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Supporting Information

Photoredox B–H Functionalization to Selective B–N(sp3) Coupling of *nido*-Carborane with Primary and Secondary Amines

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1 General Information

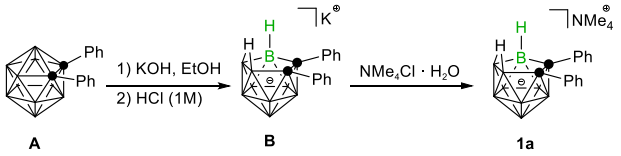
Unless otherwise noted, all experiments were all performed under an air atmosphere. Except for special instructions, solid or liquid reagents were purchased from suppliers without further purification. The process for the synthesis of *nido*-carboranes has been optimized according to literature reports.[1] 3w blue LED lights were used as the light source. Analytical thin layer chromatography (TLC) was performed on silica gel (GF 254) plates, while column chromatography was performed on silica gel (200−300 or 300−400 mesh). TLC samples for carborane-containing compounds were stained with 1 wt. % $PdCl_2$ in HCl (6 M) and were developed with high heat using a heat gun.

^{1}H, ^{11}B, $^{11}B\{^{1}H\}$, ^{13}C, ^{19}F spectra were recorded using Bruker AVANCE III 400 MHz or 500 MHz spectrometers under ambient conditions unless otherwise stated. All chemical shift (δ values) were reported in ppm with the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts. ^{11}B chemical shifts were measured utilizing external $Et_2O{\cdot}BF_3$ (δ=0 ppm) as reference. Mass spectra were conducted at Agilent 6540 Ultra-High-Definition (UHD) Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) liquid chromatography/mass spectrometry (LC/MS) system and Thermo Scientific TRACE 1300 ISQ LT gas chromatography/mass spectrometry (GC/MS) system.

Single crystal X-ray crystallographic data were collected on a Bruker SMART Apex II CCD diffractometer by means of graphitemonochromated (Mo-Kα radiation, λ = 0.7107 Å). APEX II program was used to determine the unit cell parameters and for data collection. The data were integrated and corrected for Lorentz and polarization effects using SAINT. Absorption correction was applied with SADABS. The structure was solved by direct method and refined by full-matrix least-squares method on F2 using the SHELXTL or Olex2 crystallographic software package. All non-hydrogen atom positions were determined to utilize the difference Fourier synthesis, while the hydrogen atoms were placed at geometrically calculated positions using a riding model. X-ray data can be obtained from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

2 Experimental Section

2.1 Synthesis of Starting Materials

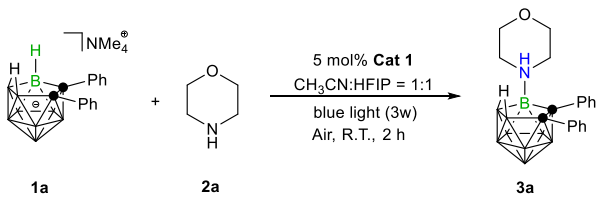


Scheme S1. Schematic presentation for the synthesis of 1a.

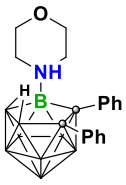
Deboronation of *closo*-carborane substrates: A 50 mL Schlenk tube was added by substituted *closo*-carborane derivatives (5.0 mmol), KOH (1.12 g, 20 mmol) and 25 mL EtOH. The mixture was refluxed for 10 hours before cooling down to room temperature. HCl (1M) was added to adjust pH to 6-7. After filtration and evaporation, the resulting white solid was dissolved in 50 mL deionized water and an aqueous solution of NMe_4Cl (602.8 mg, 5.5 mmol) was added dropwise. The resulting mixture was stirred overnight and filtered. The filter cake was washed by *n*-hexane and diethyl ether for three times, respectively. Finally, dried under vacuum to give the corresponding *nido*-carborane substrates.

2.2 General Procedure for Intermolecular B−N Coupling Reactions

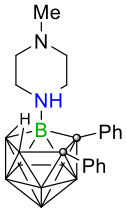
Under air atmosphere, **1a** (38.2 mg, 0.1 mmol), **2a** (17.4 mg, 0.2 mmol) and **Cat 1** (5 mol%) at ambient temperature in CH_3CN:HFIP =1:1 (1.0 mL) with the irradiation of 3W blue LEDs for 2 h. The mixture was filtered through a silica gel plug and concentrated in vacuo. The products **3a-3l, 4a-4p** were obtained by flash column chromatography on silica gel (hexane: ethyl acetate: acetone = 10:5:2, v/v).



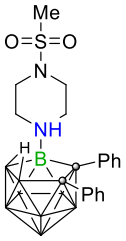
3 Detailed Descriptions for Products



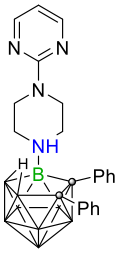
3a: Yield 81 %. White solid. **^{1}H NMR (400 MHz, Acetone-*d*$_6$)** δ 7.26 – 7.24 (m, 2H), 7.13 – 7.10 (m, 2H), 6.96 – 6.91 (m, 6H), 6.19 (br, 1H, NH), 3.93 – 3.90 (m, 1H), 3.82 – 3.79 (m, 2H), 3.62 (td, *J* = 12.7, 12.4, 2.2 Hz, 1H), 3.50 (td, *J* = 12.7, 12.3, 2.4 Hz, 1H), 3.41 – 3.30 (m, 1H), 3.20 – 3.11 (m, 1H), 3.01 – 2.98 (m, 1H), 3.03 − 0.32 (8H, B−H), −2.19 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ 139.7, 137.3, 133.1, 132.5, 128.3, 127.9, 127.0, 75.2 (Cage C), 65.3, 65.1, 62.8 (Cage C), 55.6, 53.9; **^{11}B{^{1}H} (128 MHz, Acetone-*d*$_6$)** δ −3.4 (1B), −6.6 (1B), −12.4 (1B), −15.2 (2B), −23.1 (1B), −26.4 (1B), −32.4 (1B), −36.9 (1B). **HRMS *m/z*** calcd for $C_{18}B_9NH_{28}O$ $[M+Na]^+$: 395.2942, Found: 395.2954.



3b: Yield 50%. White solid. **^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) Conformer Ⅰ:** δ 7.40 – 7.37 (m, 2H), 7.24 – 7.22 (m, 2H), 7.15 – 7.07 (m, 6H), 4.69 (br, 1H, NH), 3.82 – 3.78 (m, 1H), 3.34 – 3.24 (m, 1H), 3.13 – 3.04 (m, 1H), 2.94 – 2.88 (m, 2H), 2.76 – 2.73 (m, 1H), 2.27 (s, 3H, CH_3), 2.10 – 2.09 (m, *J* = 2.4 Hz, 1H), 2.08 – 2.07 (m, 1H), 3.25 − 0.15 (8H, B−H), −2.15 (br, 1H, B−H−B); **Conformer Ⅱ:** δ 7.40 – 7.37 (m, 2H), 7.24 – 7.22 (m, 2H), 7.15 – 7.07 (m, 6H), 4.69 (br, 1H, NH), 3.82 – 3.78 (m, 1H), 3.34 – 3.24 (m, 1H), 3.13 – 3.04 (m, 1H), 2.94 – 2.88 (m, 2H), 2.76 – 2.73 (m, 1H), 2.25 (s, 3H, CH_3), 2.14 – 2.13 (d, *J* = 2.9 Hz,1H), 2.08 – 2.07 (m, 1H), 3.25 − 0.15 (8H, B−H), −2.15 (br, 1H, B−H−B); **^{13}C NMR (400 MHz, Acetonitrile-*d*$_3$)** δ 168.4, 165.7, 161.8, 161.1, 157.1, 156.7, 155.9, 146.8, 84.1, 82.6, 82.3, 82.0, 74.2; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −3.4 (1B), −6.6 (1B), −12.4 (1B), −15.3 (2B), −23.1 (1B), −26.5 (1B), −32.4 (1B), −36.9 (1B). **HRMS *m/z*** calcd for $C_{19}B_9N_2H_{31}$ $[M + Na]^+$: 408.3259, Found: 408.3263.

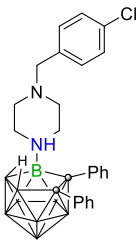


3c: Yield 70 %. White solid. **^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$)** δ 7.40 – 7.38 (m, 2H), 7.24 – 7.22 (m, 2H), 7.15 – 7.08 (m, 6H), 5.15 (br, 1H, NH), 3.92 (d, *J* = 13.4 Hz, 1H), 3.81 – 3.75 (m, 1H), 3.64 – 3.60 (m, 1H), 3.45 – 3.36 (m, 1H), 3.23 – 3.11 (m, 2H), 3.05 – 2.97 (m, 2H), 2.87 (s, 3H, Me), 2.69 − 0.20 (8H, B−H), −2.12 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$)** δ 168.2, 165.5, 161.8, 161.2, 157.2, 156.7,156.7, 156.0, 146.9, 83.4, 81.9, 72.8, 72.5(cage C), 63.9, 58.8(cage C); **^{11}B{^{1}H} (128 MHz, Acetonitrile-*d*$_3$)** δ −3.0 (1B), −6.8 (1B), −12.5 (1B), −15.3 (2B), −22.9 (1B), −26.6 (1B), −32.4 (1B), −37.1 (1B). **HRMS *m/z*** calcd for $C_{19}B_9N_2H_{31}O_2S$ $[M + Na]^+$: 472.2878, Found: 472.2892.

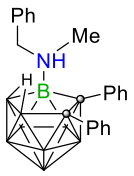


3d: Yield 80 %. White solid. **^{1}H NMR (400 MHz, Dimethylsulfoxide-*d*$_6$)** δ 8.35 – 8.34 (d, *J* = 4.8 Hz, 2H), 7.61 – 7.55 (br, 1H, NH), 7.20 – 7.18 (m, 2H), 7.06 – 7.05 (m, 2H), 6.97 – 6.89 (m, 6H), 6.70 – 6.68 (t, *J* = 4.8 Hz, 1H), 4.47 – 4.38 (dd, *J* = 22.3, 14.1 Hz, 1H), 3.52 – 3.49 (d, *J* = 12.8 Hz, 1H), 3.11 – 3.00 (m, 3H), 2.87 – 2.79 (m, 1H), 2.66– 2.57(m, 1H), 3.19 − 0.27 (8H, B−H), −2.10 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Dimethylsulfoxide-*d*$_6$)** δ 160.8, 158.0, 138.4, 136.3, 132.0, 131.4, 127.0, 126.7, 126.2, 111.2, 73.2 (Cage C), 61.5 (Cage C), 51.8, 51.7, 41.4, 41.3; **^{11}B{^{1}H} (128**

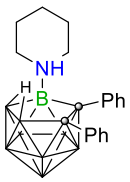
MHz, Acetone-*d*$_3$) δ −3.5 (1B), −6.6 (1B), −12.4 (1B), −15.2 (2B), −23.1 (1B), −26.5 (1B), −32.4 (1B), −36.9 (1B). **HRMS *m/z*** calcd for $C_{22}B_9N_4H_{31}$ [M + Na]$^+$: 471.3357, Found: 471.3365.



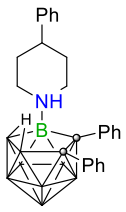
3e: Yield 67 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.31 – 7.24 (m, 4H), 7.22 – 7.19 (m, 2H), 7.09 – 7.08 (m, 3H), 7.03 – 6.96 (m, 5H), 3.63 – 3.58 (m, 1H), 3.47 – 3.40 (m, 1H), 3.39 (s, 2H), 3.19 – 3.09kk (m, 2H), 3.07 – 3.06 (br, 1H, NH), 2.95 – 2.90 (m, 1H), 2.87 – 2.82 (m, 1H), 3.32 − 0.25 (8H, B−H), 1.85– 1.76 (m, 2H), −2.50 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.9, 136.5, 136.1, 133.7, 132.6, 131.2, 130.8, 129.1, 128.8, 128.1, 127.8, 127.0, 75.6, 62.6, 61.7, 56.3, 52.6, 52.4, 30.2; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −2.7 (1B), −6.5 (1B), −11.6 (1B), −15.5 (2B), −22.7 (1B), −26.8 (1B), −32.0 (1B), −36.6 (1B). **HRMS *m/z*** calcd for $C_{25}B_9N_2ClH_{34}$ [M + Na]$^+$: 494.3321, Found: 494.3351.



3f: Yield 65 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$) Conformer Ⅰ:** δ 7.40 – 7.29 (m, 7H), 7.21 – 7.11 (m, 5H), 7.08 – 7.00 (m, 5H), 6.75 – 6.72 (m, 3H), 4.76 – 4.74 (d, *J* = 13.3 Hz, 1H), 4.07 – 4.01 (m, 1H), 3.62 (br, 1H, NH), 2.58 – 2.57 (d, *J* = 5.7 Hz, 3H), 3.46 − 0.25 (8H, B−H), −2.35 (br, 1Hz, B−H−B); **Conformer Ⅱ:** 7.40 – 7.29 (m, 7H), 7.21 – 7.11 (m, 5H), 7.08 – 7.00 (m, 5H), 6.75 – 6.72 (m, 3H), 4.32 – 4.29 (m, *J* = 12.7 Hz, 1H), 3.74 – 3.68 (t, 1H), 3.62 (br, 1H, NH), 2.83 – 2.81 (d, *J* = 5.3 Hz, 3H), 3.46 − 0.25 (8H, B−H), −2.35 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.7, 138.7, 136.6, 136.5, 132.5, 132.2, 132.0, 130.3, 130.1, 129.9, 129.8, 129.5, 129.4, 128.0, 128.0, 127.7, 127.7, 126.8, 64.4(Cage C), 62.6(Cage C), 42.5, 40.6; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −3.3 (1B), −5.9 (1B), −11.4 (1B), −15.7 (2B), −22.5 (1B), −26.8 (1B), −31.7 (1B), −36.5 (1B). **HRMS *m/z*** calcd for $C_{22}B_9NH_{30}$ [M+Na]$^+$: 429.3150, Found: 429.3167.

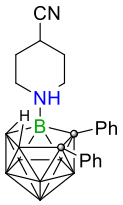


3g: Yield 40 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.32 – 7.25 (m, 2H), 7.08 (s, 3H), 7.03 – 6.98 (m, 4H), 3.74 (d, *J* = 13.2 Hz, 1H), 3.31 – 3.13 (m, 2H), 3.03 – 2.85 (m, 1H), 1.90 – 1.78 (m, 2H), 1.71 – 1.64 (m, 1H), 1.44 – 1.33 (m, 1H), 1.21 – 1.10 (m, 2H), 3.08 − 0.26 (8H, B−H), −2.44 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.9, 136.6, 132.6, 131.2, 128.7, 128.0, 127.8, 126.9, 76.1 (Cage C), 62.2 (Cage C), 58.1, 55.1, 26.3, 26.0, 22.2; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −3.2 (1B), −6.6 (1B), −11.8 (1B), −15.5 (2B), −22.8 (1B), −26.9 (1B), −32.1 (1B), −36.6 (1B). **HRMS *m/z*** calcd for $C_{19}B_9NH_{30}$ [M + Na]$^+$: 393.3150, Found: 393.3154.

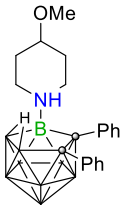


3h: Yield 52 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.31 – 7.27 (m, 4H), 7.23 – 7.20 (m, 1H), 7.11 – 7.08 (m, 6H), 7.05 – 6.99 (m, 4H), 3.92 (d, *J* = 13.4 Hz, 1H), 3.45 – 3.36 (m, 2H), 3.21 – 3.11 (m, 1H), 3.08 (br, 1H, NH), 2.80 – 2.72 (m, 1H), 2.12 – 2.01 (m, 2H), 1.47 – 1.33 (m, 1H), 3.51 − 0.32 (8H, B−H), −2.41 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 143.6, 139.0, 136.6, 132.6, 131.2, 129.3, 128.8, 128.2, 127.8, 127.6, 127.0, 126.9, 76.1 (Cage C), 62.4 (Cage C), 57.8, 55.0, 40.1, 33.7, 33.3; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −3.1 (1B), −6.5 (1B), −11.6 (1B), −15.3 (2B), −22.6 (1B), −26.8 (1B), −32.0 (1B), −36.6 (1B). **HRMS *m/z*** calcd for

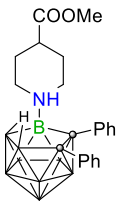
$C_{25}B_9NH_{34}$ [M + Na]$^+$: 469.3463, Found: 469.3473.



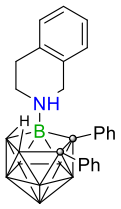
3i: Yield 78 %. White solid. **^{1}H NMR (400 MHz, Acetone-*d*$_6$) Conformer Ⅰ:** δ 7.27 – 7.24 (m, 2H), 7.13 – 7.11 (m, 2H), 7.01 – 6.90 (m, 6H), 5.76 (br, 1H, NH), 4.12 – 4.04 (m, *J* = 13.3 Hz, 1H), 3.36 – 3.30 (m, 1H), 3.25 – 3.19 (m, 1H), 3.10 – 3.04 (m, 1H), 2.18 – 2.13 (m, 2H), 1.97 – 1.87 (m, 2H), 1.81 – 1.73 (m, 1H),3.53 − 0.31 (8H, B−H), −2.21 (br, 1H, B−H−B); **Conformer Ⅱ:** δ 7.27 – 7.24 (m, 2H), 7.13 – 7.11 (m, 2H), 7.01 – 6.90 (m, 6H), 5.88 (br, 1H, NH), 4.04 – 3.99 (m, 1H), 3.48 – 3.44 (m, 1H), 3.29 – 3.26 (m, 1H), 3.14 – 3.10 (m, 1H), 2.35 – 2.29 (m, 2H), 2.03 – 1.96 (m, 2H), 1.86 – 1.83 (m, 1H), 3.53 − 0.31 (8H, B−H), −2.21 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ: 139.7, 137.2, 133.1, 132.4, 128.3, 128.3, 127.9, 127.8, 127.0, 121.6, 121.0, 55.1, 53.2, 53.0, 51.3, 28.3, 27.8, 26.9, 26.6, 24.9, 24.3; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −2.7 (1B), −6.3 (1B), −11.2 (1B), −15.5 (2B), −22.5 (1B), −26.7 (1B), −31.8 (1B), −36.6 (1B). **HRMS *m/z*** calcd for $C_{20}B_9N_2H_{29}$ [M + Na]$^+$: 418.3102, Found: 418.3115.



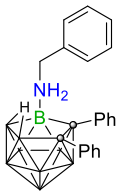
3j: Yield 60 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$) Conformer Ⅰ:** δ 7.28 – 7.26 (m, 2H), 7.10 – 7.07 (m, 3H), 7.03 – 6.98 (m, 5H), 3.81 – 3.74 (m, 1H), 3.31 – 3.29 (m, 1H), 3.25 (s, 3H, CH_3), 3.09 (br, 1H, NH), 3.06 – 2.95 (m, 2H), 2.03 – 1.93 (m, 2H), 1.21 – 1.10 (m, 3H), 3.62 − 0.22 (8H, B−H), −2.47 (br, 1H, B−H−B); **Conformer Ⅱ:** δ 7.28 – 7.26 (m, 2H), 7.10 – 7.07 (m, 3H), 7.03 – 6.98 (m, 5H), 3.58 – 3.50 (m, 2H), 3.42 – 3.38 (m, 1H), 3.28 (s, 3H, CH_3), 3.09 (br, 1H, NH), 2.26 – 2.21 (m, 3H), 1.34 – 1.21 (m, 3H), 3.62 − 0.22 (8H, B−H), −2.47 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 139.0, 138.9, 136.7, 136.5, 132.6, 132.6, 131.2, 128.8, 128.2, 128.0, 127.8, 127.8, 127.0, 126.9, 73.9, 69.6, 56.5, 56.2, 55.6, 53.0, 52.4, 49.6, 31.5, 31.3, 29.8, 29.3; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −3.0 (1B), −6.5 (1B), −11.6 (1B), −15.4 (2B), −22.6 (1B), −26.8 (1B), −32.0 (1B), −36.6 (1B). **HRMS *m/z*** calcd for $C_{20}B_9NOH_{32}$ [M + Na]$^+$: 422.3292, Found: 422.3298.



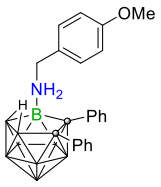
3k: Yield 72 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$) Conformer Ⅰ:** δ 7.28 – 7.26 (m, 2H), 7.10 – 7.06 (d, *J* = 1.4 Hz, 3H), 7.04 – 7.00 (m, 5H), 3.85 – 3.82 (m, 1H), 3.62 (s, 3H), 3.30 – 3.20 (m, 1H), 3.15 – 3.11 (m, 1H), 2.53 – 2.45 (m, 1H), 2.19 – 2.07 (m, 3H), 1.53 (br, 1H, NH), 1.35 – 1.29 (m, 2H), 3.46 − 0.24 (8H, B−H), −2.49 (br, 1H, B−H−B); **Conformer Ⅱ:** δ 7.28 – 7.26 (m, 2H), 7.10 – 7.06 (d, *J* = 1.4 Hz, 3H), 7.04 – 7.00 (m, 5H), 3.71 (s, 3H), 3.36 – 3.34 (m, 1H), 3.08 – 3.06 (m, 1H), 3.04 – 2.94 (m, 1H), 2.67 – 2.63 (m, 1H), 2.34 – 2.23 (m, 3H), 1.53 (br, 1H, NH), 1.50 – 1.42 (m, 2H), 3.46 − 0.24 (8H, B−H), −2.49 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 173.3, 138.7, 136.3, 132.4, 131.0, 128.7, 128.1, 127.9, 127.7, 126.8, 77.7 (Cage C), 62.3 (Cage C), 56.4, 53.7, 52.6, 52.4, 51.6, 38.8, 35.4, 28.4, 28.0, 26.9, 26.7; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −3.0 (1B), −6.5 (1B), −11.5 (1B), −15.4 (2B), −22.7 (1B), −26.9 (1B), −32.0 (1B), −36.6 (1B). **HRMS *m/z*** calcd for $C_{21}B_9NO_2H_{32}$ [M + Na]$^+$: 450.3241, Found: 450.3253.



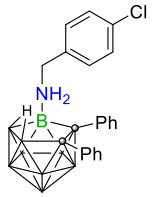
3l: Yield 77 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$) Conformer Ⅰ:** δ 7.32 – 7.29 (m, 2H), 7.25 – 7.18 (m, 2H), 7.10 – 7.00 (m, 10H), 4.50 – 4.43 (m, 1H), 4.24 (d, *J* = 15.8Hz, 1H), 4.13 – 4.08 (m, 1H), 3.74 (br, 1H, NH), 3.62 – 3.52 (m, 1H), 3.01 – 2.95 (dd, *J* = 18.4, 3.9 Hz, 1H), 2.69 – 2.60 (m, 1H), 3.43 − 0.31 (8H, B−H), −2.38 (br, 1H, B−H−B); **Conformer Ⅱ:** δ 7.32 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 7.12 – 6.98 (m, 10H), 4.73 – 4.59 (m, 2H), 4.00 – 3.90 (m, 1H), 3.51 – 3.47 (m, 1H), 3.31 – 3.19 (m, 1H), 2.92 – 2.84 (m, 1H), 2.74 – 2.69 (m, 1H), 3.43 − 0.31 (8H, B−H), −2.38 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.7, 136.4, 136.3, 132.4, 131.1, 130.8, 130.7, 129.7, 129.5, 129.2, 129.2, 128.8, 128.7, 128.5, 127.9, 127.9, 127.6, 127.6, 127.6, 126.9, 126.8, 126.6, 57.3, 55.3, 54.9, 52.5, 28.1, 27.6; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −3.1 (1B), −6.2 (1B), −11.4 (1B), −15.3 (2B), −22.5 (1B), −26.7 (1B), −32.0 (1B), −36.6 (1B). **HRMS *m/z*** calcd for $C_{23}B_9NH_{30}$ $[M + Na]^+$: 441.3150, Found: 441.3159.



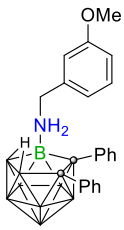
4a: Yield 70 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.41 − 7.33 (m, 3H), 7.29 − 7.27 (m, 2H), 7.11 − 6.98 (m, 10H), 4.72 (br, 1H, NH_2), 4.59 (br, 1H, NH_2), 4.34 – 4.27 (m, 1H), 4.15 – 4.08 (m, 1H), 3.50 − 0.31 (8H, B−H), −2.32 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.9, 136.8, 133.6, 132.6, 131.4, 130.4, 130.1, 129.1, 129.0, 128.1, 127.8, 76.2(cage C), 63.5 (cage C), 54.8; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.3 (1B), −5.9 (1B), −11.9 (1B), −15.5 (2B), −21.4 (1B), −26.2 (1B), −31.3 (1B), −36.7 (1B). **HRMS *m/z*** calcd for $C_{21}B_9NH_{28}$ $[M + Na]^+$: 414.3030, Found: 414.3020.



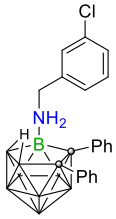
4b: Yield 58 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.29 − 7.27 (m, 2H), 7.14 − 6.94 (m, 10H), 6.87 – 6.83 (m, 2H), 4.56 (br, 1H, NH_2), 4.42 (br, 1H, NH_2), 4.28 – 4.21 (m, 1H), 4.10 – 4.03 (m, 1H), 3.77 (s, 3H, OMe), 3.14 − 0.33 (8H, B−H), −2.32 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 161.3, 139.0, 136.9, 132.6, 131.4, 130.6, 129.0, 128.1, 127.8, 127.0, 125.6, 115.4, 76.2 (cage C), 63.5(cage C), 55.9, 54.5; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.4 (1B), −5.9 (1B), −11.9 (1B), −15.5 (2B), −21.4 (1B), −26.2 (1B), −31.4 (1B), −36.7 (1B). **HRMS *m/z*** calcd for $C_{22}B_9NH_{30}O$ $[M + Na]^+$: 444.3135, Found: 444.3134.



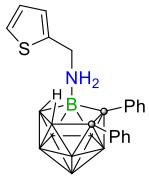
4c: Yield 65 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.36 − 7.33 (m, 2H), 7.29 − 7.25 (m, 2H), 7.15 – 7.09 (m, 3H), 7.08 – 7.03 (m, 2H), 7.02 – 6.95 (m, 5H), 4.65 (br, 1H, NH_2), 4.55 (br, 1H, NH_2), 4.31– 4.24 (m, 1H), 4.13 – 4.06 (m, 1H), 3.46 − 0.42 (8H, B−H), −2.33 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ 140.0, 137.7, 135.0, 134.2, 133.0, 132.4, 132.2, 129.5, 128.4, 127.8, 127.7, 126.9, 52.5; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.5 (1B), −5.9 (1B), −11.7 (1B), −15.5 (2B), −21.4 (1B), −26.2 (1B), −31.3 (1B), −36.7 (1B). **HRMS *m/z*** calcd for $C_{21}B_9NClH_{27}$ $[M + Na]^+$: 448.2640, Found: 448.2660.



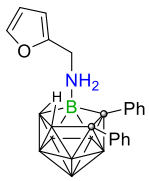
4d: Yield 64 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ7.29 – 7.25 (m, 3H), 7.14 –6.98 (m, 8H), 6.91– 6.98 (m, 1H); 6.61 (d, *J* = 7.5 Hz, 1H), 6.50 (t, *J* = 2.1 Hz, 1H), 4.68 (br, 1H, NH_2), 4.52 (br, 1H, NH_2), 4.30 – 4.23 (m, 1H), 4.12 – 4.05 (m, 1H), 3.74 (s, 3H, OMe); 3.11 − 0.41 (8H, B−H), −2.32 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.9, 136.9, 135.0, 132.6, 131.4, 129.0, 128.1, 127.8, 127.0, 121.0, 116.0, 114.3, 56.0, 54.9; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.4 (1B), −5.9 (1B), −11.9 (1B), −15.9 (2B), −21.5 (1B), −26.3 (1B), −31.6 (1B), −36.9 (1B). **HRMS *m/z*** calcd for $C_{22}B_9NH_{30}O$ [M + Na]$^+$: 444.3135, Found: 444.3136.



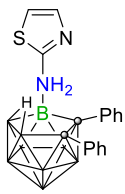
4e: Yield 60 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.40 – 7.37 (m, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.16 – 7.10 (m, 3H), 7.09 – 6.98 (m, 6H), 6.97 – 6.94 (m, 1H), 4.68 (br, 1H, NH_2), 4.58 (br, 1H, NH_2), 4.32 – 4.25 (m, 1H), 4.12 – 4.05 (m, 1H), 3.34 − 0.33 (8H, B−H), −2.28 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.8, 136.7, 135.8, 135.2, 132.6, 131.6, 131.3, 130.6, 129.3, 129.1, 128.2, 127.8, 127.4, 127.0, 76.7 (Cage C), 63.5 (Cage C), 54.0; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.3 (1B), −5.8 (1B), −11.7 (1B), −15.4 (2B), −21.3 (1B), −26.2 (1B), −31.3 (1B), −36.7 (1B). **HRMS *m/z*** calcd for $C_{21}B_9NClH_{27}$ [M + Na]$^+$: 448.2640, Found: 448.2654.



4f: Yield 65%. Yellow solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.38 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.13 – 7.08 (m, 3H), 7.03 – 6.98 (m, 6H), 6.93 (d, *J* = 3.4 Hz,1H), 4.83 (br, 1H, NH_2), 4.61 (br, 1H, NH_2), 4.57 – 4.50 (m, 1H), 4.39 – 4.32 (m, 1H), 3.33 − 0.38 (8H, B−H), −2.28 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.8, 136.5, 134.6, 132.5, 131.2, 130.0, 128.9, 128.7, 128.4, 128.0, 127.7, 126.8, 76.6 (cage C), 63.5 (cage C), 48.2; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.6 (1B), −5.9 (1B), −11.8 (1B), −15.6 (2B), −21.3 (1B), −26.1 (1B), −31.3 (1B), −36.7 (1B). **HRMS *m/z*** calcd for $C_{19}B_9NSH_{26}$ [M + Na]$^+$: 421.2557, Found: 421.2552.

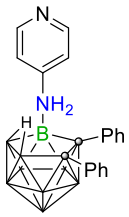


4g: Yield 60%. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.42 (s, 1H), 7.27 – 7.24 (m, 2H), 7.11 – 7.05 (m, 3H), 7.01– 6.97(m,5H), 6.41 – 6.38(m, 2H), 4.73 (br, 2H, NH2), 4.44– 4.37(m, 1H), 4.25 – 4.18(m, 1H), 3.35 − 0.30 (8H, B−H), −2.38 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 146.6, 144.8, 138.9, 136.6, 132.6, 131.4, 129.0, 128.1, 127.8, 127.0, 112.1, 111.7, 46.2; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.6 (1B), −6.0 (1B), −11.8 (1B), −15.6 (2B), −21.2 (1B), −26.2 (1B), −31.4 (1B), −36.7 (1B). **HRMS *m/z*** calcd for $C_{19}B_9NOH_{26}$ [M + Na]$^+$: 404.2822, Found: 404.2822.

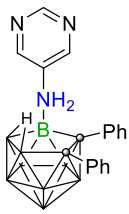


4h: Yield 61%. White solid. **^{1}H NMR (400 MHz, Acetone-*d*$_6$)** δ 8.65 (br, 2H, NH_2), 7.35 – 7.33 (m, 2H), 7.13 (d, *J* = 4.5 Hz, 1H), 7.09 – 7.06 (m, 2H), 6.98 – 6.91 (m, 3H), 6.87 – 6.81 (m, 3H), 6.57 (d, *J* = 4.5 Hz, 1H), 3.33 − 0.40 (8H, B−H), −1.91 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ 173.5, 140.1, 138.3, 136.4, 133.0, 131.7, 127.7, 127.6, 127.0, 126.9, 105.8; **^{11}B{^{1}H} (128 MHz, Acetone-d$_6$)** δ −1.1 (1B), −5.3 (1B), −11.1 (1B), −15.4 (1B), −16.4 (1B), −20.5 (1B), −25.4 (1B), −30.6 (1B), −36.3 (1B). **HRMS *m/z***

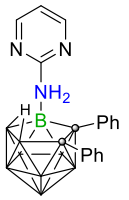
calcd for $C_{17}B_9N_2SH_{23}$ [M + Na]$^+$: 408.2353, Found: 408.2351.



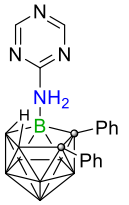
4i: Yield 60 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 8.28 (d, *J* = 7.2 Hz, 2H), 7.31 – 7.29(m, 2H), 7.07(br, 2H, NH_2), 7.00 – 6.98 (m, 2H), 6.96 – 6.88 (m, 3H), 6.83 – 6.77 (m, 3H), 6.70 – 6.67 (m, 2H), 3.10 − 0.32 (8H, B−H), −1.81 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ 158.9, 148.6, 140.3, 138.3, 133.1, 132.1, 127.7, 126.9, 126.8, 109.6; **^{11}B{^{1}H} (128 MHz, Acetone-*d*$_6$)** δ 5.3 (1B), −5.2 (1B), −13.2 (1B), −15.6 (2B), −21.9 (1B), −26.0 (1B), −31.3 (1B), −36.6 (1B). **HRMS *m/z*** calcd for $C_{19}B_9N_2H_{25}$ [M + Na]$^+$: 402.2789, Found: 402.2793.



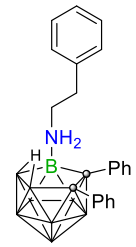
4j: Yield 53 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 8.94 (s, 1H), 8.53 – 8.52 (m, 1H), 8.48 (d, *J* = 3.2 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.04 – 7.01 (m, 2H), 6.98 – 6.91 (m, 3H), 6.84 – 6.81 (m, 3H), 6.05 (br, 2H, NH_2), 3.47 − 0.43 (8H, B−H), −1.77 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ 147.5, 146.1, 144.2, 139.9, 138.6, 137.3, 133.1, 132.0, 128.0, 127.8, 127.4, 127.0; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −3.6 (1B), −4.5 (1B), −11.7 (1B), −15.7 (2B), −21.4 (1B), −26.0 (1B), −30.7 (1B), −36.3 (1B). **HRMS *m/z*** calcd for $C_{18}B_9N_3H_{24}$ [M + Na]$^+$: 402.2778, Found: 402.2764.



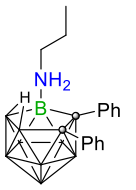
4k: Yield 34 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 8.39 – 8.37 (m, 2H), 7.31 – 7.29(m, 2H), 7.05 – 6.99(m, 3H), 6.92 – 6.88(m, 2H), 6.84 – 6.81(m, 3H), 6.56 (dd, *J* = 6.3, 4.6 Hz, 1H), 3.42 − 0.43(8H, B−H), −2.42(br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 164.8, 160.6, 154.4, 138.9, 136.8, 132.6, 131.1, 127.8, 127.7, 127.1, 111.4; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −1.3(1B), −4.3(1B), −10.1(1B), −14.8(1B), −16.5(1B), −21.1(1B), −25.4(1B), −29.5(1B), −36.0(1B). **HRMS *m/z*** calcd for $C_{18}B_9N_3H_{24}$ [M + Na]$^+$: 402.2778, Found: 402.2770.



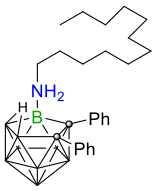
4l: Yield 67%. White solid. **^{1}H NMR (400 MHz, Acetone-*d*$_6$)** δ 8.88 (s, 2H), 8.63 (br, 2H, NH_2), 7.34 – 7.31 (m, 2H), 7.09 – 7.07 (m, 2H), 6.97 – 6.85 (m, 6H), 3.40 − 0.34 (8H, B−H), −1.83 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ 165.2, 163.1, 140.0, 137.8, 133.1, 132.1, 128.2, 127.8, 127.4, 127.0; **^{11}B{^{1}H} (128 MHz, Acetone-*d*$_6$)** δ −1.8 (1B), −4.9 (1B), −11.8 (1B), −15.8 (2B), −21.8 (1B), −25.9 (1B), −30.8 (1B), −36.5 (1B). **HRMS *m/z*** calcd for $C_{17}B_9N_4H_{23}$ [M + Na]$^+$: 403.2731, Found: 403.2732.



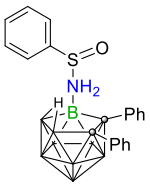
4m: Yield 52 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ7.29 – 7.27 (m, 3H), 7.23 – 7.21 (m, 2H), 7.00 – 6.94 (m, 8H), 6.89 – 6.88 (m, 2H), 4.27 (br, 1H, NH_2), 4.11 (br, 1H, NH_2), 3.52 – 3.44 (m, 1H), 3.41 – 3.33 (m, 1H), 2.95 – 2.84 (m, 2H), 3.20 − 0.37 (8H, B−H), −2.42 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.9, 136.5, 135.3, 132.6, 131.1, 130.1, 128.9, 128.4, 128.0, 127.7, 126.9, 50.7, 34.9; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.4 (1B), −6.2 (1B), −12.1 (B), −15.7 (2B), −21.3 (1B), −26.3 (1B), −31.6 (1B), −36.8 (1B). **HRMS *m/z*** calcd for $C_{22}B_9NH_{30}$ [M + Na]$^+$: 428.3186, Found: 428.3179.



4n: Yield 41 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.29 − 7.25 (m, 2H), 7.13 – 6.96 (m, 8H), 4.25 (br, 2H, NH_2), 3.24 – 3.02 (m, 2H), 1.62 – 1.53 (m, 1H), 0.83 (t, *J* = 7.5 Hz, 3H), 3.37 − 0.26 (8H, B−H), −2.33 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 139.0, 136.7, 132.6, 131.4, 128.9, 128.1, 127.8, 126.9, 76.5 (Cage C), 63.3 (Cage C), 52.2, 22.7, 10.8; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.3 (1B), −6.1 (1B), −12.1 (1B), −15.6 (2B), −21.3 (1B), −26.3 (1B), −31.6 (1B), −36.8 (1B). **HRMS *m/z*** calcd for $C_{17}B_9NH_{28}$ [M]: 343.3132, Found: 343.3170.

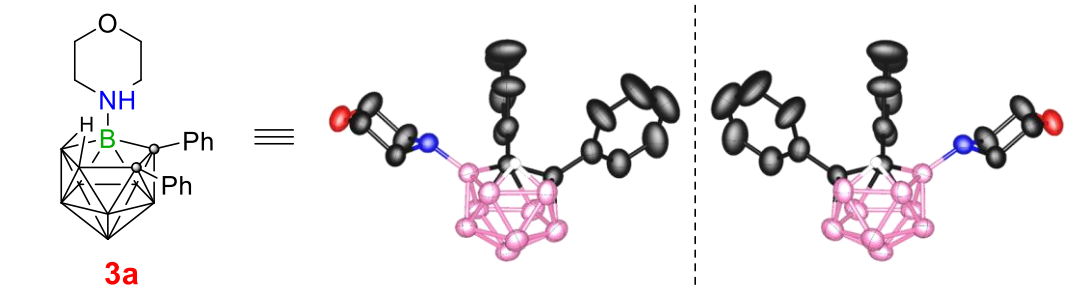


4o: Yield 43 %. White solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 7.27 – 7.24 (m, 2H), 7.12 – 6.97 (m, 8H), 4.22 (br, 2H, NH_2), 3.26 – 3.06 (m, 2H), 1.57 – 1.48 (m, 3H), 1.31 – 1.15 (m, 17H), 0.90 – 0.87 (t, *J* = 6.8 Hz, 3H), 3.35 − 0.26 (8H, B−H), −2.35 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 138.8, 136.6, 132.4, 131.2, 128.8, 127.9, 127.6, 126.8, 50.6, 32.3, 30.1, 30.0, 30.0, 29.8, 29.7, 29.6, 26.3, 29.2, 23.1, 14.3; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −0.4 (1B), −6.1 (1B), −12.1 (1B), −15.6 (2B), −21.4 (1B), −26.3 (1B), −31.6 (1B), −36.8 (1B). **HRMS *m/z*** calcd for $C_{26}B_9NH_{46}$ $[M + Na]^+$: 493.4402, Found: 493.4400.



4p: Yield 64%. Yellow solid. **^{1}H NMR (400 MHz, Methylene Cloride-*d*$_2$)** δ 10.13 (br, 1H, NH_2), 8.21 (br, 1H, NH_2), 7.73 − 7.69 (m, 1H), 7.62 − 7.59 (m, 2H), 7.53 − 7.44 (m, 2H), 7.30 − 7.26 (m, 2H), 7.03 − 6.92 (m, 8H), 3.41 − 0.51 (8H, B−H), −2.05 (br, 1H, B−H−B); **^{13}C NMR (101 MHz, Methylene Cloride-*d*$_2$)** δ 139.2, 138.6, 136.0, 133.6, 132.7, 131.8, 130.2, 127.8, 127.7, 127.7, 127.2, 127.0; **^{11}B{^{1}H} (128 MHz, Methylene Cloride-*d*$_2$)** δ −4.8 (1B), −6.5 (1B), −8.1 (1B), −14.5 (1B), −15.4 (1B), −19.7 (1B), −24.5 (1B), −29.3 (1B), −34.9 (1B). **HRMS *m/z*** calcd for $C_{21}B_9NH_{26}S$ $[M + Na]^+$: 444.2594, Found: 444.2591.

