

Supporting Information

Photoredox B–H Functionalization to Selective B–N(sp³)

Coupling of *nido*-Carborane with Primary and Secondary

Amines

Ronghui Huang, Weijia Zhao, Shengwen Xu, Jingkai Xu, Chunxiao Li, Changsheng Lu* and Hong Yan*

State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of
Advanced Organic Materials, School of Chemistry and Chemical Engineering
Nanjing University
Nanjing, 210023, P. R. China

Table of Contents

1 General Information.....	3
2 Experimental Section.....	4
3 Detailed Descriptions for Products	5
4 Crystal Structures.....	12
5 Reference	15
6 NMR Spectra.....	16

1 General Information

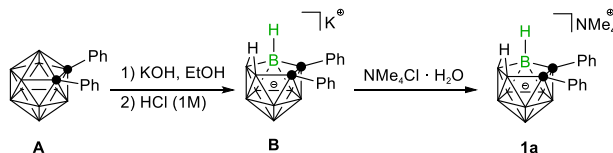
Unless otherwise noted, all experiments were all performed under an air atmosphere. Except for special instructions, solid or liquid reagents were purchased from suppliers without further purification. The process for the synthesis of *nido*-carboranes has been optimized according to literature reports.^[1] 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. % PdCl₂ in HCl (6 M) and were developed with high heat using a heat gun.

¹H, ¹¹B, ¹¹B{¹H}, ¹³C, ¹⁹F 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. ¹¹B chemical shifts were measured utilizing external Et₂O·BF₃ (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 graphite-monochromated (Mo-K α 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

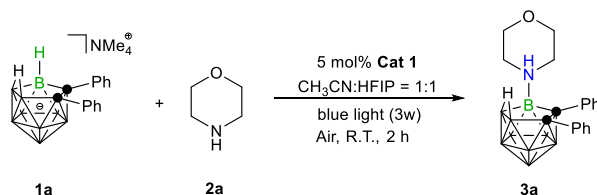


Scheme S1. Schematic presentation for the synthesis of 1a.

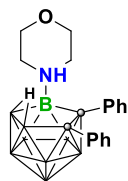
Deboronation of *closo*-carborane substrates: A 50 mL Schlenk tube was added by substituted *closo*-carborane derivatives (5.0 mmol), KOH (1.12 g, 20 mmol) and 25 mL EtOH. The mixture was refluxed for 10 hours before cooling down to room temperature. HCl (1M) was added to adjust pH to 6-7. After filtration and evaporation, the resulting white solid was dissolved in 50 mL deionized water and an aqueous solution of NMe₄Cl (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

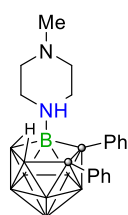
Under air atmosphere, **1a** (38.2 mg, 0.1 mmol), **2a** (17.4 mg, 0.2 mmol) and **Cat 1** (5 mol%) at ambient temperature in CH₃CN:HFIP = 1:1 (1.0 mL) with the irradiation of 3W blue LEDs for 2 h. The mixture was filtered through a silica gel plug and concentrated in vacuo. The products **3a-3l**, **4a-4p** were obtained by flash column chromatography on silica gel (hexane: ethyl acetate: acetone = 10:5:2, v/v).



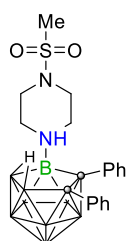
3 Detailed Descriptions for Products



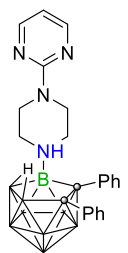
3a: Yield 81 %. White solid. ^1H NMR (400 MHz, Acetone- d_6) δ 7.26 – 7.24 (m, 2H), 7.13 – 7.10 (m, 2H), 6.96 – 6.91 (m, 6H), 6.19 (br, 1H, NH), 3.93 – 3.90 (m, 1H), 3.82 – 3.79 (m, 2H), 3.62 (td, J = 12.7, 12.4, 2.2 Hz, 1H), 3.50 (td, J = 12.7, 12.3, 2.4 Hz, 1H), 3.41 – 3.30 (m, 1H), 3.20 – 3.11 (m, 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; $^{11}\text{B}\{^1\text{H}\}$ (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 $\text{C}_{18}\text{B}_9\text{NH}_{28}\text{O}$ $[\text{M}+\text{Na}]^+$: 395.2942, Found: 395.2954.



3b: Yield 50%. White solid. ^1H 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; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- 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 $\text{C}_{19}\text{B}_9\text{N}_2\text{H}_{31}$ $[\text{M} + \text{Na}]^+$: 408.3259, Found: 408.3263.

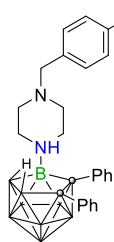


3c: Yield 70 %. White solid. ^1H NMR (400 MHz, Acetonitrile- d_3) δ 7.40 – 7.38 (m, 2H), 7.24 – 7.22 (m, 2H), 7.15 – 7.08 (m, 6H), 5.15 (br, 1H, NH), 3.92 (d, J = 13.4 Hz, 1H), 3.81 – 3.75 (m, 1H), 3.64 – 3.60 (m, 1H), 3.45 – 3.36 (m, 1H), 3.23 – 3.11 (m, 2H), 3.05 – 2.97 (m, 2H), 2.87 (s, 3H, Me), 2.69 – 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); $^{11}\text{B}\{^1\text{H}\}$ (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 $\text{C}_{19}\text{B}_9\text{N}_2\text{H}_{31}\text{O}_2\text{S}$ $[\text{M} + \text{Na}]^+$: 472.2878, Found: 472.2892.

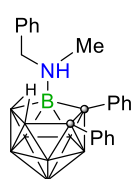


3d: Yield 80 %. White solid. ^1H NMR (400 MHz, Dimethylsulfoxide- d_6) δ 8.35 – 8.34 (d, J = 4.8 Hz, 2H), 7.61 – 7.55 (br, 1H, NH), 7.20 – 7.18 (m, 2H), 7.06 – 7.05 (m, 2H), 6.97 – 6.89 (m, 6H), 6.70 – 6.68 (t, J = 4.8 Hz, 1H), 4.47 – 4.38 (dd, J = 22.3, 14.1 Hz, 1H), 3.52 – 3.49 (d, J = 12.8 Hz, 1H), 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; $^{11}\text{B}\{^1\text{H}\}$ (128

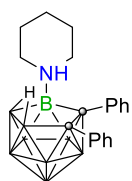
MHz, Acetone-*d*₃) δ -3.5 (1B), -6.6 (1B), -12.4 (1B), -15.2 (2B), -23.1 (1B), -26.5 (1B), -32.4 (1B), -36.9 (1B). **HRMS *m/z*** calcd for C₂₂B₉N₄H₃₁ [M + Na]⁺: 471.3357, Found: 471.3365.



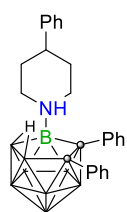
3e: Yield 67 %. White solid. **¹H NMR (400 MHz, Methylene Chloride-*d*₂)** δ 7.31 – 7.24 (m, 4H), 7.22 – 7.19 (m, 2H), 7.09 – 7.08 (m, 3H), 7.03 – 6.96 (m, 5H), 3.63 – 3.58 (m, 1H), 3.47 – 3.40 (m, 1H), 3.39 (s, 2H), 3.19 – 3.09 (m, 2H), 3.07 – 3.06 (br, 1H, NH), 2.95 – 2.90 (m, 1H), 2.87 – 2.82 (m, 1H), 3.32 – 0.25 (8H, B–H), 1.85– 1.76 (m, 2H), -2.50 (br, 1H, B–H–B); **¹³C NMR (101 MHz, Methylene Chloride-*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; **¹¹B{¹H} (128 MHz, Methylene Chloride-*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 C₂₅B₉N₂ClH₃₄ [M + Na]⁺: 494.3321, Found: 494.3351.



3f: Yield 65 %. White solid. **¹H NMR (400 MHz, Methylene Chloride-*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, 1H, 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); **¹³C NMR (101 MHz, Methylene Chloride-*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; **¹¹B{¹H} (128 MHz, Methylene Chloride-*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 C₂₂B₉NH₃₀ [M+Na]⁺: 429.3150, Found: 429.3167.

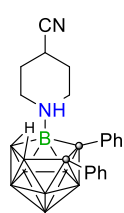


3g: Yield 40 %. White solid. **¹H NMR (400 MHz, Methylene Chloride-*d*₂)** δ 7.32 – 7.25 (m, 2H), 7.08 (s, 3H), 7.03 – 6.98 (m, 4H), 3.74 (d, *J* = 13.2 Hz, 1H), 3.31 – 3.13 (m, 2H), 3.03 – 2.85 (m, 1H), 1.90 – 1.78 (m, 2H), 1.71 – 1.64 (m, 1H), 1.44 – 1.33 (m, 1H), 1.21 – 1.10 (m, 2H), 3.08 – 0.26 (8H, B–H), -2.44 (br, 1H, B–H–B); **¹³C NMR (101 MHz, Methylene Chloride-*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; **¹¹B{¹H} (128 MHz, Methylene Chloride-*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 C₁₉B₉NH₃₀ [M + Na]⁺: 393.3150, Found: 393.3154.



3h: Yield 52 %. White solid. **¹H NMR (400 MHz, Methylene Chloride-*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); **¹³C NMR (101 MHz, Methylene Chloride-*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; **¹¹B{¹H} (128 MHz, Methylene Chloride-*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

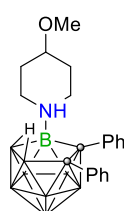
C₂₅B₉NH₃₄ [M + Na]⁺: 469.3463, Found: 469.3473.



3i: Yield 78 %. White solid. ¹H 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);

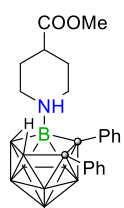
Conformer II : δ 7.27 – 7.24 (m, 2H), 7.13 – 7.11 (m, 2H), 7.01 – 6.90 (m, 6H), 5.88 (br, 1H, NH), 4.04 – 3.99 (m, 1H), 3.48 – 3.44 (m, 1H), 3.29 – 3.26 (m, 1H), 3.14 – 3.10 (m, 1H), 2.35 – 2.29 (m, 2H), 2.03 – 1.96 (m, 2H), 1.86 – 1.83 (m, 1H), 3.53 – 0.31 (8H, B–H), –2.21 (br, 1H, B–H–B); ¹³C NMR (101 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; ¹¹B{¹H} (128 MHz, Methylene Chloride-*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 C₂₀B₉N₂H₂₉ [M + Na]⁺: 418.3102, Found: 418.3115.



3j: Yield 60 %. White solid. ¹H NMR (400 MHz, Methylene Chloride-*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, CH₃), 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),

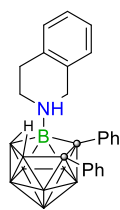
3.42 – 3.38 (m, 1H), 3.28 (s, 3H, CH₃), 3.09 (br, 1H, NH), 2.26 – 2.21 (m, 3H), 1.34 – 1.21 (m, 3H), 3.62 – 0.22 (8H, B–H), –2.47 (br, 1H, B–H–B); ¹³C NMR (101 MHz, Methylene Chloride-*d*₂) δ 139.0, 138.9, 136.7, 136.5, 132.6, 132.6, 131.2, 128.8, 128.2, 128.0, 127.8, 127.8, 127.0, 126.9, 73.9, 69.6, 56.5, 56.2, 55.6, 53.0, 52.4, 49.6, 31.5, 31.3, 29.8, 29.3; ¹¹B{¹H} (128 MHz, Methylene Chloride-*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 C₂₀B₉NOH₃₂ [M + Na]⁺: 422.3292, Found: 422.3298.



3k: Yield 72 %. White solid. ¹H NMR (400 MHz, Methylene Chloride-*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);

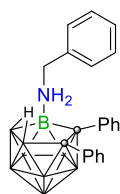
Conformer II : δ 7.28 – 7.26 (m, 2H), 7.10 – 7.06 (d, *J* = 1.4 Hz, 3H), 7.04 – 7.00 (m, 5H), 3.71 (s, 3H), 3.36 – 3.34 (m, 1H), 3.08 – 3.06 (m, 1H), 3.04 – 2.94 (m, 1H), 2.67 – 2.63 (m, 1H), 2.34 – 2.23 (m, 3H), 1.53 (br, 1H, NH), 1.50 – 1.42 (m, 2H), 3.46 – 0.24 (8H, B–H), –2.49 (br, 1H, B–H–B); ¹³C NMR (101 MHz, Methylene Chloride-*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; ¹¹B{¹H} (128 MHz, Methylene Chloride-*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 C₂₁B₉NO₂H₃₂ [M + Na]⁺: 450.3241, Found: 450.3253.



3l: Yield 77 %. White solid. ^1H NMR (400 MHz, Methylene Chloride- 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 = 15.8 Hz, 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);

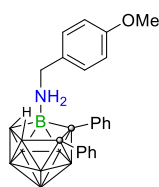
Conformer II : δ 7.32 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 7.12 – 6.98 (m, 10H), 4.73 – 4.59 (m, 2H), 4.00 – 3.90 (m, 1H), 3.51 – 3.47 (m, 1H), 3.31 – 3.19 (m, 1H), 2.92 – 2.84 (m, 1H), 2.74 – 2.69 (m, 1H), 3.43 – 0.31 (8H, B–H), –2.38 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Methylene Chloride- d_2) δ 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, 126.9, 126.8, 126.6, 57.3, 55.3, 54.9, 52.5, 28.1, 27.6; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- 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 $\text{C}_{23}\text{B}_9\text{NH}_{30}$ $[\text{M} + \text{Na}]^+$: 441.3150, Found: 441.3159.



4a: Yield 70 %. White solid. ^1H NMR (400 MHz, Methylene Chloride- 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, NH₂), 4.59 (br, 1H, NH₂), 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 Chloride- d_2) δ 138.9, 136.8, 133.6, 132.6, 131.4, 130.4, 130.1,

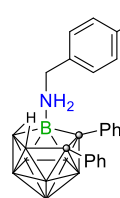
129.1, 129.0, 128.1, 127.8, 76.2 (cage C), 63.5 (cage C), 54.8; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- d_2) δ –0.3 (1B), –5.9 (1B), –11.9 (1B), –15.5 (2B), –21.4 (1B), –26.2 (1B), –31.3 (1B), –36.7 (1B). HRMS m/z calcd for $\text{C}_{21}\text{B}_9\text{NH}_{28}$ $[\text{M} + \text{Na}]^+$: 414.3030, Found: 414.3020.



4b: Yield 58 %. White solid. ^1H NMR (400 MHz, Methylene Chloride- 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, NH₂), 4.42 (br, 1H, NH₂), 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 Chloride- d_2) δ 161.3, 139.0,

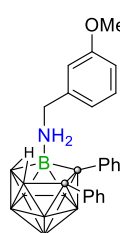
136.9, 132.6, 131.4, 130.6, 129.0, 128.1, 127.8, 127.0, 125.6, 115.4, 76.2 (cage C), 63.5 (cage C), 55.9, 54.5; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- d_2) δ –0.4 (1B), –5.9 (1B), –11.9 (1B), –15.5 (2B), –21.4 (1B), –26.2 (1B), –31.4 (1B), –36.7 (1B). HRMS m/z calcd for $\text{C}_{22}\text{B}_9\text{NH}_{30}\text{O}$ $[\text{M} + \text{Na}]^+$: 444.3135, Found: 444.3134.



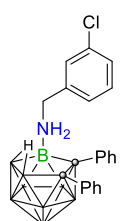
4c: Yield 65 %. White solid. ^1H NMR (400 MHz, Methylene Chloride- d_2)

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, NH₂), 4.55 (br, 1H, NH₂), 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;

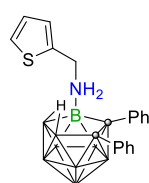
$^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- d_2) δ –0.5 (1B), –5.9 (1B), –11.7 (1B), –15.5 (2B), –21.4 (1B), –26.2 (1B), –31.3 (1B), –36.7 (1B). HRMS m/z calcd for $\text{C}_{21}\text{B}_9\text{NClH}_{27}$ $[\text{M} + \text{Na}]^+$: 448.2640, Found: 448.2660.



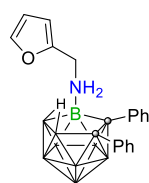
4d: Yield 64 %. White solid. ^1H NMR (400 MHz, Methylene Chloride- d_2) δ 87.29 – 7.25 (m, 3H), 7.14 – 6.98 (m, 8H), 6.91– 6.98 (m, 1H); 6.61 (d, J = 7.5 Hz, 1H), 6.50 (t, J = 2.1 Hz, 1H), 4.68 (br, 1H, NH_2), 4.52 (br, 1H, NH_2), 4.30 – 4.23 (m, 1H), 4.12 – 4.05 (m, 1H), 3.74 (s, 3H, OMe); 3.11 – 0.41 (8H, B–H), –2.32 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Methylene Chloride- 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; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- 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 $\text{C}_{22}\text{B}_9\text{NH}_{30}\text{O}$ $[\text{M} + \text{Na}]^+$: 444.3135, Found: 444.3136.



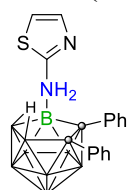
4e: Yield 60 %. White solid. ^1H NMR (400 MHz, Methylene Chloride- d_2) δ 7.40 – 7.37 (m, 1H), 7.33 (d, J = 7.7 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.16 – 7.10 (m, 3H), 7.09 – 6.98 (m, 6H), 6.97 – 6.94 (m, 1H), 4.68 (br, 1H, NH_2), 4.58 (br, 1H, NH_2), 4.32 – 4.25 (m, 1H), 4.12 – 4.05 (m, 1H), 3.34 – 0.33 (8H, B–H), –2.28 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Methylene Chloride- 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; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- 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 $\text{C}_{21}\text{B}_9\text{NClH}_{27}$ $[\text{M} + \text{Na}]^+$: 448.2640, Found: 448.2654.



4f: Yield 65%. Yellow solid. ^1H NMR (400 MHz, Methylene Chloride- 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 Chloride- 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; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- 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 $\text{C}_{19}\text{B}_9\text{NSH}_{26}$ $[\text{M} + \text{Na}]^+$: 421.2557, Found: 421.2552.

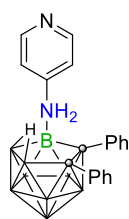


4g: Yield 60%. White solid. ^1H NMR (400 MHz, Methylene Chloride- d_2) δ 7.42 (s, 1H), 7.27 – 7.24 (m, 2H), 7.11 – 7.05 (m, 3H), 7.01 – 6.97 (m, 5H), 6.41 – 6.38 (m, 2H), 4.73 (br, 2H, NH_2), 4.44 – 4.37 (m, 1H), 4.25 – 4.18 (m, 1H), 3.35 – 0.30 (8H, B–H), –2.38 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Methylene Chloride- 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; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- 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 $\text{C}_{19}\text{B}_9\text{NOH}_{26}$ $[\text{M} + \text{Na}]^+$: 404.2822, Found: 404.2822.

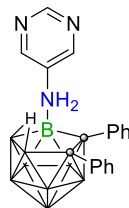


4h: Yield 61%. White solid. ^1H NMR (400 MHz, Acetone- d_6) δ 8.65 (br, 2H, NH_2), 7.35 – 7.33 (m, 2H), 7.13 (d, J = 4.5 Hz, 1H), 7.09 – 7.06 (m, 2H), 6.98 – 6.91 (m, 3H), 6.87 – 6.81 (m, 3H), 6.57 (d, J = 4.5 Hz, 1H), 3.33 – 0.40 (8H, B–H), –1.91 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Acetone- d_6) δ 173.5, 140.1, 138.3, 136.4, 133.0, 131.7, 127.7, 127.6, 127.0, 126.9, 105.8; $^{11}\text{B}\{^1\text{H}\}$ (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

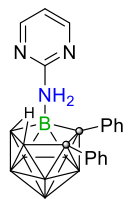
calcd for $C_{17}B_9N_2SH_{23} [M + Na]^+$: 408.2353, Found: 408.2351.



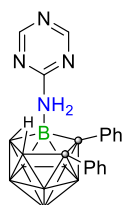
4i: Yield 60 %. White solid. 1H NMR (400 MHz, Methylene Chloride- d_2) δ 8.28 (d, J = 7.2 Hz, 2H), 7.31 – 7.29(m, 2H), 7.07(br, 2H, NH_2), 7.00 – 6.98 (m, 2H), 6.96 – 6.88 (m, 3H), 6.83 – 6.77 (m, 3H), 6.70 – 6.67 (m, 2H), 3.10 – 0.32 (8H, B–H), –1.81 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Acetone- d_6) δ 158.9, 148.6, 140.3, 138.3, 133.1, 132.1, 127.7, 126.9, 126.8, 109.6; $^{11}B\{^1H\}$ (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.



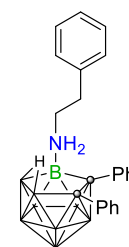
4j: Yield 53 %. White solid. 1H NMR (400 MHz, Methylene Chloride- d_2) δ 8.94 (s, 1H), 8.53 – 8.52 (m, 1H), 8.48 (d, J = 3.2 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.04 – 7.01 (m, 2H), 6.98 – 6.91 (m, 3H), 6.84 – 6.81 (m, 3H), 6.05 (br, 2H, NH_2), 3.47 – 0.43 (8H, B–H), –1.77 (br, 1H, B–H–B); ^{13}C NMR (101 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; $^{11}B\{^1H\}$ (128 MHz, Methylene Chloride- 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.



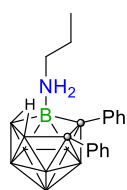
4k: Yield 34 %. White solid. 1H NMR (400 MHz, Methylene Chloride- d_2) δ 8.39 – 8.37 (m, 2H), 7.31 – 7.29(m, 2H), 7.05 – 6.99(m, 3H), 6.92 – 6.88(m, 2H), 6.84 – 6.81(m, 3H), 6.56 (dd, J = 6.3, 4.6 Hz, 1H), 3.42 – 0.43(8H, B–H), –2.42(br, 1H, B–H–B); ^{13}C NMR (101 MHz, Methylene Chloride- d_2) δ 164.8, 160.6, 154.4, 138.9, 136.8, 132.6, 131.1, 127.8, 127.7, 127.1, 111.4; $^{11}B\{^1H\}$ (128 MHz, Methylene Chloride- 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.



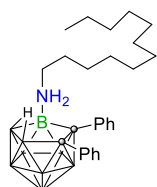
4l: Yield 67%. White solid. 1H NMR (400 MHz, Acetone- d_6) δ 8.88 (s, 2H), 8.63 (br, 2H, NH_2), 7.34 – 7.31 (m, 2H), 7.09 – 7.07 (m, 2H), 6.97 – 6.85 (m, 6H), 3.40 – 0.34 (8H, B–H), –1.83 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Acetone- d_6) δ 165.2, 163.1, 140.0, 137.8, 133.1, 132.1, 128.2, 127.8, 127.4, 127.0; $^{11}B\{^1H\}$ (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.



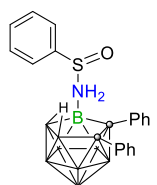
4m: Yield 52 %. White solid. 1H NMR (400 MHz, Methylene Chloride- d_2) δ 7.29 – 7.27 (m, 3H), 7.23 – 7.21 (m, 2H), 7.00 – 6.94 (m, 8H), 6.89 – 6.88 (m, 2H), 4.27 (br, 1H, NH_2), 4.11 (br, 1H, NH_2), 3.52 – 3.44 (m, 1H), 3.41 – 3.33 (m, 1H), 2.95 – 2.84 (m, 2H), 3.20 – 0.37 (8H, B–H), –2.42 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Methylene Chloride- 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; $^{11}B\{^1H\}$ (128 MHz, Methylene Chloride- 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. ^1H NMR (400 MHz, Methylene Chloride- 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 Chloride- 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; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- 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 $\text{C}_{17}\text{B}_9\text{NH}_{28}$ [M]: 343.3132, Found: 343.3170.

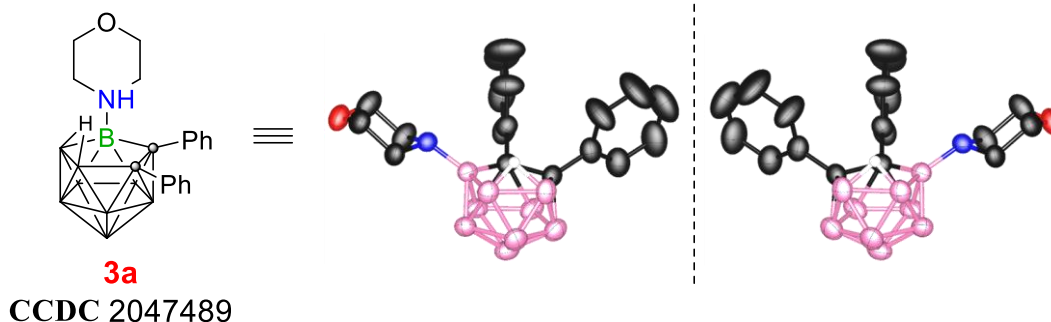


4o: Yield 43 %. White solid. ^1H NMR (400 MHz, Methylene Chloride- d_2) δ 7.27 – 7.24 (m, 2H), 7.12 – 6.97 (m, 8H), 4.22 (br, 2H, NH_2), 3.26 – 3.06 (m, 2H), 1.57 – 1.48 (m, 3H), 1.31 – 1.15 (m, 17H), 0.90 – 0.87 (t, J = 6.8 Hz, 3H), 3.35 – 0.26 (8H, B–H), –2.35 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Methylene Chloride- 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; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- 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 $\text{C}_{26}\text{B}_9\text{NH}_{46}$ [M + Na] $^+$: 493.4402, Found: 493.4400.

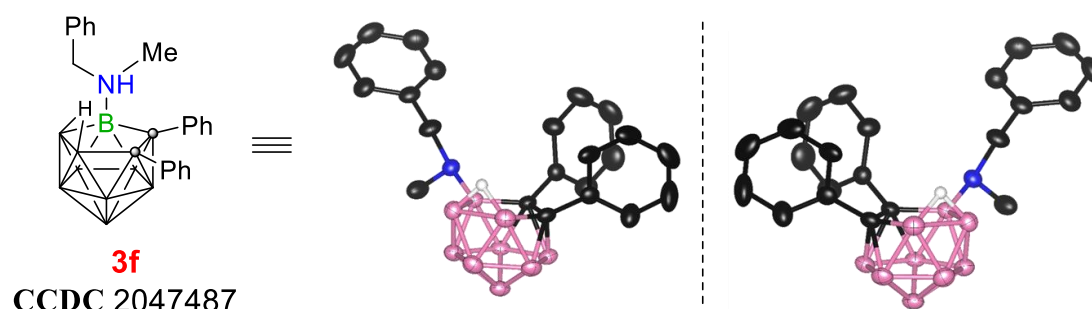


4p: Yield 64%. Yellow solid. ^1H NMR (400 MHz, Methylene Chloride- d_2) δ 10.13 (br, 1H, NH_2), 8.21 (br, 1H, NH_2), 7.73 – 7.69 (m, 1H), 7.62 – 7.59 (m, 2H), 7.53 – 7.44 (m, 2H), 7.30 – 7.26 (m, 2H), 7.03 – 6.92 (m, 8H), 3.41 – 0.51 (8H, B–H), –2.05 (br, 1H, B–H–B); ^{13}C NMR (101 MHz, Methylene Chloride- 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; $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, Methylene Chloride- 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 $\text{C}_{21}\text{B}_9\text{NH}_{26}\text{S}$ [M + Na] $^+$: 444.2594, Found: 444.2591.

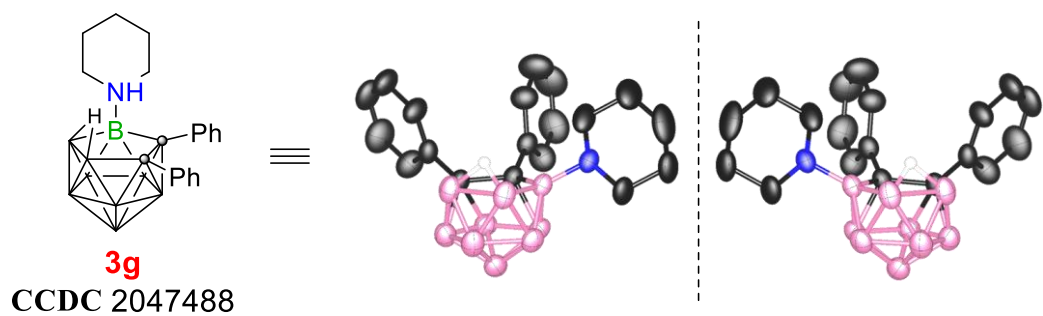
4 Crystal Structures



Identification code	3a
Empirical formula	C ₁₈ H ₂₈ B ₉ NO
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} /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



Identification code	3f
Empirical formula	C ₂₃ H ₃₂ B ₉ Cl ₂ N
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
$\rho_{\text{calc}}/\text{cm}^3$	1.229
μ/mm^{-1}	0.259
F(000)	512.0
Crystal size/mm ³	0.11 × 0.09 × 0.07
Radiation	MoK α (λ = 0.71073)
2 Θ 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 ≥ 2 σ (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



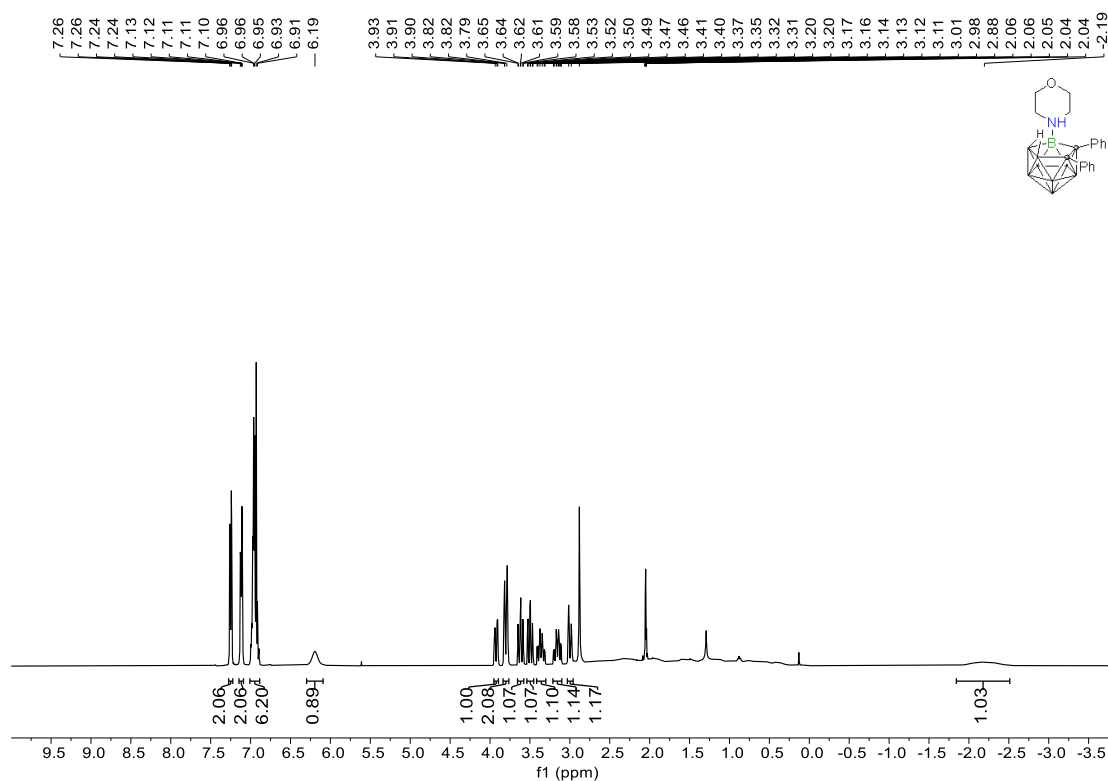
Identification code	3g
Empirical formula	C ₂₂ H ₃₆ B ₉ NO
Formula weight	427.81
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2/c
a/Å	34.119(8)
b/Å	6.9698(17)
c/Å	23.025(6)
α /°	90
β /°	107.554(4)
γ /°	90
Volume/Å ³	5220(2)
Z	8
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.089
μ/mm^{-1}	0.059
F(000)	1824.0
Crystal size/mm ³	0.13 × 0.11 × 0.1
Radiation	MoK α (λ = 0.71073)
2 Θ 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 ≥ 2 σ (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

