

Supporting Information

Pd(II)-catalyzed B(9)-alkynylation of *o*-carboranes and *m*-carboranes

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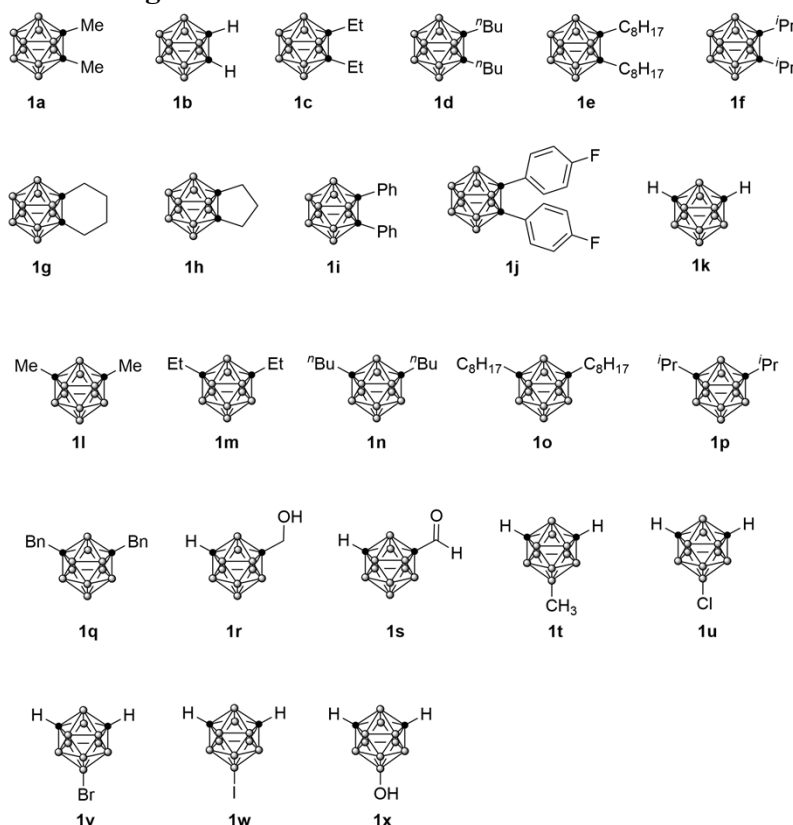
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1. General Information

^1H , ^{13}C , ^{11}B , and ^{19}F NMR spectra were recorded on Bruker Advance III600 spectrometer at 600, 151, 193, and 565 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external $\text{BF}_3 \cdot \text{OEt}_2$ (0.00 ppm) for boron chemical shifts. High-Resolution Mass Spectra (HRMS (ESI-TOF)) were recorded on a Bruker Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). GC-MS analyses were performed on SHIMADZU GCMS-QP 2020. Triisopropylsilylacetylenyl bromide can be purchased in the market. Starting *o*-carborane **1b**, 1,2-Ph₂-*o*-carborane **1i**, *m*-carborane **1k** were purchased from Zhengzhou Yuanli technology. Carboranes **1a**, **1c**-**1h**, **1j**, **1l**-**1q**, **1r**, **1s**, **1t**, **1u**-**1w**, **1x**⁷ were prepared according to literature procedures. All other chemicals were purchased from Aldrich, Acros Organics, J&K Chemicals, Energy Chemical, Aladdin, Macklin, or TCI and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm).

2. Structure of starting carboranes



3. Experimental Section

3.1 General procedure for the B(9)-alkynylation of *o/m*-carboranes

Carborane **1** (0.20 mmol), (bromoethynyl)triisopropylsilane **2a** (2.0 equiv, 0.40 mmol), $\text{Pd}(\text{OAc})_2$ (10 mol%, 0.02 mmol), AgPF_6 (3.0 equiv, 0.60 mmol) were mixed in TFA (1 ml). The resulting mixture was stirred in a closed flask at room temperature for 24 h under air atmosphere. After removal of organic solvents under reduced pressure, the residue was subjected to flash column chromatography on silica gel (200-300 mesh) to give the product.

3.2 Synthesis of terminal alkyne **4**

Compound **31** (354 mg, 1 mmol) and TBAF (2 mL, 2 mmol, 1M in THF) were mixed in THF (5 mL). The resulting mixture was stirred at 0 °C for 1 h. After hydrolysis with water (20 mL) and extraction with ethyl acetate (20 mL x 3), the organic layers were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography to give the product **4**.

3.3 Synthesis of **5**

N,N-dimethyl aniline (51 mg, 0.42 mmol) was added to the reaction mixture of **4** (39.2mg, 0.2 mmol) and B₁₀H₁₄ (26 mg, 0.21 mmol) in toluene. Then the reaction mixture was stirred at 115 °C for 24 hours. After cooling to room temperature, water (10 mL) was added to the mixture and extracted with ethyl acetate (10 mL x 3). The organic layers were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography to give the product **5**.

3.4 Synthesis of **6**

To a mixture of PPh₃ (52.4 mg, 0.2 mmol) and terminal alkyne **4** (39.2 mg, 0.2 mmol) in DCM (2.0 mL) was added NBS (71.2 mg, 0.4 mmol). The reaction mixture was stirring at room temperature for 6 hours. After removal of the solvent with a rotary evaporator, the residue was purified by column chromatography to give the product **6**. The reaction requires the recovery of raw materials and repeat again.

3.5 Synthesis of **7**

Compound **4** (39.2 mg, 0.2 mmol), PhI (81.6 mg, 0.4 mmol), Pd(PPh₃)Cl₂ (7.0 mg, 0.01 mmol), CuI (3.8 mg, 0.02 mmol) and NEt₃ (1 mL) were mixed in toluene (4 mL). The resulting mixture was heated at 80 °C for 12 h. After hydrolysis with water (10 mL) and extraction with ethyl acetate (10 mL x 3), the organic layers were combined and concentrated to dryness in vacuo. The residue was purified by column chromatography to give the product **7**.

3.6 Synthesis of **8**

Compound **4** (58.8 mg, 0.3 mmol), CrO₃ (178.2 mg, 1.8 mmol, 6 eq), H₂SO₄ (16 μL, 0.3 mmol, 1 eq), were mixed in HOAc (1.5 mL), The resulting mixture was stirring at room temperature for 1 h, quenching the mixture with saturated NaHCO₃, and extracting with EA (10 mL x 3). The residue was purified by column chromatography to give the product **8**.

3.6 Synthesis of **9 and 10**

Under N₂ atmosphere, *n*-BuLi (1.38 ml, 1.6 M / hexane, 2.2 mmol) was added to the solution of **4** in THF (20 mL) at -78 °C. After that, the reaction mixture was warmed up to room temperature and stirred for 1 hour. Then the mixture was cooled to -78 °C, benzaldehyde (224 μL, 2.2 mmol) or acetone (163μL, 2 mmol) in THF (10 mL) was added. The reaction was slowly warmed up to room temperature and was stirred for 1 hour. Saturated aqueous solution of NH₄Cl was added, and extract the aqueous layer with Et₂O. Dry the organic phase over Na₂SO₄. Filter the mixture and concentrate in vacuo. Purify the crude product by flash column chromatography on silica gel to obtain the final product.

3.7 Synthesis of product **11**

To a solution of alkyne (39.2 mg, 0.2 mmol) in acetone (50 mL) was added N-bromosuccinimide (3.36 mg, 0.02 mmol) and AgNO₃ (39.16 mg, 0.22 mmol). The reaction mixture was stirred at room

temperature under exclusion of light for 2 h. Upon completion the reaction mixture was concentrated under reduced pressure and filtered through a celite plug to afford crude **11** which was submitted to the next step without further purification.

4. Mechanistic study

(a) 1,2-Me₂-*o*-carborane **1a** (0.1 mmol) was stirred in CF₃COOH (1 mL) at room temperature for 30 minutes; (b) 1,2-Me₂-*o*-carborane **1a** (0.1 mmol) and Pd(OAc)₂ (0.01 mmol, 10 mol%) were stirred in CF₃COOH (1 mL) at room temperature for 30 minutes; (c) 1,2-Me₂-*o*-carborane **1a** (0.1 mmol), Pd(OAc)₂ (0.01 mmol, 10 mol%) and AgPF₆ (0.3 mmol) were stirred in CF₃COOH (1 mL) at room temperature for 30 minutes; (d) 1,2-Me₂-*o*-carborane **1a** (0.1 mmol) and AgPF₆ (0.3 mmol) were stirred in CF₃COOH (1 mL) at room temperature for 30 minutes.

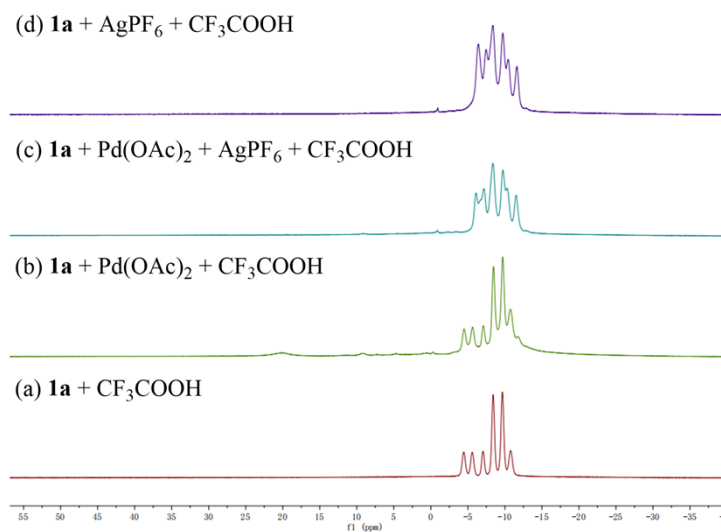


Figure S1 ¹¹B NMR.

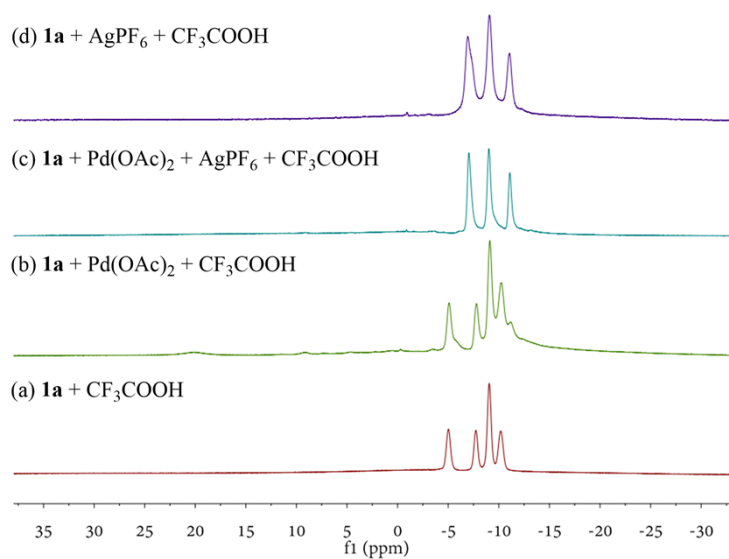
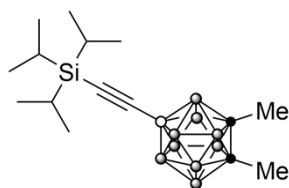


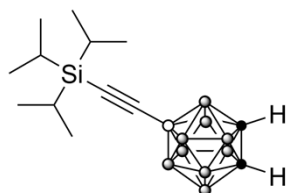
Figure S2 ¹¹B{¹H} NMR

5. Characterization data



3a. Yield 60% . Yellow liquid. **Eluent:** PE:EA = 20:1

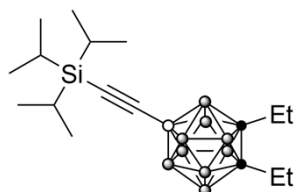
¹H NMR (400 MHz, CDCl₃) δ 2.02 (d, *J* = 3.5 Hz, 7H), 1.16 – 0.94 (m, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 29.73, 18.57, 11.33. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -4.55 (2B), -7.50 (6B), 11.93 (2B). **HRMS(ESI-TOF):** *m/z* calcd for C₁₅¹⁰B₂¹¹B₈H₃₆Si [M+Na]⁺: 375.3490. Found: 375.3463.



3b. Yield 59% . Yellow liquid. **Eluent:** PE:EA = 20:1

¹H NMR (400 MHz, CDCl₃) δ 3.58 – 3.36 (m, 2H), 1.16 – 0.95 (m, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 52.75, 49.30, 29.73, 18.63, 11.26. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -1.75 (1B), -2.46 (1B), -8.45 (2B), -13.39 (2B), -14.56 (2B), -15.66 (2B).

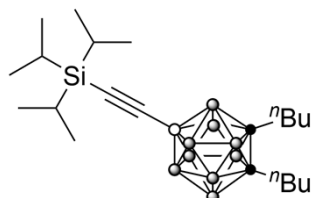
HRMS(ESI-TOF): *m/z* calcd for C₁₃¹⁰B₂¹¹B₈H₂₉Si [M+Na]⁺: 347.3176. Found: 347.3177.



3c. Yield 61% . Yellow liquid. **Eluent:** PE:EA = 20:1

¹H NMR (400 MHz, CDCl₃) δ 2.22 (dq, *J* = 7.6, 1.3 Hz, 5H), 1.24 – 1.12 (m, 7H), 1.11 – 0.96 (m, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 75.48, 28.55, 27.88, 18.64, 14.08, 14.00, 11.30. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -4.33 (2B) -9.64 (2B) -10.79 (4B) -11.94 (2B).

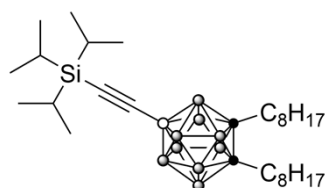
HRMS(ESI-TOF): *m/z* calcd for C₁₇¹⁰B₂¹¹B₈H₄₀Si [M+Na]⁺: 403.3804. Found: 403.3804.



3d. Yield 62% . Yellow liquid. **Eluent:** PE:EA = 20:1

¹H NMR (400 MHz, CDCl₃) δ 2.16 – 2.07 (m, 5H), 1.56 – 1.45 (m, 6H), 1.31 (dtd, *J* = 14.6, 7.5, 2.8 Hz, 5H), 1.08 – 0.98 (m, 21H), 0.92 (td, *J* = 7.3, 4.7 Hz, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 74.69, 34.83, 34.15, 31.82, 31.70, 22.43, 18.64, 13.64, 11.30. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -4.36 (2B), -9.67 (2B), -10.87 (4B), -11.79 (2B).

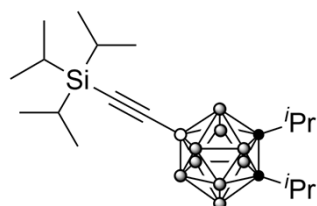
HRMS(ESI-TOF): *m/z* calcd for C₂₁¹⁰B₁¹¹B₉H₄₈Si [M+Na]⁺: 460.4402. Found: 460.4395.



3e. Yield 63%. Yellow liquid. **Eluent:** PE:EA = 20:1

¹H NMR (400 MHz, CDCl₃) δ 2.15 – 2.03 (m, 5H), 1.59 – 1.47 (m, 5H), 1.27 (s, 20H), 1.04 (d, *J* = 5.1 Hz, 20H), 0.88 (t, *J* = 6.1 Hz, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 74.73, 35.09, 34.42, 31.75, 29.75, 29.65, 29.26, 29.09, 22.61, 18.64, 14.06, 11.30. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -4.58 (2B), -11.56 (8B).

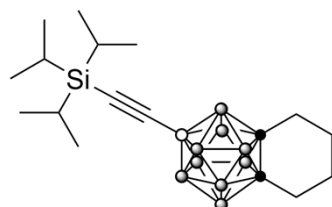
HRMS(ESI-TOF): *m/z* calcd for C₂₉¹⁰B₁¹¹B₉H₆₄Si [M+Na]⁺: 572.5660. Found: 572.5663.



3f. Yield 47%. Yellow liquid. **Eluent:** PE:EA = 20:1

¹H NMR (400 MHz, CDCl₃) δ 2.29 (dq, *J* = 13.8, 6.9, 5.9, 4.0 Hz, 3H), 1.21 (dd, *J* = 8.8, 6.9 Hz, 12H), 1.14 – 0.92 (m, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 86.97, 83.27, 30.71, 30.24, 24.45, 24.32, 18.66, 11.30. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -3.85 (2B), -8.68 (2B), -11.65 (2B) -12.78 (4B).

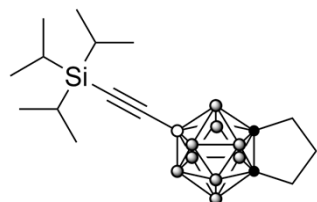
HRMS(ESI-TOF): *m/z* calcd for C₁₉¹⁰B₁¹¹B₉H₄₄Si [M+Na]⁺: 432.4088 Found: 432.4089.



3g. Yield 48%. Yellow liquid. **Eluent:** PE:EA = 20:1

¹H NMR (400 MHz, CDCl₃) δ 2.42-2.43 (m, 4H), 1.56-1.58 (m, 4H), 1.08 – 0.96 (m, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 71.48, 68.10, 32.75, 32.19, 19.74, 19.55, 18.64, 18.46, 11.28. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -5.12 (2B), -8.39 (2B), -9.33 (2B), -10.45 (2B), -12.48 (2B).

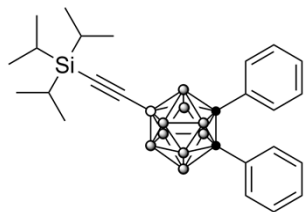
HRMS(ESI-TOF): *m/z* calcd for C₁₇¹⁰B₂¹¹B₈H₃₈Si [M+Na]⁺: 401.3648. Found: 401.3649.



3h. Yield 45%. Yellow liquid. **Eluent:** PE:EA = 20:1

¹H NMR (400 MHz, CDCl₃) δ 2.47 – 2.31 (m, 6H), 1.02 – 0.90 (m, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 82.48, 34.51, 34.01, 32.21, 18.64, 11.28. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -5.97 (2B), -7.24 (2B), -9.91 (2B), -11.41 (2B), -12.56 (2B).

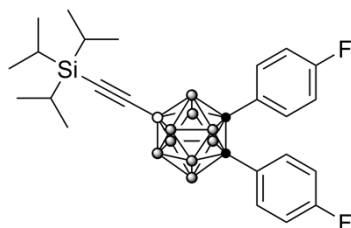
HRMS(ESI-TOF): *m/z* calcd for C₁₆¹⁰B₂¹¹B₈H₃₆Si [M+Na]⁺: 387.3491. Found: 387.3506.



3i. Yield 34%. Yellow liquid. **Eluent:** PE

¹H NMR (400 MHz, CDCl₃) δ 7.41 (dq, *J* = 7.2, 1.5 Hz, 3H), 7.26 – 7.20 (m, 2H), 7.16 – 7.10 (m, 3H), 1.19 – 0.96 (m, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 130.72, 130.61, 130.24, 128.29, 83.64, 18.66, 11.28. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -2.09 (2B), -9.54 (6B) -12.04 (2B).

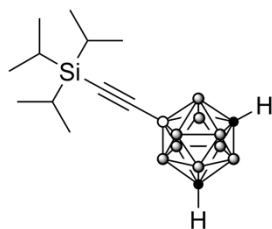
HRMS(ESI-TOF): *m/z* calcd for C₂₅¹⁰B₁¹¹B₉H₄₀Si [M+Na]⁺: 500.3780. Found: 500.3774.



3j. Yield 28%. Yellow liquid. **Eluent:** PE:EA = 20:1

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.05 (m, 6H), 6.99 – 6.85 (m, 2H), 0.98 (d, *J* = 4.7 Hz, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 163.29, 160.83, 132.41, 132.32, 132.24, 130.07, 130.06, 129.99, 129.98, 126.51, 126.48, 126.39, 126.36, 118.20, 118.09, 117.96, 117.84, 117.79, 117.58, 82.16, 18.64, 11.25. **¹⁹F NMR (376 MHz, CDCl₃)** δ -111.43. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -1.60 (2B), -9.35 (6B), -12.08 (2B).

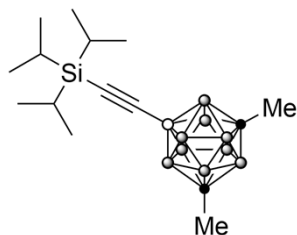
HRMS(ESI-TOF): *m/z* calcd for C₂₅¹⁰B₁¹¹B₉H₃₈SiF₂ [M+Na]⁺: 536.3591. Found: 536.3582.



3k. Yield 48%. Yellow liquid. **Eluent:** PE

¹H NMR (400 MHz, CDCl₃) δ 2.88 (s, 2H), 1.13 – 0.99 (m, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 29.71, 18.63, 11.27. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -6.08 (2B), -9.52 (2B), -12.80 (2B), -14.12 (2B), -17.81 (1B), -19.69 (1B)

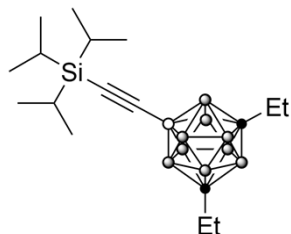
HRMS(ESI-TOF): *m/z* calcd for C₁₃¹⁰B₂¹¹B₈H₃₂Si [M+Na]⁺: 347.3176. Found: 347.3150.



3l. Yield 64%. Yellow liquid. **Eluent:** PE

¹H NMR (400 MHz, CDCl₃) δ 1.52 (s, 6H), 0.98 – 0.79 (m, 21H). **¹³C NMR (101 MHz, CDCl₃)** δ 24.33, 18.65, 11.28. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -6.80 (2B), -9.47 (4B), -10.88 (2B), -12.94 (1B), -15.88 (1B).

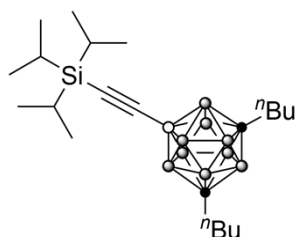
HRMS(ESI-TOF): m/z calcd for C₁₅¹⁰B₂¹¹B₈H₃₆Si [M+Na]⁺: 375.3490. Found: 375.3485.



3m. Yield 59%. Yellow liquid. **Eluent:** PE

¹H NMR (400 MHz, CDCl₃) δ 1.98 (q, *J* = 7.6 Hz, 4H), 1.17 – 1.00 (m, 21H), 0.97 (t, *J* = 7.6 Hz, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 30.31, 18.66, 14.25, 11.30. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -6.94 (2B), -10.18 (2B), -10.81 (2B), -12.19 (2B), -14.63 (1B), -16.08 (1B).

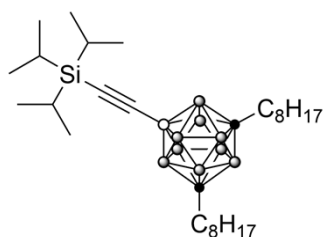
HRMS(ESI-TOF): m/z calcd for C₁₇¹⁰B₂¹¹B₈H₄₀Si [M+Na]⁺: 403.3804. Found: 403.3790.



3n. Yield 61%. Yellow liquid. **Eluent:** PE

¹H NMR (400 MHz, CDCl₃) δ 1.92 – 1.86 (m, 4H), 1.32 (ddd, *J* = 12.1, 6.0, 3.1 Hz, 4H), 1.25 – 1.19 (m, 4H), 1.13 – 0.99 (m, 20H), 0.87 (t, *J* = 7.2 Hz, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 36.73, 32.03, 22.33, 18.66, 13.70, 11.30. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -6.82 (2B), -10.38 (4B), -12.10 (2B), -14.54 (1B), -16.02 (1B).

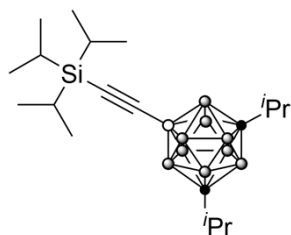
HRMS(ESI-TOF): m/z calcd for C₂₁¹⁰B₁¹¹B₉H₄₈Si [M+Na]⁺: 460.4402. Found: 460.4394.



3o. Yield 62%. Yellow liquid. **Eluent:** PE

¹H NMR (400 MHz, CDCl₃) δ 1.92 – 1.85 (m, 4H), 1.37 – 1.16 (m, 24H), 1.13 – 1.03 (m, 21H), 0.88 (t, *J* = 6.9 Hz, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 36.98, 31.78, 29.95, 29.17, 29.14, 22.62, 18.66, 14.08, 11.30. **¹¹B{¹H} NMR (128 MHz, CDCl₃)** δ -6.81 (2B), -10.32 (4B), -10.47 (4B), -14.15 (2B).

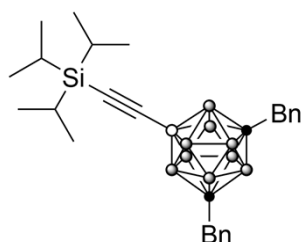
HRMS(ESI-TOF): m/z calcd for C₂₉¹⁰B₁¹¹B₉H₆₄Si [M+Na]⁺: 572.5660. Found: 572.5675.



3p. Yield 48% . Yellow liquid. **Eluent:** PE

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.19 – 2.14 (m, 2H), 1.11 – 1.04 (m, 21H), 1.03 (s, 6H), 1.02 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 80.23, 33.81, 23.89, 18.67, 11.31. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ - 6.61 (2B), -10.54 (2B), -11.49 (2B), -12.87 (2B), -15.26 (1B), -16.69 (1B).

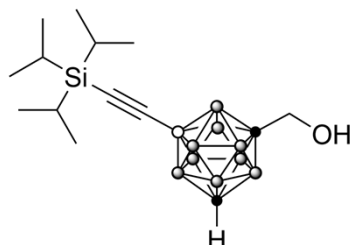
HRMS(ESI-TOF): m/z calcd for $\text{C}_{19}^{10}\text{B}_1^{11}\text{B}_9\text{H}_{44}\text{Si}$ $[\text{M}+\text{Na}]^+$: 432.4088. Found: 432.4081.



3q. Yield 38%. Yellow liquid. **Eluent:** PE

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 (d, $J = 1.9$ Hz, 2H), 7.27 (d, $J = 2.0$ Hz, 3H), 7.05 – 7.02 (m, 3H), 3.12 (s, 4H), 2.44 – 2.04 (m, 9H), 1.06 (d, $J = 4.7$ Hz, 21H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 136.82, 129.83, 128.39, 127.51, 42.97, 29.73, 18.66, 11.28. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ -6.33 (2B), - 9.85 (4B), -11.94 (2B), -14.76 (1B), -16.36 (1B).

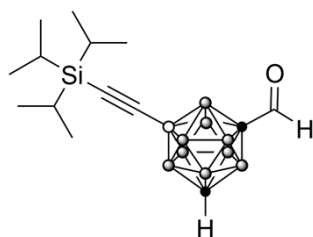
HRMS(ESI-TOF): m/z calcd for $\text{C}_{27}^{10}\text{B}_1^{11}\text{B}_9\text{H}_{44}\text{Si}$ $[\text{M}+\text{Na}]^+$: 528.4094. Found: 528.4082.



3r. Yield 37%. Yellow liquid. **Eluent:** PE

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.28 (s, 1H), 2.91 (s, 1H), 2.09 (s, 2H), 1.06 (s, 21H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 64.21, 20.46, 18.62, 11.26. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ -4.05 (2B), -20.30 – - 10.09 (8B).

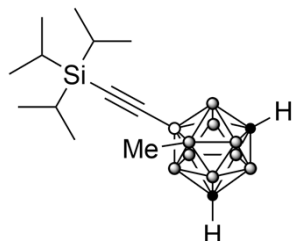
HRMS(ESI-TOF): m/z calcd for $\text{C}_{14}^{10}\text{B}_2^{11}\text{B}_8\text{H}_{34}\text{SiO}$ $[\text{M}+\text{Na}]^+$: 377.3282. Found: 377.3242.



3s. Yield 33%. Yellow liquid. **Eluent:** PE

^1H NMR (400 MHz, CDCl_3) δ 9.05 (s, 1H), 3.04 (s, 1H), 1.07 (d, J = 3.9 Hz, 21H). ^{13}C NMR (101 MHz, CDCl_3) δ 185.04, 54.02, 18.62, 11.22. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ -5.77 (2B), -9.22 (2B), -12.13 (2B), -13.42 (2B), -17.16 (1B), -18.95 (1B).

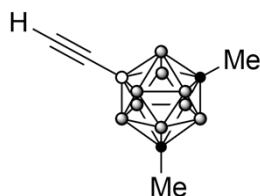
HRMS(ESI-TOF): m/z calcd for $\text{C}_{14}^{10}\text{B}_2^{11}\text{B}_8\text{H}_{32}\text{SiO}$ $[\text{M}+\text{H}]^+$: 375.3126. Found: 375.3216.



3t. Yield 27%. Yellow liquid. **Eluent:** PE

^1H NMR (400 MHz, CDCl_3) δ 2.81 (s, 2H), 1.15 – 0.98 (m, 21H), 0.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 52.23, 18.65, 11.24. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ -0.01 (2B), -5.49 (2B), -9.12 (1B), -13.63 (3B), -20.00 (1B), -21.46 (1B).

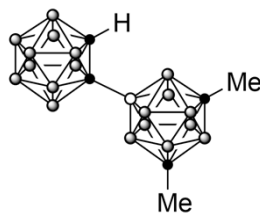
HRMS(ESI-TOF): m/z calcd for $\text{C}_{14}^{10}\text{B}_2^{11}\text{B}_8\text{H}_{34}\text{Si}$ $[\text{M}+\text{Na}]^+$: 349.3332. Found: 349.3307.



4. Yield 60%. White solid. Melting point: 46 – 48 °C. **Eluent:** PE

^1H NMR (400 MHz, CDCl_3) δ 3.40 (s, 1H), 1.72 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 70.82, 61.24, 24.28. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ -6.82 (2B), -9.64 (3B), -10.64 (3B), -12.75 (1B), -14.04 (1B).

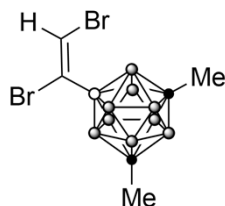
HRMS(ESI-TOF): m/z calcd for $\text{C}_6^{10}\text{B}_2^{11}\text{B}_8\text{H}_{16}$ $[\text{M}+\text{H}]^+$: 197.2331. Found: 197.2321.



5. Yield 77%. White solid. Melting point: 230 – 232 °C. **Eluent:** PE:DCM = 5:1

^1H NMR (400 MHz, CDCl_3) δ 3.40 (s, 1H), 1.72 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 70.82, 61.24, 24.28. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ -1.77 (1B), -2.78 (1B), -7.13 (1B), -8.16 (1B), -12.76 – -9.73 (5B), -14.09 (1B).

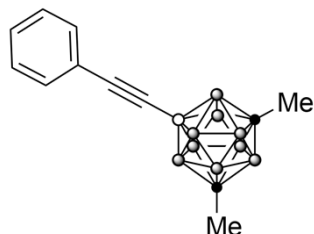
HRMS(ESI-TOF): m/z calcd for $\text{C}_6^{10}\text{B}_4^{11}\text{B}_{16}\text{H}_{26}$ $[\text{M}+\text{H}]^+$: 315.4117. Found: 315.4096.



6. Yield 60%. Yellow solid. Melting point: 53 – 55°C. **Eluent:** PE

¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, *J* = 9.1 Hz, 1H), 1.73 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 111.06, 70.18, 24.48. **¹¹B{¹H} NMR** (128 MHz, CDCl₃) δ -2.85 (1B), -6.74 (2B), -9.48 (3B), -10.71 (2B), -12.89 (2B).

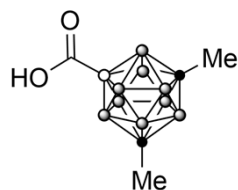
HRMS(ESI-TOF): *m/z* calcd for C₆¹¹⁰B₂¹¹B₈H₁₆Br₂ [M+H]⁺: 356.0597. Found: 356.0519.



7. Yield 90%. Yellow liquid. **Eluent:** PE

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.33 (m, 2H), 7.25 – 7.14 (m, 3H), 1.65 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 130.88, 127.00, 126.82, 122.96, 68.95, 23.34. **¹¹B{¹H} NMR** (128 MHz, CDCl₃) δ -6.86 (2B), -9.46 (3B), -10.72 (3B), -12.79 (1B), -14.24 (1B).

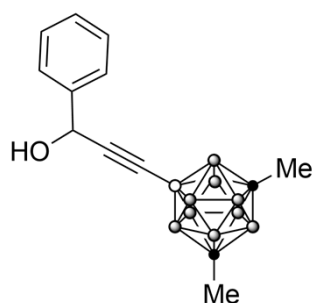
HRMS(ESI-TOF): *m/z* calcd for C₁₂¹⁰B₂¹¹B₈H₂₀ [M+H]⁺: 273.2647 Found: 273.2628.



8. Yield 65%. White solid. Melting point: 169 – 170 °C. **Eluent:** EA

¹H NMR (400 MHz, CDCl₃) δ 1.74 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 70.98, 24.25. **¹¹B{¹H} NMR** (128 MHz, CDCl₃) δ -7.36 (3B), -10.09 (5B), -12.33 (2B).

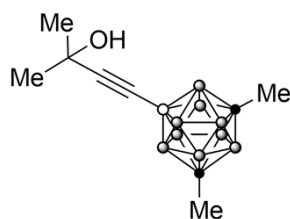
HRMS(ESI-TOF): *m/z* calcd for C₅¹⁰B₂¹¹B₈H₁₆O₂ [M+H]⁺: 241.2230. Found: 241.2219.



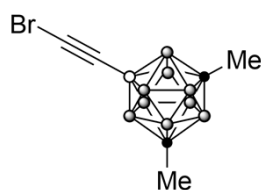
9. Yield 76% . White liquid. **Eluent:** PE:EA = 3:1

¹H NMR (400 MHz, CDCl₃) δ 7.57 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.38 (dd, *J* = 8.2, 6.4 Hz, 2H), 7.34 – 7.29 (m, 1H), 5.46 (d, *J* = 6.3 Hz, 1H), 2.13 (d, *J* = 6.5 Hz, 1H), 1.71 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 128.49, 128.17, 126.89, 65.12, 24.35. **¹¹B{¹H} NMR** (128 MHz, CDCl₃) δ -6.93 (2B), -9.62 (4B), -10.71 (2B), -12.71 (1B), -14.10 (1B).

HRMS(ESI-TOF): *m/z* calcd for C₁₃¹⁰B₂¹¹B₈H₂₂O [M+Na]⁺: 325.2573. Found: 325.2570.



10. Yield 80%. White solid. Melting point: 133 – 135 °C. **Eluent:** PE:EA = 3:1
 $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.69 (s, 6H), 1.49 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 69.92, 65.45, 31.51, 24.33. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ -6.92, -10.17 (d, $J = 162.4$ Hz), -13.63 (d, $J = 191.2$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ -5.92 (2B), -9.54 (4B), -10.81 (2B), -12.88 (1B), -14.37 (1B).
HRMS(ESI-TOF): m/z calcd for $\text{C}_9^{10}\text{B}_2^{11}\text{B}_8\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 256.2829. Found: 256.2835

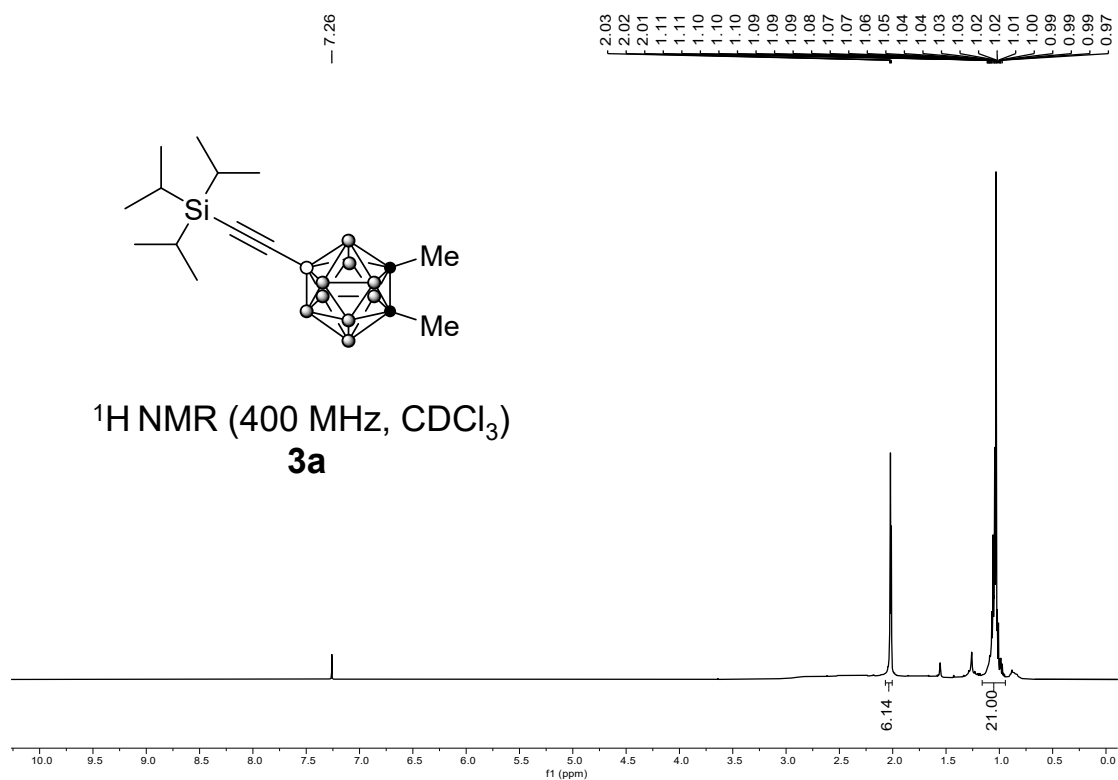
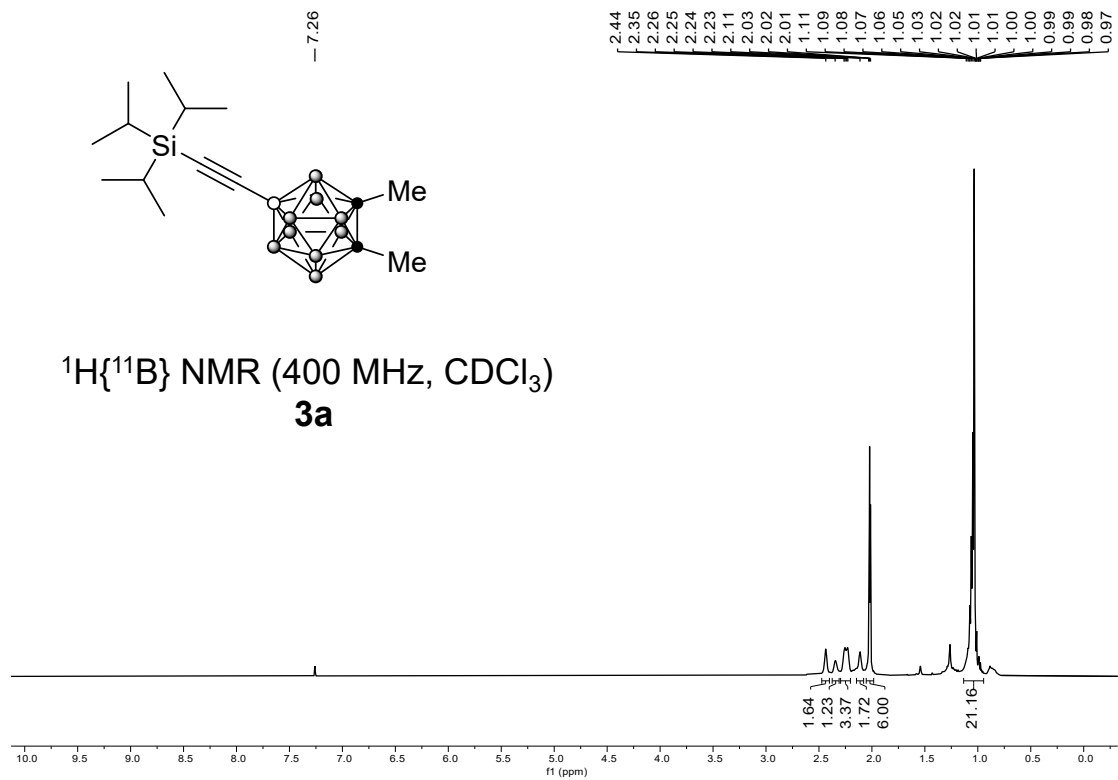


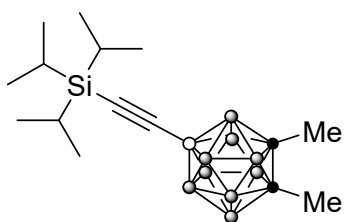
11. Yield 83%. Yellow solid. Melting point: 113 – 114 °C. **Eluent:** PE:DCM = 1:1
 $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.70 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 70.13, 24.33. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ -6.94 (2B), -9.69 (4B), -10.73 (2B), -12.83 (1B), -14.16 (1B).
HRMS(ESI-TOF): m/z calcd for $\text{C}_6^{10}\text{B}_1^{11}\text{B}_9\text{H}_{15}\text{Br}$ $[\text{M}+\text{Na}]^+$: 298.1240. Found: 298.1269.

6. References

1. T. L. Heying, J. W. Ager Jr, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid and S. I. Trotz, *Inorg. Chem.*, 1963, **2**, 1097.
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7. Y.-N. Ma, H. Ren, Y. Wu, N. Li, F. Chen and X. Chen, *J. Am. Chem. Soc.*, 2023, **145**, 7331.

