Supplementary Information

Boron-Enriched Star-Shaped Molecule via Cycloaddition Reaction

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General Methods: Reactions were generally performed under argon in oven-dried flasks. Solvents and reagents were added by syringes. Solvents were dried using standard procedures. Reagents were used as purchased without further purification unless otherwise stated. Unless otherwise stated, products were purified by column chromatography on silica gel (70-230 mesh, Aldrich). Unless otherwise stated, yields refer to analytical pure samples. ^1H and ^{13}C NMR spectra were recorded on Bruker Fourier Transform multinuclear NMR spectrometer at 500.13 MHz and 125.75 MHz respectively. Chemical shifts are reported relative to TMS (^1H: $\delta = 0.00$ ppm), $CDCl_3$ (^{13}C: $\delta = 77.0$ ppm). Integrals are in accordance with assignments; coupling constants are given in Hz. All ^{13}C spectra are proton–decoupled. ^{11}B spectra were recorded 64.2 MHz relative to $BF_3.Et_2O$. Infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. Elemental analyses were carried out with CHN-Analyzer 2400 (Perkin Elmer). Melting points were measured with a Mel-Temp II apparatus (Laboratory Devices, USA) and are uncorrected. Differential scanning calorimetry and Thermal gravimetric analysis were performed with DSC 220C and TG/DTA 320 (Seiko Instruments) respectively. UV absorption spectra and emission spectra were measured with Perkin-Elmer Lambda 19 UV-Vis spectrometer and Hitachi F-2500 Fluorescence spectrophotometer respectively. Mass spectral analyses were performed with Applied Biosystems Voyager-DE STR-MALDI-TOF System and Waters 70-VSE spectrometer.

Preparation and Analytical Data for Compound 2: To a mixture of compound **1** (100 mg, 0.26 mmol) in 4 ml dry THF and 2 ml of dry Et_3N, $PdCl_2$ $(PPh_3)_2$ (15 mg, 8 mol %),

CuI (5 mg, 10 mol %), trimethyl silyl acetylene (0.06 mL, 0.4 mmol) was added at room temperature. It was then stirred at room temperature for 5 hours and then filtered over a silicagel pad. After evaporation of the solvent the crude reaction mixture was purified by silica gel column chromatography with hexane as eluent to obtain 90 mg of pure compound **2** as a colorless solid. Yield: 98 %. M.P: 98-100 $^{\circ}$C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.47(d, 2H, J = 8.0 Hz), 7.14(d, 2H, J = 8.0 Hz), 3.45(s, 2H), 2.16 (s, 3H, cluster-CH$_3$), 0.28(s, 9H, SiMe$_3$).^{13}C NMR (CDCl$_3$, 125 MHz): δ 135.2, 132.1, 130.2, 123.0, 104.3, 95.3, 77.1, 74.8, 41.0, 23.6, -0.0., IR (KBr): 2959, 2594, 2898, 2162, 1505, 1462, 1250, 1020 cm^{-1}. ^{11}B NMR (proton decoupled): -4.03, -5.52, -10.11. B$_{10}$C$_{15}$H$_{28}$Si: calcd. C 52.28, H 8.19; Found C 52.11, H 7.93.

Preparation and Analytical Data for Compound 3: Compound **2** (70 mg, 0.2 mmol) was dissolved in 1 mL THF and 1 mL MeOH. Then K$_2$CO$_3$ (41 mg, 0.3 mmol) was added to it and the mixture was stirred at room temperature for 3 hours. The reaction mixture was quenched with saturated ammonium chloride solution and then the crude reaction mixture was extracted with dichloromethane. The combined organic layers were dried over MgSO$_4$. After evaporation of the solvent the crude reaction mixture was purified by silica gel column chromatography with 20 % ethyl acetate in hexane as eluent to obtain 53 mg of pure compound **3** as a colorless solid. Yield: 96 %. M.P: 120 $^{\circ}$C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.50 (d, 2H, J = 8.0 Hz), 7.17(d, 2H, J = 8.0 Hz), 3.47(s, 2H), 3.14 (s, 1H), 2.17(s, 3H cluster-CH$_3$).^{13}C NMR (CDCl$_3$, 125 MHz): δ 135.6, 132.3, 130.3, 122.0, 83.0, 78.1, 77.0, 74.9, 41.0, 23.6. IR (KBr): 3049, 2933, 2563, 2107, 1507, 1237, 1153, 1028 cm^{-1}. ^{11}B NMR (proton decoupled): -3.95, -5.53, -10.0. B$_{10}$C$_{12}$H$_{20}$: calcd. for C 52.91, H 7.40; Found C 52.93, H 7.31. HRMS (ES) (m/z): calcd for B$_{10}$C$_{12}$H$_{20}$: 274.2495; Found 274.2496