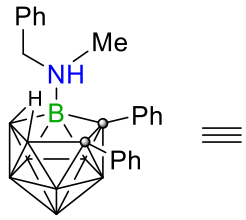
4 Crystal Structures



3a

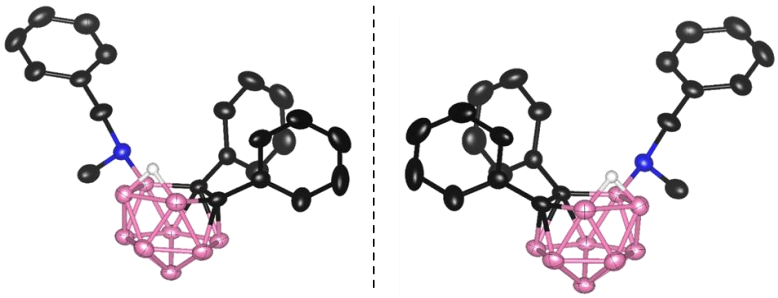
CCDC 2047489

Identification code	**3a**
Empirical formula	$C_{18}H_{28}B_9NO$
Formula weight	371.70
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2/c
a/Å	39.638(12)
b/Å	6.973(2)
c/Å	16.345(5)
α/°	90
β/°	107.786(5)
γ/°	90
Volume/Å^3	4302(2)
Z	8
ρ_{calc}g/cm^3	1.148
μ/mm^{-1}	0.062
F(000)	1568.0
Crystal size/mm^3	0.11 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.234 to 54.806
Index ranges	-50 ≤ h ≤ 51, -9 ≤ k ≤ 5, -21 ≤ l ≤ 21
Reflections collected	18526
Independent reflections	4814
Data/restraints/parameters	4814/0/338
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0583, wR_2 = 0.1456
Final R indexes [all data]	R_1 = 0.1039, wR_2 = 0.1755
Largest diff. peak/hole / e Å^{-3}	0.16/-0.19

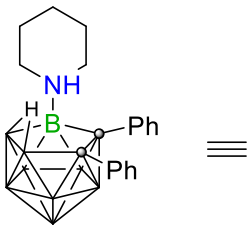


3f

CCDC 2047487

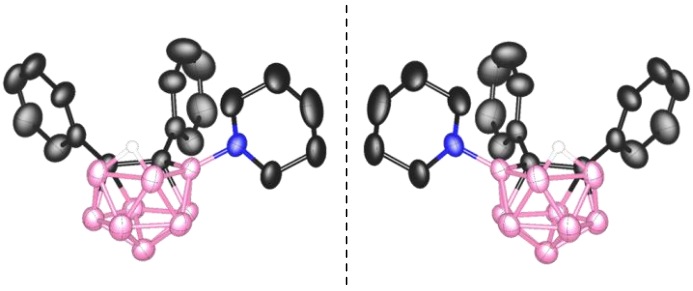


Identification code	**3f**
Empirical formula	$C_{23}H_{32}B_9Cl_2N$
Formula weight	490.68
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	6.9564(3)
b/Å	11.0803(5)
c/Å	17.5164(8)
α/°	81.973(2)
β/°	88.116(2)
γ/°	82.705(2)
Volume/Å^3	1325.94(10)
Z	2
ρ_{calc}g/cm^3	1.229
μ/mm^{-1}	0.259
F(000)	512.0
Crystal size/mm^3	0.11 × 0.09 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.136 to 55.038
Index ranges	-9 ≤ h ≤ 8, -13 ≤ k ≤ 14, -22 ≤ l ≤ 22
Reflections collected	11558
Independent reflections	5950
Data/restraints/parameters	5950/21/448
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0677, wR_2 = 0.1257
Final R indexes [all data]	R_1 = 0.0975, wR_2 = 0.1387
Largest diff. peak/hole / e Å^{-3}	0.29/-0.32



3g

CCDC 2047488



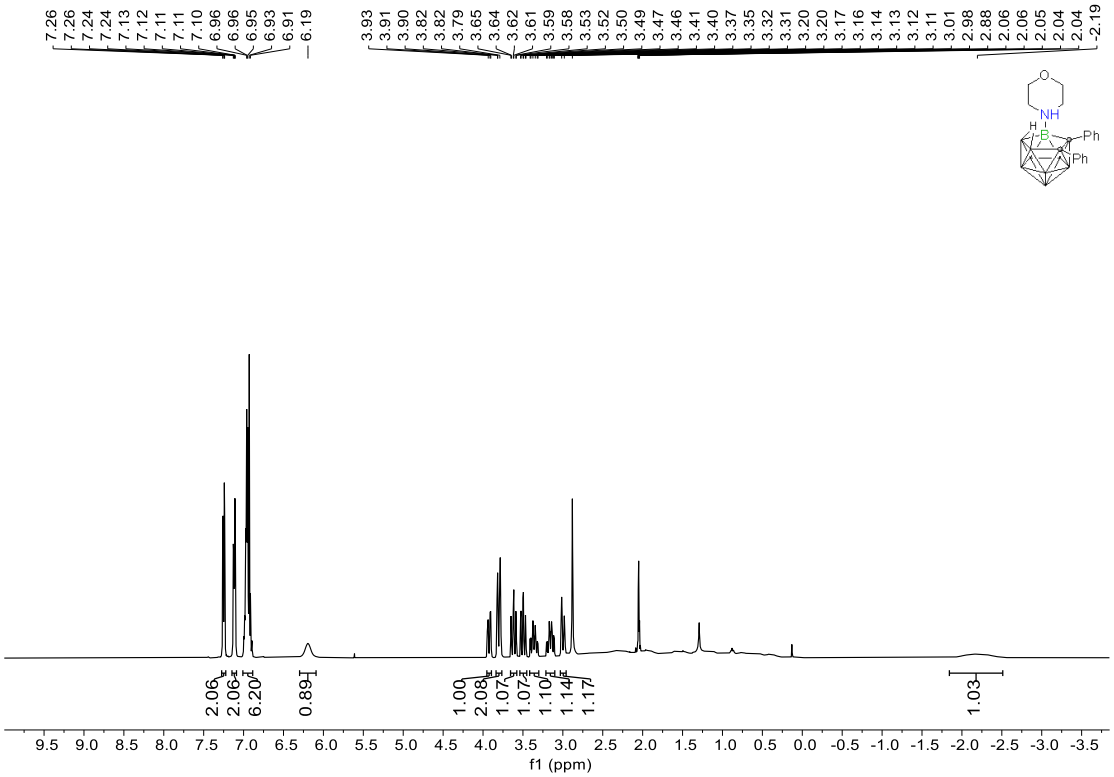
Identification code	**3g**
Empirical formula	$C_{22}H_{36}B_9NO$
Formula weight	427.81
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2/c
a/Å	34.119(8)
b/Å	6.9698(17)
c/Å	23.025(6)
α/°	90
β/°	107.554(4)
γ/°	90
Volume/Å^3	5220(2)
Z	8
ρ_{calc}/g·cm^{-3}	1.089
μ/mm^{-1}	0.059
F(000)	1824.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.504 to 54.794
Index ranges	-43 ≤ h ≤ 40, -8 ≤ k ≤ 8, -29 ≤ l ≤ 29
Reflections collected	21986
Independent reflections	5802
Data/restraints/parameters	5802/0/412
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0744, wR_2 = 0.2067
Final R indexes [all data]	R_1 = 0.1053, wR_2 = 0.2360
Largest diff. peak/hole / e Å^{-3}	0.46/-0.33

5 Reference

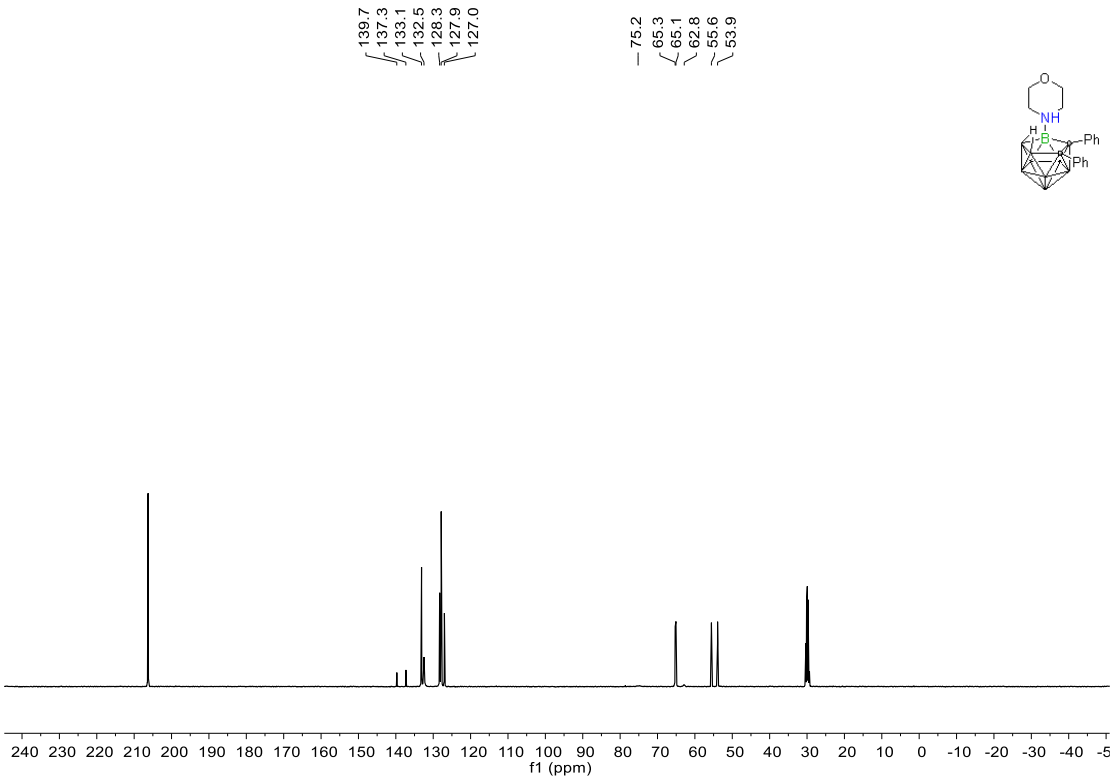
[1] Yang, Z.; Zhao, W.; Liu, W.; Wei, X.; Chen, M.; Zhang, X.; Zhang, X.; Liang, Y.; Lu, C.; Yan, H., Metal-Free Oxidative B-N Coupling of *nido*-Carborane with N-Heterocycles. *Angew. Chem. Int. Ed.* **2019,** *58*, 11886-11892.
[2] Chen, M.; Zhao, D.; Xu, J.; Li, C.; Lu, C.; Yan, H., Electrooxidative B-H Functionalization of *nido*-Carboranes. *Angew. Chem. Int. Ed.* **2021,** *60*, 7838-7844.

6. NMR Spectra

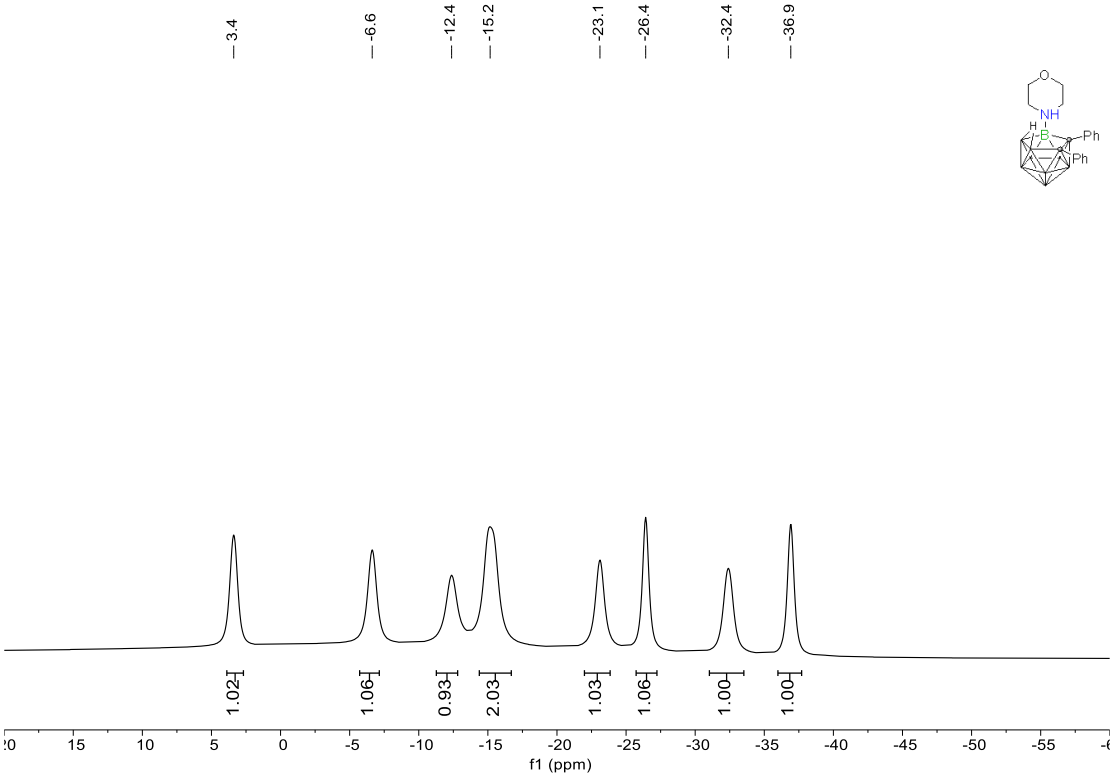
^{1}H NMR (Acetone-d_6) (Compound 3a)



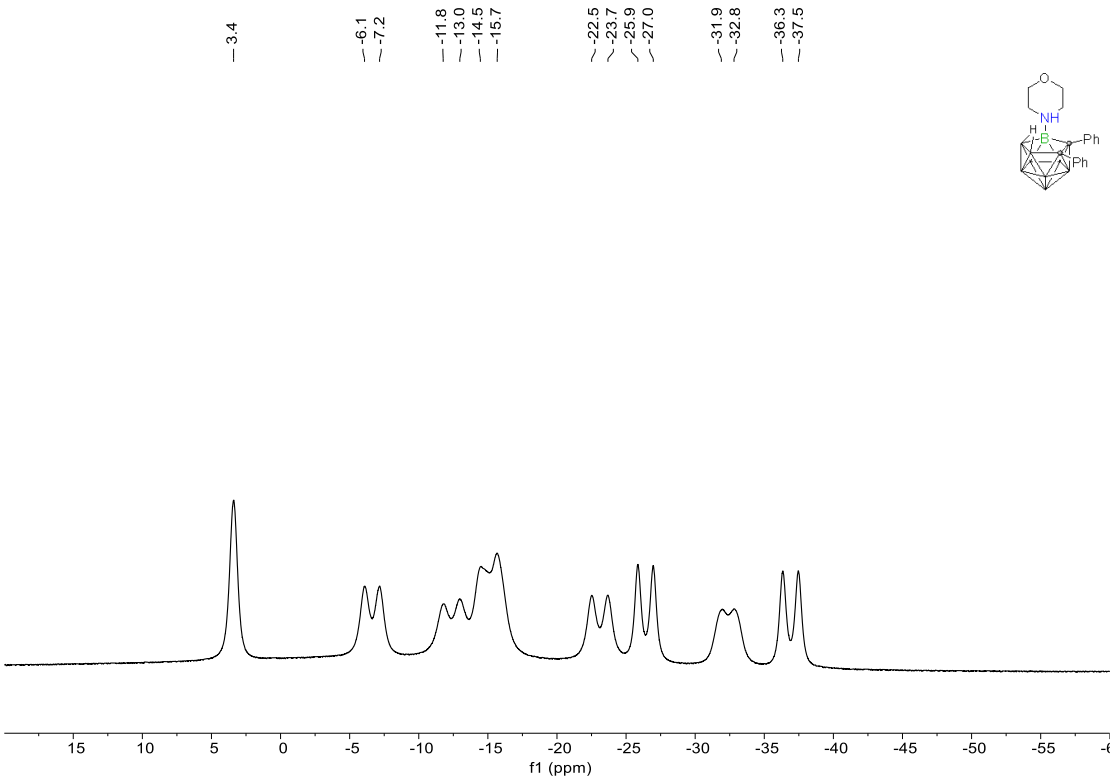
^{13}C NMR (Acetone-d_6) (Compound 3a)



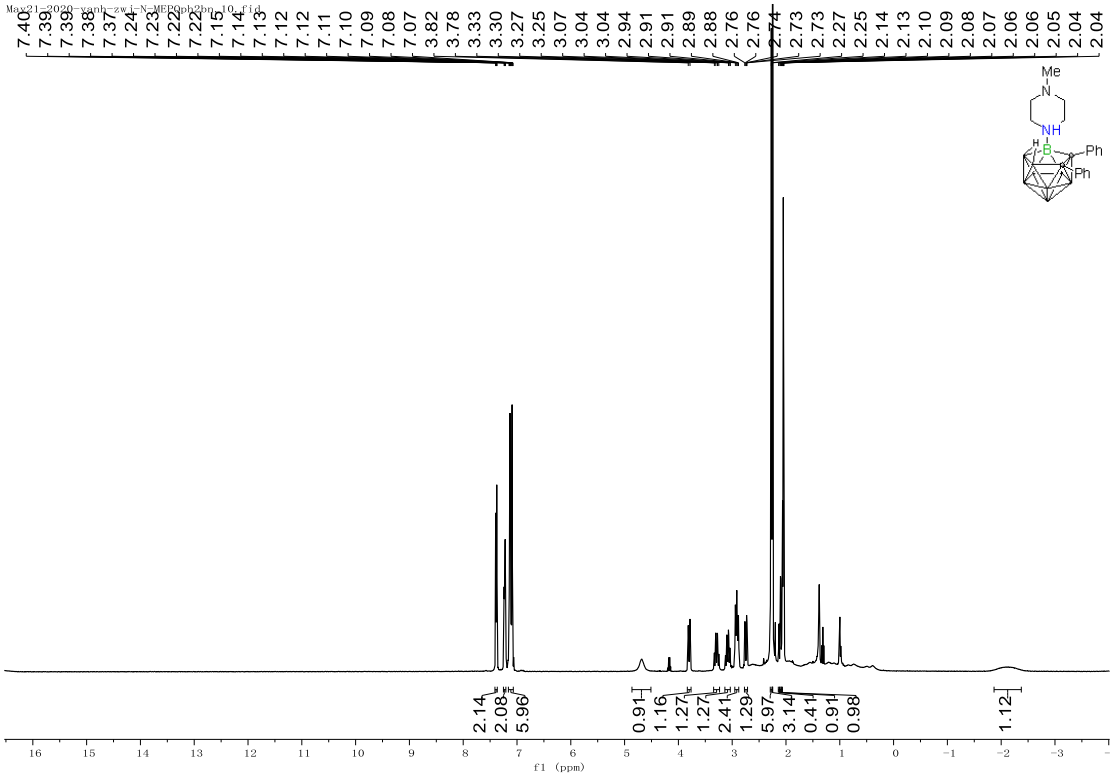
$^{11}B\{^{1}H\}$ NMR (Acetone-d_6) (Compound 3a)



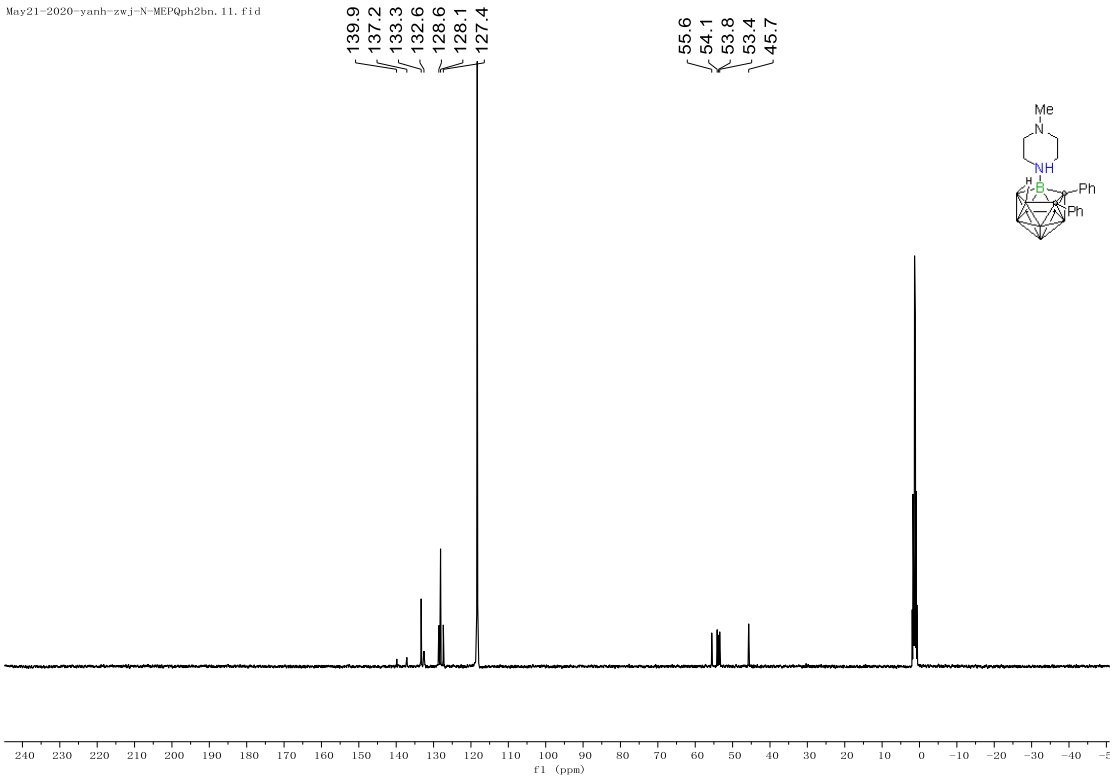
^{11}B NMR (Acetone-d_6) (Compound 3a)



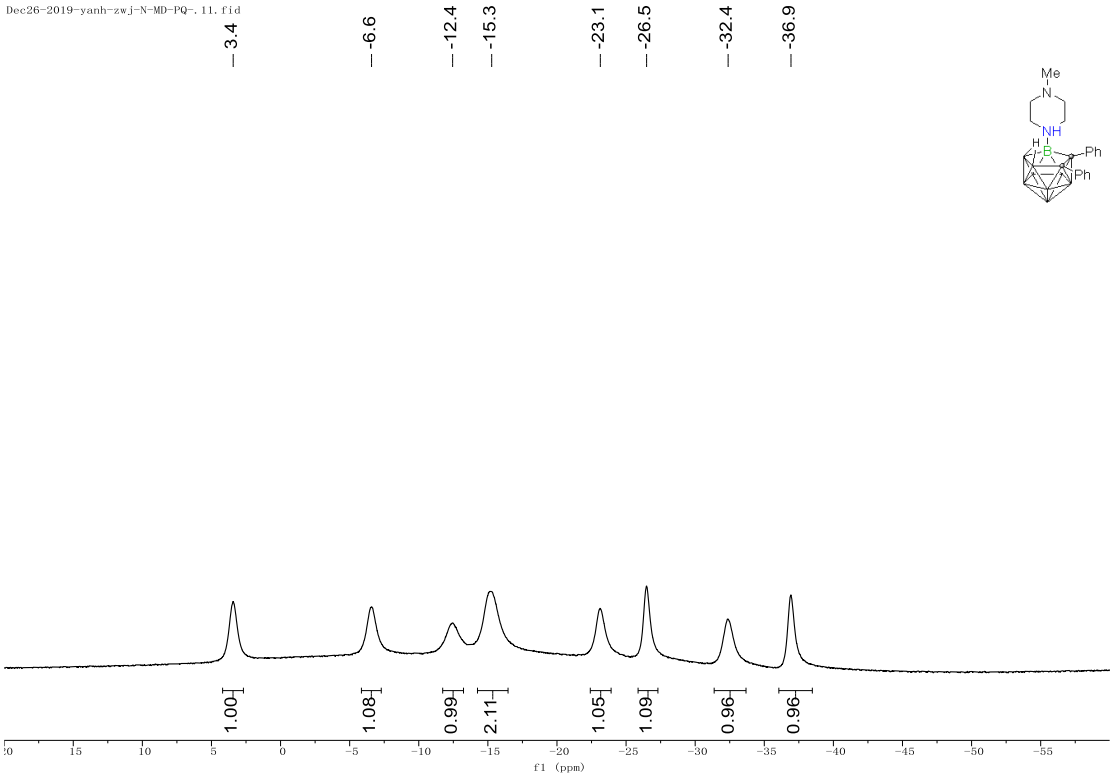
^{1}H NMR (Acetonitrile-d_3) (Compound 3b)



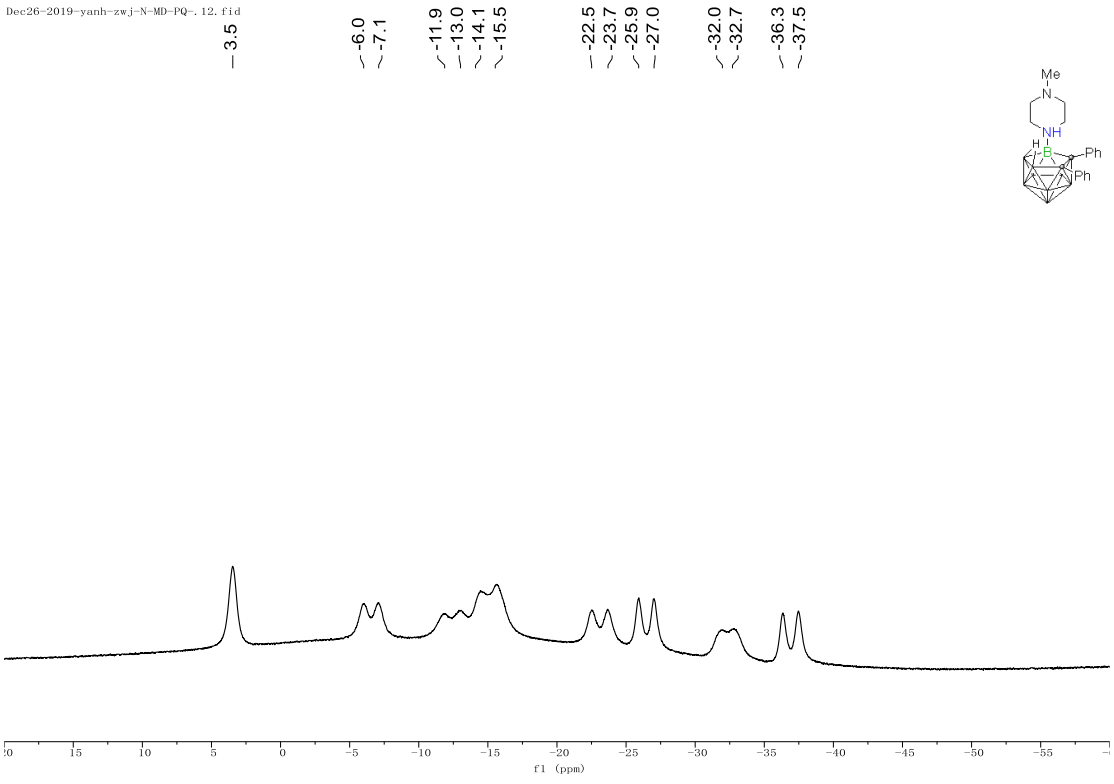
^{13}C NMR (Acetonitrile-d_3) (Compound 3b)



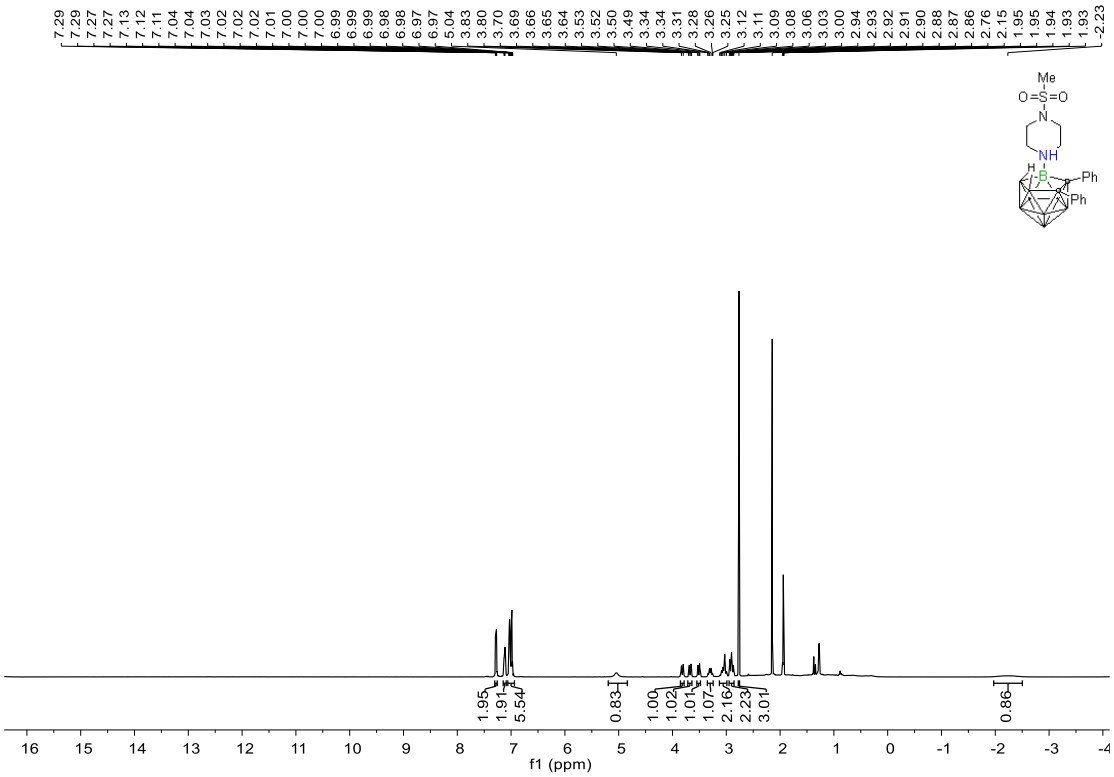
$^{11}B\{^{1}H\}$ NMR (Acetonitrile-d_3) (Compound 3b)



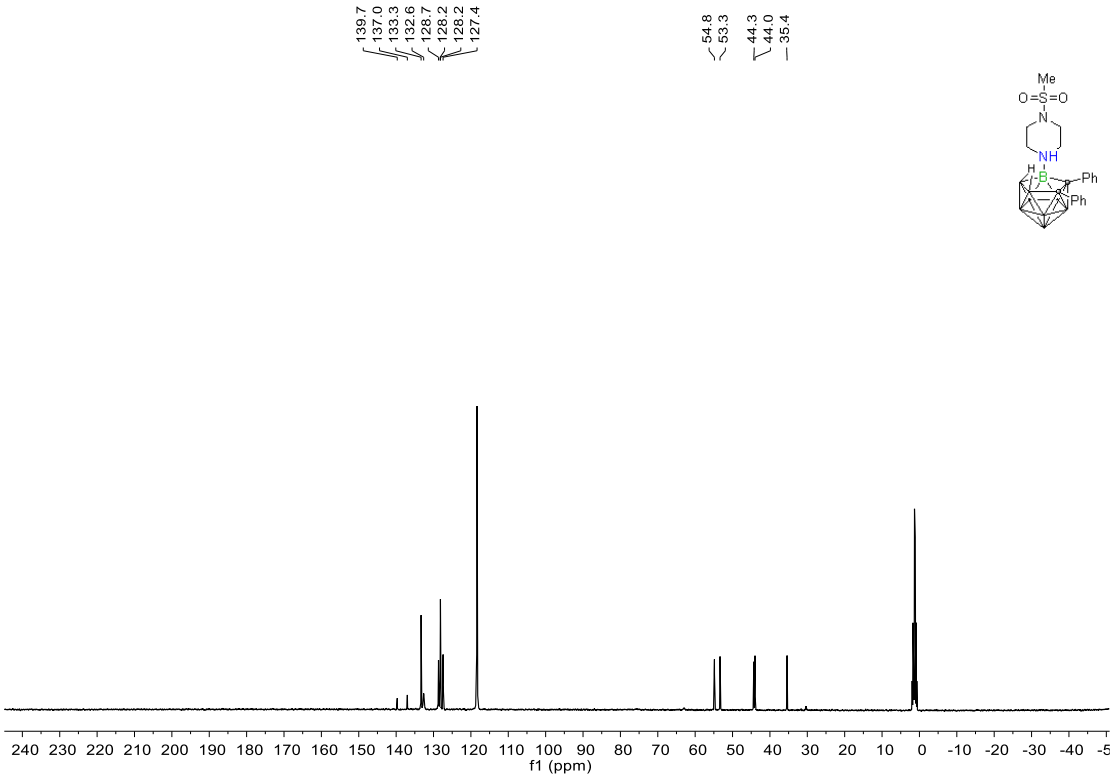
^{11}B NMR (Acetonitrile-d_3) (Compound 3b)



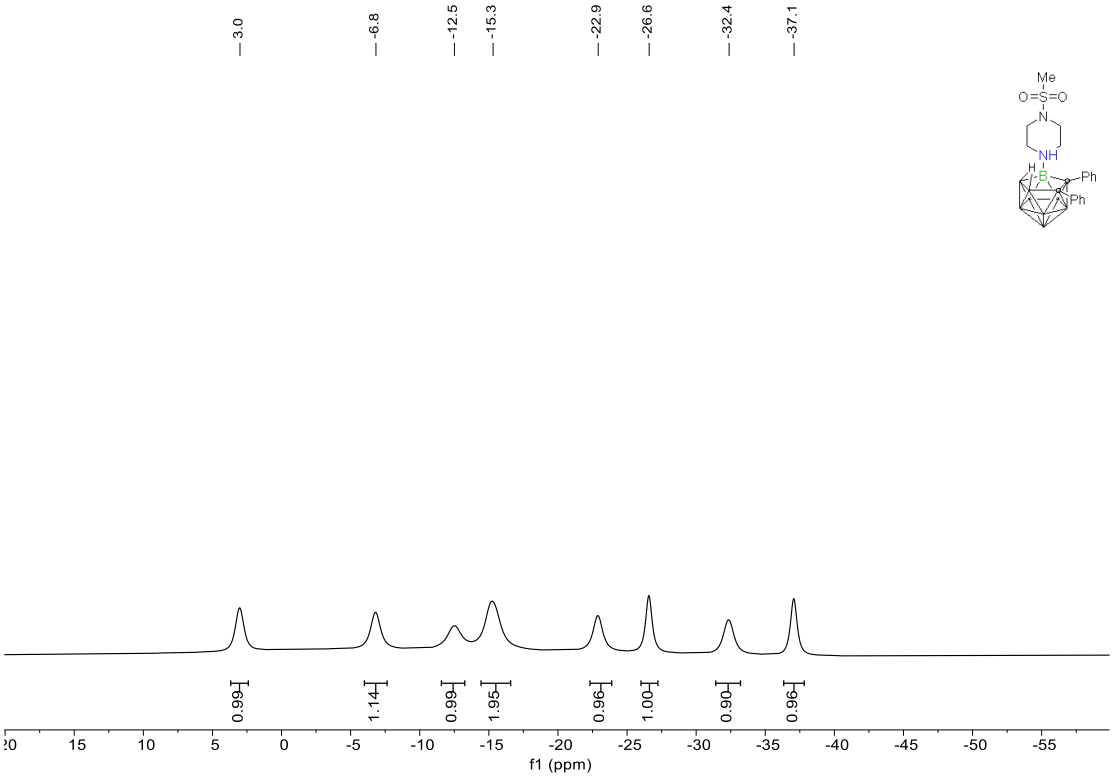
^{1}H NMR (Acetonitrile-d_3) (Compound 3c)



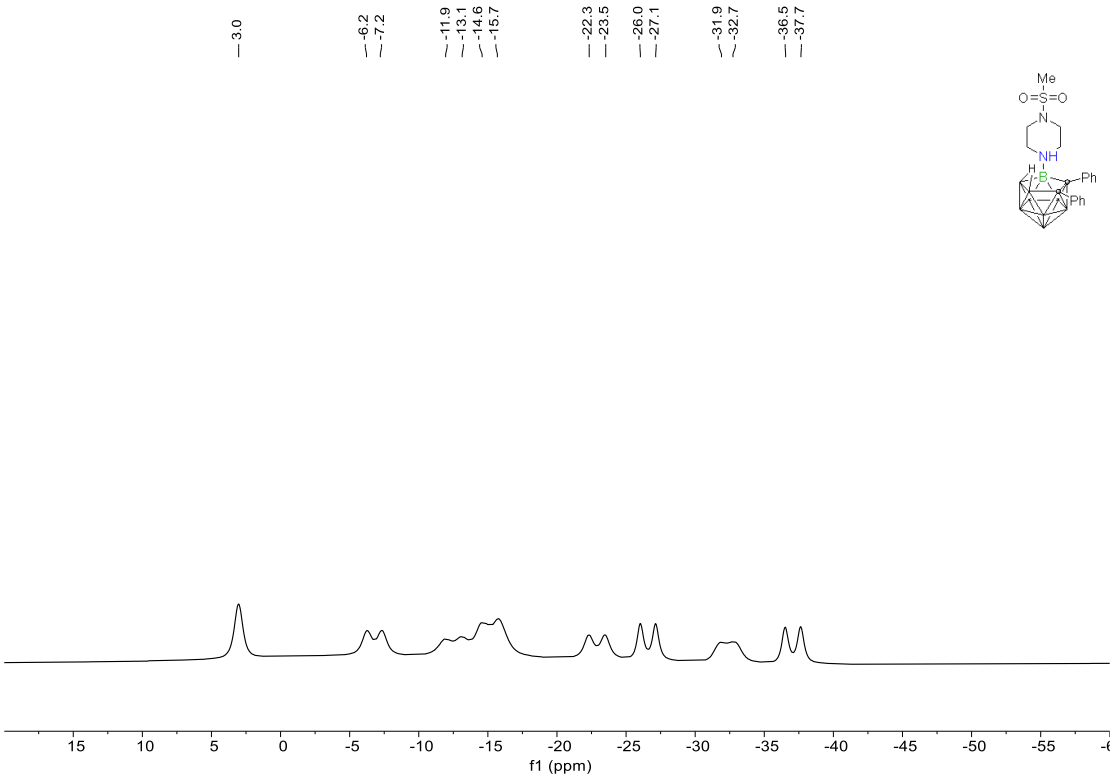
^{13}C NMR (Acetonitrile-d_3) (Compound 3c)



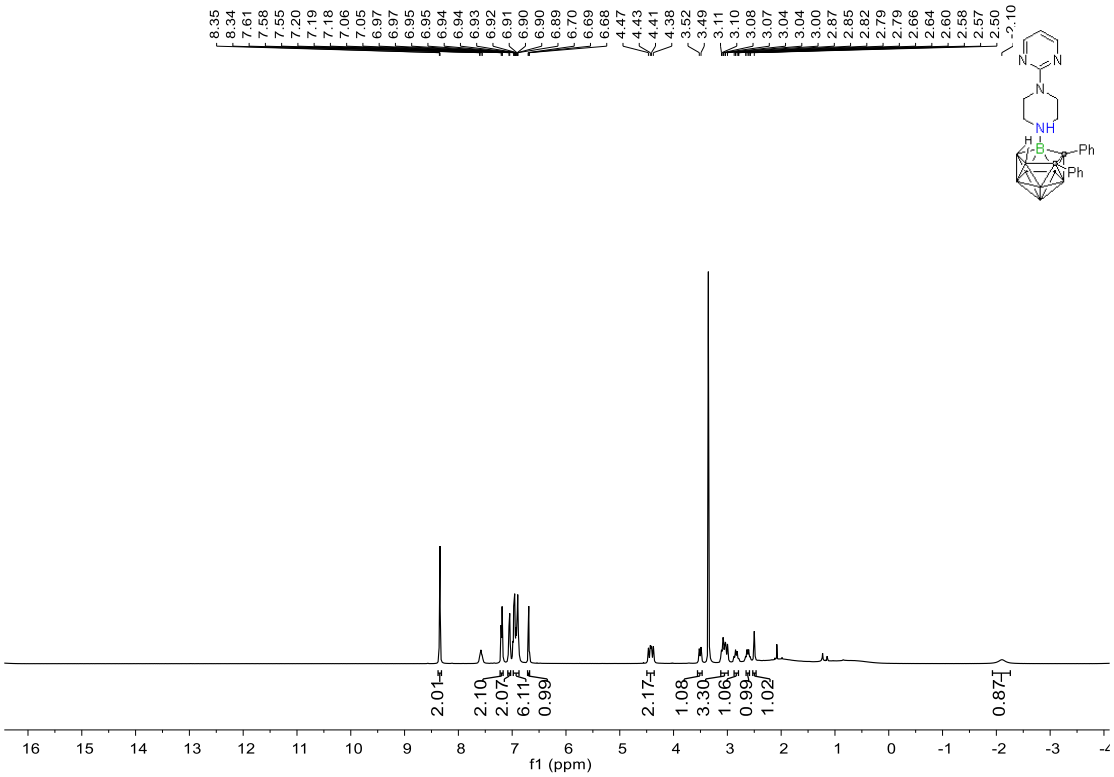
$^{11}B\{^{1}H\}$ NMR (Acetonitrile-d_3) (Compound 3c)



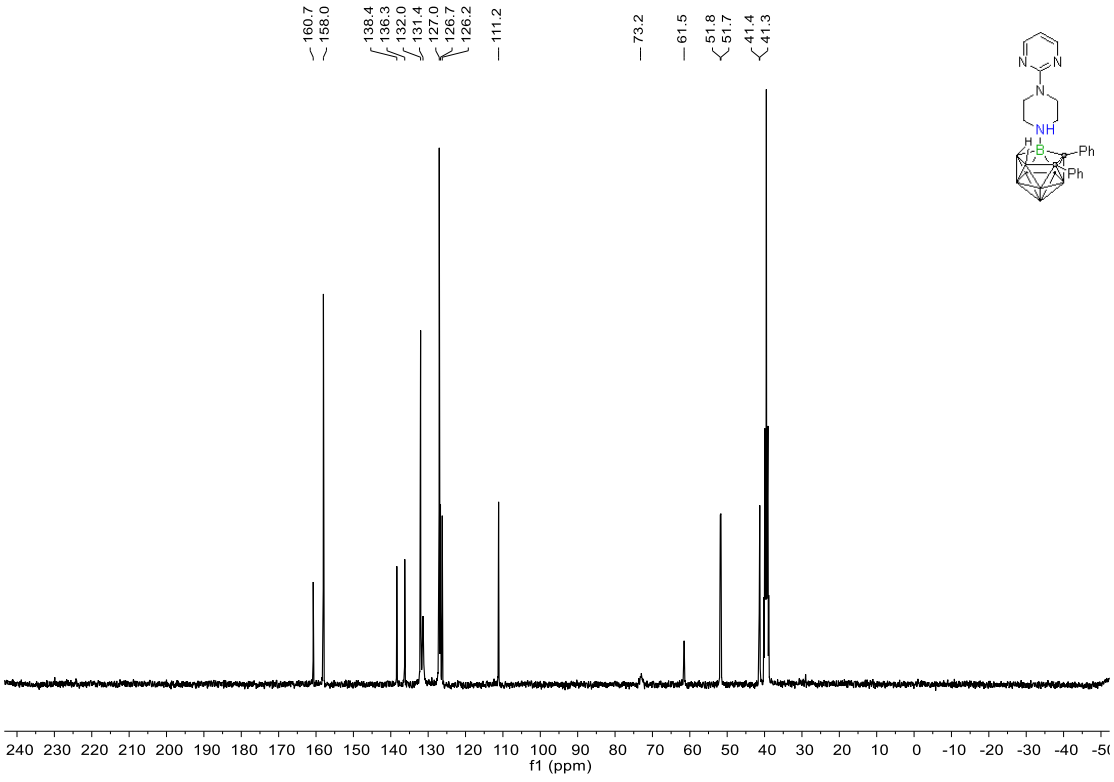
^{11}B NMR (Acetonitrile-d_3) (Compound 3c)



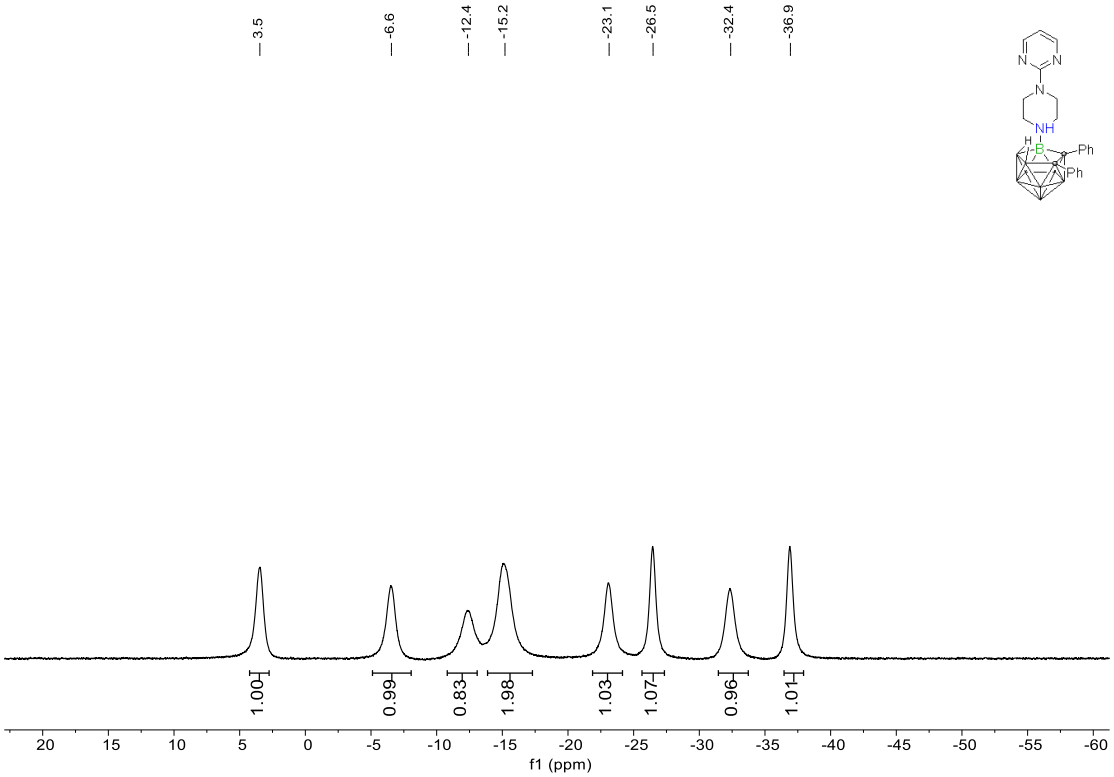
^{1}H NMR (Dimethylsulfoxide-d_6) (Compound 3d)



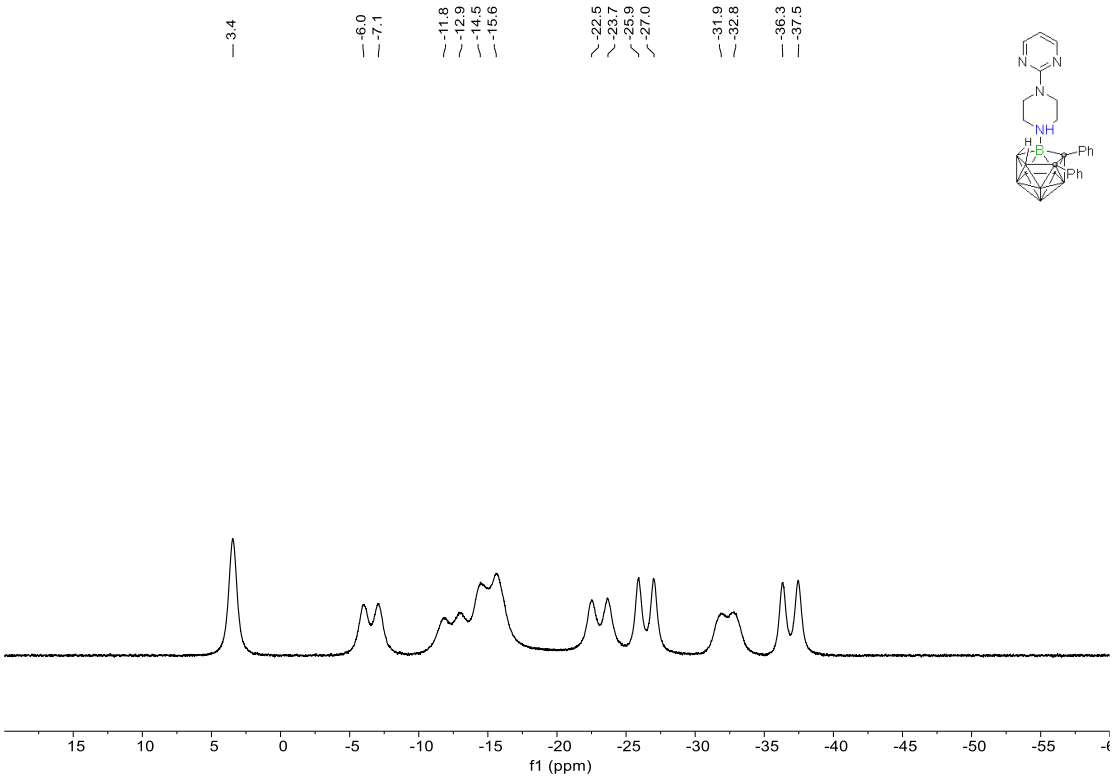
^{13}C NMR (Dimethylsulfoxide-d_6) (Compound 3d)



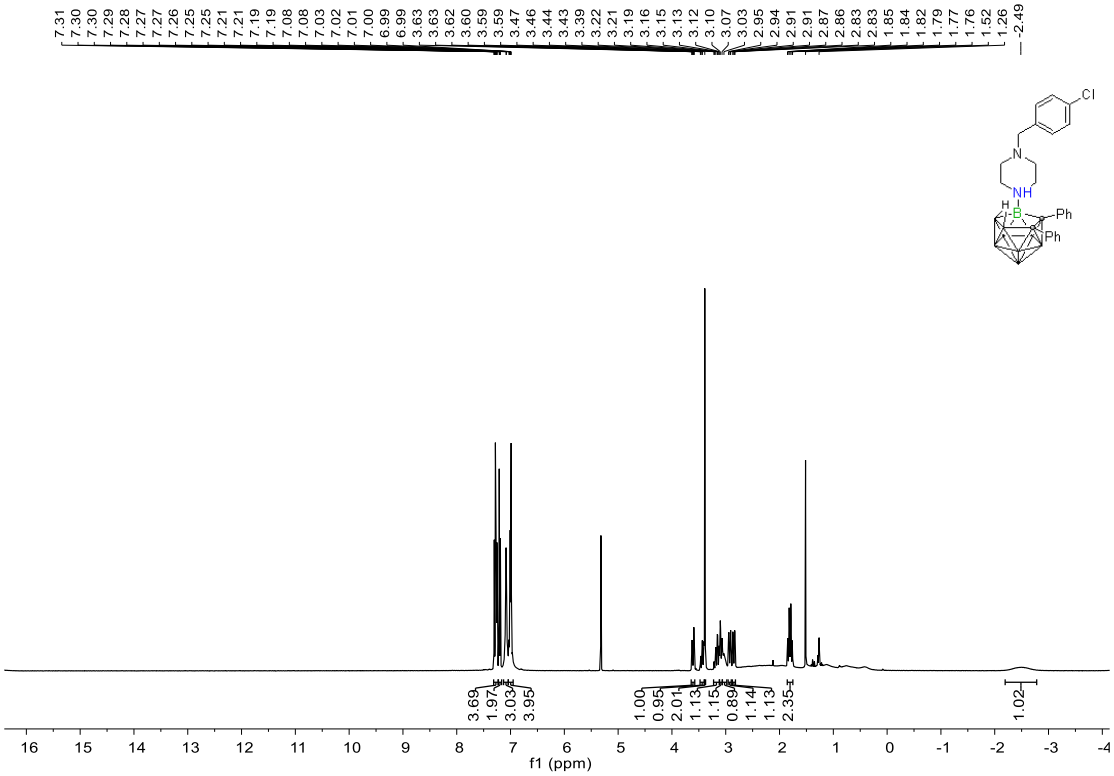
$^{11}B\{^{1}H\}$ NMR (Dimethylsulfoxide-d_6) (Compound 3d)



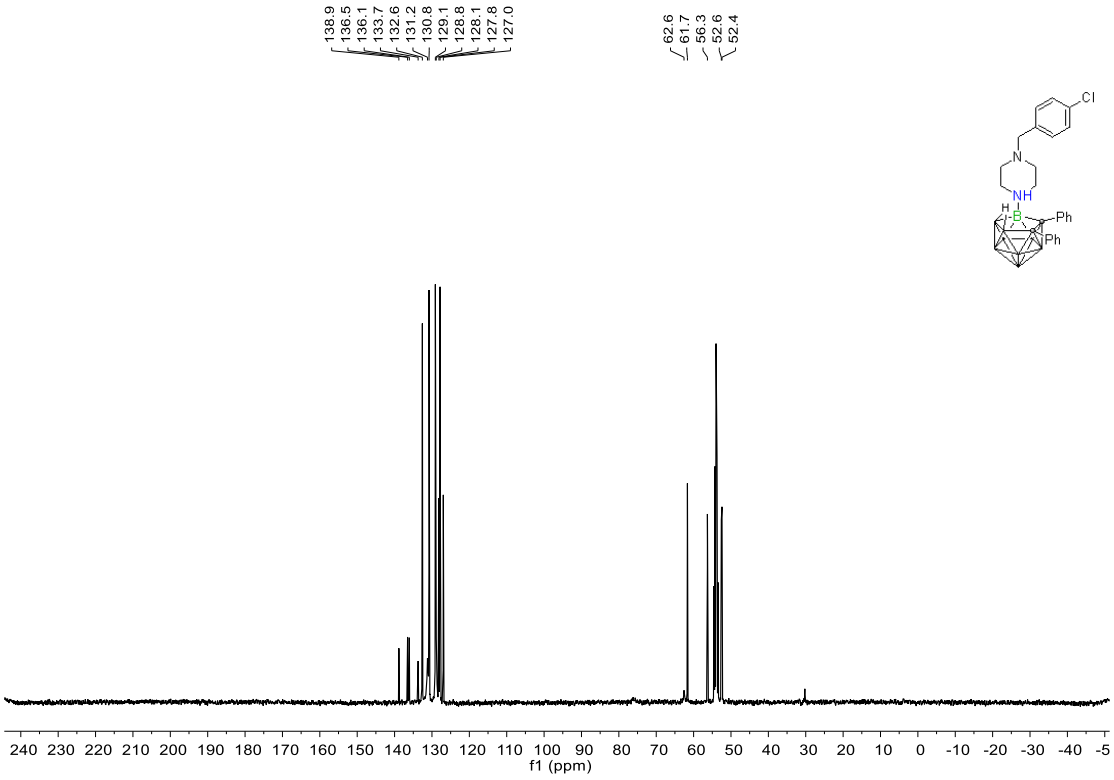
^{11}B NMR (Dimethylsulfoxide-d_6) (Compound 3d)



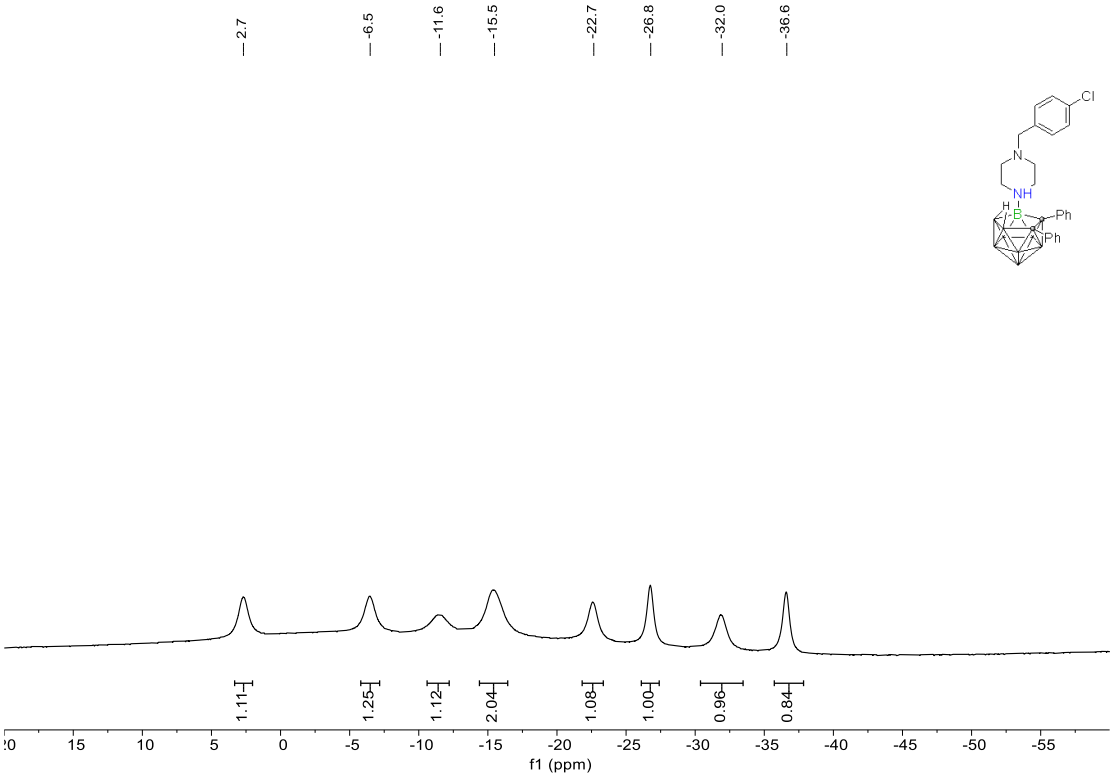
^{1}H NMR (Methylene Cloride-d_2) (Compound 3e)



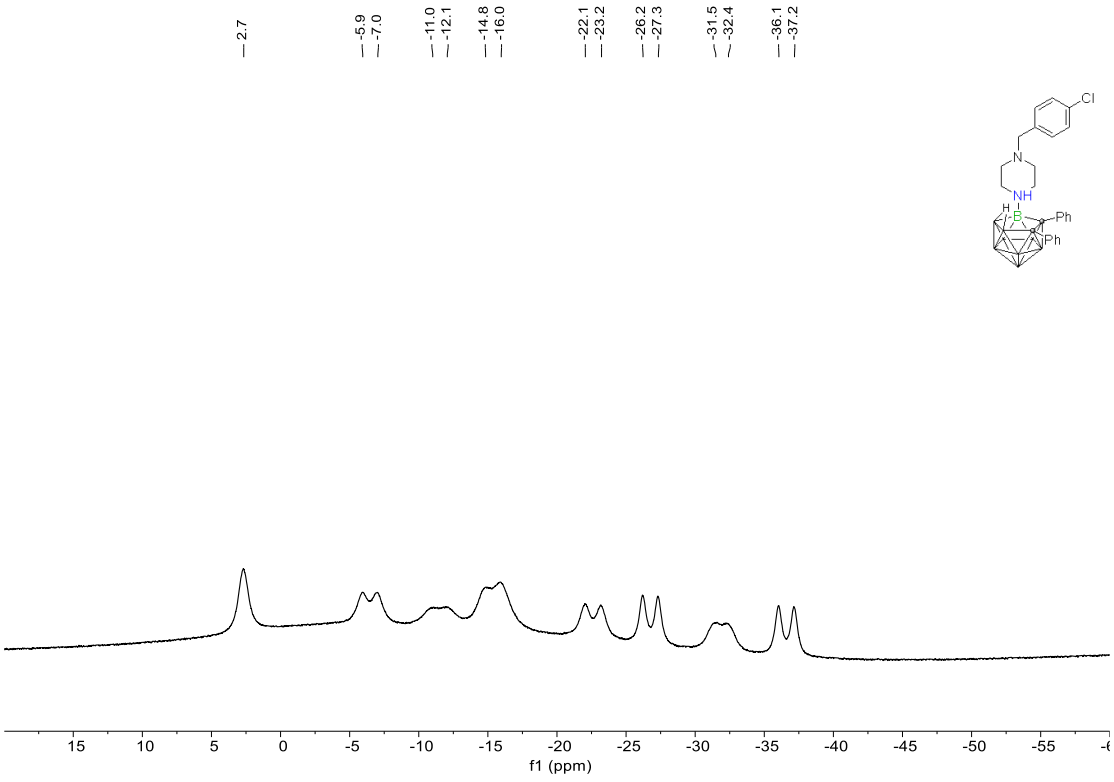
^{13}C NMR (Methylene Cloride-d_2) (Compound 3e)



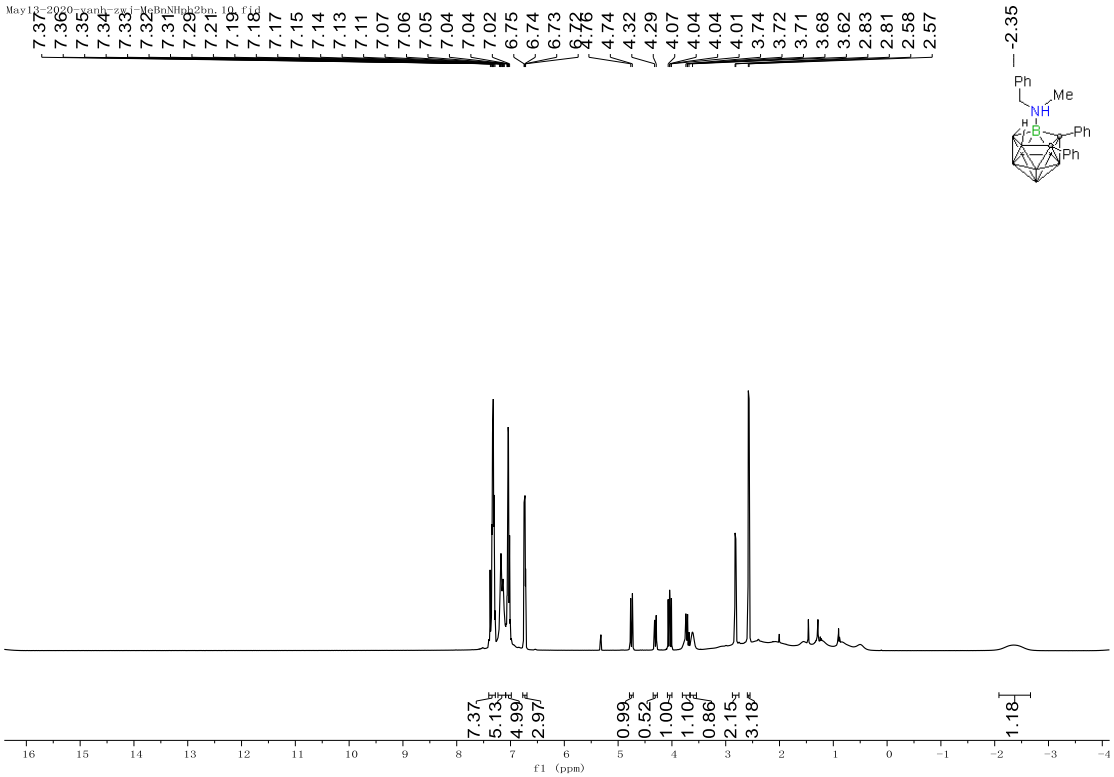
$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 3e)



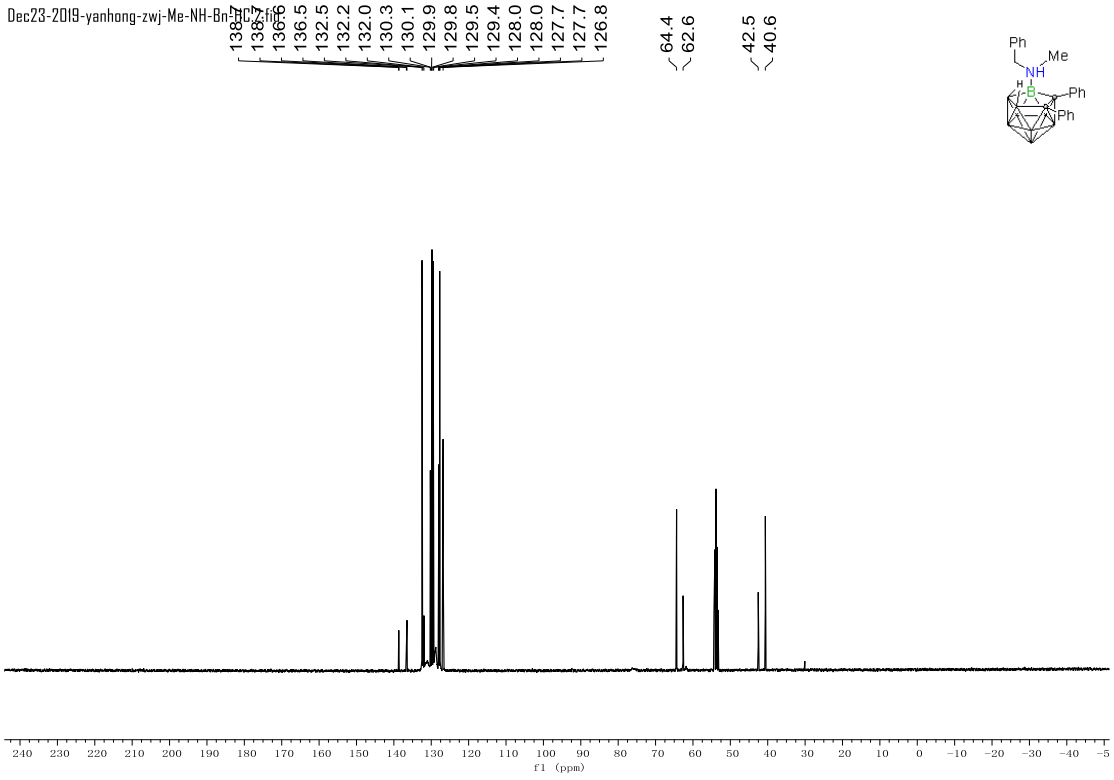
^{11}B NMR (Methylene Cloride-d_2) (Compound 3e)



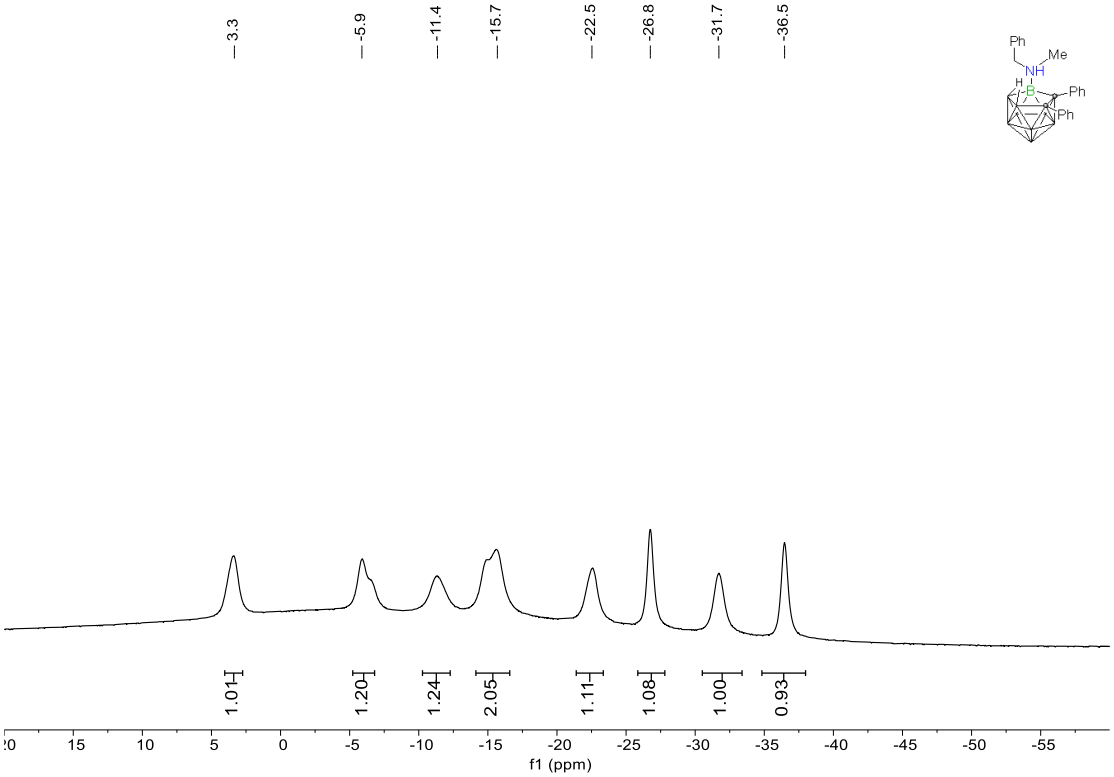
^{1}H NMR (Methylene Cloride-d_2) (Compound 3f)



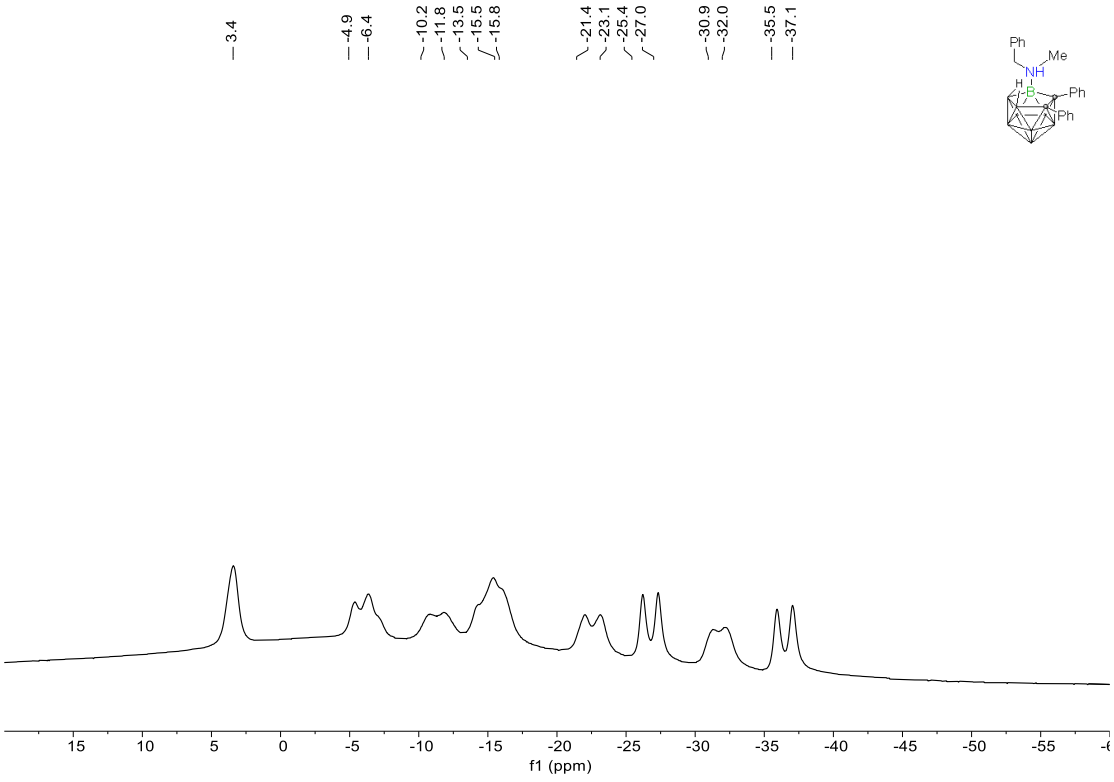
^{13}C NMR (Methylene Cloride-d_2) (Compound 3f)



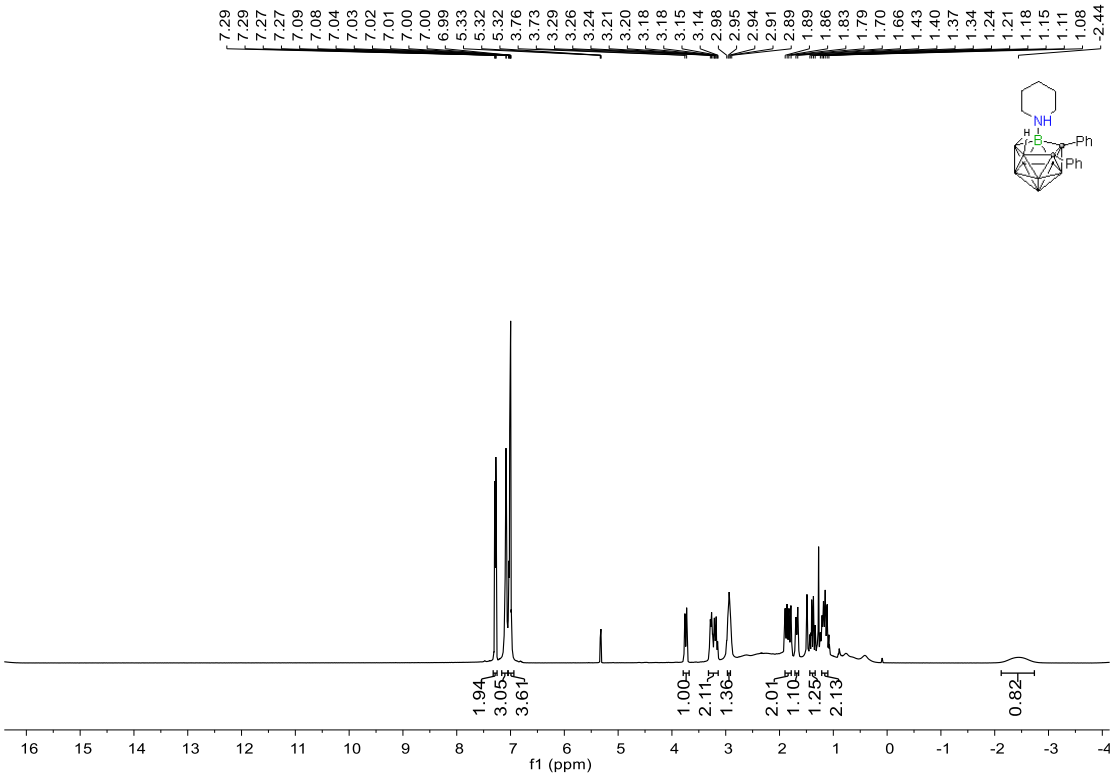
$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 3f)



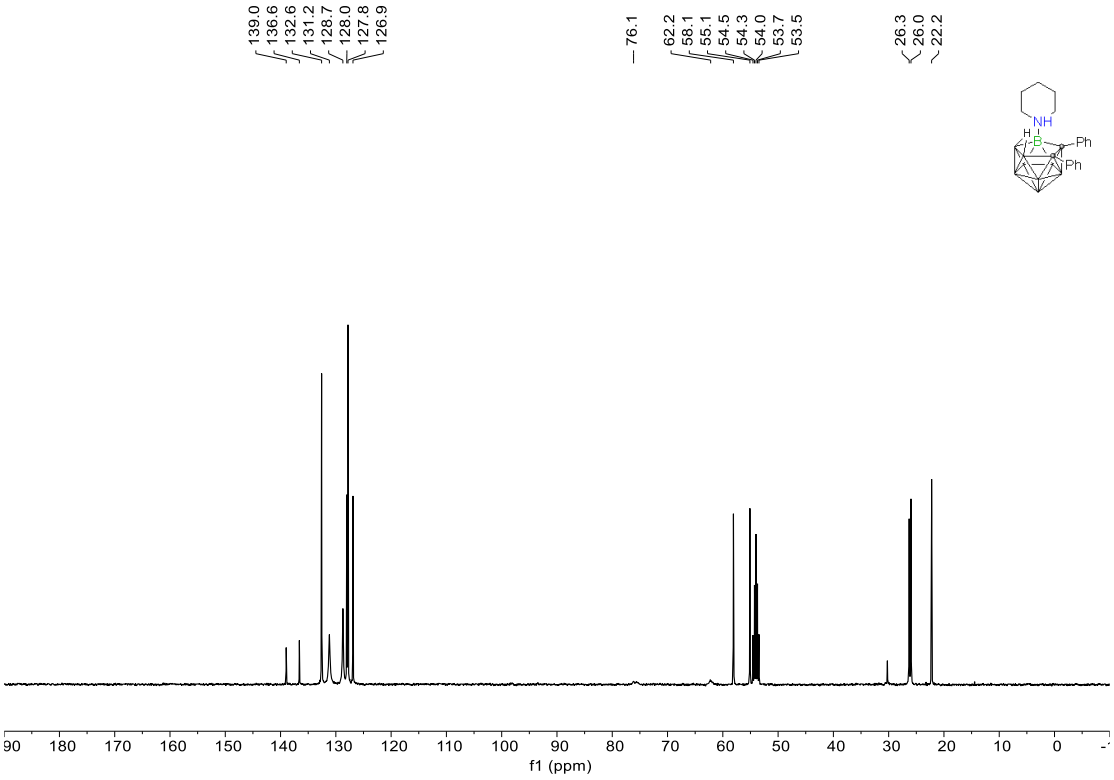
^{11}B NMR (Methylene Cloride-d_2) (Compound 3f)



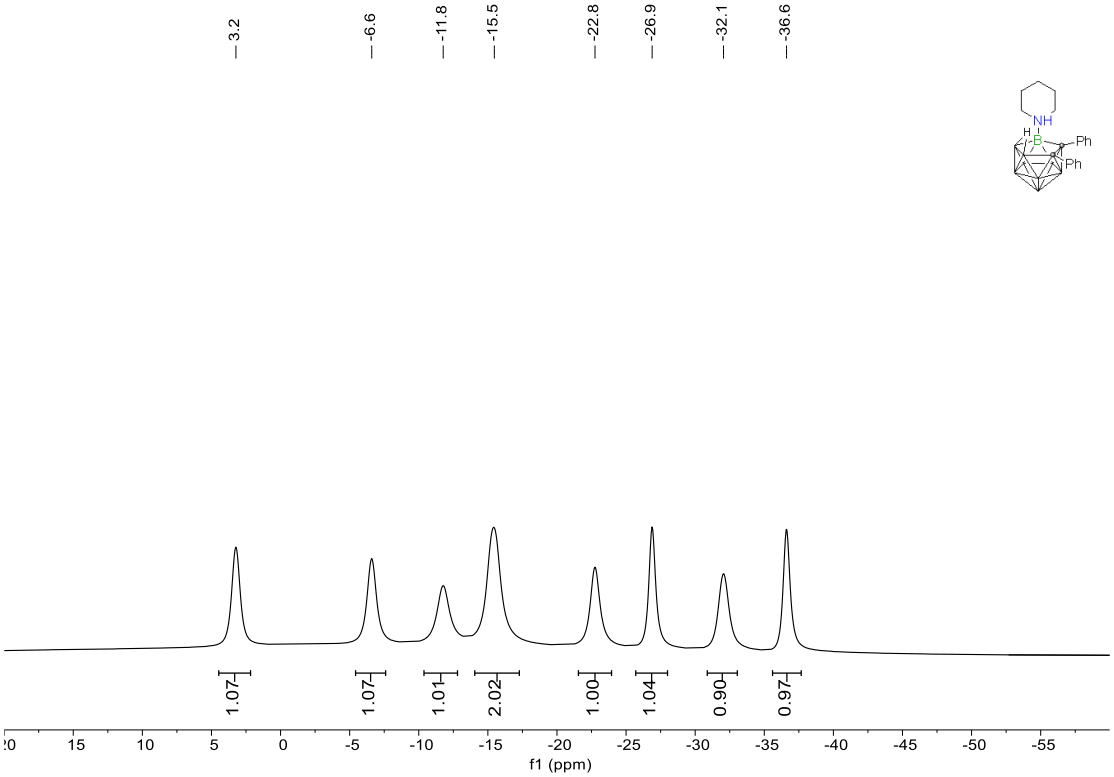
^{1}H NMR (Methylene Cloride-d_2) (Compound 3g)



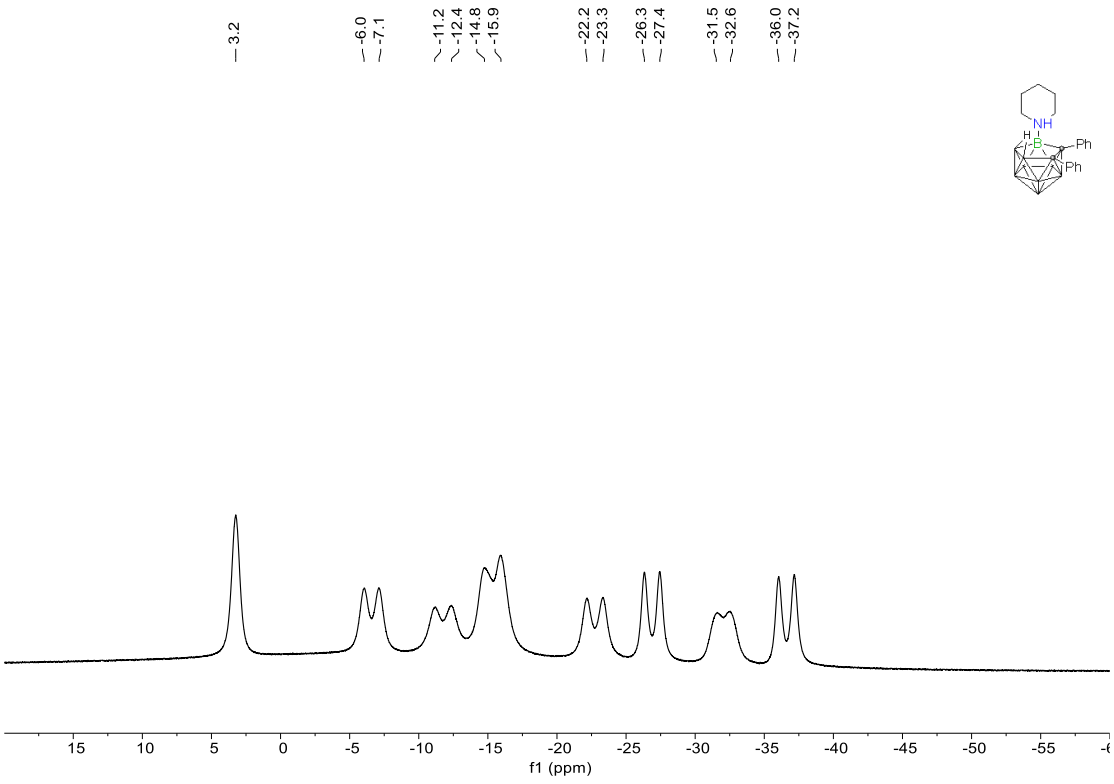
^{13}C NMR (Methylene Cloride-d_2) (Compound 3g)



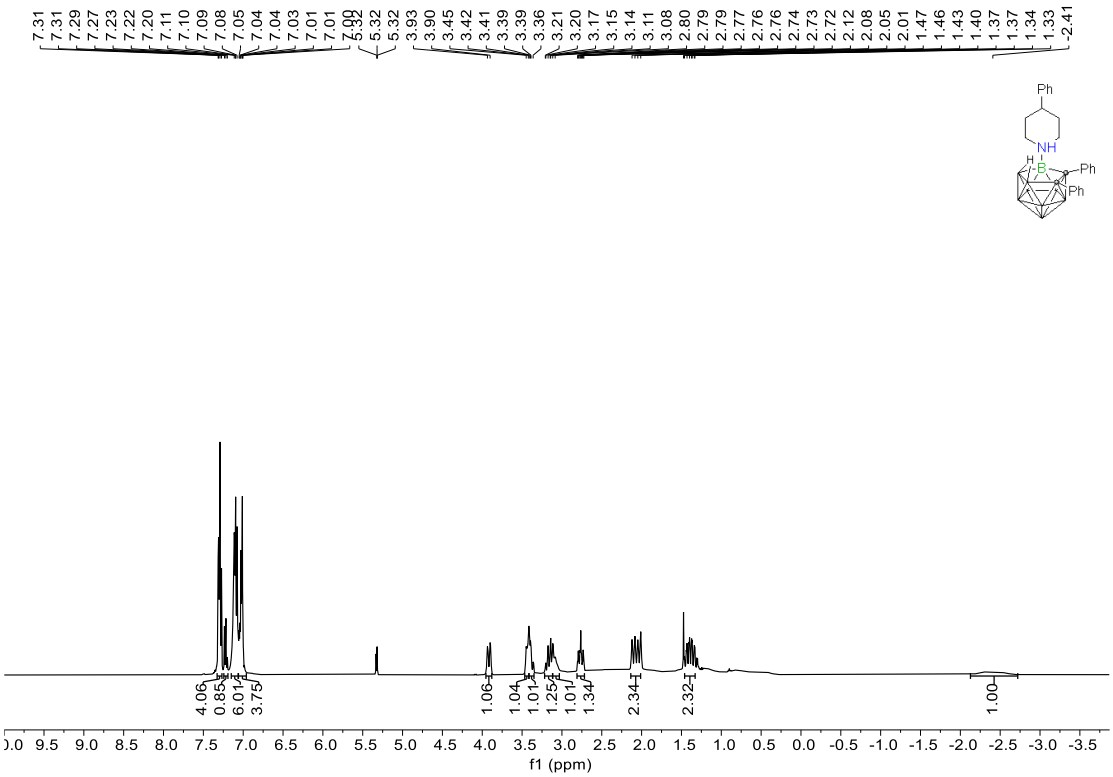
$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 3g)



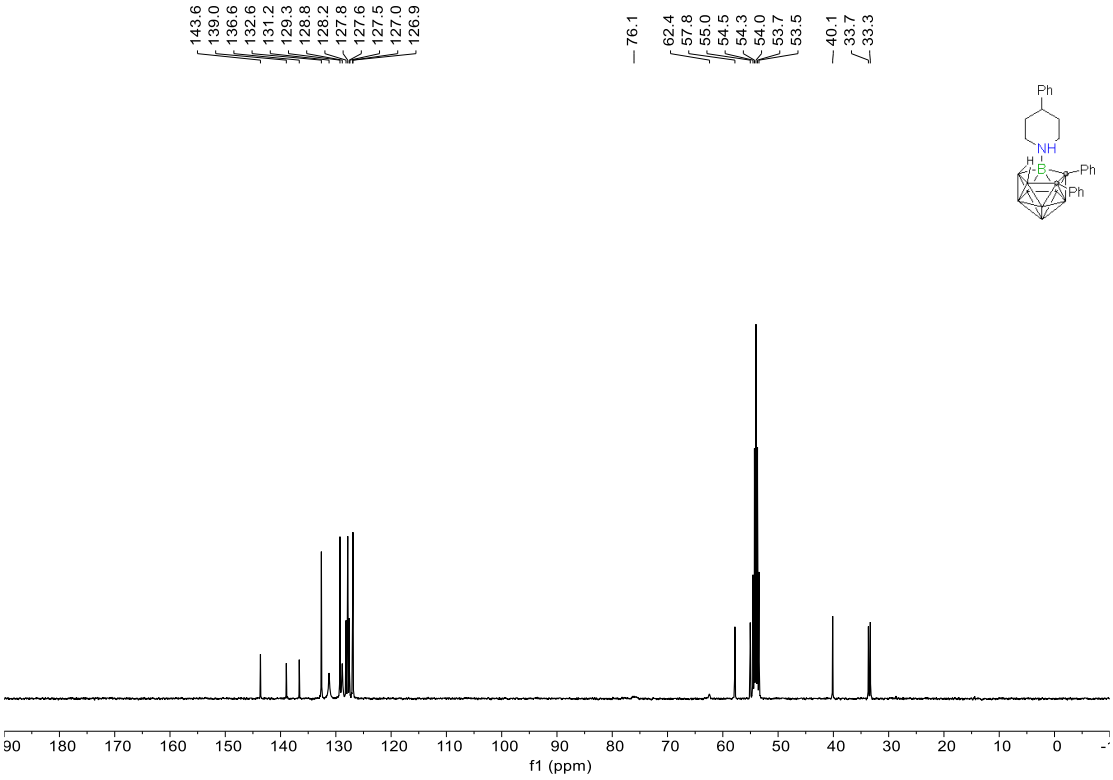
^{11}B NMR (Methylene Cloride-d_2) (Compound 3g)



^{1}H NMR (Methylene Cloride-d_2) (Compound 3h)



^{13}C NMR (Methylene Cloride-d_2) (Compound 3h)



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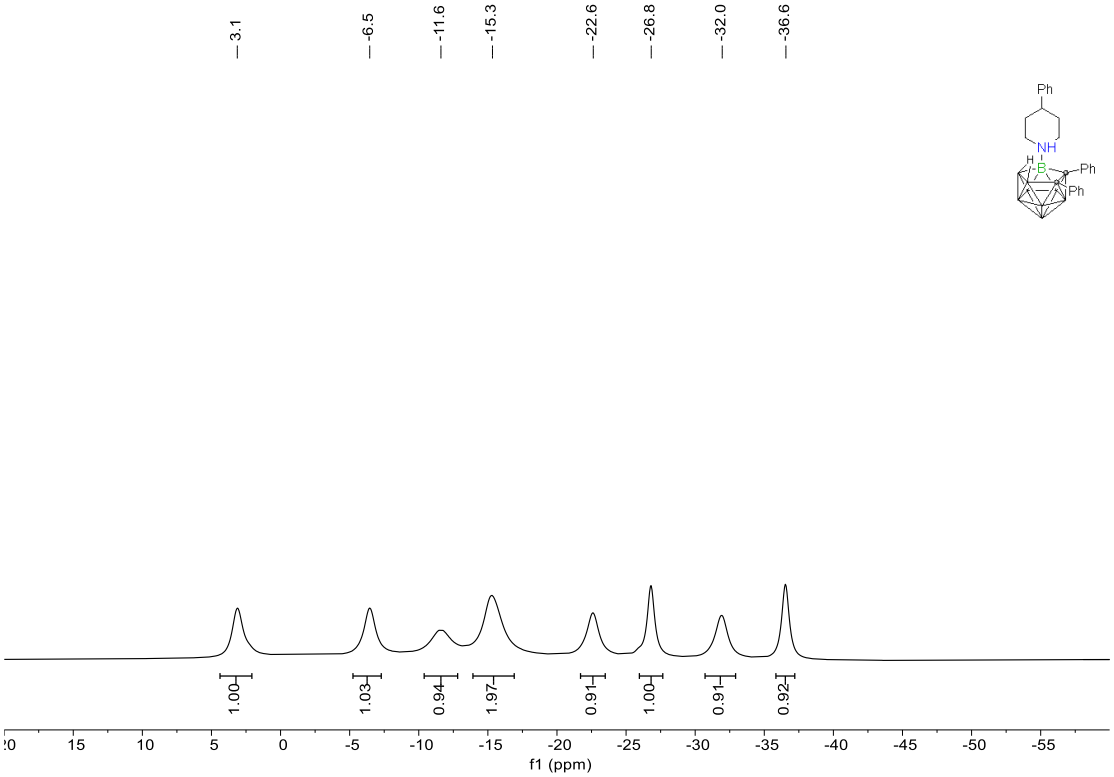

