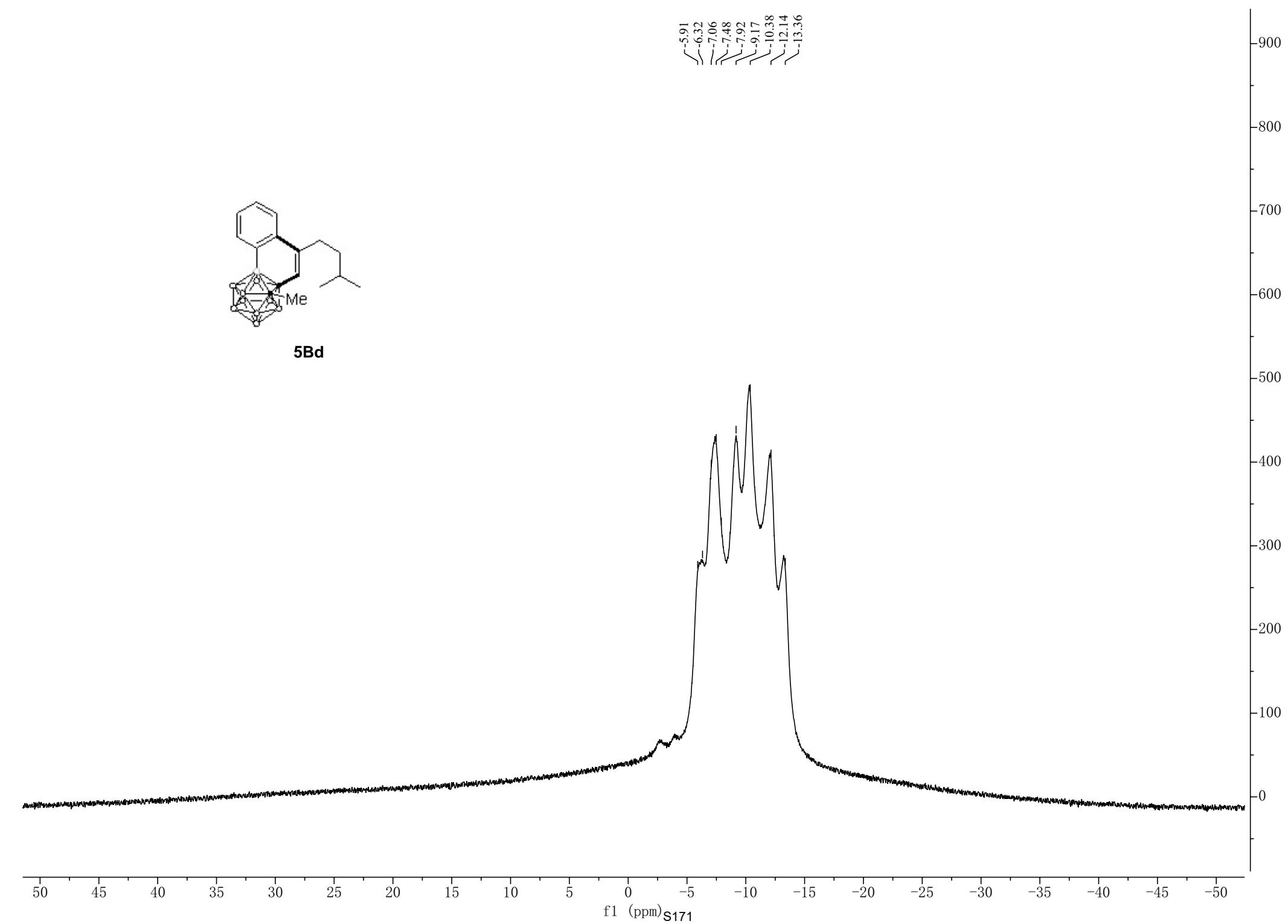
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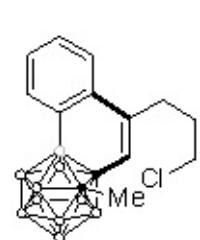




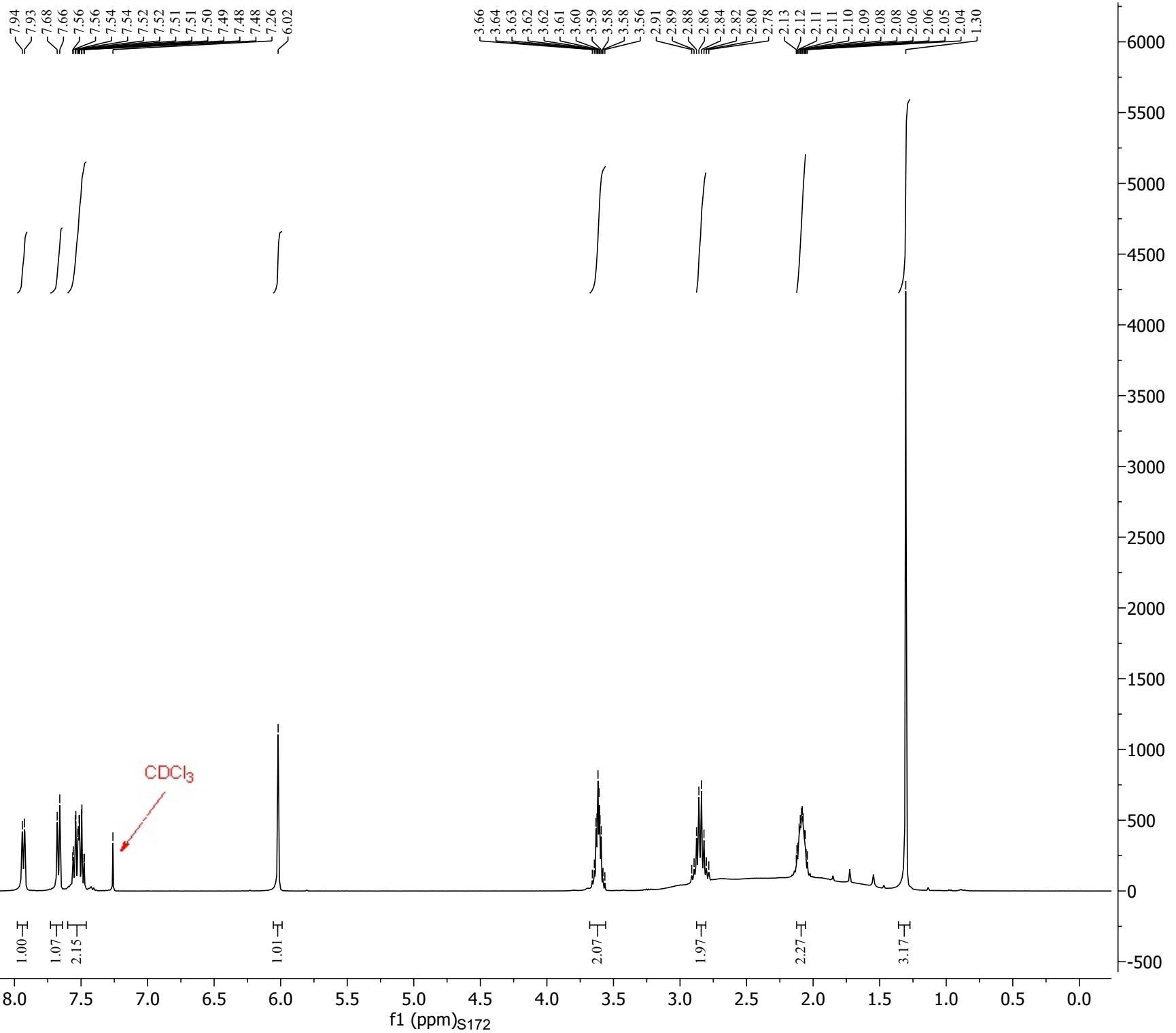
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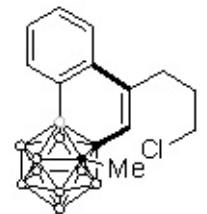
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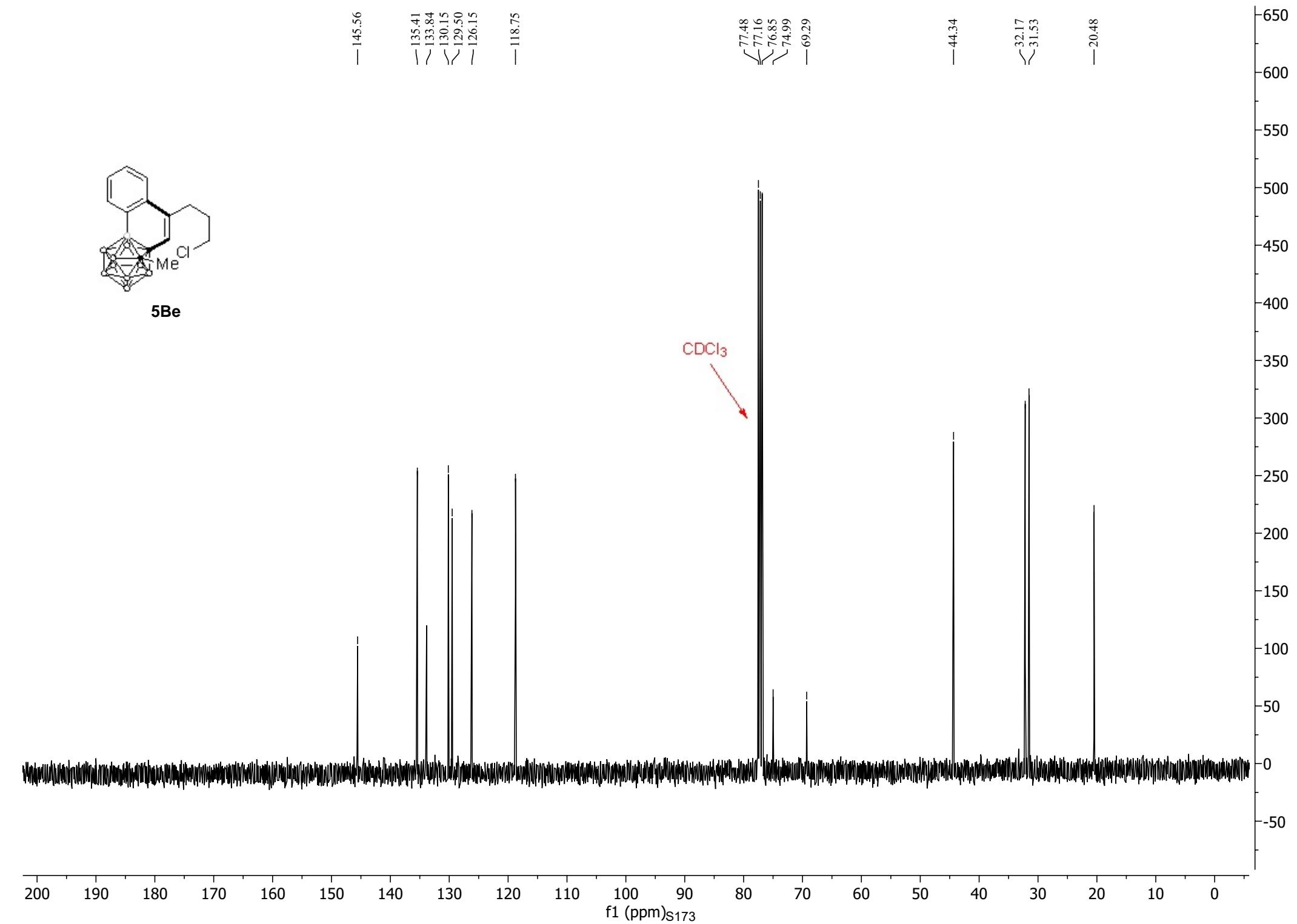


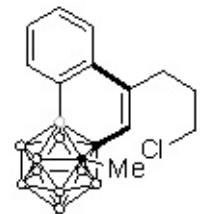
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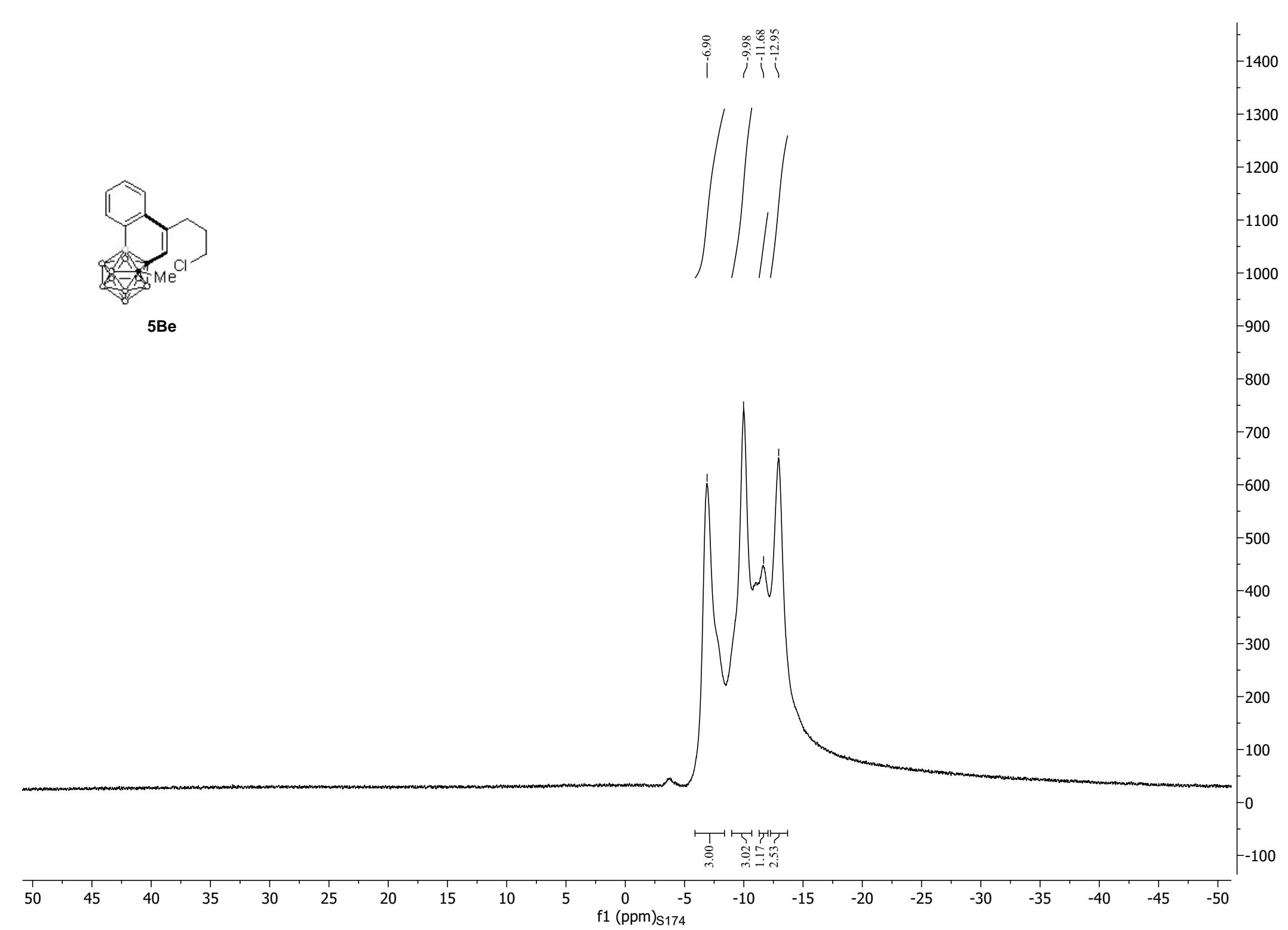


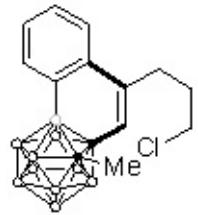
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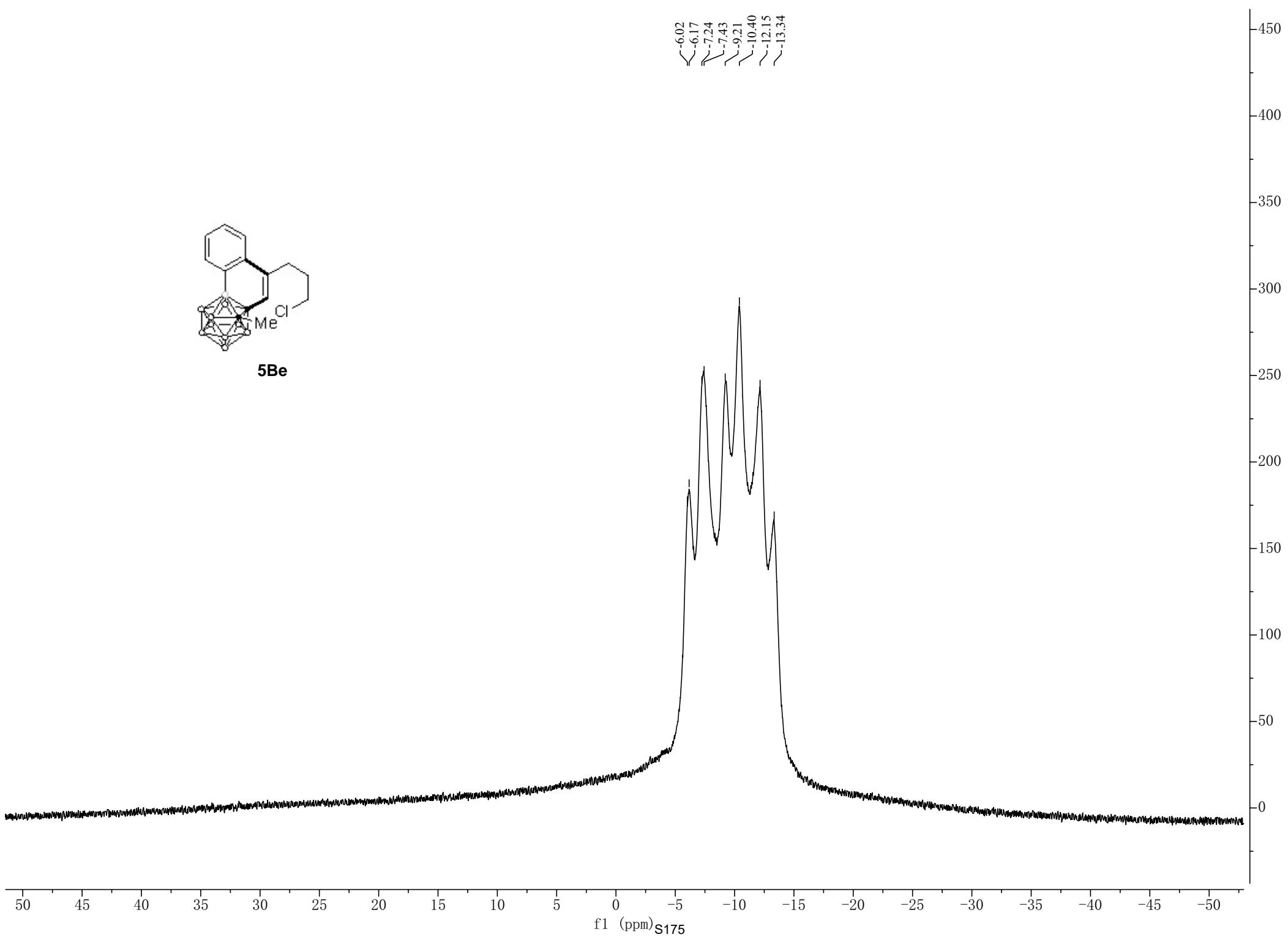
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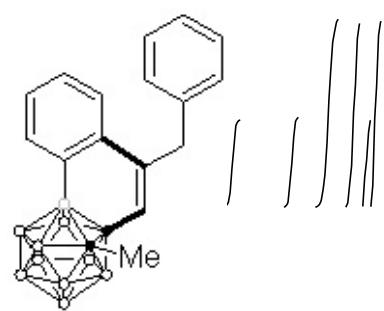




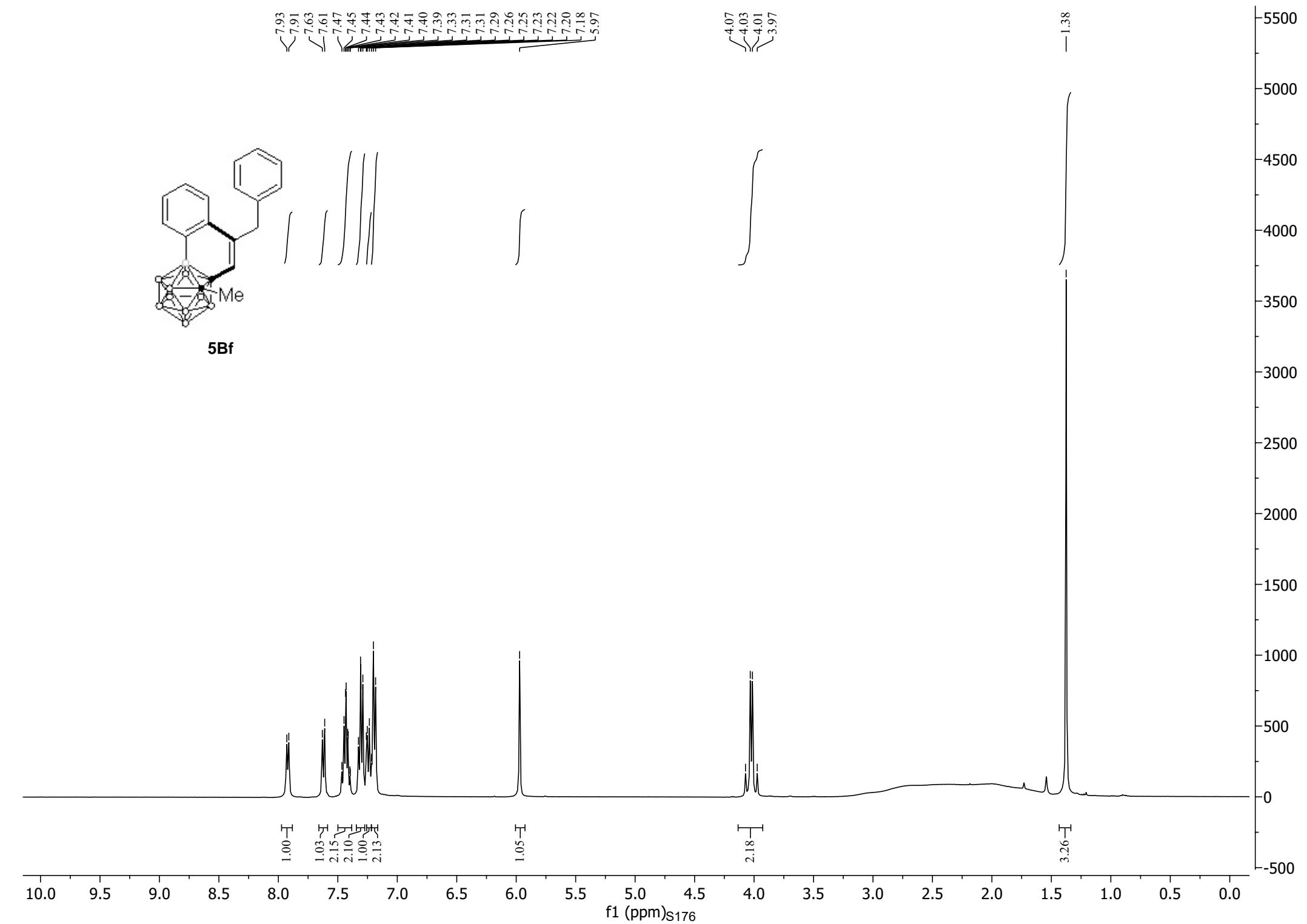
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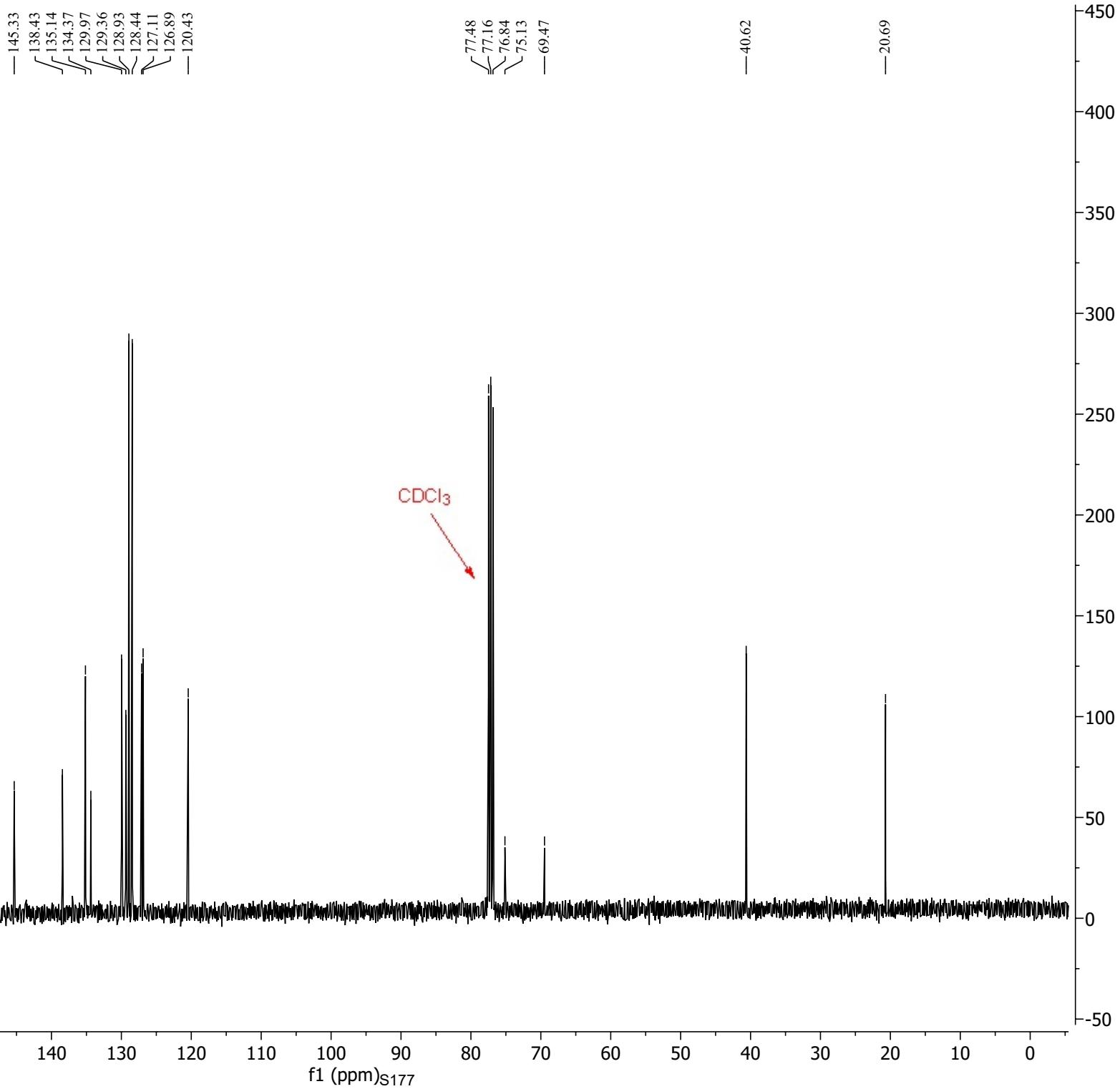
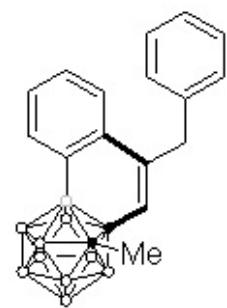
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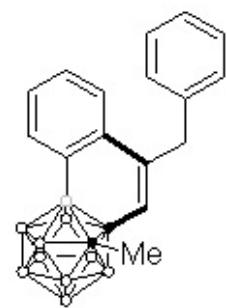




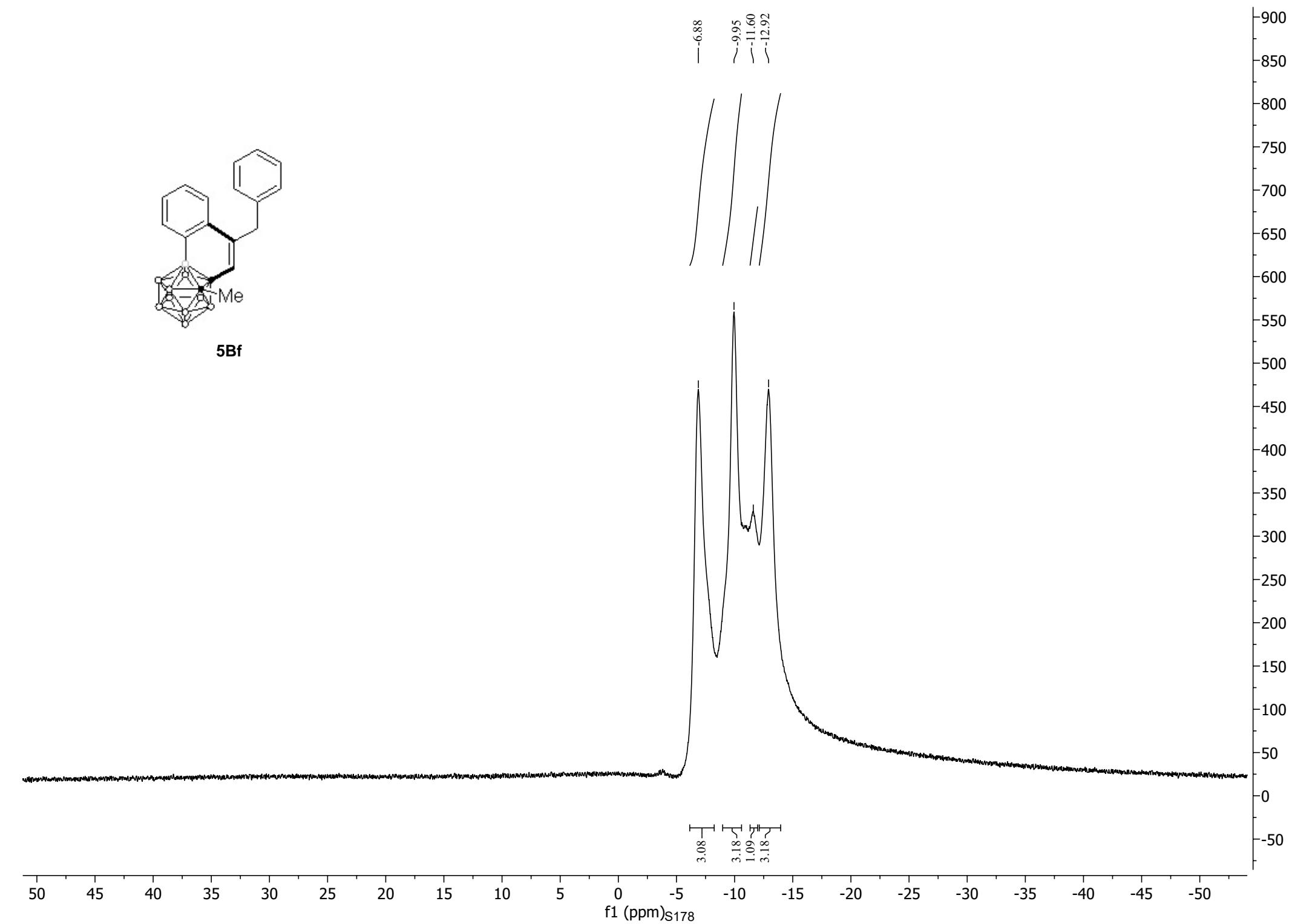
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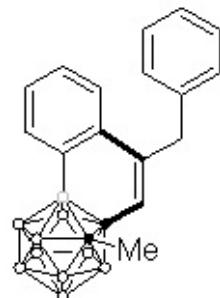






