Supporting Information

9,9'-Bis-*o*-carboranes: Synthesis and Property Exploration

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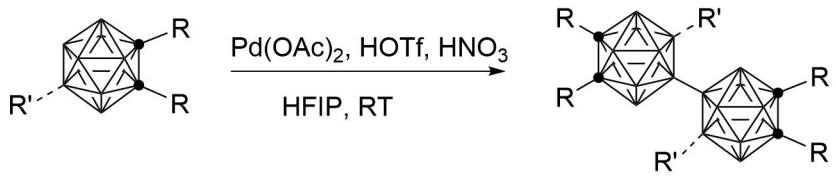
1. General information

^{1}H, ^{13}C, ^{11}B, ^{31}P NMR spectra were recorded on Bruker advance III 400 spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C, 128 MHz for ^{11}B, 162 MHz for ^{31}P). All chemical shifts were reported in units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts. The data contained properties such as chemical shift, multiplicity, peaks and coupling constants. High Resolution Mass Spectra (HRMS-ESI) were obtained on an Ultra-high-resolution electro-spray time-of-flight mass spectrometer. GC-MS analysis was performed on the agilent GC-MS 2010 spectrometer or GC-MS-QP2020 NX. The starting materials were purchased from J&K Chemicals, Macklin, Energy Chemical or TCI, and used as received. Starting *o*-carborane and *m*-carborane were purchased from Zhengzhou Yuanli technology. Thin-layer chromatography (TLC) was performed using 300 mesh silica gel plates visualized with short-wavelength UV light (254 nm). TLC samples for carborane-containing compounds were stained with 1 wt. % $PdCl_2$ in 6 M HCl and were developed with high heat using a heat gun.

2. Experimental details

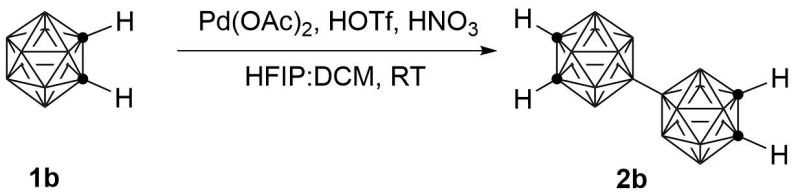
General procedure for Pd(II)-catalyzed dehydrogenative coupling of *o*/*m*-carboranes



1 **2**

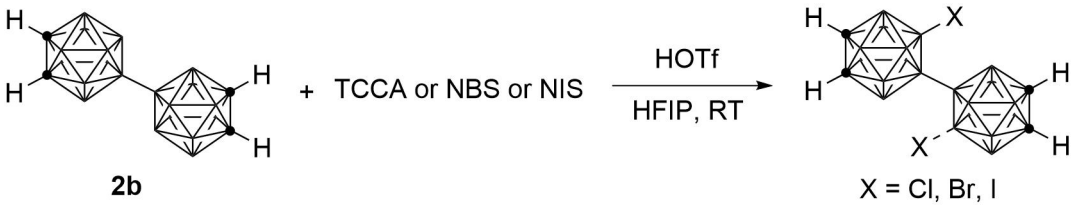
68% HNO_3 (2 mmol, 2.0 equiv) was added to the solution of carboranes **1** (1 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.1 mmol, 10 mol%) and HOTf (6 mmol, 6.0 equiv) in HFIP (10 mL). The reaction mixture was stirred at ambient temperature for 10 minutes under air atmosphere. Then, the reaction solution was added to saturated aqueous $NaHCO_3$ and was extracted with EtOAc (10 mL × 3). The organic portions were combined and dried over Na_2SO_4. After removal of organic solvents under reduced pressure, the residue was subjected to flash column chromatography on silica gel (200-300 mesh) to give the product (**2a**, **2c-2k**).

CAUTION: On this scale and under these conditions no explosions occurred. Nevertheless, this does not preclude such an event when dealing with these species. Extreme precautions should be taken! Additionally, HFIP can increase the acidity of HNO_3 and HOTf, and the oxidability of HNO_3. The solution of HNO_3 or HOTf in HFIP exhibits strong acidity even for the dilute solution. So the reaction system for the hydroxylation of carboranes is strongly acidic and oxidizing. After the reaction, Pd(0) is formed, which needs to be handled carefully.



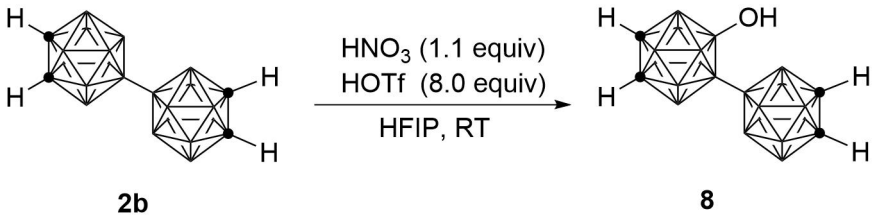
68% HNO_3 (2 mmol, 2.0 equiv) was added to the solution of carboranes **1b** (1 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.1 mmol, 10 mol%) and HOTf (6 mmol, 6.0 equiv) in the mixture solvent of HFIP (2 mL) and DCM (1 mL). The reaction mixture was stirred at ambient temperature for 10 minutes under air atmosphere. Then, the reaction solution was added to saturated aqueous $NaHCO_3$ and was extracted with EtOAc (10 mL × 3). The organic portions were combined and dried over Na_2SO_4. After removal of organic solvents under reduced pressure, the residue was subjected to flash column chromatography on silica gel (200-300 mesh) to give the product **2b**.

General procedure for the synthesis of 4-7



HOTf (1.2, mmol, 6.0 equiv) was added to the solution of **2b** (0.2 mmol, 1.0 equiv) and TCCA (0.16 mmol, 0.8 equiv) or NBS (0.44 mmol, 2.2 equiv) or NIS (0.44 mmol, 2.2 equiv) in HFIP (4 mL). The reaction mixture was stirred at ambient temperature overnight. Then, the reaction solution was added to saturated aqueous $NaHCO_3$ and was extracted with EtOAc (10 mL × 3). The organic portions were combined and dried over Na_2SO_4. After removal of organic solvents under reduced pressure, the residue was subjected to flash column chromatography on silica gel (200-300 mesh) to give the product **4** and **5**, or **6** or **7**.[1]

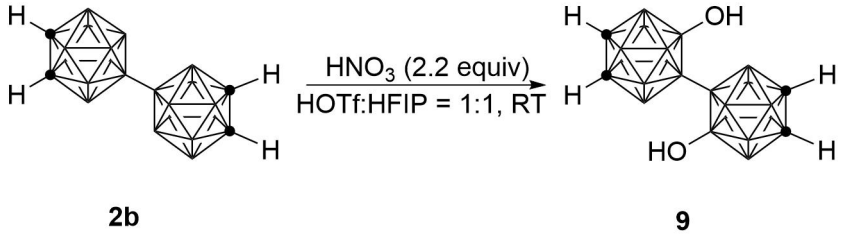
Synthesis of 8



HOTf (0.8 mmol, 8.0 equiv) was added to the solution of **2b** (0.1 mmol, 1.0 equiv) and 68% HNO_3 (0.11 mmol, 1.1 equiv) in HFIP (2 mL). The reaction mixture was stirred at ambient temperature for 0.5 h. Then, the reaction solution was added to saturated aqueous $NaHCO_3$ and was extracted with EtOAc (10 mL × 3). The organic portions were combined and dried over

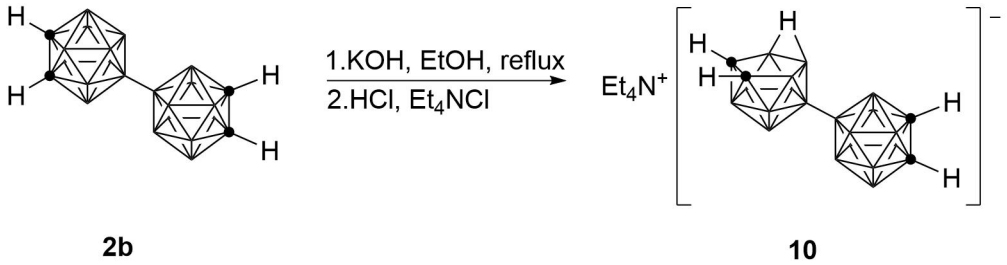
Na_2SO_4. After removal of organic solvents under reduced pressure, the residue was subjected to flash column chromatography on silica gel (200-300 mesh) to give the product **8**.[2]

Synthesis of 9



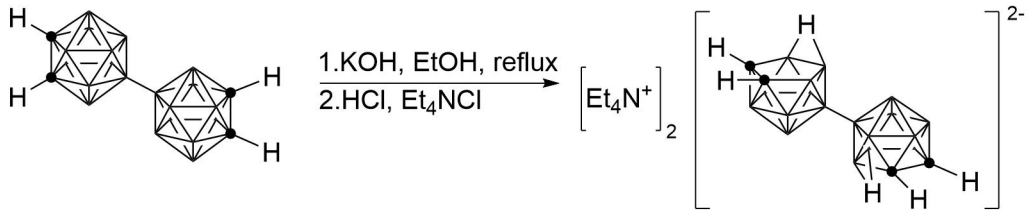
68% HNO_3 (0.22 mmol, 2.2 equiv) was added to the solution of **2b** (0.1 mmol, 1.0 equiv) in the mixture solvent of HFIP (1 mL) and HOTf (1 mL). The reaction mixture was stirred at ambient temperature for 0.5 h. Then, the reaction solution was added to saturated aqueous $NaHCO_3$ and was extracted with EtOAc (10 mL × 3). The organic portions were combined and dried over Na_2SO_4. After removal of organic solvents under reduced pressure, the residue was subjected to flash column chromatography on silica gel (200-300 mesh) to give the product **9**.[2]

Synthesis of 10



2b (0.5 mmol, 1.0 equiv) and KOH (2 mmol, 4.0 equiv) were dissolved in 5 mL of EtOH. Then the solution was stirred under reflux for 1 day. After cooling to room temperature, hydrochloric acid (1M) was added and the pH was adjusted to 6-7. After filtration and evaporation, the resulting white solid was dissolved in 5 mL of deionized water and dropped with an aqueous solution of Et_4NCl (0.55 mmol, 1.1 equiv). The resulting mixture was stirred overnight and filtered, and the filter cakes were washed three times with *n*-hexane and DCM. Finally, it was dried under vacuum to obtain the corresponding product **10**.[3]

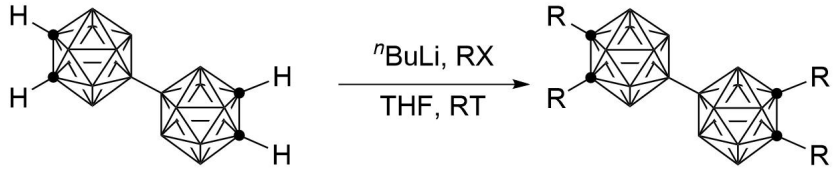
Synthesis of 11



2b **11**

2b (0.5 mmol, 1.0 equiv) and KOH (4 mmol, 8.0 equiv) were dissolved in 5 mL of EtOH. Then the solution was stirred under reflux for 5 days. After cooling to room temperature, hydrochloric acid (1M) was added and the pH was adjusted to 6-7. After filtration and evaporation, the resulting white solid was dissolved in 5 mL of deionized water and dropped with an aqueous solution of Et_4NCl (1.1 mmol, 2.2 equiv). The resulting mixture was stirred overnight and filtered, and the filter cakes were washed with *n*-hexane and DCM. Finally, it was dried under vacuum to obtain the corresponding product **11.**[3]

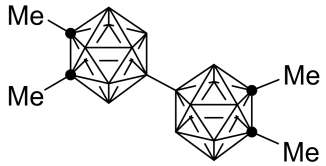
General procedure for the synthesis of 12-18



2b

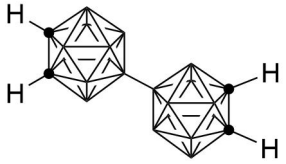
Under nitrogen atmosphere, ^{n}BuLi (1 mmol, 2.5 M, 5.0 equiv) was added to the solution of **2b** (0.2 mmol, 1.0 equiv) in 10 mL THF at room temperature. Then, RX (1 mmol, 5.0 equiv) was added after the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was further stirred at room temperature for 2 h. After that, the reaction was quenched with water, extracted with EtOAc (10 mL× 3), the organic phase was collected and dried over anhydrous Na_2SO_4. After removing the organic solvent under reduced pressure, the crude product is obtained, and then the pure product (**12-18**) was obtained by recrystallization with hexane/DCM.[4]

3. Characterization data



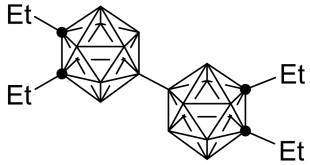
2a: White solid, Yield 48%; **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 1.97 (s, 6H), 1.96 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 74.53, 71.65, 23.23, 23.19; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 0.75 (2B), -3.97 (2B), -7.85 (4B), -9.02 (12B).

HRMS (ESI): m/z calcd for $C_8B_{20}H_{30}$ $[M + Na]^+$, 365.4251, found, 365.4251.



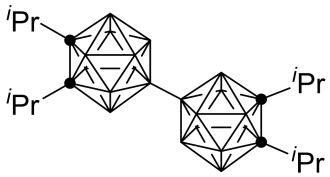
2b: White solid, Yield 42%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.53 (s, 2H), 3.44 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 55.70, 53.25; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 4.10 (2B), -1.21 (2B), -7.87 (4B), -13.05 (8B), -14.36 (4B).

HRMS (ESI): m/z calcd for $C_4B_{20}H_{22}$ $[M + Na]^+$, 309.3622, found, 309.3620.



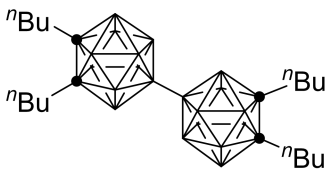
2c: White solid, Yield 37%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 2.21-2.15 (m, 8H), 1.13-1.10 (m, 12H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 81.74, 78.77, 28.48, 28.42, 14.16, 14.06; **^{11}B{^{1}H} NMR** (193 MHz, $CDCl_3$) δ: 1.42 (2B), -3.61 (2B), -9.11 (5B), -10.07 (5B), -10.59 (6B).

HRMS (ESI): m/z calcd for $C_{12}B_{20}H_{38}$ $[M + Na]^+$, 421.4879, found, 421.4878.



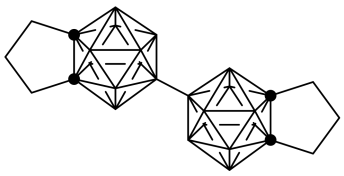
2d: White solid, Yield 46%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.29-2.22 (m, 4H), 1.21-1.17 (m, 24H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 89.54, 86.70, 30.70, 30.50, 24.52, 24.44; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 1.87 (2B), -3.20 (2B), -8.19 (4B), -11.39 (12B).

HRMS (ESI): m/z calcd for $C_{16}B_{20}H_{46}$ $[M + Na]^+$, 477.5507, found, 477.5505.



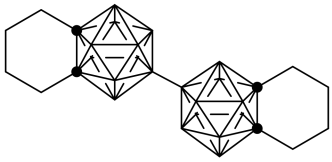
2e: White solid, Yield 24%; **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 2.10-2.05 (m, 8H), 1.50-1.46 (m, 8H), 1.33-1.27 (m, 8H), 0.92-0.89 (m, 12H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ: 80.97, 78.02, 34.85, 34.79, 31.87, 31.8, 22.6, 22.62, 13.84, 13.83; **^{11}B{^{1}H} NMR** (193 MHz, $CDCl_3$) δ: 1.43 (2B), -3.56 (2B), -9.12 (6B), -10.11 (10B).

HRMS (ESI): m/z calcd for $C_{20}B_{20}H_{54}$ $[M - H]^-$, 510.6127, found, 510.6117.



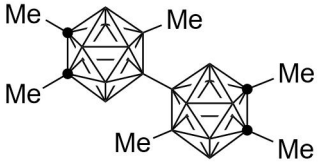
2f: White solid, Yield 35%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.46-2.41 (m, 8H), 2.38-2.32 (m, 4H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 85.00,82.02, 34.84, 34.71, 31.94; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: -1.00 (2B), -5.49 (2B), -6.64 (4B), -8.61 (4B), -11.18 (8B).

HRMS (ESI): m/z calcd for $C_{10}B_{20}H_{30}$ $[M + Na]^+$, 389.4252; found, 389.4242.



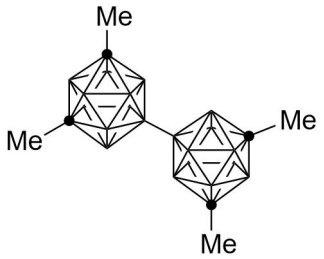
2g: White solid, Yield 47%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.43 (s, 8H), 1.58 (d, J = 2.3 Hz, 8H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 73.23, 32.93, 19.82; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 0.35 (2B), -4.50 (2B), -7.80 (4B), -9.06 (8B), -11.21 (4B).

HRMS(ESI): m/z calcd for $C_{12}B_{20}H_{34}$ $[M + NH_4]^+$, 412.5012, found, 412.5010.



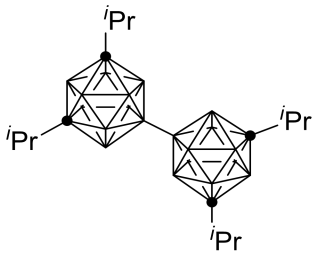
2h: White solid, Yield 35%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.96 (s, 6H), 1.94 (s, 6H), 0.20 (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 72.07, 67.83, 23.40, 22.34; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 5.32 (2B), 0.46 (2B), -8.32 (16B).

GCMS (EI): m/z calcd for $C_{10}B_{20}H_{34}$, 370, found, 370.



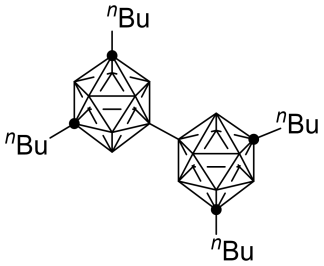
2i: oil, Yield 47%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.68 (s, 12H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 72.76, 24.54; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: -4.90 (2B), -6.32 (4B), -8.85 (6B), -9.45 (4B), -11.54 (2B), -12.67 (2B).

HRMS (ESI): m/z calcd for $C_8B_{20}H_{30}$ $[M + Na]^+$, 365.4251, found, 365.4249.



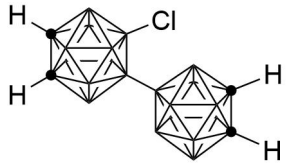
2j: oil, Yield 43%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.20-2.13 (m, 4H), 1.03 (d, J = 1.0 Hz, 12H), 1.01 (d, J = 1.0 Hz, 12H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 83.08, 33.91, 24.11, 24.09; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: -6.01 (6B), -9.75 (2B), -10.86 (2B), -11.52 (6B), -14.01 (2B), -15.26 (2B).

GCMS (EI): m/z calcd for $C_{16}B_{20}H_{46}$, 454, found, 454.



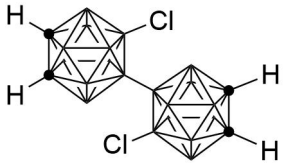
2k: oil,Yield 49%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.91-1.86 (m, 8H), 1.36-1.28 (m, 8H), 1.26-1.18 (m, 8H), 0.88-0.84 (m, 12H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 37.00, 32.21, 22.55, 13.88; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: -6.49 (5B), -10.42 (10B), -14.09 (5B).

GCMS (EI): m/z calcd for $C_{20}B_{20}H_{54}$, 510, found, 510.



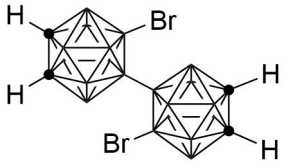
4: White solid, Yield 42%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.56 (s, 1H), 3.49 (s, 1H), 3.45 (s, 1H), 3.41 (s, 1H).; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 55.69, 54.42, 51.43, 46.26; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 7.93 (1B), 3.19 (2B), -1.11 (1B), -7.80 (4B), -13.20 (6B), -14.26 (4B), -15.96 (2B).

HRMS (ESI): m/z calcd for $C_4B_{20}H_{21}Cl$ $[M + H]^+$, 322.3386, found, 322.3382.



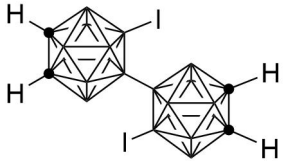
5: White solid, Yield 43%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.50 (s, 2H), 3.44 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 52.62, 46.43; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 8.01 (2B), 2.38 (2B), -7.63 (4B), -13.26 (5B), -14.06 (4B), -15.82 (3B).

HRMS (ESI): m/z calcd for $C_4B_{20}H_{20}Cl_2$ $[M + Na]^+$, 378.2823, found, 378.2824.



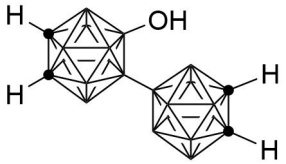
6: White solid, Yield 61%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.61 (s, 2H), 3.56 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 53.94, 48.71; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 2.22 (2B), 1.09 (2B), -7.33 (4B), -13.58 (8B), -15.53 (4B).

HRMS (ESI): m/z calcd for $C_4B_{20}H_{20}Br_2$ $[M + Na]^+$, 467.1808, found, 467.1810.



7: White solid, Yield 70%; **^{1}H NMR** (400 MHz, DMSO) δ: 5.21 (s, 2H), 4.97 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO) δ: 57.75, 54.18; **^{11}B{^{1}H} NMR** (128 MHz, DMSO) δ: 1.99 (2B), -6.63 (4B), -12.08 (8B), -14.45 (6B).

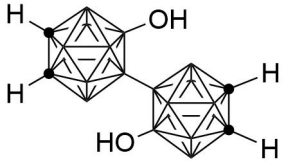
HRMS (ESI): m/z calcd for $C_4B_{20}H_{20}I_2$ $[M + Na]^+$, 561.1555, found, 561.1554.



8: White solid, Yield 76%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.59 (s, 1H), 3.51 (s, 1H), 3.25 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 55.95, 54.26, 48.27, 39.00; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$)

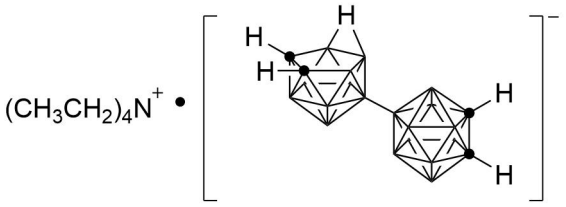
δ: 15.15 (1B), 2.34 (2B), -1.38 (1B), -8.01 (2B), -8.77 (2B), -12.09 (5B), -14.16 (2B), -14.75 (2B), -15.86 (2B), -17.27 (1B).

HRMS (ESI): m/z calcd for $C_4B_{20}H_{21}OH$ $[M + H]^+$, 303.3752, found, 303.3752.

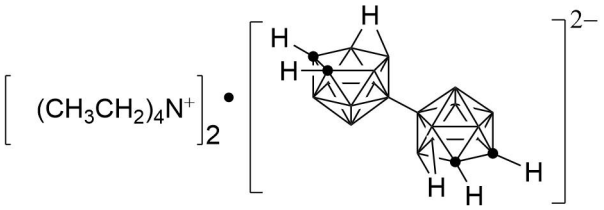


9: White solid, Yield 67%; **^{1}H NMR** (400 MHz, CD_3CN) δ: 4.24 (s, 2H), 3.67 (s, 4H); **^{13}C{^{1}H} NMR** (101 MHz, CD_3CN) δ: 49.94, 39.80; **^{11}B{^{1}H} NMR** (128 MHz, CD_3CN) δ: 14.83 (2B), 0.92 (2B), -9.27 (4B), -15.03 (4B), -16.15 (4B), -17.04 (4B).

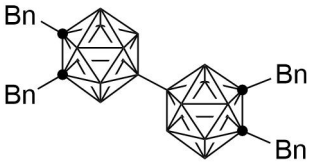
HRMS (ESI): m/z calcd for $C_4B_{20}H_{20}(OH)_2$ $[M + H]^+$, 319.3701, found, 319.3699.



10: White solid, Yield 50%; **^{1}H NMR** (400 MHz, CD_3CN) δ: 3.78 (s, 1H), 3.71 (s, 1H), 3.17 (q, *J* = 7.3 Hz, 8H), 1.77 (s, 1H), 1.66 (s, 1H), 1.24-1.19 (m, 12H); **^{13}C{^{1}H} NMR** (101 MHz, CD_3CN) δ: 57.04, 53.12, 53.09, 53.06, 52.91, 7.68; **^{11}B{^{1}H} NMR** (128 MHz, CD_3CN) δ: 8.37 (1B), -1.90 (1B), -8.24 (2B), -9.33 (1B), -10.48 (1B), -12.86 (2B), -13.93 (2B), -14.79 (4B), -17.36 (1B), -20.77 (1B), -21.80 (1B), -31.19 (1B), -35.86 (1B).

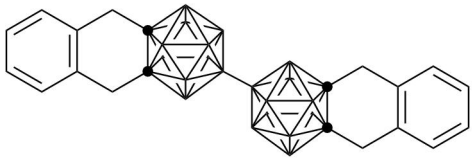


11: White solid, Yield 95%; **^{1}H NMR** (400 MHz, CD_3CN) δ: 3.18 (q, *J* = 7.3 Hz, 16H), 1.63 (s, 2H), 1.49 (s, 2H), 1.24-1.20 (m, 24H); **^{13}C{^{1}H} NMR** (101 MHz, CD_3CN) δ: 53.13, 53.10, 53.07, 7.69; **^{11}B{^{1}H} NMR** (128 MHz, CD_3CN) δ: -8.45 (4B), -11.66 (2B), -15.64 (2B), -17.91 (2B), -20.80 (2B), -21.91 (2B), -30.74 (2B), -35.50 (2B).

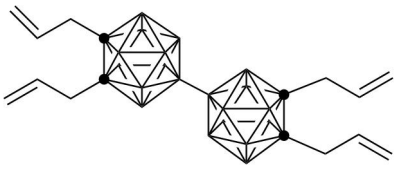


12: White solid, Yield 64%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.33-7.31 (m, 12H), 7.20-7.15 (m, 8H), 3.58 (s, 4H), 3.55 (s, 4H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 135.54, 135.38, 130.56, 128.63, 128.60, 128.01, 127.97, 80.53, 68.26, 41.41; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 1.20 (2B), -3.70 (2B), -9.34 (16B).

HRMS (ESI): m/z calcd for $C_{32}B_{20}H_{46}$ $[M + NH_4]^+$, 665.5931, found, 665.5952.

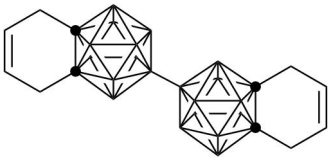


13: White solid, Yield 65%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.22-7.19 (m, 4H), 7.05-7.03 (m, 4H), 3.68 (s, 4H), 3.66 (s, 4H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 129.64, 129.50, 128.81, 128.79, 127.54, 127.53, 72.40, 69.61, 37.66; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 0.86 (2B), -3.95 (2B), -8.18 (16B).



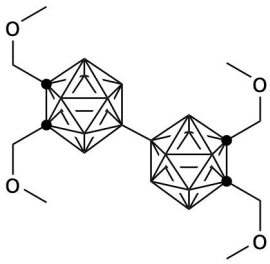
14: White solid, Yield 58%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.82-5.70 (m, 4H), 5.16-5.04 (m, 8H), 2.93-2.89 (m, 8H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 133.27, 133.08, 119.19, 119.05, 78.73, 75.86, 39.32, 39.25; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 1.93 (2B), -3.24 (2B), -8.84 (6B), -9.88 (10B).

GCMS (EI): m/z calcd for $C_{16}B_{20}H_{38}$, 446, found, 446 .



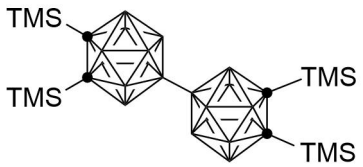
15: White solid, Yield 75%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.62 (s, 4H), 2.95 (d, J = 4.9 Hz, 8H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 120.22, 120.05, 71.18, 68.40, 33.22, 33.20; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 0.41 (2B), -4.39 (2B), -7.63 (4B), -9.15 (8B), -11.04 (4B).

GCMS (EI): m/z calcd for $C_{12}B_{20}H_{30}$, 390, found, 390.

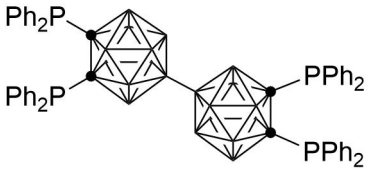


16: White solid, Yield 37%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.89 (s, 4H), 3.87 (s, 4H), 3.37 (s, 6H), 3.36 (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 77.63, 74.72, 73.02, 59.70; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 3.00 (2B), -2.13 (2B), -9.94 (16B).

HRMS (ESI): m/z calcd for $C_{12}B_{20}H_{38}O_4$ $[M + H]^+$, 463.4857, found, 463.4857.



17: White solid, Yield 62%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.29 (s, 18H), 0.28 (s, 18H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ: 75.61, 72.80, 1.78, 1.67; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$) δ: 9.08 (2B), 2.88 (2B), -4.42 (4B), -8.34 (8B), -10.58 (4B).



18: White solid, Yield 44%; **^{1}H NMR** (400 MHz, THF-d_8) δ: 7.88-7.82 (m, 16H), 7.43-7.35 (m, 24H); **^{13}C{^{1}H} NMR** (101 MHz, THF-d_8) δ: 136.70-136.34 (m), 134.73-134.36 (m), 131.21 (d, J = 2.9 Hz), 129.06-128.91 (m); **^{11}B{^{1}H} NMR** (128 MHz, THF-d_8) δ: 6.44, 0.42, -6.56, -9.63; **^{31}P NMR** (162 MHz, THF-d_8) δ: 6.07, 5.98.

HRMS (ESI): m/z calcd for $C_{52}B_{20}H_{58}P_4$ $[M + H]^+$, 1024.5568, found, 1024.5569.

4. Tables of crystal data and structure refinements

	2a	**2b**
CCDC number	2268196	2268197
Empirical formula	$C_8H_{30}B_{20}$	$C_4H_{22}B_{20}$
Formula weight	342.52	286.41
Temperature/K	293(2)	149.99(10)
Crystal system	orthorhombic	monoclinic
Space group	Pnnm	$P2_1/n$
a/Å	9.5876(5)	6.9432(3)
b/Å	11.2736(5)	10.0433(5)
c/Å	10.0616(5)	12.6587(6)
α/°	90	90
β/°	90	97.066(4)
γ/°	90	90
Volume/Å^3	1087.53(9)	876.02(7)
Z	2	2
ρ_{calc}g/cm^3	1.046	1.086
μ/mm^{-1}	0.289	0.275
F(000)	356.0	292.0
Crystal size/mm^3	0.15 × 0.12 × 0.1	0.01 × 0.01 × 0.01
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	11.79 to 134.088	11.28 to 142.922
Index ranges	$-11 \leq h \leq 7$, $-13 \leq k \leq 13$, $-12 \leq l \leq 11$	$-8 \leq h \leq 8$, $-11 \leq k \leq 12$, $-9 \leq l \leq 15$
Reflections collected	3815	5428
Independent reflections	1033 [Rint = 0.0250, Rsigma = 0.0188]	1685 [R_{int} = 0.0605, R_{sigma} = 0.0463]
Data/restraints/parameters	1033/2/75	1685/0/145
Goodness-of-fit on F^2	1.042	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0603, wR_2 = 0.1750	R_1 = 0.0659, wR_2 = 0.1841
Final R indexes [all data]	R_1 = 0.0669, wR_2 = 0.1858	R_1 = 0.0716, wR_2 = 0.1896
Largest diff. peak/hole / e Å^{-3}	0.31/-0.29	0.28/-0.25

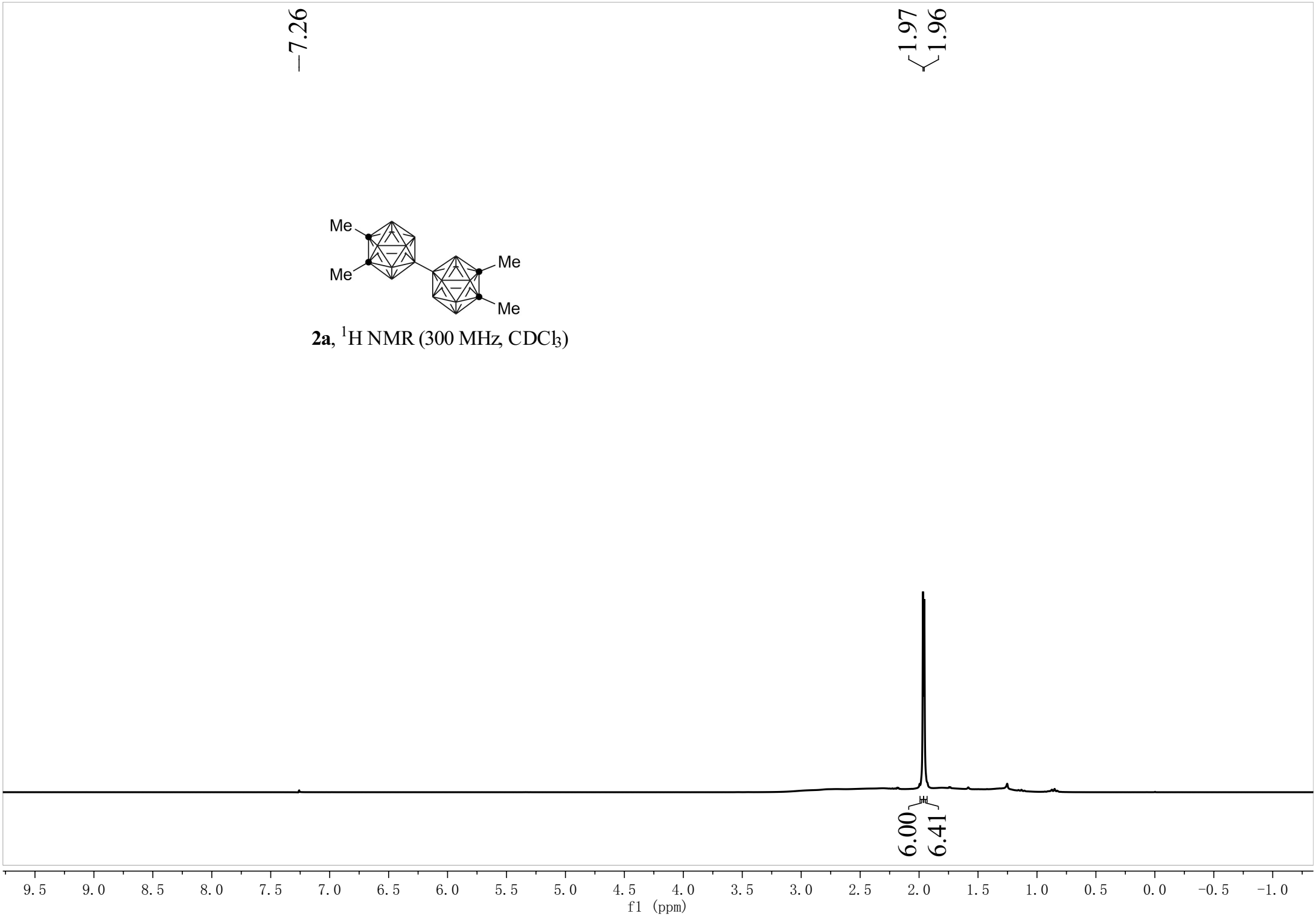
	5	**9**
CCDC number	2268198	2268199
Empirical formula	$C_{4.5}H_{20}B_{20}Cl_3$	$C_4H_{22}B_{20}O_2$
Formula weight	396.75	318.41
Temperature/K	293(2)	293(2)
Crystal system	tetragonal	monoclinic
Space group	I-4c2	$P2_1/c$
a/Å	17.7977(2)	12.3573(3)
b/Å	17.7977(2)	12.9050(3)
c/Å	13.4194(2)	13.1240(3)
α/°	90	90
β/°	90	112.213(3)
γ/°	90	90
Volume/Å^3	4250.70(11)	1937.57(8)
Z	8	4
ρ_{calc}g/cm^3	1.240	1.092
μ/mm^{-1}	3.758	0.374
F(000)	1584.0	648.0
Crystal size/mm^3	0.19 × 0.09 × 0.07	0.18 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.024 to 134.16	7.728 to 134.14
Index ranges	$-19 \leq h \leq 21$, $-20 \leq k \leq 21$, $-16 \leq l \leq 11$	$-14 \leq h \leq 14$, $-15 \leq k \leq 13$, $-15 \leq l \leq 10$
Reflections collected	8435	7051
Independent reflections	1908 [R_{int} = 0.0382, R_{sigma} = 0.0268]	3457 [R_{int} = 0.0278, R_{sigma} = 0.0420]
Data/restraints/parameters	1908/6/133	3457/1/240
Goodness-of-fit on F^2	1.079	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0595, wR_2 = 0.1638	R_1 = 0.0675, wR_2 = 0.1854
Final R indexes [all data]	R_1 = 0.0633, wR_2 = 0.1689	R_1 = 0.0800, wR_2 = 0.2037
Largest diff. peak/hole / e Å^{-3}	0.37/-0.25	0.40/-0.33

	10	**11**
CCDC number	2268200	2271213
Empirical formula	$C_{12}H_{42}B_{19}N$	$C_{20}H_{62}B_{18}N_2$
Formula weight	811.71	525.29
Temperature/K	169.99(10)	297
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	10.7318(3)	11.2612(5)
b/Å	13.0844(4)	17.2885(10)
c/Å	18.4673(5)	18.0579(11)
α/°	89.977(2)	85.761(5)
β/°	78.418(2)	87.210(4)
γ/°	88.417(2)	82.019(4)
Volume/Å^3	2539.36(13)	3469.5(3)
Z	4	4
ρ_{calc}g/cm^3	1.062	1.006
μ/mm^{-1}	0.326	0.338
F(000)	864.0	1144.0
Crystal size/mm^3	0.15 × 0.1 × 0.05	0.01 × 0.01 × 0.01
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.322 to 142.62	6.888 to 140.828
Index ranges	$-10 \leq h \leq 13$, $-15 \leq k \leq 16$, $-22 \leq l \leq 16$	$-13 \leq h \leq 8$, $-21 \leq k \leq 20$, $-20 \leq l \leq 22$
Reflections collected	18413	25502
Independent reflections	9630 [R_{int} = 0.0404, R_{sigma} = 0.0575]	12998 [R_{int} = 0.0257, R_{sigma} = 0.0419]
Data/restraints/parameters	9630/49/647	12998/69/903
Goodness-of-fit on F^2	1.041	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0628, wR_2 = 0.1740	R_1 = 0.0877, wR_2 = 0.2596
Final R indexes [all data]	R_1 = 0.0771, wR_2 = 0.1828	R_1 = 0.1235, wR_2 = 0.3027
Largest diff. peak/hole / e Å^{-3}	0.49/-0.42	0.37/-0.54

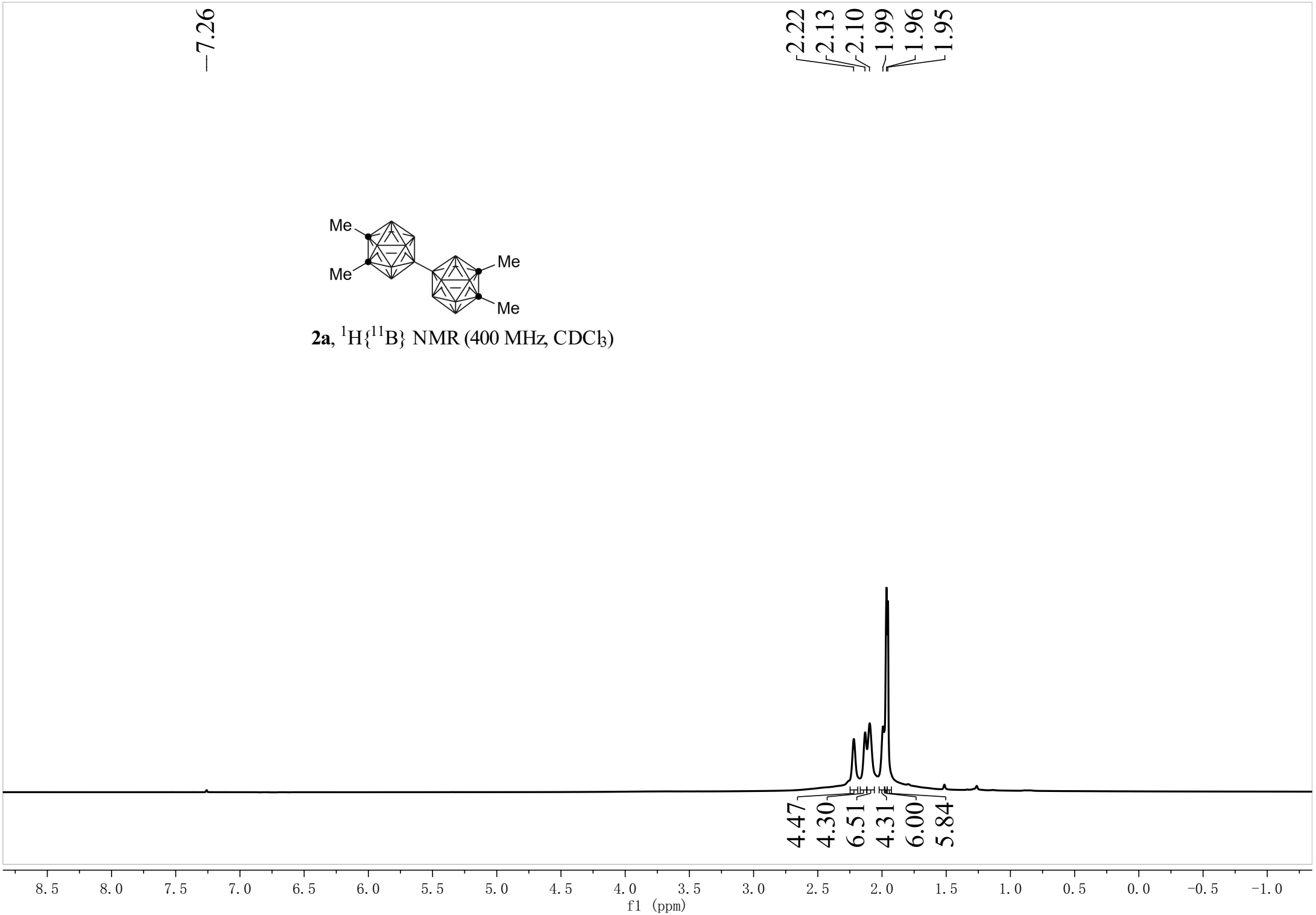
	13	**17**
CCDC number	2268201	2268202
Empirical formula	$C_{20}H_{34}B_{20}$	$C_{16}H_{54}B_{20}Si_4$
Formula weight	490.67	575.15
Temperature/K	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	P2/c	$P2_1/n$
a/Å	20.2379(7)	9.2397(4)
b/Å	7.7225(2)	17.1741(7)
c/Å	18.3961(6)	12.2399(5)
α/°	90	90
β/°	96.014(3)	109.520(5)
γ/°	90	90
Volume/$Å^3$	2859.23(16)	1830.63(15)
Z	4	2
ρ_{calc}g/cm^3	1.140	1.043
μ/mm^{-1}	0.371	1.550
F(000)	1016.0	612.0
Crystal size/mm^3	0.16 × 0.1 × 0.08	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.788 to 134.12	9.234 to 134.158
Index ranges	$-24 \leq h \leq 24$, $-9 \leq k \leq 9$, $-17 \leq l \leq 21$	$-11 \leq h \leq 11$, $-19 \leq k \leq 20$, $-9 \leq l \leq 14$
Reflections collected	5083	6630
Independent reflections	5083 [Rint = 0.0432, Rsigma = 0.0585]	3267 [R_{int} = 0.0309, R_{sigma} = 0.0426]
Data/restraints/parameters	5083/0/362	3267/0/187
Goodness-of-fit on F^2	1.066	1.053
Final R indexes [I>=2σ (I)]	R1 = 0.0988, wR2 = 0.2969	R_1 = 0.0491, wR_2 = 0.1294
Final R indexes [all data]	R1 = 0.1137, wR2 = 0.3124	R_1 = 0.0587, wR_2 = 0.1406
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.50	0.25/-0.37

5. References

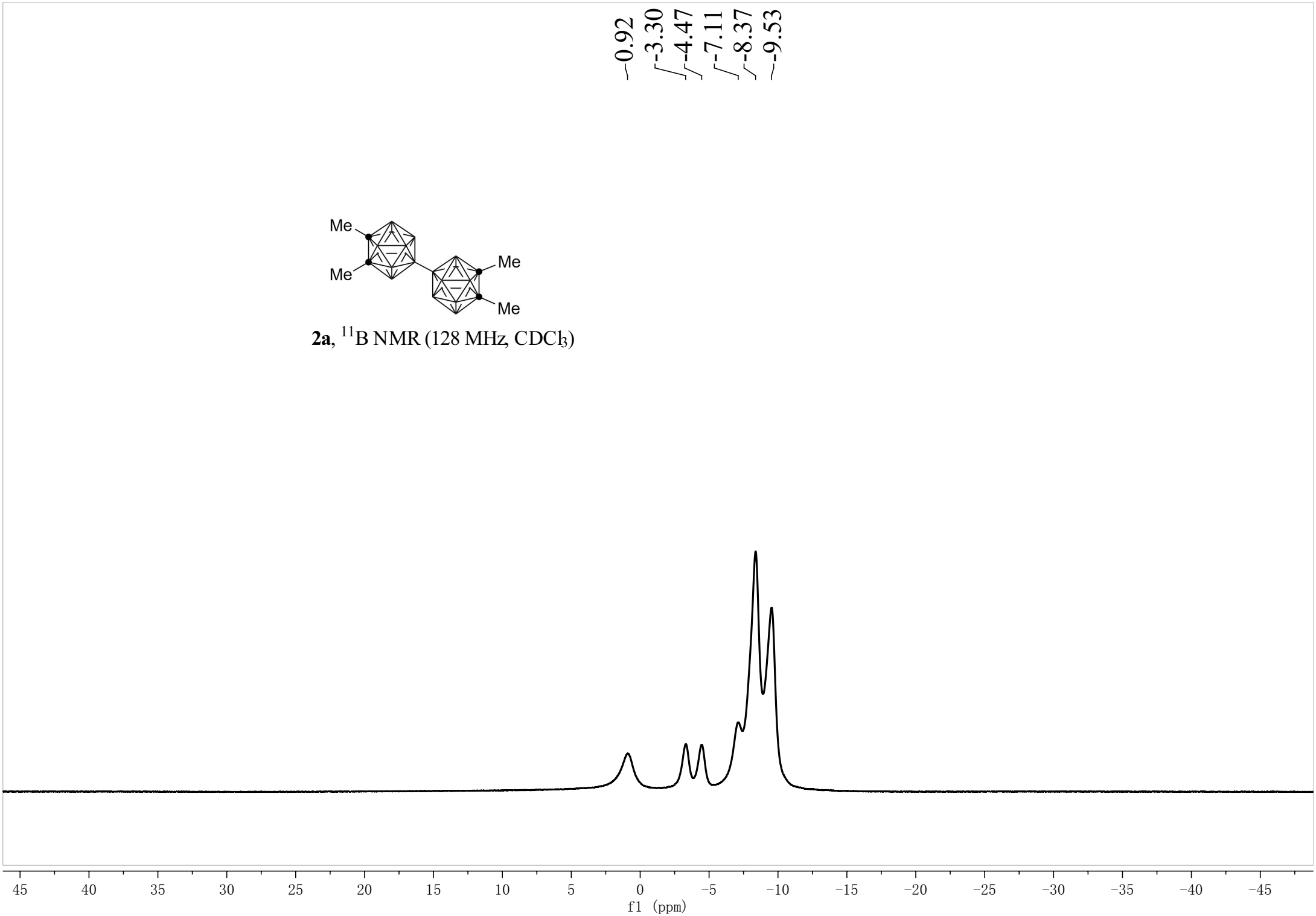
1. (a) W. Guo, C. Guo, Y. -N. Ma, X.-N. Chen, *Inorg. Chem*. 2022, **61**, 5326-5334. (b) W. Lu, Y. Wu, Y. -N. Ma, F. Chen, X. Chen, *Inorg. Chem*., 2023, **62**, 885-892.
2. Y. -N. Ma, H. Ren, Y. Wu, N. Li, F. Chen, X. Chen, *J. Am. Chem. Soc.*, 2023, **145**, 7331-7342.
3. R. A. Wiesboeck, M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1642-1643.
4. (a) T. L. Heying, J. W. Ager Jr, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, S. I. Trotz, *Inorg. Chem.*, 1963, **2**, 1097-1105. (b) M. Bai, G. Tao, Z. Liu, L. Wang, Z. Duan, *Chin. Chem. Lett.*, 2022, **33**, 201-204.



2a, ^{1}H NMR (300 MHz, $CDCl_3$)

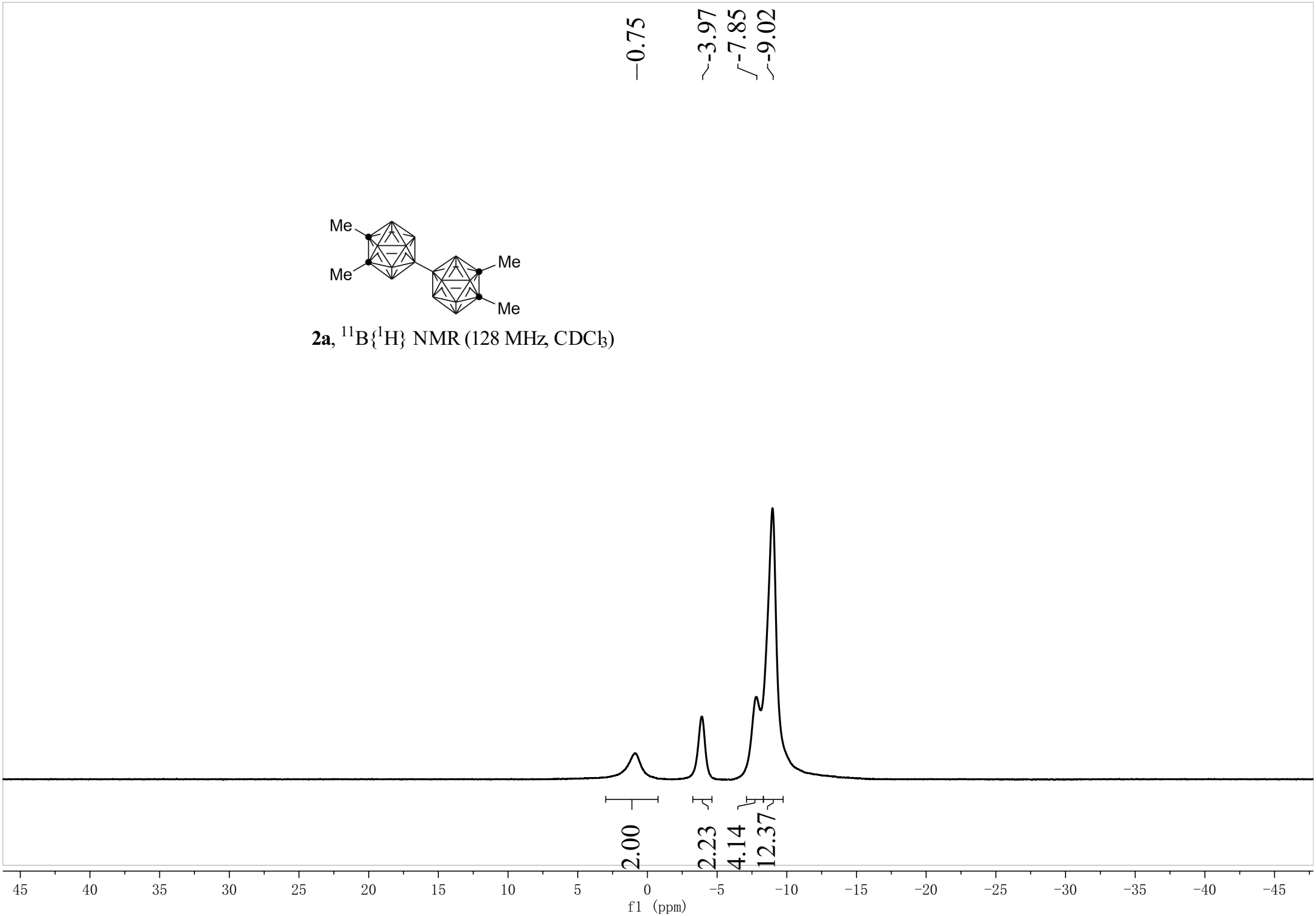


2a, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

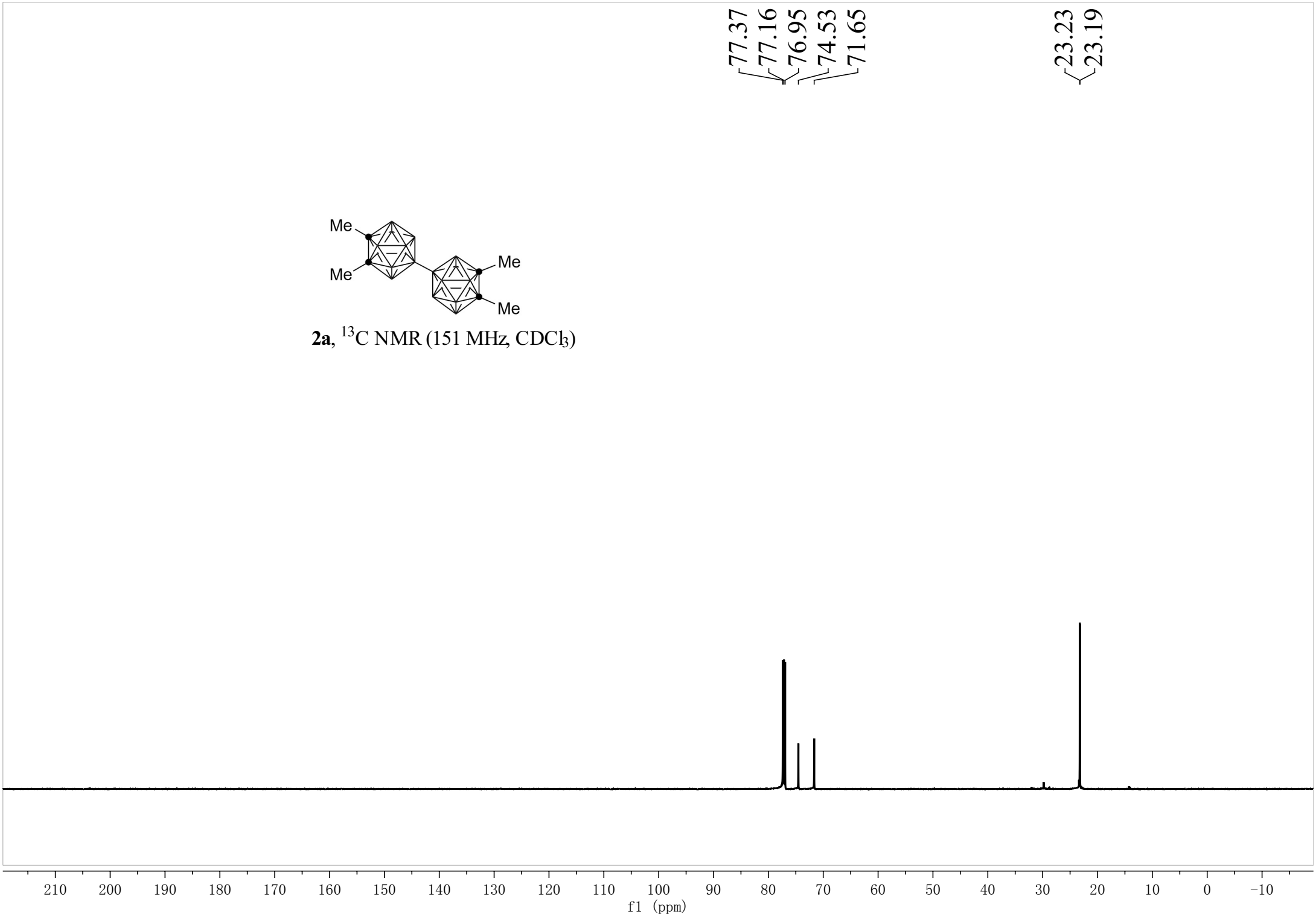


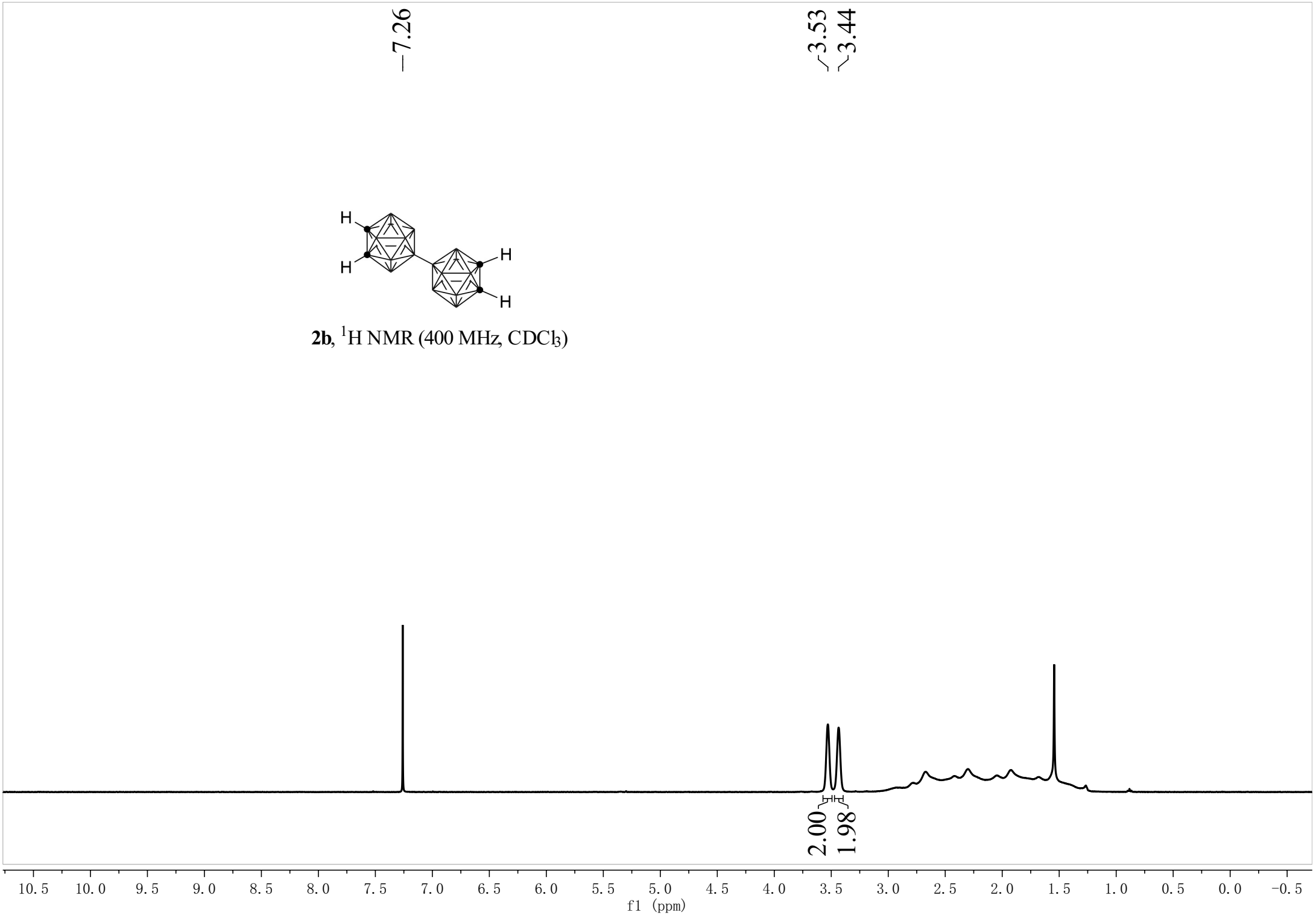
2a, ^{11}B NMR (128 MHz, $CDCl_3$)

2a, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

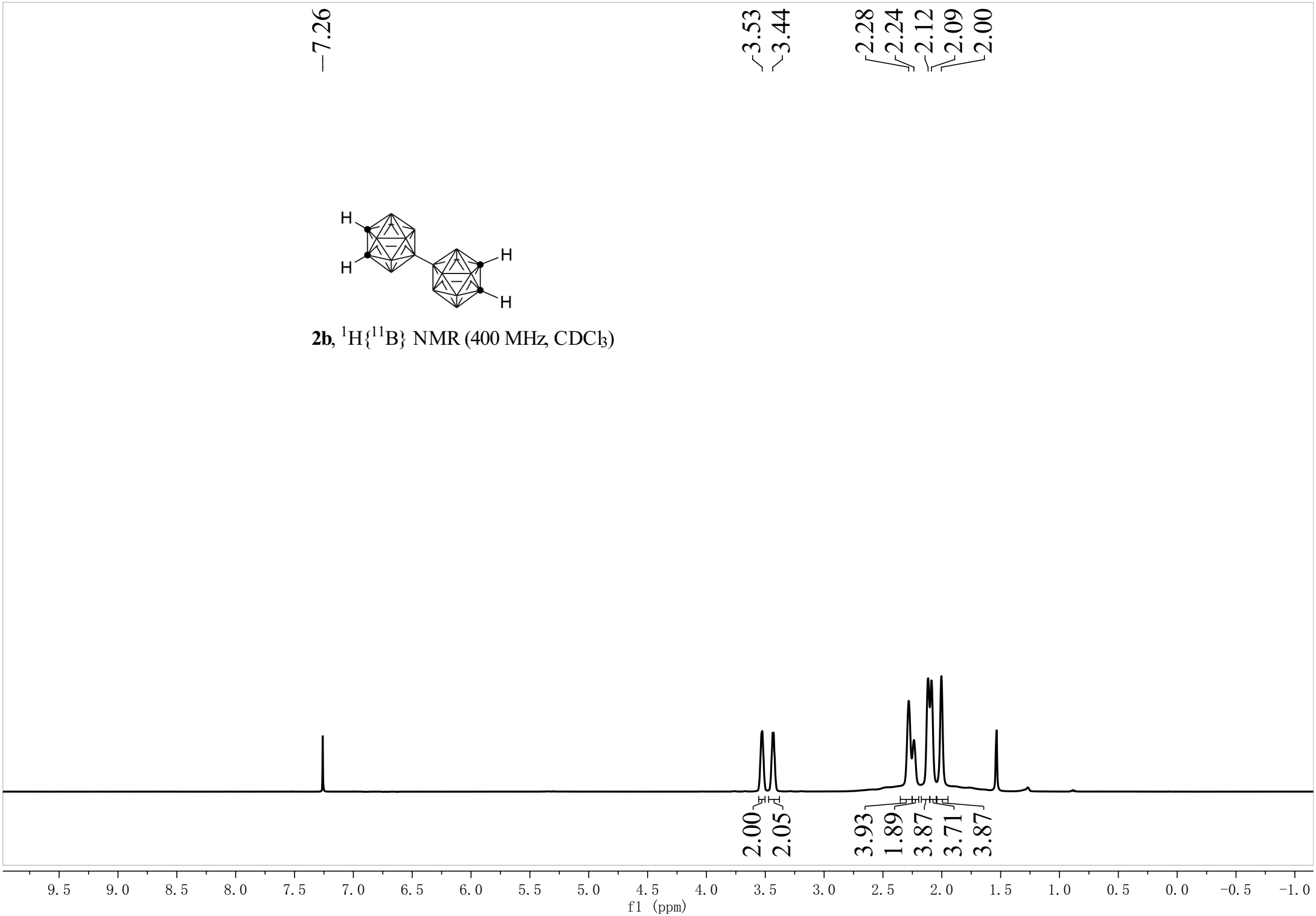


2a, ^{13}C NMR (151 MHz, $CDCl_3$)

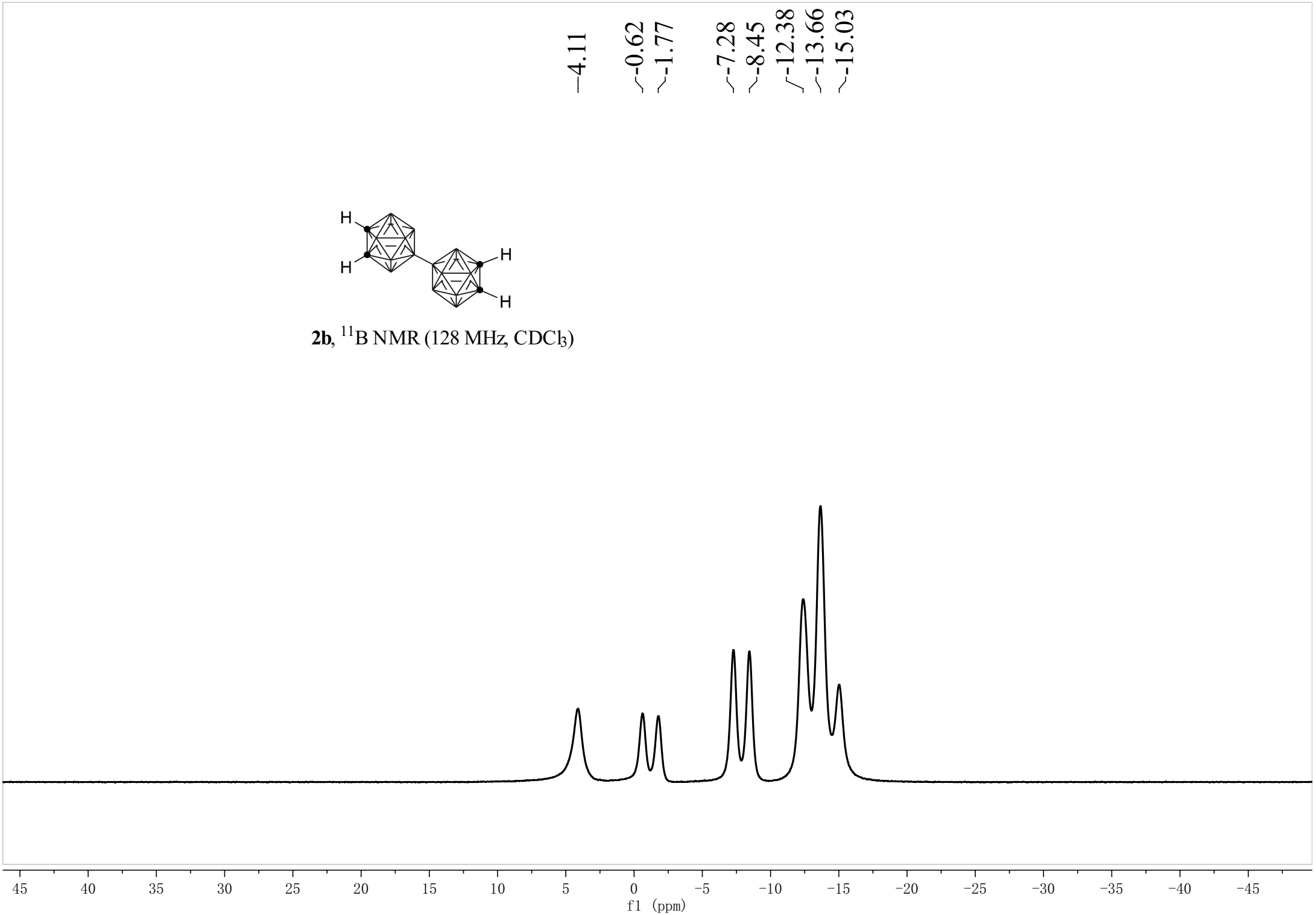




2b, ^{1}H NMR (400 MHz, $CDCl_3$)