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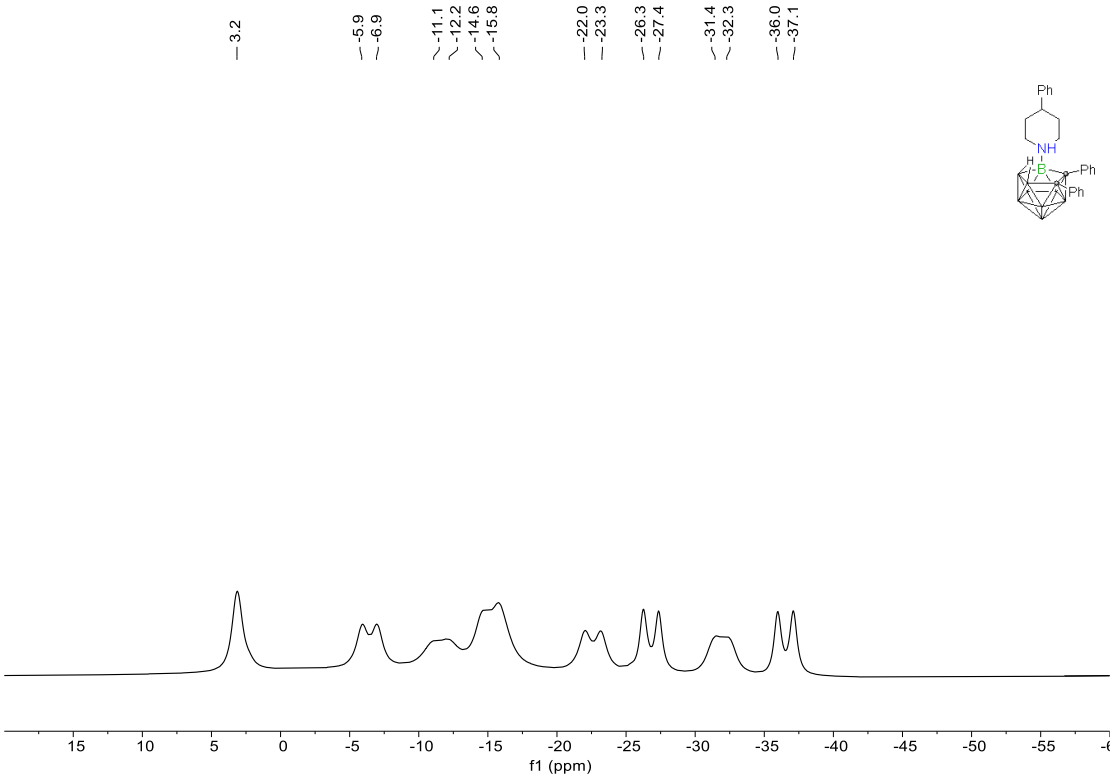
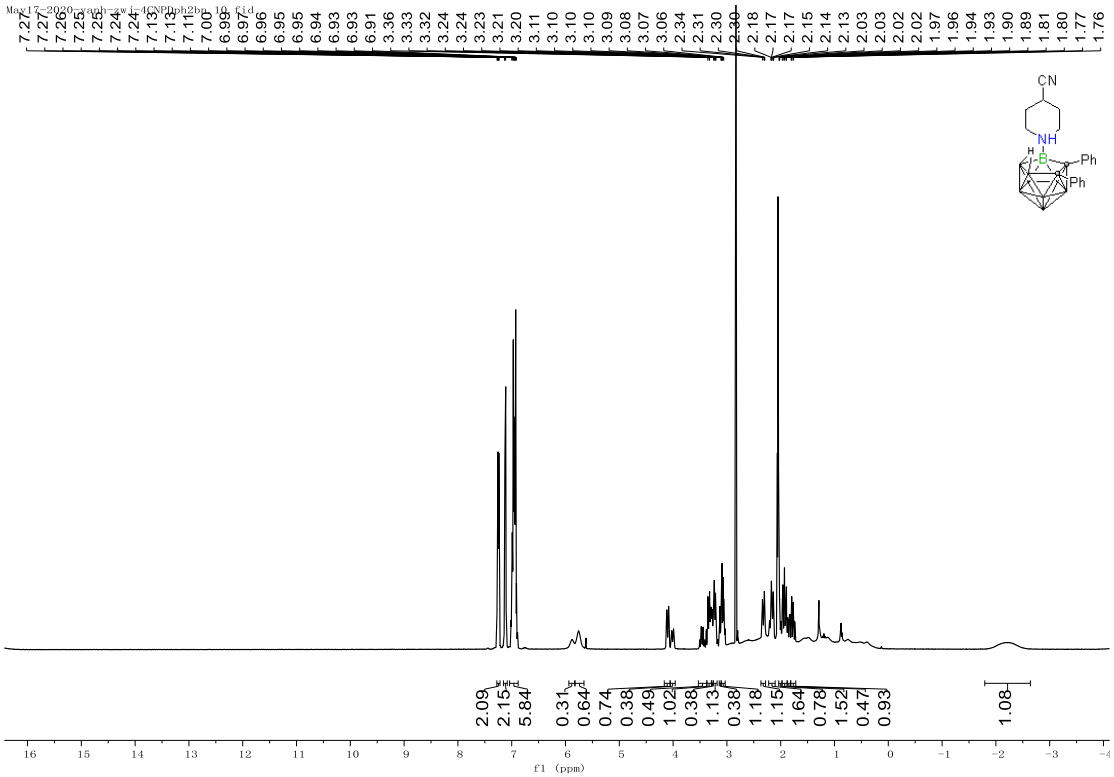
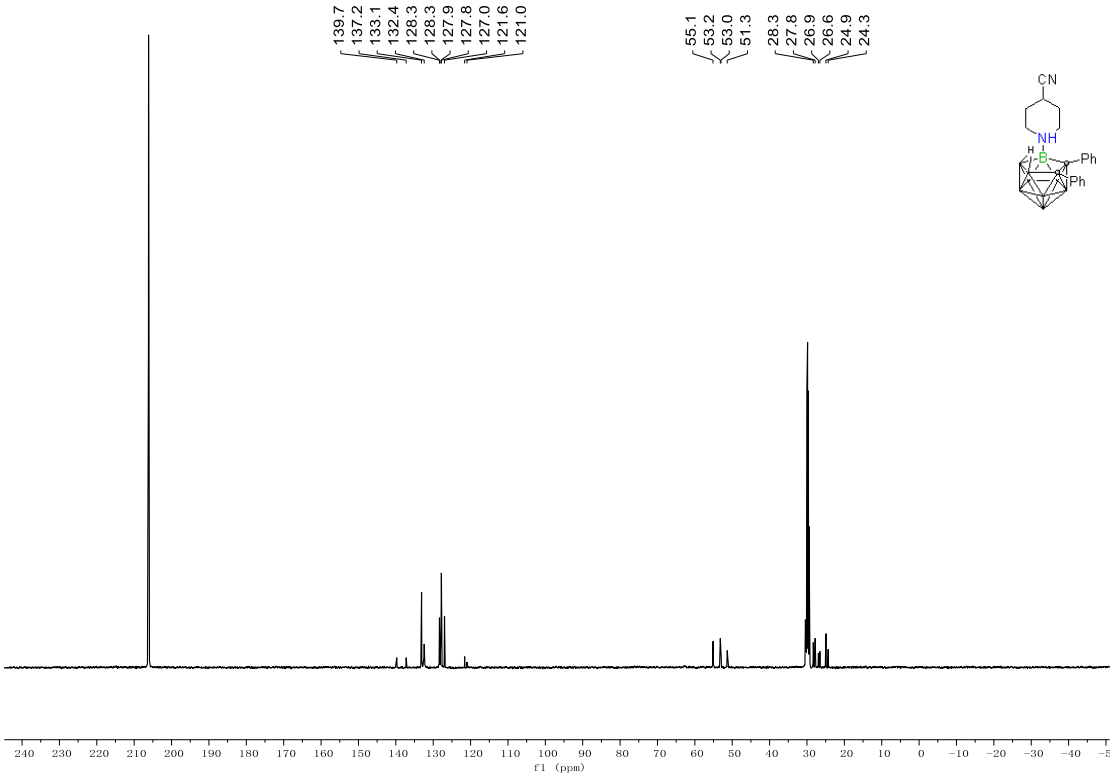


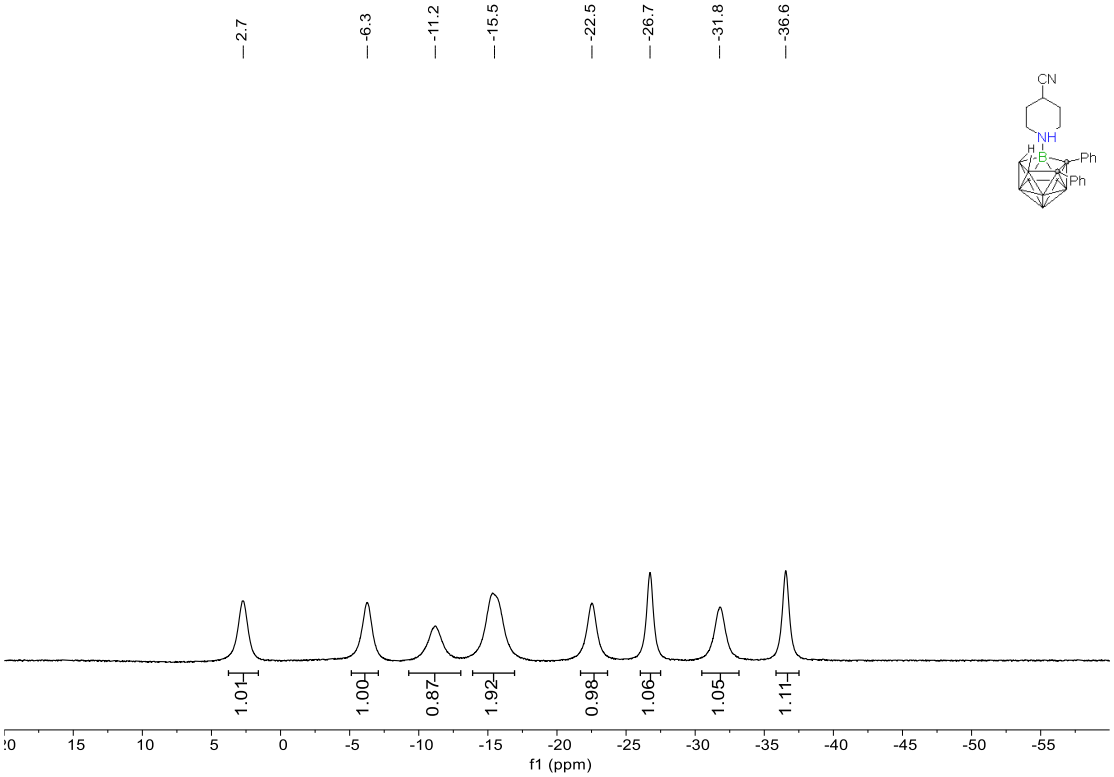
^{1}H NMR (Acetone-d_6) (Compound 3i)



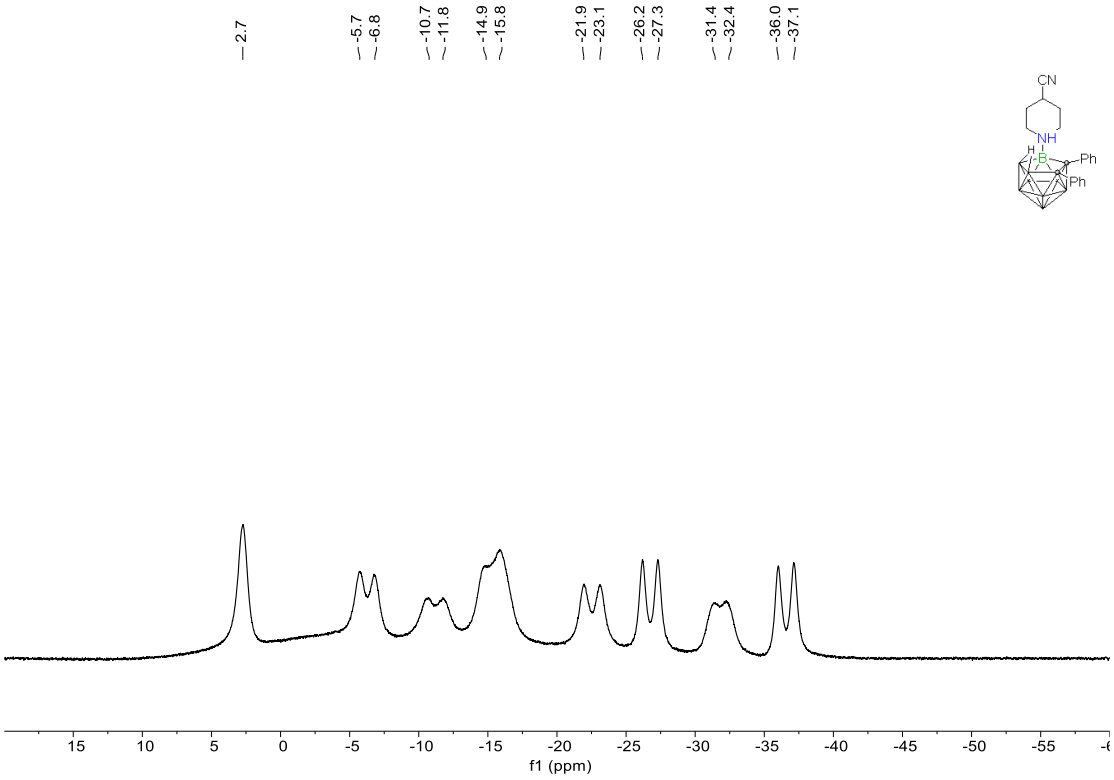
^{13}C NMR (Acetone-d_6) (Compound 3i)



$^{11}B\{^{1}H\}$ NMR (Acetone-d_6) (Compound 3i)



^{11}B NMR (Acetone-d_6) (Compound 3i)



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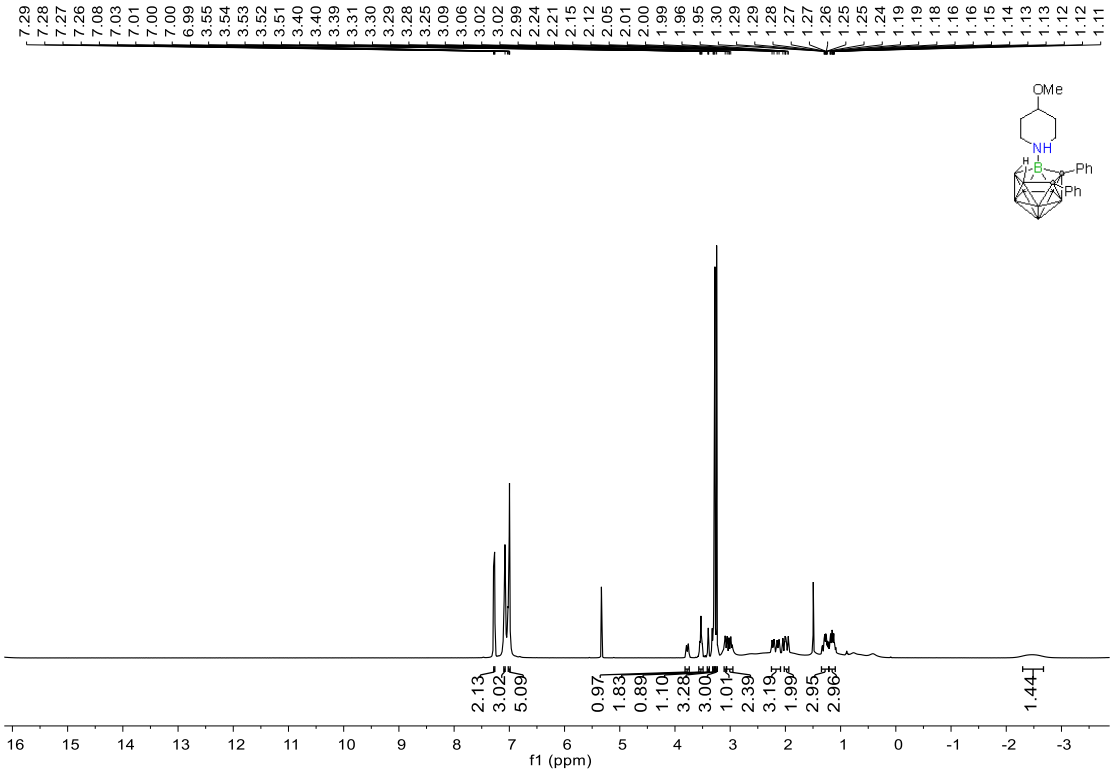
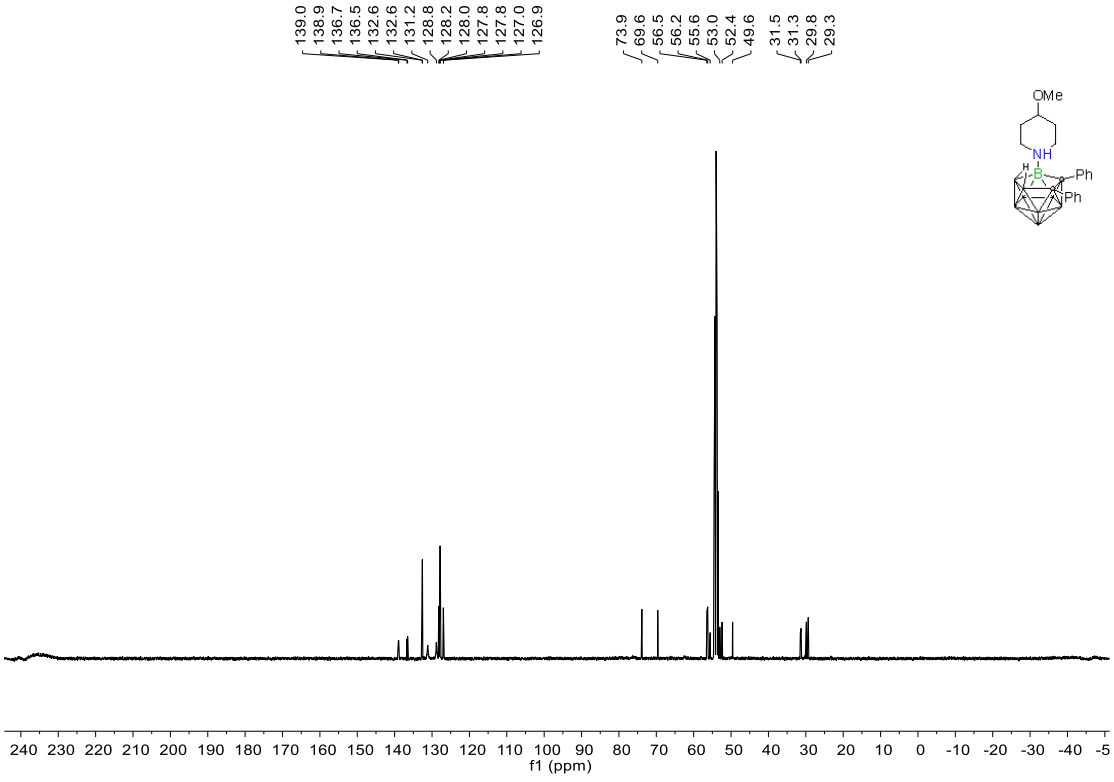
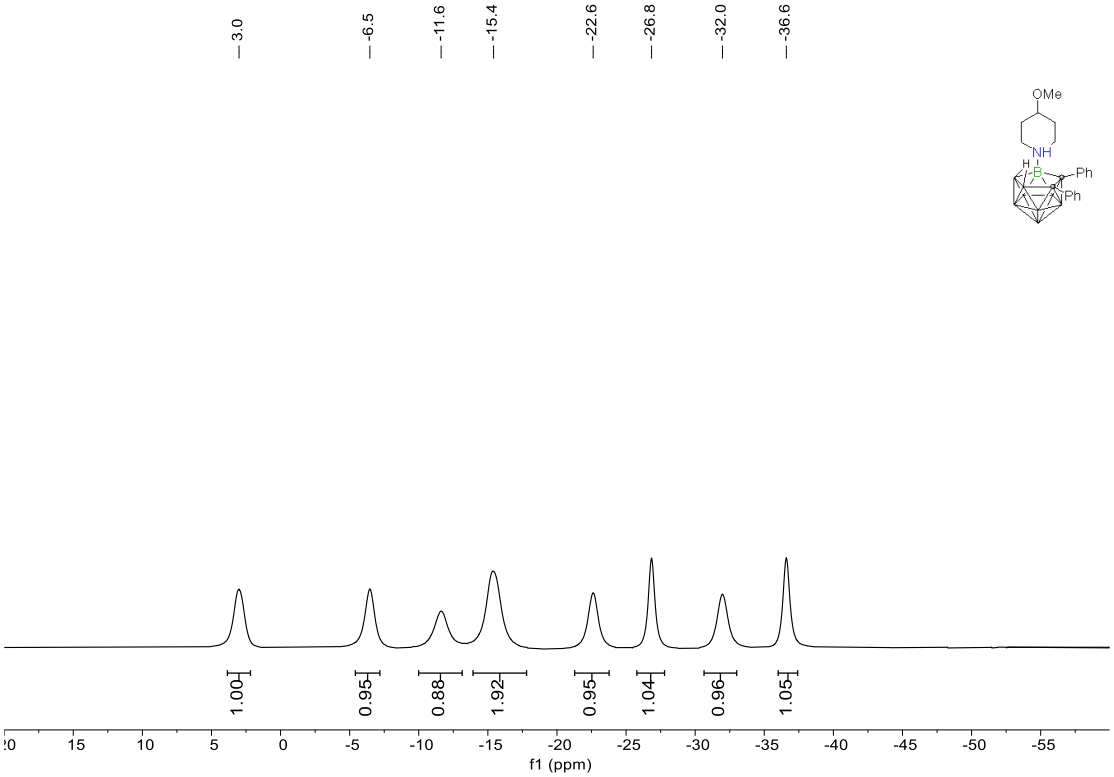


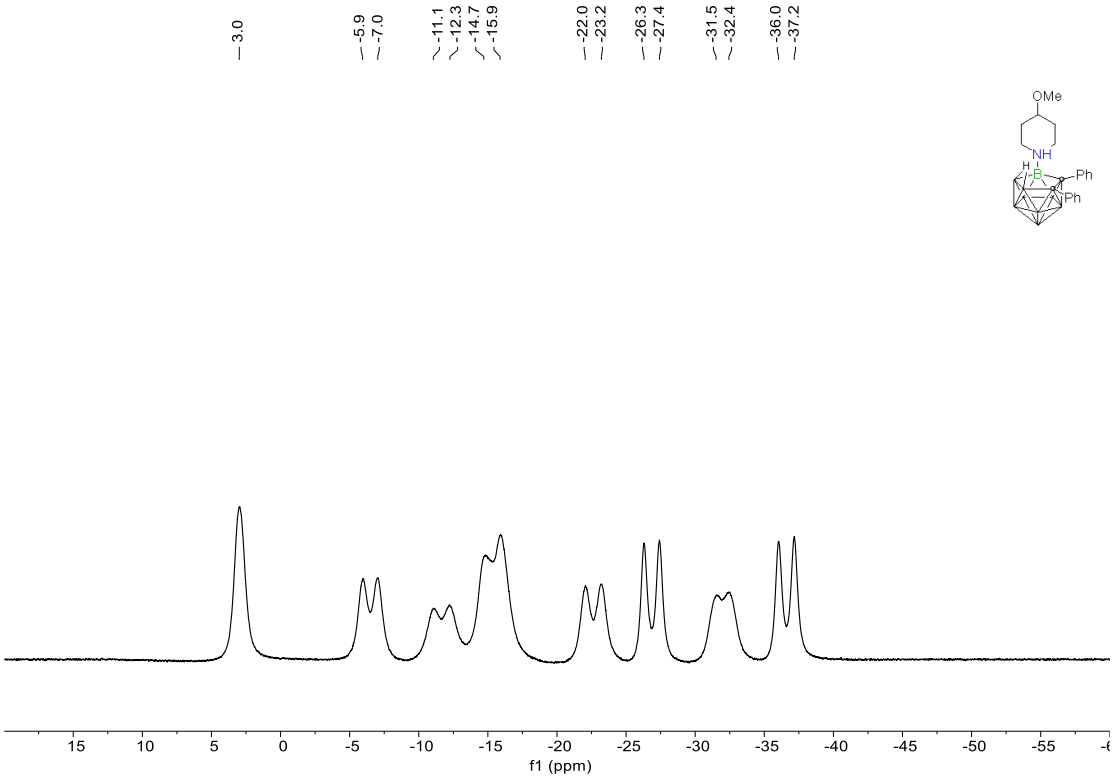
^{13}C NMR (Methylene Cloride-d_2) (Compound 3j)



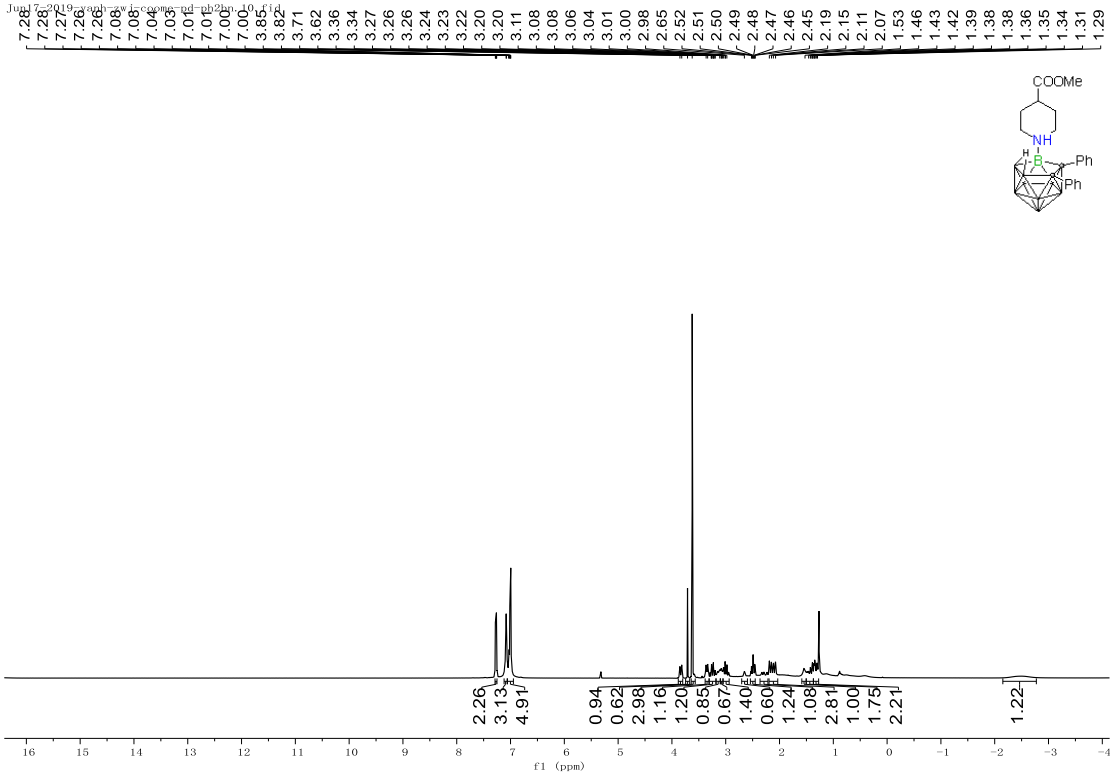
$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 3j)



^{11}B NMR (Methylene Cloride-d_2) (Compound 3j)



[1] H NMR (Methylene Cloride-d_2) (Compound 3k)



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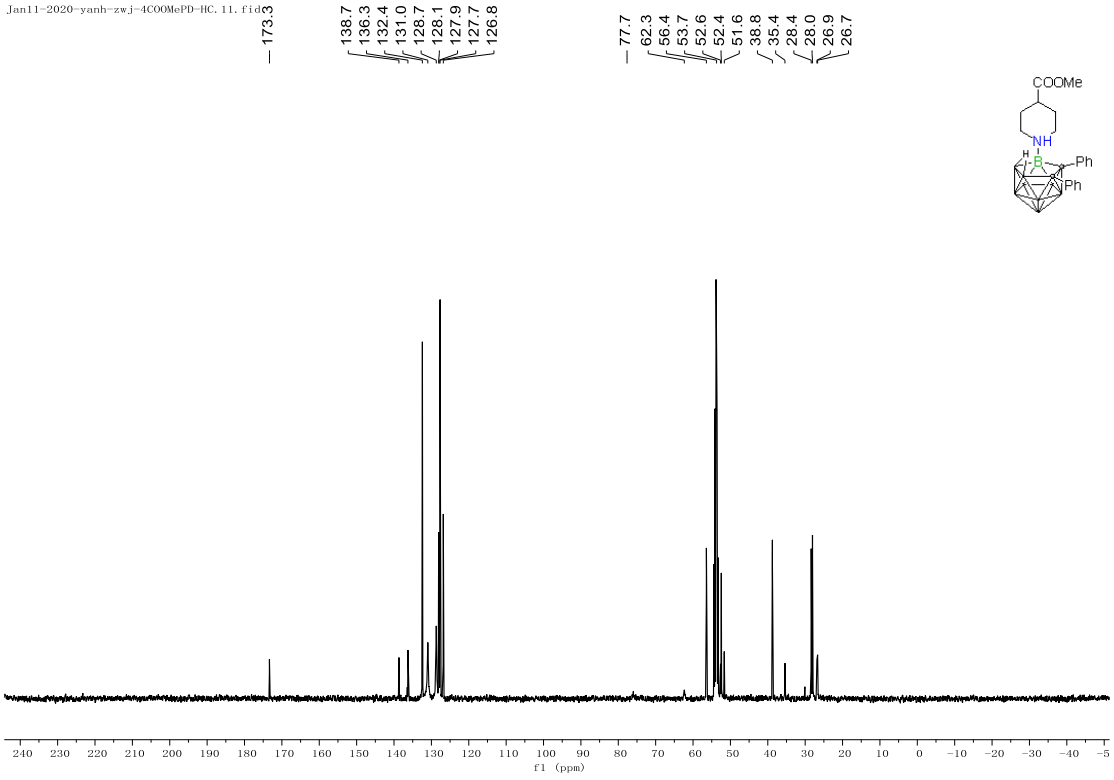
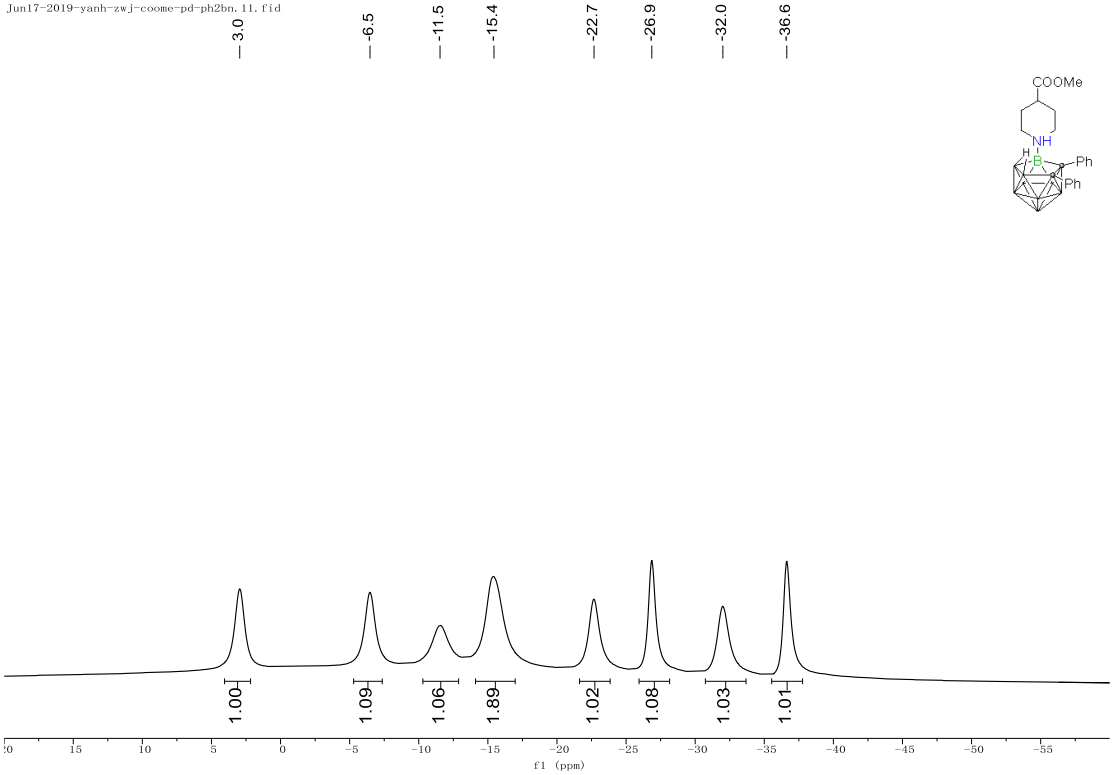


$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 3k)



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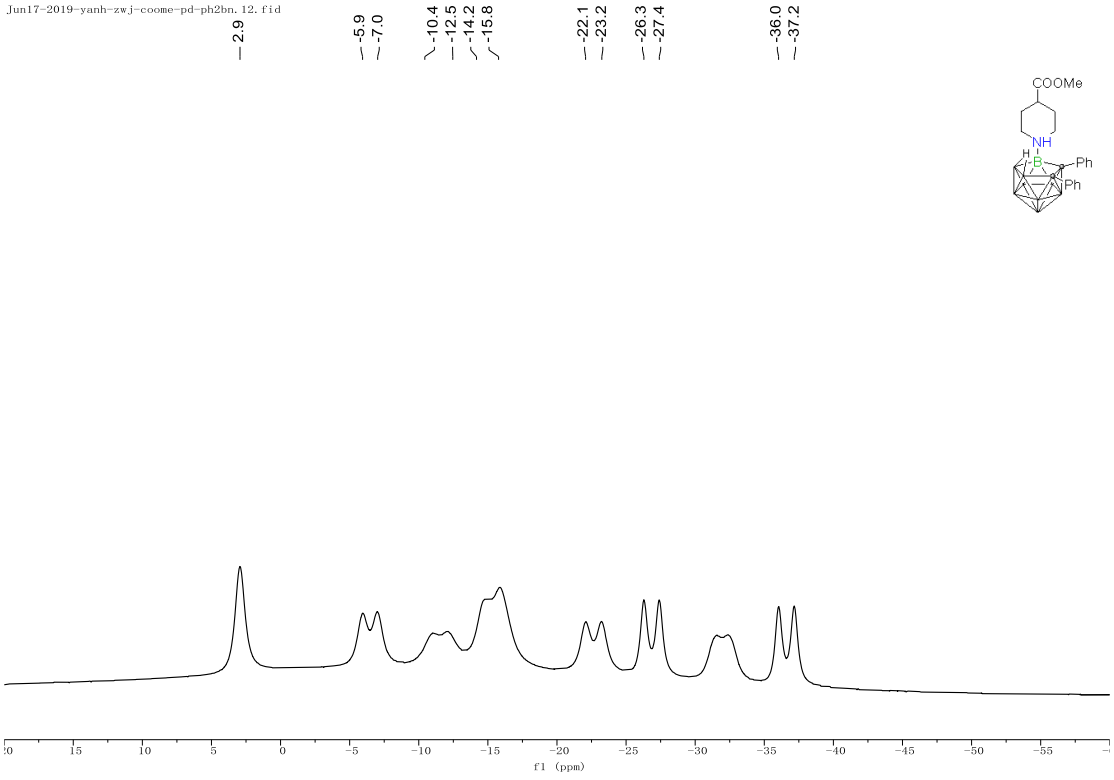
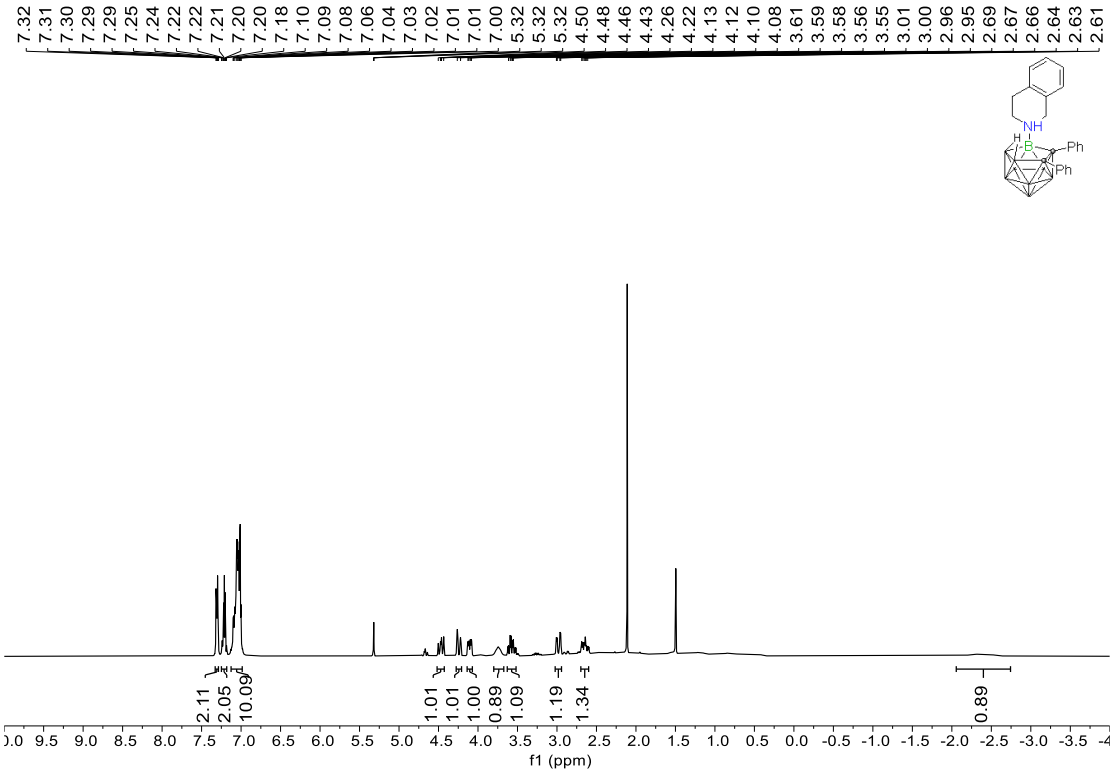


^{1}H NMR (Methylene Cloride-d_2) (Compound 3l)



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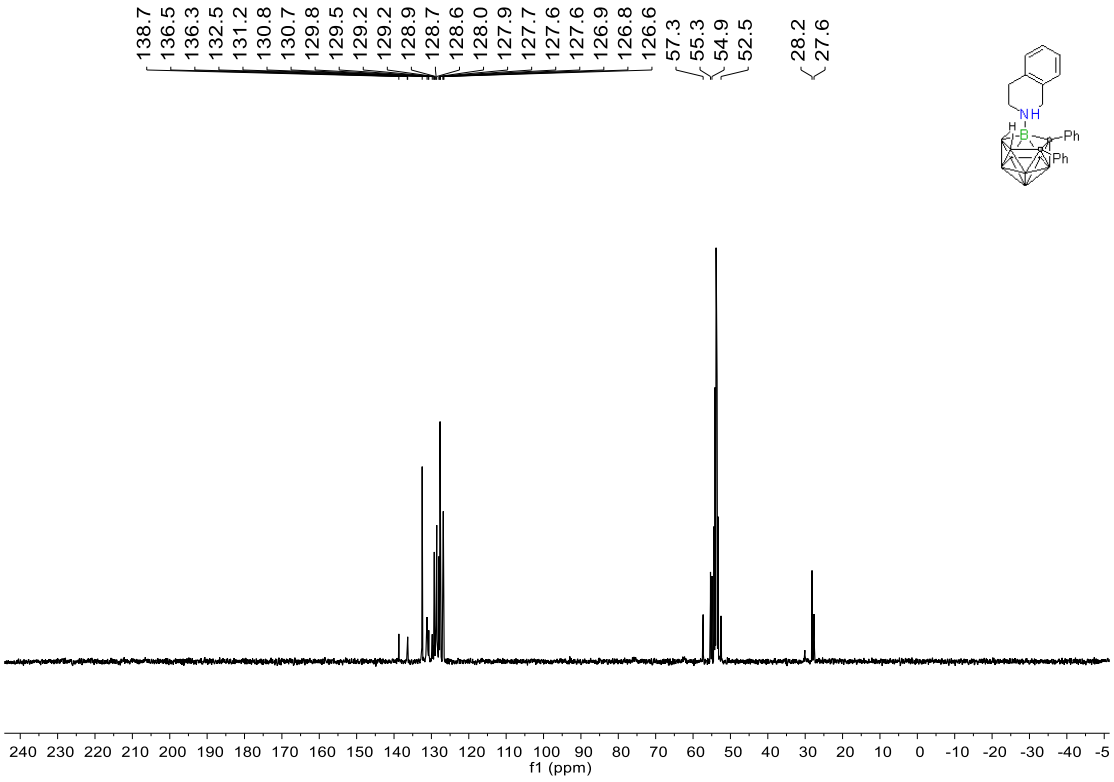
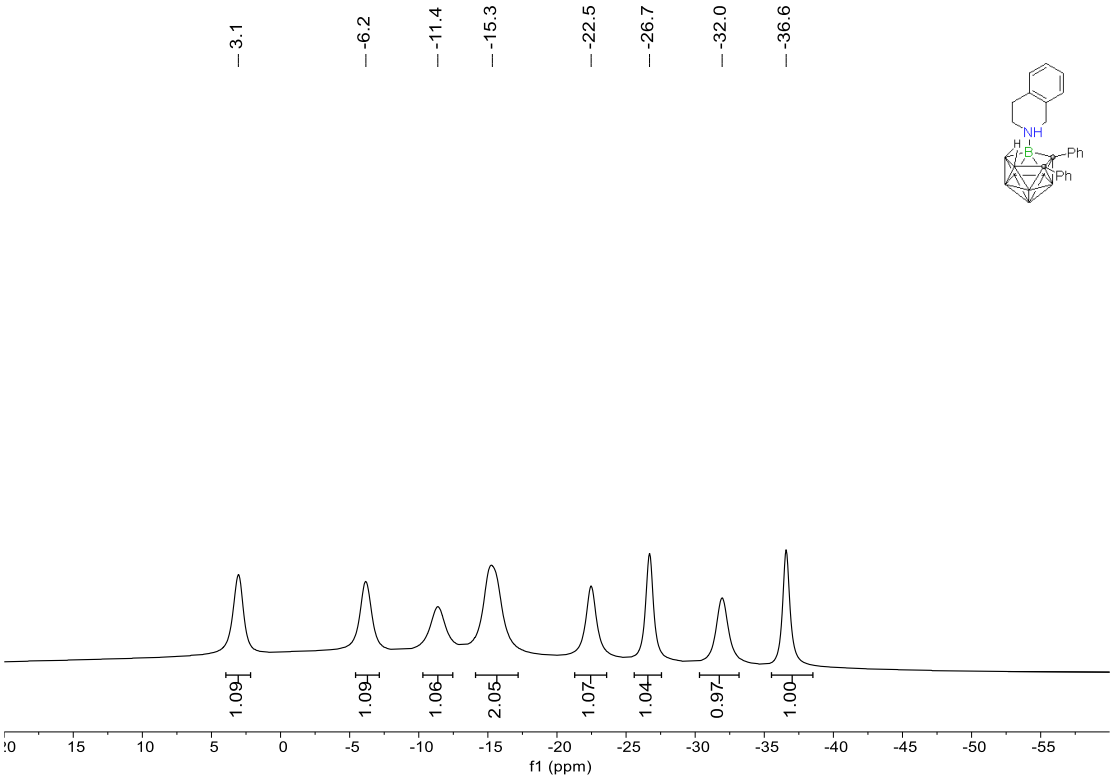


