Supporting Information

Insights into a Chemoselective Cobalt Catalyzed Hydroboration of Alkenes and Nitriles

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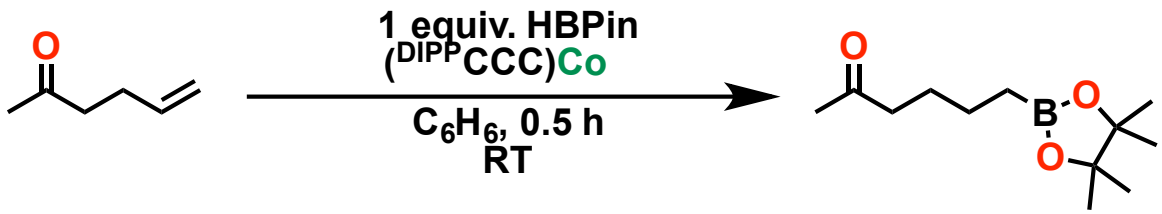
General Considerations. All manipulations of air- and moisture-sensitive compounds were carried out in the absence of water and dioxygen in an MBraun inert atmosphere drybox under a dinitrogen atmosphere except where specified otherwise. All glassware was oven dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in the drybox. Solvents for sensitive manipulations were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves purchased from Strem following drying via a literature procedure prior to use.[1] Chloroform-d_1,water- d_2, dimethyl sulfoxide- d_6,benzene-d_6 were purchased from Cambridge Isotope Labs and were degassed and stored over 4 Å molecular sieves prior to use. Celite® 545 (J. T. Baker) was used as received. NMR Spectra were recorded at room temperature on a Varian or Bruker spectrometer operating at 500 MHz or 400 MHz (^{1}H NMR), 126 MHz or 101 MHz (^{13}C NMR), and 119 MHz (^{2}H NMR) (U500, VXR500, UI500NB, CB500, U400) and referenced to the residual $CHCl_3$, C_6D_5H, HDO, or $C_2D_5HSO_2$ resonances (δ in parts per million, and J in Hz). Electrospray ionization mass spectrometry (ESI) was recorded on a Waters Q-TOF Ultima ESI instrument. Electron ionization mass spectrometry (EI) was recorded on a Waters 70-VSE EI instrument. Allyl phenyl ether were purchased from Alfa Aesar. 4-pentenenitrile was purchased from TCI Chemicals, N-allylaniline was purchased from Alfa Aesar, and the remainder of the alkene substrates were purchased from Sigma-Aldrich. All liquids were dried over 4 Å molecular sieves prior to use.

General Hydroboration Procedure for Alkenes. A 20 mL scintillation vial is charged with mesitylene or naphthalene standard (0.140 mmol), olefin (0.140 mmol), and pinacolborane (0.140 mmol) inside a glove box. Using benzene-d_6, the resulting mixture is then transferred to a vial containing the catalyst (^{DIPP}CCC)CoN$_2$ (**1**) (0.0025 g, 0.00349 mmol), which was prepared according to literature procedure.[2] A final rinse and transfer with the deuterated benzene solvent, for a total solvent volume of ca. 2 mL, completes the setup and the reaction is stirred at room temperature for 1 h. Upon completion, an NMR aliquot of the reaction is taken and the yield is determined by integration relative to the resonances of the internal standard.

Isolation Protocol for Alkylboronate Esters. A 20 mL scintillation vial is charged with **1** (10 mg, 0.0140 mmol), olefin (0.558 mmol), pinacolborane (0.558 mmol), and benzene (1.5 mL). The crude reaction was taken outside of the glovebox, concentrated under reduced pressure, and purified by flash chromatography with an ethyl acetate:hexanes solvent mixture (1:20) to afford the product.

General Hydroboration Procedure for Nitriles. A 20 mL scintillation vial is charged with nitrile (0.558 mmol) and a separate vial is charged pinacolborane (1.116 mmol) inside a glove box. Using benzene solvent, the pinacolborane is transferred to a vial containing the catalyst (^{DIPP}CCC)CoN$_2$ (**1**)[2] (0.010 g, 0.0140 mmol), followed by the nitrile. A final rinse and transfer of the resulting solution to a high-pressure glass vessel with the benzene solvent gives a total solvent volume of ca. 1.5 mL and completes the setup. The vessel is sealed, taken outside of the glovebox and heated at 70 C for 16 h. Upon completion, the crude reaction is transferred to a vial and the volatiles are removed using a rotary evaporator. Aqueous hydrochloric acid (0.95 mL of 37 wt%) is subsequently added to the vial, followed by 1 mL of deionized water, and the mixture is stirred for approximately 10 mins. The water is then removed using a rotary evaporator and the solid is filtered over Celite, using solvent to wash off impurities. The remaining solid is then flushed with methanol into a separate container and the filtrate is dried under reduced pressure to give a solid.

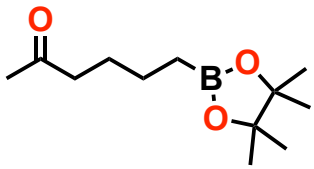
Table S1. Catalytic Optimization



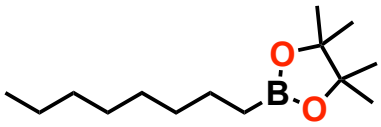
Entry	catalyst (mol %)	Additive	GC-Yield
1	Co^{I} (5 mol %)	None	>99%
2	Co^{I} (2.5 mol %)	None	82%
3	Co^{I} (1 mol %)	None	5%
4	Co^{III} (2.5 mol %)	2 equiv. $(Me_3Si)CH_2Li$	77%
5	Co^{III} (2.5 mol %)	2 equiv. $NaEt_3BH$	51%
6	Co^{III} (2.5 mol %)	2 equiv. MeMgBr	<1%

The Co^{I} complex (2.5 mol%) was employed for the investigation of the catalysis' substrate scope.

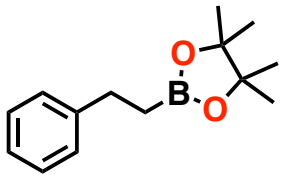
Characterization Data.



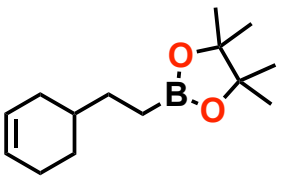
6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (2a). The isolation protocol was followed to afford **2a** as an oil (0.111 g, 0.491 mmol, 88%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.40 (t, *J* = 7.5 Hz, 2H), 2.11 (s, 3H), 1.62 – 1.52 (m, 3H), 1.46 – 1.33 (m, 2H), 1.23 (s, 12H), 0.81 – 0.74 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 83.1, 43.8, 29.9, 26.6, 25.0, 23.8, 11.2 (broad). ^{11}B NMR (161 MHz, $CDCl_3$) δ 33.9. ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy data match literature values.[3] HRMS (ES), calc. for $C_{12}H_{23}BO_3Na$ $(M + Na)^+$: 249.1638; found 225.1635.



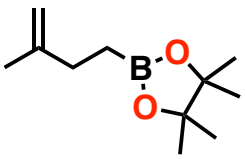
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (2b). The general procedure was followed using napthalene as the internal standard, 1-octene, pinacolborane, and benzene-d_6 (2.5 mL) (^{1}H NMR yield: 99%). The isolation protocol was followed to yield **2b** as an oil (Isolated yield: 87%). ^{1}H NMR (400 MHz, Benzene-d_6) δ 1.71 – 1.59 (m, 2H), 1.47 – 1.34 (m, 2H), 1.36 – 1.19 (m, 8H), 1.08 (s, 12H), 1.03 (t, *J* = 7.7 Hz, 2H), 0.94 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, Benzene) δ 86.2, 82.7, 32.9, 32.3, 30.0, 29.8, 25.0, 24.7, 23.1, 14.4. ^{11}B NMR (161 MHz, $CDCl_3$) δ 34.1. ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy data in $CDCl_3$ solvent match literature values.[4] HRMS (EI), calc. for $C_{13}H_{26}O_2B$ $(M - CH_3)^+$: 225.2026; found 225.2036.



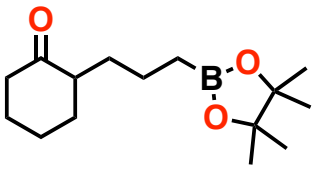
4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2c). The general procedure was followed using naphthalene as the internal standard, styrene, pinacolborane, and benzene-d_6 (^{1}H NMR yield: 99%). The isolation protocol was followed to yield **2c** as an oil (Isolated yield: 88%). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.17 – 7.10 (m, 4H), 7.04 – 6.99 (m, 1H), 2.83 (t, *J* = 8.0 Hz, 2H), 1.25 (t, *J* = 7.9 Hz, 2H), 0.97 (s, 12H). ^{13}C NMR (126 MHz, Benzene-d_6) δ 144.8, 128.5, 128.5, 125.9, 83.0, 30.6, 25.0. ^{11}B NMR (161 MHz, $CDCl_3$) δ33.9. ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy data in $CDCl_3$ solvent match literature values.[5] HRMS (EI), calc. for $C_{14}H_{21}O_2B$ $(M^{\bullet})^+$: 232.1635; found 232.1637.



2-(2-(cyclohex-3-en-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d). The general procedure was followed using mesitylene as the internal standard, 4-vinyl-1-cyclohexene, pinacolborane, and benzene-d_6 (^{1}H NMR yield: 90%). The isolation protocol was followed to yield **2d** as an oil (Isolated yield: 97%). ^{1}H NMR (400 MHz, Benzene-d_6) δ 5.82 – 5.54 (m, 2H), 2.18 – 2.05 (m, 1H), 2.04-1.88 (m, 2H), 1.78 – 1.48 (m, 5H), 1.28 – 1.14 (m, 1H), 1.06 (s, 12H), 1.03 – 0.96 (m, 2H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 127.2, 127.0, 82.8, 36.1, 32.1, 31.3, 29.1, 25.7, 25.0, 25.0. ^{11}B NMR (161 MHz, $CDCl_3$) δ 34.1. ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy data in $CDCl_3$ solvent match literature values.[6] HRMS (EI), calc. for $C_{14}H_{25}O_2B$ $(M^{\bullet})^+$: 236.1948; found 236.1955.

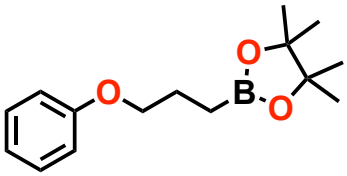


4,4,5,5-tetramethyl-2-(3-methylbut-3-en-1-yl)-1,3,2-dioxaborolane (2e). A modified isolation protocol was followed using **1** (10 mg, 0.0140 mmol), isoprene (2.232 mmol), pinacolborane (0.558 mmol), and benzene (2.5 mL). The reaction was conducted in a high-pressure vessel and sealed following addition of the borane and olefin mixture to the catalyst. The sealed vessel was then taken outside of the glove box and heated to 70 °C for 2 h. The crude reaction was concentrated under reduced pressure and purified by flash chromatography with hexanes to afford **2e** as a colorless oil (0.082 g, 0.419 mmol, 75%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.69 – 4.59 (m, 2H), 2.10 (t, *J* = 7.8 Hz, 2H), 1.71 (s, 3H), 1.23 (s, 12H), 0.91 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 108.6, 83.1, 31.8, 24.9, 22.7, 9.7. ^{11}B NMR (161 MHz, $CDCl_3$) δ 34.0. ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy data match literature values.[7]

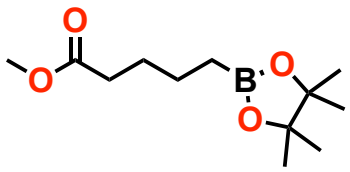


2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propyl)cyclohexan-1-one (2f). The general procedure was followed using naphthalene as the internal standard, 2-allylcyclohexanone (0.140 mmol), pinacolborane (0.140 mmol), and benzene-d_6 (^{1}H NMR yield: 95%). The isolation protocol was followed to yield **2f** as an oil (Isolated yield: 65%). ^{1}H NMR (500 MHz, Benzene-d_6) δ 2.21 (dtd, *J* = 13.4, 4.3, 1.5 Hz, 1H), 2.08 – 1.90 (m, 2H), 1.83 (dddd, *J* = 13.4, 12.4, 5.8, 1.2 Hz, 1H), 1.77 – 1.67 (m, 1H), 1.65 – 1.55 (m, 2H), 1.54 – 1.47 (m, 1H), 1.38 – 1.32 (m, 1H), 1.31 – 1.18 (m, 2H), 1.08 (s, 12H),

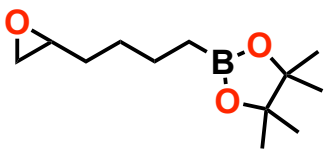
1.04 – 0.94 (m, 4H). ^{13}C NMR (126 MHz, Benzene-d_6) δ 210.5, 82.8, 50.6, 42.0, 33.9, 32.6, 28.0, 25.1, 25.0, 22.3. ^{11}B NMR (161 MHz, $CDCl_3$) δ33.8. ^{1}H and ^{13}C NMR spectroscopy data in $CDCl_3$ solvent match literature values.[8] HRMS (ES), calc. for $C_{15}H_{27}BO_3$ $(M + H)^+$: 267.2132; found 267.2130.



4,4,5,5-tetramethyl-2-(3-phenoxypropyl)-1,3,2-dioxaborolane (2g). The general procedure was followed using naphthalene as the internal standard, allyl phenyl ether, pinacolborane, and benzene-d_6 (^{1}H NMR yield: 96%). The isolation protocol was followed to yield **2g** as an oil (Isolated yield: 80%). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.15 – 7.10 (m, 2H), 6.89 (d, J = 8.1 Hz, 2H), 6.84 (t, J = 7.3 Hz, 1H), 3.75 (t, J = 6.7 Hz, 2H), 1.98 (p, J = 7.1 Hz, 2H), 1.10 – 0.97 (m, 14H). ^{13}C NMR (126 MHz, Benzene-d_6) δ 159.9, 129.7, 120.6, 115.0, 83.0, 69.6, 25.0, 24.4. ^{11}B NMR (161 MHz, $CDCl_3$) δ34.0. ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy data in $CDCl_3$ solvent match literature values.[9] HRMS (ES), calc. for $C_{15}H_{23}BO_3Na$ $(M + Na)^+$: 285.1638; found 285.1648.

