Supporting Information

Silylium Ion-Mediated Cage Opening Functionalization of *closo*-$B_{10}H_{10}^{2-}$ Salts

Yingying Wang,[a] Hui Han,[a] Jia-Xin Kang,[b] Jiamin Peng,[a] Xiongxiong Lu,[a] Hou-Ji Cao,[b] Zhenxing Liu,*[a] Xuenian Chen*[ab]

[a]College of Chemistry, Zhengzhou University, Zhengzhou, Henan 450001, China

[b]Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China

E-mail: xuenian_chen@zzu.edu.cn liuzhenxing@zzu.edu.cn

Contents Page

1. General Methods and Materials.

All manipulations were carried out on a Schlenk line or in a glovebox filled with high-purity nitrogen. Methanol, ethanol, isopropanol, phenol, butanol, 2-Propanethiol, isobutyl mercaptan, cyclohexyl mercaptan, *p*-toluenethiol, and 4-fluorothiophenol were purchased from Energy Chemical. Hexane, pentane, dichloromethane, and $CDCl_3$ (D, 99.9%) were obtained from Fisher Chemical. $Na_2B_{10}H_{10}$ was purchased from Yuanli Technology (Zhengzhou, China). All reagents were used as received. The ^{11}B NMR and $^{11}B\{^1H\}$ spectra were obtained at a 128 or 193 MHz spectrometer and ^1H NMR and $^1H\{^{11}B\}$ spectra were obtained at a 400 or 600MHz spectrometer. All ^{11}B chemical shifts are referenced to $BF_3{\cdot}OEt_2$ in C_6D_6 (δ = 0.00 ppm), with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual protons from the lock solvents (99.9% $CDCl_3$) and then referenced to $(CH_3)_4Si$ (0.0 ppm). Due to the different types of B-Hs, the integration of certain peaks in the $^1H\{^{11}B\}$ spectrum is not accurate, we use both ^1H and $^1H\{^{11}B\}$ spectra to confirm the structure.

2. Reaction of TMSOTf with $NaBH_4$, NaB_3H_8 and $Na_2B_{10}H_{10}$

The reaction of TMSOTf with $NaBH_4$ in MeCN and THF

In a nitrogen-filled glovebox, $NaBH_4$ (19 mg, 0.5 mmol) was added to a 25 mL Schlenk flask. The flask was then removed from the glovebox and connected with the Schlenk line, followed by an injection of 5 mL of MeCN into the flask. TMSOTf (0.09 mL, 0.5 mmol) was added dropwise to the flask at room temperature and the mixture was allowed to stir for another 2 minutes. The reaction mixture was identified to be $MeCN{\cdot}BH_3$ based on the ^{11}B NMR (Figure S1b). The yield of $MeCN{\cdot}BH_3$ was quantitative, based on ^{11}B NMR and $^{11}B\{^1H\}$ NMR.

^{11}B NMR (128 MHz, MeCN): δ (ppm) -25.20 (q, J = 100.8 Hz).

$^{11}B\{^1H\}$ NMR (128 MHz, MeCN): δ (ppm) -25.20 (s).

Under otherwise same conditions, we obtained $THF{\cdot}BH_3$ in the reaction solution based on ^{11}B NMR and $^{11}B\{^1H\}$ NMR.

^{11}B NMR (128 MHz, THF): δ (ppm) -0.64 (q, J = 106.7 Hz).

$^{11}B\{^1H\}$ NMR (128 MHz, THF): δ (ppm) -0.64 (s).

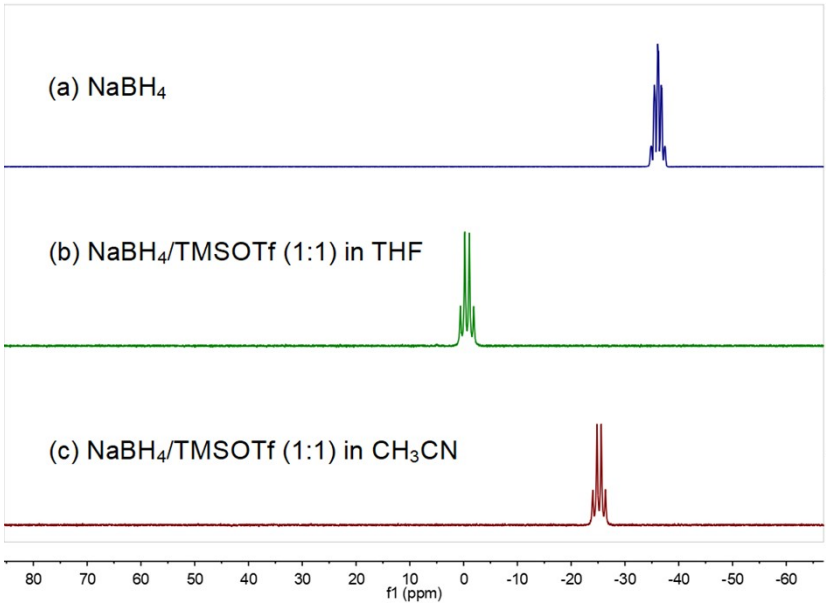


Figure S1. Comparisons of the ^{11}B NMR spectra of (a) $NaBH_4$ in DMSO, (b) TMSOTf and $NaBH_4$ (1:1) in MeCN, (c) TMSOTf and $NaBH_4$ (1:1) in THF

The reaction of TMSOTf with NaB_3H_8 in MeCN and THF

In a nitrogen-filled glovebox, NaB_3H_8·dioxane (15.2 mg, 0.1 mmol) was added to a 10 mL Schlenk flask. The flask was then removed from the glovebox and connected with the Schlenk line, followed by an injection of 1 mL of MeCN into the flask. TMSOTf (18 μL, 0.1 mmol) was added dropwise to the flask and the mixture was allowed to stir for about 2 minutes. The reaction mixture was identified to be MeCN·B_3H_7 based on the ^{11}B NMR (Figure S2b). The yield of MeCN·B_3H_7 was quantitative, based on ^{11}B NMR and $^{11}B\{^1H\}$ NMR.

^{11}B NMR (128 MHz, MeCN): δ (ppm) -6.91 (*br*, 2B, based-B), -34.44 (*br*, B, top-B).

$^{11}B\{^1H\}$ NMR (128 MHz, MeCN): δ (ppm) -6.91, -34.44.

Under otherwise same conditions, we obtained THF·B_3H_7 in the reaction solution based on ^{11}B NMR and $^{11}B\{^1H\}$ NMR.

^{11}B NMR (128 MHz, THF): δ (ppm) -7.13 (*br*, 2B, based-B), -12.01 (*br*, B, top-B).

$^{11}B\{^1H\}$ NMR (128 MHz, CH_3CN): δ (ppm) -7.13, -12.01.

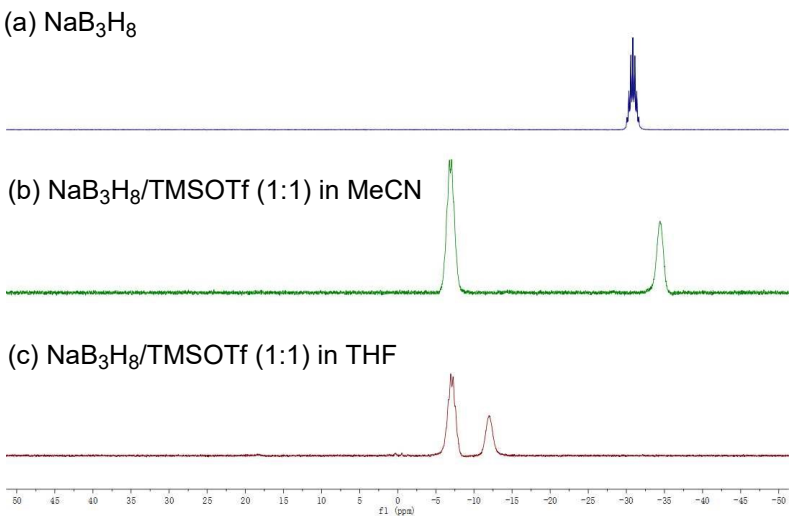


Figure S2. Comparisons of the ^{11}B NMR spectra of (a) NaB_3H_8 in THF, (b) TMSOTf and NaB_3H_8 (1:1) in MeCN, (c) TMSOTf and NaB_3H_8 (1:1) in THF

The reaction of TMSOTf with $Na_2B_{10}H_{10}$ in MeCN and THF

In a nitrogen-filled glovebox, $Na_2B_{10}H_{10}$ (8.3 mg, 0.05 mmol) was added to a 10 mL Schlenk flask. The flask was then removed from the glovebox and connected with the Schlenk line, followed by an injection of 1 mL of MeCN into the flask. TMSOTf (9 μL, 0.05 mmol) was added dropwise to the flask and stirred for about 2 minutes. ^{11}B NMR of the reaction solution is shown in Figure S3b. When THF is used as the solvent, ^{11}B NMR of the reaction solution is shown in Figure S3c.

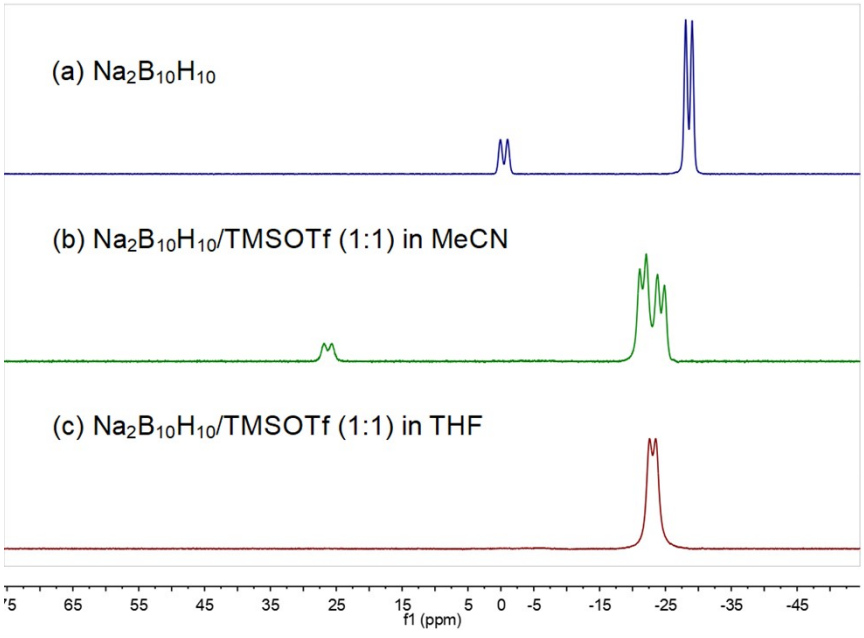
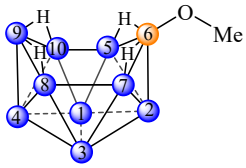


Figure S3. Comparisons of the ^{11}B NMR spectra of (a) $Na_2B_{10}H_{10}$ in THF, (b) TMSOTf and $Na_2B_{10}H_{10}$ (1:1) in MeCN, (c) TMSOTf and $Na_2B_{10}H_{10}$ (1:1) in THF

3. General Procedures and Spectral Date of Compounds.

Preparation of 6-CH_3O-$B_{10}H_{13}$ (1)[1] from *closo*-$Na_2B_{10}H_{10}$.



A mixture containing $Na_2B_{10}H_{10}$ (33.2 mg, 0.2 mmol), methanol (19.2 mg, 0.6 mmol), and TMSOTf (89 mg, 0.4 mmol) in 5 mL of hexane was stirred at room temperature for 5 h. The reaction solution was filtered, and another 5 mL hexane was used to extract the remaining residue. The solutions were combined, and the solvent was evaporated under vacuum at 0 ℃ to give **1** (26.5 mg, 85%) as a clear oil.

^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) 26.36 (s, 1B), 4.58-2.96 (m, 5B), -15.74 (d, J = 155.6 Hz, 2B), -32.14 (d, J = 156.3 Hz, 1B), -43.81 (d, J = 156.3 Hz, 1B).

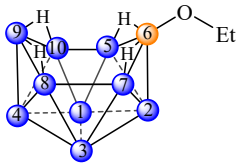
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ (ppm) 26.35 (1B), 4.65 (1B), 4.21 (2B), 3.36 (2B), -15.74 (2B), -32.14 (1B), -43.82 (1B).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 3.88 (s, 3H). Hydrides were not integrated due to multiple B-H couplings.

^{1}H{^{11}B} NMR (600 MHz, $CDCl_3$) δ (ppm) 3.89 (s, 3CH), 3.80 (s, 1BH), 3.21 (s, 4BH), 2.13 (s, 2BH), 1.40 (s, 1BH), 0.22 (s, 1BH), -0.54 (s, 2BHB), -1.83 (s, 2BHB).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 58.50.

Preparation of 6-C_2H_5O-$B_{10}H_{13}$ (2)[1] from *closo*-$Na_2B_{10}H_{10}$.



A mixture containing $Na_2B_{10}H_{10}$ (83 mg, 0.5 mmol), ethanol (69 mg, 1.5 mmol), and TMSOTf (222 mg, 1 mmol) in 10 mL of hexane was stirred at room temperature for 6 h. The reaction solution was filtered, and another 5 mL hexane was used to extract the remaining residue. The solutions were combined, and the solvent was evaporated under vacuum at 0 ℃ to give **2** (57 mg, 67%) as a clear oil.

^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) 25.89 (s, 1B), 4.24-2.88 (m, 5B), -16.20 (d, *J* = 145.6 Hz, 2B), -32.06 (d, *J* = 155.2 Hz, 1B), -44.04 (d, *J* = 152.6 Hz, 1B).

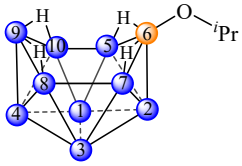
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ (ppm) 25.91 (1B), 4.23(1B), 3.88 (2B), 3.25 (2B), -16.19 (2B), -32.06 (1B), -44.03 (1B).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 4.15 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 3H). Hydrides were not integrated due to multiple B-H couplings.

^{1}H{^{11}B} NMR (600 MHz, $CDCl_3$) δ (ppm) 4.15 (q, *J* = 6.9 Hz, 2CH), 3.79 (s, 1BH), 3.20 (s, 4BH), 2.09 (s, 2BH), 1.39-1.37 (m, 1BH, 3CH), 0.20 (s, 1BH), -0.50 (s, 2BHB), -1.84 (s, 2BHB).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 67.41, 16.51.

Preparation of 6-$(CH_3)_2$CHO-$B_{10}H_{13}$ (3) from *closo*-$Na_2B_{10}H_{10}$.



A mixture containing $Na_2B_{10}H_{10}$ (33.2 mg, 0.2 mmol), isopropanol (36 mg, 0.6 mmol), and TMSOTf (89 mg, 0.4 mmol) in 10 mL of hexane was stirred at room temperature for 4 h. The reaction solution was filtered, and another 5 mL hexane was used to extract the remaining residue. The solutions were combined, and the solvent was evaporated under vacuum at 0 ℃ to give **3** (24 mg, 66%) as a light-yellow oil.

^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) 25.73 (s, 1B), 4.01-3.33 (m, 5B), -16.52 (d, *J* = 148.9 Hz, 2B), -31.81 (d, *J* = 152.9 Hz, 1B), -44.11 (d, *J* = 158.9 Hz, 1B).

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ (ppm) 25.72 (1B), 4.02-3.65 (m, 5B), -16.56 (2B), -31.81 (1B), -44.11 (1B).

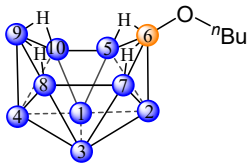
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 4.52-4.46 (m, 1H), 1.35 (d, *J* = 6.1 Hz, 6H). Hydrides were not integrated due to multiple B-H couplings.

^{1}H{^{11}B} NMR (600 MHz, $CDCl_3$) δ (ppm) 4.52-4.46 (m, 1CH), 3.78 (s, 1BH), 3.19 (s, 4BH), 2.05 (s, 2BH), 1.41 (s, 1BH), 1.35 (d, *J* = 6.1 Hz, 6CH), 0.19 (s, 1BH), -0.46 (s, 2BHB), -1.83 (s, 2BHB).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 74.90, 23.66.

HRMS (ESI): $[M-H]^-$: calculated for $^{11}B_{10}C_3H_{19}O$: 181.2366; found: 181.2363.

Preparation of 6-$CH_3(CH_2)_3O$-$B_{10}H_{13}$ (4)[2] from *closo*-$Na_2B_{10}H_{10}$.



A mixture containing $Na_2B_{10}H_{10}$ (33.2 mg, 0.2 mmol), n-butanol (44.4 mg, 0.6 mmol), and TMSOTf (89 mg, 0.4 mmol) in 10 mL of hexane was stirred at room temperature for 7 h. The reaction solution was filtered, and another 5 mL hexane was used to extract the remaining residue. The solutions were combined, and the solvent was evaporated under vacuum at 0 ℃ to give a yellow oil. The flask with the yellow oil was then put in a -78 ºC cold bath and 1 mL pentane was added to wash the oil for one time. The pentane was removed under vacuum to obtain **4** (36 mg, 92%) as an oil.

^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) 26.13 (s, 1B), 4.34-3.02 (m, 5B), -16.03 (d, J = 145.6 Hz, 2B), -31.93 (d, J = 154.8 Hz, 1B), -43.93 (d, J = 155.9 Hz, 1B).

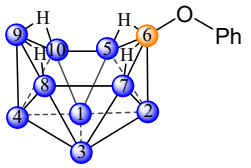
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ (ppm) 26.16 (1B), 4.38 (1B), 3.97 (2B), 3.40 (2B), -16.06 (2B), -31.94 (1B), -43.93 (1B).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 4.07 (t, J = 6.5 Hz, 2H), 1.72-1.68 (m, 2H), 1.46-1.40 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). Hydrides were not integrated due to multiple B-H couplings.

^{1}H{^{11}B} NMR (600 MHz, $CDCl_3$) δ (ppm) 4.07 (t, J = 6.5 Hz, 2CH), 3.77 (s, 1BH), 3.20 (s, 4BH), 2.09 (s, 2BH), 1.72-1.68 (m, 2CH), 1.46-1.39(m, 1BH, 2CH), 0.96 (t, J = 7.4 Hz, 3CH), 0.20 (s,1BH), -0.49 (s, 2BHB), -1.84 (s, 2BHB).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 71.45, 32.83, 18.86, 13.69.

Preparation of 6-PhO-$B_{10}H_{13}$ (5)[2] from closo-$Na_2B_{10}H_{10}$.



A mixture containing $Na_2B_{10}H_{10}$ (83 mg, 0.5 mmol), phenol (0.141 g, 1.5 mmol), and TMSOTf (222 mg, 1 mmol) in 10 mL of hexane was stirred at room temperature for 7 h. The reaction solution was filtered, and another 5 mL hexane was used to extract the remaining residue. The solutions were combined, and the solvent was evaporated under vacuum at 0 ℃ to give a light-yellow oil. The flask

with the yellow oil was then put in a -78 °C cold bath and 1 mL pentane was added to wash the oil for one time. The pentane was removed under vacuum to obtain **5** (95 mg, 88%) as a white solid.

^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) 23.52 (s, 1B), 6.42-4.70 (m, 3B), 3.10 (d, *J* = 153.0 Hz, 2B), -12.94 (d, *J* = 154.8 Hz, 2B), -32.30 (d, *J* = 158.3 Hz, 1B), -42.98 (d, *J* = 156.1 Hz, 1B).

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ (ppm) 23.55 (1B), 6.02 (1B), 5.08 (2B), 3.12 (2B), -12.94 (2B), -32.30 (1B), -42.98 (1B).

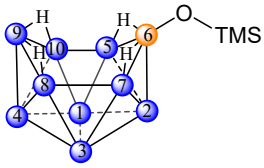
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.36 (t, *J* = 8.0 Hz, 2H), 7.17-7.13 (m, 3H). Hydrides were not integrated due to multiple B-H couplings.

^{1}H{^{11}B} NMR (600 MHz, $CDCl_3$) δ (ppm) 7.36 (t, *J* = 8.0 Hz, 2CH), 7.17-7.13 (m, 3CH), 3.87 (s, 1BH), 3.31 (s, 2BH), 3.21 (s, 2BH), 2.30 (s, 2BH), 1.58-1.57 (m, 1BH), 0.32 (s, 1BH), -0.32 (s, 2BHB), -1.75 (s, 2BHB).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 155.31, 129.99, 124.40, 119.09.

HRMS (ESI): $[M+H]^+$: calculated for $^{10}B_2{}^{11}B_8C_6H_{19}O$: 215.2436; found: 215.2435.

Preparation of 6-$(CH_3)_3SiO$-$B_{10}H_{13}$ (6)[3] from *closo*-$Na_2B_{10}H_{10}$.



A mixture containing $Na_2B_{10}H_{10}$ (83 mg, 0.5 mmol), H_2O (27 mg, 1.5 mmol), and TMSOTf (222 mg, 1 mmol) in 10 mL of hexane was stirred at room temperature for 3.5 h. The reaction solution was filtered, and another 5 mL hexane was used to extract the remaining residue. The solutions were combined, and the solvent was evaporated under vacuum at 0 ℃ to give **6** (89.7 mg, 85%) as a needle-like solid.

^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) 24.23 (s, 1B), 5.27-2.75 (m, 5B), -14.20 (d, *J* = 150.7 Hz, 2B), -32.72 (d, *J* = 154.8 Hz, 1B), -44.54 (d, *J* = 152.7 Hz, 1B).

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ (ppm) 24.23 (1B), 4.88 (1B), 3.71 (2B), 3.13 (2B), -14.28 (2B), -32.69 (1B), -44.52 (1B).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 0.29 (s, 9CH). Hydrides were not integrated due to multiple B-H couplings.

$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$) δ (ppm) 3.79 (s, 1BH), 3.16 (s, 4BH), 2.10 (s, 2BH), 1.31 (s, 1BH), 0.29 (s, 9CH), 0.15 (s, 1BH), -0.40 (s, 2BHB), -1.82 (s, 2BHB).

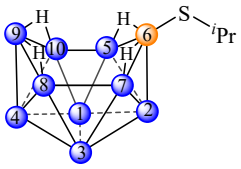
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 0.00.

General Procedure for Syntheses of 6-RS-$B_{10}H_{13}$ (7 – 9).

A mixture containing $Na_2B_{10}H_{10}$, thiols, and TMSOTf in hexane was stirred for different of time (18 h for Comp. 7, 7 h for Comp. 8, and 40 h for Comp. 9) at room temperature. The reaction solution was filtered, and another 5 mL hexane was used to extract the remaining residue. The solutions were combined, and the solvent was evaporated under vacuum. All products were chromatographed over silica gel using a 10 % dichloromethane in PE as an eluent.

6-$(CH_3)_2CHS$-$B_{10}H_{13}$ (**7**). $Na_2B_{10}H_{10}$ (33.2 mg, 0.2 mmol), 2-propanethiol (45.6 mg, 0.6 mmol), TMSOTf (89 mg, 0.4 mmol) and hexane (5 mL).

For **7**: colorless oil, 19.8 mg (0.1 mmol, 50%).



^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) 24.55 (s, 1B), 8.50 (d, J = 148.6 Hz, 2B), 7.01 (d, J = 158.3 Hz, 1B), 2.19 (d, J = 158.8 Hz, 2B), -7.88 (d, J = 151.6 Hz, 2B), -30.34 (d, J = 157.8 Hz, 1B), -38.83 (d, J = 157.7 Hz, 1B).

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ (ppm) 24.56 (1B), 8.50 (2B), 6.97 (1B), 2.19 (2B), -7.86 (2B), -30.33 (1B), -38.84 (1B).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 3.47-3.42 (m, 1H), 1.44 (d, J = 6.7 Hz, 6H). Hydrides were not integrated due to multiple B-H couplings.

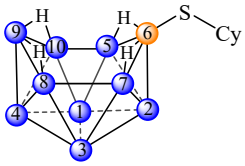
$^{1}H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$) δ (ppm) 3.85 (s, 1BH), 3.52 (s, 2BH), 3.47-3.43 (m, 1CH), 3.15 (s, 2BH), 2.59 (s, 2BH), 1.44 (d, J = 6.7 Hz, 6CH), 1.36 (s, 1BH), 0.48 (s, 1BH), -0.62 (s, 2BHB), -1.88 (s, 2BHB).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 38.51, 25.76.

HRMS (ESI): $[M-H]^-$: calculated for $^{10}B_2{}^{11}B_8C_3H_{19}S$: 195.2207; found: 195.2209.

6-$(CH_2)_5CHS$-$B_{10}H_{13}$ (**8**). $Na_2B_{10}H_{10}$ (0.083 g, 0.5 mmol), cyclohexyl mercaptan (174 mg, 1.5 mmol), TMSOTf (222 mg, 1 mmol) and hexane (10 mL).

For **8**: white solid, 59 mg (0.25 mmol, 50%).



^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 24.71 (s, 1B), 8.96-6.21 (m, 3B), 2.16 (d, *J* = 159.2 Hz, 2B), -8.03 (d, *J* = 151.5 Hz, 2B), -30.20 (d, *J* = 155.1 Hz, 1B), -38.94 (d, *J* = 155.0 Hz, 1B).

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ (ppm) 24.70 (1B), 8.39 (2B), 6.87 (1B), 2.17 (2B), -8.05 (2B), -30.22 (1B), -38.93 (1B).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 3.26-3.21 (m, 1H), 2.09 (d, *J* = 12.0 Hz, 2H), 1.79 (d, *J* = 12.8 Hz, 2H), 1.66-1.28 (m, 6H). Hydrides were not integrated due to multiple B-H couplings.

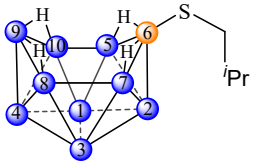
^{1}H{^{11}B} NMR (600 MHz, $CDCl_3$) δ (ppm) 3.85 (s, 1BH), 3.51 (s, 2BH), 3.21-3.19 (m, 1CH), 3.14 (s, 2BH), 2.56 (s, 2BH), 2.09 (d, *J* = 12.0 Hz, 2CH), 1.79 (d, *J* = 12.8 Hz, 2CH), 1.62 (d, *J* = 11.8 Hz, 1CH), 1.53-1.48 (m, 2CH), 1.40-1.26 (m, 1BH, 3CH), 0.47 (s, 1BH), -0.60 (s, 2BHB), -1.88 (s, 2BHB).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 46.58, 35.70, 26.13, 25.37.

HRMS (ESI): $[M-H]^-$: calculated for $^{10}B_2{}^{11}B_8C_6H_{23}S$: 235.2521; found: 235.2523.

6-$(CH_3)_2CHCH_2S$-$B_{10}H_{13}$ (**9**). $Na_2B_{10}H_{10}$ (33.2 mg, 0.2 mmol), isobutyl mercaptan (54 mg, 0.6 mmol), TMSOTf (89 mg, 0.4 mmol) and hexane (10 mL).

For **9**: colorless oil, 15.3 mg (0.072 mmol, 36%).