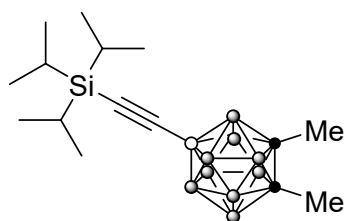
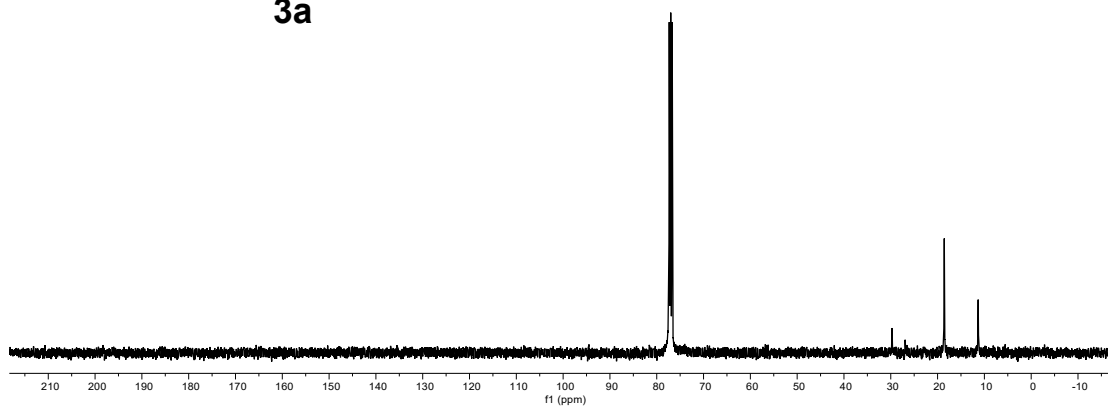
7. NMR spectra





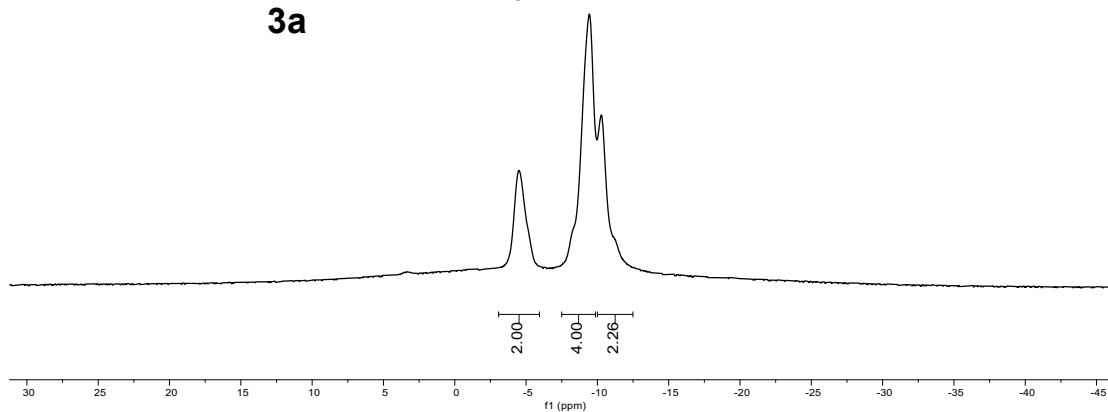
~ 29.73
 ~ 26.93
 ~ 18.57
 ~ 11.33

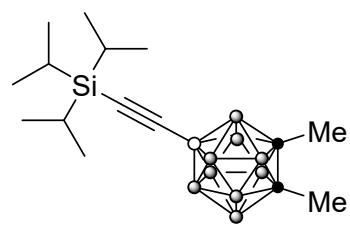
^{13}C NMR (101 MHz, CDCl_3)
3a



~ -4.55
 ~ -9.37
 ~ -9.43
 ~ -10.34

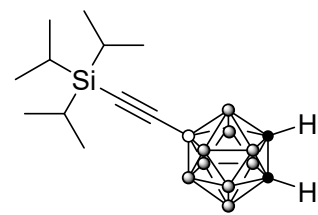
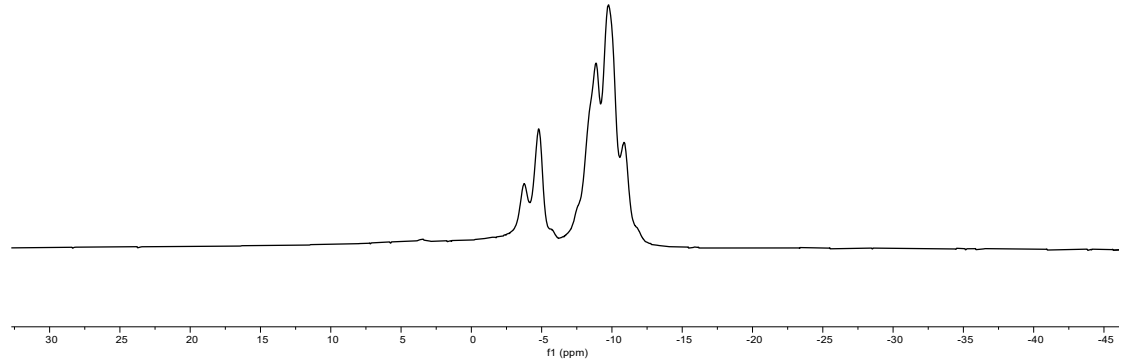
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)
3a





-3.74
-4.78
-7.59
-8.37
-8.87
-9.69
-10.08
-10.92

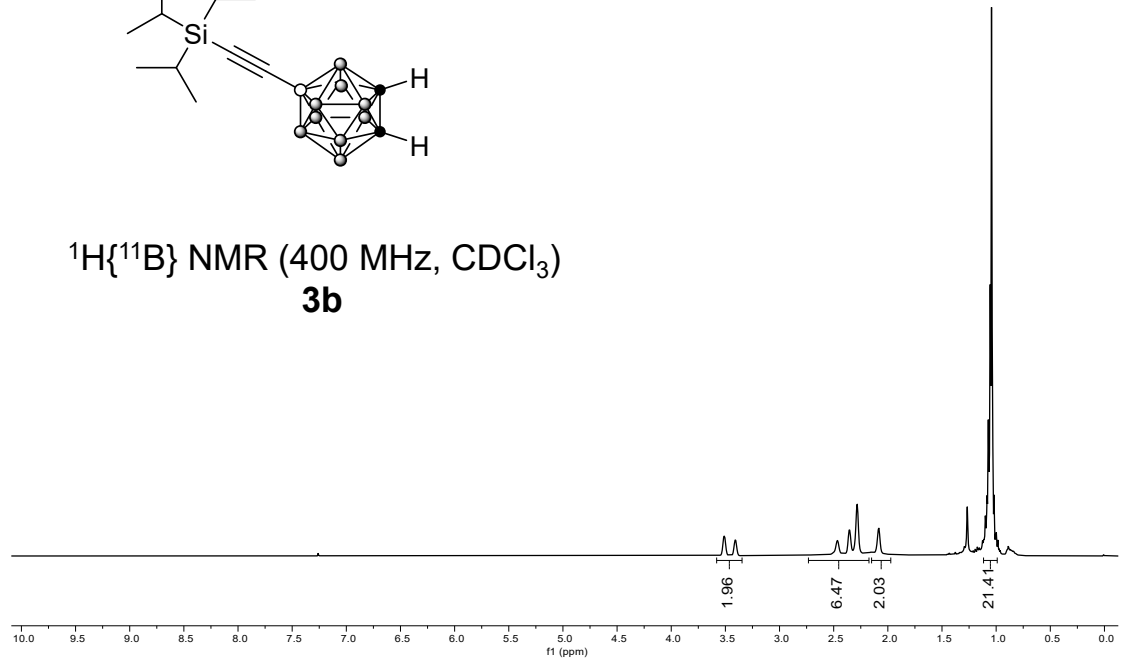
^{11}B NMR (128 MHz, CDCl_3)
3a

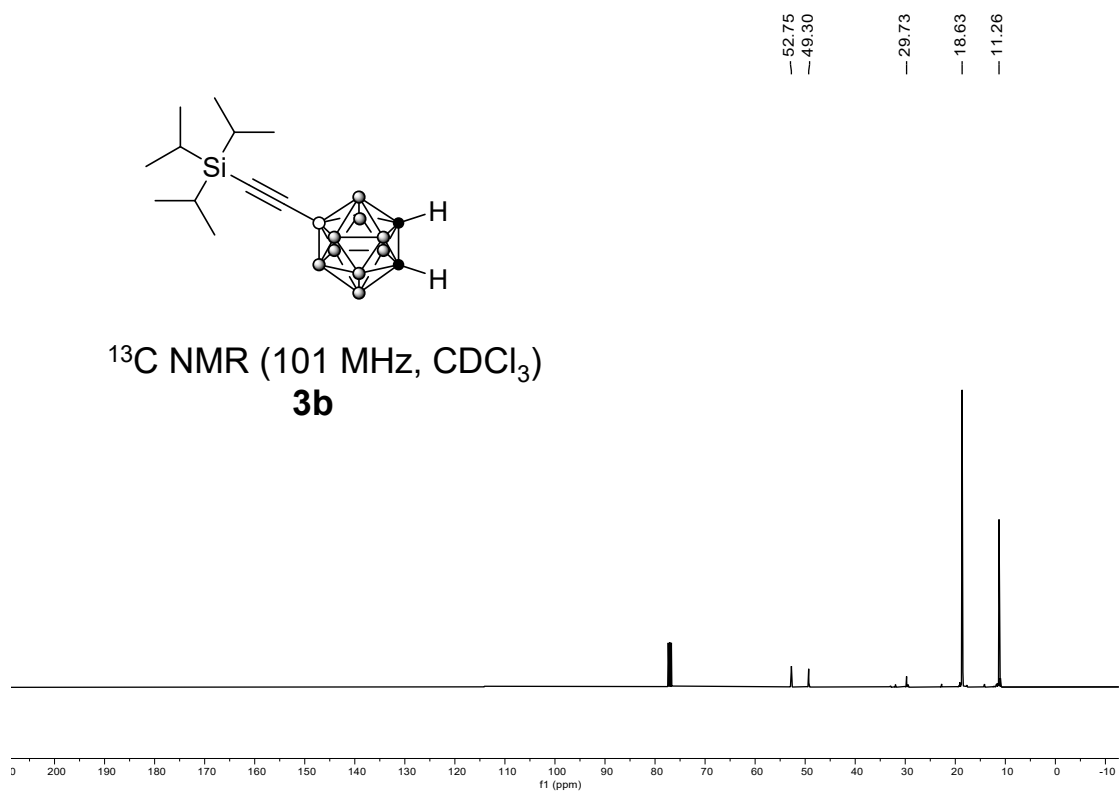
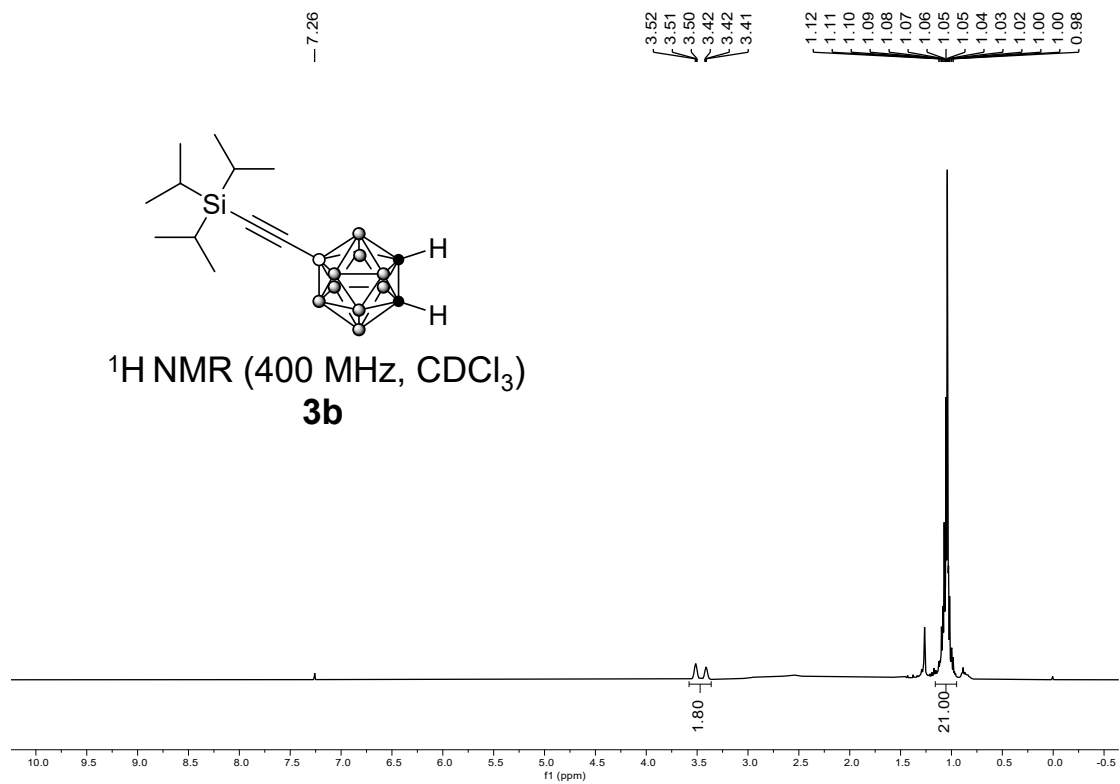


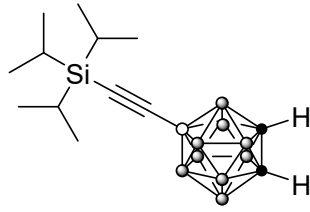
-7.26

3.52
3.51
3.51
3.50
3.42
3.41
3.41
3.39
2.36
2.35
2.28
2.08
1.11
1.10
1.08
1.07
1.06
1.05
1.04
1.03
1.02
1.02
1.01
1.01

$^1\text{H}\{^{11}\text{B}\}$ NMR (400 MHz, CDCl_3)
3b

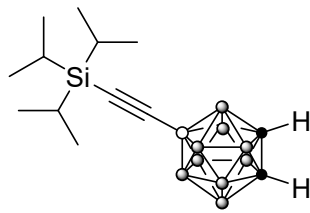
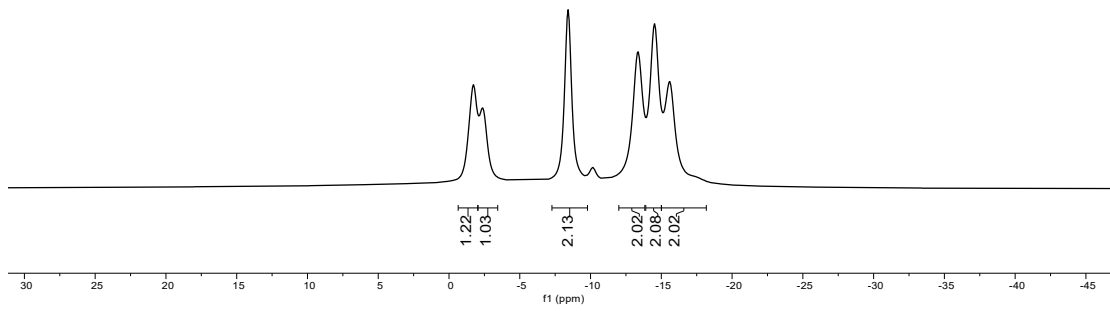






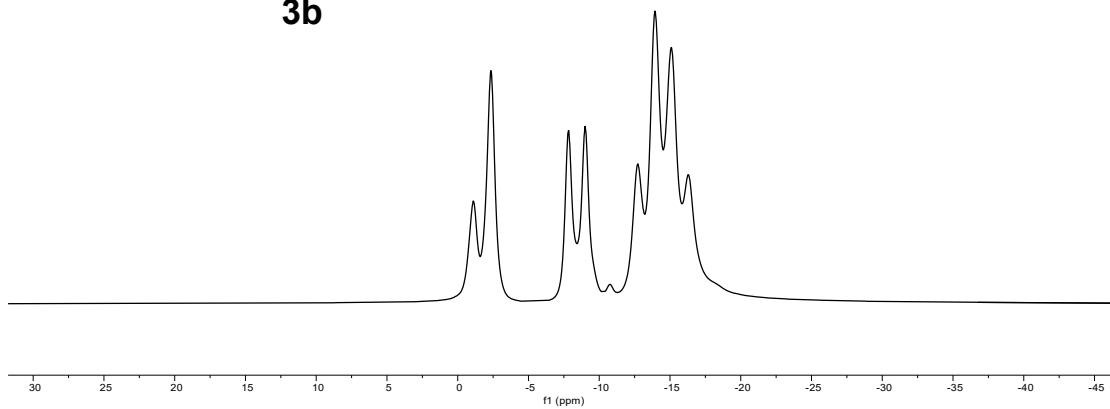
~ -1.71
~ -2.43
- -8.41
~ -13.33
~ -14.52
~ -15.61

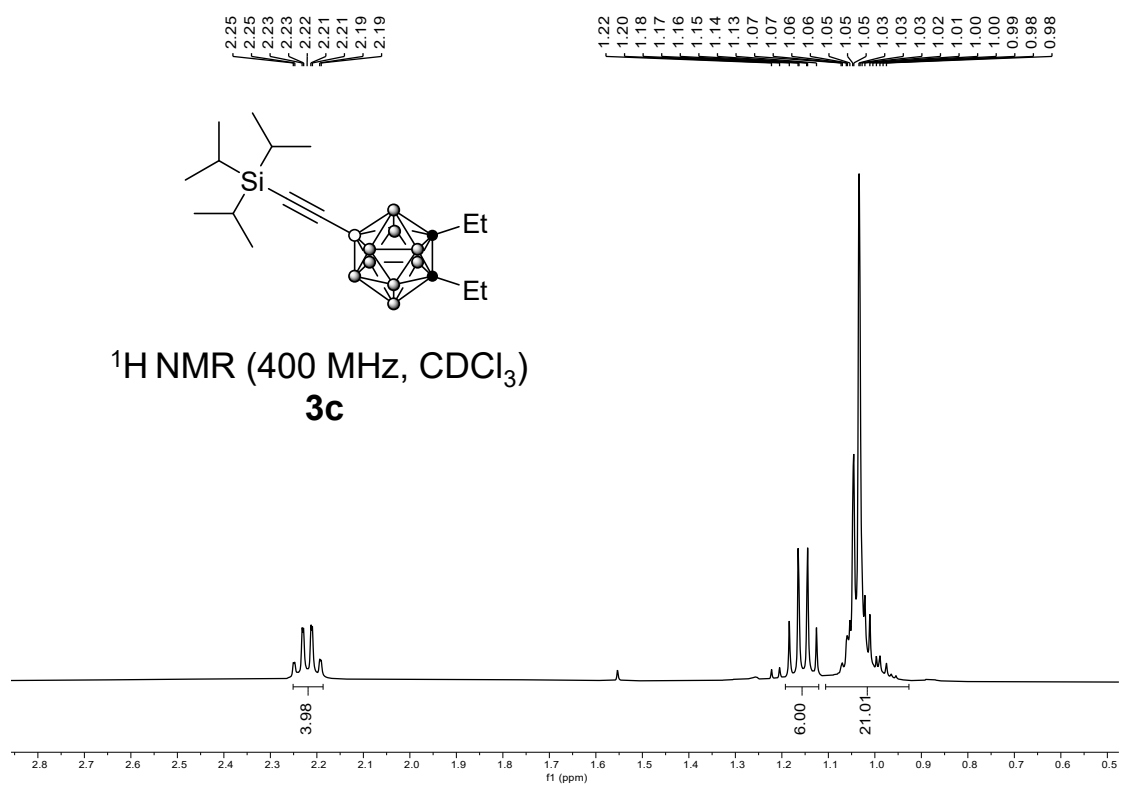
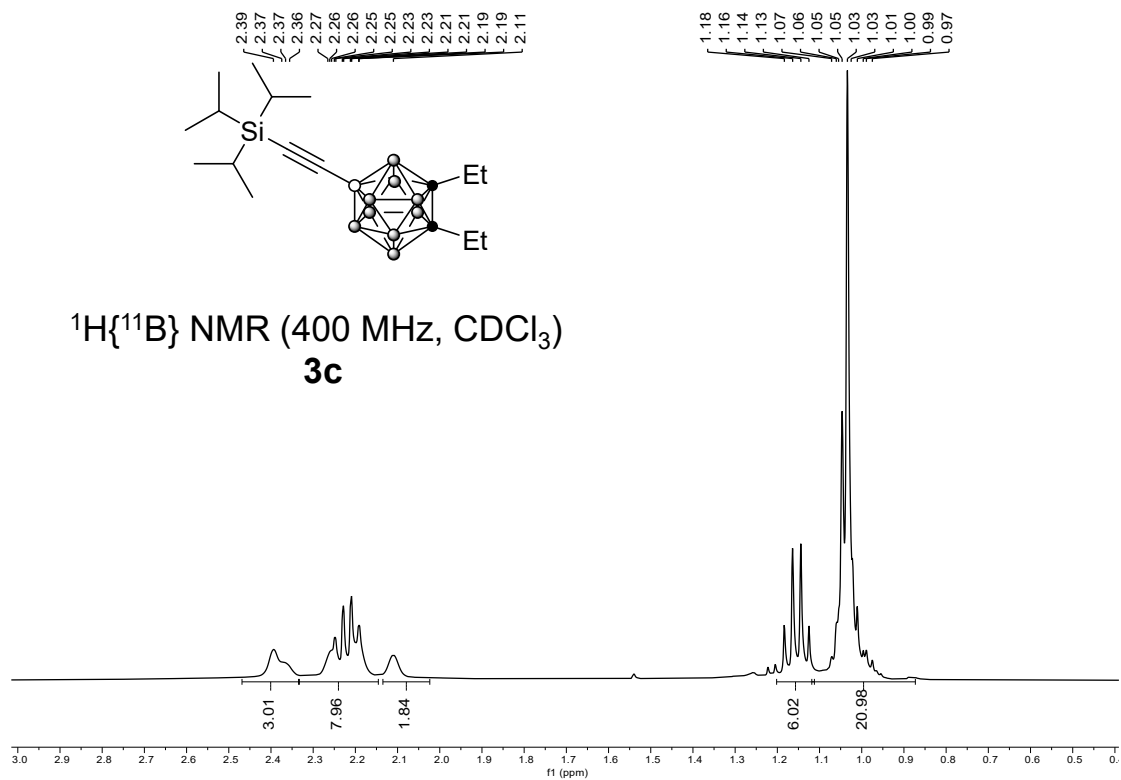
¹¹B{¹H} NMR (128 MHz, CDCl₃)
3b

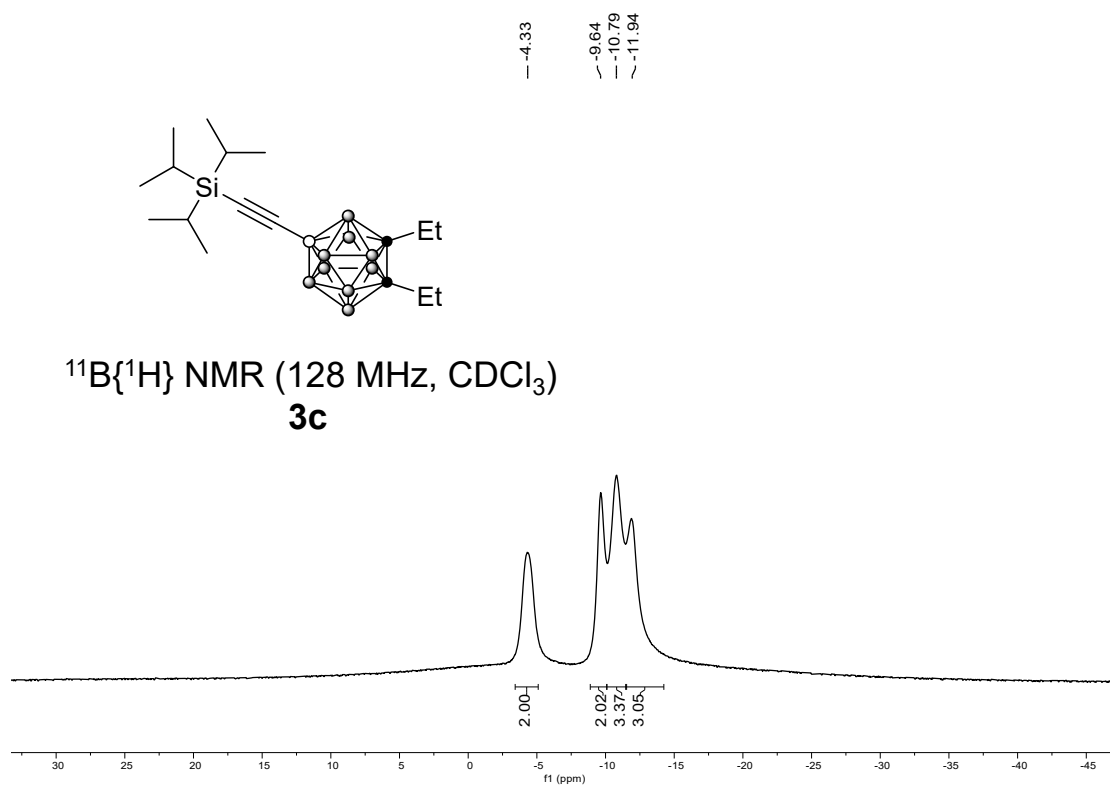
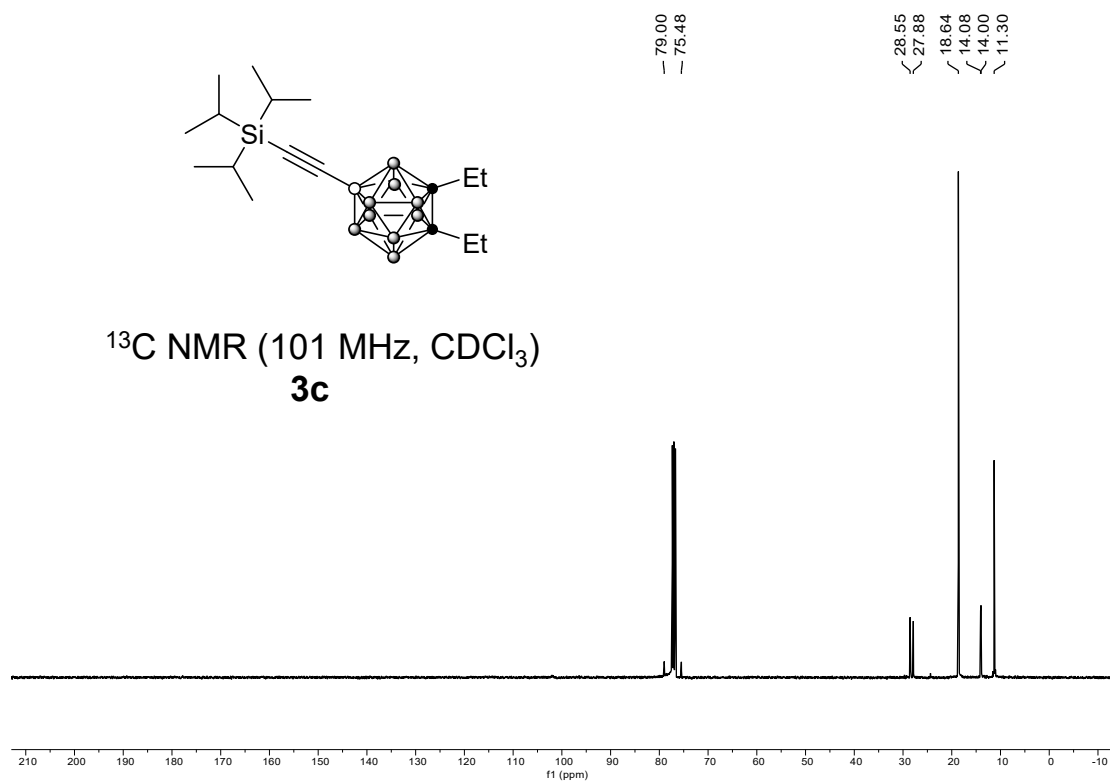


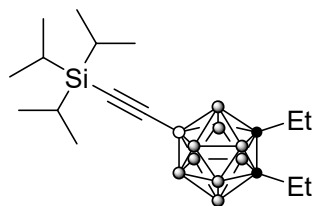
- -1.08
- -2.35
- -7.82
- -9.01
~ -12.69
~ -13.94
~ -15.10
~ -16.33

¹¹B NMR (128 MHz, CDCl₃)
3b

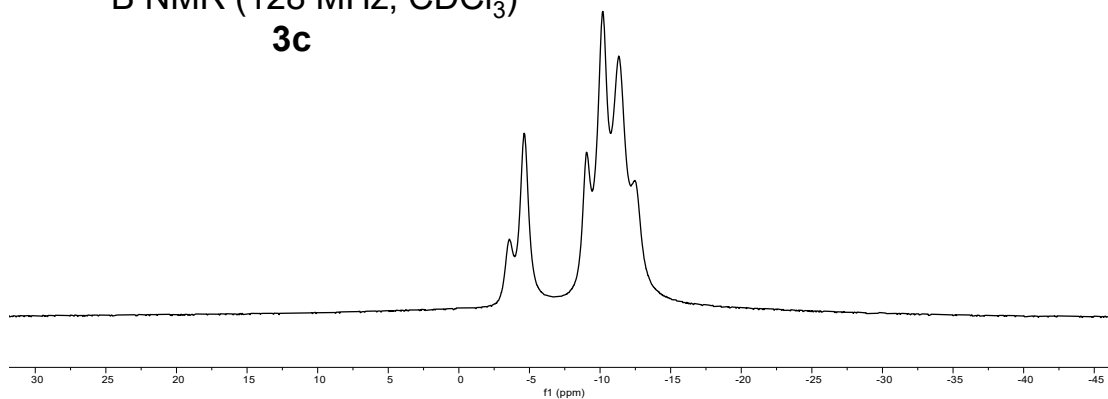






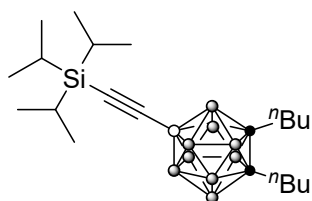


^{11}B NMR (128 MHz, CDCl_3)
3c

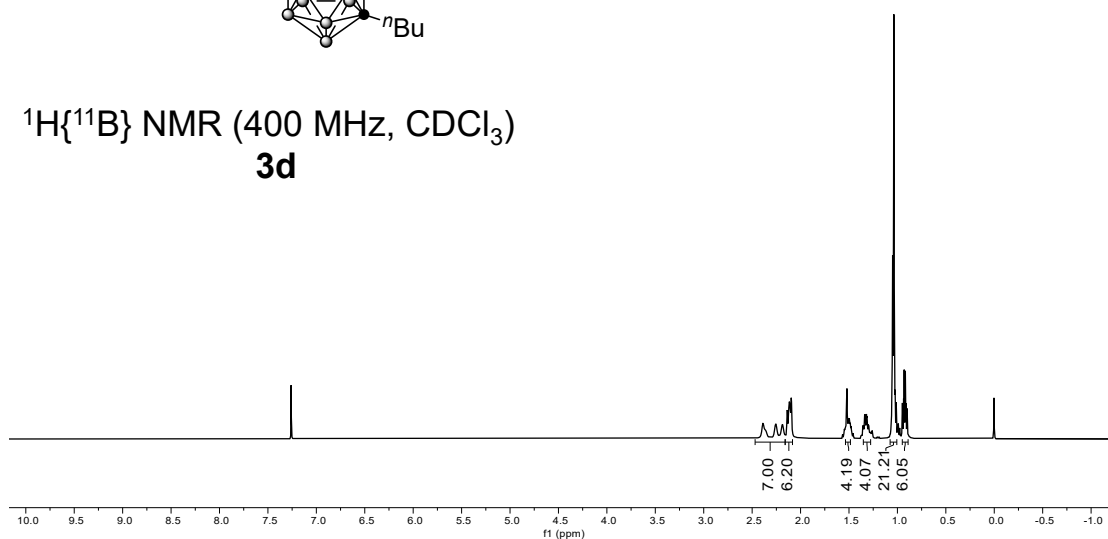


~ -3.55
~ -4.64
~ -9.04
~ -10.17
~ -11.35
~ -12.57

7.26
2.39
2.36
2.26
2.19
2.14
2.14
2.13
2.12
2.11
2.10
2.09
1.57
1.55
1.54
1.53
1.52
1.51
1.51
1.50
1.49
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1.06
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0.94
0.93
0.92
0.91
0.90



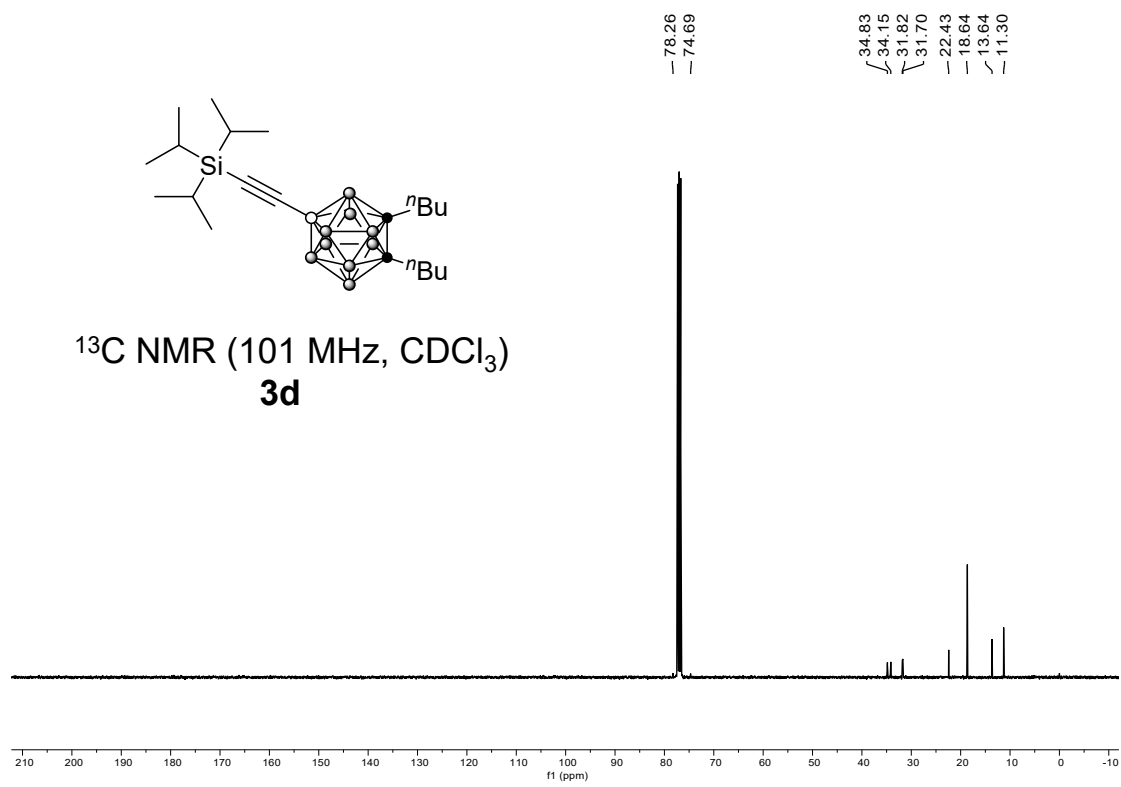
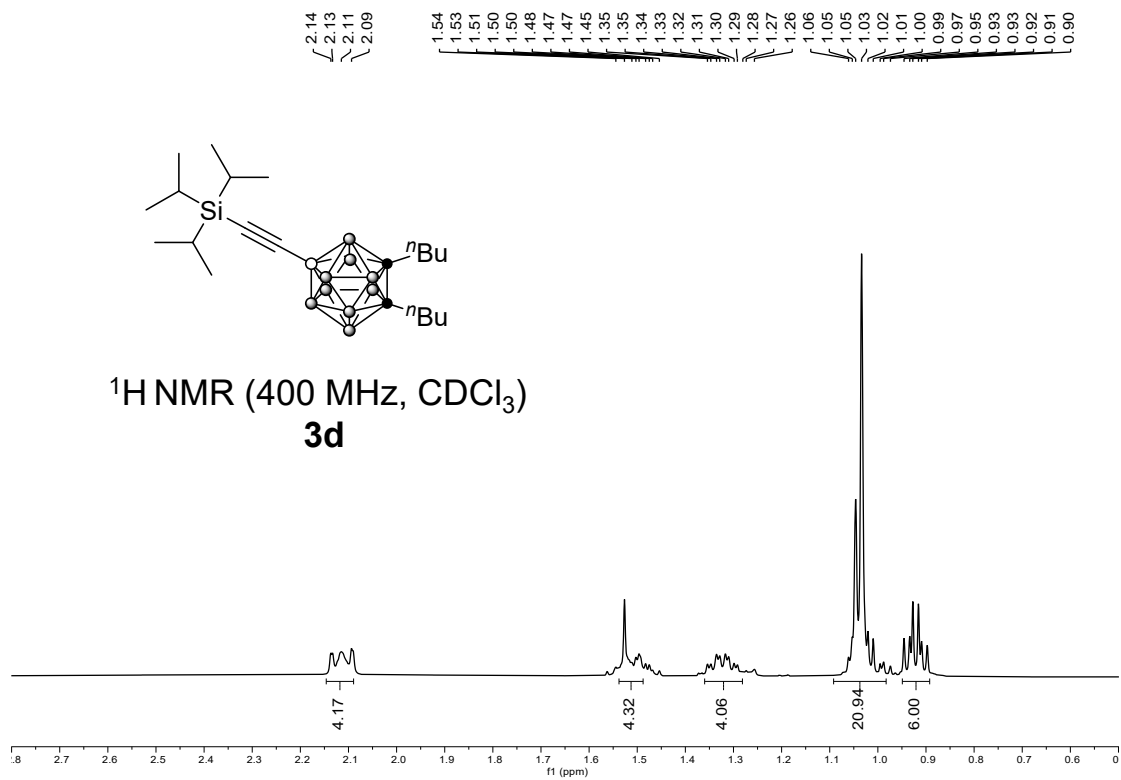
$^1\text{H}\{^{11}\text{B}\}$ NMR (400 MHz, CDCl_3)
3d

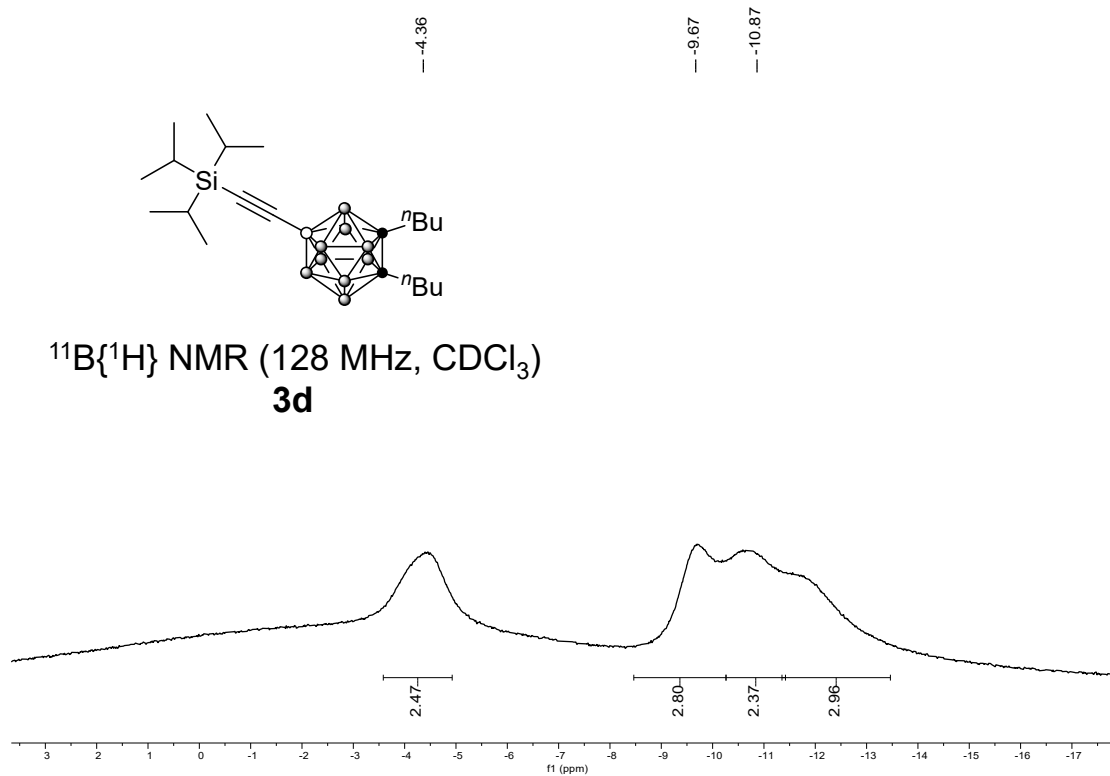


7.00
6.20

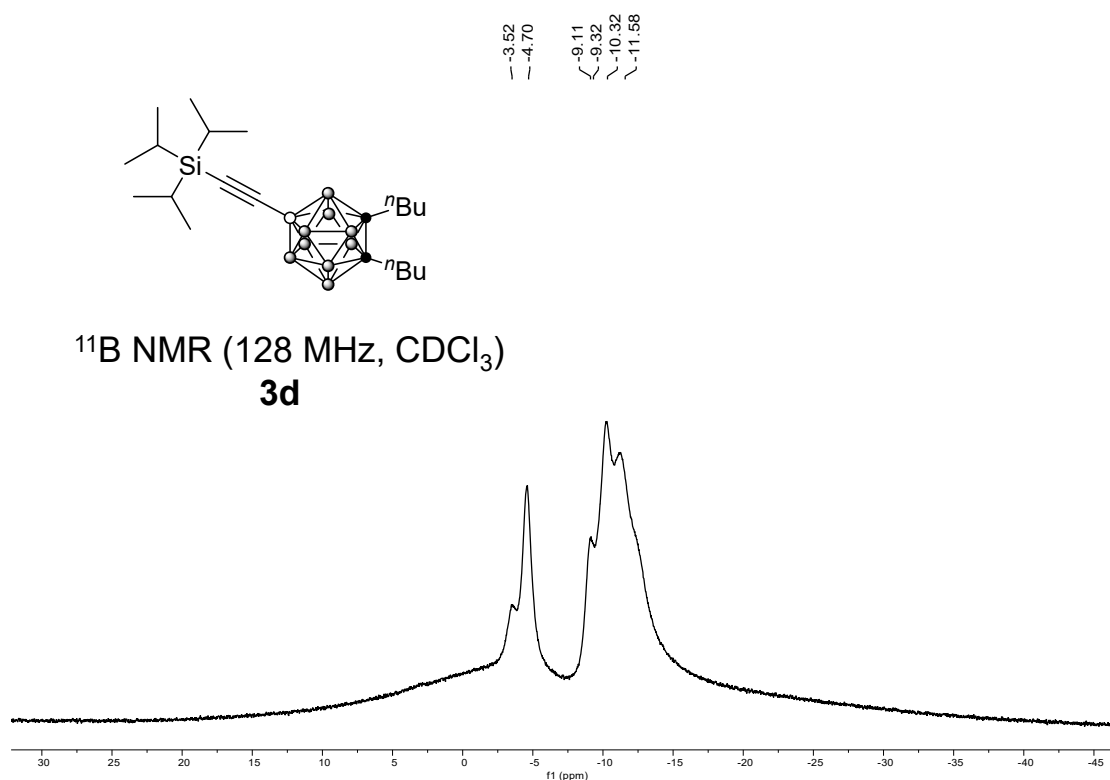
4.19
4.07

21.21
6.05



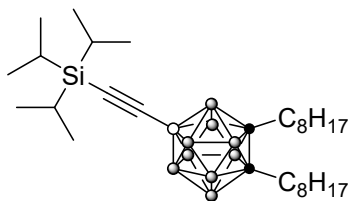


$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)
3d



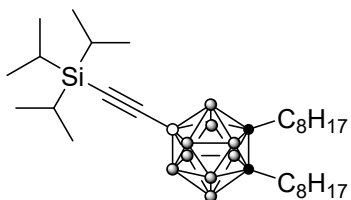
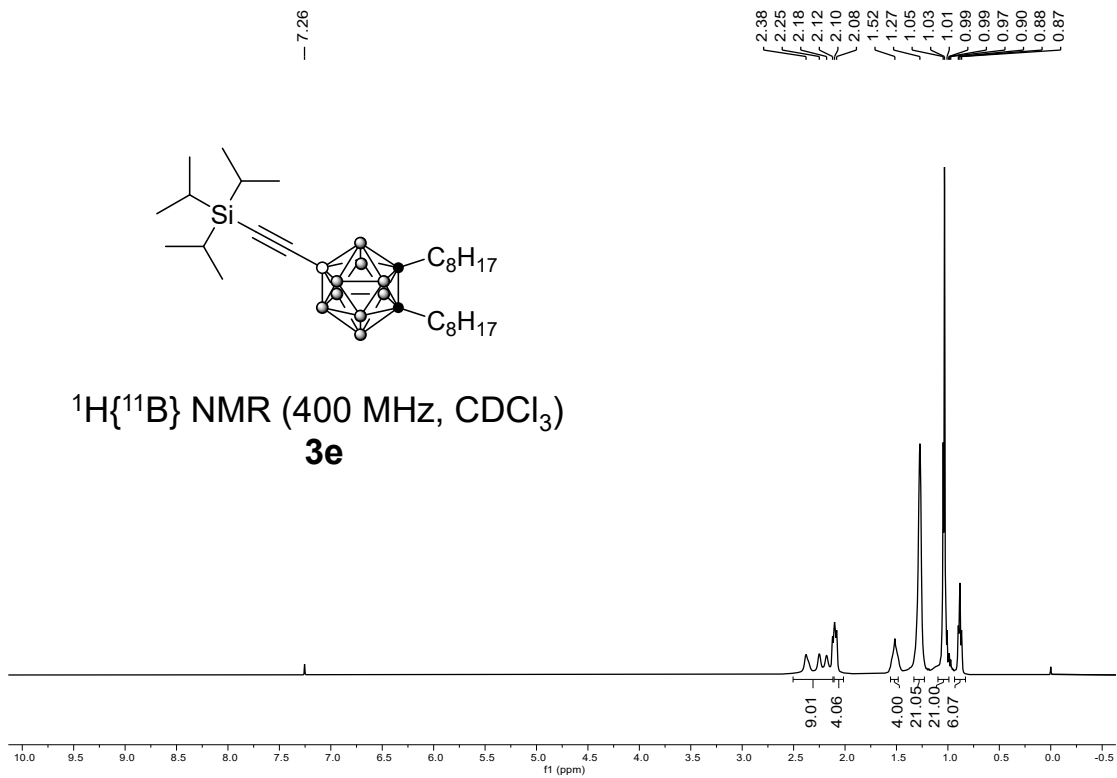
^{11}B NMR (128 MHz, CDCl_3)
3d

- 7.26



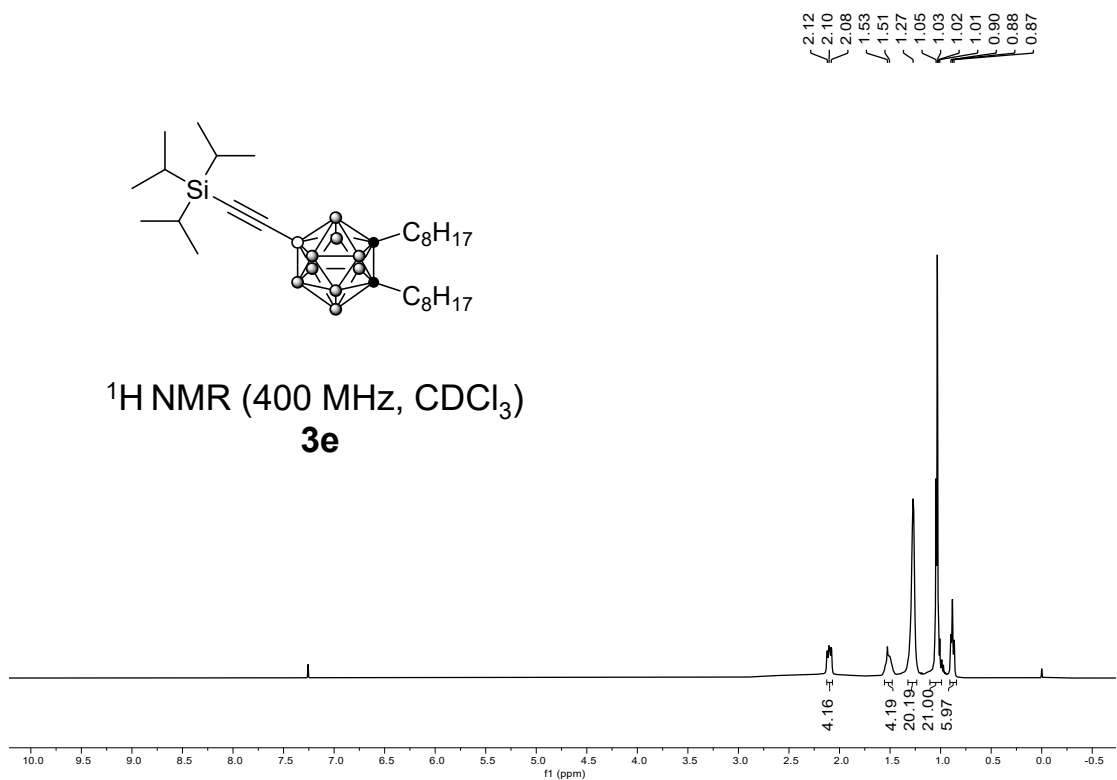
$^1\text{H}\{^{11}\text{B}\}$ NMR (400 MHz, CDCl_3)

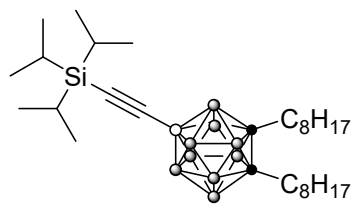
3e



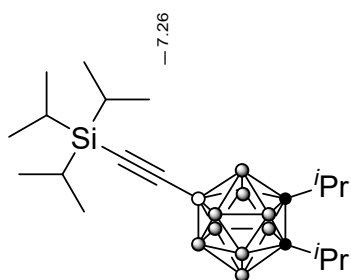
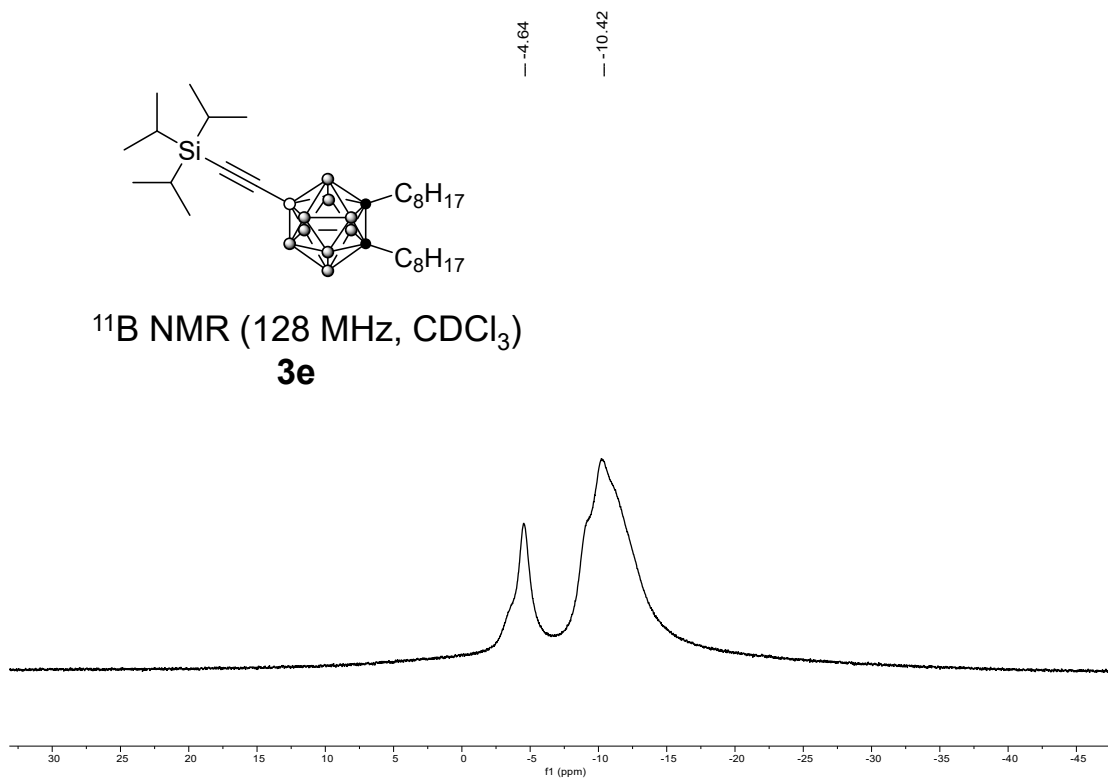
^1H NMR (400 MHz, CDCl_3)