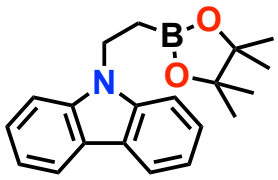


methyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (2h). The general procedure was followed using naphthalene as the internal standard, methyl 4-pentenoate, pinacolborane, and benzene-d_6 (^{1}H NMR yield: 97%). The isolation protocol was followed to yield **2h** as an oil (Isolated yield: 92%). ^{1}H NMR (400 MHz, Benzene-d_6) δ 3.31 (s, 3H), 2.13 (p, J = 7.4 Hz, 2H), 1.72 – 1.62 (m, 2H), 1.52 (p, J = 7.6 Hz, 2H), 1.04 (s, 12H), 0.90 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 173.4, 128.1, 86.2, 82.8, 50.9, 34.1, 27.9, 25.0, 24.2. ^{11}B NMR (161 MHz, $CDCl_3$) δ33.8. ^{1}H and ^{13}C NMR spectroscopy data in $CDCl_3$ solvent match literature values.[10] HRMS (ES), calc. for $C_{12}H_{23}BO_4Na$ $(M + Na)^+$: 265.1587; found 265.1582.

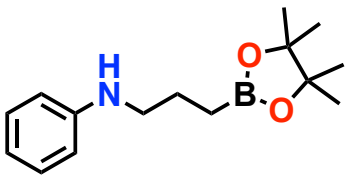


4,4,5,5-tetramethyl-2-(4-(oxiran-2-yl)butyl)-1,3,2-dioxaborolane (2i). The general procedure was followed using naphthalene as the internal standard, 1,2-epoxy-5-hexene, pinacolborane, and benzene-d_6 (^{1}H NMR yield: 86%). The isolation protocol was

followed to yield **2i** as an oil (Isolated yield: 77%). ^{1}H NMR (500 MHz, Benzene-d_6) δ 2.66 – 2.50 (m, 1H), 2.33 (t, J = 4.6 Hz, 1H), 2.08 (dd, J = 5.3, 2.6 Hz, 1H), 1.60 – 1.49 (m, 2H), 1.47 – 1.23 (m, 4H), 1.06 (s, 12H), 0.93 (t, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, Benzene-d_6) δ 82.8, 51.8, 46.4, 32.8, 29.0, 25.0, 24.4. ^{11}B NMR (161 MHz, $CDCl_3$) δ34.0. ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy data in $CDCl_3$ solvent match literature values.[11] HRMS (ES), calc. for $C_{12}H_{23}BO_3Na$ $(M + Na)^+$: 249.1638; found 249.1649.

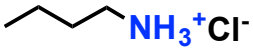


9-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-9*H*-carbazole (2j). The general procedure was followed using mesitylene as the internal standard, 9-vinylcarbazole, pinacolborane, and benzene-d_6 (^{1}H NMR yield: 80%). The compound was also isolated in a modified procedure using **1** (10 mg, 0.0140 mmol), 9-vinylcarbazole (0.558 mmol), pinacolborane (0.558 mmol), and benzene (2 mL) whereby the crude reaction was taken outside of the glovebox after 3 h of stirring, concentrated under reduced pressure, and purified by flash chromatography with an ethyl acetate:hexanes solvent mixture (1:20) to afford **2j** as a white solid (0.177 g, 0.552 mmol, 99%). ^{1}H NMR (499 MHz, Chloroform-d) δ 8.15 (d, J = 7.8 Hz, 2H), 7.58 – 7.47 (m, 4H), 7.27 (t, J = 7.2 Hz, 2H), 4.57 – 4.45 (m, 2H), 1.26 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 125.5, 123.0, 120.4, 118.7, 109.1, 83.6, 38.8, 24.9, 12.1. ^{11}B NMR (161 MHz, $CDCl_3$) δ33.4. ^{1}H and ^{13}C NMR spectroscopy data in $CDCl_3$ solvent match literature values.[8] HRMS (ES), calc. for $C_{20}H_{25}NO_2B$ $(M + H)^+$: 322.1978; found 322.1971.



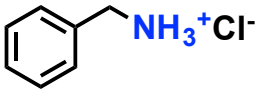
4,4,5,5-tetramethyl-2-(4-(oxiran-2-yl)butyl)-1,3,2-dioxaborolane (2k). The general procedure was followed using mesitylene as the internal standard, N-allylaniline, pinacolborane, and benzene-d_6 (^{1}H NMR yield: 93%). The isolation protocol was followed to yield **2k** as a viscous oil (Isolated yield: 92%). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.22 – 7.15 (m, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.50 (d, J = 7.6 Hz, 2H), 3.35 (s, 1H), 3.00 – 2.85 (m, 2H), 1.65 (p, J = 7.3 Hz, 2H), 1.04 (s, 12H), 0.89 (t, J = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 149.2, 129.5, 117.2, 113.0, 83.0, 46.2, 25.0, 25.0, 24.3.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.21 – 7.13 (m, 2H), 6.68 (tt, J = 7.3, 1.2 Hz, 1H), 6.64 – 6.59 (m, 2H), 3.78 (s, 2H), 3.11 (t, J = 7.1 Hz, 2H), 1.69 – 1.83 (m, 2H), 0.89 (t, J = 7.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 129.3, 117.0, 112.7, 83.2, 46.2, 25.0, 24.0. ^{11}B NMR (161 MHz, $CDCl_3$) δ 33.9. HRMS (ES), calc. for $C_{15}H_{25}BNO_2$ $(M + H)^+$: 262.1978; found 262.1979.

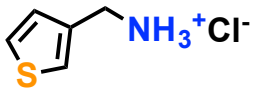


4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (3a). The general procedure for nitriles was followed with ethyl acetate (15 mL) used for washes (isolated yield: 79%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 3H), 2.97 (t, *J* = 7.5 Hz, 2H), 1.73 (t, *J* = 7.6 Hz, 2H), 1.39 (q, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 40.1, 29.6, 20.0, 13.6. ^{1}H and ^{13}C NMR spectroscopy data match literature values.[12]

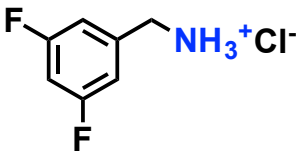
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (3b). The general procedure for nitriles was followed with ethyl acetate (5 mL) and DCM (10 mL) used for washes (isolated yield: 52%). ^{1}H NMR (500 MHz, Deuterium Oxide) δ 2.87 (q, *J* = 7.0 Hz, 2H), 1.10 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, D_2O) δ 35.1, 12.0. ^{1}H and ^{13}C NMR spectroscopy data match literature values.[13]



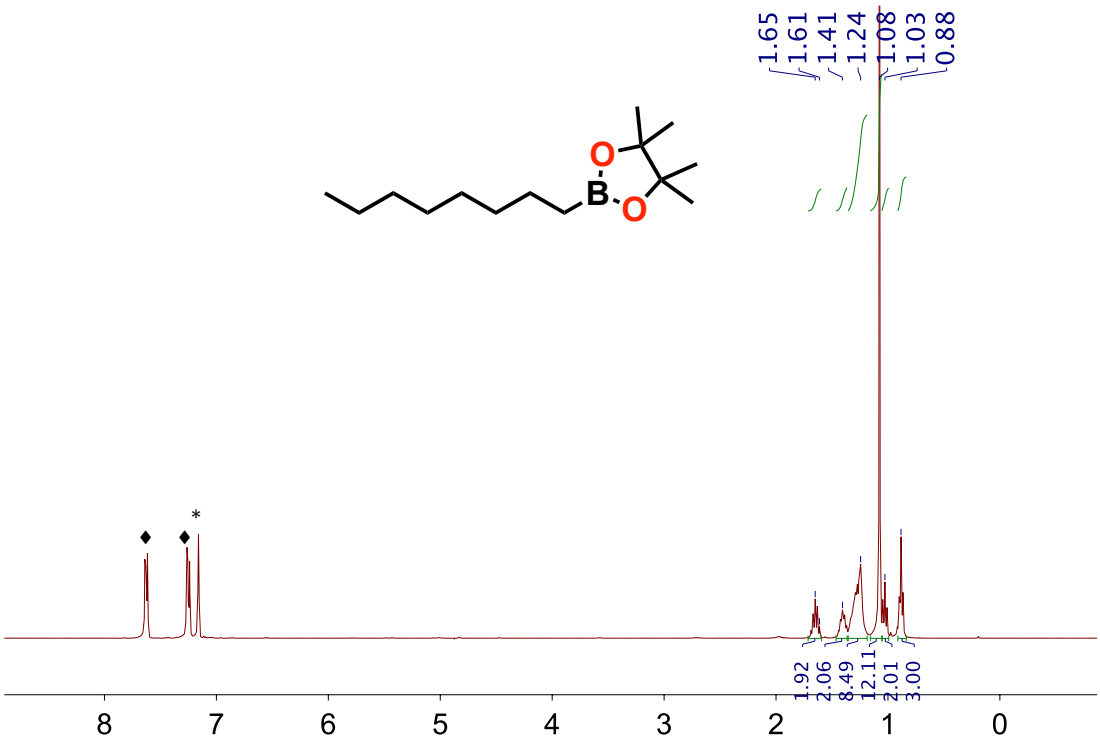
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (3c). The general procedure for nitriles was followed with ethyl acetate (18 mL) and DCM (3 mL) used for washes (isolated yield: 67%). ^{1}H NMR (400 MHz, D_2O) δ 7.44, 4.15. ^{13}C NMR (101 MHz, D_2O) δ 132.5, 129.1, 128.7, 43.0. ^{1}H and ^{13}C NMR spectroscopy data match literature values.[14]



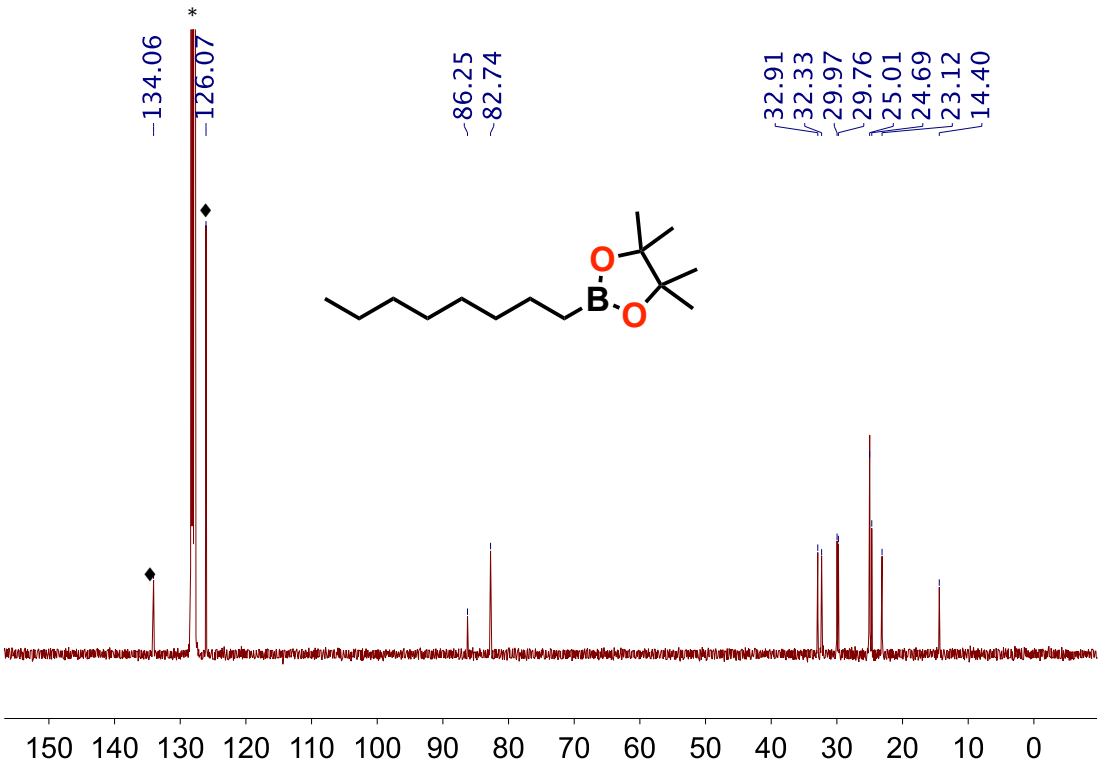
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (3d). The general procedure for nitriles was followed with ethyl acetate (18 mL) and DCM (12 mL) used for washes (isolated yield: 79%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.64 (s, 3H), 7.68 – 7.62 (m, 1H), 7.57 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.38 – 7.23 (m, 1H), 3.99 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 134.8, 128.2, 126.9, 125.1, 37.2. ^{1}H NMR spectroscopy data match literature values.[15]



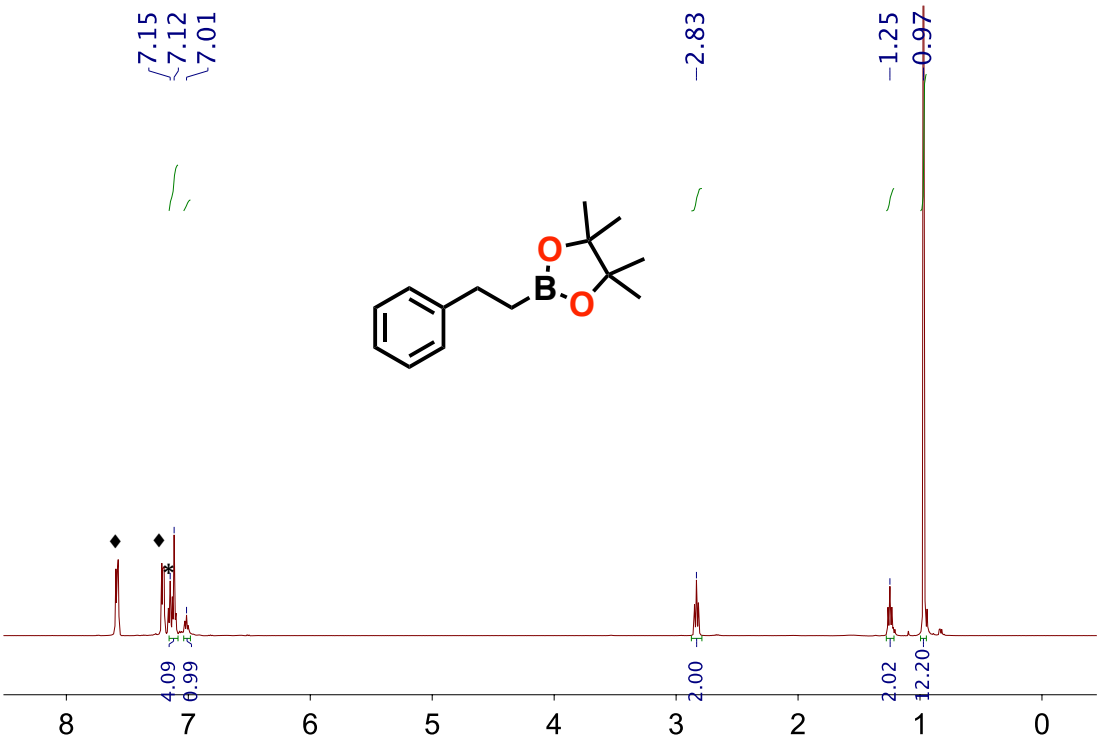
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (3e). The general procedure for nitriles was followed with ethyl acetate (8 mL) and DCM (3 mL) used for washes (isolated yield: 85%). ^{1}H NMR (500 MHz, Deuterium Oxide) δ 7.11 – 7.04 (m, 2H), 7.06 – 6.98 (m, 1H), 4.20 (s, 2H). ^{13}C NMR (126 MHz, Deuterium Oxide) δ 164.1 (d, *J* = 13.3 Hz), 162.1 (d, *J* = 12.9 Hz), 136.2 (t, *J* = 9.6 Hz), 112.1 (q), 104.7 (t, *J* = 25.5 Hz), 42.4. HRMS (EI), calc. for $C_7H_8NF_2$ $(M)^+$: 144.0625; found 144.0624.



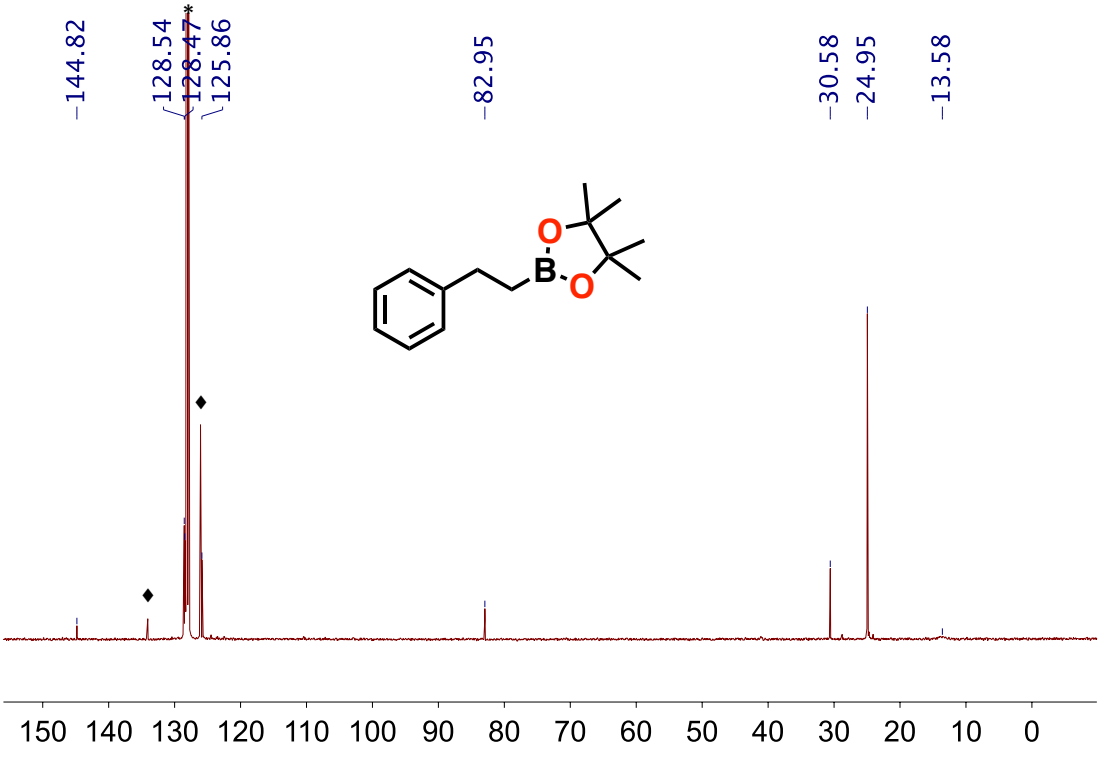
(**2b** ^{1}H NMR, * denotes C_6D_6 reference at 7.16 ppm, ♦ denotes naphthalene)



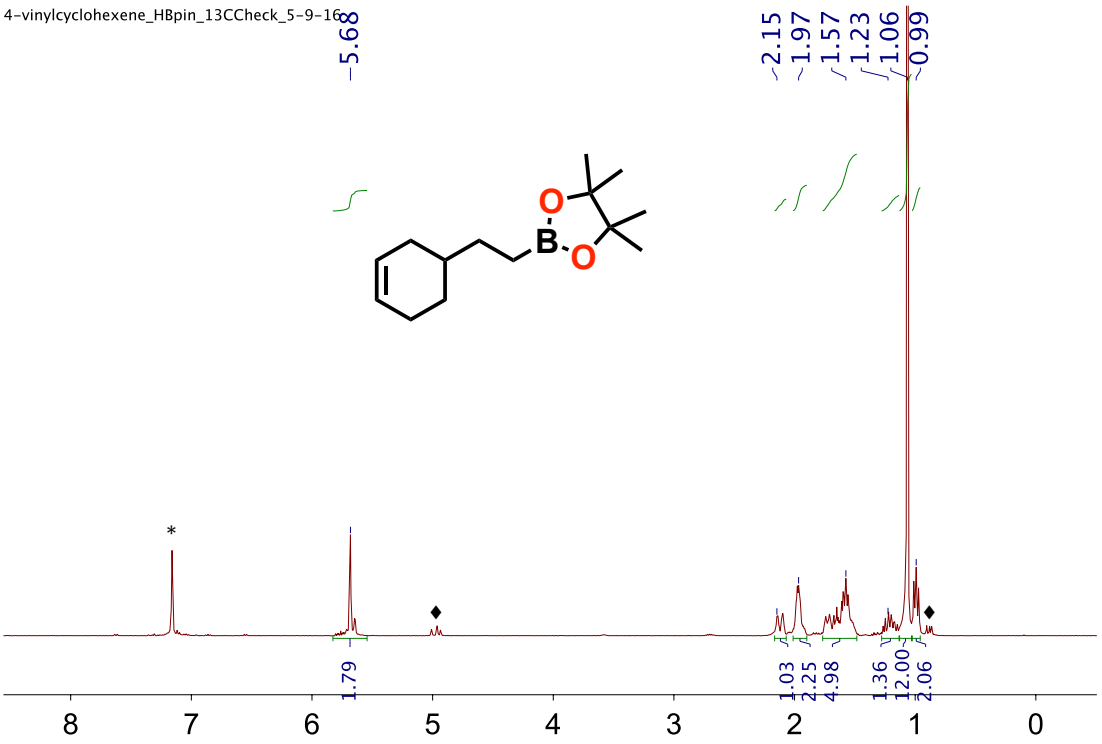
(**2b** ^{13}C{^{1}H} NMR, * denotes C_6D_6 reference at 128.06 ppm, ♦ denotes naphthalene)



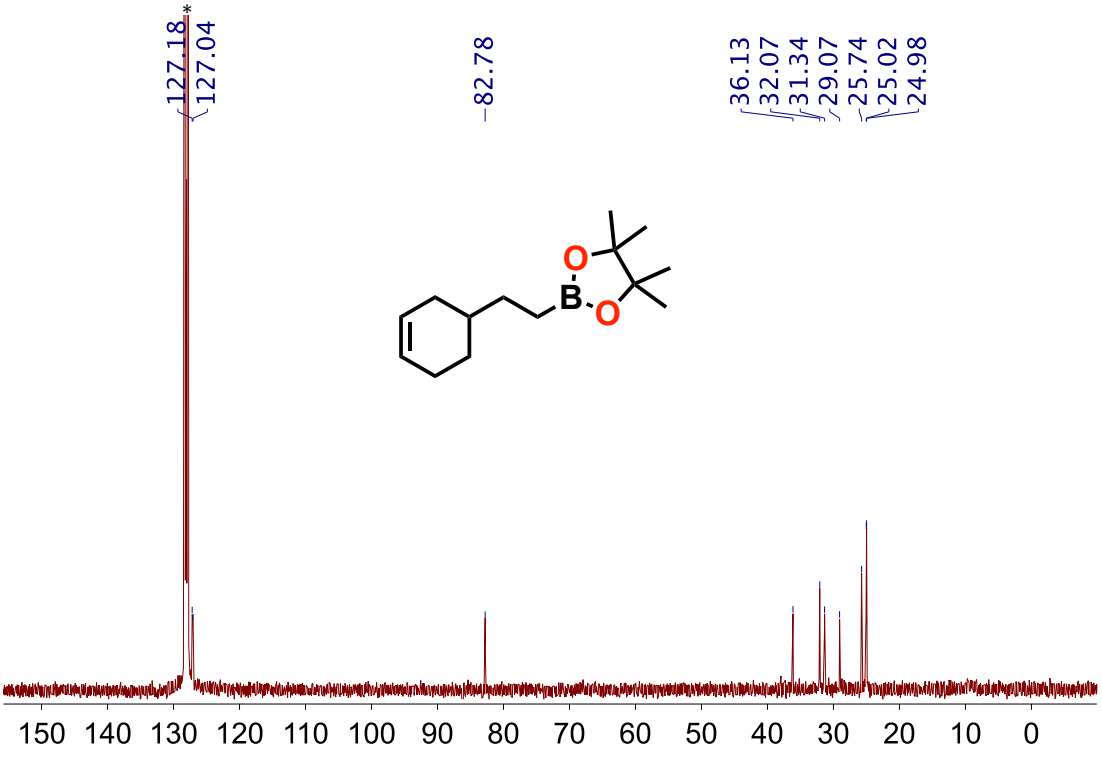
(**2c** ^{1}H NMR, * denotes C_6D_6 reference at 7.16 ppm, ♦ denotes naphthalene)



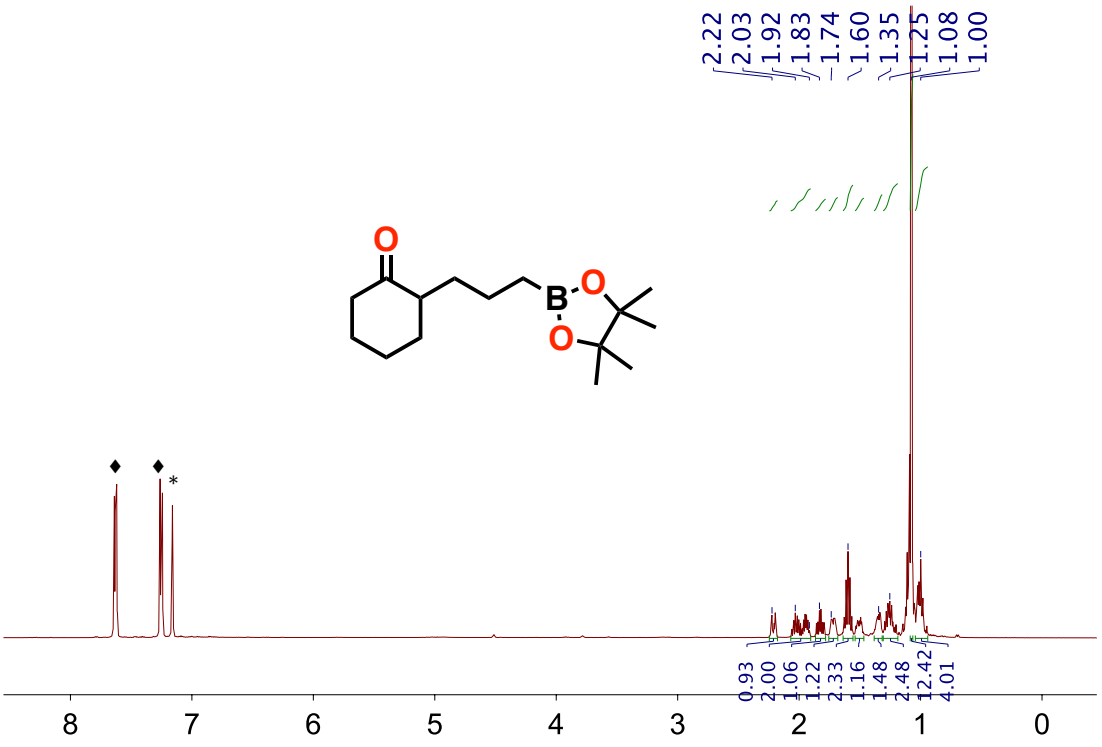
(**2c** ^{13}C{^{1}H} NMR, * denotes C_6D_6 reference at 128.06 ppm, ♦ denotes naphthalene)



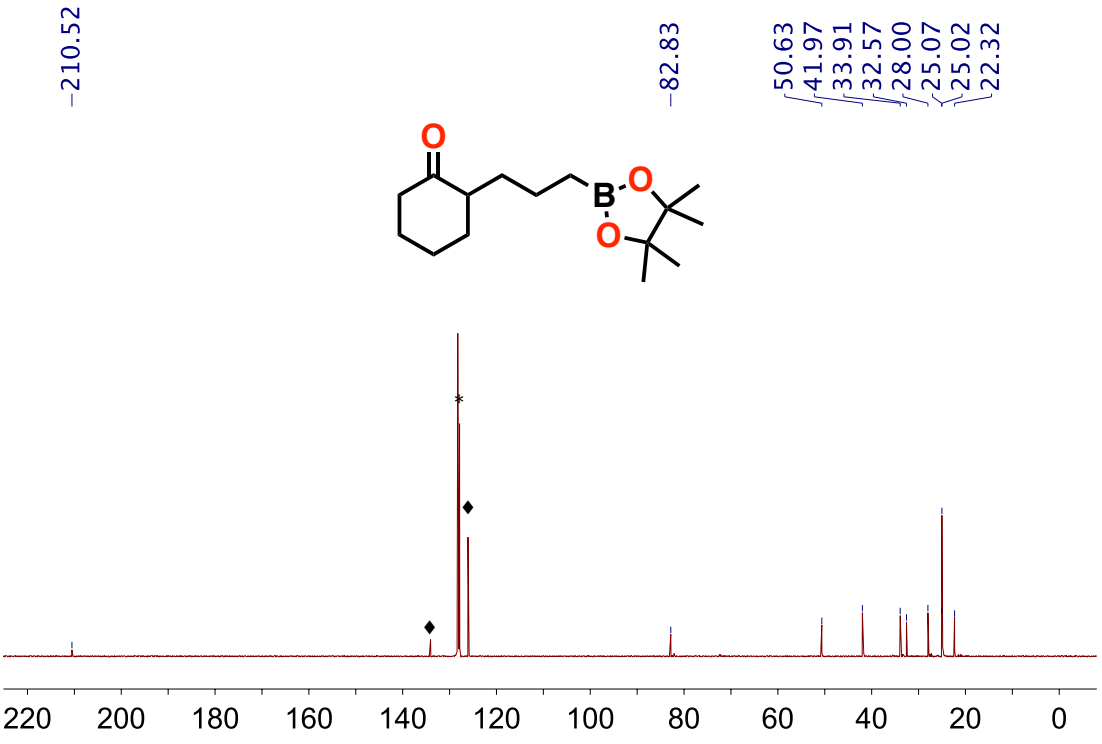
(**2d** ^{1}H NMR, * denotes C_6D_6 reference at 7.16 ppm, ♦ denotes 4-vinylcyclohexene)