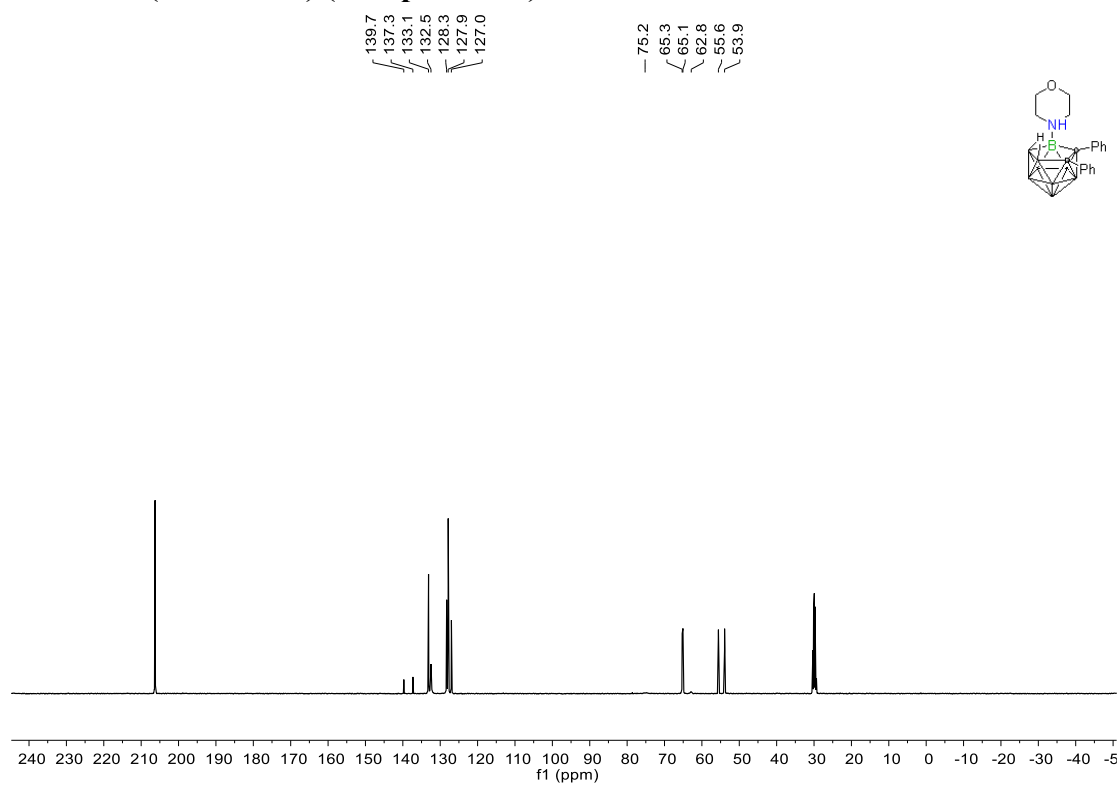
- [1] Yang, Z.; Zhao, W.; Liu, W.; Wei, X.; Chen, M.; Zhang, X.; Zhang, X.; Liang, Y.; Lu, C.; Yan, H., Metal-Free Oxidative B-N Coupling of *nido*-Carborane with N-Heterocycles. *Angew. Chem. Int. Ed.* **2019**, *58*, 11886-11892.
- [2] Chen, M.; Zhao, D.; Xu, J.; Li, C.; Lu, C.; Yan, H., Electrooxidative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

6. NMR Spectra

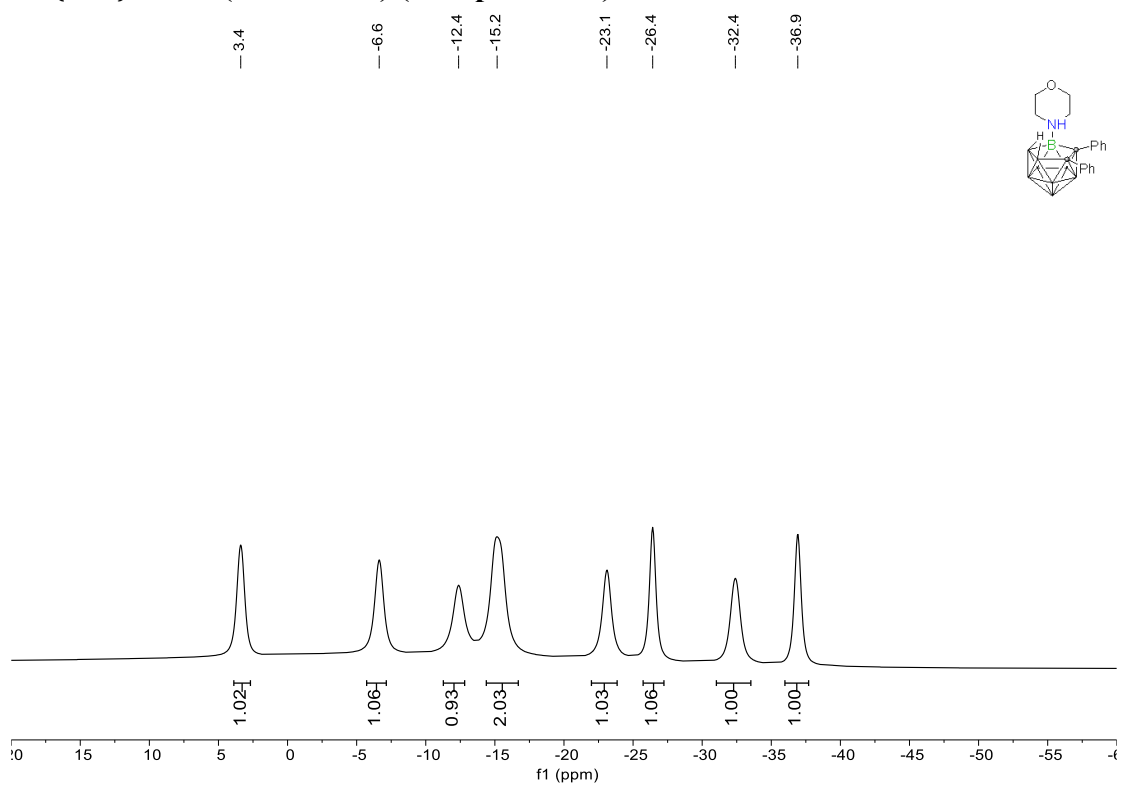
^1H NMR (Acetone- d_6) (Compound 3a)



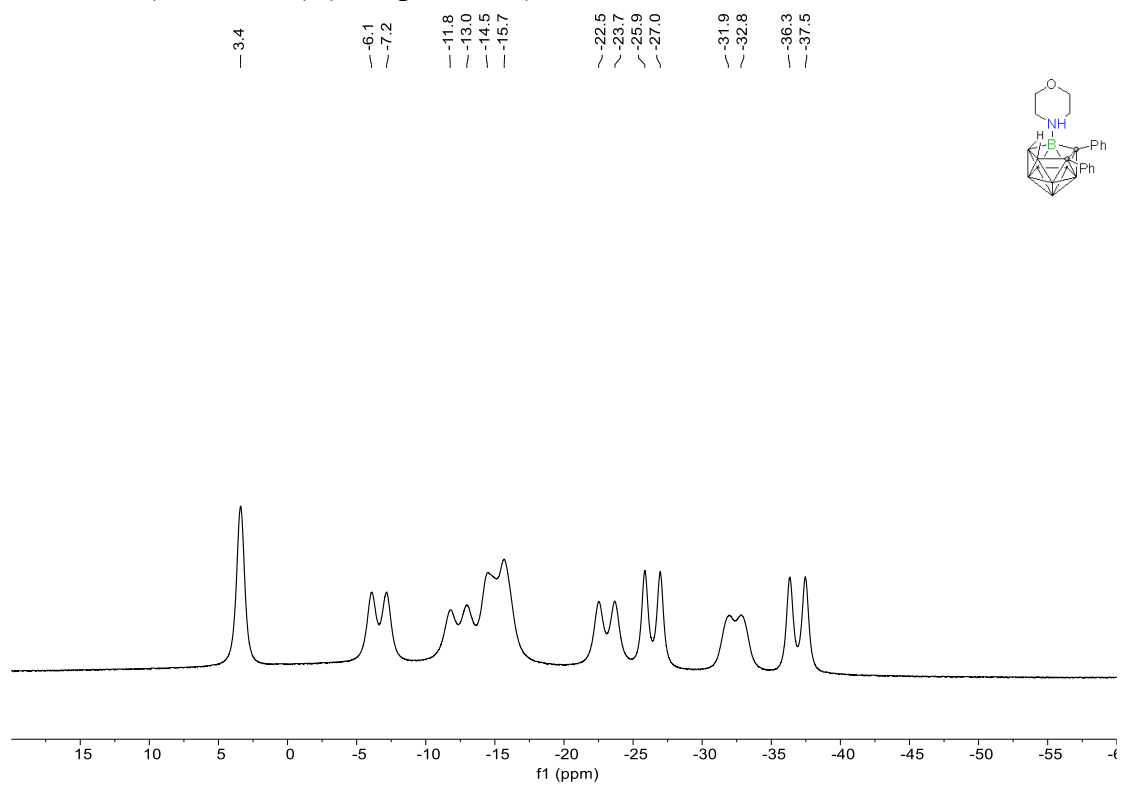
^{13}C NMR (Acetone- d_6) (Compound 3a)



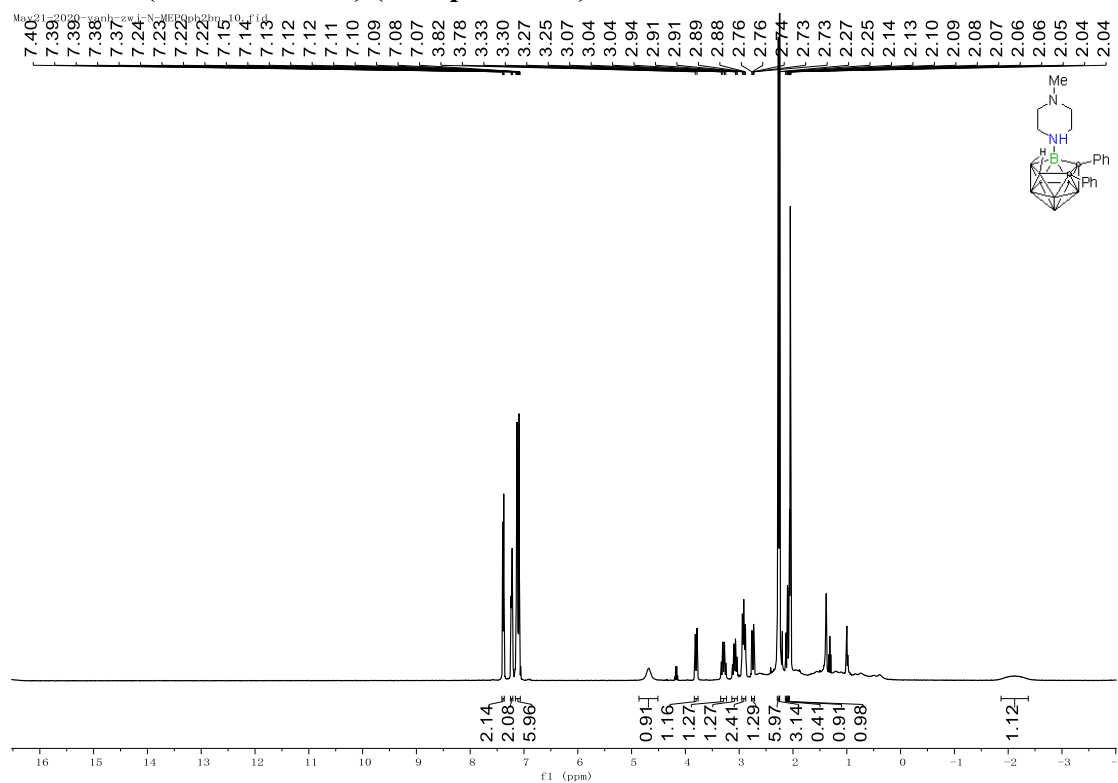
$^{11}\text{B}\{^1\text{H}\}$ NMR (Acetone- d_6) (Compound 3a)



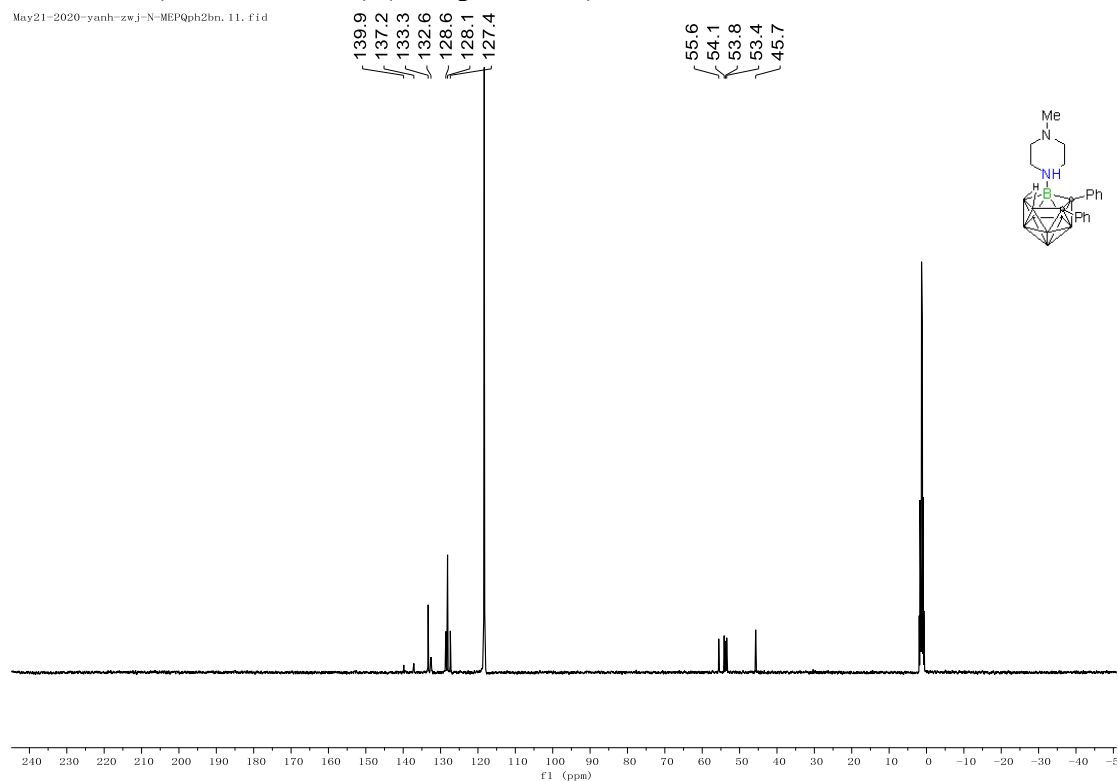
^{11}B NMR (Acetone- d_6) (Compound 3a)



¹H NMR (Acetonitrile-*d*₃) (Compound 3b)

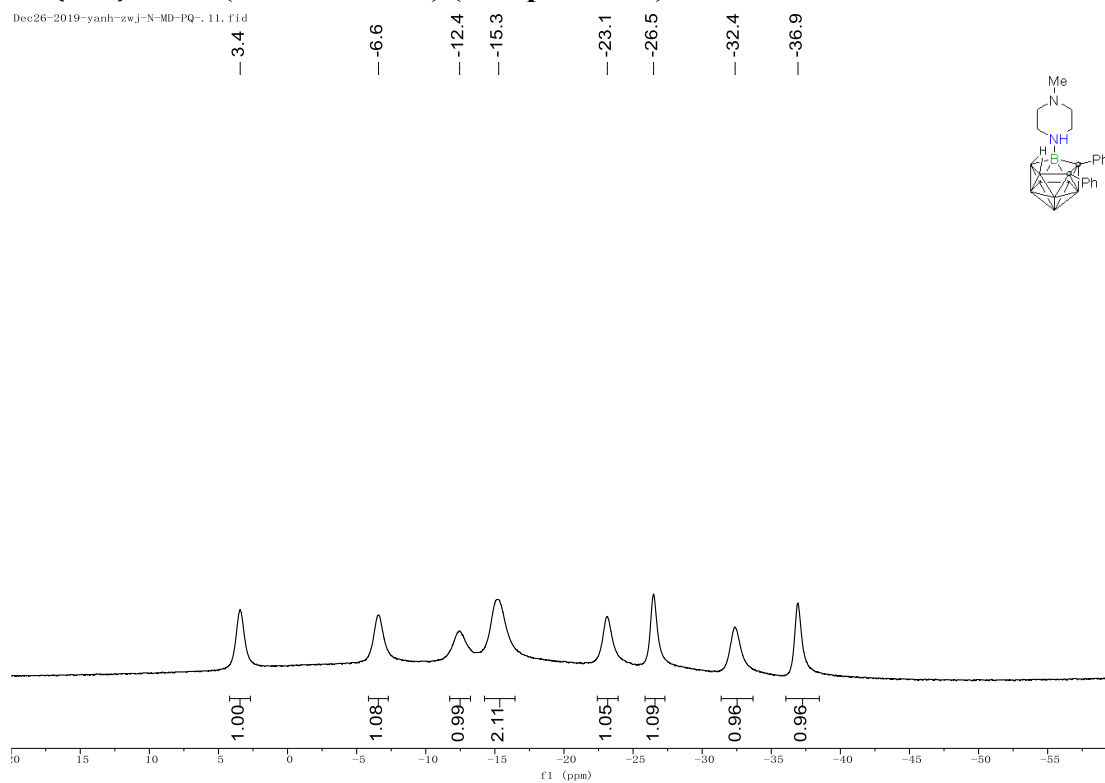


¹³C NMR (Acetonitrile-*d*₃) (Compound 3b)



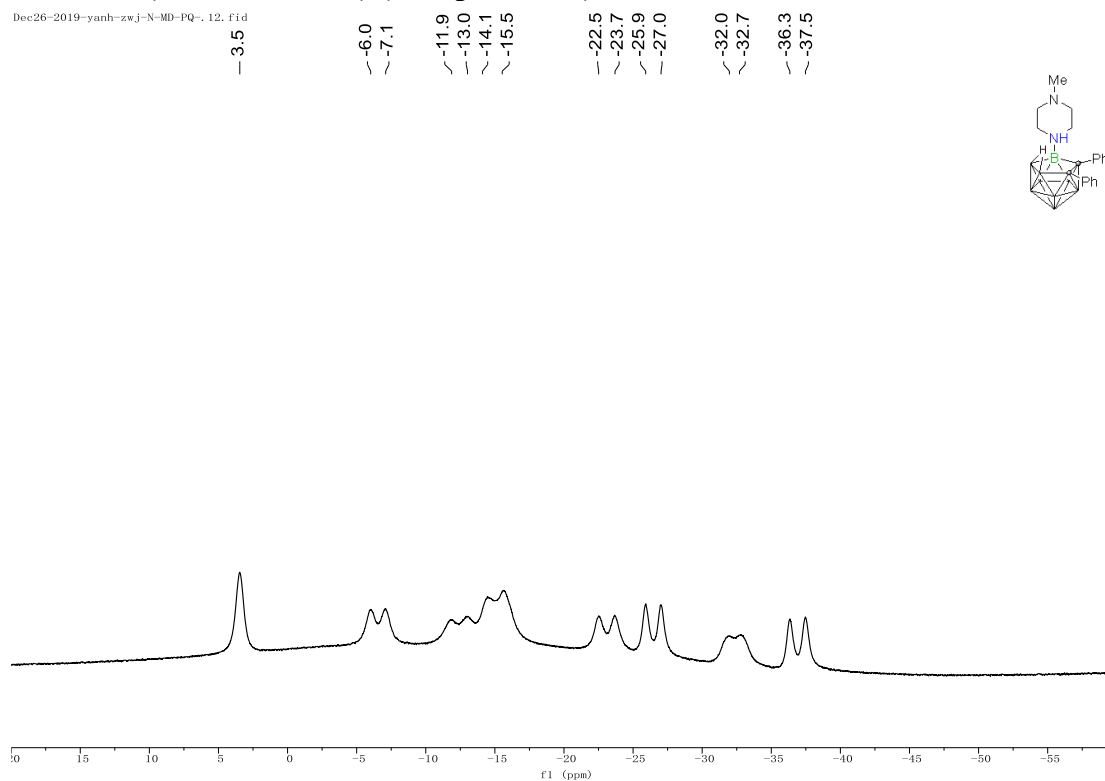
$^{11}\text{B}\{^1\text{H}\}$ NMR (Acetonitrile- d_3) (Compound 3b)

Dec26-2019-yanh-zwj-N-MD-PQ-, 11, f1d

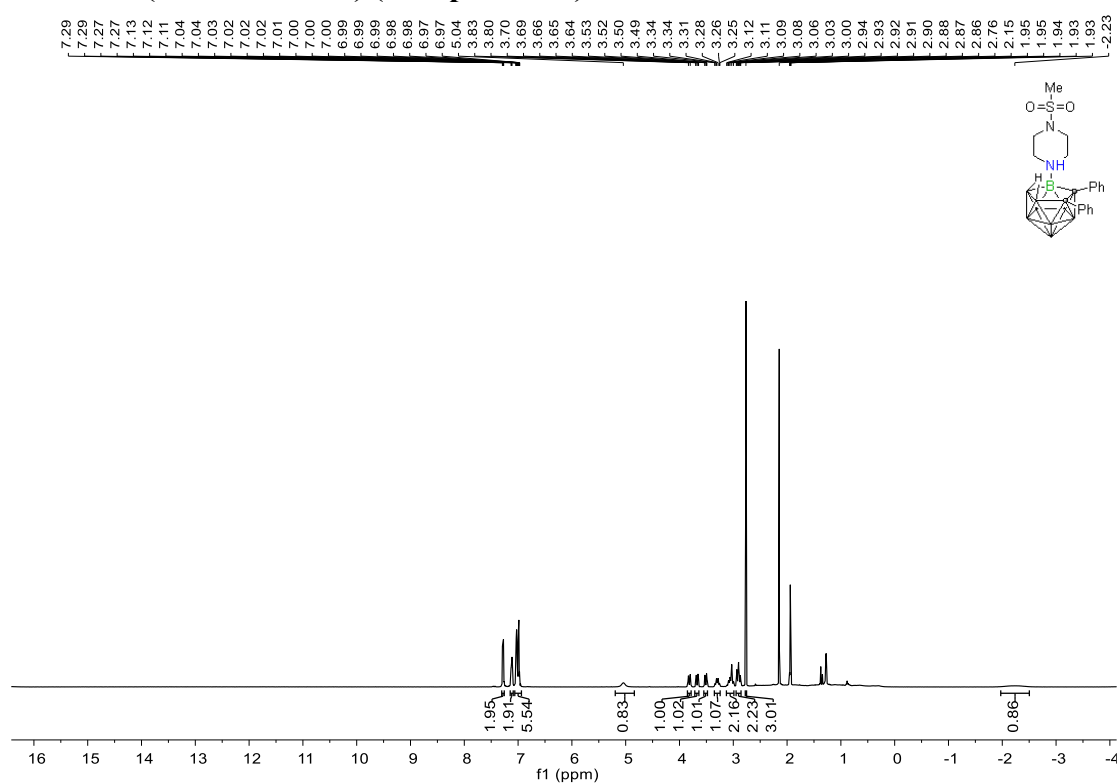


^{11}B NMR (Acetonitrile- d_3) (Compound 3b)

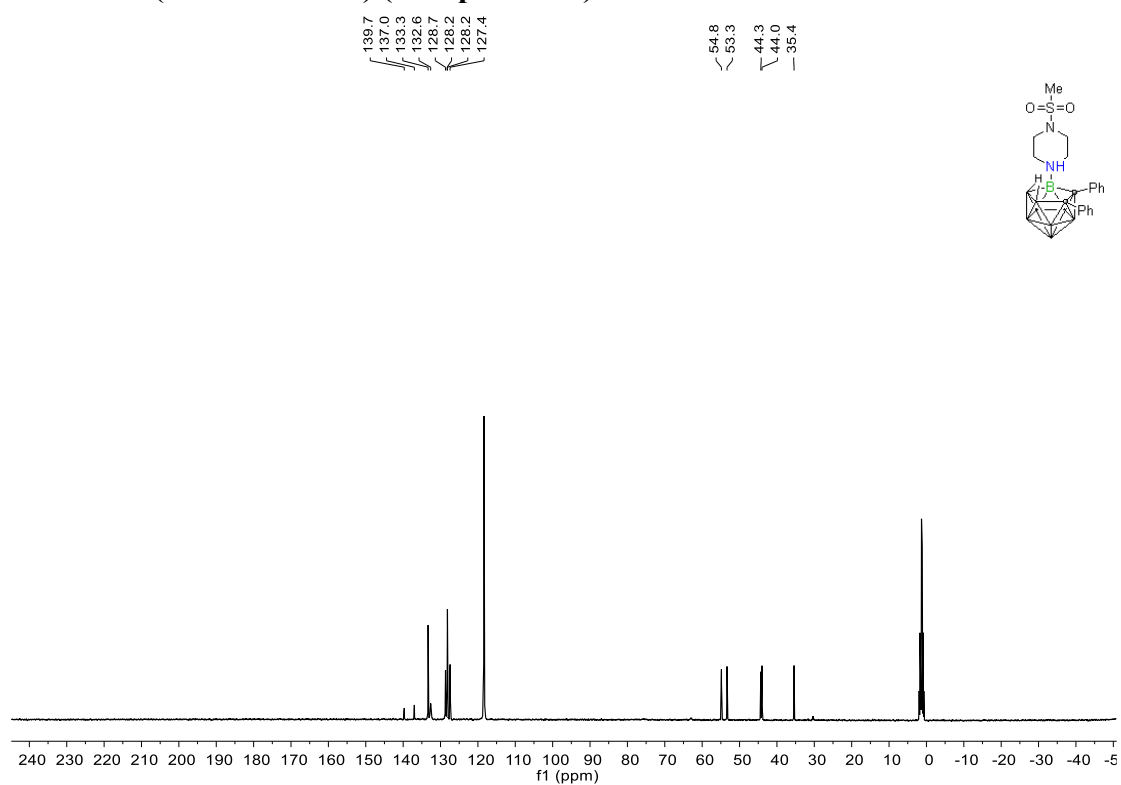
Dec26-2019-yanh-zwj-N-MD-PQ-, 12, f1d



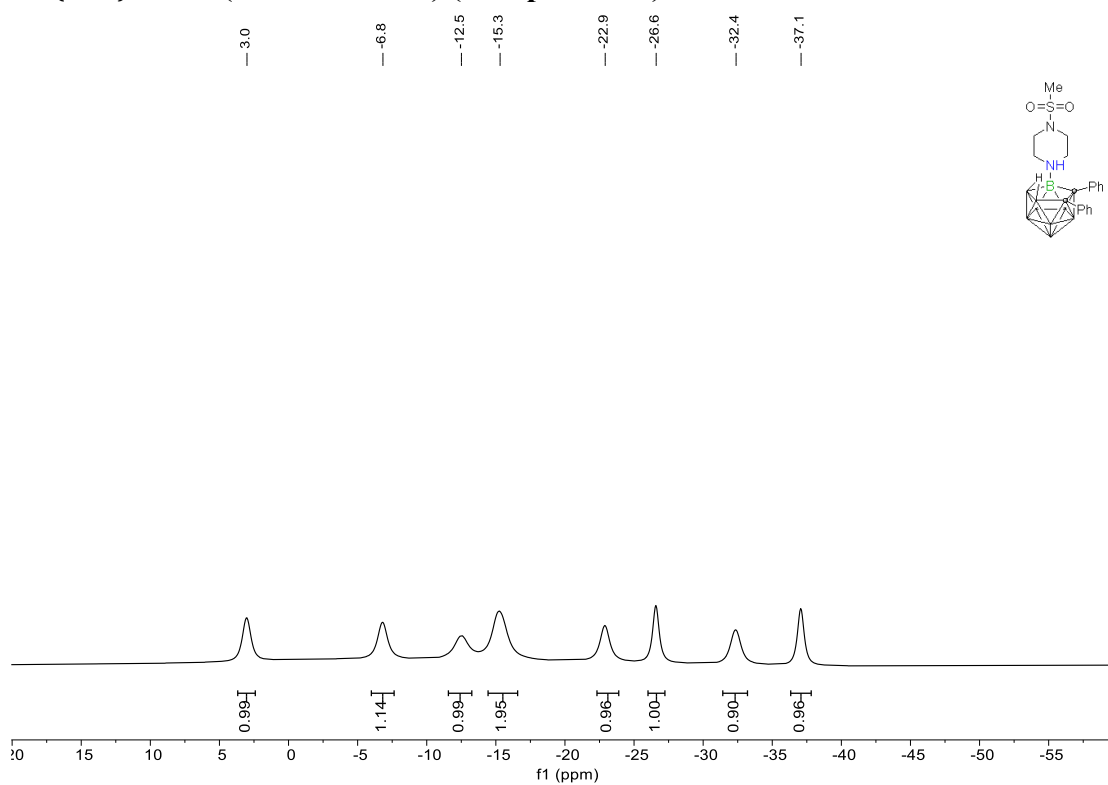
¹H NMR (Acetonitrile-*d*₃) (Compound 3c)



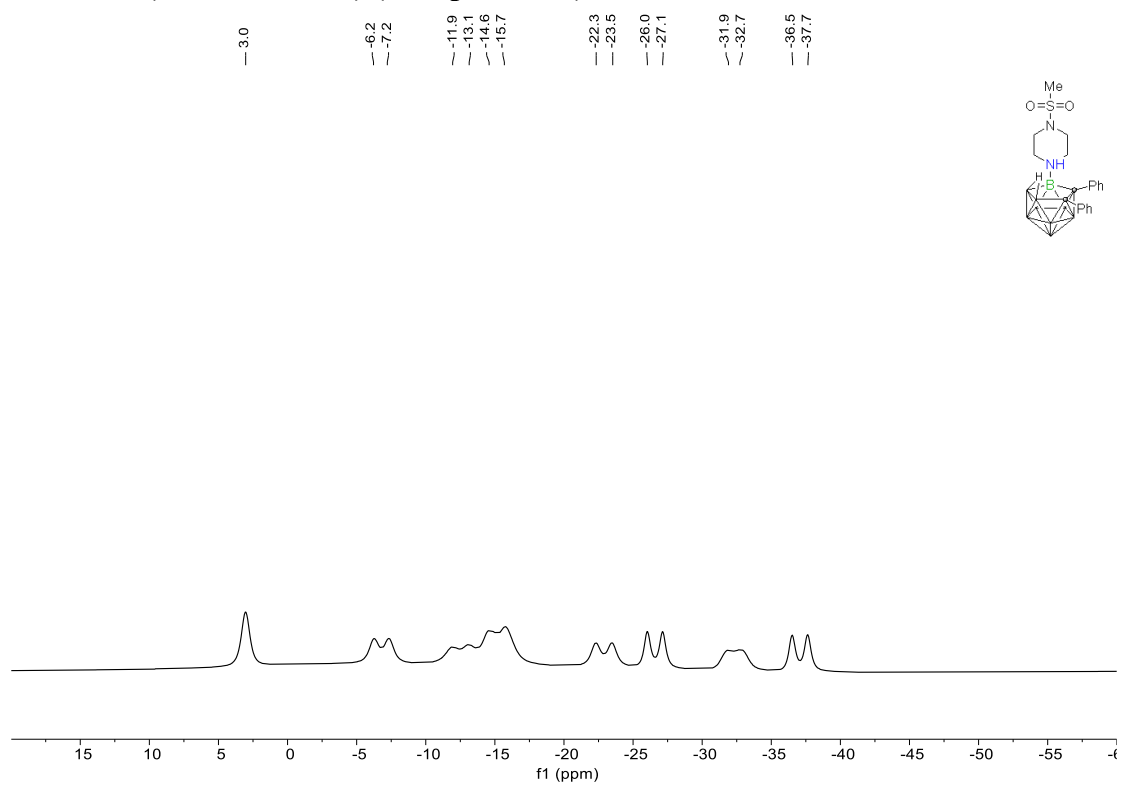
¹³C NMR (Acetonitrile-*d*₃) (Compound 3c)



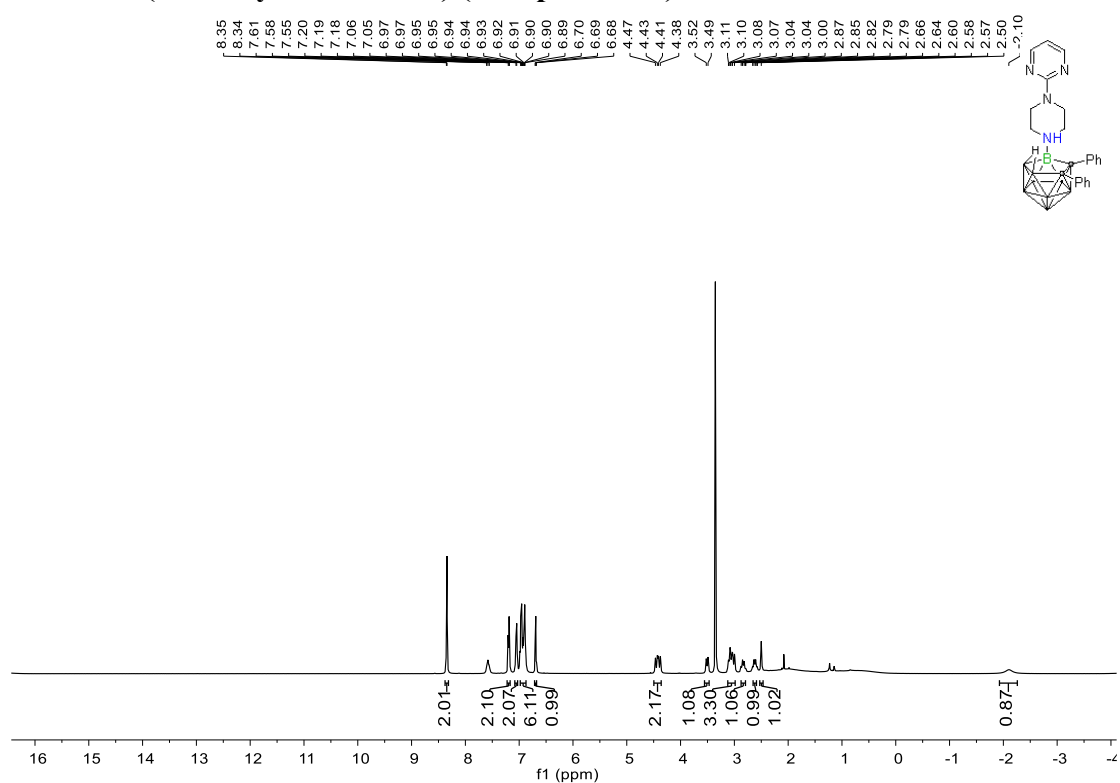
$^{11}\text{B}\{^1\text{H}\}$ NMR (Acetonitrile- d_3) (Compound 3c)



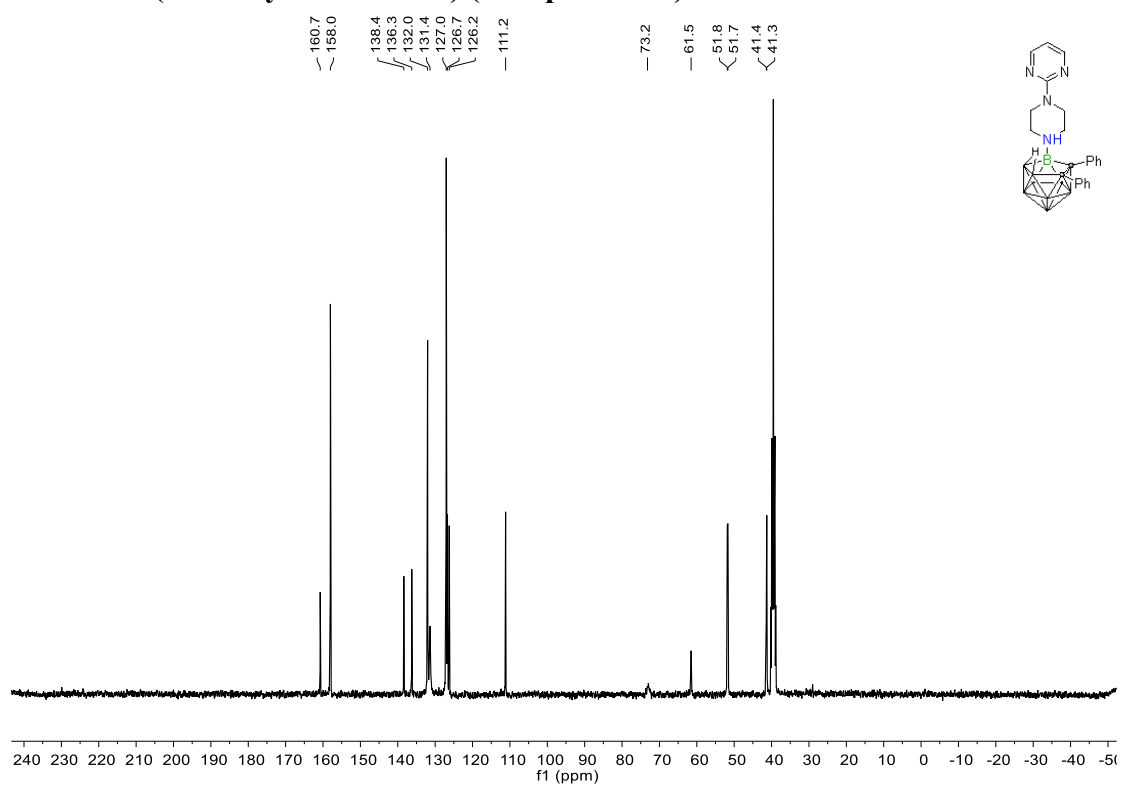
^{11}B NMR (Acetonitrile- d_3) (Compound 3c)



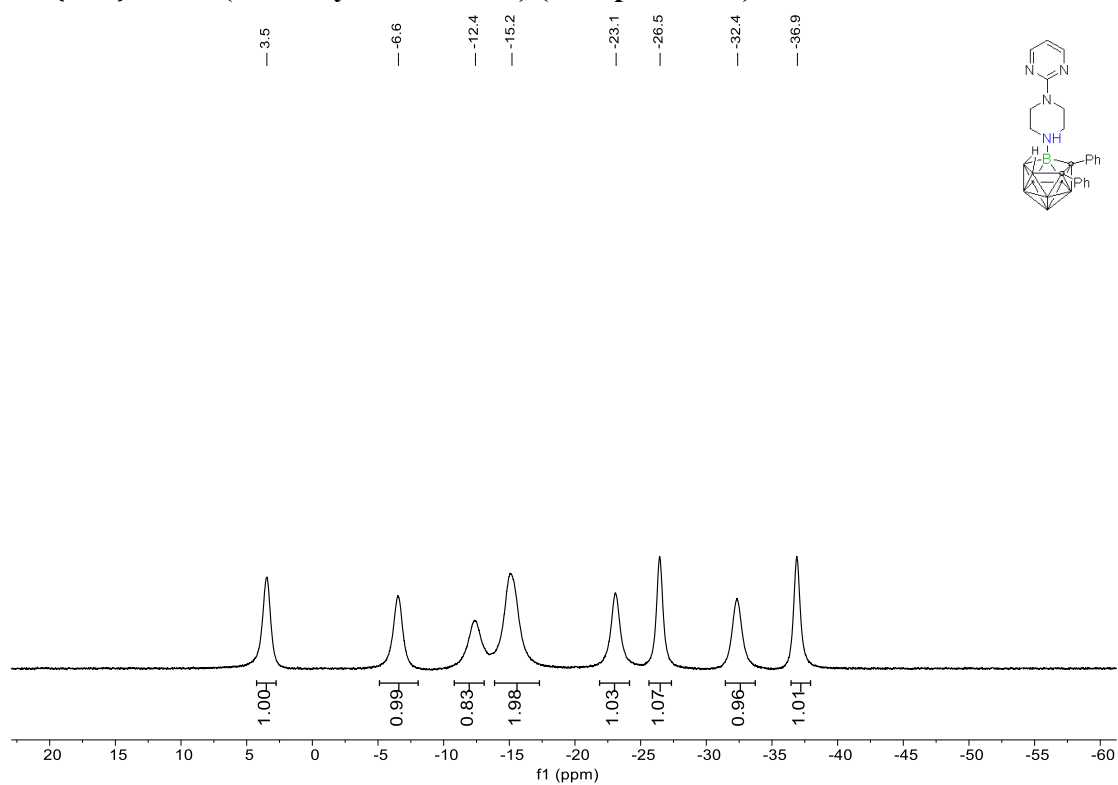
¹H NMR (Dimethylsulfoxide-*d*₆) (Compound 3d)



¹³C NMR (Dimethylsulfoxide-*d*₆) (Compound 3d)



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

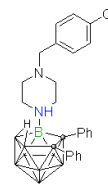


Chemical structure of the compound is shown in the top right corner. The structure is a complex molecule featuring a central boron atom (B) coordinated by a nitrogen atom (N) and a chlorine atom (Cl). The nitrogen atom is part of a piperidine ring, which is further substituted with a phenyl group (Ph) and a 4-chlorophenyl group (4-Cl-Ph). The boron atom is also coordinated by two phenyl groups (Ph) and a chlorine atom (Cl). The chemical structure is labeled with the following atoms: B, N, Cl, Ph, and 4-Cl-Ph.

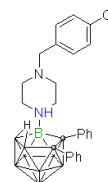
The ¹³C NMR spectrum shows the following chemical shifts (ppm): 138.9, 136.5, 136.1, 133.7, 132.5, 131.2, 129.1, 130.6, 128.8, 128.1, 127.8, 127.0, 62.6, 61.7, 56.3, 52.6, and 52.4.

The ¹³C NMR spectrum displays several sharp peaks in the aromatic region (127-139 ppm) and a cluster of peaks in the aliphatic region (52-63 ppm). A solvent peak is visible at approximately 30 ppm.

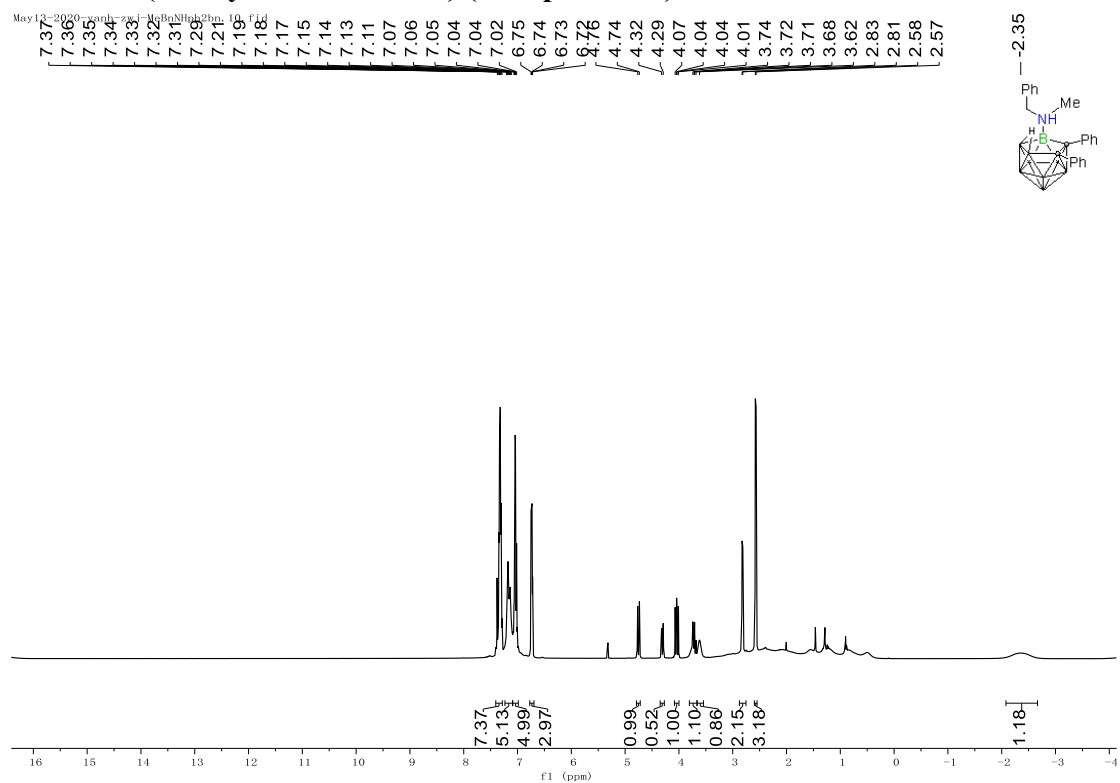
Chemical structure of compound 10 is shown in the top right corner. The structure is a complex organotin compound featuring a central tin atom (Sn) bonded to a phenyl group (Ph), a chlorine atom (Cl), and a complex ligand system. The ligand system includes a tin atom (Sn) bonded to a phenyl group (Ph), a chlorine atom (Cl), and a complex ligand system. The ligand system includes a tin atom (Sn) bonded to a phenyl group (Ph), a chlorine atom (Cl), and a complex ligand system.



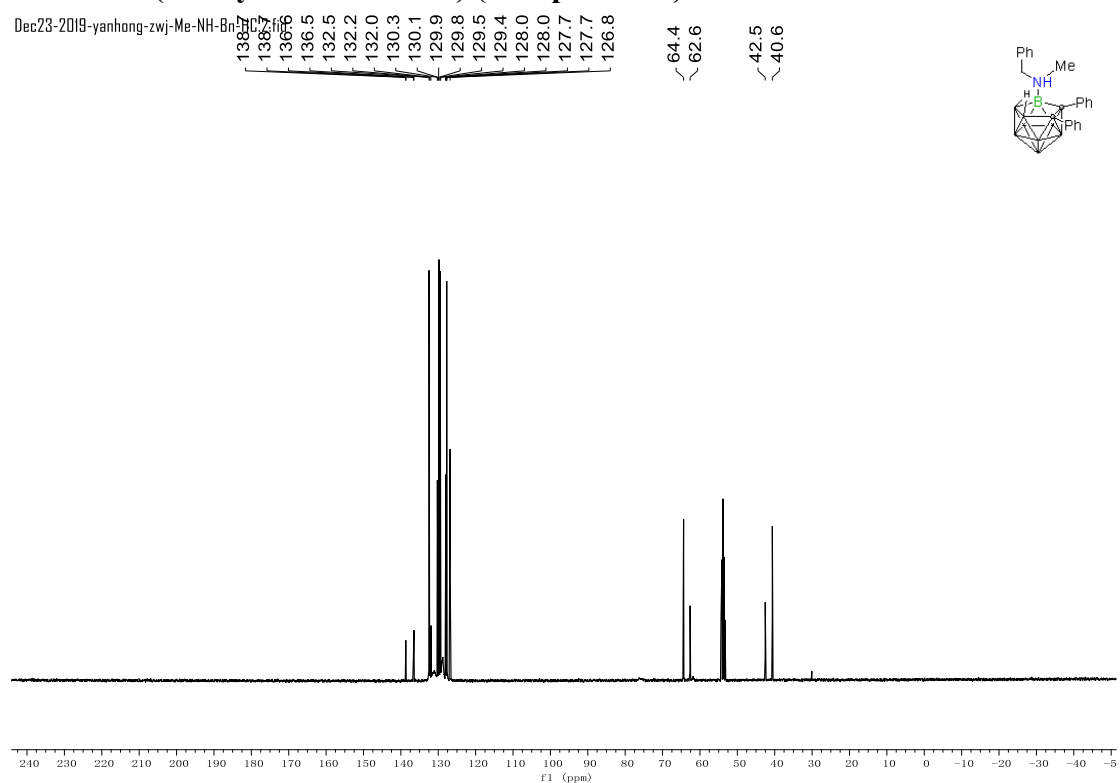
Chemical structure of compound 10 is shown in the top right corner. The structure is a complex molecule with a central core and various substituents, including a chlorine atom and a phenyl group.



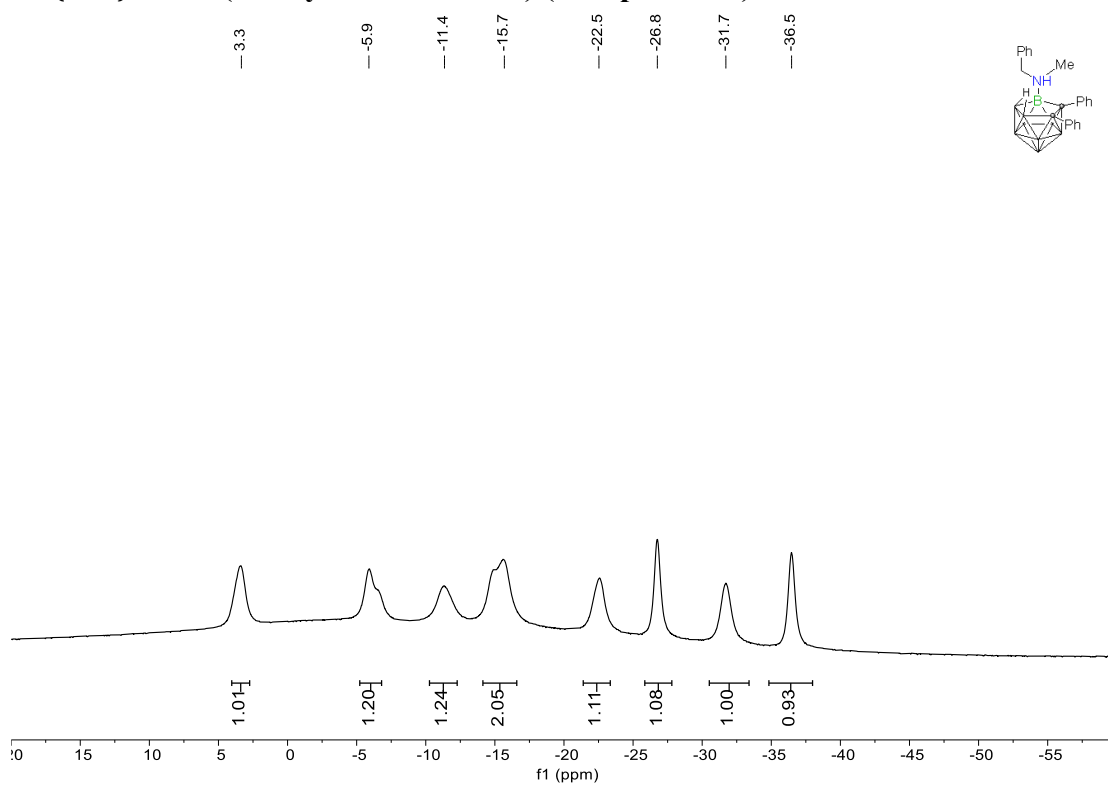
¹H NMR (Methylene Chloride-*d*₂) (Compound 3f)



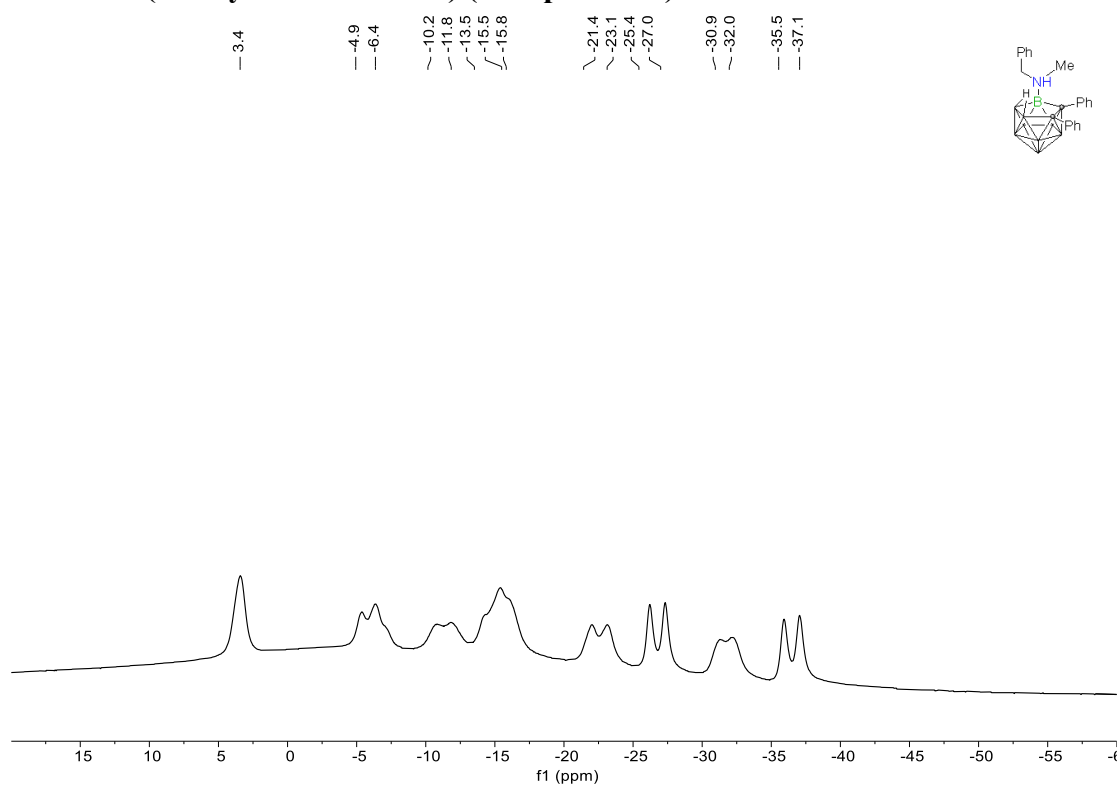
¹³C NMR (Methylene Chloride-*d*₂) (Compound 3f)



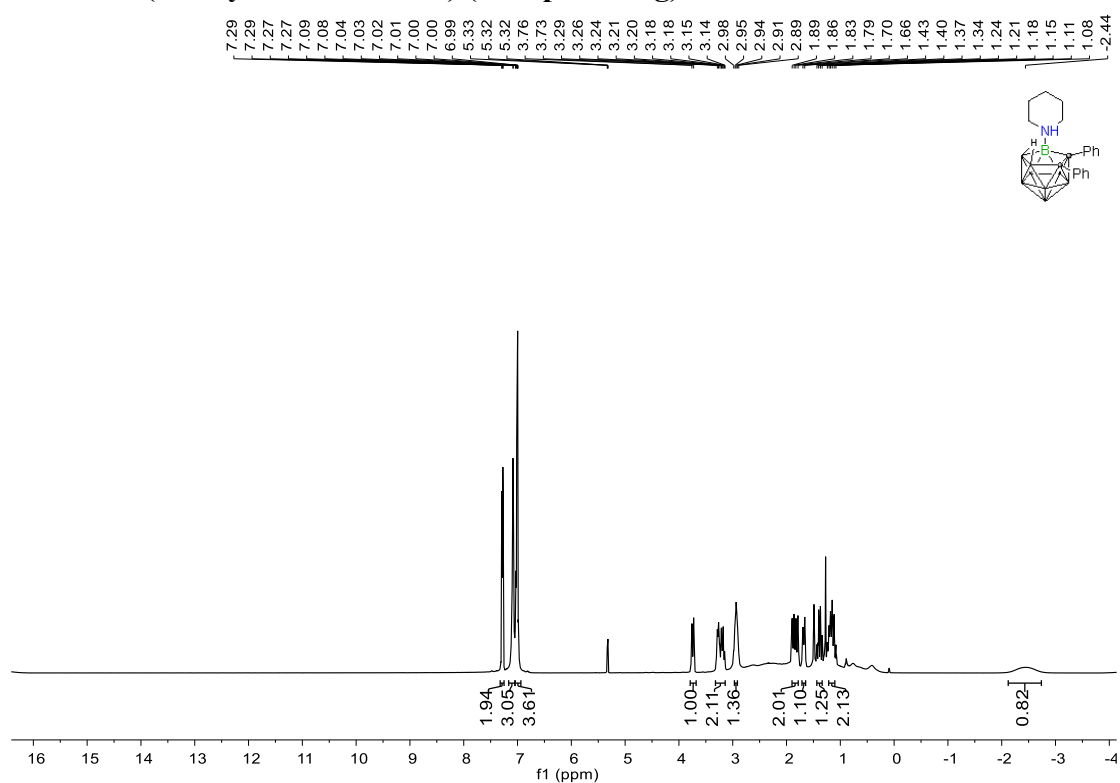
¹¹B{ ¹H } NMR (Methylene Chloride-*d*₂) (Compound 3f)



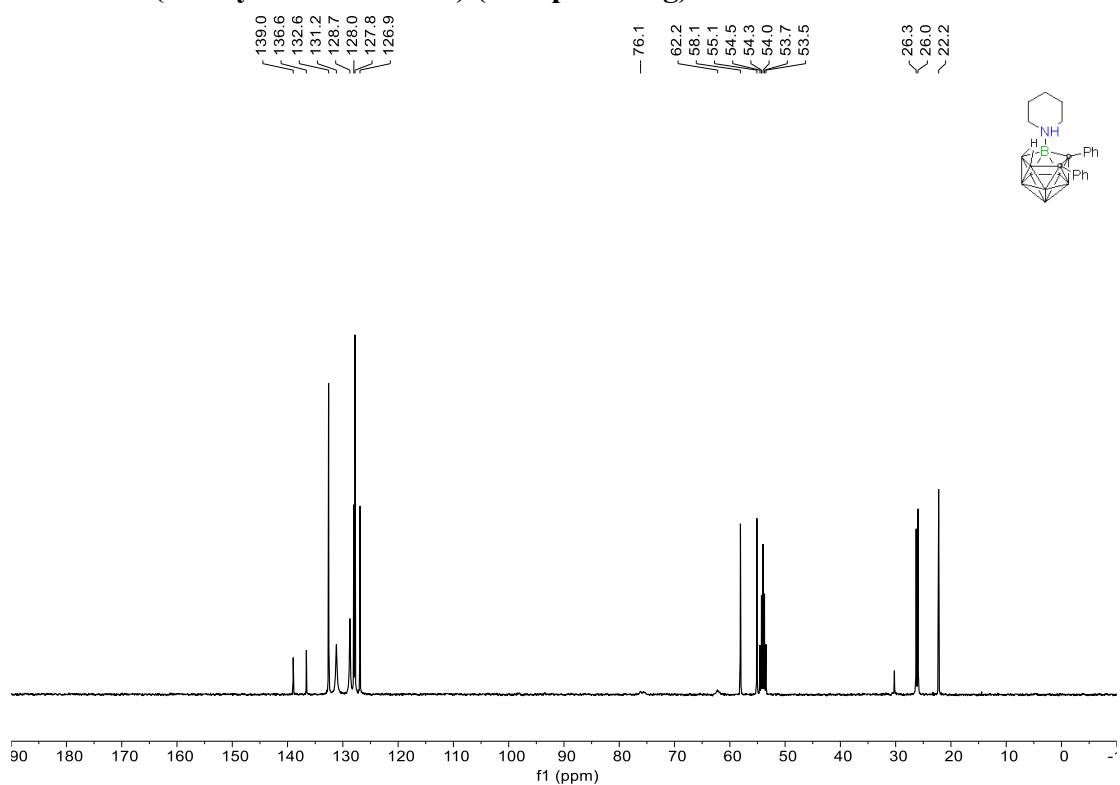
¹¹B NMR (Methylene Chloride-*d*₂) (Compound 3f)



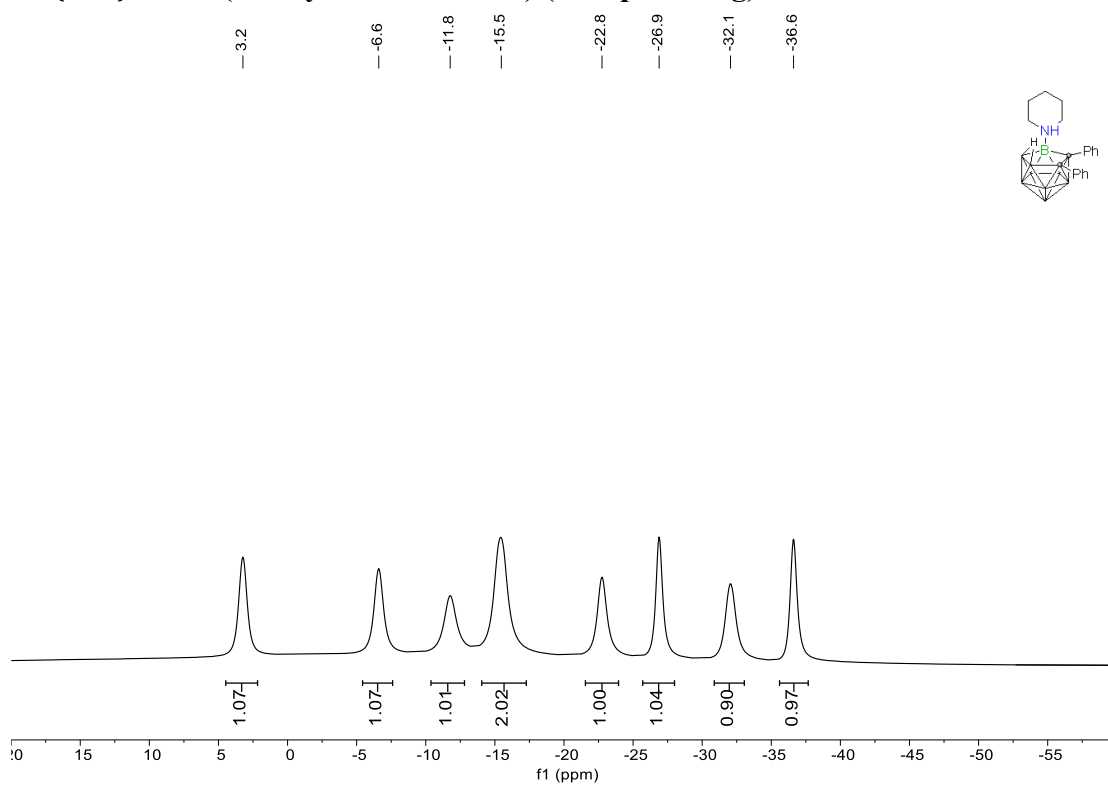
¹H NMR (Methylene Chloride-*d*₂) (Compound 3g)



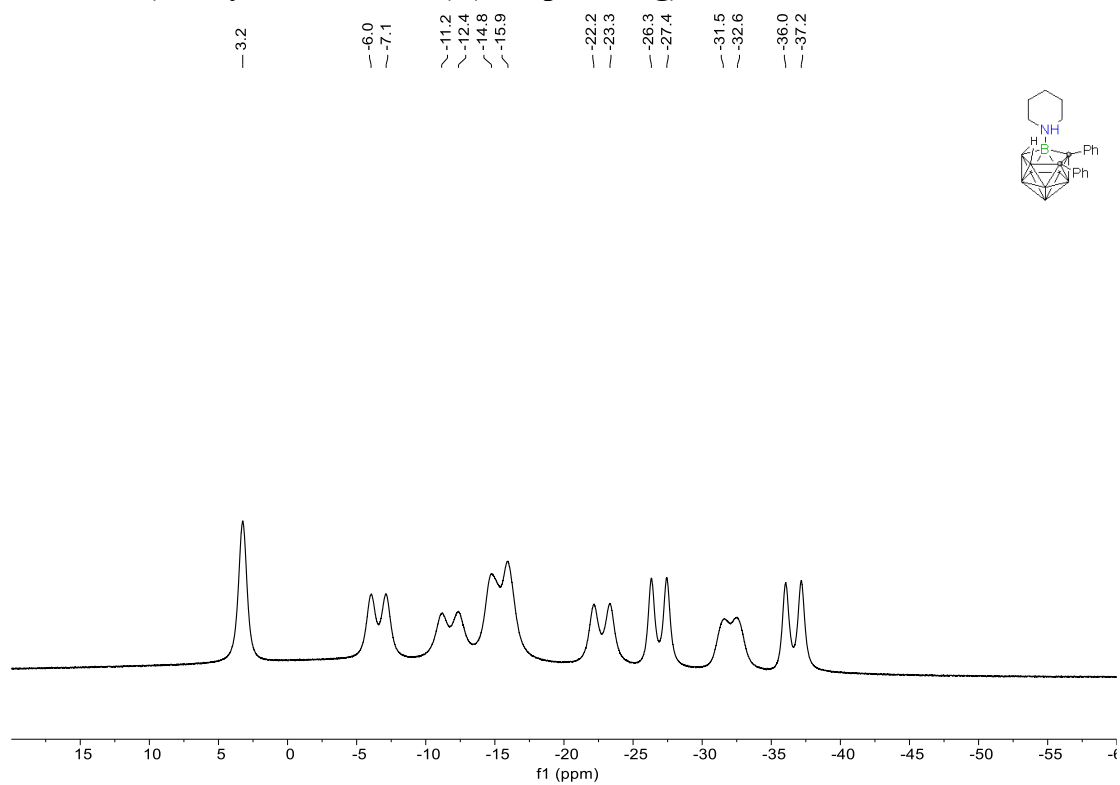
¹³C NMR (Methylene Chloride-*d*₂) (Compound 3g)



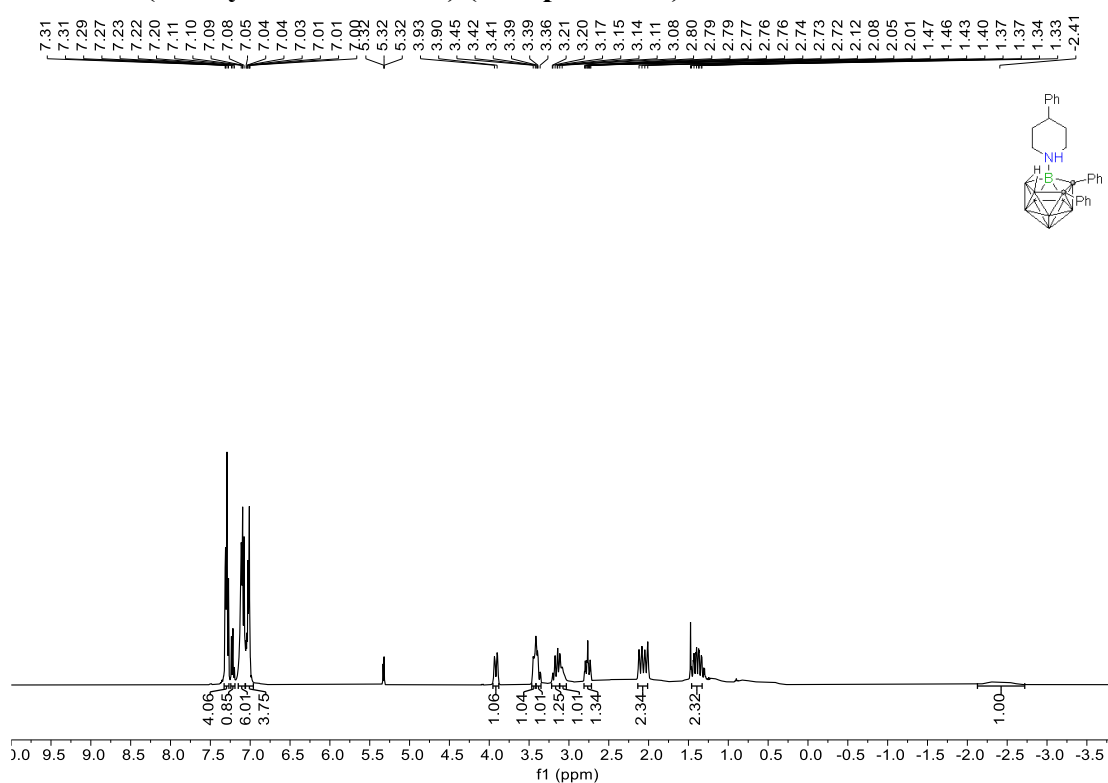
$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 3g)



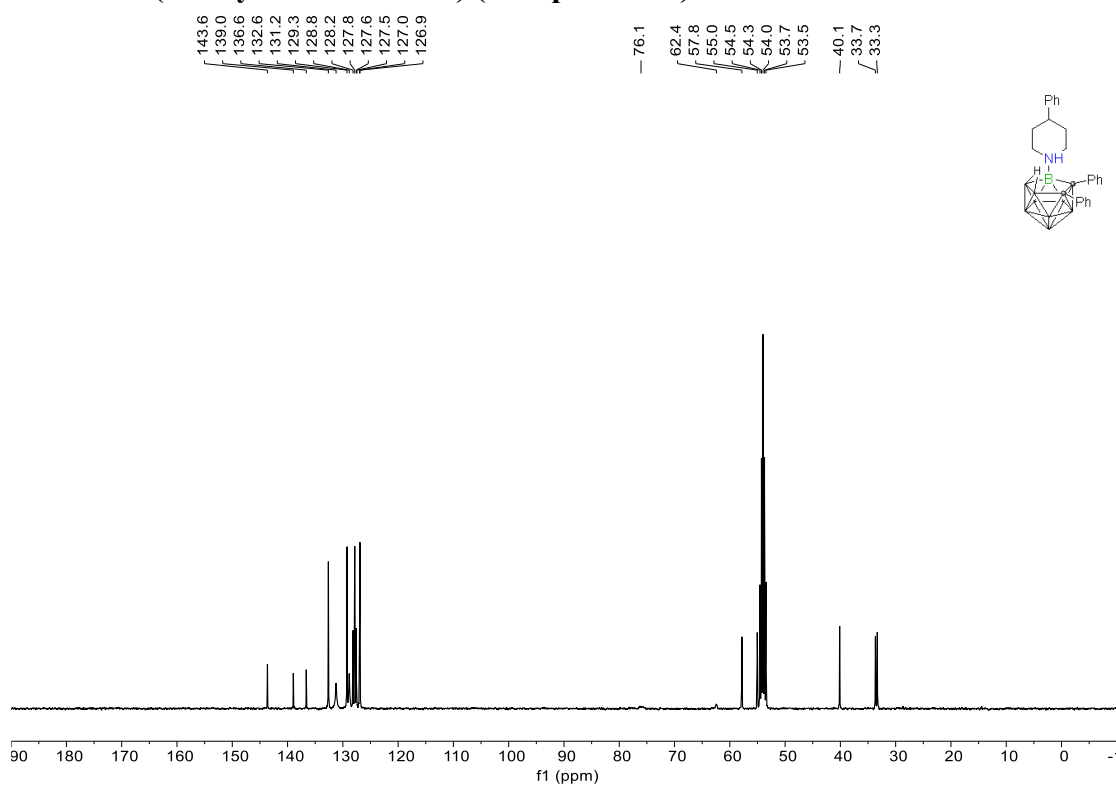
^{11}B NMR (Methylene Chloride- d_2) (Compound 3g)



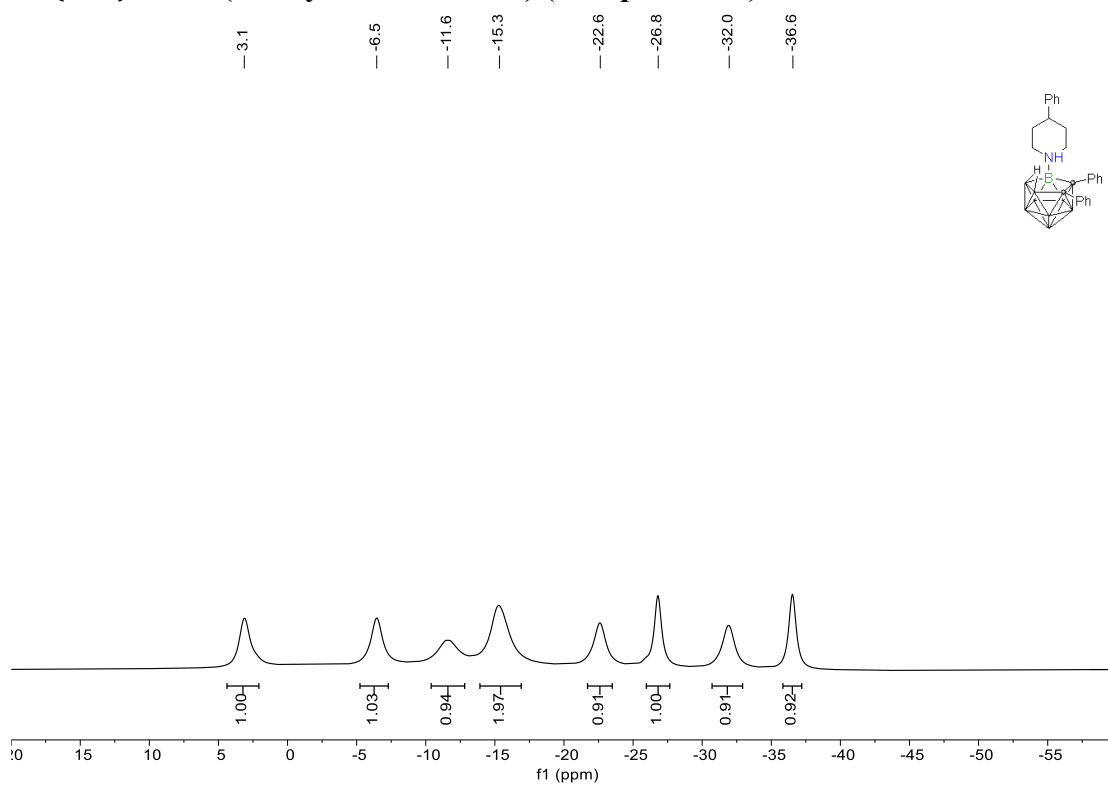
^1H NMR (Methylene Chloride- d_2) (Compound 3h)



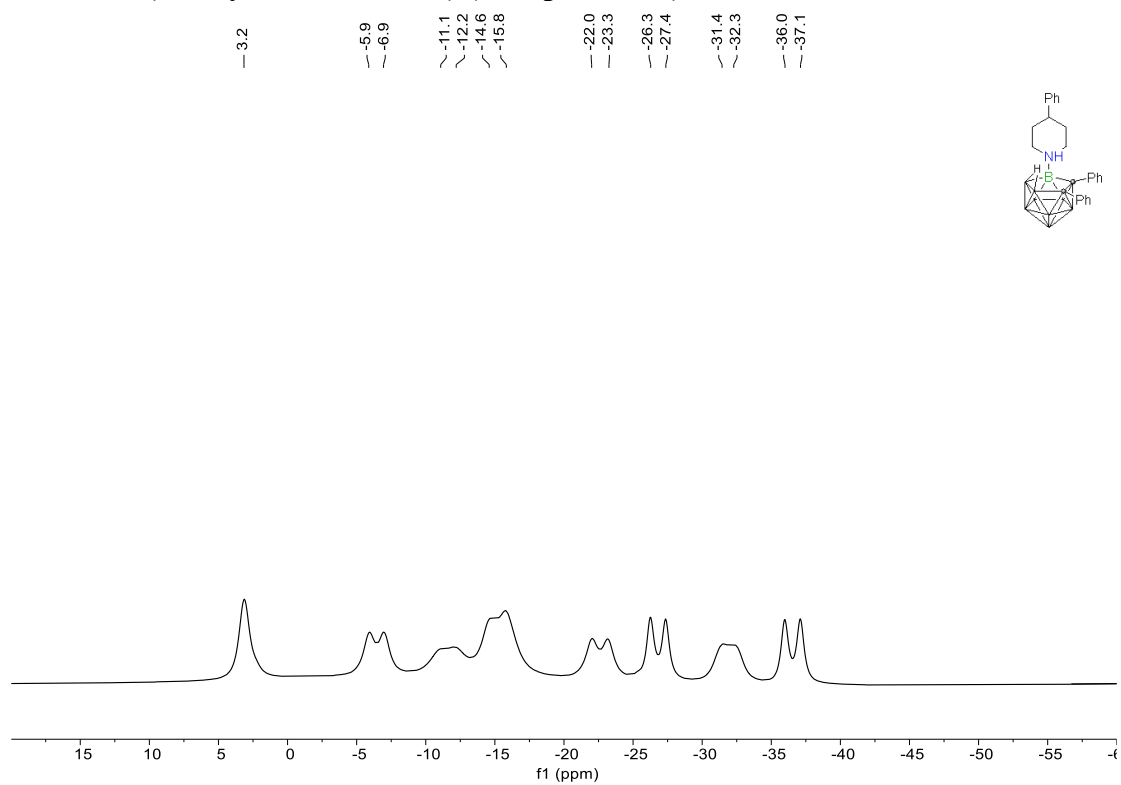
^{13}C NMR (Methylene Chloride- d_2) (Compound 3h)



$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 3h)



^{11}B NMR (Methylene Chloride- d_2) (Compound 3h)



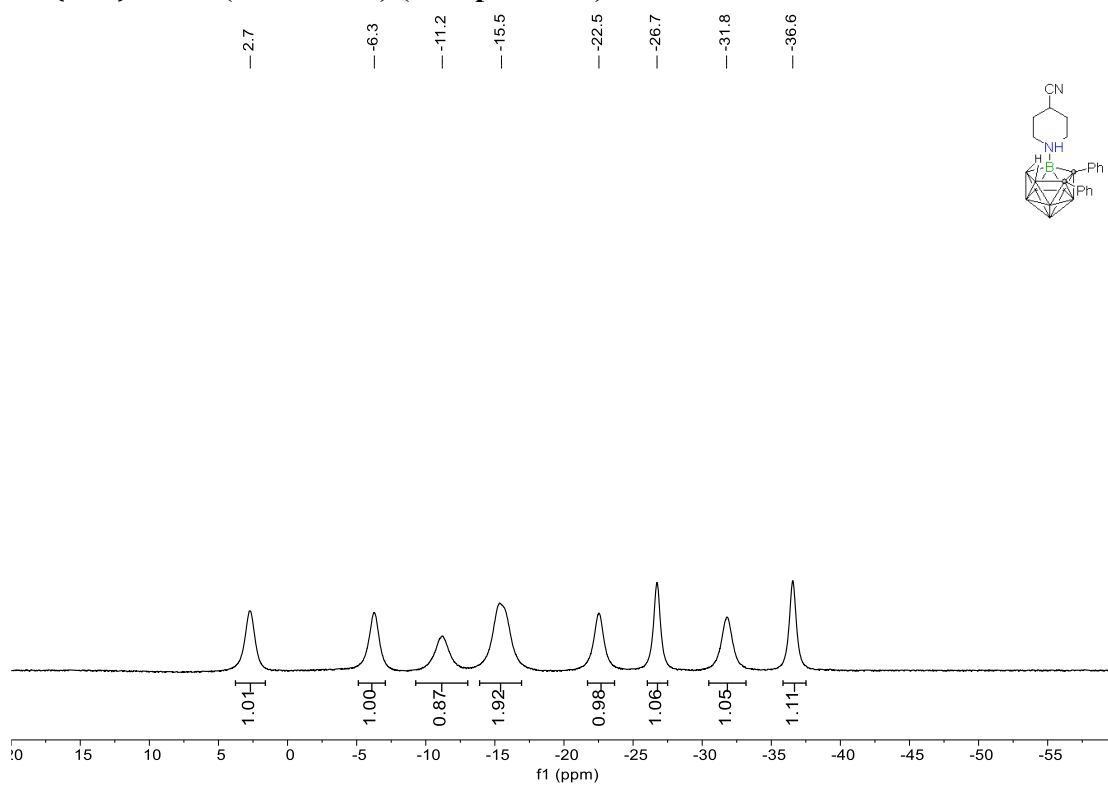
[illegible]

Chemical Structure: 1-(4-cyanophenyl)-1,2,3,4,5,6-hexaphenylbenzene

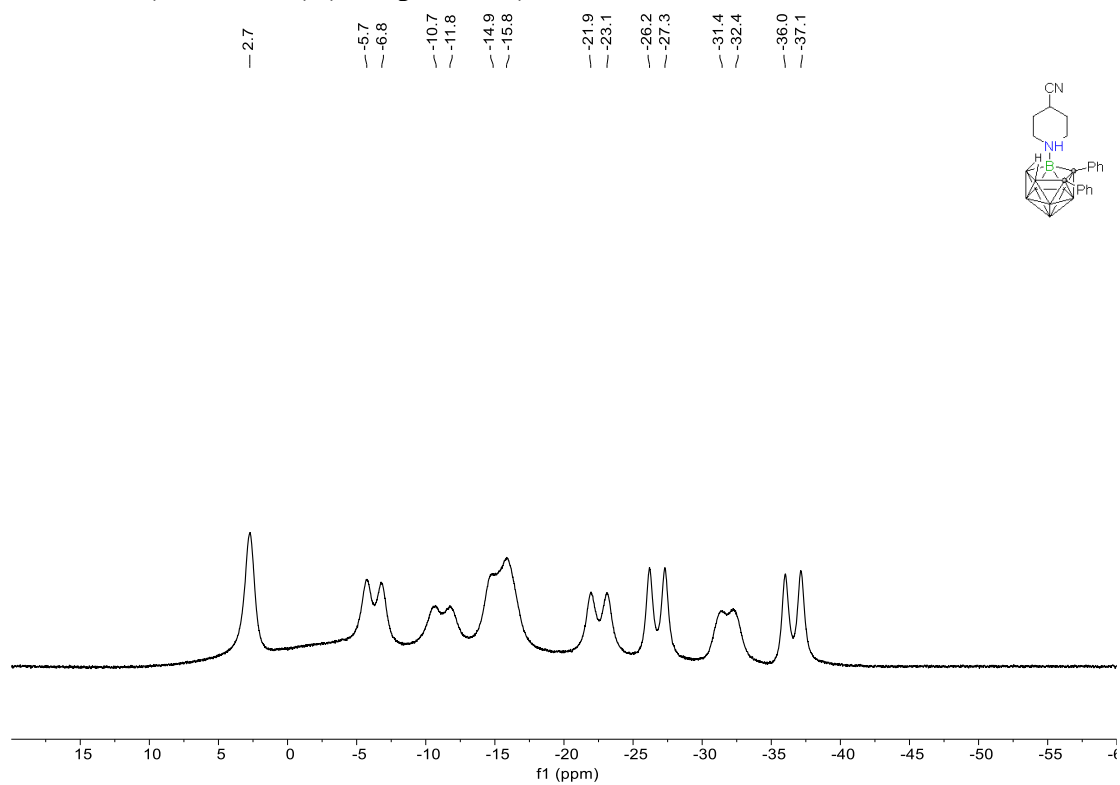
¹³C NMR Peaks (ppm):

- 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

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



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



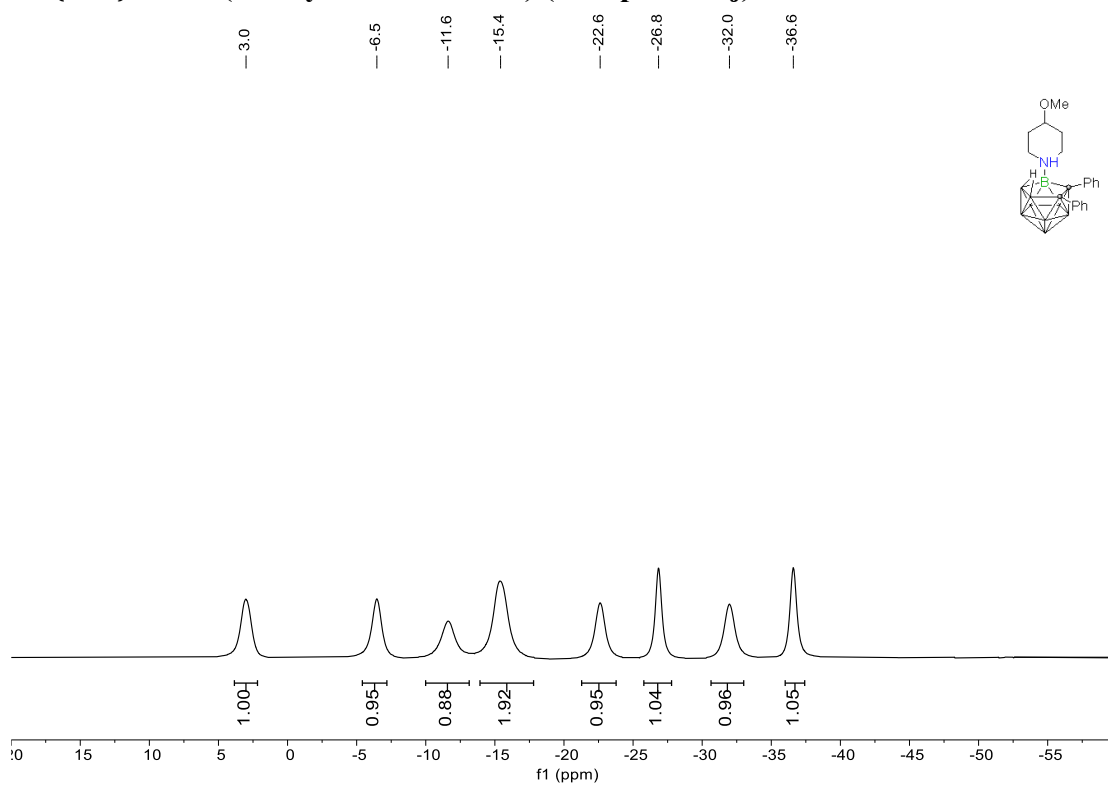
[illegible]

Chemical structure of compound 10 is shown in the top right corner. The structure is a naphthalene derivative with a 4-methoxyphenyl group and a 2-phenyl-2-phenyl-1H-imidazole substituent.

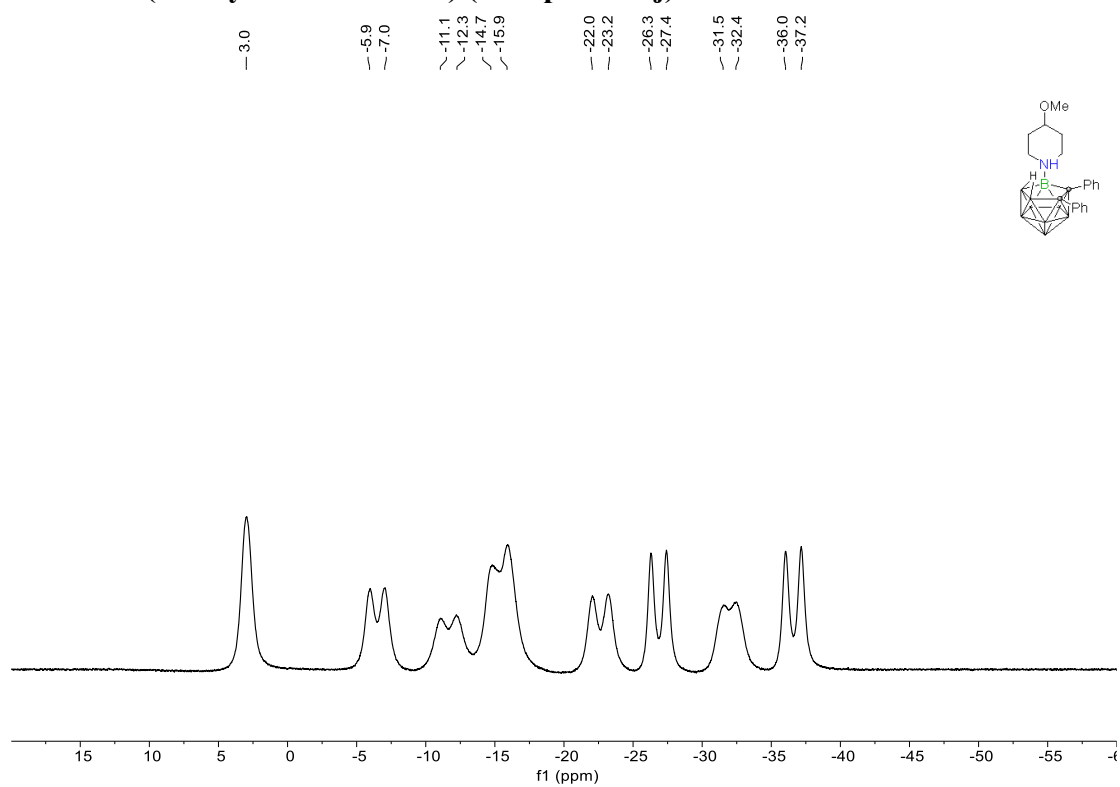
The ^{13}C NMR spectrum (f1 (ppm)) shows the following chemical shifts (ppm):

- 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

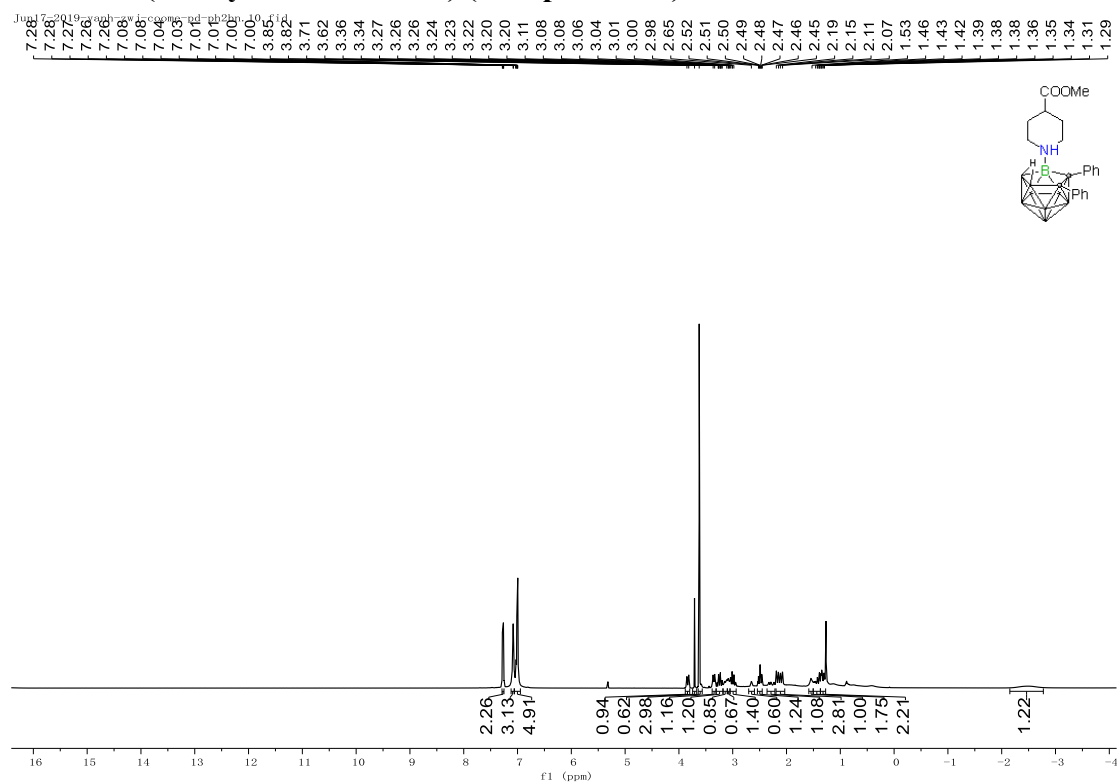
$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 3j)



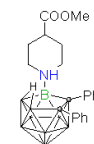
^{11}B NMR (Methylene Chloride- d_2) (Compound 3j)



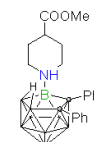
¹H NMR (Methylene Chloride-*d*₂) (Compound 3k)



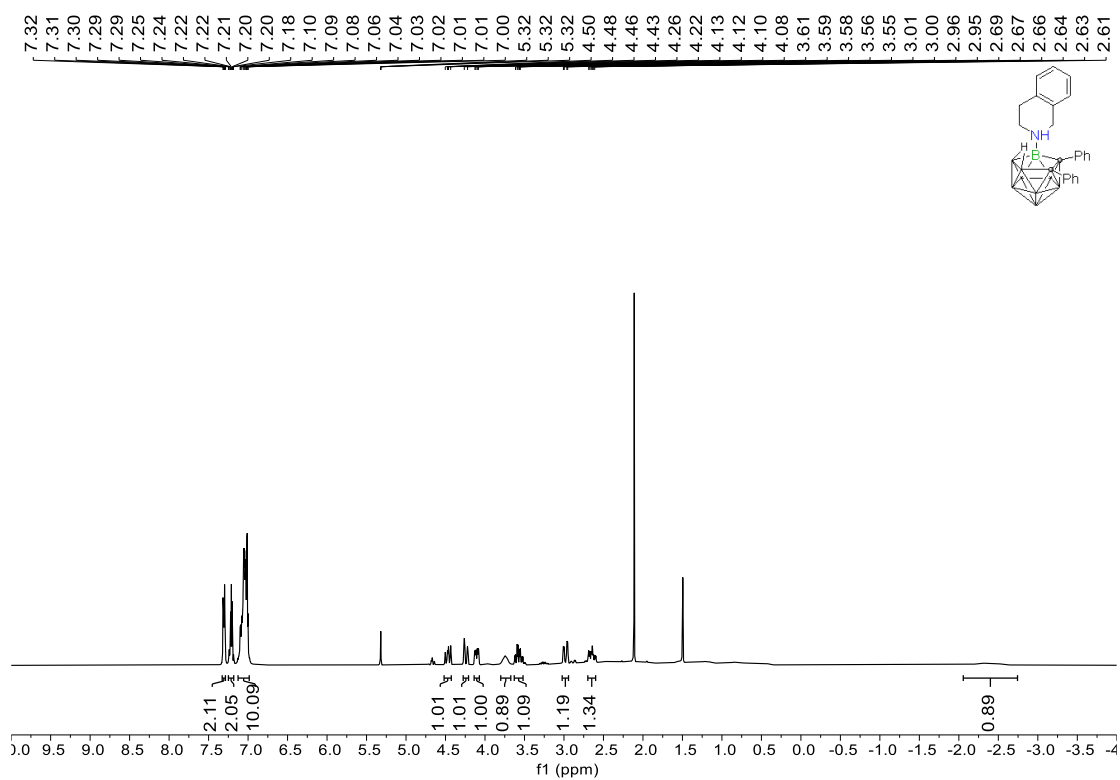
Jun17-2019-yanh-zwj-coome-pd-ph2bn.11.fid



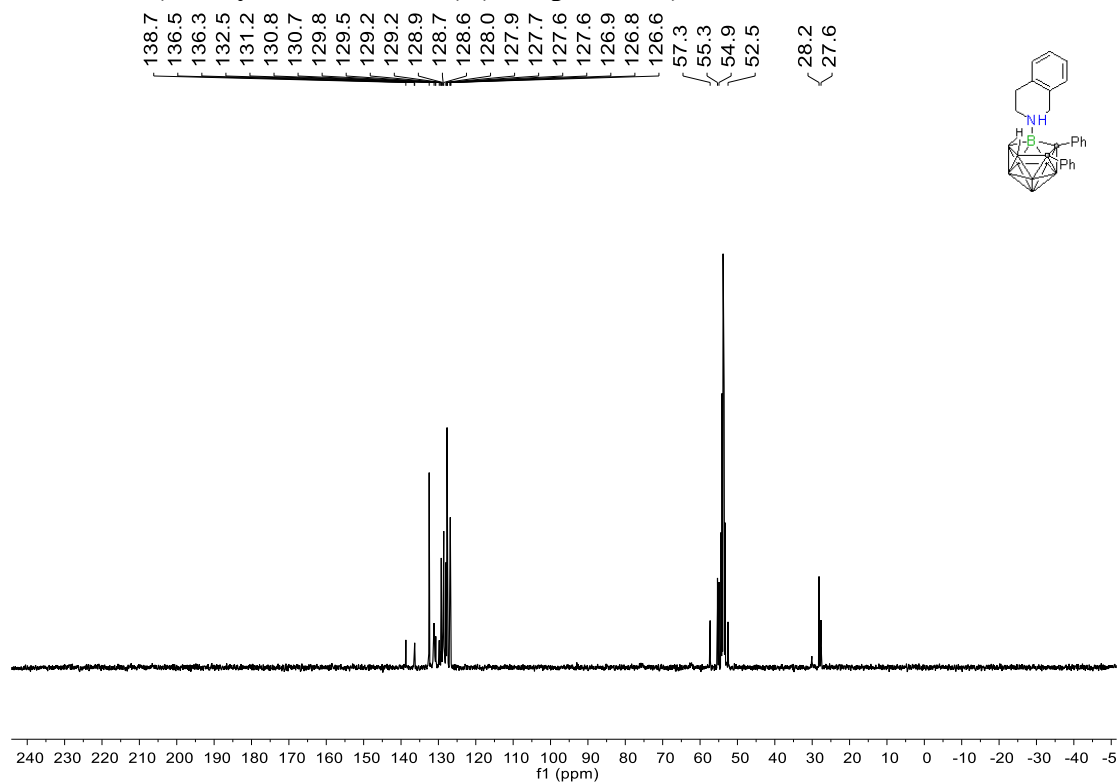
Jun17-2019-yanh-zwj-coome-pd-ph2bn. 12. fid



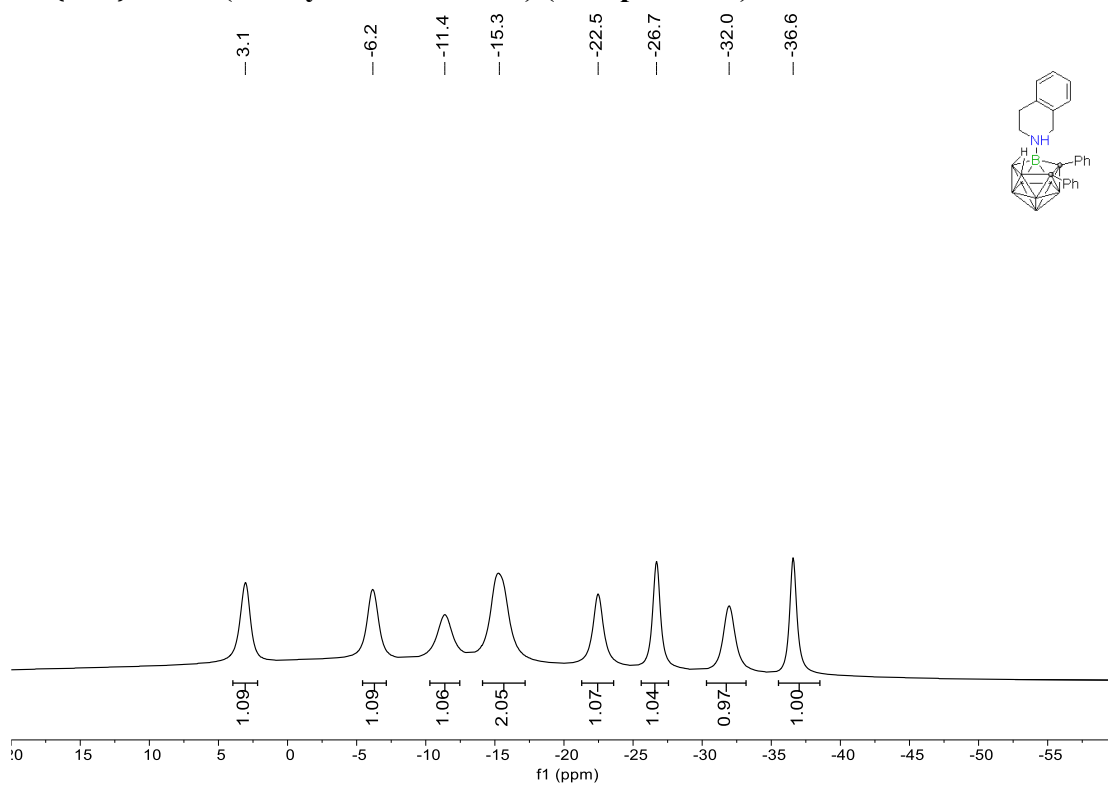
^1H NMR (Methylene Chloride- d_2) (Compound 3l)



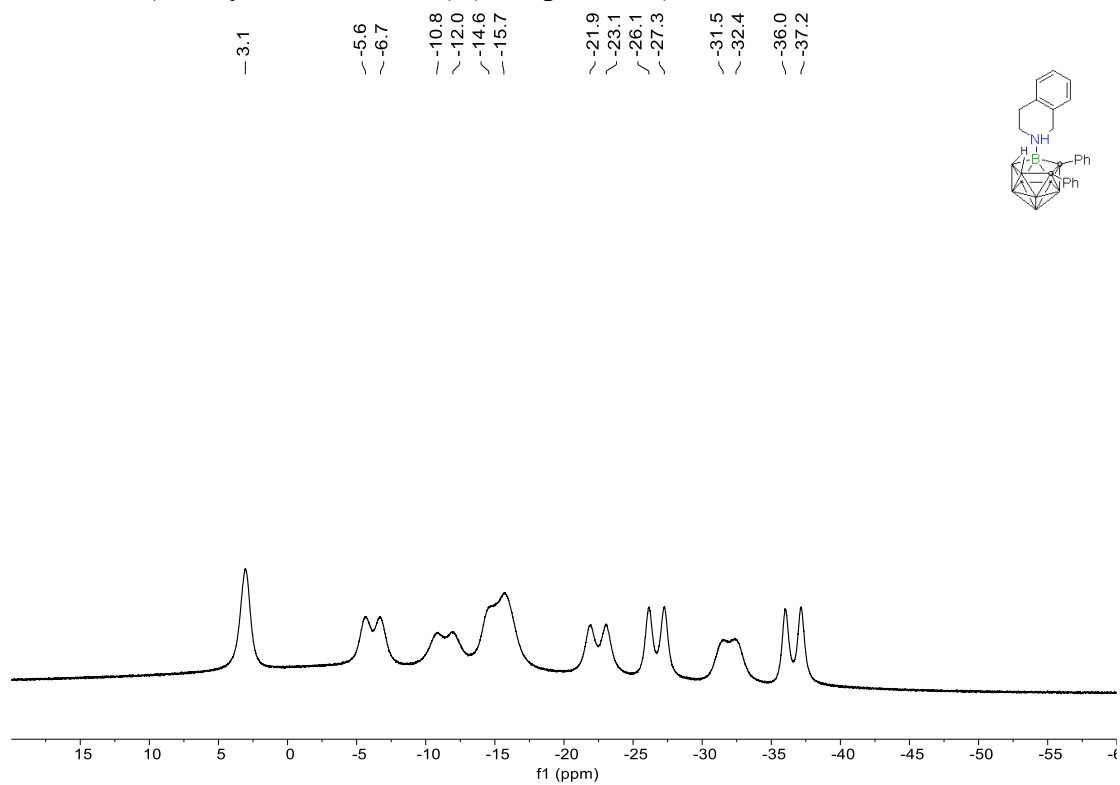
^{13}C NMR (Methylene Chloride- d_2) (Compound 3l)



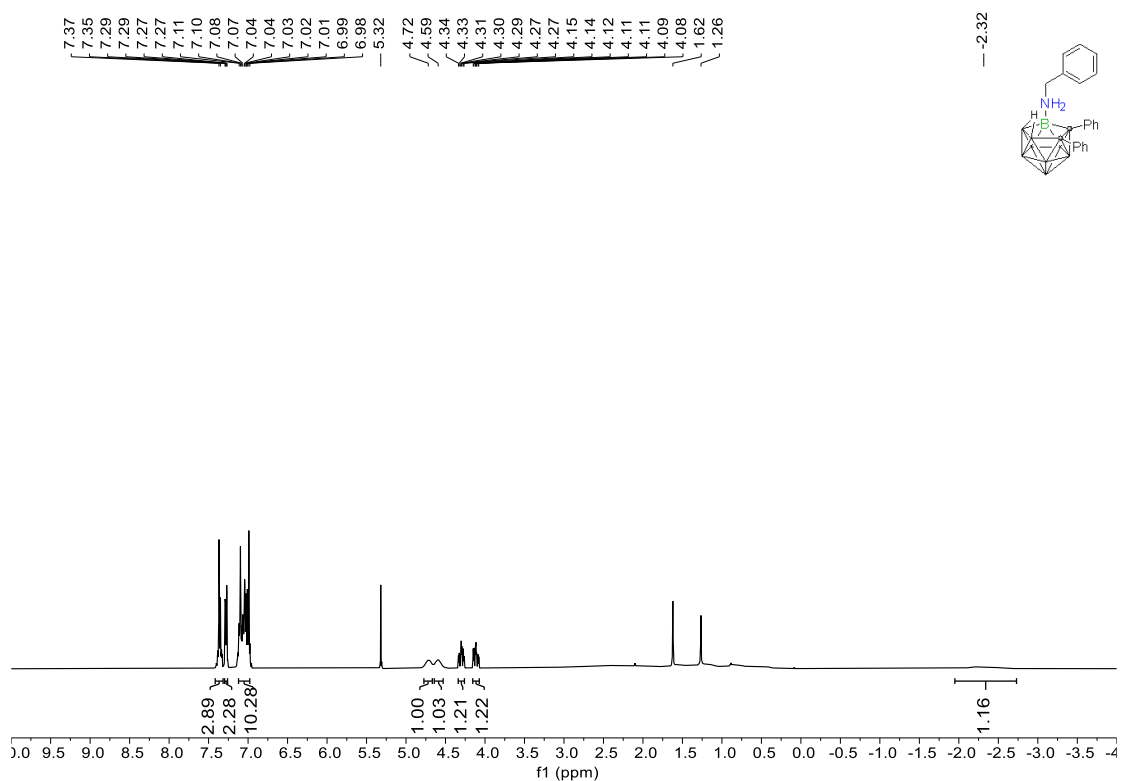
$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 3l)



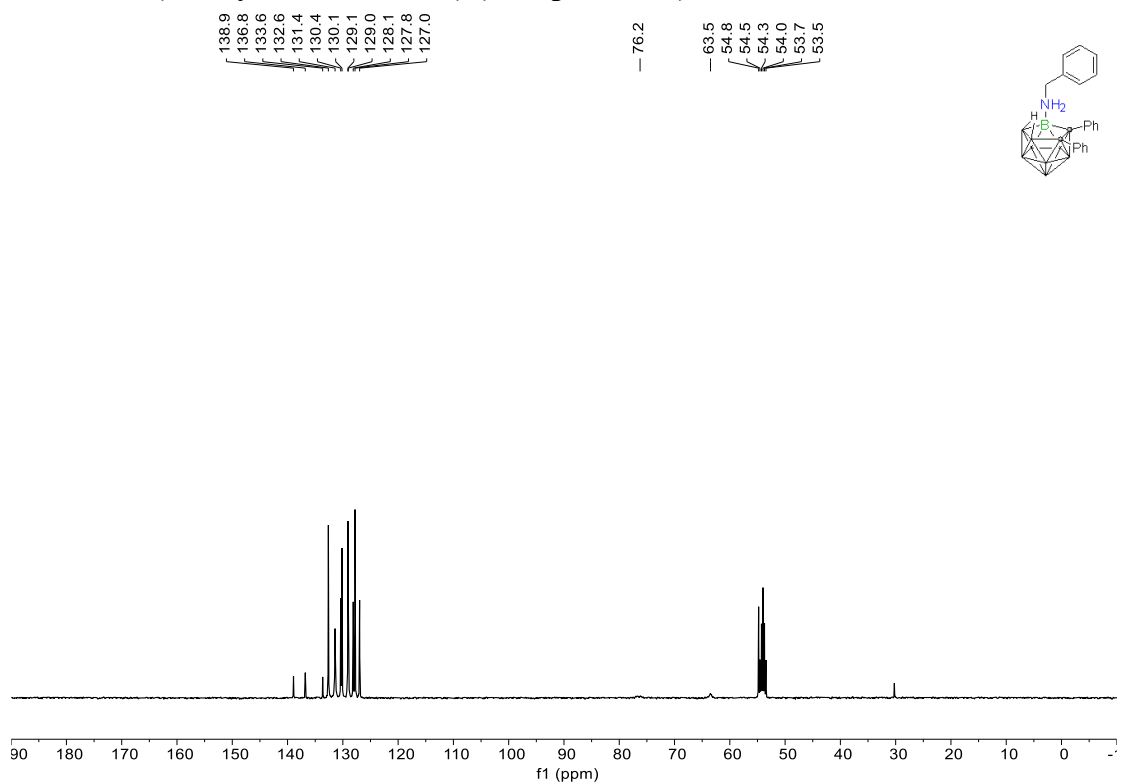
^{11}B NMR (Methylene Chloride- d_2) (Compound 3l)



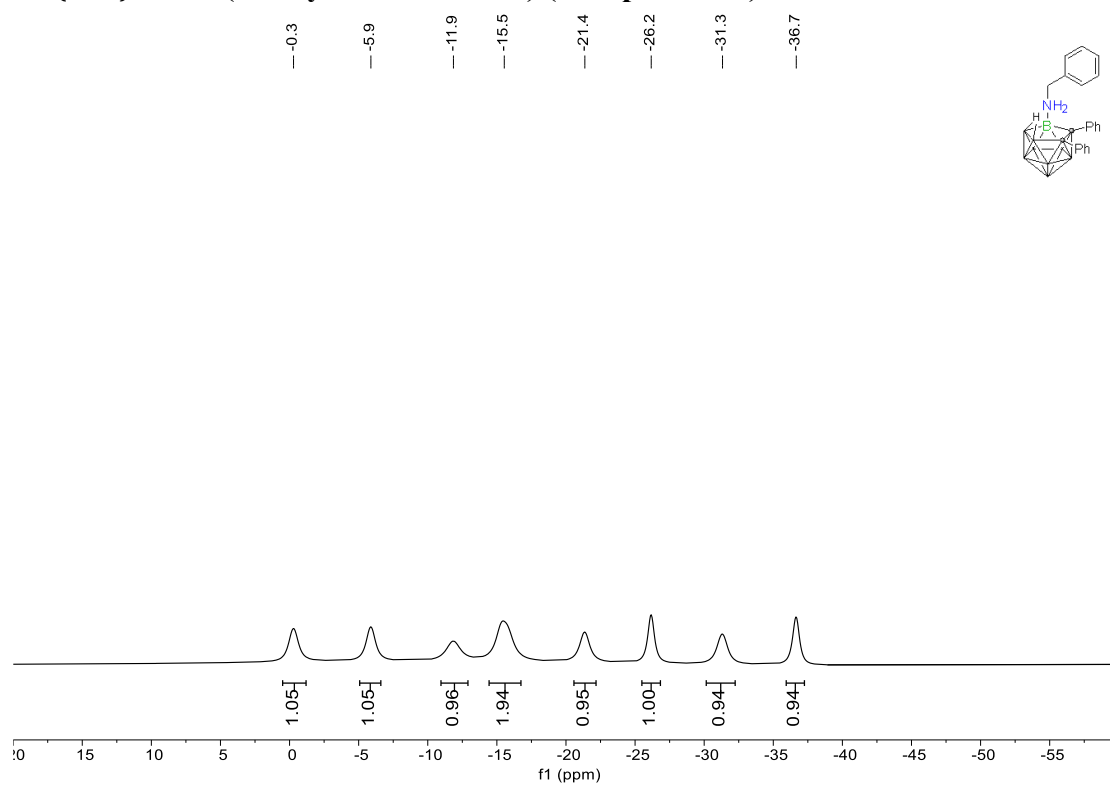
^1H NMR (Methylene Chloride- d_2) (Compound 4a)



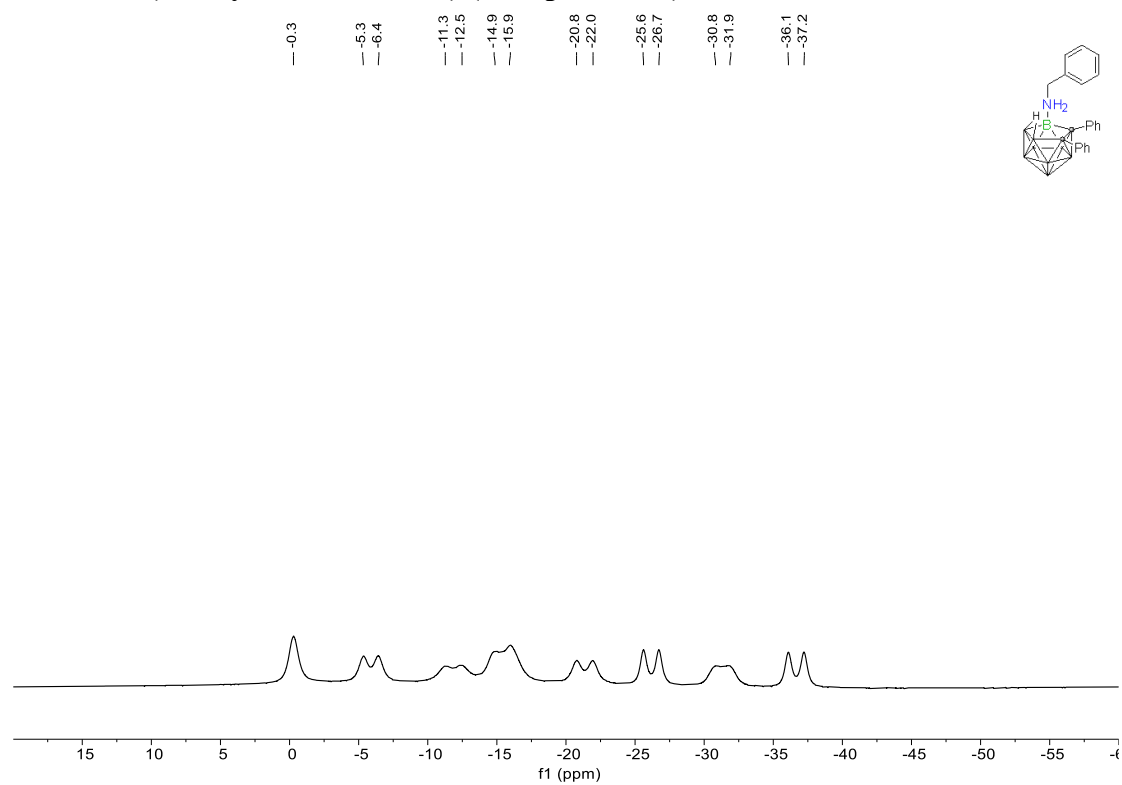
^{13}C NMR (Methylene Chloride- d_2) (Compound 4a)



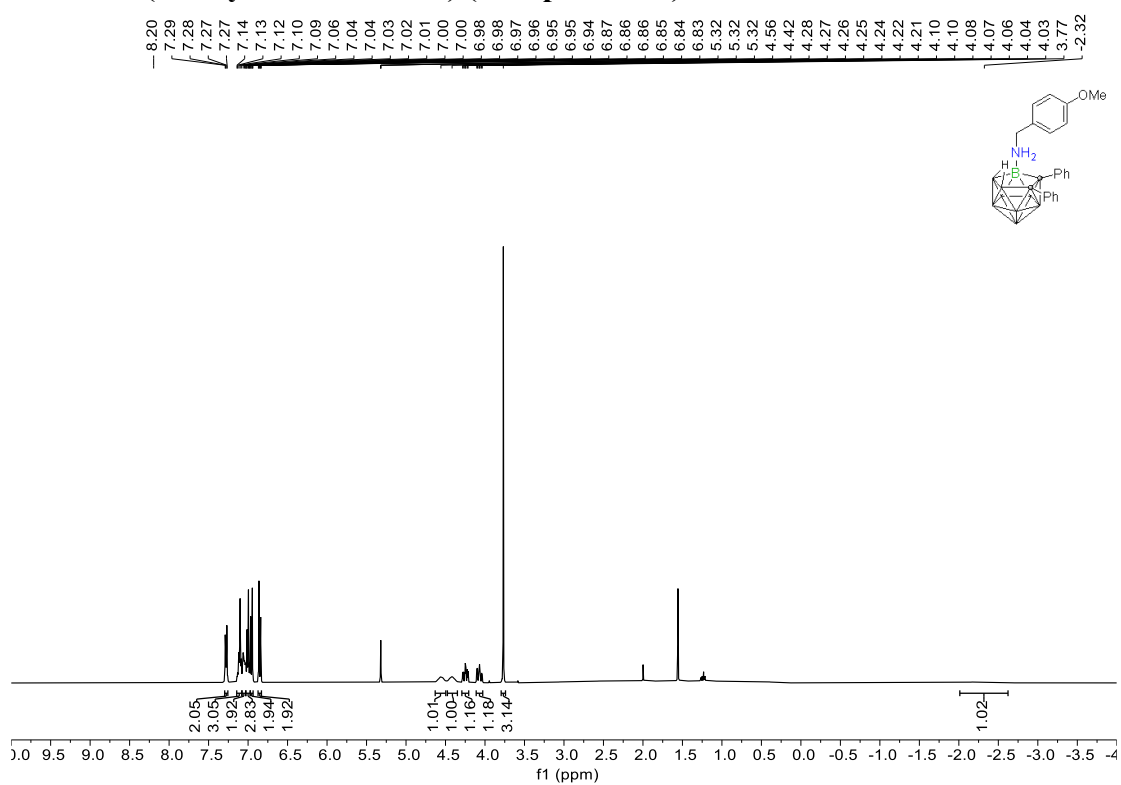
$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 4a)



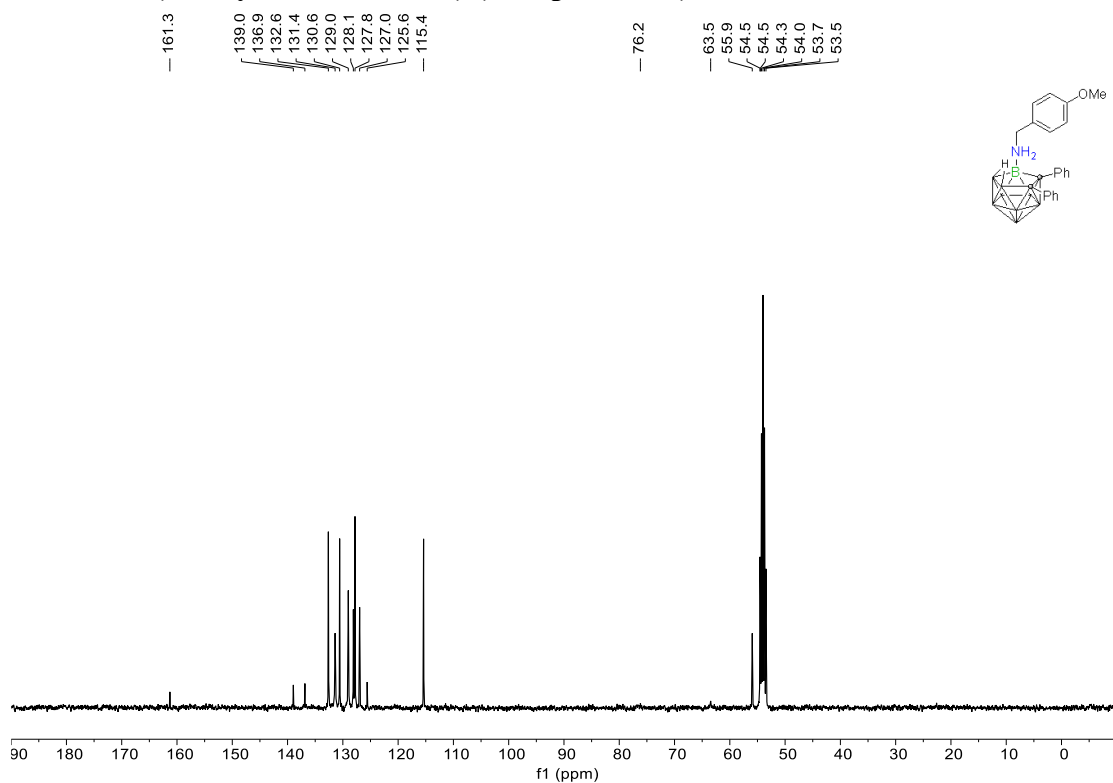
^{11}B NMR (Methylene Chloride- d_2) (Compound 4a)



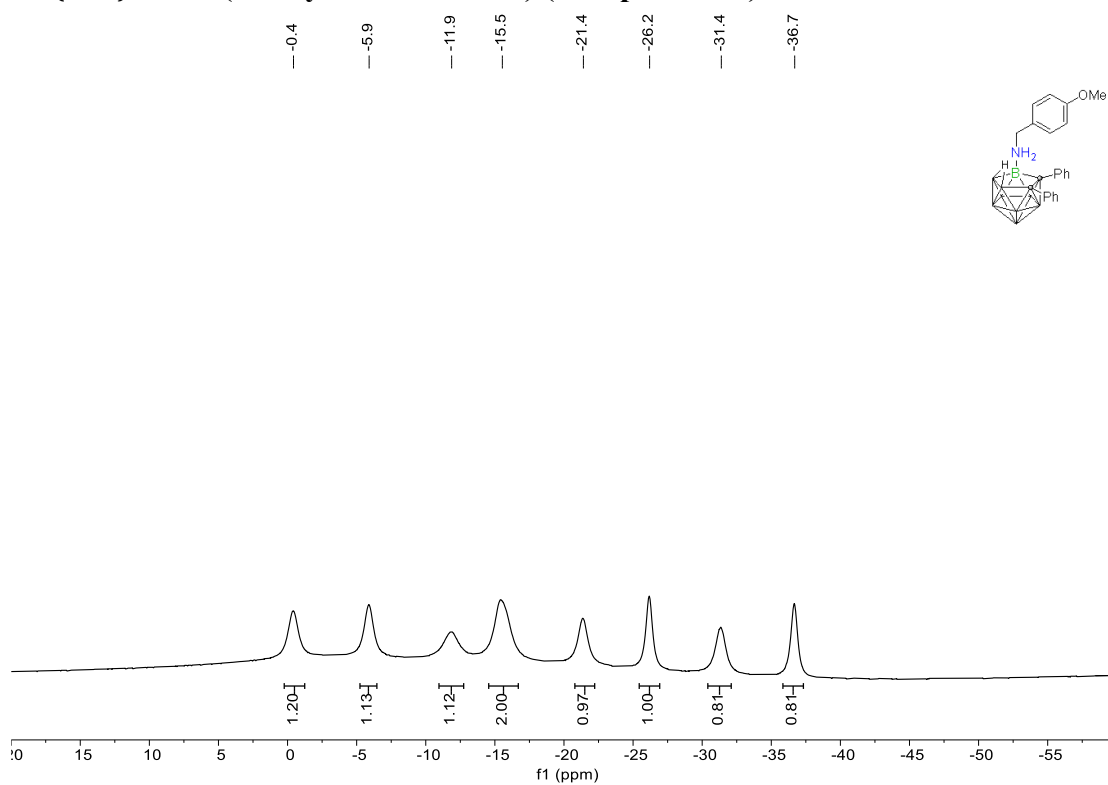
^1H NMR (Methylene Chloride- d_2) (Compound 4b)



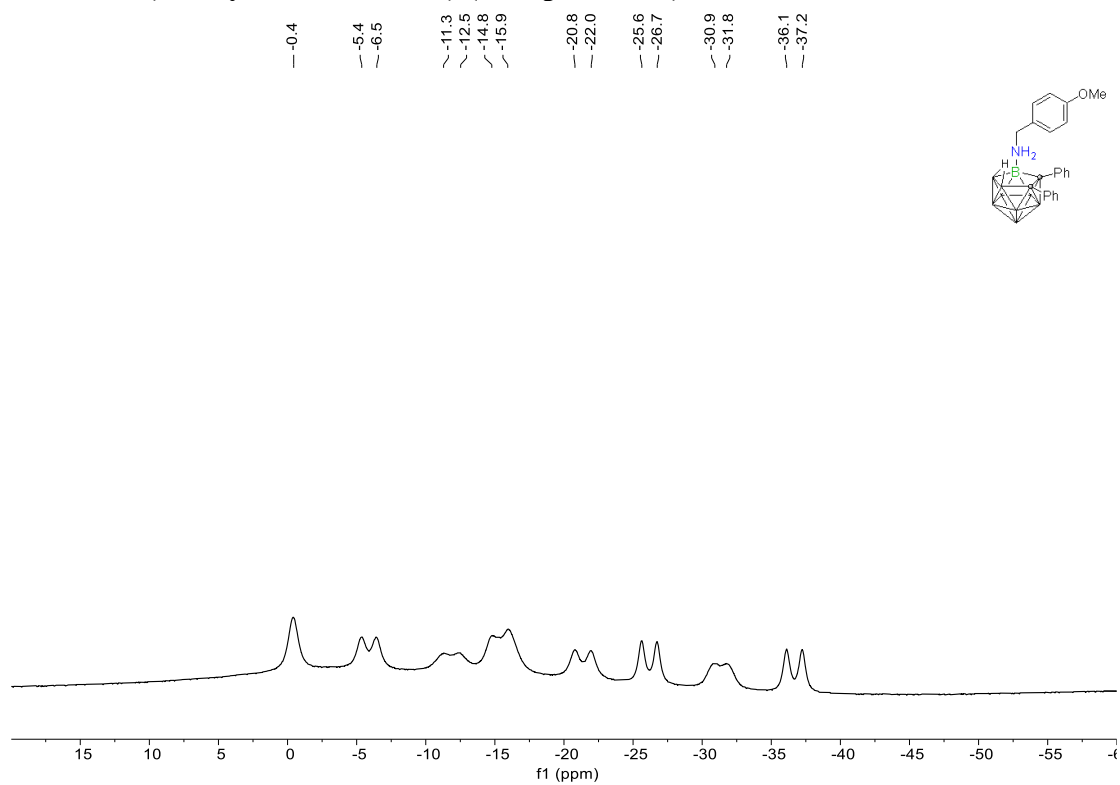
^{13}C NMR (Methylene Chloride- d_2) (Compound 4b)



$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 4b)



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



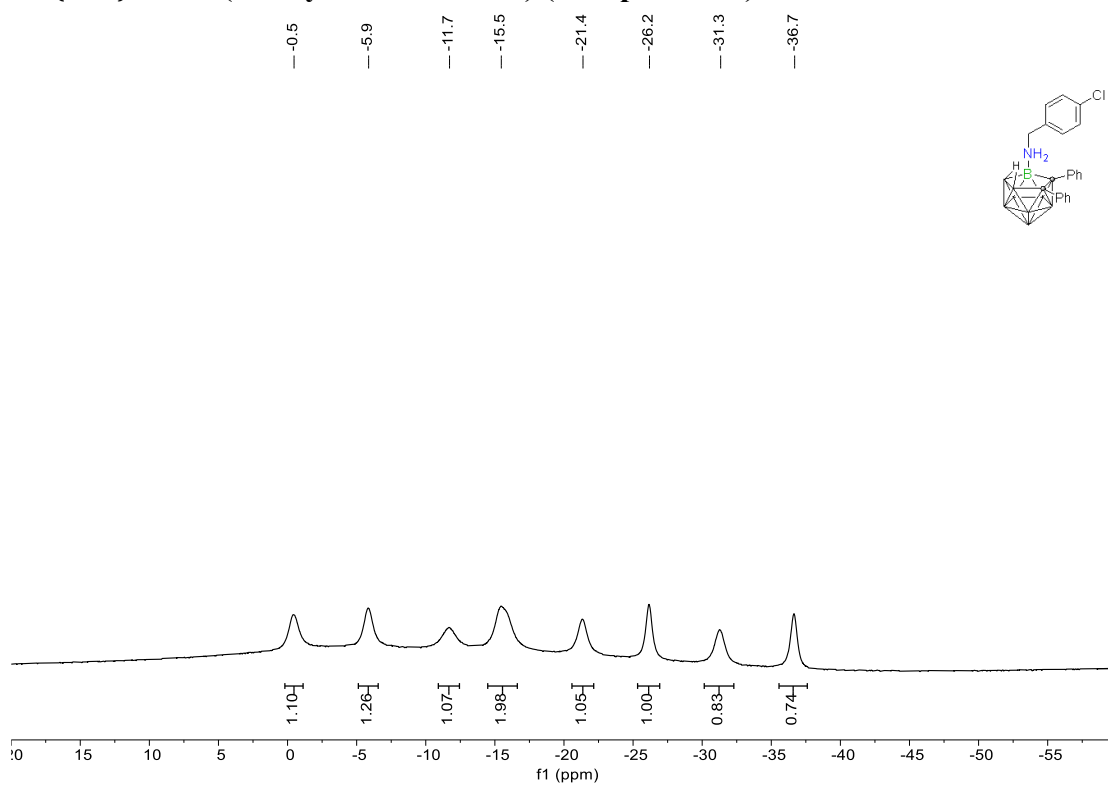
¹H NMR spectrum of compound **10** in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from 0 to 10. The spectrum shows several peaks, with integration values provided below the baseline. The chemical structure of compound **10** is shown in the top right corner.

Chemical structure of compound **10**: N[C@@H]1[C@H]2[C@H]3[C@H]4[C@H]1[C@@H]5[C@H]2[C@@H]([C@H]3[C@H]4[C@H]5)C6=CC=CC=C6

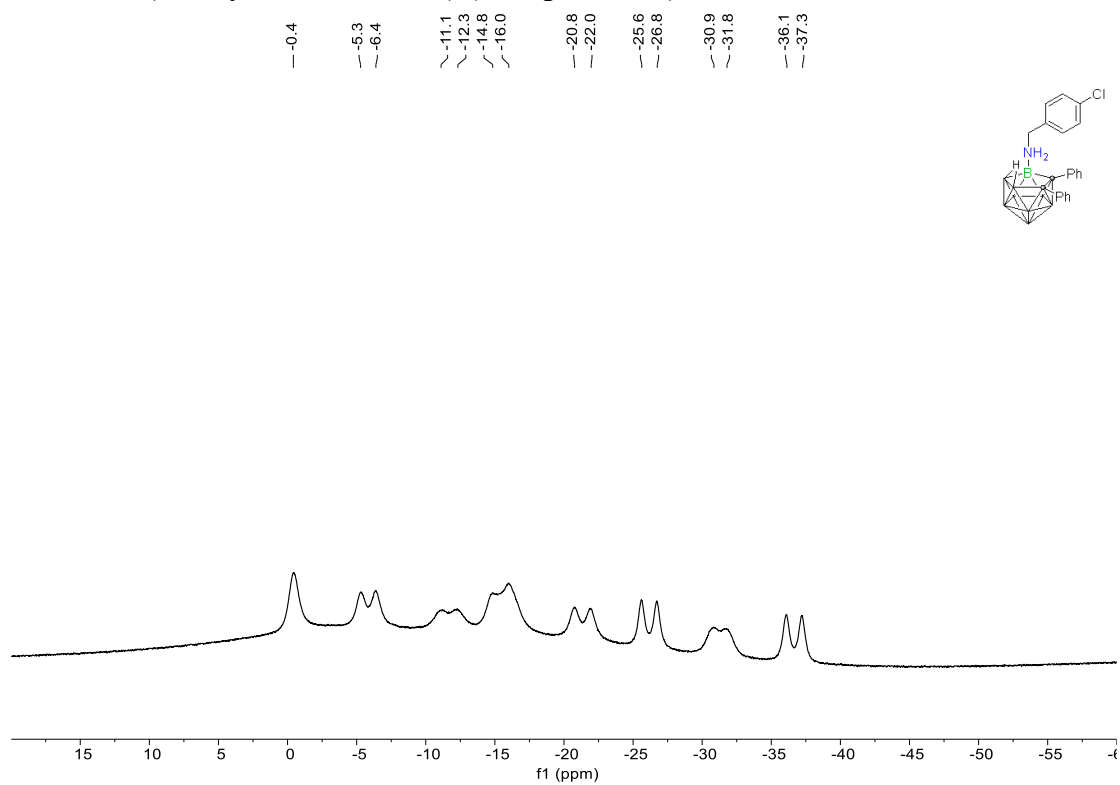
Integration values (from left to right): 1.77, 2.12, 3.08, 1.90, 4.96, 1.06, 1.05, 1.15, 1.11, and 0.94.

Chemical structure of compound 10 is shown in the top right corner. The structure is a complex molecule featuring a central boron atom (B) coordinated by a phenyl group (Ph) and a chlorine atom (Cl). The boron atom is also bonded to a nitrogen atom (N) which is part of a five-membered ring system. The nitrogen atom is further bonded to a phenyl group (Ph) and a chlorine atom (Cl). The structure is labeled with 'H' and 'NH₂' groups.