Analytical Data for Compound 4: Yield: 40 %. M.P: >260 $^{\circ}$C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.53 (d, 4H, J = 6.55 Hz), 7.21(d, 4H, J = 5.50 Hz), 3.50 (s, 4H), 2.19 (s, 6H, cluster-CH$_3$).^{13}C NMR (CDCl$_3$, 125 MHz): δ 135.1, 131.8, 130.4, 122.9, 89.5, 81.2, 74.8, 41.0, 23.7. IR (KBr): 3029, 2940, 2581, 2049, 1517, 1326, 1114 cm^{-1}. ^{11}B NMR (proton decoupled): -3.87, -5.47, -9.93. B$_{20}$C$_{22}$H$_{38}$: calcd. C 50.94, H 7.38; Found C 51.1, H 7.25. MALDI-TOF-MS (m/z): calcd. 518.75; Found 518.8 (M^{+}, 100 %).

Analytical Data for Compound 5: Yield: 62 %. M.P: >260 °C. . ^{1}H NMR (CDCl$_3$, 500MHz): δ 6.79 (d, 12H, J = 7.85 Hz), 6.72 (d, 12H, J = 7.85 Hz), 3.21 (s, 12H), 2.0(s, 18H, cluster-CH$_3$).^{13}C NMR (CDCl$_3$, 125 MHz): δ 140.0, 139.9, 132.3, 131.5, 129.1, 77.6, 74.8, 40.5, 23.5. IR (KBr): 3038, 2963, 2583 (B-H), 1517, 1261, 1097 cm^{-1}. ^{11}B NMR (proton decoupled): -10.32. C$_{66}$H$_{114}$B$_{60}$: calcd. C 50.94, H 7.38; Found C 50.97, H 7.29. MALDI-TOF-MS (m/z): calcd. 1556.2; Found 1555.1 (M-1, 100 %).

NMR Spectra of Compounds

^{1}H NMR of Compound 2:

3
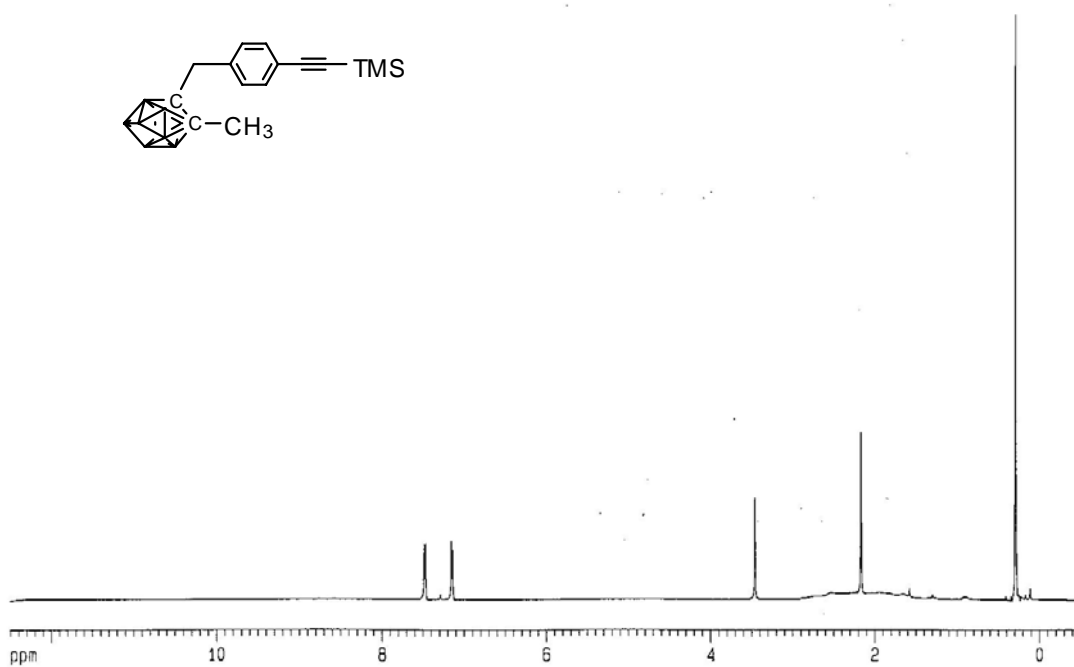
^{13}C NMR of Compound 2:
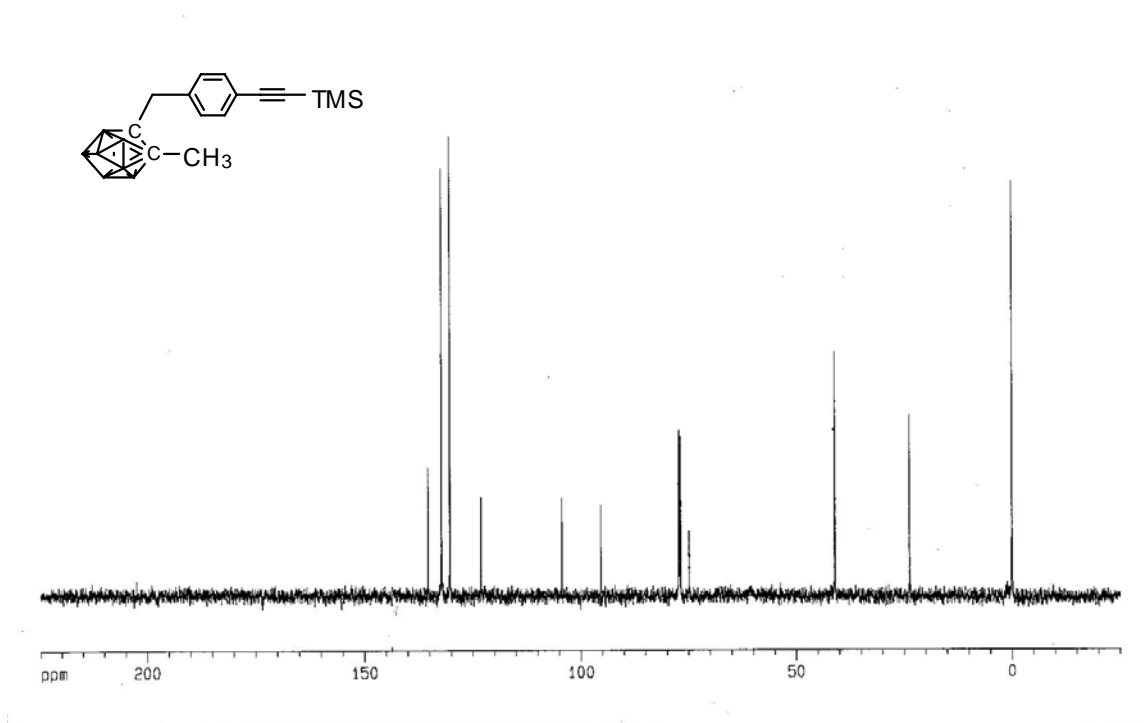
^{11}B NMR (proton decoupled) of Compound 2:

4
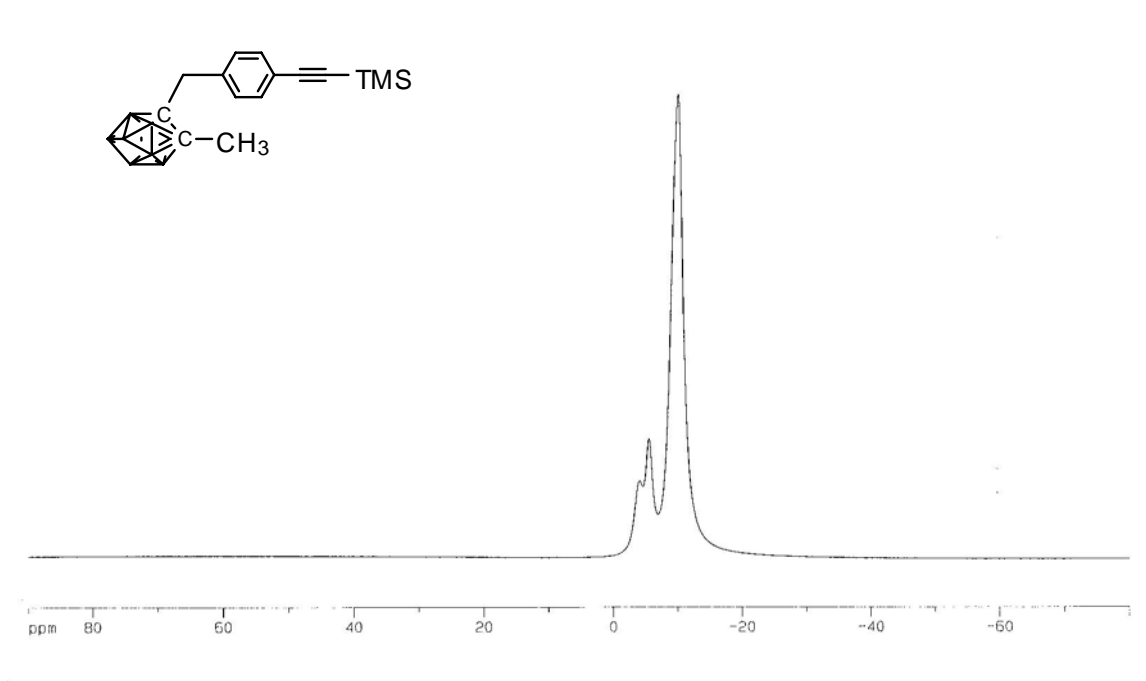
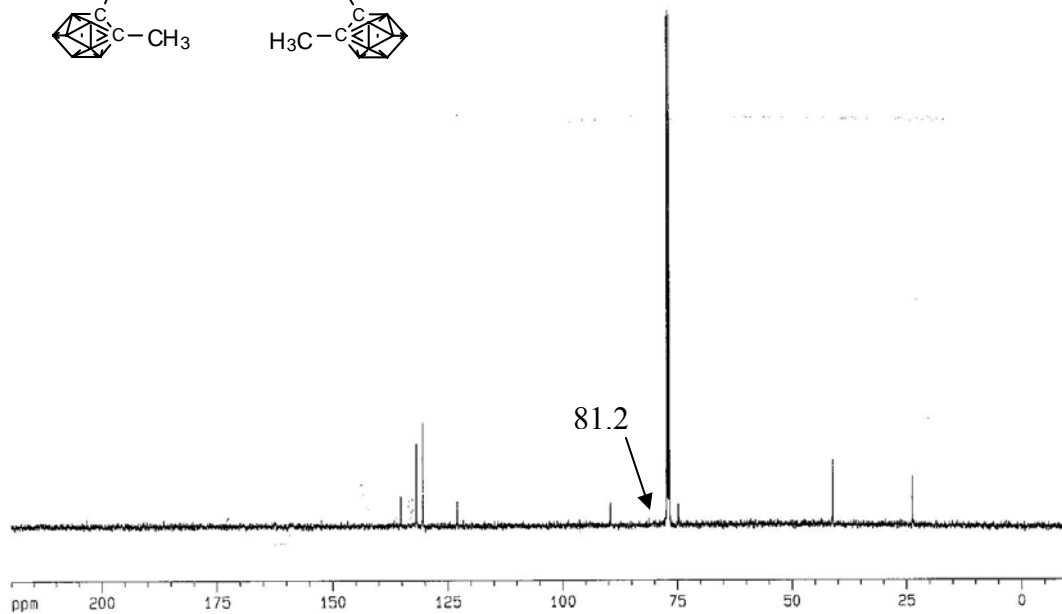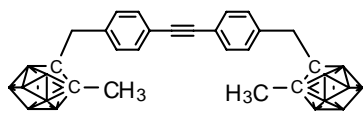