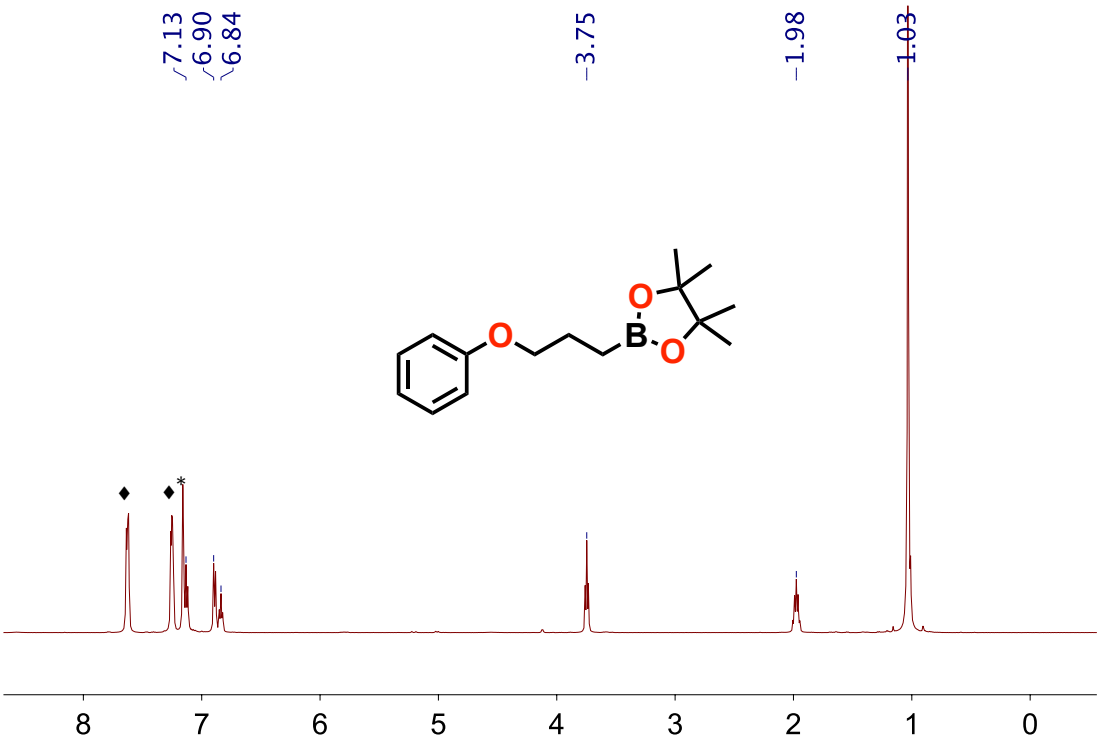
(**2d** $^{13}C\{^{1}H\}$ NMR, * denotes C_6D_6 reference at 128.06 ppm)



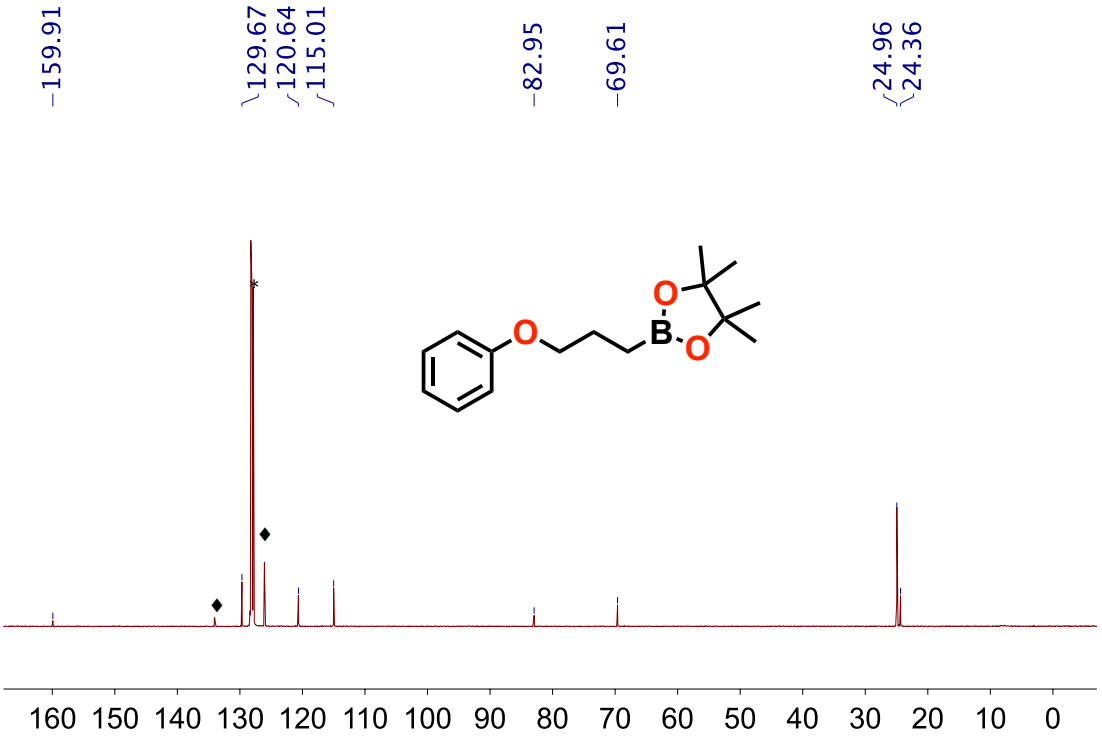
(**2f** ^{1}H NMR, * denotes C_6D_6 reference at 7.16 ppm, ♦ denotes naphthalene)



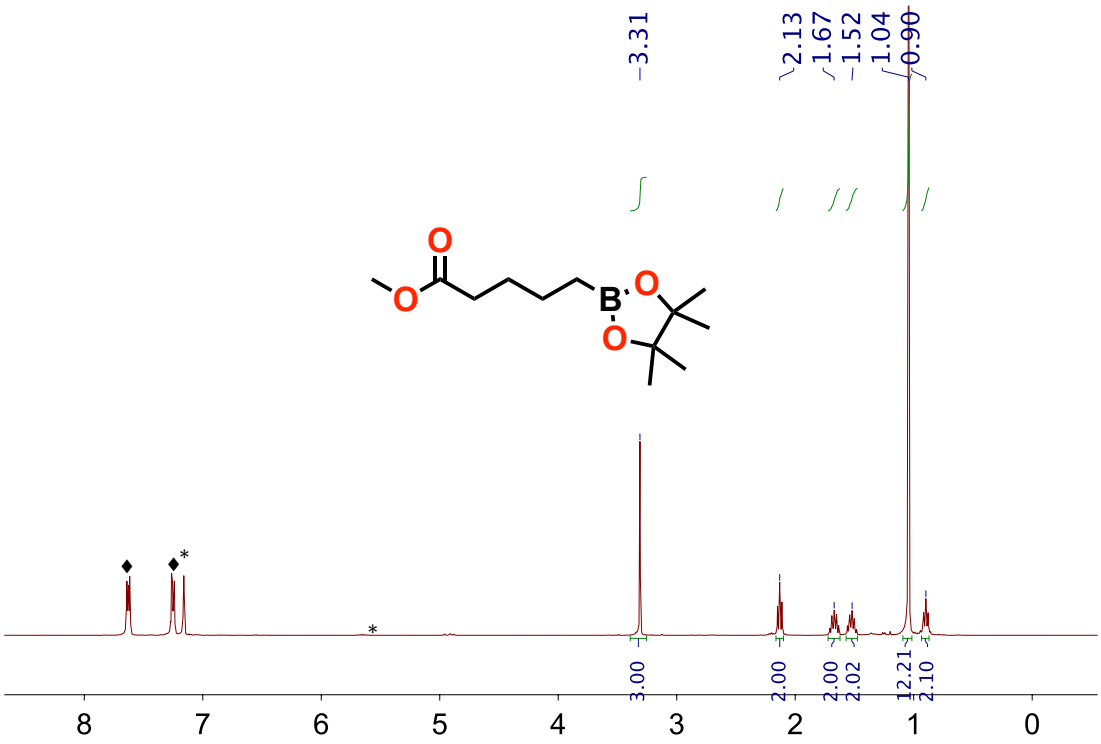
(**2f** ^{13}C{^{1}H} NMR, * denotes C_6D_6 reference at 128.06 ppm, ♦ denotes naphthalene)



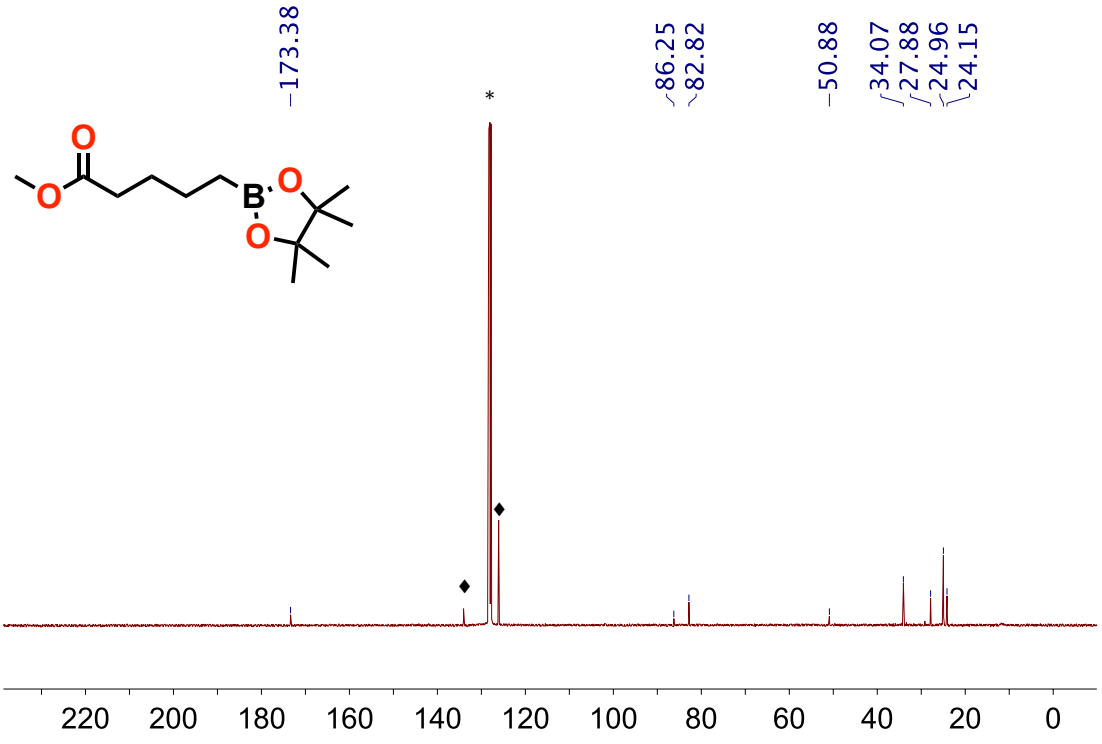
(**2g** ^{1}H NMR, * denotes C_6D_6 reference at 7.16 ppm, ♦ denotes naphthalene)



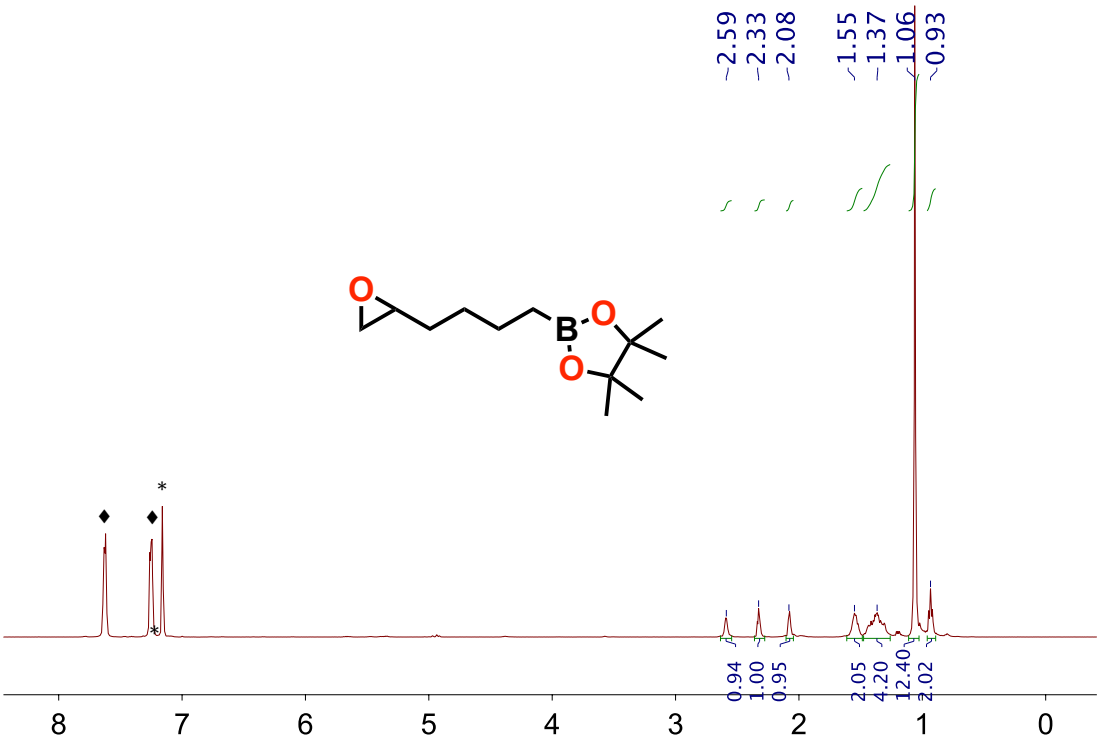
(**2g** ^{13}C{^{1}H} NMR, * denotes C_6D_6 reference at 128.06 ppm, ♦ denotes naphthalene)