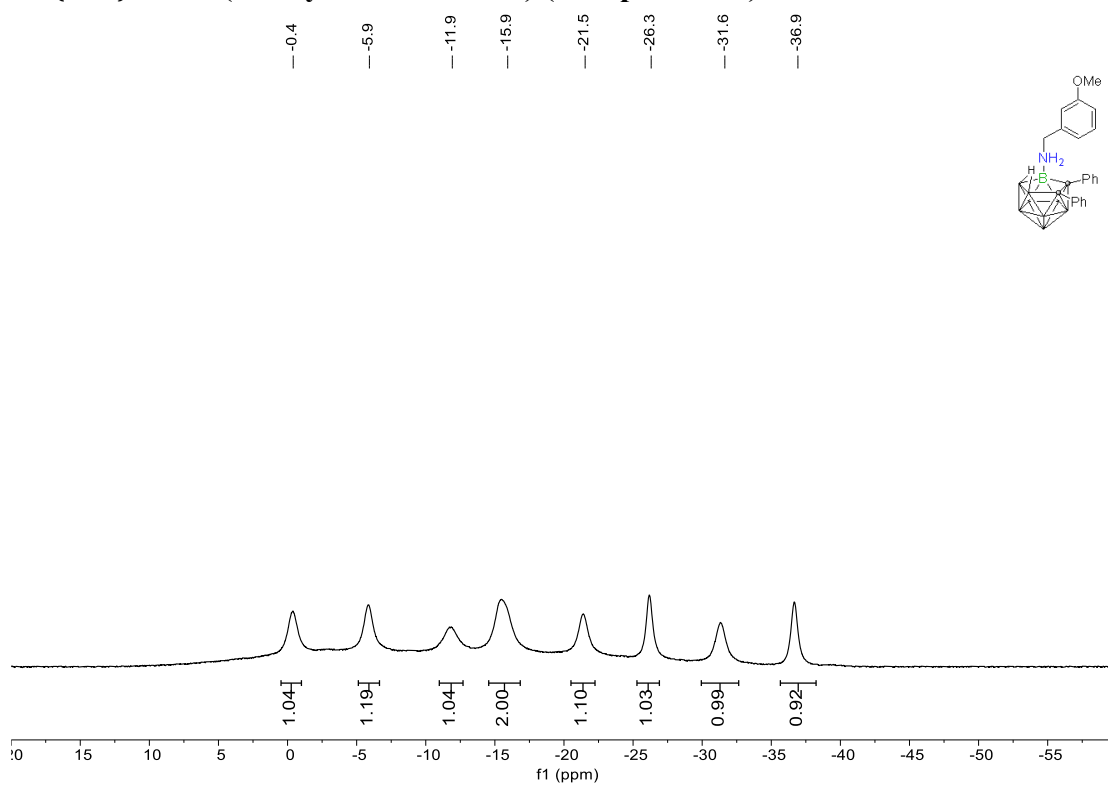
$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 4c)



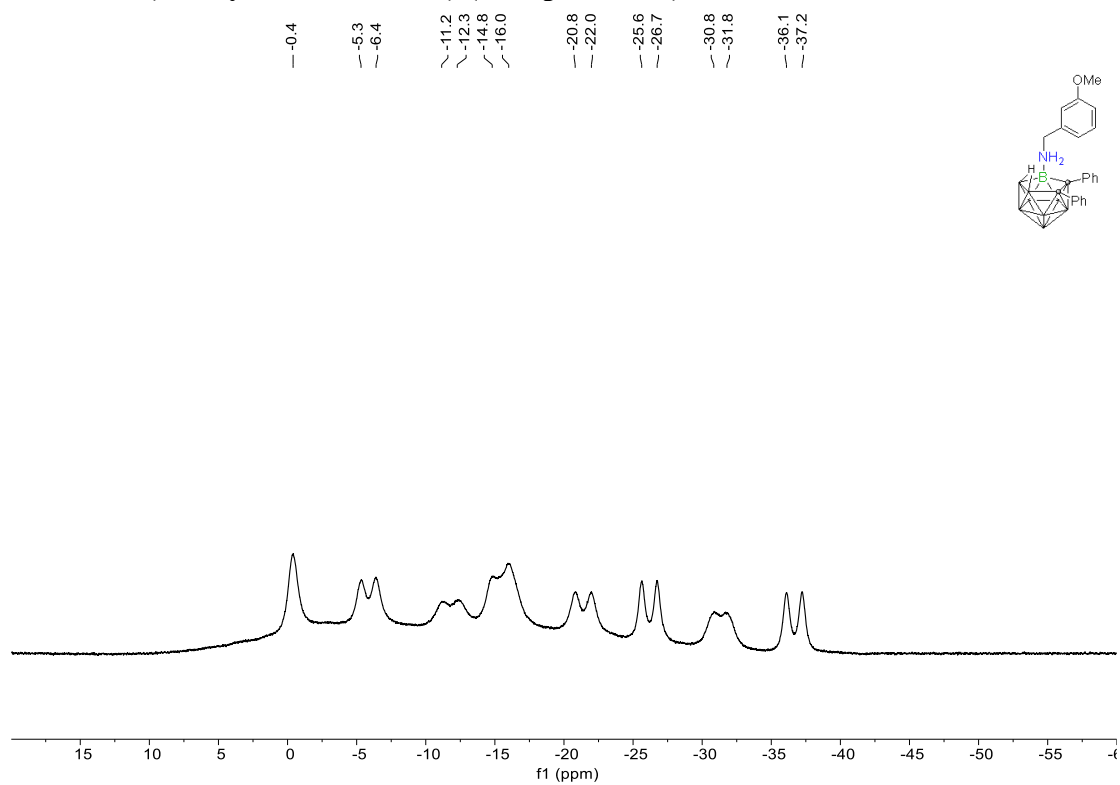
^{11}B NMR (Methylene Chloride- d_2) (Compound 4c)



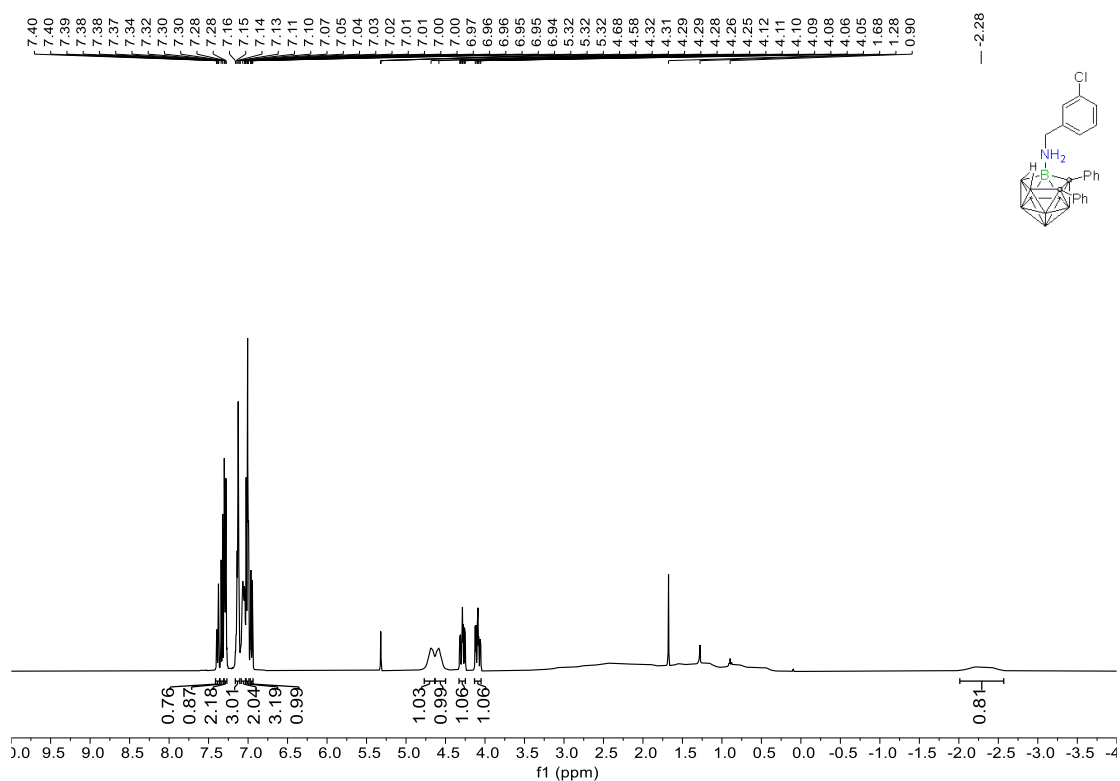
$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 4d)



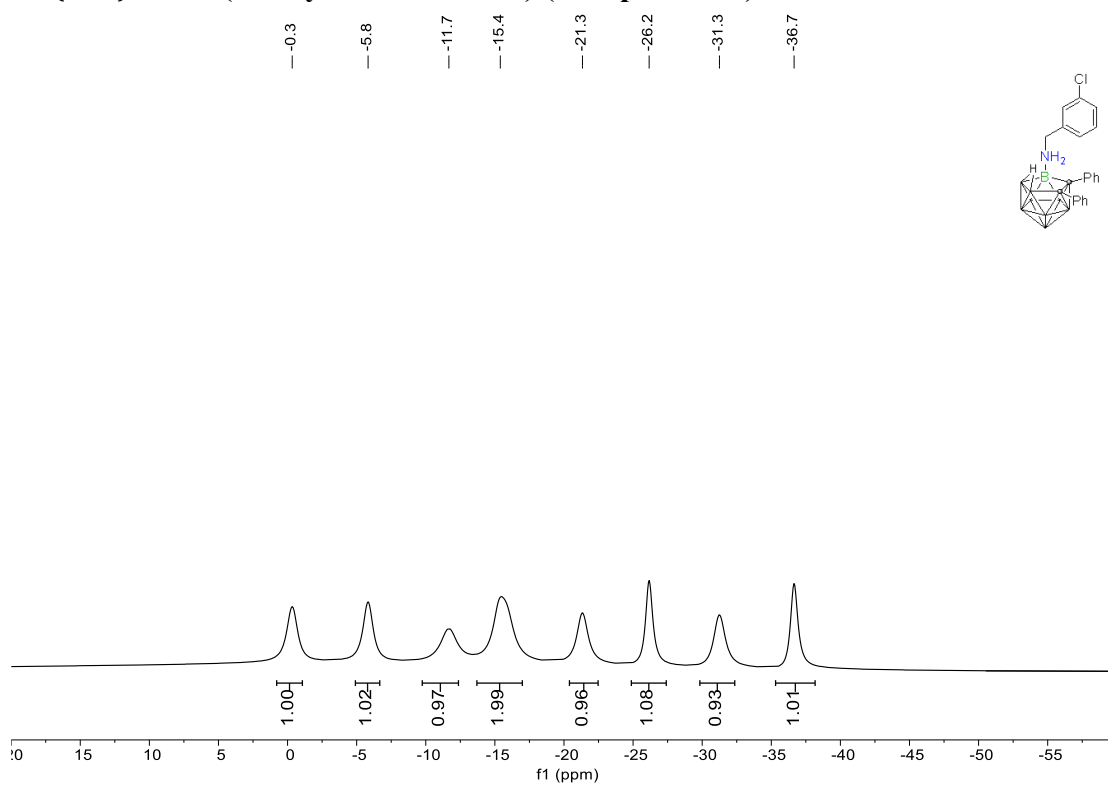
^{11}B NMR (Methylene Chloride- d_2) (Compound 4d)



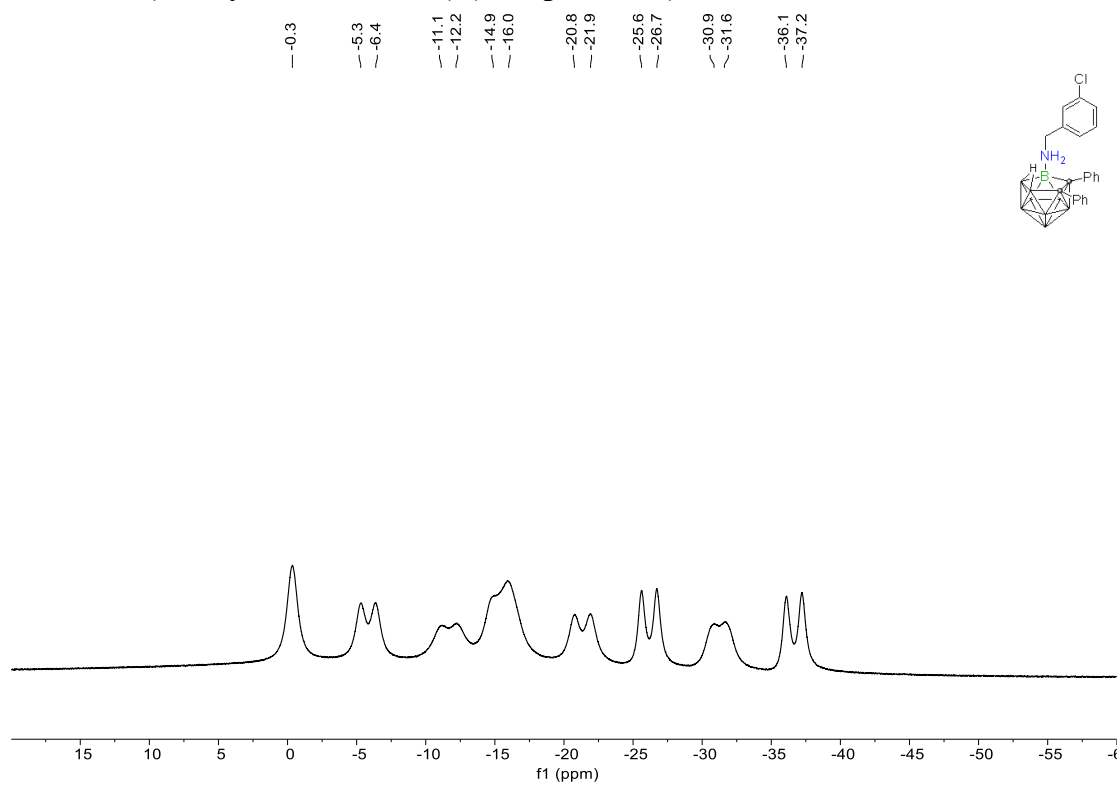
¹H NMR (Methylene Chloride-*d*₂) (Compound 4e)



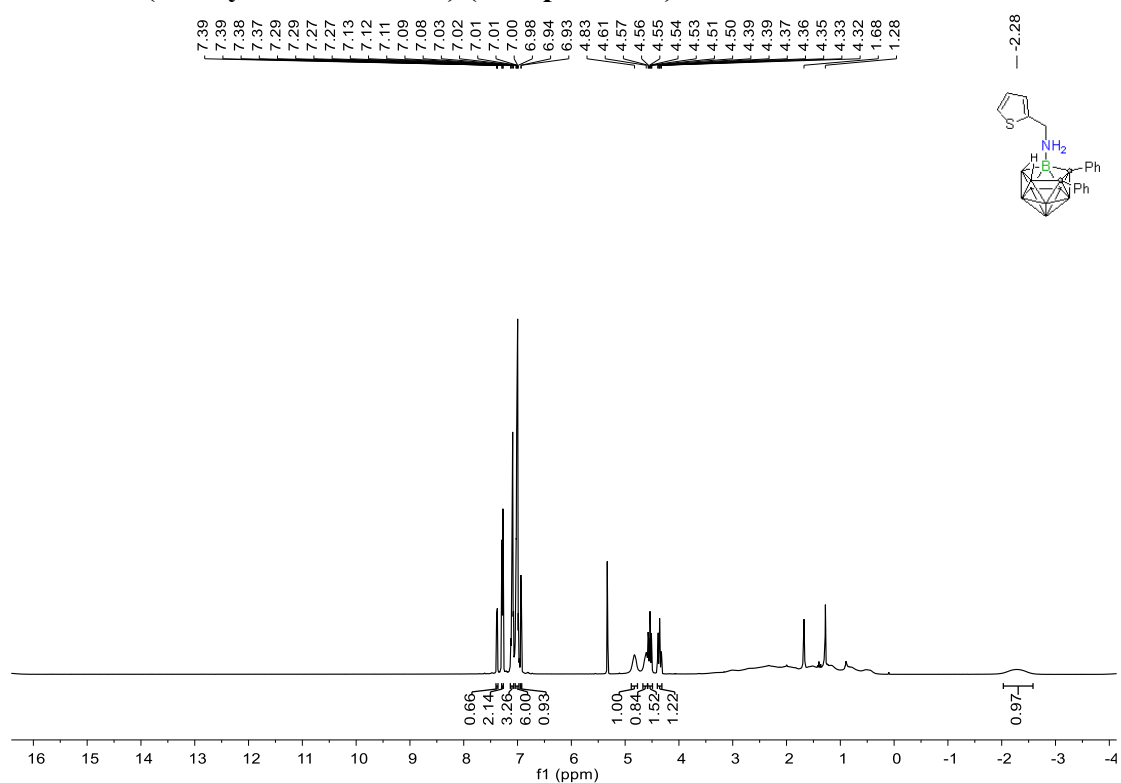
$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 4e)



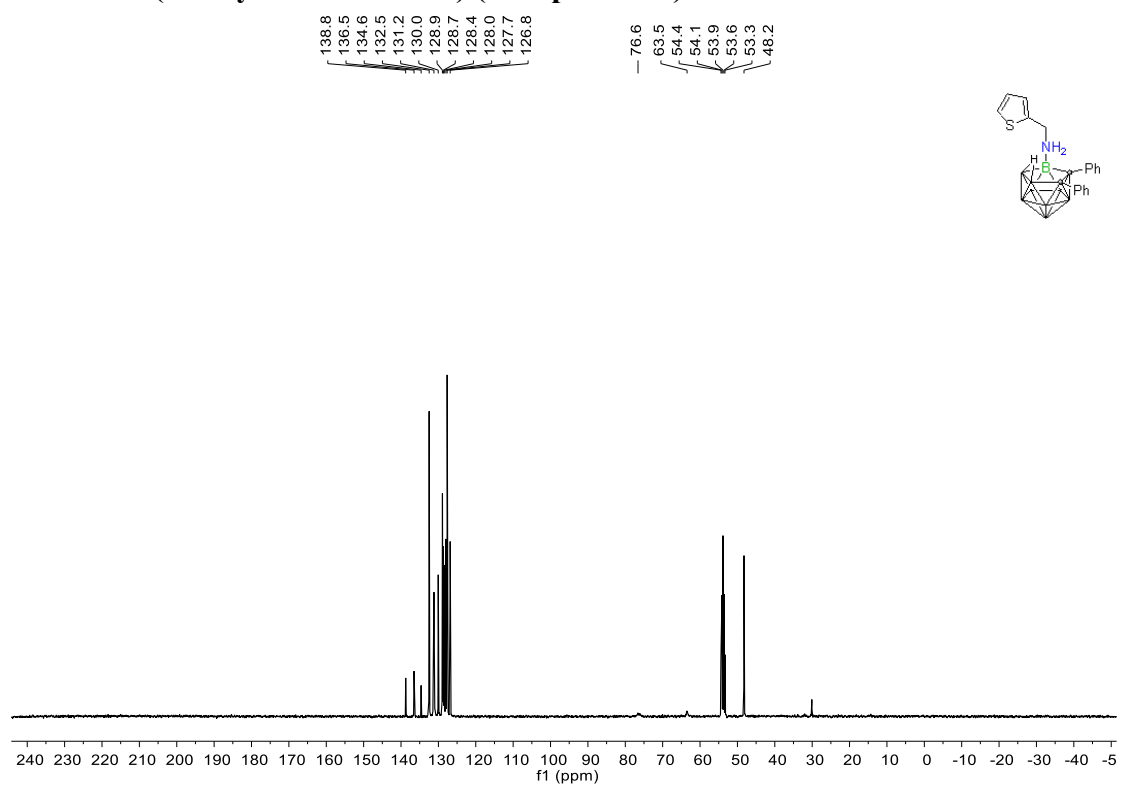
^{11}B NMR (Methylene Chloride- d_2) (Compound 4e)



^1H NMR (Methylene Chloride- d_2) (Compound 4f)



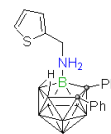
^{13}C NMR (Methylene Chloride- d_2) (Compound 4f)



Chemical structure of compound 10 is shown in the top right corner. The structure is a complex cage-like molecule with a central boron atom (B) bonded to a phenyl group (Ph) and a thienyl group (S). The boron atom is also bonded to a nitrogen atom (N) which is part of a five-membered ring containing a sulfur atom (S). The cage structure is composed of carbon and boron atoms, with various hydrogen atoms (H) attached.

¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from 0 to -55. The spectrum shows several peaks with corresponding integration values:

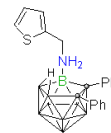
Chemical Shift (ppm)	Integration
0.6	0.97
5.9	1.04
11.8	0.94
15.6	1.95
21.3	0.96
26.1	1.00
31.3	0.89
36.7	0.95



Chemical shift (ppm):

- 0.6
- 5.3
- 6.4
- 11.2
- 12.4
- 15.0
- 15.9
- 20.7
- 21.9
- 25.6
- 26.7
- 30.9
- 31.8
- 36.1
- 37.2

Chemical structure of the compound is shown in the top right corner.



¹H NMR spectrum of compound **1** in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from -4 to 16. The spectrum shows several peaks, with integration values provided below the baseline. The chemical structure of compound **1** is shown in the top right corner.

Chemical structure of compound **1**: Nc1ccc(cc1)C23C4C1CC5C2(C1C3C(C(C5)C)C)C4

Integration values (from left to right): 0.73, 2.02, 3.08, 5.00, 1.61, 1.98, 1.09, 1.08, 1.04.

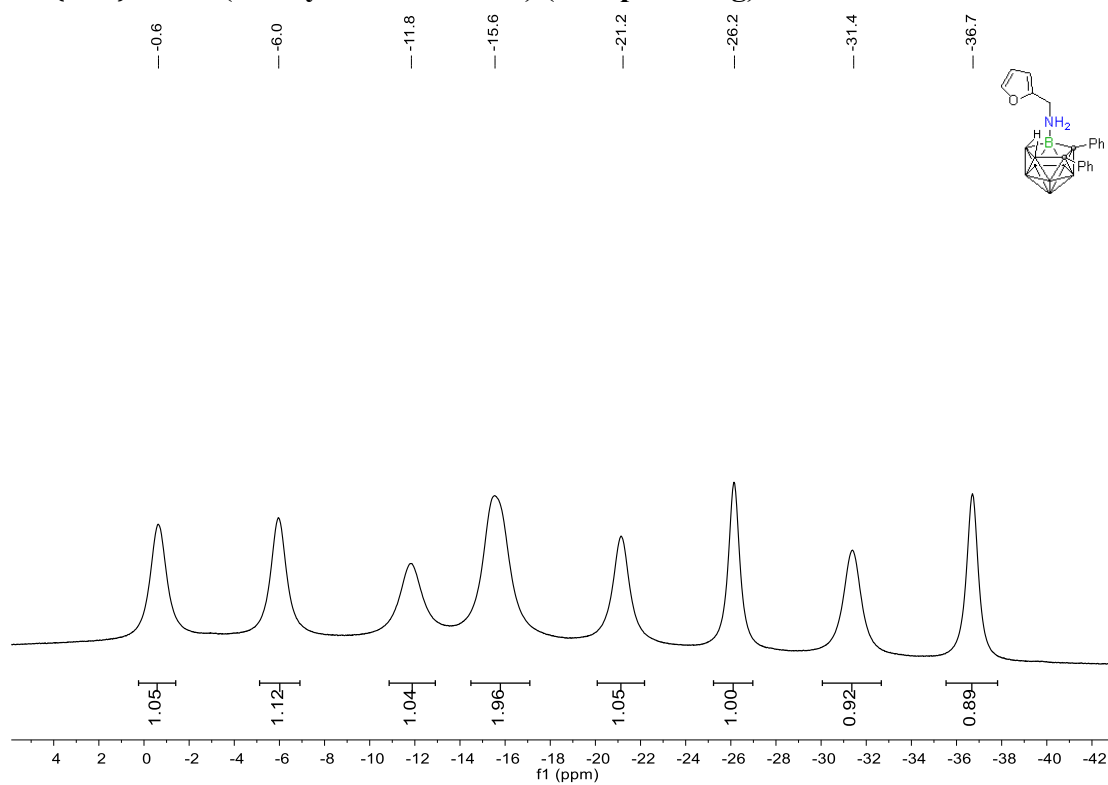
Chemical shift values (ppm) labeled above the peaks: 7.42, 7.42, 7.27, 7.26, 7.25, 7.24, 7.11, 7.10, 7.09, 7.09, 7.08, 7.07, 7.07, 7.05, 7.01, 7.00, 7.00, 6.99, 6.99, 6.97, 6.97, 6.41, 6.40, 6.40, 6.39, 6.38, 4.73, 4.44, 4.44, 4.42, 4.40, 4.39, 4.38, 4.37, 4.25, 4.24, 4.23, 4.21, 4.20, 4.18, -2.38.

Chemical structure of compound 10 is shown in the top right corner. The structure is a naphthalene derivative with a phenyl group, an NH₂ group, and a 2-(benzyloxy)ethyl group.

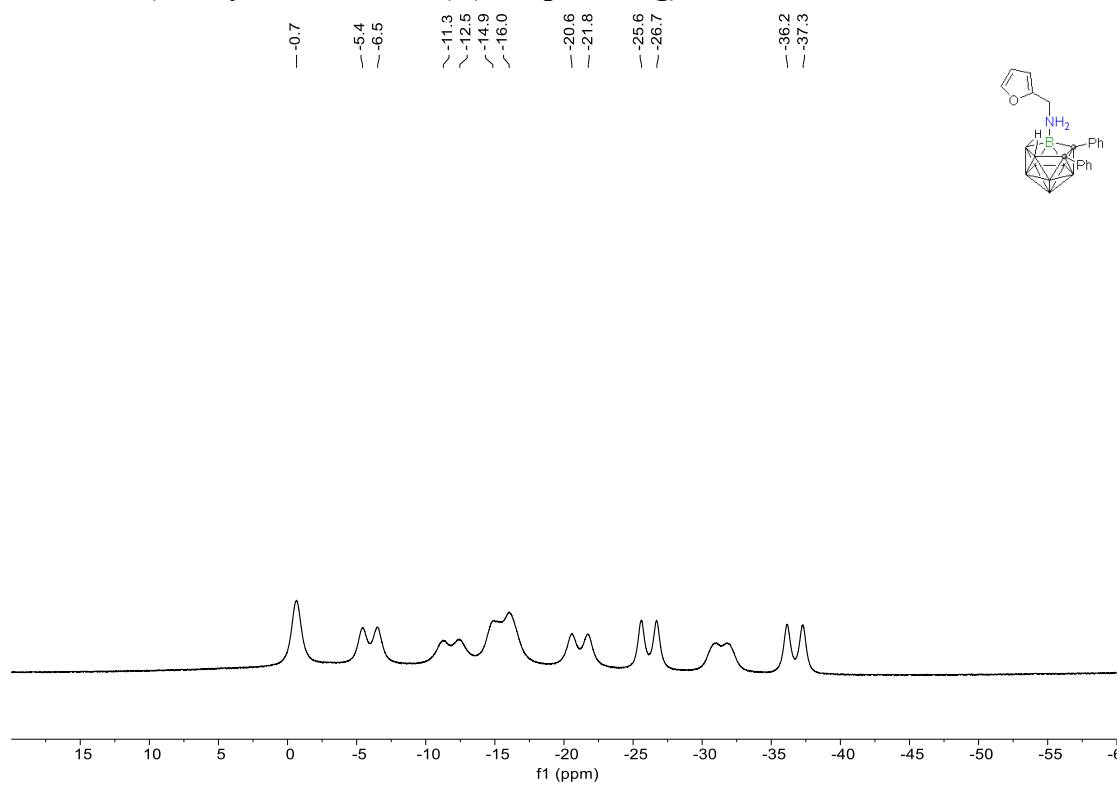
1H NMR spectrum (CDCl₃) of compound 10. The x-axis is labeled f1 (ppm) and ranges from 240 to -5. The spectrum shows several peaks, with the following chemical shifts (ppm) labeled above the peaks:

- 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

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



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



Chemical Structure of Compound 10:

Nc1nc2c(c1)C3C(C2)C4C(C3)C5C(C4)C6C(C5)C7C(C6)C8C(C7)C9C(C8)C10C(C9)C11C(C10)C12C(C11)C13C(C12)C14C(C13)C15C(C14)C16C(C15)C17C(C16)C18C(C17)C19C(C18)C20C(C19)C21C(C20)C22C(C21)C23C(C22)C24C(C23)C25C(C24)C26C(C25)C27C(C26)C28C(C27)C29C(C28)C30C(C29)C31C(C30)C32C(C31)C33C(C32)C34C(C33)C35C(C34)C36C(C35)C37C(C36)C38C(C37)C39C(C38)C40C(C39)C41C(C40)C42C(C41)C43C(C42)C44C(C43)C45C(C44)C46C(C45)C47C(C46)C48C(C47)C49C(C48)C50C(C49)C51C(C50)C52C(C51)C53C(C52)C54C(C53)C55C(C54)C56C(C55)C57C(C56)C58C(C57)C59C(C58)C60C(C59)C61C(C60)C62C(C61)C63C(C62)C64C(C63)C65C(C64)C66C(C65)C67C(C66)C68C(C67)C69C(C68)C70C(C69)C71C(C70)C72C(C71)C73C(C72)C74C(C73)C75C(C74)C76C(C75)C77C(C76)C78C(C77)C79C(C78)C80C(C79)C81C(C80)C82C(C81)C83C(C82)C84C(C83)C85C(C84)C86C(C85)C87C(C86)C88C(C87)C89C(C88)C90C(C89)C91C(C90)C92C(C91)C93C(C92)C94C(C93)C95C(C94)C96C(C95)C97C(C96)C98C(C97)C99C(C98)C100C(C99)C101C(C100)C102C(C101)C103C(C102)C104C(C103)C105C(C104)C106C(C105)C107C(C106)C108C(C107)C109C(C108)C110C(C109)C111C(C110)C112C(C111)C113C(C112)C114C(C113)C115C(C114)C116C(C115)C117C(C116)C118C(C117)C119C(C118)C120C(C119)C121C(C120)C122C(C121)C123C(C122)C124C(C123)C125C(C124)C126C(C125)C127C(C126)C128C(C127)C129C(C128)C130C(C129)C131C(C130)C132C(C131)C133C(C132)C134C(C133)C135C(C134)C136C(C135)C137C(C136)C138C(C137)C139C(C138)C140C(C139)C141C(C140)C142C(C141)C143C(C142)C144C(C143)C145C(C144)C146C(C145)C147C(C146)C148C(C147)C149C(C148)C150C(C149)C151C(C150)C152C(C151)C153C(C152)C154C(C153)C155C(C154)C156C(C155)C157C(C156)C158C(C157)C159C(C158)C160C(C159)C161C(C160)C162C(C161)C163C(C162)C164C(C163)C165C(C164)C166C(C165)C167C(C166)C168C(C167)C169C(C168)C170C(C169)C171C(C170)C172C(C171)C173C(C172)C174C(C173)C175C(C174)C176C(C175)C177C(C176)C178C(C177)C179C(C178)C180C(C179)C181C(C180)C182C(C181)C183C(C182)C184C(C183)C185C(C184)C186C(C185)C187C(C186)C188C(C187)C189C(C188)C190C(C189)C191C(C190)C192C(C191)C193C(C192)C194C(C193)C195C(C194)C196C(C195)C197C(C196)C198C(C197)C199C(C198)C200C(C199)C201C(C200)C202C(C201)C203C(C202)C204C(C203)C205C(C204)C206C(C205)C207C(C206)C208C(C207)C209C(C208)C210C(C209)C211C(C210)C212C(C211)C213C(C212)C214C(C213)C215C(C214)C216C(C215)C217C(C216)C218C(C217)C219C(C218)C220C(C219)C221C(C220)C222C(C221)C223C(C222)C224C(C223)C225C(C224)C226C(C225)C227C(C226)C228C(C227)C229C(C228)C230C(C229)C231C(C230)C232C(C231)C233C(C232)C234C(C233)C235C(C234)C236C(C235)C237C(C236)C238C(C237)C239C(C238)C240C(C239)C241C(C240)C242C(C241)C243C(C242)C244C(C243)C245C(C244)C246C(C245)C247C(C246)C248C(C247)C249C(C248)C250C(C249)C251C(C250)C252C(C251)C253C(C252)C254C(C253)C255C(C254)C256C(C255)C257C(C256)C258C(C257)C259C(C258)C260C(C259)C261C(C260)C262C(C261)C263C(C262)C264C(C263)C265C(C264)C266C(C265)C267C(C266)C268C(C267)C269C(C268)C270C(C269)C271C(C270)C272C(C271)C273C(C272)C274C(C273)C275C(C274)C276C(C275)C277C(C276)C278C(C277)C279C(C278)C280C(C279)C281C(C280)C282C(C281)C283C(C282)C284C(C283)C285C(C284)C286C(C285)C287C(C286)C288C(C287)C289C(C288)C290C(C289)C291C(C290)C292C(C291)C293C(C292)C294C(C293)C295C(C294)C296C(C295)C297C(C296)C298C(C297)C299C(C298)C300C(C299)C301C(C300)C302C(C301)C303C(C302)C304C(C303)C305C(C304)C306C(C305)C307C(C306)C308C(C307)C309C(C308)C310C(C309)C311C(C310)C312C(C311)C313C(C312)C314C(C313)C315C(C314)C316C(C315)C317C(C316)C318C(C317)C319C(C318)C320C(C319)C321C(C320)C322C(C321)C323C(C322)C324C(C323)C325C(C324)C326C(C325)C327C(C326)C328C(C327)C329C(C328)C330C(C329)C331C(C330)C332C(C331)C333C(C332)C334C(C333)C335C(C334)C336C(C335)C337C(C336)C338C(C337)C339C(C338)C340C(C339)C341C(C340)C342C(C341)C343C(C342)C344C(C343)C345C(C344)C346C(C345)C347C(C346)C348C(C347)C349C(C348)C350C(C349)C351C(C350)C352C(C351)C353C(C352)C354C(C353)C355C(C354)C356C(C355)C357C(C356)C358C(C357)C359C(C358)C360C(C359)C361C(C360)C362C(C361)C363C(C362)C364C(C363)C365C(C364)C366C(C365)C367C(C366)C368C(C367)C369C(C368)C370C(C369)C371C(C370)C372C(C371)C373C(C372)C374C(C373)C375C(C374)C376C(C375)C377C(C376)C378C(C377)C379C(C378)C380C(C379)C381C(C380)C382C(C381)C383C(C382)C384C(C383)C385C(C384)C386C(C385)C387C(C386)C388C(C387)C389C(C388)C390C(C389)C391C(C390)C392C(C391)C393C(C392)C394C(C393)C395C(C394)C396C(C395)C397C(C396)C398C(C397)C399C(C398)C400C(C399)C401C(C400)C402C(C401)C403C(C402)C404C(C403)C405C(C404)C406C(C405)C407C(C406)C408C(C407)C409C(C408)C410C(C409)C411C(C410)C412C(C411)C413C(C412)C414C(C413)C415C(C414)C416C(C415)C417C(C416)C418C(C417)C419C(C418)C420C(C419)C421C(C420)C422C(C421)C423C(C422)C424C(C

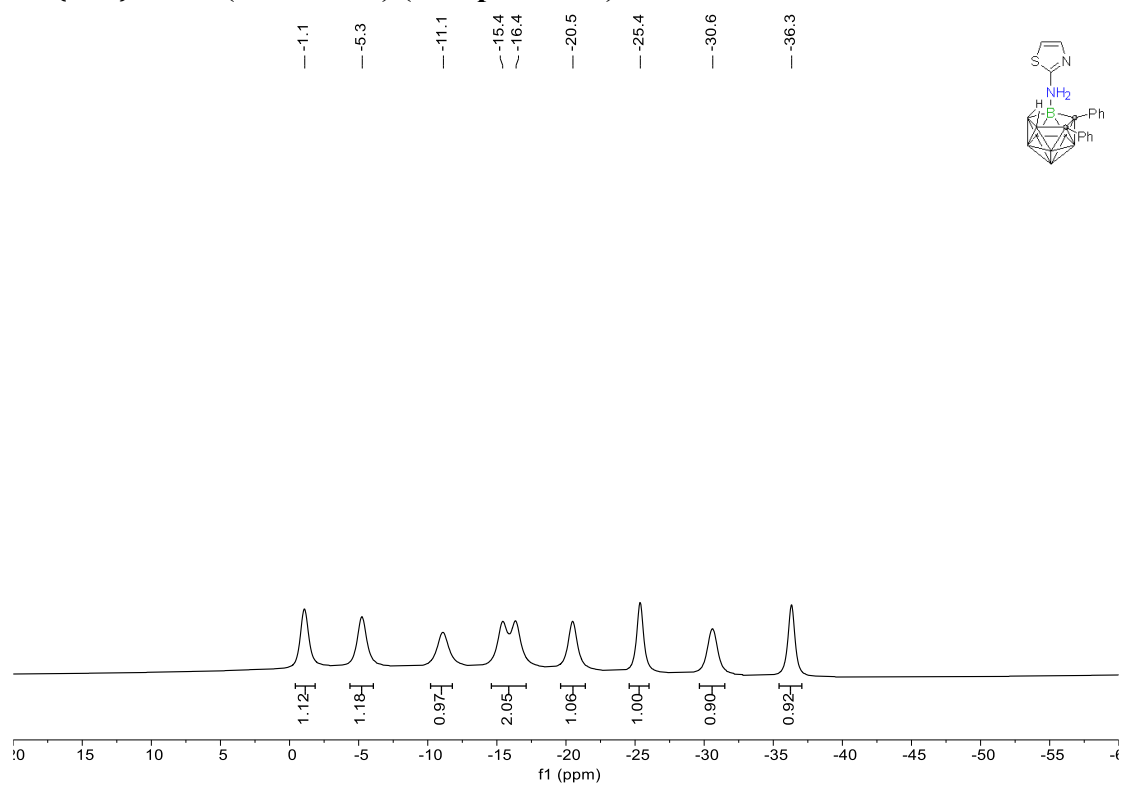
Chemical structure of the compound is shown in the top right corner. The structure is a complex molecule featuring a central boron atom (B) coordinated by a thiazole ring (S, N) and a phenyl group (Ph). The boron atom is also bonded to a hydrogen atom (H) and a phenyl group (Ph). The chemical structure is labeled with the following atoms: S, N, H, B, and Ph.

The ¹³C NMR spectrum (f1 (ppm)) shows the following peaks (ppm):

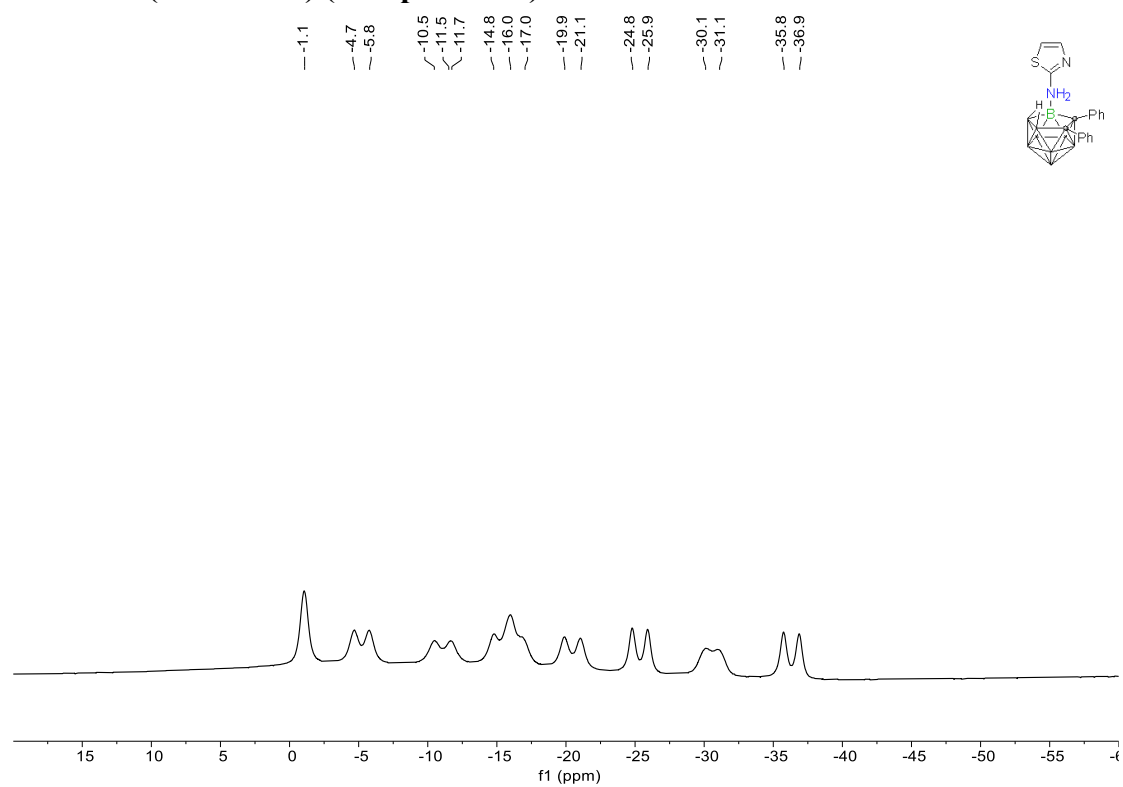
- 173.5
- 140.1
- 136.3
- 136.4
- 133.0
- 131.7
- 127.7
- 127.6
- 127.0
- 126.9
- 105.8

The spectrum displays a series of sharp peaks in the aromatic region (105.8 to 140.1 ppm) and a single sharp peak at 173.5 ppm, characteristic of a carbonyl group. The x-axis ranges from -5 to 240 ppm.

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



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



Chemical structure of compound 10: Nc1ccc(cc1)[C@H]2[C@H](c3ccccc3)[C@H](c4ccccc4)[C@H]5[C@@H]2C6=CC=CC=C6[C@H]5C6=CC=CC=C6

¹H NMR spectrum (CDCl₃):

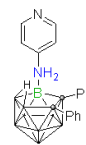
Chemical Shift (ppm)	Integration
8.29	2.11
7.31	2.15
7.29	2.00
7.28	2.14
7.07	3.06
7.00	3.02
6.98	2.00
6.96	
6.95	
6.94	
6.92	
6.91	
6.90	
6.89	
6.88	
6.89	
6.88	
6.83	
6.81	
6.79	
6.78	
6.79	
6.77	
6.77	
6.70	
6.69	
6.69	
6.69	
1.19	1.19

Chemical structure of the compound is shown in the top right corner. The structure is a complex cage-like molecule with a central nitrogen atom (N) and a central carbon atom (C). The cage is composed of several fused rings, including a cyclohexane ring and a cyclopentane ring. The central nitrogen atom is bonded to a phenyl group (Ph) and a hydrogen atom (H). The central carbon atom is bonded to a phenyl group (Ph) and a hydrogen atom (H). The chemical structure is labeled with the following chemical shift values (ppm): 158.9, 148.6, 140.3, 138.3, 133.1, 132.1, 127.7, 126.9, 126.8, and 109.6.

Chemical structure of compound 1: Nc1ccc(cc1)[C@H]2[C@@H](c3ccccc3)[C@H](c4ccccc4)[C@H]5[C@@H](c6ccccc6)[C@H]25

¹H NMR spectrum (CDCl₃) of compound 1. The x-axis represents the chemical shift in ppm, ranging from 0 to -55. The spectrum shows several peaks with corresponding integration values:

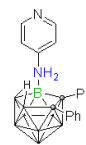
Chemical Shift (ppm)	Integration
5.3	1.03
5.2	1.08
13.2	0.92
15.6	1.81
21.9	1.00
26.0	1.00
31.3	0.90
36.6	0.99



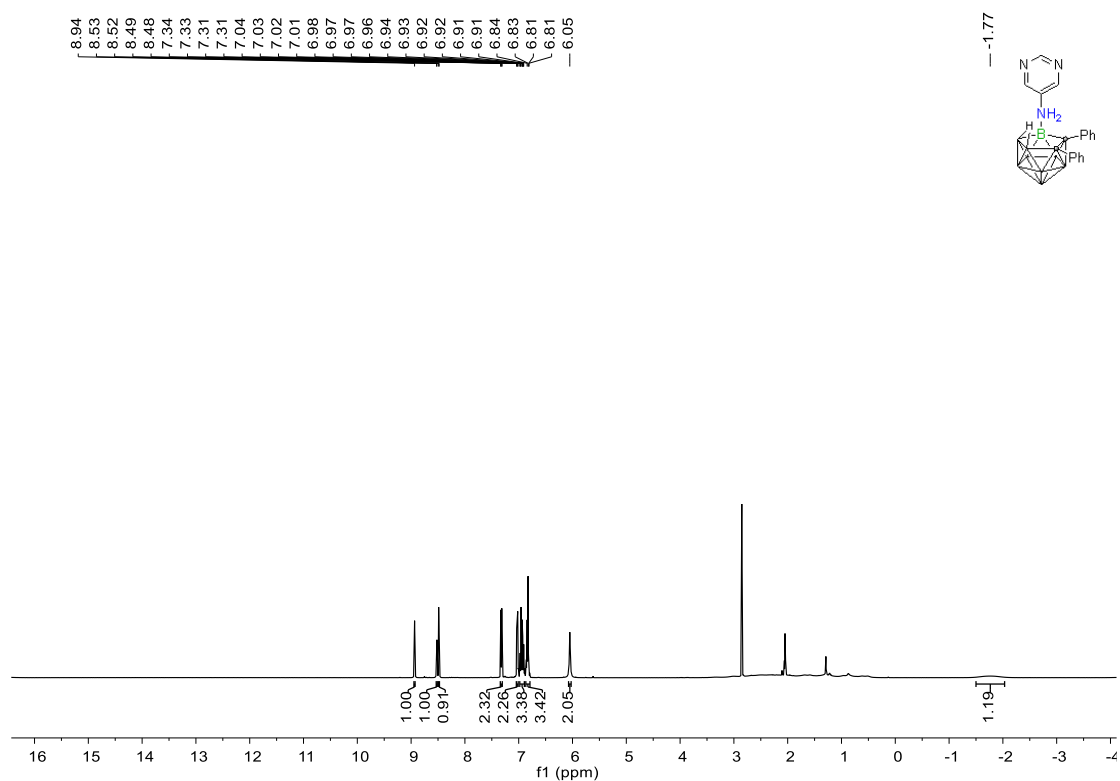
Chemical shift (ppm):

- 5.3
- 4.7
- 5.8
- 12.6
- 13.8
- 15.1
- 16.3
- 21.3
- 22.5
- 25.4
- 26.5
- 30.8
- 31.7
- 36.1
- 37.2

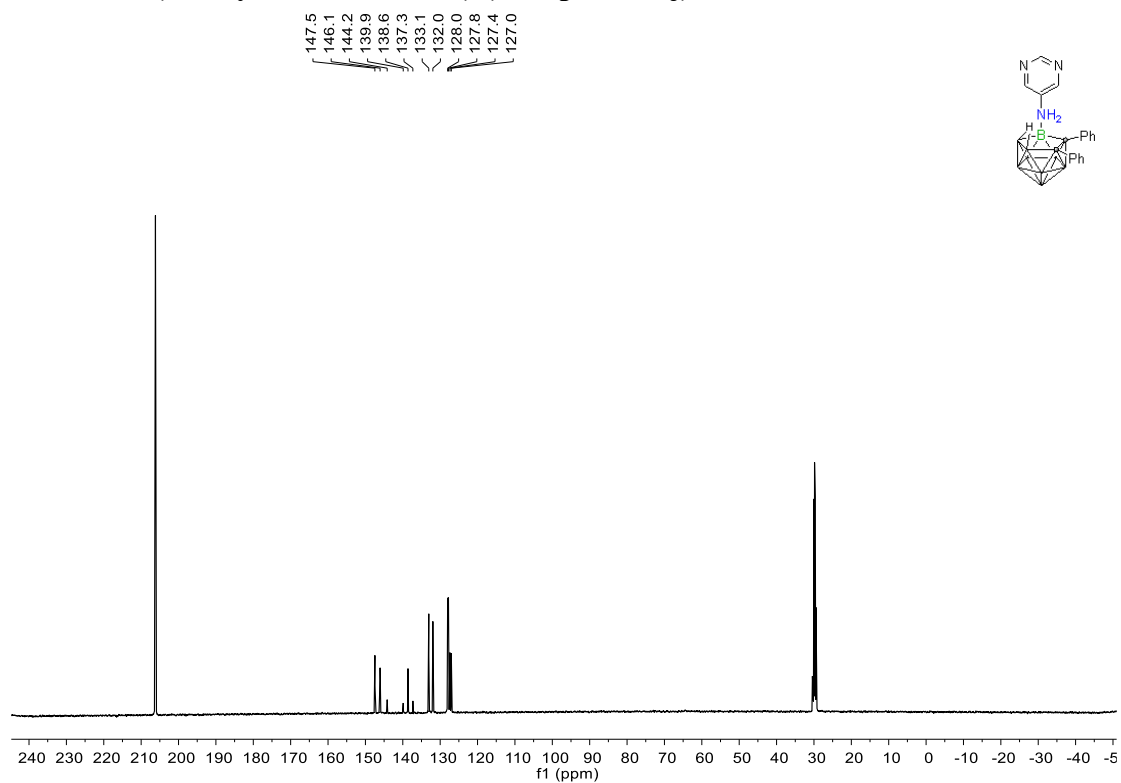
Chemical structure:



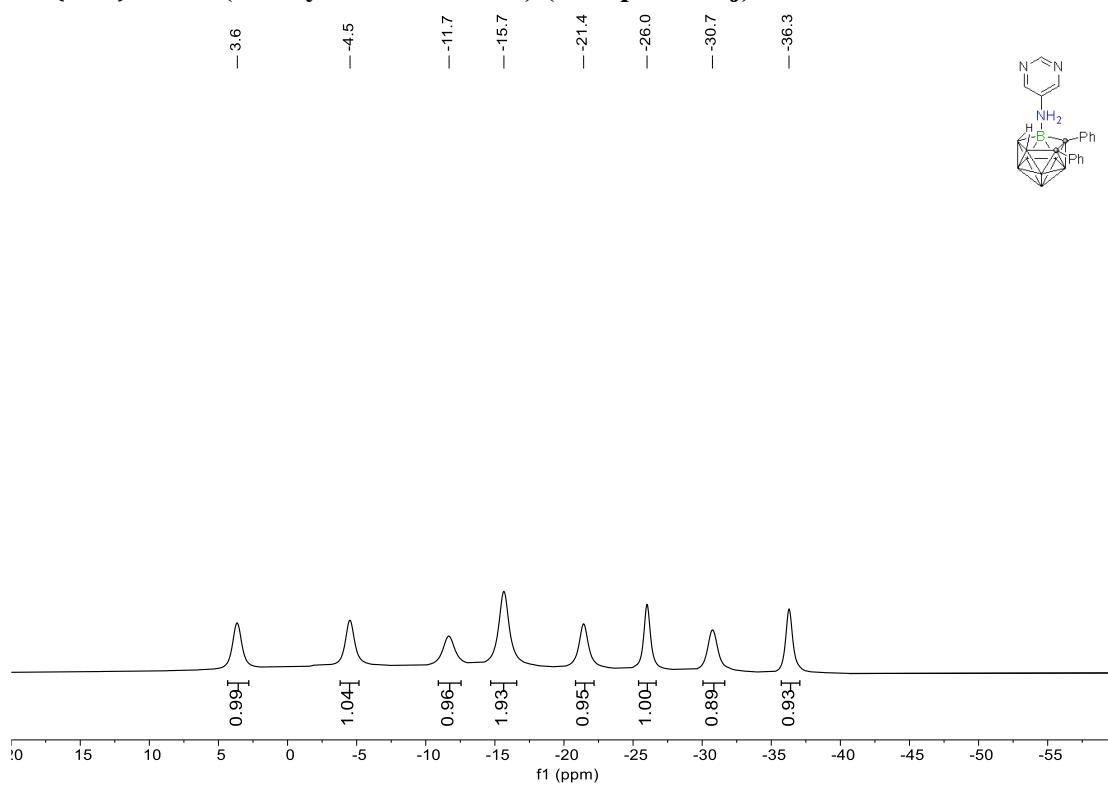
^1H NMR (Methylene Chloride- d_2) (Compound 4j)



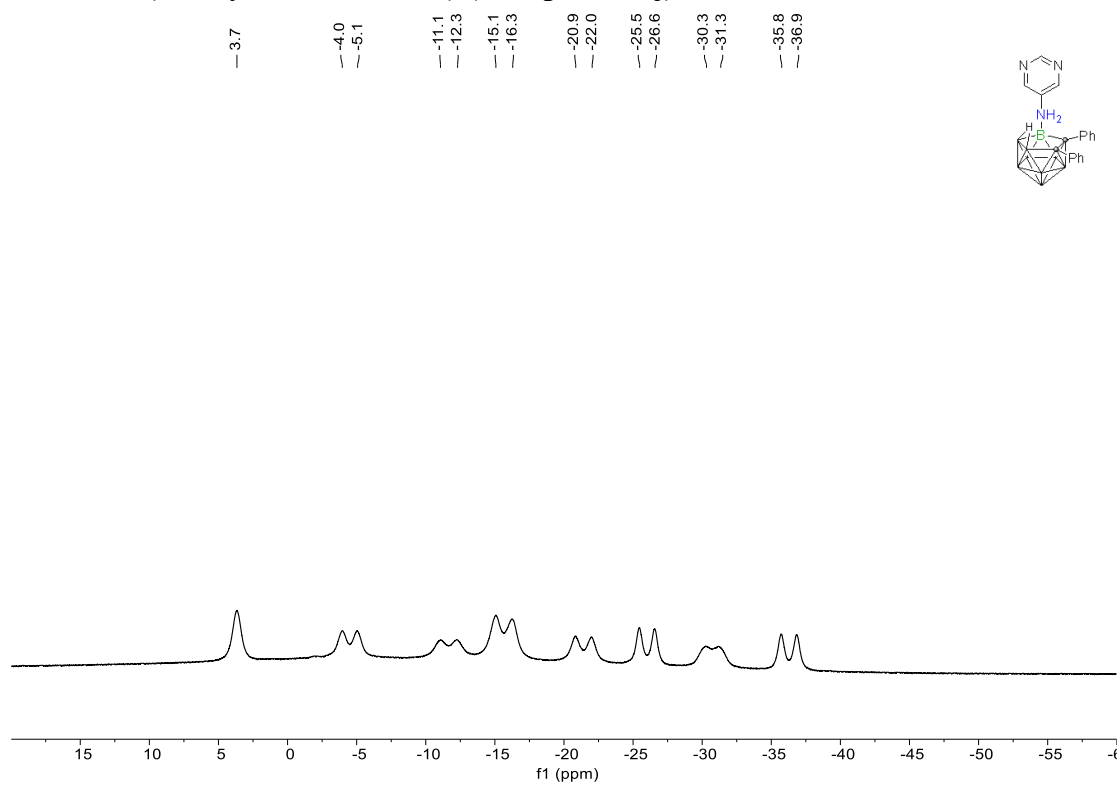
^{13}C NMR (Methylene Chloride- d_2) (Compound 4j)



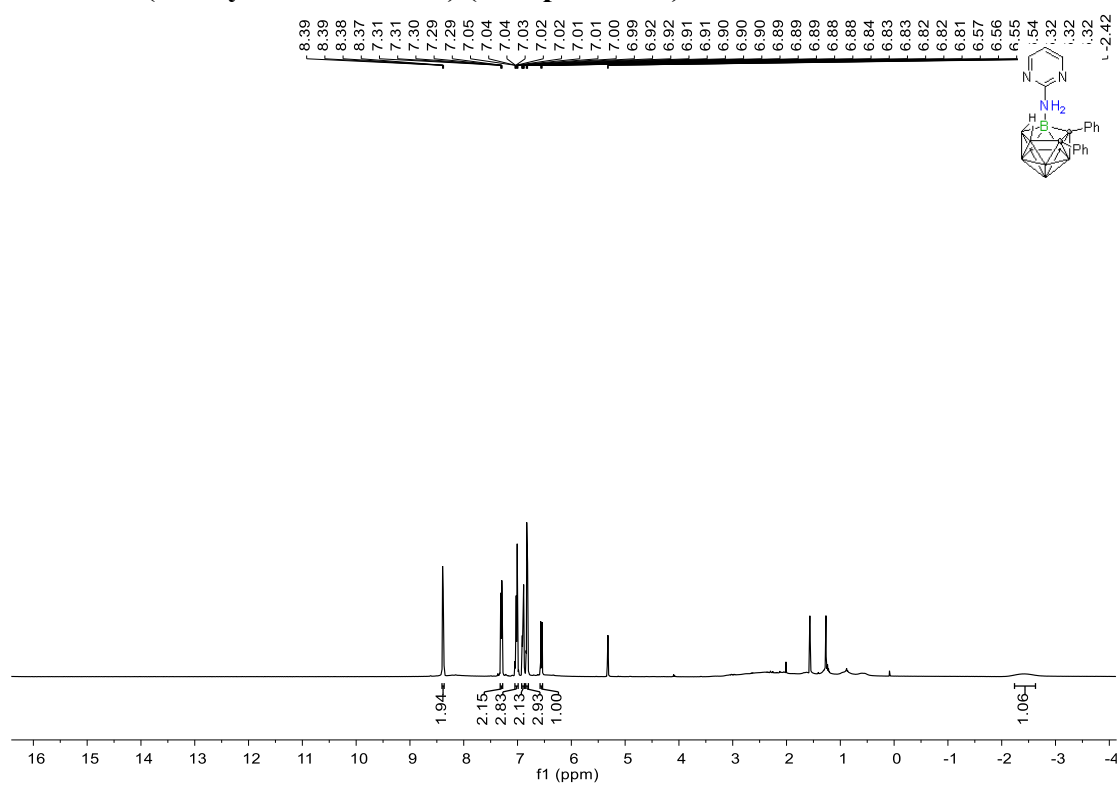
$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 4j)



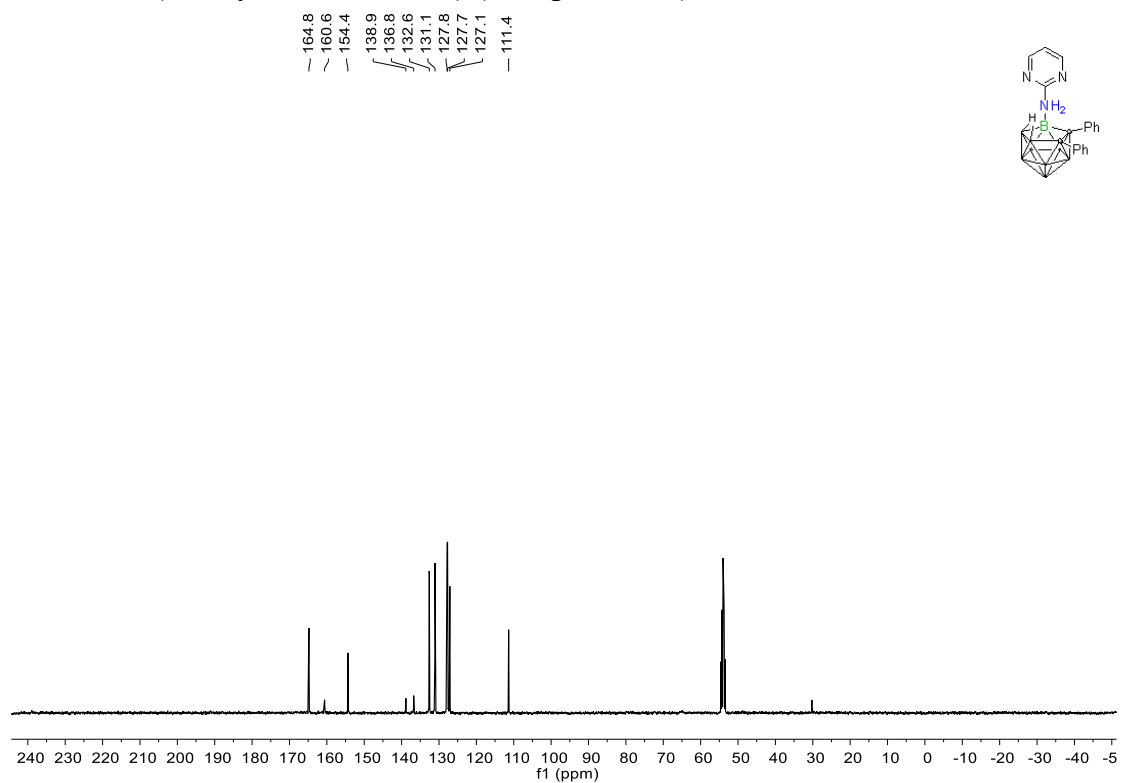
^{11}B NMR (Methylene Chloride- d_2) (Compound 4j)



¹H NMR (Methylene Chloride-*d*₂) (Compound 4k)



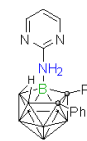
¹³C NMR (Methylene Chloride-*d*₂) (Compound 4k)



Chemical structure of compound 1: Nc1ccncc1[C@H]2[C@H](c3ccccc3)[C@H](c4ccccc4)[C@H]5[C@H]2C6=C(C(=O)O)C(=O)N6

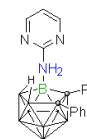
¹H NMR spectrum (CDCl₃) of compound 1. The x-axis represents the chemical shift in ppm, ranging from 0 to -55. The spectrum shows several peaks with corresponding integration values:

Chemical Shift (ppm)	Integration
1.3	0.99
4.3	1.07
10.1	1.03
14.8	0.96
16.5	0.95
21.1	0.98
25.4	1.00
29.5	0.90
36.0	0.89

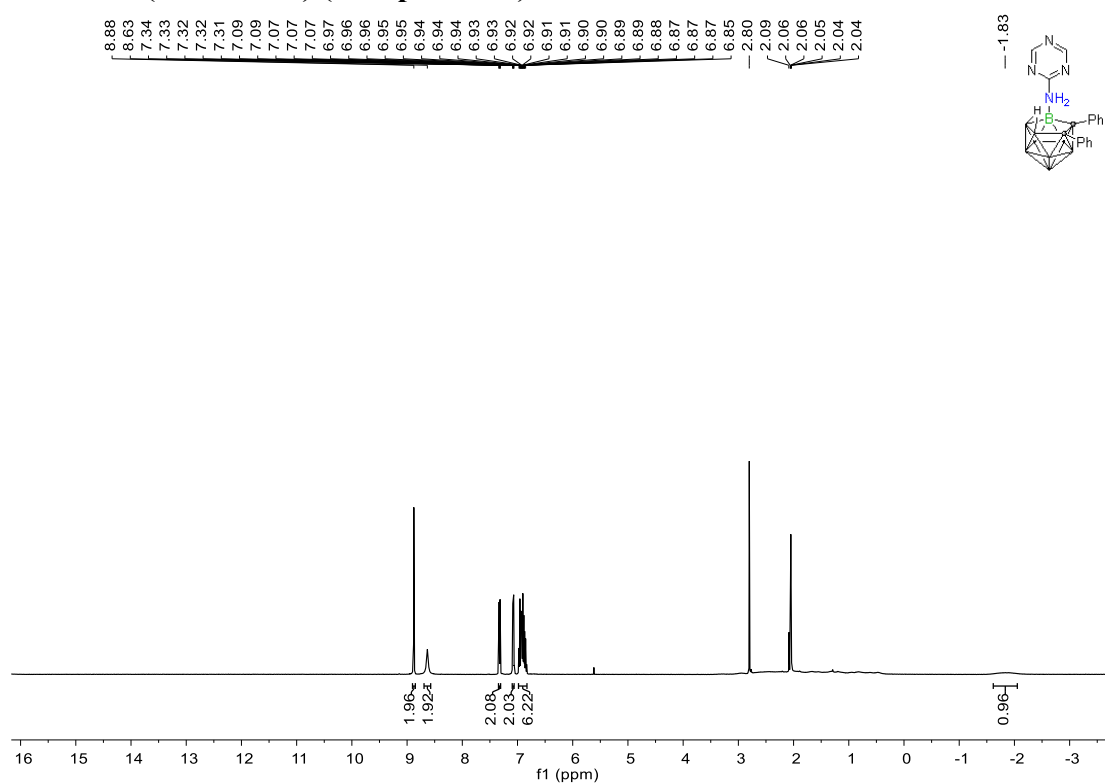


Chemical shift (ppm): 1.3, -3.8, -4.9, -9.5, -10.8, -14.2, -15.6, -16.9, -20.5, -21.7, -24.8, -25.9, -29.0, -30.0, -35.4, -36.5.

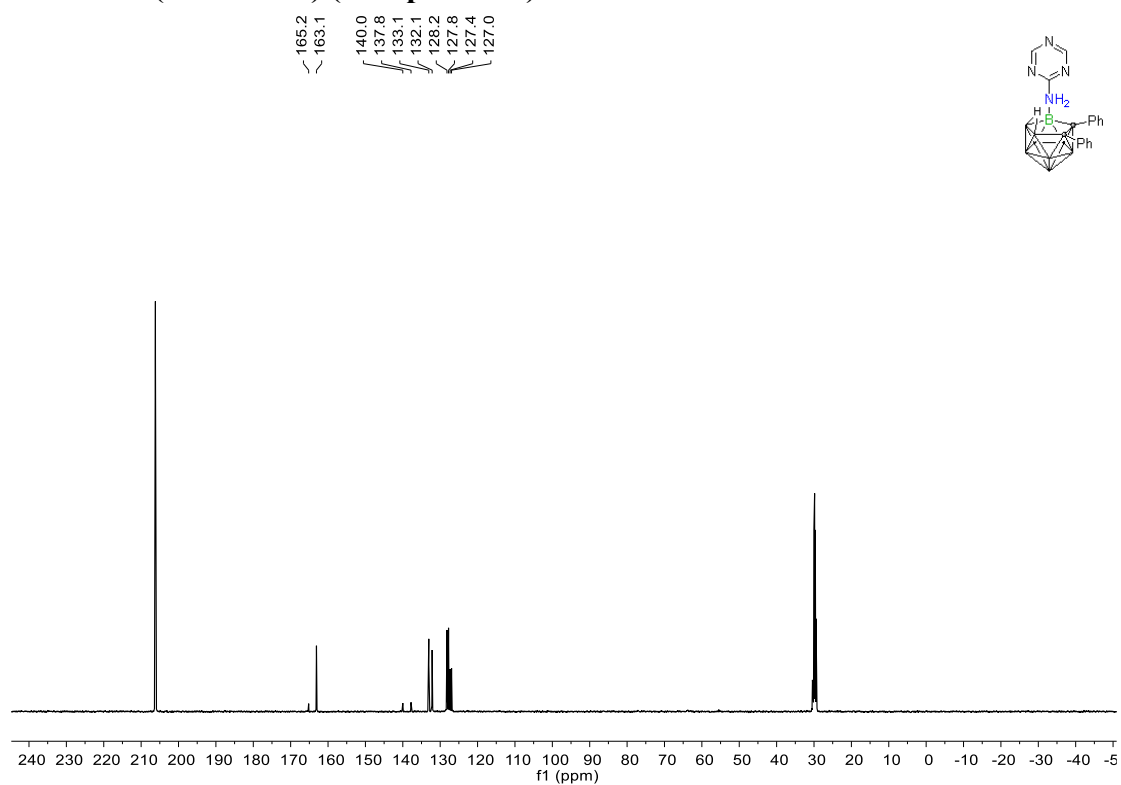
Chemical structure:



¹H NMR (Acetone-*d*₆) (Compound 4l)



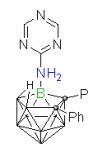
¹³C NMR (Acetone-*d*₆) (Compound 4l)



Chemical structure of compound 1 is shown in the top right corner. The structure is a complex molecule featuring a central boron atom (B) coordinated by a phenyl group (Ph) and a pyridine ring. The boron atom is also bonded to a hydrogen atom (H) and a nitrogen atom (N). The pyridine ring is substituted with a phenyl group (Ph) and a hydrogen atom (H). The chemical structure is labeled with 'Ph' for phenyl and 'H' for hydrogen.