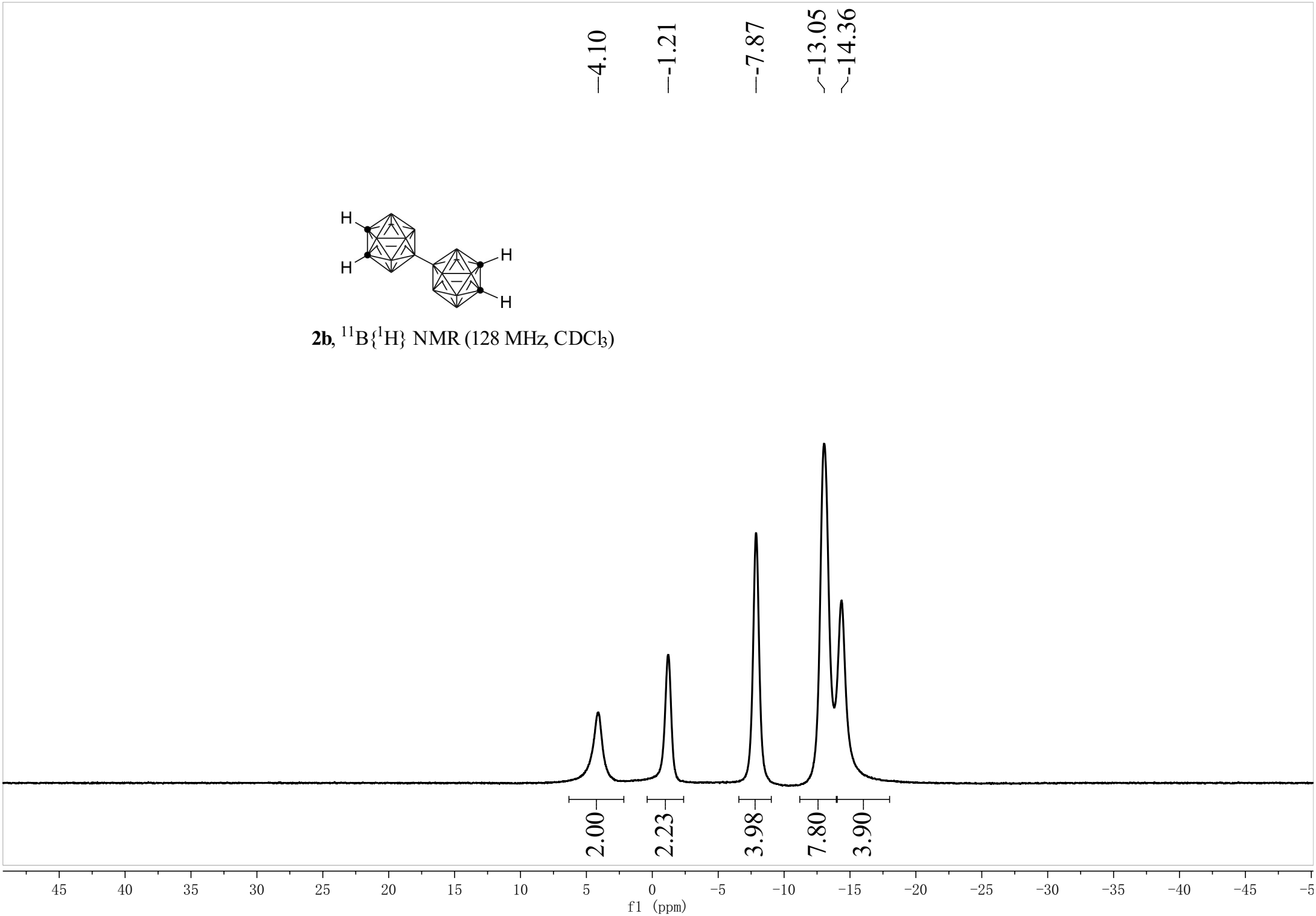


2b, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

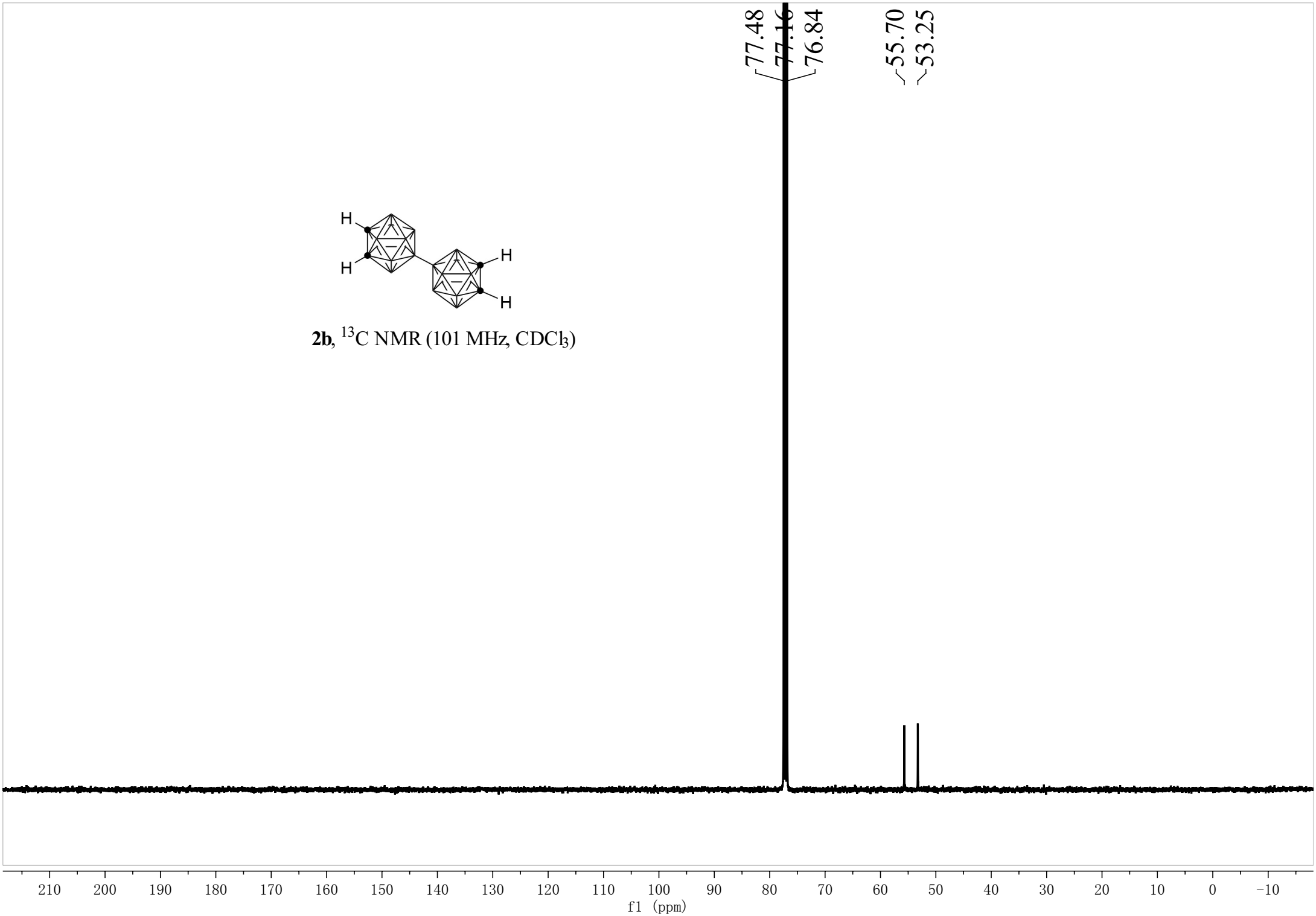


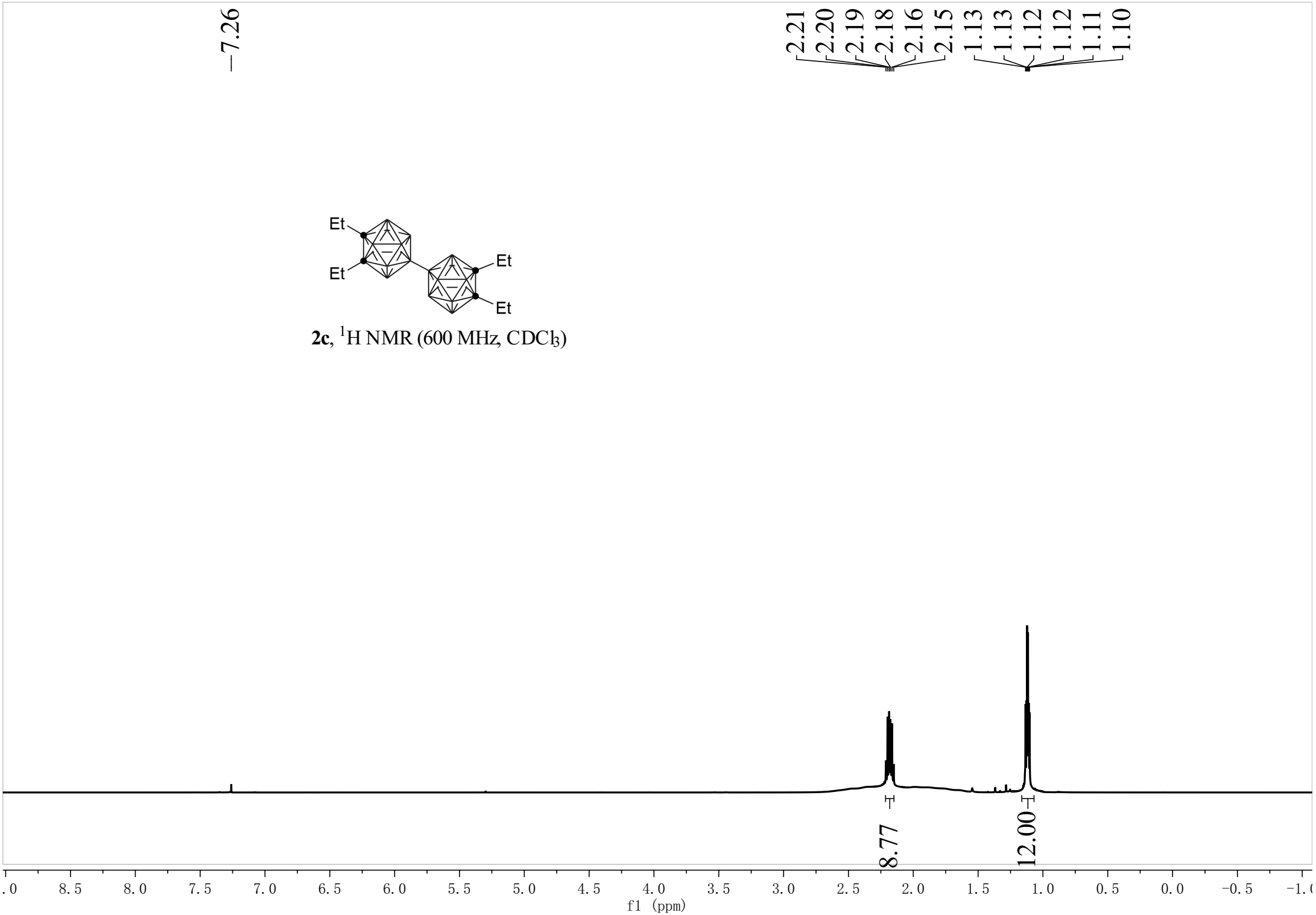
2b, ^{11}B NMR (128 MHz, $CDCl_3$)

2b, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

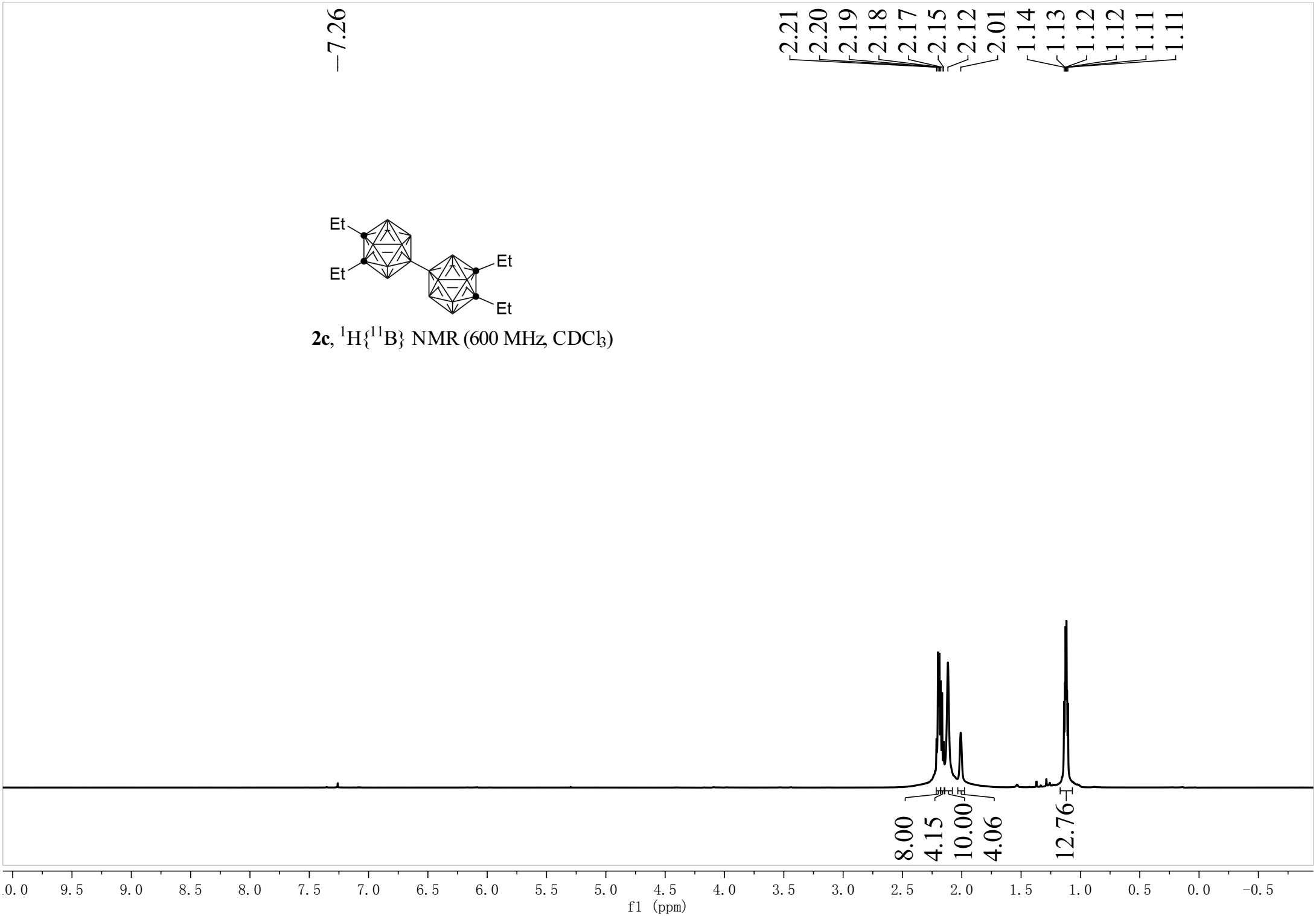


2b, ^{13}C NMR (101 MHz, $CDCl_3$)



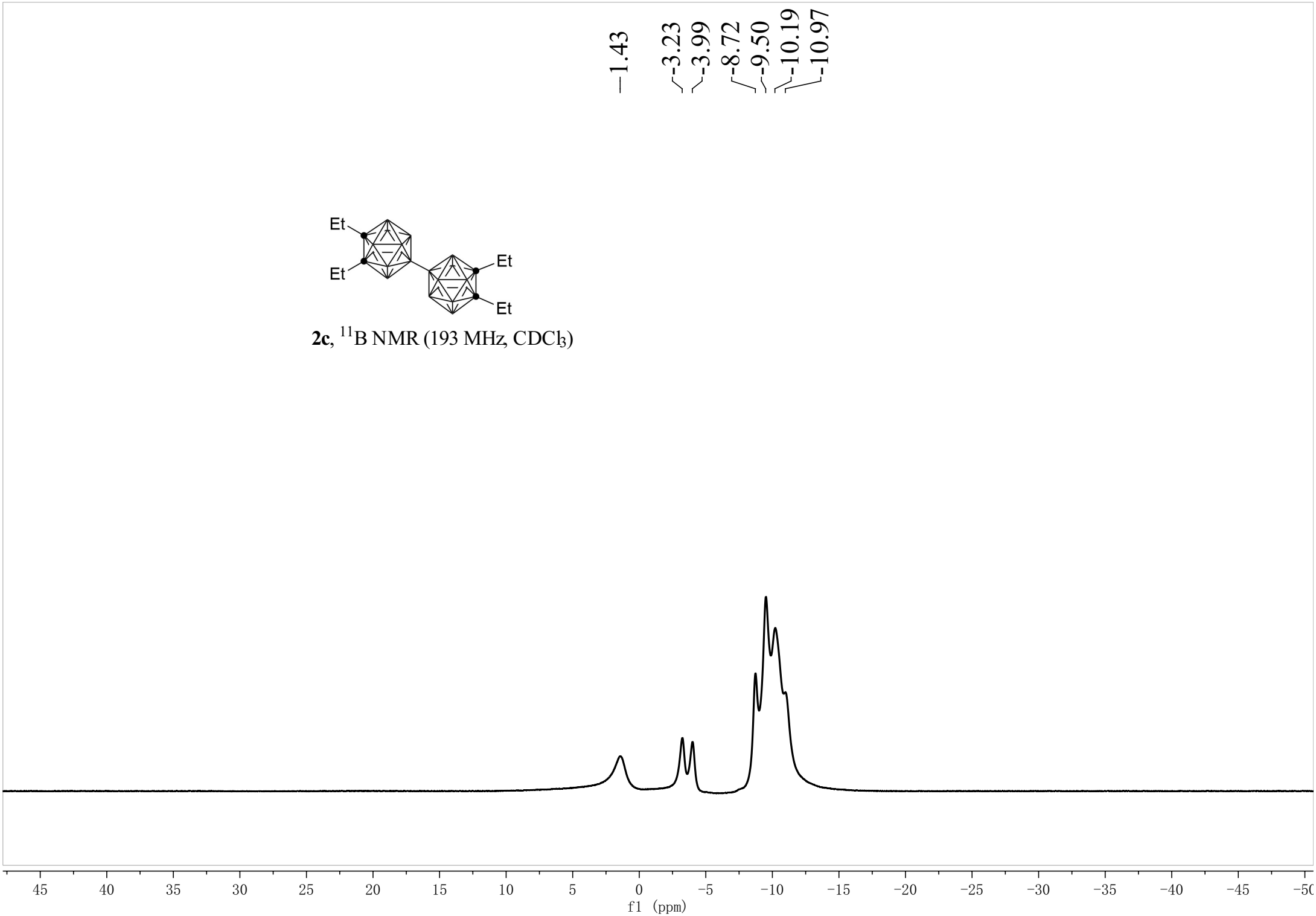


2c, ^{1}H NMR (600 MHz, $CDCl_3$)

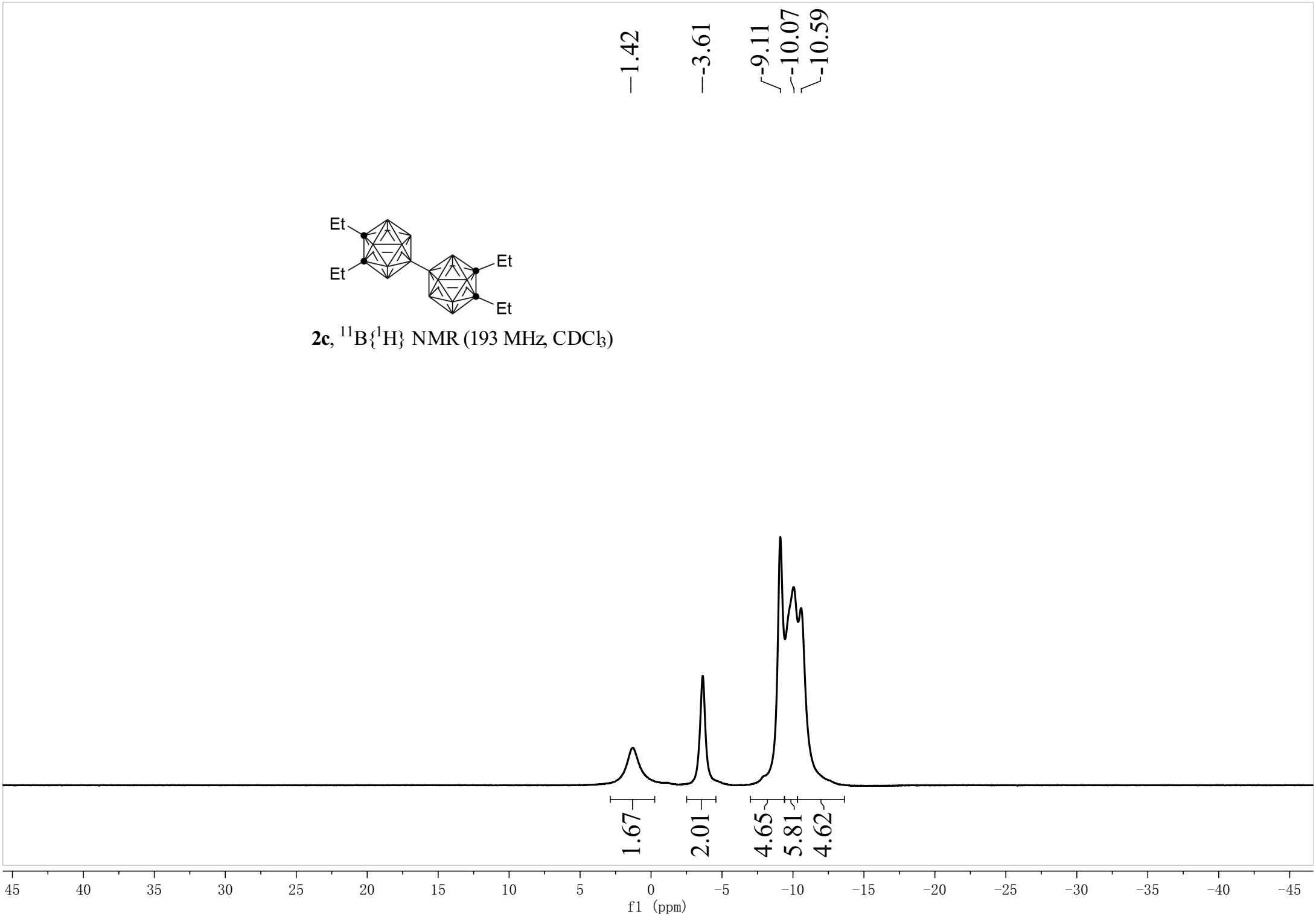


2c, $^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)

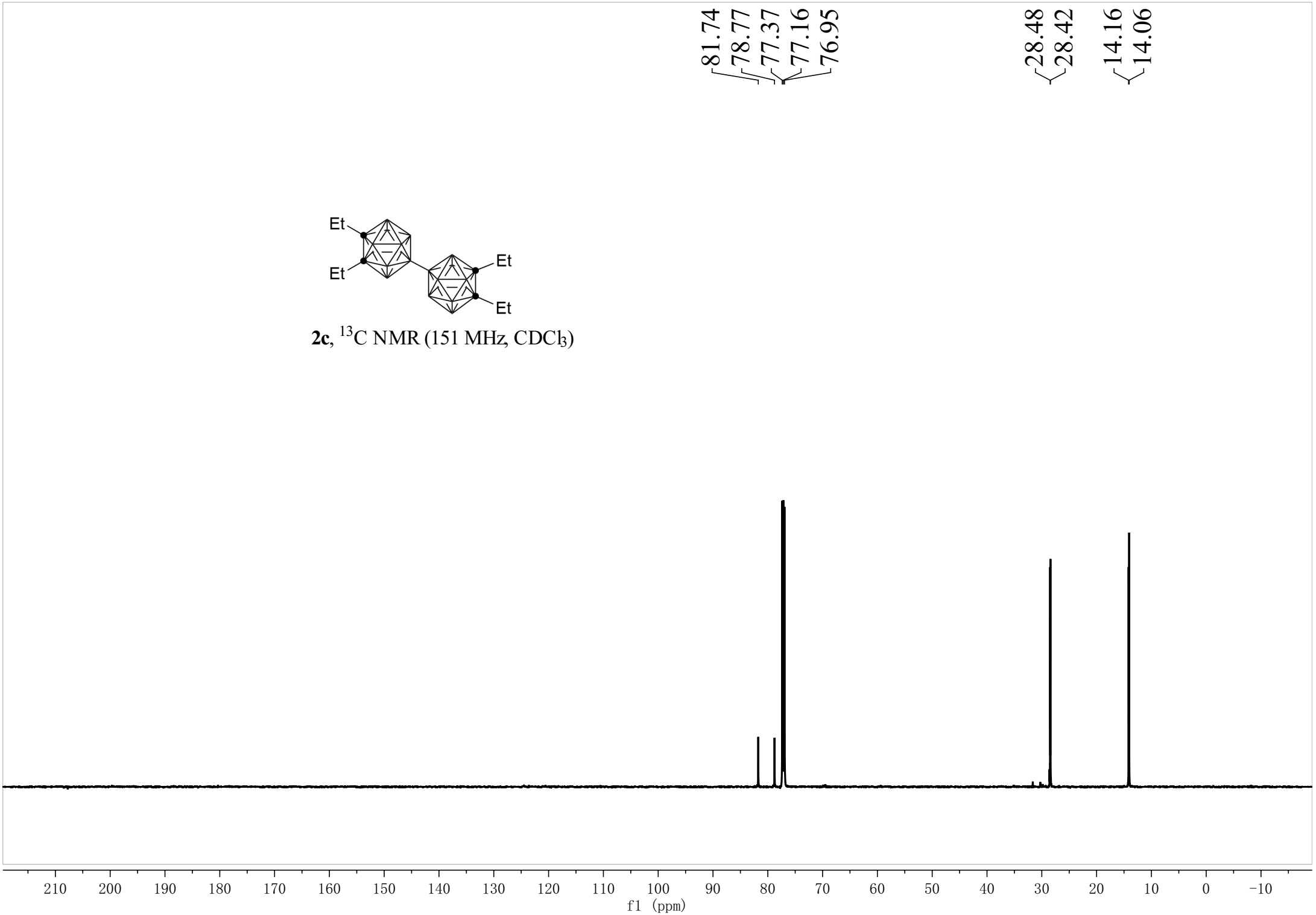
2c, ^{11}B NMR (193 MHz, $CDCl_3$)

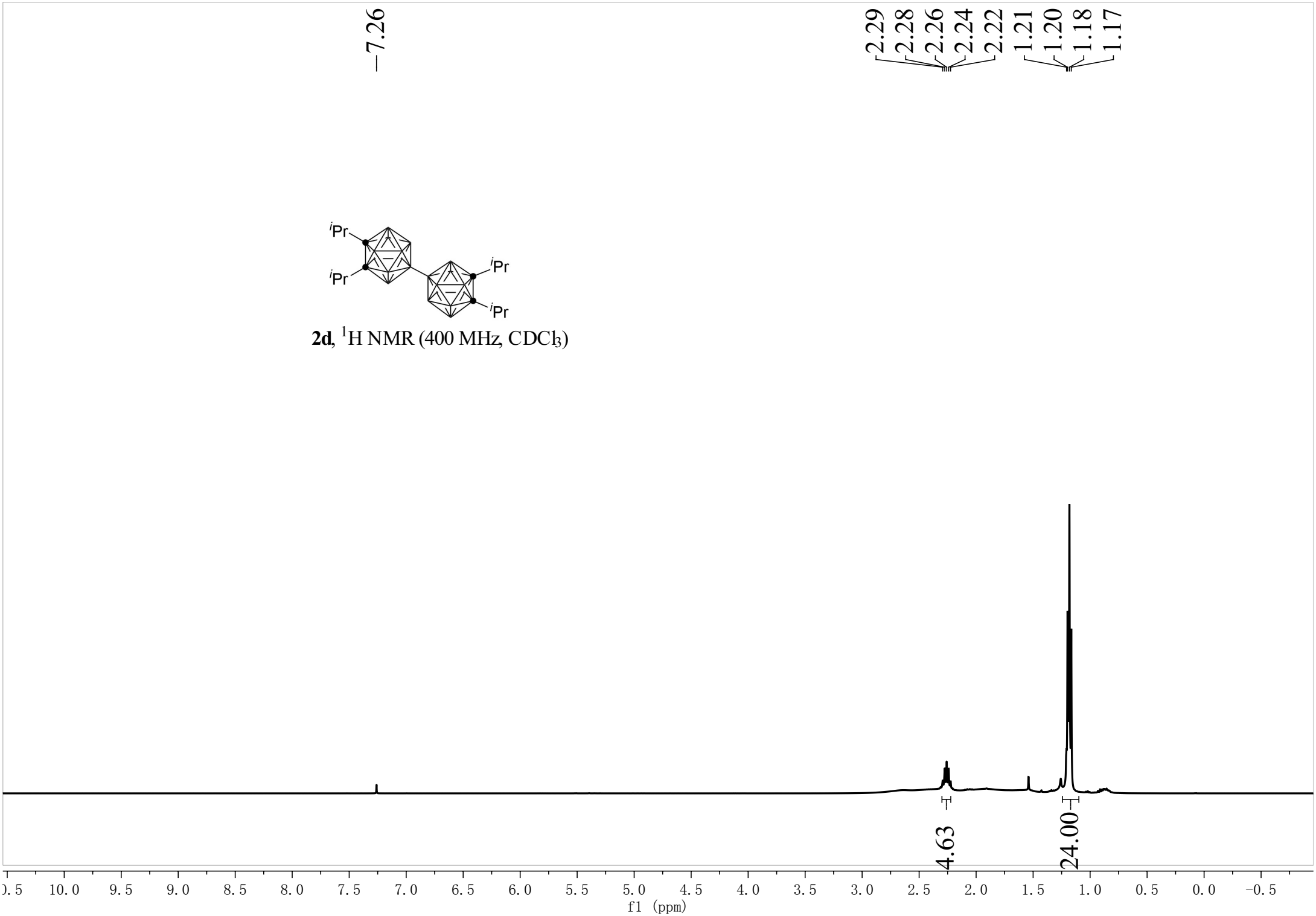


2c, $^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)



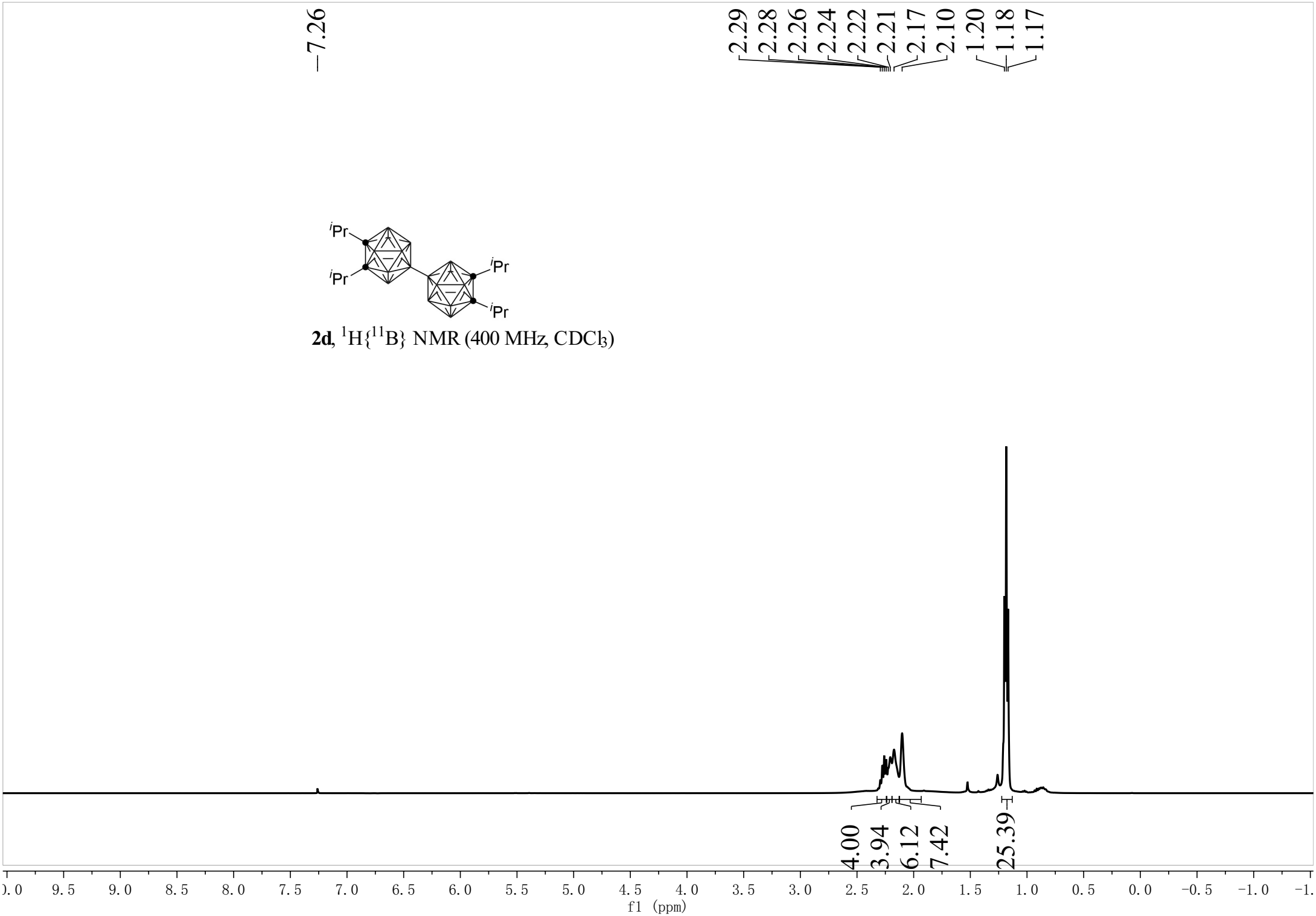
2c, ^{13}C NMR (151 MHz, $CDCl_3$)

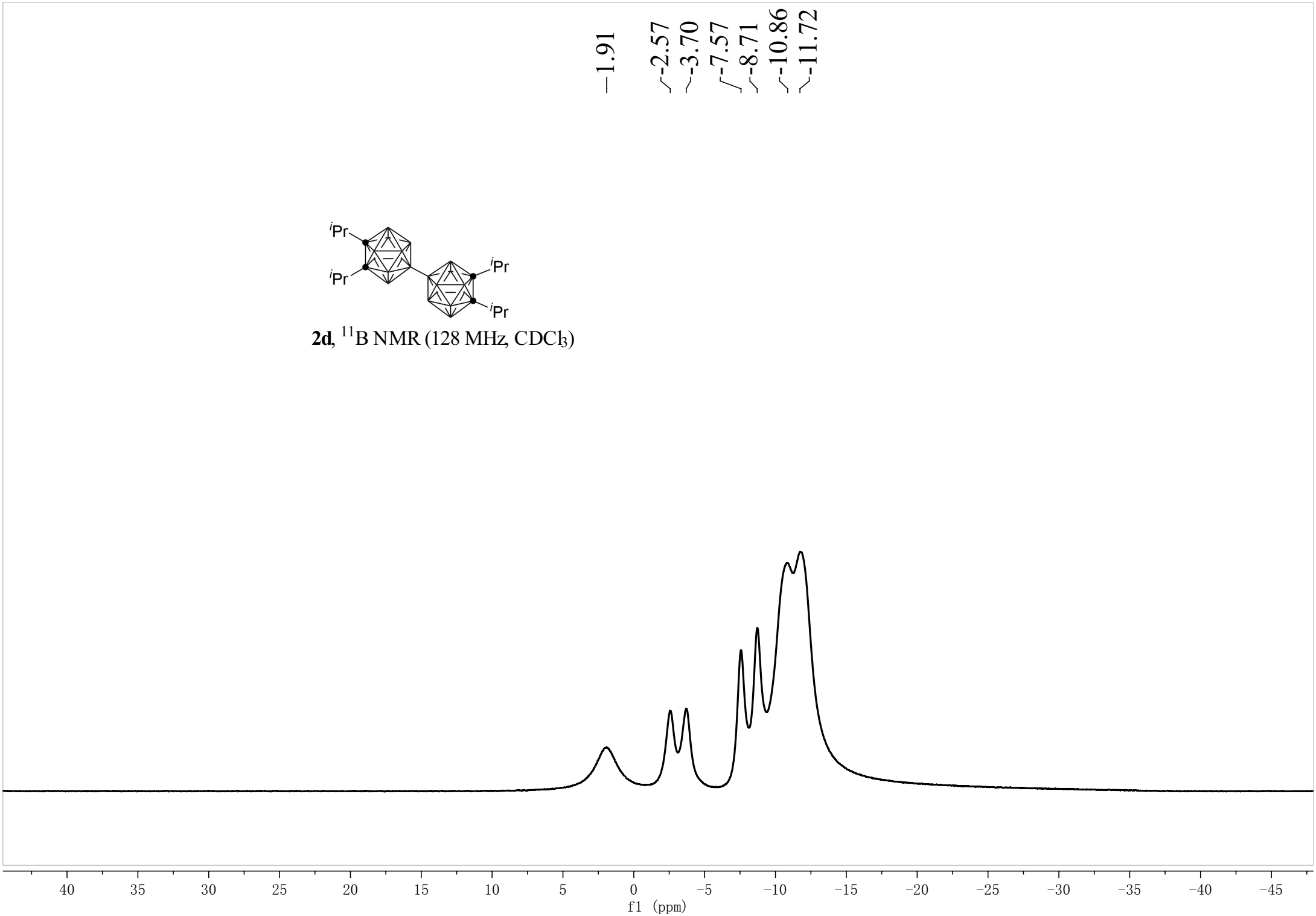




2d, ^{1}H NMR (400 MHz, $CDCl_3$)

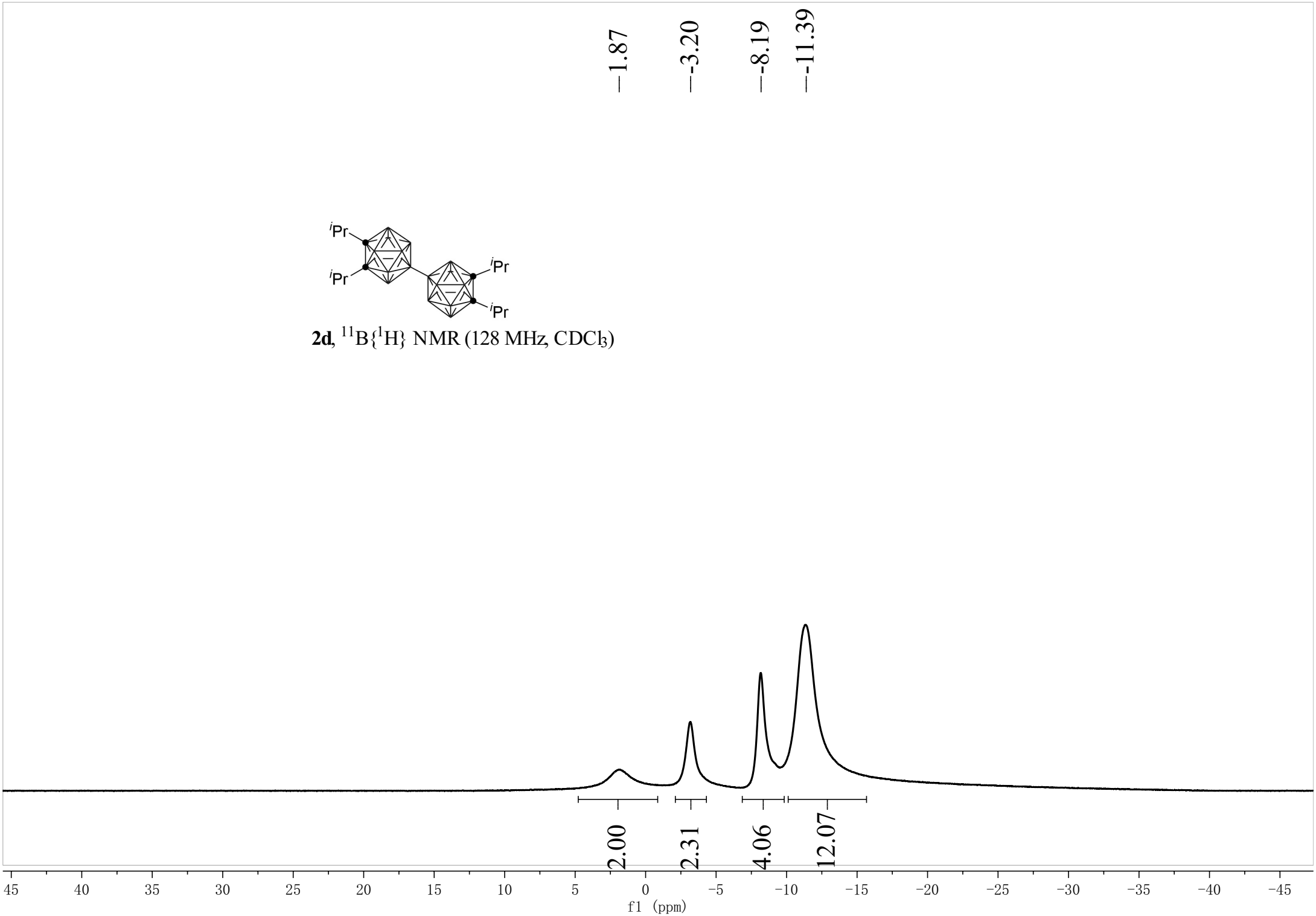
2d, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)



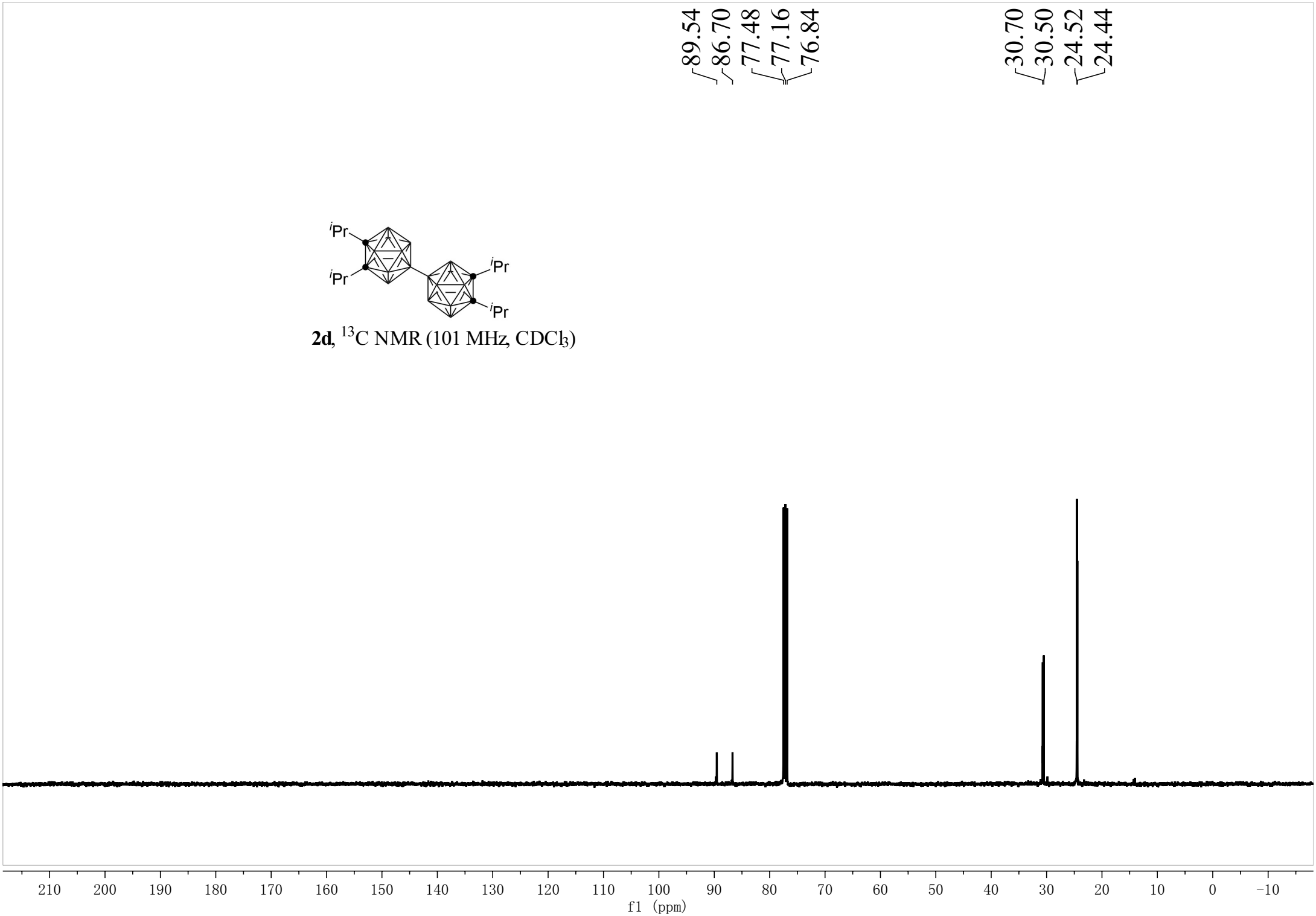


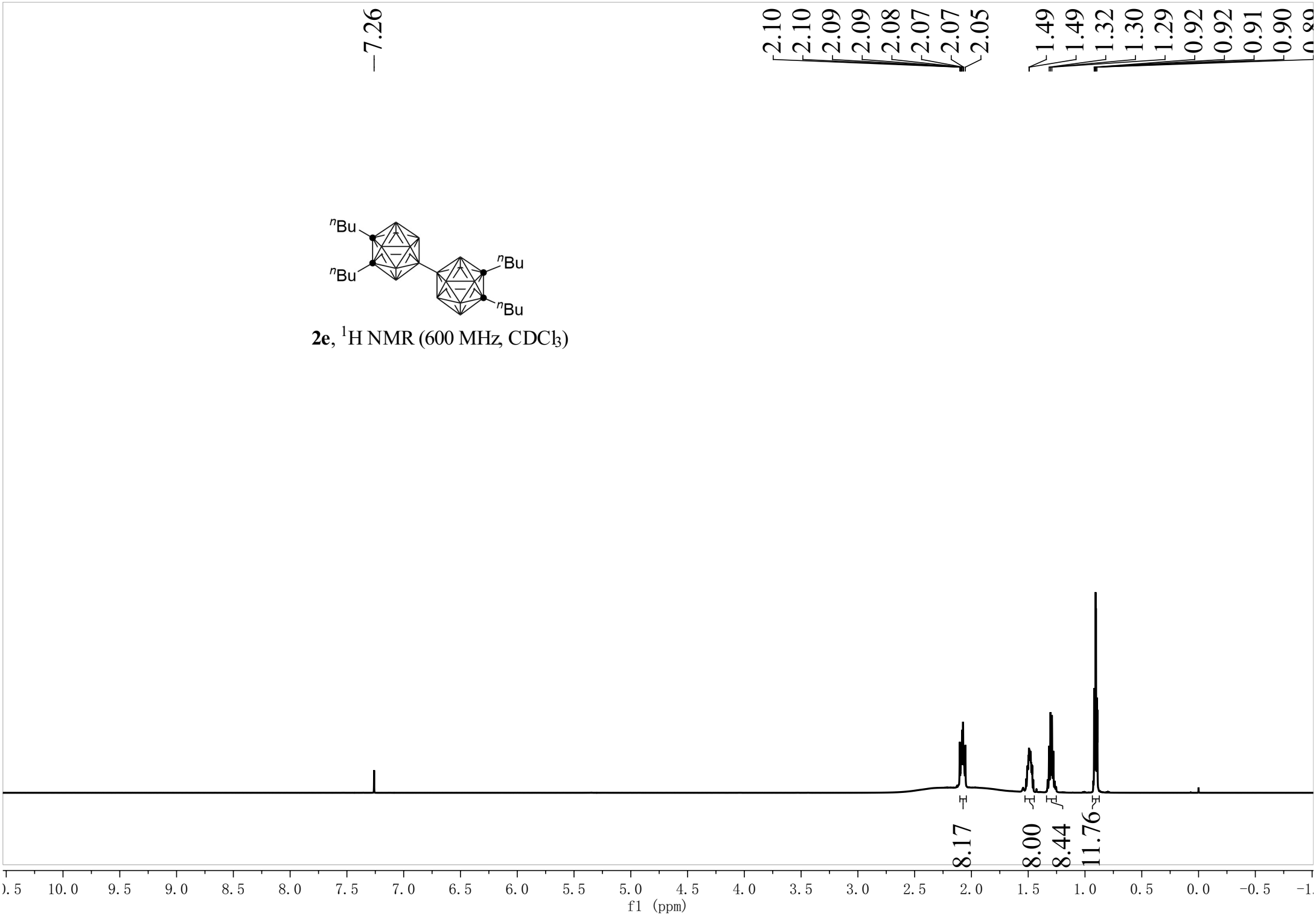
2d, ^{11}B NMR (128 MHz, $CDCl_3$)

2d, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

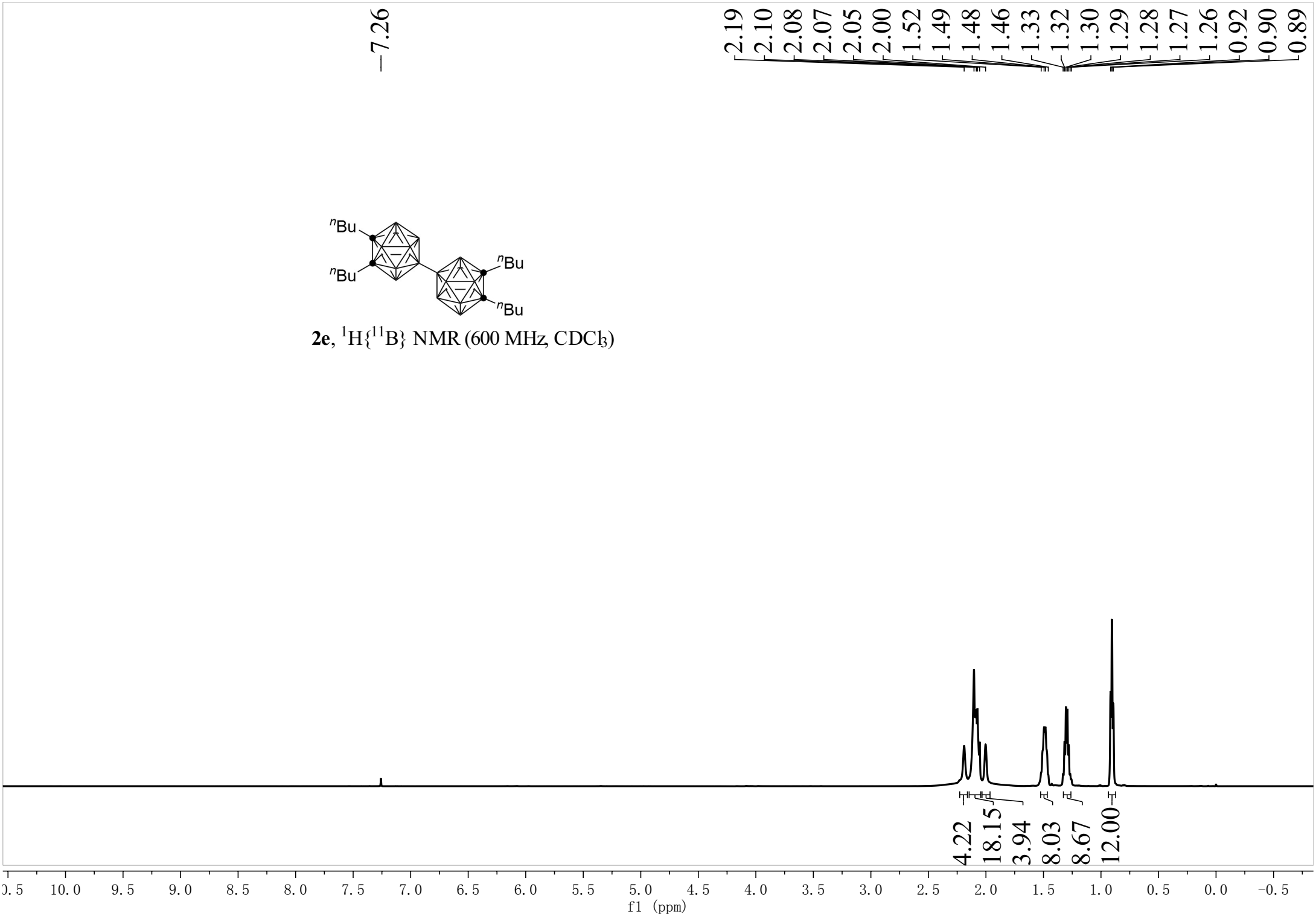


2d, ^{13}C NMR (101 MHz, $CDCl_3$)



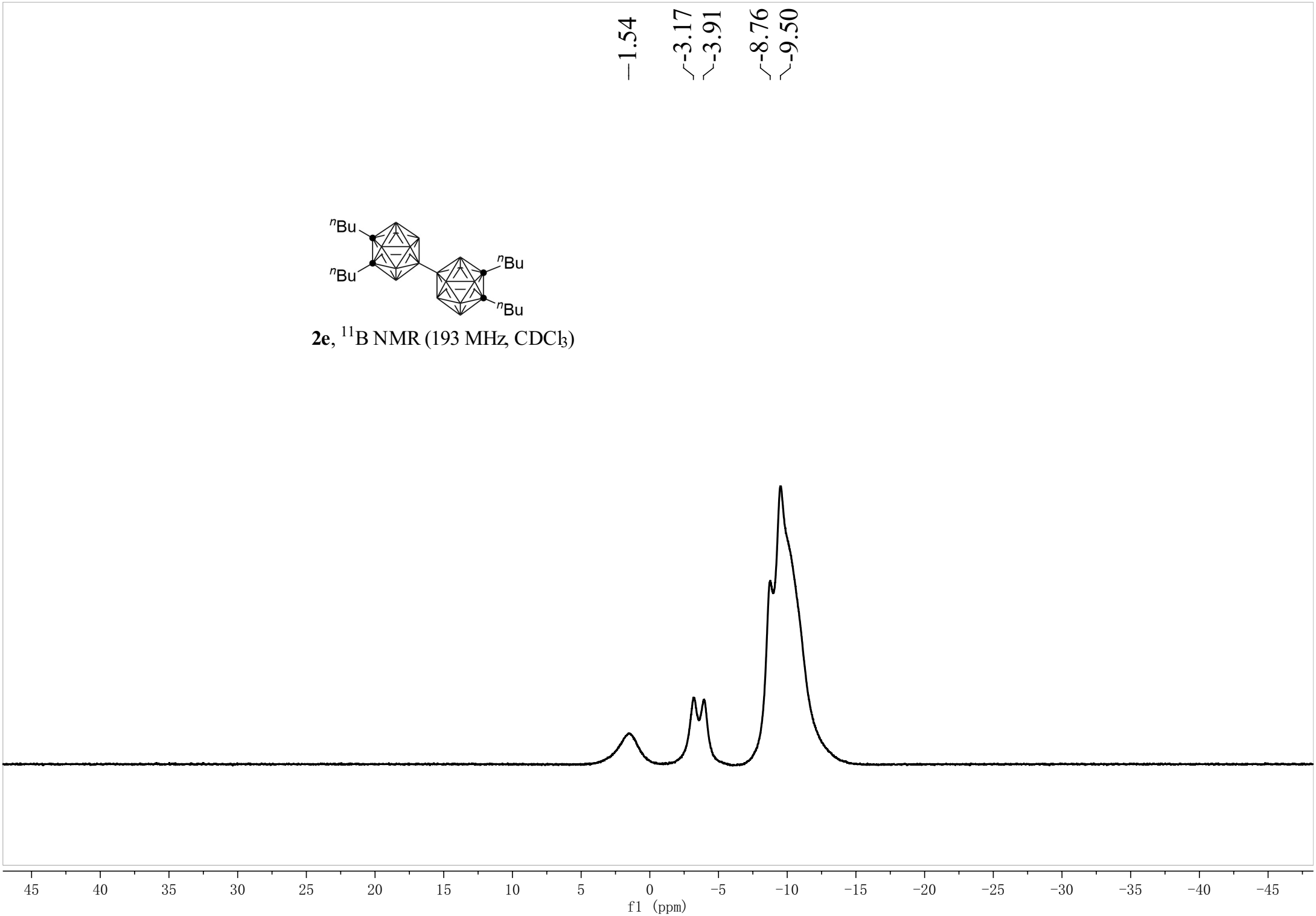


2e, ^{1}H NMR (600 MHz, $CDCl_3$)

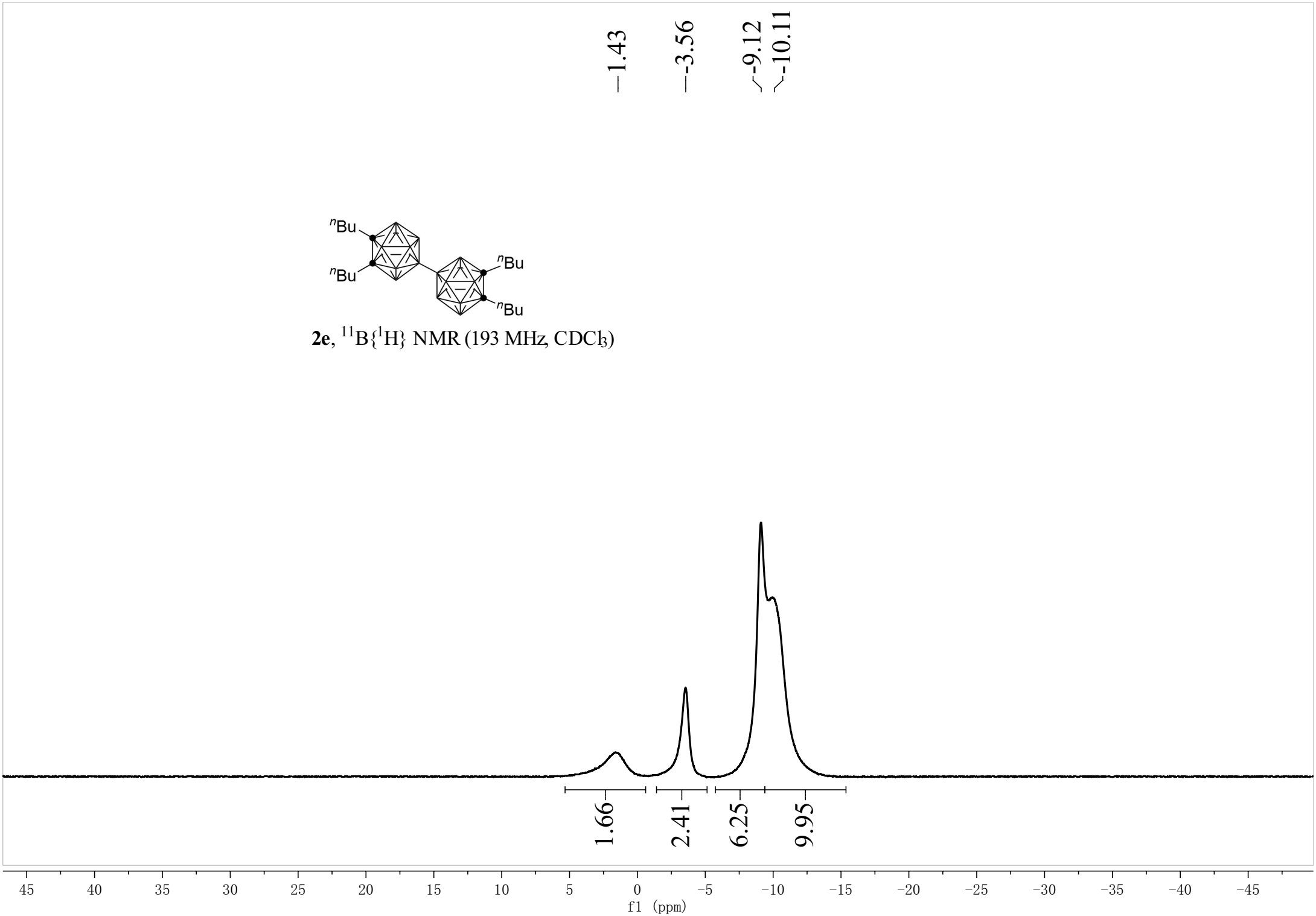


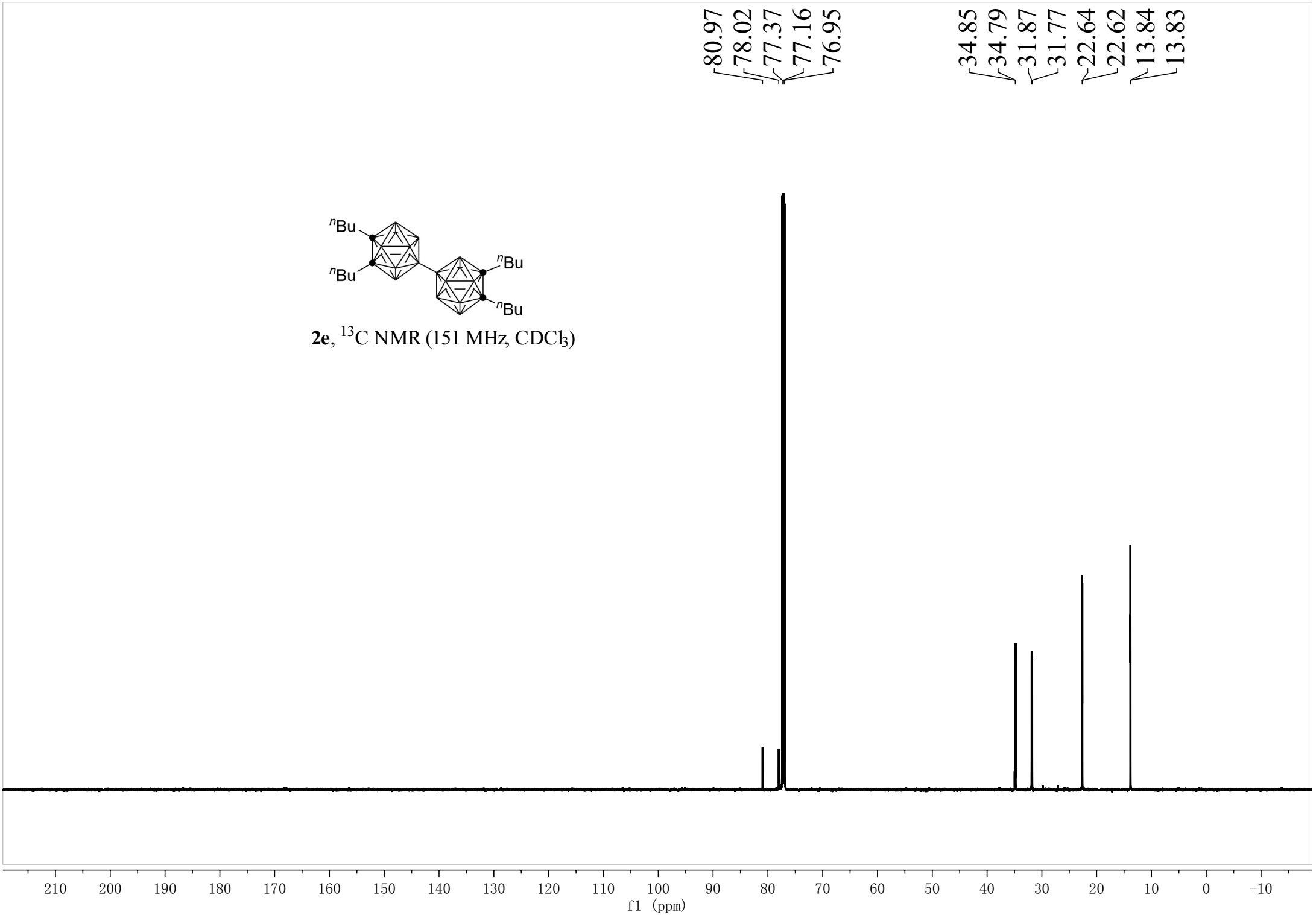
2e, $^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)

2e, ^{11}B NMR (193 MHz, $CDCl_3$)