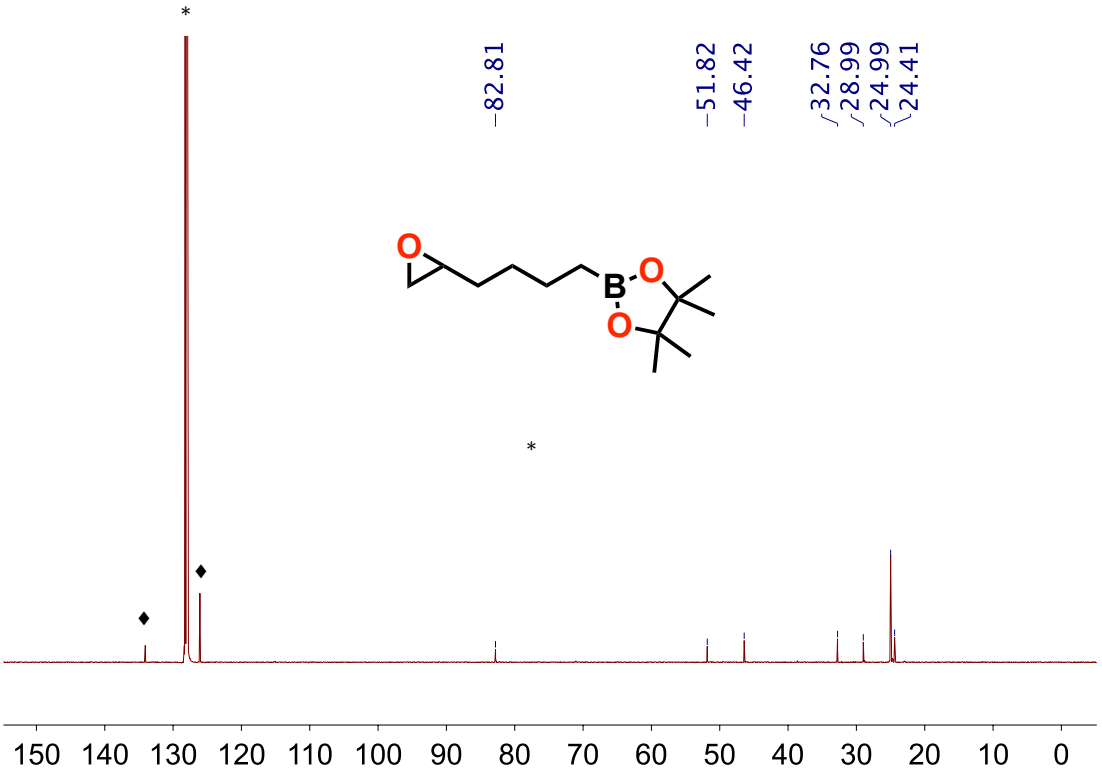
(**2h** ^{1}H NMR, * denotes C_6D_6 reference at 7.16 ppm, ♦ denotes naphthalene)



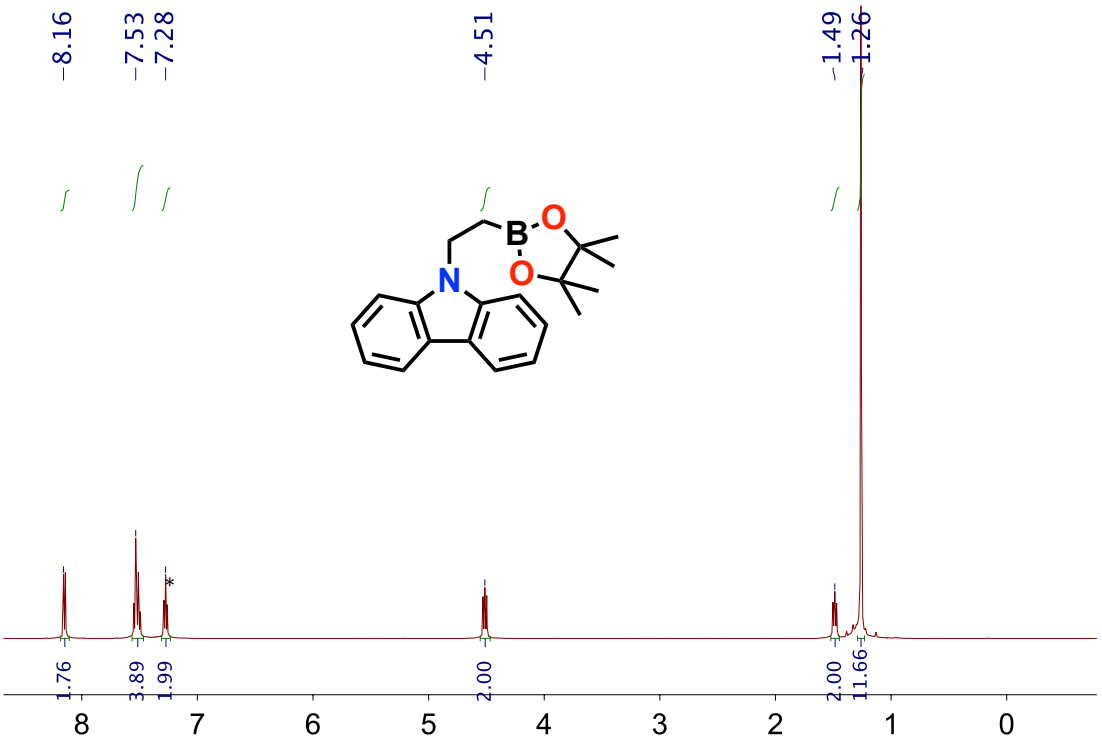
(**2h** ^{13}C{^{1}H} NMR, * denotes C_6D_6 reference at 128.06 ppm, ♦ denotes naphthalene)



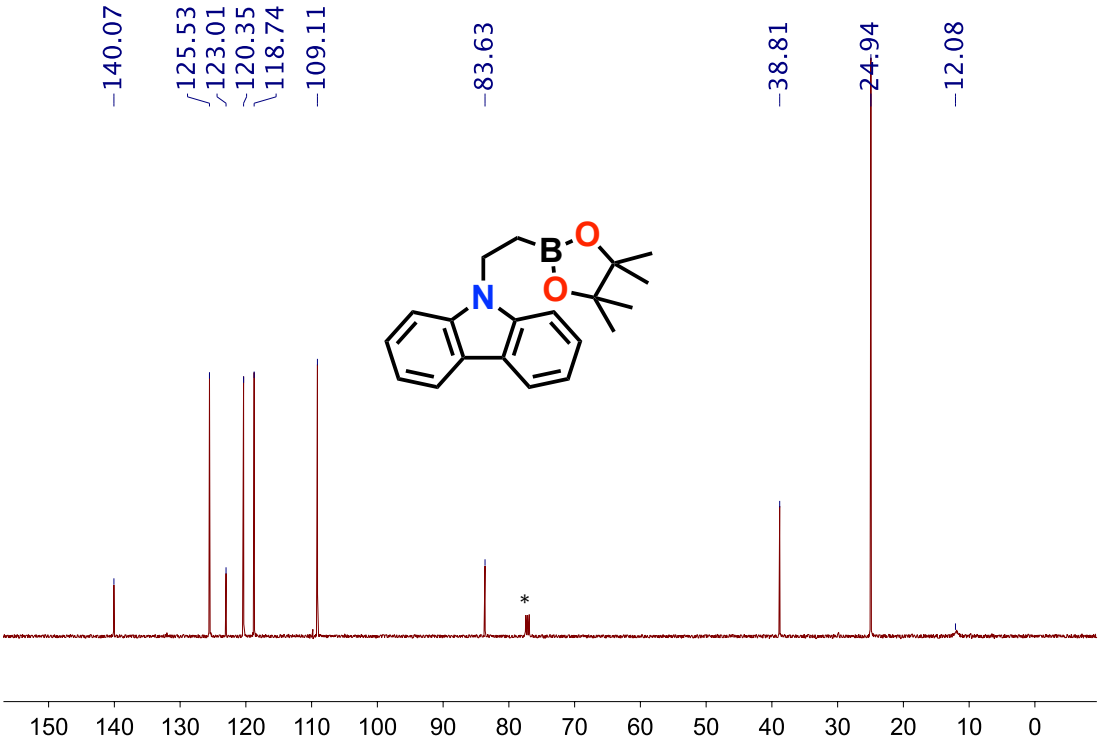
(**2i** ^{1}H NMR, * denotes C_6D_6 reference at 7.16 ppm, ♦ denotes naphthalene)



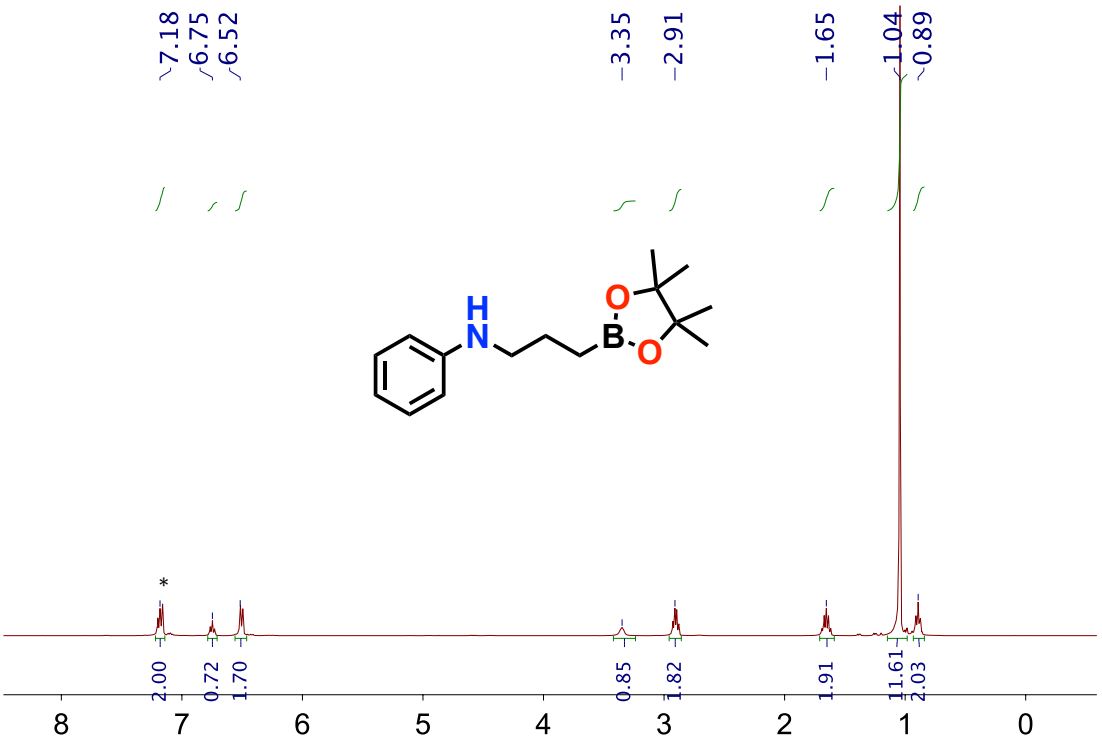
(**2i** ^{13}C{^{1}H} NMR, * denotes C_6D_6 reference at 128.06 ppm, ♦ denotes naphthalene)



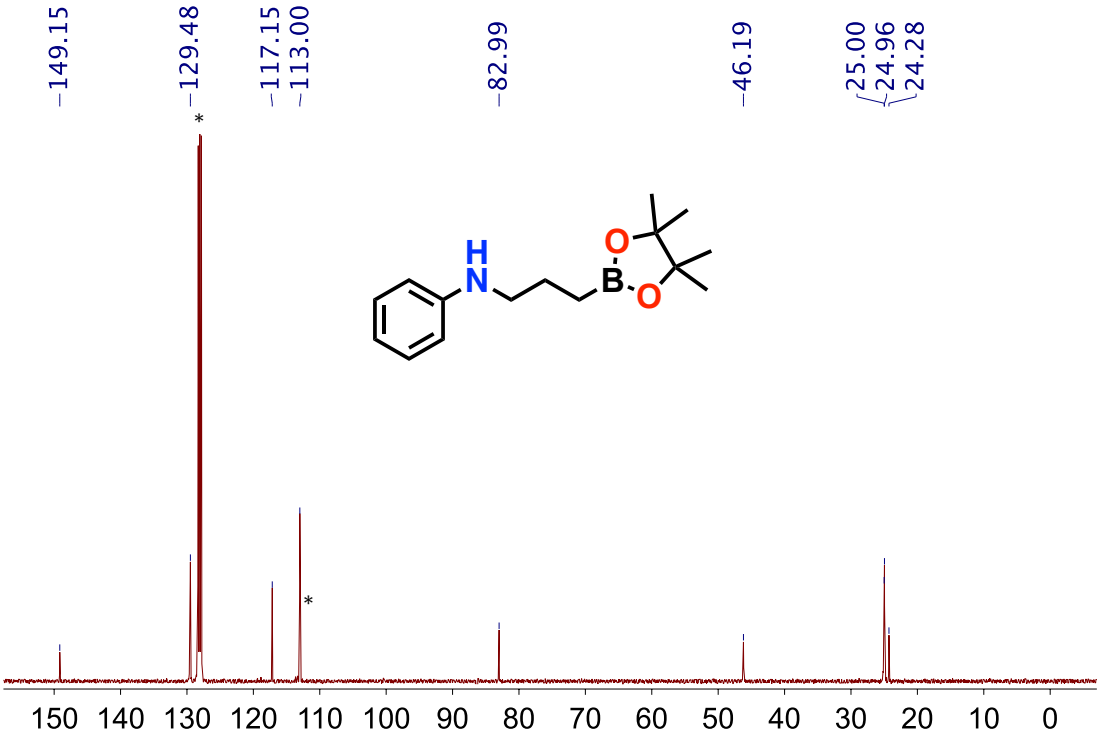
(**2j** ^{1}H NMR, * denotes $CDCl_3$ reference at 7.26 ppm)



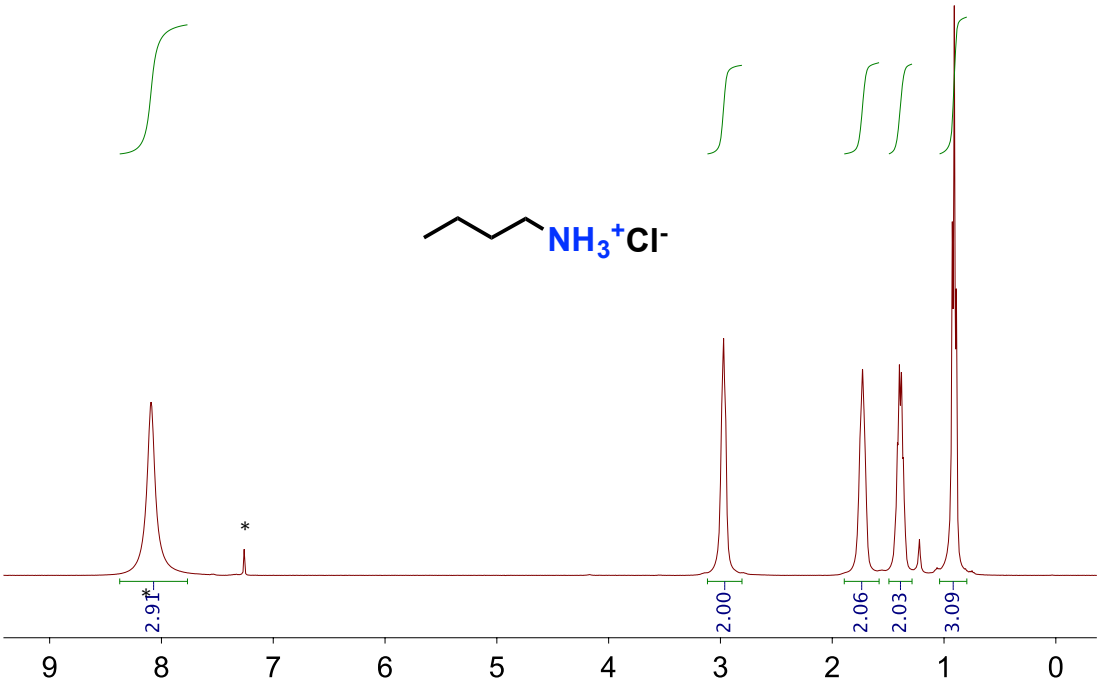
(**2j** $^{13}C\{^{1}H\}$ NMR, * denotes $CDCl_3$ reference at 77.16 ppm)



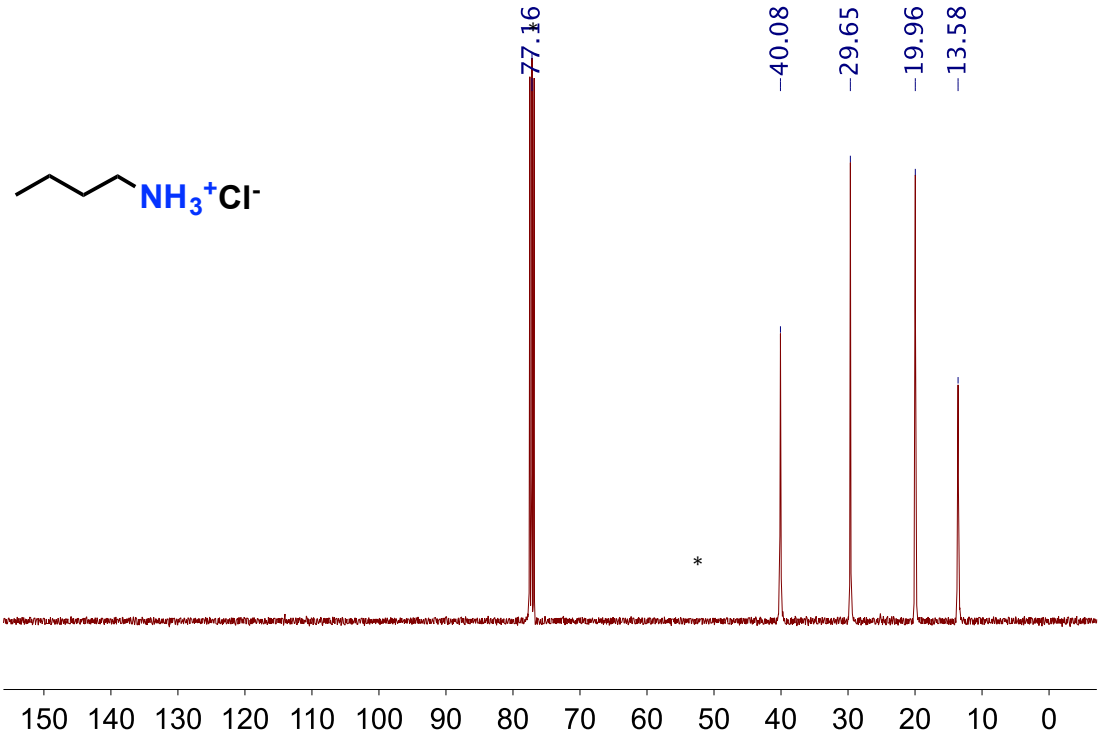
(**2k** ^{1}H NMR, * denotes C_6D_6 reference at 7.16 ppm)



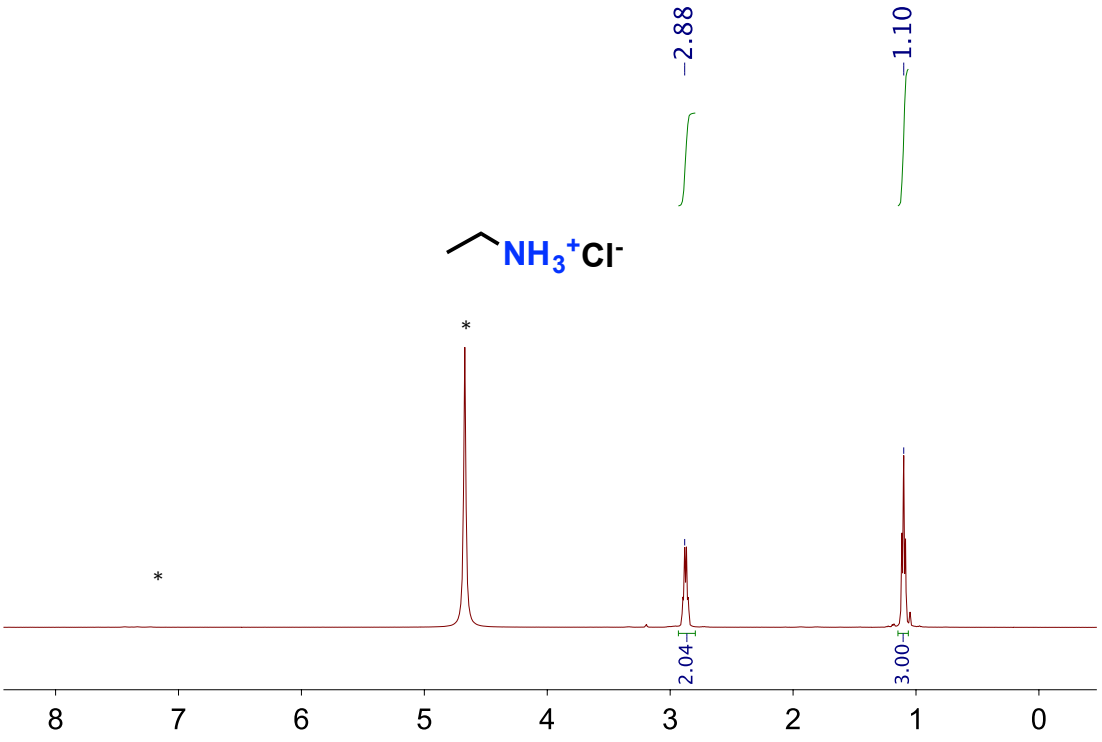
(**2k** ^{13}C{^{1}H} NMR, * denotes C_6D_6 reference at 128.06 ppm



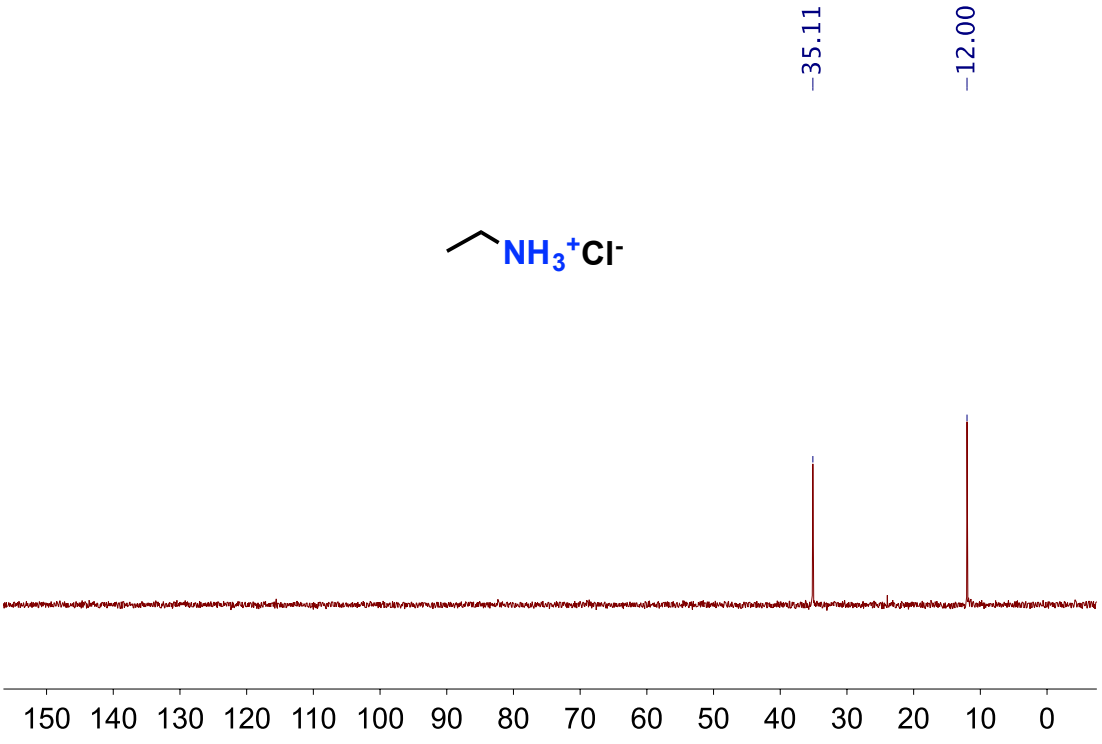
(**3a** ^{1}H NMR, * denotes $CDCl_3$ reference at 7.26 ppm)



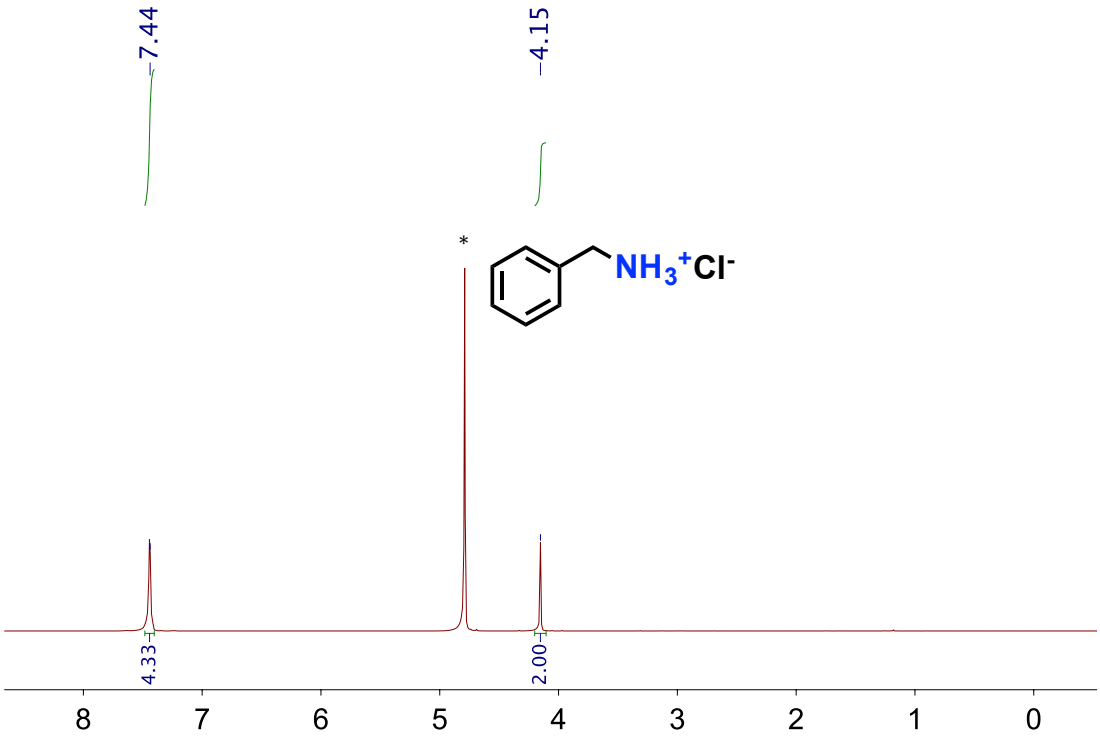
(**3a** $^{13}C\{^{1}H\}$ NMR, * denotes $CDCl_3$ reference at 77.16 ppm)



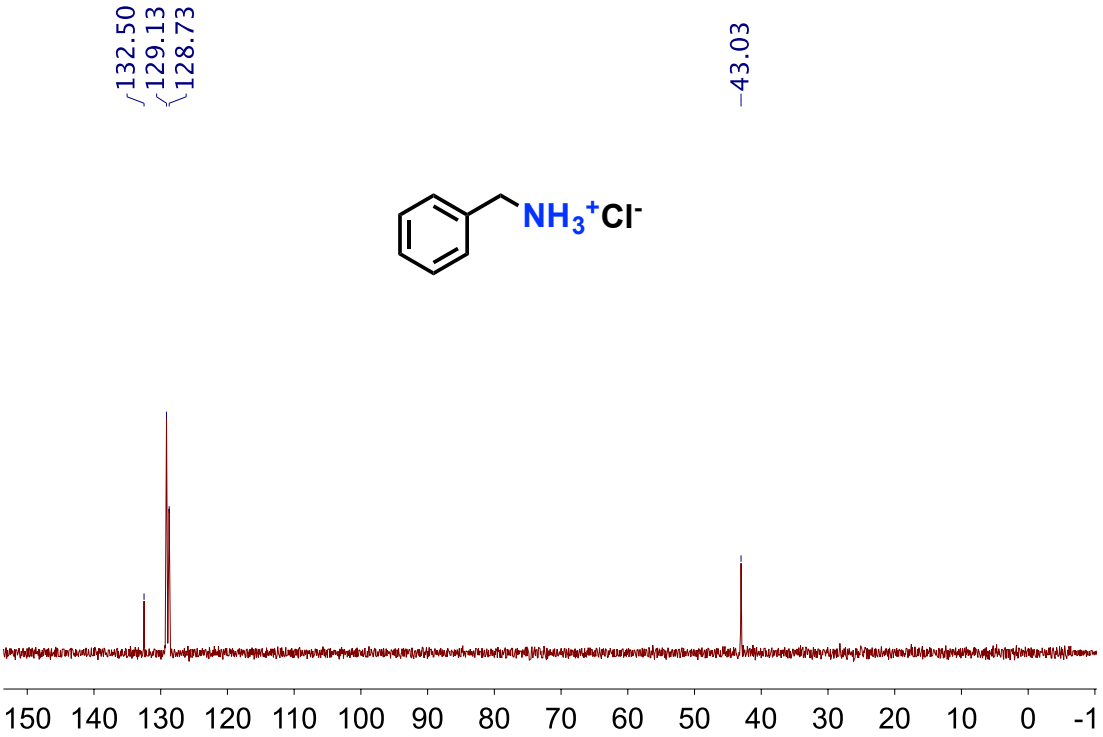
(**3b** ^{1}H NMR, * denotes D_2O reference at 4.79 ppm)



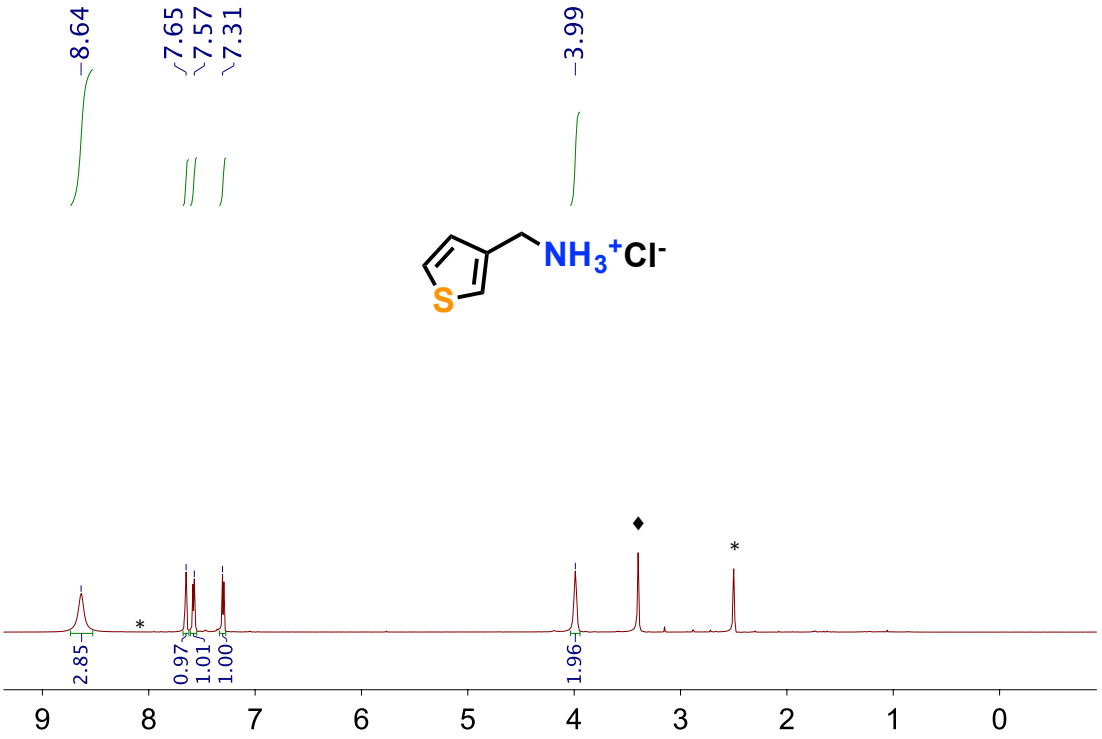
(**3b** ^{13}C{^{1}H} NMR)



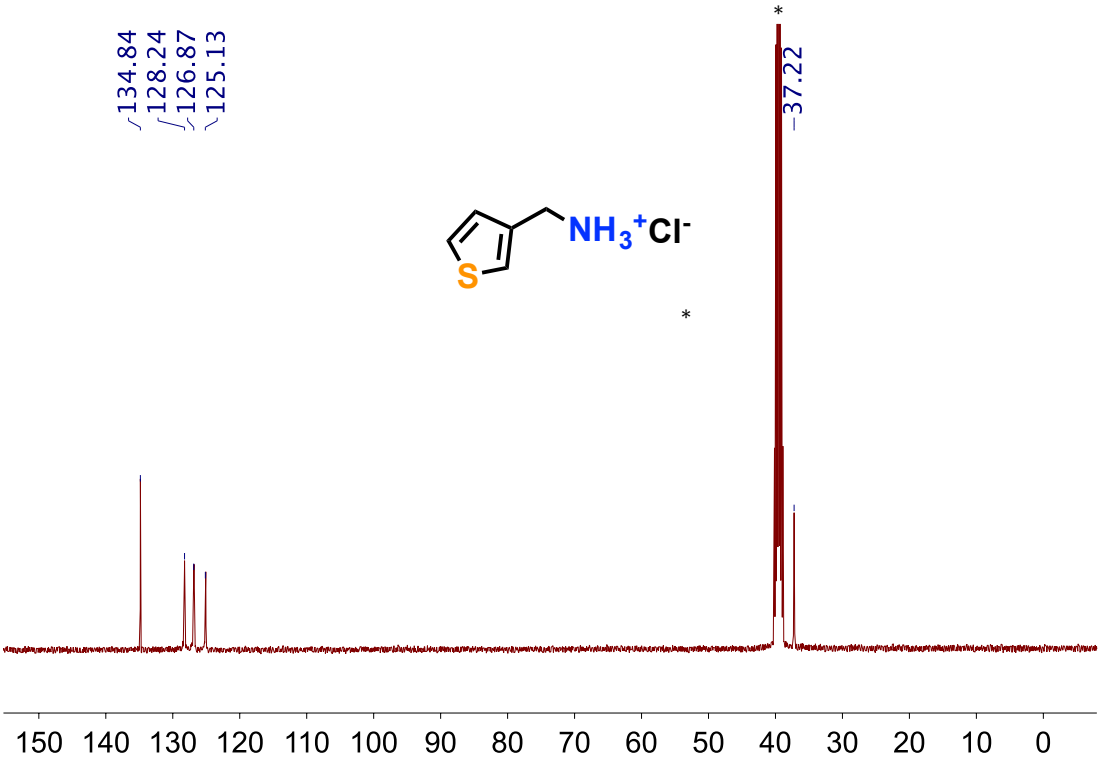
(**3c** ^{1}H NMR, * denotes D_2O reference at 4.79 ppm)



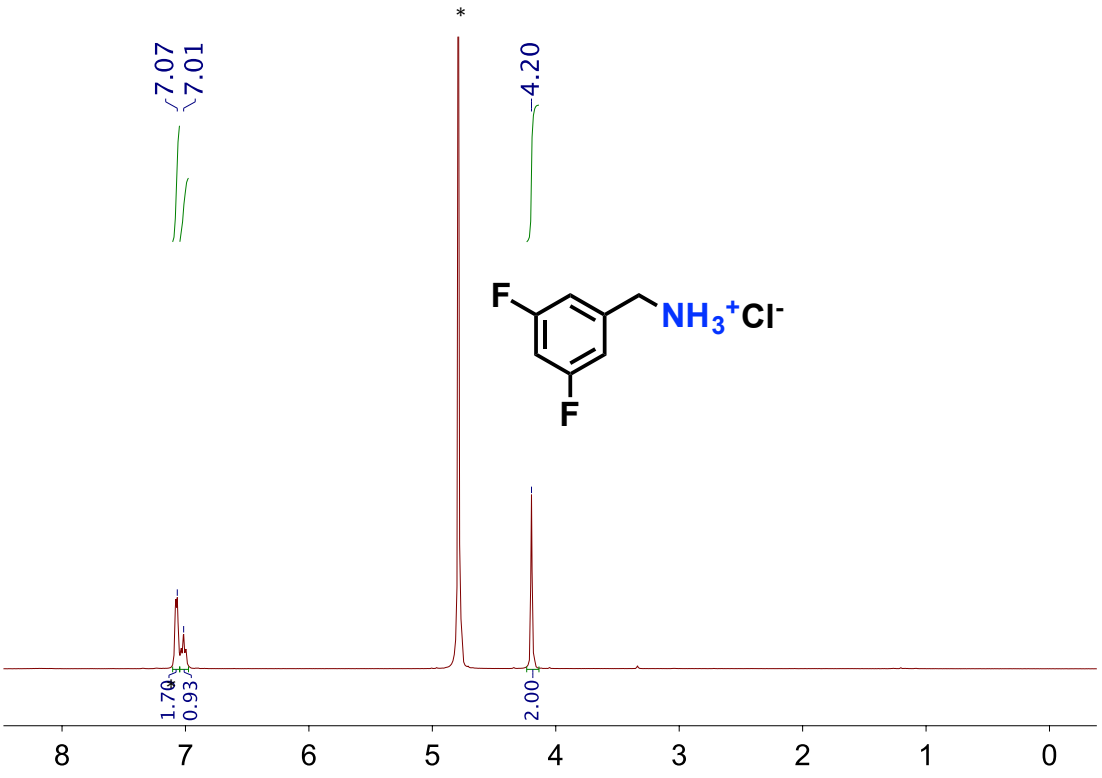
(**3c** ^{13}C{^{1}H} NMR)



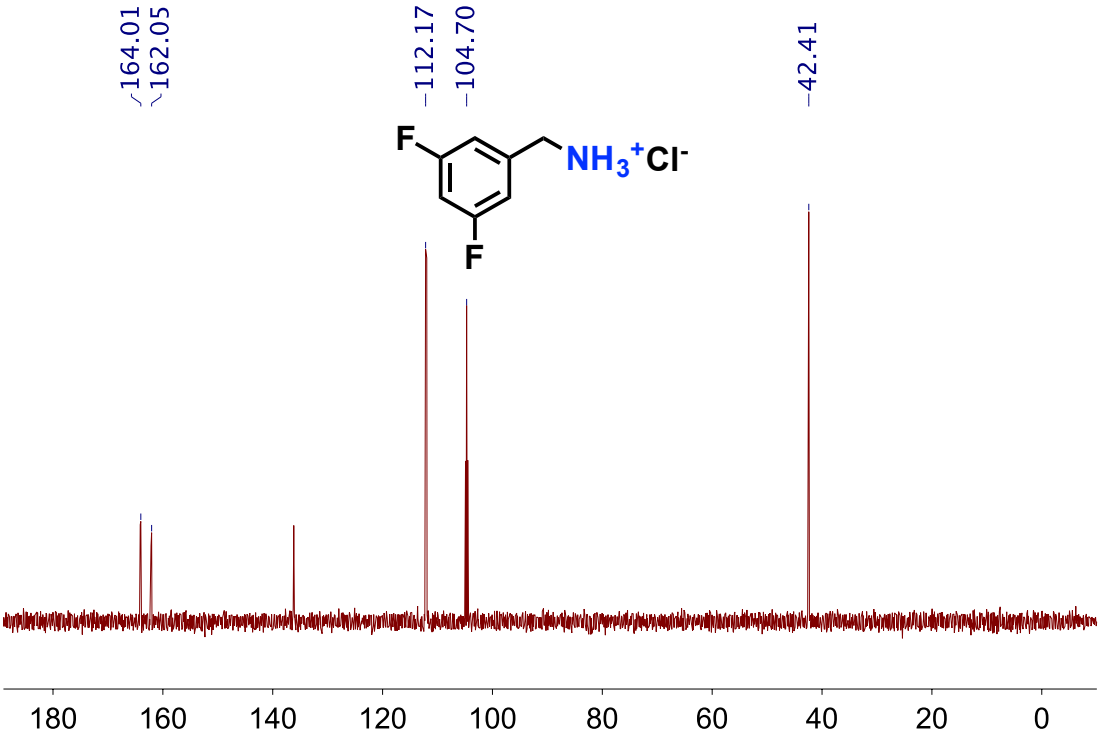
(**3d** ^{1}H NMR, * denotes $(CD_3)_2SO$ reference at 2.50 ppm, ♦denotes water)



(**3d** $^{13}C\{^{1}H\}$ NMR, * denotes $(CD_3)_2SO$ reference at 39.52 ppm)



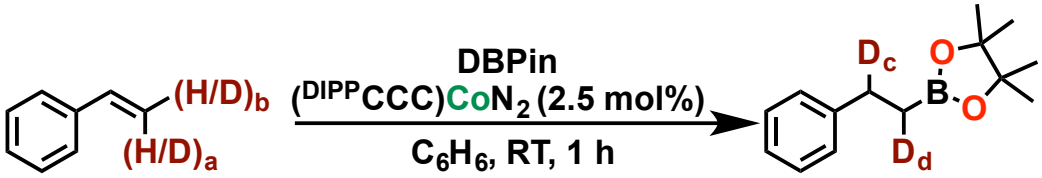
(**3e** ^{1}H NMR, * denotes D_2O reference at 4.79 ppm)