¹H NMR spectrum (CDCl₃) of compound 1. The x-axis represents the chemical shift in ppm, ranging from 0 to -60. The spectrum shows several peaks with corresponding integration values:

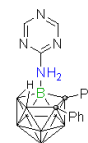
Chemical Shift (ppm)	Integration
1.8	1.04
4.9	1.09
11.8	0.97
15.8	2.00
21.8	1.01
25.9	1.00
30.8	0.86
36.5	0.91



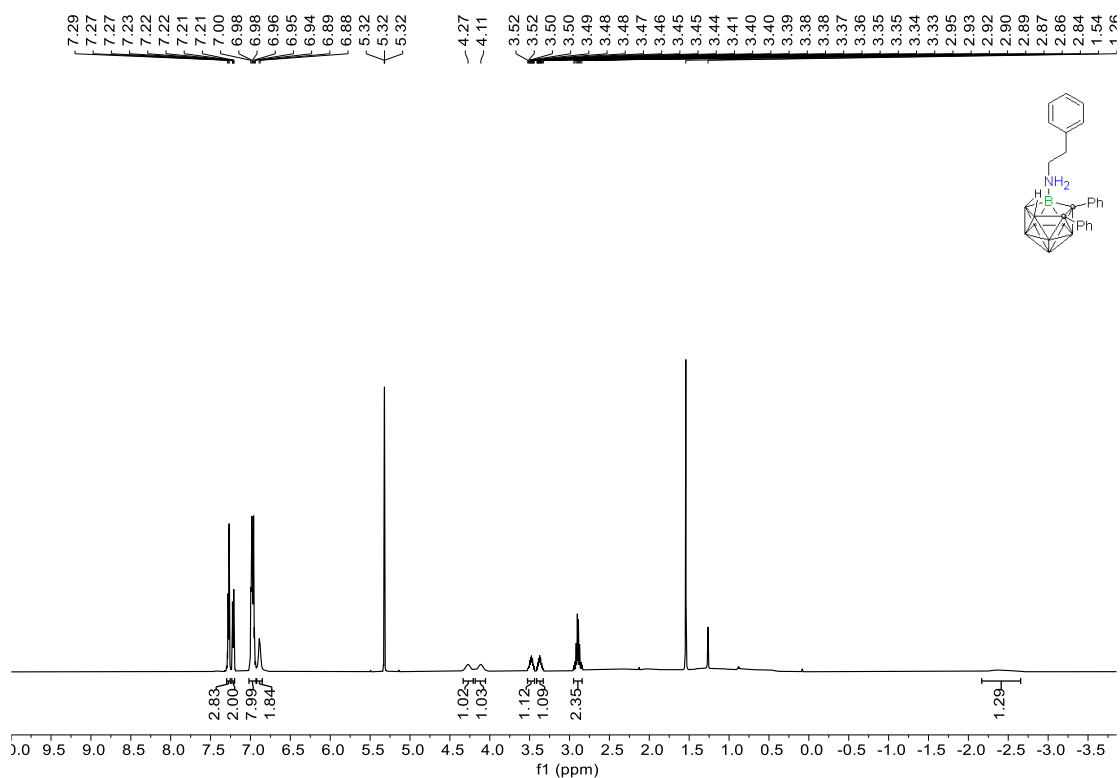
Chemical structure of 2-((1,2,3,4,5,6-hexaphenyl-1,3,5-triazin-4-ylidene)amino)phenylboronic acid is shown. The structure features a central triazine ring substituted with six phenyl groups and an amino group, which is further substituted with a phenylboronic acid moiety.

The ¹H NMR spectrum (DMSO-d₆) displays the following chemical shifts (ppm) and integration values:

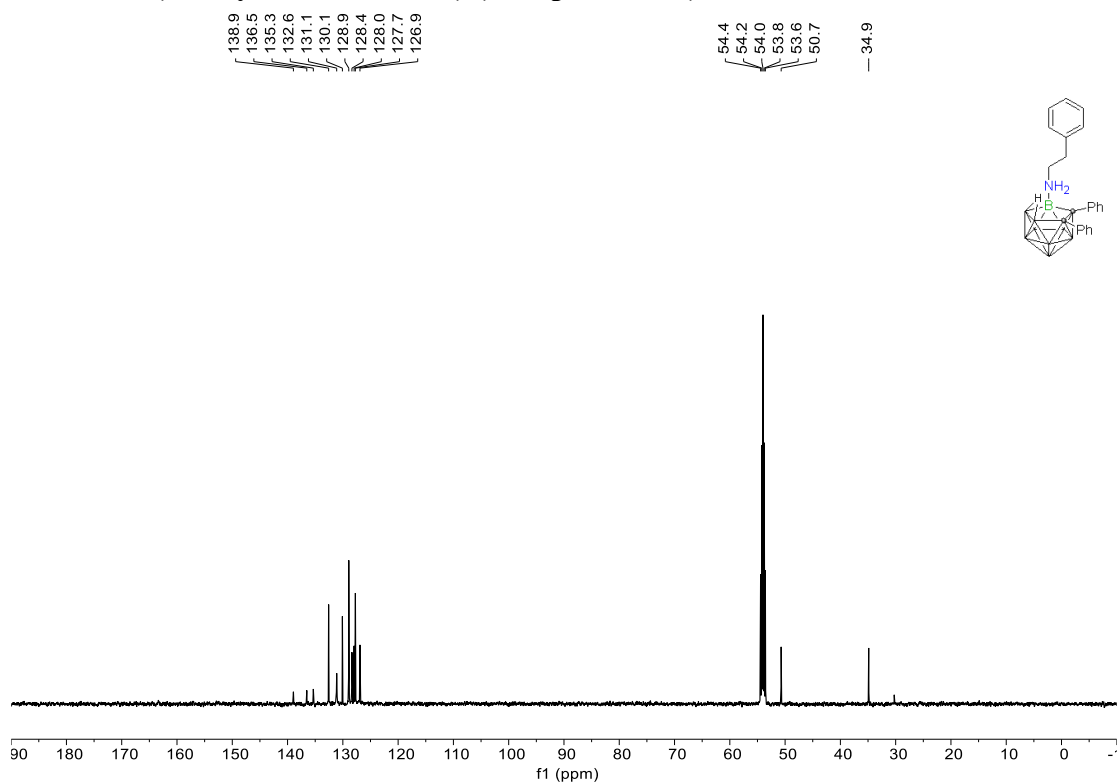
Chemical Shift (ppm)	Integration
~1.7	1.7
~4.4	4.4
~5.5	5.5
~11.3	11.3
~12.4	12.4
~15.2	15.2
~16.4	16.4
~21.2	21.2
~22.4	22.4
~25.3	25.3
~26.4	26.4
~30.3	30.3
~31.3	31.3
~35.9	35.9
~37.1	37.1



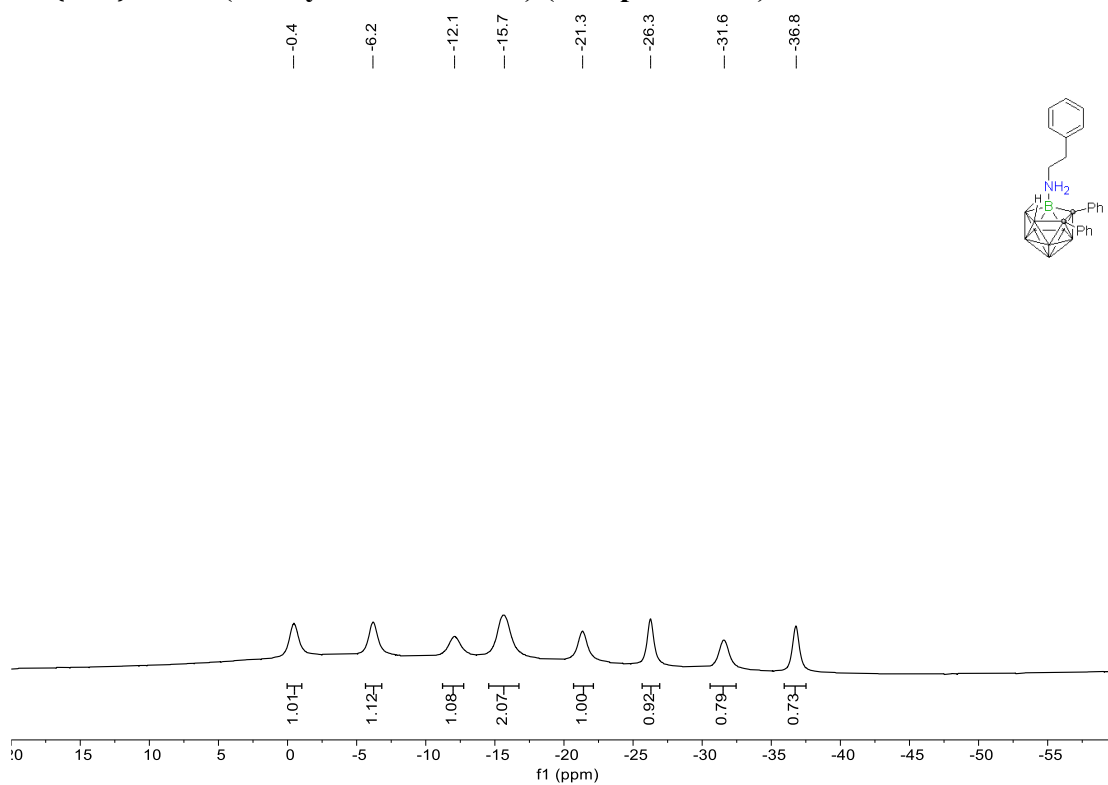
^1H NMR (Methylene Chloride- d_2) (Compound 4m)



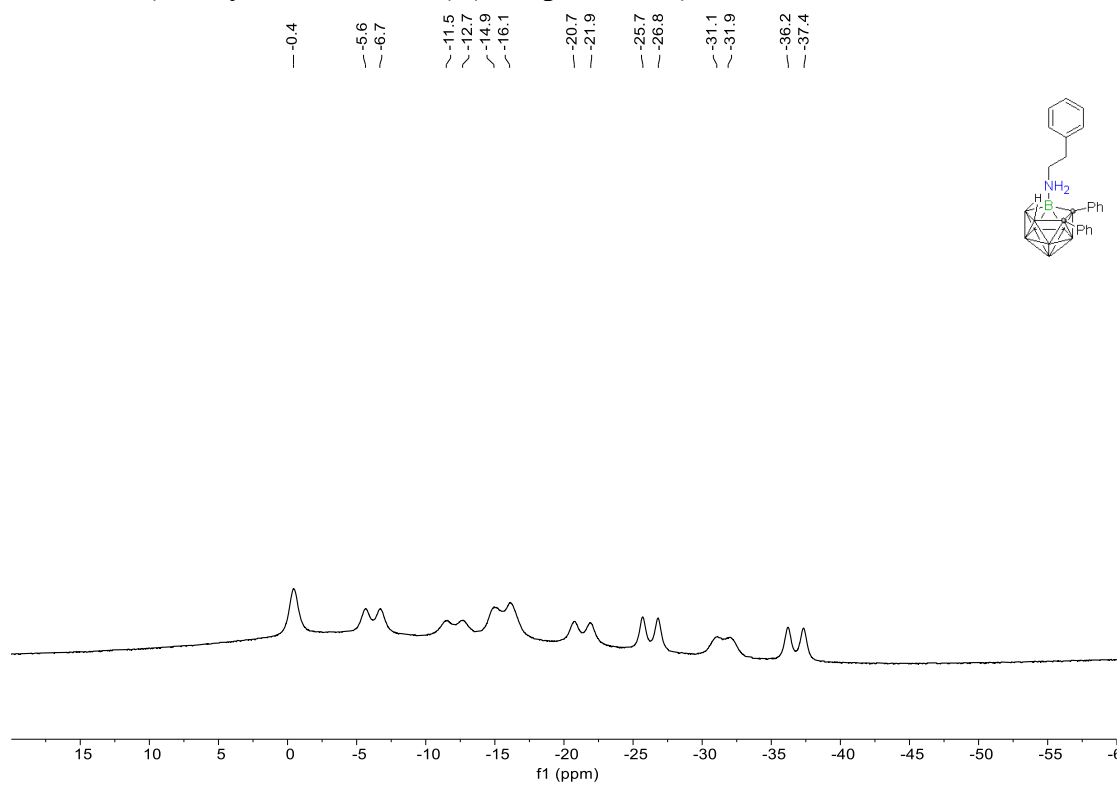
^{13}C NMR (Methylene Chloride- d_2) (Compound 4m)



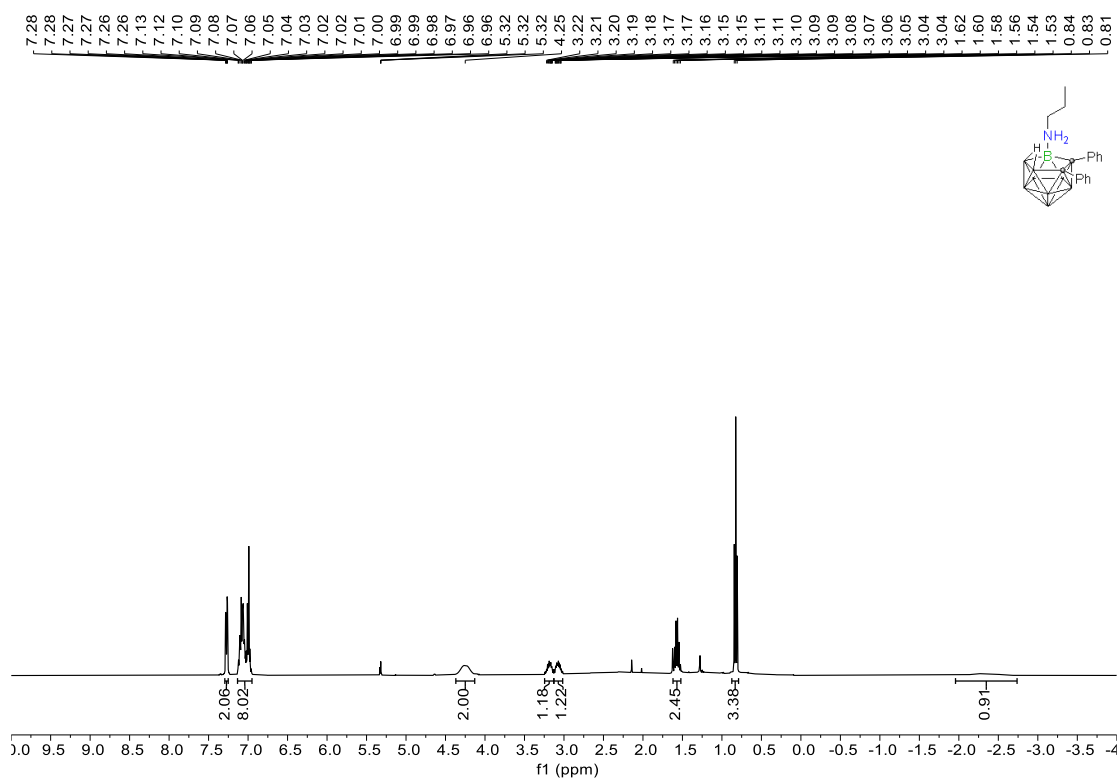
$^{11}\text{B}\{^1\text{H}\}$ NMR (Methylene Chloride- d_2) (Compound 4m)



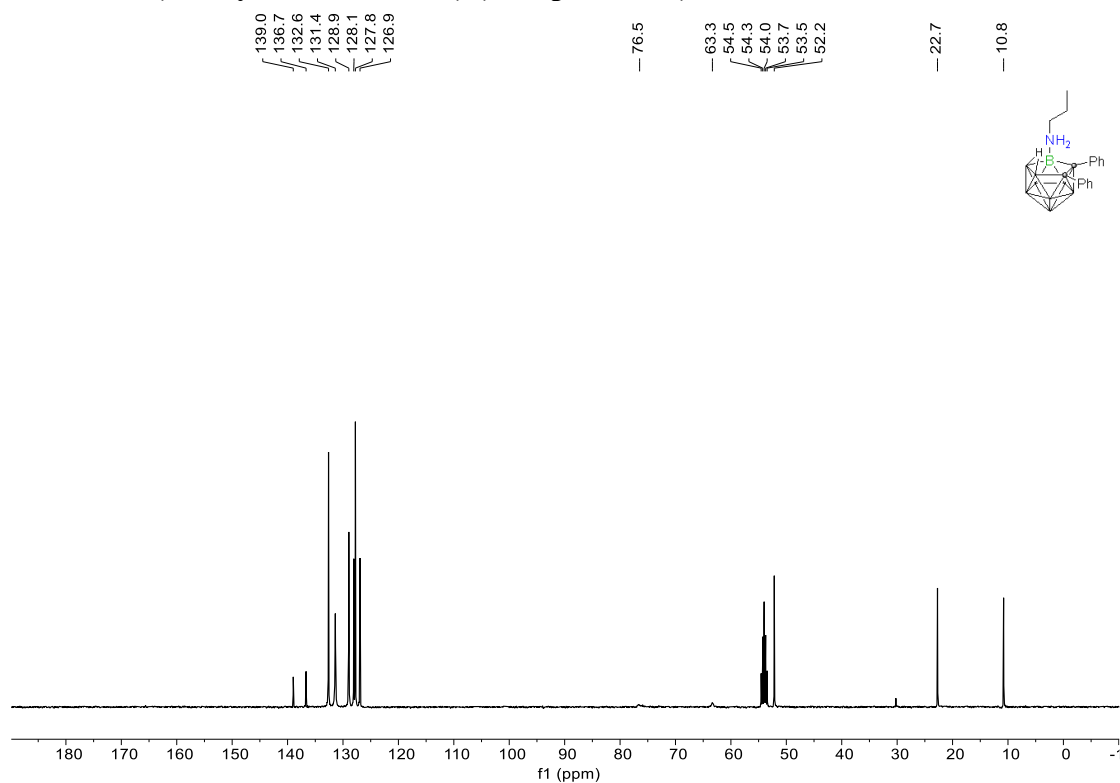
^{11}B NMR (Methylene Chloride- d_2) (Compound 4m)



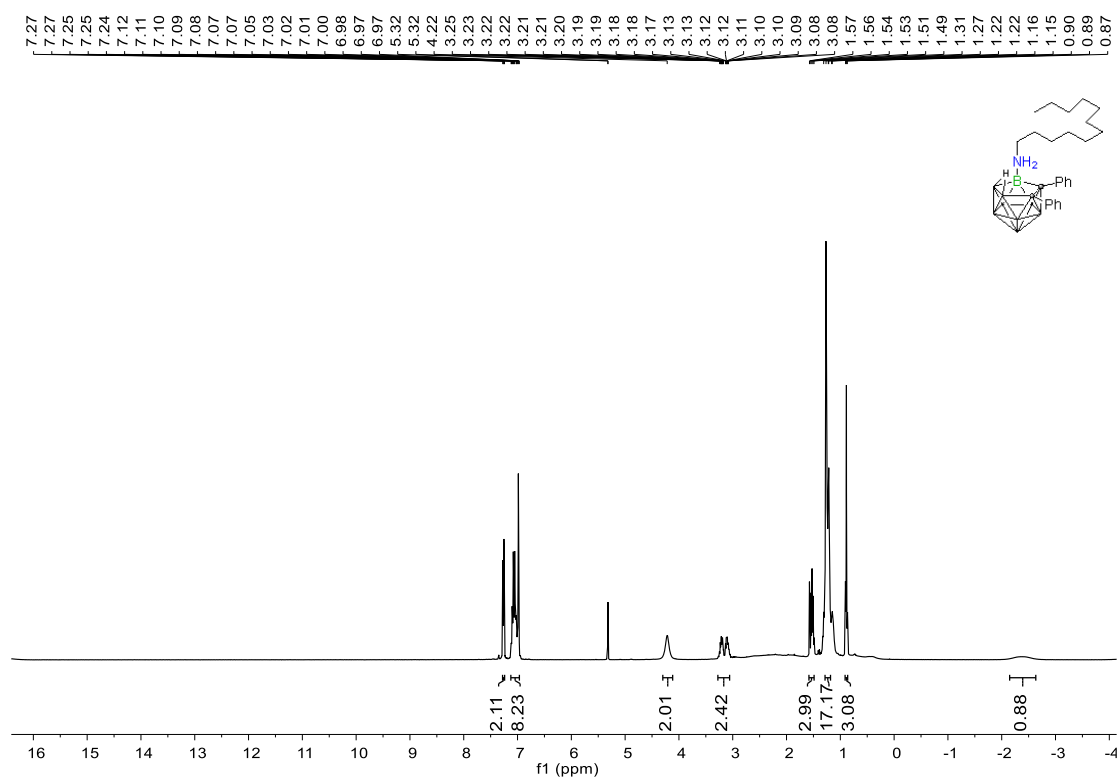
^1H NMR (Methylene Chloride- d_2) (Compound 4n)



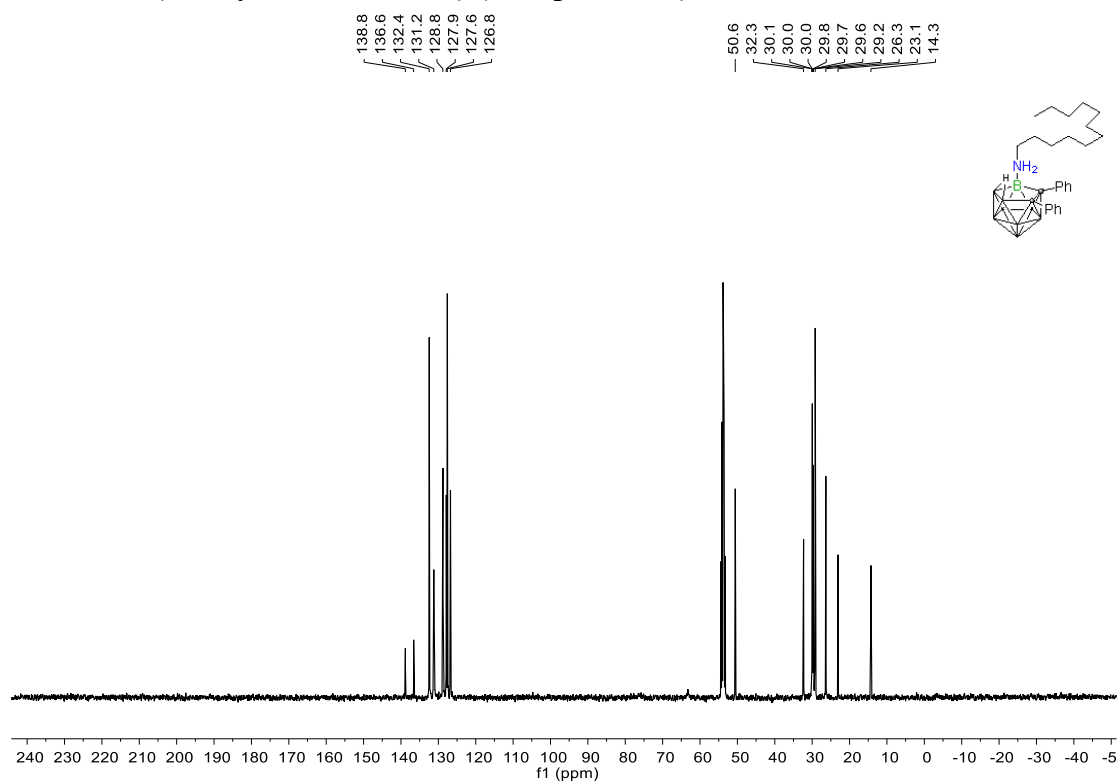
^{13}C NMR (Methylene Chloride- d_2) (Compound 4n)



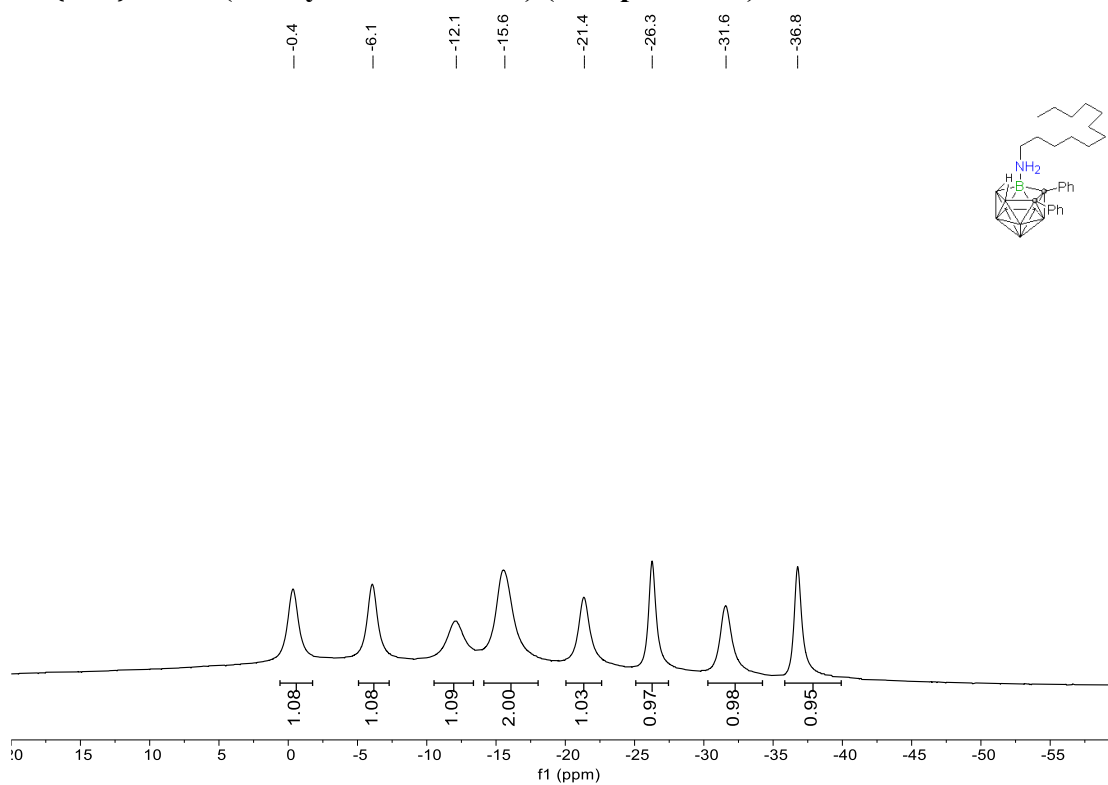
^1H NMR (Methylene Chloride- d_2) (Compound 4o)



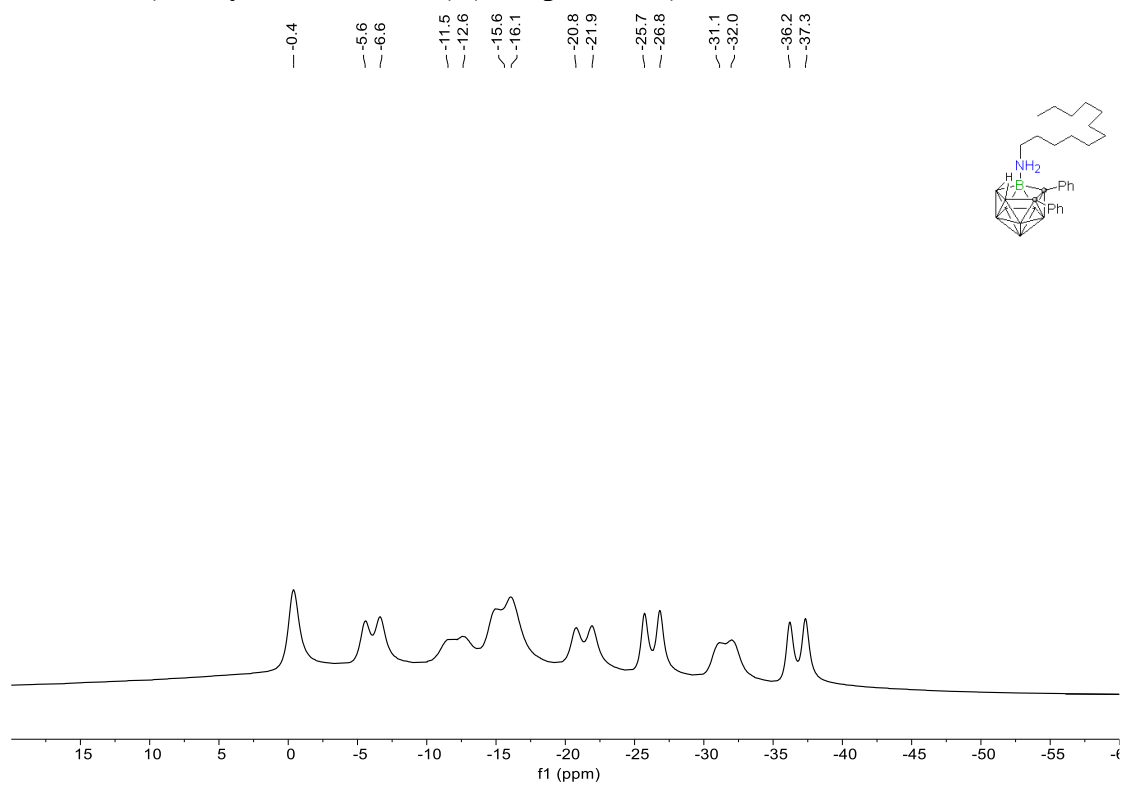
^{13}C NMR (Methylene Chloride- d_2) (Compound 4o)



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



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



139.2
138.6
136.0
133.6
132.7
131.8
130.2
127.8
127.7
127.7
127.2
127.0

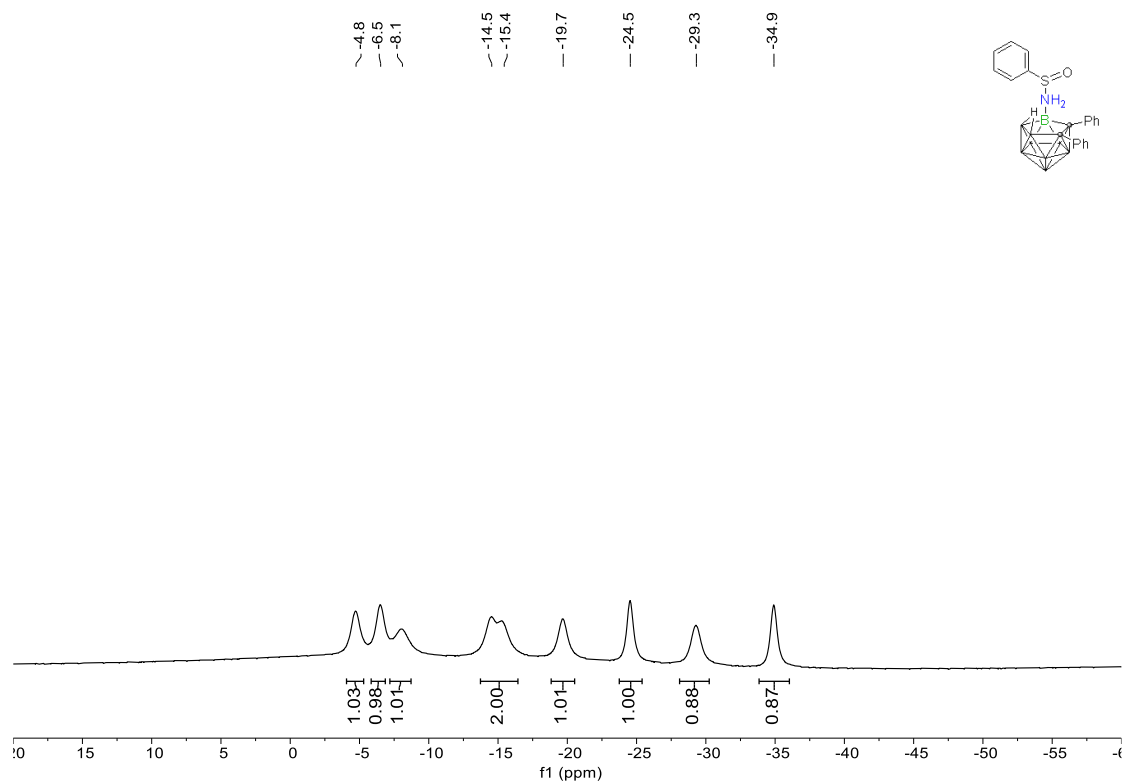
198.2

55.5

f1 (ppm)

Chemical structure: NS(=O)(=O)c1ccc(cc1)C23CC4C(C2)C(C(C3)C4)C5=CC=CC=C5

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



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