3e

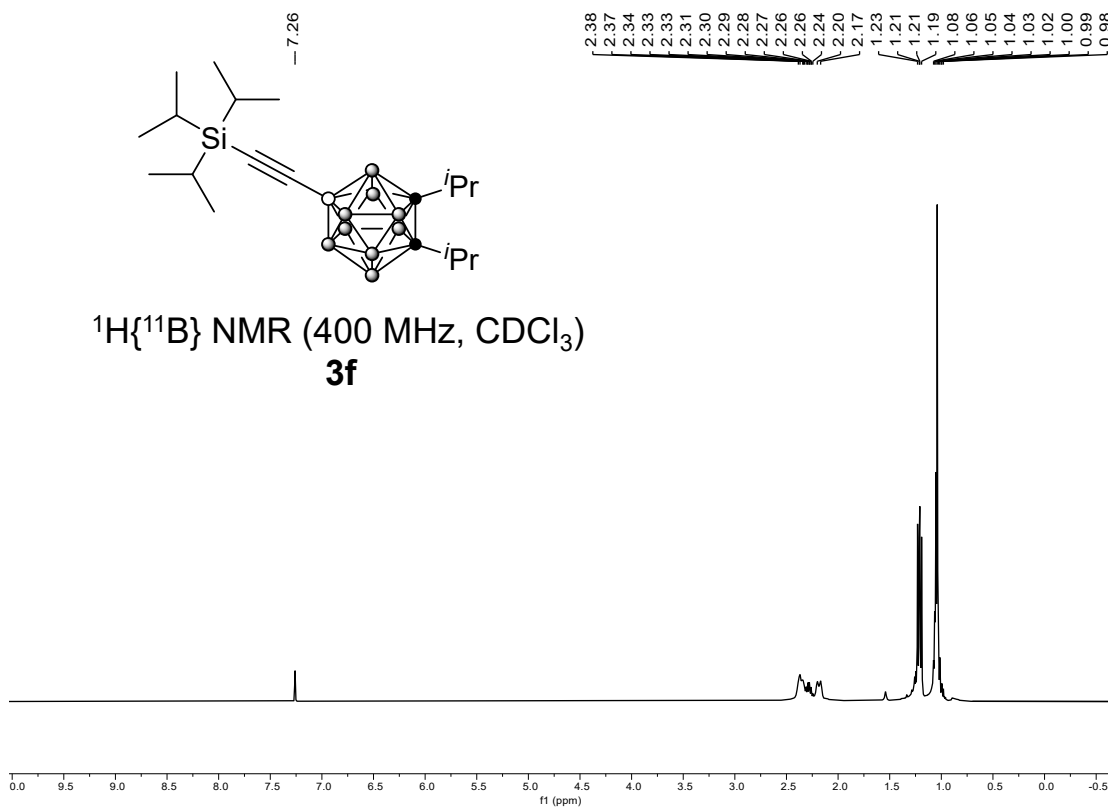


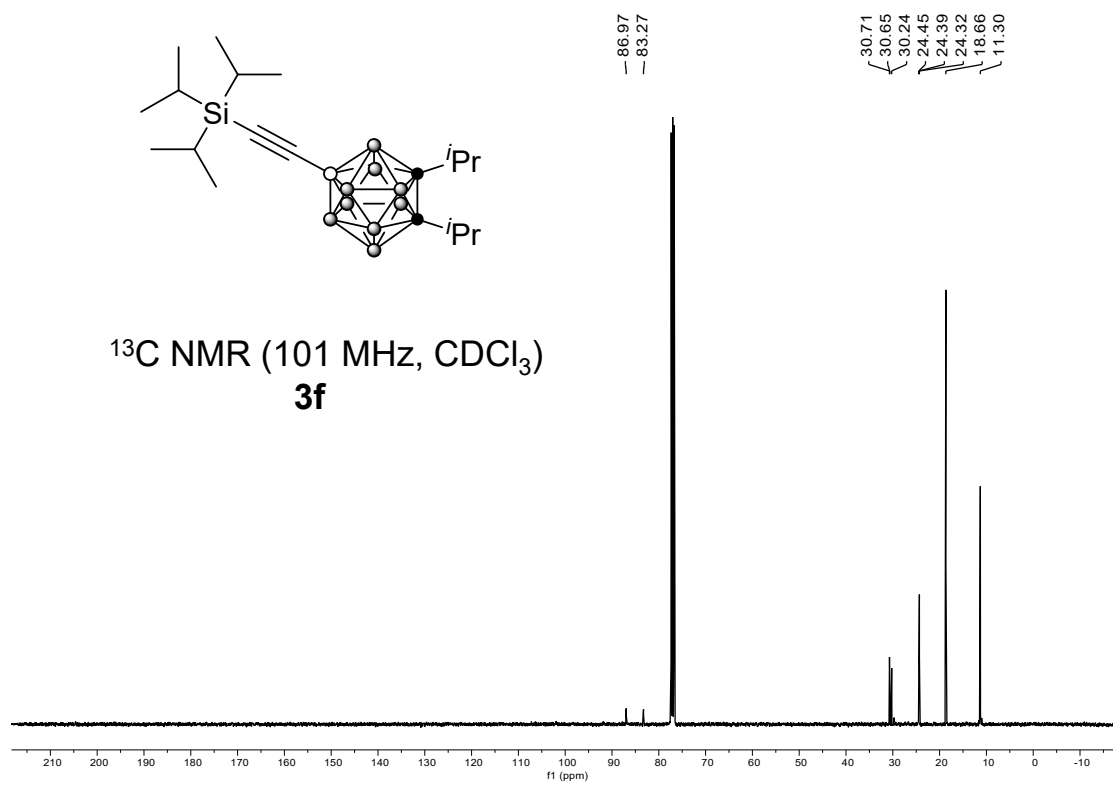
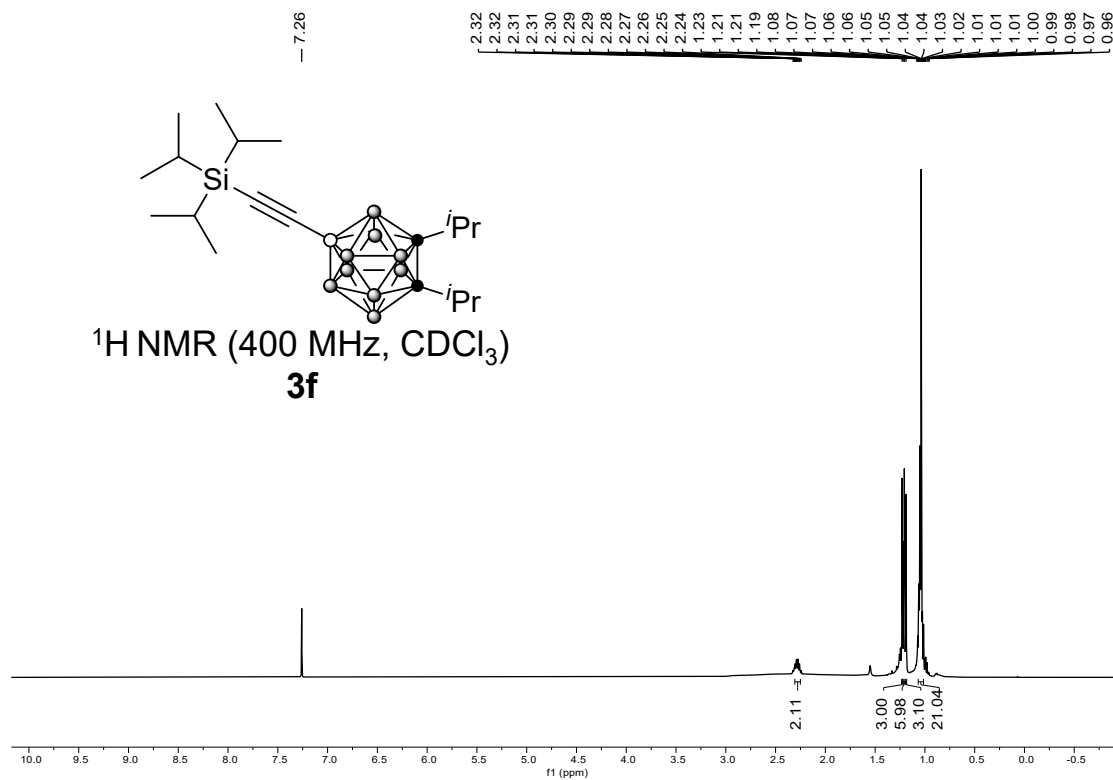


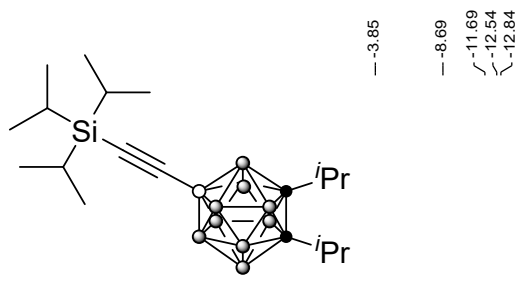
^{11}B NMR (128 MHz, CDCl_3)
3e



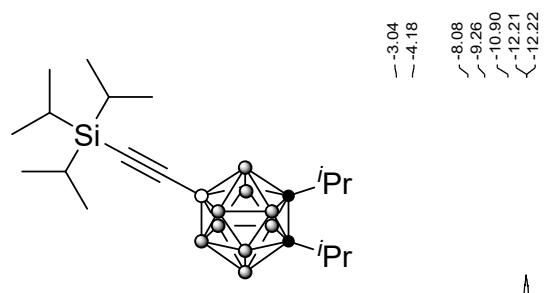
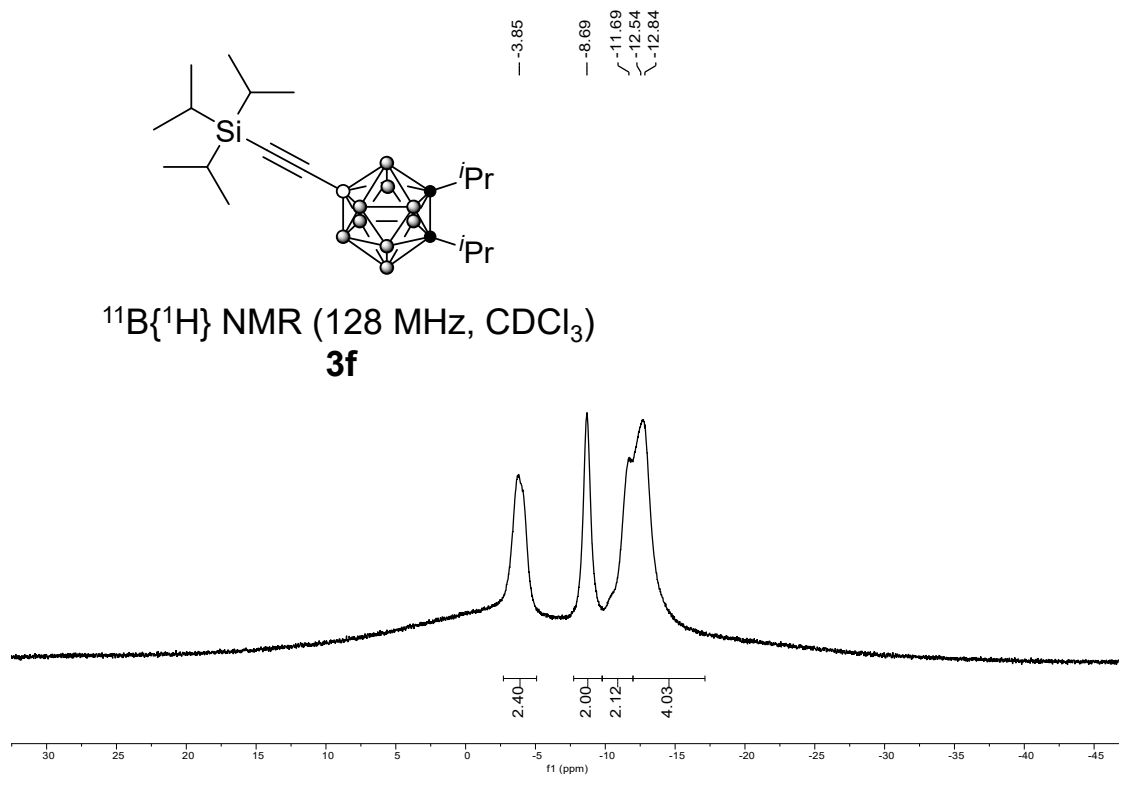
$^1\text{H}\{^{11}\text{B}\}$ NMR (400 MHz, CDCl_3)
3f



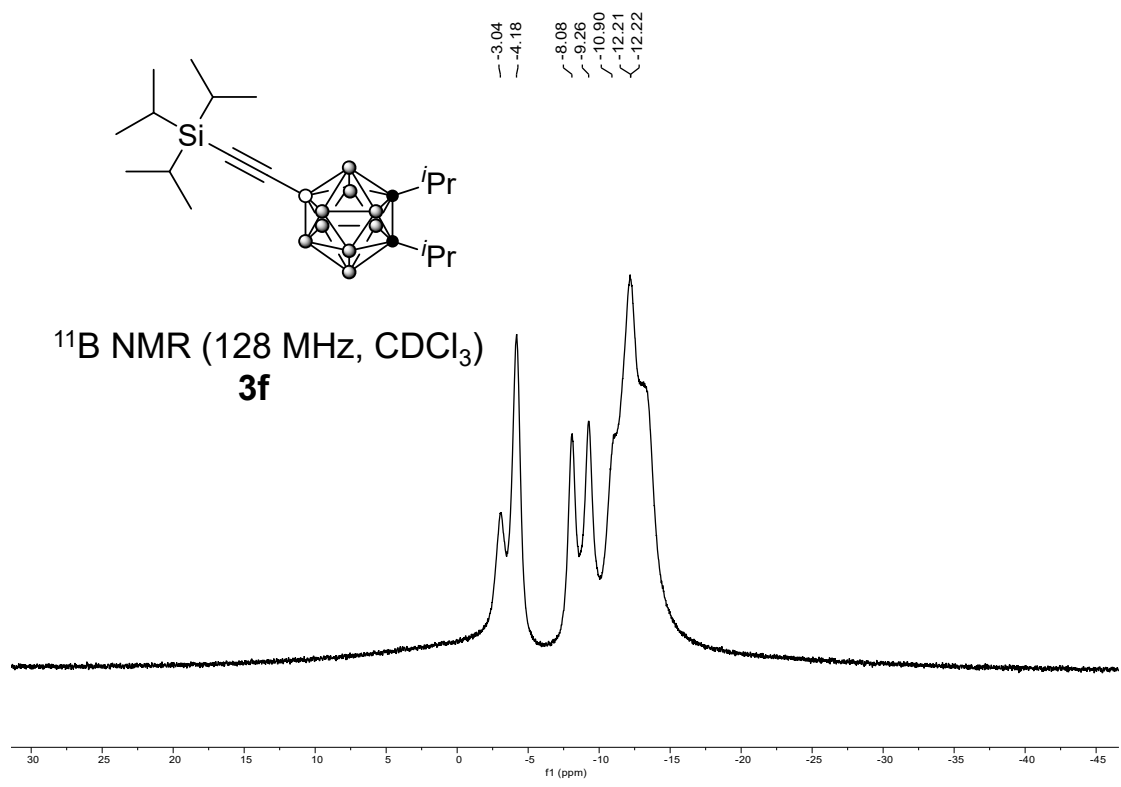


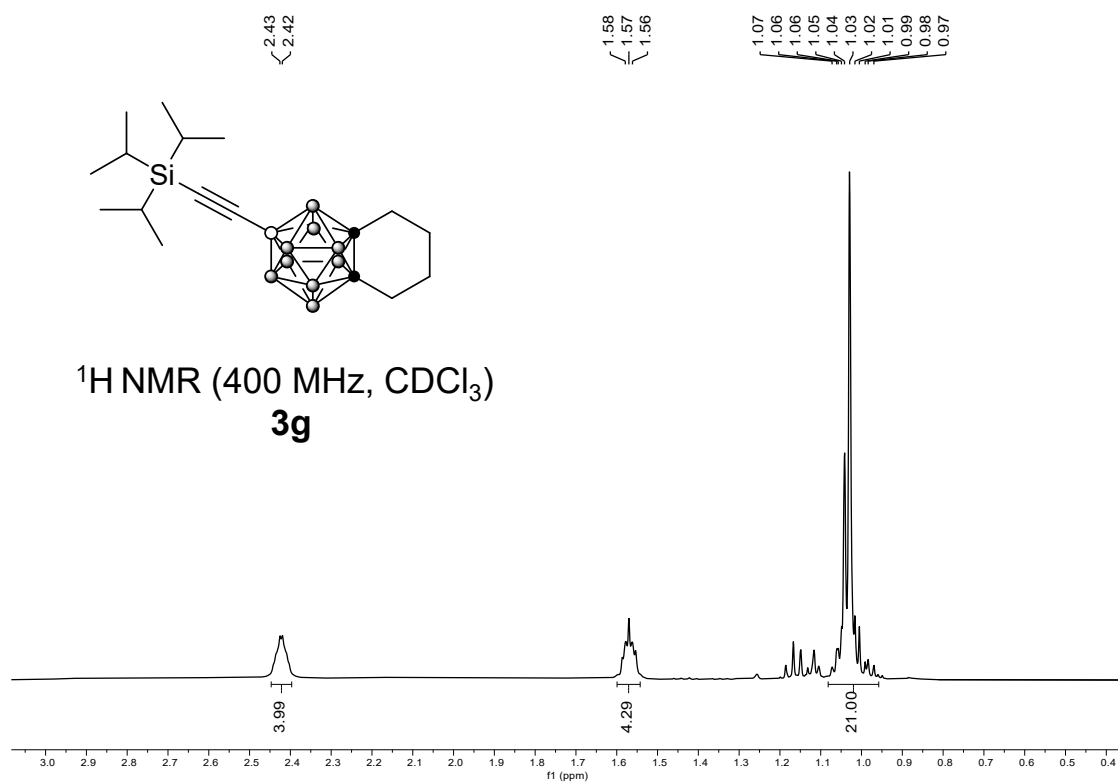
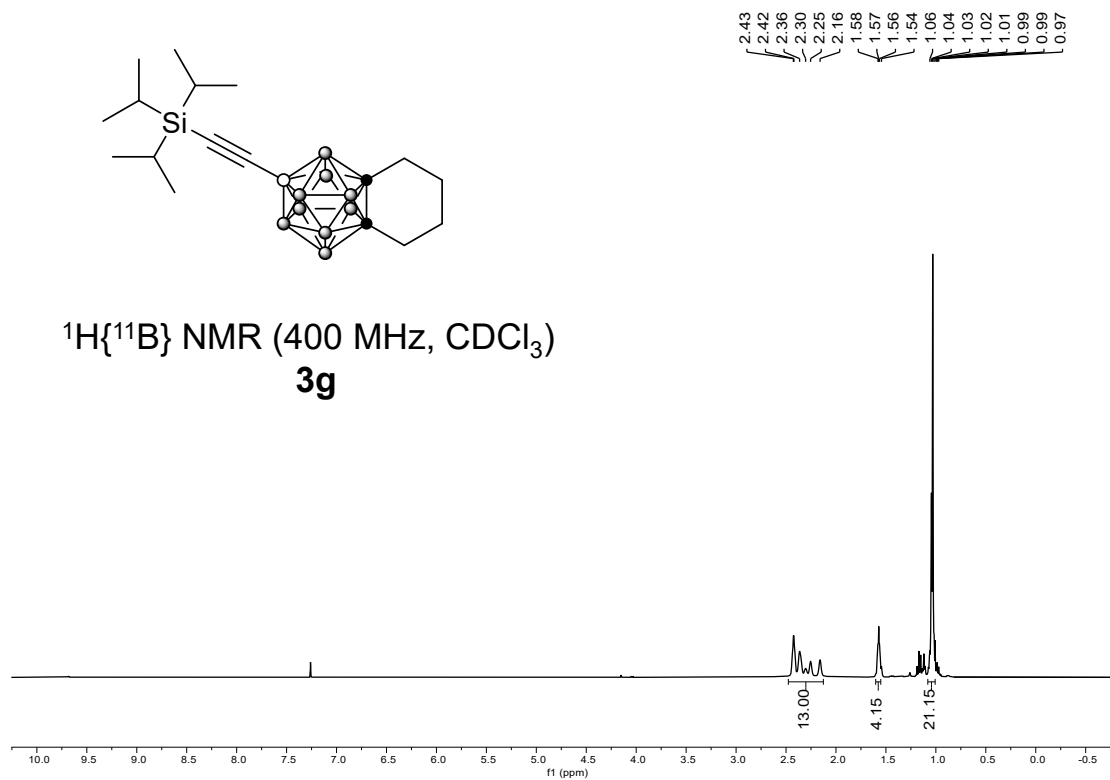


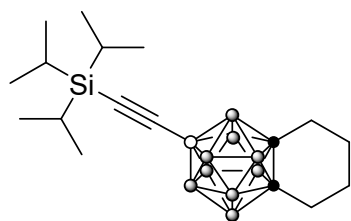
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)
3f



^{11}B NMR (128 MHz, CDCl_3)
3f

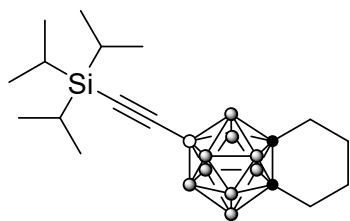
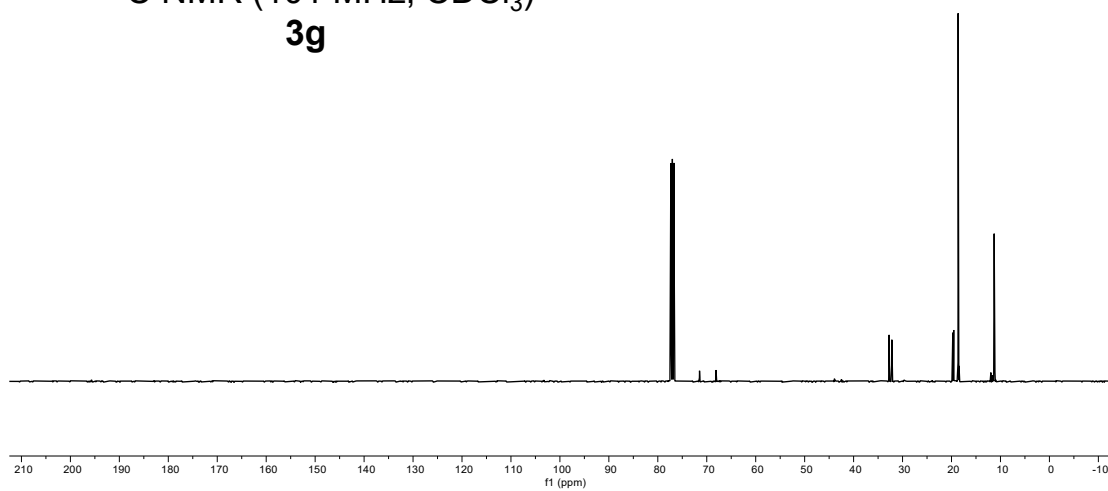






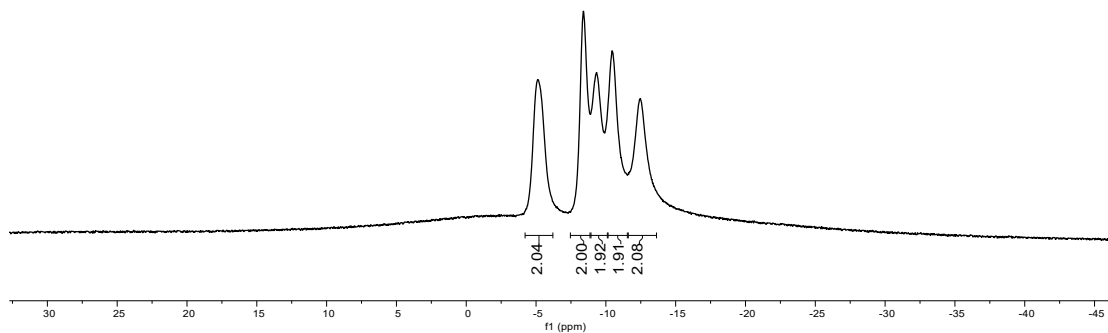
71.48
68.10
32.75
32.19
19.74
19.55
18.64
18.46
11.28

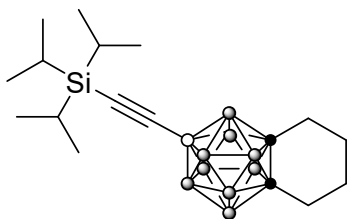
^{13}C NMR (101 MHz, CDCl_3)
3g



-5.12
-8.39
-9.33
-10.45
-12.48

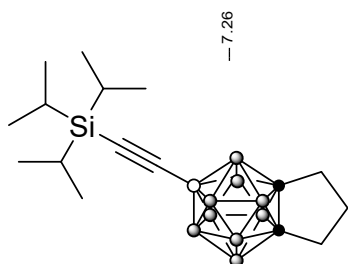
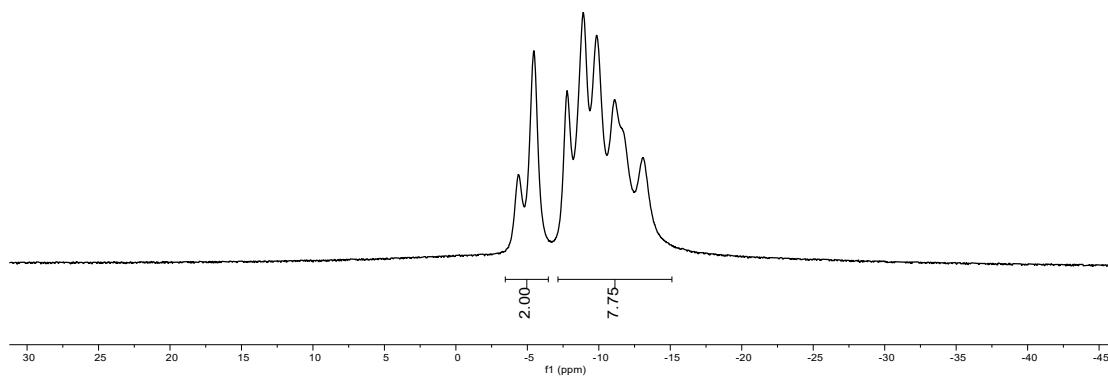
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)
3g





~-4.41
 ~-5.48
 ~-7.81
 ~-8.94
 ~-9.88
 ~-11.13
 ~-13.13

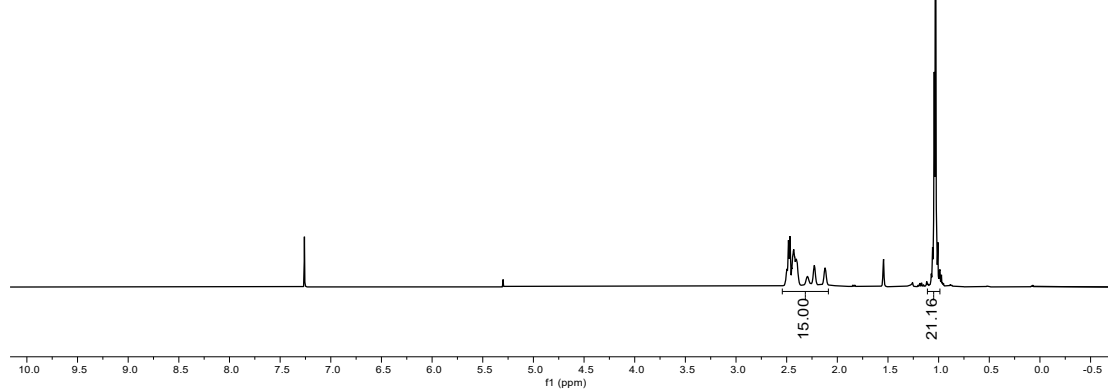
^{11}B NMR (128 MHz, CDCl_3)
3g

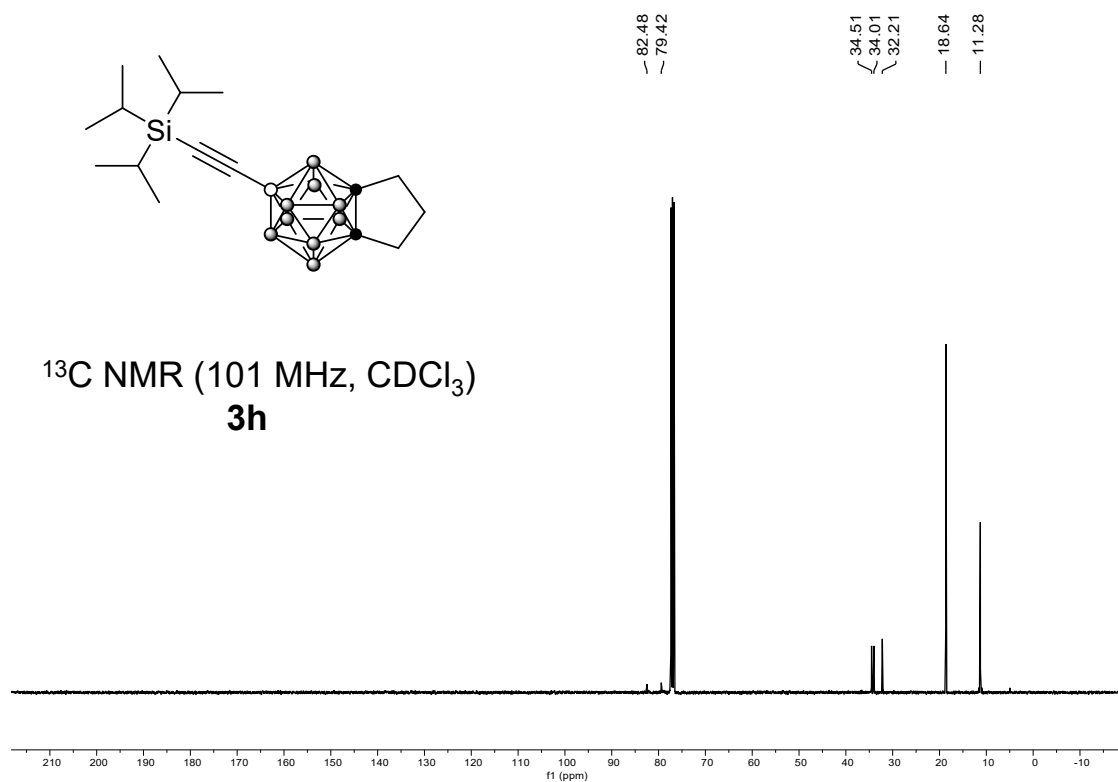
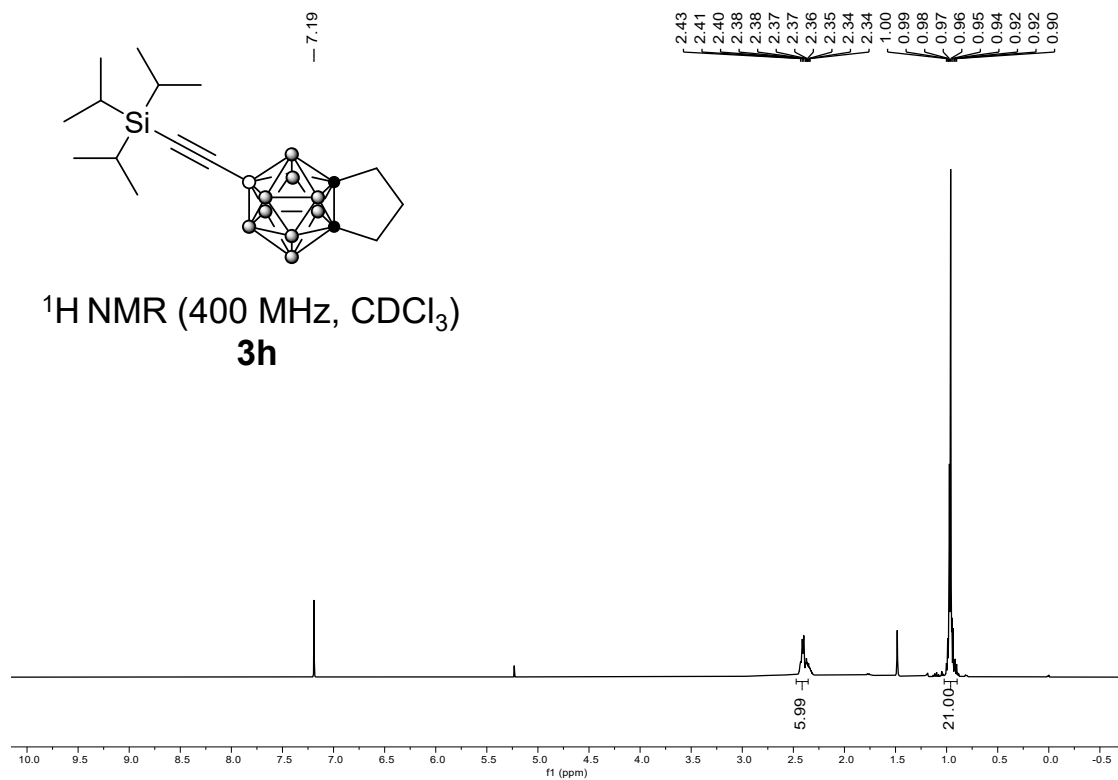


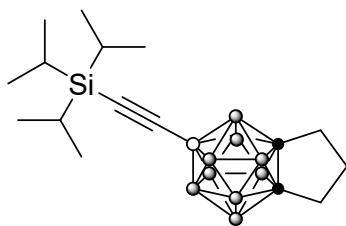
~ 7.26

2.51
 2.50
 2.48
 2.47
 2.45
 2.44
 2.43
 2.42
 2.41
 2.40
 2.30
 2.23
 2.12
 1.07
 1.06
 1.04
 1.03
 1.02
 1.01
 0.99
 0.99
 0.97

$^1\text{H}\{^{11}\text{B}\}$ NMR (400 MHz, CDCl_3)
3h

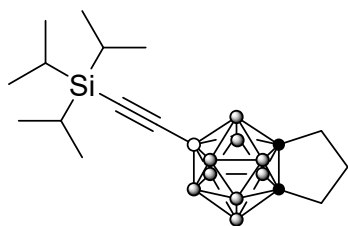
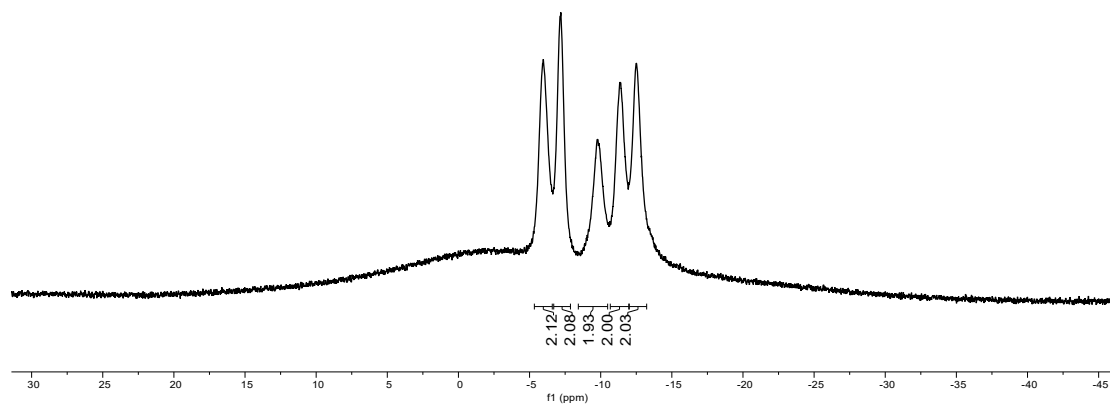






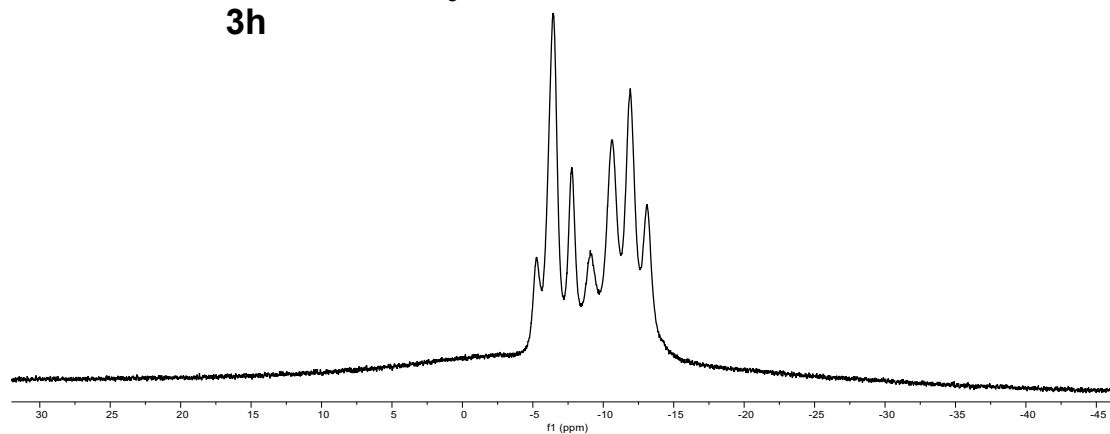
-5.97
 -7.24
 -9.91
 -11.41
 -12.56

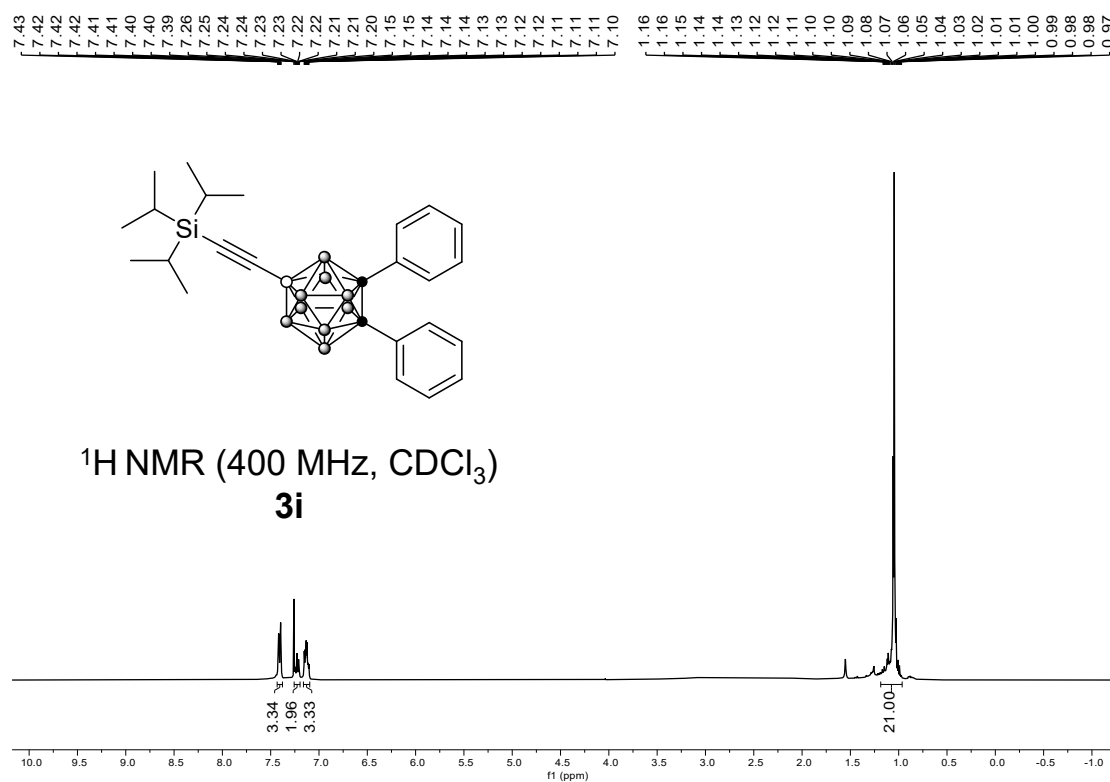
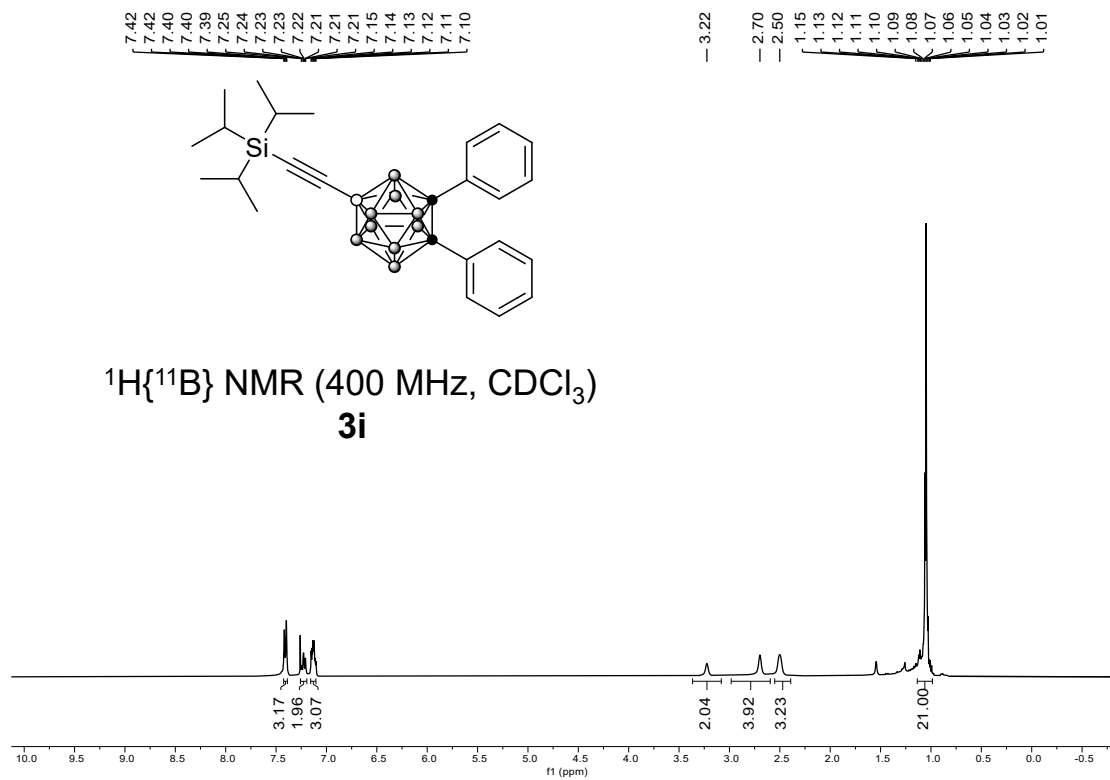
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)
3h

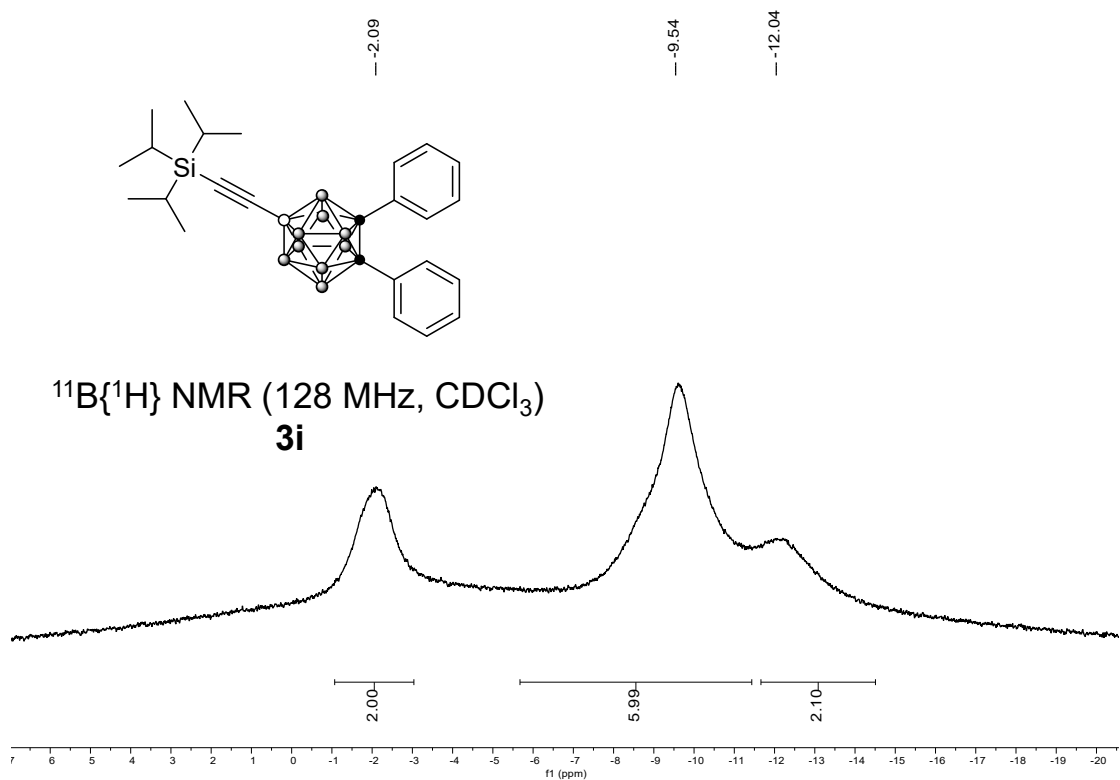
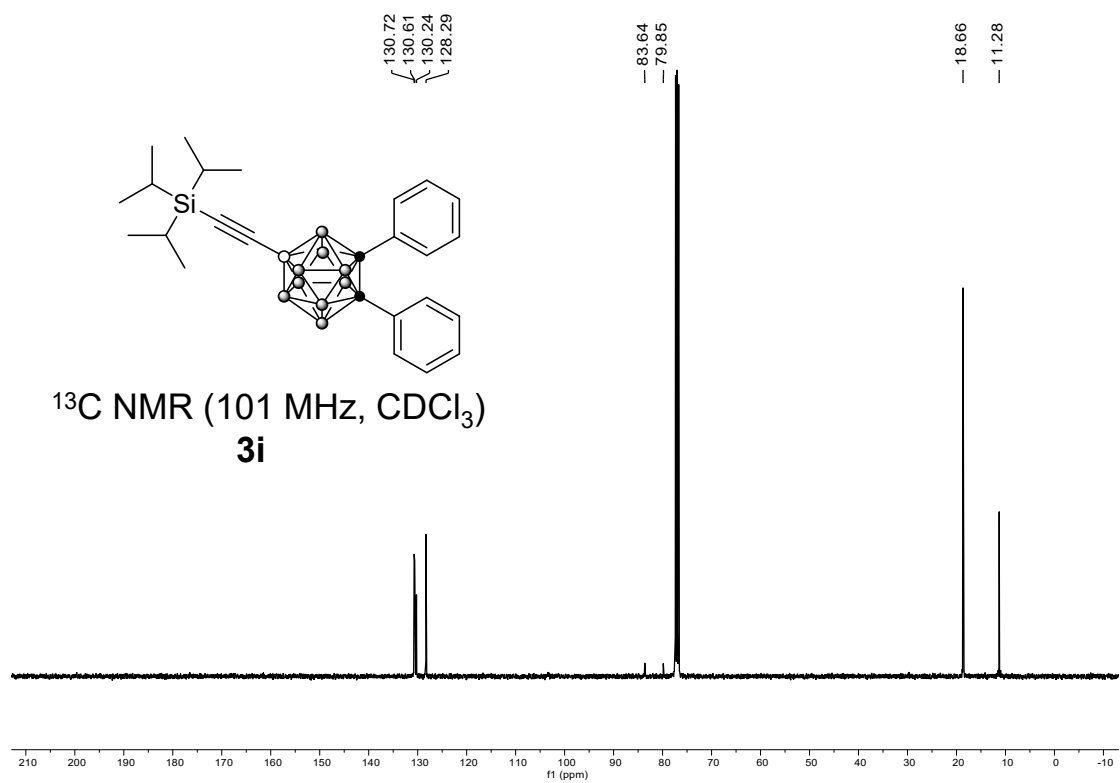


