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Supporting Information

HSAB Theory Guiding Electrophilic Substitution Reactions of *o*-Carborane

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1. General Information

^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on Bruker Advance III600 (400) spectrometer at 600 (400), 151 (101), 193 (128) and 565 (377) MHz, respectively. 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, and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. High Resolution Mass Spectra (HRMS (ESI-TOF)) were recorded on an Bruker Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). GC-MS analyses were performed on SHIMADZU GCMS-QP 2020. Starting *o*-carborane and *m*-carborane were purchased from Zhengzhou Yuanli technology. All other chemicals were purchased from Aldrich, Acros Organics, J&K Chemicals, Energy Chemical, Aladdin, Macklin or TCI and used without further purification. 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 Section

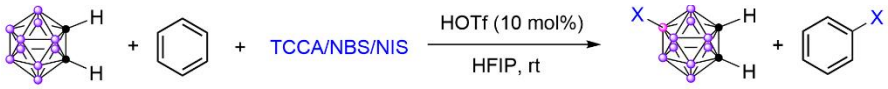
2.1 Comparison of electrophilic substitution reactions between *o*-carborane and benzene

(a) Catalyst-free electrophilic halogenation.

X = Cl	0%	98%
X = Br	79%	12%
X= I	88%	0%

General procedure: *o*-Carborane (2.0 equiv, 0.40 mmol) and electrophile TCCA (0.067 mmol), TBCA (0.067 mmol) or NIS (0.02 mmol) were mixed in HFIP (4.0 mL). Then to this solution was added benzene (2.0 equiv, 0.4 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

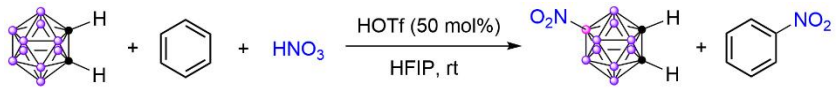
(b) HOTf-promoted electrophilic halogenation.



X = Cl	0%	99%
X = Br	73%	27%
X= I	95%	trace

General procedure: *o*-Carborane (2.0 equiv, 0.40 mmol) and electrophile TCCA (0.067 mmol), TBCA (0.067 mmol) or NIS (0.02 mmol) were mixed in HFIP (4.0 mL). Then to this solution was added benzene (2.0 equiv, 0.40 mmol), HOTf (10 mol%) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

(c) Electrophilic nitration.

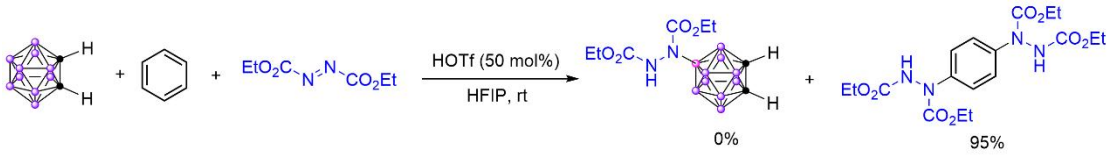


0% 99%

General procedure: Benzene (2.0 equiv, 0.40 mmol), 68% HNO_3 (1.0 equiv, 0.20 mmol) and

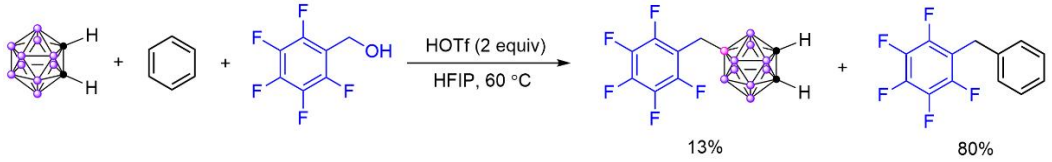
HOTf (50 mol%) were successively added to the solution of *o*-carborane (2.0 equiv, 0.40 mmol) in HFIP (4.0 mL). The resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

(d) Electrophilic amination.



General procedure: Benzene (2.0 equiv, 0.40 mmol), DEAD (1.0 equiv, 0.20 mmol), HOTf (50 mol%) were successively added to the solution of *o*-carborane (2.0 equiv, 0.40 mmol) in HFIP (4.0 mL). The resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

(e) Friedel-Crafts alkylation.



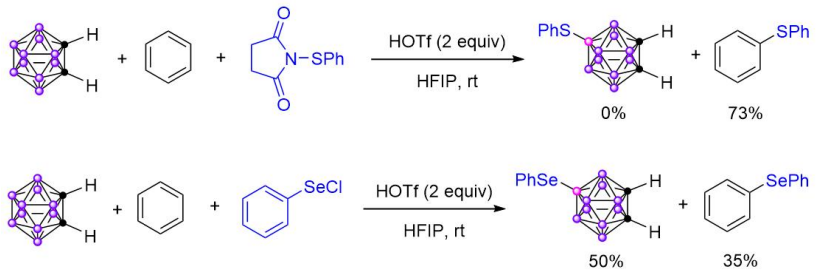
General procedure: *o*-Carborane (2.0 equiv, 0.40 mmol) and 2,3,4,5,6-pentafluorobenzyl alcohol (1.0 equiv, 0.20 mmol) were mixed in HFIP (4.0 mL). Then to this solution was added benzene (2.0 equiv, 0.40 mmol), HOTf (2.0 equiv, 0.40 mmol) and the resulting mixture was stirred in a closed flask at 60 °C for 12 h under air atmosphere. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

2.2 Electrophilic chalcogenation/Friedel-Crafts acylation/sulfonylation

(a) Electrophilic chalcogenation [1]

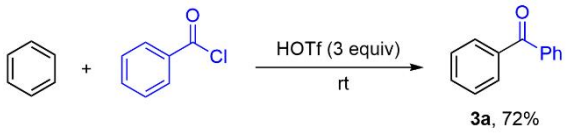
General procedure: *o*-Carborane (1.0 equiv, 0.20 mmol) and 1-(phenylthio)pyrrolidine-2,5-dione or phenylselenenyl chloride (2.0 equiv, 0.40 mmol) were mixed in HFIP (2.0 mL). Then to this solution was added HOTf (2.0 equiv, 0.40 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. After the reaction was completed, the solution was portioned between EtOAc and saturated aqueous $NaHCO_3$. The organic portions were combined. Then 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.

(b) Competing experiments towards electrophilic chalcogenation



General procedure: *o*-Carborane (2.0 equiv, 0.40 mmol) and electrophiles (1.0 equiv, 0.20 mmol) were mixed in HFIP (4.0 mL). Then to this solution was added benzene (2.0 equiv, 0.40 mmol), HOTf (2.0 equiv, 0.40 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. The reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

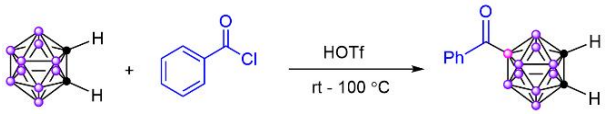
(c) Friedel-Crafts acylation of benzene. [2]



3a, 72%

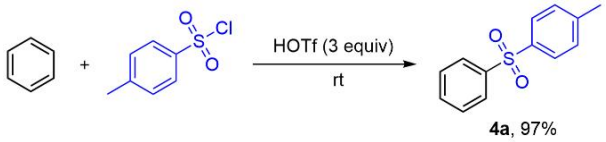
General procedure: Benzene (1.0 equiv, 0.20 mmol) and benzoyl chloride (2.0 equiv, 0.4 mmol) were mixed in a glass tube, then HOTf (3.0 equiv, 0.60 mmol) was carefully and slowly added, the reaction was stirred at ambient temperature for 12 h under air atmosphere. 1 mL of EtOAc was added to the reaction tube for dilution, then saturated aqueous $NaHCO_3$ was added to neutralize to pH = 6 – 7, and then extracted with EtOAc (20 mL × 3). The organic phase was collected and dried with Na_2SO_4. Then 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 **3a**.

(d) Friedel-Crafts acylation of *o*-carborane.



General procedure: *o*-Carborane (1.0 equiv, 0.20 mmol) was mixed in HOTf (1.0 mL). Then to this solution was added benzoyl chloride (2.0 equiv, 0.40 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. After the reaction solution was portioned between EtOAc and saturated aqueous $NaHCO_3$. The organic portions were combined. No product was detected by ^{11}B NMR and GC-MS.

(e) Electrophilic sulfonylation of benzene. [3]

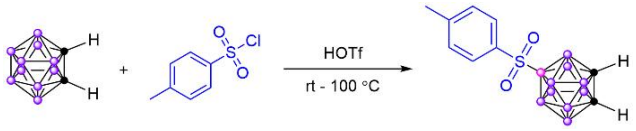


4a, 97%

General procedure: Benzene (1.0 equiv, 0.20 mmol) and tosyl chloride (2.0 equiv, 0.4 mmol) were weighed into a glass reaction tube, then HOTf (3.0 equiv, 0.60 mmol) was carefully and slowly added, the reaction was stirred at ambient temperature for 12 h under air atmosphere. 1 mL of EtOAc was added to the reaction tube for dilution, then saturated aqueous $NaHCO_3$ was added to neutralize to pH = 6 – 7, and then extracted with EtOAc (20 mL × 3). The organic phase was

collected and dried with Na_2SO_4. Then 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 **4a**.

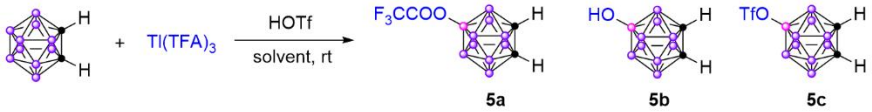
(f) Electrophilic sulfonylation of *o*-carborane.



General procedure: *o*-Carborane (1.0 equiv, 0.20 mmol) was mixed in HOTf (1.0 mL). Then to this solution was added tosyl chloride (2.0 equiv, 0.4 mmol and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. After the reaction solution was portioned between EtOAc and saturated aqueous $NaHCO_3$. The organic portions were combined. No product was detected by ^{11}B NMR and GC-MS.

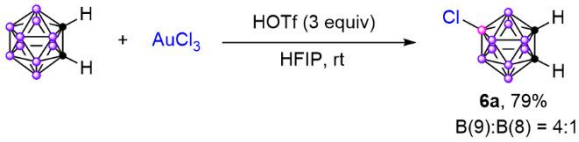
2.3 Electrophilic metallization

(a) Electrophilic thallation of *o*-carborane [4]



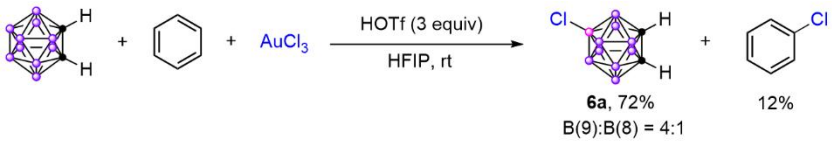
General procedure: *o*-Carborane (1.0 equiv, 0.20 mmol) and thallium(III) trifluoroacetate (2.0 equiv, 0.40 mmol) were mixed in HFIP or TFA (2.0 mL). Then to this solution was added HOTf (6.0 equiv, 1.20 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. After the reaction solution was portioned between EtOAc and saturated aqueous $NaHCO_3$. The organic portions were combined. Then 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 **5a, 5b** and **5c**.

(b) Electrophilic auration of *o*-carborane [5]



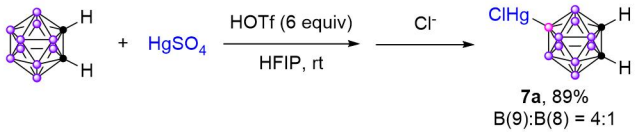
General procedure: *o*-Carborane (1.0 equiv, 0.20 mmol) and $AuCl_3$ (2.0 equiv, 0.40 mmol) were mixed in HFIP (2.0 mL). Then to this solution was added HOTf (3.0 equiv, 0.60 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. After the reaction solution was portioned between EtOAc and saturated aqueous $NaHCO_3$. The organic portions were combined. Then 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 **6a**.

(c) Competing experiment towards electrophilic auration.



General procedure: *o*-Carborane (2.0 equiv, 0.40 mmol) and $AuCl_3$ (1.0 equiv, 0.20 mmol) were mixed in HFIP (4.0 mL). Then to this solution was added benzene (2.0 equiv, 0.40 mmol), HOTf (3.0 equiv, 0.60 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

(d) Electrophilic mercuration of *o*-carborane.

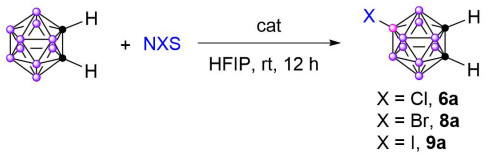


General procedure: *o*-Carborane (1.0 equiv, 0.20 mmol) and $HgSO_4$ (2.0 equiv, 0.40 mmol) were mixed in HFIP (2.0 mL). Then to this solution was added HOTf (6.0 equiv, 1.20 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. After the reaction solution was portioned between EtOAc and saturated aqueous $NaHCO_3$. The organic portions were combined. Then 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 **7a**.

2.4 Pd(II)-catalyzed B(9)-functionalization of *o*-carborane

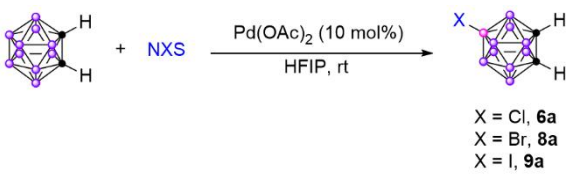
(a) Pd(II)-catalyzed B(9)-halogenation of *o*-carborane [5]

Table S1. B(9)–halogenation of *o*-carborane.[a]



entry	NXS (1.0 equiv)	Cat (10 mol%)	Yield (%)
1	NCS	w/o	n.r.
2	NCS	$Pd(OAc)_2$	36 (trace)[b]
3	NBS	w/o	26
4	NBS	$Pd(OAc)_2$	69 (6)[b]
5	NIS	w/o	74
6	NIS	$Pd(OAc)_2$	71 (13)[b]

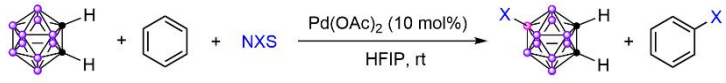
[a] reaction conditions: *o*-carborane (0.2 mmol), NXS (0.2 mmol) in 2 mL HFIP was stirred at room temperature for 12 hours. [b] yields of the dihalogenated products.



General procedure: *o*-Carborane (1.0 equiv, 0.20 mmol), NXS (2.0 equiv, 0.40 mmol) and $Pd(OAc)_2$ (10 mol%) were mixed in HFIP (2.0 mL). Then the resulting mixture was stirred in a

closed flask at ambient temperature for 12 h under air atmosphere. After the reaction solution was portioned between EtOAc and saturated aqueous $NaHCO_3$. The organic portions were combined. Then 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 **6a/8a/9a**.

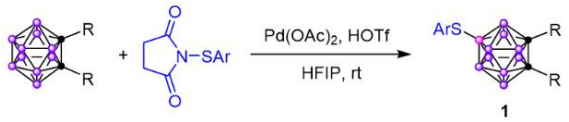
(b) Comparison of Pd(II)-catalyzed B-H/C-H halogenation of *o*-carborane and benzene



X = Cl	29%	0%
X = Br	76%	0%
X= I	83%	0%

General procedure: *o*-Carborane (2.0 equiv, 0.40 mmol), NXS (1.0 equiv, 0.20 mmol) and $Pd(OAc)_2$ (10 mol%) were mixed in HFIP (4.0 mL). Then to this solution was added benzene (2.0 equiv, 0.40 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

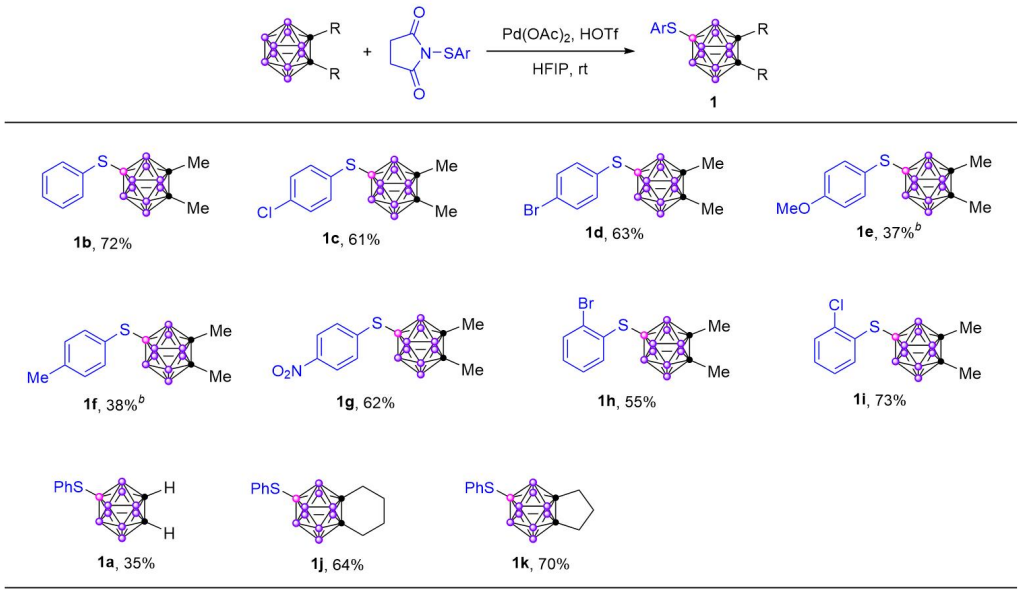
(c) Pd(II)-catalyzed B(9)-thiolation of *o*-carborane



1

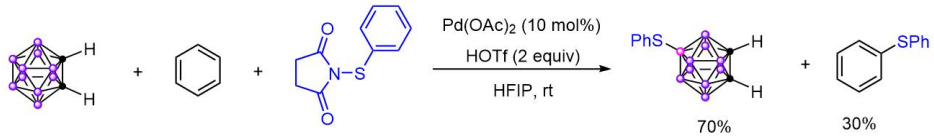
General procedure: *o*-Carborane (1.0 equiv, 0.20 mmol), the sulfur reagent (1.5 equiv, 0.30 mmol) and $Pd(OAc)_2$ (10 mol%) were mixed in HFIP (2.0 mL). Then to this solution was added HOTf (1.0 equiv, 0.20 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature or 60℃ for 12 h – 24 h under air atmosphere. After the reaction solution was portioned between EtOAc and saturated aqueous $NaHCO_3$. The organic portions were combined. Then 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 **1a-1k**.

Table *S2*. Scope of Pd(II)-catalyzed B(9)-thiolation of *o*-carborane.[a]



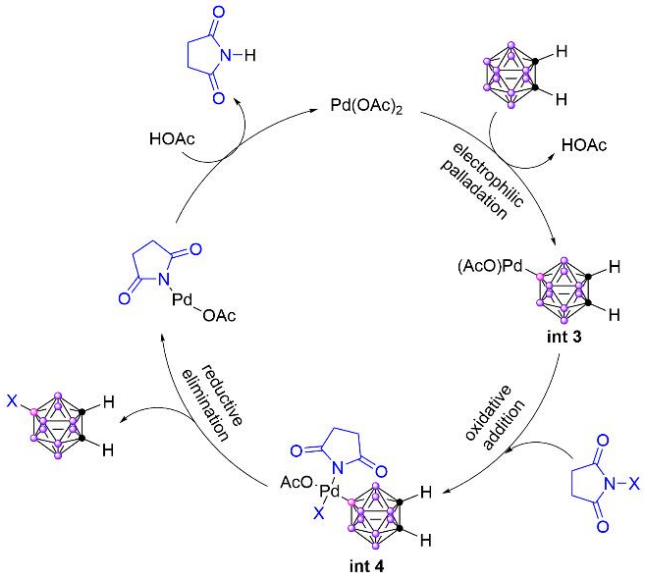
[a] Reaction conditions: carboranes (0.2 mmol, 1.0 equiv), arylthiolation reagent (0.3 mmol, 1.5 equiv), Pd(OAc)2 (10 mol%) and HOTf (0.2 mmol, 1.0 equiv) in HFIP (2 mL) at room temperature under an air atmosphere. [b] At 60 °C for 24 hours.

(d) Comparison of Pd(II)-catalyzed B-H/C-H thiolation of *o*-carborane and benzene



General procedure: *o*-Carborane (2.0 equiv, 0.40 mmol), 1-(phenylthio)pyrrolidine-2,5-dione (1.0 equiv, 0.20 mmol) and $Pd(OAc)_2$ (10 mol%) were mixed in HFIP (4.0 mL). Then to this solution was added benzene (2.0 equiv, 0.40 mmol), HOTf (2.0 equiv, 0.40 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

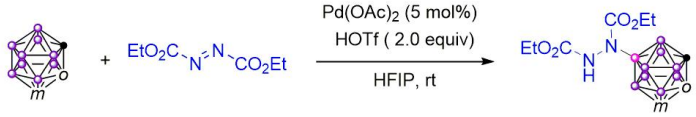
(e) Proposed mechanism for Pd(II)-catalyzed B(9)-H halogenation/thiolation of *o*-carborane



Scheme *S1*. The plausible mechanism of Pd(II)-catalyzed B(9)-halogenation of *o*-carborane

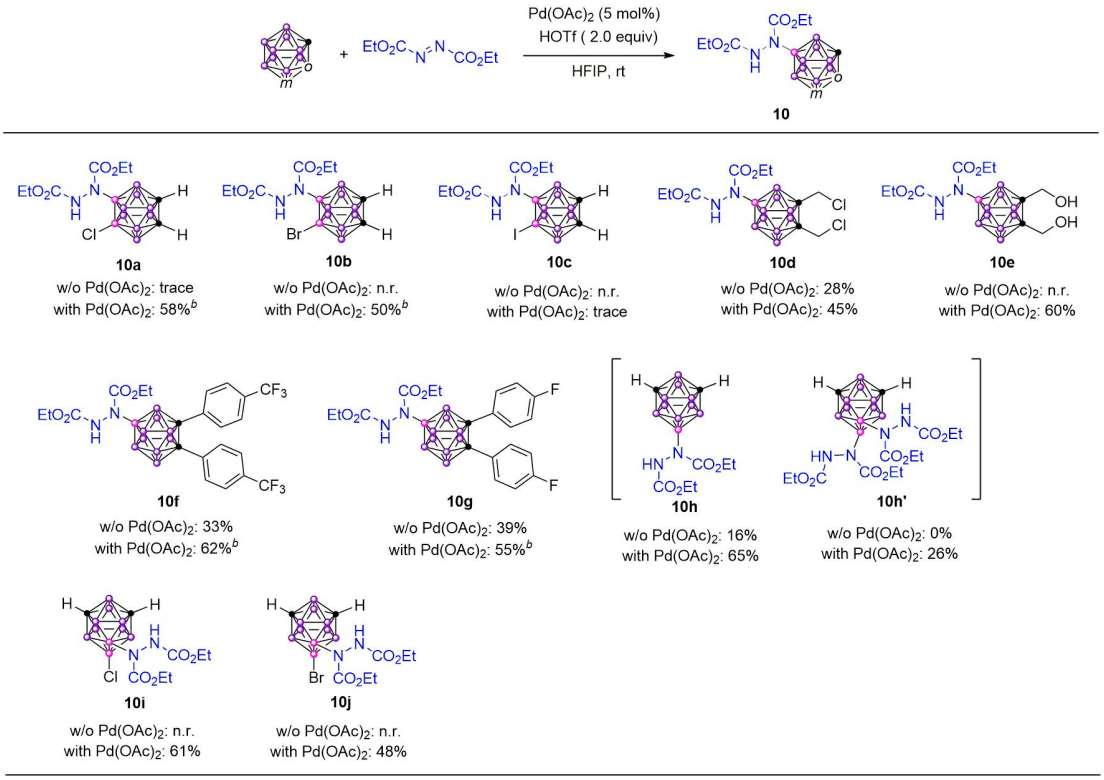
Based on the experiment results and our previous mechanism studies, a plausible mechanism of Pd(II)-catalyzed B(9)-halogenation and thiolation of *o*-carborane is proposed, as shown in **Scheme *S1***. We consider that the first step in the catalytic cycle is the formation of B−Pd intermediate **int 3** through electrophilic palladation process. Then the halogenating reagent oxidative addition occurs to form the Pd(IV) intermediate **int 4**. B−X reductive elimination from **int 4** produces the target product, meanwhile the catalyst palladium is reduced from the Pd(IV) to the Pd(II), entering the catalytic cycle.

(f) Pd(II)-catalyzed B(9)-amination of *o*-carborane [6]



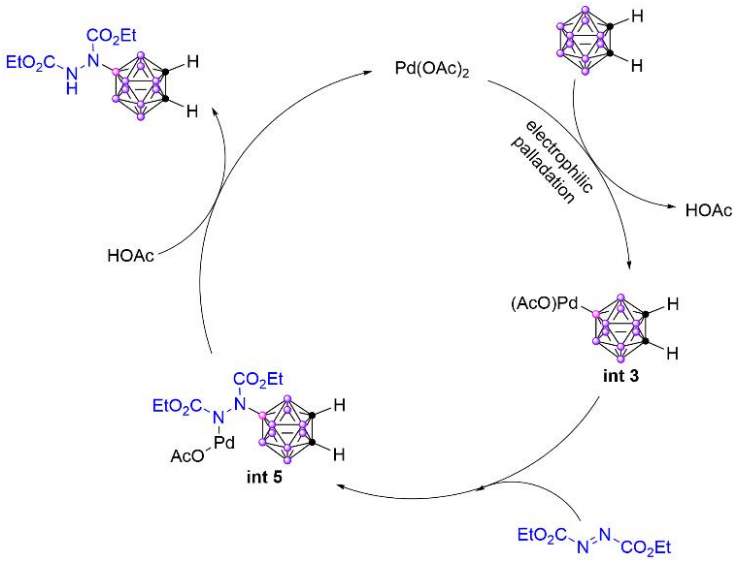
General procedure: *o*/*m*-Carborane (1.0 equiv, 0.20 mmol), DEAD (1.1 equiv, 0.22 mmol) and $Pd(OAc)_2$ (5 mol%) were mixed in HFIP (2.0 mL). Then to this solution was added HOTf (1.0 equiv, 0.20 mmol) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. After the reaction solution was portioned between EtOAc and saturated aqueous $NaHCO_3$. The organic portions were combined. Then 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 (**10a-10j**).

Table S3. Selective B(9)-amination of *o*-carborane.[a]



[a] Reaction conditions: carboranes (0.2 mmol, 1.0 equiv), DEAD (0.22 mmol, 1.1 equiv), Pd(OAc)2 (5 mol%) and HOTf (0.2 mmol, 1.0 equiv) in HFIP (2 mL) at room temperature under an air atmosphere. [b] At 60 °C for 12 hours.

(g) Proposed mechanism for Pd(II)-catalyzed B(9)-amination of *o*-carborane

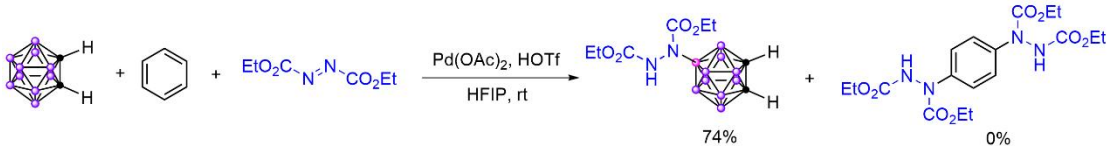


Scheme *S2*. The plausible mechanism of Pd(II)-catalyzed B(9)-amination of *o*-carborane

Based on the experiment results and our previous mechanism studies, a plausible mechanism of Pd(II)-catalyzed B(9)-amination of *o*-carborane is proposed, as shown in **Scheme *S2***. We consider that the first step in the catalytic cycle is the formation of B−Pd intermediate **int 3** through electrophilic palladation process. Then the aminating reagent (DEAD) electrophilic addition occurs to form the B−N intermediate **int 5**, following protonation to form the target product and

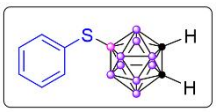
the catalyst palladium enters the catalytic cycle.

(h) Comparison of Pd(II)-catalyzed B-H/C-H amination of *o*-carborane and benzene

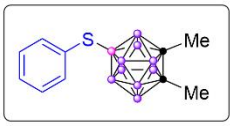


General procedure: *o*-Carborane (2.0 equiv, 0.40 mmol), DEAD (1.0 equiv, 0.20 mmol) and $Pd(OAc)_2$ (10 mol%) were mixed in HFIP (4.0 mL). Then to this solution was added benzene (2.0 equiv, 0.40 mmol), HOTf (50 mol%) and the resulting mixture was stirred in a closed flask at ambient temperature for 12 h under air atmosphere. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield. Then, the reaction solution was monitored by ^{11}B NMR and ^{1}H NMR spectroscopy to gain the product yield.

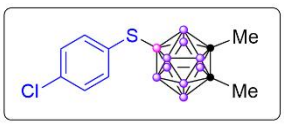
3. Characterization data



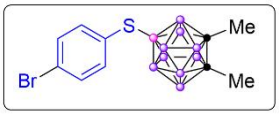
1a: Yield 35%; White solid; **Eluent**: PE/EA = 50:1 (R_f = 0.28), Mp:124-126 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 5.2 Hz, 2H), 7.24 (s, 1H), 7.23 (d, *J* = 1.4 Hz, 2H),, 3.50 (s, 1H), 3.41 (s, 1H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ: 135.4, 134.9, 128.5, 126.9, 52.7, 47.5. **^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$)** δ: 7.5 (1B), -2.3 (1B), -8.6 (2B), -13.9 (2B), -14.6 (2B), -15.5 (2B). **IR**: 621, 718, 1069, 2603, 3258 cm^{-1}.
HRMS (ESI-TOF): m/z calcd for $C_8B_{10}H_{17}S$ $[M+H]^+$: 253.2053. Found: 253.2051.



1b: Yield 72%; White solid; **Eluent**: PE/EA = 25:1 (R_f = 0.32).
^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 5.5 Hz, 2H), 7.25 (s, 1H), 7.23 (d, *J* = 0.8 Hz, 2H), 1.99 (s, 3H), 1.98 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ: 135.8, 134.8, 128.4, 126.7, 71.9, 66.5, 23.2, 21.9. **^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$)** δ: 5.3 (1B), -4.8 (1B), -8.9 (2B), -9.8 (4B), -10.3 (2B).
HRMS (ESI-TOF): m/z calcd for $C_{10}B_{10}H_{21}S$ $[M+H]^+$: 281.2367. Found: 281.2366.



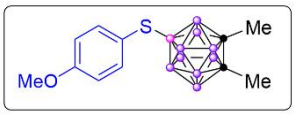
1c: Yield 61%; White solid; **Eluent**: PE/EA = 25:1 (R_f = 0.28).
^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 1.99 (s, 3H), 1.98 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ: 136.1, 134.4, 132.9, 128.6, 71.9, 66.7, 23.2, 22.0. **^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$)** δ: 5.1 (1B), -4.8 (1B), -8.9 (2B), -9.8 (4B), -10.3 (2B).
HRMS (ESI-TOF): m/z calcd for $C_{10}B_{10}H_{20}SCl$ $[M+H]^+$: 316.1951. Found: 316.1953.



1d: Yield 63%; White solid; **Eluent**: PE/EA = 100:1 (R_f = 0.28).

^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.34 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 1.99 (s, 3H), 1.98 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)** δ: 136.5, 135.0, 131.5, 121.1, 71.9, 66.7, 23.3, 22.0. **^{11}B{^{1}H} NMR (193 MHz, CDCl$_3$)** δ: 5.0 (1B), -4.8 (1B), -8.9 (2B), -9.8 (4B), -10.2 (2B).

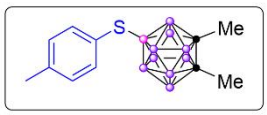
HRMS (ESI-TOF): m/z calcd for $C_{10}B_{10}H_{20}SBr$ $[M+H]^+$: 360.1458. Found: 360.1456.



1e: Yield 37%; White solid; **Eluent**: PE/EA = 25:1 (R_f = 0.26).

^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.33 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)** δ: 158.8, 136.2, 126.7, 114.0, 71.8, 66.2, 55.2, 23.3, 22.0. **^{11}B{^{1}H} NMR (193 MHz, CDCl$_3$)** δ: 5.7 (1B), -4.7 (1B), -8.9 (2B), -9.8 (4B), -10.3 (2B).

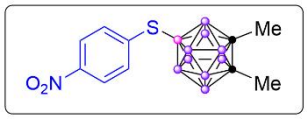
HRMS (ESI-TOF): m/z calcd for $C_{11}B_{10}H_{23}SO$ $[M+H]^+$: 311.2473. Found: 311.2468.



1f: Yield 38%; White solid; **Eluent**: PE (R_f = 0.26).

^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.31 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 2.31 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)** δ: 136.5, 134.8, 132.2, 129.2, 71.8, 66.3, 23.2, 22.0, 21.1. **^{11}B{^{1}H} NMR (193 MHz, CDCl$_3$)** δ: 5.5 (1B), -4.7 (1B), -8.9 (2B), -9.7 (4B), -10.3 (2B).

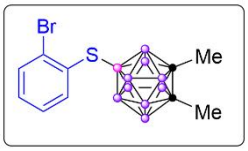
HRMS (ESI-TOF): m/z calcd for $C_{11}B_{10}H_{22}SNH_4$ $[M+NH_4]^+$: 312.2790. Found: 312.2785.



1g: Yield 62%; White solid; **Eluent**: PE/EA = 25:1 (R_f = 0.32).

^{1}H NMR (600 MHz, CDCl$_3$) δ: 8.06 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 2.02 (s, 3H), 2.01 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)** δ: 146.4, 145.8, 134.3, 123.3, 72.2, 67.7, 23.3, 22.0. **^{11}B{^{1}H} NMR (193 MHz, CDCl$_3$)** δ: 4.2 (1B), -4.8 (1B), -8.8 (2B), -9.8 (6B).

HRMS (ESI-TOF): m/z calcd for $C_{10}B_{10}H_{20}SNO_2$ $[M+H]^+$: 326.2218. Found: 326.2216.

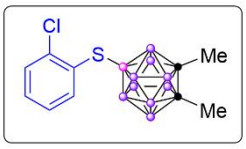


1h: Yield 55%; White solid; **Eluent**: PE/EA = 25:1 (R_f = 0.26).

^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.57 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 1.99 (s, 3H), 1.98 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)** δ: 137.6, 137.2, 132.9, 130.3, 128.4, 127.2, 71.9, 66.9, 23.3, 22.0. **^{11}B{^{1}H} NMR (193 MHz, CDCl$_3$)** δ: 4.9 (1B), -4.7

(1B), -9.0 (2B), -9.8 (4B), -10.3 (2B).

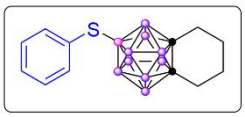
HRMS (ESI-TOF): m/z calcd for $C_{10}B_{10}H_{20}SBr$ $[M+H]^+$: 360.1458. Found: 360.1457.



1i: Yield 73%; White solid; **Eluent**: PE/EA = 25:1 (R_f = 0.28).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.11 (m, 2H), 1.99 (s, 3H), 1.98 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ: 139.0, 137.8, 135.0, 129.5, 128.4, 126.6, 71.9, 66.8, 23.3, 22.0. **^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$)** δ: 4.8 (1B), -4.8 (1B), -9.0 (2B), -9.8 (4B), -10.3 (2B).

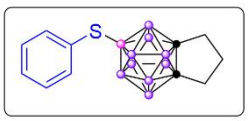
HRMS (ESI-TOF): m/z calcd for $C_{10}B_{10}H_{20}SCl$ $[M+H]^+$: 316.1951. Found: 316.1950.



1j: Yield 64%; White solid; **Eluent**: PE/EA = 50:1 (R_f = 0.32).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 6.4 Hz, 2H), 7.23 (s, 1H), 7.22 (s, 2H), 2.39 (s, 4H), 1.56 – 1.51 (m, 4H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ: 135.9, 134.9, 128.4, 126.7, 71.6, 66.2, 32.7, 31.6, 19.7, 19.4.**^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$)** δ: 4.7 (1B), -5.2 (1B), -8.7 (2B), -9.8 (2B), -10.4 (2B), -12.3 (2B).

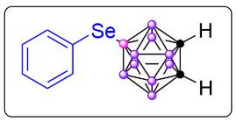
HRMS (ESI-TOF): m/z calcd for $C_{12}B_{10}H_{23}S$ $[M+H]^+$: 307.2525. Found: 307.2524.



1k: Yield 70%; White solid; **Eluent:** PE/EA = 50:1 (R_f = 0.32).

^{1}H NMR (600 MHz, CD_2Cl_2) δ: 7.44 (d, *J* = 6.2 Hz, 2H), 7.23 (s, 1H), 7.22 (s, 2H), 2.48 – 2.38 (m, 6H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ: 135.9, 134.9, 128.4, 126.7, 82.9, 77.8, 34.4, 33.3, 32.3. **^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$)** δ: 4.2 (1B), -6.0 (1B), -7.5 (2B), -9.7 (2B), -11.8 (2B), -12.5 (2B).

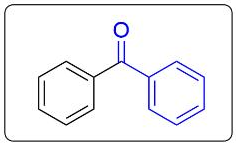
HRMS (ESI-TOF) m/z calcd for $C_{11}B_{10}H_{21}S$ $[M+H]^+$: 293.2368. Found: 293.2369.



2a: White solid; **Eluent**: PE/EA = 50:1 (R_f = 0.28), Mp: 94-97 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 3.2 Hz, 1H), 7.26 – 7.20 (m, 2H), 3.55 (s, 2H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 136.2, 129.1, 128.6, 127.0, 53.7, 49.4. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** δ: 3.0 (1B), -2.0 (1B), -8.4 (2B), -14.0 (4B), -15.1 (2B). **IR**: 720, 846, 1023, 1134, 2556, 3052 cm^{-1}.

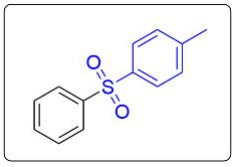
HRMS (ESI-TOF): m/z calcd for $C_8B_{10}H_{16}SeK$ $[M+K]^+$: 339.1047. Found: 339.1070. [1]



3a: Yield 72%; White solid; **Eluent:** PE/EA = 50:1 (R_f = 0.32), Mp: 47-49 ºC.

^{1}H NMR (400 MHz, CD_3CN) δ: 7.76 (d, *J* = 7.2 Hz, 4H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 4H). **^{13}C{^{1}H} NMR (101 MHz, CD_3CN)** δ: 197.2, 138.5, 133.4, 130.7, 129.3. **IR**: 634, 688, 943, 1269, 1448, 1646 cm^{-1}.

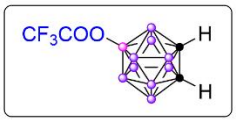
HRMS (ESI-TOF): m/z calcd for $C_{13}H_{10}ONH_4$ $[M+NH_4]^+$: 200.1070. Found: 200.1076. [2]



4a: Yield 97%; White solid; **Eluent:** DCM/EA = 20:1 (R_f = 0.28), Mp: 127-129 ºC.

^{1}H NMR (400 MHz, CD_3CN) δ: 8.59 (d, *J* = 7.2 Hz, 2H), 8.49 (d, *J* = 8.1 Hz, 2H), 8.29 (t, *J* = 7.3 Hz, 1H), 8.23 (t, *J* = 7.4 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H), 3.05 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, CD_3CN)** δ: 145.8, 142.9, 139.6, 134.3, 131.1, 130.5, 128.4, 128.2, 21.5. **IR**: 548, 651, 688, 723, 813, 1101, 1155, 1293, 1448 cm^{-1}.

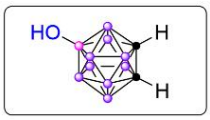
HRMS (ESI-TOF): m/z calcd for $C_{13}H_{12}O_2SNa$ $[M+Na]^+$: 225.0450. Found: 255.0456. [3]



5a: White solid; **Eluent:** PE/DCM = 3:1 (R_f = 0.28), Mp: 100-102 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.54 (s, 2H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 155.8 (q, *J* = 41.41), 114.5 (q, *J* = 286.84), 50.5, 44.3. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** δ: 10.0 (1B), -3.5 (1B), -10.4 (2B), -115.0 (2B), -16.1 (2B), -17.2 (2B). **^{19}F NMR (377 MHz, $CDCl_3$)** δ: -75.88. **IR**: 506, 725, 873, 1028, 1162, 1388, 1771, 2613, 3091 cm^{-1}.

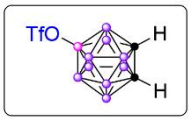
HRMS (ESI-TOF): m/z calcd for $C_4B_{10}H_{11}O_2F_3$ $[M+H]^+$: 257.1789. Found: 257.1791. [4]



5b: White solid; **Eluent:** PE/DCM = 1:1 (R_f = 0.28), Mp:312-314 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.38 (s, 1H), 3.26 (s, 1H), 1.84 (s, 1H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 49.1, 37.1. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** δ: 14.7 (1B), -3.8 (1B), -10.2 (2B), -15.2 (2B), -16.8 (2B), -17.7 (2B). **IR**: 465, 721, 1028, 1122, 2548, 3070, 3272 cm^{-1}.

HRMS (ESI-TOF): m/z calcd for $C_2B_{10}H_{12}O_1$ $[M+H]^+$: 161.1965. Found: 161.1961. [4]

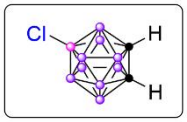


5c: Colorless oil; **Eluent:** PE/DCM = 4:1 (R_f = 0.26).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.55 (s, 2H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 118.3 (q, *J* = 319.16 Hz), 50.6, 44.1. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** δ: 9.8 (1B), -3.6 (1B), -10.4 (2B), -15.2

(2B), -16.0 (2B), -17.1 (2B). **^{19}F NMR (377 MHz, $CDCl_3$)** δ: -75.91. **IR**: 509, 612, 886, 968, 1028, 1096, 1209, 1388, 2601, 3076 cm^{-1}.

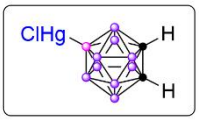
HRMS (ESI-TOF): m/z calcd for $C_3B_{10}H_{11}SF_3O_3$ $[M+H]^+$: 293.1459. Found: 293.1463. [4]



6a: White solid; **Eluent:** DCM/EA = 50:1 (R_f = 0.32), Mp: 221-223 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.57 (s, 1H), 3.45 (s, 1H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 52.1, 44.4. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** δ: 7.4 (1B), -2.1 (1B), -8.8 (2B), -13.8 (2B), -15.1 (2B), -16.3 (2B). **IR**: 531, 723, 873, 972, 1007, 1140, 1713, 2570, 3063 cm^{-1}.

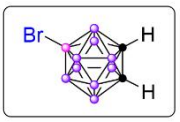
HRMS (ESI-TOF): m/z calcd for $C_2B_{10}H_{12}Cl$ $[M+H]^+$: 180.1599. Found: 180.1598. [5]



7a: White solid; **Eluent:** PE/EA = 3:1 (R_f = 0.26), Mp: 266-268 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.74 (s, 1H), 3.54 (s, 1H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 58.9, 57.0. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** 3.5 (1B), -1.0 (1B), -8.1 (2B), -12.5 (4B), -13.7 (2B). **IR**: 716, 852, 966, 1141, 1211, 2564, 3031 cm^{-1}.

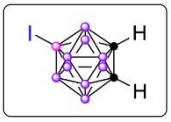
HRMS (ESI-TOF): m/z calcd for $C_2B_{10}H_{11}HgClNH_4$ $[M+NH_4]^+$: 397.1574. Found: 397.1581.



8a: White solid; **Eluent:** DCM/EA = 50:1 (R_f = 0.32), Mp: 182-184 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.62 (s, 2H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 53.2, 46.7. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** δ: 0.1 (1B), -1.6 (1B), -8.3 (2B), -13.5 (2B), -14.5 (2B), -15.7 (2B). **IR**: 725, 846, 966, 1137, 1207, 2595, 3058 cm^{-1}.

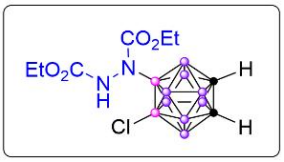
HRMS (ESI-TOF): m/z calcd for $C_2B_{10}H_{11}BrNH_4$ $[M+NH_4]^+$: 241.1372. Found: 241.1390. [5]



9a: White solid; **Eluent:** DCM/EA = 50:1 (R_f = 0.32), Mp: 119-120 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.87 (s, 1H), 3.66 (s, 1H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ: 54.8, 50.7. **^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$)** δ: -0.9 (1B), -7.5 (2B), -12.8 (2B), -13.4 (2B), -14.8 (2B), -16.6 (1B). **IR**: 725, 832, 966, 1137, 1204, 2579, 3048 cm^{-1}.

HRMS (ESI-TOF): m/z calcd for $C_2B_{10}H_{11}IK$ $[M+K]^+$: 309.0542. Found: 309.0525. [5]

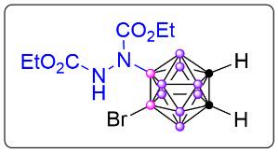


10a: Yield 58%; White solid; **Eluent:** PE/EA = 2:1 (R_f = 0.26).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.70 – 6.30 (m, 1H), 4.13 (s, 4H), 3.66 (s, 1H), 3.56 (s, 1H), 1.24 (t, J = 7.1 Hz, 6H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ: 157.7, 156.3, 62.5, 61.6, 44.4, 43.1, 14.4,

14.2. **$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$)** δ: 7.3 (1B), 6.4 (1B), -9.7 (1B), -10.8 (1B), -16.2 (4B), -18.8 (2B).

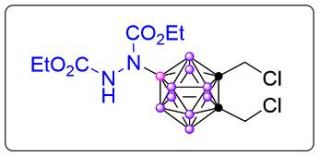
HRMS (ESI-TOF): m/z calcd for $C_8B_{10}H_{22}N_2O_4Cl$ $[M+H]^+$: 354.2243. Found: 354.2245.



10b: Yield 50%; White solid; **Eluent:** PE/EA = 2:1 (R_f = 0.32).

^1H NMR (600 MHz, $CDCl_3$) δ: 6.75 – 6.35 (m, 1H), 4.22 – 4.08 (m, 4H), 3.59 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 6H). **$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$)** δ: 157.6, 156.3, 62.6, 61.6, 45.3, 45.2, 14.5, 14.2. **$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$)** δ: 7.6 (1B), -0.4 (1B), -9.1 (1B), -10.4 (1B), -16.0 (4B), -18.3 (2B).

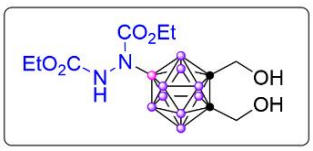
HRMS (ESI-TOF): m/z calcd for $C_8B_{10}H_{22}N_2O_4Br$ $[M+H]^+$: 398.1750. Found: 398.1749.



10d: Yield 45%; White solid; **Eluent:** PE/EA = 2:1 (R_f = 0.26).

^1H NMR (400 MHz, $CDCl_3$) δ: 6.52 – 6.05 (m, 1H), 4.20 (s, 2H), 4.15 (s, 4H), 1.25 (t, *J* = 7.1 Hz, 6H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ: 157.9, 156.4, 62.4, 61.7, 43.9, 42.9, 14.4, 14.3. **$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)** 8.5 (1B), -4.3 (1B), -10.9 (4B), -12.5 (4B).

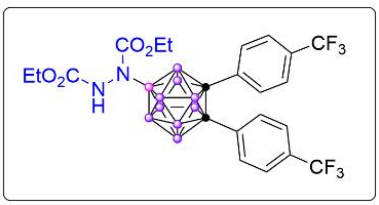
HRMS (ESI-TOF): m/z calcd for $C_{10}B_{10}H_{25}N_2O_4Cl_2$ $[M+H]^+$: 416.2173. Found: 416.2174. [6]



10e: Yield 60%; White solid; **Eluent:** PE/EA = 4:1 (R_f = 0.32)

^1H NMR (400 MHz, $CDCl_3$) δ: 6.50 – 6.10 (m, 1H), 4.17 – 4.01 (m, 4H), 2.01 (s, 3H), 2.00 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ: 158.0, 156.3, 69.5, 64.4, 62.0, 61.3, 23.5, 21.4, 14.3, 14.2. **$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)** 8.7 (1B), -6.2 (1B), -10.9 (8B).

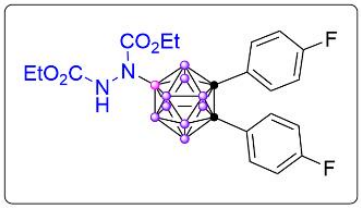
HRMS (ESI-TOF): m/z calcd for $C_{10}B_{10}H_{26}N_2O_4Na$ $[M+Na]^+$: 369.2793. Found: 369.2798.



10f: Yield 62%; White solid; **Eluent:** PE/EA = 4:1 (R_f = 0.28).

^1H NMR (400 MHz, $CDCl_3$) δ: 7.56 (t, *J* = 8.0 Hz, 4H), 7.44 (d, *J* = 8.2 Hz, 4H), 6.55 – 6.13 (m, 1H), 4.26 – 4.05 (m, 4H), 1.29 – 1.21 (m, 6H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ: 157.9, 156.6, 132.7 (dd, J_1 = 71.71 Hz, J_2 = 31.31 Hz), 131.2, 131.0, 125.6 (q, *J* = 3.03 Hz), 123.1 (q, *J* = 273.71 Hz), 79.4, 74.4, 62.4, 61.7, 14.5, 14.3. **$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)** δ: 9.8 (1B), -3.0 (1B), -10.7 (8B). **^{19}F NMR (377 MHz, $CDCl_3$)** δ: -63.23 (d, *J* = 2.6 Hz).

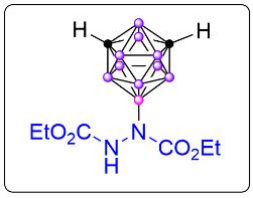
HRMS (ESI-TOF): m/z calcd for $C_{22}B_{10}H_{29}N_2O_4F_6$ $[M+H]^+$: 607.3040. Found: 607.3041. [6]



10g: Yield 55%; White solid; **Eluent:** PE/EA = 4:1 (R_f = 0.28).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 – 7.36 (m, 4H), 6.84 (t, *J* = 8.4 Hz, 4H), 6.54 – 6.15 (m, 1H), 4.27 – 4.06 (m, 4H), 1.32 – 1.20 (m, 6H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 163.7 (d, *J* = 253.51 Hz), 158.0, 156.6, 132.9 (d, *J* = 9.09 Hz), 126.3, 125.3, 115.6 (d, *J* = 22.22 Hz), 80.6, 75.2, 62.3, 61.6, 14.4, 14.3. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** δ: 9.5 (1B), -3.0 (1B), -10.7 (8B). **^{19}F NMR (377 MHz, $CDCl_3$)** δ: -109.24.

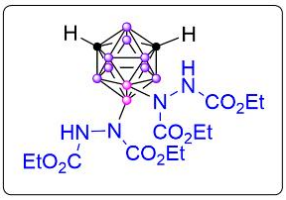
HRMS (ESI-TOF): m/z calcd for $C_{20}B_{10}H_{29}N_2O_4F_2$ $[M+H]^+$: 507.3103. Found: 507.3101. [6]



10h: Yield 65%; White solid; **Eluent:** PE/EA = 4:1 (R_f = 0.26), Mp:115-117 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.61 – 6.26 (m, 1H), 4.27 – 4.05 (m, 4H), 2.84 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 6H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 158.1, 156.5, 62.4, 61.7, 51.4, 14.4, 14.3. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** δ: 2.2 (1B), -7.4 (2B), -11.0 (1B), -14.0 (2B), -15.5 (2B), -19.0 (1B), -22.0 (1B). **IR**: 743, 1065, 1225, 1277, 1674, 2613, 3056, 3262 cm^{-1}.

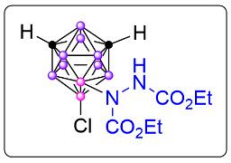
HRMS (ESI-TOF): m/z calcd for $C_8B_{10}H_{23}N_2O_4$ $[M+H]^+$: 319.2660. Found: 319.2661. [6]



10h′: Yield 26%; White solid; **Eluent:** PE/EA = 2:1 (R_f = 0.28).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 – 6.69 (m, 2H), 4.17 (s, 8H), 2.73 (s, 2H), 1.31 – 1.17 (m, 12H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 157.6, 156.4, 62.2, 61.6, 46.0, 14.5, 14.3. **^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)** δ: 0.8 (1B), 0.5 (1B), -9.5 (2B), -16.0 (4B), -24.0 (2B).

HRMS (ESI-TOF): m/z calcd for $C_{14}B_{10}H_{32}N_4O_8K$ $[M+K]^+$: 503.2801. Found: 503.2839.

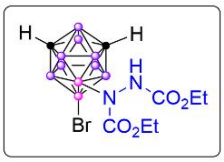


10i: Yield 61%; White solid; **Eluent:** PE/EA= 4:1 (R_f = 0.32).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.75 – 6.30 (m, 1H), 4.21 (d, *J* = 7.0 Hz, 4H), 2.83 (s, 1H), 2.79 (s, 1H), 1.28 – 1.24 (m, 6H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)** δ: 156.5, 62.7, 61.8, 47.6, 14.5,

14.3. **$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$)** δ: 1.3 (1B), -0.3 (1B), -7.5 (1B), -8.4 (1B), -15.3 (4B), -23.9 (2B).

HRMS (ESI-TOF): m/z calcd for $C_8B_{10}H_{22}N_2O_4Cl$ $[M+H]^+$: 354.2243. Found: 354.2247.



10j: Yield 48%; White solid; **Eluent:** PE/EA = 4:1 (R_f = 0.32).

^1H NMR (600 MHz, $CDCl_3$) δ: 6.80 – 6.45 (m, 1H), 4.20 (s, 4H), 2.90 (s, 1H), 2.86 (s, 1H), 1.32 – 1.20 (m, 6H). **$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$)** δ: 157.8, 156.6, 62.7, 61.8, 49.2, 48.9, 14.3, 14.2. **$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$)** δ: 1.6 (1B), -7.2 (3B), -14.8 (4B), -22.7 (2B).

HRMS (ESI-TOF): m/z calcd for $C_8B_{10}H_{22}N_2O_4Br$ $[M+H]^+$: 398.1750. Found: 398.1751.

4. References

1. Bai, F.; Yan, H. **2021**. DOI:10.27235/d.cnki.gnjiu.2021.002442.
2. Chena, J.; Chena, S.; Tanga, Y.; Moub, C.; Tsaia, F. *J. Mol. Catal. A. Chem.* **2009**, *307*, 88–92.
3. Falconnet, A.; Arndt, J.; Hashmi, A. S. K.; Schaub, T. *Eur. J. Org. Chem.* **2022**, e202200477, 1-5.
4. Ma, Y.-N.; Ren, H.; Wu, Y.; Li, N.; Chen, F.; Chen, X.-N. *J. Am. Chem. Soc.* **2023***, 145,* 7331−7342.
5. Lu, W.; Wu, Y.; Ma, Y.-N.; Chen, F.; Chen, X.-N. *Inorg. Chem.* **2023**, *62*, 885−892.
6. Wang, Y.; Gao, Y.; Guo, W.; Zhao, Q.-Y.; Ma, Y.-N.; Chen, X.-N. *Org. Chem. Front.,* **2022***, 9,* 4975–4980.

5. X-ray Structure Determination

Single crystal XRD analysis of the **7a** compound was recorded on a SuperNova Dual diffractometer using graphite-monochromated Cu Kα radiation, λ = 1.54184 Å. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography. Empirical absorption corrections were applied. Structures were solved using direct methods (SHELXT) and refined by full-matrix least-squares (SHELXL) interfaced with the programme OLEX2. Crystal data and details of data collection and structure refinements are given in **Table S2**.

Further details on the crystal structure investigations can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/ by quoting the depository numbers CCDC- 2358875 (**7a**).

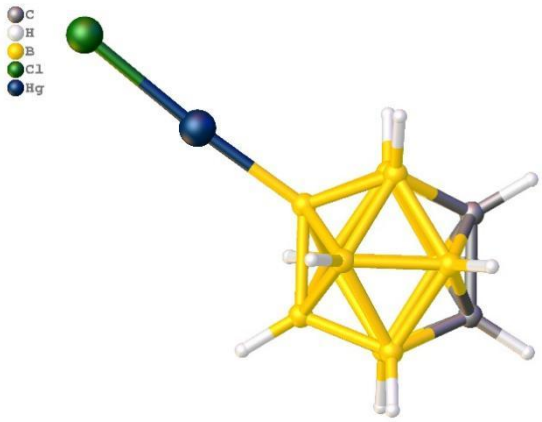
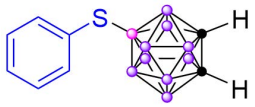


Figure S2. Molecular Structure of **7a**

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

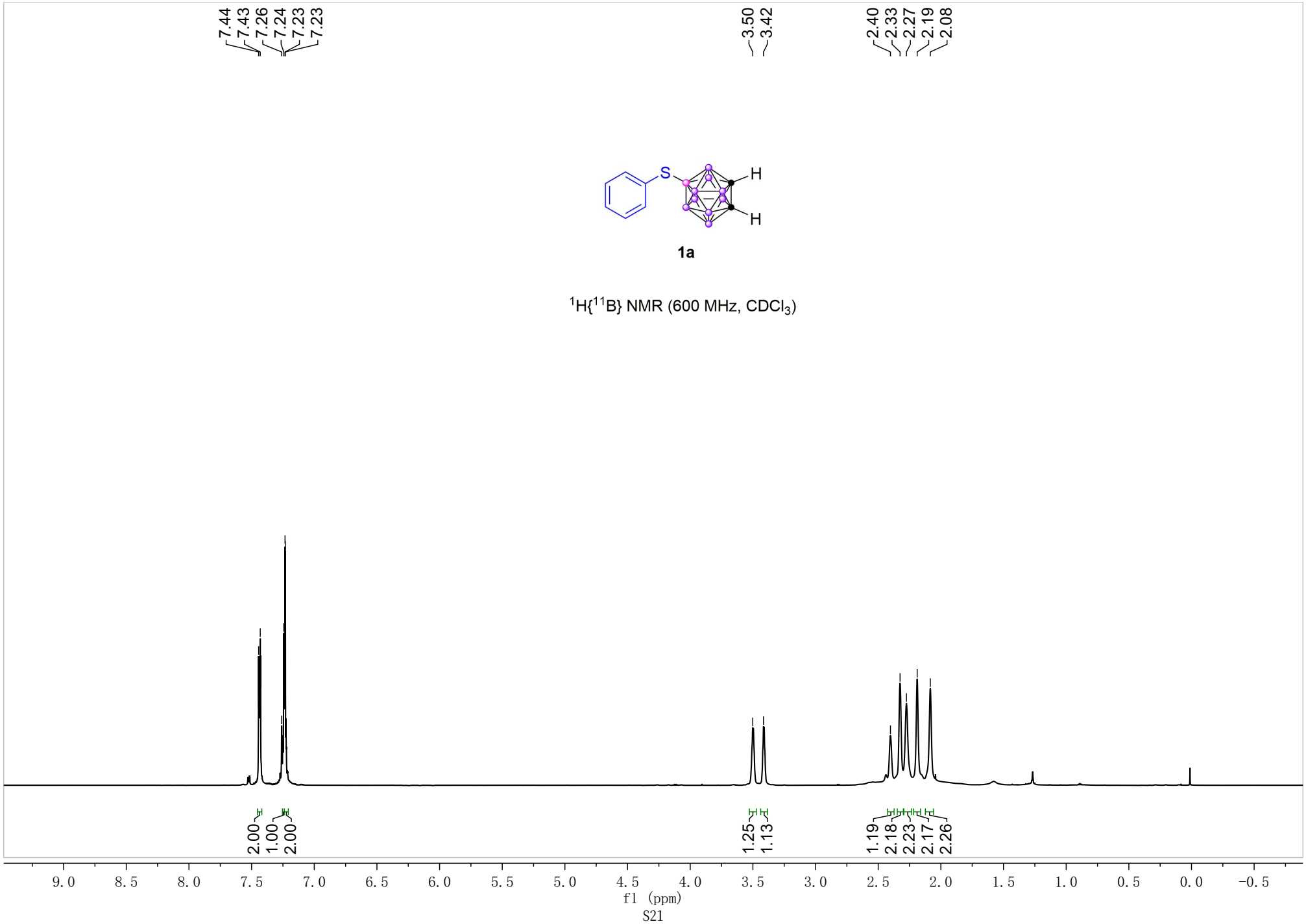
compound	**7a**
formula	$C_2H_{11}B_{10}ClHg$
Formula weight	379.25
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.73953(18)
b/Å	21.6921(6)
c/Å	7.3452(2)
α/°	90
β/°	91.737(2)
γ/°	90
Volume/Å^3	1073.33(5)
Z	4
ρ_{calc}g/cm^3	2.347
μ/mm^{-1}	27.444
F(000)	680.0
Crystal size/mm^3	0.138 × 0.123 × 0.059
Radiation	Cu Kα (λ = 1.54184)
Reflections collected	3825
Independent reflections	[R_{int} = 0.0512, R_{sigma} = 0.0634]
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R1 = 0.0434, wR2 = 0.1166
Final R indexes [all data]	R1 = 0.0508, wR2 = 0.1238

6. NMR spectra



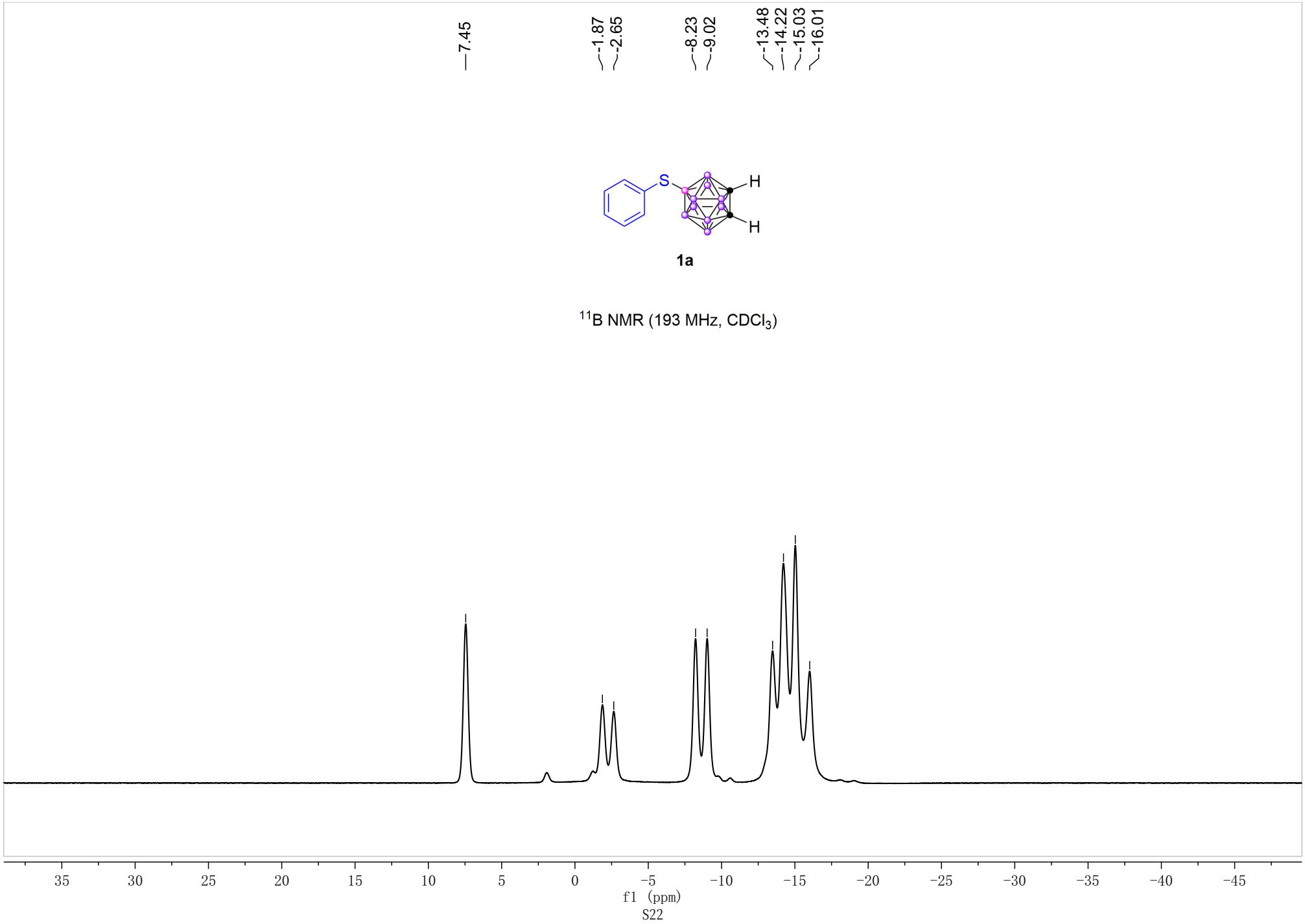
1a

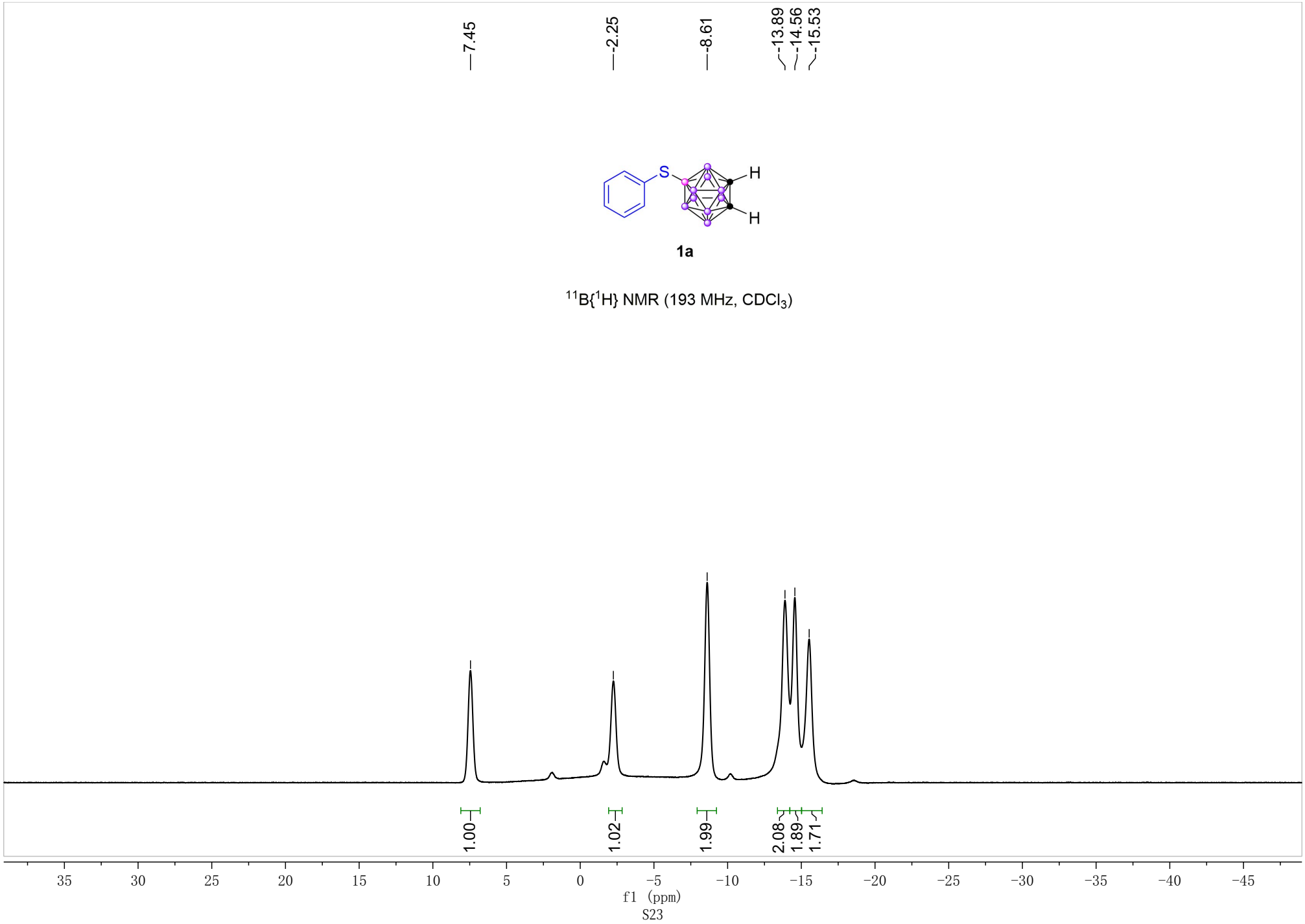
^{1}H NMR (600 MHz, $CDCl_3$)

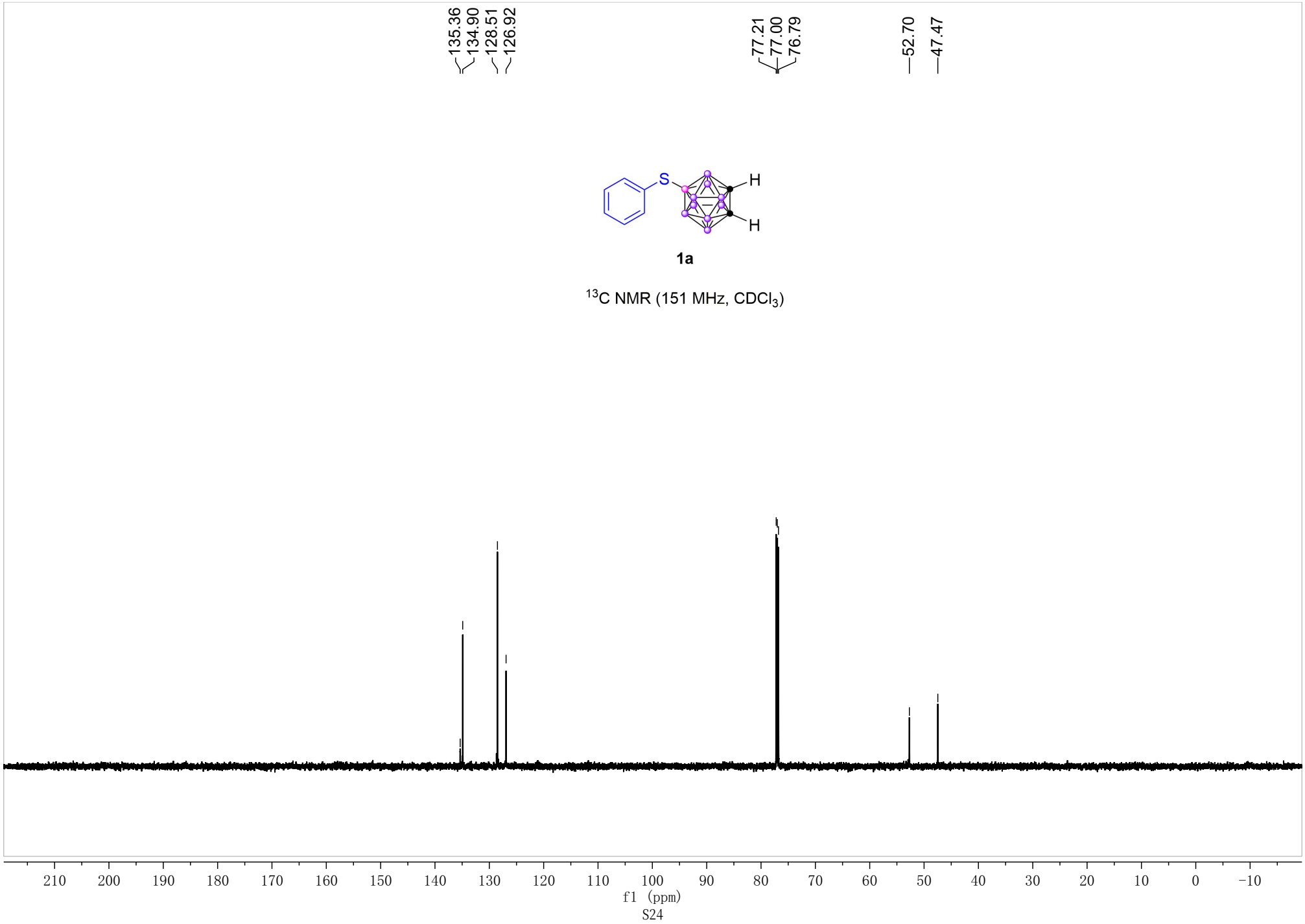


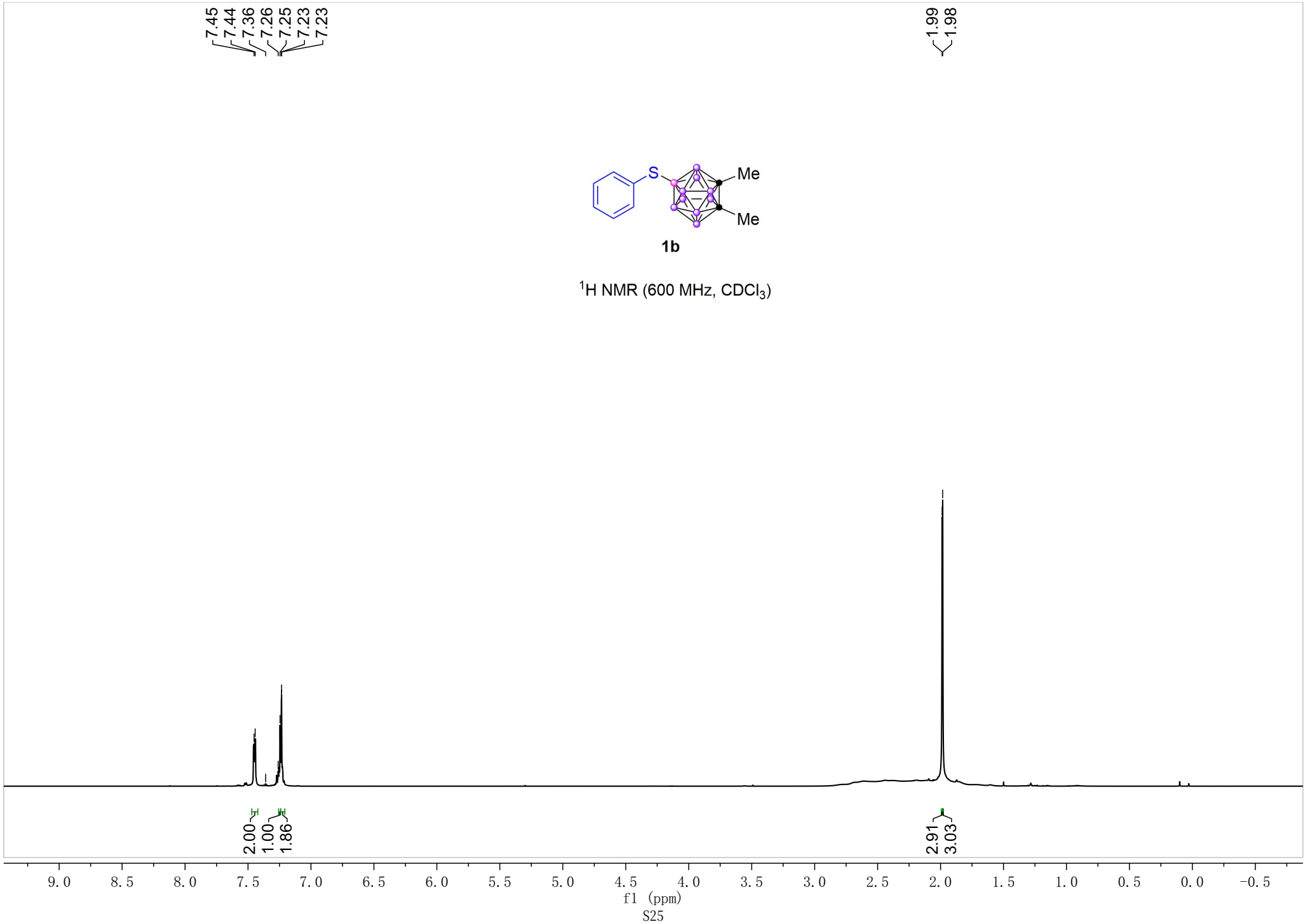
1a

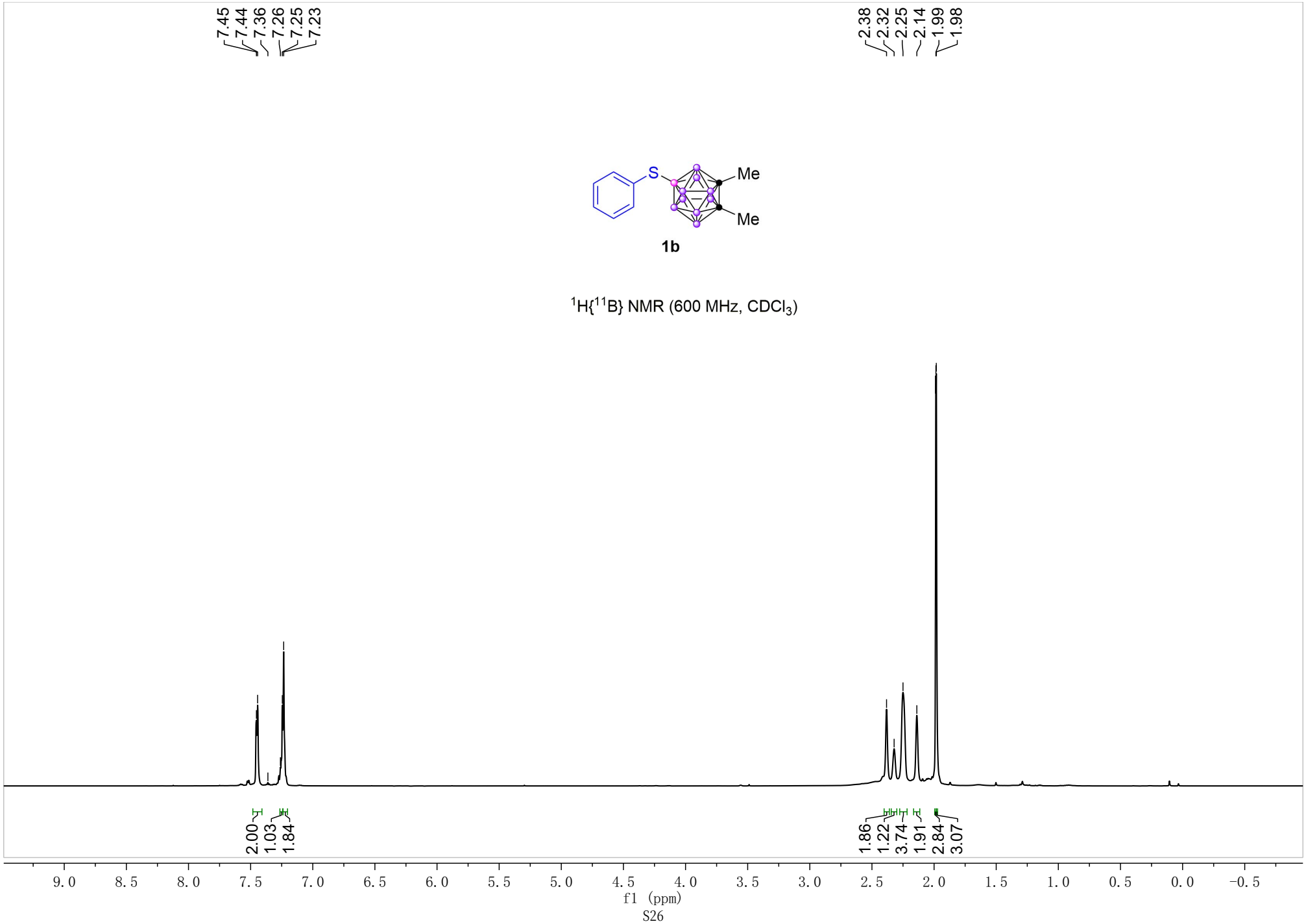
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)

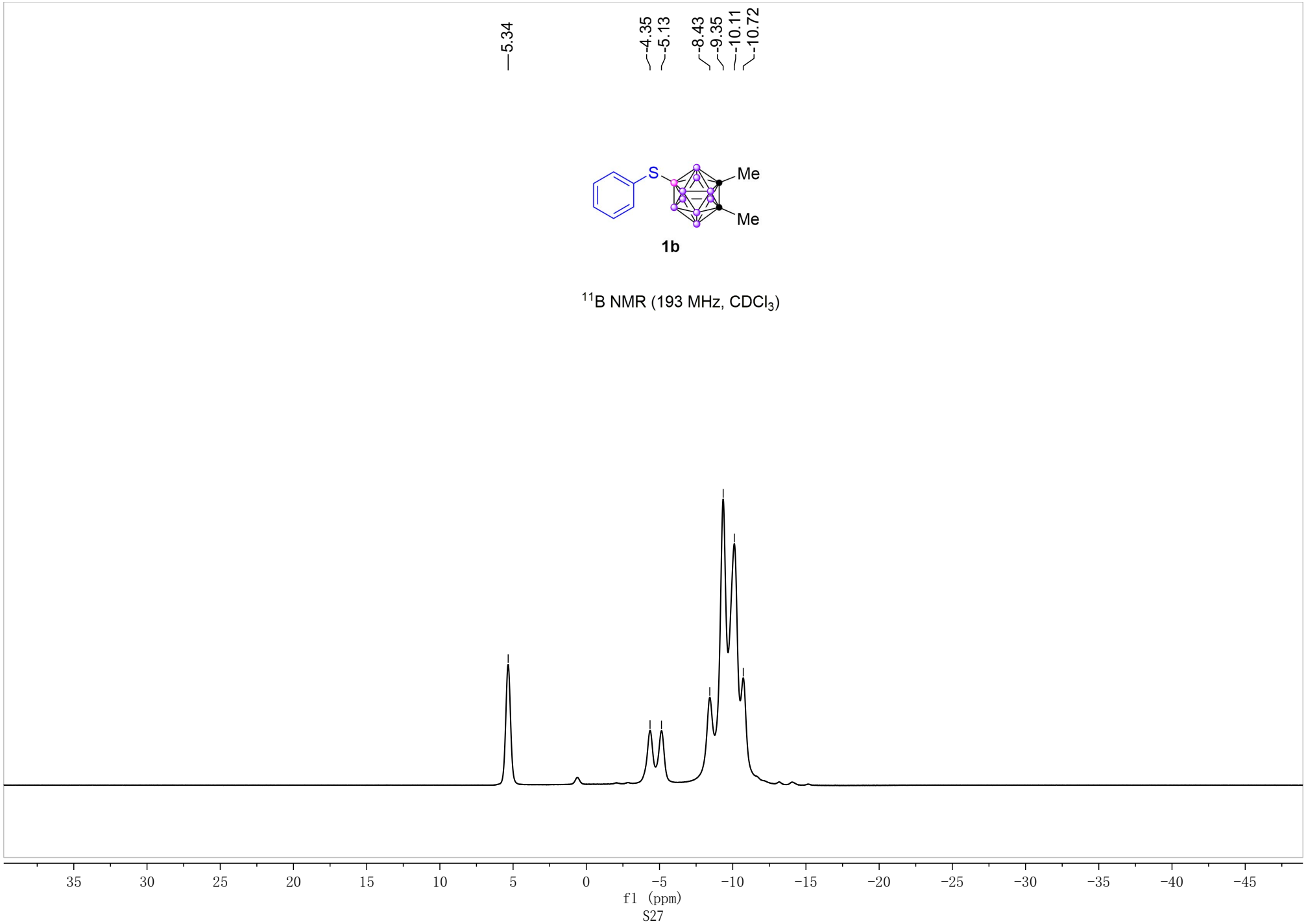

7.45
1.87
2.65
8.23
9.02
13.48
14.22
15.03
16.01
S
H
H
1a
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

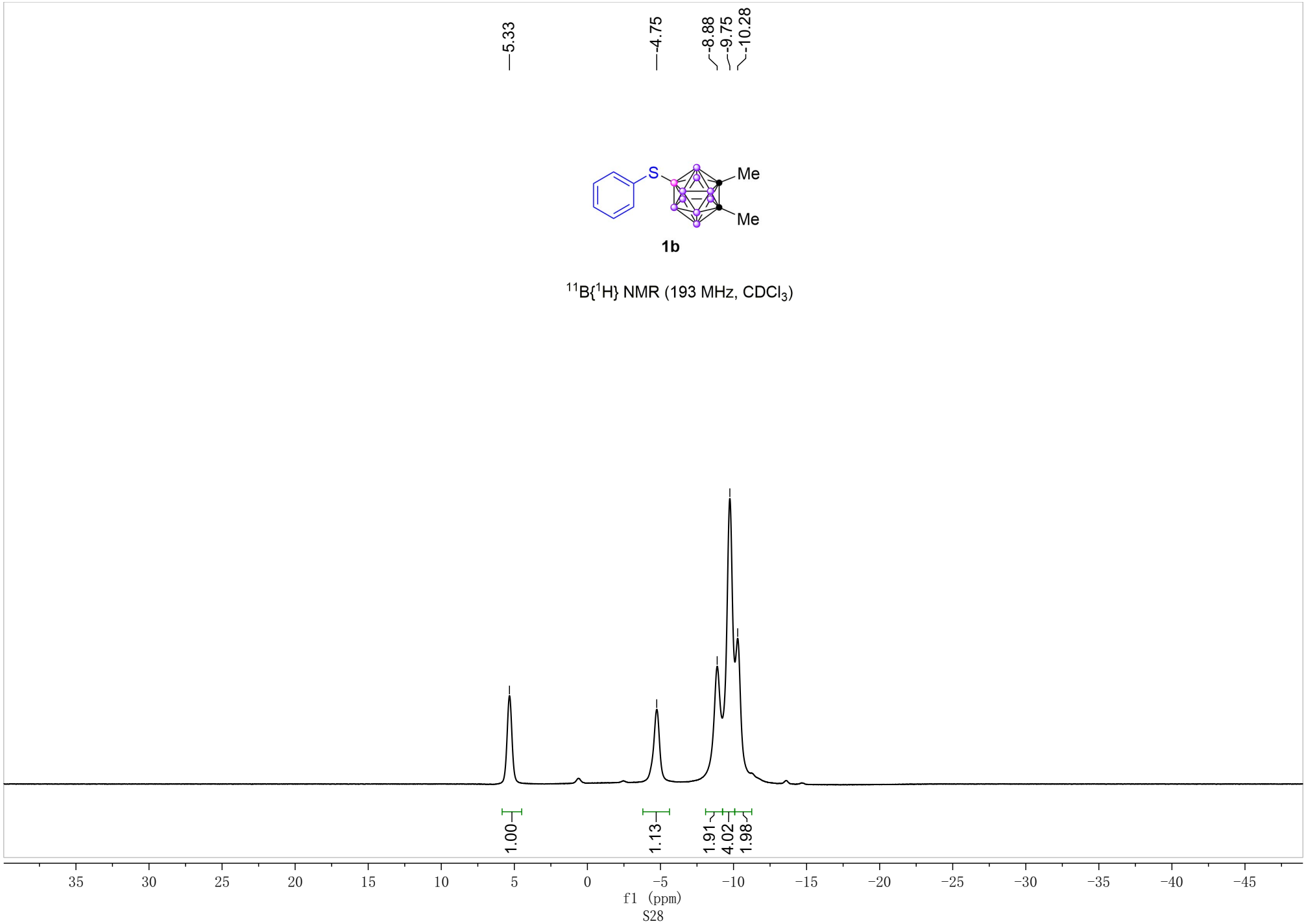

7.45
-2.25
-8.61
-13.89
-14.56
-15.53
S
H
H
1a
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
1.02
1.99
2.08
1.89
1.71
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

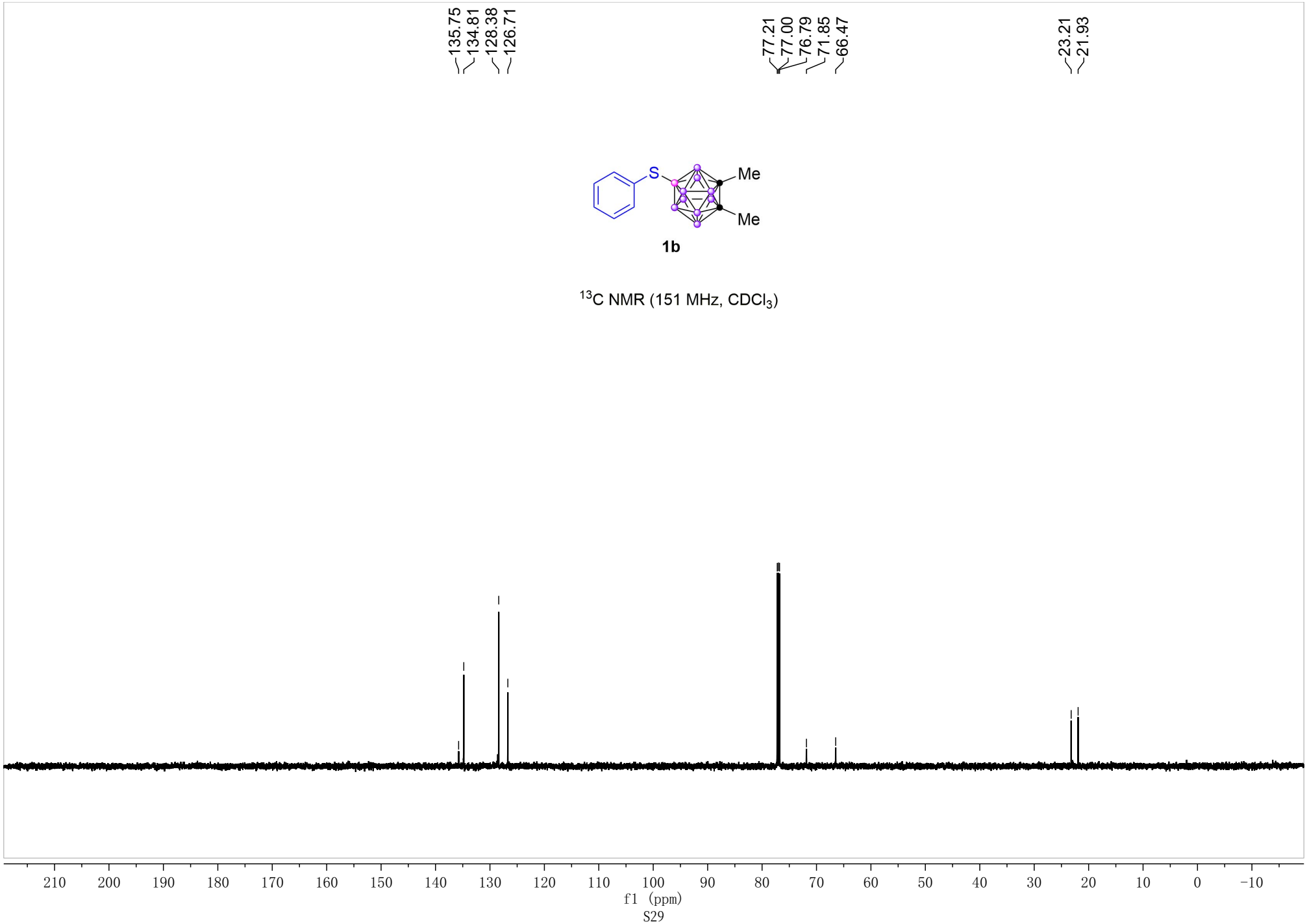

135.36
134.90
128.51
126.92
77.21
77.00
76.79
52.70
47.47
S
H
H
1a
^{13}C NMR (151 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

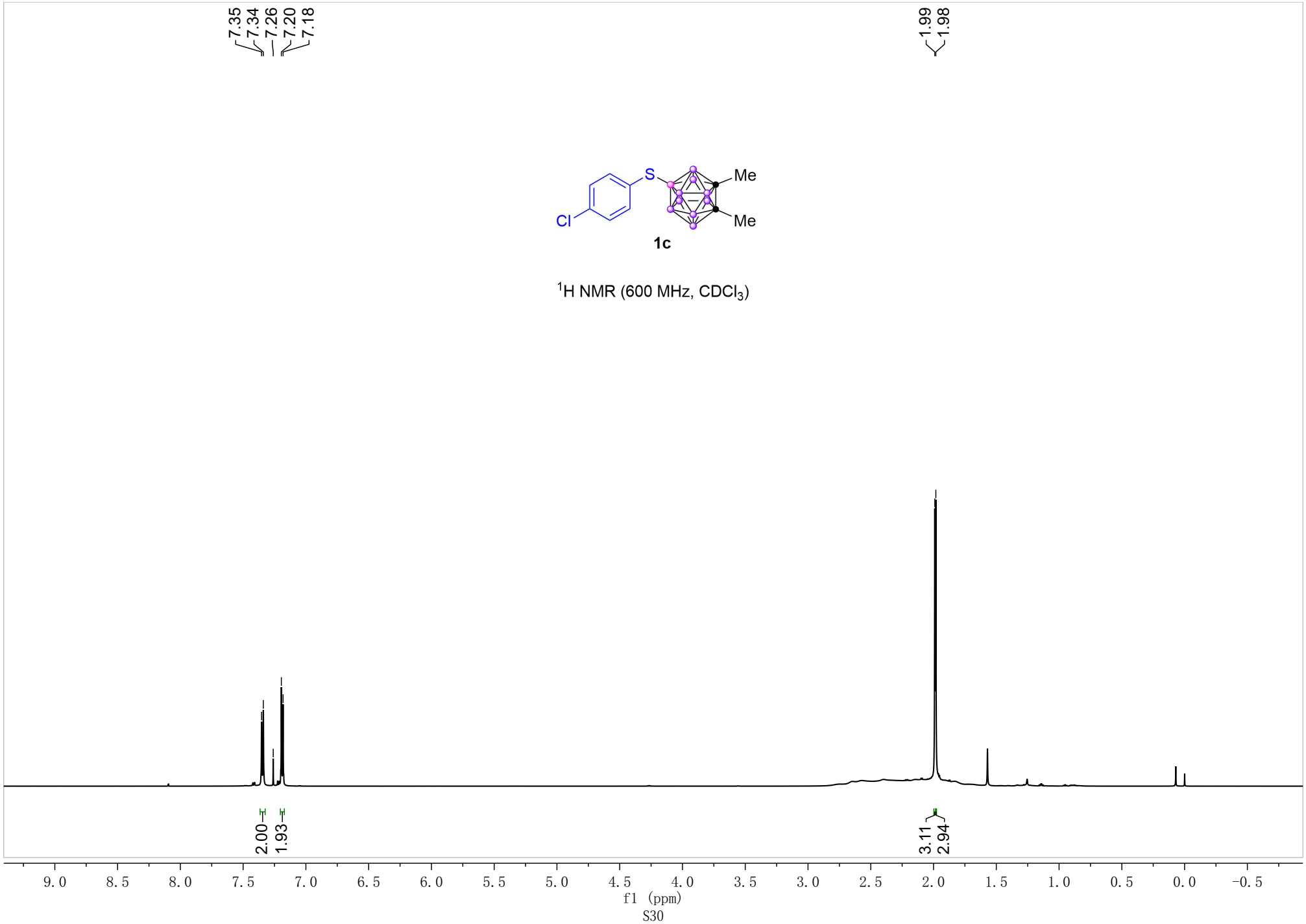

7.45
7.44
7.36
7.26
7.25
7.23
7.23
1.99
1.98
S
Me
Me
1b
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
1.00
1.86
2.91
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

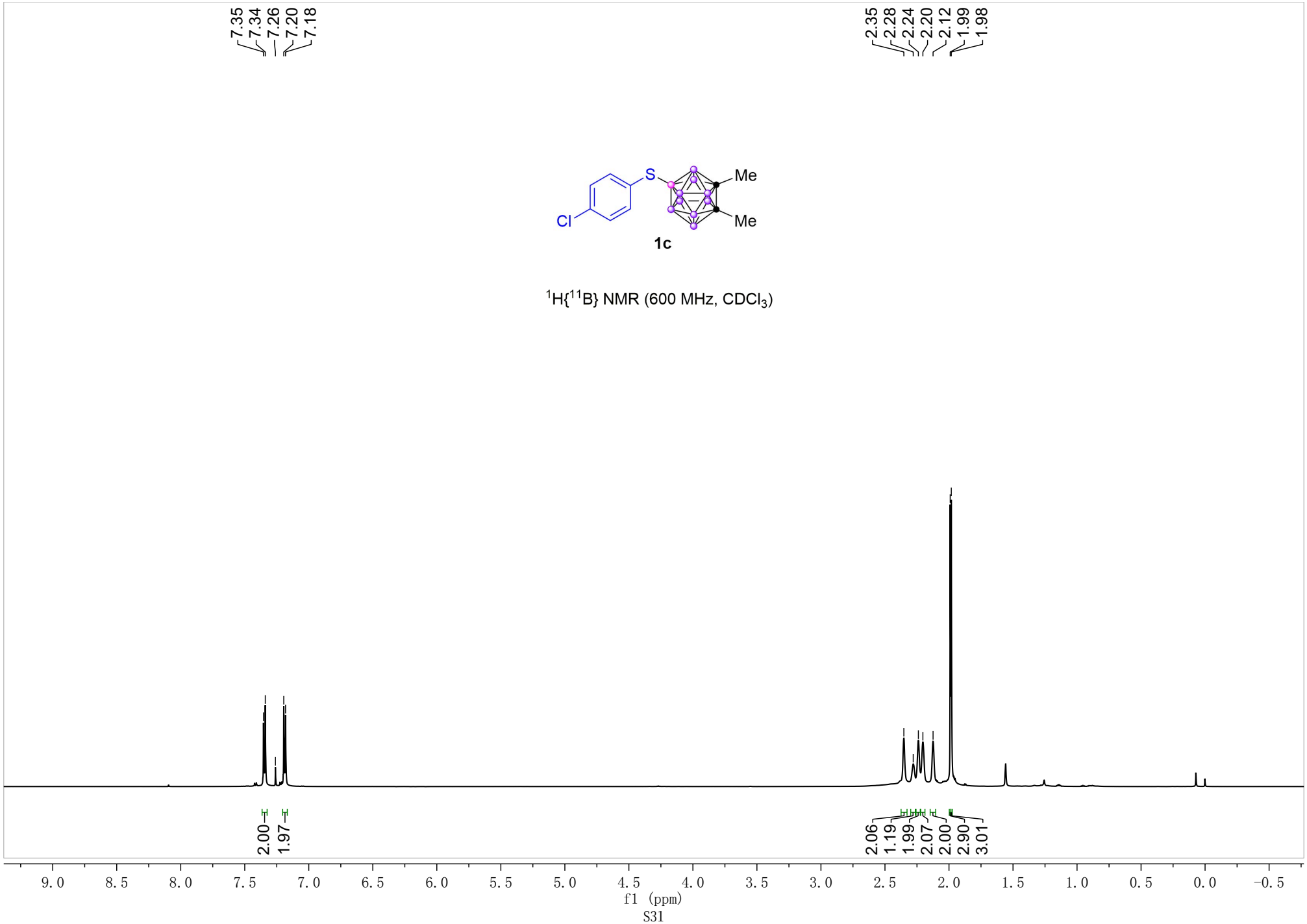

7.45
7.44
7.36
7.26
7.25
7.23
2.38
2.32
2.25
2.14
1.99
1.98
S
Me
Me
1b
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)
2.00
1.03
1.84
1.86
1.22
3.74
1.91
2.84
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

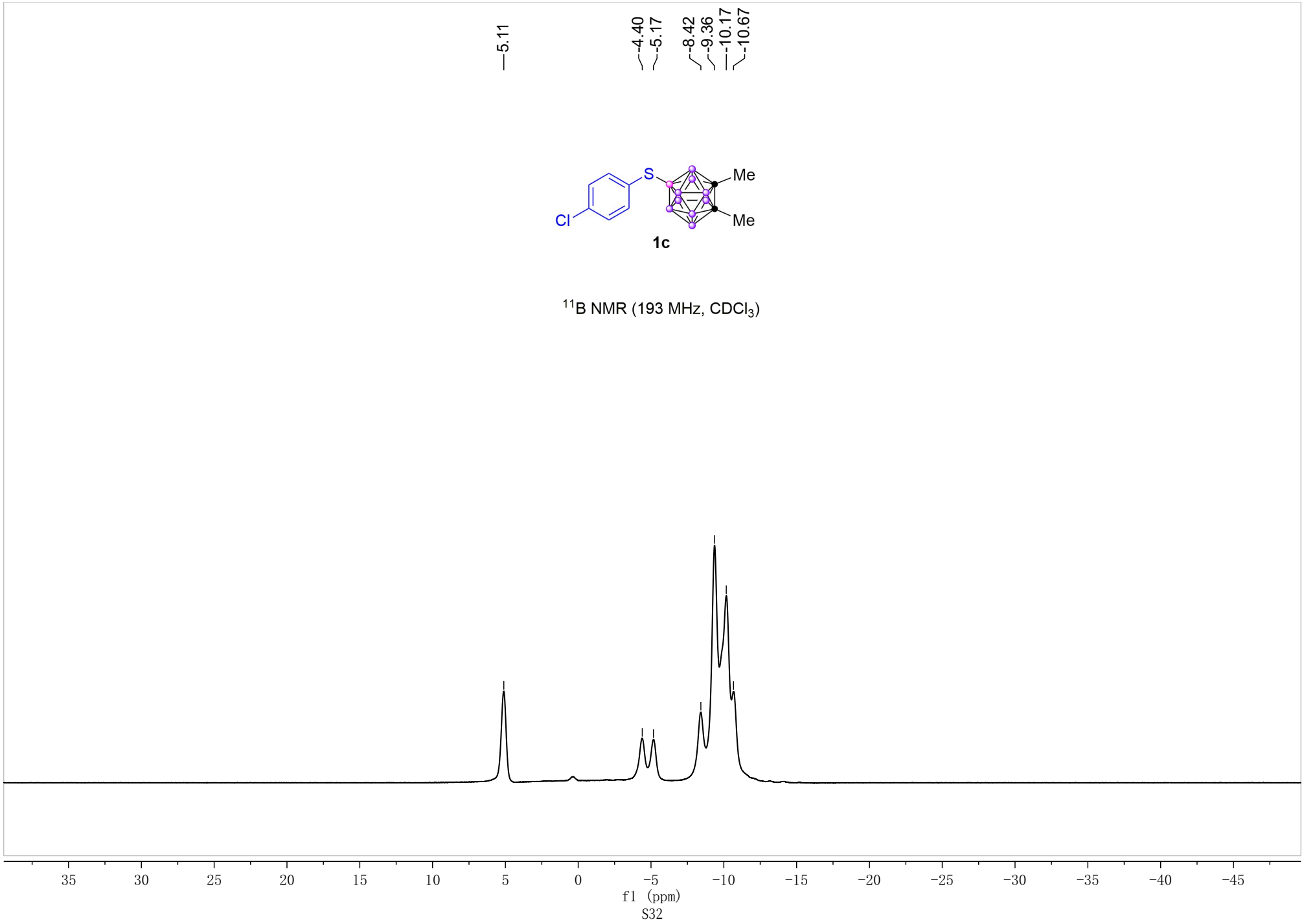

5.34
-4.35
-5.13
-8.43
-9.35
-10.11
-10.72
S
Me
Me
1b
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

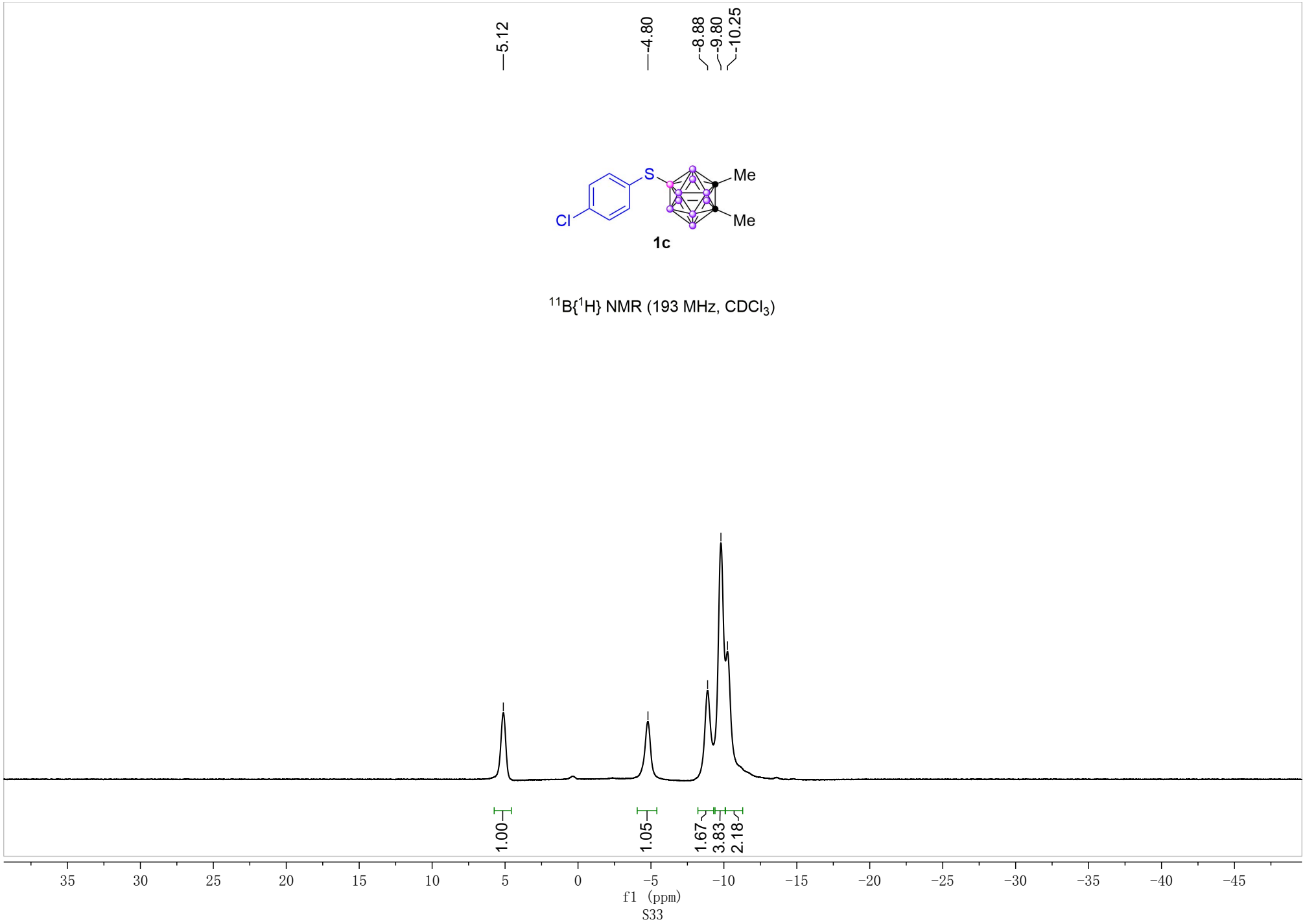

5.33
-4.75
-8.88
-9.75
-10.28
S
Me
Me
1b
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
1.13
1.91
4.02
1.98
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

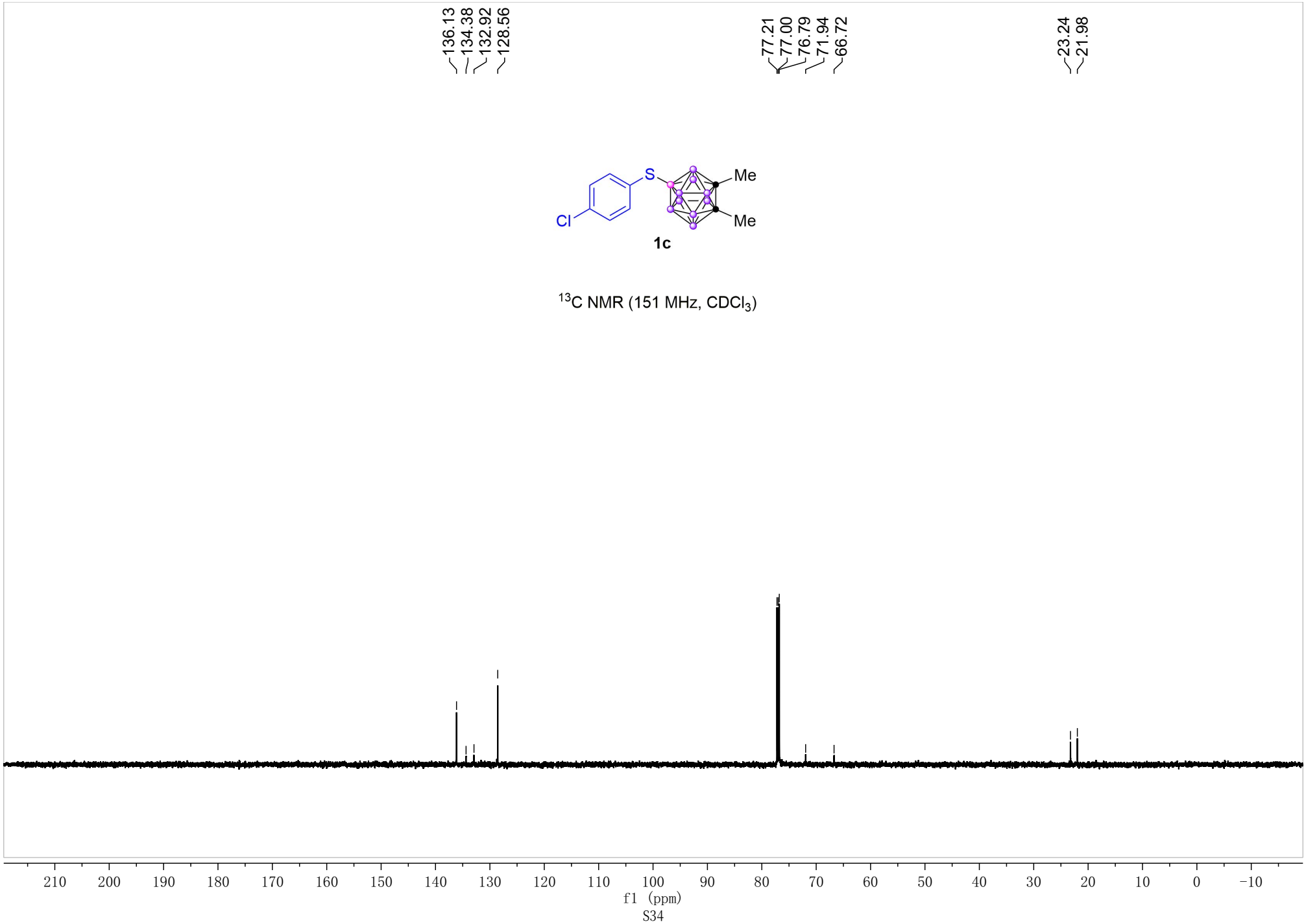

135.75
134.81
128.38
126.71
77.21
77.00
76.79
71.85
66.47
23.21
21.93
S
Me
Me
1b
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

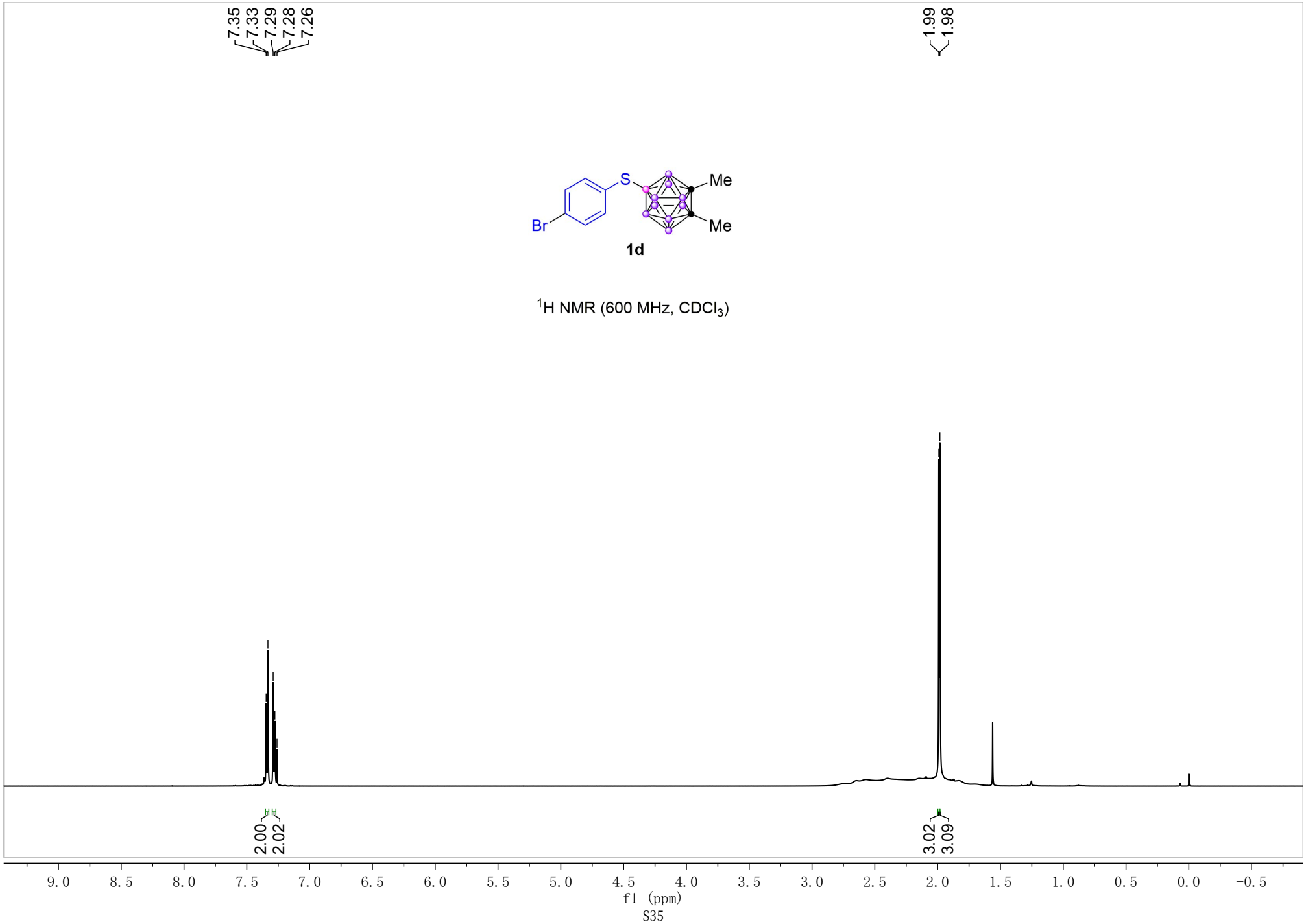

7.35
7.34
7.26
7.20
7.18
1.99
1.98
S
Cl
Me
Me
1c
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
1.93
3.11
2.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

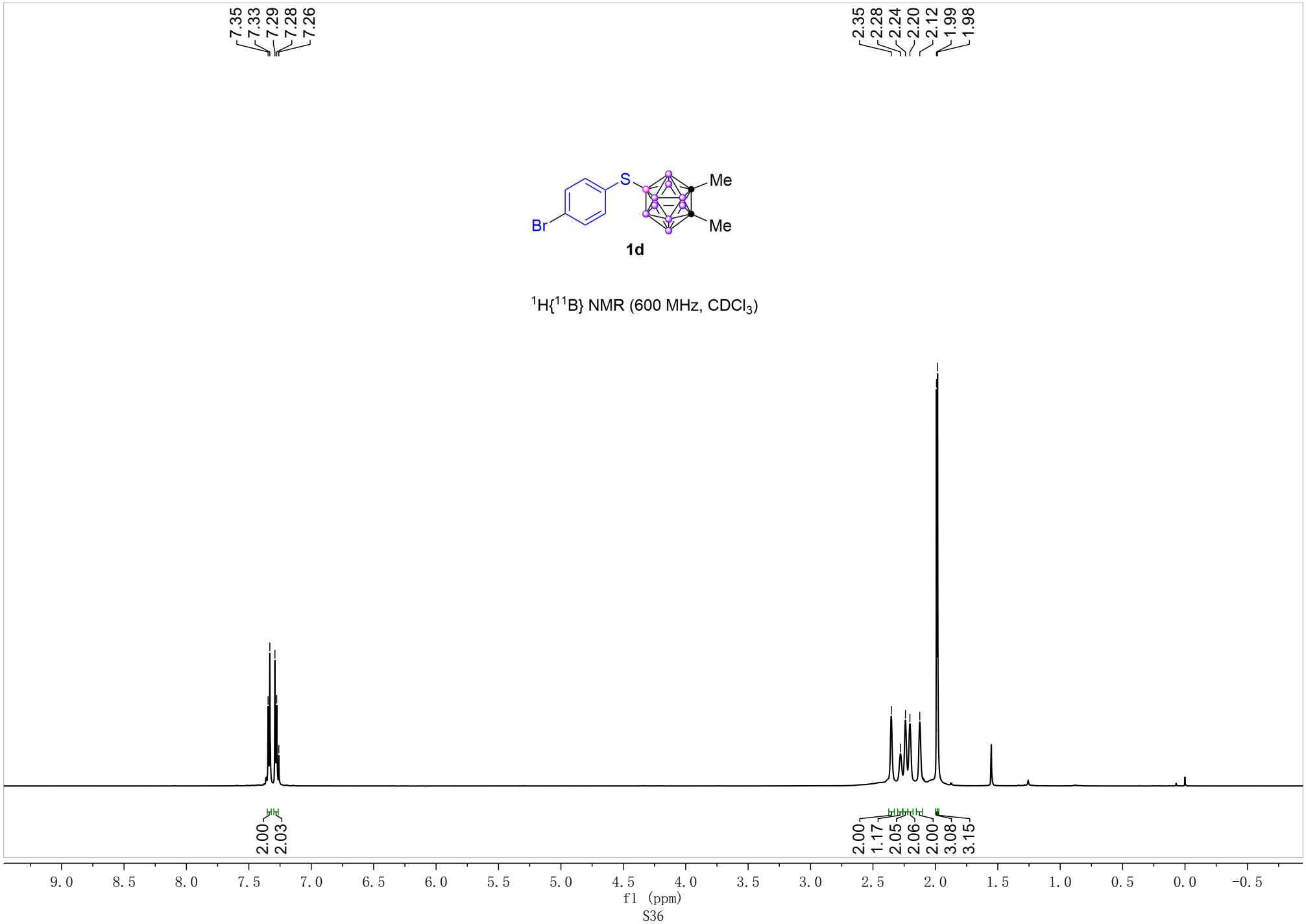

7.35
7.34
7.26
7.20
7.18
2.35
2.28
2.24
2.20
2.12
1.99
1.98
S
Me
Me
Cl
1c
$^1H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)
2.00
1.97
2.06
1.19
1.99
2.07
2.00
2.90
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


5.11
-4.40
-5.17
-8.42
-9.36
-10.17
-10.67
S
Me
Me
Cl
1c
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)


5.12
4.80
8.88
9.80
10.25
S
Cl
Me
Me
1c
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
1.05
1.67
3.83
2.18
35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45
f1 (ppm)

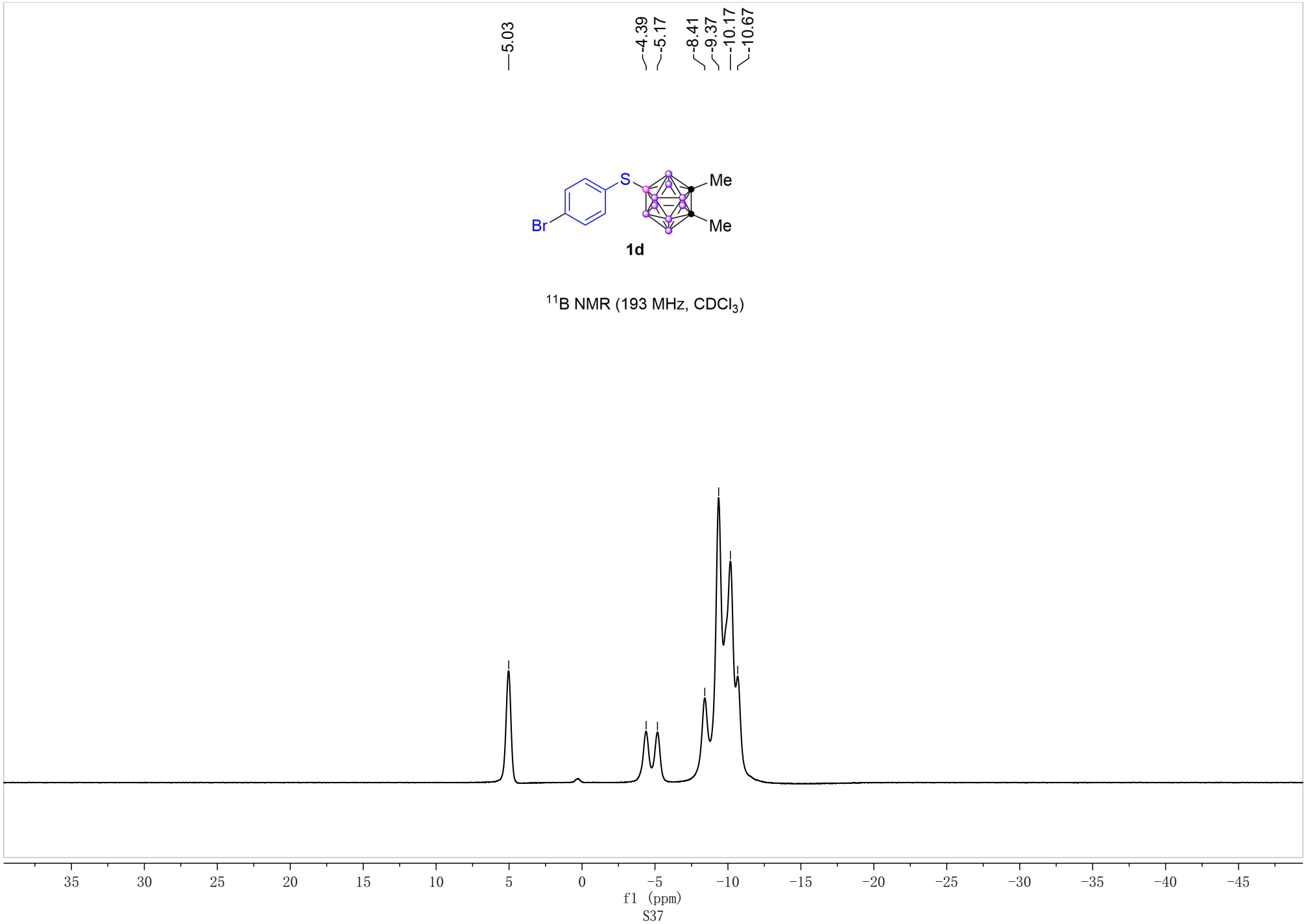

136.13
134.38
132.92
128.56
77.21
77.00
76.79
71.94
66.72
23.24
21.98
S
Me
Me
Cl
1c
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

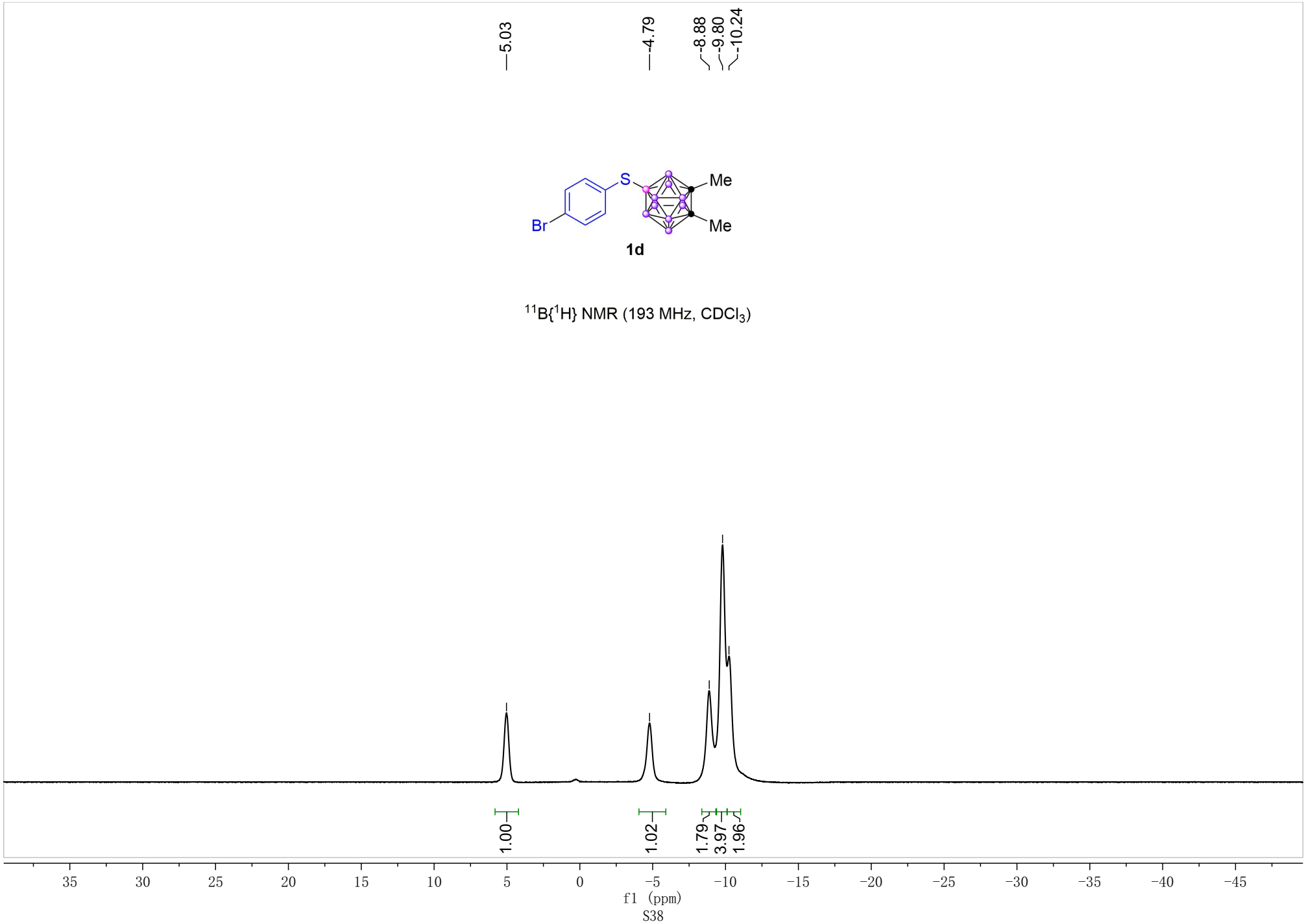

7.35
7.33
7.29
7.28
7.26
1.99
1.98
S
Me
Me
Br
1d
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
2.02
3.02
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

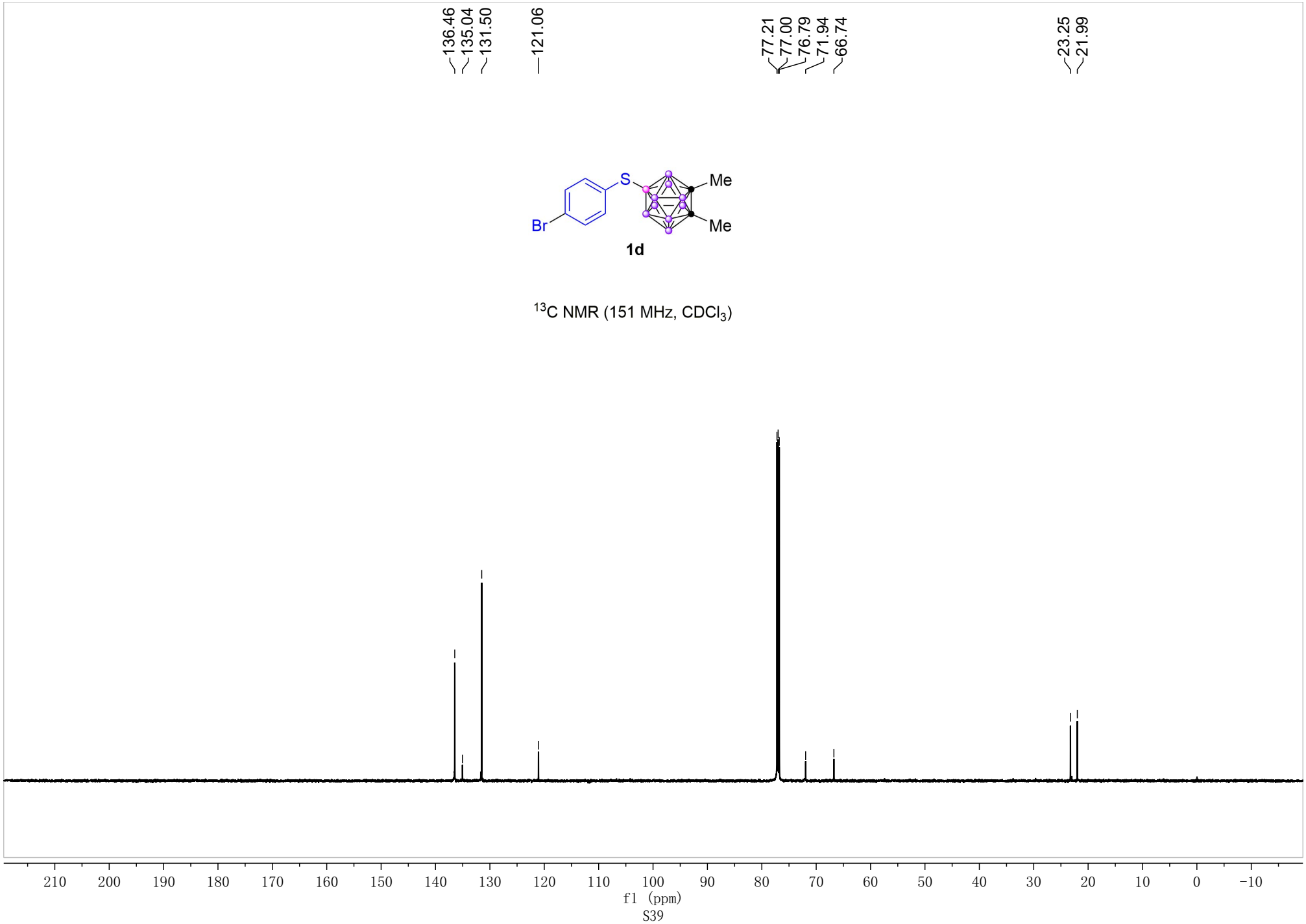


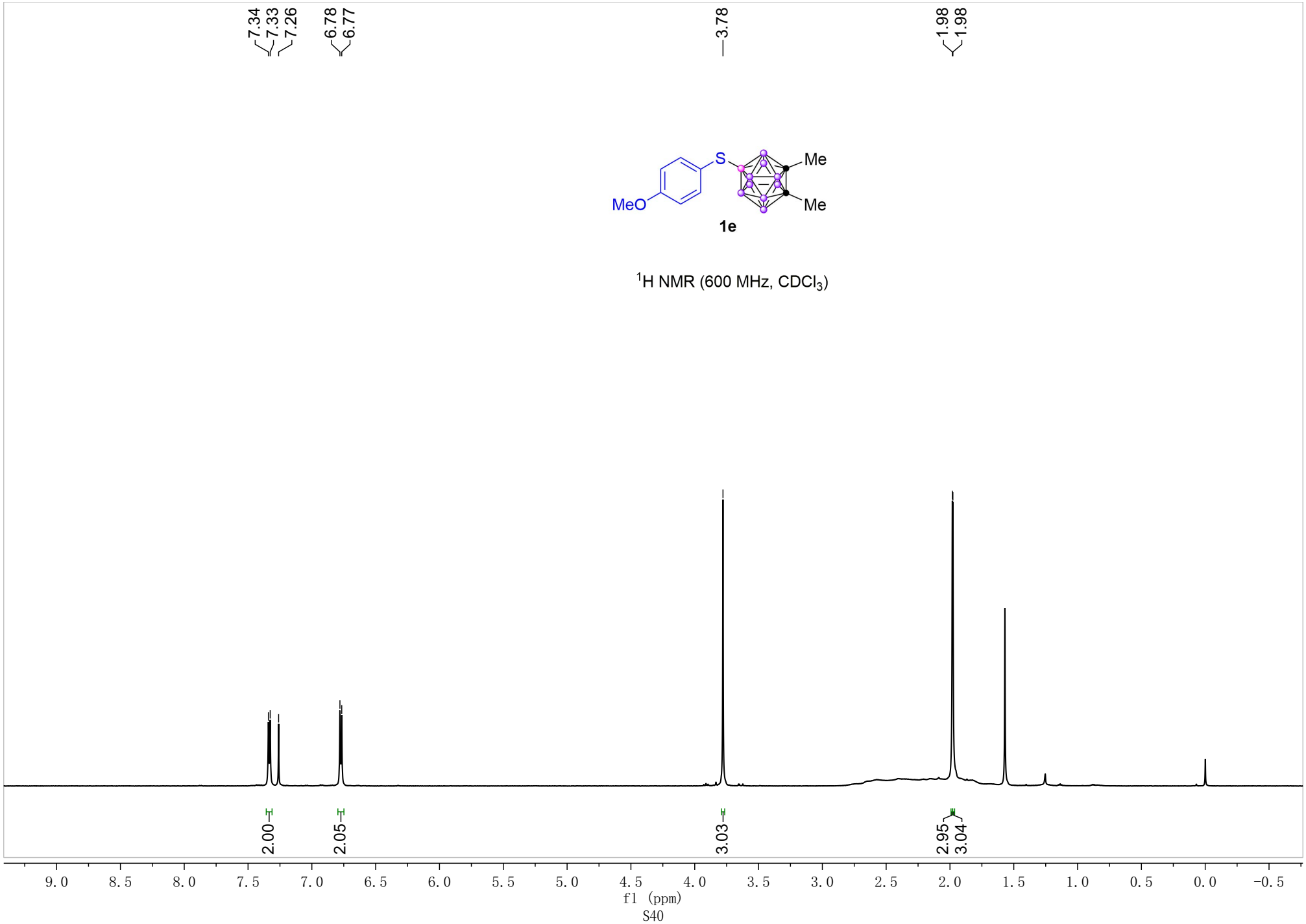
1d

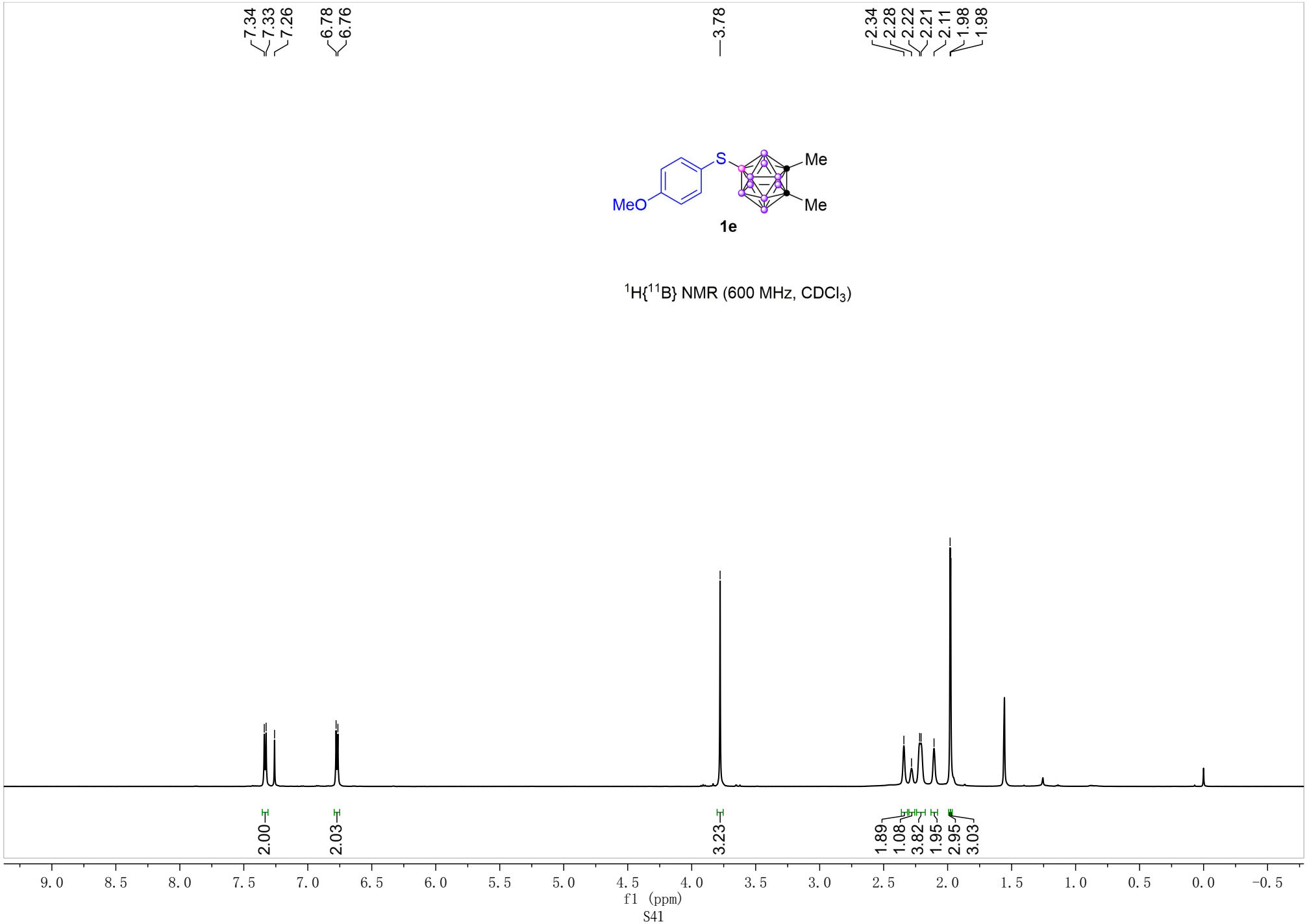
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)

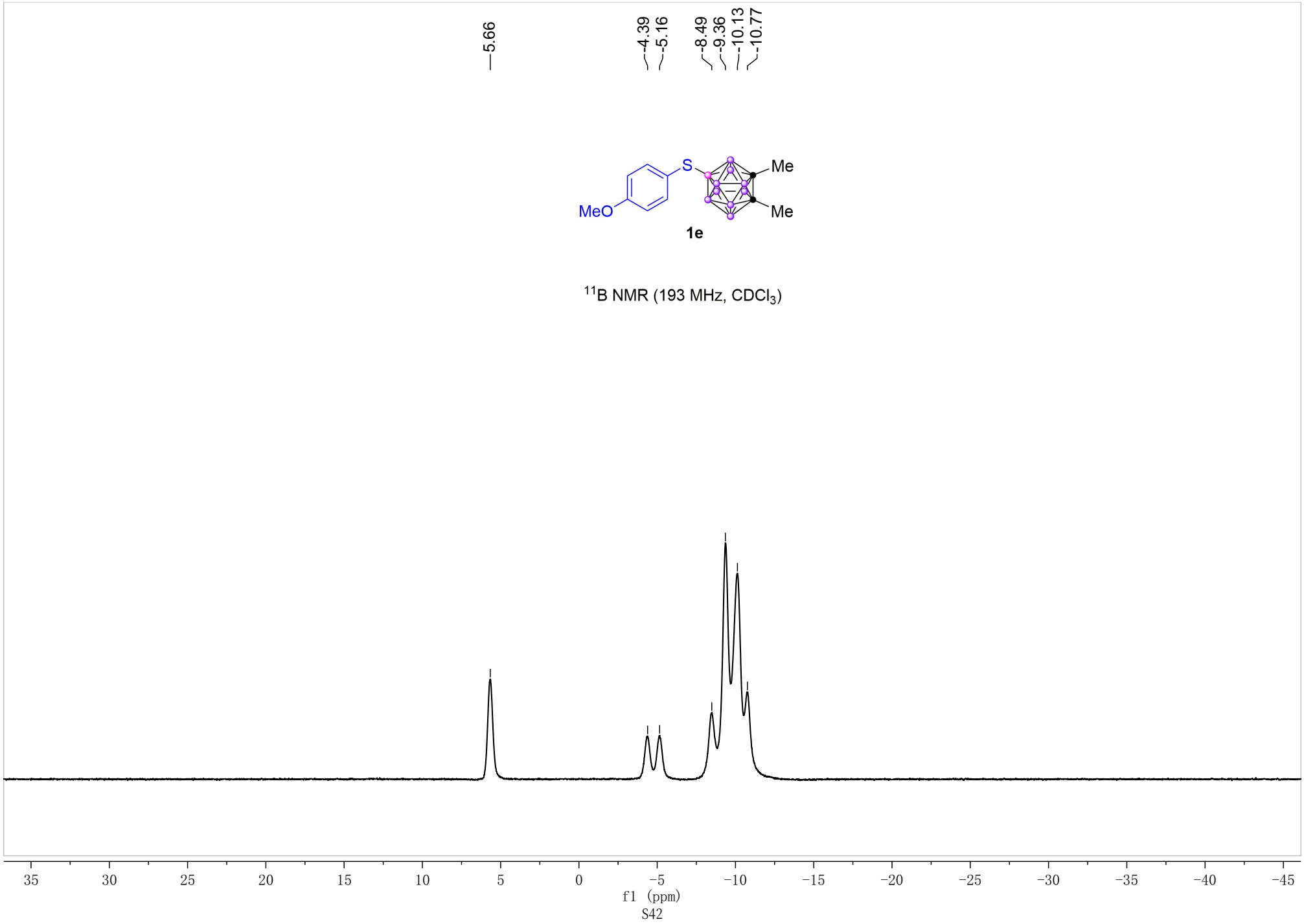

5.03
-4.39
-5.17
-8.41
-9.37
-10.17
-10.67
S
Me
Me
Br
1d
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

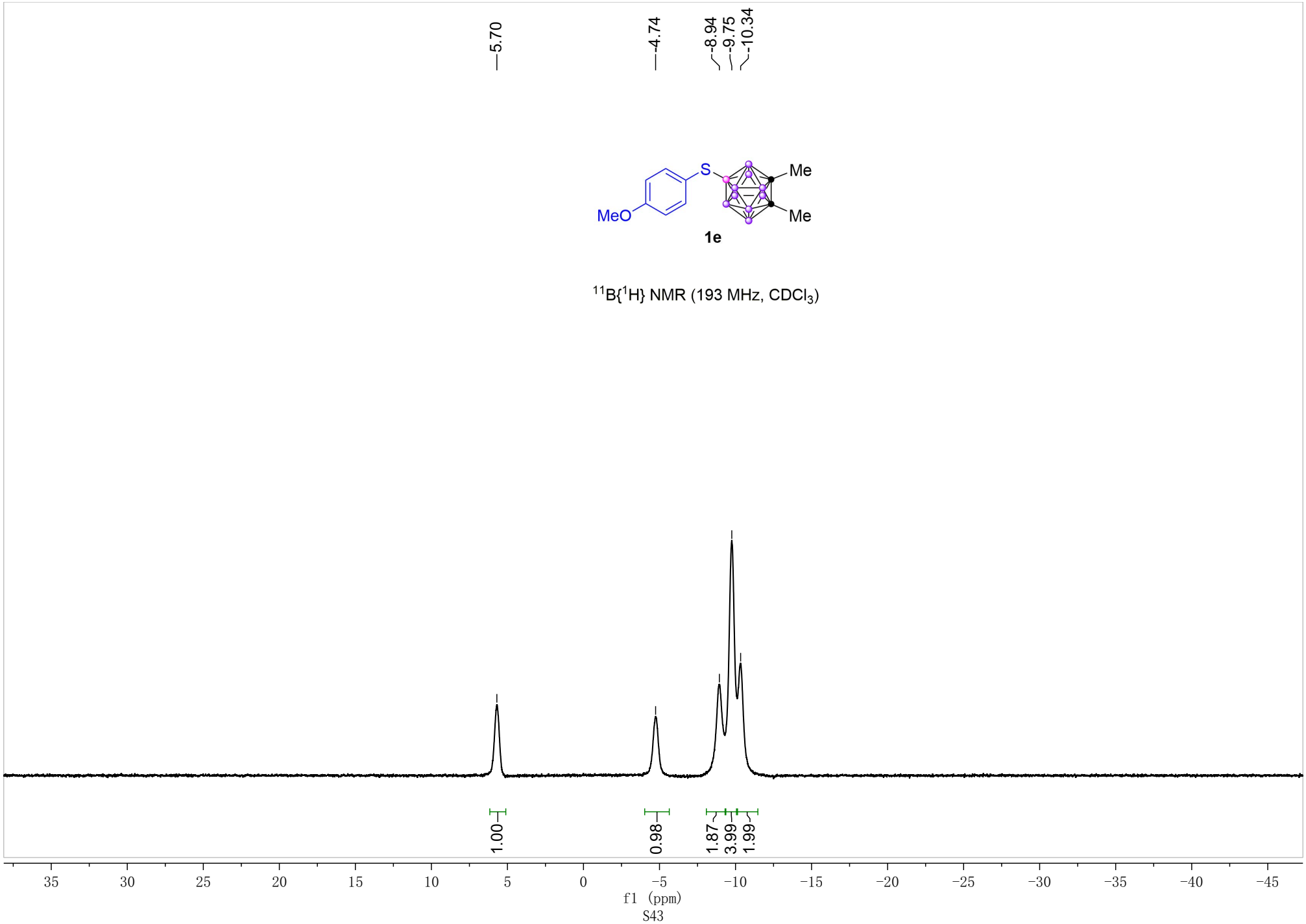

5.03
4.79
8.88
9.80
10.24
S
Me
Me
Br
1d
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
1.02
1.79
3.97
1.96
35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45
f1 (ppm)

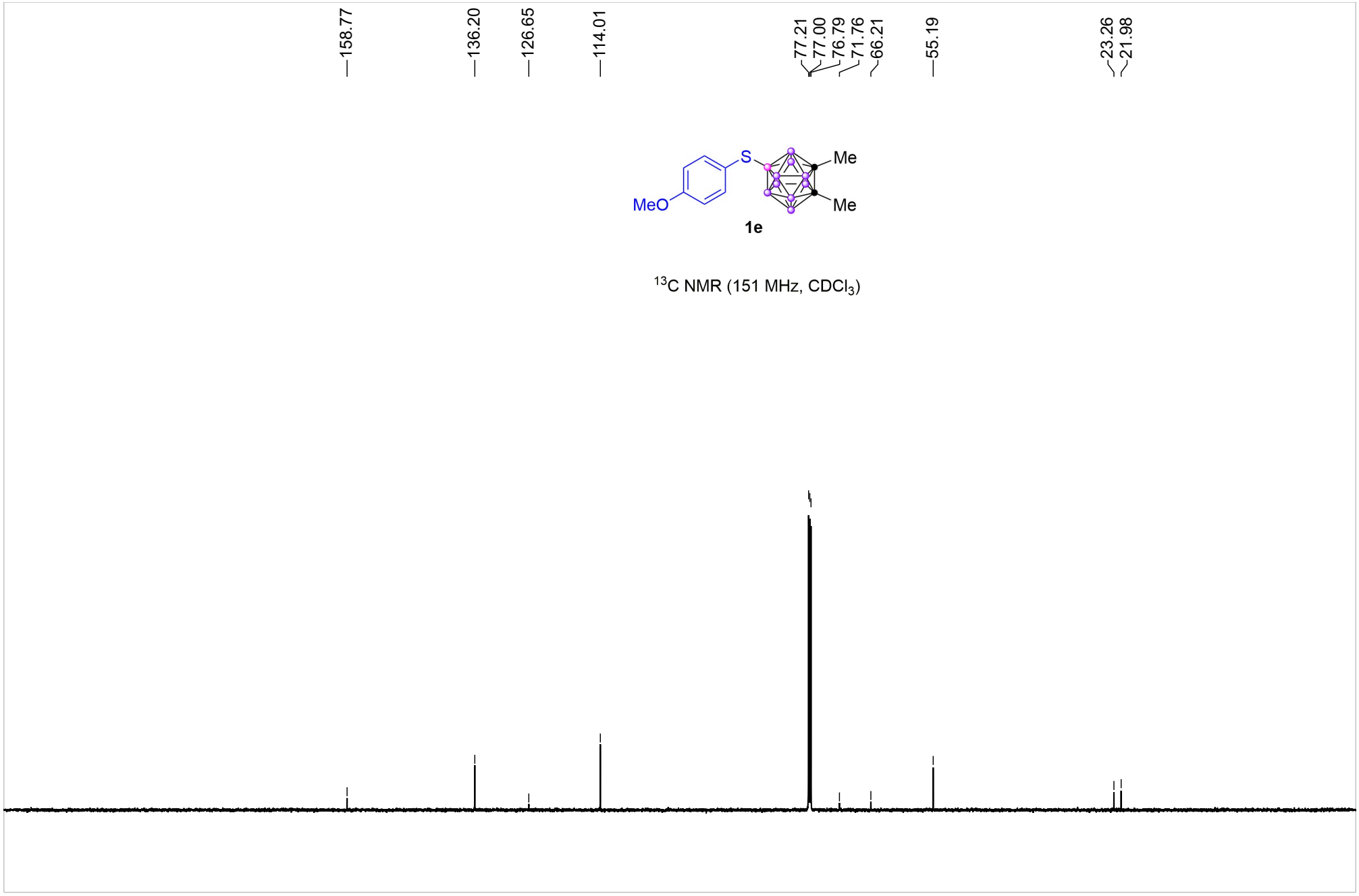

136.46
135.04
131.50
121.06
77.21
77.00
76.79
71.94
66.74
23.25
21.99
S
Me
Me
Br
1d
^{13}C NMR (151 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

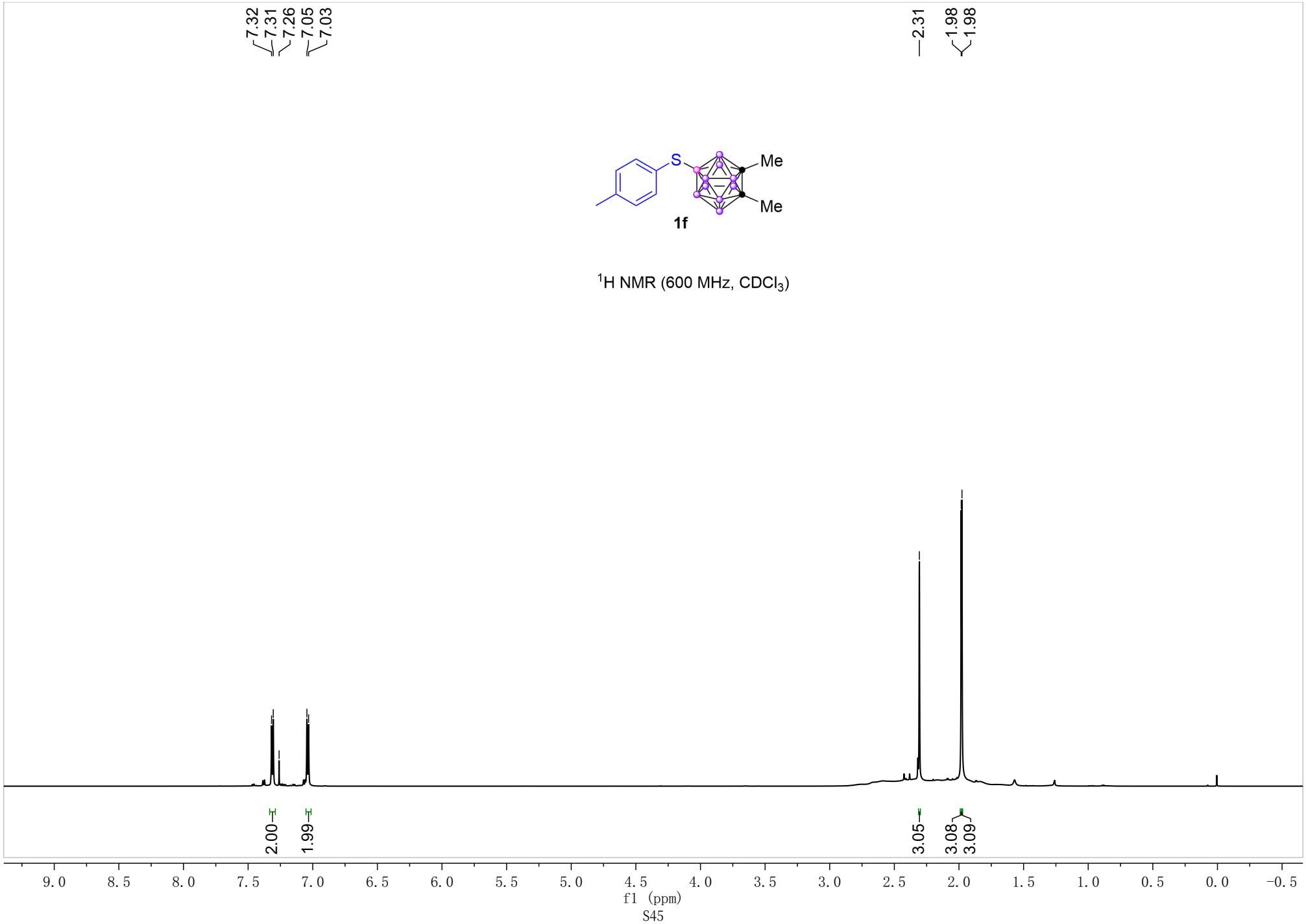

7.34
7.33
7.26
6.78
6.77
3.78
1.98
1.98
S
Me
Me
MeO
1e
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
2.05
3.03
2.95
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

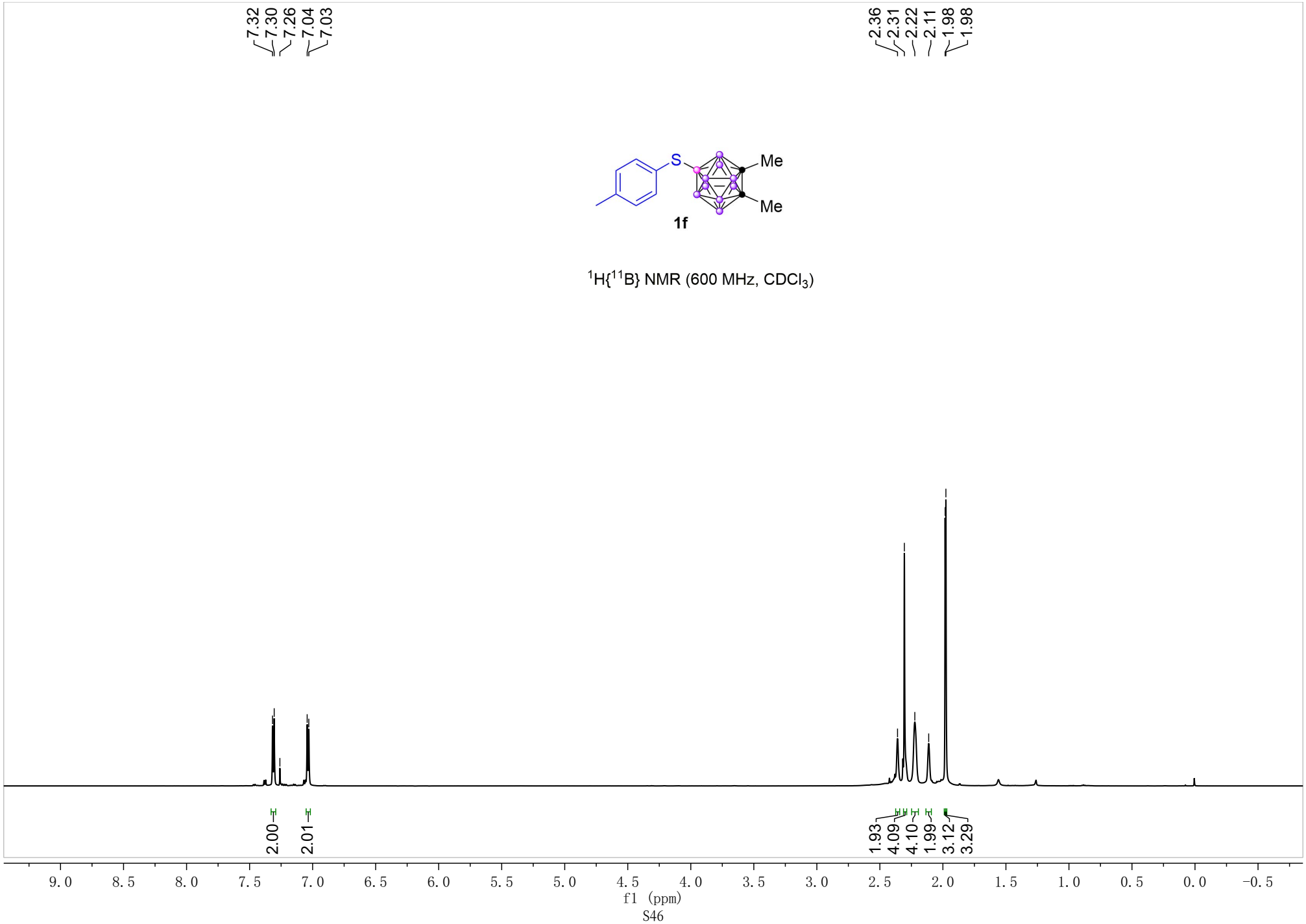

7.34
7.33
7.26
6.78
6.76
3.78
2.34
2.28
2.22
2.21
2.11
1.98
1.98
S
Me
Me
MeO
1e
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)
2.00
2.03
3.23
1.89
1.08
3.82
1.95
2.95
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

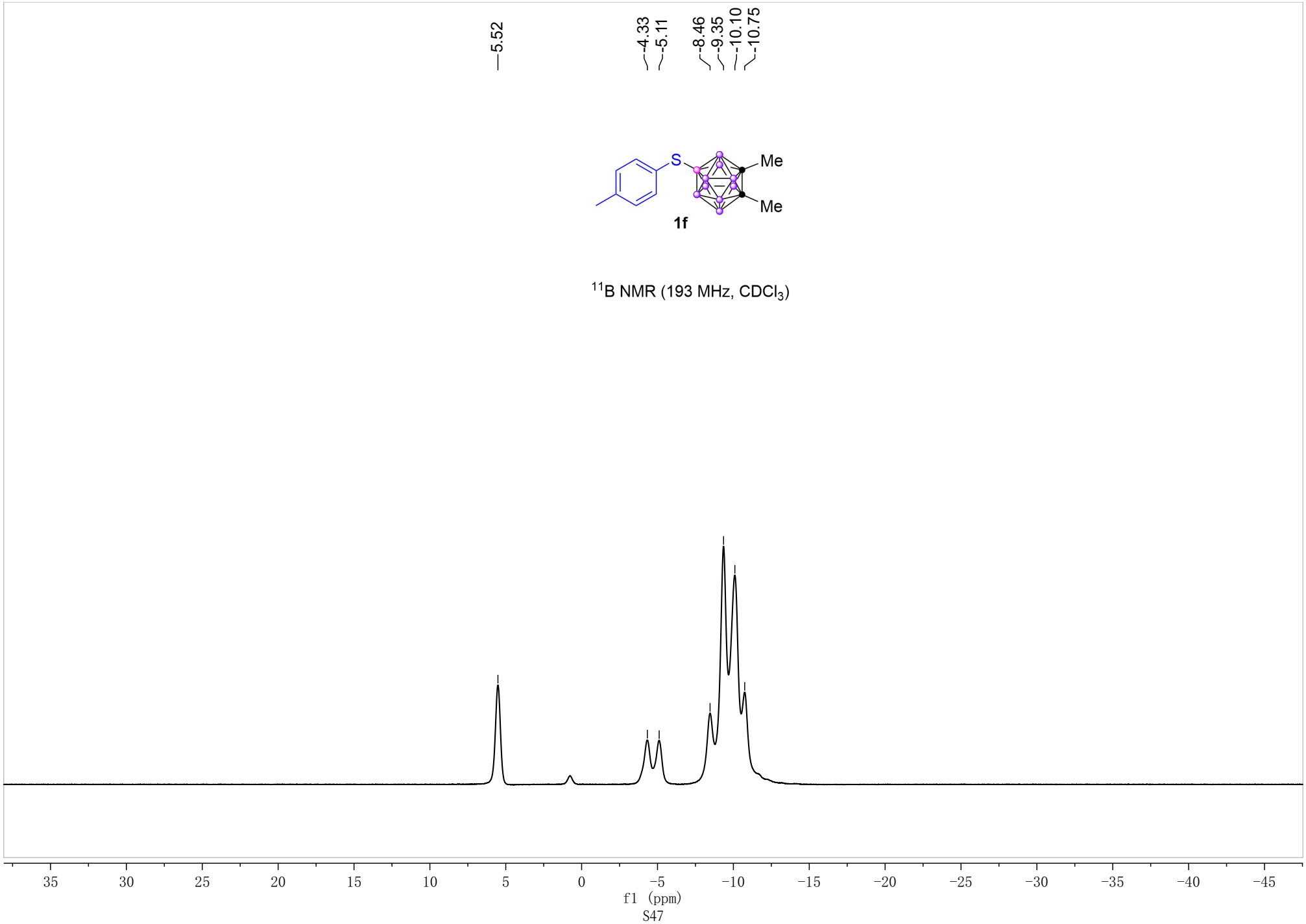

-5.66
-4.39
-5.16
-8.49
-9.36
-10.13
-10.77
S
Me
Me
MeO
1e
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

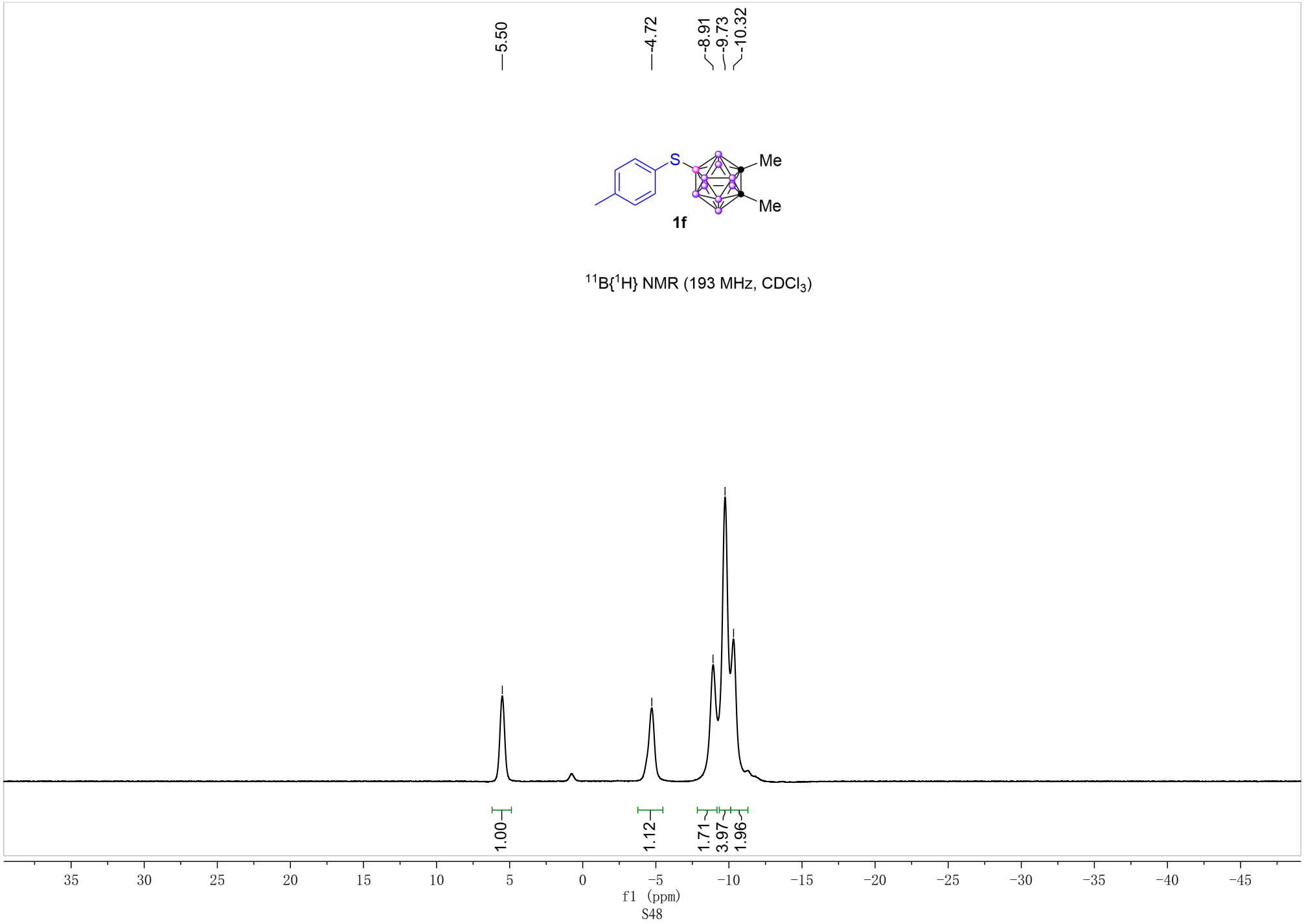

-5.70
-4.74
-8.94
-9.75
-10.34
S
Me
Me
MeO
1e
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
0.98
1.87
3.99
1.99
35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45
f1 (ppm)

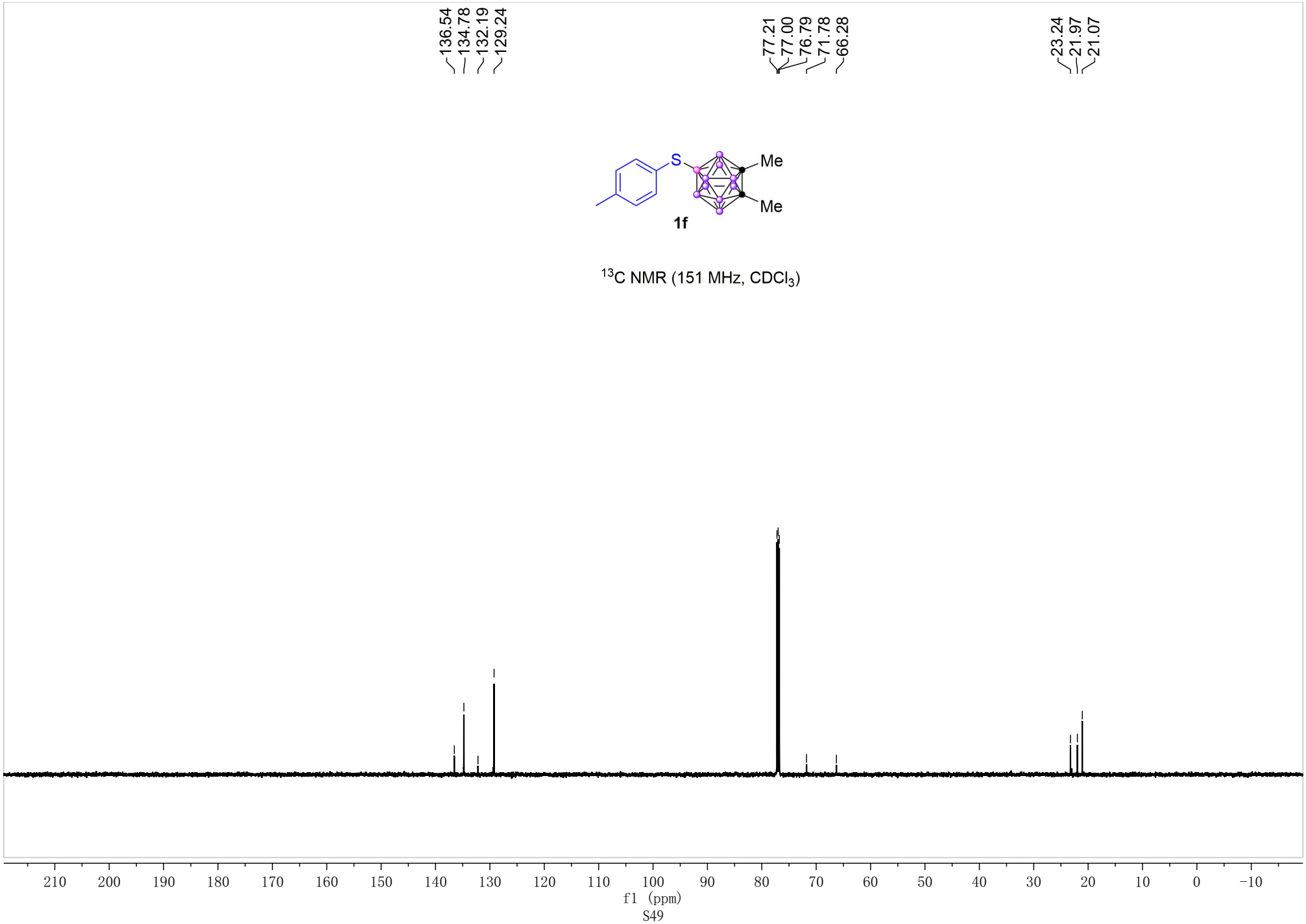

158.77
136.20
126.65
114.01
77.21
77.00
76.79
71.76
66.21
55.19
23.26
21.98
S
Me
Me
MeO
1e
^{13}C NMR (151 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

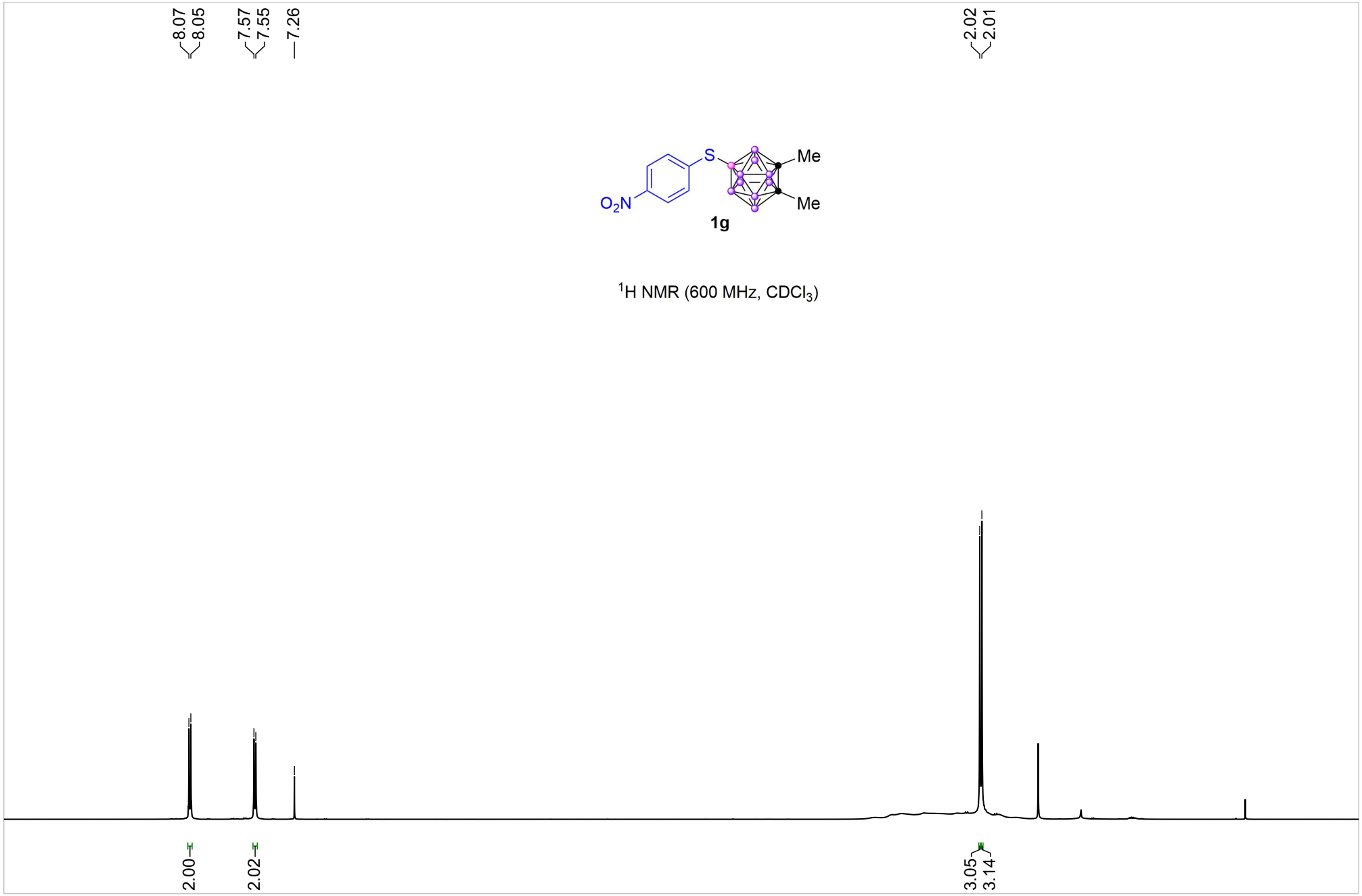

7.32
7.31
7.26
7.05
7.03
2.31
1.98
1.98
S
Me
Me
1f
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
1.99
3.05
3.08
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

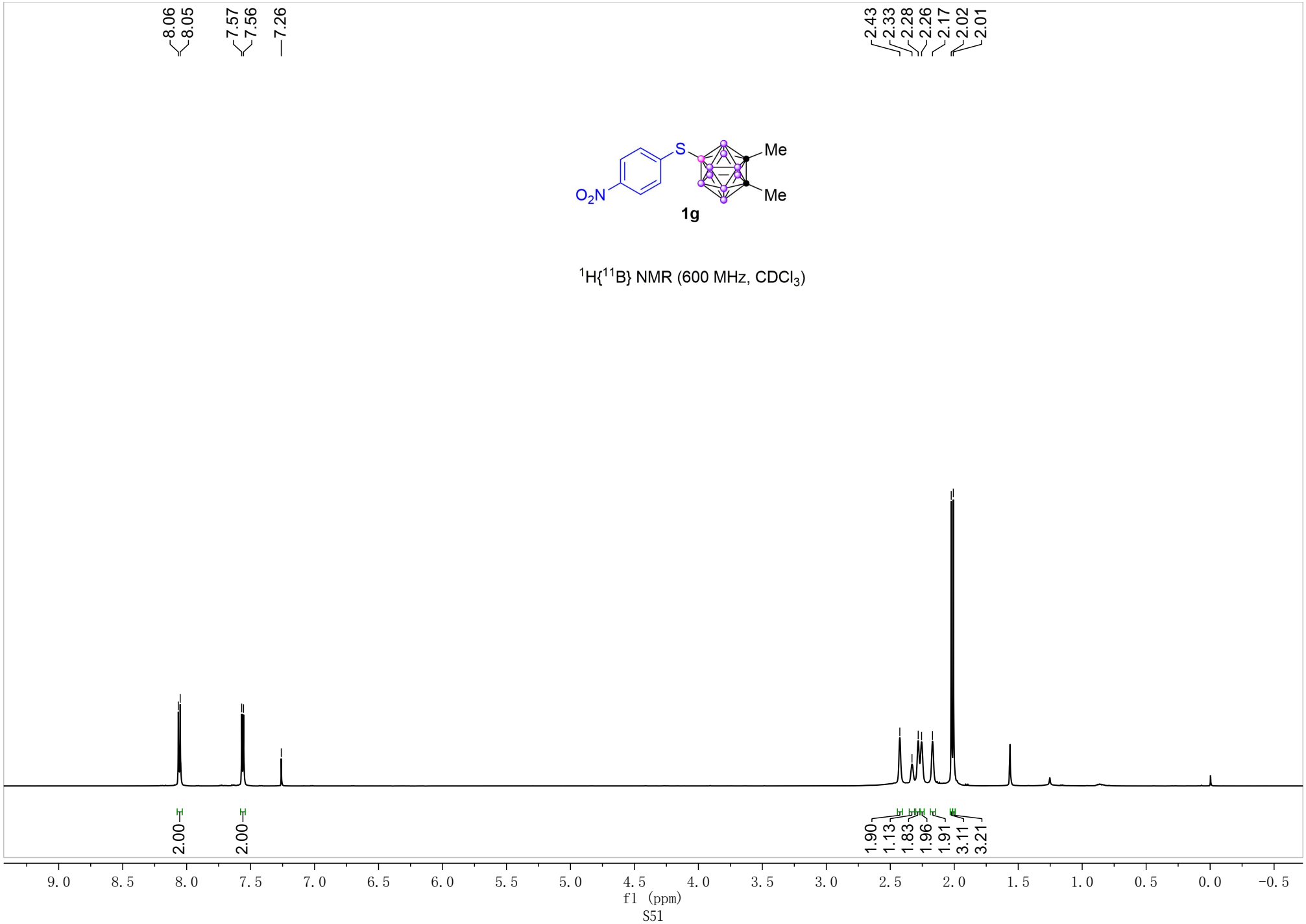

7.32
7.30
7.26
7.04
7.03
2.36
2.31
2.22
2.11
1.98
1.98
S
Me
Me
1f
$^1H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)
2.00
2.01
1.93
4.09
4.10
1.99
3.12
3.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

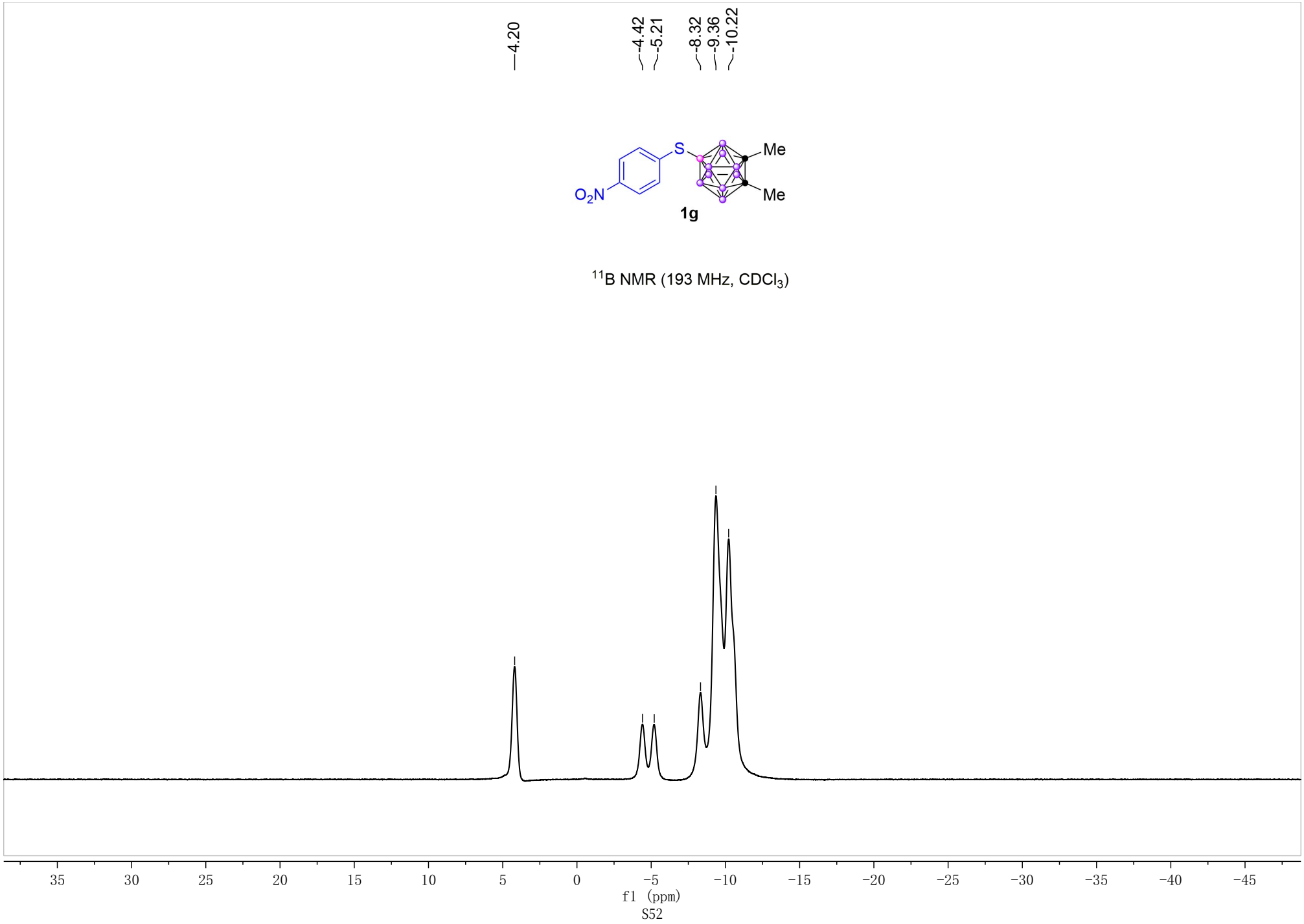

5.52
4.33
5.11
8.46
9.35
10.10
10.75
S
Me
Me
1f
^{11}B NMR (193 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

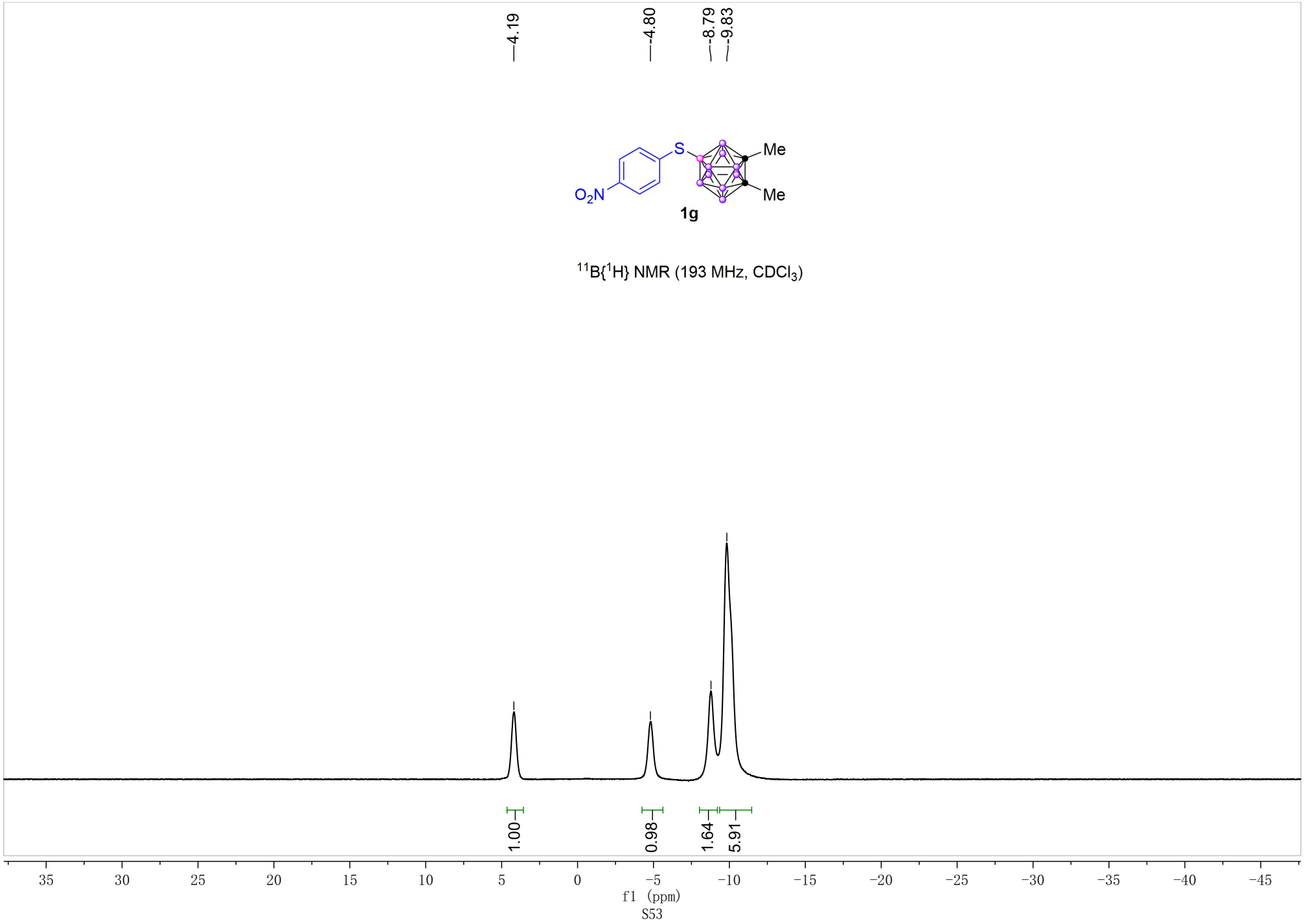

5.50
4.72
8.91
9.73
10.32
S
Me
Me
1f
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
1.12
1.71
3.97
1.96
35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45
f1 (ppm)

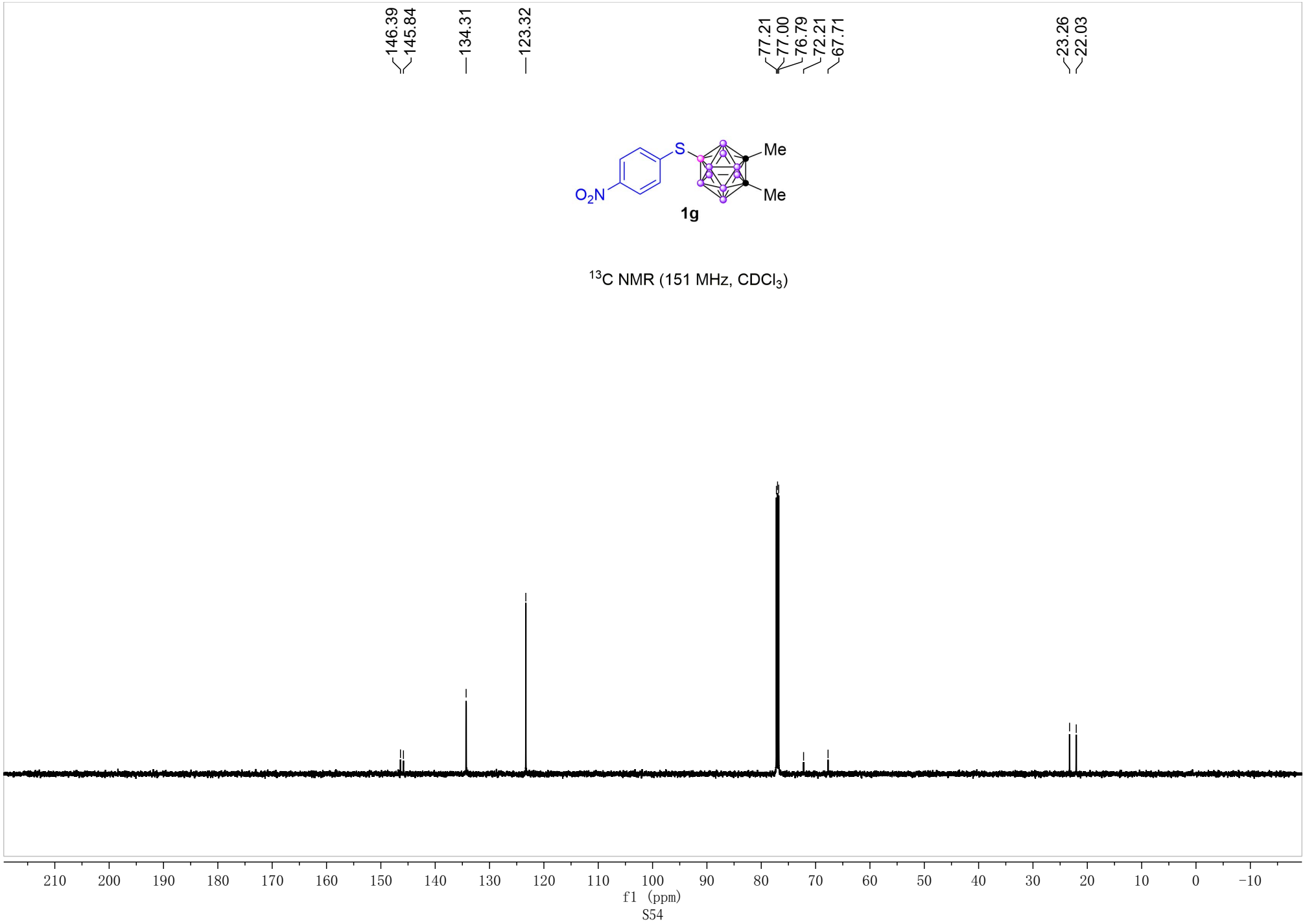

136.54
134.78
132.19
129.24
77.21
77.00
76.79
71.78
66.28
23.24
21.97
21.07
S
Me
Me
1f
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

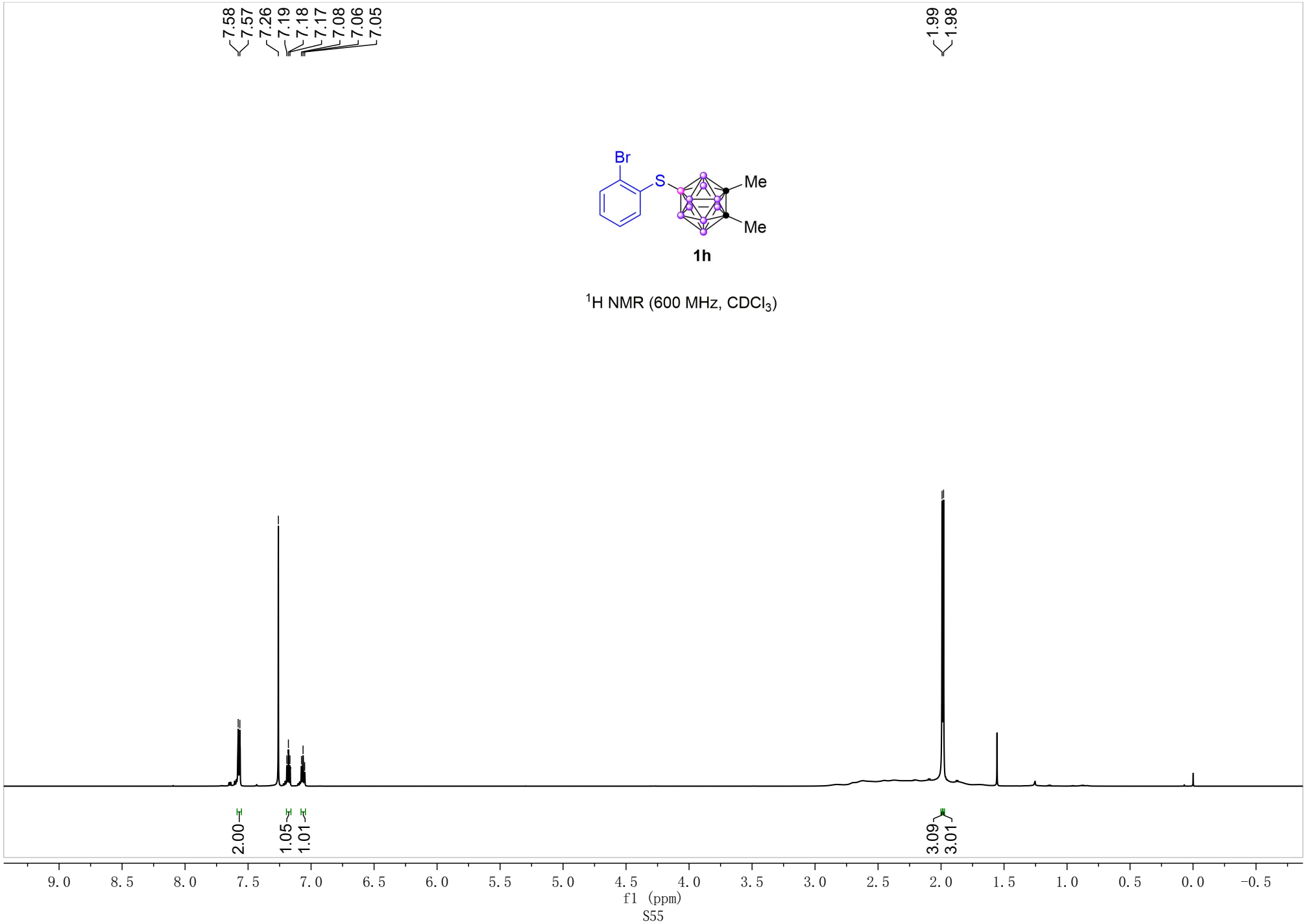

8.07
8.05
7.57
7.55
7.26
2.02
2.01
S
Me
Me
O_2N
1g
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
2.02
3.05
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

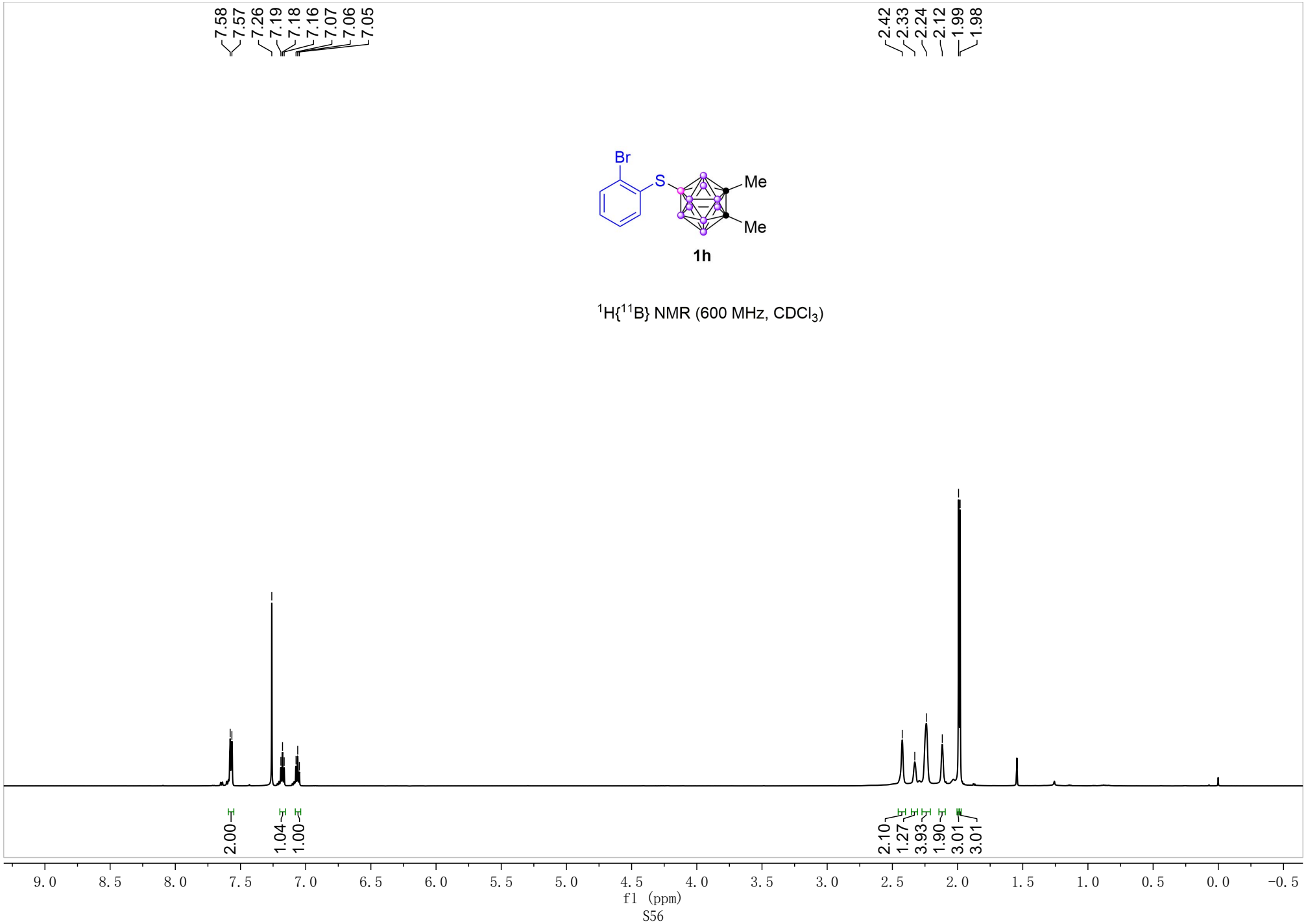

8.06
8.05
7.57
7.56
7.26
2.43
2.33
2.28
2.26
2.17
2.02
2.01
S
Me
Me
O_2N
1g
$^1H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)
2.00
2.00
1.90
1.13
1.83
1.96
1.91
3.11
3.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

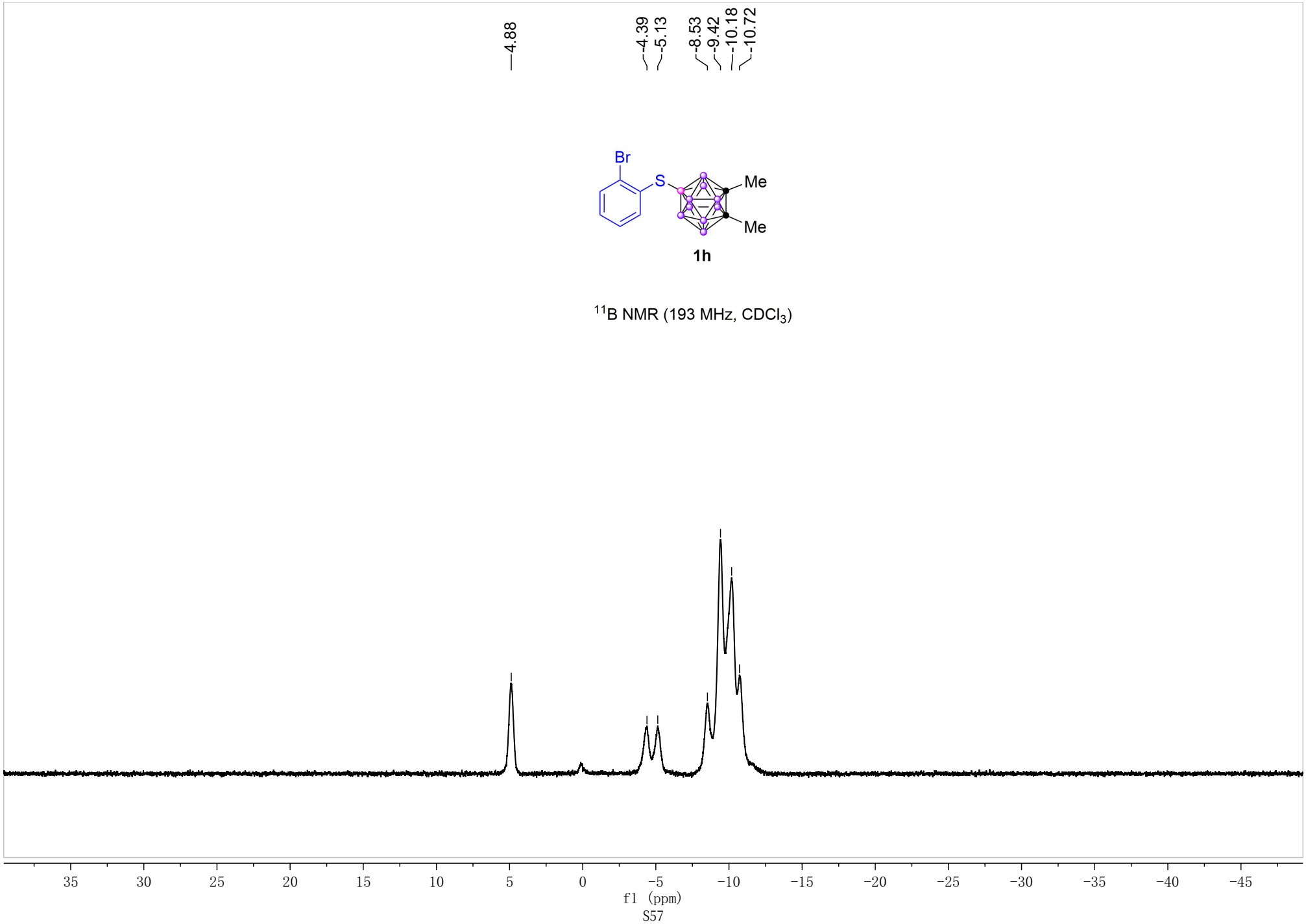

-4.20
-4.42
-5.21
-8.32
-9.36
-10.22
S
Me
Me
O_2N
1g
^{11}B NMR (193 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

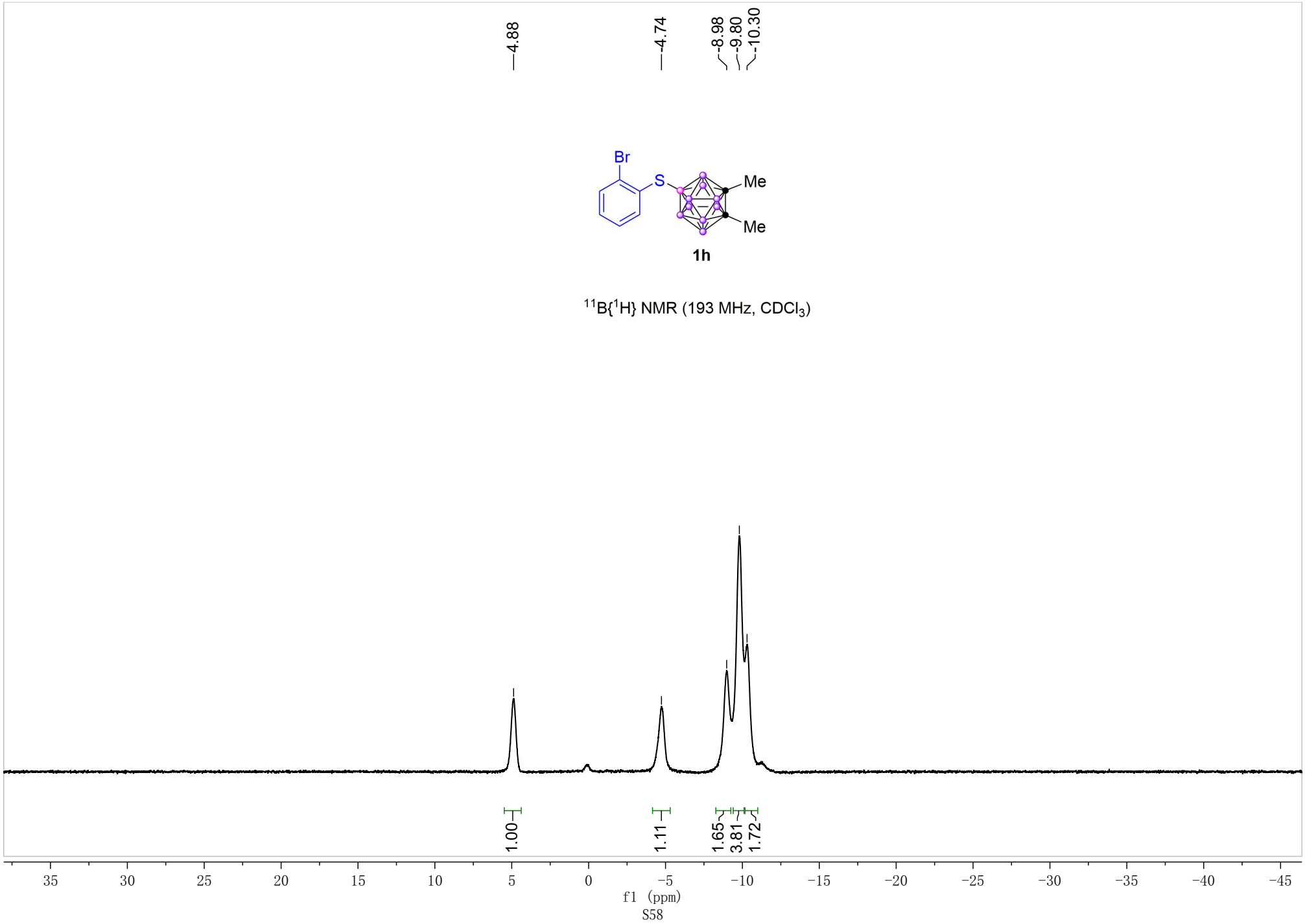

-4.19
-4.80
-8.79
-9.83
S
Me
Me
O_2N
1g
$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$)
1.00
0.98
1.64
5.91
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

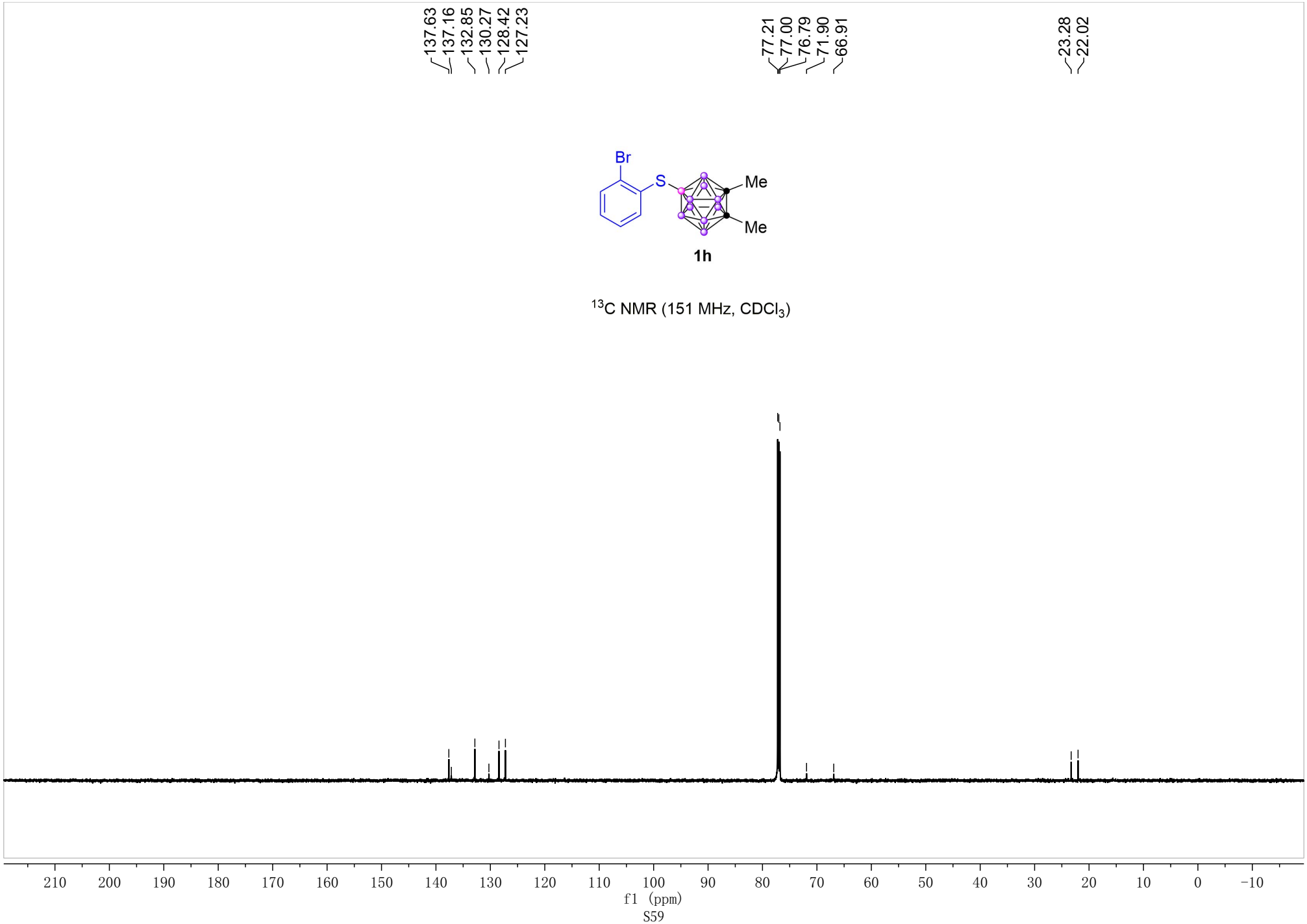

146.39
145.84
134.31
123.32
77.21
77.00
76.79
72.21
67.71
23.26
22.03
S
Me
Me
O_2N
1g
^{13}C NMR (151 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

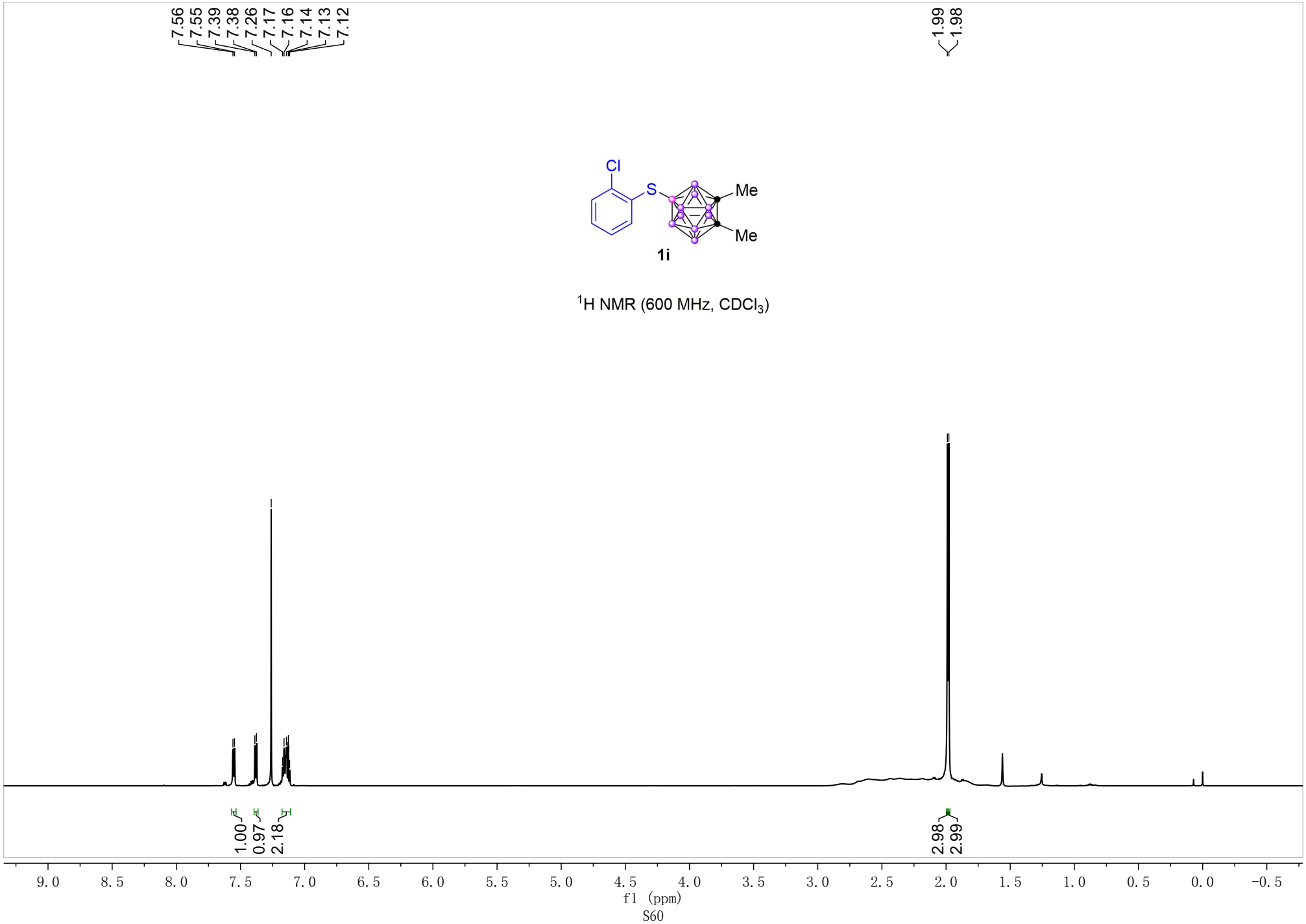

7.58
7.57
7.26
7.19
7.18
7.17
7.08
7.06
7.05
1.99
1.98
Br
S
Me
Me
1h
^{1}H NMR (600 MHz, CDCl$_3$)
2.00
1.05
1.01
3.09
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

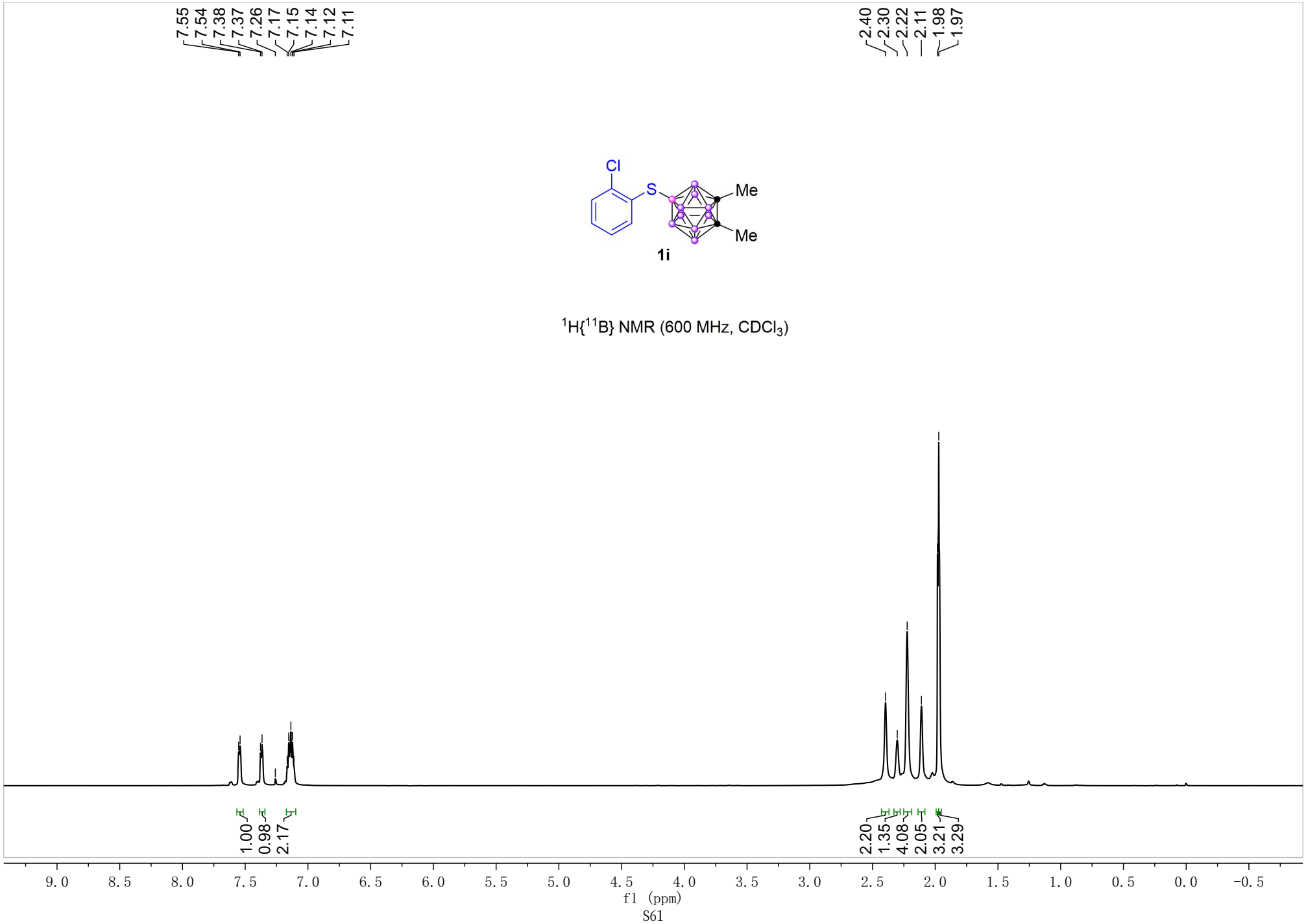

7.58
7.57
7.26
7.19
7.18
7.16
7.07
7.06
7.05
2.42
2.33
2.24
2.12
1.99
1.98
Br
S
Me
Me
1h
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)
2.00
1.04
1.00
2.10
1.27
3.93
1.90
3.01
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

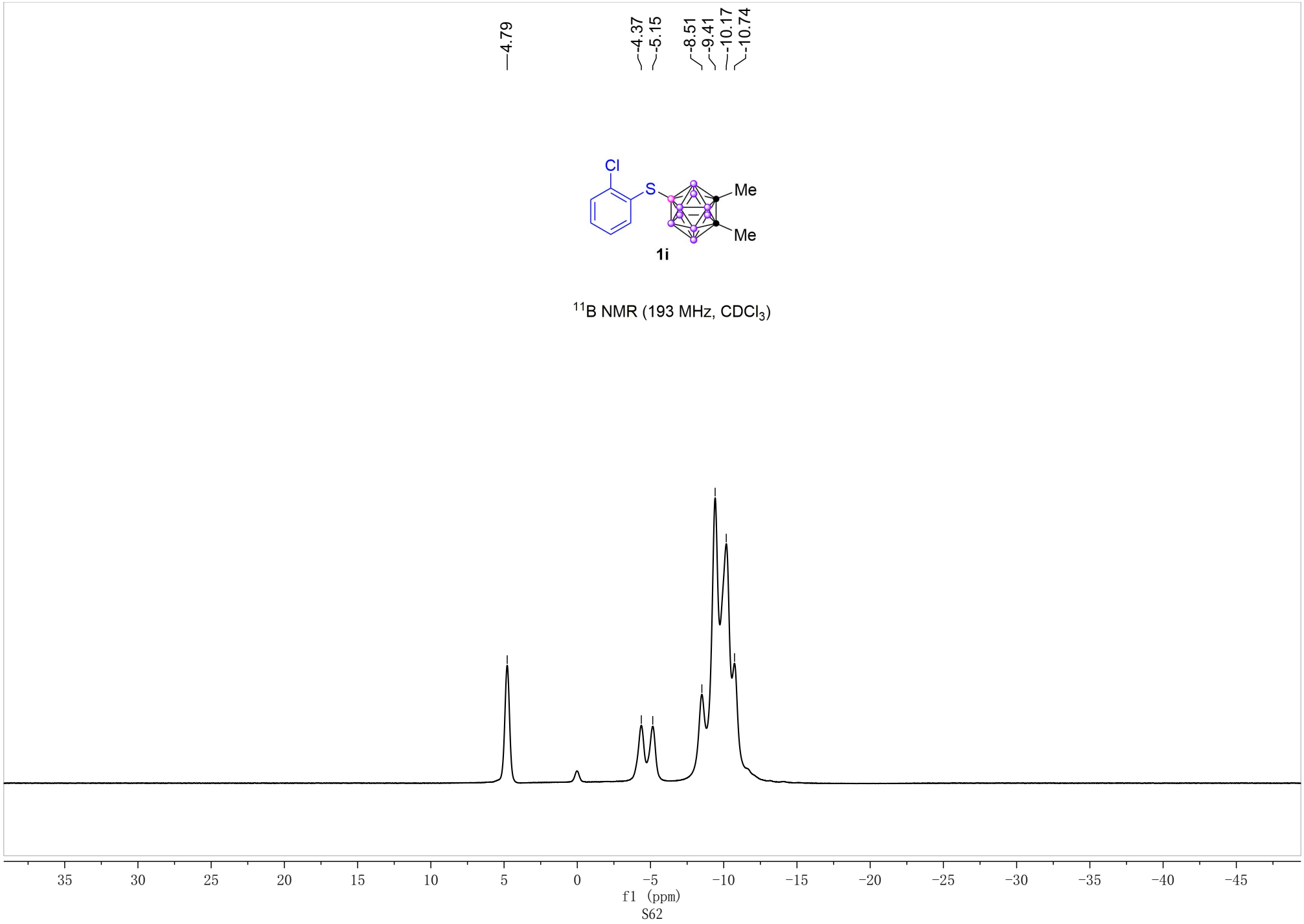

-4.88
-4.39
-5.13
-8.53
-9.42
-10.18
-10.72
Br
S
Me
Me
1h
^{11}B NMR (193 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

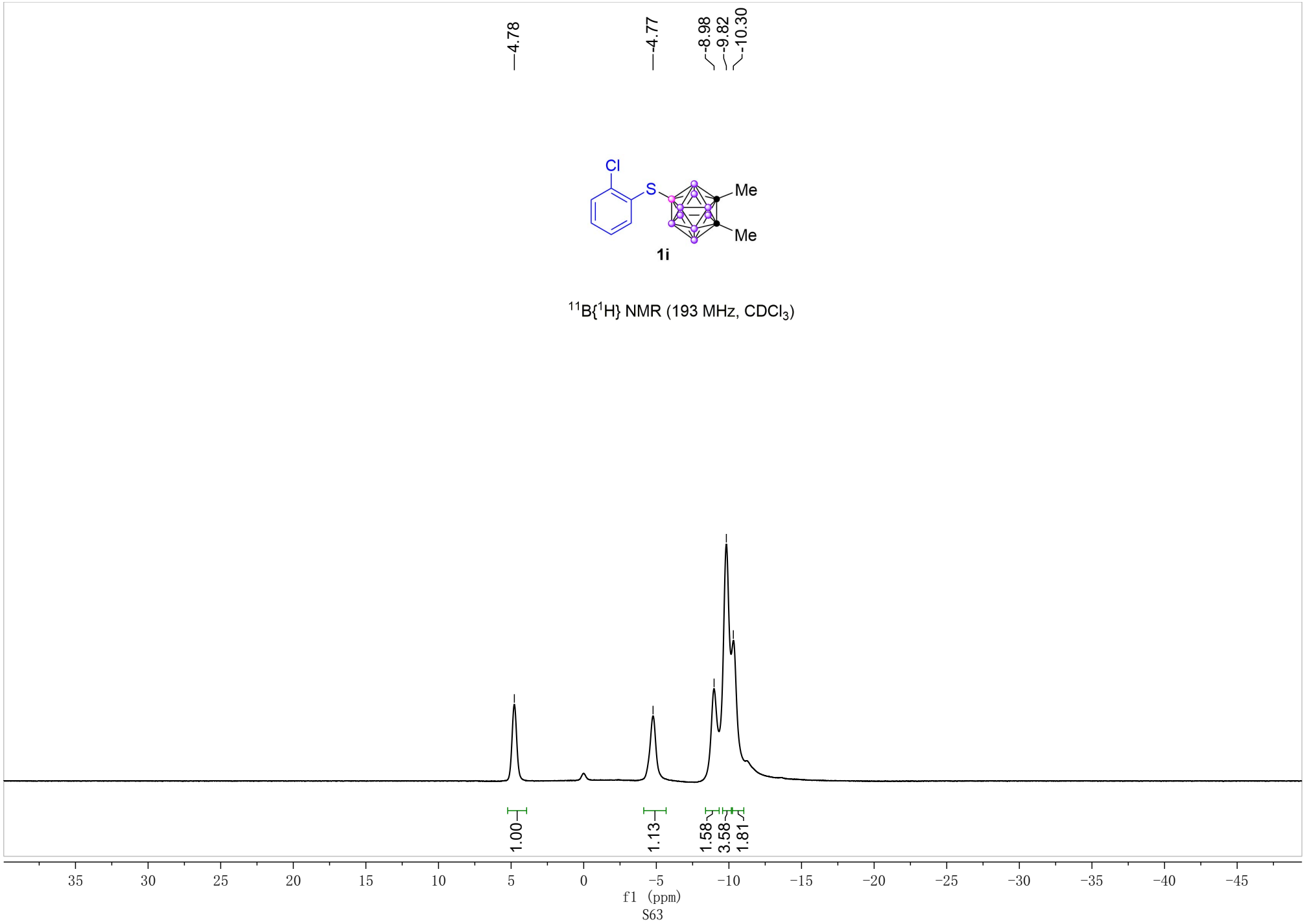

-4.88
-4.74
-8.98
-9.80
-10.30
Br
S
Me
Me
1h
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
1.11
1.65
3.81
1.72
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

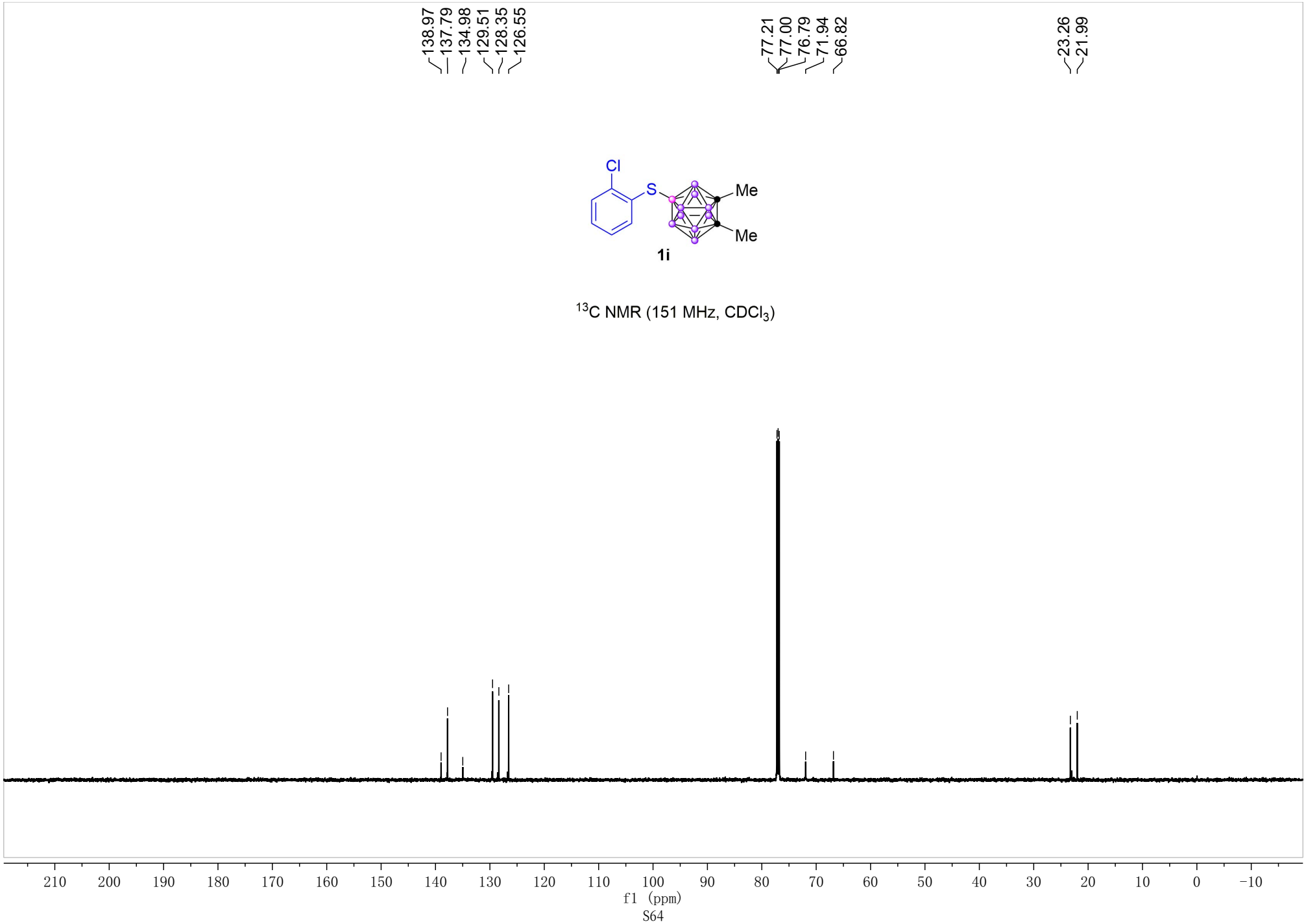

137.63
137.16
132.85
130.27
128.42
127.23
77.21
77.00
76.79
71.90
66.91
23.28
22.02
Br
S
Me
Me
1h
^{13}C NMR (151 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

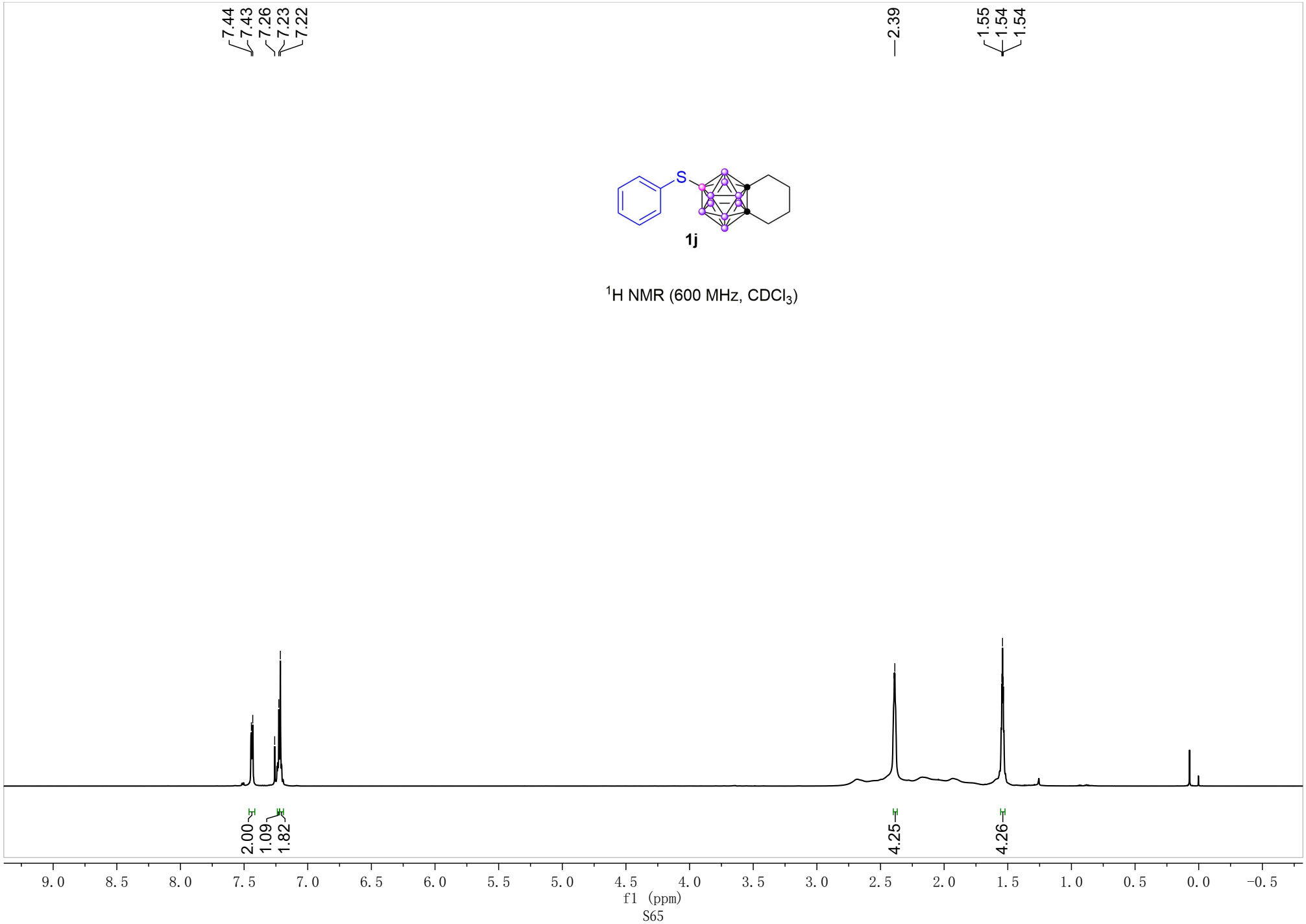

7.56
7.55
7.39
7.38
7.26
7.17
7.16
7.14
7.13
7.12
1.99
1.98
Cl
S
Me
Me
1i
1H NMR (600 MHz, CDCl3)
1.00
0.97
2.18
2.98
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

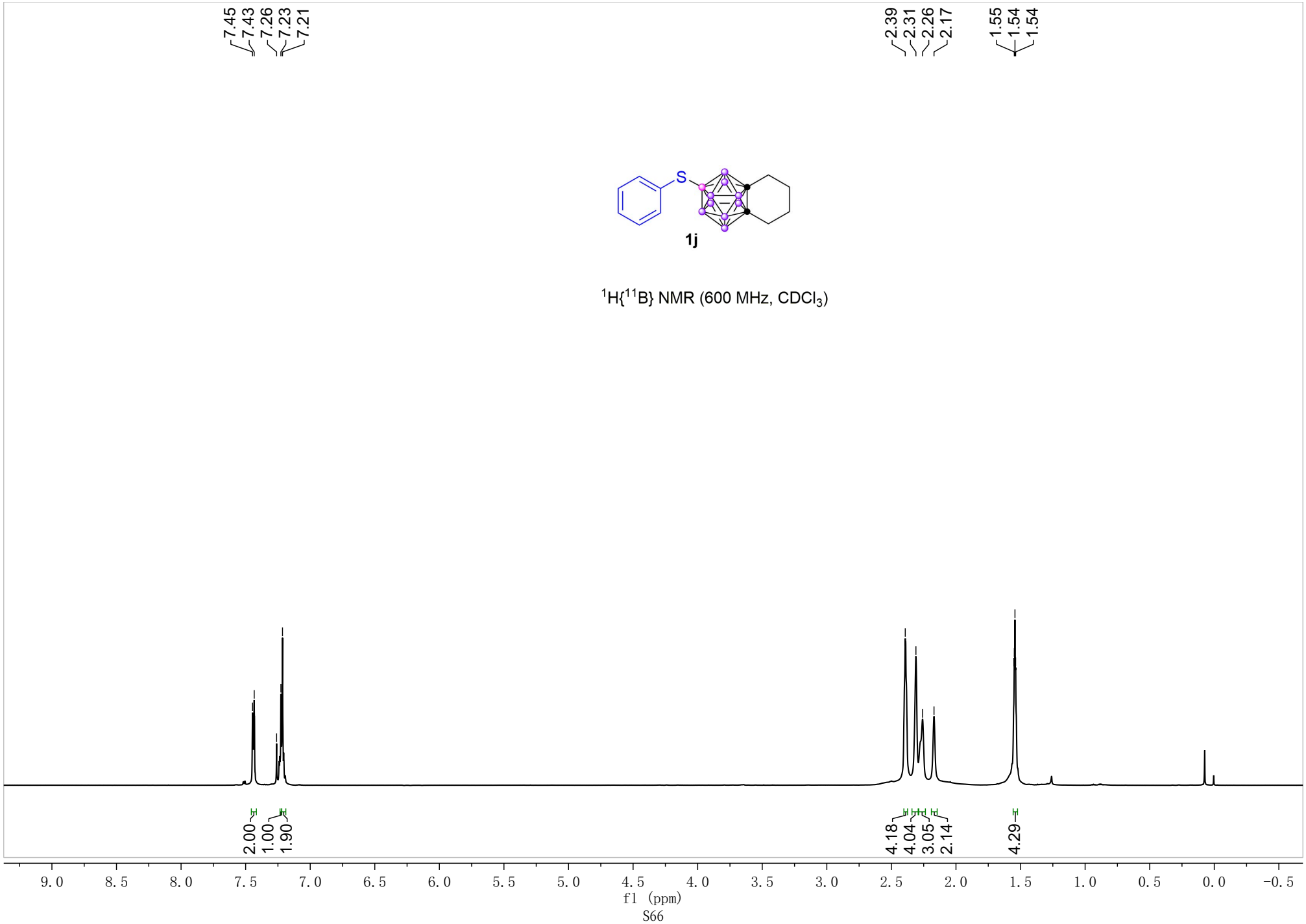

7.55
7.54
7.38
7.37
7.26
7.17
7.15
7.14
7.12
7.11
2.40
2.30
2.22
2.11
1.98
1.97
Cl
S
Me
Me
1i
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)
1.00
0.98
2.17
2.20
1.35
4.08
2.05
3.21
3.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

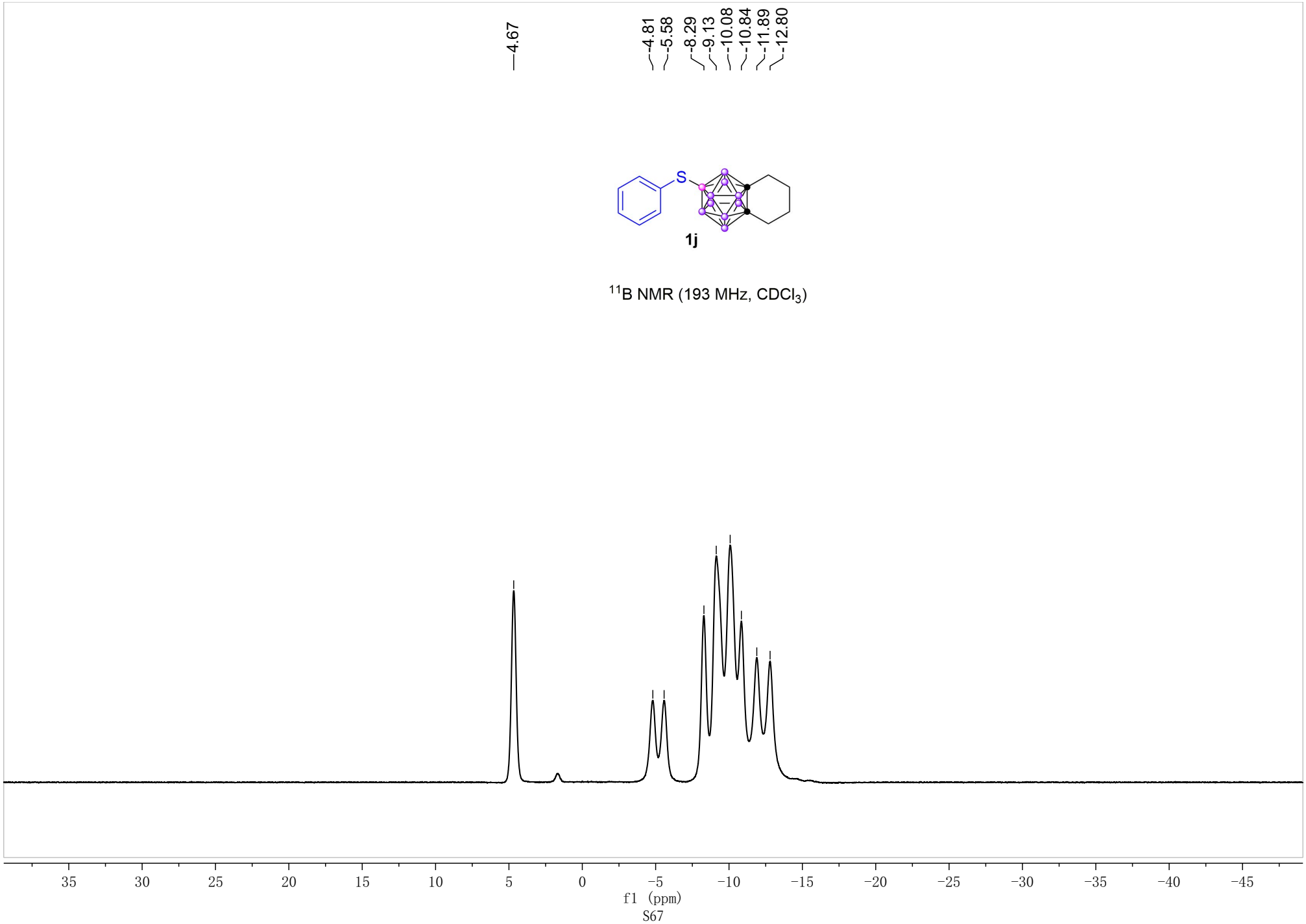

4.79
-4.37
-5.15
-8.51
-9.41
-10.17
-10.74
Cl
S
Me
Me
1i
^{11}B NMR (193 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

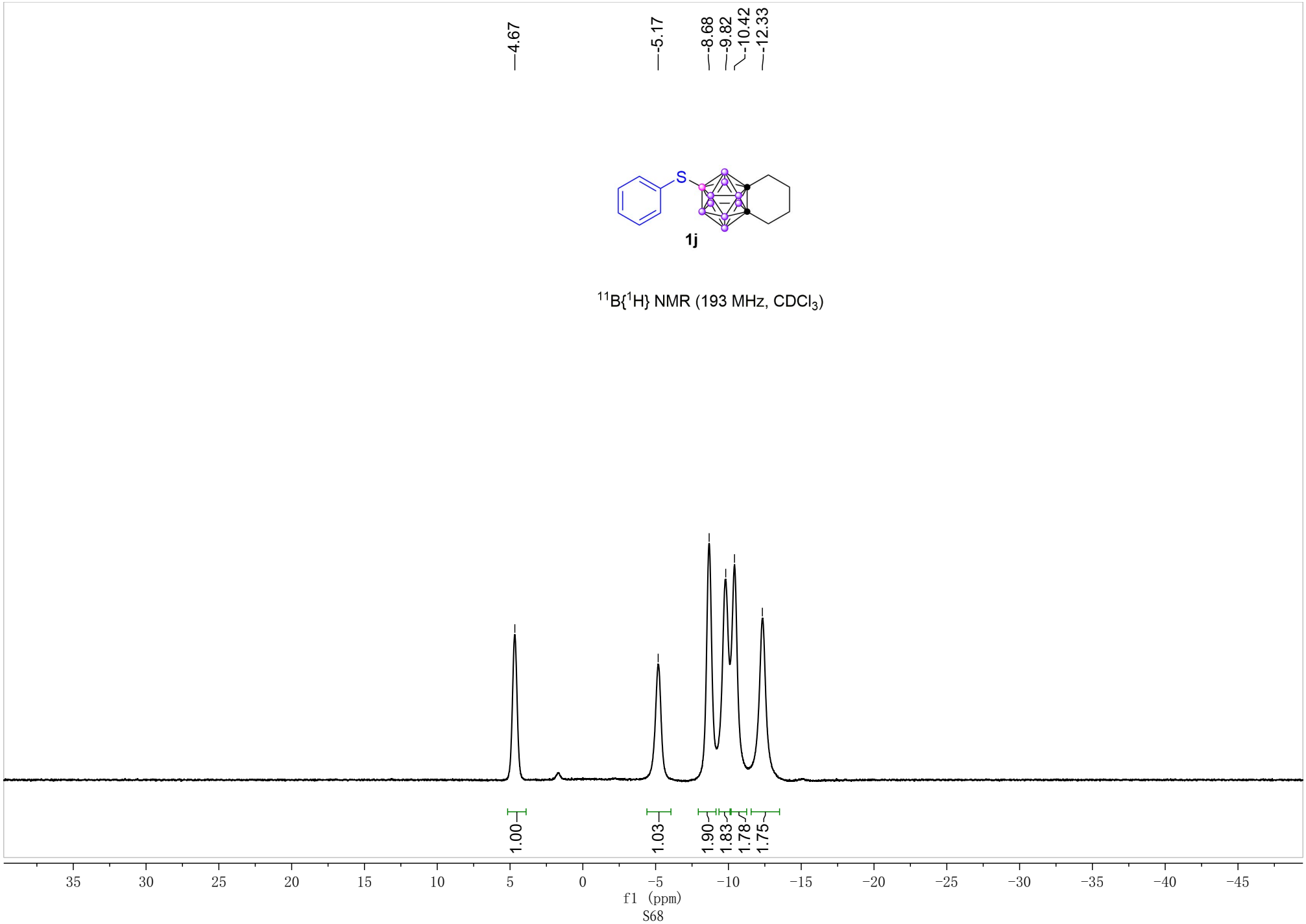

-4.78
-4.77
-8.98
-9.82
-10.30
Cl
S
Me
Me
1i
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
1.13
1.58
3.58
1.81
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