^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 25.05 (s, 1B), 9.04-6.41 (m, 3B), 2.19 (d, *J* = 153.2 Hz, 2B), -7.80 (d, *J* = 155.4 Hz, 2B), -30.40 (d, *J*= 160.3 Hz, 1B), -38.98 (d, *J* = 159.0 Hz, 1B).

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ (ppm) 25.05 (1B), 8.43 (2B), 6.93 (1B), 2.13 (2B), -7.80 (2B), -30.44 (1B), -38.97 (1B).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.80 (d, *J* = 6.7 Hz, 2H), 1.97-1.87 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 6H). Hydrides were not integrated due to multiple B-H couplings.

$^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$) δ (ppm) 3.86 (s, 1BH), 3.52 (s, 2BH), 3.15 (s, 2BH), 2.80 (d, *J* = 6.7 Hz, 2CH), 2.59 (s, 2BH), 1.97-1.87 (m, 1CH), 1.35-1.33 (m, 1BH), 1.04 (d, *J* = 6.6 Hz, 6CH), 0.48-0.47 (m, 1BH), -0.65 (s, 2BHB), -1.89 (s, 2BHB).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 41.69, 30.14, 21.72.

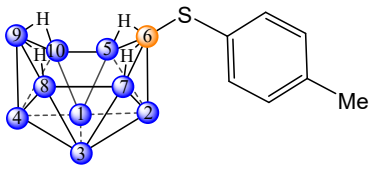
HRMS (ESI): $[M-H]^-$: calculated for $^{10}B_2{}^{11}B_8C_4H_{21}S$: 209.2364; found: 209.2364.

Preparation of 6-*p*-$CH_3C_6H_4S$-$B_{10}H_{13}$ (10) and 6-*p*-FC_6H_4S-$B_{10}H_{13}$ (11) from *closo*-$Na_2B_{10}H_{10}$.

A mixture containing $Na_2B_{10}H_{10}$, thiophenols, and TMSOTf in hexane was stirred for different of time (40 h for comp. 10 and 34 h for comp. 11) at room temperature. The reaction solution was filtered, and another 5 mL hexane was used to extract the remaining residue. The solutions were combined, and the solvent was evaporated under vacuum. All products were chromatographed over silica gel using PE as eluent.

6-*p*-$CH_3C_6H_4S$-$B_{10}H_{13}$ (**10**). $Na_2B_{10}H_{10}$ (33.2 mg, 0.2 mmol), p-toluenethiol (74.4 mg, 0.6 mmol), TMSOTf (89 mg, 0.4 mmol) and hexane (5 mL).

For **10**: light yellow solid, 28.7 mg (0.116 mmol, 58%).



^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 24.55 (s, 1B), 9.50-7.39 (m, 3B), 1.90 (d, *J* = 166.1 Hz, 2B), -6.02 (d, *J* = 151.6 Hz, 2B), -31.03 (d, *J* = 157.8 Hz, 1B), -38.62 (d, *J* = 157.7 Hz, 1B).

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ (ppm) 23.81 (1B), 9.01 (2B), 7.99 (1B), 2.00 (2B), -5.99 (2B), -30.98 (1B), -38.52 (1B).

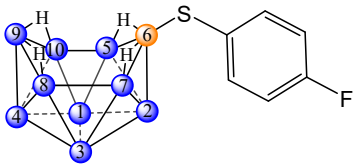
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H). Hydrides were not integrated due to multiple B-H couplings.

$^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (d, *J* = 8.1 Hz, 2CH), 7.15 (d, *J* = 7.9 Hz, 2CH), 3.86 (s, 1BH), 3.51 (s, 2BH), 3.08 (s, 2BH), 2.48 (s, 2BH), 2.35 (s, 3CH), 1.37-1.34 (m, 1BH), 0.48-0.47 (m, 1BH), -0.59 (s, 2BHB), -1.90 (s, 2BHB).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 138.67, 134.15, 130.41, 127.32, 21.15.

6-*p*-FC_6H_4S-$B_{10}H_{13}$ (**11**). $Na_2B_{10}H_{10}$ (33.2 mg, 0.2 mmol), 4-fluorothiophenol (76.2 mg, 0.6 mmol), TMSOTf (89 mg, 0.4 mmol) and hexane (5 mL).

For **11**: light yellow solid, 15.7 mg (0.063 mmol, 31%).



^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 23.35 (s, 1B), 9.69-7.65 (m, 3B), 1.97 (d, *J* = 159.9 Hz, 2B). -5.82 (d, *J* = 151.6 Hz, 2B), -31.16 (d, *J* = 157.8 Hz, 1B), -38.46 (d, *J* = 157.7 Hz, 1B).

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ (ppm) 23.31 (1B), 9.13 (2B), 8.28 (1B), 1.97 (2B), -5.82 (2B), -31.16 (1B), -38.47 (1B).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50-7.53 (m, 2H), 7.08-7.03 (m, 2H). Hydrides were not integrated due to multiple B-H couplings.

^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50-7.53 (m, 2H), 7.08-7.03 (m, 2H), 3.89 (s, 1BH), 3.52 (s, 2BH), 3.09 (s, 2BH), 2.48 (s, 2BH), 1.35-1.32 (m, 1BH), 0.51-0.49 (m, 1BH), -0.64 (s, 2BHB), -1.89 (s, 2BHB).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 163.04 (d, *J* = 249.2 Hz), 136.29 (d, *J* = 8.4 Hz), 125.94 (d, *J* = 3.3 Hz), 116.81 (d, *J* = 22.1 Hz).

HRMS (ESI): $[M-H]^-$: calculated for $^{11}B_{10}C_6H_{16}FS$: 249.1887; found: 249.1892.

4. Mechanistic studies

(a) Variable-Temperature NMR experiments.

$Na_2B_{10}H_{10}$ (4.1 mg, 0.025 mmol) was added to a 10 mL reaction flask in a glove box, then 1 mL of CD_3CN was injected. TMSOTf (5 μL, 0.025 mmol) was added dropwise to the flask and stirred for about 2 minutes. The reaction solution was monitored by $^{1}H\{^{11}B\}$ NMR at room temperature, 30 °C, 40 °C, 50 °C, and 60 °C, respectively. The spectra were also monitored at 50 °C, 40 °C, 30 °C, and room temperature when the temperature cooled down (from up to down, Fig. **S4**).

The spectra showed similar results to Prof. Shore's report when the mixture was heated (1:5:4 peaks to one single peak). However, the unidentified peaks around 0 ppm and -30 to -20 ppm indicated decomposition when the mixture was cooled down. The structure of the decomposed compounds was not clear at this moment. Besides, the single peak at 60 °C went back to 1:5:4 peaks when cooled down, suggesting the reversibility of the reaction between TMSOTf and $Na_2B_{10}H_{10}$.

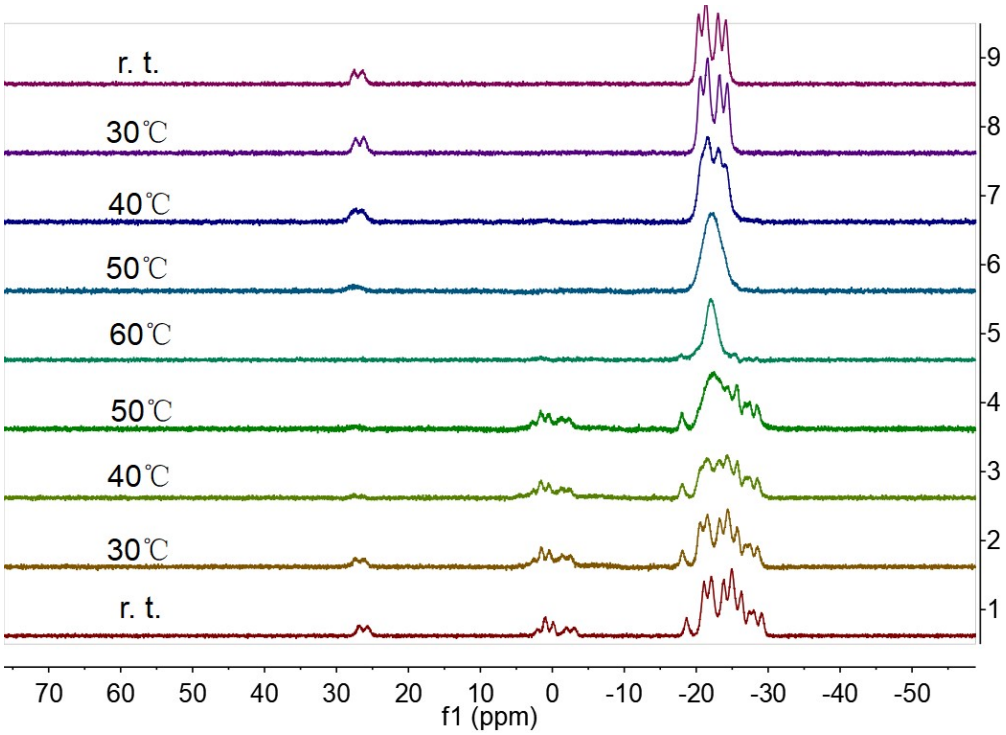


Figure S4. $^{11}B\{^{1}H\}$ Variable-Temperature NMR spectra of the reaction mixture (TMSOTf/$Na_2B_{10}H_{10}$ = 1:1) in CD_3CN

(b) ^{29}Si NMR spectra of TMSOTf under different conditions.

For figure S5a, pure TMSOTf was added to the NMR tube and measured. For figures S5b-d, TMSOTf (222 mg, 1.0 mmol) was added to an NMR tube containing 0.6 mL solvents (hexane for 5b, MeCN for 5c, and THF for 5d). All the NMR spectra were measured at room temperature.

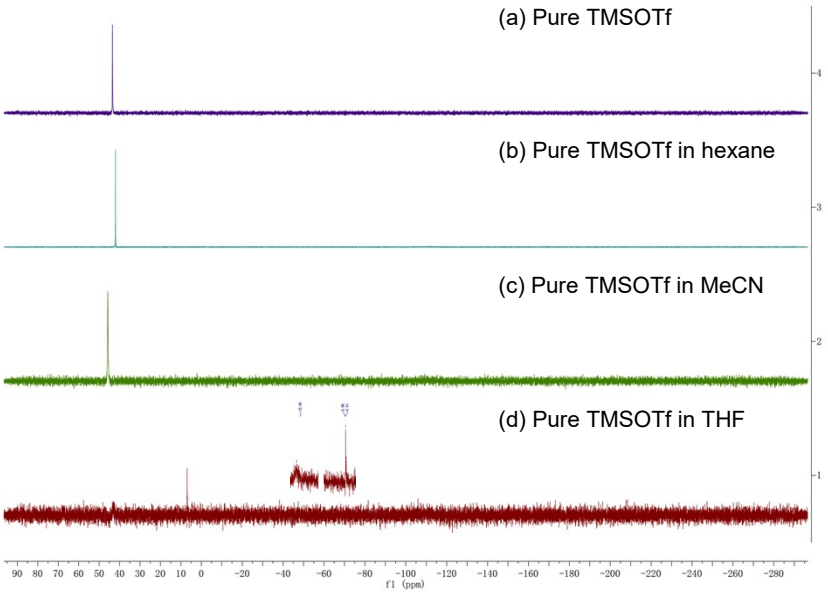
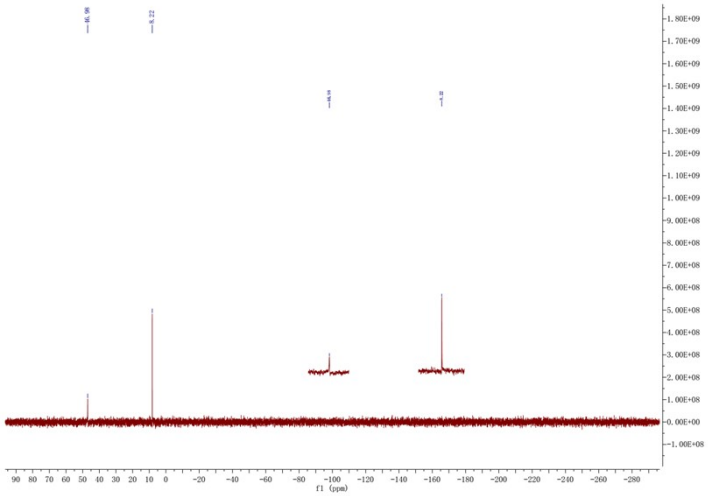


Figure S5. ^{29}Si NMR spectra of TMSOTf under different conditions

(c) ^{29}Si NMR spectra of TMSOTf :Na2B10H10 (1:1) under different conditions.

$Na_2B_{10}H_{10}$ (49.8 mg, 0.03 mmol) was added to a NMR tube. Solvents (0.6 mL, MeCN for 6a and THF for 6b) and TMSOTf (66.7 mg, 0.03 mmol) were added successively. The mixture was shaken with hands for about 2 minutes. All the NMR spectra were measured at room temperature.

(a) TMSOTf/$Na_2B_{10}H_{10}$ (1:1) in MeCN



(b) TMSOTf/$Na_2B_{10}H_{10}$ (1:1) in THF

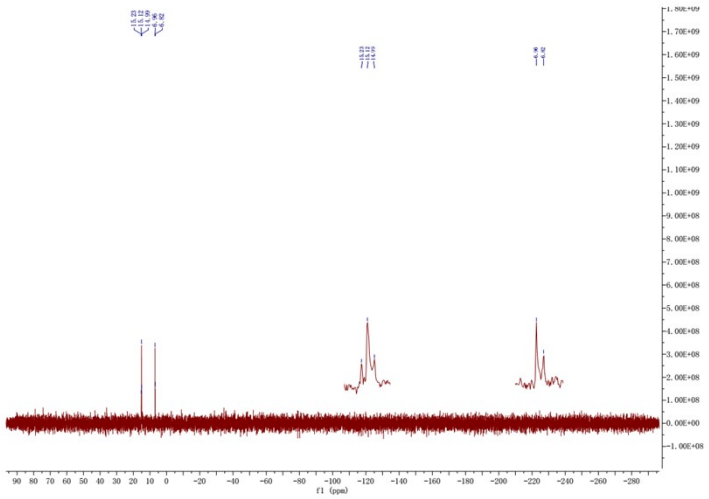


Figure S6. ^{29}Si NMR spectra of TMSOTf:$Na_2B_{10}H_{10}$ (1:1) with different solvents

Preparation of 6-CD_3O-$B_{10}H_{10}D_3$ from *closo*-$Na_2B_{10}H_{10}$.

A mixture containing $Na_2B_{10}H_{10}$ (0.0332 g, 0.2 mmol), CD_3OD (21.6 mg, 0.6 mmol), and TMSOTf (89 mg, 0.4 mmol) in 5 mL hexane was stirred at room temperature for 5 h. The reaction solution was filtered, and another 5 mL hexane was used to extract the remaining residue. The solutions were combined, and the solvent was evaporated under vacuum at 0 ℃ to give 6-CD_3O-$B_{10}H_{10}D_3$ (28.2 mg, 88%) as a clear oil.

The yield calculation was based on the assumed structure with 3 bridging D atoms, which is the most possible structure.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 26.28 (s, 1B), 4.72-2.71 (m, 5B), -15.78 (d, *J* = 132.3 Hz, 2B), -32.22 (d, *J* = 148.9 Hz, 1B), -43.90 (d, *J* = 148.4 Hz, 1B).

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ (ppm) 26.23 (1B), 4.18 (3B), 3.26 (2B), -15.80 (2B), -32.27 (1B), -43.91 (1B).

^{1}H NMR (400 MHz, $CDCl_3$) Hydrides were not integrated due to multiple B-H couplings.

^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$) δ (ppm) 3.79 (s, 1BH), 3.20 (s, 4BH), 2.12 (s, 2BH), 1.38 (s, 1BH), 0.21 (s, 1BH), -0.56 (s, BHB), -1.85 (s, BHB).

^{2}H NMR (61 MHz, $CHCl_3$): δ (ppm) 3.88 (s, CD_3), -0.57 (s, B^{2}HB), -1.93 (s, B^{2}HB).

5. References

[1] W. C. Ewing, P. J. Carroll, L. G. Sneddon, *Inorg. Chem.* **2011**, *50*, 4054-4064.

[2] M. F. Hawthorne, J. J. Miller, *J. Am. Chem. Soc.* **1960**, *82*, 500-500.

[3] R. E. Loffredo, L. F. Drullinger, J. A. Slater, C. A. Turner, A. D. Norman, *Inorg. Chem.* **1976**, *15*, 478-480.

6. NMR Spectra

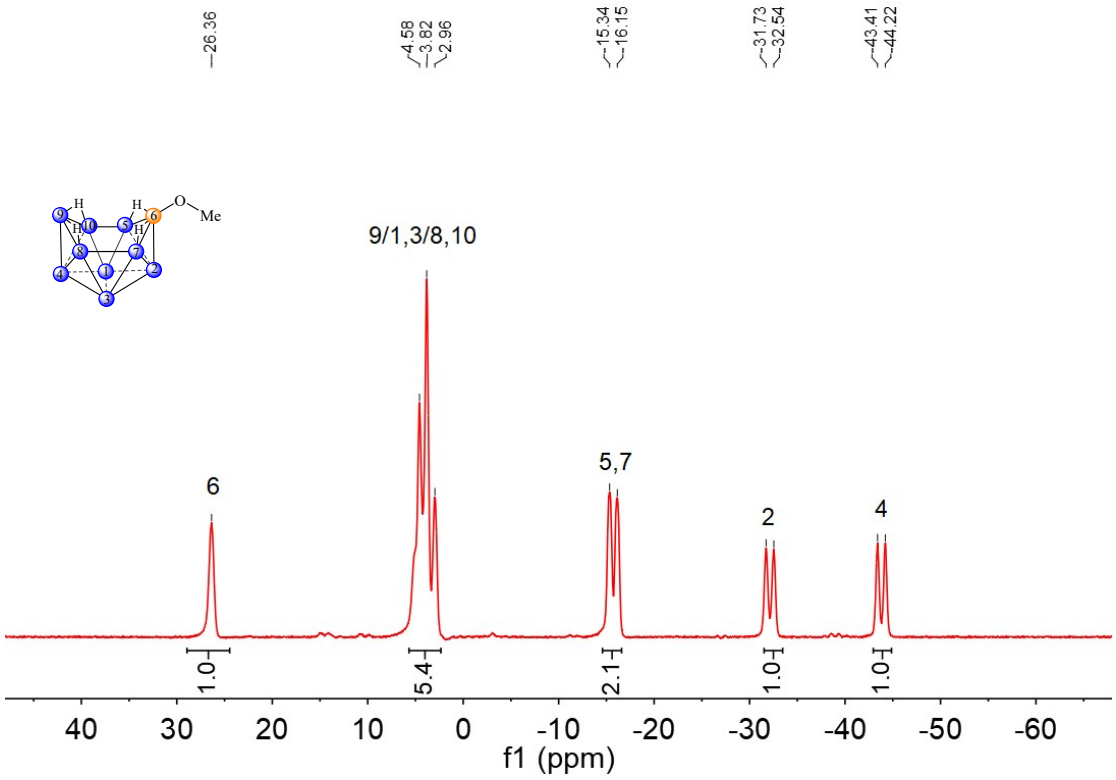


Figure S7. ^{11}B NMR spectrum of *nido*-6-CH_3O-$B_{10}H_{13}$ (**1**) in $CDCl_3$

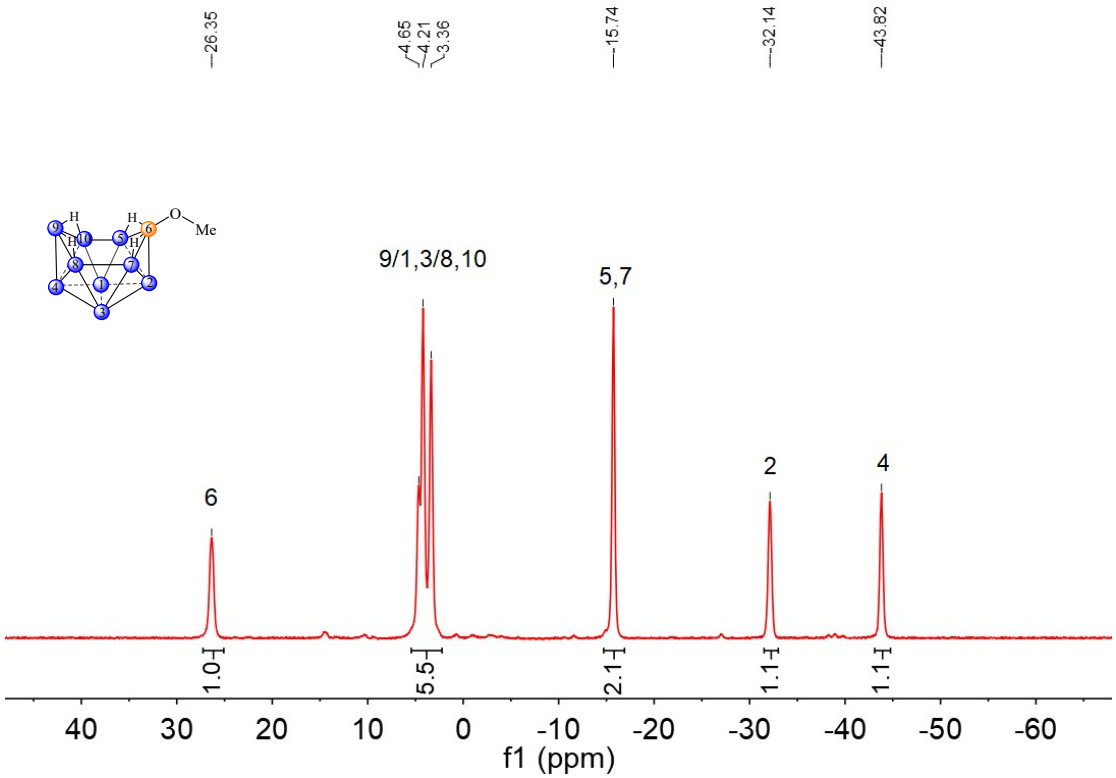


Figure S8. ^{11}B{^{1}H} NMR spectrum of *nido*-6-CH_3O-$B_{10}H_{13}$ (**1**) in $CDCl_3$

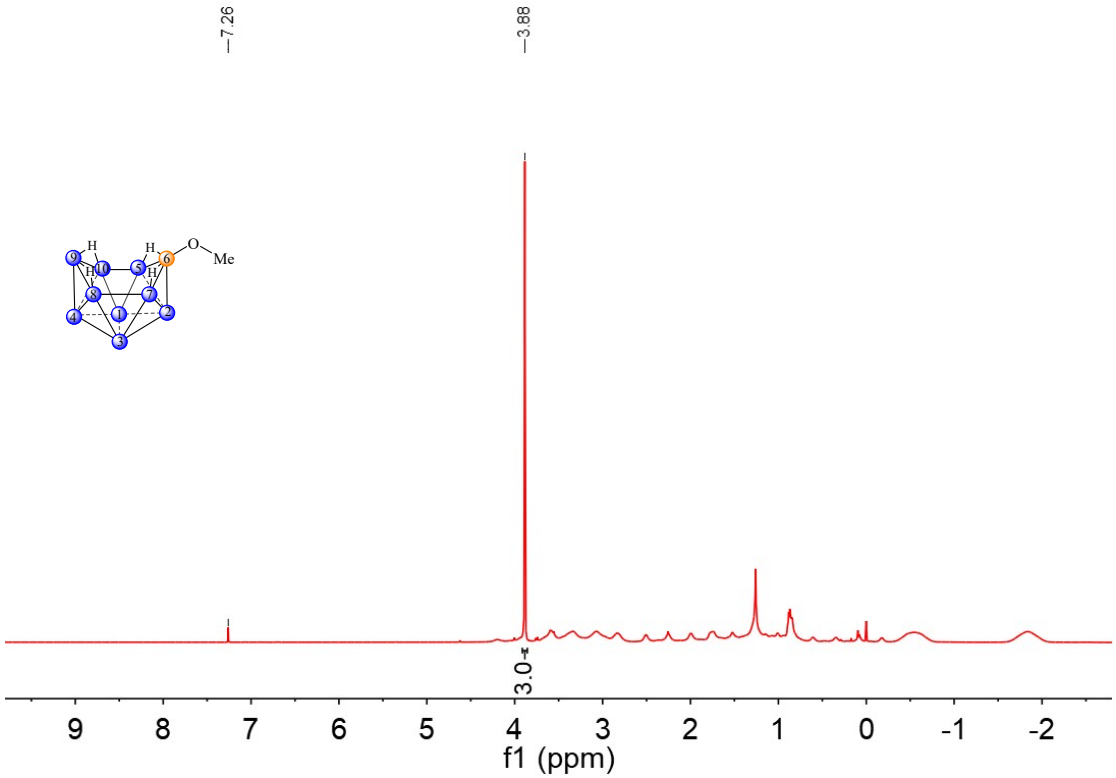


Figure S9. ^{1}H NMR spectrum of *nido*-6-CH_3O-$B_{10}H_{13}$ (**1**) in $CDCl_3$

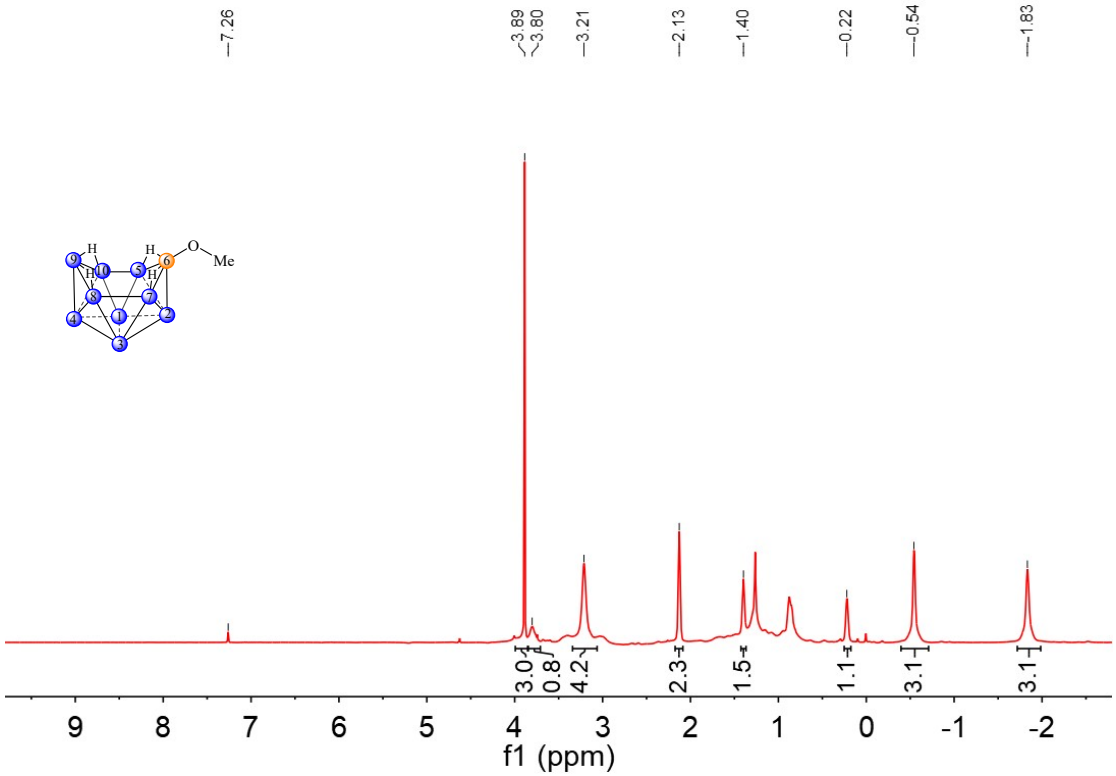


Figure S10. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-CH_3O-$B_{10}H_{13}$ (**1**) in $CDCl_3$