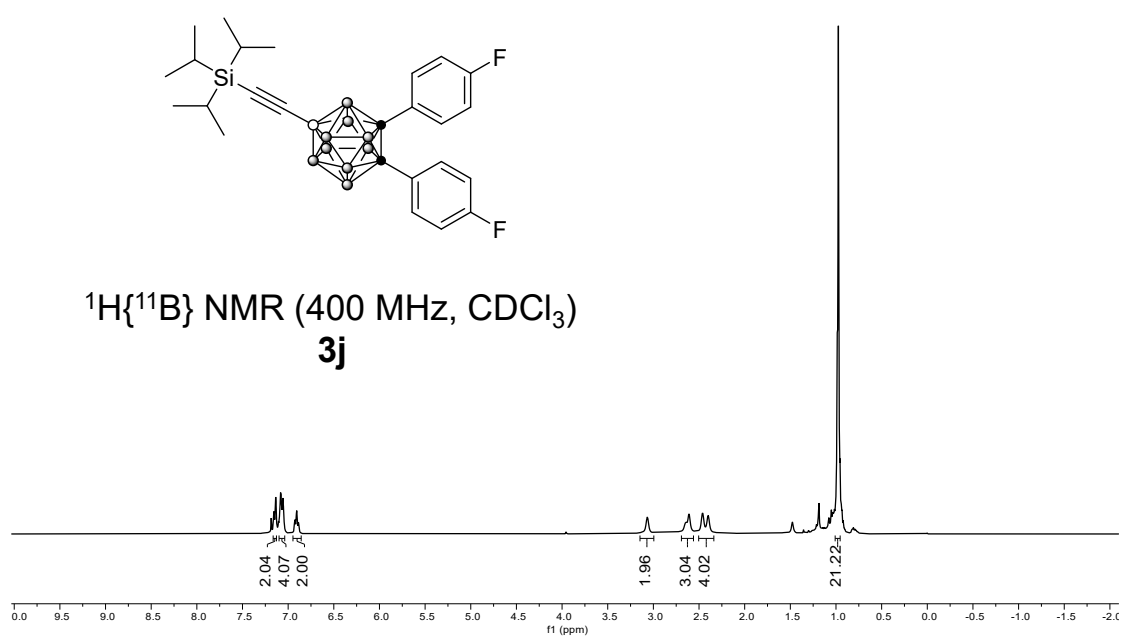
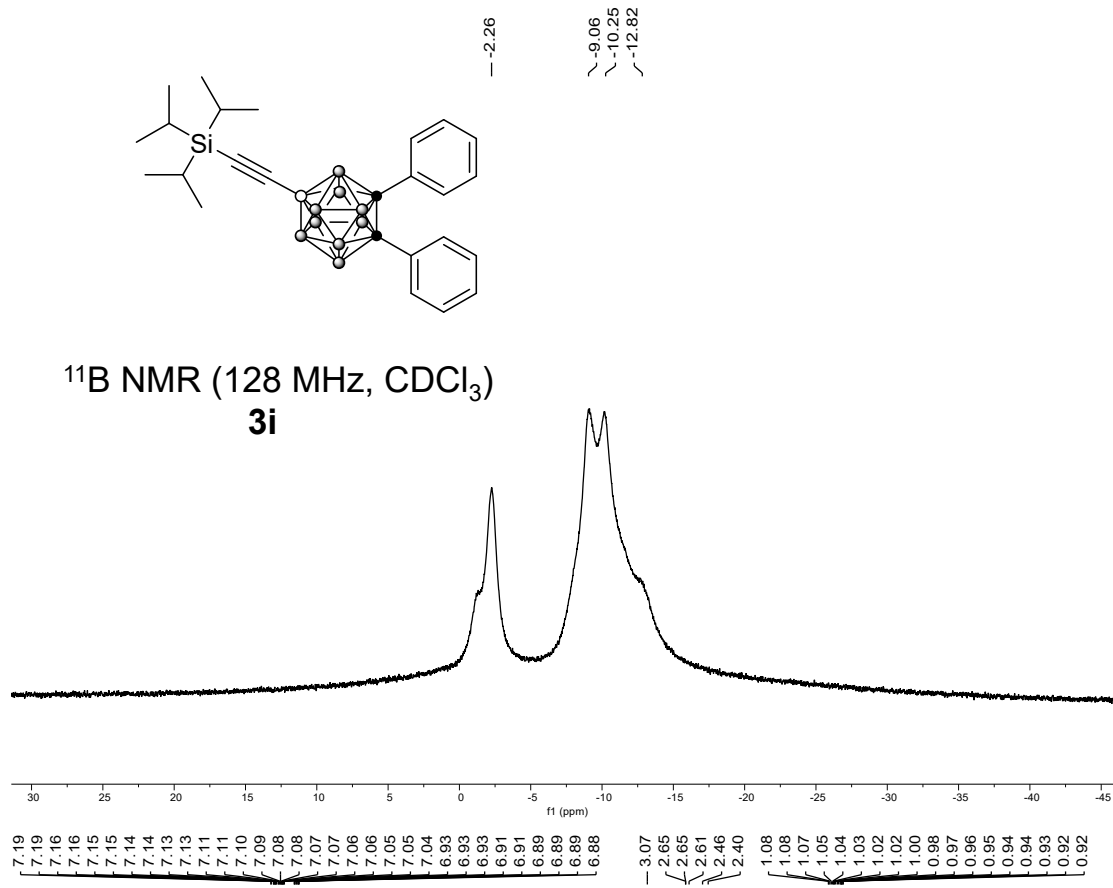
-5.25
 -6.43
 -7.76
 -9.09
 -10.65
 -11.92
 -13.11

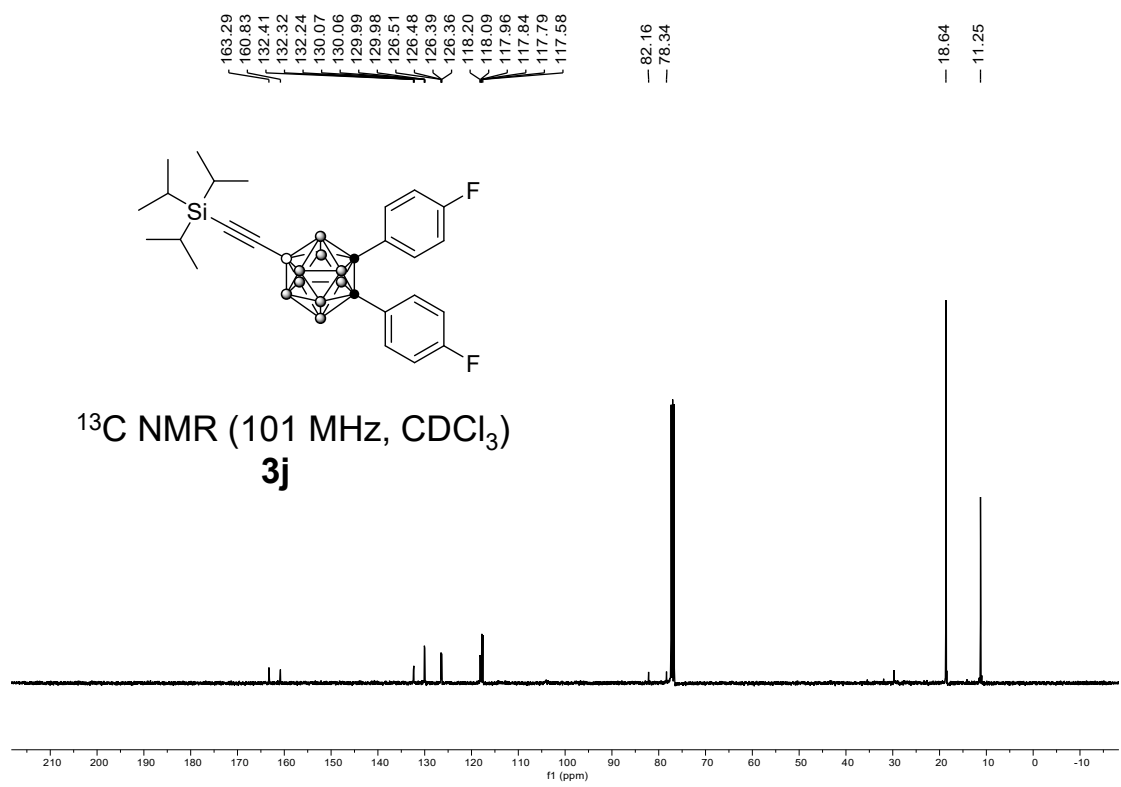
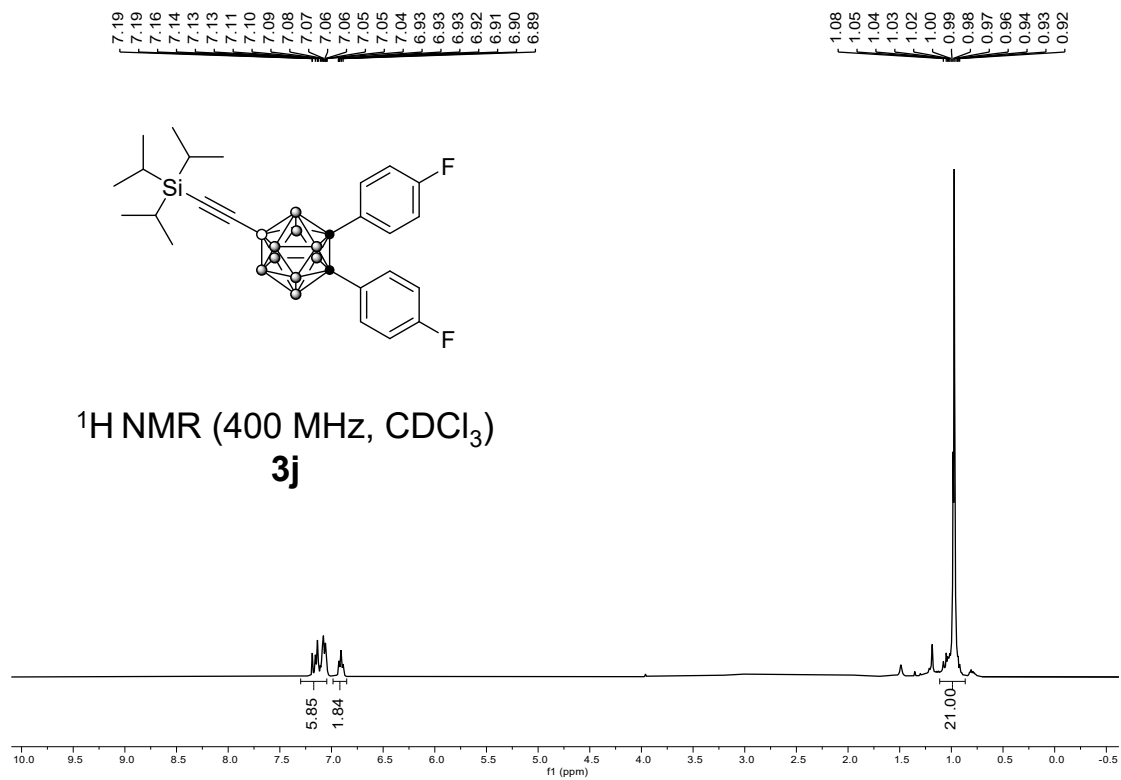
^{11}B NMR (128 MHz, CDCl_3)
3h

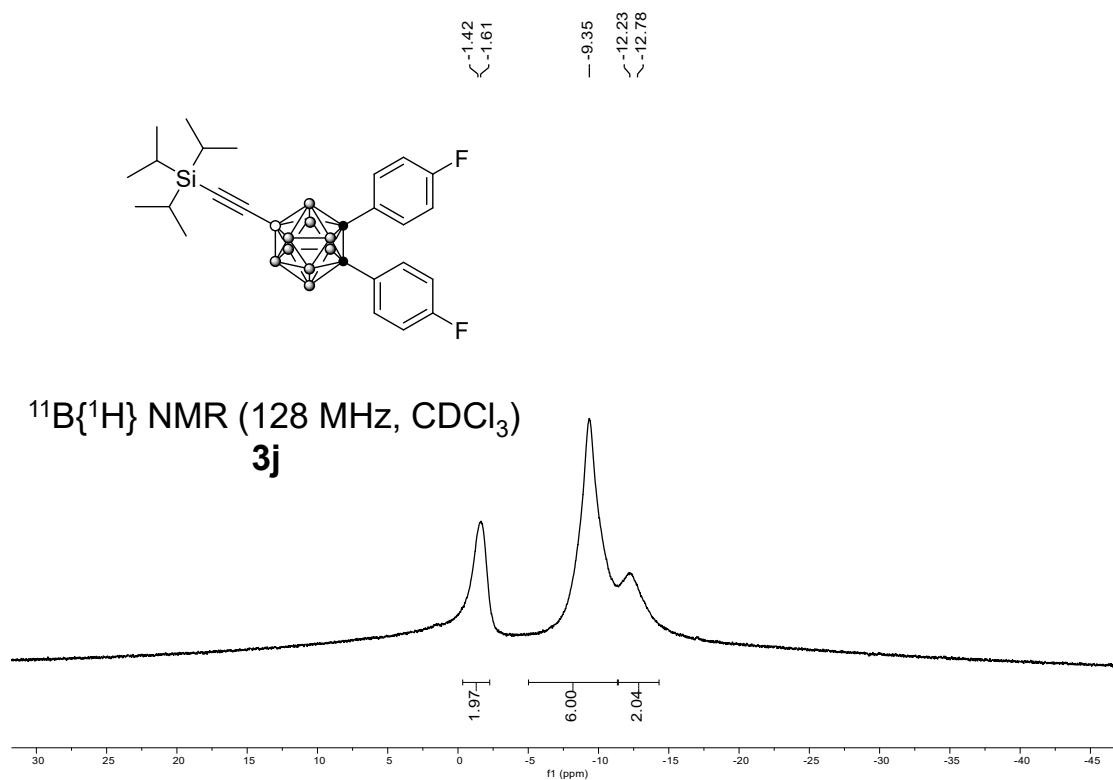
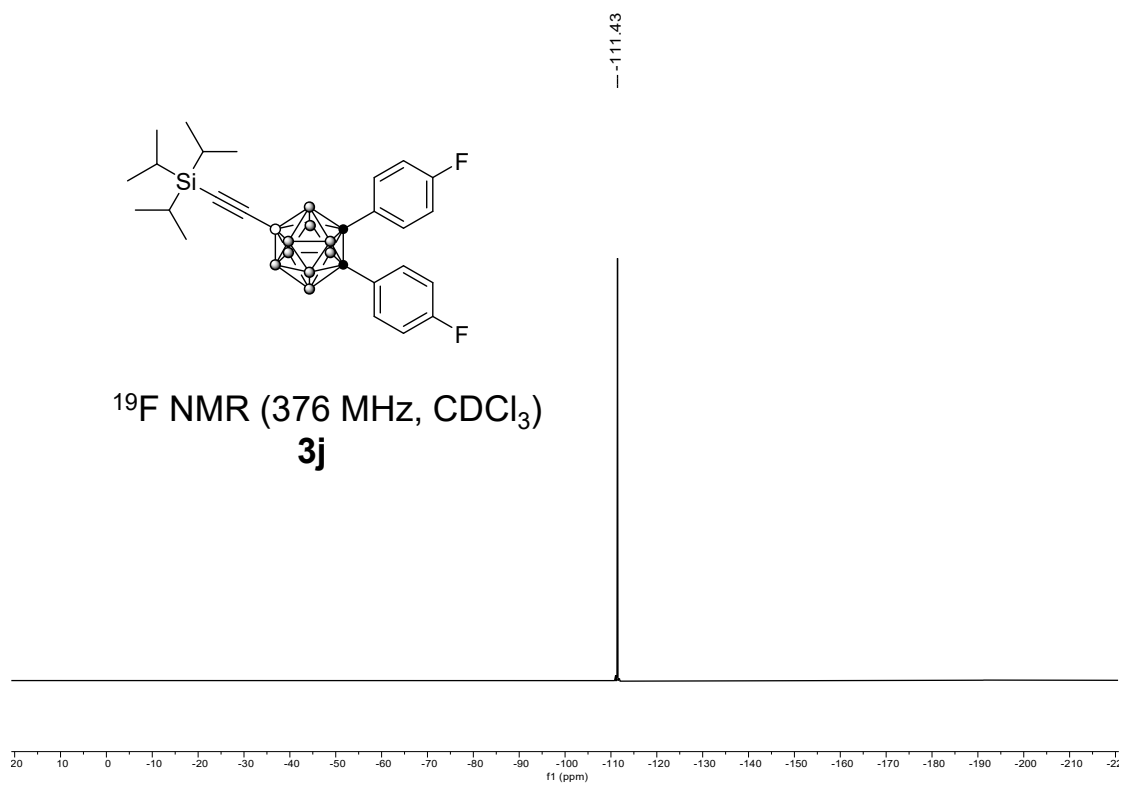


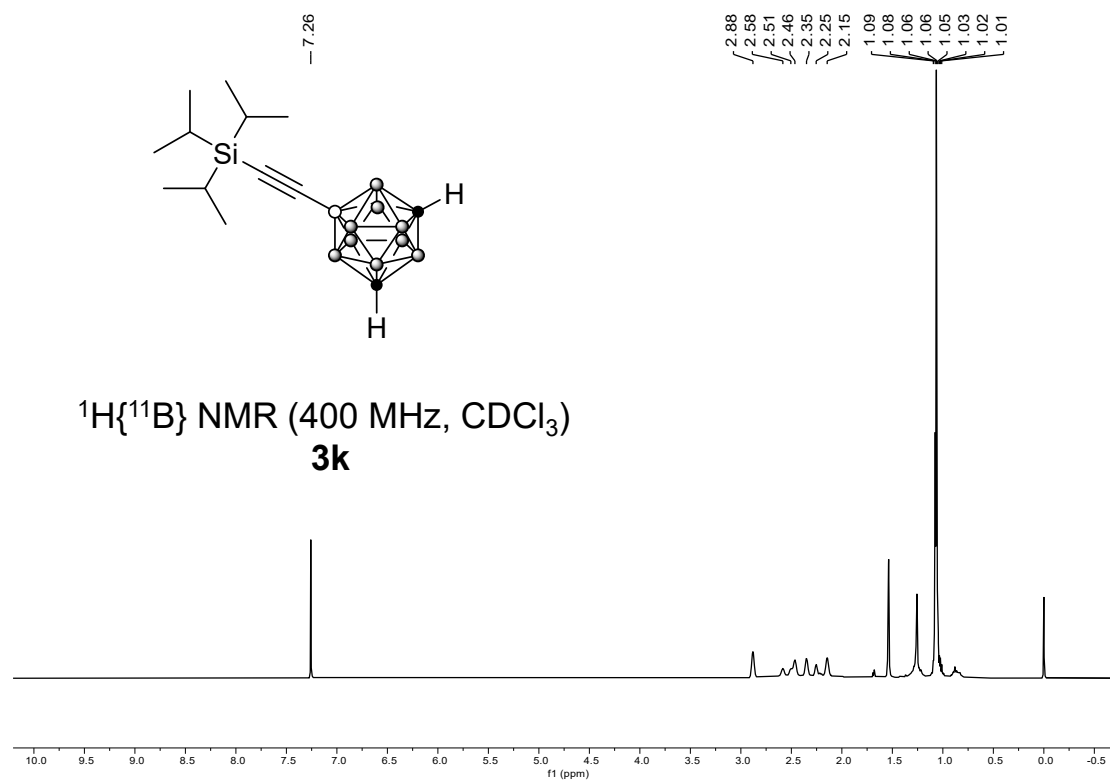
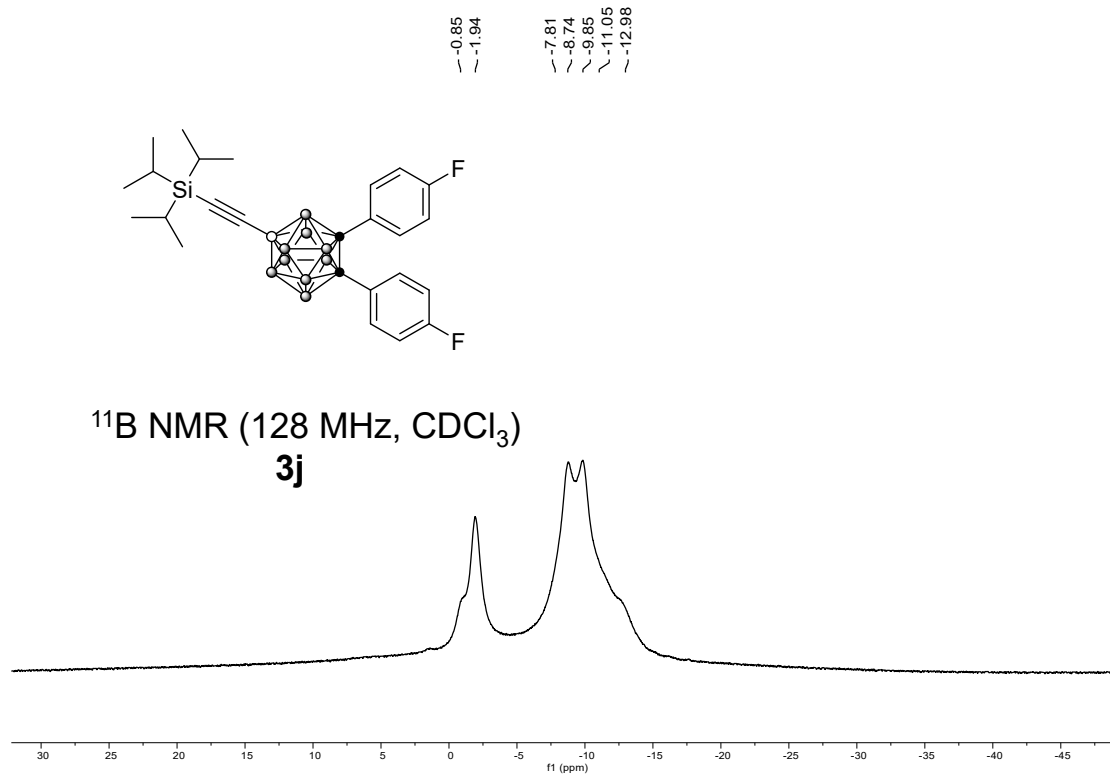


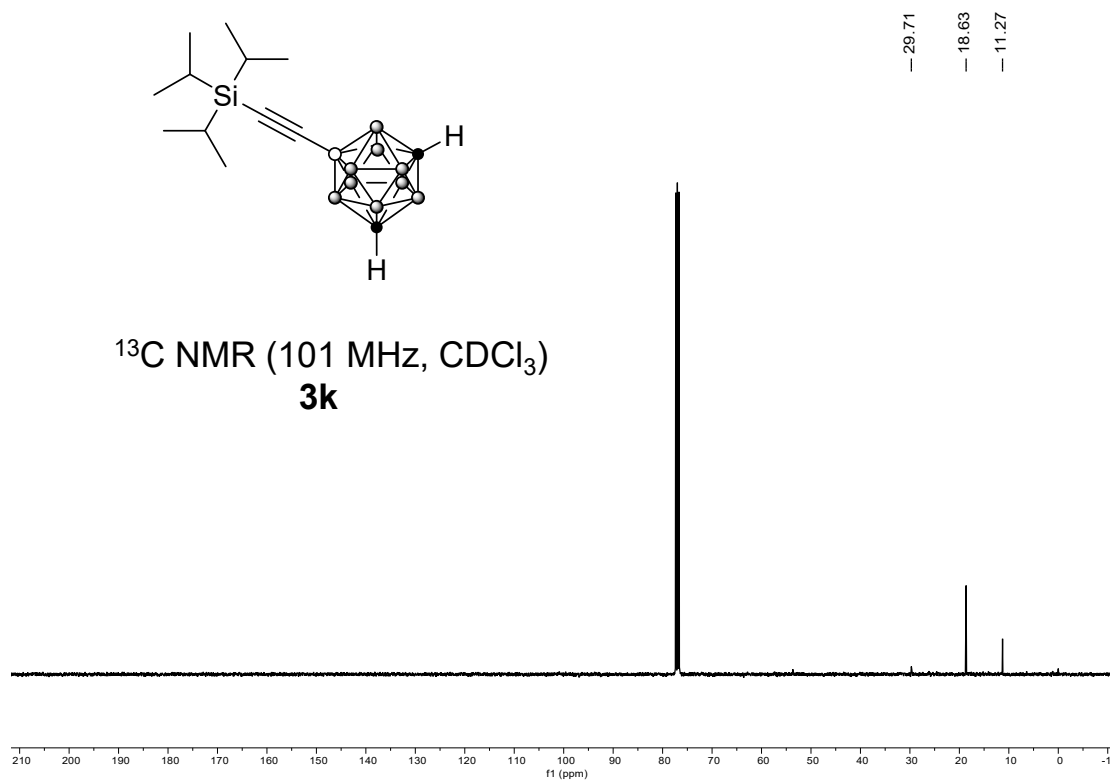
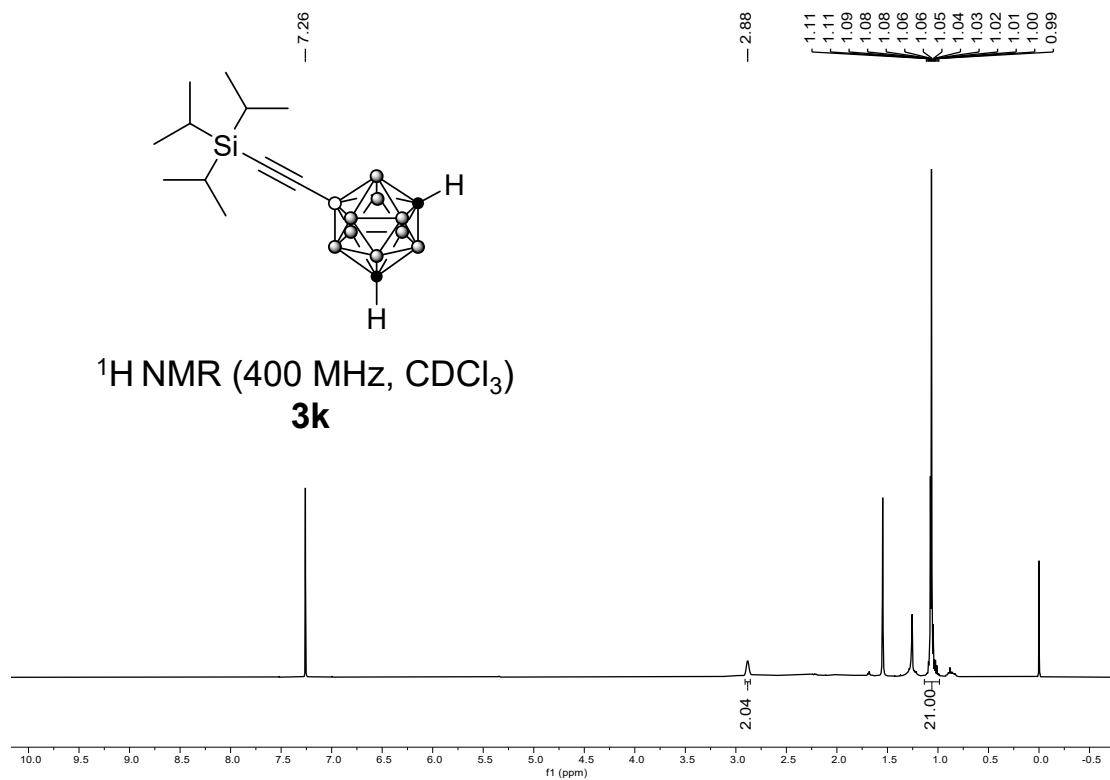


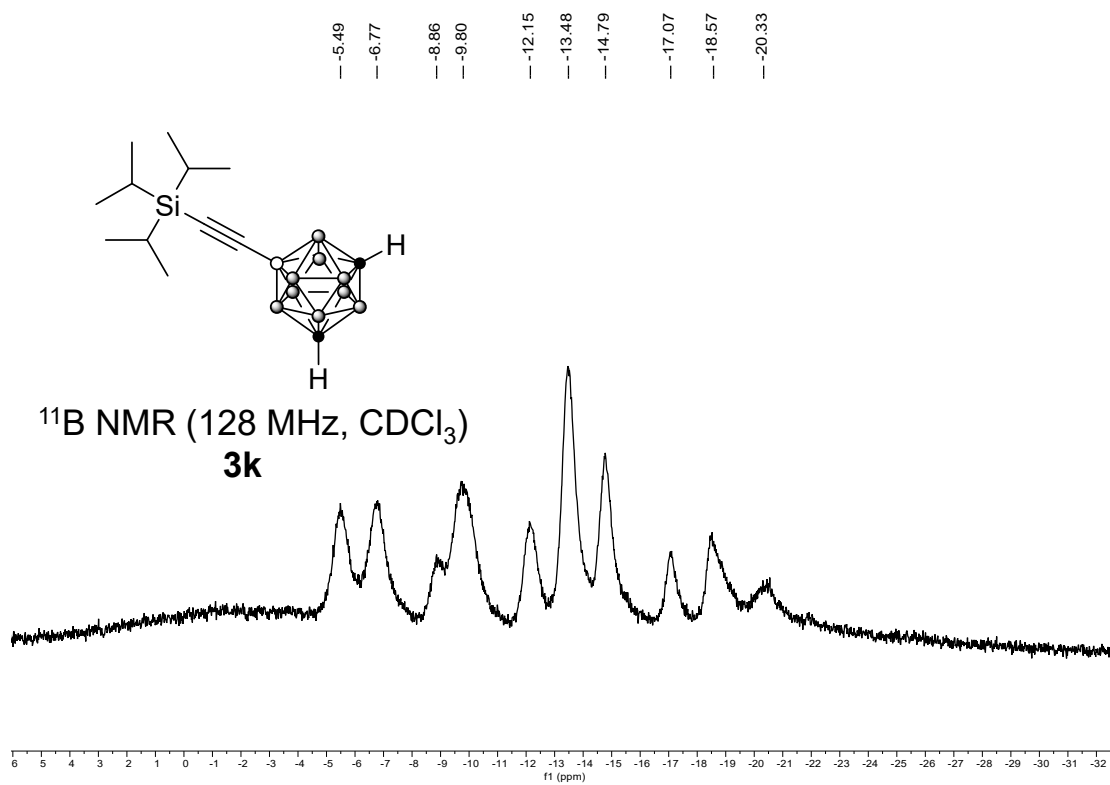
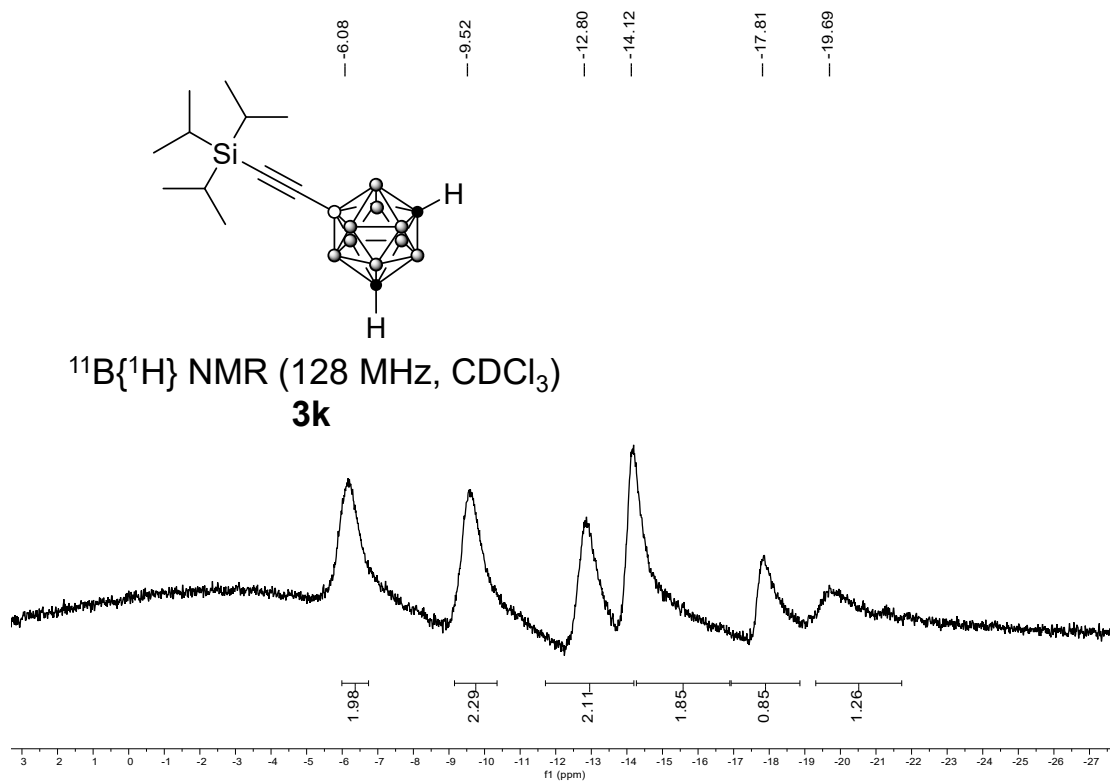


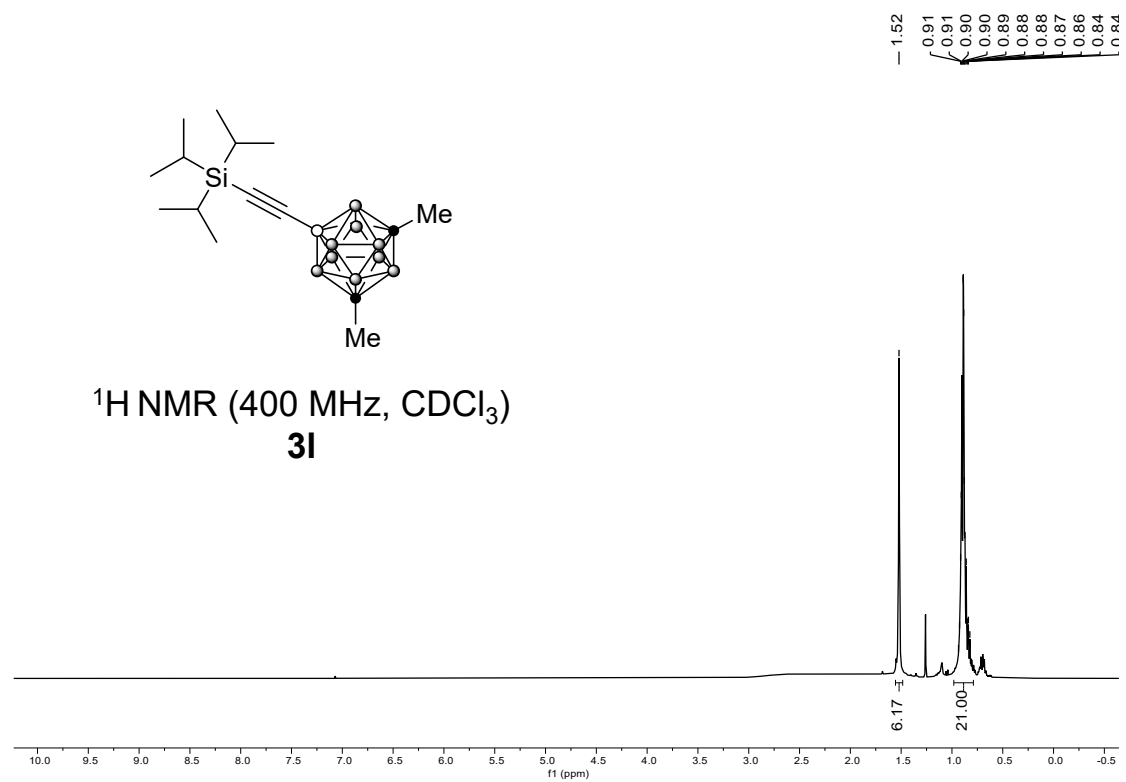
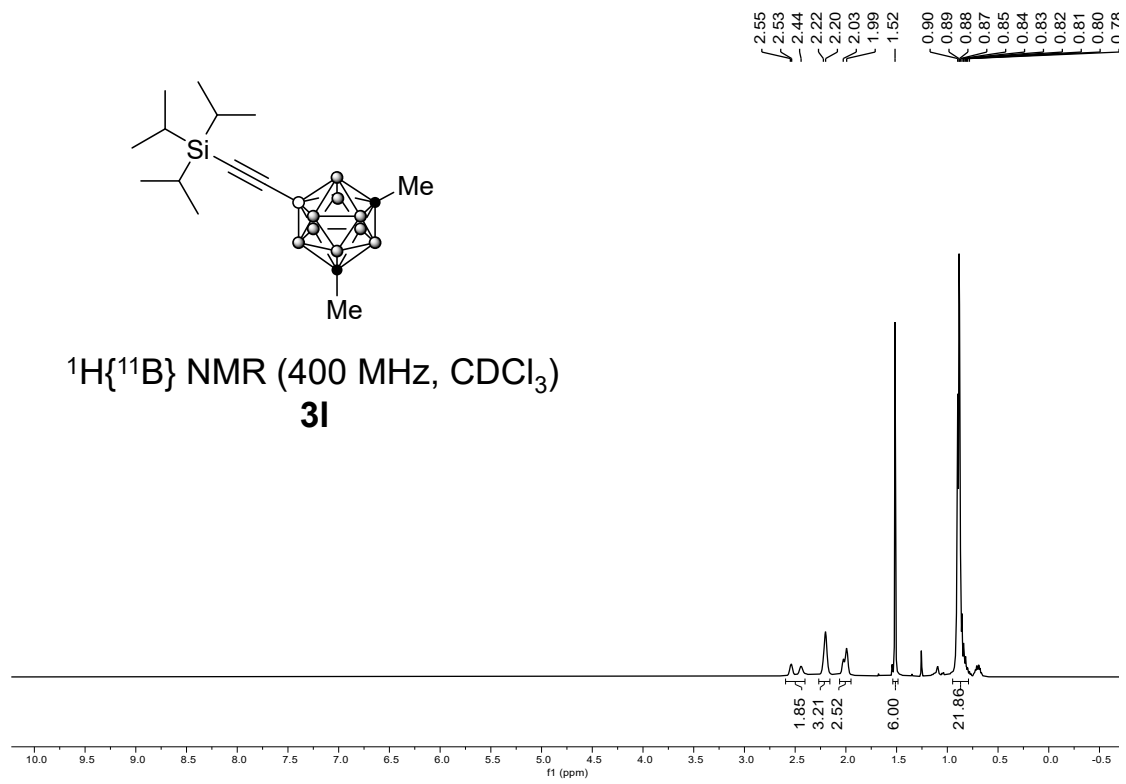


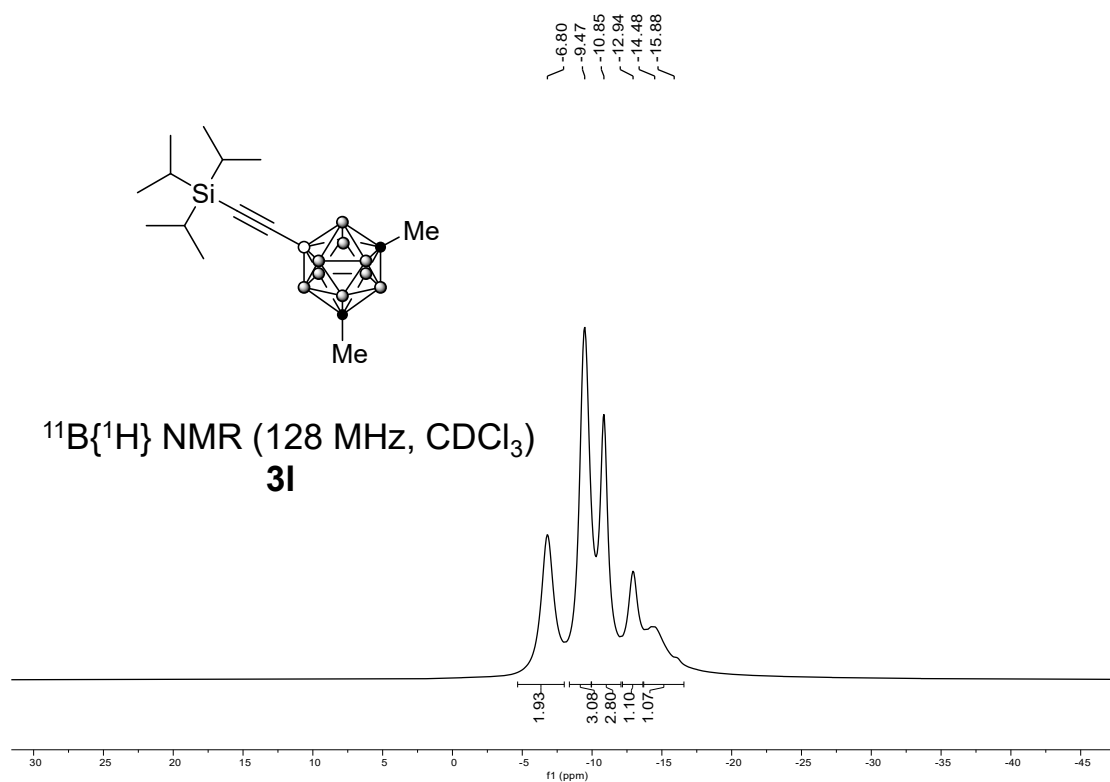
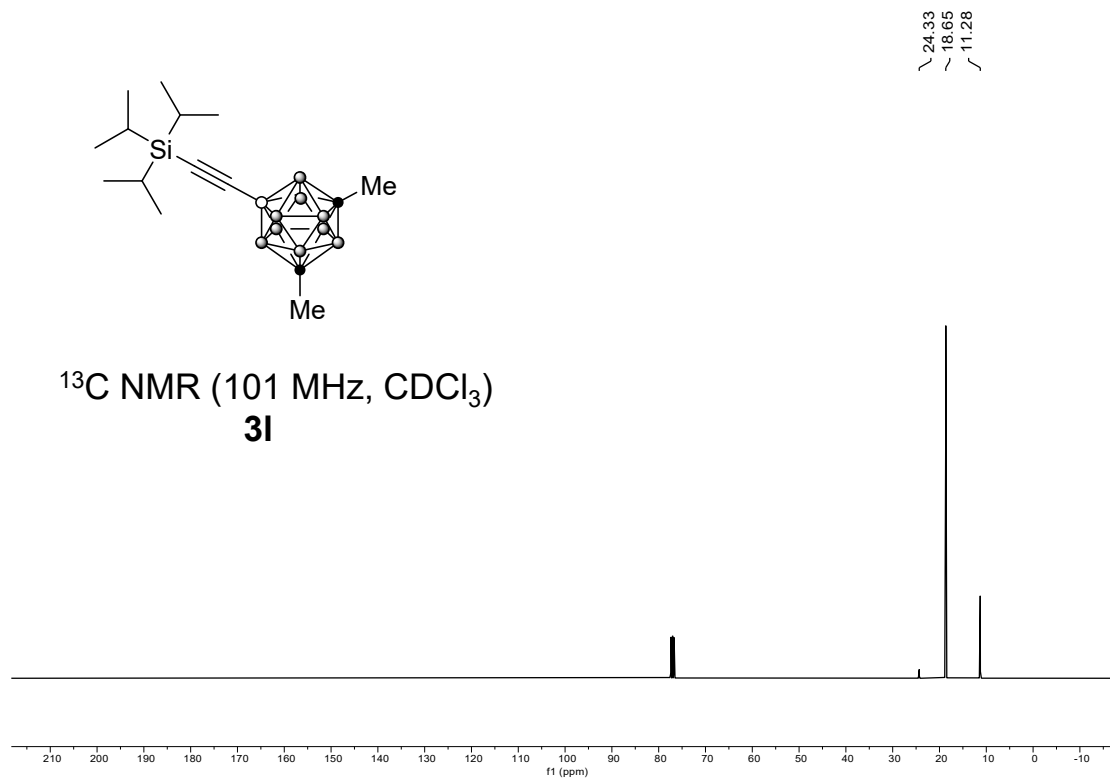


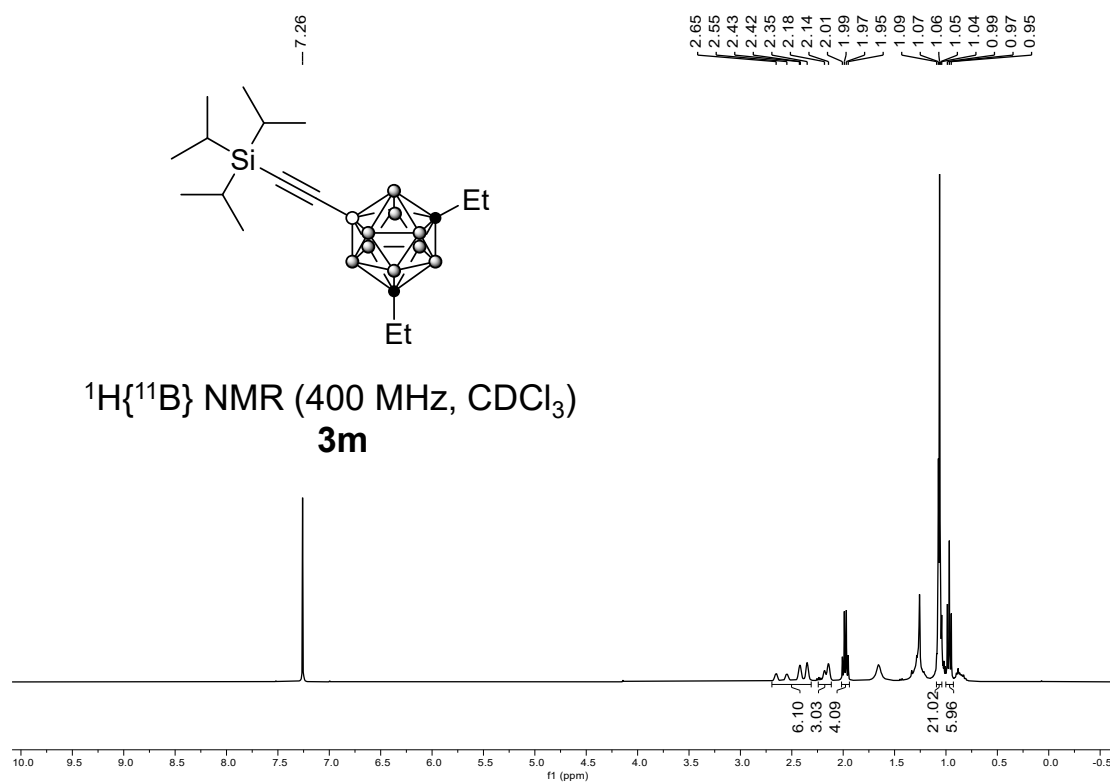
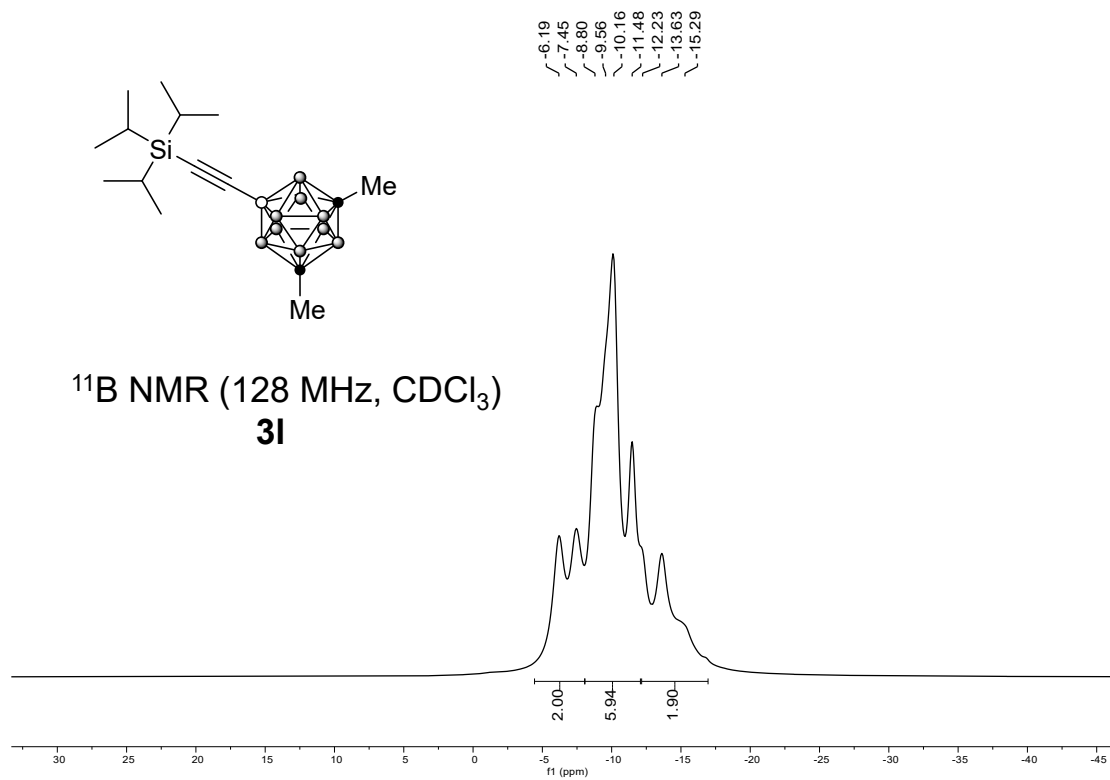