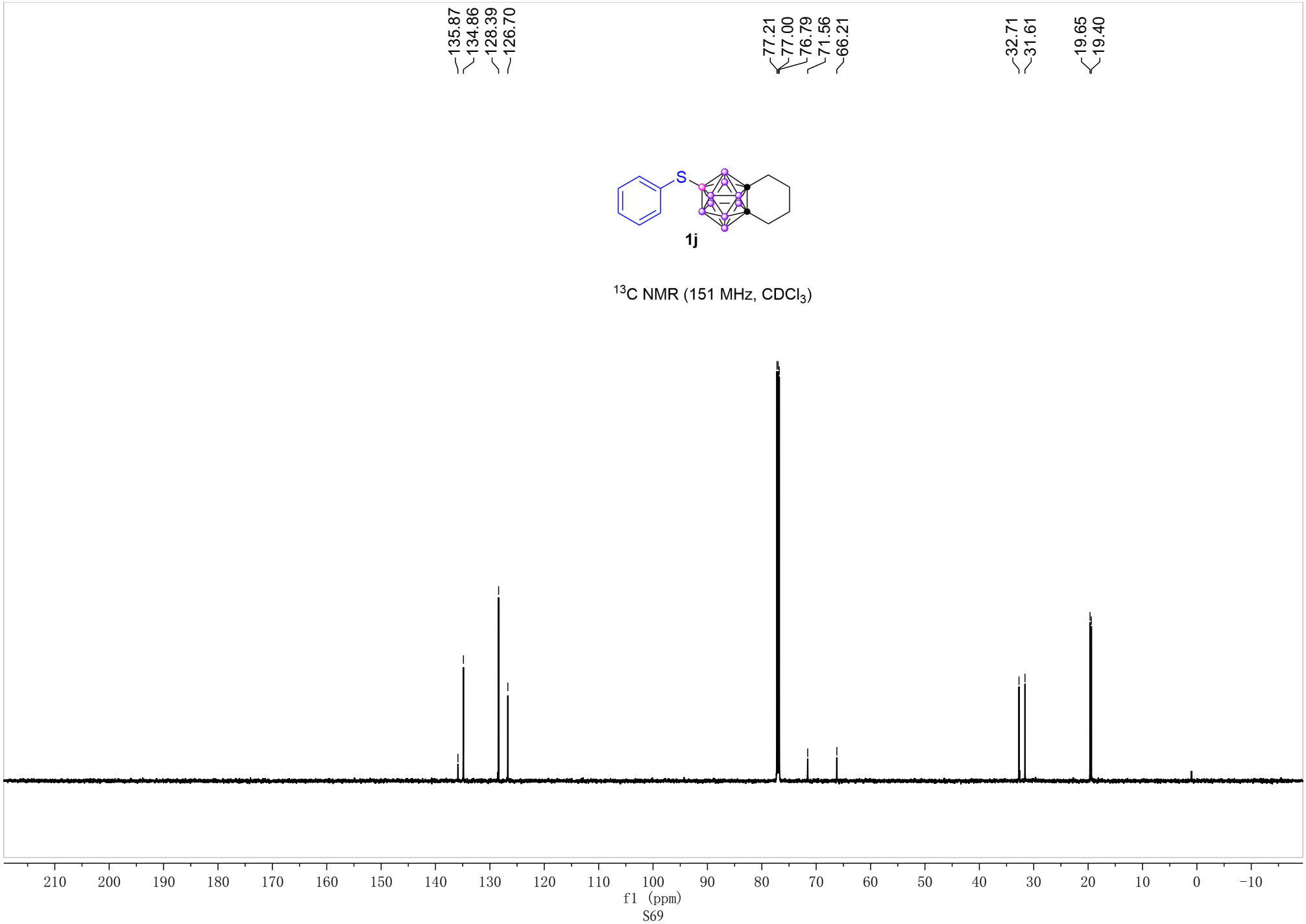

138.97
137.79
134.98
129.51
128.35
126.55
77.21
77.00
76.79
71.94
66.82
23.26
21.99
Cl
S
Me
Me
1i
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

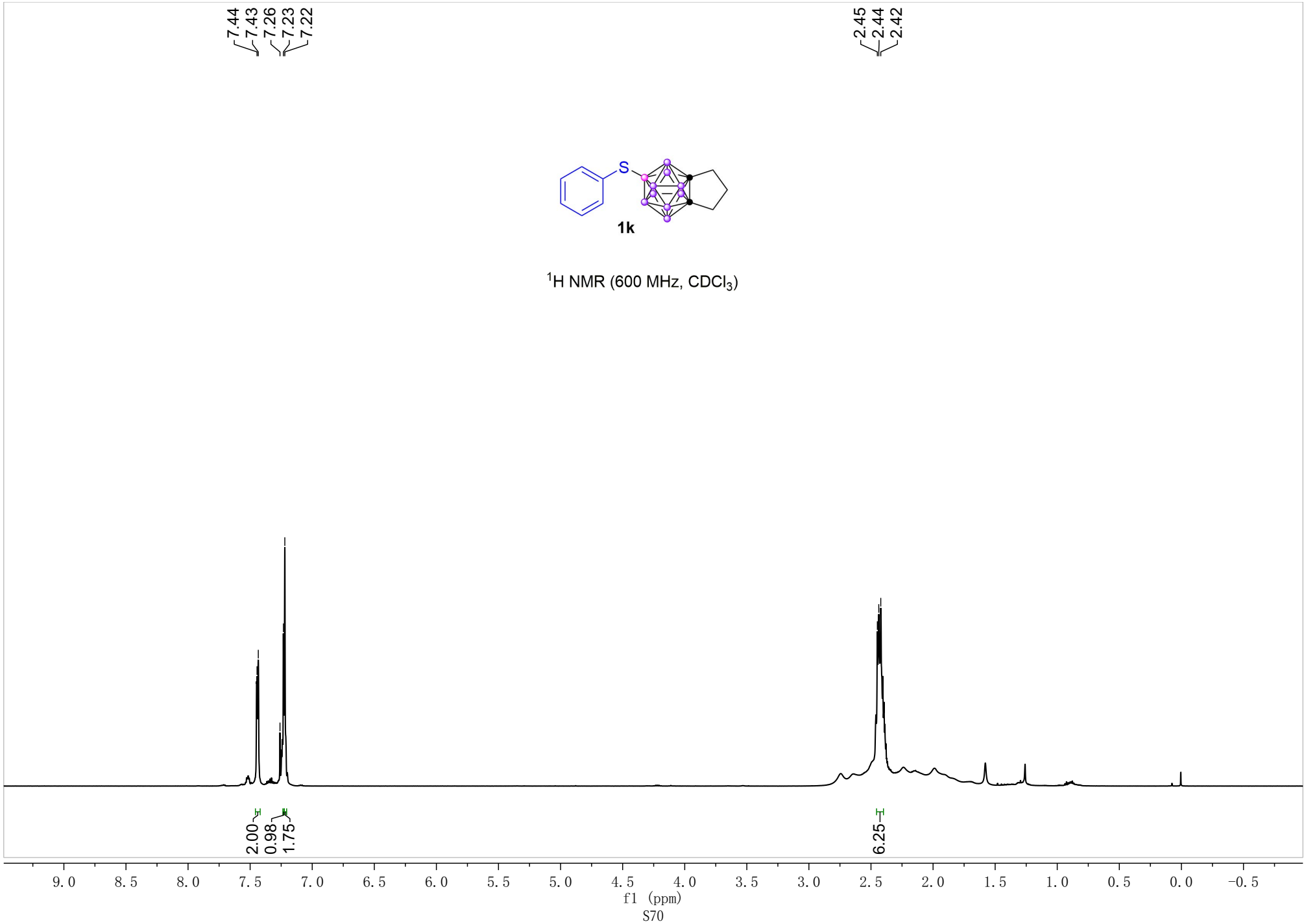

7.44
7.43
7.26
7.23
7.22
2.39
1.55
1.54
1.54
S
1j
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
1.09
1.82
4.25
4.26
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

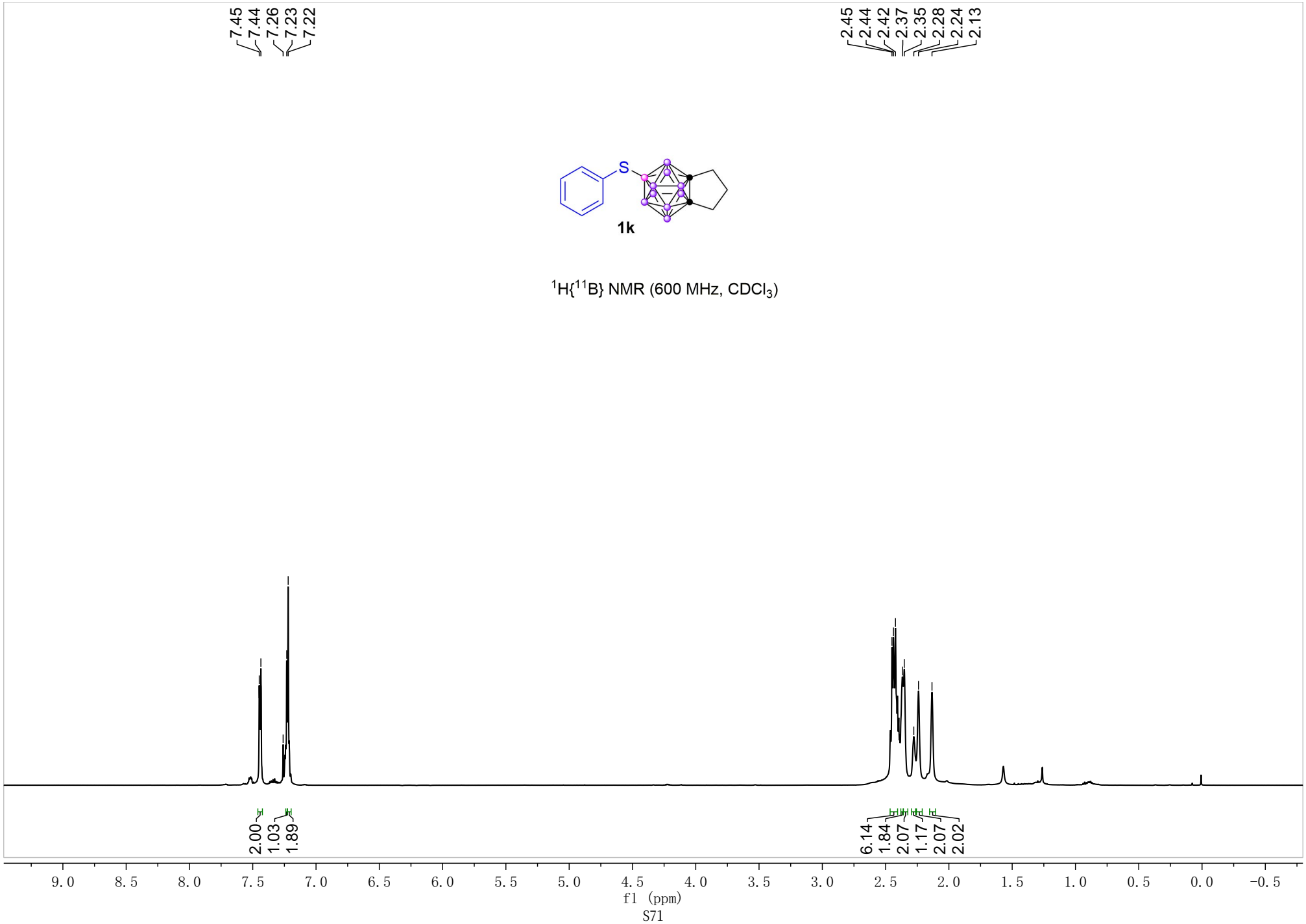

7.45
7.43
7.26
7.23
7.21
2.39
2.31
2.26
2.17
1.55
1.54
1.54
S
1j
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)
2.00
1.00
1.90
4.18
4.04
3.05
2.14
4.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


4.67
-4.81
-5.58
-8.29
-9.13
-10.08
-10.84
-11.89
-12.80
S
1j
^{11}B NMR (193 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

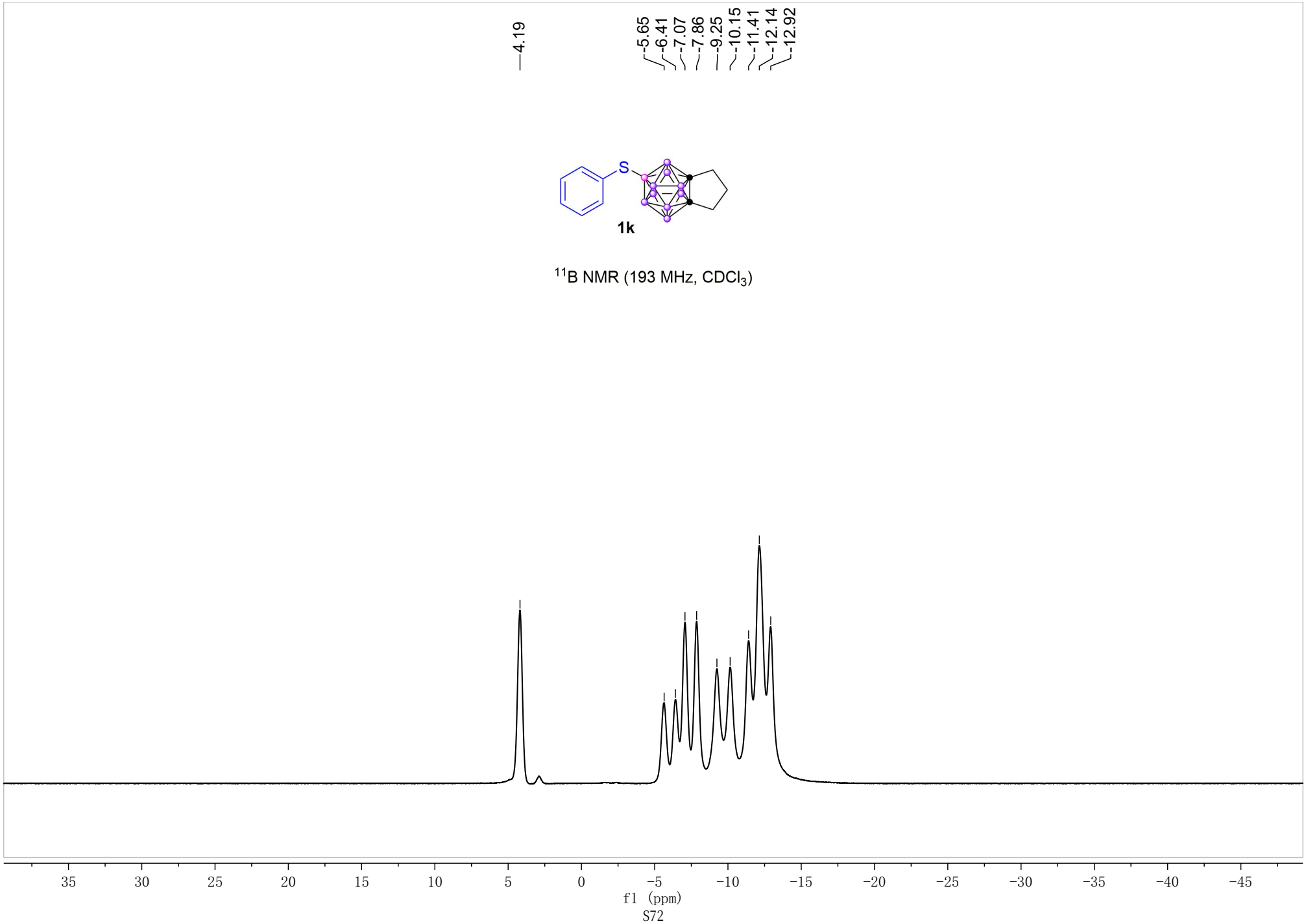

4.67
-5.17
-8.68
-9.82
-10.42
-12.33
S
1j
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
1.03
1.90
1.83
1.78
1.75
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

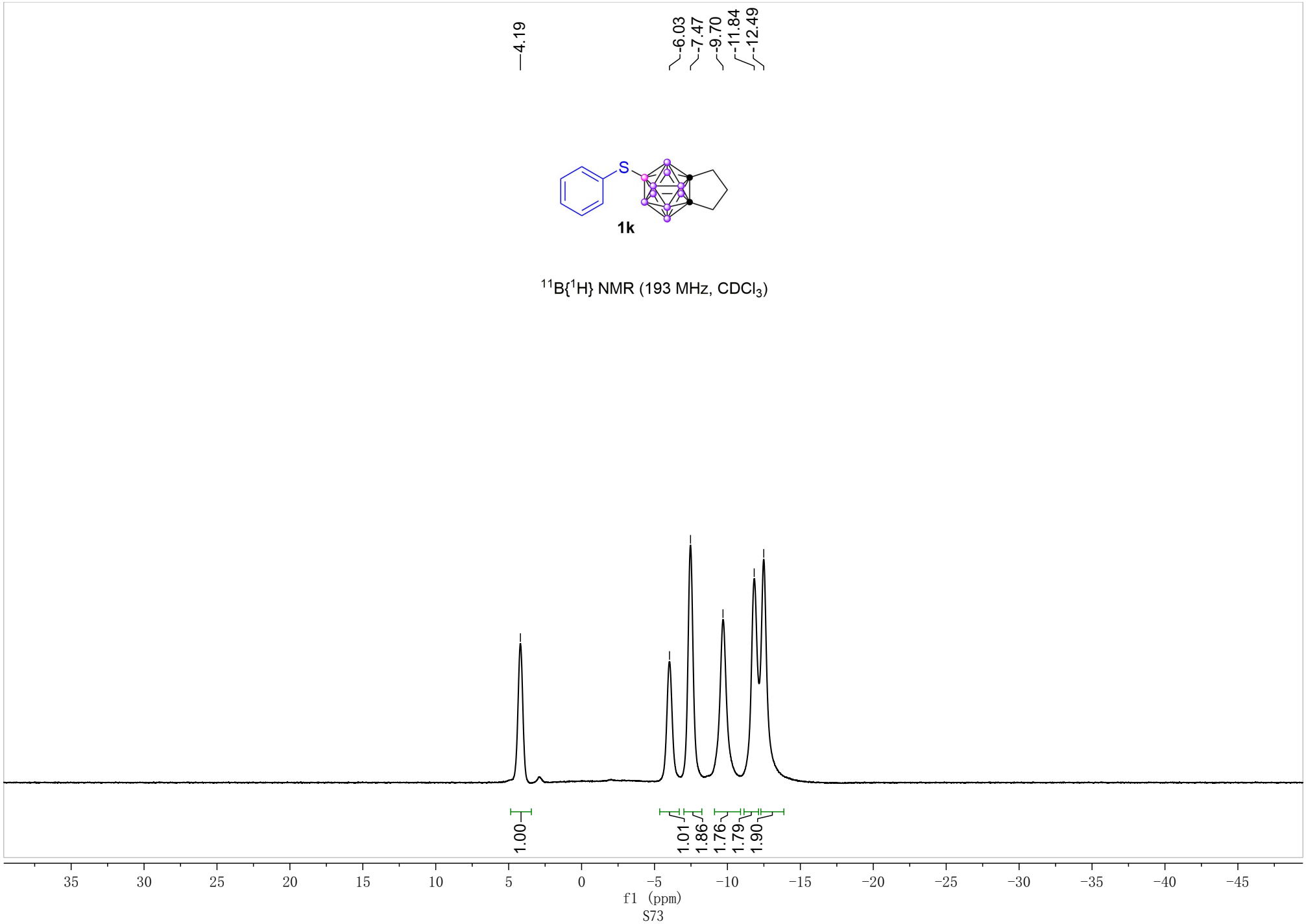

135.87
134.86
128.39
126.70
77.21
77.00
76.79
71.56
66.21
32.71
31.61
19.65
19.40
S
1j
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

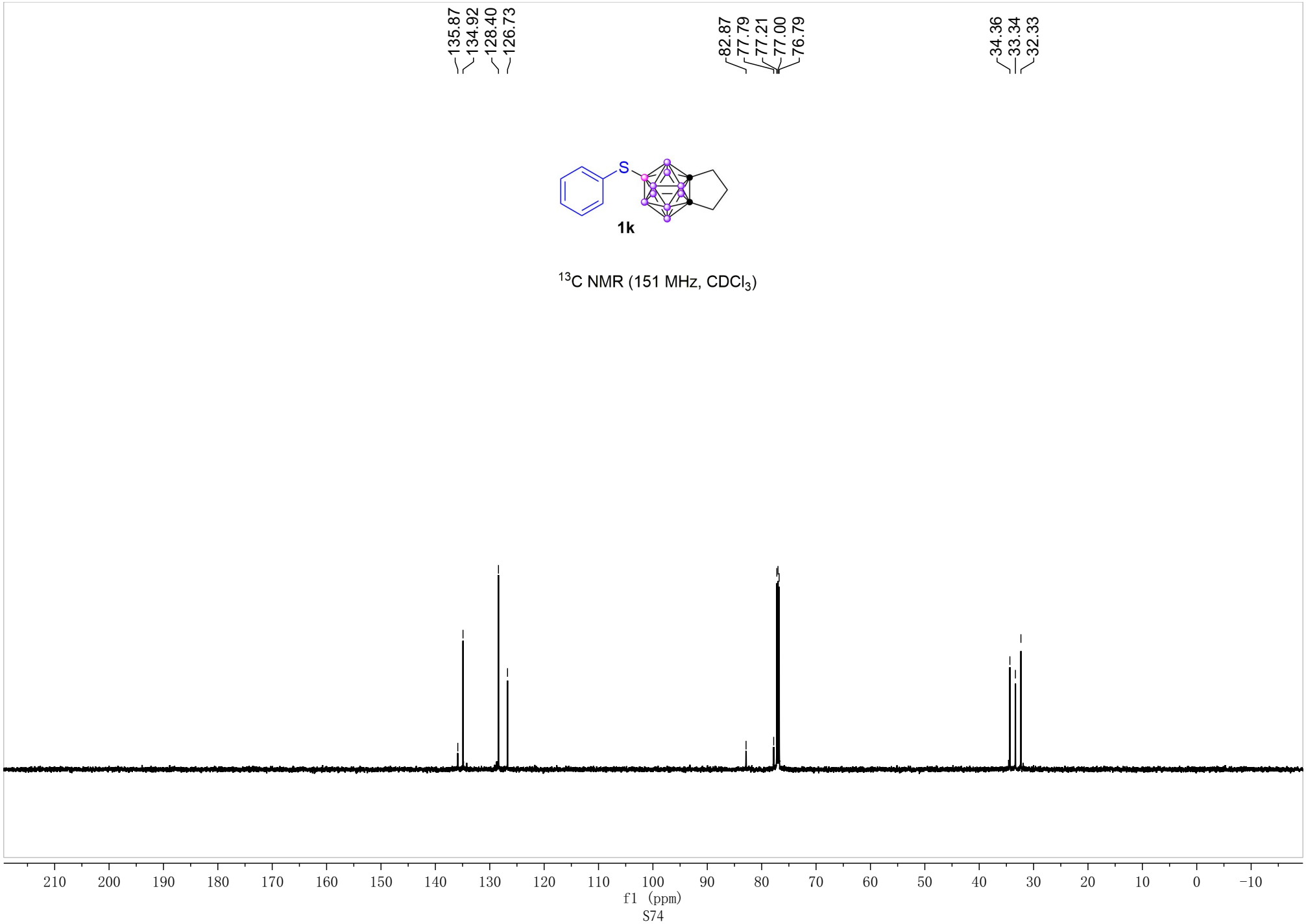

7.44
7.43
7.26
7.23
7.22
2.45
2.44
2.42
S
1k
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
0.98
1.75
6.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

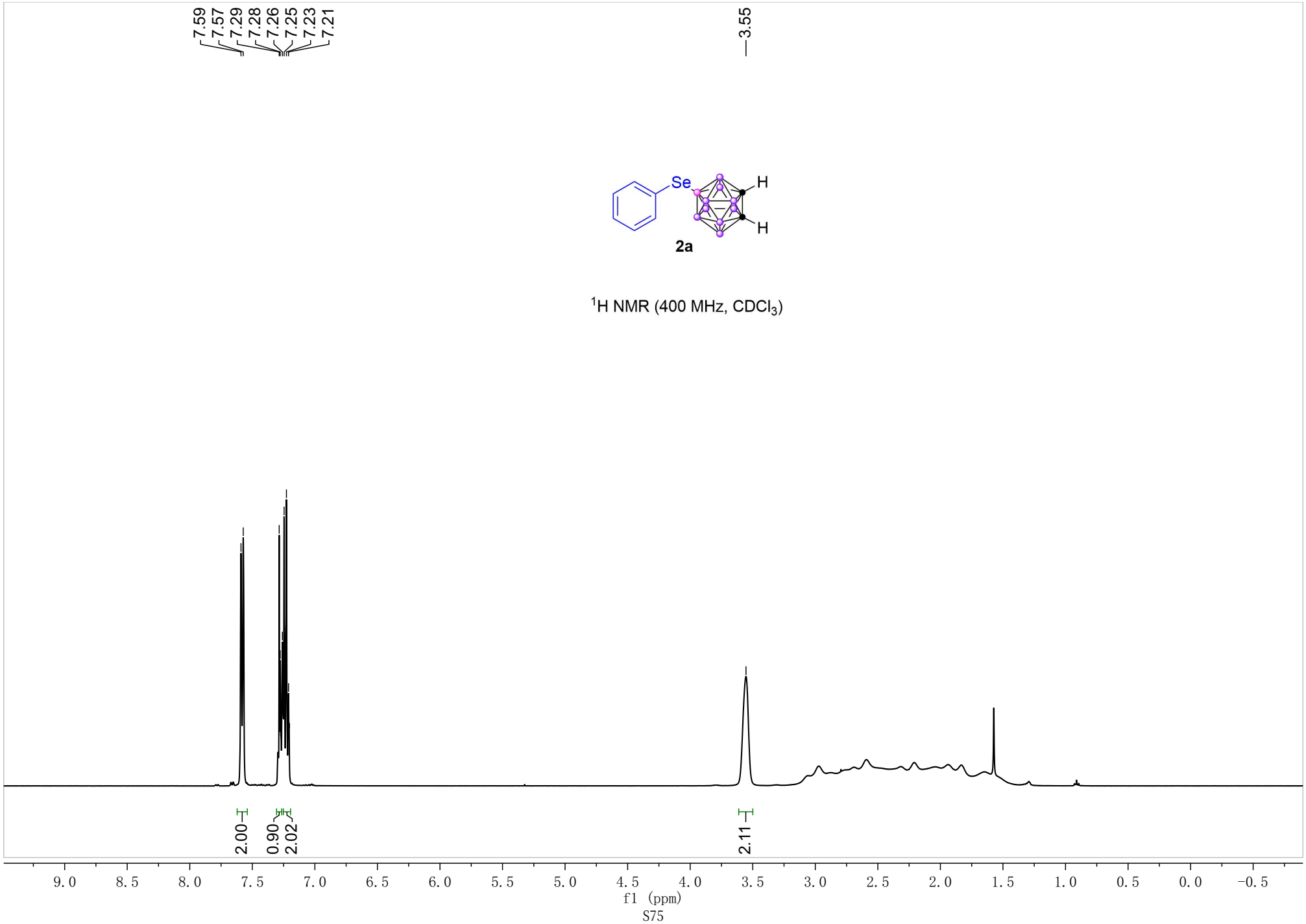


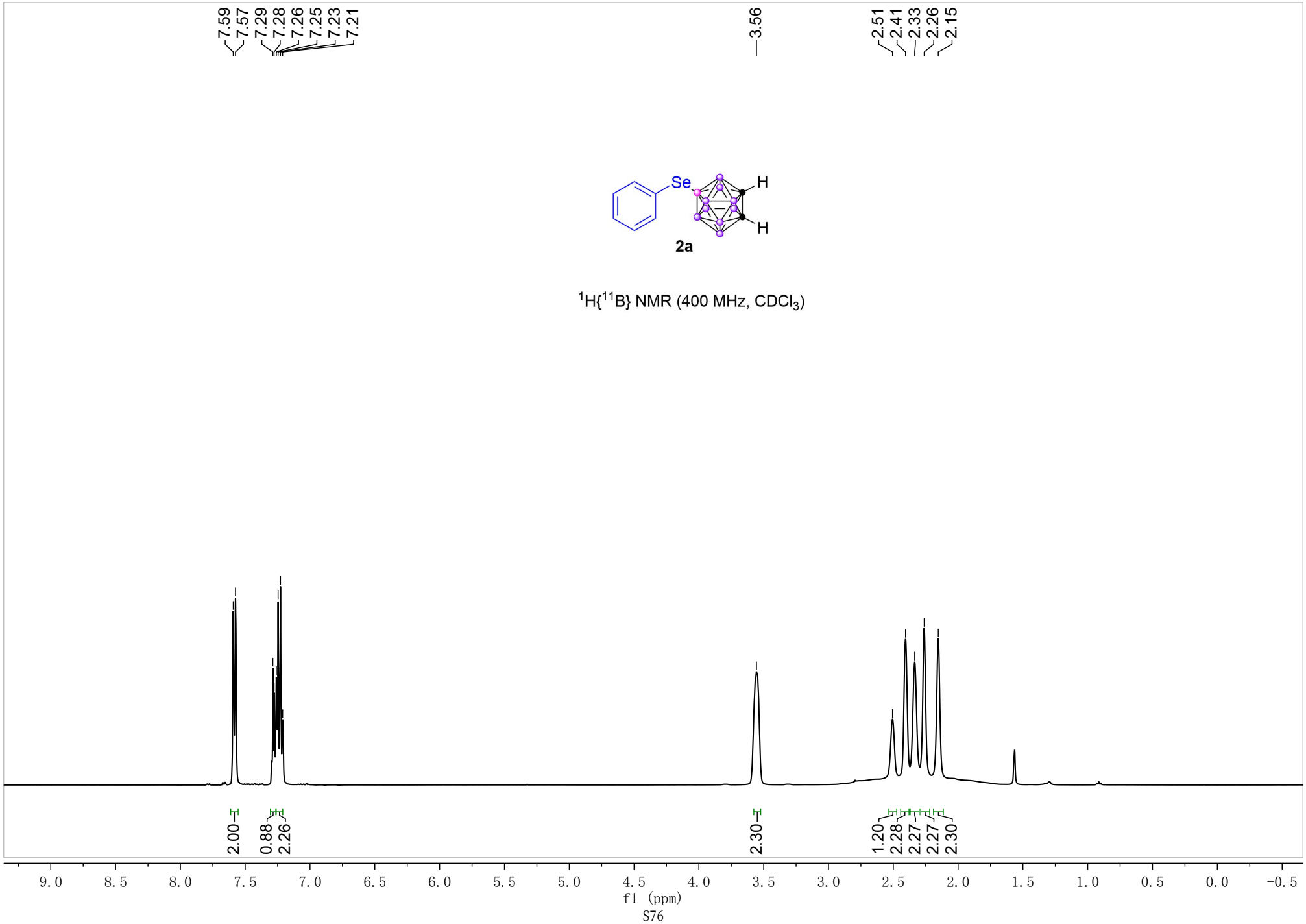
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)

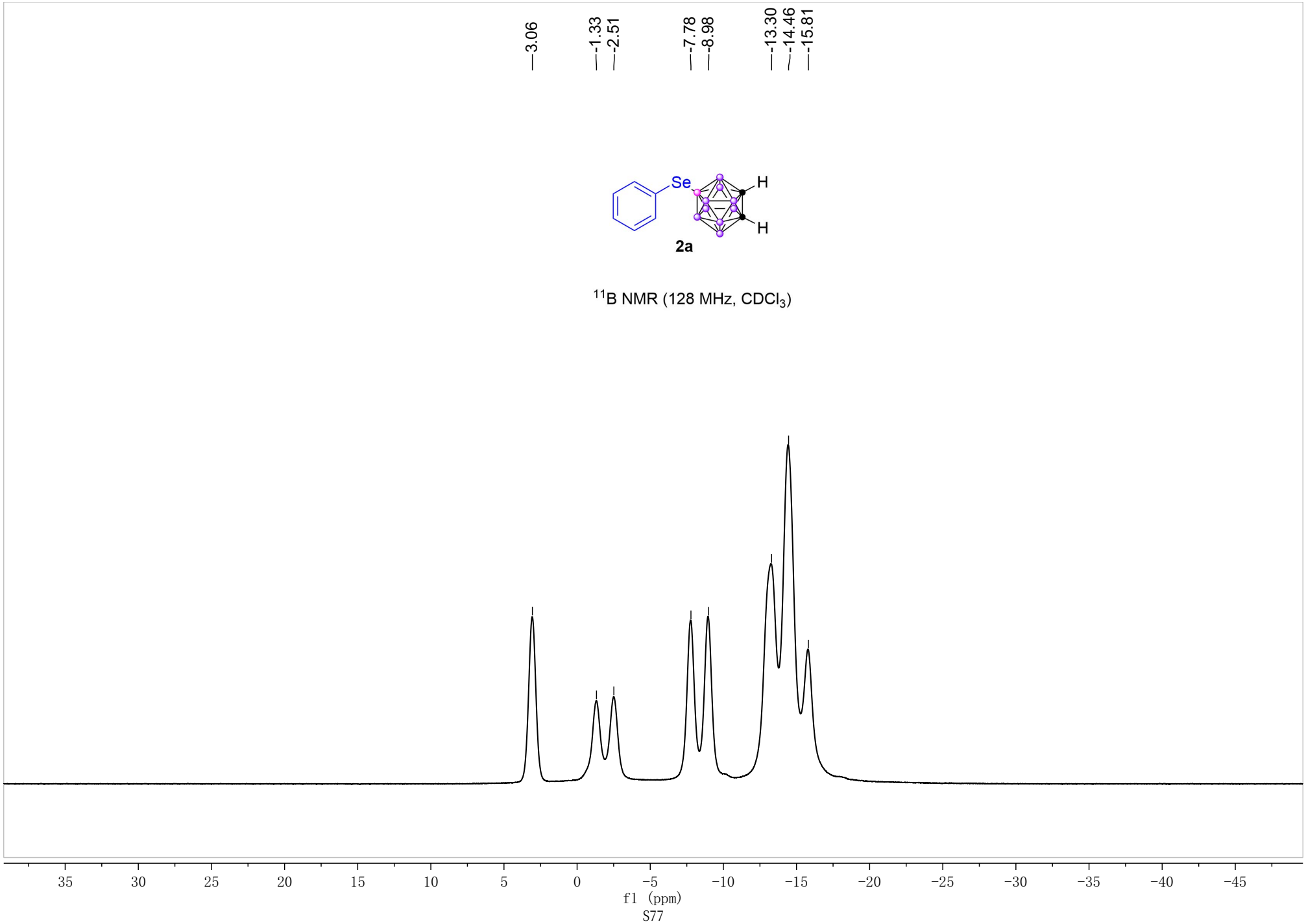

4.19
-5.65
-6.41
-7.07
-7.86
-9.25
-10.15
-11.41
-12.14
-12.92
S
1k
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

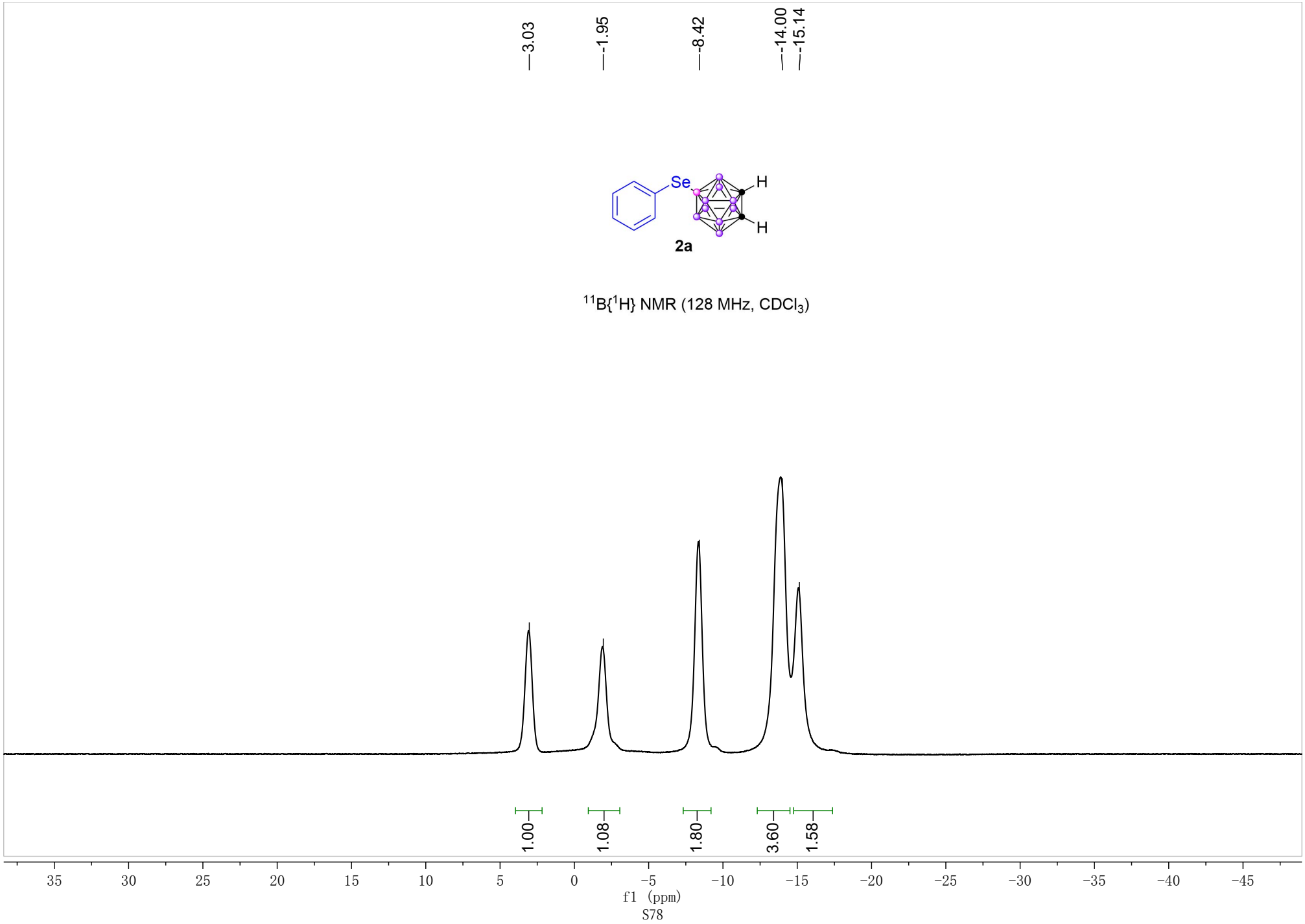

4.19
-6.03
-7.47
-9.70
-11.84
-12.49
S
1k
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)
1.00
1.01
1.86
1.76
1.79
1.90
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

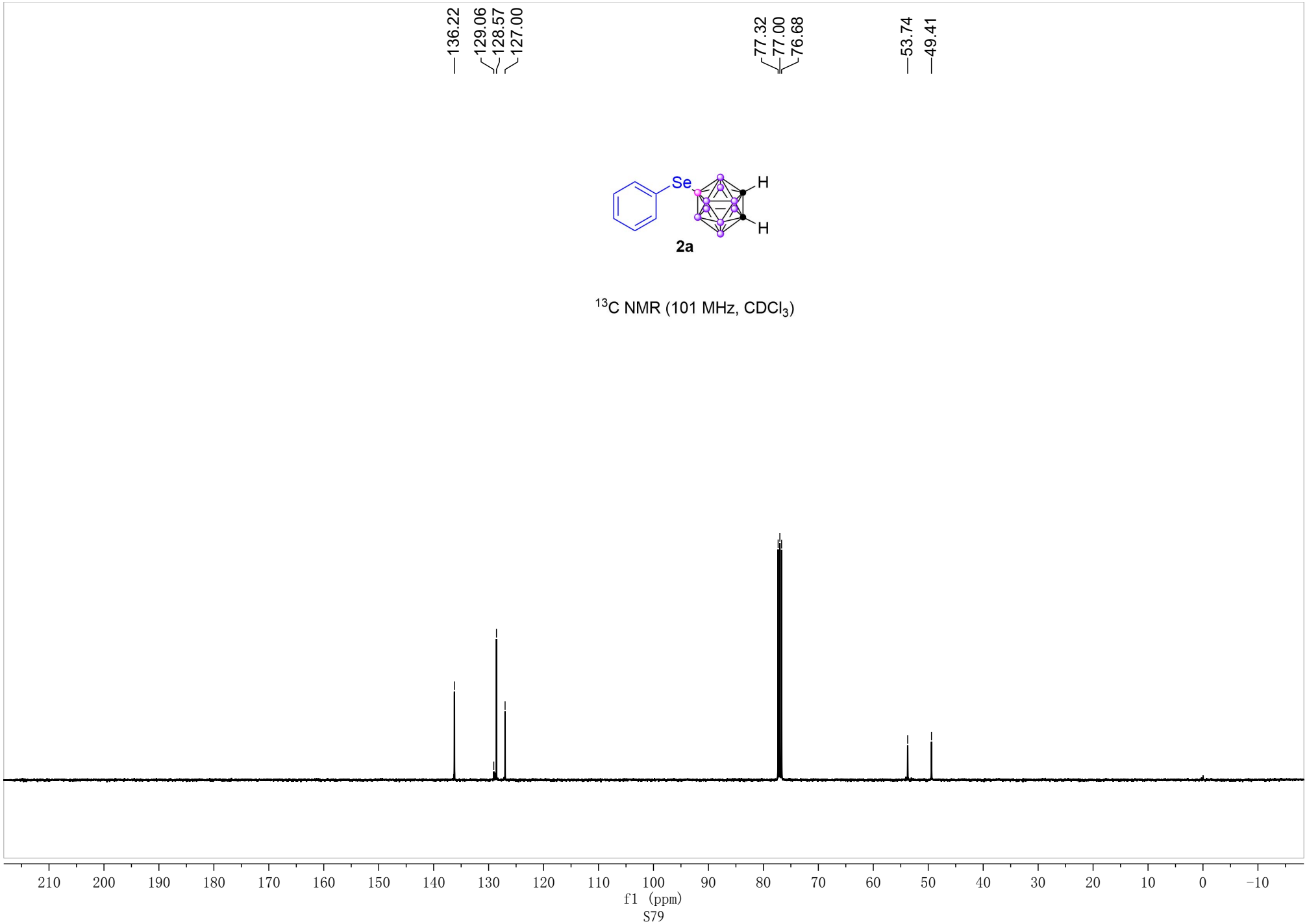

135.87
134.92
128.40
126.73
82.87
77.79
77.21
77.00
76.79
34.36
33.34
32.33
S
1k
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

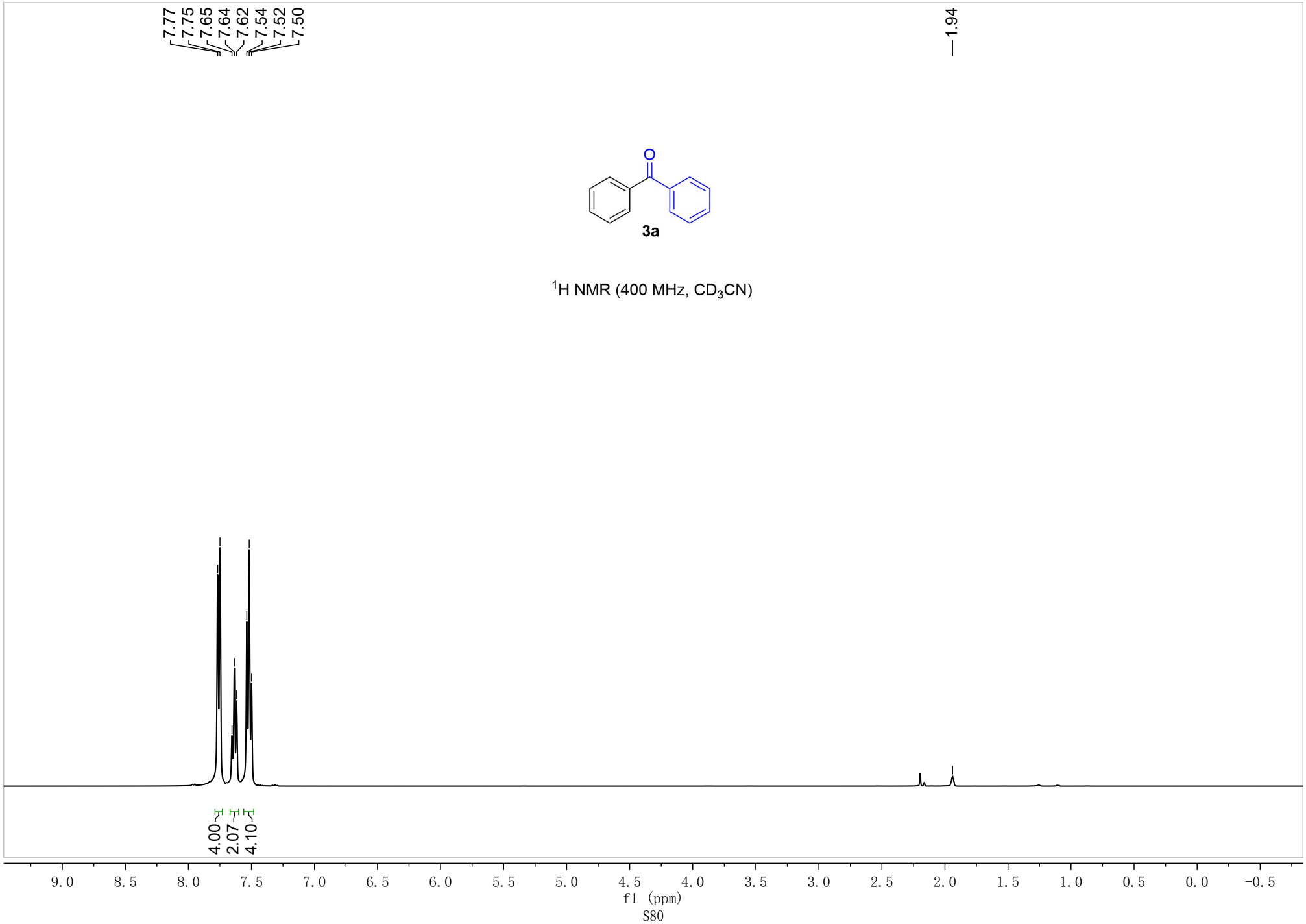

7.59
7.57
7.29
7.28
7.26
7.25
7.23
7.21
3.55
Se
H
H
2a
^{1}H NMR (400 MHz, $CDCl_3$)
2.00
0.90
2.02
2.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

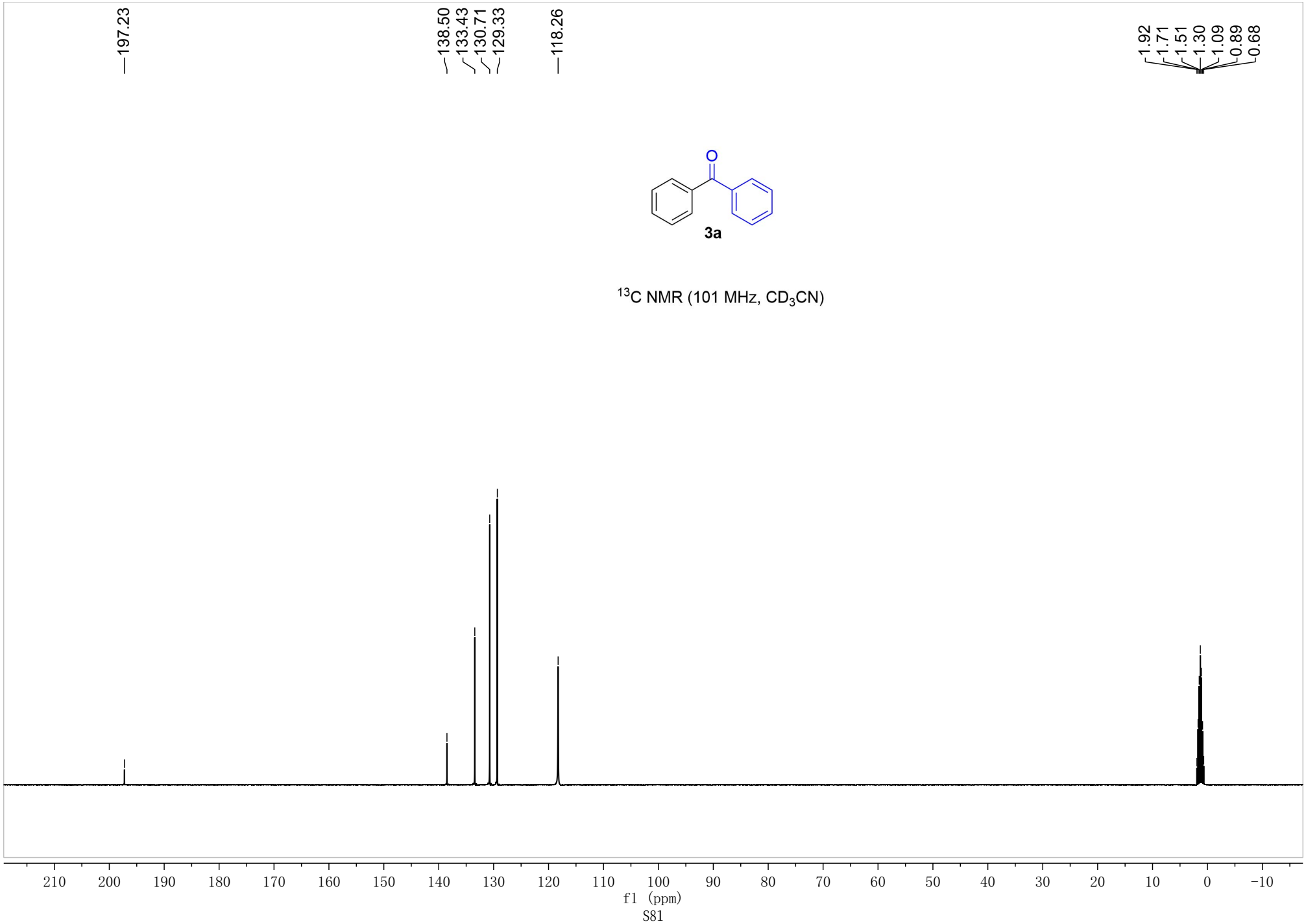

7.59
7.57
7.29
7.28
7.26
7.25
7.23
7.21
3.56
2.51
2.41
2.33
2.26
2.15
Se
H
H
2a
$^1H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)
2.00
0.88
2.26
2.30
1.20
2.28
2.27
2.27
2.30
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

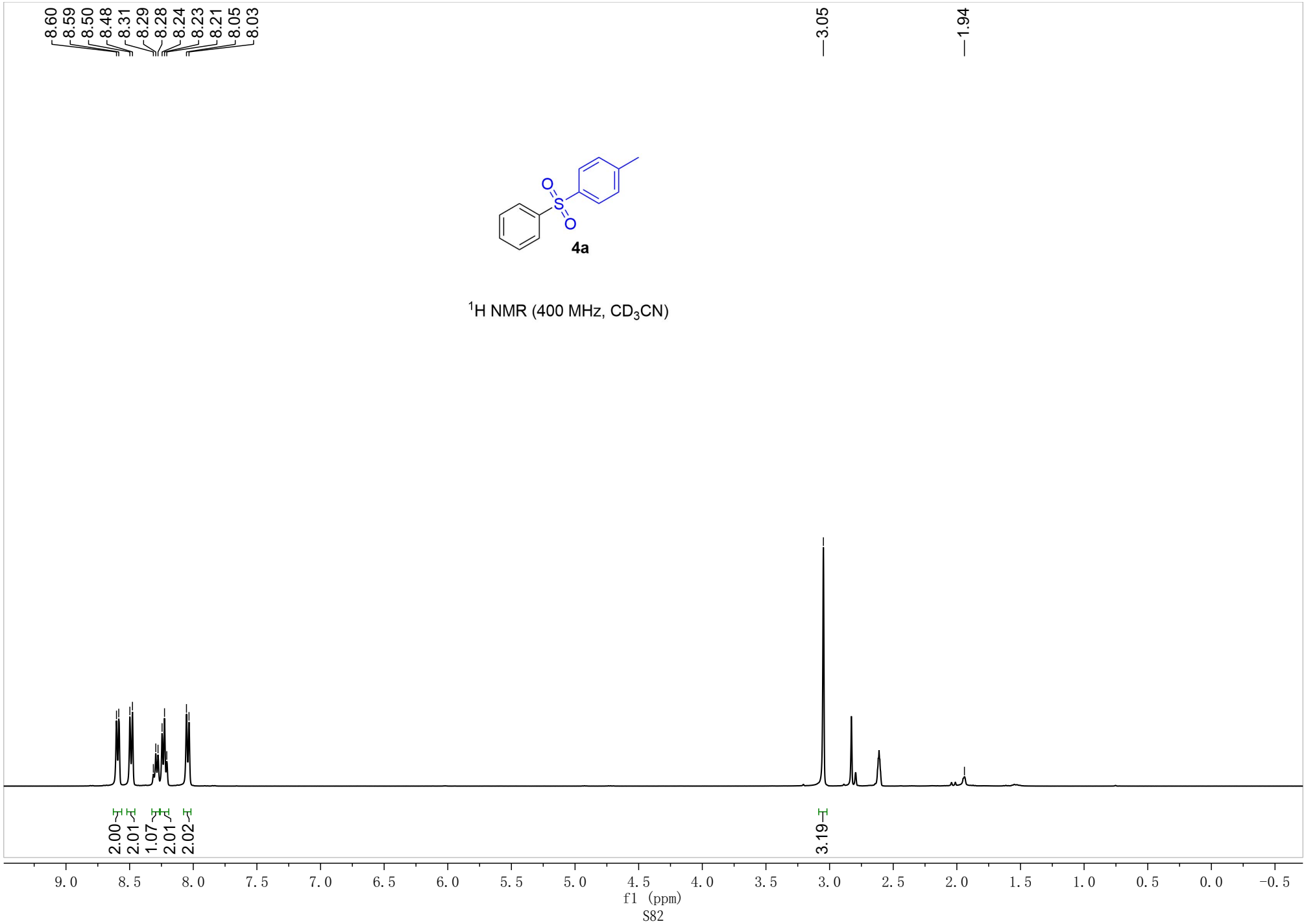

-3.06
-1.33
-2.51
-7.78
-8.98
-13.30
-14.46
-15.81
Se
H
H
2a
^{11}B NMR (128 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

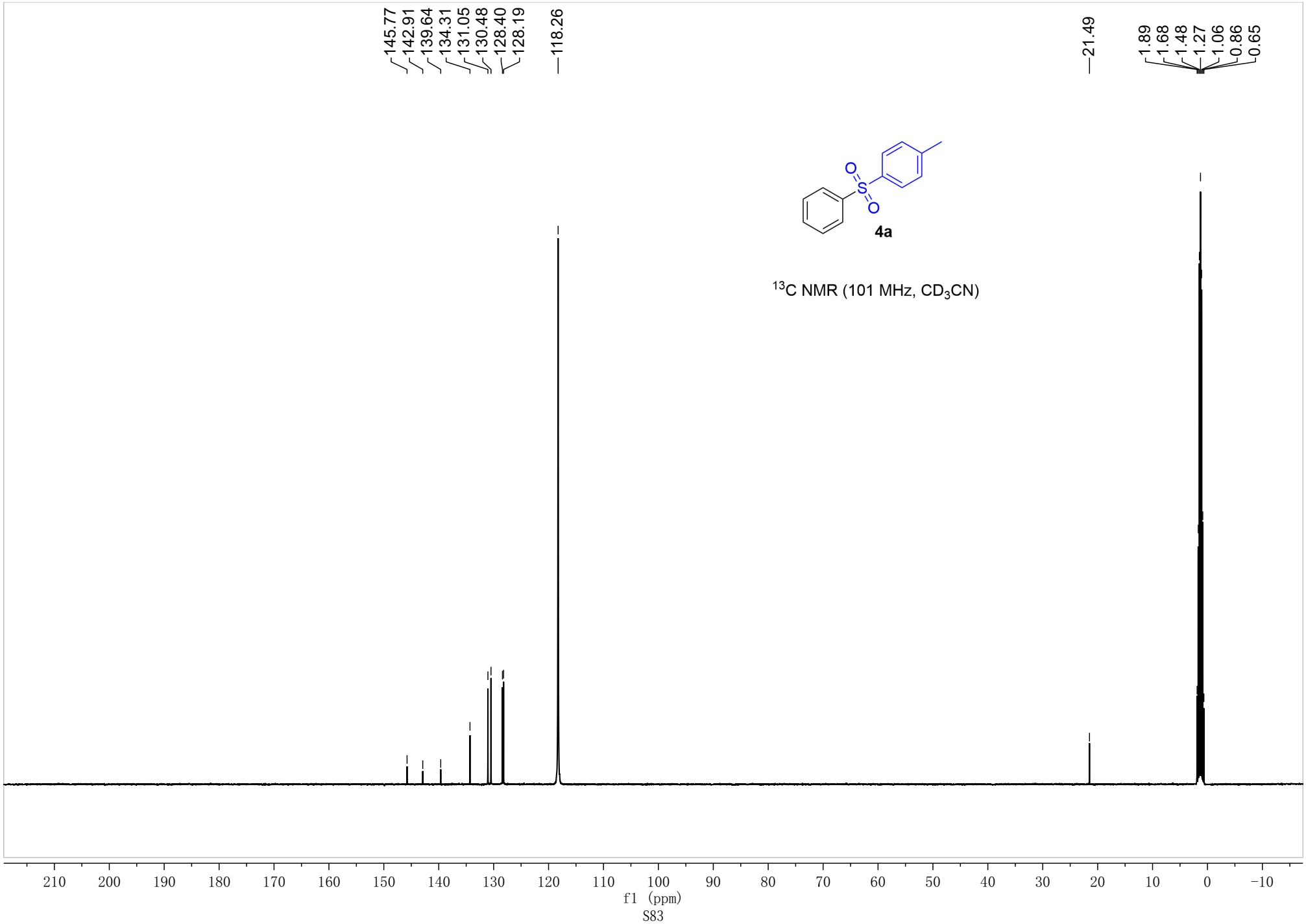

-3.03
-1.95
-8.42
-14.00
-15.14
Se
H
H
2a
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)
1.00
1.08
1.80
3.60
1.58
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

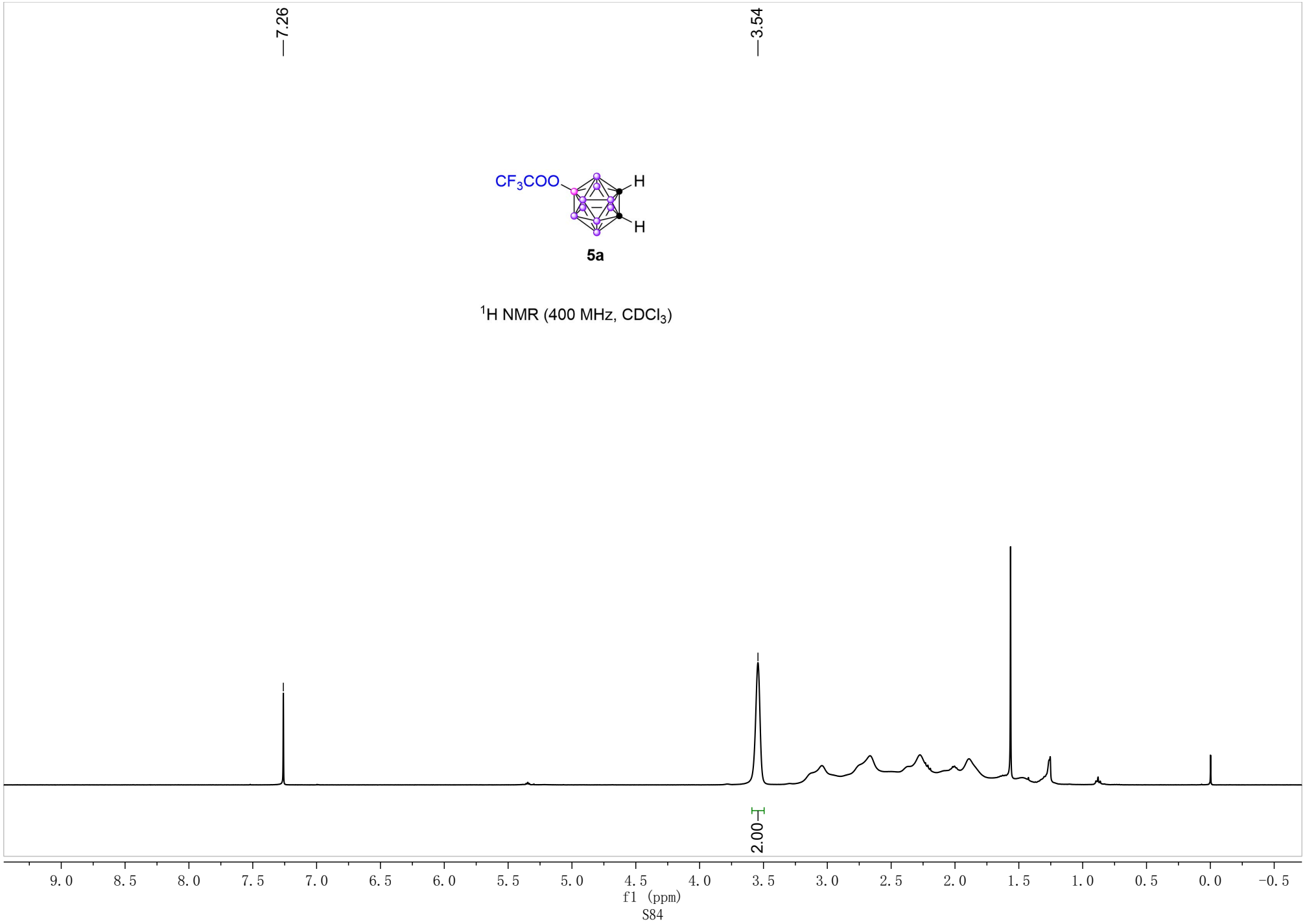

136.22
129.06
128.57
127.00
77.32
77.00
76.68
53.74
49.41
Se
H
H
2a
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

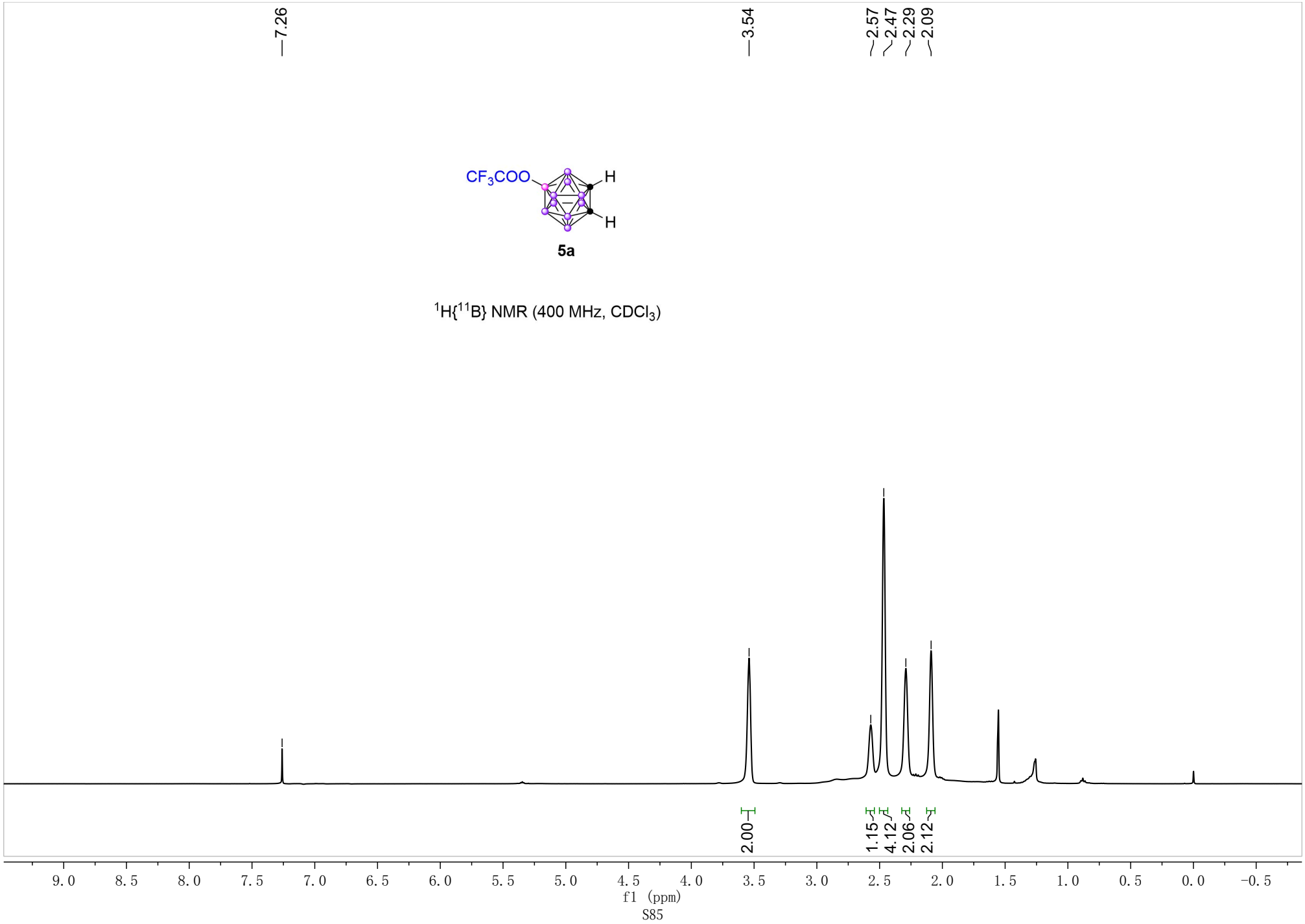

7.77
7.75
7.65
7.64
7.62
7.54
7.52
7.50
1.94
3a
^{1}H NMR (400 MHz, CD_3CN)
4.00
2.07
4.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

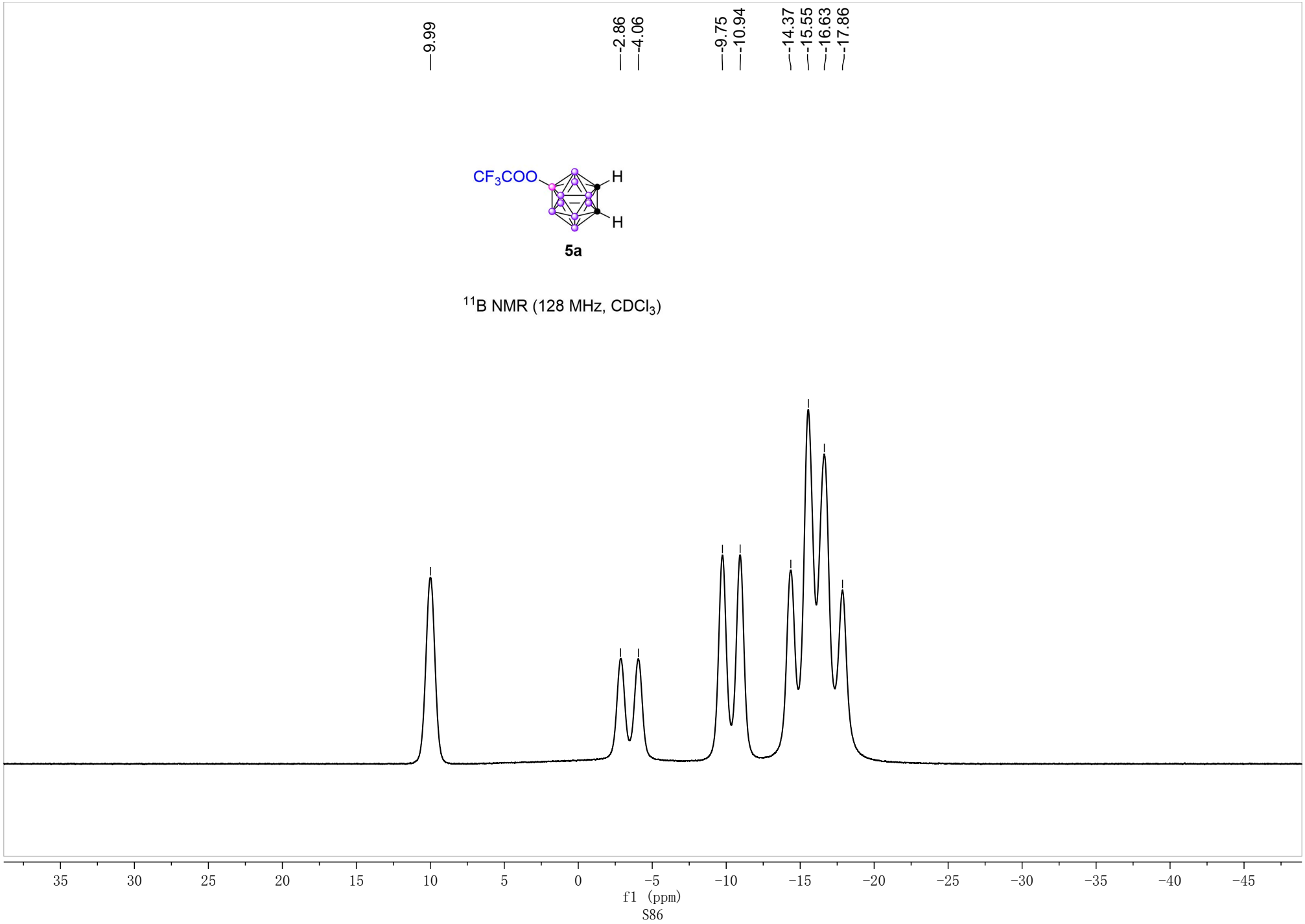

197.23
138.50
133.43
130.71
129.33
118.26
1.92
1.71
1.51
1.30
1.09
0.89
0.68
O
3a
13C NMR (101 MHz, CD3CN)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

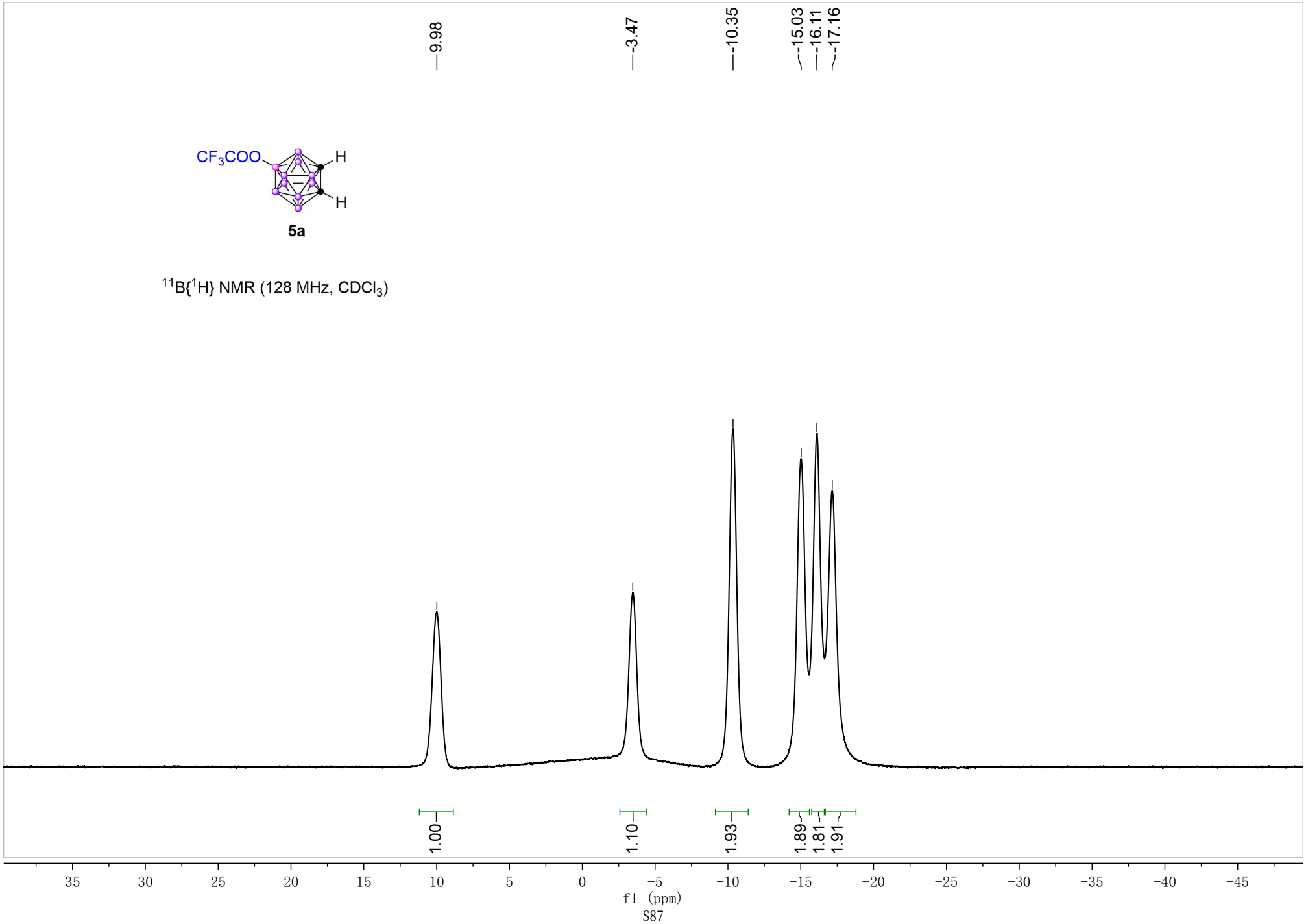

8.60
8.59
8.50
8.48
8.31
8.29
8.28
8.24
8.23
8.21
8.05
8.03
3.05
1.94
4a
^{1}H NMR (400 MHz, CD_3CN)
2.00
2.01
1.07
2.01
2.02
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

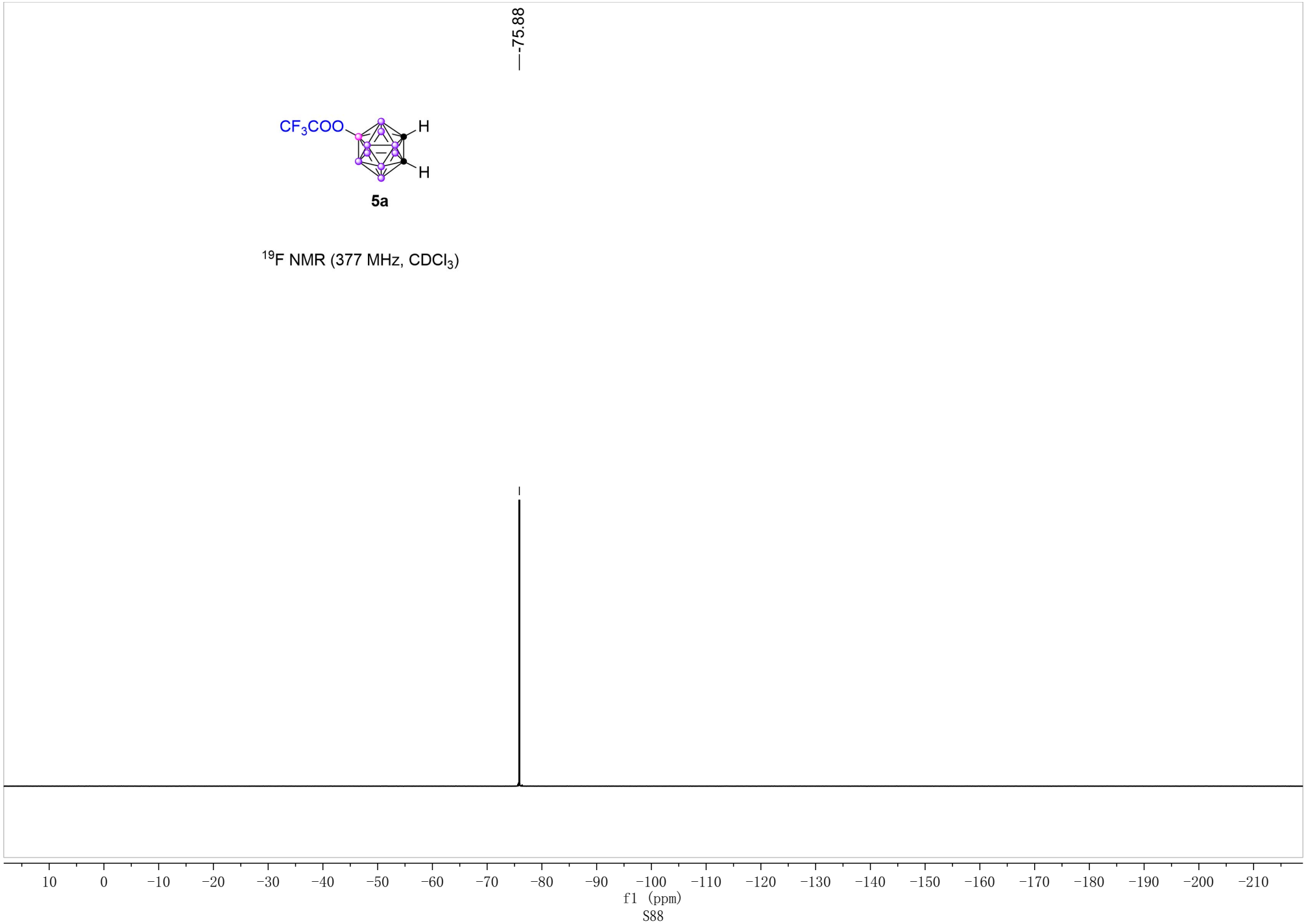

145.77
142.91
139.64
134.31
131.05
130.48
128.40
128.19
118.26
21.49
1.89
1.68
1.48
1.27
1.06
0.86
0.65
4a
^{13}C NMR (101 MHz, CD$_3$CN)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

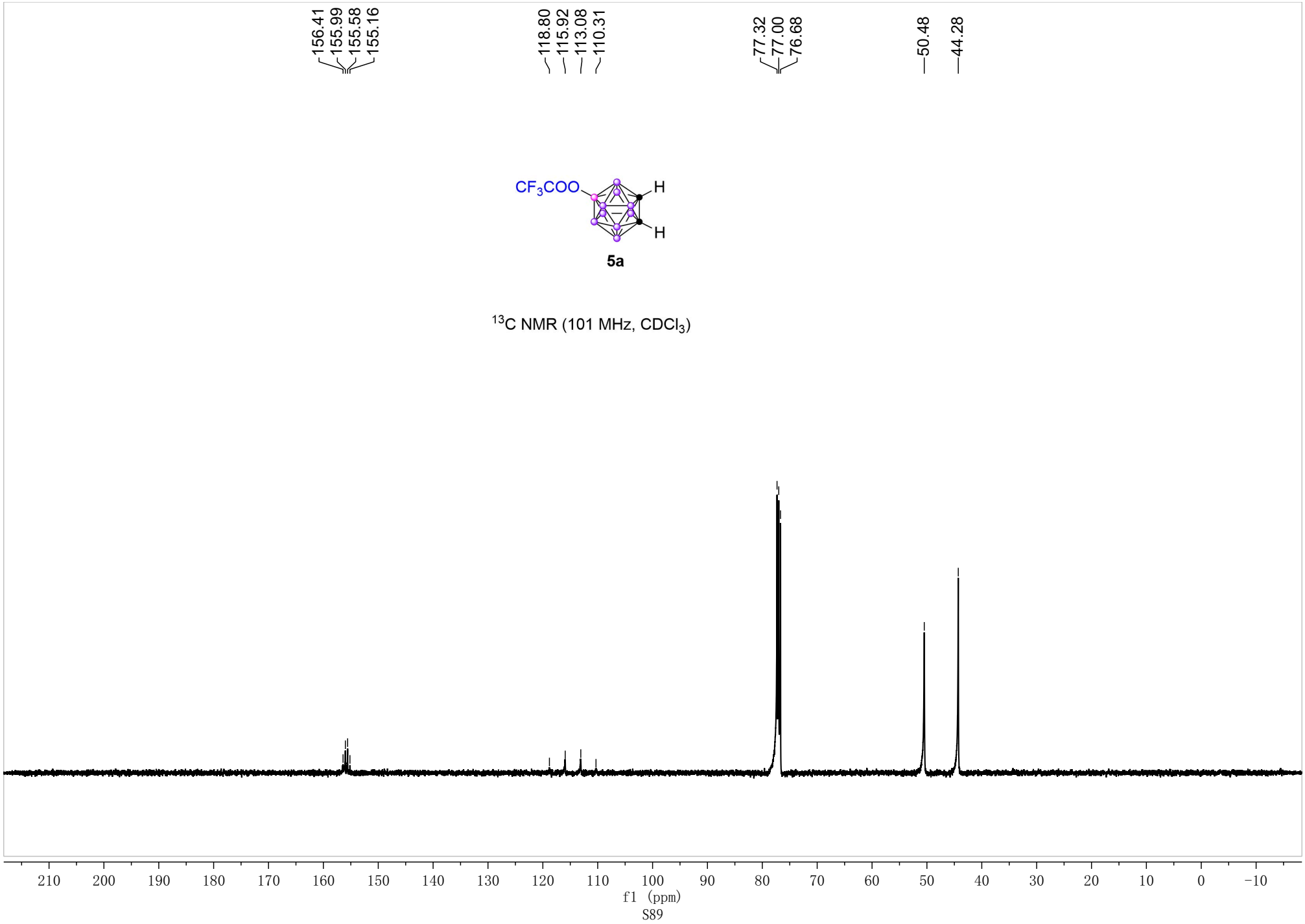

7.26
3.54
CF3COO
H
H
5a
1H NMR (400 MHz, CDCl3)
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

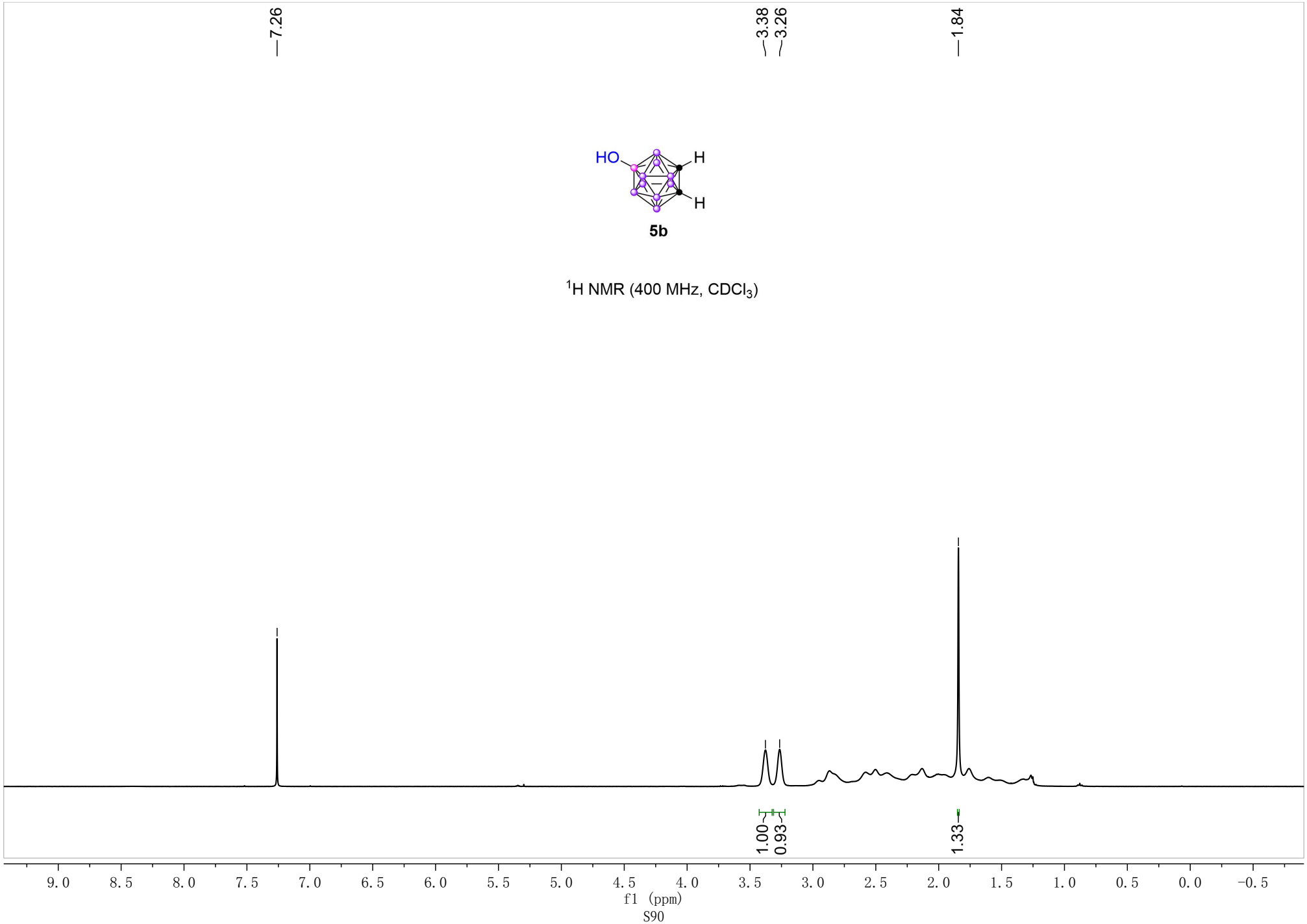

7.26
3.54
2.57
2.47
2.29
2.09
CF3COO
H
H
5a
1H{11B} NMR (400 MHz, CDCl3)
2.00
1.15
4.12
2.06
2.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

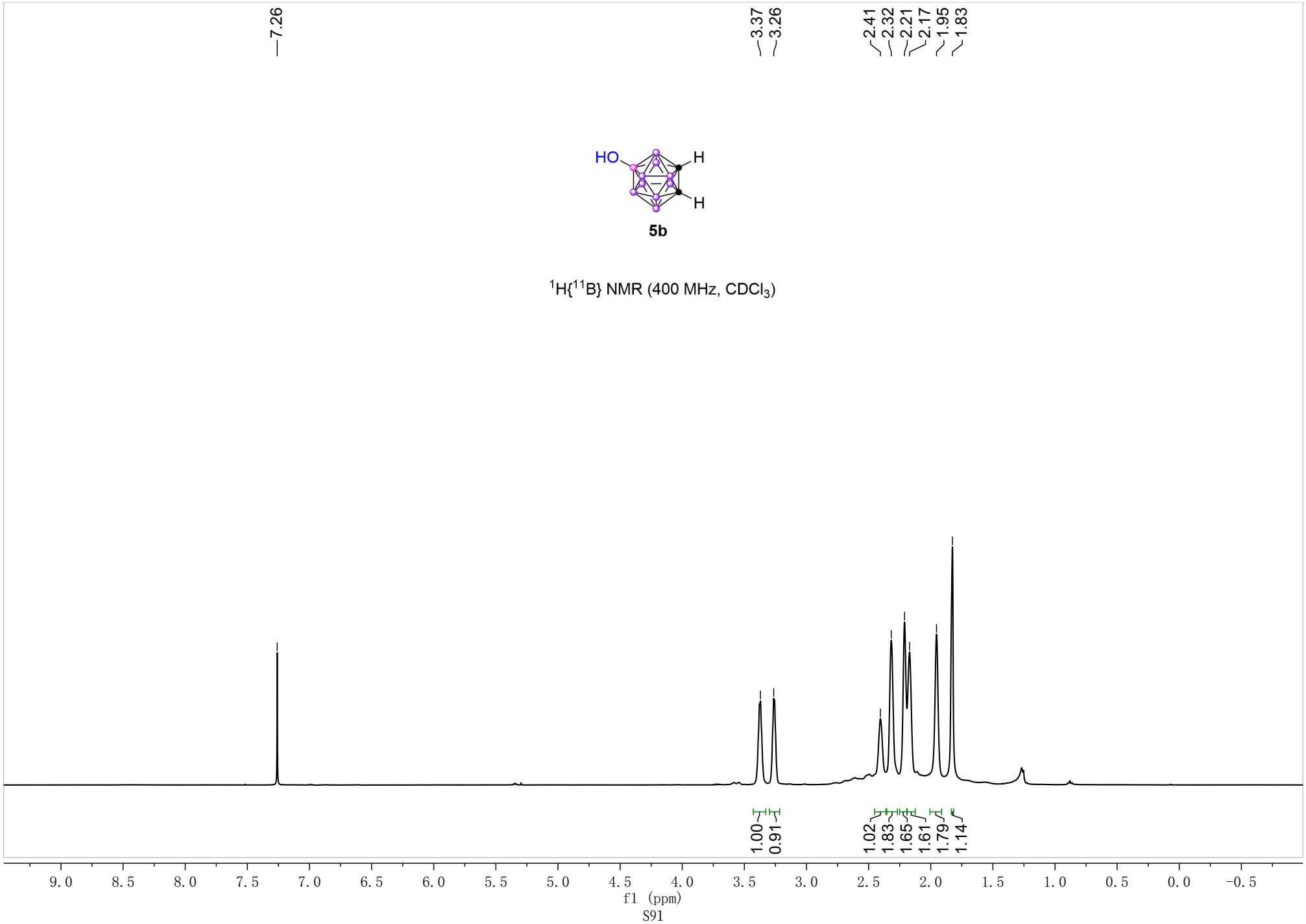

-9.99
-2.86
-4.06
-9.75
-10.94
-14.37
-15.55
-16.63
-17.86
CF3COO
H
H
5a
11B NMR (128 MHz, CDCl3)
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

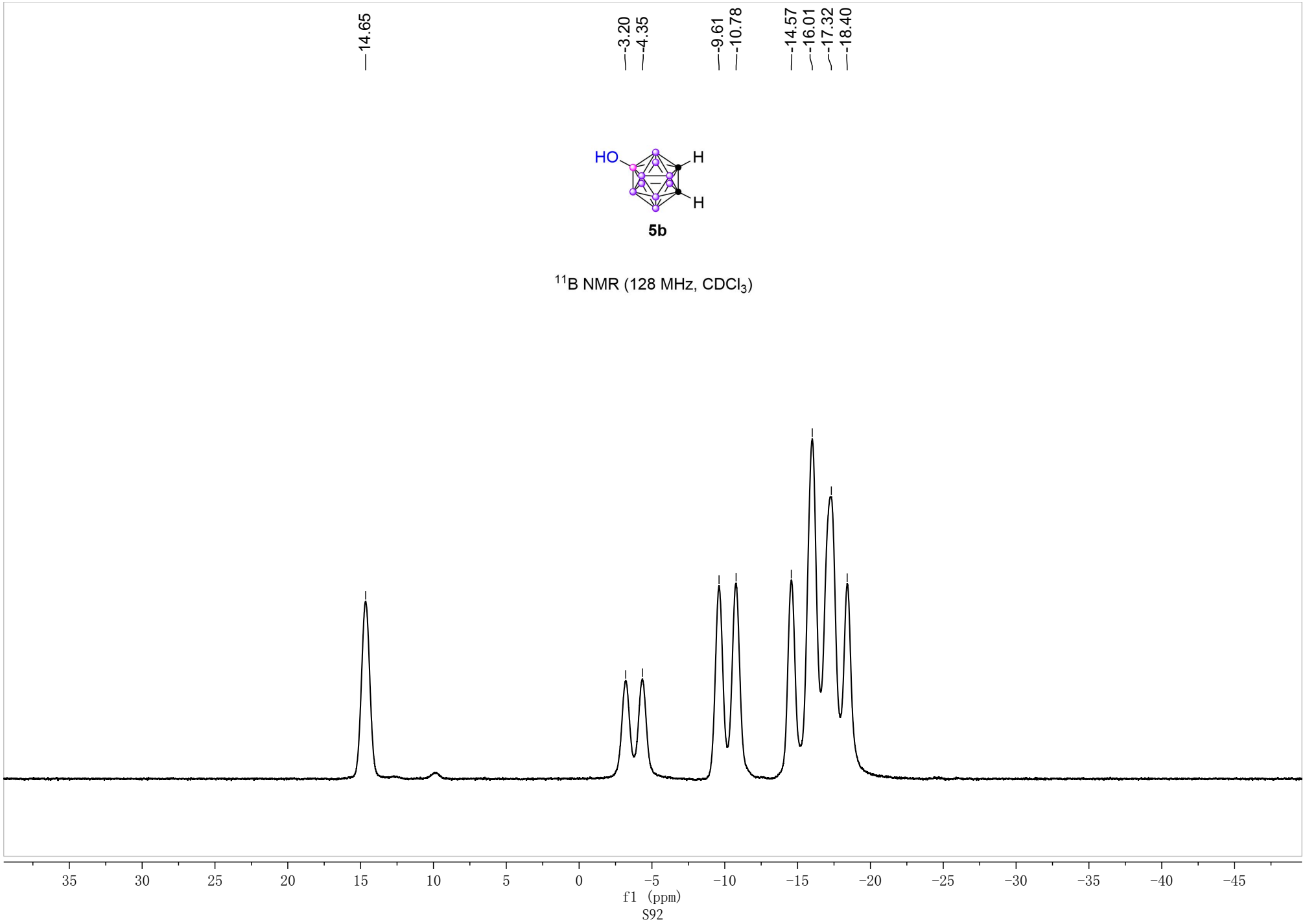

-9.98
-3.47
-10.35
-15.03
-16.11
-17.16
CF3COO
H
H
5a
11B{1H} NMR (128 MHz, CDCl3)
1.00
1.10
1.93
1.89
1.81
1.91
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

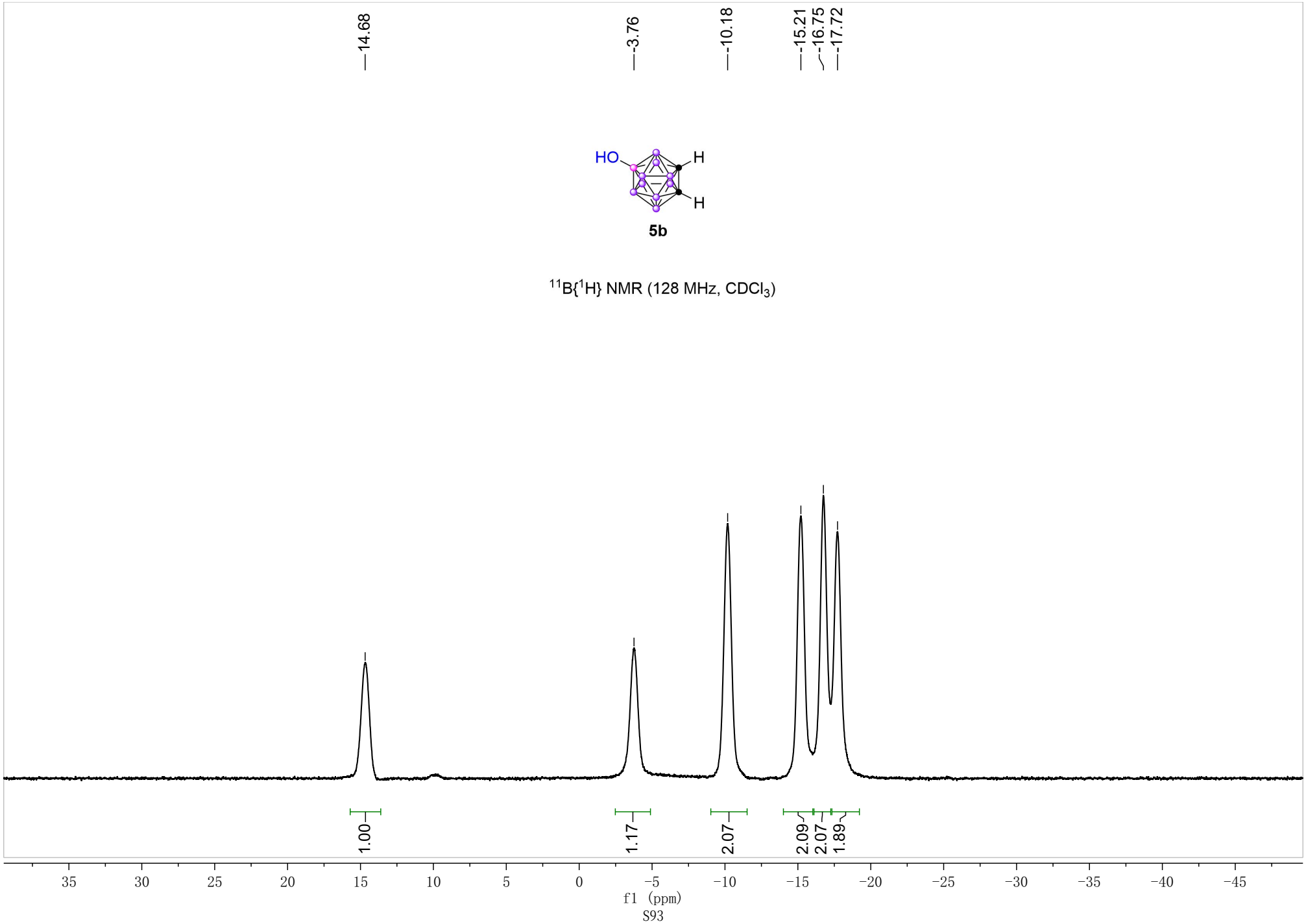

-75.88
CF3COO
H
H
5a
19F NMR (377 MHz, CDCl3)
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

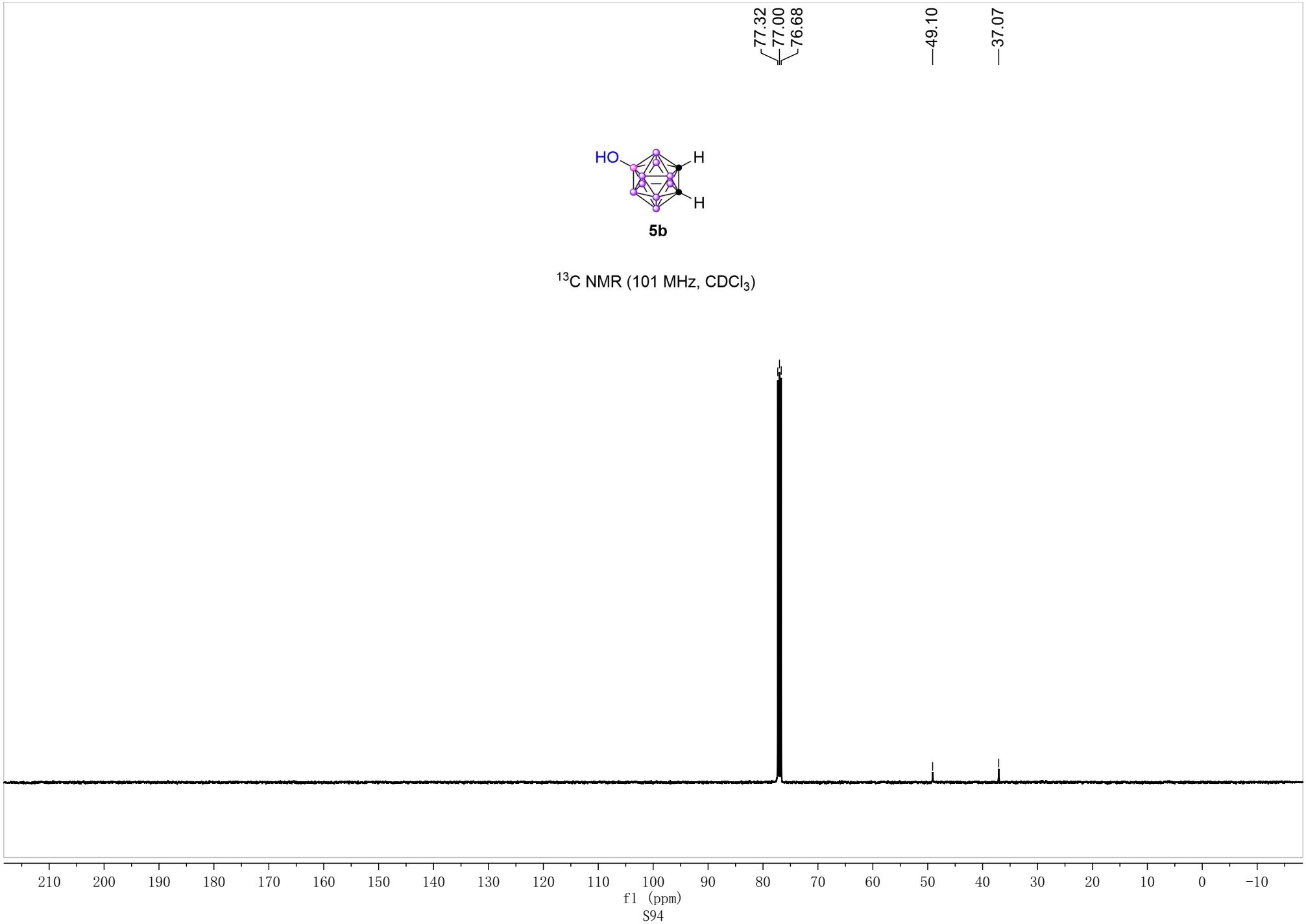

156.41
155.99
155.58
155.16
118.80
115.92
113.08
110.31
77.32
77.00
76.68
50.48
44.28
CF3COO
H
H
5a
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

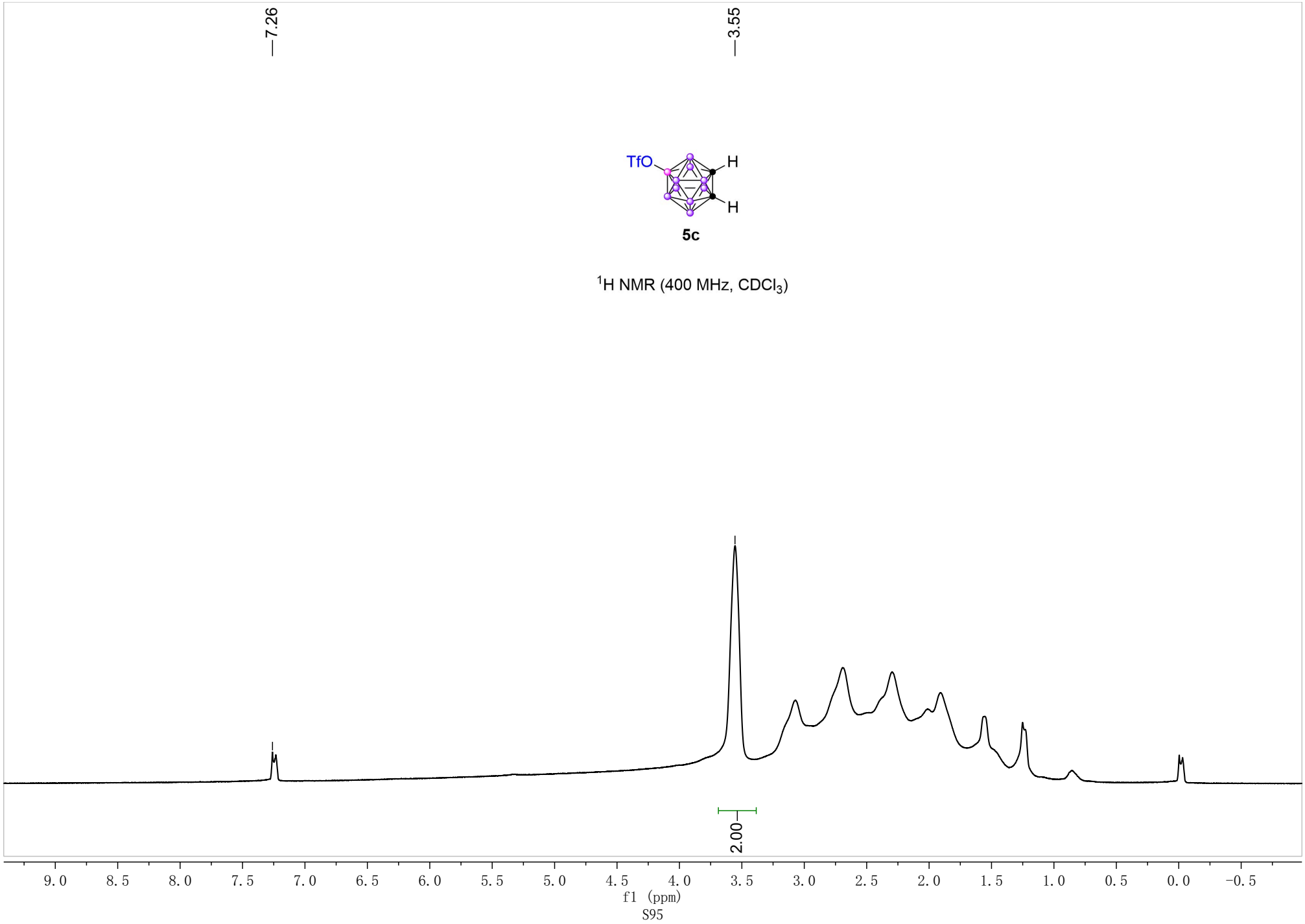

7.26
3.38
3.26
1.84
HO
H
H
5b
1H NMR (400 MHz, CDCl3)
1.00
0.93
1.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

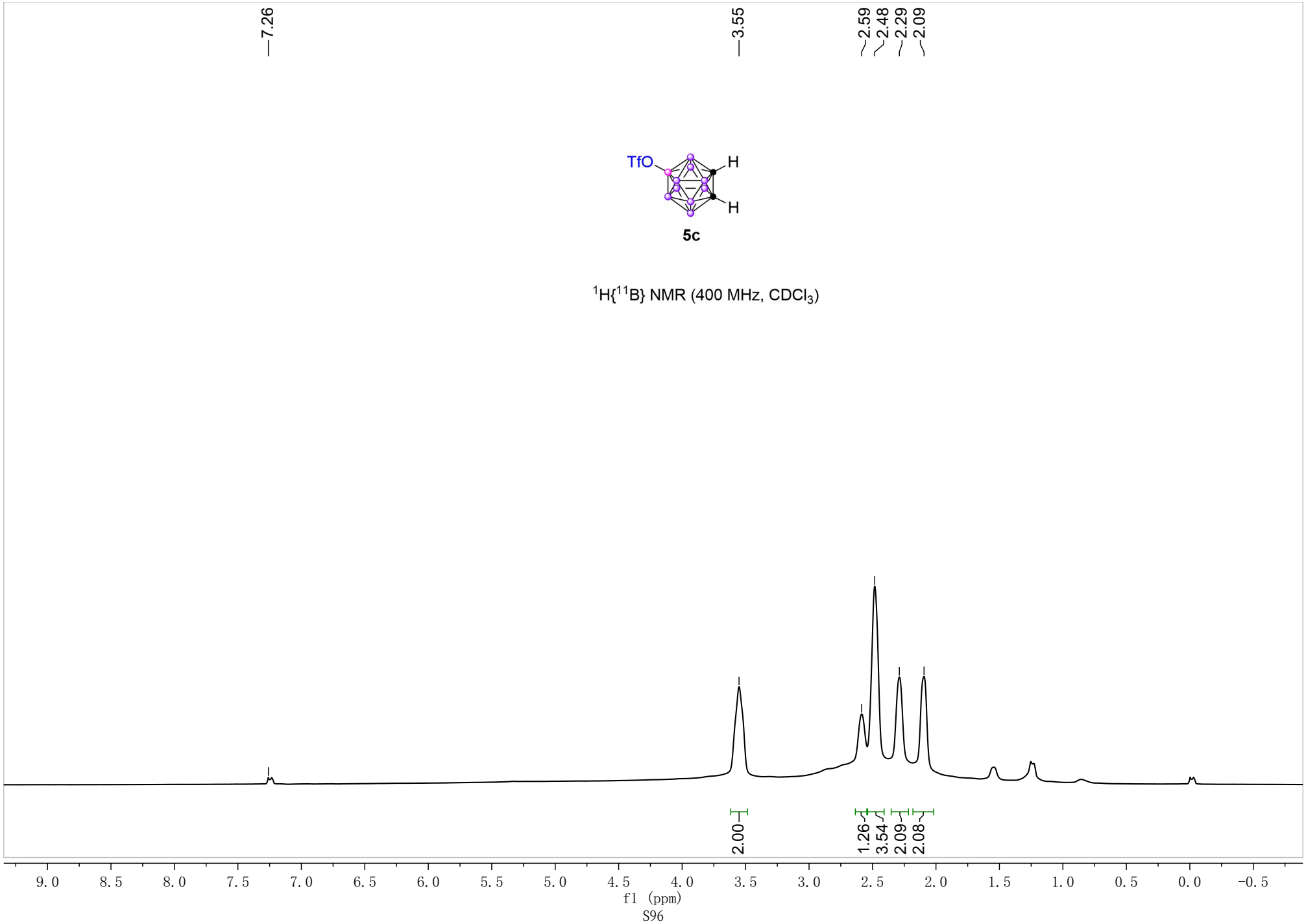

7.26
3.37
3.26
2.41
2.32
2.21
2.17
1.95
1.83
HO
H
H
5b
1H{11B} NMR (400 MHz, CDCl3)
1.00
0.91
1.02
1.83
1.65
1.61
1.79
1.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

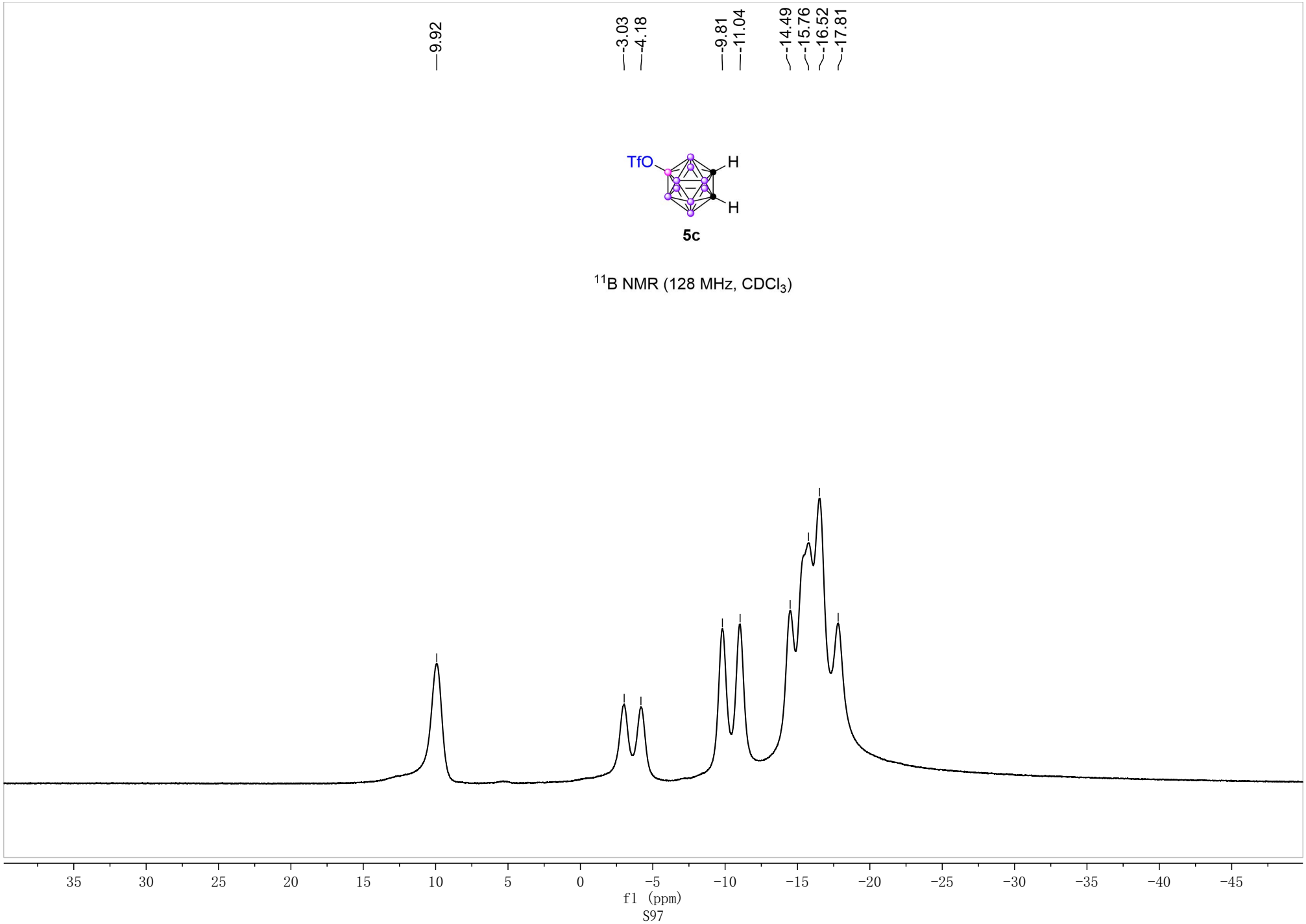

14.65
-3.20
-4.35
-9.61
-10.78
-14.57
-16.01
-17.32
-18.40
HO
H
H
5b
^{11}B NMR (128 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

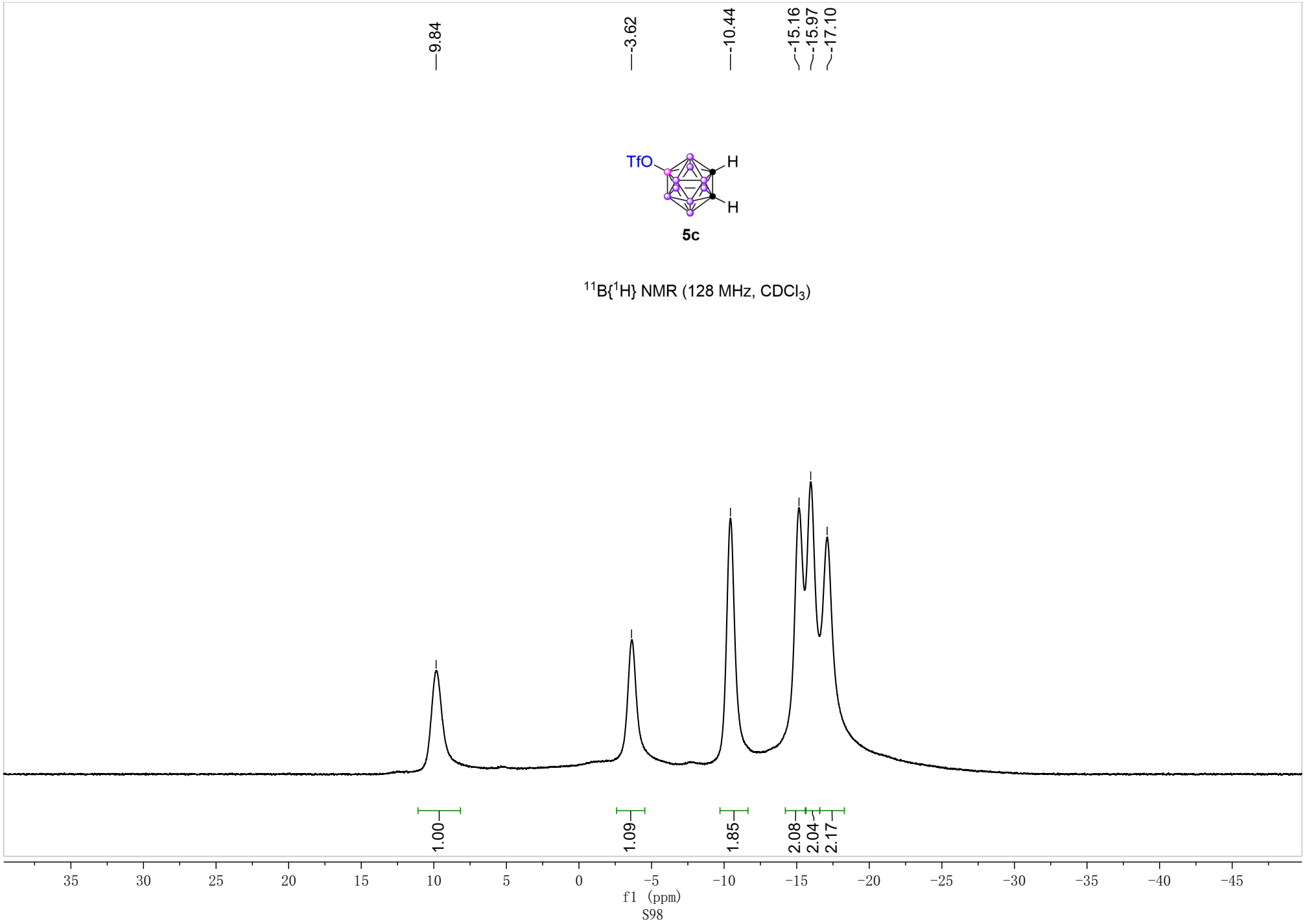

14.68
-3.76
-10.18
-15.21
-16.75
-17.72
HO
H
H
5b
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)
1.00
1.17
2.07
2.09
2.07
1.89
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

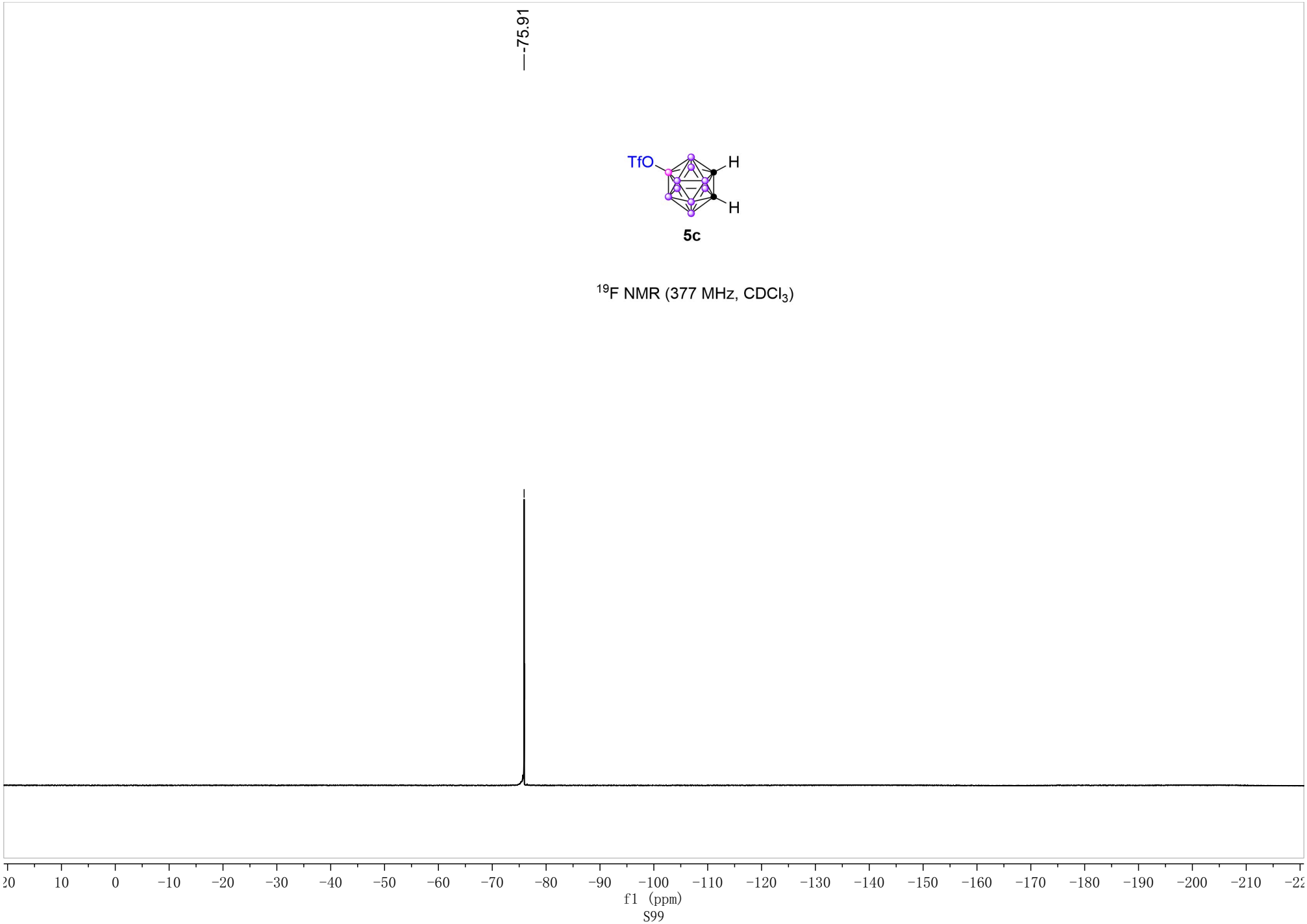

77.32
77.00
76.68
49.10
37.07
HO
H
H
5b
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

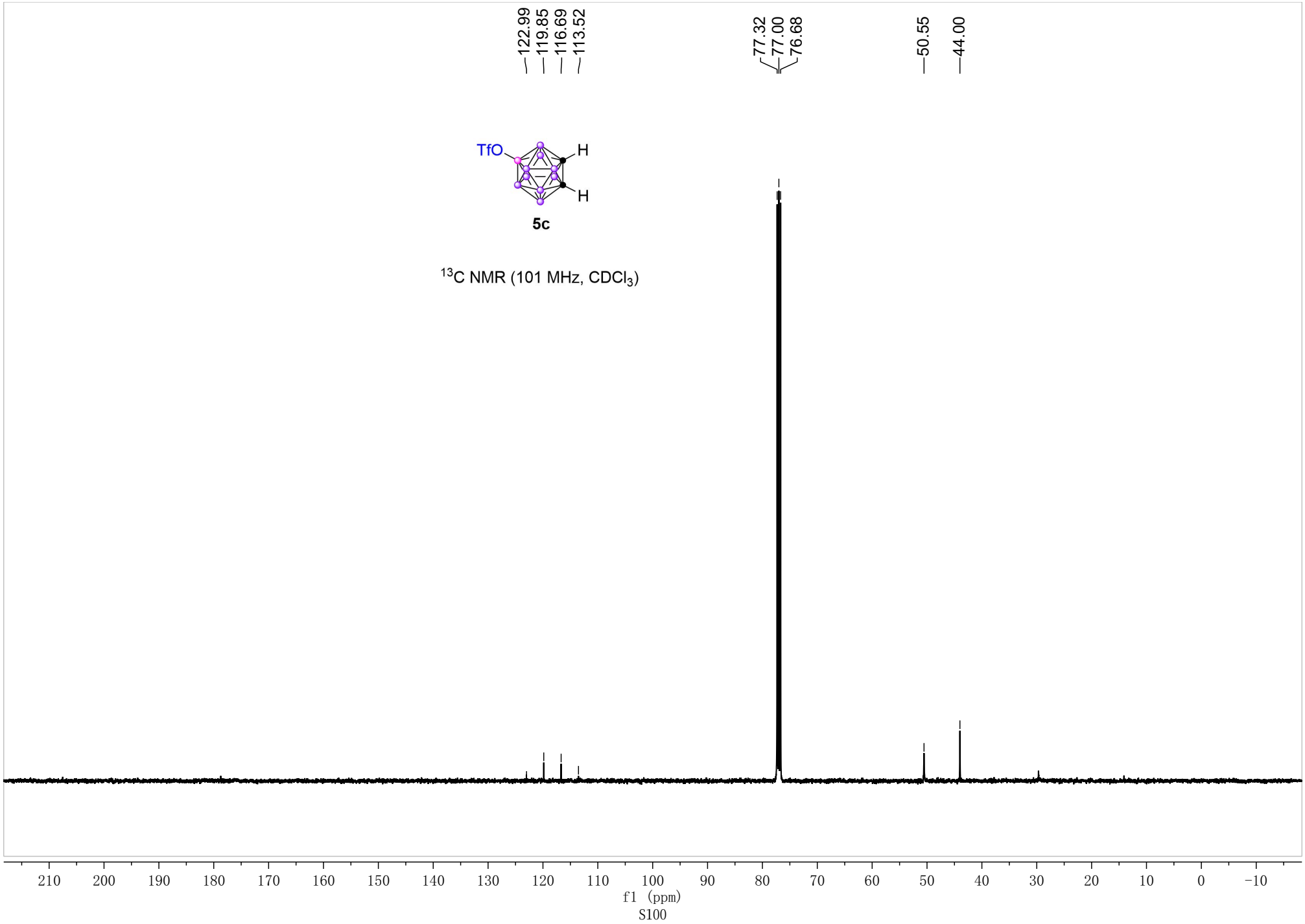

7.26
3.55
TfO
H
H
5c
^{1}H NMR (400 MHz, $CDCl_3$)
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

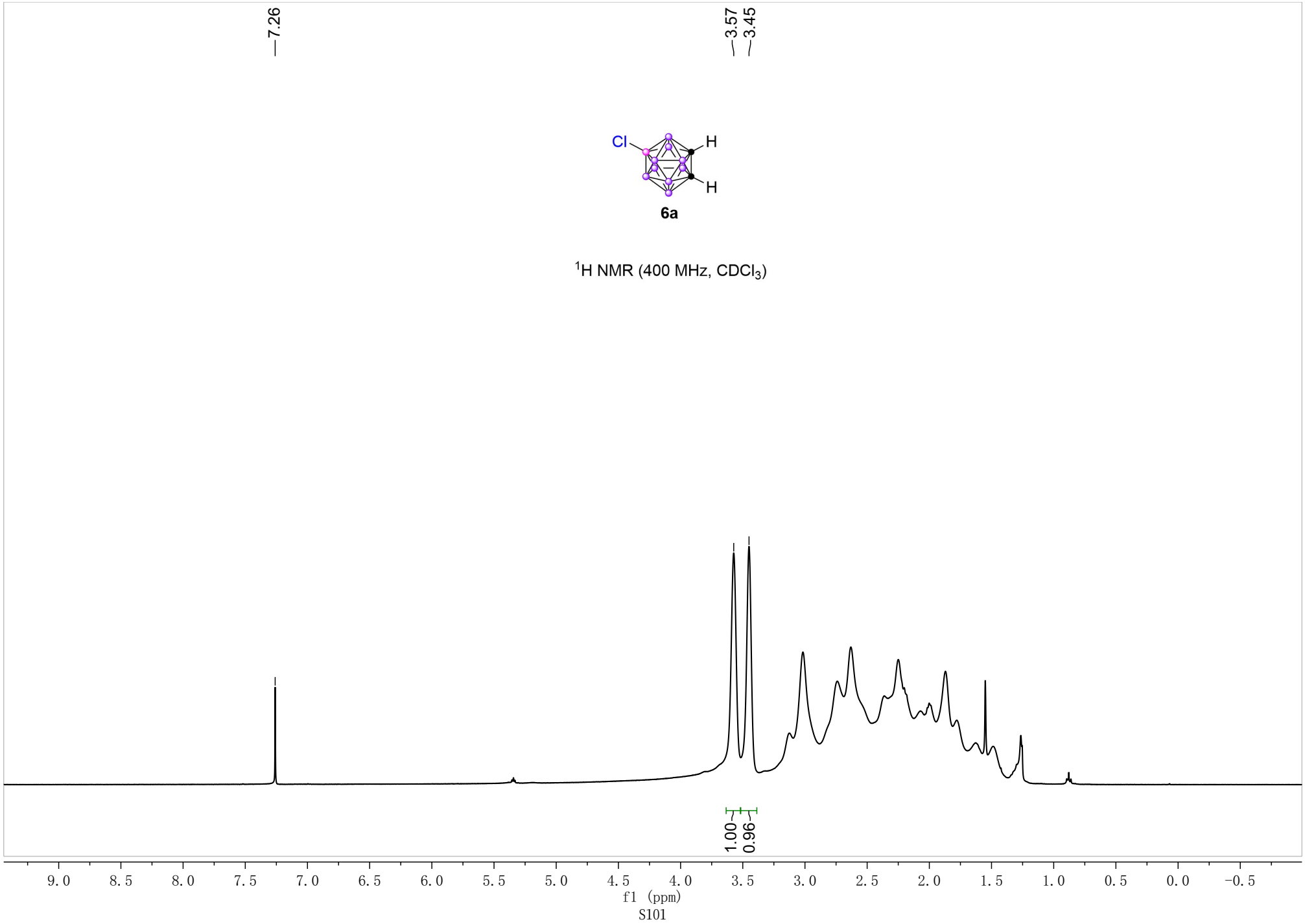

7.26
3.55
2.59
2.48
2.29
2.09
TfO
H
H
5c
$^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)
2.00
1.26
3.54
2.09
2.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

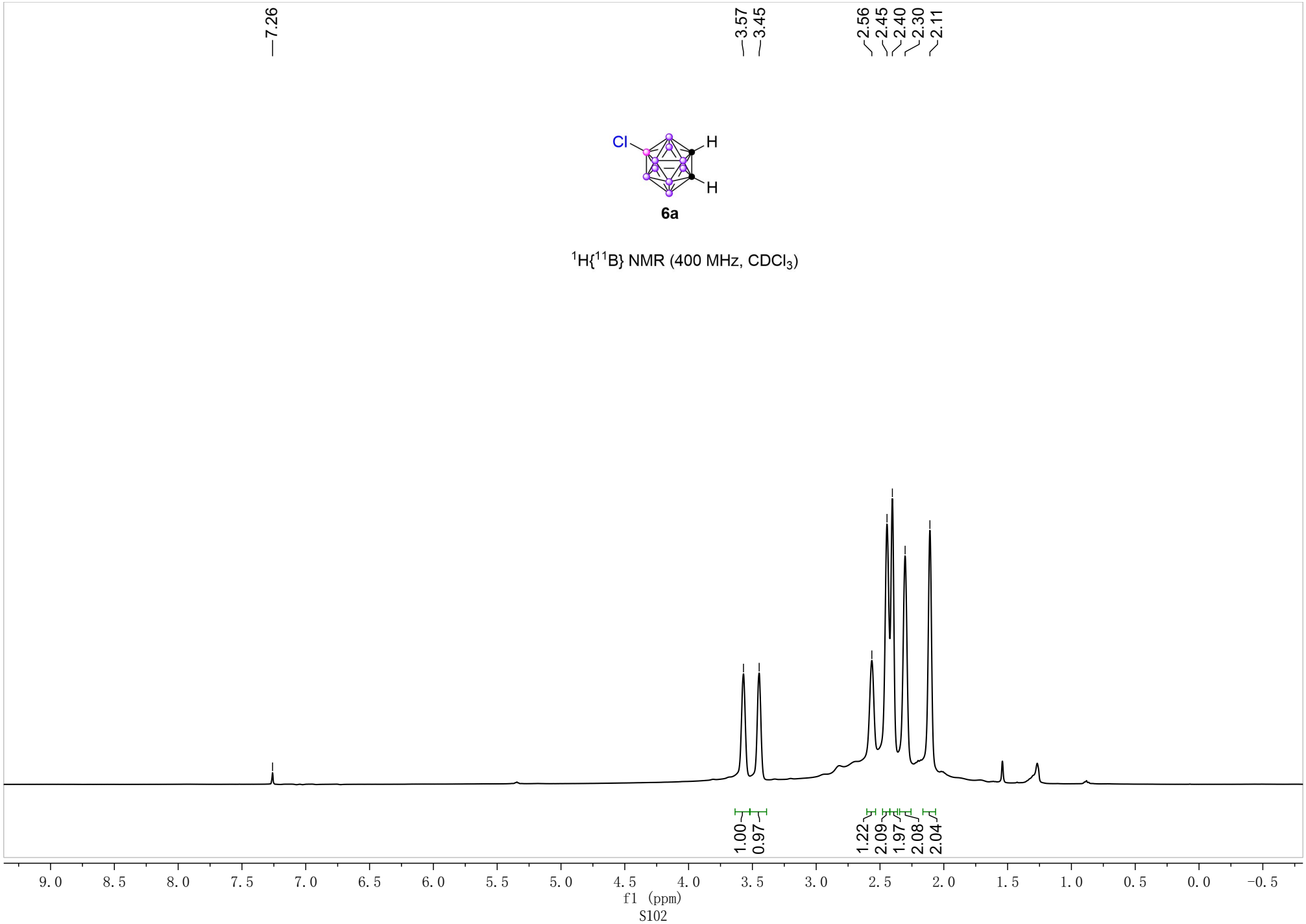

-9.92
-3.03
-4.18
-9.81
-11.04
-14.49
-15.76
-16.52
-17.81
TfO
H
H
5c
^{11}B NMR (128 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

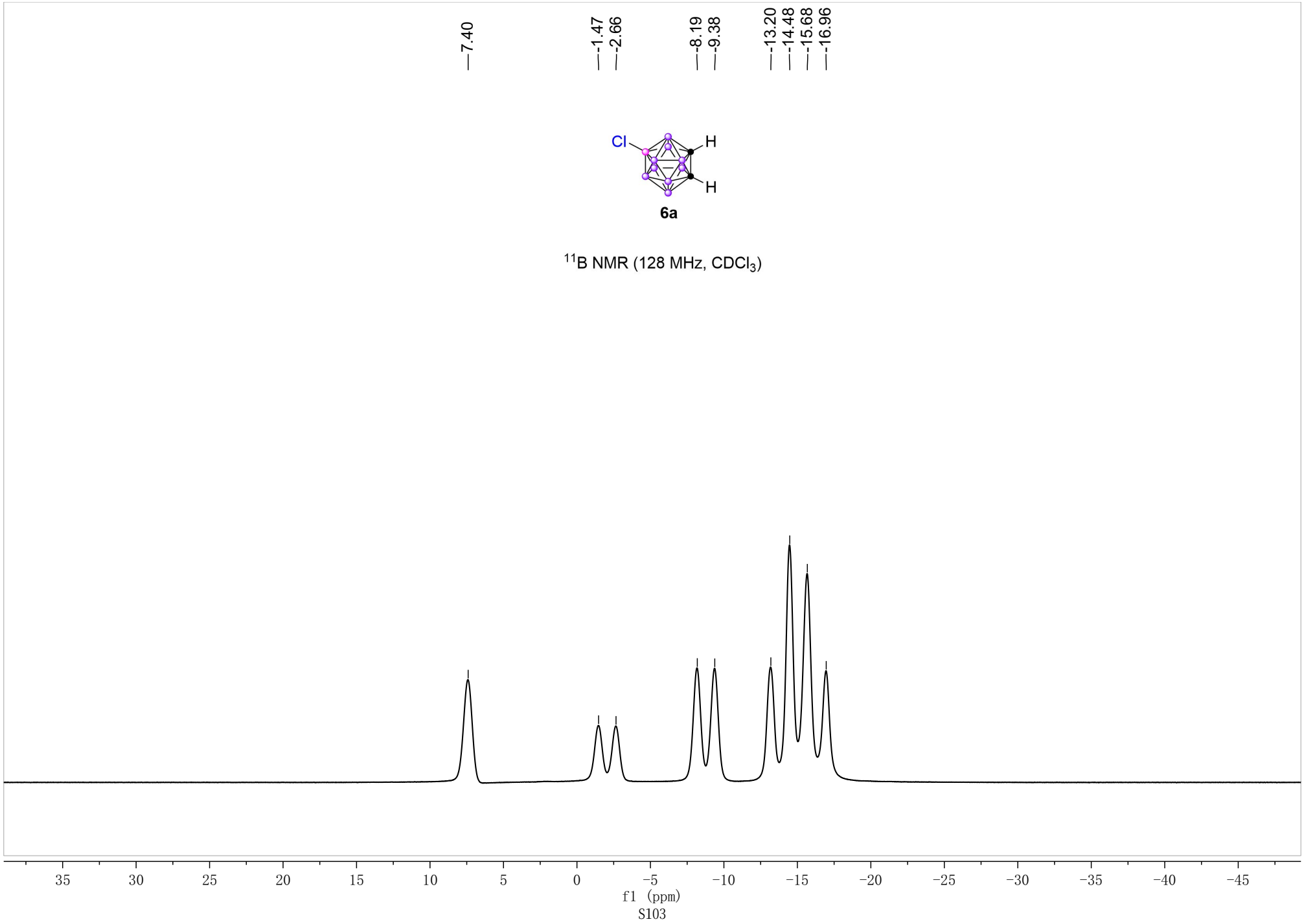

-9.84
-3.62
-10.44
-15.16
-15.97
-17.10
TfO
H
H
5c
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)
1.00
1.09
1.85
2.08
2.04
2.17
35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45
f1 (ppm)
S98

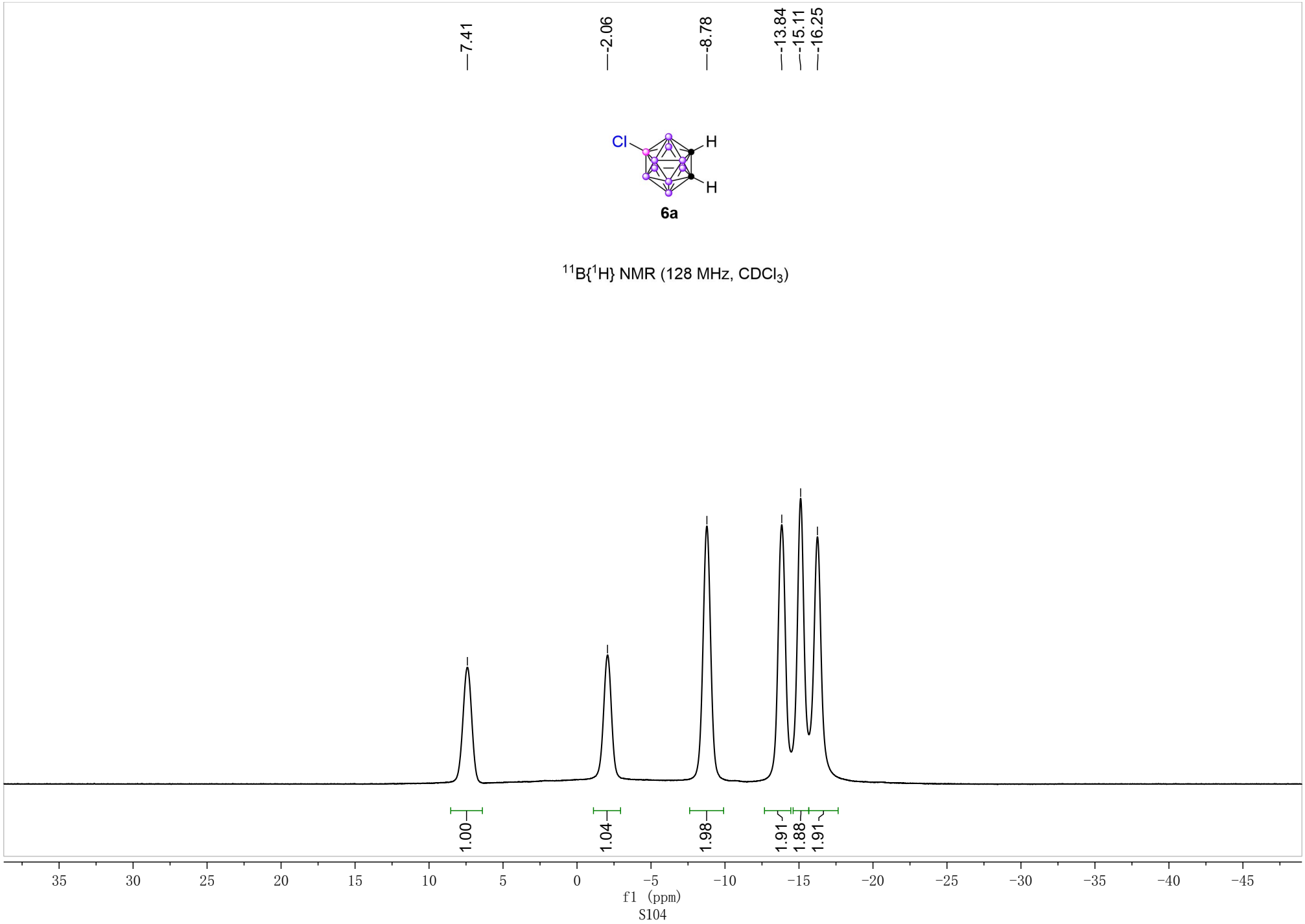

-75.91
TfO
H
H
5c
^{19}F NMR (377 MHz, $CDCl_3$)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

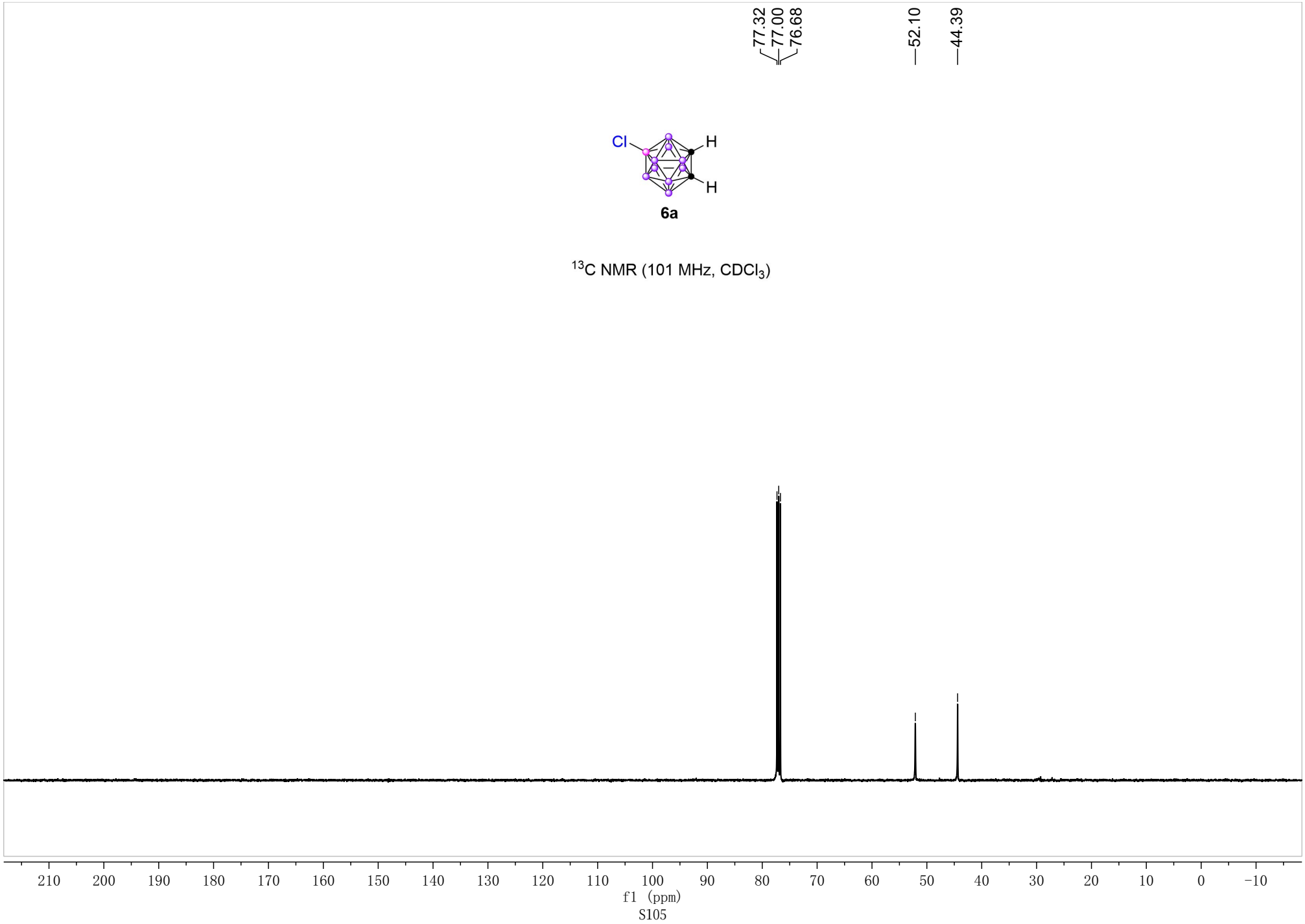

122.99
119.85
116.69
113.52
77.32
77.00
76.68
50.55
44.00
TfO
H
H
5c
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

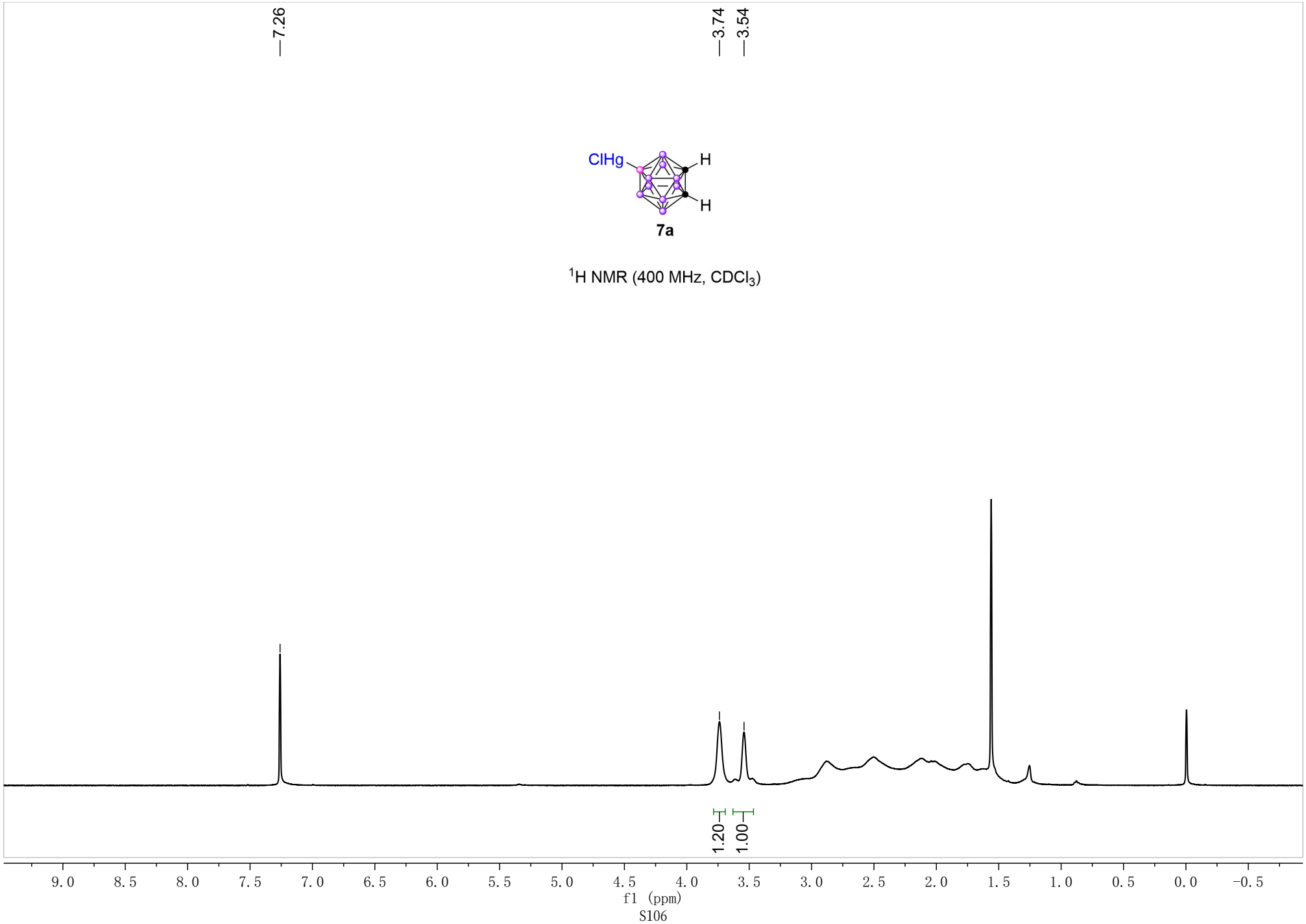

7.26
3.57
3.45
Cl
H
H
6a
1H NMR (400 MHz, CDCl3)
1.00
0.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

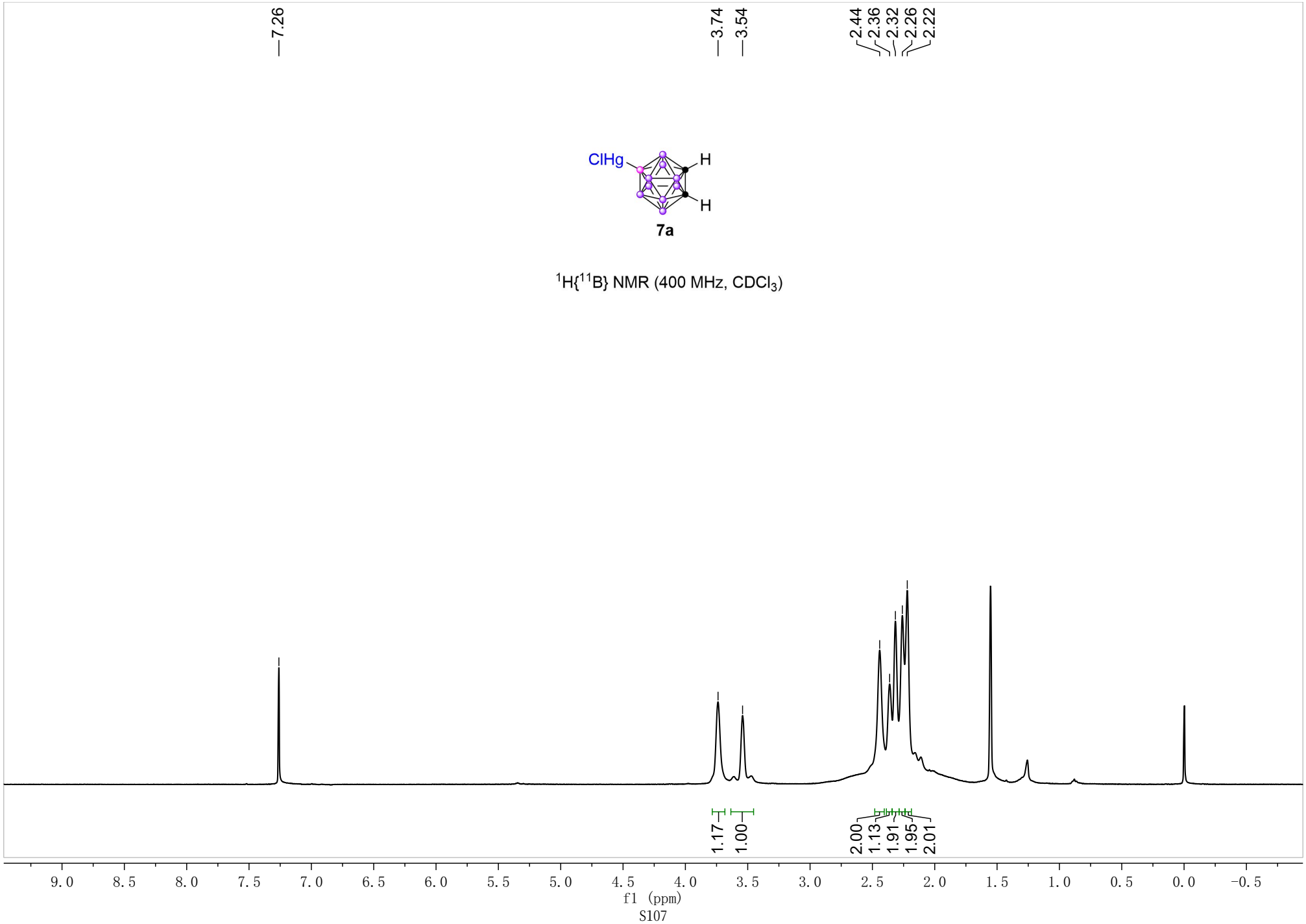

7.26
3.57
3.45
2.56
2.45
2.40
2.30
2.11
Cl
H
H
6a
$^1H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)
1.00
0.97
1.22
2.09
1.97
2.08
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

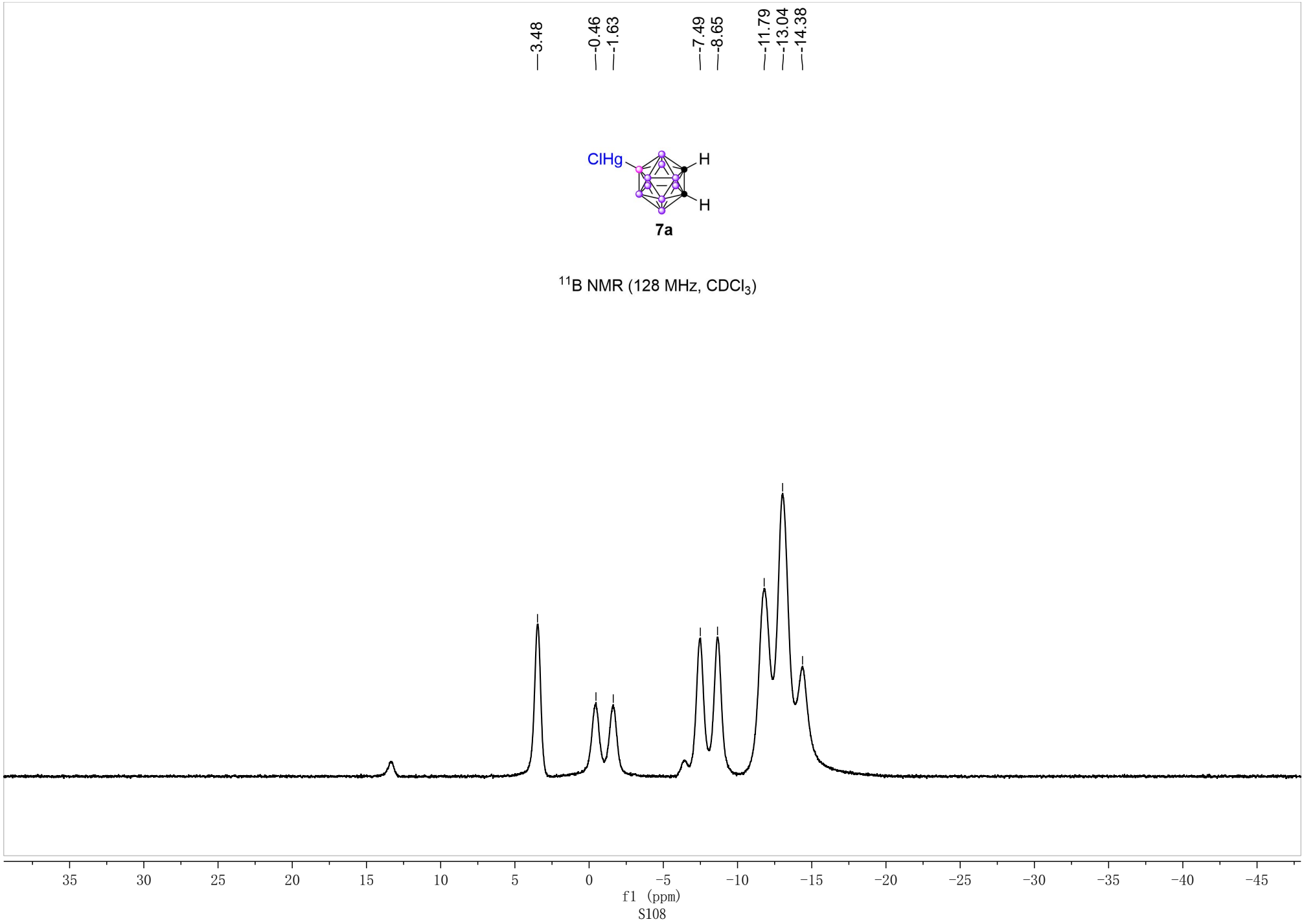

-7.40
-1.47
-2.66
-8.19
-9.38
-13.20
-14.48
-15.68
-16.96
Cl
H
H
6a
^{11}B NMR (128 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

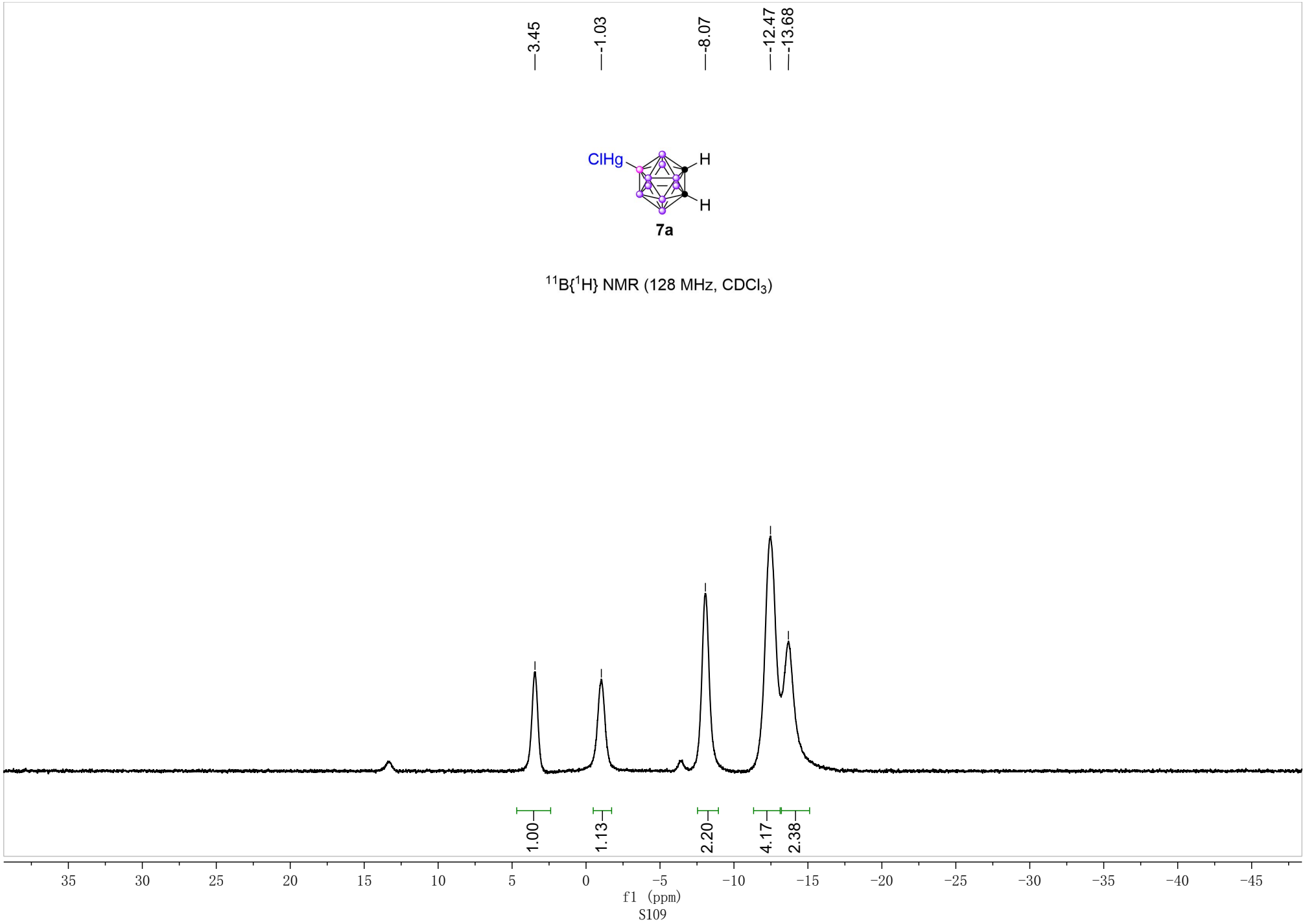

-7.41
-2.06
-8.78
-13.84
-15.11
-16.25
Cl
H
H
6a
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)
1.00
1.04
1.98
1.91
1.88
1.91
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

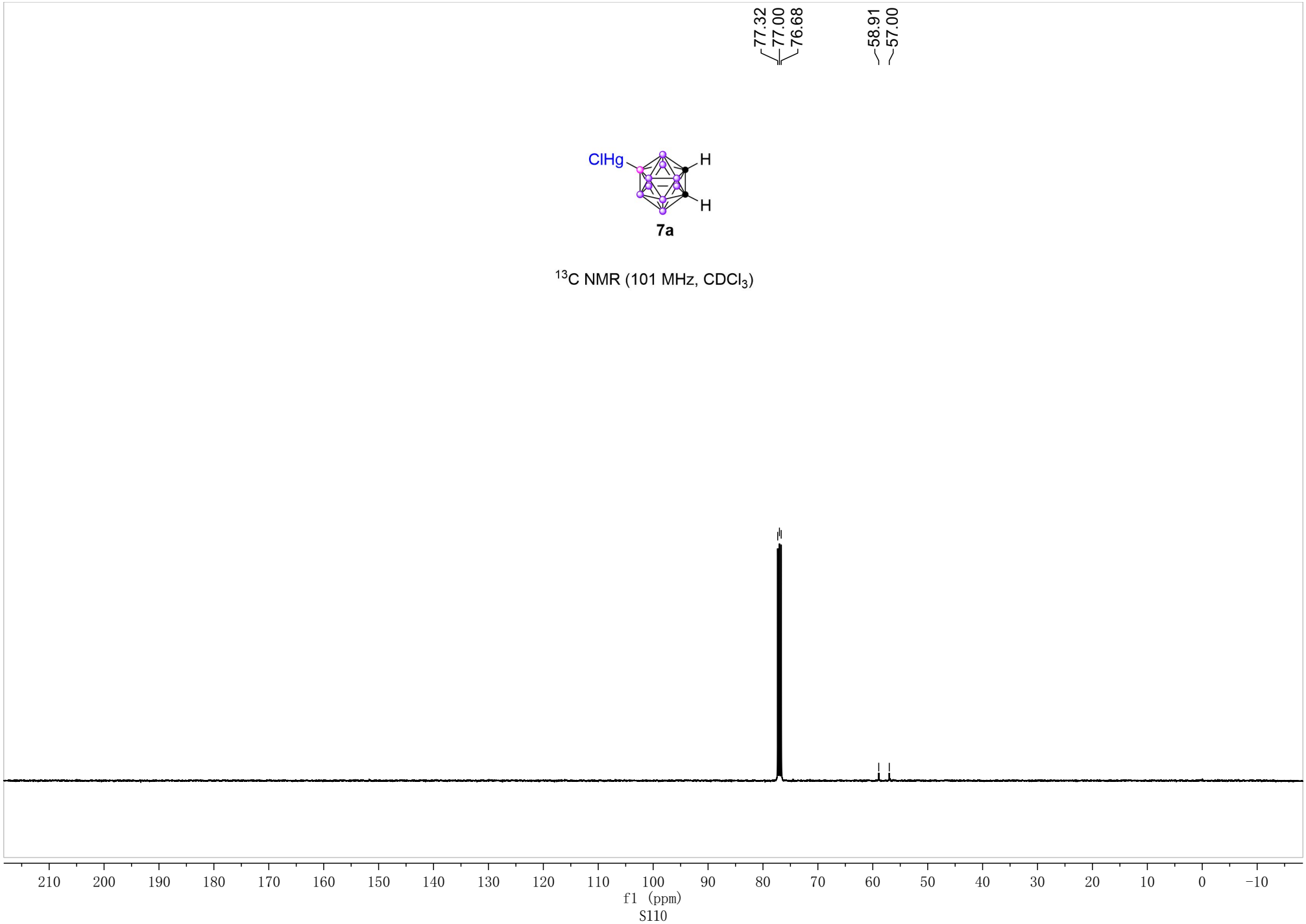

77.32
77.00
76.68
52.10
44.39
Cl
H
H
6a
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