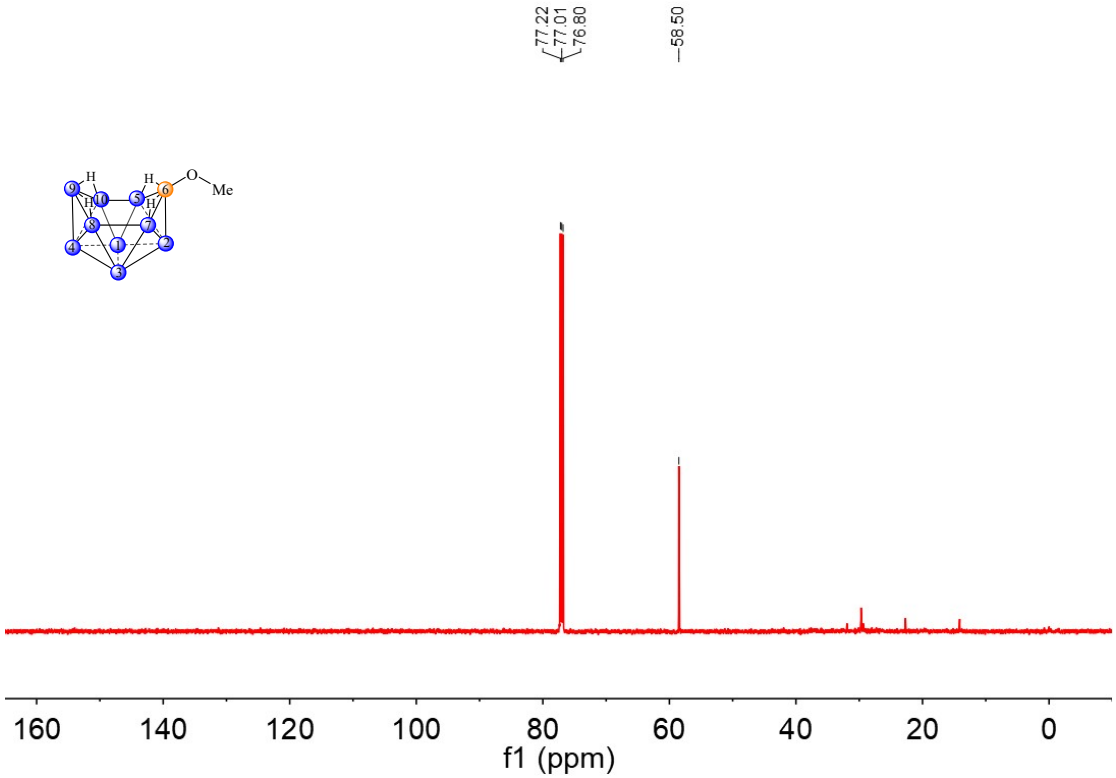


Figure S11. ^{13}C NMR spectrum of *nido*-6-CH_3O-$B_{10}H_{13}$ (**1**) in $CDCl_3$

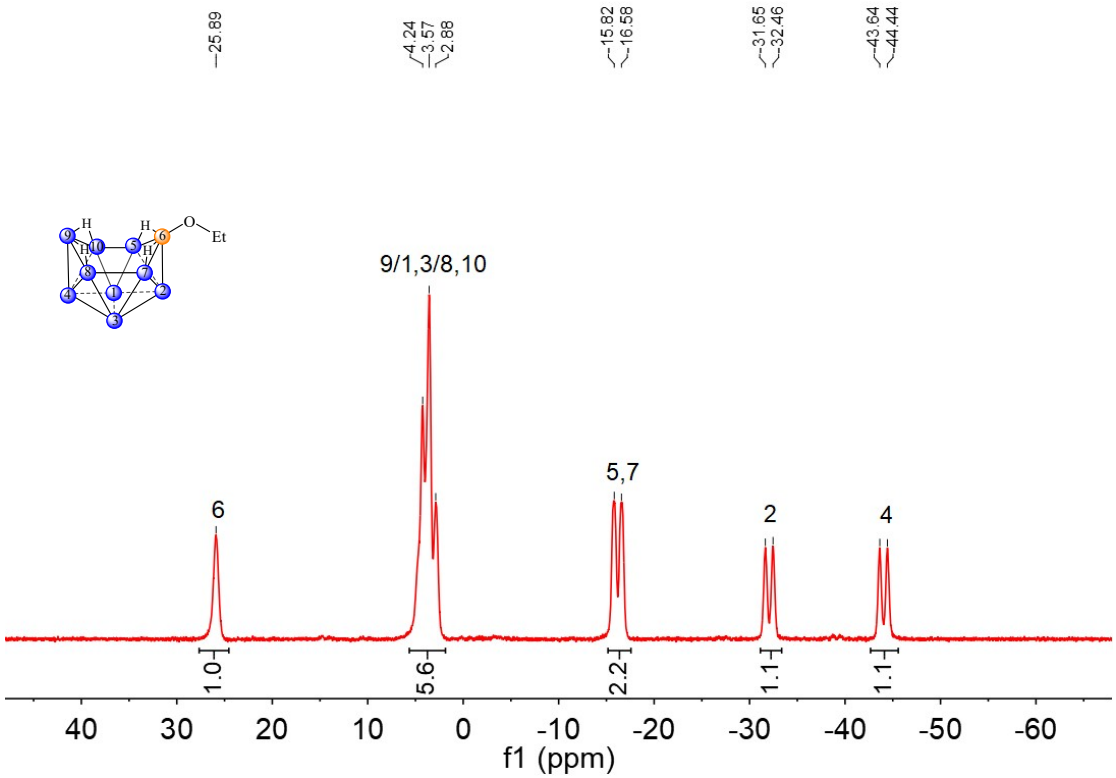


Figure S12. ^{11}B NMR spectrum of *nido*-6-CH_3CH_2O-$B_{10}H_{13}$ (**2**) in $CDCl_3$

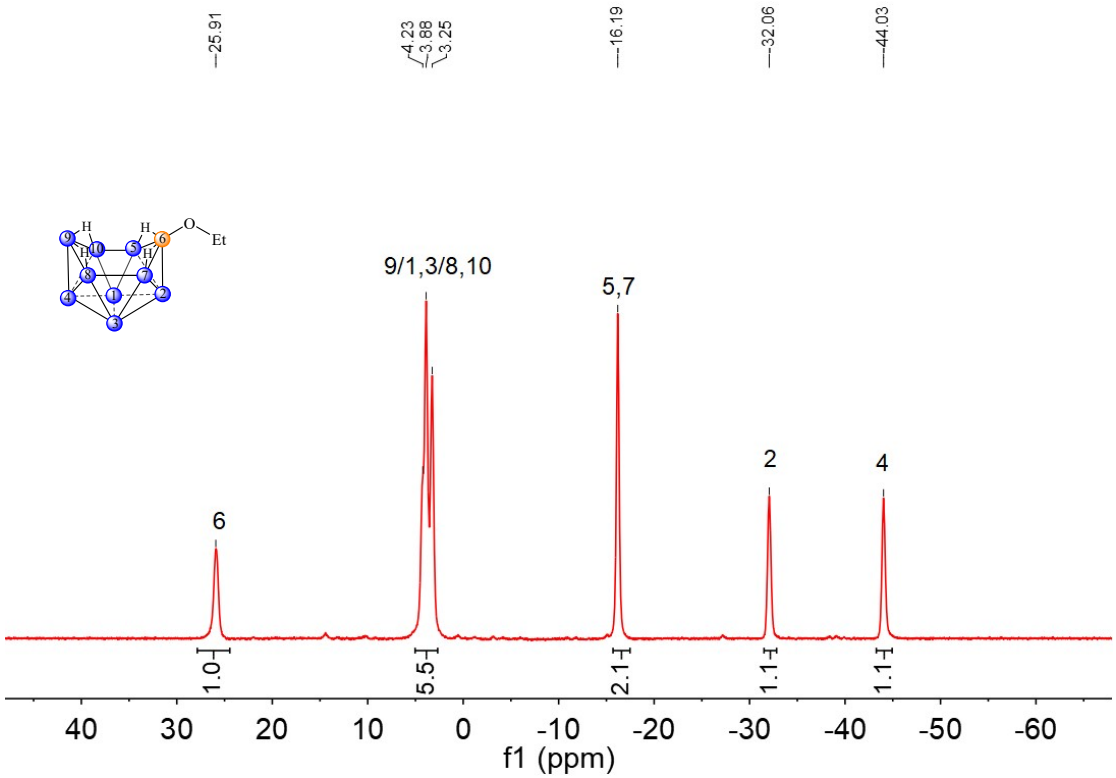


Figure S13. $^{11}B\{^1H\}$ NMR spectrum of *nido*-6-CH_3CH_2O-$B_{10}H_{13}$ (**2**) in $CDCl_3$

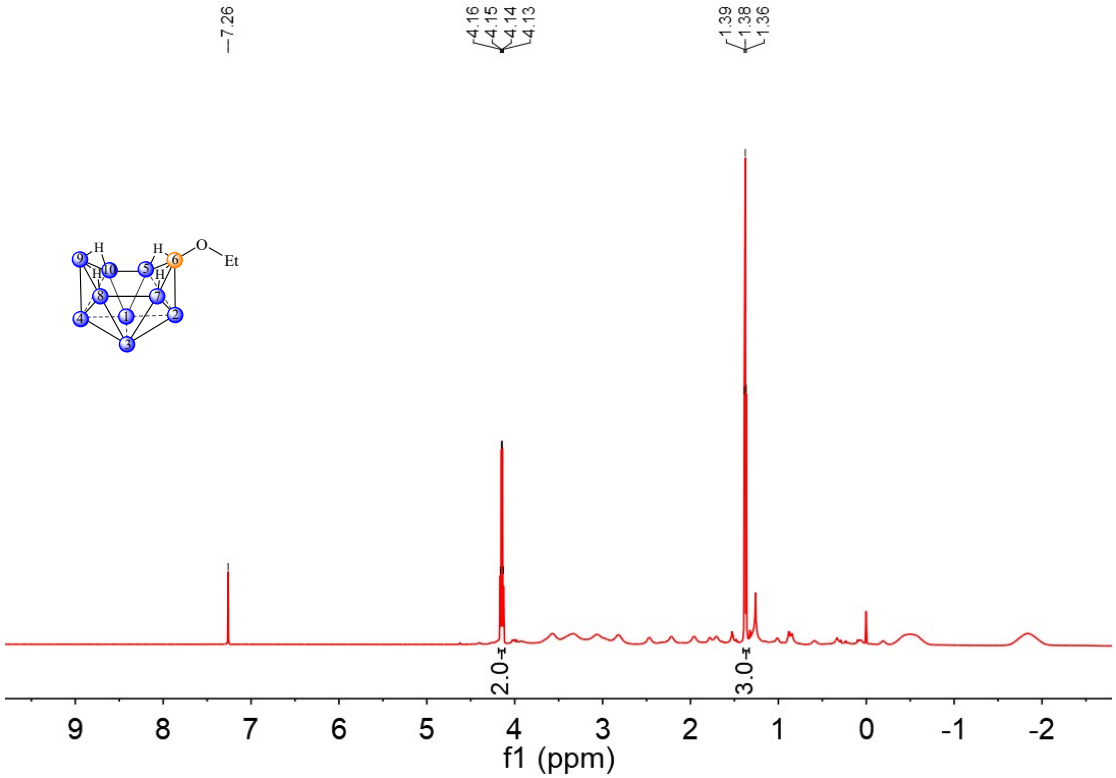


Figure S14. ^{1}H NMR spectrum of *nido*-6-CH_3CH_2O-$B_{10}H_{13}$ (**2**) in $CDCl_3$

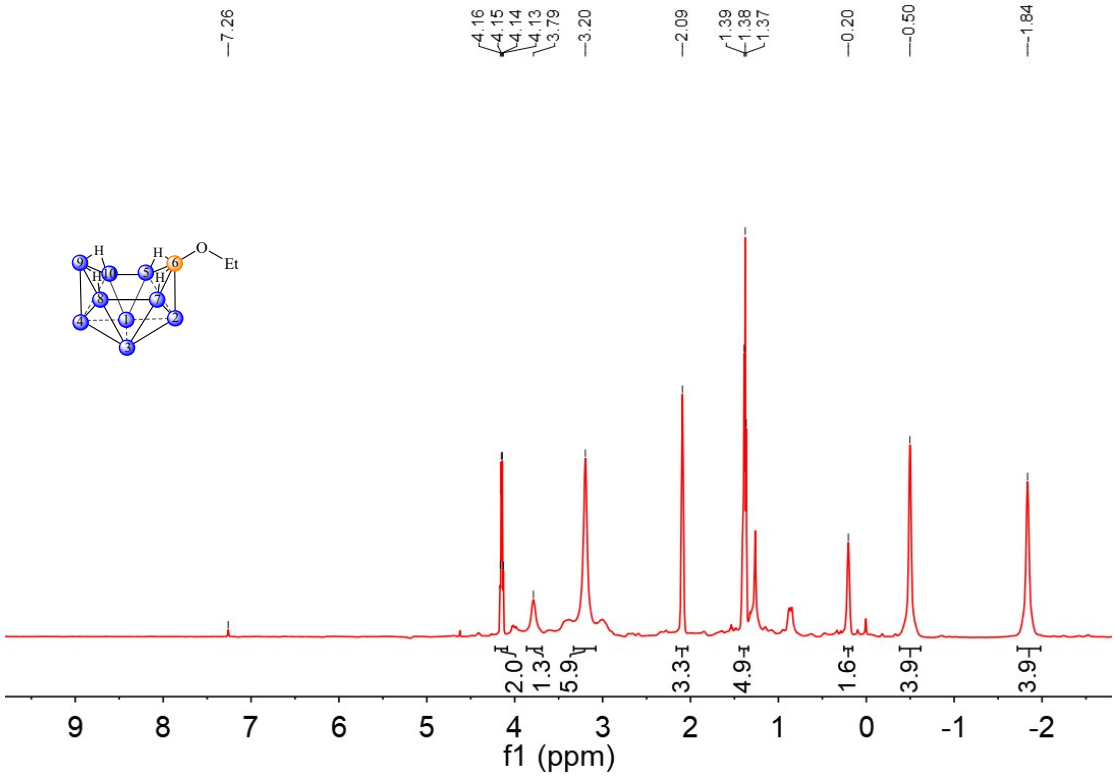


Figure S15. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-CH_3CH_2O-$B_{10}H_{13}$ (**2**) in $CDCl_3$

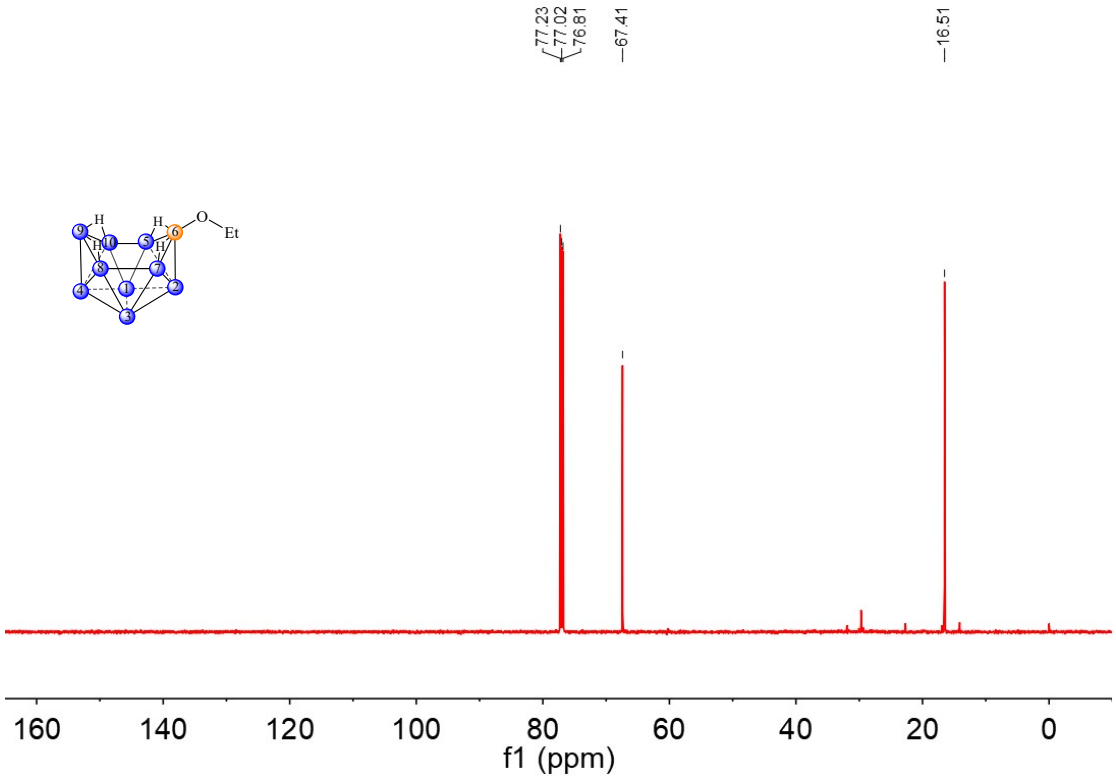


Figure S16. ^{13}C NMR spectrum of *nido*-6-CH_3CH_2O-$B_{10}H_{13}$ (**2**) in $CDCl_3$

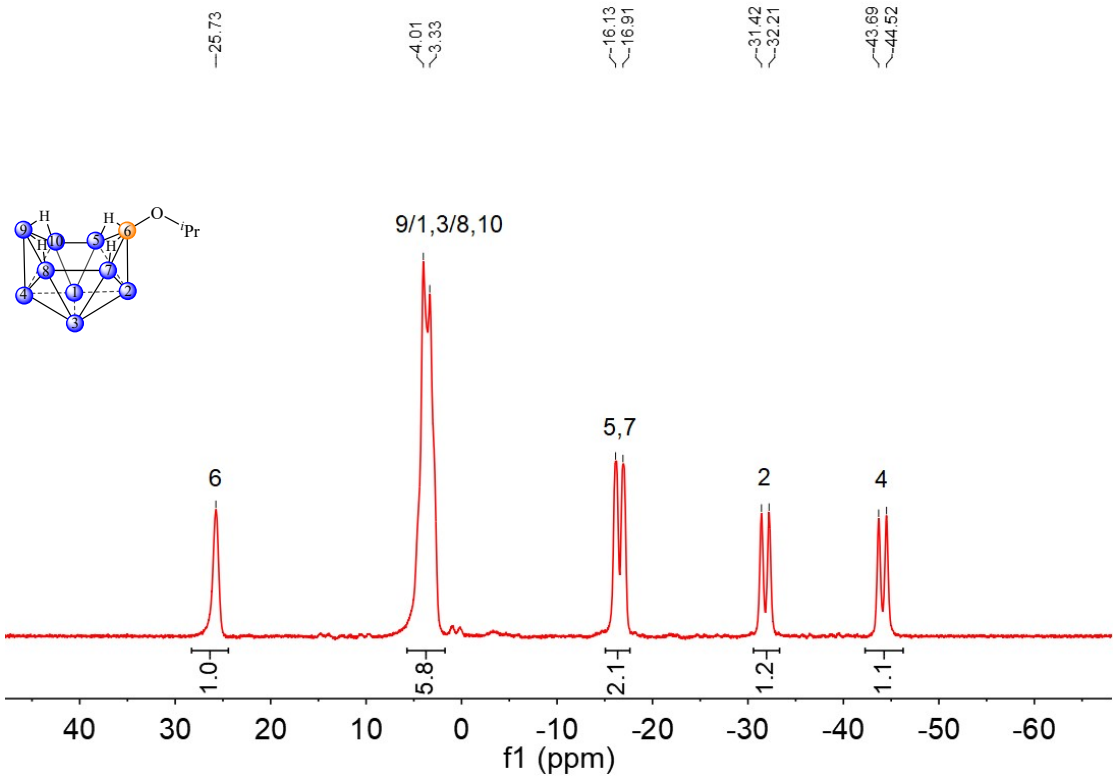


Figure S17. ^{11}B NMR spectrum of *nido*-6-$(CH_3)_2CHO$-$B_{10}H_{13}$ (**3**) in $CDCl_3$

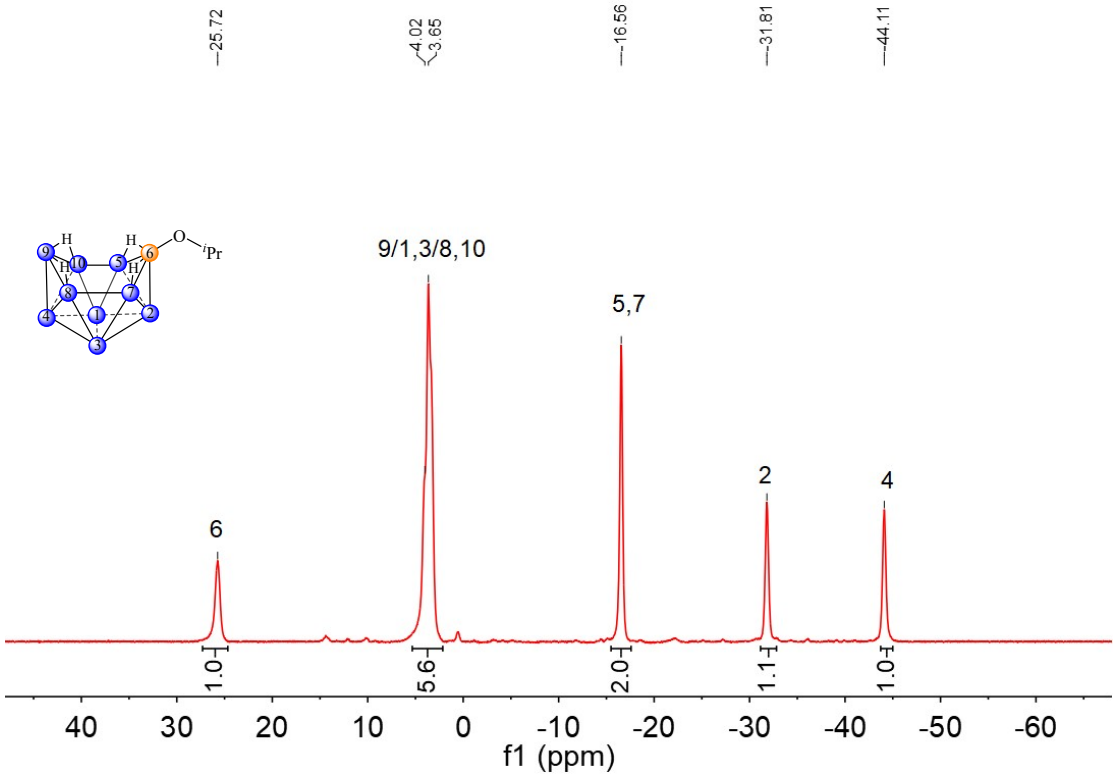


Figure S18. $^{11}B\{^1H\}$ NMR spectrum of *nido*-6-$(CH_3)_2CHO$-$B_{10}H_{13}$ (**3**) in $CDCl_3$

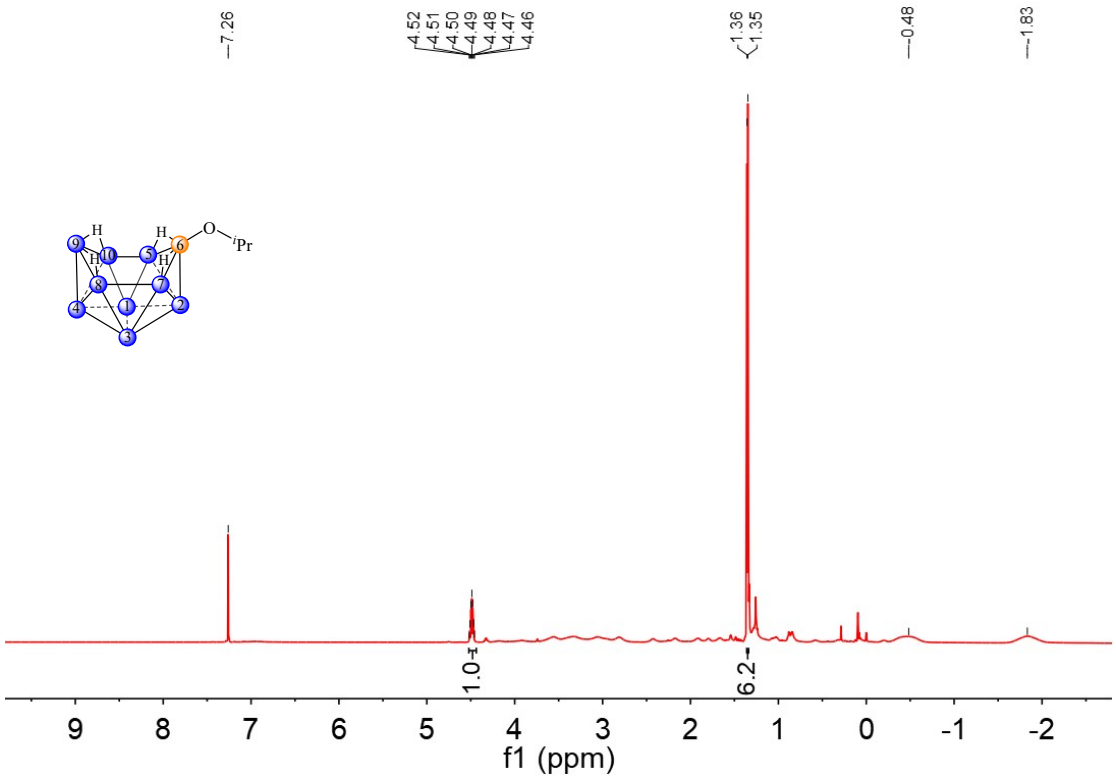


Figure S19. ^{1}H NMR spectrum of *nido*-6-$(CH_3)_2CHO$-$B_{10}H_{13}$ (**3**) in $CDCl_3$

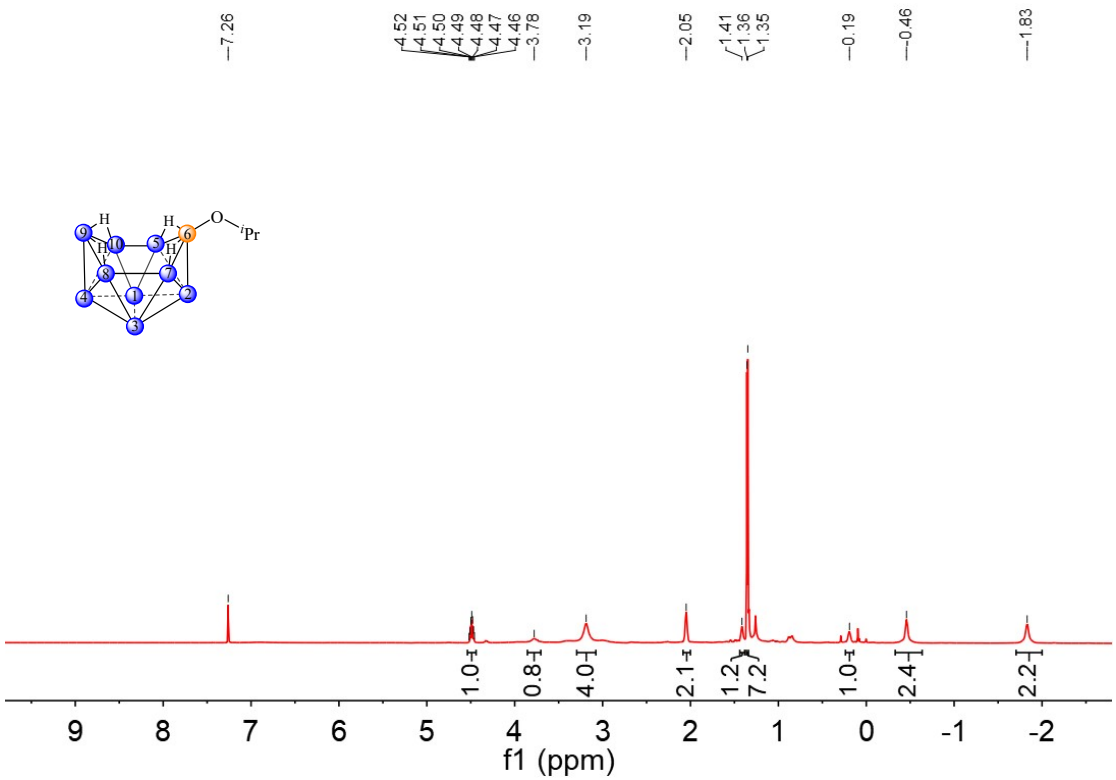


Figure S20. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-$(CH_3)_2CHO$-$B_{10}H_{13}$ (**3**) in $CDCl_3$

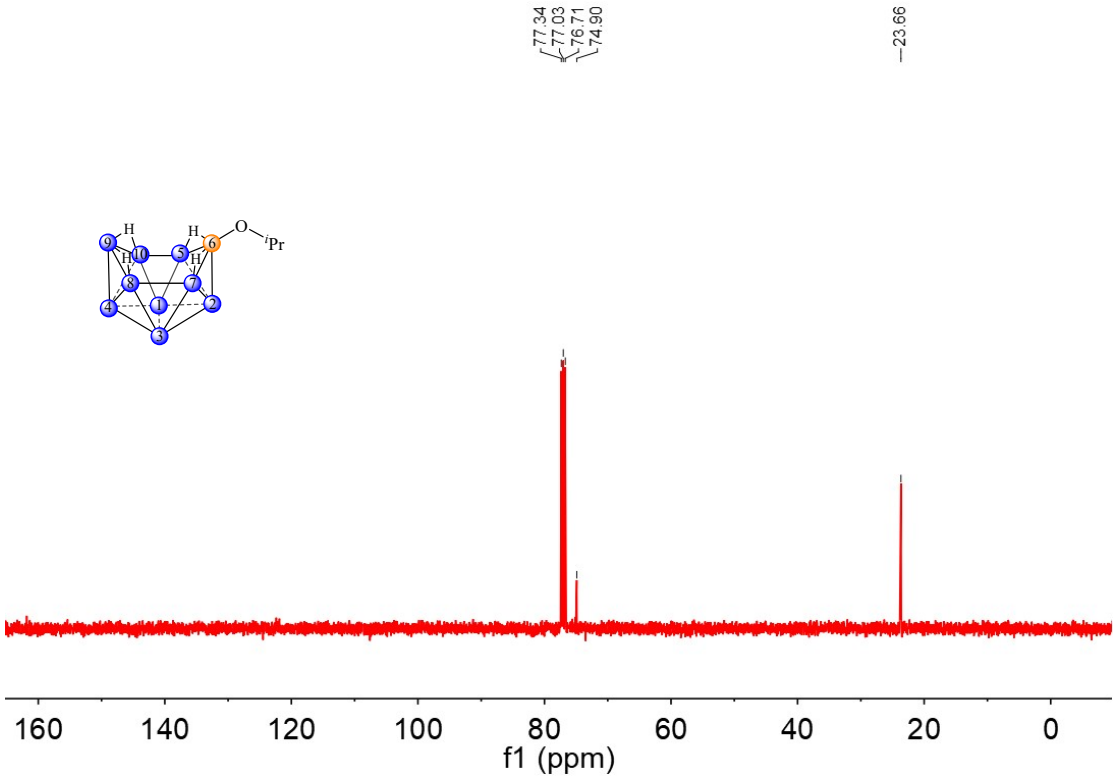


Figure S21. ^{13}C NMR spectrum of *nido*-6-$(CH_3)_2CHO$-$B_{10}H_{13}$ (**3**) in $CDCl_3$

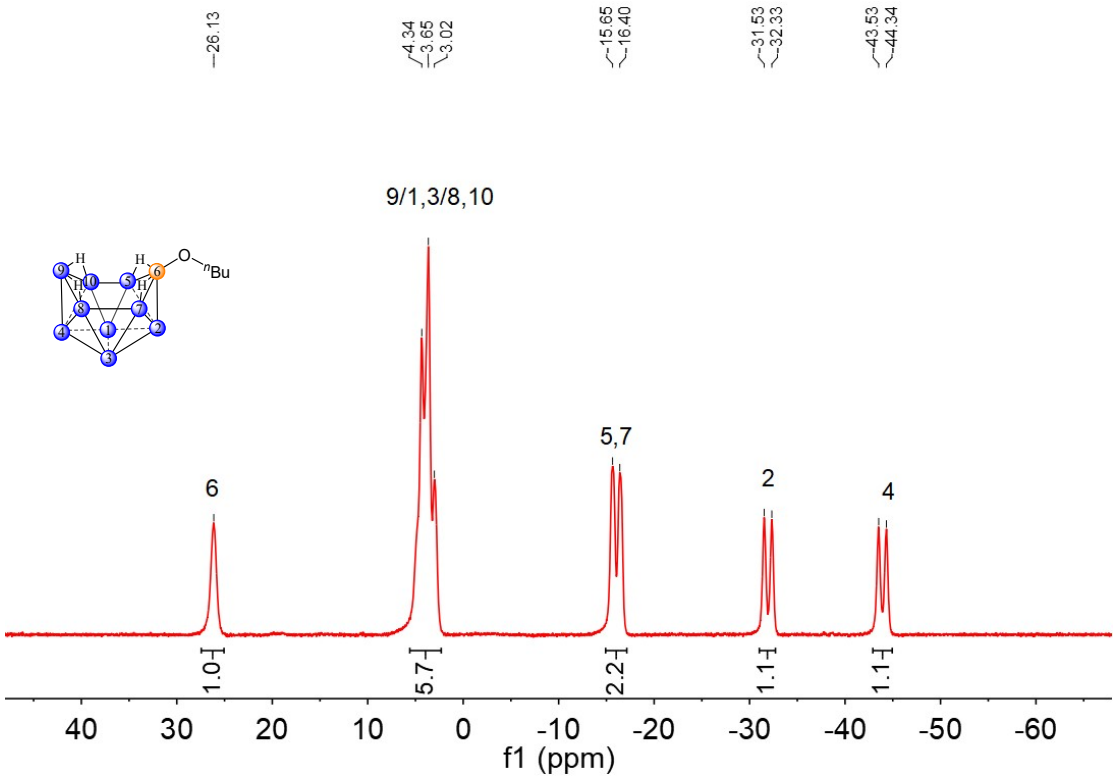


Figure S22. ^{11}B NMR spectrum of *nido*-6-$CH_3(CH_2)_3O$-$B_{10}H_{13}$ (**4**) in $CDCl_3$

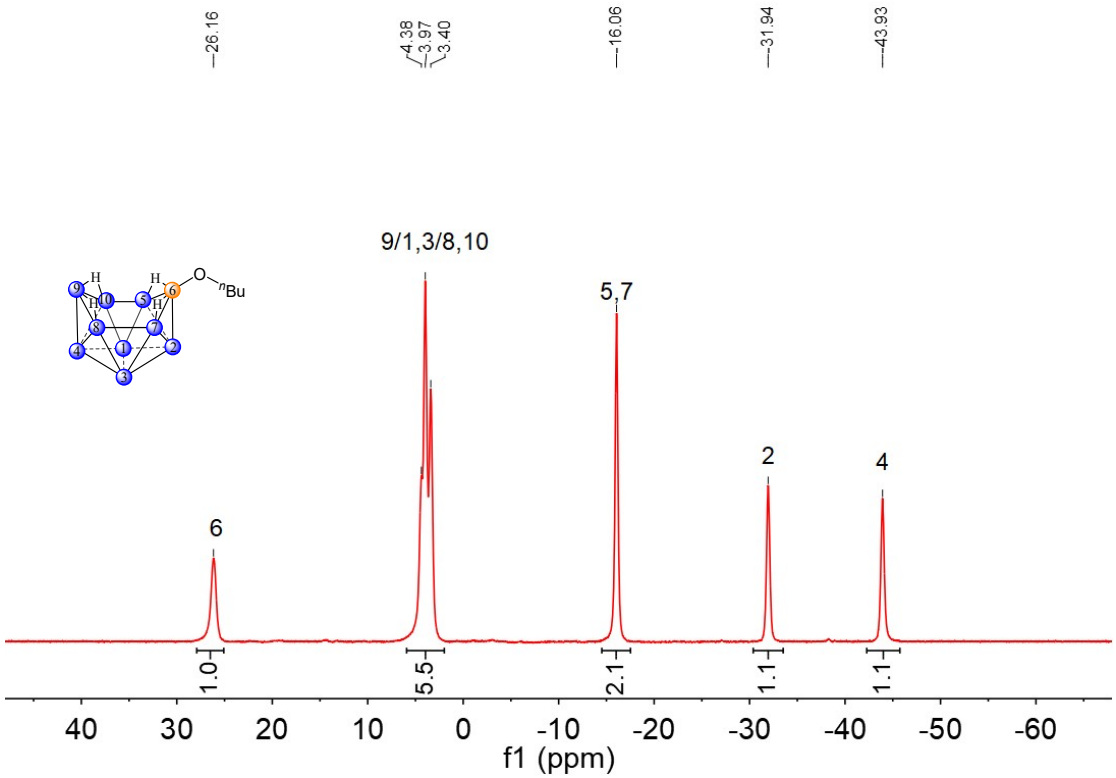


Figure S23. ^{11}B{^{1}H} NMR spectrum of *nido*-6-$CH_3(CH_2)_3O$-$B_{10}H_{13}$ (**4**) in $CDCl_3$

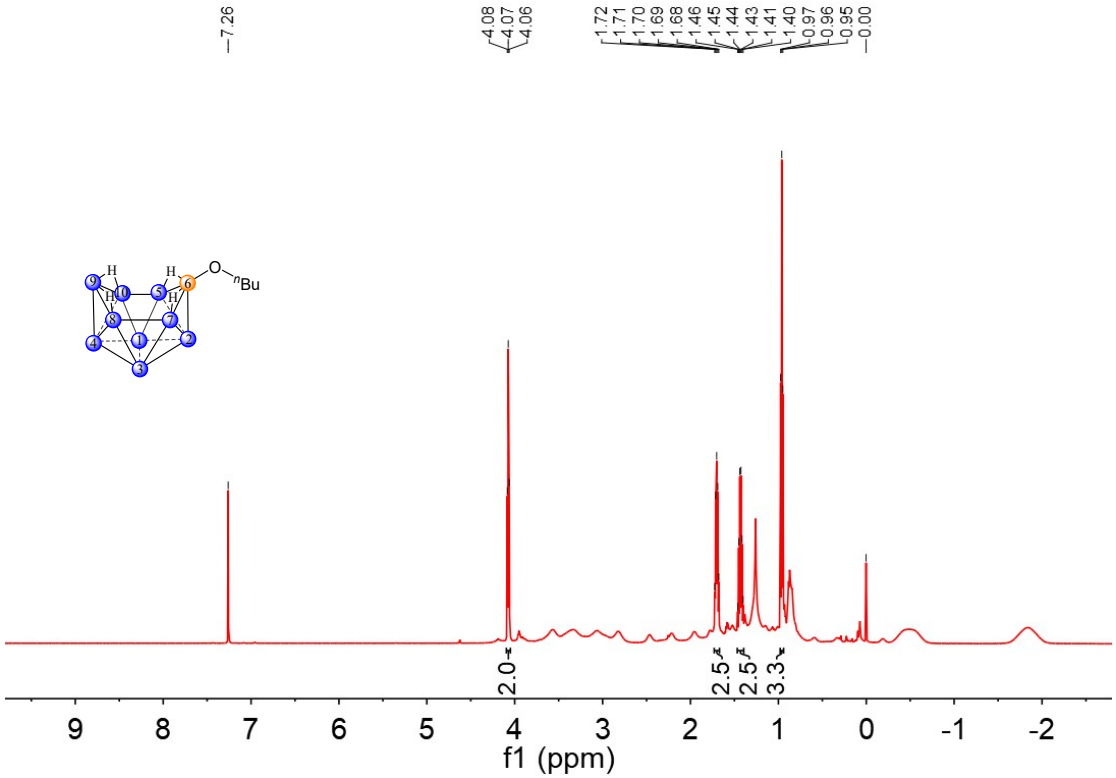


Figure S24. ^{1}H NMR spectrum of *nido*-6-$CH_3(CH_2)_3O$-$B_{10}H_{13}$ (**4**) in $CDCl_3$

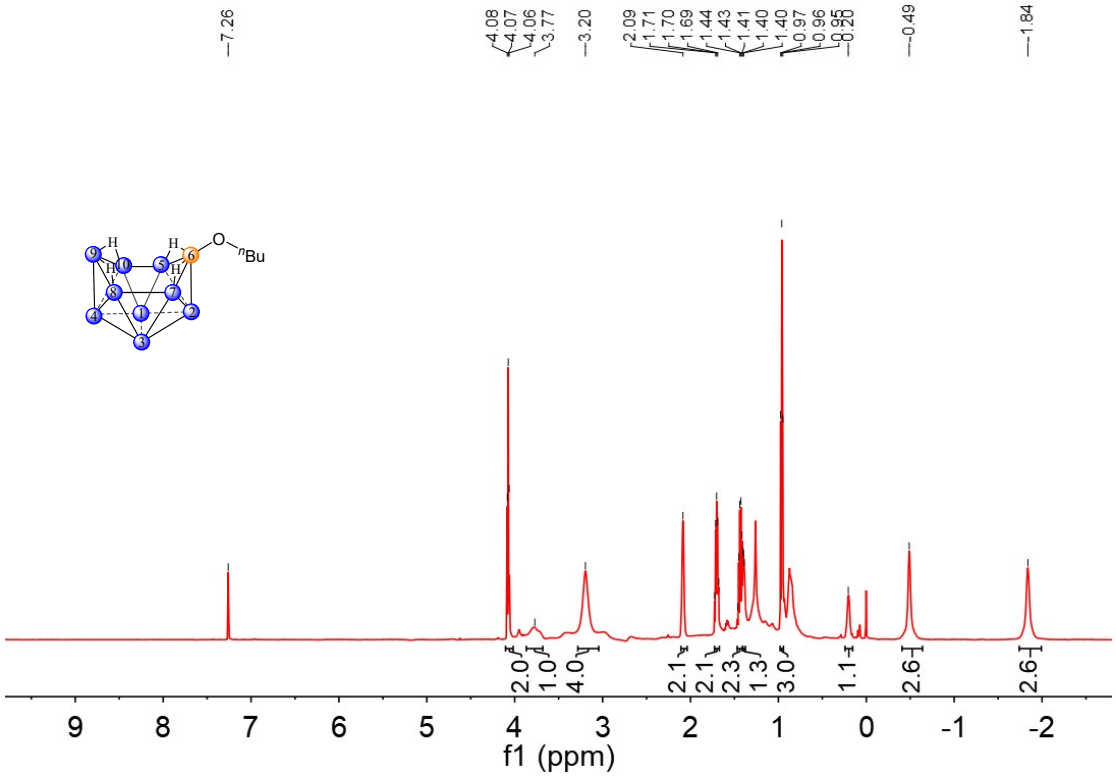


Figure S25. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-$CH_3(CH_2)_3O$-$B_{10}H_{13}$ (**4**) in $CDCl_3$

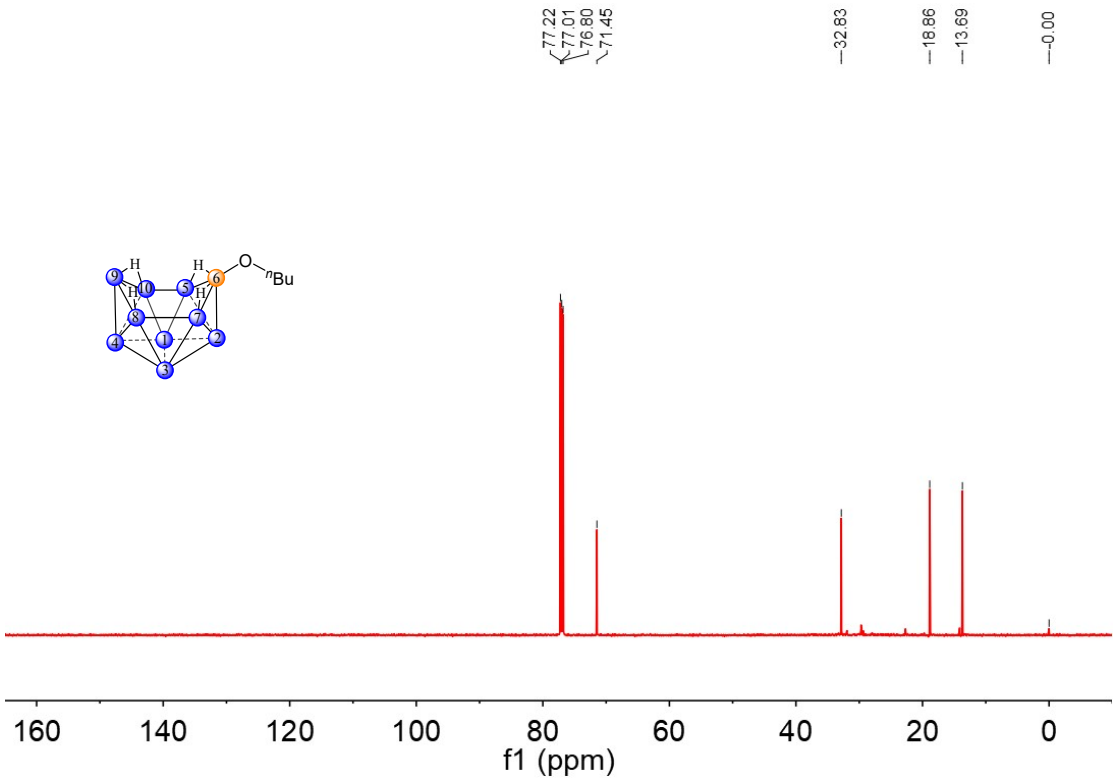


Figure S26. ^{13}C NMR spectrum of *nido*-6-$CH_3(CH_2)_3O$-$B_{10}H_{13}$ (**4**) in $CDCl_3$

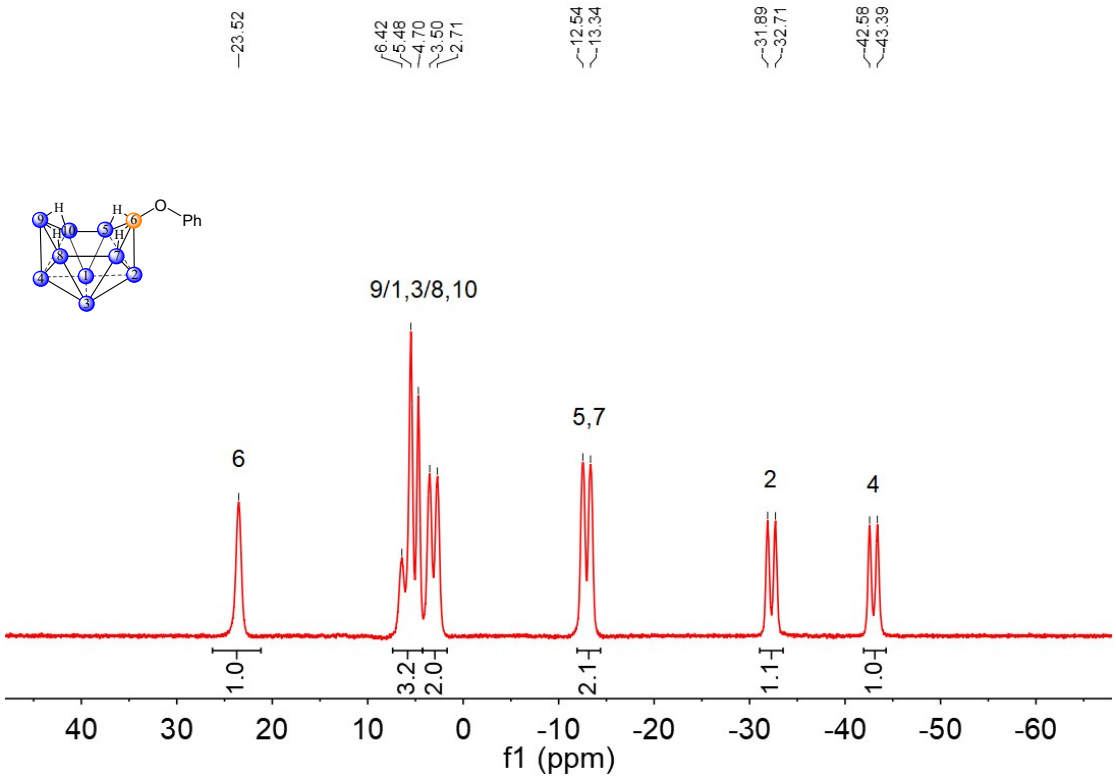


Figure S27. ^{11}B NMR spectrum of *nido*-6-PhO-$B_{10}H_{13}$ (**5**) in $CDCl_3$

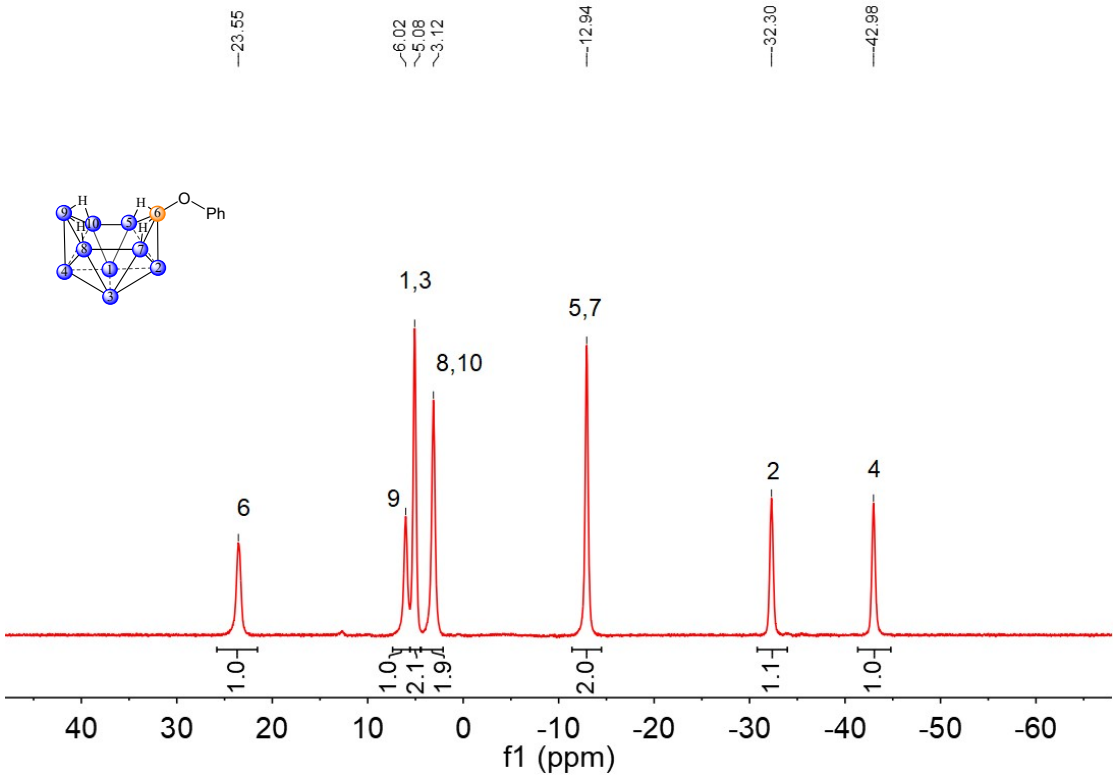


Figure S28. ^{11}B{^{1}H} NMR spectrum of *nido*-6-PhO-$B_{10}H_{13}$ (**5**) in $CDCl_3$