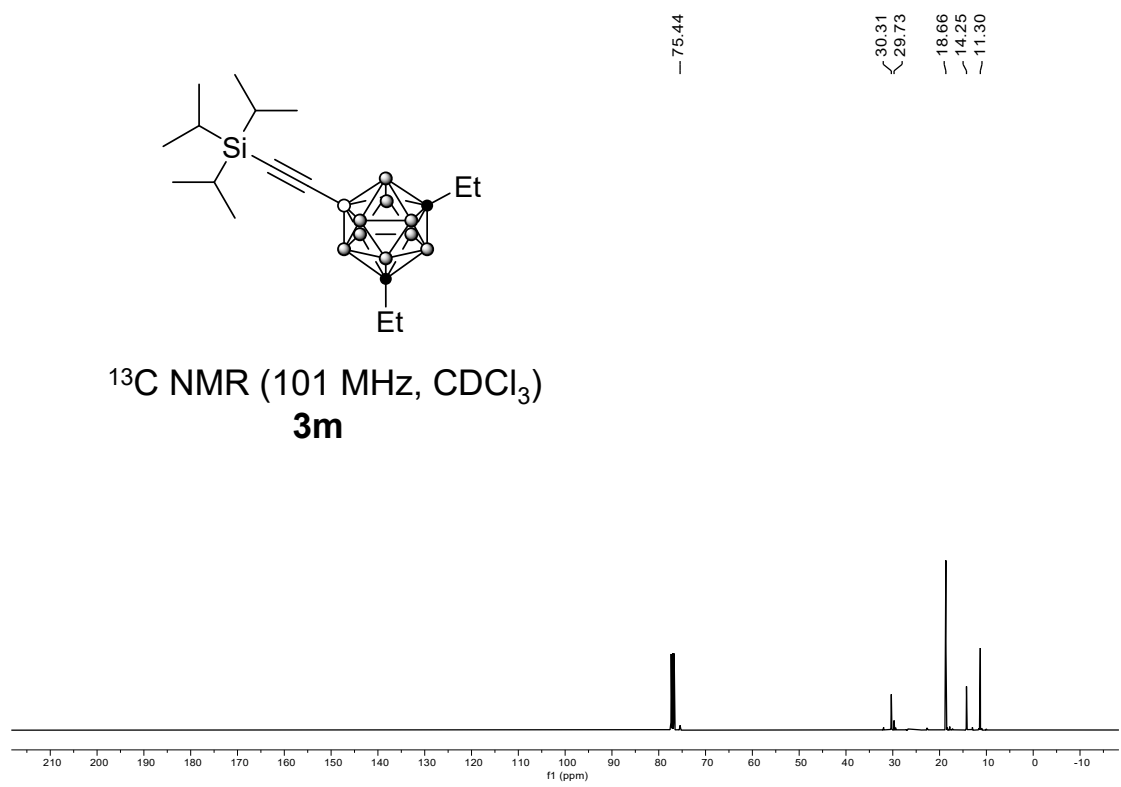
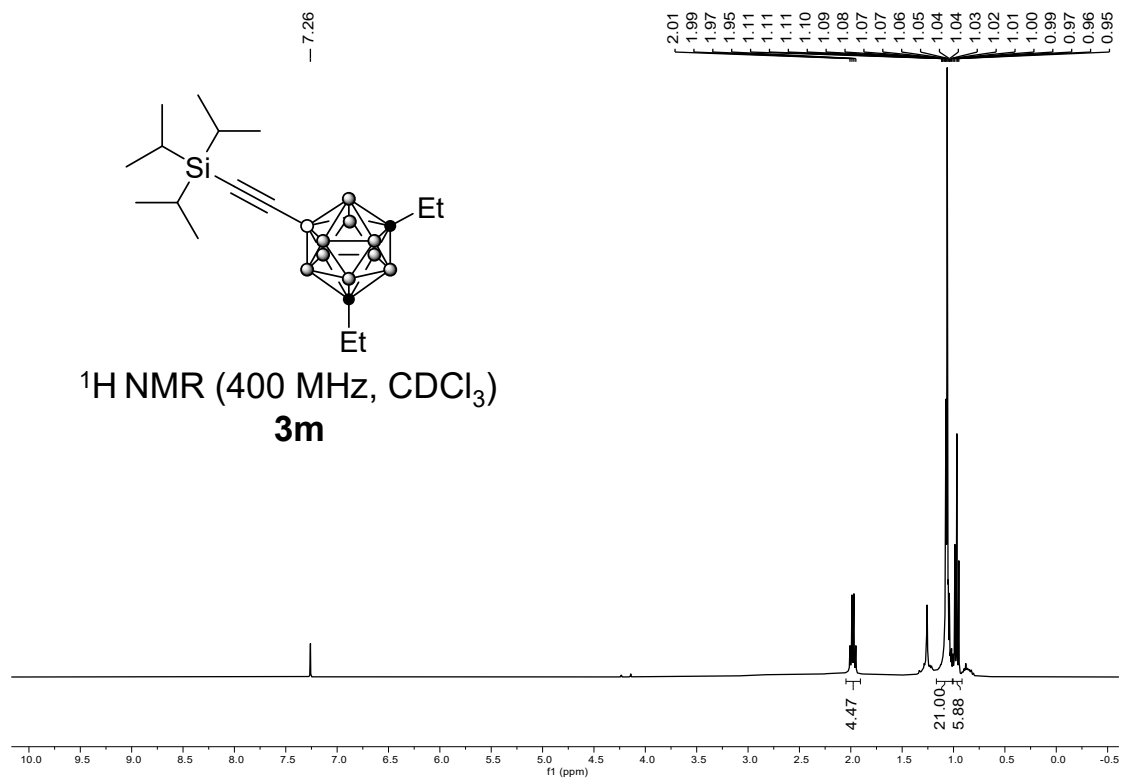


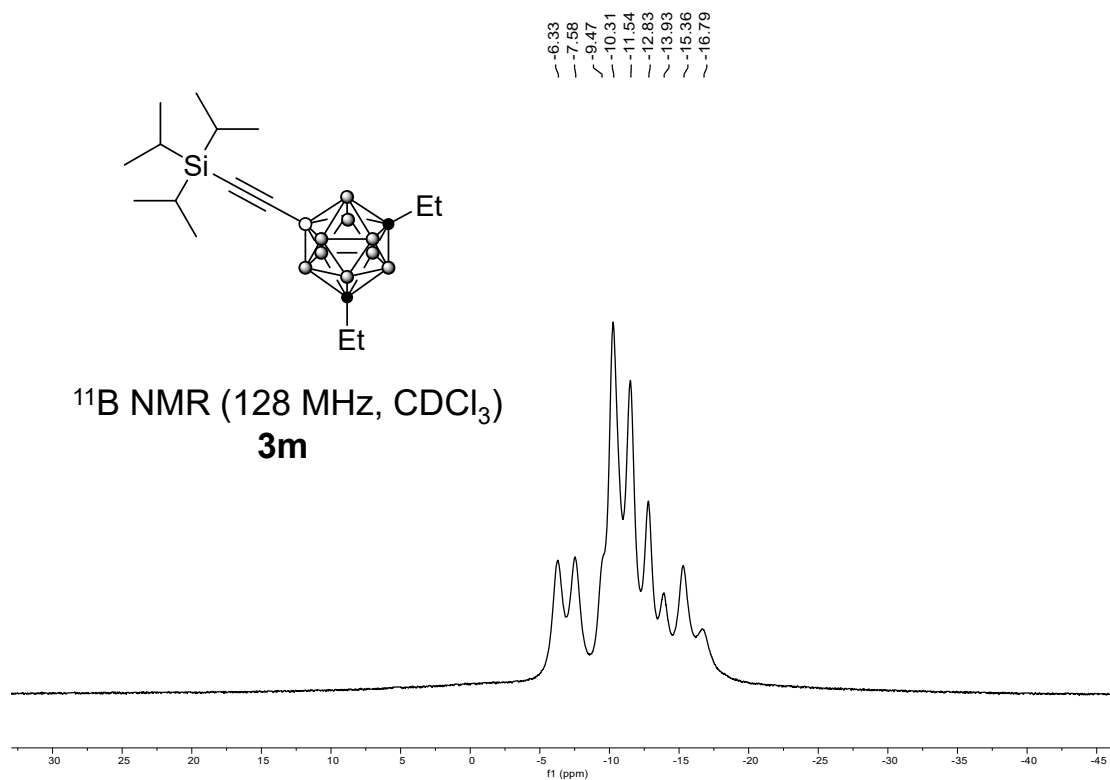
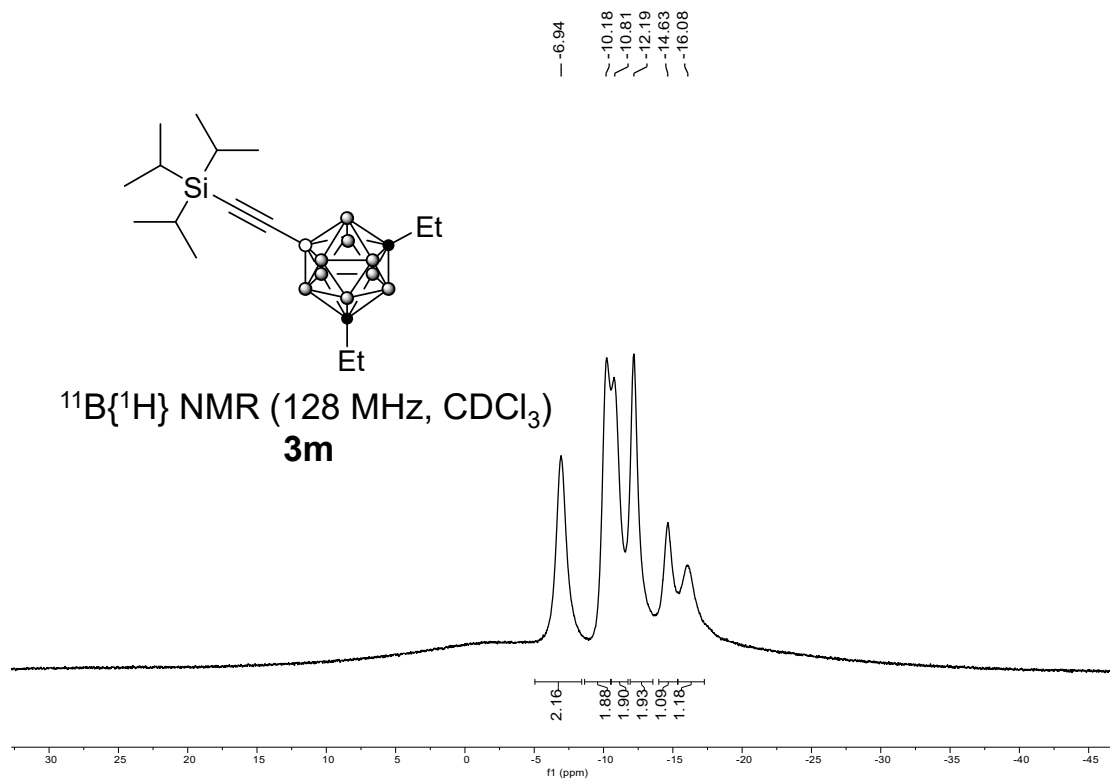


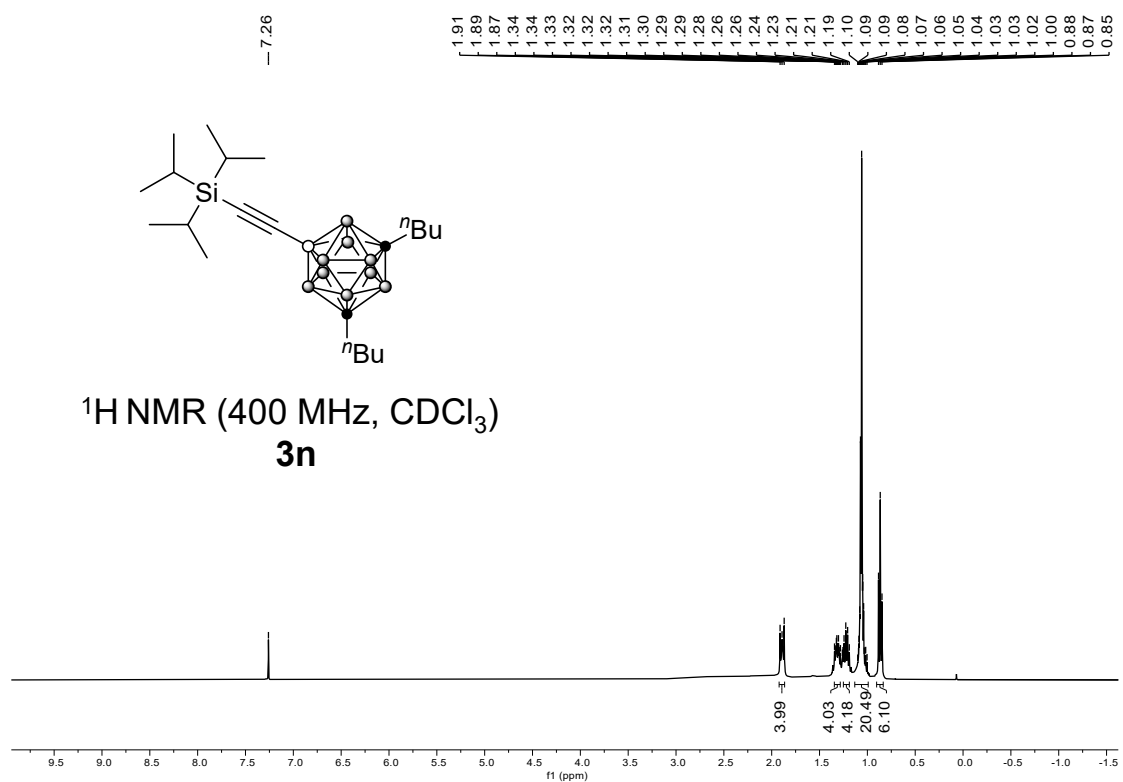
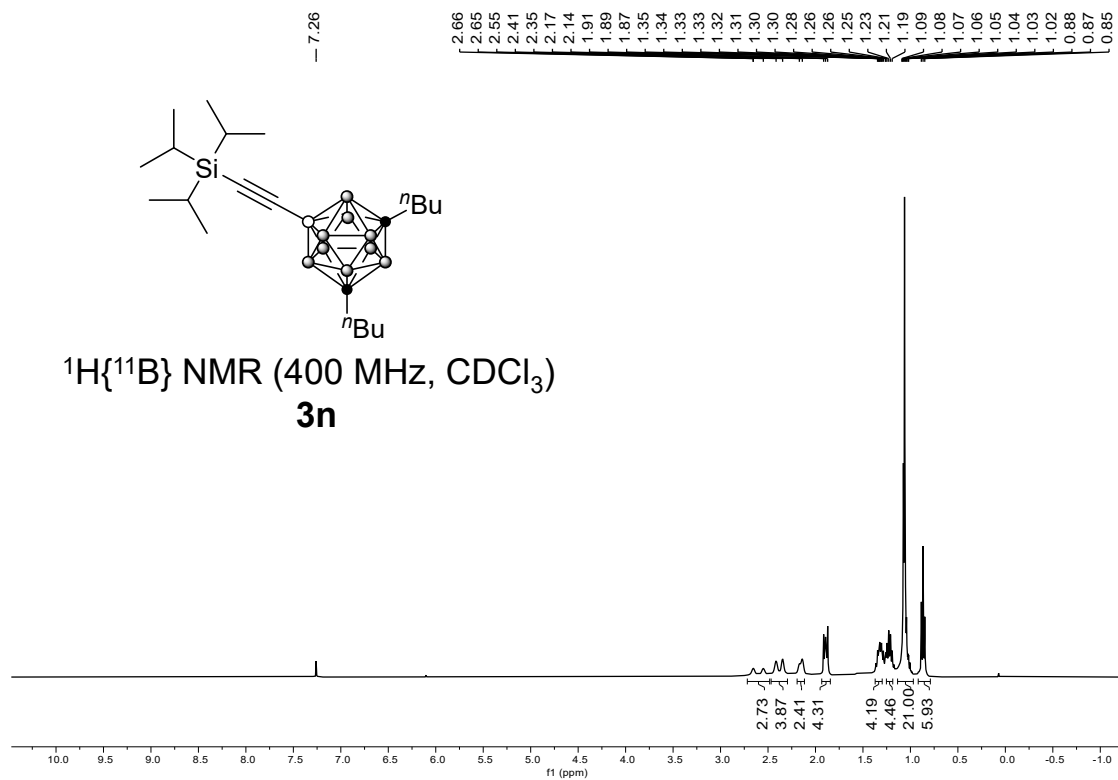


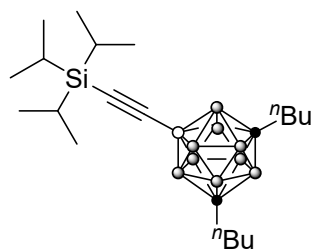




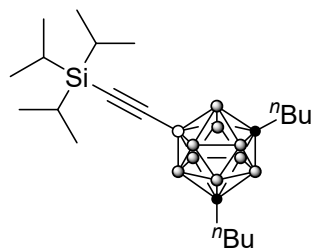
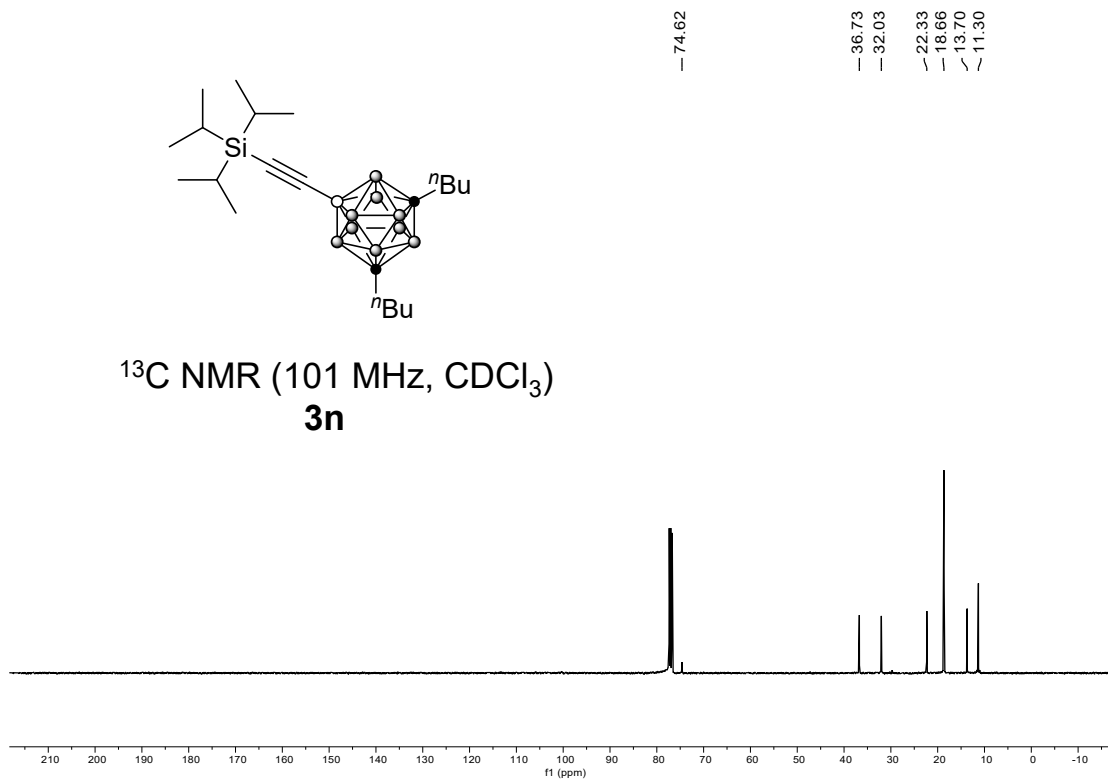




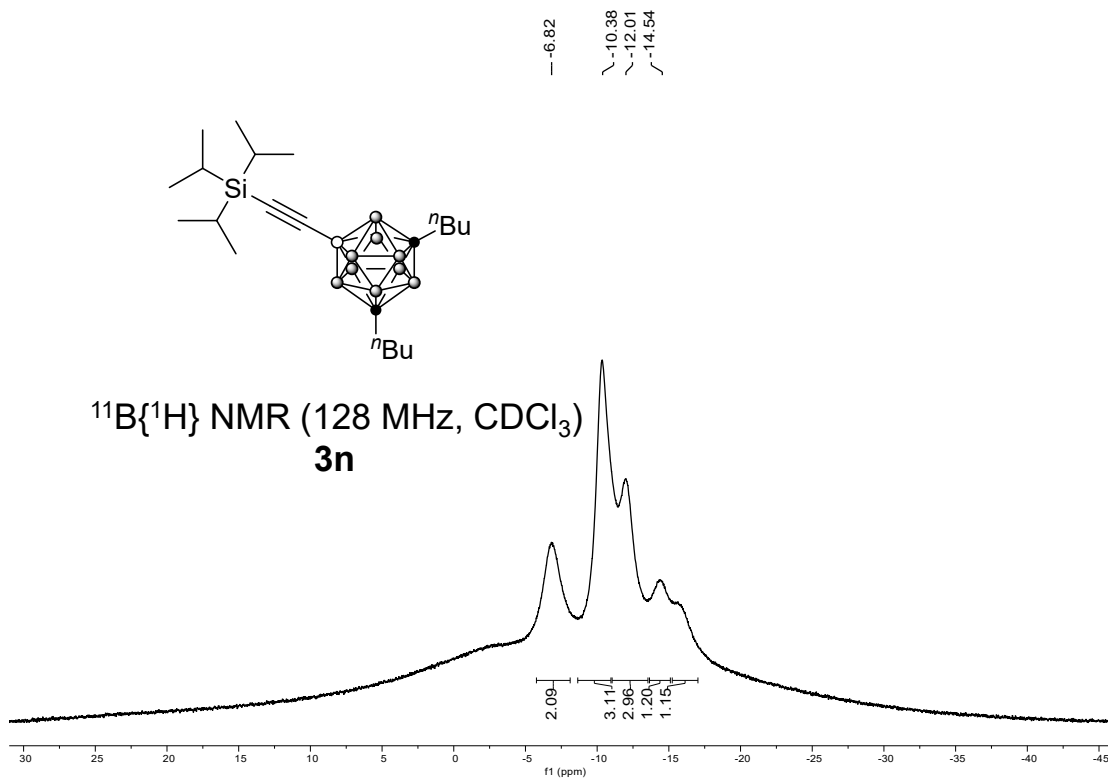


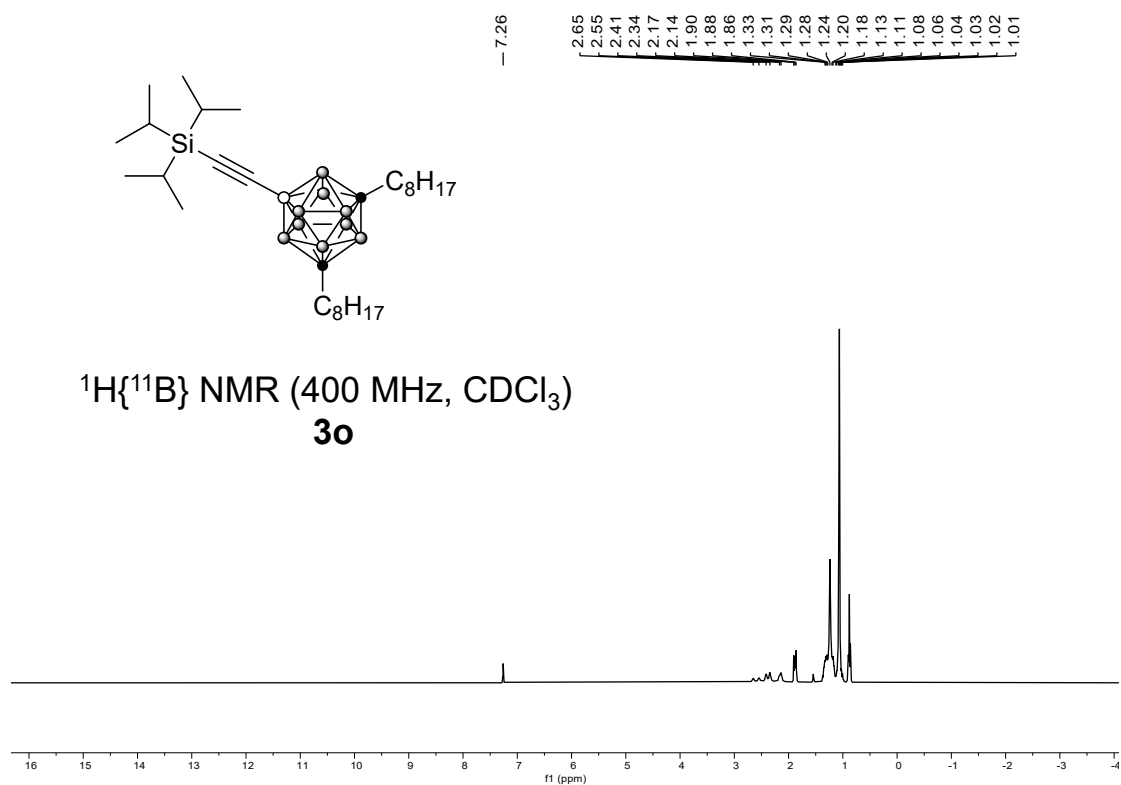
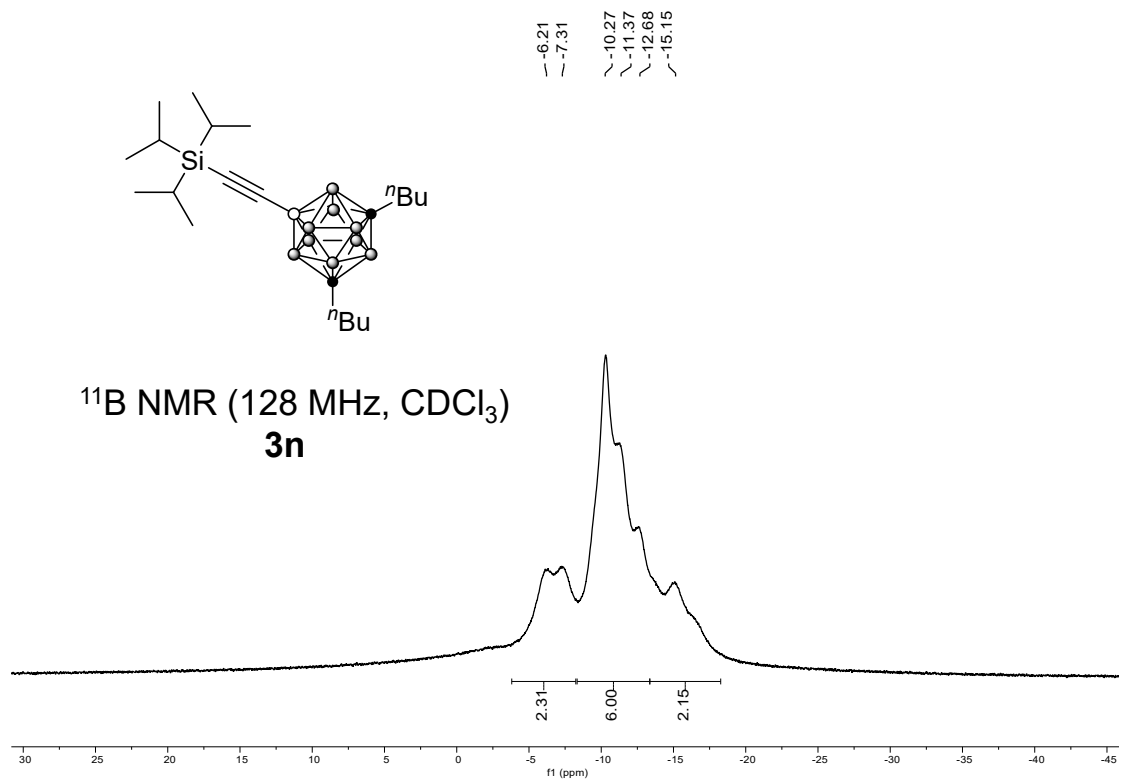


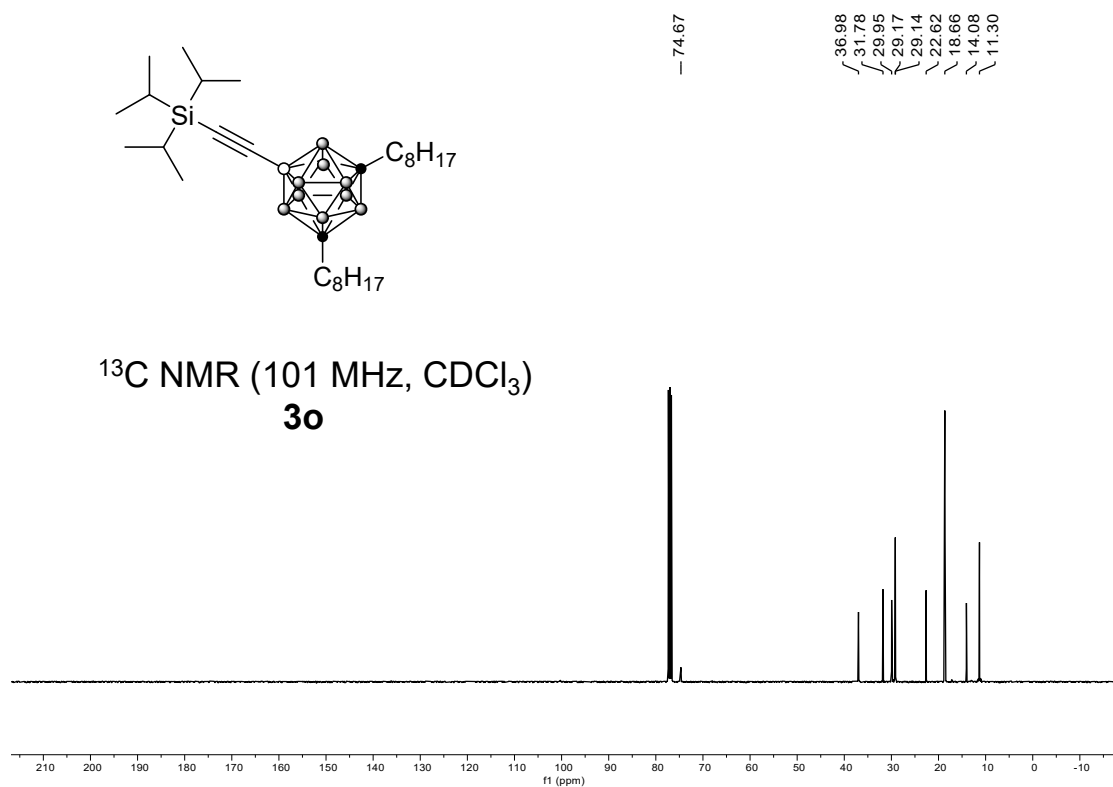
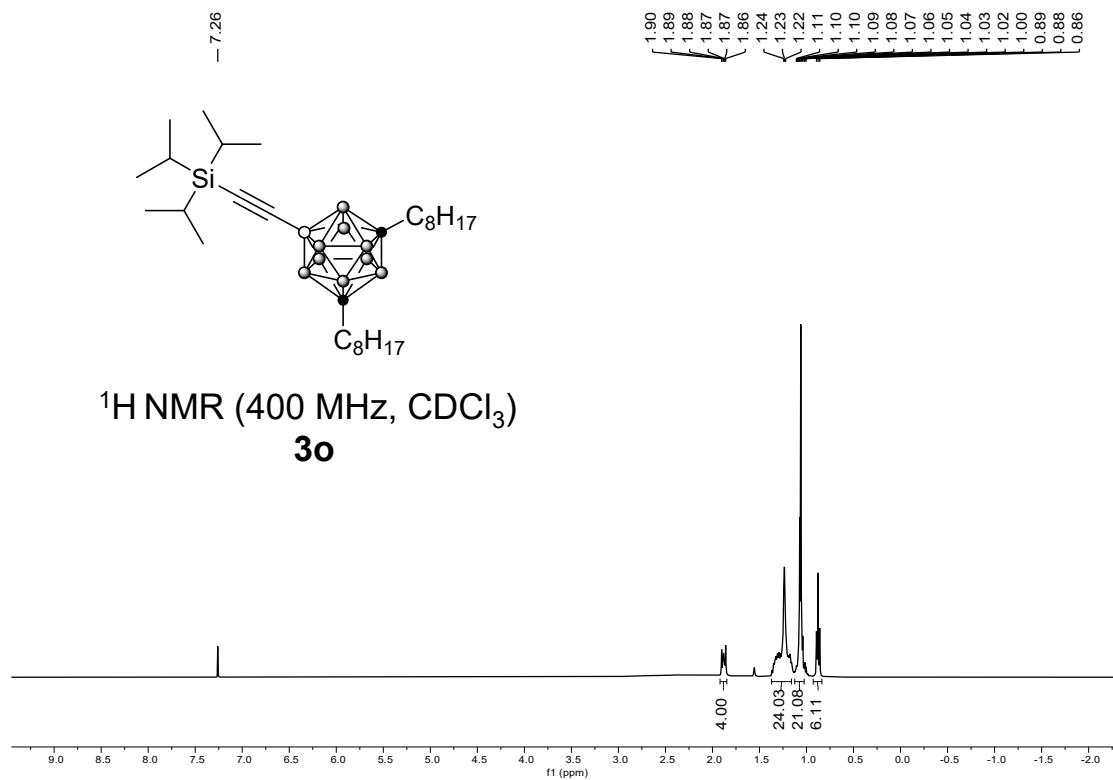
^{13}C NMR (101 MHz, CDCl_3)
3n

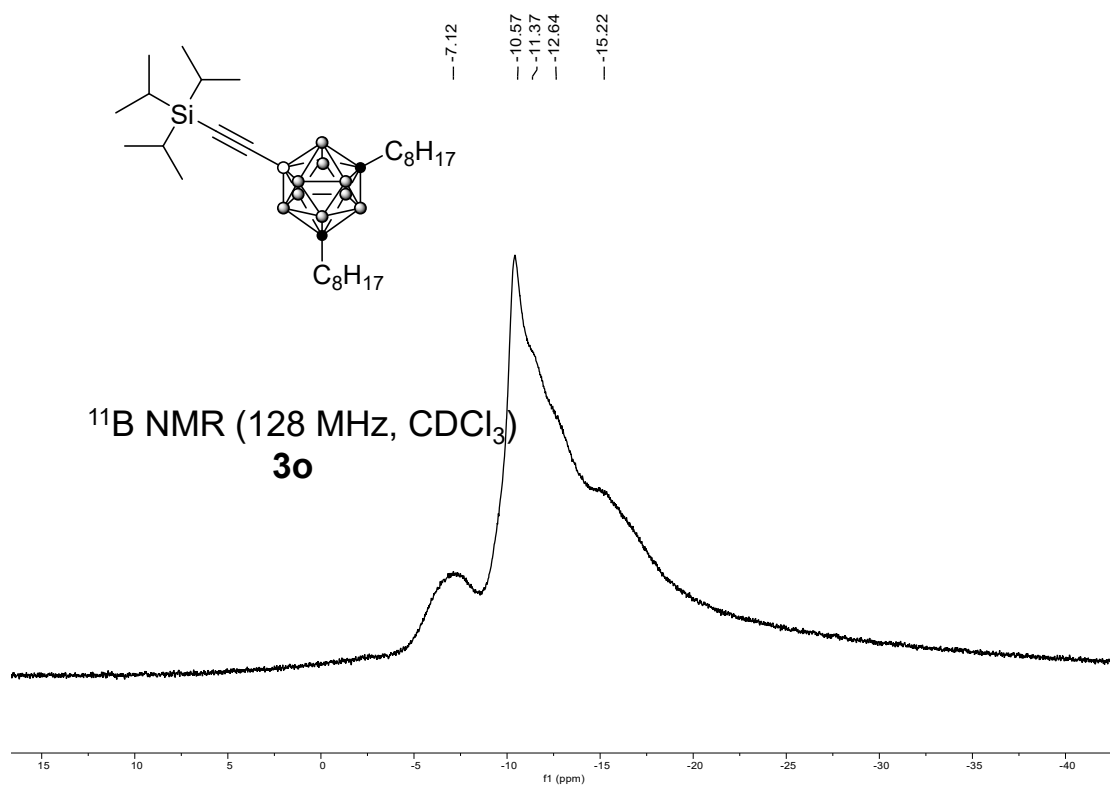
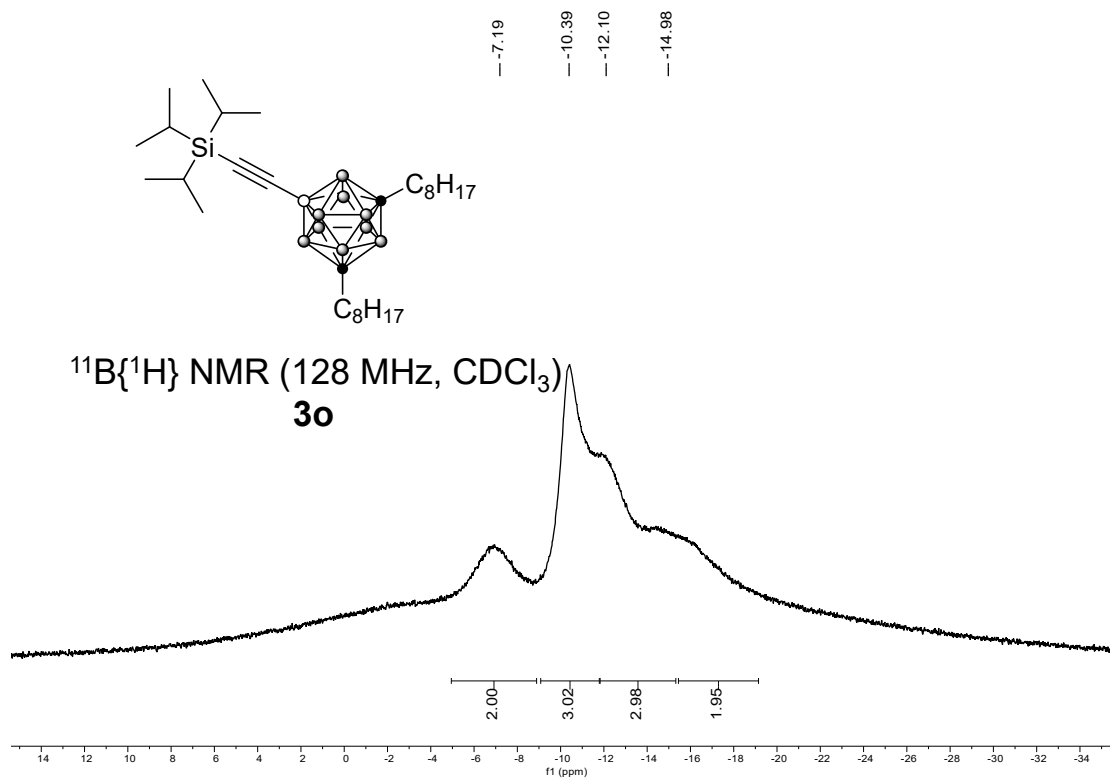


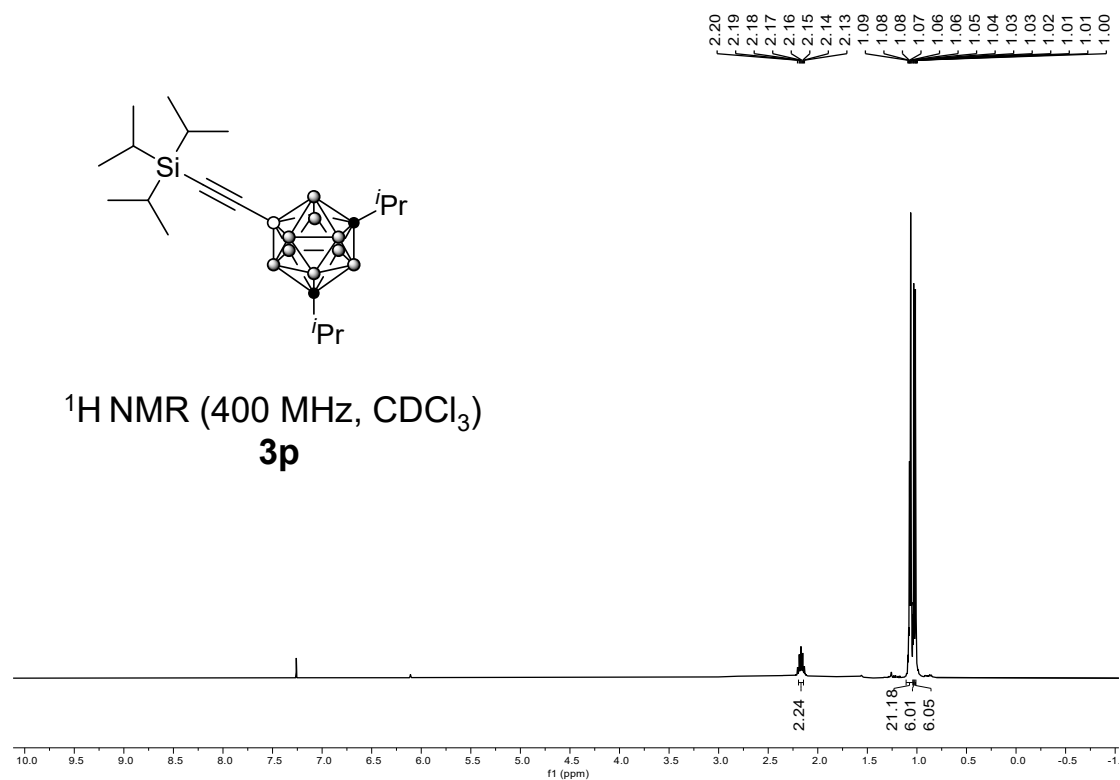
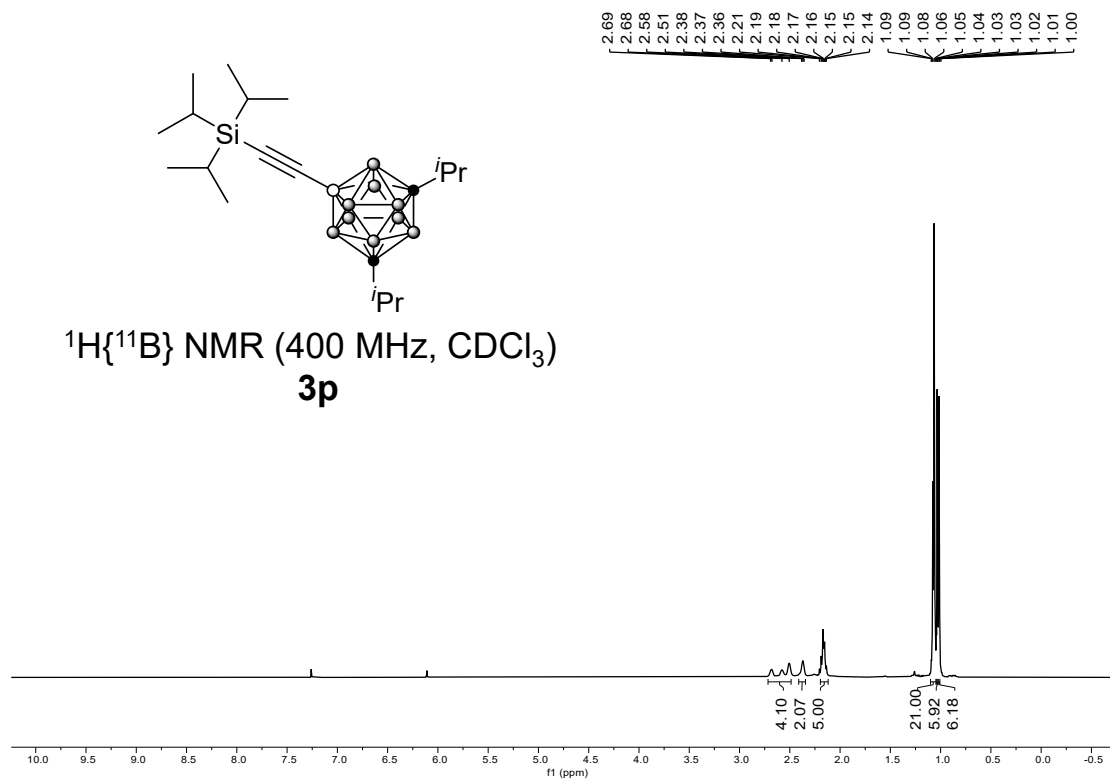
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)
3n