$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 3l)



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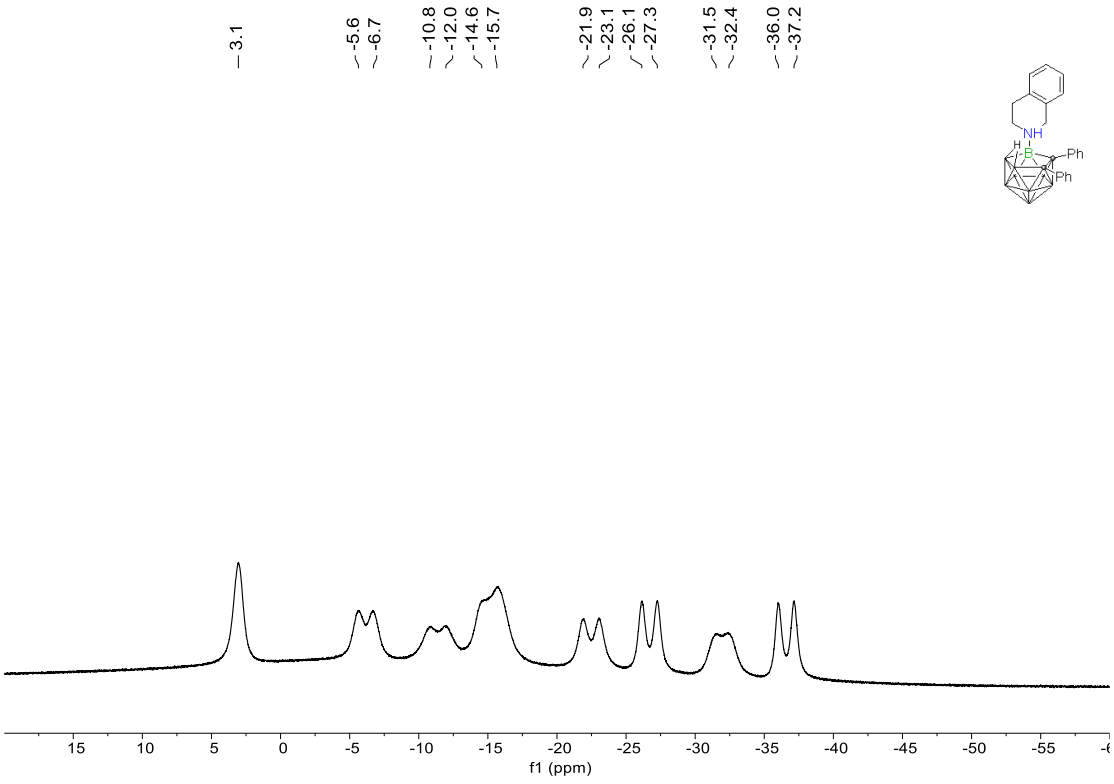
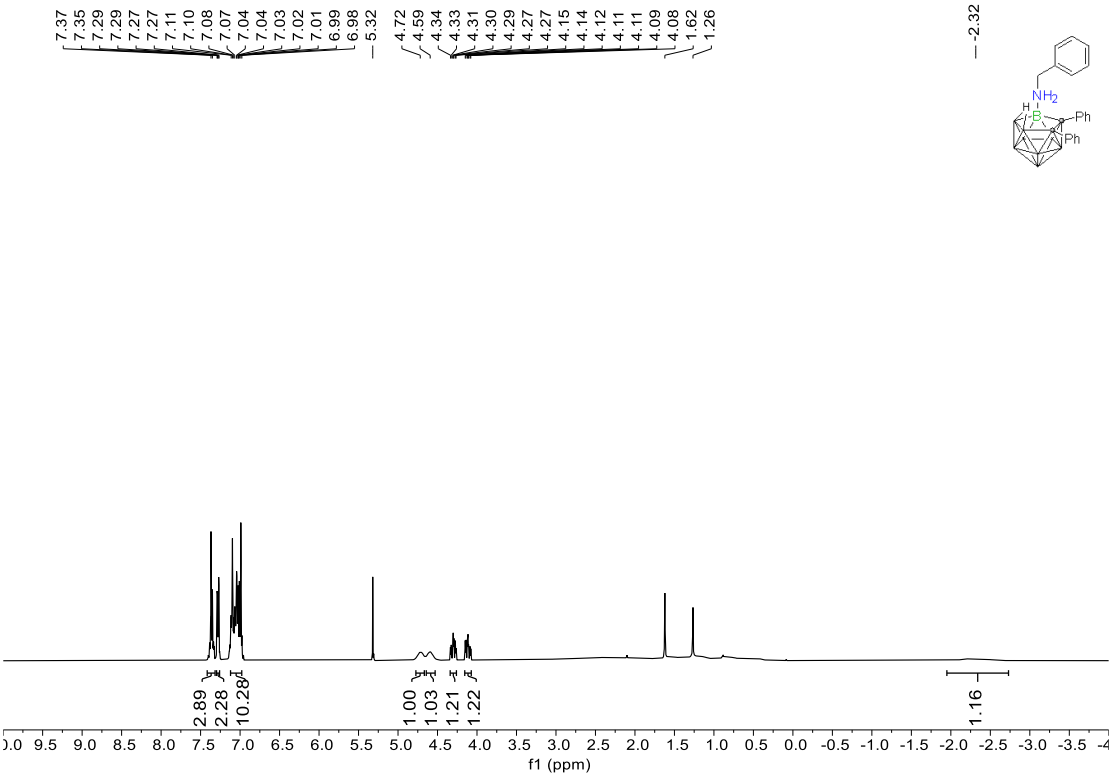


^{1}H NMR (Methylene Cloride-d_2) (Compound 4a)



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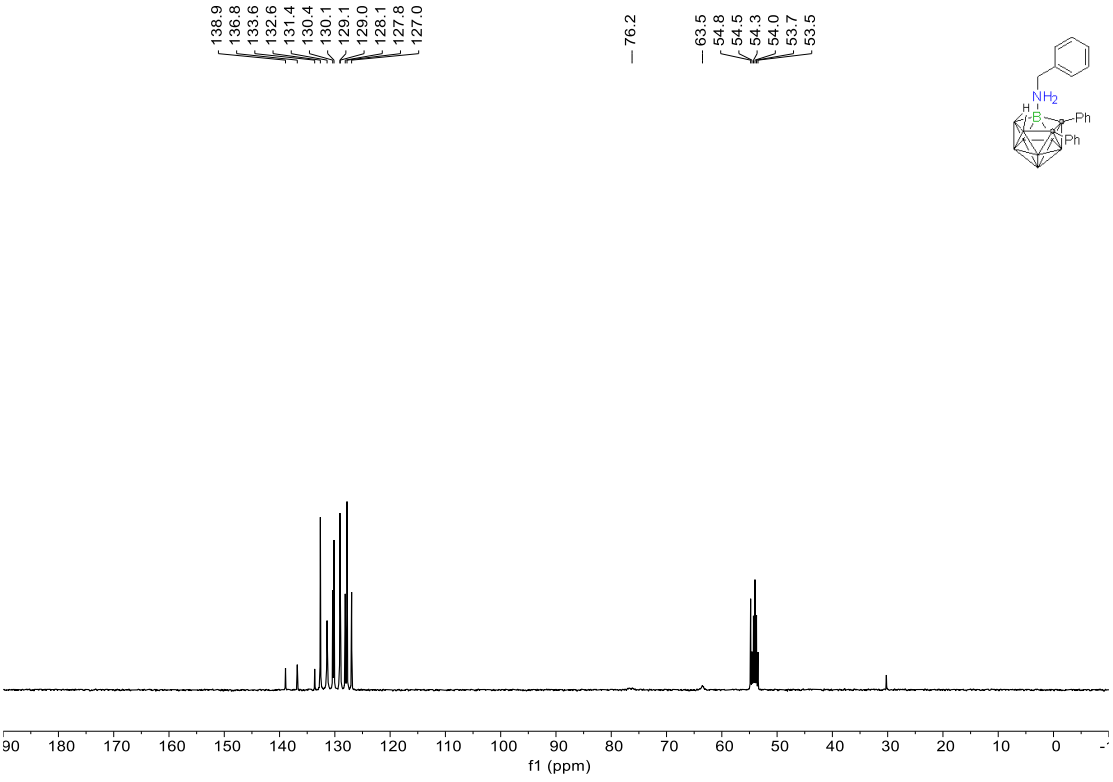
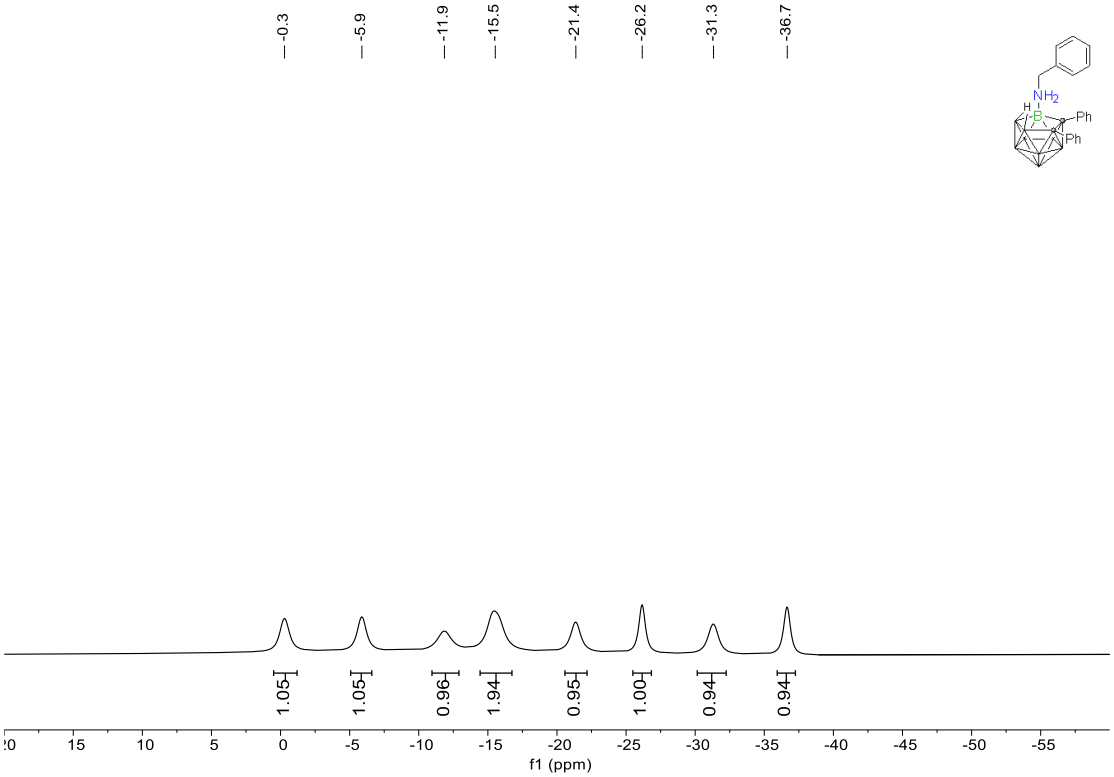


$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 4a)



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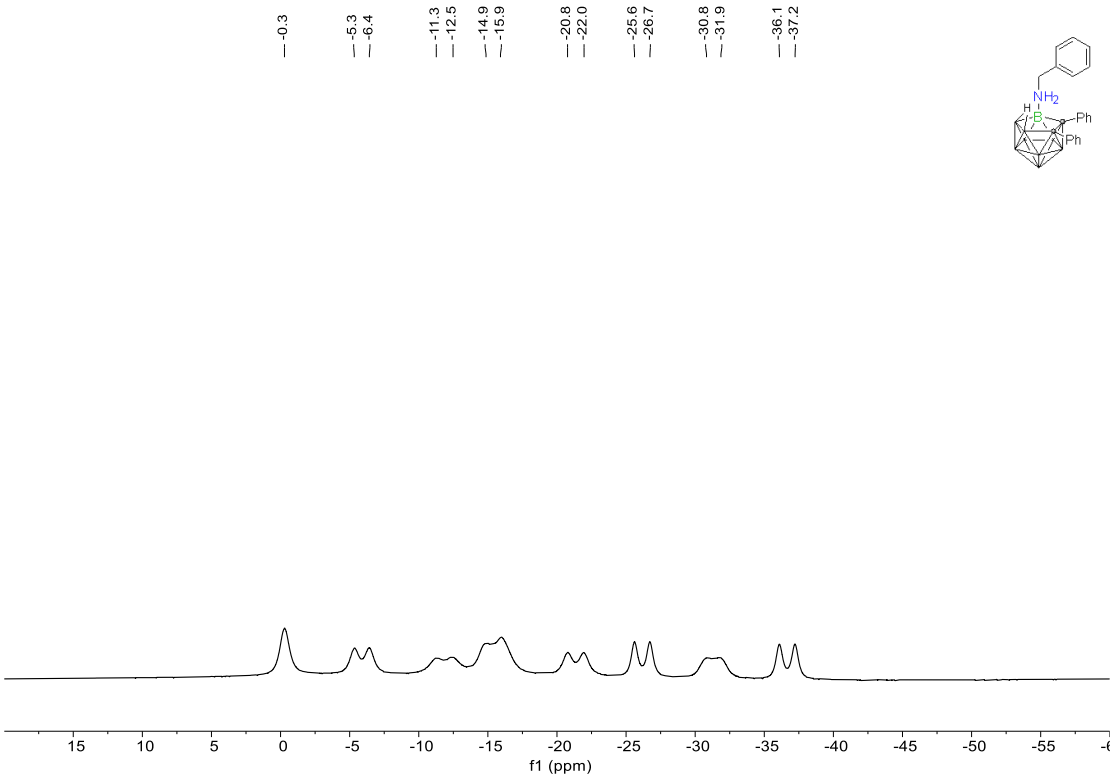
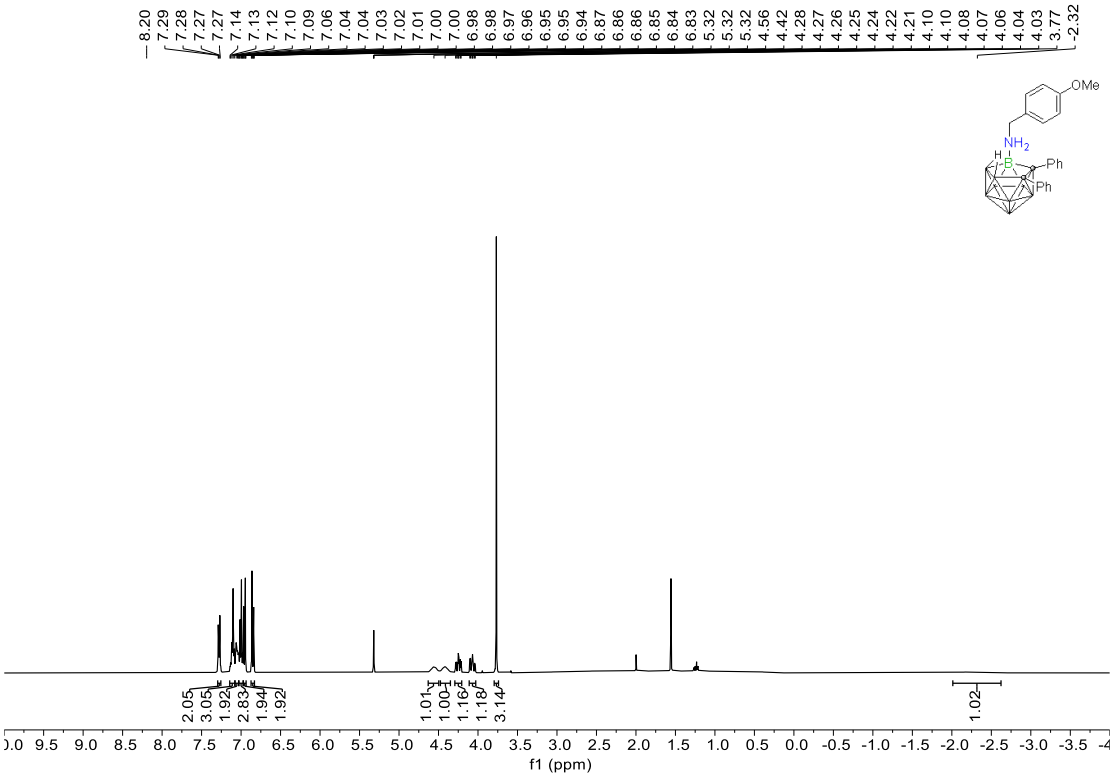
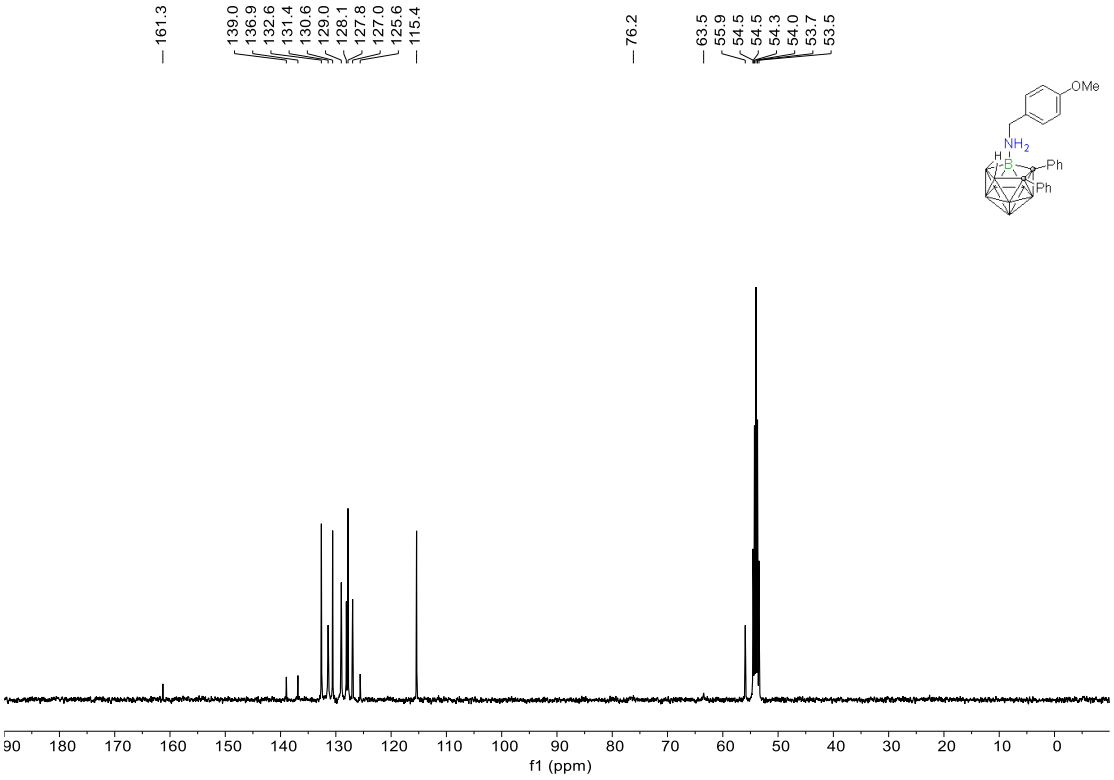


^{1}H NMR (Methylene Cloride-d_2) (Compound 4b)



^{13}C NMR (Methylene Cloride-d_2) (Compound 4b)



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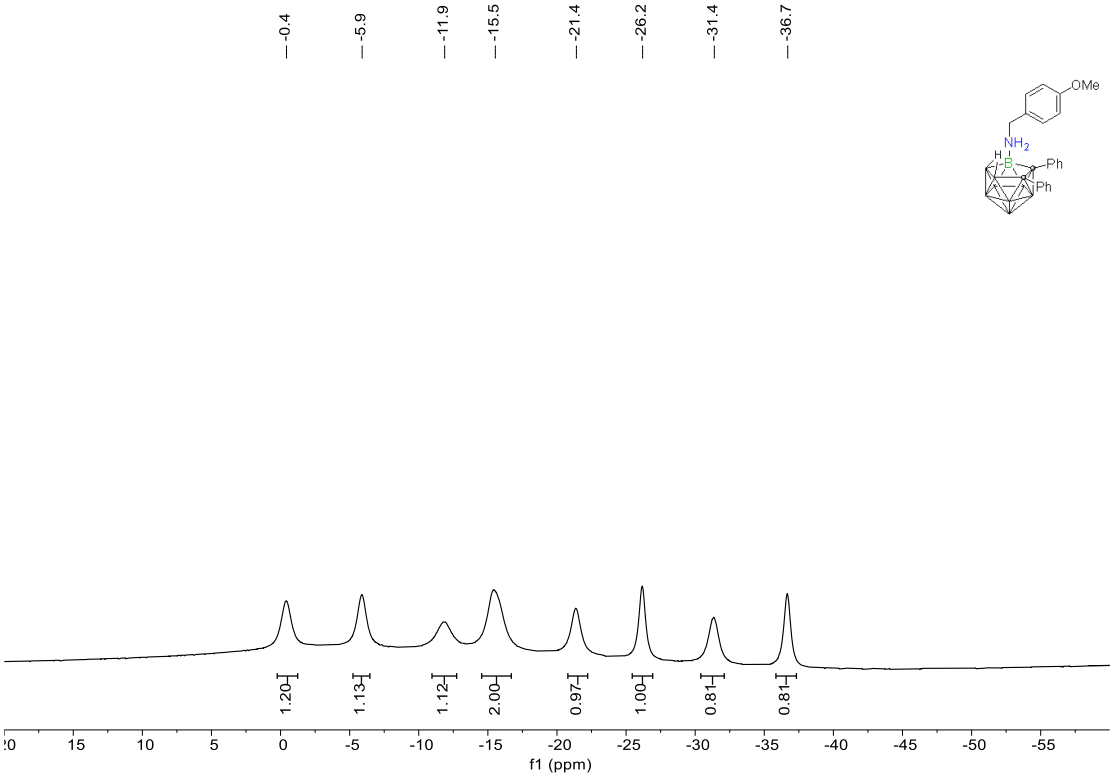
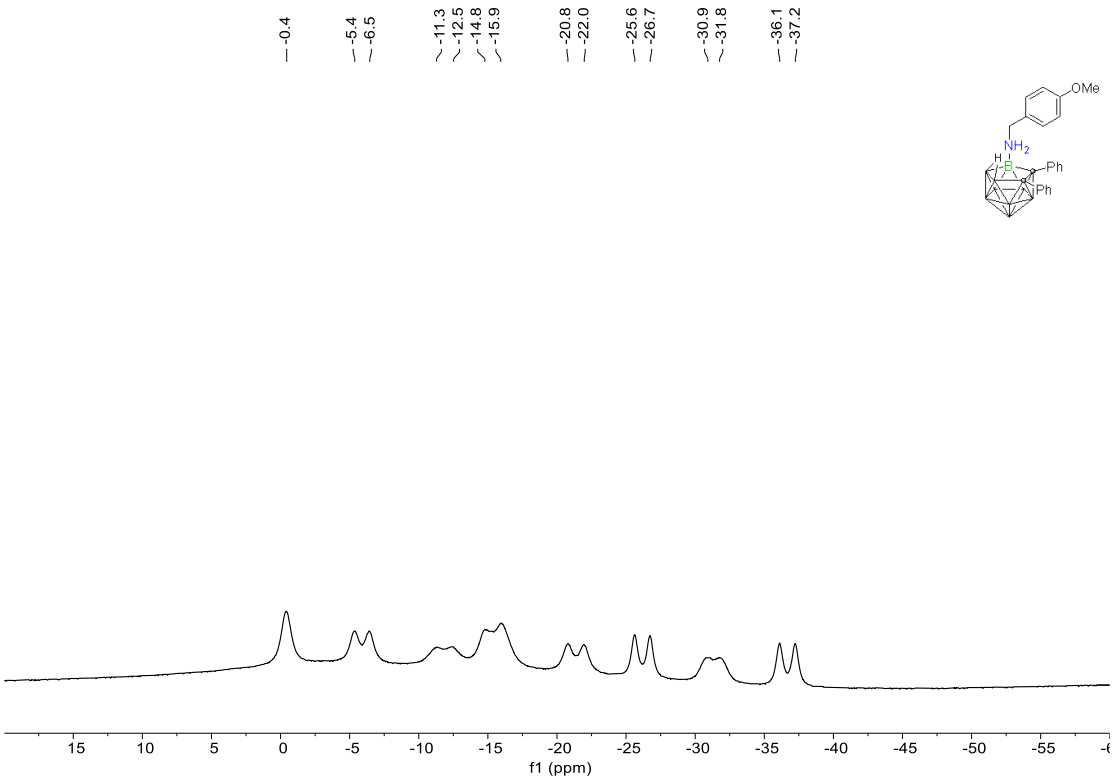
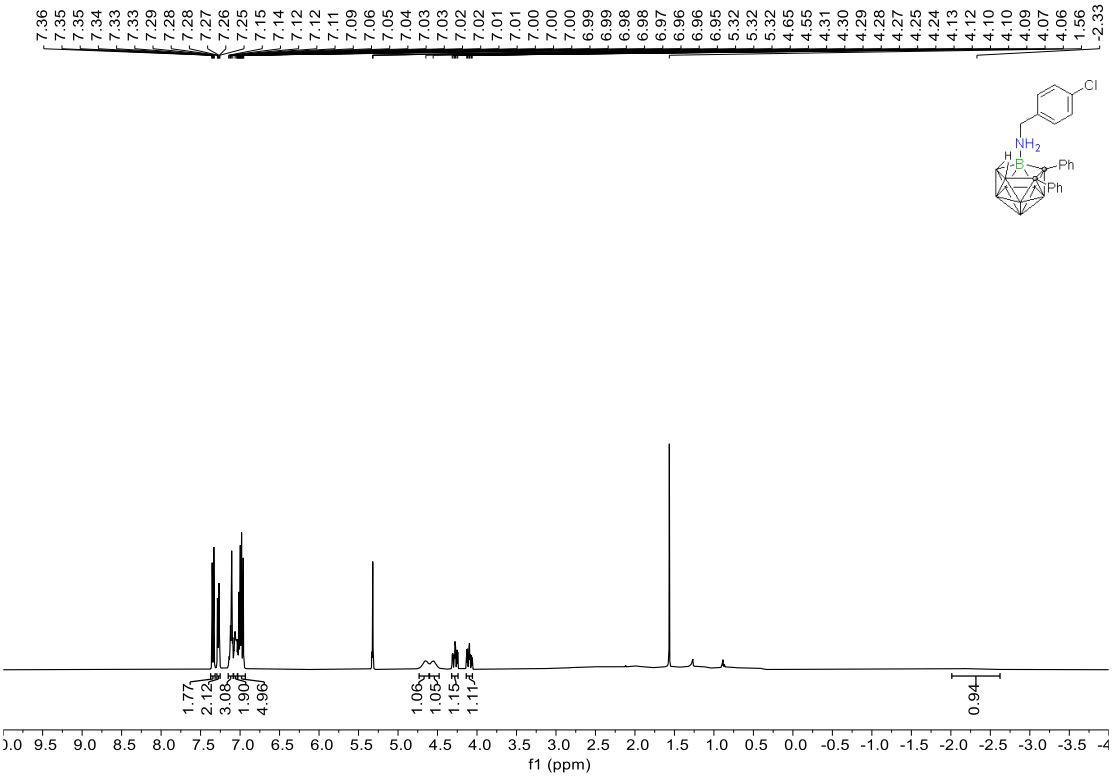


^{11}B NMR (Methylene Cloride-d_2) (Compound 4b)



^{1}H NMR (Methylene Cloride-d_2) (Compound 4c)



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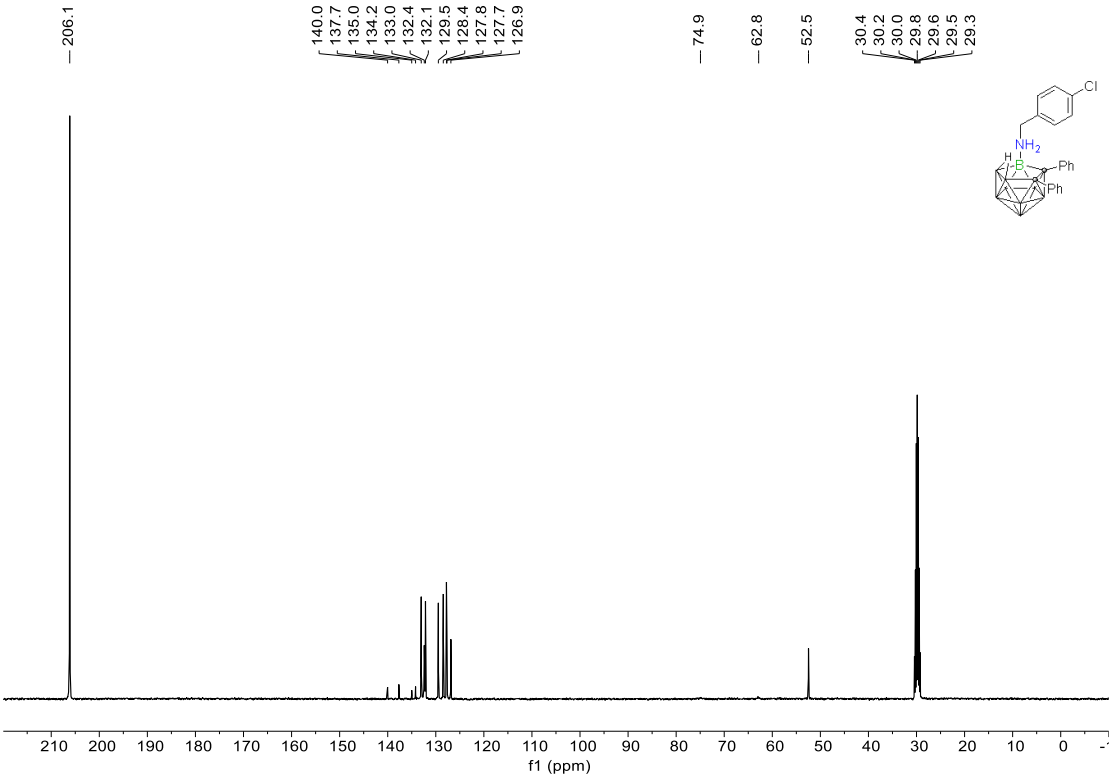

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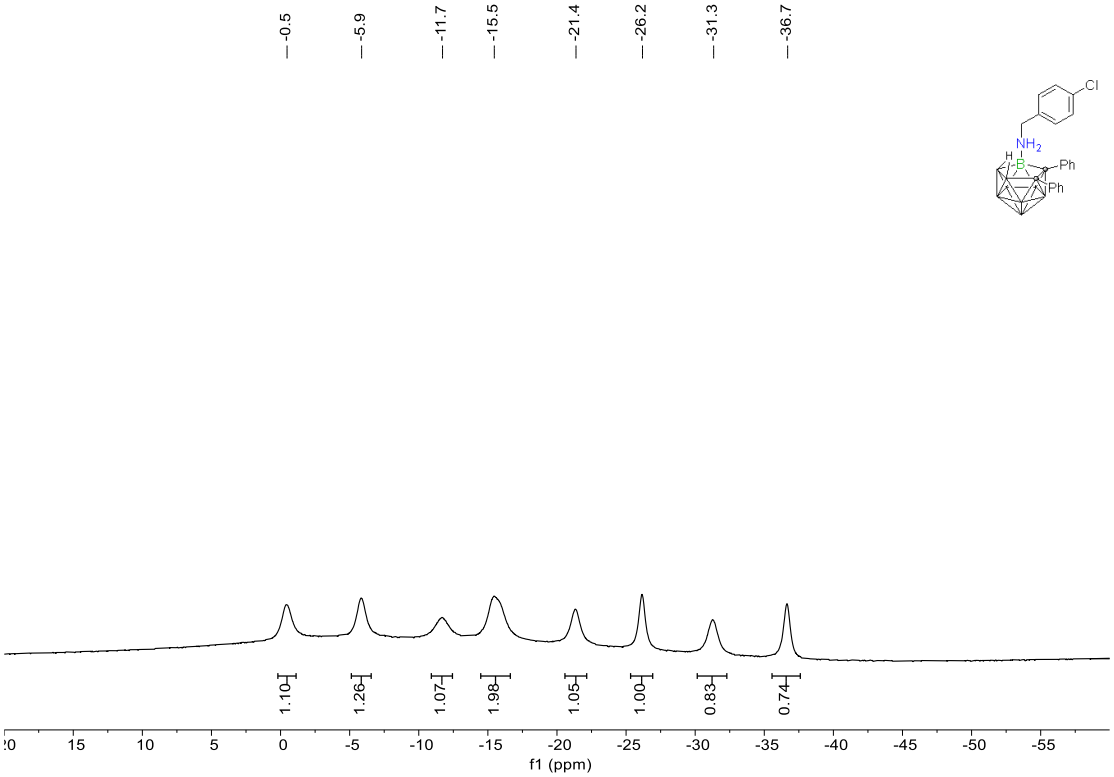

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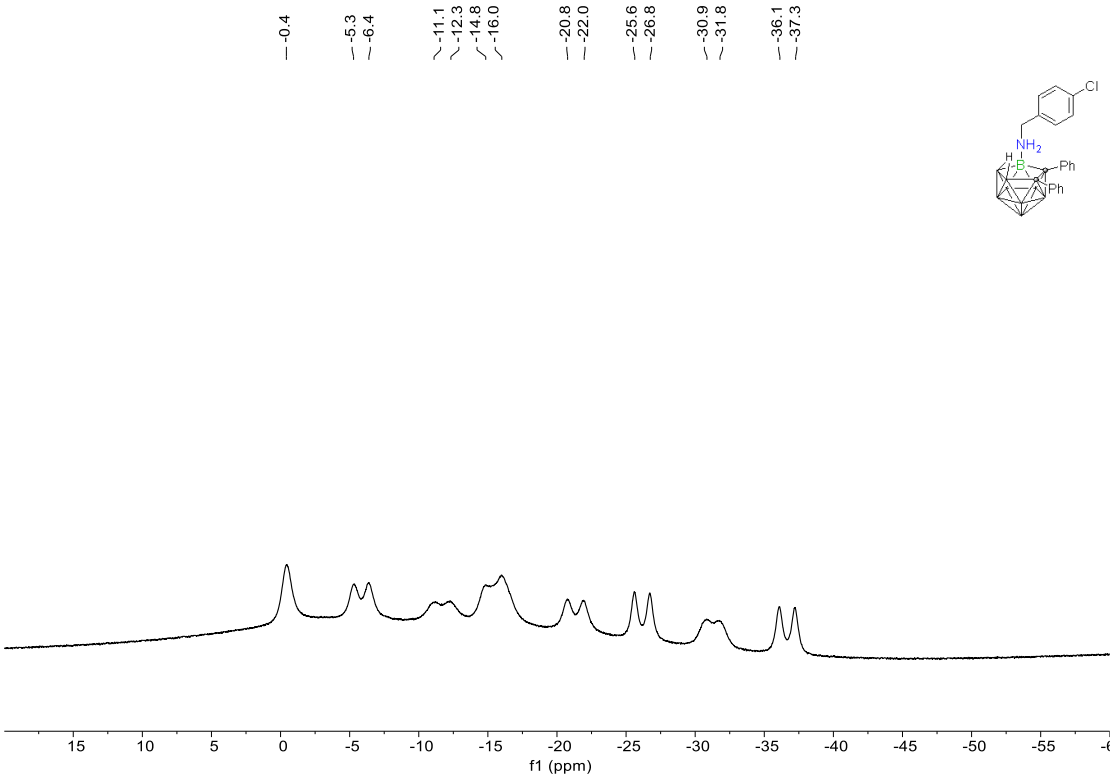

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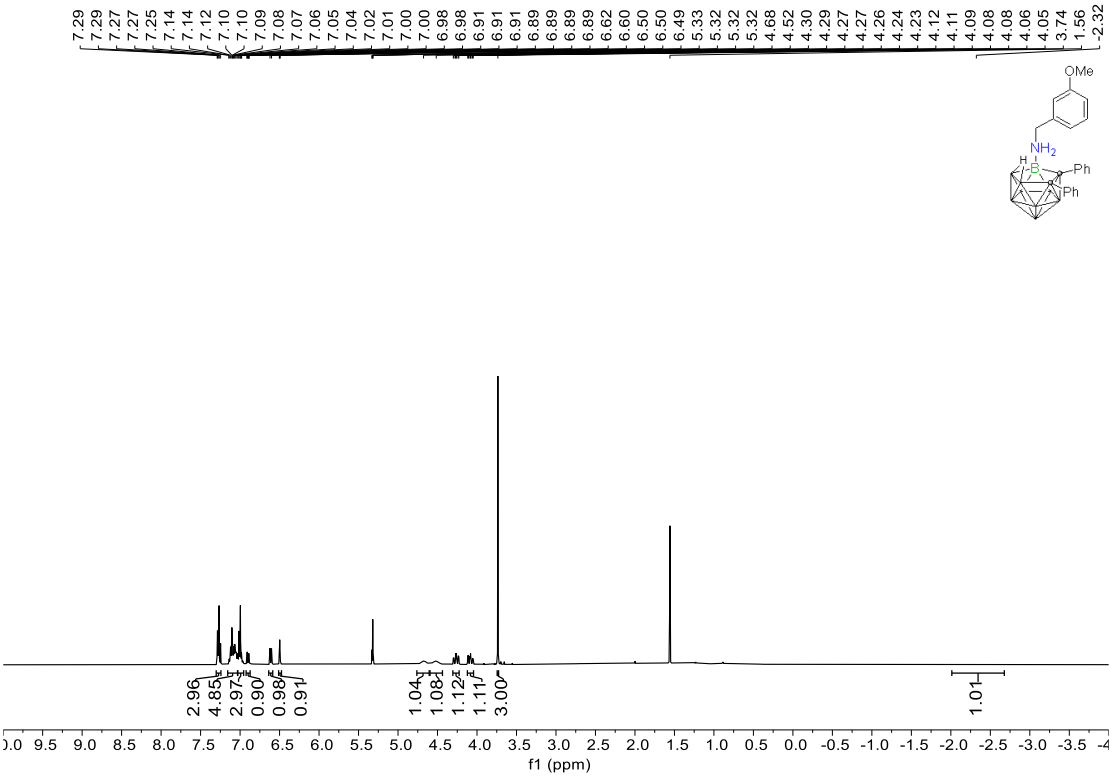

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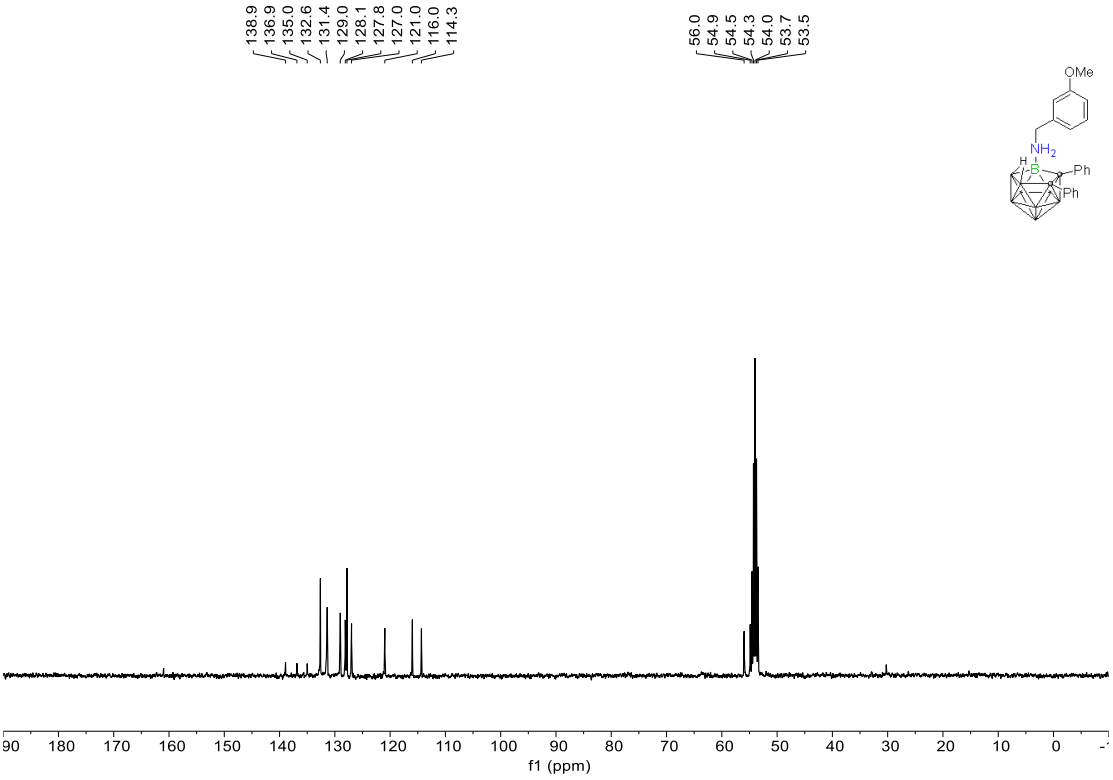

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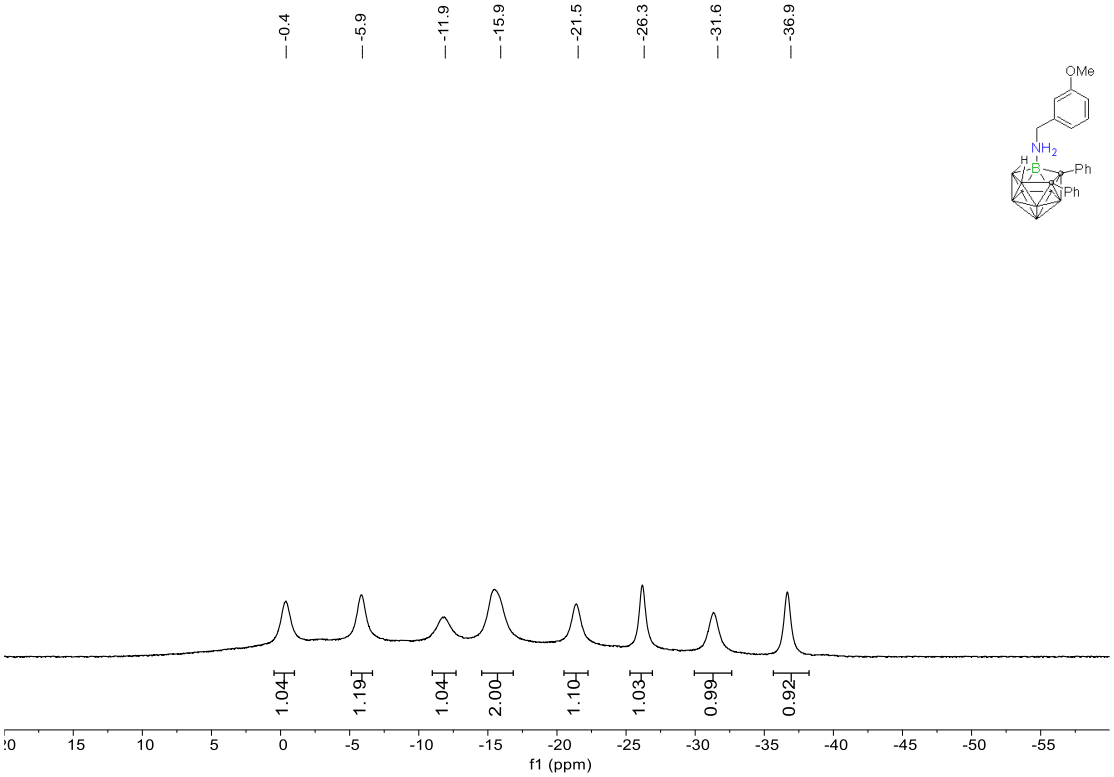

