Electronic Supplementary Information

Diboration of Alkenes and Alkynes with a Carborane-fused Four-Membered Boracycle Bearing an Electron-Precise B-B Bond

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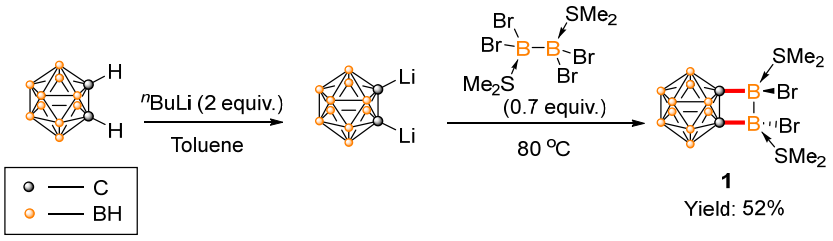
Experimental Section

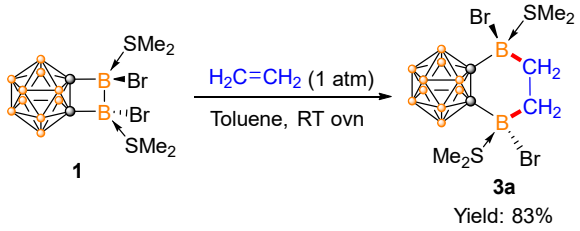
General Procedure. All operations were carried out under a dry argon atmosphere using standard Schlenk and glovebox techniques. All organic solvents were dried and distilled by standard methods prior to use. ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on Bruker DPX 400/500 spectrometer at 400/500, 100/125 and 128/160 MHz, respectively. All chemical shifts were reported in δ unit with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, q = quartet, m = multiplet, br = broad signal. Compound $B_2Br_4(SMe_2)_2$[1] was prepared according to literature procedures. All other chemicals were purchased from either Aldrich, J&K or Acros Chemical Co. and used as received unless otherwise specified.



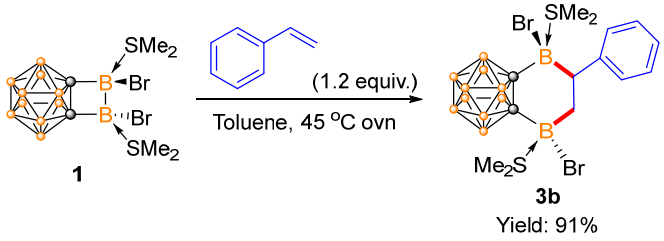
1

Yield: 52%

Preparation of 1,2-[$B_2Br_2(SMe_2)_2$]-1,2-$C_2B_{10}H_{10}$ (1). To a toluene solution (25 mL) of *o*-$C_2B_{10}H_{12}$ (691.0 mg, 4.8 mmol) was slowly added via syringe n-BuLi (1.6 M in n-hexane, 6.0 mL, 9.6 mmol) at 0 °C under stirring. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight, to which was slowly added via cannula a toluene solution (25 mL) of $B_2Br_4(SMe_2)_2$ (1582.0 mg, 3.4 mmol). The reaction mixture was heated and stirred at 80 °C overnight. The formed inorganic salts were removed by filtration, the residue was extracted with warm toluene (3×40 mL). All the toluene solutions were combined and concentrated to about 3 mL, from which compound **1** was isolated as a pale-yellow powder (777.0 mg, 52% according to $B_2Br_4(SMe_2)_2$) via filtration. X-ray quality crystals of **1** were obtained by slow evaporation from a toluene solution at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 1.35 ppm (s,12H, $S(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6): δ 21.10 ($S(CH_3)_2$), 18.67 ppm ($S(CH_3)_2$); cage C atoms were not observed. ^{11}B NMR (160 MHz, C_6D_6): δ -1.29 (d, J_{BH} = 144.1 Hz, 3B), -3.05 (s, 2B), -6.34 (d, J_{BH} = 151.4 Hz, 3B), -9.58 ppm (d, J_{BH} = 167.1 Hz, 4B). HRMS (ESI-MS): calcd for $C_2H_{10}B_{12}Br_2$ $[M+CH_3OH-H]^-$: 355.05088. Found: 355.05080. M.p.: 201.5−203.7 °C.

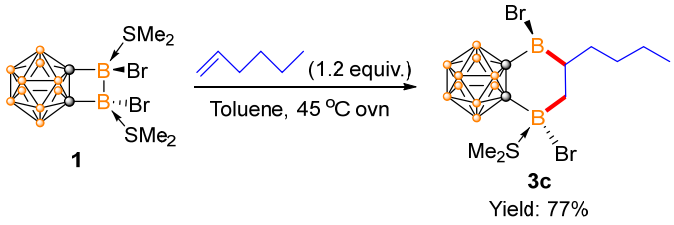


Preparation of 1,2-[$B_2Br_2C_2H_4(SMe_2)_2$]-1,2-$C_2B_{10}H_{10}$ (3a). In a 100 mL J-Young tube, a toluene solution (20 mL) of **1** (90.0 mg, 0.2 mmol) was subjected to ethylene (1 atm) at room temperature. The reaction mixture was then stirred at room temperature overnight. After filtration, the volatiles were removed in vacuo. Compound **3a** was isolated as a white powder (79.0 mg, 83%). X-ray quality crystals of **3a** were obtained by slow evaporation from a toluene solution at room temperature. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.39 (s, 12H, S(CH_3)$_2$), 0.93 ppm (s, 4H, B-CH_2). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 82.10 (cage *C*), 23.52 (S(CH_3)$_2$), 21.39 (S(CH_3)$_2$), 17.07 ppm (B-CH_2). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 4.40 (s, 2B), -2.10 (d, J_{BH} = 146.7 Hz, 2B), -5.61 (d, J_{BH} = 149.8 Hz, 2B), -9.58 (unresolved, 4B), -11.09 ppm (unresolved, 2B). HRMS (ESI-MS): calcd for $C_4H_{14}B_{12}Br_2$ [M+Cl]$^-$: 387.03280. Found: 387.03269. M.p.: 187.5−188.5 °C.

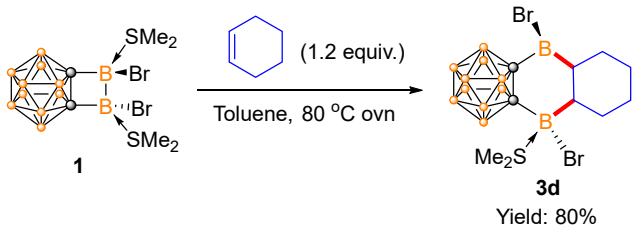


Preparation of 1,2-[$B_2Br_2C_8H_8(SMe_2)_2$]-1,2-$C_2B_{10}H_{10}$ (3b). To a toluene solution (10 mL) of **1** (45.0 mg, 0.1 mmol) was added a toluene solution (5 mL) of styrene (13.0 mg, 14 μL, 0.12 mmol) at room temperature. The reaction mixture was heated and stirred at 45 °C overnight. After removal of the precipitates, the volatiles were removed in vacuo. The residue was washed by hexane (2×2mL). Compound **3b** was isolated as a white powder (50.0 mg, 91%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.35 (brs, 2H, aromatic *H*), 7.23 (t, J = 7.9 Hz, 2H, aromatic *H*), 7.13 (m, 1H, aromatic *H*), 2.63 (d, J = 12.9 Hz, 1H, B-C*H*), 2.20 (brs, 12H, S(CH_3)$_2$), 1.60 (t, J = 13.3 Hz, 1H, B-CH_2), 0.87 ppm (d, J = 13.5 Hz, 1H, B-CH_2). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 148.82 (aromatic *C*), 129.33 (aromatic *C*), 128.42 (aromatic *C*), 126.04 (aromatic *C*), 34.04 (B-*C*H), 29.24 (B-CH_2), 22.28 ppm (S(CH_3)$_2$); cage C were not observed. ^{11}B NMR (128 MHz, CD_2Cl_2): δ 6.65 (s, 1B), 3.84 (s, 1B), -1.98 (d, J_{BH} = 148.6 Hz, 2B), -5.77 (d, J_{BH} = 148.9 Hz, 2B), -9.93 ppm (unresolved, 6B). HRMS (ESI-MS): calcd for

$C_{10}H_{18}B_{12}Br_2$ [M+Cl]$^-$: 463.06441. Found: 463.06490. M.p.: 203.5−204.9 °C.

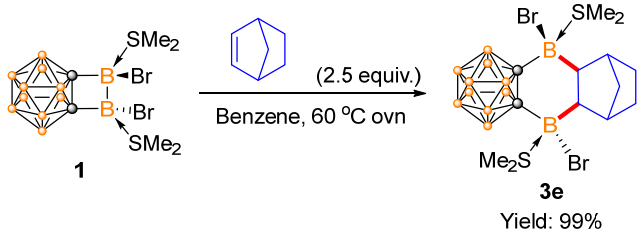


Preparation of 1,2-[$B_2Br_2C_6H_{12}(SMe_2)_2$]-1,2-$C_2B_{10}H_{10}$ (3c). To a toluene solution (10 mL) of **1** (45.0 mg, 0.1 mmol) was added a toluene solution (5 mL) of 1-hexene (10.0 mg, 15 μL, 0.12 mmol) at room temperature. The reaction mixture was heated and stirred at 45 °C overnight. After removal of the precipitates, the volatiles were removed in vacuo. The residue was washed by hexane (2×2mL). Compound **3c** was isolated as a pale yellow powder (36.0 mg, 77%). X-ray quality crystals of **3c** were obtained by slow evaporation from a toluene solution at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 1.66-1.44 (m, 10H, S(C*H*$_3$)$_2$, C*H*$_2$-CH$_2$CH$_2$CH$_3$, 2H of C*H*$_2$-C*H*$_2$-CH$_3$), 1.34 (m, 2H of C*H*$_2$-C*H*$_2$-CH$_3$) 1.08 (m, 1H, B-C*H*), 0.99 (t, J = 6.9 Hz, 3H, CH$_2$-C*H*$_3$), 0.86 ppm (m, 2H, B-C*H*$_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 83.26 (cage *C*), 81.74 (cage *C*), 35.17 ((*C*H$_2$-CH$_2$-CH$_2$-CH$_3$), 30.72 (CH$_2$-*C*H$_2$-CH$_2$-CH$_3$), 26.15 (B-*C*H), 24.25 (B-*C*H$_2$), 23.61 (CH$_2$-CH$_2$-*C*H$_2$-CH$_3$), 19.93 (S(*C*H$_3$)$_2$), 14.61 ppm (CH$_2$-*C*H$_3$). ^{11}B NMR (128 MHz, C_6D_6): δ 14.84 (s, 1B), 3.61 (s, 1B), -1.23 (m, unresolved, 2B), -5.46 (d, J_{BH} = 148.6 Hz, 2B), -9.90 ppm (br, unresolved, 6B). HRMS (ESI-MS): calcd for $C_8H_{22}B_{12}Br_2$ [M+Cl]$^-$: 443.09619. Found: 443.09547. M.p.: 150.9−152.0 °C.

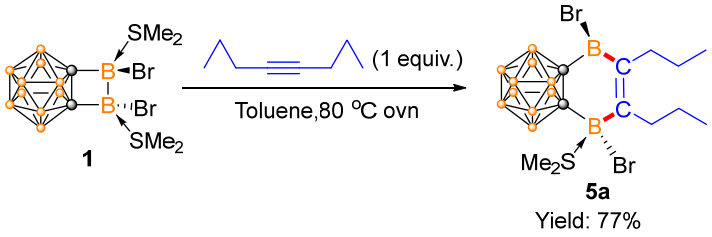


Preparation of 1,2-[$B_2Br_2C_6H_{10}(SMe_2)_2$]-1,2-$C_2B_{10}H_{10}$ (3d). To a toluene solution (10 mL) of **1** (45.0 mg, 0.1 mmol) was added a toluene solution (5 mL) of cyclohexene (10.0 mg, 12 μL, 0.12 mmol) at room temperature. The reaction mixture was heated and stirred at 80 °C overnight. After removal of the precipitates, the volatiles were removed in vacuo. The residue was washed by hexane (2×2mL). Compound **3d** was isolated as a white powder (38.0 mg, 80%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.56 (s, 3H, S(C*H*$_3$)$_2$), 2.46 (br, 1H, C*H*$_2$), 2.34 (s, 3H, S(C*H*$_3$)$_2$), 1.83(s, 1H, B-C*H*), 1.73 (m, 1H, C*H*$_2$), 1.68 (m, 1H, C*H*$_2$), 1.50 (m, 4H, 3H of C*H*$_2$, 1H of B-C*H*), 1.24 (m, 1H, C*H*$_2$), 1.17 ppm (m, 1H, C*H*$_2$). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 79.92 (cage C),

75.20 (cage C), 40.63 (B-C), 38.49 (B-C), 32.37 (CH_2), 31.42 (CH_2), 28.88 (CH_2), 25.50 (CH_2), 23.36 (S(CH_3)$_2$), 22.17 ppm (S(CH_3)$_2$). ^{11}B NMR (160 MHz, CD_2Cl_2): δ 75.85 (s, 1B), 4.37 (s, 1B), 0.48 to -0.17 (unresolved, 2B), -5.34 (unresolved, 1B), -6.57 (unresolved, 1B), -8.76 (unresolved, 5B), -11.82 ppm (d, J_{BH} = 174.1 Hz, 1B). HRMS (ESI-MS): calcd for $C_8H_{20}B_{12}Br_2$ [M+H_2O-H]$^-$: 423.11420. Found: 423.11304. M.p.: 183.1−184.2 °C.

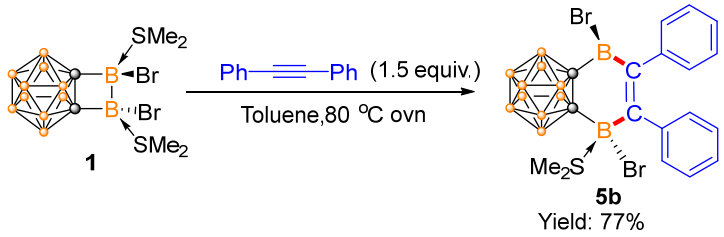


Preparation of 1,2-[$B_2Br_2C_7H_{10}(SMe_2)_2$]-1,2-$C_2B_{10}H_{10}$ (3e). To a benzene solution (10 mL) of **1** (45.0 mg, 0.1 mmol) was added a toluene solution (5 mL) of norbornene (240.0 mg, 0.25 mmol) at room temperature. The reaction mixture was heated and stirred at 60 °C overnight. After cooling down to room temperature, colorles crystals were generated immediately. The supernatant was removed with a syringe, and the volatiles in the residue were removed in vacuo. Compound **3e** was isolated as a white solid (54.0 mg, 99 %). Owing to poor solubility of **3e** in C_6D_6 or CD_2Cl_2, ^{13}C NMR spectrum was not feasible. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.58 (br, 2H), 2.35 (br, 12H, S(CH_3)$_2$), 1.62 (d, J = 7.9 Hz, 2H), 1.31 (d, J = 7.3 Hz, 2H), 1.25 ppm (d, J = 7.1 Hz, 2H). ^{11}B NMR (160 MHz, C_6D_6): δ -0.36 (d, J_{BH} = 138.4 Hz, 2B), -7.04 (d, J_{BH} = 125.2 Hz, 4B), -9.93 (unresolved, 4B), -11.72 ppm (d, J_{BH} = 163.0 Hz, 2B). HRMS (ESI-MS): calcd for $C_2H_{10}B_{12}Br_2$ [M+H_2O-H]$^-$: 435.11426. Found: 435.11382. M.p.: 202.9−204.3 °C.

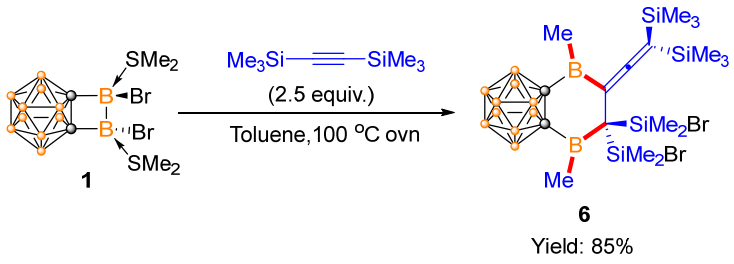


Preparation of 1,2-[$B_2Br_2C_8H_{14}(SMe_2)$]-1,2-$C_2B_{10}H_{10}$ (5a). To a toluene solution (20 mL) of **1** (90.0 mg, 0.2 mmol) was added a toluene solution (5 mL) of 4-octyne (23.0 mg, 31 μL, 0.2 mmol) at room temperature. The reaction mixture was heated and stirred at 80 °C overnight. After removal of the precipitates, the volatiles

were removed in vacuo. The residue was washed by hexane (2 × 2 mL). Compound **5a** was isolated as a yellow powder (72.0 mg, 77%). X-ray quality crystals of **5a** were obtained by recrystallization from toluene at -30 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 2.25 (m, 4H, CH_2), 1.33 (m, 4H, CH_2), 1.23 (s, 6H, S(CH_3)$_2$), 0.92 ppm (t, J = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 37.69 (*C*H$_3$), 24.44 (*C*H$_2$), 21.22 (S(*C*H$_3$)$_2$), 14.92 ppm (*C*H$_2$); cage C were not observed. ^{11}B NMR (160 MHz, C_6D_6): δ 34.39 (s, 2B), 1.05 (d, J_{BH} = 139.6 Hz, 2B), -7.76 (unresolved, 2B), -9.15 ppm (unresolved, 6B). HRMS (ESI-MS): calcd for $C_{10}H_{24}B_{12}Br_2$ [M+H$_2$O-H]$^-$: 451.14561. Found: 451.14539. M.p.: 128.9−131.4 °C.



Preparation of 1,2-[$B_2Br_2C_{14}H_{10}(SMe_2)$]-1,2-$C_2B_{10}H_{10}$ (5b). To a toluene solution (20 mL) of **1** (45.0 mg, 0.1 mmol) was added a toluene solution (5 mL) of diphenylacetylene (27.0 mg, 0.15 mmol) at room temperature. The reaction mixture was heated and stirred at 80 °C overnight. After removal of the precipitates, the volatiles were removed in vacuo. The residue was washed by hexane (2×3mL). Compound **5b** was isolated as an orange powder (43.0 mg, 77%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.82 (m, 6H, aromatic *H*), 6.74 (m, 4H, aromatic *H*), 1.15 ppm (s, 6H, S(CH_3)$_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 143.25 (aromatic *C*), 129.08 (aromatic *C*), 127.63 (aromatic *C*), 126.54 (aromatic *C*), 21.75 ppm (S(*C*H$_3$)$_2$), cage C were not observed. ^{11}B NMR (128 MHz, CD_2Cl_2): δ 28.66 (brs, 2B), -0.55 (d, J_{BH} = 149.3 Hz, 2B), -8.08 (unresolved, 2B), -10.19 ppm (unresolved, 6B). HRMS (ESI-MS): calcd for $C_{16}H_{20}B_{12}Br_2$ [M+H$_2$O-H]$^-$: 519.11463. Found: 519.11368. M.p.: 155.5−157.1 °C.



Preparation of 1,2-[$B_2C_{16}H_{36}Br_2Si_4$]-1,2-$C_2B_{10}H_{10}$ (6). To a toluene solution (20 mL) of **1** (45.0 mg, 0.1 mmol) was added a toluene solution (5 mL) of bis(trimethylsilyl)acetylene (25.0 mg, 34 μL, 0.15 mmol) at room temperature. The

reaction mixture was heated and stirred at 100 °C overnight. After removal of the precipitates, the volatiles were removed in vacuo. The residue was washed by hexane (2×3mL). Compound **6** was isolated as a pale-yellow powder (56.0 mg, 85%). X-ray quality crystals of **6** were obtained by slow evaporation from a toluene solution at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 1.24 (s, 3H, B-CH_3), 0.99 (s, 3H, B-CH_3), 0.65 (s, 6H, Si(CH_3)$_2$Br), 0.62 (s, 6H, Si(CH_3)$_2$Br), 0.13 ppm (s, 18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 207.89 (C=*C*=C), 85.34 (C=*C*(TMS)$_2$), 18.26 (B-*C*H$_3$), 12.03 (B-*C*H$_3$), 9.05 (Si(*C*H$_3$)$_2$Br), 8.27 (Si(*C*H$_3$)$_2$Br), 1.27 ppm (Si(*C*H$_3$)$_3$), cage *C* were not observed. ^{11}B NMR (160 MHz, C_6D_6): δ 73.95 (brs, 1B), 69.17 (brs, 1B), 2.32 (unresolved, 1B), 1.31 (unresolved, 1B), -6.72 (unresolved, 3B), -8.54 to -9.66 (unresolved, 4B), -12.80 ppm (unresolved, 1B). HRMS (FT-MS): calcd for $C_{18}H_{46}B_{12}Br_2Si_4$ [M]$^-$: 664.22322. Found: 664.22411. M.p.: 132.9 °C(decom.).