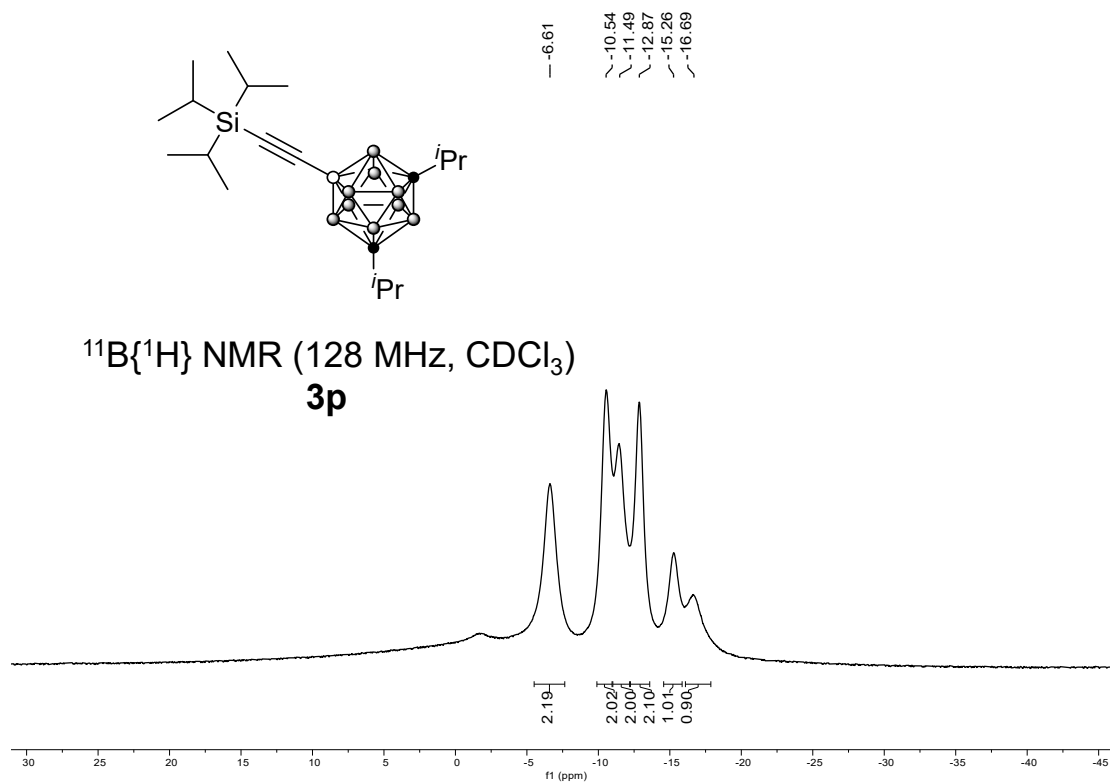
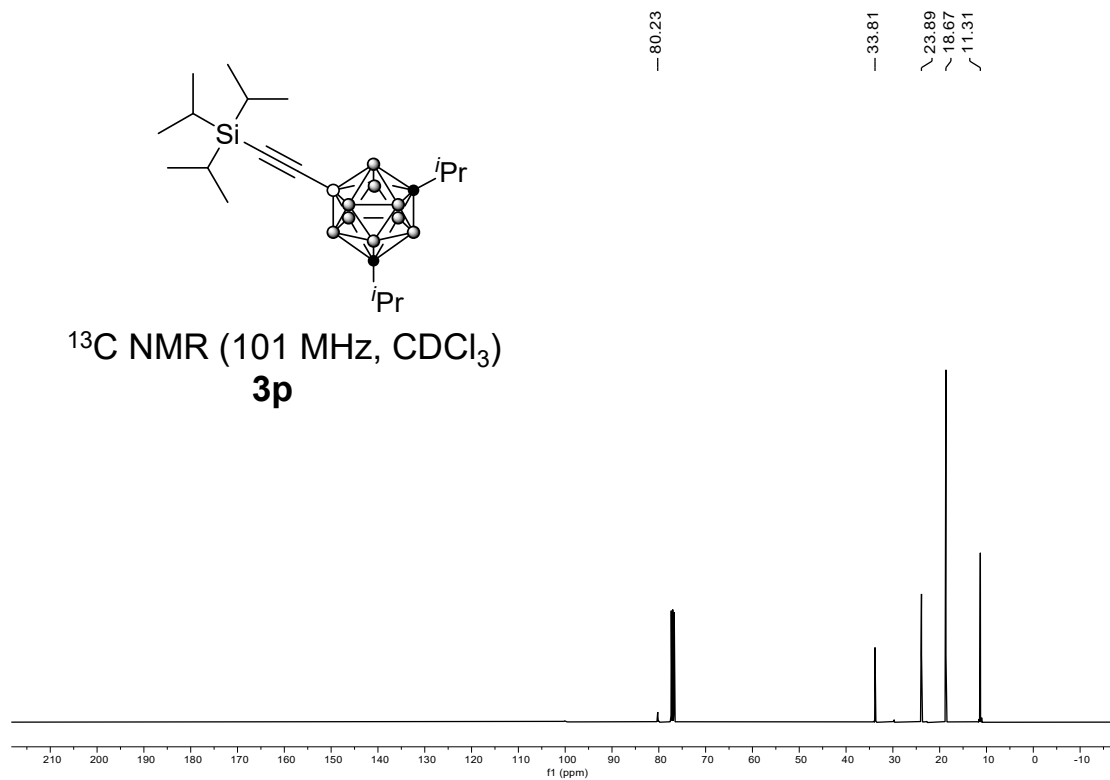


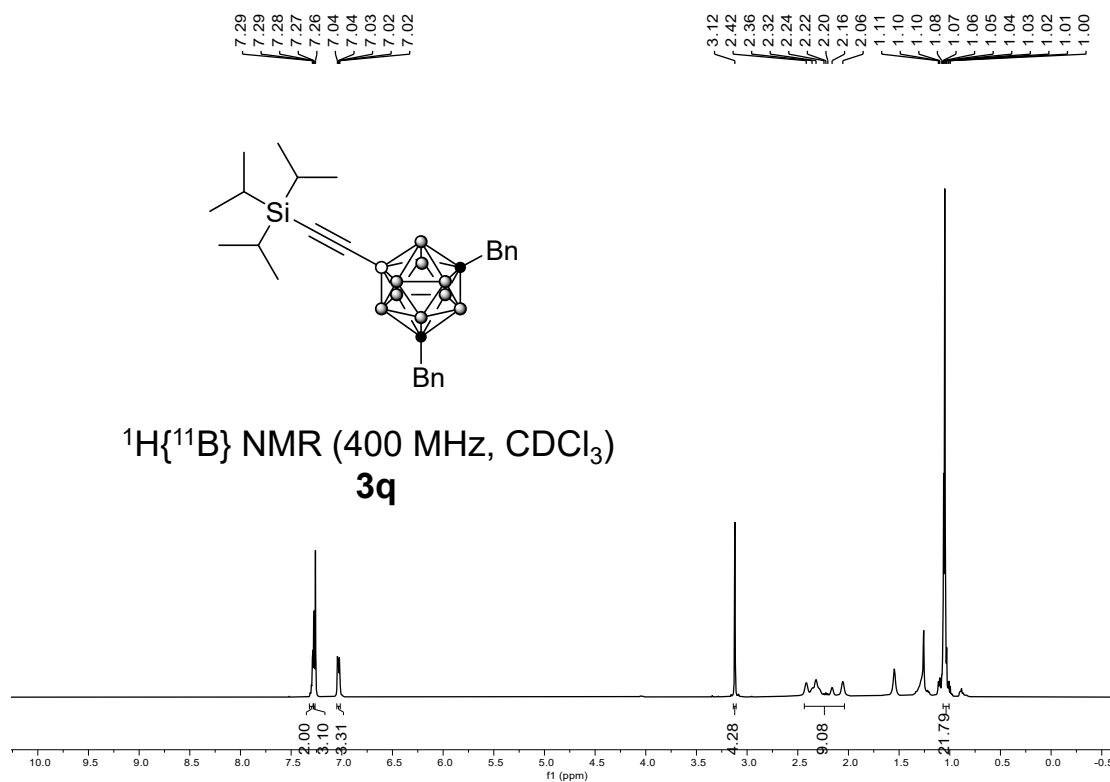
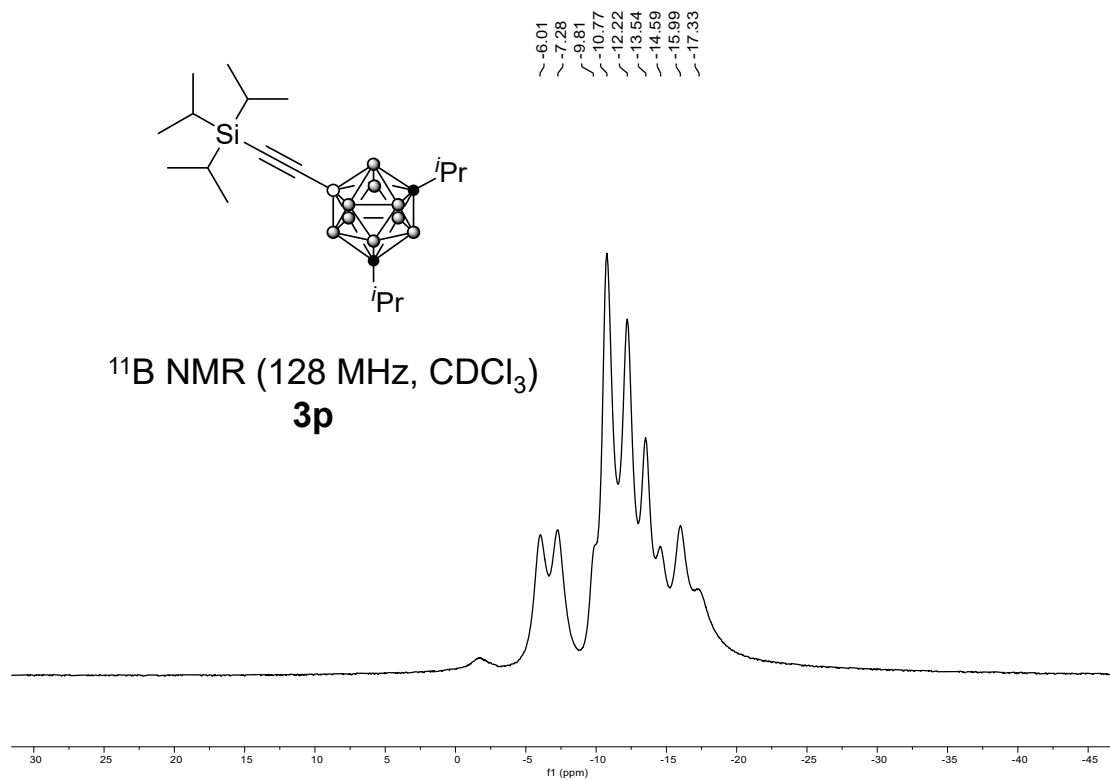


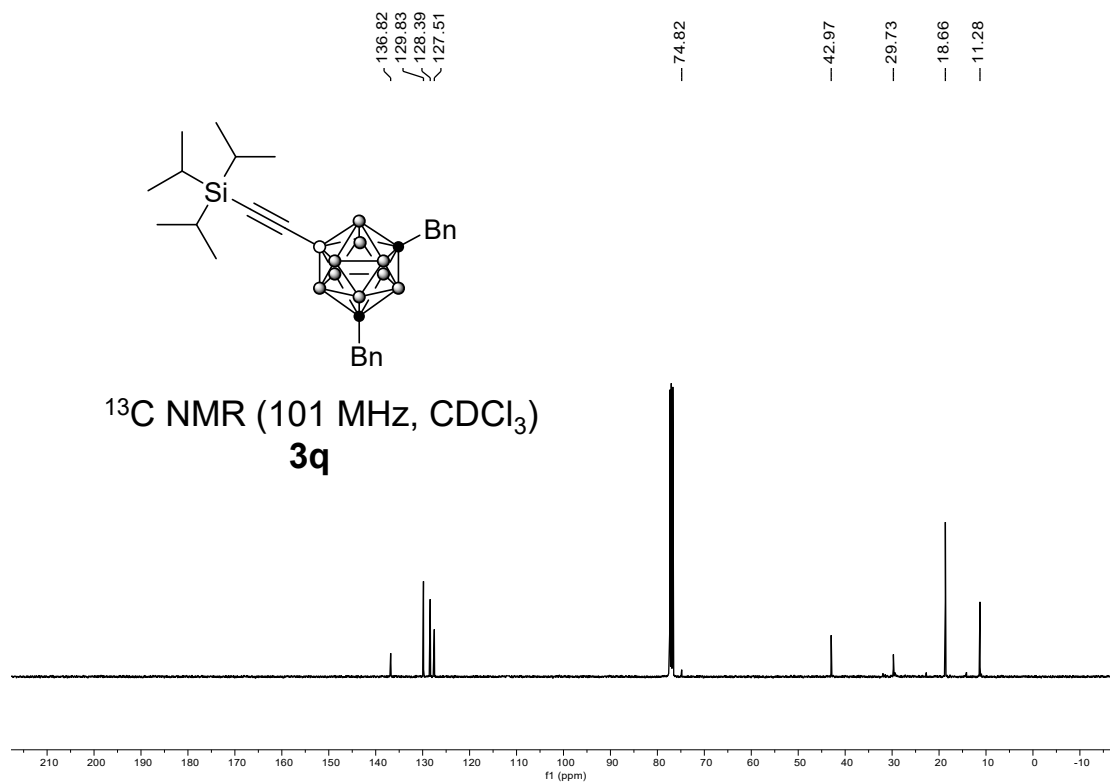
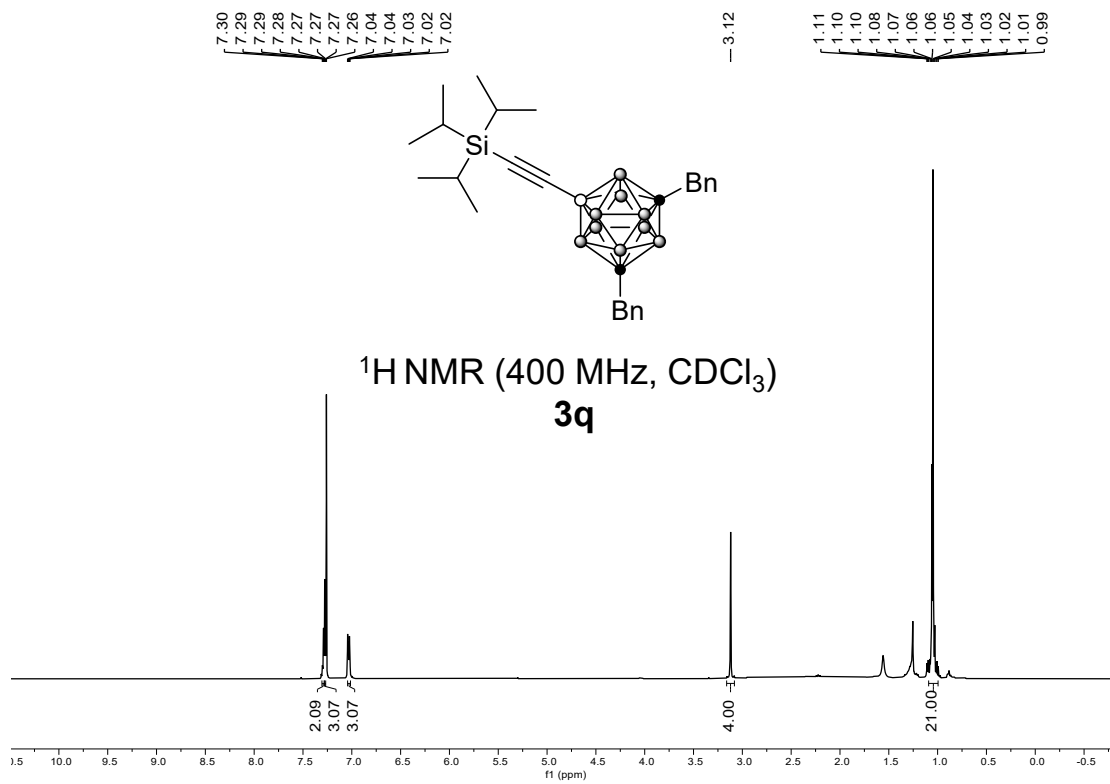


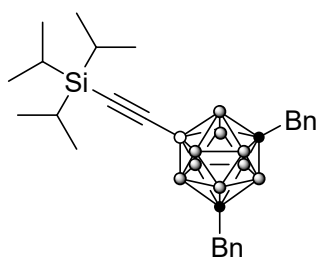






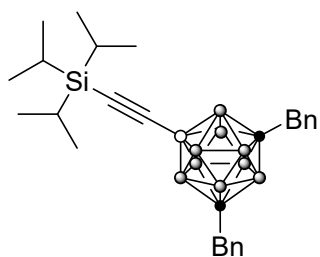
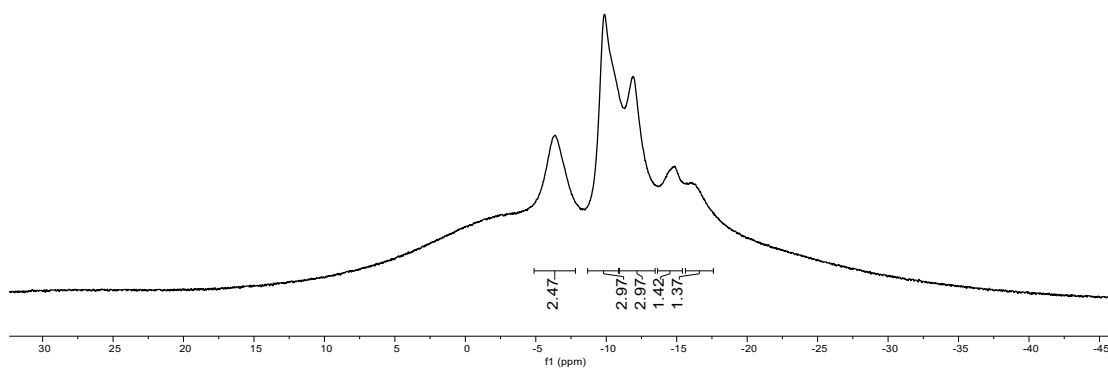






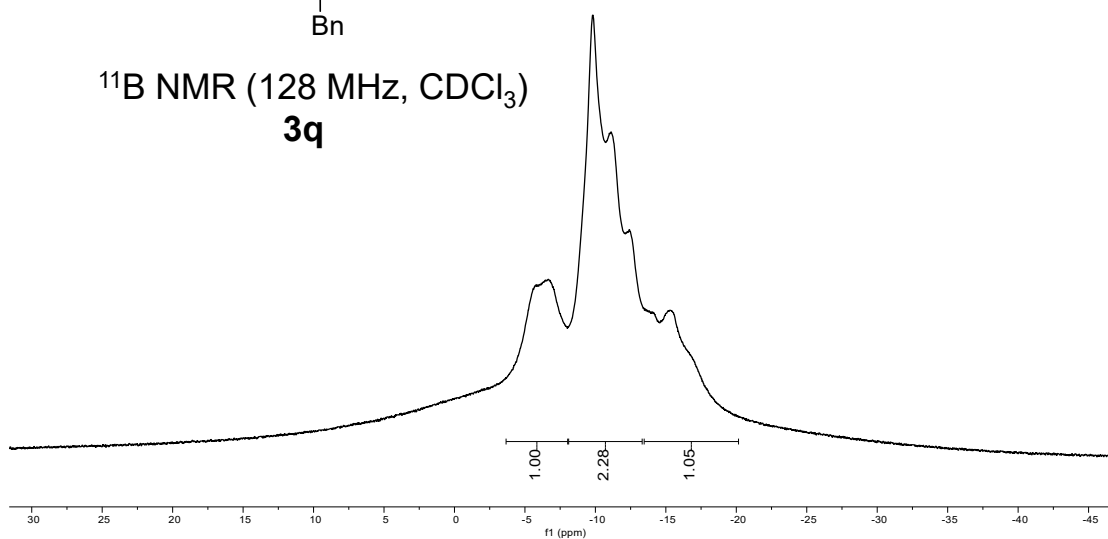
— -6.34
 — -9.99
 — -11.88
 — -14.98

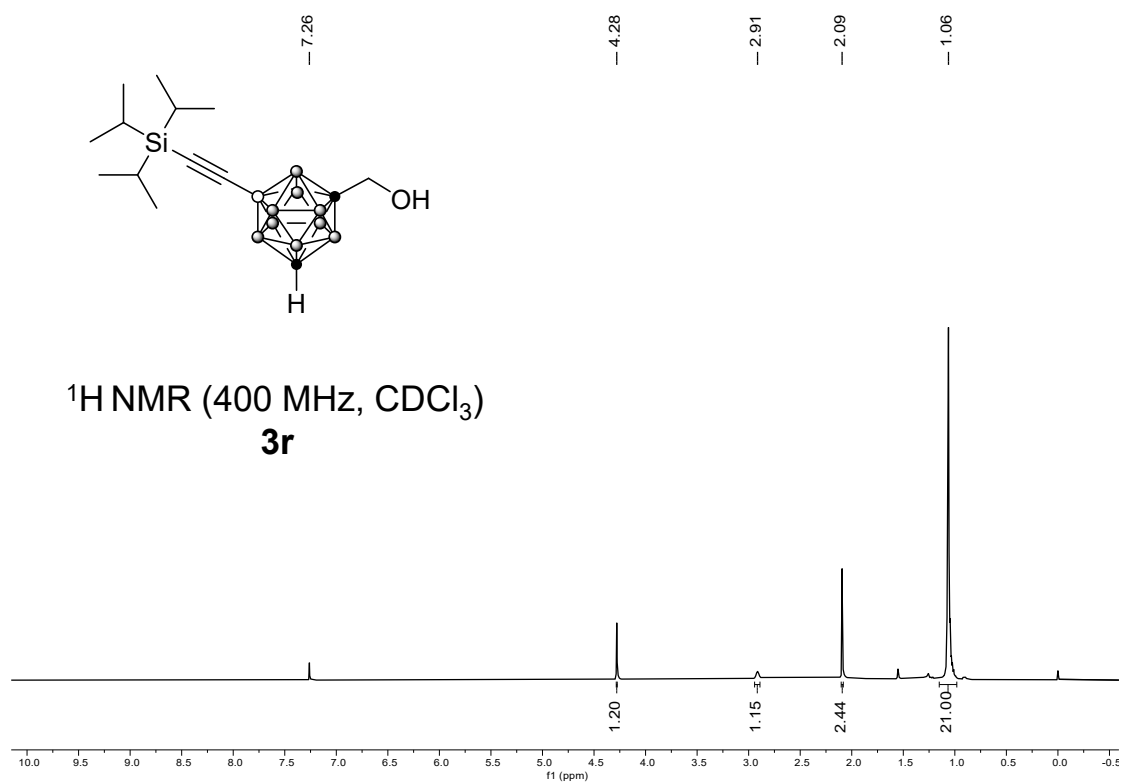
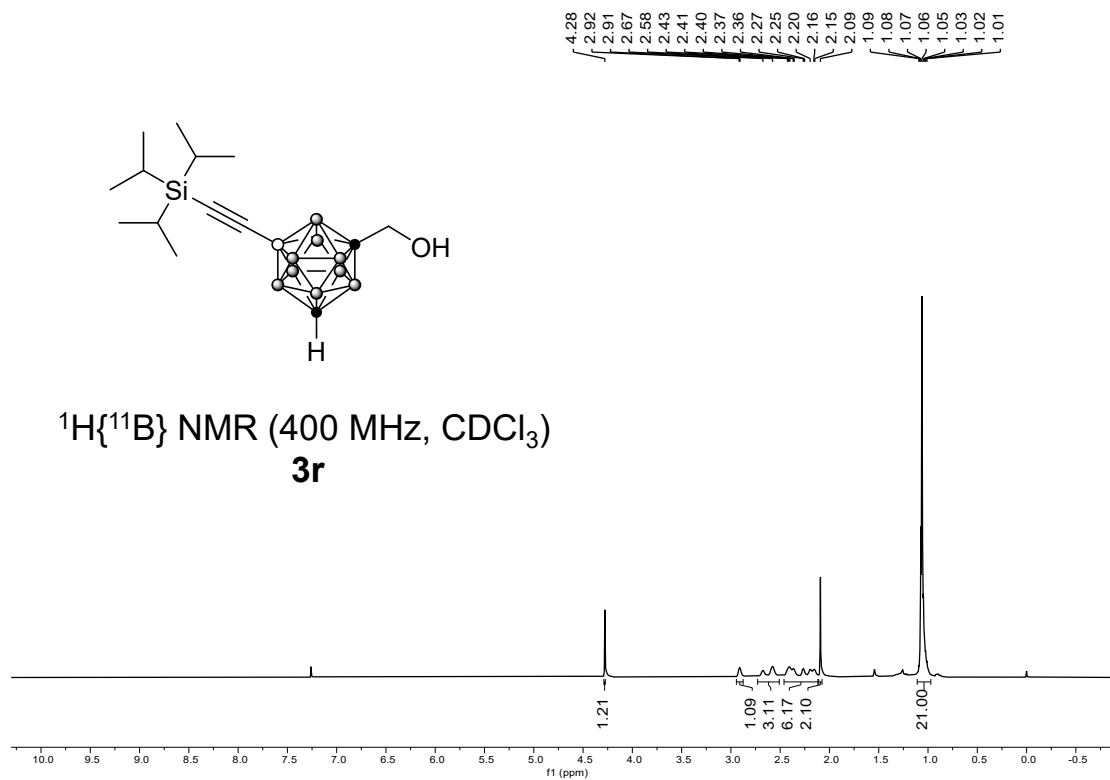
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)
3q

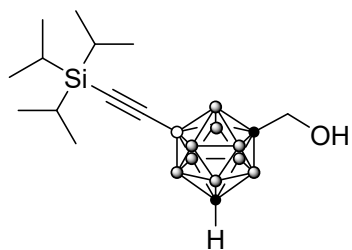


— -6.51
 / -9.81
 / -11.14
 / -11.39
 / -12.53
 / -15.38
 / -15.54

^{11}B NMR (128 MHz, CDCl_3)
3q



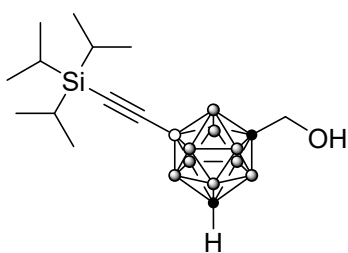
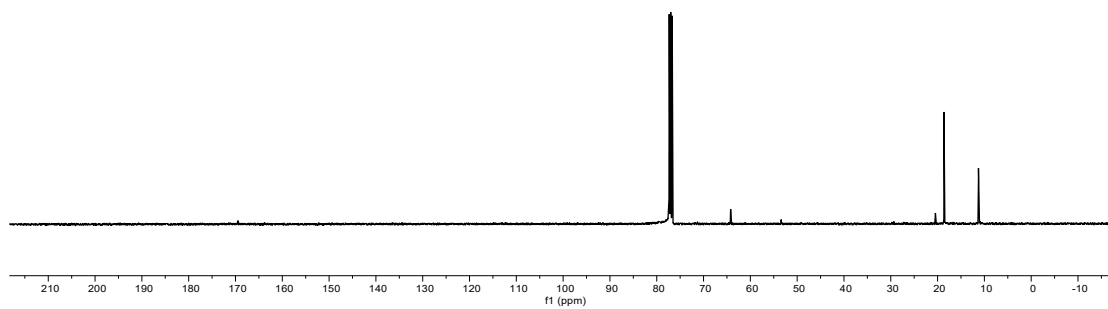




-64.21

-20.46
-18.62
-11.26

^{13}C NMR (101 MHz, CDCl_3)
3r



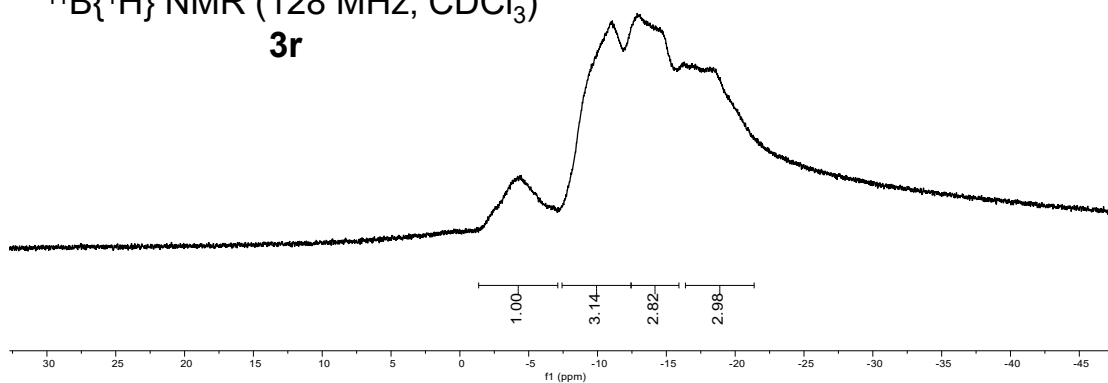
-4.30

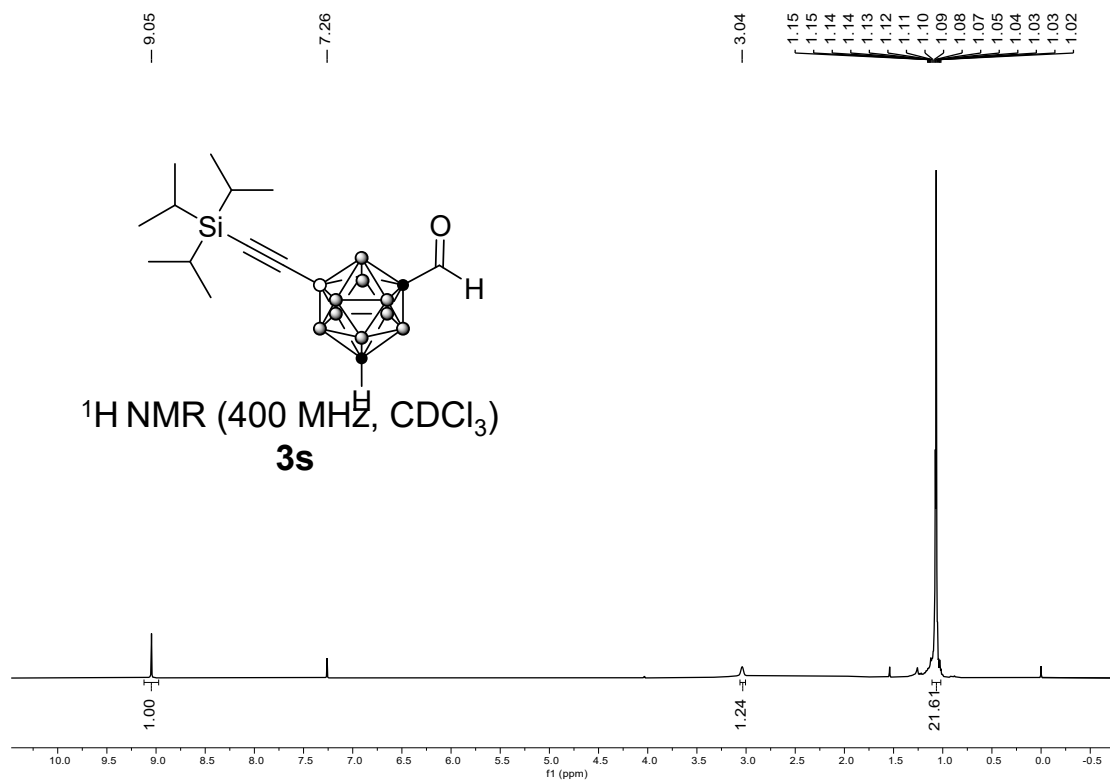
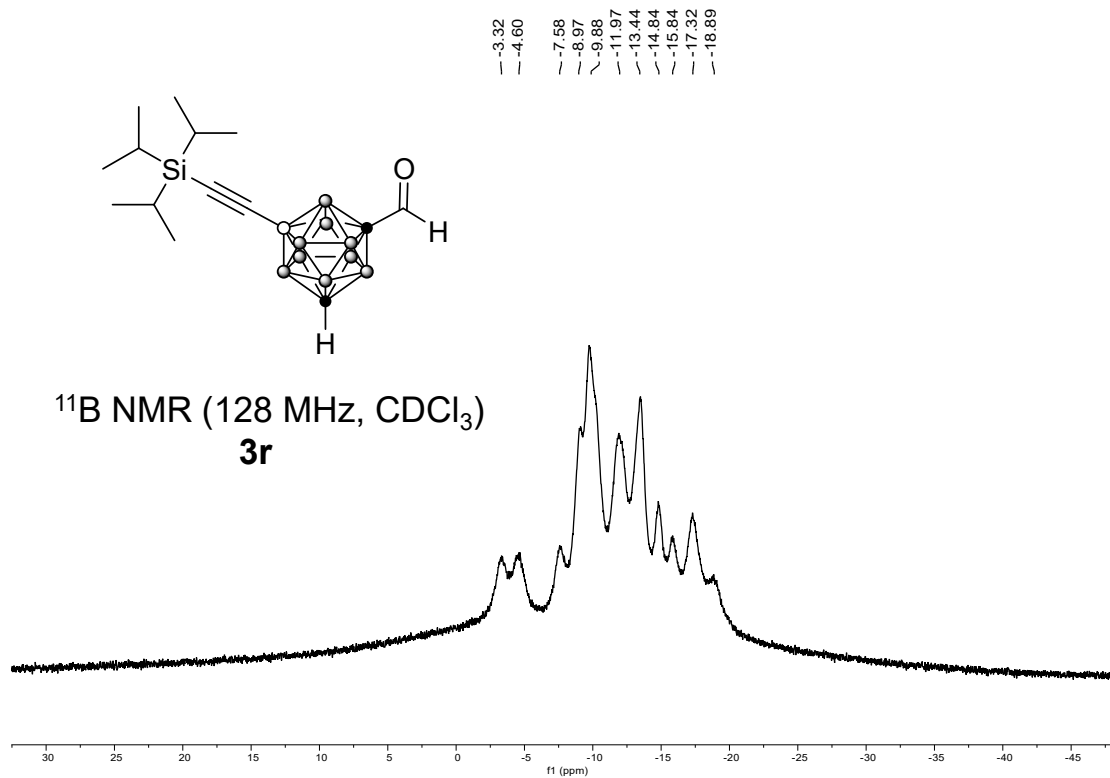
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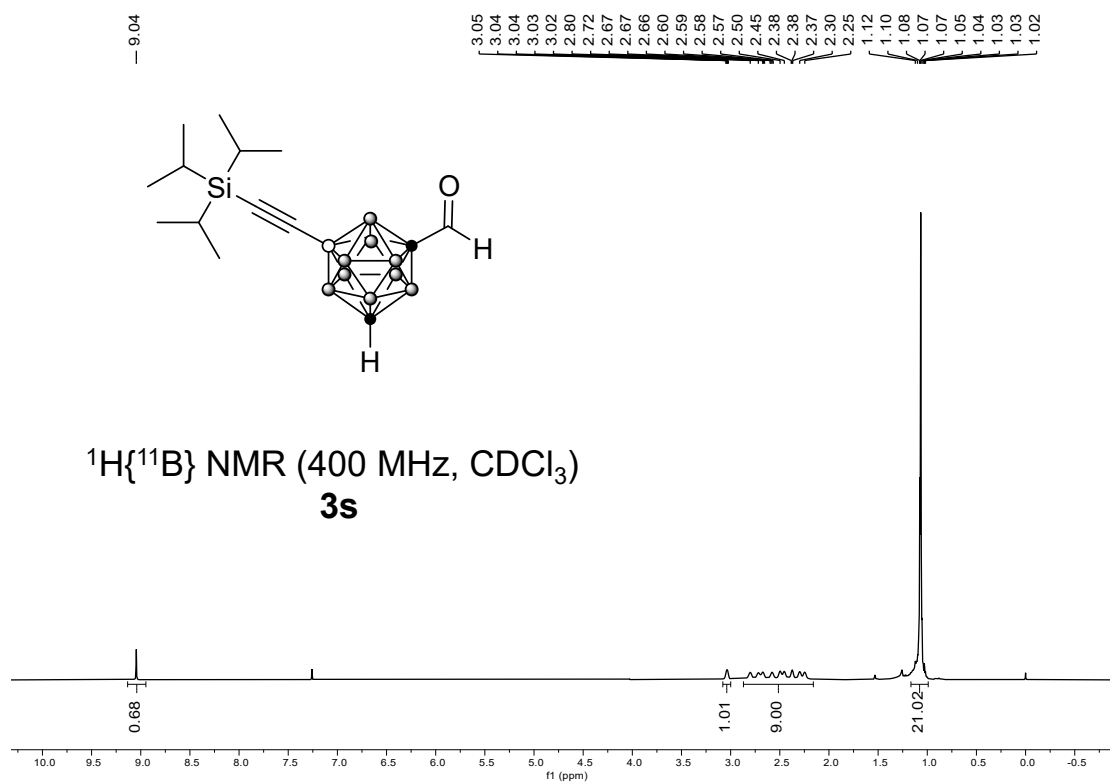
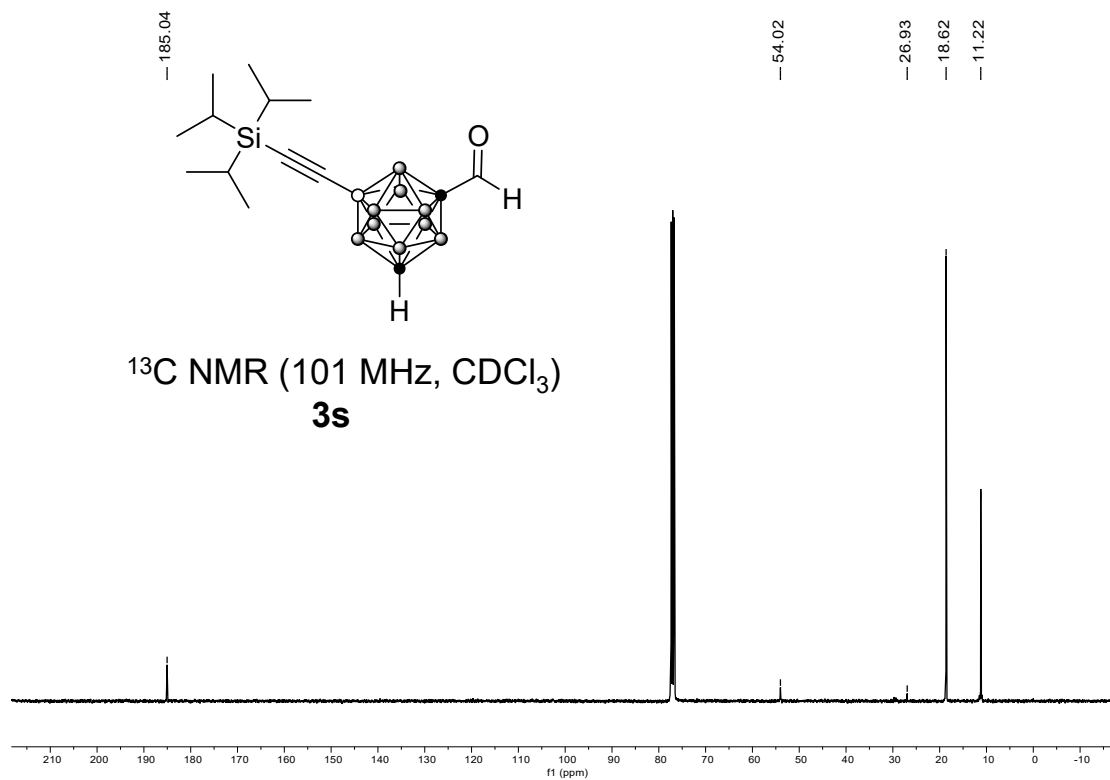
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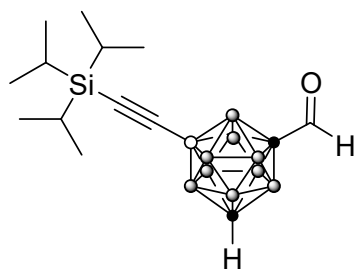
-21.86

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)
3r



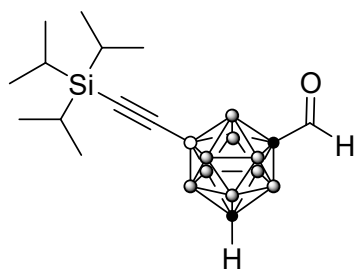
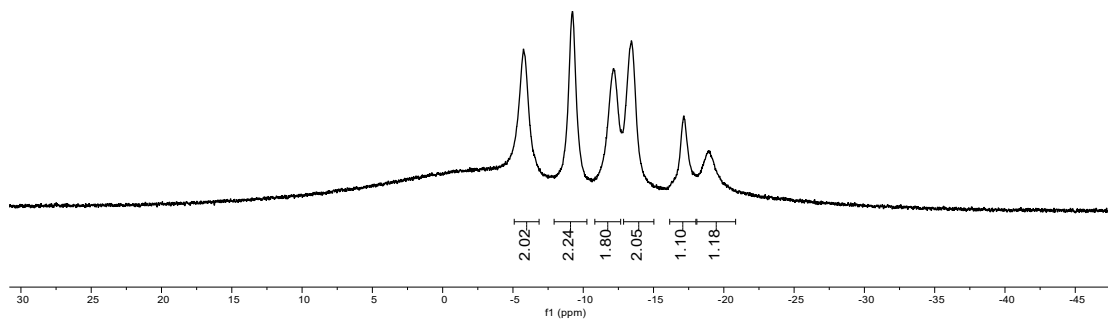






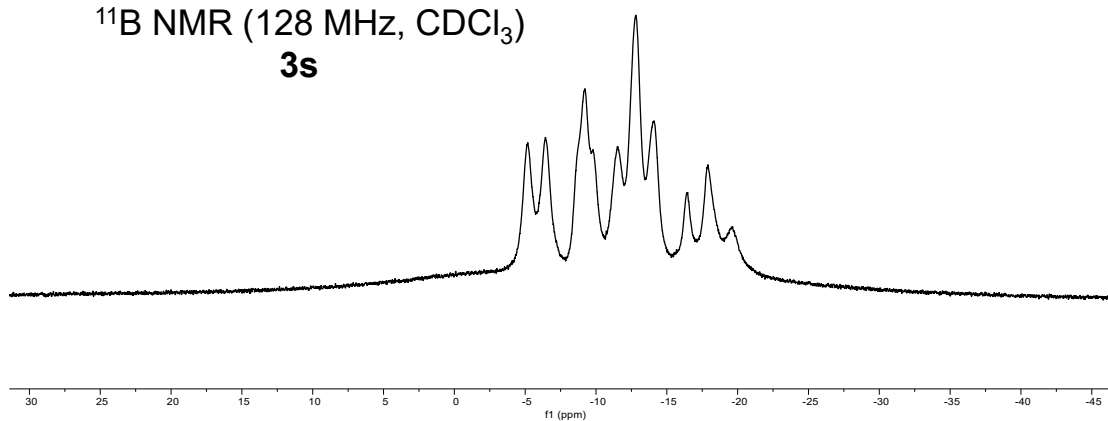
-5.77
 -9.23
 -12.14
 -13.43
 -17.13
 -17.18
 -18.94

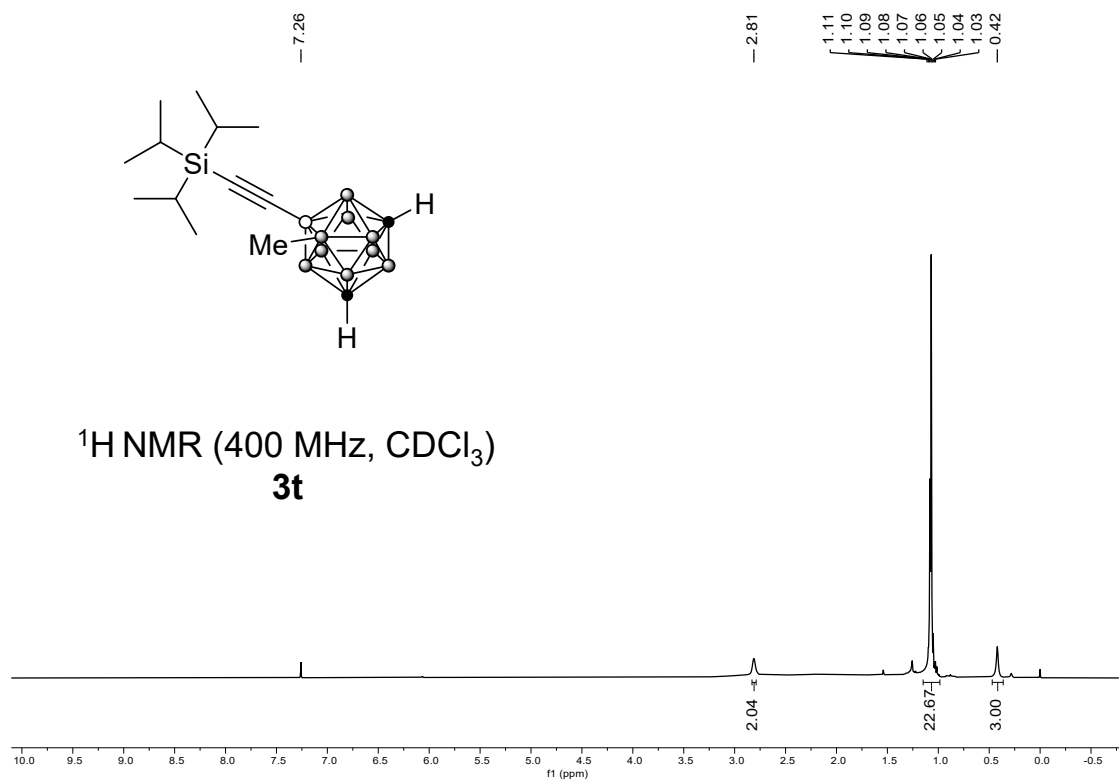
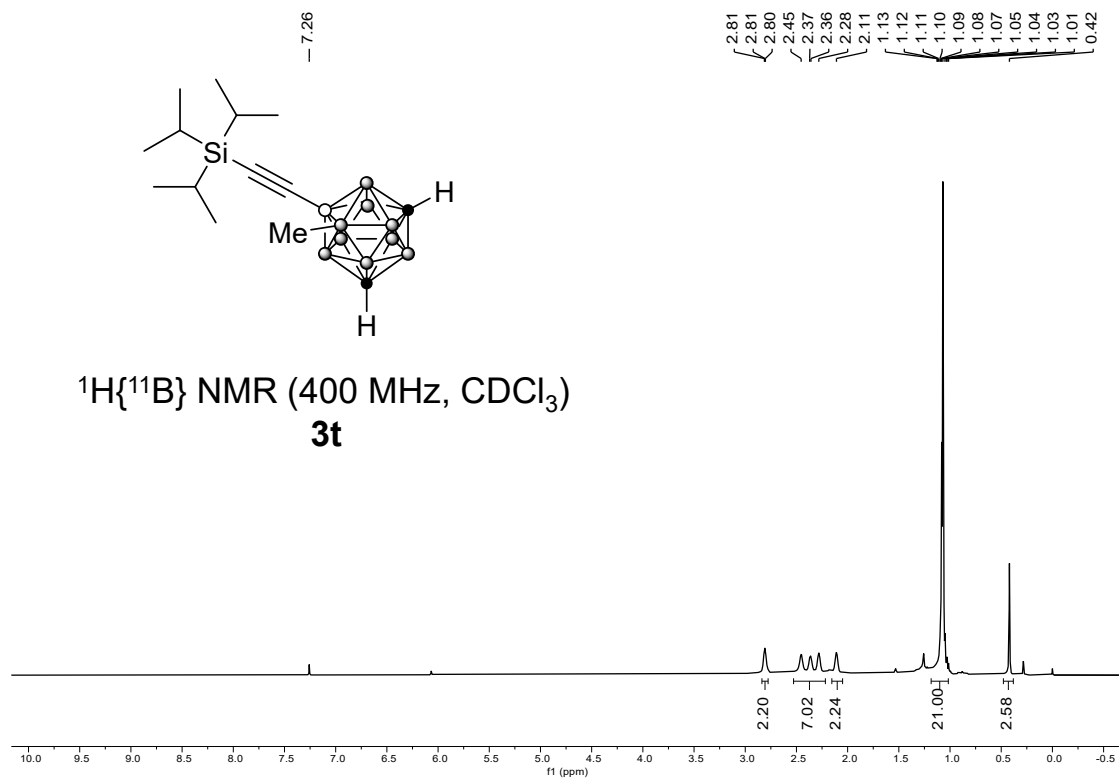
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)
3s