# ^{1}H NMR of Compound 3:
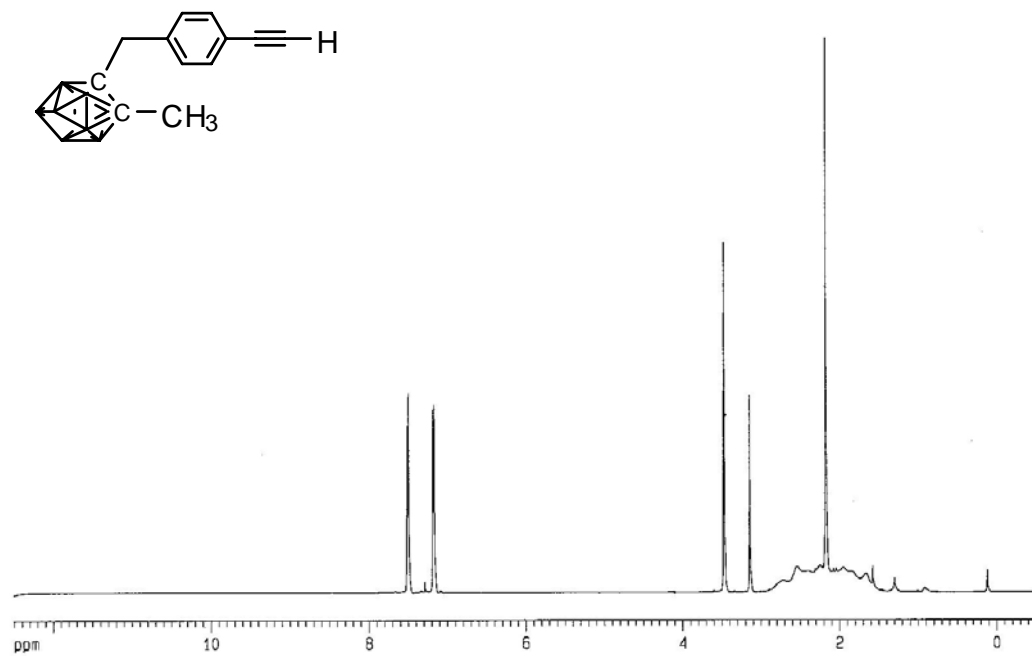
^{13}C NMR of Compound 3:

5
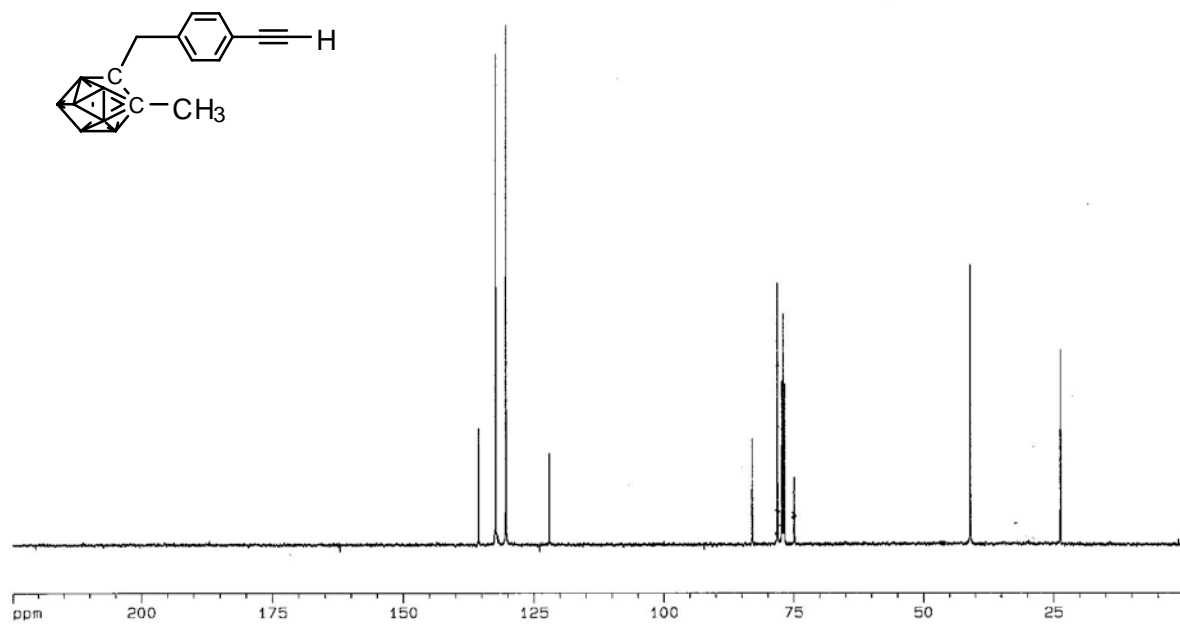
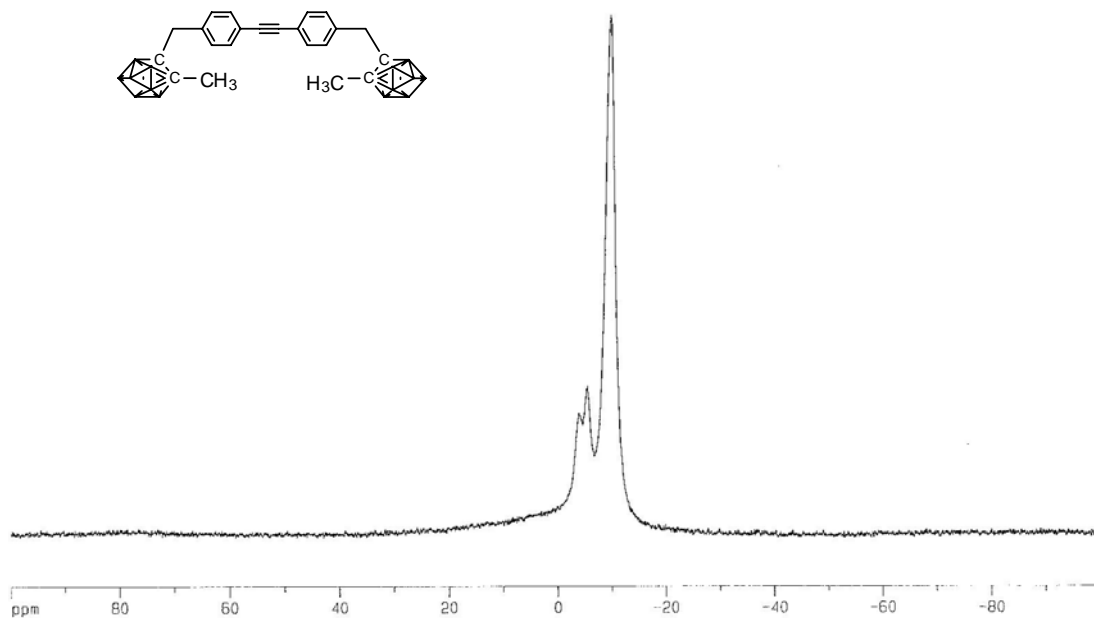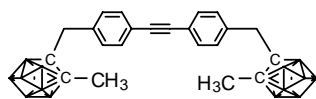