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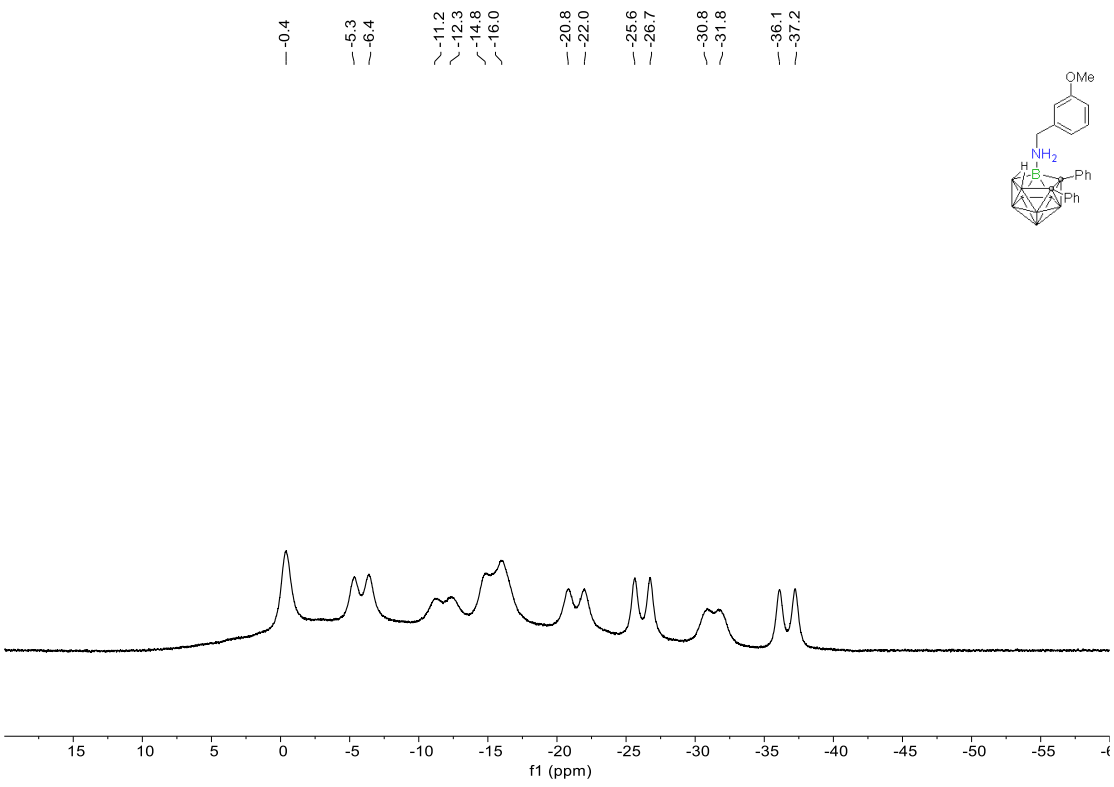

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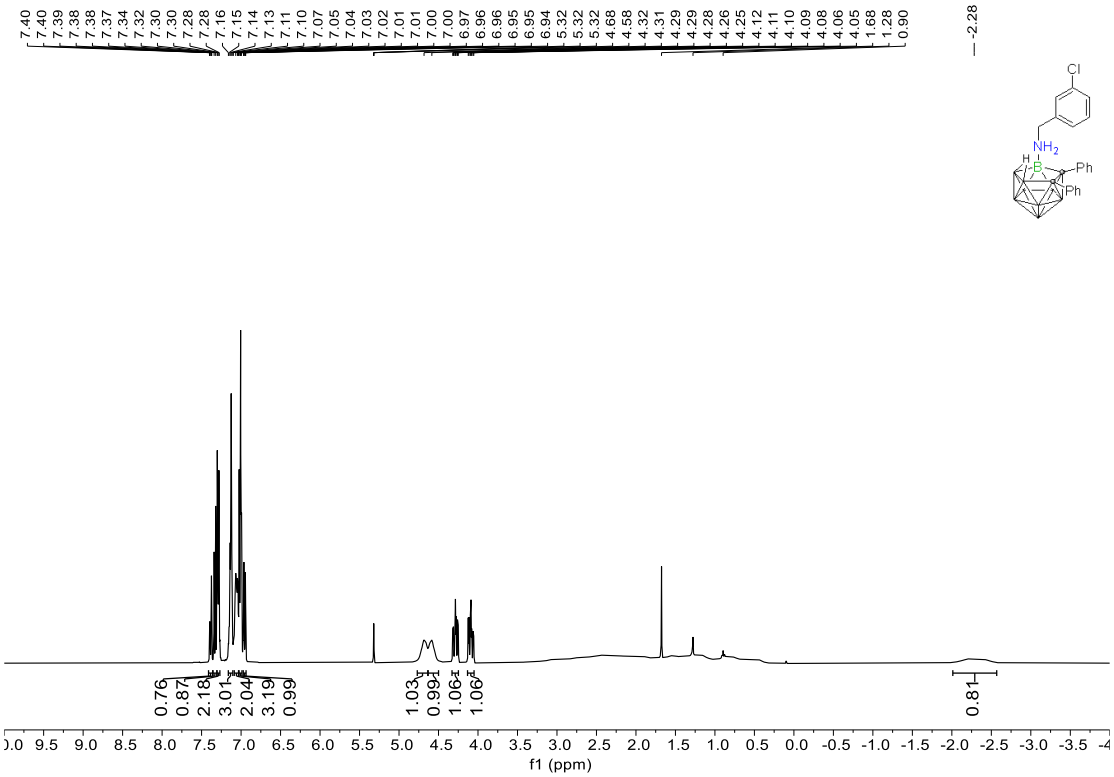

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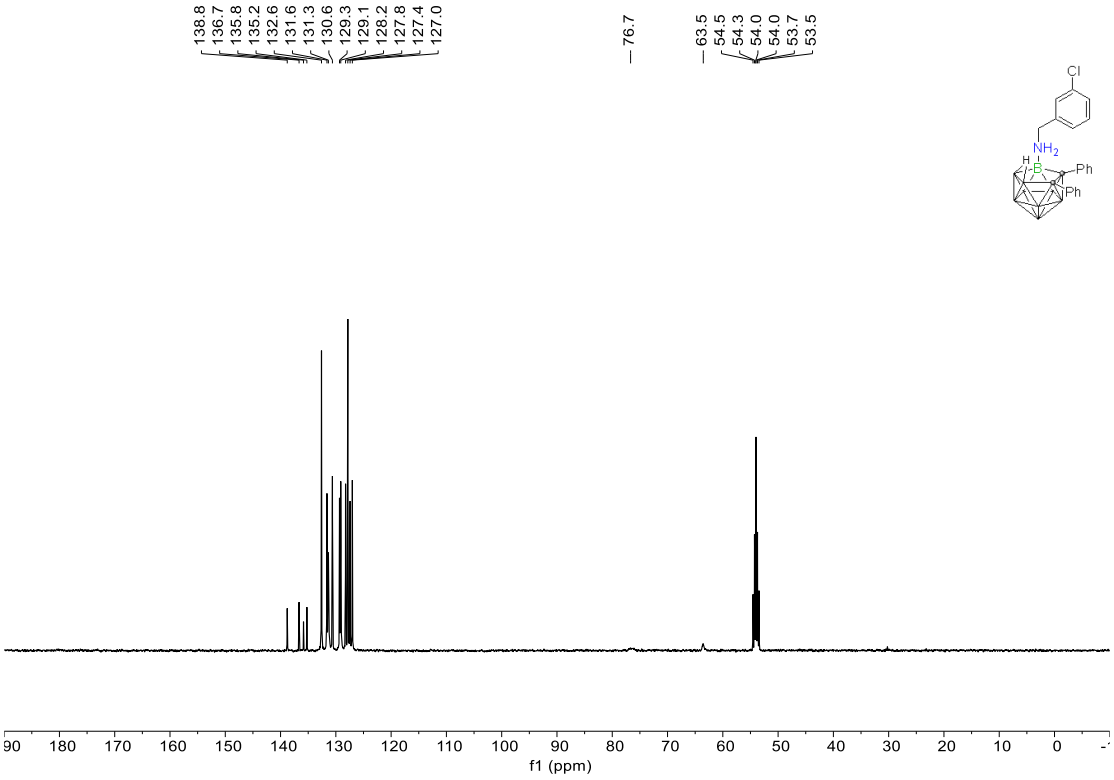

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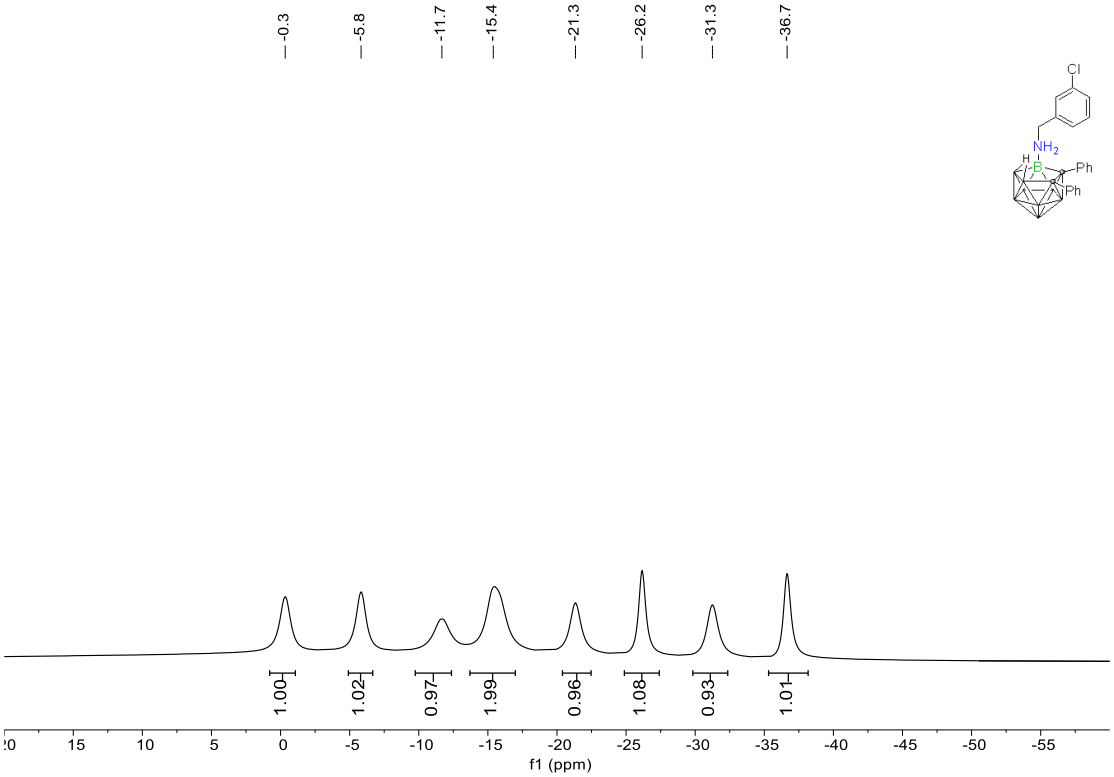

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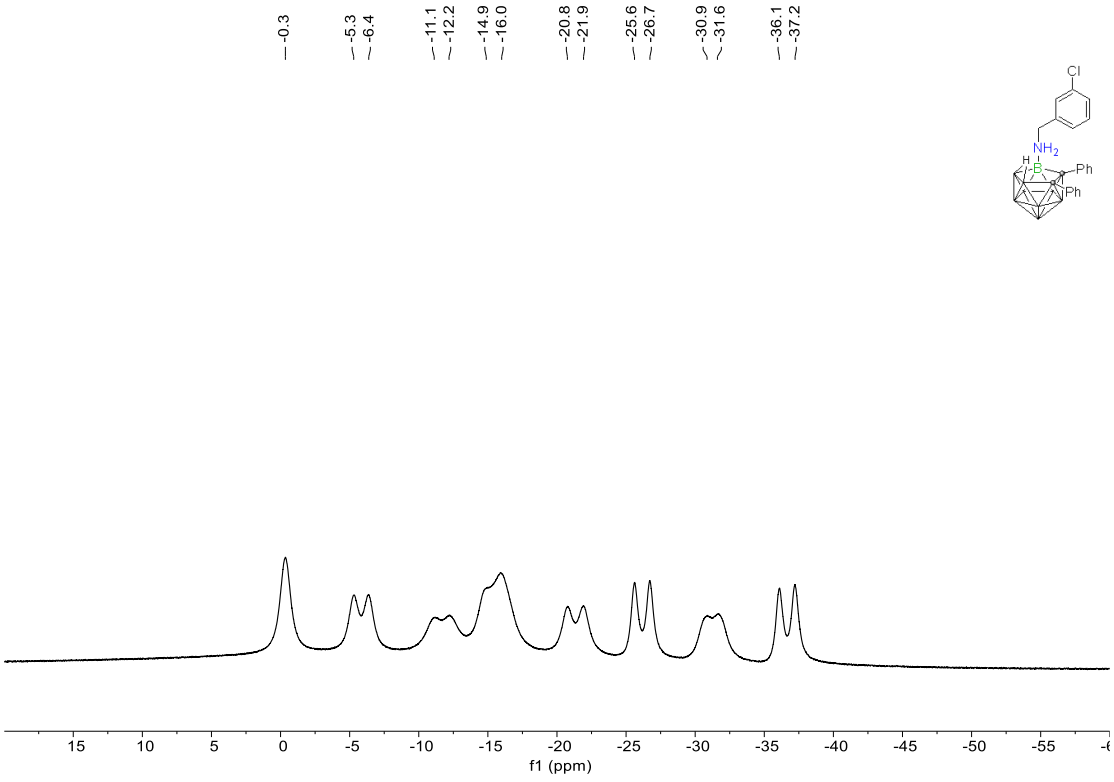

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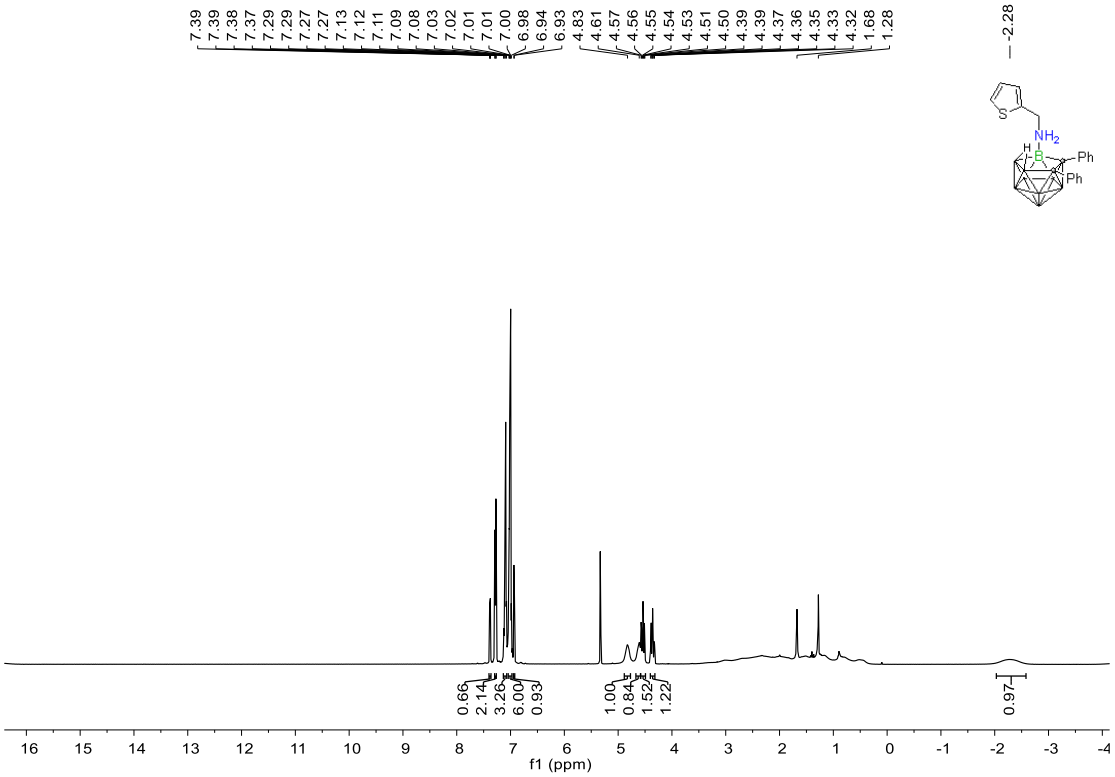

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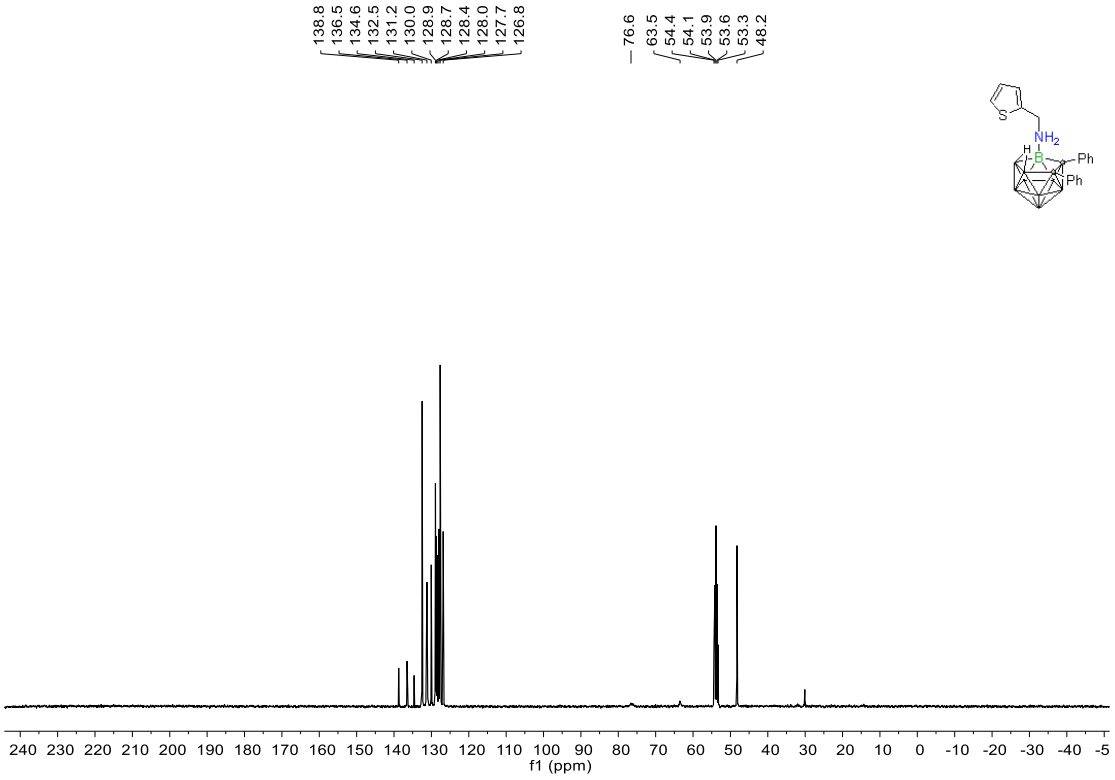

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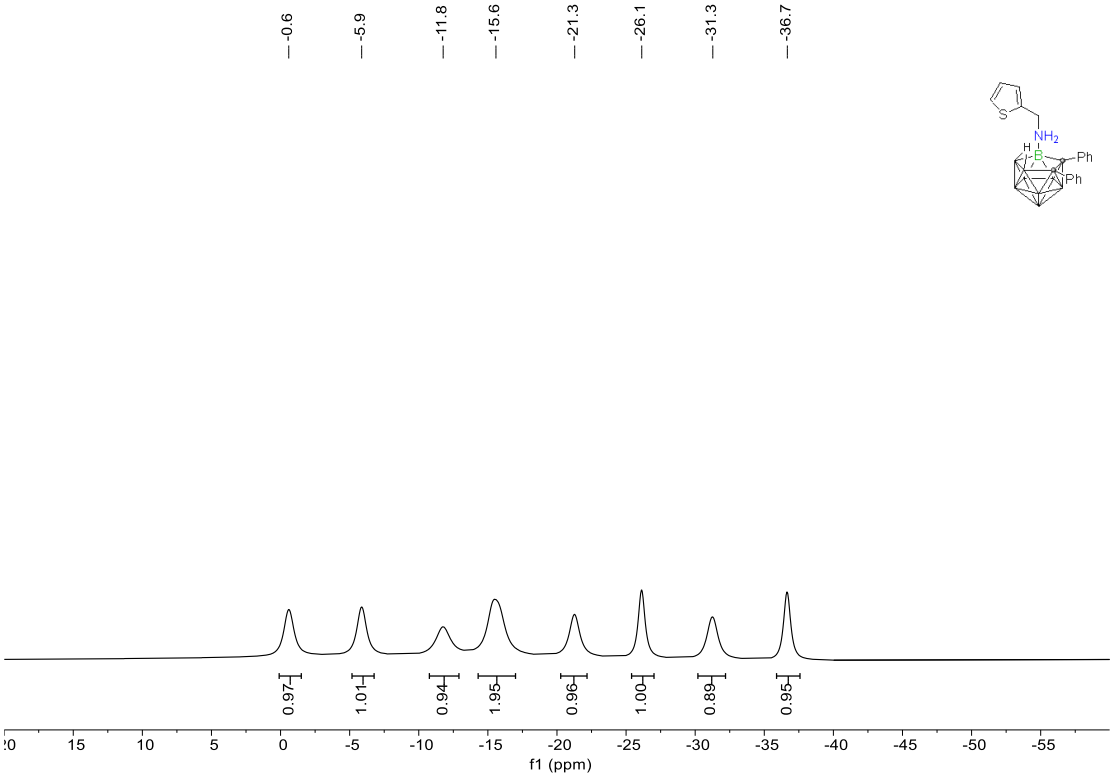
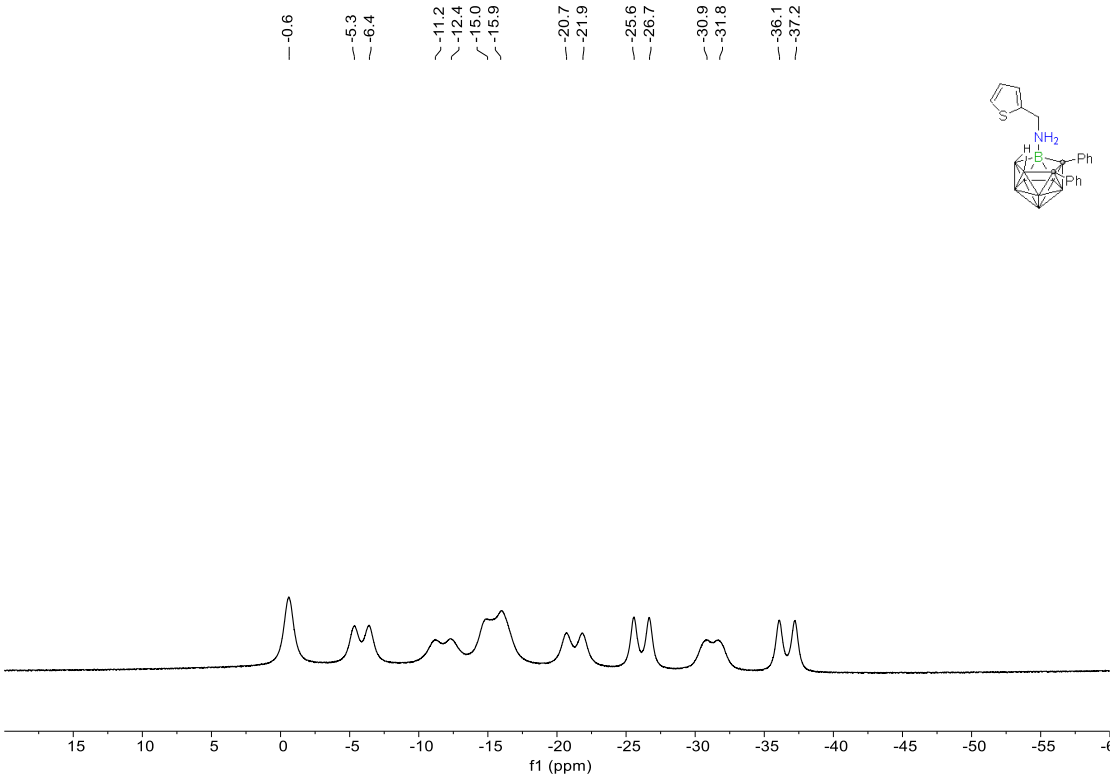


^{11}B NMR (Methylene Cloride-d_2) (Compound 4f)



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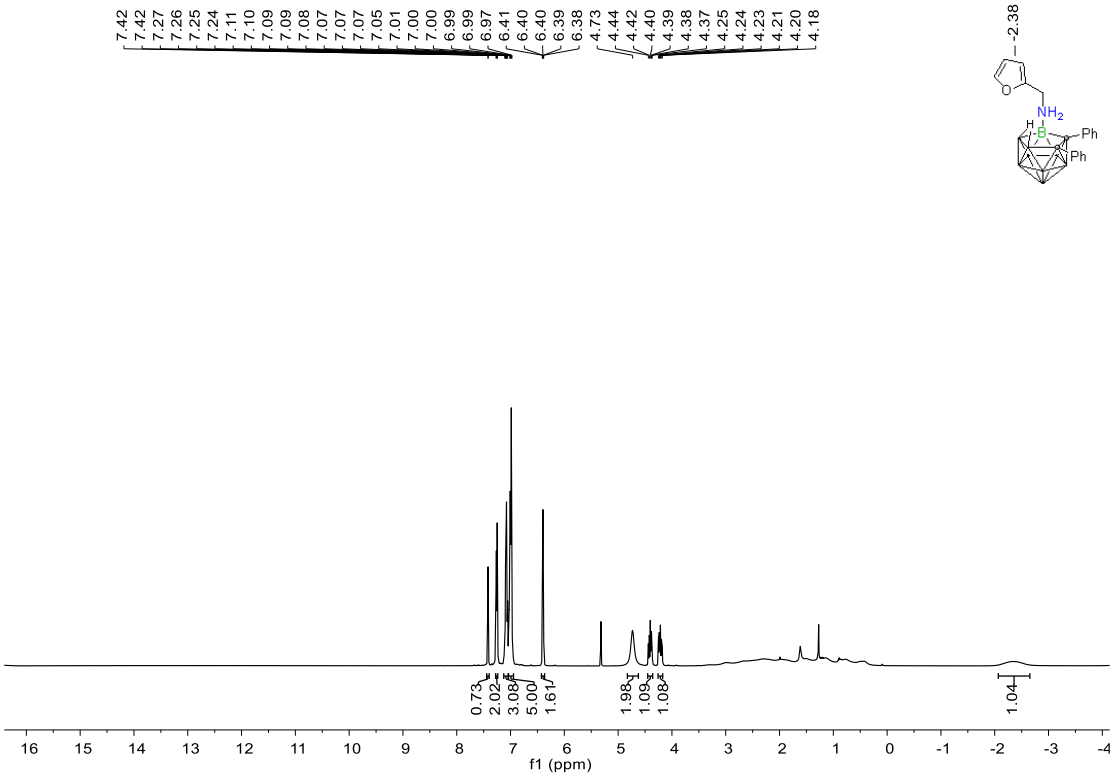
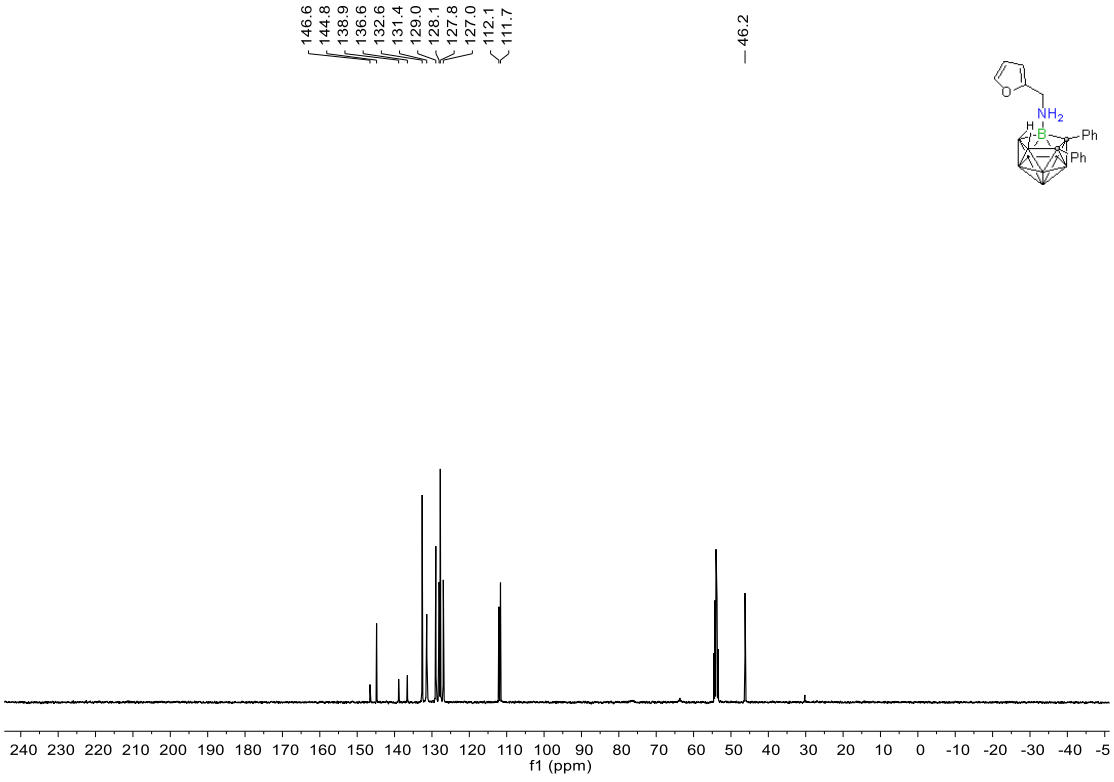
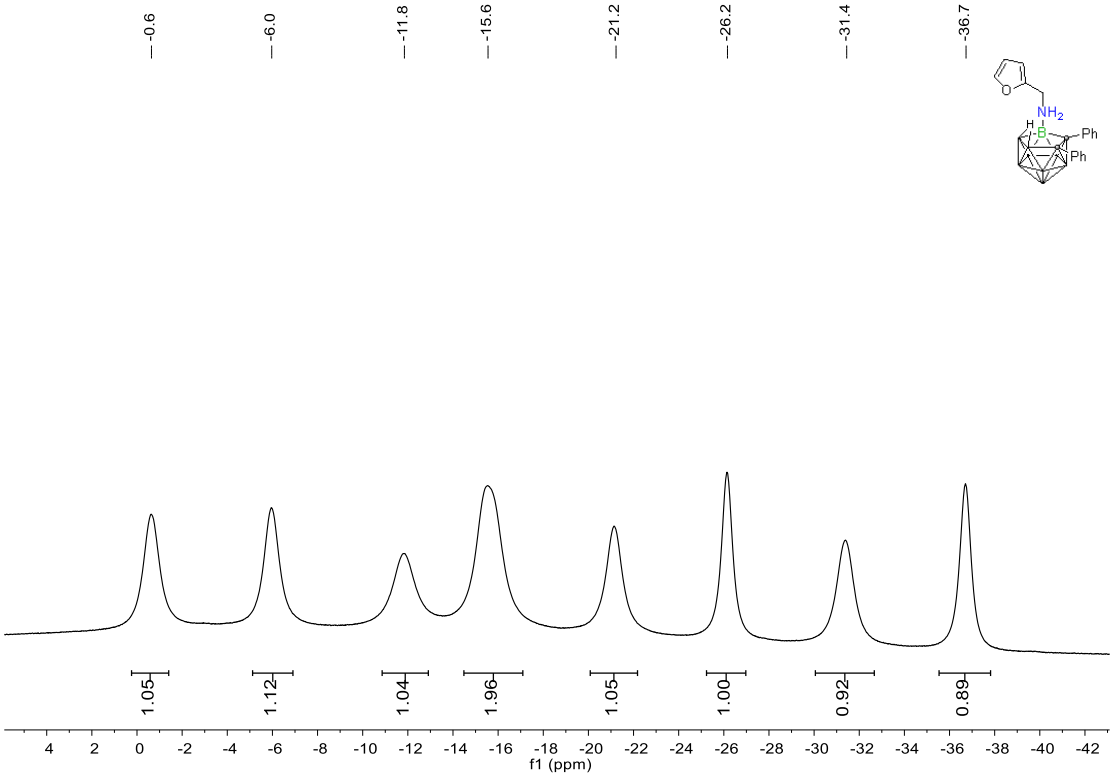


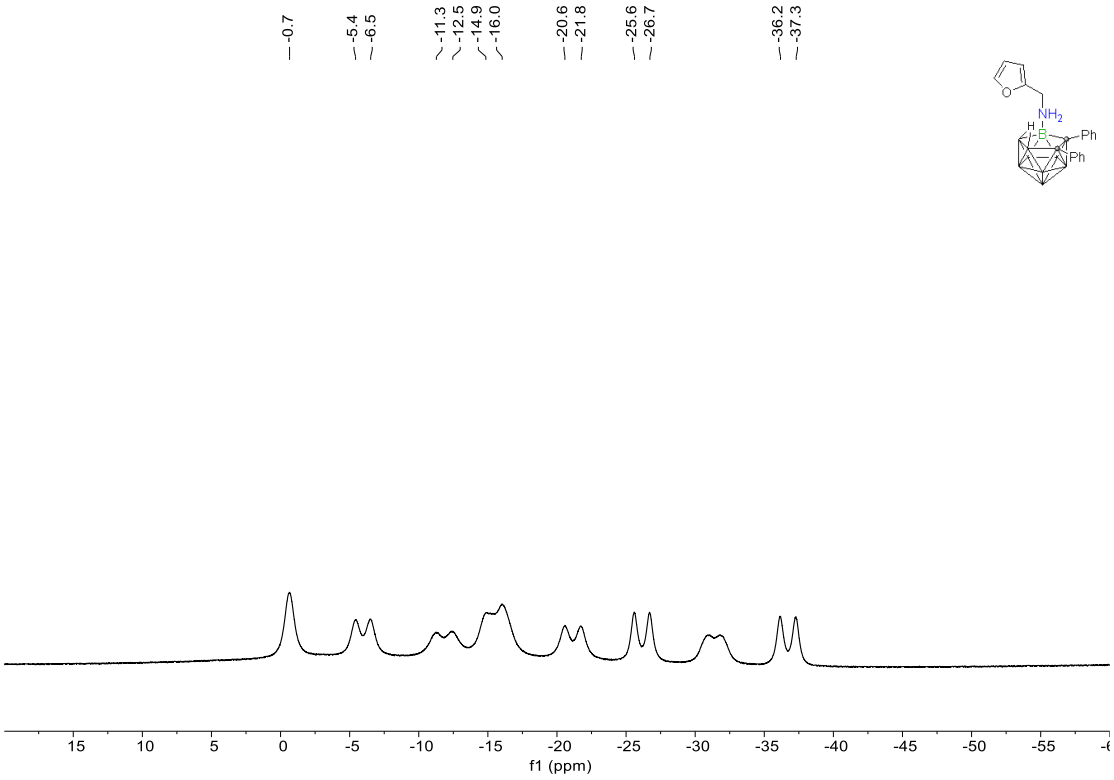
^{13}C NMR (Methylene Cloride-d_2) (Compound 4g)



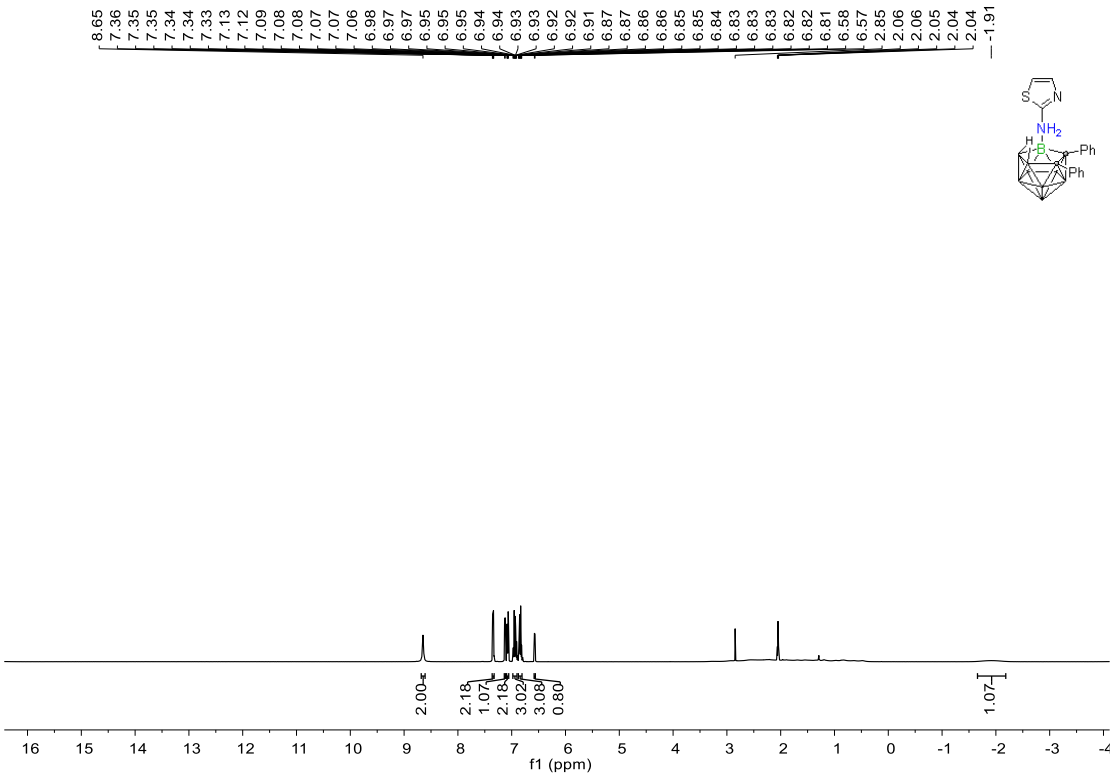
$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 4g)



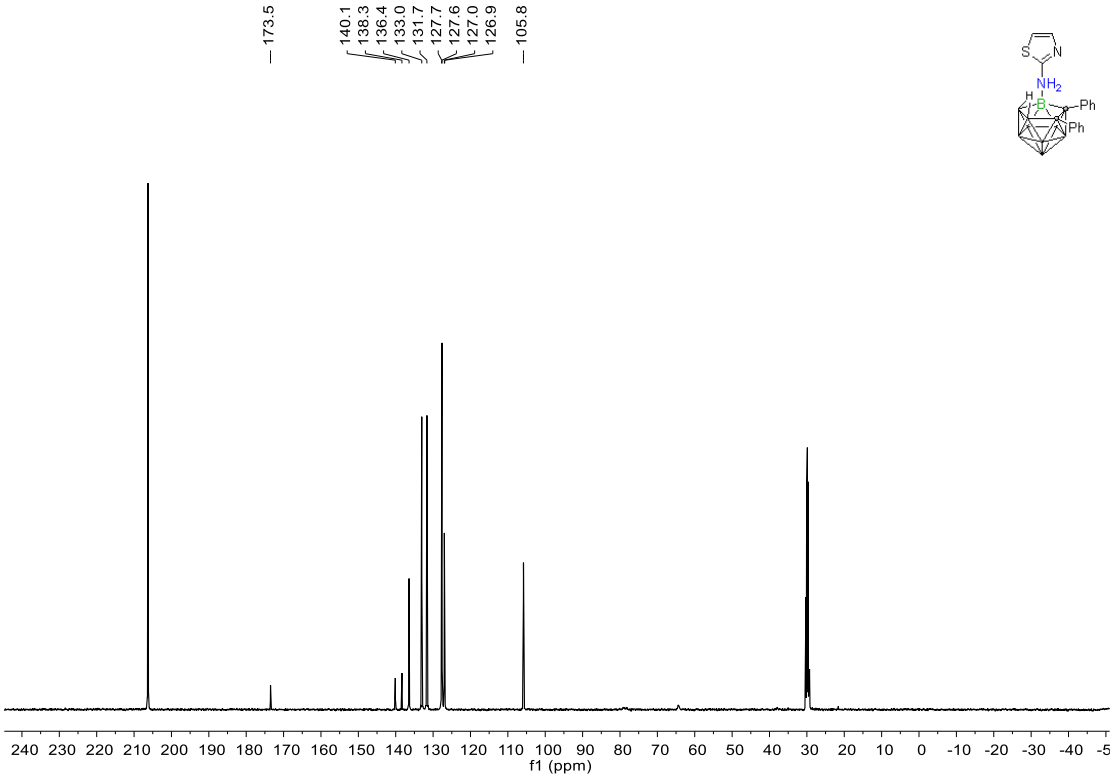
^{11}B NMR (Methylene Cloride-d_2) (Compound 4g)



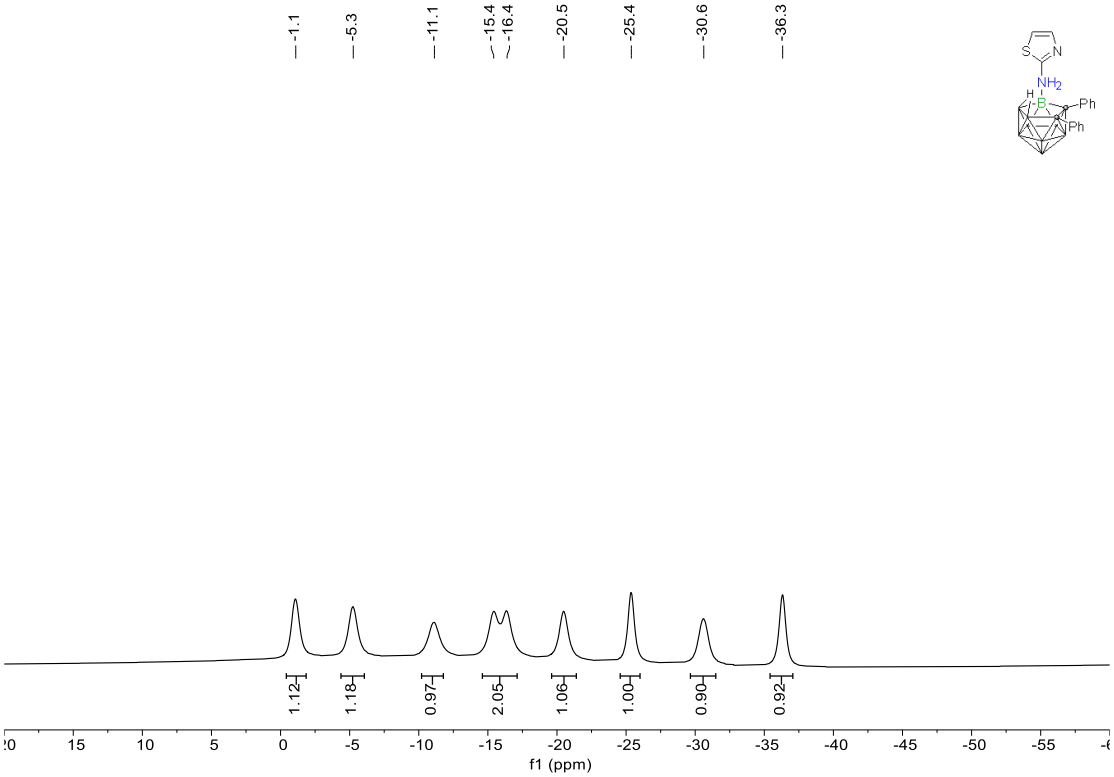
[1] H NMR (Acetone-*d*$_6$) (Compound 4h)