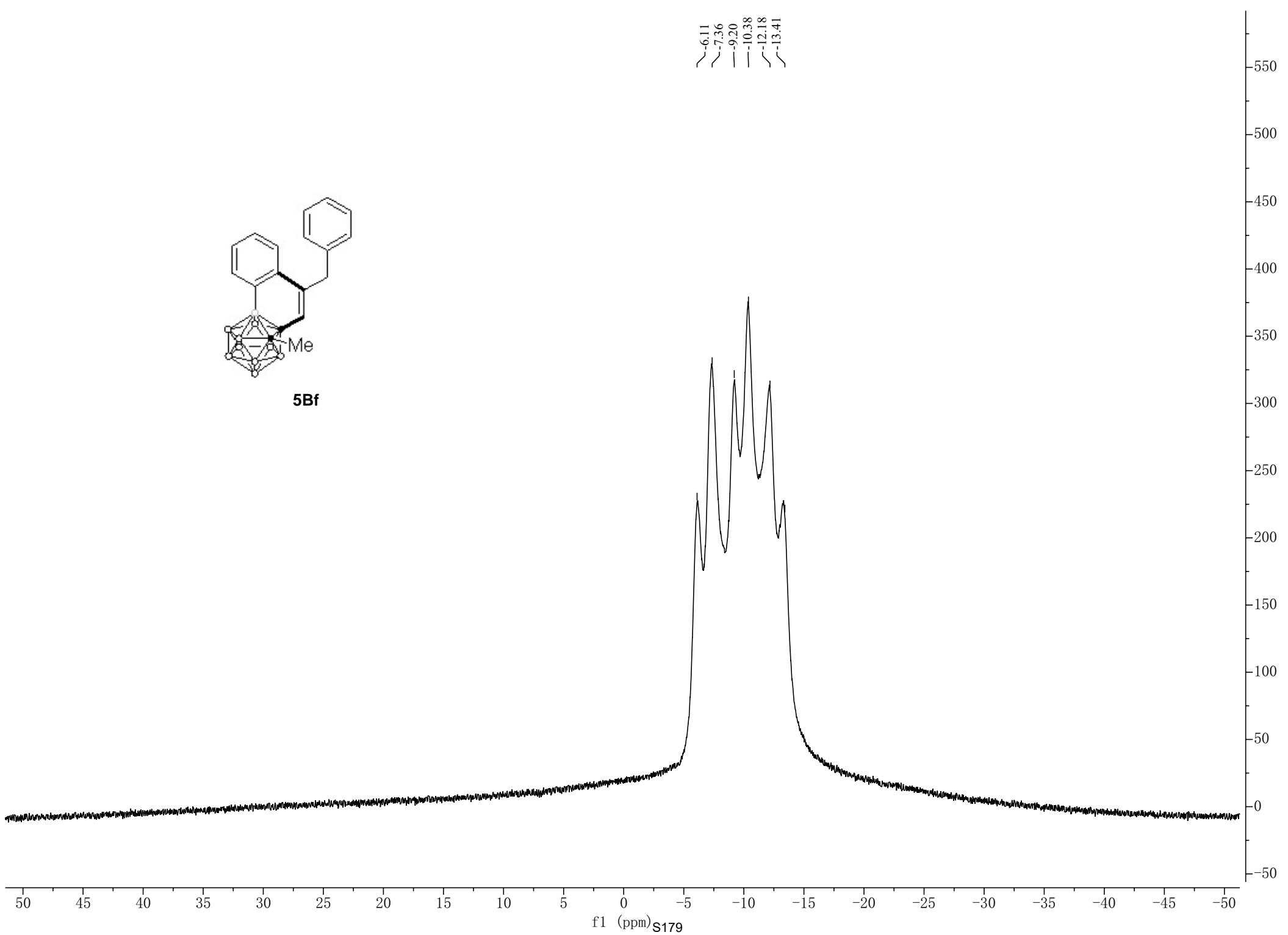
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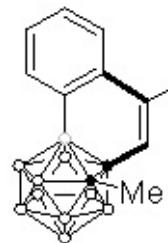




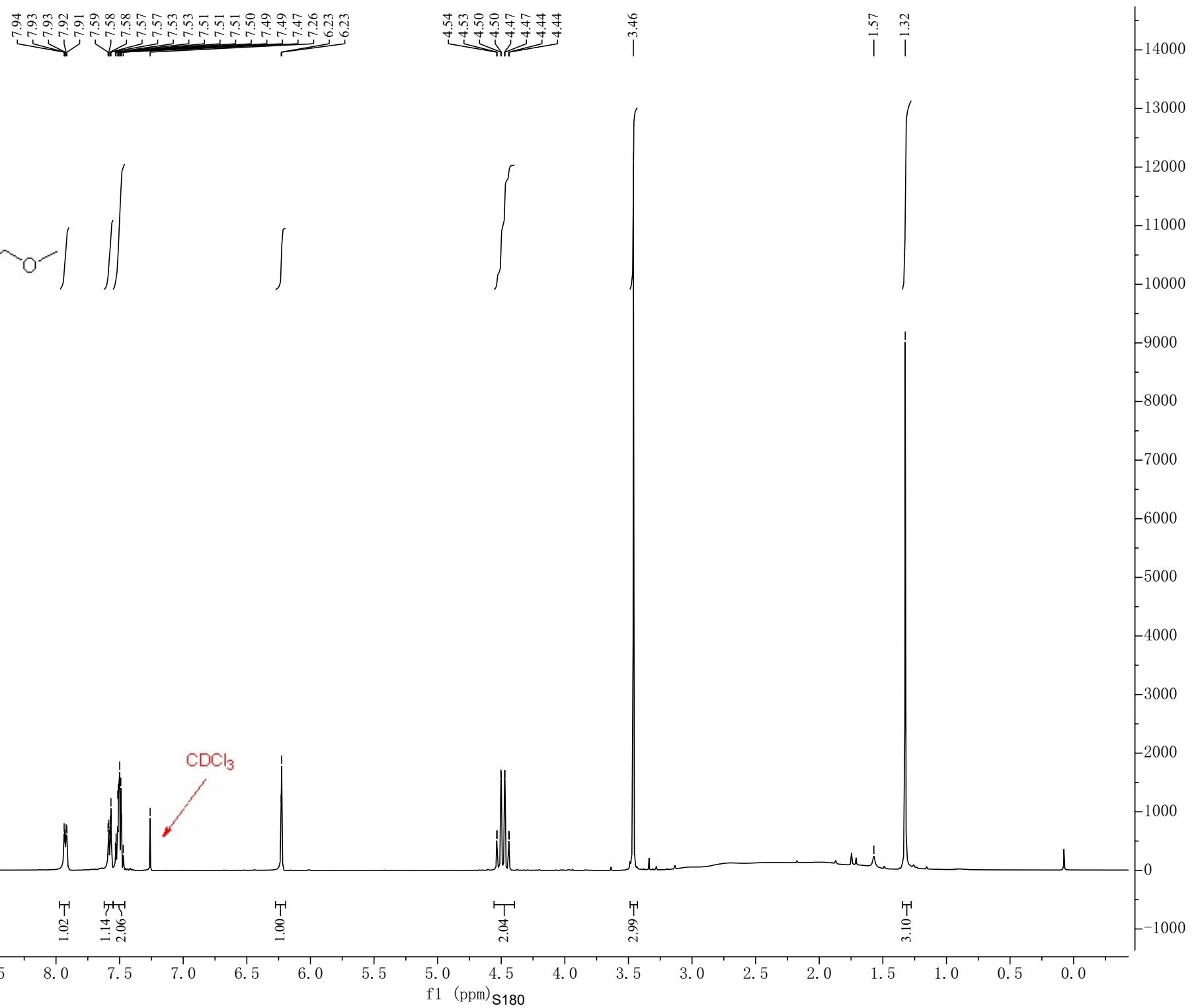
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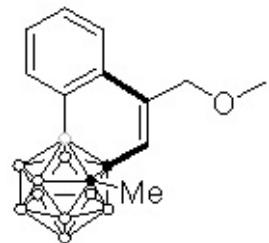
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~ -7.36
— -9.20
— -10.38
~ -12.18
~ -13.41



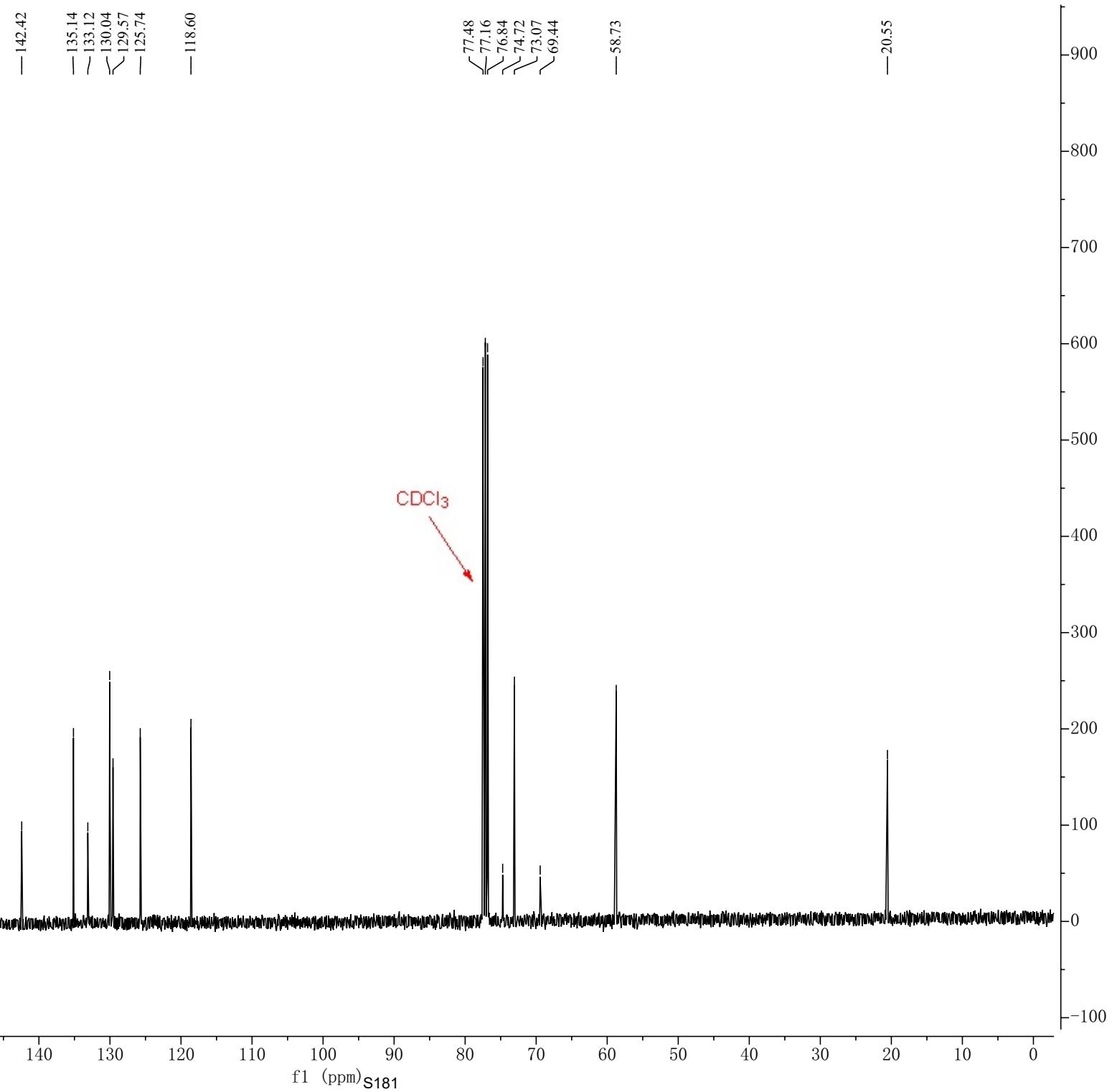


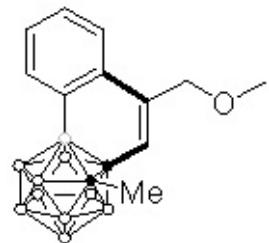
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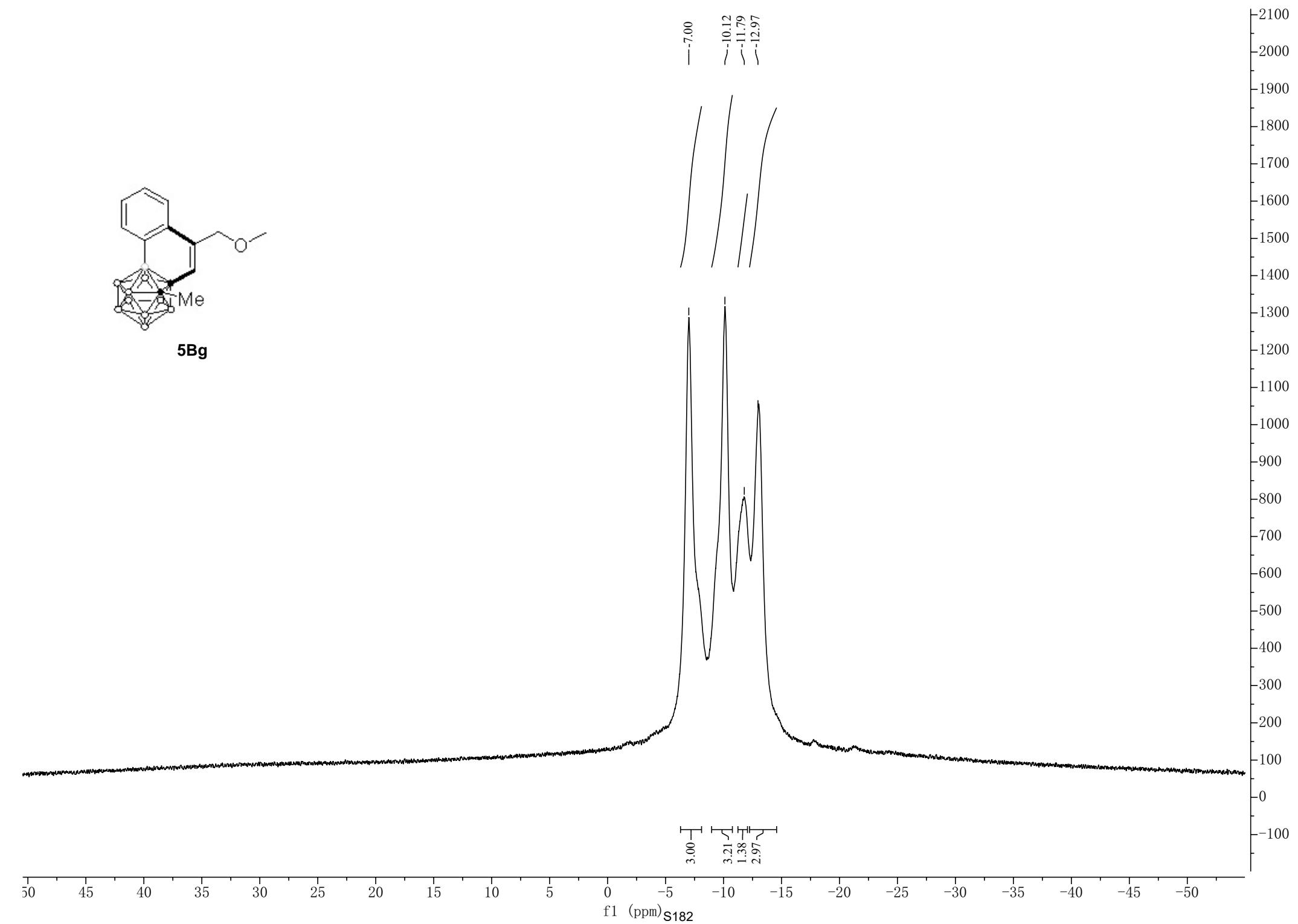


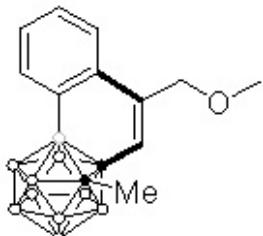
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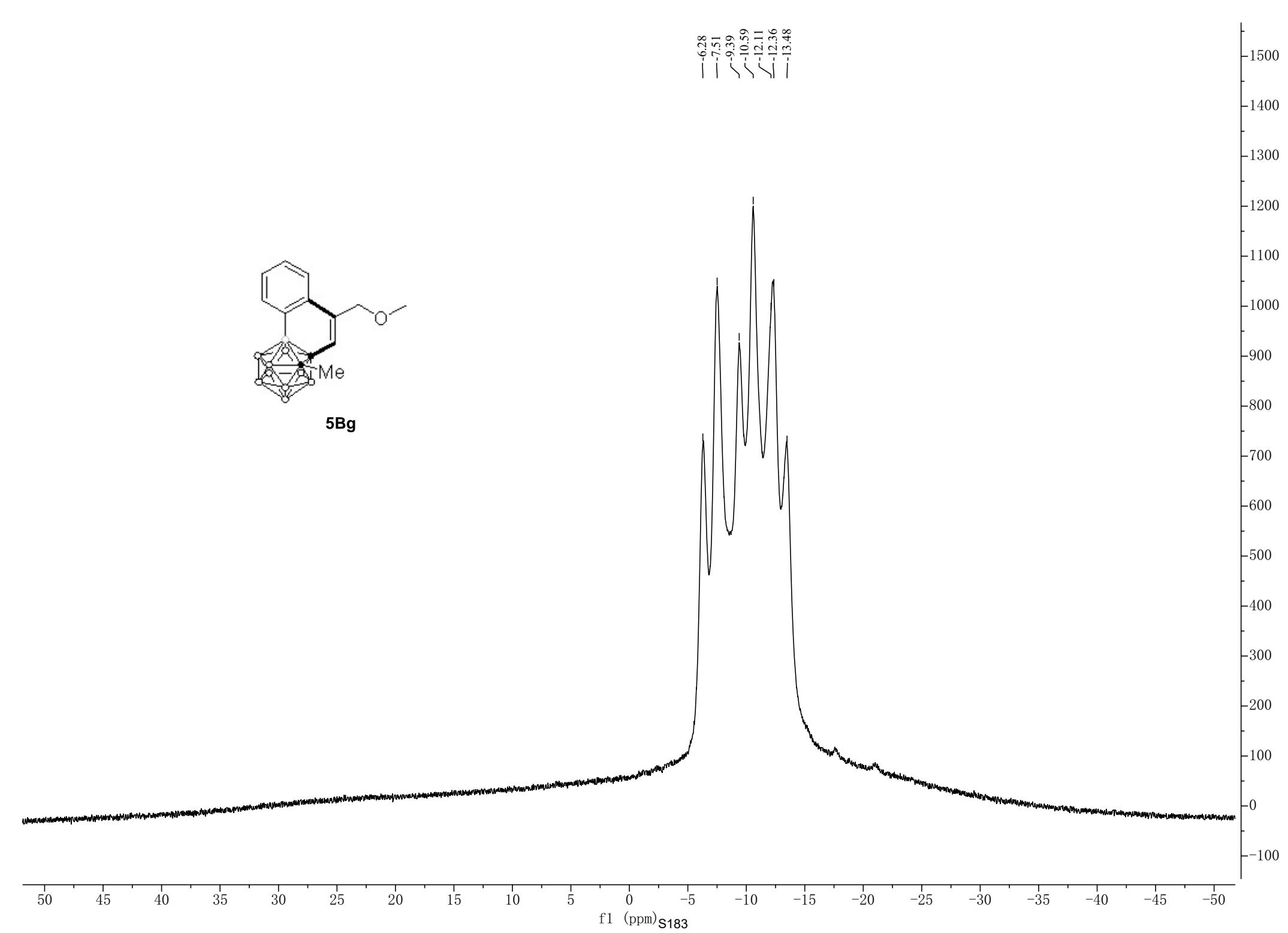


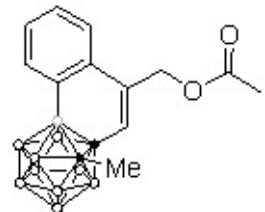
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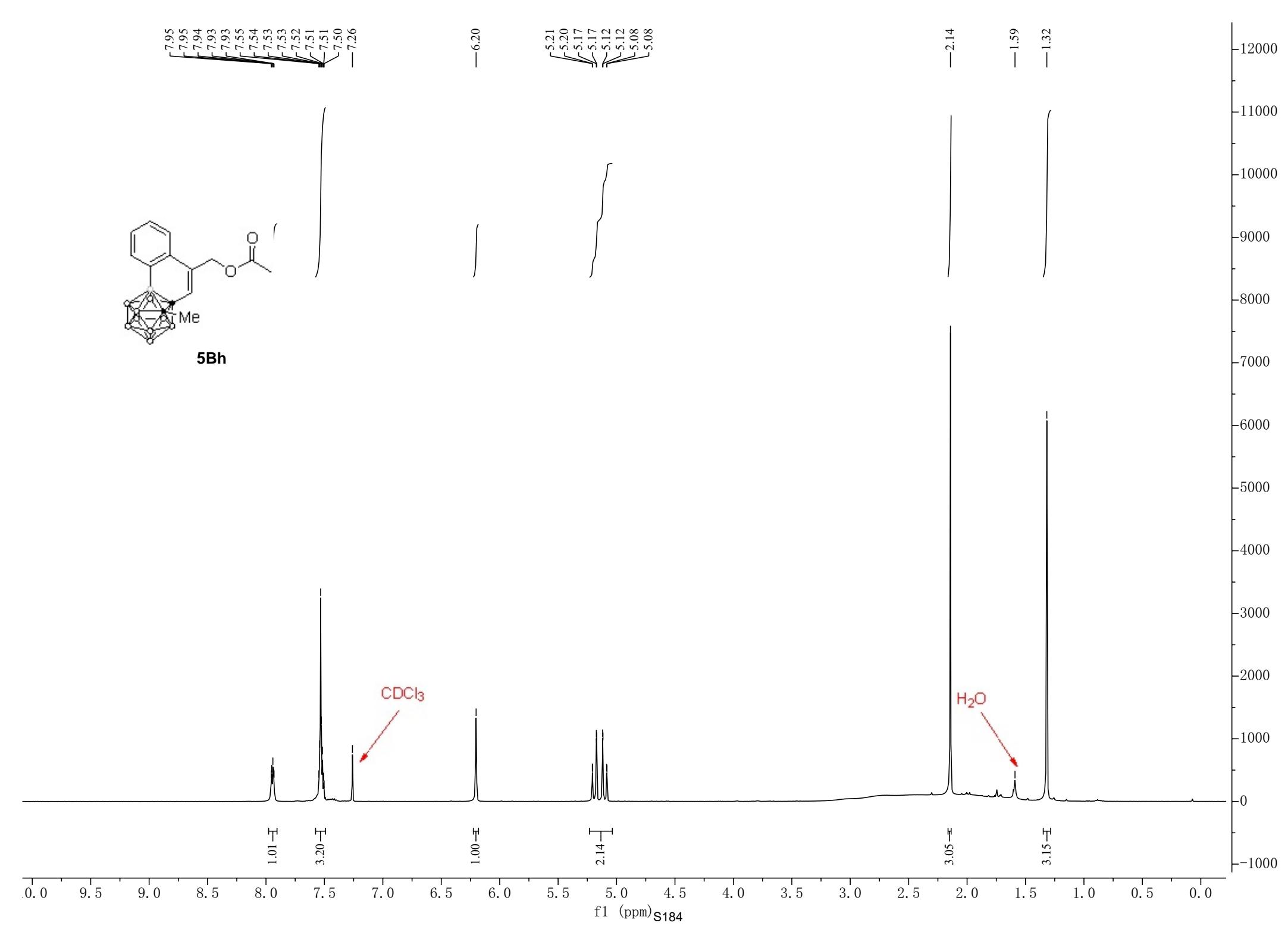


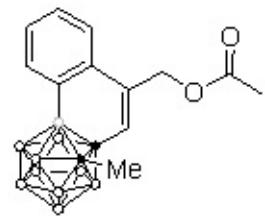
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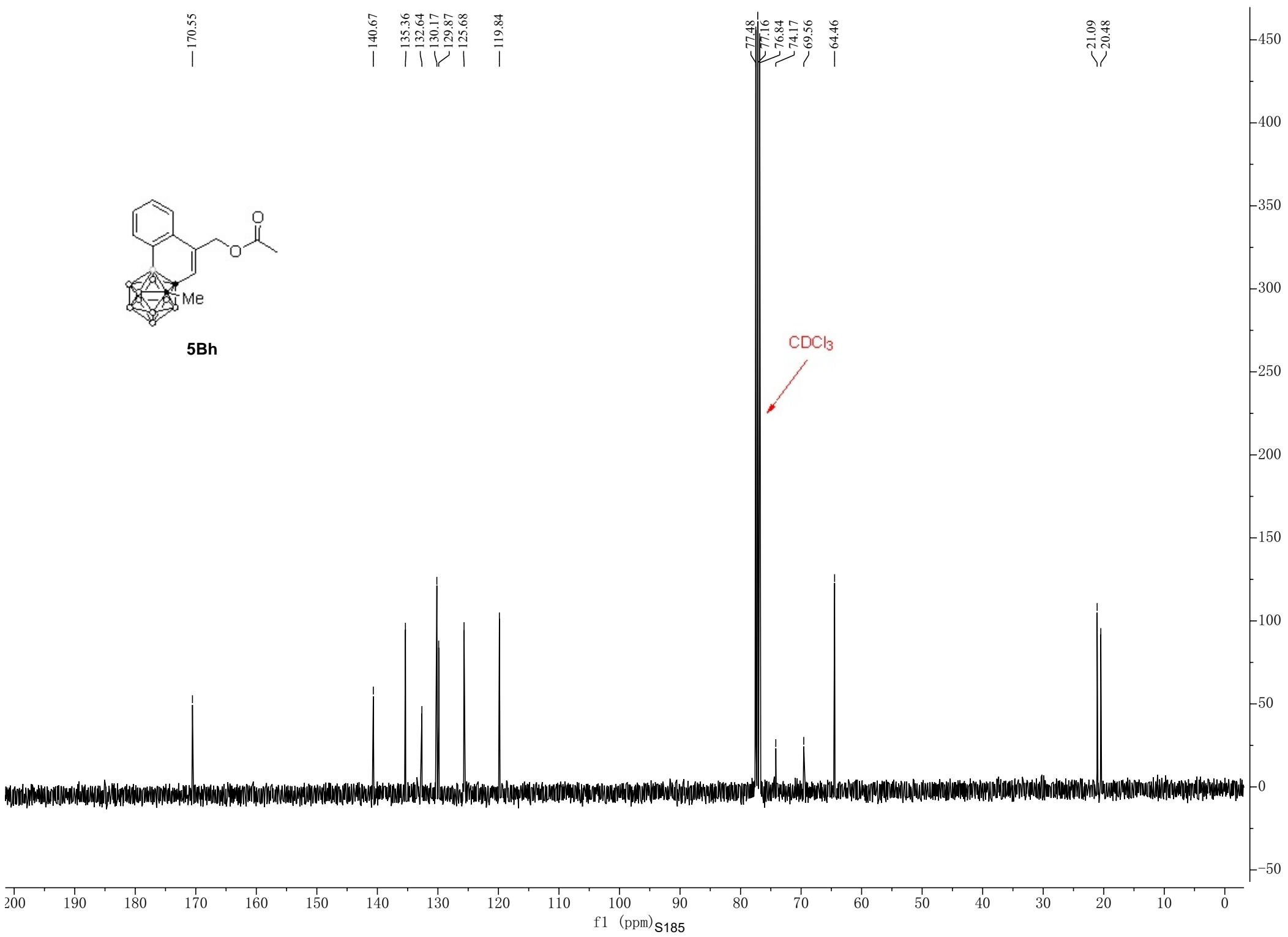


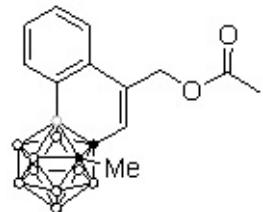
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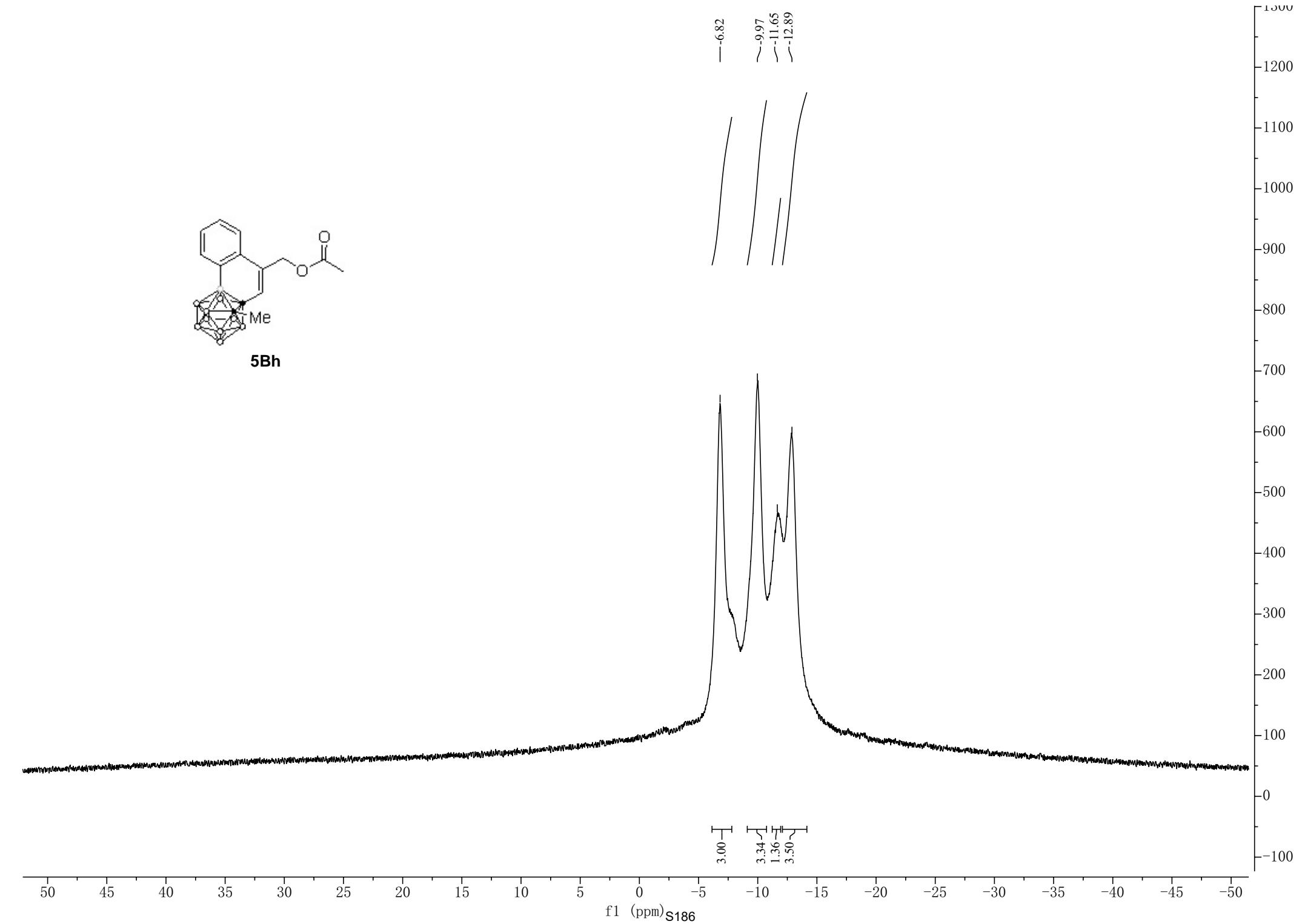


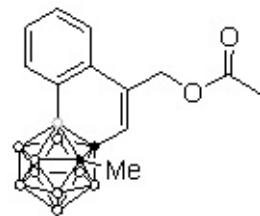
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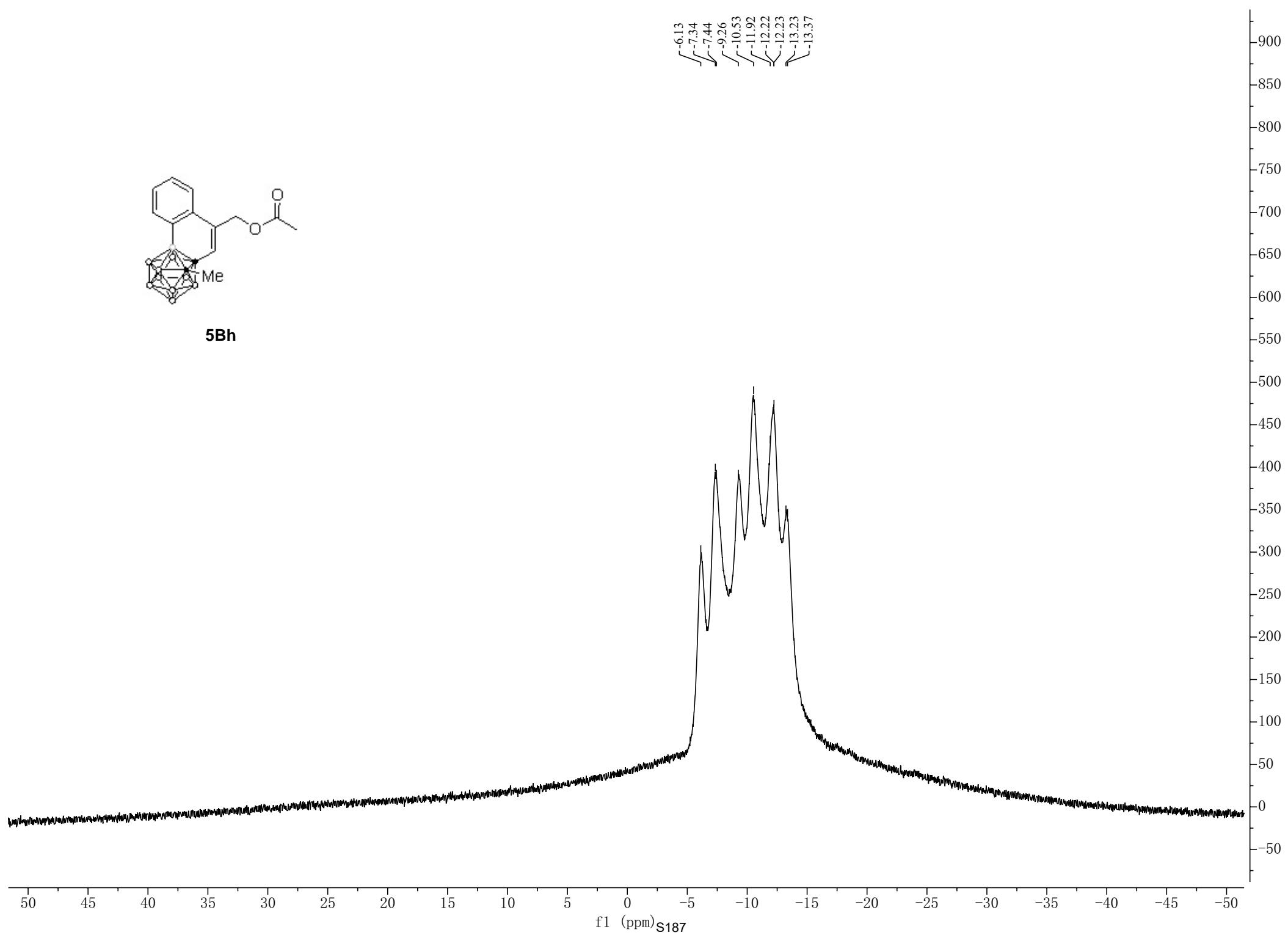


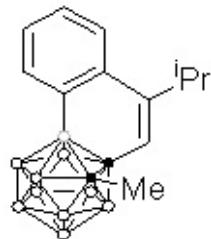
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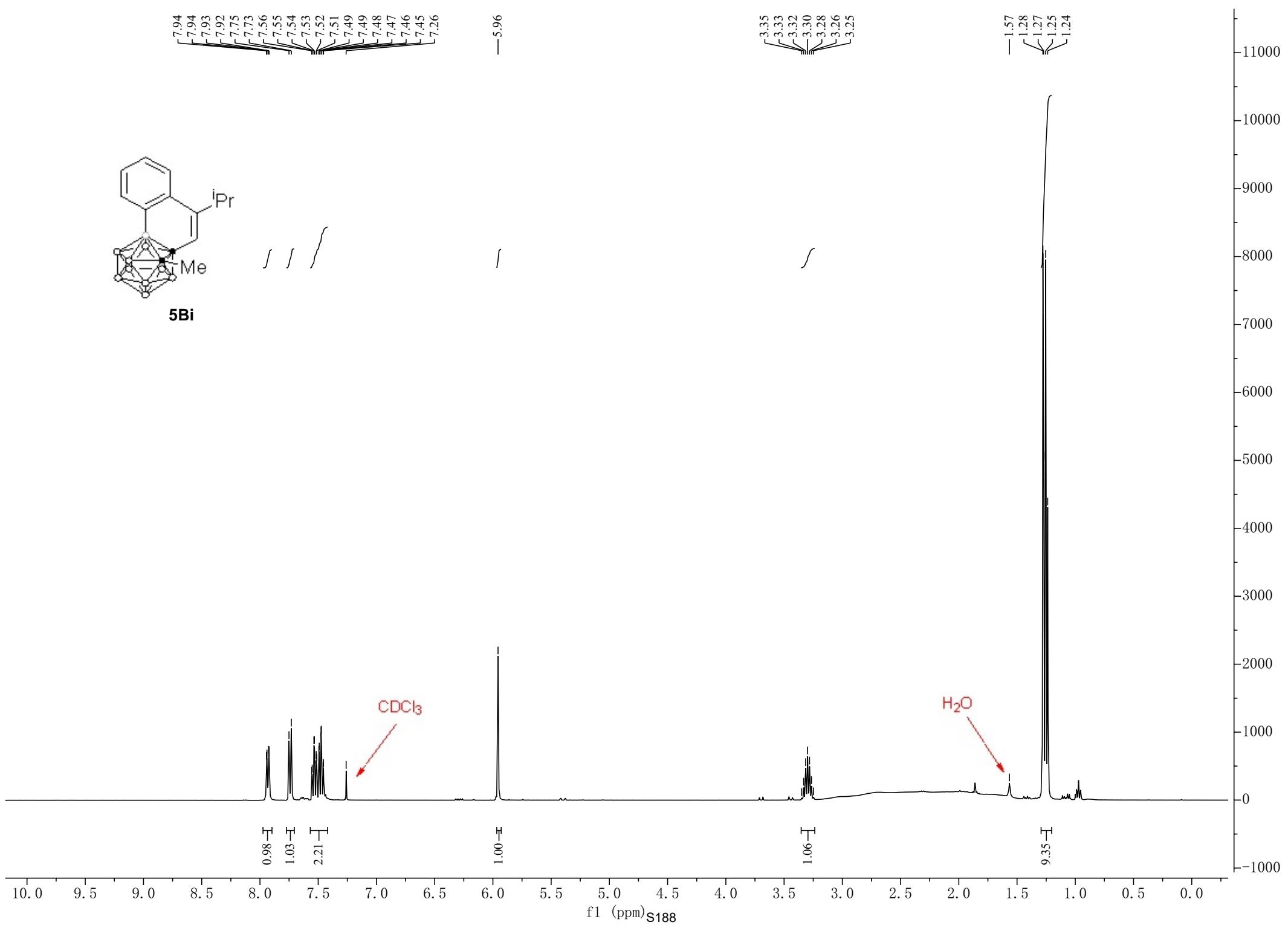


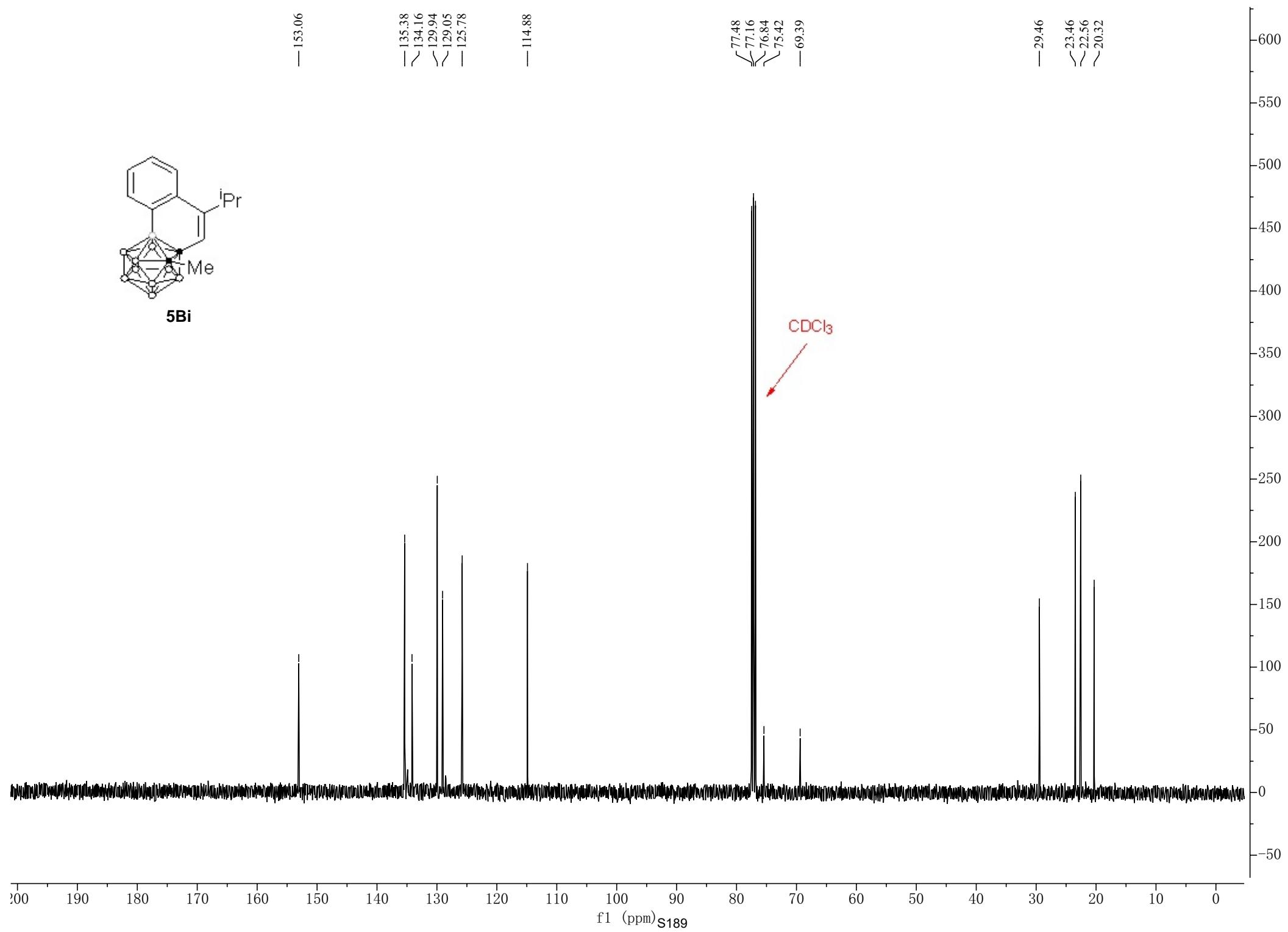
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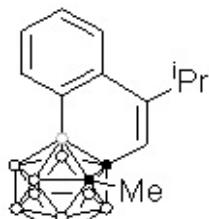




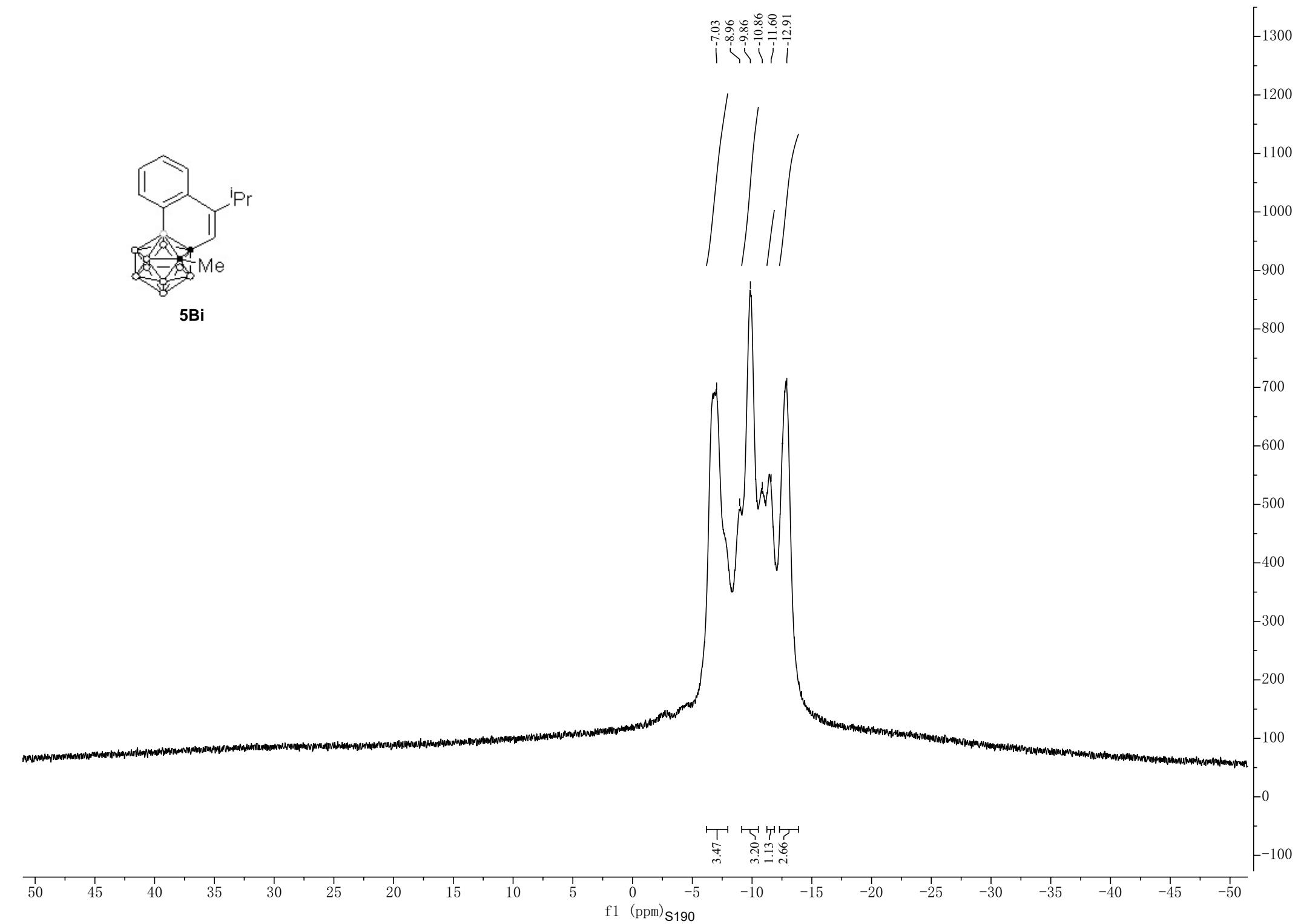
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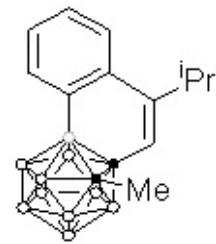




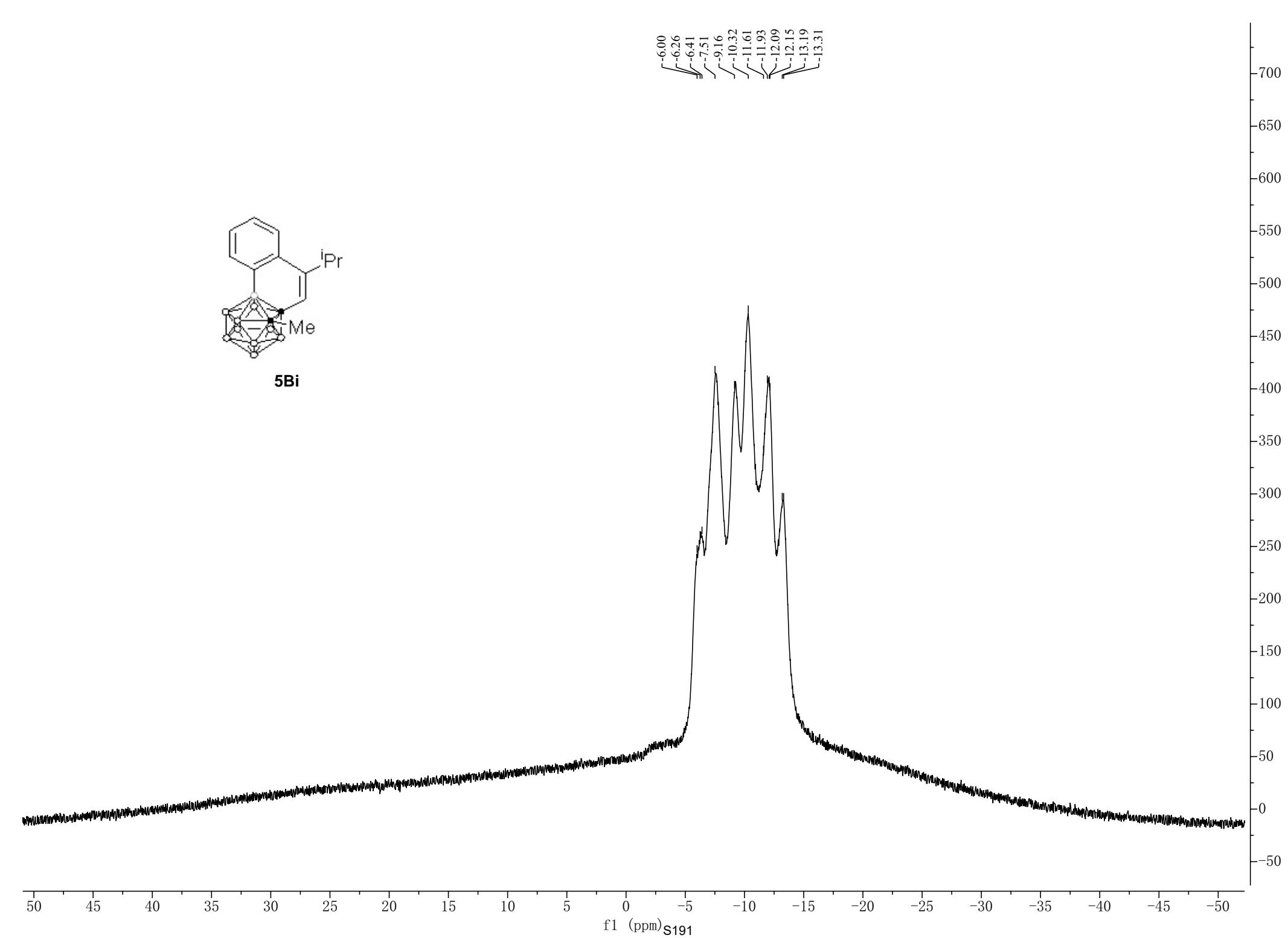


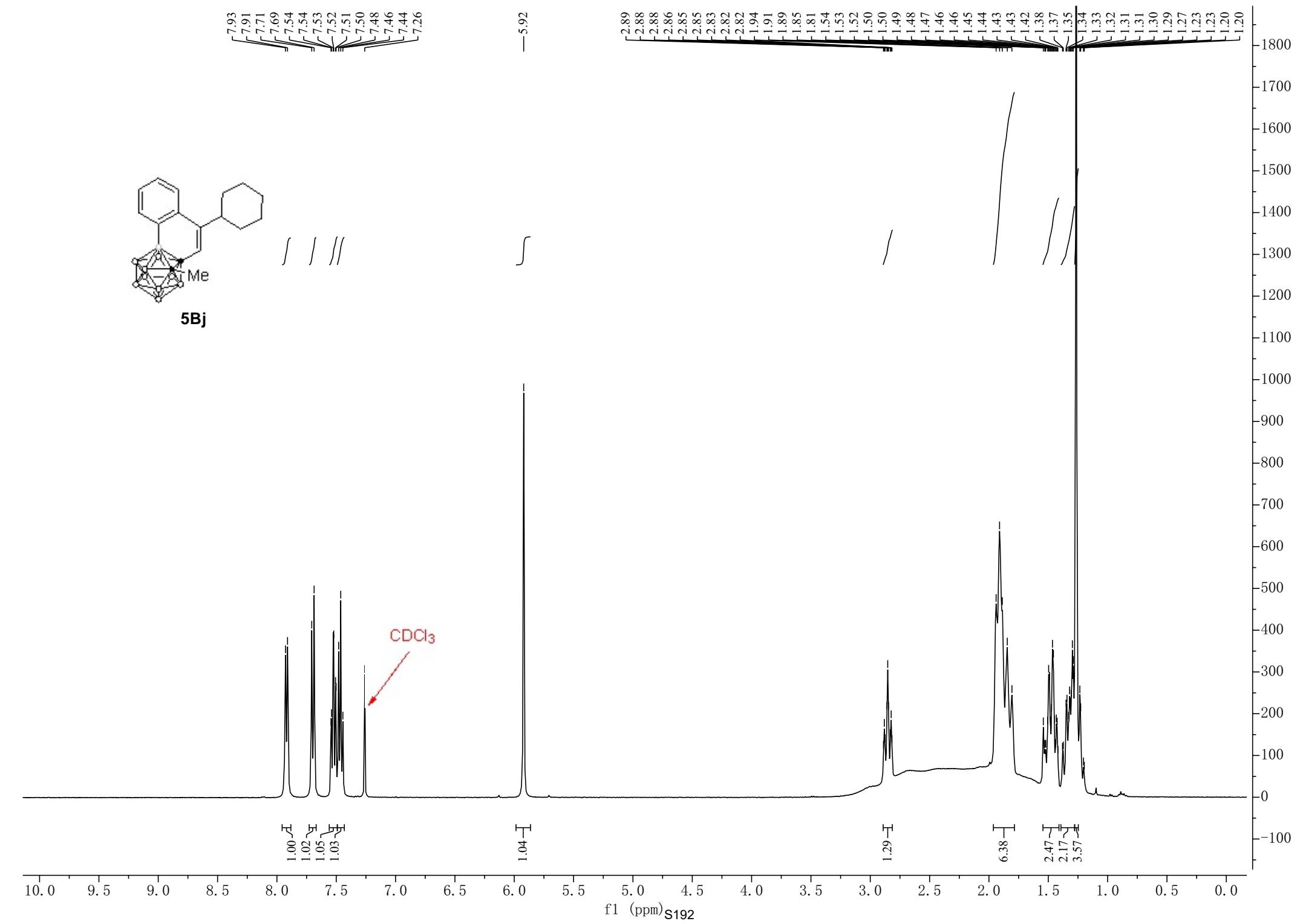
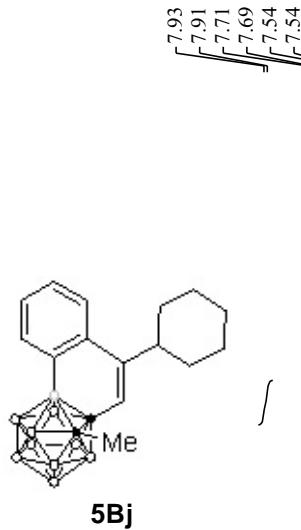
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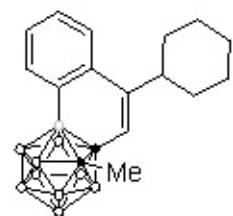




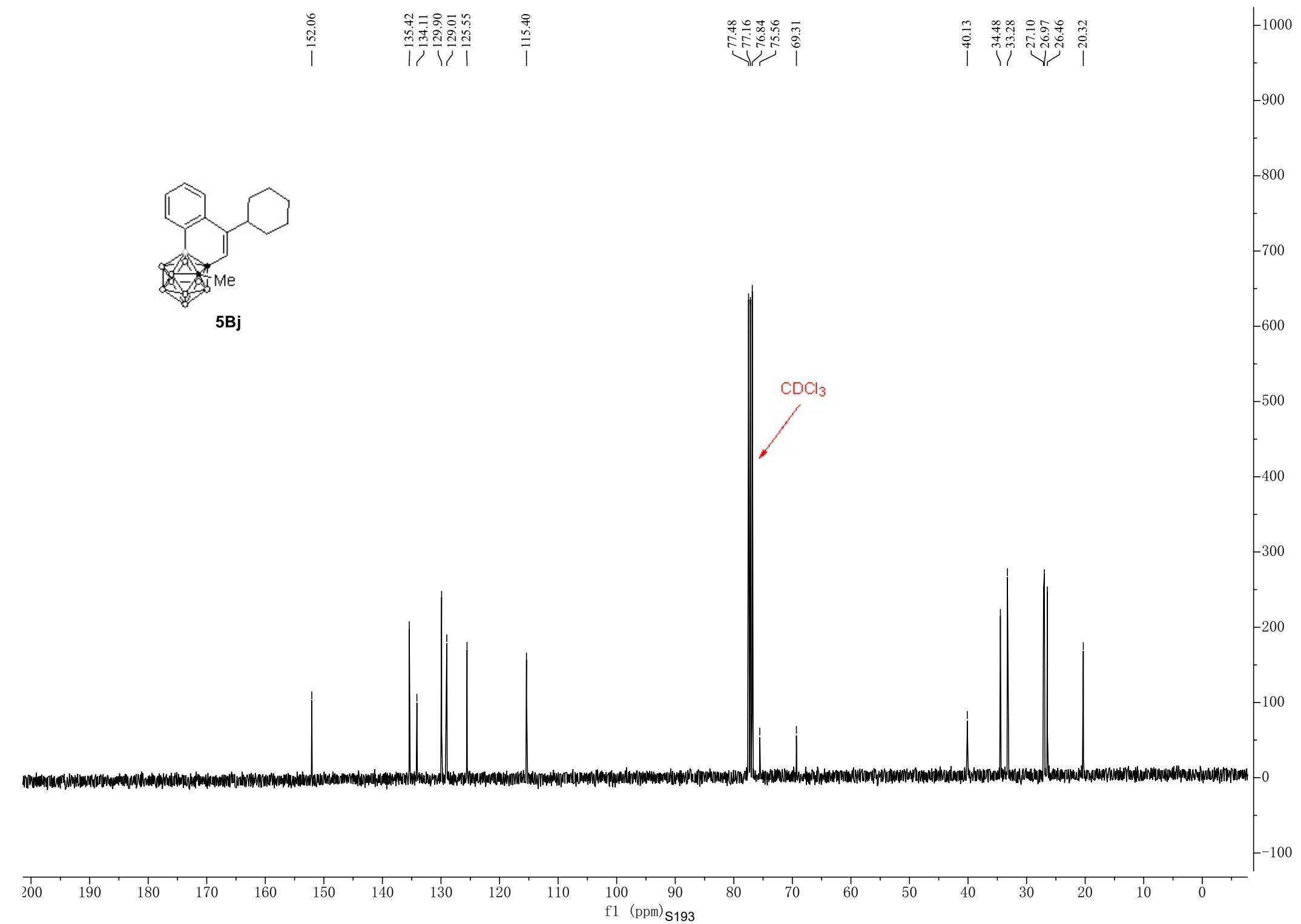
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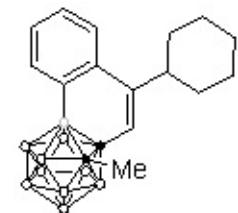




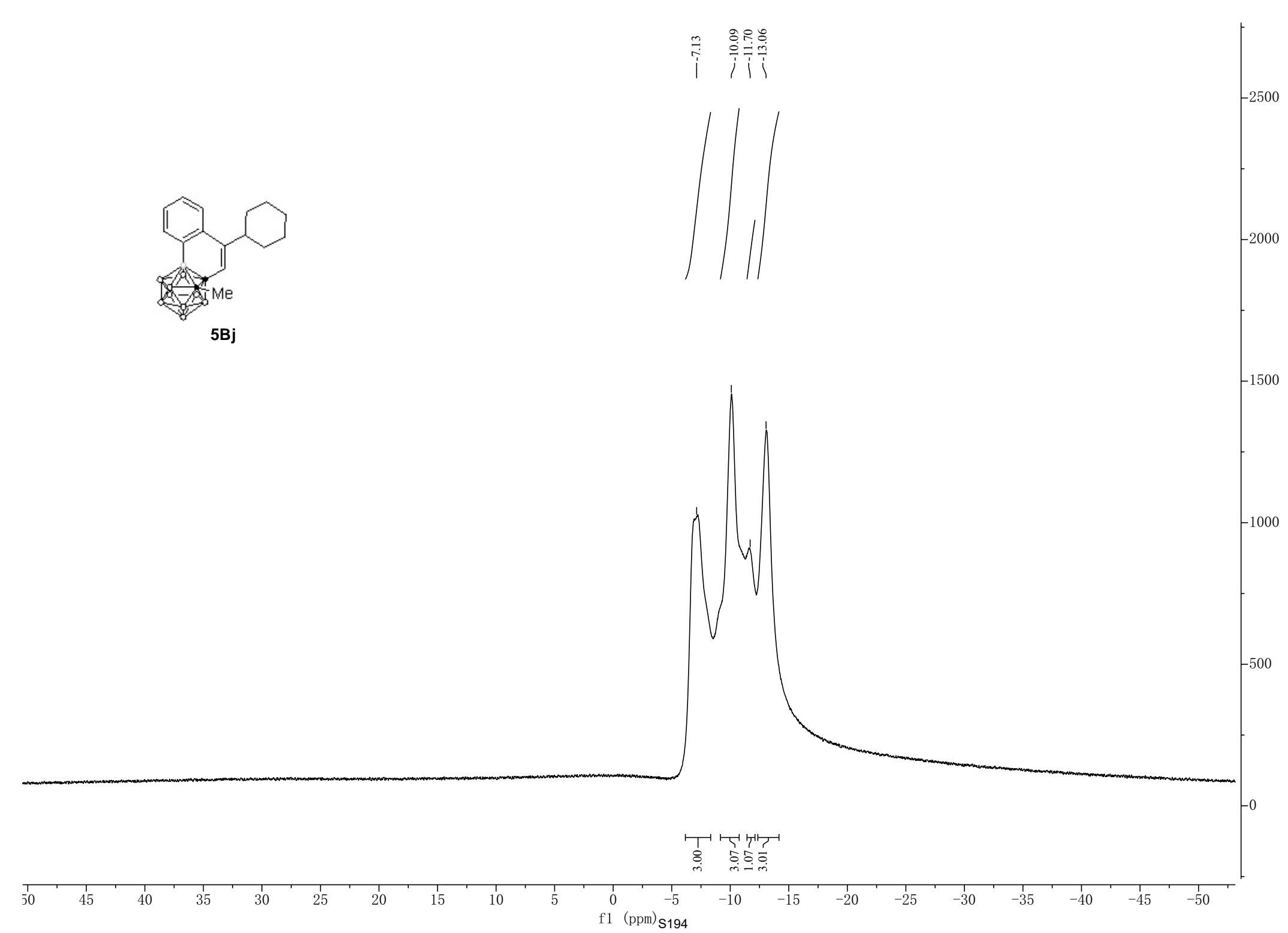


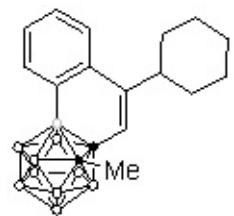
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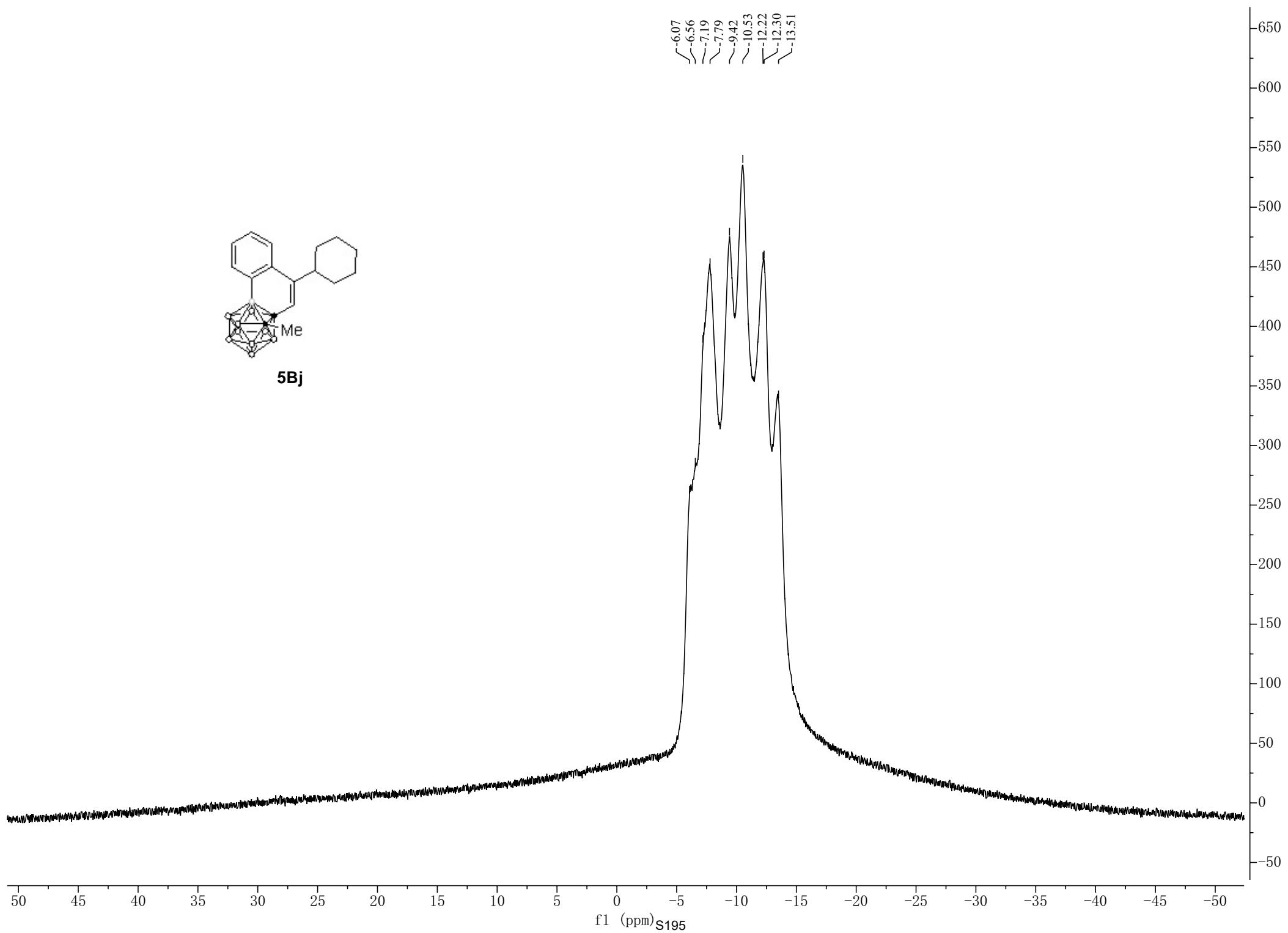


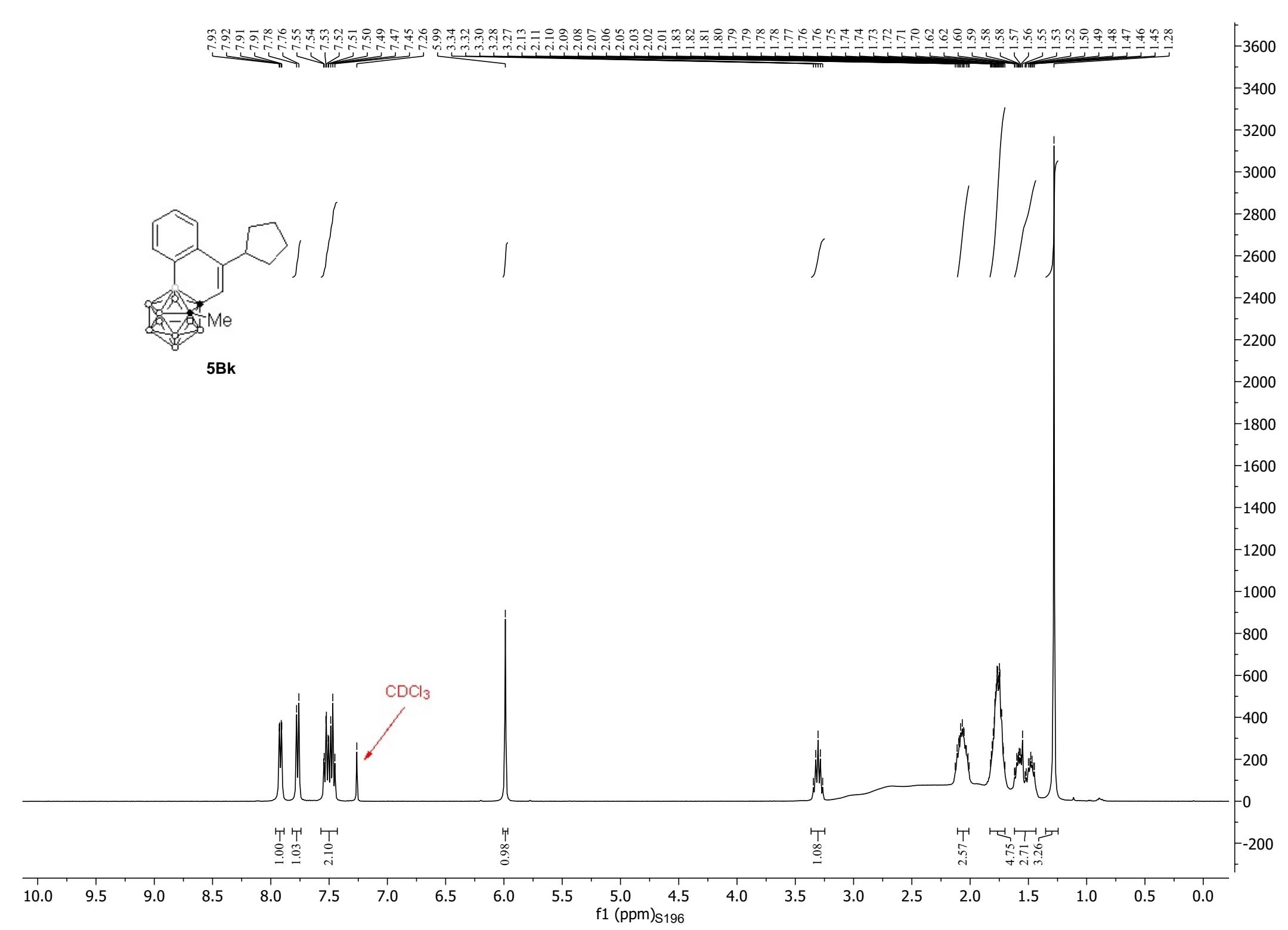
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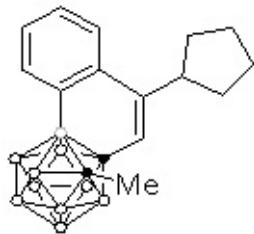




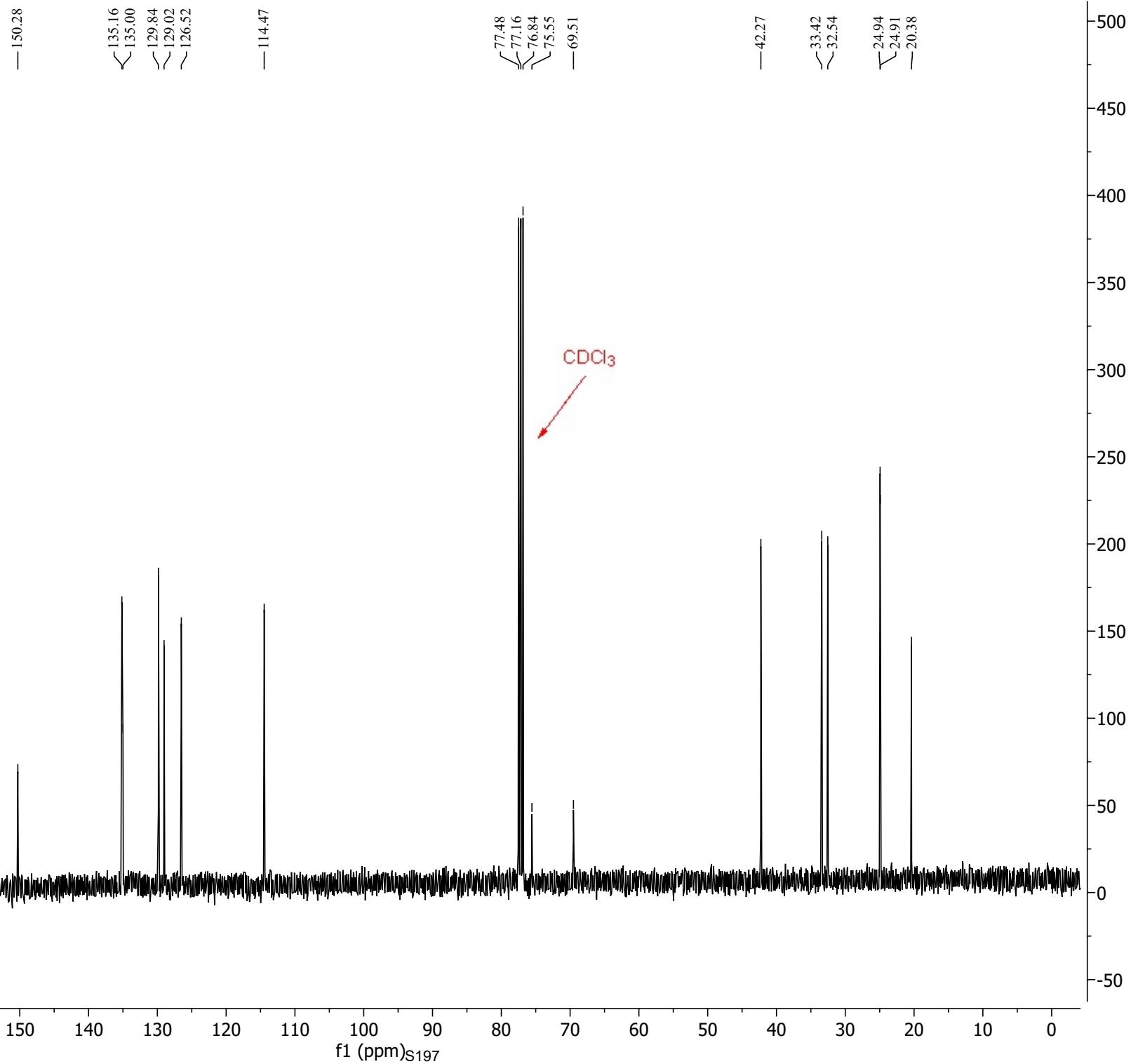
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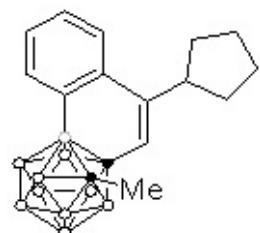




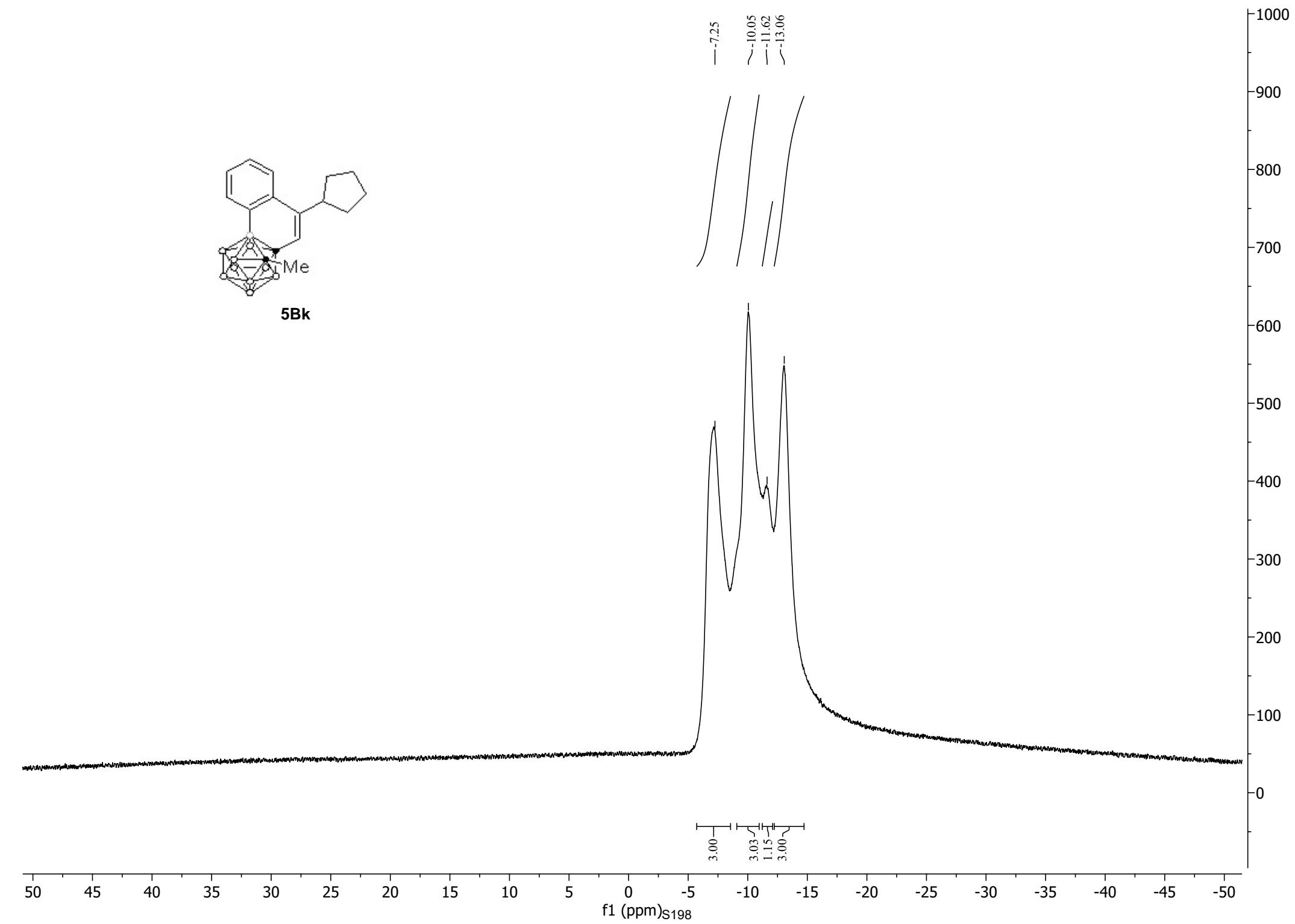


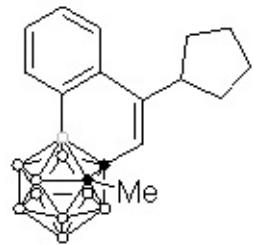
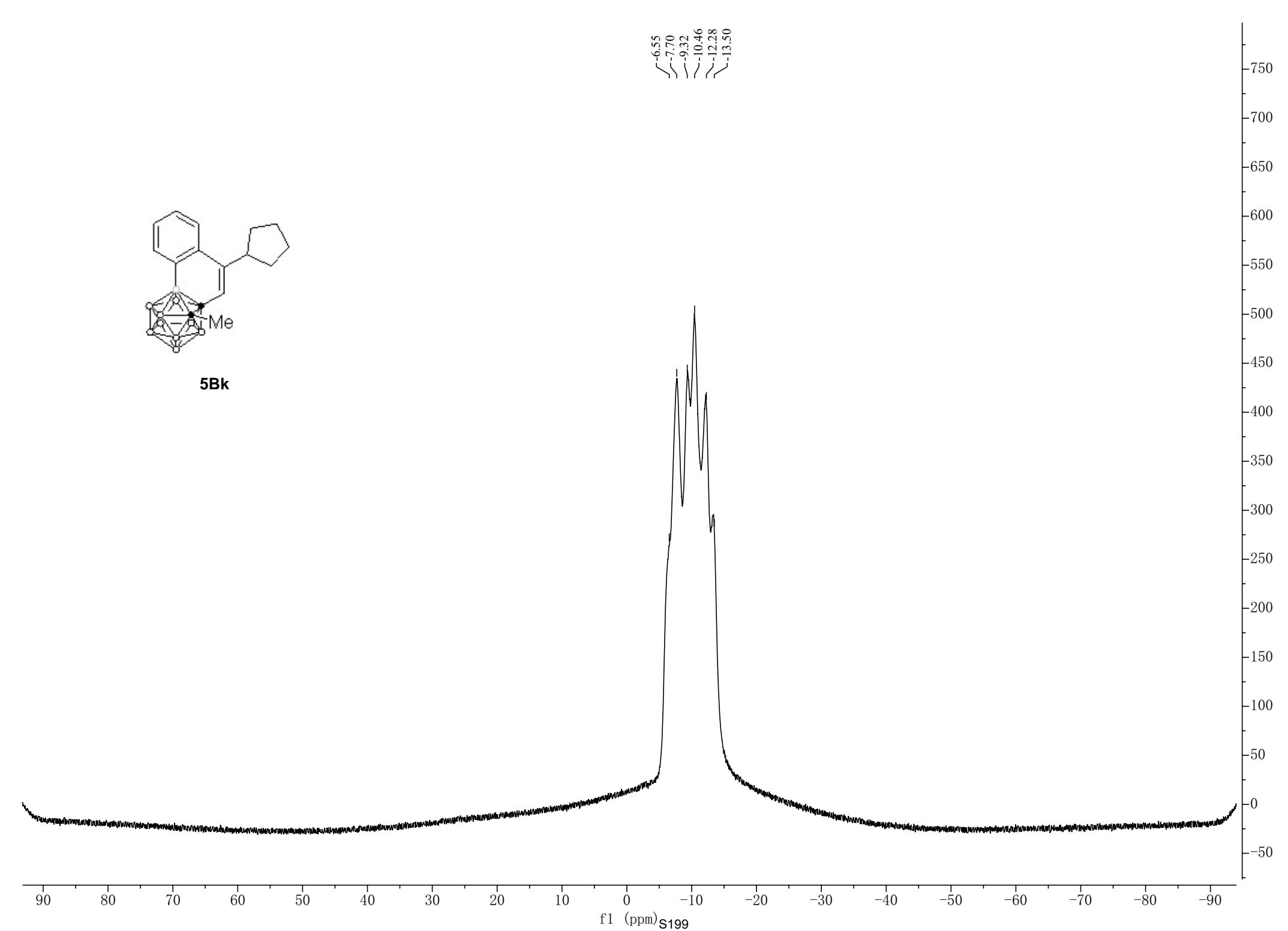
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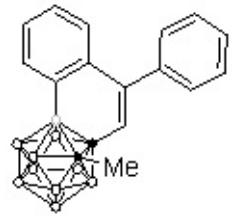


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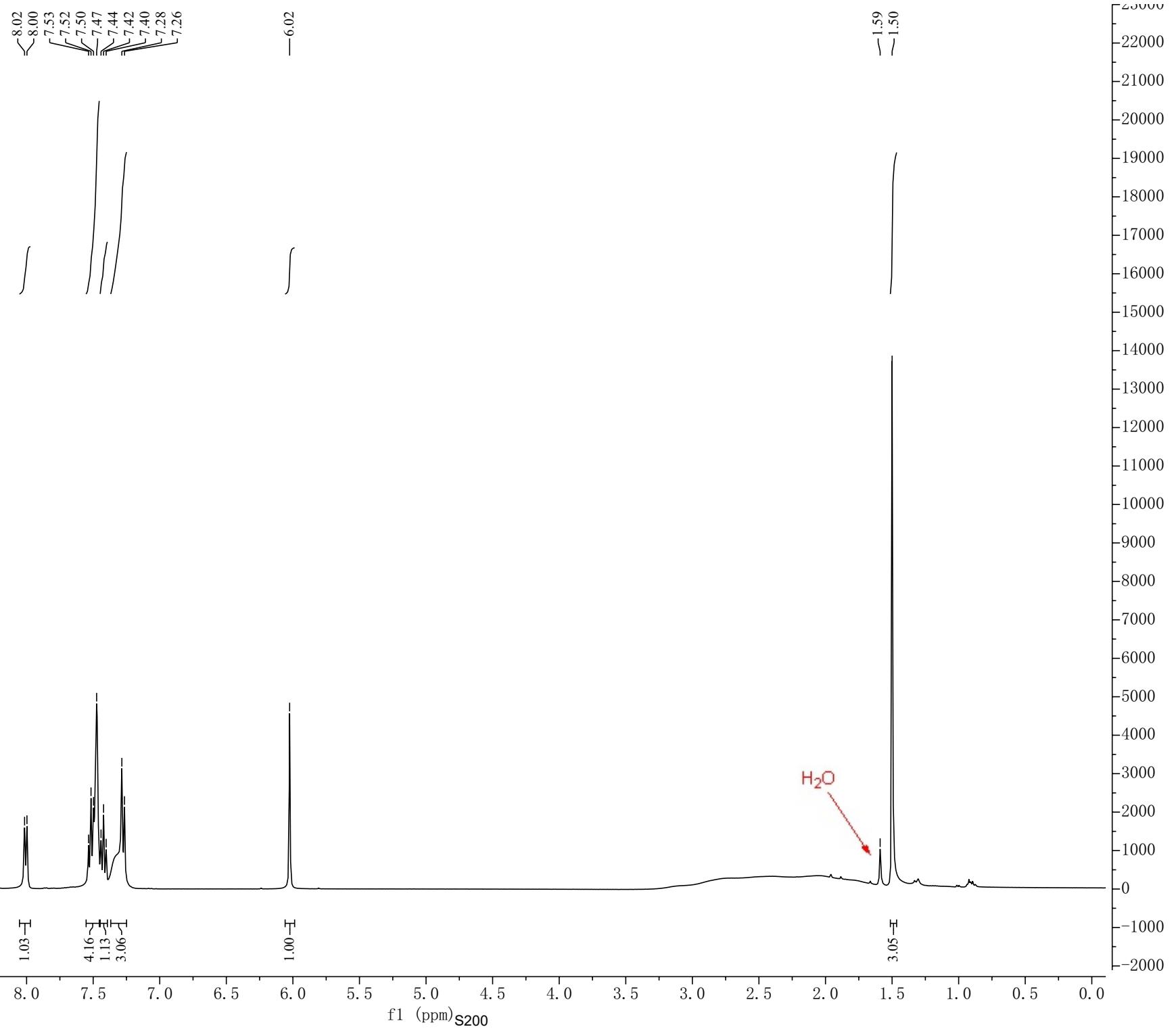


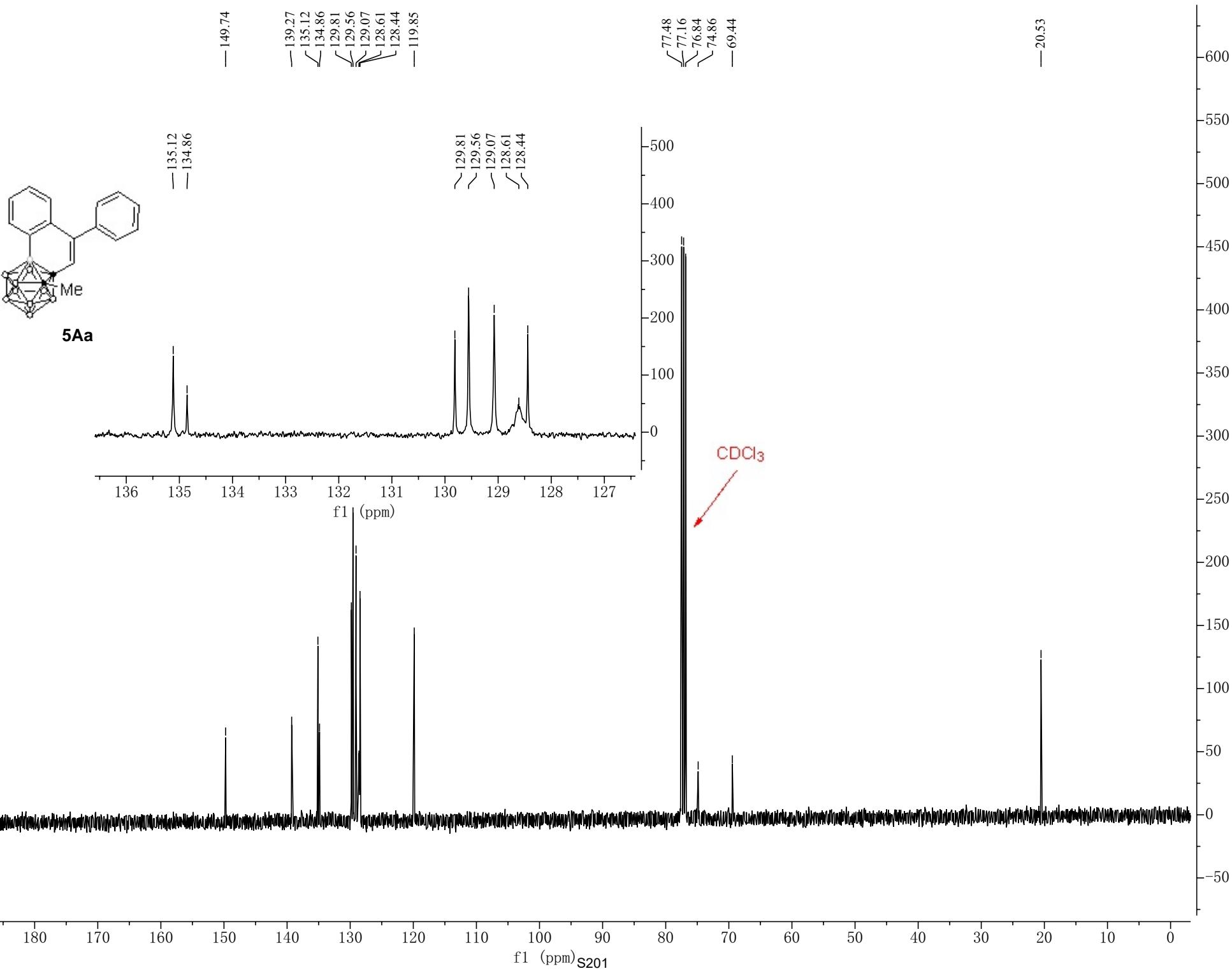


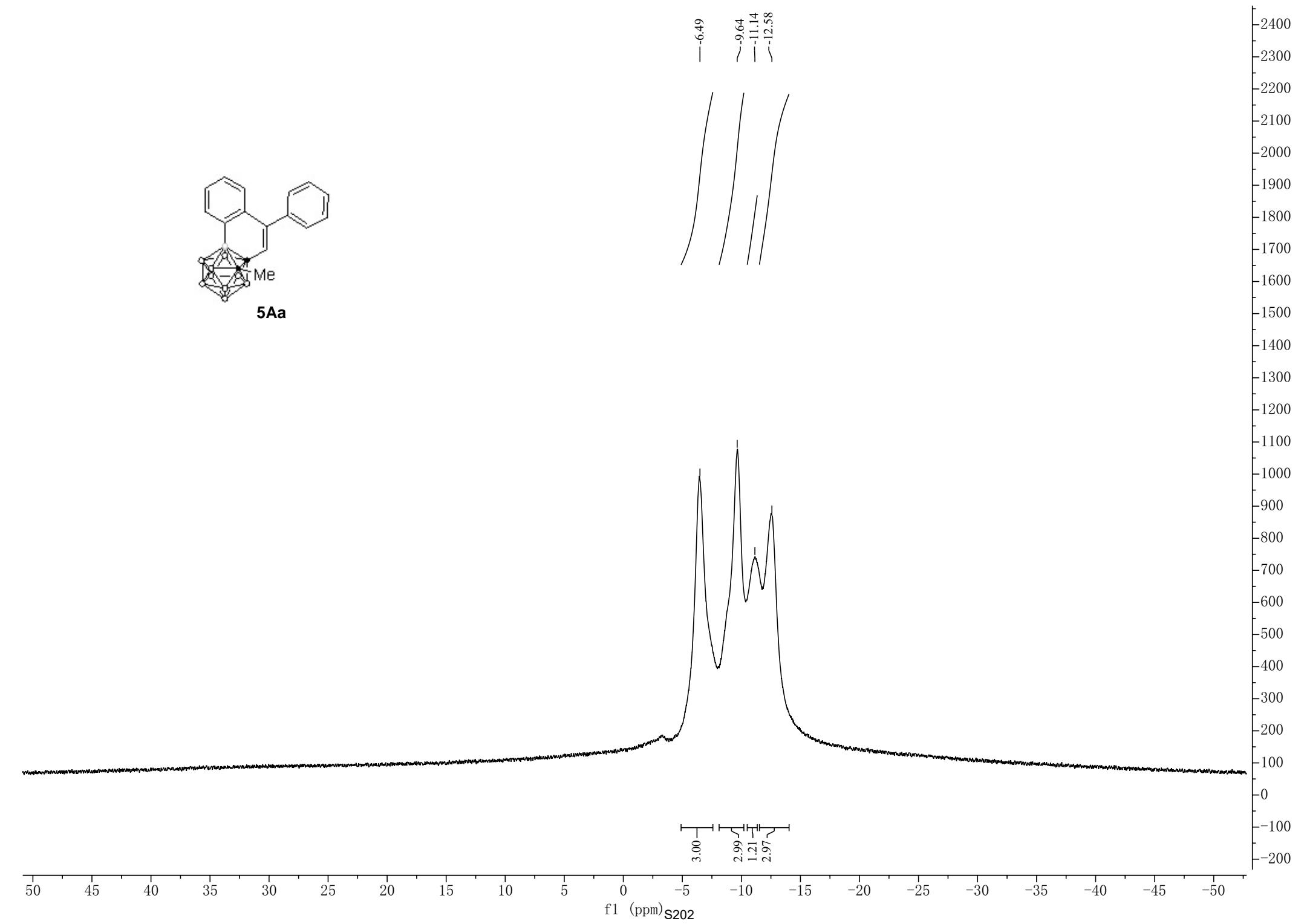
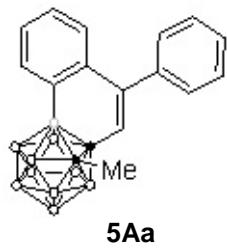
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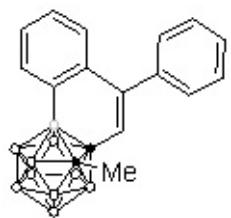


5Aa

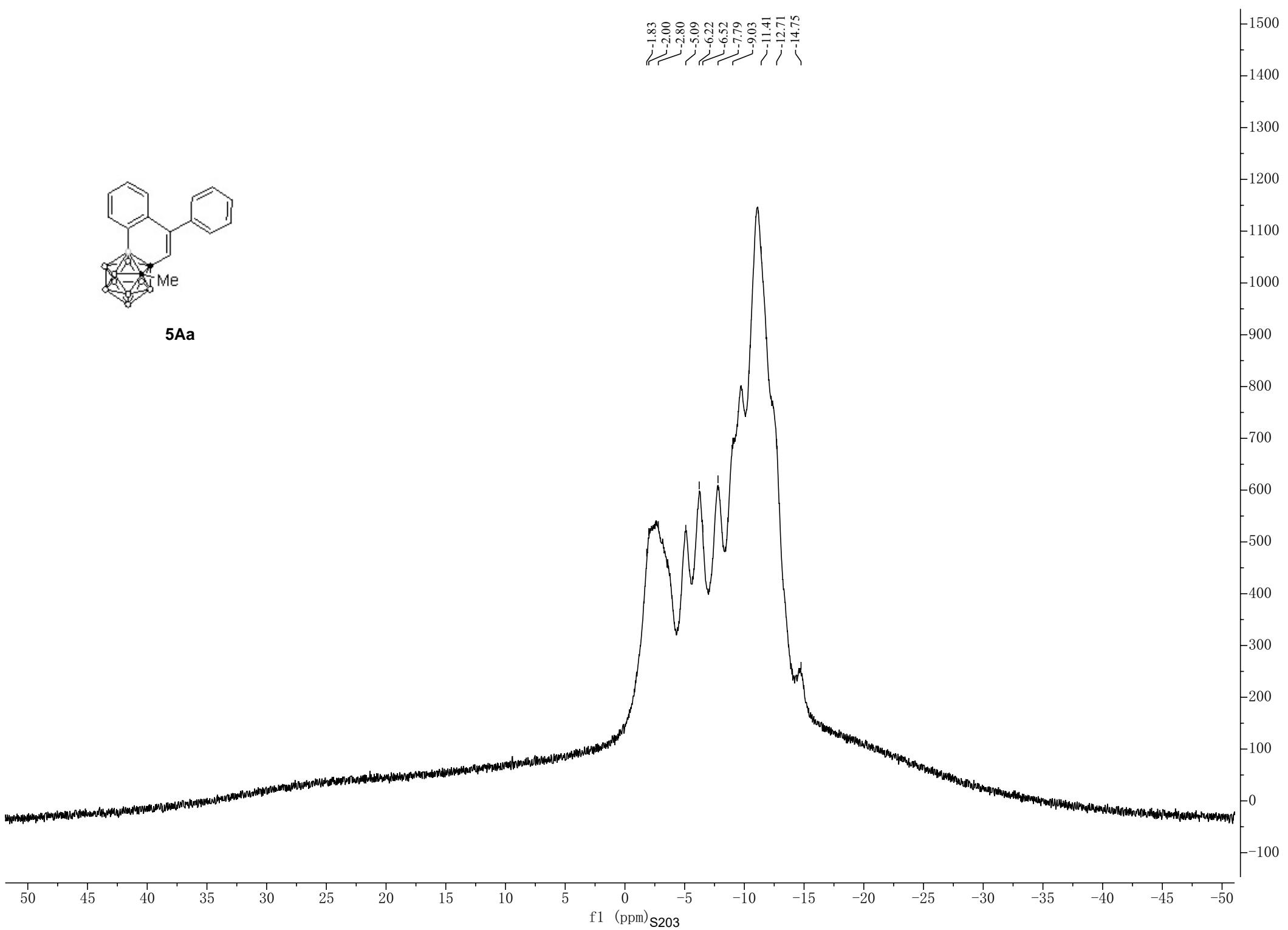


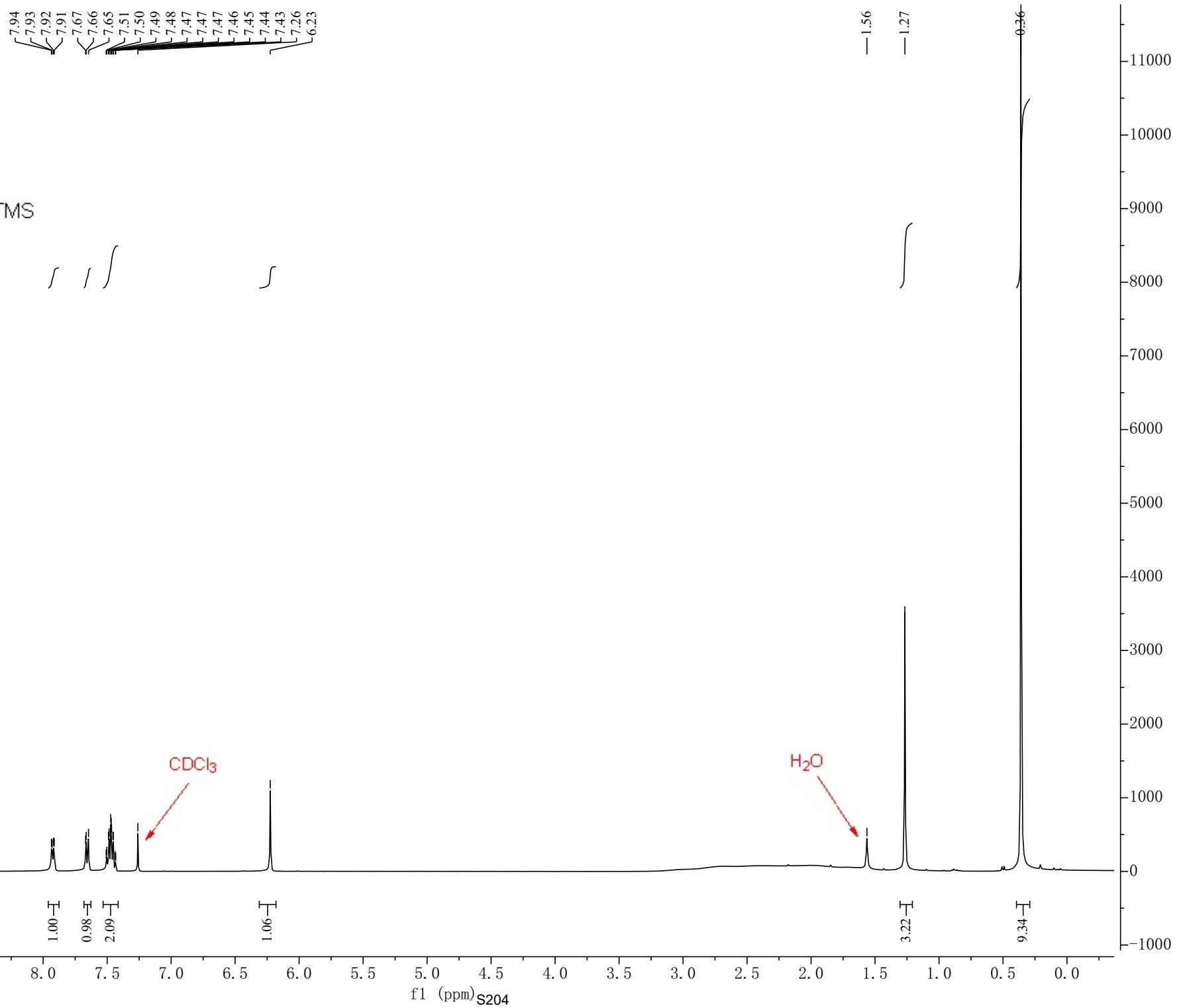
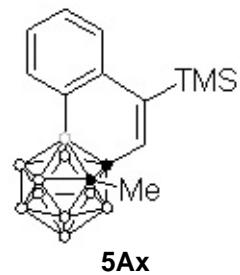


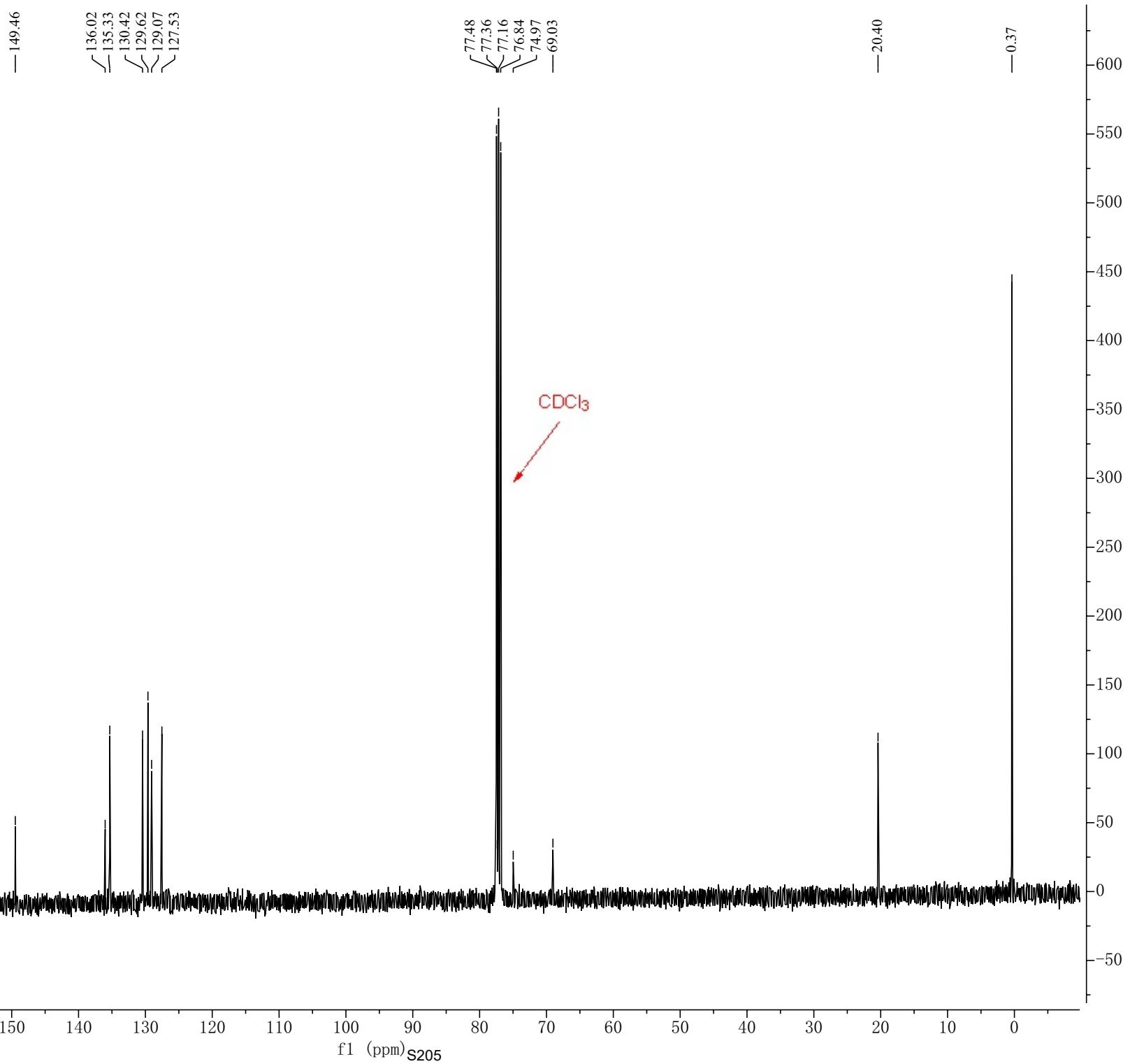
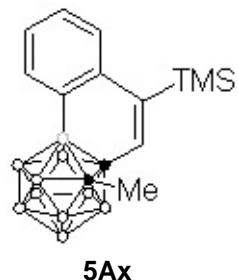


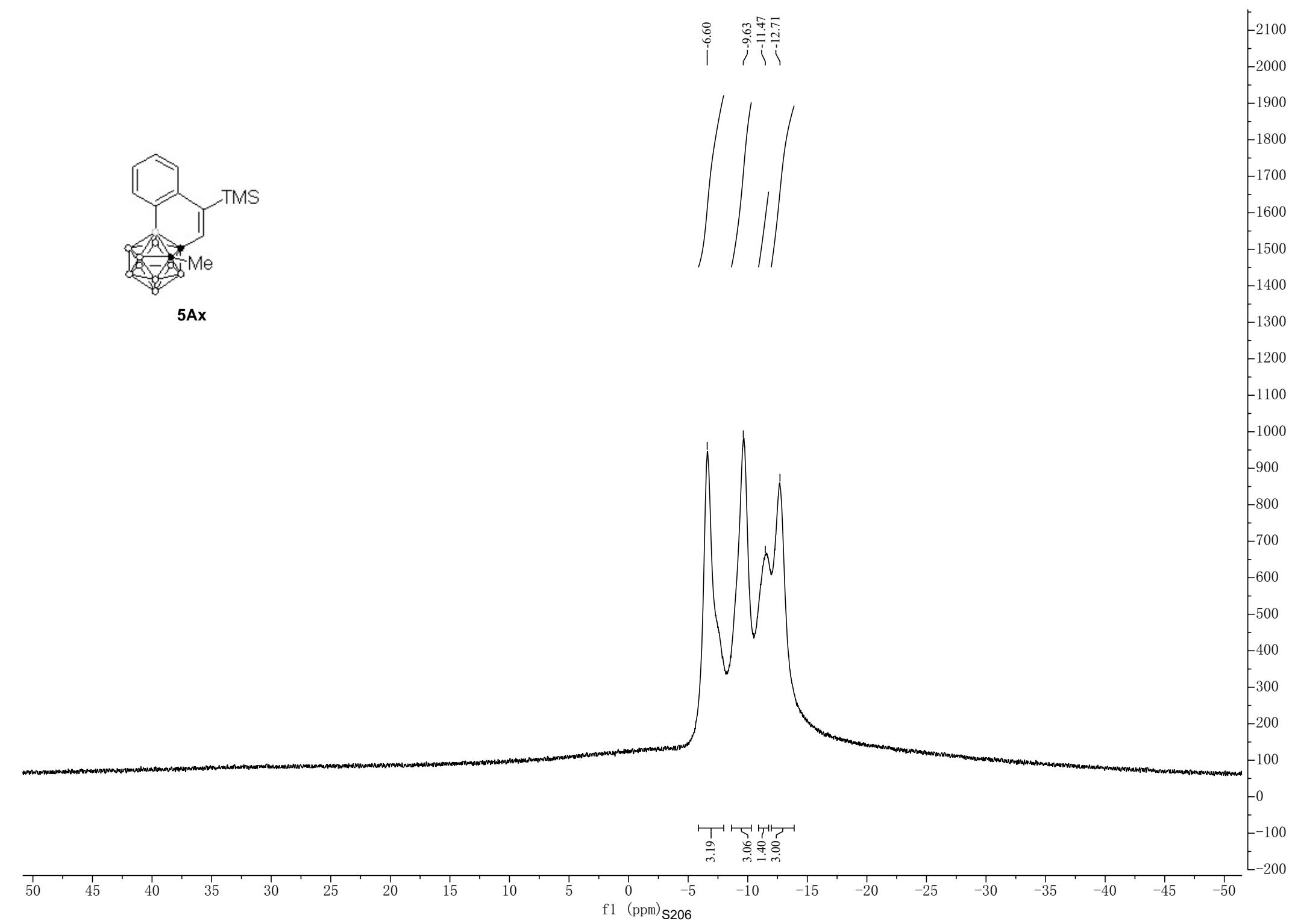
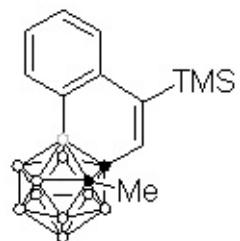


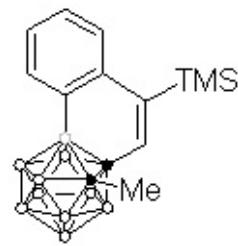
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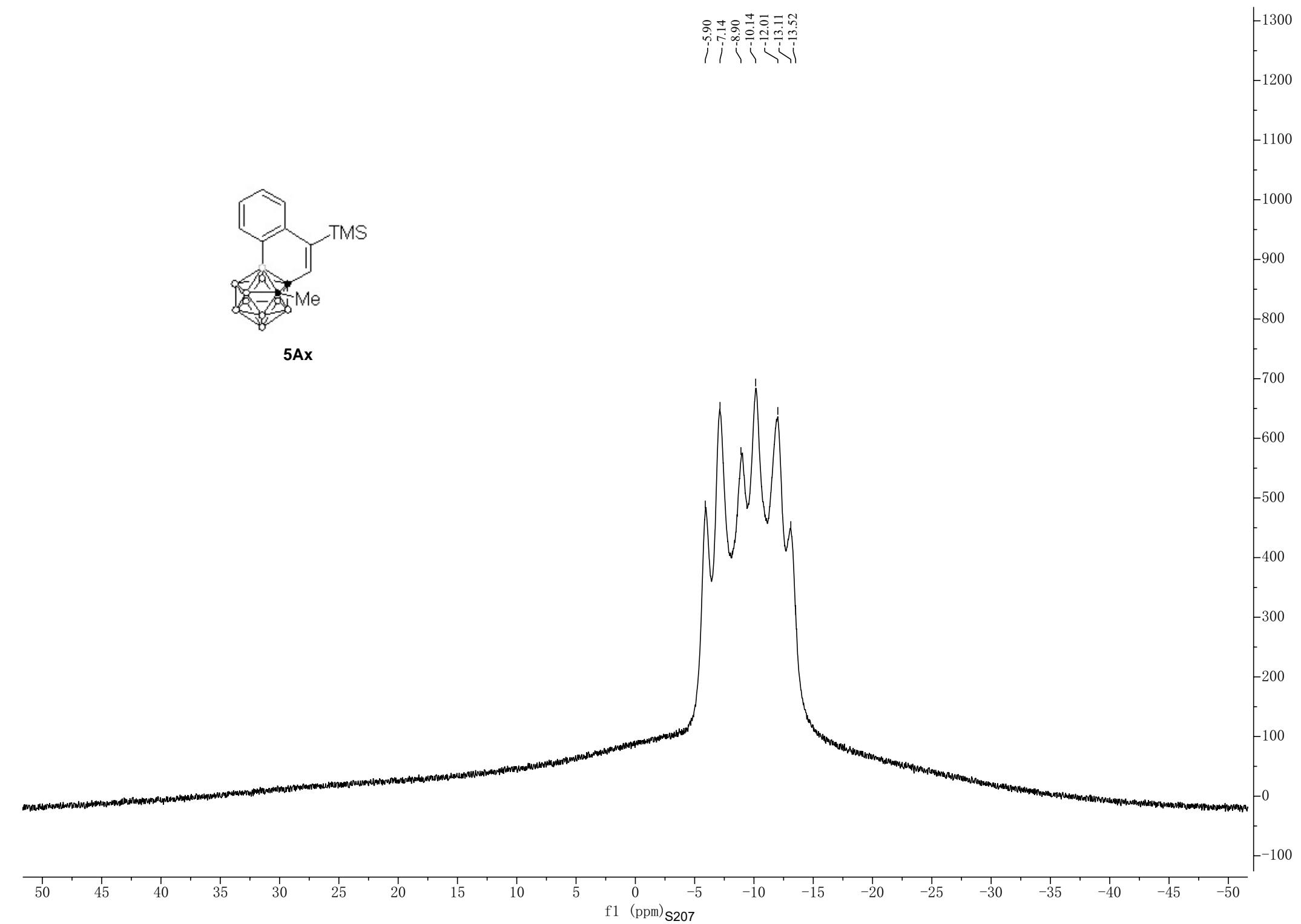


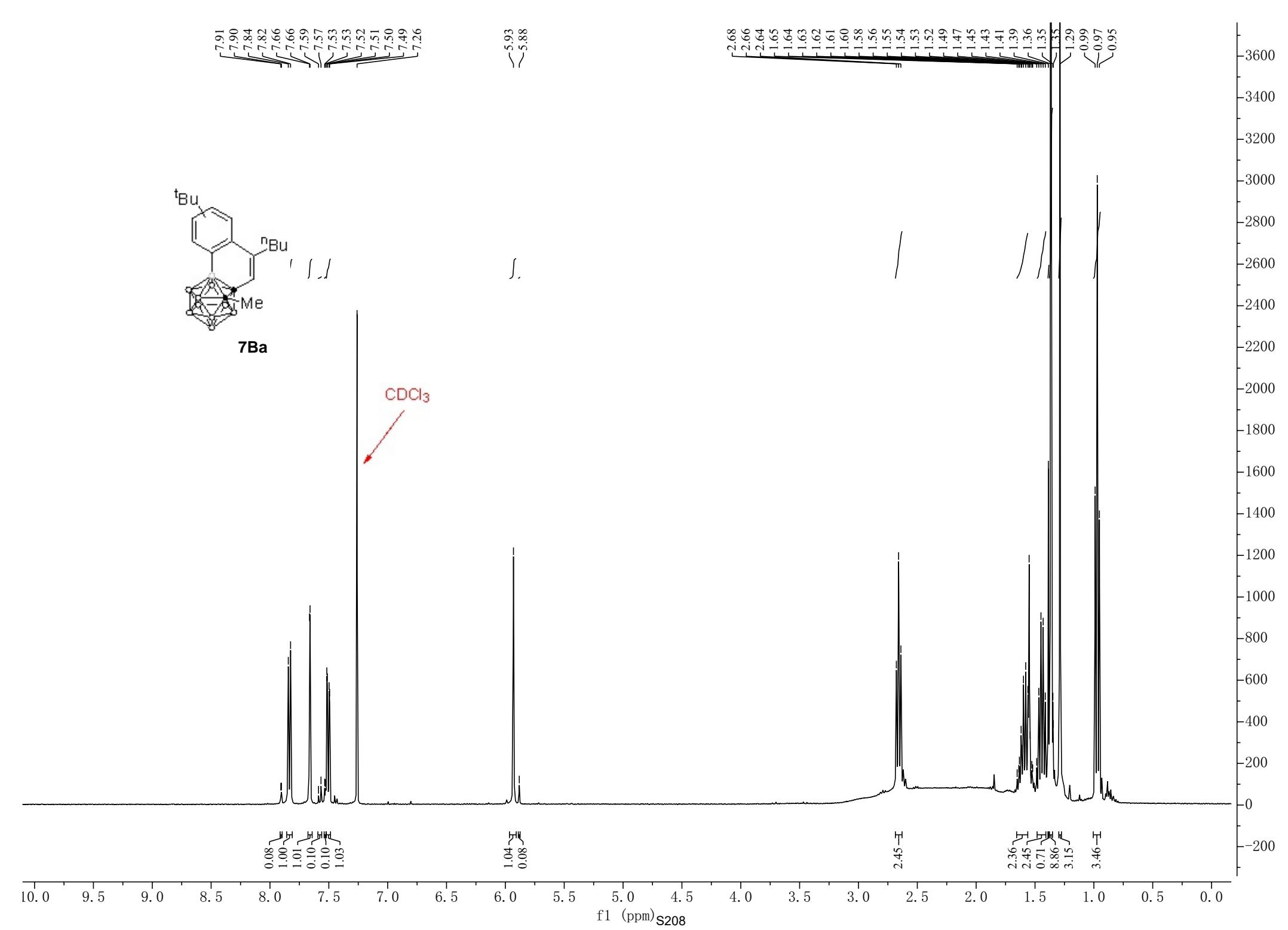


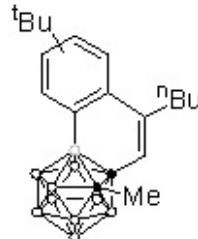




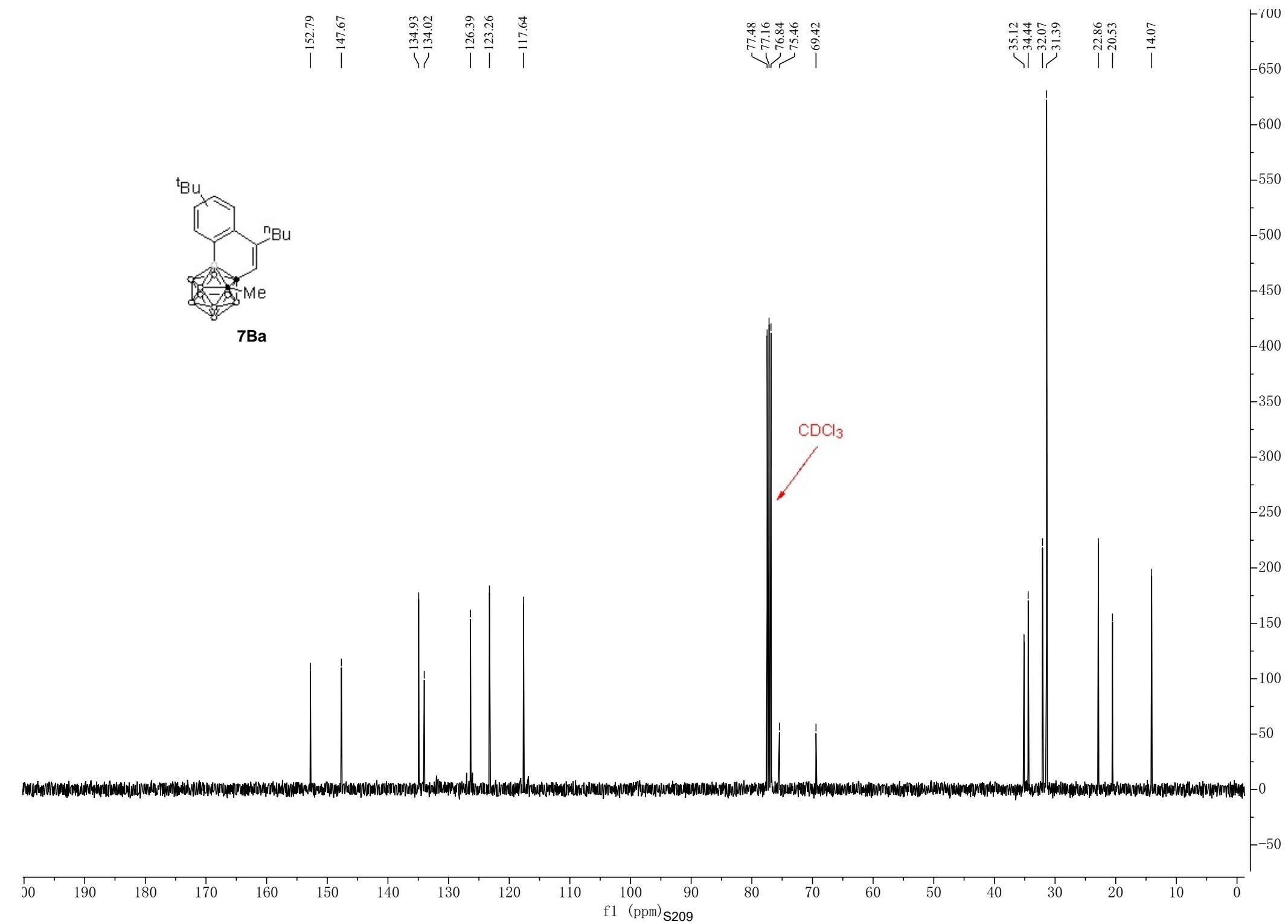
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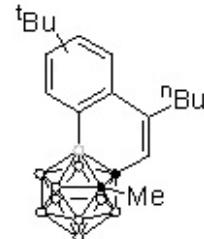