Proposed reaction mechanism for the formation of 6 [2]

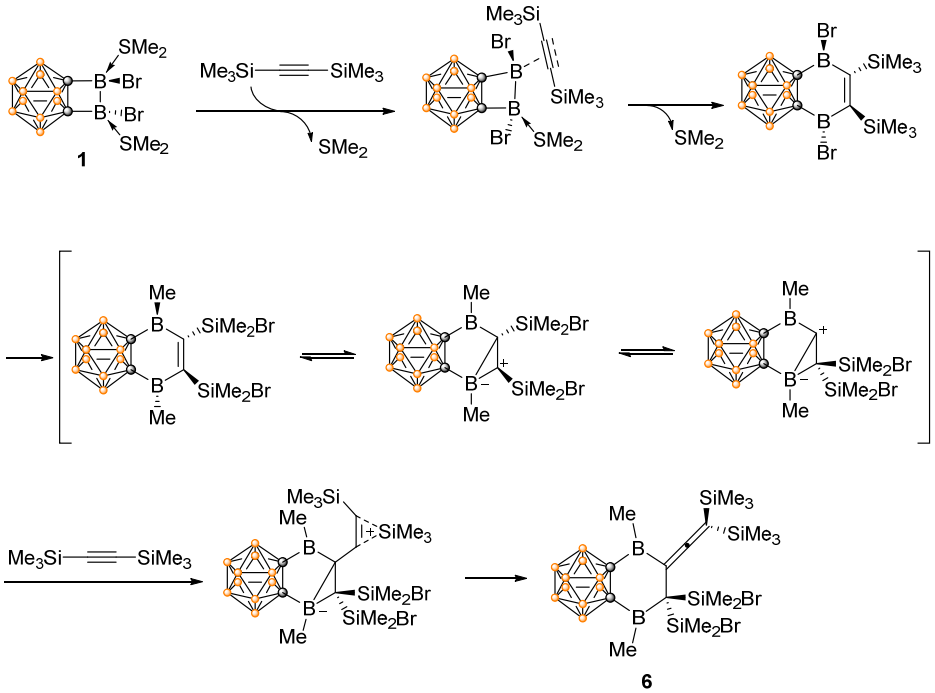


Figure S1. Proposed reaction mechanism for the formation of **6**

Crystal Data

X-ray Structure Determination. Single crystals were immersed in Paraton-N oil and sealed under argon in thin-walled glass capillaries. All data were collected at 296 K or 173 K on a Bruker Kappa ApexII Duo Diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[3] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[4] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and refinement are given in Table S1. Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC 2104196-2104201 for **1**, **3a**, **3c**, **3e**, **5a** and **6**, respectively.

Table S1. Crystal Data and Summary of Data Collection and Refinement for **1**, **3a**·0.5toluene, **3c**, **3e**, **5a** and **6**.

Compound	**1**	**3a**·0.5toluene	**3c**
Formula	$C_6H_{22}B_{12}Br_2S_2$	$C_{11.5}H_{30}B_{12}Br_2S_2$	$C_{10}H_{28}B_{12}Br_2S$
M_W	447.89	522.01	469.92
Crystal size (mm^3)	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20
Crystal system	monoclinic	triclinic	triclinic
Space Group	I2/a	P-1	P-1
a, Å	13.0965(6)	7.1932(5)	10.2053(6)
b, Å	10.4041(5)	9.4805(6)	10.4663(7)
c, Å	14.1531(6)	18.3732(12)	11.7394(7)
α, deg	90	76.724(2)	90.808(2)
β, deg	99.845(3)	86.032(2)	111.709(2)
γ, deg	90	73.8340(2)	108.033(2)
V, $Å^3$	1900.06(15)	1171.24(13)	1095.94(12)
Z	4	2	2
D_{calcd} Mg/m^3	1.566	1.480	1.424
Radiation (Å)	0.71073	0.71073	0.71073
2θ range, deg	5.030 to 55.844	5.712 to 50.496	4.566 to 50.496
μ, mm^{-1}	4.468	3.636	3.786
F(000)	880	522	468
No. of obsd reflns	2278	4236	3945
No. of params refnd	103	262	226
Goodness of fit	1.023	1.051	1.043
R1	0.0254	0.0418	0.0417
wR2	0.0625	0.1094	0.1025

Compound	**3e**	**5a**	**6**
Formula	$C_{13}H_{31}B_{12}Br_2S_2$	$C_{12}H_{30}B_{12}Br_2S$	$C_{18}H_{46}B_{12}Br_2Si_4$
M_W	541.04	495.96	664.45
Crystal size (mm^3)	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30
Crystal system	orthorhombic	monoclinic	triclinic
Space Group	Pnma	Cc	P-1
a, Å	13.4739(3)	9.8716(5)	9.2458(3)
b, Å	14.7910(3)	26.4281(15)	13.6832(5)
c, Å	11.6500(3)	9.6977(5)	14.5973(5)
α, deg	90	90	75.7550(10)
β, deg	90	114.1930(10)	85.9640(10)
γ, deg	90	90	87.7300(10)
V, $Å^3$	2321.76(9)	2307.8(2)	1785.04(11)
Z	4	4	2
D_{calcd} Mg/m^3	1.551	1.427	1.236
Radiation (Å)	0.71073	0.71073	1.54178
2θ range, deg	4.622 to 50.496	5.194 to 50.496	6.666 to 136.840
μ, mm^{-1}	3.672	3.600	4.216
F(000)	1088	992	680
No. of obsd reflns	2151	4155	6401
No. of params refnd	139	244	350
Goodness of fit	1.054	1.035	1.090
R1	0.0239	0.0273	0.0528
wR2	0.0597	0.0698	0.1429

Computational Data

Geometry optimizations were carried out with the Gaussian09 program, Revision D.01[5] at the B3LYP[6]-D3[7]/6-31++G(d,p) level of density functional theory. Frequency calculations were made to determine the characteristics of all stationary points as energy minimum or transition states and obtain thermal corrections. Intrinsic reaction coordinates (IRC)[8] were calculated to confirm that transition states lead to relevant intermediates. The solvent effect of toluene was taken into consideration by performing single-point solvation energy calculations with the conductor-like polarizable continuum model (CPCM)[9] using UAKS radii.

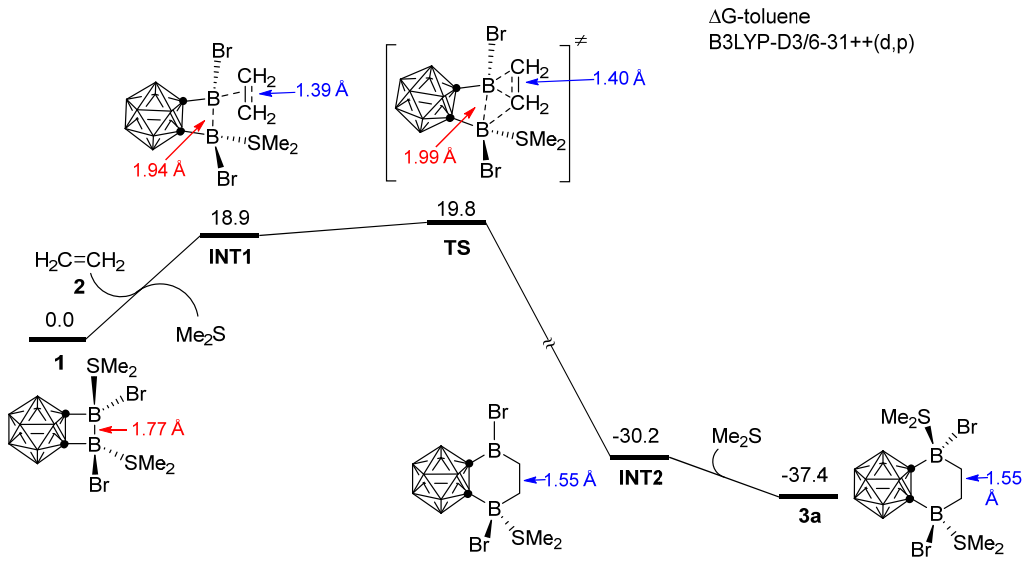


Figure S2. Energy profile calculated for the reaction of **1** with ethylene at the B3LYP-D3/6-31++g** level of theory.

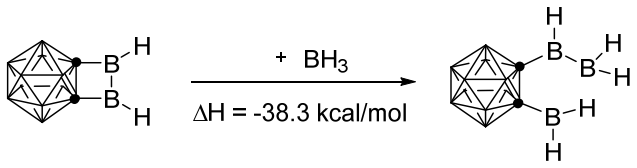


Figure S3. Calculated ring strain energy for carborane-fused diborane at the B3LYP-D3/6-31++g** level of theory.

Cartesian coordinates:

2

C	-1.04977300	0.15664400	0.00000000
H	-0.53443700	-0.80069400	0.00000000
H	-2.13649800	0.12375300	0.00000000
C	-0.38279600	1.31245100	0.00000000
H	-0.89813200	2.26978900	0.00000000
H	0.70392900	1.34534200	0.00000000

Me_2S

S	-4.27067500	6.04322200	2.92830400
C	-4.14292600	7.86377600	2.83005500
H	-3.35623800	8.17321300	3.52245400
H	-3.87043200	8.18449700	1.81983700
H	-5.08226000	8.34065800	3.12653500
C	-5.60952400	5.78881700	1.71047100
H	-5.80146200	4.71443700	1.65671400
H	-6.52735100	6.29623400	2.02311500
H	-5.31203200	6.14464500	0.71921400

1

Br	-1.46926700	6.19687900	5.03257000
S	0.32745000	6.11758800	2.31272000
C	-1.32695400	3.74416400	3.10148800
C	0.03438600	7.91113100	2.43862000
H	-0.91683500	8.09283100	1.93606000
H	-0.02578800	8.20100400	3.48863600
H	0.83726300	8.43446400	1.91701900
C	1.67491300	5.87779700	3.51792500
H	1.88970300	4.80754200	3.53592900
H	2.55156800	6.42749800	3.17006200
H	1.35369100	6.21649400	4.50452500
B	-1.35646500	2.42254400	4.18411000
H	-0.92397500	2.57016000	5.27714500
B	-0.29877700	2.42258600	2.76496300
H	0.87457900	2.57100300	2.87476800
B	-1.13324300	3.27147500	1.45128100

H	-0.58286000	4.00719400	0.71500500
B	-1.27237400	0.97761100	3.13935200
H	-0.76686200	-0.02759300	3.52125700
B	-1.12334100	1.52658800	1.44268300
H	-0.50133100	0.94514200	0.61487400
B	-1.29942600	5.38019300	3.15709700
Br	-2.51143300	6.19694300	0.16682300
S	-4.30816400	6.11760700	2.88667700
C	-2.65378900	3.74418000	2.09784900
C	-4.01514500	7.91115100	2.76069400
H	-3.06394000	8.09289200	3.26327200
H	-3.95496000	8.20098000	1.71066700
H	-4.81804800	8.43449200	3.28224800
C	-5.65569400	5.87772600	1.68156300
H	-5.87045800	4.80746500	1.66361200
H	-6.53234100	6.42741900	2.02946100
H	-5.33454100	6.21639200	0.69493100
B	-2.62429100	2.42257800	1.01520400
H	-3.05677900	2.57021600	-0.07782800
B	-3.68197800	2.42260700	2.43435100
H	-4.85533200	2.57103800	2.32454800
B	-2.84750400	3.27146400	3.74804800
H	-3.39788000	4.00717600	4.48433600
B	-2.70839600	0.97762800	2.05993800
H	-3.21391900	-0.02756500	1.67801600
B	-2.85742400	1.52657700	3.75661600
H	-3.47944000	0.94512500	4.58441500
B	-2.68129900	5.38021200	2.04227200

INT1

Br	0.98858200	2.70593600	-0.28684800
C	-1.33927200	0.68975500	0.33774900
B	-2.67130600	1.37374600	-0.49807300
H	-2.72134100	2.54770500	-0.64056900
B	-2.88286400	0.63090000	1.09517800
H	-3.07046300	1.30192300	2.05423300
B	-1.74856500	-0.72143400	1.22515200
H	-1.13261300	-0.95904500	2.20319300

B	-4.01682300	0.22960200	-0.21119600
H	-5.14254800	0.60659700	-0.18415300
B	-3.42322000	-1.06399300	0.87259000
H	-4.09570100	-1.60586900	1.68696900
B	0.16296200	1.15464400	0.77413900
Br	1.44610400	-2.13646400	1.09339100
S	1.77263500	-0.26642200	-1.53296900
C	-0.92521300	-0.77050500	-0.28873600
C	3.42621300	-0.03326600	-0.80451600
H	3.38242300	0.90156000	-0.24411100
H	3.66513400	-0.87134600	-0.14854900
H	4.14560300	0.05926000	-1.61995300
C	1.94393700	-1.91166100	-2.30661600
H	0.96147300	-2.17551900	-2.70246800
H	2.66081700	-1.82130500	-3.12520200
H	2.26562100	-2.64758200	-1.56865500
B	-2.12119300	-1.95468500	0.00666600
H	-1.78080000	-3.06971300	0.21579900
B	-1.92866300	-1.21769800	-1.59382200
H	-1.45754000	-1.83053800	-2.49471800
B	-1.42564700	0.46918800	-1.36958200
H	-0.61712100	0.99096900	-2.04656200
B	-3.55283900	-1.37082600	-0.88373300
H	-4.35337900	-2.12809000	-1.32685000
B	-3.09666000	0.13794300	-1.73744100
H	-3.53727300	0.45548600	-2.79308700
B	0.64012900	-0.58490500	0.06967200
C	0.05555500	1.81482300	2.45835000
H	0.28143600	2.87193200	2.39617800
H	-0.89409300	1.54028300	2.90337500
C	1.04240900	0.84307200	2.30514300
H	0.89586500	-0.15559700	2.69239400
H	2.07003500	1.11437900	2.08525500

TS

Br	0.98396100	2.71617800	-0.26310400
C	-1.33914200	0.69299900	0.34656500
B	-2.66854500	1.38225500	-0.48826100

H	-2.71740800	2.55696100	-0.62384600
B	-2.88406100	0.63081800	1.10120400
H	-3.07134600	1.29697900	2.06336700
B	-1.75183400	-0.72297100	1.22653000
H	-1.13672100	-0.96865400	2.20285800
B	-4.01527500	0.23749600	-0.21082500
H	-5.14092100	0.61465600	-0.18513400
B	-3.42531900	-1.06248900	0.86671800
H	-4.09997800	-1.60940900	1.67587300
B	0.14247600	1.18304200	0.80726100
Br	1.43313200	-2.17603400	1.05387700
S	1.77669400	-0.23030400	-1.51356700
C	-0.92442600	-0.76023800	-0.28556000
C	3.42634200	-0.01653600	-0.77080200
H	3.37963400	0.90378800	-0.18728000
H	3.66259200	-0.87174200	-0.13632400
H	4.14929400	0.09724400	-1.58034300
C	1.95078300	-1.85538000	-2.32925800
H	0.96680900	-2.11362200	-2.72508100
H	2.66124700	-1.73933600	-3.15021900
H	2.28129600	-2.60881000	-1.61335300
B	-2.12133300	-1.94786400	-0.00077600
H	-1.78001000	-3.06366200	0.20207400
B	-1.92413100	-1.20242700	-1.59677900
H	-1.45009700	-1.81097700	-2.49906100
B	-1.42175400	0.48304500	-1.36282300
H	-0.61078500	1.00740200	-2.03494000
B	-3.55015700	-1.35923900	-0.89163400
H	-4.34913400	-2.11443000	-1.34106800
B	-3.09167500	0.15386900	-1.73576800
H	-3.52957600	0.47744700	-2.79069300
B	0.63978400	-0.59836300	0.07267200
C	0.09207200	1.77564400	2.46244600
H	0.35593600	2.82604100	2.45905100
H	-0.84503200	1.50819400	2.93826800
C	1.06255200	0.77842900	2.27743200
H	0.90441200	-0.21798700	2.66447400
H	2.09443500	1.03434000	2.05885600

INT2

Br	-1.28175200	3.74619900	1.21731400
C	-1.56421100	0.89087900	0.39404500
B	-2.78752400	1.26294800	-0.75634600
H	-2.90087400	2.39430300	-1.07901100
B	-3.20197300	0.74395600	0.88422800
H	-3.59354500	1.53054300	1.67601200
B	-1.96107100	-0.43111500	1.42321500
H	-1.52724300	-0.43493700	2.52068300
B	-4.04756300	0.03838700	-0.51280400
H	-5.18702700	0.29243600	-0.72594200
B	-3.53703400	-0.99724300	0.85763500
H	-4.29548600	-1.48991300	1.62645900
B	-0.61921400	1.94978900	1.06727300
Br	1.22785900	-2.72673400	0.72965800
S	1.89481000	-0.06007200	-1.06701500
C	-0.86947800	-0.62236600	0.09190200
C	3.57863100	-0.46602900	-0.49808800
H	3.82451500	0.21229400	0.31916500
H	3.61466400	-1.50186800	-0.15608900
H	4.26435700	-0.29406400	-1.32976600
C	1.73834600	-1.22461900	-2.45951800
H	0.79742500	-1.00618800	-2.96222700
H	2.57399400	-1.04912000	-3.13965300
H	1.73969500	-2.24890700	-2.08186900
B	-2.05255200	-1.84979800	0.36382400
H	-1.69028200	-2.89021400	0.78264600
B	-1.62053400	-1.32363000	-1.26842600
H	-0.96049400	-2.02198600	-1.95840300
B	-1.29406900	0.42388300	-1.22659900
H	-0.43024000	0.95970200	-1.83016800
B	-3.33129900	-1.55927100	-0.83266600
H	-3.95117000	-2.46632000	-1.28237000
B	-2.84898800	-0.15254500	-1.82929900
H	-3.11286900	-0.04213800	-2.98247200
B	0.70918400	-0.77922000	0.49729700
C	0.81425200	1.62057700	1.59670600

H	1.48952000	2.11195300	0.87372700
H	0.99079000	2.16817300	2.53132400
C	1.16989900	0.12307700	1.73886300
H	0.66474000	-0.28758000	2.61986100
H	2.23792500	-0.00047500	1.94988600

3a

Br	5.08688800	10.83836200	10.79440700
Br	5.55026200	11.81354200	16.88346300
S	8.12929400	10.58270100	12.00754400
S	2.53908500	11.11403600	15.76763800
C	5.80412900	9.36280700	13.40086600
C	4.91671900	9.58368700	14.85666300
C	6.02350400	12.08447200	13.36506100
H	6.79972700	12.16982600	14.13909500
H	6.14808600	12.93610500	12.68687600
C	4.63731400	12.17918200	14.04426800
H	3.86272300	12.01360000	13.28163200
H	4.49720900	13.19495900	14.43055200
C	8.21308800	9.45803800	10.57207700
H	8.02523800	8.44757200	10.93219700
H	7.44987200	9.74700400	9.84810300
H	9.21767700	9.52496600	10.14980400
C	8.38464300	12.17411000	11.15521800
H	8.39569100	12.95587400	11.91491200
H	9.35258000	12.13738700	10.65202600
H	7.57317000	12.34347900	10.44421800
C	2.22174600	12.88679300	16.05195000
H	2.20161600	13.37829800	15.07912200
H	1.24596100	12.98356500	16.53165400
H	3.01380800	13.30611300	16.67620900
C	2.44662100	10.51360400	17.48877100
H	2.71266500	9.45754600	17.48330700
H	3.15365600	11.07451700	18.10142700
H	1.41942200	10.64108700	17.83588300
B	4.15707300	8.89333400	13.46807700
H	3.35448000	9.53997000	12.89646300
B	5.38378500	7.87433100	12.67400700

H	5.40188000	7.83103100	11.49179500
B	6.87642700	8.04322100	13.60225400
H	7.93767200	8.09320000	13.07956200
B	6.57648400	9.16957800	14.93461600
H	7.35553700	9.98766200	15.27074700
B	3.88718000	8.23447200	15.08805800
H	2.82407600	8.41551100	15.57695400
B	4.16624300	7.13406200	13.73139300
H	3.28914100	6.46500800	13.29415400
B	5.86955300	6.60520400	13.82384700
H	6.22817100	5.54103200	13.43447300
B	6.62436700	7.41610700	15.23636000
H	7.52006300	6.94640400	15.85703300
B	5.37889900	8.41151500	16.01375500
H	5.35499100	8.73841600	17.15061400
B	4.93979700	6.83040700	15.32278300
H	4.61322100	5.93189400	16.02884800
B	6.16045500	10.71135400	12.55418800
B	4.51531100	11.11925700	15.23757600

BH_3

B	0.00000000	0.00000000	0.00000000
H	0.00000000	1.19332400	0.00000000
H	1.03344900	-0.59666200	0.00000000
H	-1.03344900	-0.59666200	0.00000000

1-(BH_2BH)-2-BH_2-1,2-$C_2B_{10}H_{10}$

B	-0.86344100	1.40710400	0.88599700
B	-2.23345300	0.69960900	0.00127700
B	-0.55233000	-1.47330300	0.88310100
B	-2.04356400	-1.06613300	0.00054200
B	-0.55345900	-1.47271300	-0.88415700
B	0.19448300	0.05913500	-1.43921600
B	-1.56778200	-0.12440300	1.45731100
B	0.19620800	0.05821800	1.43800800
H	-0.80570800	2.42646300	1.48551600
H	-3.29456200	1.23001500	0.00203500

H	-0.28896500	-2.45806800	1.48438300
H	-2.96895300	-1.80854900	0.00096500
H	-0.29109800	-2.45724700	-1.48623300
H	0.95792300	0.14636700	-2.33871300
H	-2.14424200	-0.18628400	2.49188900
H	0.96066800	0.14494100	2.33663700
B	-0.86445700	1.40758500	-0.88471600
H	-0.80766800	2.42722100	-1.48386500
B	-1.56970300	-0.12341600	-1.45617800
H	-2.14777200	-0.18449300	-2.48990300
C	0.71032400	-0.73941000	-0.00140200
C	0.51949100	0.94296200	-0.00042000
B	2.18192600	-1.28641600	-0.00037700
H	2.27244900	-2.47823200	0.00010300
B	1.79908300	1.80854500	-0.00042600
H	1.74767900	2.99296500	0.00095300
H	2.89746300	1.30603500	-0.00214400
B	3.53358900	-0.32371400	0.00039400
H	4.12334400	-0.08584300	1.01746000
H	4.12505500	-0.08709200	-1.01594600