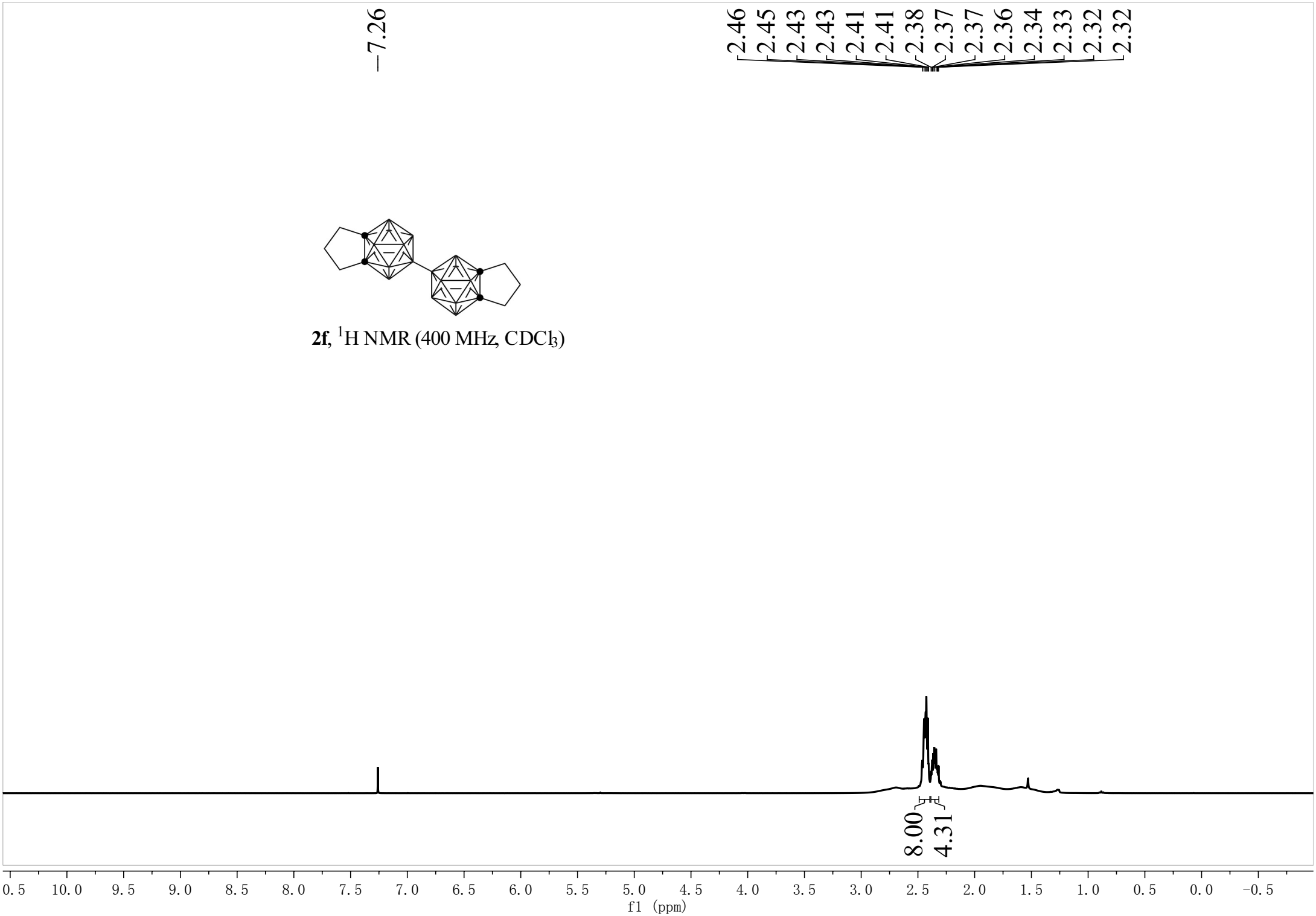


2e, $^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)



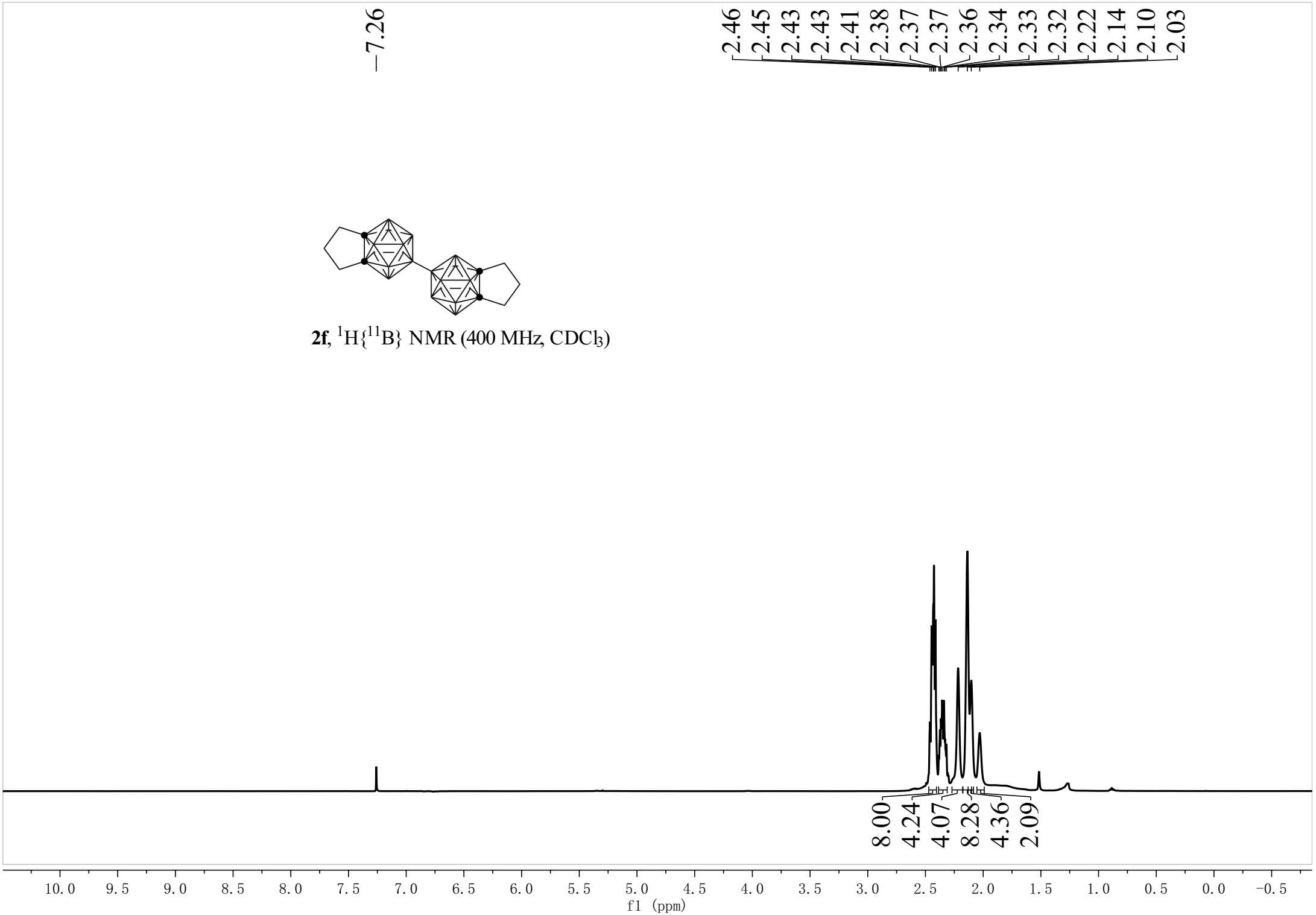


2e, ^{13}C NMR (151 MHz, $CDCl_3$)

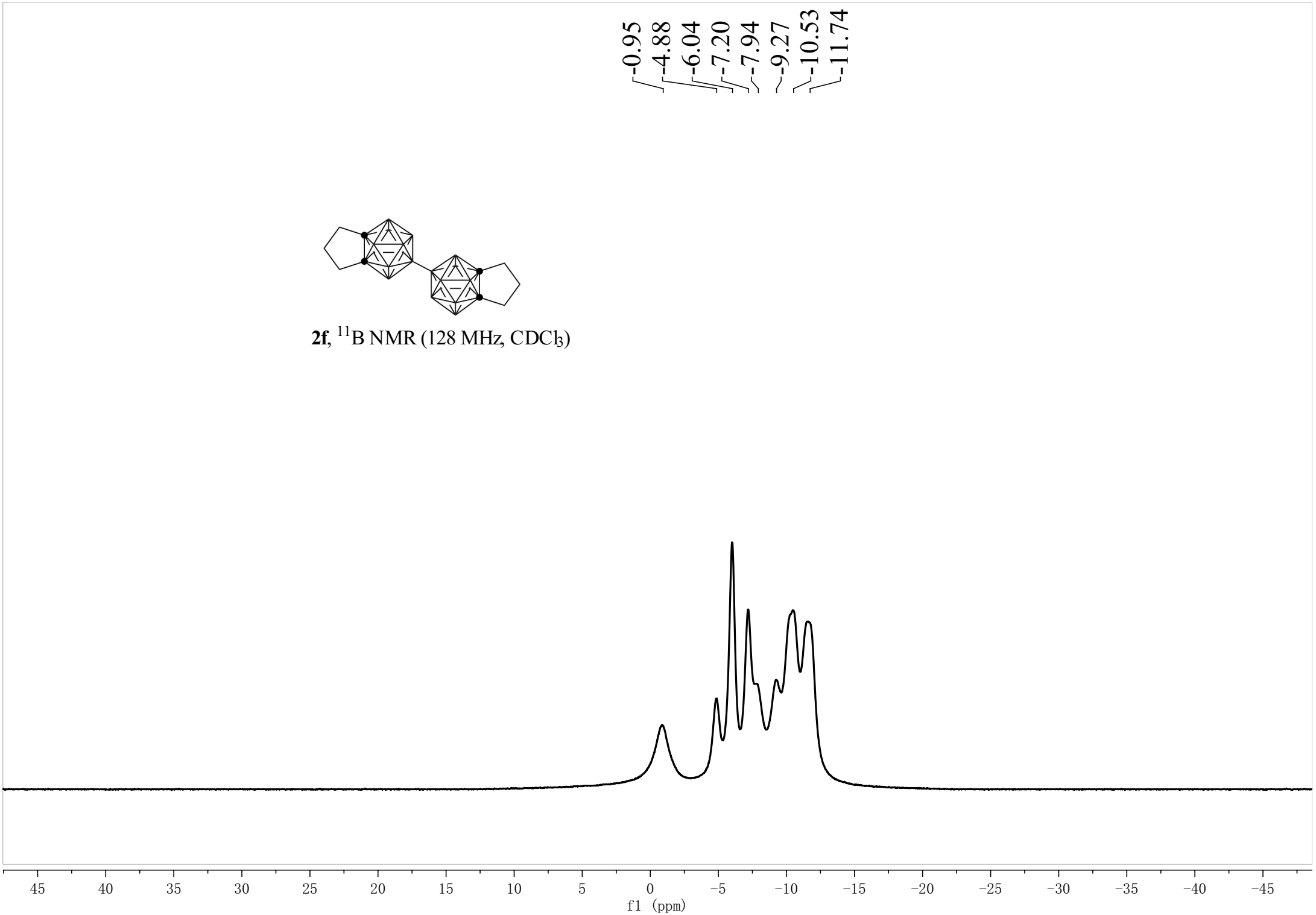


2f, ^{1}H NMR (400 MHz, $CDCl_3$)

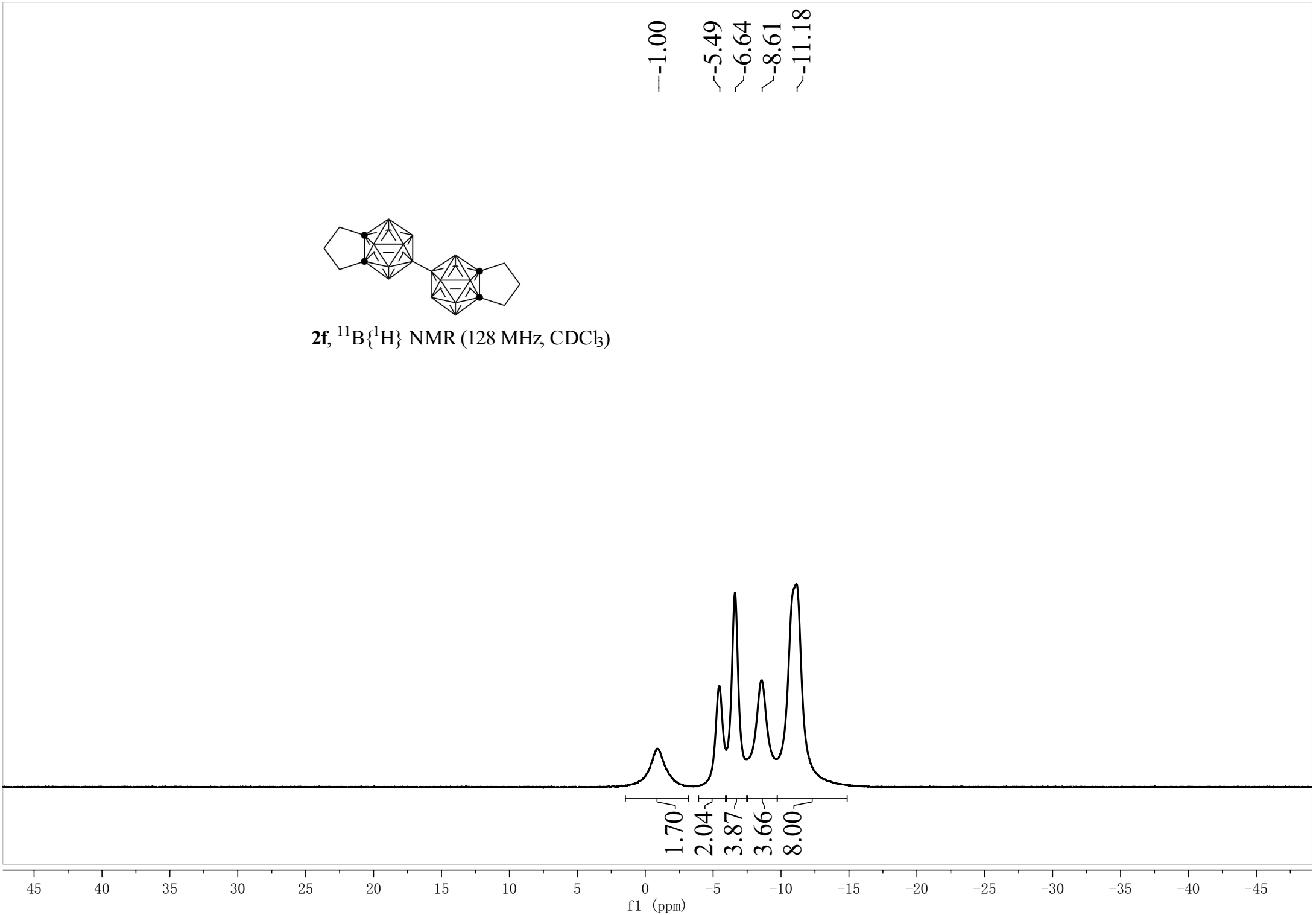
2f, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)



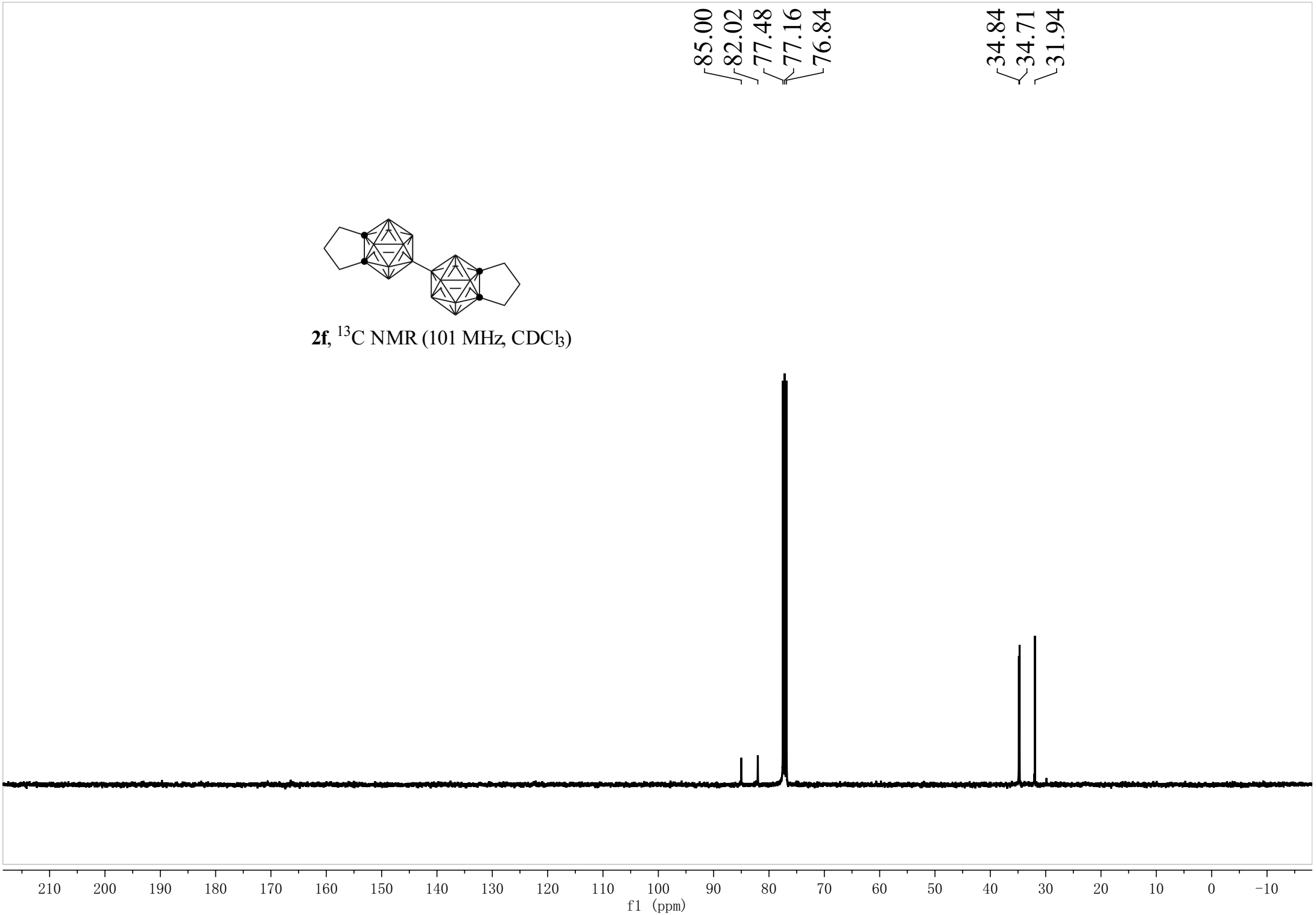
2f, ^{11}B NMR (128 MHz, $CDCl_3$)

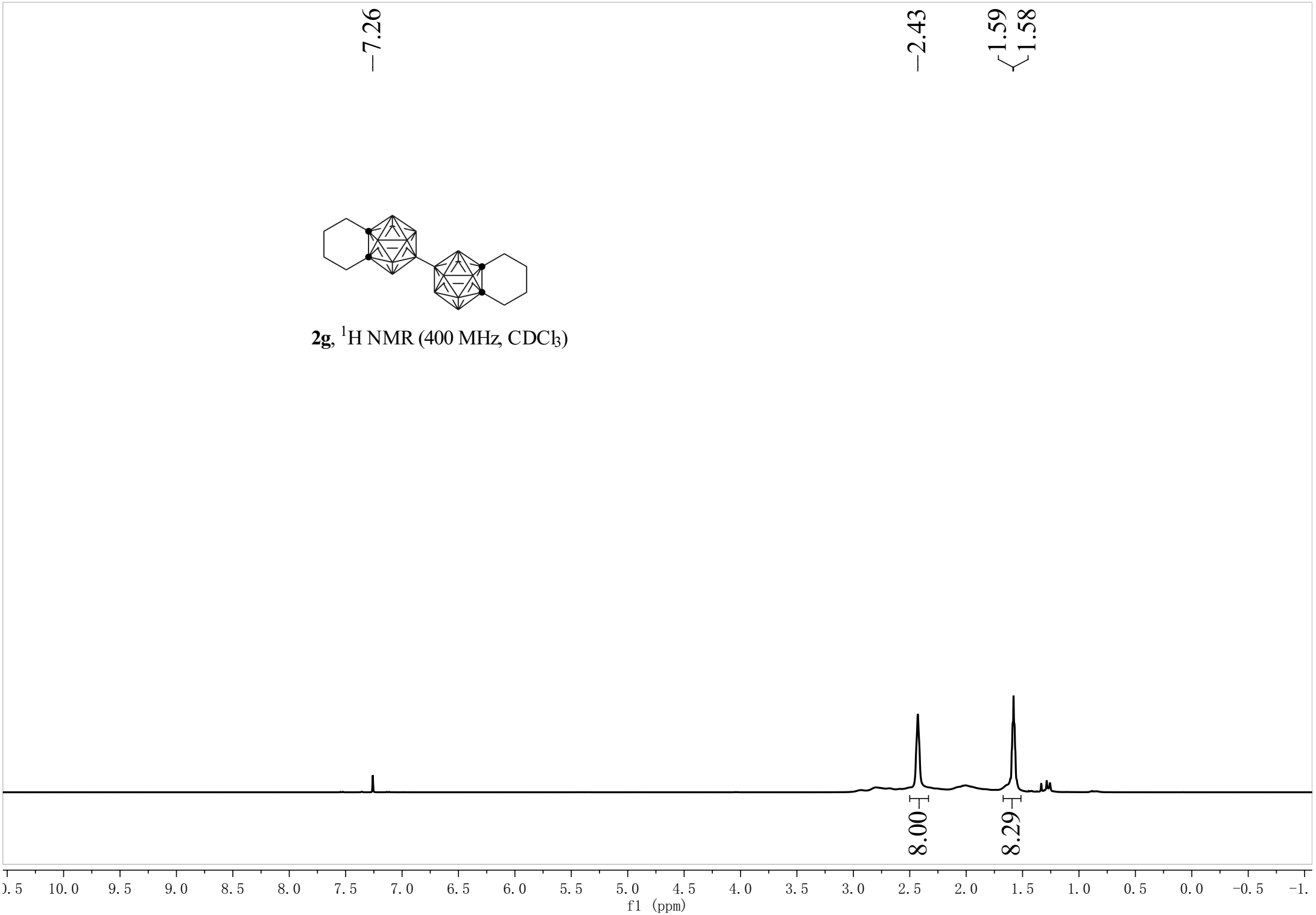


2f, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



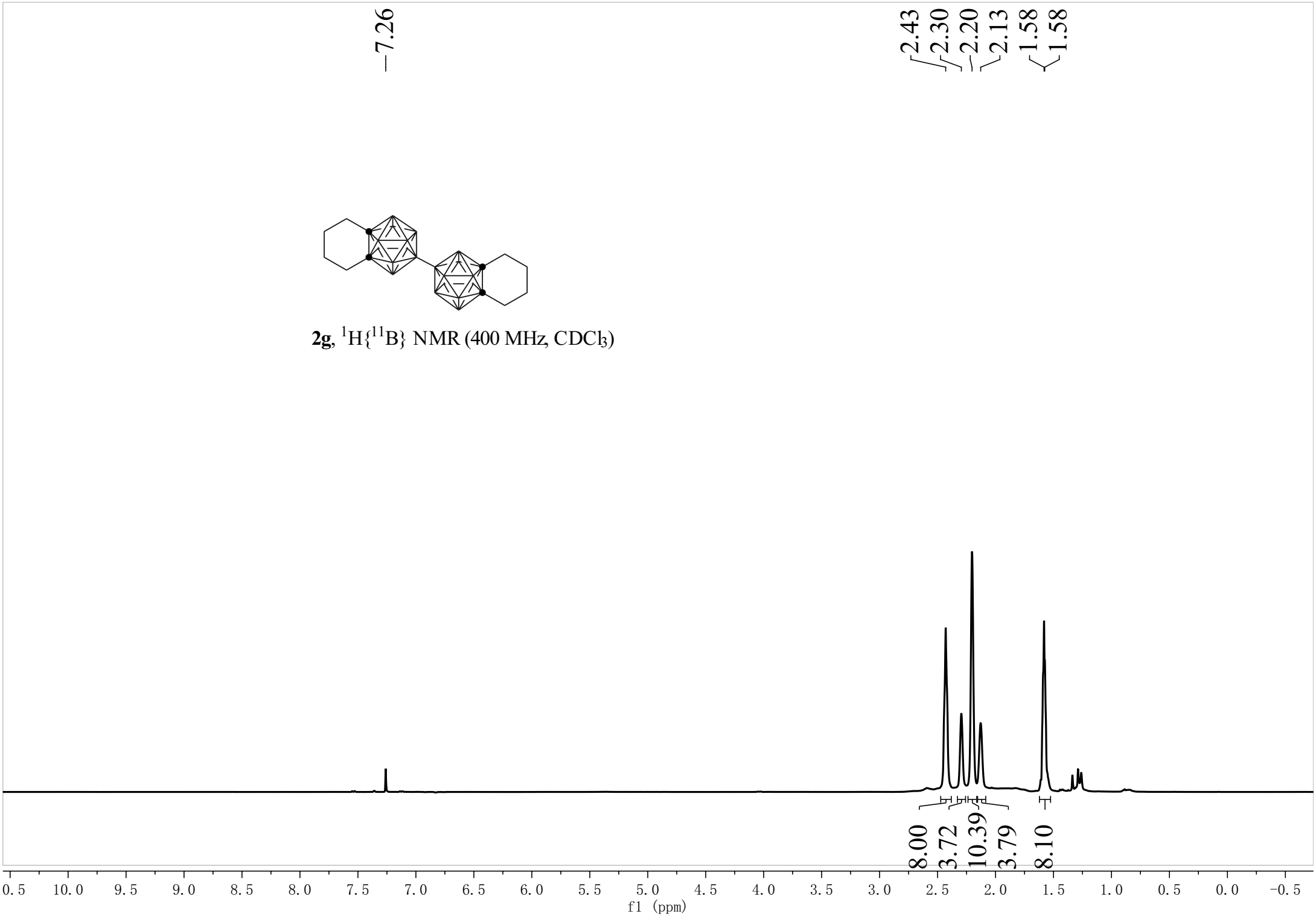
2f, ^{13}C NMR (101 MHz, $CDCl_3$)

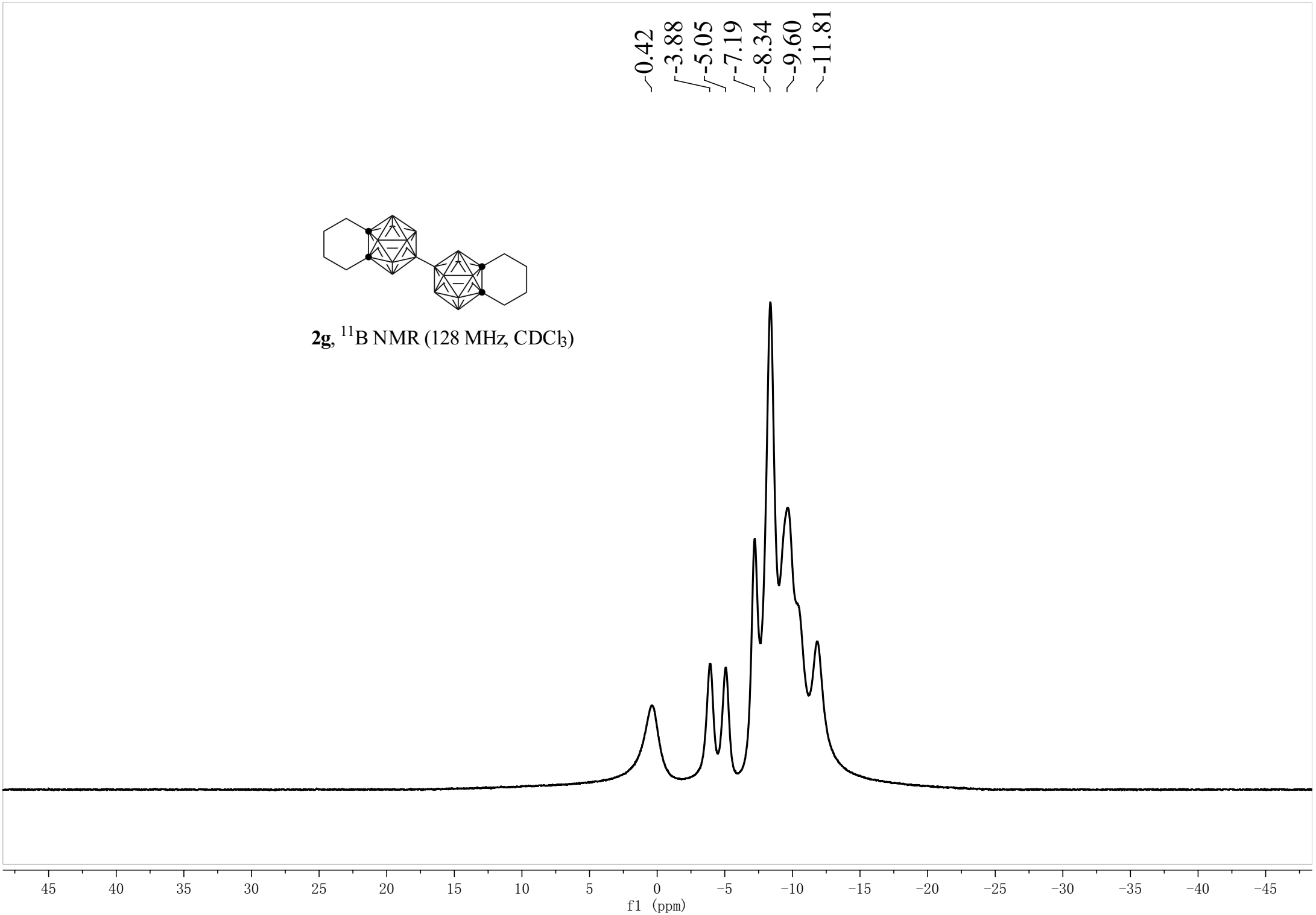




2g, ^{1}H NMR (400 MHz, $CDCl_3$)

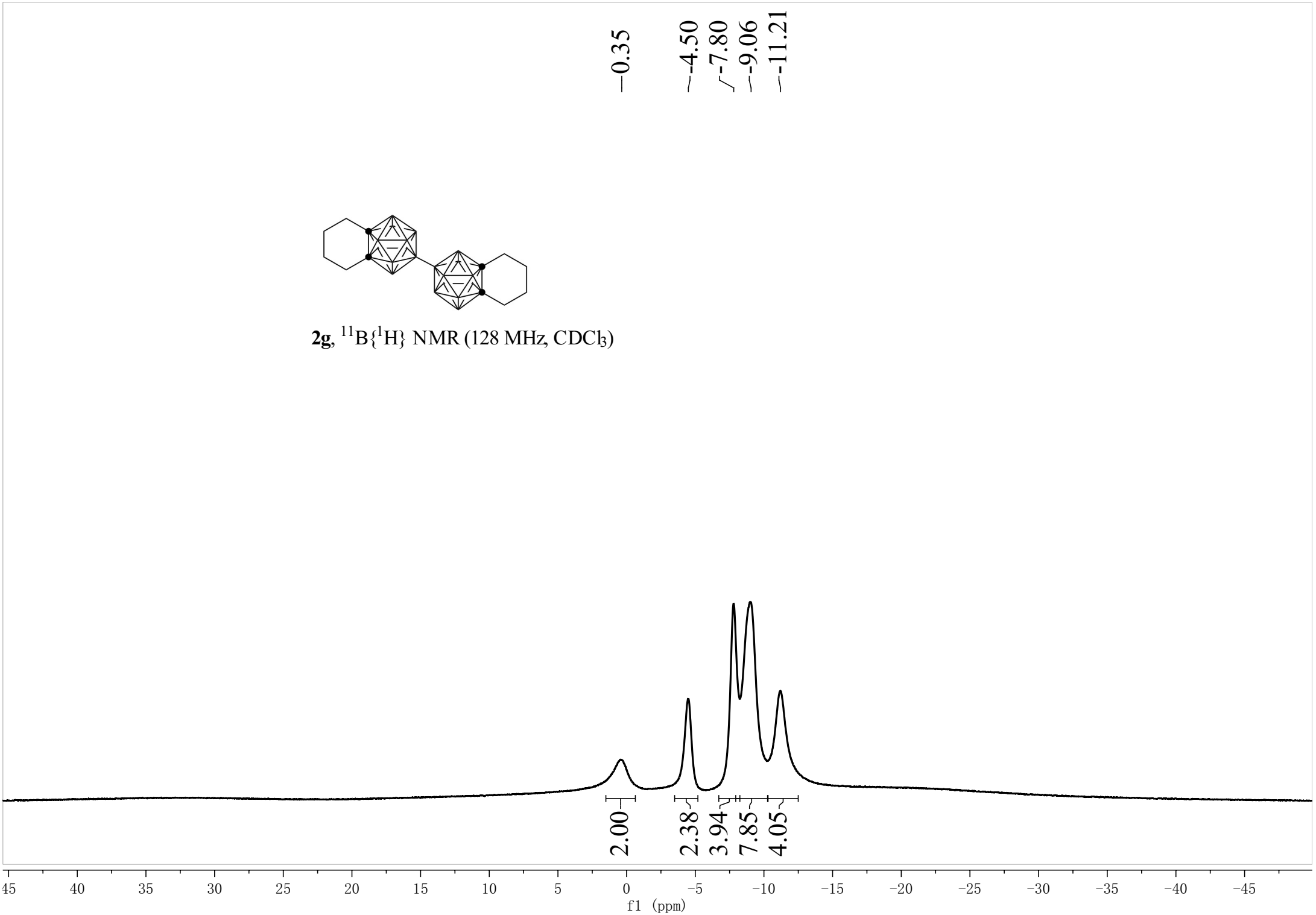
2g, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)



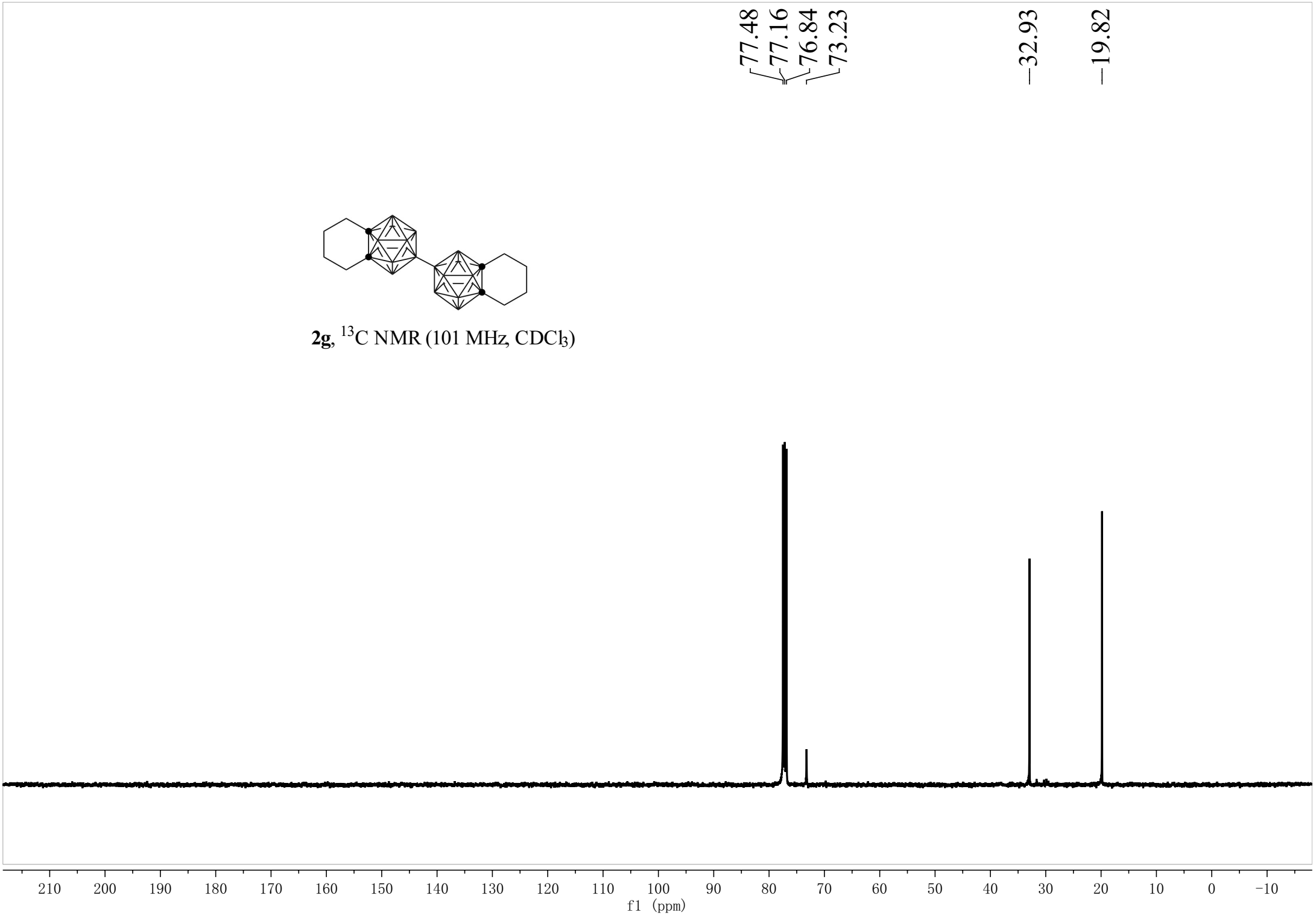


2g, ^{11}B NMR (128 MHz, $CDCl_3$)

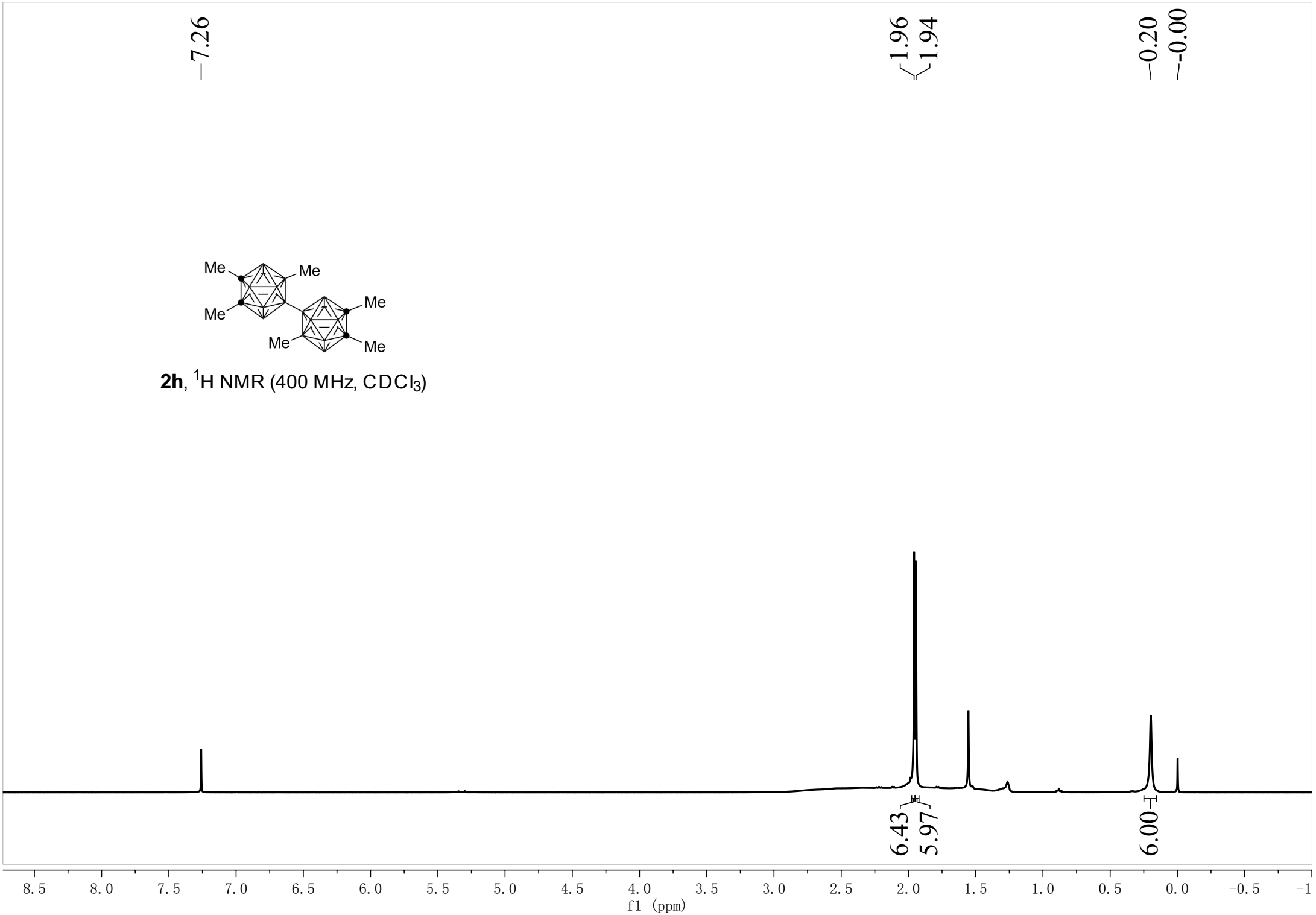
2g, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



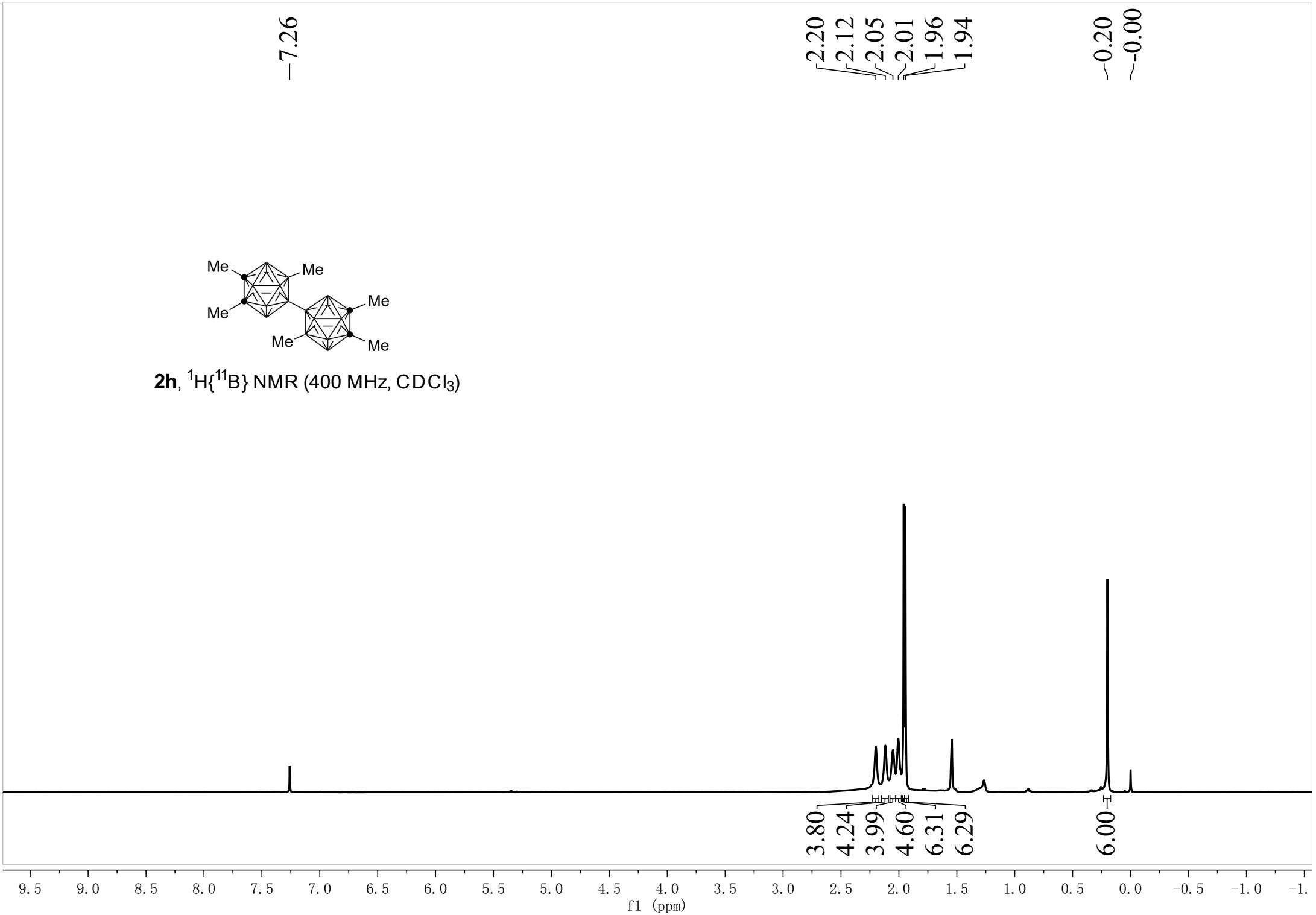
2g, ^{13}C NMR (101 MHz, $CDCl_3$)



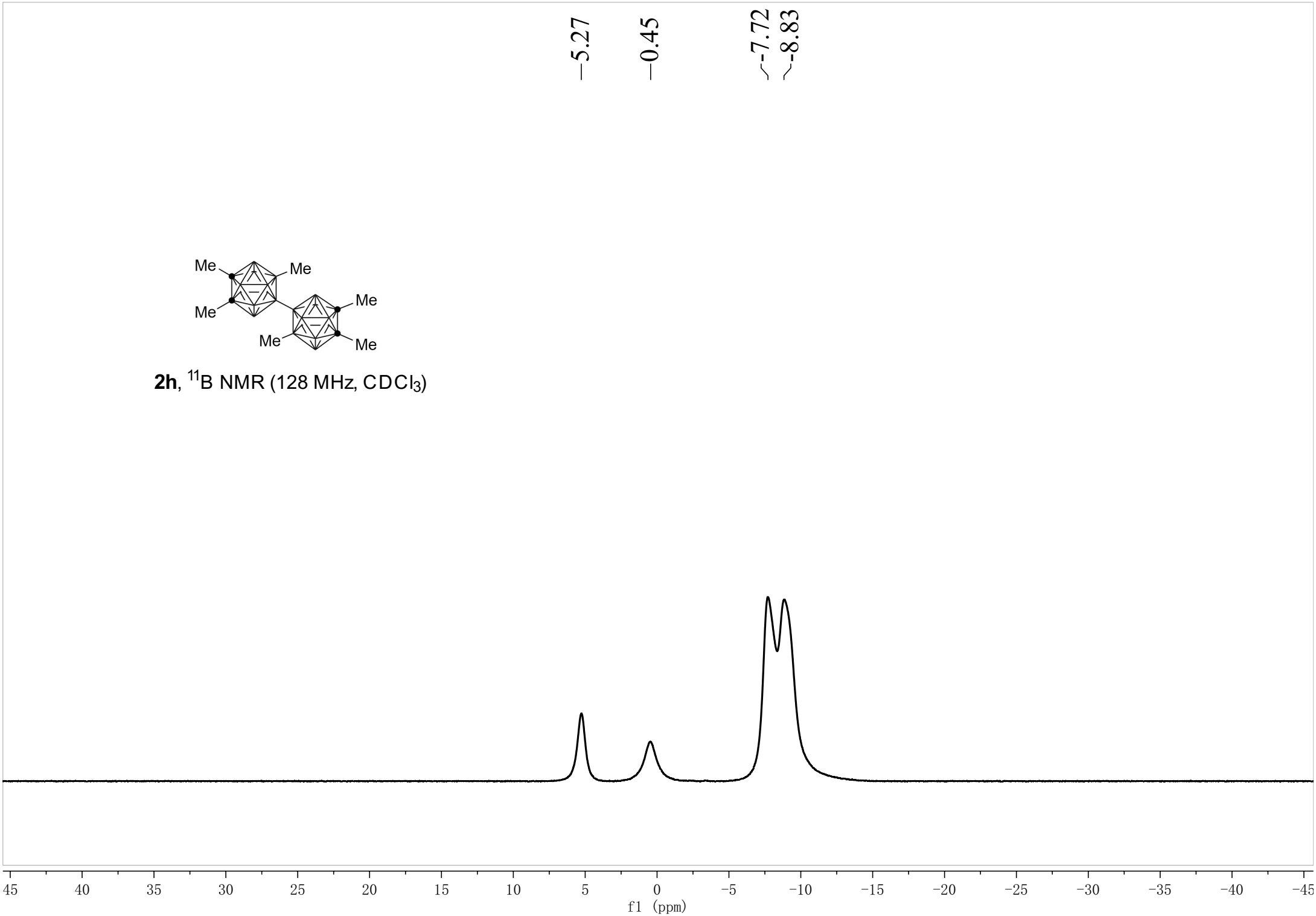
2h, ^{1}H NMR (400 MHz, $CDCl_3$)



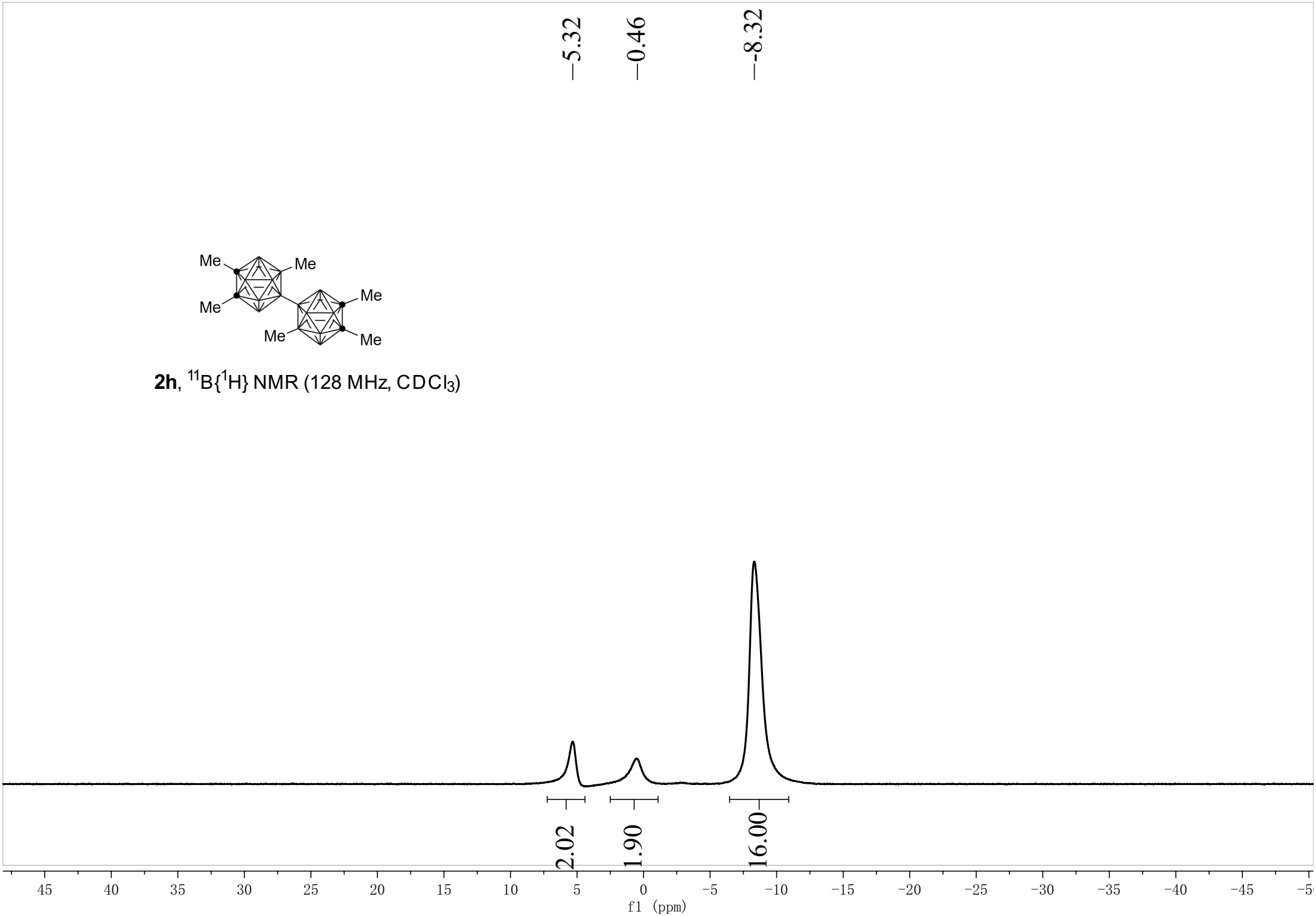
2h, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)



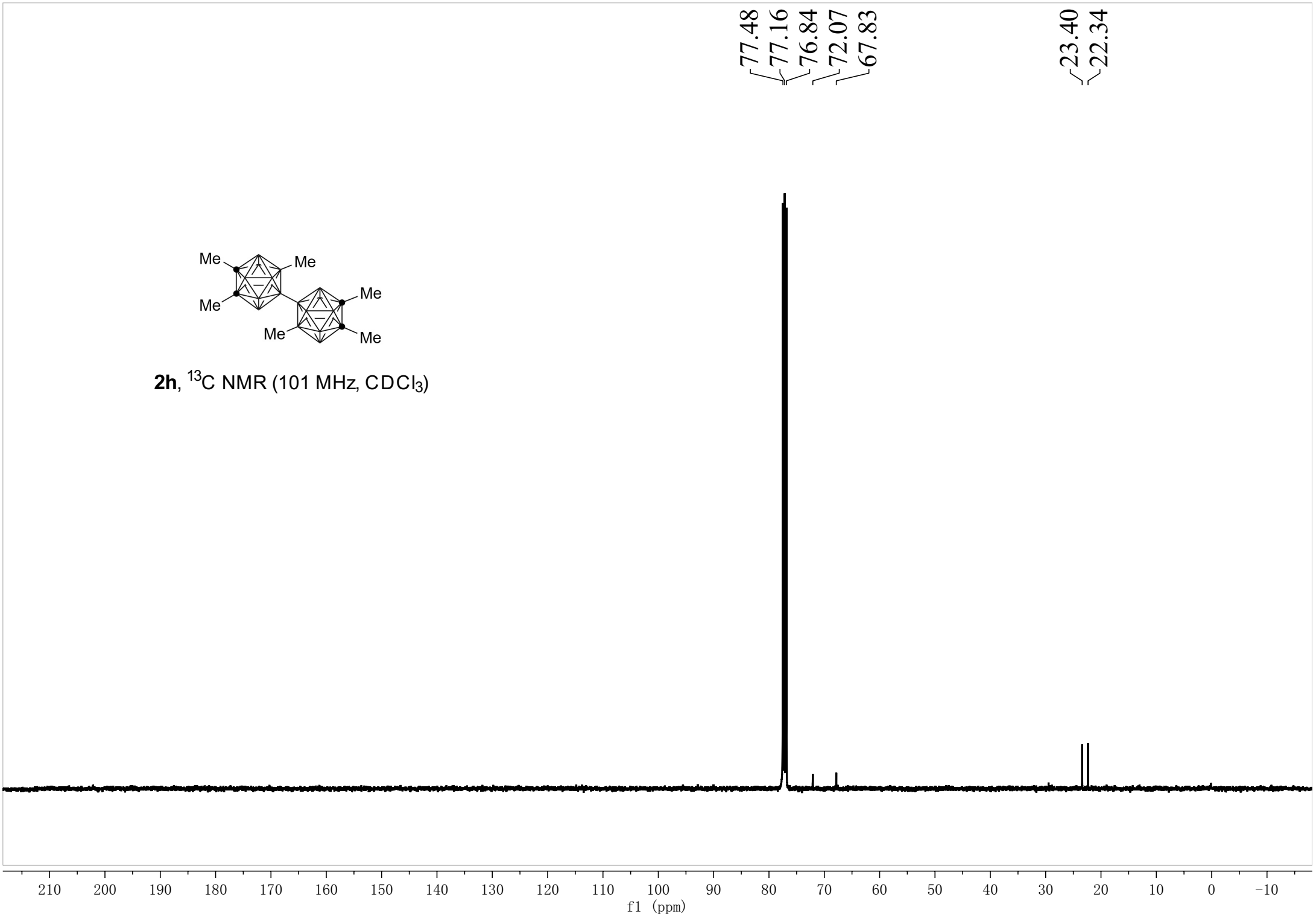
2h, ^{11}B NMR (128 MHz, $CDCl_3$)



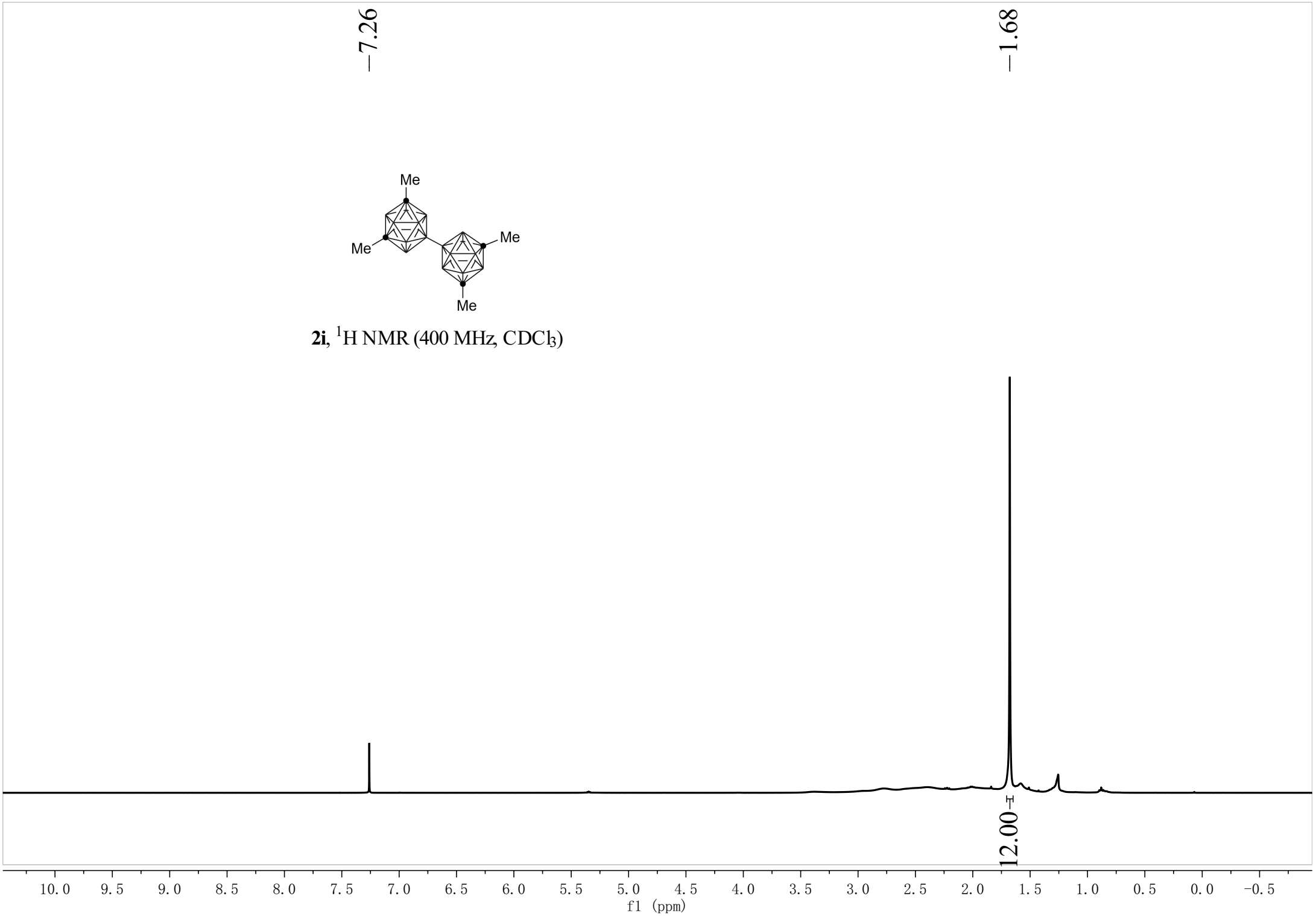
2h, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

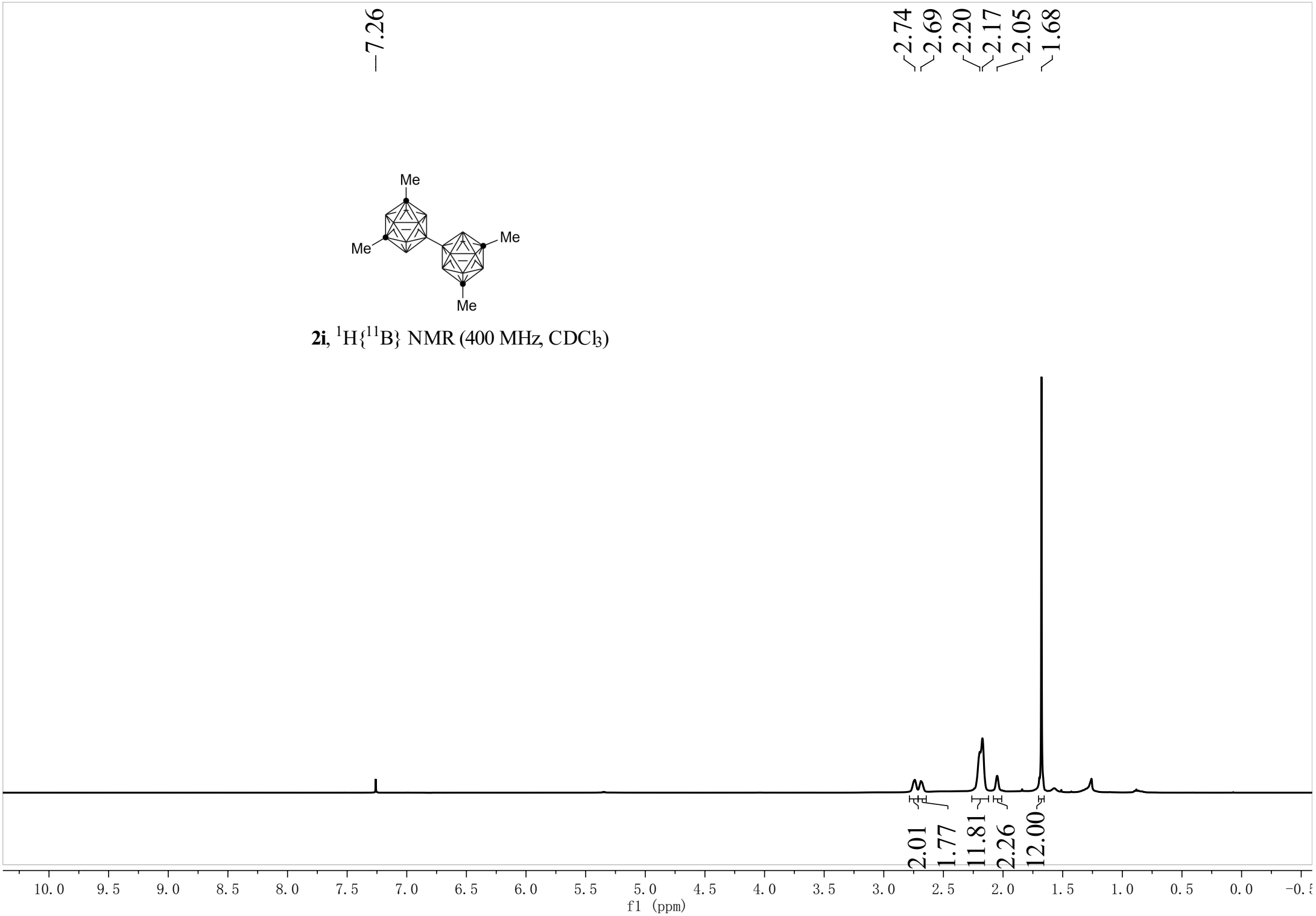


2h, ^{13}C NMR (101 MHz, $CDCl_3$)



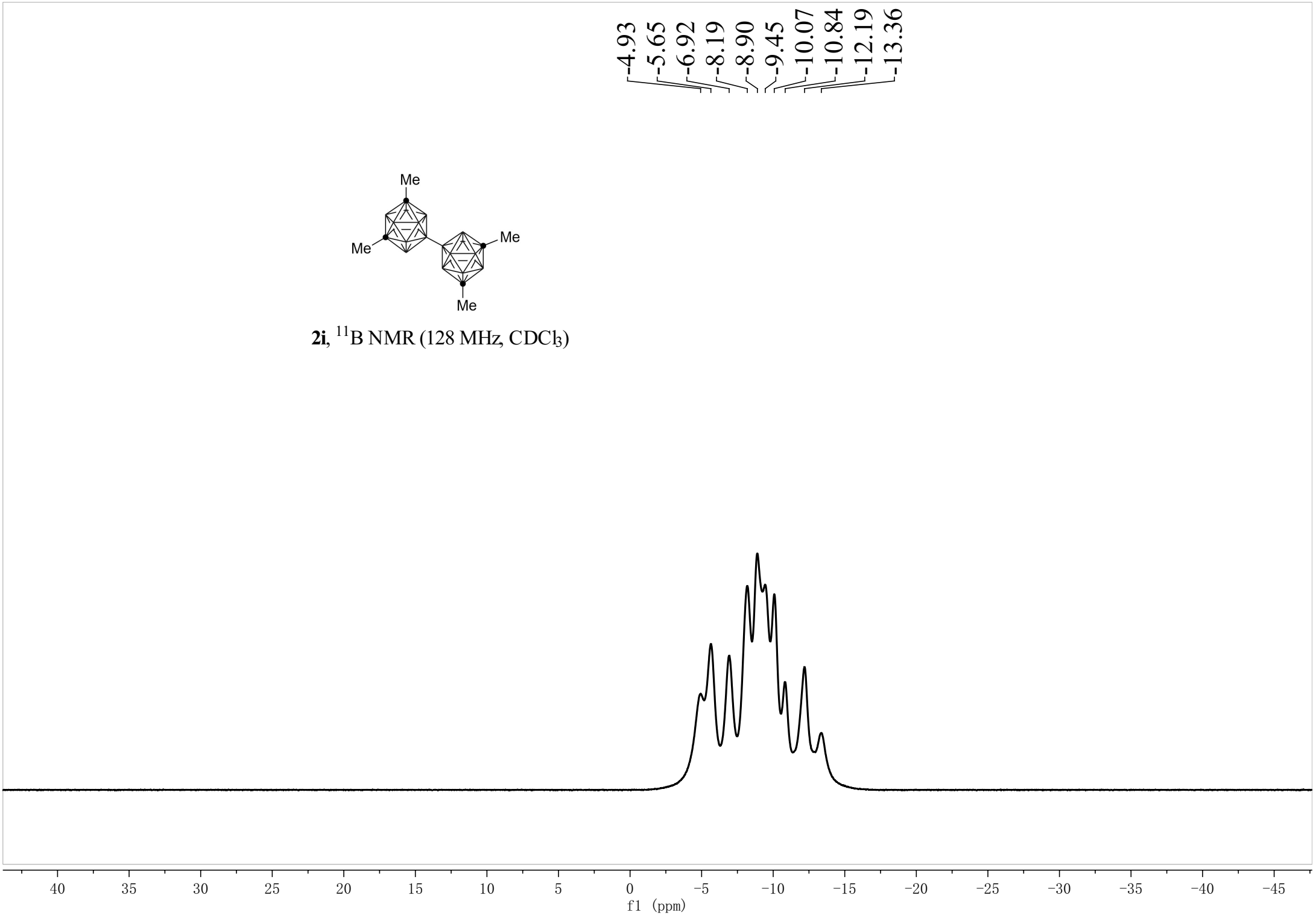
2i, ^{1}H NMR (400 MHz, $CDCl_3$)