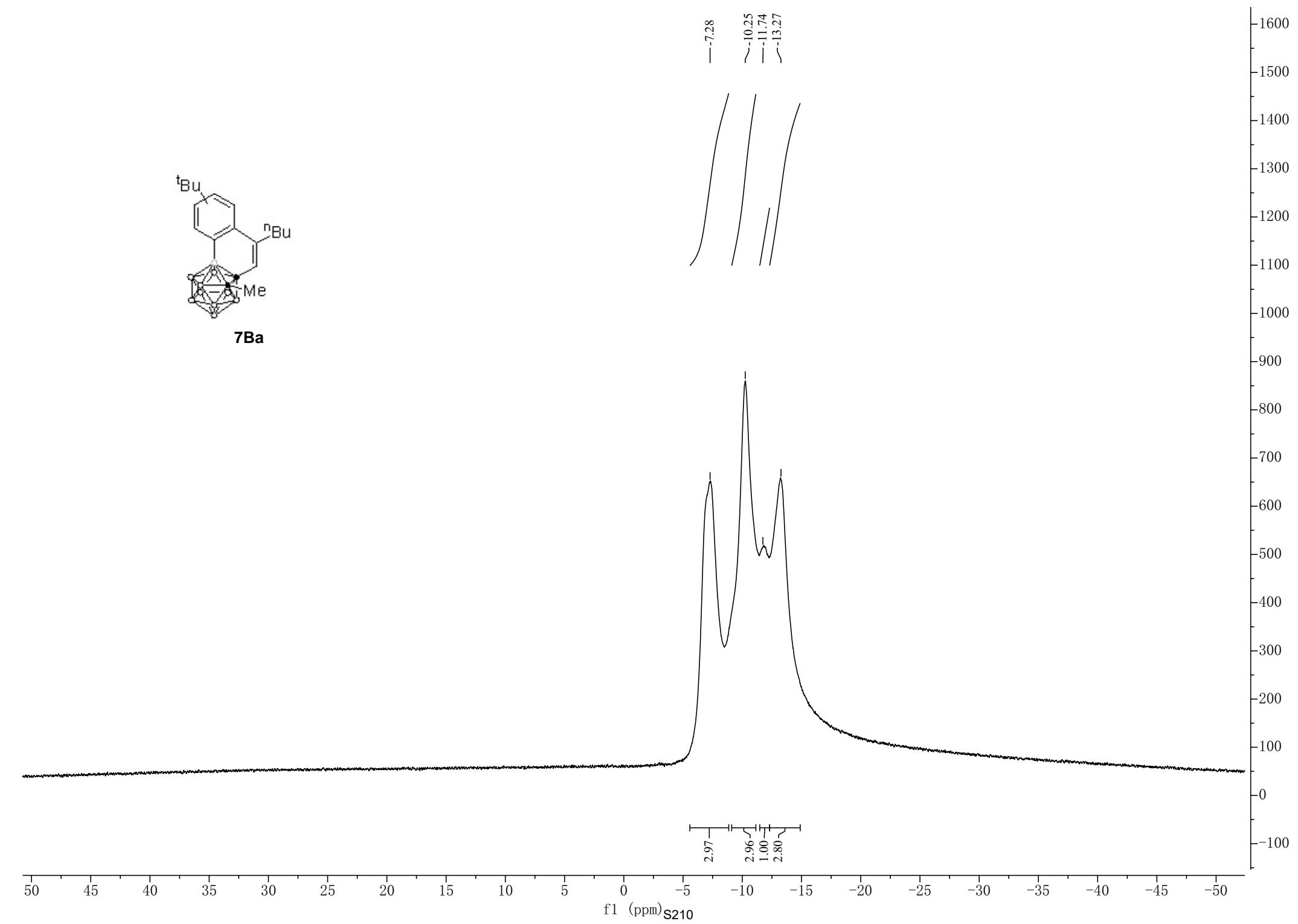


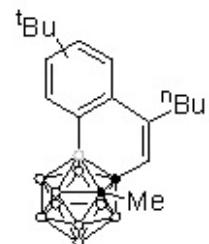
7Ba



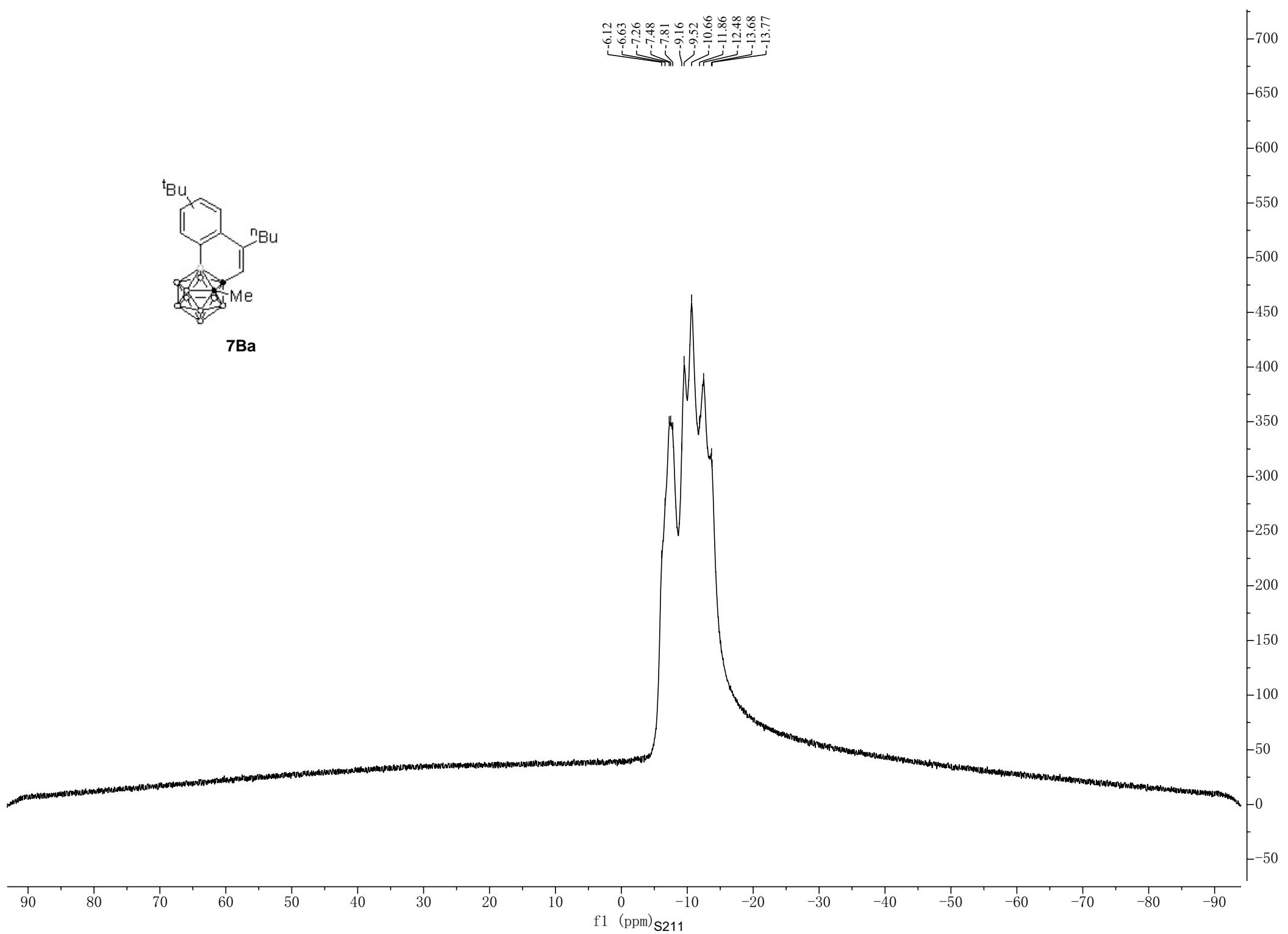


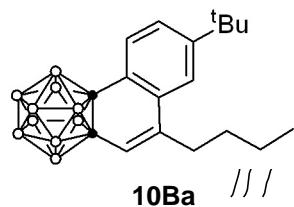
7Ba





7Ba





1.00
0.92
0.99

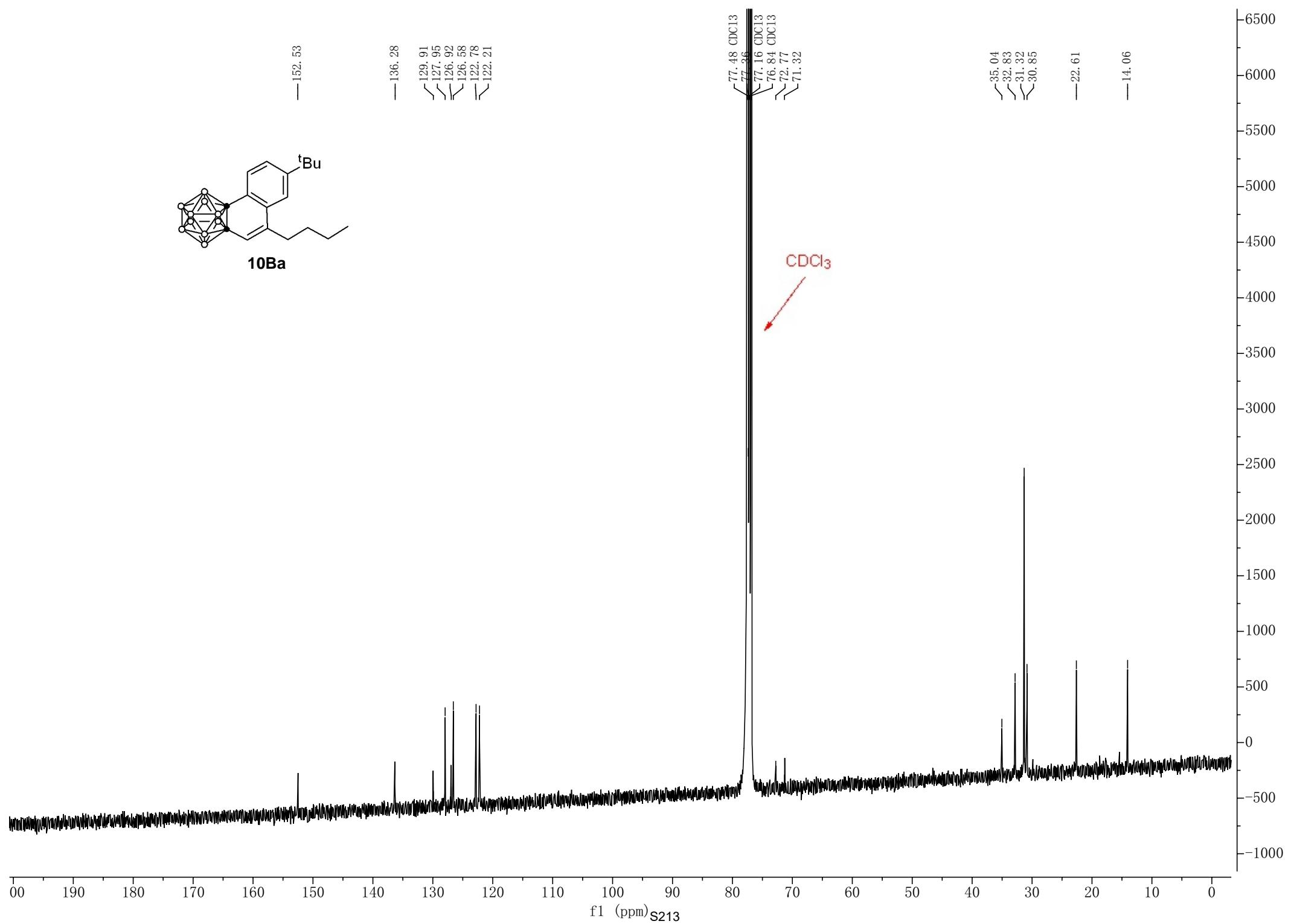
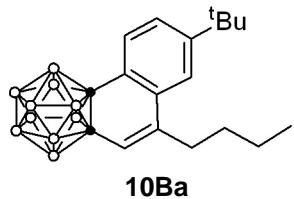
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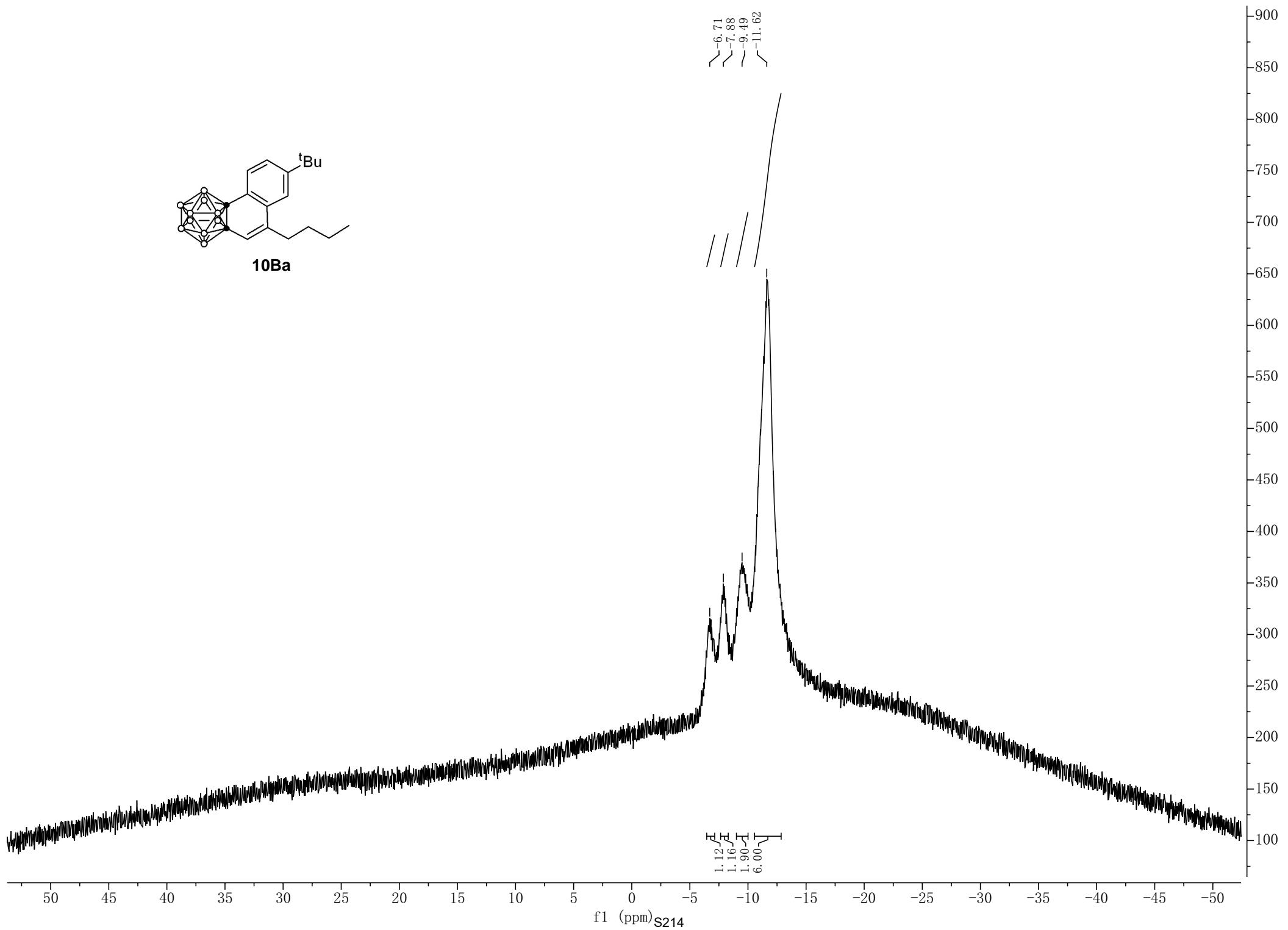
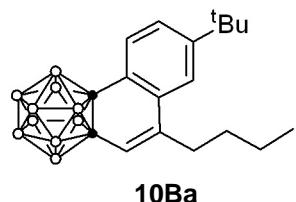
1.93

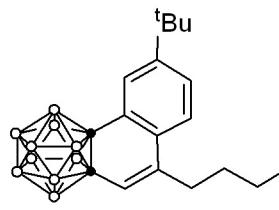
2.21
2.20
9.00
2.95

10.0 9.5 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

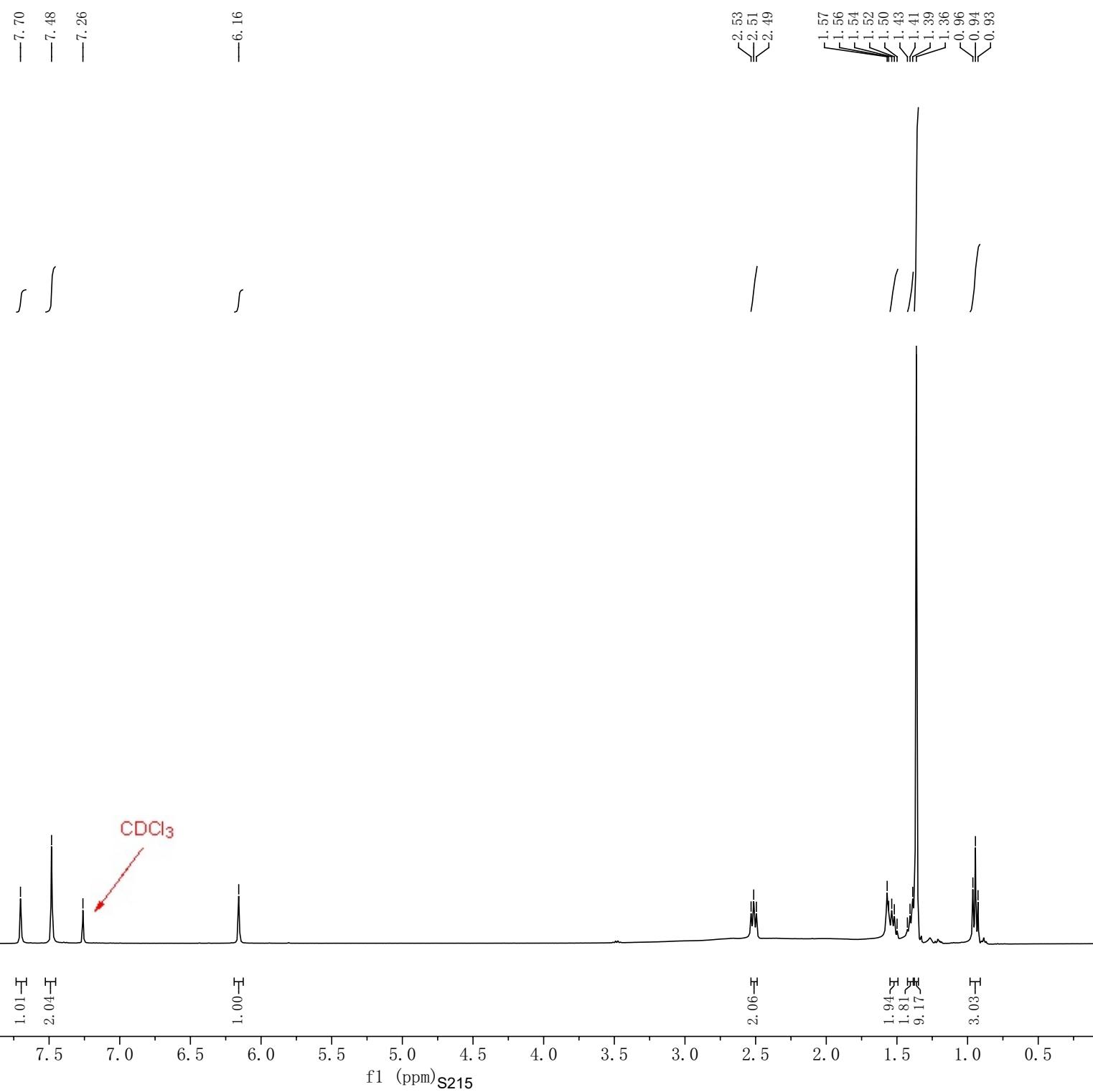
f1 (ppm) S212

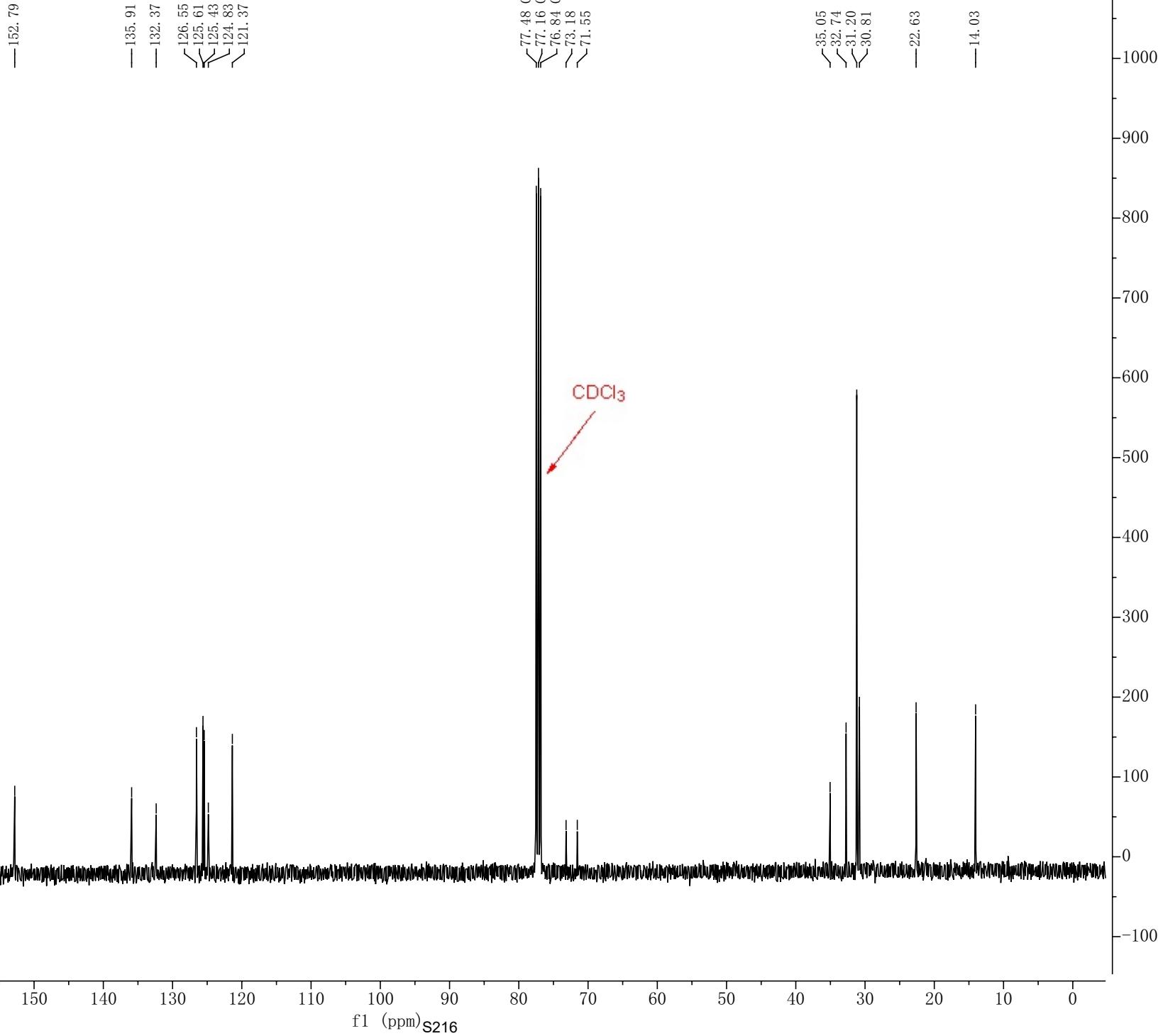
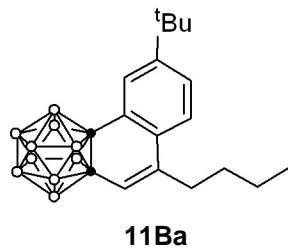


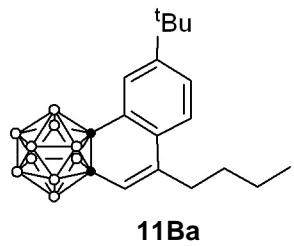




11Ba





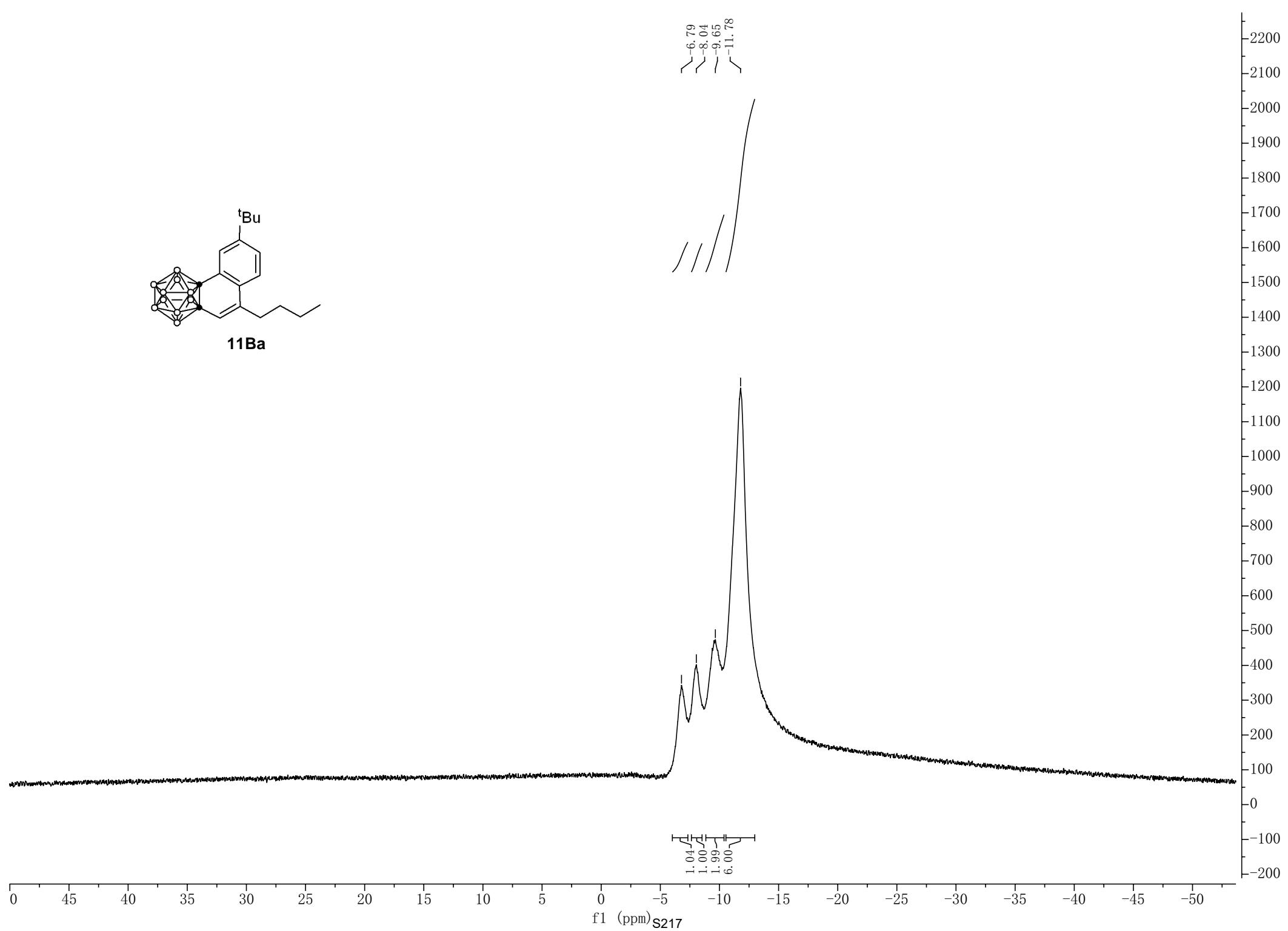


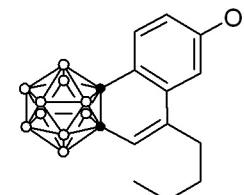
-6.79
-8.04
-9.65
-11.78

2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
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0
-100
-200

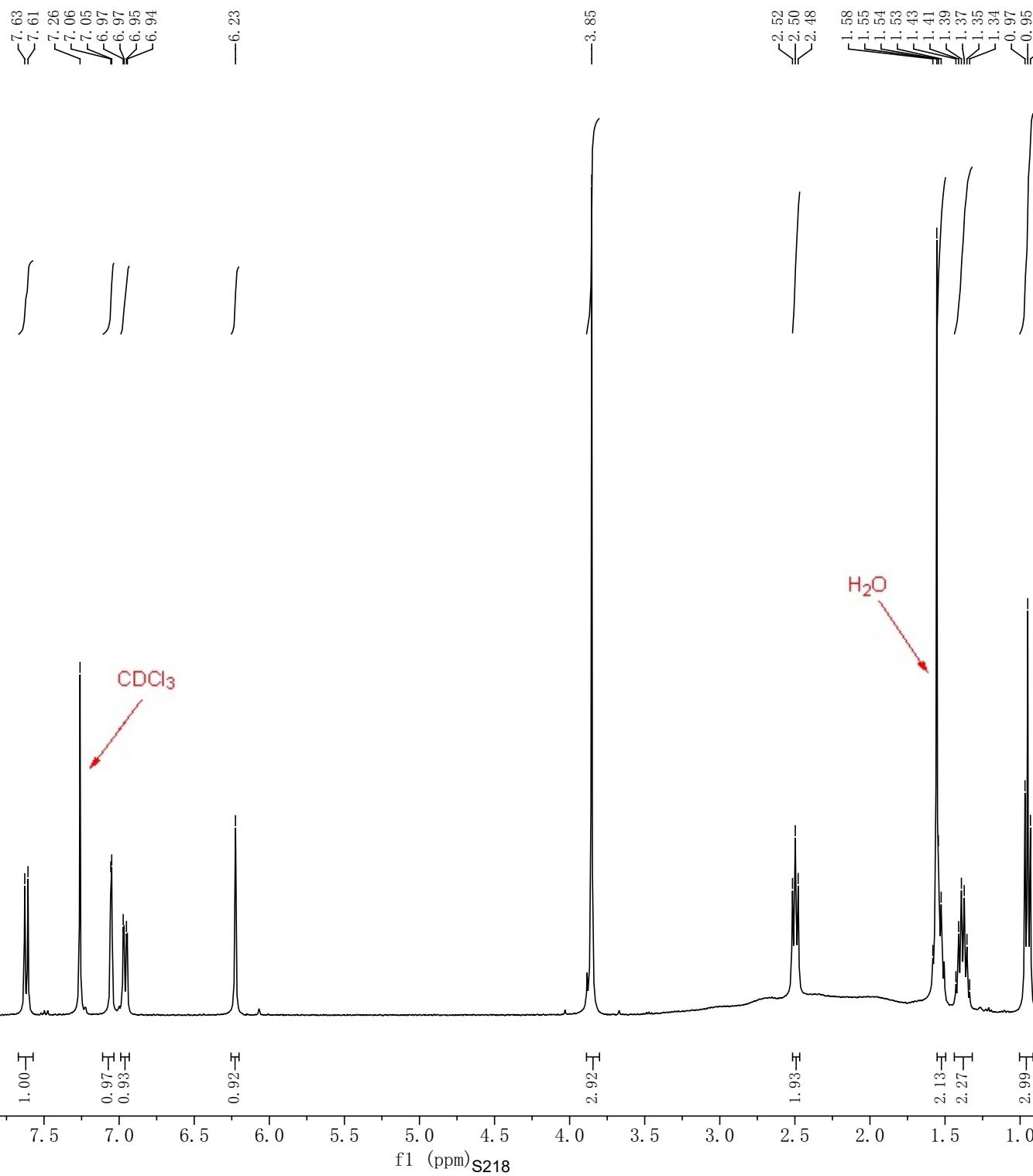
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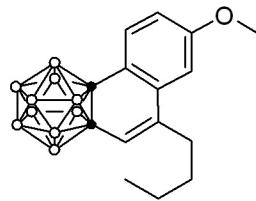
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1.00
1.99
6.00



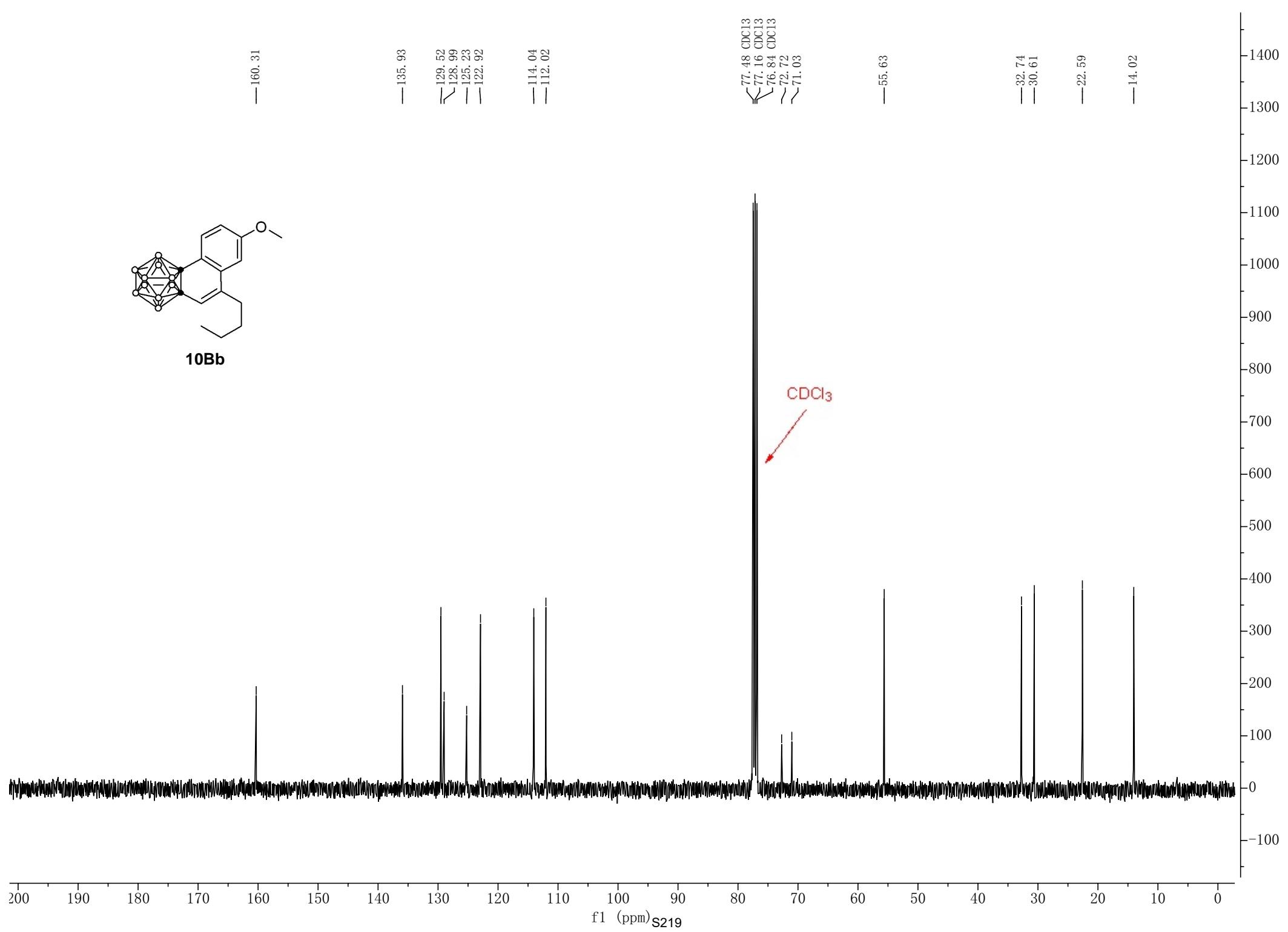


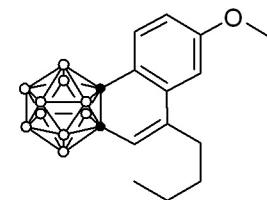
10Bb





10Bb

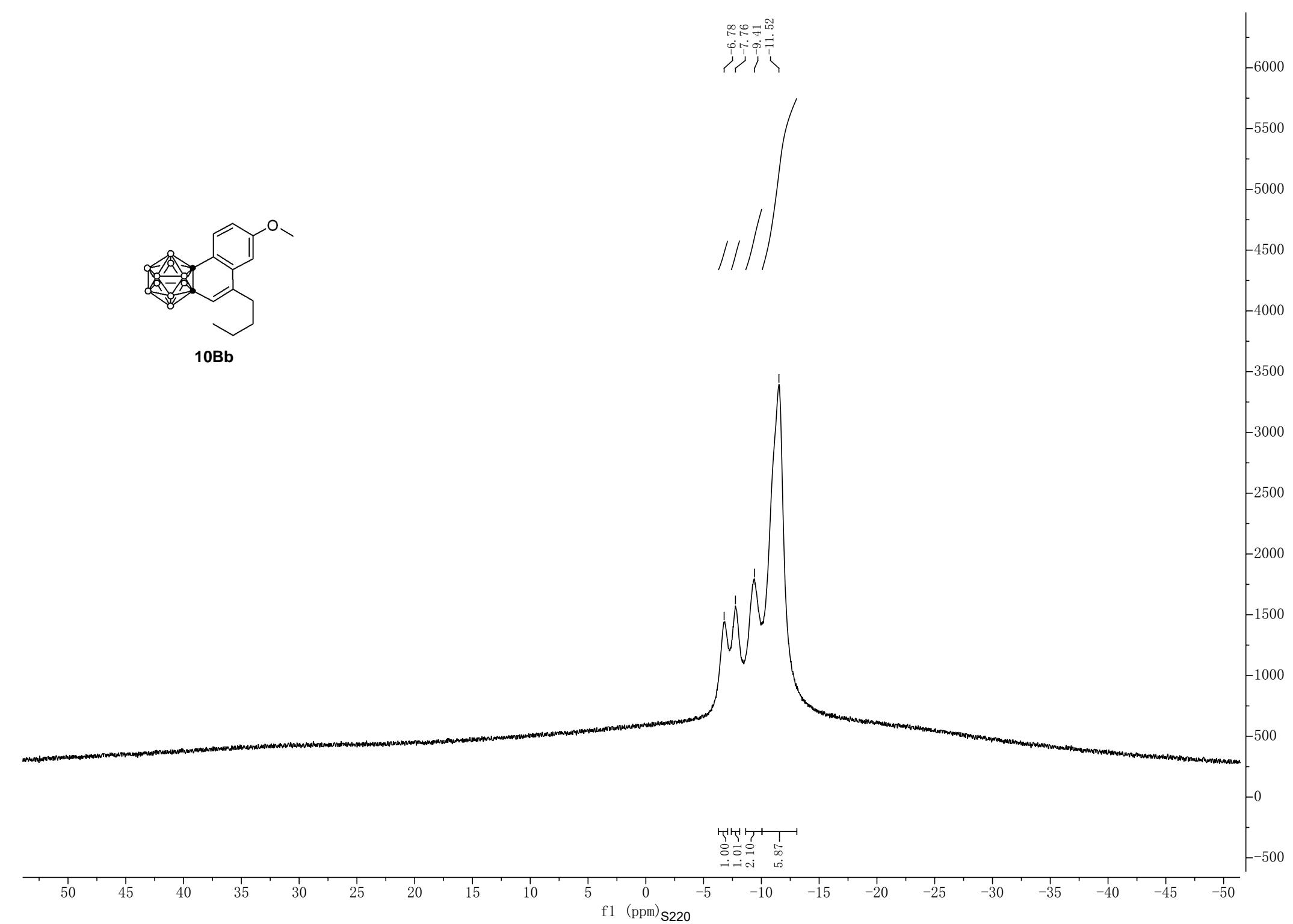


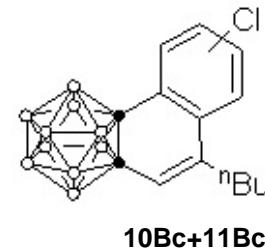


10Bb

-6.78
-7.76
-9.41
-11.52

1.00
1.01
2.10
5.87



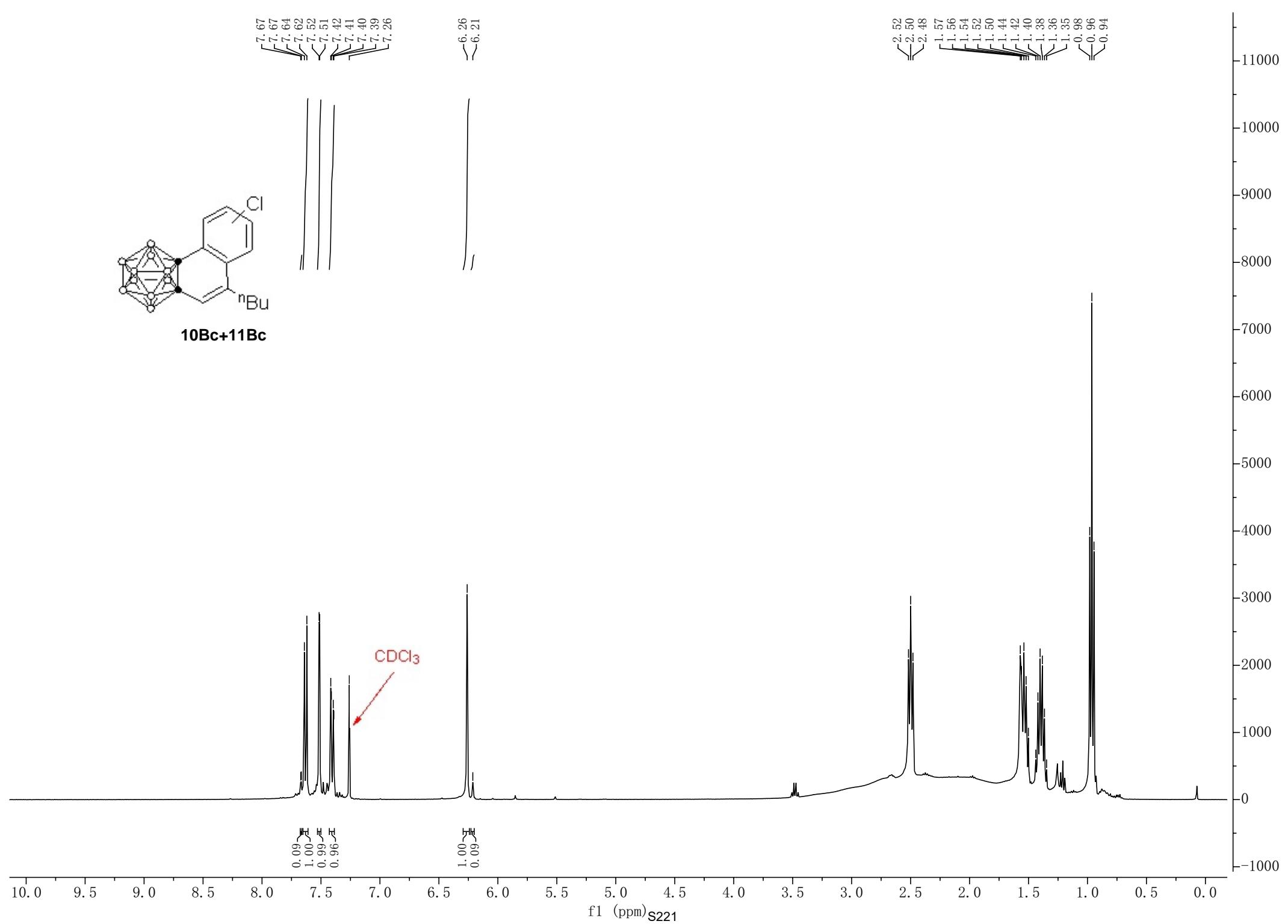


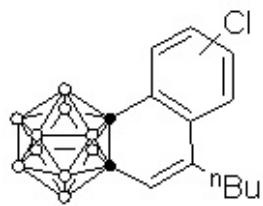
7.67
7.67
7.64
7.62
7.52
7.51
7.42
7.41
7.40
7.39
7.26

6.26
6.21

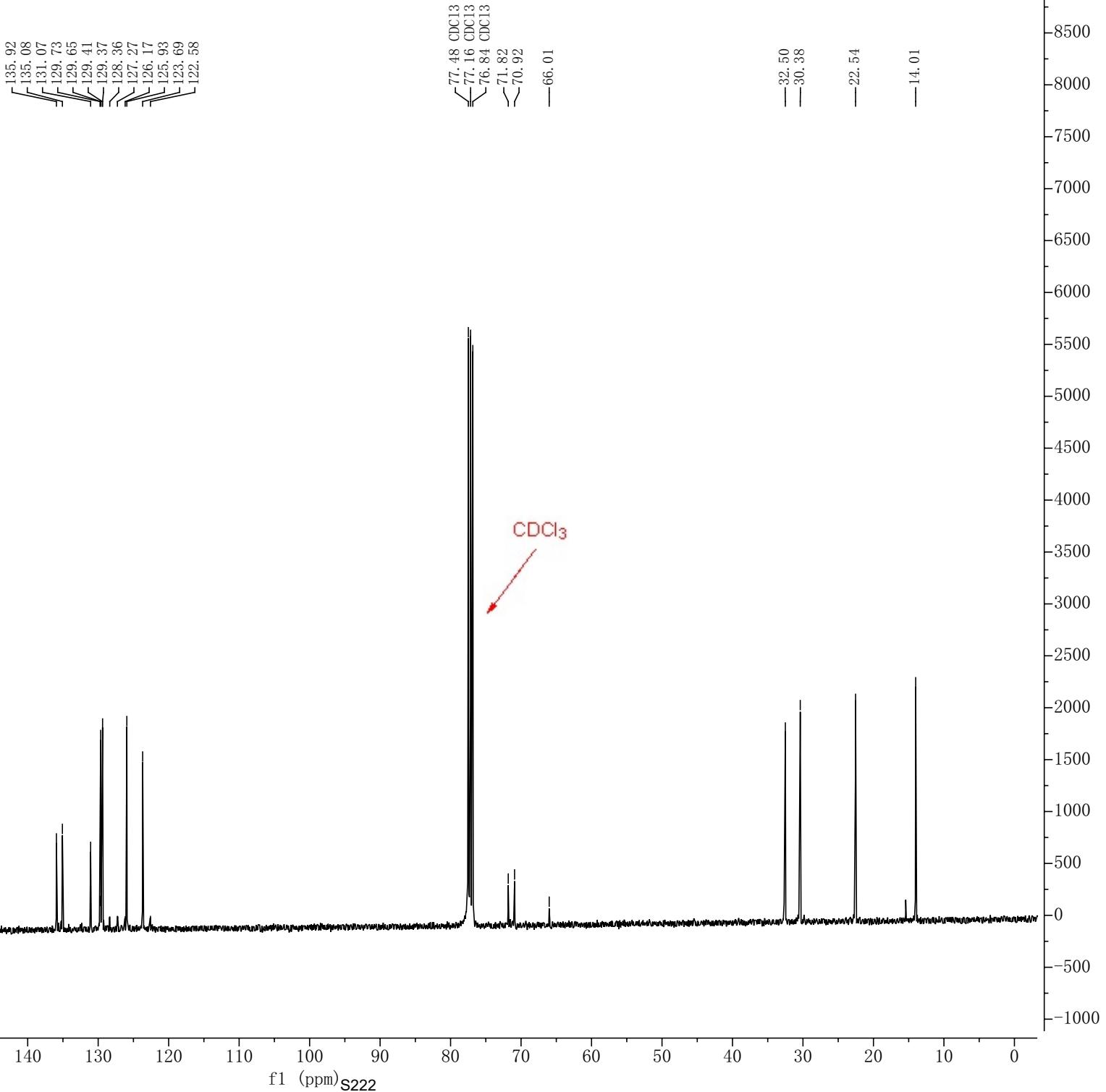
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2.50
2.48

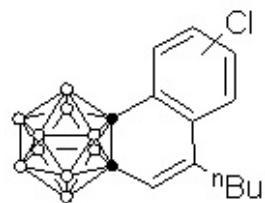
1.57
1.56
1.54
1.52
1.50
1.44
1.42
1.40
1.38
1.36
1.35
0.98
0.96
0.94





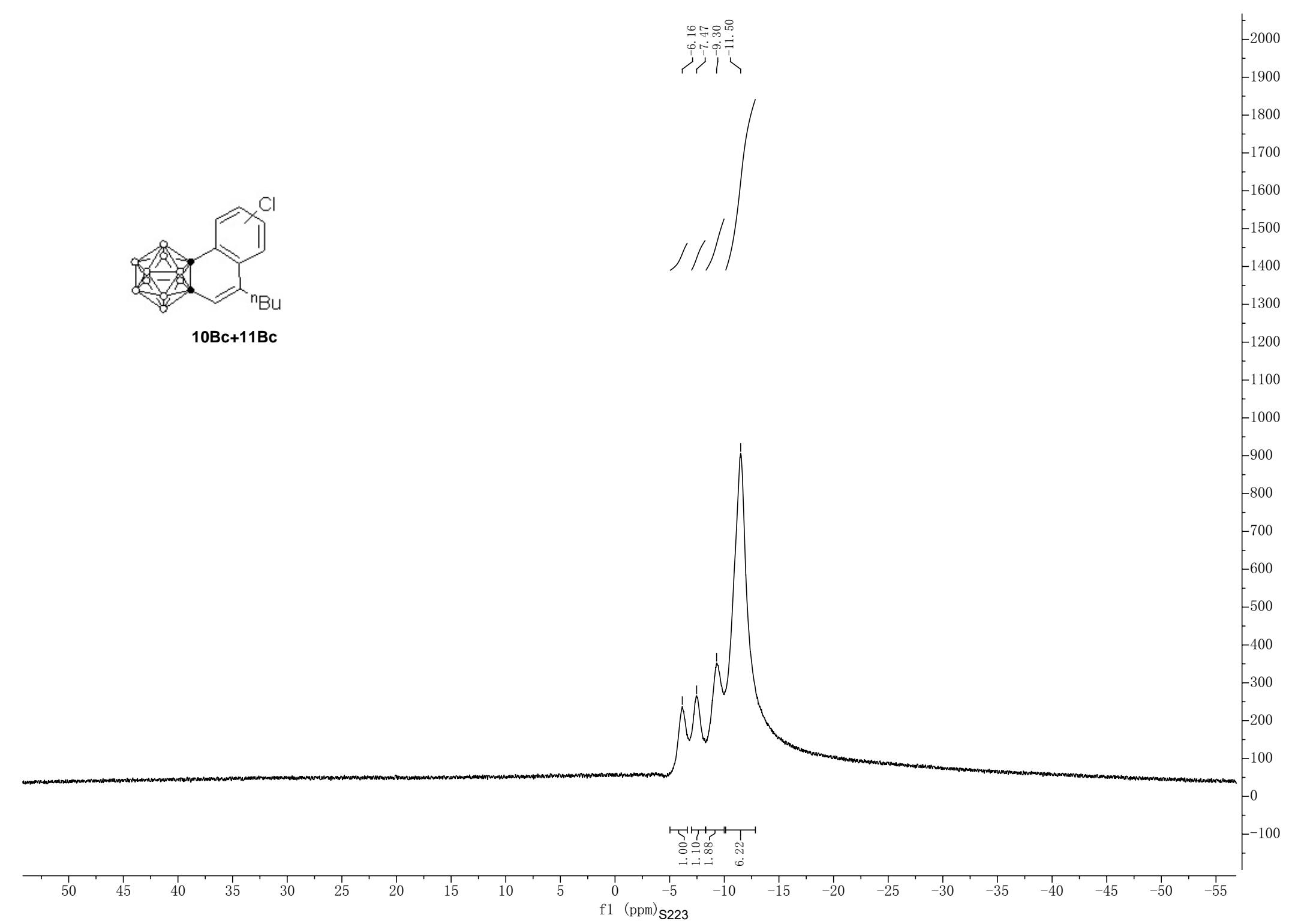
10Bc+11Bc

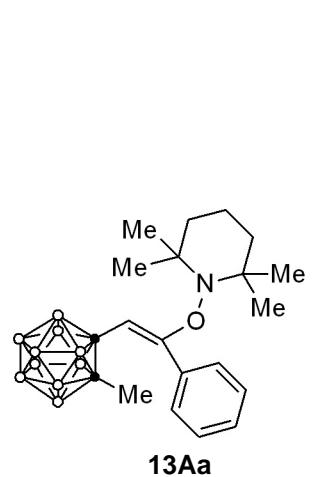




10Bc+11Bc

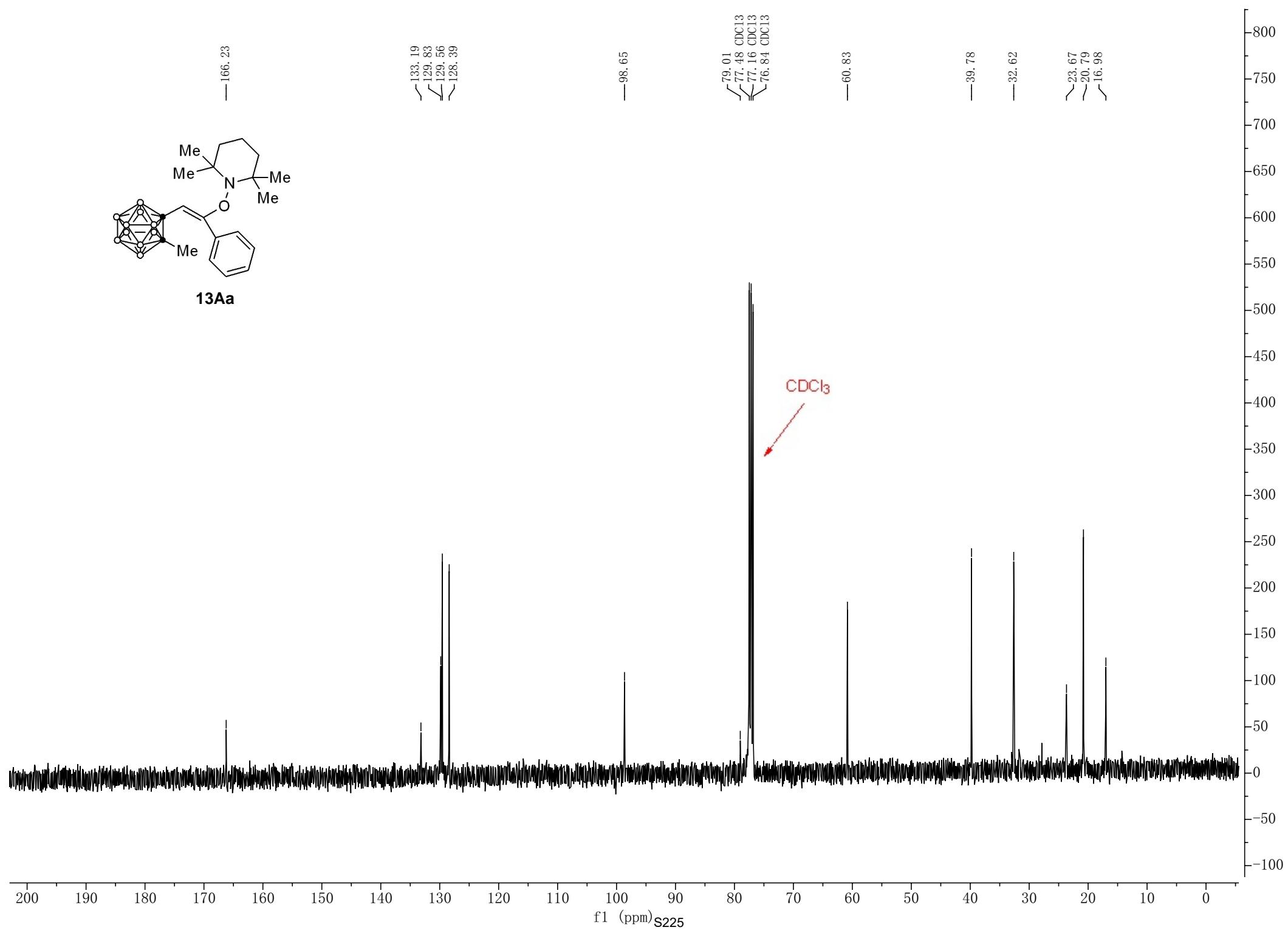
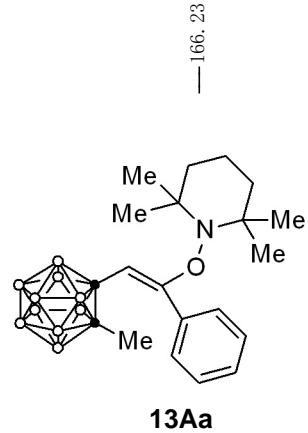
✓ -6.16
✓ -7.47
✓ -9.30
✓ -11.50

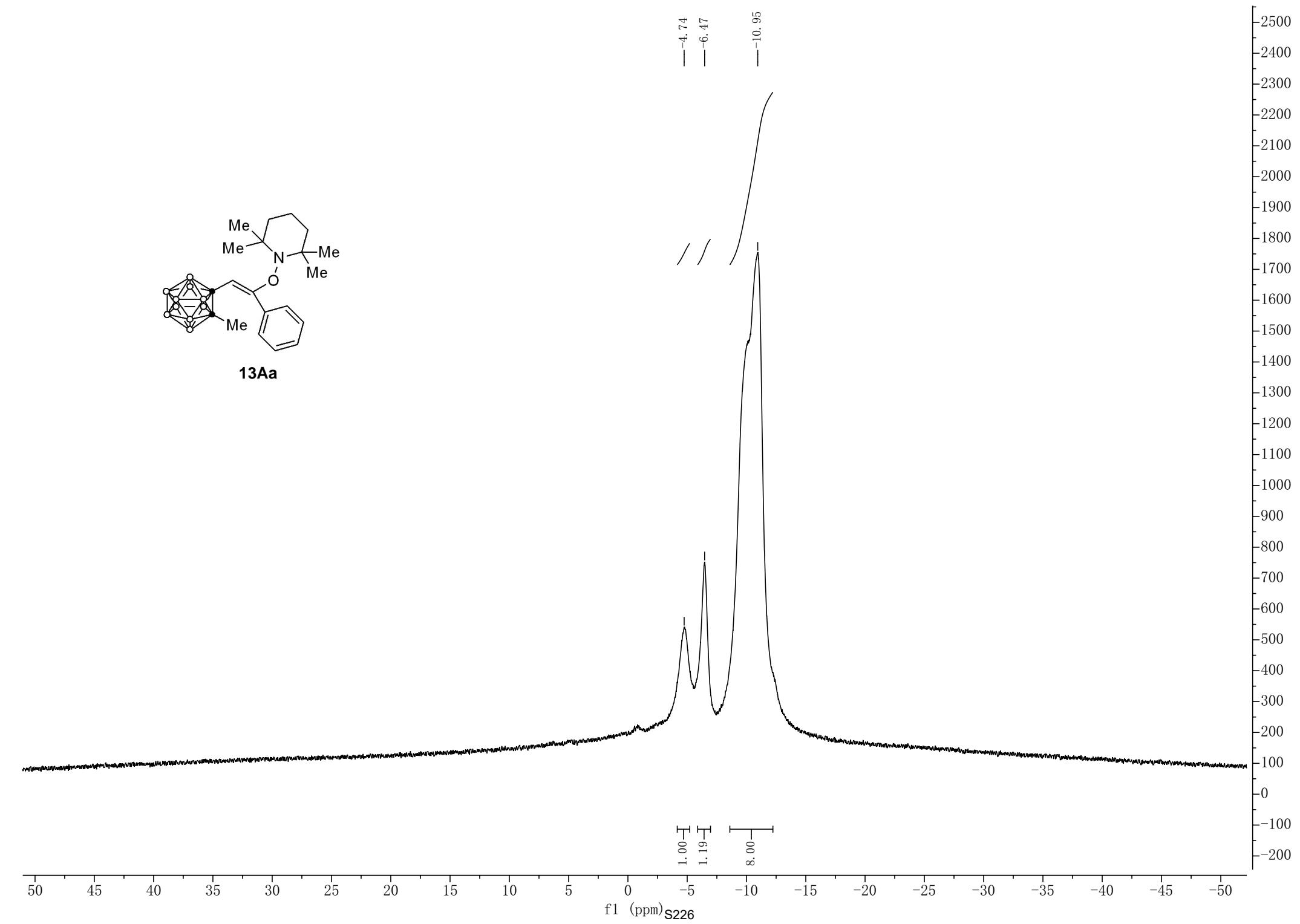
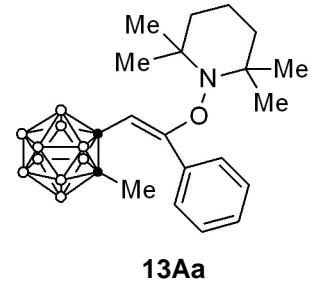