NMR Spectra

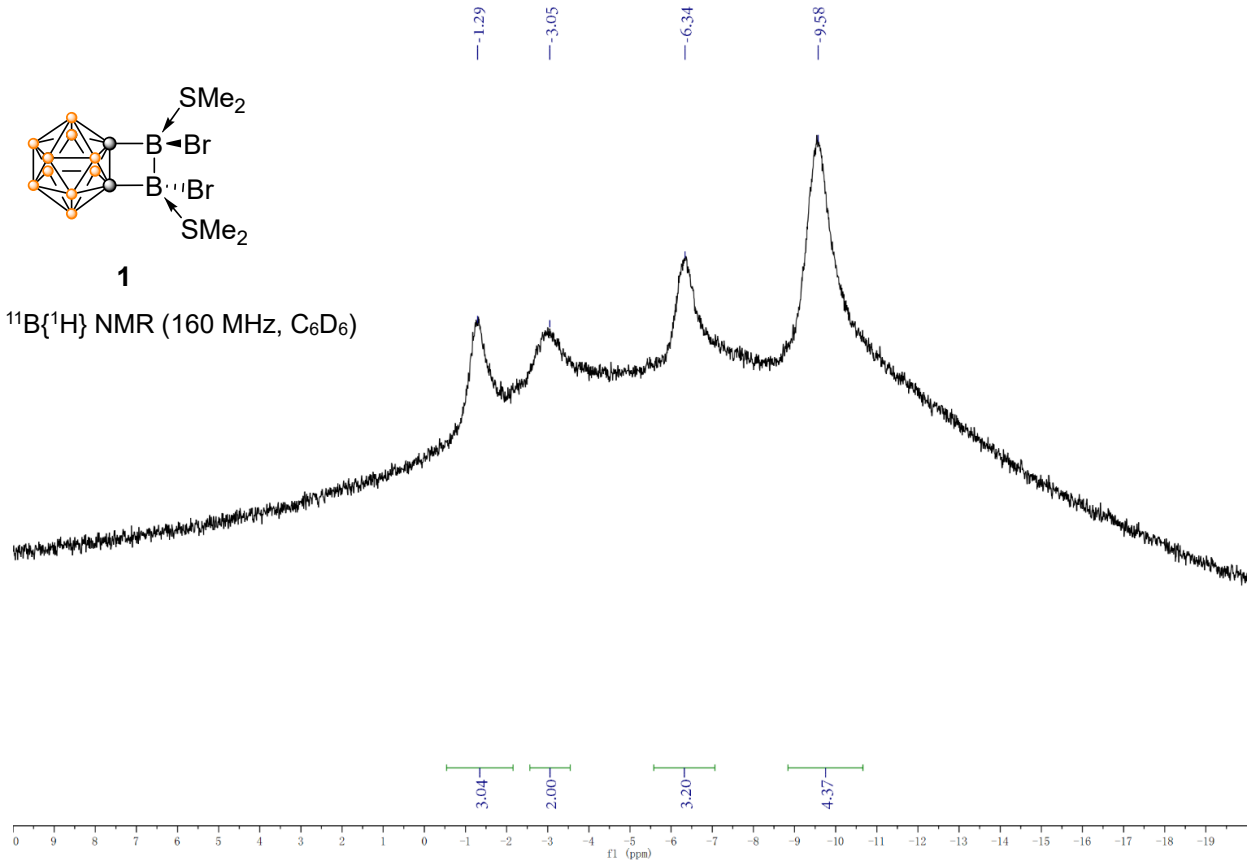


Figure S4. $^{11}B\{^{1}H\}$ NMR spectrum of compound **1.**

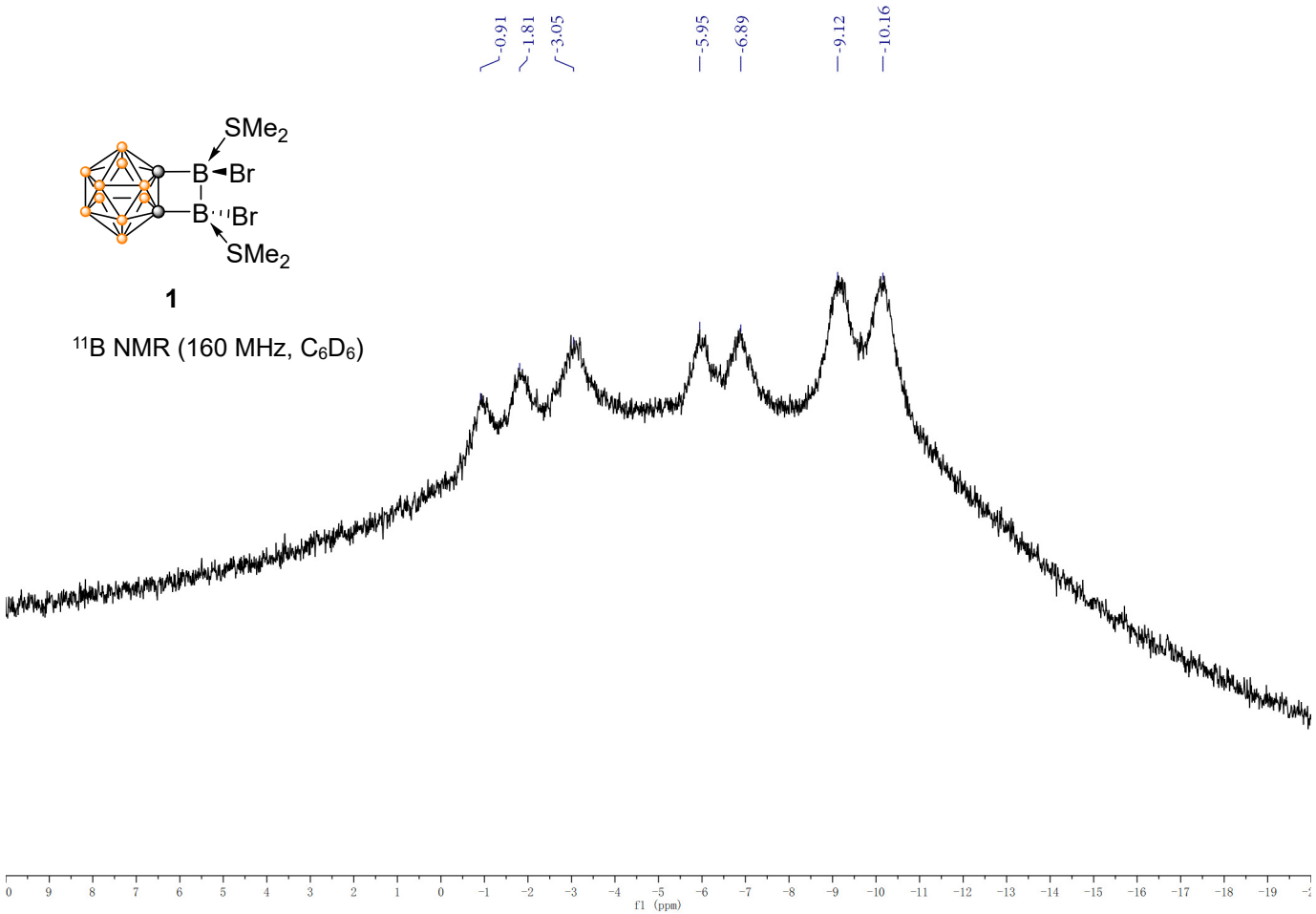


Figure S5. ^{11}B NMR spectrum of compound **1**.

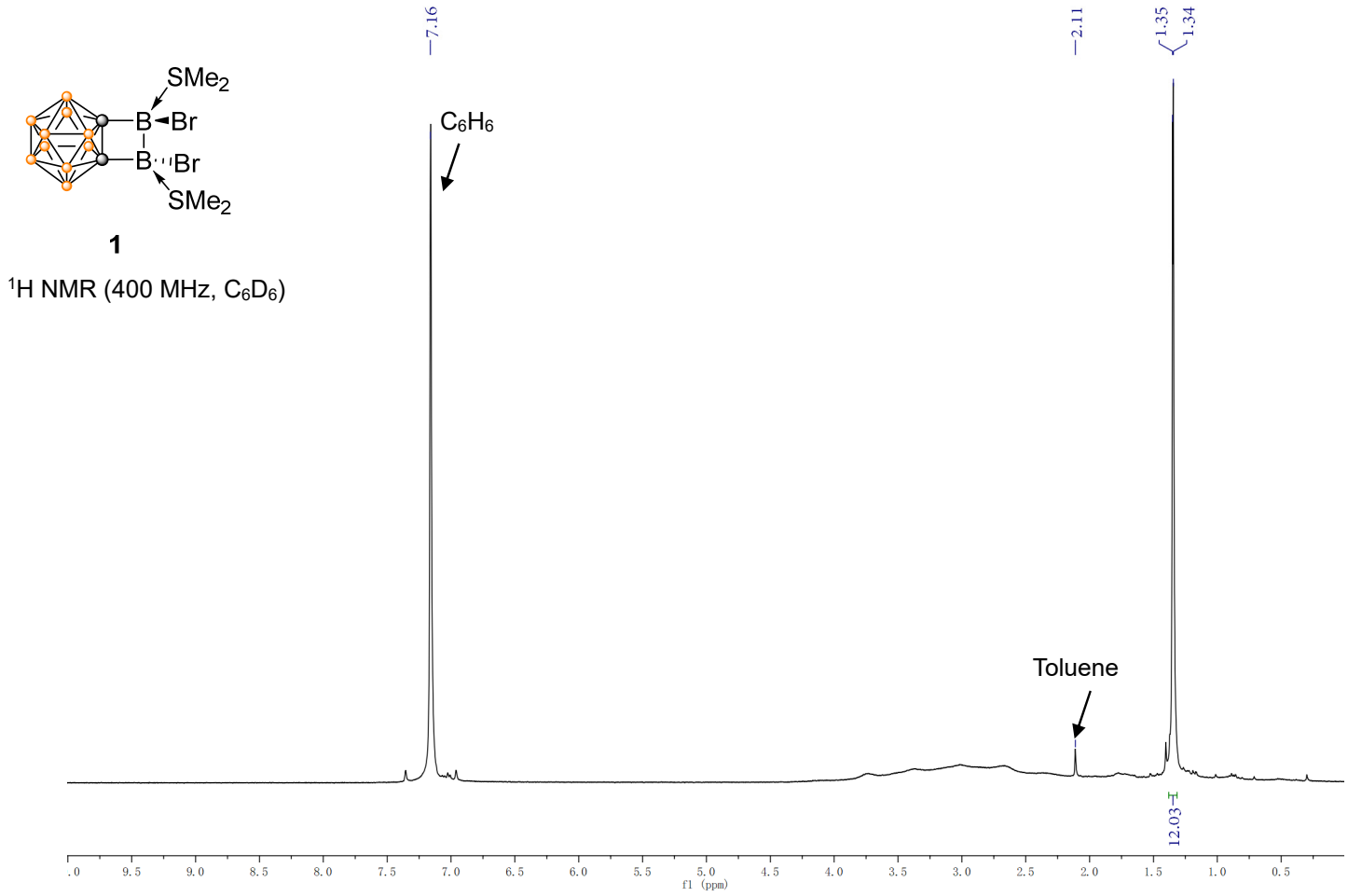


Figure S6. ^{1}H NMR spectrum of compound **1**.

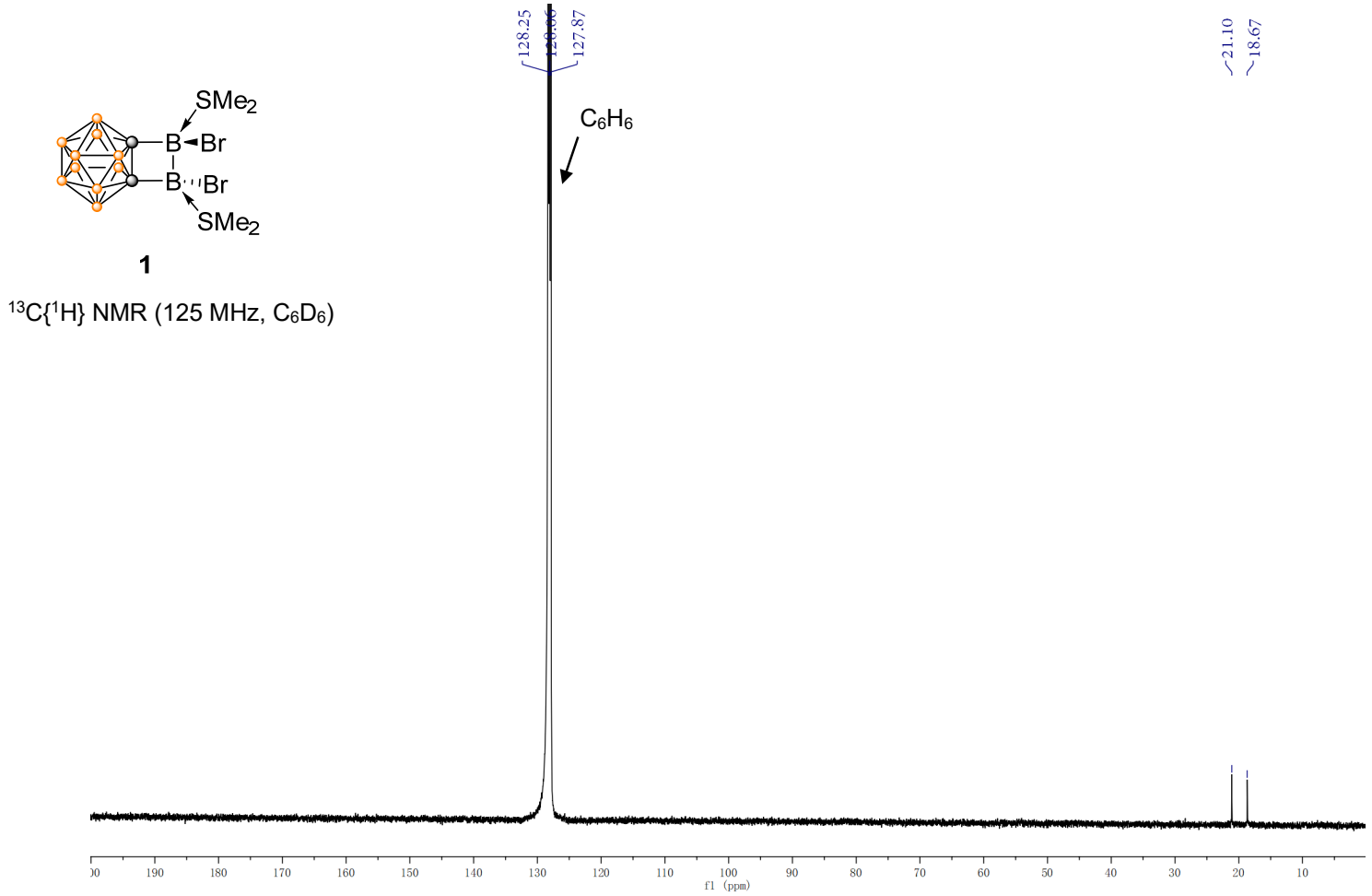


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1**.

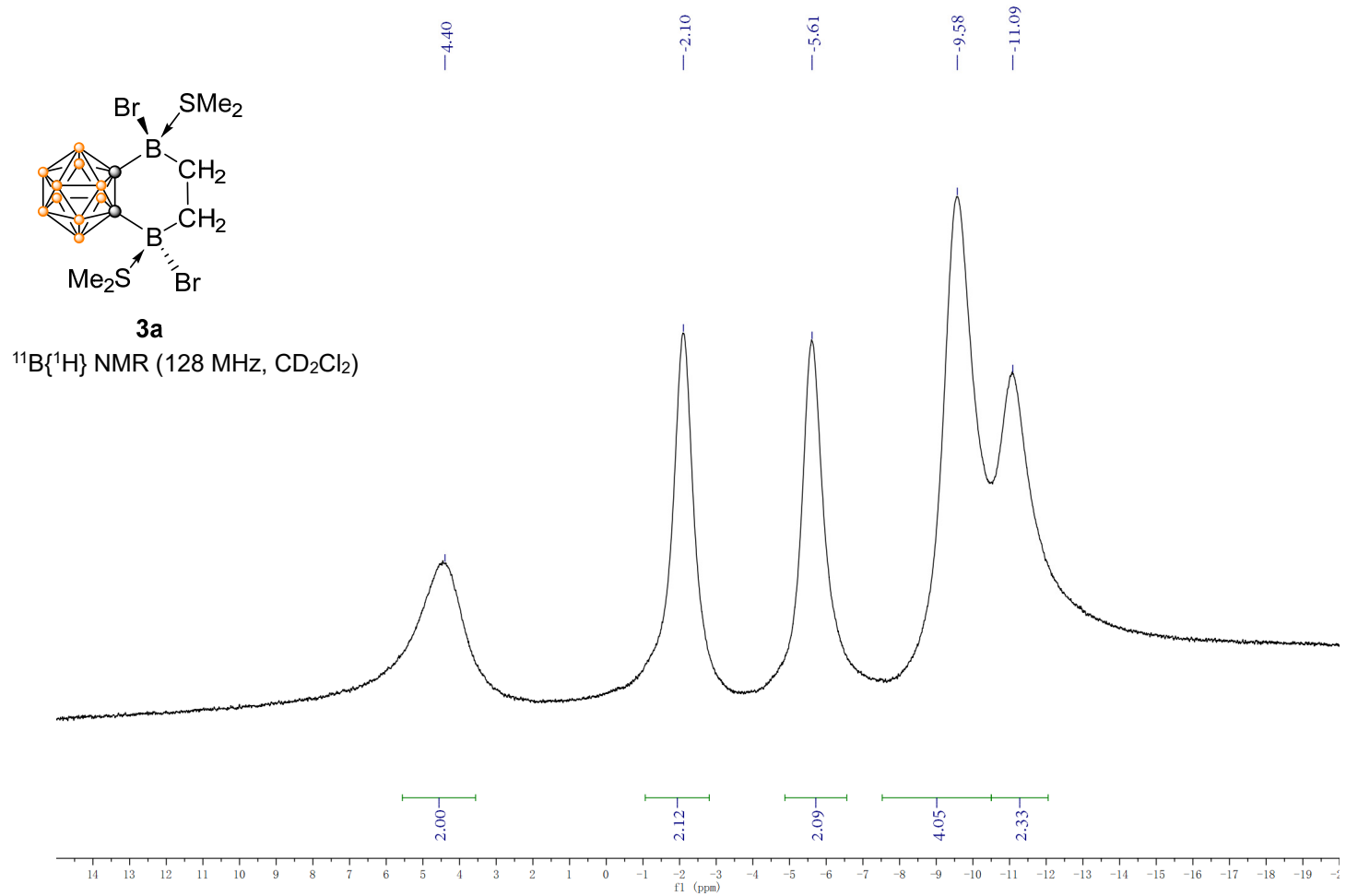


Figure S8. $^{11}B\{^{1}H\}$ NMR spectrum of compound **3a**.

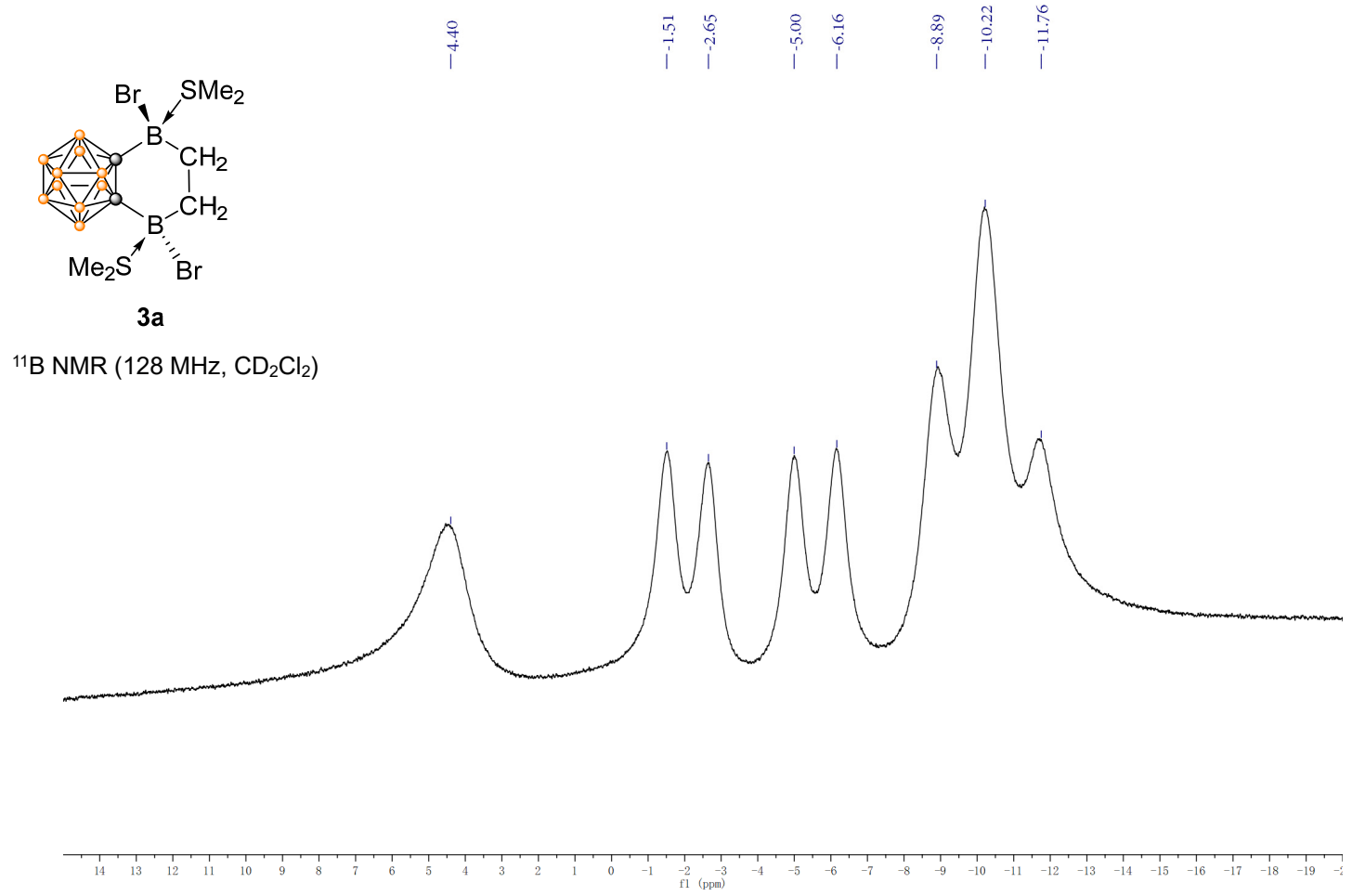


Figure S9. ^{11}B NMR spectrum of compound **3a**.

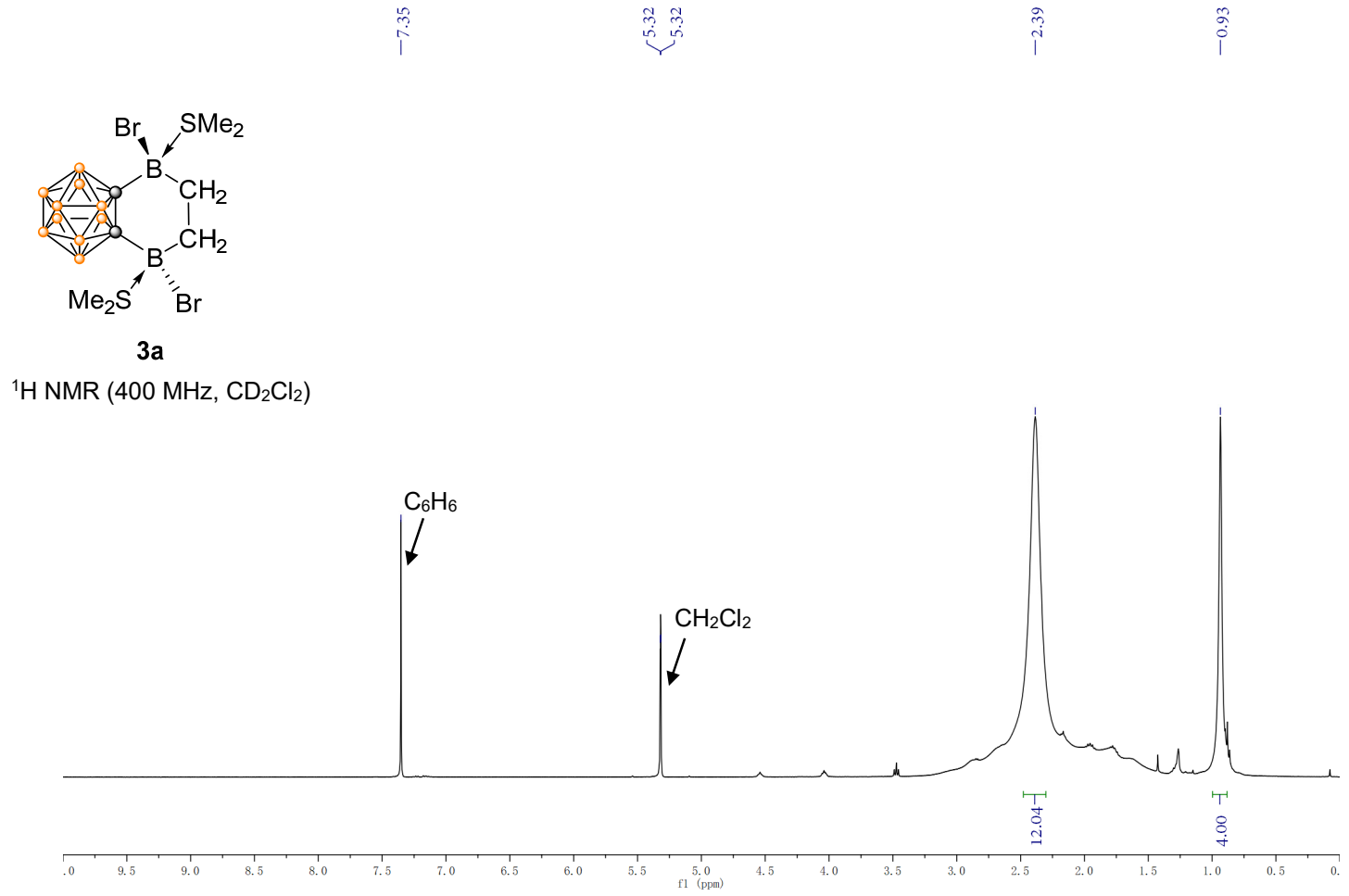


Figure S10. ^{1}H NMR spectrum of compound **3a**.

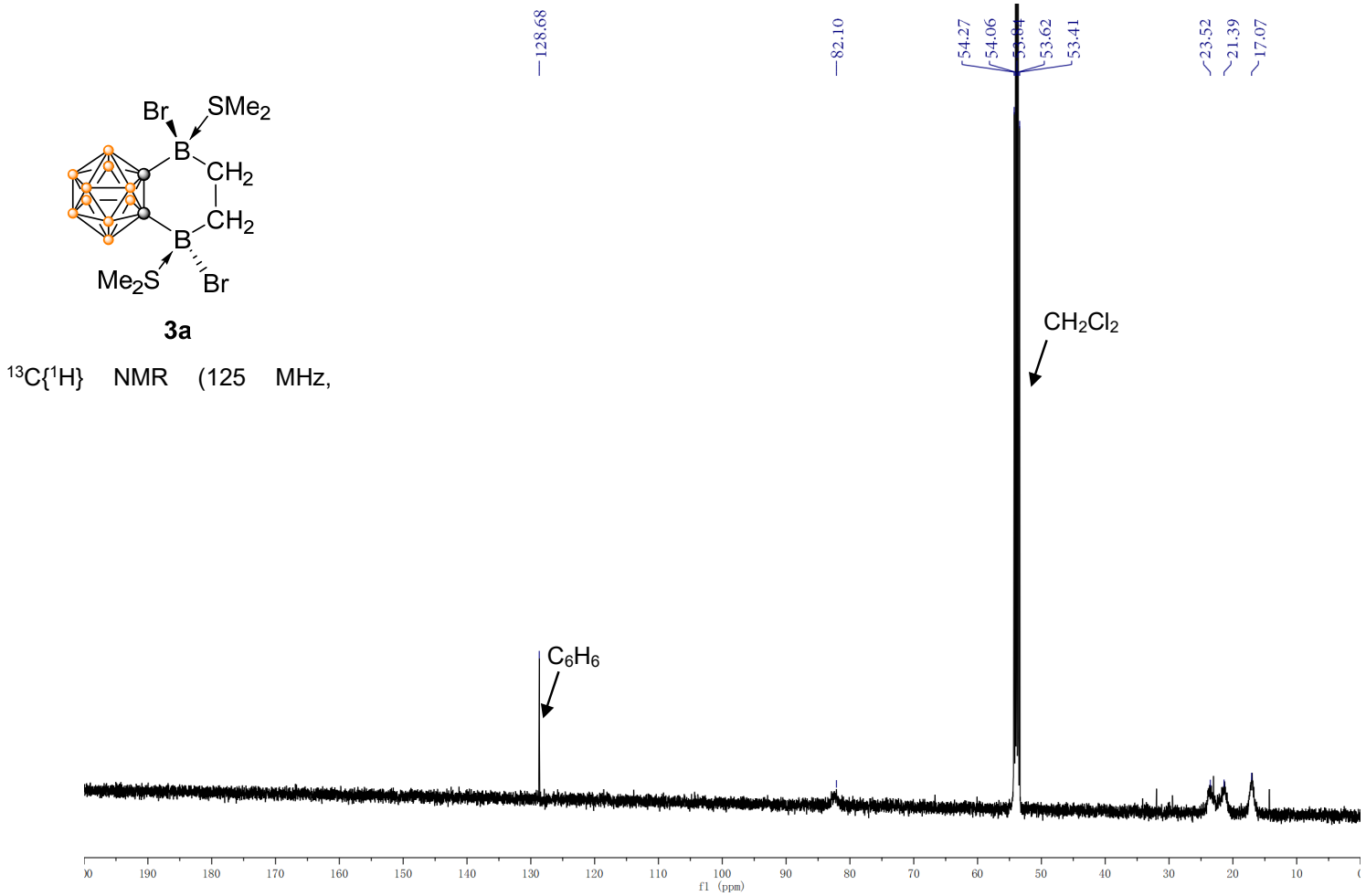


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3a**.

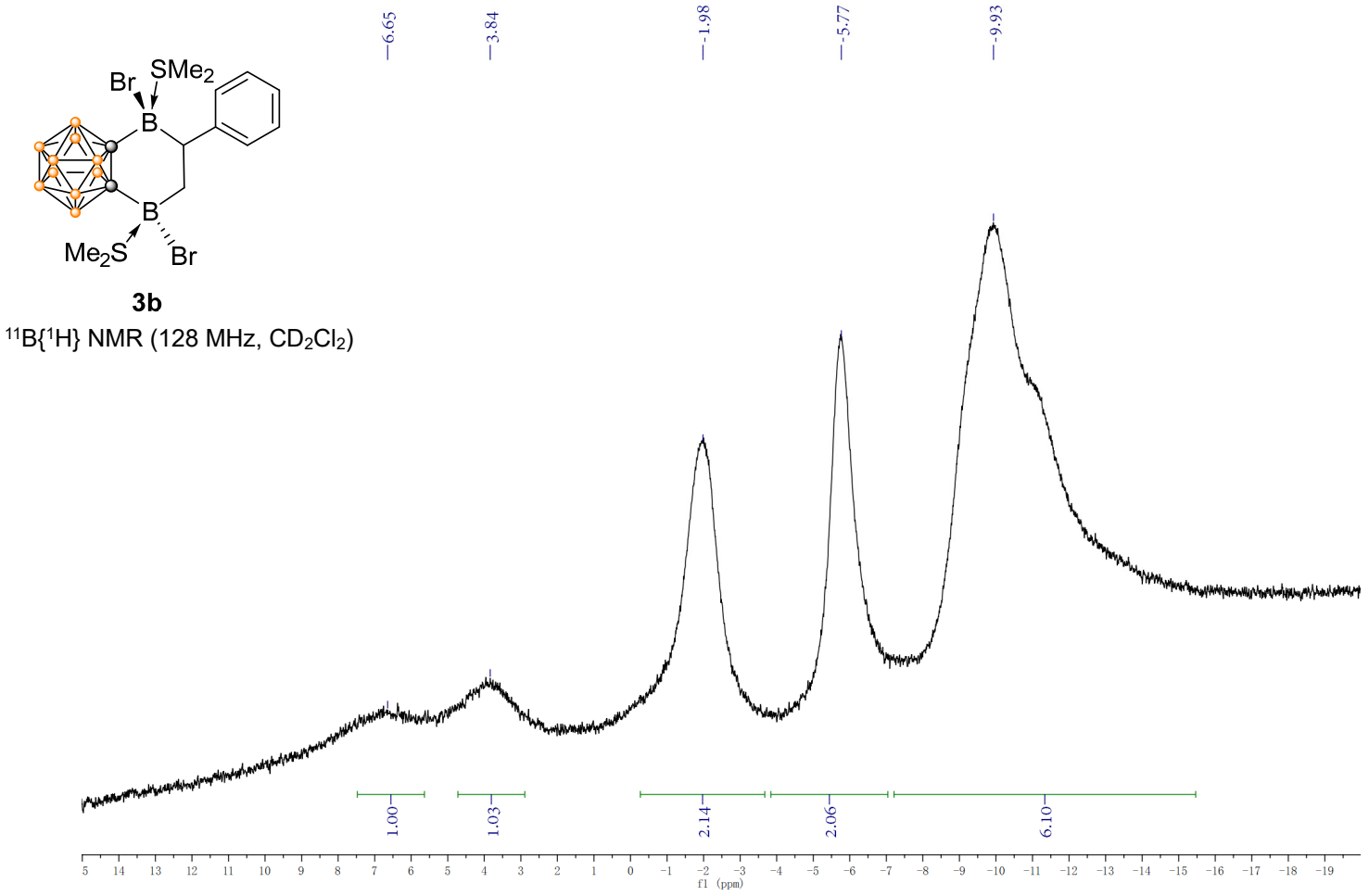


Figure S12. $^{11}B\{^{1}H\}$ NMR spectrum of compound **3b**.

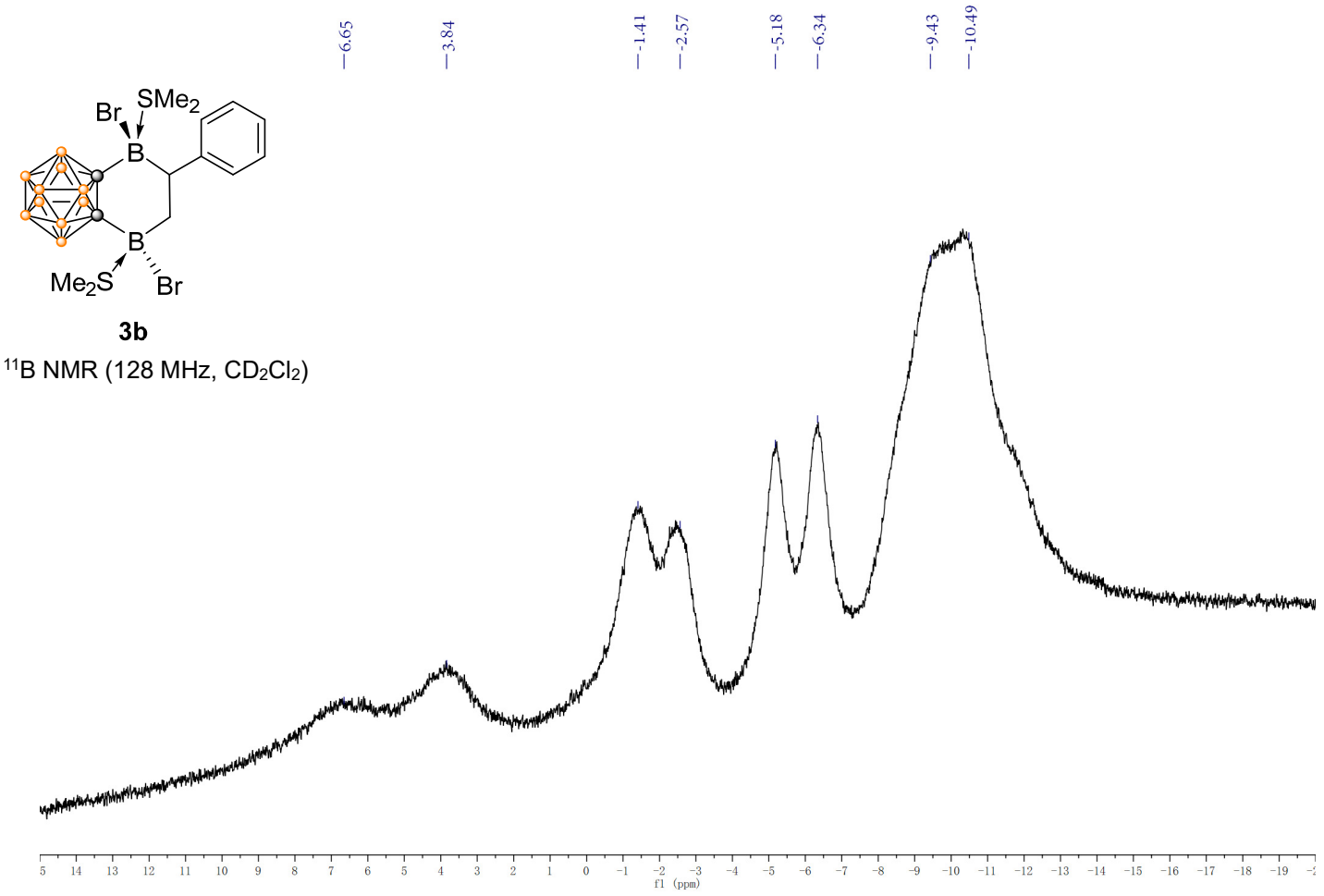


Figure S13. ^{11}B NMR spectrum of compound **3b**.

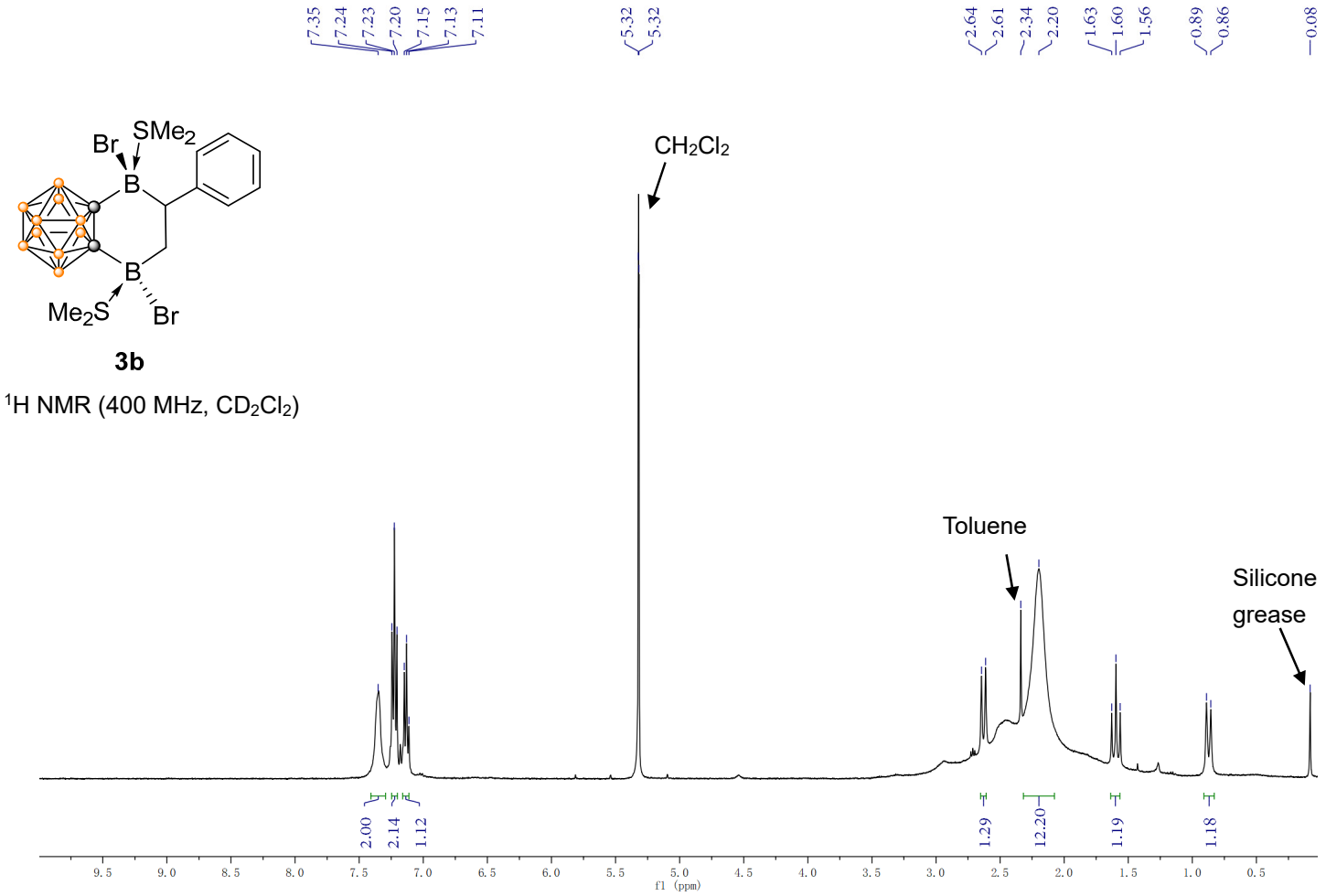


Figure S14. ^{1}H NMR spectrum of compound **3b**.

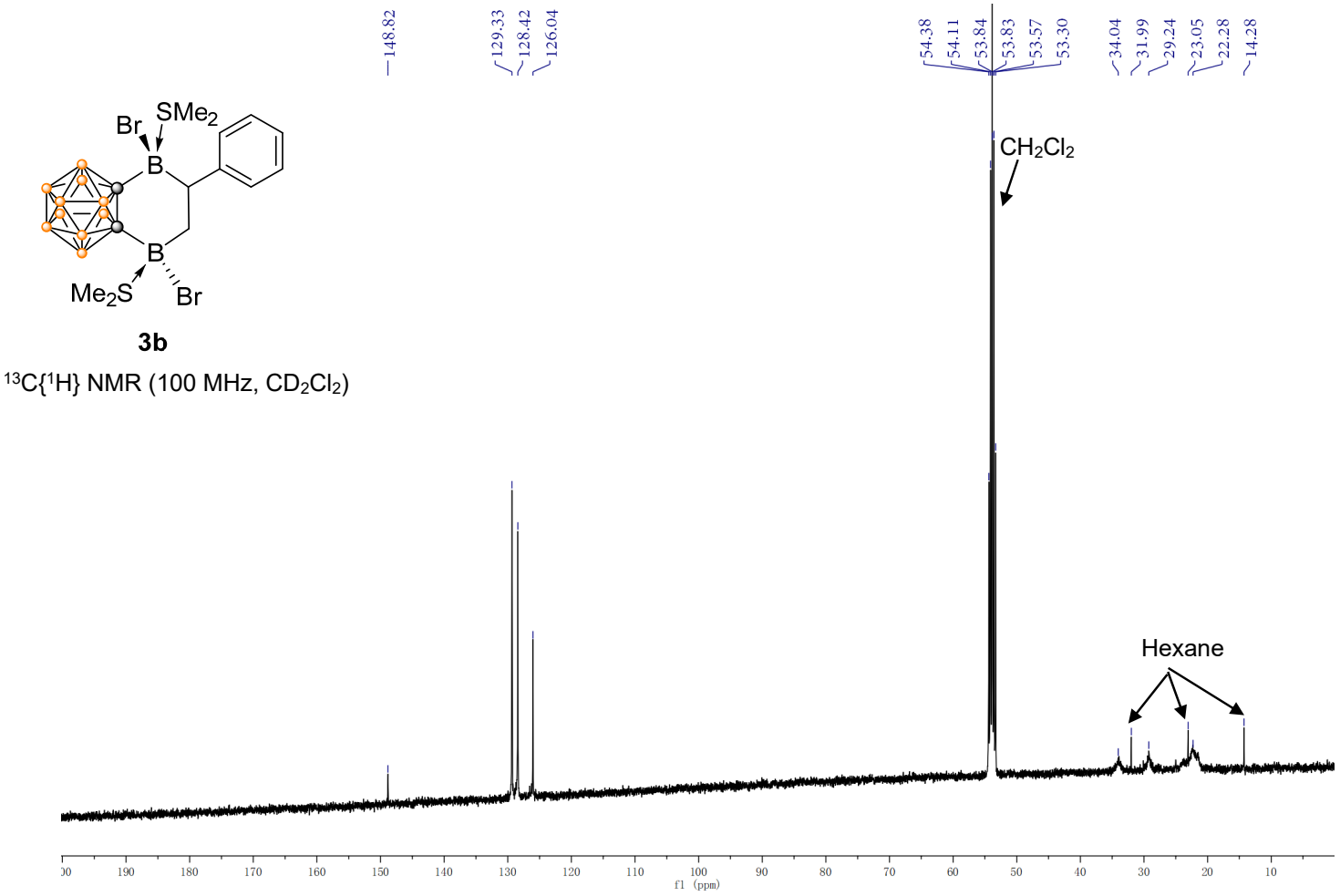


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3b**.

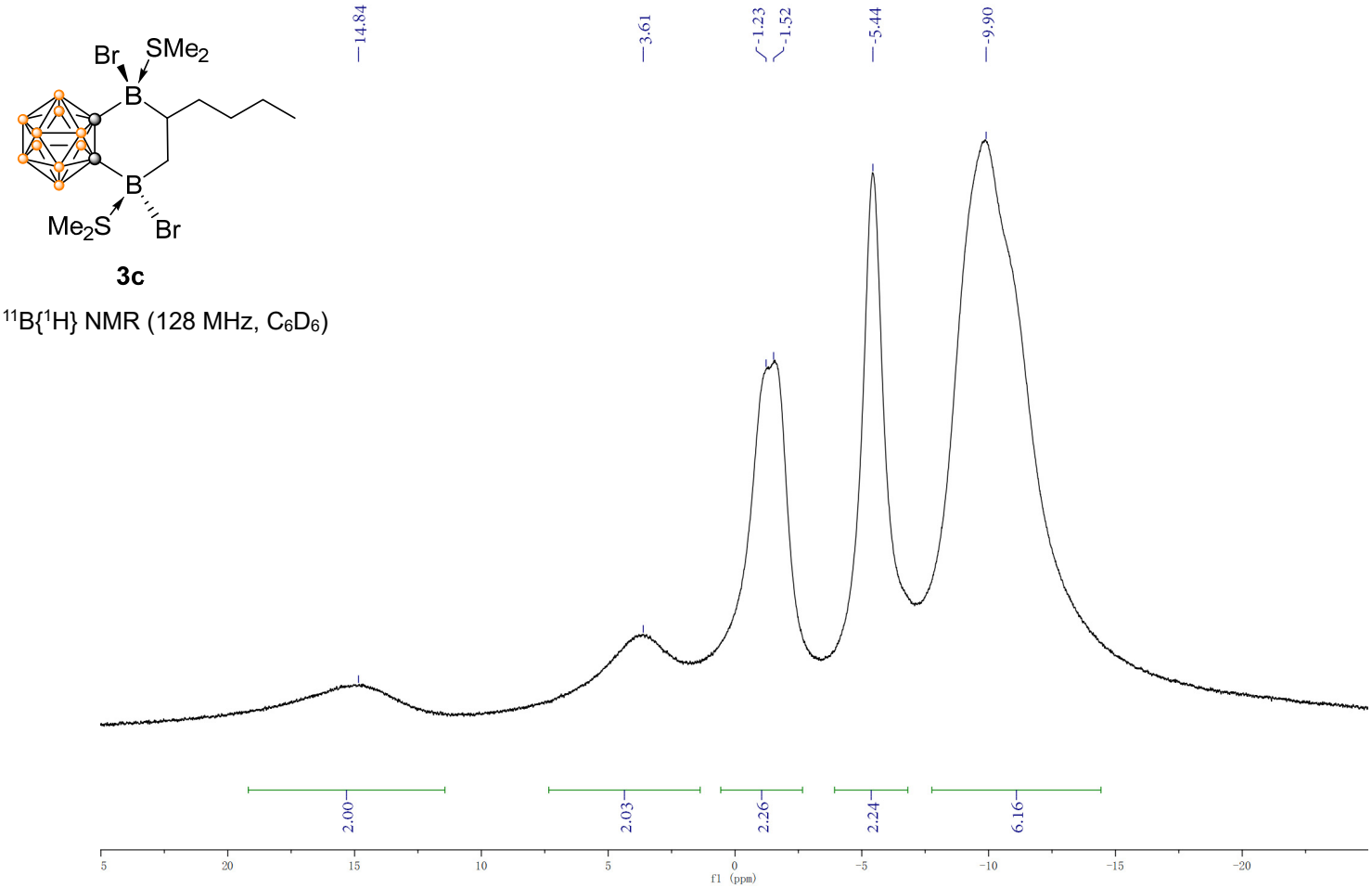


Figure S16. $^{11}B\{^{1}H\}$ NMR spectrum of compound **3c**.

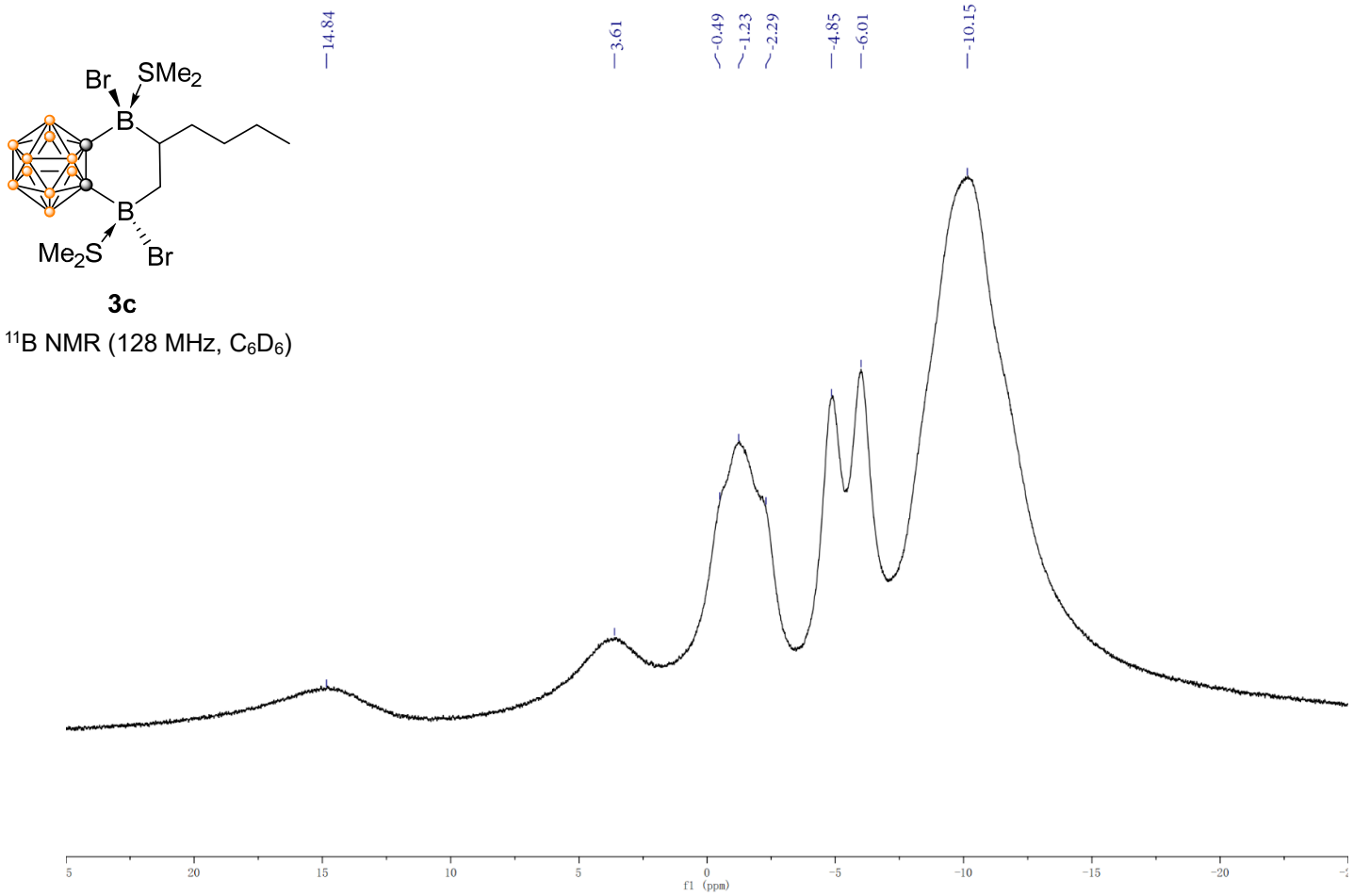


Figure S17. ^{11}B NMR spectrum of compound **3c**.

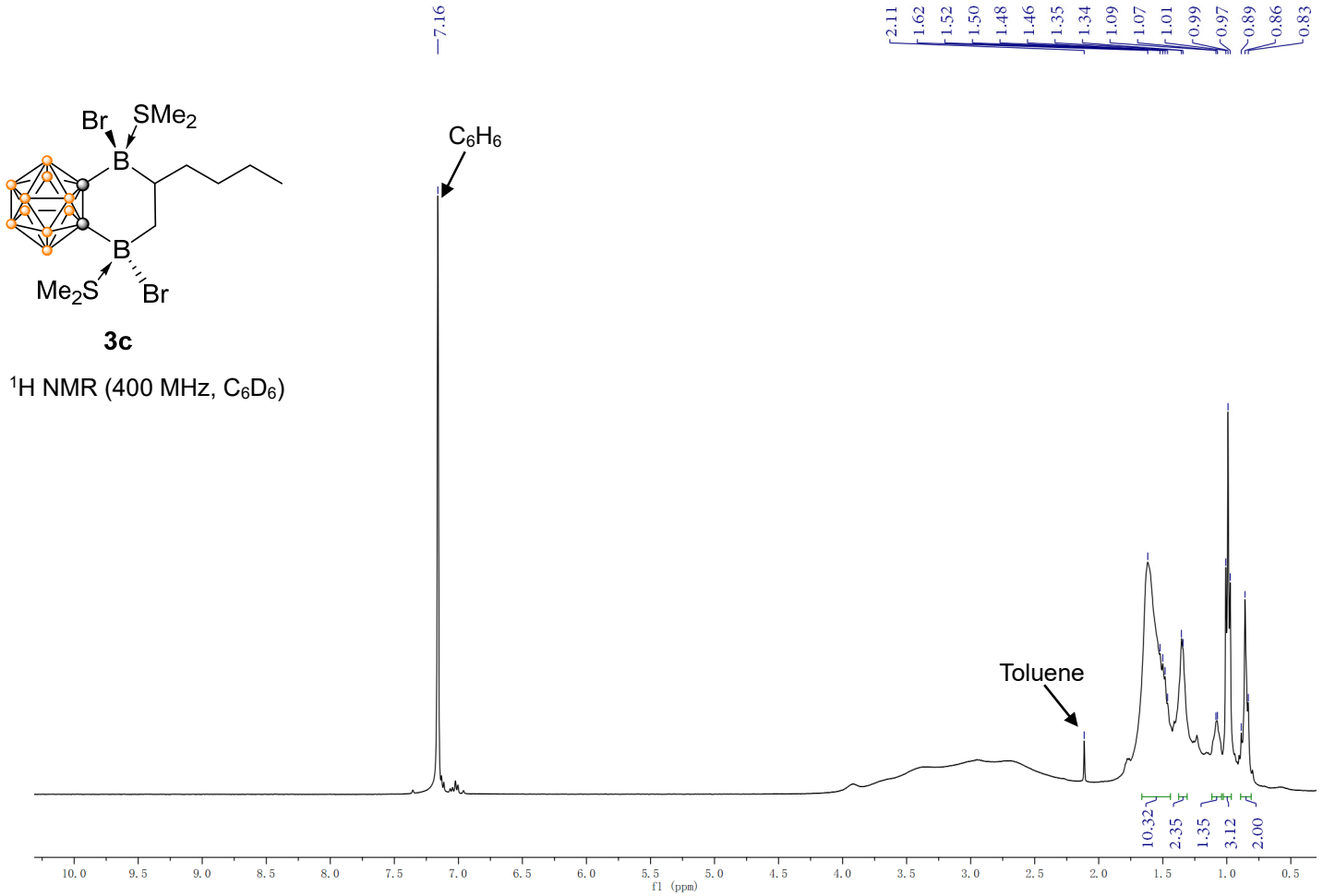


Figure S18. ^{1}H NMR spectrum of compound **3c**.

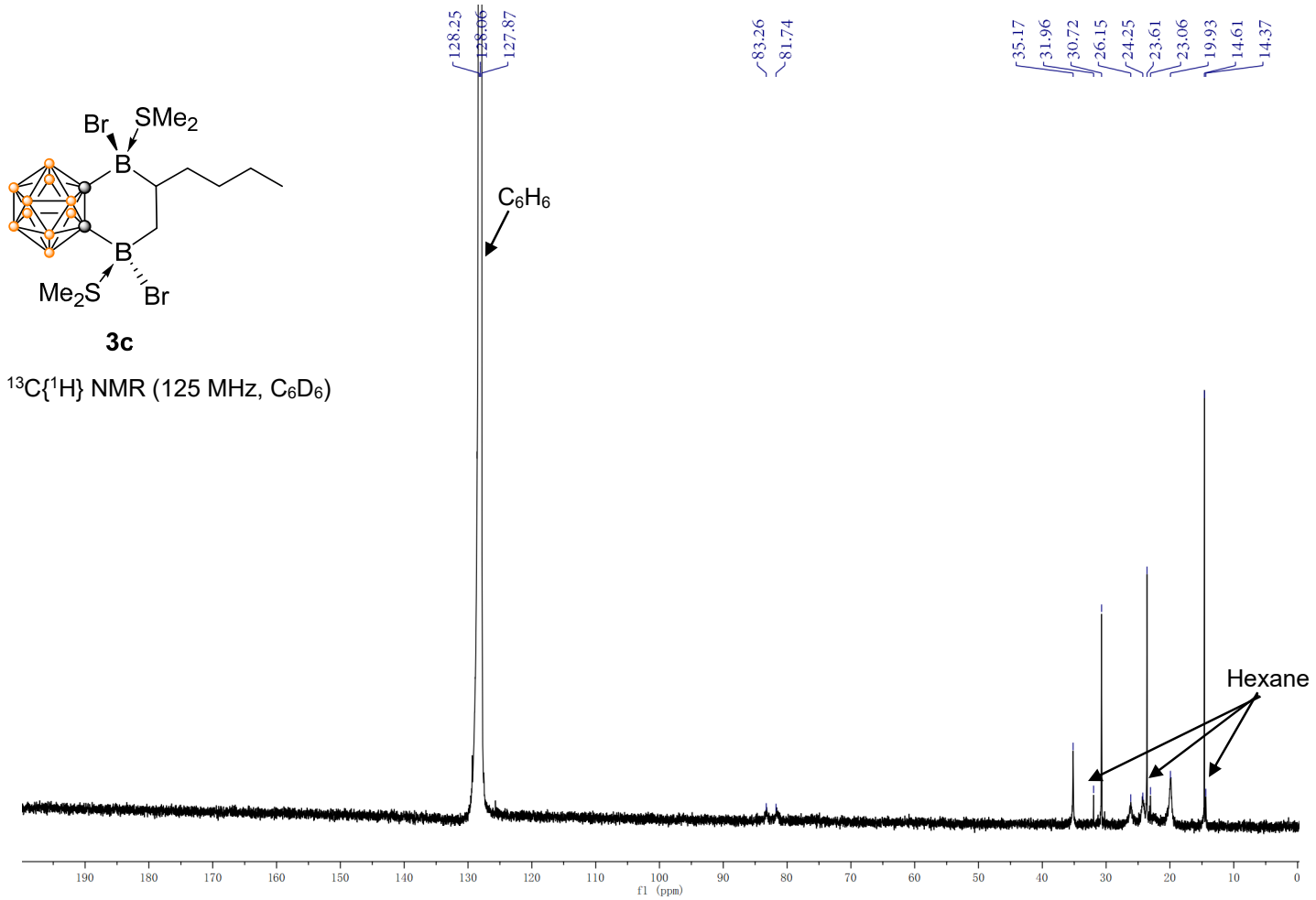


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3c**.

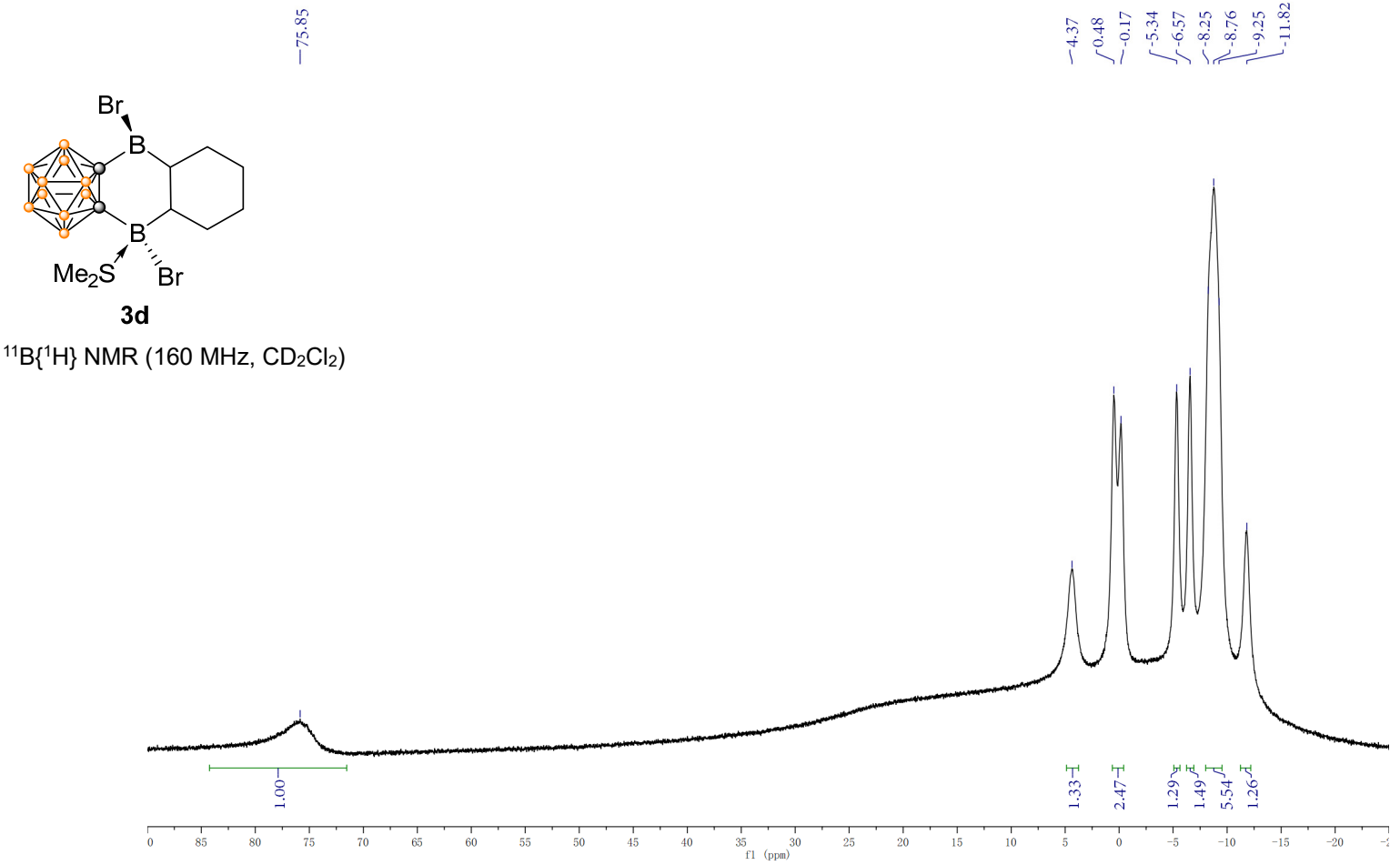


Figure S20. $^{11}B\{^{1}H\}$ NMR spectrum of compound **3d**.

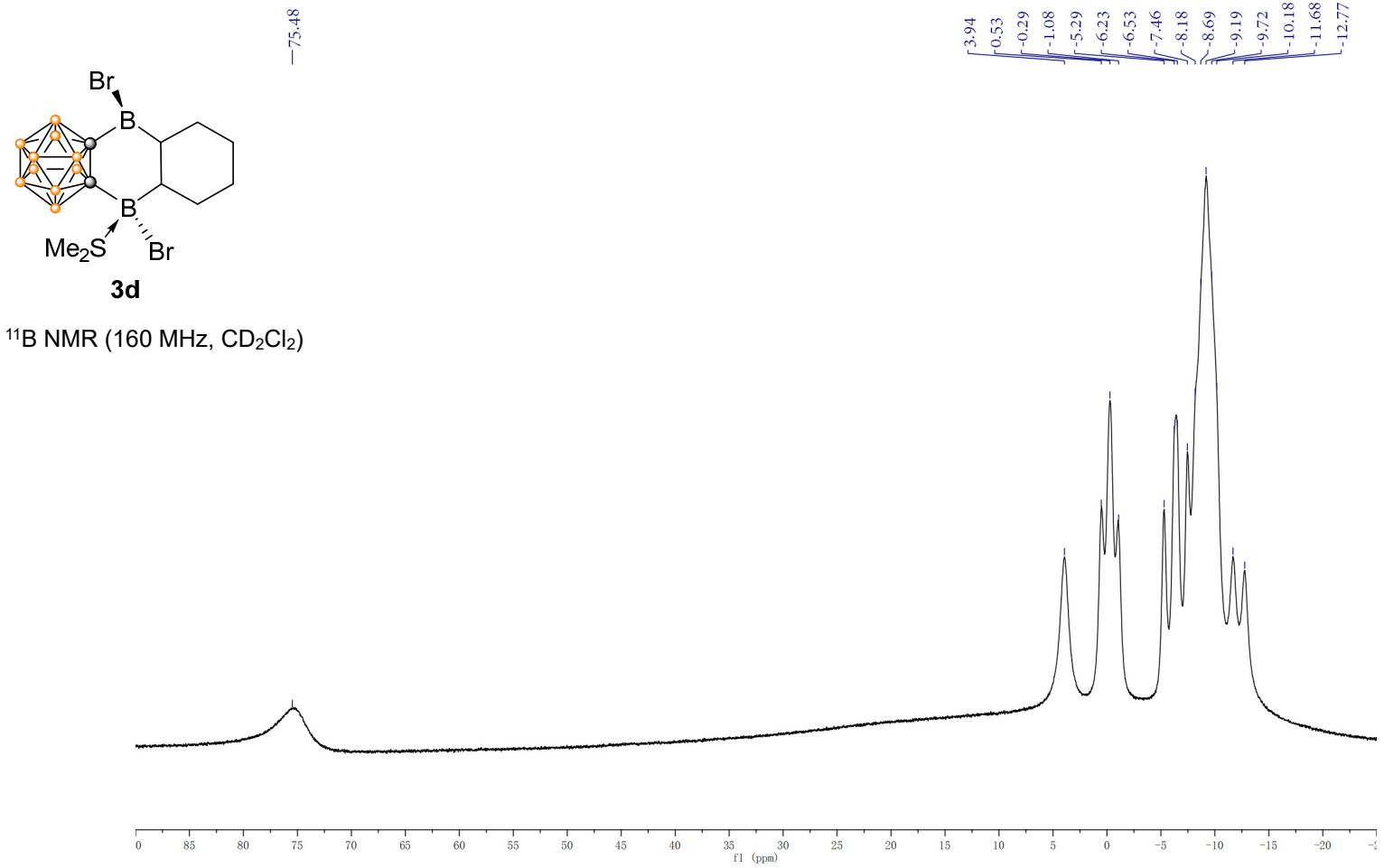


Figure S21. ^{11}B NMR spectrum of compound **3d**.

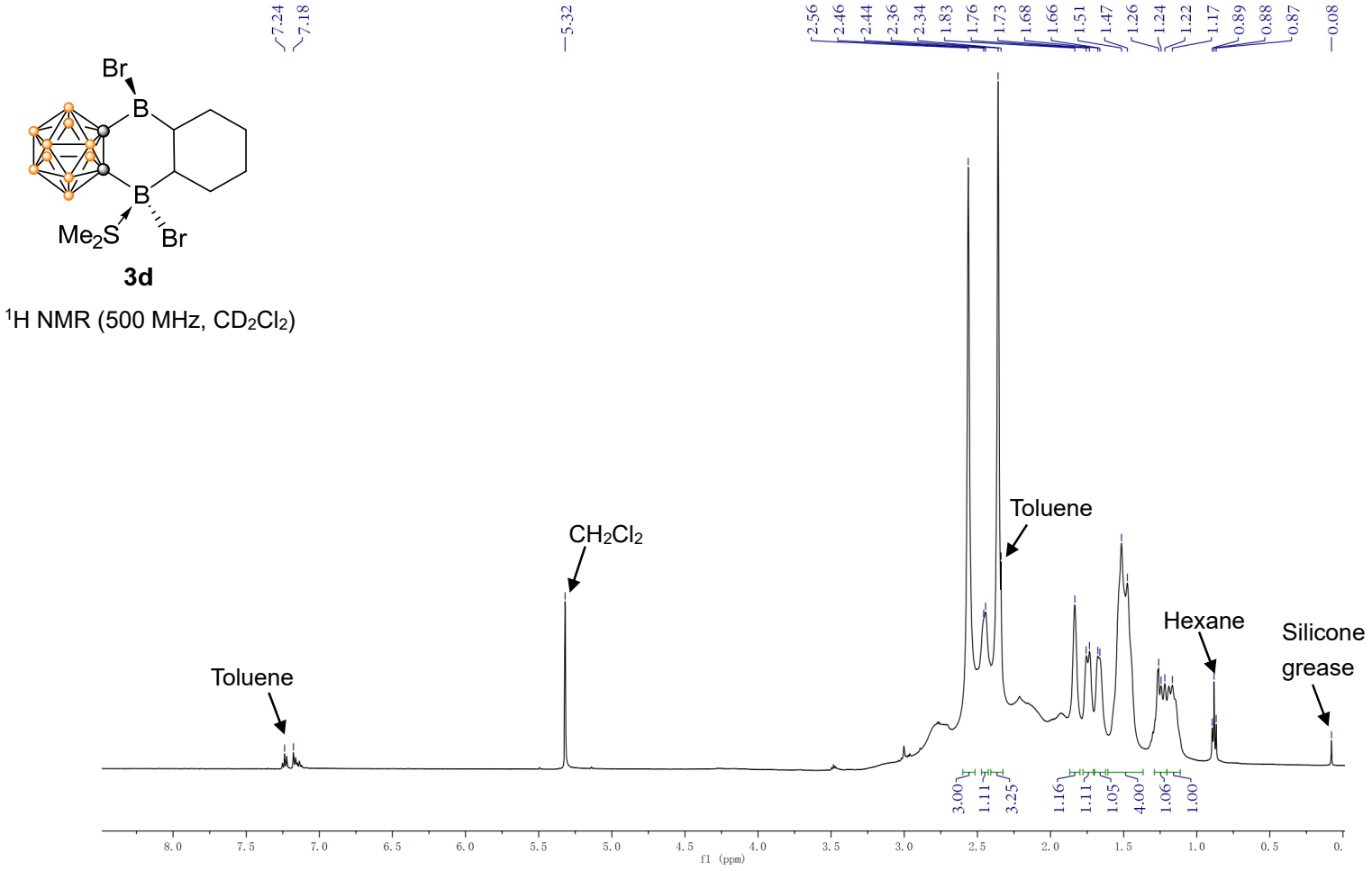


Figure S22. ^{1}H NMR spectrum of compound **3d**.

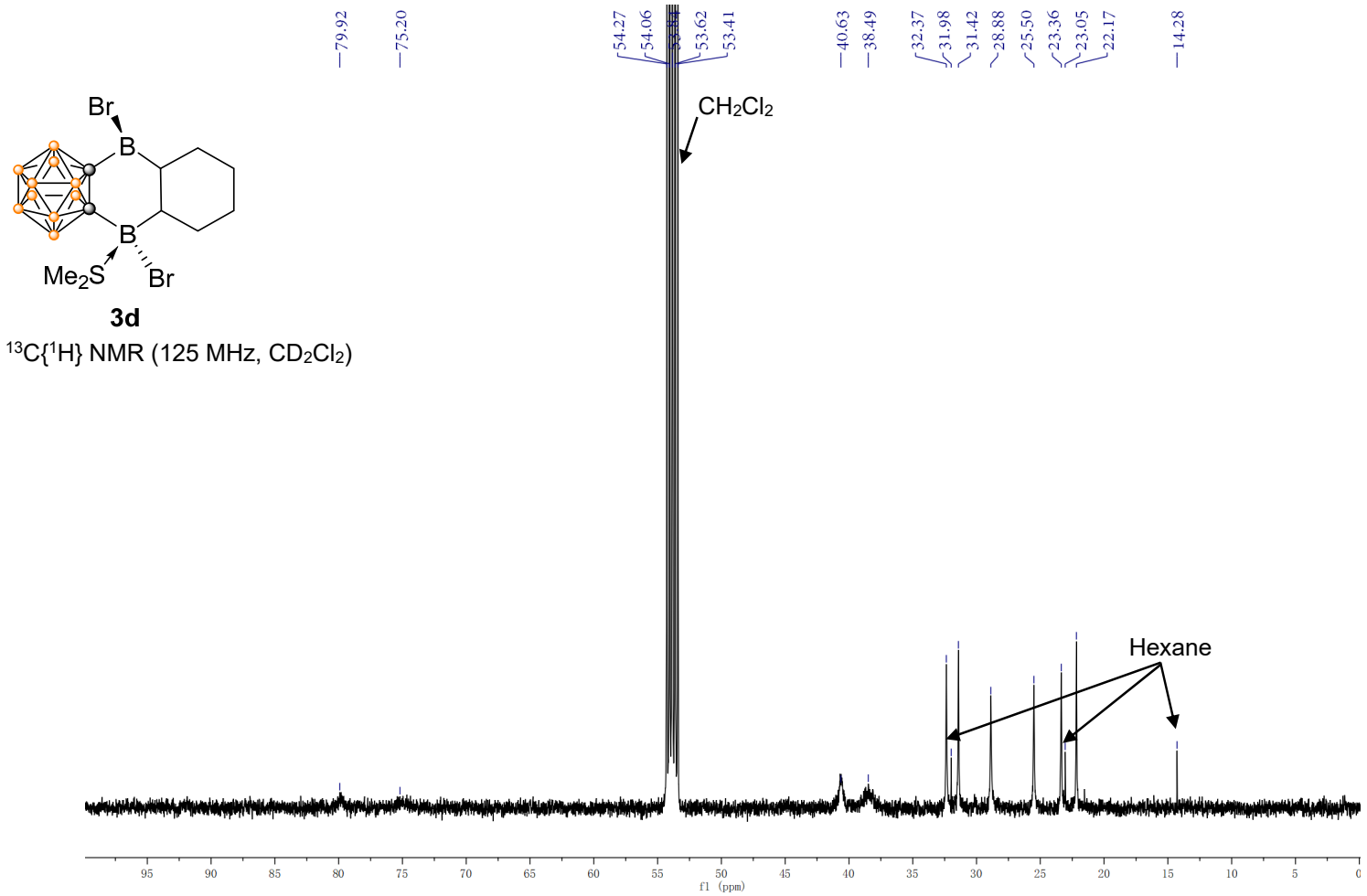


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3d**.

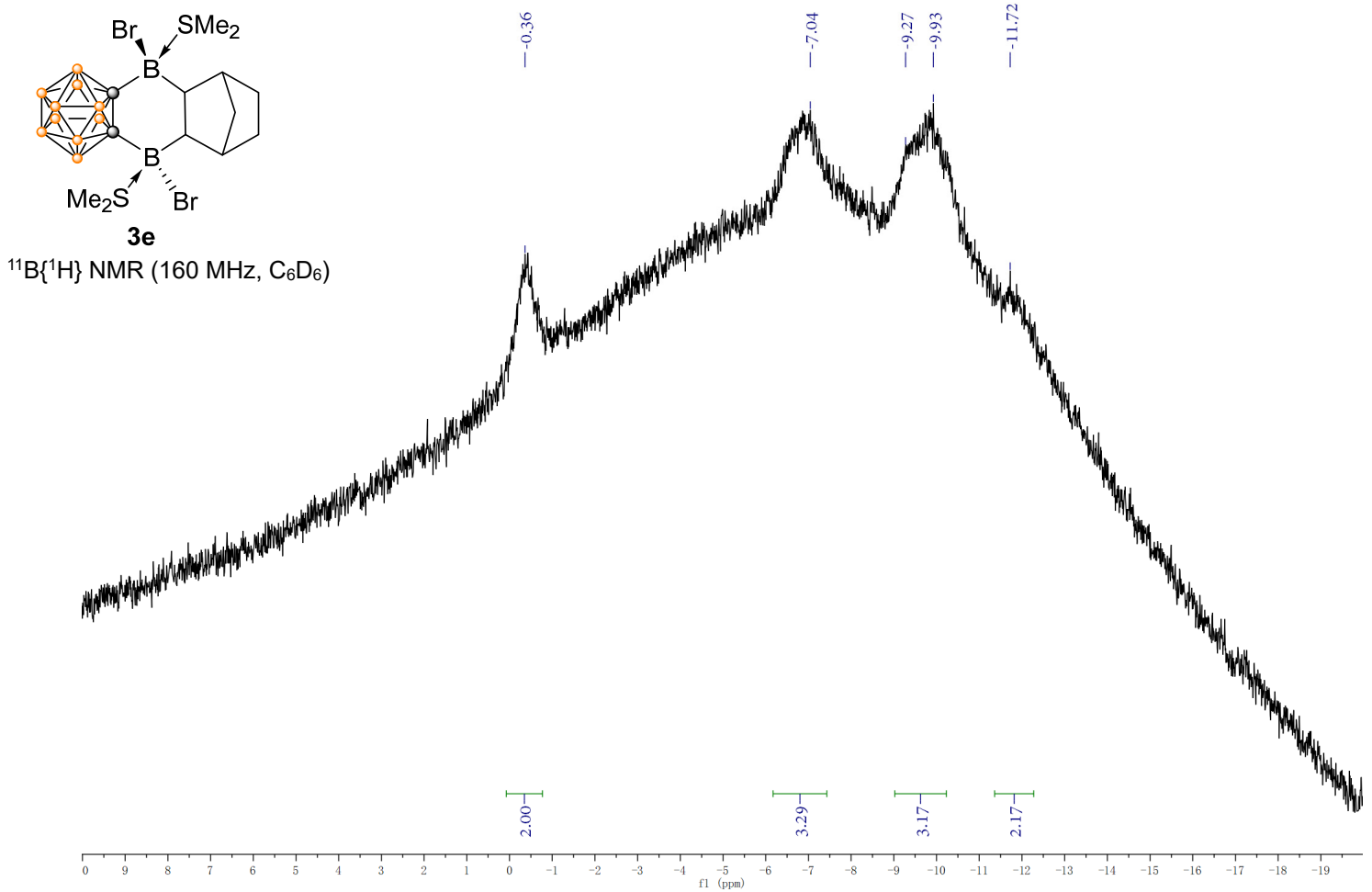


Figure S24. $^{11}B\{^{1}H\}$ NMR spectrum of compound **3e**.

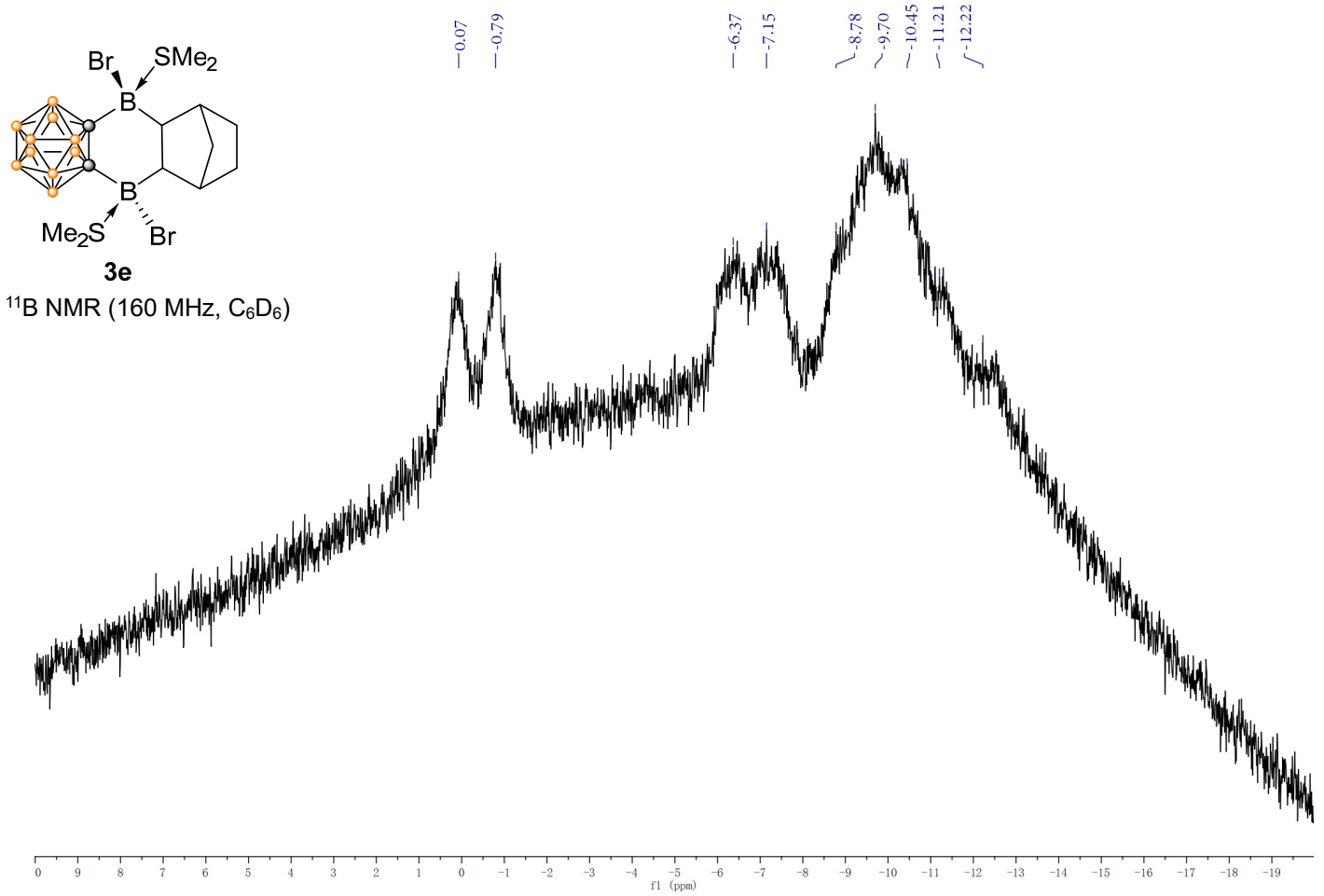


Figure S25. ^{11}B NMR spectrum of compound **3e**.

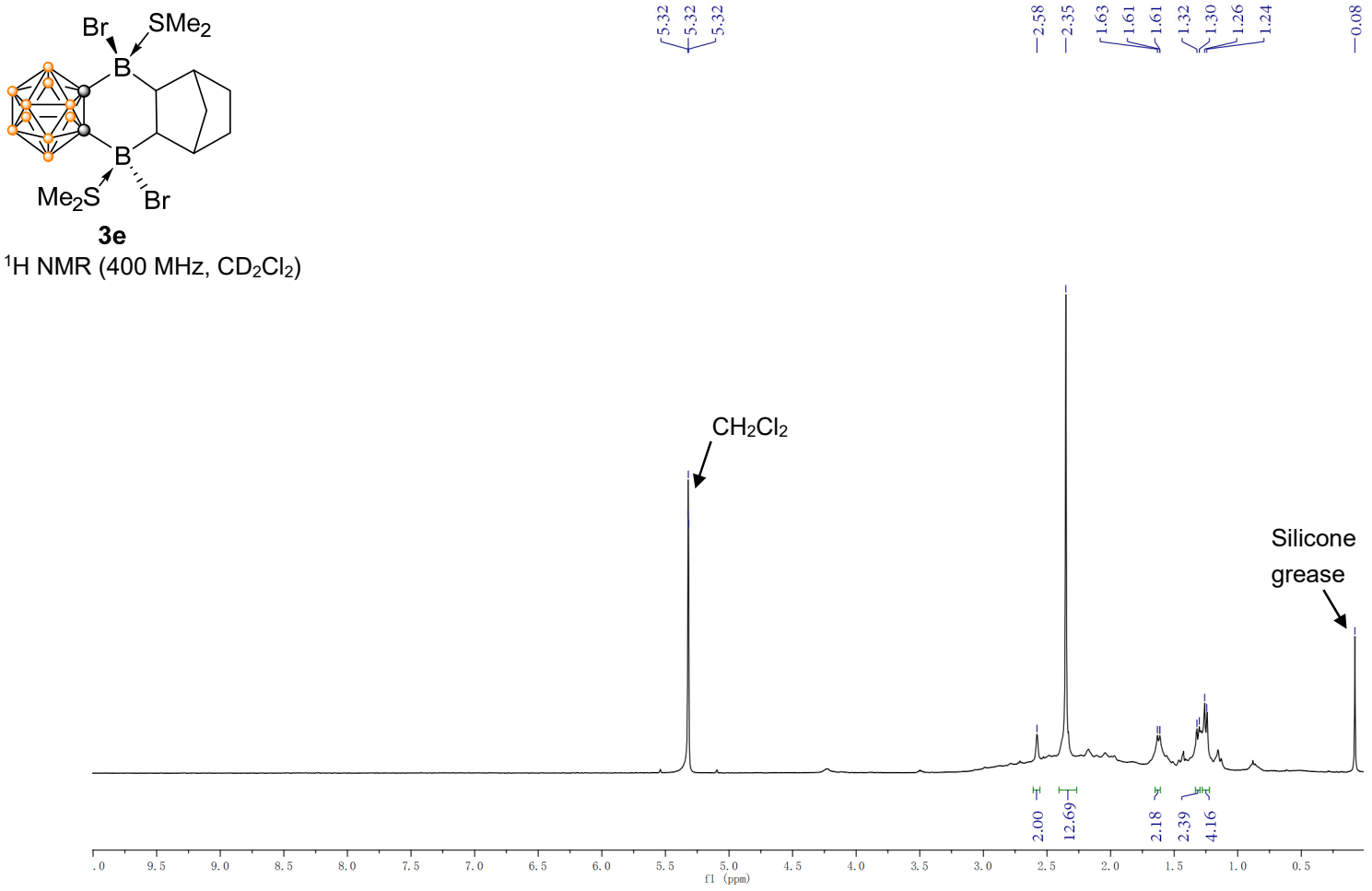


Figure S26. ^{1}H NMR spectrum of compound **3e**.

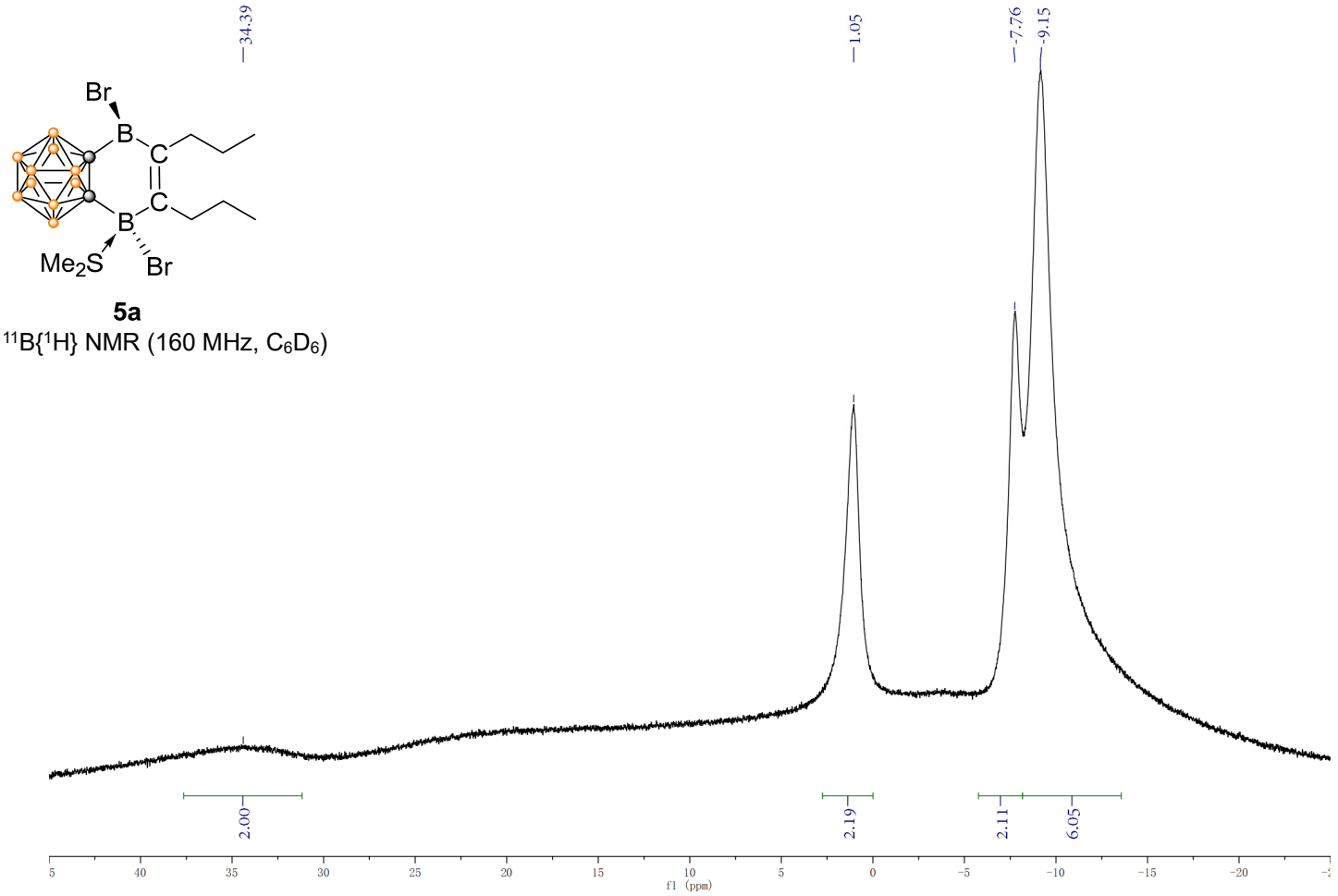


Figure S27. $^{11}B\{^{1}H\}$ NMR spectrum of compound **5a**.

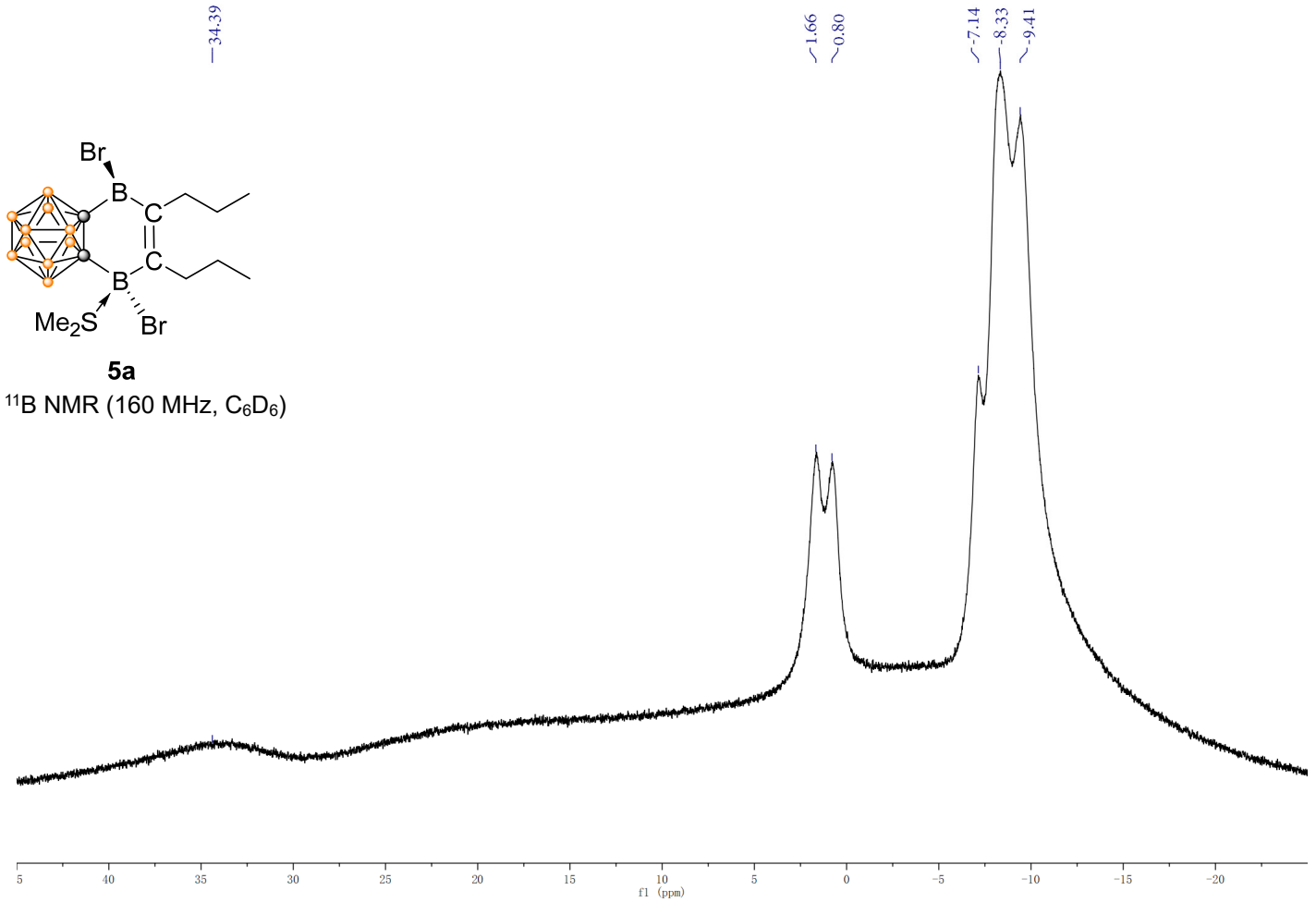


Figure S28. ^{11}B NMR spectrum of compound **5a**.

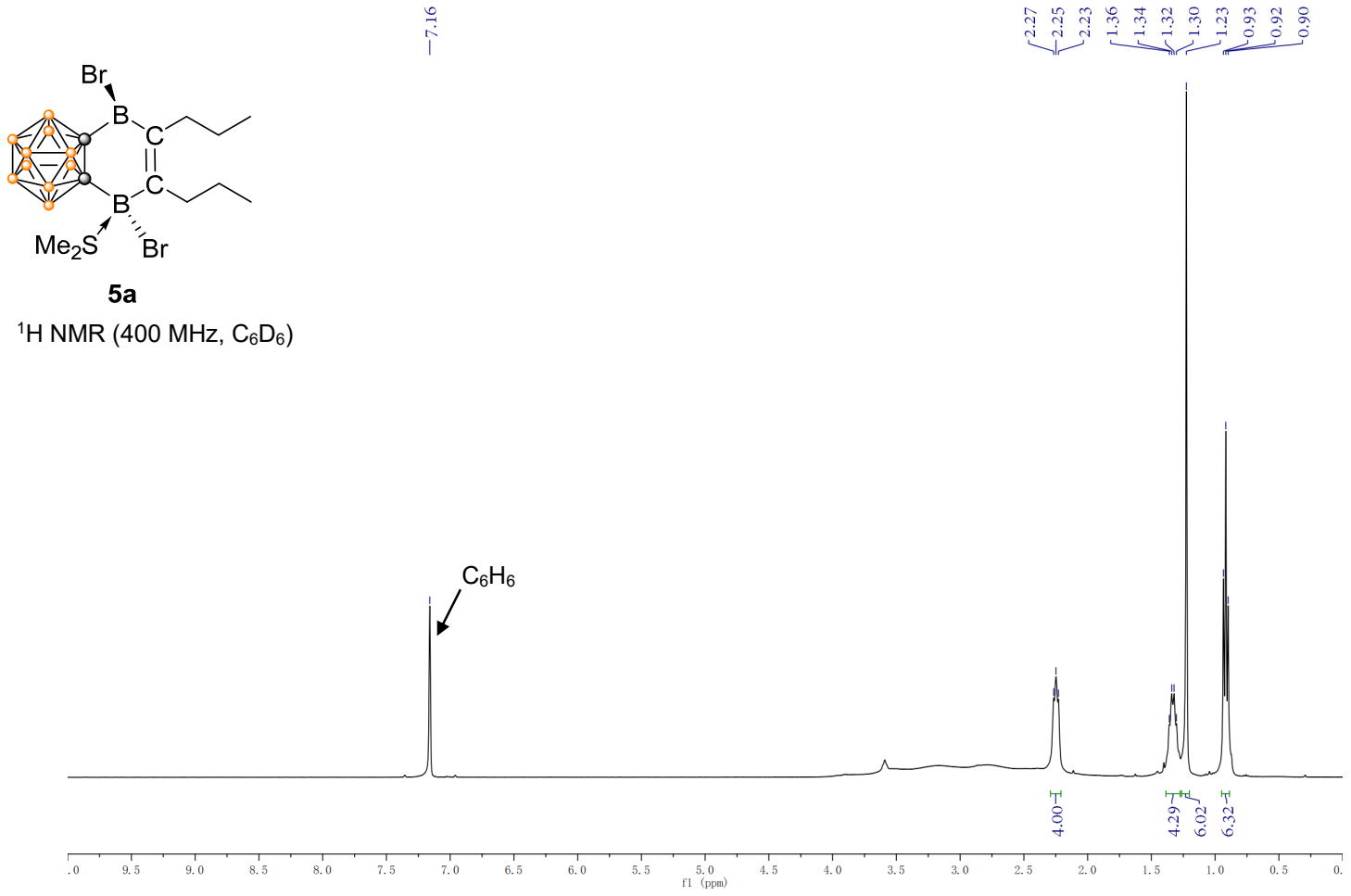


Figure S29. ^{1}H NMR spectrum of compound **5a**.

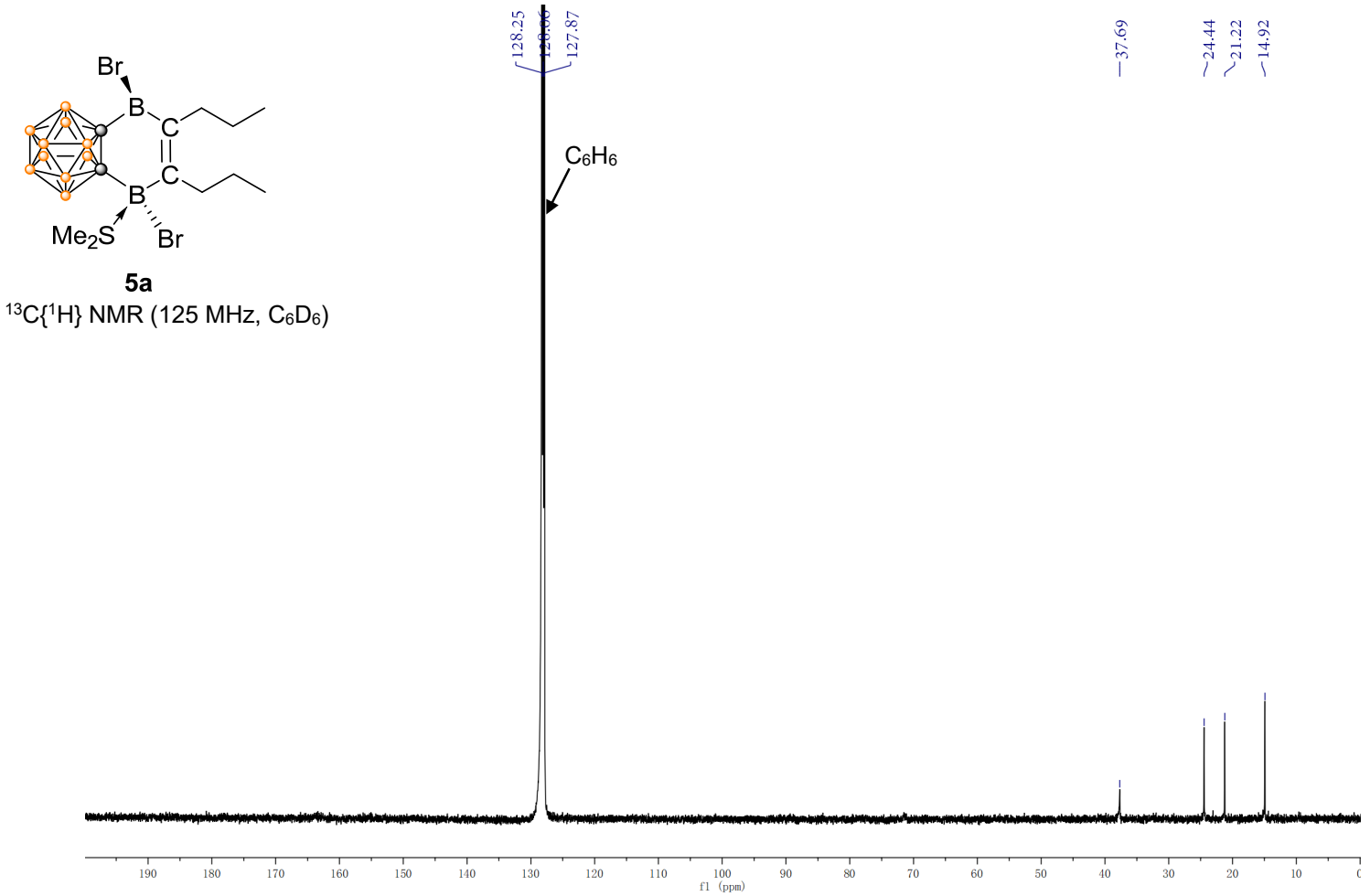


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5a**.

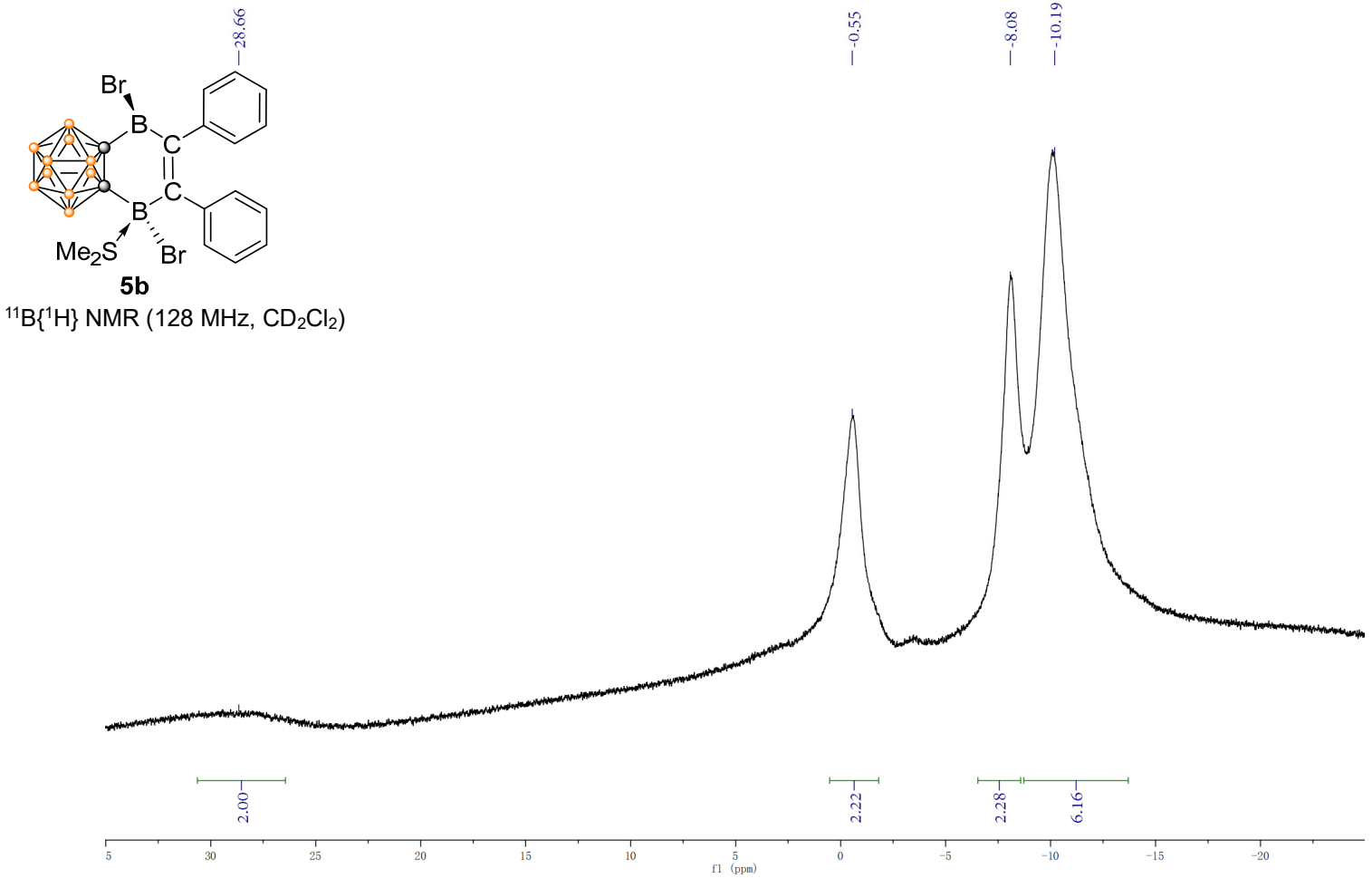


Figure S31. $^{11}B\{^{1}H\}$ NMR spectrum of compound **5b**.

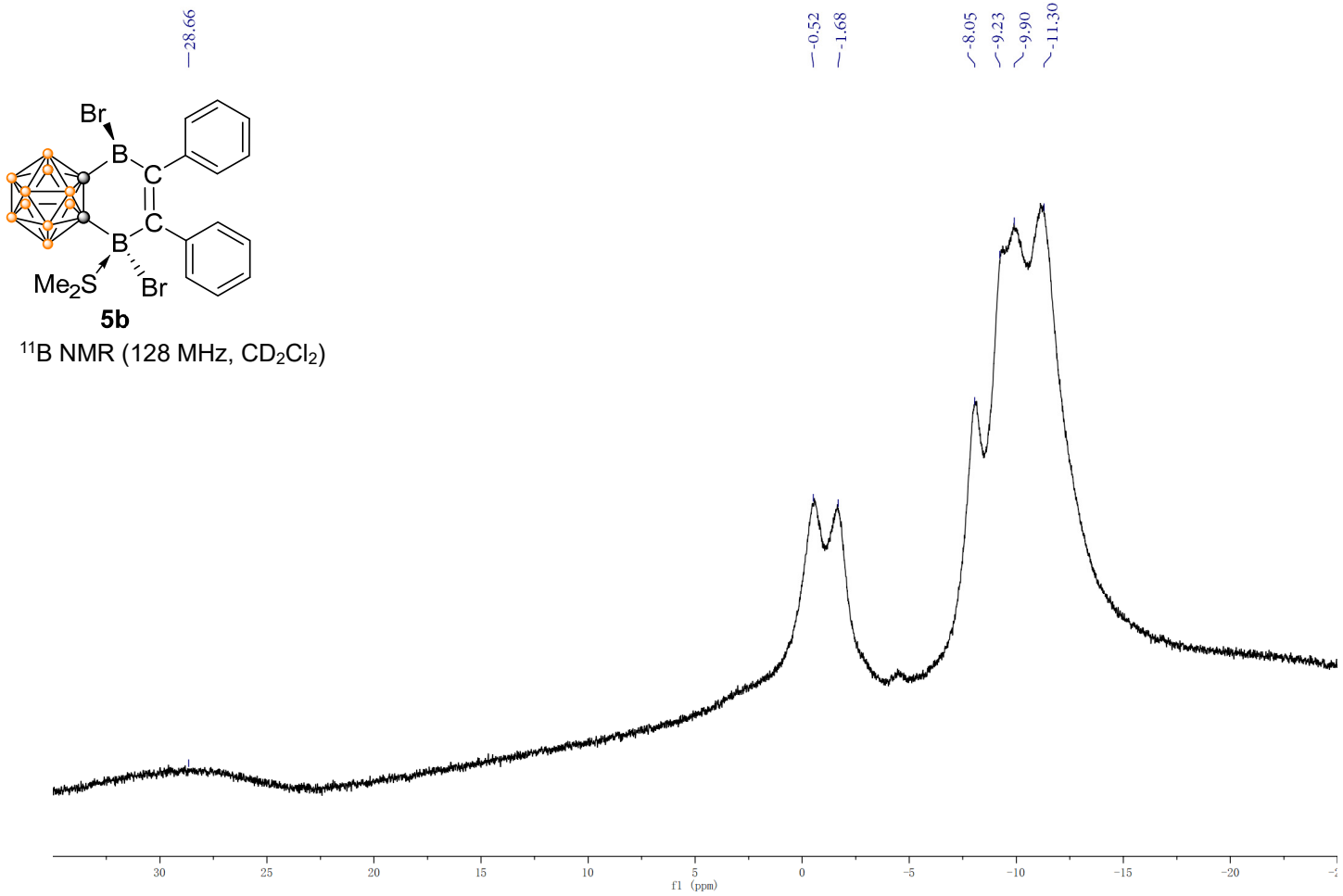


Figure S32. ^{11}B NMR spectrum of compound **5b**.

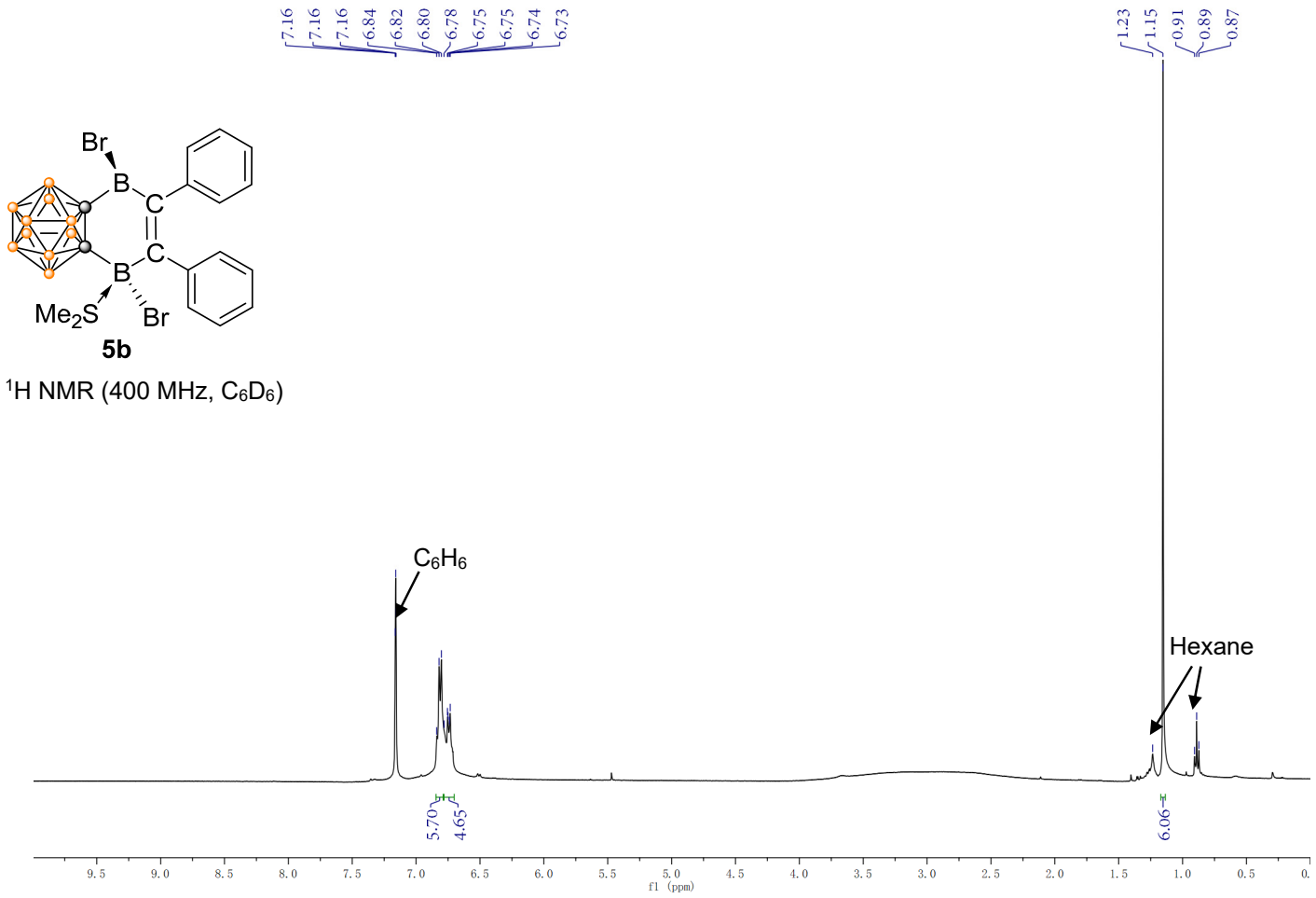


Figure S33. ^{1}H NMR spectrum of compound **5b**.

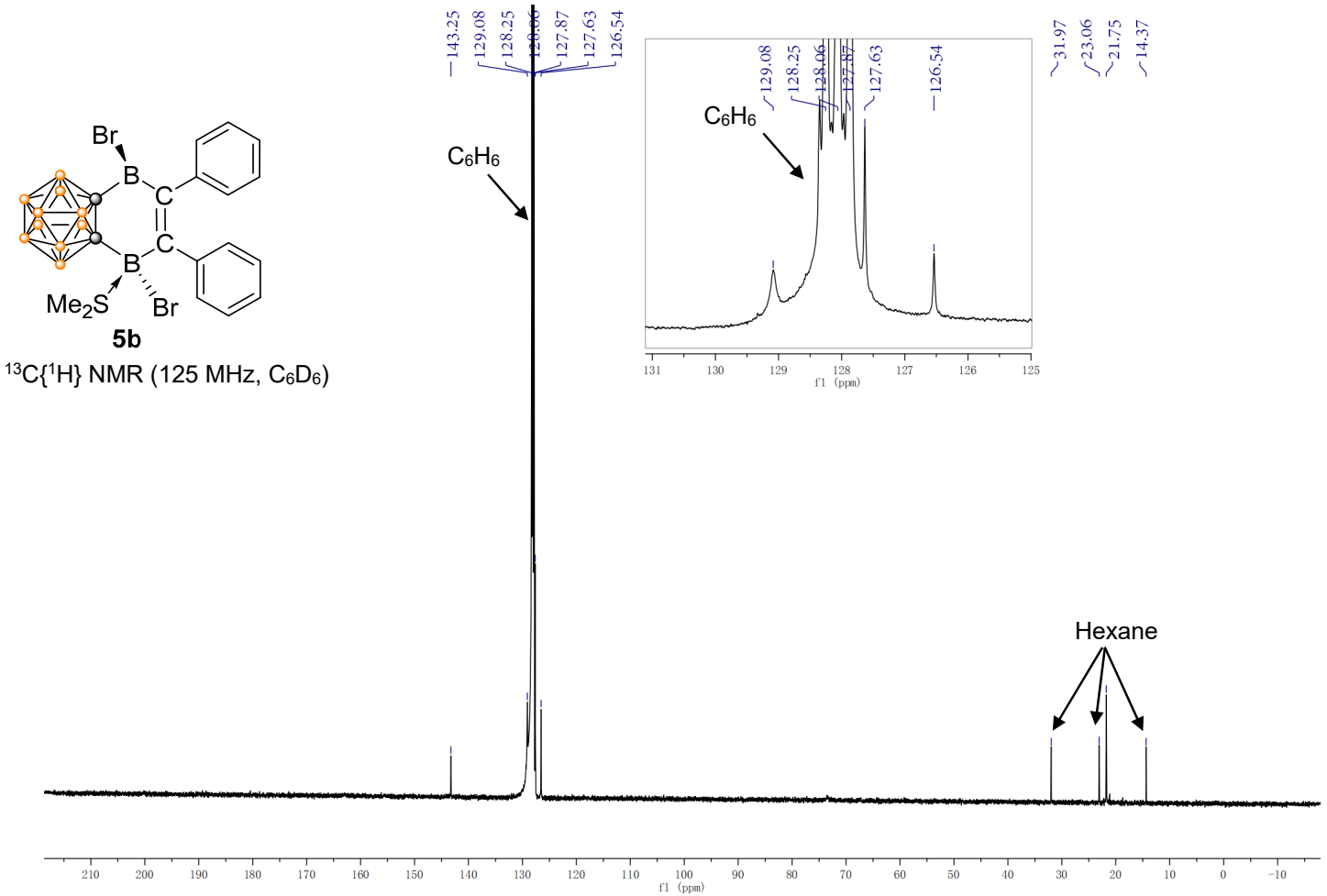


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5b**.

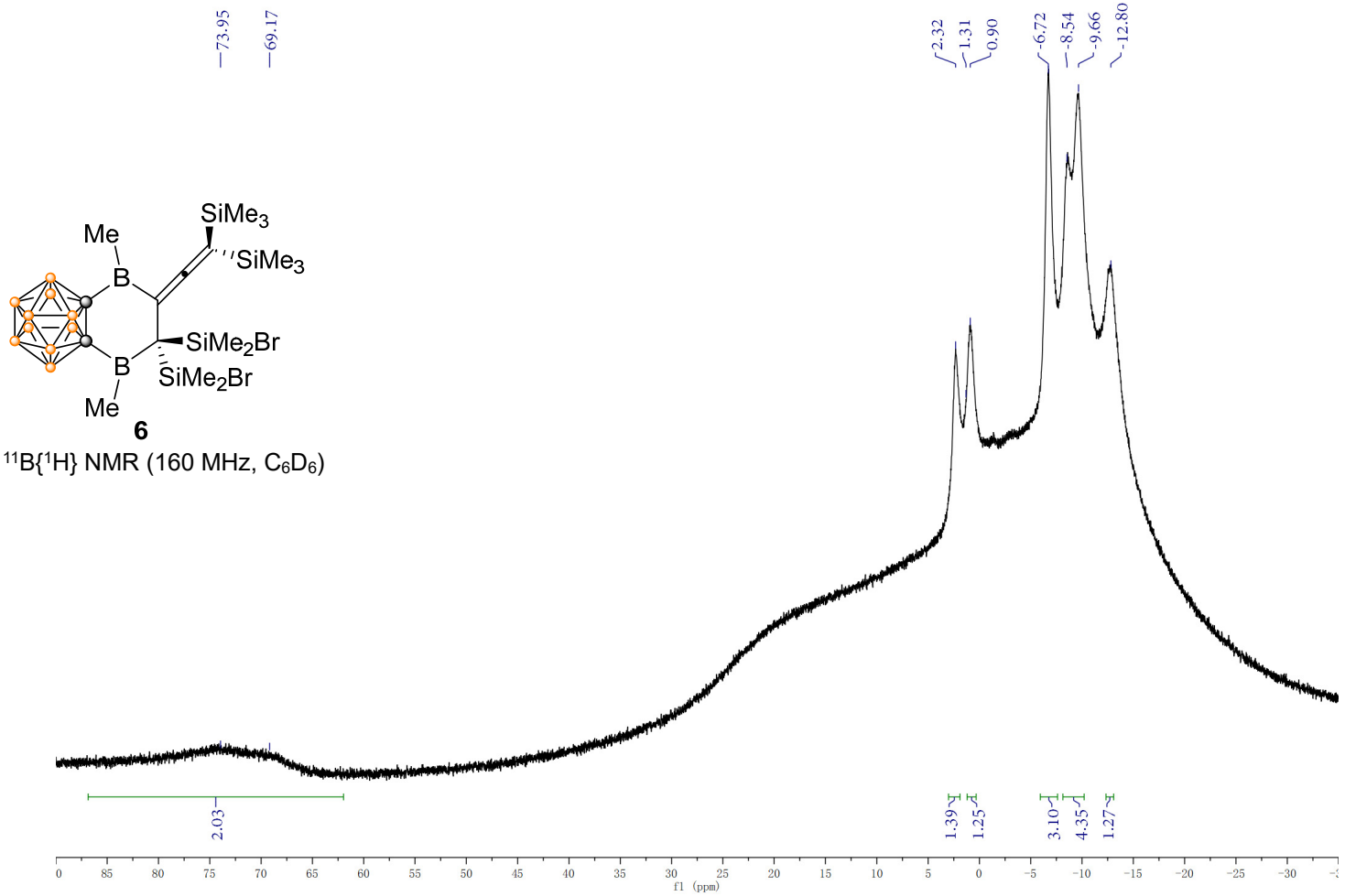


Figure S35. $^{11}B\{^{1}H\}$ NMR spectrum of compound **6**.

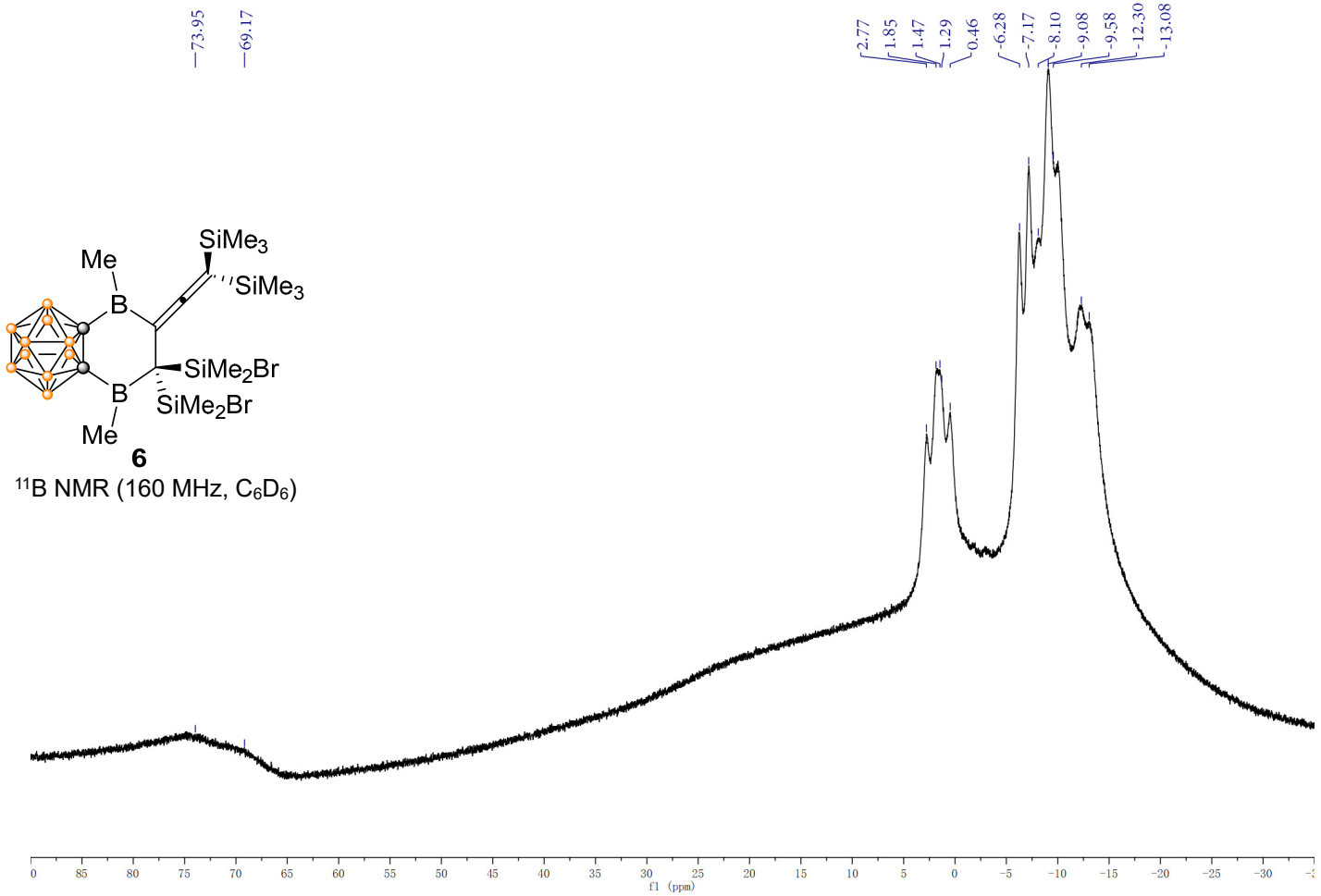


Figure S36. ^{11}B NMR spectrum of compound **6**.

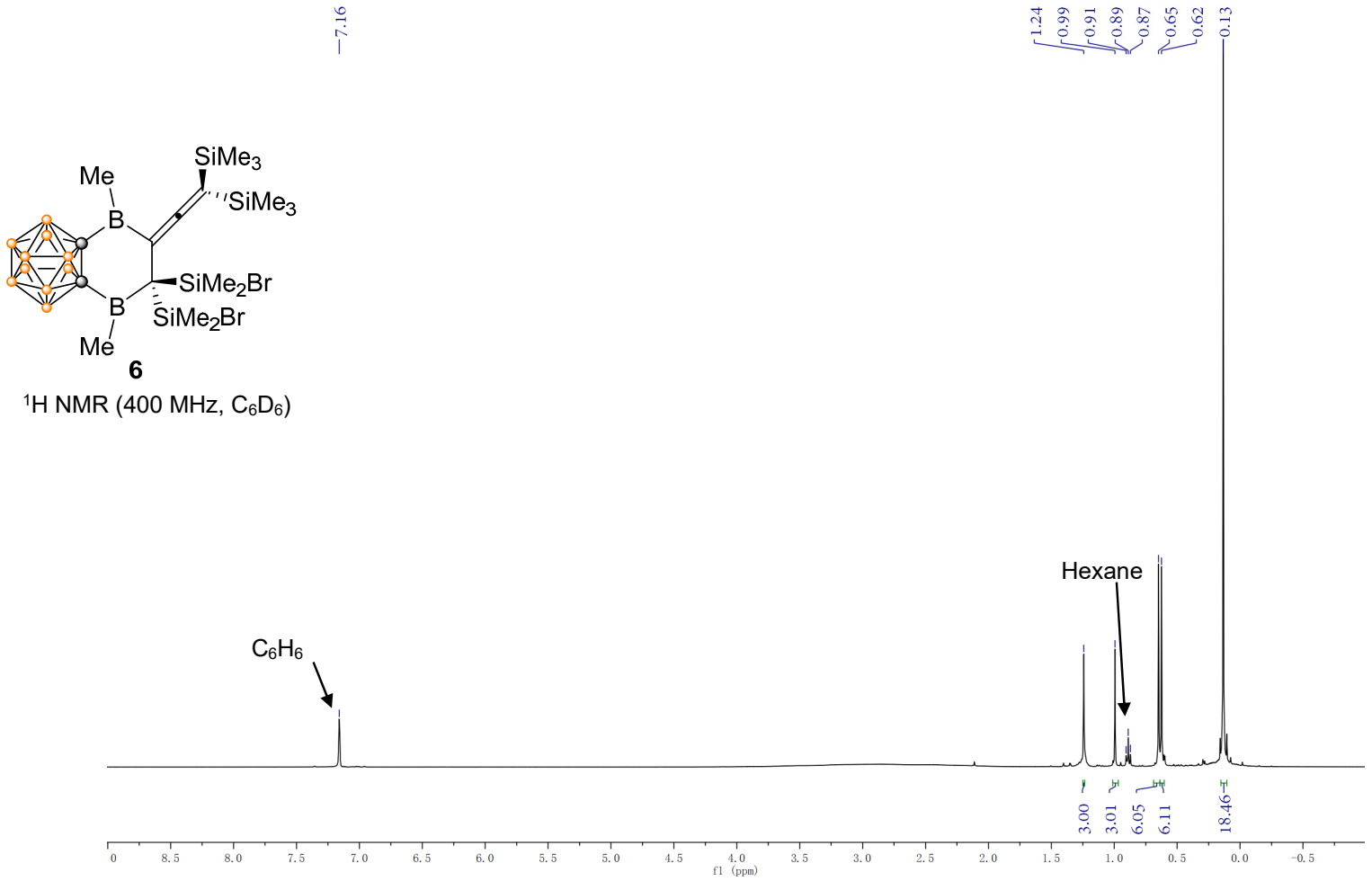


Figure S37. ^{1}H NMR spectrum of compound **6**.

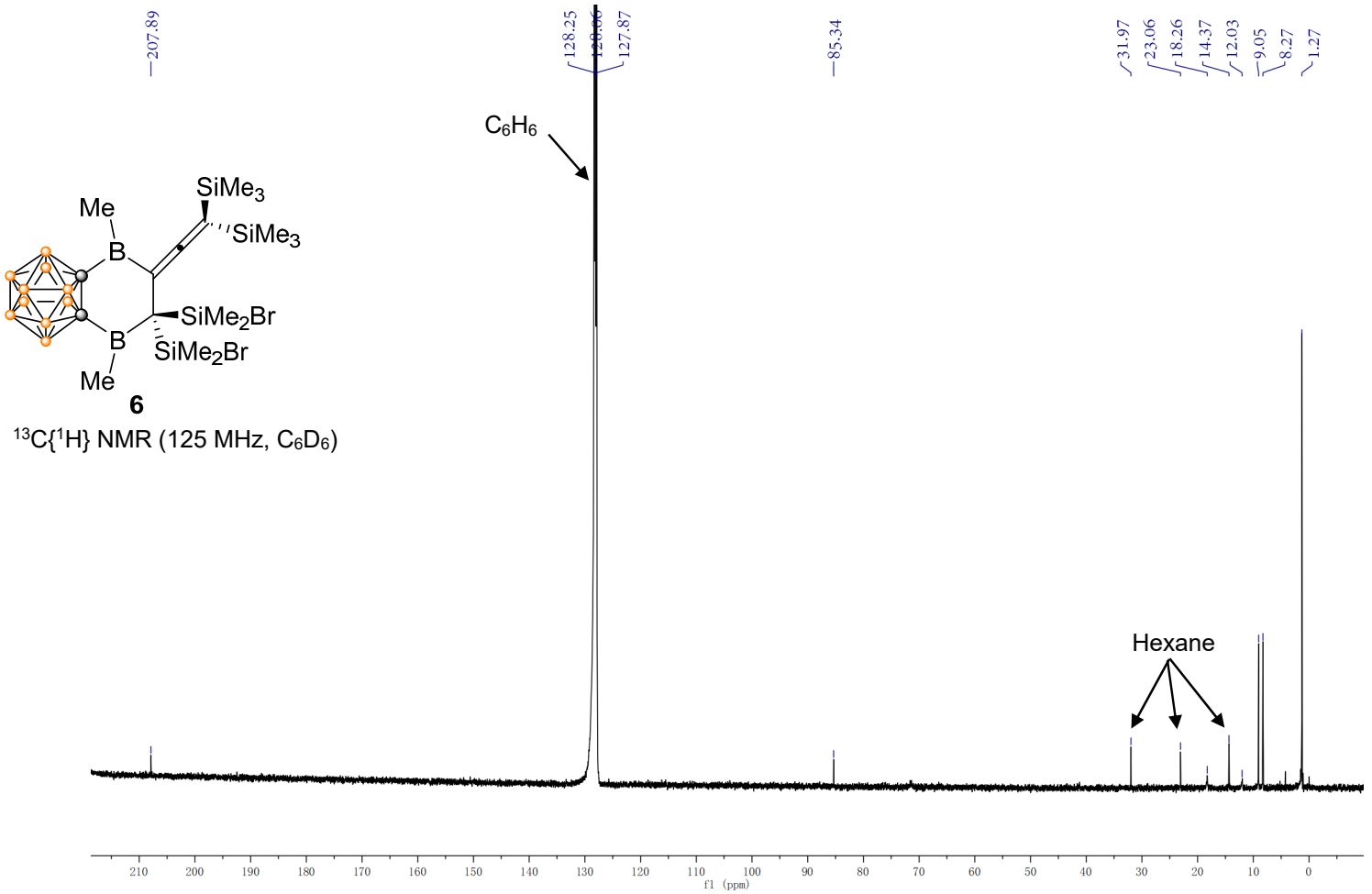


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6**.

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