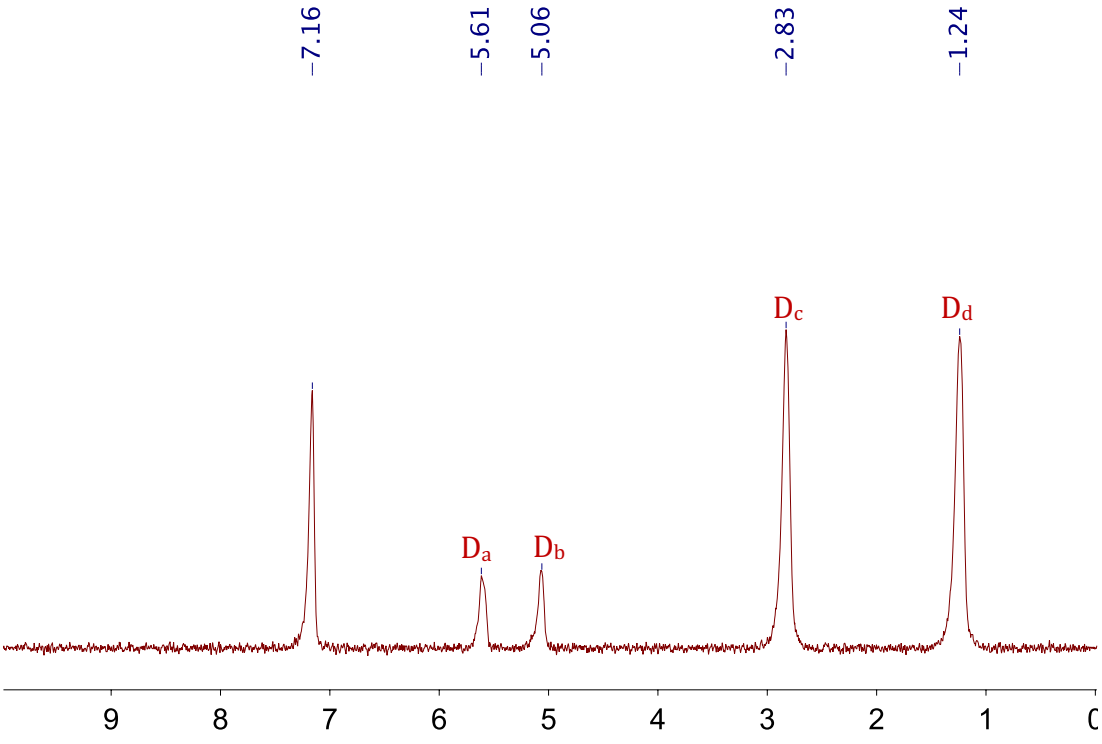


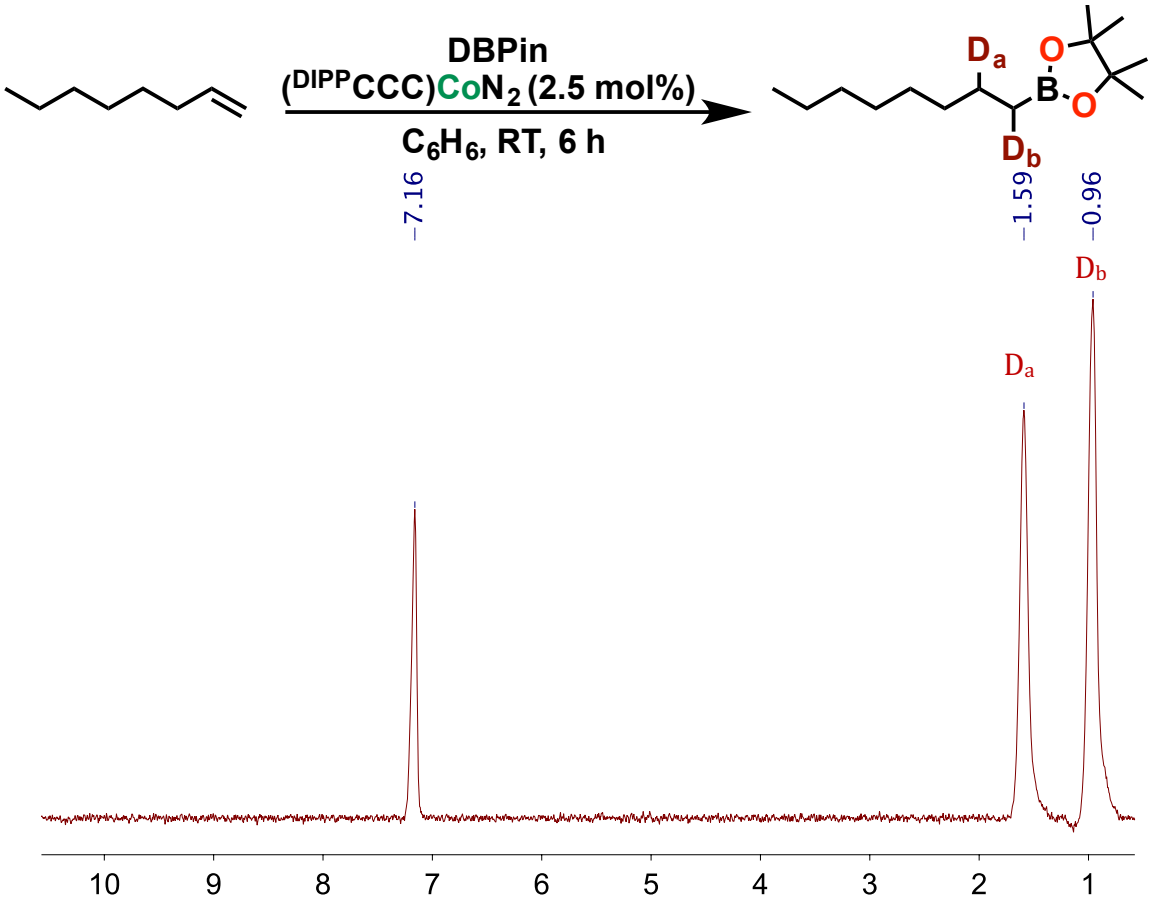
(**3e** ^{13}C{^{1}H} NMR)

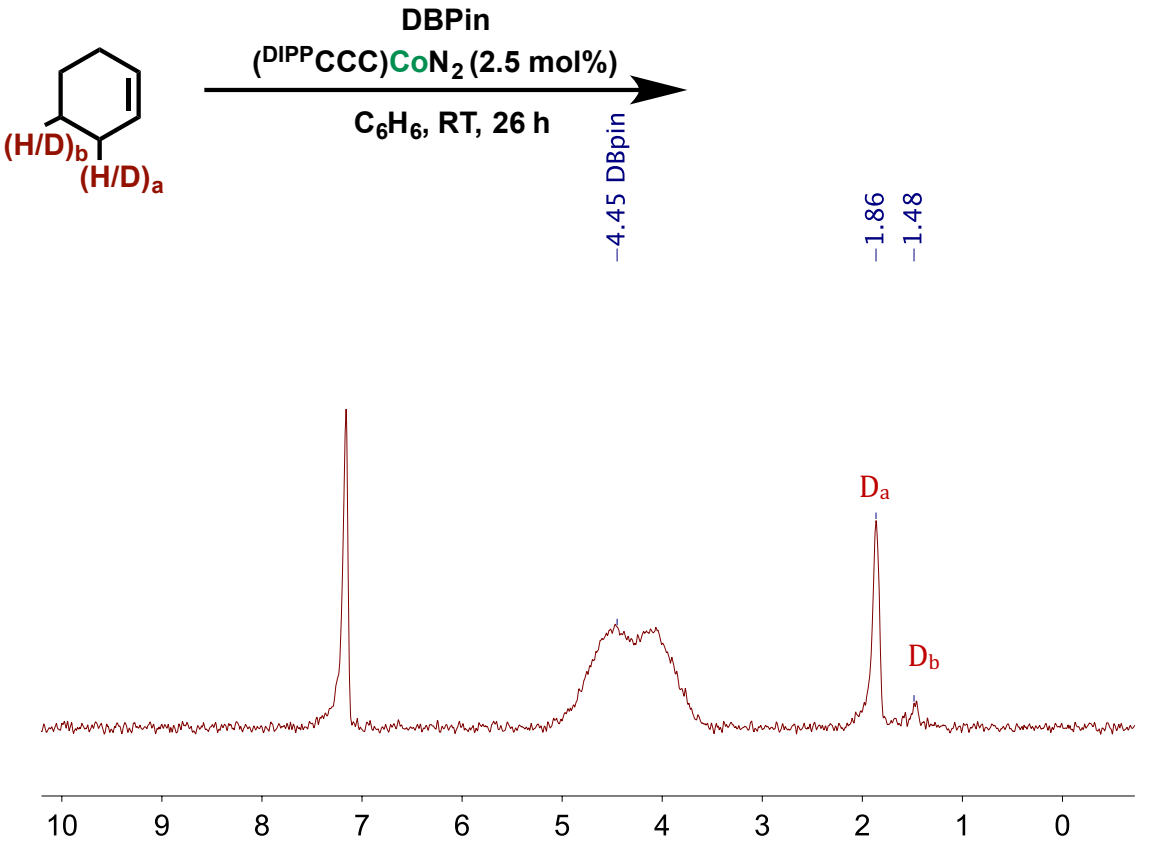
Deuterium Labelling Experiments

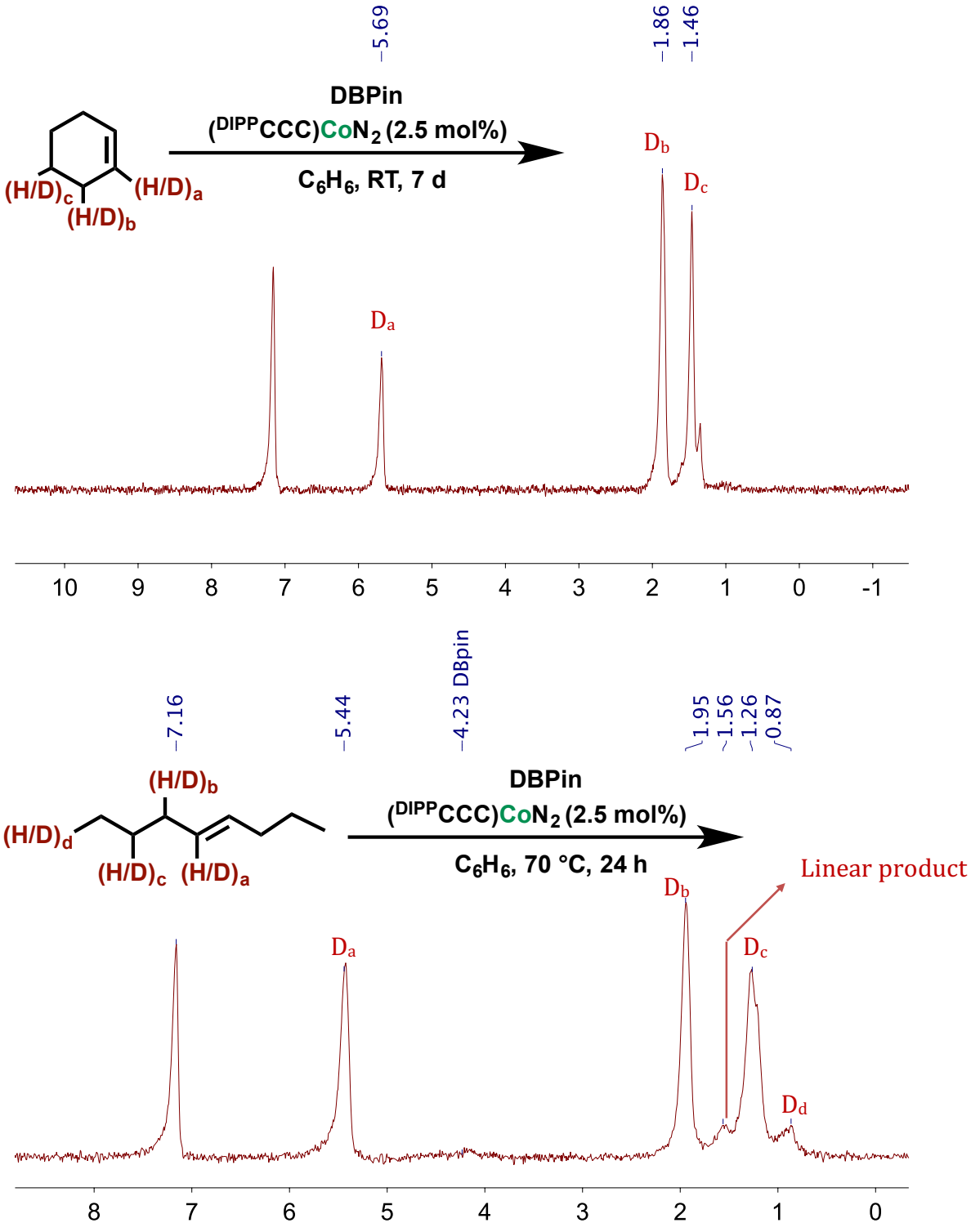
General Protocol for Deuterium Labelling Experiments. A 20 mL scintillation vial is charged with olefin (0.140 mmol) and deuterated pinacolborane (0.140 mmol), which was prepared according to literature procedure, inside a glove box.[16] Using benzene solvent, the resulting mixture is then transferred to a vial containing the catalyst (^{DIPP}CCC)CoN$_2$ (**1**) (0.0025 g, 0.00349 mmol), which was prepared according to literature procedure.[2] A final rinse and transfer with the benzene solvent, for a total solvent volume of ca. 2 mL, completes the setup and the reaction is stirred. Upon completion, an NMR aliquot of the reaction is taken.






DBPin
(DIPPCCC)CoN2 (2.5 mol%)
C6H6, RT, 6 h
Da
Db
−7.16
−1.59
−0.96
Db
Da
10
9
8
7
6
5
4
3
2
1


DBPin
(DIPPCCC)CoN2 (2.5 mol%)
C6H6, RT, 26 h
(H/D)b
(H/D)a
−4.45 DBpin
−1.86
−1.48
Da
Db
10
9
8
7
6
5
4
3
2
1
0


−5.69
−1.86
−1.46
DBPin
(DIPPCCC)CoN2 (2.5 mol%)
C6H6, RT, 7 d
(H/D)c
(H/D)a
(H/D)b
Db
Dc
Da
10 9 8 7 6 5 4 3 2 1 0 -1
−7.16
−5.44
−4.23 DBpin
1.95
1.56
1.26
0.87
(H/D)b
(H/D)d
(H/D)c
(H/D)a
DBPin
(DIPPCCC)CoN2 (2.5 mol%)
C6H6, 70 °C, 24 h
Linear product
Db
Da
Dc
Dd
8 7 6 5 4 3 2 1 0

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