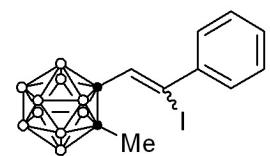


10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

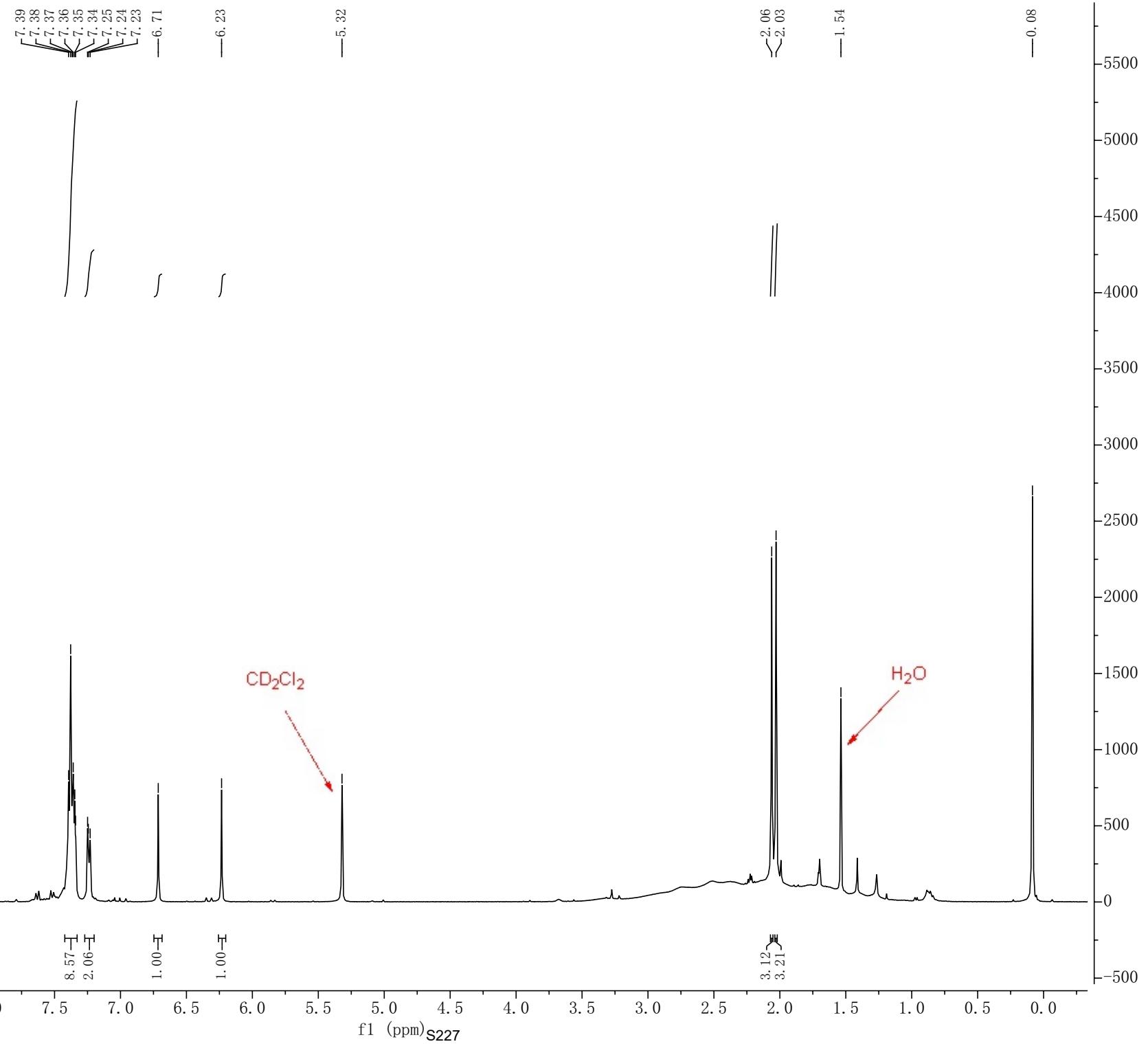
f1 (ppm) S224

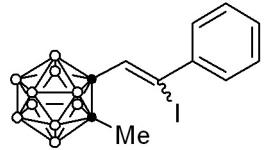




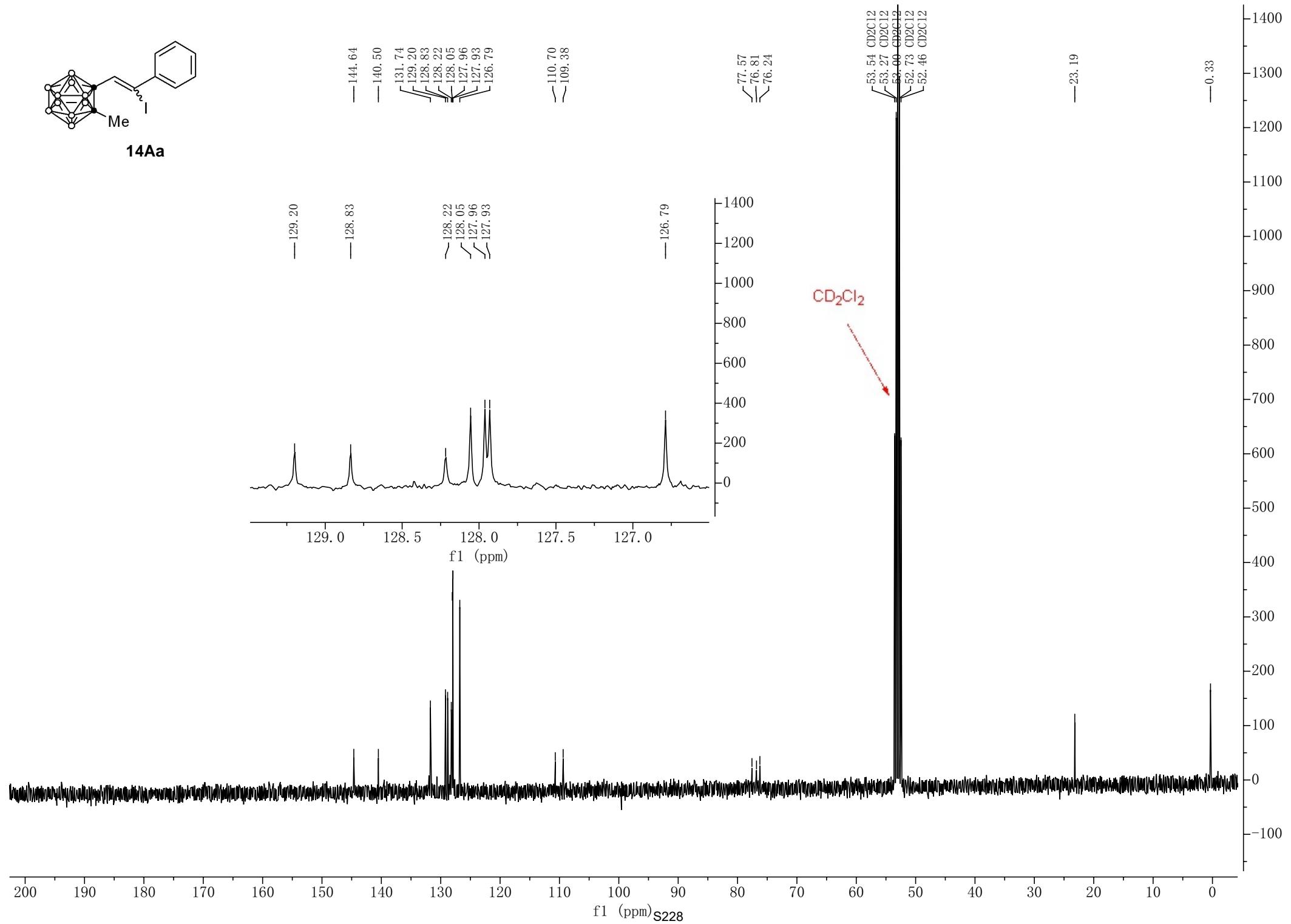


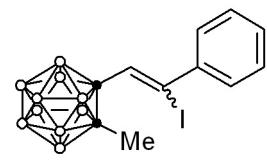
14Aa



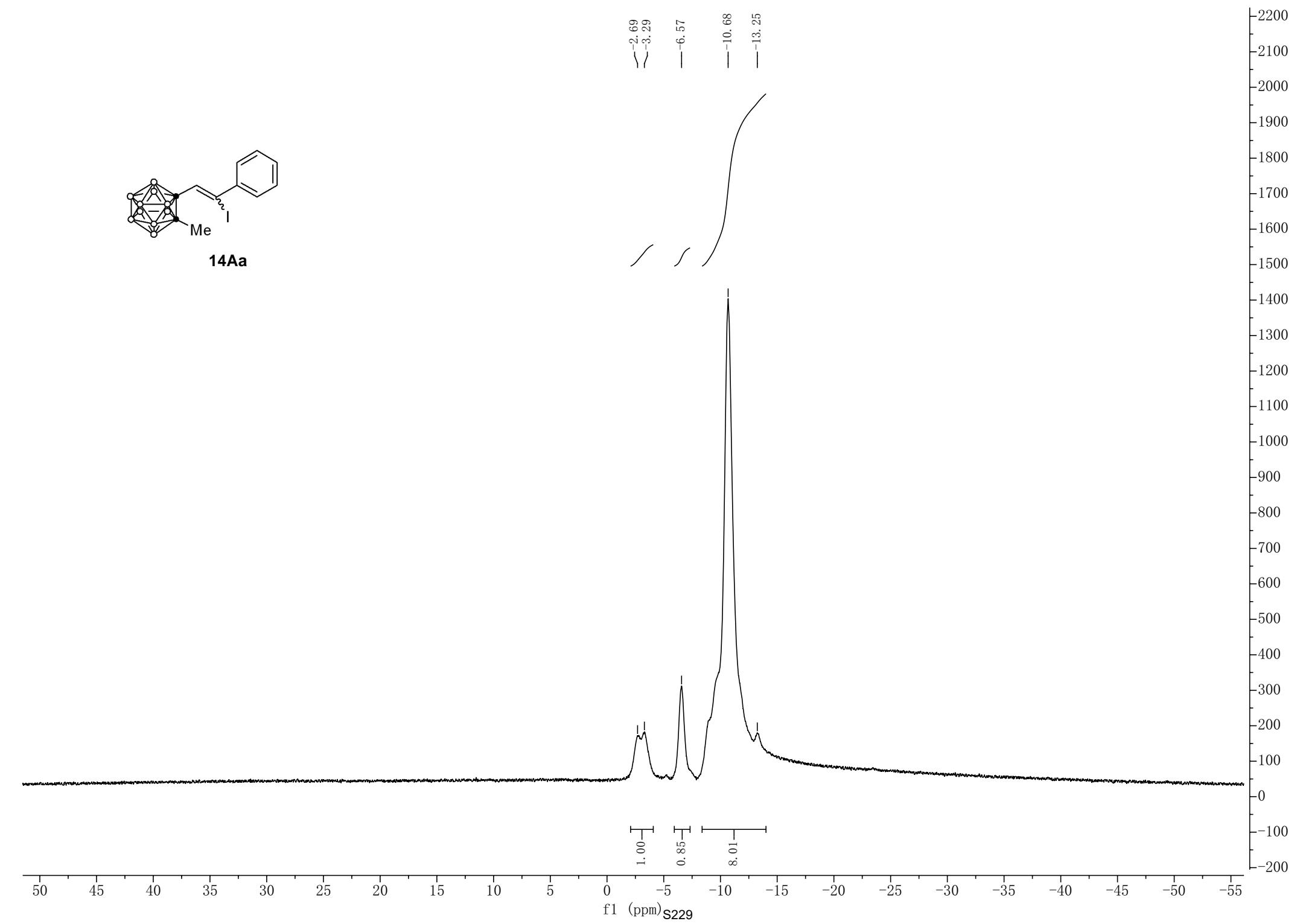


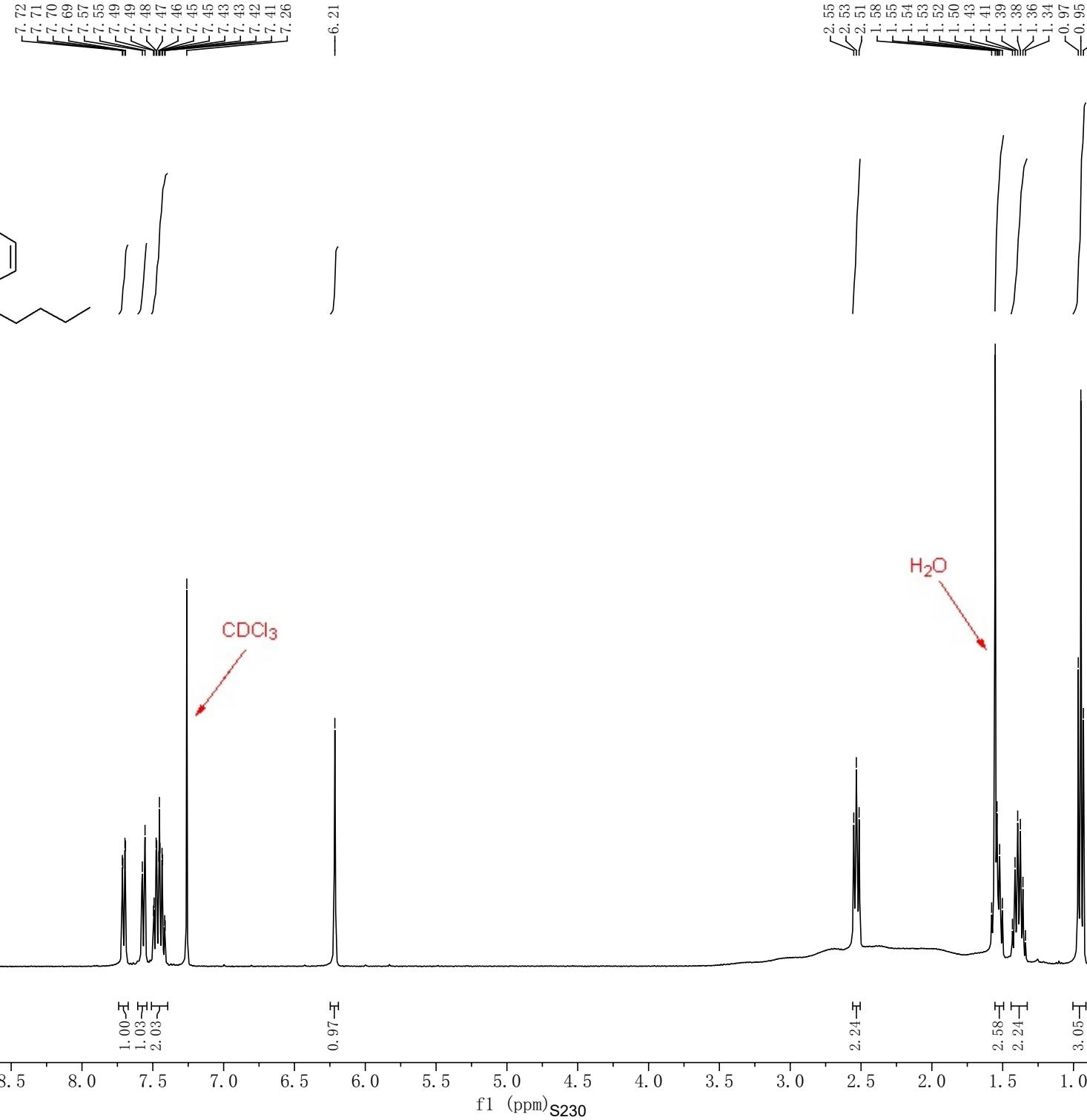
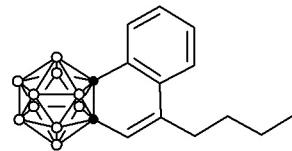
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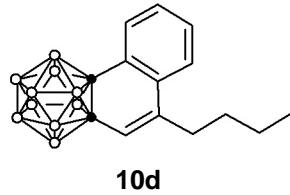




14Aa

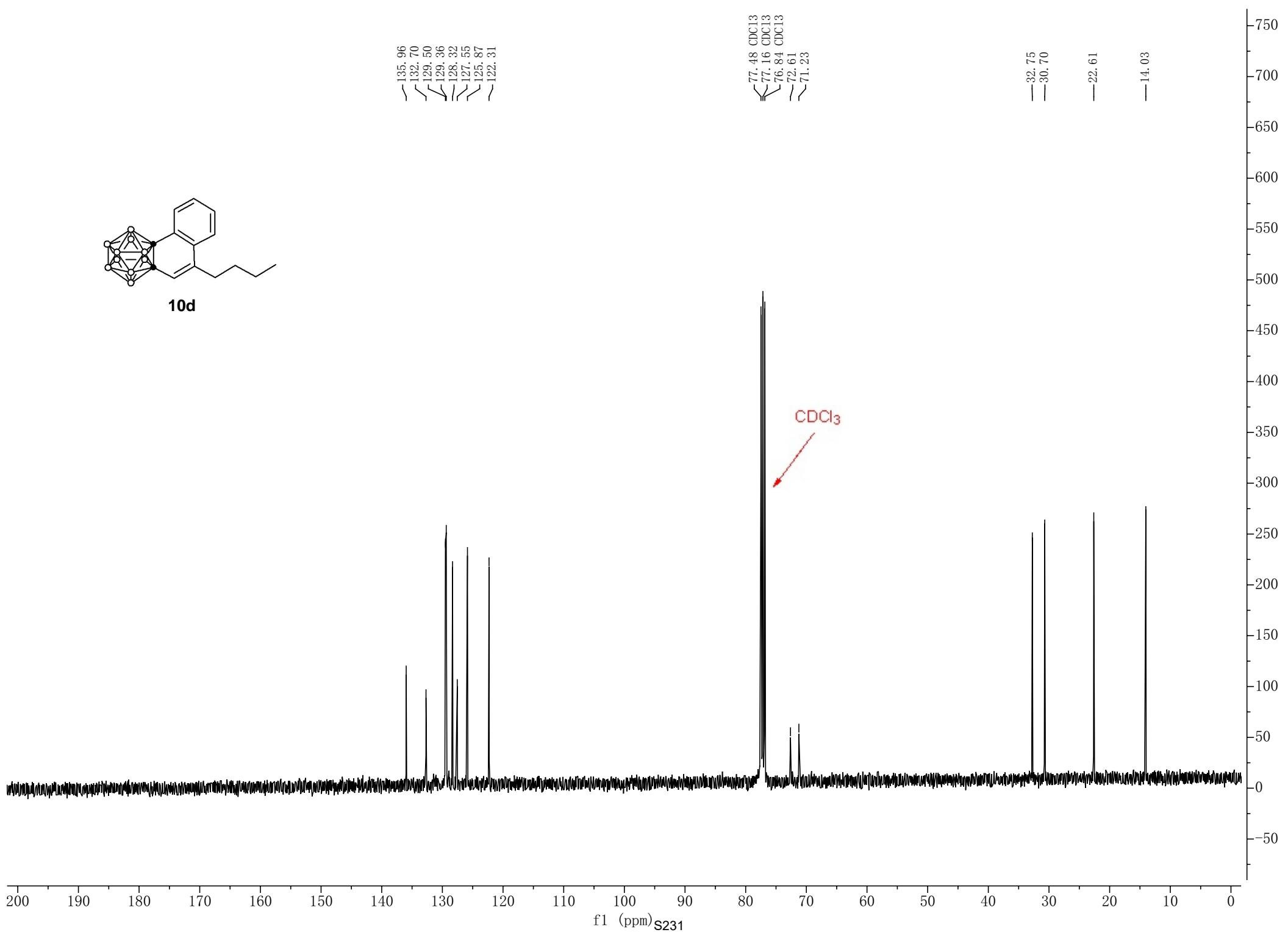


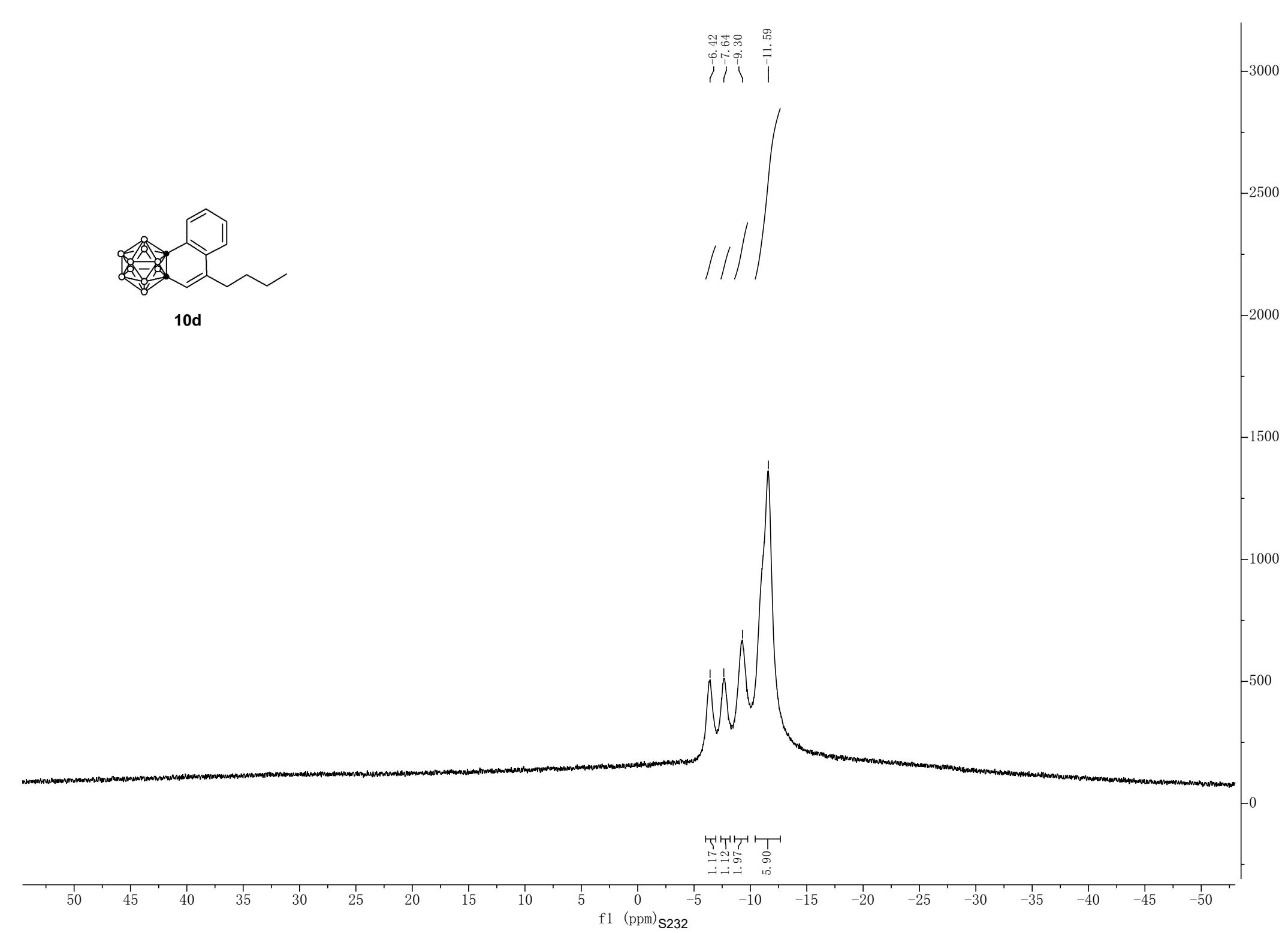
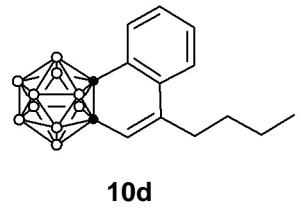


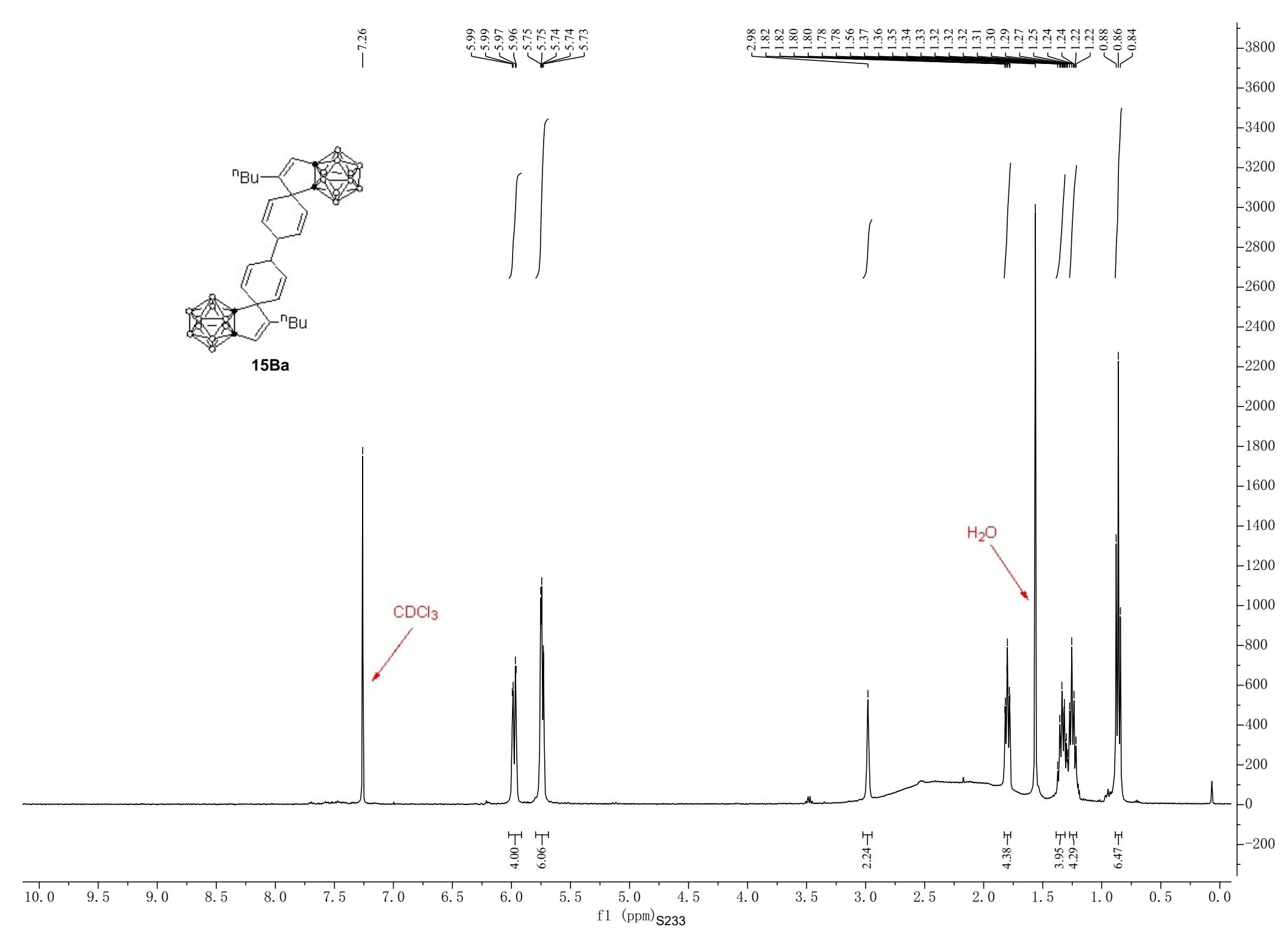


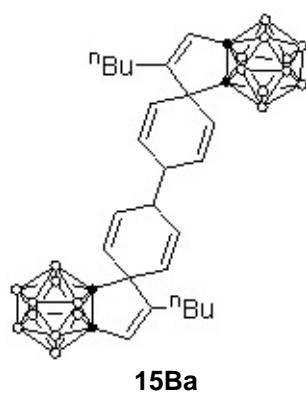
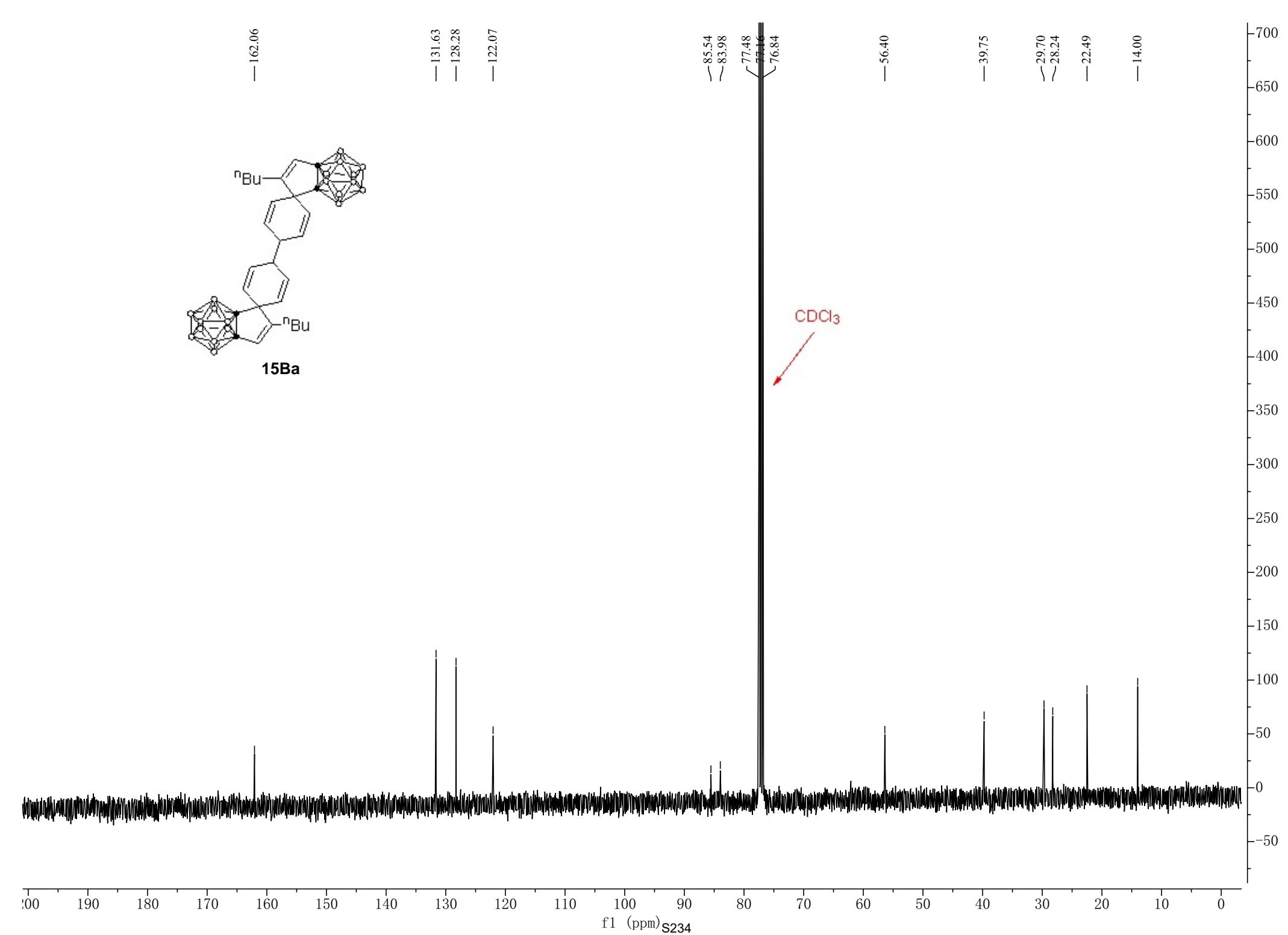
— 135.96 — 132.70 — 129.50 — 129.36 — 128.32 — 127.55 — 125.87 — 122.31

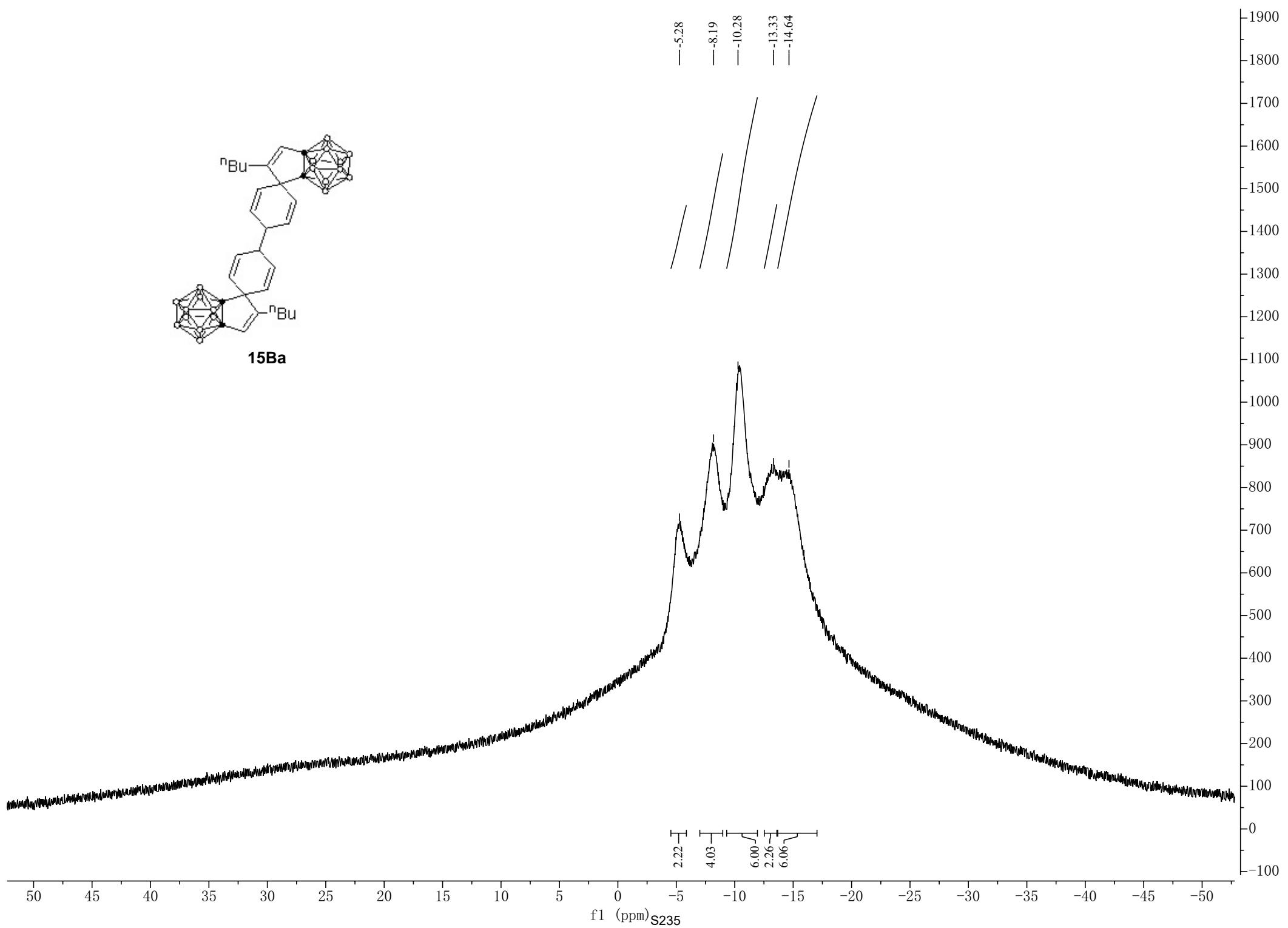
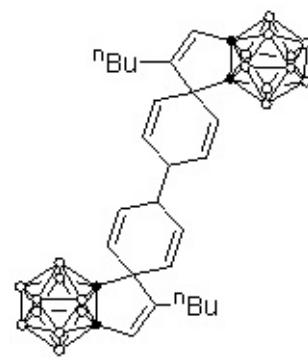
— 77.48 CDCl₃ — 77.16 CDCl₃ — 76.84 CDCl₃ — 72.61 — 71.23











8. References

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