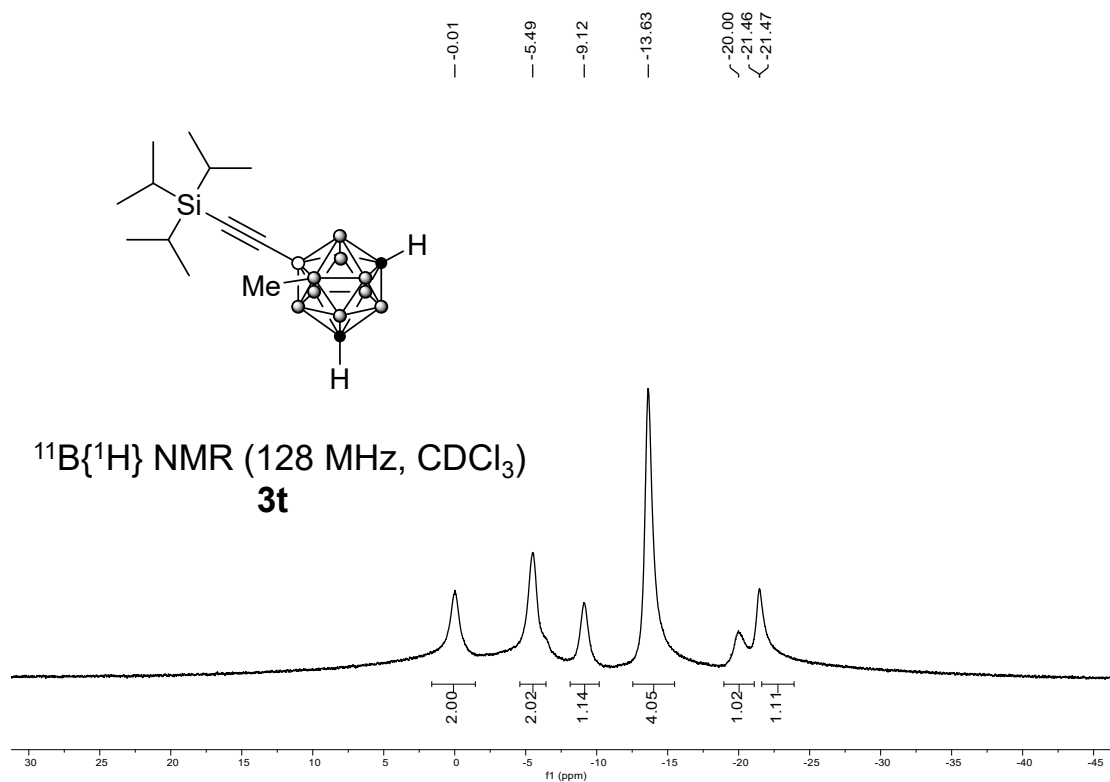
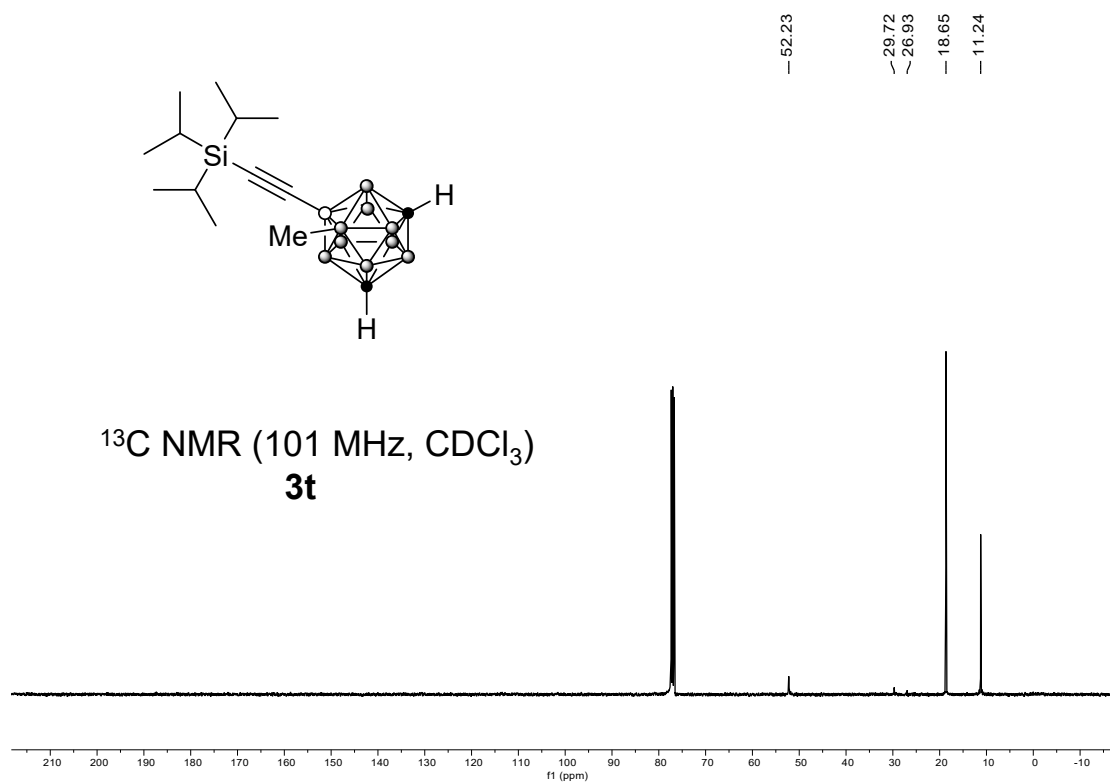


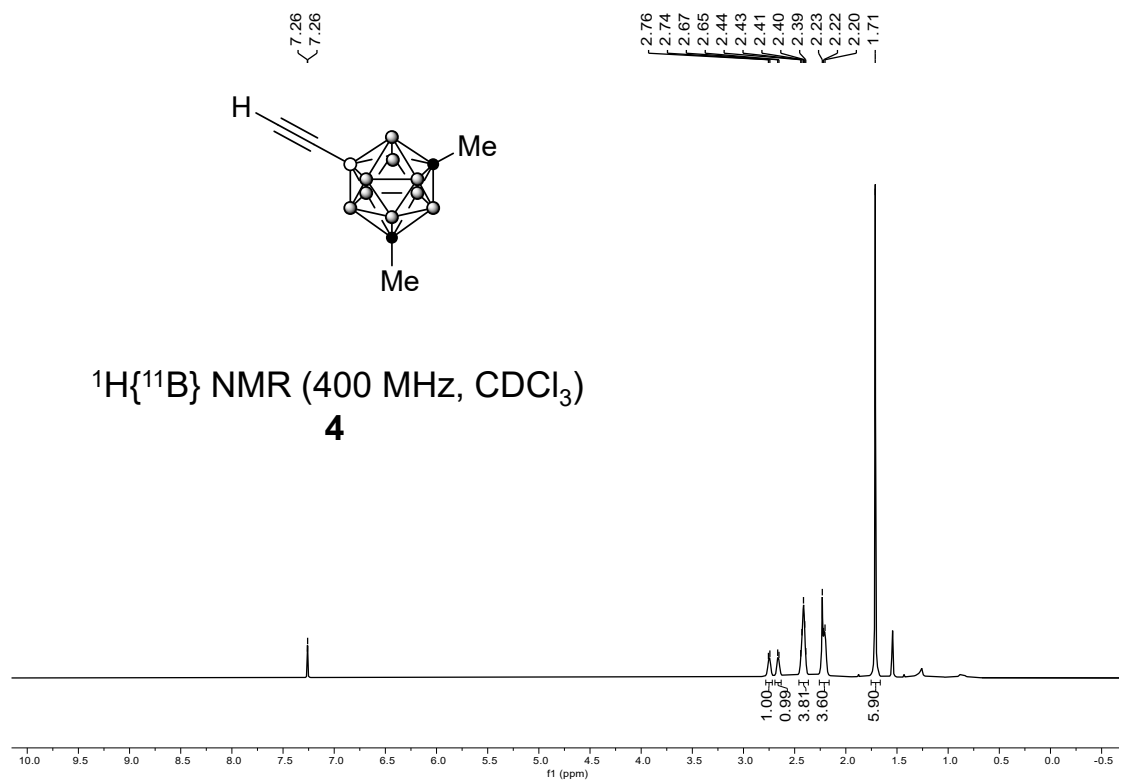
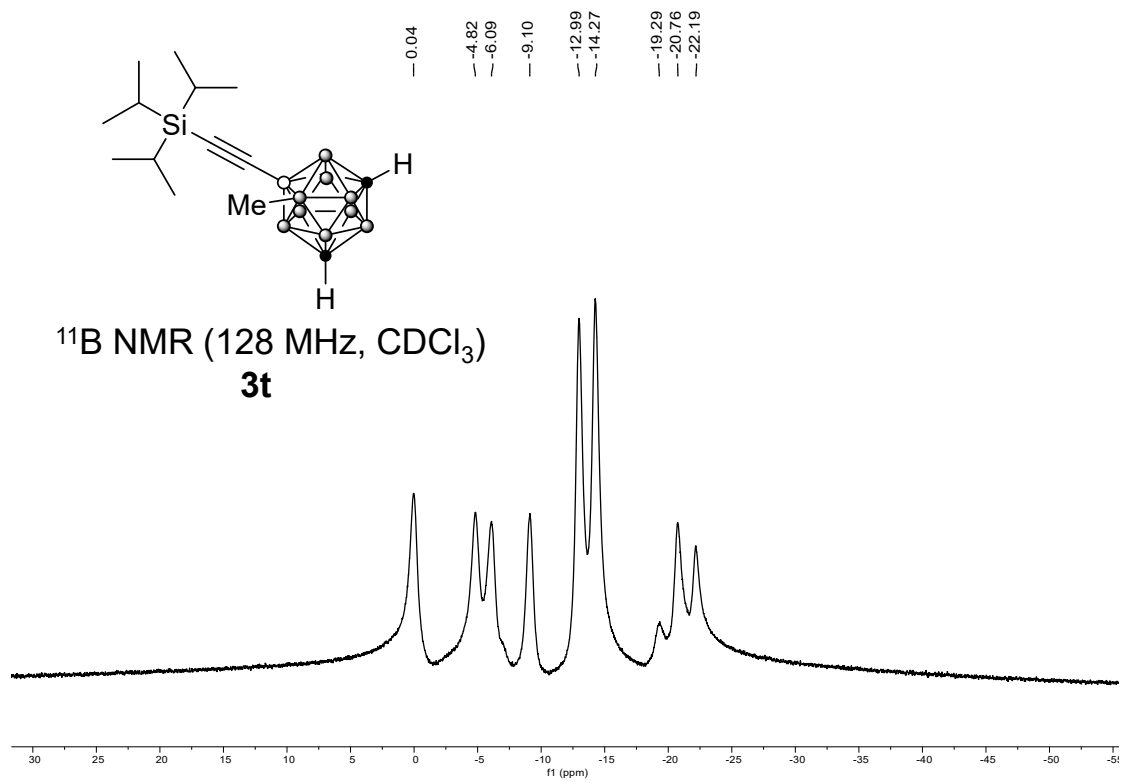
-5.16
 -6.45
 -8.67
 -9.23
 -9.89
 -11.49
 -12.79
 -14.09
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 -17.94
 -19.61

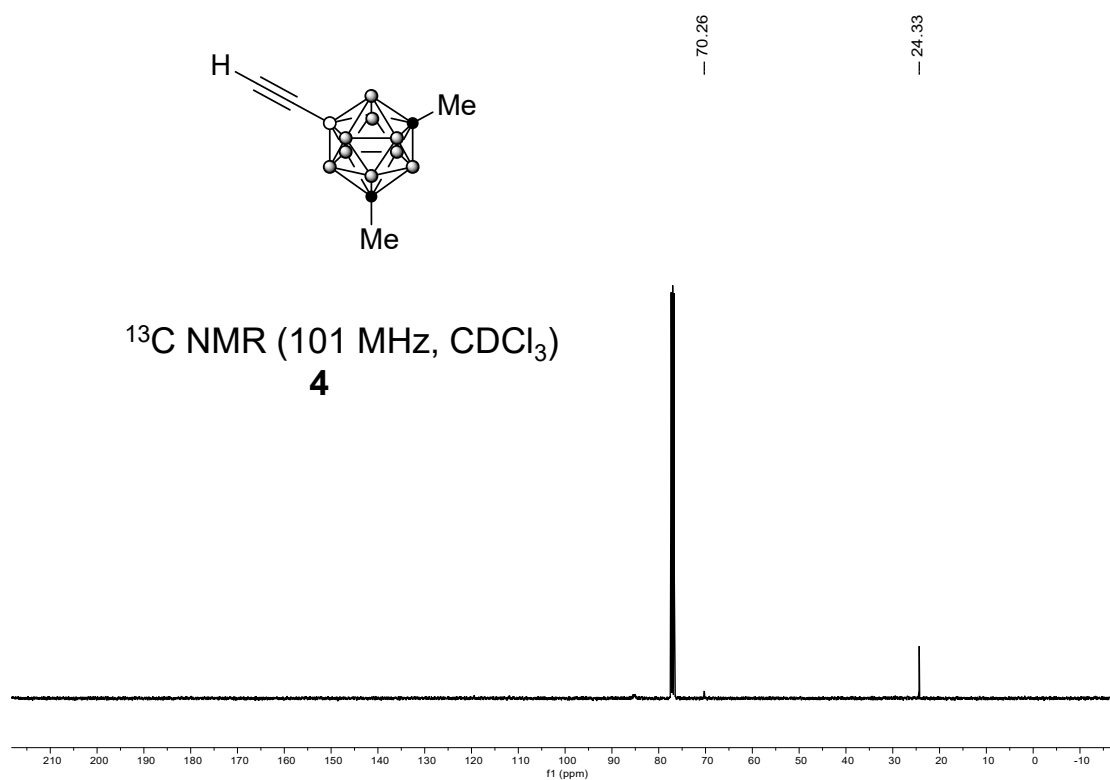
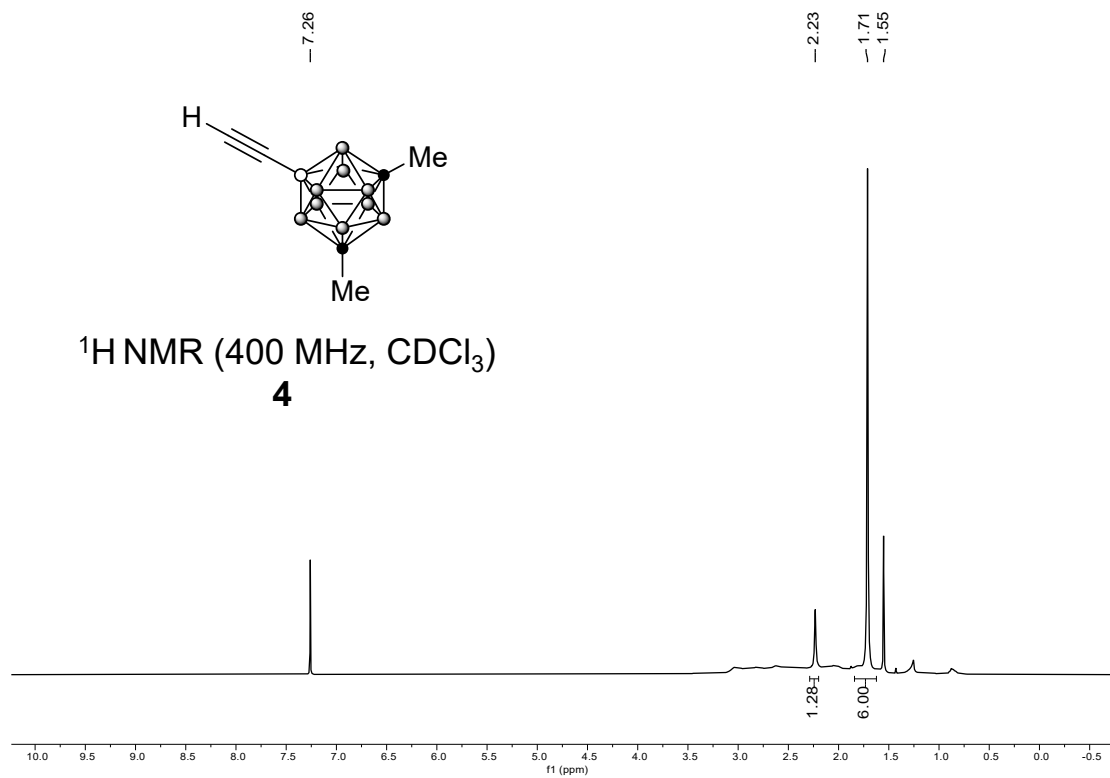
^{11}B NMR (128 MHz, CDCl_3)
3s

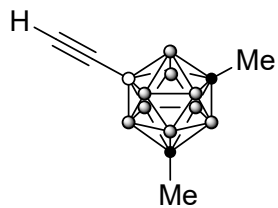








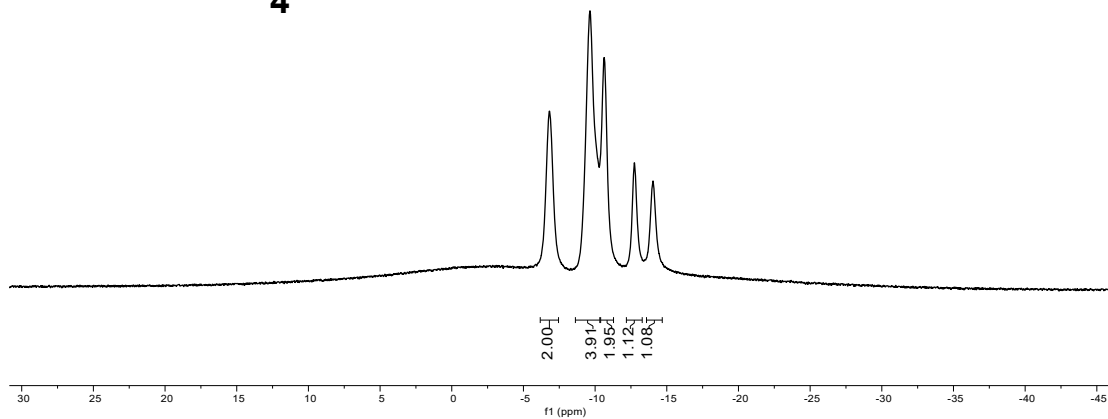




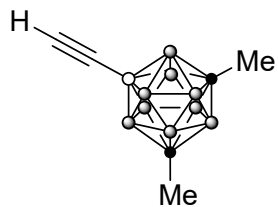
-6.82
 -9.63
 -10.12
 -10.64
 -12.75
 -14.04

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)

4

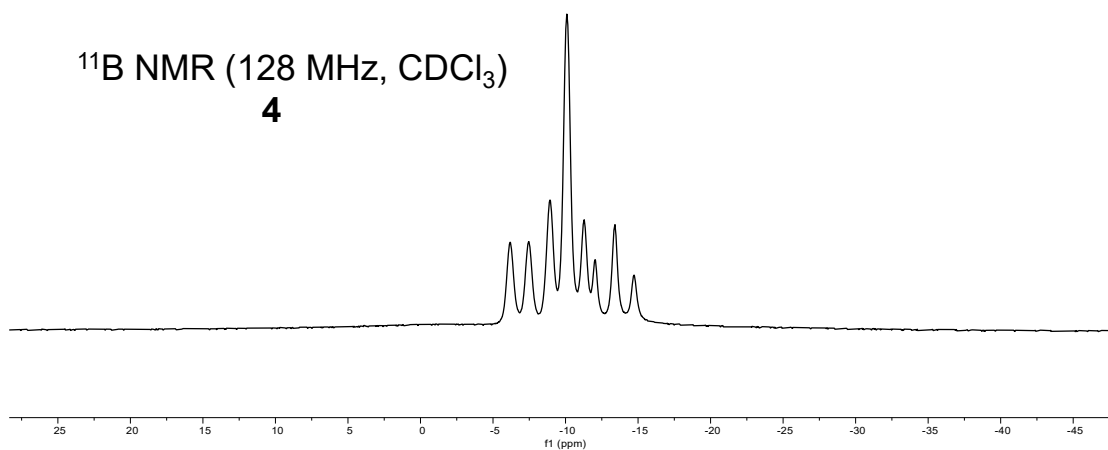


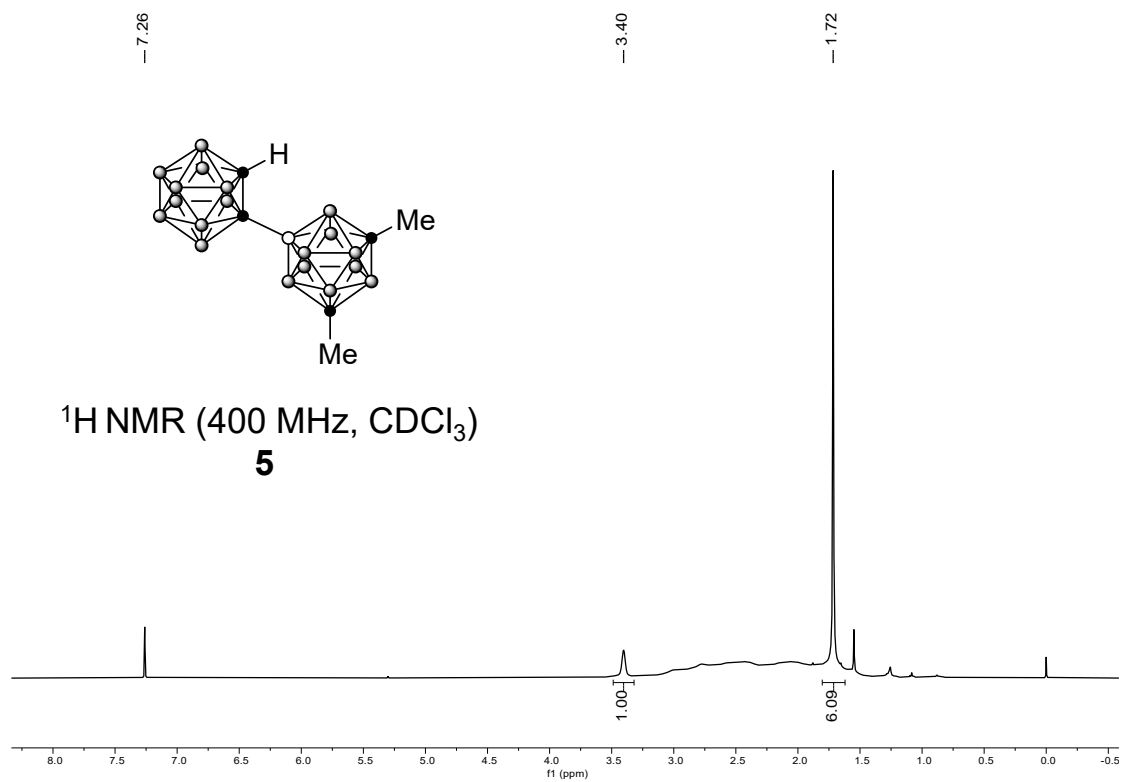
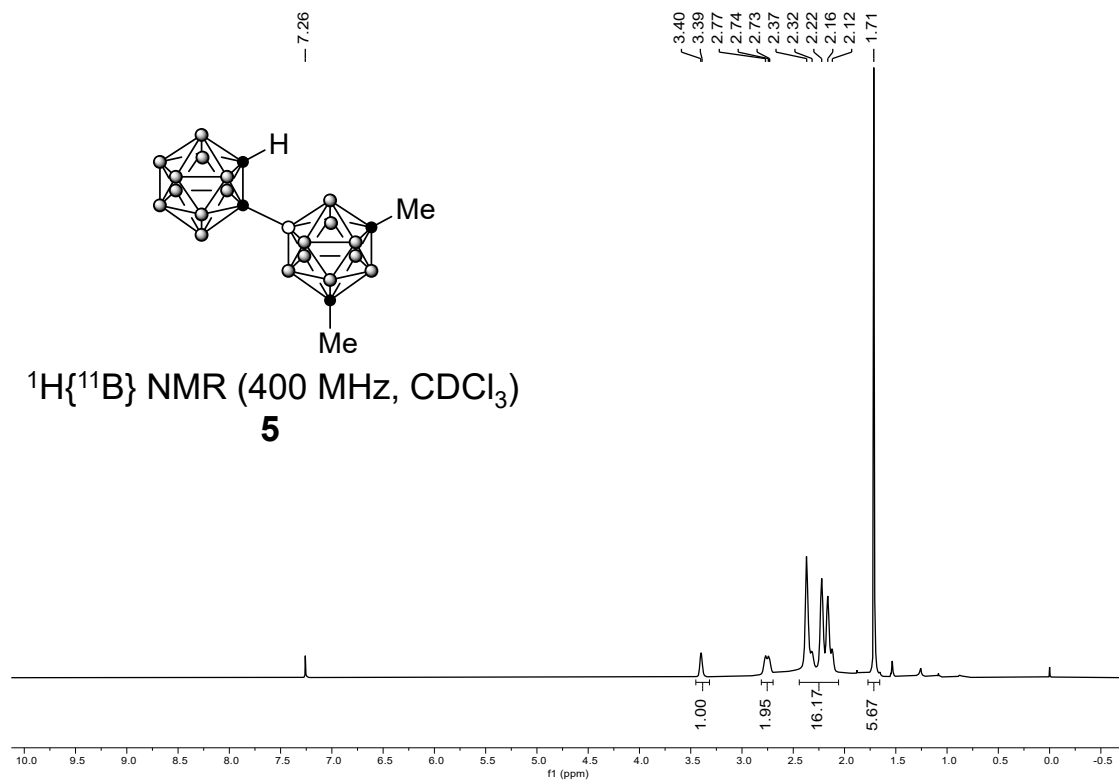
-6.18
 -7.46
 -8.92
 -10.10
 -11.28
 -12.04
 -13.40
 -14.72

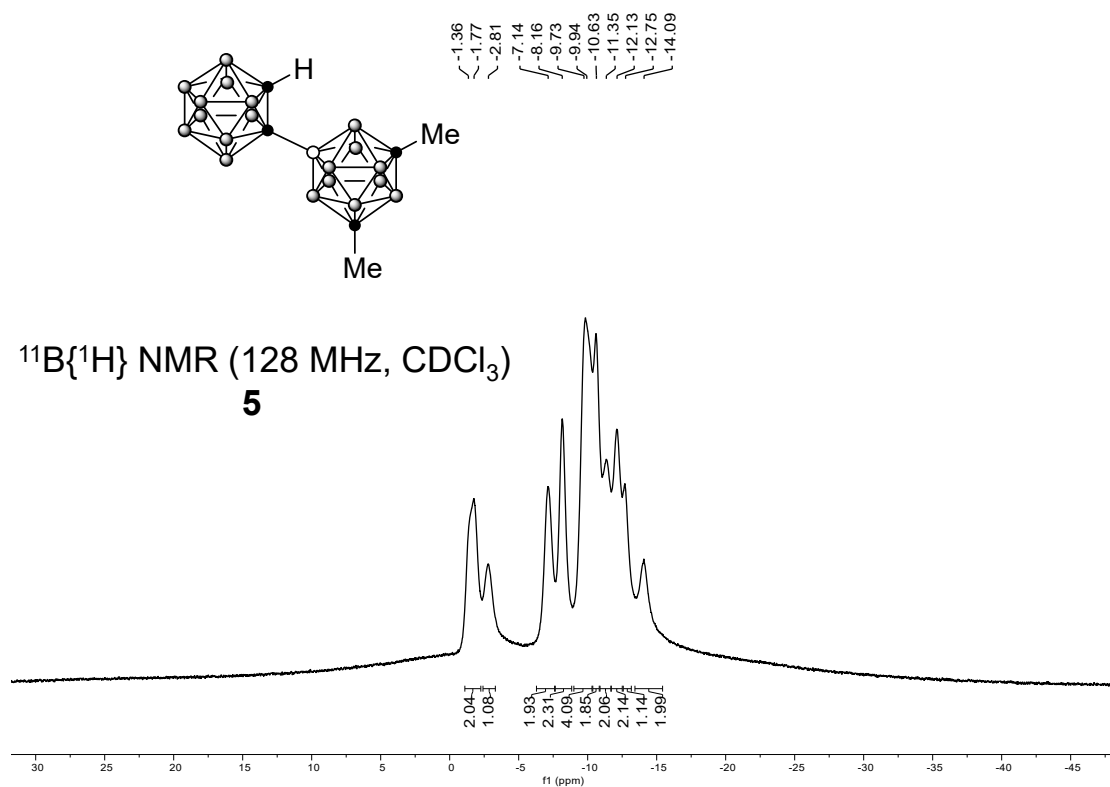
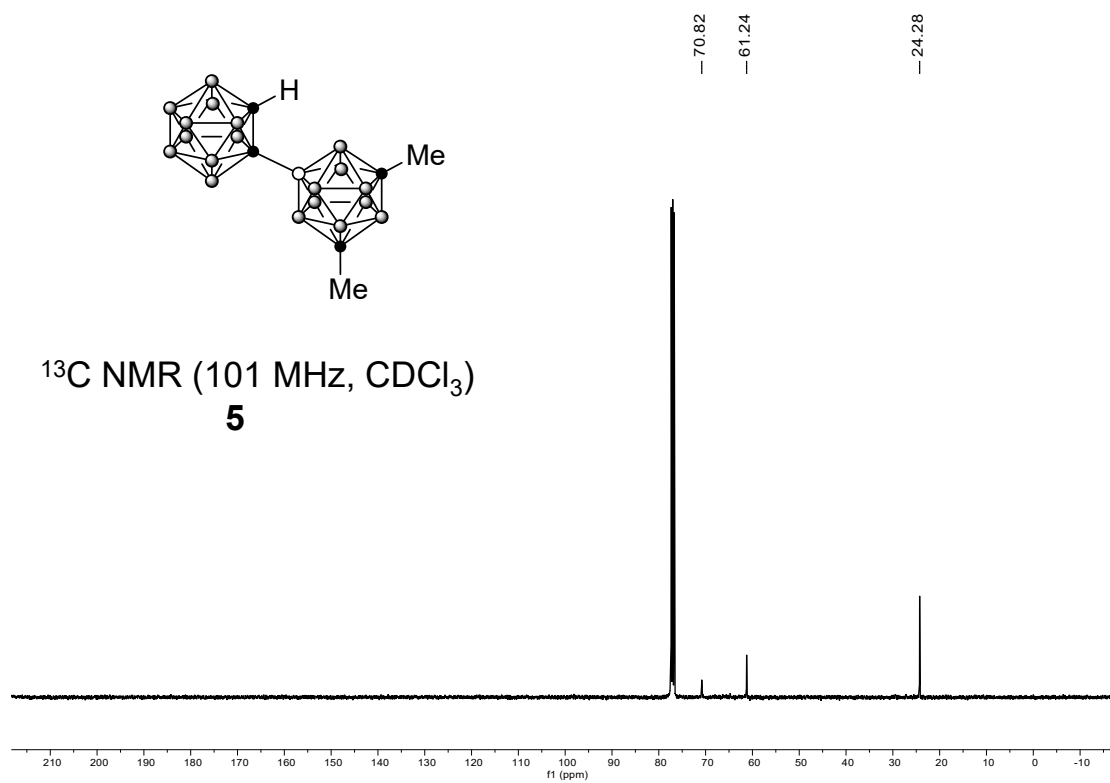


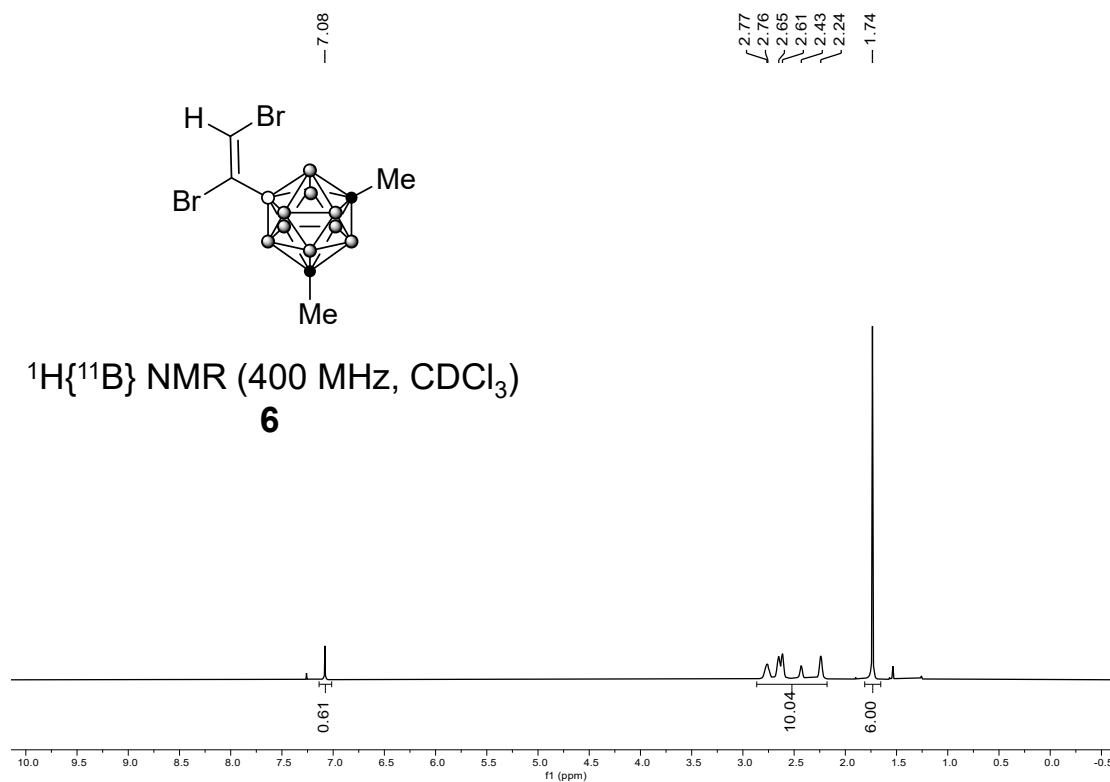
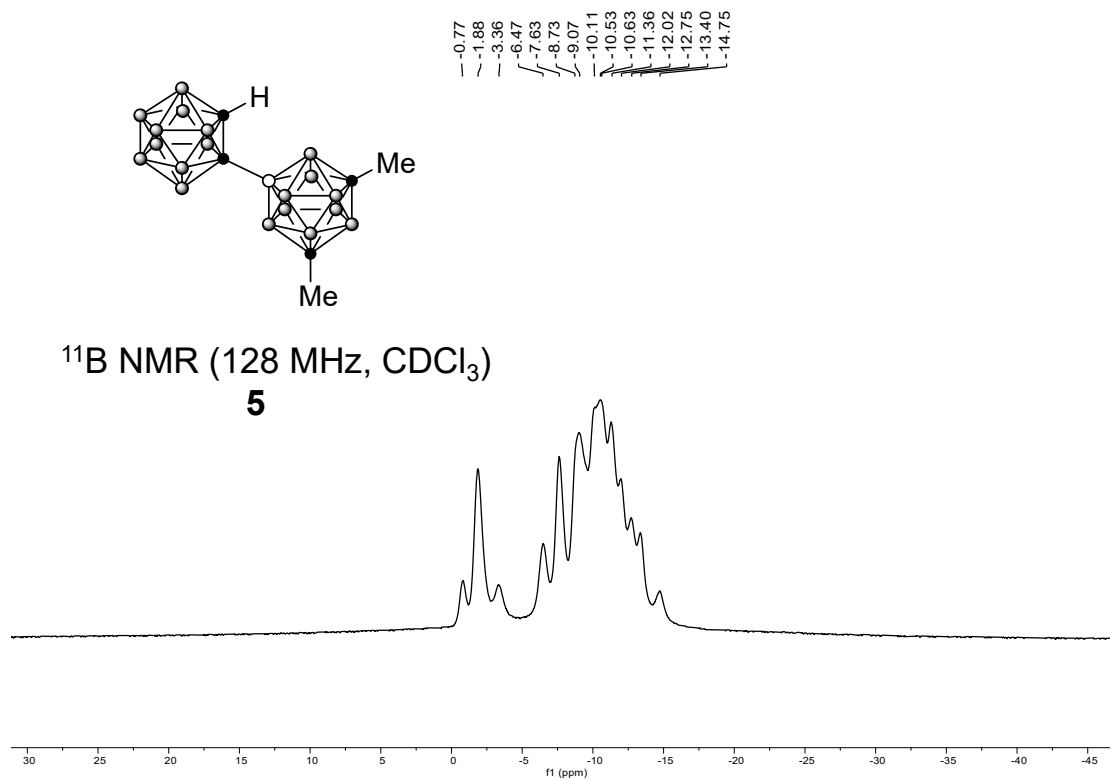
^{11}B NMR (128 MHz, CDCl_3)

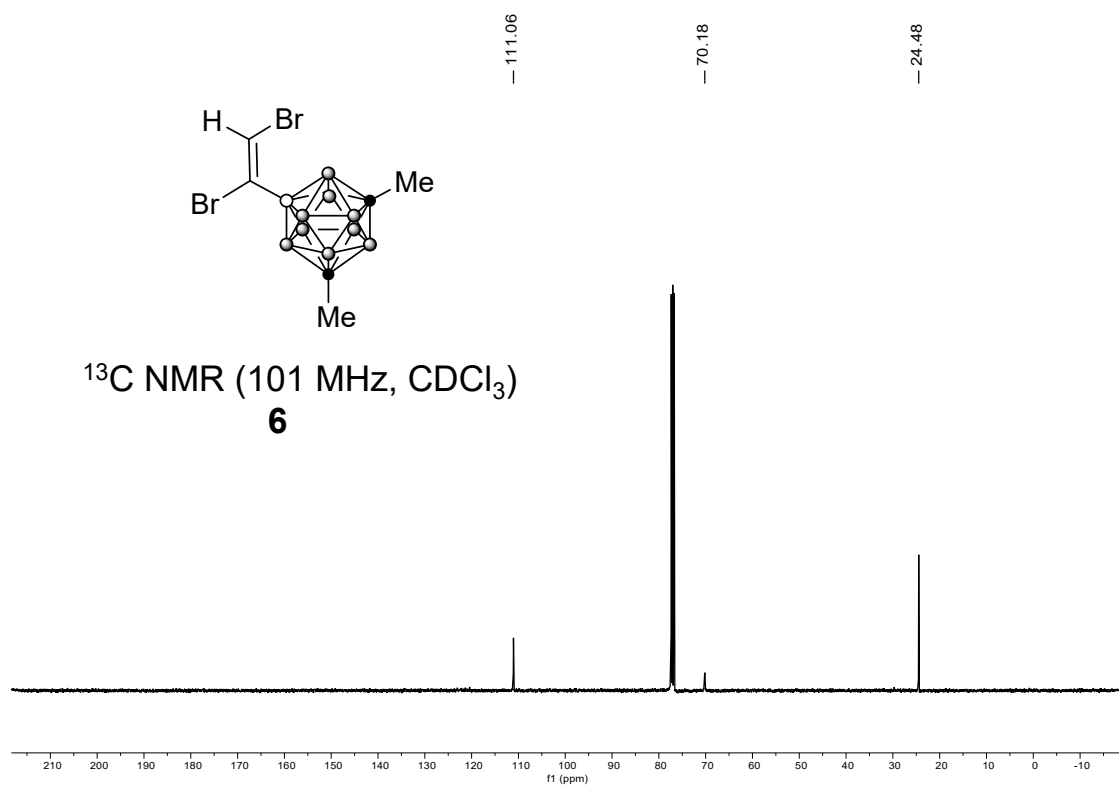
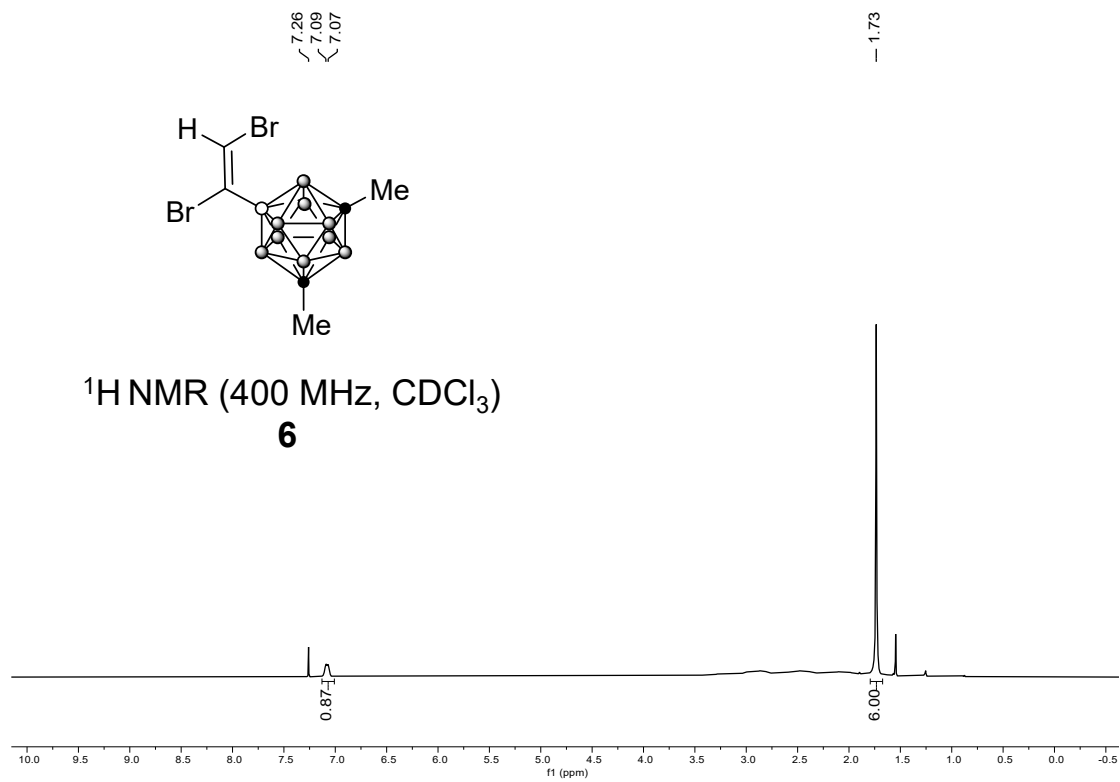
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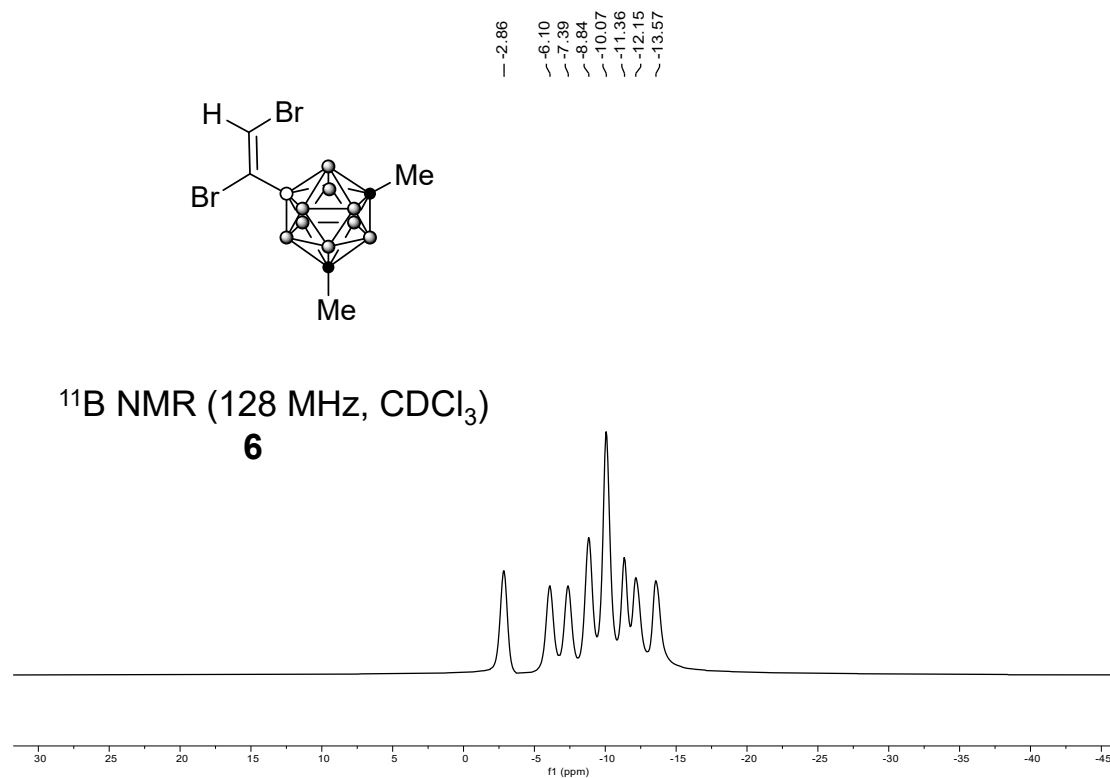
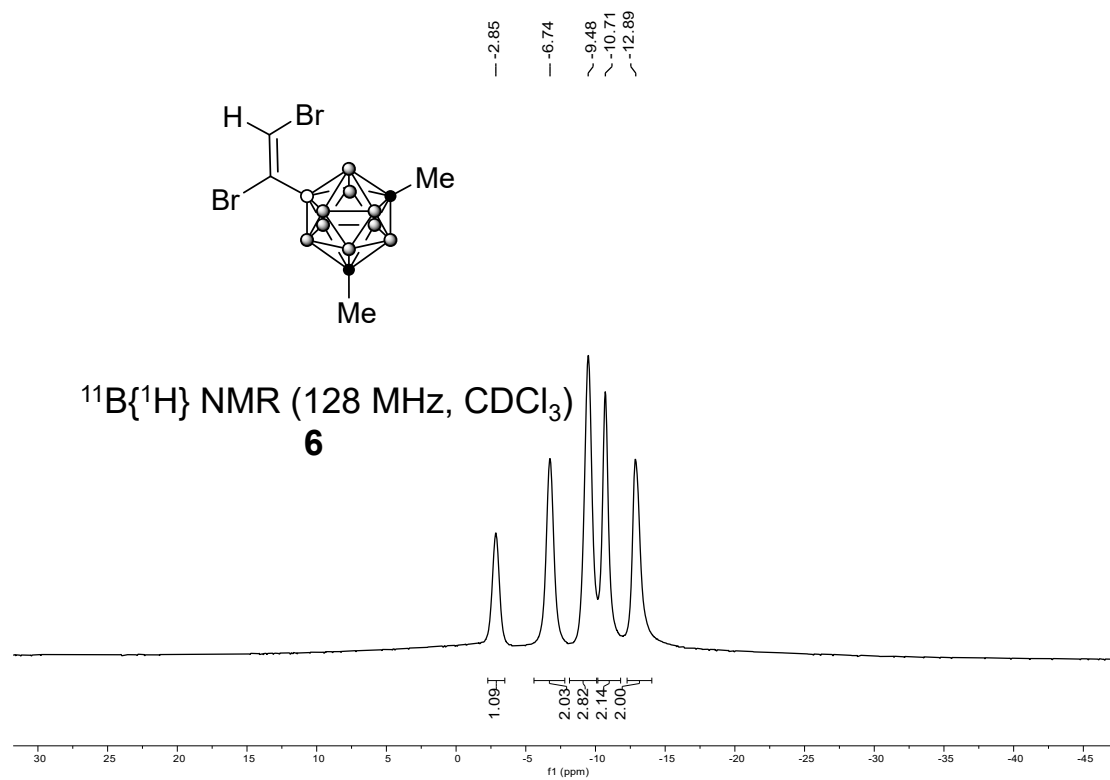