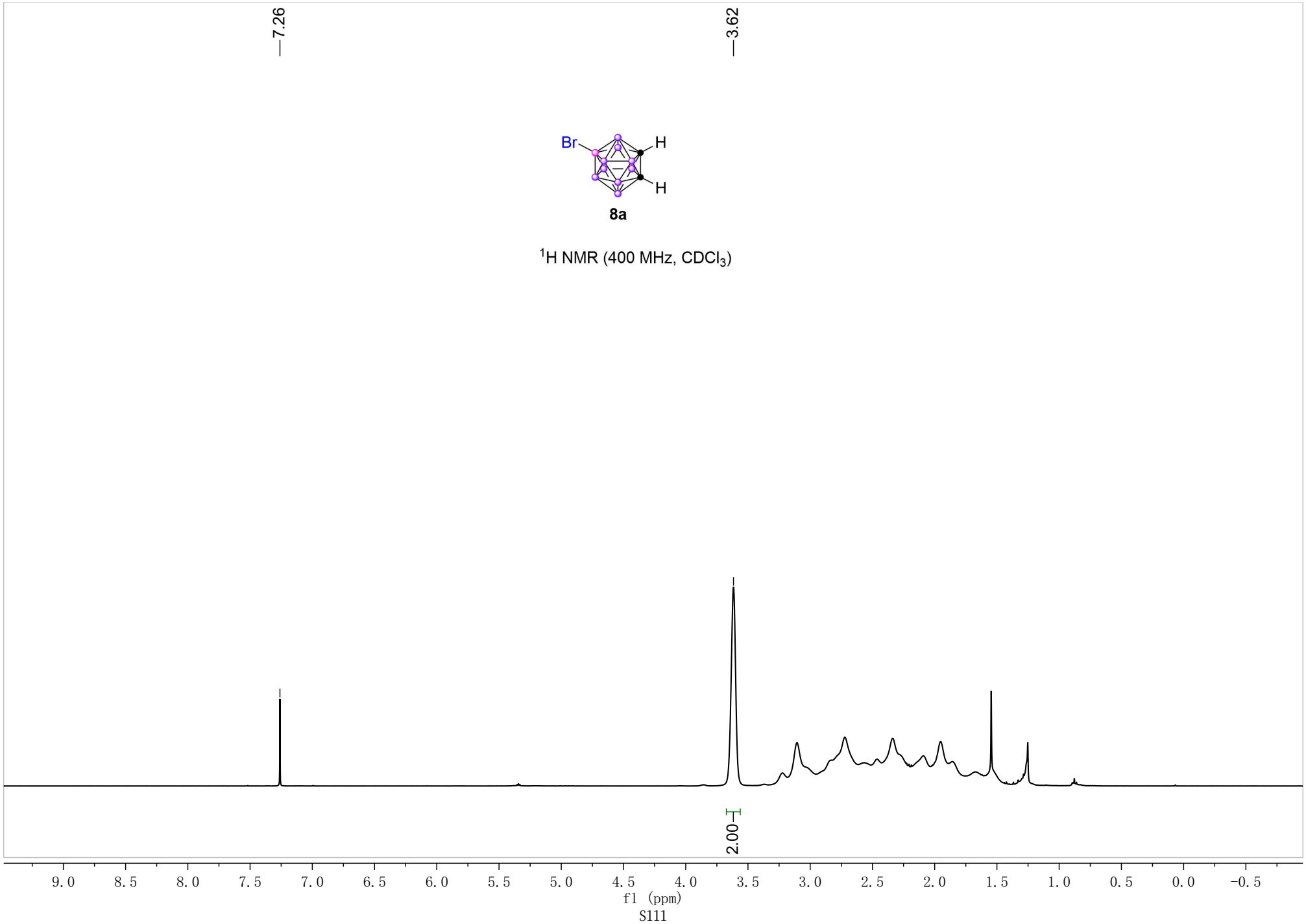

7.26
3.74
3.54
ClHg
H
H
7a
^{1}H NMR (400 MHz, $CDCl_3$)
1.20
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

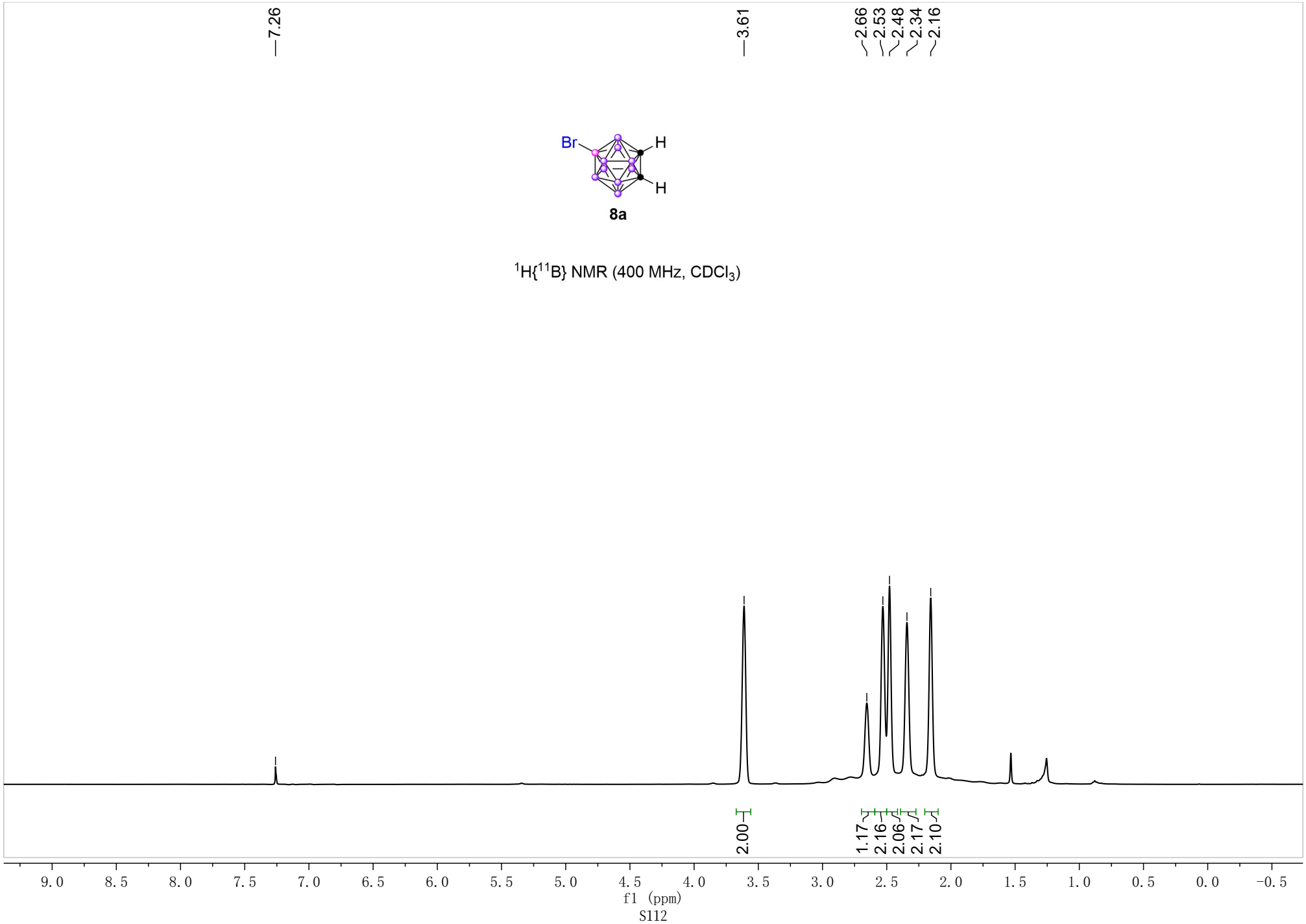

7.26
3.74
3.54
2.44
2.36
2.32
2.26
2.22
ClHg
H
H
7a
$^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)
1.17
1.00
2.00
1.13
1.91
1.95
2.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

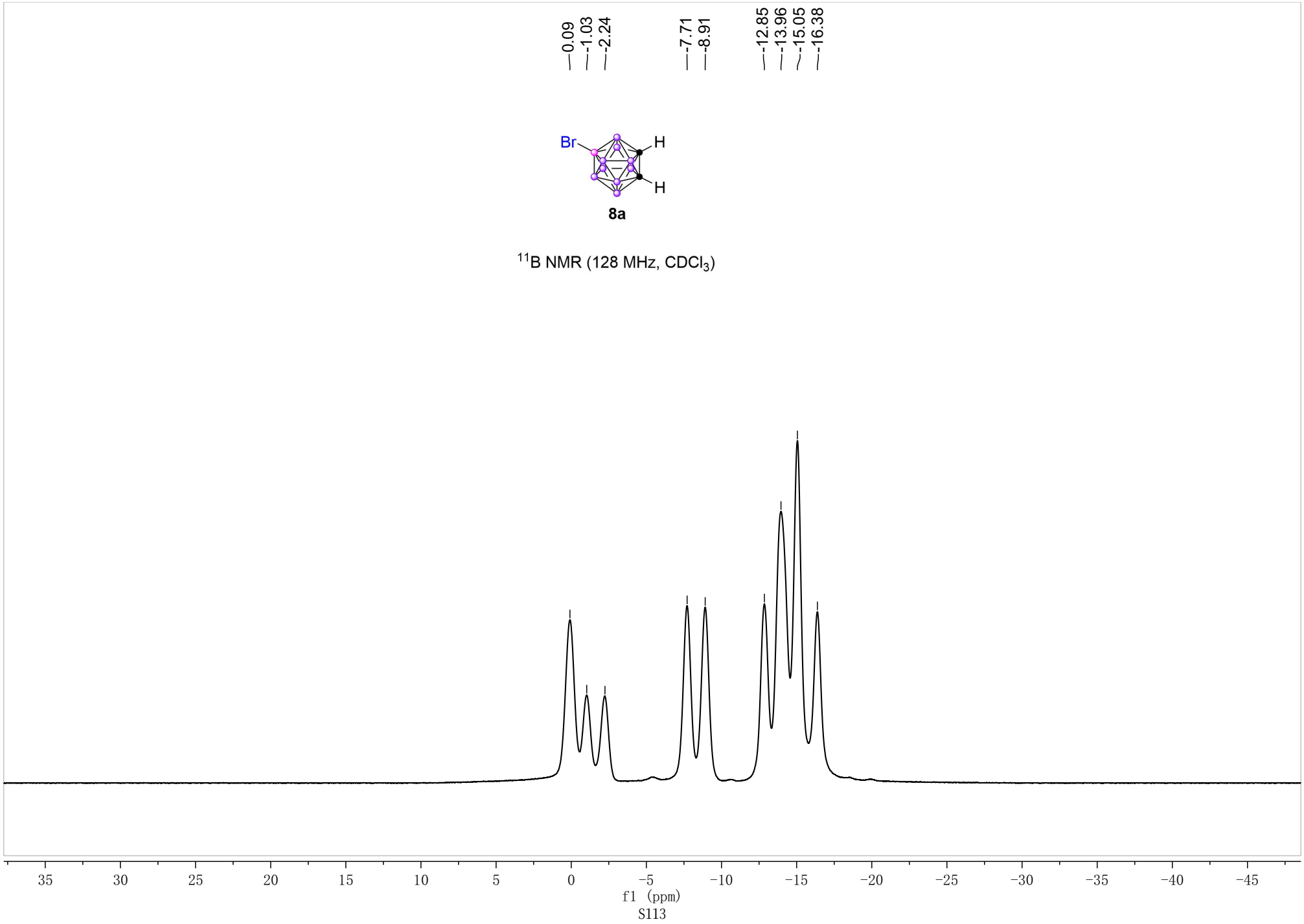

3.48
-0.46
-1.63
-7.49
-8.65
-11.79
-13.04
-14.38
ClHg
H
H
7a
11B NMR (128 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

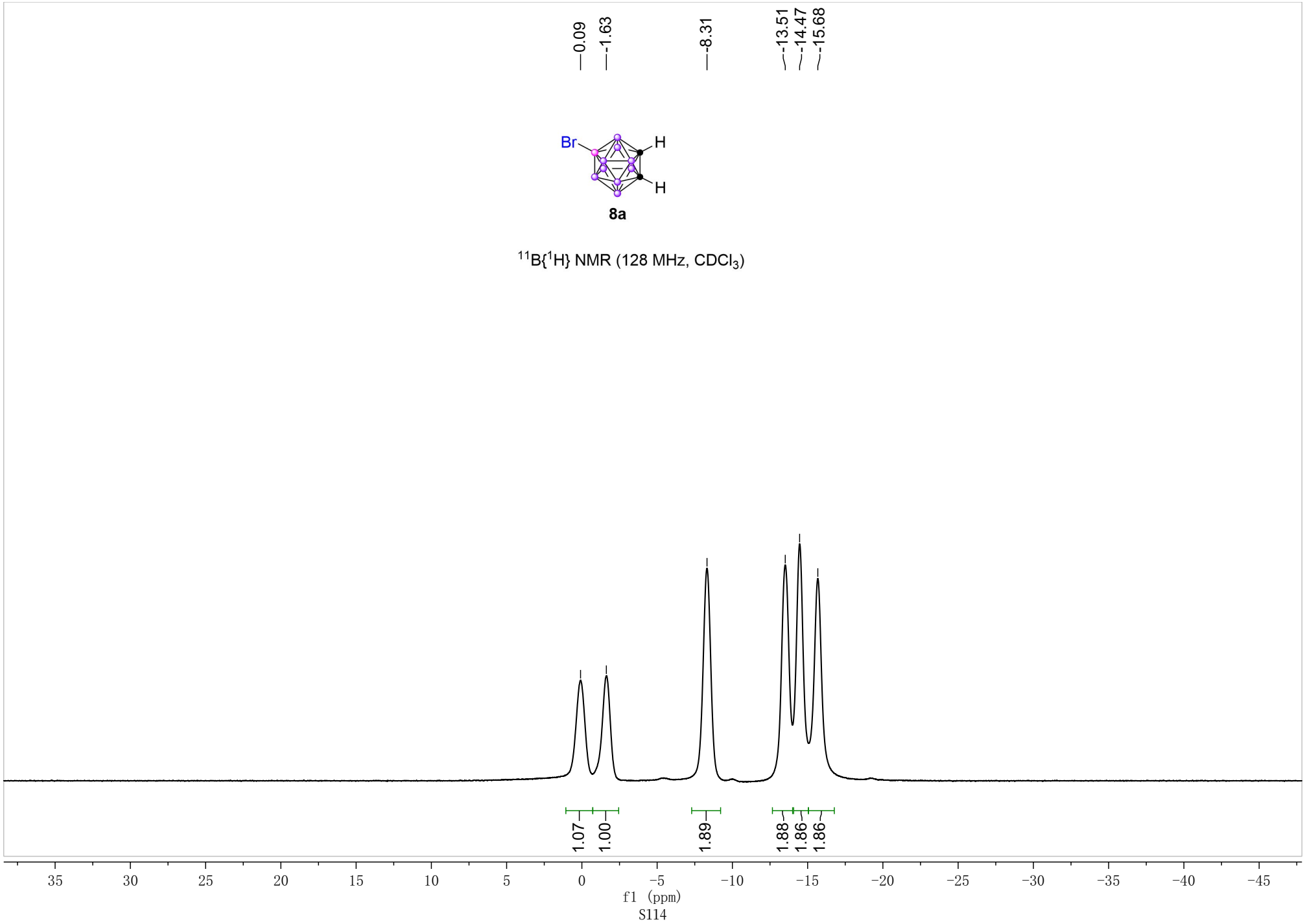

-3.45
-1.03
-8.07
-12.47
-13.68
ClHg
H
H
7a
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)
1.00
1.13
2.20
4.17
2.38
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

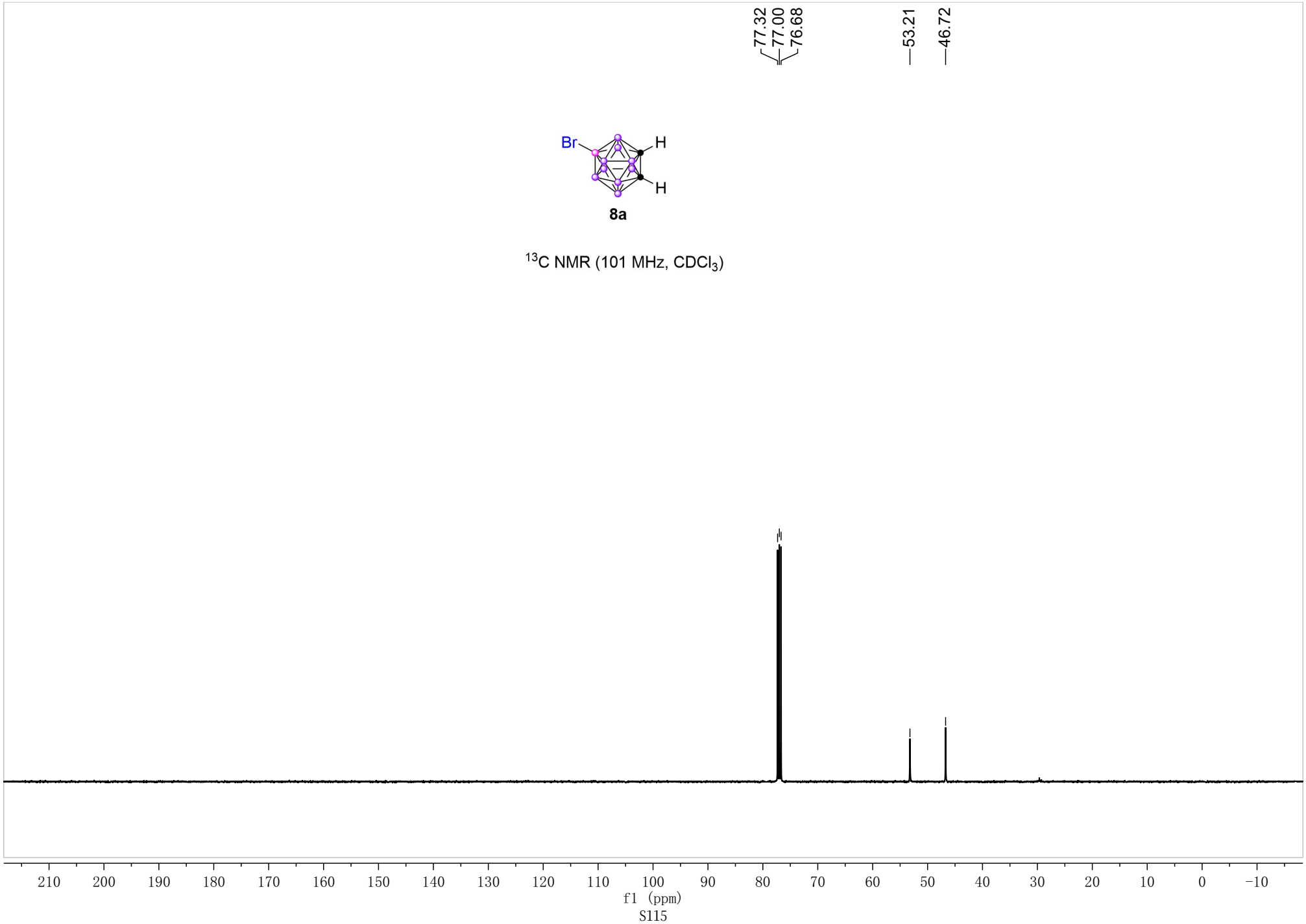

77.32
77.00
76.68
58.91
57.00
ClHg
H
H
7a
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

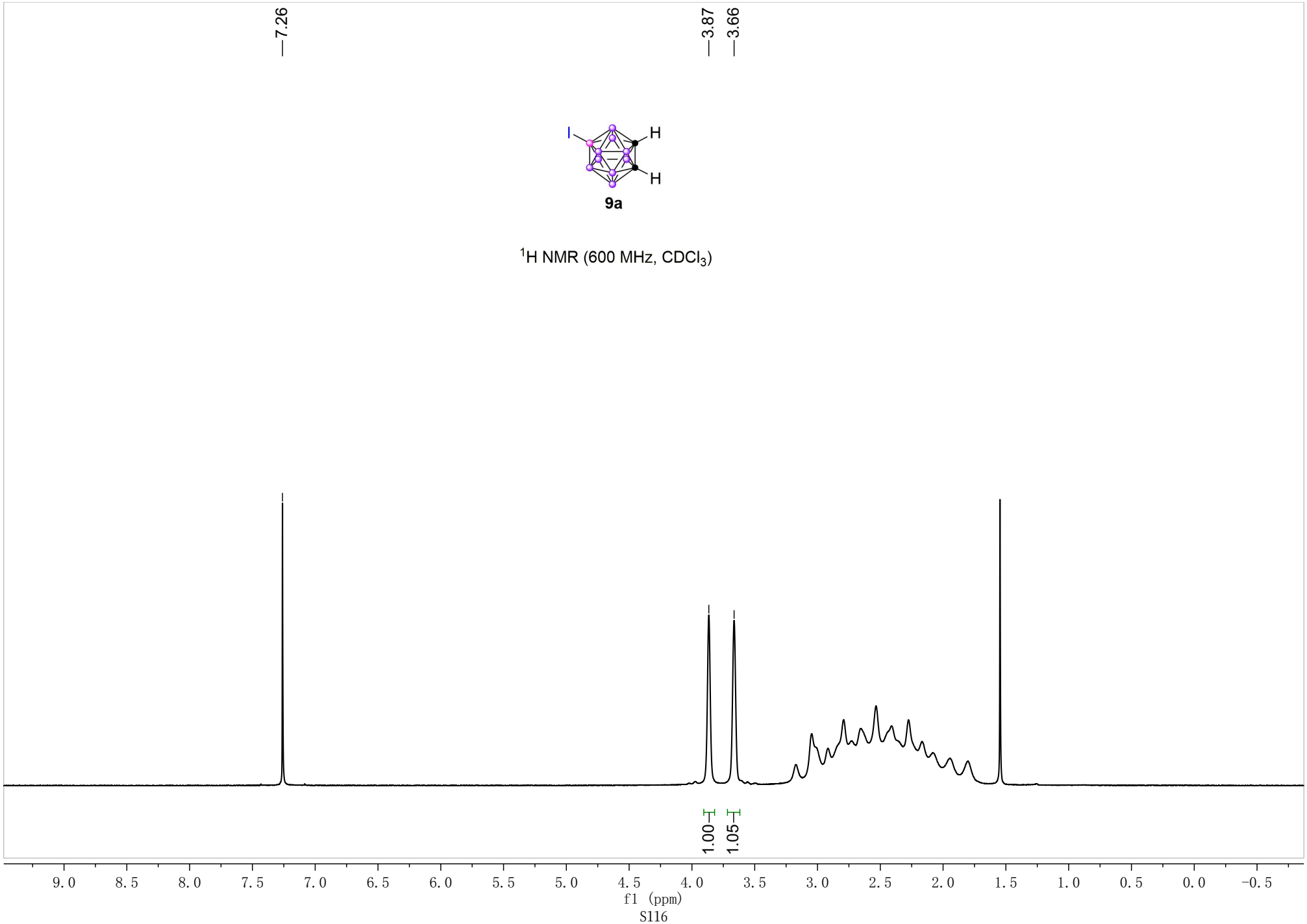

7.26
3.62
Br
H
H
8a
1H NMR (400 MHz, CDCl3)
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
S111

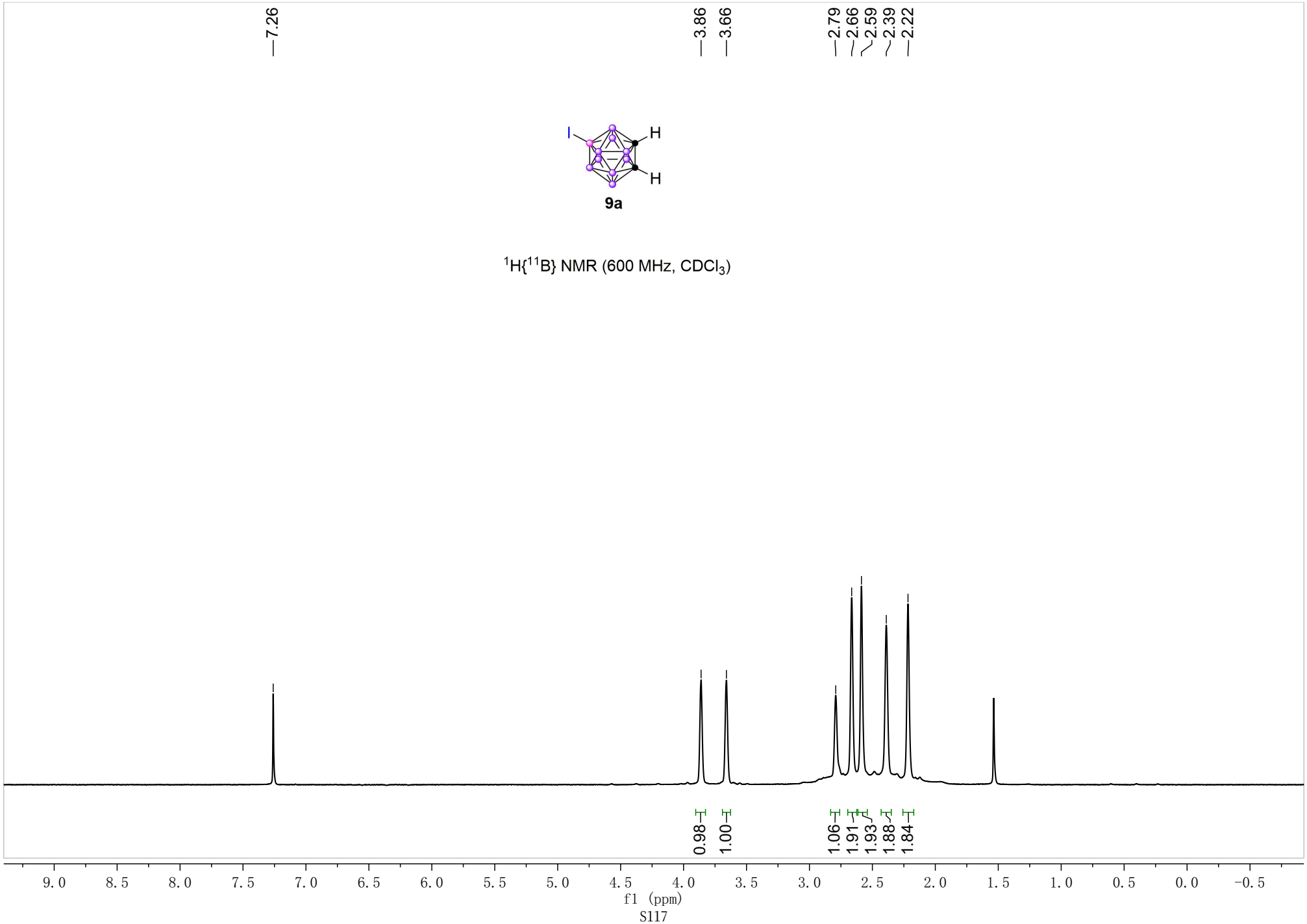

7.26
3.61
2.66
2.53
2.48
2.34
2.16
Br
H
H
8a
$^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)
2.00
1.17
2.16
2.06
2.17
2.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

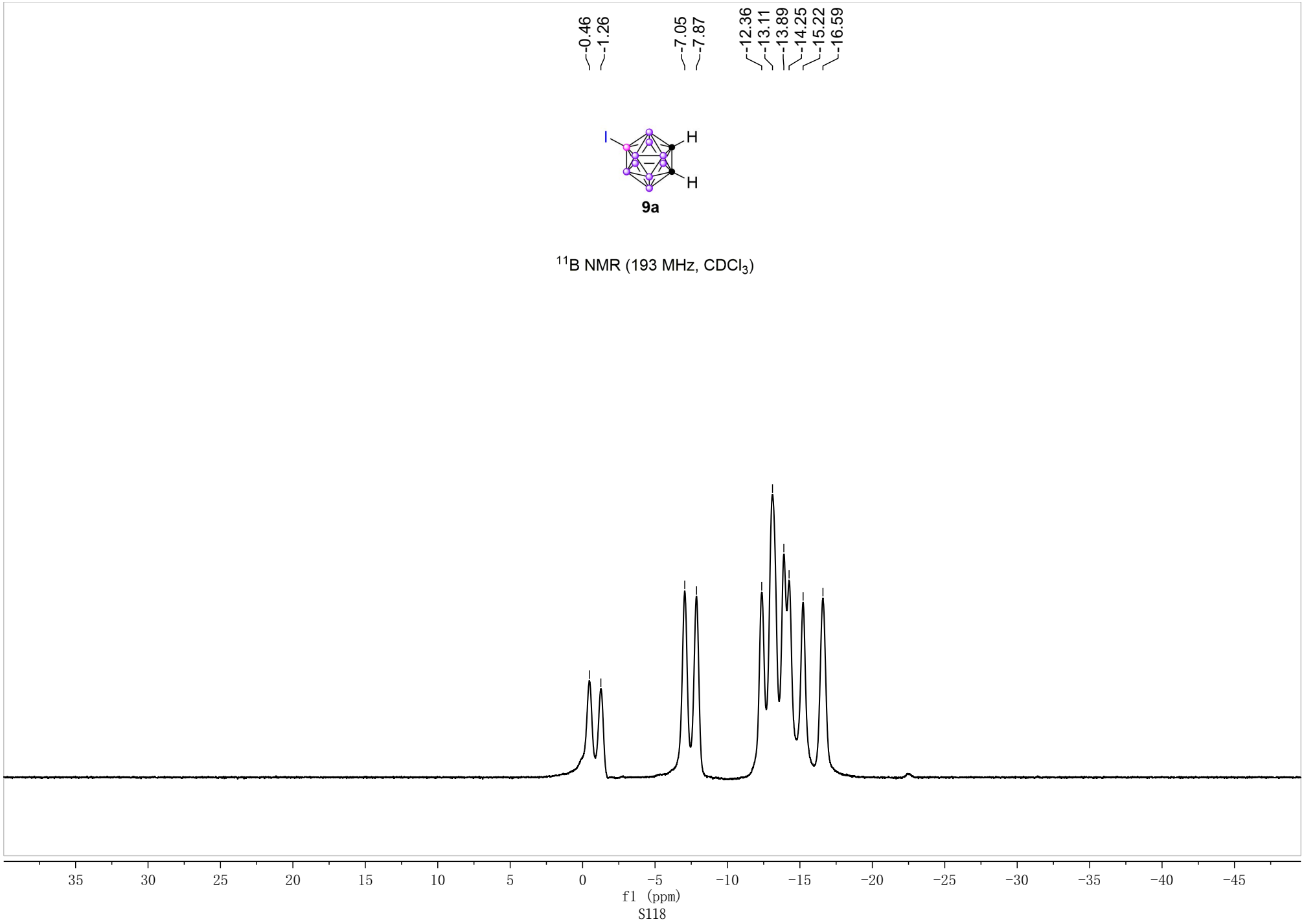

0.09
-1.03
-2.24
-7.71
-8.91
-12.85
-13.96
-15.05
-16.38
Br
H
H
8a
11B NMR (128 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

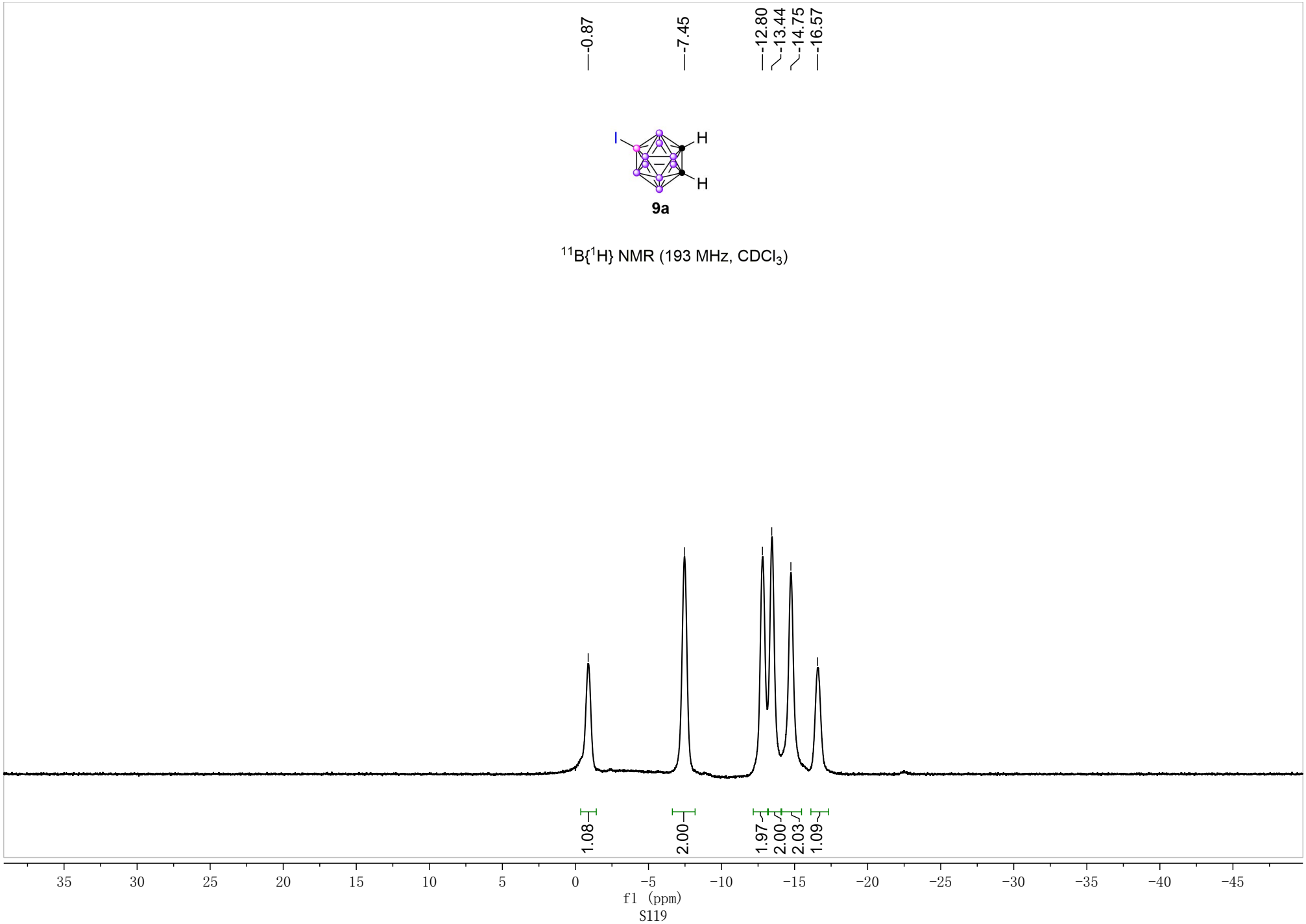

0.09
-1.63
-8.31
-13.51
-14.47
-15.68
Br
H
H
8a
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)
1.07
1.00
1.89
1.88
1.86
1.86
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)


77.32
77.00
76.68
53.21
46.72
Br
H
H
8a
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.26
3.87
3.66
I
H
H
9a
^{1}H NMR (600 MHz, $CDCl_3$)
1.00
1.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

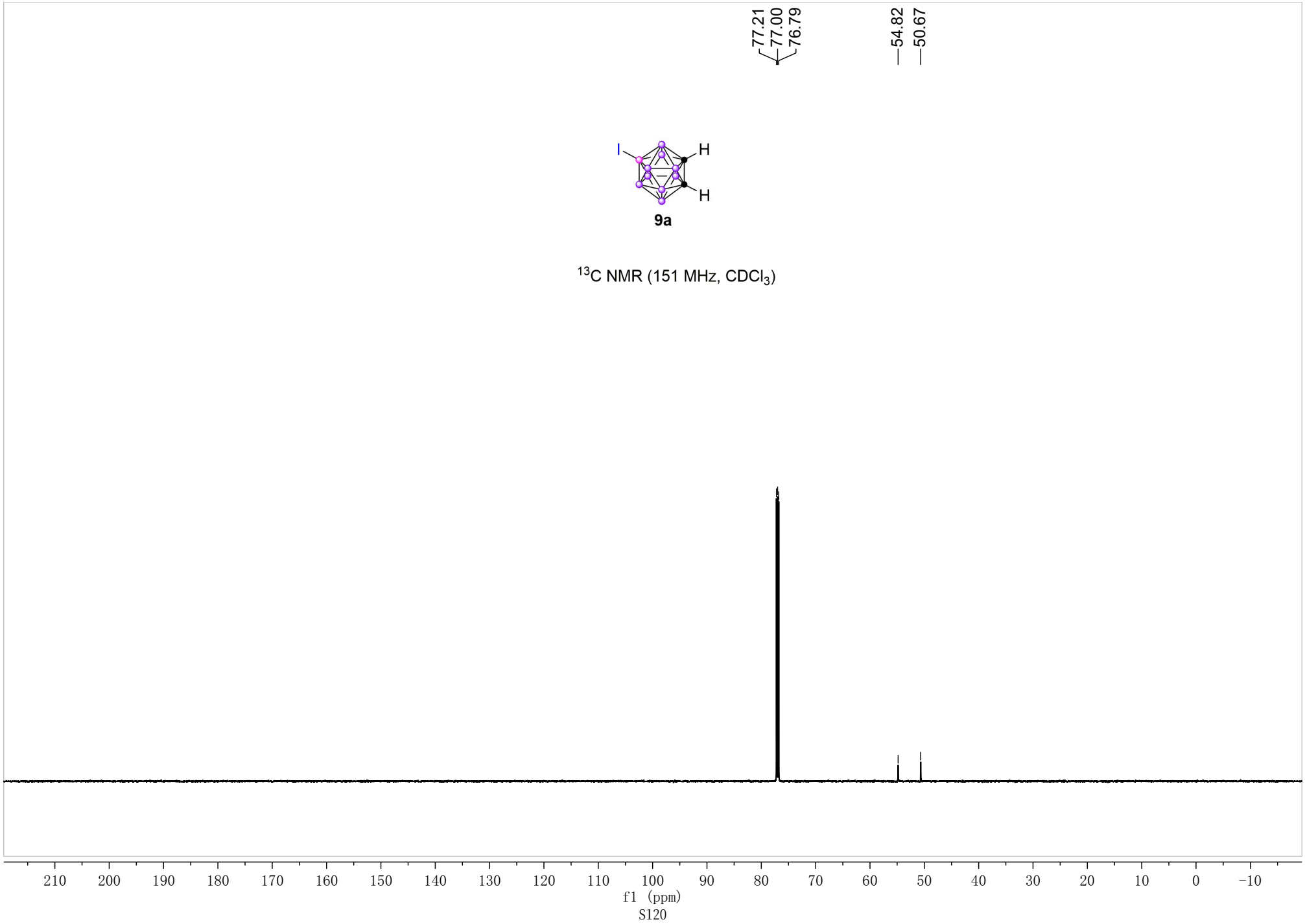

7.26
3.86
3.66
2.79
2.66
2.59
2.39
2.22
I
H
H
9a
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$)
0.98
1.00
1.06
1.91
1.93
1.88
1.84
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

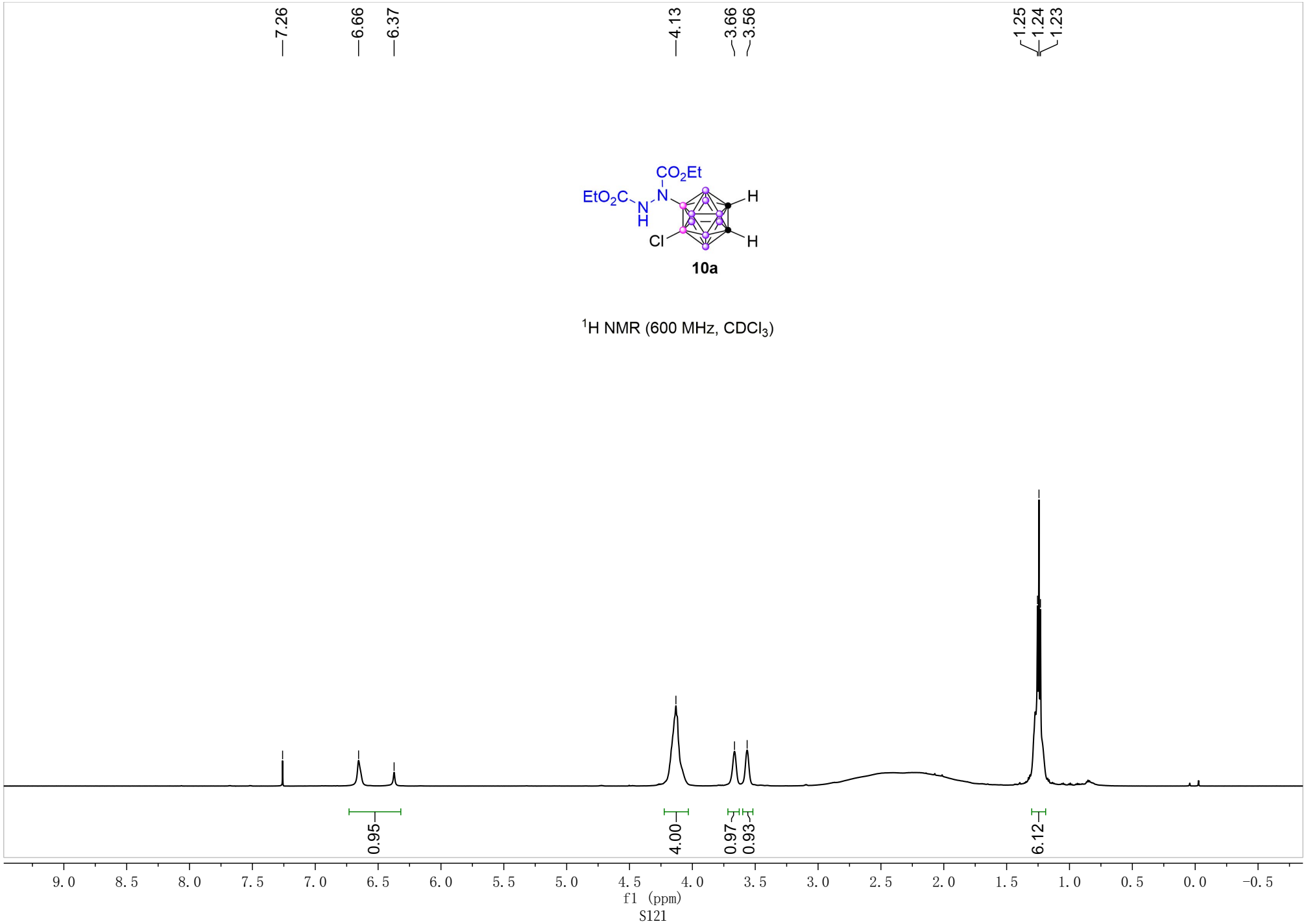

-0.46
-1.26
-7.05
-7.87
-12.36
-13.11
-13.89
-14.25
-15.22
-16.59
I
H
H
9a
^{11}B NMR (193 MHz, $CDCl_3$)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

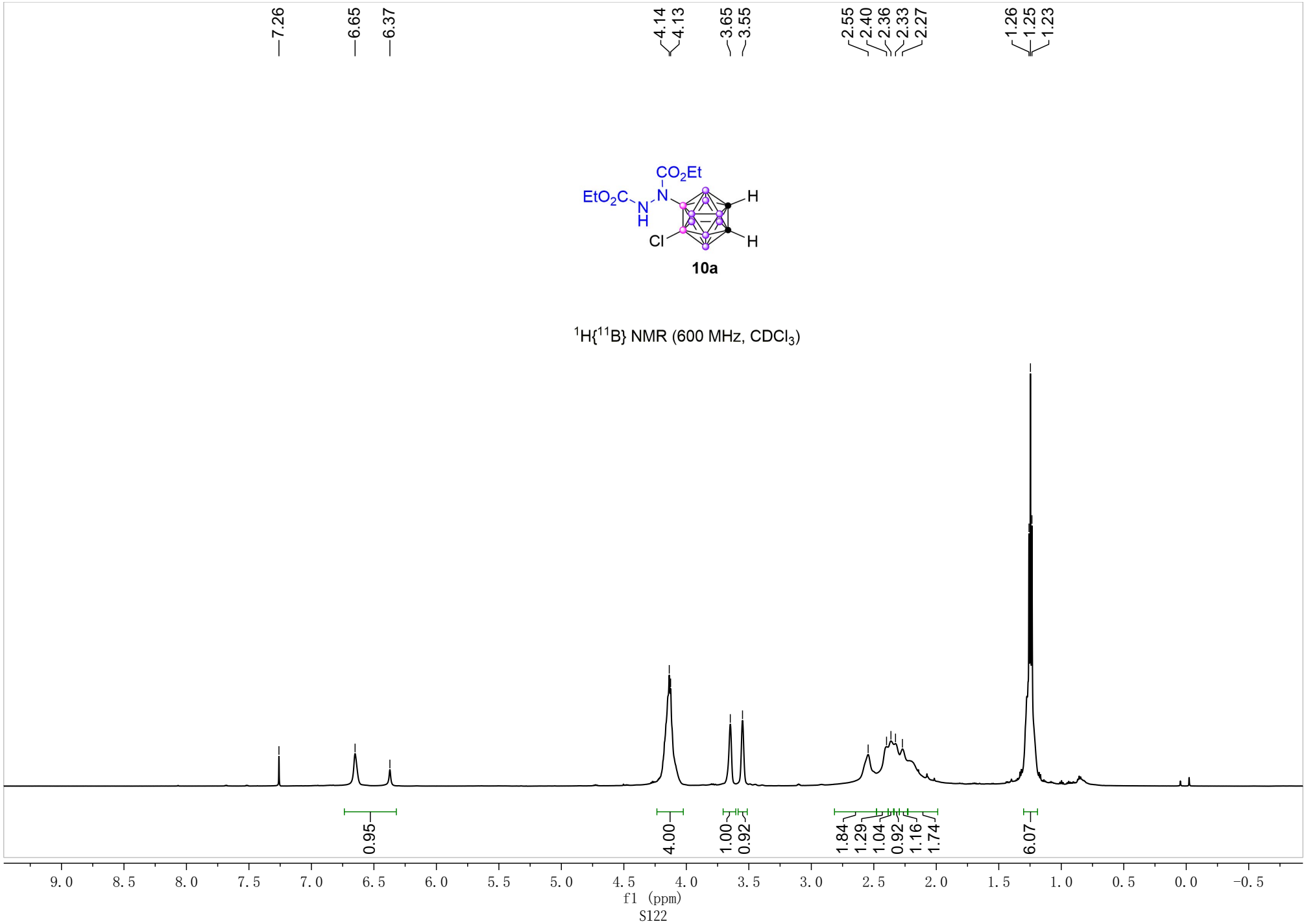


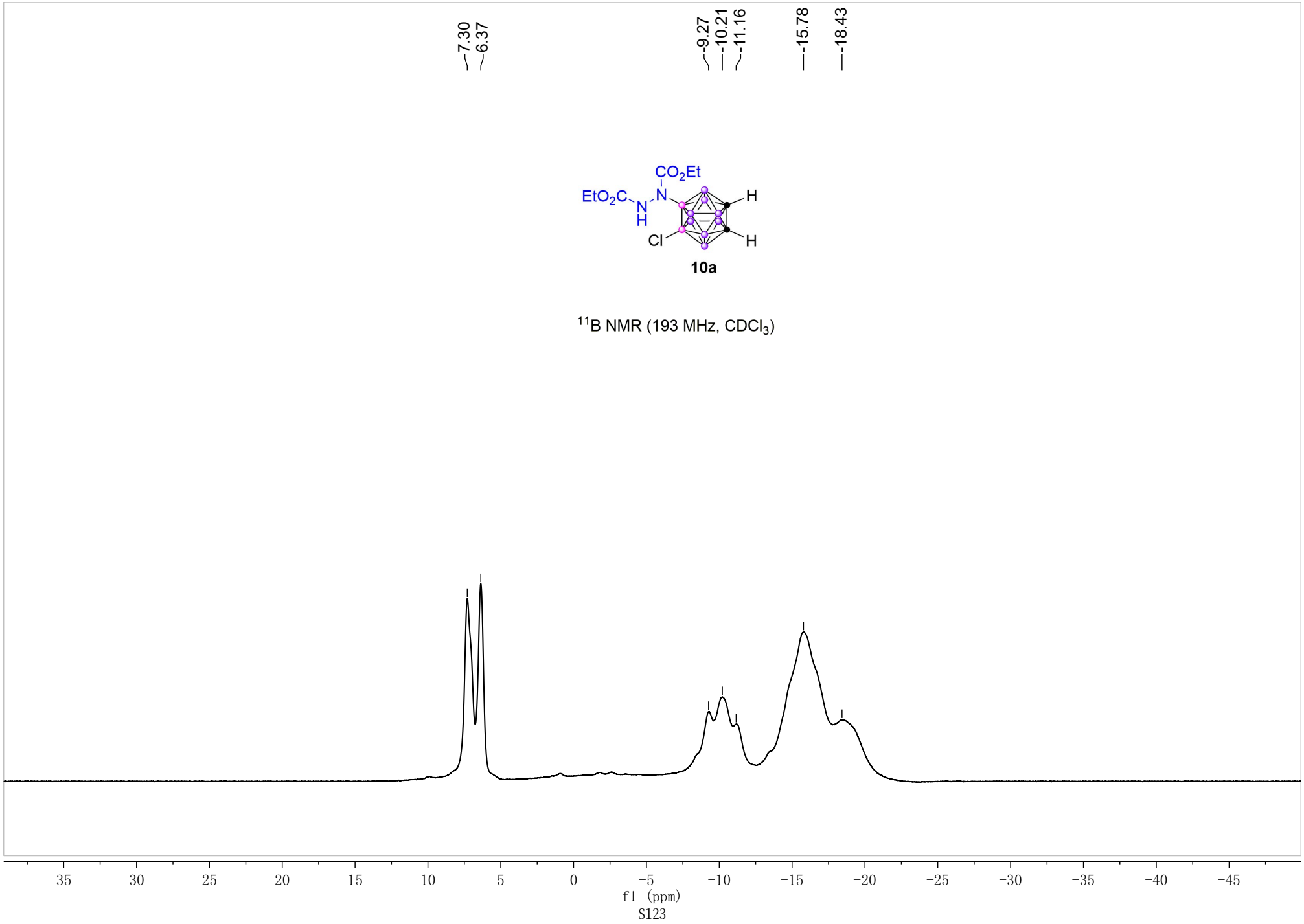
9a

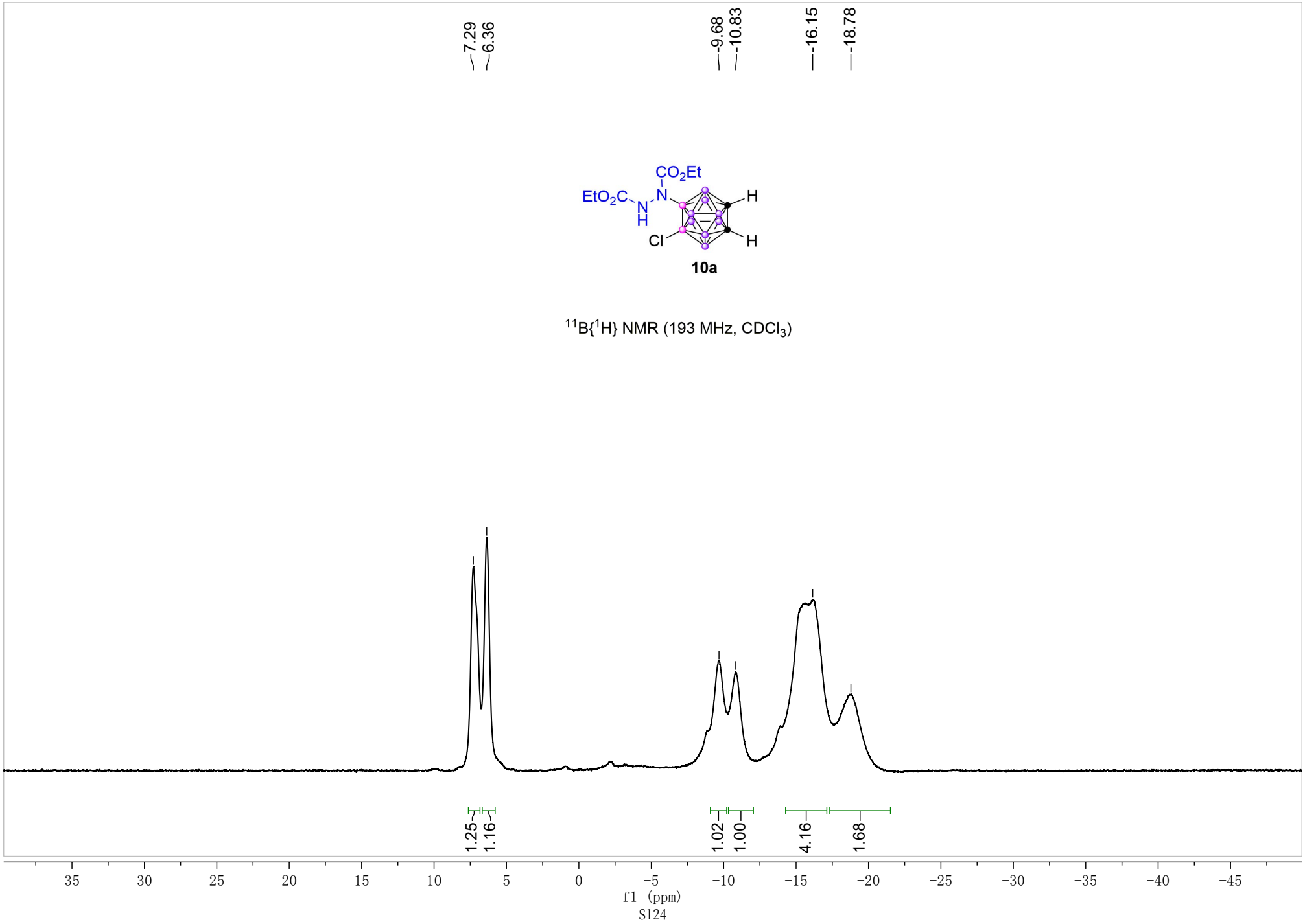
$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)

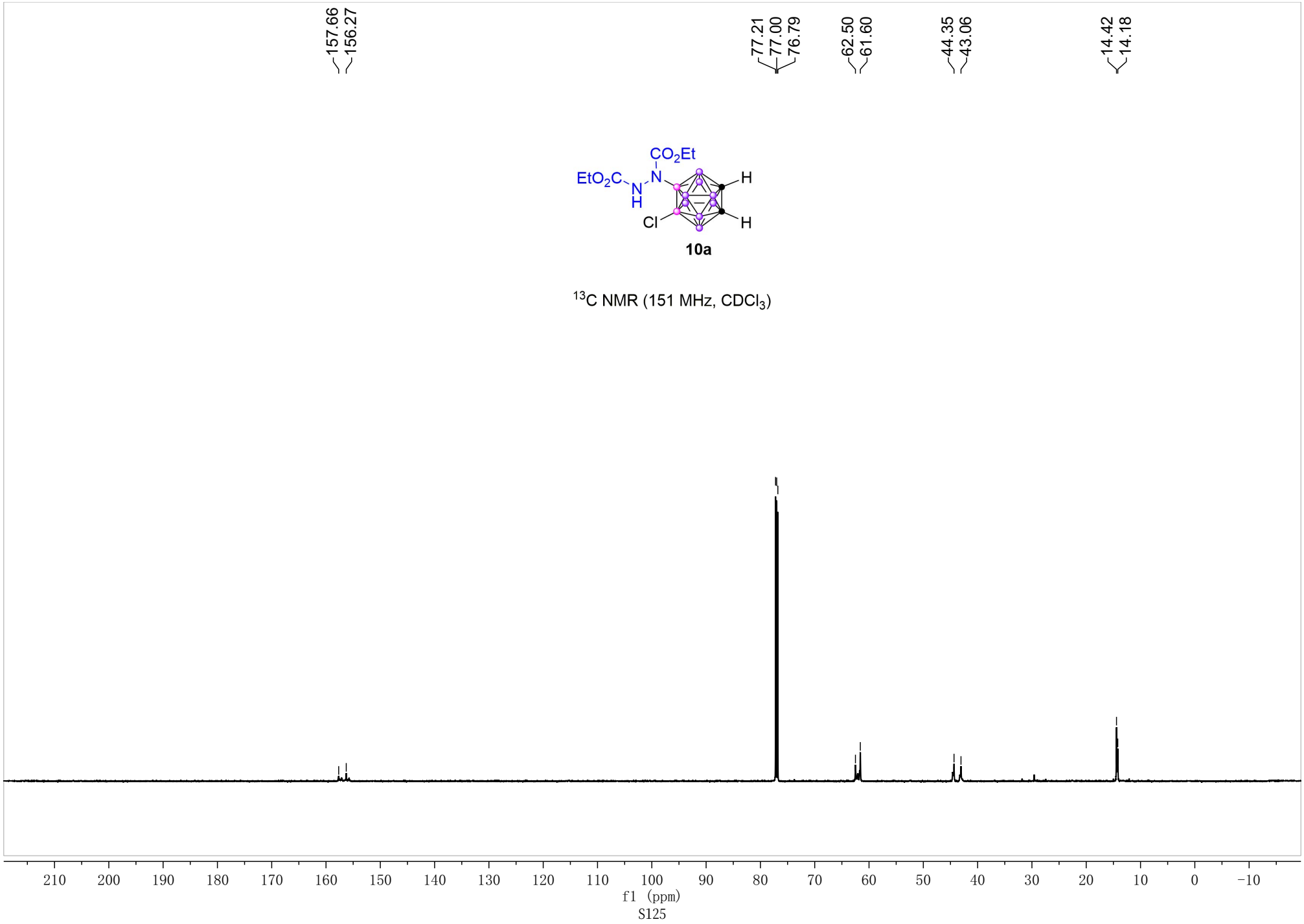

77.21
77.00
76.79
54.82
50.67
I
H
H
9a
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

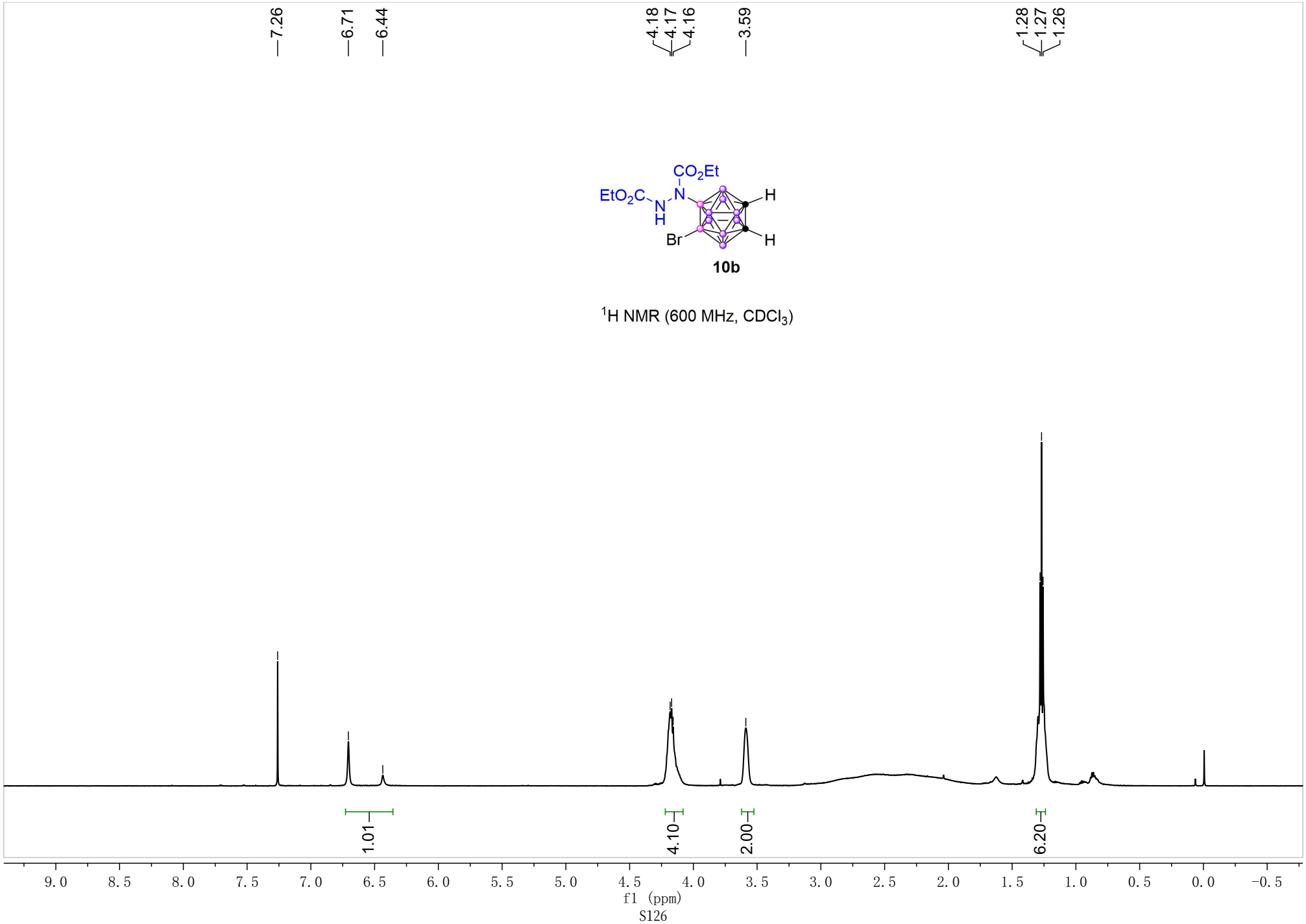

7.26
6.66
6.37
4.13
3.66
3.56
1.25
1.24
1.23
CO2Et
EtO2C
N
N
H
H
Cl
H
10a
1H NMR (600 MHz, CDCl3)
0.95
4.00
0.97
0.93
6.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

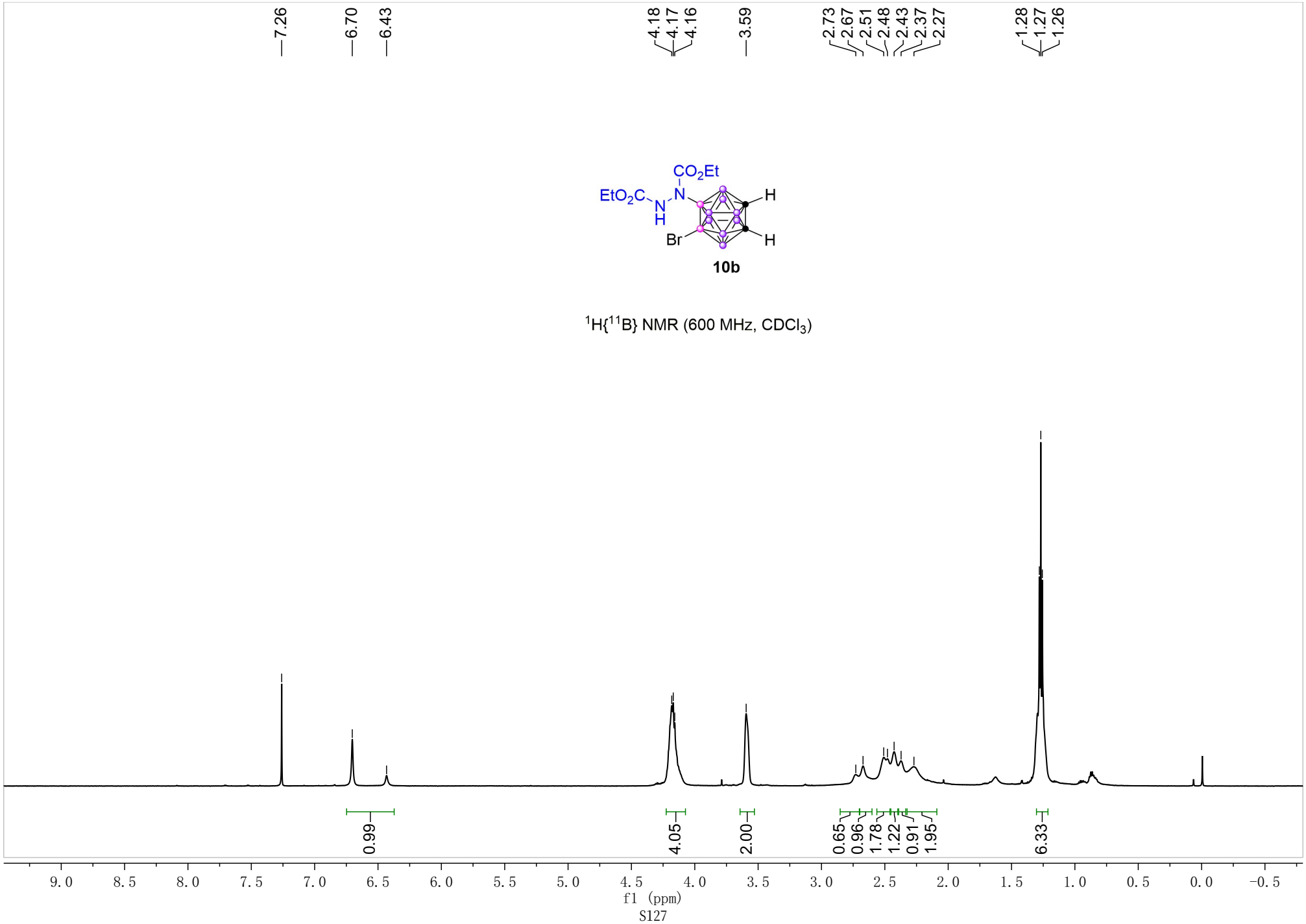

7.26
6.65
6.37
4.14
4.13
3.65
3.55
2.55
2.40
2.36
2.33
2.27
1.26
1.25
1.23
CO2Et
EtO2C
N
N
H
H
Cl
H
10a
1H{11B} NMR (600 MHz, CDCl3)
0.95
4.00
1.00
0.92
1.84
1.29
1.04
0.92
1.16
1.74
6.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

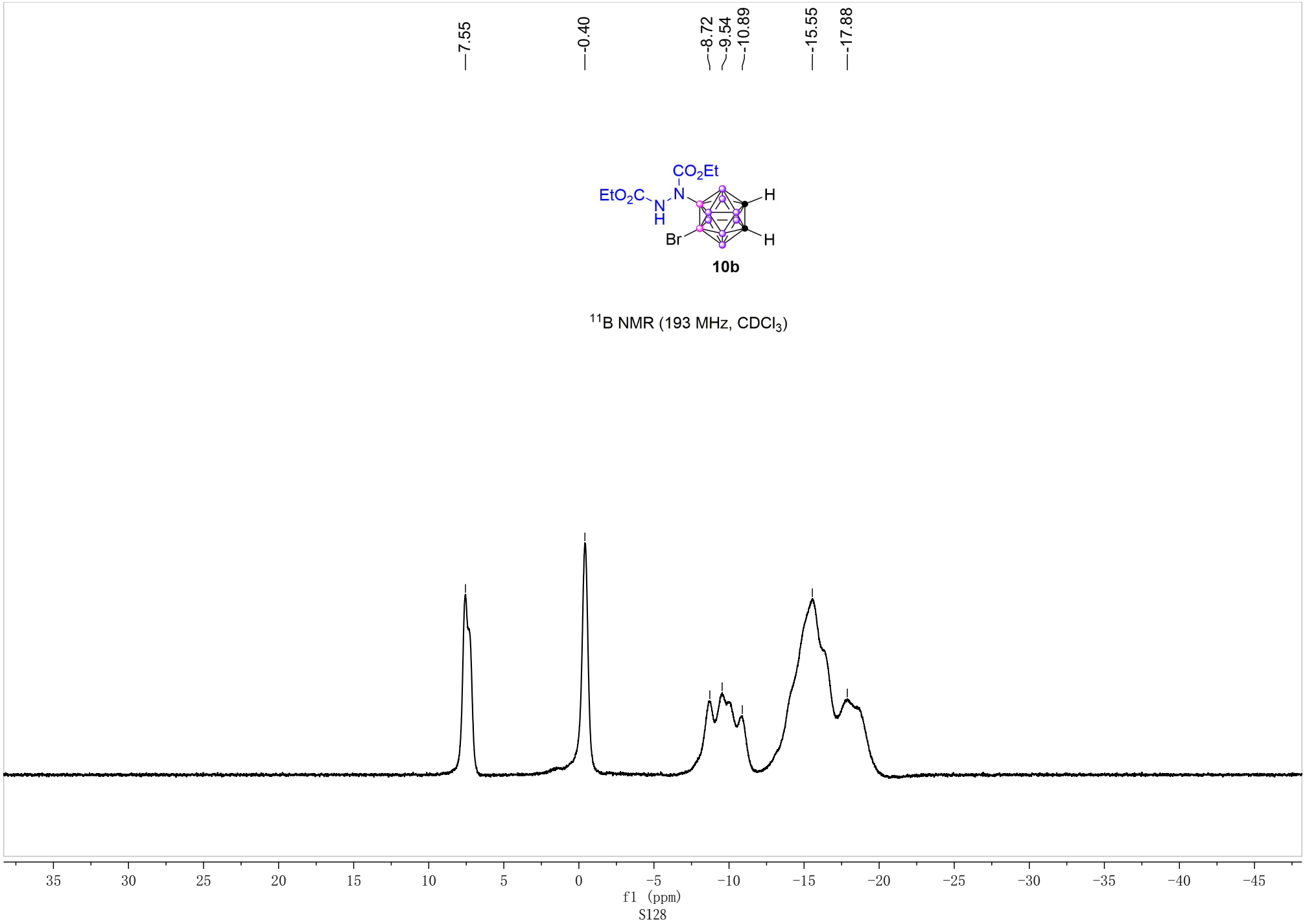

-7.30
-6.37
-9.27
-10.21
-11.16
-15.78
-18.43
CO2Et
EtO2C
N
N
H
H
Cl
H
10a
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

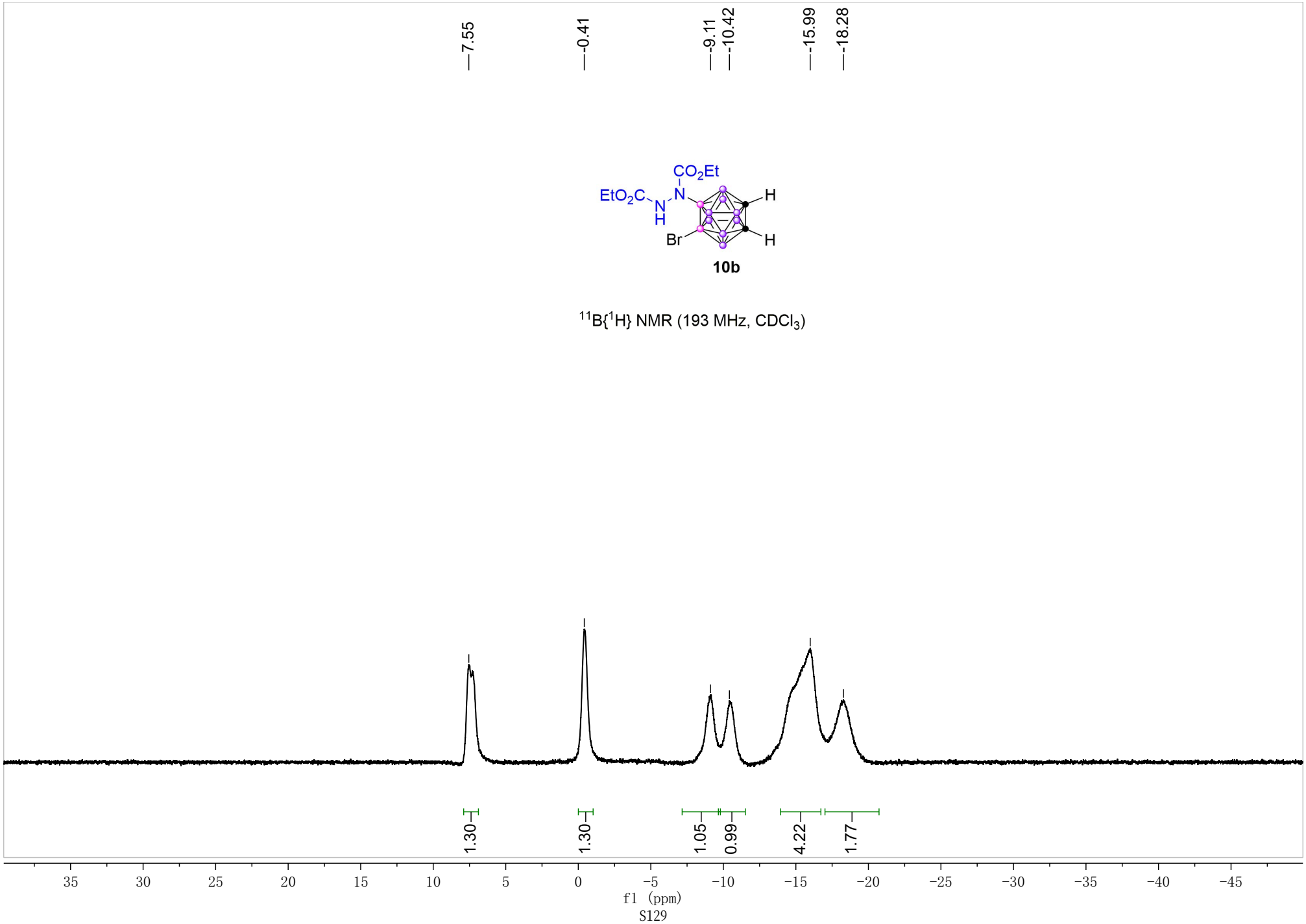

7.29
6.36
-9.68
-10.83
-16.15
-18.78
CO2Et
EtO2C
N
N
H
H
Cl
H
10a
11B{1H} NMR (193 MHz, CDCl3)
1.25
1.16
1.02
1.00
4.16
1.68
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

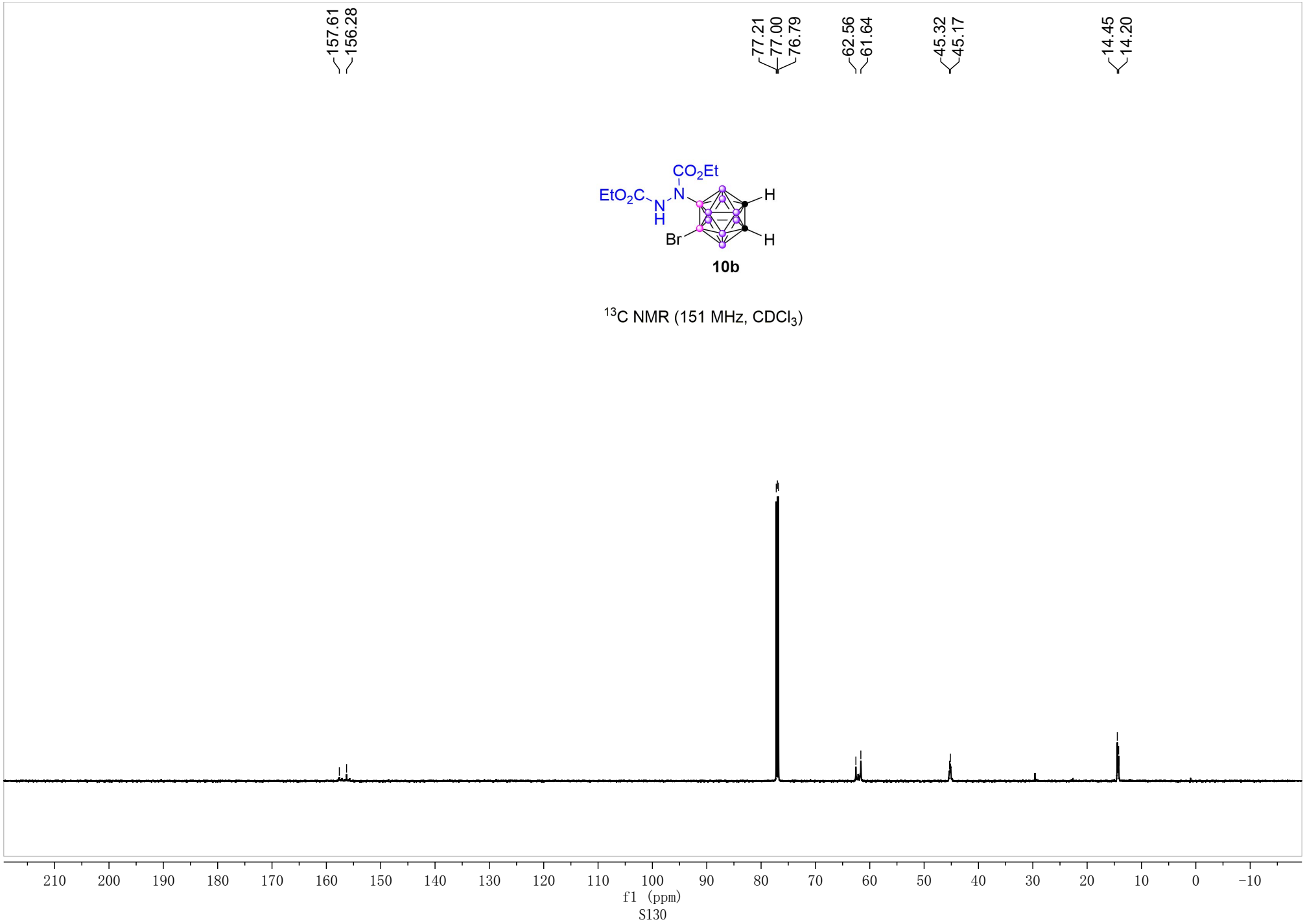

157.66
156.27
77.21
77.00
76.79
62.50
61.60
44.35
43.06
14.42
14.18
CO2Et
EtO2C
N
H
Cl
H
H
10a
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

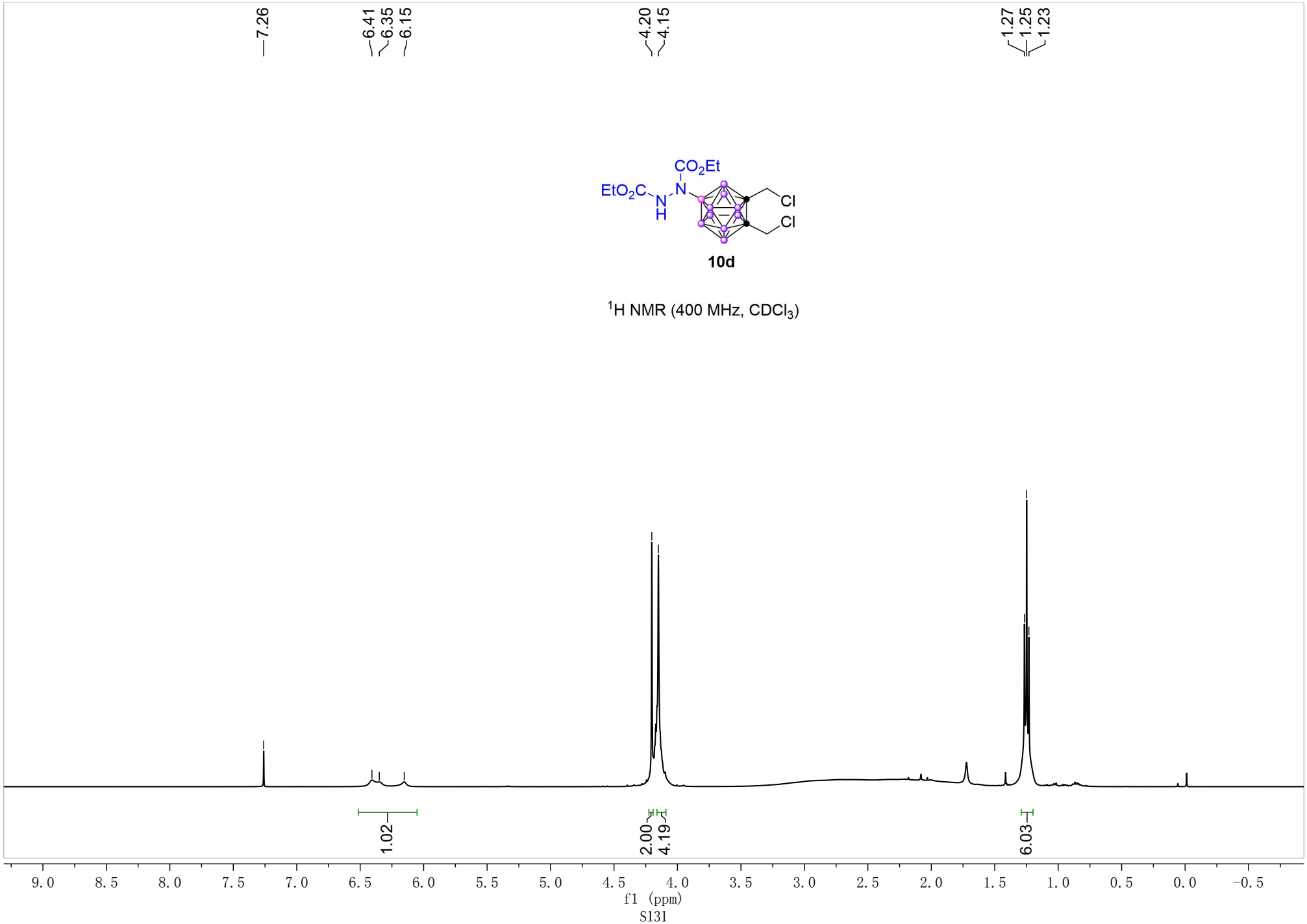

7.26
6.71
6.44
4.18
4.17
4.16
3.59
1.28
1.27
1.26
CO2Et
EtO2C
N
N
H
H
Br
H
10b
1H NMR (600 MHz, CDCl3)
1.01
4.10
2.00
6.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

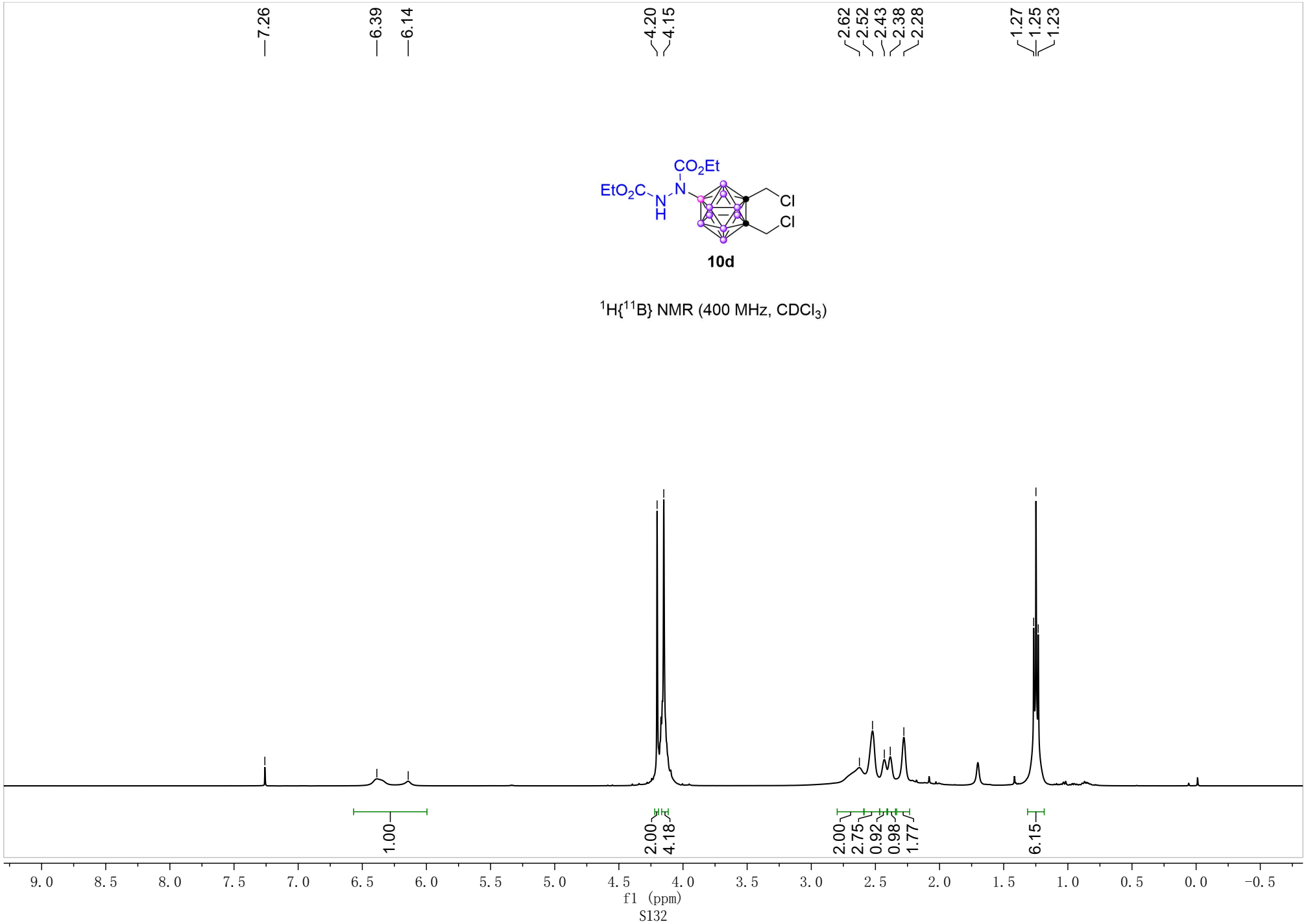

7.26
6.70
6.43
4.18
4.17
4.16
3.59
2.73
2.67
2.51
2.48
2.43
2.37
2.27
1.28
1.27
1.26
CO2Et
EtO2C
N
N
H
H
Br
H
H
10b
1H{11B} NMR (600 MHz, CDCl3)
0.99
4.05
2.00
0.65
0.96
1.78
1.22
0.91
1.95
6.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

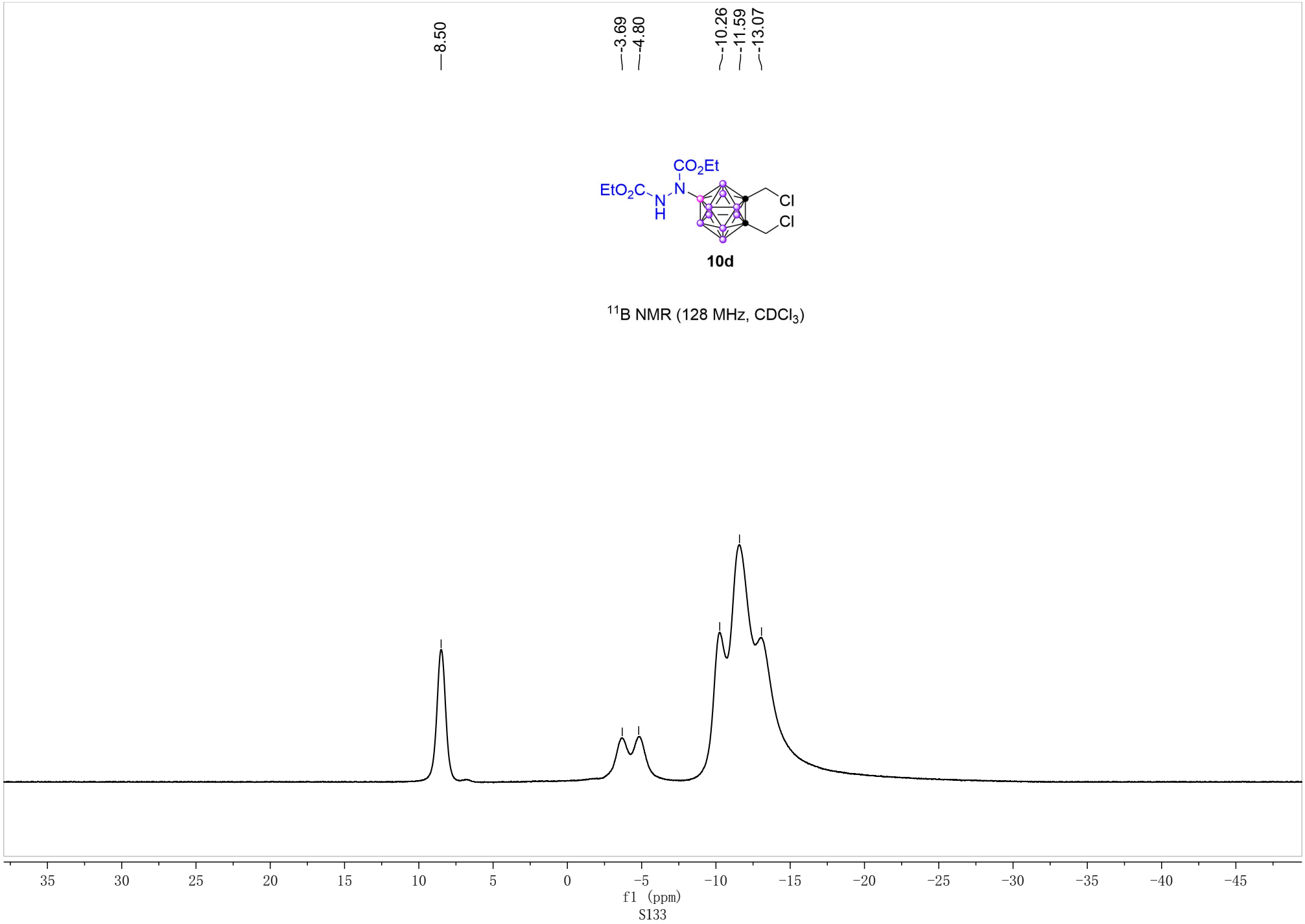

7.55
0.40
8.72
9.54
10.89
15.55
17.88
CO2Et
EtO2C
N
H
N
H
Br
H
H
10b
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

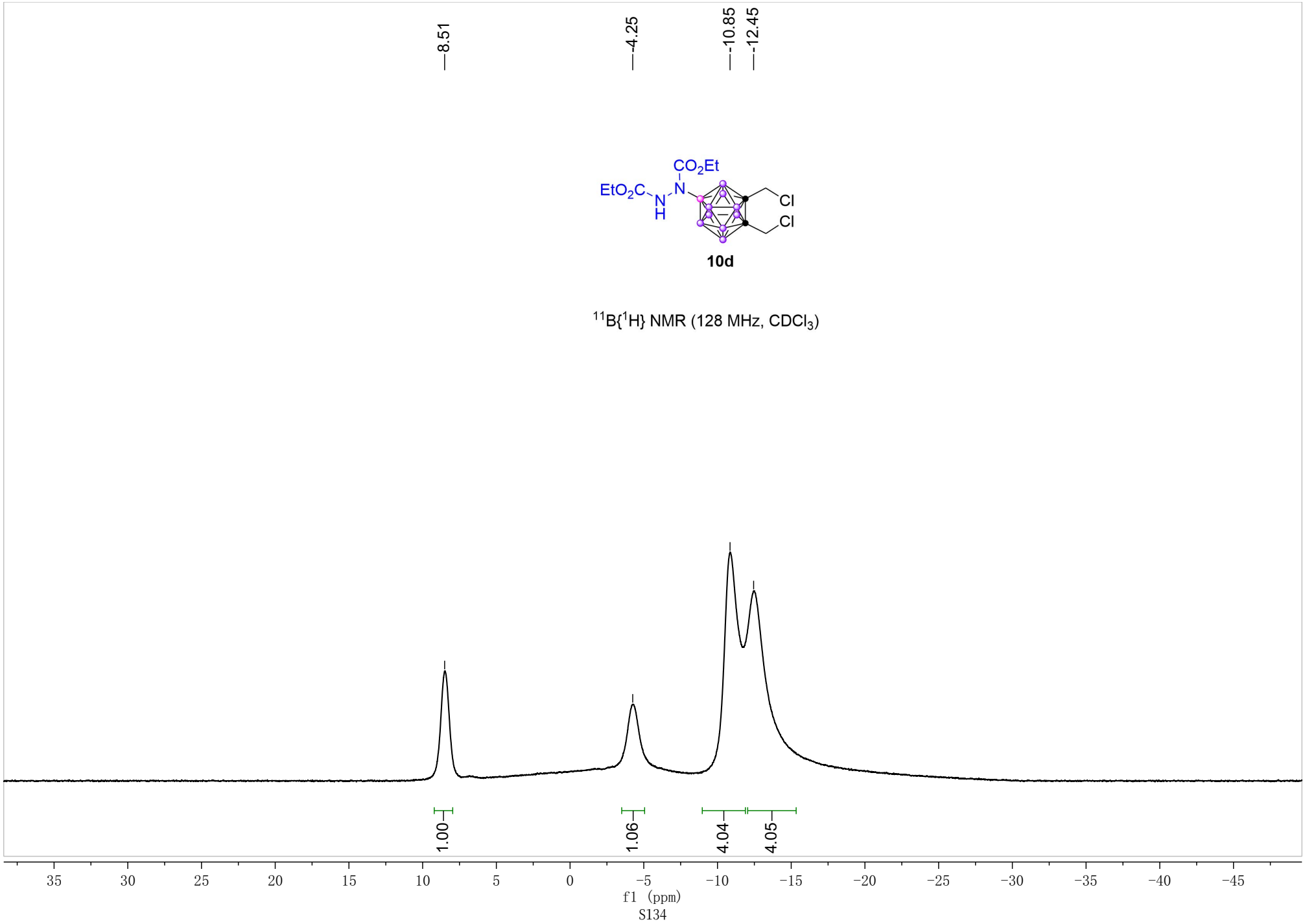

7.55
0.41
-9.11
-10.42
-15.99
-18.28
CO2Et
EtO2C
N
H
Br
H
H
10b
11B{1H} NMR (193 MHz, CDCl3)
1.30
1.30
1.05
0.99
4.22
1.77
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

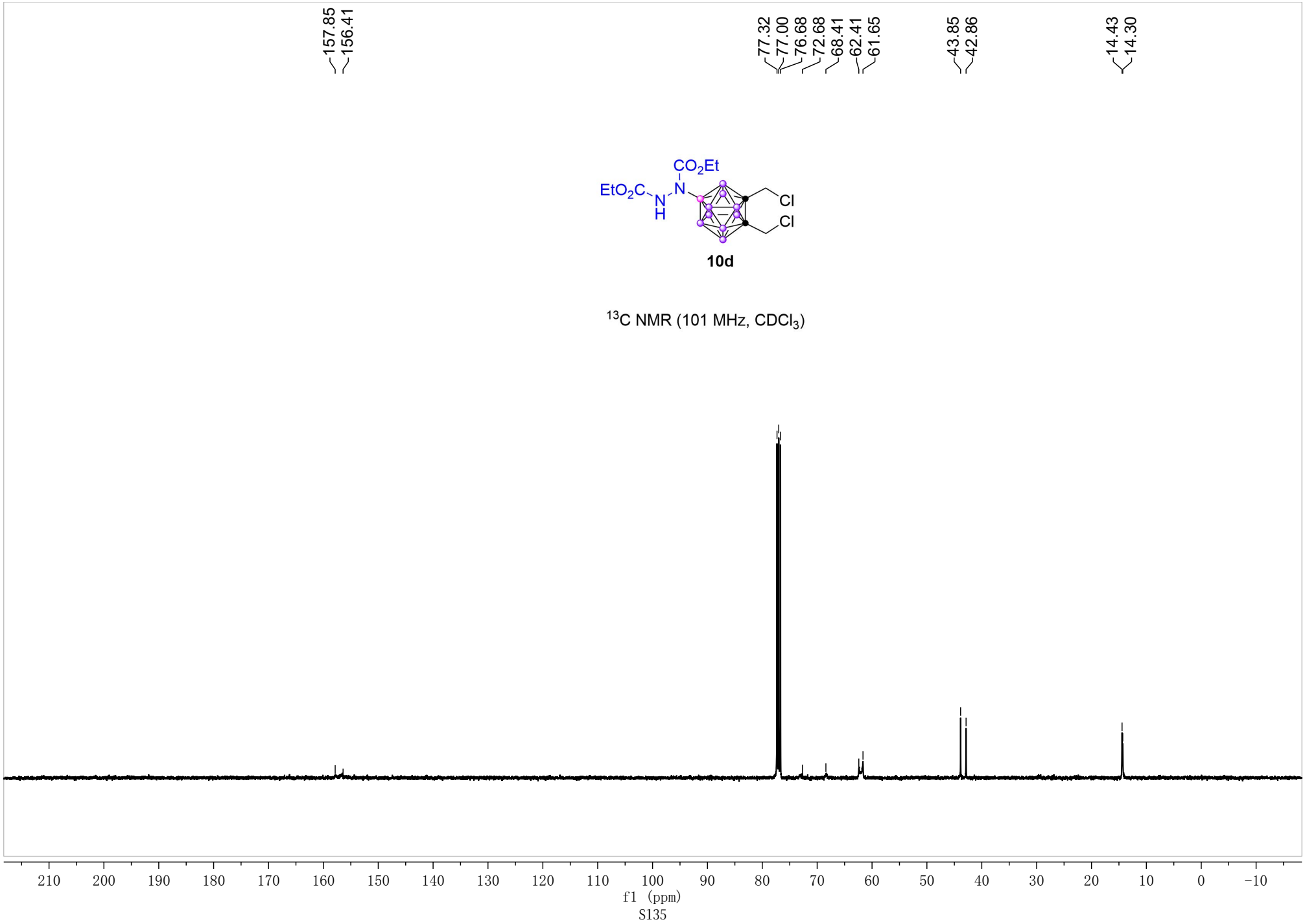

157.61
156.28
77.21
77.00
76.79
62.56
61.64
45.32
45.17
14.45
14.20
CO2Et
EtO2C
N
N
H
H
Br
H
10b
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

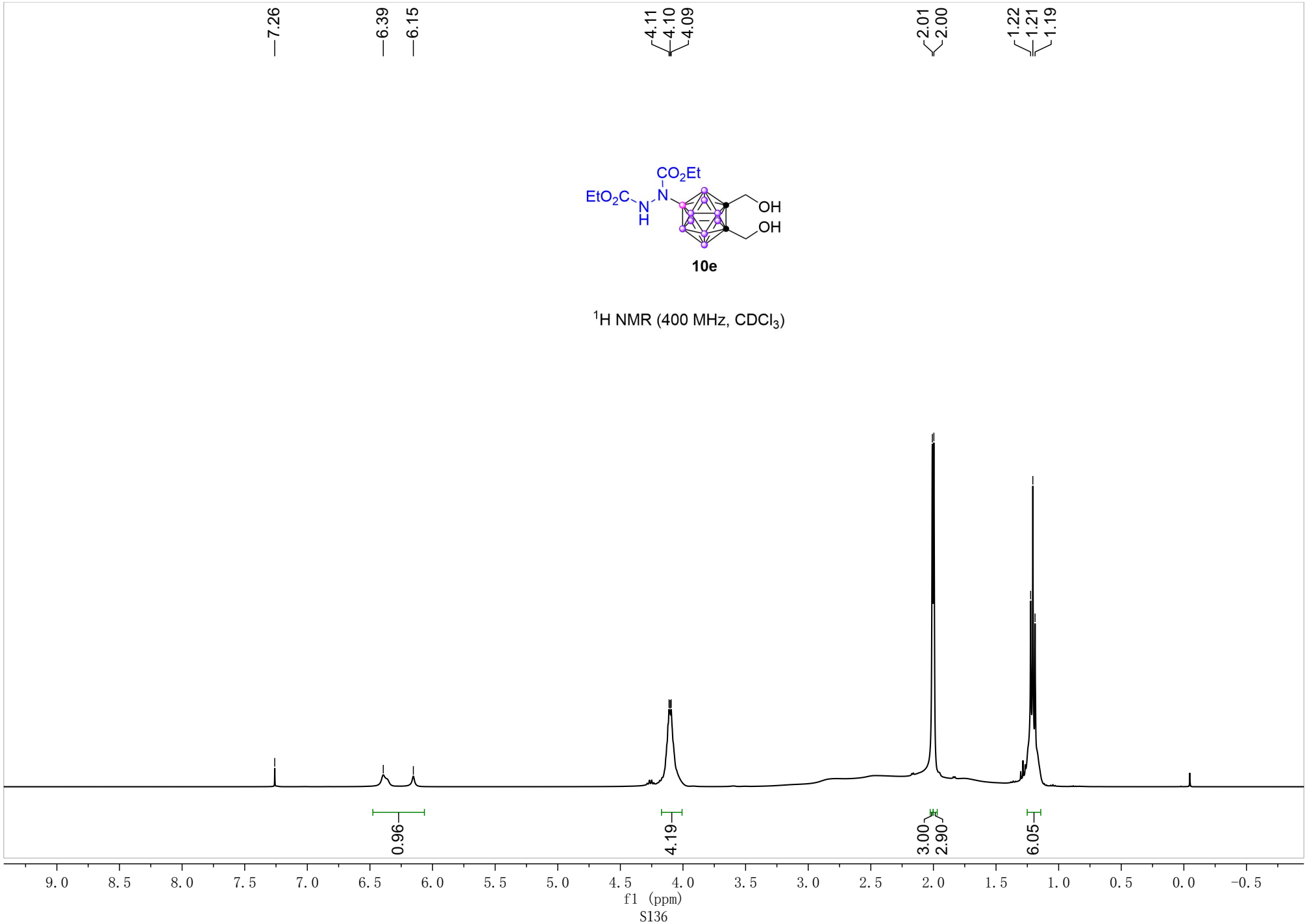

7.26
6.41
6.35
6.15
4.20
4.15
1.27
1.25
1.23
CO2Et
EtO2C
N
N
H
Cl
Cl
10d
1H NMR (400 MHz, CDCl3)
1.02
2.00
4.19
6.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

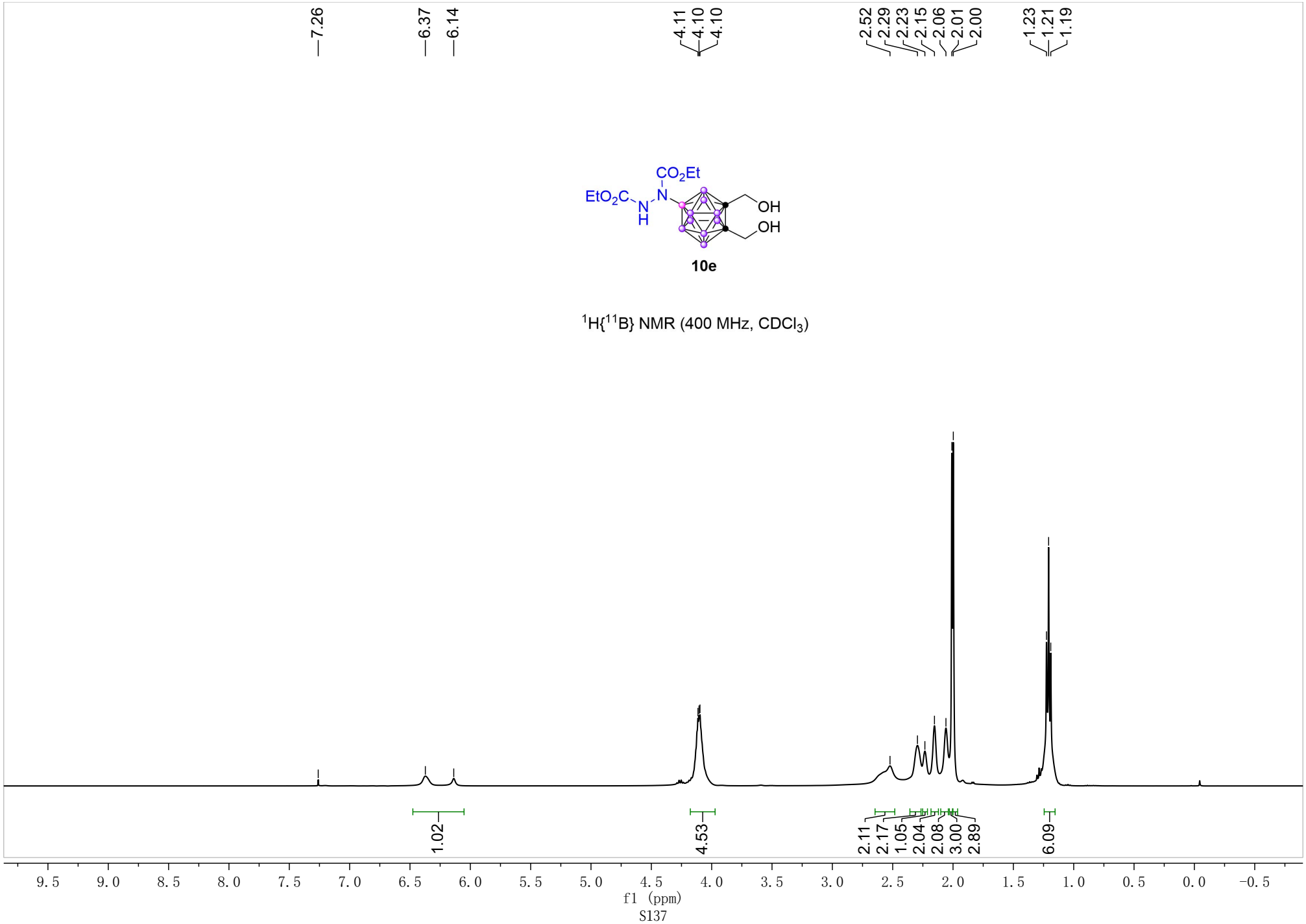

7.26
6.39
6.14
4.20
4.15
2.62
2.52
2.43
2.38
2.28
1.27
1.25
1.23
CO2Et
EtO2C
N
N
H
Cl
Cl
10d
1H{11B} NMR (400 MHz, CDCl3)
1.00
2.00
4.18
2.00
2.75
0.92
0.98
1.77
6.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

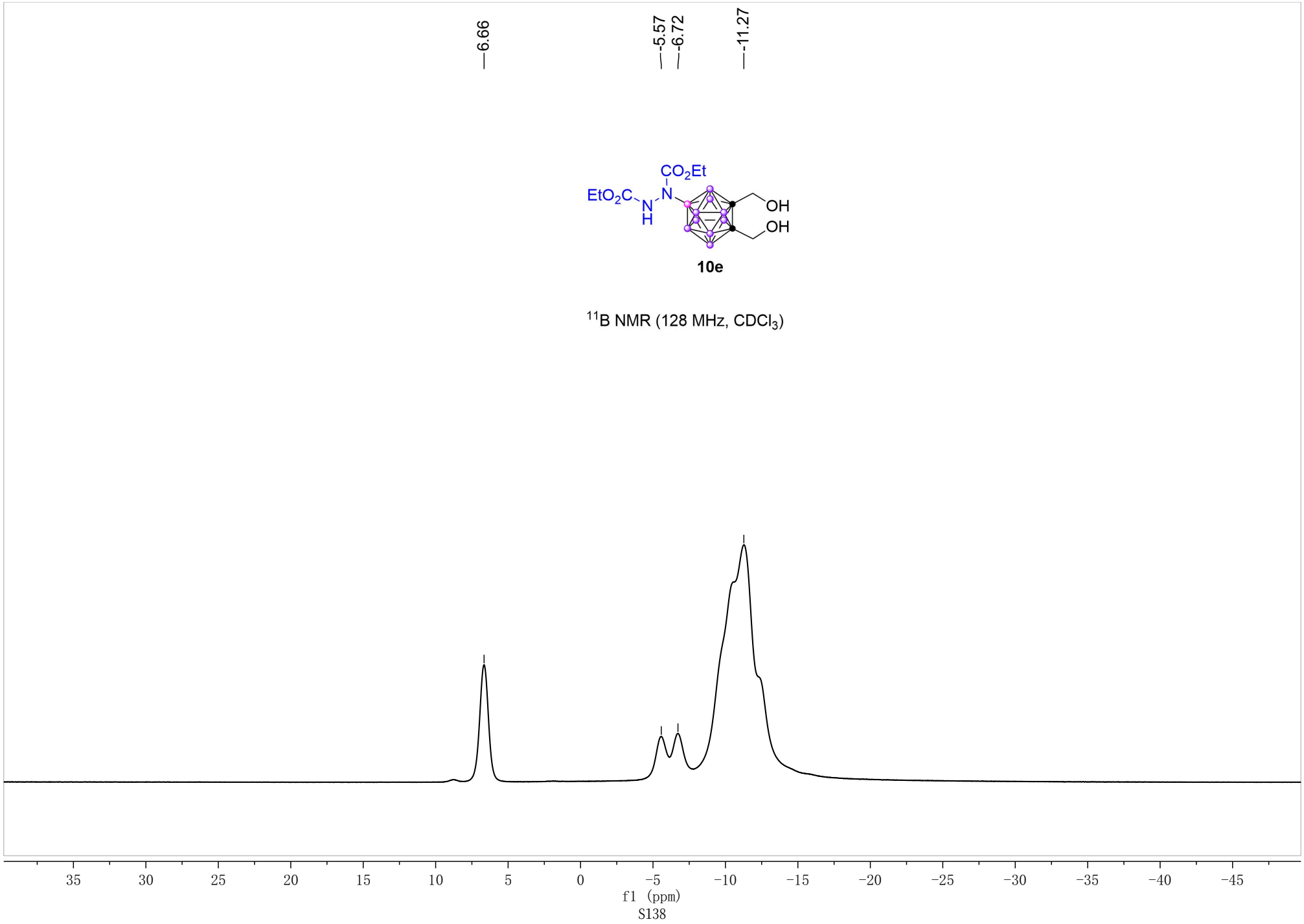

8.50
-3.69
-4.80
-10.26
-11.59
-13.07
CO2Et
EtO2C
N
N
H
Cl
Cl
10d
11B NMR (128 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

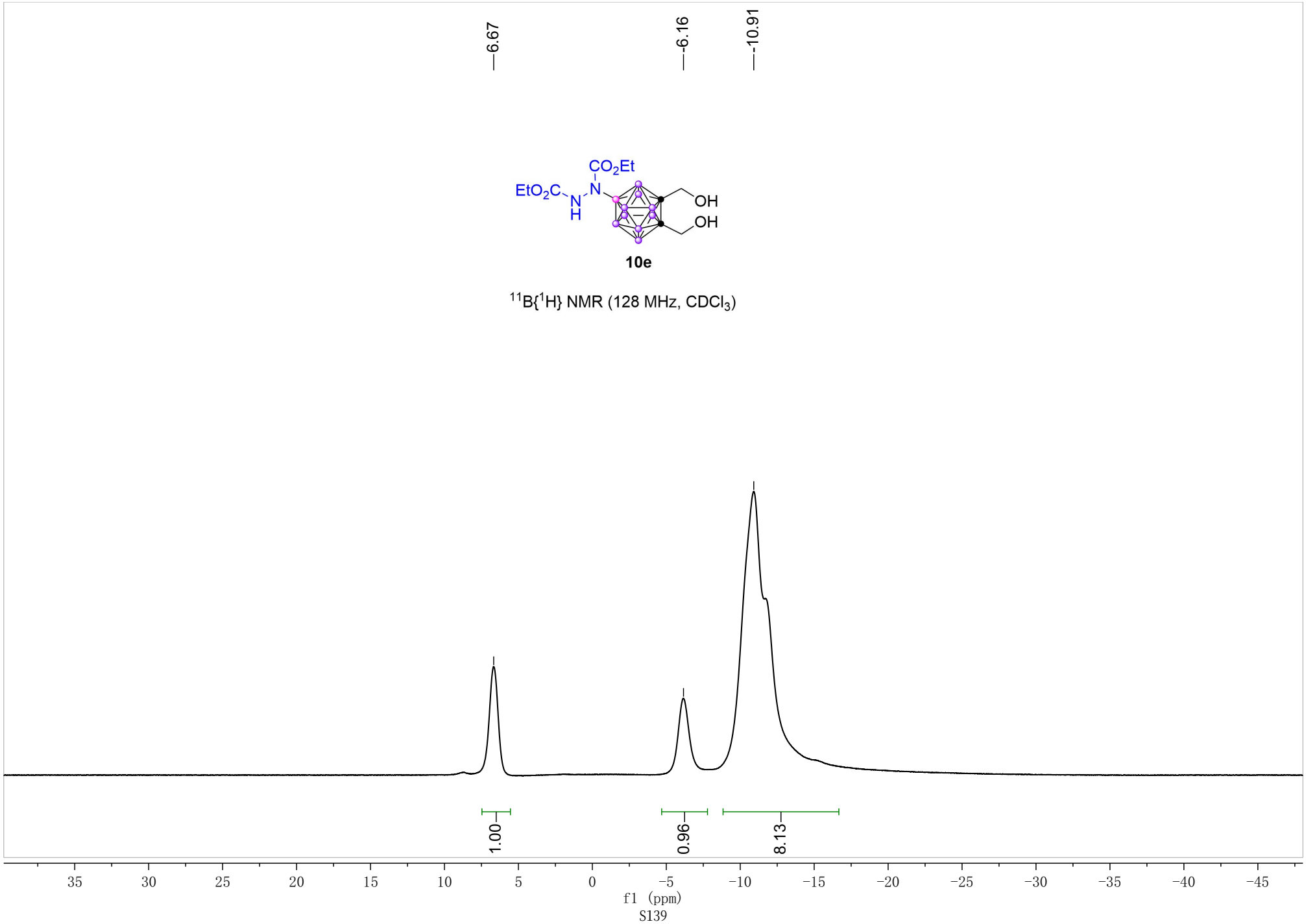

8.51
4.25
-10.85
-12.45
CO2Et
EtO2C
N
N
H
Cl
Cl
10d
11B{1H} NMR (128 MHz, CDCl3)
1.00
1.06
4.04
4.05
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

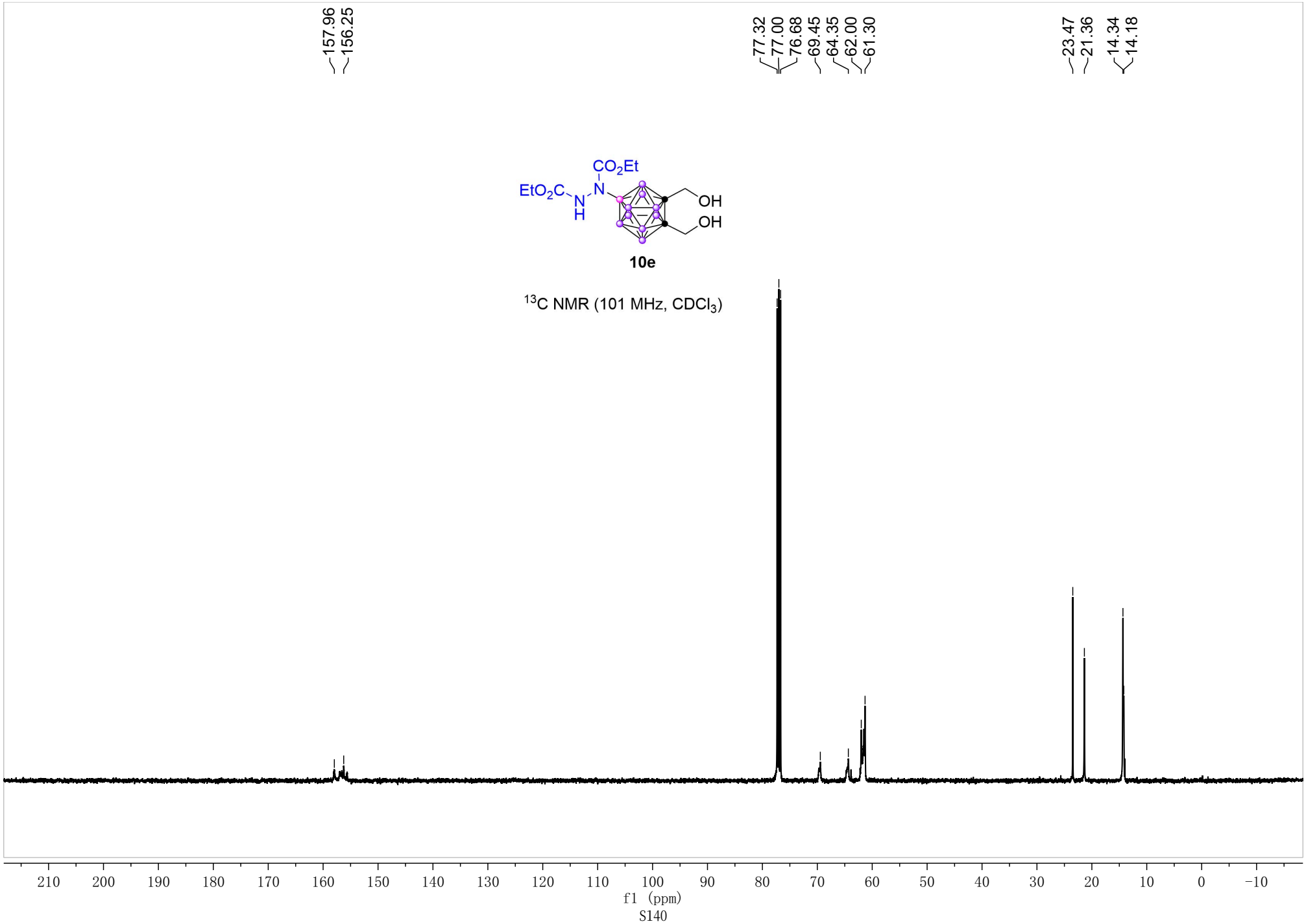

157.85
156.41
77.32
77.00
76.68
72.68
68.41
62.41
61.65
43.85
42.86
14.43
14.30
CO2Et
EtO2C
N
N
H
Cl
Cl
10d
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

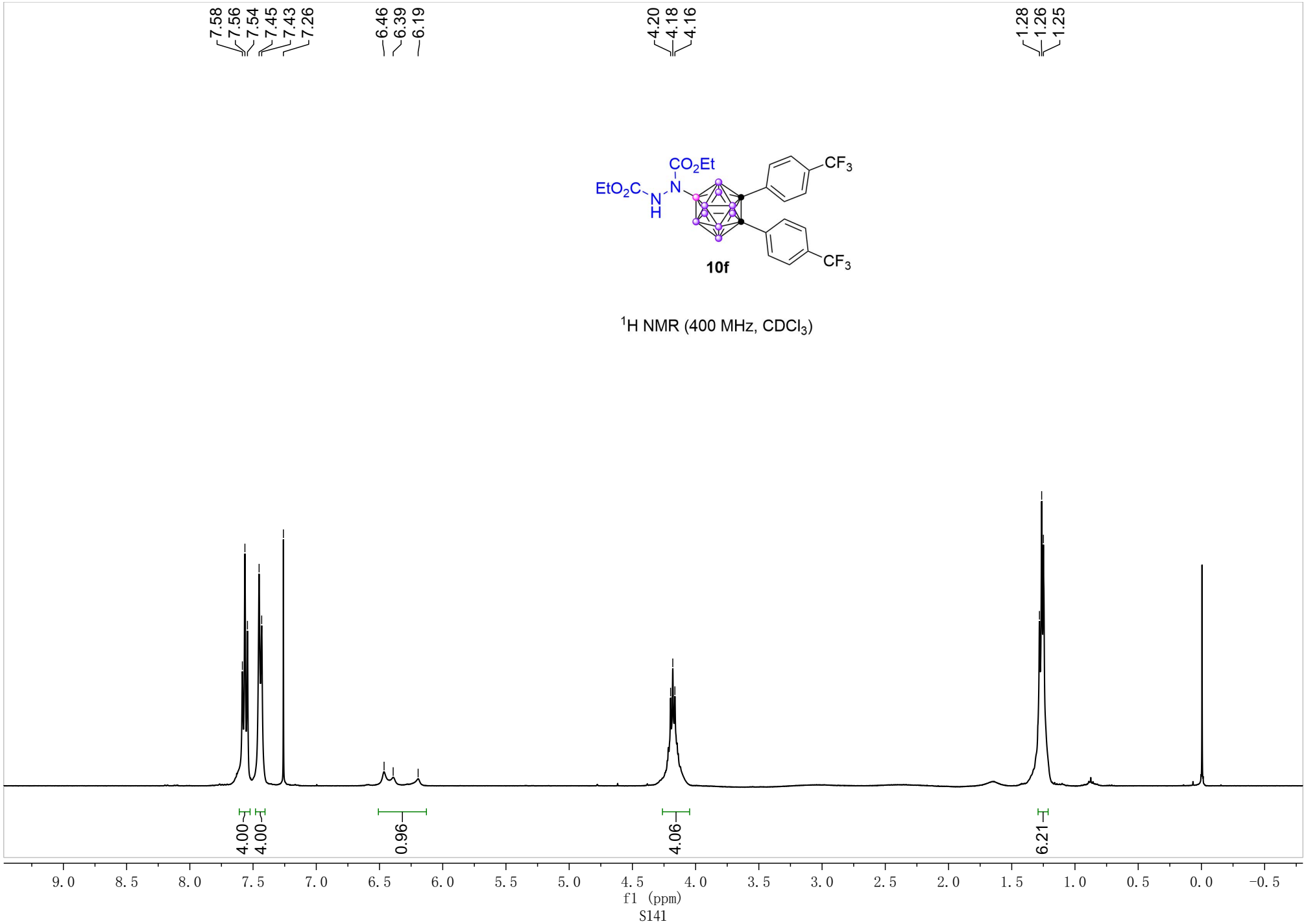

7.26
6.39
6.15
4.11
4.10
4.09
2.01
2.00
1.22
1.21
1.19
CO2Et
EtO2C
N
N
H
OH
OH
10e
1H NMR (400 MHz, CDCl3)
0.96
4.19
3.00
2.90
6.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

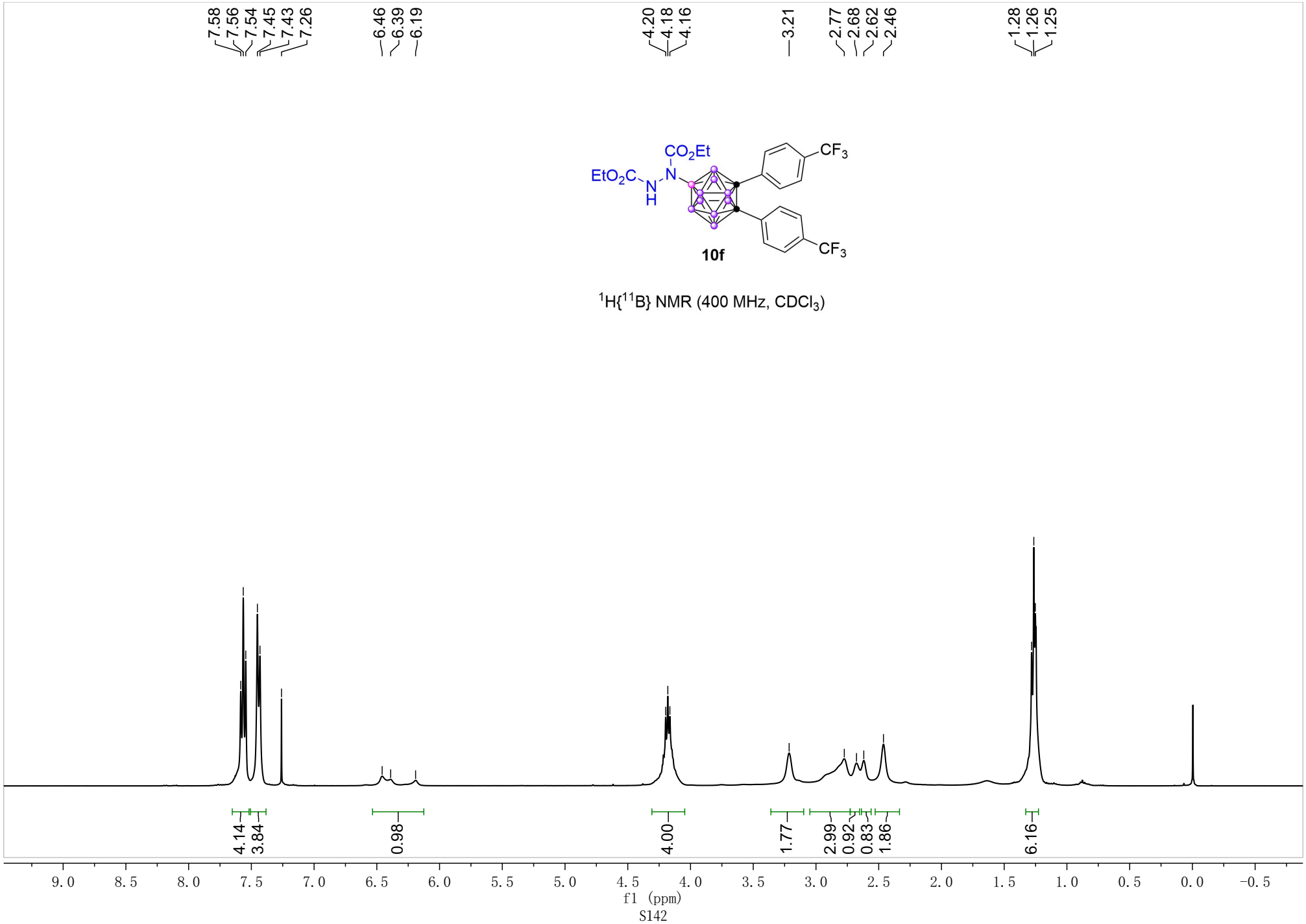

7.26
6.37
6.14
4.11
4.10
4.10
2.52
2.29
2.23
2.15
2.06
2.01
2.00
1.23
1.21
1.19
CO2Et
EtO2C
N
N
H
OH
OH
10e
1H{11B} NMR (400 MHz, CDCl3)
1.02
4.53
2.11
2.17
1.05
2.04
2.08
3.00
2.89
6.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

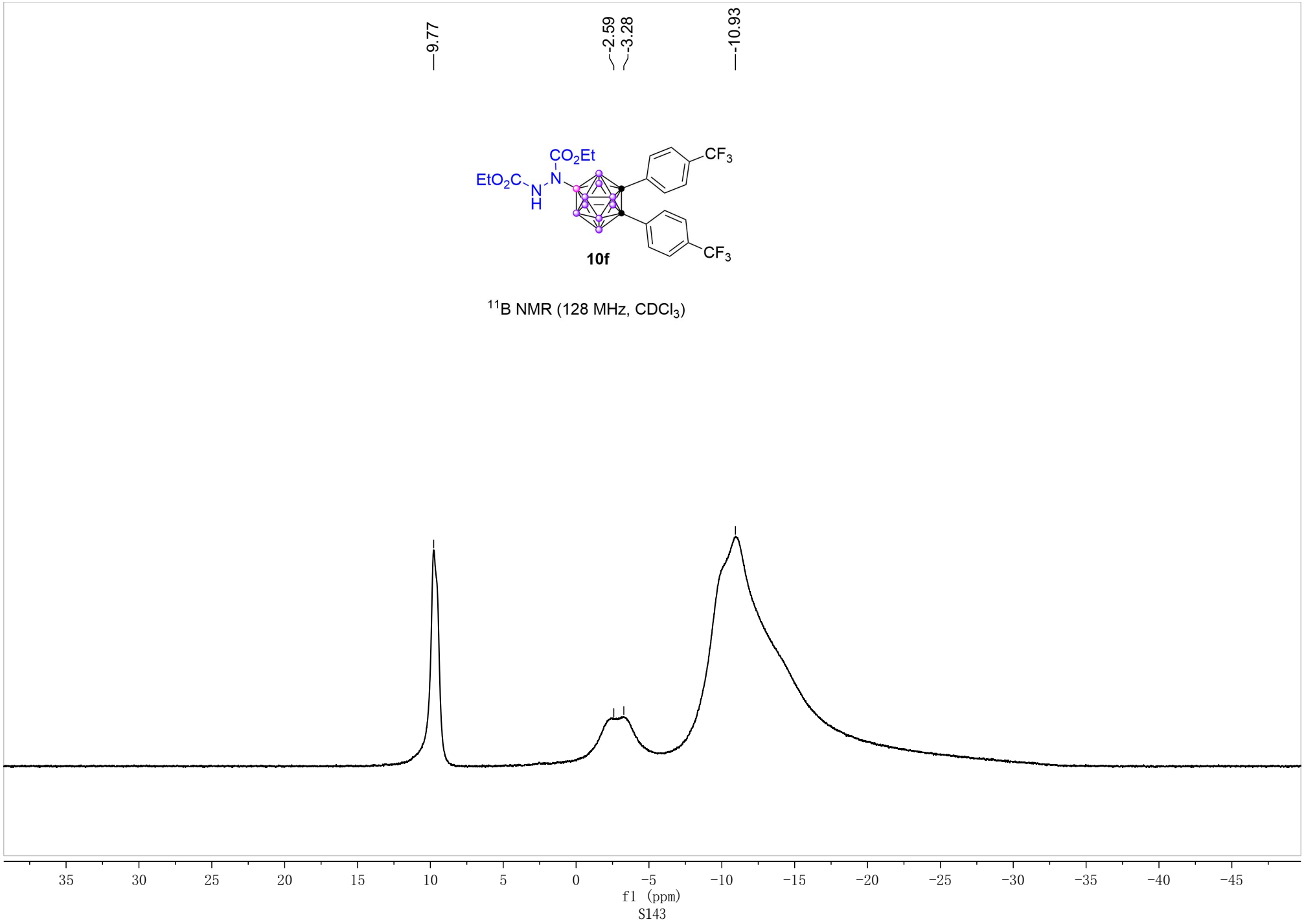

-6.66
-5.57
-6.72
-11.27
CO2Et
EtO2C
N
N
H
OH
OH
10e
11B NMR (128 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

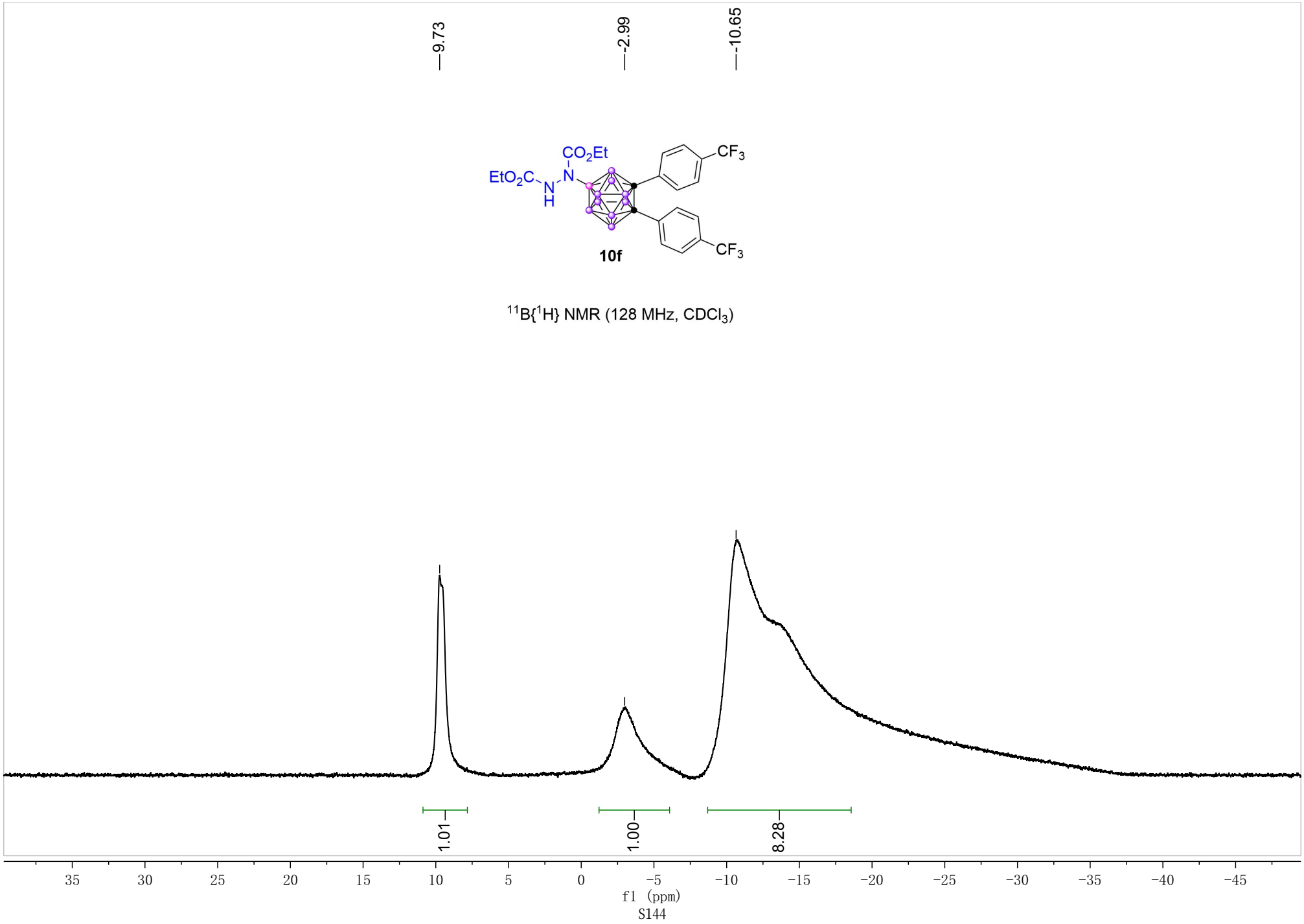

-6.67
-6.16
-10.91
CO2Et
EtO2C
N
N
H
OH
OH
10e
11B{1H} NMR (128 MHz, CDCl3)
1.00
0.96
8.13
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

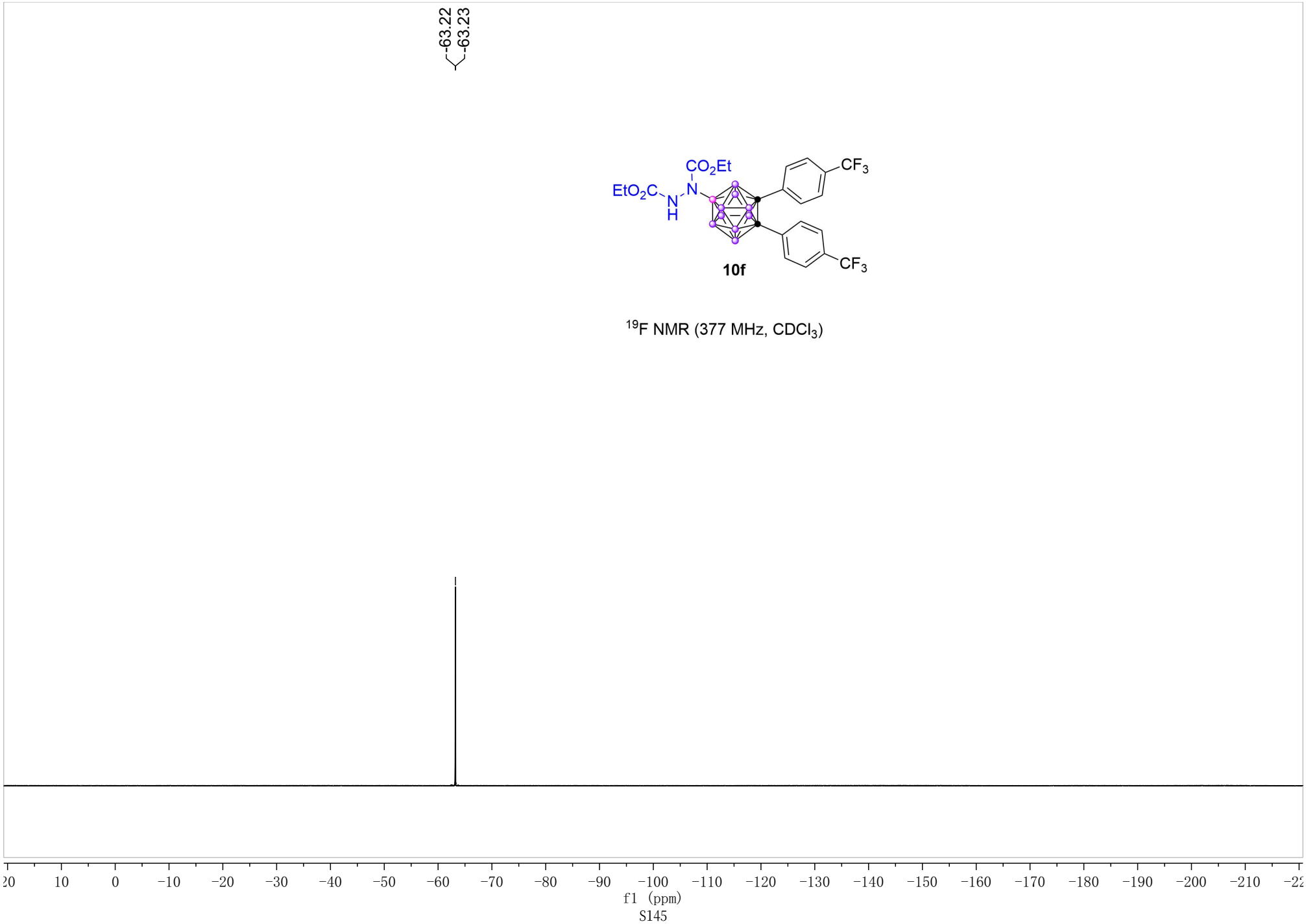

157.96
156.25
77.32
77.00
76.68
69.45
64.35
62.00
61.30
23.47
21.36
14.34
14.18
CO2Et
EtO2C
N
N
H
OH
OH
10e
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

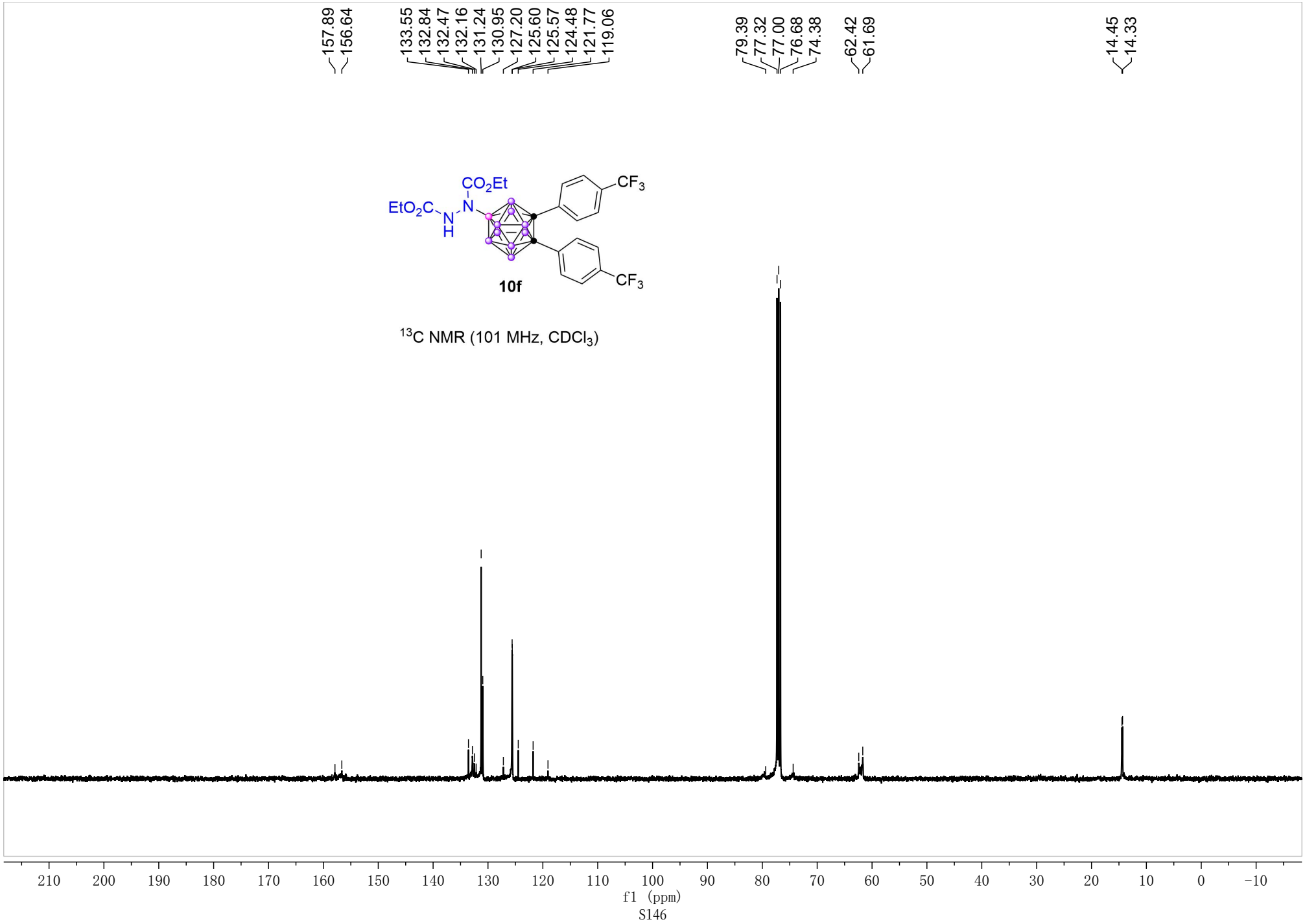

7.58
7.56
7.54
7.45
7.43
7.26
6.46
6.39
6.19
4.20
4.18
4.16
1.28
1.26
1.25
CO2Et
EtO2C
N
N
H
CF3
CF3
10f
1H NMR (400 MHz, CDCl3)
4.00
4.00
0.96
4.06
6.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

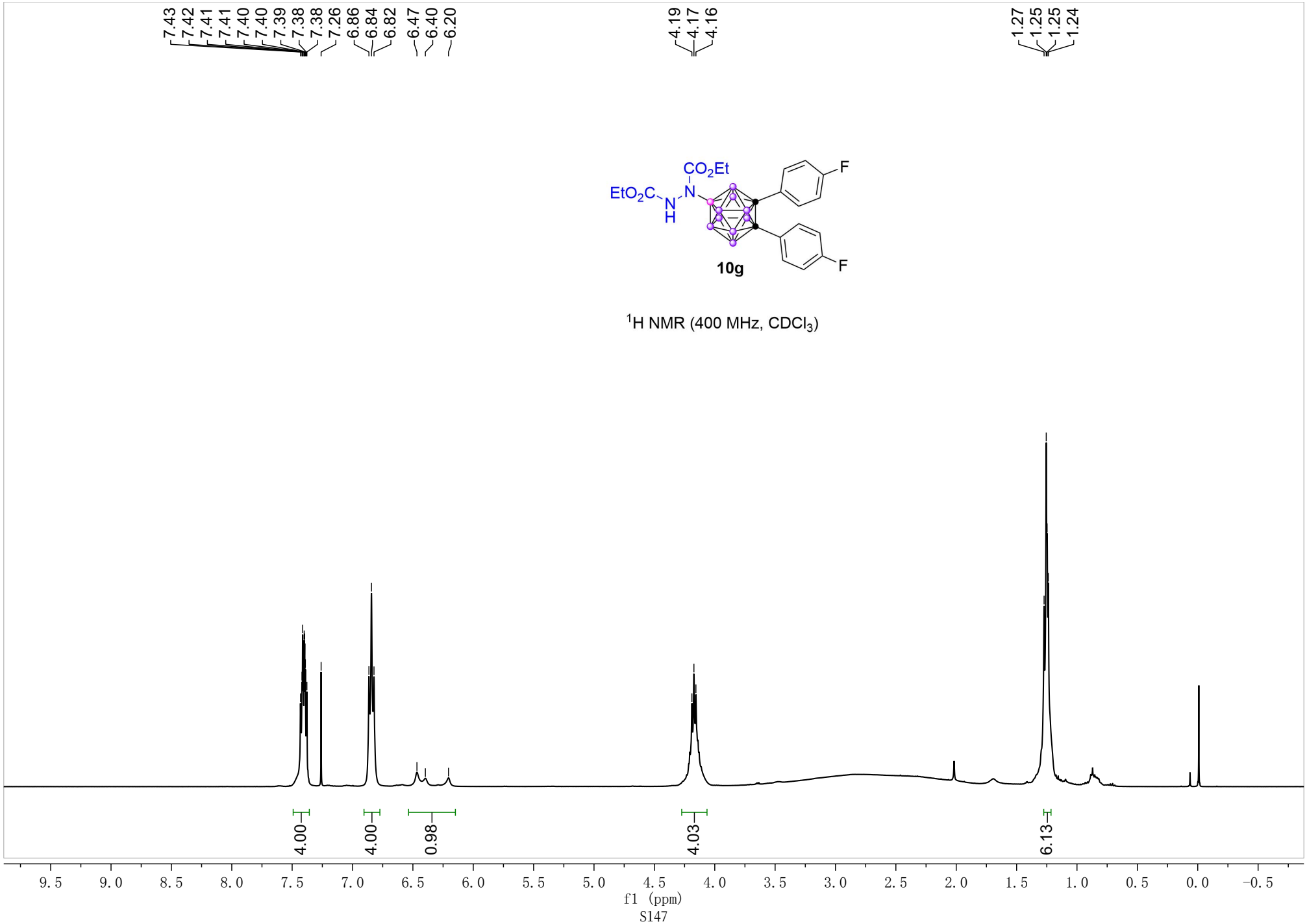

7.58
7.56
7.54
7.45
7.43
7.26
6.46
6.39
6.19
4.20
4.18
4.16
3.21
2.77
2.68
2.62
2.46
1.28
1.26
1.25
CO2Et
EtO2C
N
N
H
CF3
CF3
10f
1H{11B} NMR (400 MHz, CDCl3)
4.14
3.84
0.98
4.00
1.77
2.99
0.92
0.83
1.86
6.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

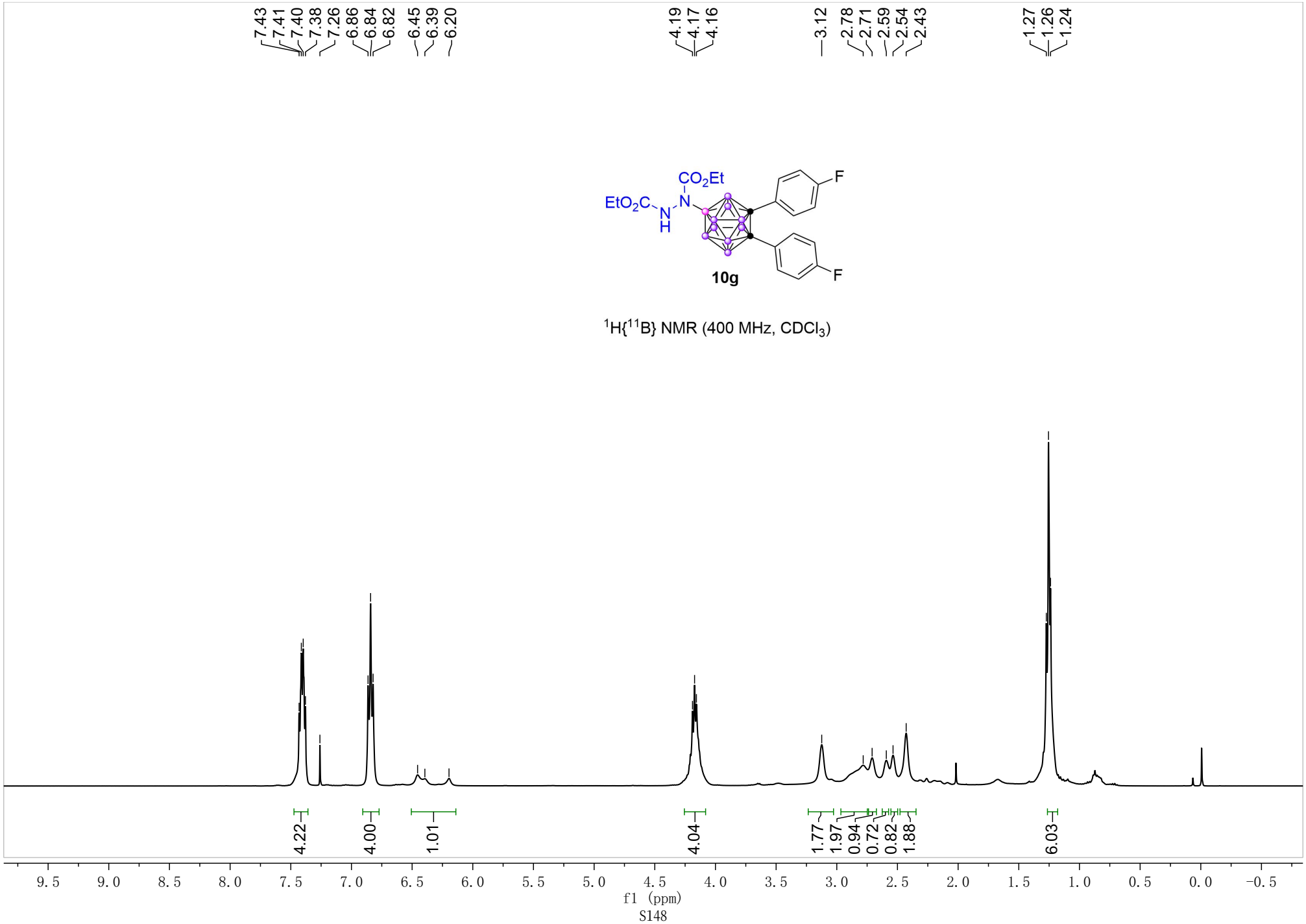

-9.77
-2.59
-3.28
-10.93
CO2Et
EtO2C
N
H
CF3
CF3
10f
11B NMR (128 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

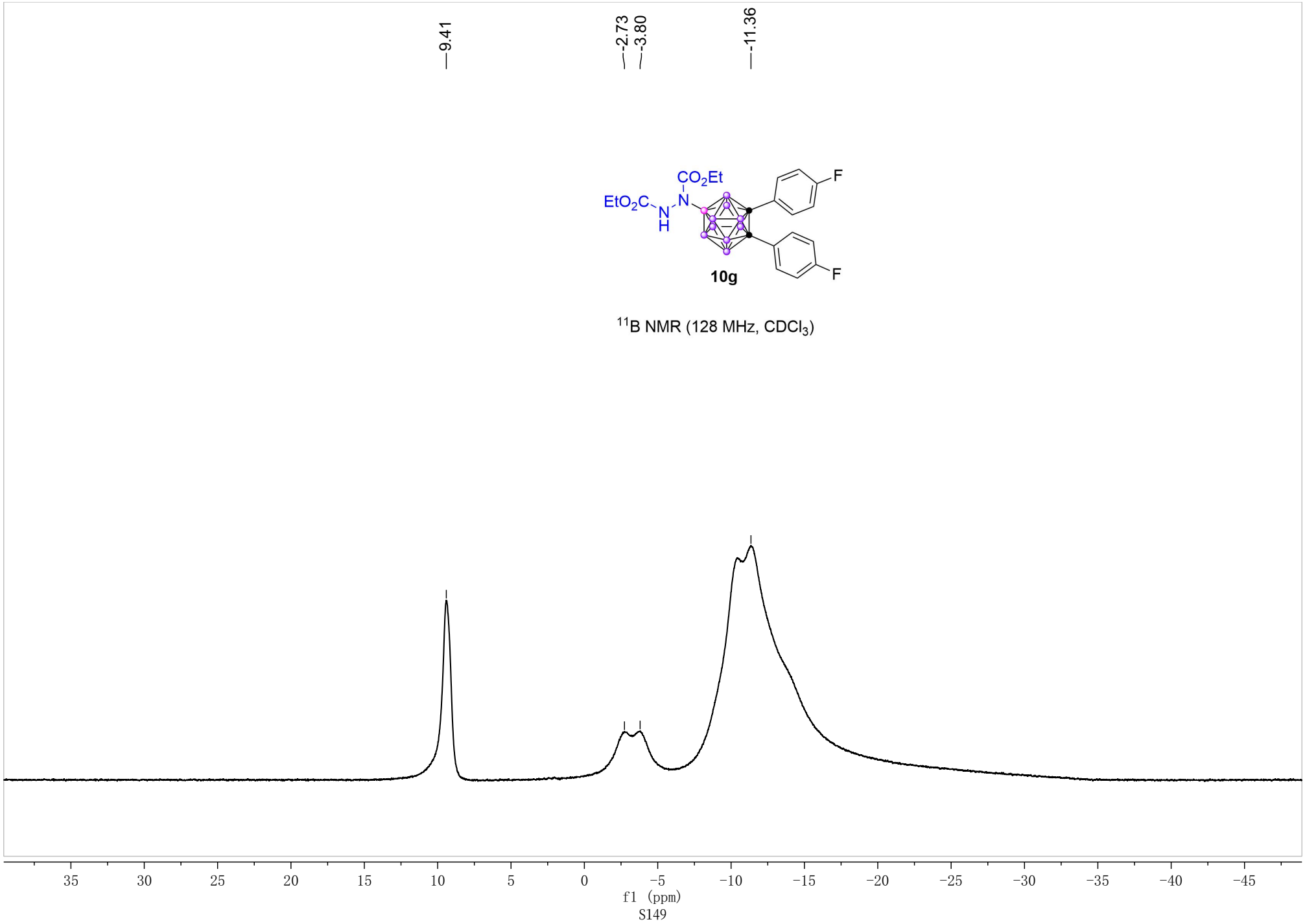

-9.73
-2.99
-10.65
CO2Et
EtO2C
N
N
H
CF3
CF3
10f
11B{1H} NMR (128 MHz, CDCl3)
1.01
1.00
8.28
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

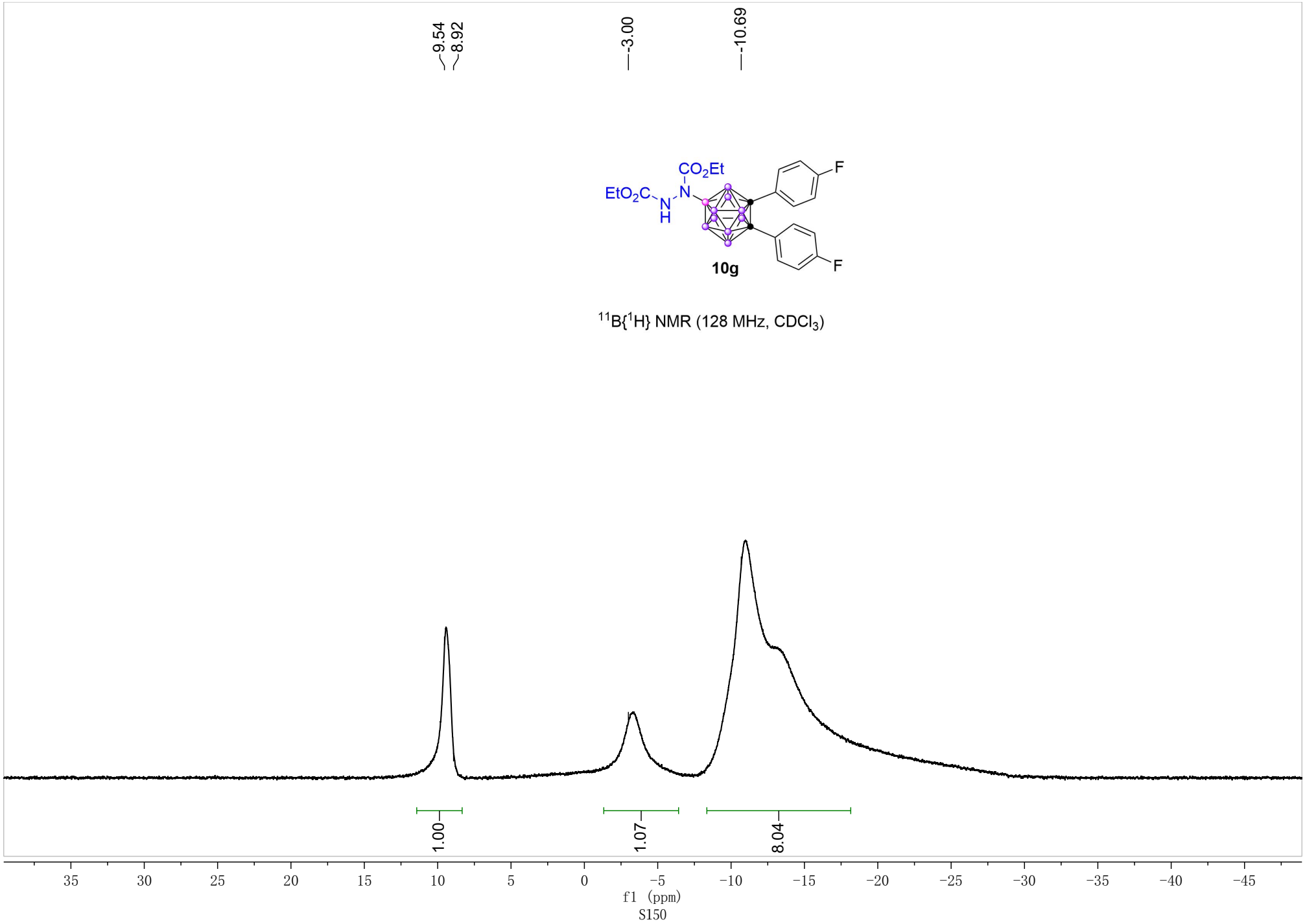

-63.22
-63.23
CO2Et
EtO2C
N
N
H
CF3
CF3
10f
19F NMR (377 MHz, CDCl3)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

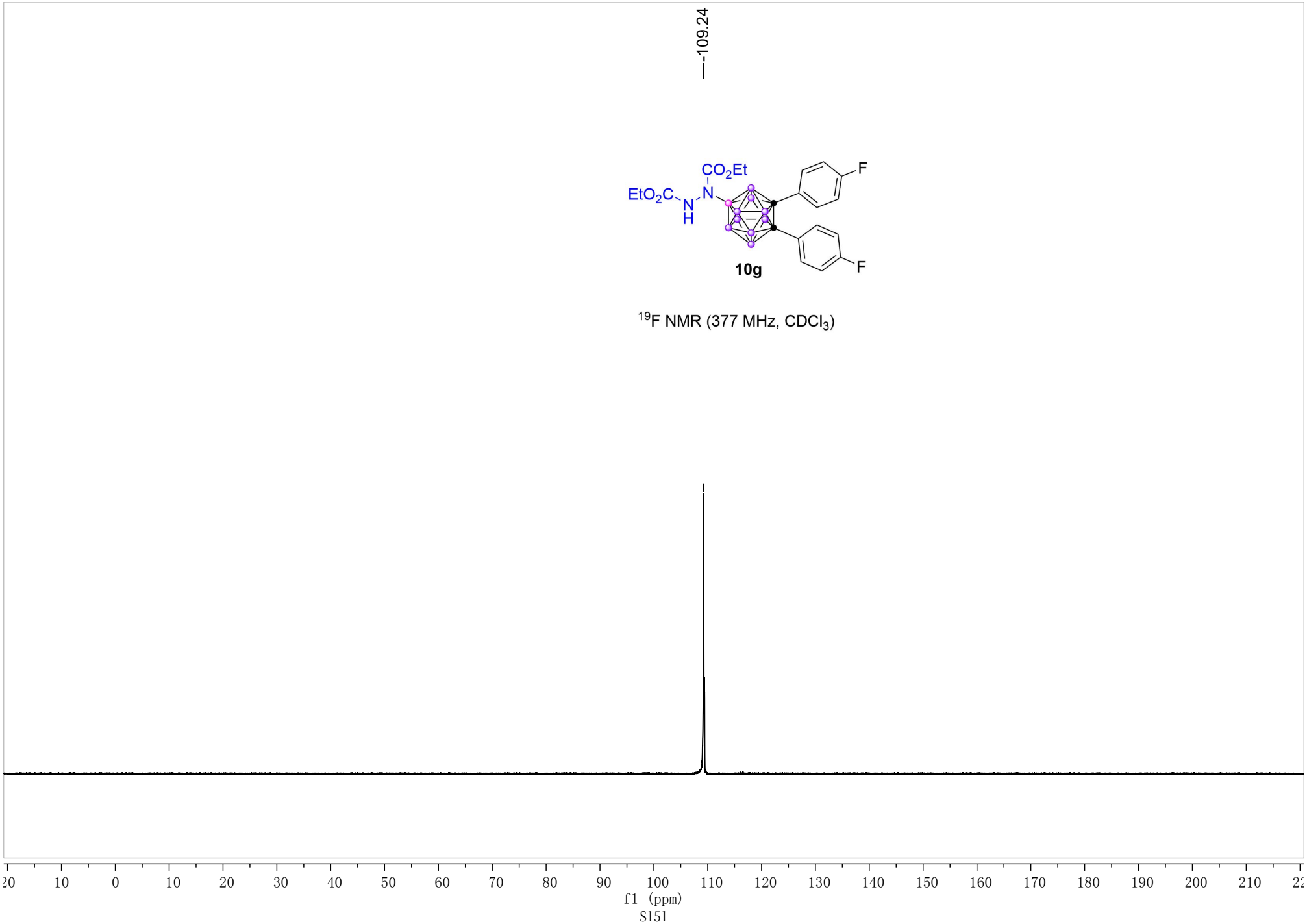

157.89
156.64
133.55
132.84
132.47
132.16
131.24
130.95
127.20
125.60
125.57
124.48
121.77
119.06
79.39
77.32
77.00
76.68
74.38
62.42
61.69
14.45
14.33
CO2Et
EtO2C
N
N
H
CF3
CF3
10f
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

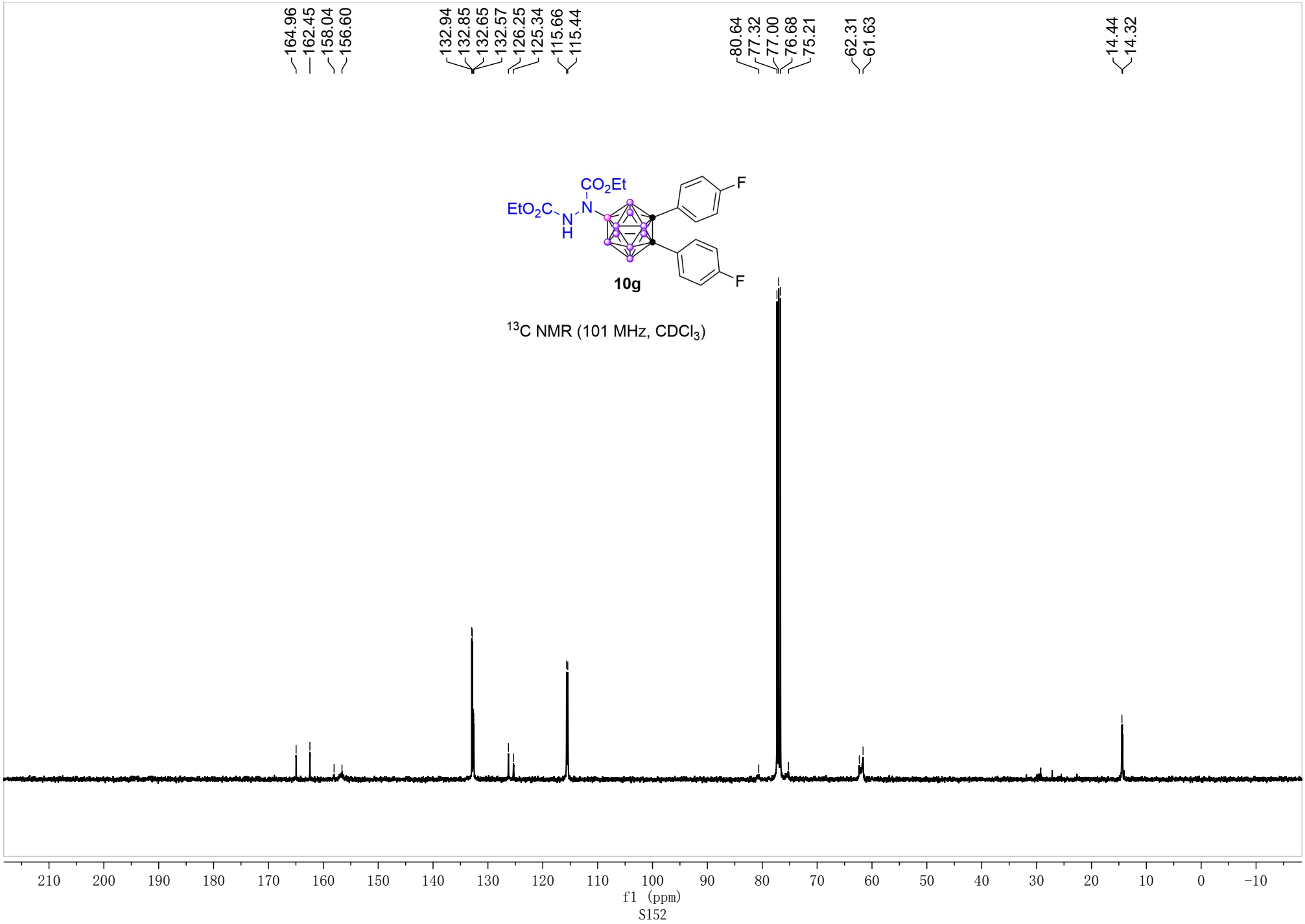

7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.26
6.86
6.84
6.82
6.47
6.40
6.20
4.19
4.17
4.16
1.27
1.25
1.25
1.24
CO2Et
EtO2C
N
N
H
F
F
10g
1H NMR (400 MHz, CDCl3)
4.00
4.00
0.98
4.03
6.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

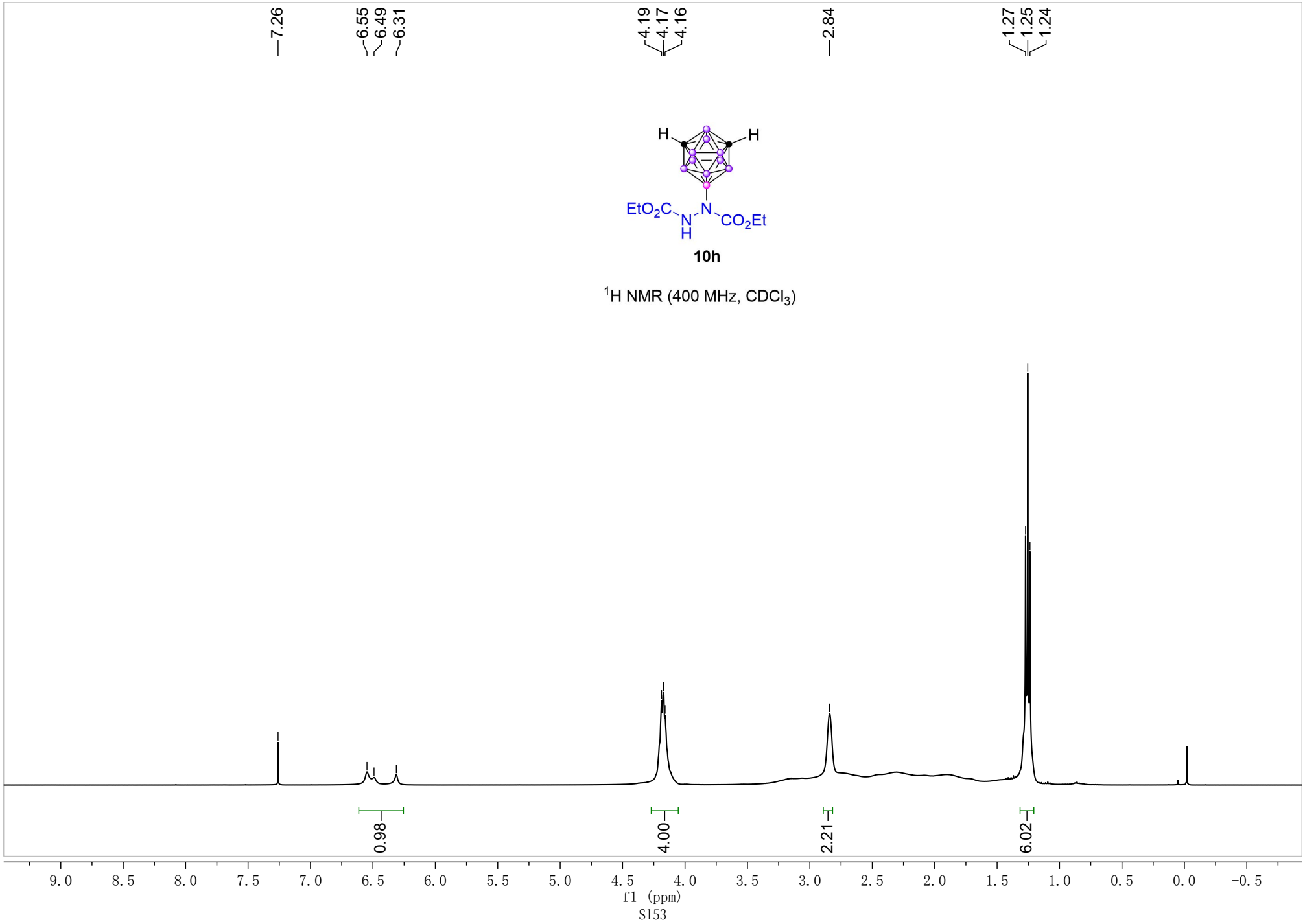

7.43
7.41
7.40
7.38
7.26
6.86
6.84
6.82
6.45
6.39
6.20
4.19
4.17
4.16
3.12
2.78
2.71
2.59
2.54
2.43
1.27
1.26
1.24
CO2Et
EtO2C
N
H
F
F
10g
1H{11B} NMR (400 MHz, CDCl3)
4.22
4.00
1.01
4.04
1.77
1.97
0.94
0.72
0.82
1.88
6.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

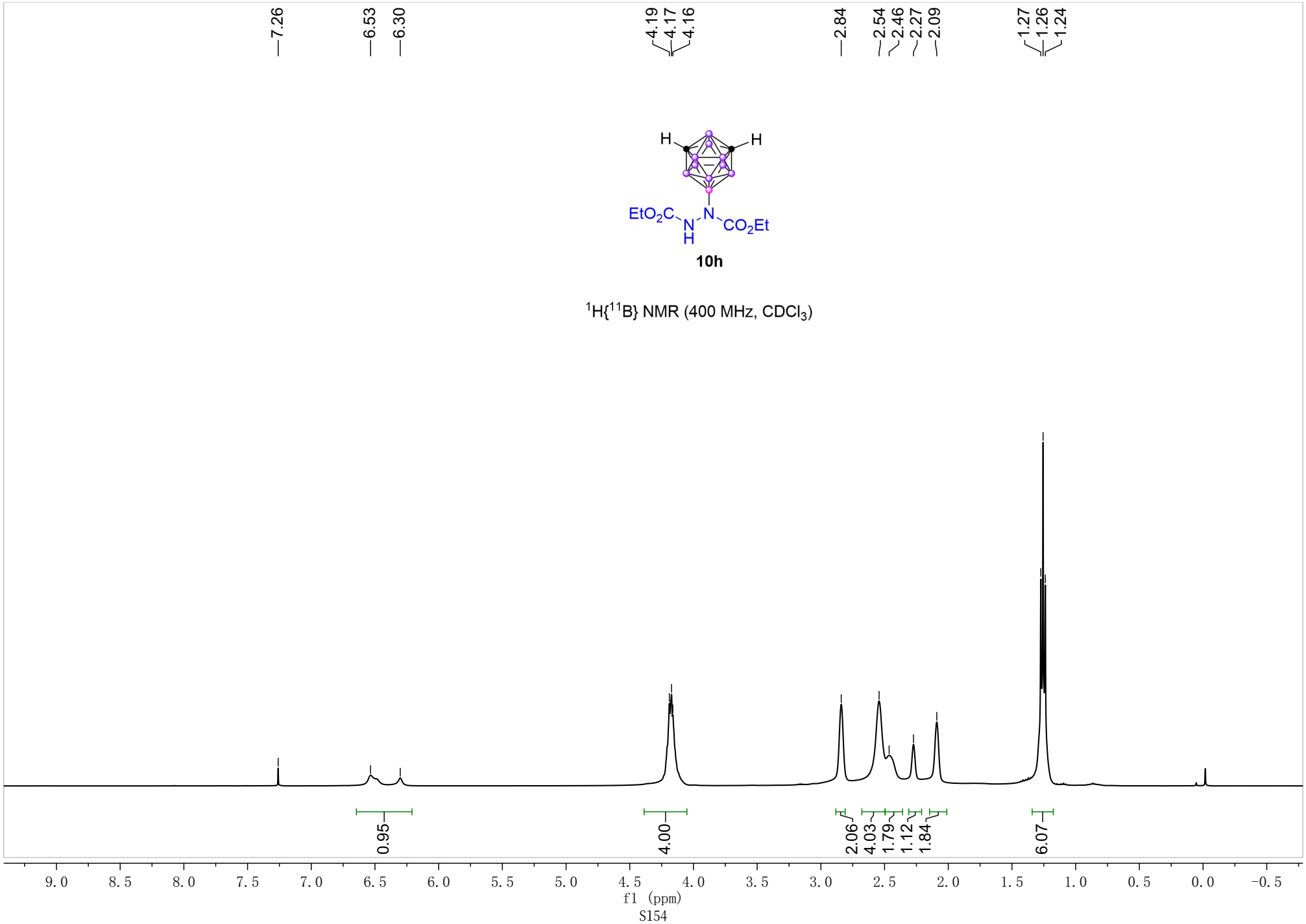

-9.41
-2.73
-3.80
-11.36
CO2Et
EtO2C
N
H
N
F
F
10g
11B NMR (128 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

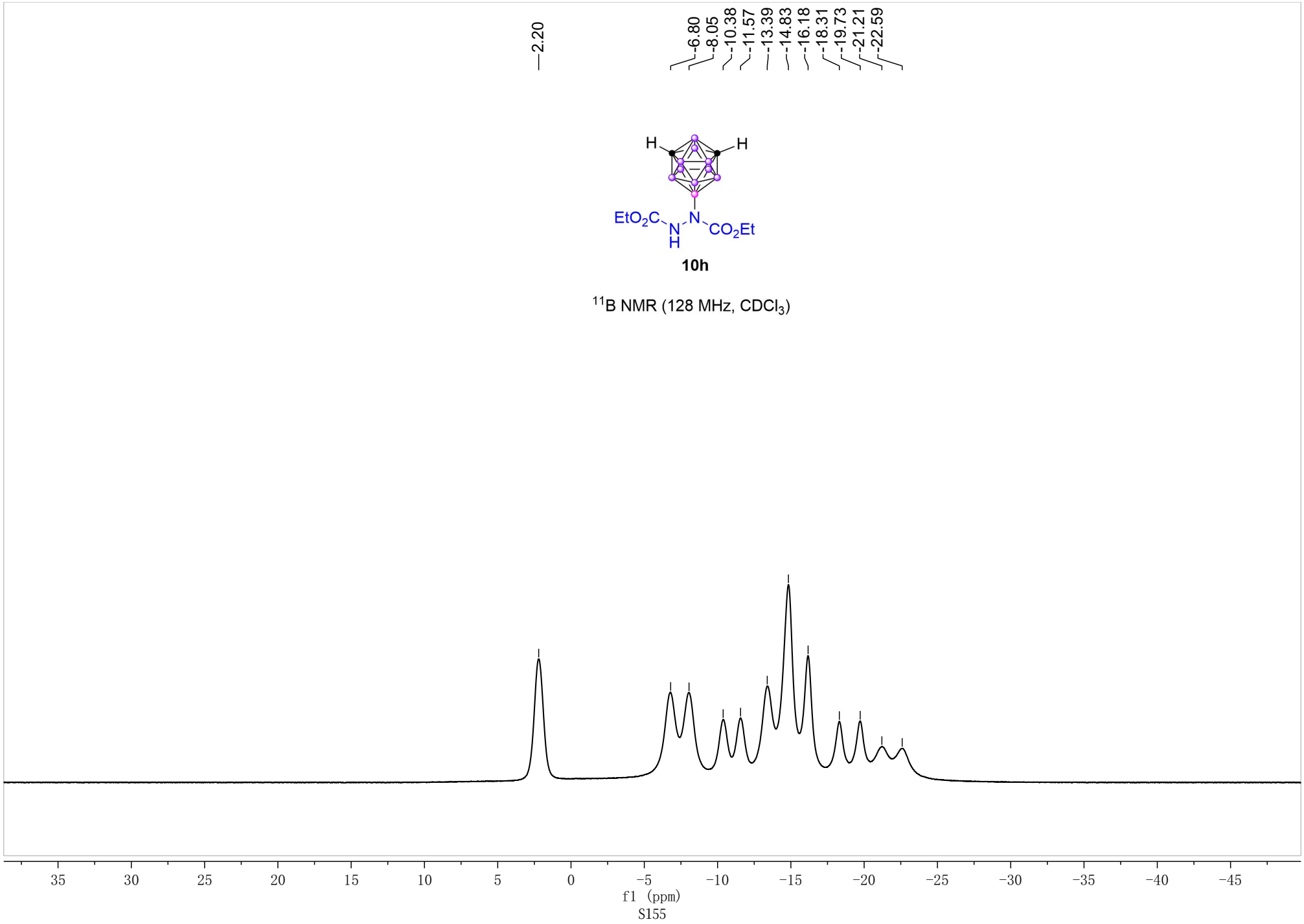

9.54
8.92
-3.00
-10.69
CO2Et
EtO2C
N
N
H
F
F
10g
11B{1H} NMR (128 MHz, CDCl3)
1.00
1.07
8.04
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

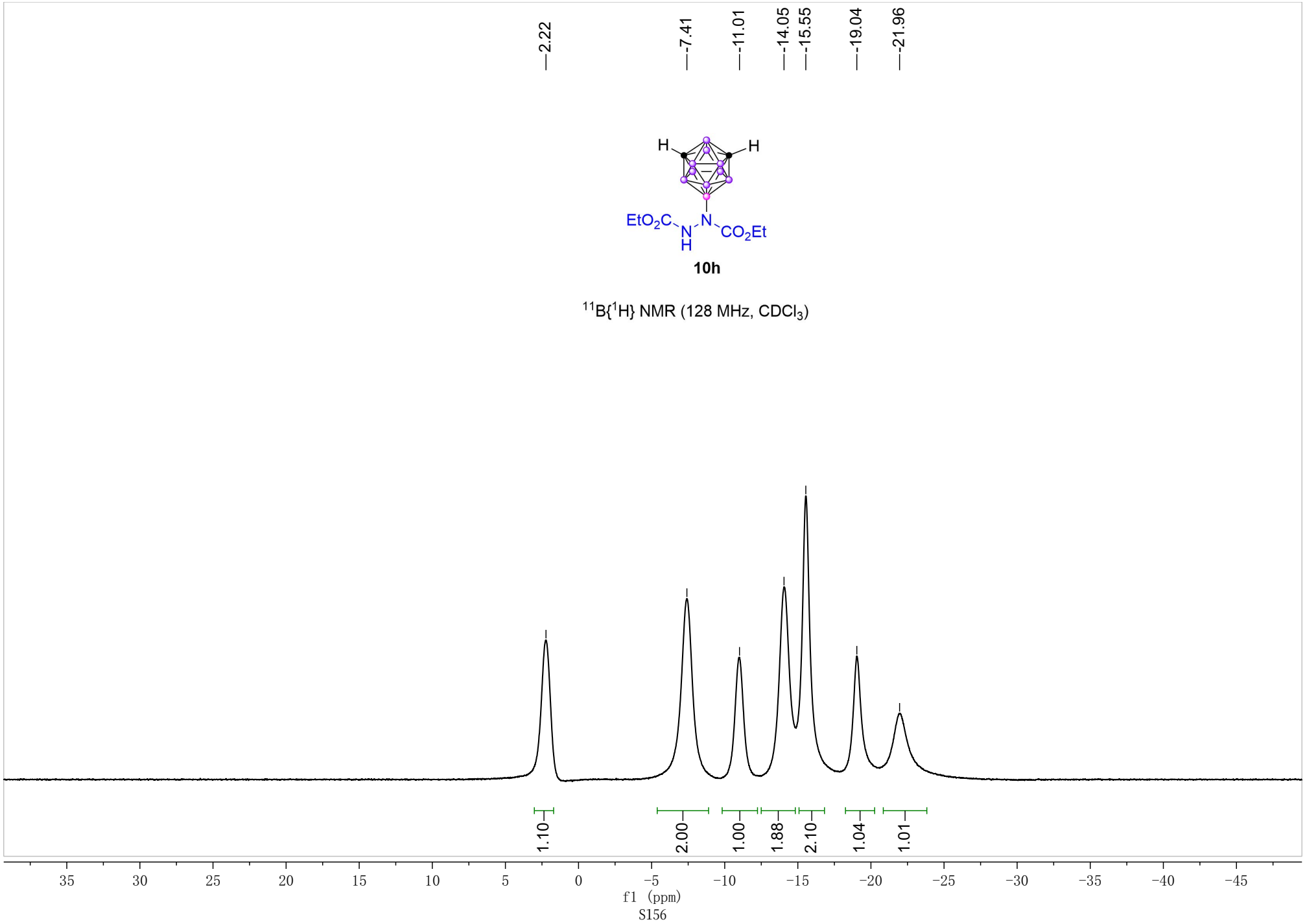

-109.24
CO2Et
EtO2C
N
N
H
F
F
10g
19F NMR (377 MHz, CDCl3)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

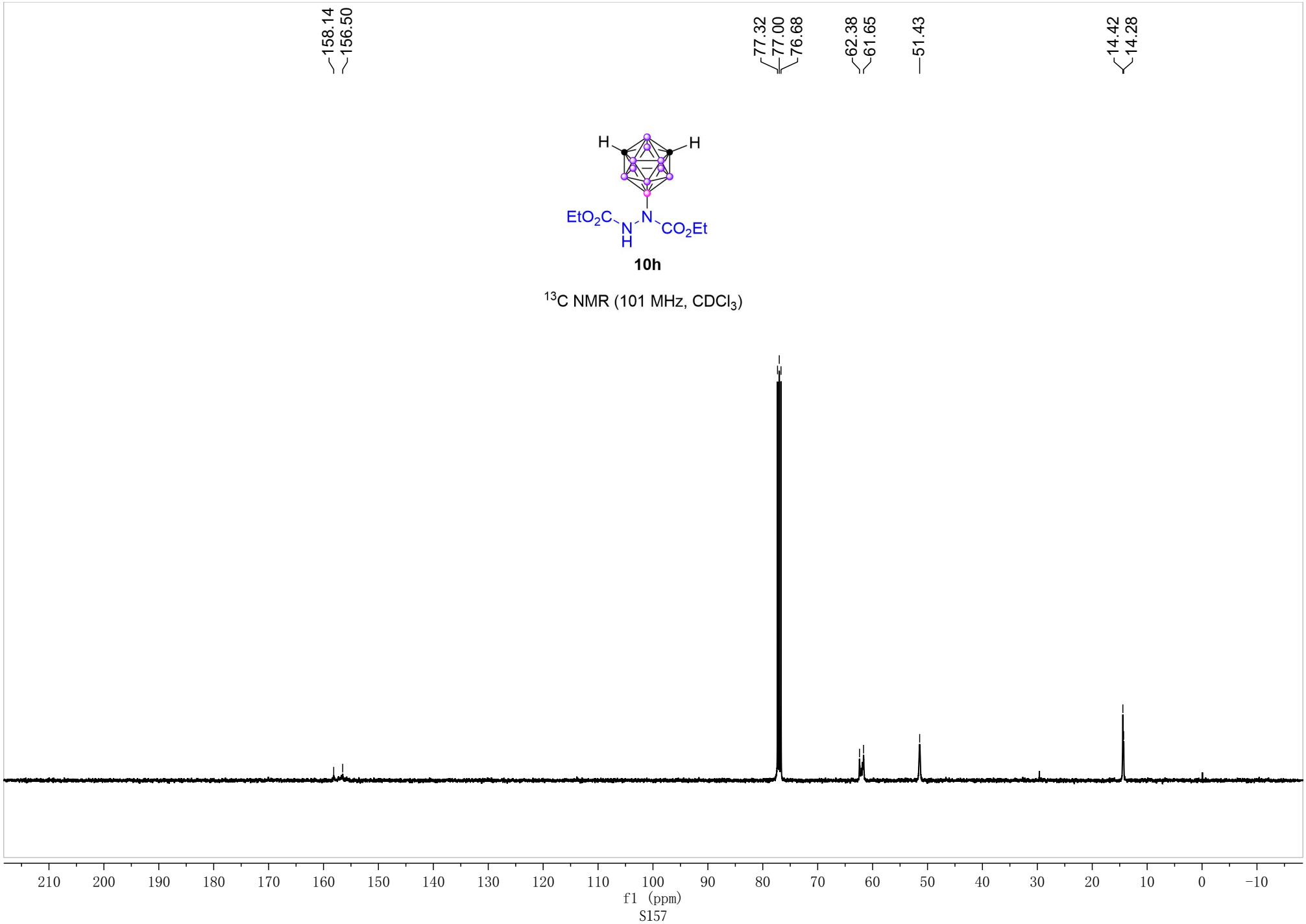

164.96
162.45
158.04
156.60
132.94
132.85
132.65
132.57
126.25
125.34
115.66
115.44
80.64
77.32
77.00
76.68
75.21
62.31
61.63
14.44
14.32
CO2Et
EtO2C
N
N
H
F
F
10g
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

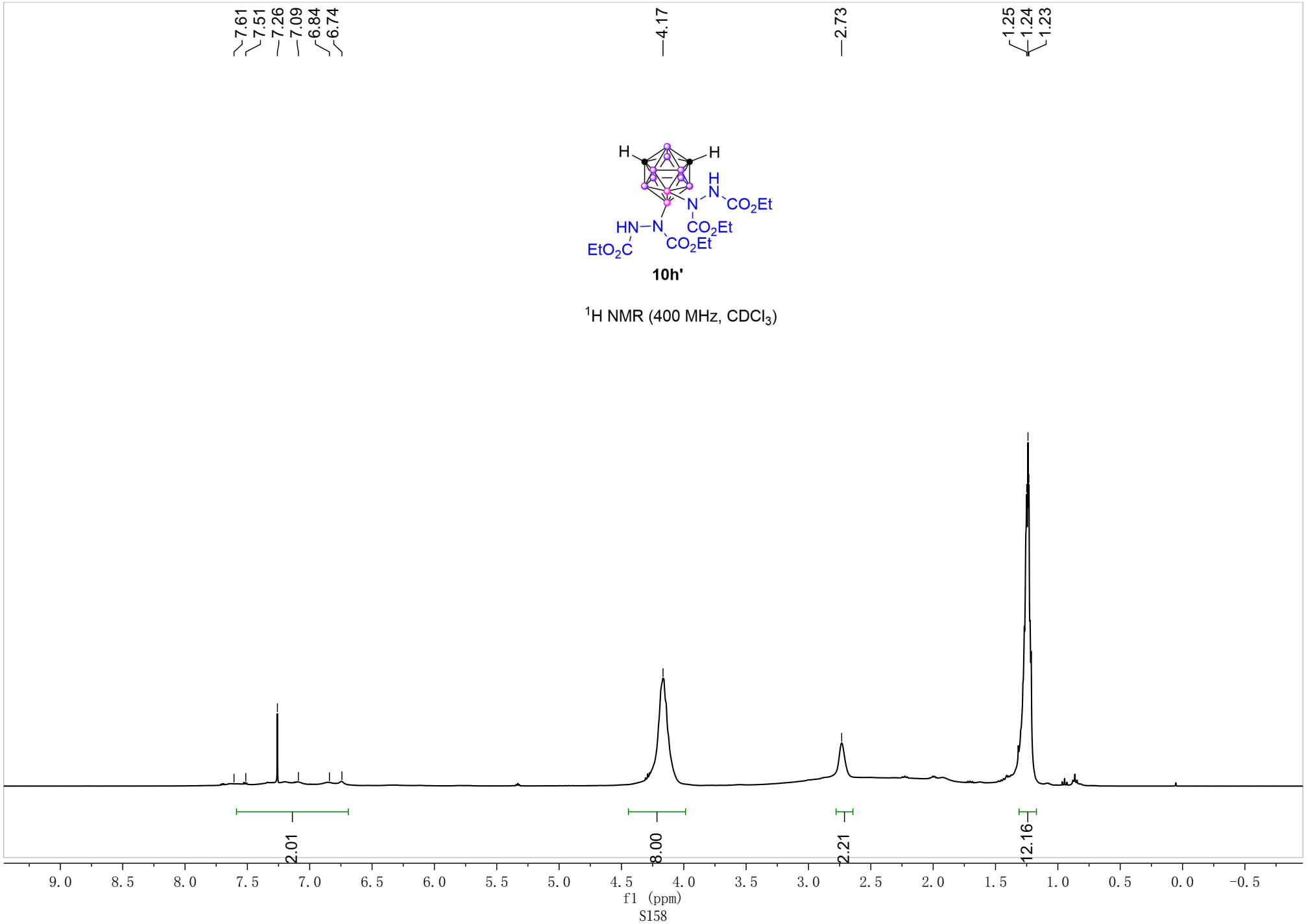

7.26
6.55
6.49
6.31
4.19
4.17
4.16
2.84
1.27
1.25
1.24
H
H
EtO2C
N
H
N
CO2Et
10h
1H NMR (400 MHz, CDCl3)
0.98
4.00
2.21
6.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

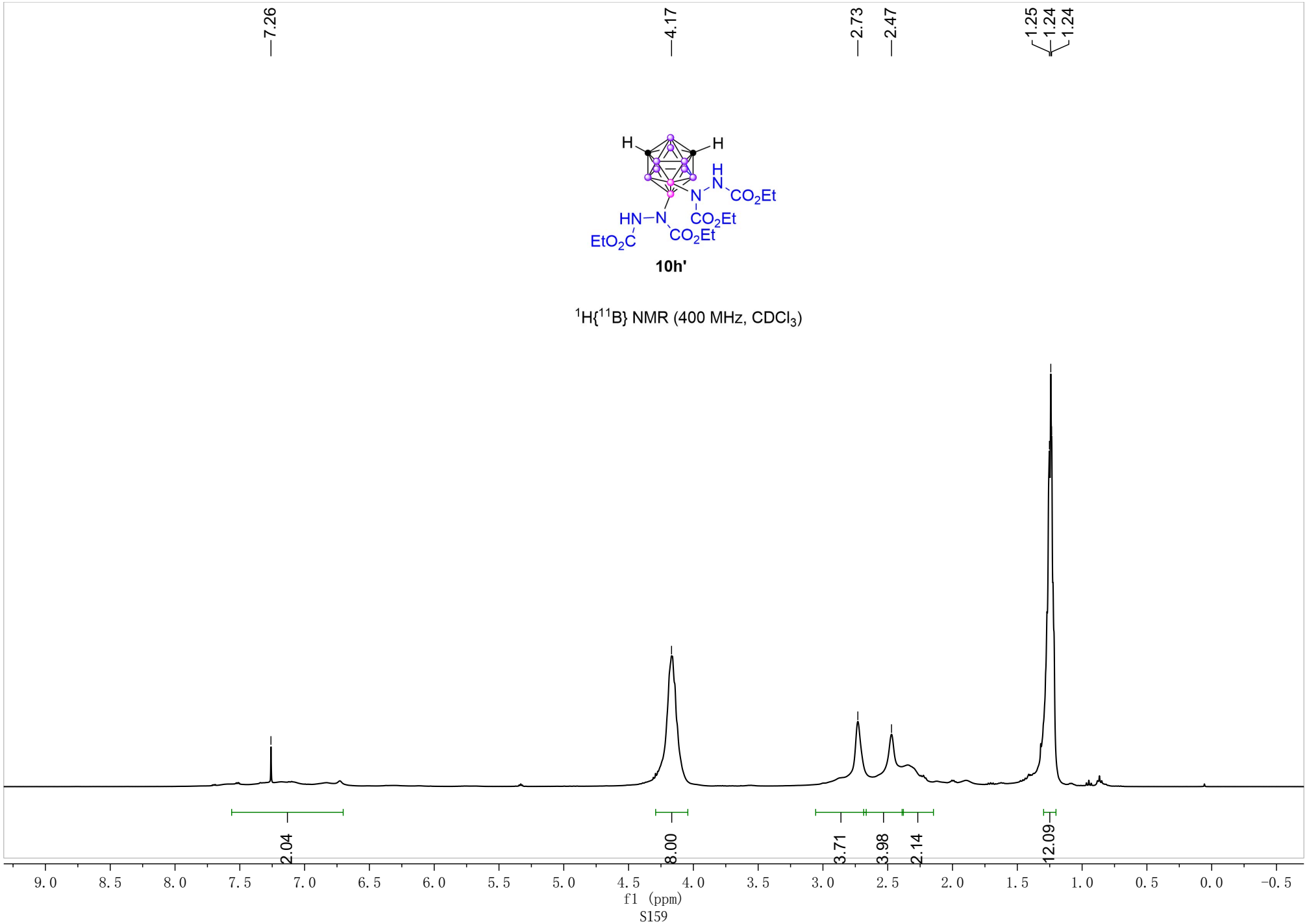

7.26
6.53
6.30
4.19
4.17
4.16
2.84
2.54
2.46
2.27
2.09
1.27
1.26
1.24
H
H
EtO2C
N
H
N
CO2Et
10h
1H{11B} NMR (400 MHz, CDCl3)
0.95
4.00
2.06
4.03
1.79
1.12
1.84
6.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

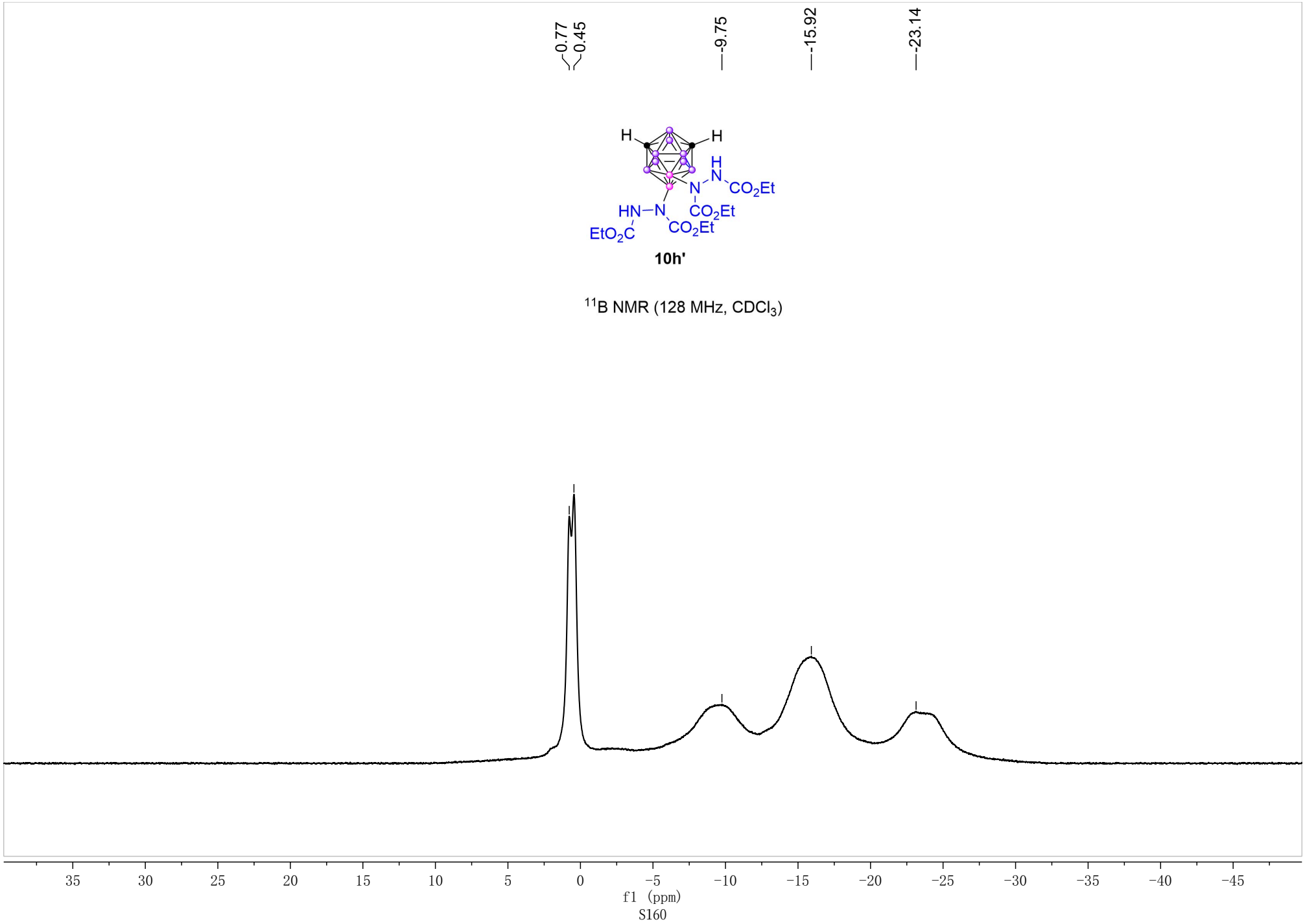

-2.20
-6.80
-8.05
-10.38
-11.57
-13.39
-14.83
-16.18
-18.31
-19.73
-21.21
-22.59
H
H
EtO2C
N
N
CO2Et
H
10h
11B NMR (128 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

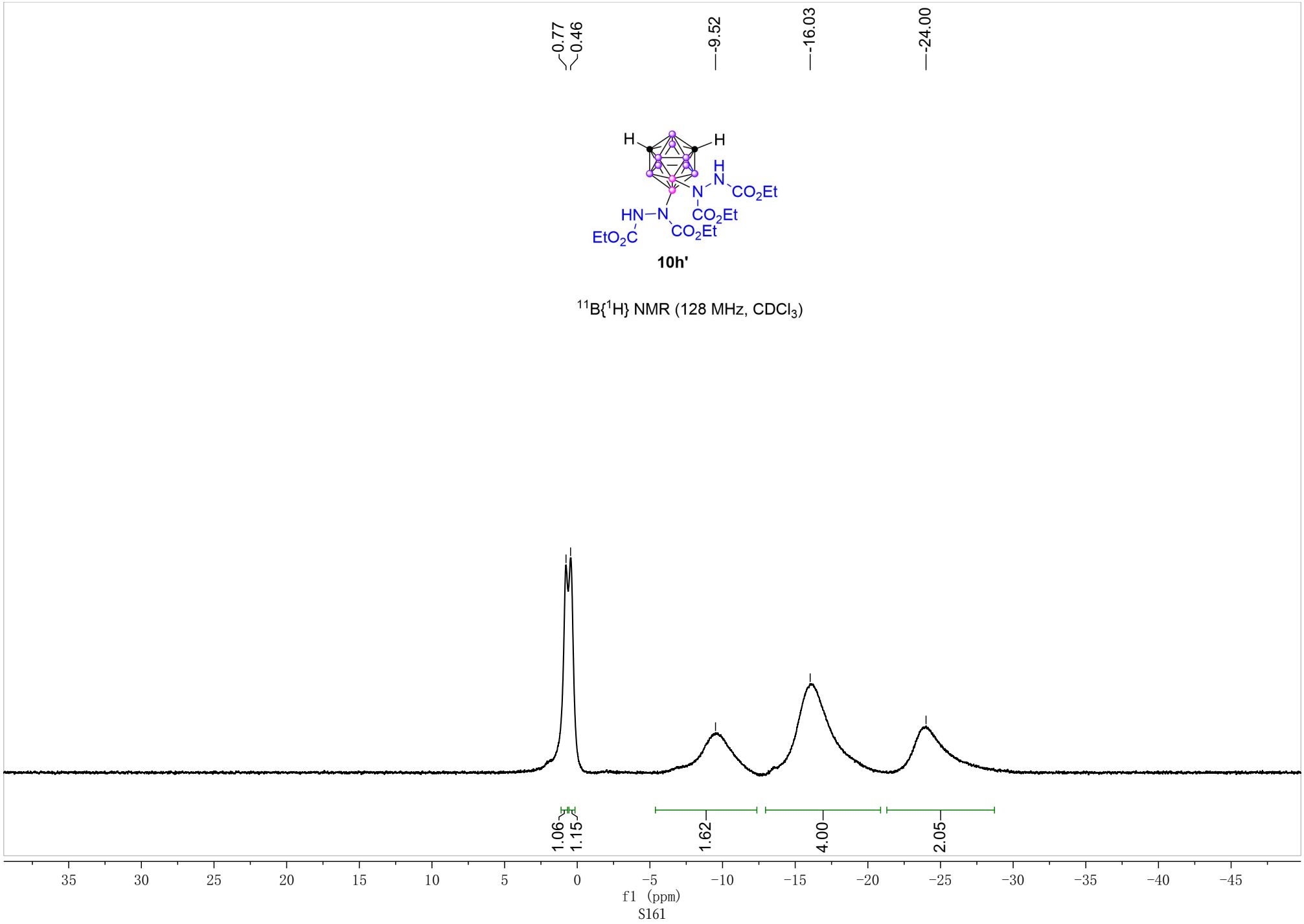

-2.22
-7.41
-11.01
-14.05
-15.55
-19.04
-21.96
H
H
EtO2C
N
H
N
CO2Et
10h
11B{1H} NMR (128 MHz, CDCl3)
1.10
2.00
1.00
1.88
2.10
1.04
1.01
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)


158.14
156.50
77.32
77.00
76.68
62.38
61.65
51.43
14.42
14.28
H
H
EtO2C
N
H
N
CO2Et
10h
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.61
7.51
7.26
7.09
6.84
6.74
4.17
2.73
1.25
1.24
1.23
H
H
H
N
N
CO2Et
HN
N
CO2Et
EtO2C
CO2Et
10h'
1H NMR (400 MHz, CDCl3)
2.01
8.00
2.21
12.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

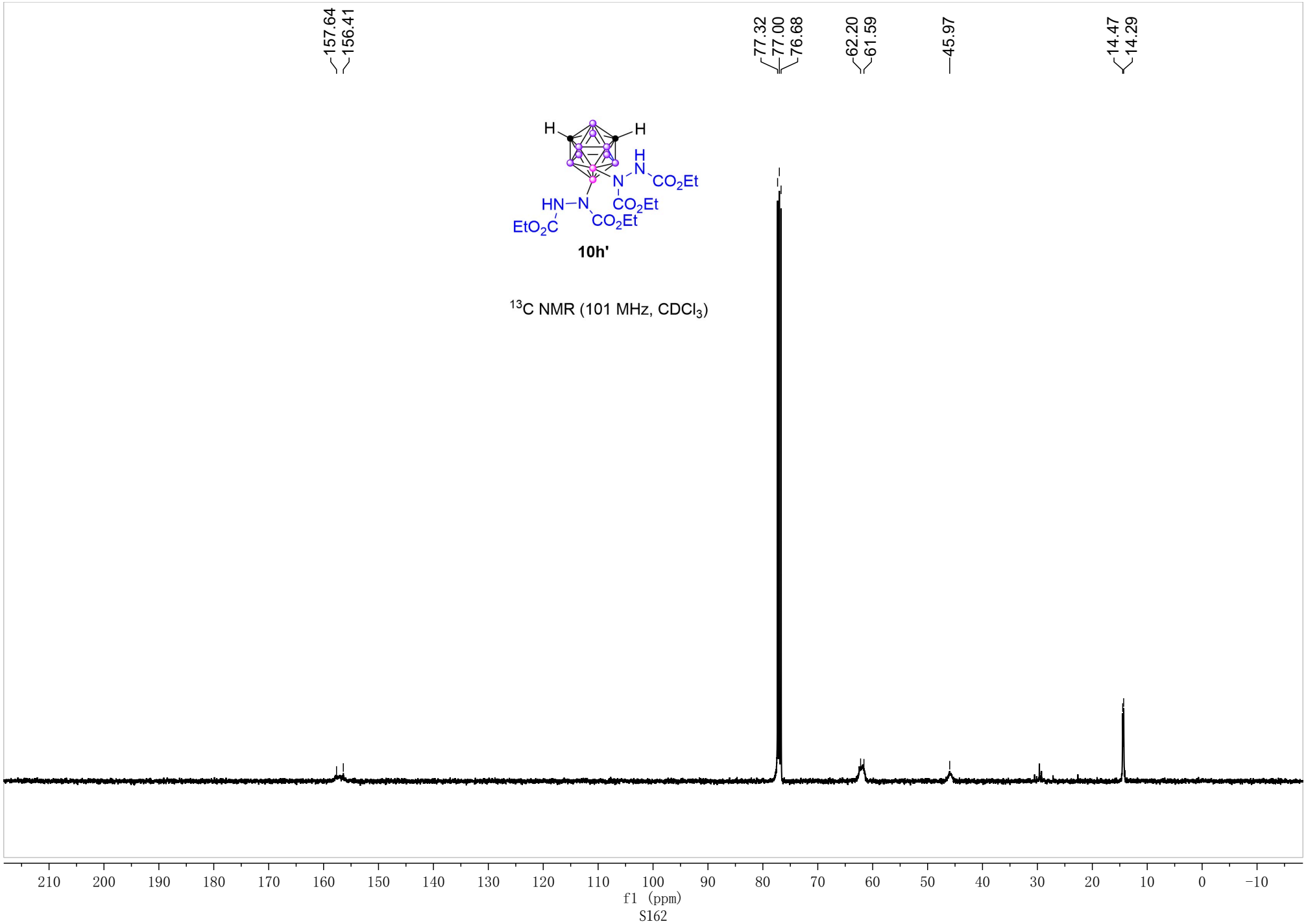

7.26
4.17
2.73
2.47
1.25
1.24
1.24
H
H
H
N
CO2Et
N
CO2Et
HN
N
CO2Et
EtO2C
CO2Et
10h'
1H{11B} NMR (400 MHz, CDCl3)
2.04
8.00
3.71
3.98
2.14
12.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

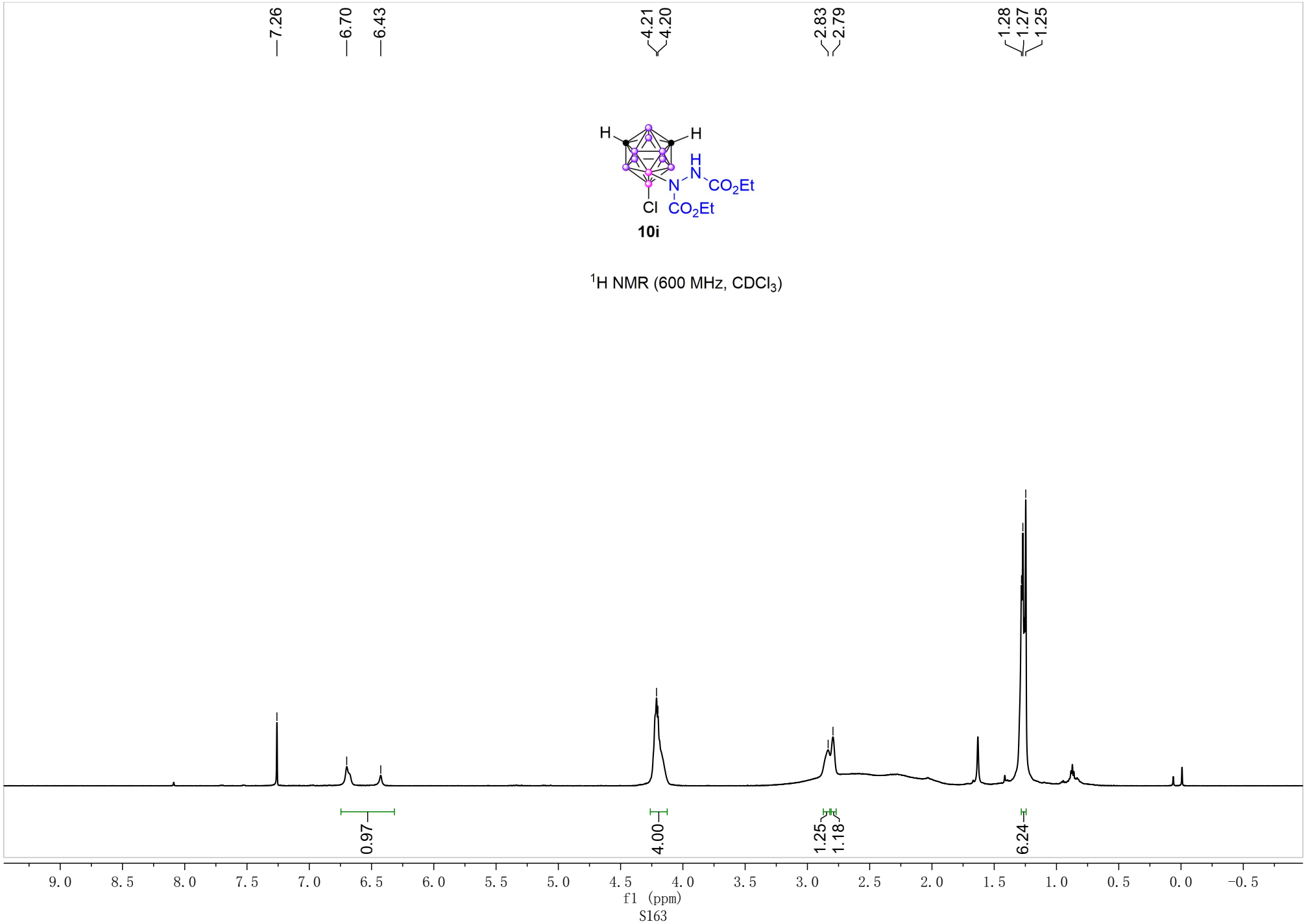

0.77
0.45
-9.75
-15.92
-23.14
H
H
H
N
N
CO2Et
HN
N
CO2Et
EtO2C
CO2Et
10h'
11B NMR (128 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

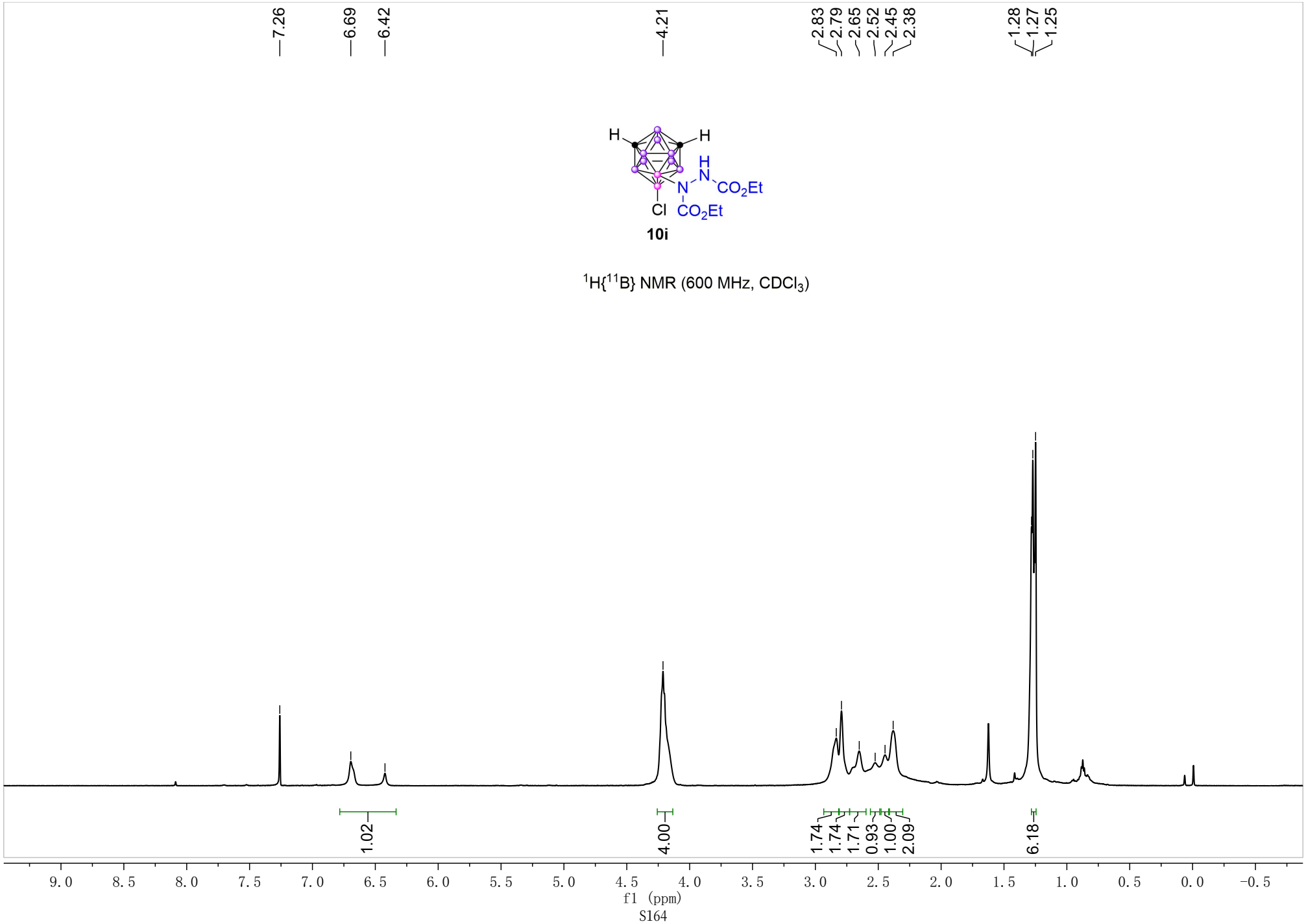


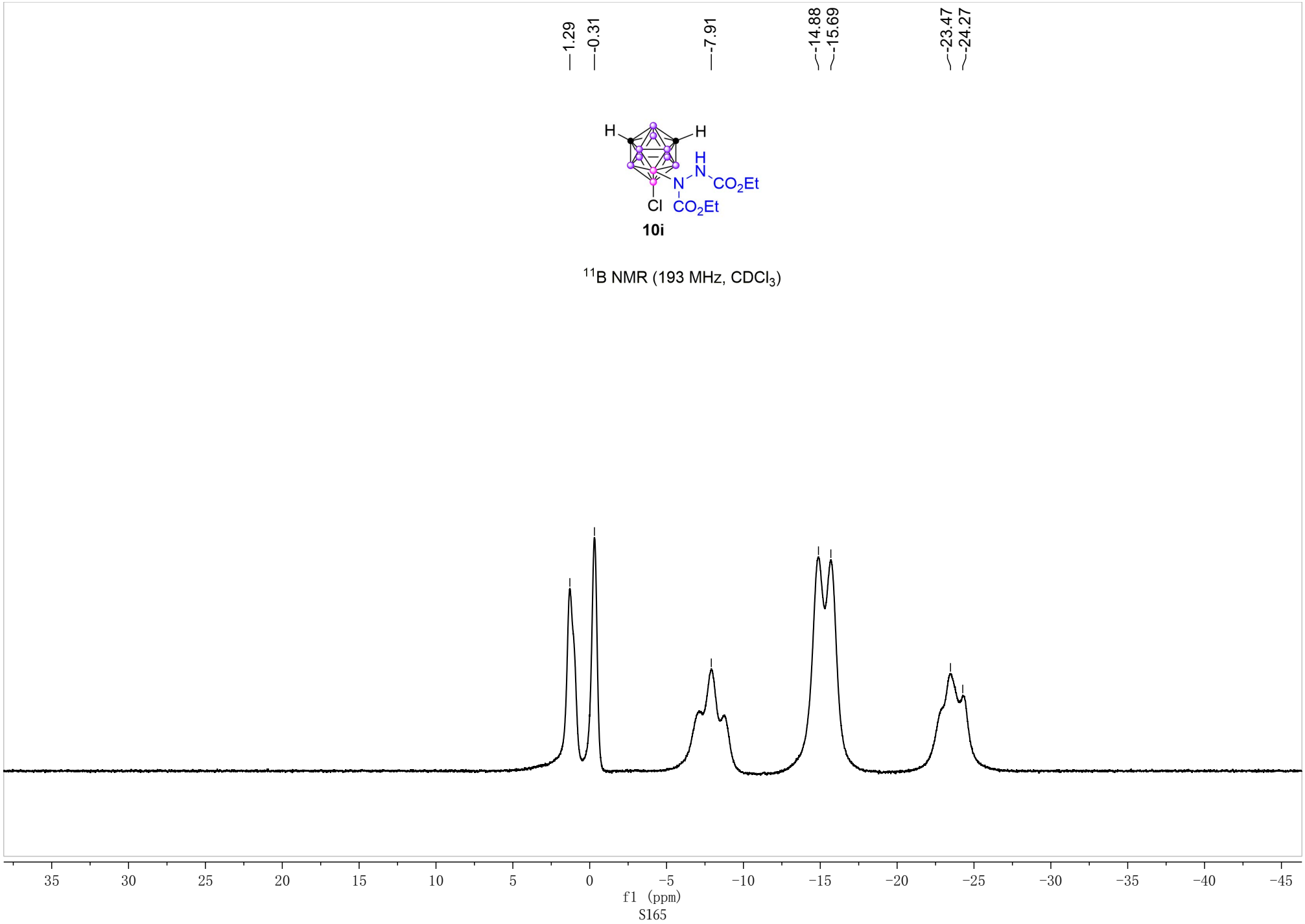
10h'

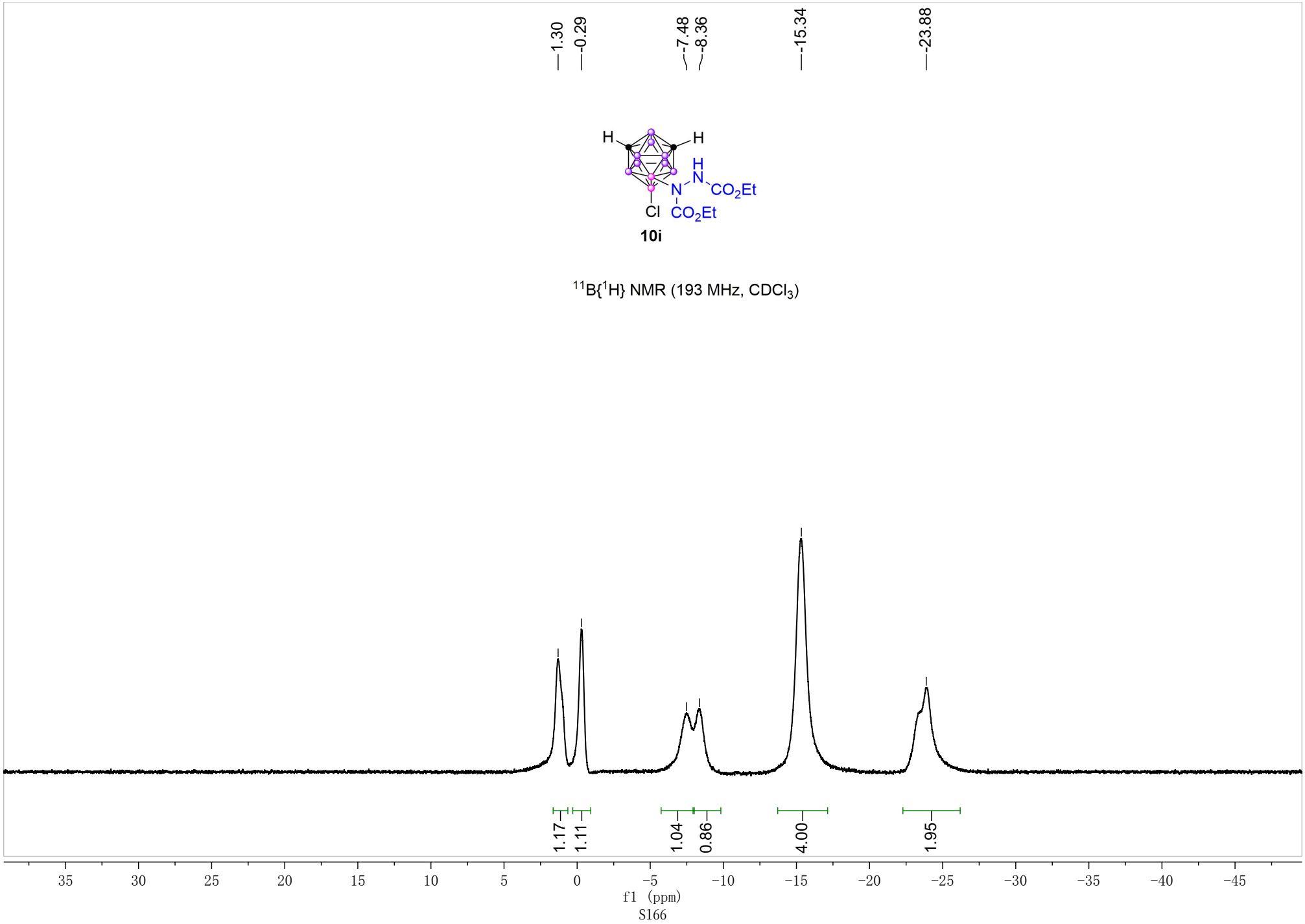
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

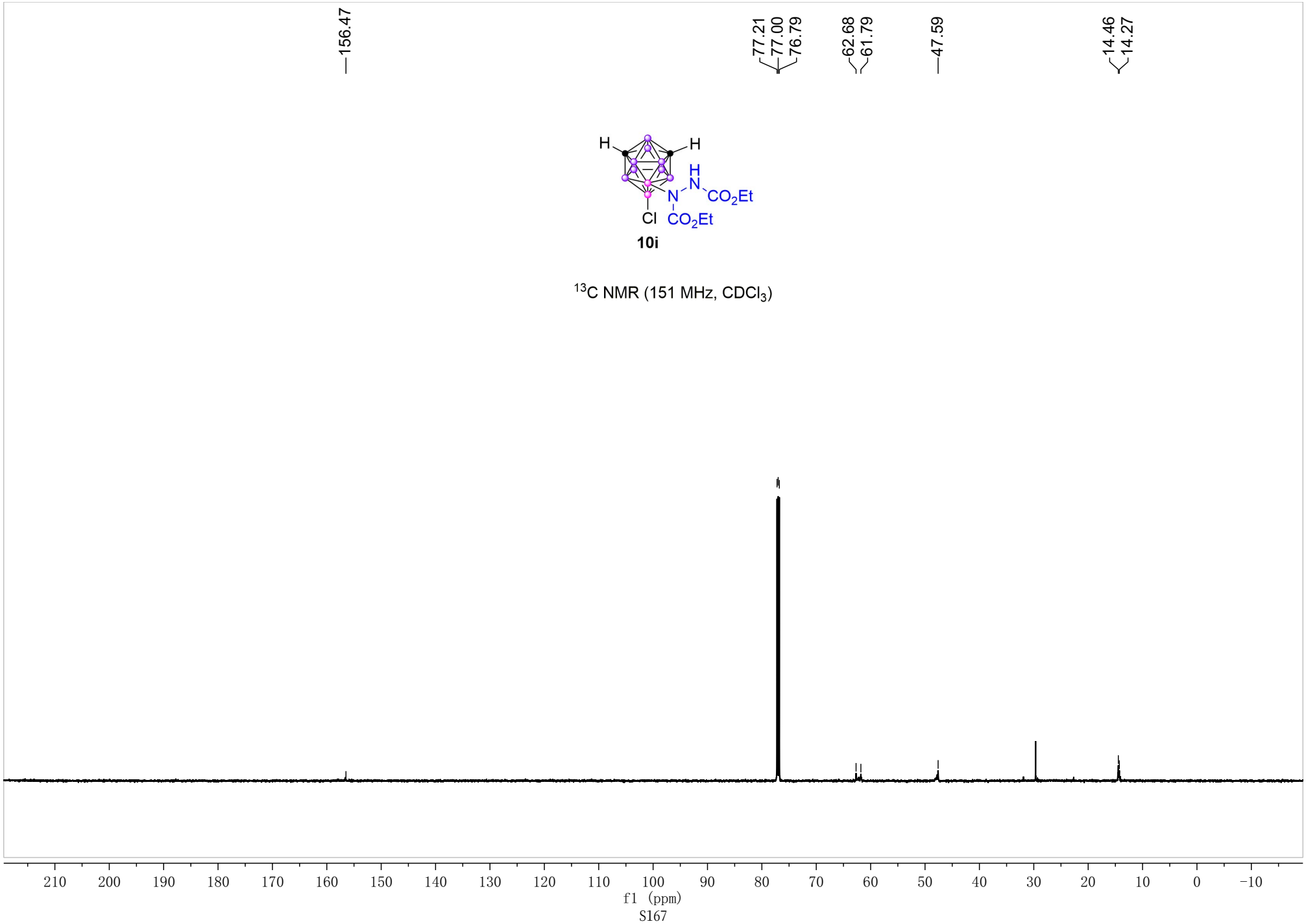

157.64
156.41
77.32
77.00
76.68
62.20
61.59
45.97
14.47
14.29
H
H
H
N
N
CO2Et
HN
N
CO2Et
EtO2C
CO2Et
10h'
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

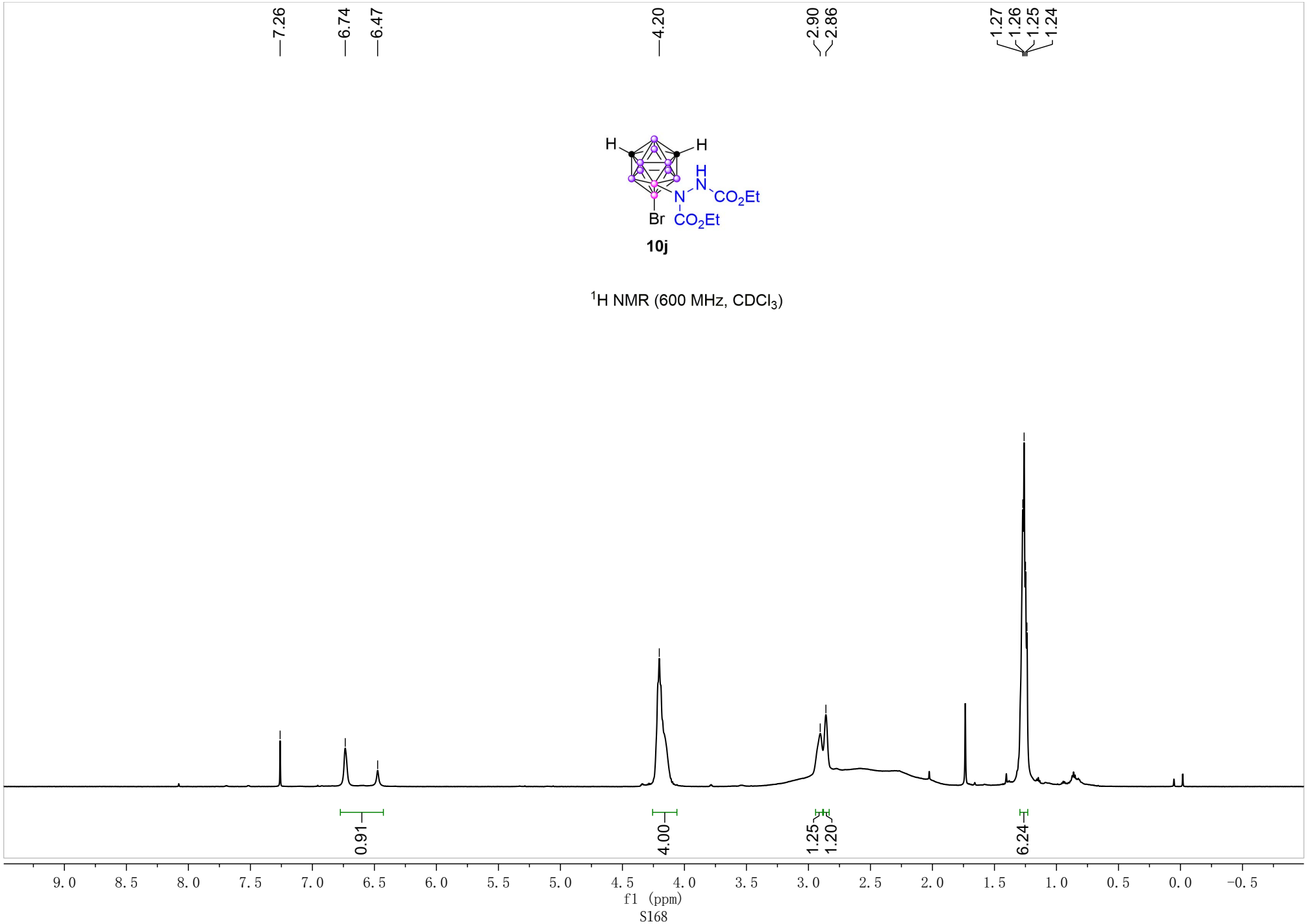

7.26
6.70
6.43
4.21
4.20
2.83
2.79
1.28
1.27
1.25
H
H
H
N
N
CO2Et
Cl
CO2Et
10i
1H NMR (600 MHz, CDCl3)
0.97
4.00
1.25
1.18
6.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

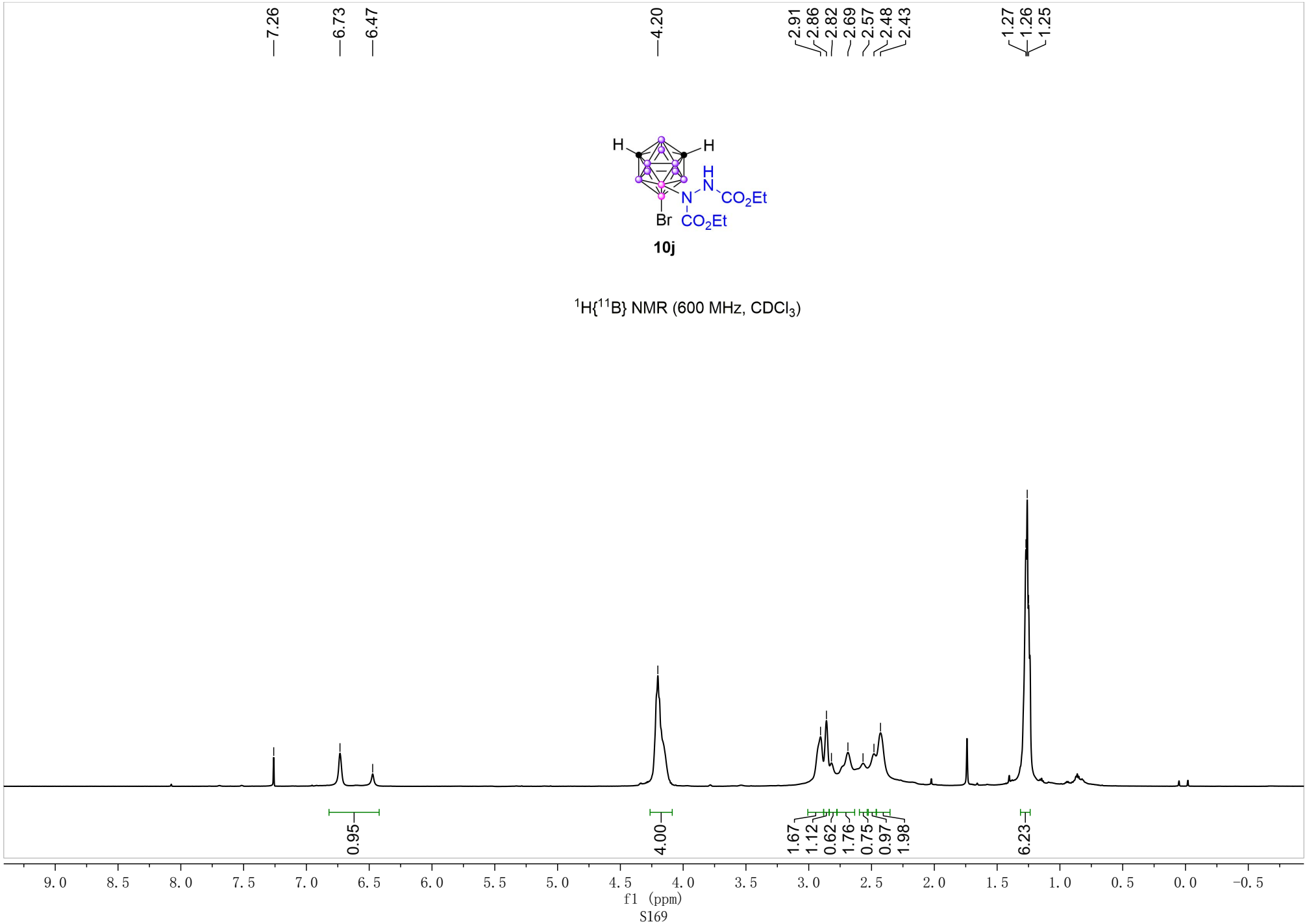

7.26
6.69
6.42
4.21
2.83
2.79
2.65
2.52
2.45
2.38
1.28
1.27
1.25
H
H
H
N
N
CO2Et
N
Cl
CO2Et
10i
1H{11B} NMR (600 MHz, CDCl3)
1.02
4.00
1.74
1.74
1.71
0.93
1.00
2.09
6.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

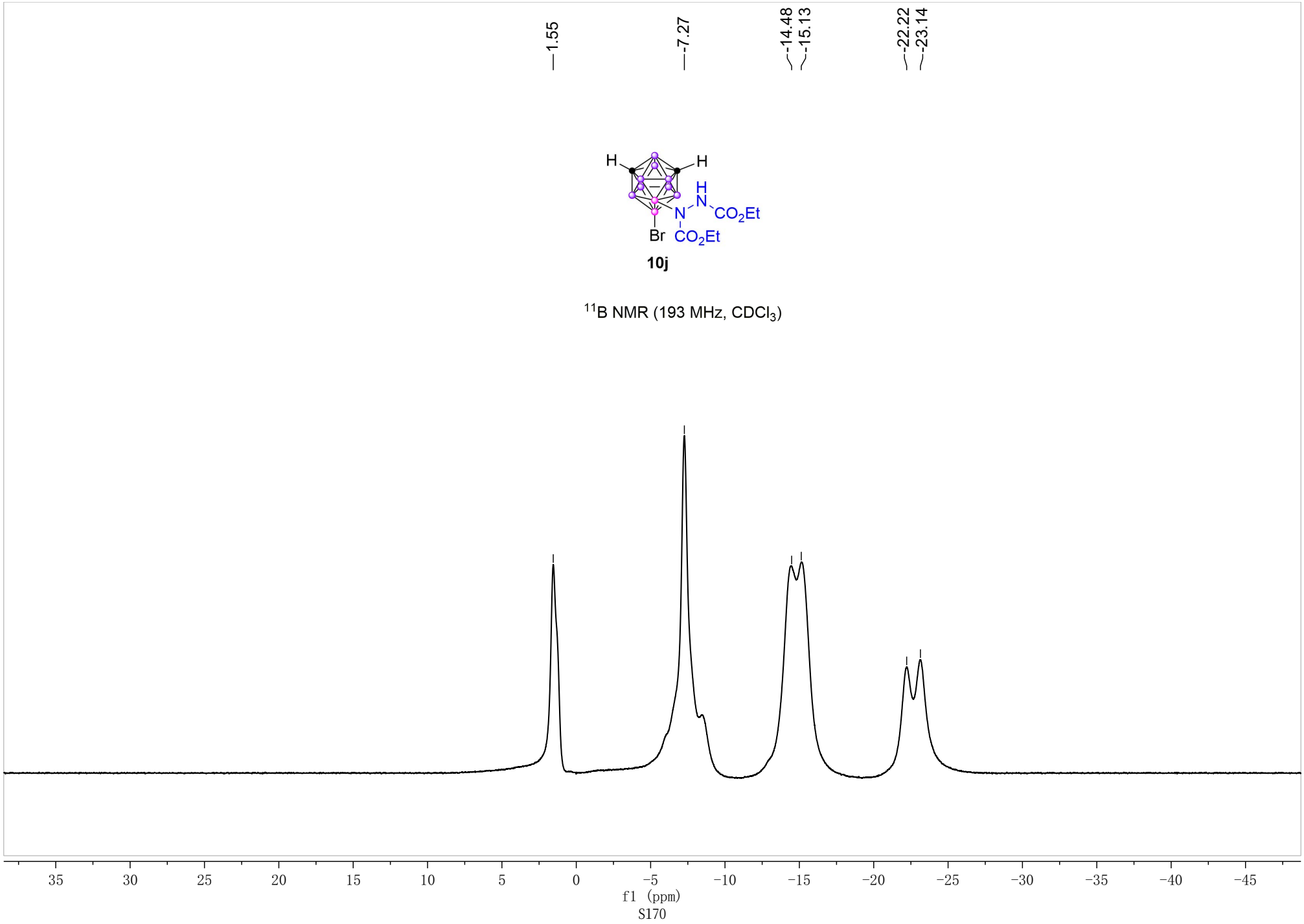

1.29
-0.31
-7.91
-14.88
-15.69
-23.47
-24.27
H
H
H
N
N
CO2Et
Cl
CO2Et
10i
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

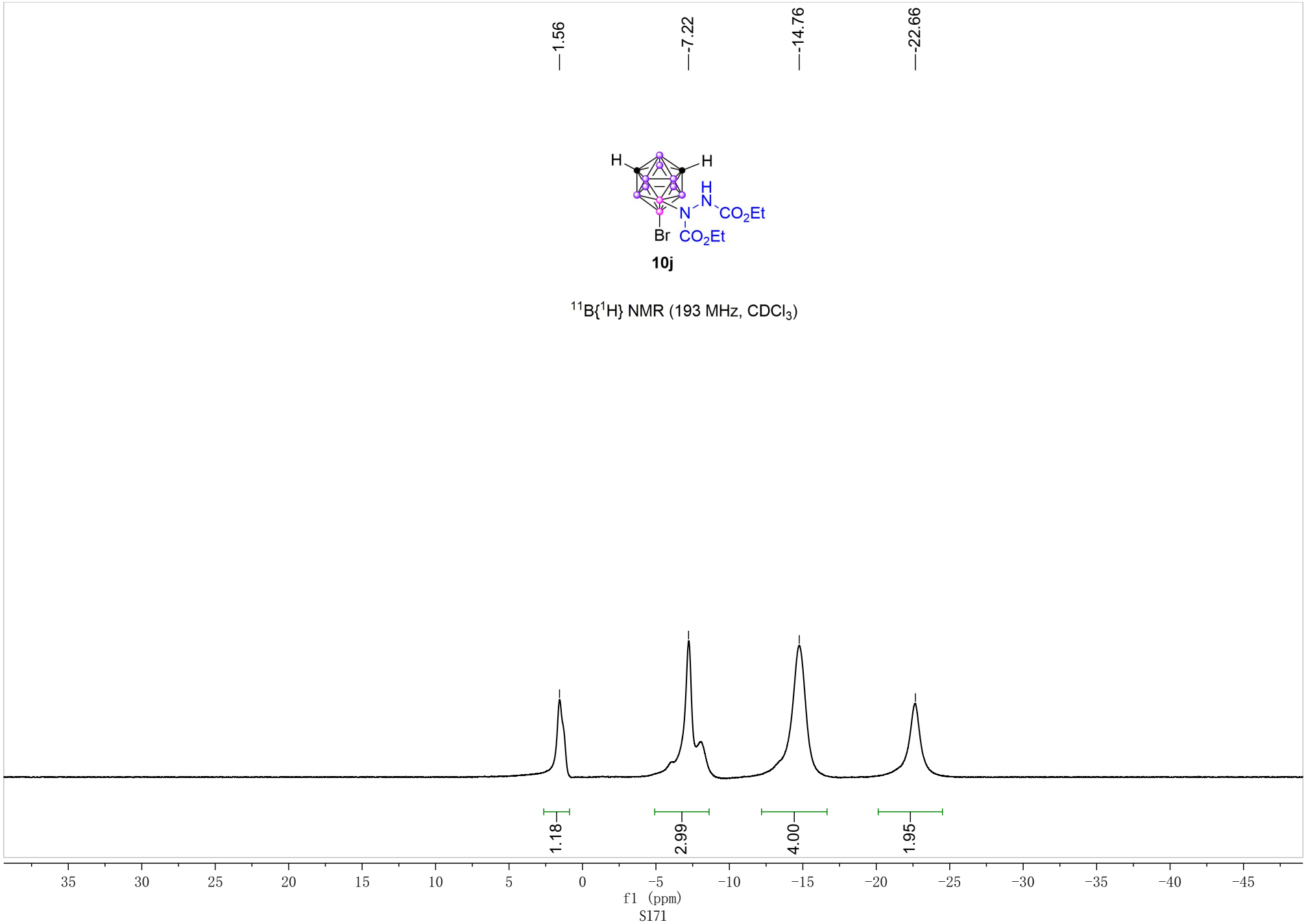

1.30
-0.29
-7.48
-8.36
-15.34
-23.88
H
H
H
N
N
CO2Et
N
Cl
CO2Et
10i
11B{1H} NMR (193 MHz, CDCl3)
1.17
1.11
1.04
0.86
4.00
1.95
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

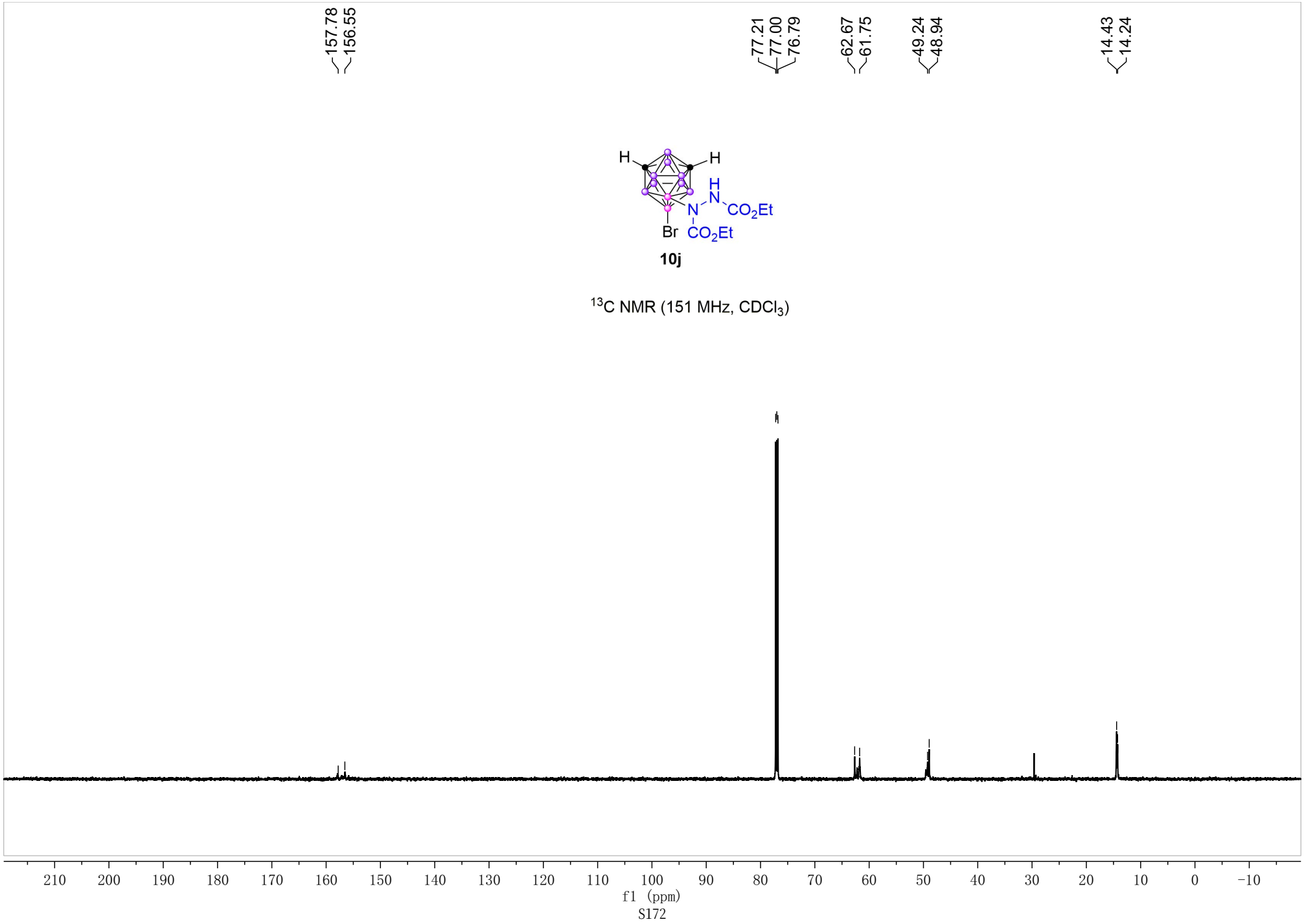

156.47
77.21
77.00
76.79
62.68
61.79
47.59
14.46
14.27
H
H
H
N
N
CO2Et
Cl
CO2Et
10i
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.26
6.74
6.47
4.20
2.90
2.86
1.27
1.26
1.25
1.24
H
H
H
N
N
CO2Et
Br
CO2Et
10j
1H NMR (600 MHz, CDCl3)
0.91
4.00
1.25
1.20
6.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


7.26
6.73
6.47
4.20
2.91
2.86
2.82
2.69
2.57
2.48
2.43
1.27
1.26
1.25
H
H
H
N
N
CO2Et
Br
N
CO2Et
10j
1H{11B} NMR (600 MHz, CDCl3)
0.95
4.00
1.67
1.12
0.62
1.76
0.75
0.97
1.98
6.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


-1.55
-7.27
-14.48
-15.13
-22.22
-23.14
H
H
H
N
N
CO2Et
Br
CO2Et
10j
11B NMR (193 MHz, CDCl3)
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)


-1.56
-7.22
-14.76
-22.66
H
H
H
N
N
CO2Et
Br
N
CO2Et
10j
11B{1H} NMR (193 MHz, CDCl3)
1.18
2.99
4.00
1.95
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)


157.78
156.55
77.21
77.00
76.79
62.67
61.75
49.24
48.94
14.43
14.24
H
H
H
N
N
CO2Et
Br
CO2Et
10j
13C NMR (151 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)