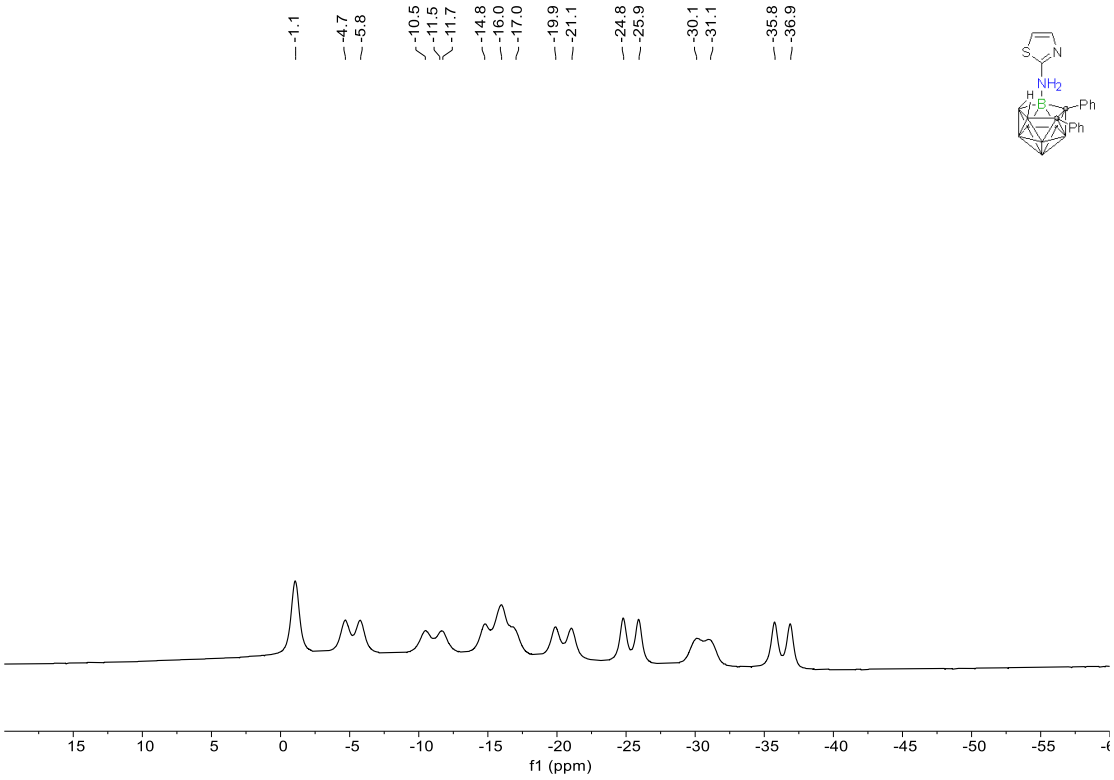
[13] C NMR (Acetone-*d*$_6$) (Compound 4h)



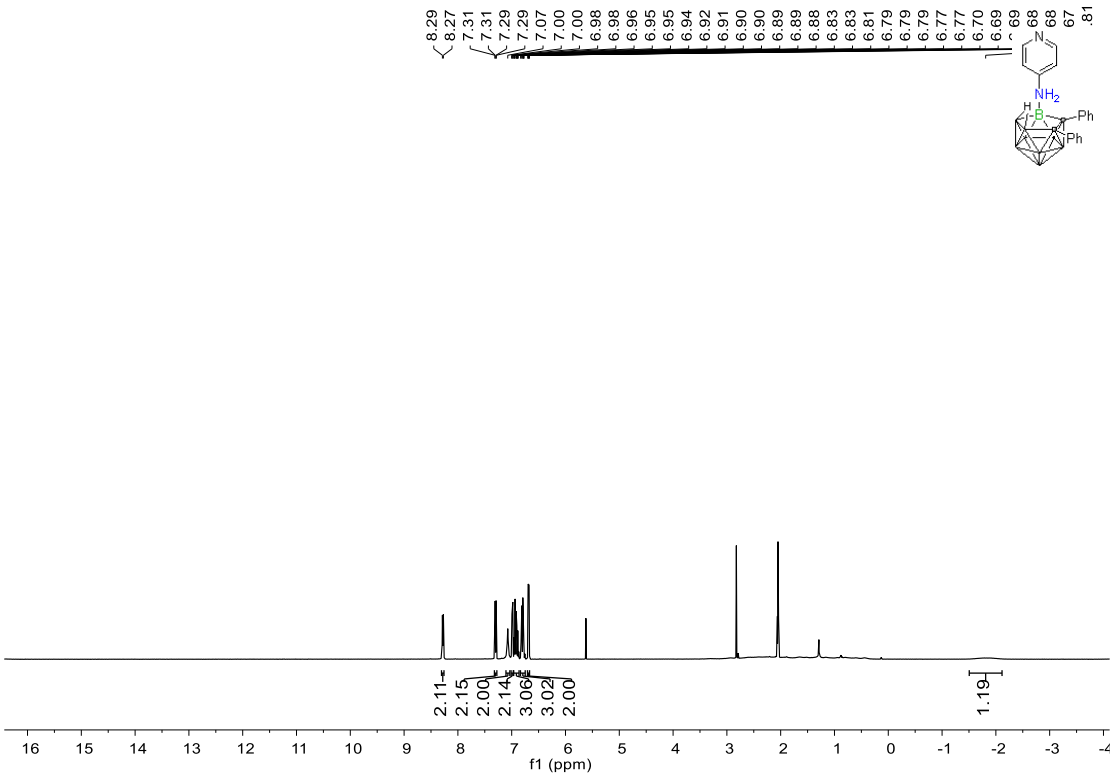
$^{11}B\{^{1}H\}$ NMR (Acetone-d_6) (Compound 4h)



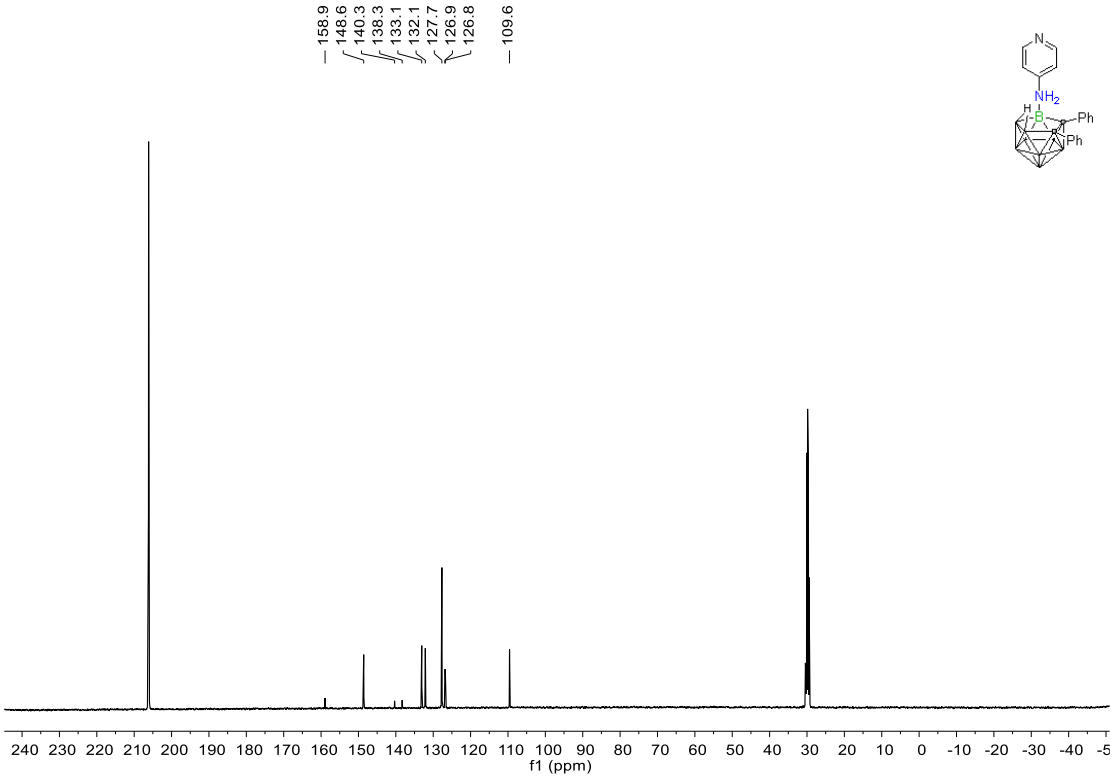
^{11}B NMR (Acetone-d_6) (Compound 4h)



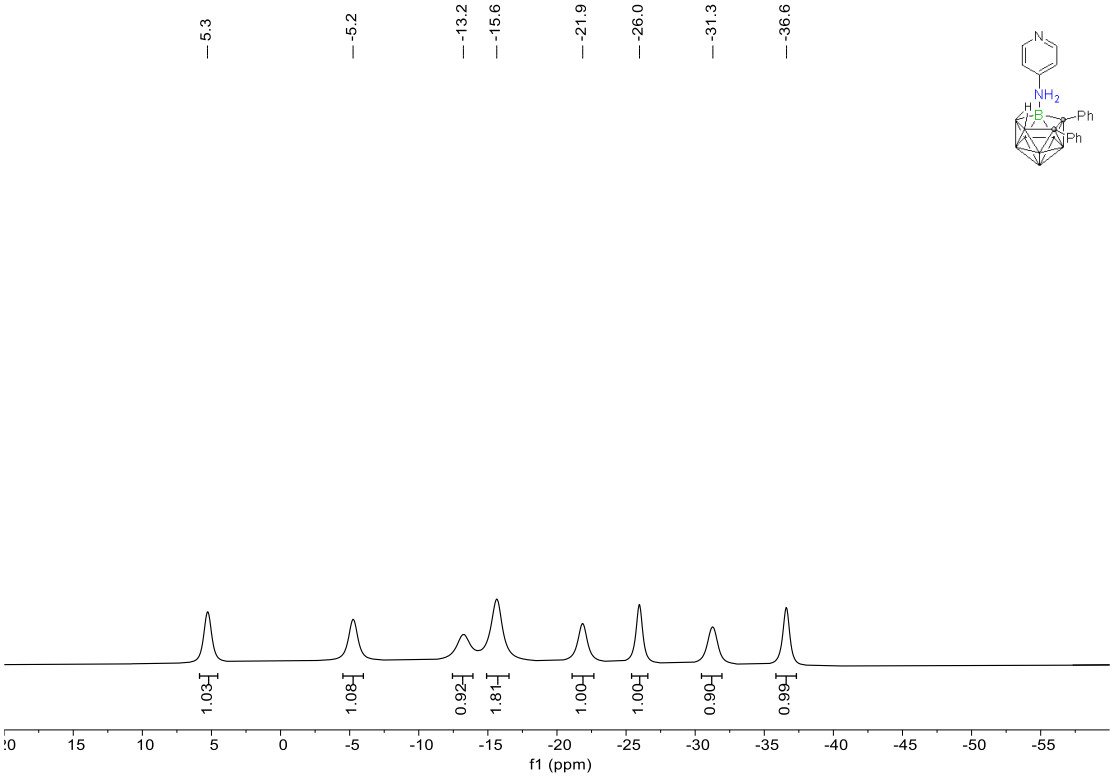
[1] H NMR (Methylene Cloride-d_2) (Compound 4i)



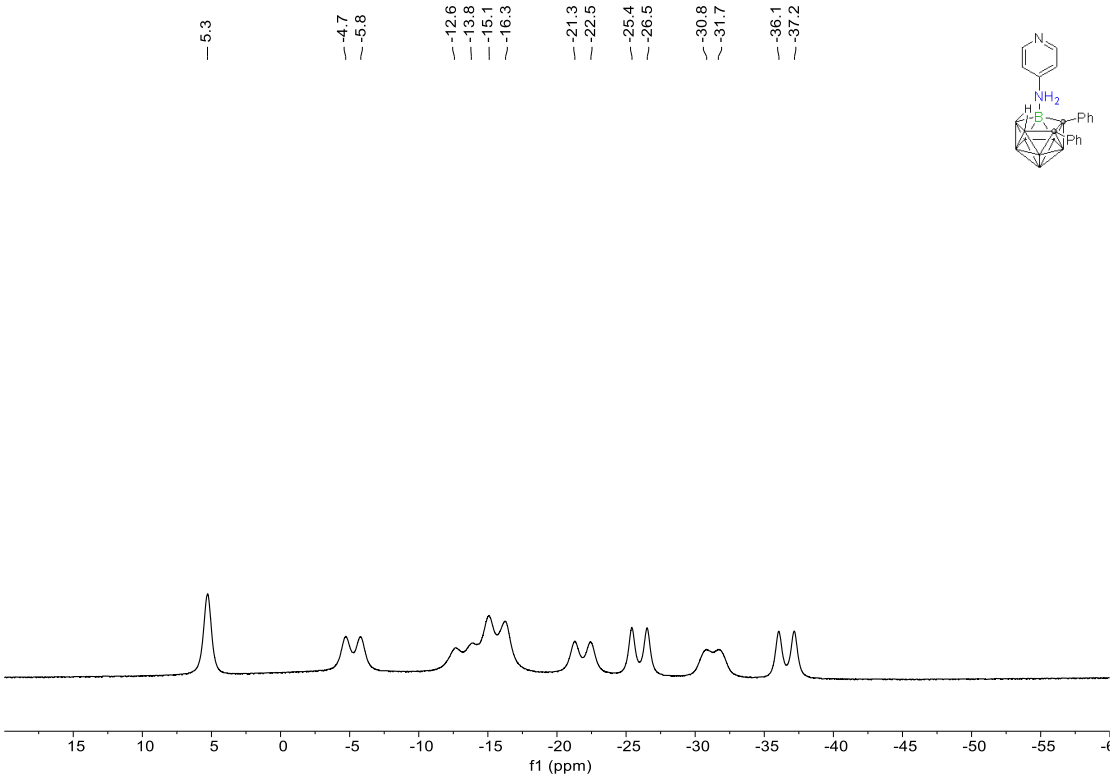
[13] C NMR (Methylene Cloride-d_2) (Compound 4i)



$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 4i)



^{11}B NMR (Methylene Cloride-d_2) (Compound 4i)



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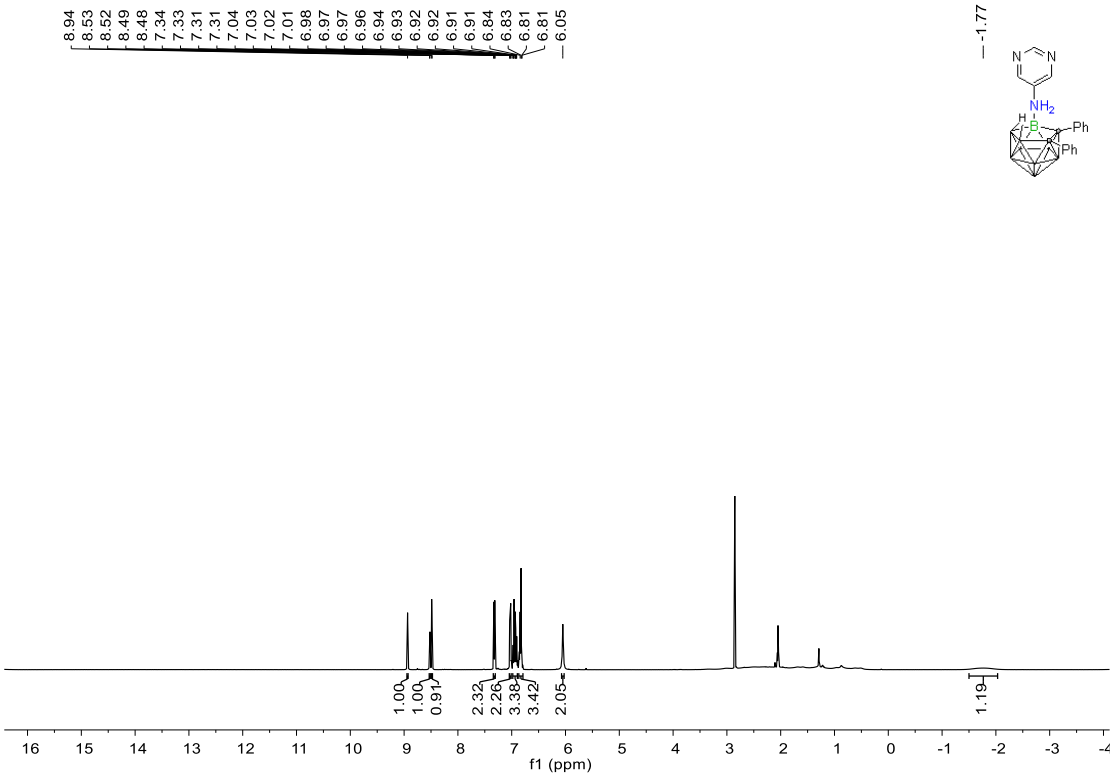
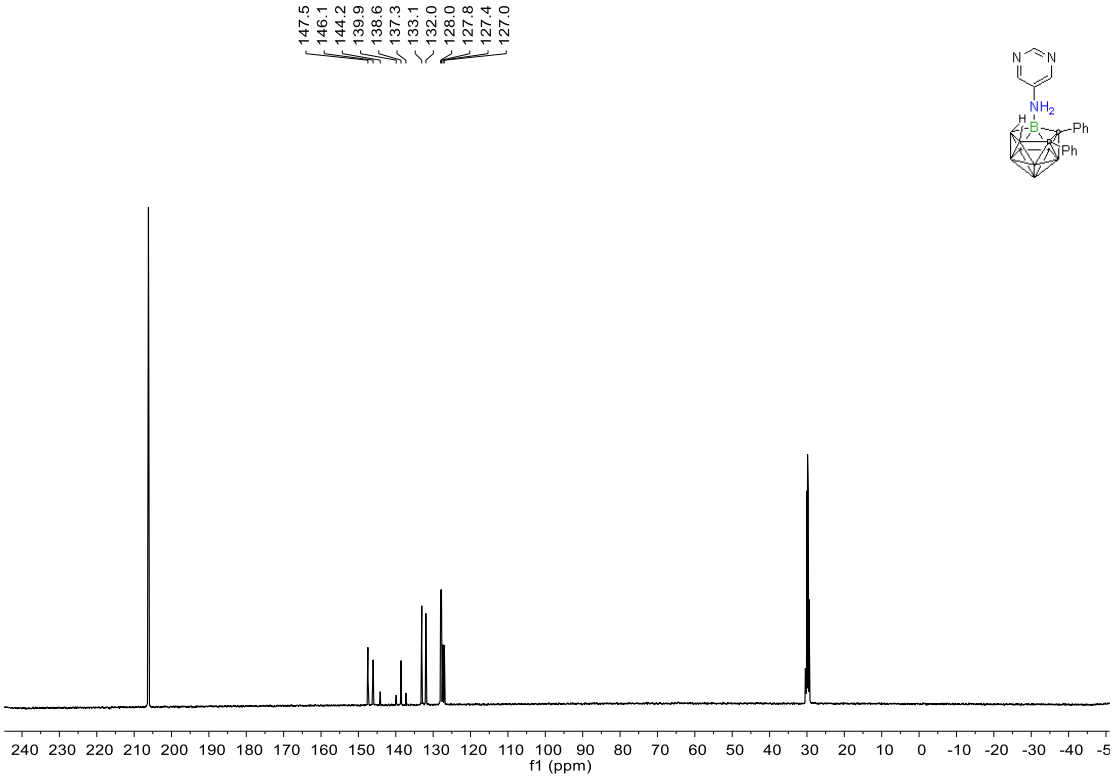
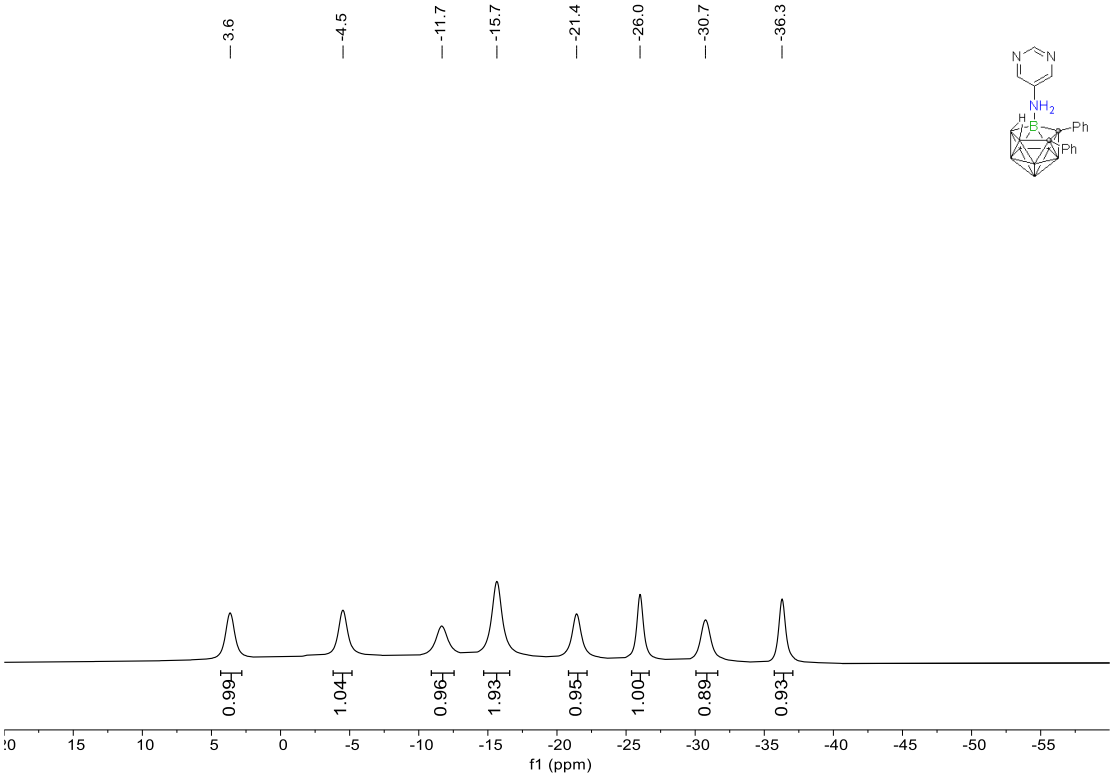


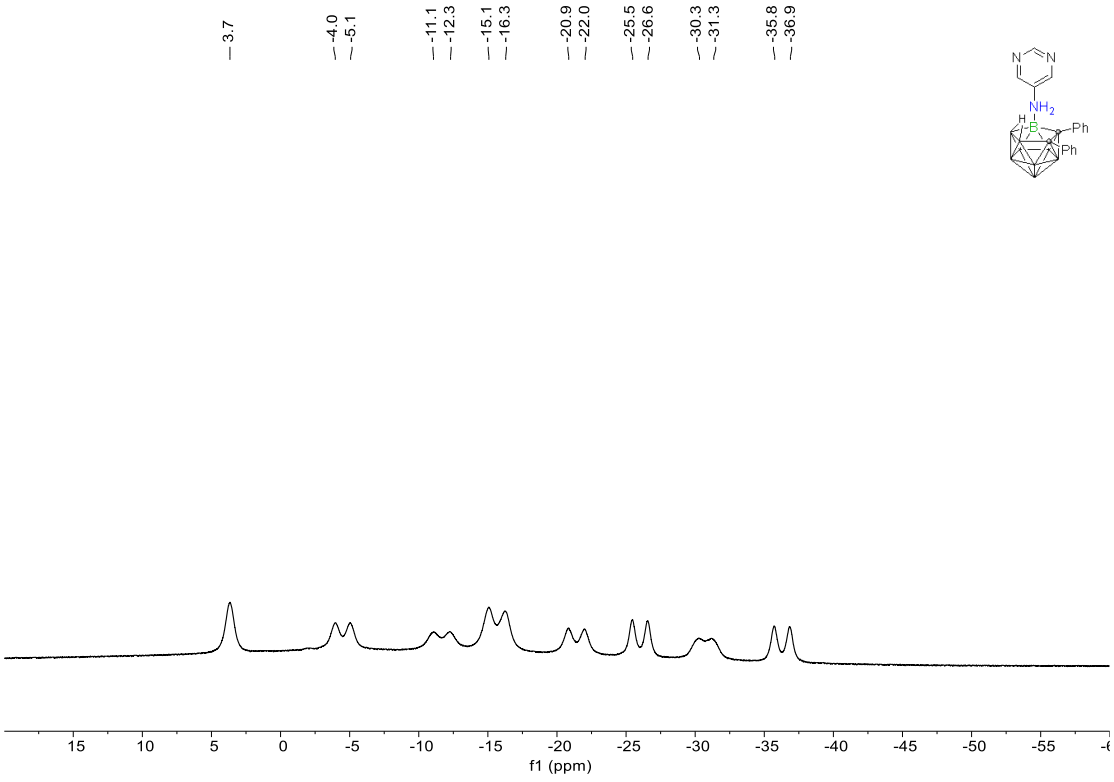
[13] C NMR (Methylene Cloride-d_2) (Compound 4j)



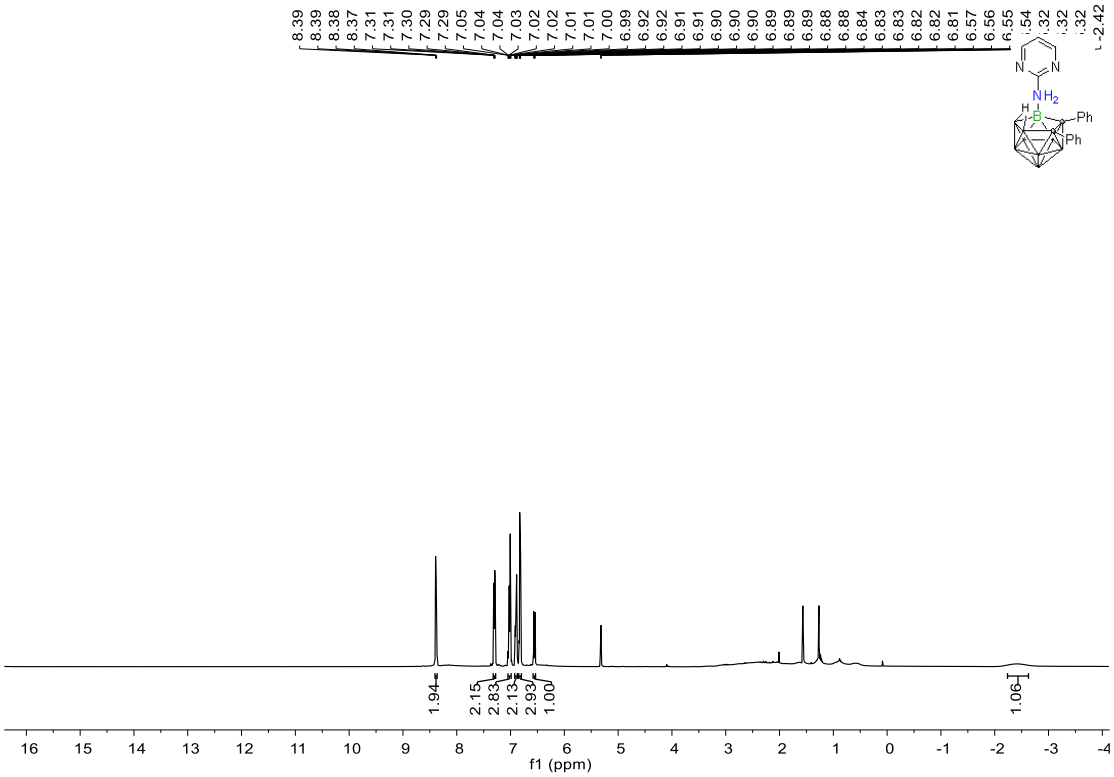
$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 4j)



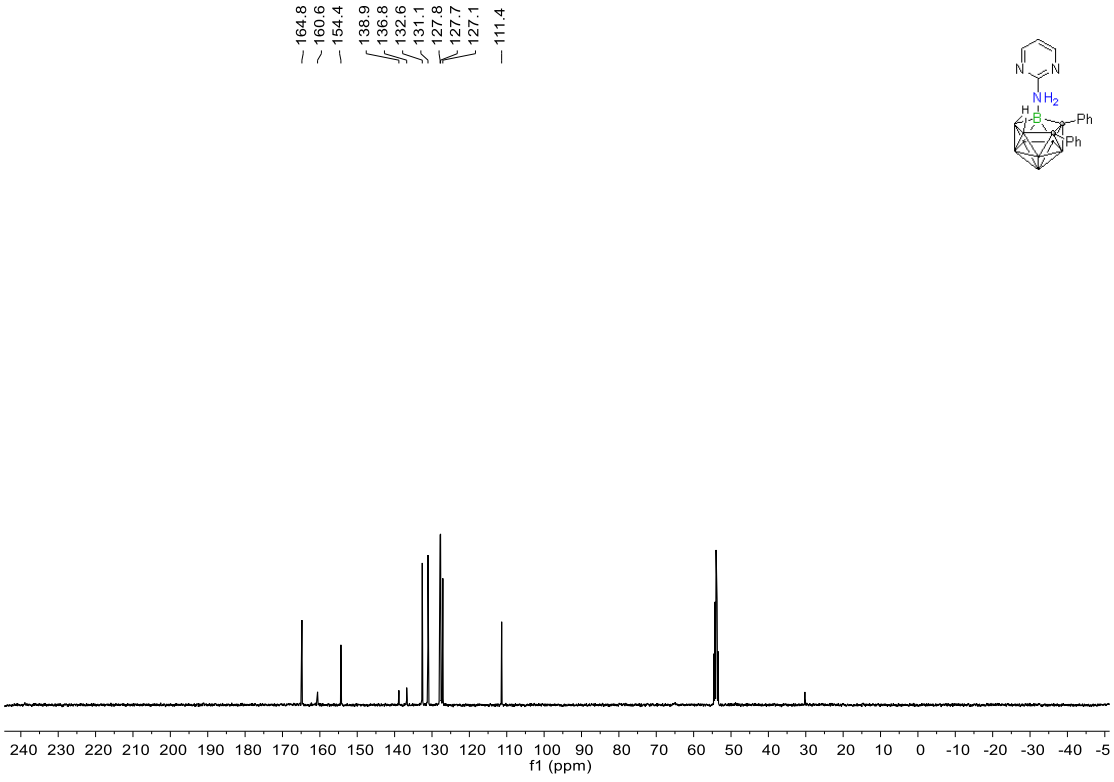
^{11}B NMR (Methylene Cloride-d_2) (Compound 4j)



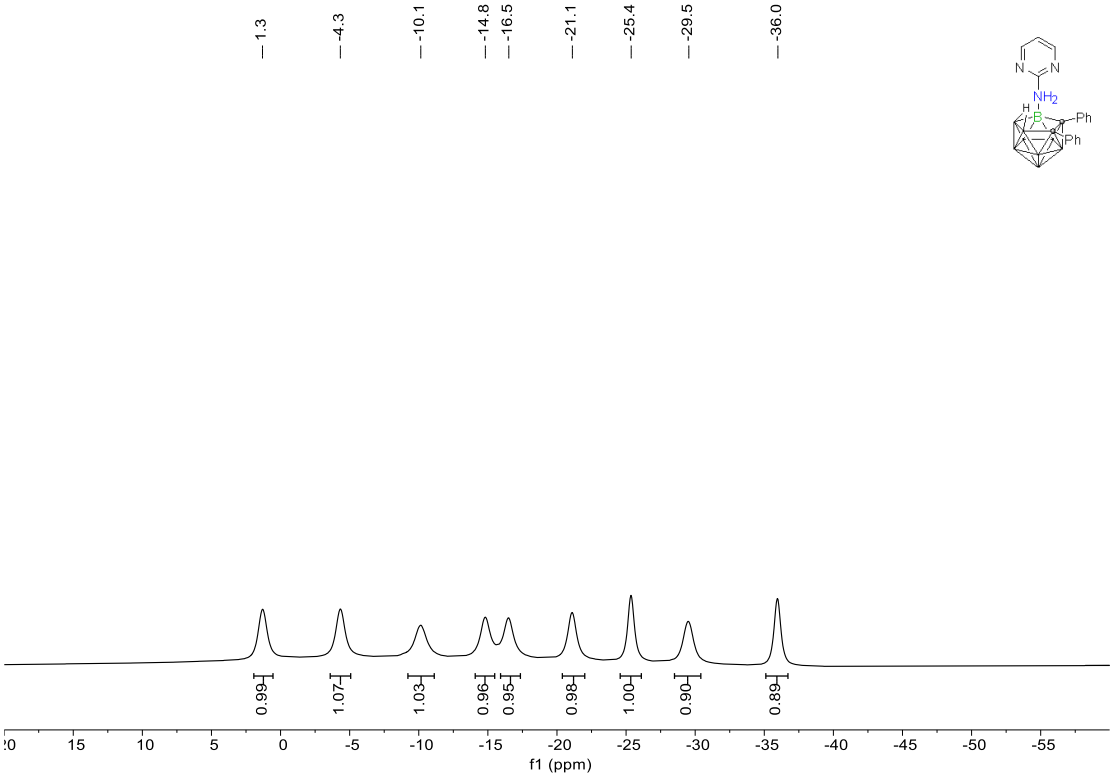
^{1}H NMR (Methylene Cloride-d_2) (Compound 4k)



^{13}C NMR (Methylene Cloride-d_2) (Compound 4k)



$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 4k)



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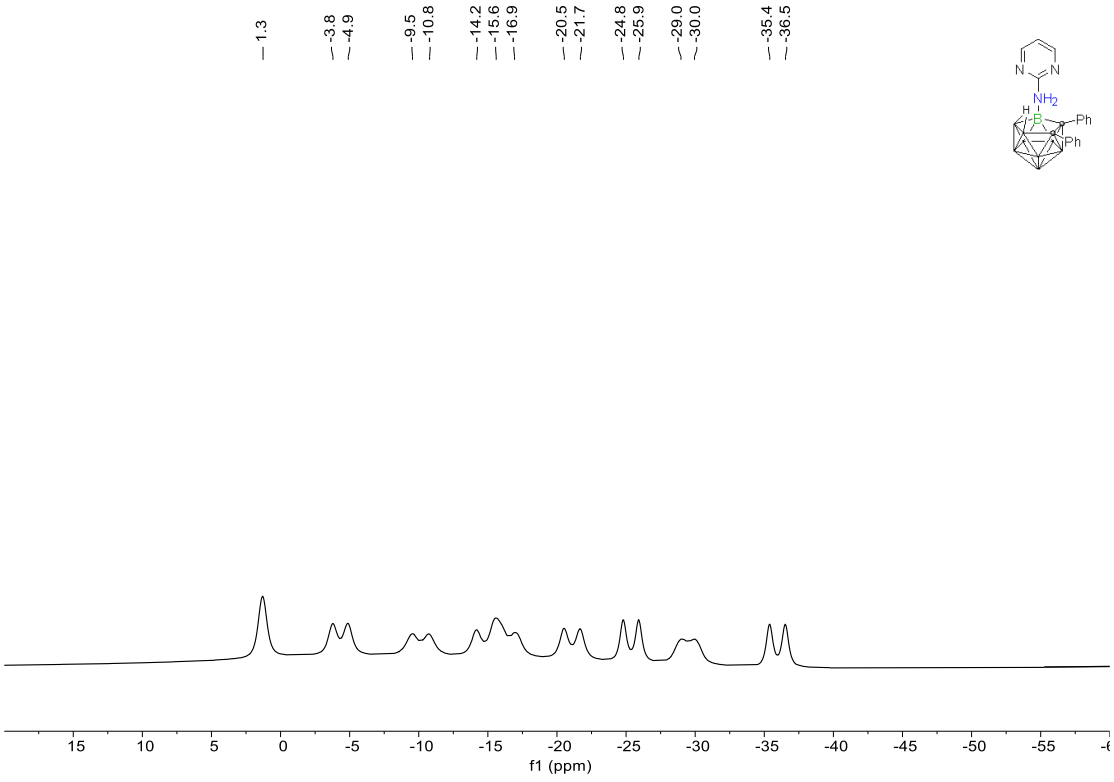
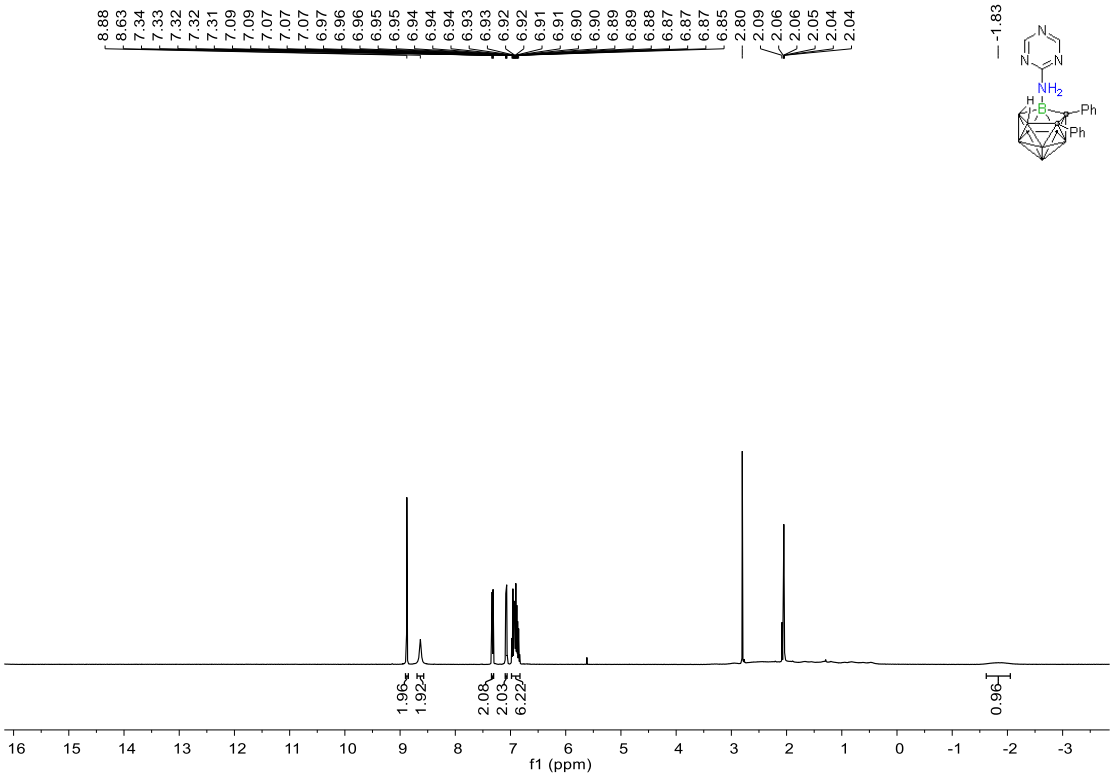
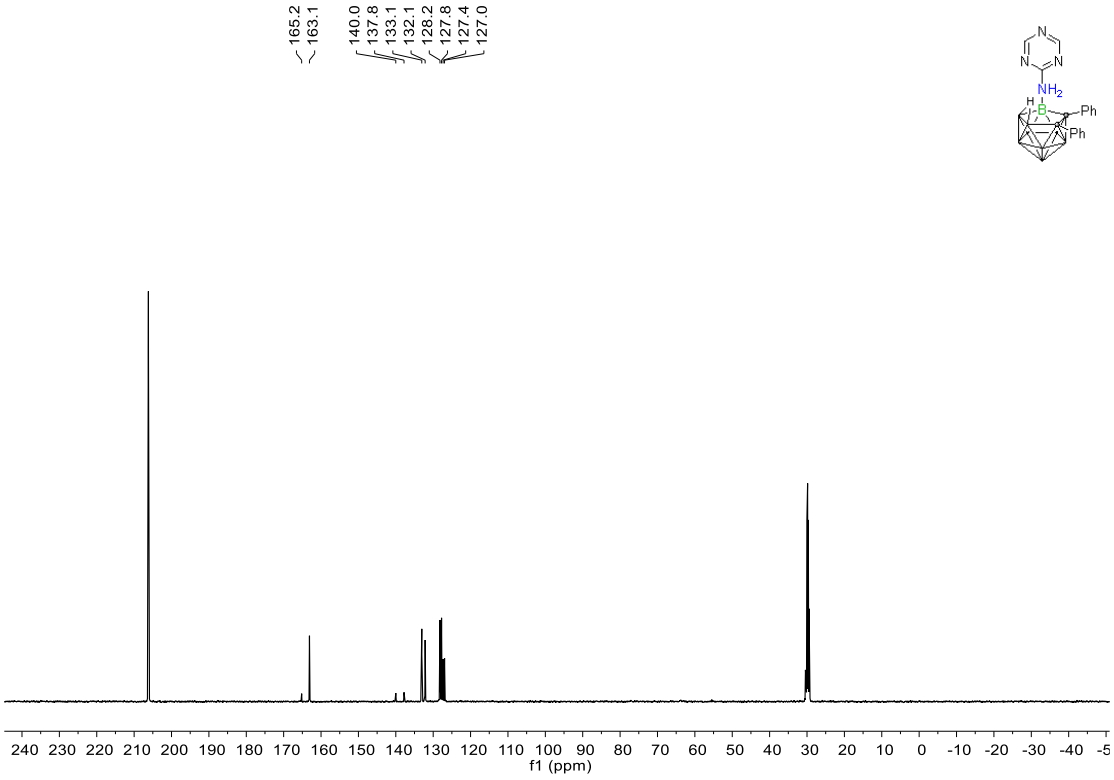


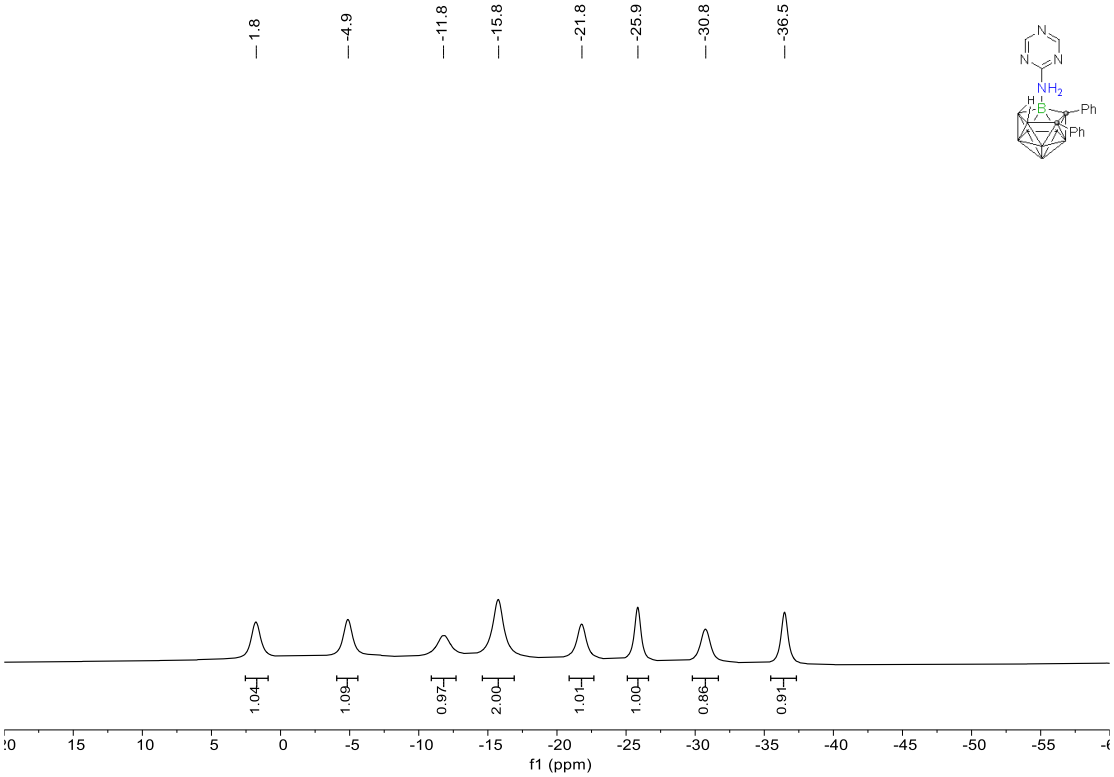
[1] H NMR (Acetone-*d*$_6$) (Compound 4l)



[13] C NMR (Acetone-*d*$_6$) (Compound 4l)



$^{11}B\{^{1}H\}$ NMR (Acetone-d_6) (Compound 4l)