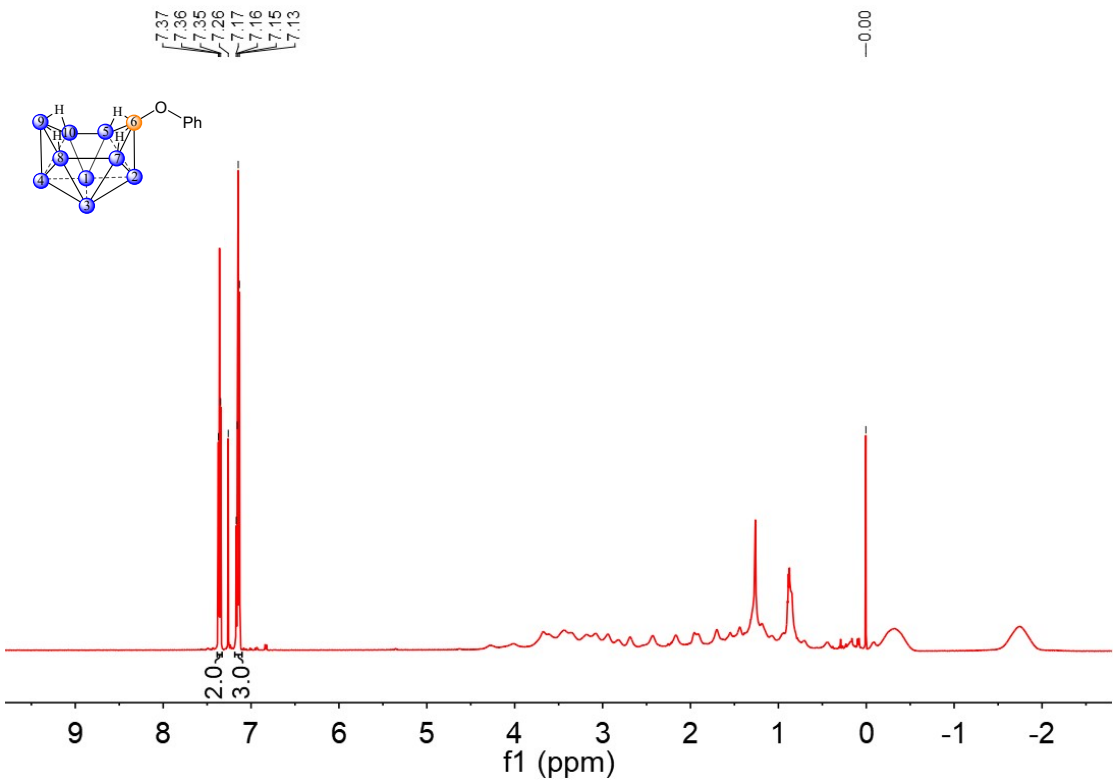


Figure S29. ^{1}H NMR spectrum of *nido*-6-PhO-$B_{10}H_{13}$ (**5**) in $CDCl_3$

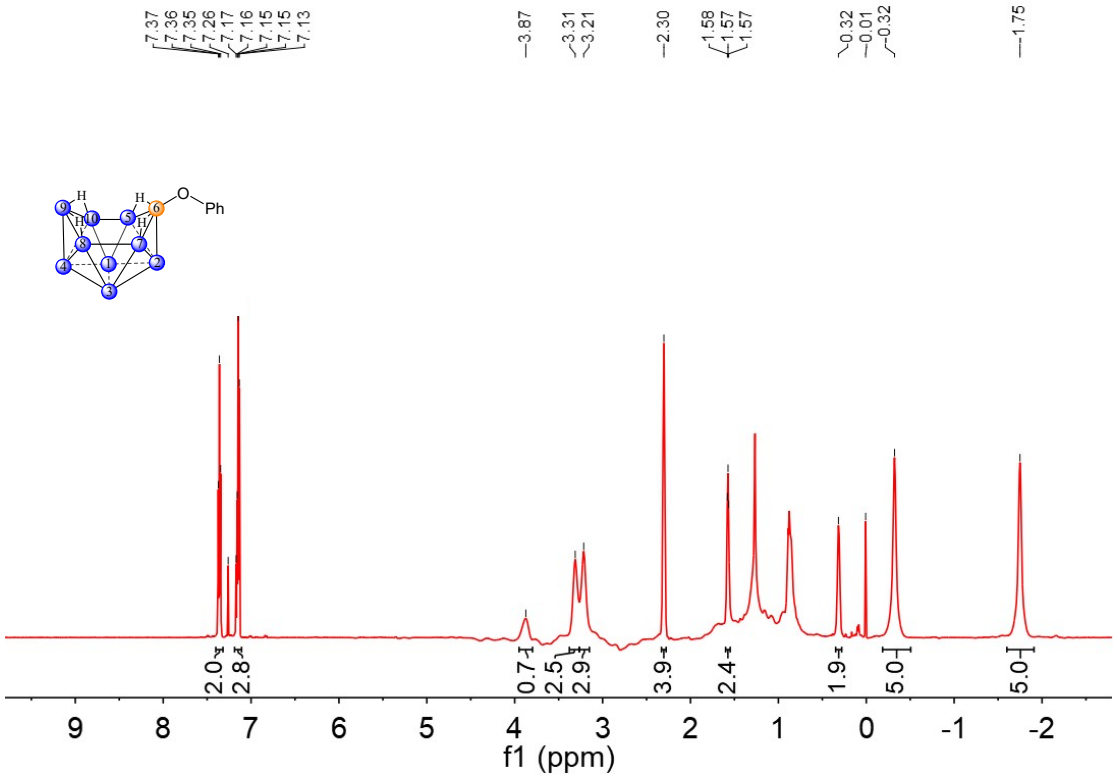


Figure S30. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-PhO-$B_{10}H_{13}$ (**5**) in $CDCl_3$

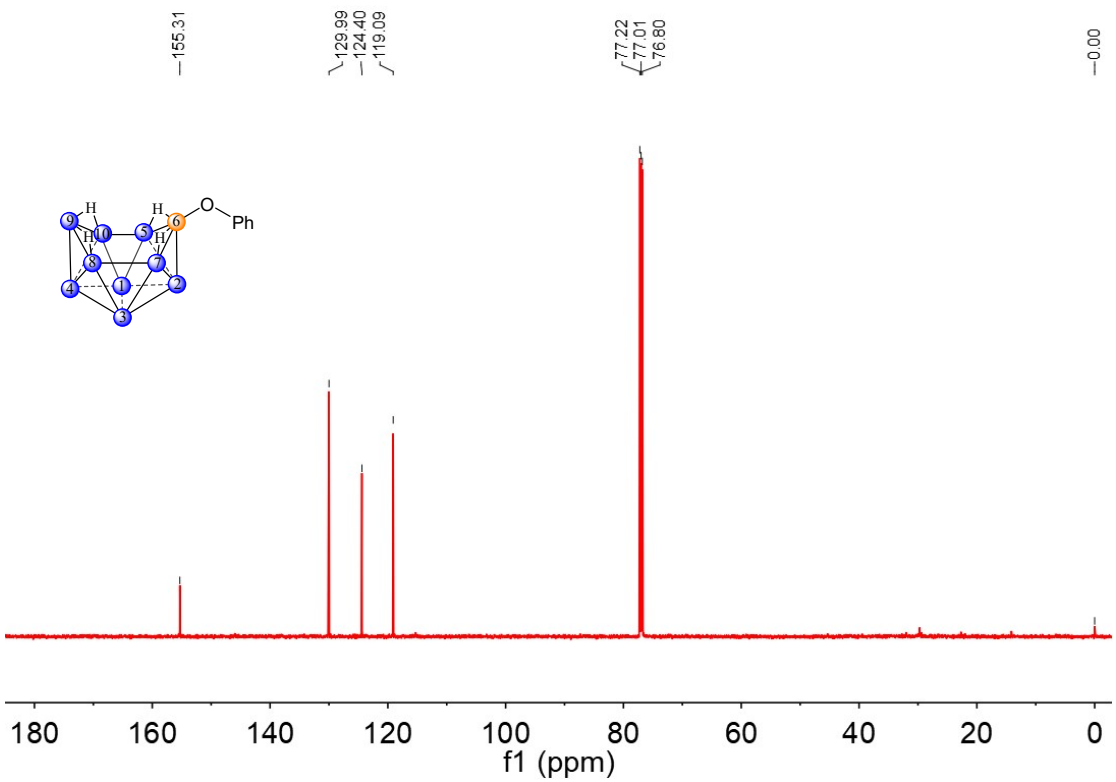


Figure S31. ^{13}C NMR spectrum of *nido*-6-PhO-$B_{10}H_{13}$ (**5**) in $CDCl_3$

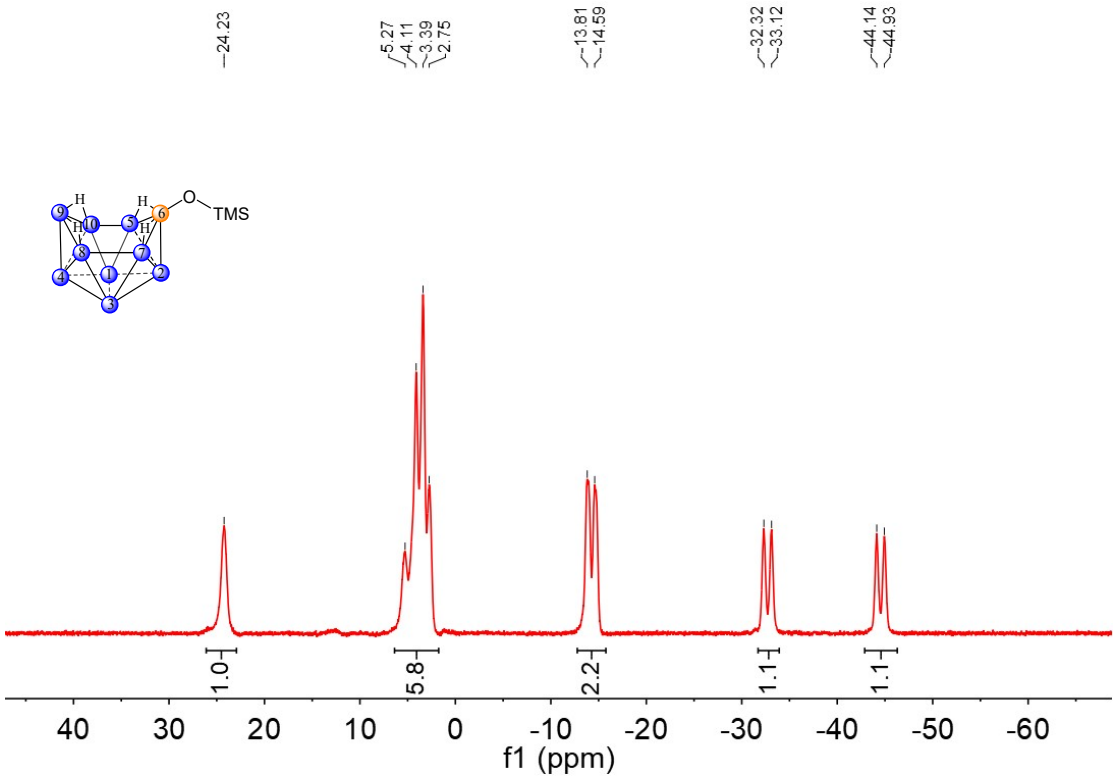


Figure S32. ^{11}B NMR spectrum of *nido*-6-$(CH_3)_3SiO$-$B_{10}H_{13}$ (**6**) in $CDCl_3$

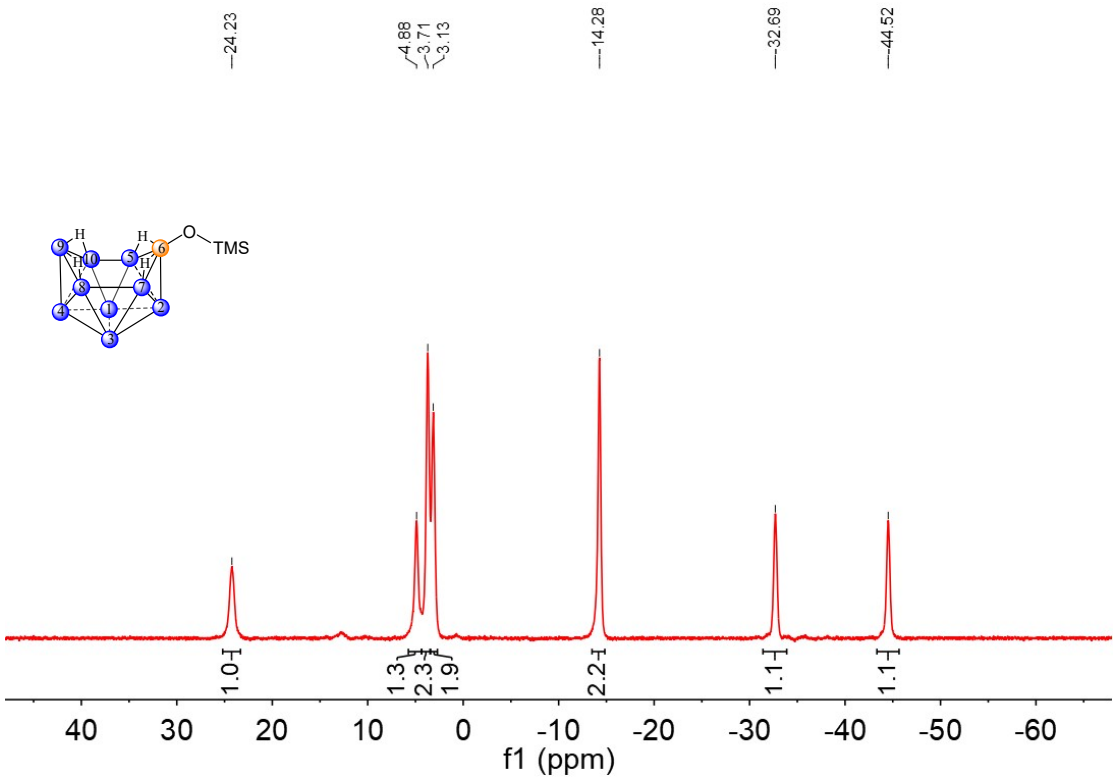


Figure S33. $^{11}B\{^1H\}$ NMR spectrum of *nido*-6-$(CH_3)_3SiO$-$B_{10}H_{13}$ (**6**) in $CDCl_3$

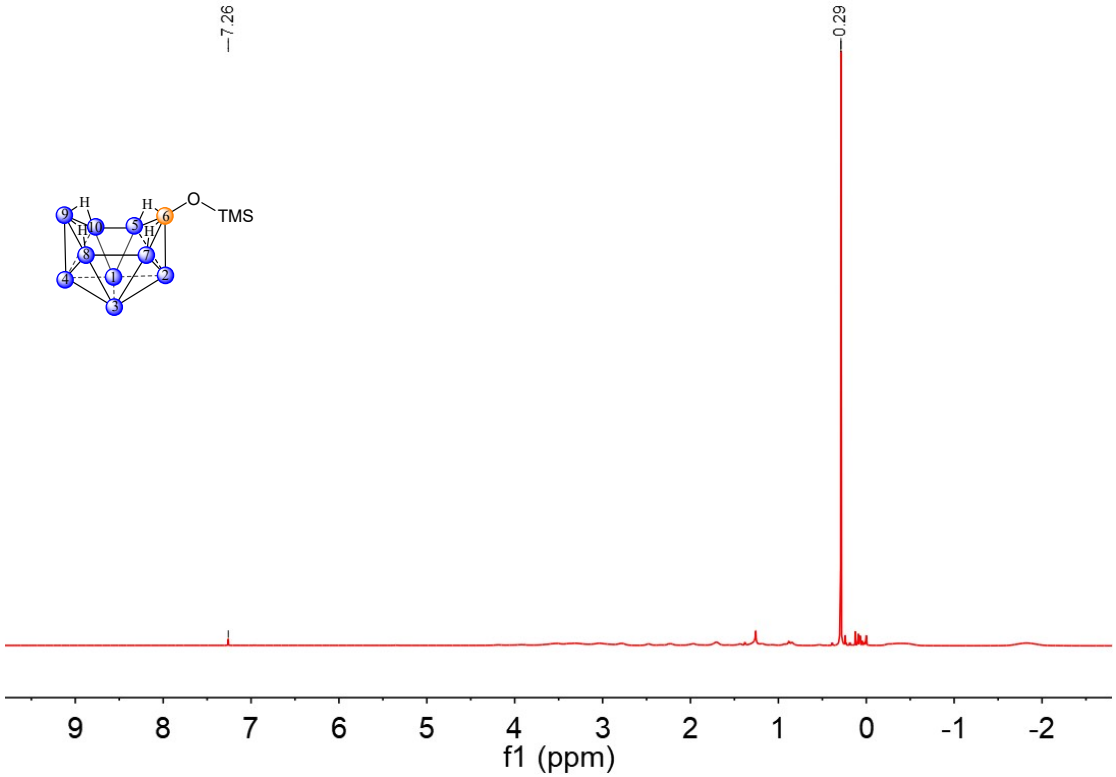


Figure S34. ^{1}H NMR spectrum of *nido*-6-$(CH_3)_3SiO$-$B_{10}H_{13}$ (**6**) in $CDCl_3$

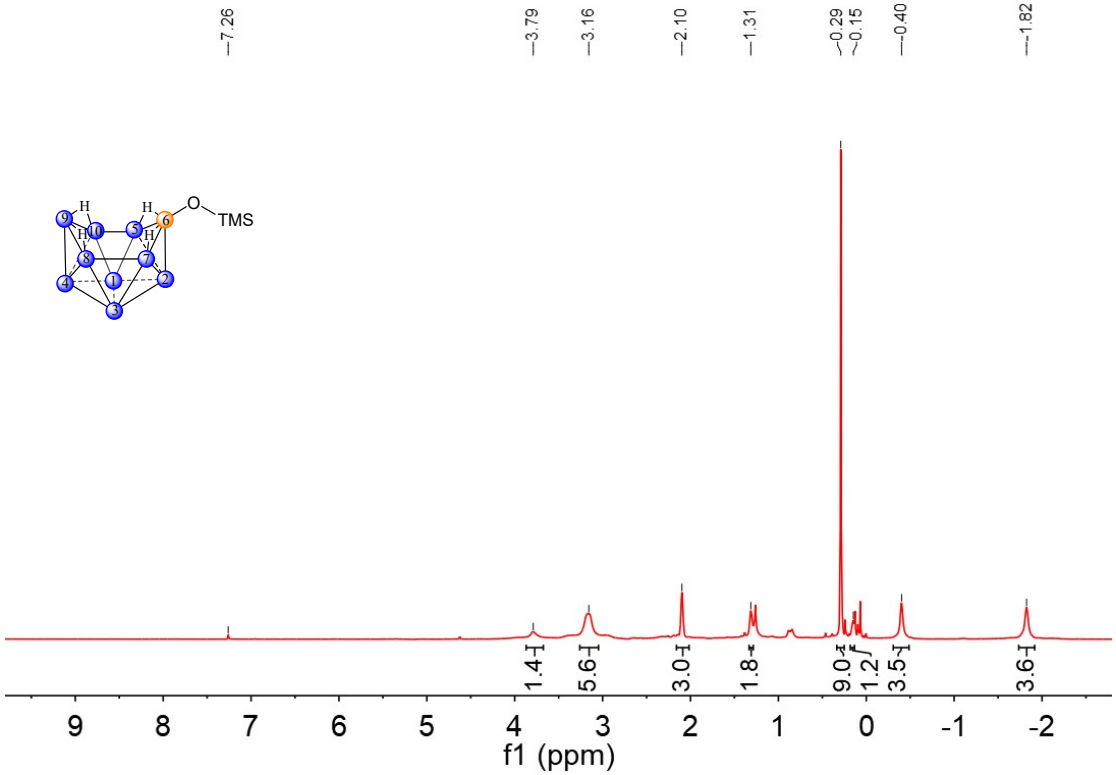


Figure S35. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-$(CH_3)_3SiO$-$B_{10}H_{13}$ (**6**) in $CDCl_3$

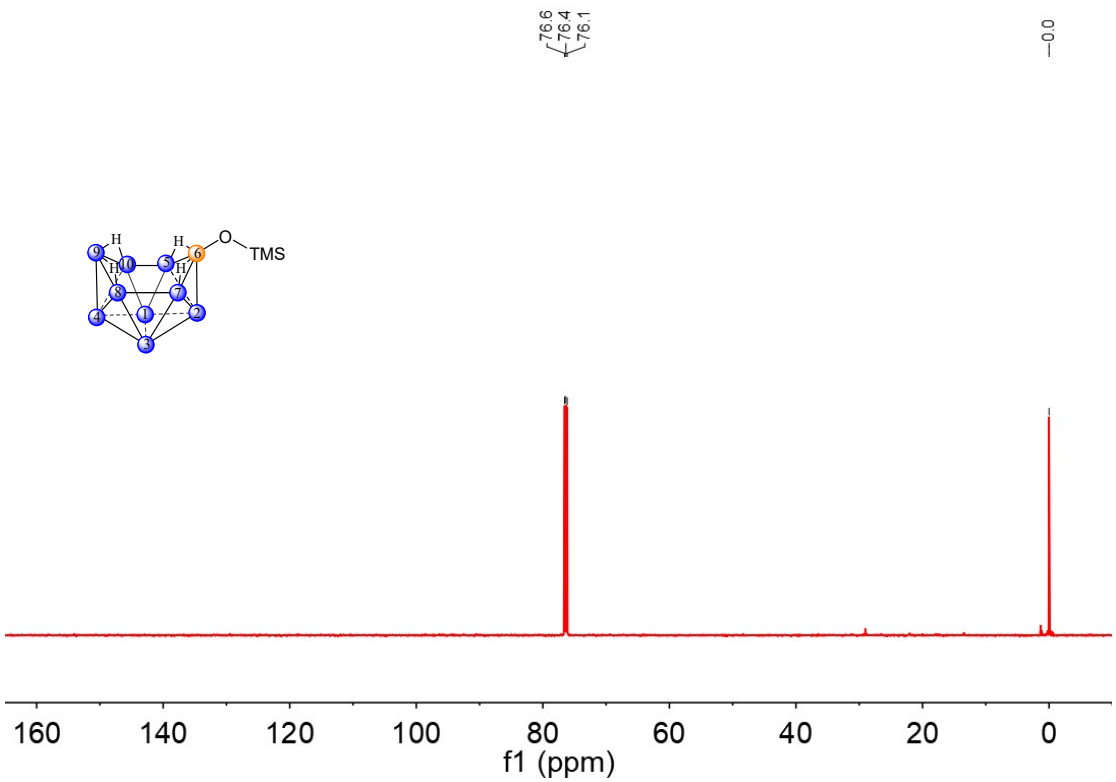


Figure S36. ^{13}C NMR spectrum of *nido*-6-$(CH_3)_3SiO$-$B_{10}H_{13}$ (**6**) in $CDCl_3$

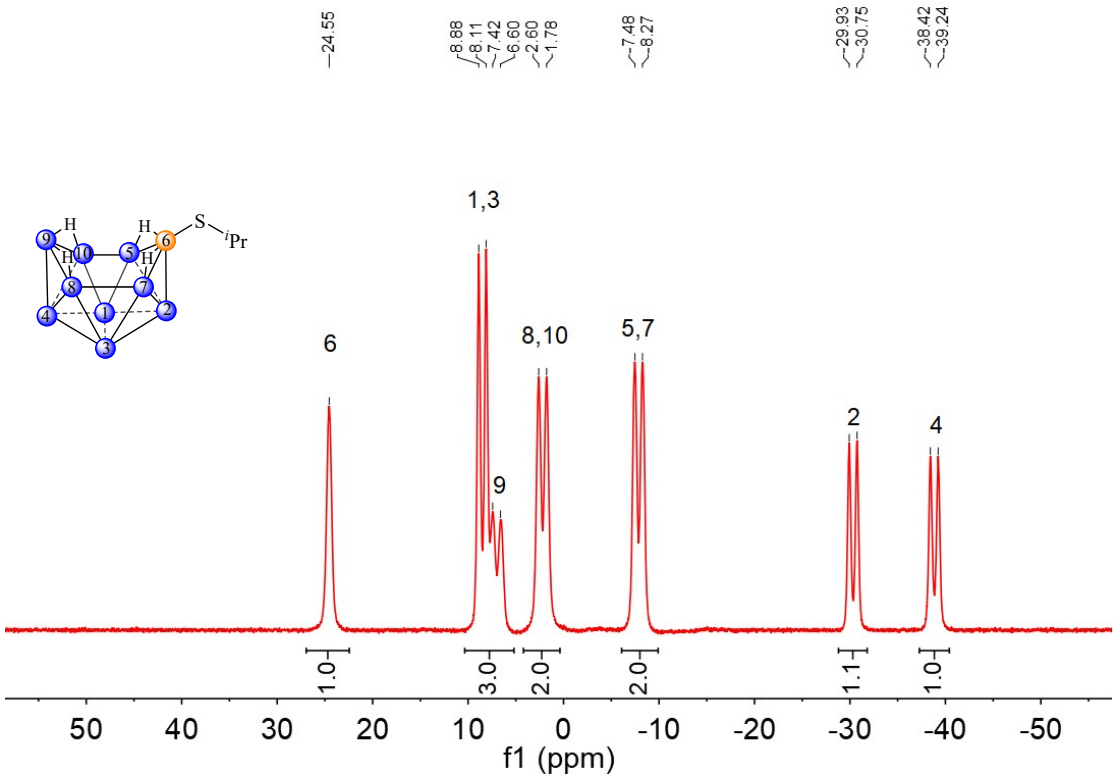


Figure S37. ^{11}B NMR spectrum of *nido*-6-$(CH_3)_2CHS$-$B_{10}H_{13}$ (**7**) in $CDCl_3$

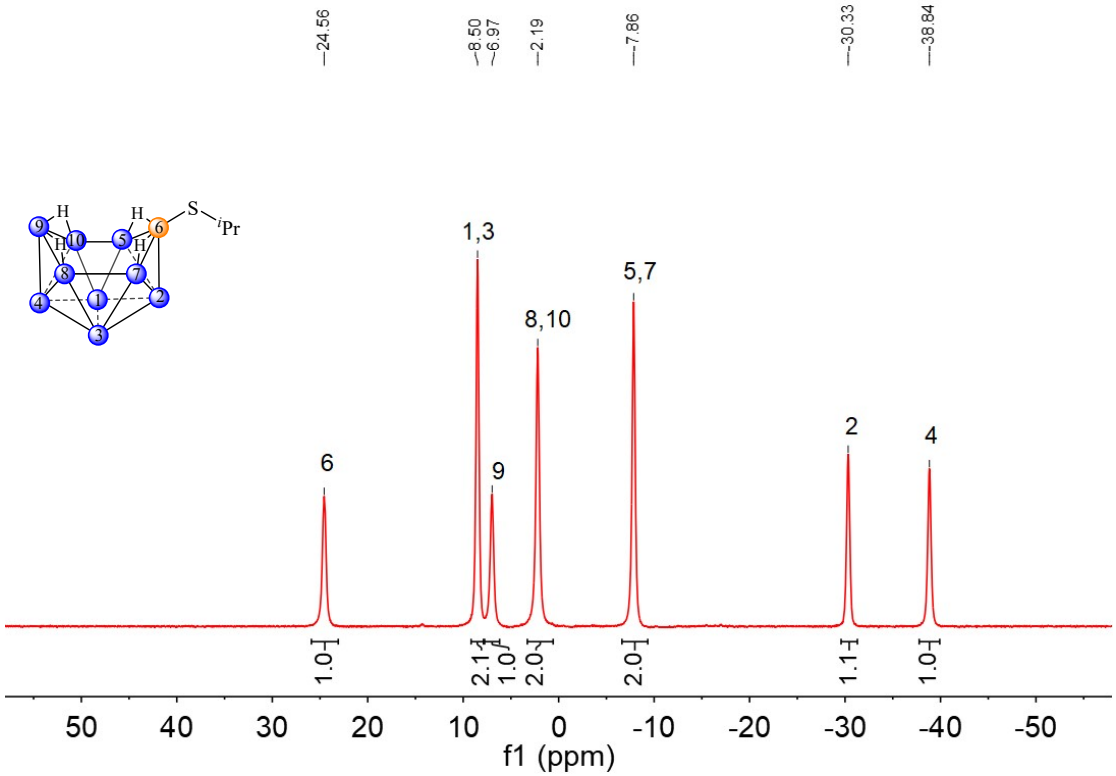


Figure S38. $^{11}B\{^1H\}$ NMR spectrum of *nido*-6-$(CH_3)_2CHS$-$B_{10}H_{13}$ (**7**) in $CDCl_3$

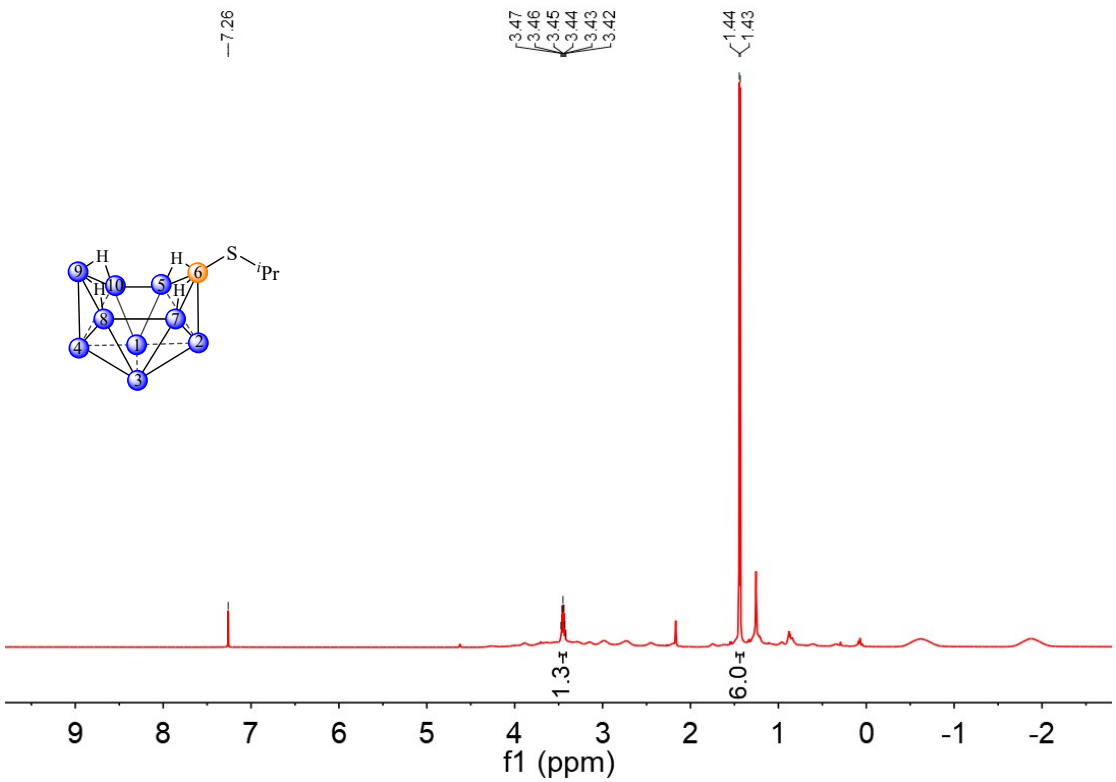


Figure S39. ^{1}H NMR spectrum of *nido*-6-$(CH_3)_2CHS$-$B_{10}H_{13}$ (**7**) in $CDCl_3$

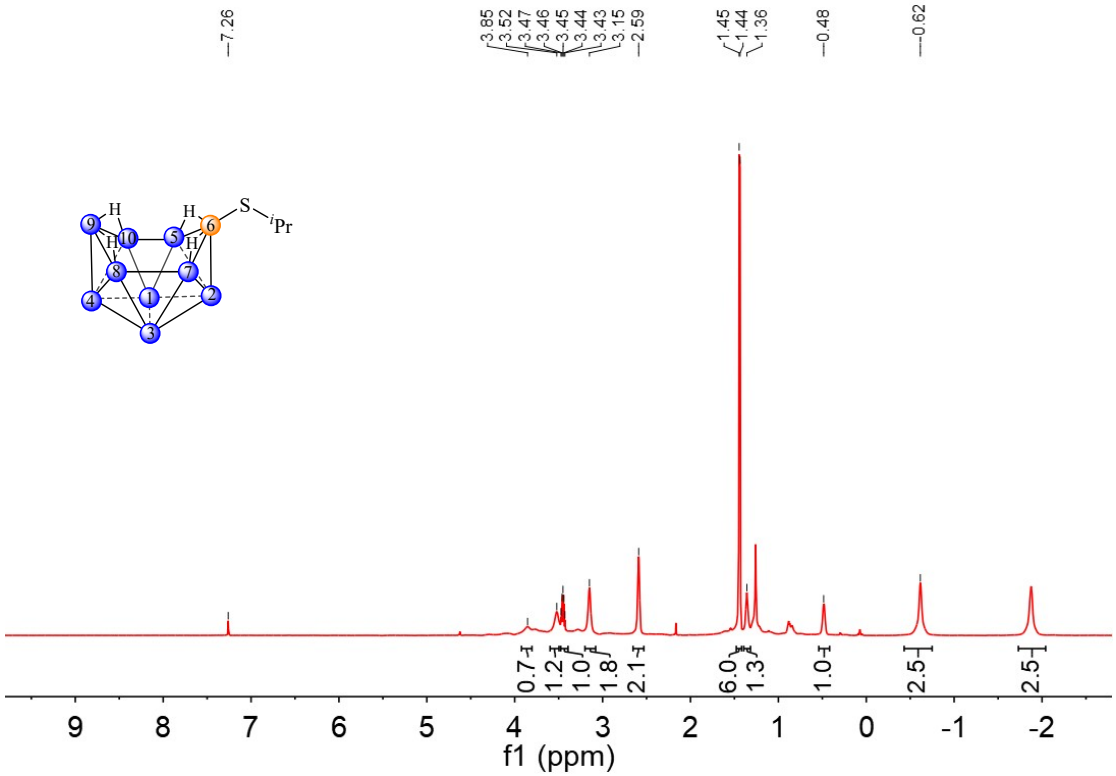


Figure S40. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-$(CH_3)_2CHS$-$B_{10}H_{13}$ (**7**) in $CDCl_3$

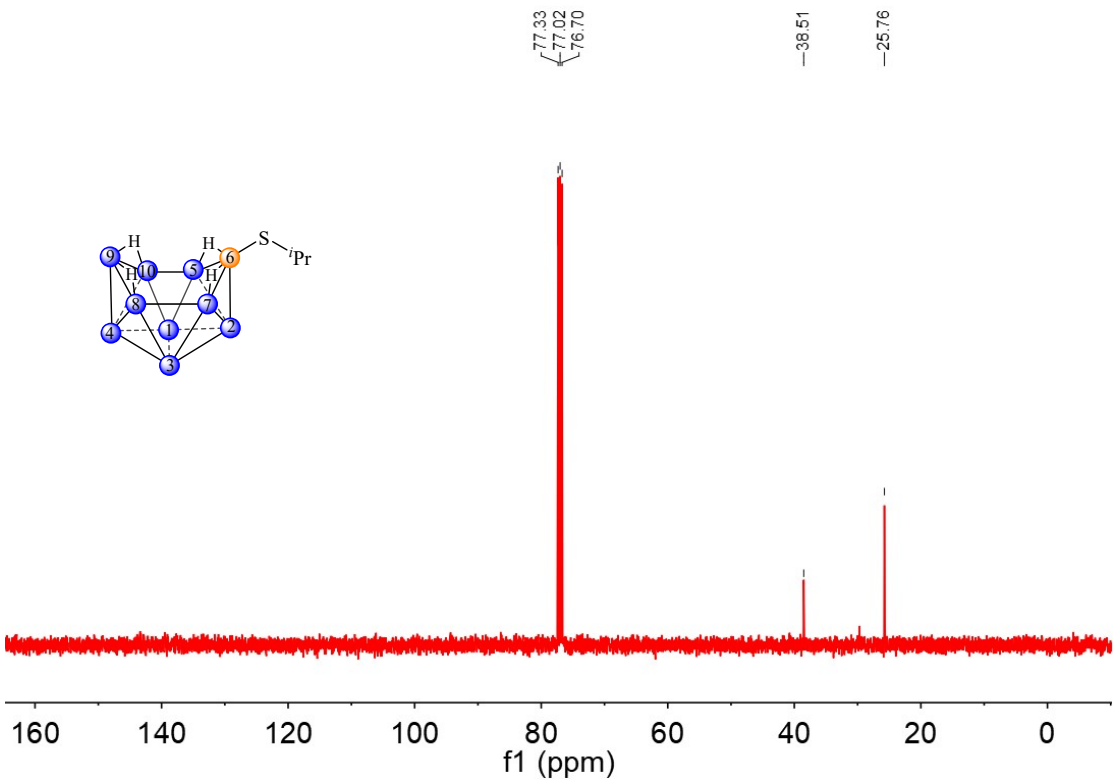


Figure S41. ^{13}C NMR spectrum of *nido*-6-$(CH_3)_2CHS$-$B_{10}H_{13}$ (**7**) in $CDCl_3$

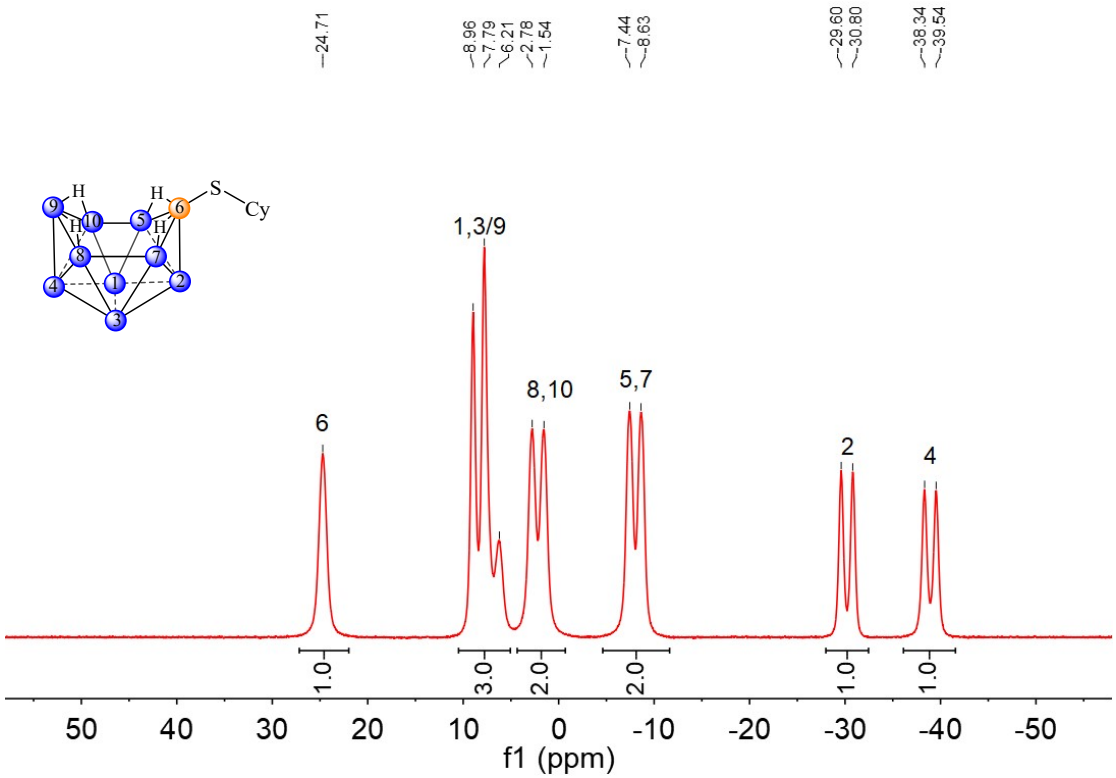


Figure S42. ^{11}B NMR spectrum of *nido*-6-$C_6H_{11}S$-$B_{10}H_{13}$ (**8**) in $CDCl_3$

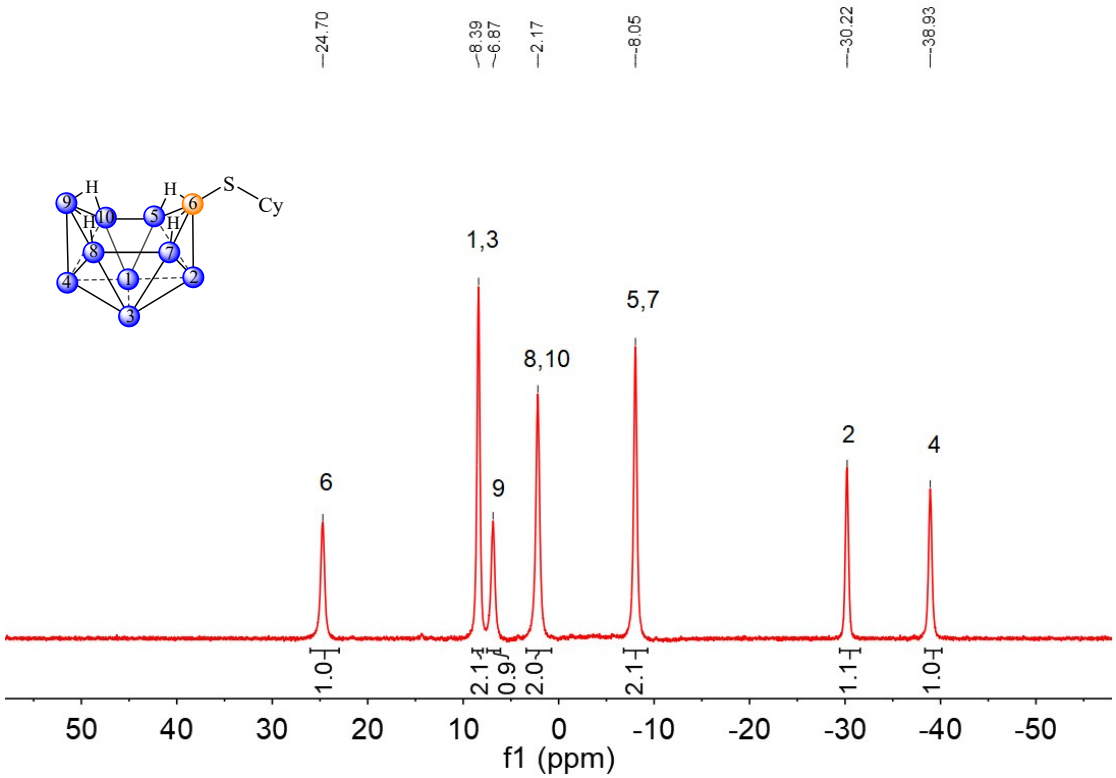


Figure S43. $^{11}B\{^1H\}$ NMR spectrum of *nido*-6-$C_6H_{11}S$-$B_{10}H_{13}$ (**8**) in $CDCl_3$

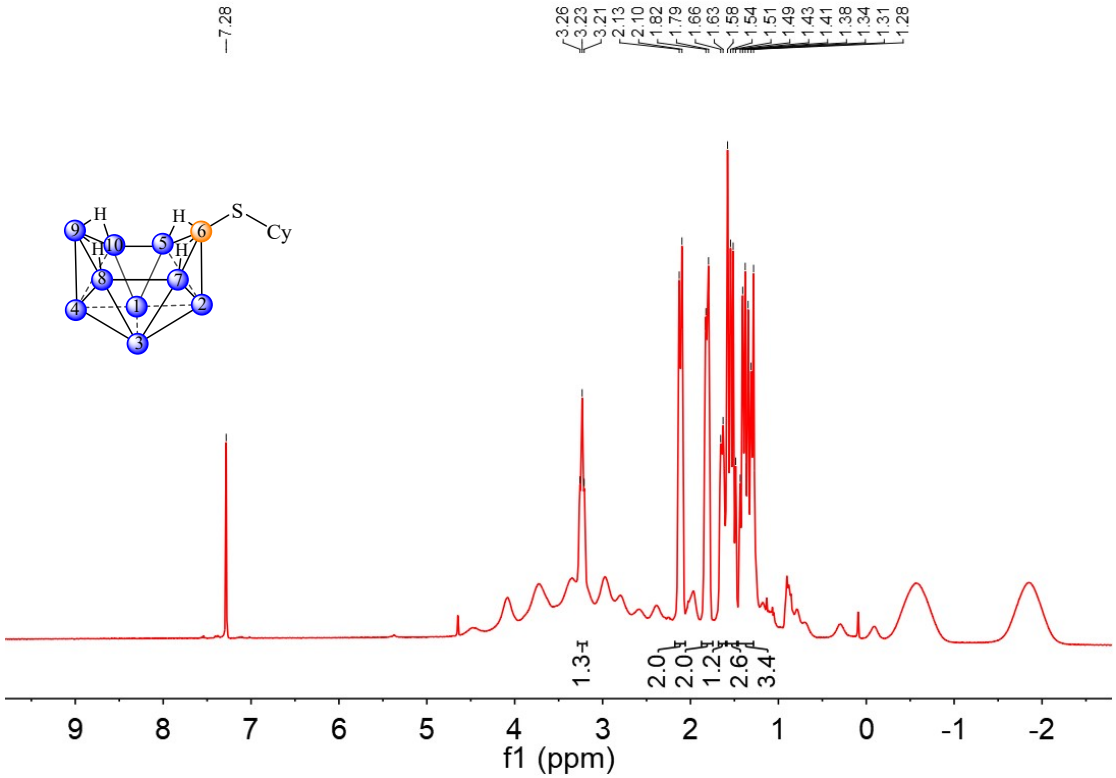


Figure S44. ^{1}H NMR spectrum of *nido*-6-$C_6H_{11}S$-$B_{10}H_{13}$ (**8**) in $CDCl_3$

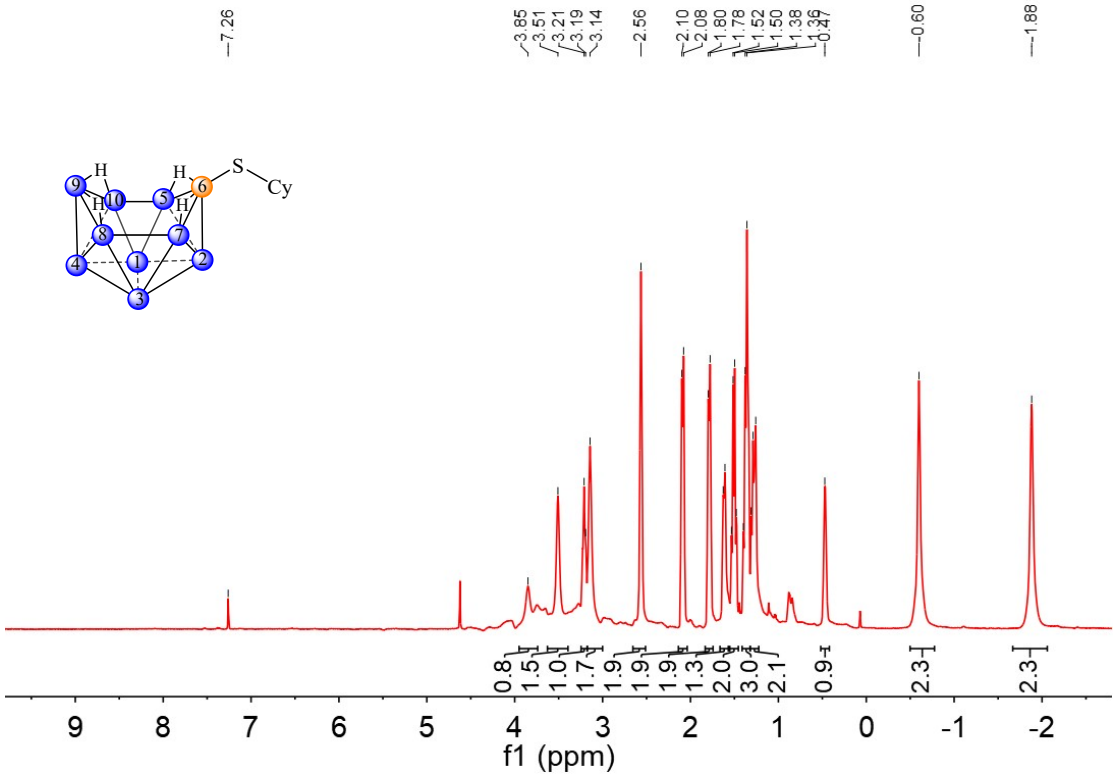


Figure S45. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-$C_6H_{11}S$-$B_{10}H_{13}$ (**8**) in $CDCl_3$

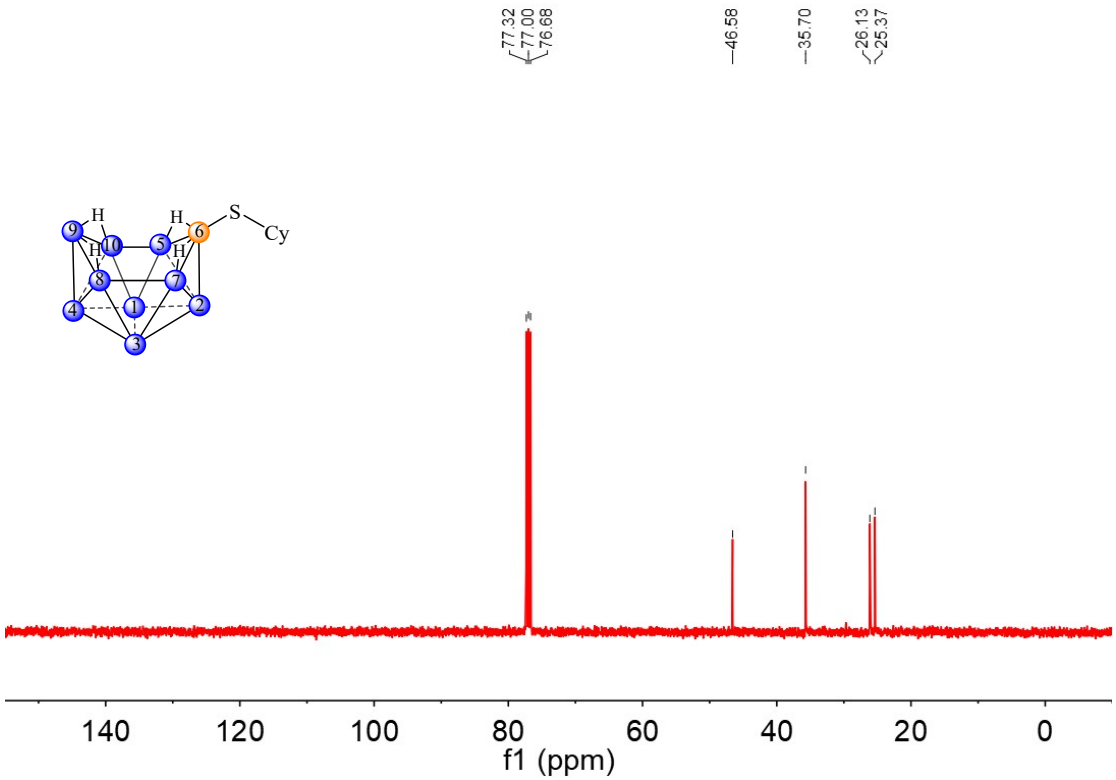


Figure S46. ^{13}C NMR spectrum of *nido*-6-$C_6H_{11}S$-$B_{10}H_{13}$ (**8**) in $CDCl_3$

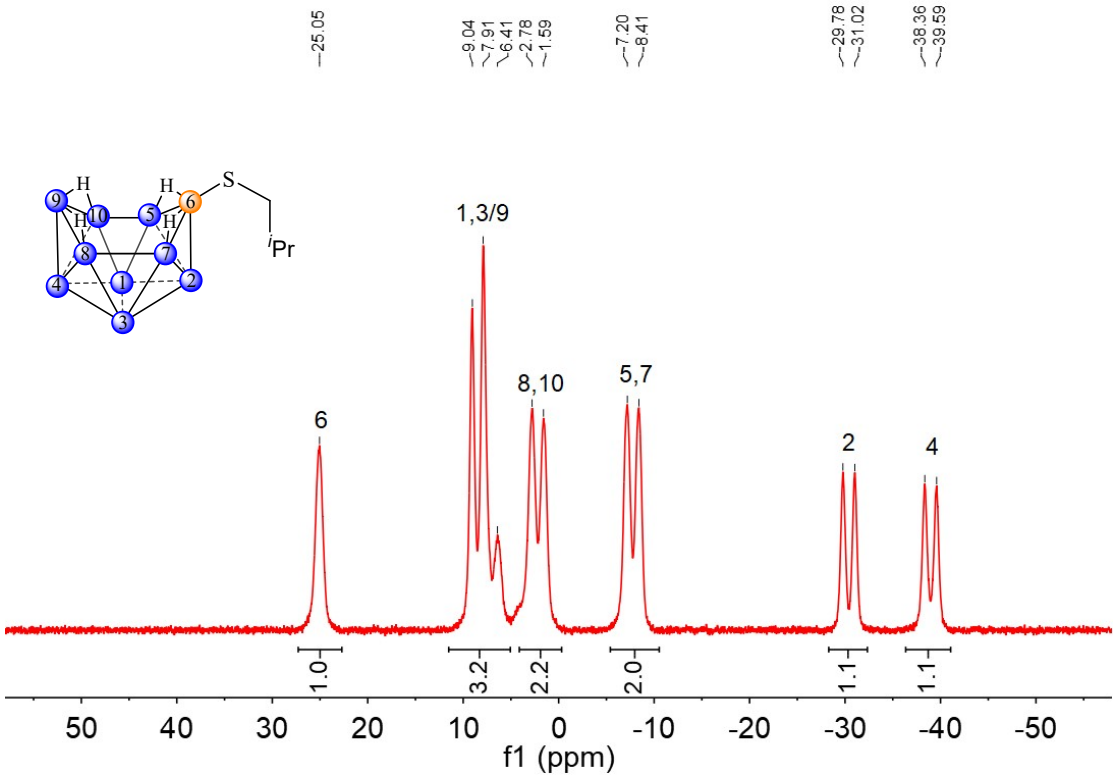


Figure S47. ^{11}B NMR spectrum of *nido*-6-$(CH_3)_2CHCH_2S$-$B_{10}H_{13}$ (**9**) in $CDCl_3$

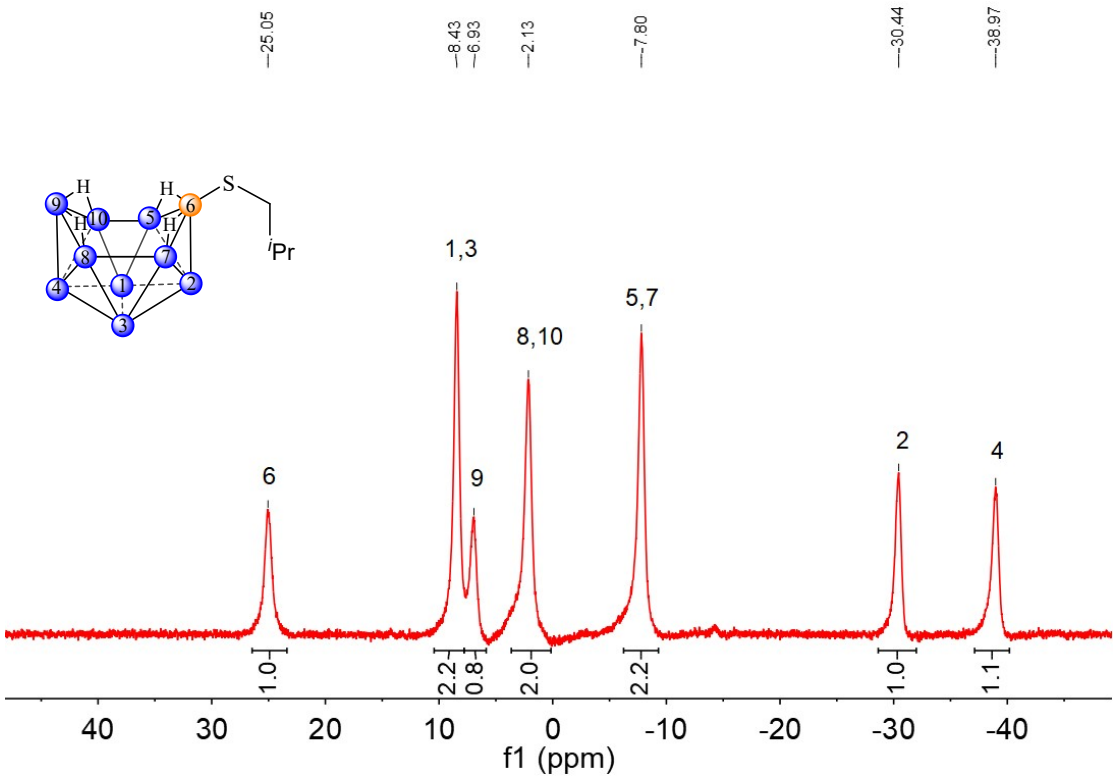


Figure S48. ^{11}B{^{1}H} NMR spectrum of *nido*-6-$(CH_3)_2CHCH_2S$-$B_{10}H_{13}$ (**9**) in $CDCl_3$

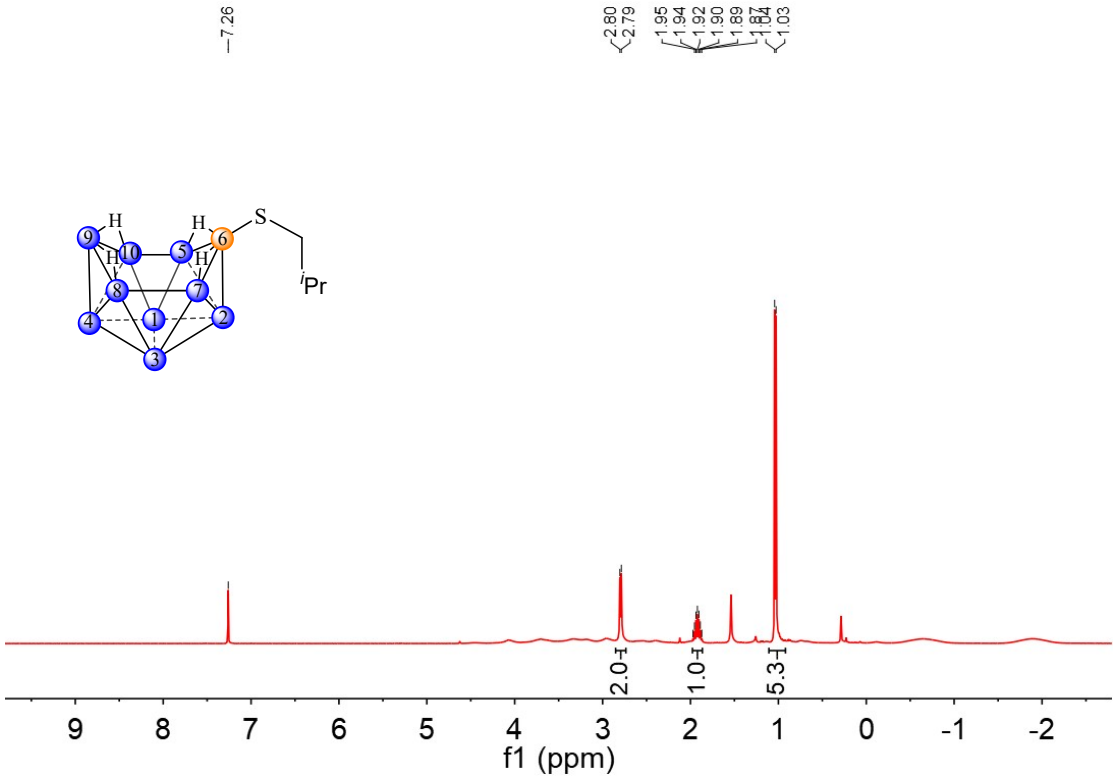


Figure S49. ^{1}H NMR spectrum of *nido*-6-$(CH_3)_2CHCH_2S$-$B_{10}H_{13}$ (**9**) in $CDCl_3$

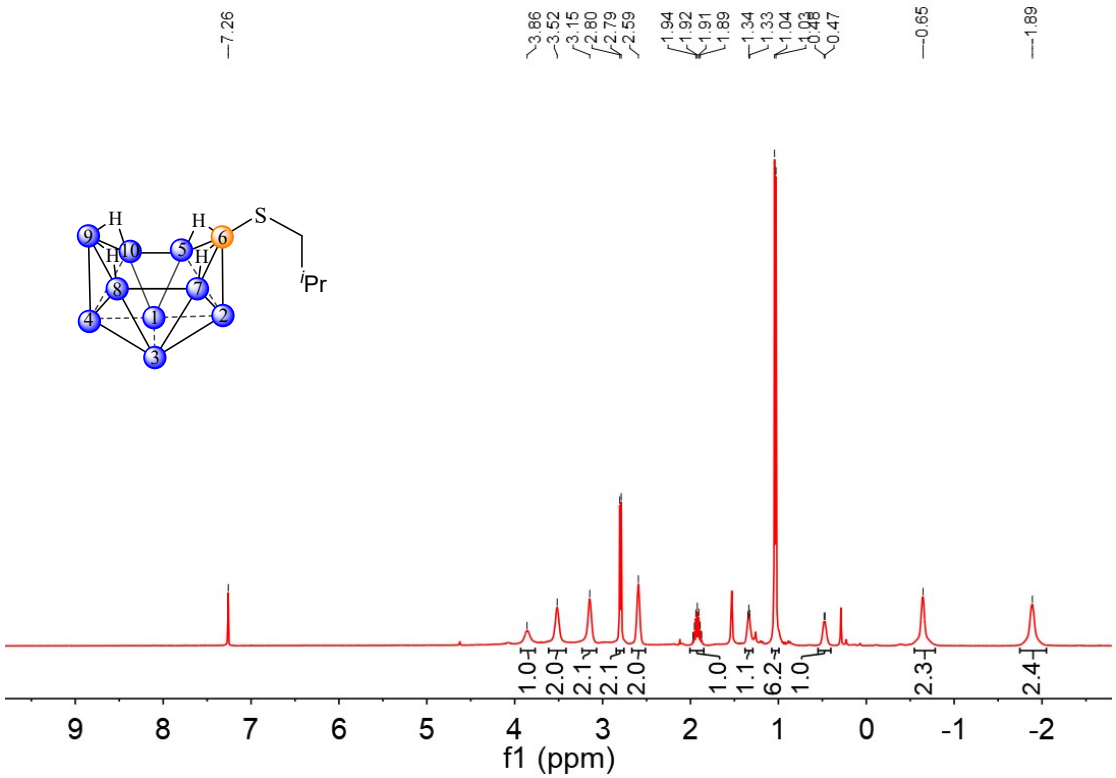


Figure S50. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-$(CH_3)_2CHCH_2S$-$B_{10}H_{13}$ (**9**) in $CDCl_3$

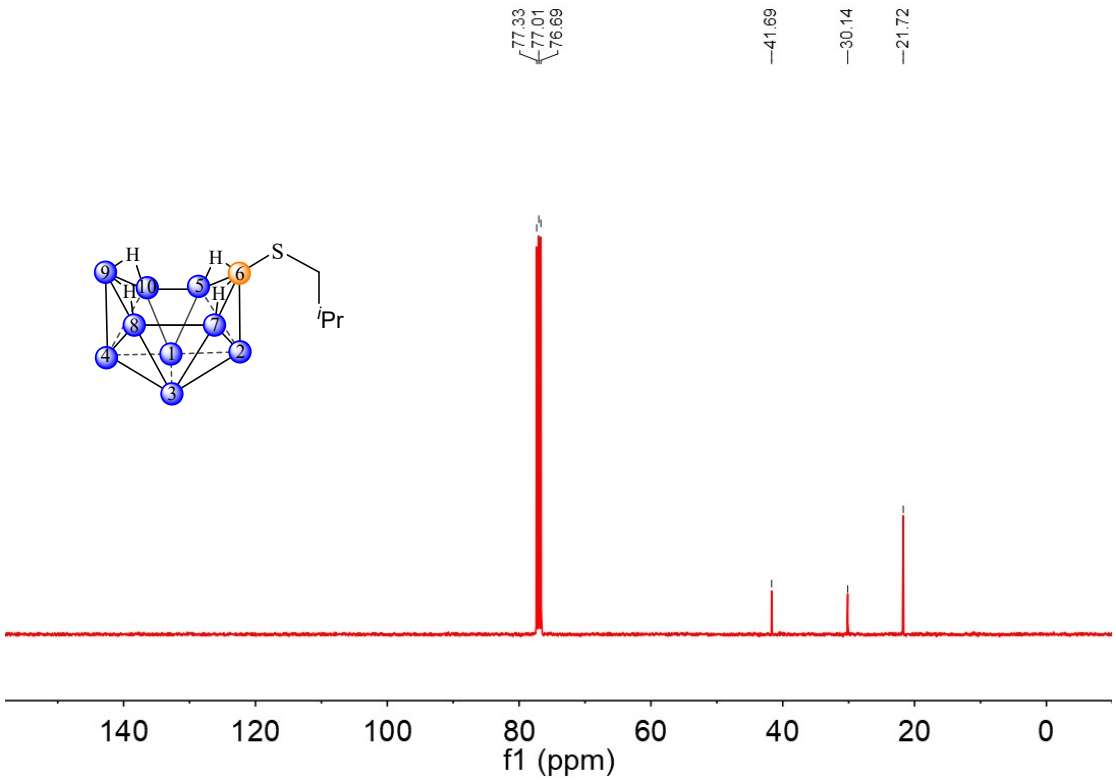


Figure S51. ^{13}C NMR spectrum of *nido*-6-$(CH_3)_2CHCH_2S$-$B_{10}H_{13}$ (**9**) in $CDCl_3$

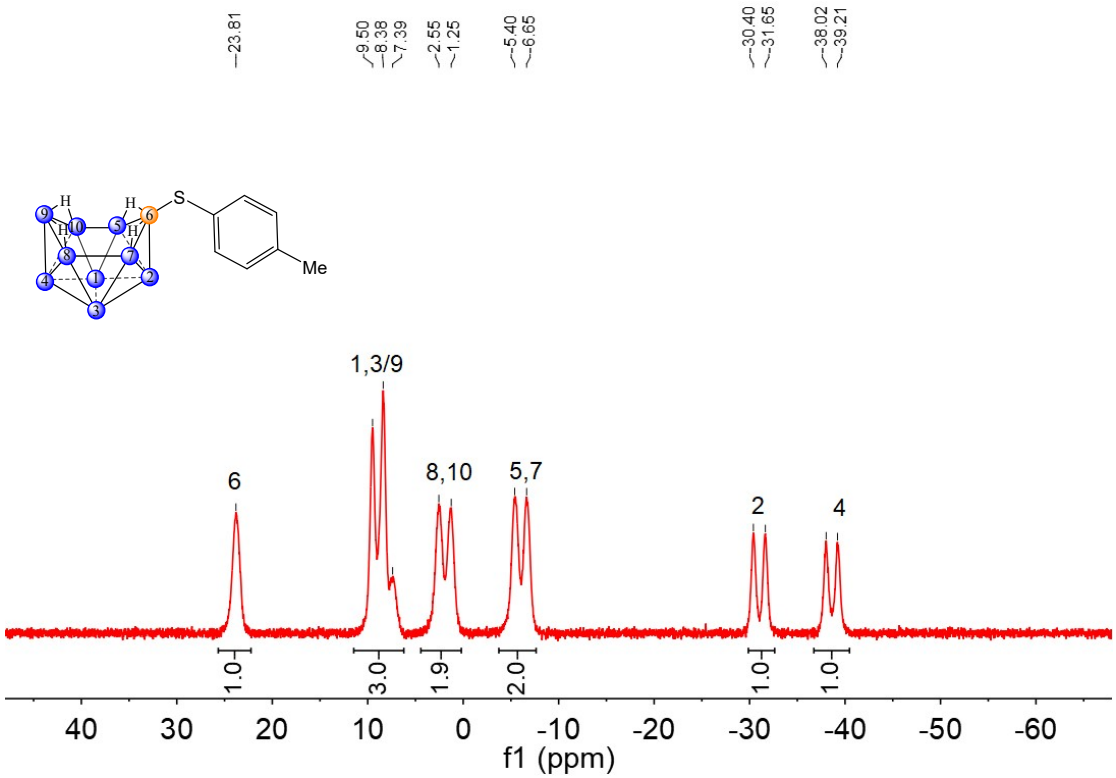


Figure S52. ^{11}B NMR spectrum of *nido*-6-*p*-CH_3-PhS-$B_{10}H_{13}$ (**10**) in $CDCl_3$

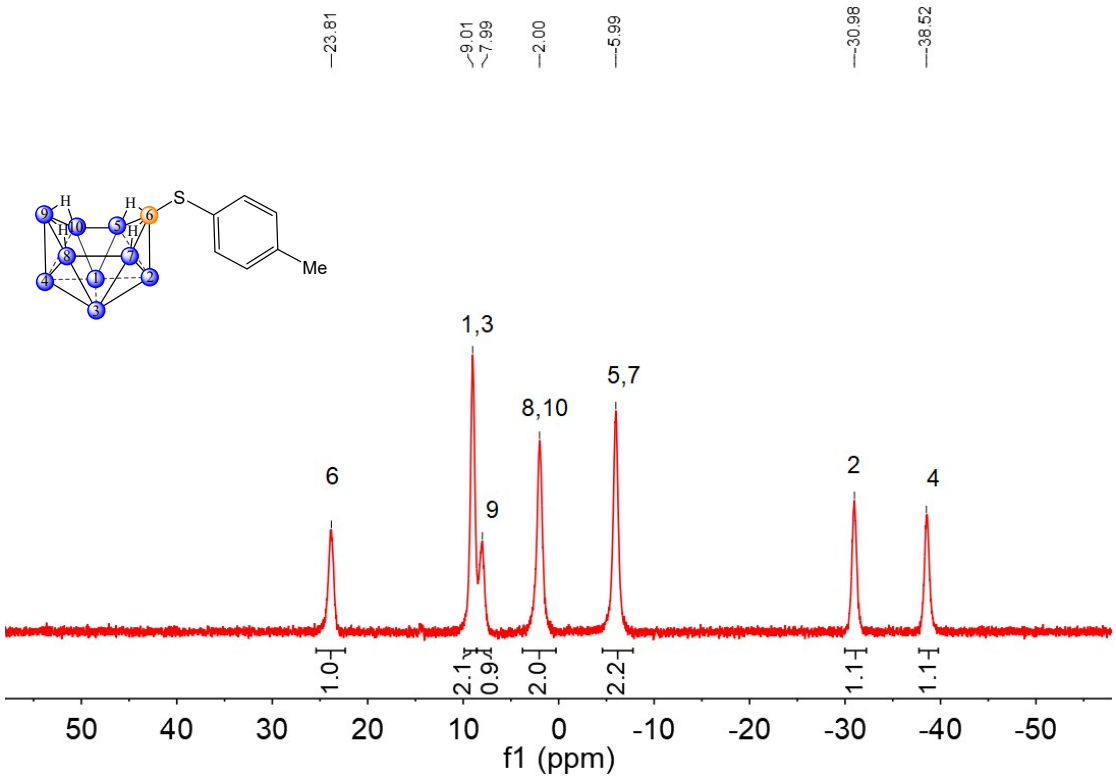


Figure S53. $^{11}B\{^1H\}$ NMR spectrum of *nido*-6-*p*-CH_3-PhS-$B_{10}H_{13}$ (**10**) in $CDCl_3$

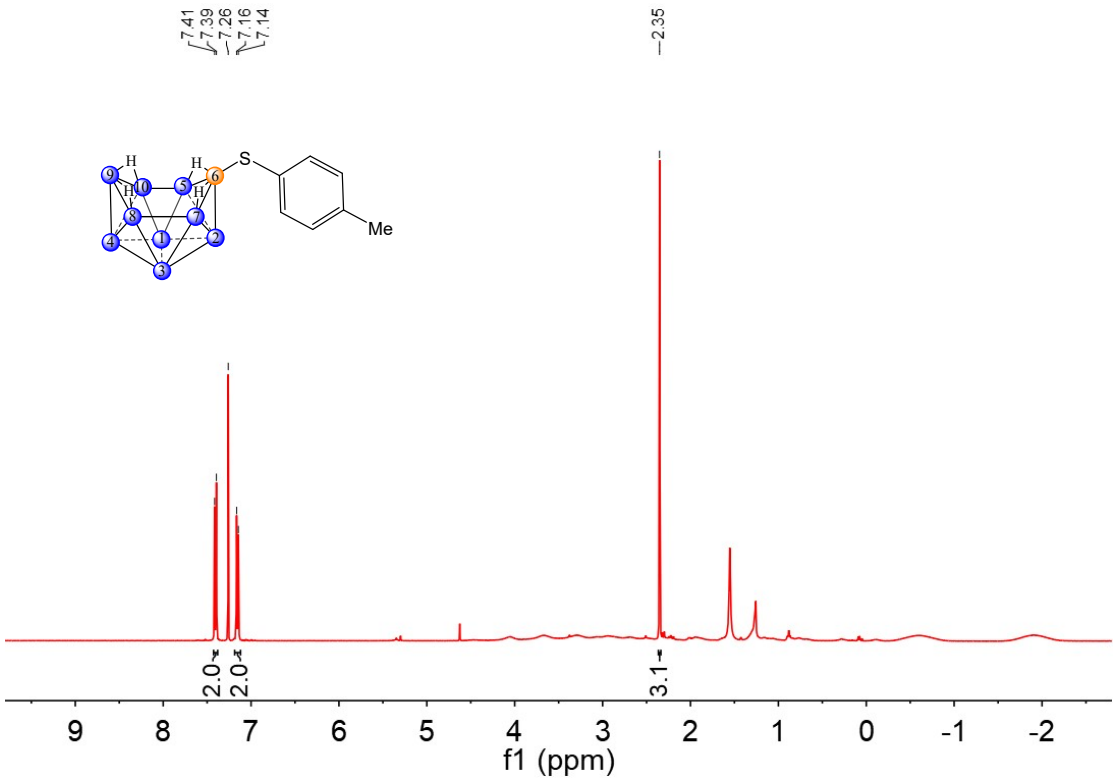


Figure S54. ^{1}H NMR spectrum of *nido*-6-*p*-CH_3-PhS-$B_{10}H_{13}$ (**10**) in $CDCl_3$

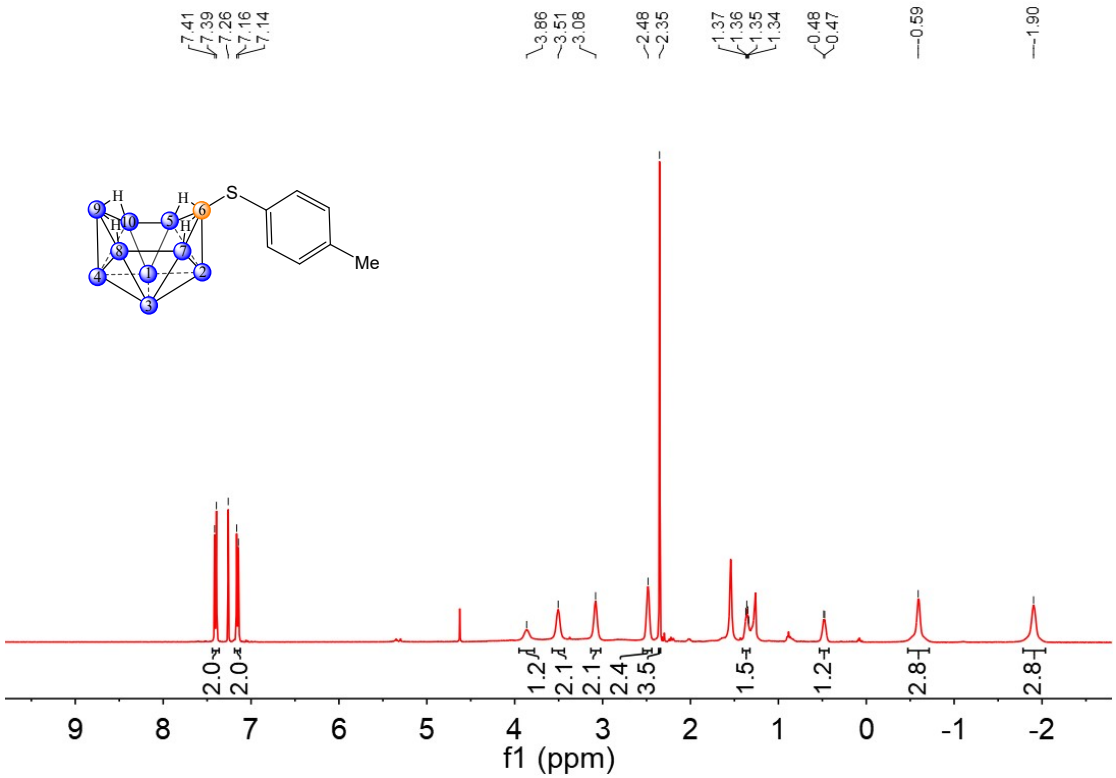


Figure S55. ^{1}H{^{11}B} NMR spectrum of *nido*-6-*p*-CH_3-PhS-$B_{10}H_{13}$ (**10**) in $CDCl_3$

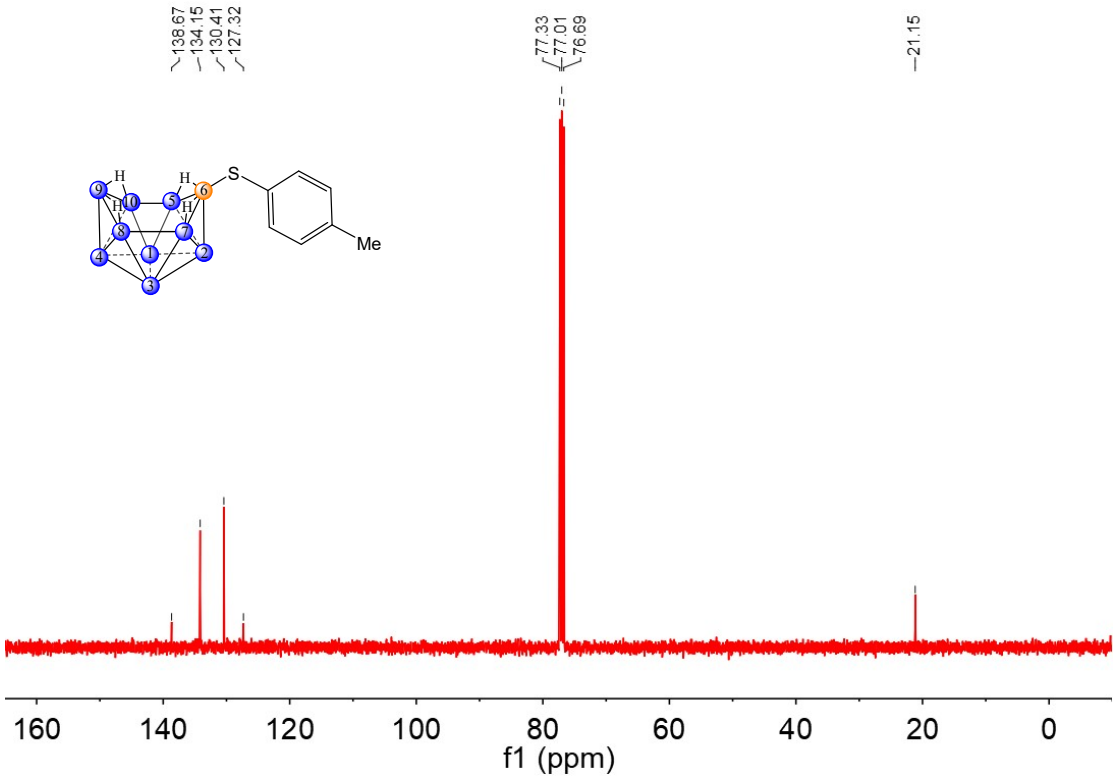


Figure S56. ^{13}CNMR spectrum of *nido*-6-*p*-CH_3-PhS-$B_{10}H_{13}$ (**10**) in $CDCl_3$

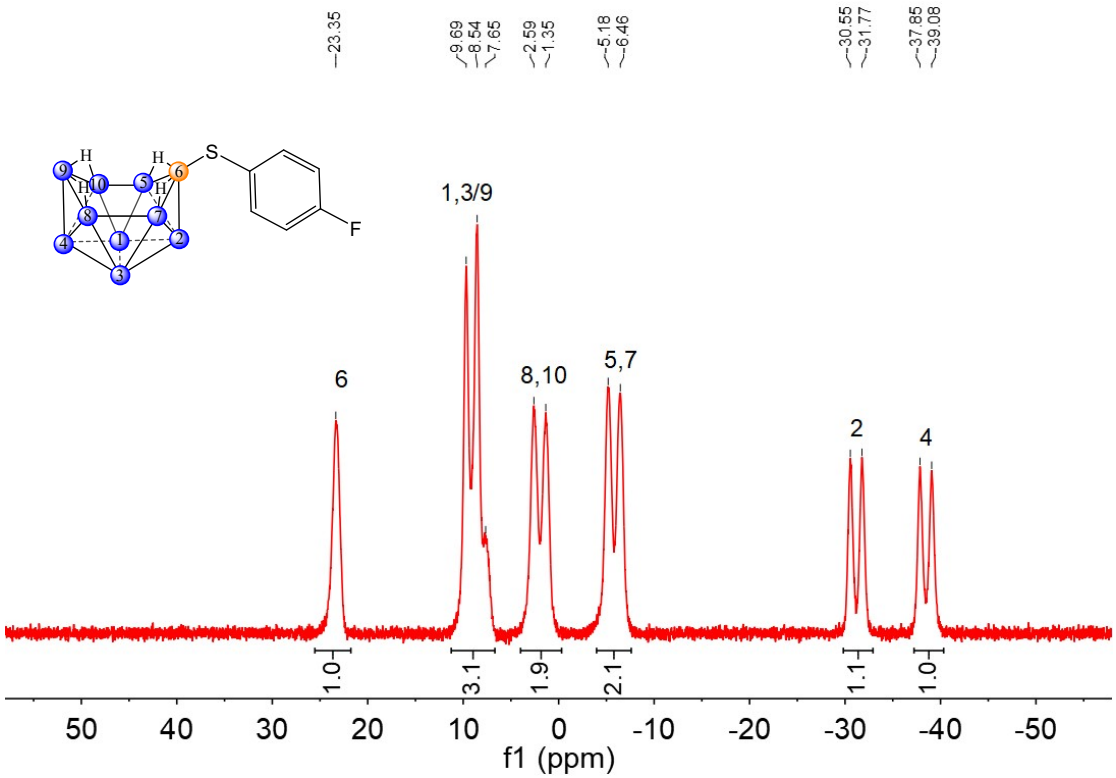


Figure S57. ^{11}B NMR spectrum of *nido*-6-*p*-F-PhS-$B_{10}H_{13}$ (**11**) in $CDCl_3$

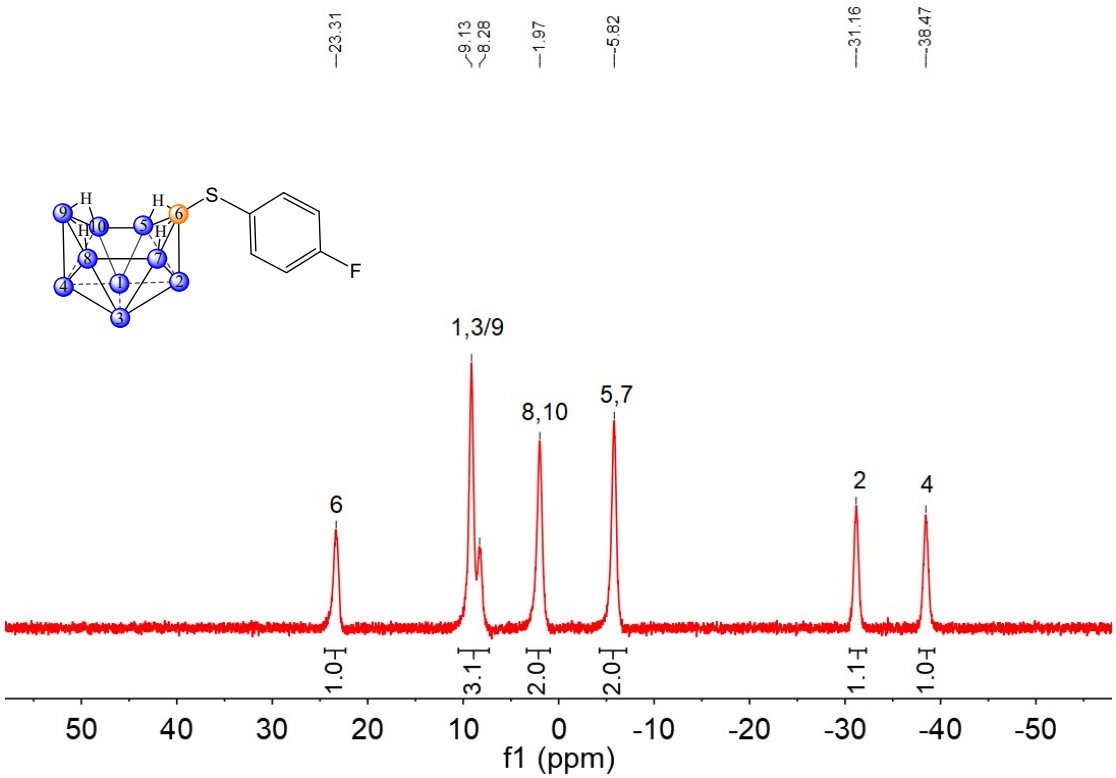


Figure S58. $^{11}B\{^1H\}$ NMR spectrum of *nido*-6-*p*-F-PhS-$B_{10}H_{13}$ (**11**) in $CDCl_3$

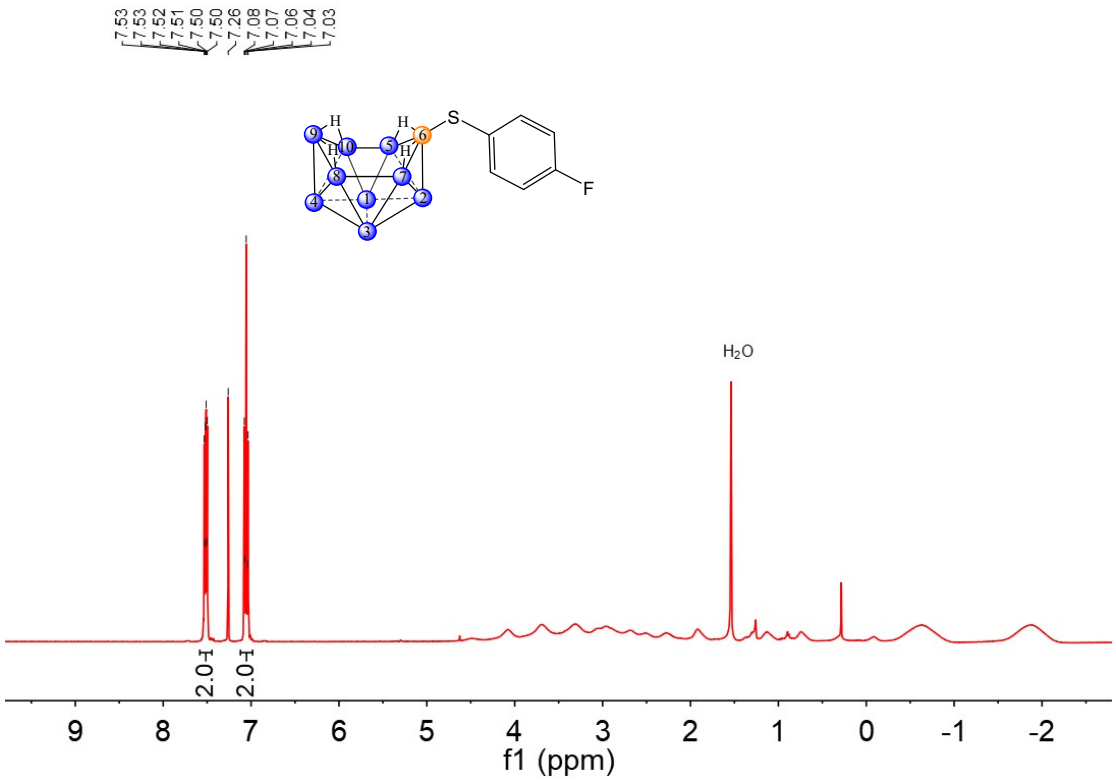


Figure S59. ^{1}H NMR spectrum of *nido*-6-*p*-F-PhS-$B_{10}H_{13}$ (**11**) in $CDCl_3$

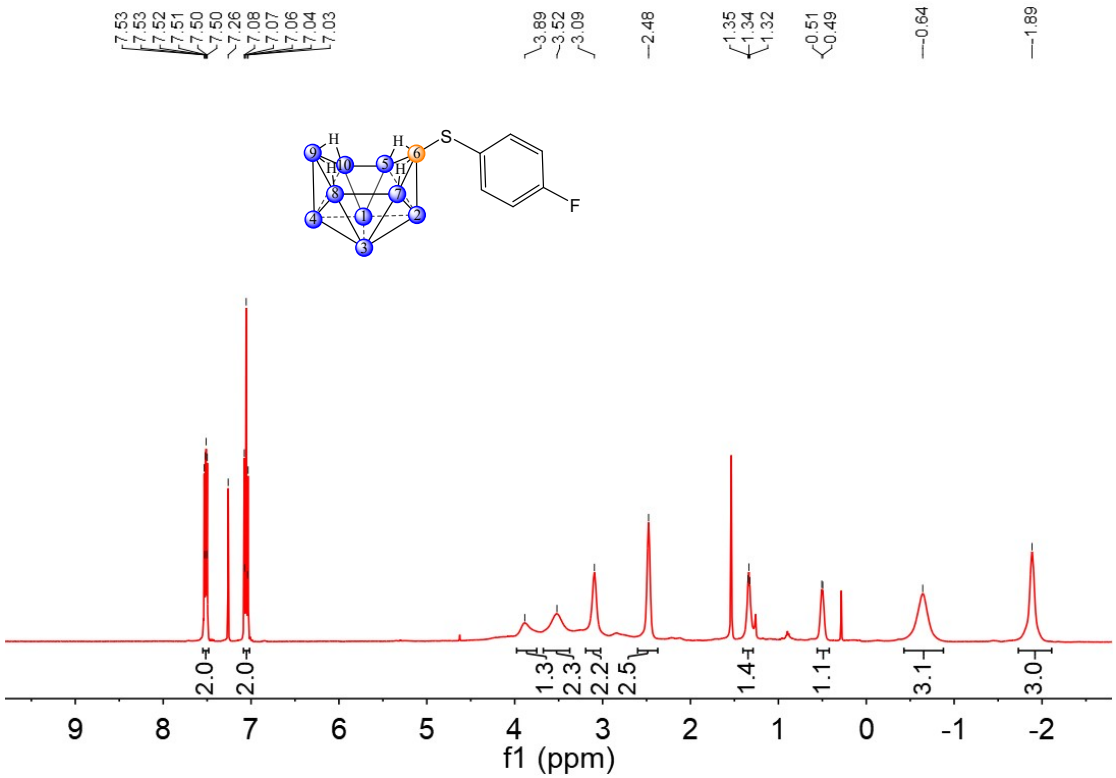


Figure S60. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-*p*-F-PhS-$B_{10}H_{13}$ (**11**) in $CDCl_3$

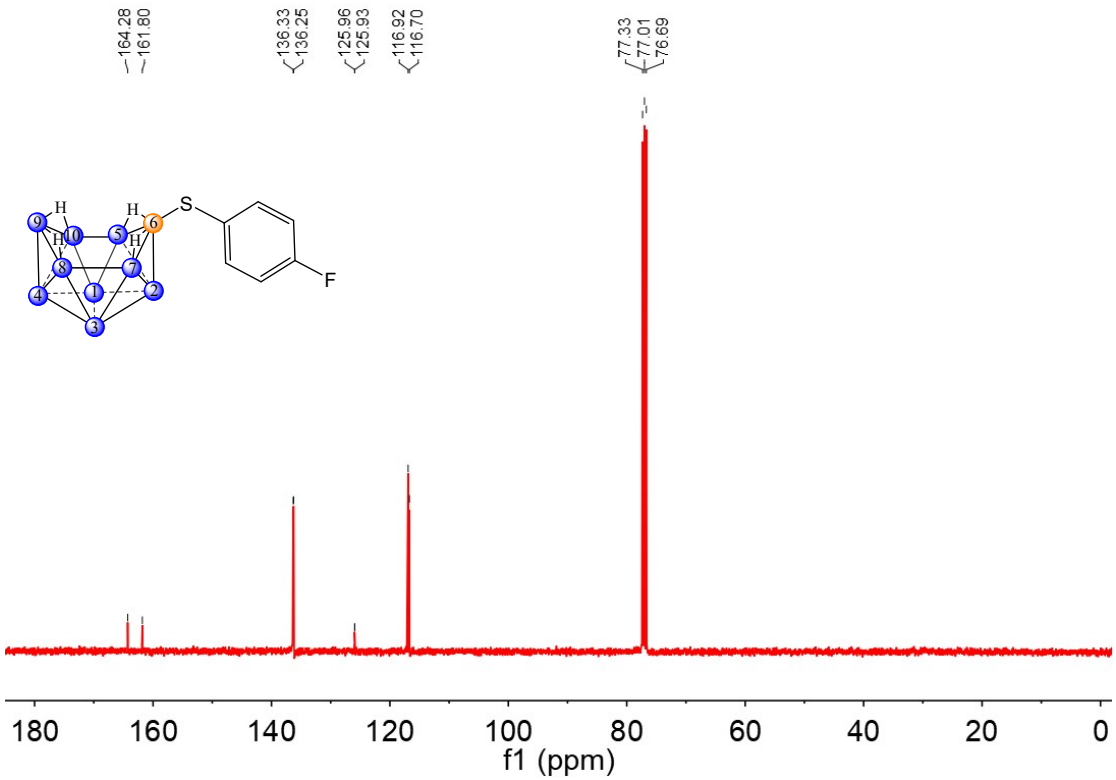


Figure S61. ^{13}C NMR spectrum of *nido*-6-*p*-F-PhS-$B_{10}H_{13}$ (**11**) in $CDCl_3$

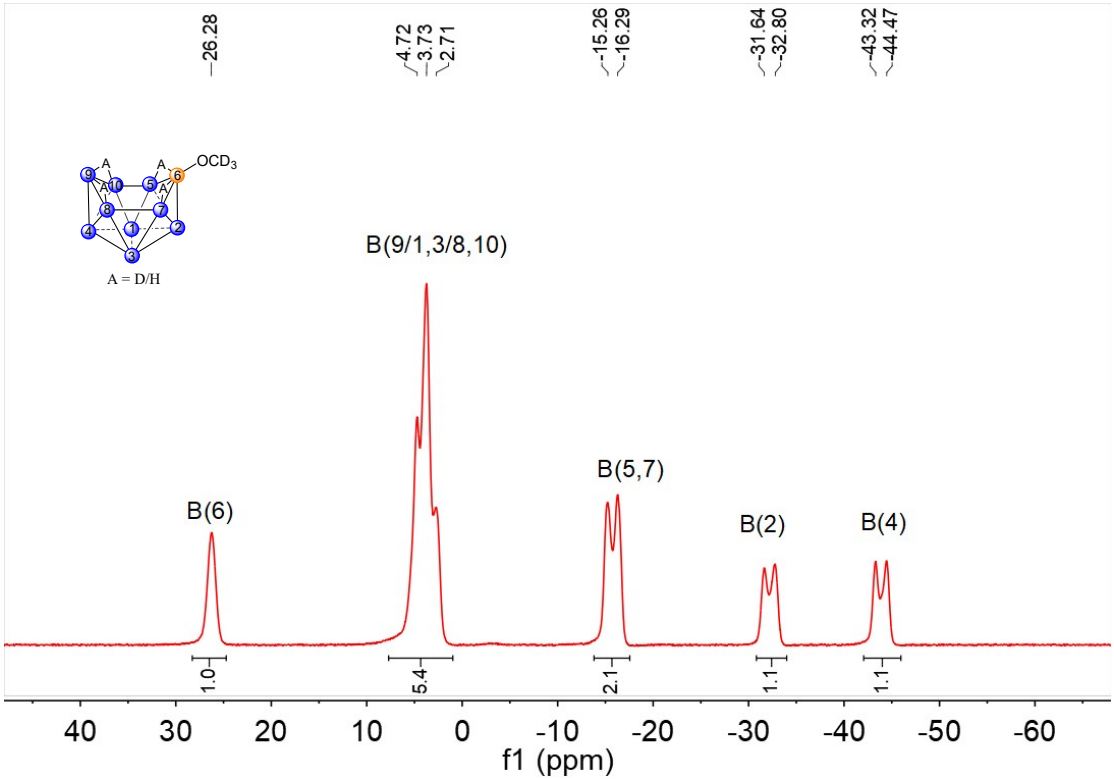


Figure S62. ^{11}B NMR spectrum of *nido*-6-CD_3O-$B_{10}H_{10}D_3$ in $CDCl_3$

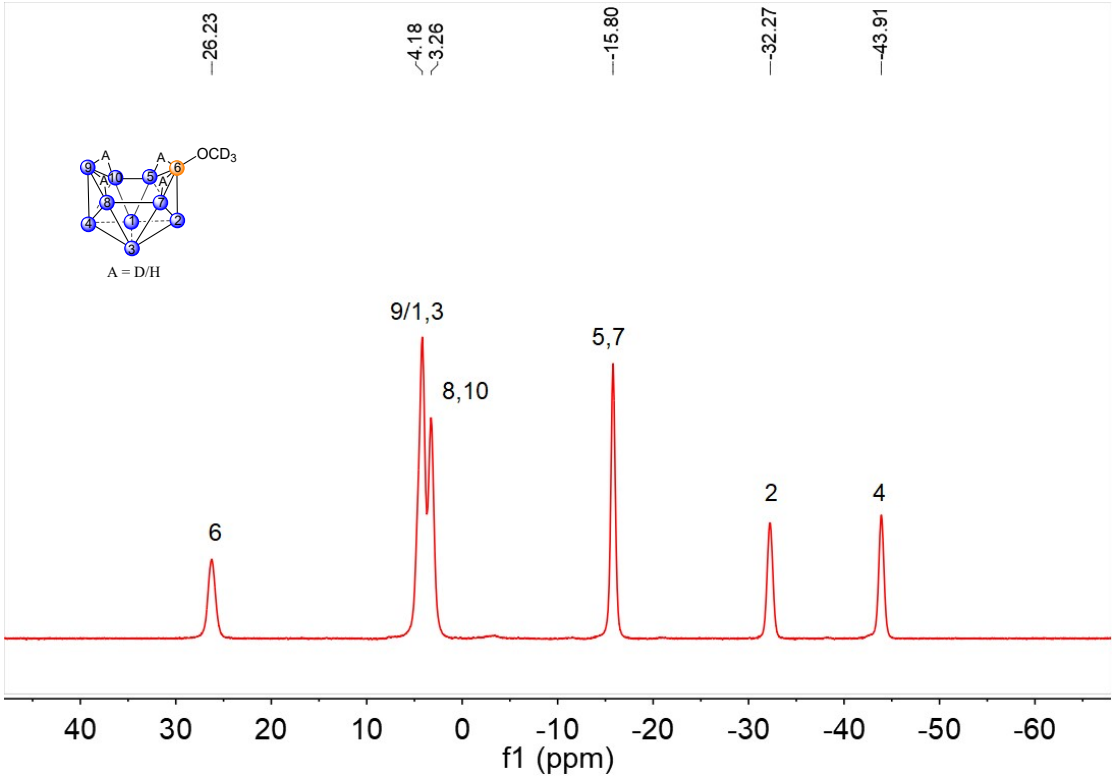


Figure S63. $^{11}B\{^1H\}$ NMR spectrum of *nido*-6-CD_3O-$B_{10}H_{10}D_3$ in $CDCl_3$

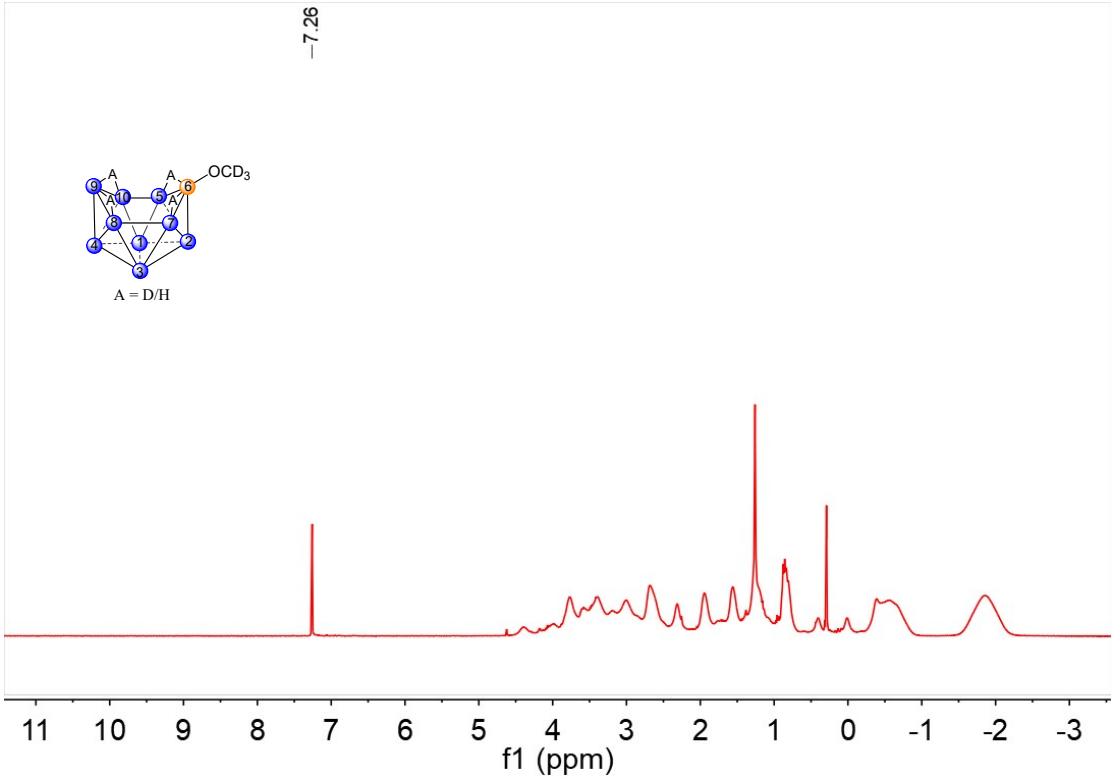


Figure S64. ^{1}H NMR spectrum of *nido*-6-CD_3O-$B_{10}H_{10}D_3$ in $CDCl_3$

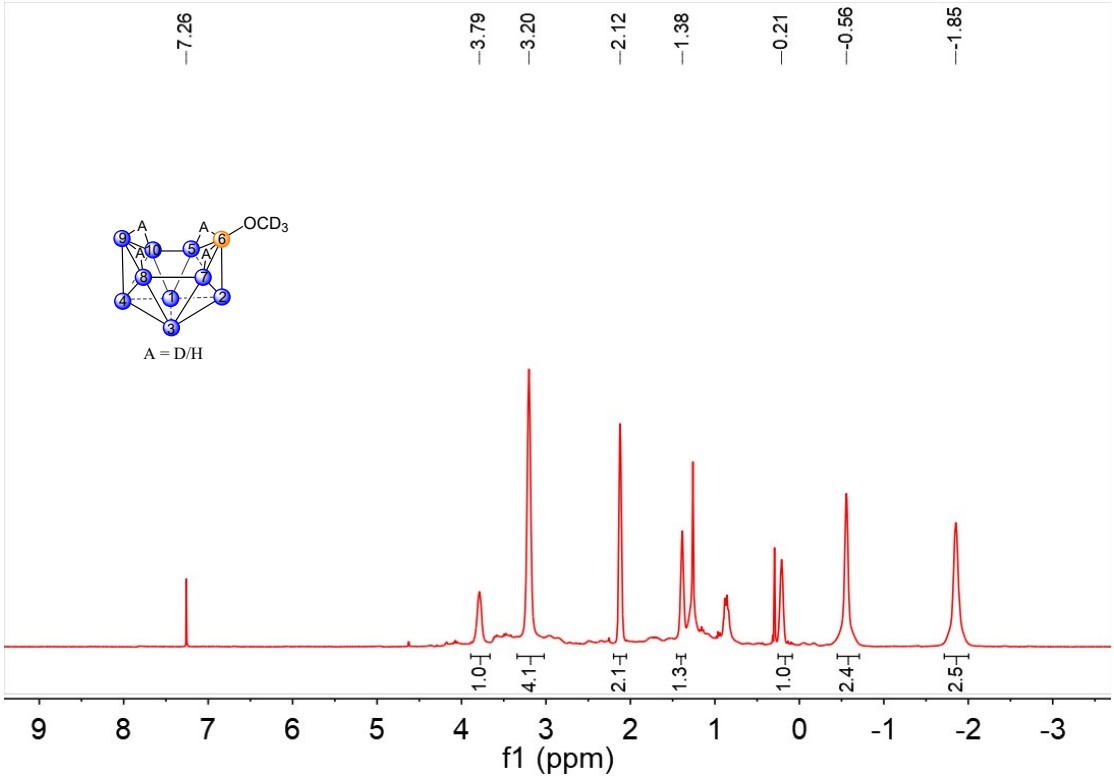


Figure S65. $^{1}H\{^{11}B\}$ NMR spectrum of *nido*-6-CD_3O-$B_{10}H_{10}D_3$ in $CDCl_3$

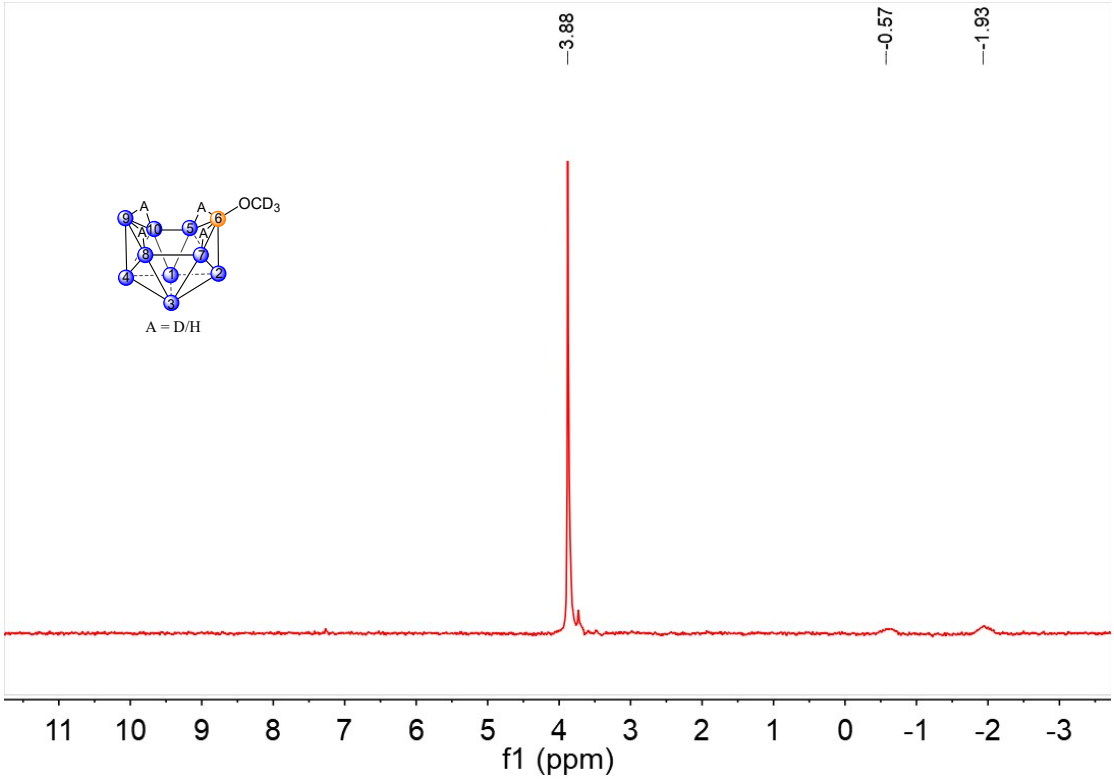


Figure S66. ^{2}H NMR spectrum of *nido*-6-CD_3O-$B_{10}H_{10}D_3$ in $CHCl_3$