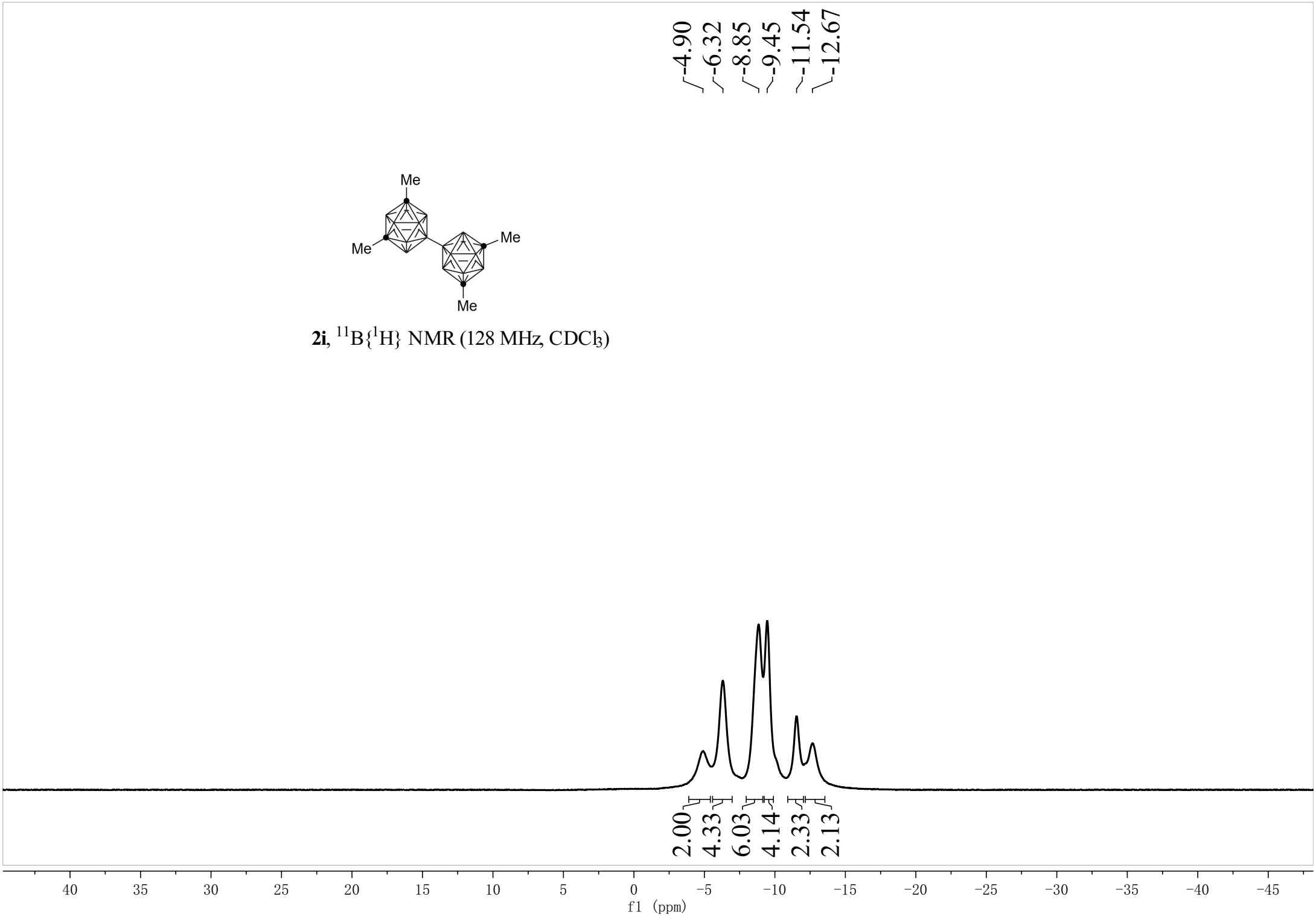


2i, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

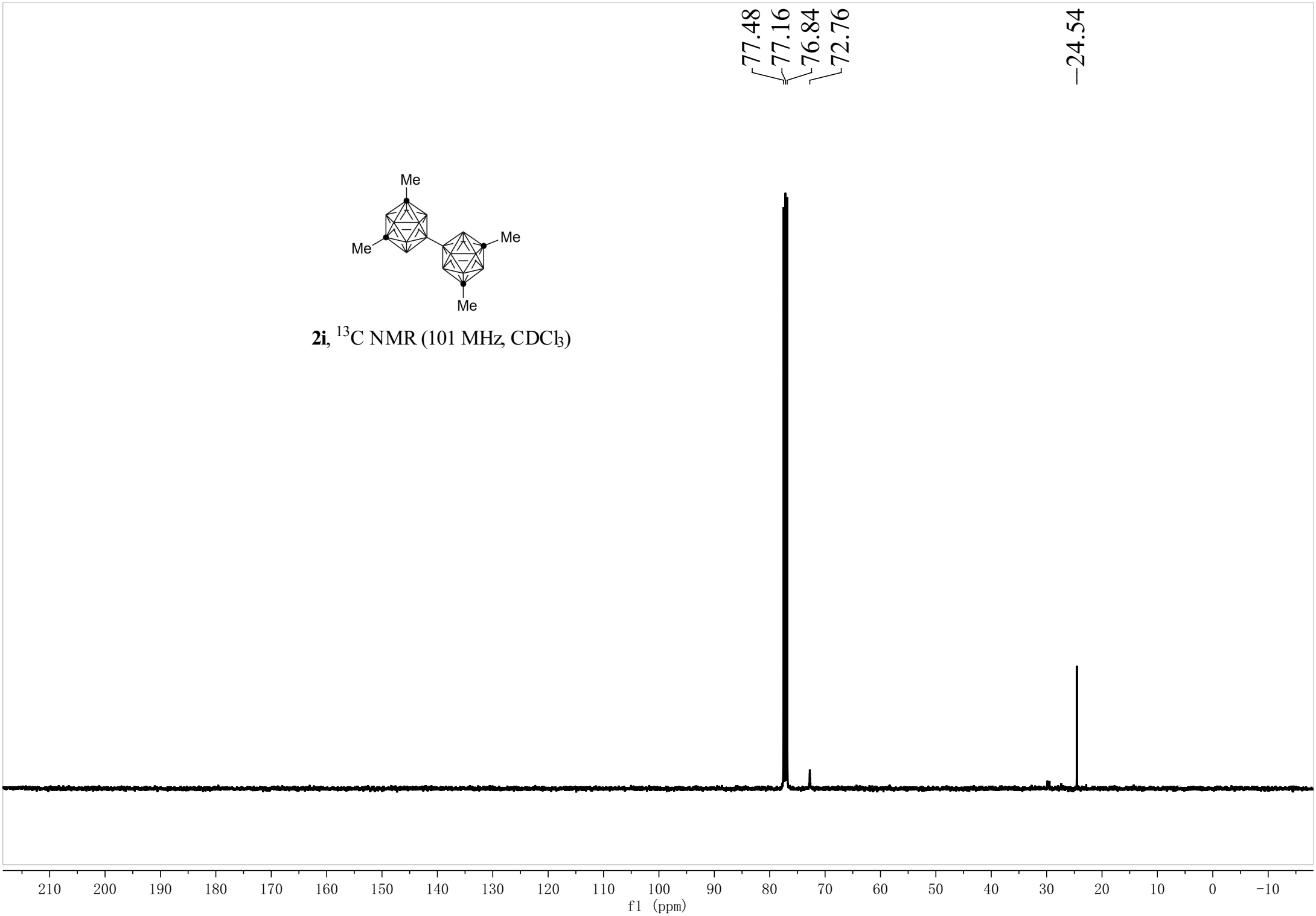
2i, ^{11}B NMR (128 MHz, $CDCl_3$)

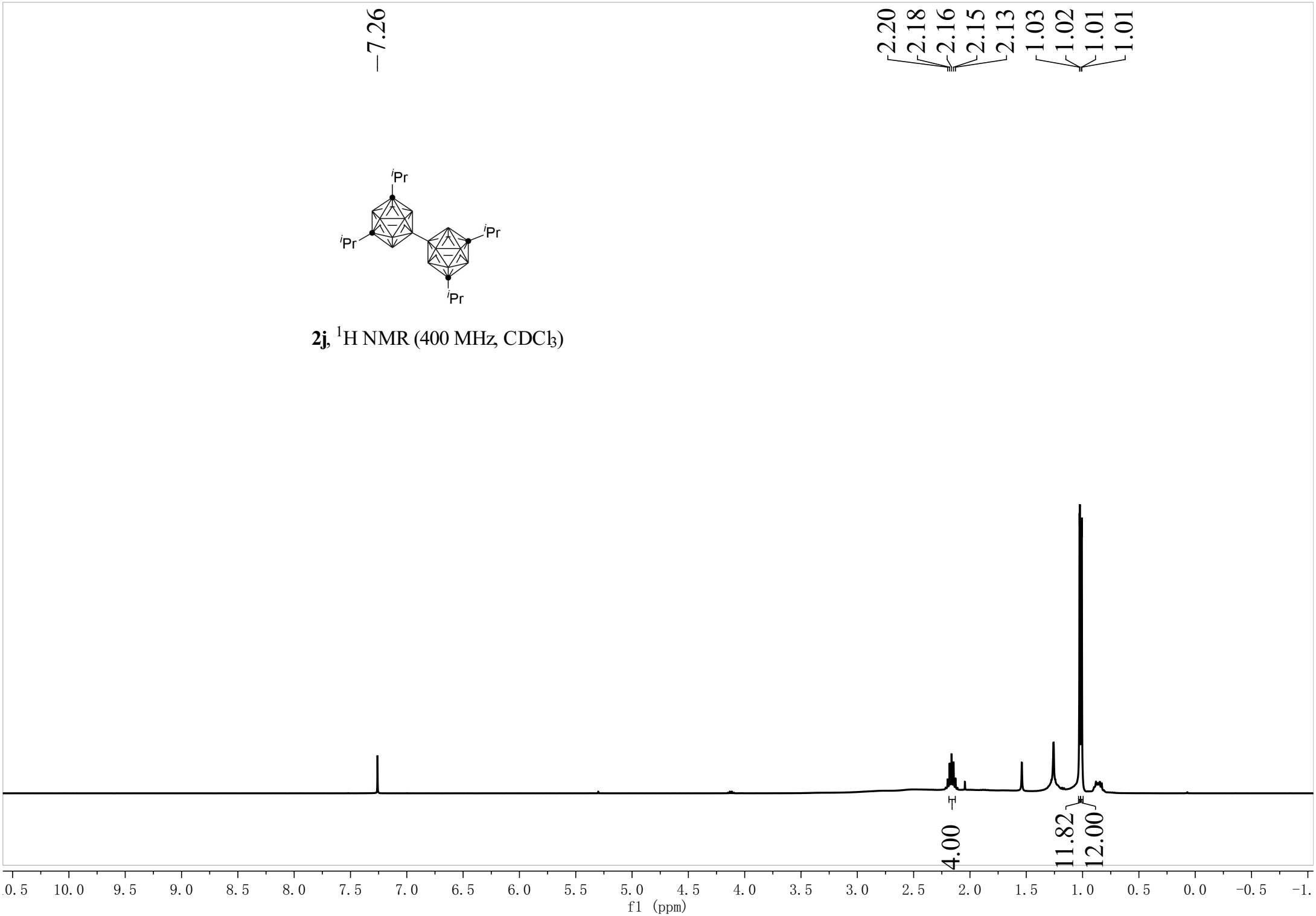


2i, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



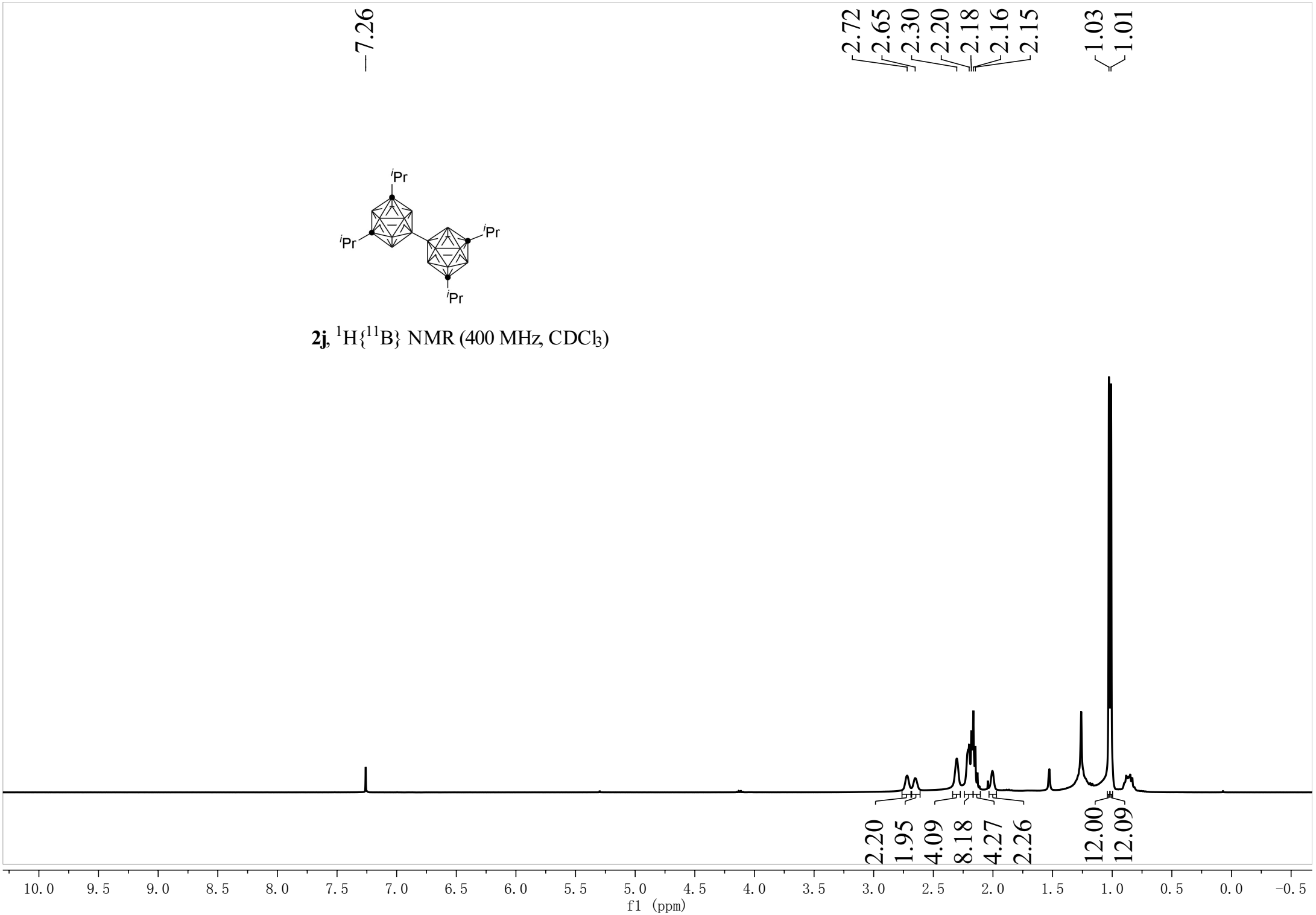
2i, ^{13}C NMR (101 MHz, $CDCl_3$)



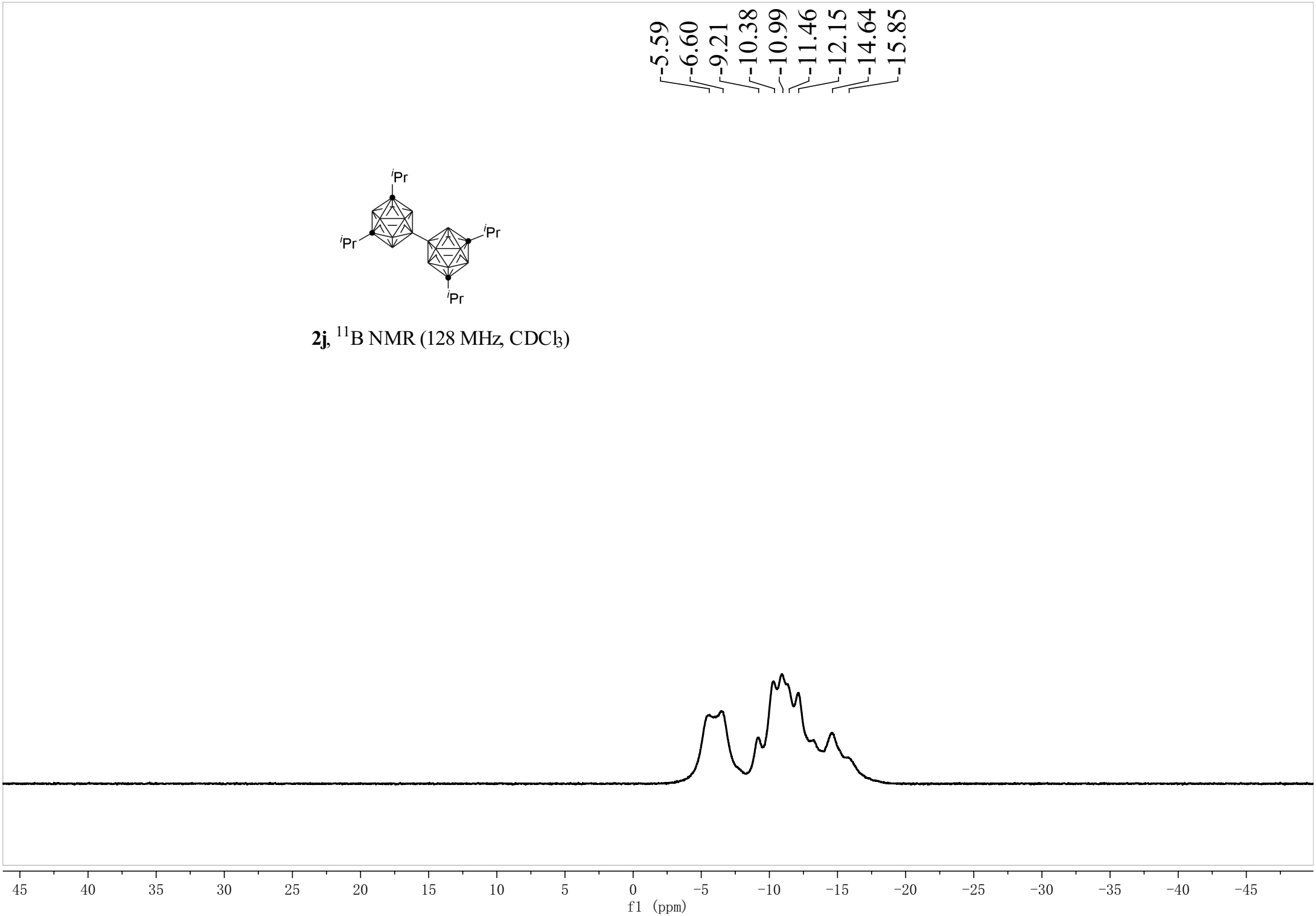


2j, ^{1}H NMR (400 MHz, $CDCl_3$)

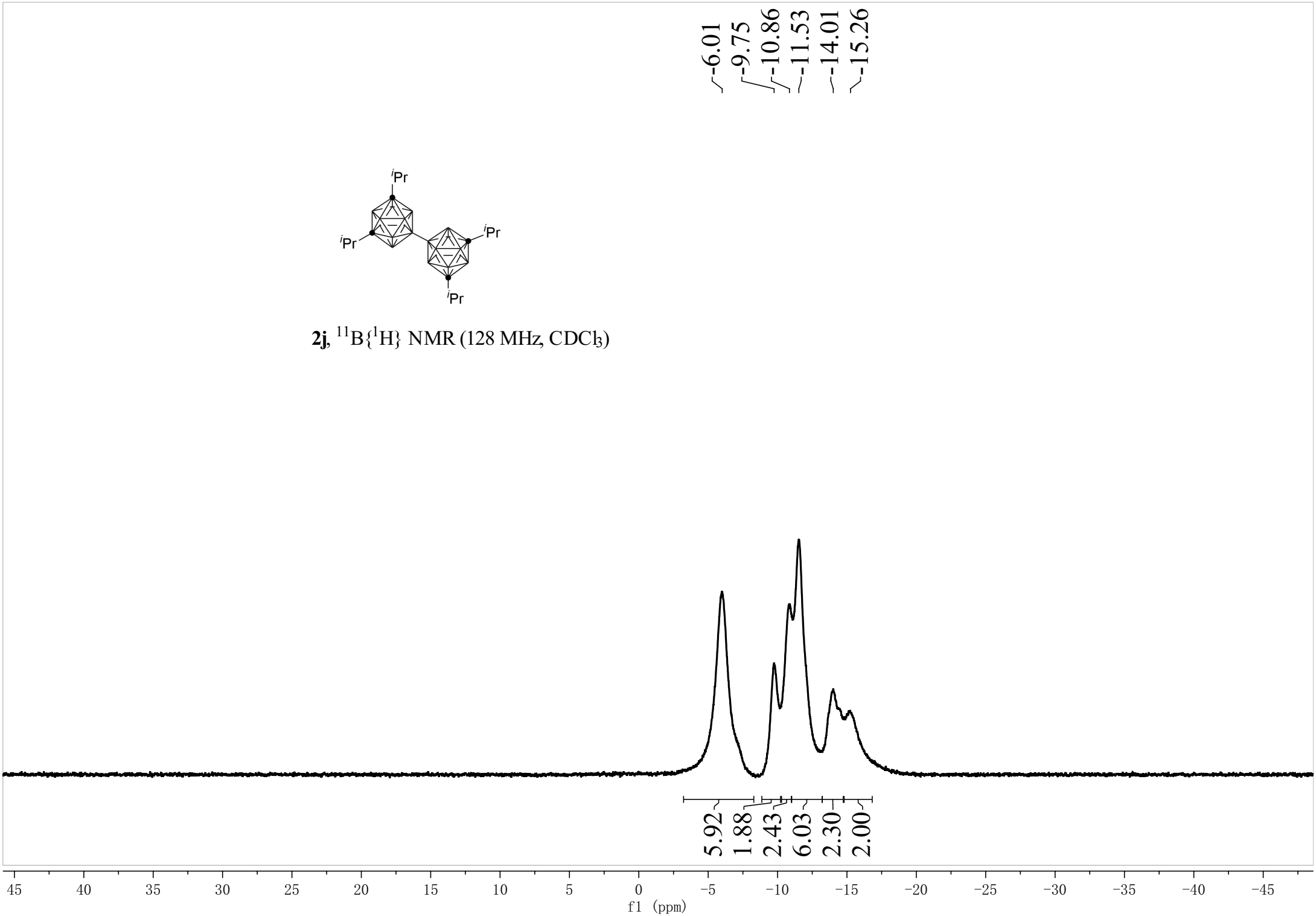
2j, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)



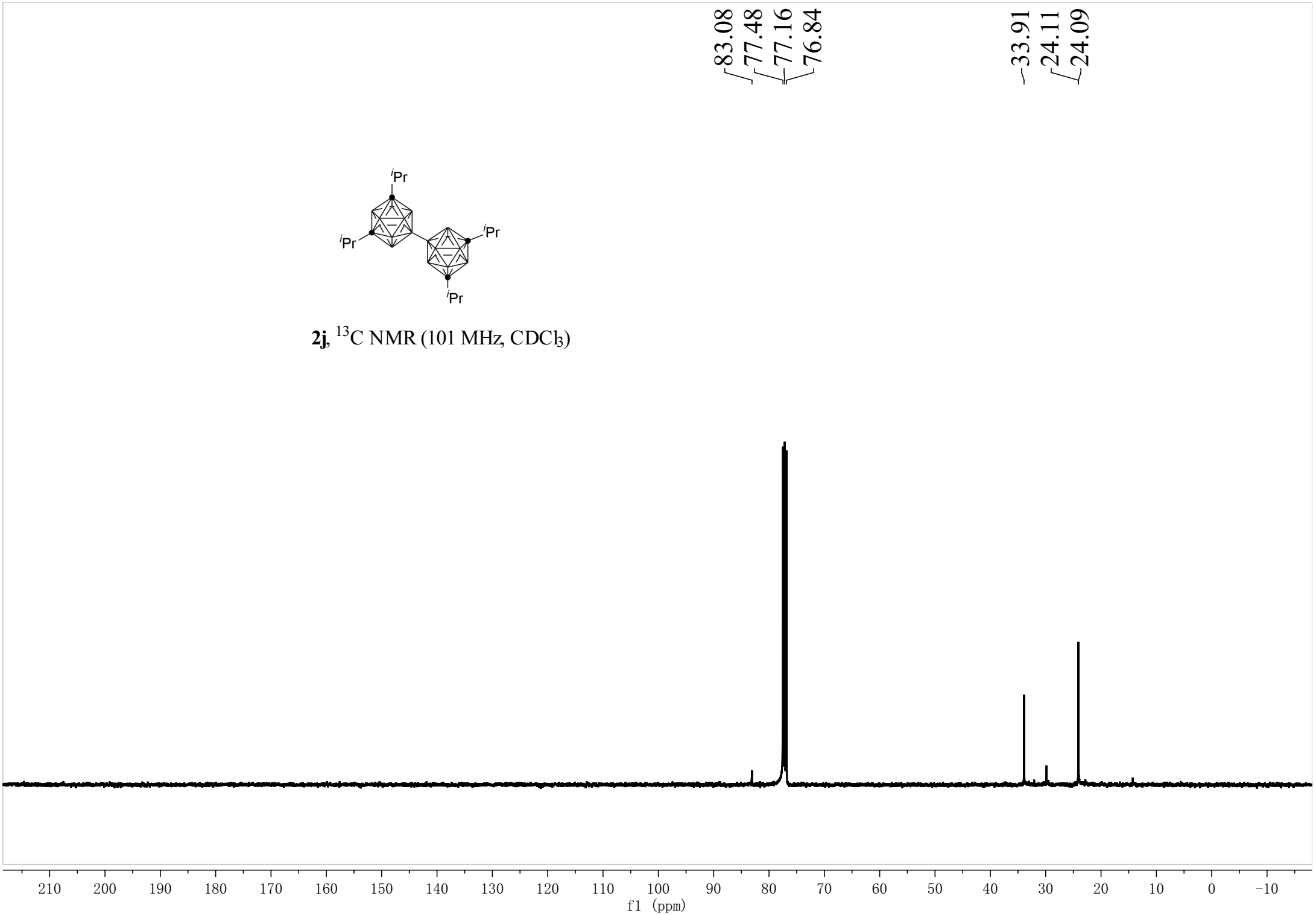
2j, ^{11}B NMR (128 MHz, $CDCl_3$)

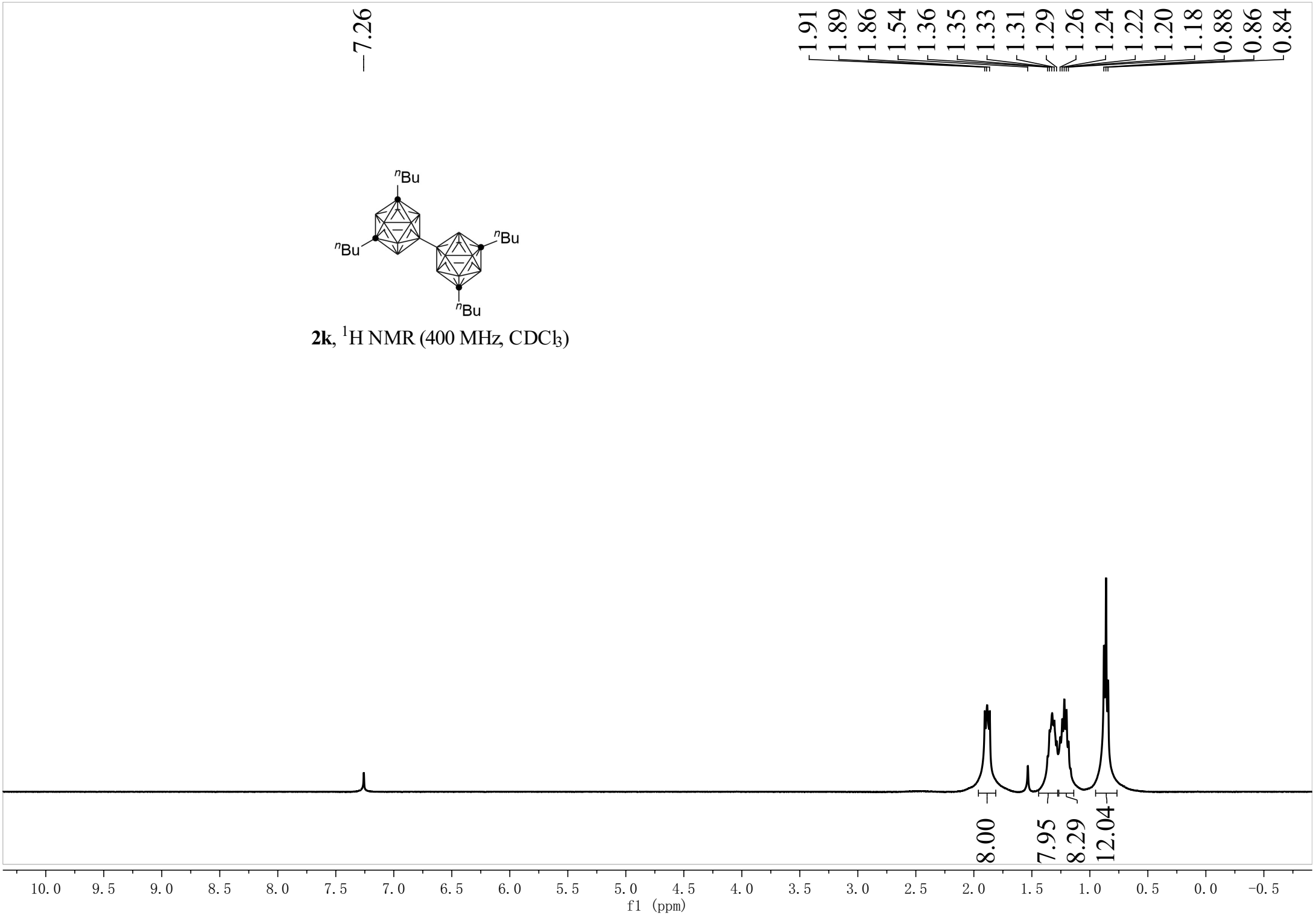


2j, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

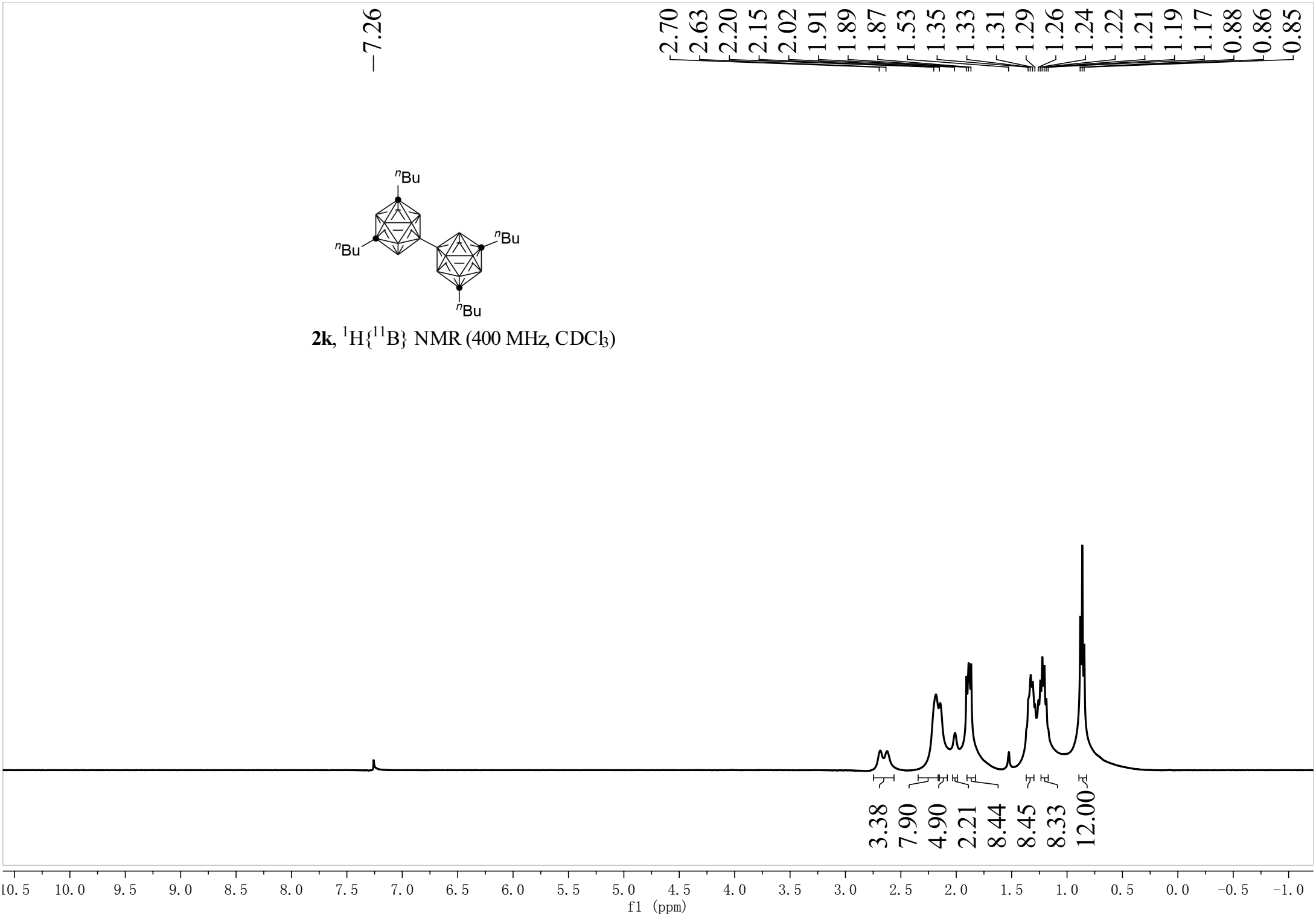


2j, ^{13}C NMR (101 MHz, $CDCl_3$)



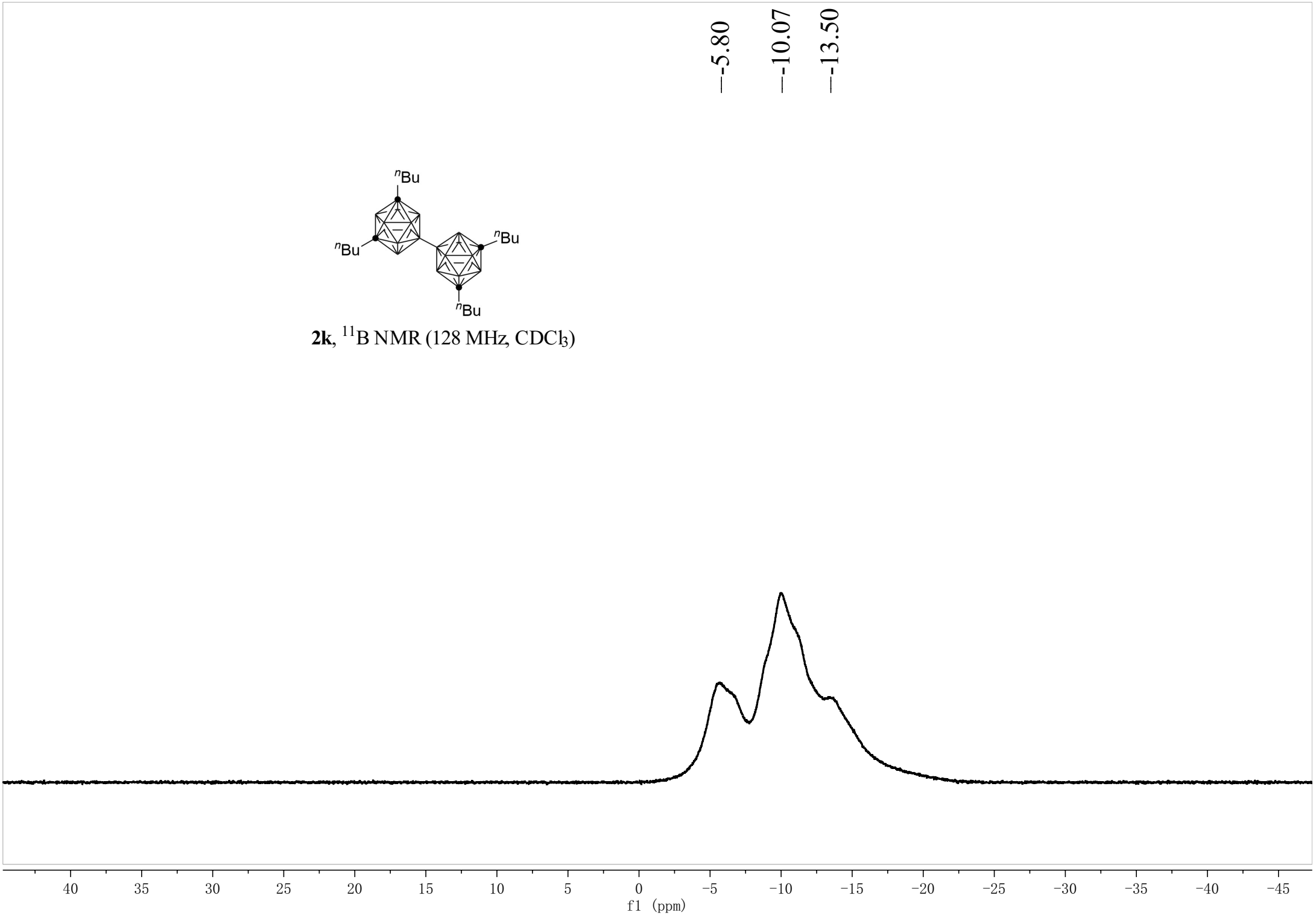


2k, ^{1}H NMR (400 MHz, $CDCl_3$)

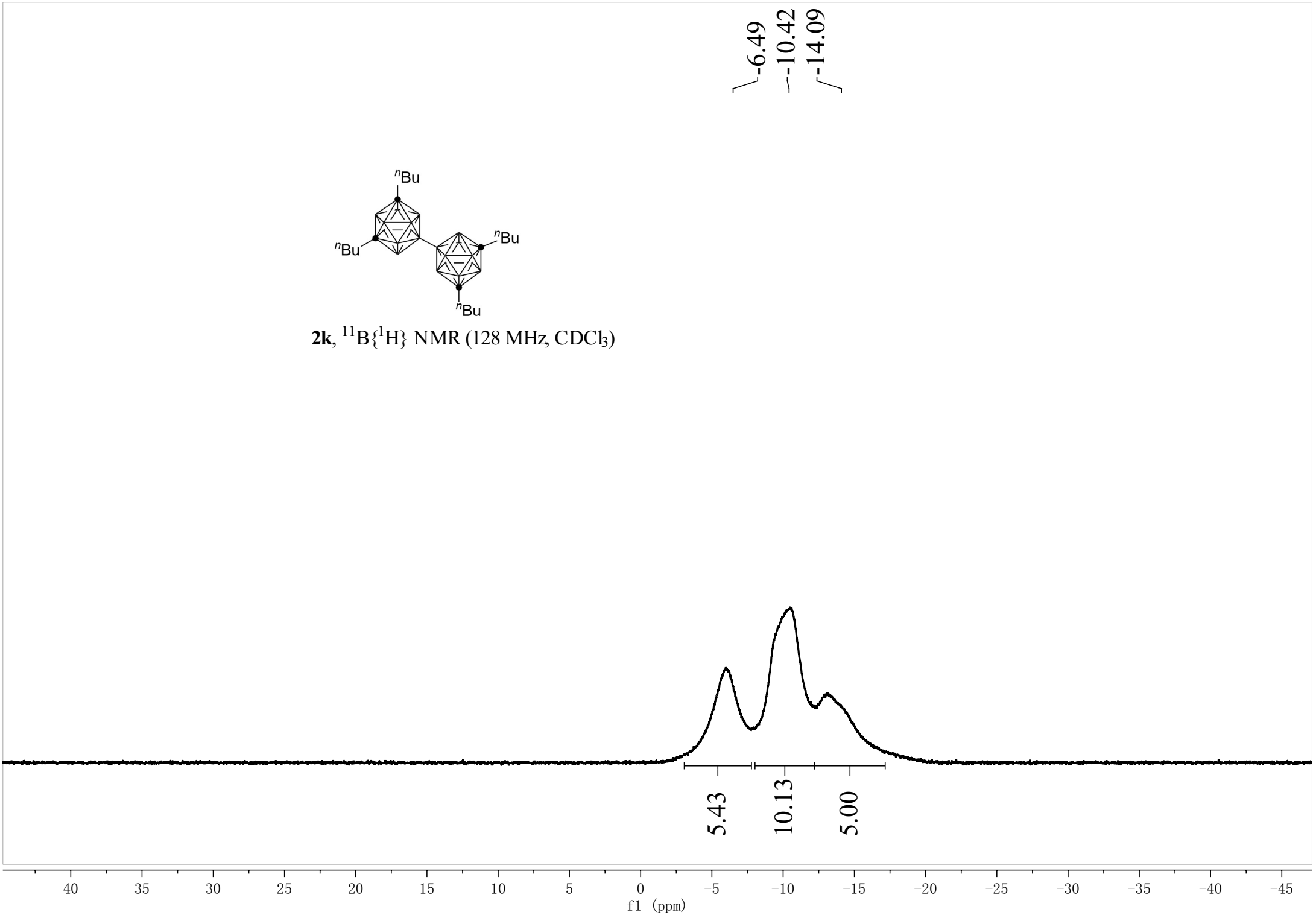


2k, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

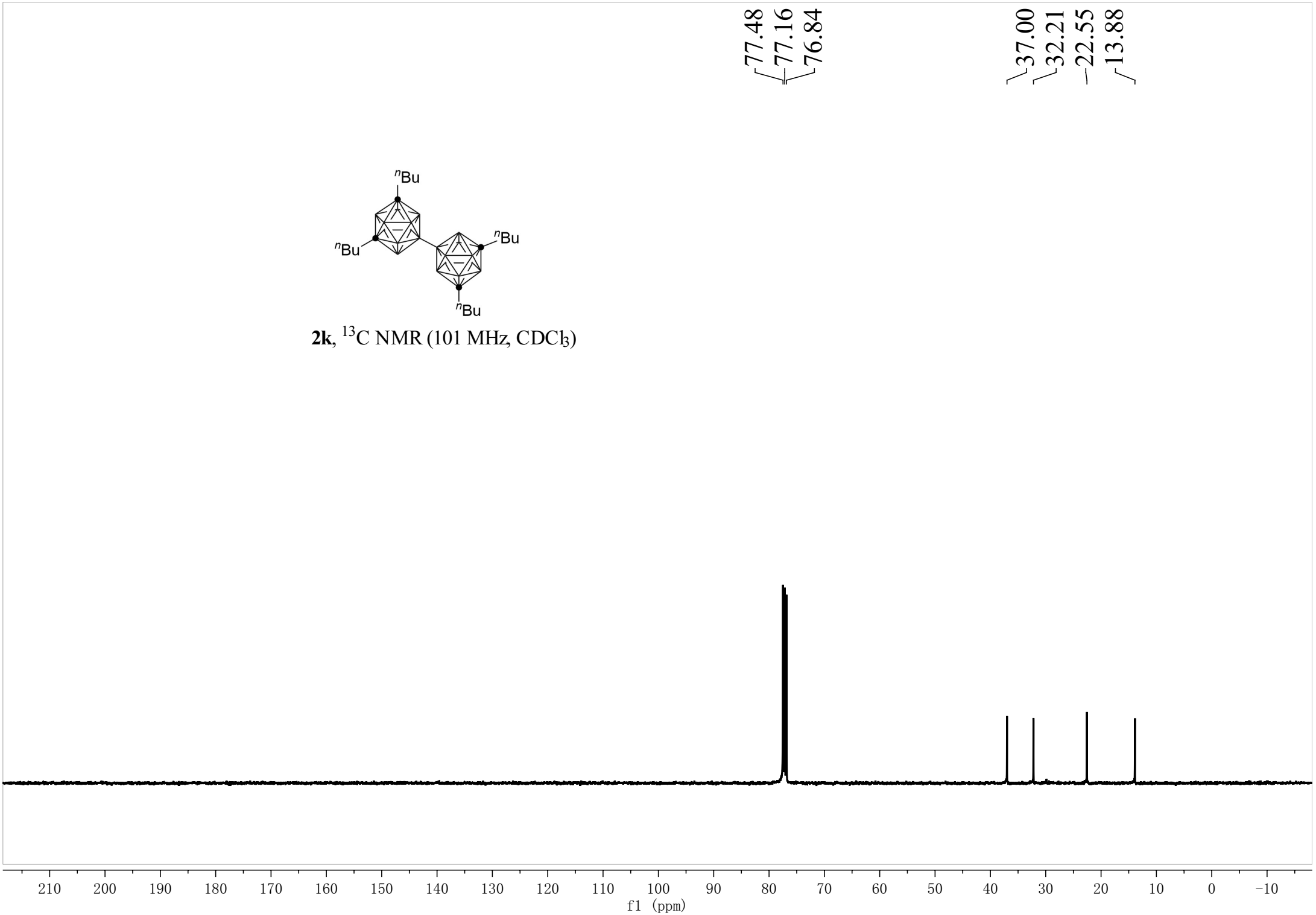
2k, ^{11}B NMR (128 MHz, $CDCl_3$)

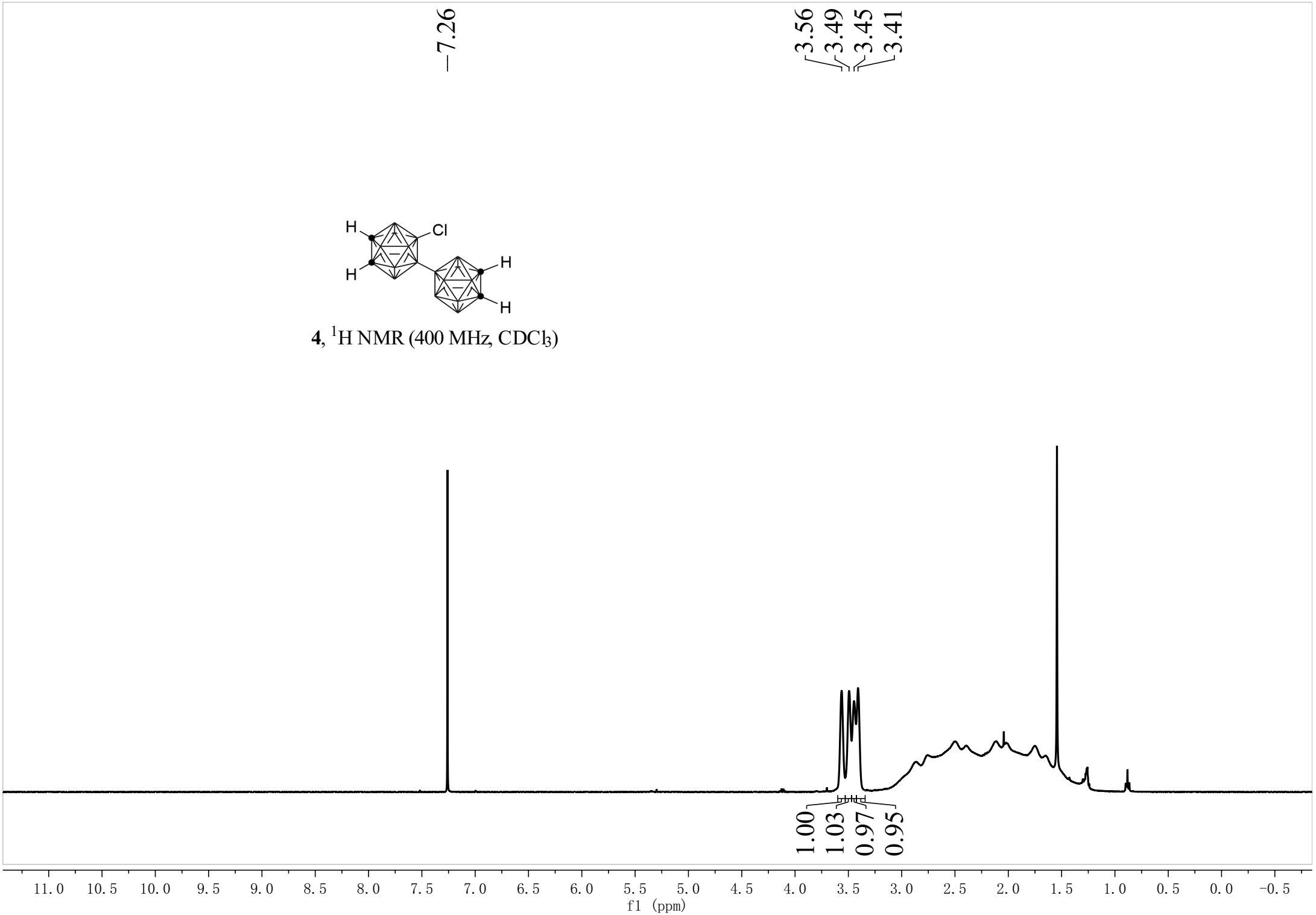


2k, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

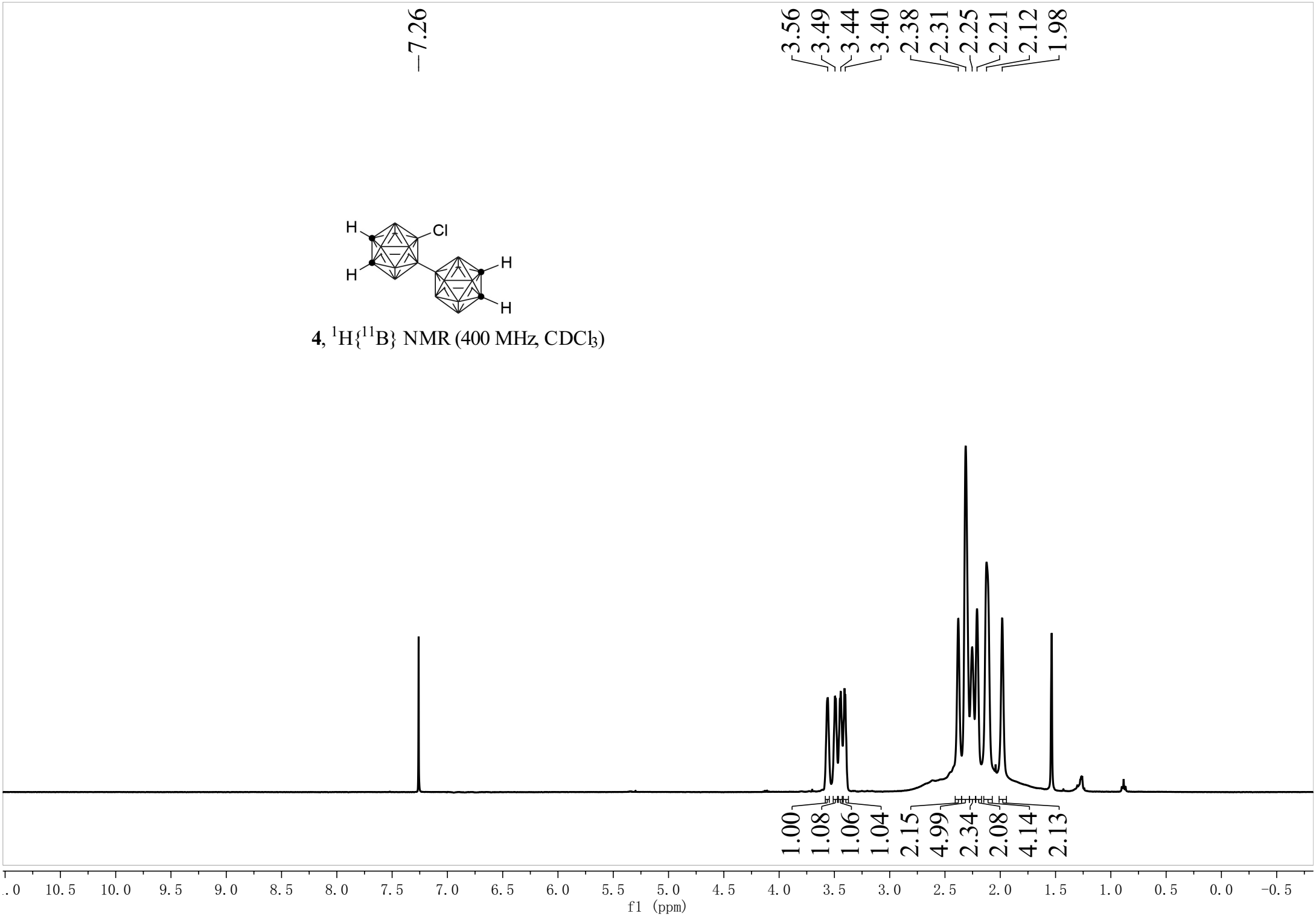


2k, ^{13}C NMR (101 MHz, $CDCl_3$)

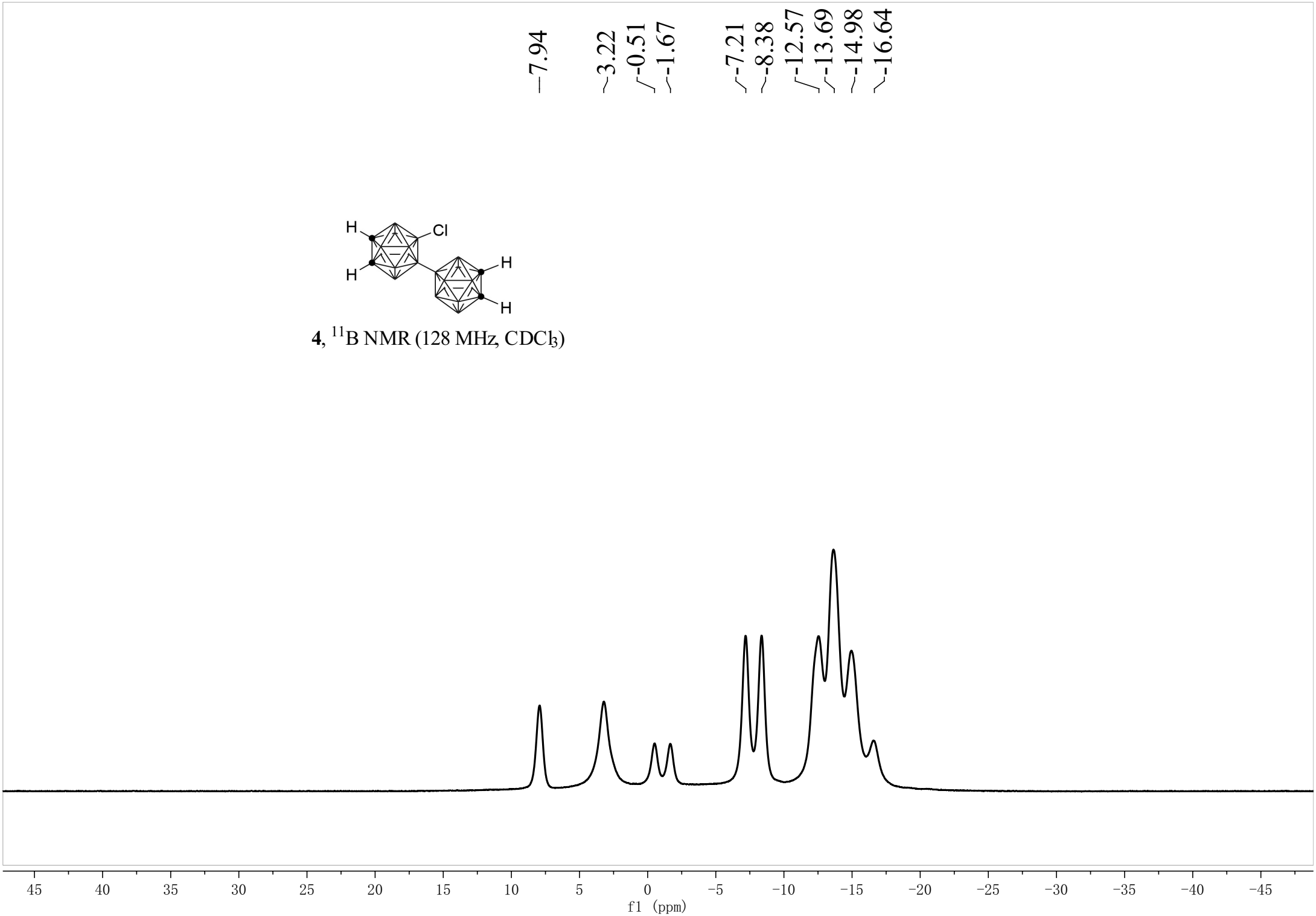




4, ^{1}H NMR (400 MHz, $CDCl_3$)

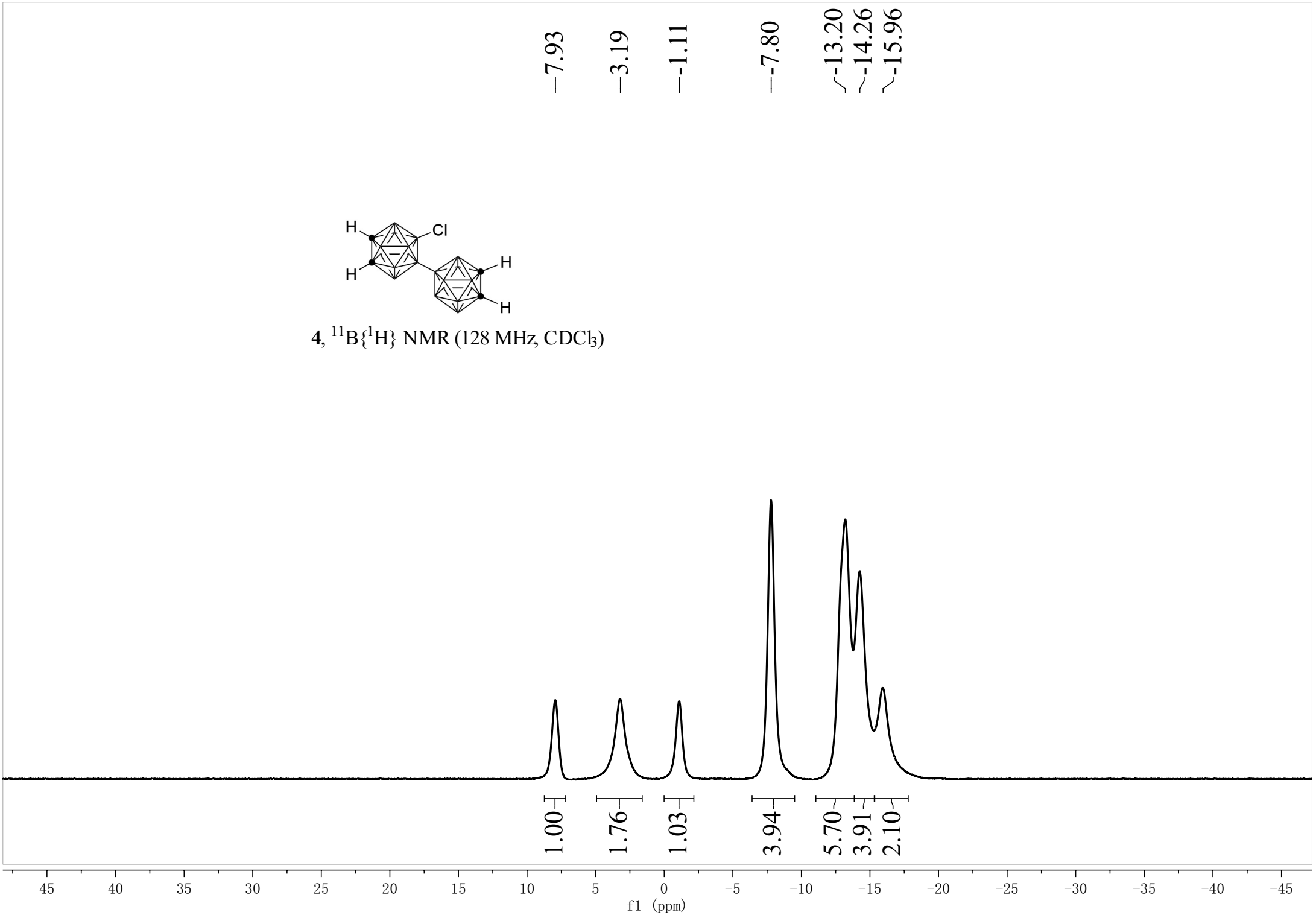


4, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

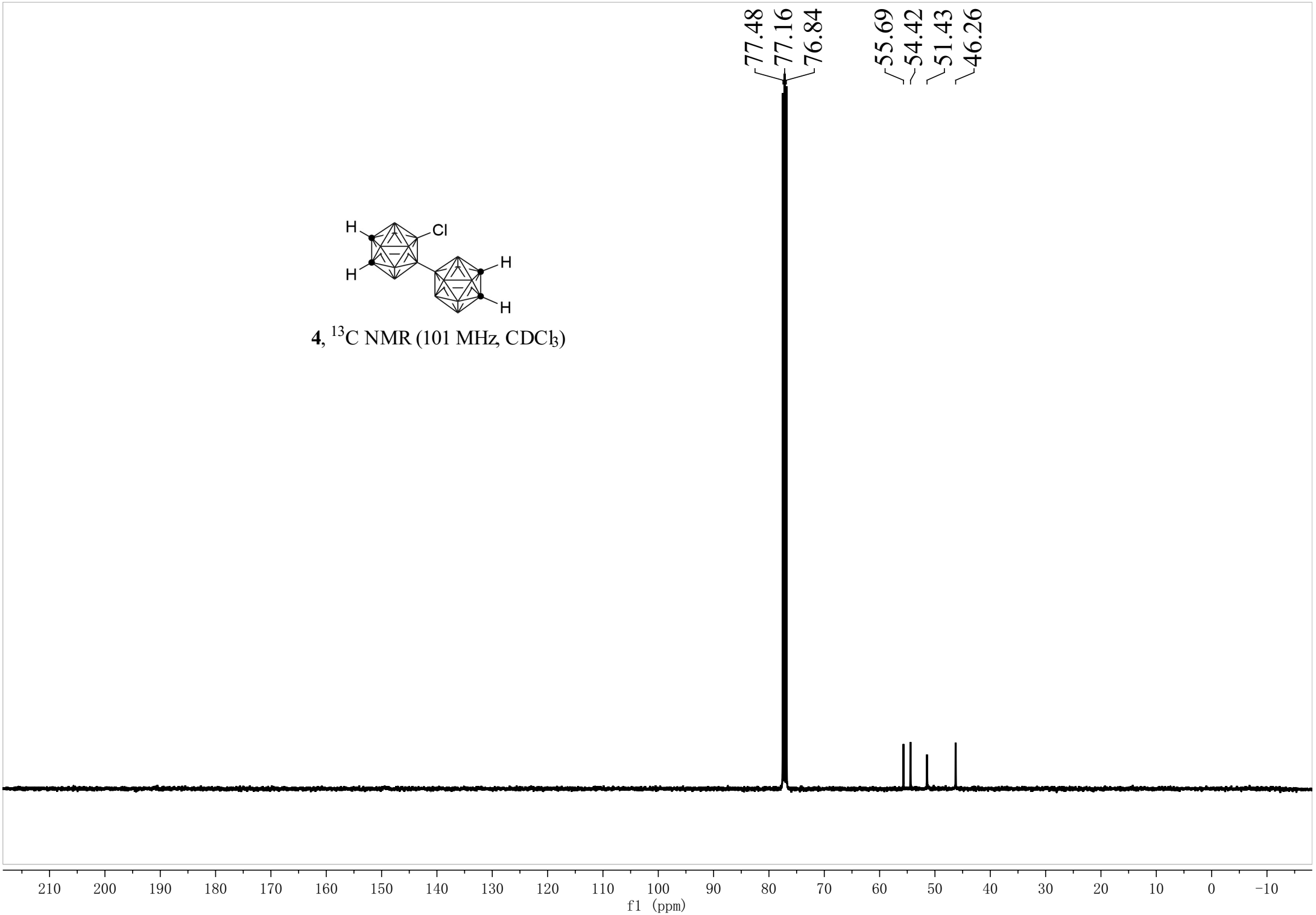


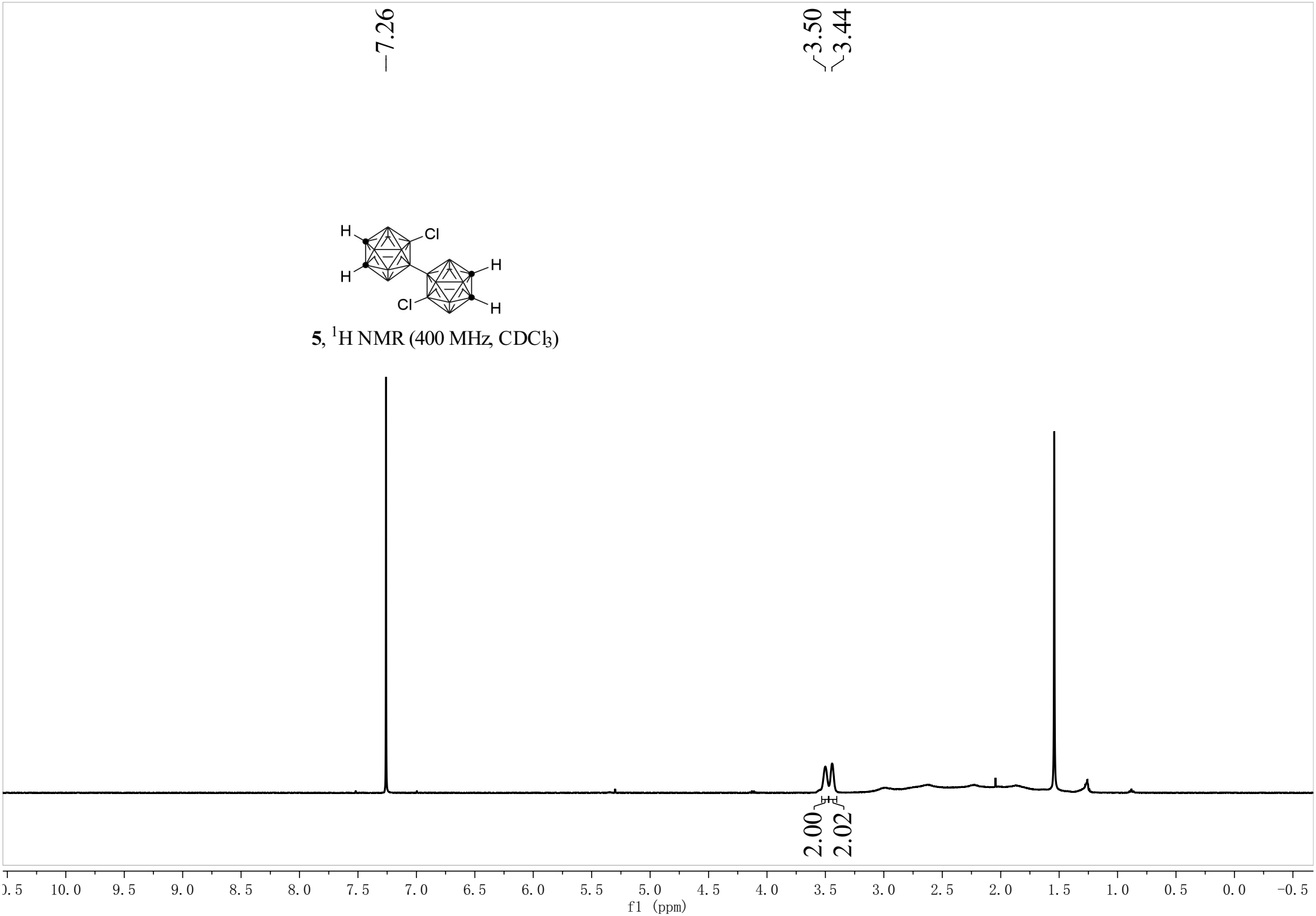
4, ^{11}B NMR (128 MHz, $CDCl_3$)

4, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

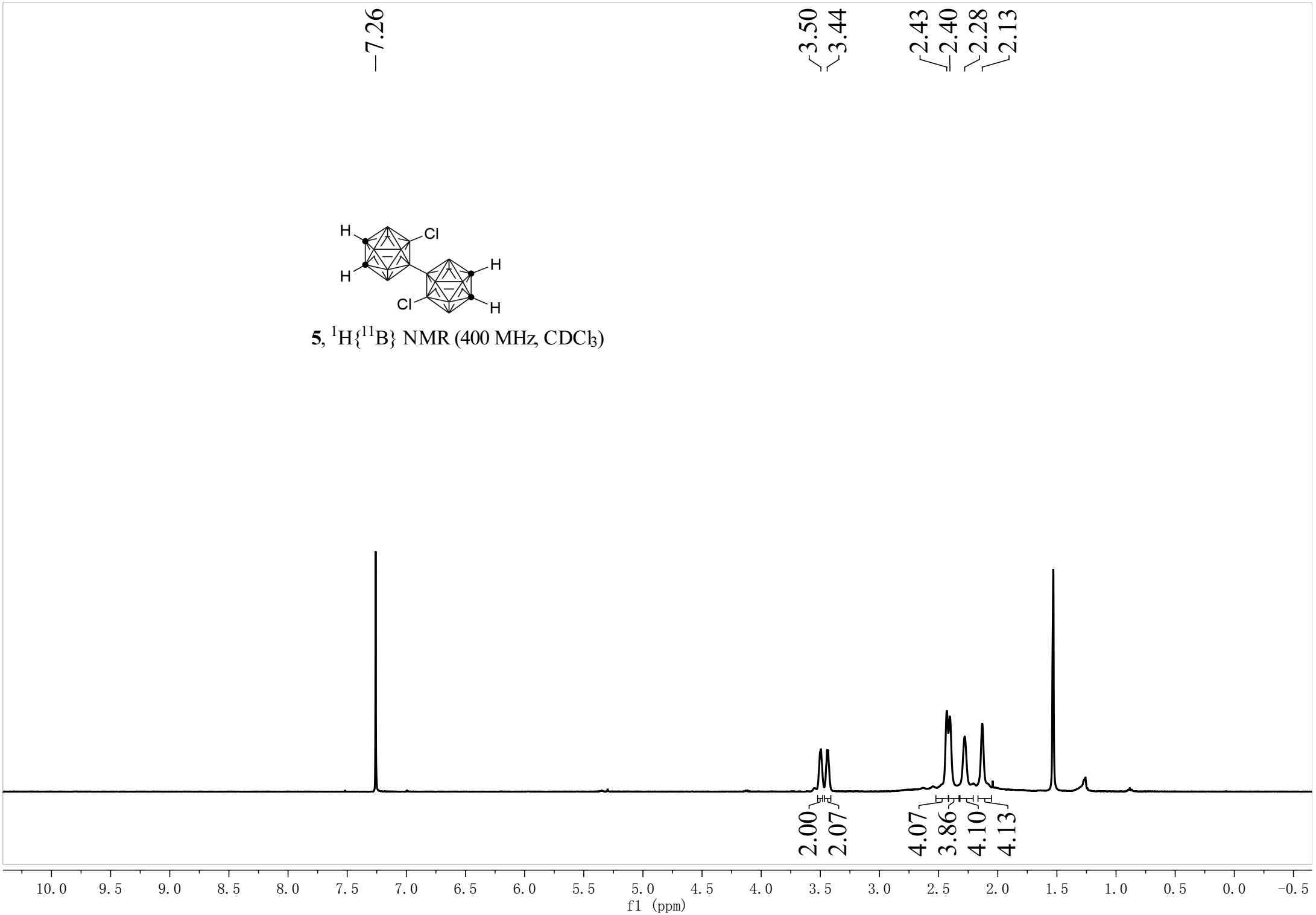


4, ^{13}C NMR (101 MHz, $CDCl_3$)



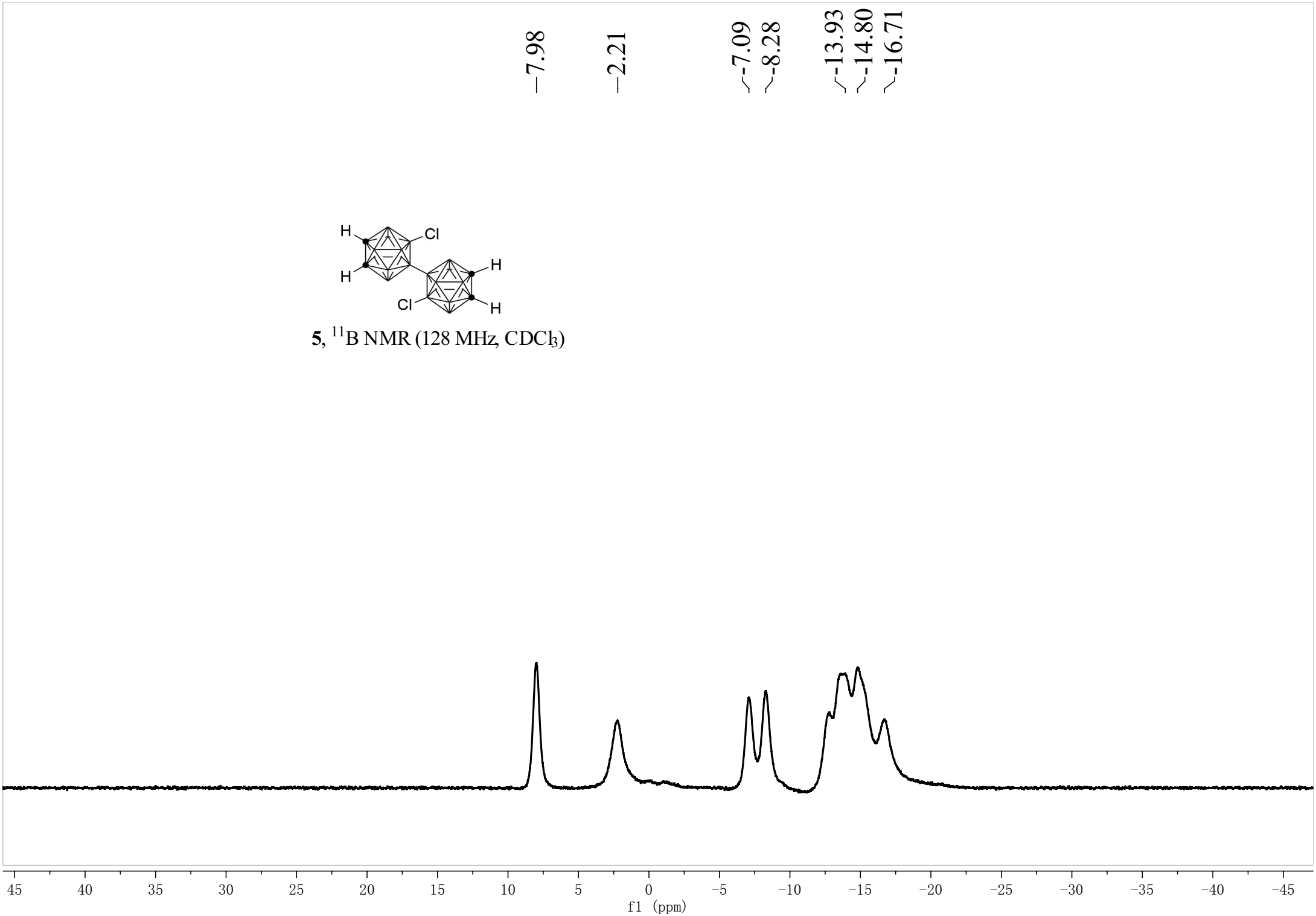


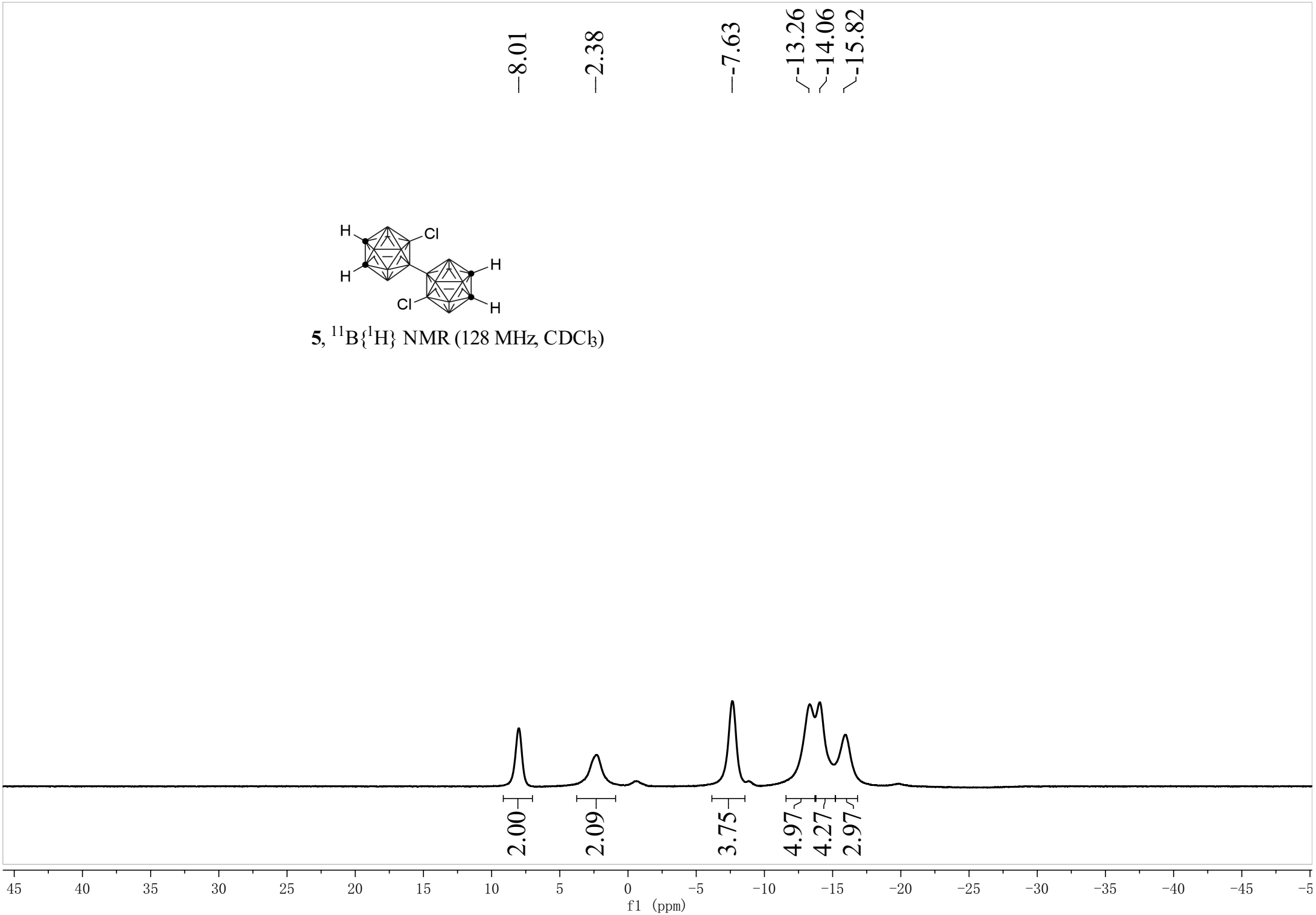
5, ^{1}H NMR (400 MHz, $CDCl_3$)



5, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

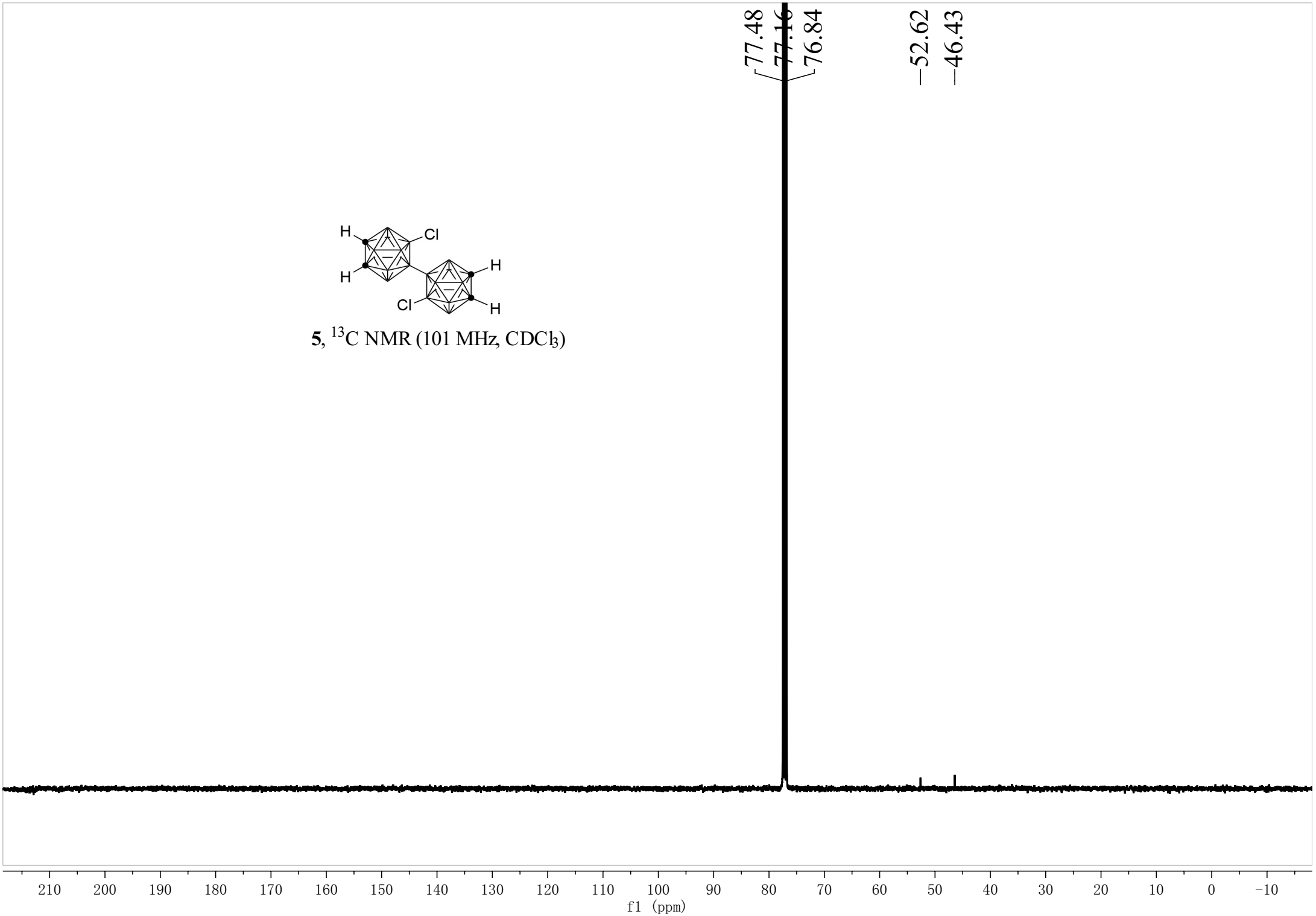
5, ^{11}B NMR (128 MHz, $CDCl_3$)



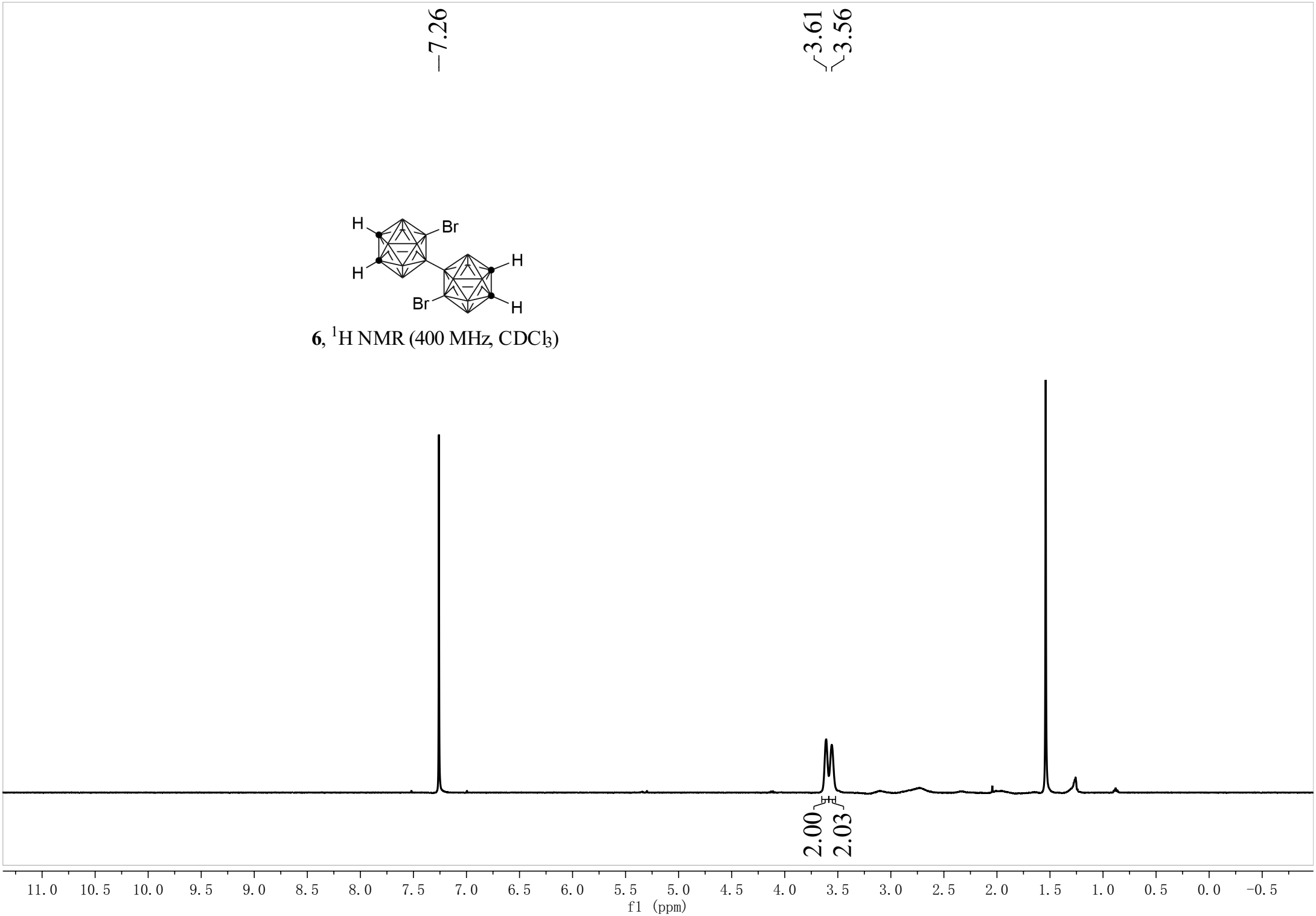


5, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

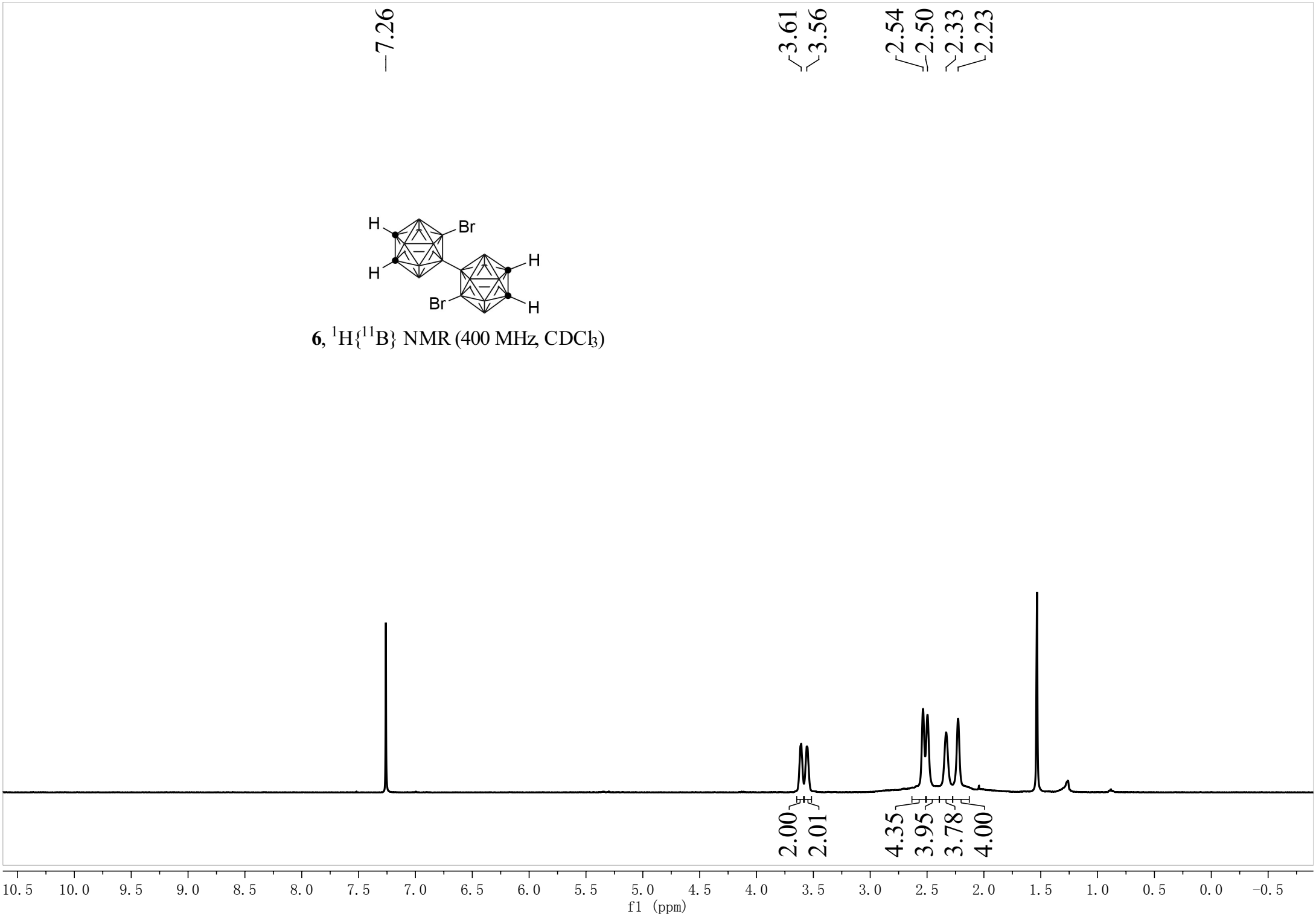
5, ^{13}C NMR (101 MHz, $CDCl_3$)



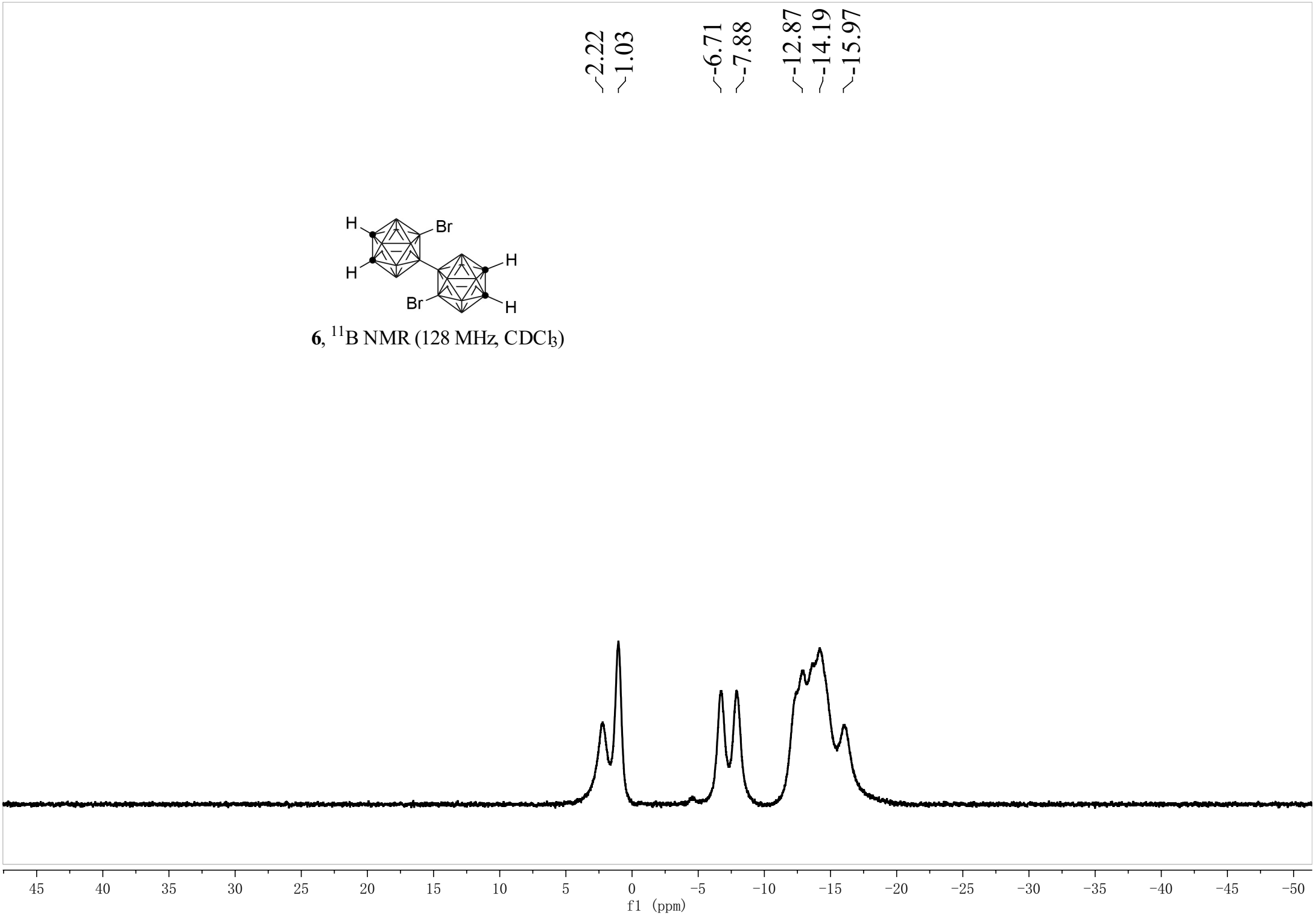
6, ^{1}H NMR (400 MHz, $CDCl_3$)



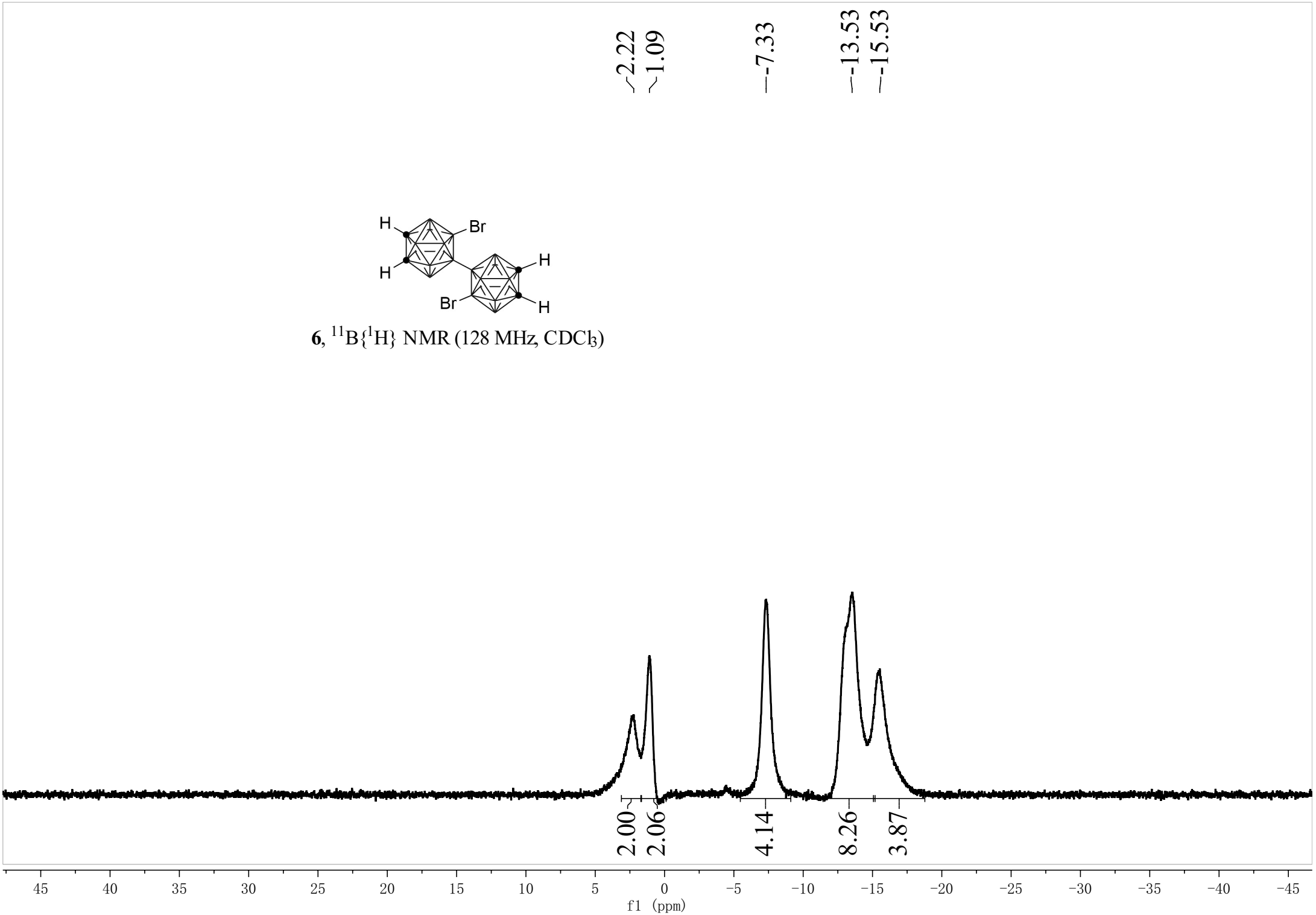
6, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)



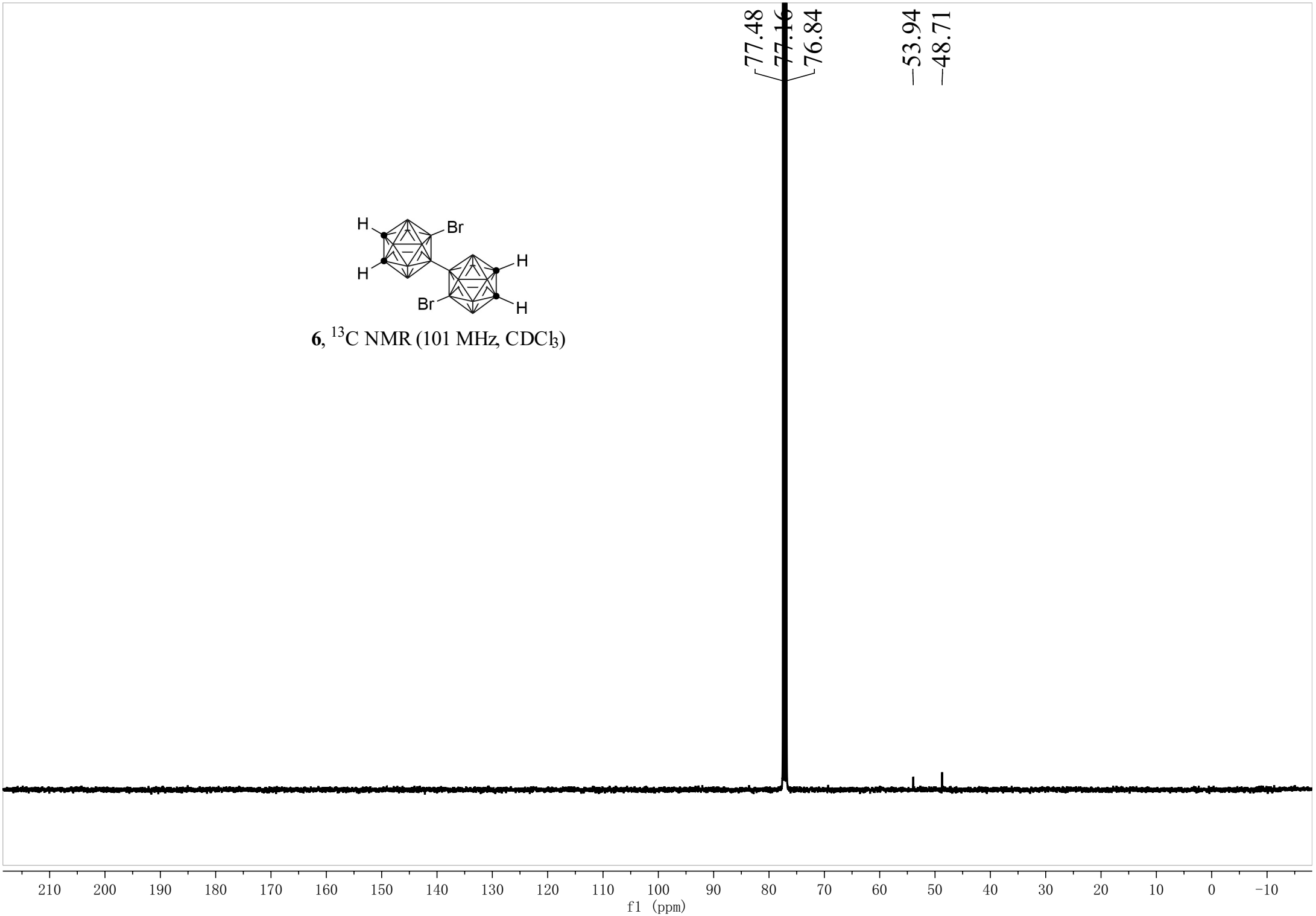
6, ^{11}B NMR (128 MHz, $CDCl_3$)



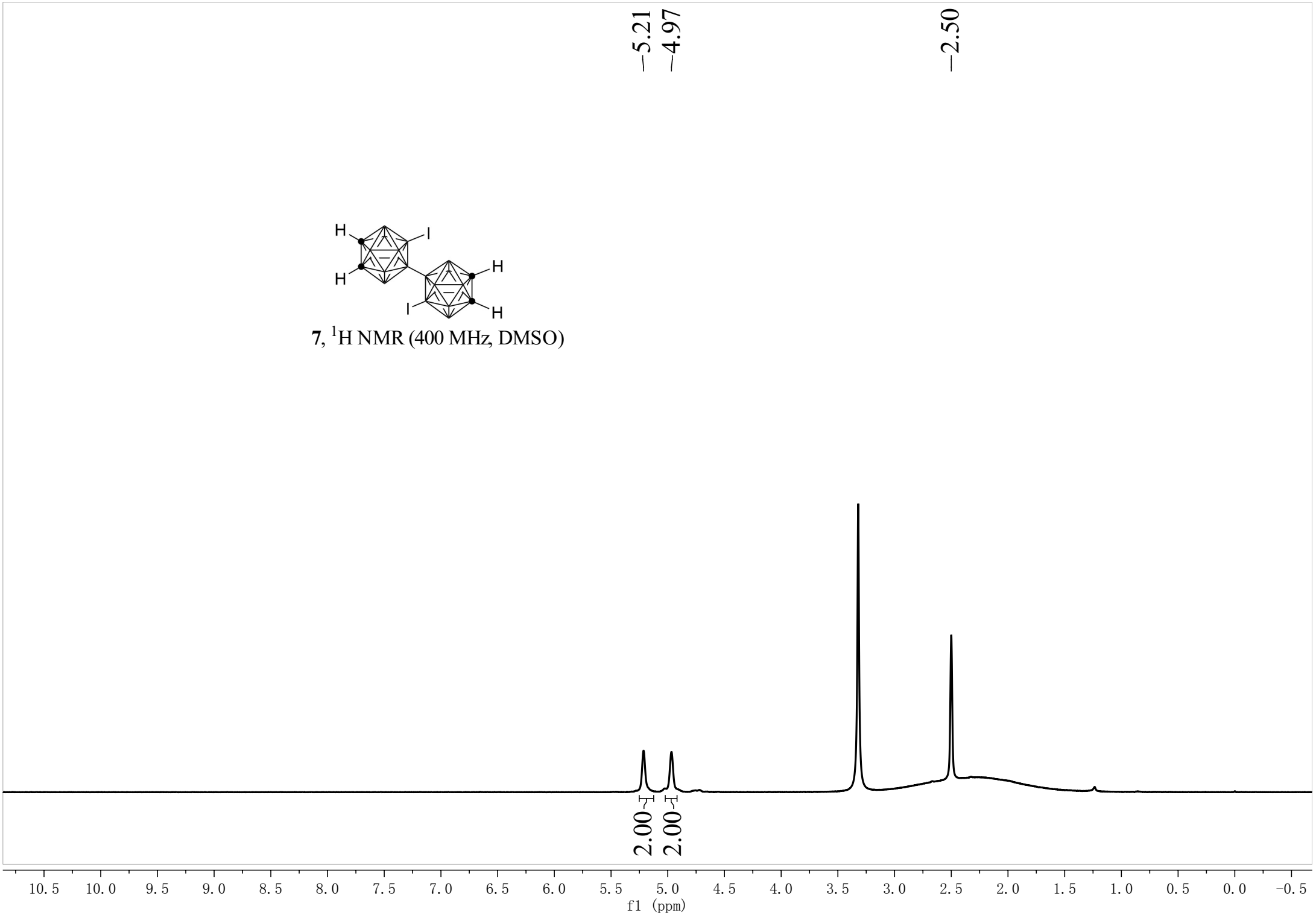
6, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



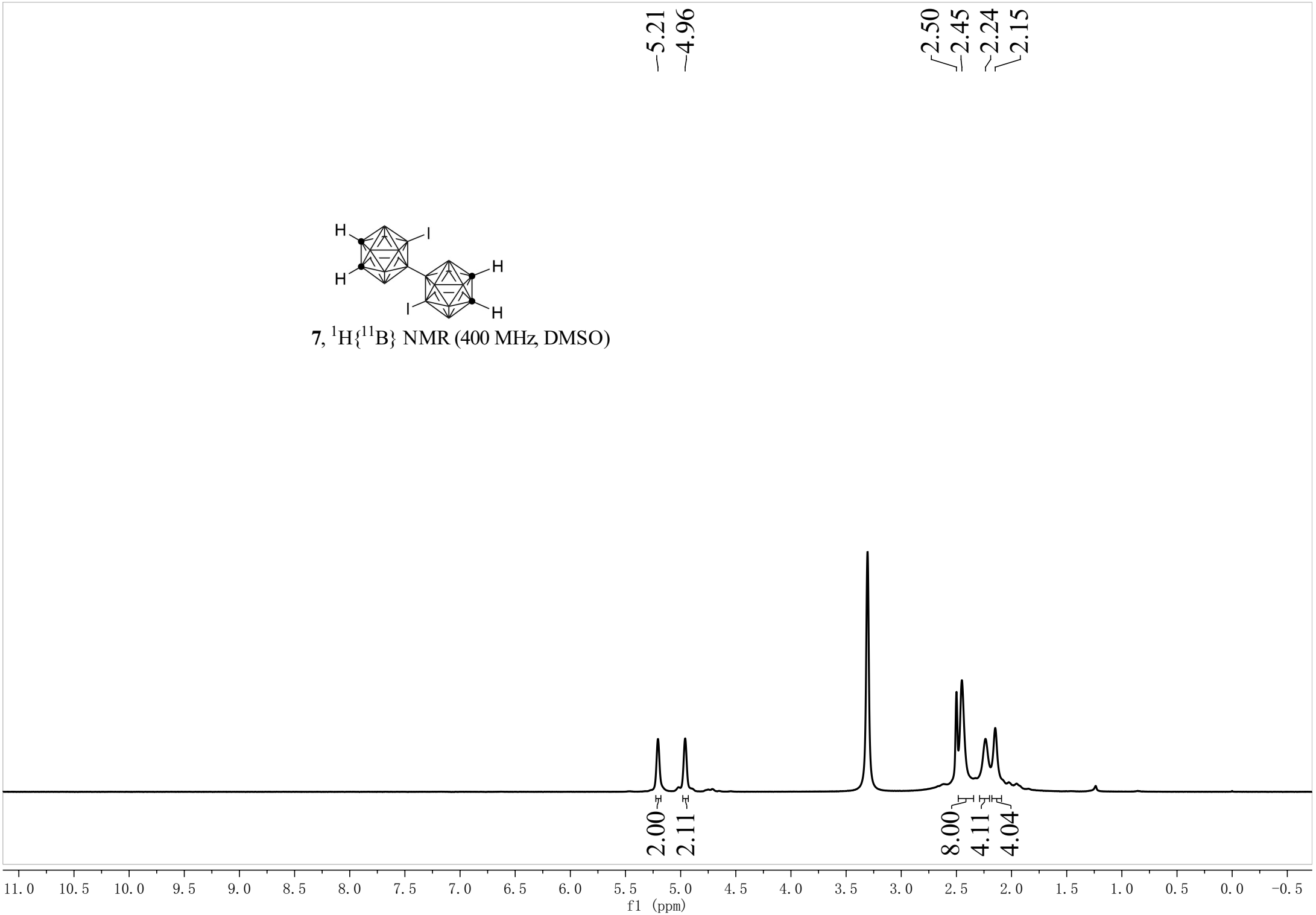
6, ^{13}C NMR (101 MHz, $CDCl_3$)



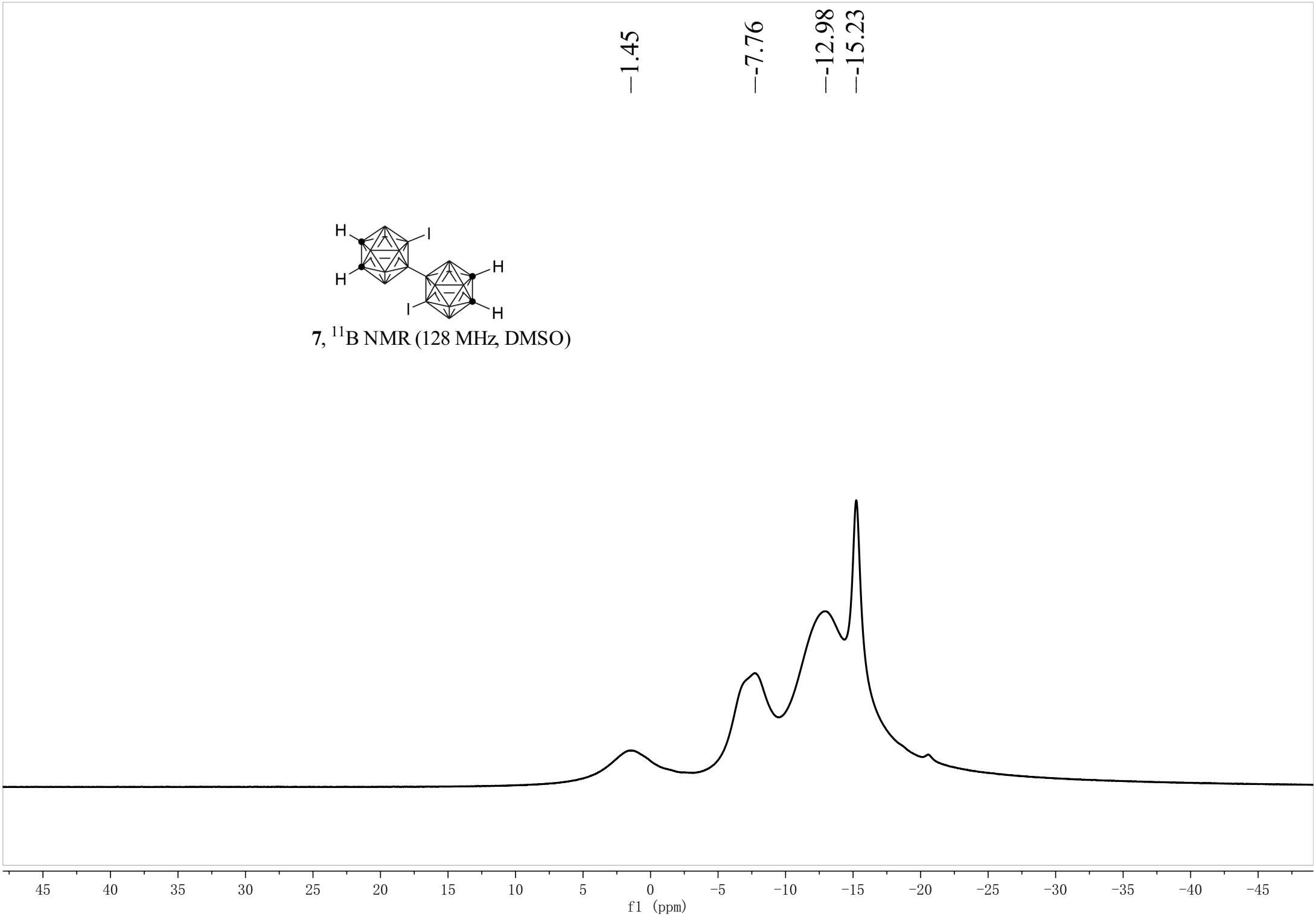
7, ^{1}H NMR (400 MHz, DMSO)



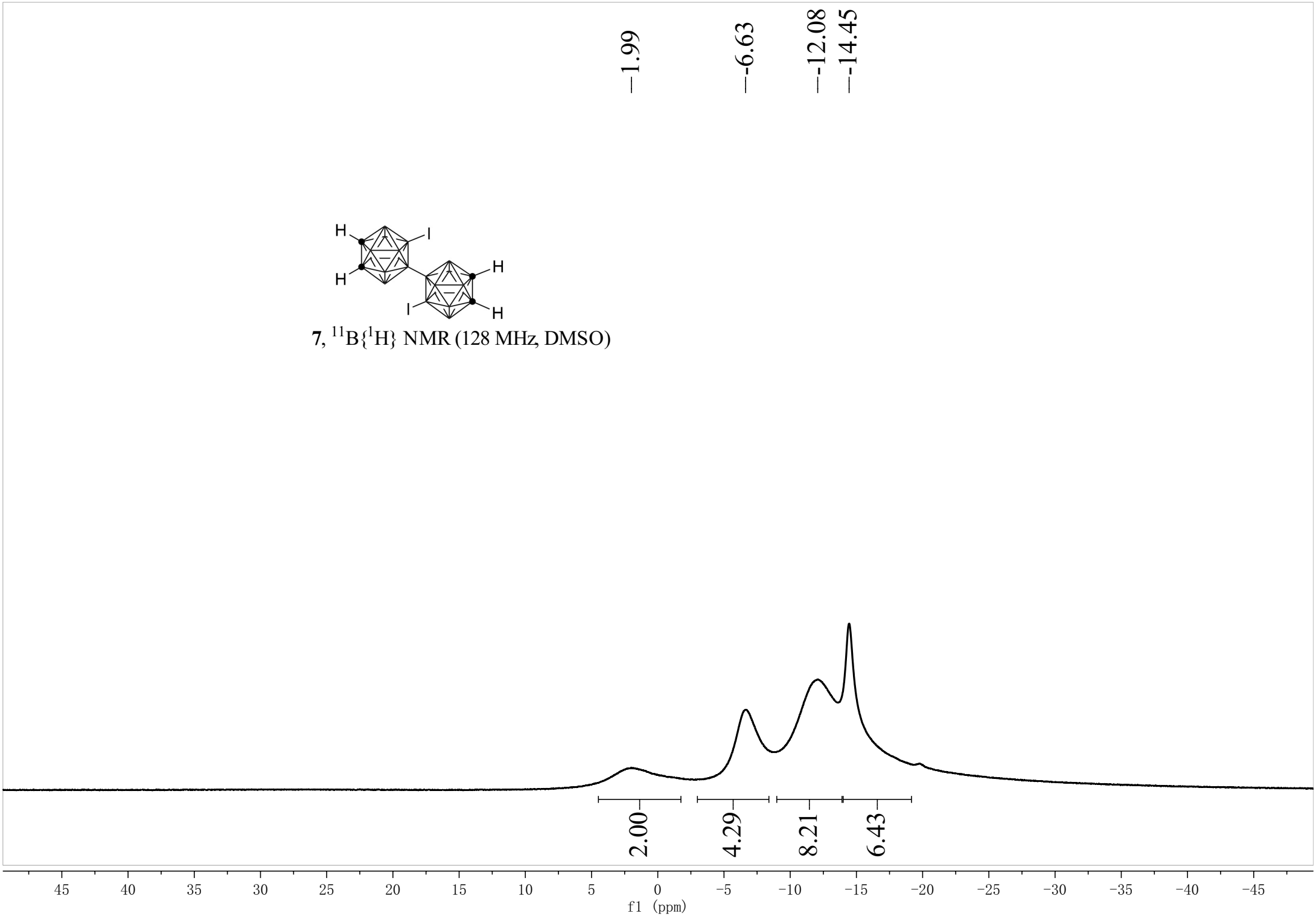
7, $^{1}H\{^{11}B\}$ NMR (400 MHz, DMSO)



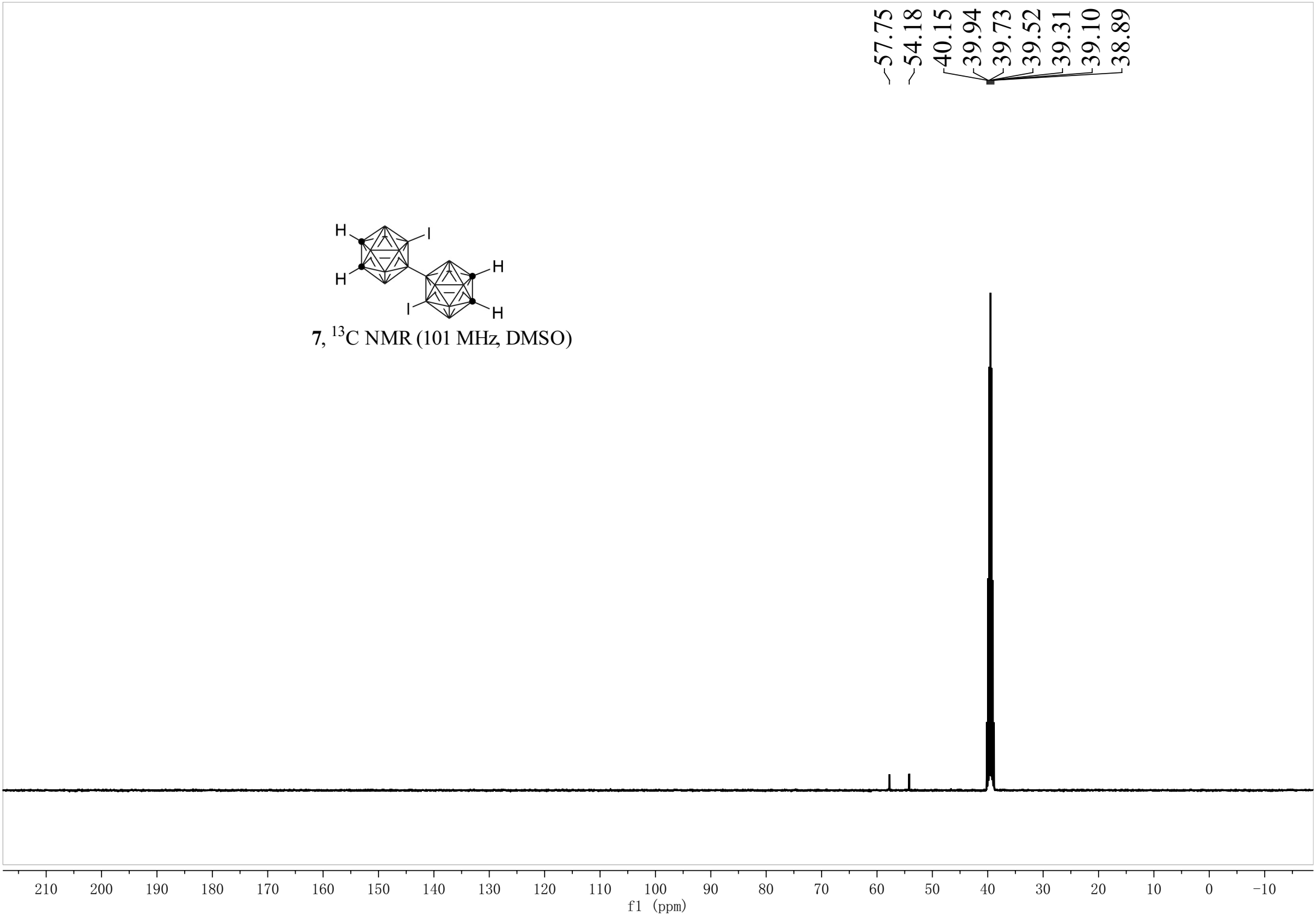
7, ^{11}B NMR (128 MHz, DMSO)

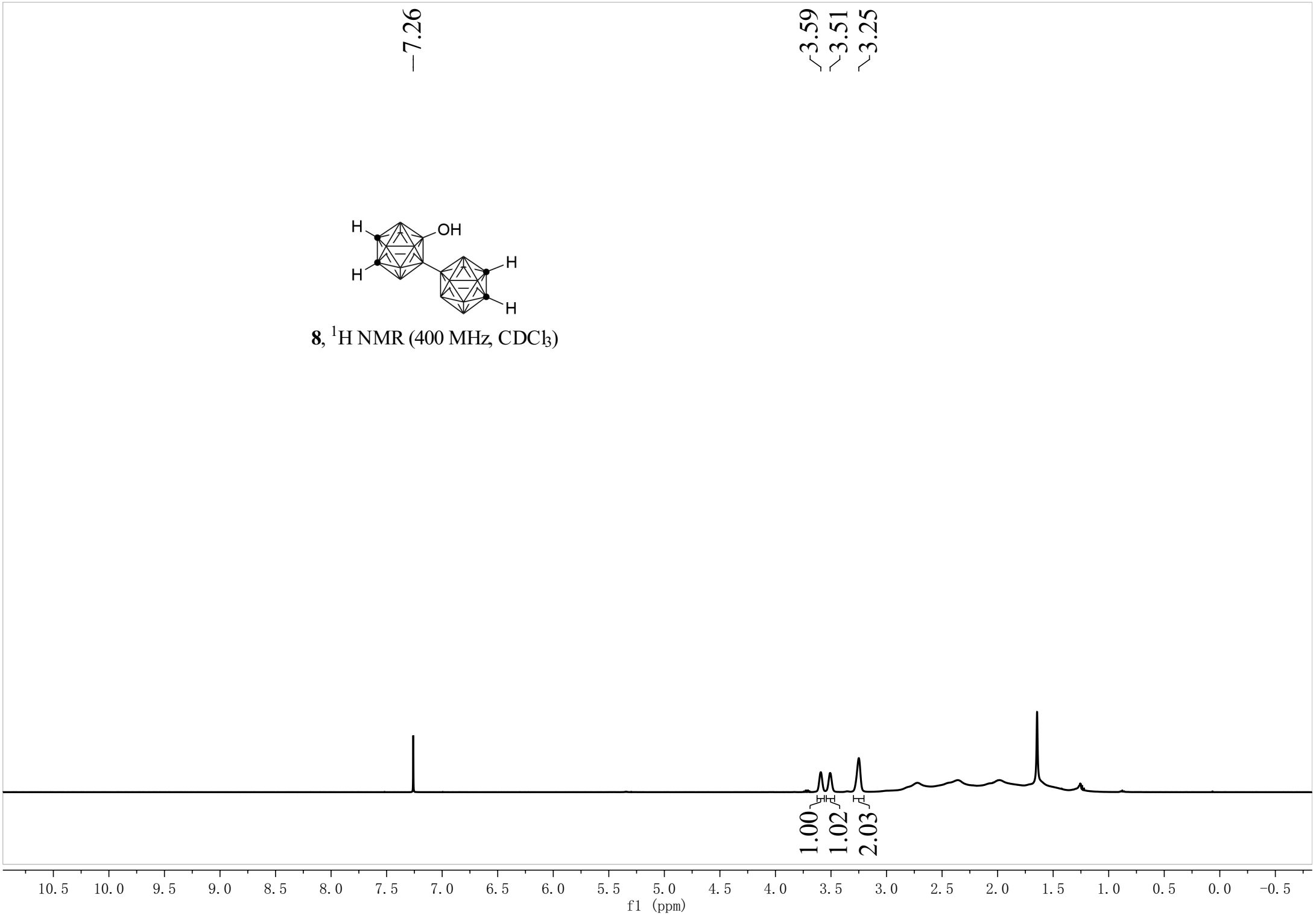


7, $^{11}B\{^{1}H\}$ NMR (128 MHz, DMSO)

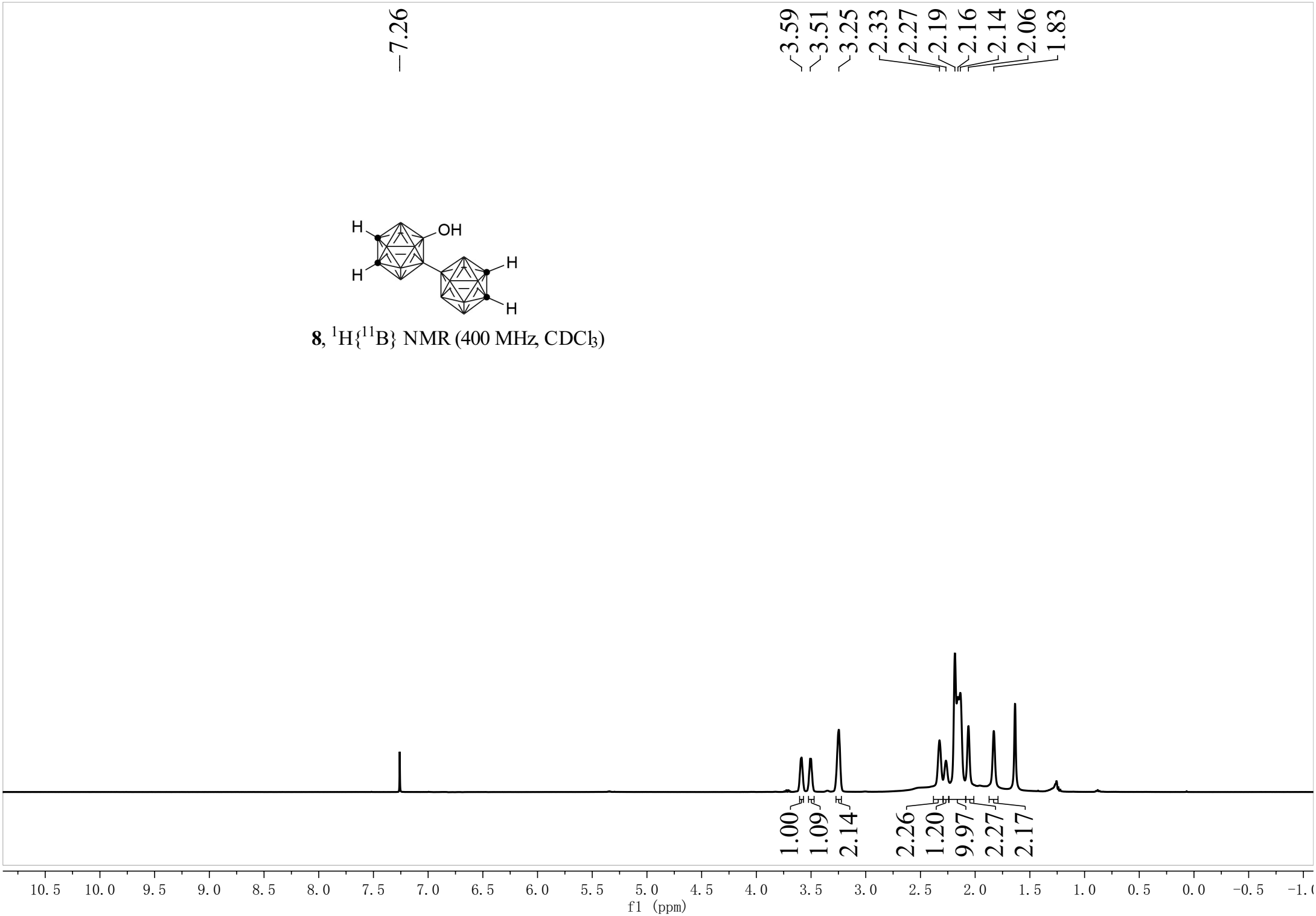


7, ^{13}C NMR (101 MHz, DMSO)

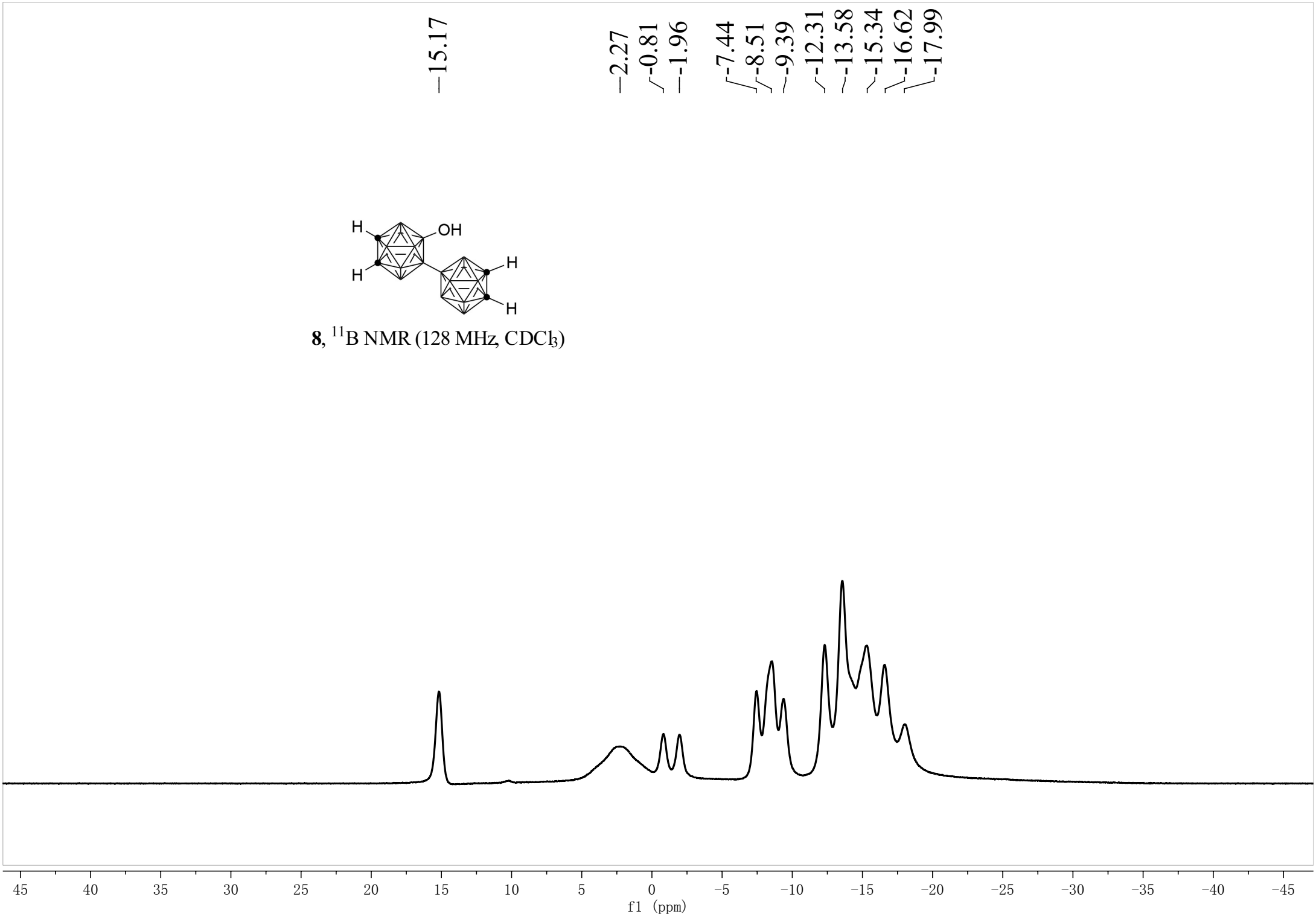




8, ^{1}H NMR (400 MHz, $CDCl_3$)