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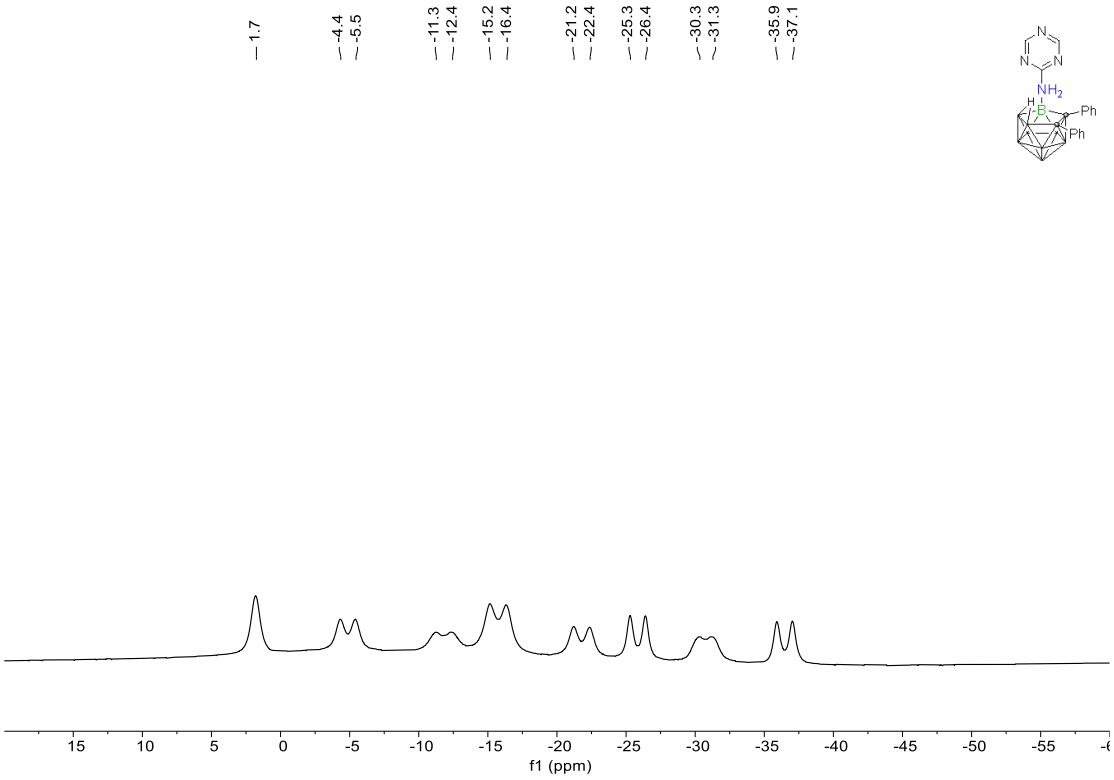

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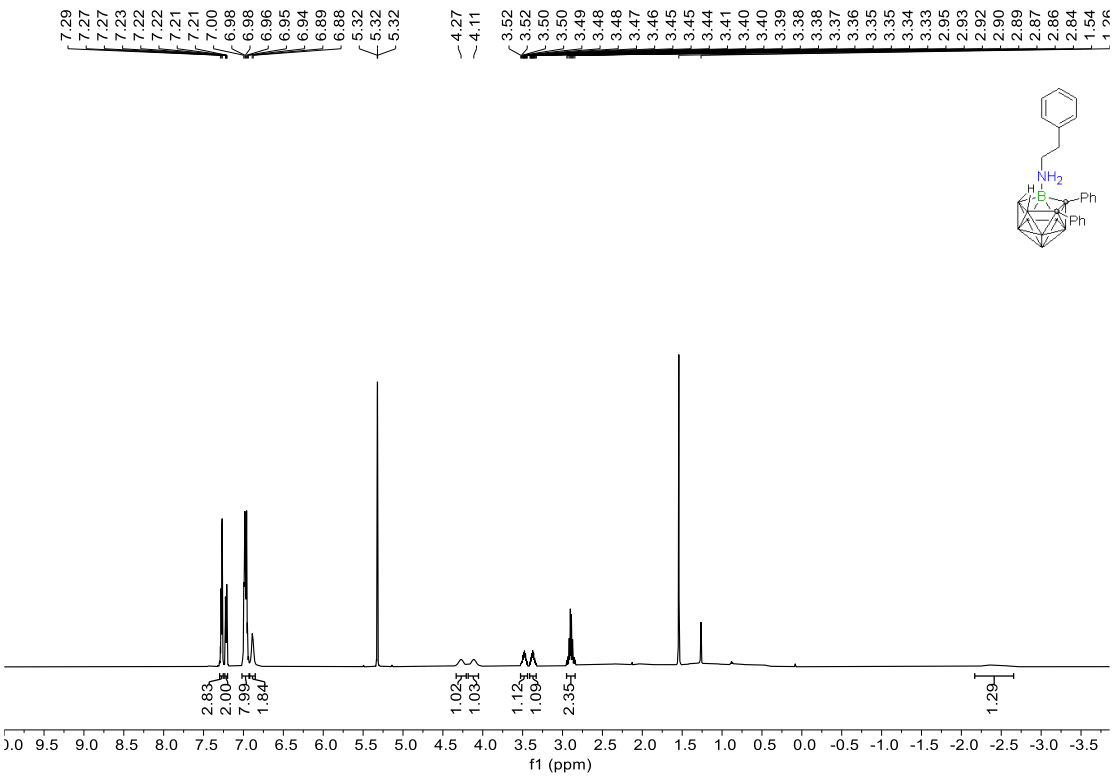

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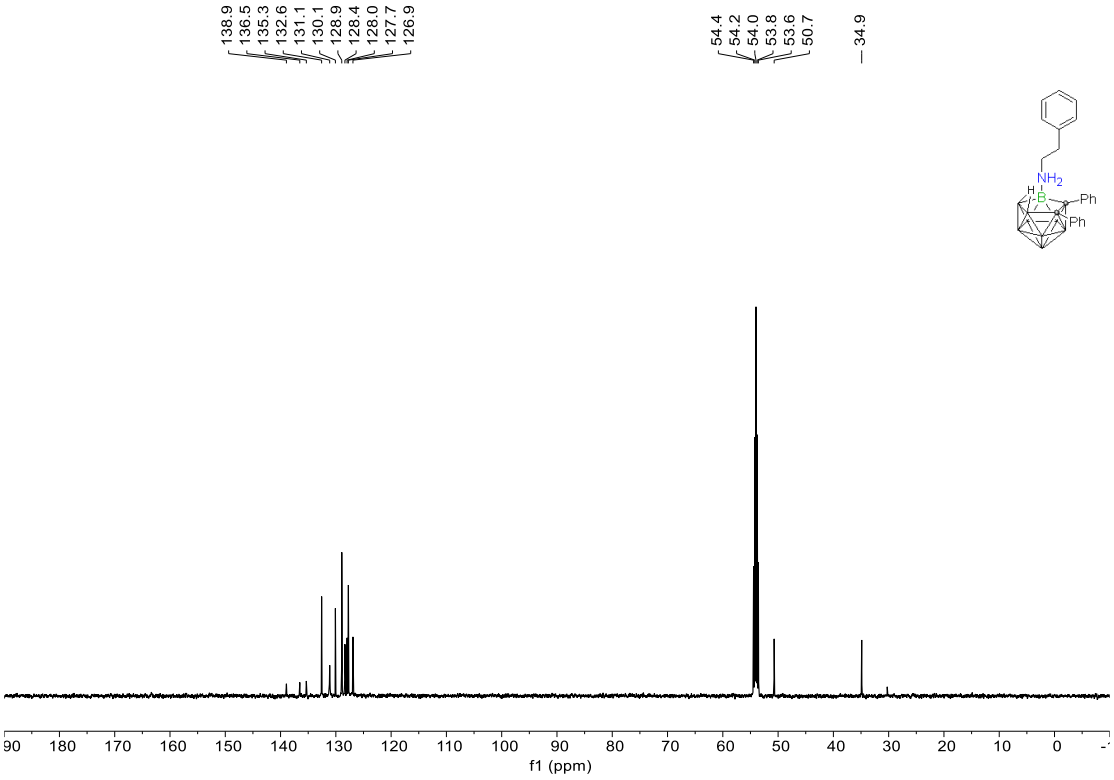
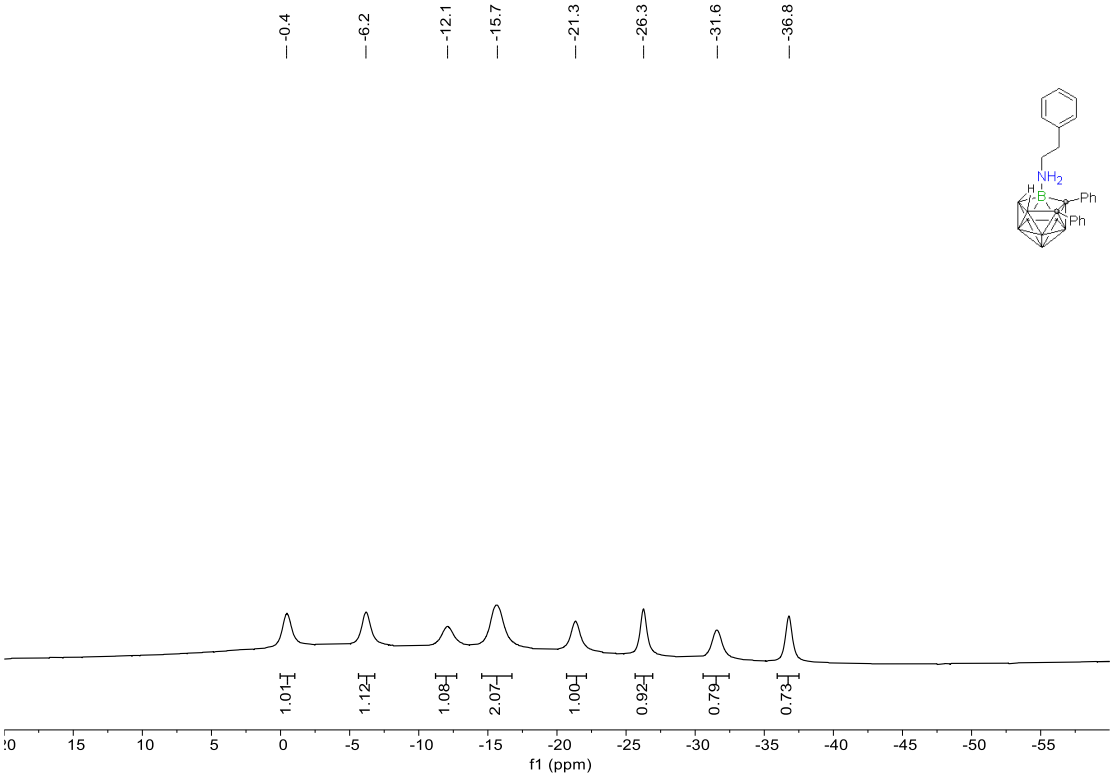


$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 4m)



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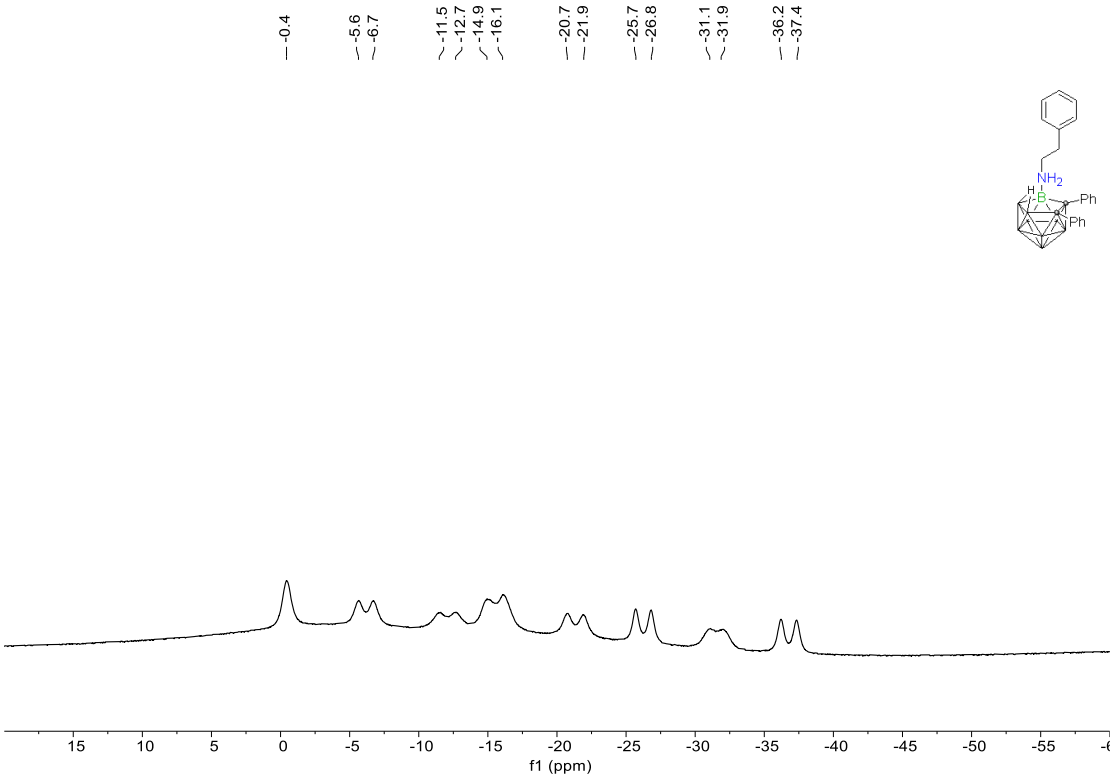
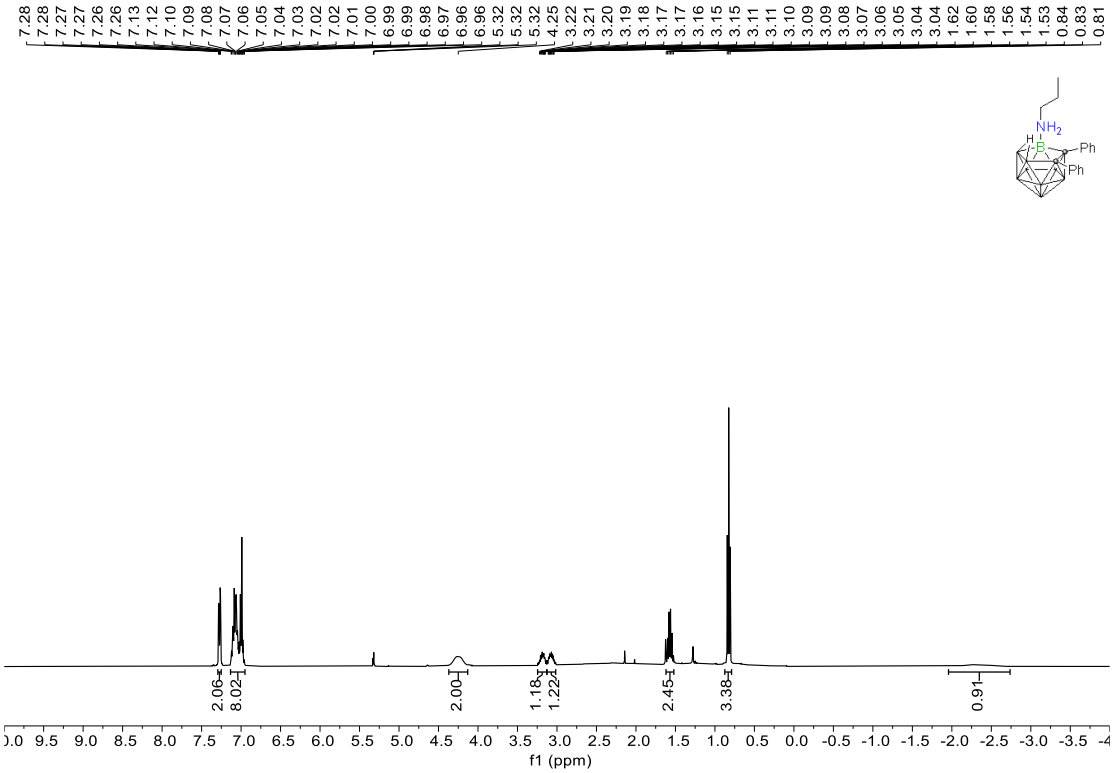
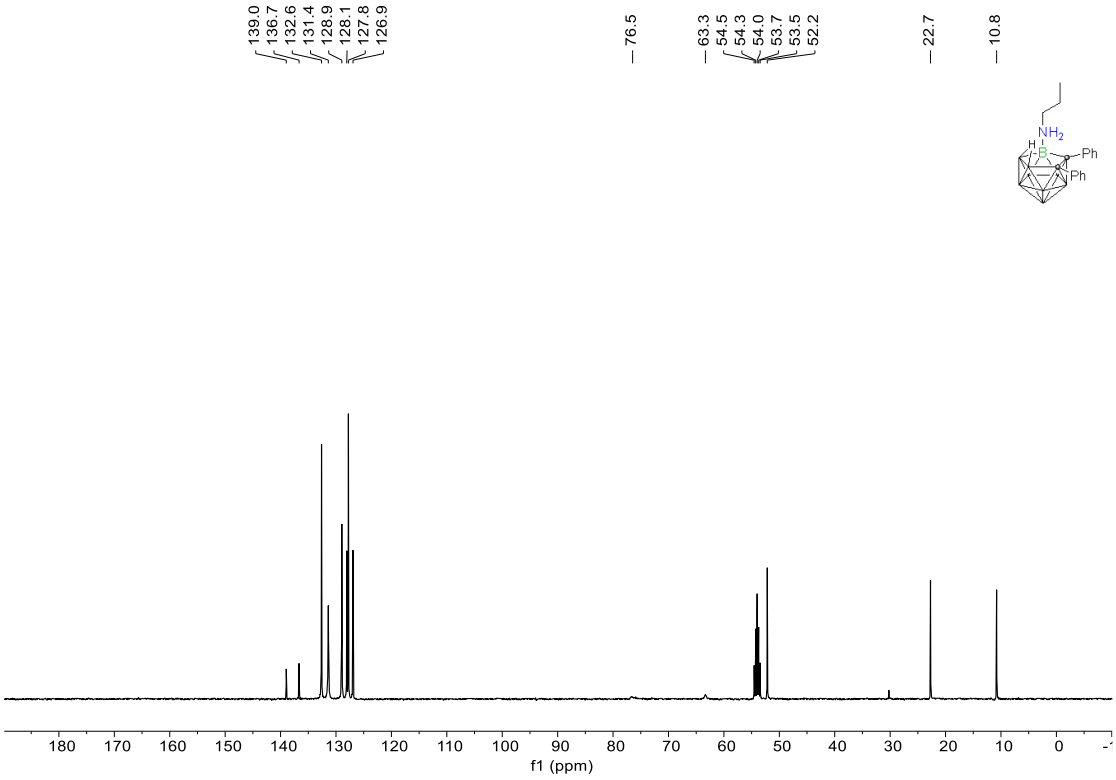


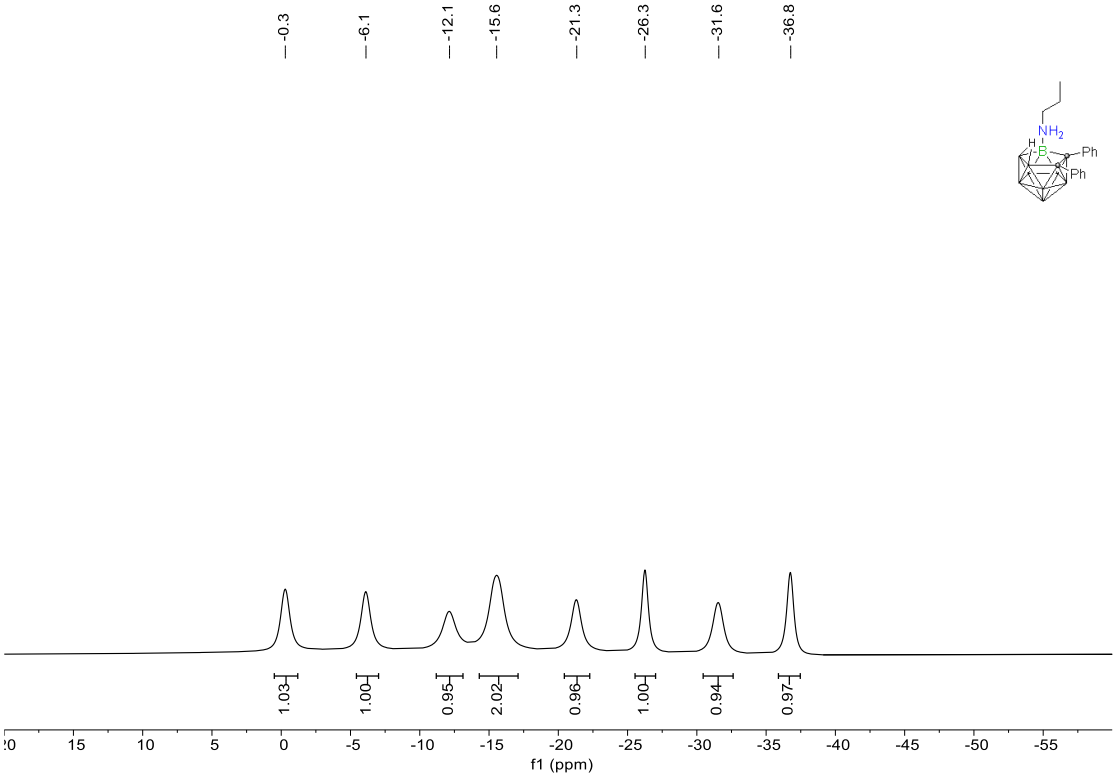
^{1}H NMR (Methylene Cloride-d_2) (Compound 4n)



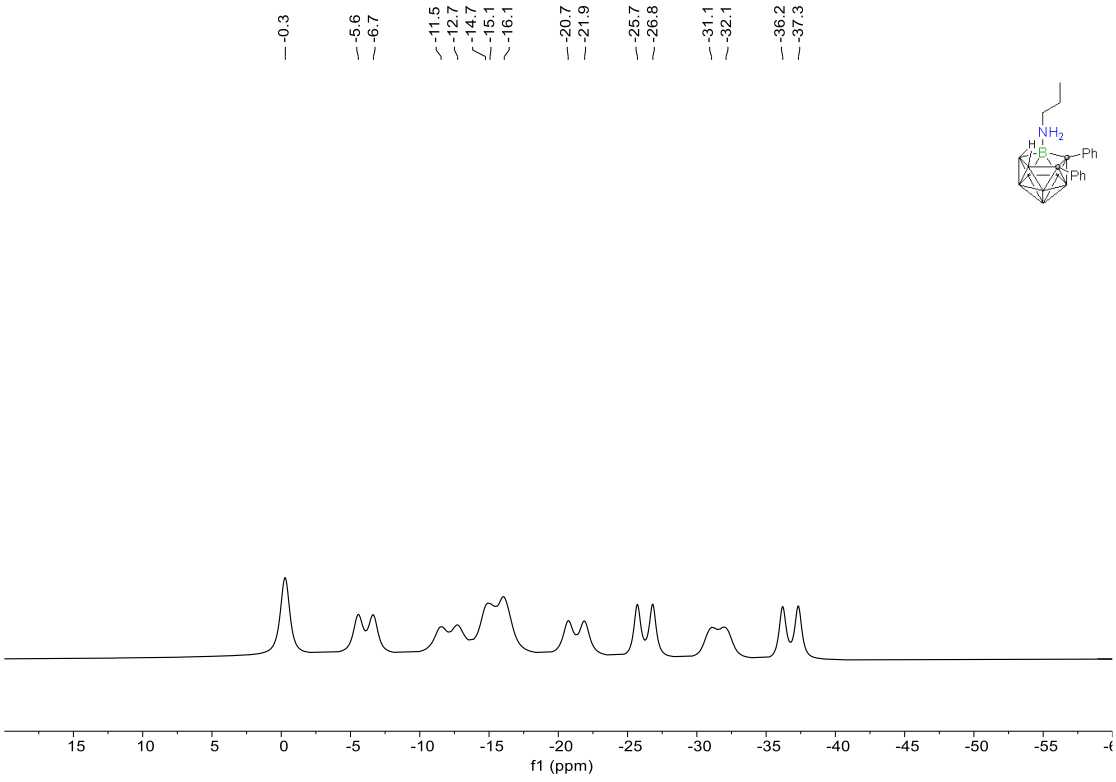
^{13}C NMR (Methylene Cloride-d_2) (Compound 4n)



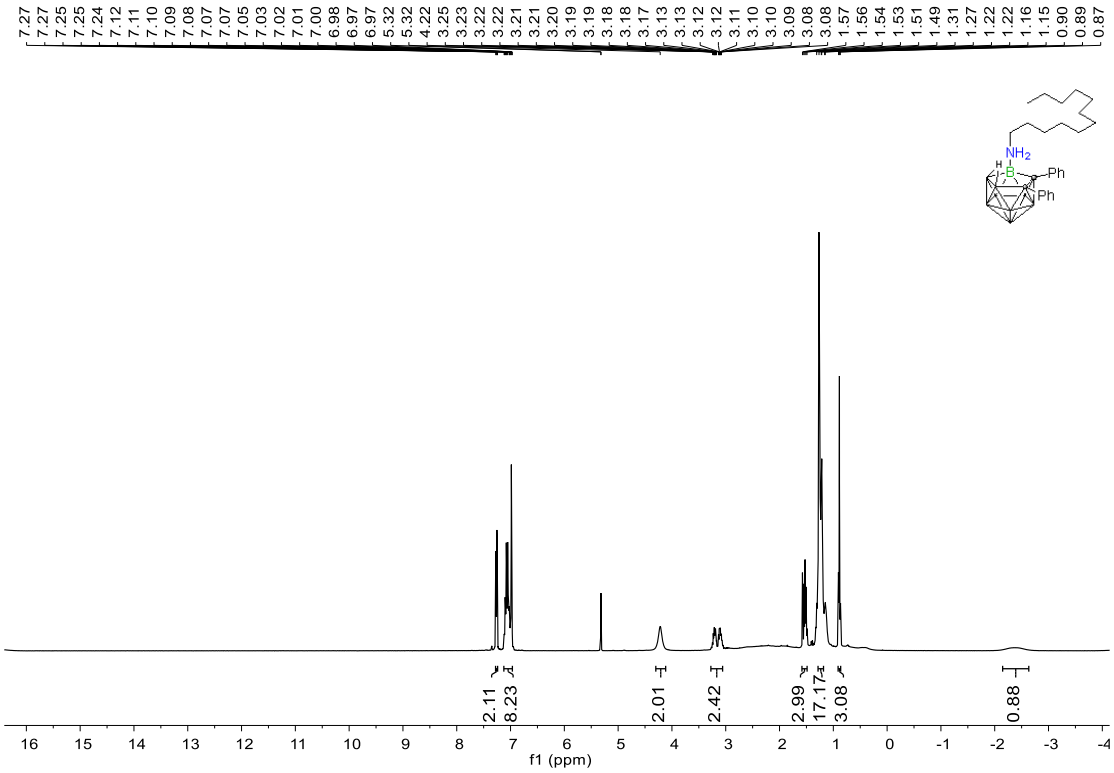
$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 4n)



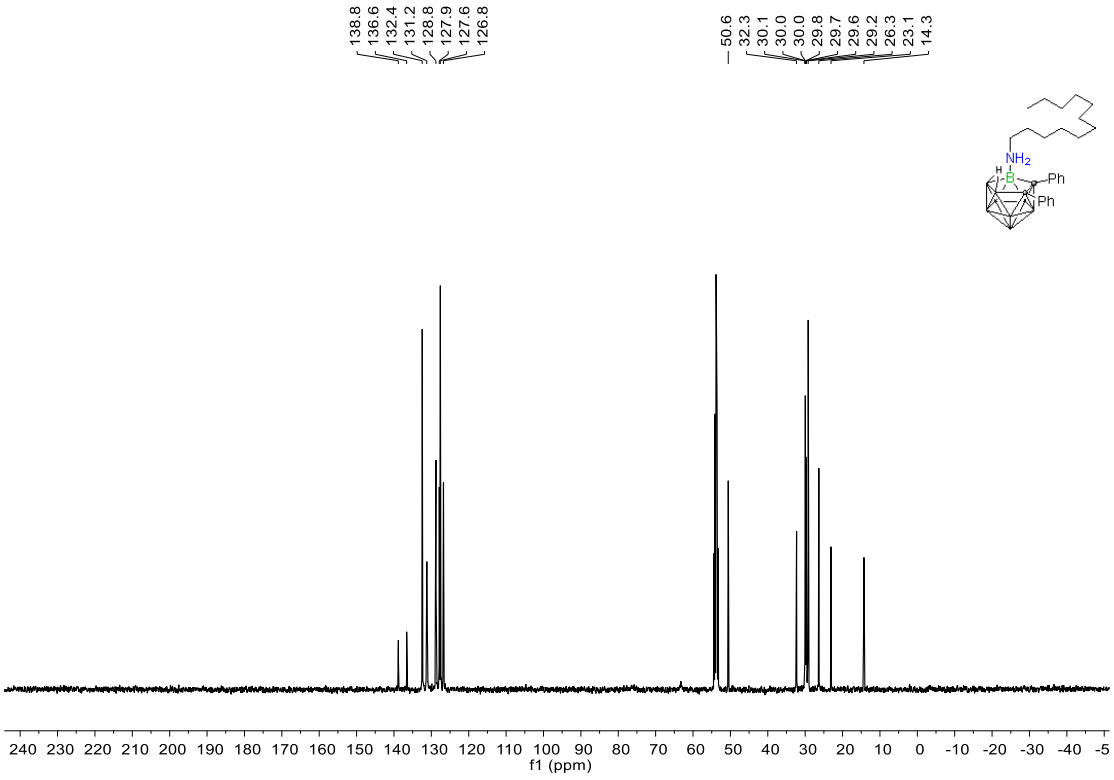
^{11}B NMR (Methylene Cloride-d_2) (Compound 4n)



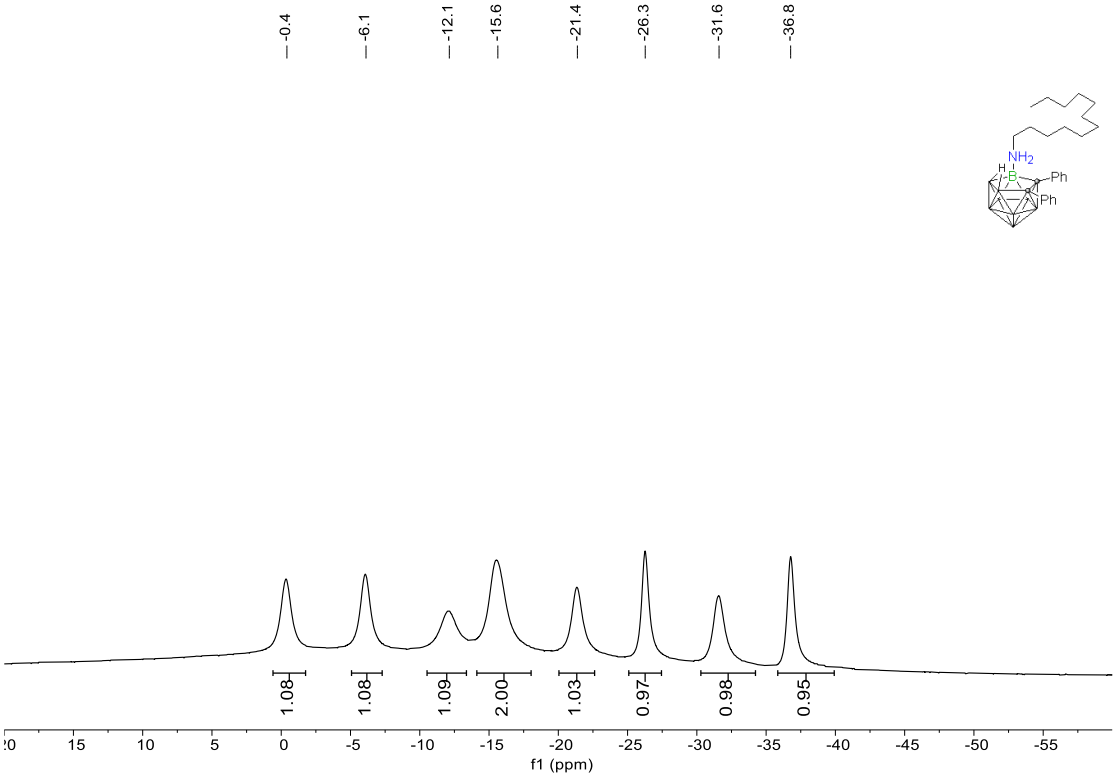
^{1}H NMR (Methylene Cloride-d_2) (Compound 4o)



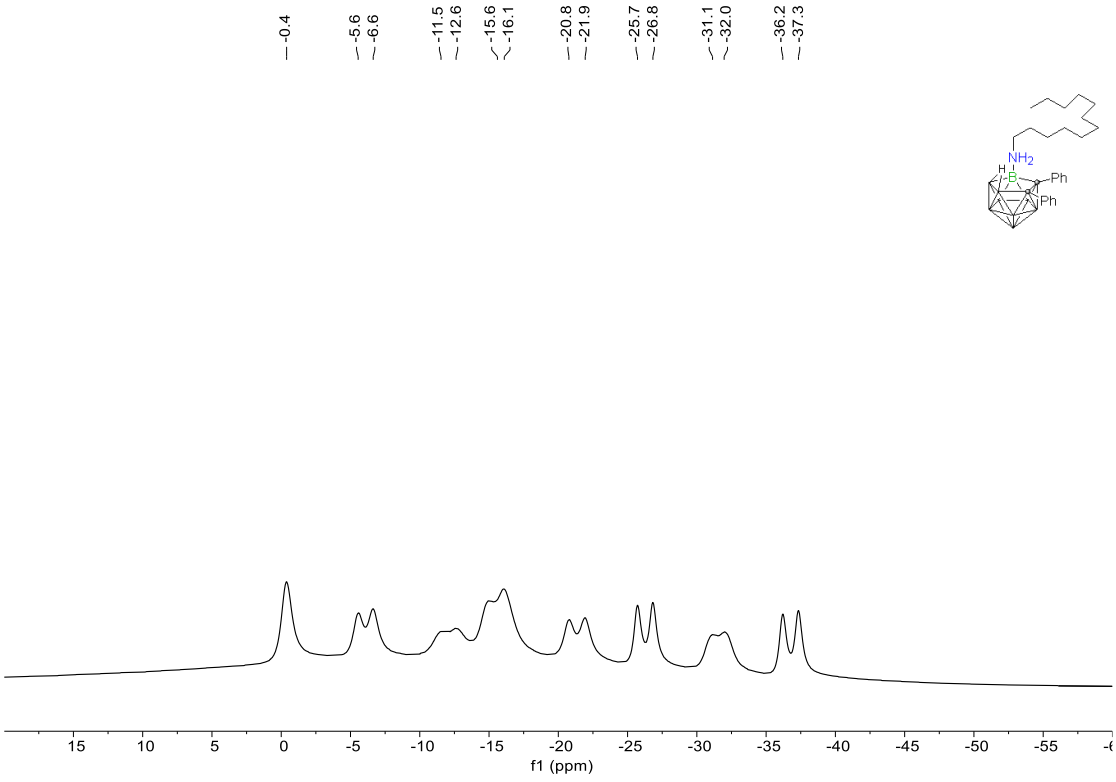
^{13}C NMR (Methylene Cloride-d_2) (Compound 4o)



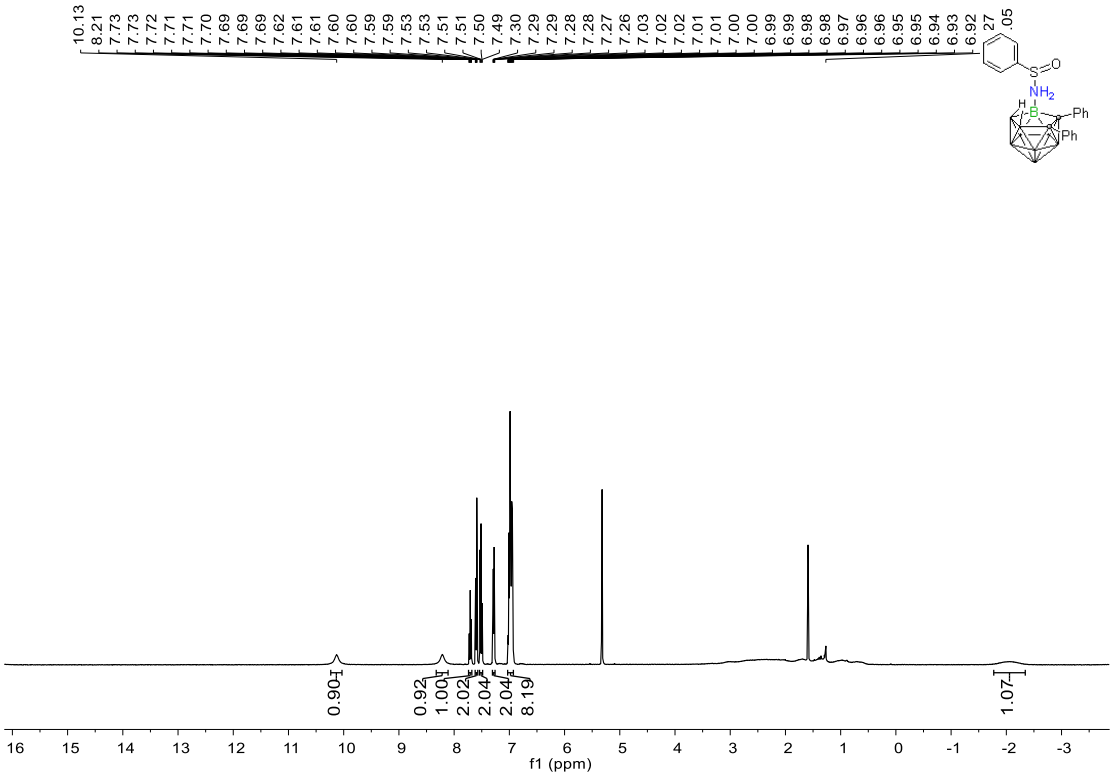
$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 4o)



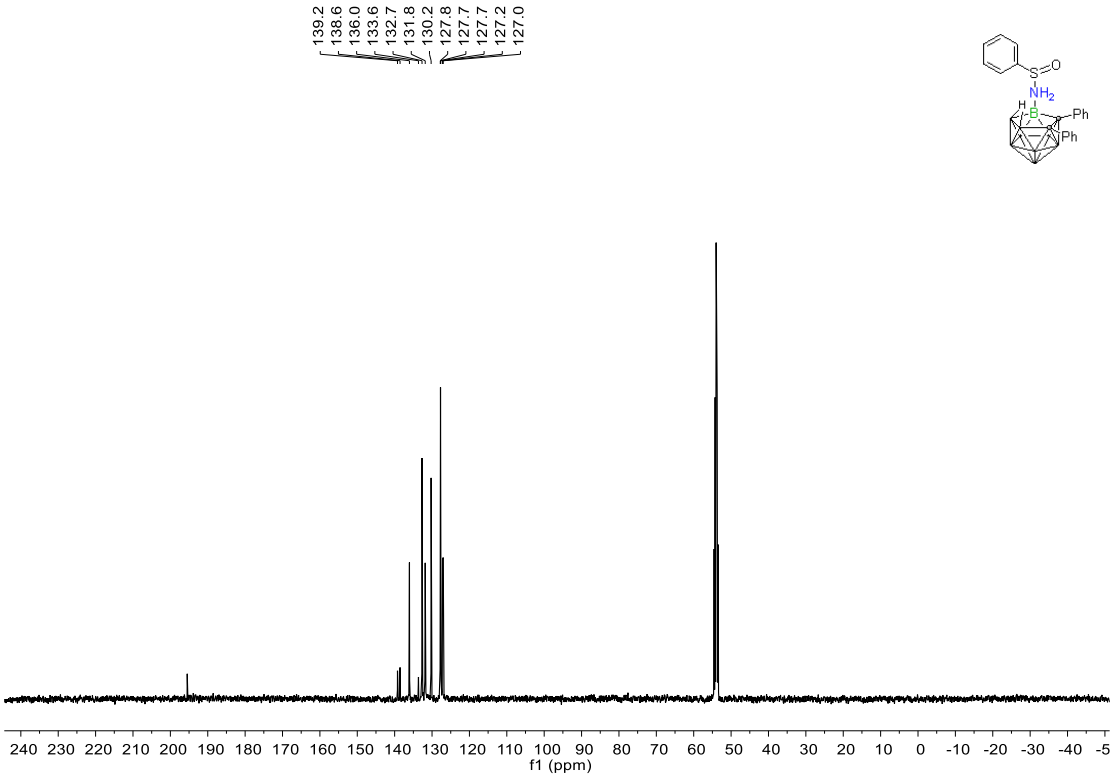
^{11}B NMR (Methylene Cloride-d_2) (Compound 4o)



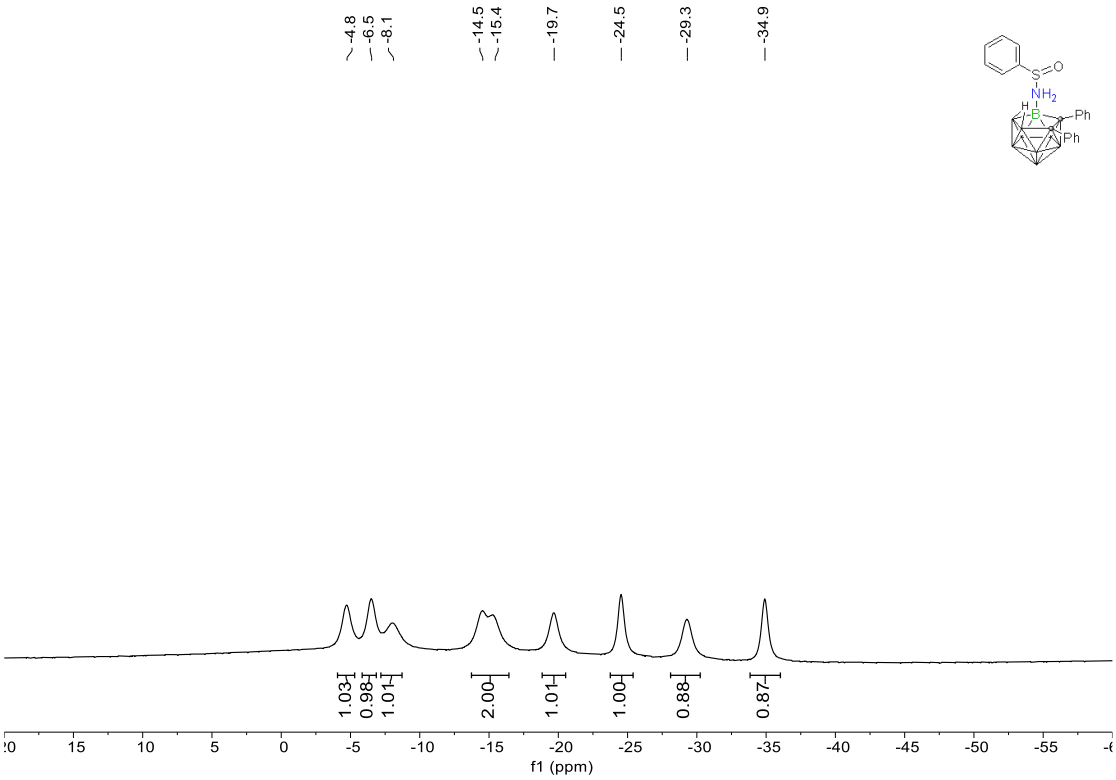
[1] H NMR (Methylene Cloride-d_2) (Compound 4p)



[13] C NMR (Methylene Cloride-d_2) (Compound 4p)



$^{11}B\{^{1}H\}$ NMR (Methylene Cloride-d_2) (Compound 4p)



^{11}B NMR (Methylene Cloride-d_2) (Compound 4p)