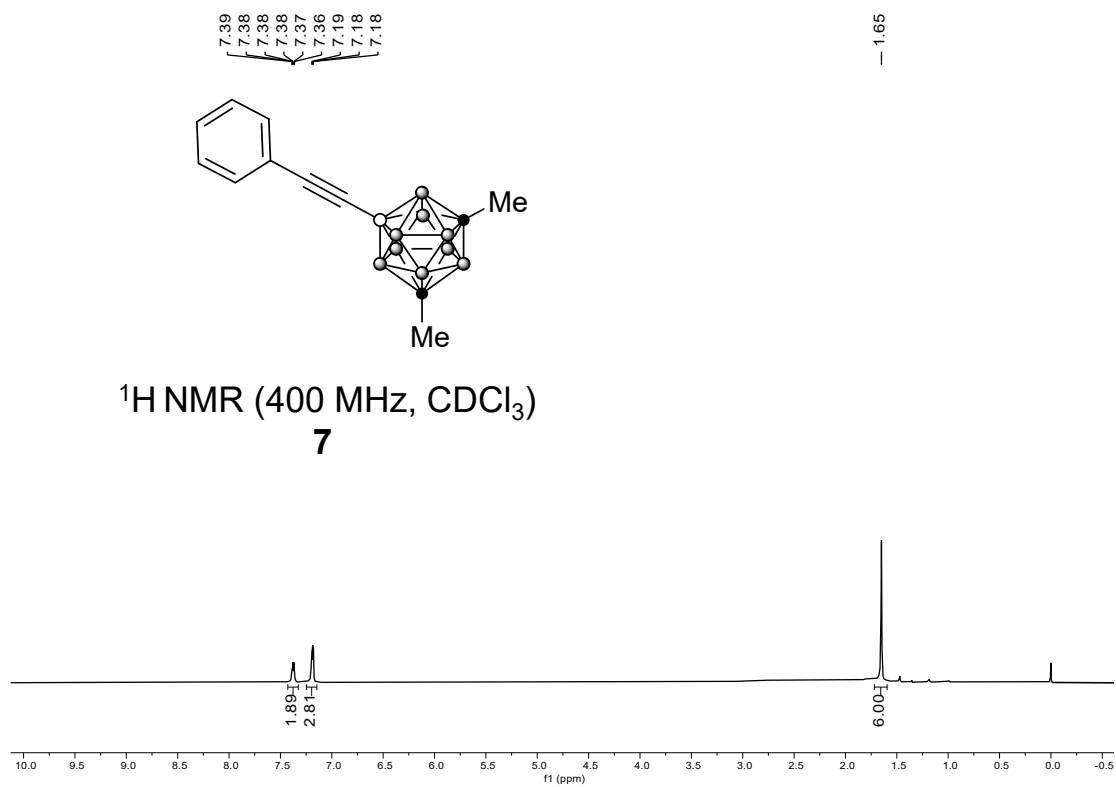
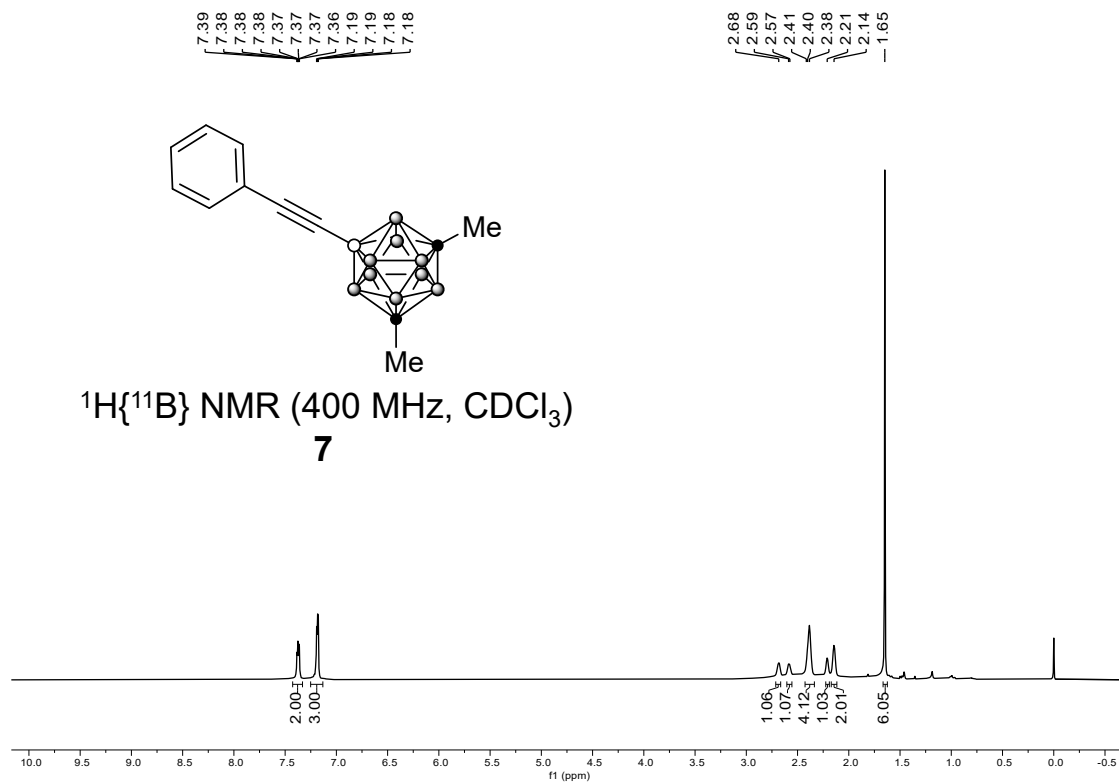


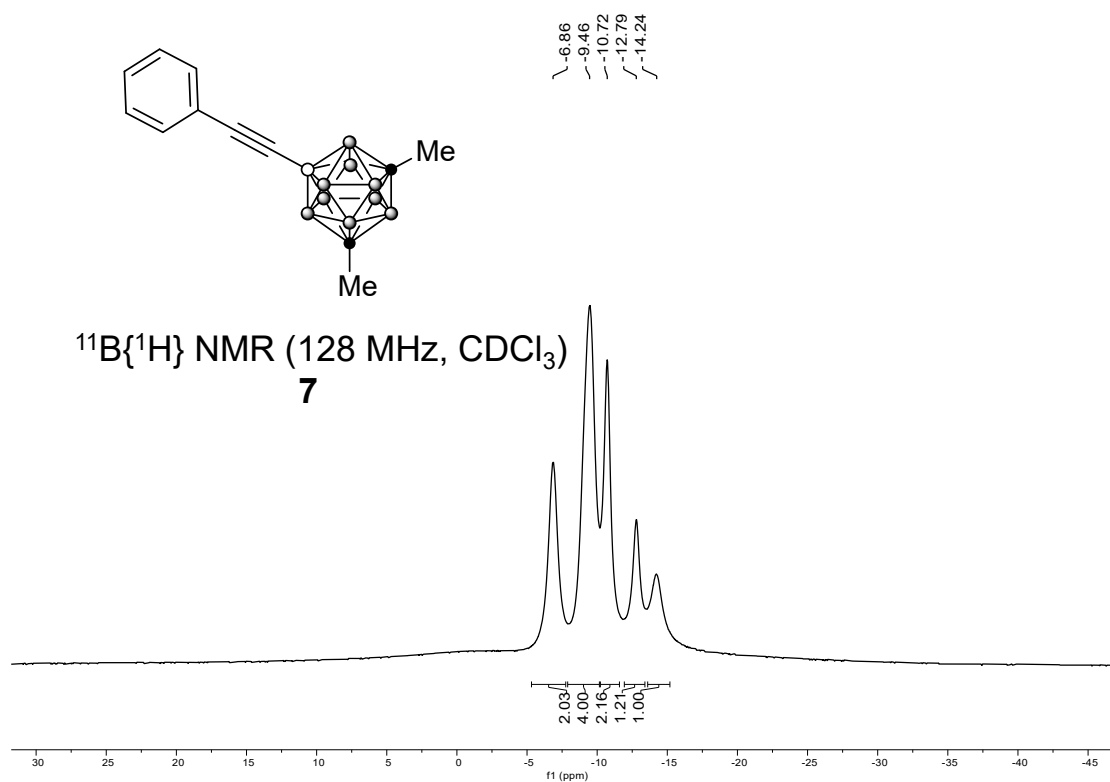
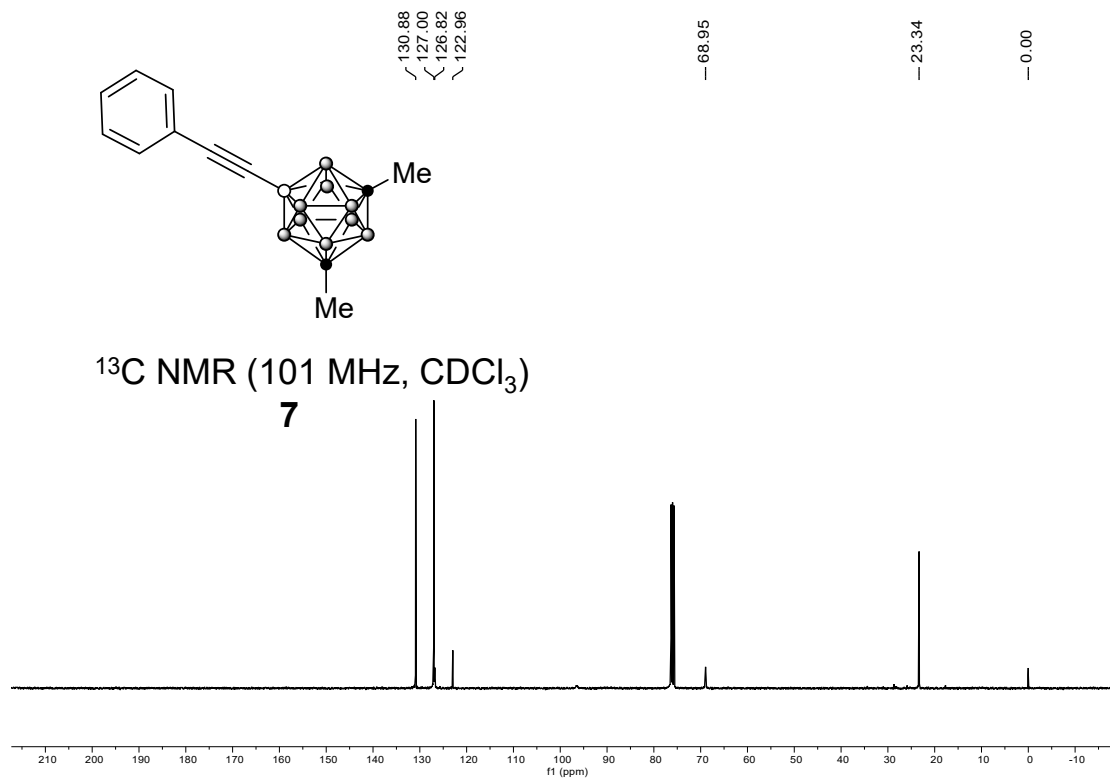


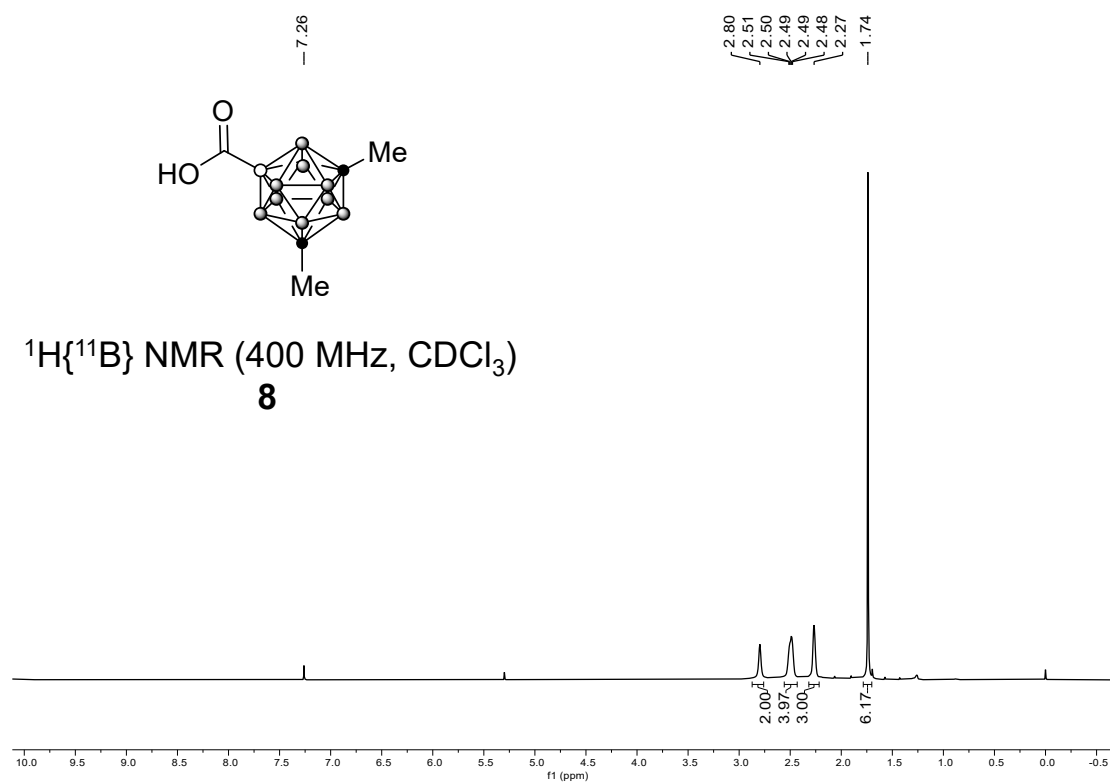
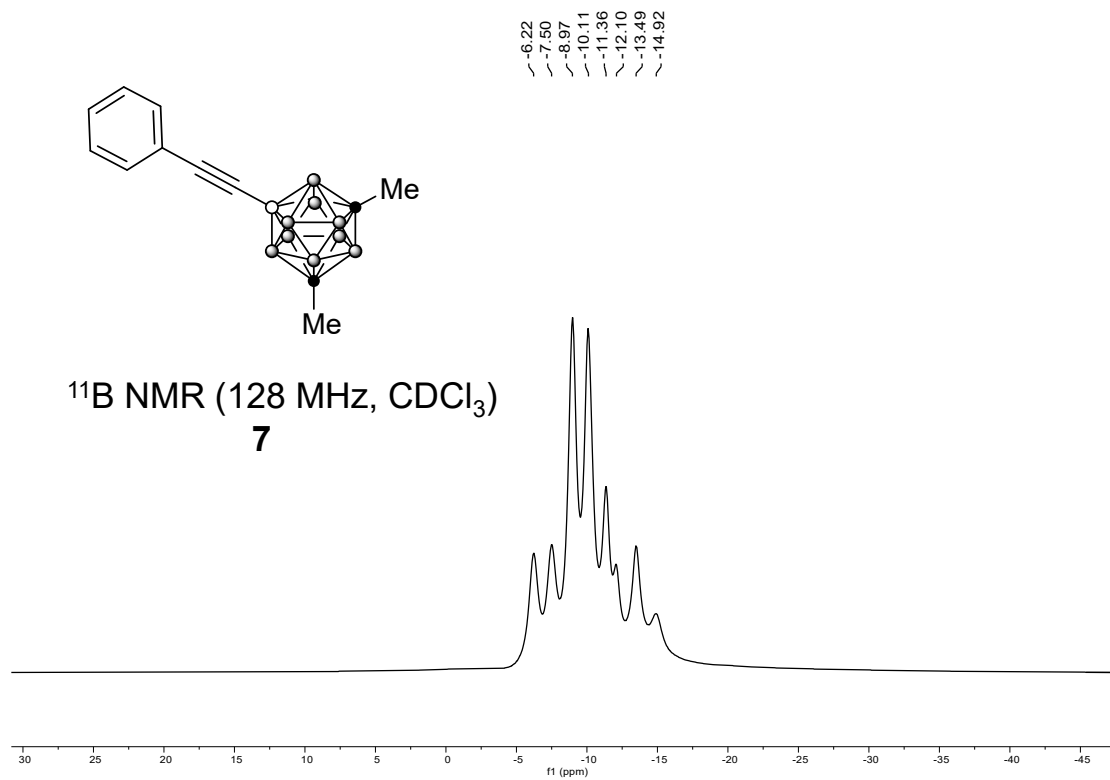


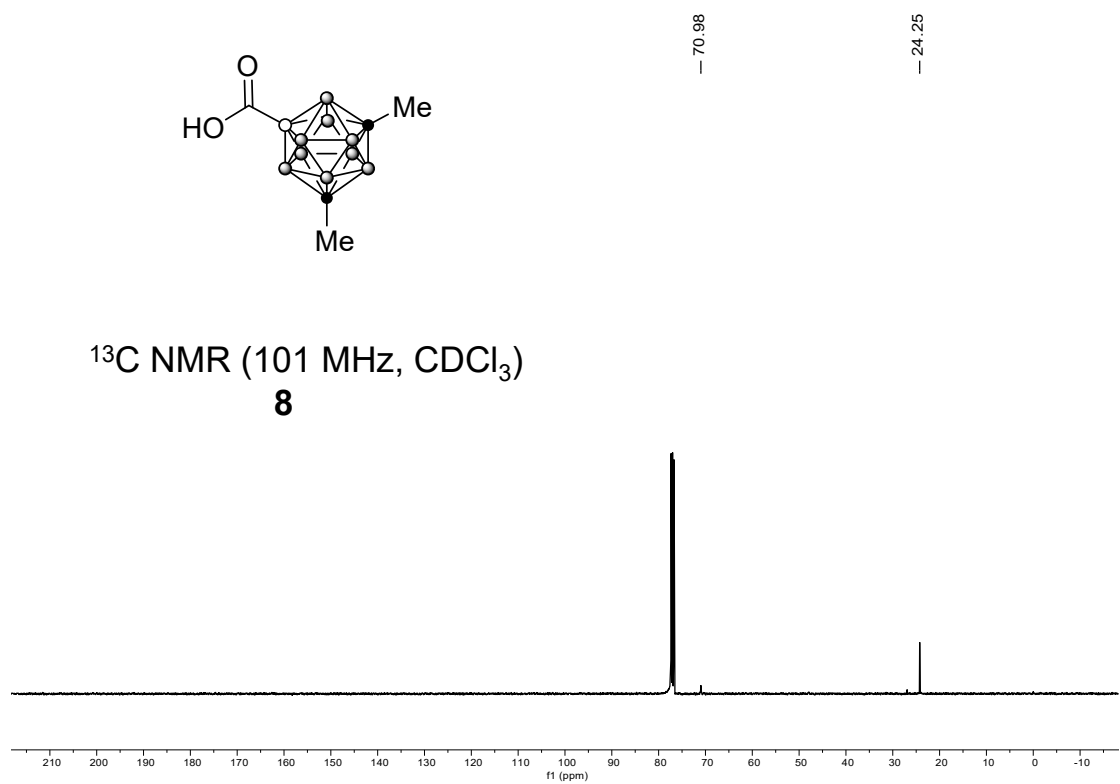
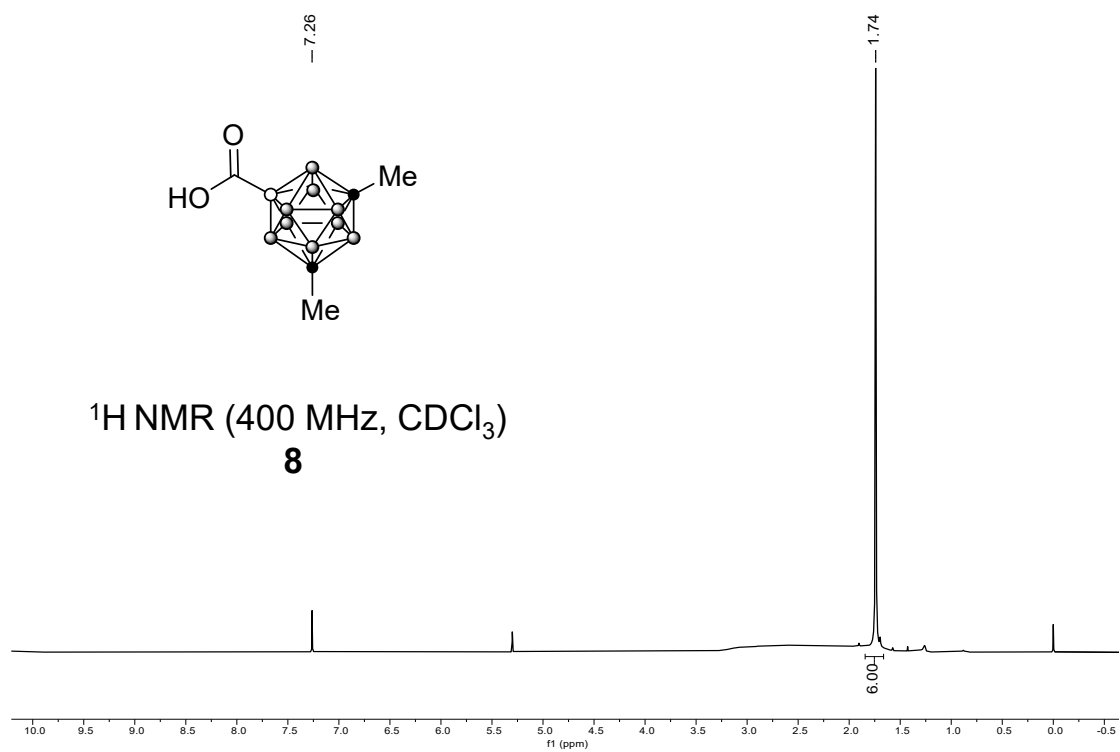


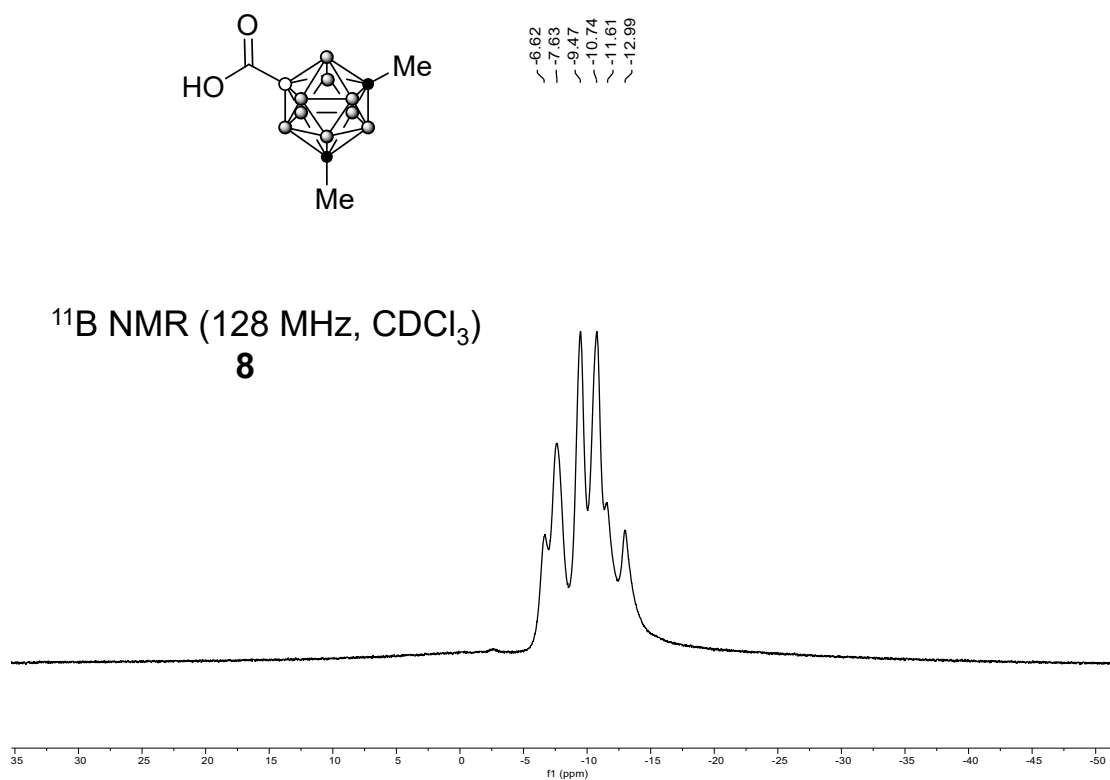
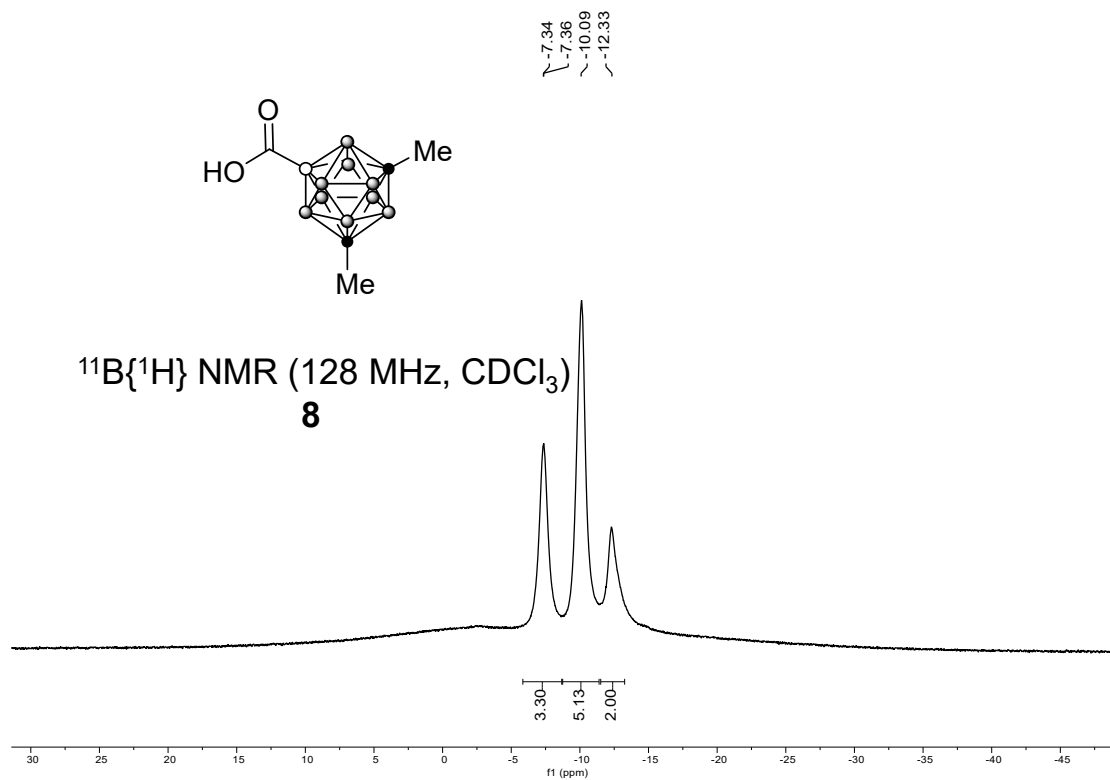


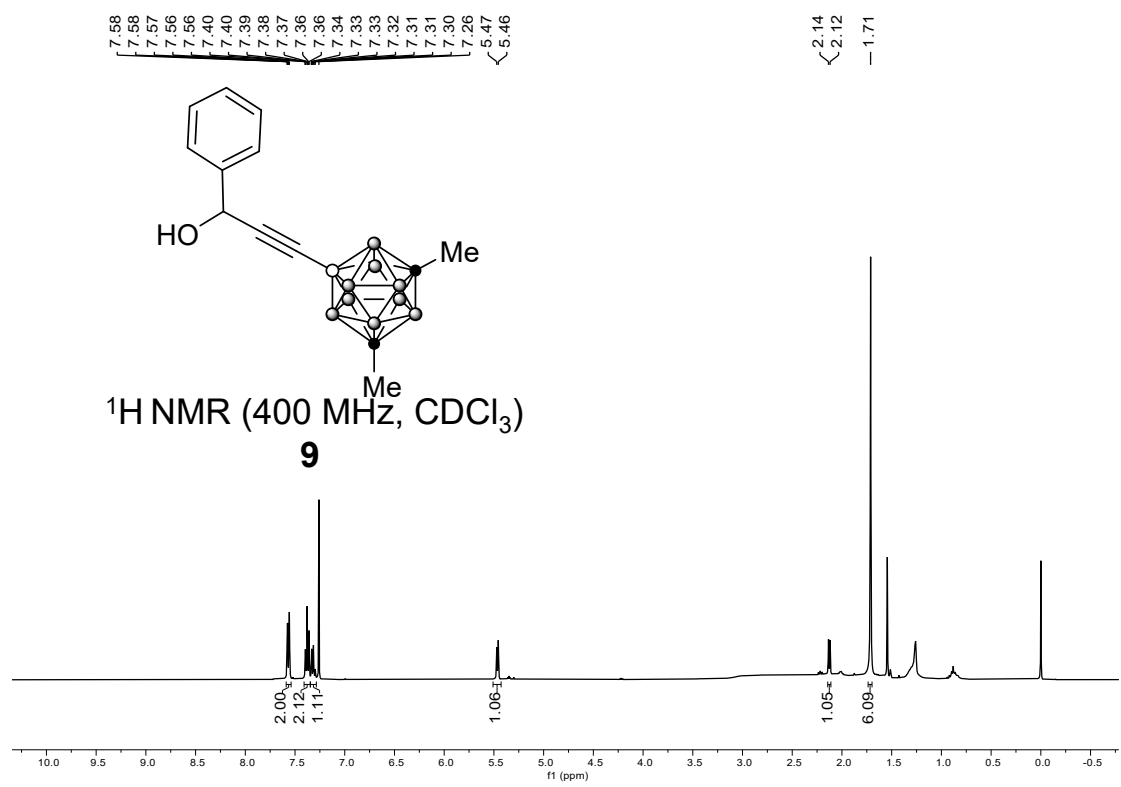
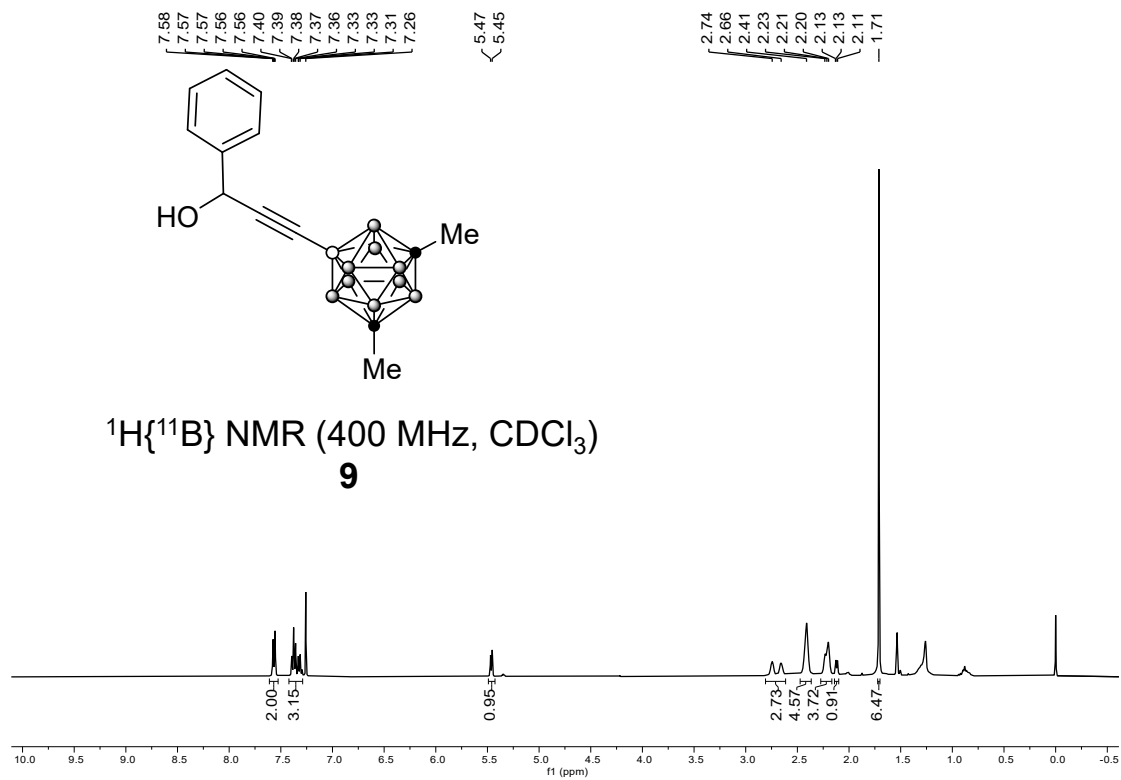


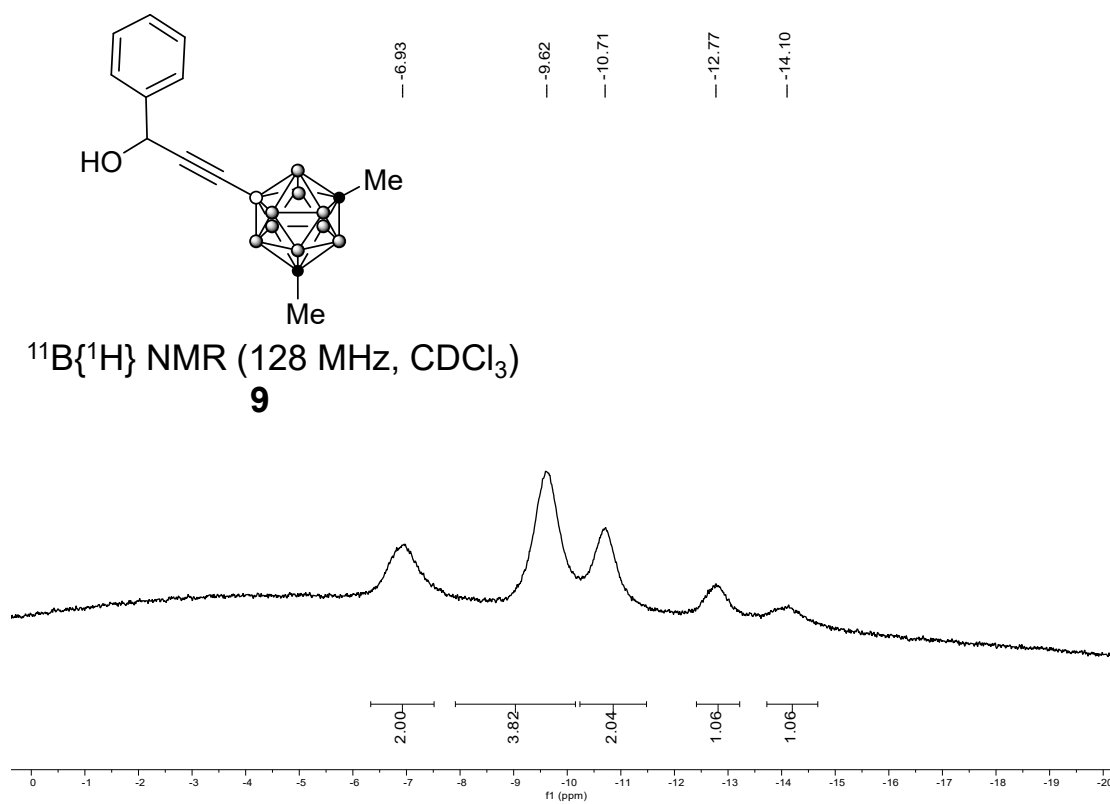
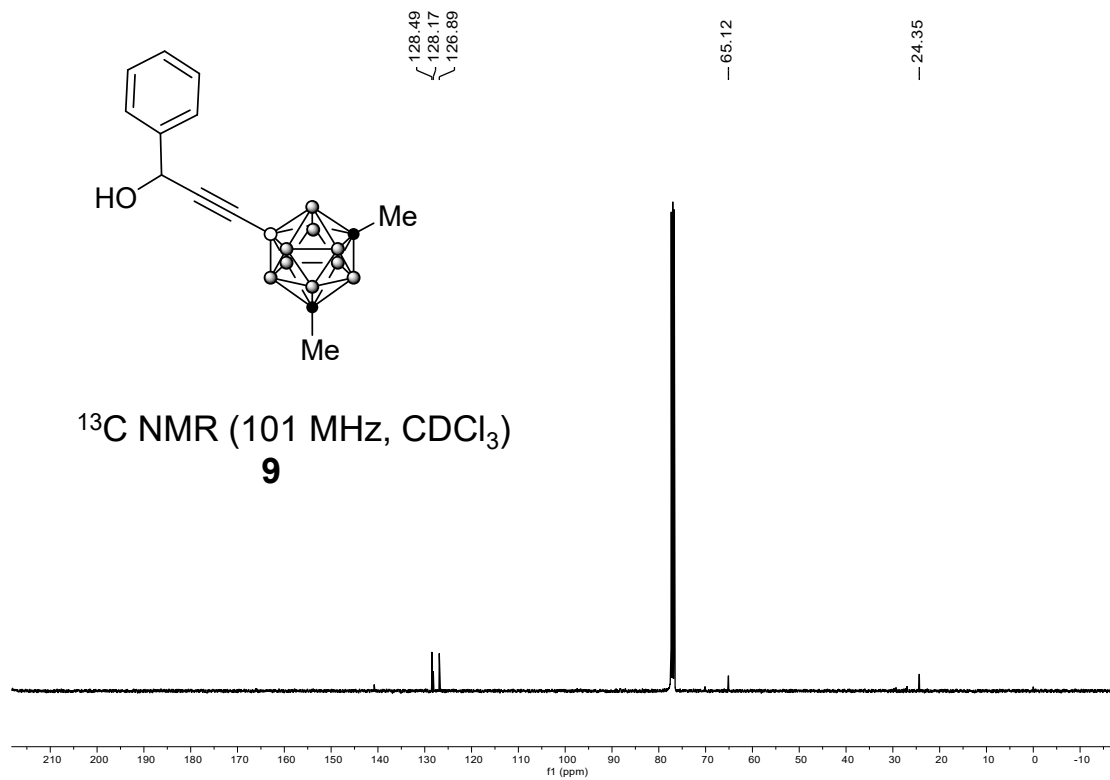


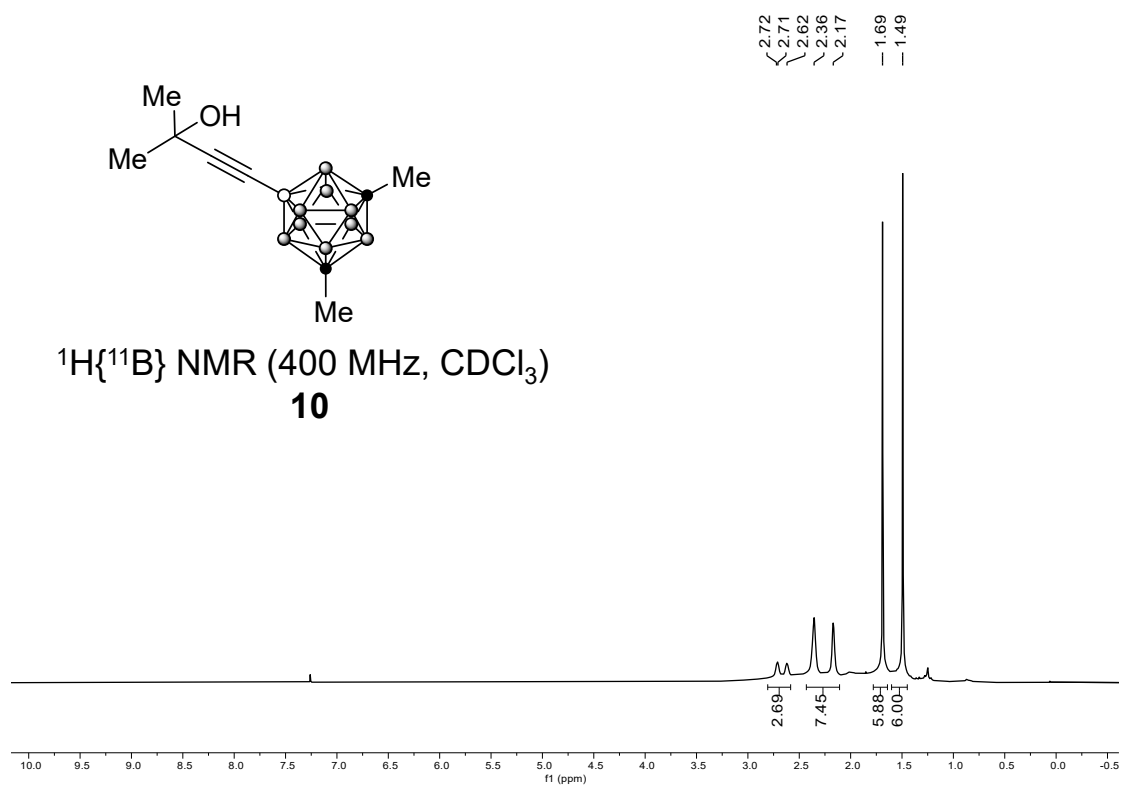
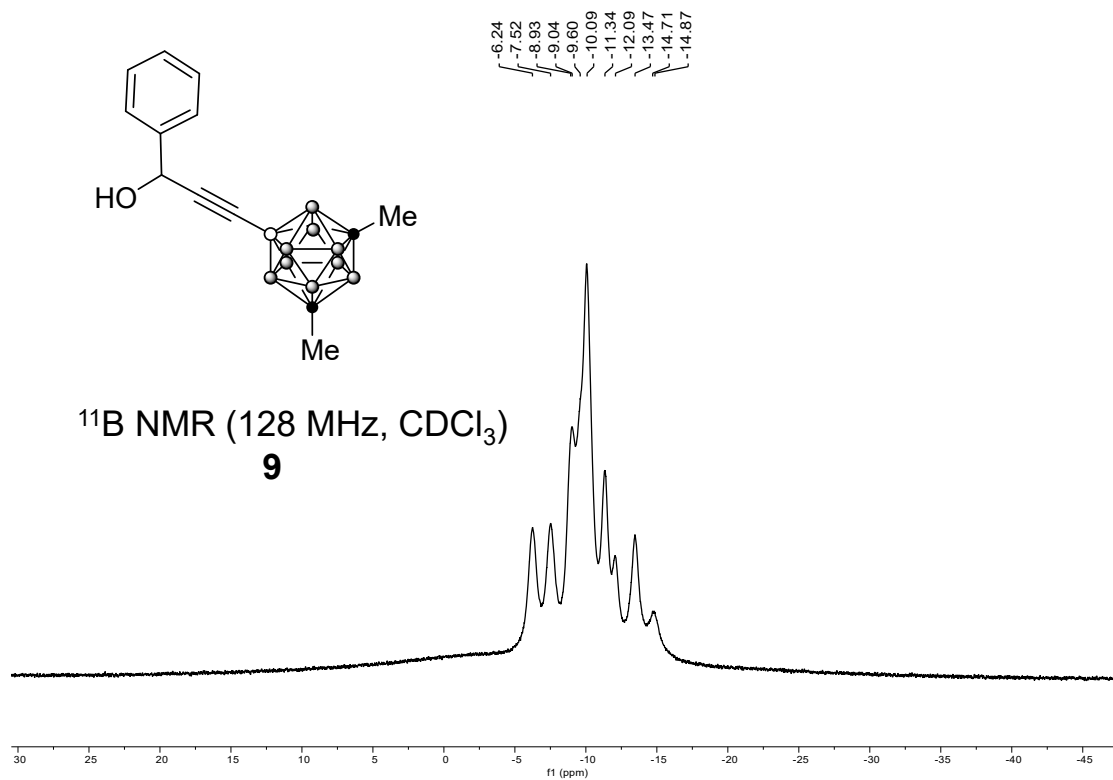


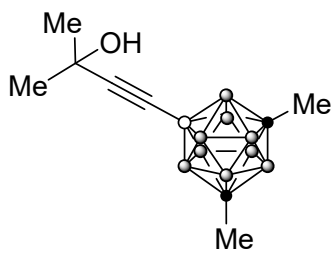




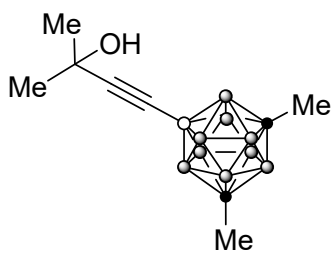
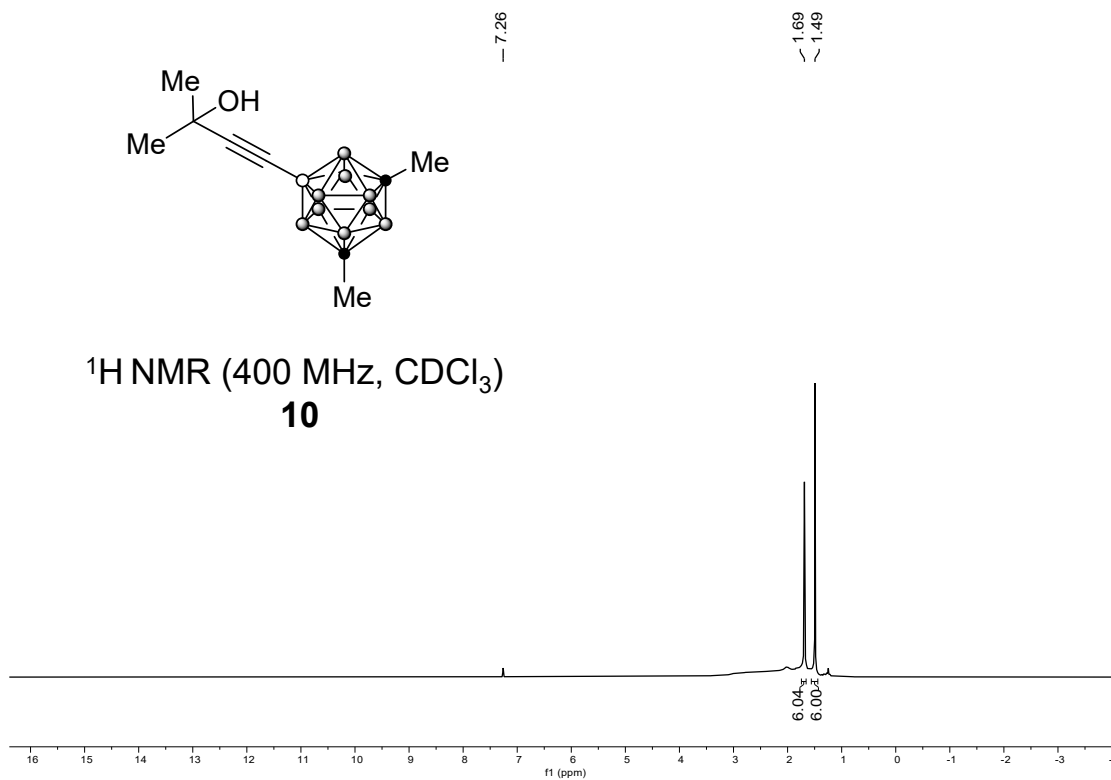








^1H NMR (400 MHz, CDCl_3)
10



^{13}C NMR (101 MHz, CDCl_3)
10