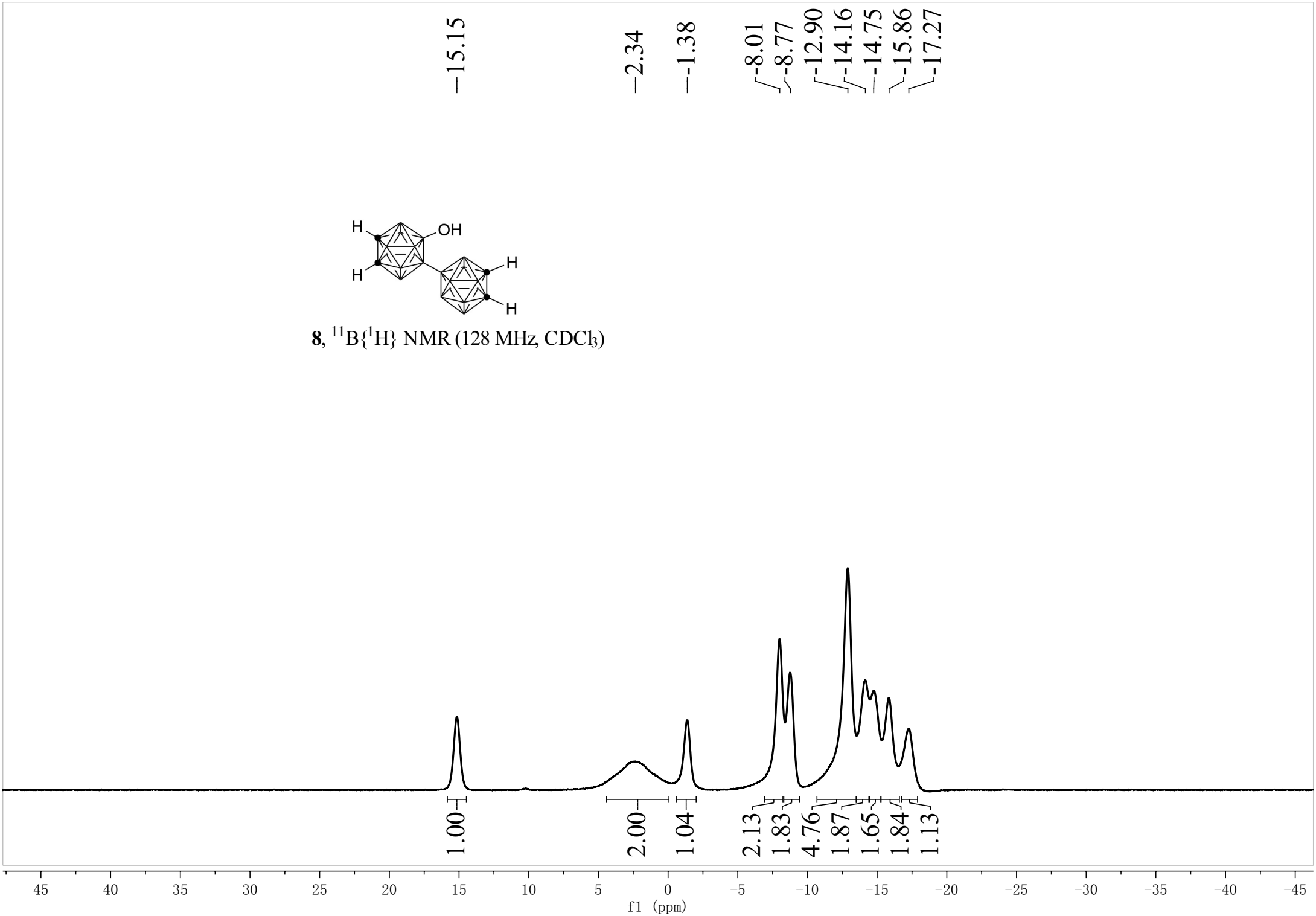


8, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

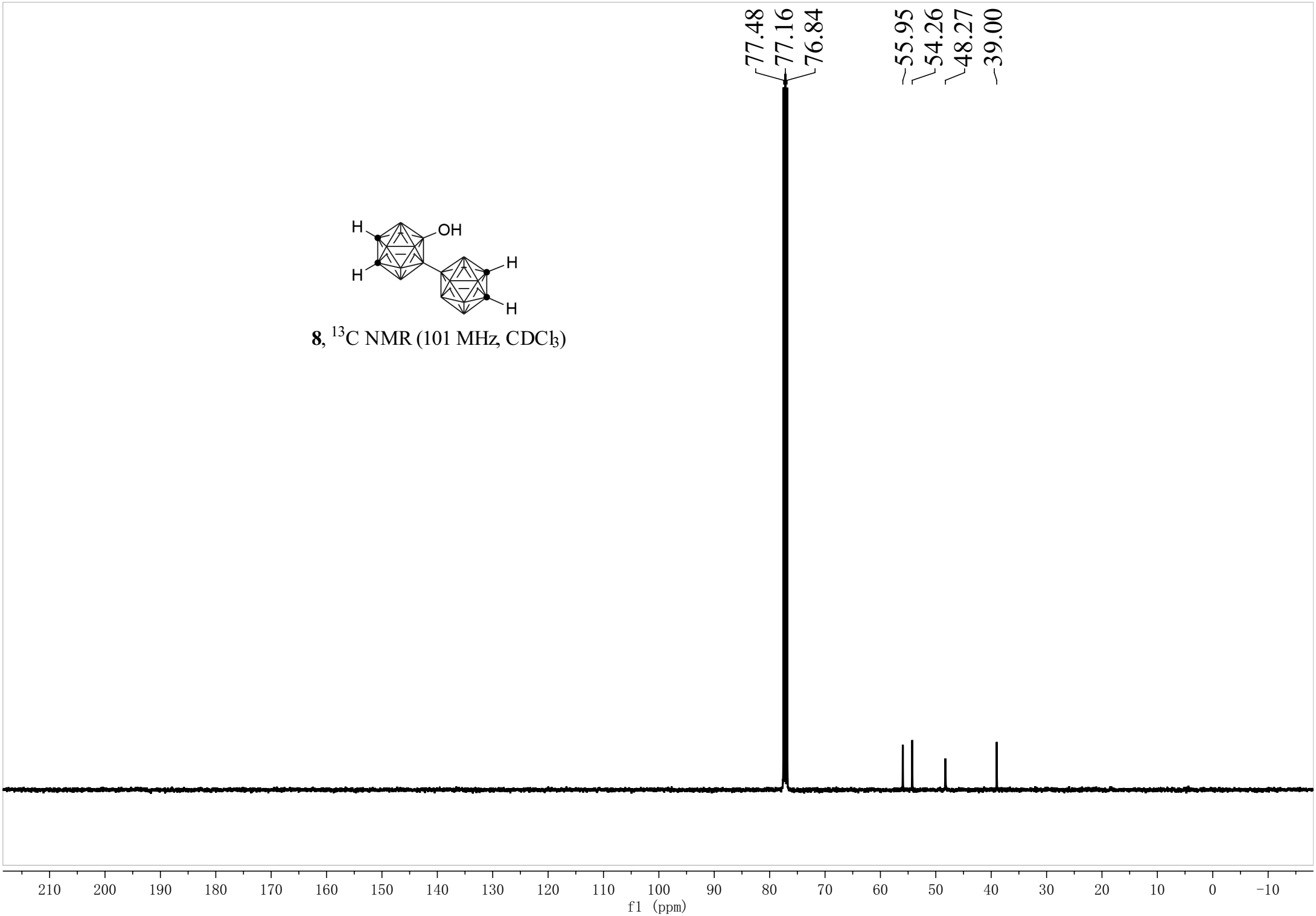


8, ^{11}B NMR (128 MHz, $CDCl_3$)

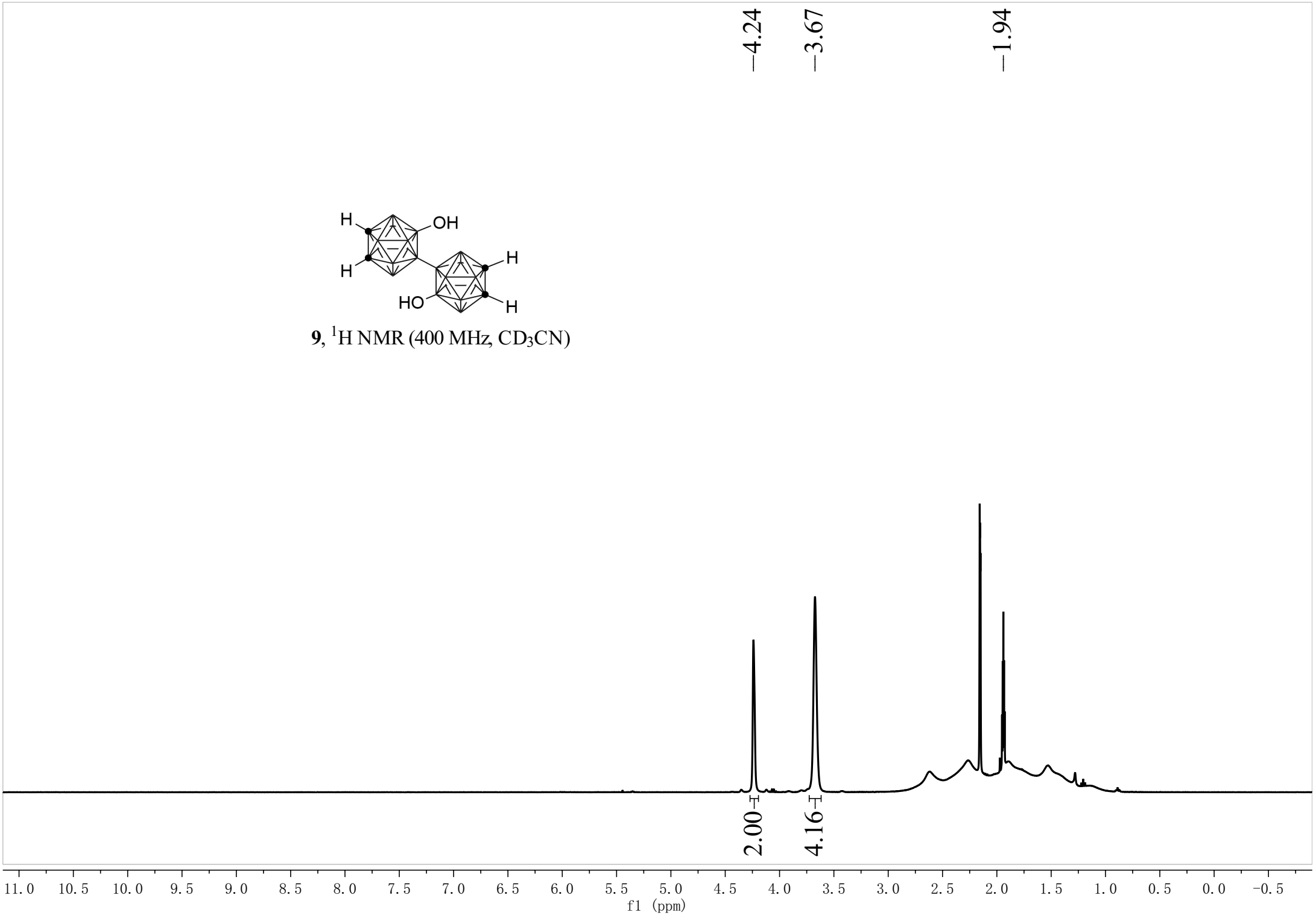
8, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



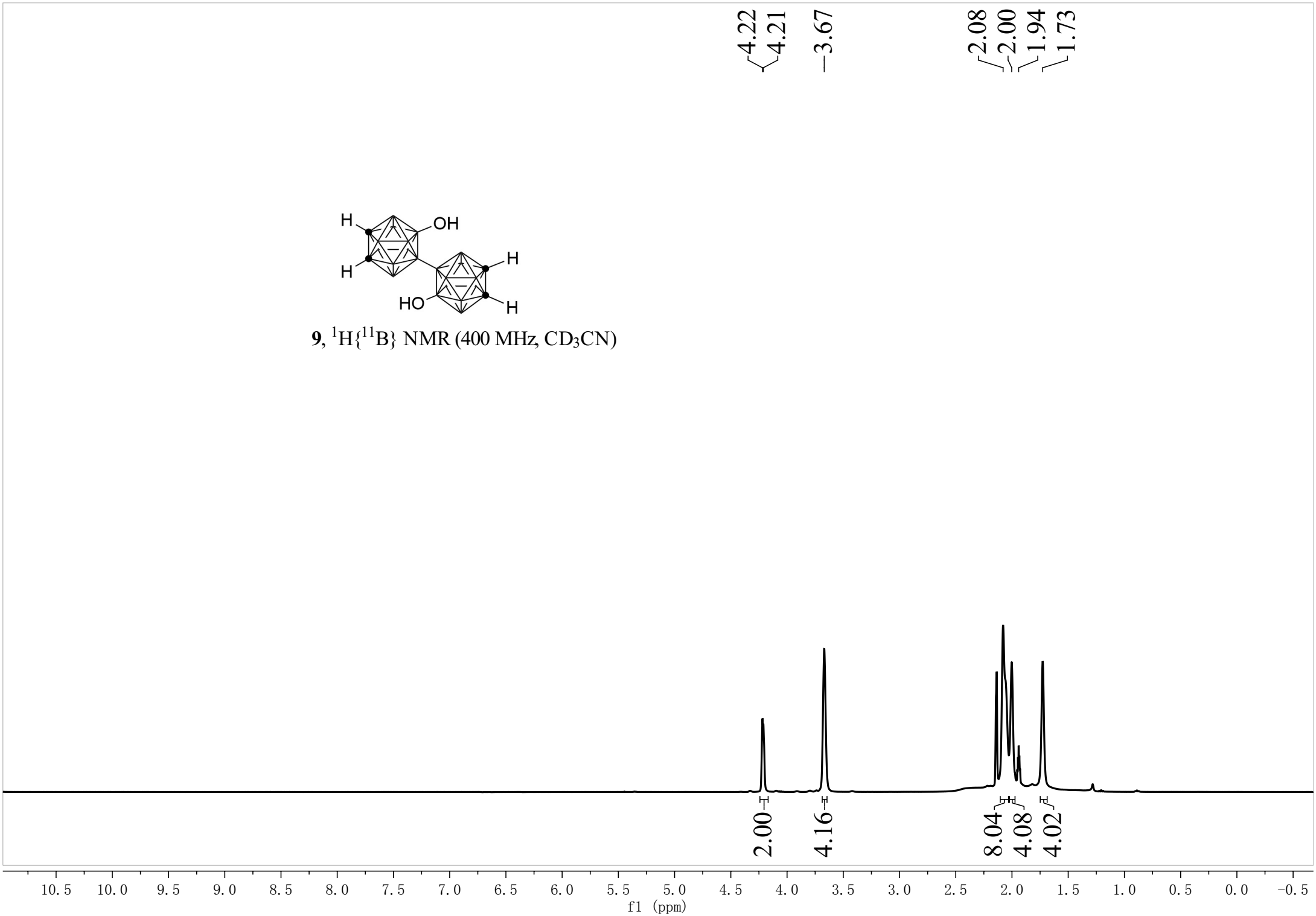
8, ^{13}C NMR (101 MHz, $CDCl_3$)

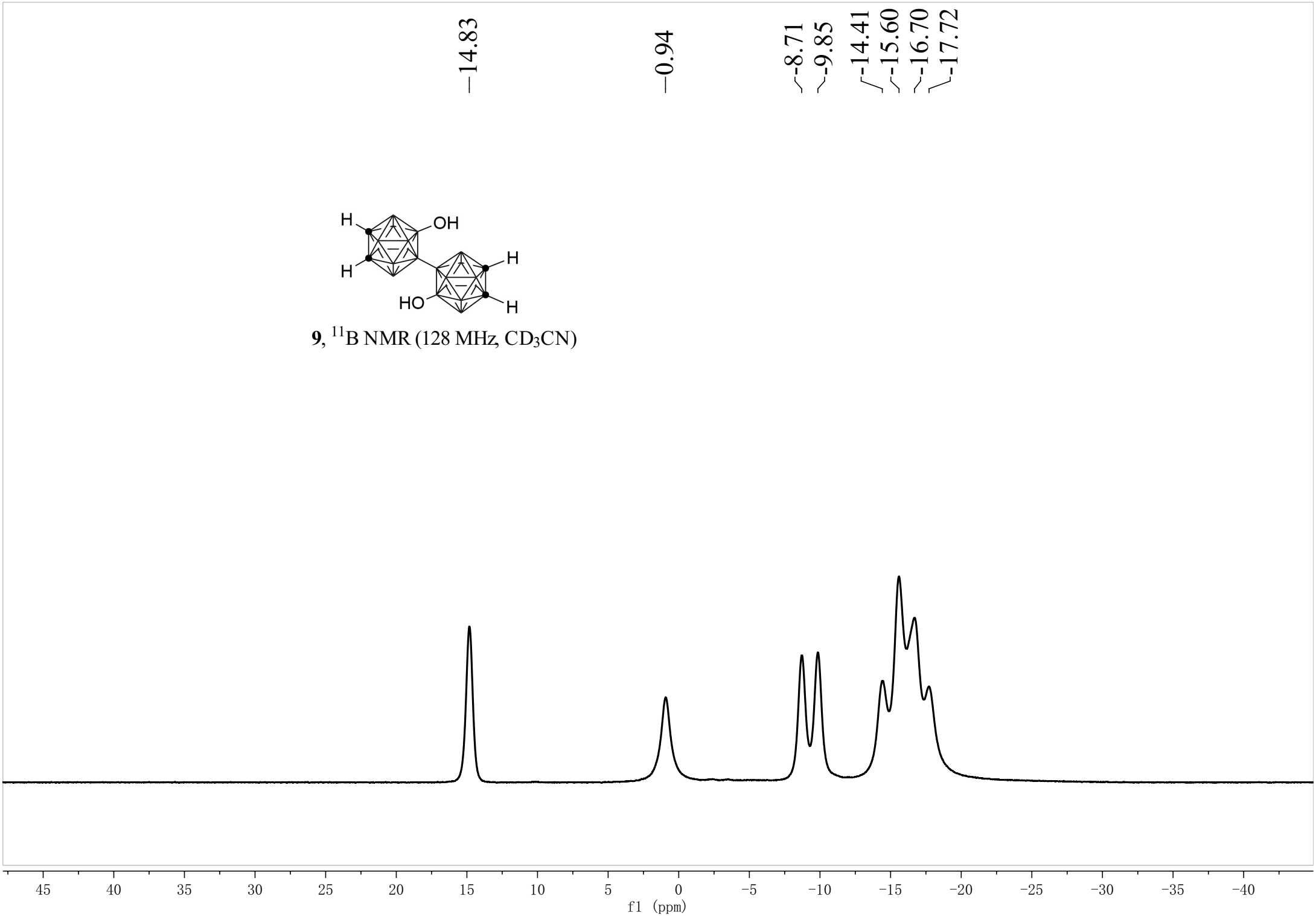


9, ^{1}H NMR (400 MHz, CD_3CN)

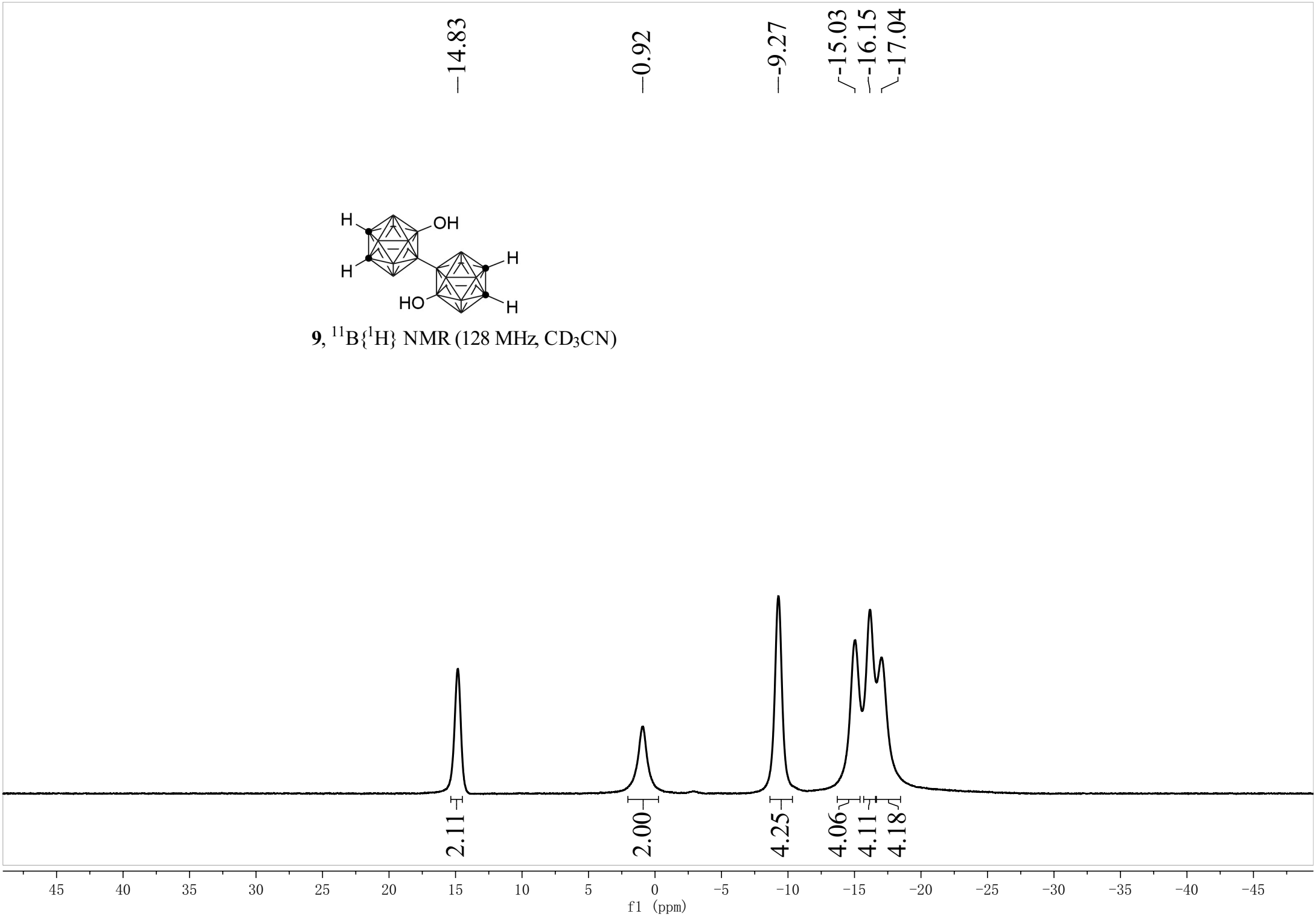


9, $^{1}H\{^{11}B\}$ NMR (400 MHz, CD_3CN)

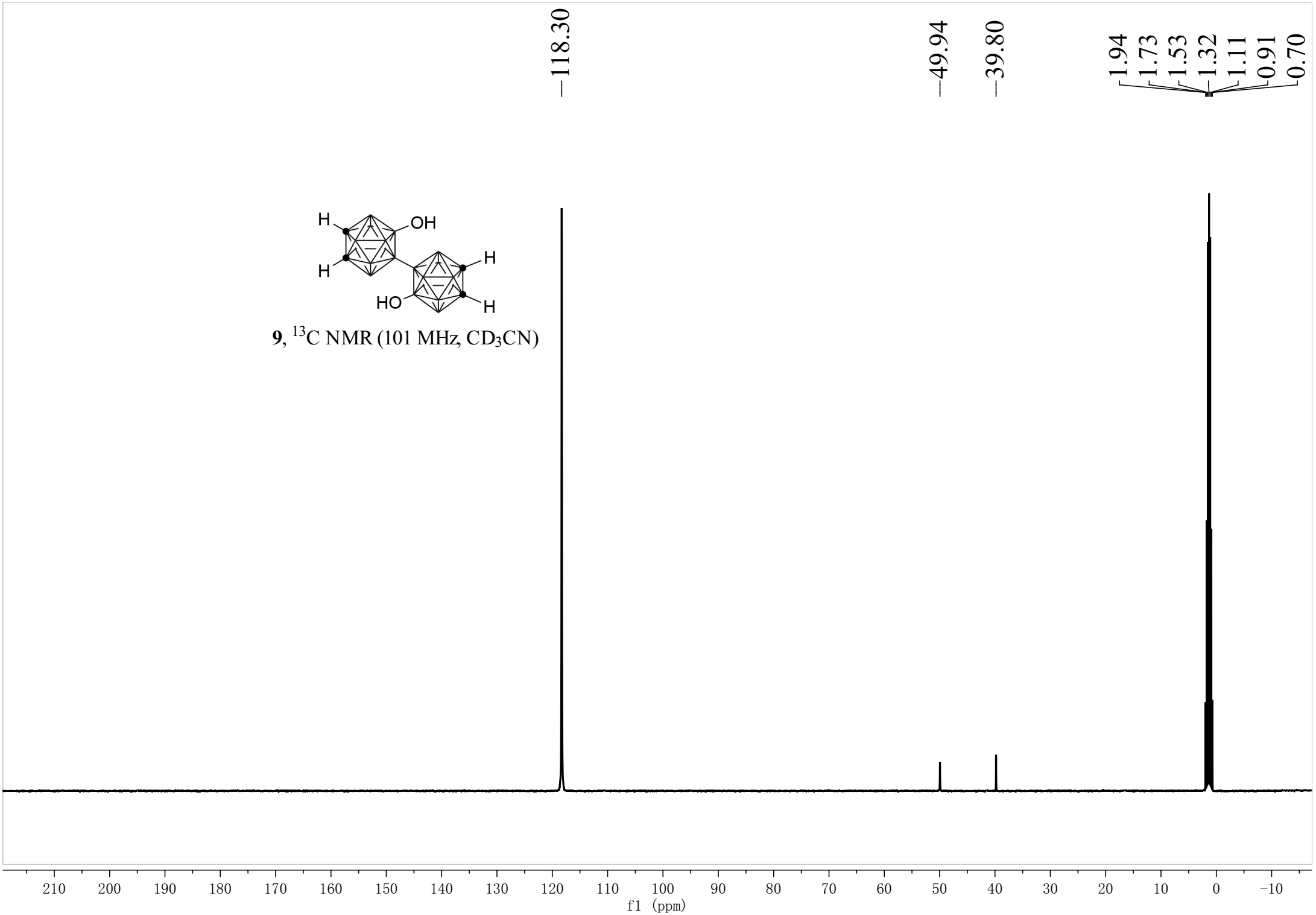




9, ^{11}B NMR (128 MHz, CD_3CN)

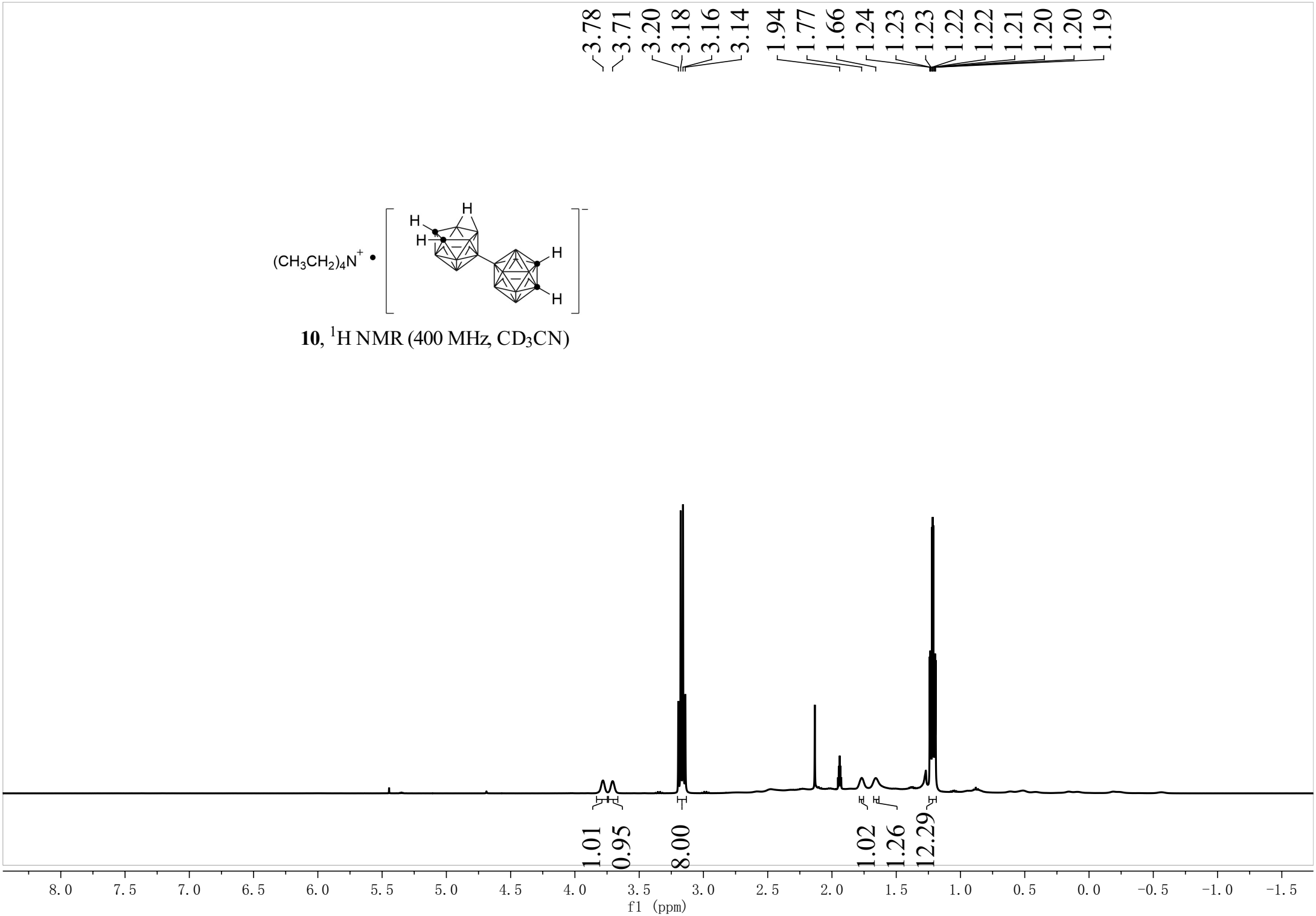


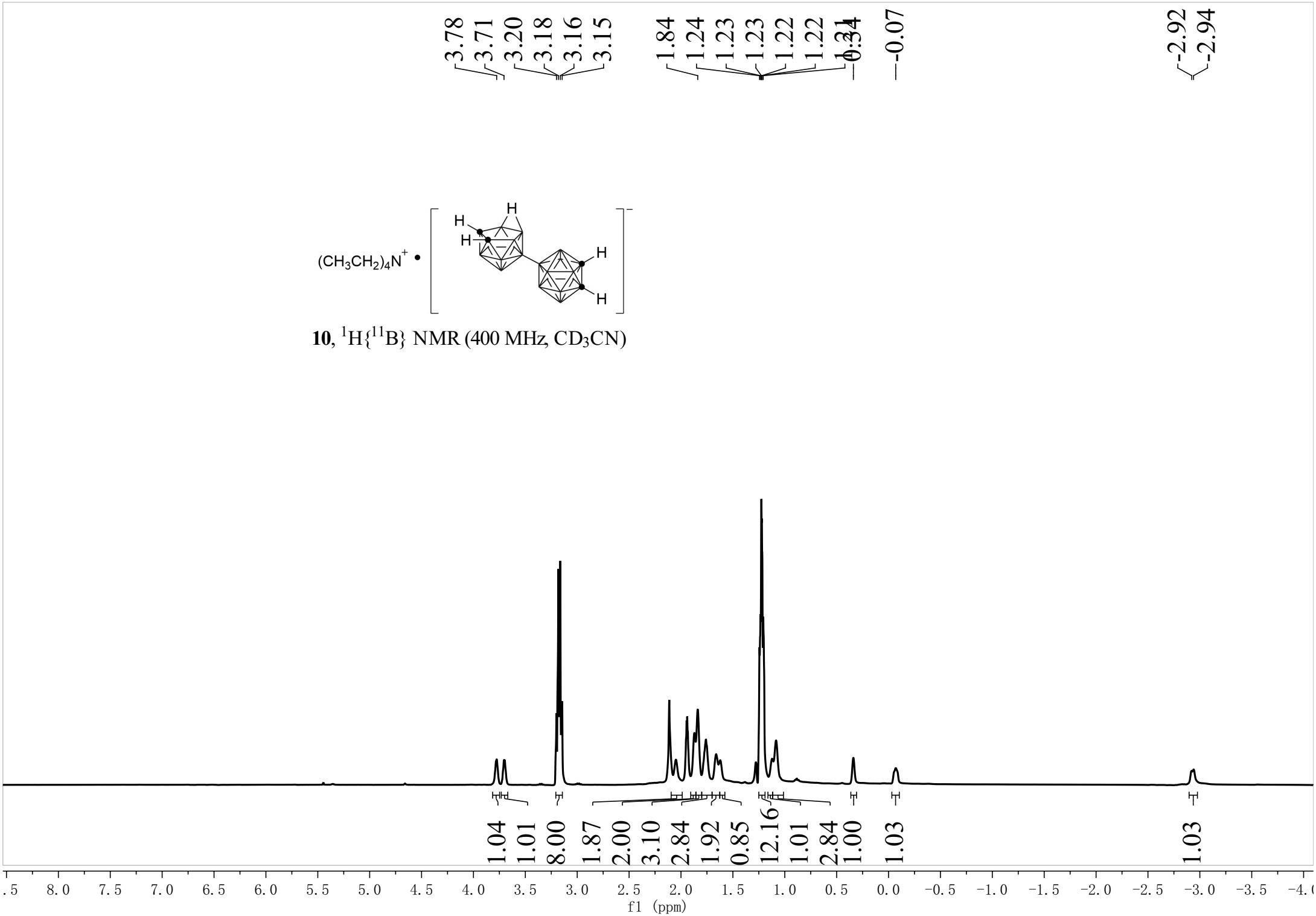
9, $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_3CN)



9, ^{13}C NMR (101 MHz, CD_3CN)

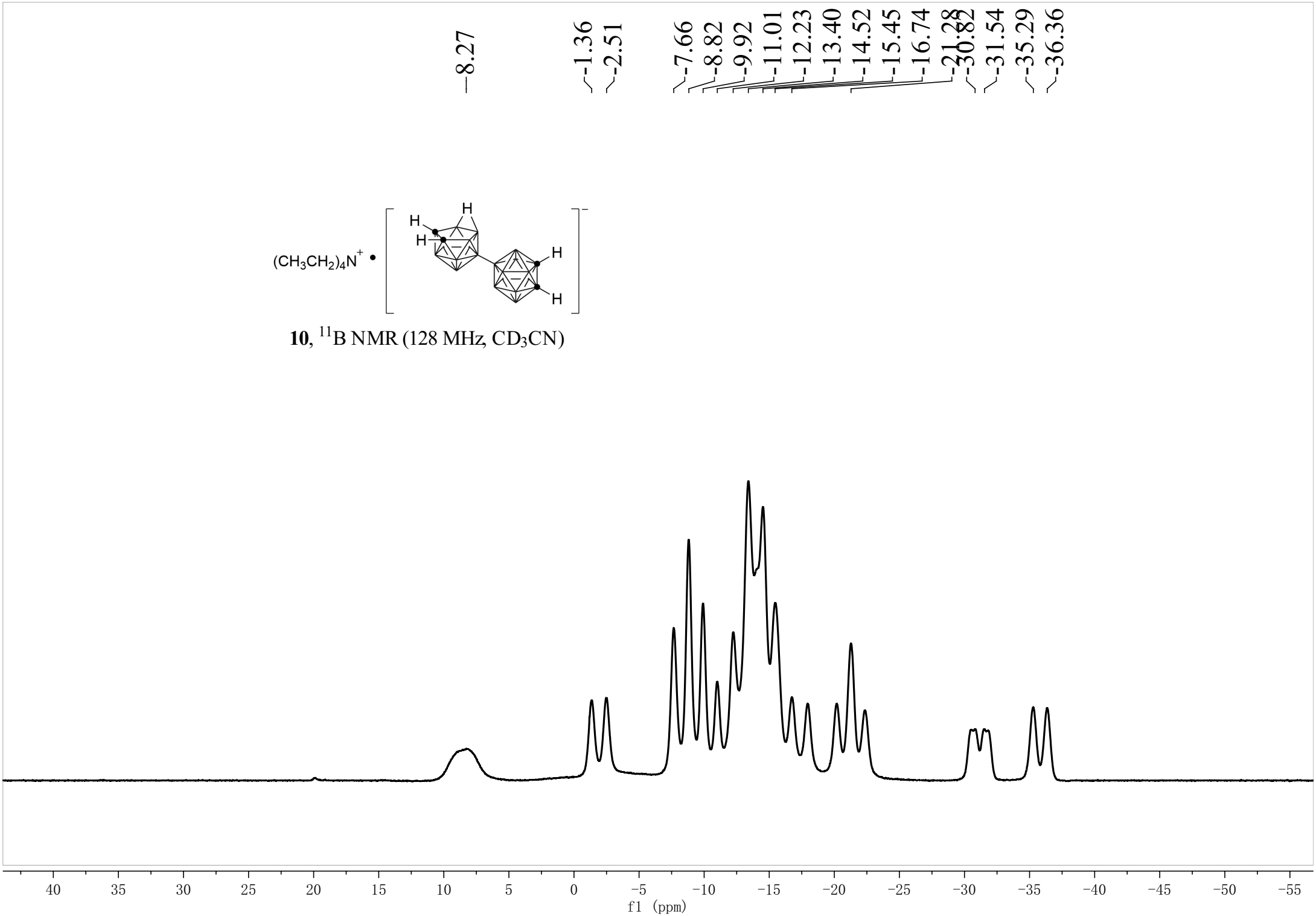
10, ^{1}H NMR (400 MHz, CD_3CN)



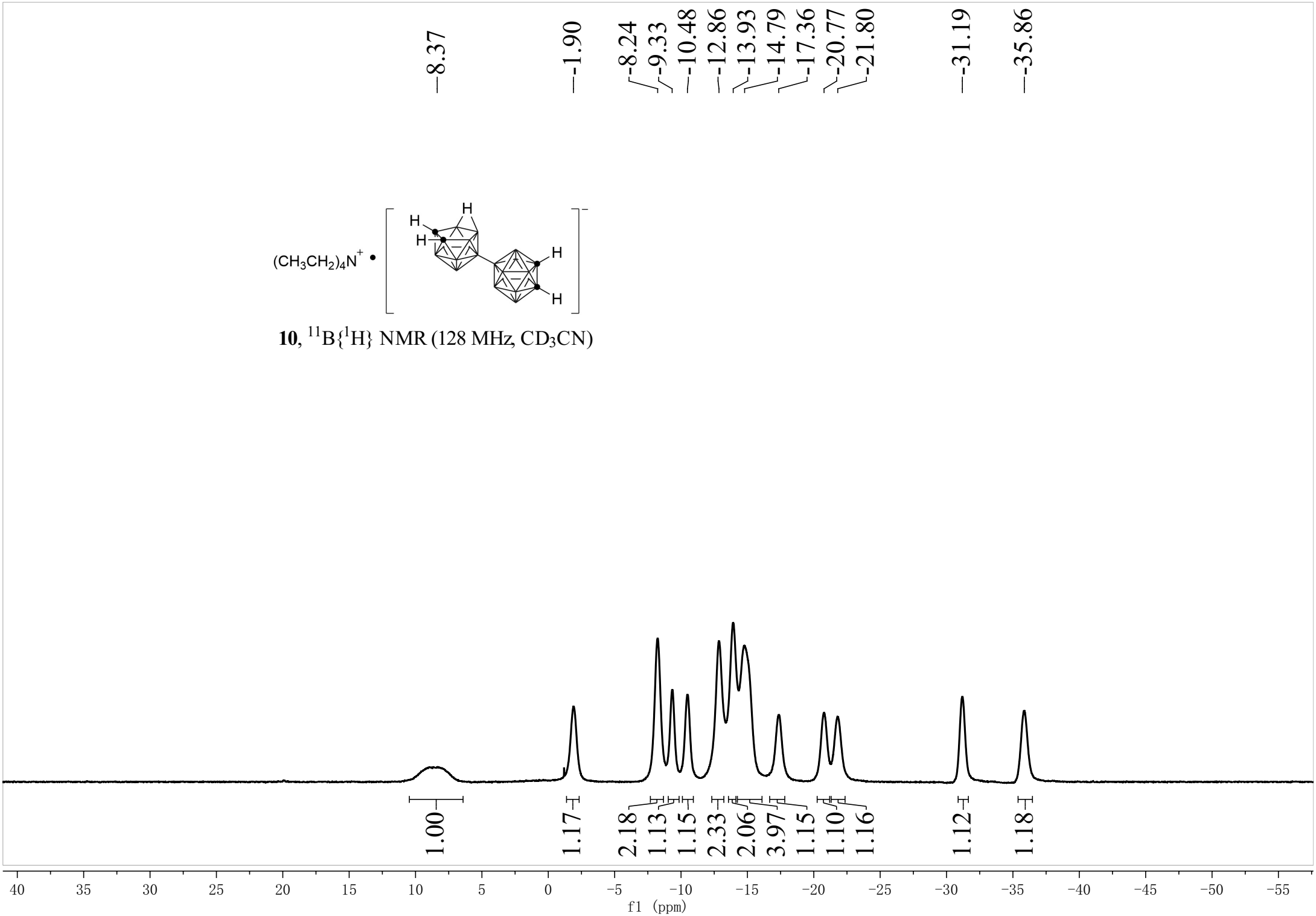


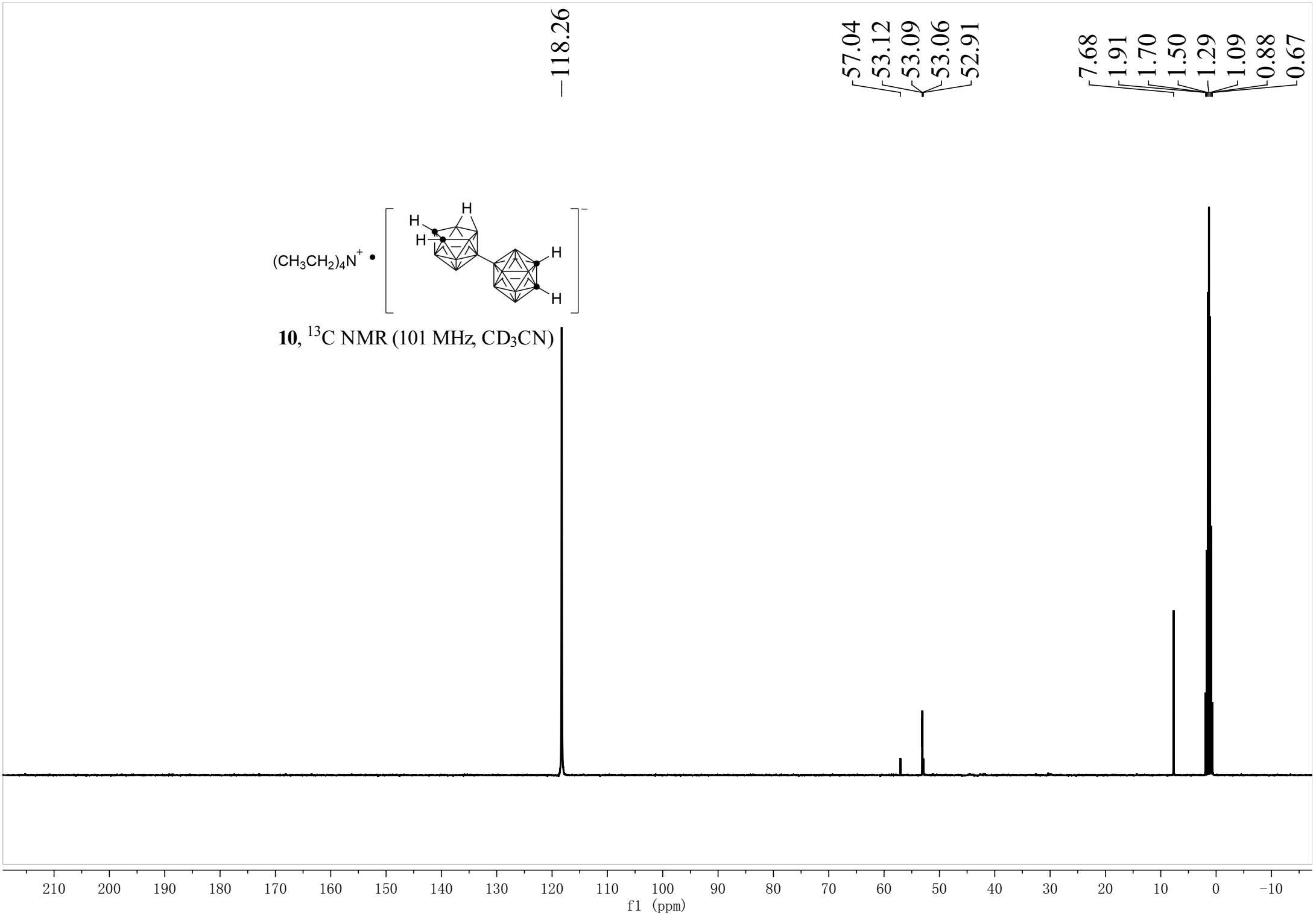
10, $^{1}H\{^{11}B\}$ NMR (400 MHz, CD_3CN)

10, ^{11}B NMR (128 MHz, CD_3CN)



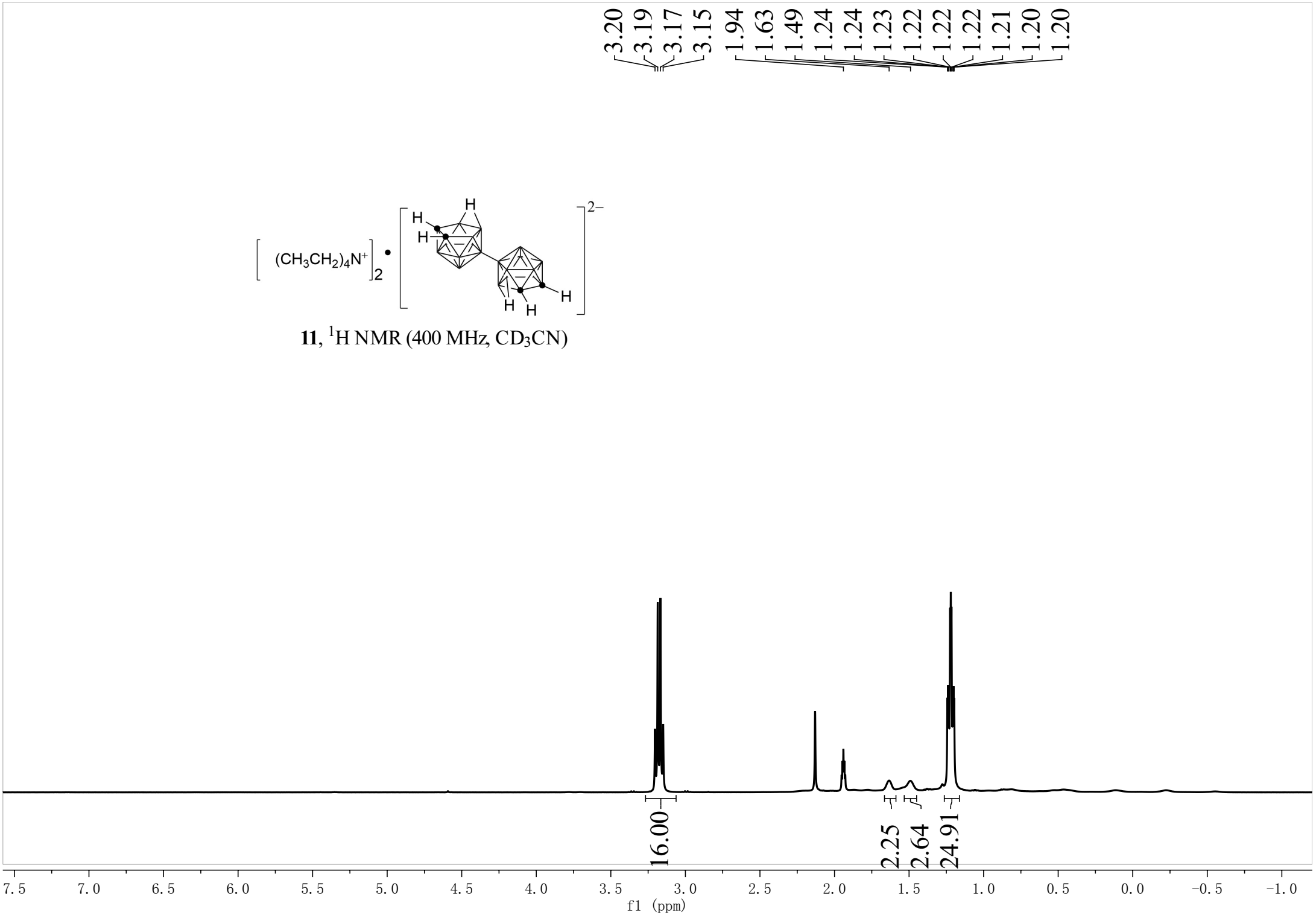
10, $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_3CN)



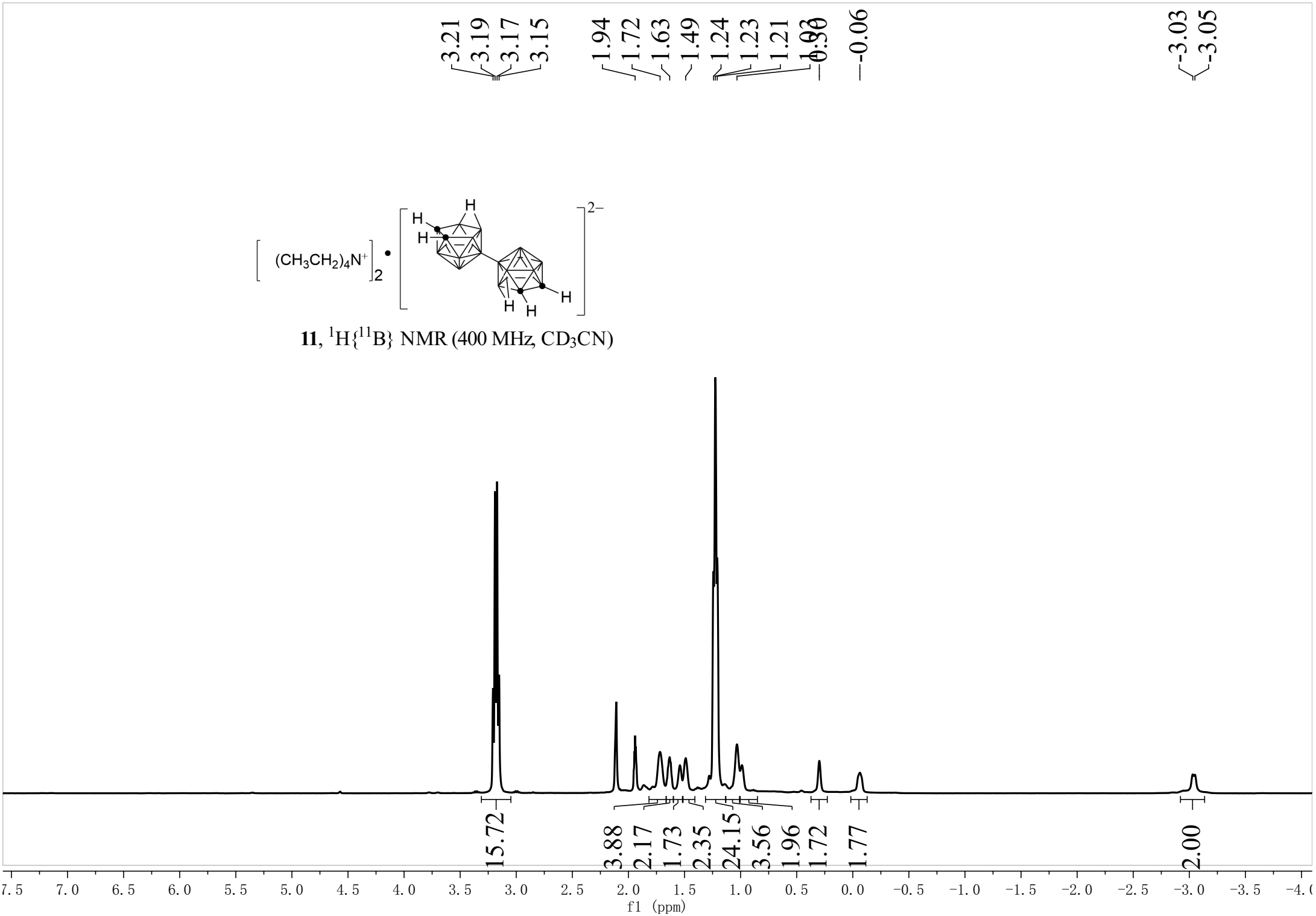


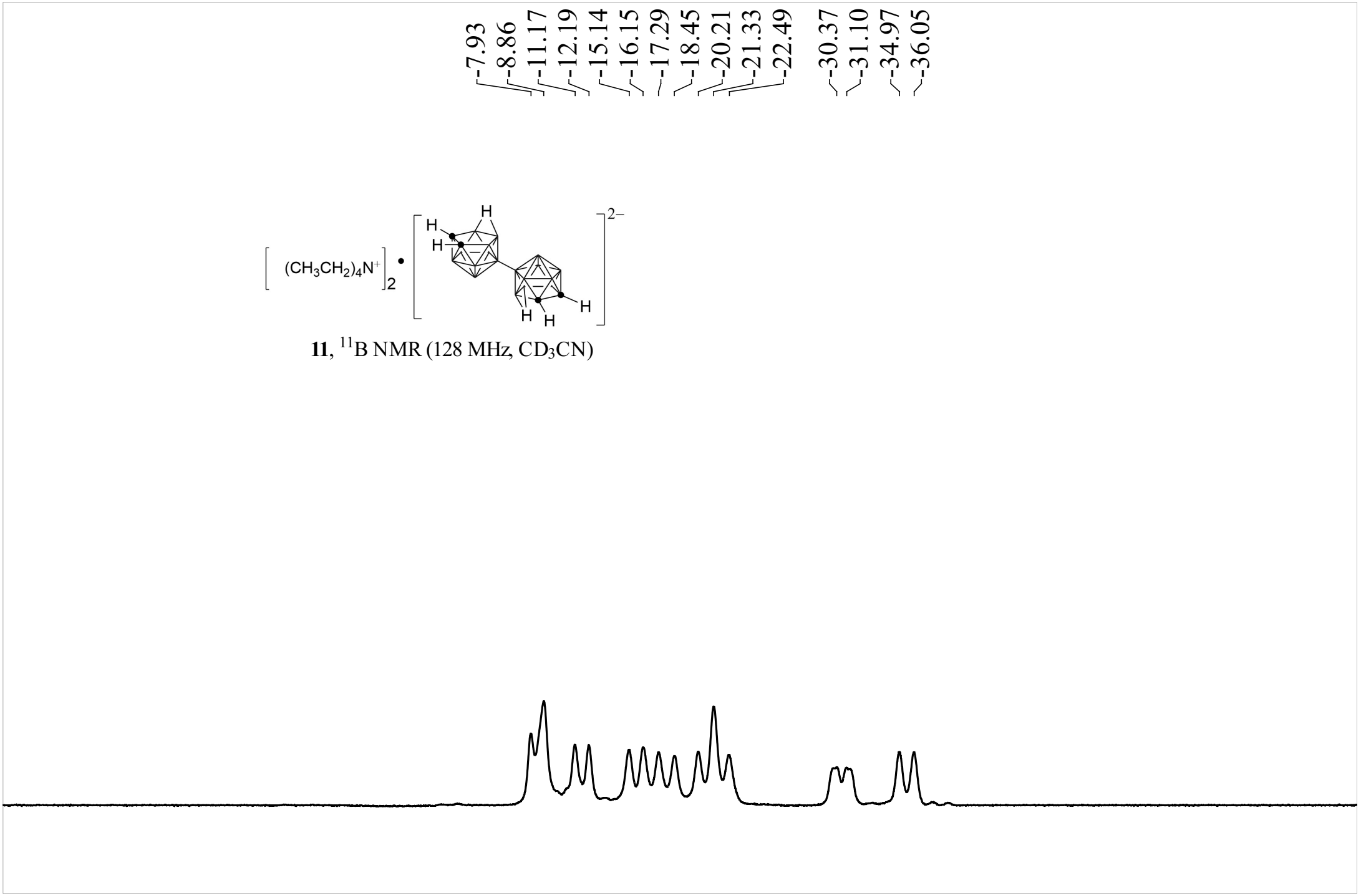
10, ^{13}C NMR (101 MHz, CD_3CN)

11, ^{1}H NMR (400 MHz, CD_3CN)



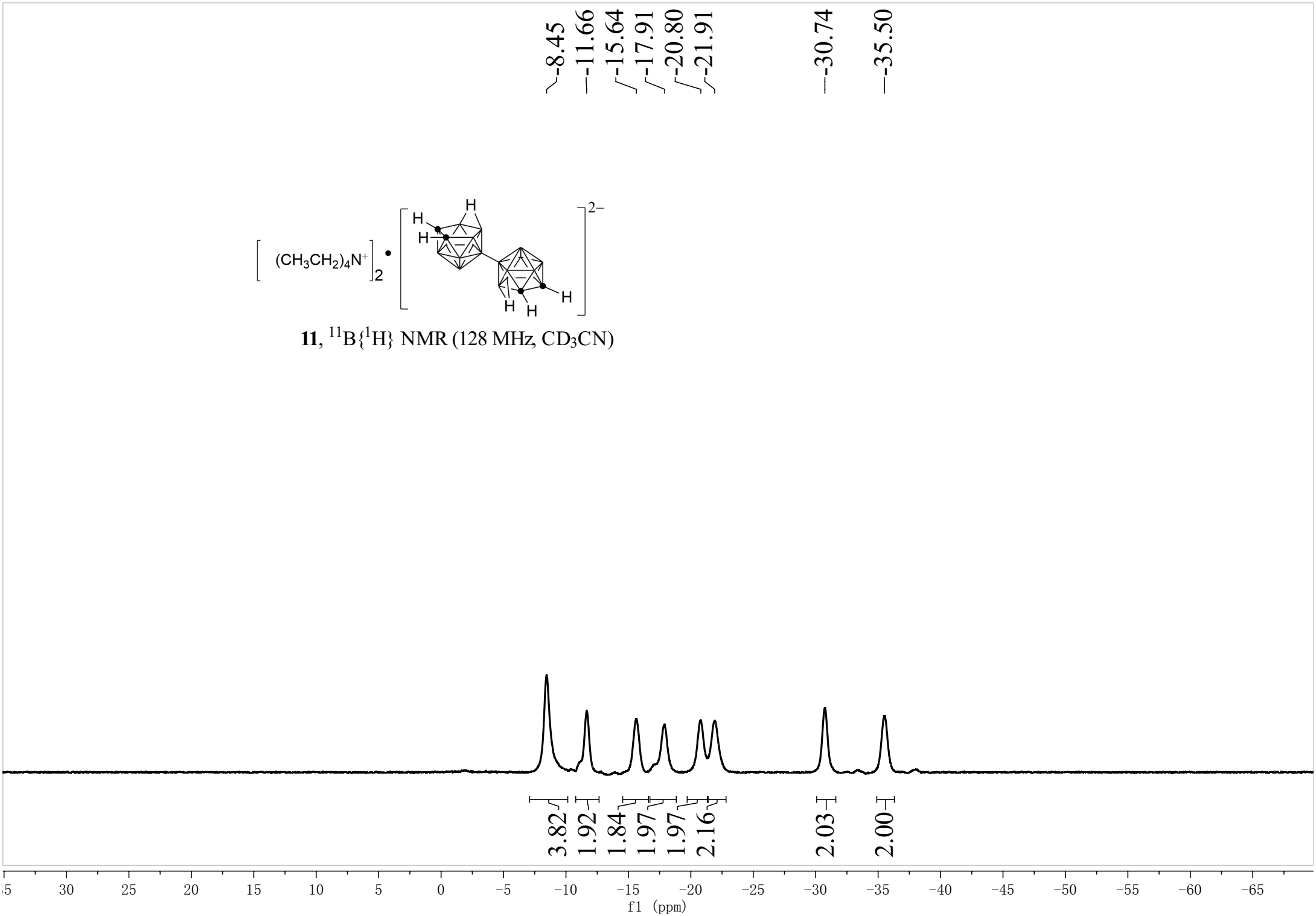
11, $^{1}H\{^{11}B\}$ NMR (400 MHz, CD_3CN)

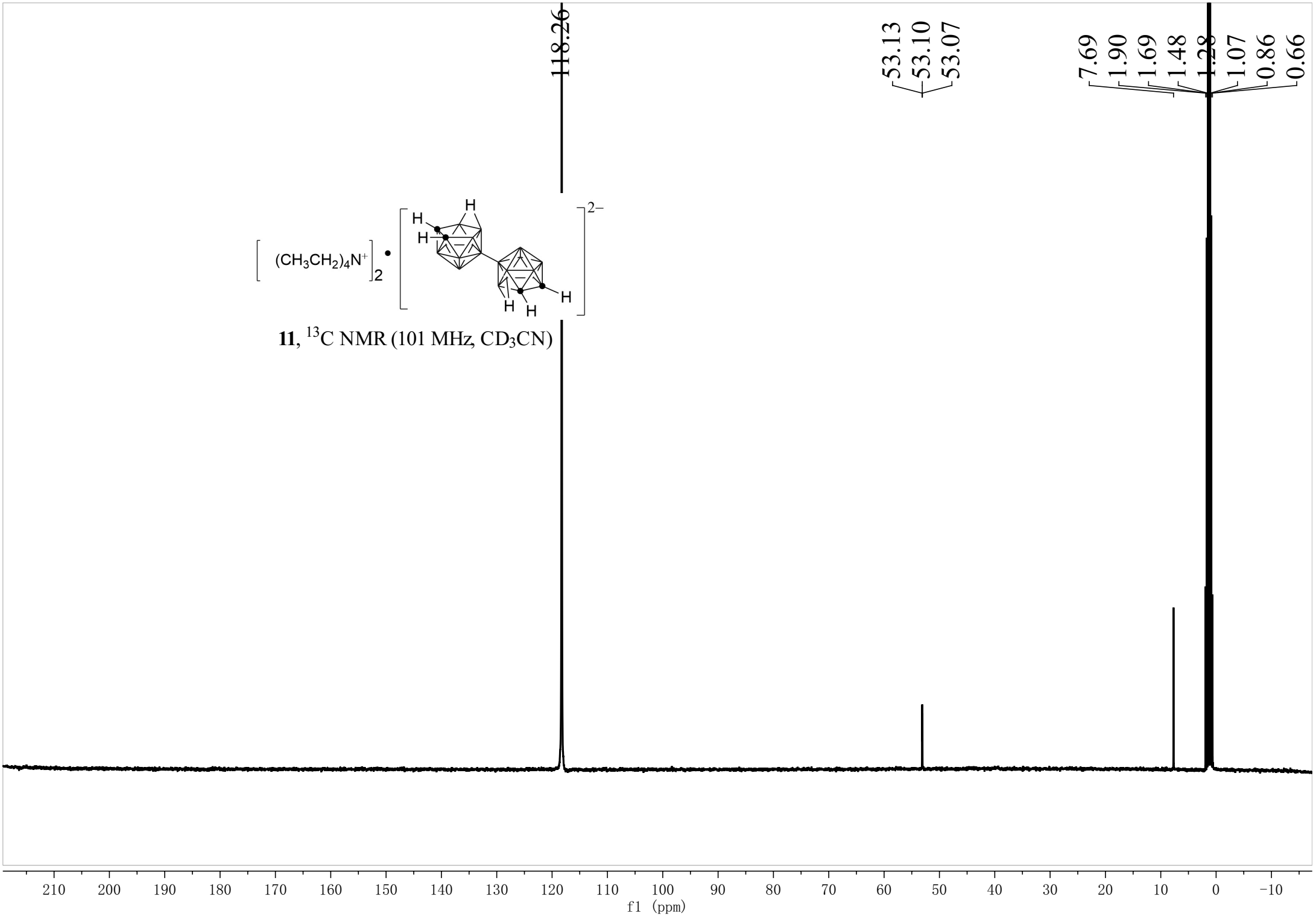




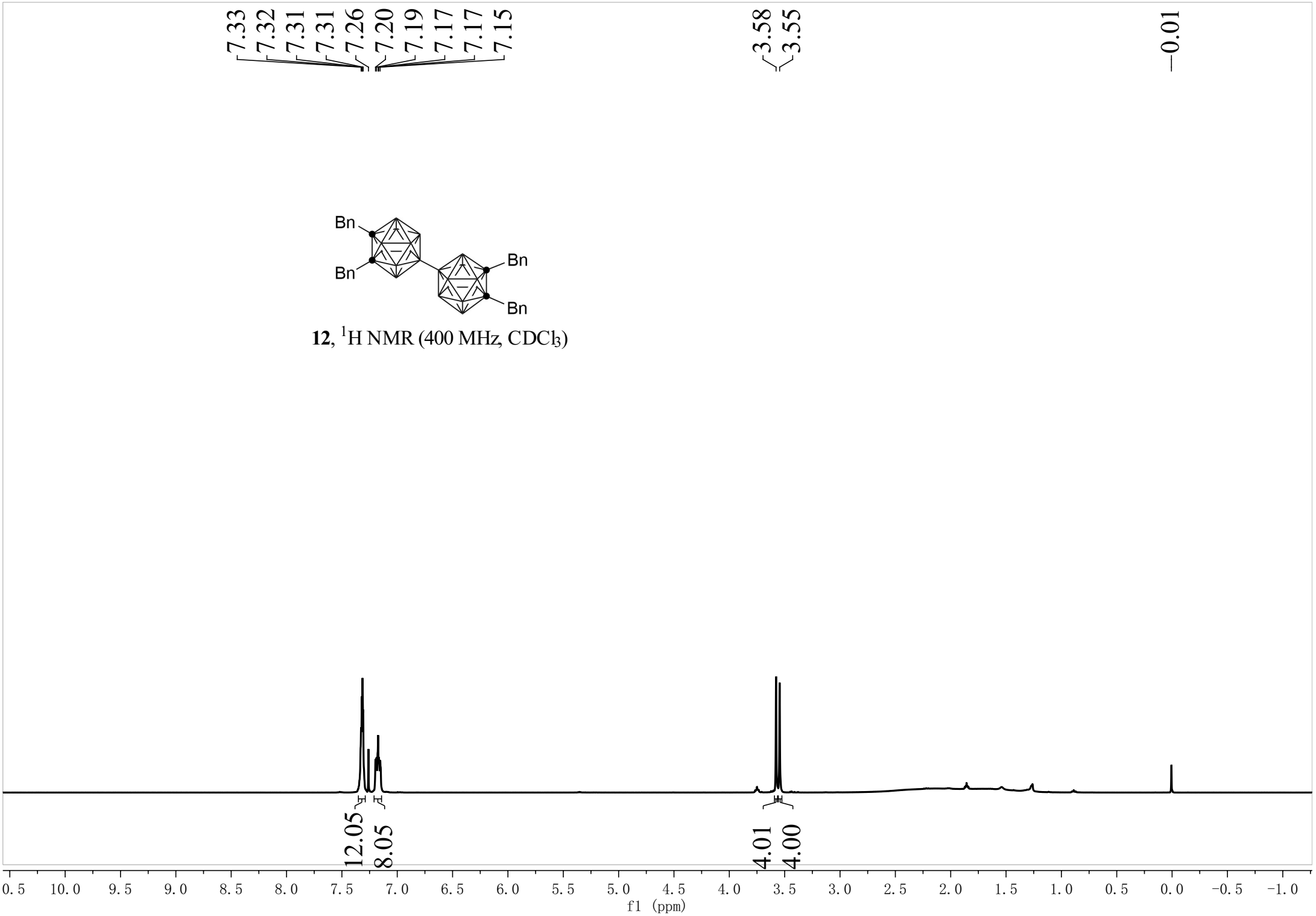
11, ^{11}B NMR (128 MHz, CD_3CN)

11, $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_3CN)

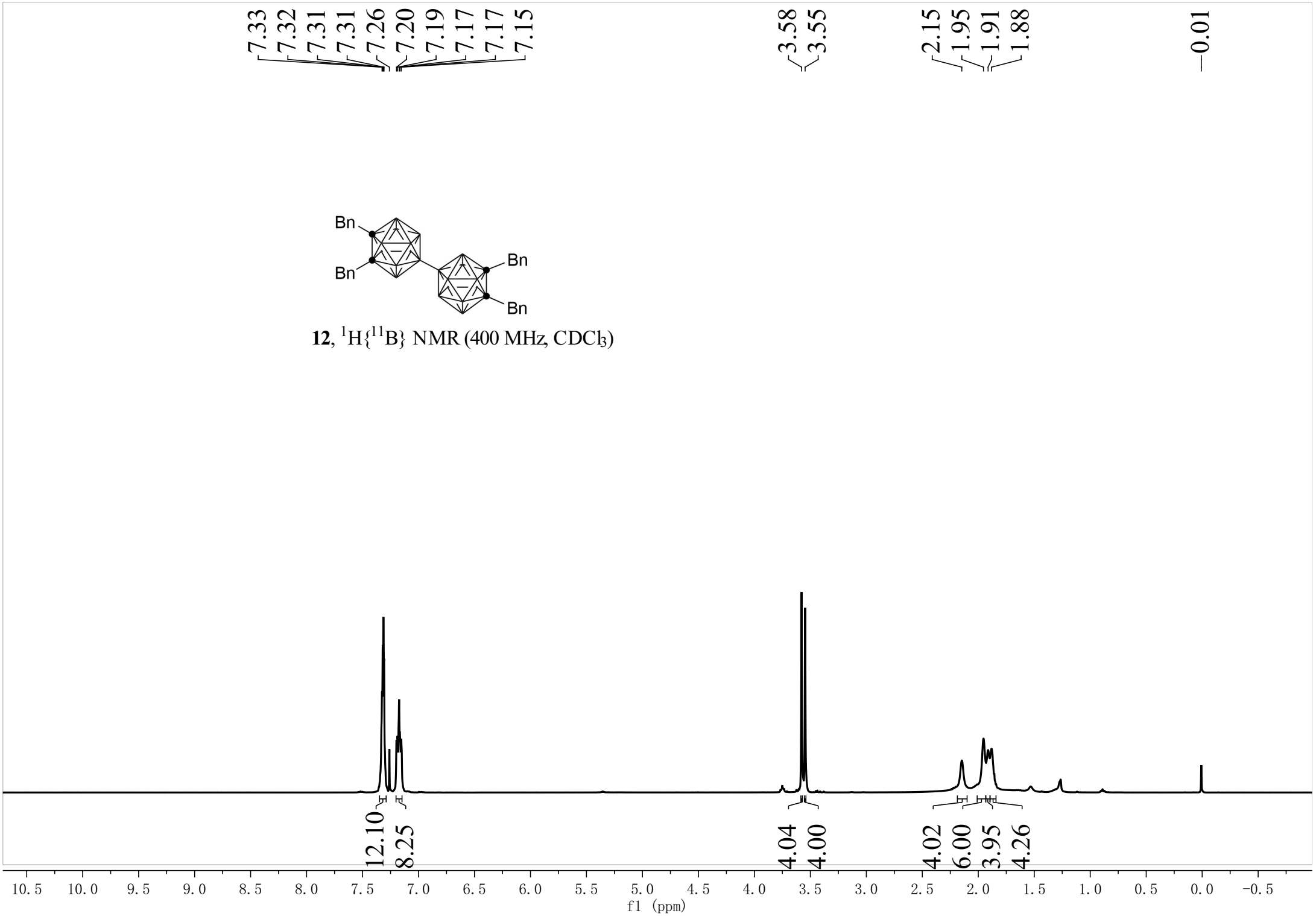




11, ^{13}C NMR (101 MHz, CD_3CN)

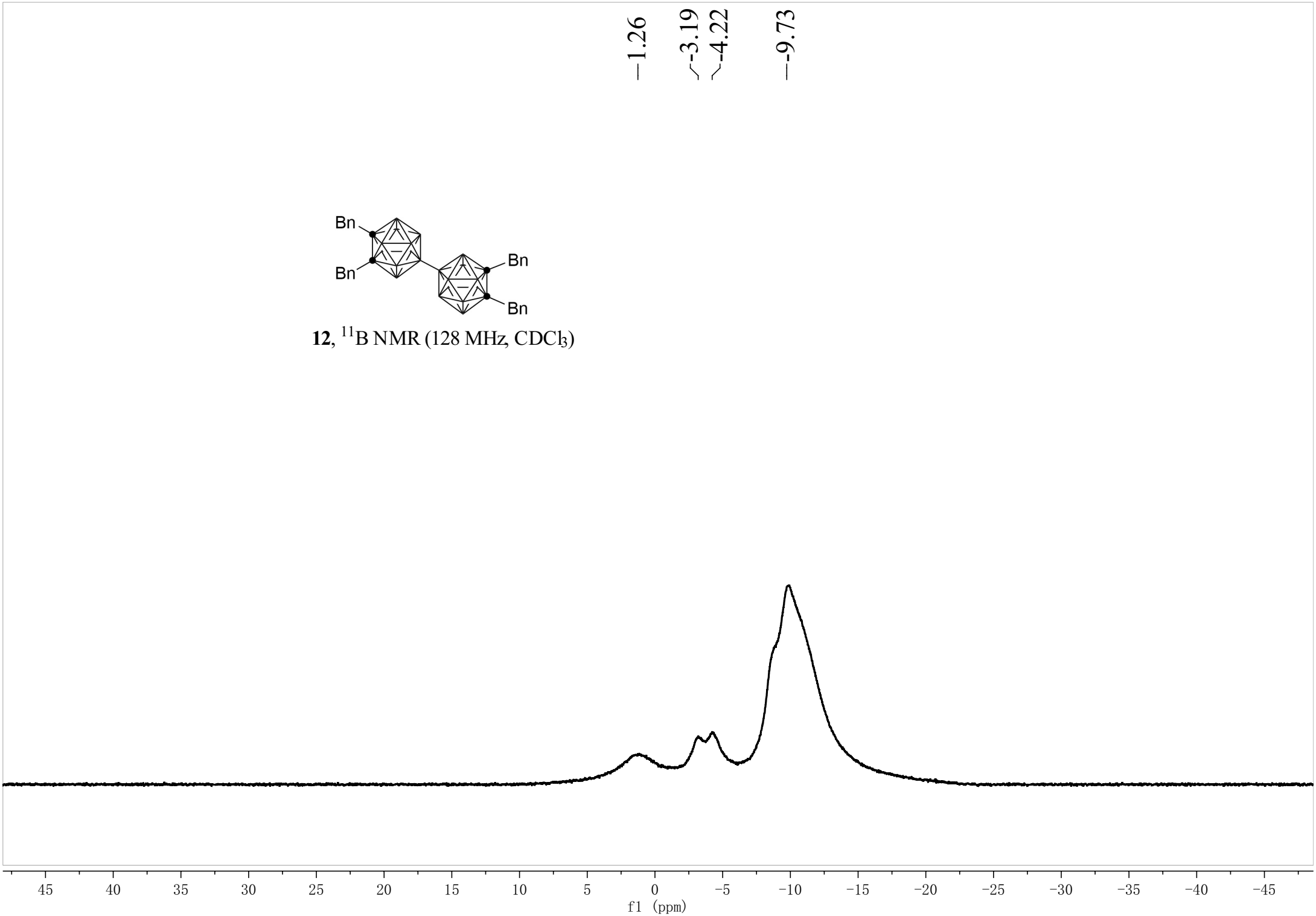


12, ^{1}H NMR (400 MHz, $CDCl_3$)

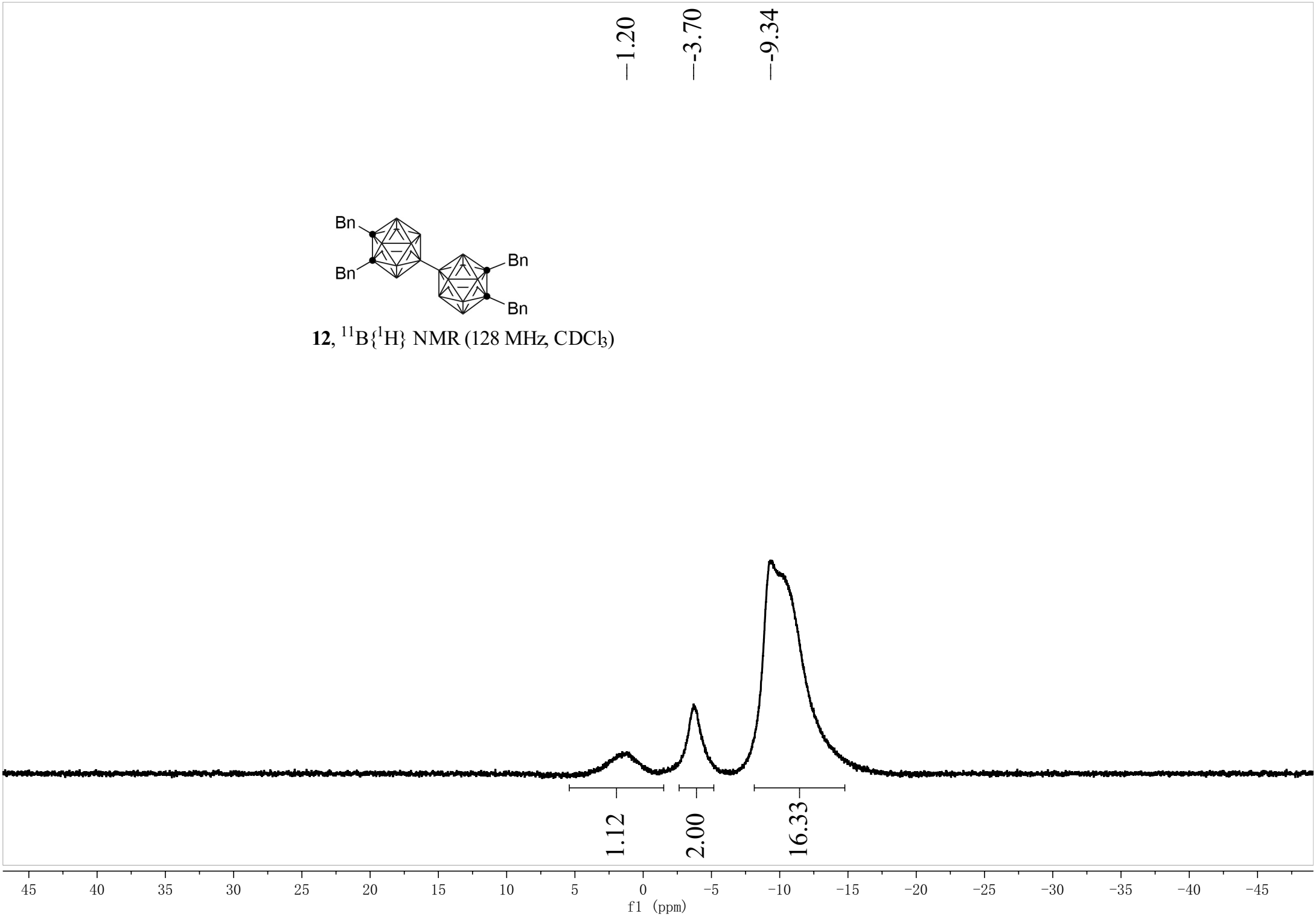


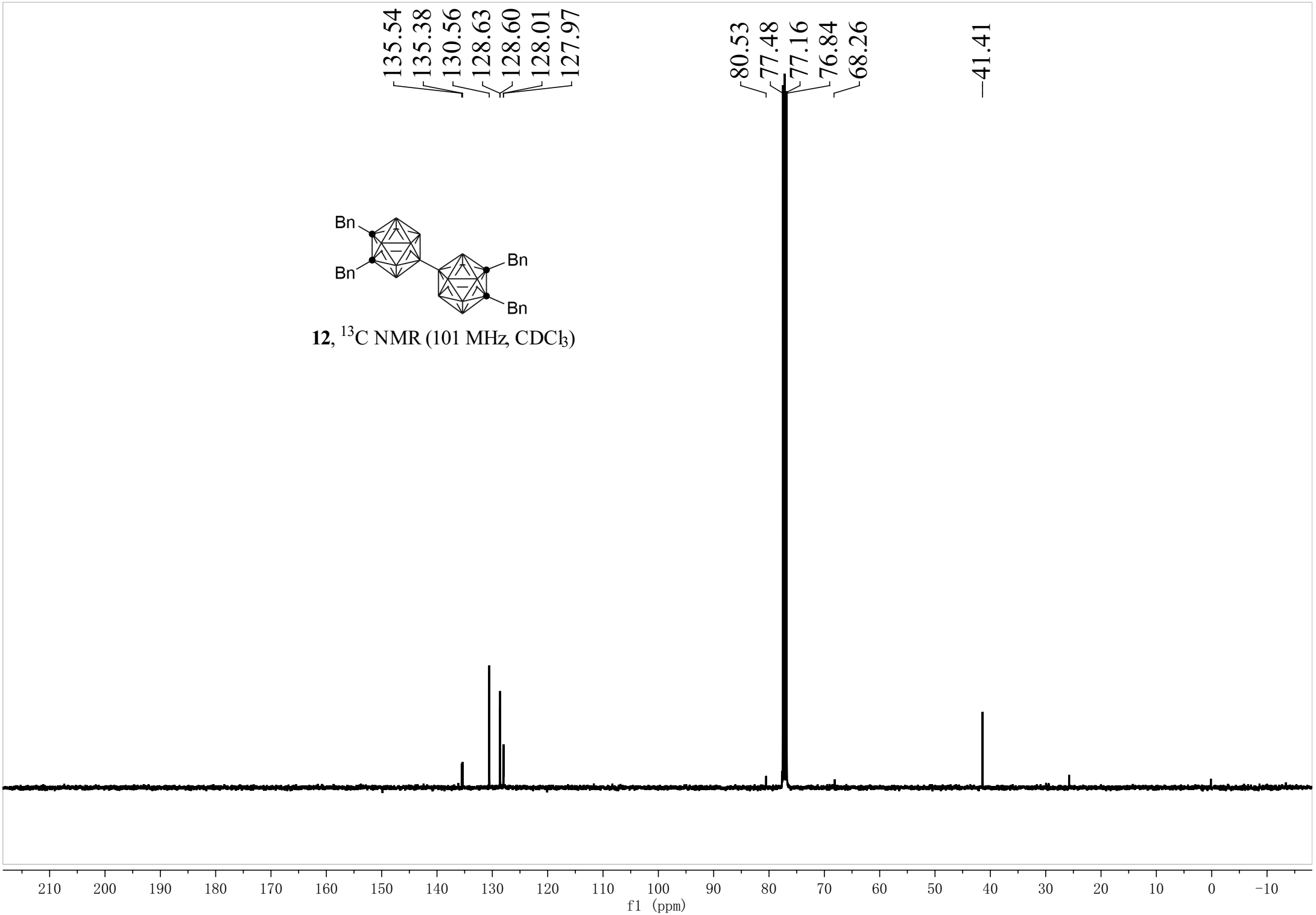
12, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

12, ^{11}B NMR (128 MHz, $CDCl_3$)

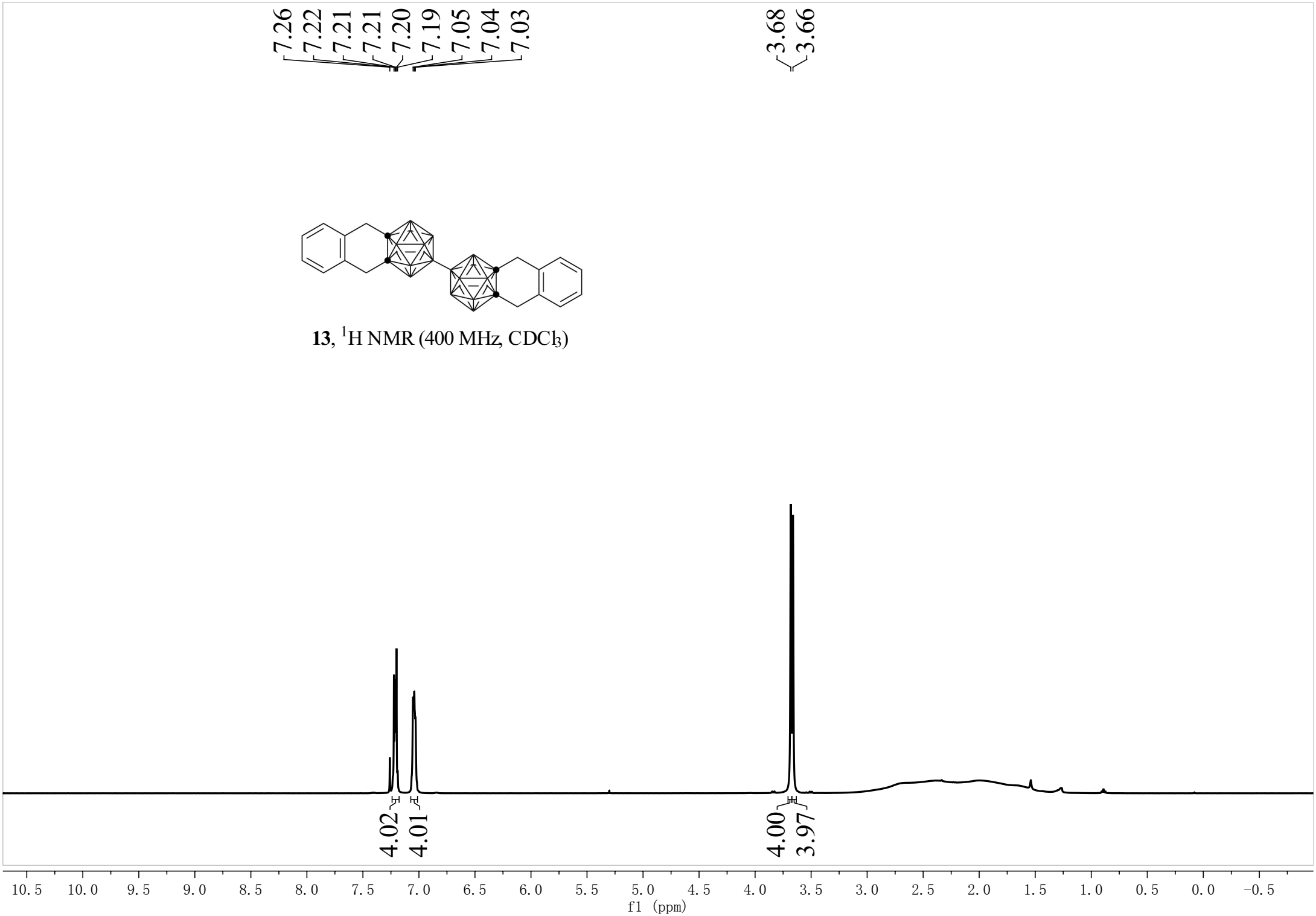


12, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

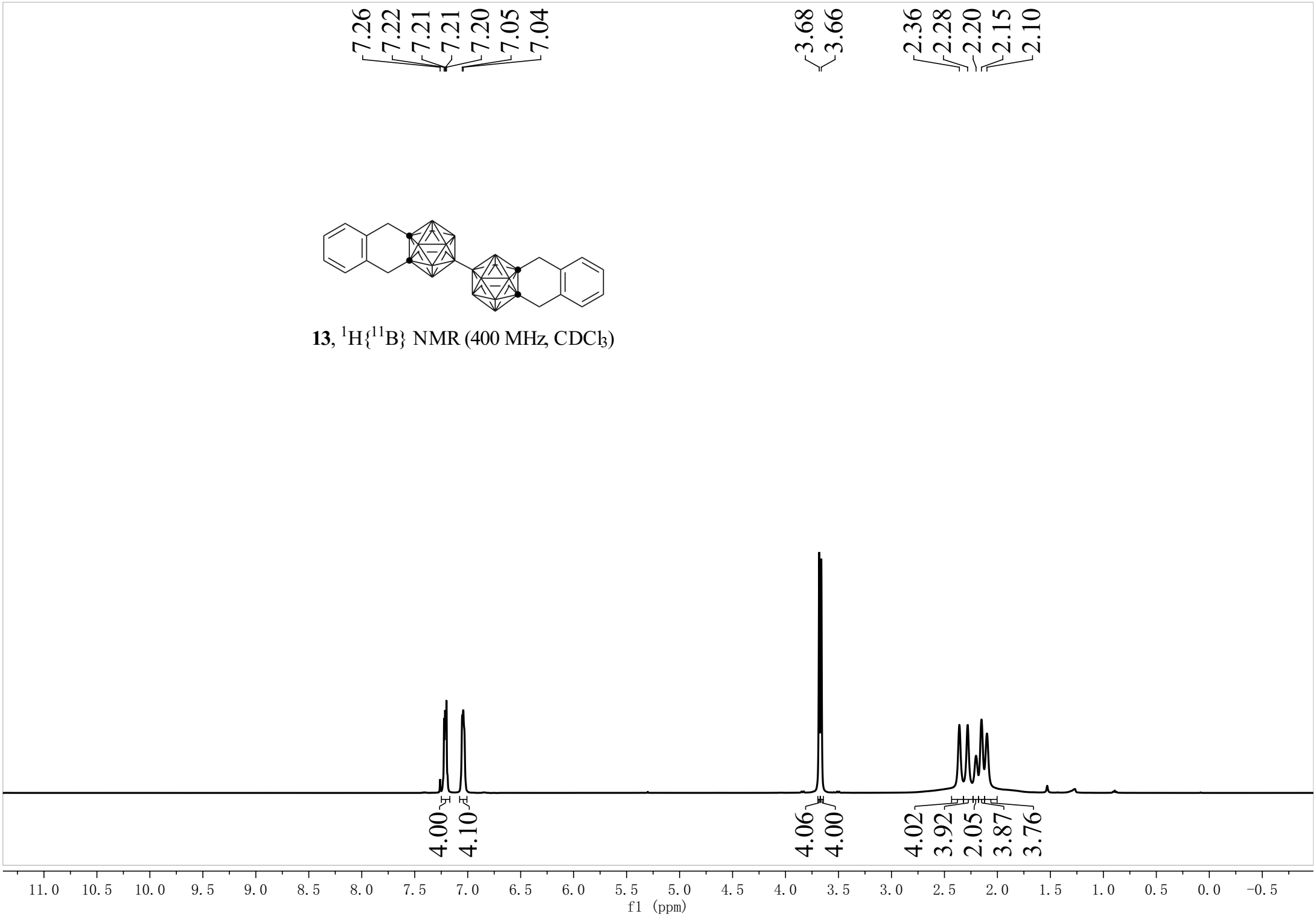




12, ^{13}C NMR (101 MHz, $CDCl_3$)

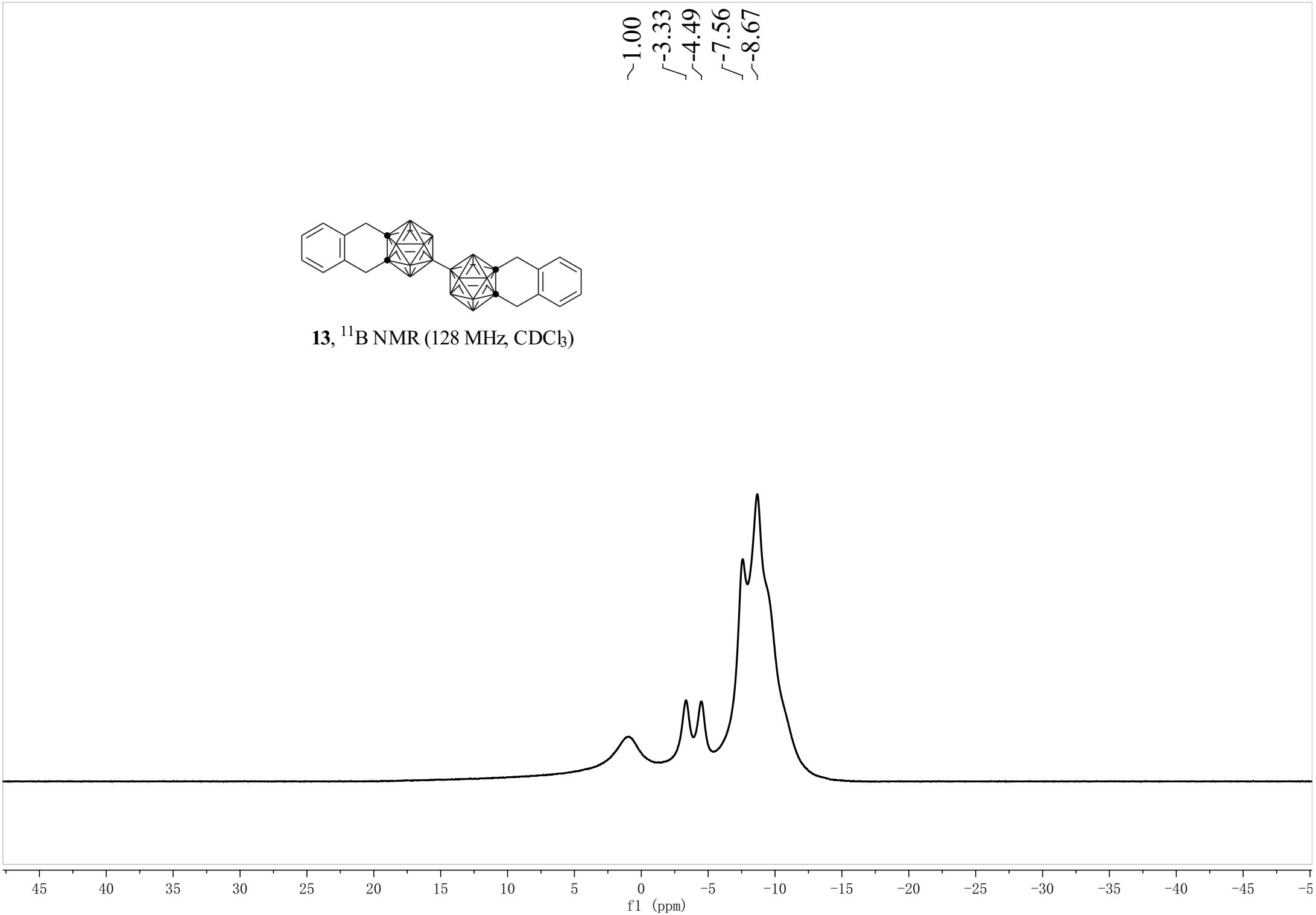


13, ^{1}H NMR (400 MHz, $CDCl_3$)

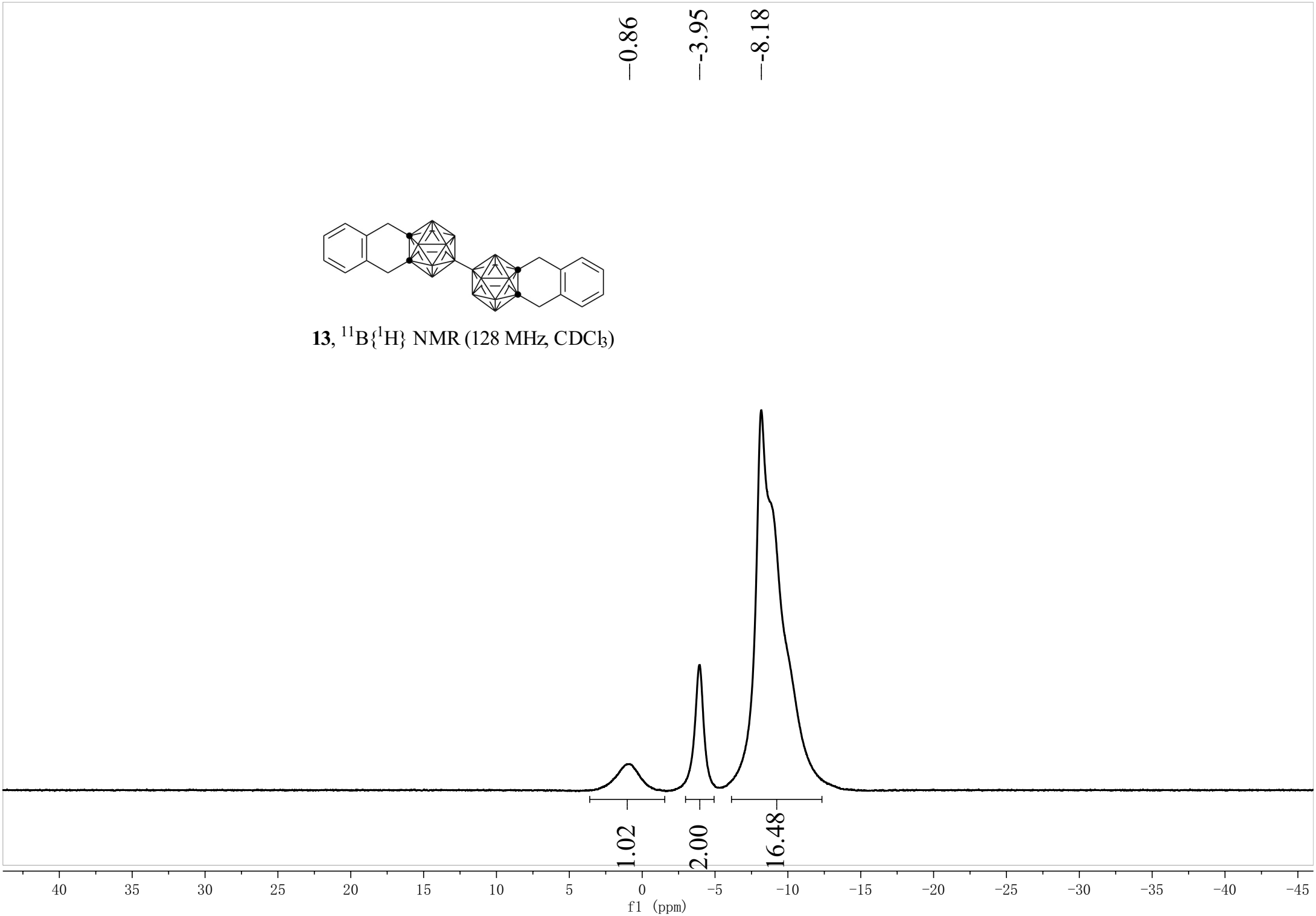


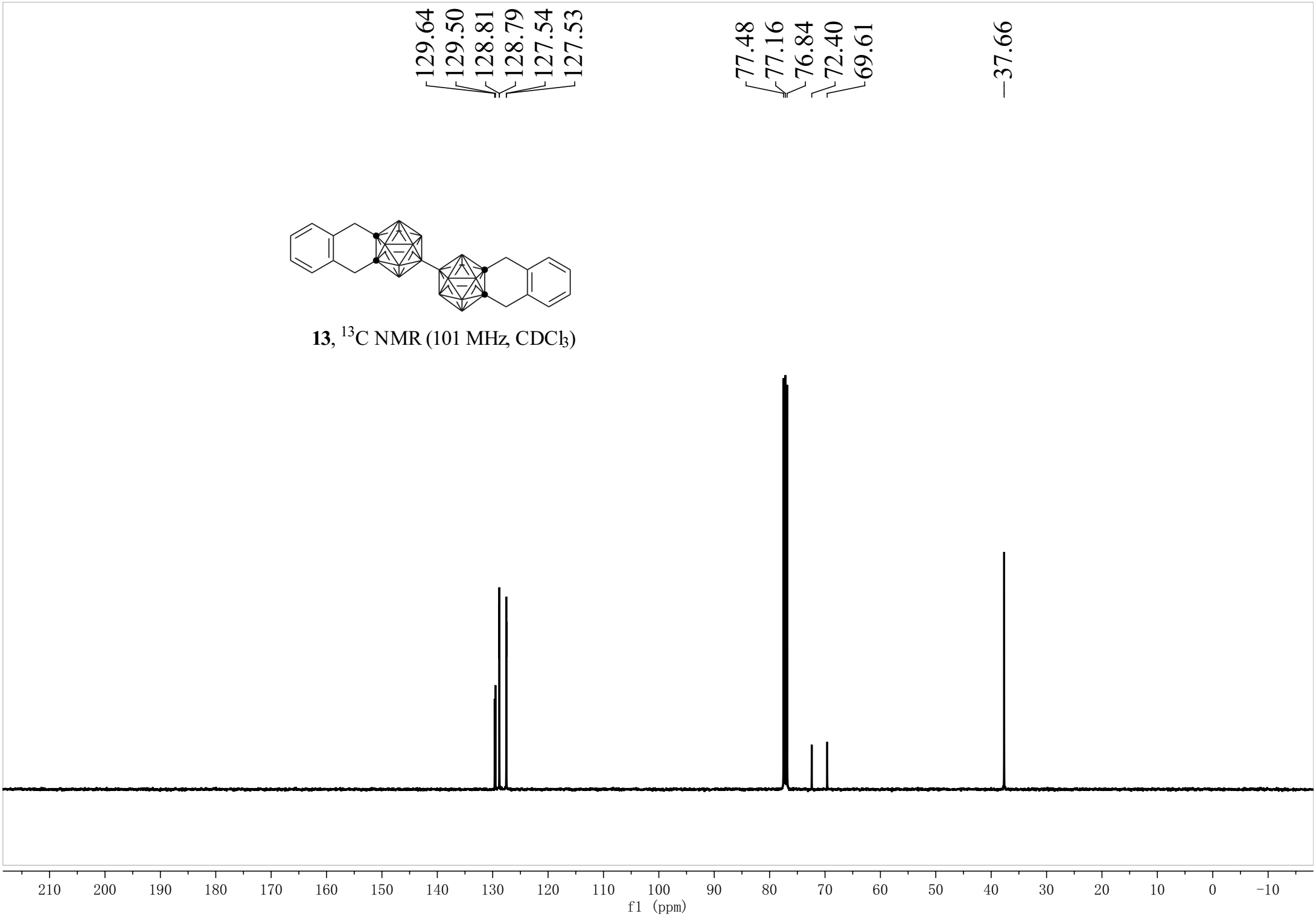
13, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

13, ^{11}B NMR (128 MHz, $CDCl_3$)

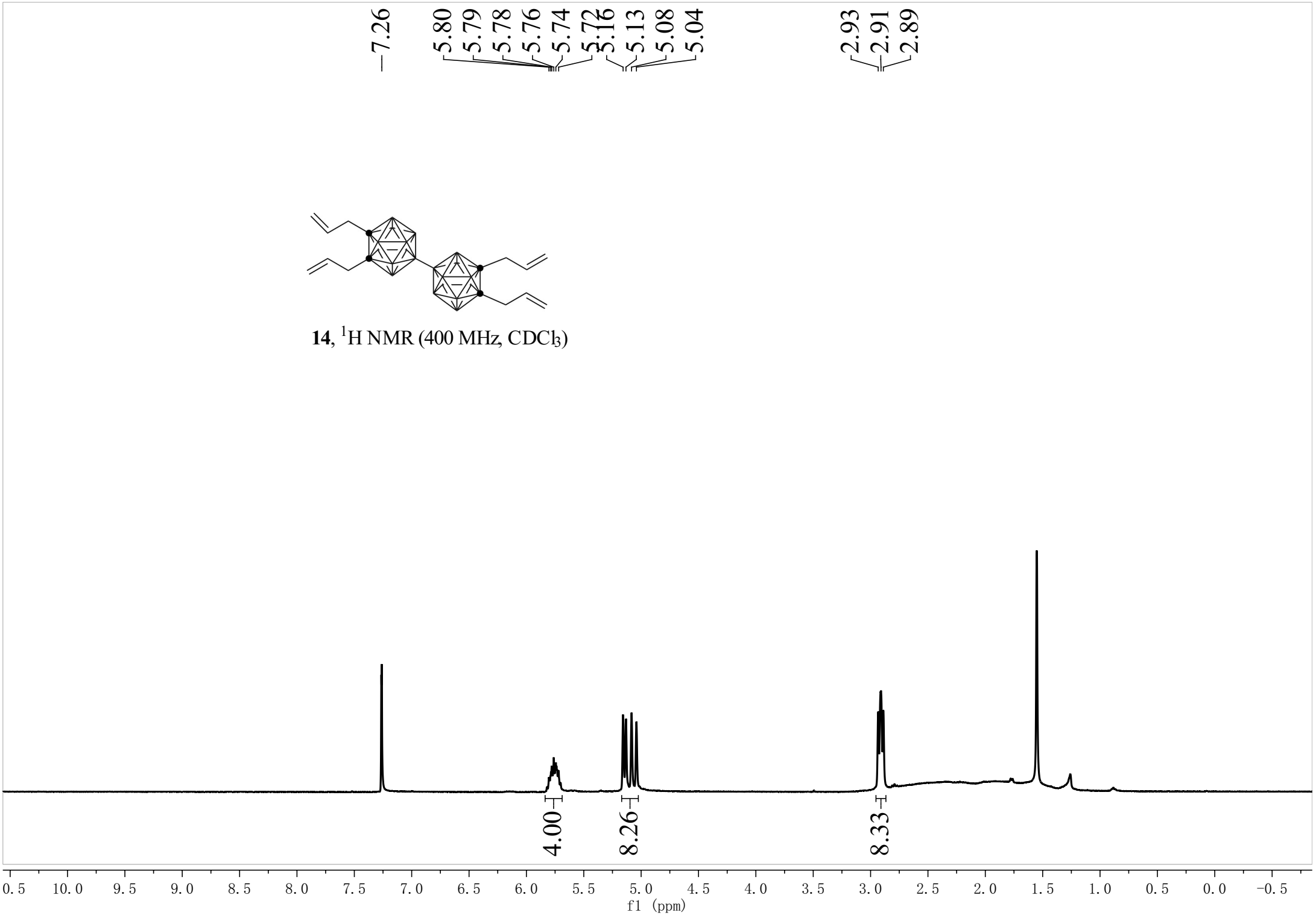


13, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



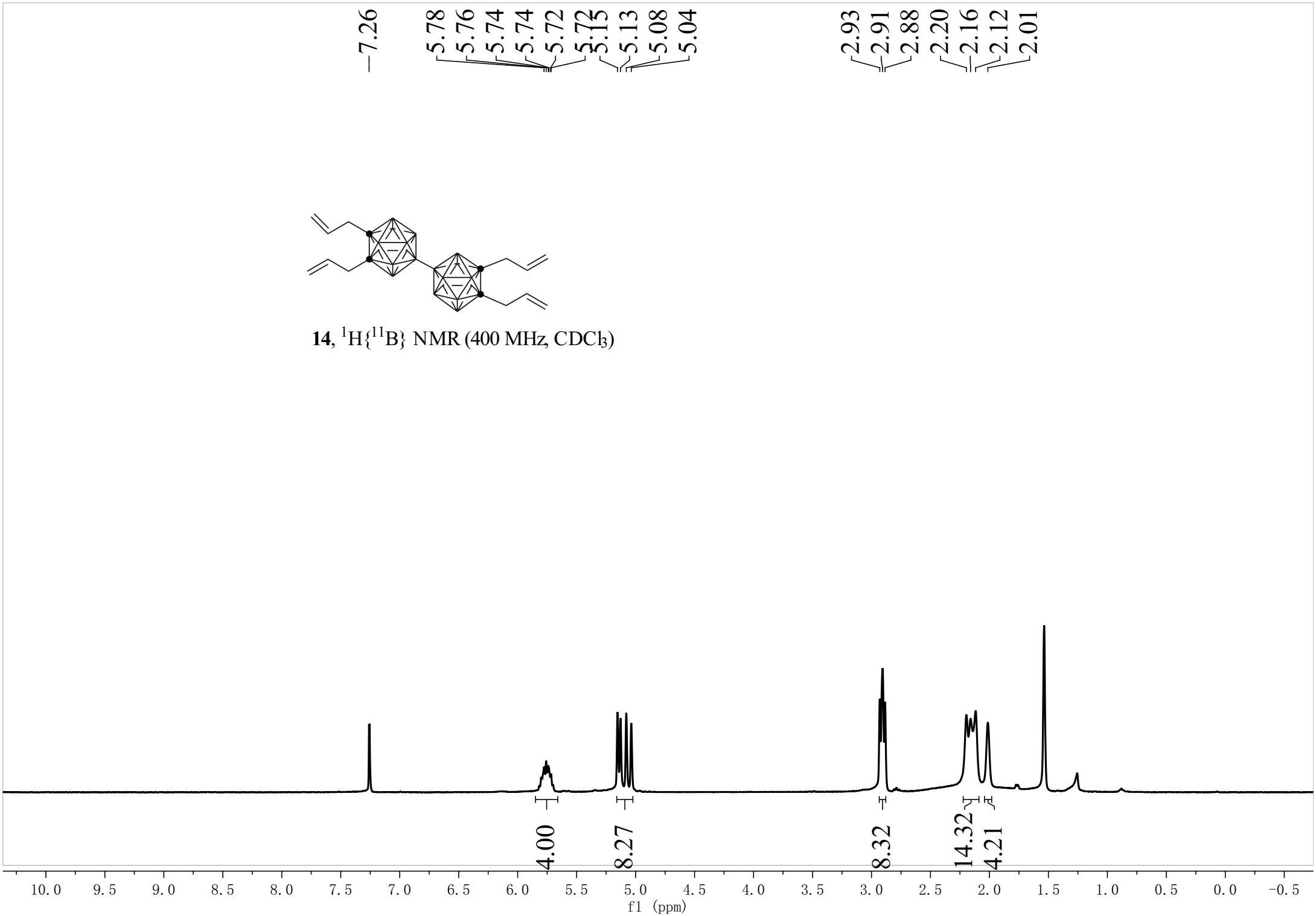


13, ^{13}C NMR (101 MHz, $CDCl_3$)

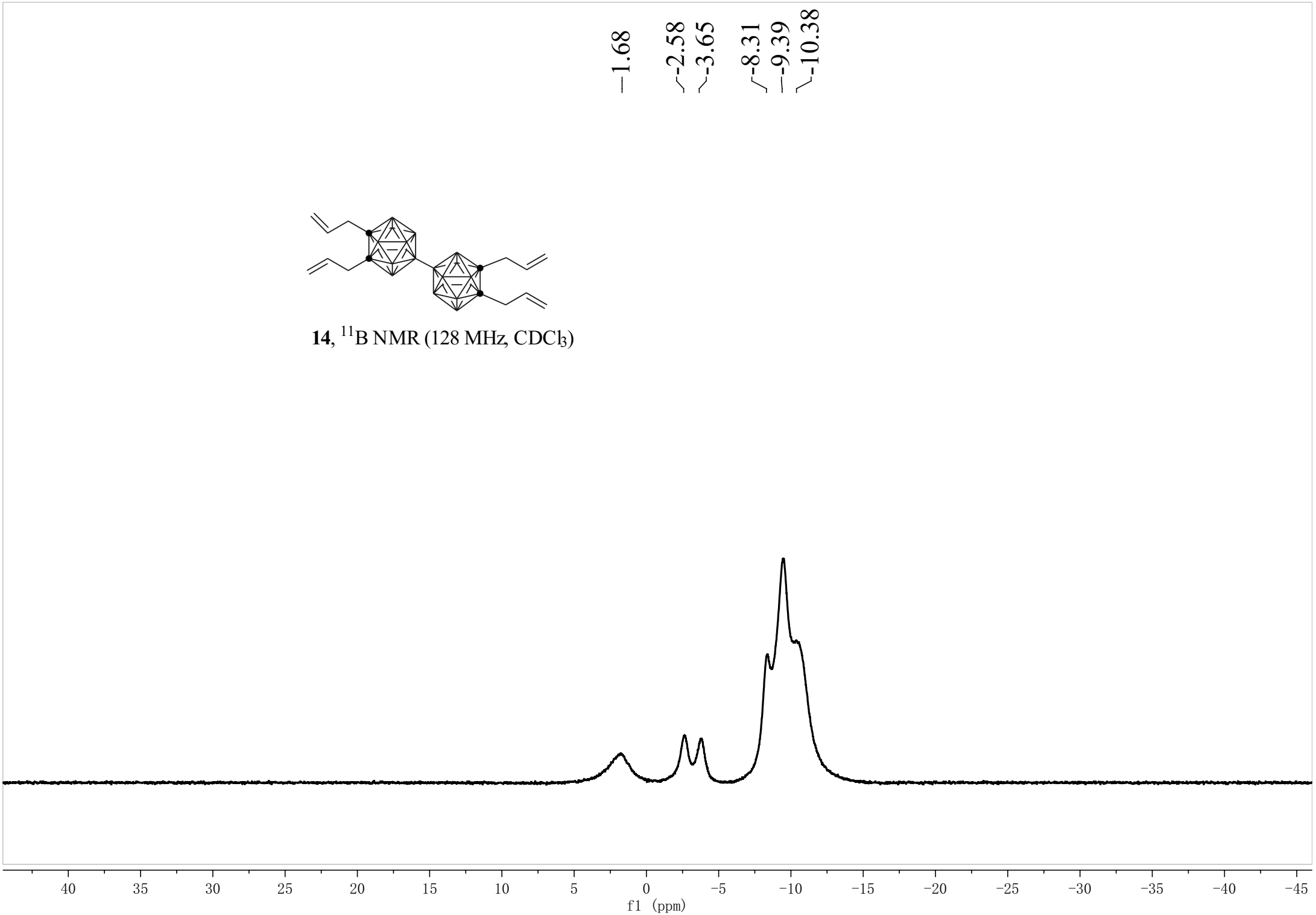


14, ^{1}H NMR (400 MHz, $CDCl_3$)

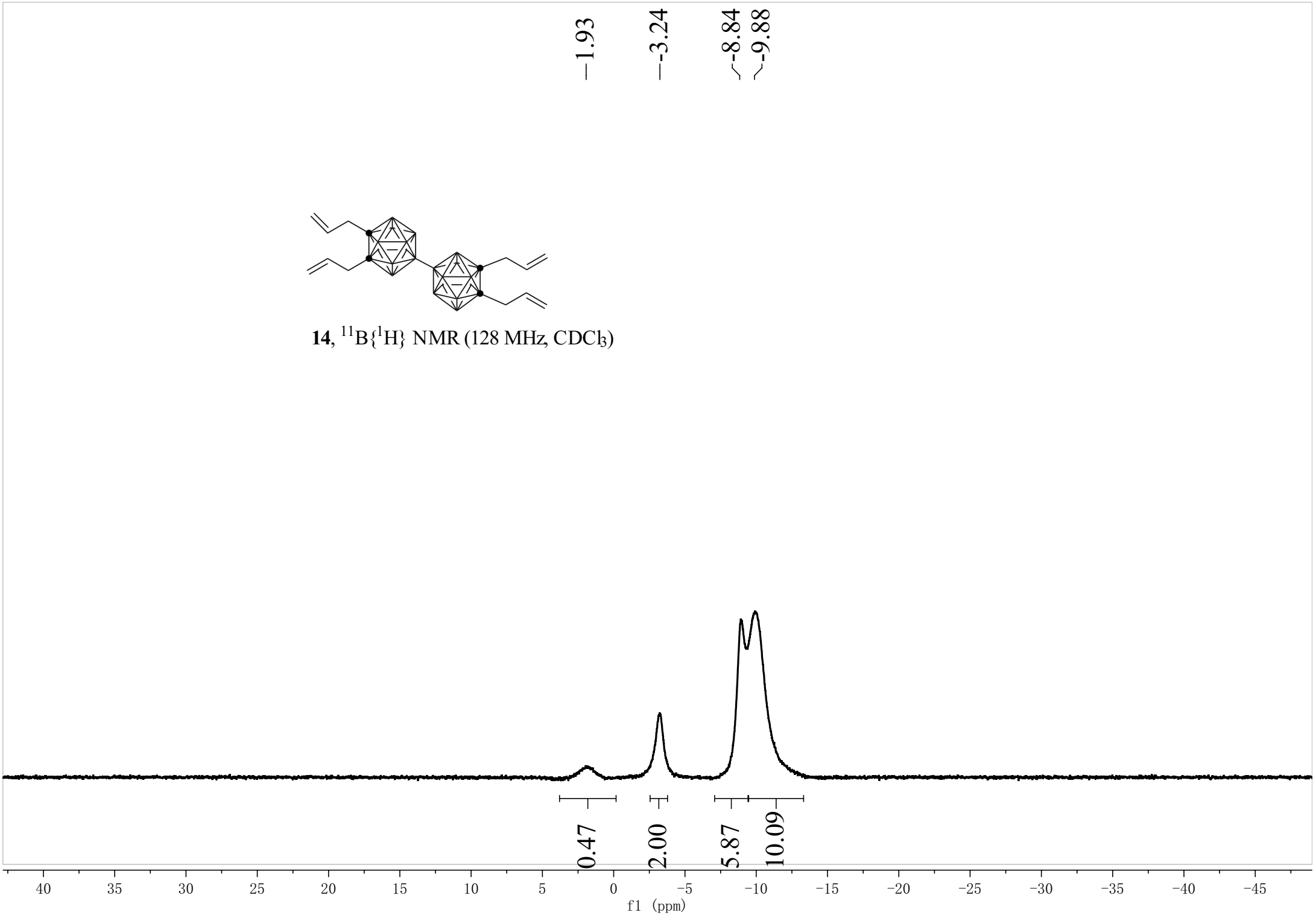
14, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)



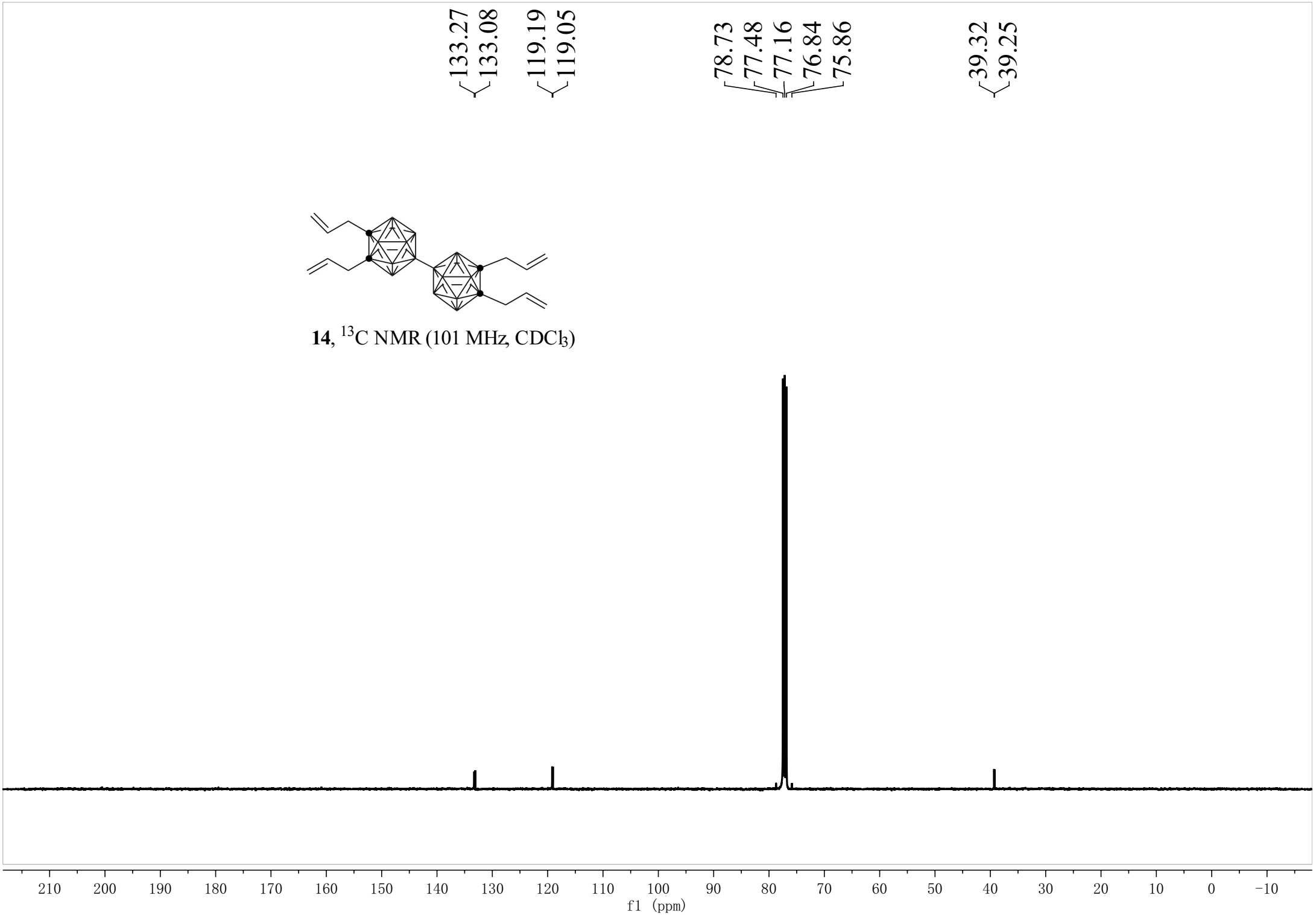
14, ^{11}B NMR (128 MHz, $CDCl_3$)

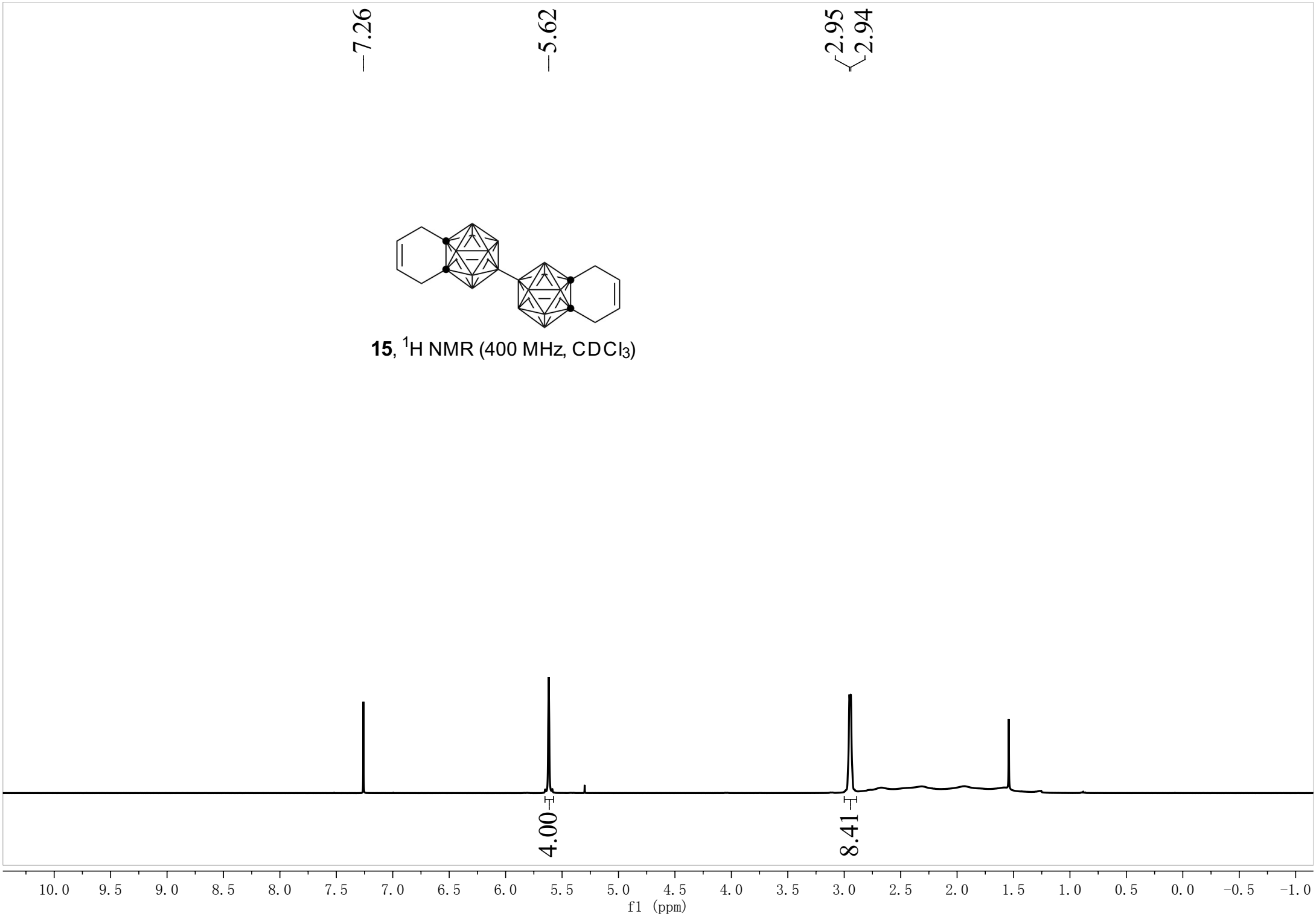


14, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

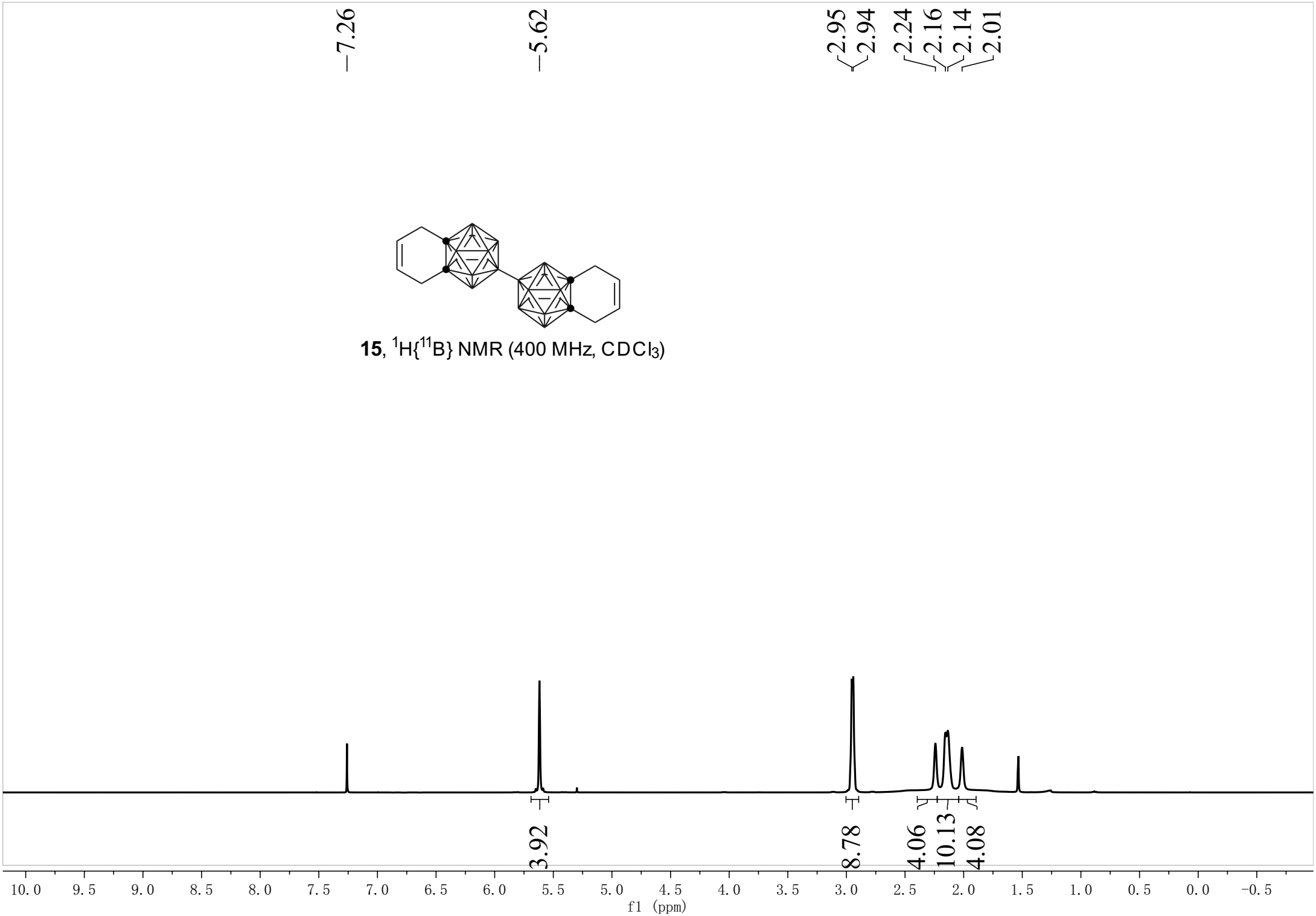


14, ^{13}C NMR (101 MHz, $CDCl_3$)



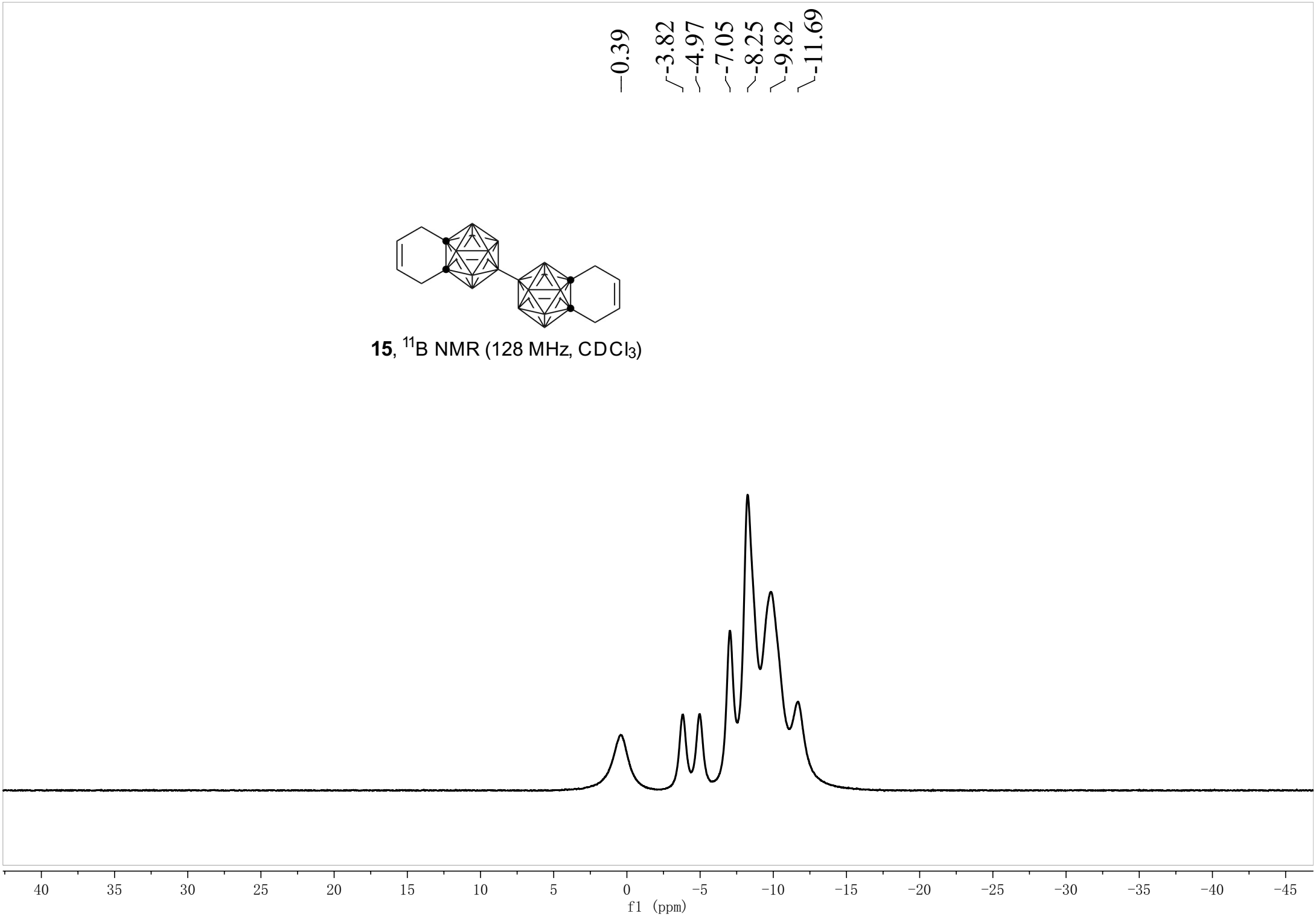


15, ^{1}H NMR (400 MHz, $CDCl_3$)

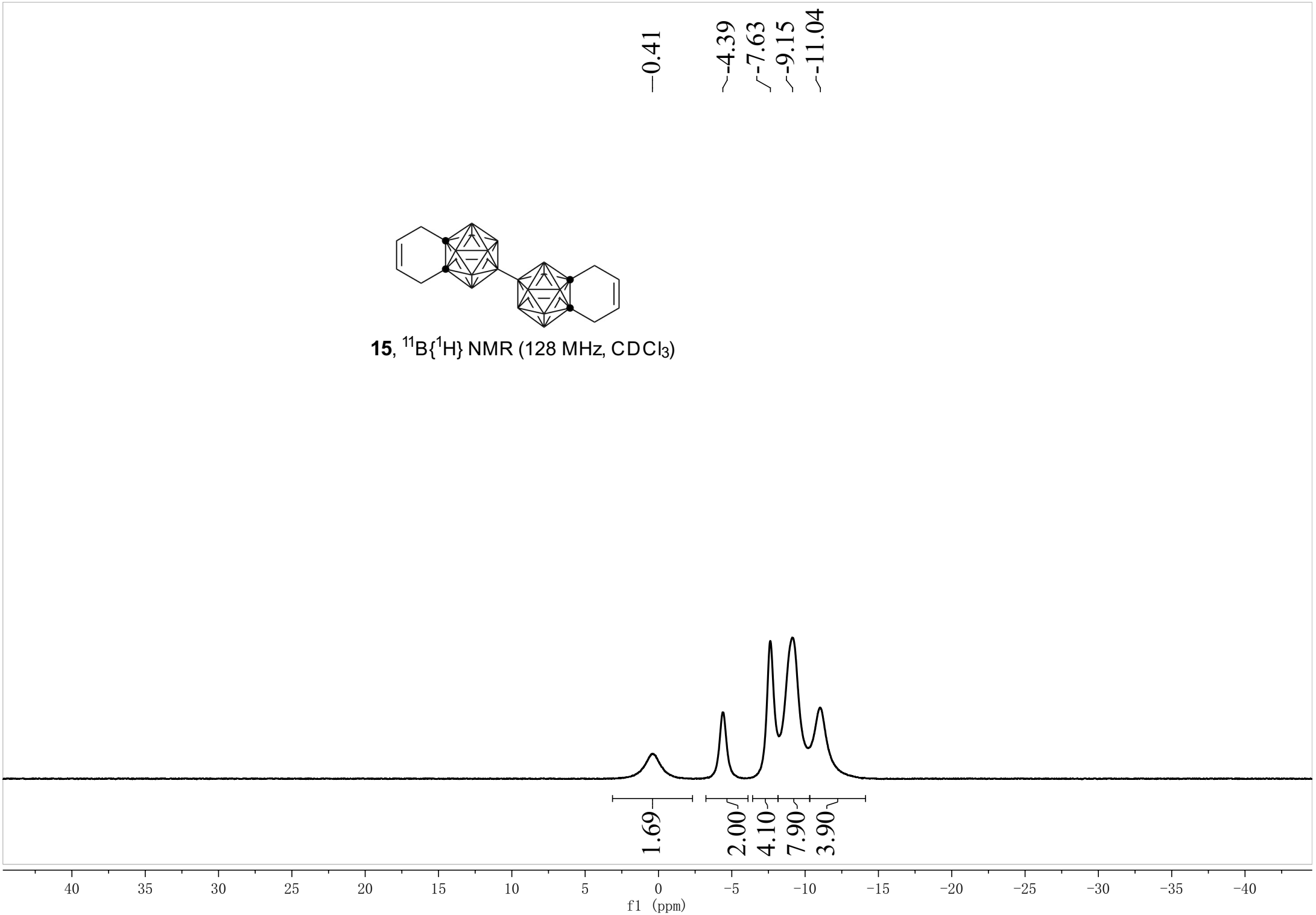


15, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

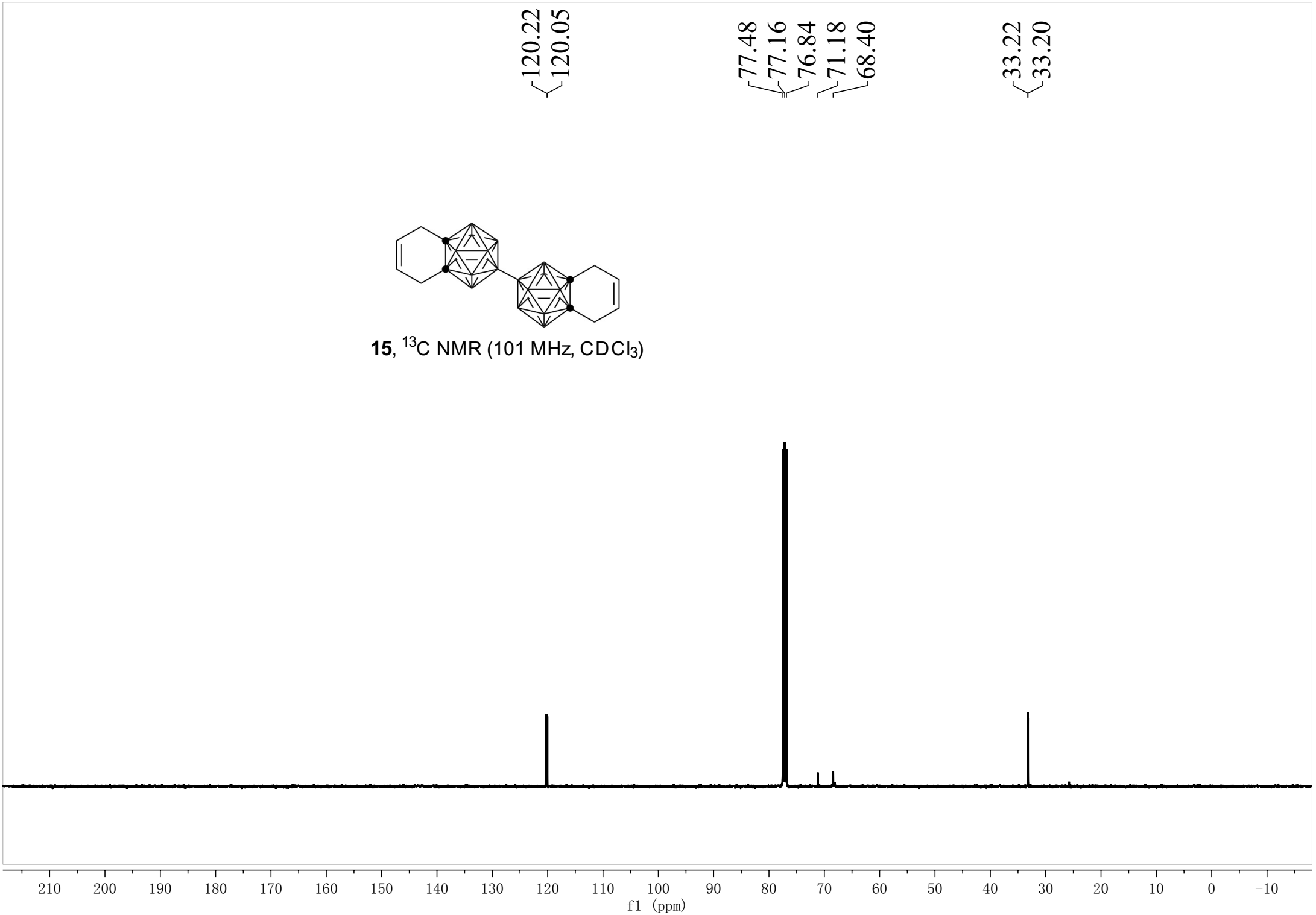
15, ^{11}B NMR (128 MHz, $CDCl_3$)

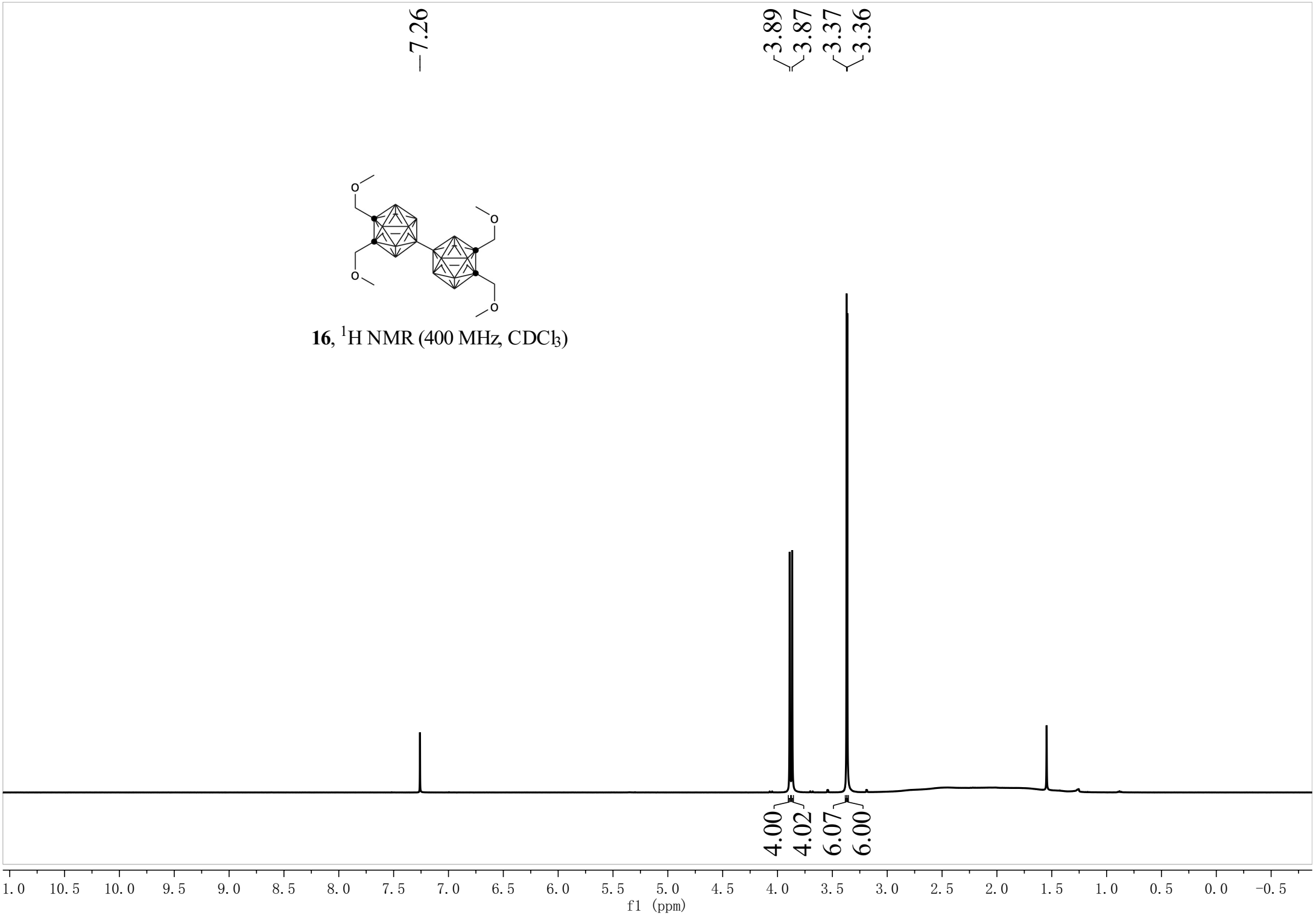


15, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

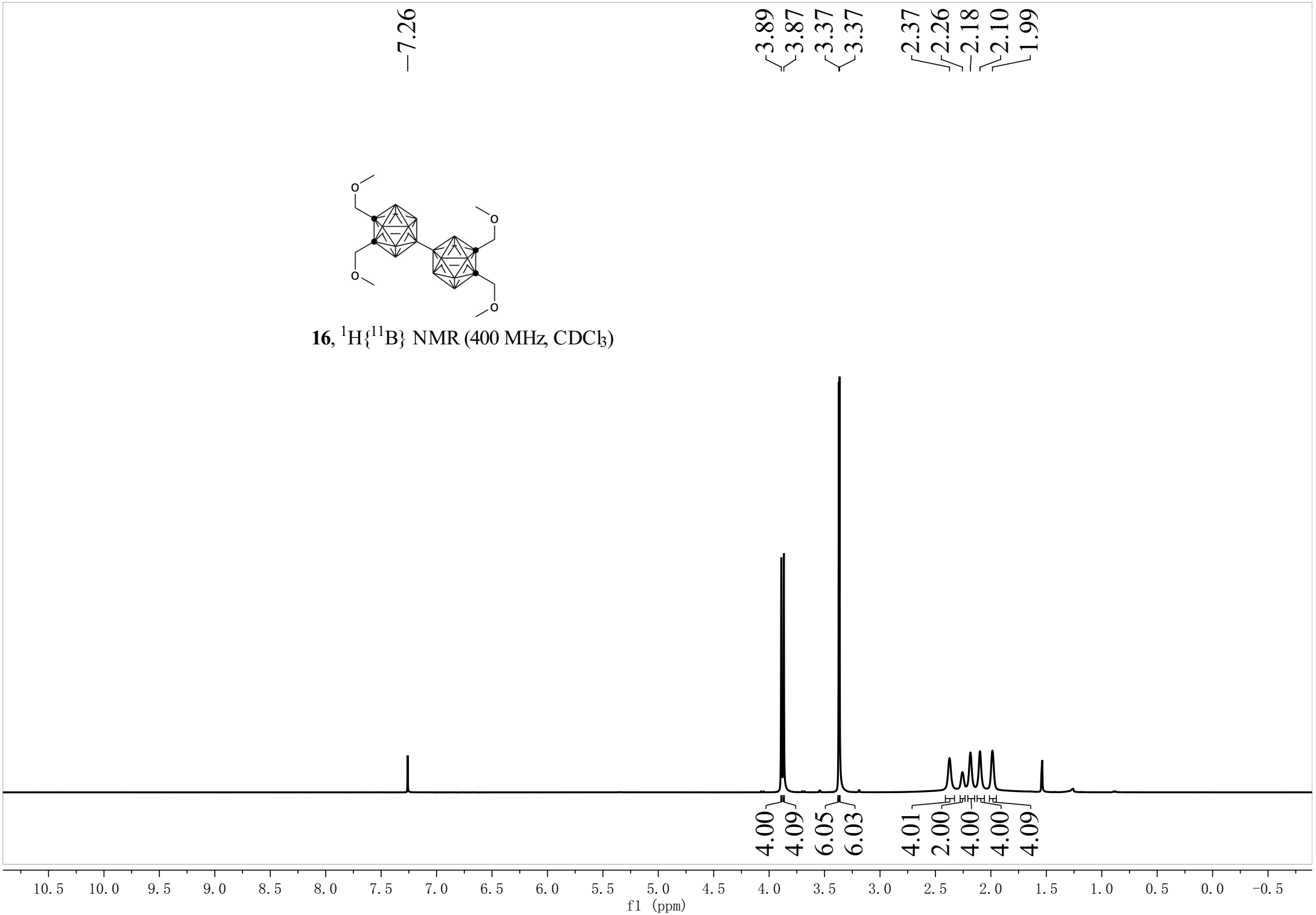


15, ^{13}C NMR (101 MHz, $CDCl_3$)



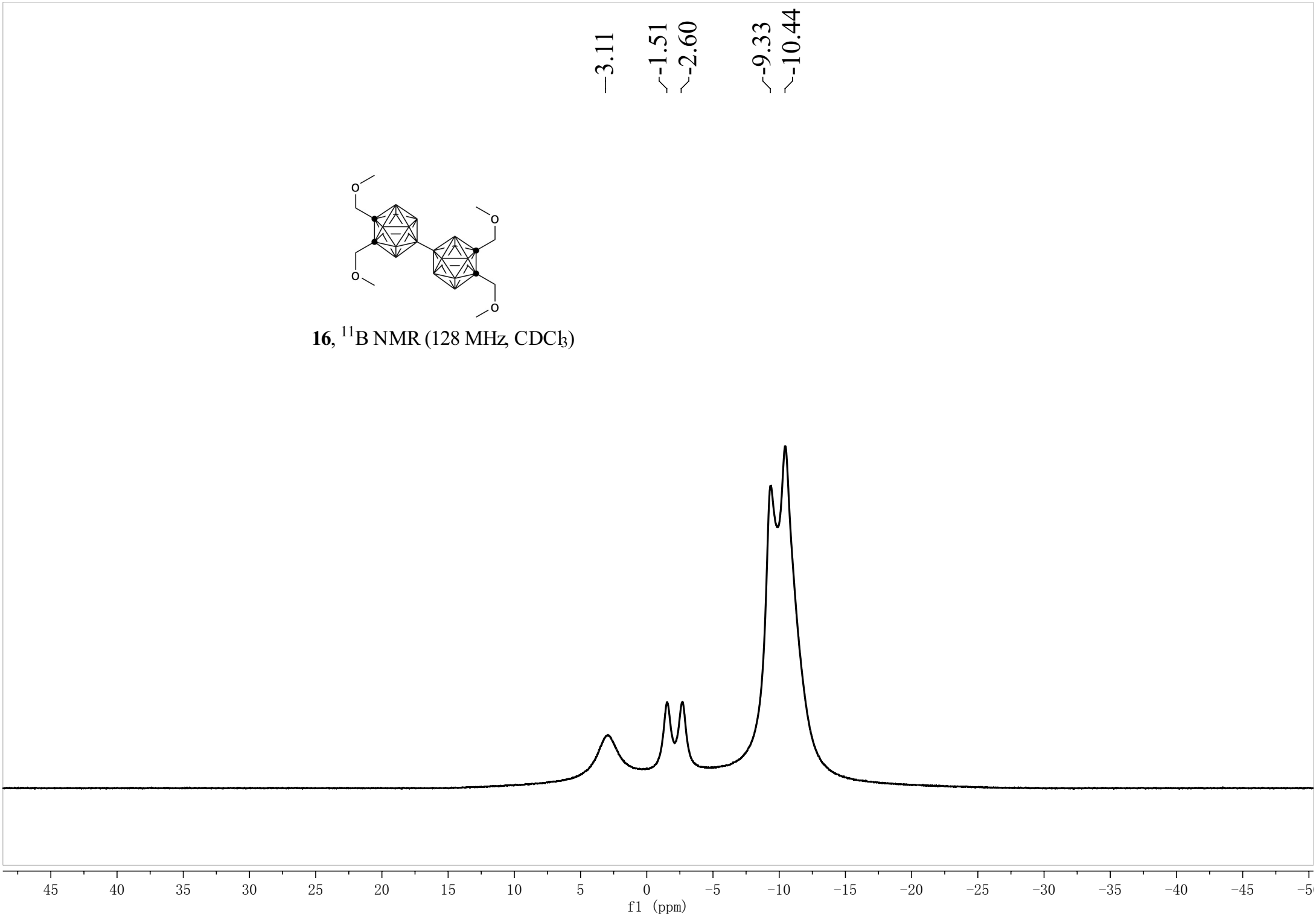


16, ^{1}H NMR (400 MHz, $CDCl_3$)

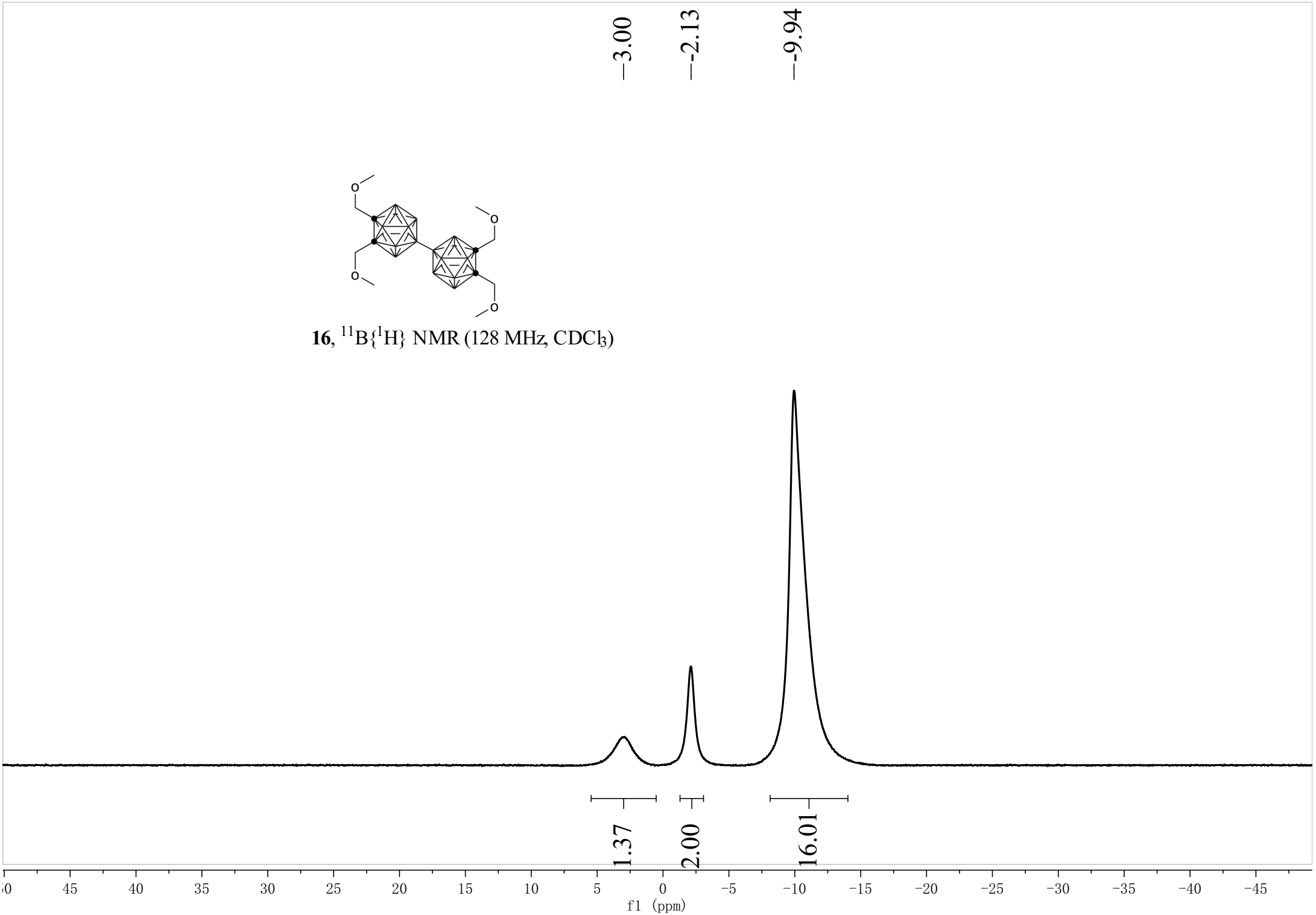


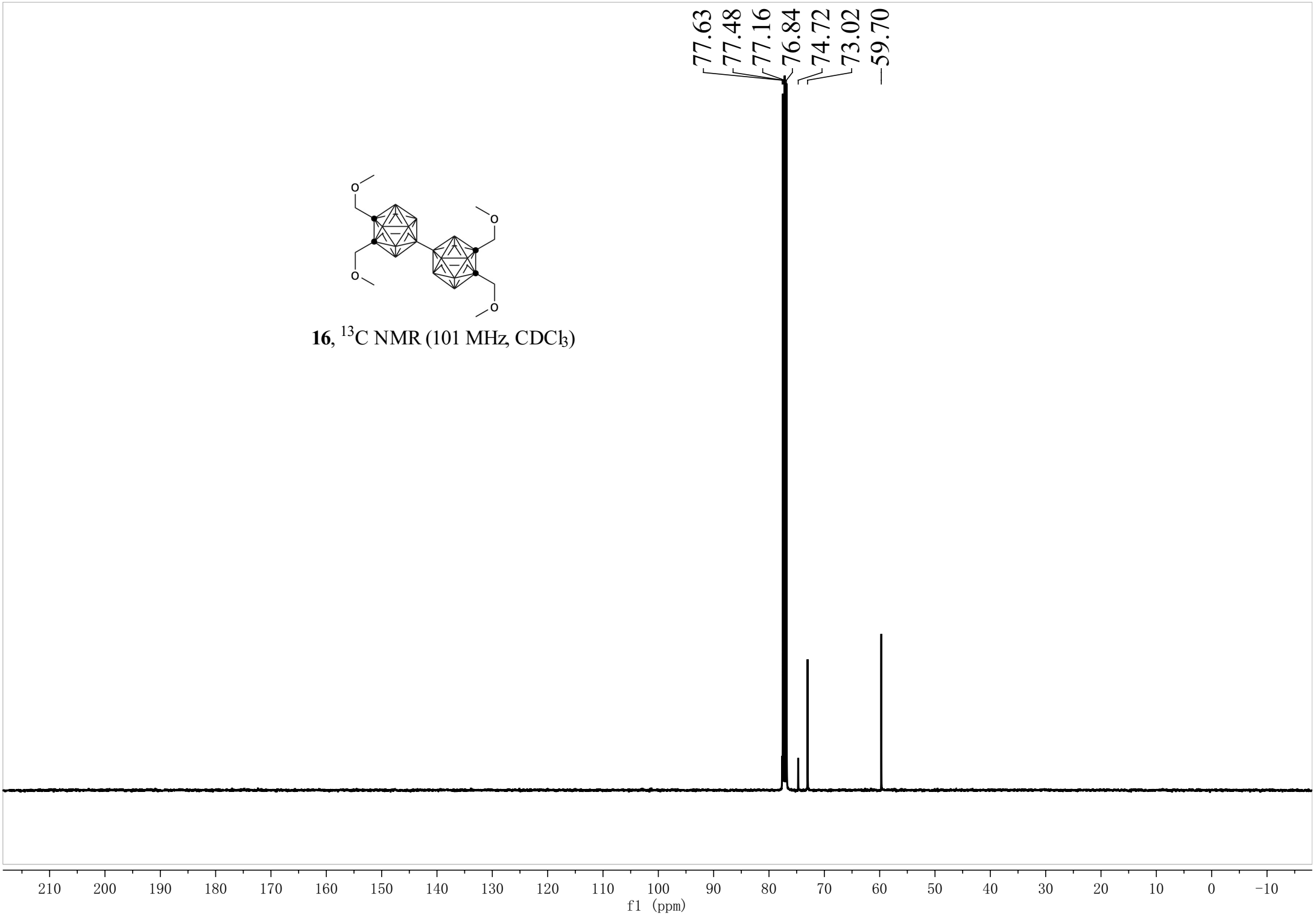
16, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

16, ^{11}B NMR (128 MHz, $CDCl_3$)

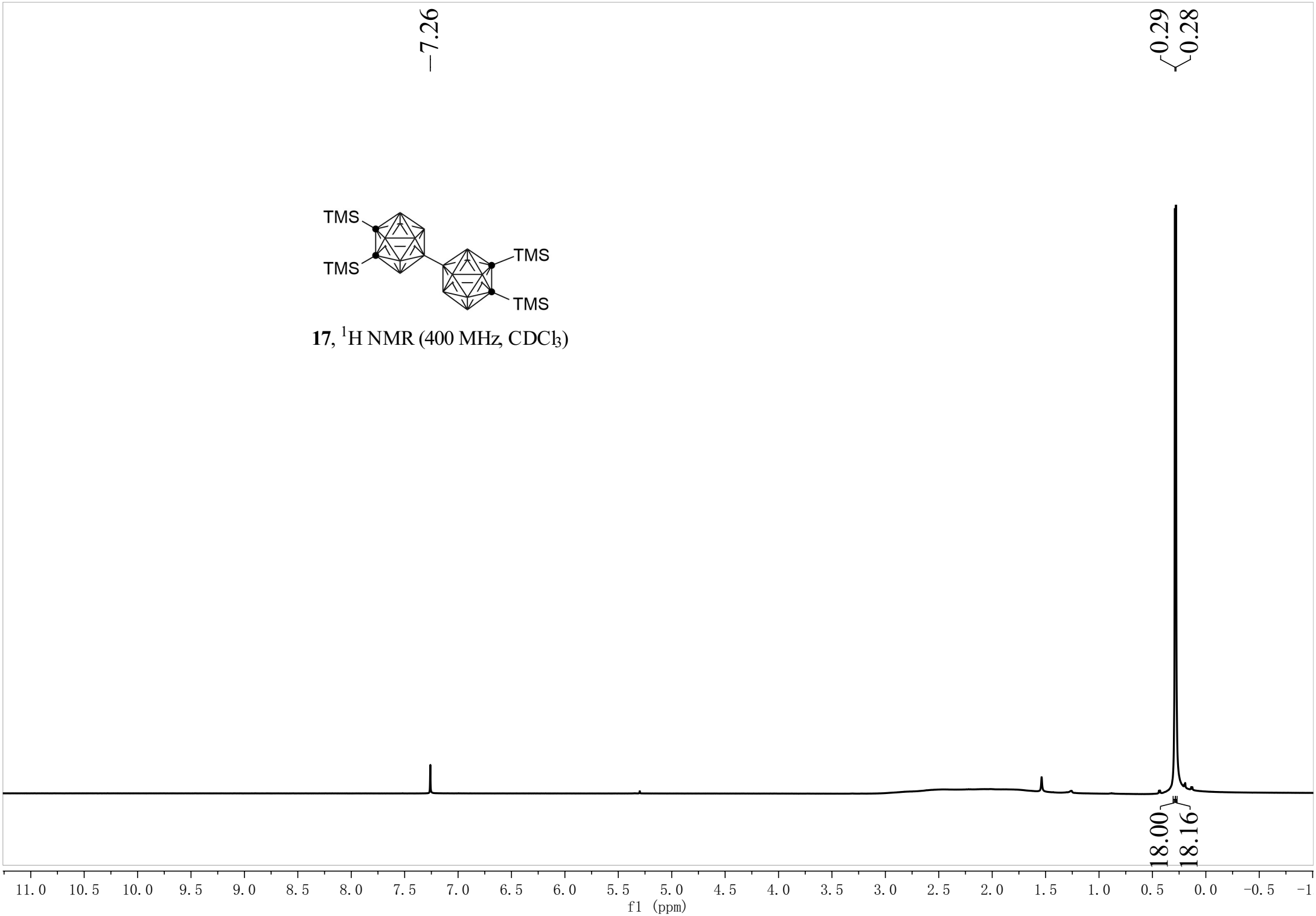


16, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



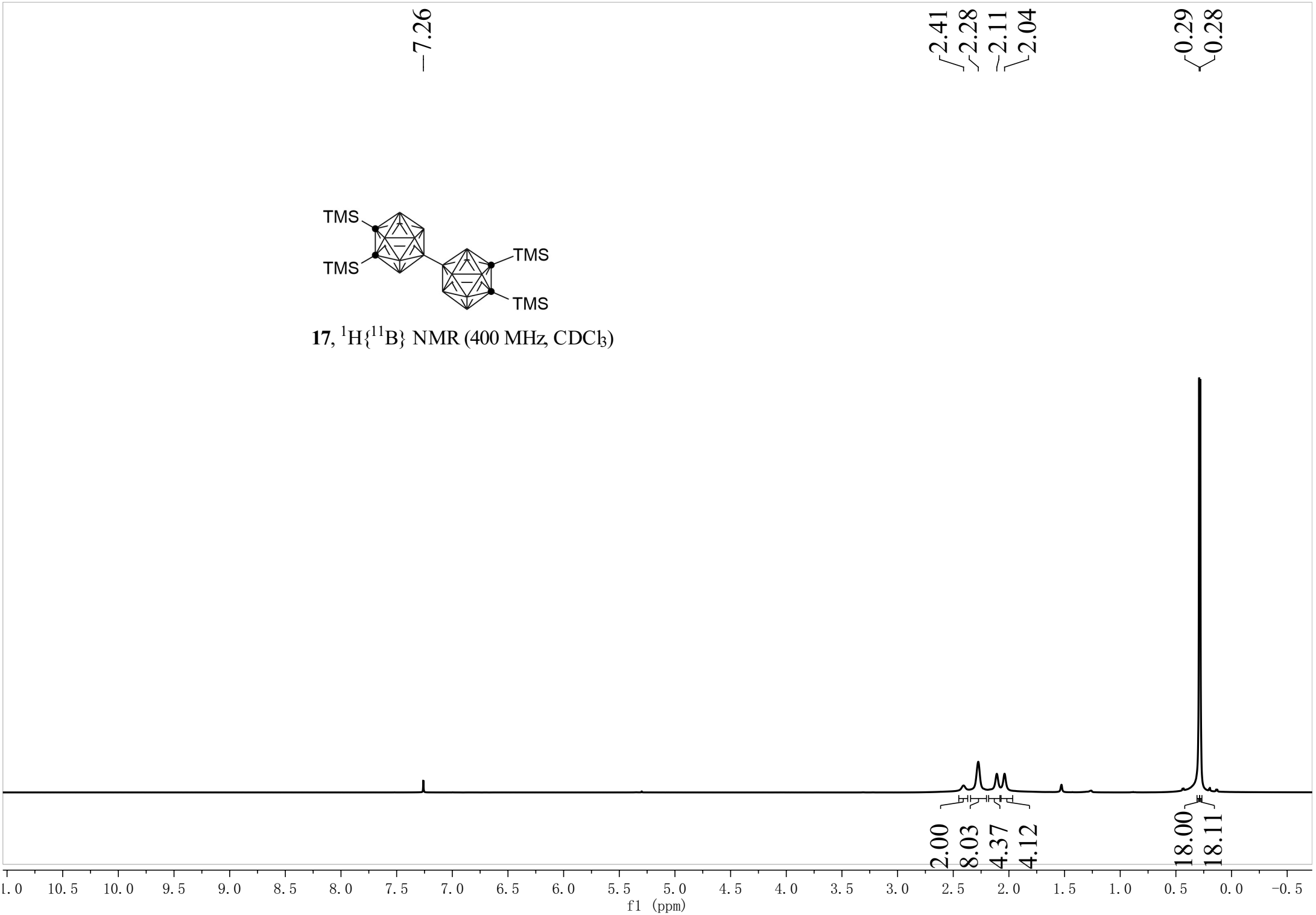


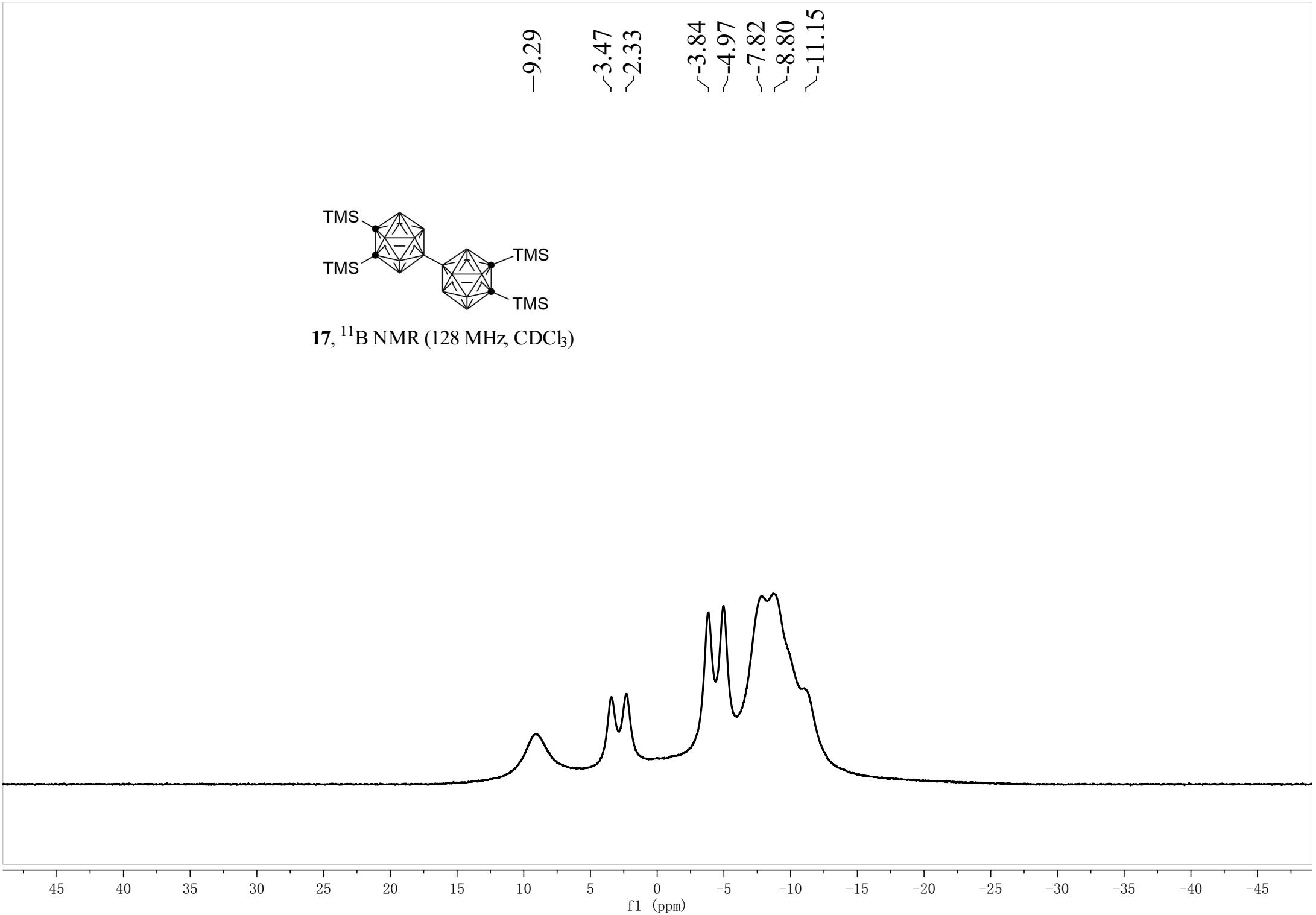
16, ^{13}C NMR (101 MHz, $CDCl_3$)



17, ^{1}H NMR (400 MHz, $CDCl_3$)

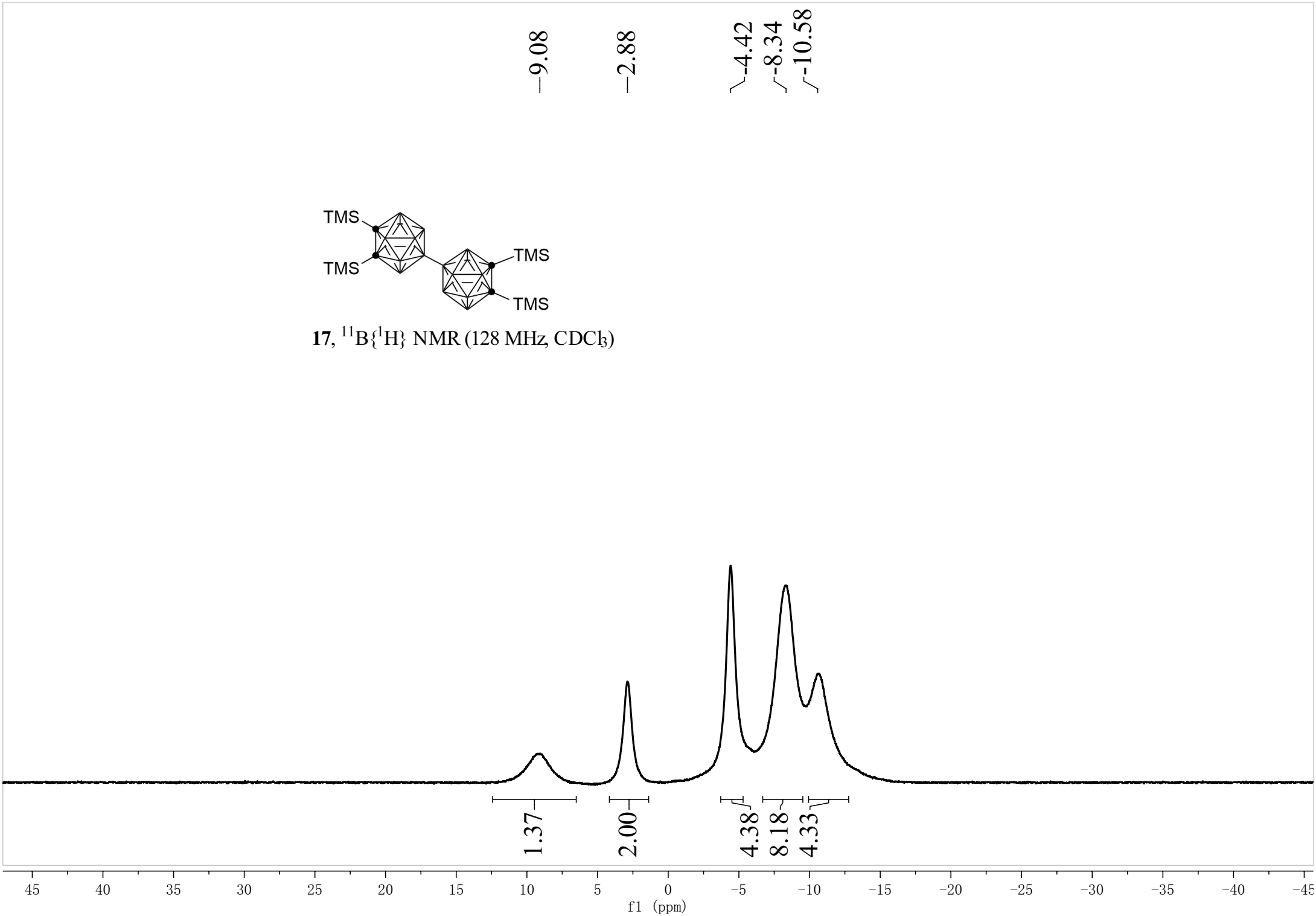
17, $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)

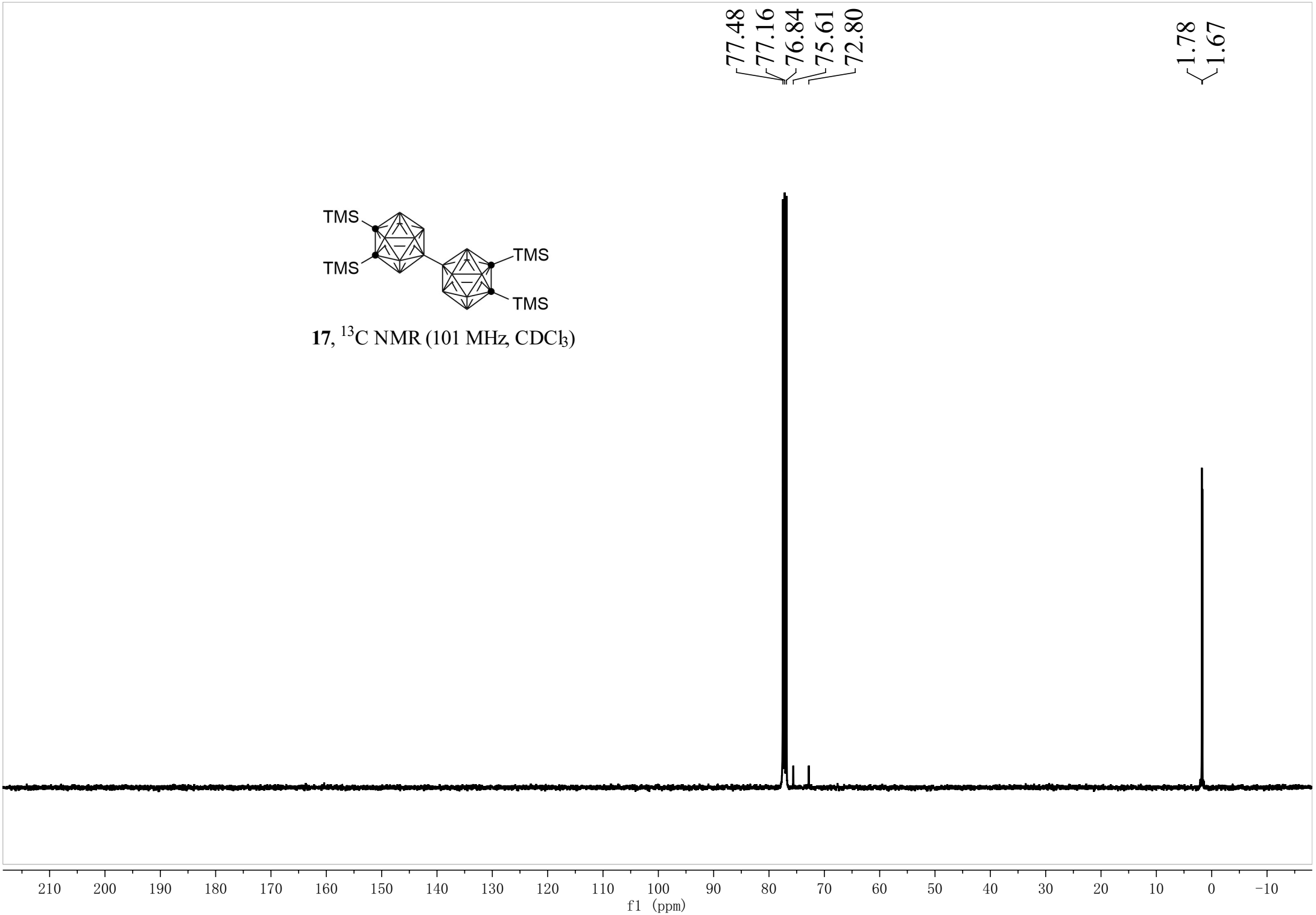




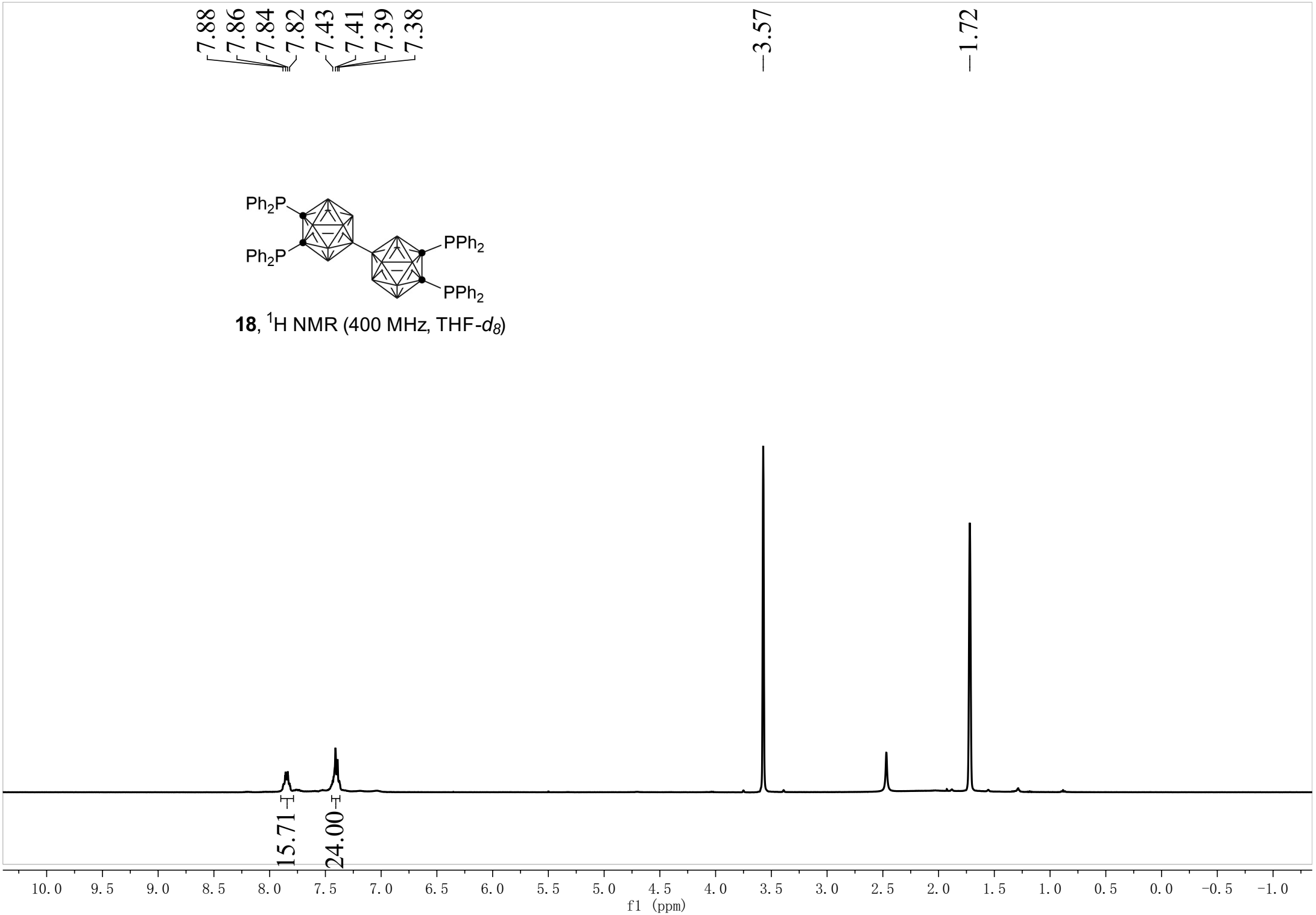
17, ^{11}B NMR (128 MHz, $CDCl_3$)

17, $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

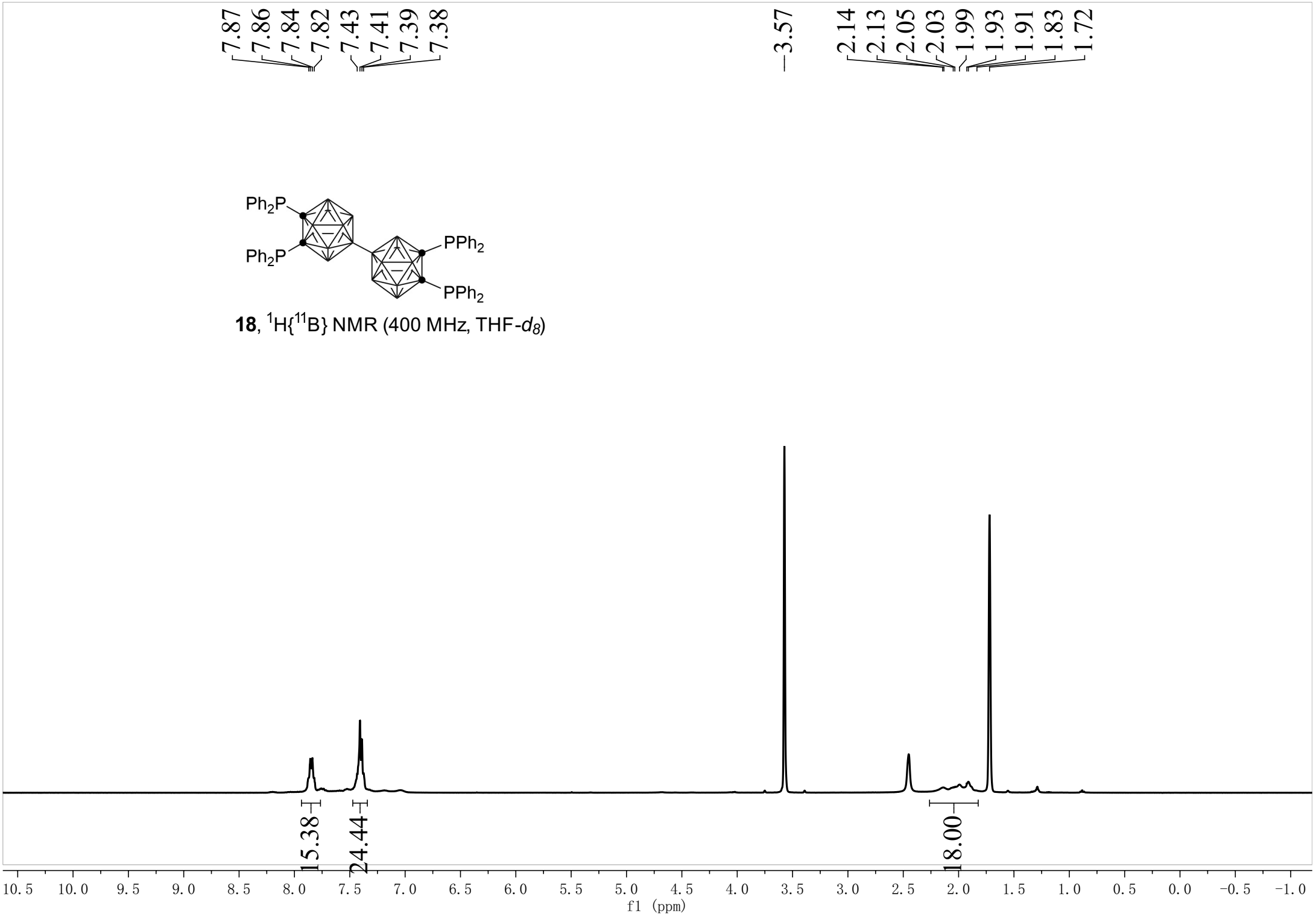




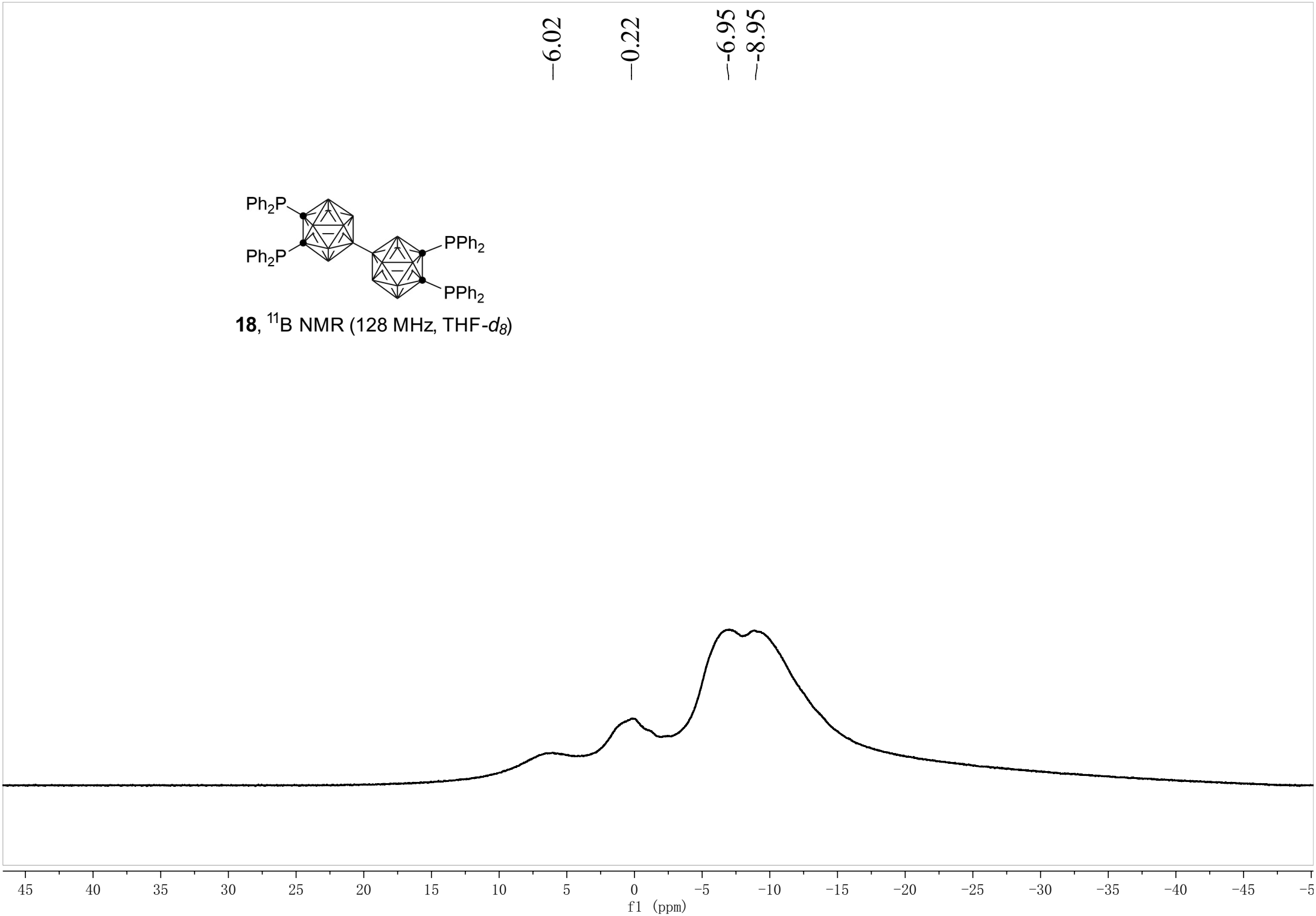
17, ^{13}C NMR (101 MHz, $CDCl_3$)



18, ^{1}H NMR (400 MHz, THF-d_8)

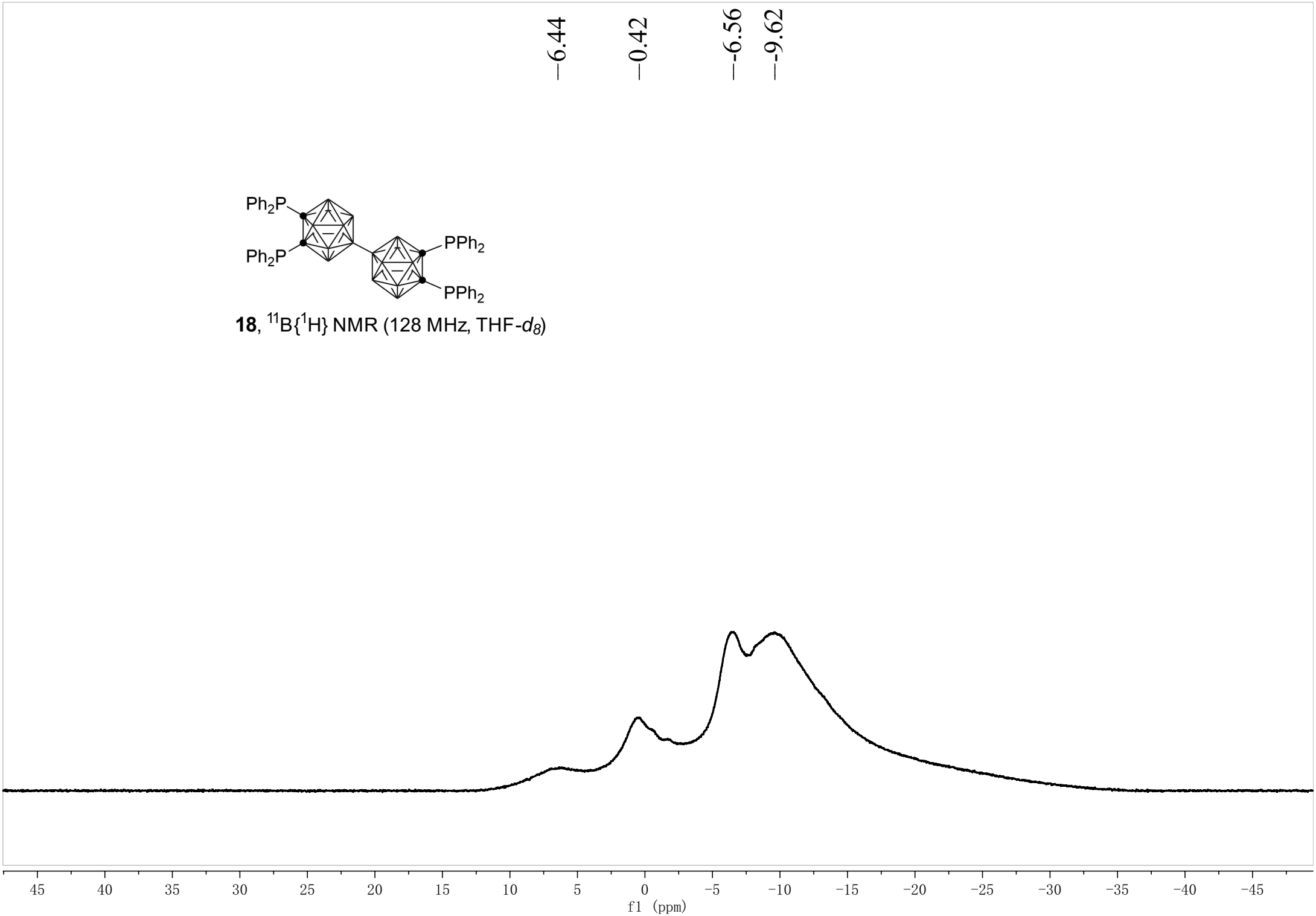


18, $^{1}H\{^{11}B\}$ NMR (400 MHz, THF-d_8)

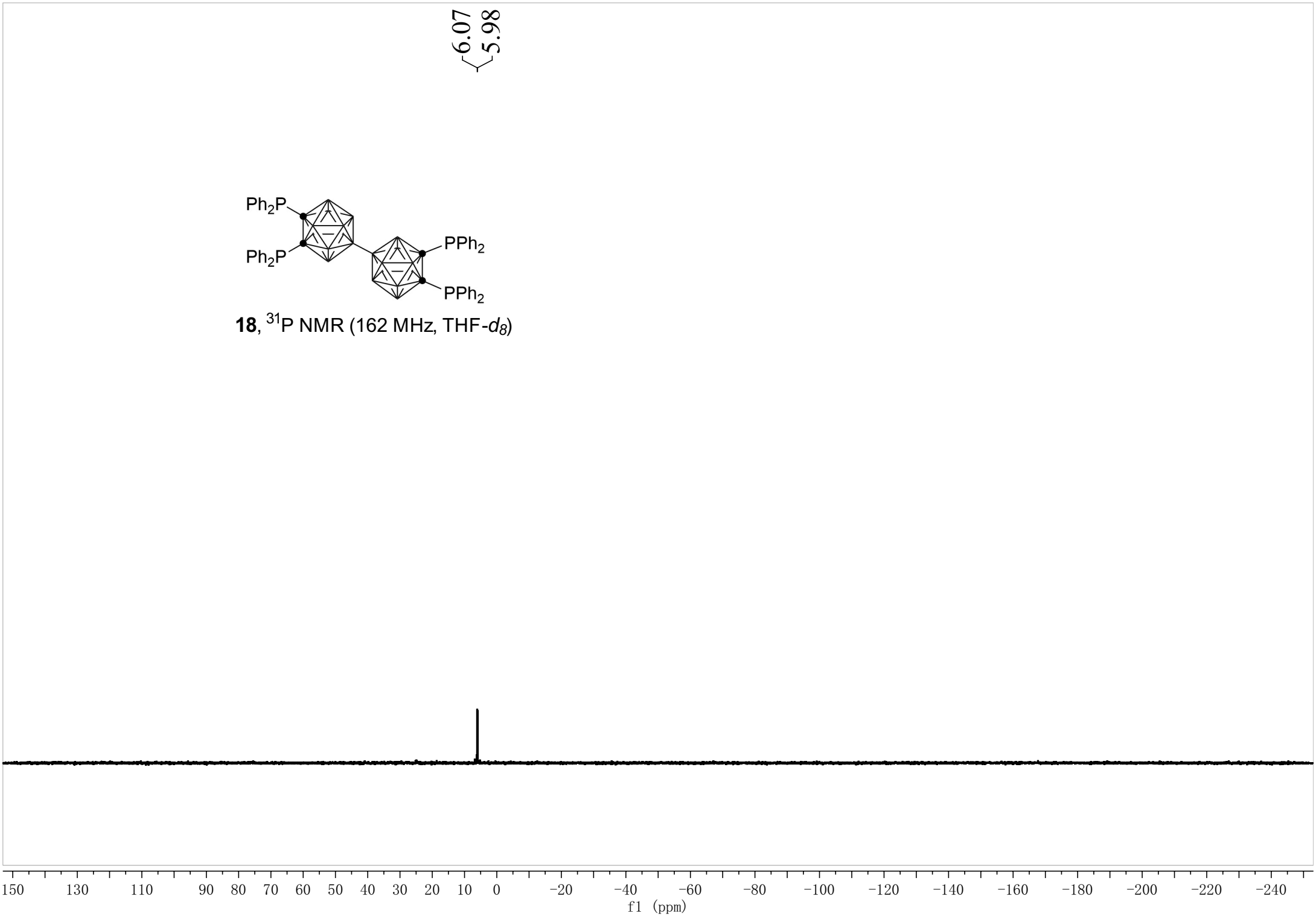


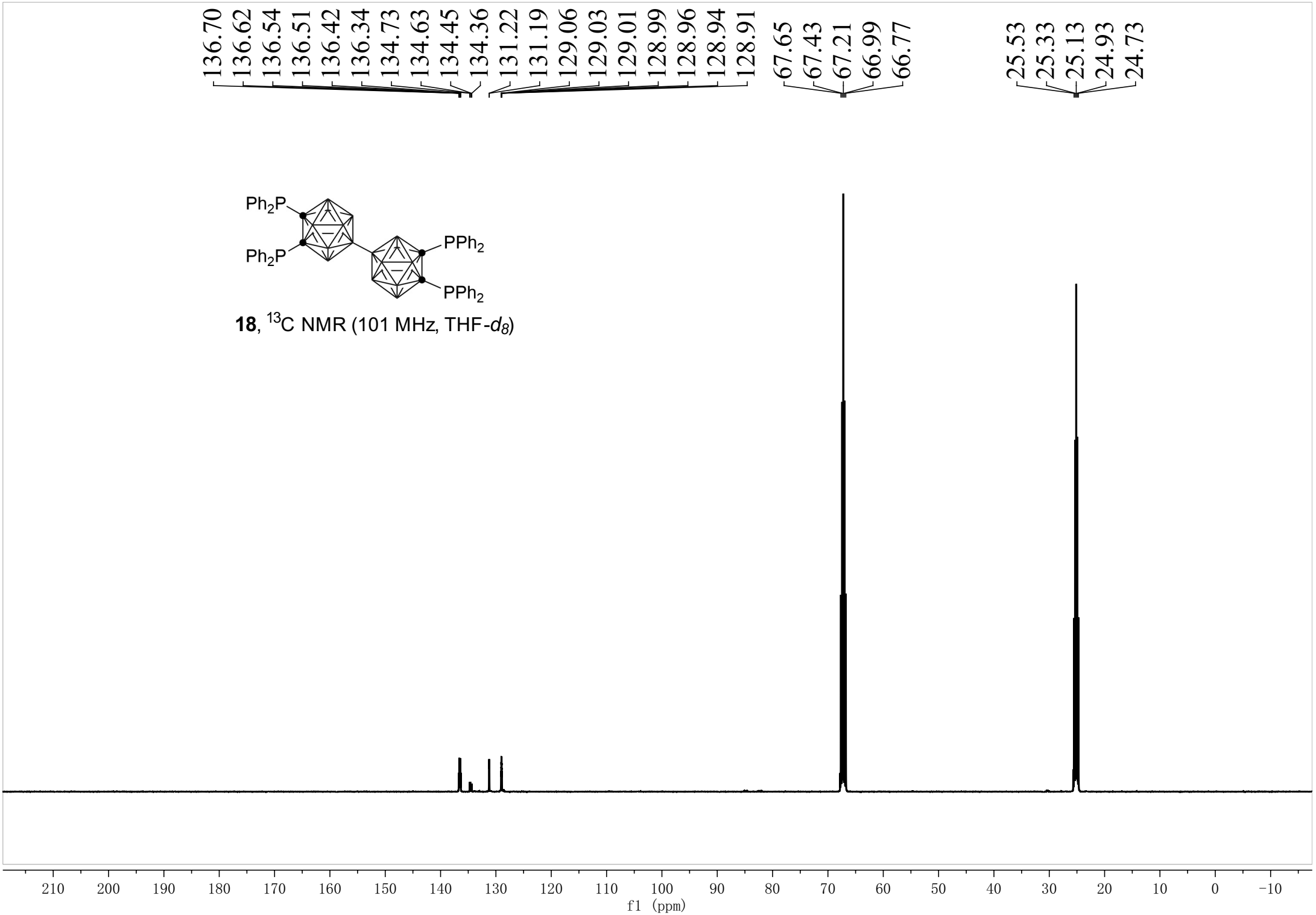
18, ^{11}B NMR (128 MHz, THF-d_8)

18, $^{11}B\{^{1}H\}$ NMR (128 MHz, THF-d_8)



18, ^{31}P NMR (162 MHz, THF-d_8)





18, ^{13}C NMR (101 MHz, THF-d_8)