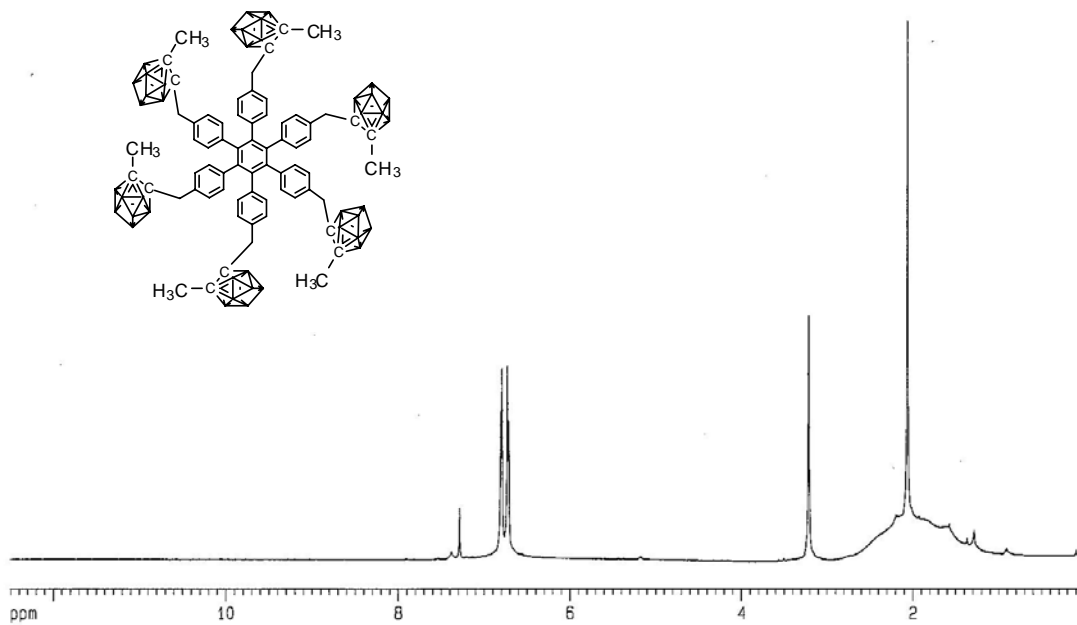# ^{11}B NMR (proton decoupled) of Compound 3:
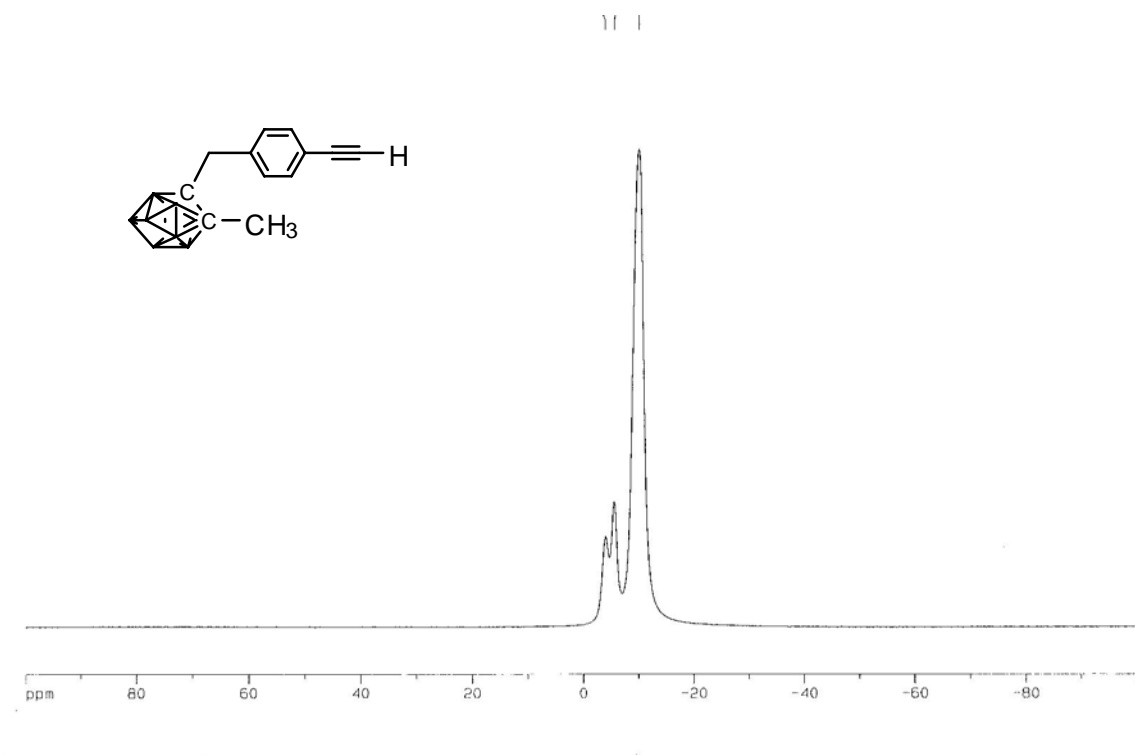
^{1}H NMR of Compound 4:

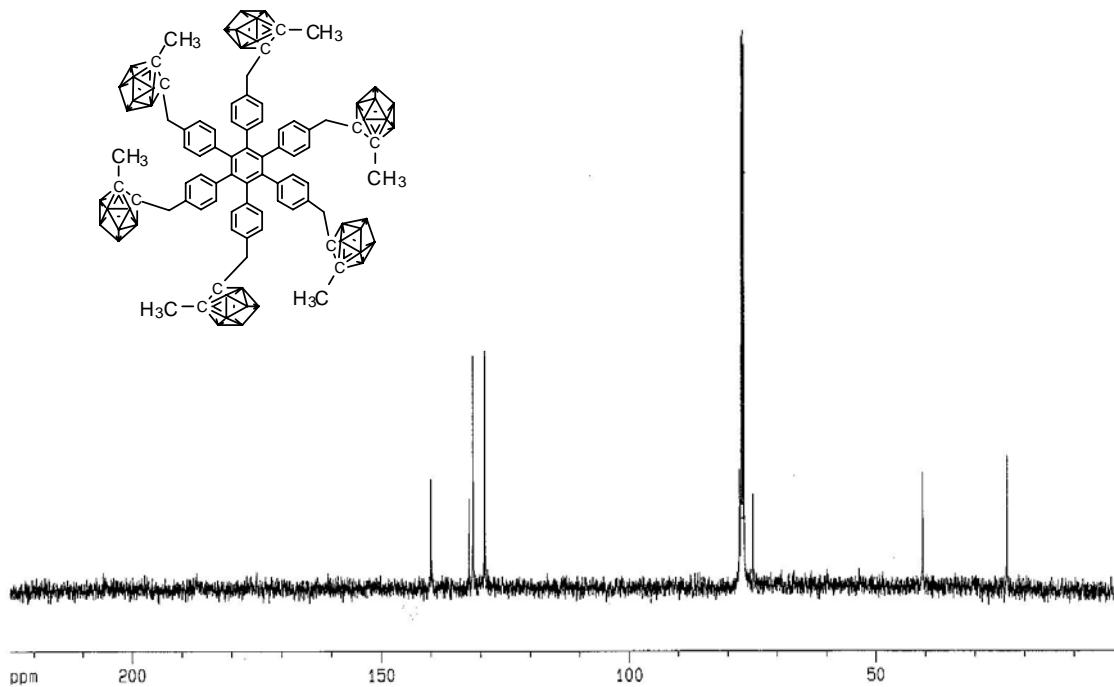
6
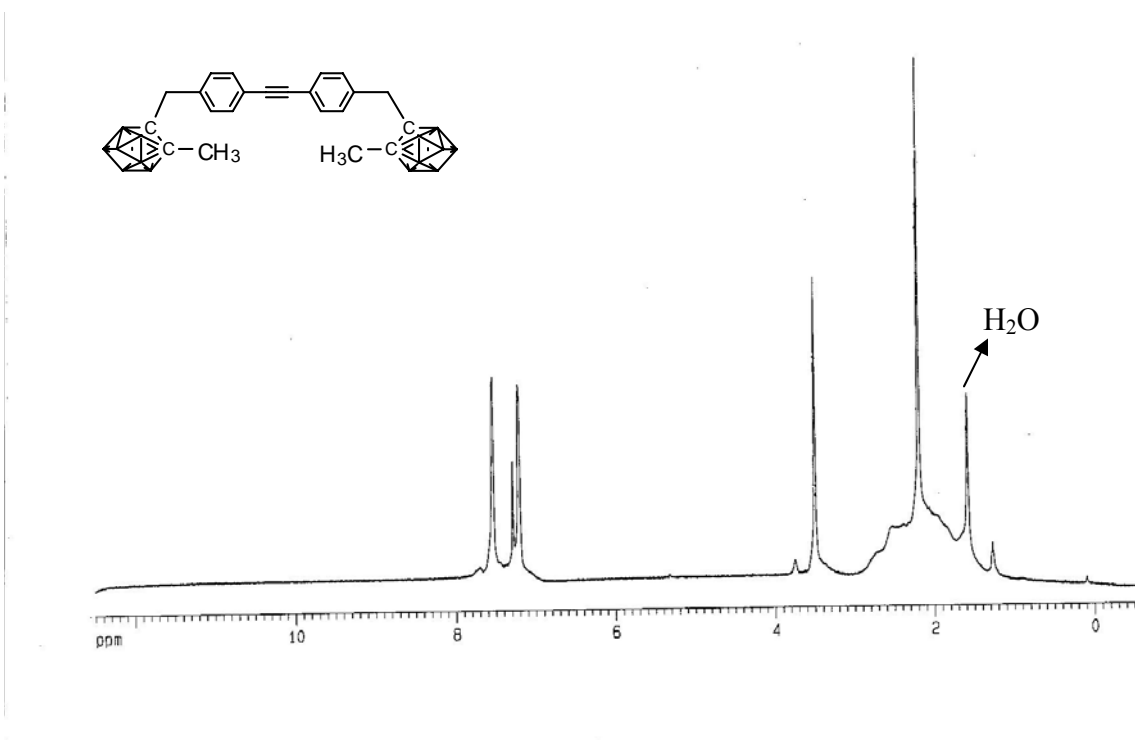
¹³C NMR of Compound 4:

¹¹B NMR (proton decoupled) of Compound 4:

¹H NMR of Compound 5:

¹³C NMR of Compound 5:

¹¹B NMR (proton decoupled) of Compound 5: