

Supporting Information

Highly Stereoselective Synthesis of *cis*-Alkenyl Pinacolboronates and Potassium Organotrifluoroborates *via* a Hydroboration/ Protodeboration Approach

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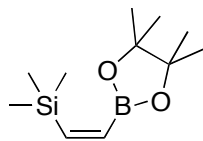
Philadelphia, Pennsylvania 19104-6323

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General. THF and Et₂O were distilled from sodium/benzophenone prior to use. Standard benchtop techniques were employed for handling air-sensitive reagents. Melting points (°C) are uncorrected. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a 500 MHz spectrometer. ¹¹B NMR spectra were recorded on a 400 or 500 MHz spectrometer with appropriate decoupling accessories. Analytical thin-layer chromatography (TLC) was performed on silica gel (60F-254) plates (0.25 mm) precoated with a fluorescent indicator. Standard flash chromatography procedures¹ were followed using 32–63 μm silica gel. Visualization was effected with ultraviolet light or KMnO₄ stain. AcOH and ethanolamine were handled in open air and stored on the benchtop. All alkynyl pinacolboronates were synthesized according to literature methods² on a 5.0 mmol scale.

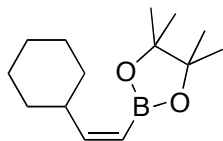
Compound Characterization:



(Z)-Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane

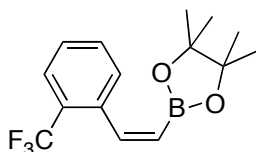
(1b). According to the general procedure, the product was obtained in 86% yield (389 mg, 1.72 mmol) as a transparent oil. ¹H-NMR (500 MHz, CDCl₃) δ: 6.87 (d, *J* = 18.7 Hz, 1H), 6.42 (d, *J* = 18.7 Hz, 1H), 1.27 (s, 12H), 0.15 (s, 9H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 157.9, 83.3, 24.9, -0.24.

The spectral data were in agreement with those reported in the literature.³



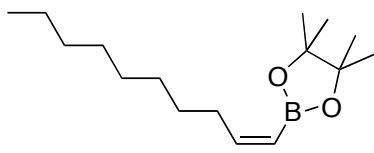
(Z)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b).

According to the general procedure, the product was obtained in 84% yield (396 mg, 1.68 mmol) as a transparent oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 6.25 (dd, $J = 13.0, 9.5$ Hz, 1H), 5.22 (d, $J = 13.0$ Hz, 1H), 2.64-2.76 (m, 1H), 1.58-1.78 (m, 4H), 1.01-1.41 (m, 18H); $^{13}\text{C-NMR}$ (125.8 MHz, CDCl_3) δ : 160.5, 82.7, 40.6, 33.4, 26.0, 25.8, 24.8; $^{11}\text{B-NMR}$ (128.37 MHz, CDCl_3) δ : 28.24; IR (neat) = 2978, 2926, 2851, 1709, 1626 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{14}\text{H}_{26}\text{BO}_2$ ($\text{M}+\text{H}$) $^+$ 237.2025, found 237.2017.



(Z)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-

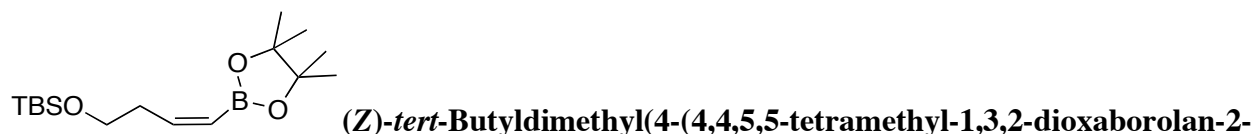
dioxaborolane (4b). According to the general procedure, the product was obtained in 78% yield (465 mg, 1.56 mmol) as a transparent oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 8.03 (s, 1H), 7.59 (d, $J = 7.9$ Hz, 1H), 7.51 (d, $J = 7.9$ Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.22 (d, $J = 15.0$ Hz, 1H), 5.70 (d, $J = 15.0$ Hz, 1H), 1.28 (s, 12H); $^{13}\text{C-NMR}$ (125.8 MHz, CDCl_3) δ : 146.9, 139.0, 132.3, 128.3, 125.3 (q, $J = 3.8$ Hz), 124.5 (q, $J = 3.8$ Hz), 83.7, 24.8; $^{19}\text{F-NMR}$ (471 MHz, CDCl_3) δ : -63.12; $^{11}\text{B-NMR}$ (128.37 MHz, CDCl_3) δ : 33.51; IR (neat) = 2980, 2933, 2199 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{18}\text{BF}_3\text{O}_2$ 298.1352, found 298.1363.



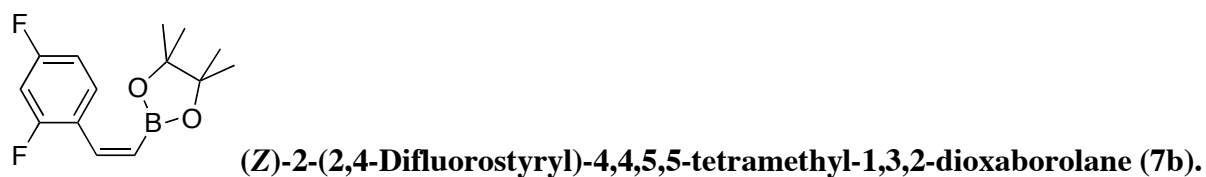
(Z)-2-(Dec-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b).

According to the general procedure, the product was obtained in 77% yield (410 mg, 1.54 mmol) as a transparent oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 6.37-6.52 (m, 1H), 5.32 (d, $J = 13.2$ Hz, 1H), 2.34-2.43 (m, 2H), 1.2-1.45 (m, 24H), 0.88 (t, $J = 6.6$ Hz, 3H); $^{13}\text{C-NMR}$ (125.8 MHz, CDCl_3) δ : 155.2, 82.8, 32.2, 32.0, 29.5, 29.4, 29.3, 29.1, 24.8, 22.7, 14.1.

The spectral data were in agreement with those reported in the literature.³

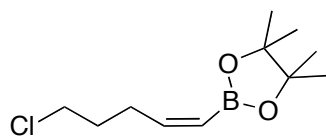


According to the general procedure, the product was obtained in 77% yield (480 mg, 1.54 mmol) as a transparent oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 6.41-6.53 (m, 1H), 5.42 (d, $J = 13.4$ Hz, 1H), 3.66 (t, $J = 7.0$ Hz, 2H), 2.60-2.66 (m, 2H), 1.26 (s, 12H), 0.89 (s, 9H), 0.06 (s, 6H); $^{13}\text{C-NMR}$ (125.8 MHz, CDCl_3) δ : 151.1, 82.9, 63.1, 36.0, 26.0, 24.9, 18.4, -5.2; $^{11}\text{B-NMR}$ (128.37 MHz, CDCl_3) δ : 28.04; IR (neat) = 2978, 2929, 2857, 1629 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{16}\text{H}_{34}\text{BO}_3\text{Si}$ ($\text{M}+\text{H}$)⁺ 313.2370, found 313.2369.



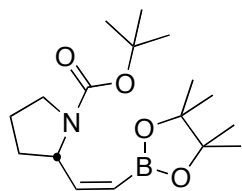
According to the general procedure, the product was obtained in 71% yield (377 mg, 1.42 mmol) as a transparent oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 7.58-7.71 (m, 1H), 7.23 (d, $J = 14.9$ Hz, 1H), 6.67-6.87 (m, 2H), 5.71 (d, $J = 14.9$ Hz, 1H), 1.26 (s, 12H); $^{13}\text{C-NMR}$ (125.8 MHz, CDCl_3) δ : 163.7, 161.6, 159.5, 139.5 (d, $J = 3.0$ Hz), 131.1 (q, $J = 4.8$ Hz), 121.5, 110.5 (dd, $J = 21.0, 3.8$

Hz), 103.4 (t, $J = 25.9$ Hz), 83.6, 24.8; ^{19}F -NMR (471 MHz, CDCl_3) δ : -110.72, -112.40; ^{11}B -NMR (128.37 MHz, CDCl_3) δ : 28.43; IR (neat) = 2979, 2929, 2853, 1625 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{17}\text{BF}_2\text{O}_2$ 266.1289, found 266.1293.



(Z)-2-(5-Chloropent-1-enyl)-4,4,5,5-tetramethyl-1,3,2-

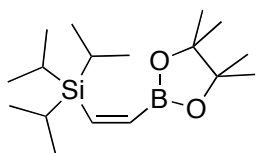
dioxaborolane (8b). According to the general procedure, the product was obtained in 66% yield (302 mg, 1.32 mmol) as a transparent oil (90:10 *cis/trans*). ^1H -NMR (500 MHz, CDCl_3) δ : 6.3-6.46 (m, 1H), 5.40 (d, $J = 13.4$ Hz, 1H), 3.52 (t, $J = 6.8$ Hz, 2H), 2.53 (m, 2H), 1.87 (m, 2H), 1.26 (s, 12H); ^{13}C -NMR (125.8 MHz, CDCl_3) δ : 152.5, 83.0, 44.4, 32.5, 29.6, 24.9; ^{11}B -NMR (128.37 MHz, CDCl_3) δ : 30.11; IR (neat) = 2979, 2933, 1629 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{11}\text{H}_{21}\text{BClO}_2$ (M+H) $^+$ 231.1323, found 231.1305.



(2S,Z)-tert-Butyl 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

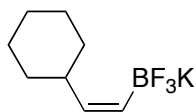
yl)vinyl)pyrrolidine-1-carboxylate (9b). According to the general procedure for polar compounds, the product was obtained in 57% yield (368 mg, 1.14 mmol) as a transparent oil after chromatography using 10% EtOAc/Hex. ^1H -NMR (500 MHz, CDCl_3) δ : 6.32 (bs, 1H) 5.31 (d, $J = 13.6$ Hz, 1H), 4.82 (dd, $J = 13.6, 7.2$ Hz, 1H), 3.48 (bs, 1H), 3.34-3.41 (m, 1H), 2.12-2.22 (m, 1H), 1.71-1.9 (m, 2H), 1.57-1.66 (m, 1H), 1.41 (bs, 9H), 1.26 (bs, 6H), 1.25 (bs, 6H); ^{13}C -NMR (125.8 MHz, CDCl_3) δ : 157.03, 154.6, 116.3, 82.9, 79.0, 58.2, 46.6, 34.1, 28.4, 24.8, 23.8;

^{11}B -NMR (128.37 MHz, CDCl_3) δ : 28.73; IR (neat) = 2976, 1697, 1632, 1391 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{17}\text{H}_{31}\text{BNO}_4$ ($\text{M}+\text{H}$) $^+$ 324.2346, found 324.2362.



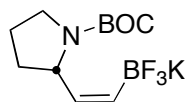
(Z)-Triisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)vinyl)silane (10b). According to the general procedure, the product was obtained in 93% yield (575 mg, 1.86 mmol) as a transparent oil (90% pure). ^1H -NMR (500 MHz, CDCl_3) δ : 6.72 (d, $J = 19.4$ Hz, 1H), 6.57 (d, $J = 19.4$ Hz, 1H), 1.25 (s, 12H), 1.05 (m, 21H); ^{13}C -NMR (125.8 MHz, CDCl_3) δ : 152.0, 83.2, 24.8, 19.0, 11.7; ^{11}B -NMR (128.37 MHz, CDCl_3) δ : 22.10; IR (neat) = 2941, 2865, 1687, 1582 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{17}\text{H}_{36}\text{BO}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$ 311.2577, found 311.2583.



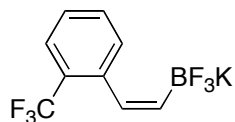
(Z)-2-Cyclohexylethenyltrifluoroborate (2c). According to the general

procedure for the preparation of potassium *cis*-alkenyltrifluoroborates, the product was obtained in 83% yield (359 mg, 1.66 mmol) as a white crystalline solid. mp: > 250 $^\circ\text{C}$. ^1H -NMR (500 MHz, Acetone- d_6) δ : 5.43 (m, 1H), 5.17 (m, 1H), 2.55 (m, 1H), 1.64 (m, 5H), 1.26 (m, 2H), 1.13 (m, 1H), 0.90 (m, 2H); ^{13}C -NMR (125.8 MHz, Acetone- d_6) δ : 143.9 (q, $J = 4.8$ Hz), 39.3, 33.9, 26.2, 26.0; ^{19}F -NMR (471 MHz, Acetone- d_6) δ : -136.36; ^{11}B -NMR (128.37 MHz, Acetone- d_6) δ : 3.64; IR (KBr) = 2932, 1624 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_8\text{H}_{13}\text{BF}_3$ ($\text{M}-\text{K}$) $^-$ 177.1062, found 177.1078.



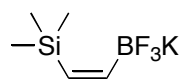
(*S,Z*)-*tert*-butyl-2-(2-(trifluoroborato)vinyl)pyrrolidine-1-carboxylate (**9c**).

Following the general procedure for the preparation of potassium *cis*-alkenyltrifluoroborates, but only stirring with KHF_2 (aq) for 0.5 h, the product was obtained in 83% yield (503 mg, 1.66 mmol) as a white crystalline solid. mp: > 250 °C. $^1\text{H-NMR}$ (500 MHz, Acetone- d_6) δ : 5.55 (m, 1H), 5.33 (m, 1H), 4.80 (m, 1H), 3.33 (m, 2H), 2.03 (m, 1H), 1.83 (m, 1H), 1.71 (m, 1H), 1.57 (m, 1H), 1.41 (s, 9H); $^{13}\text{C-NMR}$ (125.8 MHz, Acetone- d_6) δ : 154.4, 139.2, 77.6, 57.9, 46.7, 34.9, 28.5, 23.7; $^{19}\text{F-NMR}$ (471 MHz, Acetone- d_6) δ : -136.63; $^{11}\text{B-NMR}$ (128.37 MHz, Acetone- d_6) δ : 3.08; IR (KBr) = 2978, 2884, 1690, 1407 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{11}\text{H}_{18}\text{BF}_3\text{NO}_2$ (M-K) $^-$ 264.1383, found 264.1388.



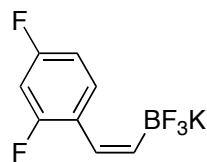
(*Z*)-2-(2-(Trifluoromethyl)phenyl)ethenyltrifluoroborate (**4c**). According to

the general procedure for the preparation of potassium *cis*-alkenyltrifluoroborates, the product was obtained in 82% yield (456 mg, 1.64 mmol) as a white crystalline solid. mp: > 250 °C. $^1\text{H-NMR}$ (500 MHz, Acetone- d_6) δ : 7.96 (s, 1H), 7.89 (d, $J = 6.6$ Hz, 1H), 7.34-7.43 (m, 2H), 6.65 (d, $J = 14.7$ Hz, 1H), 5.77-5.88 (m, 1H); $^{13}\text{C-NMR}$ (125.8 MHz, Acetone- d_6) δ : 142.2, 134.4 (q, $J = 4.8$ Hz), 132.1, 129.2 (q, $J = 31.7$ Hz), 128.1, 126.0, 125.1 (m), 123.9, 121.8 (q, $J = 3.8$ Hz); $^{19}\text{F-NMR}$ (471 MHz, Acetone- d_6) δ : -63.29, -136.82; $^{11}\text{B-NMR}$ (128.37 MHz, Acetone- d_6) δ : 3.10; IR (KBr) = 3090, 2987, 1613 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_9\text{H}_6\text{BF}_6$ (M-K) $^-$ 239.0467, found 239.0475.



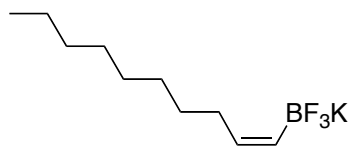
(Z)-2-Trimethylsilylethenyltrifluoroborate (1c). According to the general

procedure for the preparation of potassium *cis*-alkenyltrifluoroborates, the product was obtained in 78% yield (321 mg, 1.56 mmol) as a white crystalline solid. mp: > 250 °C. ¹H-NMR (500 MHz, Acetone-*d*₆) δ: 6.58 (dq, *J* = 18.7, 5.7 Hz, 1H), 5.89 (bs, 1H), 0.03 (s, 9H); ¹³C-NMR (125.8 MHz, Acetone-*d*₆) δ: 136.2, -0.16; ¹⁹F-NMR (471 MHz, Acetone-*d*₆) δ: -138.26; ¹¹B-NMR (128.37 MHz, Acetone-*d*₆) δ: 2.30; IR (KBr) = 2952, 1371 cm⁻¹; HRMS (ESI) calcd. for C₅H₁₁BF₃Si (M-K)⁻ 167.0675, found 167.0658.

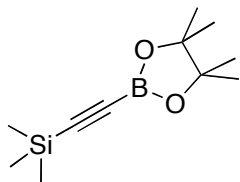


(Z)-2-(2,4-Difluorostyryl)ethenyltrifluoroborate (7c). According to the

general procedure for the preparation of potassium *cis*-alkenyltrifluoroborates, the product was obtained in 78% yield (384 mg, 1.56 mmol) as a white crystalline solid. mp: > 250 °C. ¹H-NMR (500 MHz, Acetone-*d*₆) δ: 8.11 (m, 1H), 6.79 (m, 2H), 6.66 (bd, *J* = 12.1 Hz, 1H), 5.81 (m, 1H); ¹³C-NMR (125.8 MHz, Acetone-*d*₆) δ: 161.5 (dd, *J* = 151.6, 11.5 Hz), 159.6 (dd, *J* = 152.6, 12.5 Hz), 132.0 (m), 125.4 (m), 125.2 (dd, *J* = 12.5, 3.8 Hz), 110.0 (dd, *J* = 21.1, 3.8 Hz), 101.9 (t, *J* = 25.9 Hz); ¹⁹F-NMR (471 MHz, Acetone-*d*₆) δ: -116.42, -117.18, -136.86; ¹¹B-NMR (128.37 MHz, Acetone-*d*₆) δ: 2.01; IR (KBr) = 3082, 2982, 1618 cm⁻¹; HRMS (ESI) calcd. for C₈H₅BF₅ (M-K)⁻ 207.0404, found 207.0390.

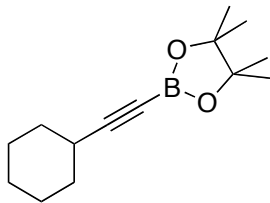


(Z)-1-Decenyltrifluoroborate (5c). According to the general procedure for the preparation of potassium *cis*-alkenyltrifluoroborates, the product was obtained in 72% yield (354 mg, 1.44 mmol) as a white crystalline solid. mp: > 250 °C. ¹H-NMR (500 MHz, Acetone-*d*₆) δ: 5.57 (s, 1H), 5.27 (m, 1H), 2.06 (m, 2H), 1.16 (bs, 12H), 0.75 (t, *J* = 7.0 Hz, 3H); ¹³C-NMR (125.8 MHz, Acetone-*d*₆) δ: 136.4 (q, *J* = 4.8 Hz), 31.8, 31.1, 30.6, 29.6, 29.4, 29.2, 22.4, 13.4; ¹⁹F-NMR (471 MHz, Acetone-*d*₆) δ: -136.39; ¹¹B-NMR (128.37 MHz, Acetone-*d*₆) δ: 3.75; IR (KBr) = 2926, 2854, 1638, 1406 cm⁻¹; HRMS (ESI) calcd. for C₁₀H₁₉BF₃ (M-K)⁻ 207.1532, found 207.1539.



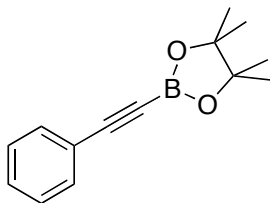
Trimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)silane

(1a). According to the literature procedure,² the product was obtained in 70% yield (780 mg, 3.5 mmol) as a transparent oil. ¹H-NMR (500 MHz, CDCl₃) δ: 1.27 (s, 12H), 0.18 (s, 9H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 84.4, 24.7, -0.05. The carbons bound to boron and silicon were not observed due to low intensity; ¹¹B-NMR (128.37 MHz, CDCl₃) δ: 22.66; IR (neat) = 2982, 2143 cm⁻¹; HRMS (CI) calcd. for C₁₁H₂₂BO₂Si (M+H)⁺ 225.1482, found 225.1489.



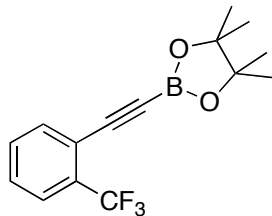
2-(Cyclohexylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a).

According to the literature procedure,² the product was obtained in 72% yield (834 mg, 3.6 mmol) as a transparent oil. ¹H-NMR (500 MHz, CDCl₃) δ: 2.3-2.47 (m, 1H), 1.76-1.86 (m, 2H), 1.64-1.75 (m, 2H), 1.41-1.55 (m, 4H), 1.27 (s, 14H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 84.0, 32.1, 29.8, 29.7, 25.8, 24.8, 24.7, 24.6; ¹¹B-NMR (128.37 MHz, CDCl₃) δ: 21.7; IR (neat) = 2978, 2930, 2854, 2202, 1449 cm⁻¹; Compound was found to be too unstable for mass spectral analysis.



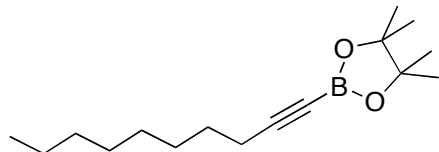
4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (3a).

According to the literature procedure,² the product was obtained in 95% yield (1.08 g, 4.75 mmol) as a transparent oil. ¹H-NMR (500 MHz, CDCl₃) δ: 7.49-7.54 (m, 2H), 7.29-7.42 (m, 3H), 1.29 (s, 12H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 132.3, 129.4, 128.4, 121.8, 84.3, 24.4. The quaternary carbon and the carbon bound to boron were not observed due to low intensity; ¹¹B-NMR (128.37 MHz, CDCl₃) δ: 23.17; IR (neat) = 2979, 2930, 2243, 2193 cm⁻¹; HRMS (CI) calcd. for C₁₄H₁₈BO₂ (M+H)⁺ 229.1340, found 229.1395.



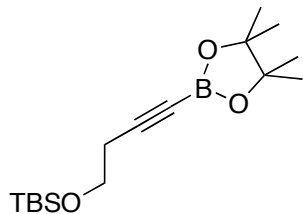
4,4,5,5-Tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-

dioxaborolane (4a). According to the literature procedure,² the product was obtained in 82% yield (1.23 g, 4.1 mmol) as a transparent oil. ¹H-NMR (500 MHz, CDCl₃) δ: 7.28 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 1.31 (s, 12H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 135.4, 131.2 (d, *J* = 32.6 Hz), 129.3 (q, *J* = 3.8 Hz), 128.9, 125.9 (q, *J* = 3.8 Hz), 122.9, 99.7, 84.7, 78.8, 24.7; ¹⁹F-NMR (471 MHz, CDCl₃) δ: -62.37; ¹¹B-NMR (128.37 MHz, CDCl₃) δ: 23.01; IR (neat) = 2980, 2933, 2199 cm⁻¹; HRMS (ESI) calcd. for C₁₅H₁₆BF₃O₂ 296.1195, found 296.1210.

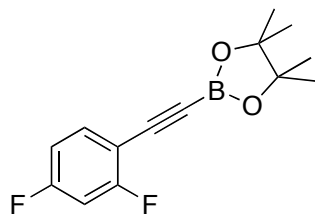


2-(Dec-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(5a). According to the literature procedure,² the product was obtained in 81% yield (1.05 g, 4.05 mmol) as a transparent oil. ¹H-NMR (500 MHz, CDCl₃) δ: 2.20 (t, *J* = 7.2 Hz, 2H), 1.43-1.54 (m, 2H), 1.28-1.40 (m, 2H), 1.22 (bs, 20H), 0.83 (t, *J* = 7.1 Hz, 3H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 84.0, 31.8, 29.1, 29.0, 28.8, 28.1, 24.8, 24.6, 24.5, 22.6, 19.5, 14.1; ¹¹B-NMR (128.37 MHz, CDCl₃) δ: 22.40; IR (neat) = 2978, 2929, 2856, 2209 cm⁻¹; HRMS (CI) calcd. for C₁₆H₃₀BO₂ (M+H)⁺ 265.2338, found 265.2347.



tert-Butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-ynoxy)silane (6a). According to the literature procedure,² the product was obtained in 86% yield (1.33 g, 4.3 mmol) as a transparent oil. ¹H-NMR (500 MHz, CDCl₃) δ: 3.73 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.3 Hz, 2H), 1.24 (s, 12H), 0.86 (s, 9H), 0.03 (s, 6H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 101.3, 84.1, 61.5, 25.9, 24.6, 23.9, 18.3, -5.4; ¹¹B-NMR (128.37 MHz, CDCl₃) δ: 22.39; IR (neat) = 2929, 2857, 2213 cm⁻¹; HRMS (CI) calcd. for C₁₆H₃₂BO₃Si (M+H)⁺ 311.2214, found 311.2209.

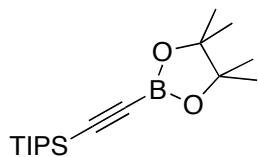


2-((2,4-Difluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7a). According to the literature procedure,² the product was obtained in 85% yield (1.12 g, 4.25 mmol) as a transparent oil. ¹H-NMR (500 MHz, CDCl₃) δ: 7.44-7.53 (m, 1H), 6.78-6.88 (m, 2H), 1.32 (s, 12H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 164.7 (dd, *J* = 66.2, 12.5 Hz), 162.6 (dd, *J* = 62.4, 12.5 Hz), 135.4 (dd, *J* = 9.6, 1.9 Hz), 111.65 (dd, *J* = 22.1, 3.8 Hz), 107.1 (dd, *J* = 15.4, 3.8 Hz), 104.4 (t, *J* = 2.5 Hz), 93.6, 84.6, 24.7; ¹⁹F-NMR (471 MHz, CDCl₂) δ: -104.23, -105.31; ¹¹B-NMR (128.37 MHz, CDCl₃) δ: 23.27; IR (neat) = 2980, 2933, 2201, 1615, 1588 cm⁻¹; HRMS (CI) calcd. for C₁₄H₁₆BF₂O₂ (M+H)⁺ 265.1211, found 265.1202.



2-(5-Chloropent-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(8a). According to the general procedure,² the product was obtained in 93% yield (1.06 g, 1.32 mmol) as a transparent oil (90:10 *cis/trans*). ¹H-NMR (500 MHz, CDCl₃) δ: 3.59 (td, *J* = 6.4, 1.7 Hz, 2H), 2.41 (t, *J* = 6.8 Hz, 2H), 1.94 (m, 2H), 1.22 (s, 12H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 102.5, 84.1, 43.4, 30.9, 24.6, 16.9; ¹¹B-NMR (128.37 MHz, CDCl₃) δ: 22.76; IR (neat) = 2978, 2932, 2209 cm⁻¹; HRMS (CI) calcd. for C₁₁H₁₉BClO₂ (M+H)⁺ 229.1167, found 229.1160.



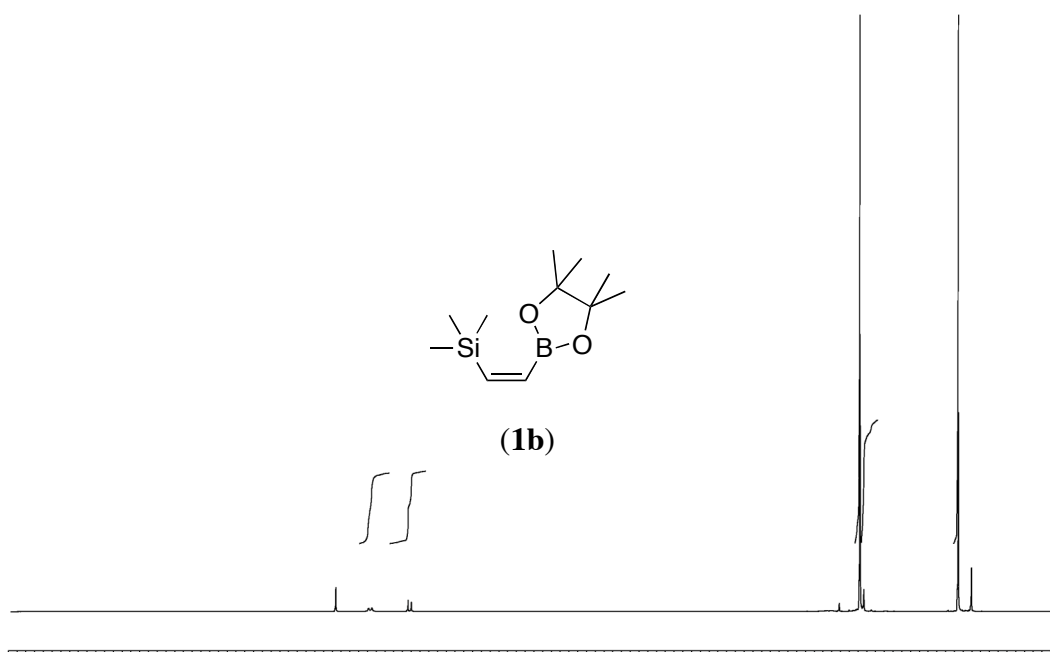
Triisopropyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)silane

(10a). According to the literature procedure,² the product was obtained in 77% yield (1.19 g, 3.85 mmol) as a transparent oil. ¹H-NMR (500 MHz, CDCl₃) δ: 1.27 (bs, 12H), 1.08 (m, 21H); ¹³C-NMR (125.8 MHz, CDCl₃) δ: 107.5, 84.17, 24.7, 18.5, 11.1; ¹¹B-NMR (128.37 MHz, CDCl₃) δ: 22.54; IR (neat) = 2962, 2142 cm⁻¹; HRMS (CI) calcd. for C₁₇H₃₄BO₂Si (M+H)⁺ 309.2421, found 309.2427.

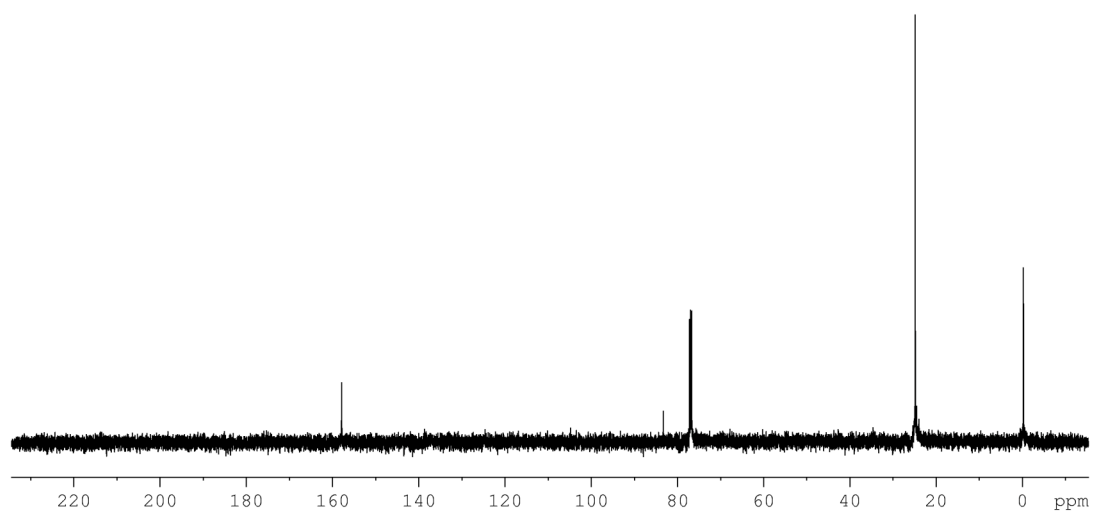
¹ Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *14*, 2923-2925.

² Brown, H. C.; Bhat, N. G.; Srebnik, M. *Tetrahedron Lett.* **1988**, *29*, 2631-2634.

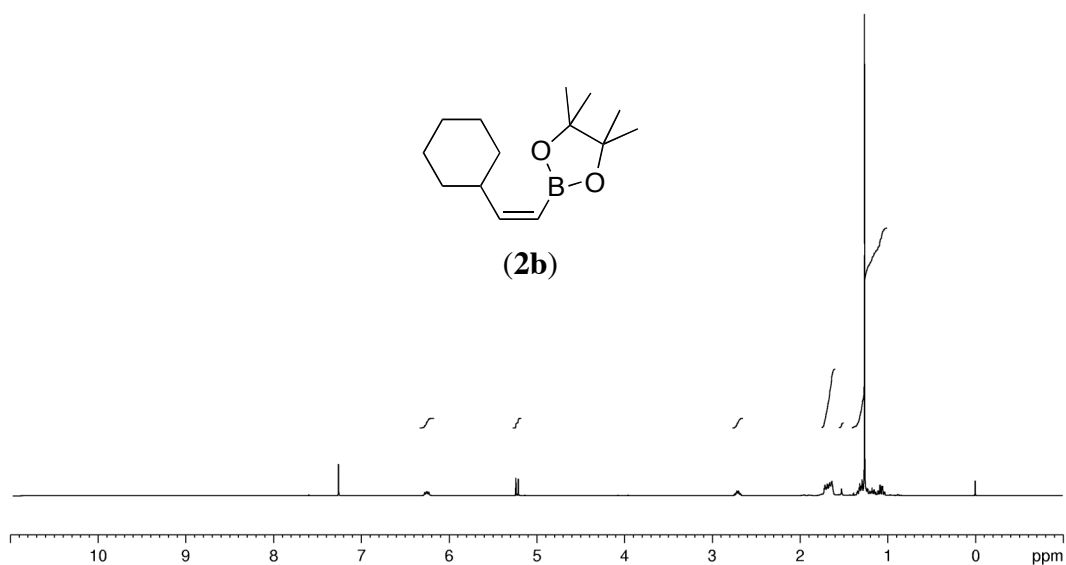
³ Miyaura, N.; Ohmura, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 4990-4991.



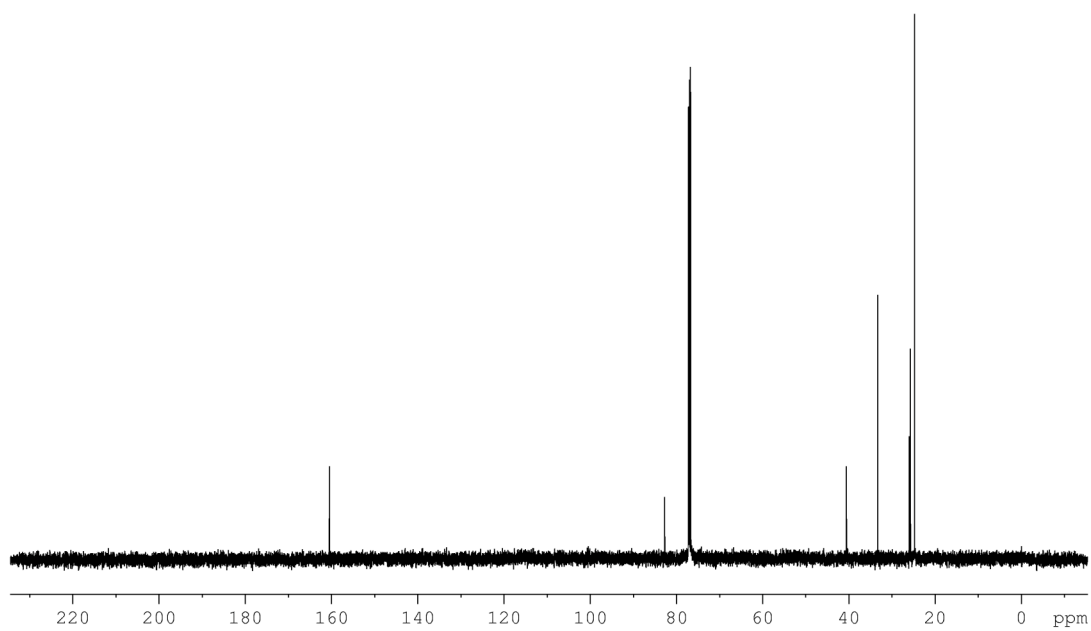
^1H NMR (500 MHz, CDCl_3) Spectrum of (Z)-Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**1b**)



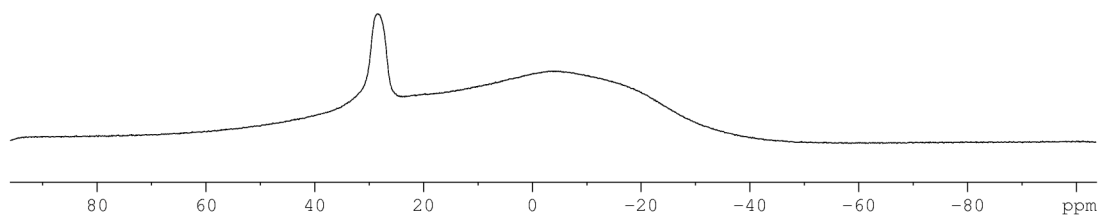
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of (Z)-Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**1b**)



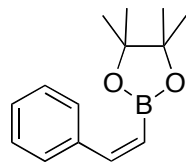
^1H NMR (500 MHz, CDCl_3) Spectrum of (*Z*)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b**)



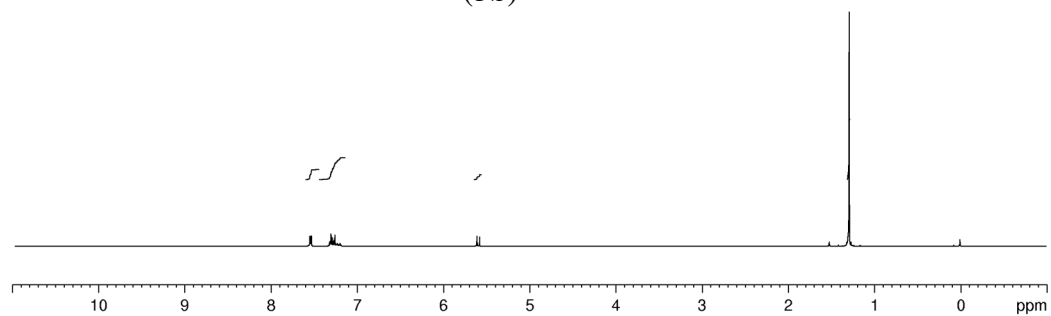
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of (*Z*)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b**)



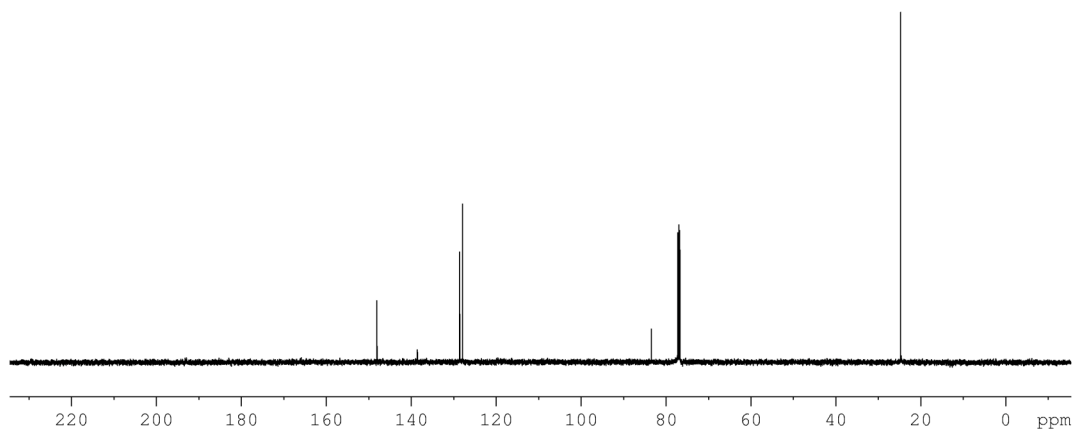
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of (*Z*)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b**)



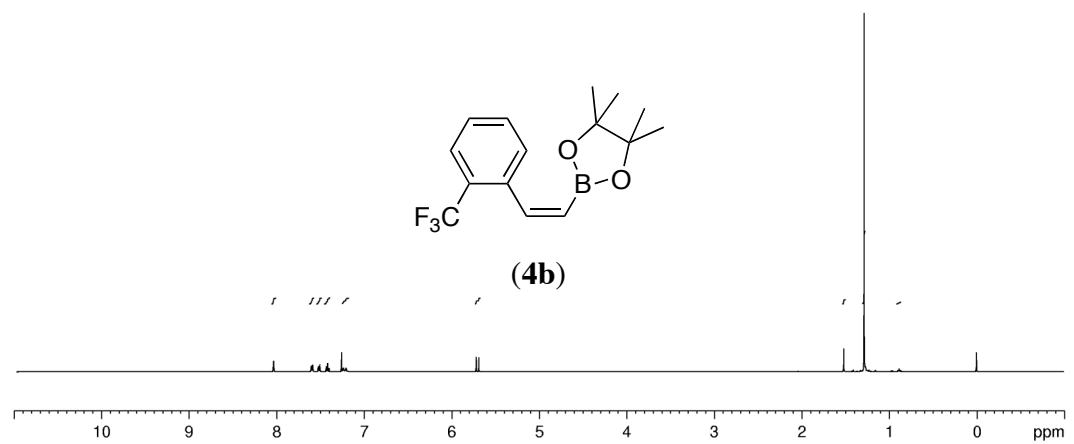
(**3b**)



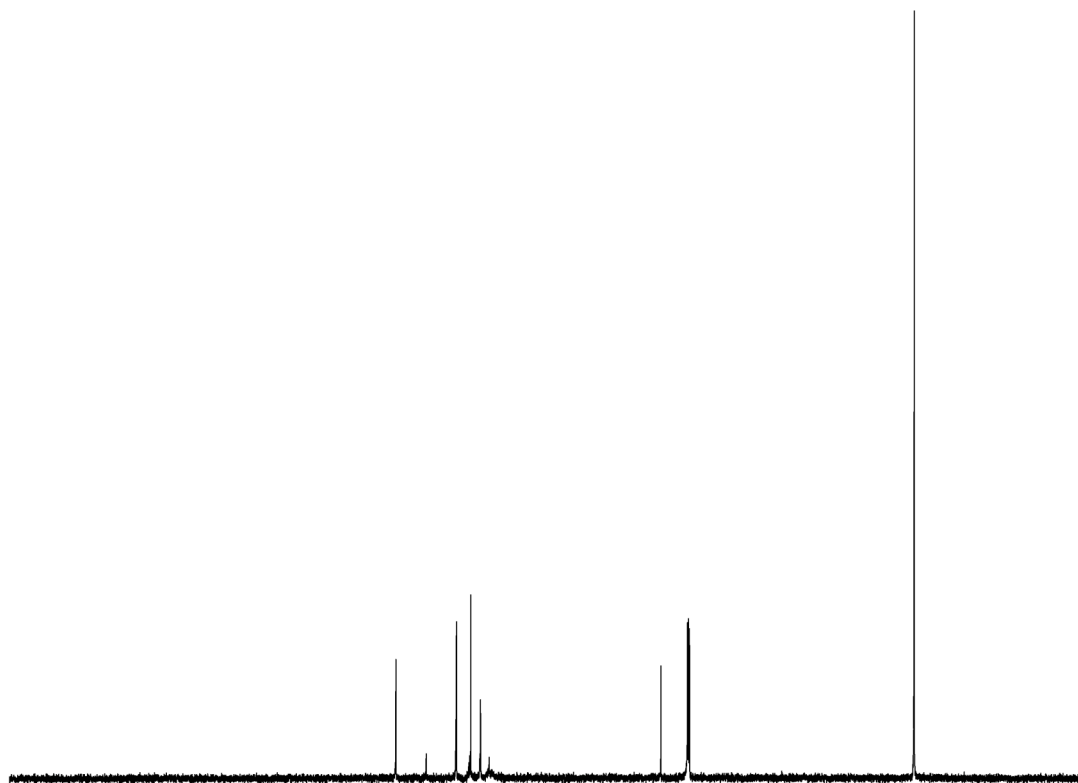
^1H NMR (500 MHz, CDCl_3) Spectrum of (*Z*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**3b**)



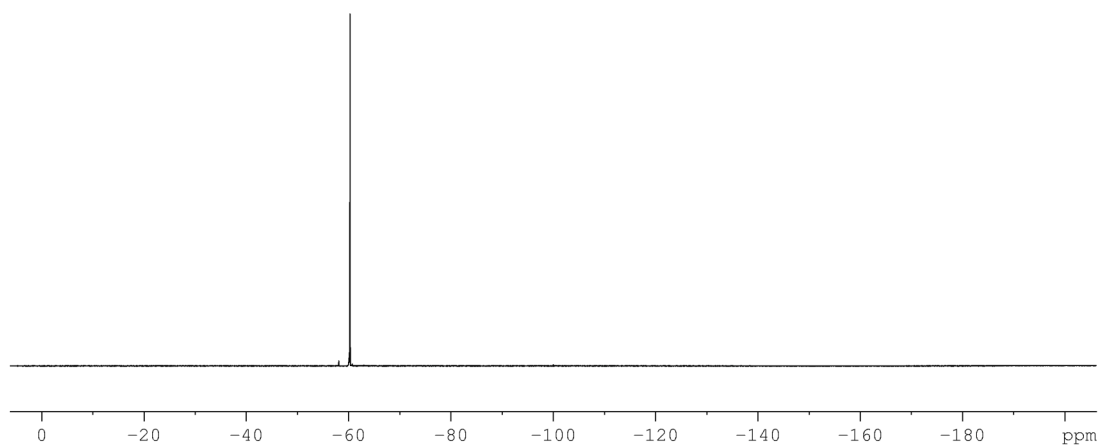
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of (*Z*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**3b**)



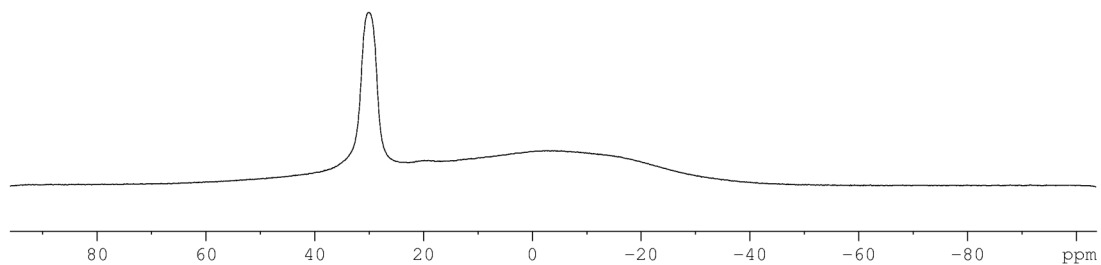
^1H NMR (500 MHz, CDCl_3) Spectrum of (*Z*)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (**4b**)



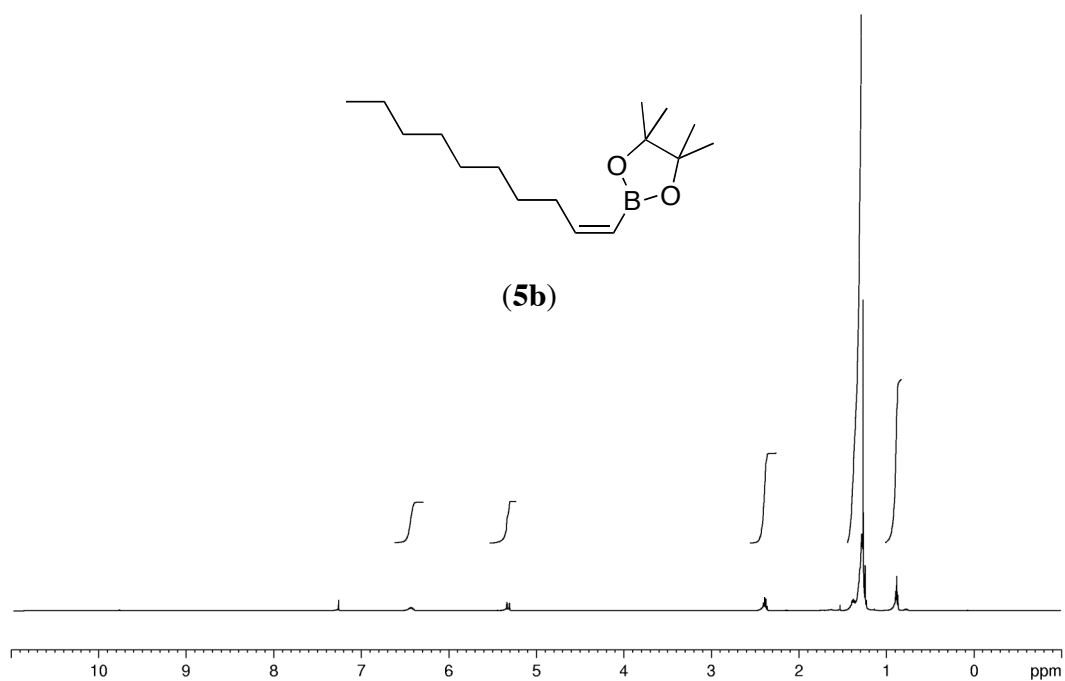
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of (*Z*)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (**4b**)



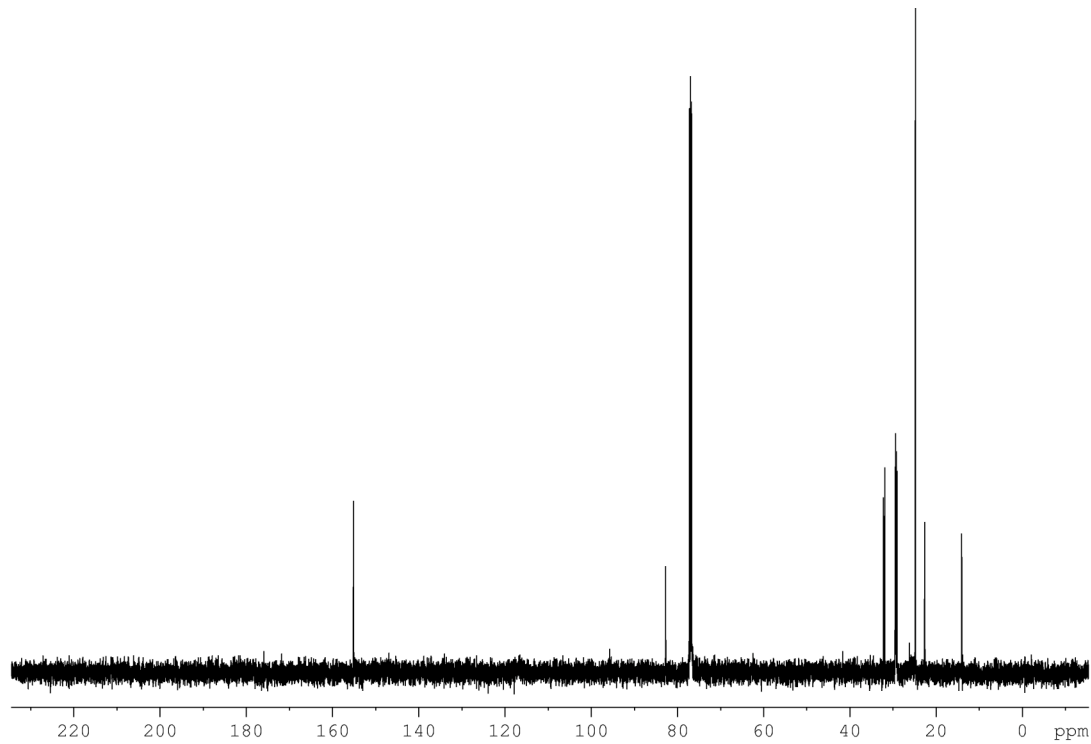
^{19}F NMR (471 MHz, CDCl_3) Spectrum of (*Z*)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (**4b**)



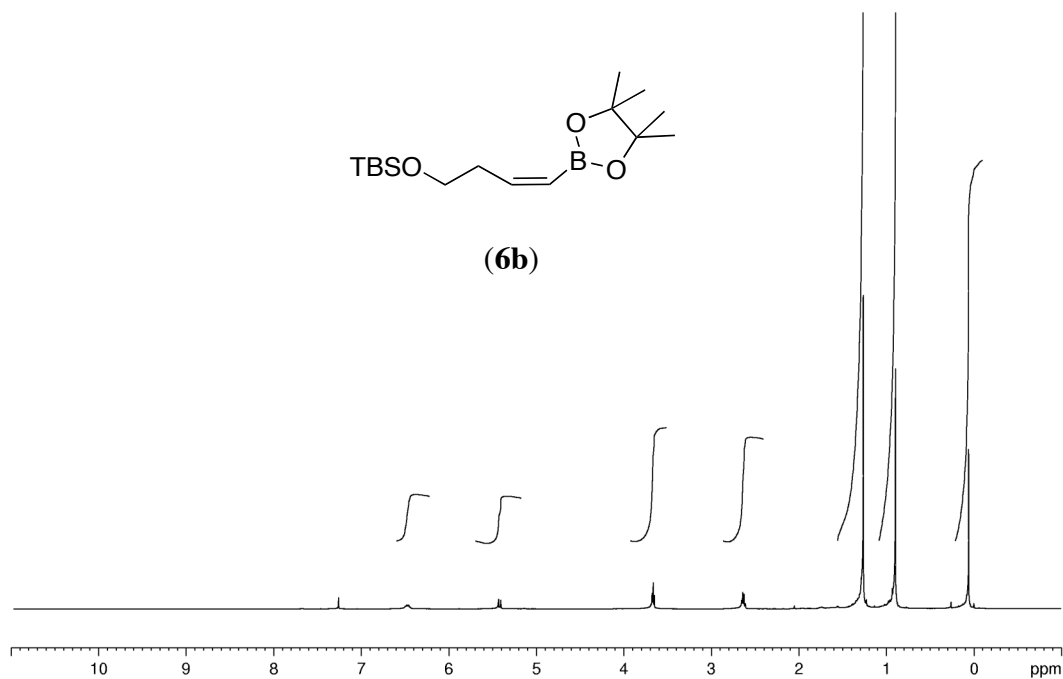
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of (*Z*)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (**4b**)



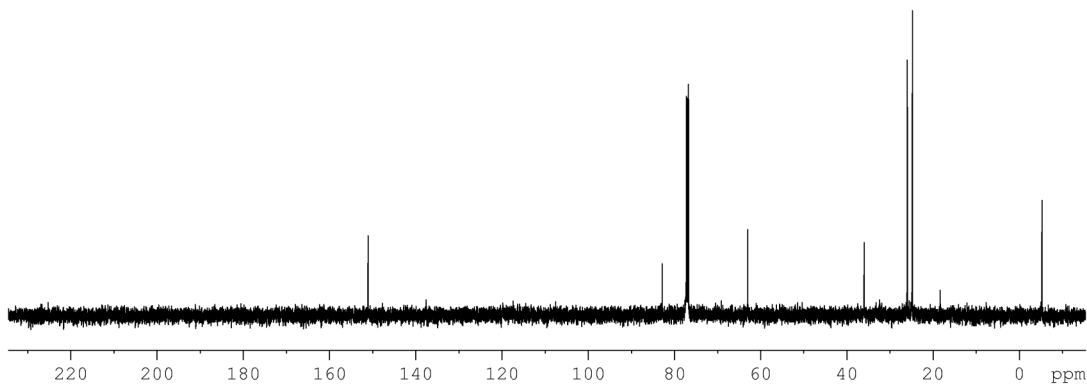
^1H NMR (500 MHz, CDCl_3) Spectrum of (*Z*)-2-(Dec-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5b**)



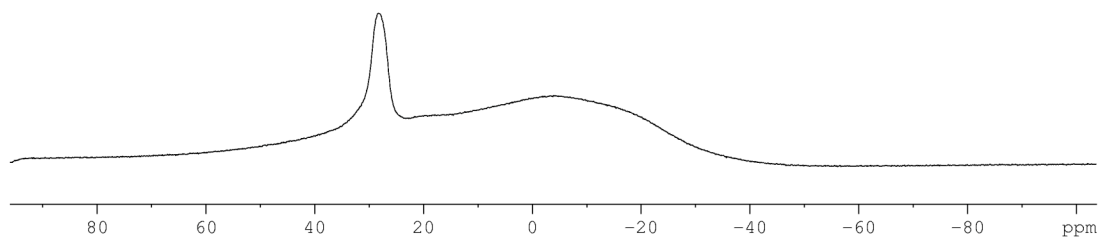
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of (*Z*)-2-(Dec-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5b**)



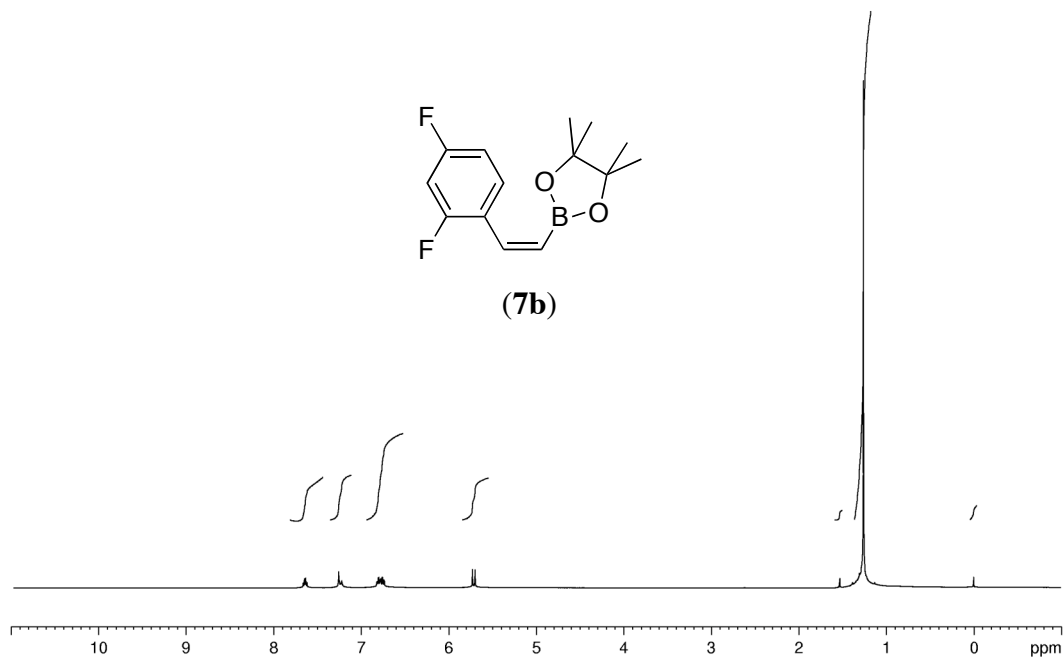
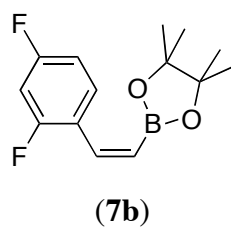
^1H NMR (500 MHz, CDCl_3) Spectrum of (*Z*)-*tert*-Butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enyloxy)silane (**6b**)



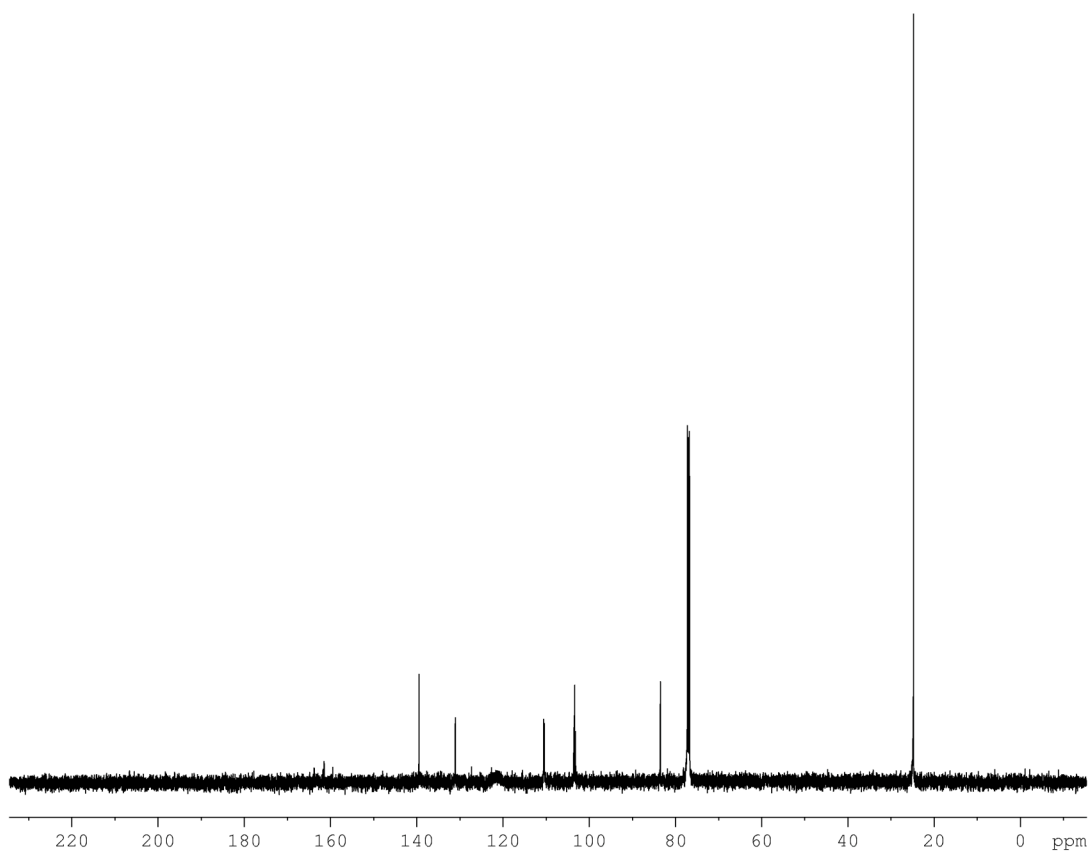
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of (*Z*)-*tert*-Butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enyloxy)silane (**6b**)



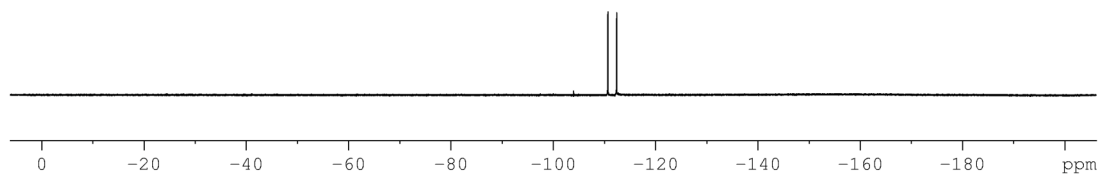
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of (*Z*)-*tert*-Butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enyloxy)silane (**6b**)



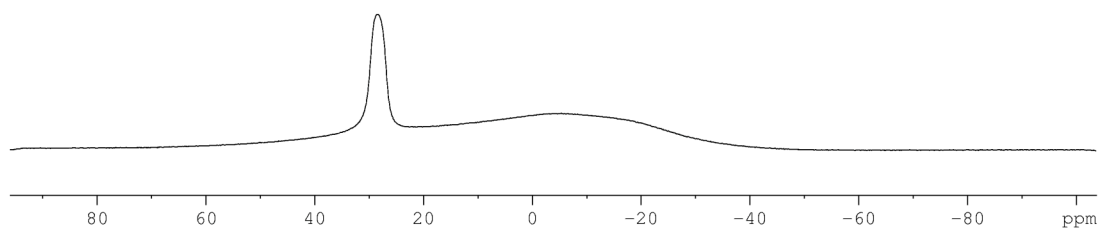
^1H NMR (500 MHz, CDCl_3) Spectrum of (Z)-2-(2,4-Difluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7b**)



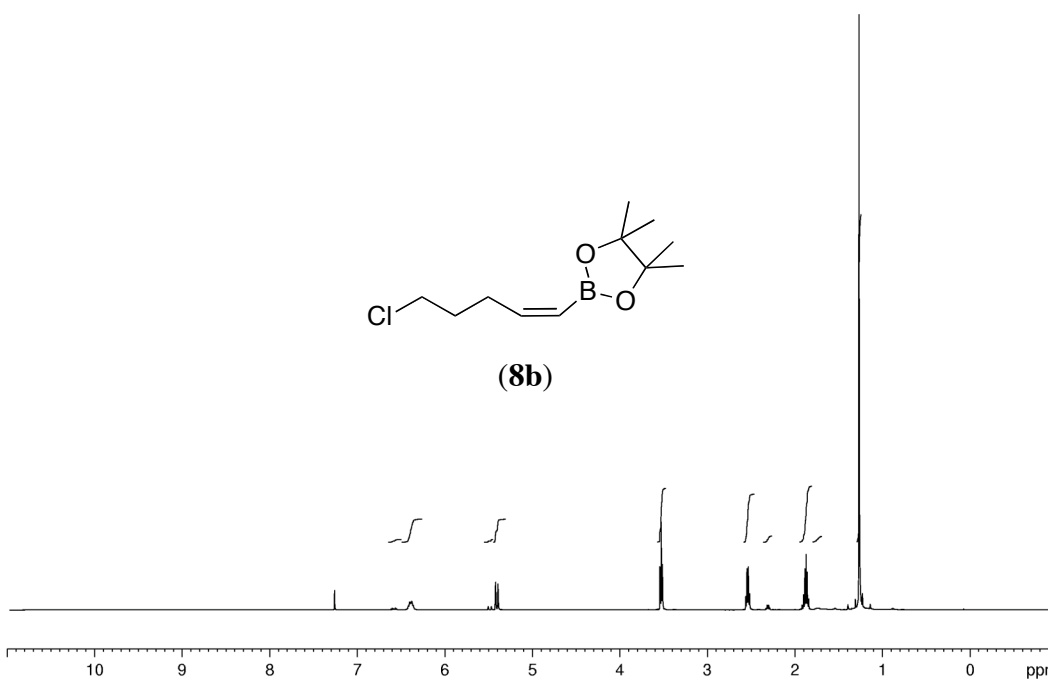
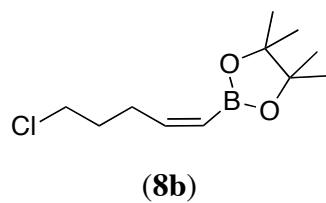
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of (Z)-2-(2,4-Difluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7b**)



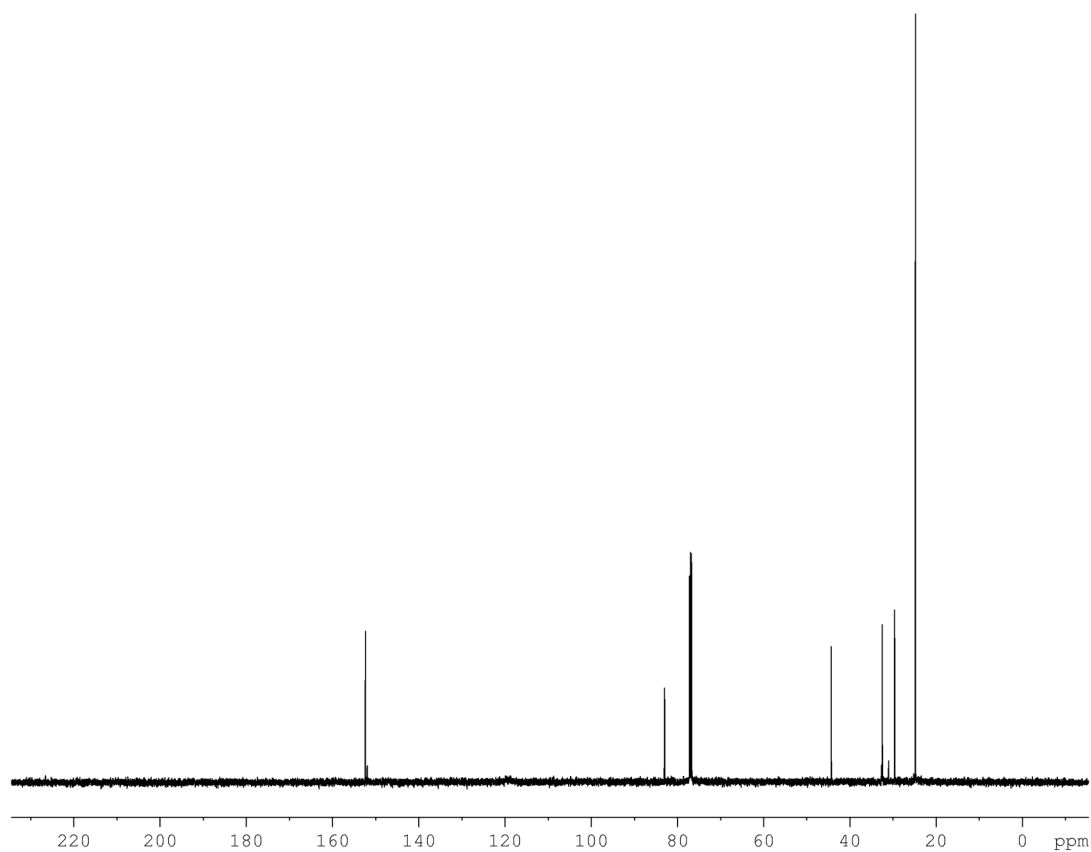
^{19}F NMR (471 MHz, CDCl_3) Spectrum of (*Z*)-2-(2,4-Difluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7b**)



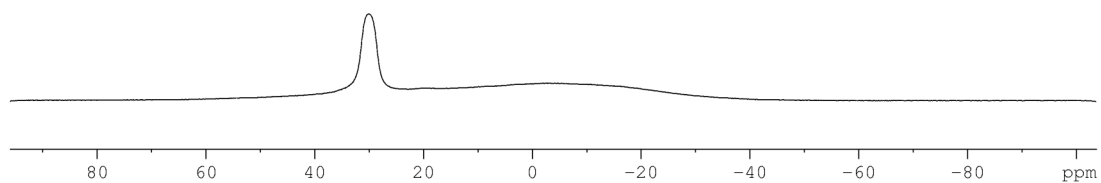
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of (*Z*)-2-(2,4-Difluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7b**)



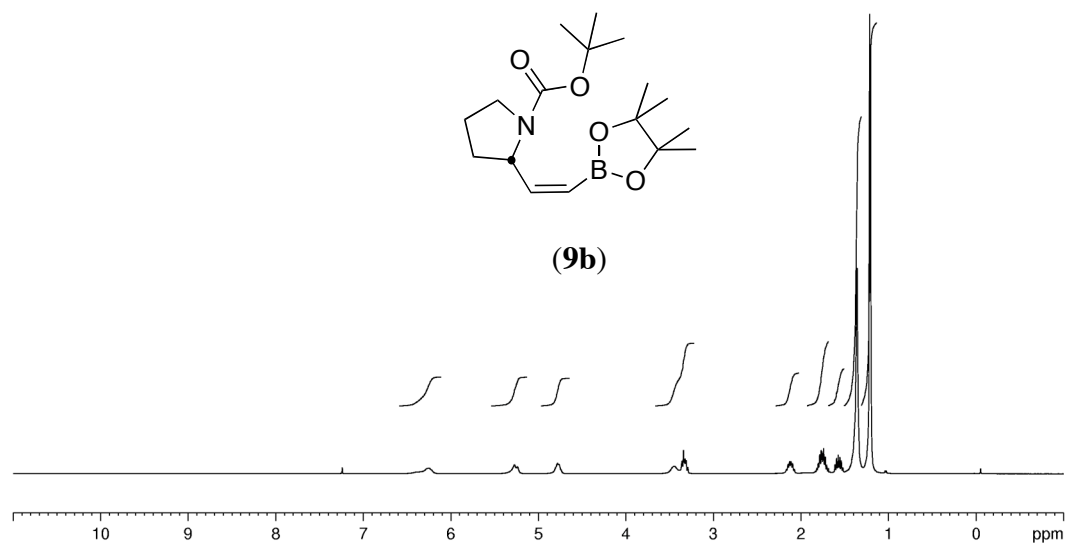
¹H NMR (500 MHz, CDCl₃) Spectrum of (Z)-2-(5-Chloropent-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8b**)



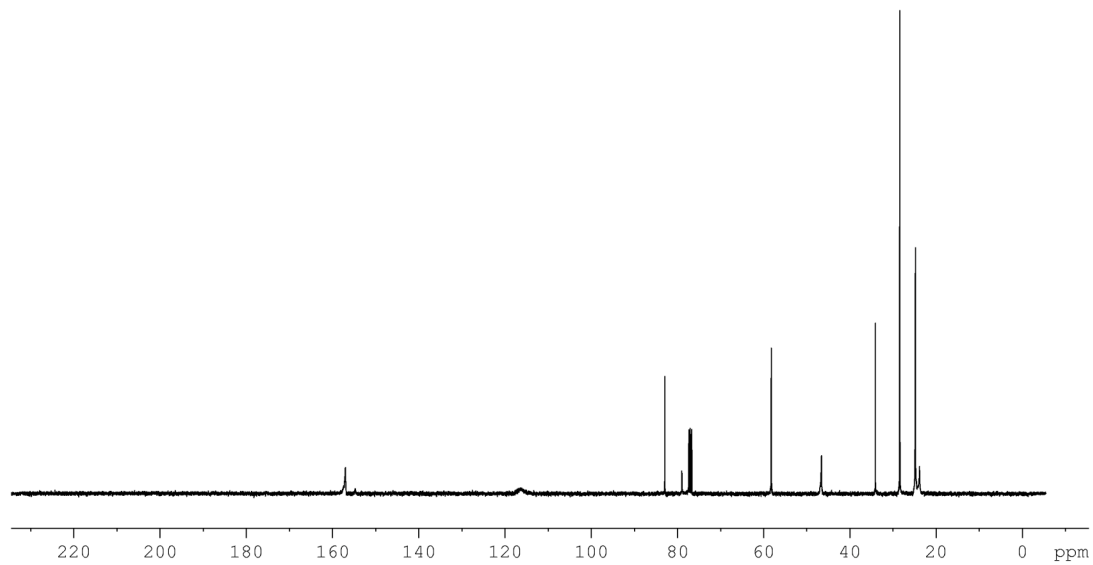
¹³C NMR (125.8 MHz, CDCl₃) Spectrum of (Z)-2-(5-Chloropent-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8b**)



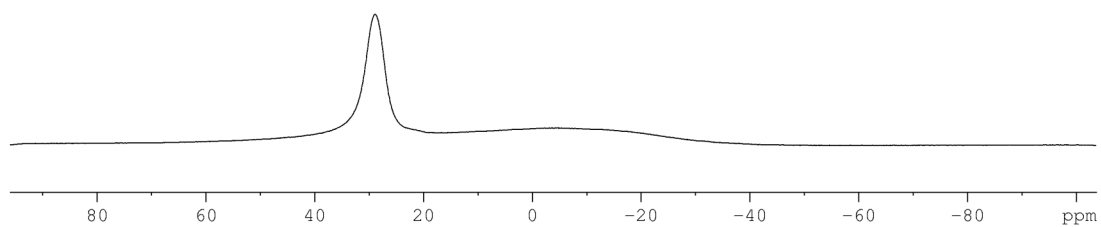
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of (Z)-2-(5-Chloropent-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8b**)



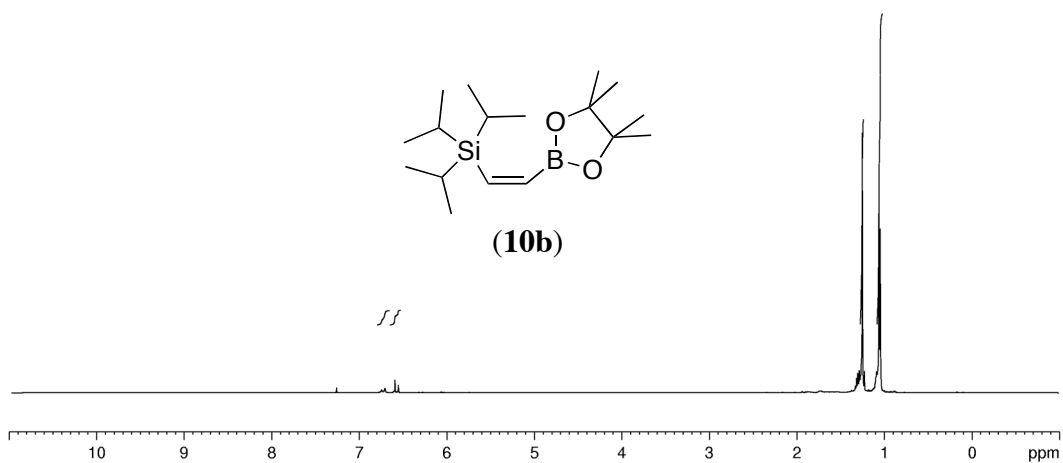
^1H NMR (500 MHz, CDCl_3) Spectrum of (2*S*,*Z*)-*tert*-Butyl 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyrrolidine-1-carboxylate (**9b**)



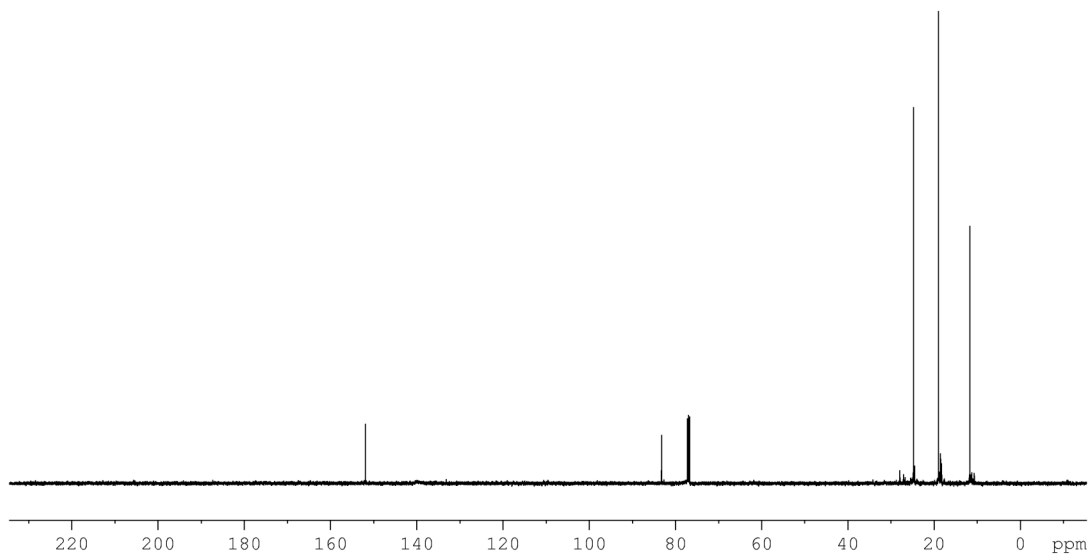
¹³C NMR (125.8 MHz, CDCl₃) Spectrum of (2*S*,*Z*)-*tert*-Butyl 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyrrolidine-1-carboxylate (**9b**)



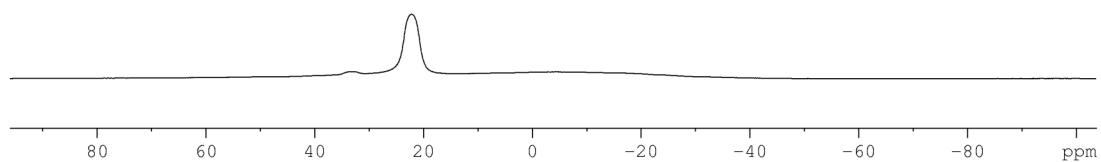
¹¹B NMR (128.37 MHz, CDCl₃) Spectrum of (2*S*,*Z*)-*tert*-Butyl 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyrrolidine-1-carboxylate (**9b**)



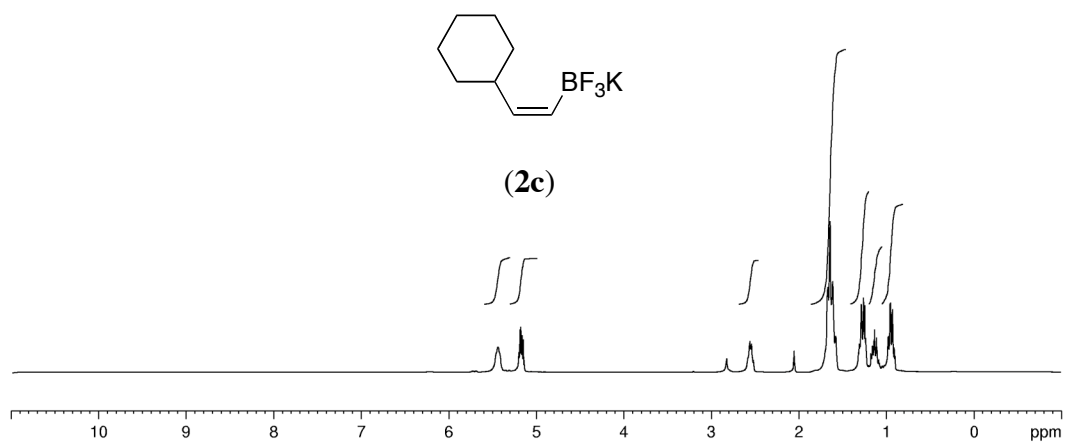
^1H NMR (500 MHz, CDCl_3) Spectrum of (Z)-Triisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**10b**)



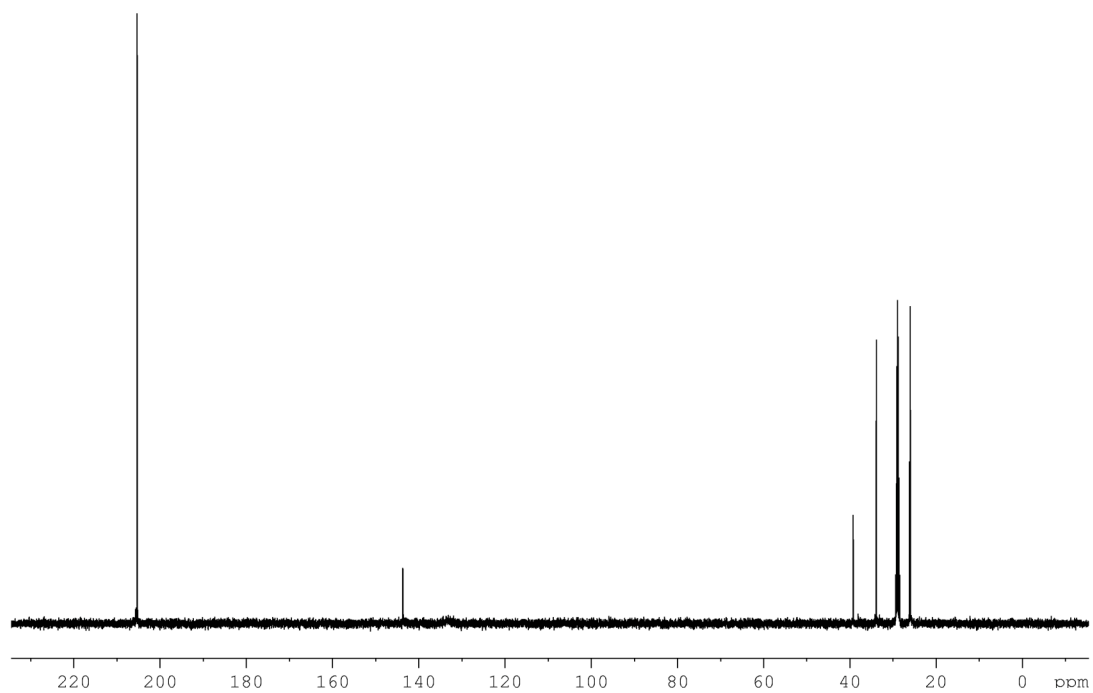
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of (Z)-Triisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**10b**)



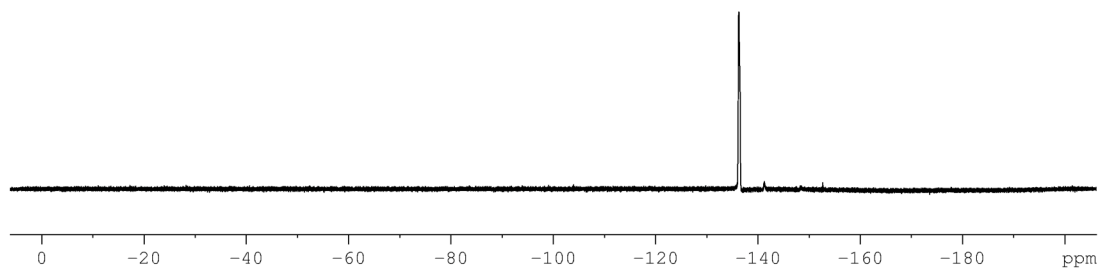
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of (Z)-Triisopropyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**10b**)



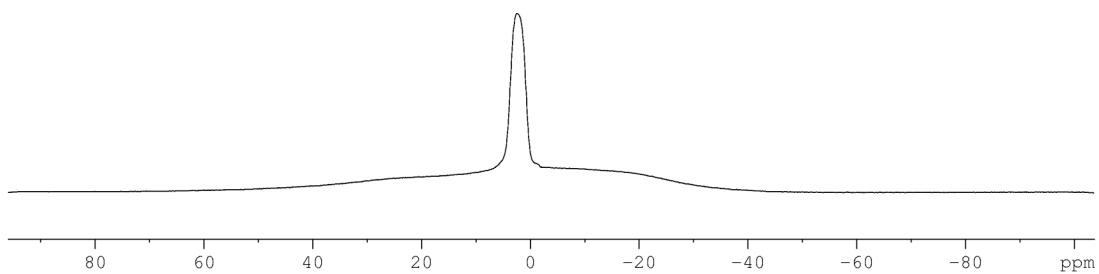
^1H NMR (500 MHz, $\text{Acetone-}d_6$) Spectrum of (Z)-2-Cyclohexylethenyltrifluoroborate (**2c**)



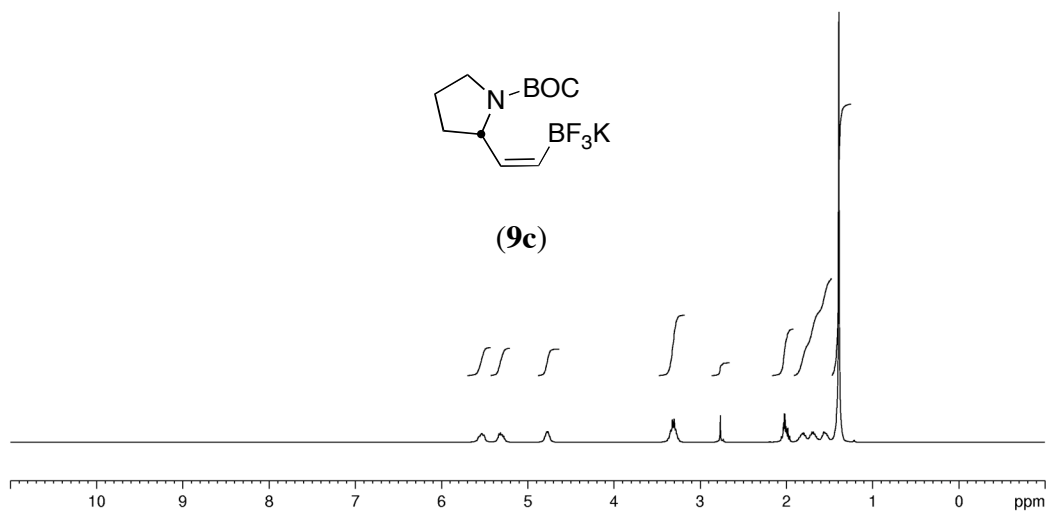
^{13}C NMR (125.8 MHz, Acetone- d_6) Spectrum of (*Z*)-2-Cyclohexylethenyltrifluoroborate (**2c**)



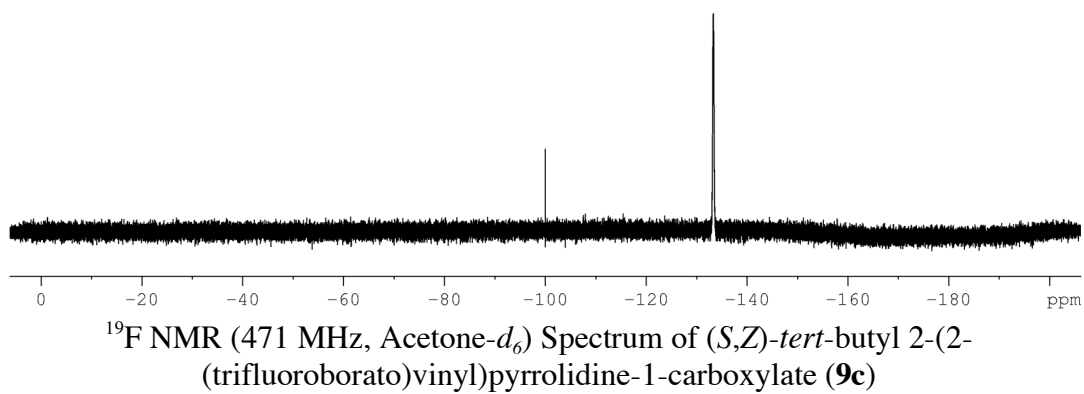
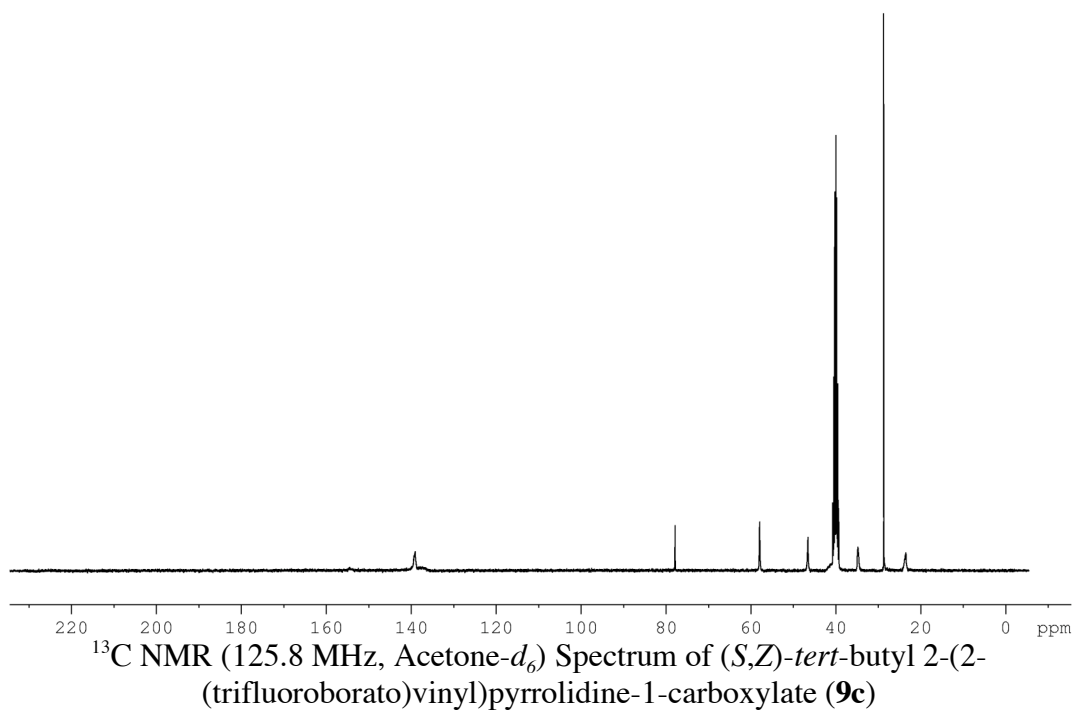
^{19}F NMR (471 MHz, Acetone- d_6) Spectrum of (*Z*)-2-Cyclohexylethenyltrifluoroborate (**2c**)

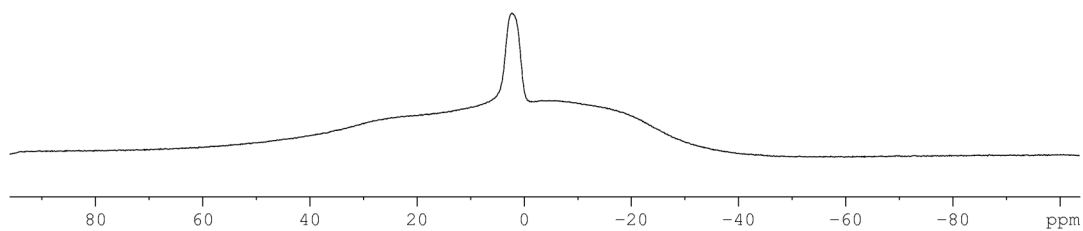


^{11}B NMR (128.37 MHz, Acetone- d_6) Spectrum of (*Z*)-2-Cyclohexylethenyltrifluoroborate (**2c**)

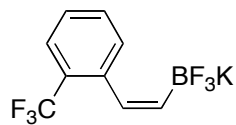


^1H NMR (500 MHz, Acetone- d_6) Spectrum of (*S,Z*)-*tert*-butyl 2-(2-(trifluoroborato)vinyl)pyrrolidine-1-carboxylate (**9c**)

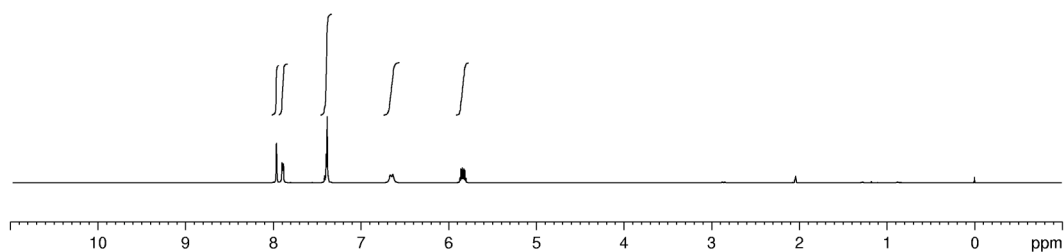




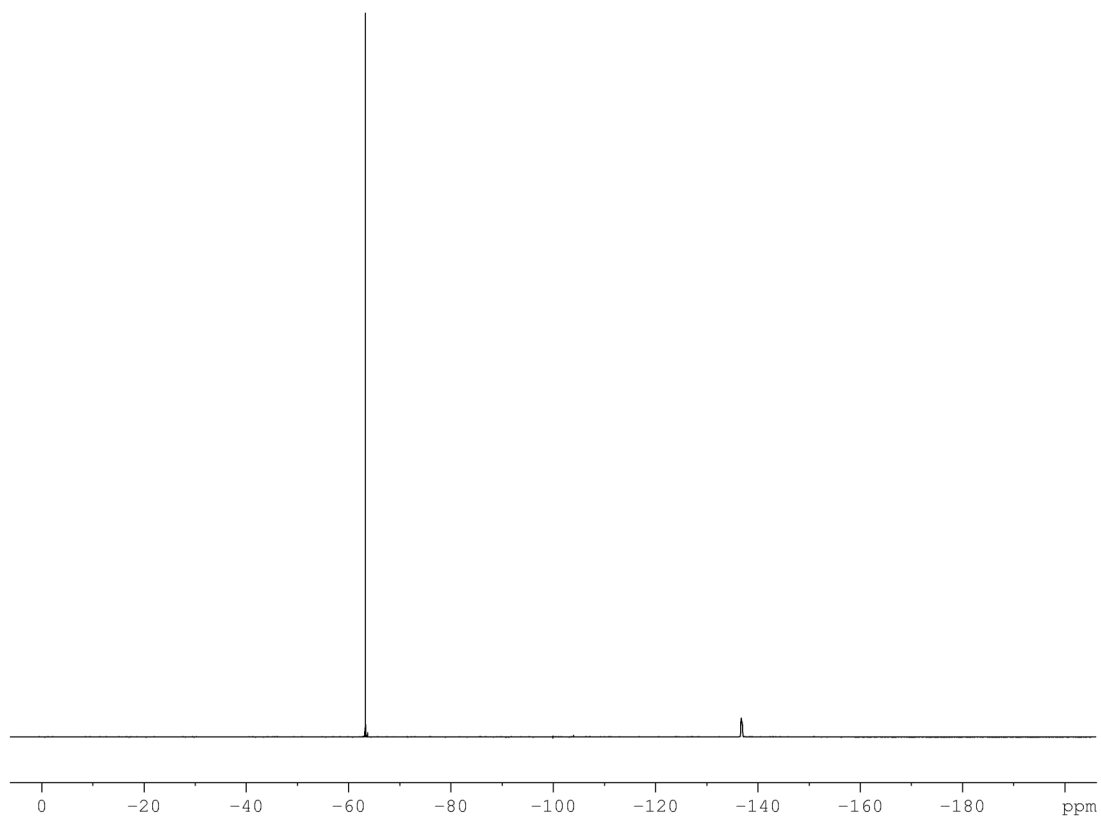
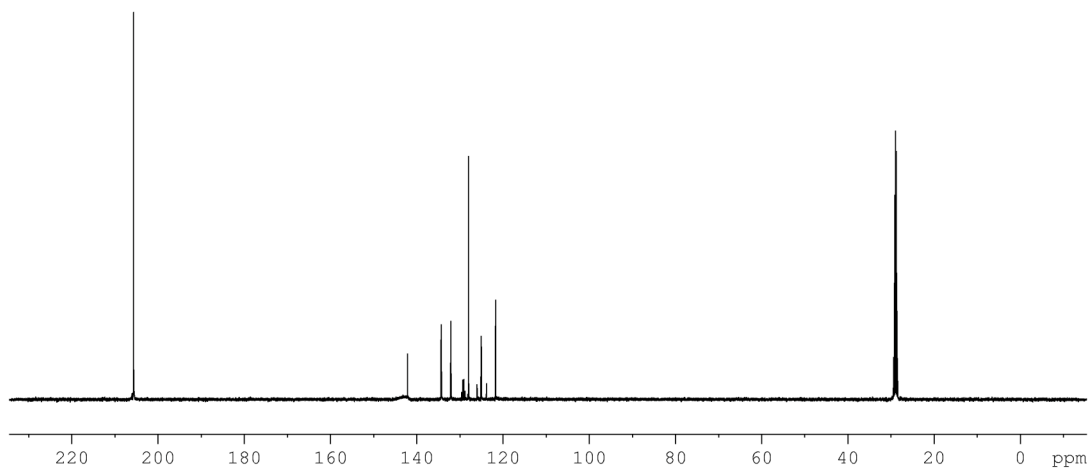
^{11}B NMR (128.37 MHz, Acetone- d_6) Spectrum of (*S,Z*)-*tert*-butyl 2-(2-(trifluoroborato)vinyl)pyrrolidine-1-carboxylate (**9c**)

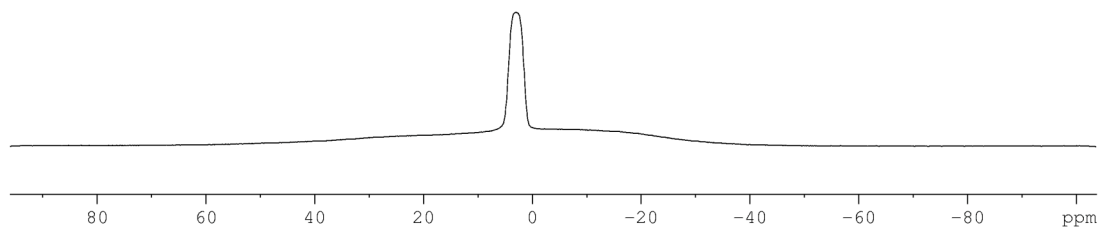


(**4c**)

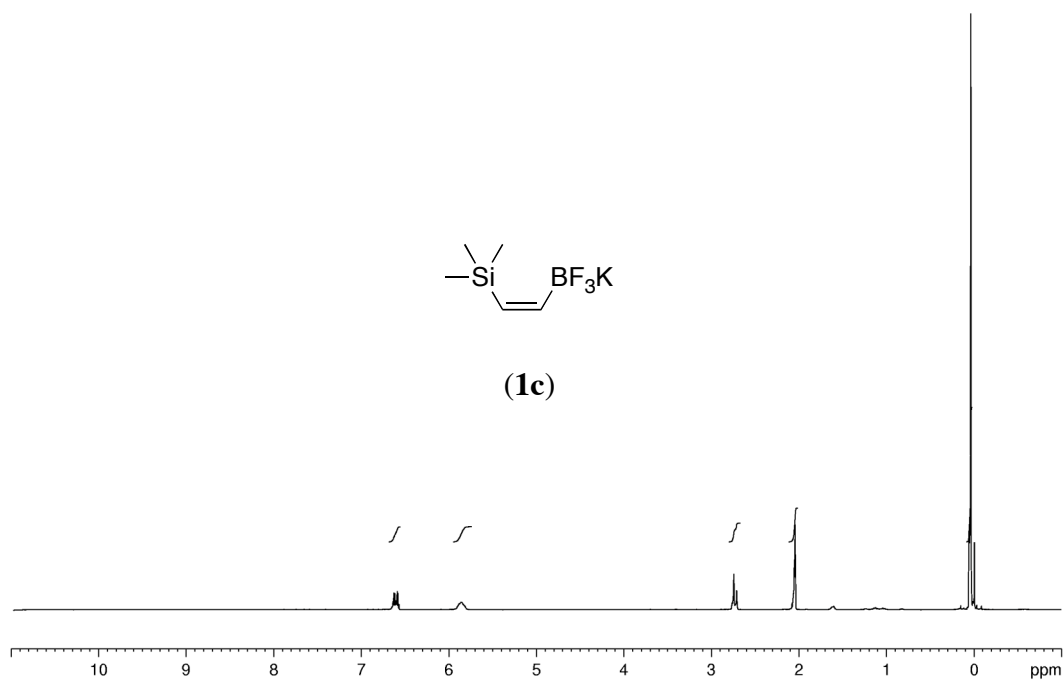


^1H NMR (500 MHz, Acetone- d_6) Spectrum of (*Z*)-2-(2-(Trifluoromethyl)phenyl)ethenyltrifluoroborate (**4c**)

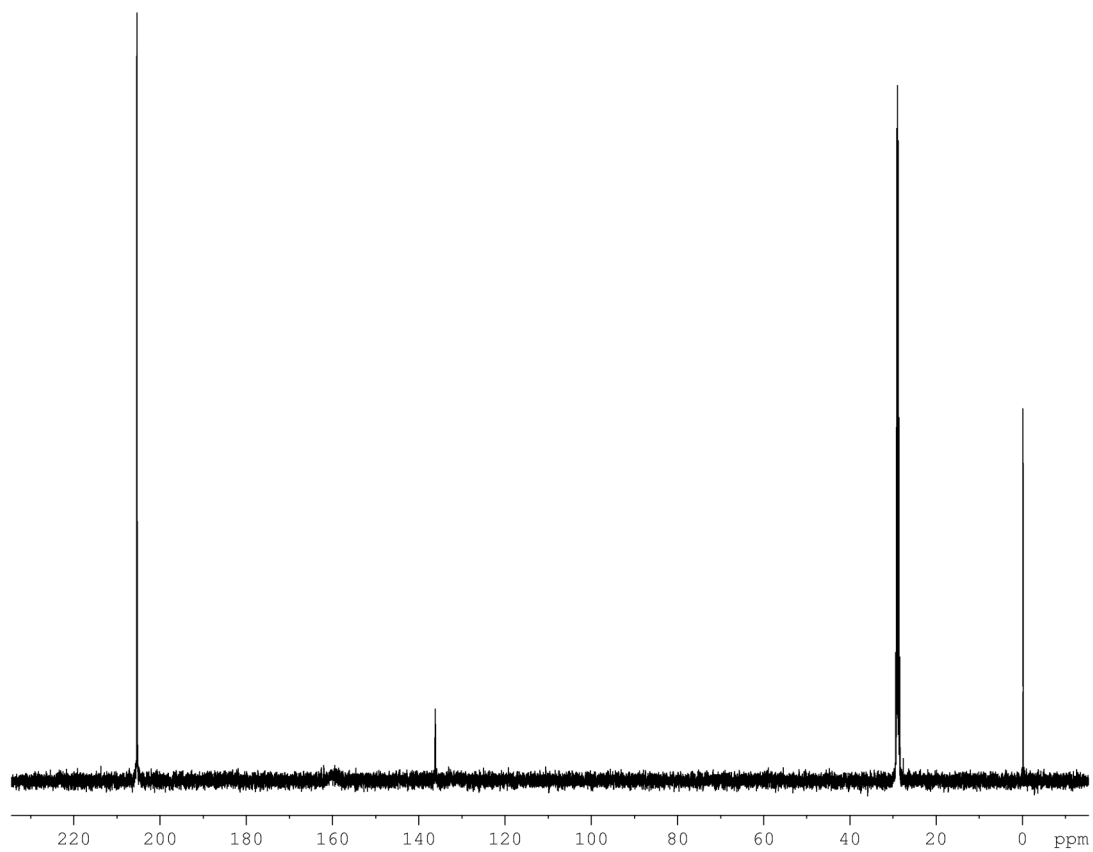




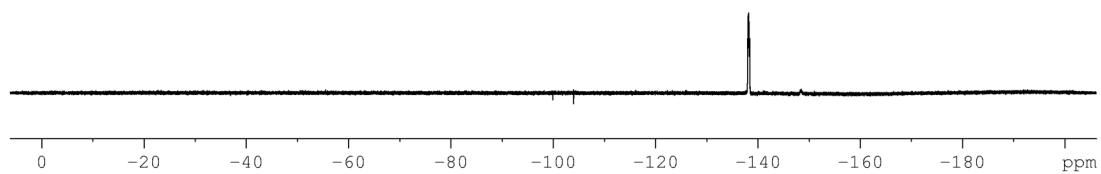
^{11}B NMR (128.37 MHz, Acetone- d_6) Spectrum of (Z)-2-(2-(Trifluoromethyl)phenyl)ethenyltrifluoroborate (**4c**)



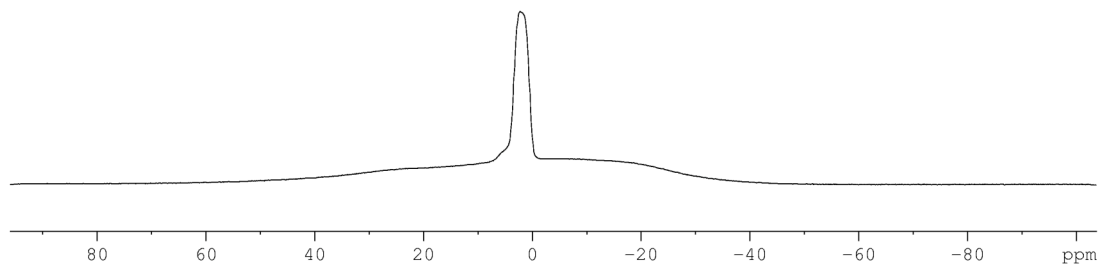
^1H NMR (500 MHz, Acetone- d_6) Spectrum of (Z)-2-Trimethylsilylethenyltrifluoroborate (**1c**)



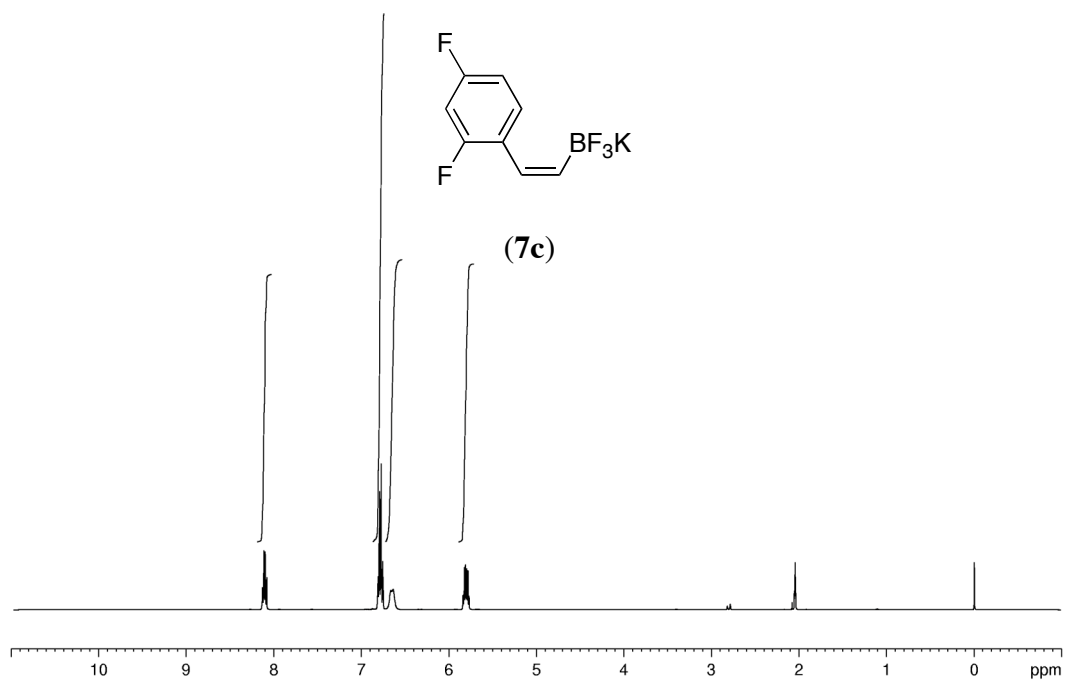
^{13}C NMR (125.8 MHz, Acetone- d_6) Spectrum of (*Z*)-2-Trimethylsilylethenyltrifluoroborate (**1c**)



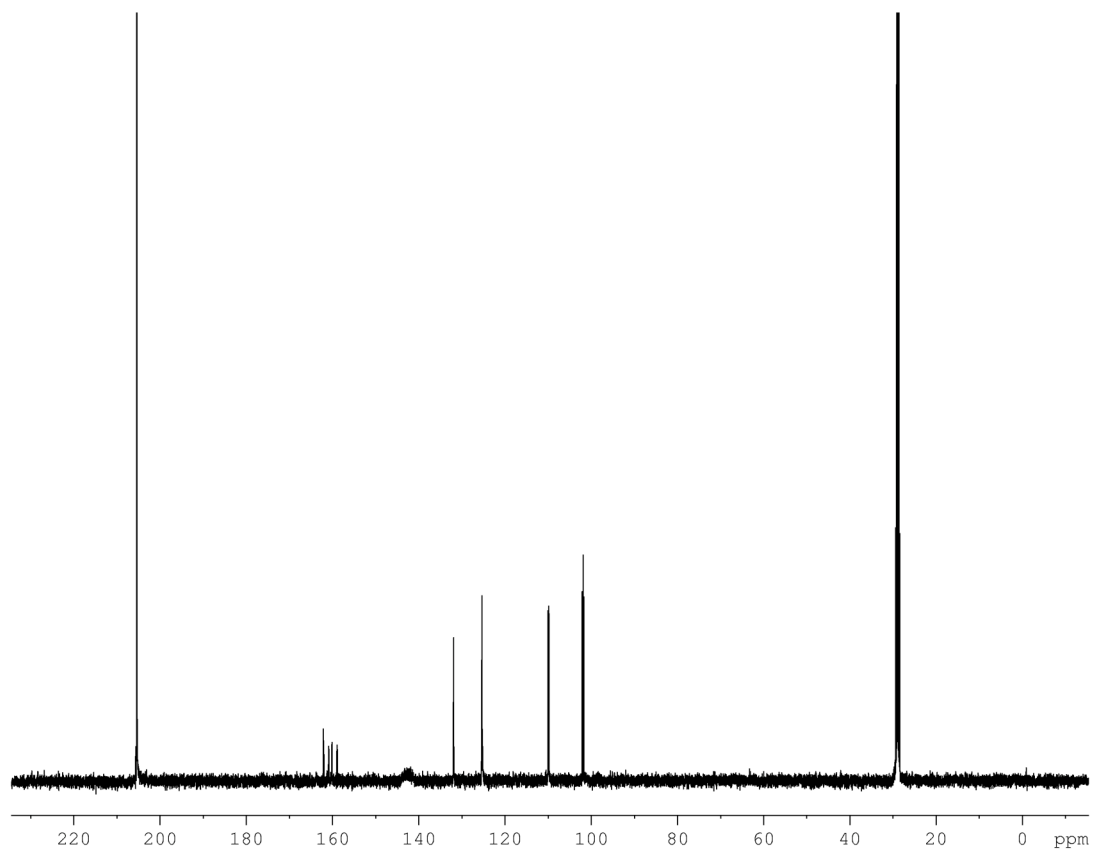
^{19}F NMR (471 MHz, Acetone- d_6) Spectrum of (*Z*)-2-Trimethylsilylethenyltrifluoroborate (**1c**)



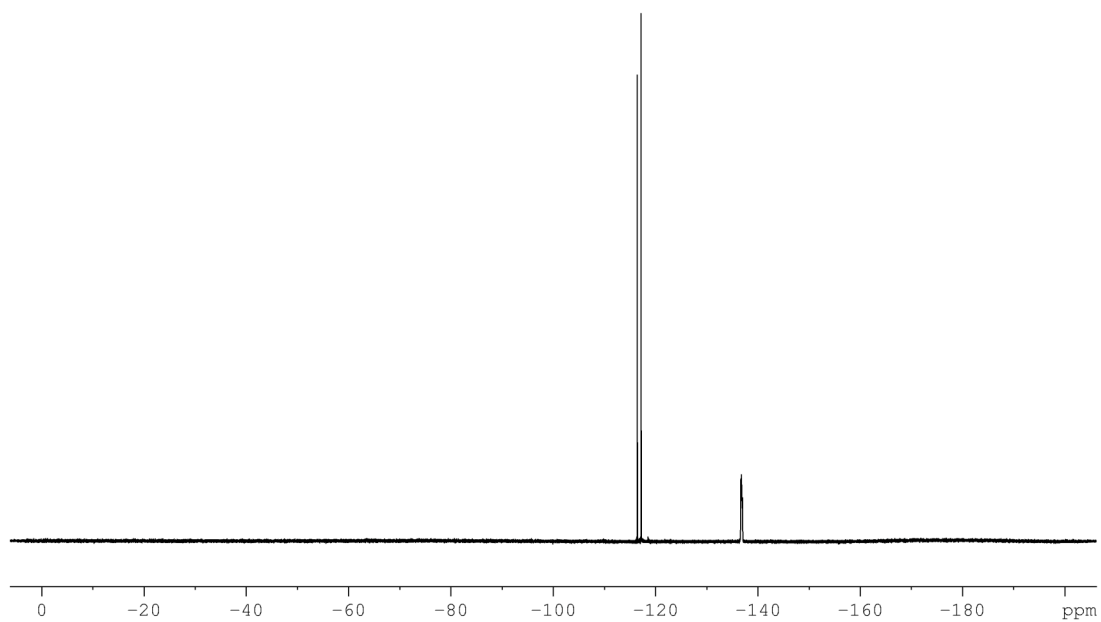
^{11}B NMR (128.37 MHz, Acetone- d_6) Spectrum of (Z)-2-Trimethylsilylethenyltrifluoroborate (**1c**)



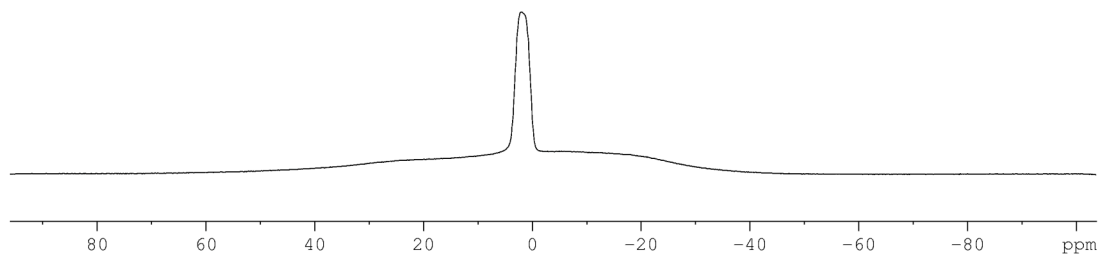
^1H NMR (500 MHz, Acetone- d_6) Spectrum of (Z)-2-(2,4-Difluorostyryl)ethenyltrifluoroborate (**7c**)



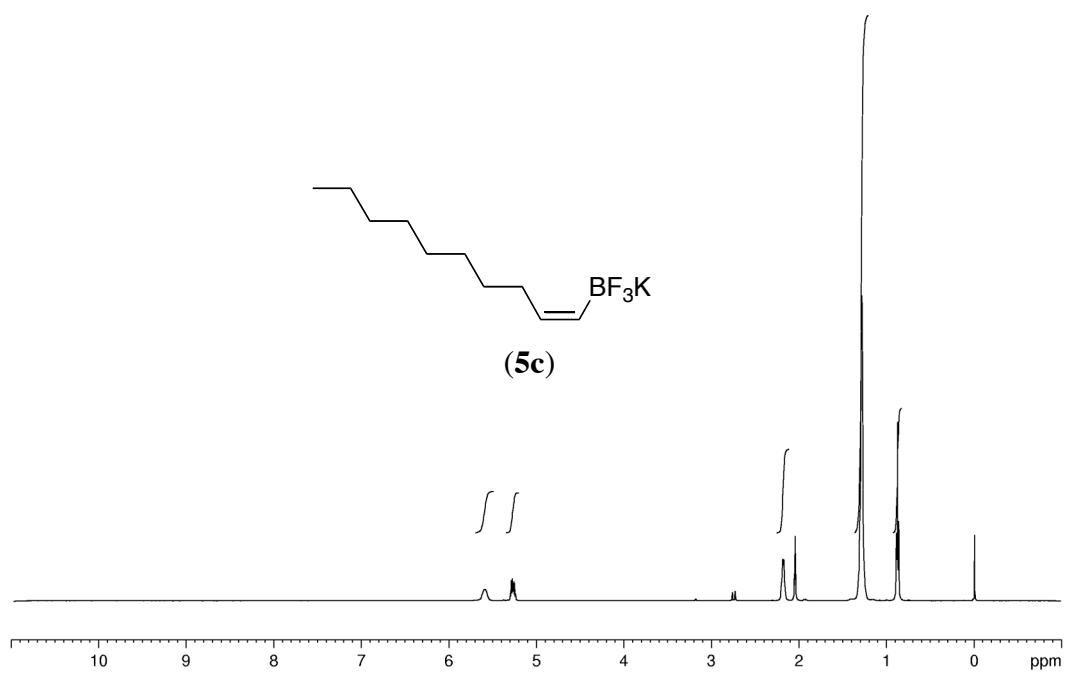
^{13}C NMR (125.8 MHz, Acetone- d_6) Spectrum of (Z)-2-(2,4-Difluorostyryl)ethenyltrifluoroborate
(7c)



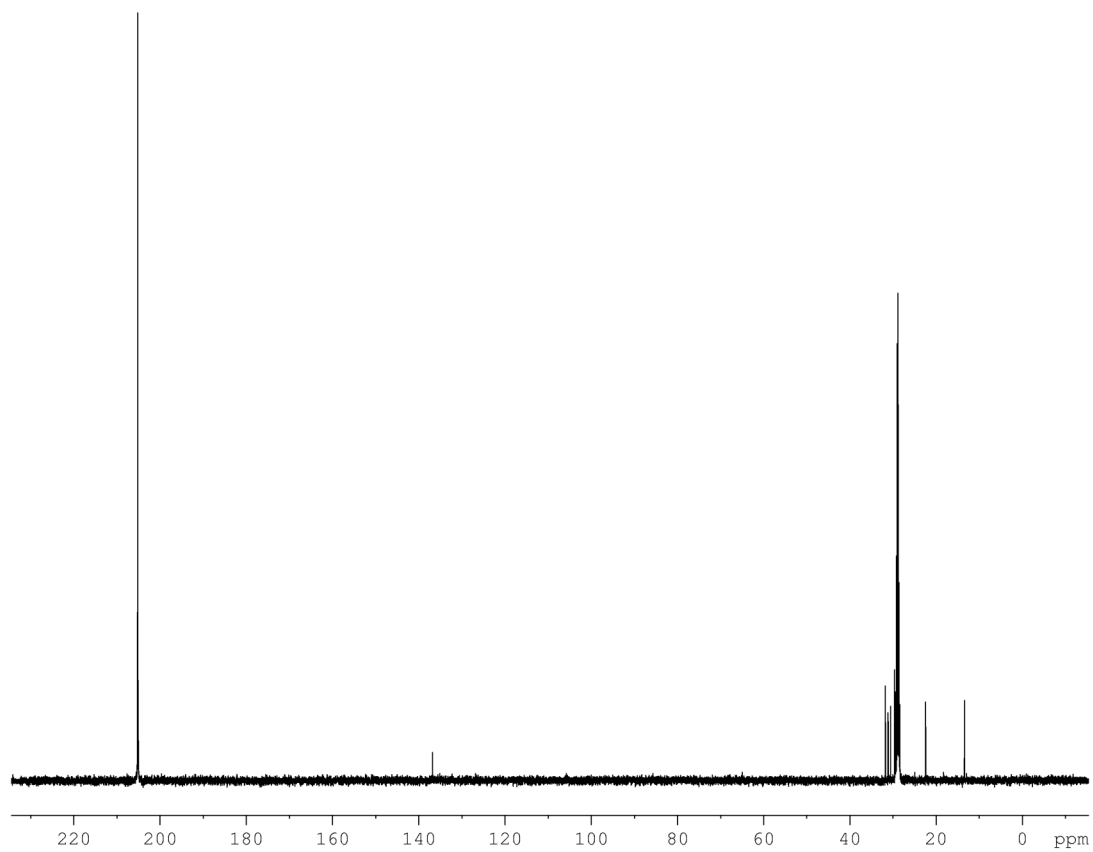
^{19}F NMR (471 MHz, Acetone- d_6) Spectrum of (Z)-2-(2,4-Difluorostyryl)ethenyltrifluoroborate
(7c)
S37



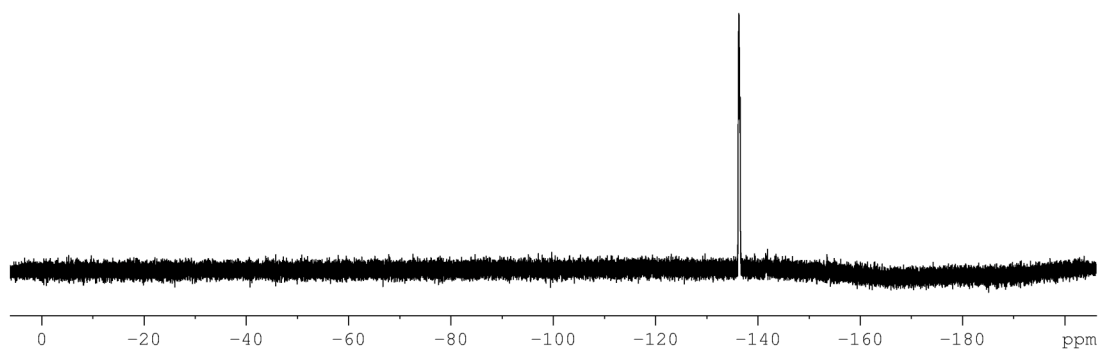
^{11}B NMR (128.37 MHz, Acetone- d_6) Spectrum of (*Z*)-2-(2,4-Difluorostyryl)ethenyltrifluoroborate (**7c**)



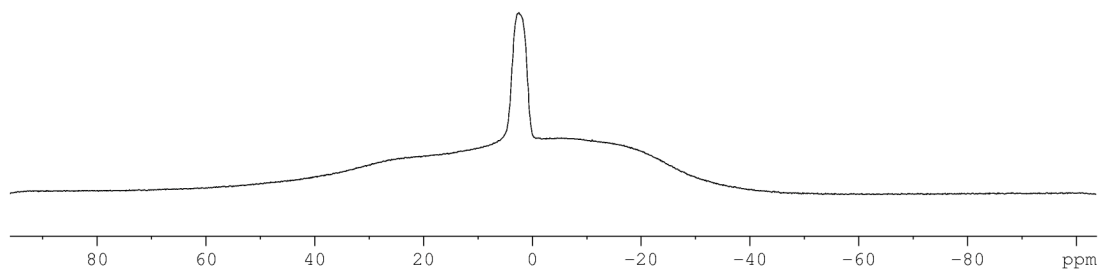
^1H NMR (500 MHz, Acetone- d_6) Spectrum of (*Z*)-1-Decenyltrifluoroborate (**5c**)



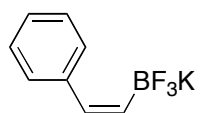
^{13}C NMR (125.8 MHz, Acetone- d_6) Spectrum of (Z)-1-Decenyltrifluoroborate (**5c**)



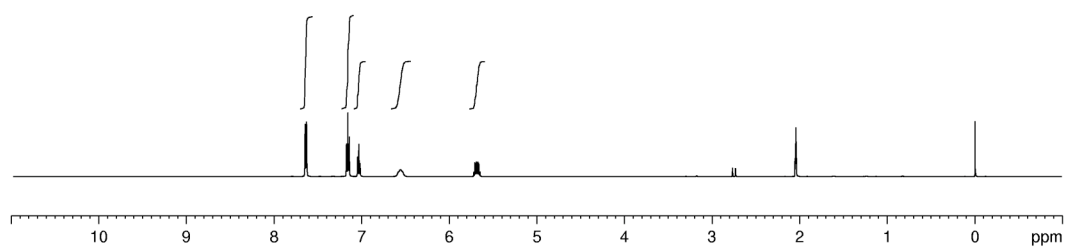
^{19}F NMR (471 MHz, Acetone- d_6) Spectrum of (Z)-1-Decenyltrifluoroborate (**5c**)



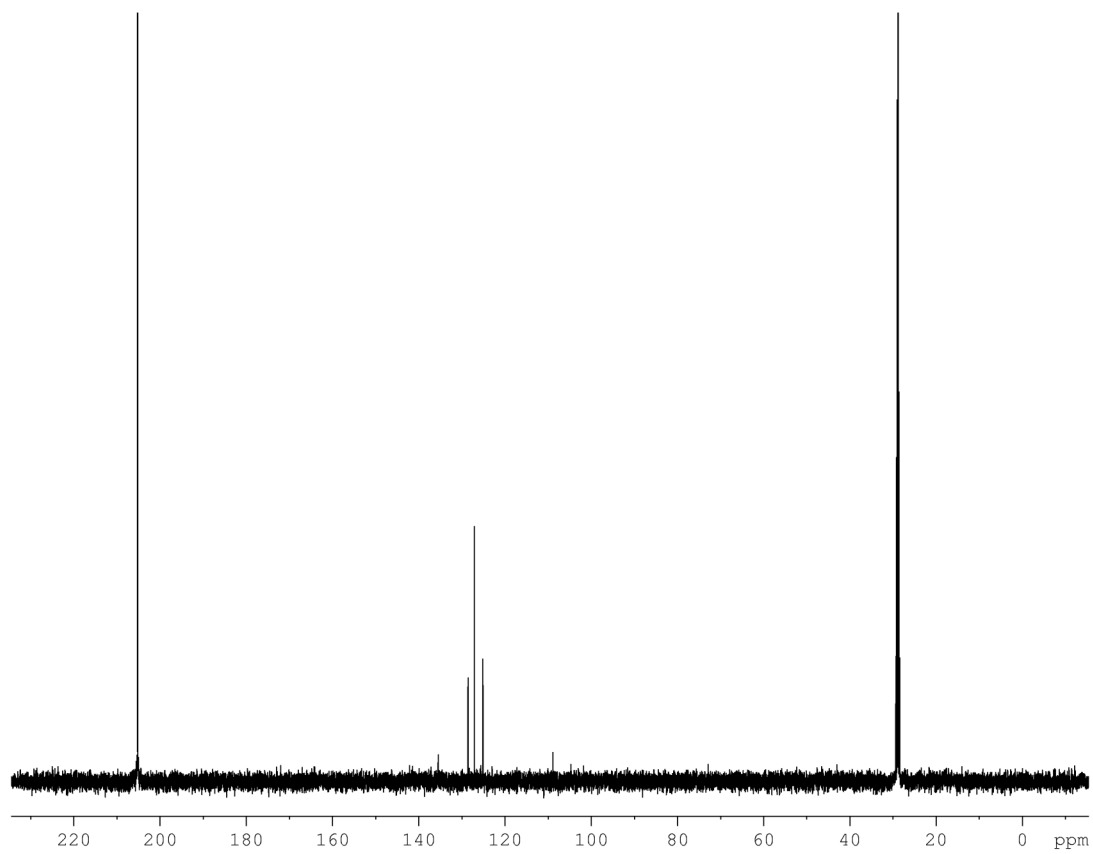
^{11}B NMR (128.37 MHz, Acetone- d_6) Spectrum of (Z)-1-Decenyltrifluoroborate (**5c**)



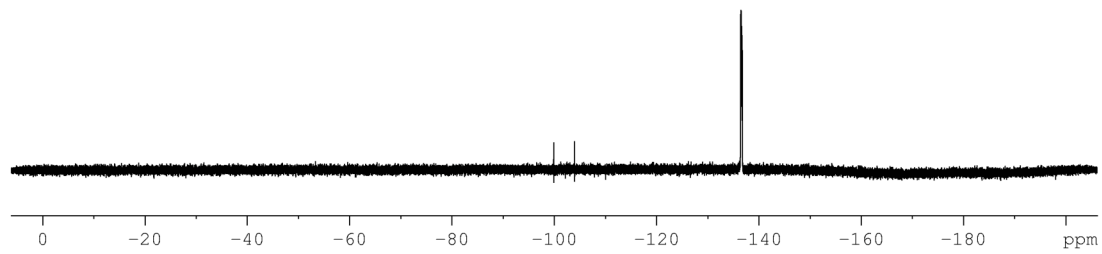
3c



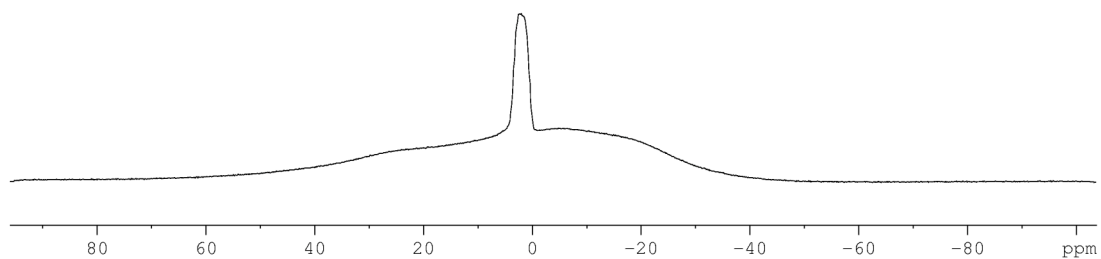
^1H NMR (500 MHz, Acetone- d_6) Spectrum of (Z)-2-(Phenyl)ethenyltrifluoroborate (**3c**)



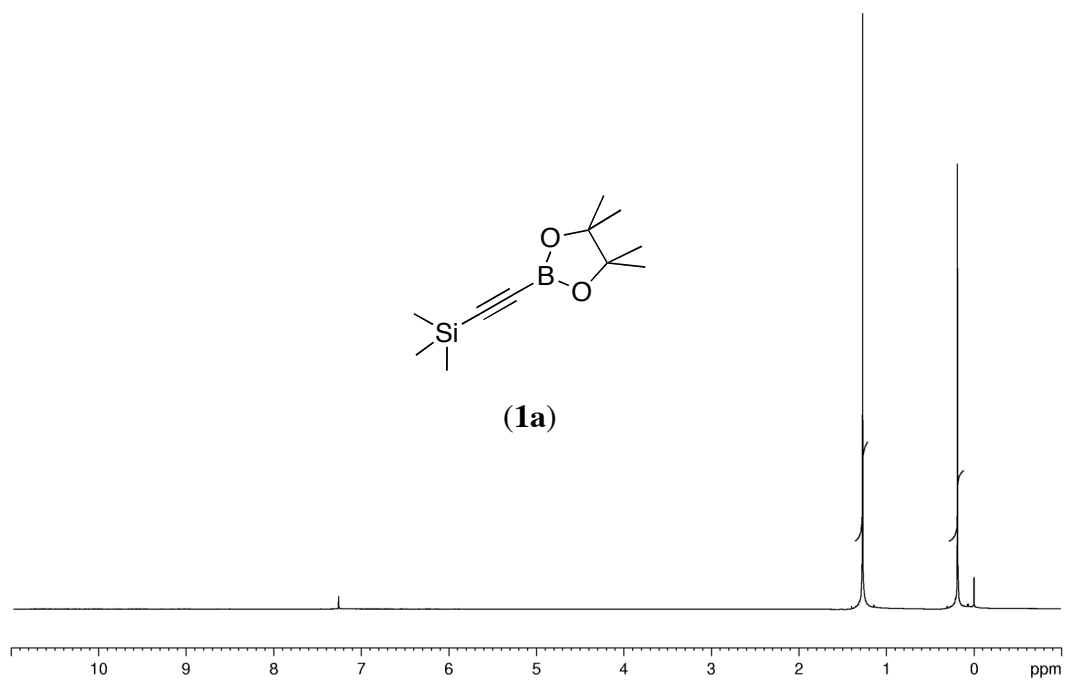
^{13}C NMR (125.8 MHz, Acetone- d_6) Spectrum of (*Z*)-2-(Phenyl)ethenyltrifluoroborate (**3c**)



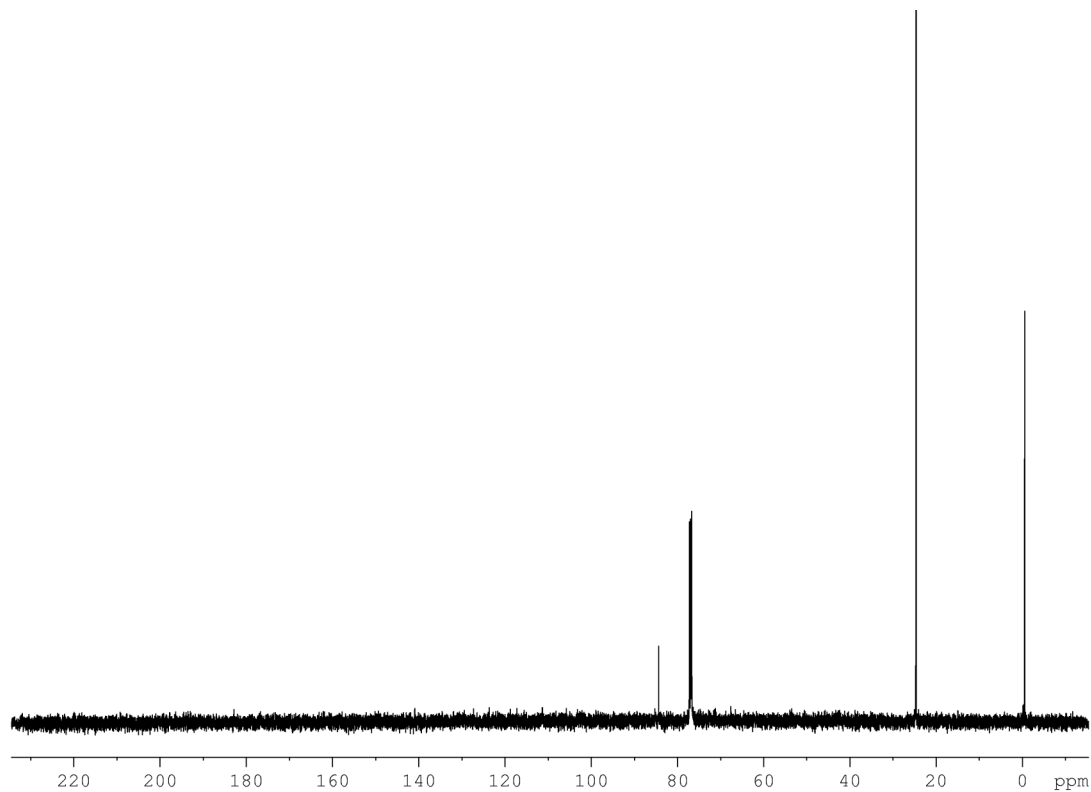
^{19}F NMR (471 MHz, Acetone- d_6) Spectrum of (*Z*)-2-(Phenyl)ethenyltrifluoroborate (**3c**)



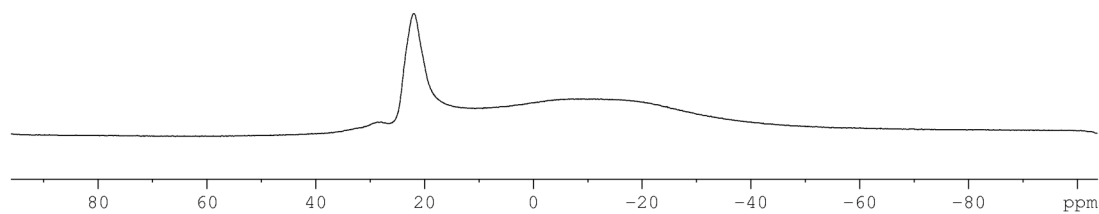
^{11}B NMR (128.37 MHz, Acetone- d_6) Spectrum of (*Z*)-2-(Phenyl)ethenyltrifluoroborate (**3c**)



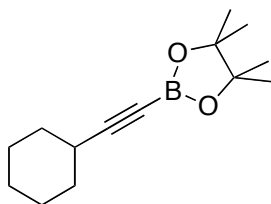
^1H NMR (500 MHz, CDCl_3) Spectrum of Trimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)silane (**1a**)



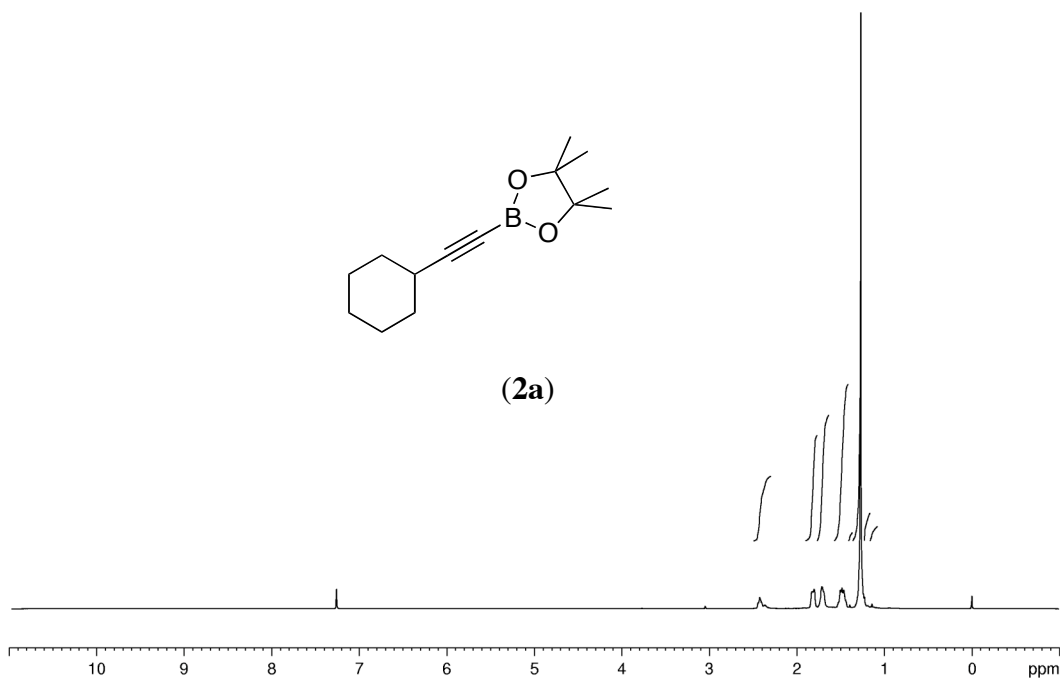
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of Trimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)silane (**1a**)



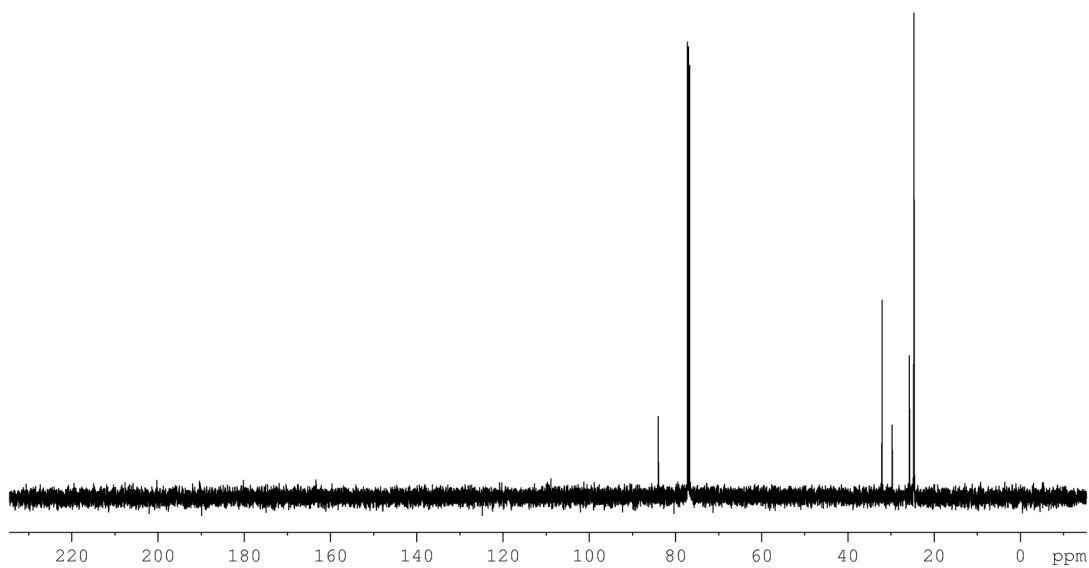
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of Trimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)silane (**1a**)



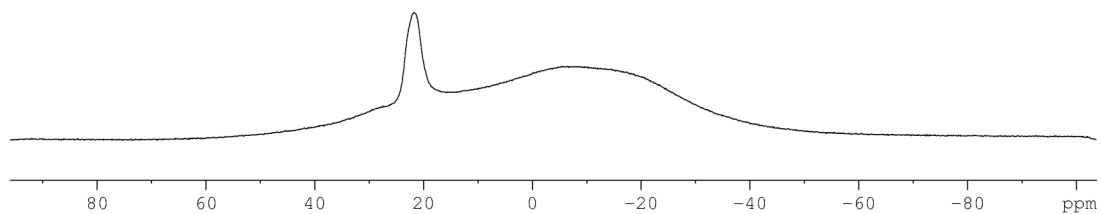
(2a)



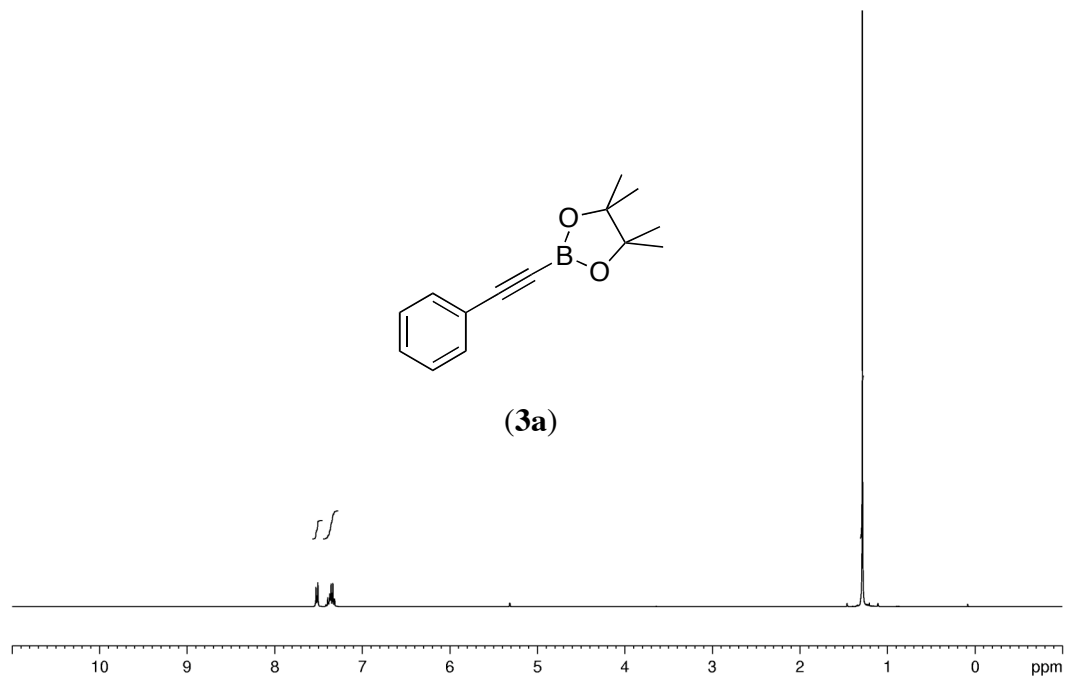
¹H NMR (500 MHz, CDCl₃) Spectrum of 2-(Cyclohexylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a**)



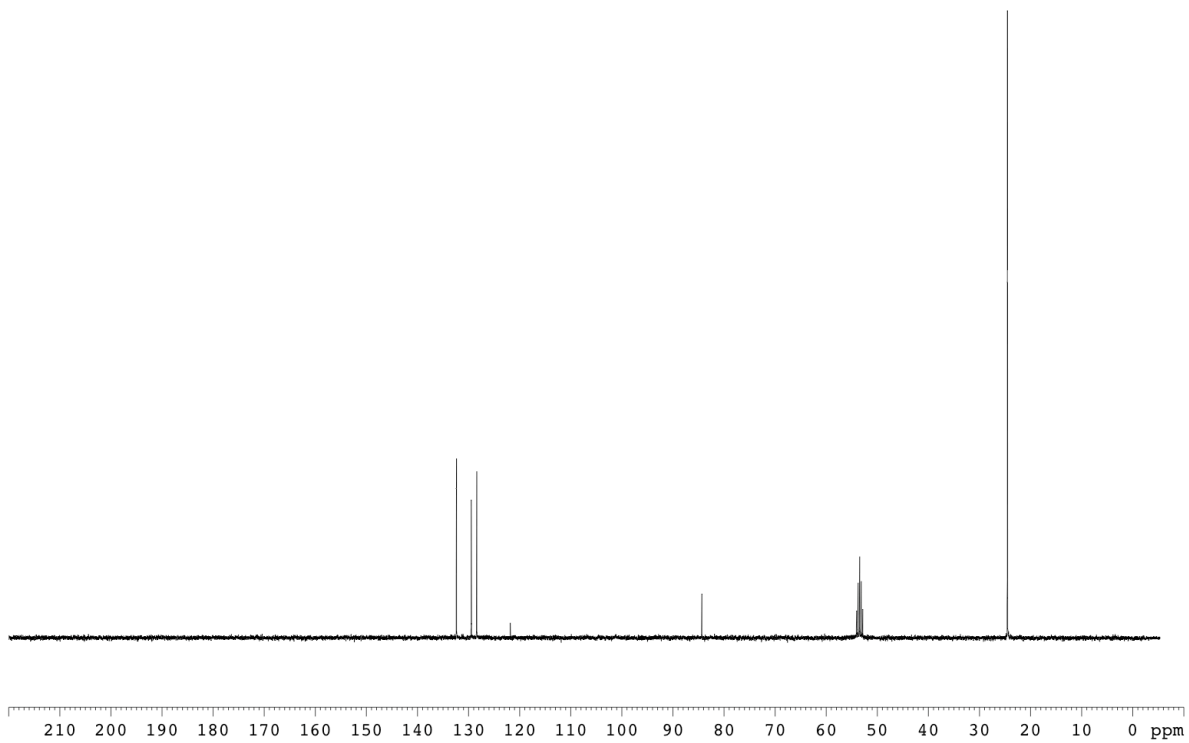
¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 2-(Cyclohexylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a**)



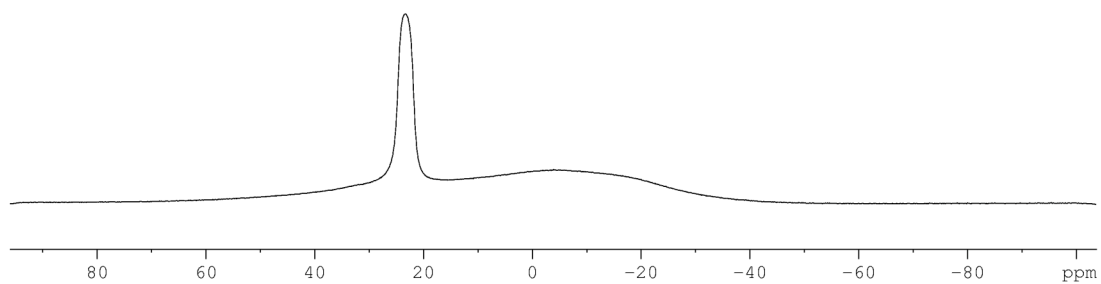
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of 2-(Cyclohexylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a**)



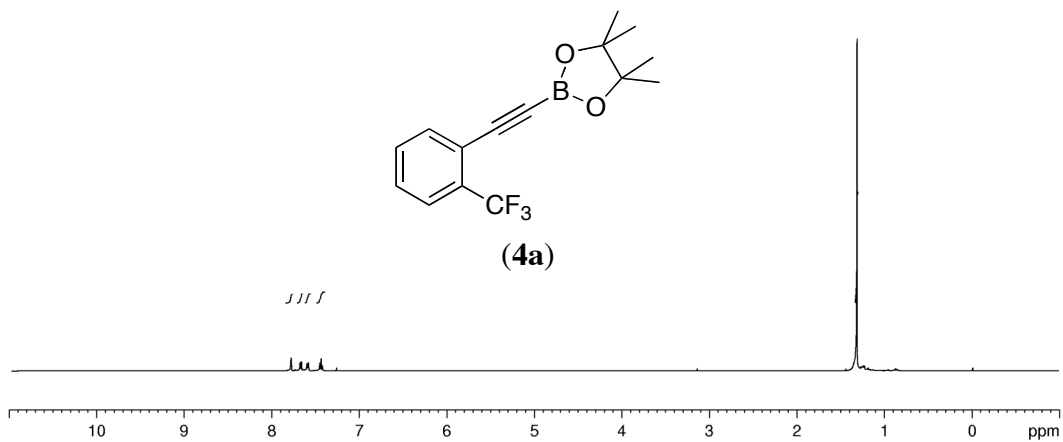
^1H NMR (500 MHz, CDCl_3) Spectrum of 4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (**3a**)



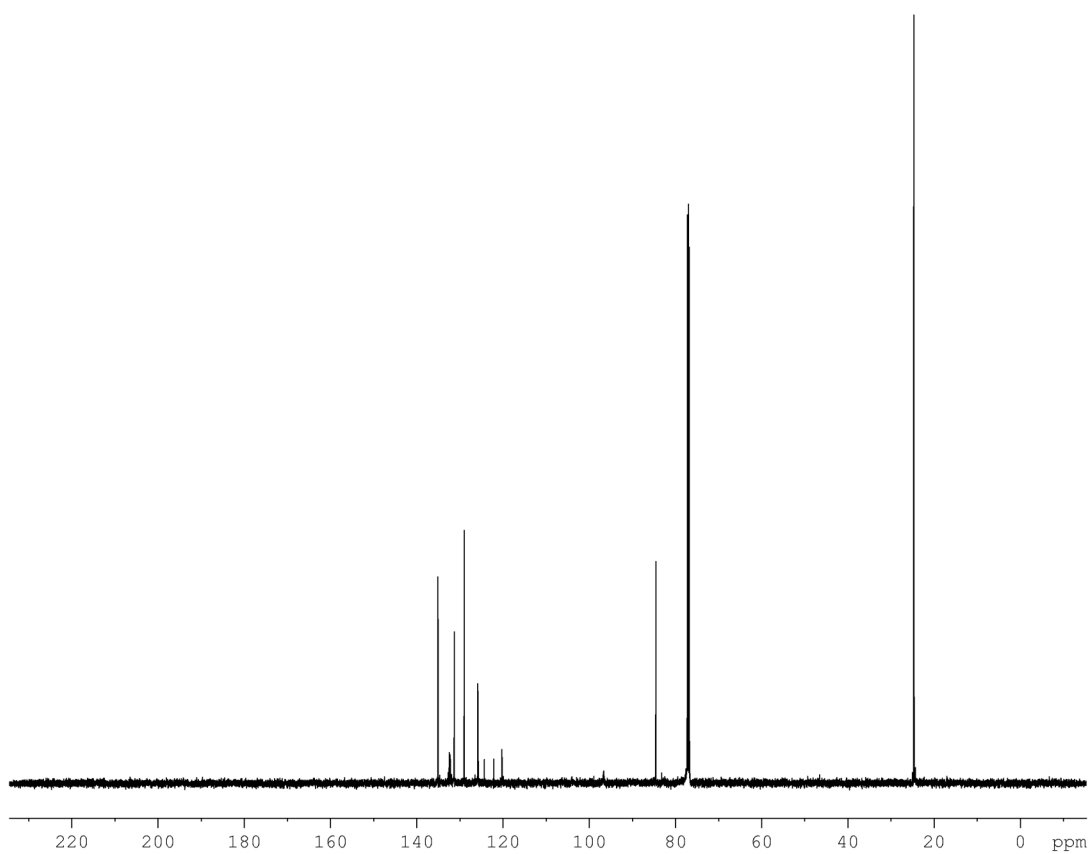
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of 4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (**3a**)



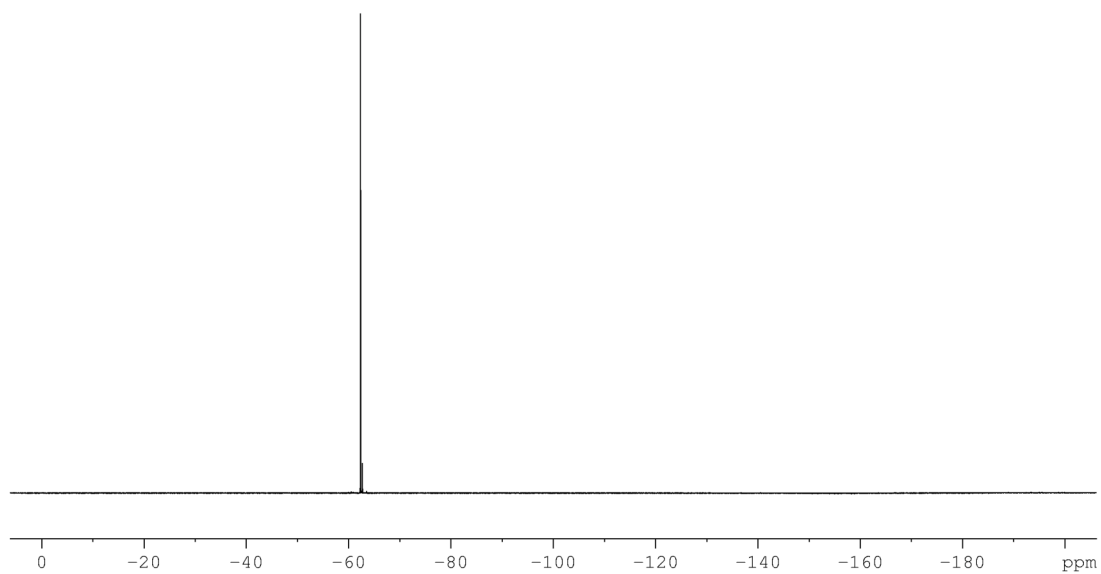
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of 4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (**3a**)



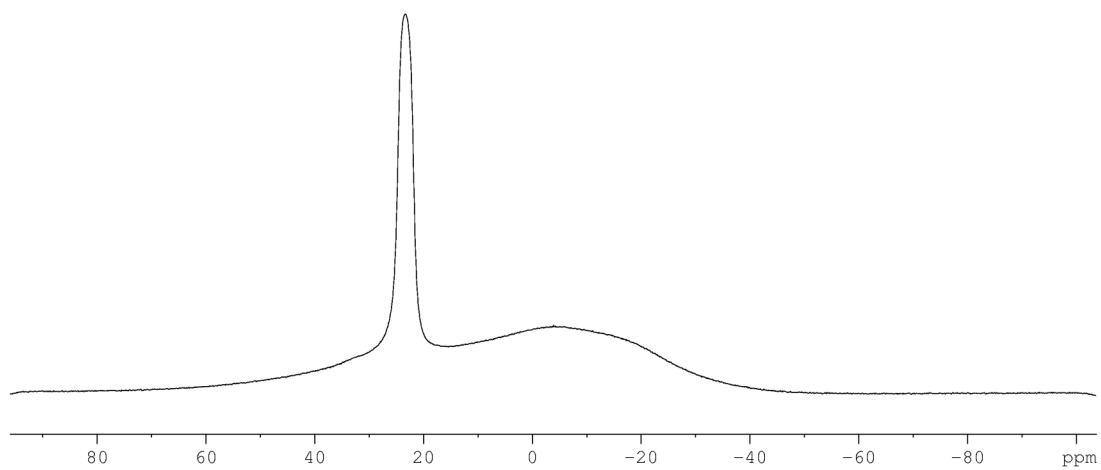
¹H NMR (500 MHz, CDCl₃) Spectrum of 4,4,5,5-Tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (**4a**)



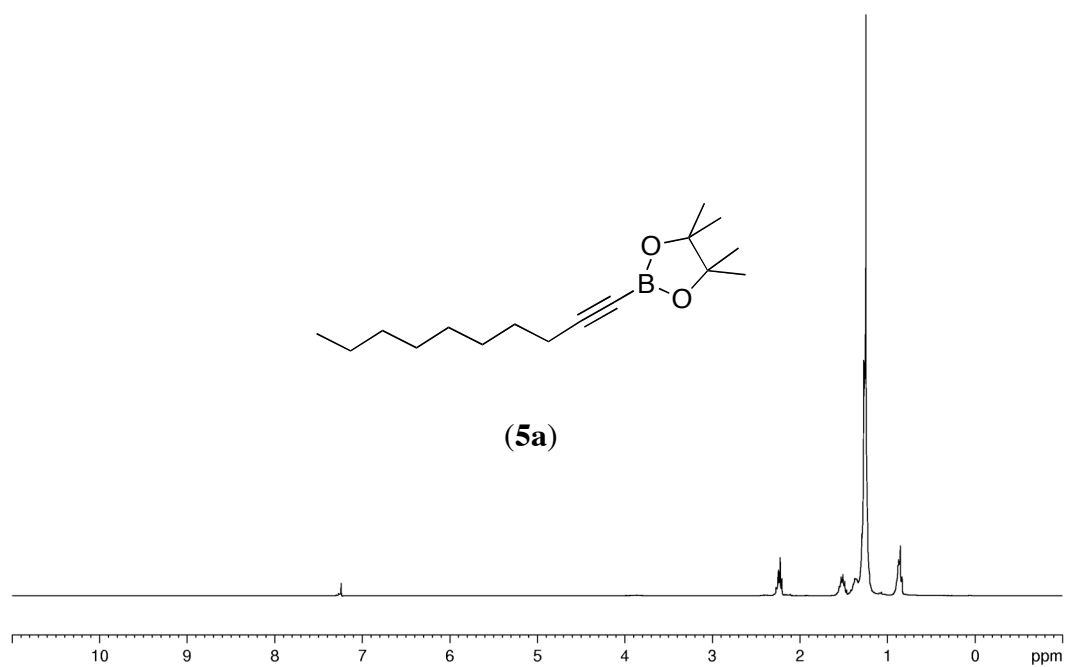
¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4,4,5,5-Tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (**4a**)



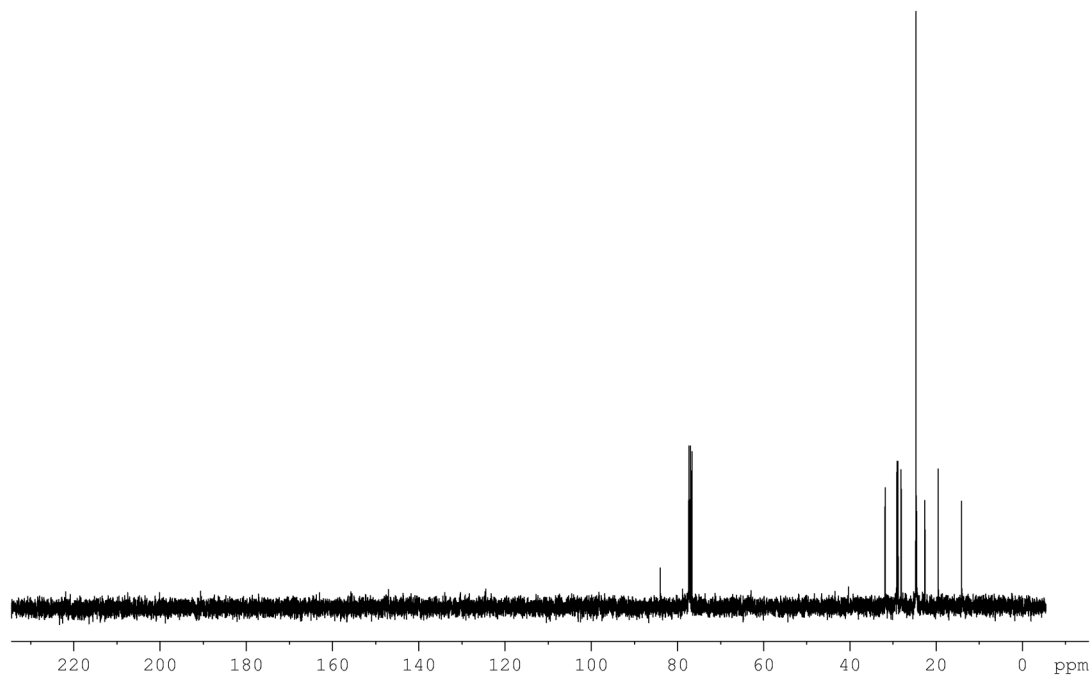
^{19}F NMR (471 MHz, CDCl_3) Spectrum of 4,4,5,5-Tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (**4a**)



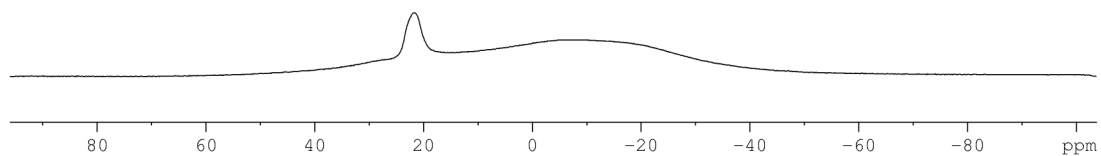
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of 4,4,5,5-Tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (**4a**)



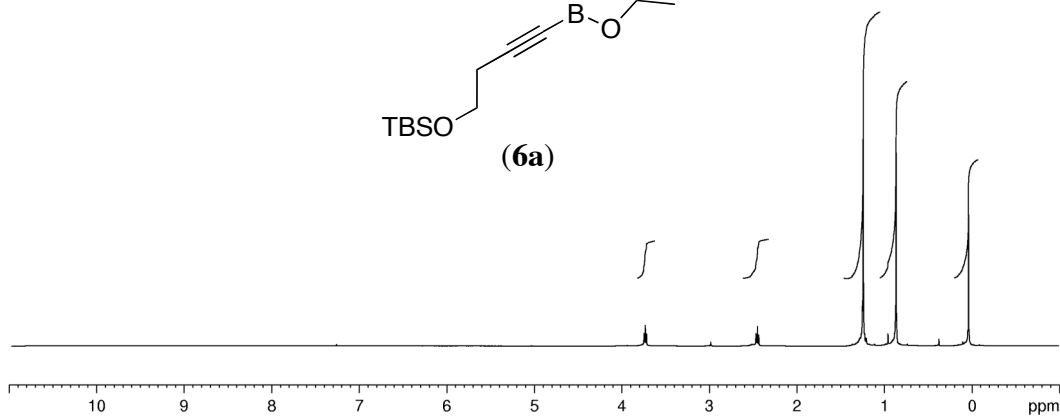
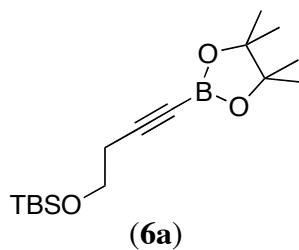
¹H NMR (500 MHz, CDCl₃) Spectrum of 2-(Dec-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5a**)



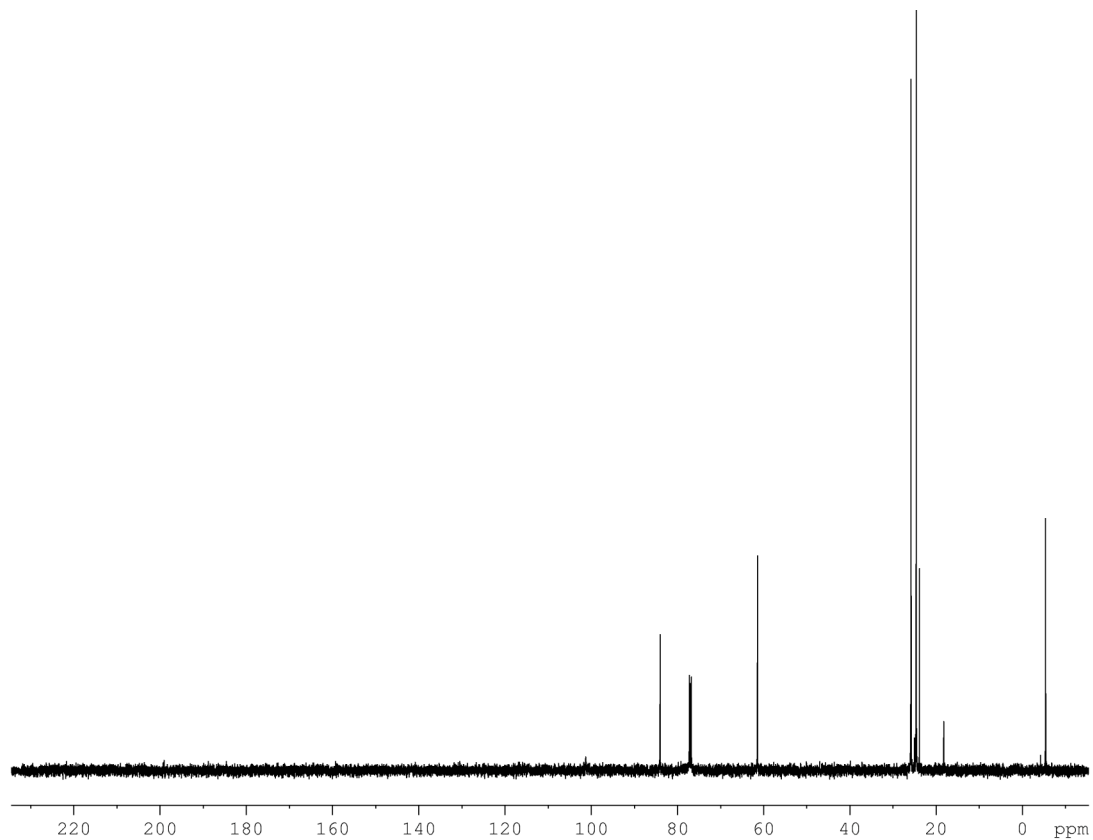
¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 2-(Dec-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5a**)



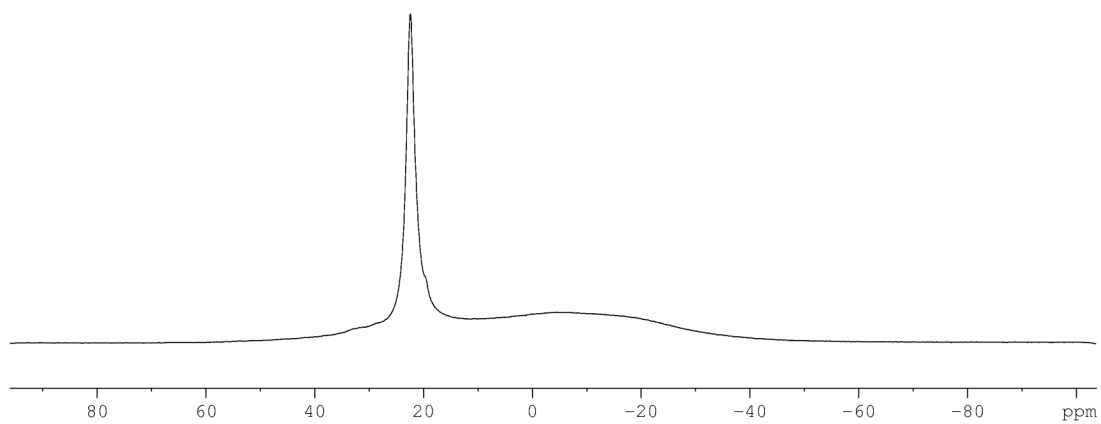
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of 2-(Dec-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5a**)



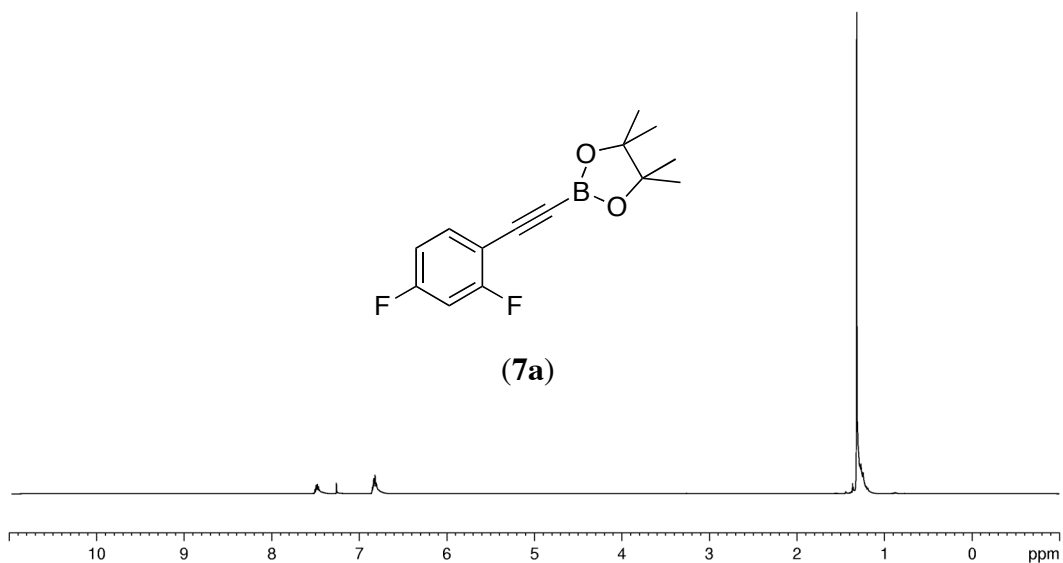
^1H NMR (500 MHz, CDCl_3) Spectrum of *tert*-Butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-ynyl)oxy)silane (**6a**)



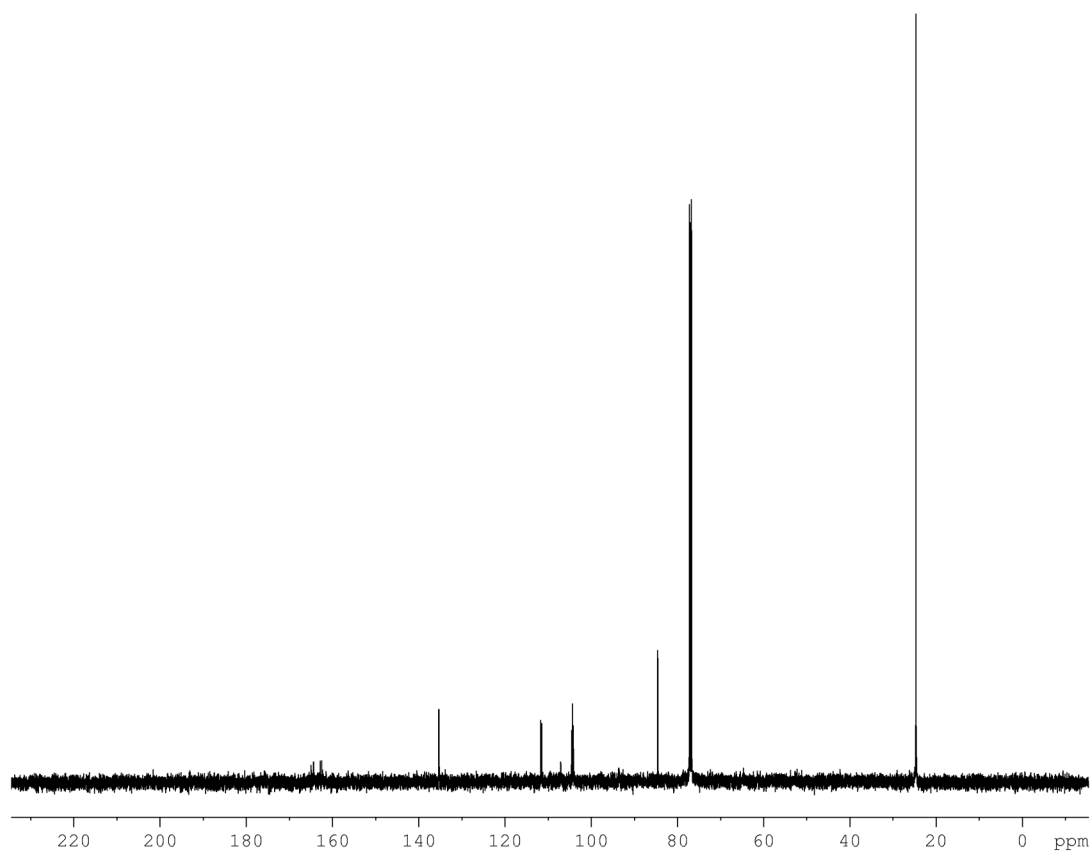
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of *tert*-Butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-ynoxy)silane (**6a**)



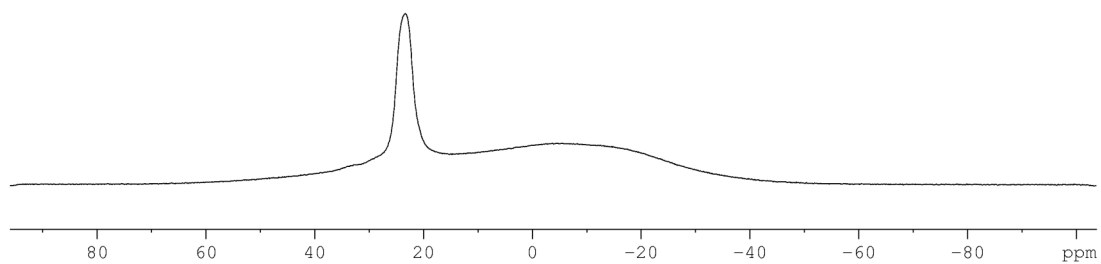
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of *tert*-Butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-ynoxy)silane (**6a**)



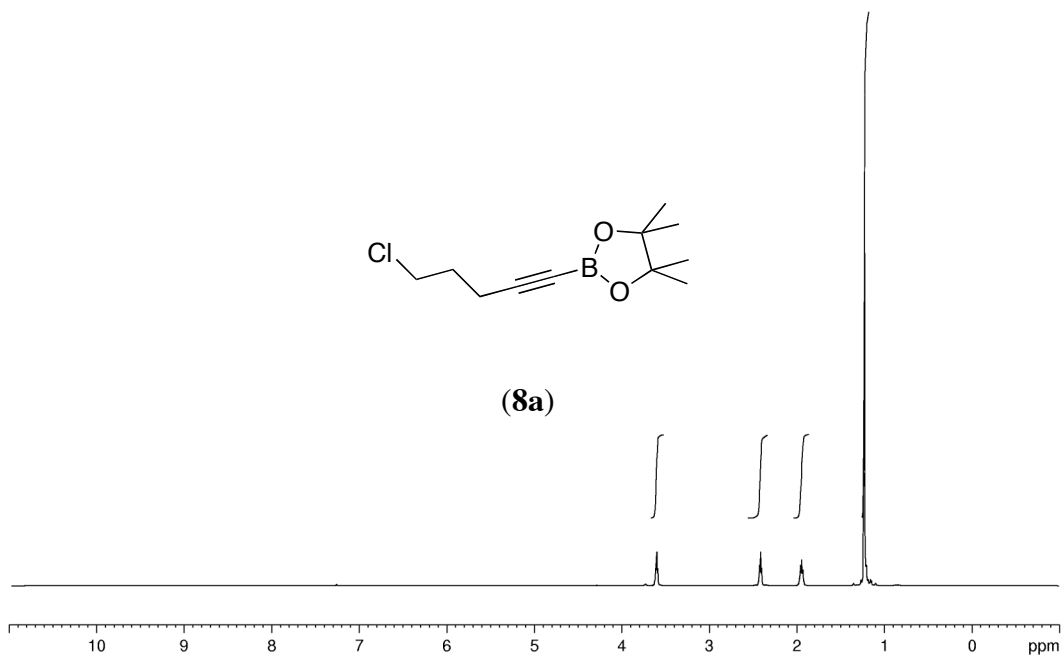
¹H NMR (500 MHz, CDCl₃) Spectrum of 2-((2,4-Difluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7a**)



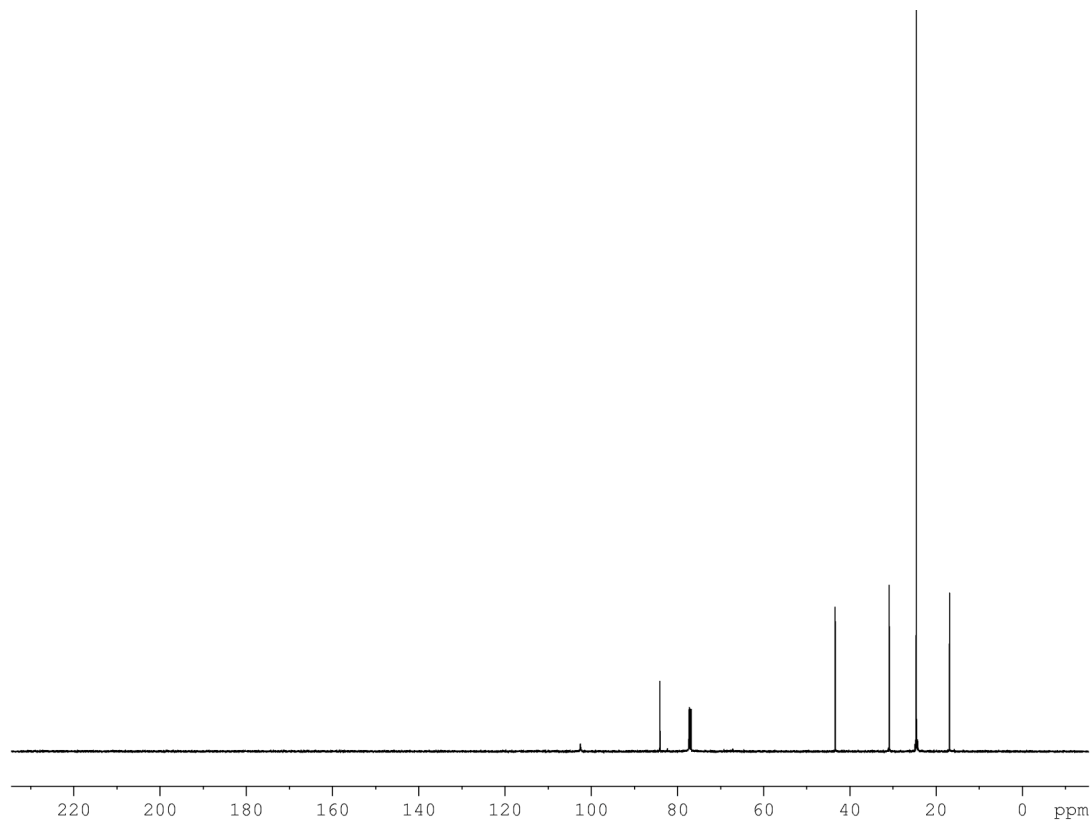
¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 2-((2,4-Difluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7a**)



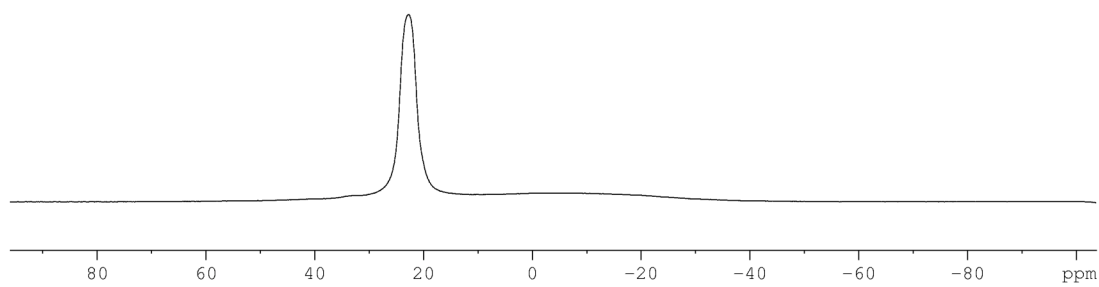
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of 2-((2,4-Difluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7a**)



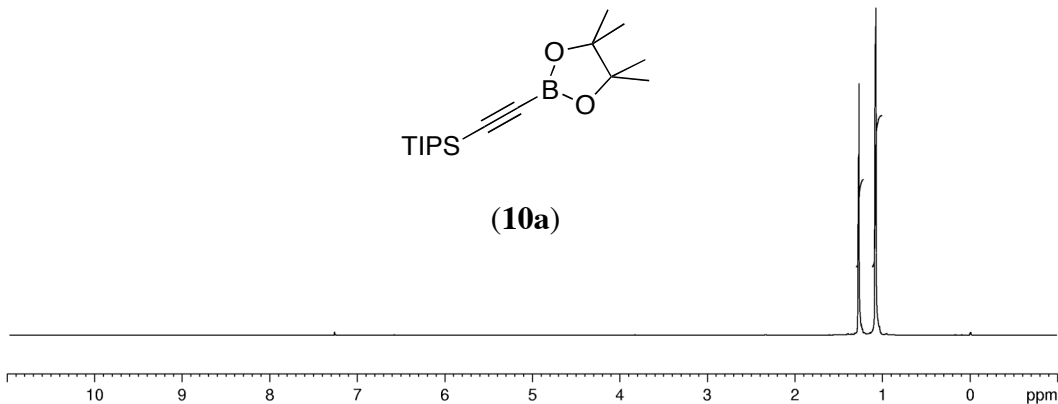
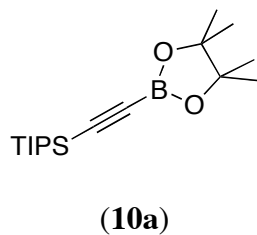
^1H NMR (500 MHz, CDCl_3) Spectrum of 2-(5-Chloropent-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8a**)



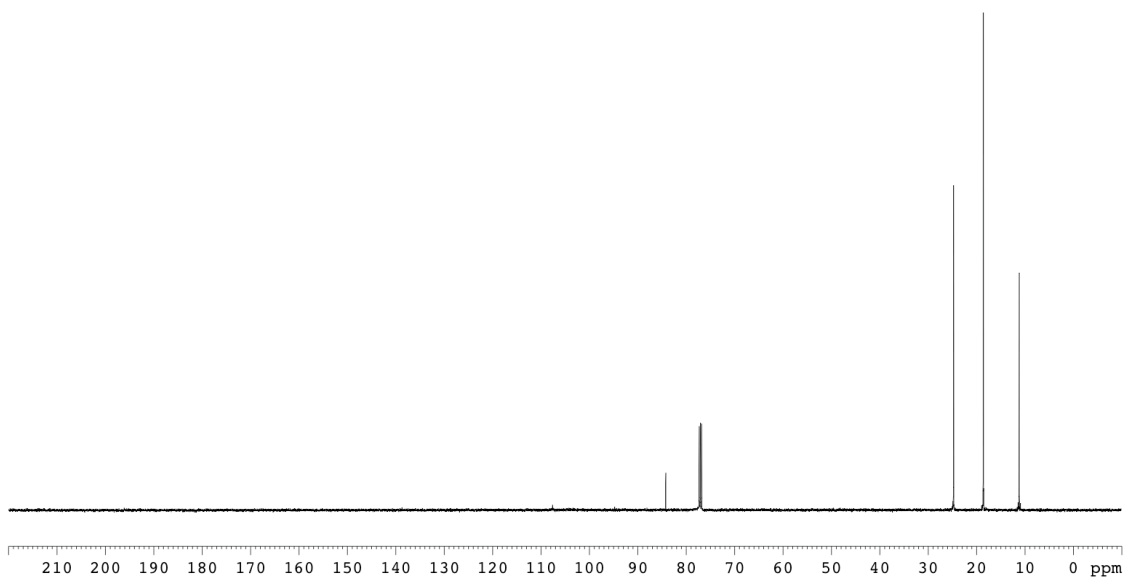
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of 2-(5-Chloropent-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8a**)



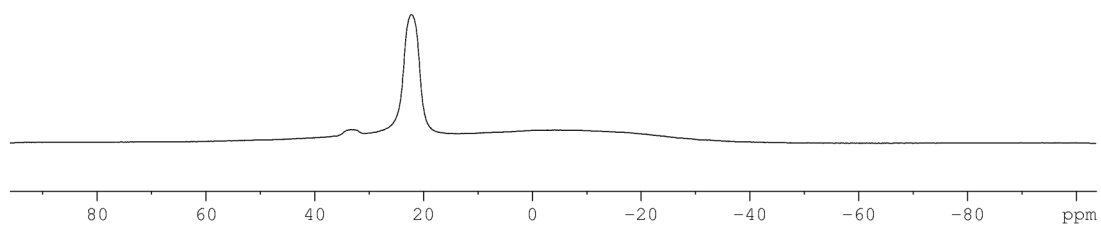
^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of 2-(5-Chloropent-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8a**)



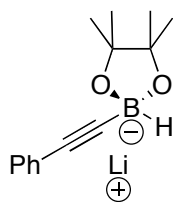
^1H NMR (500 MHz, CDCl_3) Spectrum of Triisopropyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)silane (**10a**)



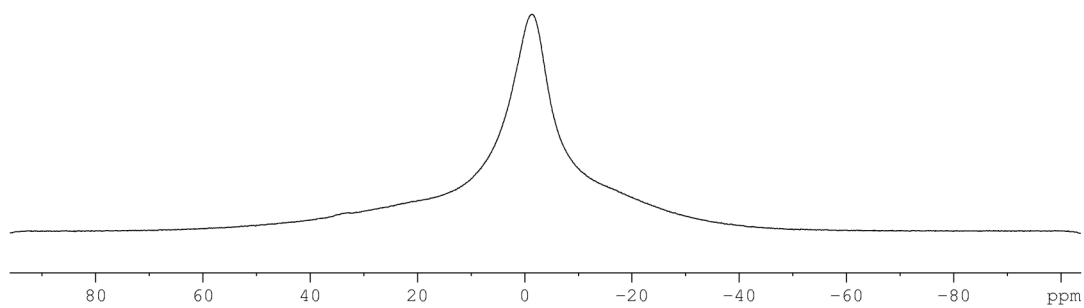
^{13}C NMR (125.8 MHz, CDCl_3) Spectrum of Triisopropyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)silane (**10a**)



^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of Triisopropyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)silane (**10a**)



(**14**)



^{11}B NMR (128.37 MHz, CDCl_3) Spectrum of lithium 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolan-2-uide (**14**)