Supporting Information

Transition Metal-Free 1,2-Carboboration of Unactivated Alkenes

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1 General Information

^{1}H NMR spectra were recorded on Bruker DPX 300 spectrometer (300 MHz) or Agilent DD2 600 spectrometer (600 MHz). Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to 7.26 ppm for $CDCl_3$ or the center line of a multiplet at 2.50 ppm of dmso-d6. Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Bruker DPX 300 spectrometer (75 MHz) or Agilent DD2 600 spectrometer (150 MHz). Chemical shifts are reported in ppm relative to the central line of the triplet at 77.0 ppm for $CDCl_3$ or the center line of a multiplet at 39.5 ppm of dmso-d6. ^{19}F NMR spectra were recorded on Bruker DPX 300 spectrometer (282 MHz) or Agilent DD2 600 spectrometer (564 MHz). Chemical shifts are reported in ppm relative to an external standard ($CFCl_3$: ^{19}F NMR: δ = 0.0). ^{11}B NMR spectra were recorded on Bruker DPX 300 spectrometer (96 MHz) or Agilent DD2 600 spectrometer (192 MHz). Infrared spectra (IR) were measured on Digilab 3100 FT-IR Excalibur Series spectrometer and the position of the absorption bands is given in wave numbers ν (cm^{-1}). High resolution mass spectra (HRMS) were performed on Bruker MicroTof and Thermo-Fisher Scientific LTQ XL Orbitrap. Melting points were

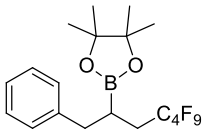
determined in open-end capillary tubes on Stuart SMP10 melting point apparatus.

Reactions were monitored by thin layer chromatography (TLC) with silica gel 60 F254 plates from Merck and flash column chromatography purifications were performed using silica gel 60 (40 – 63 μm) from Merck. Unless otherwise noted, material were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods.

Substituted alkenes **1a**[1], **1e**[1], **1f**[1], **1i**[2], **1m**[3], **1s**[4], **1t**[5], **1w**[6], **1x**[6], **1aa**[6], **1ab-ae**[7], **1af**[8], **1ag**[9], **1ak**[10] were prepared according to the literature. Substituted alkenes **1b-d**, **1g**, 1**h**, **1j-l**, **1n-r**, **1u**, 1**v**, **1y**, 1**z**, **1ah-aj, 1al** and the iodide **2a-j** were purchased from commercial source and used without further purification.

2 General Procedure and Characterization Data

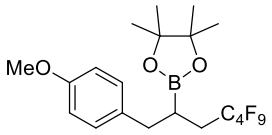
To a Schlenk tube were added alkene **1** (0.50 mmol) and bis(catecholato)diboron **3a** (95 mg, 0.40 mmol). The reaction vessel was evacuated and backfilled with Argon for three times. Dimethylformamide (0.40 mL) and the iodide or carbon tetrachloride **2** (0.20 mmol) were added. (If the alkene is a low boiling point liquid, add it after solvent.) The reaction mixture was stirred under blue LED irradiation at room temperature for 24 hours. A solution of pinacol (95 mg, 0.80 mmol) in triethylamine (0.70 mL) was added to the mixture. After 1 hour, water (15 mL) was added and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate as eluent to give the corresponding product **4** or **5**.



4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylheptan-2-yl)-1,3,2-dioxaborolane (4b)

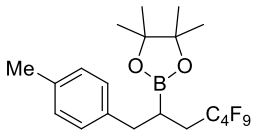
Following general procedure using allylbenzene **1b** (66 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4b** (65 mg, 70% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.30 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 2.83 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.73 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.35 – 2.24 (m, 1H), 2.13 – 2.04 (m, 1H), 1.82 – 1.77 (m, 1H), 1.19 (s, 6H), 1.13 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 140.0, 128.9, 128.4, 126.3, 118.6, 117.4, 110.4, 108.8, 83.6, 36.8, 31.6, 24.7, 24.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.7, 3.1 Hz, 3F), -111.6 – -113.7 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.0. **FTIR** (neat): ν = 2981, 2946, 2362, 2340, 1390, 1333, 1217, 1131, 1077, 1015, 966, 747, 699 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{19}H_{22}BF_9O_2+Na]^+$: 487.1461.

Found: 487.1478.



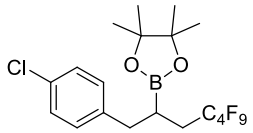
4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-methoxyphenyl)heptan-2-yl)-1,3,2-dioxaborolane (4c)

Following general procedure using 4-allylanisole **1c** (77 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4c** (79 mg, 80% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.13 – 7.11 (m, 2H), 6.83 – 6.81 (m, 2H), 3.78 (s, 3H), 2.77 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.65 (dd, *J* = 13.9, 8.4 Hz, 1H), 2.32 – 2.21 (m, 1H), 2.11 – 2.01 (m, 1H), 1.76 – 1.71 (m, 1H), 1.18 (s, 6H), 1.13 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 158.1, 132.1, 129.8, 118.6, 117.4, 113.8, 110.4, 108.8, 83.6, 55.2, 35.9, 31.5, 24.7, 24.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.0 Hz, 3F), -111.5 – -113.7 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (192 MHz, $CDCl_3$) δ (ppm) 33.4. **FTIR** (neat): ν = 2982, 2840, 2363, 2337, 1613, 1513, 1468, 1390, 1331, 1216, 1179, 1131, 1078, 840, 728, 668 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{20}H_{24}BF_9O_3+Na]^+$: 517.1567. Found: 517.1579.



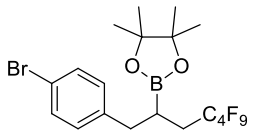
4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(*p*-tolyl)heptan-2-yl)-1,3,2-dioxaborolane (4d)

Following general procedure using 4-allyltoluene **1d** (76 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4d** (75 mg, 79% yield) as a white solid after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). Melting point: 67 – 69 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.09 (s, 4H), 2.81 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.66 (dd, *J* = 13.8, 8.5 Hz, 1H), 2.33 – 2.22 (m, 4H), 2.12 – 2.03 (m, 1H), 1.79 – 1.74 (m, 1H), 1.20 (s, 6H), 1.14 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 136.9, 135.8, 129.0, 128.7, 118.6, 117.4, 110.4, 108.8, 83.6, 36.3, 31.5, 24.7, 24.5, 21.0. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.7, 3.0 Hz, 3F), -111.5 – -113.8 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.9. **FTIR** (neat): ν = 2981, 2933, 2363, 2337, 1517, 1420, 1390, 1329, 1215, 1168, 1130, 1062, 840, 724 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{20}H_{24}BF_9O_2+Na]^+$: 501.1618. Found: 501.1634.



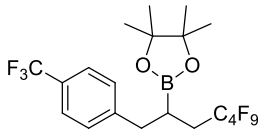
2-(1-(4-Chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)

Following general procedure using 1-allyl-4-chlorobenzene **1e** (77 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4e** (75 mg, 75% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.26 – 7.24 (m, 2H), 7.15 – 7.13 (m, 2H), 2.79 (dd, *J* = 13.9, 8.3 Hz, 1H), 2.69 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.33 – 2.22 (m, 1H), 2.10 – 2.00 (m, 1H), 1.77 – 1.72 (m, 1H), 1.18 (s, 6H), 1.13 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 138.5, 132.1, 130.2, 128.5, 118.5, 117.4, 110.4, 108.8, 83.7, 36.1, 31.5, 24.7, 24.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.7, 3.0 Hz, 3F), -111.7 – -113.7 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.8. **FTIR** (neat): ν = 2981, 2943, 2361, 2339, 1493, 1390, 1331, 1217, 1131, 1016, 966, 840 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{19}H_{21}BClF_9O_2+Na]^+$: 521.1072. Found: 521.1079.



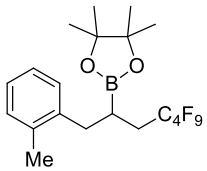
2-(1-(4-Bromophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4f)

Following general procedure using 1-allyl-4-bromobenzene **1f** (99 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4f** (75 mg, 69% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.41 – 7.39 (m, 2H), 7.10 – 7.07 (m, 2H), 2.77 (dd, *J* = 13.9, 8.3 Hz, 1H), 2.68 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.33 – 2.22 (m, 1H), 2.10 – 2.00 (m, 1H), 1.77 – 1.72 (m, 1H), 1.18 (s, 6H), 1.13 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 139.1, 131.4, 130.6, 120.1, 118.5, 117.4, 110.4, 108.7, 83.8, 36.1, 31.5, 24.7, 24.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.0 Hz, 3F), -111.7 – -113.6 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.7. **FTIR** (neat): ν = 2980, 2943, 2361, 2336, 1489, 1390, 1331, 1217, 1131, 1073, 1012, 966, 838 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{19}H_{21}BBrF_9O_2+Na]^+$: 565.0566. Found: 565.0582.



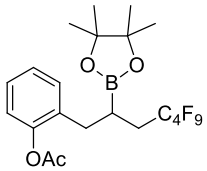
4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-(trifluoromethyl)phenyl)heptan-2-yl)-1,3,2-dioxaborolane (4g)

Following general procedure using 1-allyl-4-(trifluoromethyl)benzene **1g** (84 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4g** (76 mg, 71% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.54 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.87 (dd, *J* = 13.9, 8.5 Hz, 1H), 2.80 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.36 – 2.25 (m, 1H), 2.12 – 2.02 (m, 1H), 1.83 – 1.78 (m, 1H), 1.17 (s, 6H), 1.11 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ (ppm) 144.3, 129.2, 128.8 (q, *J* = 32.5 Hz), 125.3 (q, *J* = 3.5 Hz), 124.3 (q, *J* = 270.0 Hz), 83.8, 36.5, 31.6 (t, *J* = 21.8 Hz), 24.7, 24.5. The signal of the *α*-B-carbon was not observed. $CF_2CF_2CF_2CF_3$ could not be assigned. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -62.6 (s, 3F), -81.2 (t, *J* = 9.6 Hz, 3F), -111.7 – -113.6 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.8. **FTIR** (neat): ν = 2987, 2938, 2364, 2337, 1390, 1325, 1218, 1165, 1127, 1068, 1019, 880, 843 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{20}H_{21}BF_{12}O_2+Na]^+$: 555.1335. Found: 555.1346.



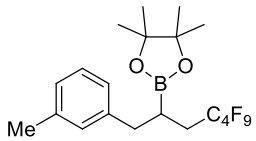
4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(*o*-tolyl)heptan-2-yl)-1,3,2-dioxaborolane (4h)

Following general procedure using 1-allyl-2-methylbenzene **1h** (74 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4h** (69 mg, 72% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.17 – 7.16 (m, 1H), 7.14 – 7.10 (m, 3H), 2.81 (dd, *J* = 14.0, 8.6 Hz, 1H), 2.68 (dd, *J* = 14.0, 8.3 Hz, 1H), 2.38 – 2.27 (m, 4H), 2.14 – 2.06 (m, 1H), 1.81 – 1.76 (m, 1H), 1.18 (s, 6H), 1.10 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 138.2, 136.3, 130.4, 129.3, 126.4, 125.8, 118.5, 117.4, 110.4, 108.8, 83.6, 34.1, 32.1, 24.8, 24.4, 19.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.1 Hz, 3F), -111.6 – -113.8 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.1. **FTIR** (neat): ν = 2981, 2360, 2339, 1390, 1330, 1216, 1131, 1078, 1014, 967, 744 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{20}H_{24}BF_9O_2+Na]^+$: 501.1618. Found: 501.1631.



2-(4,4,5,5,6,6,7,7,7-Nonafluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)phenyl acetate (4i)

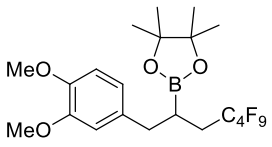
Following general procedure using 2-allylphenyl acetate **1i** (88 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4i** (66 mg, 63% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1 to 50:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.28 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24 (td, *J* = 7.7, 1.7 Hz, 1H), 7.16 (td, *J* = 7.5, 1.3 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.73 (dd, *J* = 14.1, 8.1 Hz, 1H), 2.60 (dd, *J* = 14.0, 8.3 Hz, 1H), 2.35 – 2.24 (m, 4H), 2.11 – 2.01 (m, 1H), 1.83 – 1.77 (m, 1H), 1.18 (s, 6H), 1.13 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 169.3, 149.3, 132.0, 130.6, 127.6, 125.9, 122.4, 118.5, 117.4, 110.4, 108.7, 83.7, 31.7, 31.4, 24.7, 24.4, 20.9. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.0 Hz, 3F), -111.8 – -113.7 (m, 2F), -124.6 – -124.64 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.1. **FTIR** (neat): ν = 2982, 2365, 2337, 1767, 1490, 1373, 1204, 1171, 1131, 1079, 1012, 750 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{21}H_{24}BF_9O_4+Na]^+$: 545.1516. Found: 545.1526.



4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(*m*-tolyl)heptan-2-yl)-1,3,2-dioxaborolane (4j)

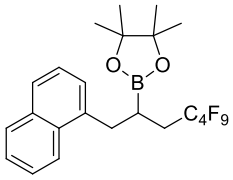
Following general procedure using 1-allyl-3-methylbenzene **1j** (76 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4j** (73 mg, 77% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.17 (t, *J* = 7.5 Hz, 1H), 7.03 – 7.00 (m, 3H), 2.79 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.69 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.34 – 2.23 (m, 4H), 2.14 – 2.04 (m, 1H), 1.81 – 1.75 (m, 1H), 1.19 (s, 6H), 1.13 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 139.9, 137.8, 129.7, 128.2, 127.0, 125.9, 118.6, 117.4, 110.4, 108.8, 83.6, 36.7, 31.7, 24.7, 24.5, 21.3. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.7, 2.9 Hz, 3F), -111.5 – -113.7 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.0. **FTIR** (neat): ν = 2981, 2947, 2832, 2360, 2336, 1390, 1331, 1218, 1169, 1134, 1076, 1019, 879, 779

(cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{20}H_{24}BF_9O_2+Na]^+$: 501.1618. Found: 501.1626.



2-(1-(3,4-Dimethoxyphenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k)

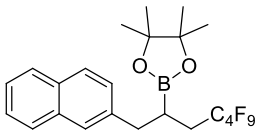
Following general procedure using 4-allyl-1,2-dimethoxybenzene **1k** (86 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4k** (78 mg, 75% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 70:1 to 20:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 6.78 – 6.76 (m, 1H), 6.73 – 6.72 (m, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.77 (dd, *J* = 13.9, 7.9 Hz, 1H), 2.63 (dd, *J* = 13.9, 8.6 Hz, 1H), 2.31 – 2.20 (m, 1H), 2.10 – 2.01 (m, 1H), 1.77 – 1.72 (m, 1H), 1.17 (s, 6H), 1.13 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 148.8, 147.5, 132.5, 120.9, 118.6, 117.4, 111.9, 111.1, 110.4, 108.7, 83.6, 55.9, 55.7, 36.2, 31.4, 24.7, 24.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.6, 2.8 Hz, 3F), -111.5 – -113.8 (m, 2F), -124.66 – -124.7 (m, 2F), -126.1 – -126.12 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.2. **FTIR** (neat): ν = 2943, 2833, 2361, 2339, 1516, 1390, 1332, 1217, 1130, 1074, 1031, 968, 849, 727 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{21}H_{26}BF_9O_4+Na]^+$: 547.1673. Found: 547.1685.



4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-1-yl)heptan-2-yl)-1,3,2-dioxaborolane (4l)

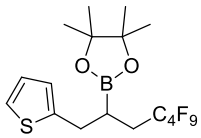
Following general procedure using 1-allylnaphthalene **1l** (84 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4l** (73 mg, 71% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.06 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.53 (m, 1H), 7.50 – 7.47 (m, 1H), 7.41 – 7.37 (m, 2H), 3.35 (dd, *J* = 14.2, 8.2 Hz, 1H), 3.13 (dd, *J* = 14.2, 8.3 Hz, 1H), 2.48 – 2.38 (m, 1H), 2.24 – 2.14 (m, 1H), 2.02 – 1.97 (m, 1H), 1.19 (s, 6H), 1.11 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 136.0, 134.0, 131.9, 128.8, 127.2, 126.7, 126.0, 125.5, 125.2, 123.7, 118.6, 117.4, 110.4, 108.8, 83.6, 33.9, 32.3, 24.8, 24.4. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.0 Hz, 3F),

-111.4 – -113.6 (m, 2F), -124.6 – -124.65 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.6. **FTIR** (neat): ν = 2981, 2946, 2890, 2877, 2361, 2340, 1441, 1391, 1234, 1221, 1168, 1133, 1073, 1014, 777 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{23}H_{24}BF_9O_2+Na]^+$: 537.1618. Found: 537.1629.



4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-2-yl)heptan-2-yl)-1,3,2-dioxaborolane (4a)

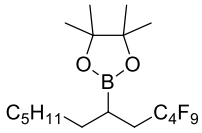
Following general procedure using 2-allylnaphthalene **1a** (84 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4a** (72 mg, 70% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.82 – 7.77 (m, 3H), 7.66 (s, 1H), 7.48 – 7.43 (m, 2H), 7.37 (dd, *J* = 8.4, 1.7 Hz, 1H), 3.02 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.90 (dd, *J* = 13.9, 8.2 Hz, 1H), 2.41 – 2.30 (m, 1H), 2.18 – 2.09 (m, 1H), 1.94 – 1.89 (m, 1H), 1.18 (s, 6H), 1.11 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 137.6, 133.5, 132.2, 128.1, 127.6, 127.5, 127.3, 127.2, 126.0, 125.3, 118.6, 117.4, 110.4, 108.8, 83.7, 36.9, 31.6, 24.7, 24.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (282 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.2 Hz, 3F), -111.1 – -113.8 (m, 2F), -124.4 – -124.5 (m, 2F), -125.9 – -126.0 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.9. **FTIR** (neat): ν = 2981, 2946, 2360, 1390, 1337, 1219, 1168, 1133, 1077, 1019, 881, 851 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{23}H_{24}BF_9NaO_2+Na]^+$: 537.1618. Found: 537.1623.



4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(thiophen-2-yl)heptan-2-yl)-1,3,2-dioxaborolane (4m)

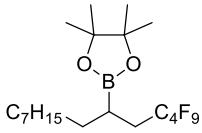
Following general procedure using 2-allylthiophene **1m** (61 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4m** (56 mg, 60% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.83 (dd, *J* = 3.4, 1.1 Hz, 1H), 3.07 (dd, *J* = 14.8, 7.7 Hz, 1H), 2.94 (dd, *J* = 14.8, 7.9 Hz, 1H), 2.35 – 2.25 (m, 1H), 2.20 – 2.10 (m, 1H), 1.82 – 1.77 (m, 1H), 1.20 (s, 6H), 1.17 (s, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 142.7, 126.6, 125.5, 123.7, 118.6, 117.4, 110.4, 108.8, 83.8, 31.1, 30.8, 24.7, 24.6. The signal

of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.1 Hz, 3F), -111.7 – -113.6 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (192 MHz, $CDCl_3$) δ (ppm) 33.4. **FTIR** (neat): ν = 2982, 2947, 2361, 2340, 1390, 1335, 1216, 1132, 1076, 1020, 965, 851, 693 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{17}H_{20}BF_9O_2S + Na]^+$: 493.1026. Found: 493.1047.



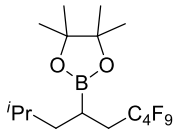
4,4,5,5-Tetramethyl-2-(1,1,1,2,2,3,3,4,4-nonafluorododecan-6-yl)-1,3,2-dioxaborolane (4n)

Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4n** (83 mg, 91% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.35 – 2.24 (m, 1H), 2.08 – 1.98 (m, 1H), 1.53 – 1.47 (m, 1H), 1.43 – 1.23 (m, 22H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.7, 117.5, 110.5, 108.8, 83.5, 32.2, 31.7, 31.4, 29.3, 28.6, 24.7, 24.6, 22.6, 14.0. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.7, 3.1 Hz, 3F), -112.2 – -113.9 (m, 2F), -124.7 – -124.75 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.0. **FTIR** (neat): ν = 2980, 2932, 2859, 2361, 2337, 1457, 1391, 1328, 1216, 1166, 1132, 1078, 879, 724, 668 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{18}H_{28}BF_9O_2+Na]^+$: 481.1931. Found: 481.1951.



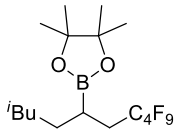
4,4,5,5-Tetramethyl-2-(1,1,1,2,2,3,3,4,4-nonafluorotetradecan-6-yl)-1,3,2-dioxaborolane (4o)

Following general procedure using 1-decene **1o** (95 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4o** (82 mg, 84% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.35 – 2.24 (m, 1H), 2.07 – 1.98 (m, 1H), 1.53 – 1.47 (m, 1H), 1.42 – 1.35 (m, 2H), 1.34 – 1.23 (m, 24H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.7, 117.5, 110.5, 108.8, 83.5, 32.3, 31.9, 31.4, 29.6, 29.4, 29.2, 28.6, 24.7, 24.6, 22.7, 14.1. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (t, *J* = 8.7 Hz, 3F), -112.2 – -113.9 (m, 2F), -124.7 – -124.8 (m, 2F), -126.1 – -126.12 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.0. **FTIR** (neat): ν = 2979, 2927, 2858, 2365, 2337, 1391, 1328, 1216, 1166, 1132, 1076, 879, 725, 668 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{20}H_{32}BF_9O_2+Na]^+$: 509.2244. Found: 509.2259.



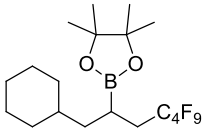
4,4,5,5-Tetramethyl-2-(6,6,7,7,8,8,9,9,9-nonafluoro-2-methylnonan-4-yl)-1,3,2-dioxaborolane (4p)

Following general procedure using 4-methylpent-1-ene **1p** (63 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4p** (72 mg, 83% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.32 – 2.21 (m, 1H), 2.06 – 1.97 (m, 1H), 1.63 – 1.56 (m, 1H), 1.48 – 1.39 (m, 2H), 1.23 – 1.19 (m, 13H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.6, 117.5, 110.5, 108.8, 83.4, 40.5, 32.4, 26.9, 24.7, 24.6, 22.8, 22.3. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.7, 3.1 Hz, 3F), -111.9 – -113.9 (m, 2F), -124.7 – -124.8 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.2. **FTIR** (neat): ν = 2979, 2962, 2935, 2364, 2337, 1471, 1373, 1217, 1167, 1133, 1077, 880, 727 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{16}H_{24}BF_9O_2+Na]^+$: 453.1618. Found: 453.1623.



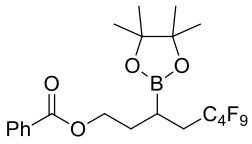
4,4,5,5-Tetramethyl-2-(7,7,8,8,9,9,10,10,10-nonafluoro-2-methyldecan-5-yl)-1,3,2-dioxaborolane (4q)

Following general procedure using 5-methylhex-1-ene **1q** (71 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4q** (78 mg, 88% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 2.41 – 2.20 (m, 1H), 2.13 – 1.93 (m, 1H), 1.57 – 1.32 (m, 4H), 1.29 – 1.13 (m, 14H), 0.87 (dd, *J* = 6.6, 0.7 Hz, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.6, 117.5, 110.5, 108.8, 83.5, 37.9, 32.3, 29.2, 28.1, 24.7, 24.6, 22.6, 22.4. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (282 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.3 Hz, 3F), -111.8 – -114.2 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 34.0. **FTIR** (neat): ν = 2980, 2960, 2933, 2874, 2364, 2337, 1391, 1327, 1218, 1134, 1079, 878, 725, 631 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{17}H_{26}BF_9O_2+Na]^+$: 467.1774. Found: 467.1777.



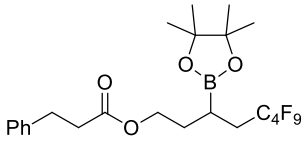
2-(1-Cyclohexyl-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4r)

Following general procedure using allylcyclohexane **1r** (77 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4r** (81 mg, 86% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 150:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.31 – 2.20 (m, 1H), 2.05 – 1.96 (m, 1H), 1.81 – 1.78 (m, 1H), 1.71 – 1.62 (m, 4H), 1.51 – 1.46 (m, 1H), 1.42 – 1.36 (m, 1H), 1.27 – 1.10 (m, 17H), 0.90 – 0.81 (m, 2H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.6, 117.5, 110.5, 108.8, 83.4, 39.0, 36.6, 33.6, 33.0, 32.6, 26.6, 26.4, 26.3, 24.8, 24.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.7, 3.1 Hz, 3F), -111.9 – -113.9 (m, 2F), -124.7 – -124.8 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.2. **FTIR** (neat): ν = 2930, 2854, 2361, 2339, 1452, 1327, 1217, 1131, 1075, 1013, 968 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{19}H_{28}BF_9O_2+Na]^+$: 493.1931. Found: 493.1928.



5,5,6,6,7,7,8,8,8-Nonafluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl benzoate (4s)

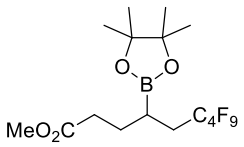
Following general procedure using 3-butenyl benzoate **1s** (88 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4s** (64 mg, 62% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1 to 40:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.05 – 8.03 (m, 2H), 7.56 – 7.54 (m, 1H), 7.45 – 7.42 (m, 2H), 4.43 – 4.32 (m, 2H), 2.45 – 2.35 (m, 1H), 2.24 – 2.14 (m, 1H), 2.04 – 1.90 (m, 2H), 1.63 – 1.58 (m, 1H), 1.24 (d, *J* = 3.3 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 166.5, 132.9, 130.2, 129.6, 128.3, 118.6, 117.4, 110.4, 108.8, 83.9, 63.7, 31.8, 29.9, 24.7, 24.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.0 Hz, 3F), -112.2 – -113.6 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.05 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.1. **FTIR** (neat): ν = 2980, 2947, 2360, 1724, 1452, 1383, 1336, 1275, 1233, 1133, 1071, 1027, 713 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{21}H_{24}BF_9O_4+Na]^+$: 545.1516. Found: 545.1531.



5,5,6,6,7,7,8,8,8-Nonafluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl

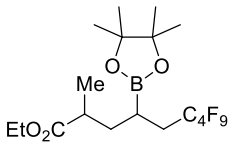
3-phenylpropanoate (4t)

Following general procedure using but-3-en-1-yl 3-phenylpropanoate **1t** (102 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4t** (64 mg, 59% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 80:1 to 40:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.30 – 7.27 (m, 2H), 7.21 – 7.19 (m, 3H), 4.17 – 4.07 (m, 2H), 2.95 (t, *J* = 7.9 Hz, 2H), 2.63 (dd, *J* = 8.3, 7.3 Hz, 2H), 2.39 – 2.28 (m, 1H), 2.15 – 2.05 (m, 1H), 1.87 – 1.81 (m, 1H), 1.78 – 1.72 (m, 1H), 1.50 – 1.45 (m, 1H), 1.24 (d, *J* = 2.9 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 172.8, 140.5, 128.5, 128.2, 126.2, 118.6, 117.4, 110.4, 108.8, 83.8, 63.2, 35.8, 31.7, 30.9, 29.8, 24.7, 24.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.0 Hz, 3F), -112.2 – -113.8 (m, 2F), -124.7 – -124.71 (m, 2F), -126.0 – -126.04 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 34.2. **FTIR** (neat): ν = 2981, 2947, 2360, 2340, 1737, 1383, 1332, 1217, 1132, 1077, 737, 698 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{23}H_{28}BF_9O_4+Na]^+$: 573.1829. Found: 573.1844.



Methyl 6,6,7,7,8,8,9,9,9-nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanoate (4u)

Following general procedure using methyl pent-4-enoate **1u** (57 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4u** (57 mg, 62% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1 to 30:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 3.66 (s, 3H), 2.41 – 2.27 (m, 3H), 2.10 – 2.00 (m, 1H), 1.86 – 1.76 (m, 2H), 1.41 – 1.36 (m, 1H), 1.23 (d, *J* = 2.4 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 173.5, 118.6, 117.4, 110.4, 108.8, 83.8, 51.6, 33.0, 31.9, 26.3, 24.7, 24.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.7, 3.1 Hz, 3F), -111.4 – -114.5 (m, 2F), -124.6 – -124.9 (m, 2F), -125.5 – -127.0 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.0. **FTIR** (neat): ν = 2983, 2364, 2337, 1741, 1437, 1331, 1216, 1167, 1131, 1074, 1017, 878, 848, 735 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{16}H_{22}BF_9O_4+Na]^+$: 483.1360. Found: 483.1378.

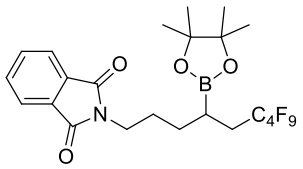


Ethyl

6,6,7,7,8,8,9,9,9-nonafluoro-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanoa

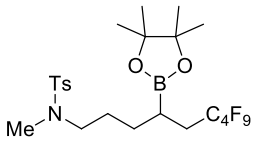
te (4v)

Following general procedure using ethyl 2-methylpent-4-enoate **1v** (81 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4v** in an inseparable diastereomeric mixture (64 mg, 66% yield, *dr* = 1.6:1) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 70:1 to 50:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 4.14 – 4.09 (m, 2H), 2.52 – 2.45 (m, 1H), 2.35 – 2.20 (m, 1H), 2.14 – 2.01 (m, 1H), 1.93 – 1.88 and 1.79 – 1.74 (m, 1H), 1.57 – 1.53 and 1.50 – 1.45 (m, 1H), 1.42 – 1.37 (m, 1H), 1.26 – 1.22 (m, 15H), 1.17 and 1.15 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 176.3, 176.2, 118.5, 118.48, 117.4, 110.4, 108.8, 83.7, 83.6, 60.3, 38.7, 38.1, 35.1, 34.8, 32.1, 31.9, 24.7, 24.6, 17.7, 16.9, 14.15, 14.1. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.3, 2.8 Hz, 3F), -111.8 – -113.9 (m, 2F), -124.7 – -124.8 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.4. **FTIR** (neat): ν = 2983, 2938, 2364, 2336, 1734, 1374, 1329, 1216, 1166, 1131, 1077, 863, 727 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{18}H_{26}BF_9O_4+Na]^+$: 511.1673. Found: 511.1692.



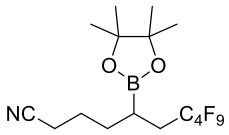
2-(6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)isoindoline-1,3-dione (4w)

Following general procedure using 2-(pent-4-en-1-yl)isoindoline-1,3-dione **1w** (108 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4w** (56 mg, 50% yield) as a white solid after purification by flash chromatography (*n*-pentane/ ethyl acetate = 40:1 to 20:1). Melting point: 62 – 64 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 3.68 (t, *J* = 7.1 Hz, 2H), 2.34 – 2.24 (m, 1H), 2.07 – 1.97 (m, 1H), 1.75 – 1.68 (m, 2H), 1.58 – 1.45 (m, 2H), 1.42 – 1.38 (m, 1H), 1.21 (s, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 168.3, 133.8, 132.1, 123.2, 118.5, 117.4, 110.4, 108.7, 83.7, 37.9, 32.1, 28.6, 27.7, 24.7, 24.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 2.9 Hz, 3F), -112.3 – -113.8 (m, 2F), -124.7 – -124.72 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.6. **FTIR** (neat): ν = 2987, 2938, 2866, 2364, 2336, 1712, 1469, 1374, 1330, 1215, 1131, 1066, 1020, 849, 717 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{23}H_{25}BF_9NO_4+Na]^+$: 584.1625. Found: 584.1642.



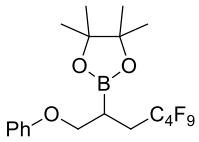
***N*,4-Dimethyl-*N*-(6,6,7,7,8,8,9,9,9-nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) nonyl)benzenesulfonamide (4x)**

Following general procedure using *N*,4-dimethyl-*N*-(pent-4-en-1-yl)benzenesulfonamide **1x** (127 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4x** (85 mg, 71% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 40:1 to 20:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.65 – 7.63 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.02 – 2.92 (m, 2H), 2.69 (s, 3H), 2.41 (s, 3H), 2.36 – 2.25 (m, 1H), 2.06 – 1.96 (m, 1H), 1.59 – 1.50 (m, 3H), 1.49 – 1.42 (m, 1H), 1.37 – 1.32 (m, 1H), 1.22 (d, *J* = 3.7 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 143.2, 134.6, 129.6, 127.4, 118.6, 117.4, 110.4, 108.7, 83.6, 50.0, 34.6, 32.1, 28.2, 26.8, 24.7, 24.6, 21.4. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.2 Hz, 3F), -112.3 – -113.8 (m, 2F), -124.7 – -124.72 (m, 2F), -126.0 – -126.05 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.6. **FTIR** (neat): ν = 2981, 2942, 2873, 2360, 2340, 1457, 1339, 1216, 1160, 1131, 816, 716, 652 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{23}H_{31}BF_9NO_4S+Na]^+$: 622.1815. Found: 622.1842.



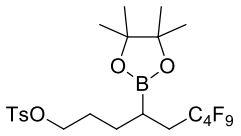
7,7,8,8,9,9,10,10,10-Nonafluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decanenitrile (4y)

Following general procedure using 5-hexenenitrile **1y** (57 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4y** (42 mg, 47% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 50:1 to 20:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.39 – 2.29 (m, 3H), 2.09 – 1.99 (m, 1H), 1.75 – 1.84 (m, 3H), 1.63 – 1.55 (m, 1H), 1.41 – 1.37 (m, 1H), 1.24 (d, *J* = 2.7 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 119.3, 118.5, 117.4, 110.4, 108.7, 83.9, 31.9, 30.3, 24.7, 24.6, 24.6, 17.2. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 11.7, 3.9 Hz, 3F), -112.3 – -113.7 (m, 2F), -124.7 – -124.71 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.1. **FTIR** (neat): ν = 2983, 2936, 2363, 2336, 1392, 1333, 1217, 1168, 1131, 1073, 879, 725, 632 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{16}H_{21}BF_9NO_2+Na]^+$: 464.1414. Found: 464.1429.



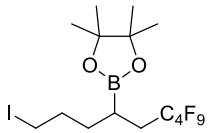
4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-phenoxyheptan-2-yl)-1,3,2-dioxaborola ne (4z)

Following general procedure using (allyloxy)benzene **1z** (69 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4z** (39 mg, 40% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 150:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.30 – 7.26 (m, 2H), 6.95 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.91 – 6.89 (m, 2H), 4.10 (d, *J* = 6.0 Hz, 2H), 2.52 – 2.35 (m, 2H), 1.96 – 1.92 (m, 1H), 1.26 (d, *J* = 8.3 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 158.8, 129.4, 120.9, 118.8, 117.4, 114.6, 110.4, 108.8, 84.0, 68.4, 28.7, 24.7, 24.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.1 Hz, 3F), -113.1 – -113.2 (m, 2F), -124.5 – -124.55 (m, 2F), -125.9 – -126.0 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.9. **FTIR** (neat): ν = 2982, 2364, 2337, 1601, 1499, 1473, 1338, 1235, 1171, 1134, 1079, 878, 753, 691 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{19}H_{22}BF_9O_3+Na]^+$: 503.1410. Found: 503.1426.



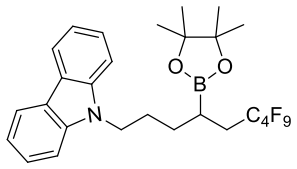
6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl 4-methylbenzenesulfonate (4aa)

Following general procedure using pent-4-en-1-yl 4-methylbenzenesulfonate **1aa** (120 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4aa** (32 mg, 27% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 25:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.79 – 7.77 (m, 2H), 7.34 – 7.33 (m, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 2.33 – 2.22 (m, 1H), 2.01 – 1.91 (m, 1H), 1.69 – 1.66 (m, 2H), 1.54 – 1.40 (m, 2H), 1.31 – 1.26 (m, 1H), 1.21 (d, *J* = 3.9 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 144.7, 133.1, 129.8, 127.9, 118.5, 117.4, 110.4, 108.7, 83.7, 70.2, 31.9, 28.0, 27.0, 24.7, 24.6, 21.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.0 Hz, 3F), -112.3 – -113.8 (m, 2F), -124.7 – -124.71 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.6. **FTIR** (neat): ν = 2864, 2361, 2337, 1457, 1388, 1358, 1214, 1188, 1177, 1134, 1072, 827, 811, 727 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{22}H_{28}BF_9O_5S +Na]^+$: 609.1499. Found: 609.1516.



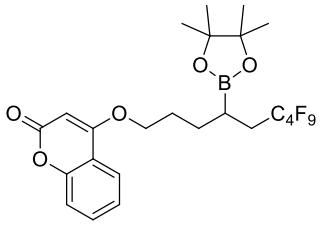
4,4,5,5-Tetramethyl-2-(6,6,7,7,8,8,9,9,9-nonafluoro-1-iodononan-4-yl)-1,3,2-dioxaborolane (4aa')

Following general procedure using pent-4-en-1-yl 4-methylbenzenesulfonate **1aa** (120 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4aa'** (34 mg, 31%) as a colorless oil after purification by flash chromatography (*n*-pentane). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 3.21 – 3.15 (m, 2H), 2.39 – 2.28 (m, 1H), 2.09 – 1.99 (m, 1H), 1.89 – 1.84 (m, 2H), 1.65 – 1.51 (m, 2H), 1.43 – 1.38 (m, 1H), 1.24 (d, *J* = 3.6 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.6, 117.4, 110.4, 108.8, 83.7, 32.5, 32.2, 32.1, 24.8, 24.6, 6.1. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.1 Hz, 3F), -112.3 – -113.8 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.01 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.6. **FTIR** (neat): ν = 2982, 2933, 2859, 2363, 2337, 1457, 1391, 1331, 1217, 1167, 1132, 1078, 1017, 878, 571 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{15}H_{21}BF_9IO_2+Na]^+$: 565.0428. Found: 565.0429.



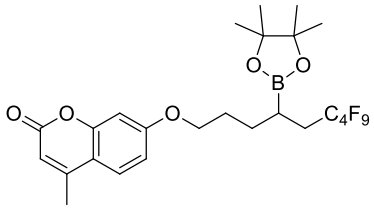
9-(6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)-9*H*-carbazole (4ab)

Following general procedure using 9-(pent-4-en-1-yl)-9*H*-carbazole **1ab** (118 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4ab** (81 mg, 70% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 150:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.13 – 8.11 (m, 2H), 7.49 – 7.46 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.23 (m, 2H), 4.39 – 4.28 (m, 2H), 2.37 – 2.27 (m, 1H), 2.06 – 1.90 (m, 3H), 1.68 – 1.62 (m, 1H), 1.59 – 1.53 (m, 1H), 1.50 – 1.45 (m, 1H), 1.18 (d, *J* = 3.3 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 140.3, 125.6, 122.9, 120.3, 118.8, 118.6, 117.4, 110.4, 108.8, 108.6, 83.7, 42.8, 32.2, 29.0, 27.9, 24.6, 24.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 2.9 Hz, 3F), -112.2 – -113.7 (m, 2F), -124.6 – -124.7 (m, 2F), -125.9 – -126.0 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.6. **FTIR** (neat): ν = 2979, 2935, 2364, 2337, 1453, 1391, 1326, 1215, 1167, 1131, 1073, 878, 848, 748, 722 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{27}H_{29}BF_9NO_2+Na]^+$: 604.2040. Found: 604.2043.



4-((6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)oxy)-2*H*-chromen-2-one (4ac)

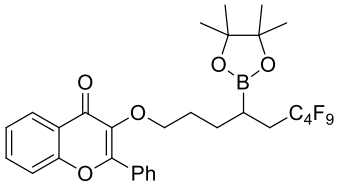
Following general procedure using 4-(pent-4-en-1-yloxy)-2*H*-chromen-2-one **1ac** (115 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4ac** (85 mg, 74% yield) as a white solid after purification by flash chromatography (*n*-pentane/ ethyl acetate = 15:1). Melting point: 76 – 78 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.82 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.31 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.27 – 7.25 (m, 1H), 5.66 (s, 1H), 4.13 (t, *J* = 6.2 Hz, 2H), 2.37 (ddd, *J* = 30.6, 15.5, 9.1 Hz, 1H), 2.15 – 2.05 (m, 1H), 1.99 – 1.91 (m, 2H), 1.78 – 1.65 (m, 2H), 1.50 – 1.46 (m, 1H), 1.25 (d, *J* = 2.7 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 165.6, 162.9, 153.3, 132.3, 123.8, 123.0, 118.6, 117.4, 116.8, 115.7, 110.4, 108.8, 90.5, 83.8, 69.0, 31.9, 27.6, 24.7, 24.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.0 Hz, 3F), -112.3 – -113.6 (m, 2F), -124.6 – -124.7 (m, 2F), -125.9 – -126.0 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.3. **FTIR** (neat): ν = 2980, 2362, 2340, 1723, 1627, 1458, 1355, 1219, 1131, 1076, 1017, 751 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{24}H_{26}BF_9O_5+Na]^+$: 599.1622. Found: 599.1627.



4-Methyl-7-((6,6,7,7,8,8,9,9,9-nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)oxy)-2*H*-chromen-2-one (4ad)

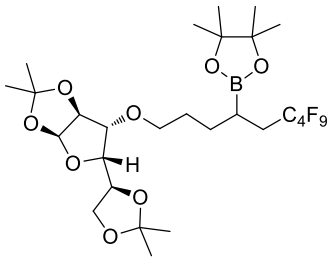
Following general procedure using 4-methyl-7-(pent-4-en-1-yloxy)-2*H*-chromen-2-one **1ad** (122 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4ad** (92 mg, 78% yield) as a white solid after purification by flash chromatography (*n*-pentane/ diethyl ether = 5:1 to 3:1). Melting point: 82 – 84 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.47 (d, *J* = 8.8 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 6.11 (s, 1H), 4.01 (t, *J* = 6.3 Hz, 2H), 2.39 – 2.30 (m, 4H), 2.12 – 2.04 (m, 1H), 1.88 – 1.83 (m, 2H), 1.72 – 1.59 (m, 2H), 1.46 – 1.41 (m, 1H), 1.23 (d, *J* = 2.8 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 162.0, 161.3, 155.2, 152.5, 125.4, 118.6, 117.4, 113.5, 112.5, 111.8, 110.4, 108.8, 101.4, 83.7, 68.2, 32.0, 28.0, 27.7, 24.7, 24.6, 18.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (t, *J* = 9.6 Hz, 3F), -112.2 – -113.7 (m, 2F), -124.7 – -124.71 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm)

31.6. **FTIR** (neat): ν = 2987, 2944, 2364, 2337, 1718, 1605, 1476, 1391, 1372, 1331, 1266, 1205, 1131, 1068, 846, 743 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{25}H_{28}BF_9O_5+Na]^+$: 613.1778. Found: 613.1793.



3-((6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)oxy)-2-phenyl-4*H*-chromen-4-one (4ae)

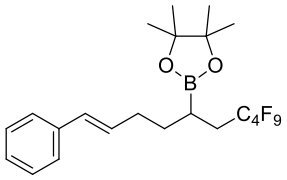
Following general procedure using 3-(pent-4-en-1-yloxy)-2-phenyl-4*H*-chromen-4-one **1ae** (153 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4ae** (66 mg, 51% yield) as a light yellow oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 20:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.26 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.08 – 8.06 (m, 2H), 7.68 – 7.65 (m, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.48 (m, 3H), 7.41 – 7.38 (m, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 2.30 – 2.20 (m, 1H), 1.98 – 1.89 (m, 1H), 1.77 – 1.66 (m, 2H), 1.56 – 1.44 (m, 2H), 1.29 (ddd, *J* = 16.3, 6.0, 3.2 Hz, 1H), 1.20 (d, *J* = 5.6 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 175.1, 155.9, 155.3, 140.5, 133.4, 131.1, 130.6, 128.7, 128.3, 125.8, 124.6, 124.2, 118.5, 118.0, 117.4, 110.4, 108.8, 83.5, 72.4, 32.2, 29.1, 27.8, 24.7, 24.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.2 Hz, 3F), -112.1 – -113.8 (m, 2F), -124.65 – -124.7 (m, 2F), -126.0 – -126.02 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 31.9. **FTIR** (neat): ν = 2979, 2938, 2363, 2337, 1643, 1468, 1373, 1216, 1167, 1131, 1075, 758, 691 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{30}H_{30}BF_9O_5+Na]^+$: 675.1935. Found: 675.1946.



2-(1-(((3a*S*,5*S*,6*R*,6a*S*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)-6,6,7,7,8,8,9,9,9-nonafluorononan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4af)

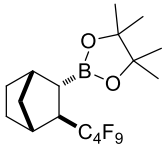
Following general procedure using (3a*S*,5*S*,6*R*,6a*S*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(pent-4-en-1-yloxy)tetrahydrofuro[2,3-*d*][1,3]dioxole **1af** (164 mg, 500 μmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4af** in an inseparable diastereomeric mixture (96 mg, 71% yield, *dr* = 1:1) as a

colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 20:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 5.84 (d, *J* = 3.7 Hz, 1H), 4.50 (dd, *J* = 3.7, 2.1 Hz, 1H), 4.30 – 4.26 (m, 1H), 4.10 – 4.04 (m, 2H), 3.97 (dd, *J* = 8.5, 5.8 Hz, 1H), 3.83 (d, *J* = 3.1 Hz, 1H), 3.61 – 3.58 (m, 1H), 3.53 – 3.49 (m, 1H), 2.36 – 2.25 (m, 1H), 2.06 – 1.98 (m, 1H), 1.62 – 1.53 (m, 3H), 1.51 – 1.44 (m, 4H), 1.40 (s, 3H), 1.39 – 1.34 (m, 1H), 1.32 (s, 3H), 1.30 (s, 3H), 1.22 (d, *J* = 3.6 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.6, 117.4, 111.7, 111.71, 110.4, 108.9, 108.89, 108.8, 105.3, 83.6, 82.5, 82.51, 82.15, 82.1, 81.2, 72.5, 72.4, 70.3, 70.2, 67.2, 67.23, 32.2, 32.1, 28.7, 27.8, 27.7, 26.8, 26.7, 26.2, 26.18, 25.3, 25.27, 24.7, 24.71, 24.6, 24.55. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.1 Hz, 3F), -112.2 – -113.8 (m, 2F), -124.7 – -124.73 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.6. **FTIR** (neat): ν = 2987, 2938, 2360, 2337, 1457, 1373, 1330, 1215, 1166, 1131, 1073, 1018, 846, 752 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{27}H_{40}BF_9O_8+Na]^+$: 697.2565. Found: 697.2594.



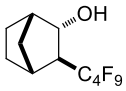
(*E*)-4,4,5,5-Tetramethyl-2-(7,7,8,8,9,9,10,10,10-nonafluoro-1-phenyldec-1-en-5-yl)-1,3,2-dioxaborolane (4ag)

Following general procedure using (*E*)-hexa-1,5-dien-1-ylbenzene **1ag** (79 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4ag** (66 mg, 65% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.34 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.30 – 7.28 (m, 2H), 7.21 – 7.18 (m, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.22 – 6.17 (m, 1H), 2.40 – 2.29 (m, 1H), 2.28 – 2.24 (m, 2H), 2.15 – 2.05 (m, 1H), 1.74 – 1.68 (m, 1H), 1.62 – 1.55 (m, 1H), 1.49 – 1.44 (m, 1H), 1.26 (d, *J* = 2.6 Hz, 12H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 137.6, 130.5, 129.9, 128.5, 126.9, 126.0, 118.6, 117.4, 110.5, 108.8, 83.6, 32.0, 32.0, 31.0, 24.8, 24.6. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.1 Hz, 3F), -112.1 – -113.7 (m, 2F), -124.6 – -124.7 (m, 2F), -126.0 – -126.02 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.9. **FTIR** (neat): ν = 2980, 2943, 2360, 2340, 1329, 1216, 1131, 1073, 1020, 964, 692 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{22}H_{26}BF_9O_2+Na]^+$: 527.1774. Found: 527.1798.



***trans*-4,4,5,5-Tetramethyl-2-(3-(perfluorobutyl)bicyclo[2.2.1]heptan-2-yl)-1,3,2-dioxaborolan e (4ah)**

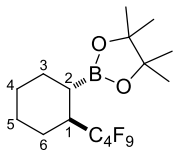
Following general procedure using norbornene **1ah** (47 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4ah** (77 mg, 87% yield, *dr* > 98:2) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 150:1). The relative stereochemistry was assigned by analogy to compound **S1**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.58 (s, 1H), 2.45 (s, 1H), 2.41 – 2.34 (m, 1H), 1.56 – 1.53 (m, 2H), 1.49 – 1.46 (m, 2H), 1.30 – 1.22 (m, 15H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.8, 117.5, 111.3, 108.9, 83.5, 45.5, 39.5, 38.5, 37.6, 30.1, 26.6, 24.9, 24.5. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.6 Hz, 3F), -114.7 – -117.7 (m, 2F), -121.9 – -122.0 (m, 2F), -126.0 – -126.1 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.2. **FTIR** (neat): ν = 2961, 2932, 2880, 2361, 2337, 1457, 1367, 1327, 1233, 1215, 1145, 1132, 1099, 1028 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{17}H_{22}BF_9O_2+Na]^+$: 463.1461. Found: 463.1484.



***trans*-3-(Perfluorobutyl)bicyclo[2.2.1]heptan-2-ol (S1)**

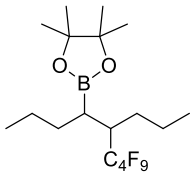
The title compound was prepared according to a literature procedure[11].

To a solution of **4ah** (88 mg, 0.20 mmol) in tetrahydrofuran (2.0 mL) at 0 °C was added aqueous sodium hydroxide solution (1.0 mL, 3.0 mmol, 3 M). Aqueous hydrogen peroxide solution (0.50 mL, 30 % w/w) was added dropwise. The mixture was stirred at room temperature for 4 hours. Upon the completion of the reaction as determined by TLC, the mixture was cooled to 0 °C and saturated aqueous sodium thiosulfate solution (2.0 mL) was added dropwise. The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate (30:1) as eluent to give the corresponding product **S1** (57 mg, 86% yield) as a white solid. The assignment of compound **S1** is based on NMR experiments. Melting point: 39 – 41 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 4.39 (t, *J* = 4.6 Hz, 1H), 2.53 (d, *J* = 4.3 Hz, 1H), 2.37 – 2.35 (m, 1H), 1.96 – 1.84 (m, 2H), 1.75 (s, 1H), 1.69 – 1.60 (m, 2H), 1.50 – 1.39 (m, 2H), 1.29 (d, *J* = 10.6 Hz, 1H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.5, 117.5, 111.1, 108.8, 73.2, 52.1, 41.6, 37.9, 35.7, 30.6, 19.1. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.0 (tt, *J* = 9.8, 3.4 Hz, 3F), -116.1 – -116.3 (m, 2F), -121.7 – -123.2 (m, 2F), -125.5 – -126.7 (m, 2F). **FTIR** (neat): ν = 3288, 2966, 2882, 1461, 1354, 1296, 1234, 1216, 1161, 1129, 1105, 1053, 1032 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{11}H_{11}F_9O+Na]^+$: 353.0558. Found: 353.0556.



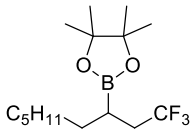
***trans*-4,4,5,5-Tetramethyl-2-(2-(perfluorobutyl)cyclohexyl)-1,3,2-dioxaborolane (4ai)**

Following general procedure using cyclohexene **1ai** (51 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4ai** (26 mg, 30% yield, *dr* > 98:2) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). The 1-H was found to have small H, H couplings (< 6 Hz) with 2-H indicating that the assignment of the major product is *trans*. 1-H: **^{1}H NMR {^{19}F}** (600 MHz, $CDCl_3$) δ (ppm) 2.42 (td, *J* = 11.3, 3.5 Hz). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.46 – 2.38 (m, 1H), 1.92 – 1.68 (m, 4H), 1.36 – 1.10 (m, 17H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 119.1, 117.5, 111.5, 108.8, 83.2, 41.1, 27.2, 25.8, 25.3, 24.9, 24.6, 24.4. The signal of the α-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.0 (tt, *J* = 9.7, 3.5 Hz, 3F), -107.8 – -108.4 (m, 1F), -119.7 – -120.3 (m, 1F), -121.4 – -121.5 (m, 2F), -124.9 – -127.6 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 32.7. **FTIR** (neat): ν = 2982, 2935, 2859, 2361, 1454, 1382, 1328, 1233, 1212, 1146, 1132, 1104, 1021, 991 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{16}H_{22}BF_9O_2+Na]^+$: 451.1461. Found: 451.1458.



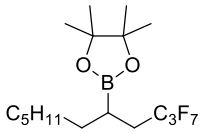
4,4,5,5-Tetramethyl-2-(6,6,7,7,8,8,9,9,9-nonafluoro-5-propylnonan-4-yl)-1,3,2-dioxaborolane (4aj)

Following general procedure using (*E*)-4-octene **1aj** (56 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **4aj** (18 mg, 20% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). The product was formed as a 10:1 mixture of diastereoisomers. The relative configuration could not be assigned. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.49 – 2.40 (m, 1H), 1.65 – 1.59 (m, 1H), 1.54 – 1.22 (m, 20H), 0.93 – 0.89 (m, 6H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 120.3, 117.6, 111.5, 108.9, 83.3, 42.5, 42.1, 29.6, 28.5, 24.9, 24.8, 24.7, 24.5, 22.7, 20.9, 14.3, 14.2. The signal of the α-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.0 (tt, *J* = 9.9, 3.4 Hz, 3F), -109.0 – -114.2 (m, 2F), -121.0 – -122.4 (m, 2F), -125.4 – -126.7 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.5. **FTIR** (neat): ν = 2963, 2935, 2877, 2360, 1469, 1329, 1234, 1213, 1165, 1133, 1099, 1020, 969 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{18}H_{28}BF_9O_2+Na]^+$: 481.1931. Found: 481.1935.



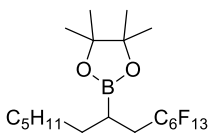
4,4,5,5-Tetramethyl-2-(1,1,1-trifluorononan-3-yl)-1,3,2-dioxaborolane (5a)

Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol) and prepared trifluoroiodomethane solution in dimethylformamide (**2c**, 612 mg, 200 μmol, 6.4% w/w) in absence of additional dimethylformamide provided the product **5a** (40 mg, 66% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 2.36 – 1.98 (m, 2H), 1.52 – 1.24 (m, 23H), 0.87 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm) 127.5 (q, *J* = 275.0 Hz), 83.5, 35.3 (q, *J* = 27.8 Hz), 31.7, 30.9, 29.3, 28.5, 24.8, 24.6, 22.6, 14.0. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (282 MHz, $CDCl_3$) δ (ppm) -65.1. **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.6. **FTIR** (neat): ν = 2929, 2858, 1463, 1373, 1260, 1215, 1139, 1117, 1077, 966, 863, 840, 669 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{15}H_{28}BF_3O_2+Na]^+$: 331.2027. Found: 331.2028.



2-(1,1,1,2,2,3,3-Heptafluoroundecan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)

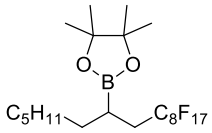
Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol) and perfluoropropyl iodide **2d** (29 μL, 0.20 mmol) provided the product **5b** (67 mg, 82% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.33 – 2.23 (m, 1H), 2.06 – 1.97 (m, 1H), 1.53 – 1.47 (m, 1H), 1.43 – 1.23 (m, 22H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.1, 118.0, 108.9, 83.5, 32.1, 31.7, 31.4, 29.3, 28.6, 24.7, 24.6, 22.6, 14.0. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -80.6 (t, *J* = 9.6 Hz, 3F), -112.9 – -114.7 (m, 2F), -128.1 – -128.07 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.3. **FTIR** (neat): ν = 2959, 2930, 2860, 1469, 1391, 1353, 1329, 1224, 1168, 1144, 1111, 1075, 949 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{17}H_{28}BF_7O_2+Na]^+$: 431.1963. Found: 431.1967.



4,4,5,5-Tetramethyl-2-(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecan-7-yl)-1,3,2-dioxaborolane (5c)

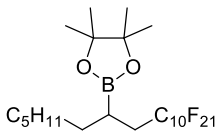
Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol) and perfluorohexyl iodide **2e** (43

μL, 0.20 mmol) provided the product **5c** (87 mg, 78% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.35 – 2.24 (m, 1H), 2.07 – 1.98 (m, 1H), 1.53 – 1.47 (m, 1H), 1.43 – 1.23 (m, 22H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.8, 117.2, 111.1, 111.0, 110.3, 108.5, 83.5, 32.4, 31.7, 31.4, 29.3, 28.6, 24.7, 24.6, 22.6, 14.0. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.0 (tt, *J* = 9.9, 2.6 Hz, 3F), -112.0 – -113.6 (m, 2F), -121.9 – -122.0 (m, 2F), -122.9 – -123.0 (m, 2F), -123.8 – -123.9 (m, 2F), -126.2 – -126.3 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.2. **FTIR** (neat): ν = 2982, 2930, 2859, 1391, 1329, 1238, 1207, 1196, 1167, 1144, 1077, 703 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{20}H_{28}BF_{13}O_2+Na]^+$: 581.1867. Found: 581.1871.



2-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluorohexadecan-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d)

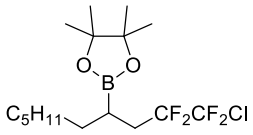
Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol) and heptadecafluoro-1-iodooctane **2f** (53 μL, 0.20 mmol) provided the product **5d** (105 mg, 80% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.35 – 2.24 (m, 1H), 2.08 – 1.99 (m, 1H), 1.53 – 1.47 (m, 1H), 1.43 – 1.20 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.8, 117.1, 111.2, 111.0, 110.8, 110.8, 110.2, 108.4, 83.5, 32.4, 31.7, 31.4, 29.3, 28.6, 24.7, 24.6, 22.6, 14.0. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -80.4 – -81.3 (m, 3F), -111.9 – -113.6 (m, 2F), -121.7 (s, 2F), -122.0 (s, 4F), -122.8 (s, 2F), -123.7 (s, 2F), -126.1 – -126.2 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ 32.9. **FTIR** (neat): ν = 2955, 2919, 2850, 1463, 1378, 1329, 1240, 1205, 1145, 719 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{22}H_{28}BF_{17}O_2+Na]^+$: 681.1803. Found: 681.1812.



2-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-Henicosafluorooctadecan-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e)

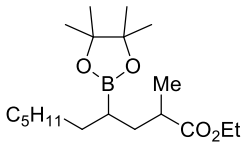
Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol), perfluorodecyl iodide **2g** (129 mg, 200 μmol) and DMF (1 mL) provided the product **5e** (110 mg, 73% yield) as a white solid after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). Melting point: 39 – 41 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.35 – 2.24 (m, 1H), 2.08 – 1.99 (m, 1H), 1.53 – 1.47 (m, 1H), 1.43

– 1.23 (m, 22H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 118.8, 117.1, 111.2, 111.1, 110.9, 110.8, 110.7, 110.2, 108.4, 83.5, 32.4, 31.7, 31.4, 29.3, 28.6, 24.7, 24.6, 22.6, 14.0. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -80.9 (t, *J* = 9.9 Hz, 3F), -112.0 – -113.6 (m, 2F), -121.7 – -122.0 (m, 10F), -122.8 (s, 2F), -123.8 (s, 2F), -126.2 – -126.3 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ 32.7. **FTIR** (neat): ν = 2983, 2928, 2859, 1471, 1373, 1328, 1243, 1200, 1139, 1111, 1078, 963 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{24}H_{28}BF_{21}O_2+Na]^+$: 781.1739. Found: 781.1737.



2-(1-Chloro-1,1,2,2-tetrafluorodecan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f)

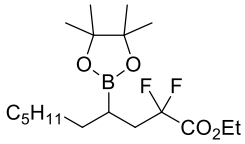
Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol) and 1-chloro-1,1,2,2-tetrafluoro-2-iodoethane **2h** (52 mg, 0.20 mmol) provided the product **5f** (62 mg, 82% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.34 – 2.23 (m, 1H), 2.09 – 1.99 (m, 1H), 1.53 – 1.46 (m, 1H), 1.43 – 1.23 (m, 22H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 123.8, 117.7, 83.4, 32.0, 31.7, 31.4, 29.3, 28.6, 24.8, 24.6, 22.6, 14.0. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (282 MHz, $CDCl_3$) δ (ppm) -71.2 – -71.19 (m, 2F), -111.4 – -113.8 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.6. **FTIR** (neat): ν = 2981, 2928, 2858, 1461, 1372, 1327, 1262, 1144, 1076, 933 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{16}H_{28}BClF_4O_2+Na]^+$: 397.1699. Found: 397.1713.



Ethyl 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decanoate (5g)

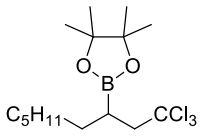
Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol) and ethyl 2-iodopropanoate **2i** (27 μL, 0.20 mmol) provided the product **5g** in an inseparable diastereomeric mixture (25 mg, 36% yield, *dr* = 1.3:1) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 150:1 to 70:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 4.10 (q, *J* = 7.1 Hz, 2H), 2.50 – 2.43 (m, 1H), 1.83 – 1.63 (m, 1H), 1.49 – 1.22 (m, 27H), 1.11 (dd, *J* = 6.9, 1.9 Hz, 3H), 0.88 – 0.84 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) 177.1, 177.0, 82.93, 82.9, 60.0, 59.97, 39.1, 38.6, 35.6, 35.0, 31.8, 31.76, 31.4, 31.1, 29.6, 29.5, 29.0, 28.8, 24.81, 24.8, 24.7, 24.69, 22.6, 17.7, 16.9, 14.25, 14.2, 14.1. The signal of the *α*-B-carbon was not observed. **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.4. **FTIR** (neat):

ν = 2976, 2925, 2857, 2364, 2337, 1734, 1457, 1318, 1257, 1145, 668, 631 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{19}H_{37}BO_4+Na]^+$: 363.2677. Found: 363.2687.



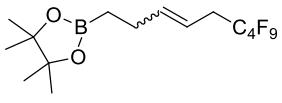
Ethyl 2,2-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decanoate (5h)

Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol) and ethyl 2,2-difluoro-2-iodoacetate **2j** (29 μL, 0.20 mmol) provided the product **5h** (19 mg, 27% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 150:1 to 70:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 4.32 – 4.28 (m, 2H), 2.29 – 2.19 (m, 1H), 2.12 – 2.03 (m, 1H), 1.49 – 1.43 (m, 1H), 1.40 – 1.33 (m, 4H), 1.30 – 1.20 (m, 21H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 164.5, 116.5, 83.3, 62.6, 35.9, 31.7, 31.4, 29.3, 28.6, 24.7, 24.7, 22.6, 14.0, 13.9. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -103.4 (ddd, *J* = 258.1, 22.1, 11.0 Hz, 1F), -105.9 (ddd, *J* = 258.1, 22.8, 15.8 Hz, 1F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.0. **FTIR** (neat): ν = 2979, 2925, 2856, 2362, 2338, 1768, 1465, 1372, 1323, 1189, 1144, 1069, 967, 863 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{18}H_{33}BF_2O_4+Na]^+$: 385.2332. Found: 385.2351.



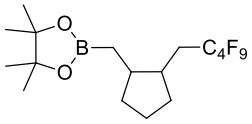
4,4,5,5-Tetramethyl-2-(1,1,1-trichlorononan-3-yl)-1,3,2-dioxaborolane (5i)

Following general procedure using 1-octene **1n** (79 μL, 0.50 mmol) and carbon tetrachloride **2k** (19 μL, 0.20 mmol) provided the product **5i** (17 mg, 23% yield) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 200:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 3.07 (dd, *J* = 14.5, 9.2 Hz, 1H), 2.60 (dd, *J* = 14.5, 2.0 Hz, 1H), 1.55 – 1.24 (m, 23H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ (ppm) 100.8, 83.4, 56.7, 31.7, 31.5, 29.4, 28.4, 24.9, 24.8, 22.6, 14.1. The signal of the *α*-B-carbon was not observed. **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.0. **FTIR** (neat): ν = 2959, 2926, 2856, 1458, 1321, 1258, 1143, 706, 668, 631 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{15}H_{28}BCl_3O_2+Na]^+$: 379.1140. Found: 379.1137.



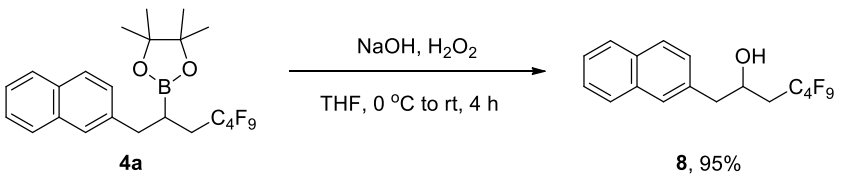
4,4,5,5-Tetramethyl-2-(6,6,7,7,8,8,9,9,9-nonafluorononen-3-en-1-yl)-1,3,2-dioxaborolane (6)

Following general procedure using vinylcyclopropane **1ak** (34 mg, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **6** in an inseparable isomeric mixture (54 mg, 66% yield, *E*:*Z* = 3.3:1) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 5.79 – 5.73 (m, 1H), 5.41 – 5.33 (m, 1H), 2.88 and 2.76 (td, *J* = 18.5, 7.1 Hz, 2H), 2.20 – 2.14 (m, 2H), 1.23 (d, *J* = 1.5 Hz, 12H), 0.88 (q, *J* = 7.7 Hz, 2H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 140.7, 138.8, 117.5, 117.43, 117.4, 117.2, 115.2, 114.6, 110.6, 108.8, 108.7, 83.2, 83.1, 34.6, 29.3, 26.9, 24.8, 21.9. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.6, 3.3 Hz, 3F), -113.5 – -113.7 (m, 2F), -124.1 – -124.2 (m, 2F), -126.1 – -126.2 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.7. **FTIR** (neat): ν = 2982, 2921, 2849, 2362, 2336, 1373, 1233, 1218, 1145, 1133, 1019, 969 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{15}H_{20}BF_9O_2+Na]^+$: 437.1305. Found: 437.1301.



4,4,5,5-Tetramethyl-2-((2-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)cyclopentyl)methyl)-1,3,2-dioxaborolane (7)

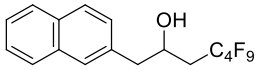
Following general procedure using hepta-1,6-diene **1al** (67 μL, 0.50 mmol) and nonafluoro-1-iodobutane **2a** (35 μL, 0.20 mmol) provided the product **7** in an inseparable diastereomeric mixture (69 mg, 78% yield, *cis:trans* = 7.3:1) as a colorless oil after purification by flash chromatography (*n*-pentane/ ethyl acetate = 100:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 2.26 – 2.00 (m, 3H), 1.90 – 1.76 (m, 3H), 1.73 – 1.66 (m, 1H), 1.62 – 1.54 (m, 1H), 1.46 – 1.40 (m, 1H), 1.34 – 1.26 (m, 1H), 1.24 (d, *J* = 3.7 Hz, 12H), 0.72 (dd, *J* = 15.2, 5.1 Hz, 1H), 0.61 (dd, *J* = 15.3, 9.6 Hz, 1H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 119.0, 118.7, 117.5, 110.5, 110.0, 108.8, 83.1, 83.08, 42.4, 40.7, 38.6, 35.9, 34.7, 33.4, 32.8, 32.76, 30.9, 30.1, 24.9, 24.85, 24.7, 24.65, 23.3, 22.3. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.2 (tt, *J* = 9.7, 3.3 Hz, 3F), -112.1 – -115.0 (m, 2F), -124.6 – -124.61 (m, 2F), -125.9 – -126.0 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ (ppm) 33.6. **FTIR** (neat): ν = 2979, 2942, 2879, 2364, 1373, 1346, 1321, 1219, 1165, 1133, 1022, 968, 880 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{17}H_{24}BF_9O_2+Na]^+$: 465.1618. Found: 465.1621.



4a **8**, 95%

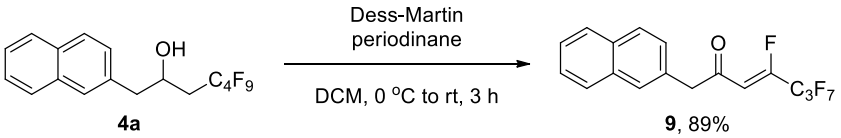
The title compound was prepared according to a literature procedure[11].

To a solution of **4a** (103 mg, 200 μmol) in tetrahydrofuran (2 mL) at 0 °C was added aqueous sodium hydroxide solution (1 mL, 3 mmol, 3 M). Aqueous hydrogen peroxide solution (0.5 mL, 30 % w/w) was added dropwise. The mixture was stirred at room temperature for 4 hours. Upon the completion of the reaction as determined by TLC, the mixture was cooled to 0 °C and saturated aqueous sodium thiosulfate solution (2 mL) was added dropwise. The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate (25:1 to 20:1) as eluent to give the corresponding product **8** (77 mg, 95% yield) as a white solid.



4,4,5,5,6,6,7,7,7-Nonafluoro-1-(naphthalen-2-yl)heptan-2-ol (8)

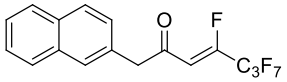
Melting point: 50 – 52 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.85 – 7.82 (m, 3H), 7.69 (s, 1H), 7.52 – 7.47 (m, 2H), 7.37 (dd, *J* = 8.4, 1.7 Hz, 1H), 4.47 (tt, *J* = 8.3, 4.4 Hz, 1H), 3.08 (dd, *J* = 13.7, 4.6 Hz, 1H), 2.97 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.45 – 2.29 (m, 2H), 1.95 (s, 1H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 134.3, 133.5, 132.5, 128.6, 128.2, 127.7, 127.6, 127.4, 126.3, 125.8, 118.1, 117.4, 110.3, 108.7, 66.1, 44.2, 37.3. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.7, 3.1 Hz, 3F), -112.3 – -113.6 (m, 2F), -124.5 – -124.53 (m, 2F), -125.9 – -126.0 (m, 2F). **FTIR** (neat): ν = 3432, 2929, 2363, 1349, 1214, 1190, 1132, 1049, 864, 809, 750, 717 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{17}H_{13}F_9O+Na]^+$: 427.0715. Found: 427.0717.



4a **9**, 89%

The title compound was prepared according to a literature procedure[11].

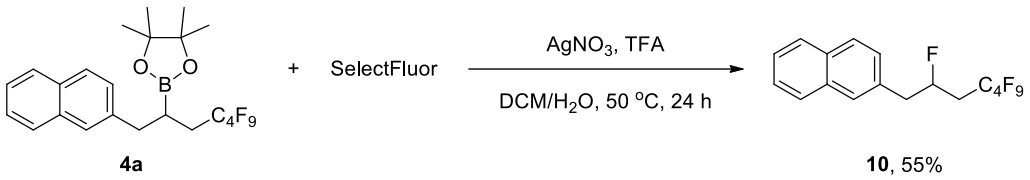
8 (77 mg, 0.19 mmol) was dissolved in dichloromethane (5 mL) and the mixture was cooled to 0 °C. Dess-Martin periodinane (204 mg, 480 μmol) was added in one portion. The reaction mixture was stirred at room temperature for 3 hours, concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl acetate (150:1) as eluent to give the corresponding product **9** (64 mg, 89% yield) as a white solid.



(*Z*)-4,5,5,6,6,7,7,7-Octafluoro-1-(naphthalen-2-yl)hept-3-en-2-one (9)

Melting point: 65 – 67 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.85 – 7.80 (m, 3H), 7.68 (s, 1H), 7.52 – 7.48 (m, 2H), 7.31 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.16 (d, *J* = 34.1 Hz, 1H), 4.15 (s, 2H). **^{13}C NMR {^{19}F}**

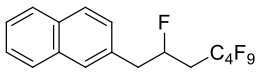
(150 MHz, $CDCl_3$) δ (ppm) 192.9, 152.5, 133.5, 132.6, 129.7, 128.7, 128.5, 127.7, 127.7, 127.2, 126.4, 126.1, 117.3, 112.4, 109.5, 108.1, 50.7. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -80.7 (td, *J* = 8.7, 1.6 Hz, 3F), -109.1 – -109.3 (m, 1F), -119.5 – -119.6 (m, 2F), -127.0 – -127.02 (m, 2F). **FTIR** (neat): ν = 3059, 2928, 2363, 1684, 1335, 1211, 1123, 1051, 936, 816, 734 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{17}H_{10}F_8O+Na]^+$: 405.0496. Found: 405.0480.



4a **10**, 55%

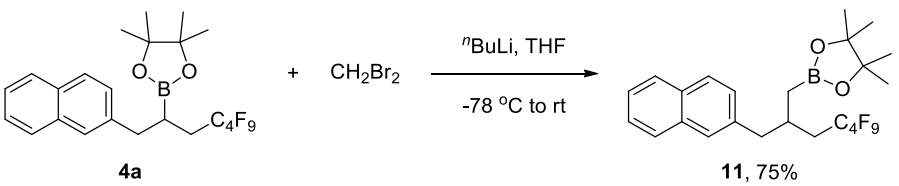
The title compound was prepared according to a literature procedure[12].

4a (103 mg, 200 μmol), silver nitrate (7 mg, 0.04 mmol), SelectFluor (213 mg, 600 μmol) were added into a 25 mL Schlenk tube. The reaction vessel was evacuated and backfilled with Argon for three times. Dichloromethane (1 mL), water (1 mL) and trifluoroacetic acid (62 μL, 0.80 mmol) were added. The reaction mixture was stirred under an argon atmosphere at 50 °C for 24 hours. After cooling to room temperature, the aqueous layer was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane as eluent to give the corresponding product **10** (44 mg, 55% yield) as a white solid.



2-(2,4,4,5,5,6,6,7,7,7-Decafluoroheptyl)naphthalene (10)

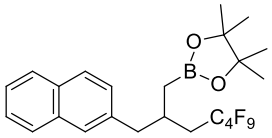
Melting point: 72 – 74 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.86 – 7.82 (m, 3H), 7.70 (s, 1H), 7.52 – 7.47 (m, 2H), 7.36 (dd, *J* = 8.4, 1.4 Hz, 1H), 5.33 – 5.21 (m, 1H), 3.27 – 3.15 (m, 2H), 2.58 – 2.32 (m, 2H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 133.5, 132.7 (d, *J* = 4.5 Hz), 132.5, 128.5, 128.2, 127.7, 127.6, 127.4, 126.3, 125.9, 117.3, 117.1, 110.2, 108.7, 87.0 (d, *J* = 174.0 Hz), 41.8 (d, *J* = 21.0 Hz), 35.7 (d, *J* = 22.5 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.5, 3.1 Hz, 3F), -112.5 – -113.7 (m, 2F), -124.4 – -124.44 (m, 2F), -126.0 – -126.01 (m, 2F), -177.5 – -177.8 (m, 1F). **FTIR** (neat): ν = 2362, 2337, 1436, 1398, 1357, 1267, 1215, 1198, 1134, 1114, 1050, 1034, 967 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{17}H_{12}F_{10}+Na]^+$: 429.0672. Found: 429.0671.



4a **11**, 75%

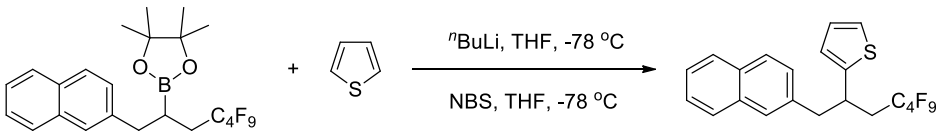
The title compound was prepared according to a literature procedure[13].

4a (103 mg, 200 μmol) was dissolved in tetrahydrofuran (2 mL), and dibromomethane (35 μL, 0.50 mmol) was added. The mixture was cooled to -78 °C, *n*-butyllithium (0.28 mL, 0.44 mmol, 1.6 M in hexane) was added dropwise. The reaction mixture was stirred at -78 °C for 20 min, and then warmed to room temperature for another 2 hours. The mixture was quenched with saturated aqueous ammonium chloride solution, extracted with diethyl ether (3 x 15 mL), dried over magnesium sulfate, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (150:1 to 100:1) as eluent to give the corresponding product **11** (79 mg, 75% yield) as a white solid.



4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-2-(naphthalen-2-ylmethyl)heptyl)-1,3,2-dioxaborolane (11)

Melting point: 43 – 45 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.82 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.61 (s, 1H), 7.48 – 7.43 (m, 2H), 7.34 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.97 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.83 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.59 – 2.52 (m, 1H), 2.29 – 2.11 (m, 2H), 1.25 (d, *J* = 2.0 Hz, 12H), 1.05 (dd, *J* = 16.3, 6.2 Hz, 1H), 0.95 (dd, *J* = 16.3, 6.6 Hz, 1H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 137.4, 133.5, 132.2, 128.0, 127.8, 127.75, 127.6, 127.5, 125.9, 125.3, 119.1, 117.4, 110.4, 108.8, 83.2, 43.2, 35.1, 29.9, 24.8, 24.77. The signal of the *α*-B-carbon was not observed. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.1 Hz, 3F), -111.8 – -113.0 (m, 2F), -124.7 – -124.72 (m, 2F), -125.86 – -126.0 (m, 2F). **^{11}B NMR** (96 MHz, $CDCl_3$) δ 32.8. **FTIR** (neat): ν = 2979, 2363, 1373, 1323, 1218, 1166, 1132, 1019, 967, 881, 845, 748, 718 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{24}H_{26}BF_9O_2+Na]^+$: 551.1774. Found: 551.1776.

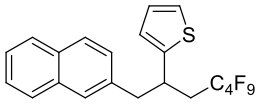


4a **12**, 64%

The title compound was prepared according to a literature procedure[14].

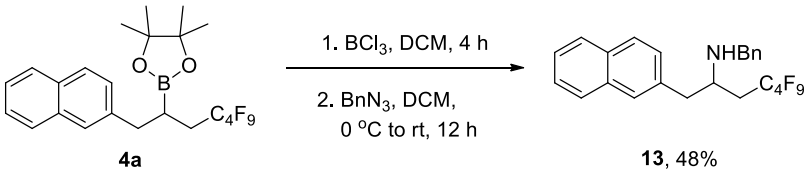
Thiophene (25 μL, 0.32 mmol) in tetrahydrofuran (1 mL) was cooled to -78 °C and *n*-butyllithium (0.20 mL, 0.32 mmol, 1.6 M in hexane) was added dropwise. Then the mixture was allowed to warm up to 0 °C and stirred for 30 minutes. After cooling to -78 °C again, a solution of **4a** (138 mg, 260 μmol) in tetrahydrofuran (0.5 mL) was added dropwise. The reaction mixture was allowed to stir at -78 °C for

1 hour. *N*-bromosuccinimide (57 mg, 0.32 mmol) in tetrahydrofuran (1 mL) was added dropwise and the mixture was stirred at -78 °C for 1 hour. Saturated aqueous sodium thiosulfate solution (2 mL) was added. The reaction mixture was allowed to warm to room temperature and diluted with water and ethyl acetate. The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified by flash column chromatography on silica gel with *n*-pentane as eluent to give the corresponding product **12** (78 mg, 64% yield) as a colorless oil.



2-(4,4,5,5,6,6,7,7,7-Nonafluoro-1-(naphthalen-2-yl)heptan-2-yl)thiophene (12)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.82 – 7.81 (m, 1H), 7.77 – 7.75 (m, 2H), 7.51 (s, 1H), 7.49 – 7.44 (m, 2H), 7.20 – 7.17 (m, 2H), 6.87 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.74 – 6.73 (m, 1H), 3.88 – 3.84 (m, 1H), 3.28 (dd, *J* = 13.7, 6.4 Hz, 1H), 3.17 (dd, *J* = 13.7, 8.5 Hz, 1H), 2.62 – 2.54 (m, 2H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 146.4, 135.9, 133.4, 132.3, 128.0, 127.7, 127.6, 127.56, 127.2, 126.6, 126.0, 125.5, 124.7, 123.6, 118.1, 117.4, 110.3, 108.7, 44.8, 37.1, 35.8. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.0 Hz, 3F), -113.0 – -113.1 (m, 2F), -124.4 – -124.44 (m, 2F), -125.9 – -125.94 (m, 2F). **FTIR** (neat): ν = 2361, 2337, 1354, 1219, 1169, 1133, 1096, 881, 815, 747, 695, 631 (cm^{-1}). **HRMS** (APCI) *m/z*: Calcd for $[C_{21}H_{15}F_9S+H]^+$: 471.0824. Found: 471.0821.

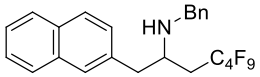


4a **13**, 48%

The title compound was prepared according to a literature procedure[15].

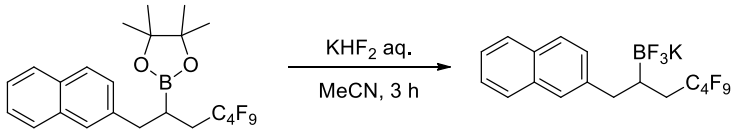
4a (103 mg, 200 μmol) was added into a flame-dried round bottom flask. The reaction vessel was evacuated and backfilled with Argon for three times. Dichloromethane (0.40 mL) was added followed by dropwise addition of boron trichloride (1.0 mL, 1.0 mmol, 1 M in dichloromethane). The reaction mixture was stirred under an argon atmosphere at room temperature for 4 hours. The volatiles were removed under vacuum and the reaction vessel was evacuated and backfilled with Argon for three times again. The resulting mixture was dissolved in dichloromethane (1.2 mL). Benzyl azide (76 μL, 0.60 mmol) was added dropwise at 0 °C. After warming to room temperature, the reaction mixture was allowed to stir for 12 hours. The reaction was quenched with aqueous sodium hydroxide solution (5.0 mL, 3 M) and the aqueous layer was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified

by flash column chromatography on silica gel with *n*-pentane/ethyl acetate (100:1 to 20:1) as eluent to give the corresponding product **13** (47 mg, 48% yield) as a colorless syrup.



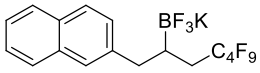
***N*-Benzyl-4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-2-yl)heptan-2-amine (13)**

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.84 (d, *J* = 7.2 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 2H), 7.62 (s, 1H), 7.51 – 7.46 (m, 2H), 7.29 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.25 – 7.22 (m, 3H), 7.15 (dd, *J* = 7.2, 2.0 Hz, 2H), 3.84 (d, *J* = 13.3 Hz, 1H), 3.75 (d, *J* = 13.3 Hz, 1H), 3.48 – 3.44 (m, 1H), 3.14 (dd, *J* = 13.9, 5.4 Hz, 1H), 2.99 (dd, *J* = 13.7, 7.9 Hz, 1H), 2.40 – 2.23 (m, 2H), 2.11 – 1.35 (br, 1H). **^{13}C NMR {^{19}F}** (150 MHz, $CDCl_3$) δ (ppm) 135.1, 133.5, 132.4, 128.4, 128.4, 128.1, 127.9, 127.6, 127.5, 127.3, 127.2, 126.2, 125.7, 118.5, 117.4, 110.3, 108.8, 51.9, 51.0, 41.5, 34.8. **^{19}F NMR** (564 MHz, $CDCl_3$) δ (ppm) -81.1 (tt, *J* = 9.6, 3.0 Hz, 3F), -112.4 – -112.6 (m, 2F), -124.4 – -124.5 (m, 2F), -125.8 – -125.9 (m, 2F). **FTIR** (neat): ν = 2360, 2337, 1465, 1355, 1220, 1133, 1018, 881, 856, 818, 738, 718 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{24}H_{20}F_9N+H]^+$: 494.1525. Found: 494.1534.



4a **14**, 77%

4a (411 mg, 800 μmol) was dissolved in acetonitrile (5 mL) and saturated aqueous potassium hydrogenfluoride solution (0.90 mL, 4.1 mmol, 4.5 M) was added. The reaction mixture was stirred at room temperature for 3 hours, concentrated, azeotroped with methanol and placed on the vacuum overnight. The crude product was dissolved in acetone, filtered and concentrated. The resulting crude product was washed with hexane several times to give the desired product **14** (303 mg, 77% yield) as a white solid.



Potassium trifluoro(4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-2-yl)heptan-2-yl)borate (14)

Melting point: 164 – 166 °C. **^{1}H NMR** (600 MHz, dmso-d6) δ (ppm) 7.80 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.43 – 7.40 (m, 1H), 7.35 – 7.34 (m, 2H), 2.89 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.54 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.19 – 2.11 (m, 1H), 1.80 – 1.69 (m, 1H), 0.97 (s, 1H). **^{13}C NMR** (150 MHz, dmso-d6) δ (ppm) 141.9, 133.0, 131.2, 128.4, 127.2, 127.1, 126.7, 126.5, 125.4, 124.5, 37.6, 24.9. The signal of the *α*-B-carbon was not observed. $CF_2CF_2CF_2CF_3$ could not be assigned. **^{19}F NMR** (282 MHz, acetone-d6) δ (ppm) -82.0 (tt, *J* = 9.9, 3.5 Hz, 3F), -111.9 –

-114.1 (m, 2F), -125.1 – -125.2 (m, 2F), -126.4 – -126.5 (m, 2F), -147.1 (s, 3F). **^{11}B NMR** (96 MHz, acetone-d6) δ (ppm) 4.9. **FTIR** (neat): ν = 2361, 2337, 1439, 1355, 1216, 1181, 1130, 1046, 957, 862, 818, 751 (cm^{-1}). **HRMS** (ESI) *m/z*: Calcd for $[C_{17}H_{12}BF_{12}\text{-}K]^-$: 455.0846. Found: 455.0867.

3 DFT Calculations

All structures were optimized without geometry constraints using the PBE0 hybrid functional[16,17] and an atom-pairwise dispersion correction (D3)[18]. A flexible triple zeta basis set (def2-TZVP)[19] was used in all calculations. For the calculation of the free enthalpy contributions (G^{RRHO}(298K)), a rotor approximation was applied for vibrational modes with wave numbers below 100 cm^{-1}.[20] The nature of all optimized stationary points was proven by the presence of either 0 (minimum) or 1 (transition structure) imaginary vibrational frequency. Free energies of solvation ($G(solv)_{298}$) were obtained with the COSMO-RS model[21] for 298 K using DMF as solvent.

Electronic energies were recalculated with the double hybrid functional PWPB95(-D3)[22] using the structures optimized with PBE0-D3. PWPB95 includes a component of the correlation energy which is computed by perturbation theory and performs more accurately in the determination of energies, even for open shell molecules such as radicals. The final value for the free enthalpy ΔG(298) was obtained using the PWPB95-D3 electronic energies and G^{RRHO}(298K), obtained with PBE0-D3.

All geometry optimizations and vibrational frequency calculations were performed with the TURBOMOLE 7.2 program.[23] PWPB95-D3 calculations were performed with the ORCA (4.0.2) program.[24]

Results

Scheme S1. Free energies of intermediates and transition structures for the reaction.

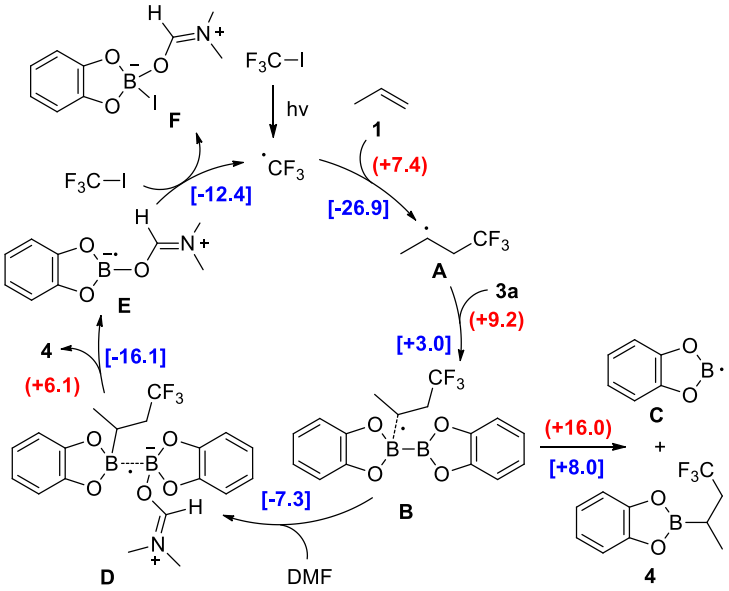


Table S1. DFT-calculated electronic energies after geometry optimization with PBE0-D3. Single point electronic energies obtained with PWPB95-D3. Free energy corrections $G(stat)_{298}$ using harmonic vibrational frequencies obtained with PBE0-D3. $G(SOLV)_{298}$: COSMO-RS calculated free energy of solvation in DMF. The def2-TZVP basis set was used in all calculations.

	E (PBE0-D3) [E_h]	E(PWPB95-D3) [E_h]	$G(stat)_{298}$ [kcal/mol]	$G(solv)_{298}$ [kcal/mol]
1	-117.800542	-117.854272	34.346	1.679
4	-861.475134	-861.920953	96.477	-5.833
3a	-812.283146	-812.718702	93.895	-10.135
A	-455.256602	-455.481345	38.935	0.486
B	-1267.560136	-1268.219055	150.379	-12.294
C	-406.051603	-406.266951	39.114	-3.257
CF3	-337.393942	-337.571163	-8.583	3.748
CF3I	-635.180681	-635.233776	-10.095	1.029
D	-1515.917196	-1516.693609	212.183	-19.593
DMF	-248.327512	-248.446565	46.178	-1.921
E	-654.451271	-654.783891	99.877	-6.976
F	-952.240420	-952.450166	98.651	-20.032
TS(1-A)	-455.195959	-455.424233	36.745	1.065
TS(A-B)	-1267.548267	-1268.207634	148.973	-11.879
TS(B-C)	-1267.532927	-1268.193316	149.539	-11.660
TS(D-E)	-1515.909384	-1516.685077	211.166	-17.855
3b	-821.927427	-822.329130	200.280	-9.864
Bb	-1277.186864	-1277.812267	257.194	-9.323

Figure S1. Spin density (PBE0/def2-TZVP, 0.01 a.u.) of **B**

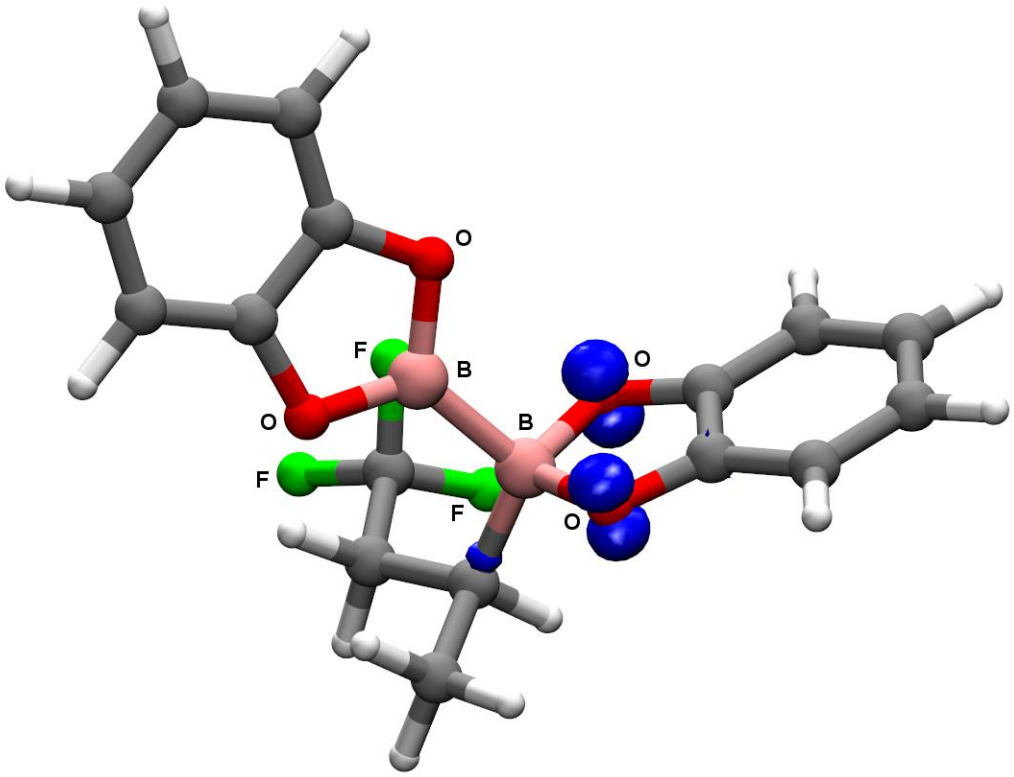


Figure S2. Spin density (PBE0/def2-TZVP, 0.02 a.u.) of **D**

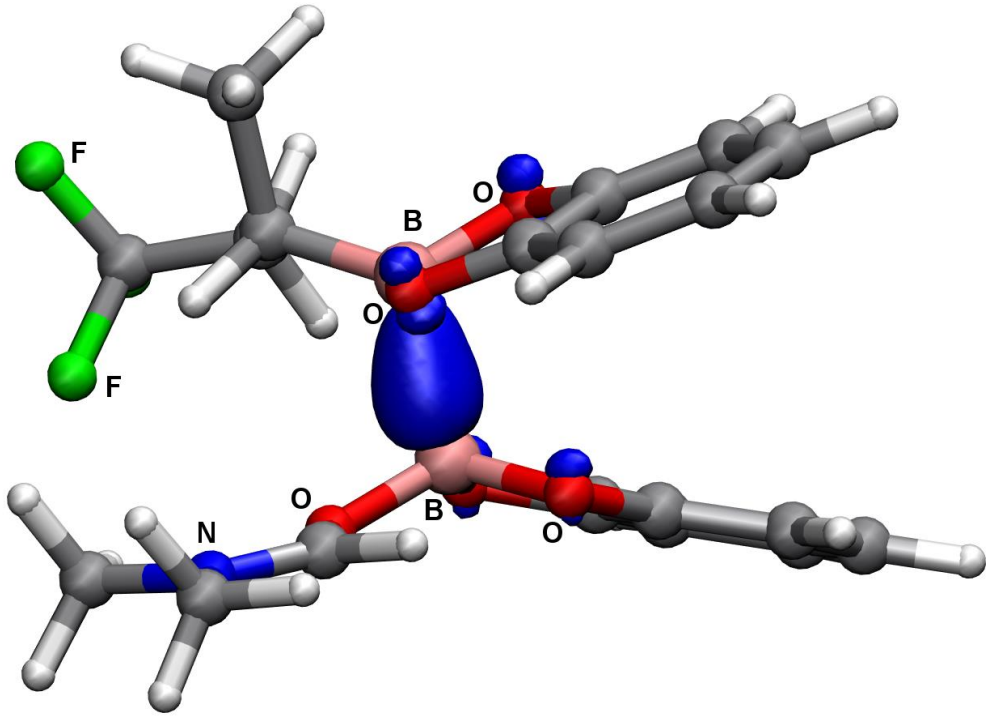
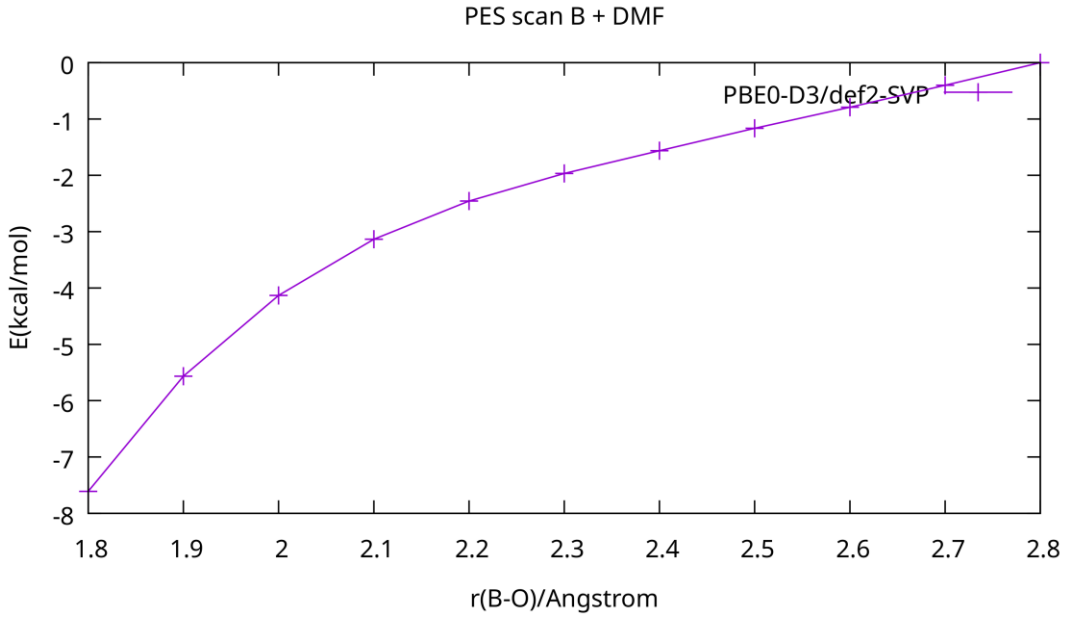
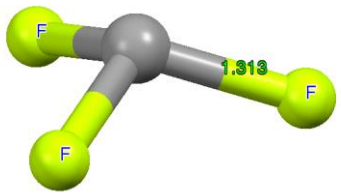


Figure S3. Potential energy surface scan of the approach of DMF to **B** (PBE0-D3/def2-SVP): Constrained optimization of **D** with fixed B...O(**DMF**) distance.



Geometries and Energies of All Intermediates and TS



CF3

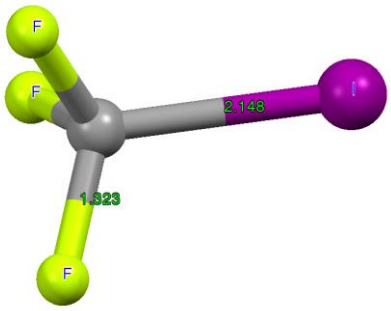
E (TPSS-D3/def2-TZVP) = -337.3939420252 (conv)

Lowest Freq. = 513.11 cm^-1

4

CF3 (CF3/c1/pbe0-d3.def2-TZVP)

C	-0.0894667	-0.0024504	-0.0041928
F	-0.4421228	-1.0635623	-0.6919150
F	-0.4823243	1.1027369	-0.5937699
F	-0.5252531	-0.0667025	1.2324418



CF3I

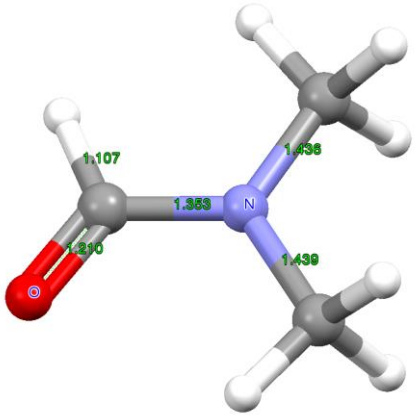
E (TPSS-D3/def2-TZVP) = -635.1806805178 (conv)

Lowest Freq. = 269.20 cm^-1

5

CF3I (CF3I/c1/pbe0-d3.def2-TZVP)

I	2.0682682	0.0355338	0.0716944
C	-0.0776539	-0.0019502	-0.0034619
F	-0.4958151	-1.0547840	-0.6876073
F	-0.5370556	1.0916663	-0.5902982
F	-0.5799703	-0.0669840	1.2191881



DMF

E (TPSS-D3/def2-TZVP) = -248.3275120827 (conv)

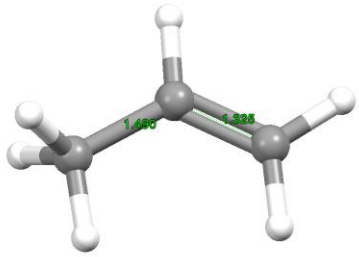
Lowest Freq. = 124.19 cm^-1

12

DMF (004/c1/pbe0-d3.def2-TZVP)

N	0.0063489	0.0109098	-0.0253071
C	-0.7608215	1.2282665	0.0031127
H	-1.5037339	1.2360705	-0.8007643

H	-0.0770583	2.0647875	-0.1280614
H	-1.2848703	1.3334988	0.9584378
C	-0.6969991	-1.2317201	0.1248916
H	-1.2229316	-1.2740997	1.0846410
H	0.0113221	-2.0602493	0.0835639
H	-1.4342338	-1.3669808	-0.6736620
C	1.3482694	0.0525800	-0.1896236
O	2.0129704	1.0550629	-0.3232147
H	1.7938006	-0.9602722	-0.1896422



1

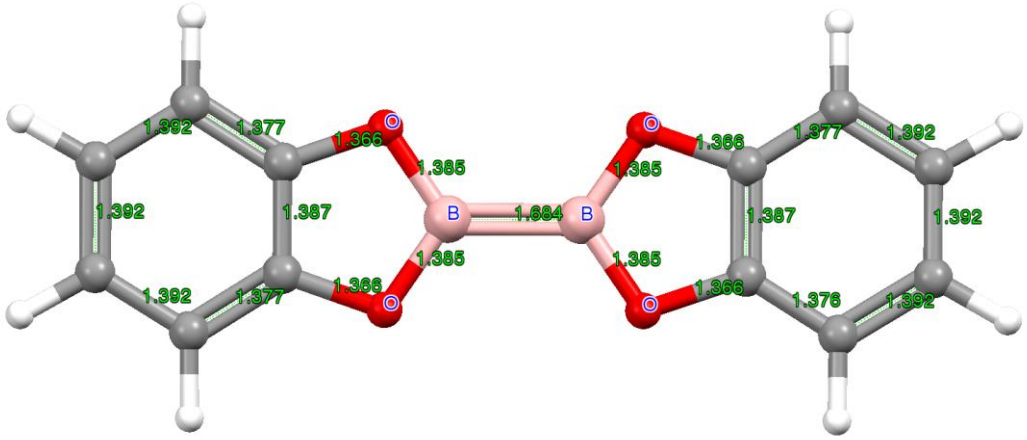
E (TPSS-D3/def2-TZVP) = -117.8005417747 (conv)

Lowest Freq. = 208.43 cm^-1

9

1 (008/c1/pbe0-d3.def2-TZVP)

C	1.5175112	0.0168614	0.0267036
H	1.7787463	1.0587487	0.2368422
H	2.0269498	-0.2512423	-0.9042116
H	1.9184295	-0.6057567	0.8286272
C	0.0428936	-0.1476889	-0.1054849
C	-0.7054453	-0.9436690	0.6448868
H	-0.4380387	0.4403825	-0.8850238
H	-1.7765075	-1.0199007	0.4990052
H	-0.2710442	-1.5494128	1.4345137



3a

E (TPSS-D3/def2-TZVP) = -812.2831464999 (conv)

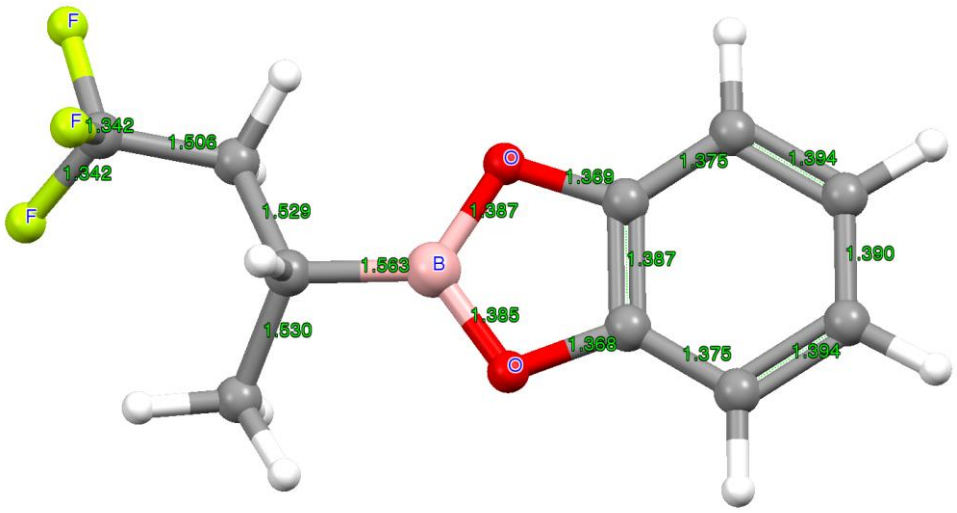
Lowest Freq. = 20.88 cm^-1

26

3a (009/c1/pbe0-d3.def2-TZVP)

O	0.8482701	-0.8352938	-1.5867769
B	0.1324190	0.0762052	-0.8284401
O	-0.4026025	1.0674950	-1.6342787
B	-0.0571356	-0.0088675	0.8430167
O	0.3923316	-1.0532665	1.6338656
O	-0.6802858	0.9558895	1.6171832
C	0.7529854	-0.3973880	-2.8773202
C	-0.0099459	0.7610186	-2.9064354
C	1.2903933	-0.9468599	-4.0193200
C	1.0268234	-0.2783658	-5.2118347
C	-0.2776913	1.4298425	-4.0794124
C	0.2602530	0.8827815	-5.2412623
H	1.8850812	-1.8505723	-3.9852118
H	1.4283286	-0.6722286	-6.1375471
H	-0.8747490	2.3325787	-4.0910118
H	0.0774818	1.3735394	-6.1894182
C	-0.6113614	0.4986907	2.9028031
C	-1.0808256	1.0853840	4.0561954
C	0.0410387	-0.7256781	2.9127771
C	0.2566100	-1.4289455	4.0763178
C	-0.8676971	0.3834072	5.2395404

C	-0.2145174	-0.8454016	5.2493306
H	-1.5878116	2.0414986	4.0373879
H	0.7663216	-2.3837859	4.0727444
H	-1.2190135	0.8045444	6.1736110
H	-0.0681828	-1.3606334	6.1908437



4

E (TPSS-D3/def2-TZVP) = -861.4751335607 (conv)

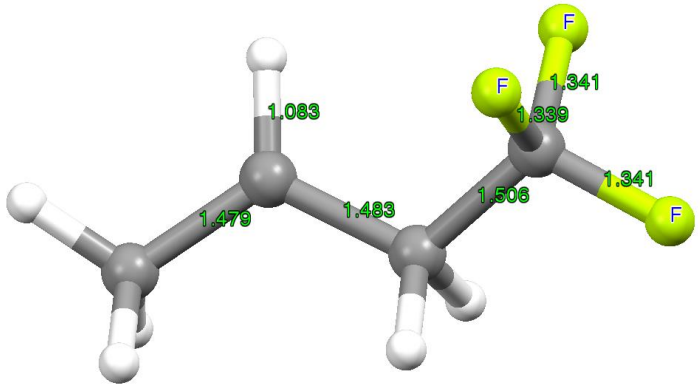
Lowest Freq. = 16.58 cm^-1

26

4 (013/c1/pbe0-d3.def2-TZVP)

B	-0.0320235	-0.0481871	0.8905365
O	0.3889353	-1.0853817	1.7064719
O	-0.6330477	0.9524844	1.6389098
C	-0.5888085	0.5178141	2.9366158
C	-1.0536093	1.1389079	4.0719544
C	0.0328121	-0.7217077	2.9768445
C	0.2217817	-1.4042197	4.1557300
C	-0.8684578	0.4566501	5.2729748
C	-0.2455118	-0.7854423	5.3137141
H	-1.5372295	2.1063501	4.0292962
H	0.7084588	-2.3708098	4.1770850
H	-1.2187005	0.9057566	6.1942647
H	-0.1194869	-1.2852214	6.2663621

C	0.1207606	-0.0283674	-0.6650960
H	-0.7564066	-0.5779900	-1.0385885
C	0.0168532	1.4034828	-1.1915022
H	0.9196530	1.9744352	-0.9583515
H	-0.8195187	1.9222622	-0.7182517
C	-0.2059676	1.5274006	-2.6756076
C	1.3744390	-0.7801823	-1.1170156
H	1.3974705	-0.9190030	-2.1976315
H	1.4204406	-1.7634585	-0.6468074
H	2.2793051	-0.2364167	-0.8323432
F	0.8574948	1.1484083	-3.4011219
F	-0.4680815	2.7995713	-3.0126811
F	-1.2455850	0.7883601	-3.0931511



A

E (TPSS-D3/def2-TZVP) = -455.2566022060 (conv)

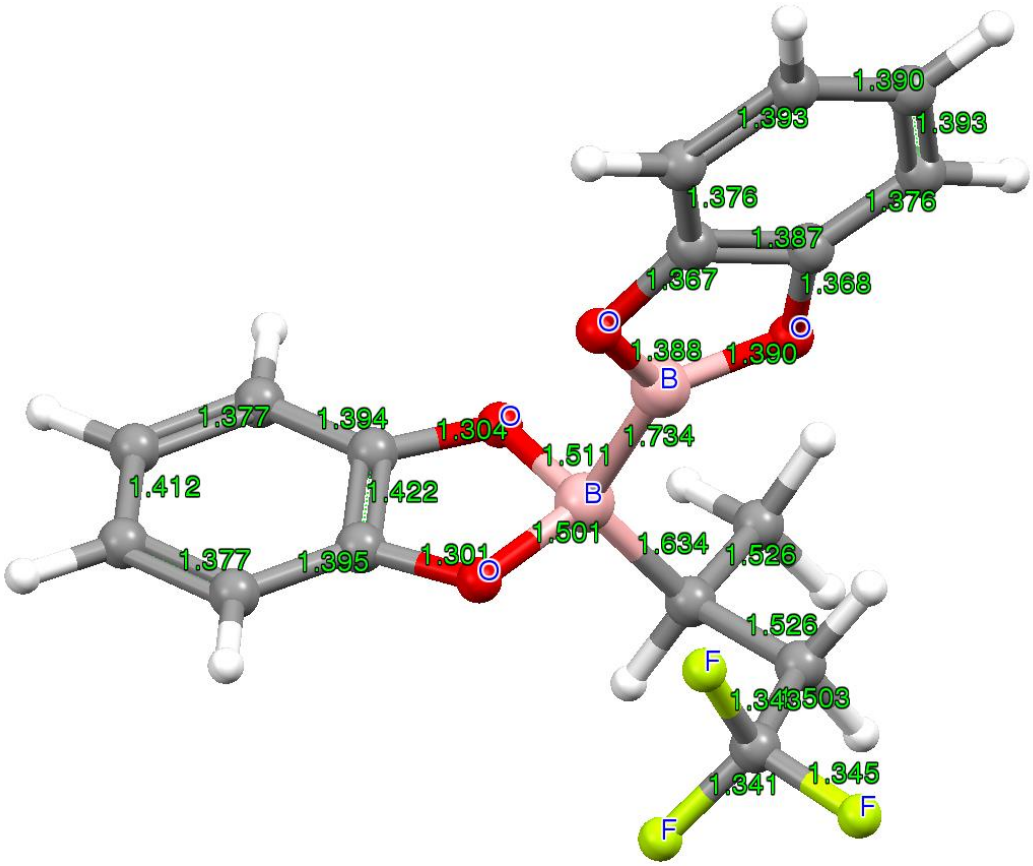
Lowest Freq. = 39.88 cm^-1

13

A (002/c1/pbe0-d3.def2-TZVP)

C	0.0426308	0.1254609	0.0915602
H	-0.5189066	0.5570402	-0.7278756
C	1.5084030	-0.0346460	-0.0201026
H	2.0496884	0.8040086	0.4450206
H	1.8306243	-0.0854219	-1.0609151
H	1.8543597	-0.9408267	0.4896019
C	-0.6258166	-0.0238705	1.4064696

H	-0.2391958	-0.8909741	1.9527528
H	-0.4540915	0.8485130	2.0559370
C	-2.1193622	-0.1895281	1.3095879
F	-2.6999428	0.8523206	0.6955233
F	-2.6745746	-0.2890344	2.5263763
F	-2.4633802	-1.2891772	0.6275117



B

E (TPSS-D3/def2-TZVP) = -1267.560136535 (conv)

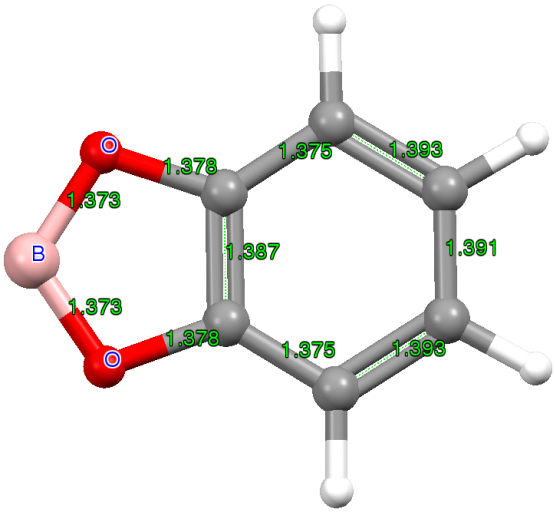
Lowest Freq. = 16.88 cm^-1

39

B (017/c1/pbe0-d3.def2-TZVP)

O	1.0265688	-0.1238417	-0.8687362
B	-0.3468971	-0.2713113	-0.7377881
O	-0.9724419	-0.0395781	-1.9571511
B	-1.1592479	-0.6623344	0.7431073
O	-0.2245070	-1.4418184	1.6217470
O	-1.3413839	0.6101120	1.5373830
C	1.2463601	0.1949687	-2.1792695

C	0.0296259	0.2482279	-2.8429273
C	2.4376682	0.4374777	-2.8235234
C	2.3608255	0.7435518	-4.1807311
C	-0.0597273	0.5502751	-4.1819534
C	1.1404123	0.7995588	-4.8447037
H	3.3828639	0.3900448	-2.2980990
H	3.2734055	0.9416473	-4.7297520
H	-1.0149499	0.5896859	-4.6897620
H	1.1204897	1.0406672	-5.9005668
C	-0.6018681	0.5335946	2.6087533
C	-0.4364043	1.4865396	3.6128207
C	0.0740512	-0.7165987	2.6599356
C	0.9238808	-1.0362176	3.7192695
C	0.4042611	1.1552241	4.6523140
C	1.0736165	-0.0866043	4.7045149
H	-0.9519120	2.4368147	3.5644820
H	1.4341493	-1.9899636	3.7478689
H	0.5613775	1.8648690	5.4556659
H	1.7238541	-0.2914666	5.5464159
C	-2.5974682	-1.4113981	0.5442801
H	-2.8619406	-1.8143315	1.5308729
C	-3.6647940	-0.4025401	0.1294783
H	-3.7645752	0.3963409	0.8641765
H	-4.6394220	-0.8896867	0.0240649
H	-3.4193191	0.0566361	-0.8317083
C	-2.6154167	-2.5617154	-0.4577959
H	-2.4308398	-2.1910816	-1.4696601
H	-3.6073496	-3.0243812	-0.4630883
C	-1.6393368	-3.6815211	-0.2283518
F	-1.9074036	-4.7206005	-1.0386889
F	-0.3705653	-3.3210746	-0.4802992
F	-1.6754883	-4.1502727	1.0276376



C

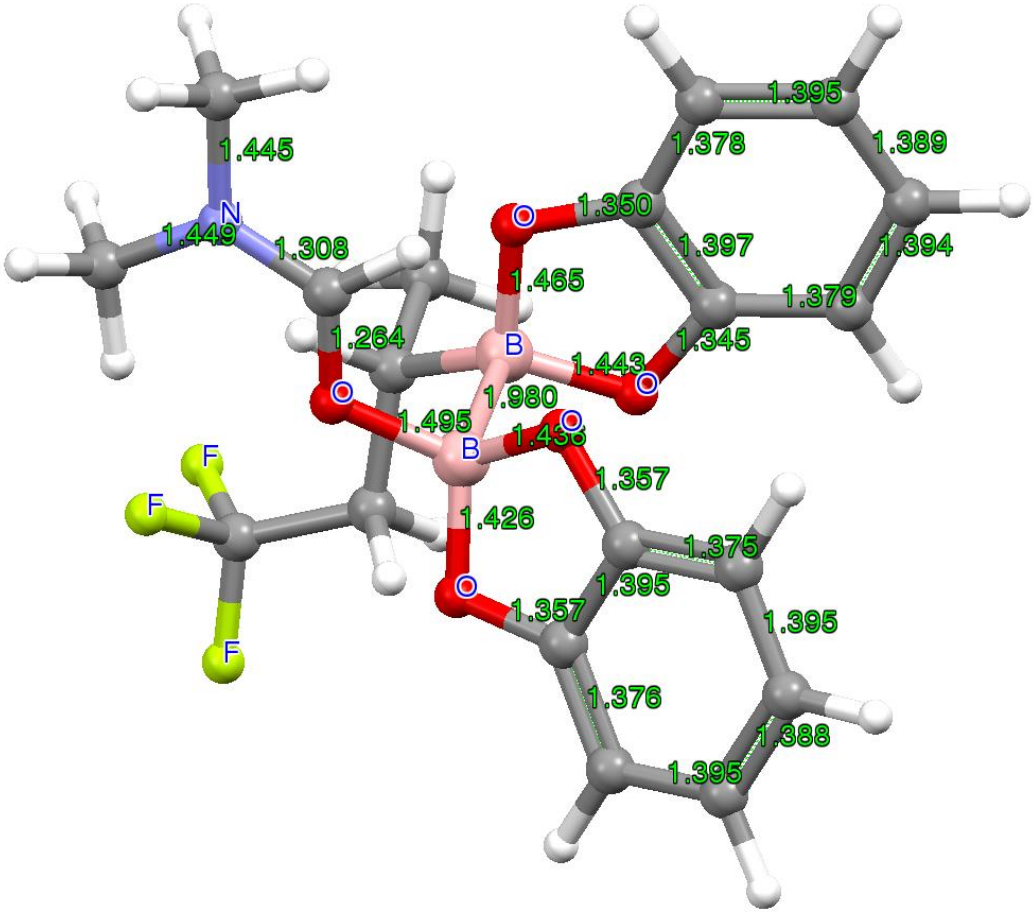
E (TPSS-D3/def2-TZVP) = -406.0516026773 (conv)

Lowest Freq. = 236.05 cm^-1

13

C (010/c1/pbe0-d3.def2-TZVP)

B	0.0857631	0.0350090	0.9922265
O	0.4926313	-1.0251666	1.7634166
O	-0.5504974	1.0083437	1.7218656
C	-0.5419252	0.5338597	3.0157335
C	-1.0514876	1.1170969	4.1515626
C	0.0911259	-0.6997516	3.0410156
C	0.2491203	-1.4164787	4.2034346
C	-0.8980689	0.4006372	5.3366821
C	-0.2627714	-0.8360683	5.3620870
H	-1.5441960	2.0802481	4.1206848
H	0.7449516	-2.3784869	4.2119662
H	-1.2832616	0.8184142	6.2587900
H	-0.1629715	-1.3621744	6.3036055



D

E (TPSS-D3/def2-TZVP) = -1515.917196168 (conv)

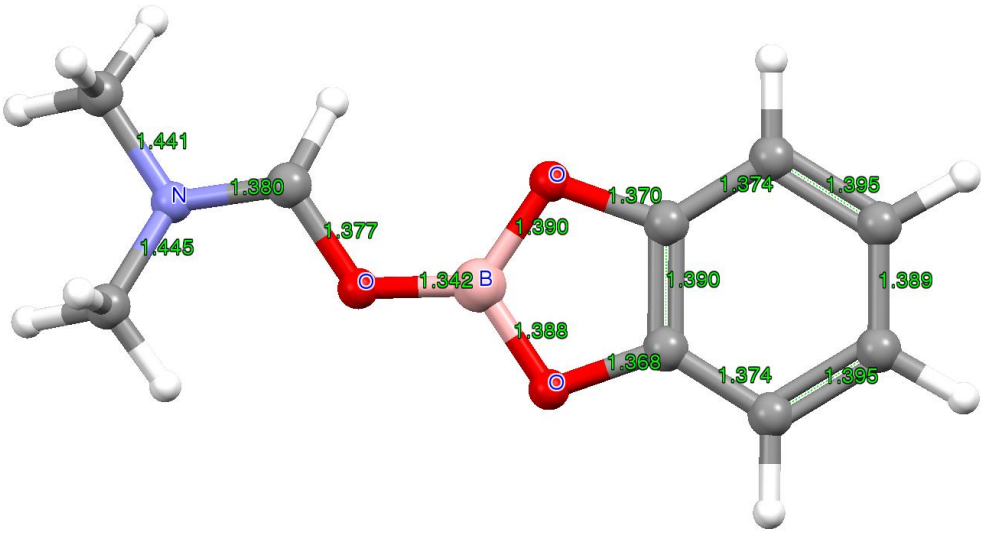
51

D (024/c4/pbe0-d3.def2-TZVP)

O	1.4590127	-0.4912885	-1.9932942
B	0.4511799	0.3511988	-1.4391167
O	-0.5903451	0.5268226	-2.4119114
B	-0.4266921	-0.3562382	0.1888291
O	-1.4459554	0.6803726	0.3677349
O	-1.1148578	-1.5319269	-0.2858754
C	0.9188578	-0.9814260	-3.1380030
C	-0.3107753	-0.3733334	-3.3887229
C	1.4338387	-1.9385203	-3.9821732
C	0.6717565	-2.2748233	-5.1015832
C	-1.0724848	-0.7056916	-4.4846745
C	-0.5547999	-1.6729516	-5.3470872
H	2.3878139	-2.4080780	-3.7778027

H	1.0446759	-3.0251444	-5.7883910
H	-2.0340440	-0.2388899	-4.6574588
H	-1.1257702	-1.9623074	-6.2211620
C	-2.3765488	-1.1511024	-0.5551551
C	-3.3831502	-1.8865300	-1.1441960
C	-2.5805383	0.1733939	-0.1595268
C	-3.7976372	0.7973173	-0.3290453
C	-4.6160710	-1.2601077	-1.3167777
C	-4.8212679	0.0543379	-0.9160517
H	-3.2106793	-2.9073428	-1.4610194
H	-3.9503877	1.8222880	-0.0122240
H	-5.4298900	-1.8104053	-1.7737312
H	-5.7929265	0.5112366	-1.0612717
C	0.6298197	-0.4827833	1.3862476
H	1.0279427	0.5254100	1.5505380
C	-0.1229495	-0.9125831	2.6498113
H	-0.9448771	-0.2251786	2.8607559
H	0.5281352	-0.9428959	3.5260238
H	-0.5538793	-1.9084728	2.5155425
C	1.8047097	-1.4070602	1.0682138
H	2.0710275	-1.3666615	0.0106461
H	1.5541256	-2.4464271	1.2949912
C	3.0656896	-1.0785769	1.8130154
F	4.0700302	-1.8998700	1.4692909
F	3.4907514	0.1768324	1.5519206
F	2.9424134	-1.1605319	3.1489366
N	0.5362504	3.6250896	0.0253126
C	1.7807139	3.6525653	0.7679830
H	2.3189990	4.5749708	0.5421120
H	2.3894311	2.7945529	0.4967124
H	1.5665788	3.6188896	1.8385393
C	-0.3812587	4.7244247	0.2219751
H	-0.6530988	4.7952230	1.2774049
H	-1.2835176	4.5622766	-0.3651377
H	0.0848132	5.6624578	-0.0872215

C	0.2126805	2.6181113	-0.7449144
O	0.9975051	1.6431591	-0.9225925
H	-0.7568130	2.6374500	-1.2362939



E

E (TPSS-D3/def2-TZVP) = -654.4512705255 (conv)

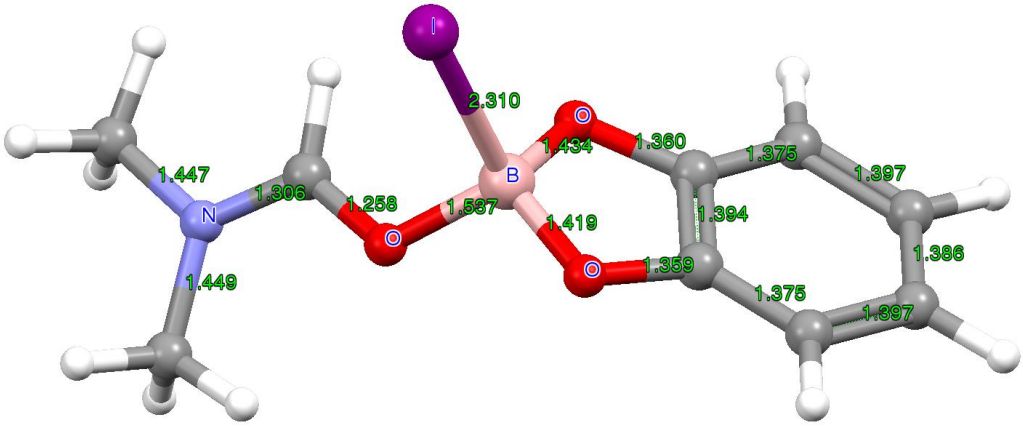
Lowest Freq. = 23.87 cm^-1

25

E (011/c1/pbe0-d3.def2-TZVP)

B	-2.2745432	-0.3915620	0.7807995
O	-1.6697036	0.8404680	0.5602187
O	-1.3430221	-1.4163068	0.8715525
O	-3.5939474	-0.6102219	0.8922575
C	-4.5084595	0.4196500	0.8918422
H	-4.2065503	1.3225679	0.3670741
N	-5.8033047	0.0018440	0.6615882
C	-6.2740472	-1.1416150	1.4093253
H	-7.1901895	-1.5158996	0.9492340
H	-6.4869066	-0.8871549	2.4589915
H	-5.5249411	-1.9301801	1.3880086
C	-6.7643010	1.0697980	0.5514316
H	-7.6827302	0.6845443	0.1048626
H	-6.3723432	1.8557222	-0.0964287
H	-7.0129103	1.5154737	1.5261264

C	-0.3290666	0.5626174	0.5099498
C	0.7195587	1.4277490	0.3112426
C	-0.1341878	-0.8007948	0.6978909
C	1.1210382	-1.3607827	0.6940606
C	1.9981012	0.8697403	0.3056105
C	2.1937126	-0.4922032	0.4926777
H	0.5553835	2.4879445	0.1669091
H	1.2628927	-2.4237974	0.8409728
H	2.8546762	1.5147066	0.1522461
H	3.2006134	-0.8914238	0.4822959



F

E (TPSS-D3/def2-TZVP) = -952.2404204601 (conv)

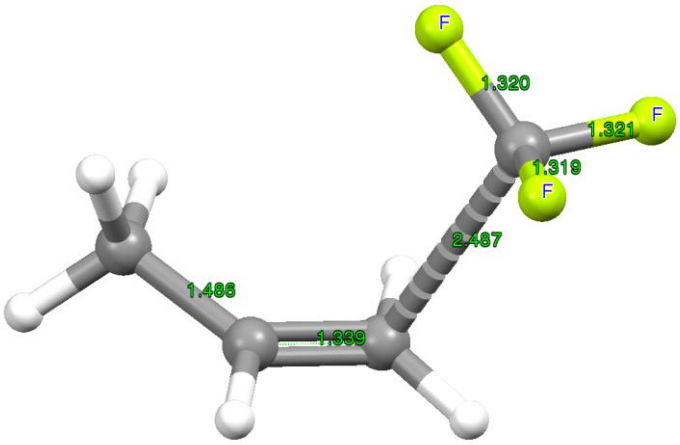
Lowest Freq. = 21.97 cm^-1

26

F (014/c1/pbe0-d3.def2-TZVP)

B	-2.1263145	0.0513037	1.9510488
O	-1.6221987	1.0707435	1.0781948
O	-1.2210819	-1.0415290	1.9621013
O	-3.4959390	-0.4354289	1.4516021
C	-4.4173451	0.4121320	1.3260579
H	-4.2424152	1.4566427	1.5818355
N	-5.6092582	0.0863261	0.9021712
C	-5.9534679	-1.2801976	0.5633859
H	-6.2528509	-1.3326035	-0.4853094
H	-6.7862792	-1.6094341	1.1878405

H	-5.0935447	-1.9221945	0.7318141
C	-6.6476409	1.0859857	0.7739627
H	-6.9910374	1.1364544	-0.2613498
H	-6.2621603	2.0595962	1.0712116
H	-7.4925821	0.8268315	1.4151207
C	-0.4036450	0.6216437	0.6735572
C	0.5140656	1.2505471	-0.1335790
C	-0.1645120	-0.6441411	1.2055984
C	1.0022804	-1.3237434	0.9475881
C	1.7018513	0.5655777	-0.4029429
C	1.9401935	-0.6933879	0.1259462
H	0.3204584	2.2368471	-0.5366720
H	1.1802510	-2.3050617	1.3692587
H	2.4497167	1.0315918	-1.0333469
H	2.8721407	-1.1991520	-0.0967420
I	-2.5792328	0.8978474	4.0516047



TS(1-A)

E (TPSS-D3/def2-TZVP) = -455.1959587745 (conv)

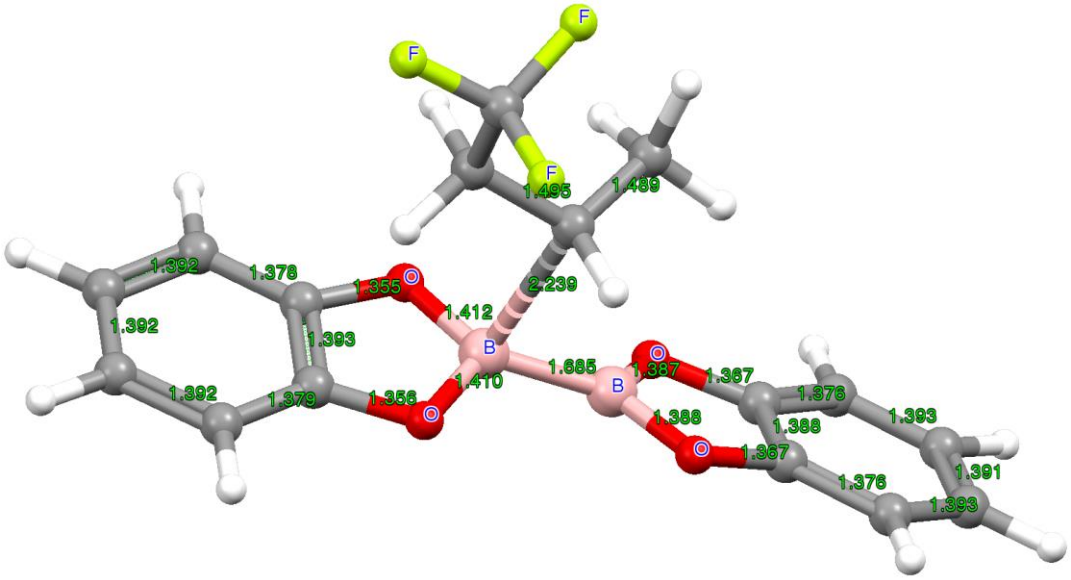
Lowest Freq. = -150.59 cm^-1

13

TS(1-A) (TS010/c1/pbe0-d3.def2-TZVP)

C	-0.0869814	-0.4665001	-1.0331173
H	-0.6063369	-0.0128156	-1.8742186
C	1.3910331	-0.5772901	-1.1444139
H	1.8489963	0.4126827	-1.2437696

H	1.6775631	-1.1436824	-2.0360235
H	1.8238768	-1.0661149	-0.2700133
C	-0.8008174	-0.8338423	0.0381699
H	-1.8824465	-0.7705836	0.0435659
H	-0.3351251	-1.3470357	0.8736420
C	-0.7716593	1.1869365	1.4882725
F	0.4946773	1.5284146	1.6335849
F	-1.3205986	0.9519443	2.6672359
F	-1.4321812	2.1378865	0.8570852



TS(A-B)

E (TPSS-D3/def2-TZVP) = -1267.548267064 (conv)

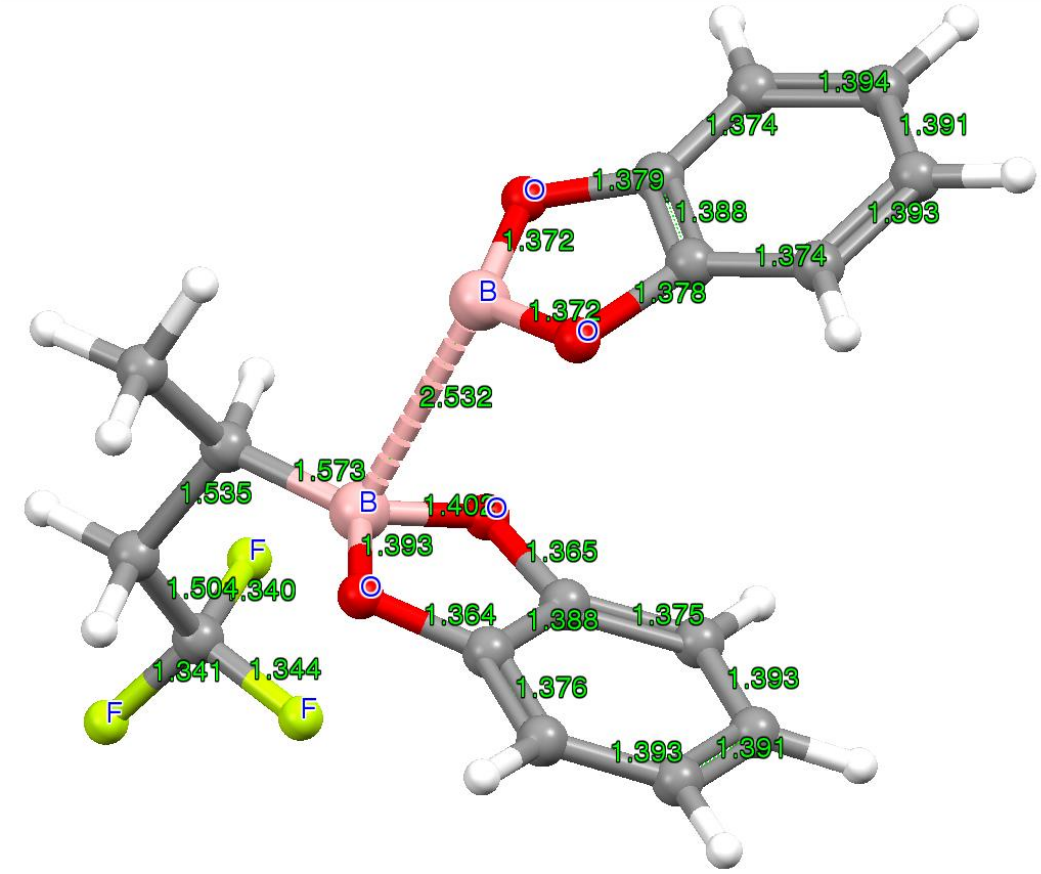
Lowest Freq. = -154.75 cm^-1

39

TS(A-B) (TS002/c2/pbe0-d3.def2-TZVP)

O	1.6906771	-0.7478082	-1.7367032
B	1.0247586	0.2663980	-1.0642125
O	0.7012016	1.2963132	-1.9369966
B	0.6068271	0.2219632	0.5671331
O	0.8787829	-0.8817667	1.4038029
O	0.4750422	1.3778555	1.3644762
C	1.7683755	-0.3401160	-3.0388139
C	1.1669145	0.9045281	-3.1606857

C	2.3294789	-0.9878083	-4.1157113
C	2.2624956	-0.3286410	-5.3409684
C	1.0965647	1.5660291	-4.3654760
C	1.6602382	0.9193263	-5.4629070
H	2.7973750	-1.9580600	-4.0093547
H	2.6898308	-0.7996124	-6.2178144
H	0.6270894	2.5377229	-4.4494190
H	1.6282723	1.4006038	-6.4327683
C	0.6042428	0.9646095	2.6491820
C	0.5121763	1.7070307	3.8073496
C	0.8471848	-0.4071714	2.6729350
C	1.0084497	-1.0960105	3.8559470
C	0.6771535	1.0182919	5.0054480
C	0.9202657	-0.3523881	5.0291482
H	0.3204133	2.7719731	3.7778557
H	1.1964473	-2.1620310	3.8642532
H	0.6144567	1.5619357	5.9401784
H	1.0433211	-0.8524495	5.9820572
C	-1.5200130	-0.1714149	-0.0111743
H	-1.6560725	0.8269923	-0.4185939
C	-1.5206814	-1.3023480	-0.9802848
H	-1.0672248	-1.0328523	-1.9346815
H	-2.5513456	-1.6165314	-1.1883548
H	-0.9947147	-2.1726479	-0.5787284
C	-2.1334395	-0.3956949	1.3330611
H	-1.7529378	0.3099688	2.0757664
H	-1.9344839	-1.4056386	1.6979665
C	-3.6350095	-0.2067481	1.3455617
F	-4.1263557	-0.3872322	2.5781435
F	-3.9859941	1.0248902	0.9537694
F	-4.2697632	-1.0714609	0.5396135



TS(B-C)

E (TPSS-D3/def2-TZVP) = -1267.532927372 (conv)

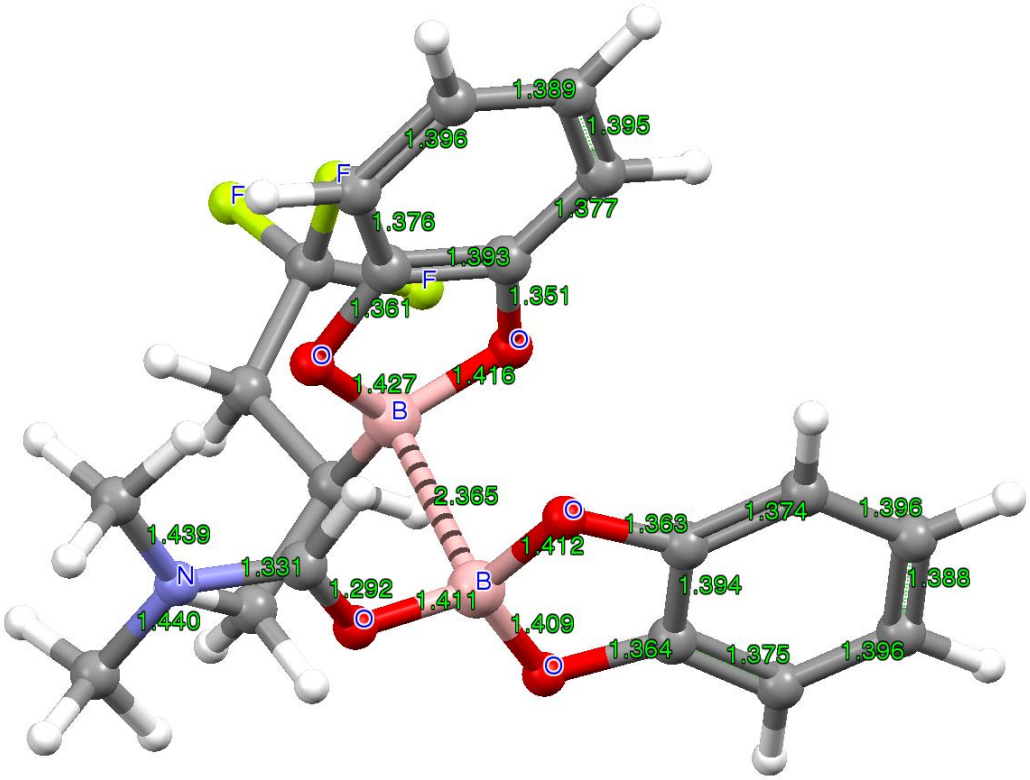
Lowest Freq. = -72.37 cm^-1

39

TS(B-C) (TS005/c1/pbe0-d3.def2-TZVP)

O	1.3313139	-0.6445700	-1.3749194
B	-0.0286539	-0.8045546	-1.4552870
O	-0.5969129	-0.0671847	-2.4636468
B	-0.9894530	-0.7957145	0.8876352
O	0.0313887	-1.4088173	1.6096582
O	-0.6822059	0.5551671	0.6756739
C	1.6260593	0.2848531	-2.3484789
C	0.4577836	0.6321989	-3.0115587
C	2.8428189	0.8352776	-2.6716846
C	2.8440852	1.7638972	-3.7107397
C	0.4461652	1.5453420	-4.0388125
C	1.6744910	2.1094694	-4.3786558
H	3.7449211	0.5615239	-2.1402272

H	3.7785679	2.2274696	-4.0023783
H	-0.4702870	1.8109222	-4.5495964
H	1.7163679	2.8362478	-5.1806869
C	0.5320206	0.7529584	1.2672056
C	1.2870633	1.9016466	1.3133202
C	0.9653406	-0.4394628	1.8308456
C	2.1753199	-0.5387948	2.4778312
C	2.5117446	1.8133956	1.9705289
C	2.9449201	0.6206081	2.5401465
H	0.9413252	2.8216837	0.8599680
H	2.5082918	-1.4731991	2.9107909
H	3.1392675	2.6936279	2.0388750
H	3.9037086	0.5907138	3.0434438
C	-2.3963334	-1.4534471	0.6393453
H	-2.9473425	-0.8151713	-0.0586295
C	-2.2822667	-2.8577131	0.0469630
H	-1.7859282	-2.8353571	-0.9248126
H	-3.2701912	-3.3065622	-0.0876083
H	-1.6999438	-3.5128624	0.6996467
C	-3.2077148	-1.5470450	1.9391062
H	-2.7023482	-2.1919108	2.6629410
H	-4.1845716	-1.9928358	1.7321246
C	-3.4722915	-0.2403222	2.6341987
F	-4.2911558	-0.4108630	3.6828873
F	-2.3465808	0.3195386	3.1082433
F	-4.0487836	0.6598464	1.8263436



TS(D-E)

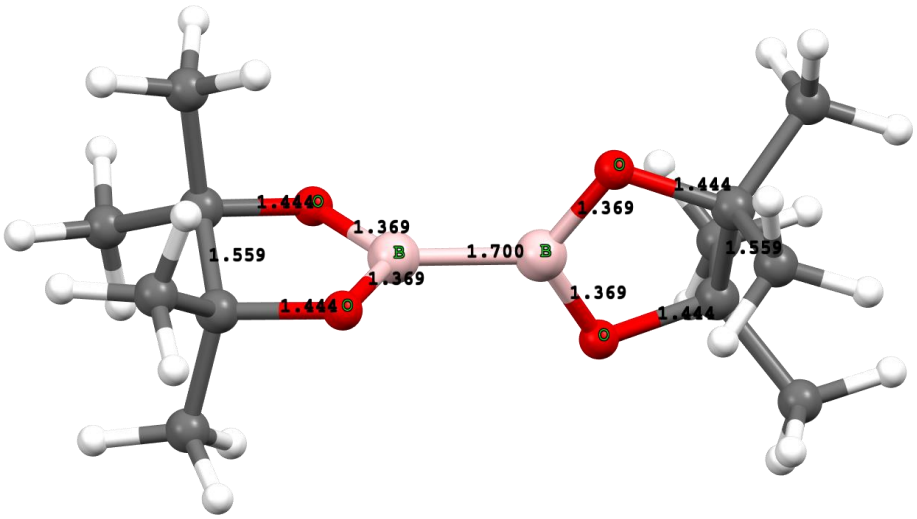
E (TPSS-D3/def2-TZVP) = -1515.909383966 (conv)

51

TS(D-E) (TS012/c1c/pbe0-d3.def2-TZVP)

O	2.2229463	-0.4021479	-1.3996695
B	1.1243264	0.3922372	-1.0160991
O	0.0790493	0.2920592	-1.9597146
B	0.1275401	-0.6794863	0.8415263
O	-0.7447241	0.4057021	1.1524377
O	-0.5895288	-1.6312545	0.0758743
C	1.7571107	-1.1302331	-2.4546857
C	0.4677834	-0.7191319	-2.7871946
C	2.3893510	-2.1415518	-3.1391160
C	1.6803745	-2.7381200	-4.1828654
C	-0.2408911	-1.3044751	-3.8087058
C	0.3947784	-2.3303235	-4.5099901
H	3.3896253	-2.4584494	-2.8725263
H	2.1442517	-3.5396924	-4.7449237
H	-1.2464424	-0.9816231	-4.0468278
H	-0.1289242	-2.8188562	-5.3227648

C	-1.8087452	-1.0934932	-0.1455704
C	-2.8466335	-1.5971868	-0.8966171
C	-1.9120770	0.1313462	0.5091209
C	-3.0541223	0.8963724	0.4442819
C	-4.0088654	-0.8296990	-0.9672775
C	-4.1127376	0.3899699	-0.3112024
H	-2.7533235	-2.5468917	-1.4076901
H	-3.1296608	1.8415582	0.9687866
H	-4.8495208	-1.1954102	-1.5446484
H	-5.0330423	0.9572273	-0.3816208
C	1.3109181	-1.1349570	1.7947915
H	1.7539903	-2.0231303	1.3324419
C	2.4154026	-0.1026246	2.0012015
H	2.9247860	0.1278075	1.0666373
H	3.1642137	-0.4718043	2.7086723
H	2.0117975	0.8290752	2.4076698
C	0.7932531	-1.5362606	3.1853249
H	0.3352917	-0.6787843	3.6863102
H	1.6332442	-1.8620221	3.8064729
C	-0.2148639	-2.6516322	3.2406563
F	-0.4123608	-3.0442169	4.5133572
F	-1.4157176	-2.2938444	2.7636565
F	0.1786064	-3.7340145	2.5571683
N	0.5226268	3.5265648	0.5898305
C	1.7118993	3.7313618	1.3759239
H	2.0533525	4.7649259	1.2691626
H	2.4954098	3.0569955	1.0414679
H	1.5090566	3.5402267	2.4346350
C	-0.5999729	4.3894289	0.8480615
H	-0.9416985	4.2768496	1.8822037
H	-1.4231956	4.1349806	0.1818541
H	-0.3244640	5.4348593	0.6838268
C	0.3954590	2.5138713	-0.2651516
O	1.3374432	1.6374370	-0.3869420
H	-0.5323759	2.4004606	-0.8115506



3b

E (PBE0-D3/def2-TZVP) = -821.9274271372 (conv)

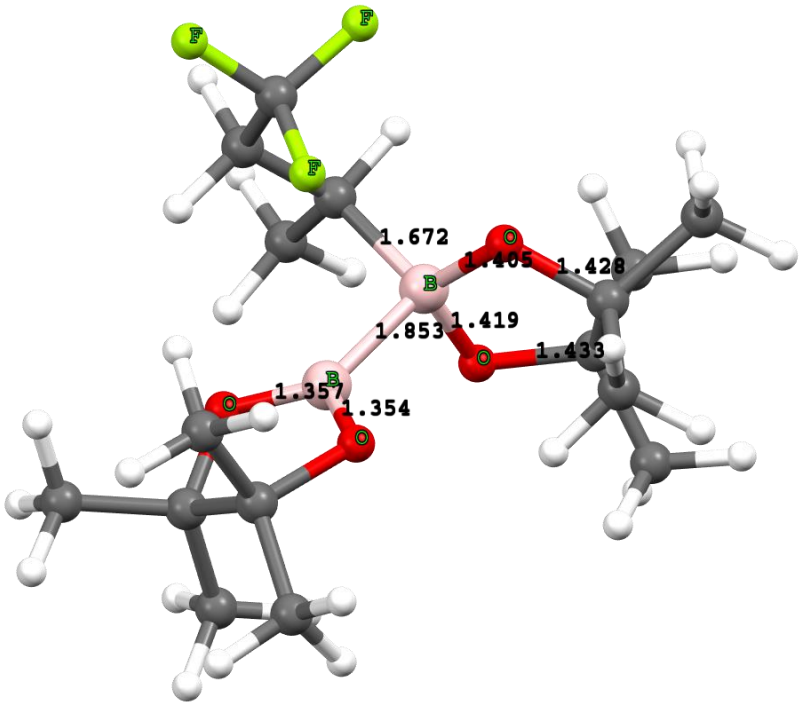
Lowest Freq. = 13.53 cm^-1

42

3b (001/c1c/pbe0-d3.def2-TZVP)

C	1.7902422	-0.7590532	-3.2377176
C	0.2922287	-0.7228139	-2.9807898
C	-0.4193066	-1.6980254	-3.8923796
O	0.0950508	-1.1336651	-1.6110155
B	-0.0000173	0.0000919	-0.8496300
O	-0.0950594	1.1335578	-1.6114507
C	-0.2921333	0.7221812	-2.9810854
C	-1.7901268	0.7583206	-3.2381435
C	0.4194716	1.6970402	-3.8929979
B	-0.0000417	0.0003903	0.8499145
O	1.1328433	0.1037676	1.6115005
C	0.7203164	0.2977892	2.9812209
C	1.7005091	-0.4067324	3.8929134
C	0.7456127	1.7959969	3.2383545
C	-0.7204290	-0.2969879	2.9811903
C	-0.7457164	-1.7952289	3.2381366
C	-1.7006258	0.4074123	3.8929707
O	-1.1329500	-0.1028207	1.6114891
H	-2.3179068	0.0572362	-2.5890358
H	-2.0244912	0.5185362	-4.2769084
H	-2.1589313	1.7624140	-3.0232844
H	0.0491046	-2.6804302	-3.8123157
H	-0.3498451	-1.3725956	-4.9331935
H	-1.4706183	-1.8003037	-3.6270805
H	2.1590324	-1.7630606	-3.0224308

H	2.3179703	-0.0577097	-2.5888474
H	2.0246873	-0.5196811	-4.2765594
H	-0.5043668	-2.0278822	4.2769283
H	-0.0407049	-2.3178324	2.5890973
H	-1.7470574	-2.1713341	3.0231012
H	-1.3746676	0.3400445	4.9337627
H	-2.6796621	-0.0679829	3.8128306
H	-1.8104104	1.4580296	3.6279098
H	2.6795308	0.0687161	3.8129043
H	1.8103452	-1.4572958	3.6276586
H	1.3745049	-0.3395738	4.9337046
H	1.4707616	1.7994253	-3.6276540
H	-0.0489490	2.6794746	-3.8133547
H	0.3500951	1.3712042	-4.9336902
H	1.7469511	2.1721274	3.0233486
H	0.5042864	2.0285129	4.2771823
H	0.0405887	2.3186880	2.5893996



Bb

E (PBE0-D3/def2-TZVP) = -1277.186863558 (conv)

Lowest Freq. = 18.24 cm^-1

55

Bb (025/c1/pbe0-d3.def2-TZVP)

O	1.0974257	-0.2738182	-0.8307069
B	-0.2474962	-0.3701628	-0.7056744
O	-0.9354194	-0.1087001	-1.8464180
B	-1.0778337	-0.6907987	0.9196608

O	-0.2605783	-1.4066778	1.8105371
O	-1.2396350	0.6359257	1.3976113
C	-2.4743133	-1.4688658	0.4296583
H	-2.7670331	-1.8880618	1.4022894
C	-3.5334453	-0.4797583	-0.0262649
H	-3.6704606	0.3137356	0.7072654
H	-4.4932560	-0.9876753	-0.1701271
H	-3.2554867	-0.0157279	-0.9742919
C	-2.3911385	-2.6156146	-0.5652134
H	-2.1535100	-2.2431482	-1.5642870
H	-3.3694176	-3.1026272	-0.6321329
C	-1.4084611	-3.7115941	-0.2623510
F	-1.5766415	-4.7425683	-1.1139081
F	-0.1331538	-3.3154487	-0.3990685
F	-1.5439304	-4.2044287	0.9736021
C	0.2913368	-0.5037322	2.7695061
C	-0.7079561	0.6980786	2.7265653
C	1.3737620	-0.1230204	-2.2484780
C	0.0234049	0.4445551	-2.7869217
C	2.5599251	0.7992125	-2.4109544
H	2.4033877	1.7488243	-1.9012926
H	2.7494008	0.9958411	-3.4689165
H	3.4487840	0.3270278	-1.9898502
C	1.6971981	-1.5071996	-2.7812657
H	2.5327555	-1.9162035	-2.2118555
H	1.9806786	-1.4698742	-3.8346133
H	0.8515420	-2.1864915	-2.6667984
C	-0.3484520	-0.0090868	-4.1792922
H	0.3939658	0.3343086	-4.9036172
H	-1.3140294	0.4164769	-4.4572166
H	-0.4207063	-1.0938941	-4.2424910
C	-0.0794578	1.9549280	-2.6697381
H	0.1781366	2.2911272	-1.6637914
H	-1.1083821	2.2551738	-2.8729059
H	0.5744126	2.4549622	-3.3862556
C	-0.0782959	2.0569060	2.9456135
H	-0.8456835	2.8306336	2.8826590
H	0.6821742	2.2670048	2.1945733
H	0.3825234	2.1144505	3.9345879
C	-1.8931569	0.5149618	3.6661495
H	-2.6340732	1.2874696	3.4536519
H	-1.5924204	0.6026411	4.7119500
H	-2.3633527	-0.4593418	3.5216572
C	1.6989490	-0.1304761	2.3274569

H	2.2756362	-1.0475713	2.1975782
H	2.1952218	0.4871752	3.0790144
H	1.6982997	0.3964048	1.3748585
C	0.3586897	-1.2137251	4.1080389
H	0.7006881	-0.5327373	4.8913436
H	1.0688275	-2.0395185	4.0414377
H	-0.6089541	-1.6230936	4.3948410

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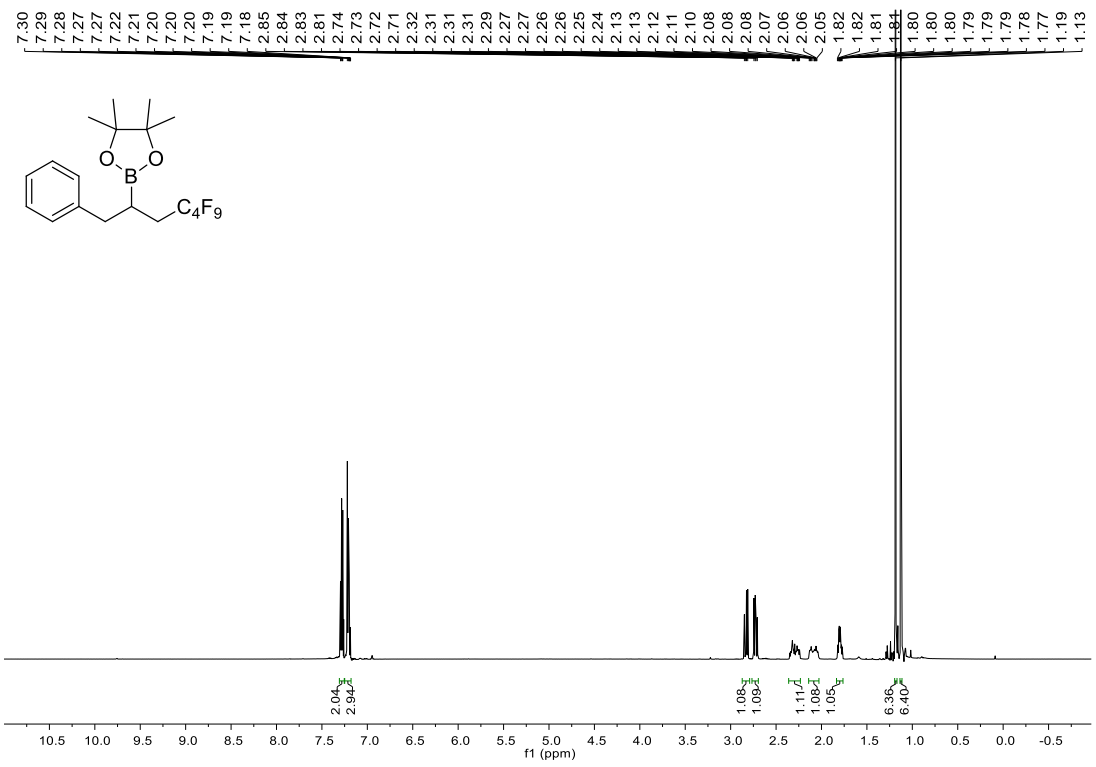
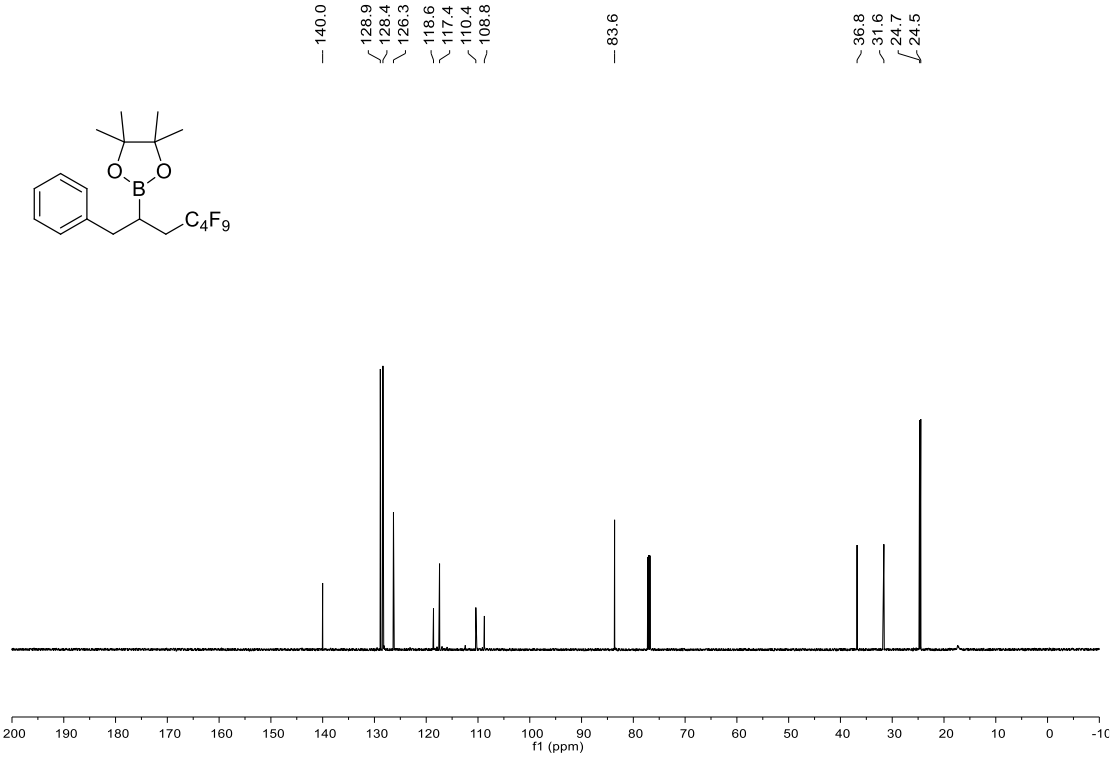
5 NMR Spectra

4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylheptan-2-yl)-1,3,2-dioxaborolane (4b)

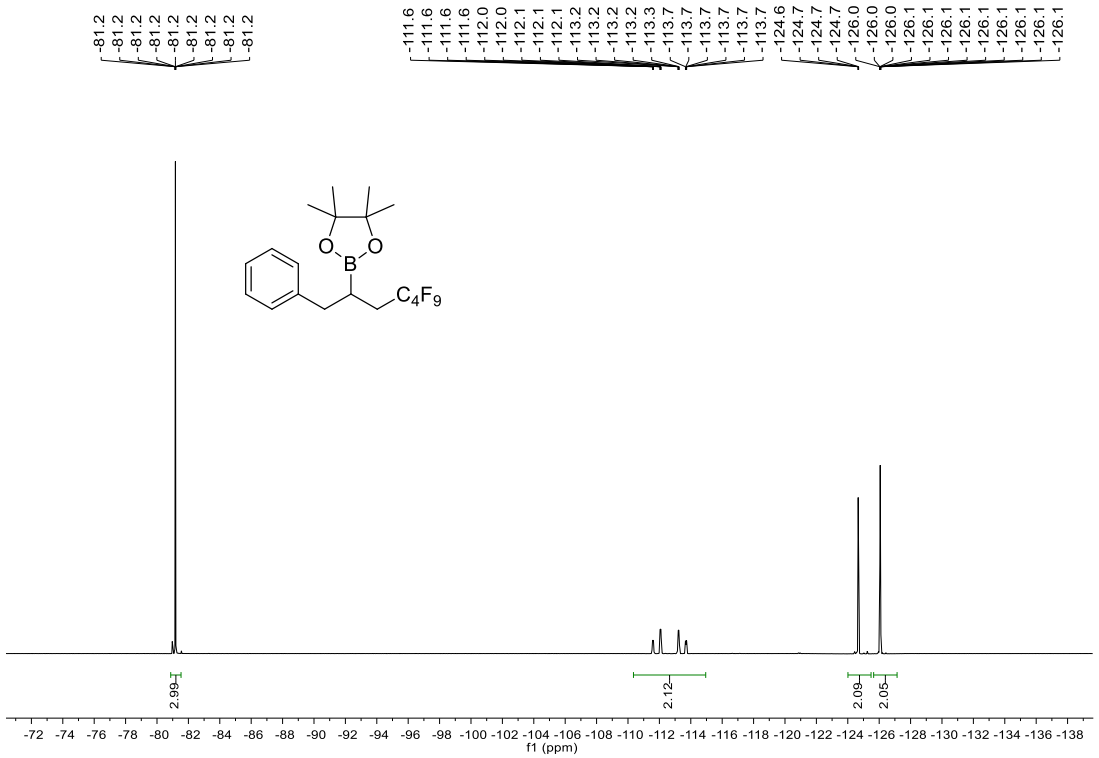
^{1}H NMR (600 MHz, $CDCl_3$)



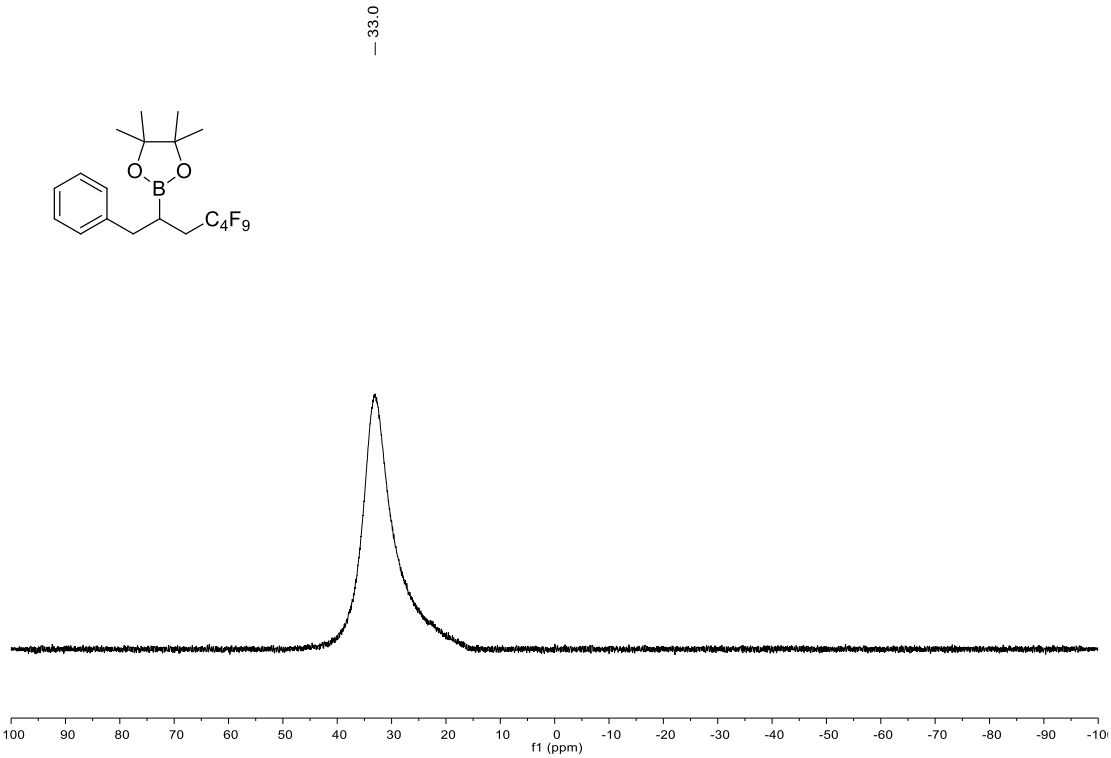
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

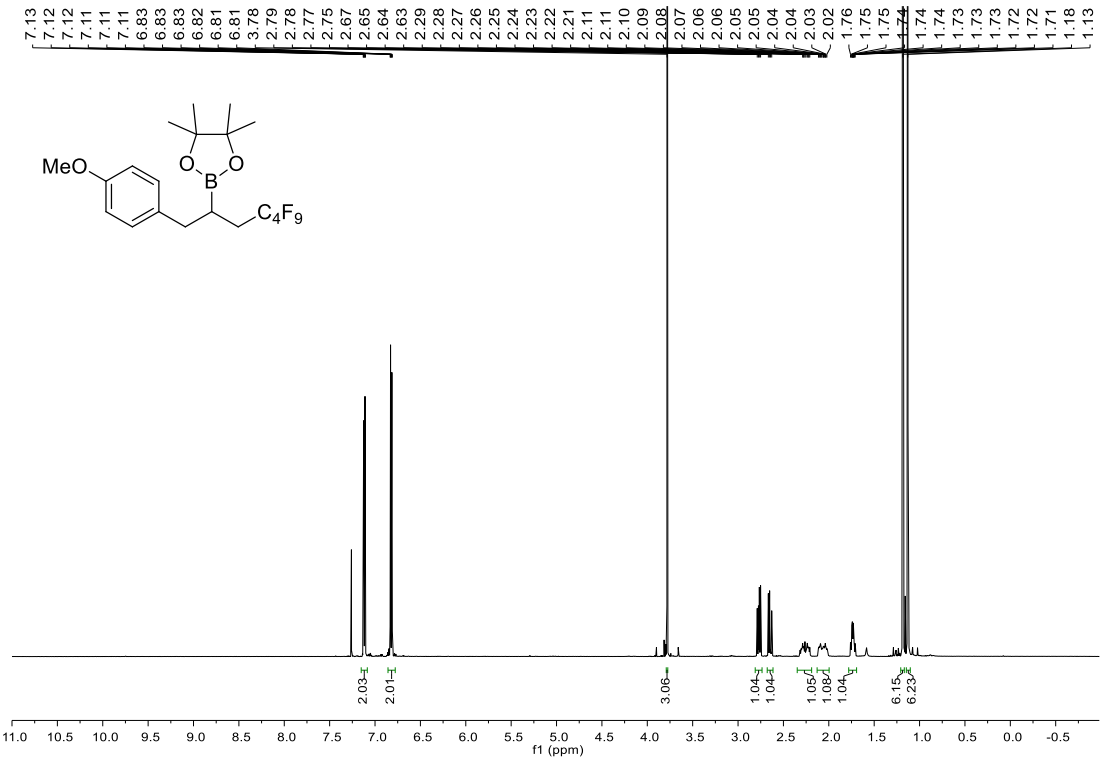


^{11}B NMR (96 MHz, $CDCl_3$)

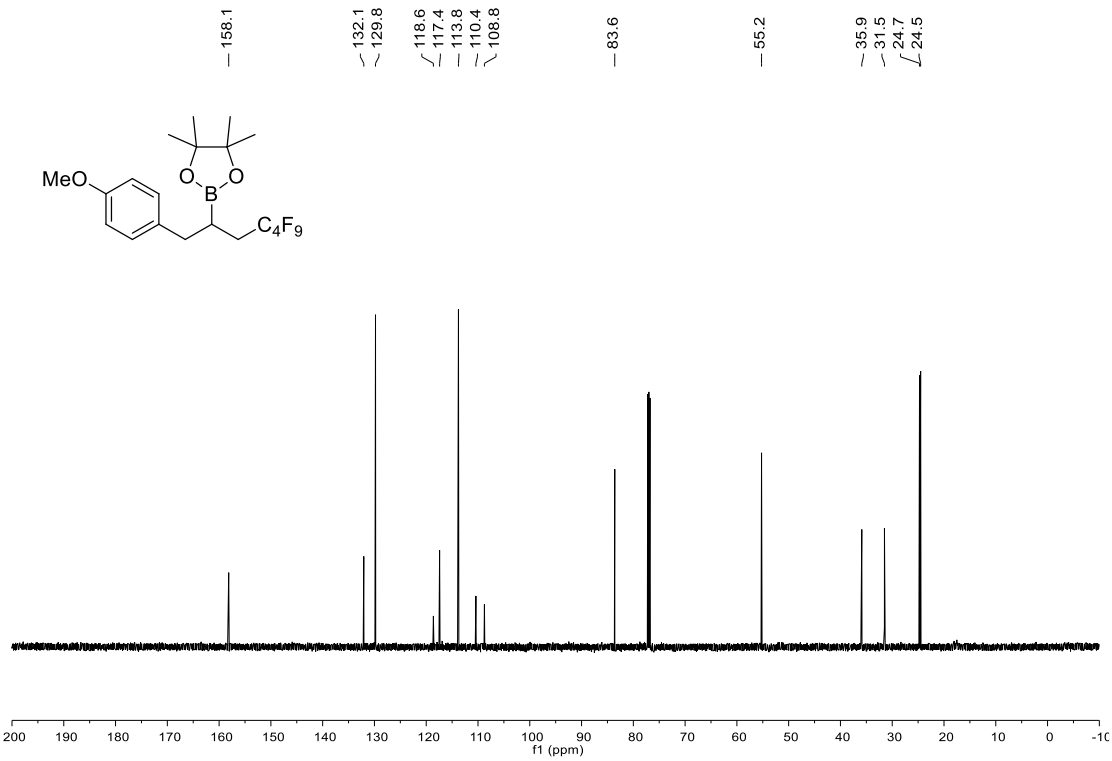


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-methoxyphenyl)heptan-2-yl)-1,3,2-dioxaborolane (4c)

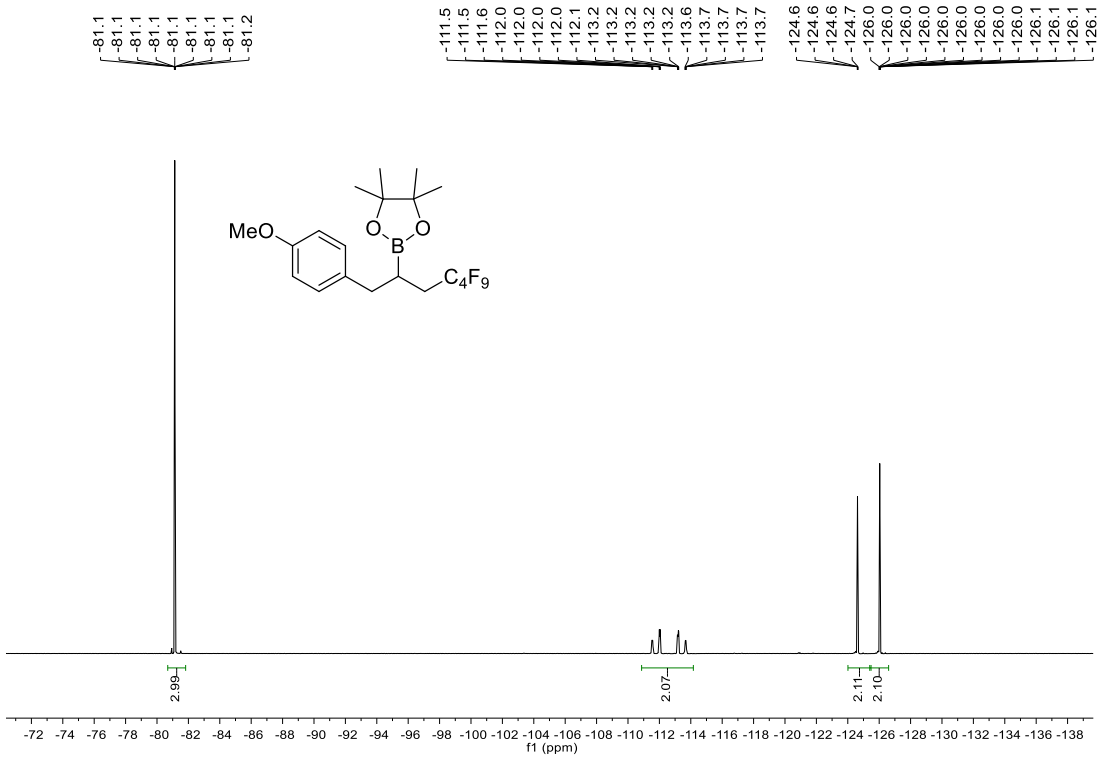
^{1}H NMR (600 MHz, $CDCl_3$)



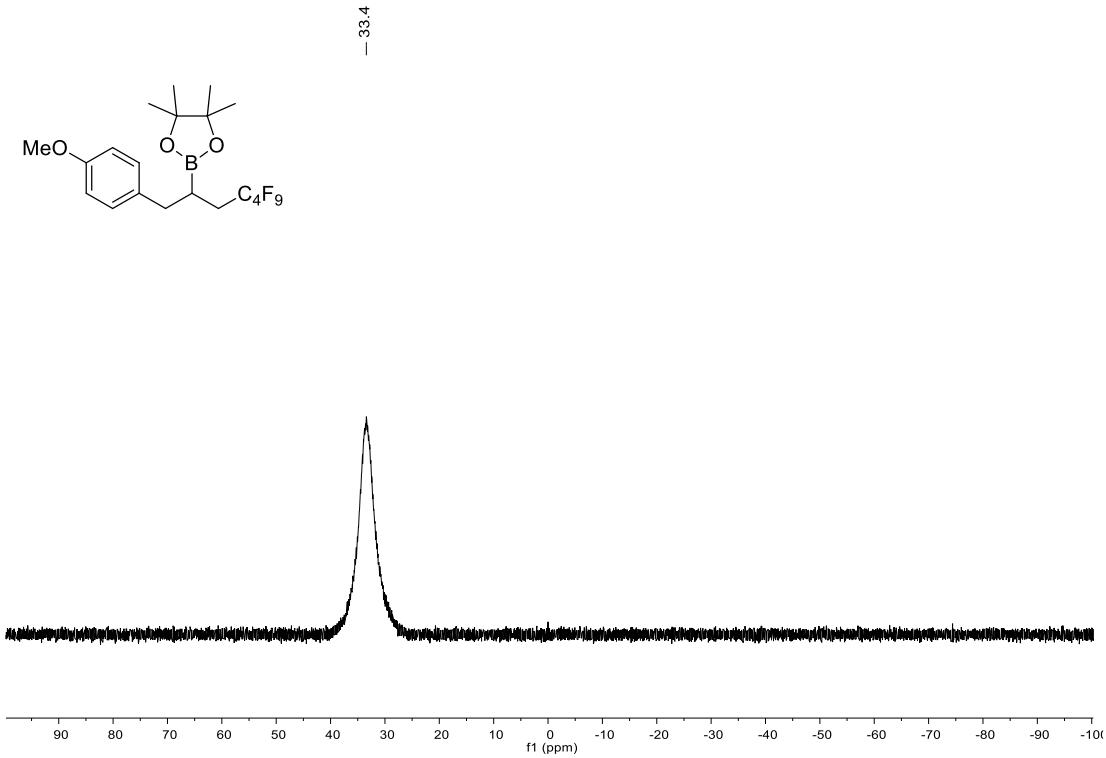
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

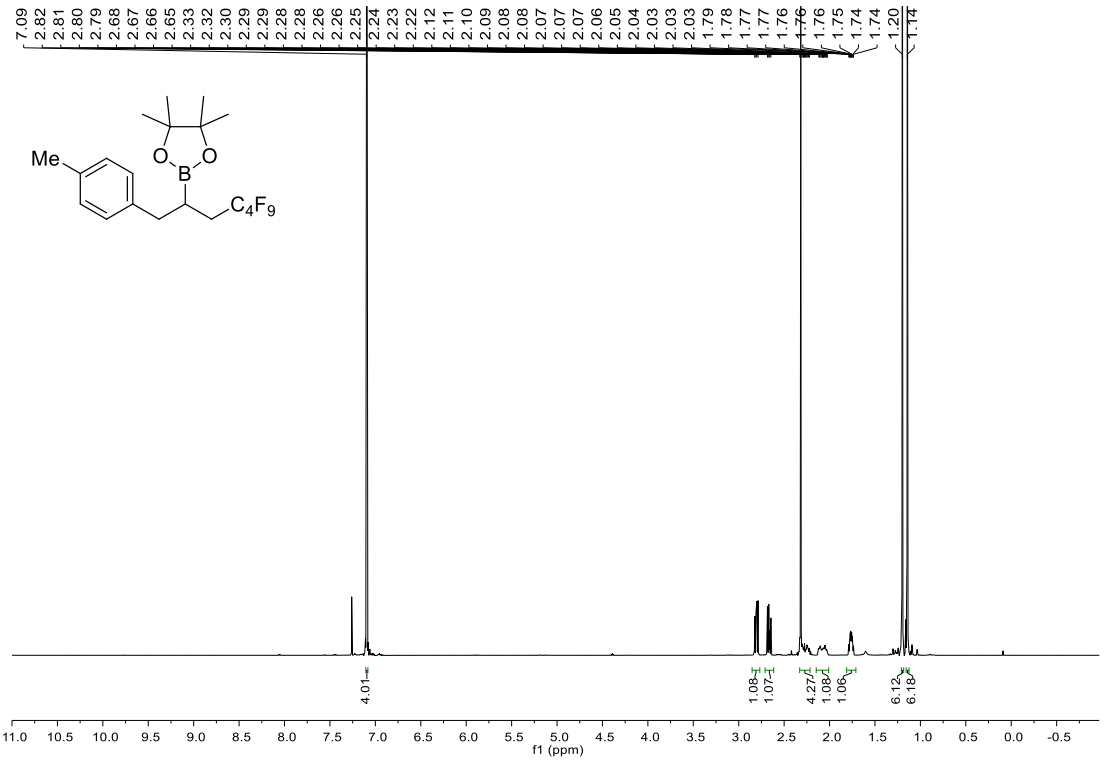


^{11}B NMR (192 MHz, $CDCl_3$)

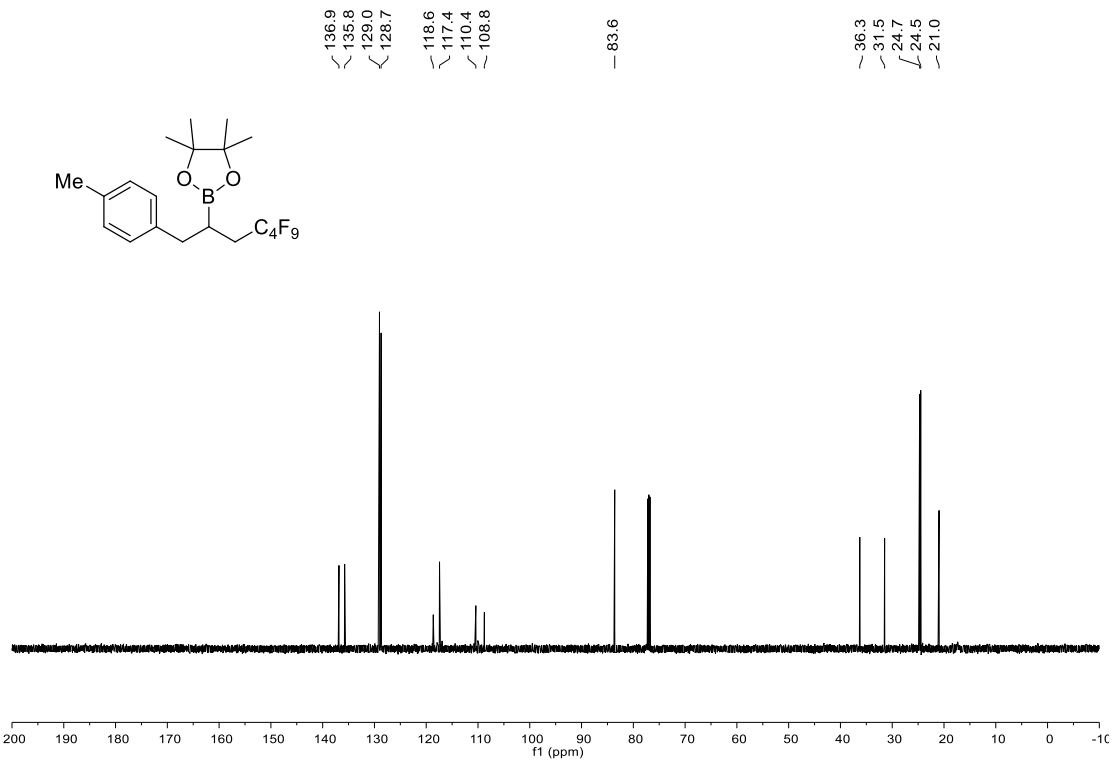


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(*p*-tolyl)heptan-2-yl)-1,3,2-dioxaborolan e (4d)

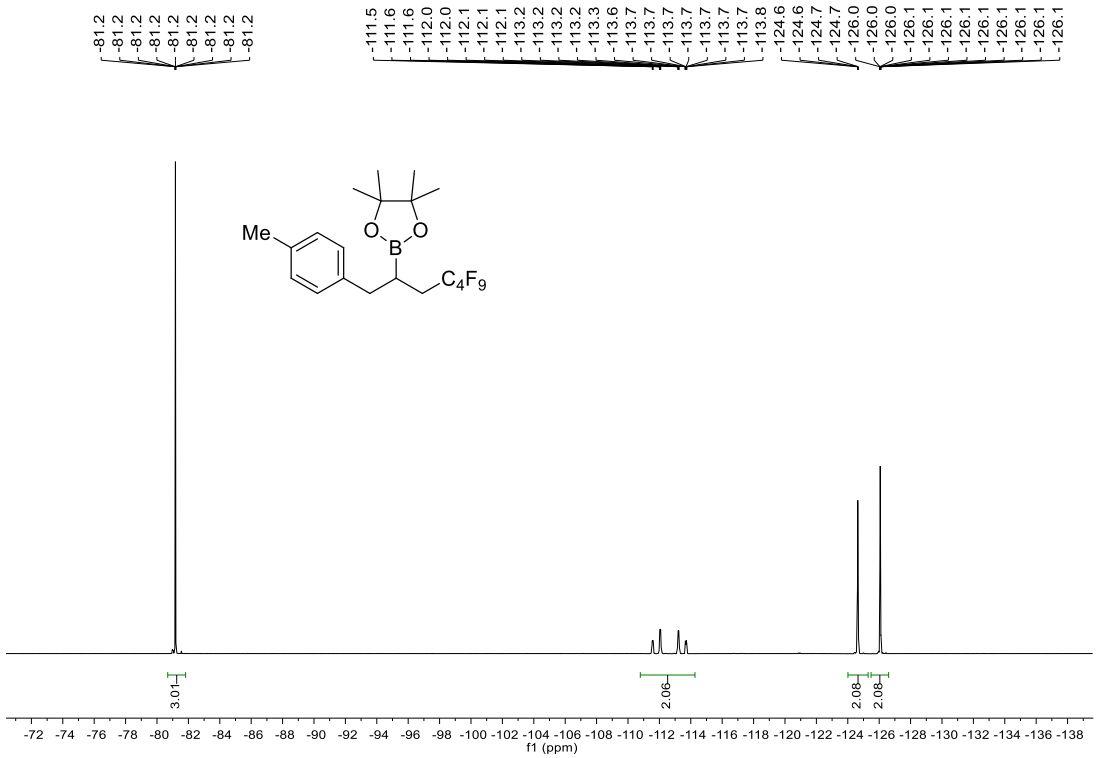
^{1}H NMR (600 MHz, $CDCl_3$)



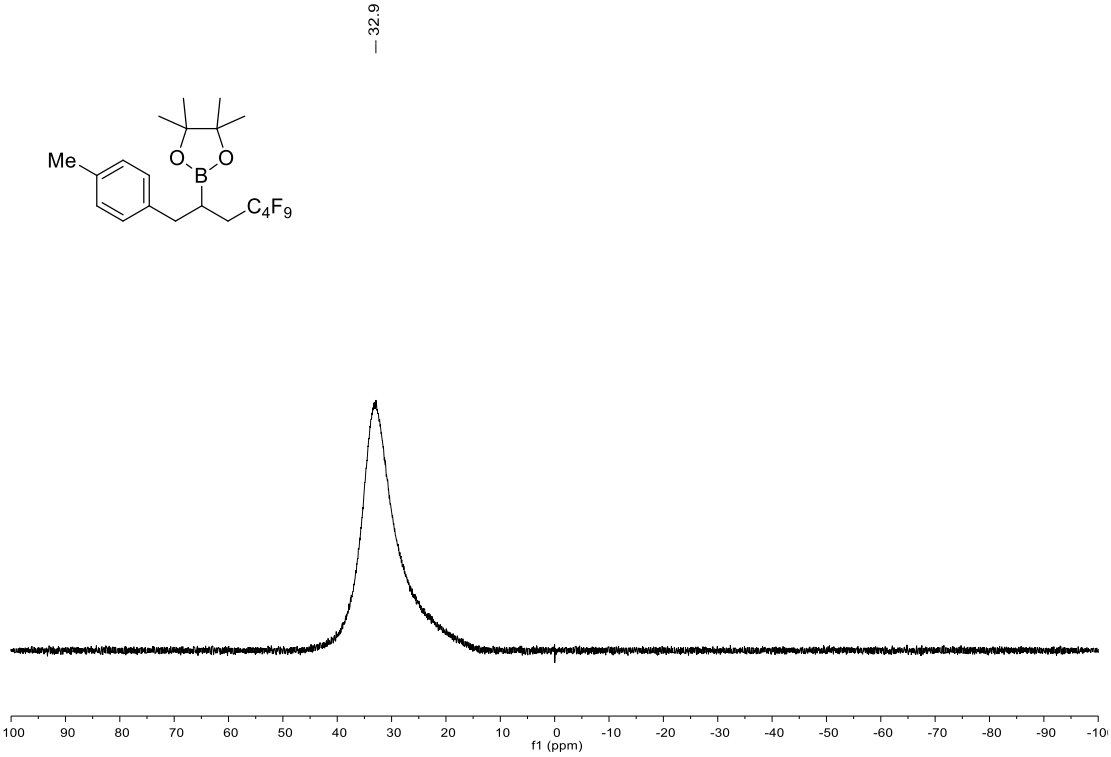
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

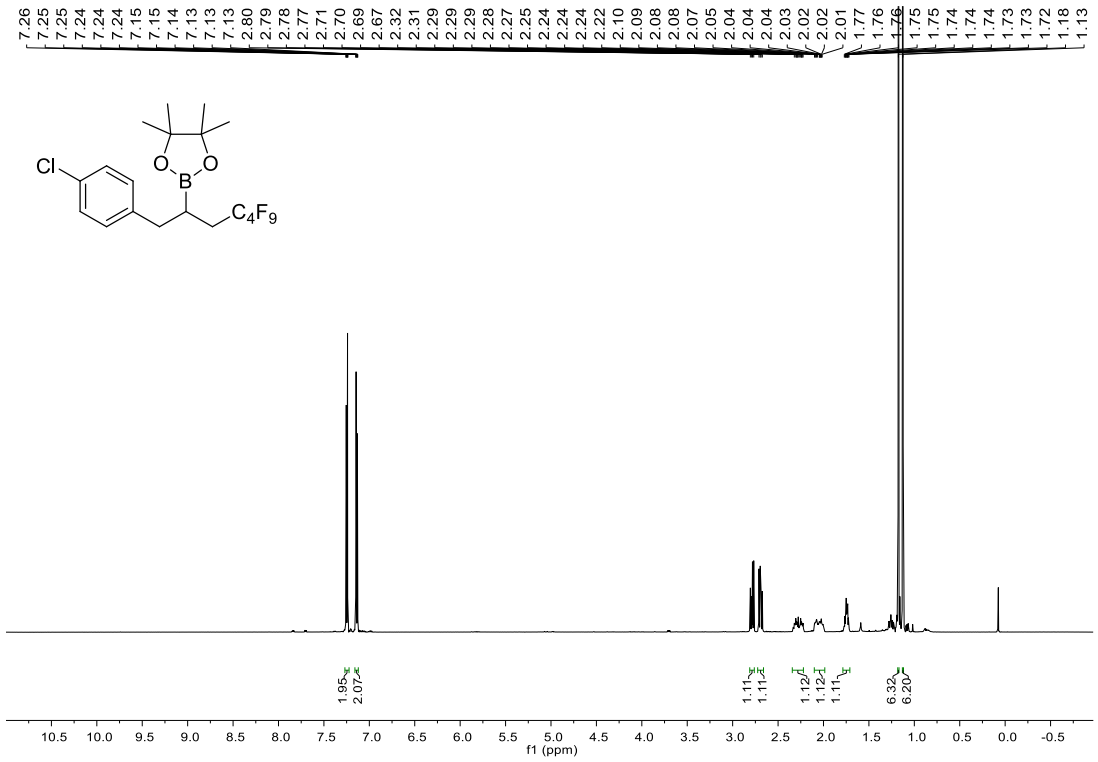


^{11}B NMR (96 MHz, $CDCl_3$)

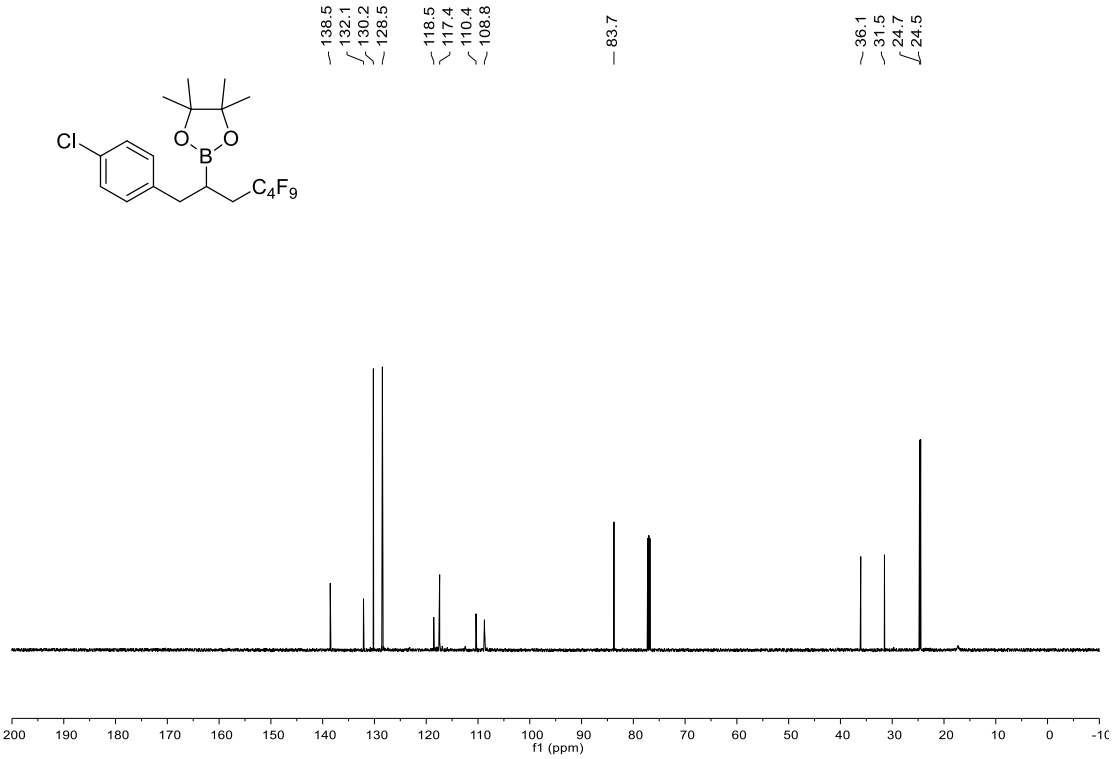


2-(1-(4-Chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)

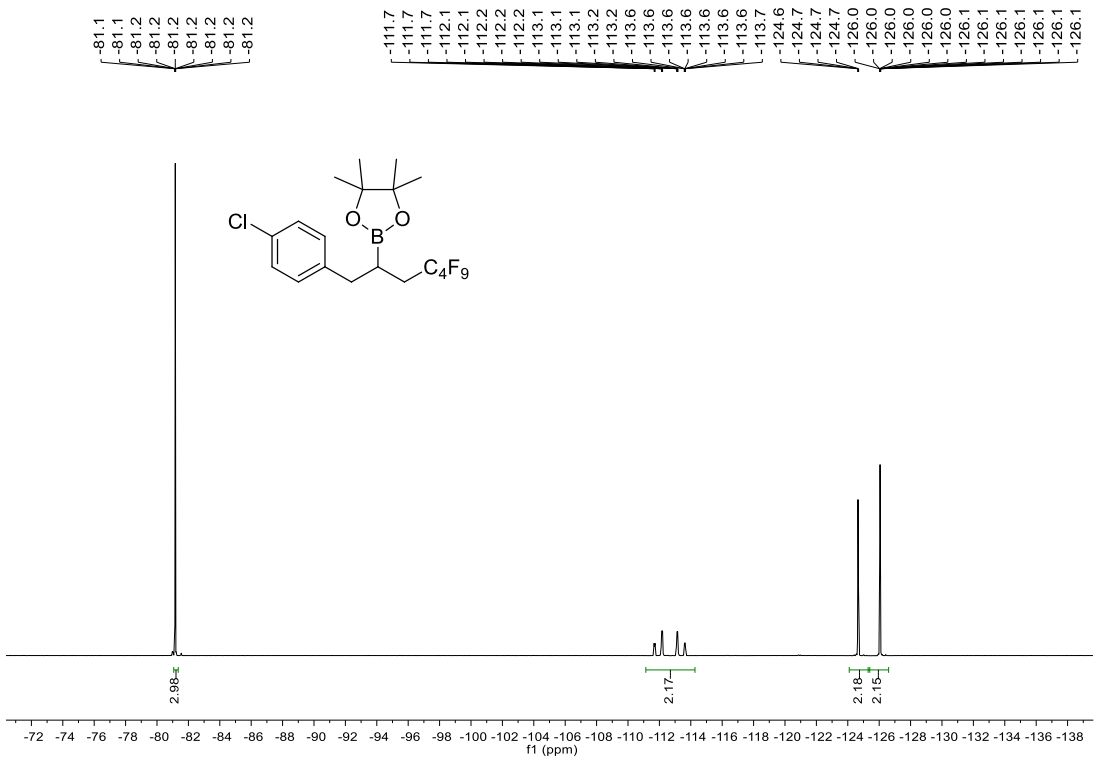
^{1}H NMR (600 MHz, $CDCl_3$)



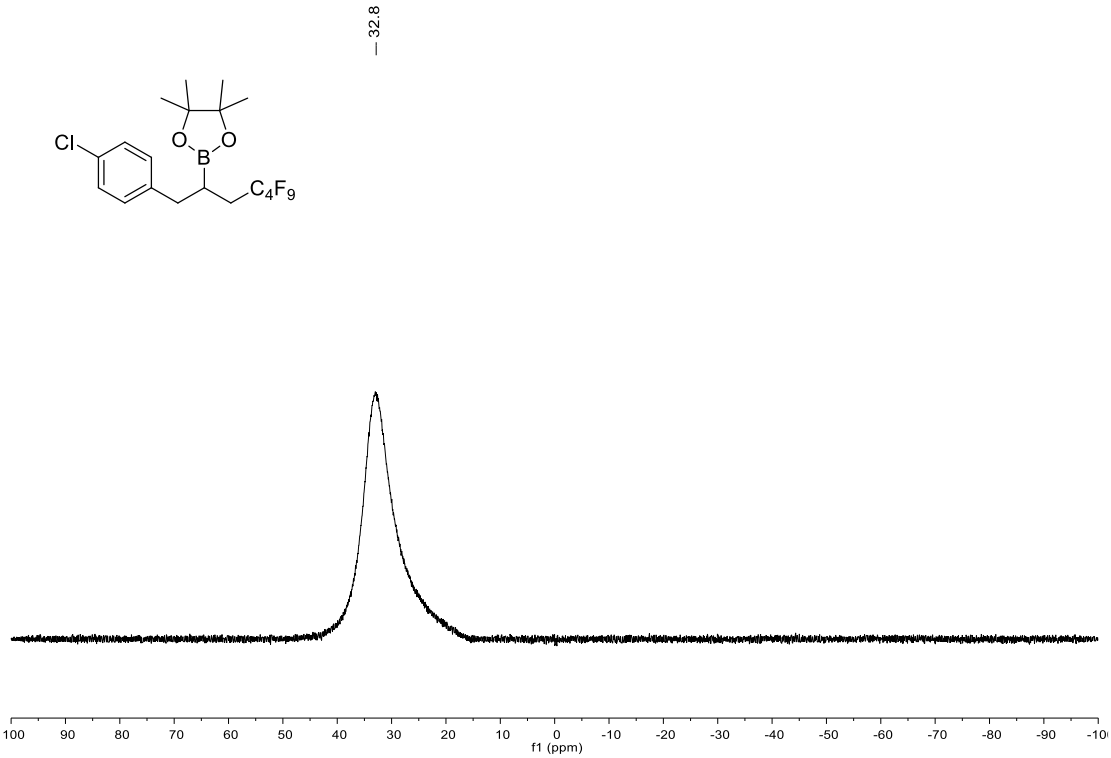
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

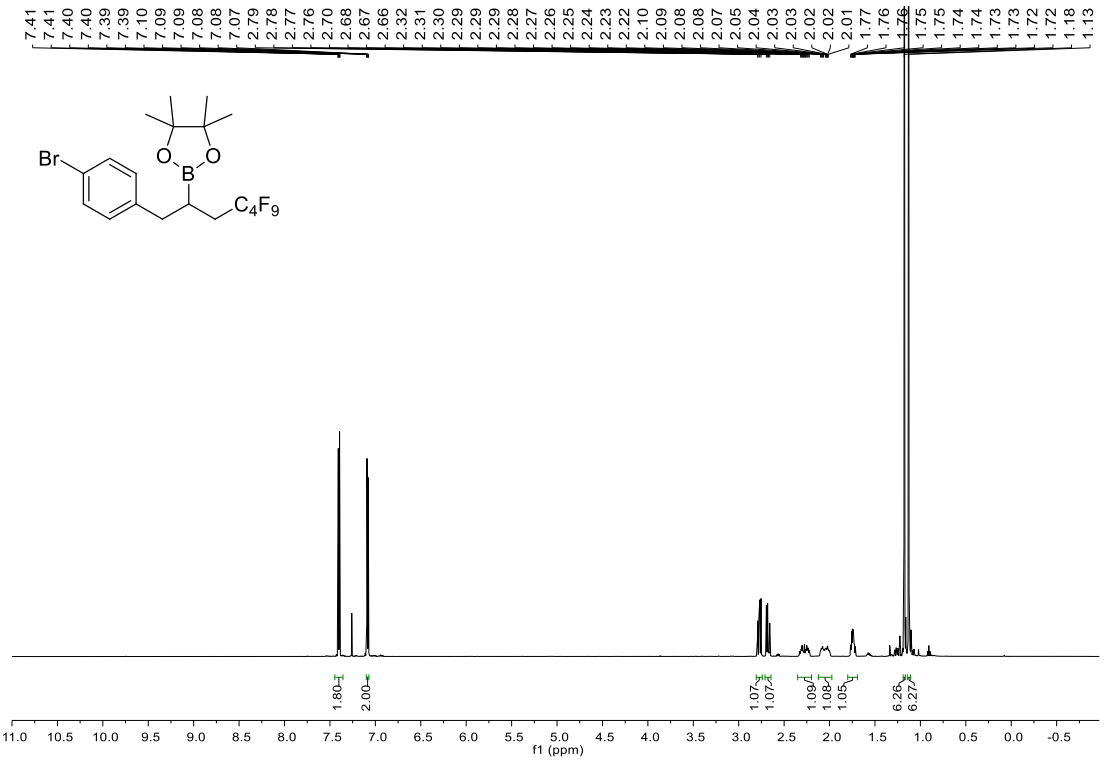


^{11}B NMR (96 MHz, $CDCl_3$)

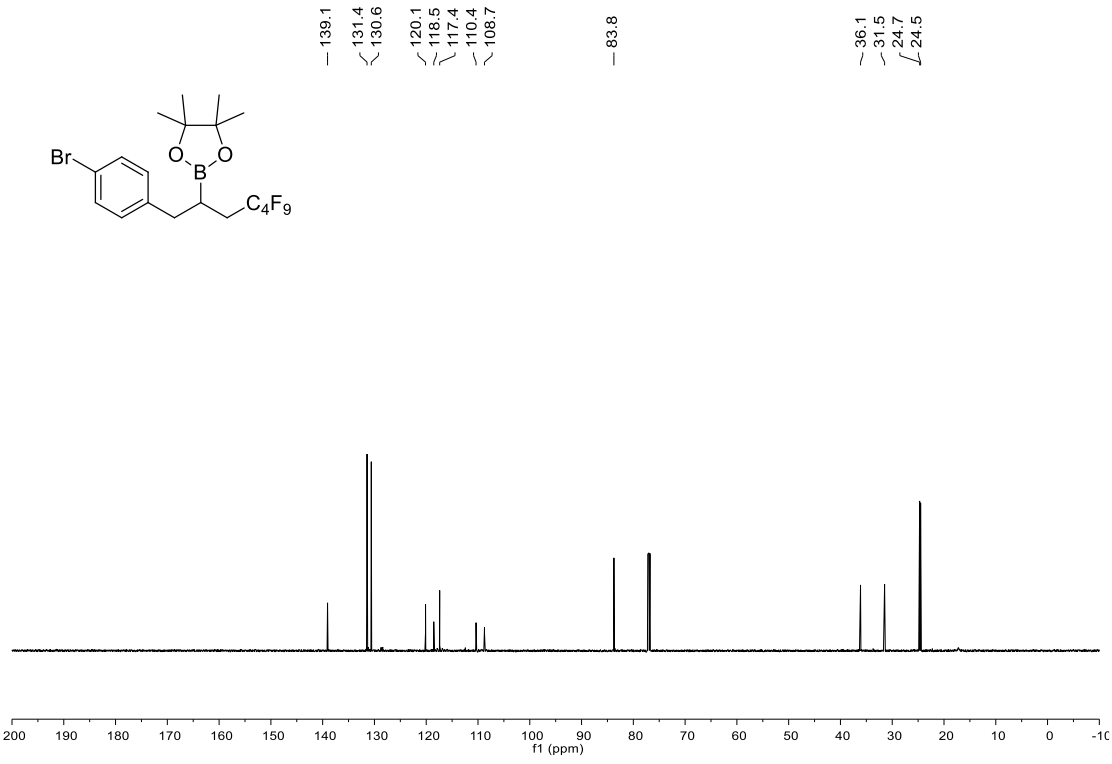


2-(1-(4-Bromophenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4f)

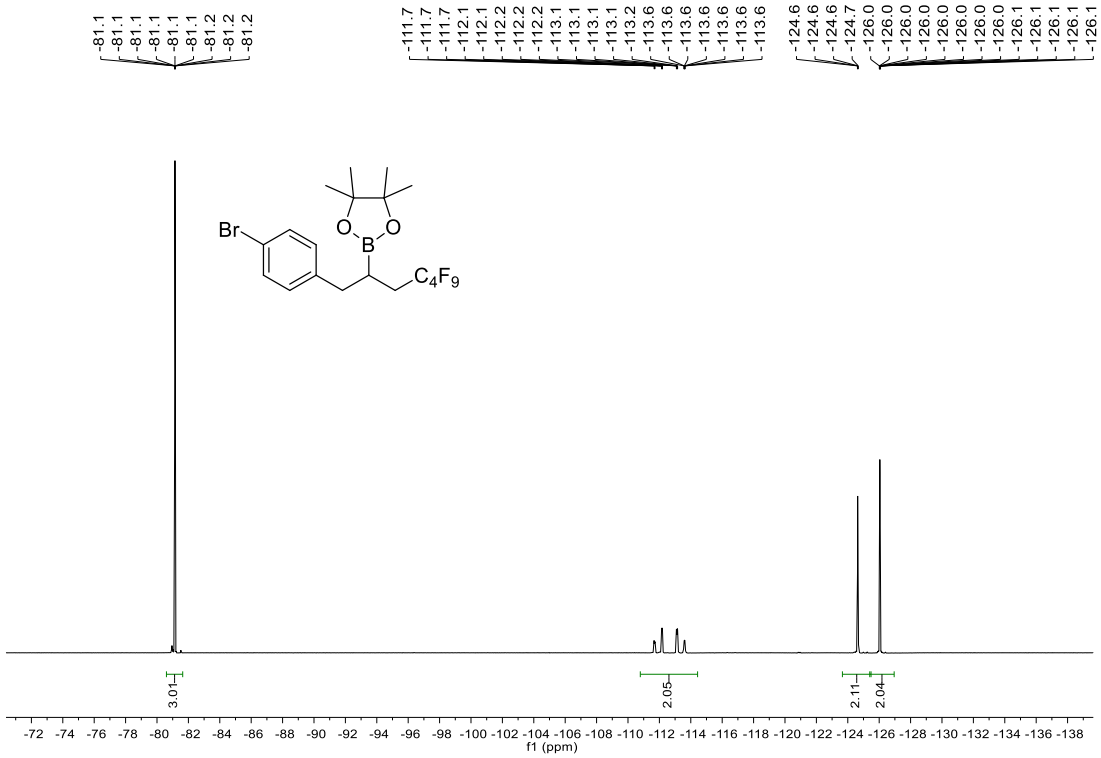
^{1}H NMR (600 MHz, $CDCl_3$)



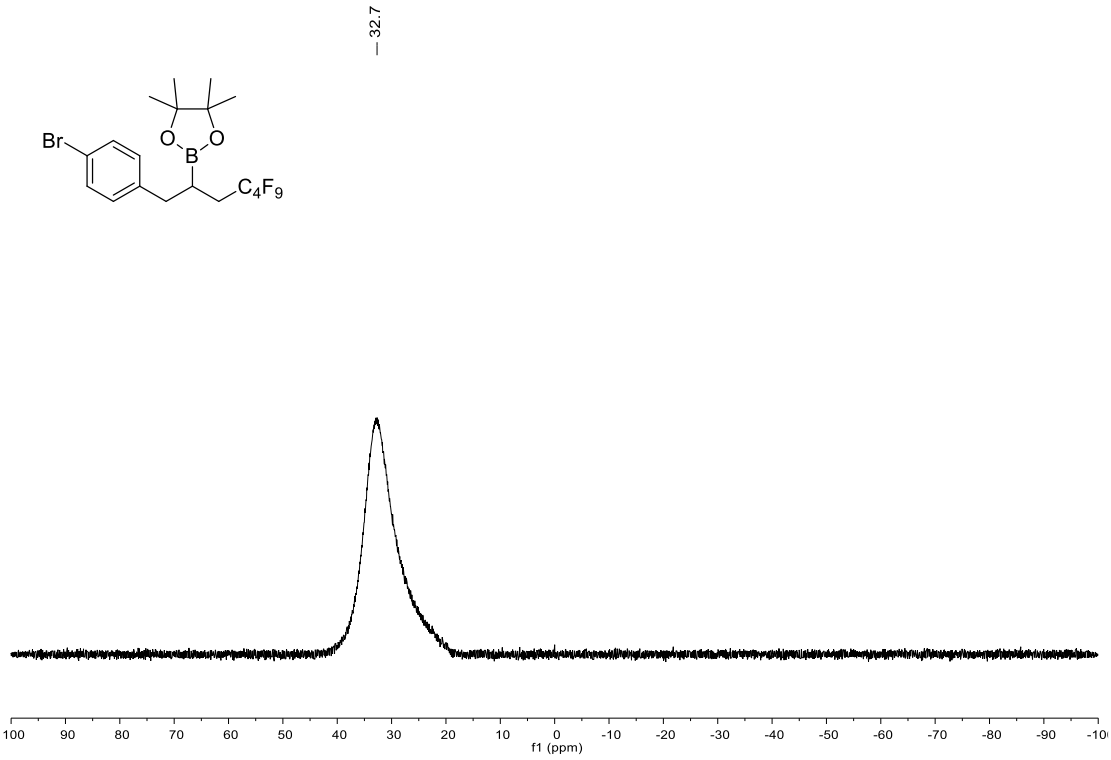
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

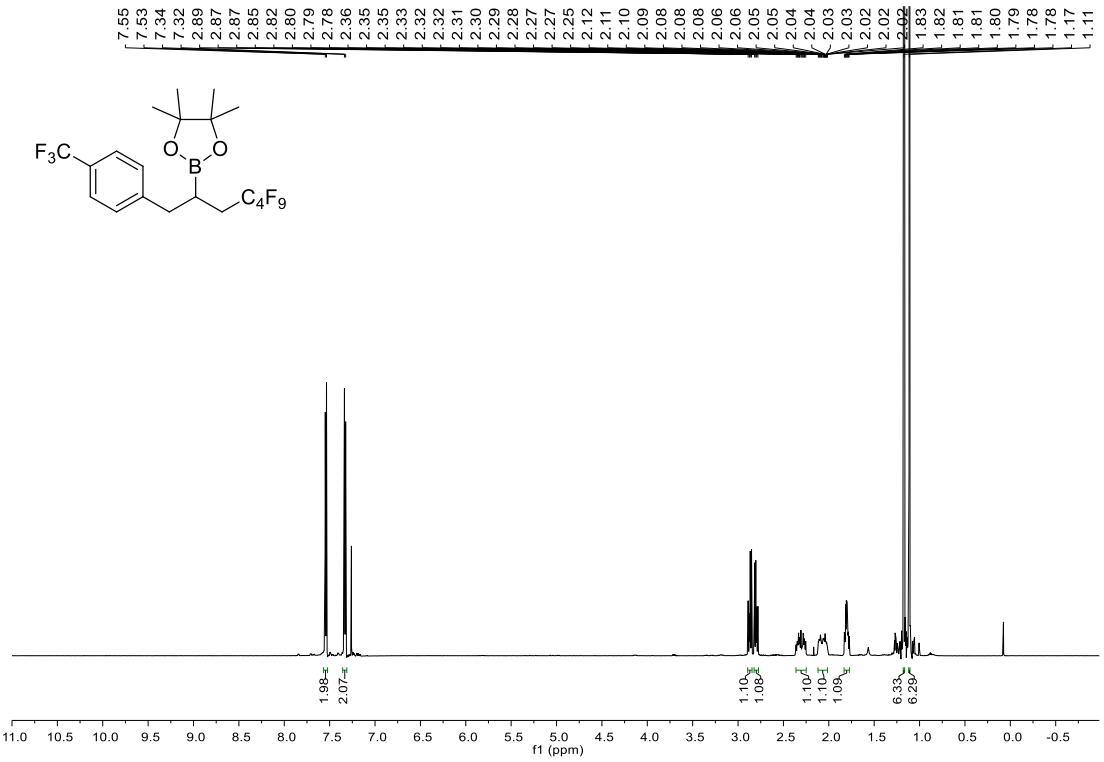


^{11}B NMR (96 MHz, $CDCl_3$)

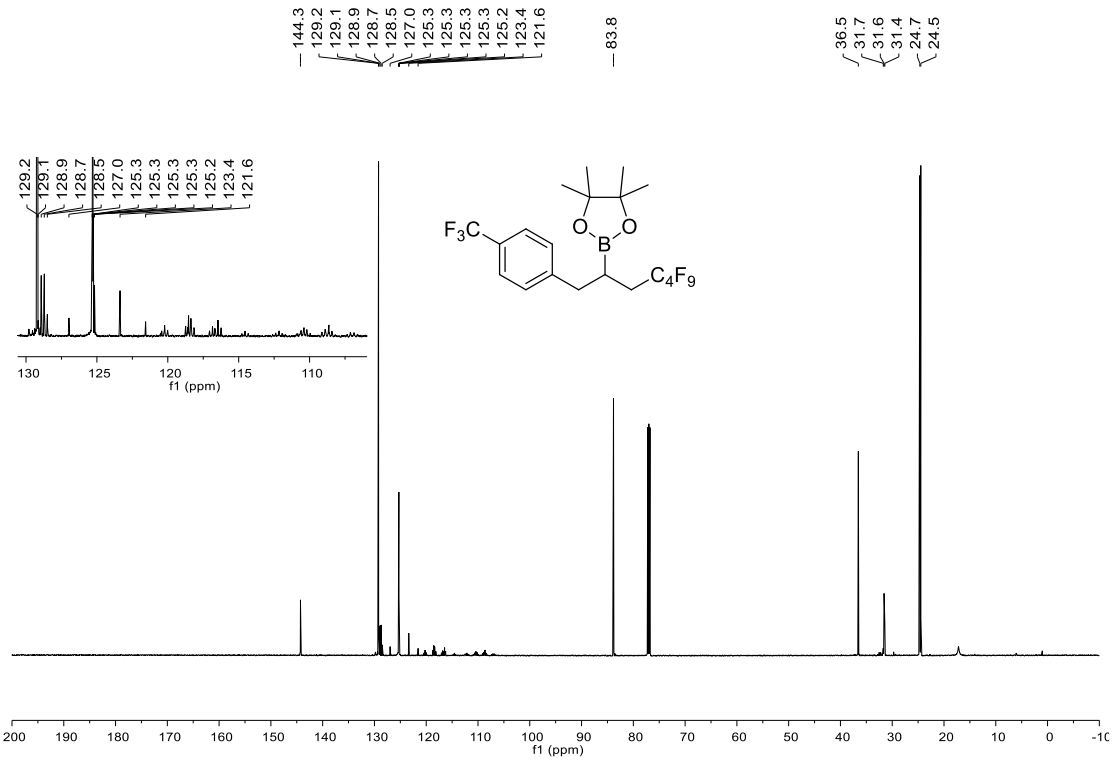


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-(trifluoromethyl)phenyl)heptan-2-yl)-1,3,2-dioxaborolane (4g)

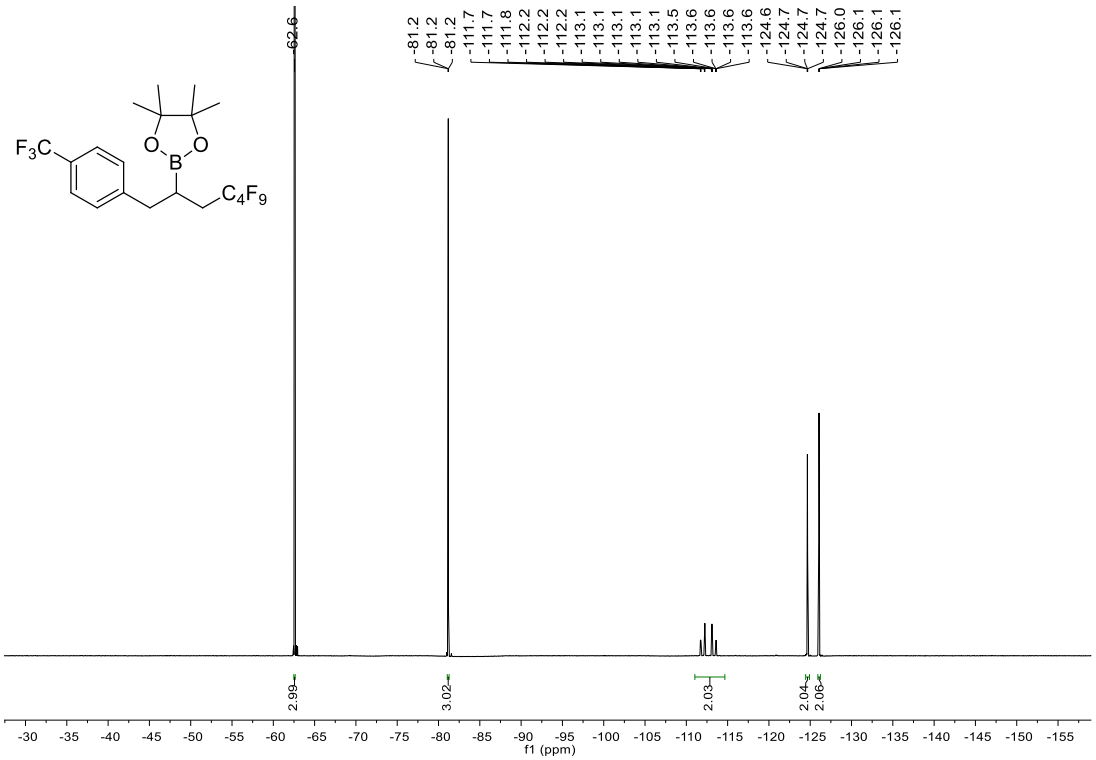
^{1}H NMR (600 MHz, $CDCl_3$)



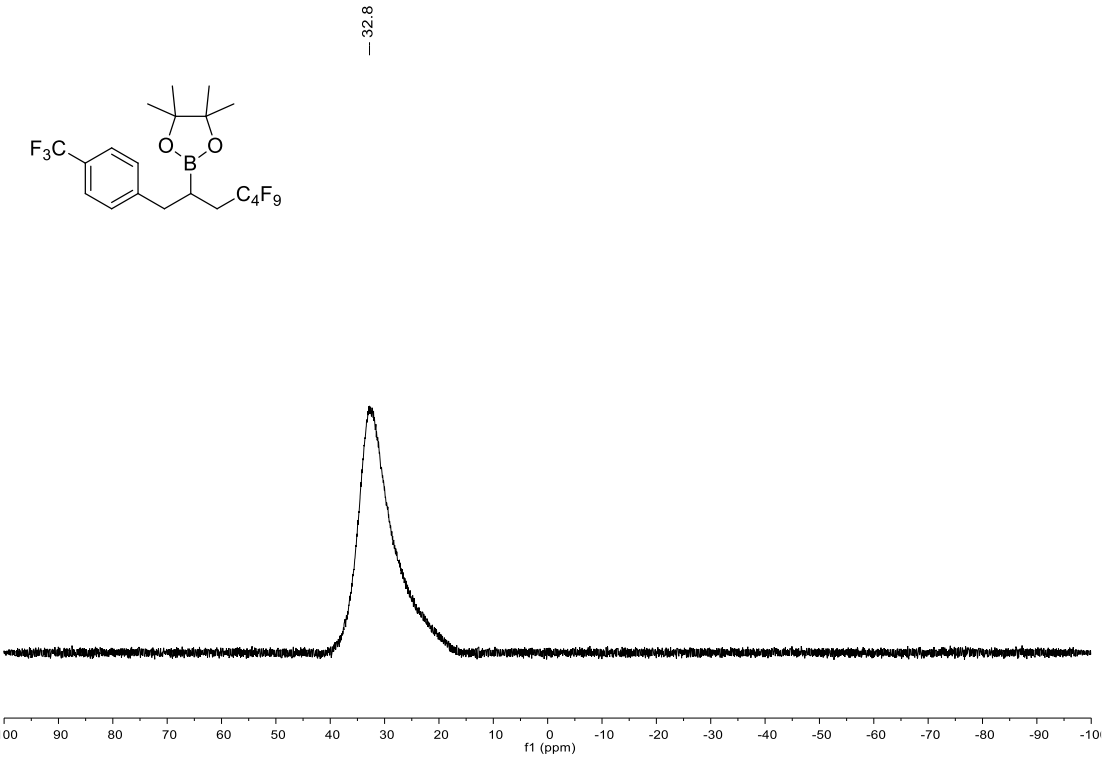
^{13}C NMR (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

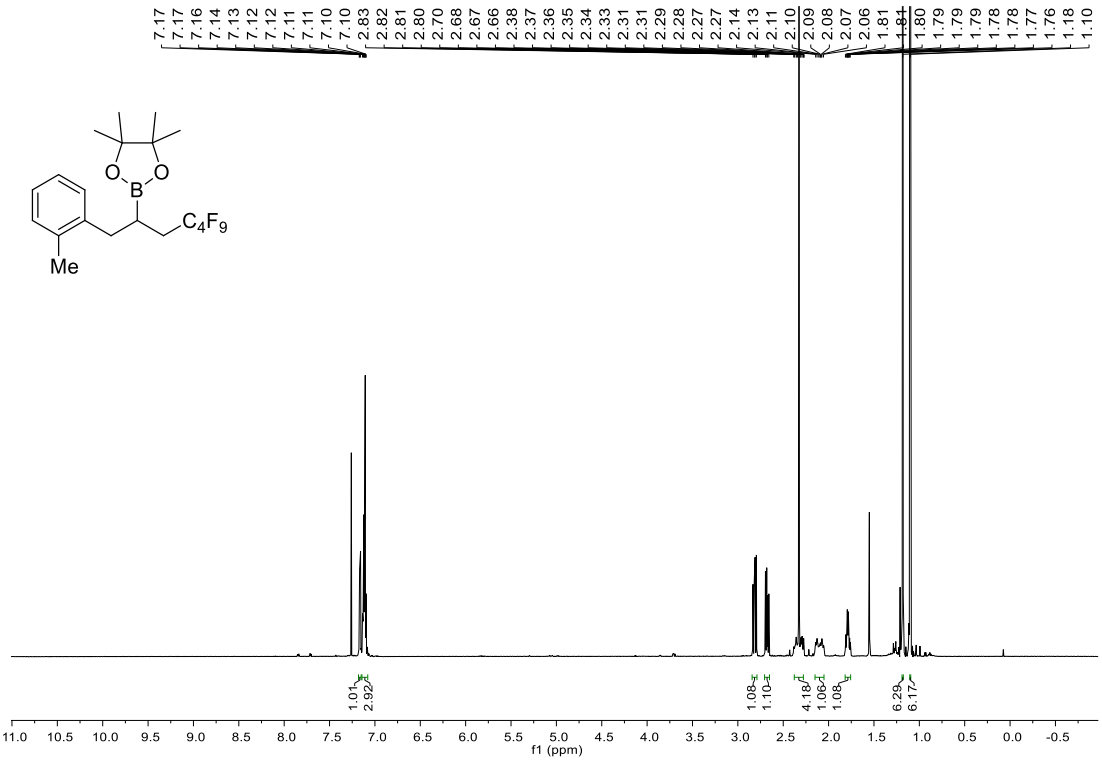


^{11}B NMR (96 MHz, $CDCl_3$)

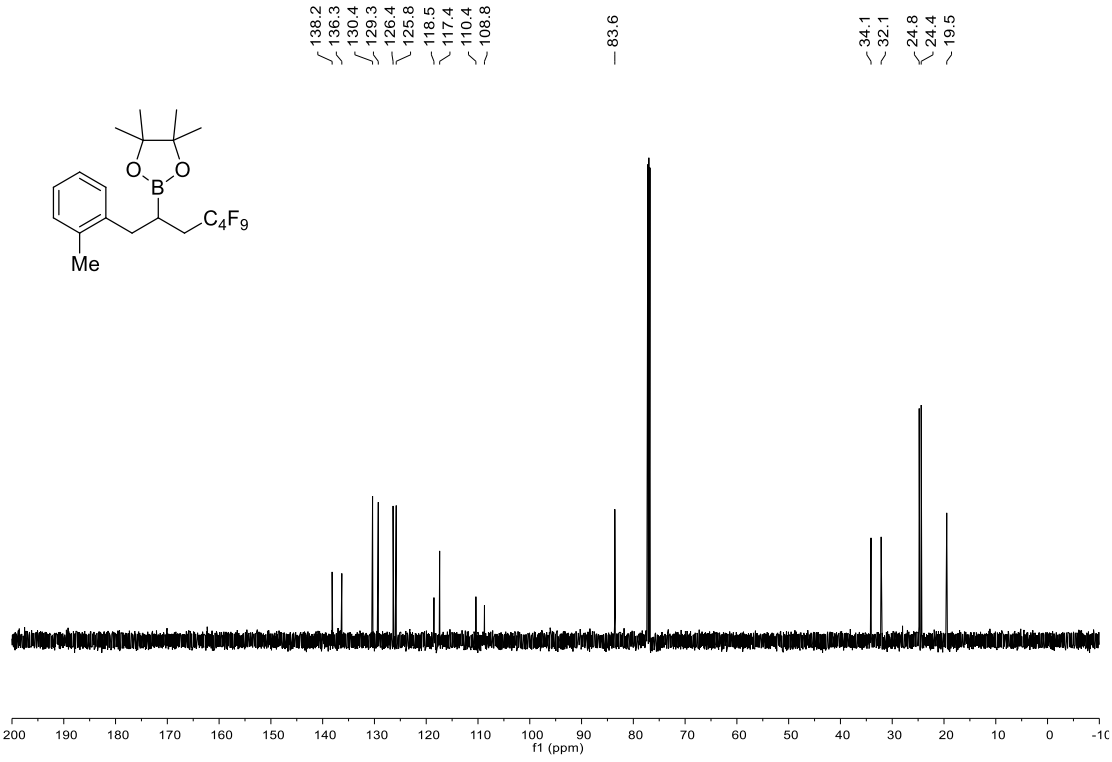


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(*o*-tolyl)heptan-2-yl)-1,3,2-dioxaborolan e (4h)

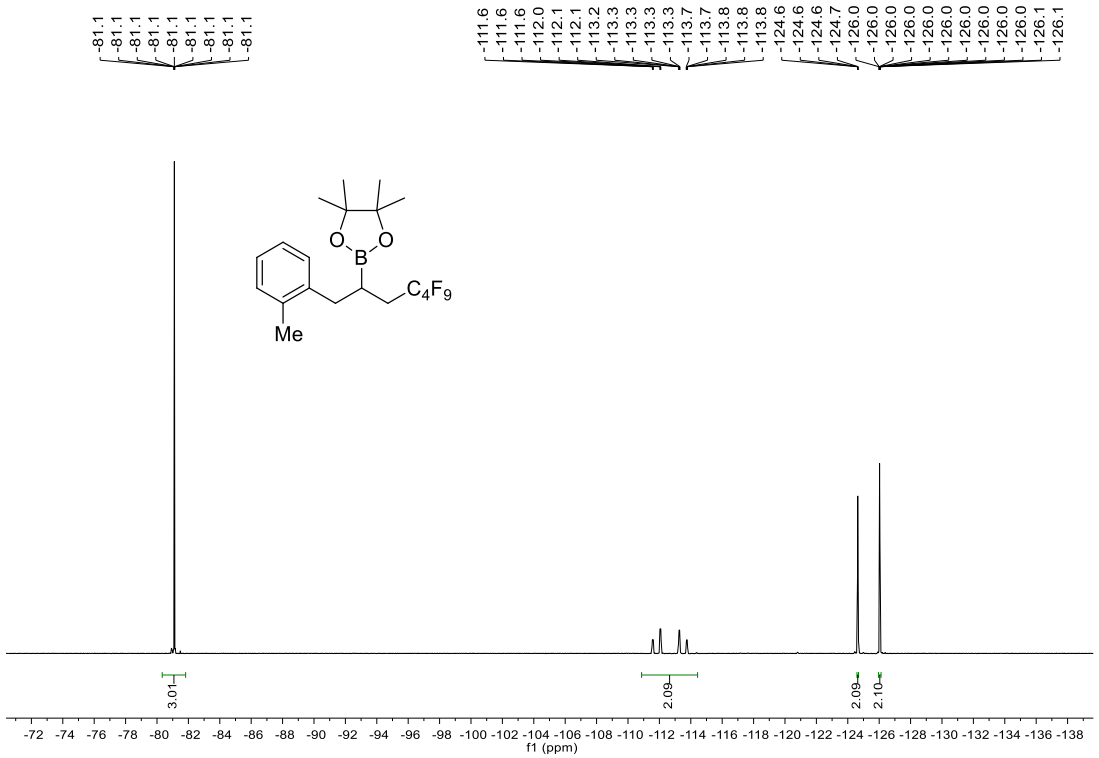
^{1}H NMR (600 MHz, $CDCl_3$)



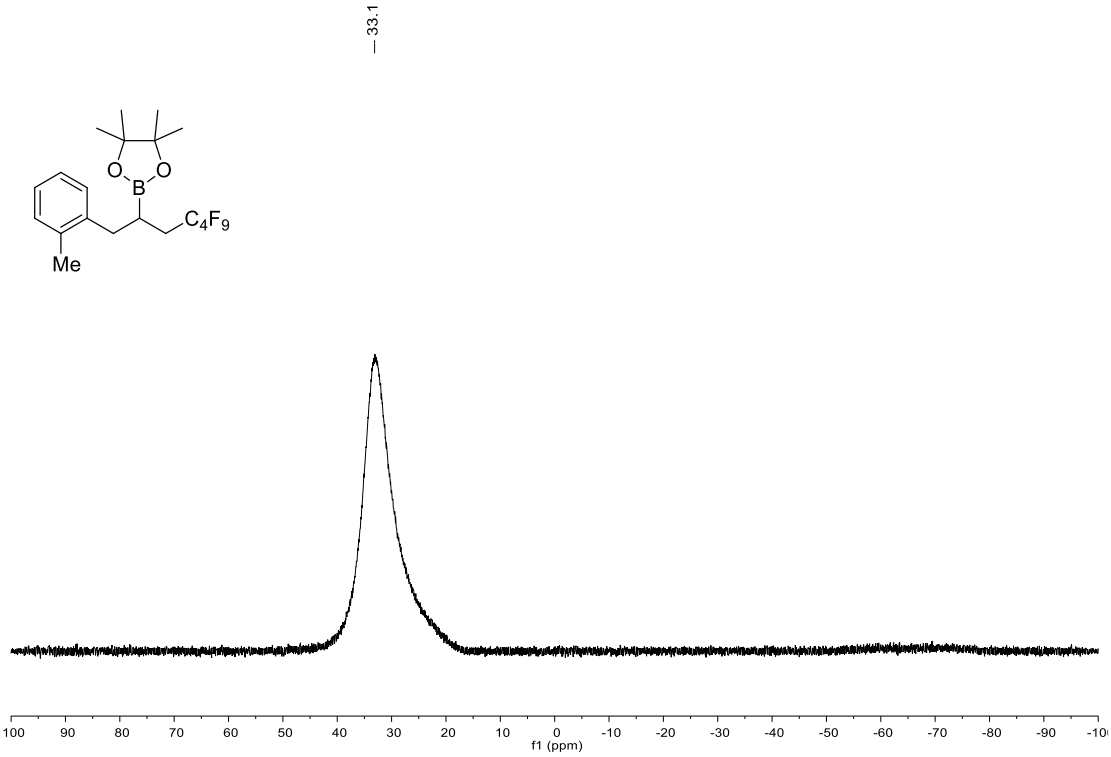
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

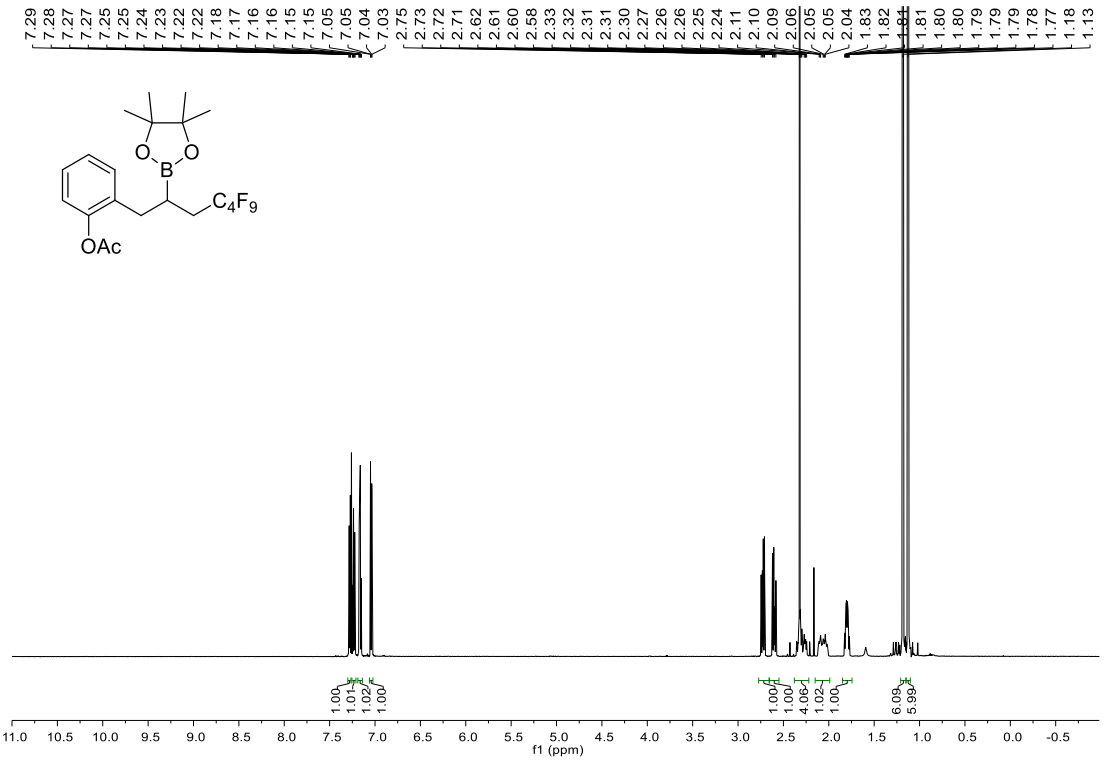


^{11}B NMR (96 MHz, $CDCl_3$)

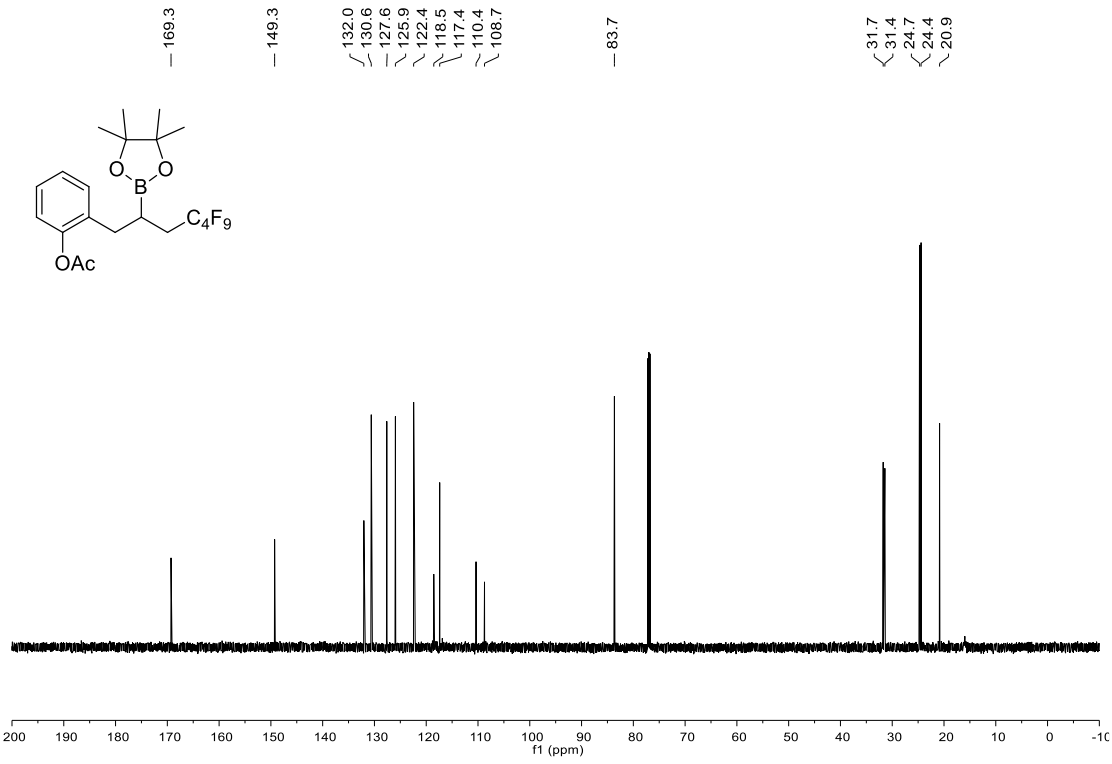


2-(4,4,5,5,6,6,7,7,7-Nonafluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)phenyl acetate (4i)

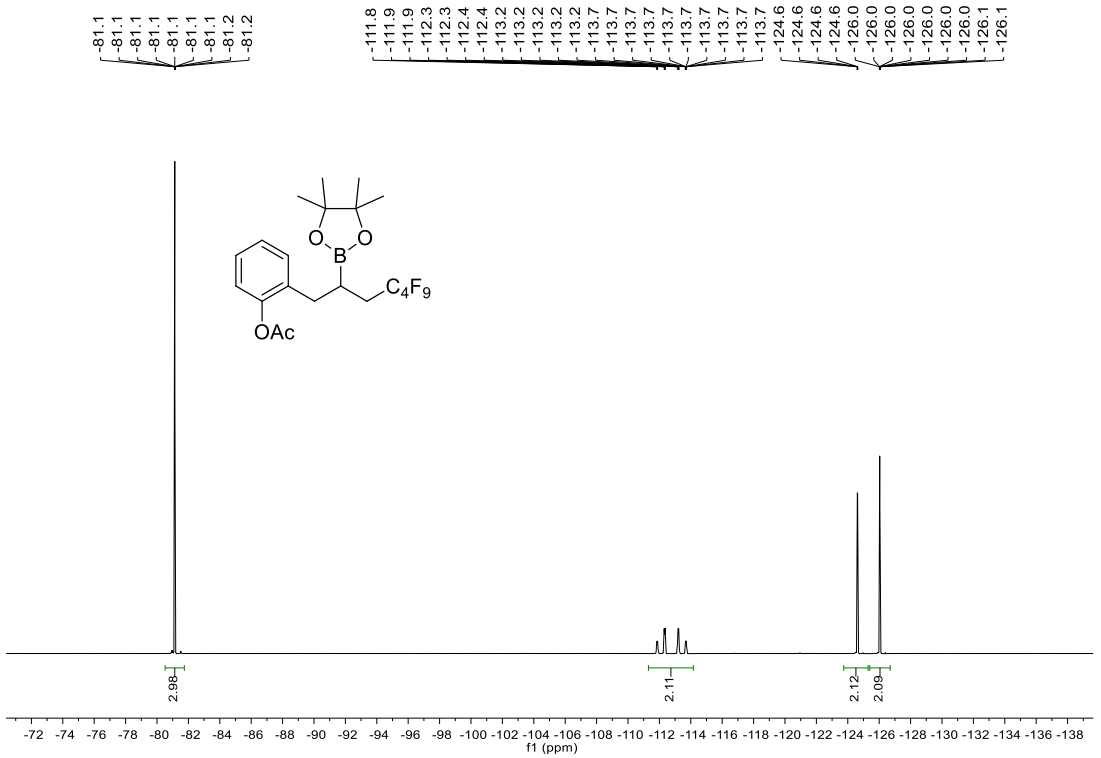
^{1}H NMR (600 MHz, $CDCl_3$)



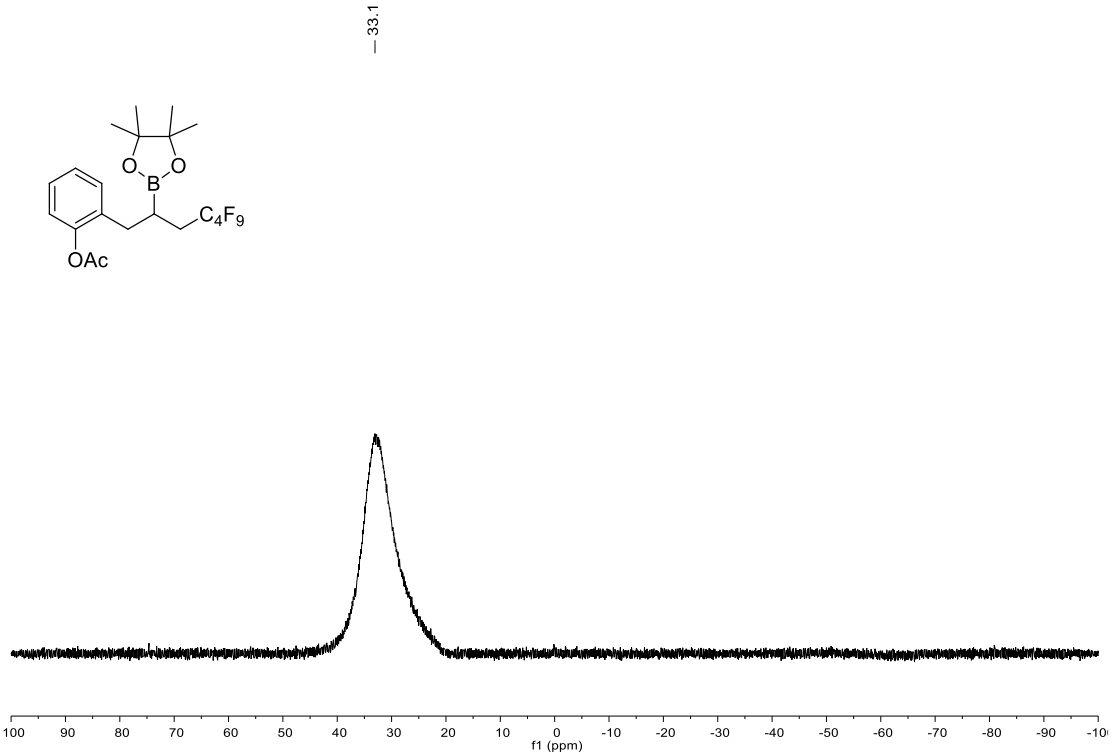
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

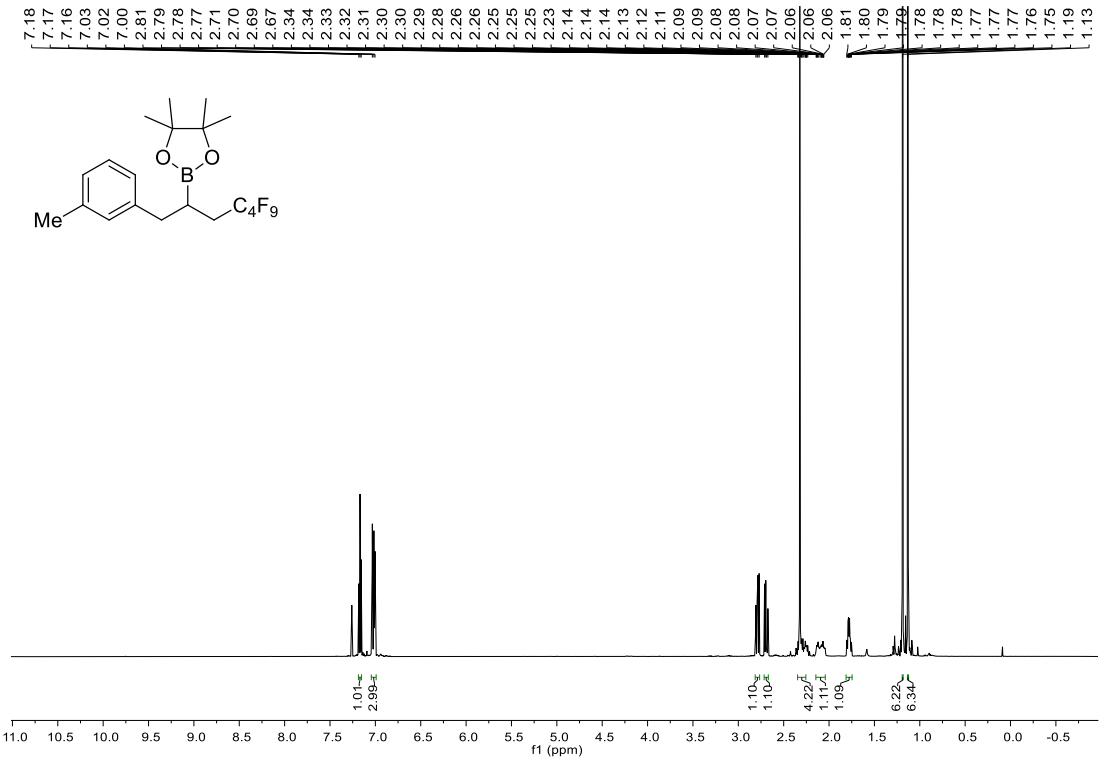


^{11}B NMR (96 MHz, $CDCl_3$)

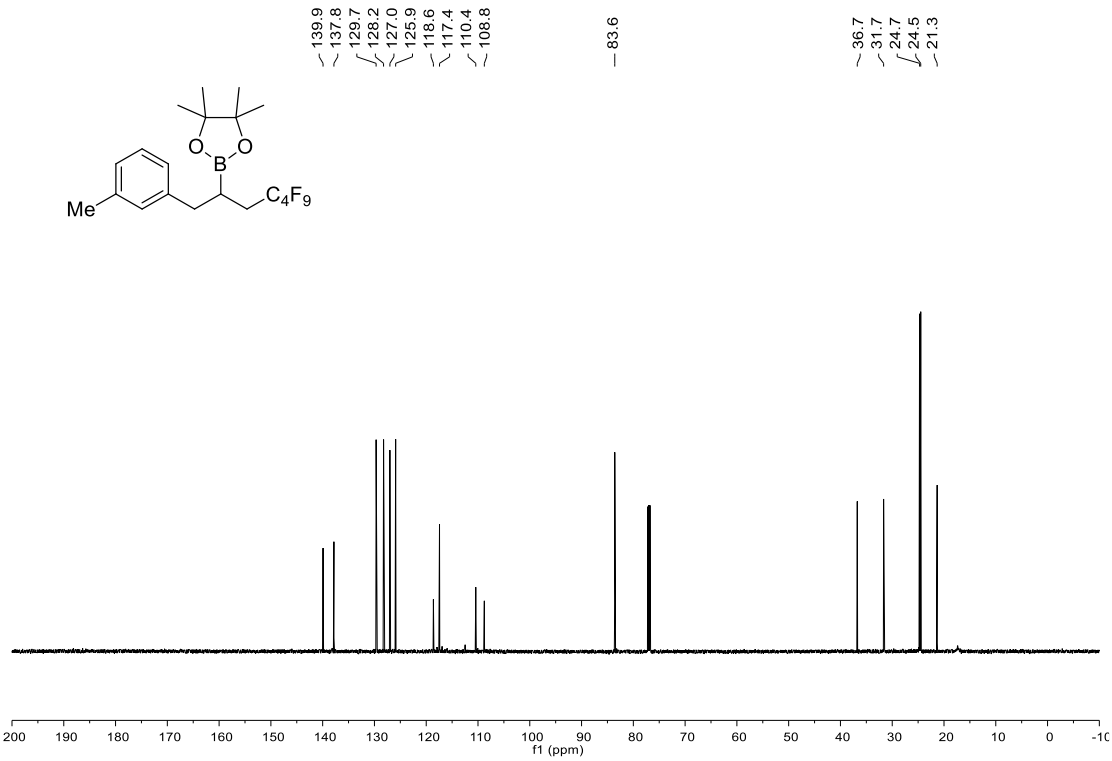


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(*m*-tolyl)heptan-2-yl)-1,3,2-dioxaborolane (4j)

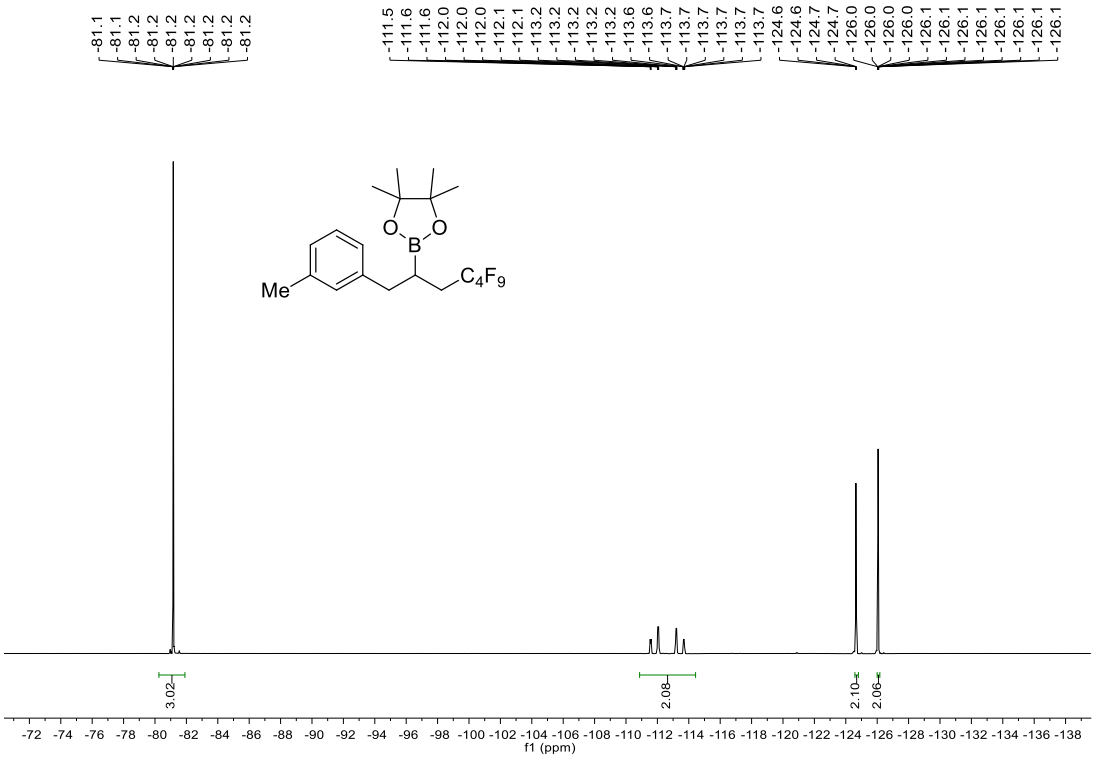
^{1}H NMR (600 MHz, $CDCl_3$)



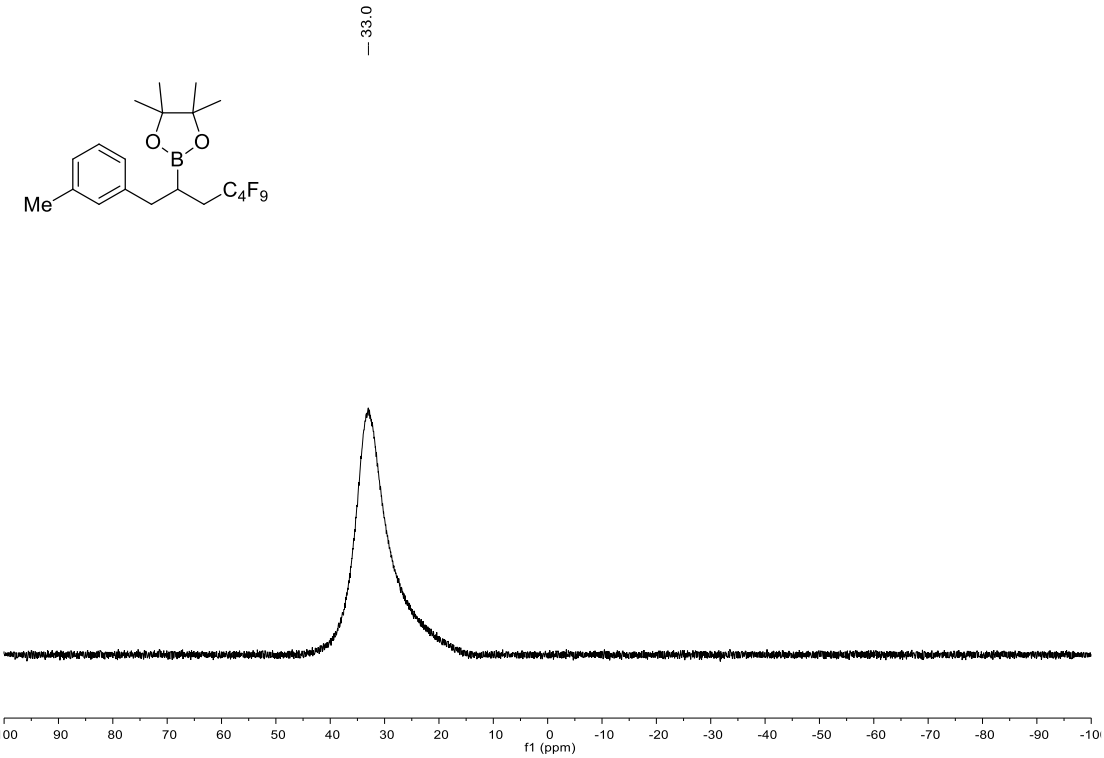
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

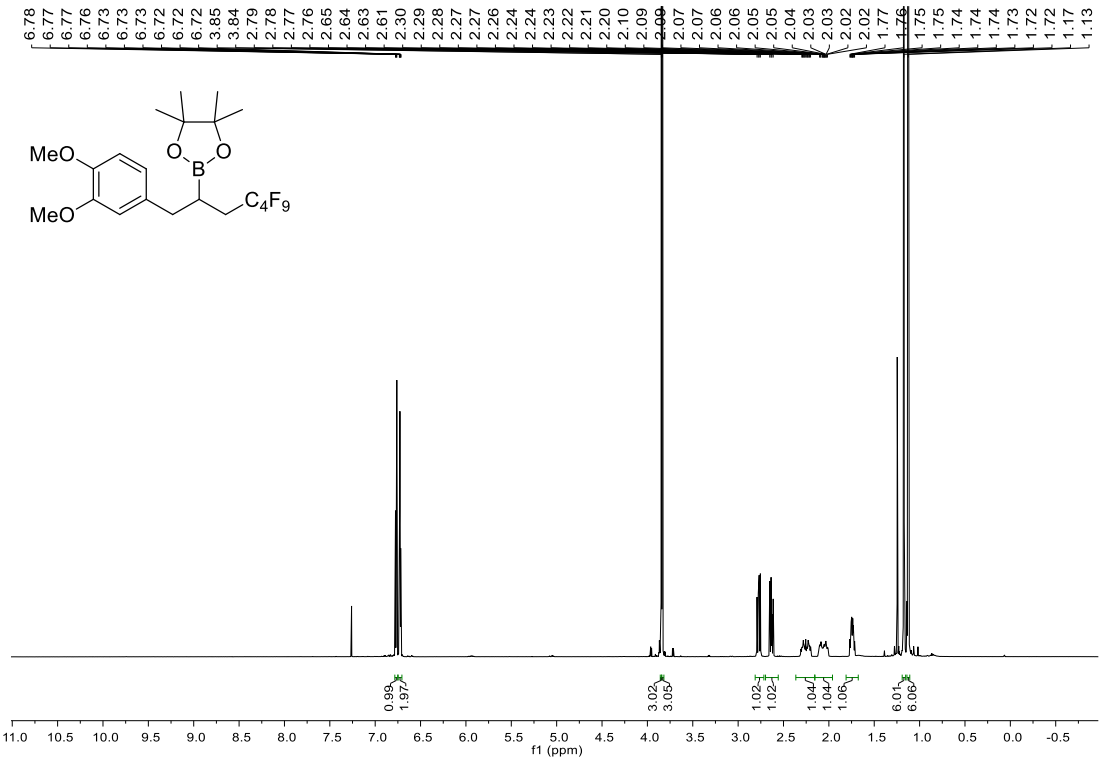


^{11}B NMR (96 MHz, $CDCl_3$)

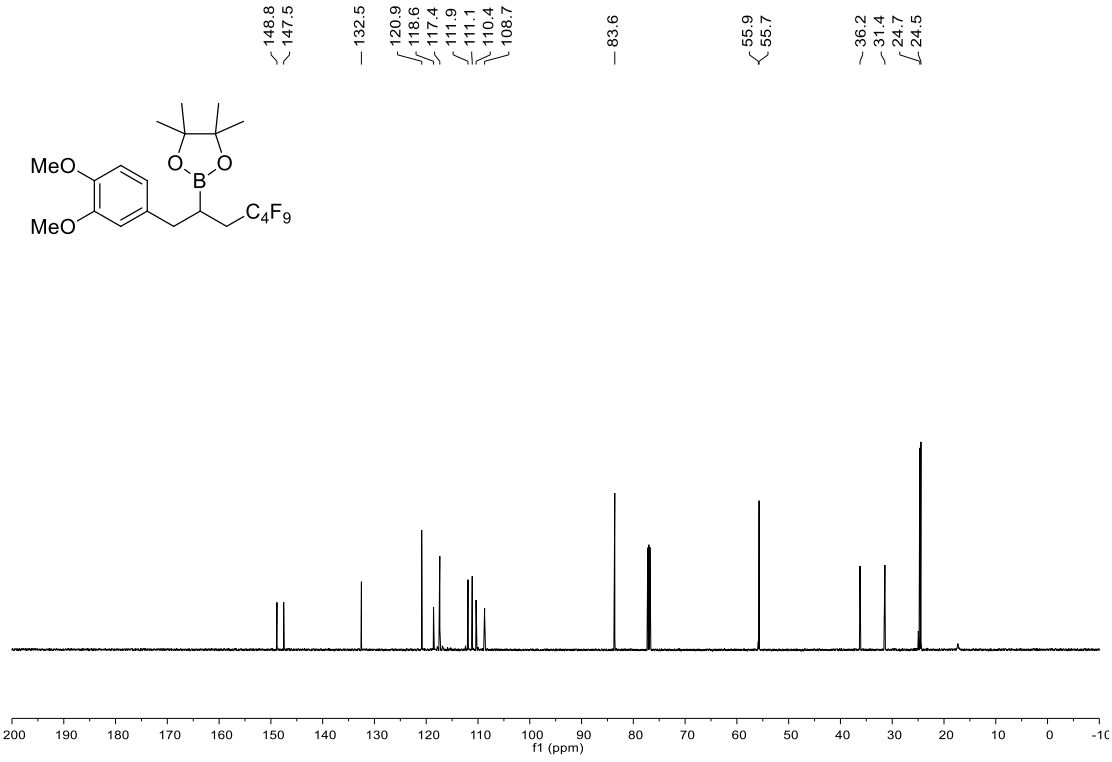


2-(1-(3,4-Dimethoxyphenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k)

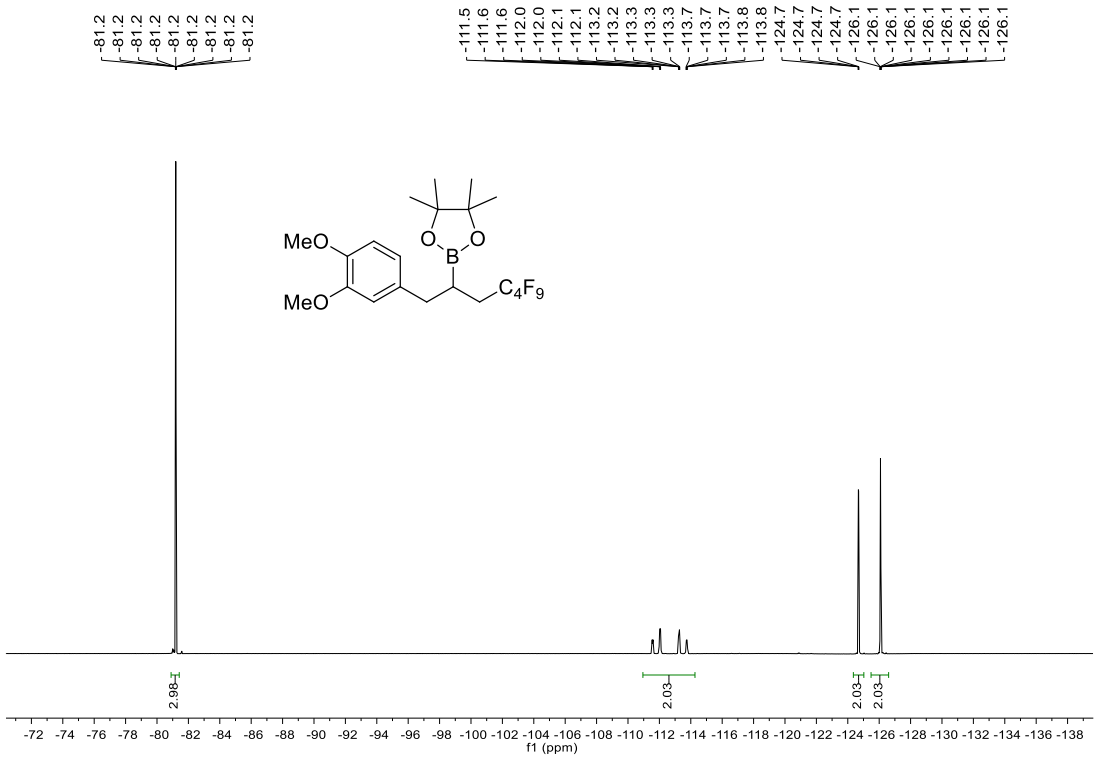
^{1}H NMR (600 MHz, $CDCl_3$)



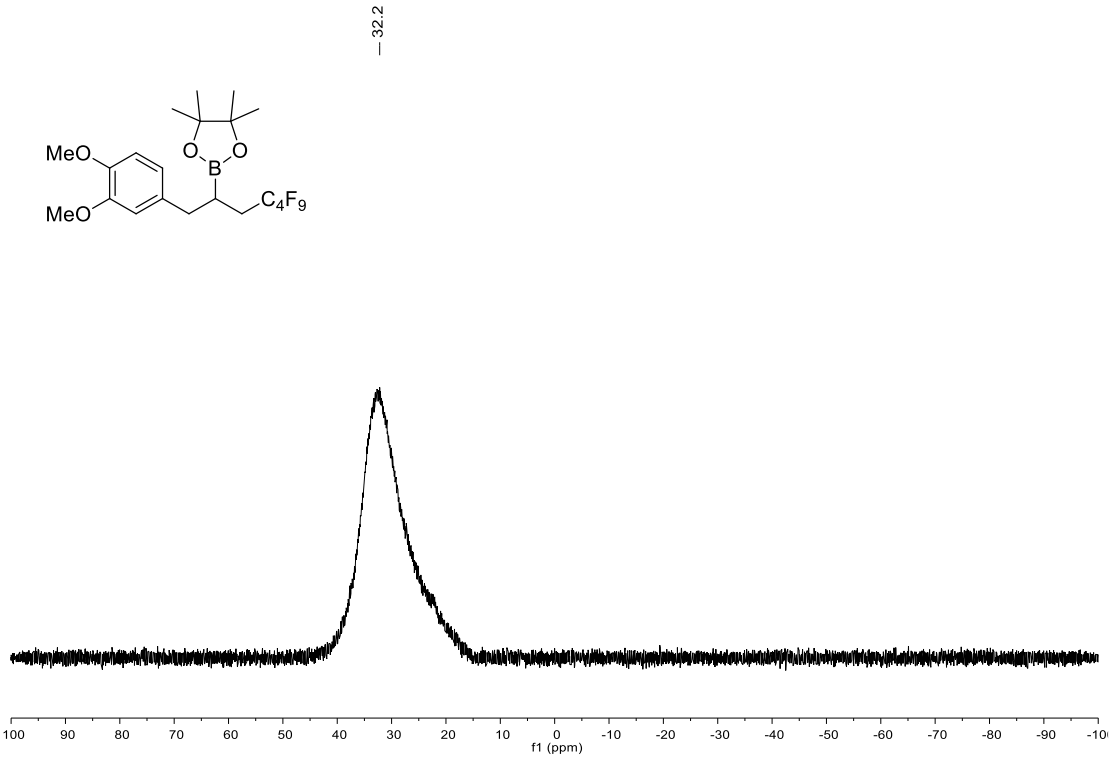
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

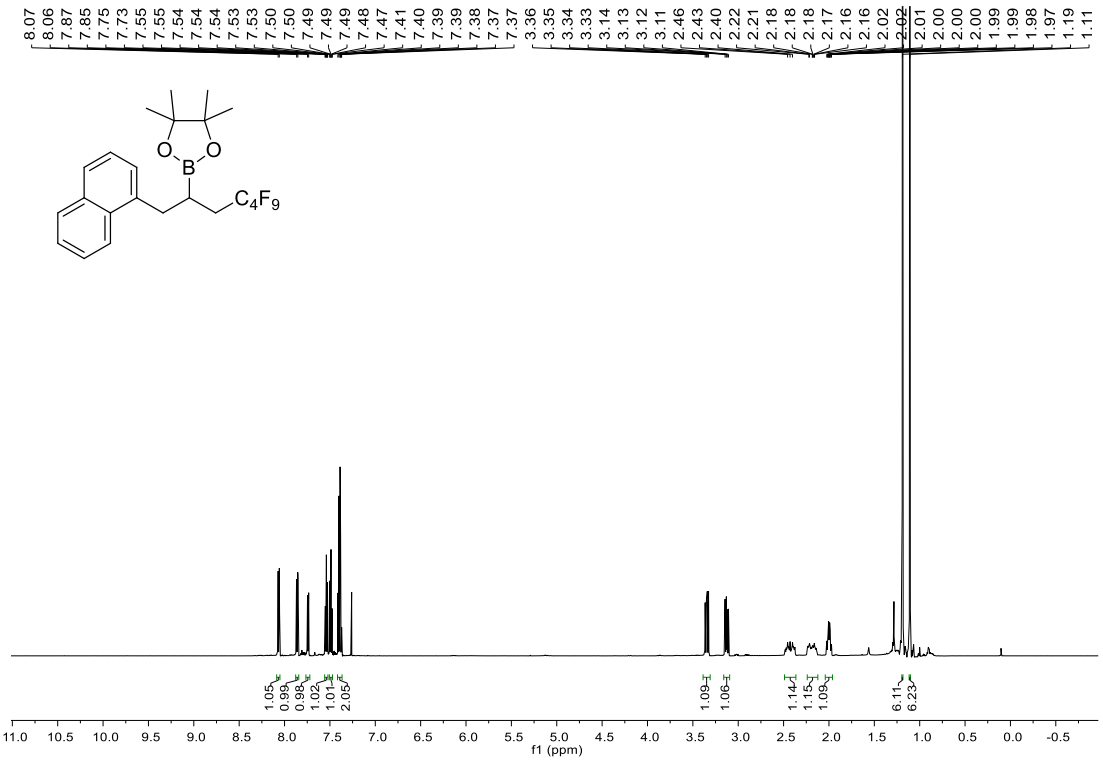


^{11}B NMR (96 MHz, $CDCl_3$)

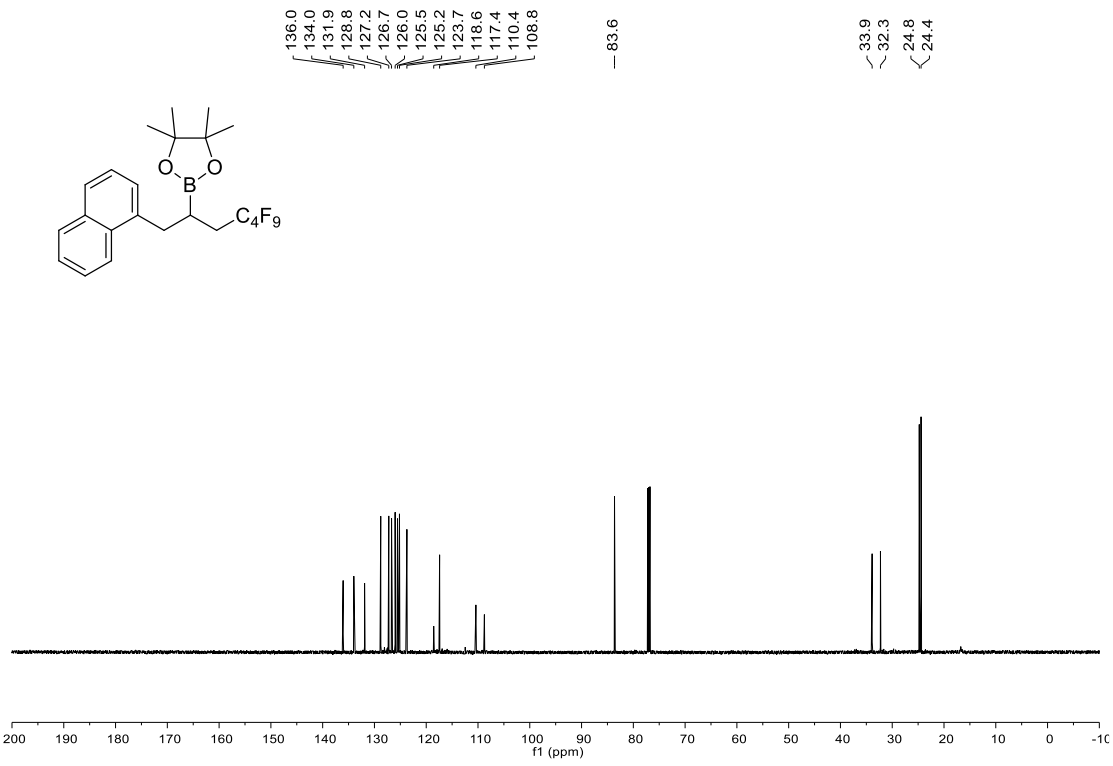


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-1-yl)heptan-2-yl)-1,3,2-dioxaborolane (4l)

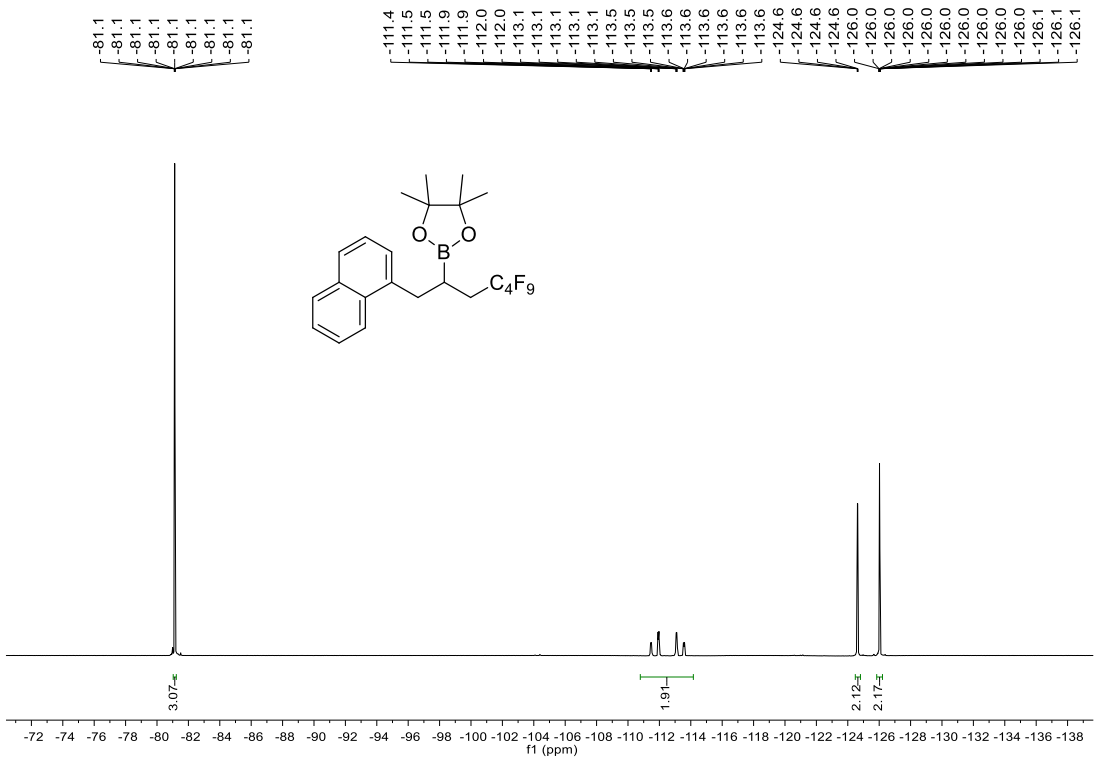
^{1}H NMR (600 MHz, $CDCl_3$)



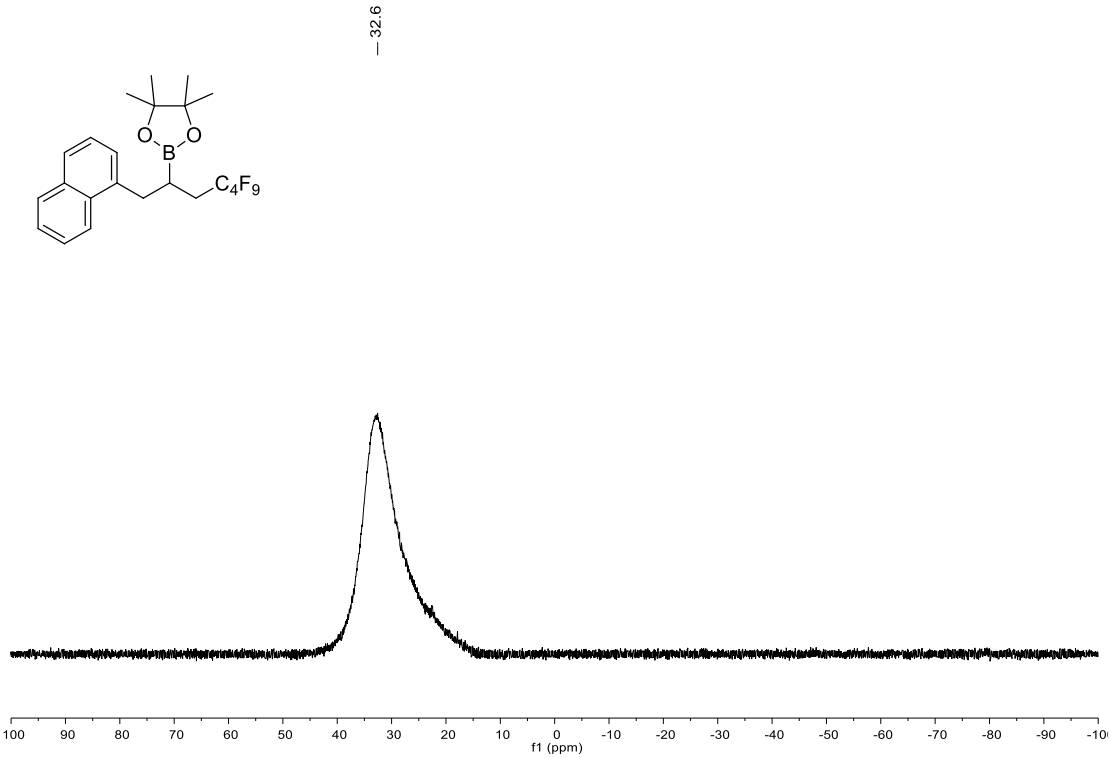
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

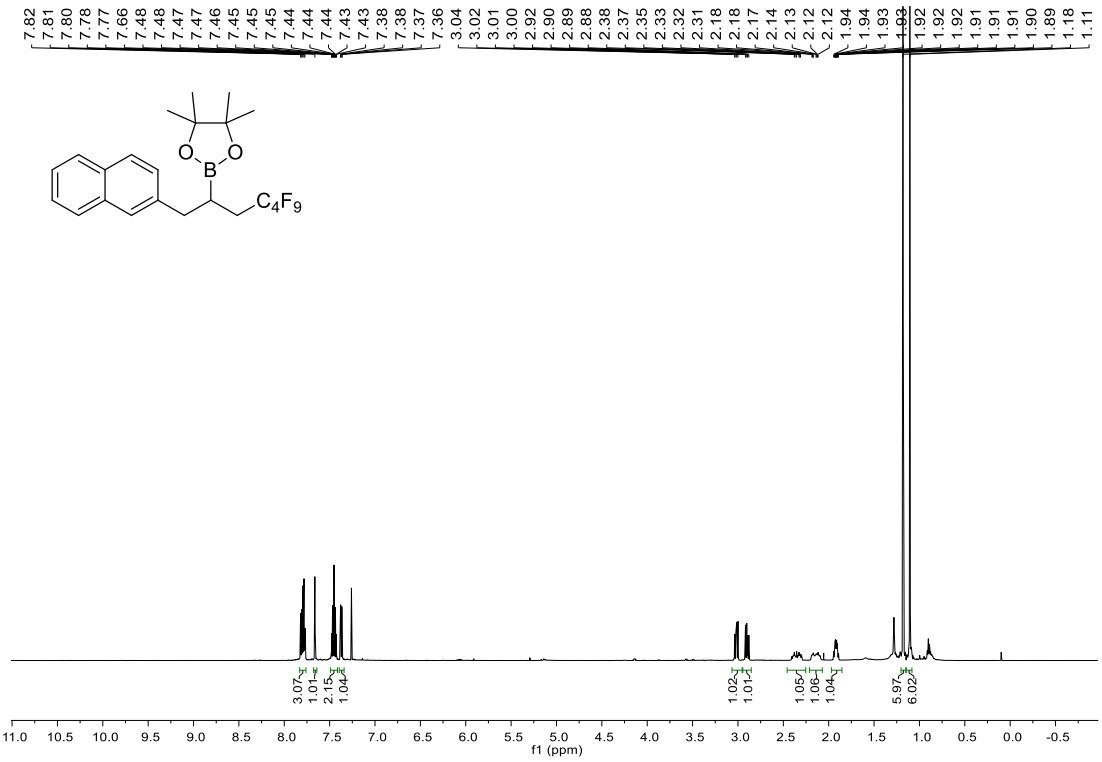


^{11}B NMR (96 MHz, $CDCl_3$)

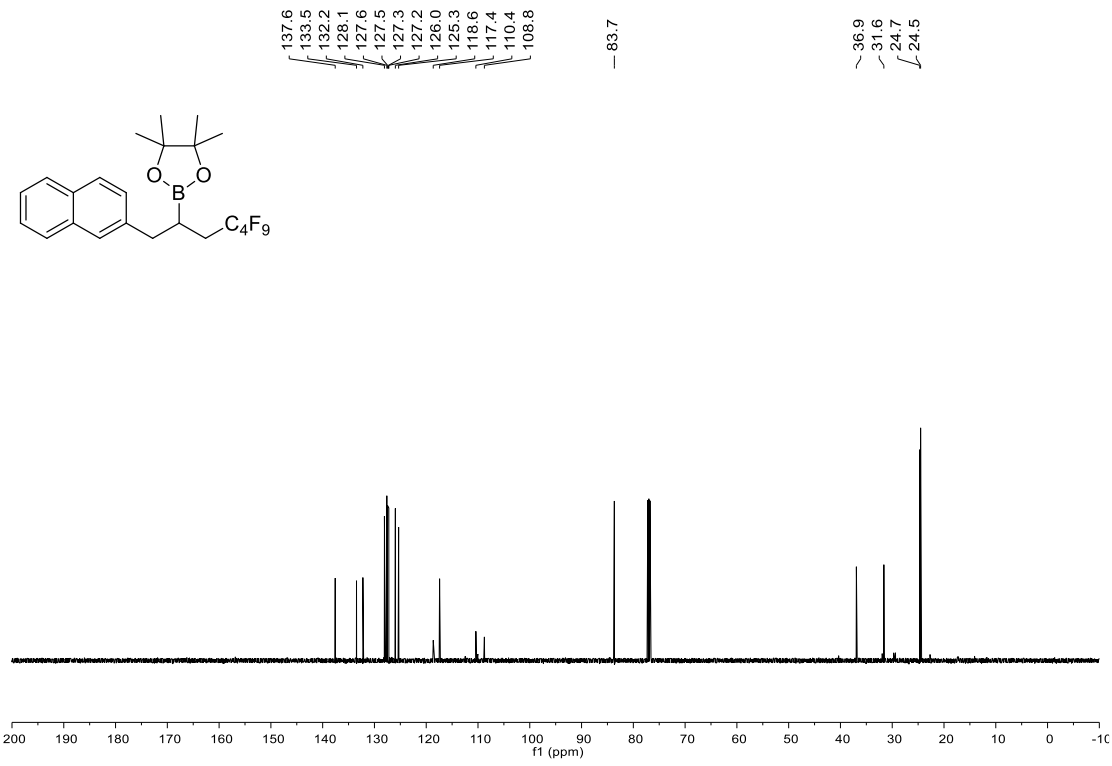


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-2-yl)heptan-2-yl)-1,3,2-dioxaborolane (4a)

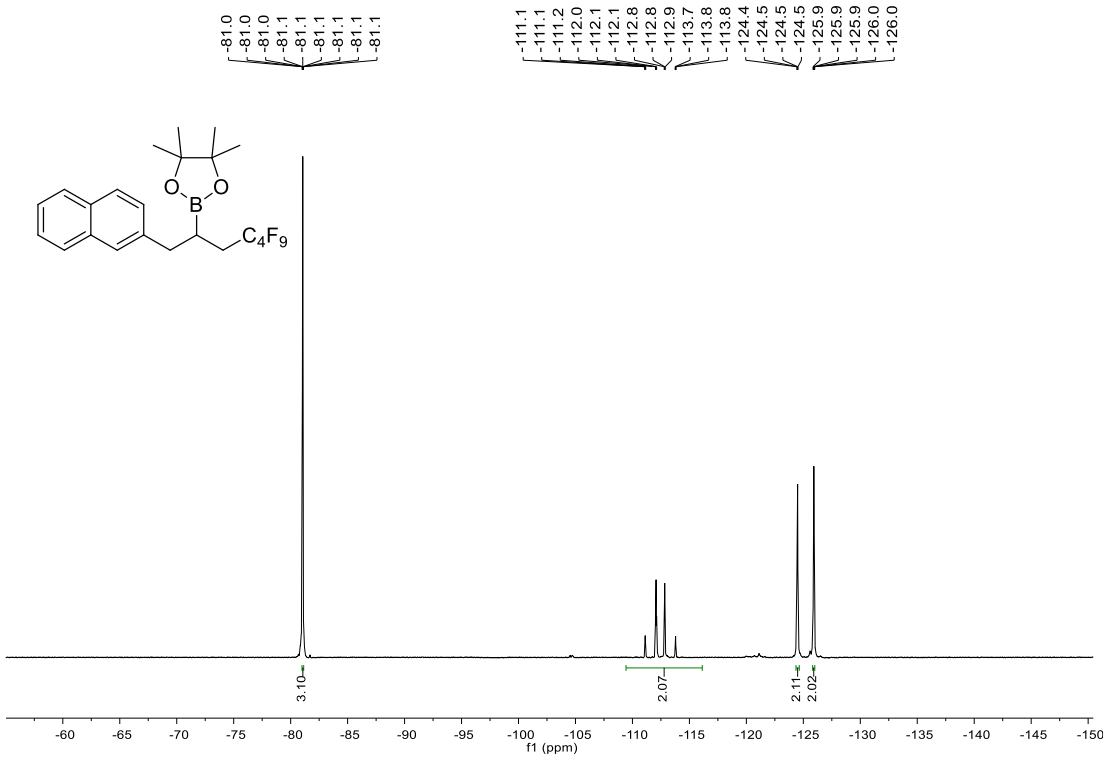
^{1}H NMR (600 MHz, $CDCl_3$)



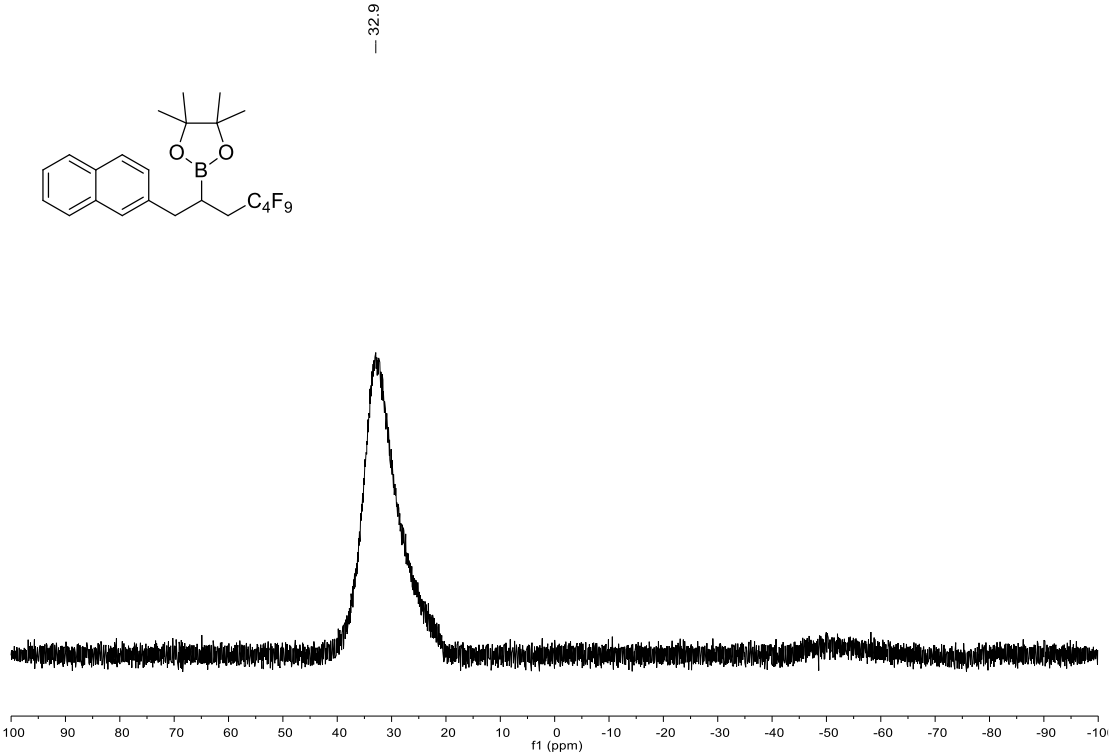
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (282 MHz, $CDCl_3$)

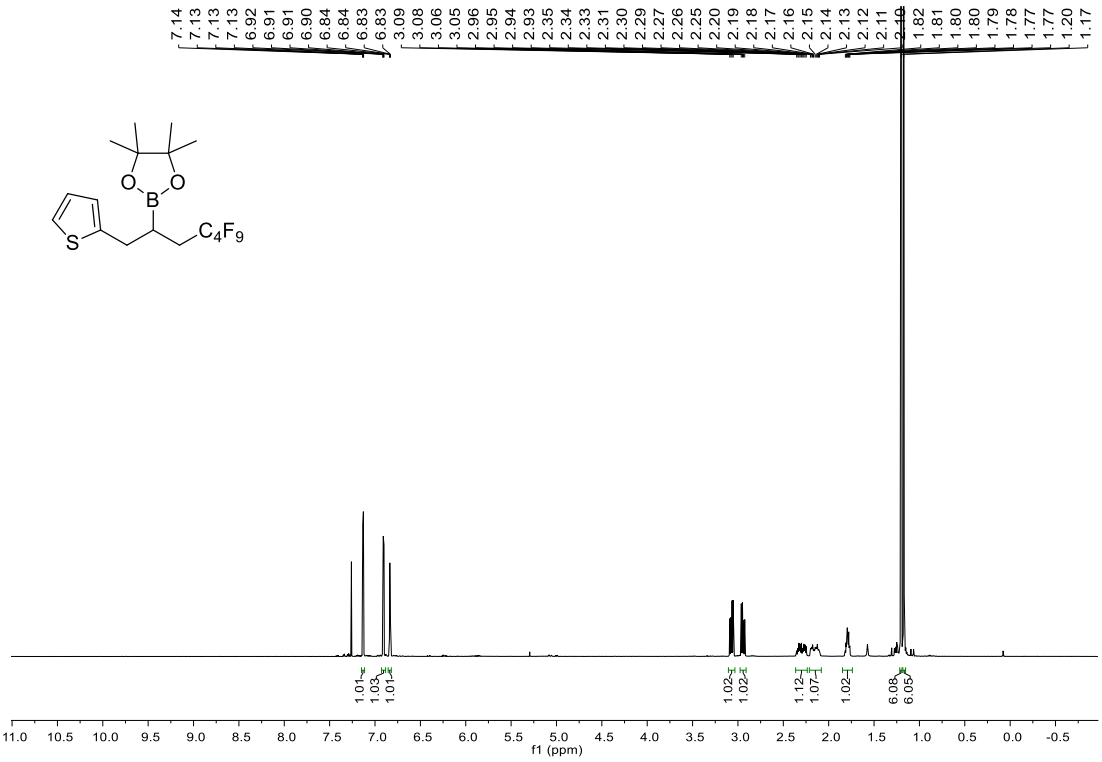


^{11}B NMR (96 MHz, $CDCl_3$)

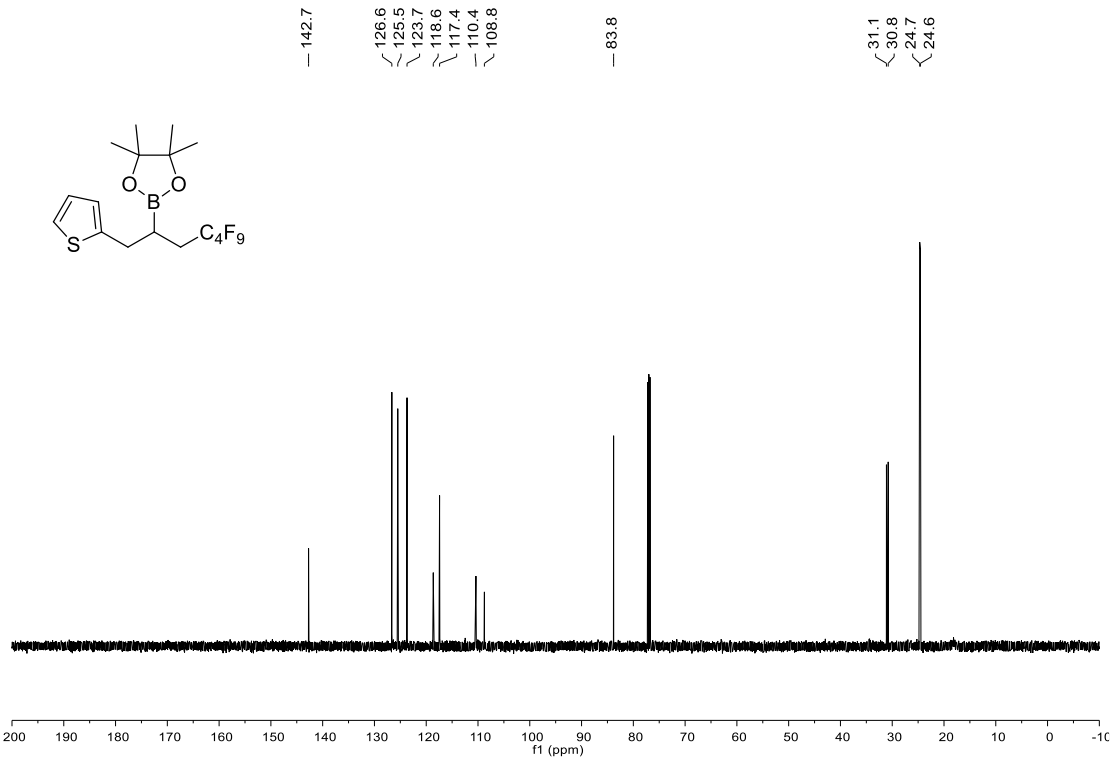


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(thiophen-2-yl)heptan-2-yl)-1,3,2-dioxaborolane (4m)

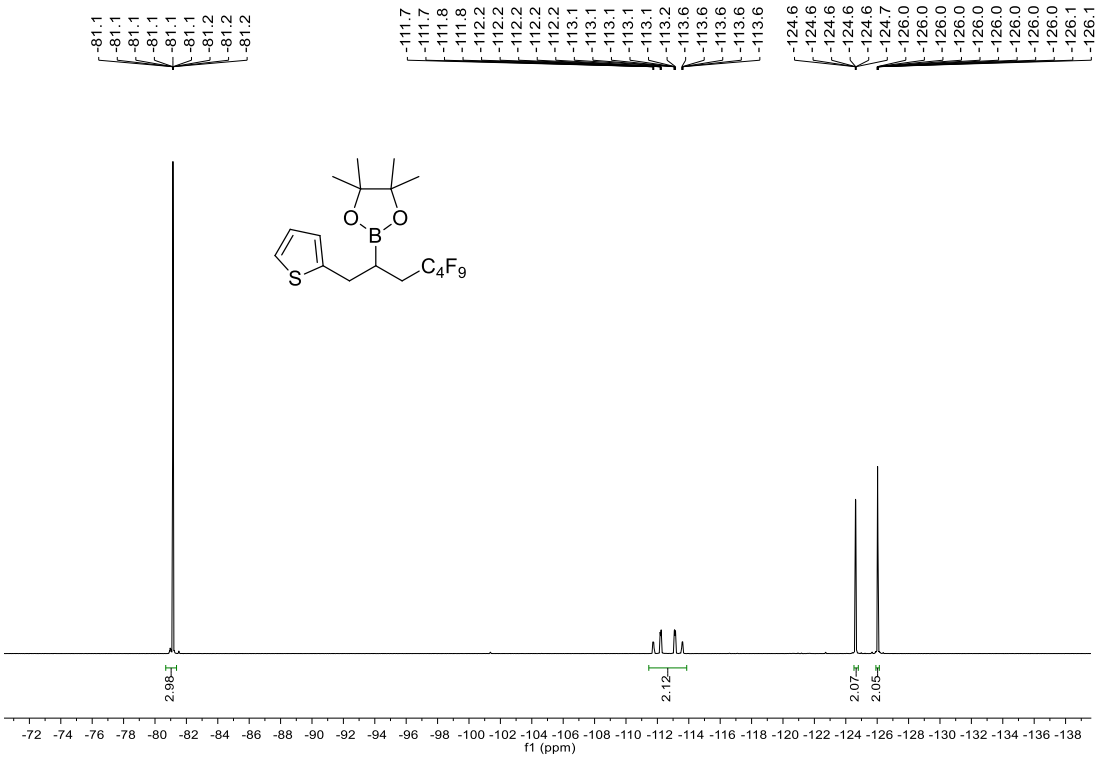
^{1}H NMR (600 MHz, $CDCl_3$)



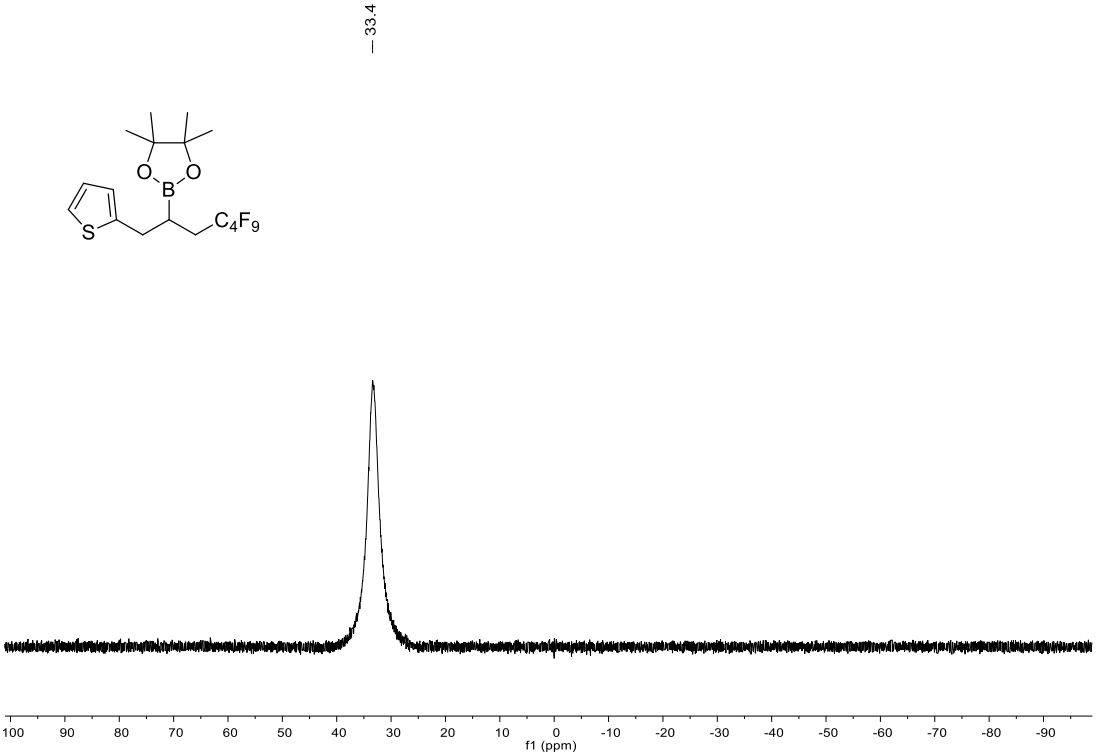
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

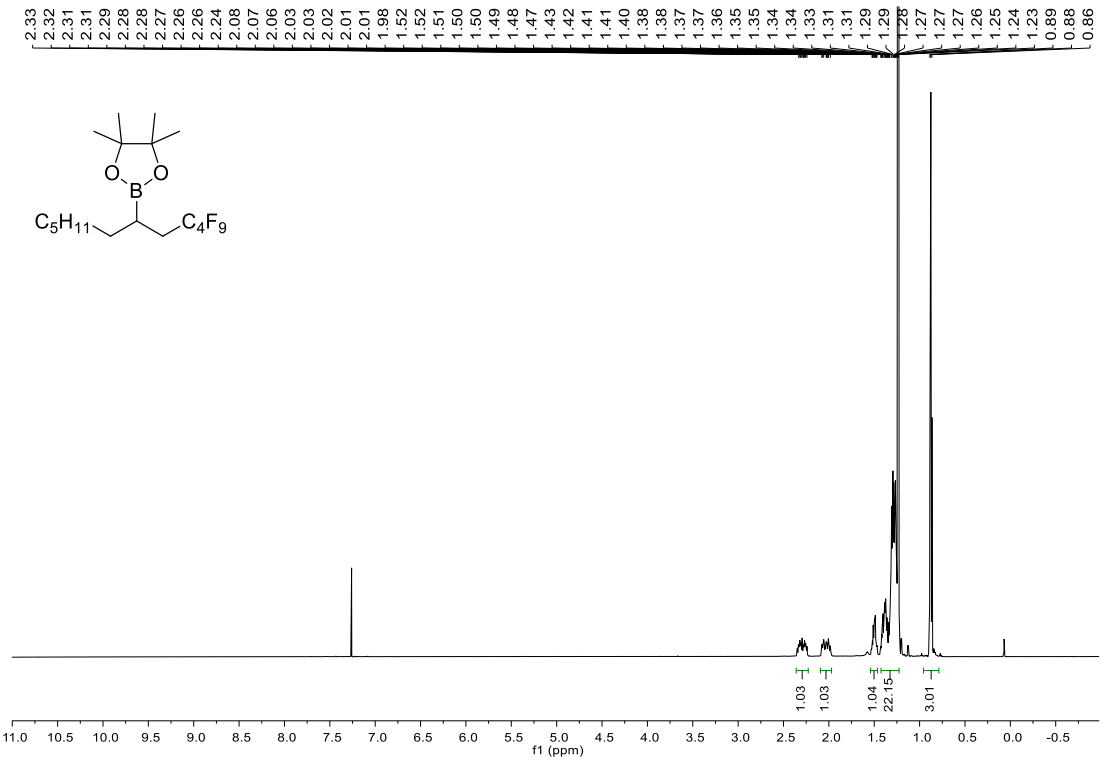


^{11}B NMR (192 MHz, $CDCl_3$)

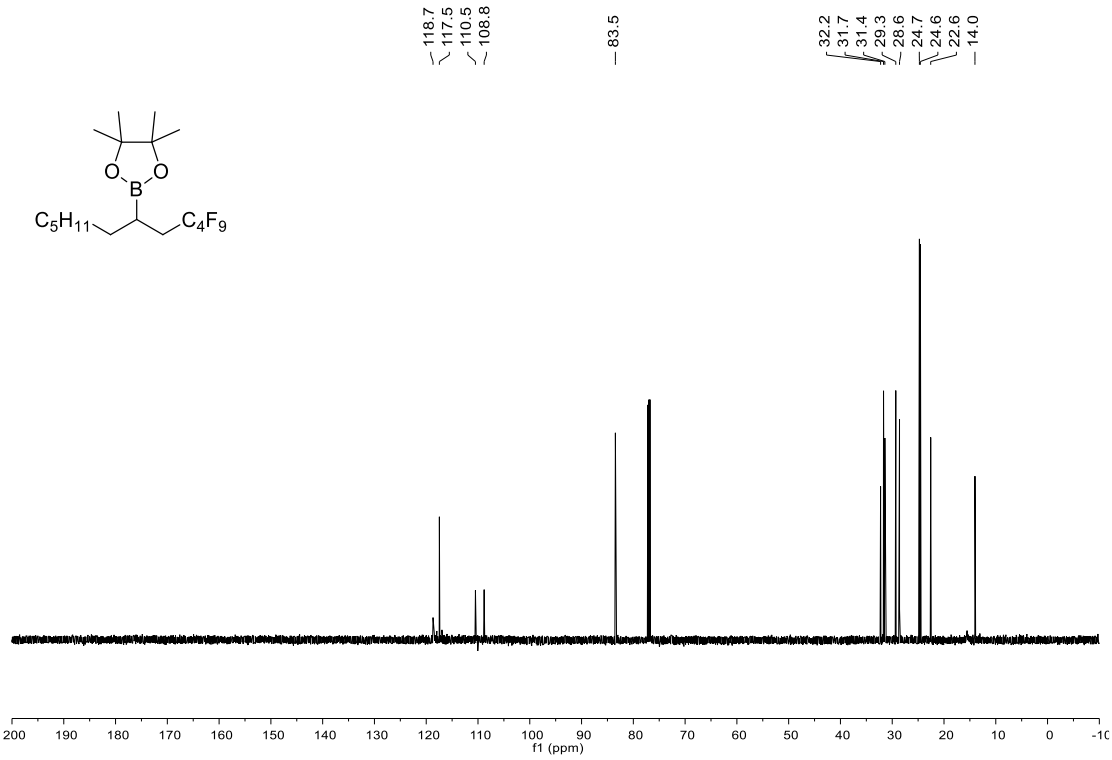


4,4,5,5-Tetramethyl-2-(1,1,1,2,2,3,3,4,4-nonafluorododecan-6-yl)-1,3,2-dioxaborolane (4n)

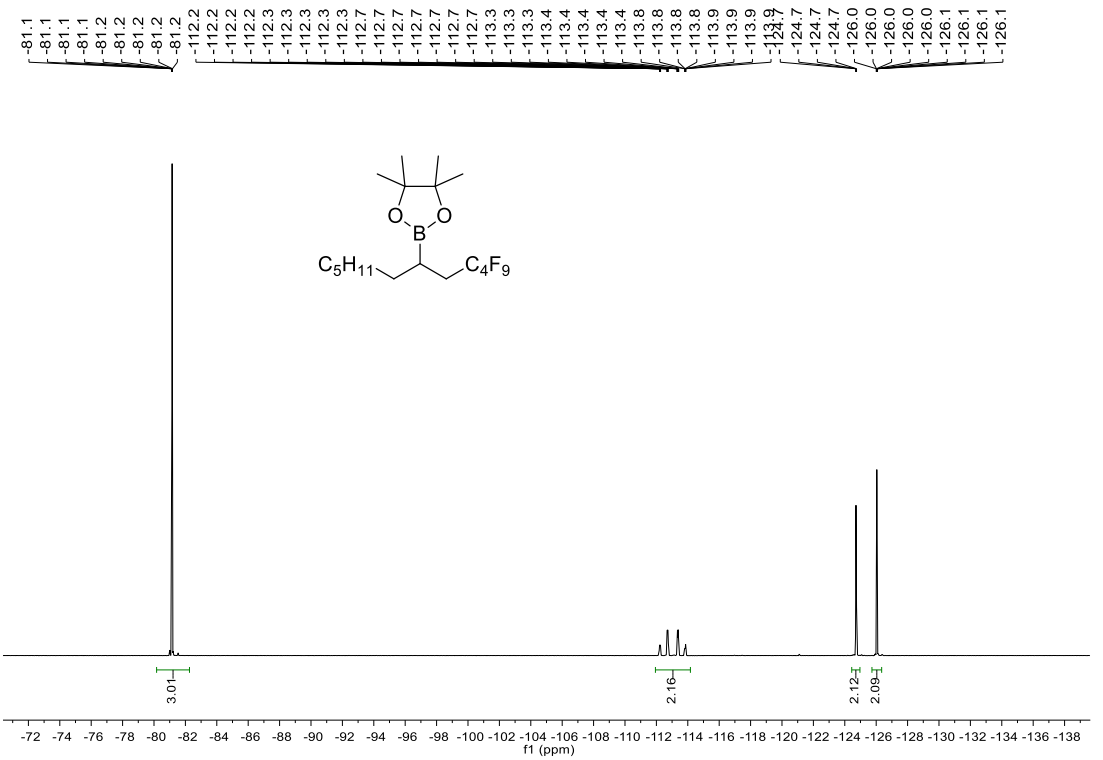
^{1}H NMR (600 MHz, $CDCl_3$)



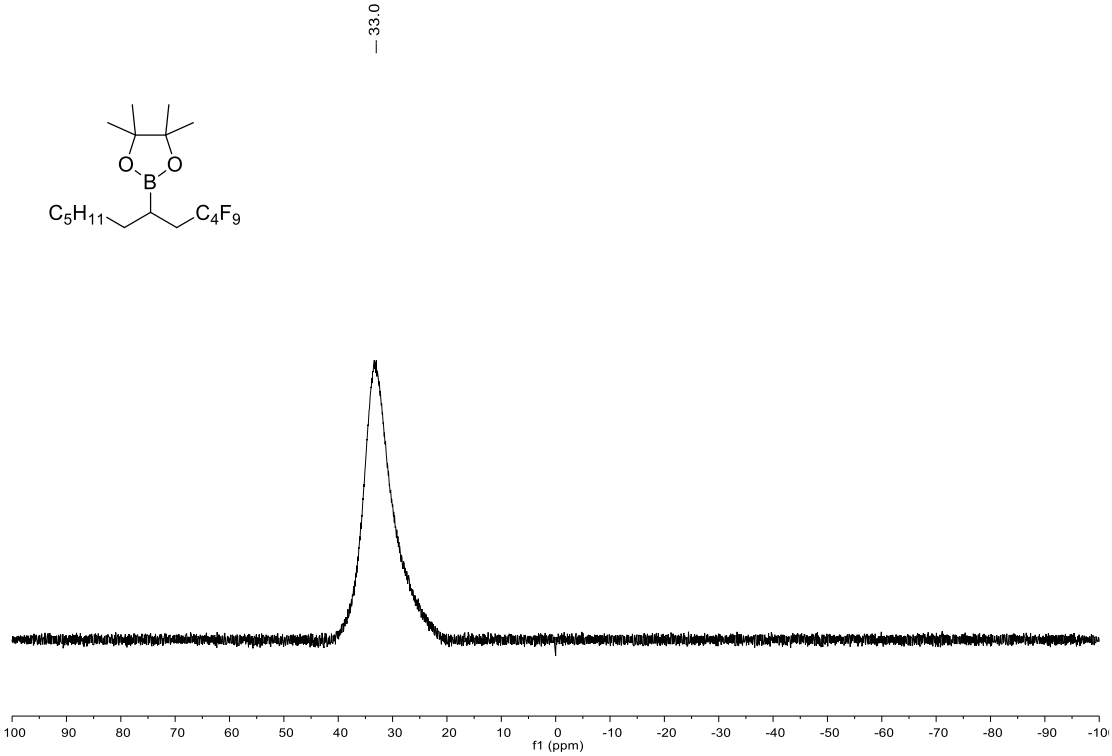
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

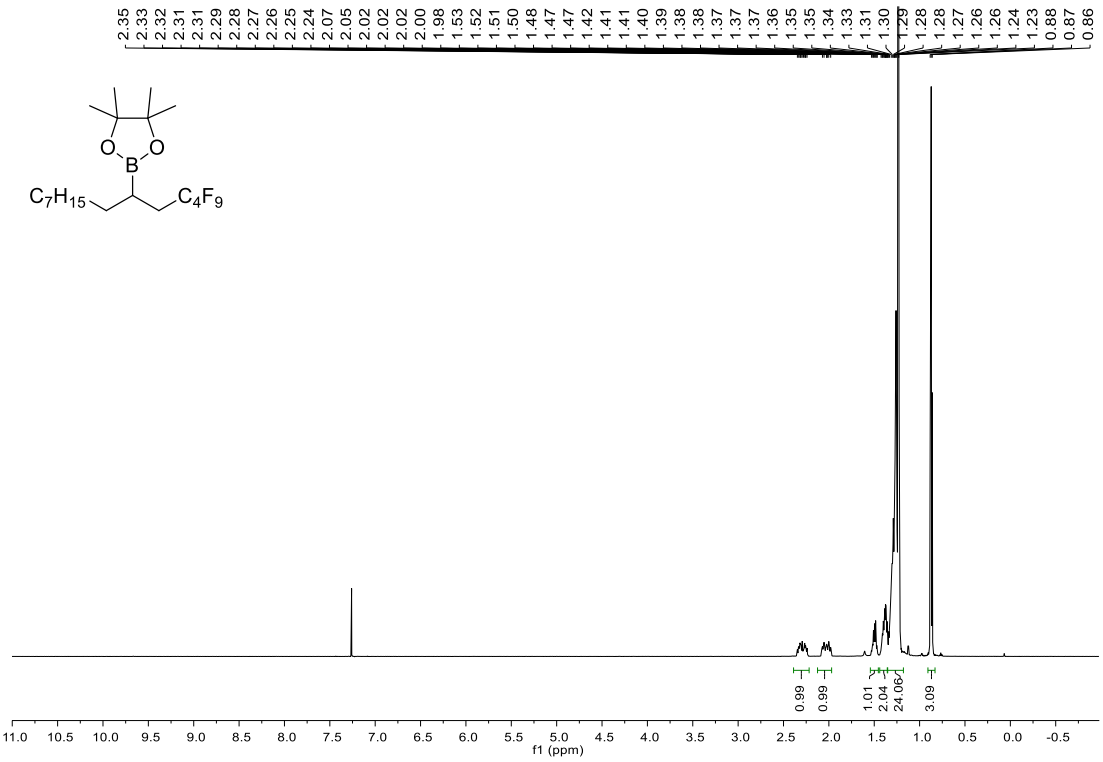


^{11}B NMR (96 MHz, $CDCl_3$)

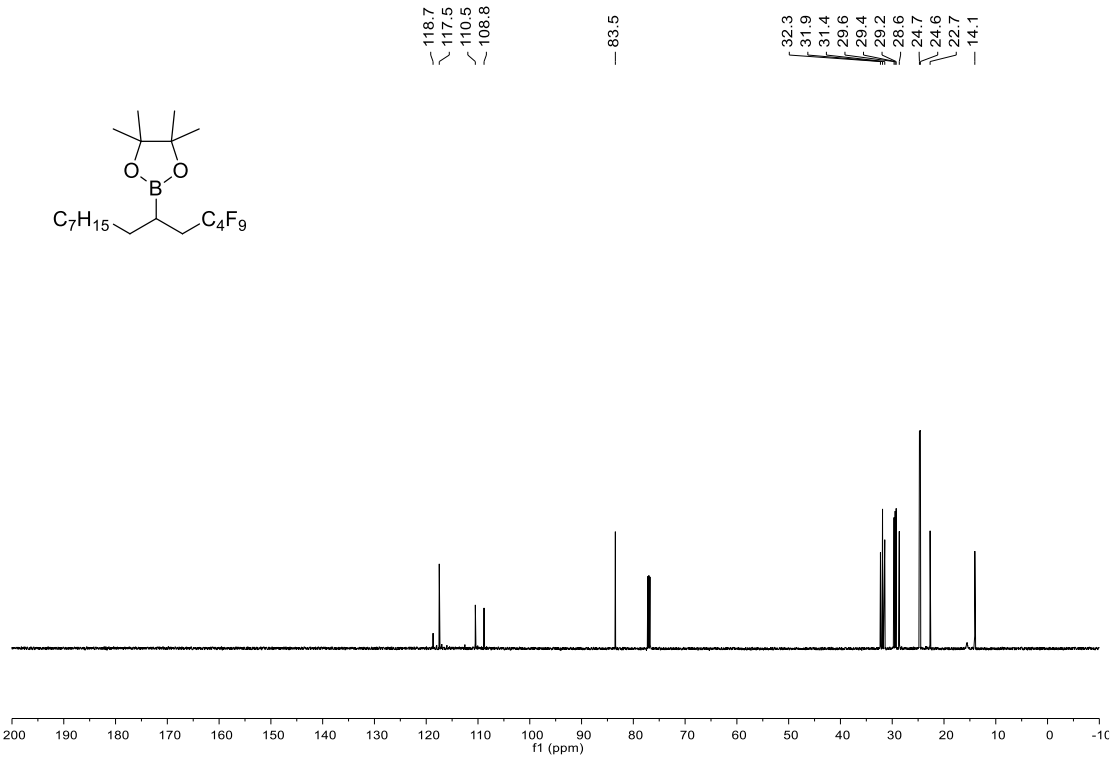


4,4,5,5-Tetramethyl-2-(1,1,1,2,2,3,3,4,4-nonafluorotetradecan-6-yl)-1,3,2-dioxaborolane (4o)

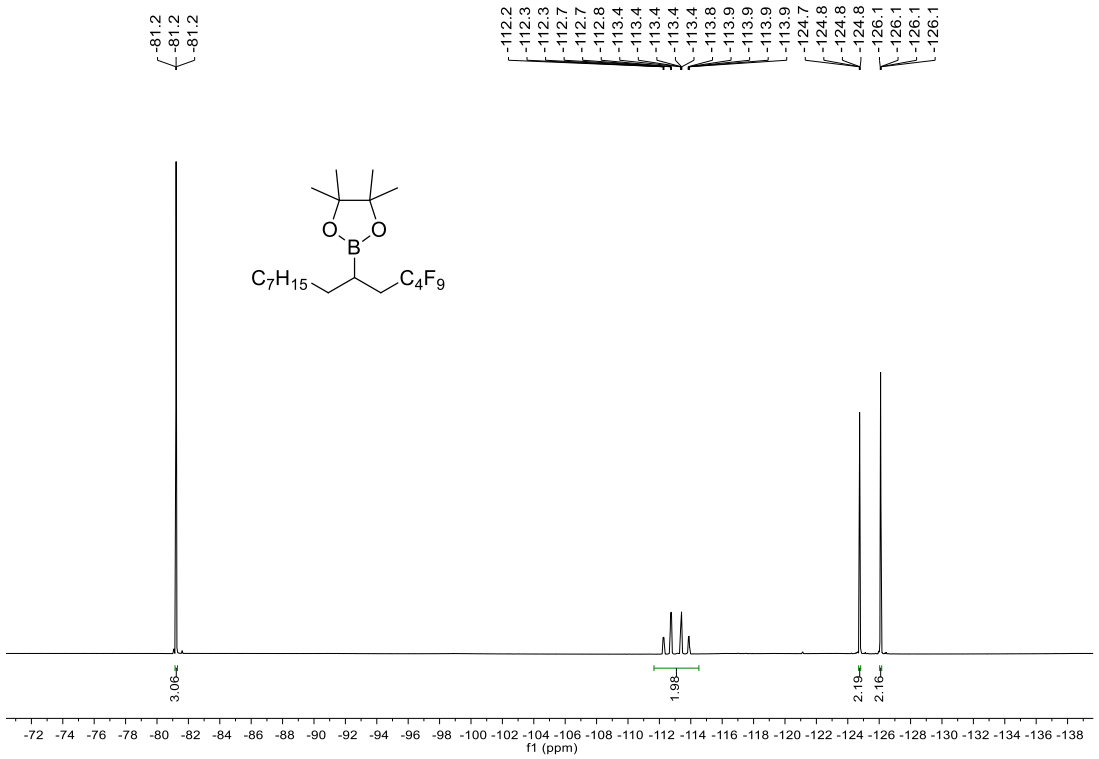
^{1}H NMR (600 MHz, $CDCl_3$)



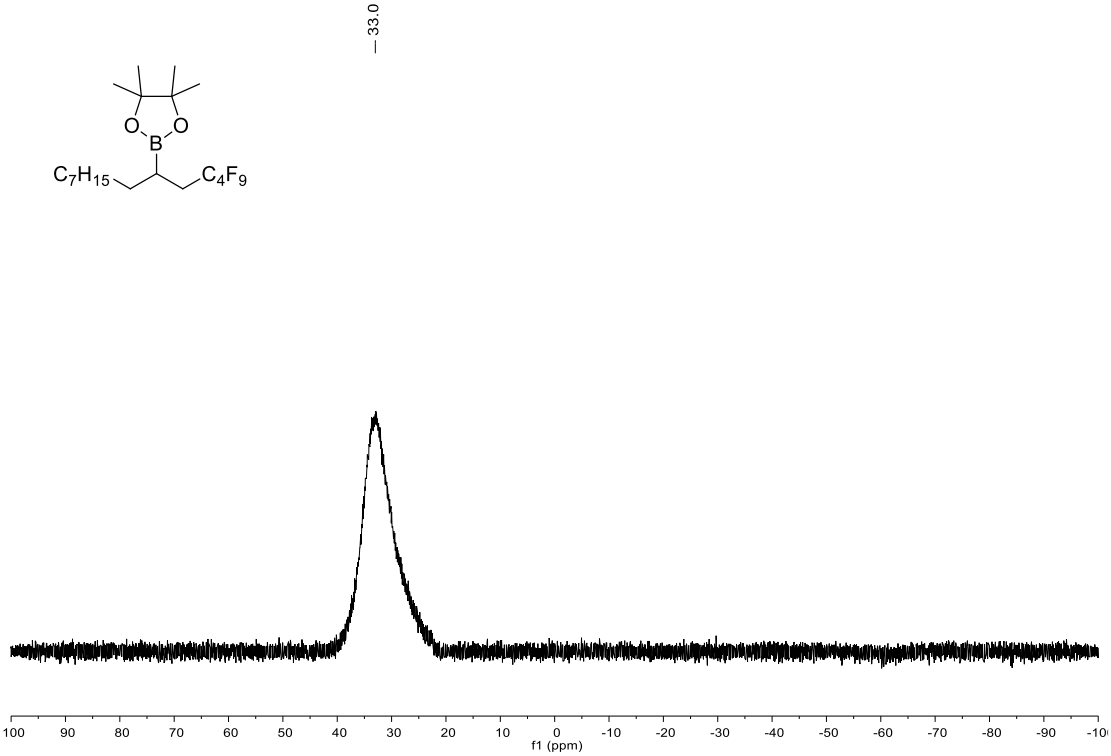
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

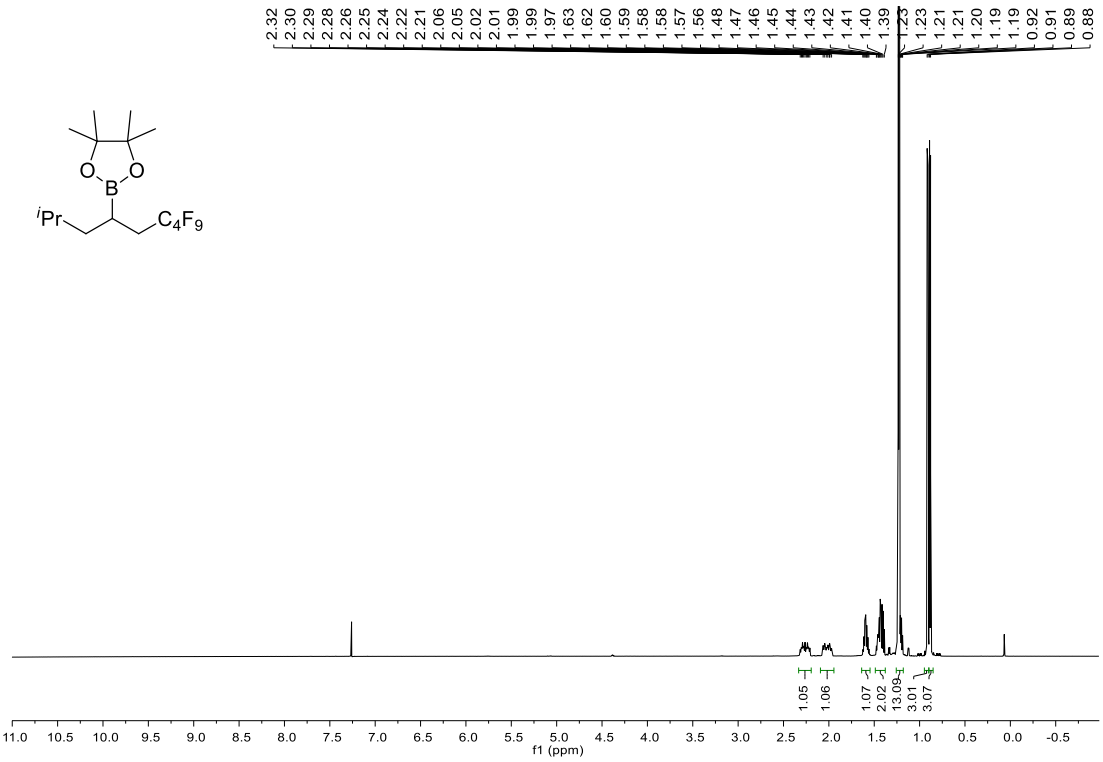


^{11}B NMR (96 MHz, $CDCl_3$)

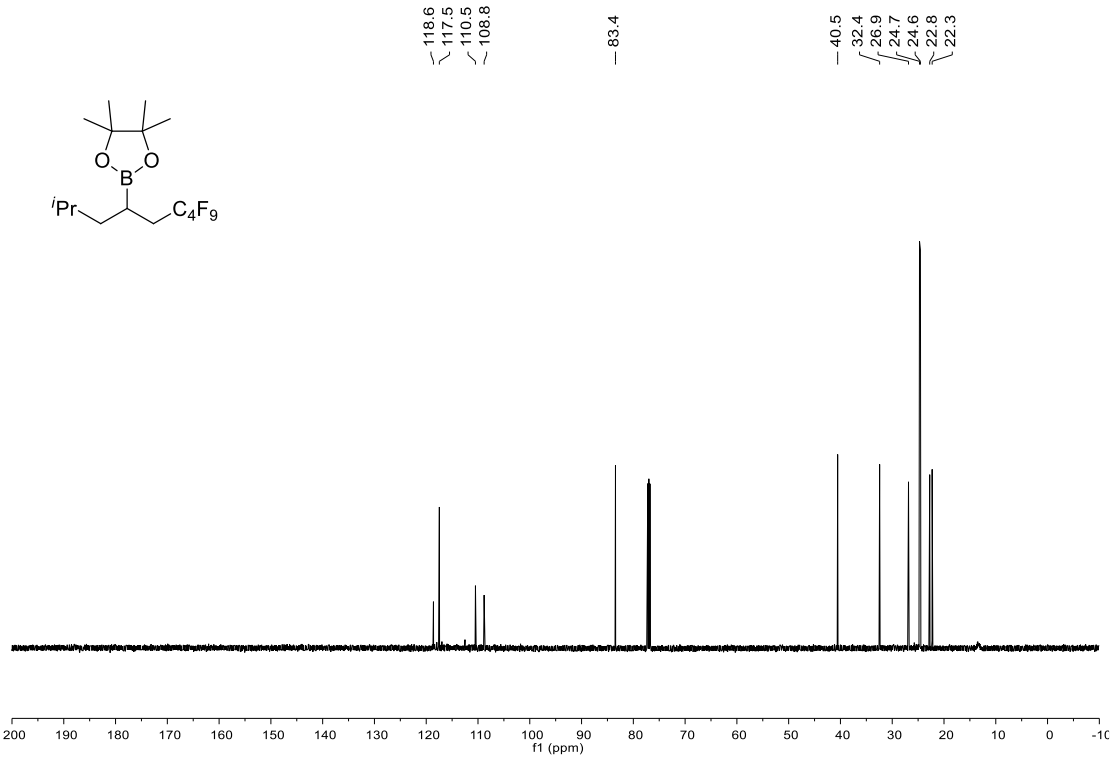


4,4,5,5-Tetramethyl-2-(6,6,7,7,8,8,9,9,9-nonafluoro-2-methylnonan-4-yl)-1,3,2-dioxaborolane (4p)

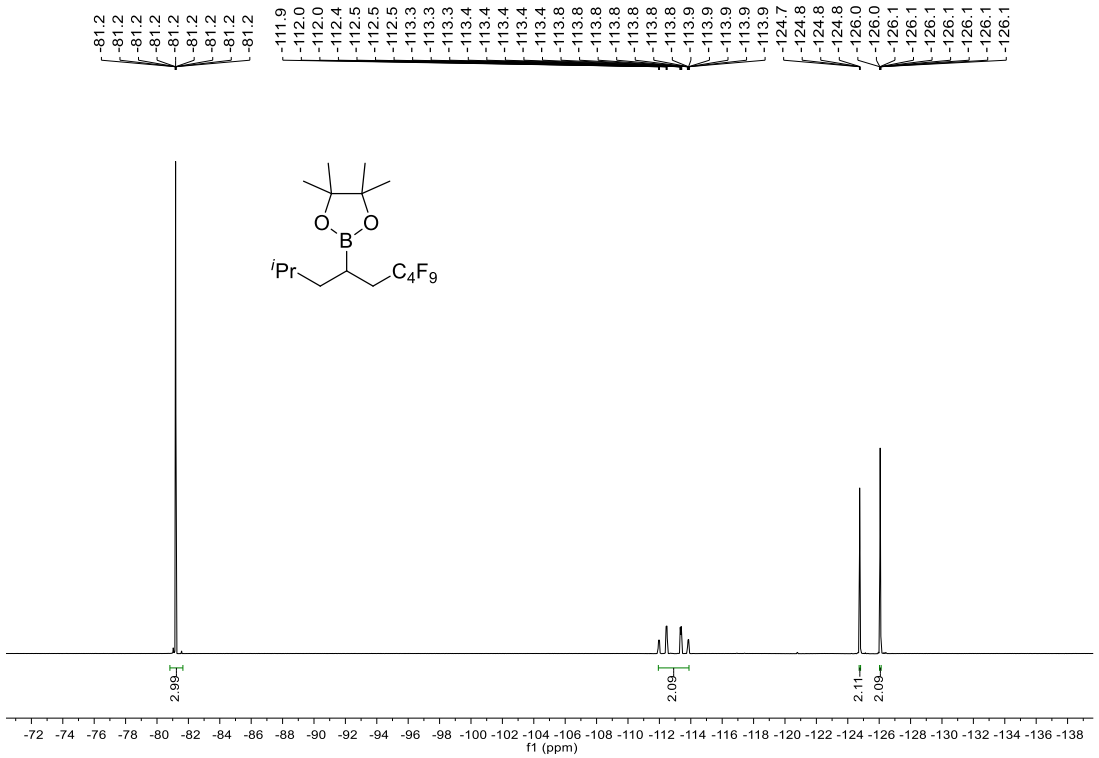
^{1}H NMR (600 MHz, $CDCl_3$)



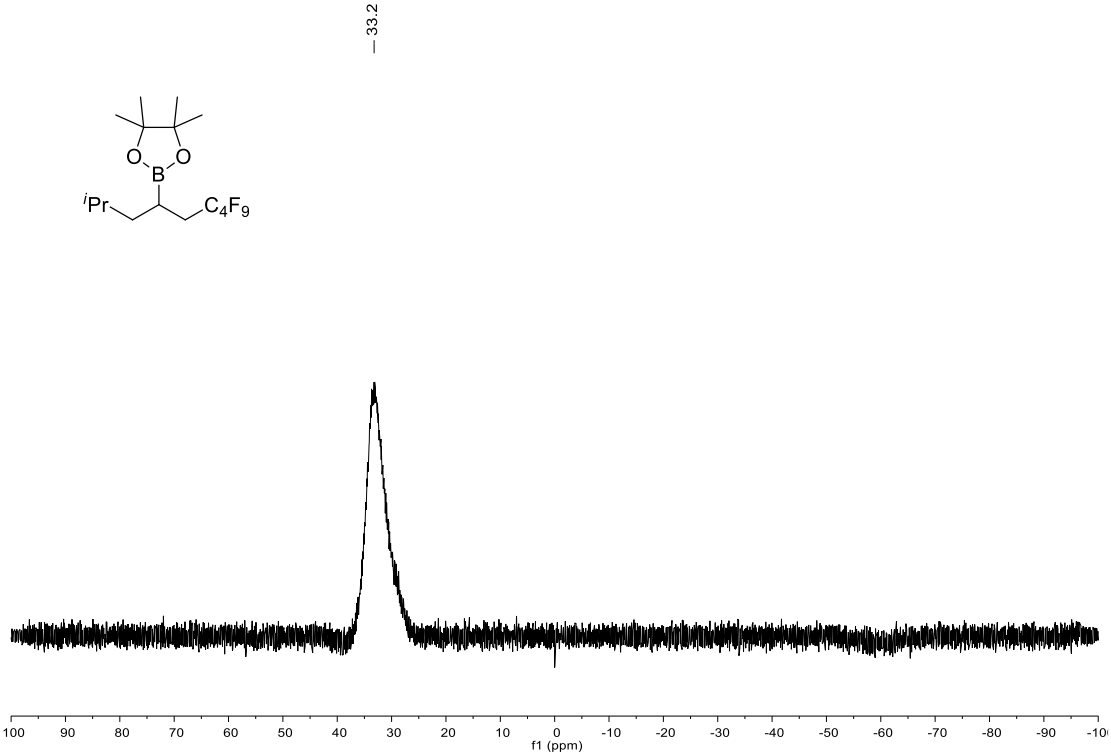
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

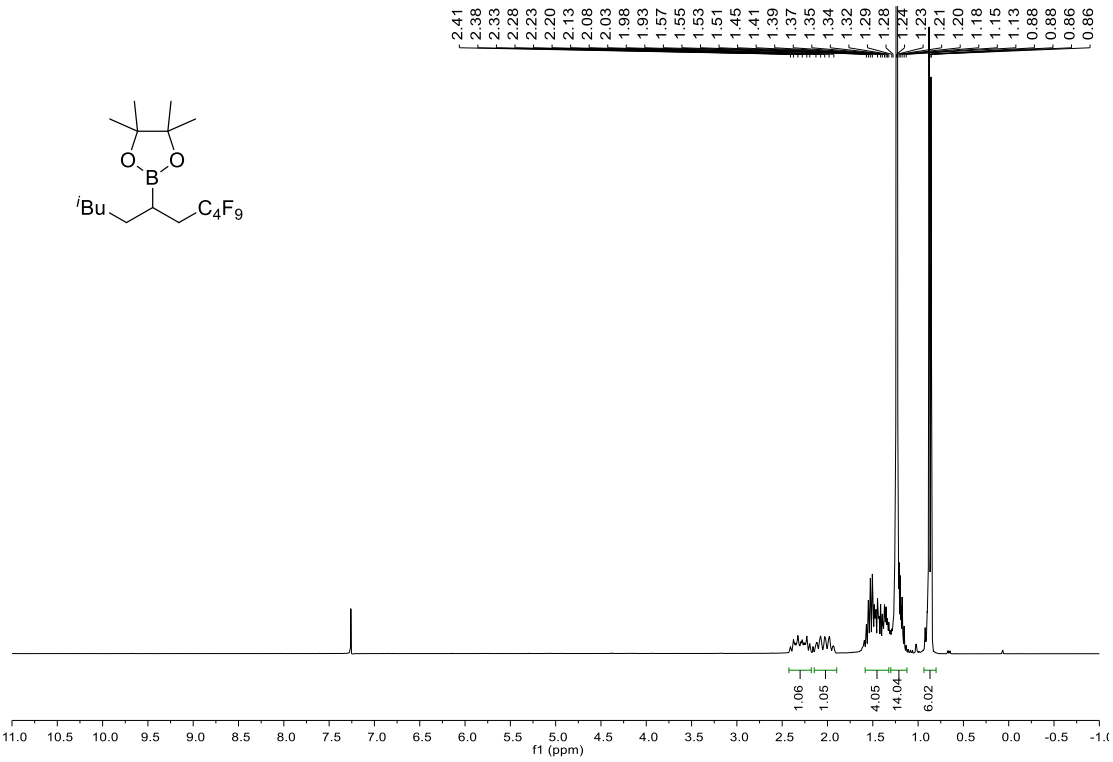


^{11}B NMR (96 MHz, $CDCl_3$)

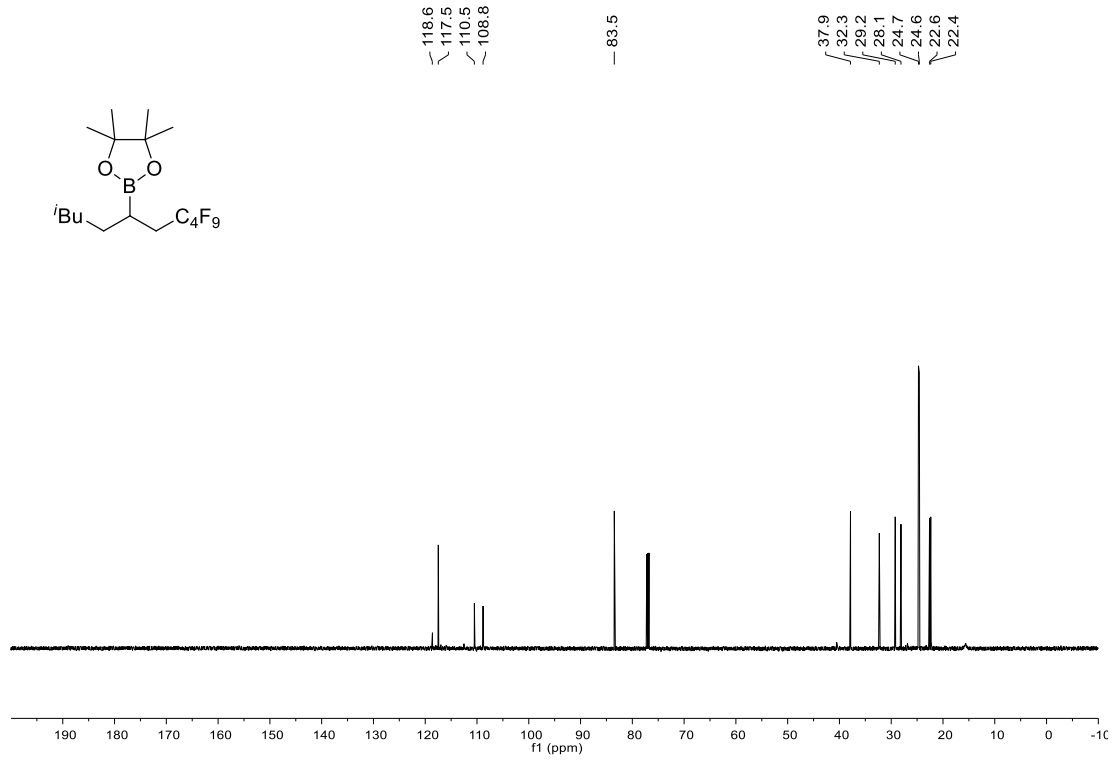


4,4,5,5-Tetramethyl-2-(7,7,8,8,9,9,10,10,10-nonafluoro-2-methyldecan-5-yl)-1,3,2-dioxaborolane (4q)

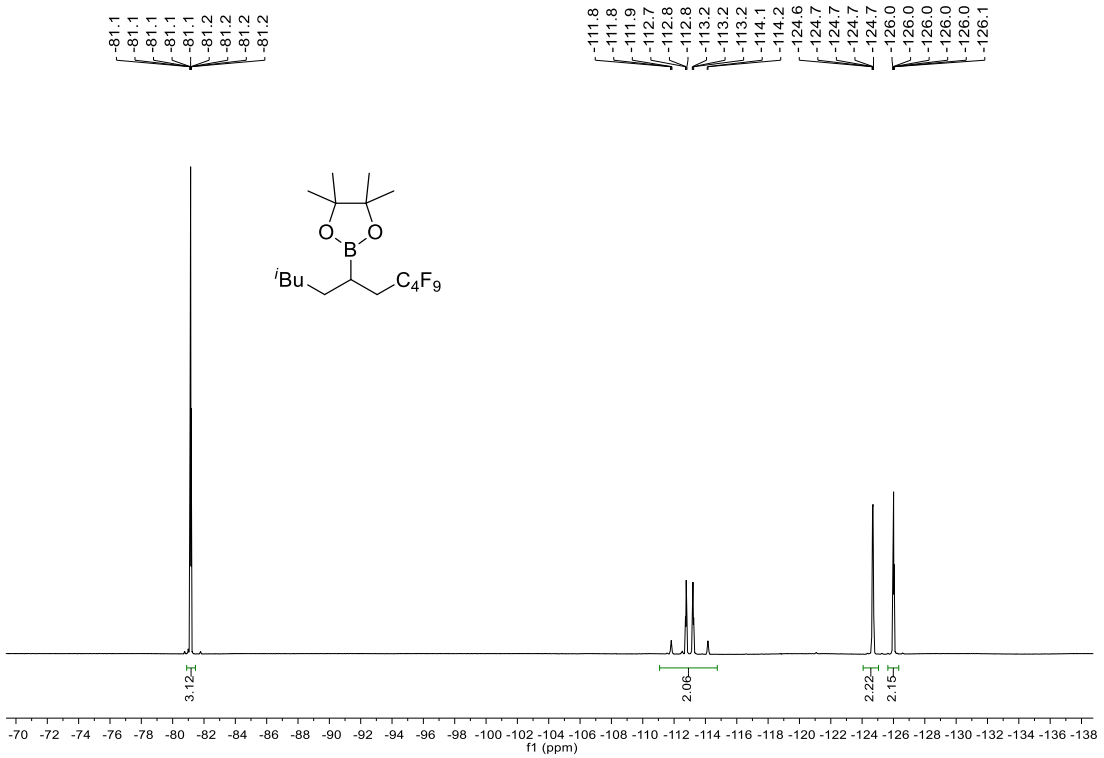
^{1}H NMR (300 MHz, $CDCl_3$)



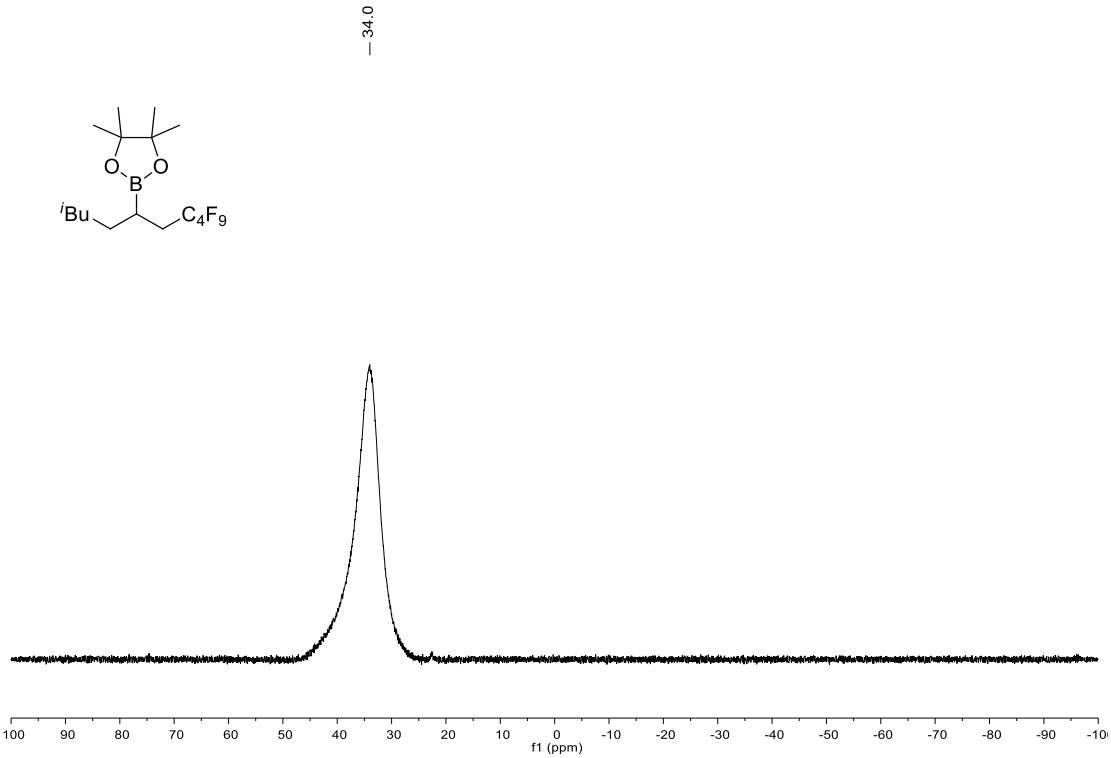
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (282 MHz, $CDCl_3$)

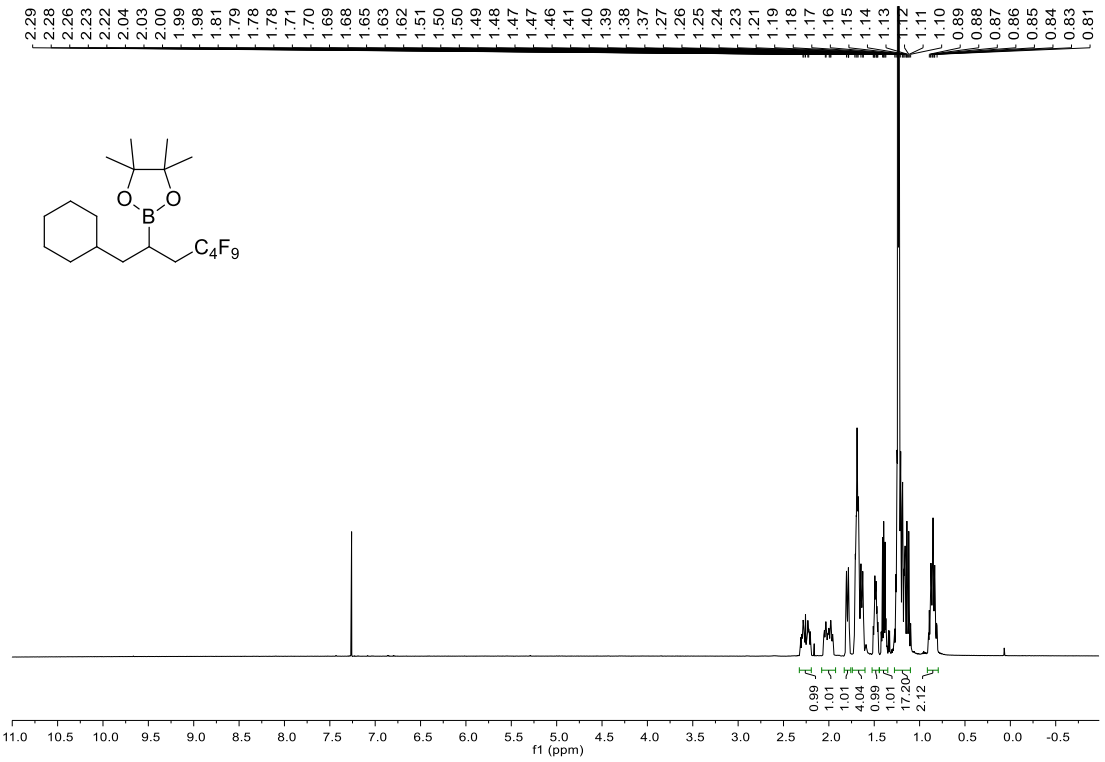


^{11}B NMR (96 MHz, $CDCl_3$)

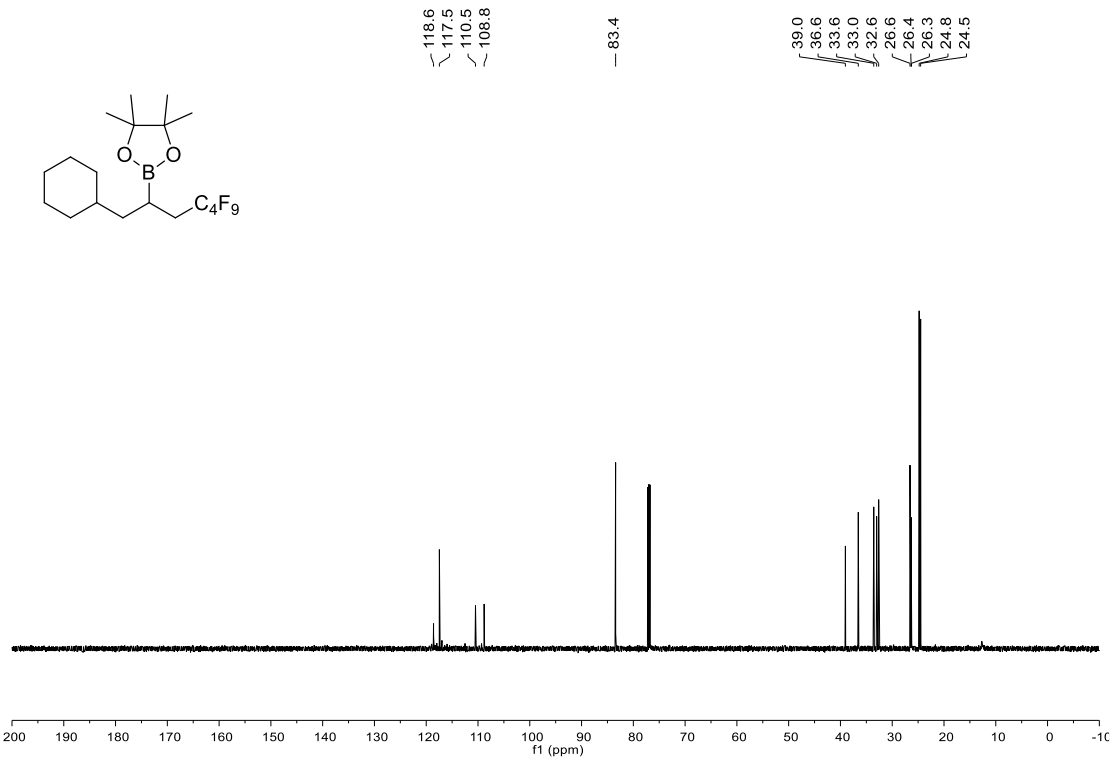


2-(1-Cyclohexyl-4,4,5,5,6,6,7,7,7-nonafluoroheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4r)

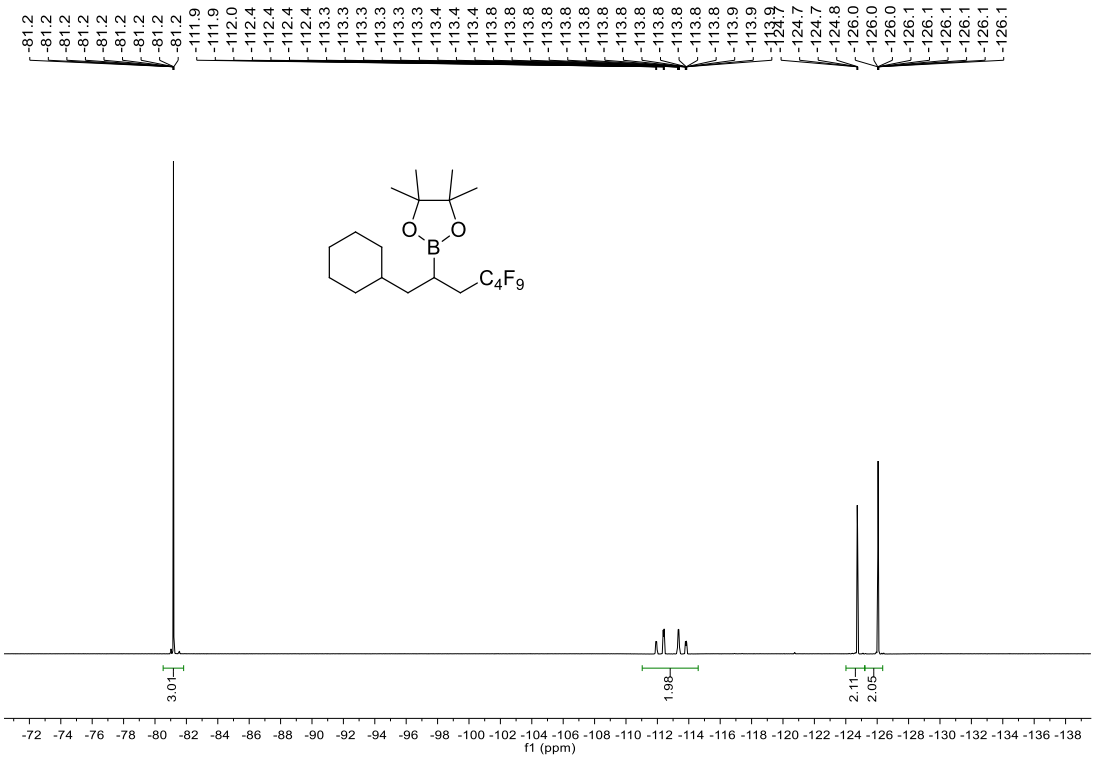
^{1}H NMR (600 MHz, $CDCl_3$)



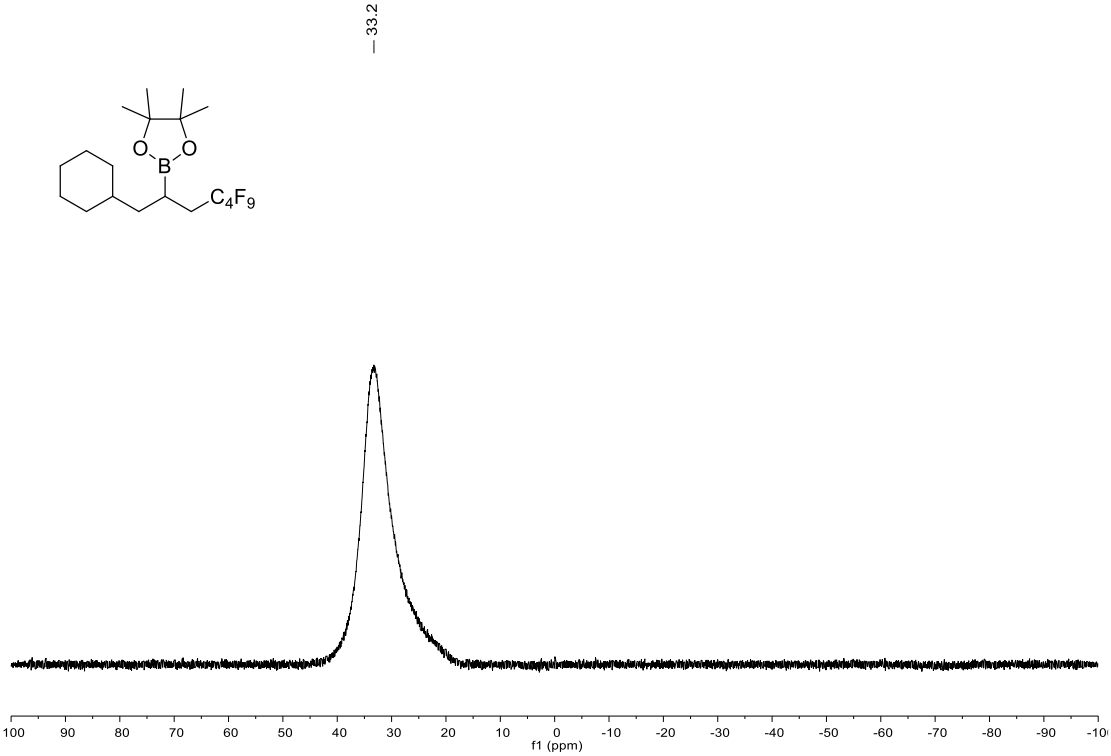
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

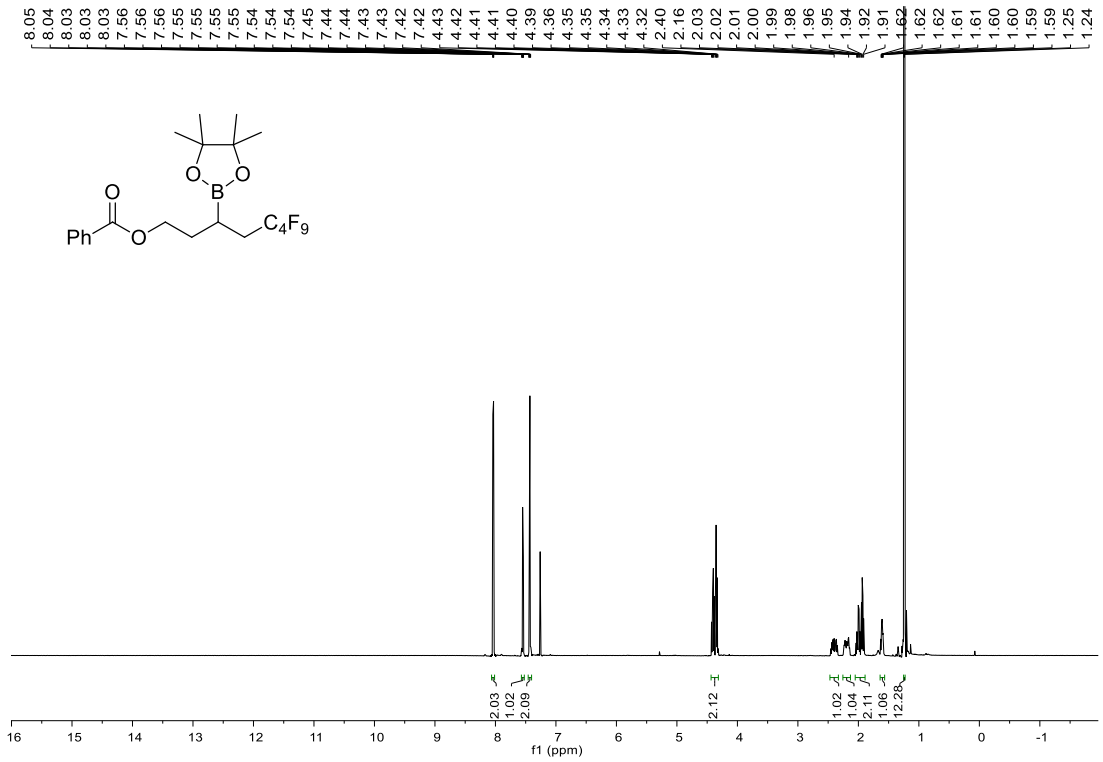


^{11}B NMR (96 MHz, $CDCl_3$)

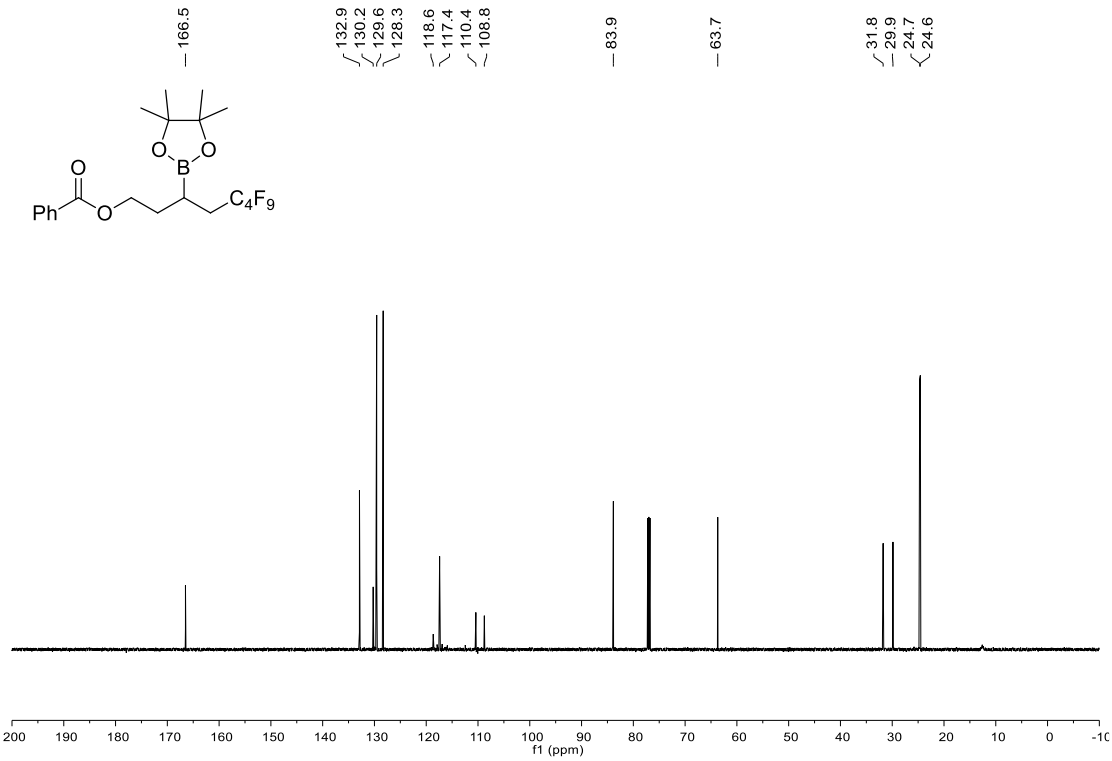


5,5,6,6,7,7,8,8,8-Nonafluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl benzoate (4s)

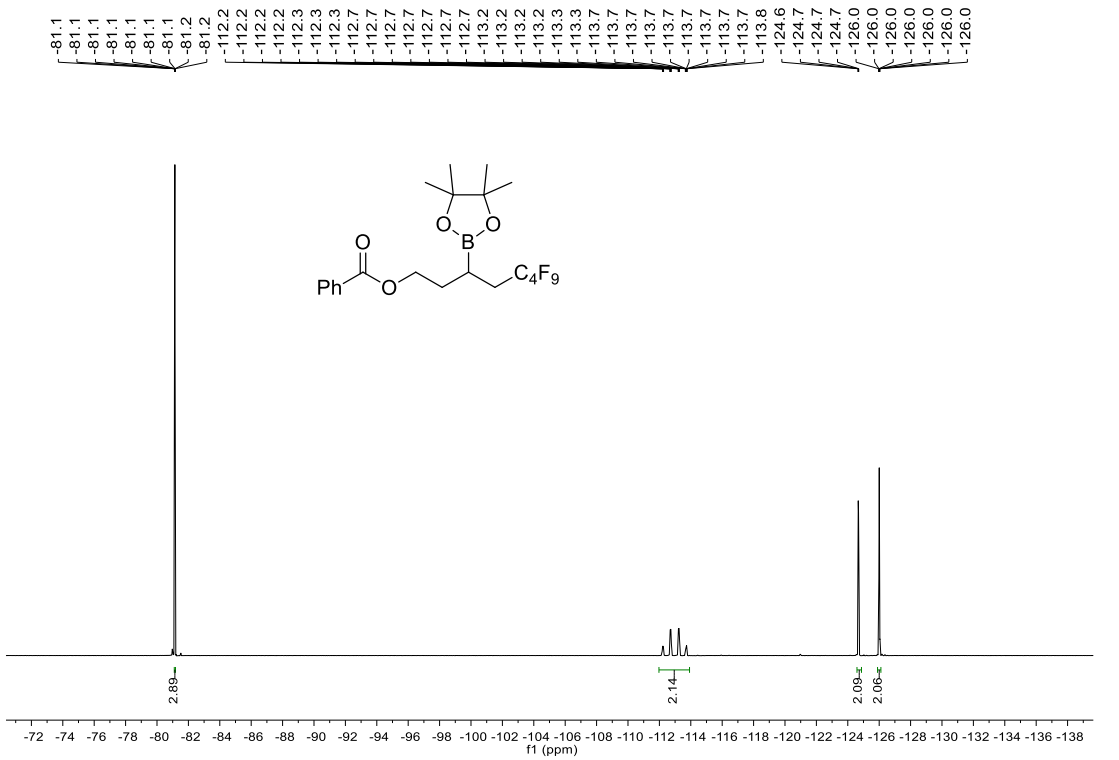
^{1}H NMR (600 MHz, $CDCl_3$)



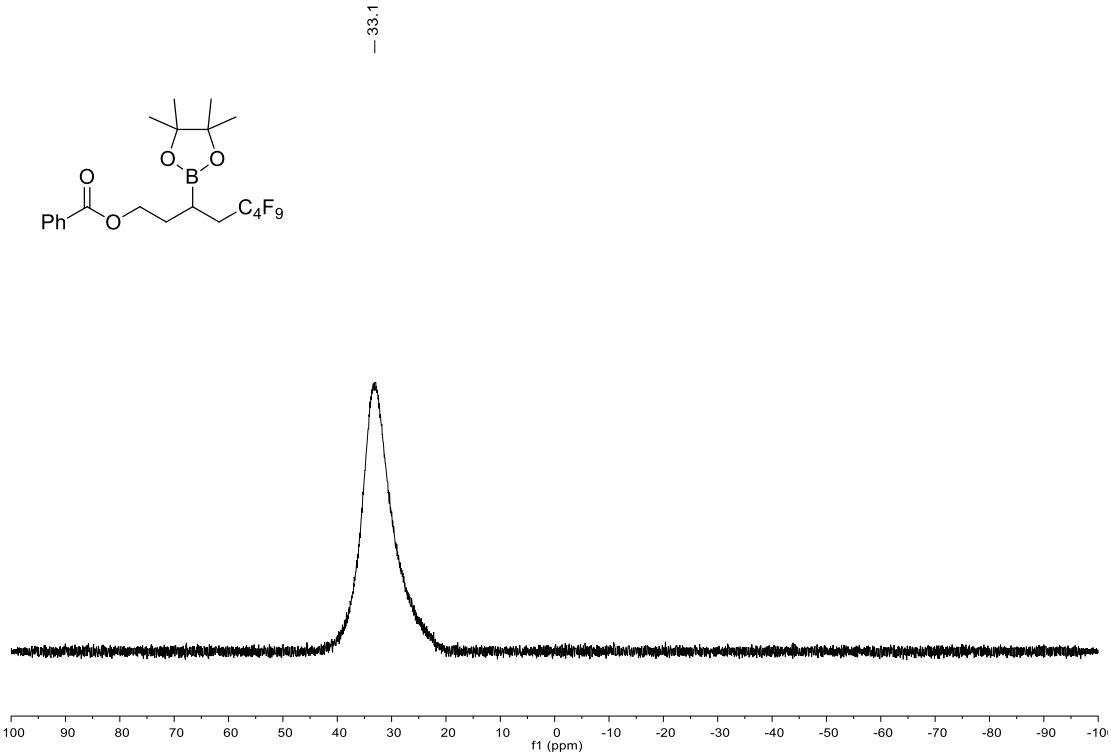
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

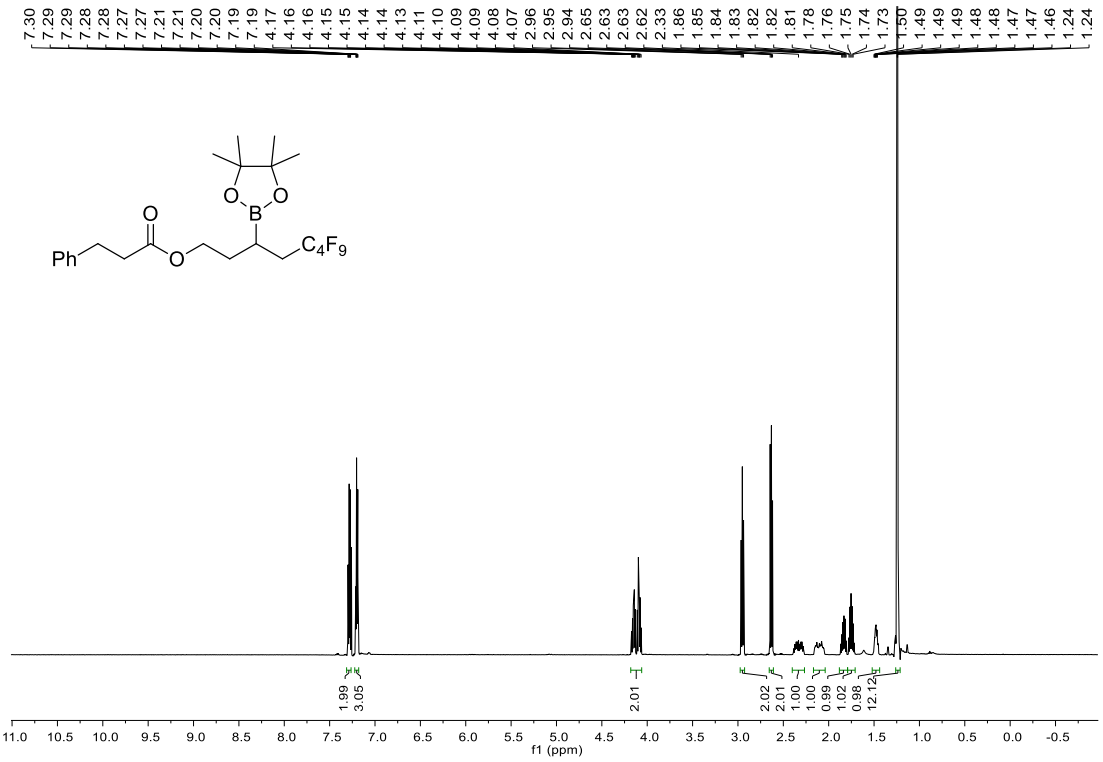


^{11}B NMR (96 MHz, $CDCl_3$)

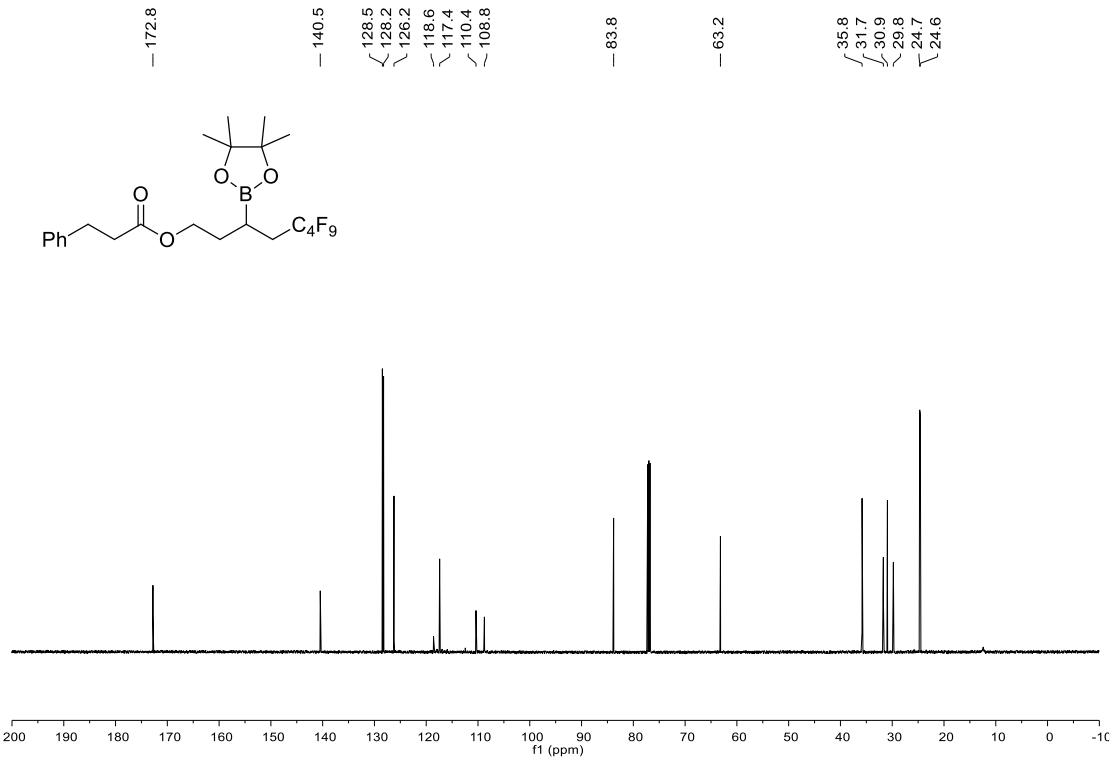


5,5,6,6,7,7,8,8,8-Nonafluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl 3-phenylpropanoate (4t)

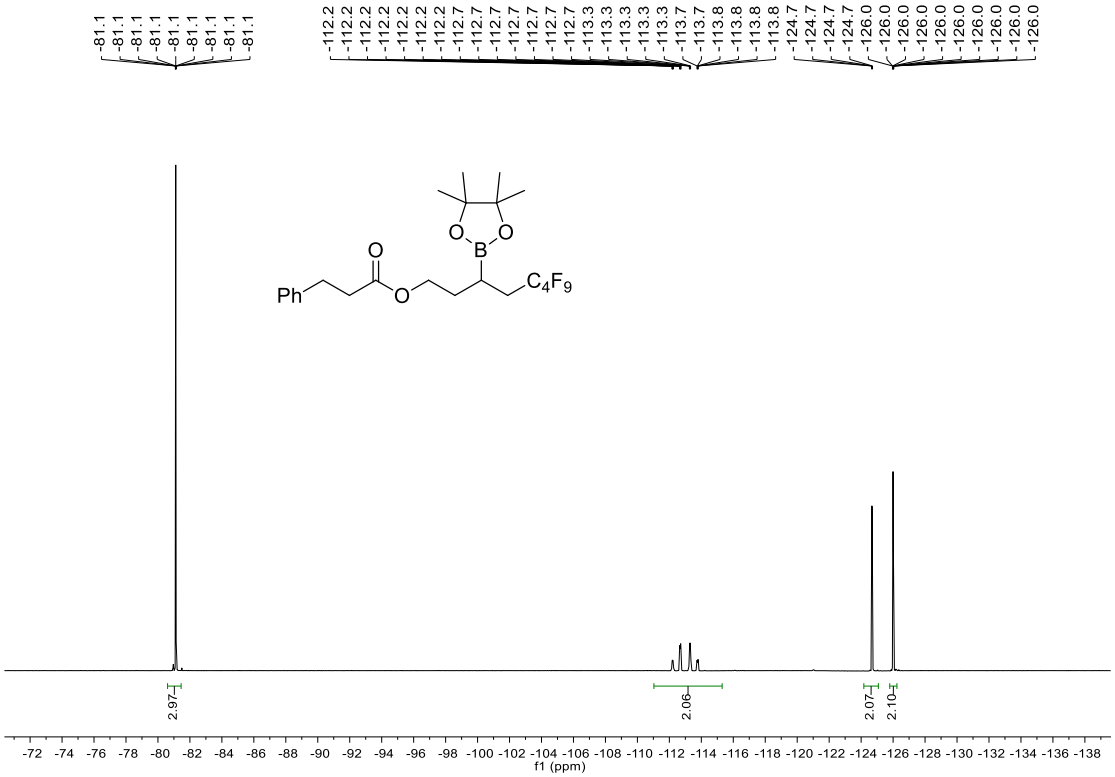
^{1}H NMR (600 MHz, $CDCl_3$)



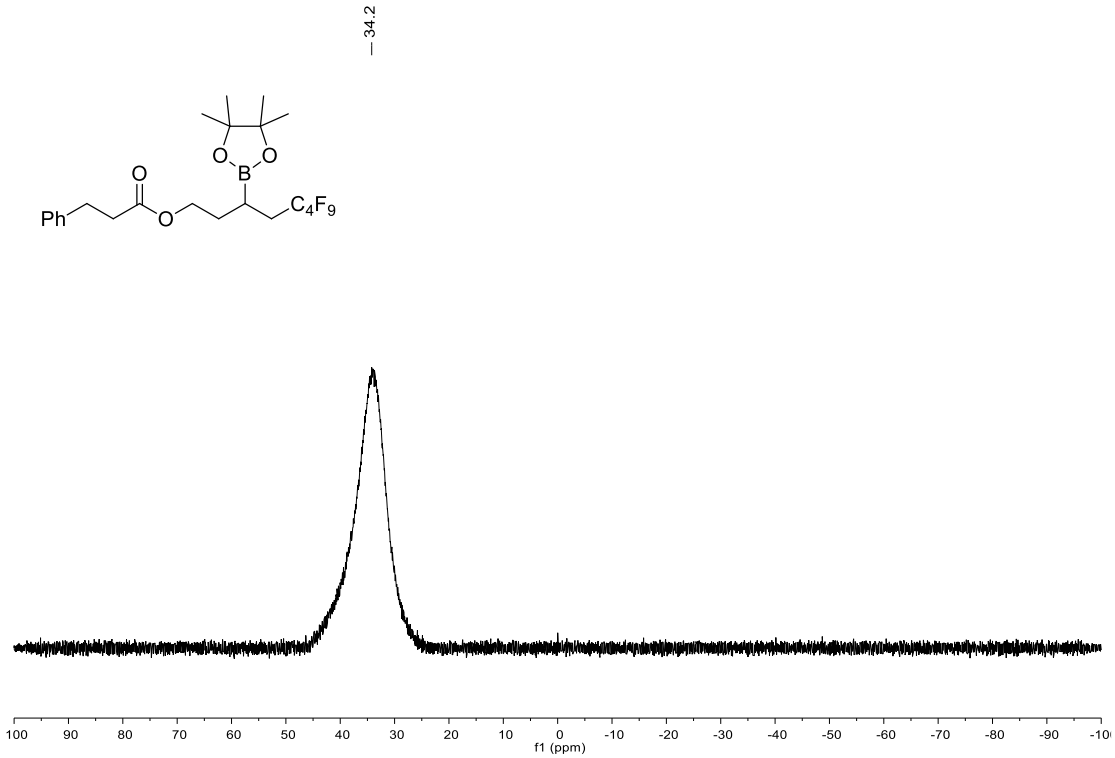
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

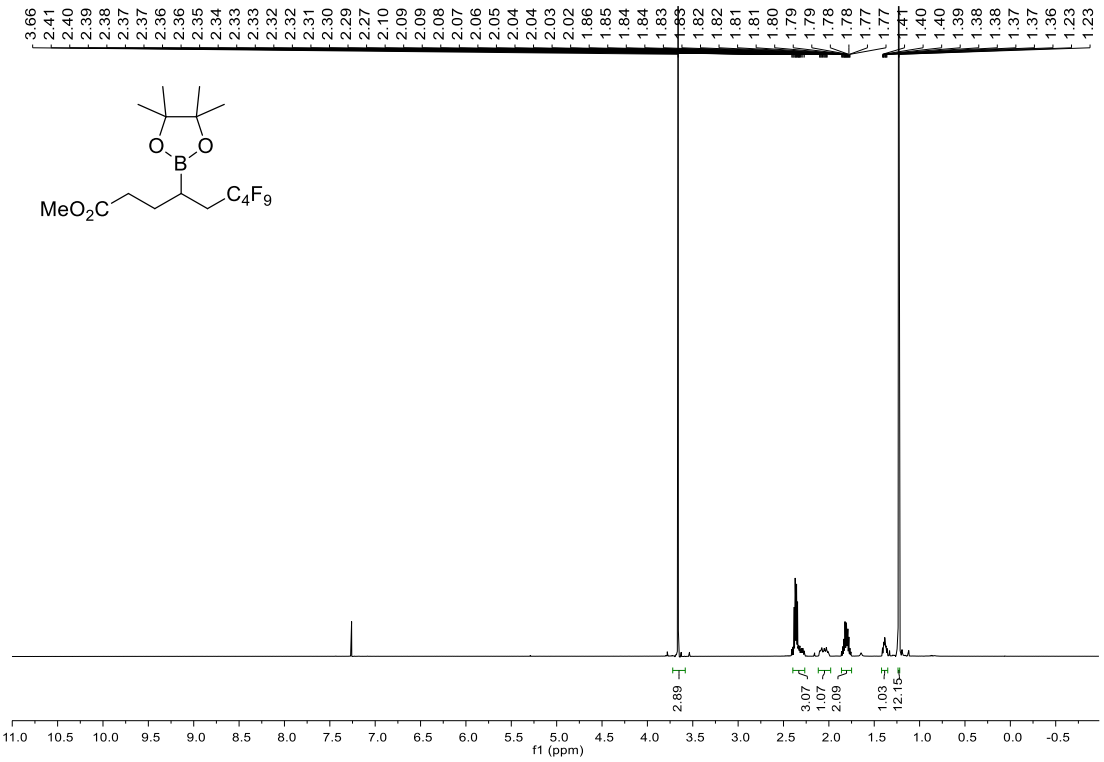


^{11}B NMR (96 MHz, $CDCl_3$)

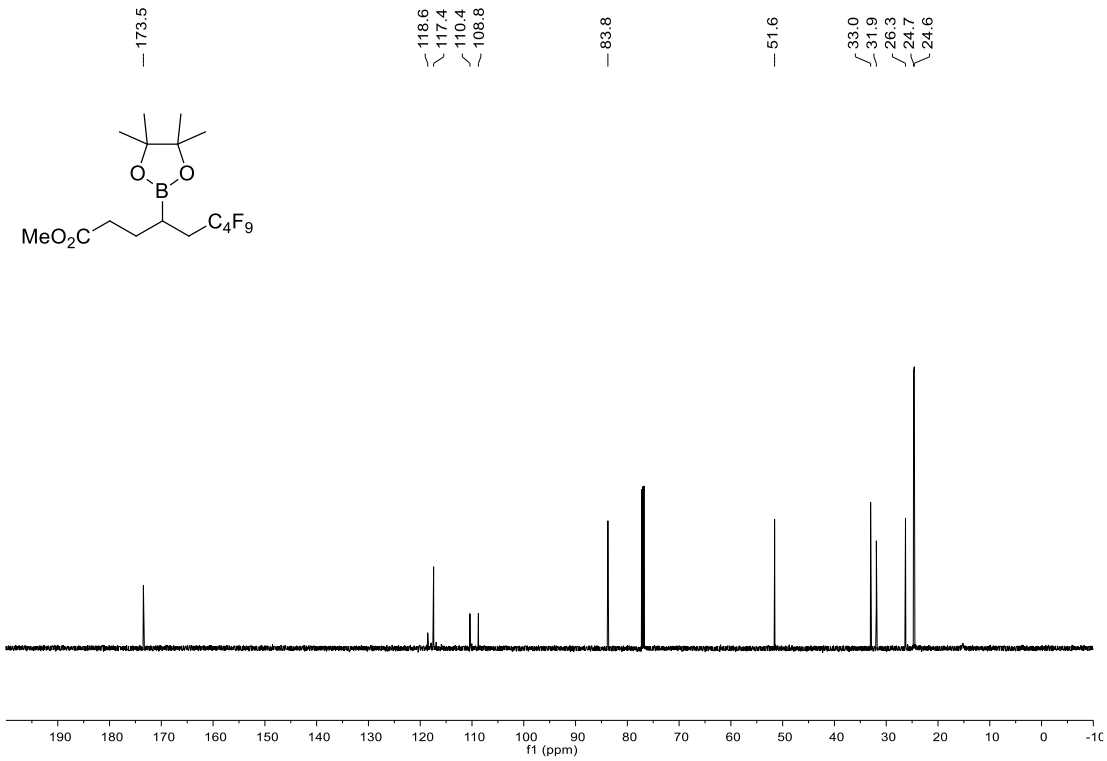


Methyl 6,6,7,7,8,8,9,9,9-nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanoate (4u)

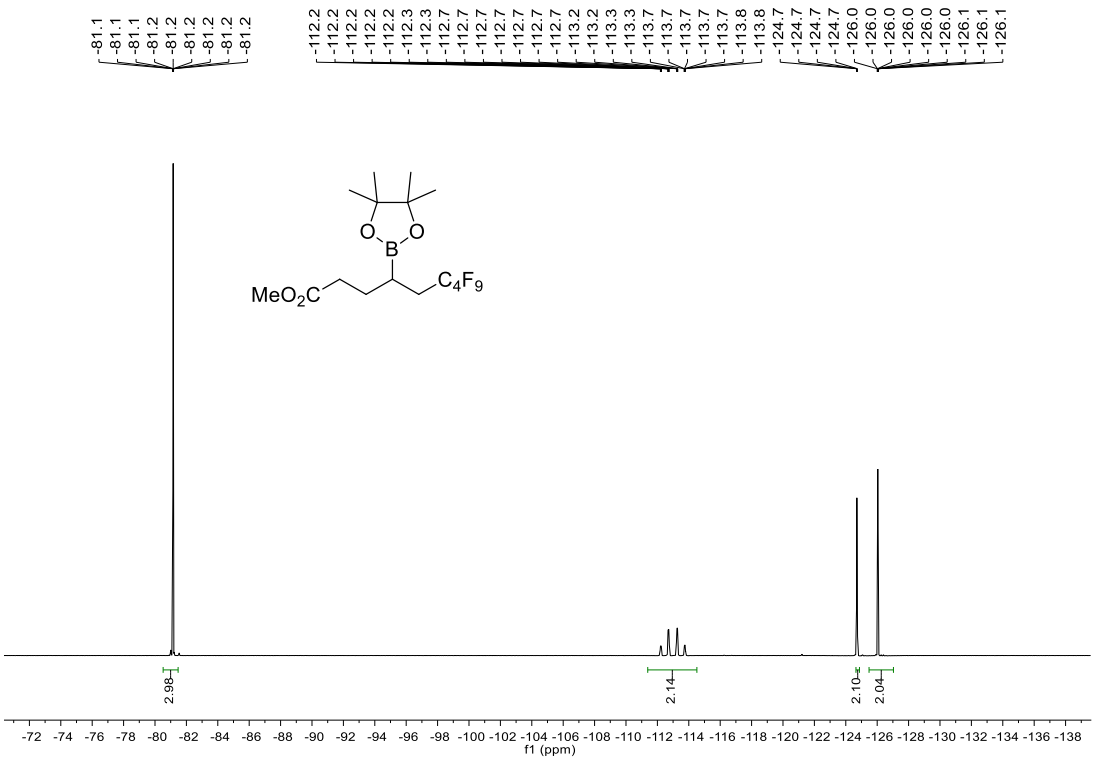
^{1}H NMR (600 MHz, $CDCl_3$)



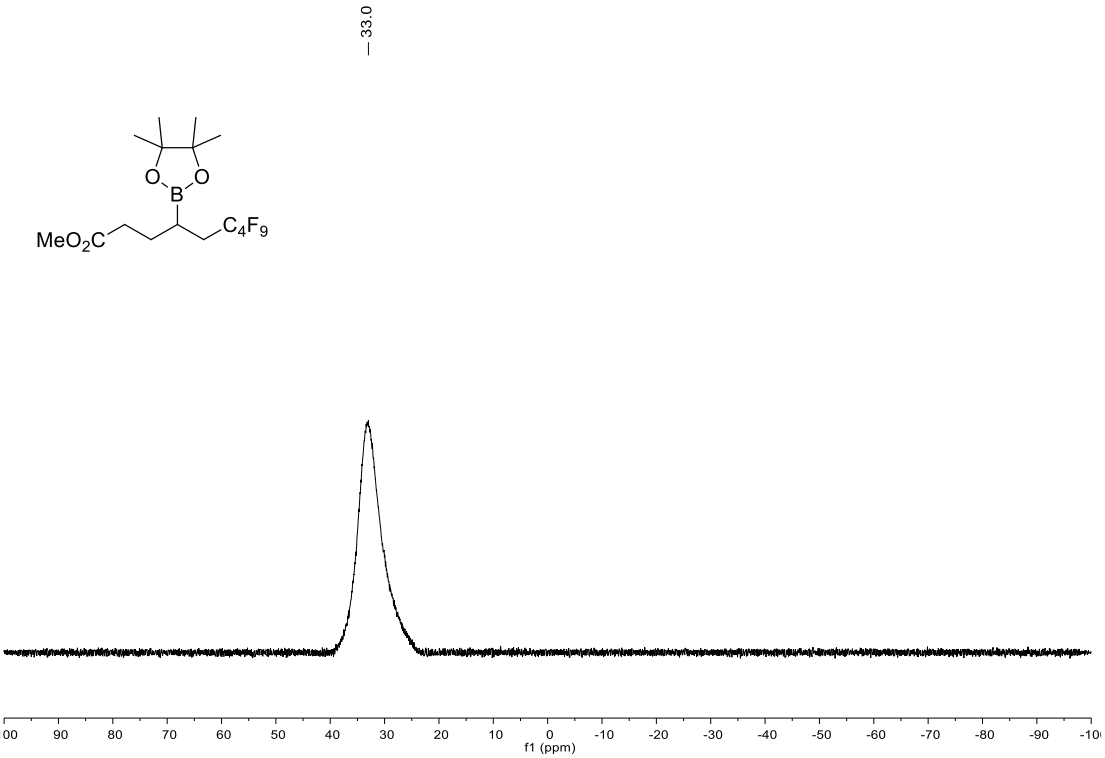
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)



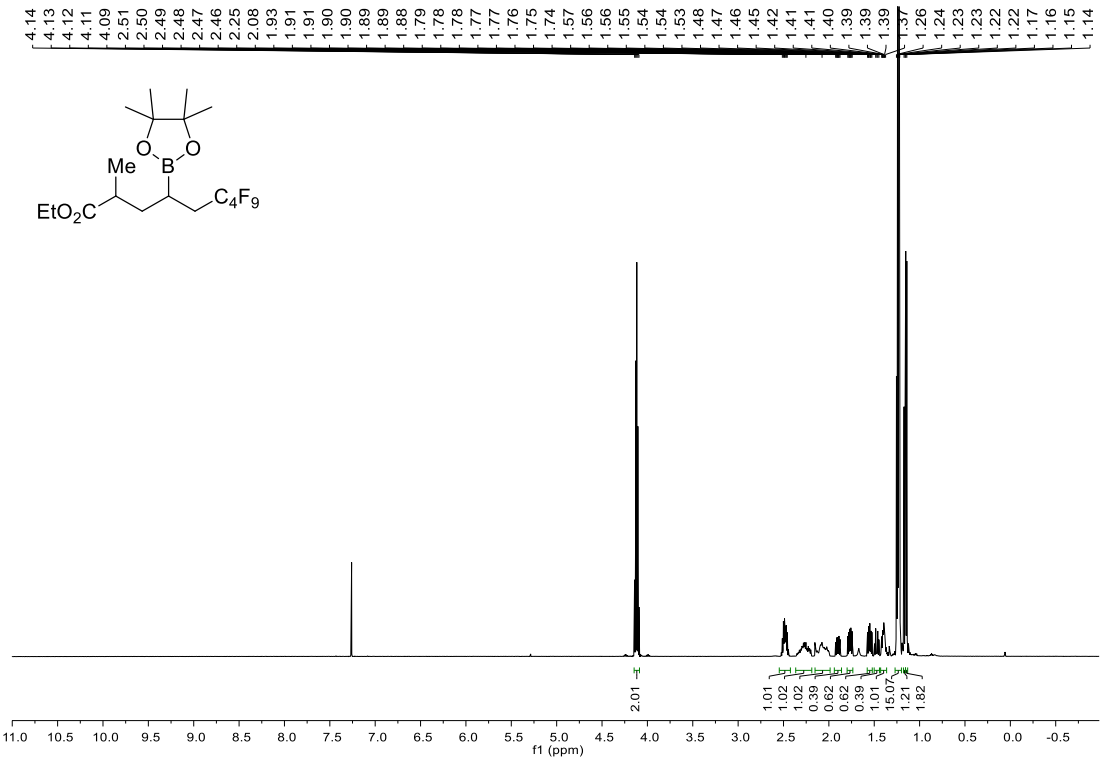
^{11}B NMR (96 MHz, $CDCl_3$)



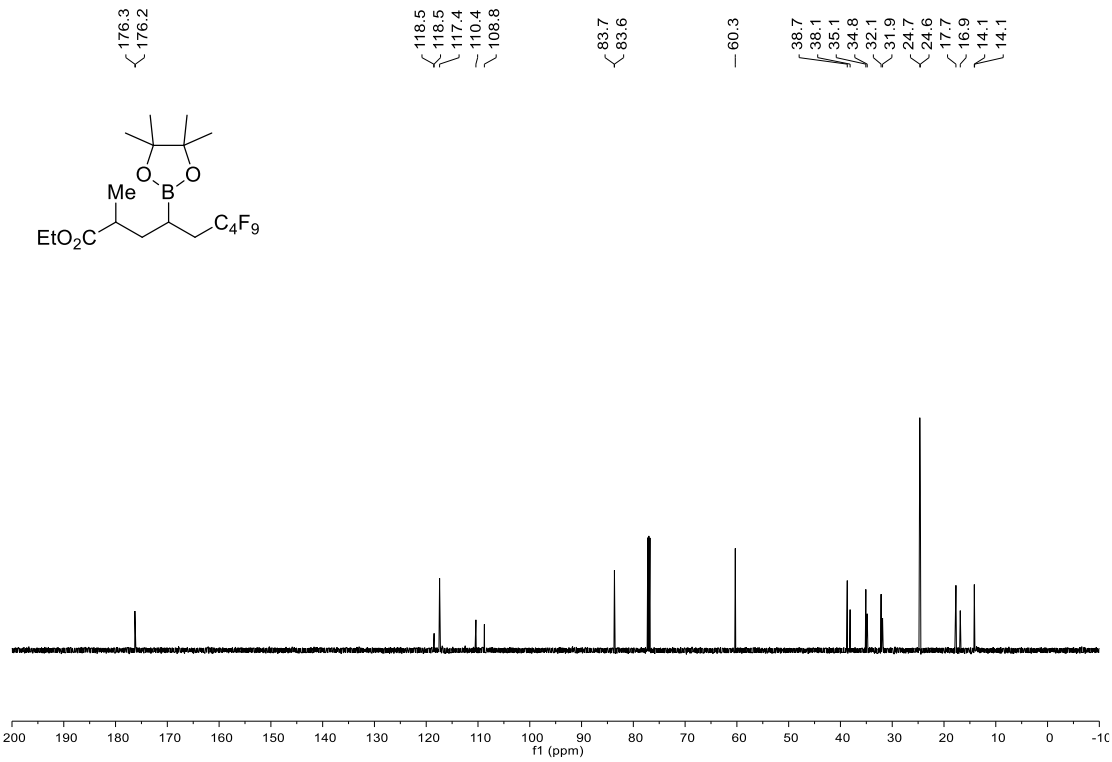
Ethyl

6,6,7,7,8,8,9,9,9-nonafluoro-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanoate (4v)

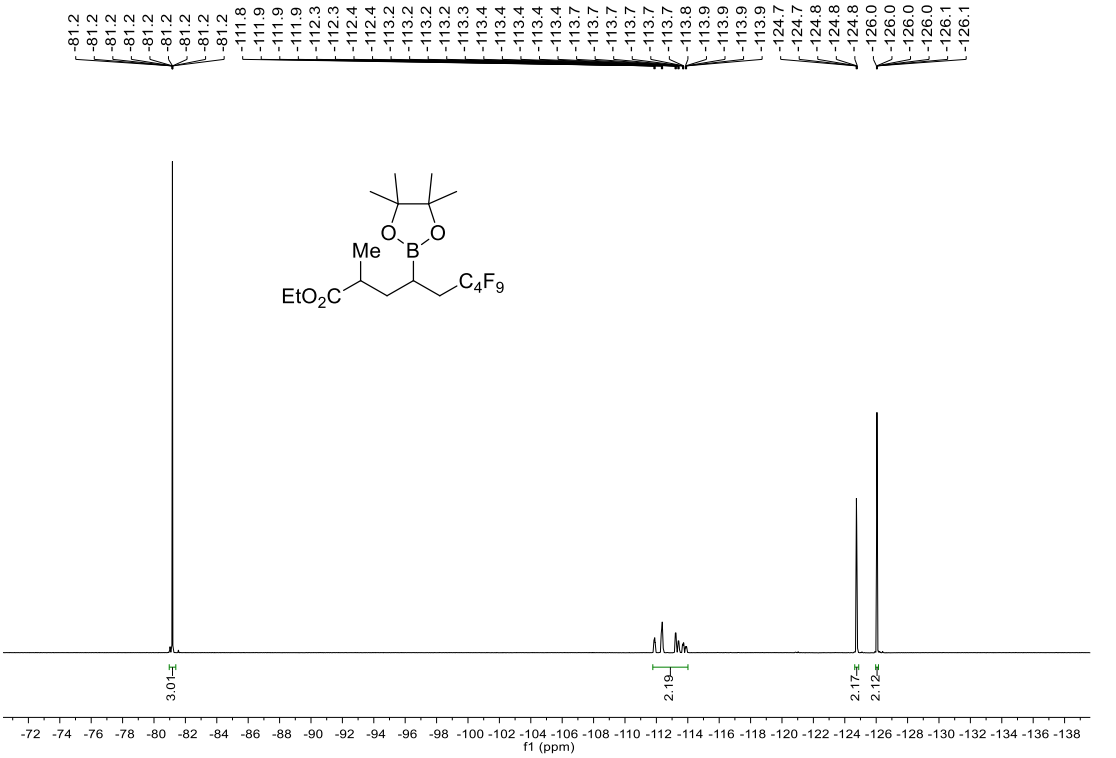
^{1}H NMR (600 MHz, $CDCl_3$)



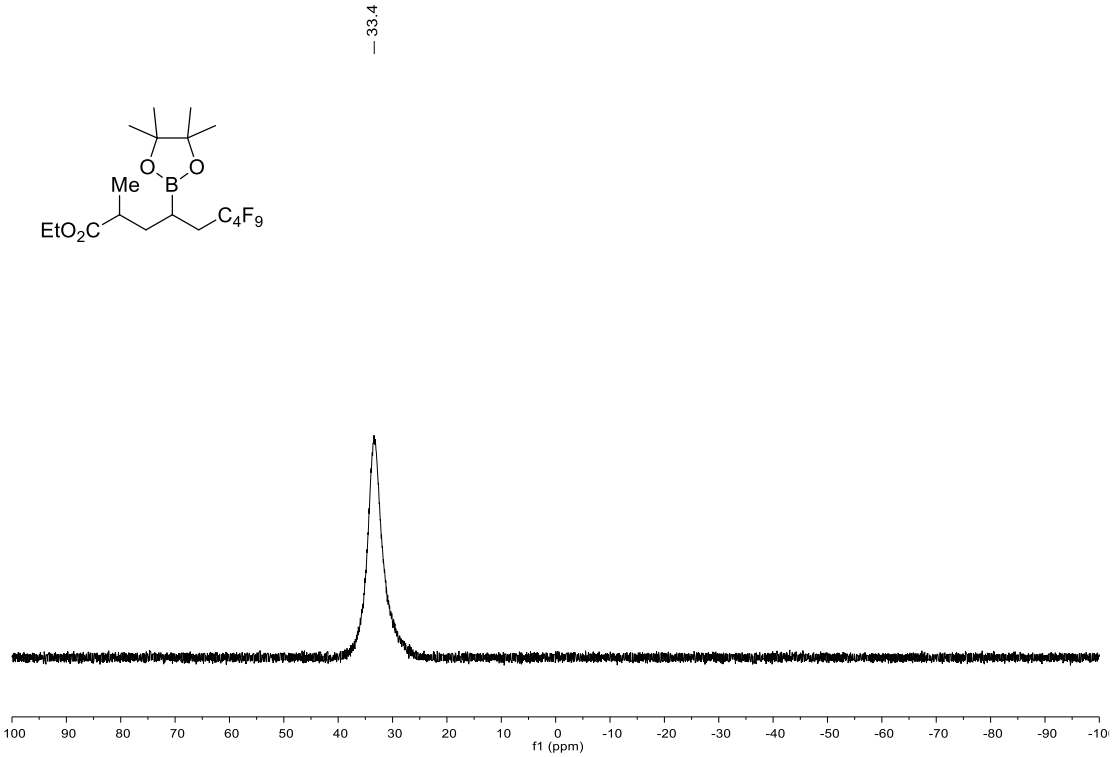
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

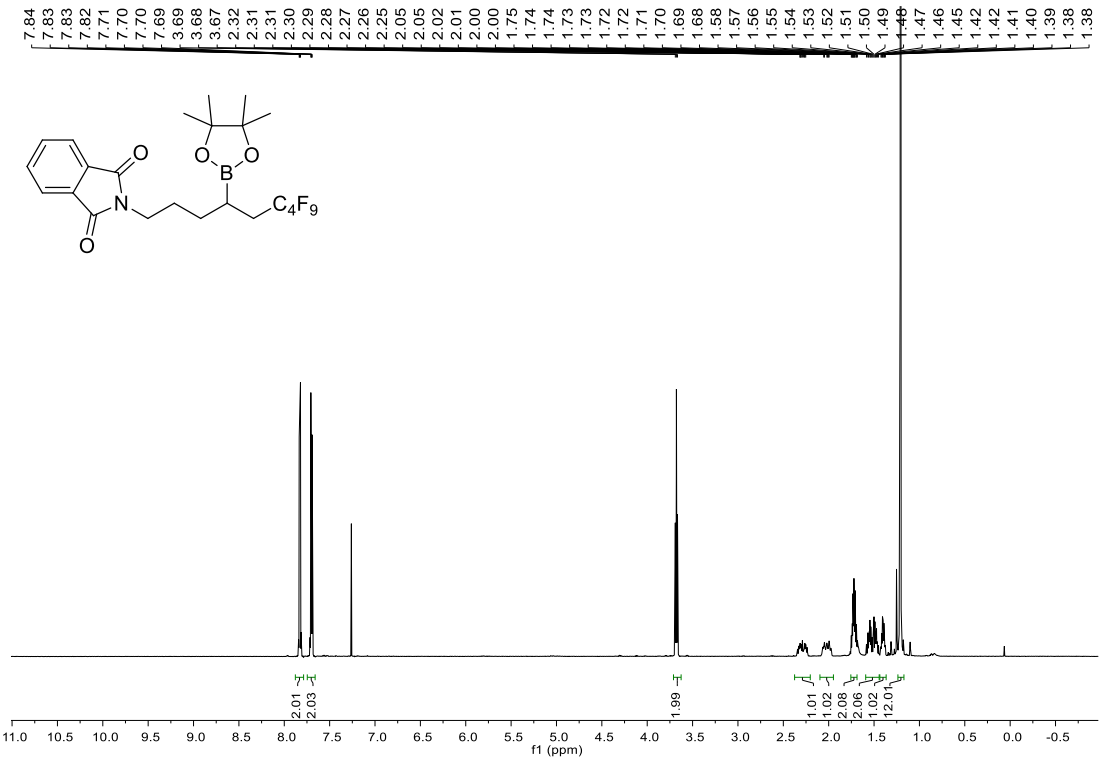


^{11}B NMR (96 MHz, $CDCl_3$)

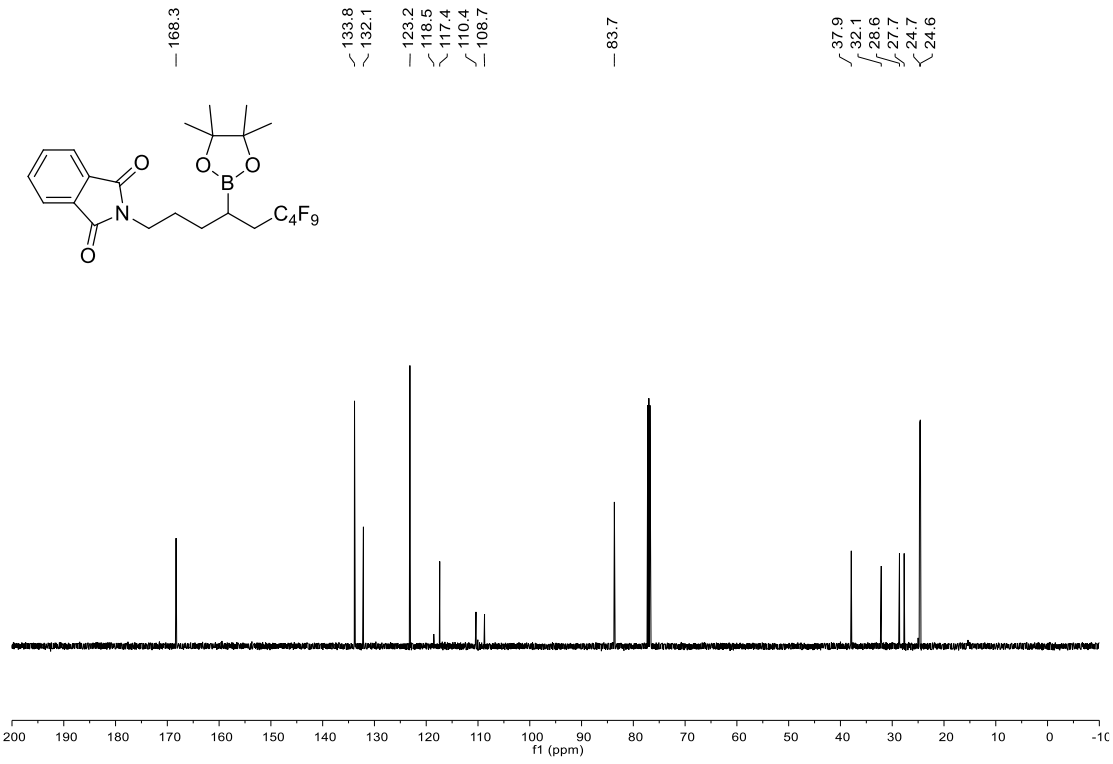


2-(6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)isoindoline-1,3-dione (4w)

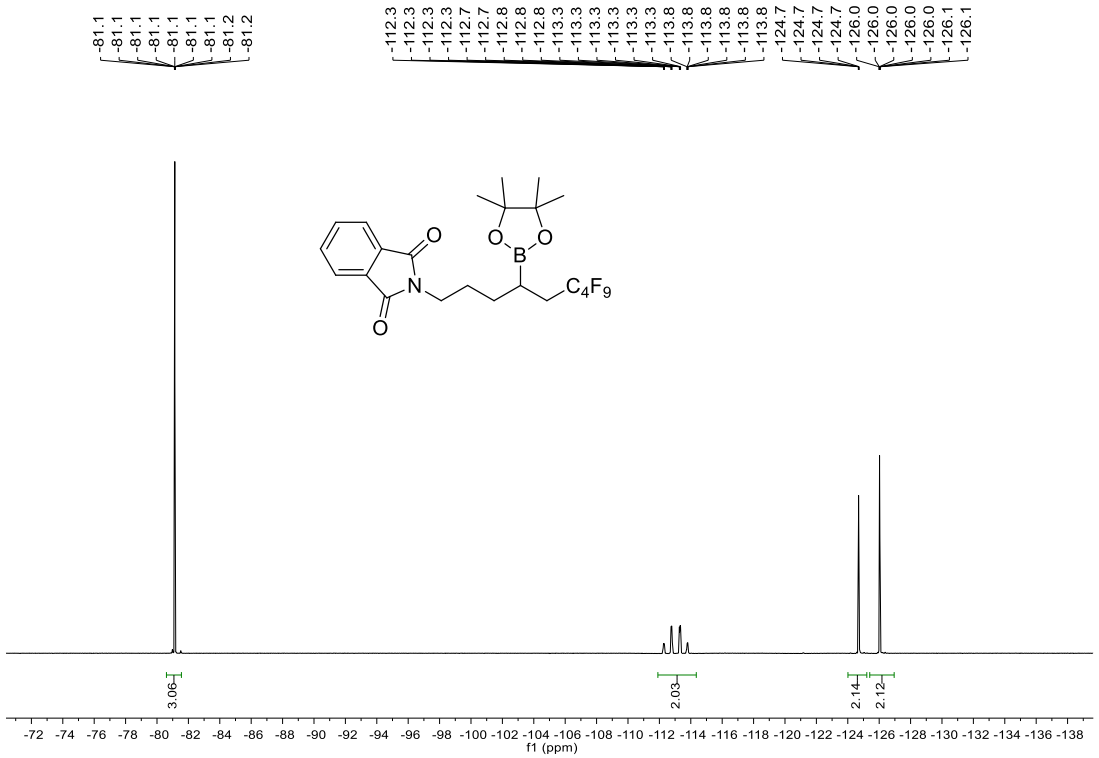
^{1}H NMR (600 MHz, $CDCl_3$)



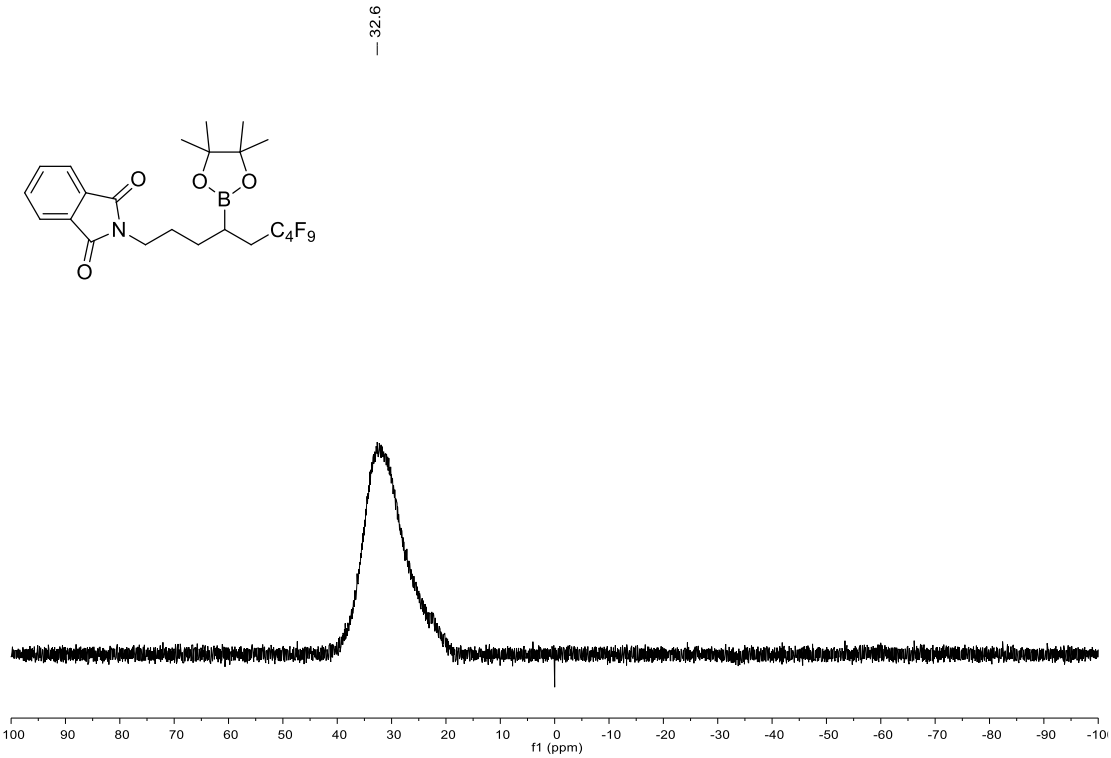
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

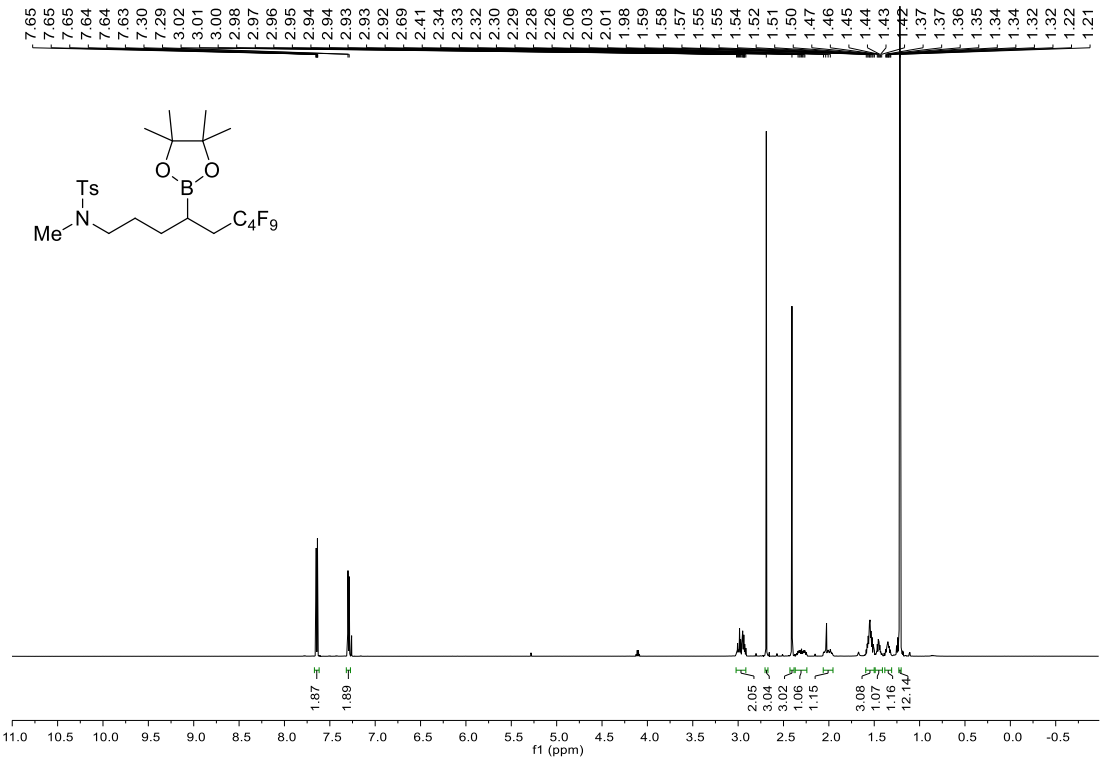


^{11}B NMR (96 MHz, $CDCl_3$)

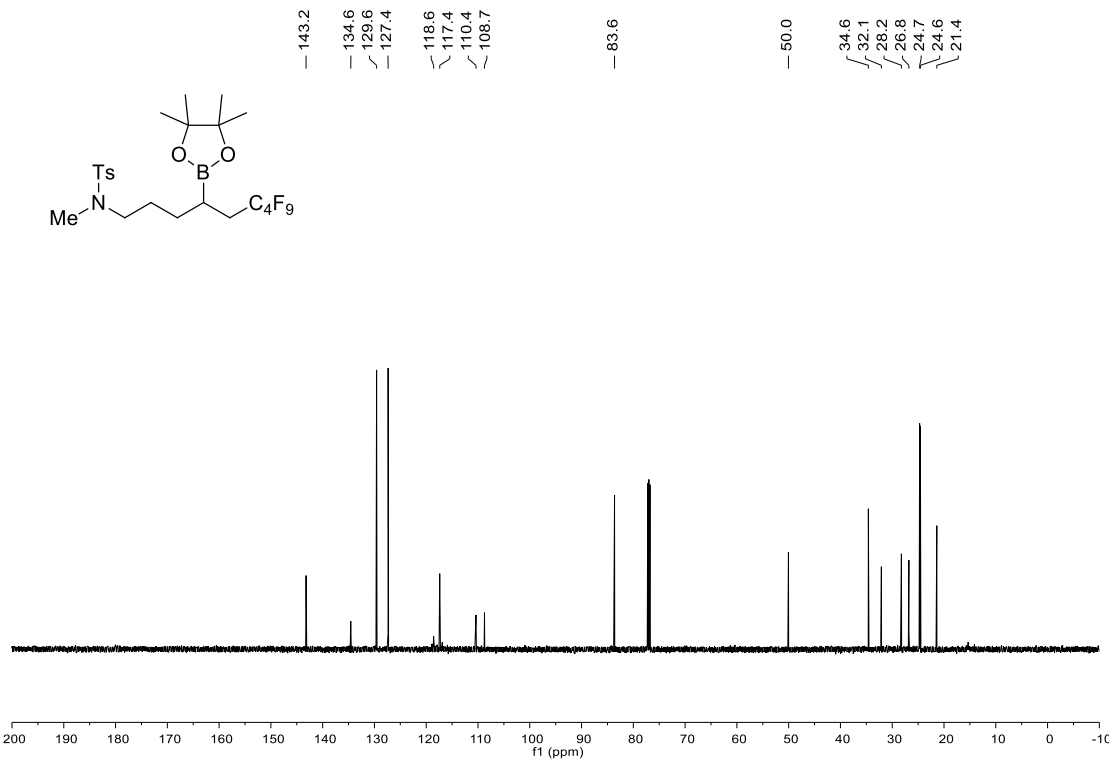


***N*,4-Dimethyl-*N*-(6,6,7,7,8,8,9,9,9-nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) nonyl)benzenesulfonamide (4x)**

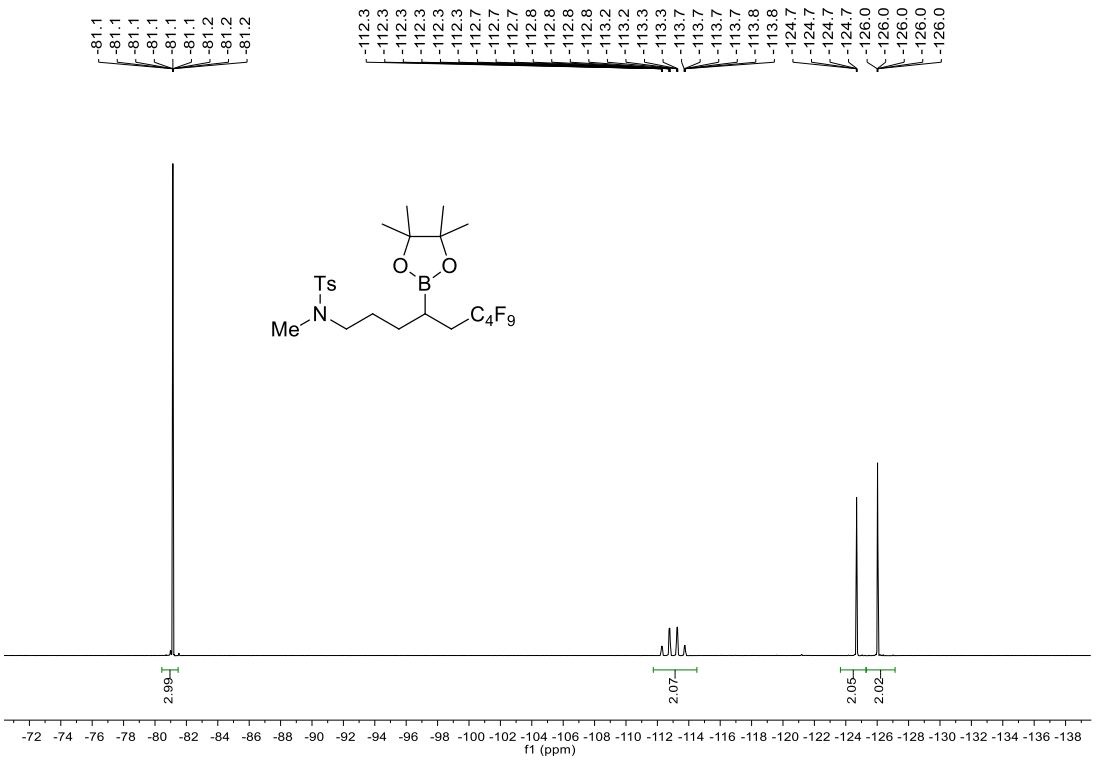
^{1}H NMR (600 MHz, $CDCl_3$)



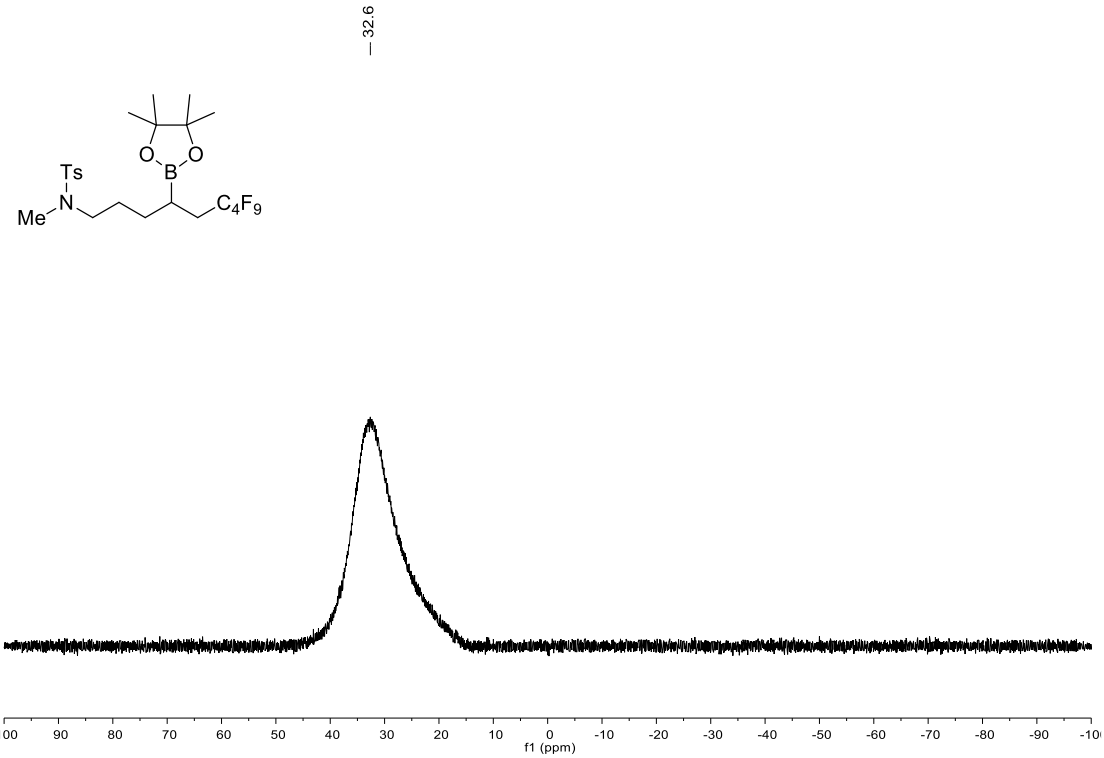
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

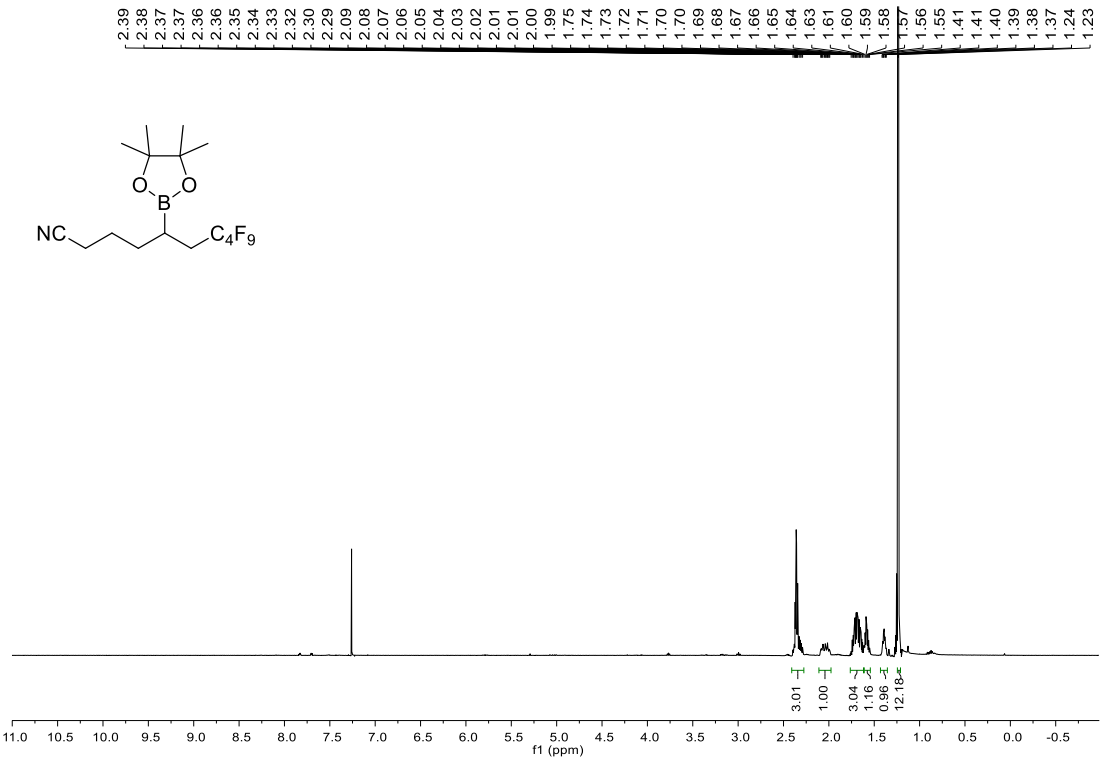


^{11}B NMR (96 MHz, $CDCl_3$)

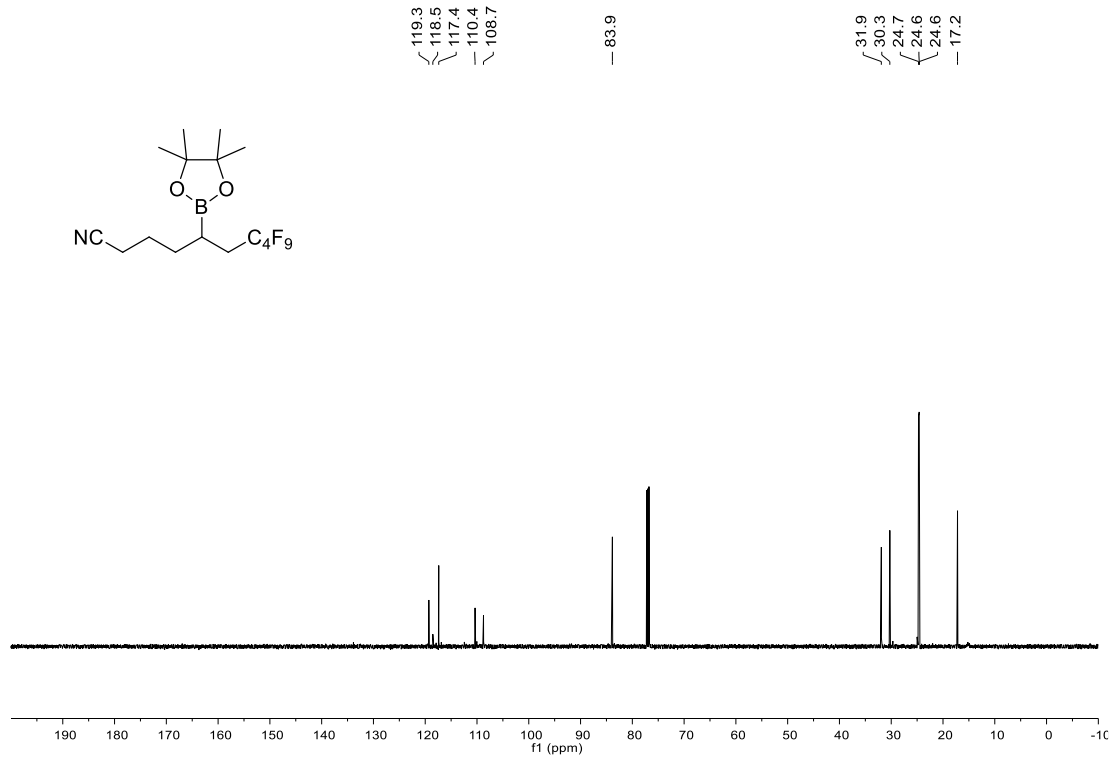


7,7,8,8,9,9,10,10,10-Nonafluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decanenitrile (4y)

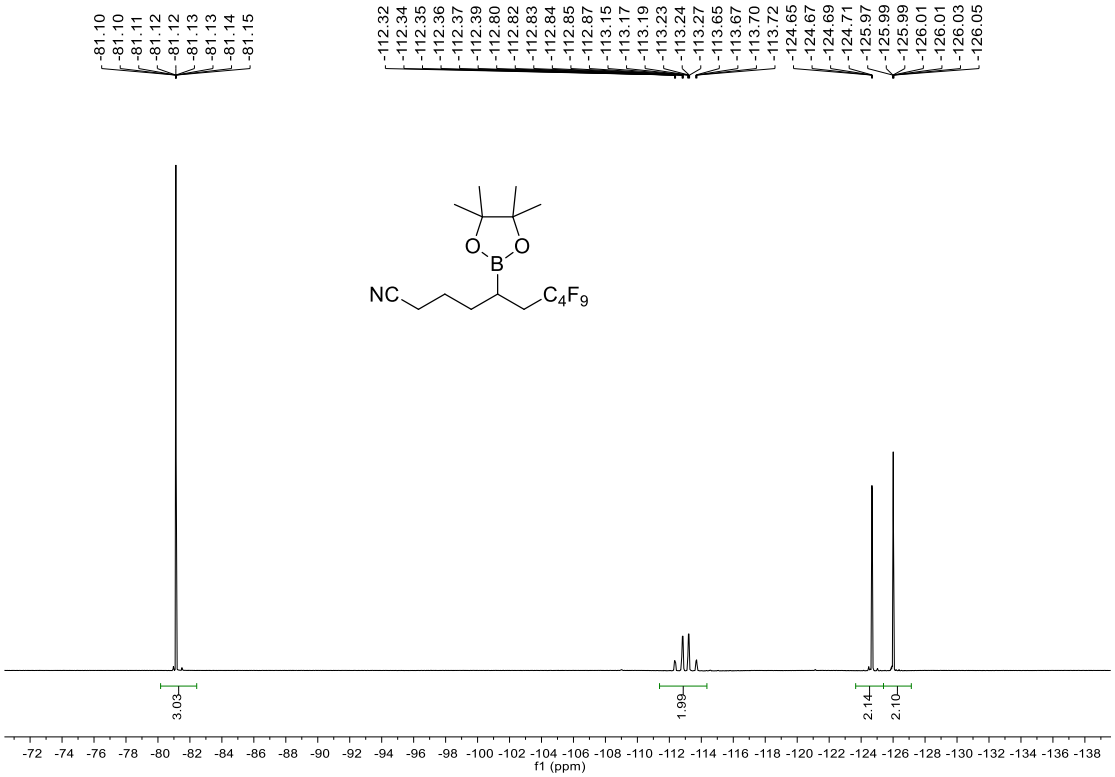
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm)



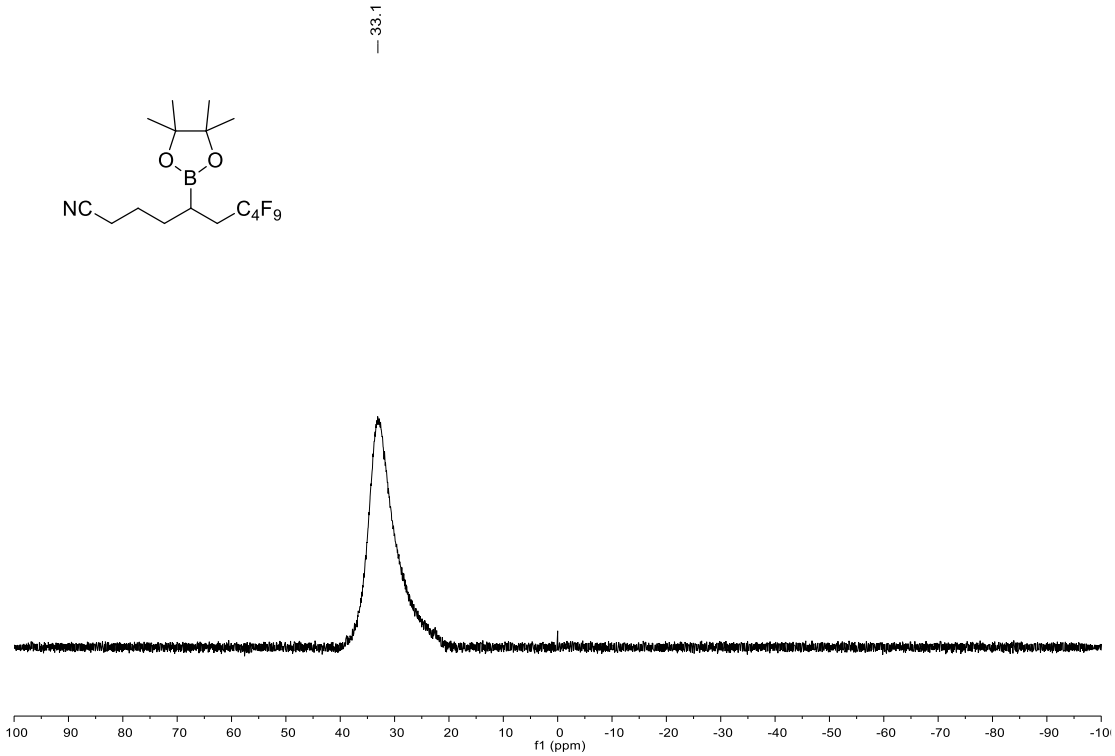
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

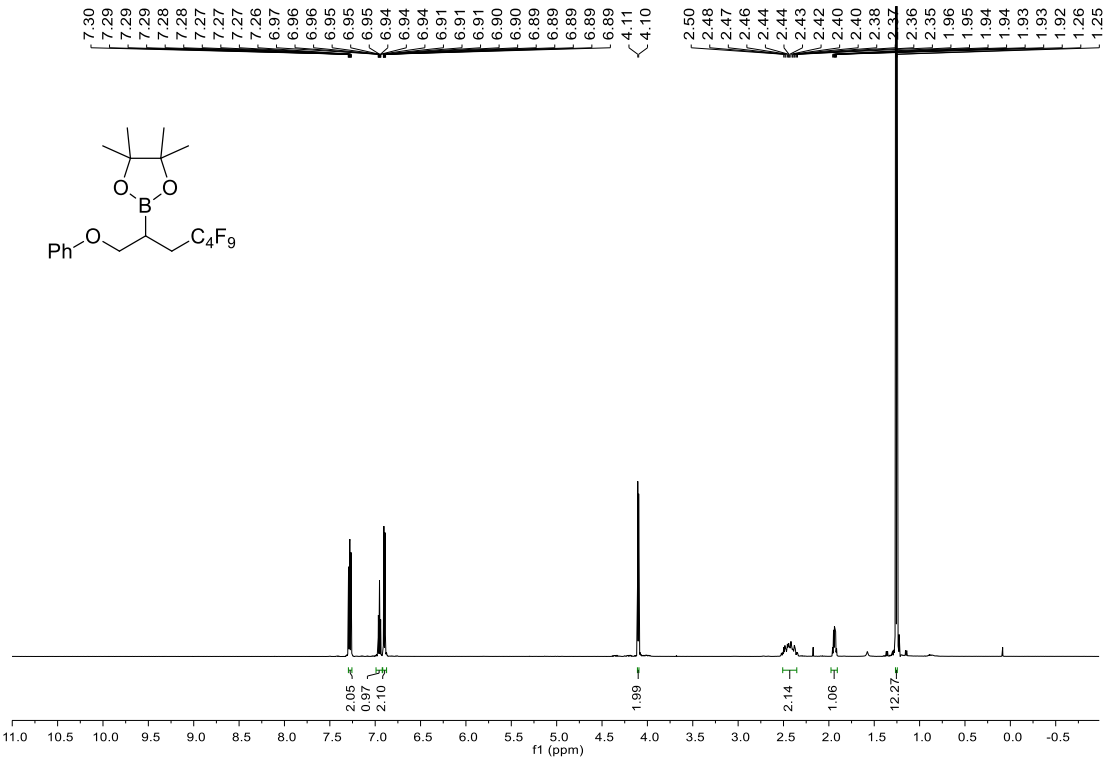


^{11}B NMR (96 MHz, $CDCl_3$)

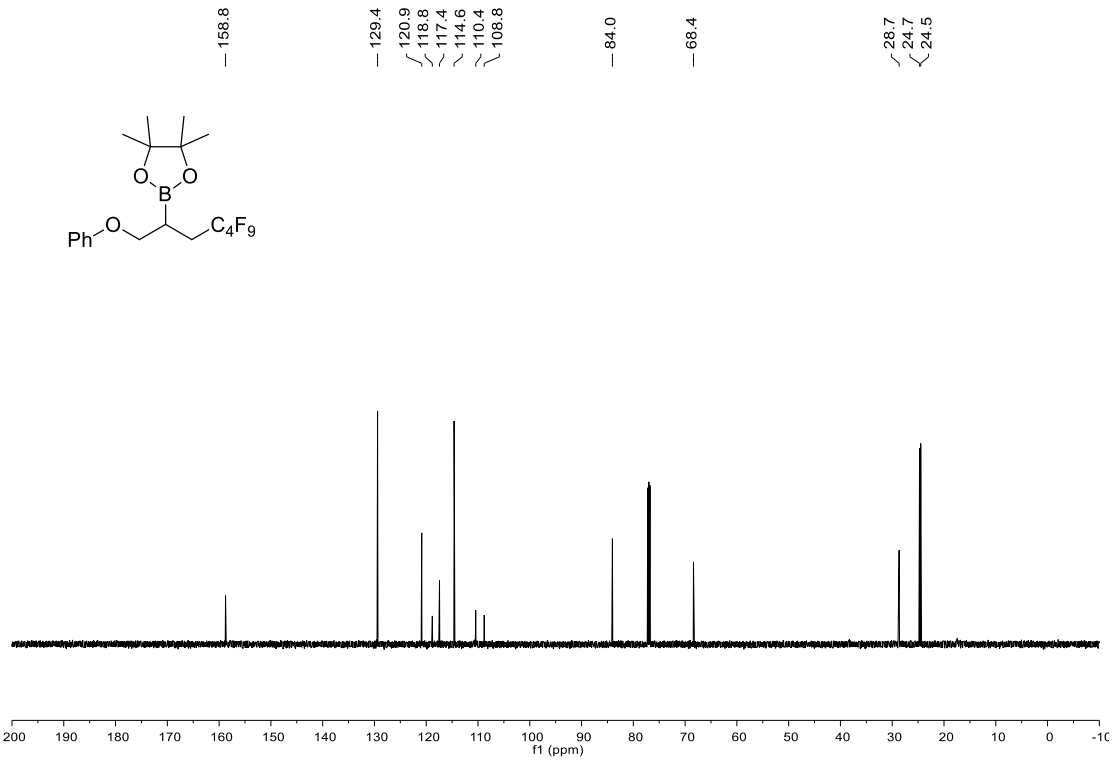


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-phenoxyheptan-2-yl)-1,3,2-dioxaborolane (4z)

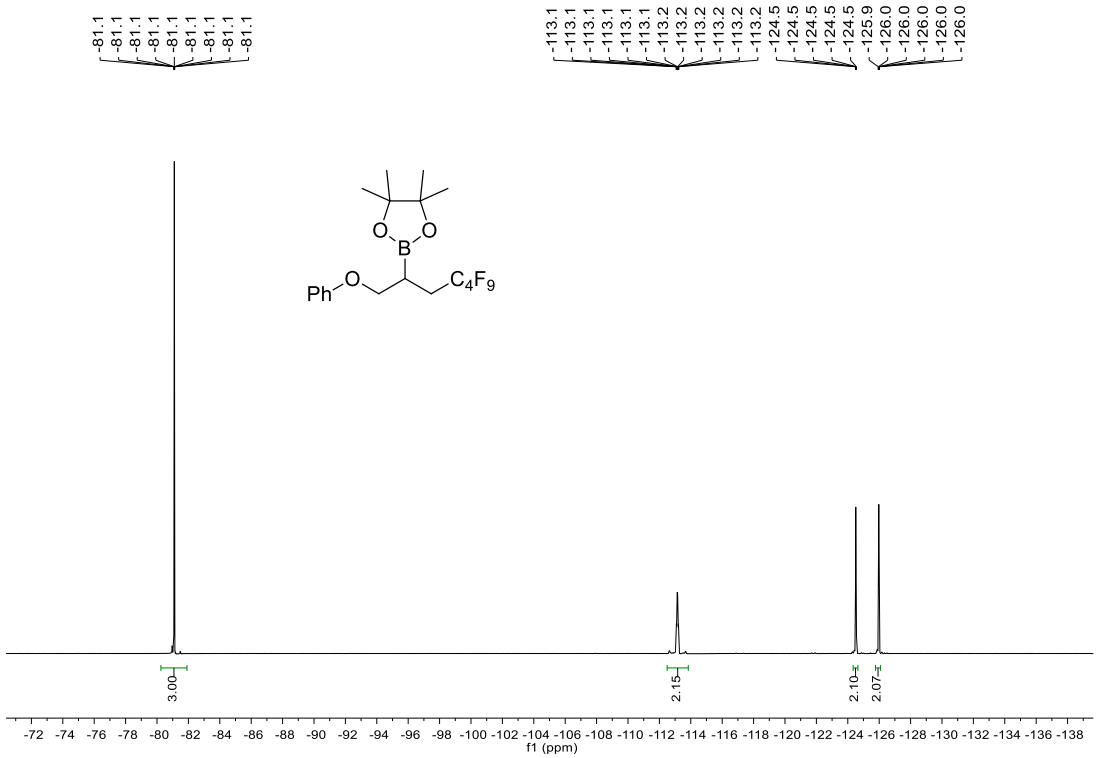
^{1}H NMR (600 MHz, $CDCl_3$)



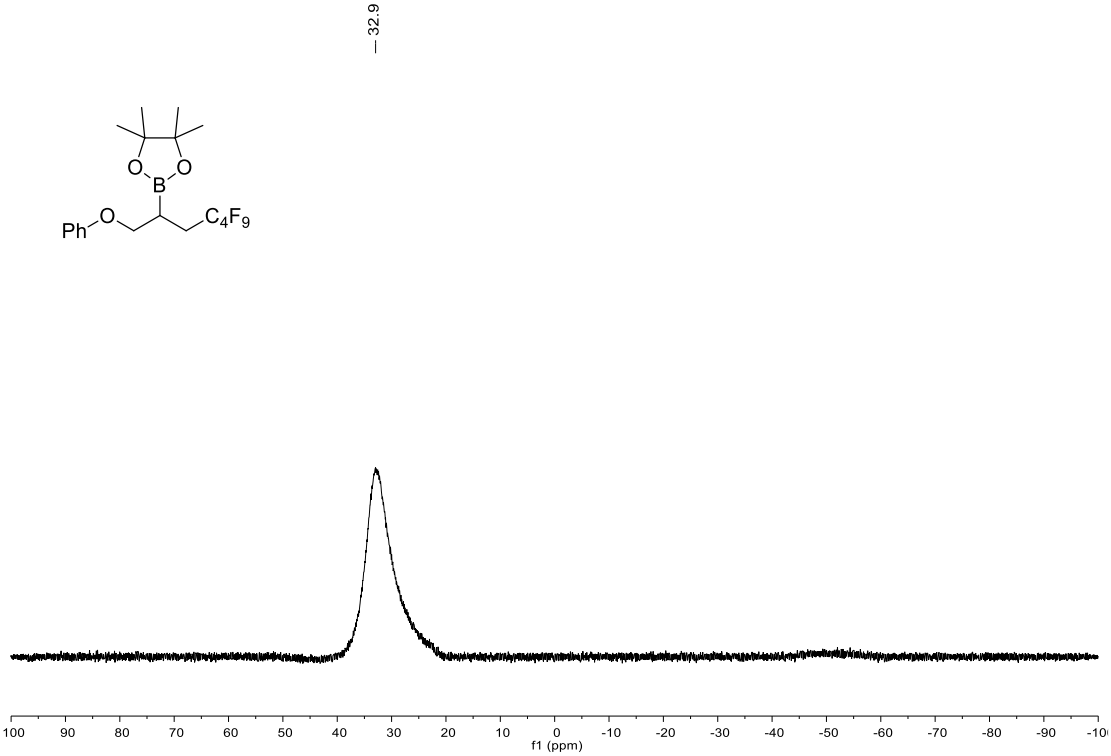
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

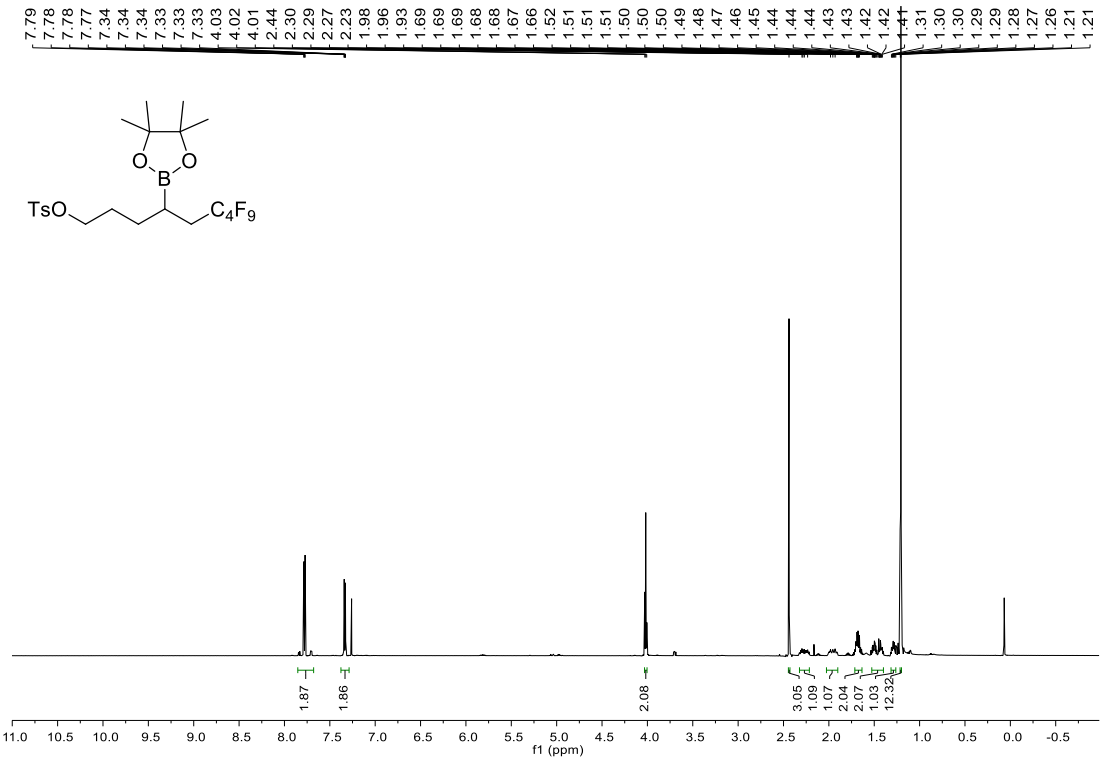


^{11}B NMR (96 MHz, $CDCl_3$)

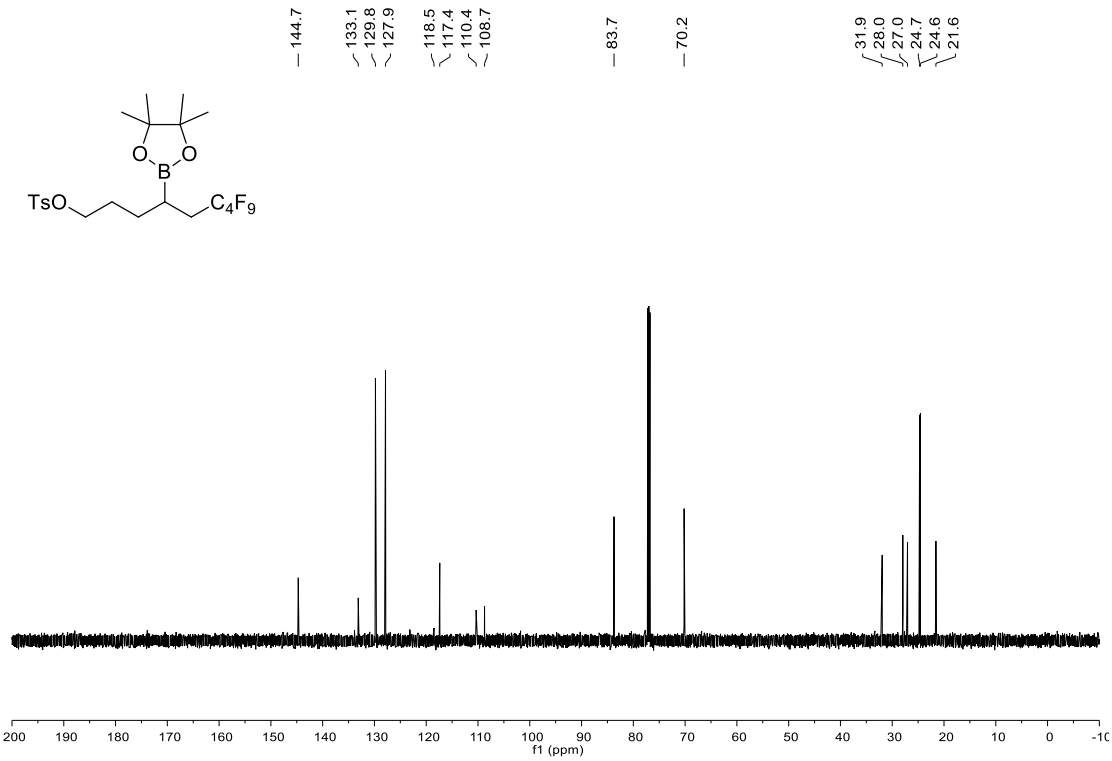


6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl 4-methylbenzenesulfonate (4aa)

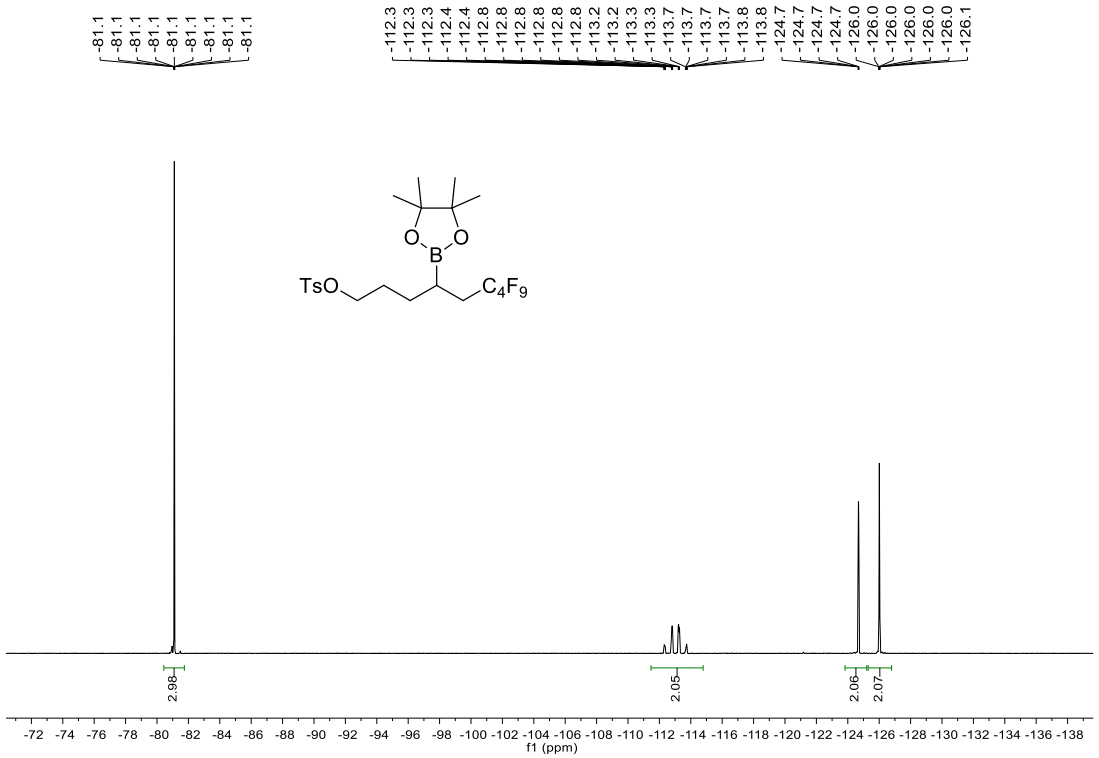
^{1}H NMR (600 MHz, $CDCl_3$)



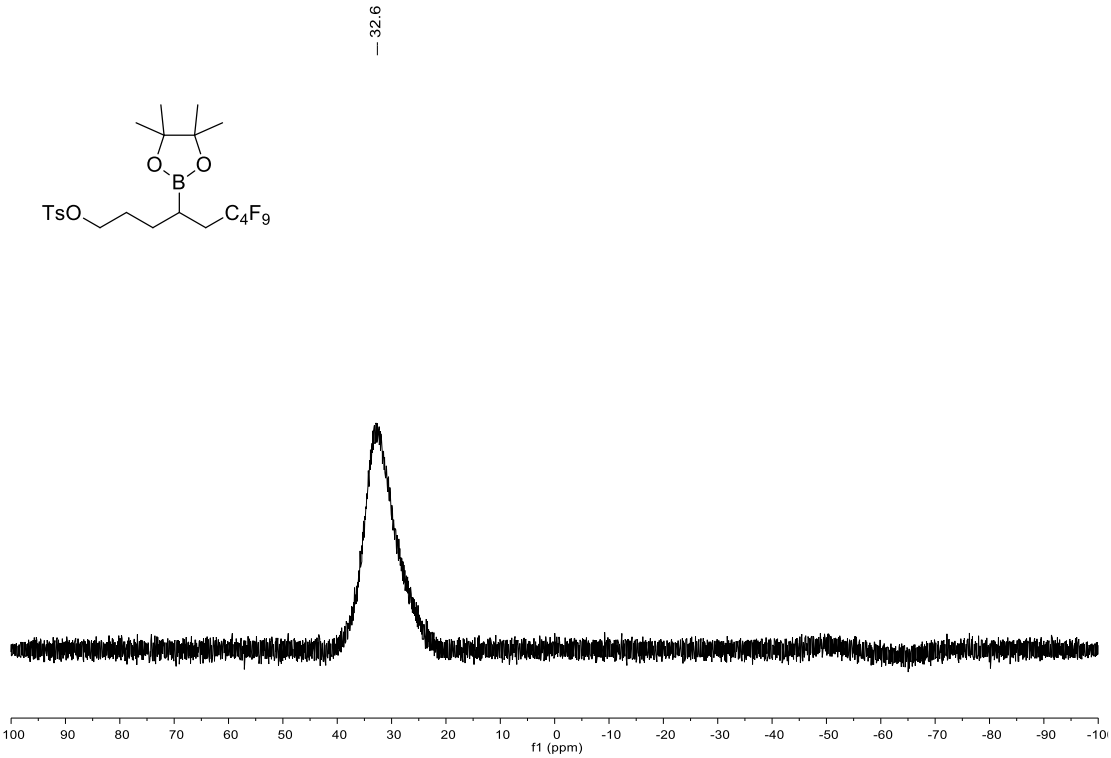
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

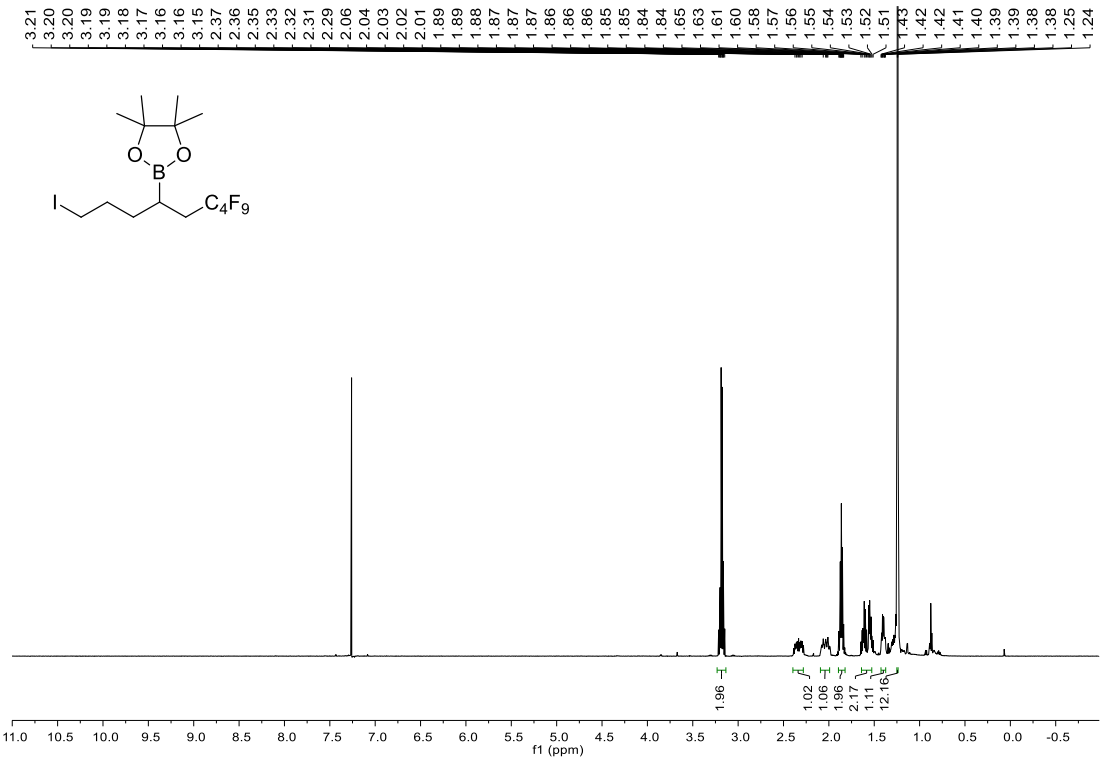


^{11}B NMR (96 MHz, $CDCl_3$)

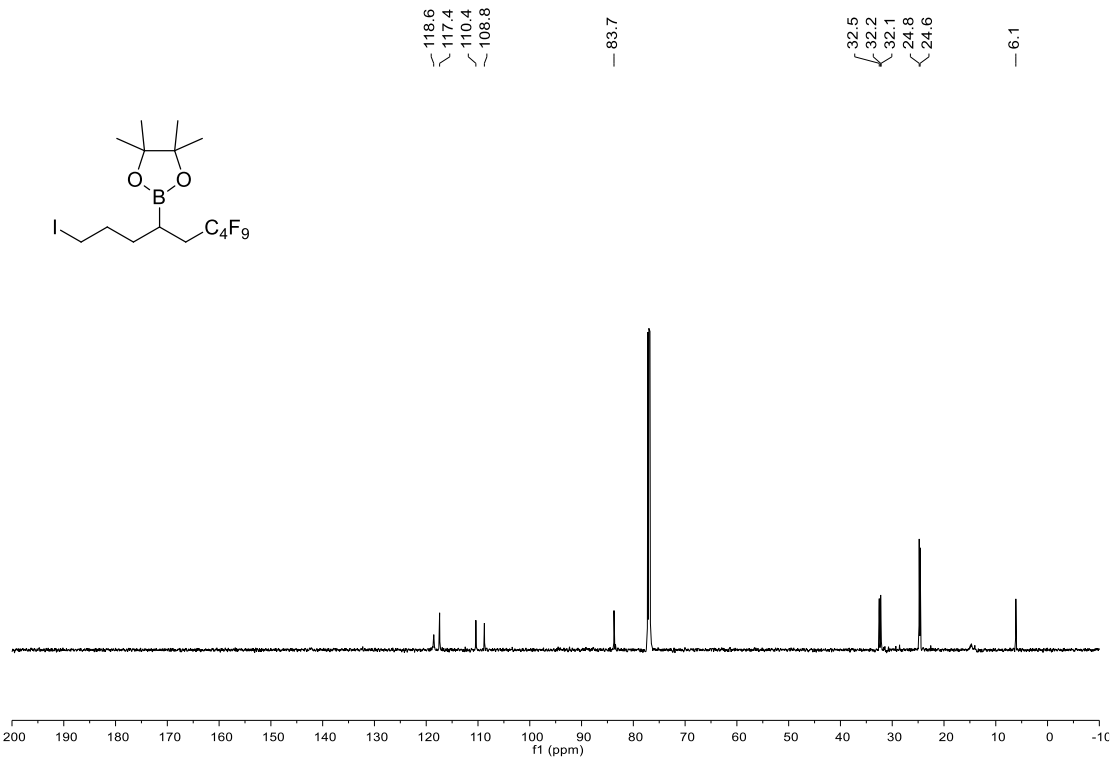


4,4,5,5-Tetramethyl-2-(6,6,7,7,8,8,9,9,9-nonafluoro-1-iodononan-4-yl)-1,3,2-dioxaborolane (4aa')

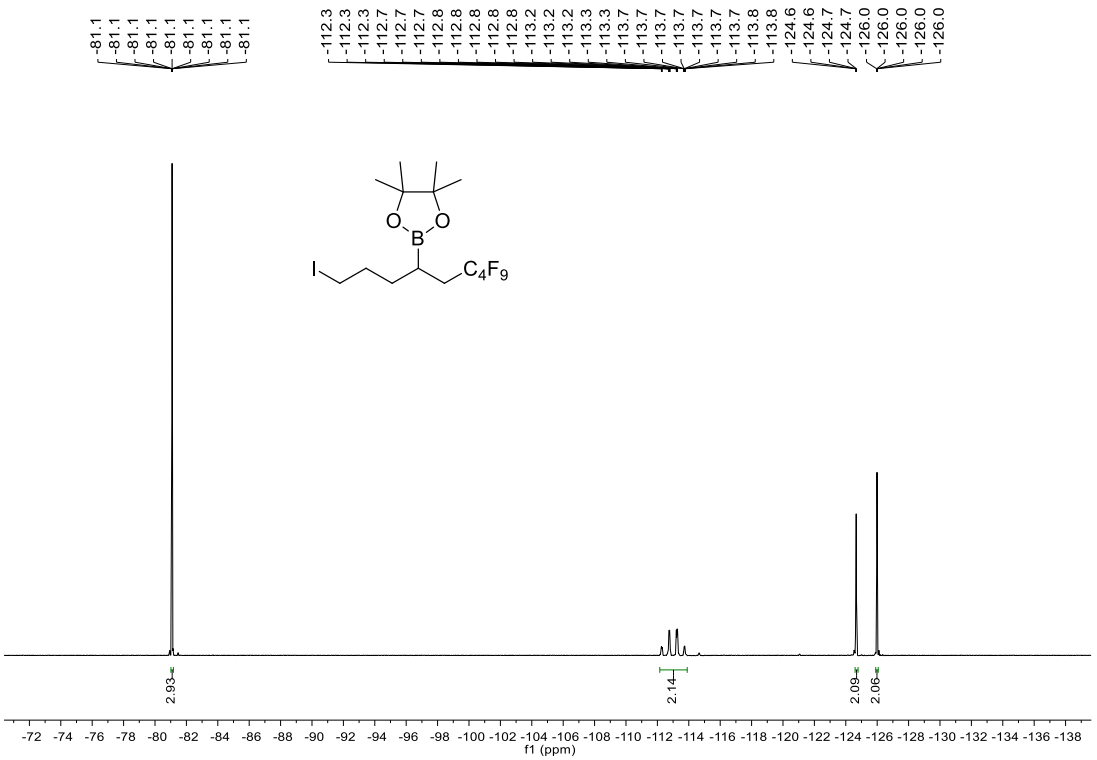
^{1}H NMR (600 MHz, $CDCl_3$)



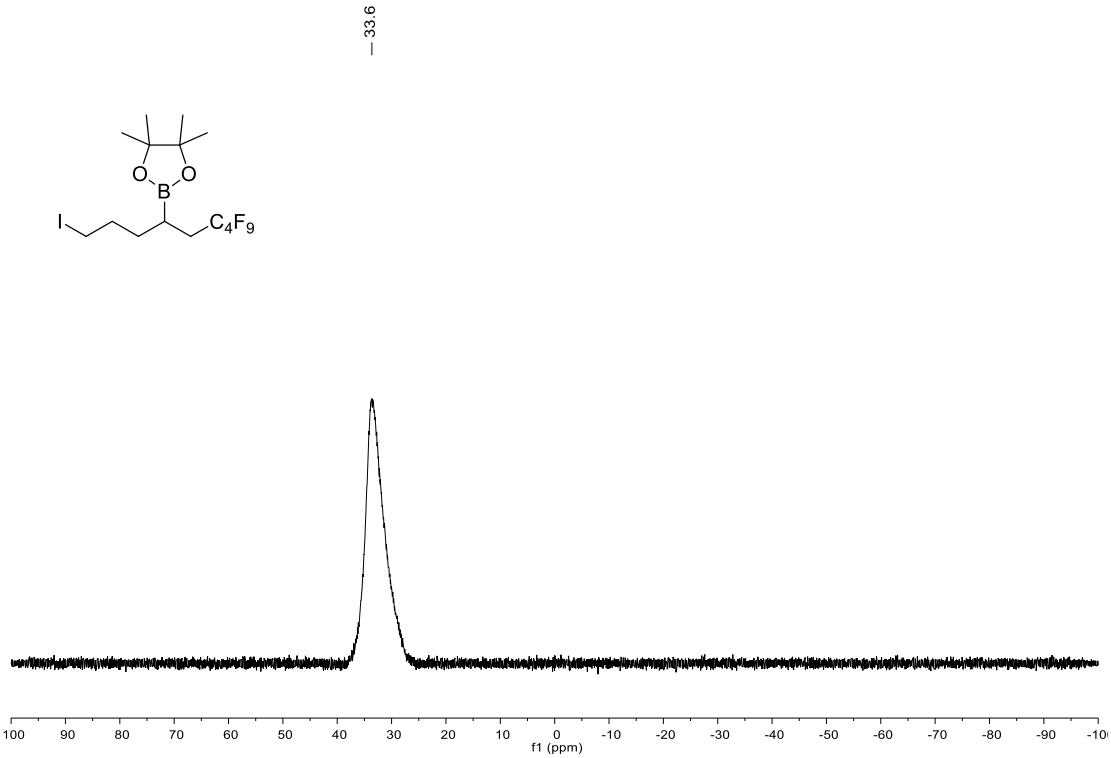
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

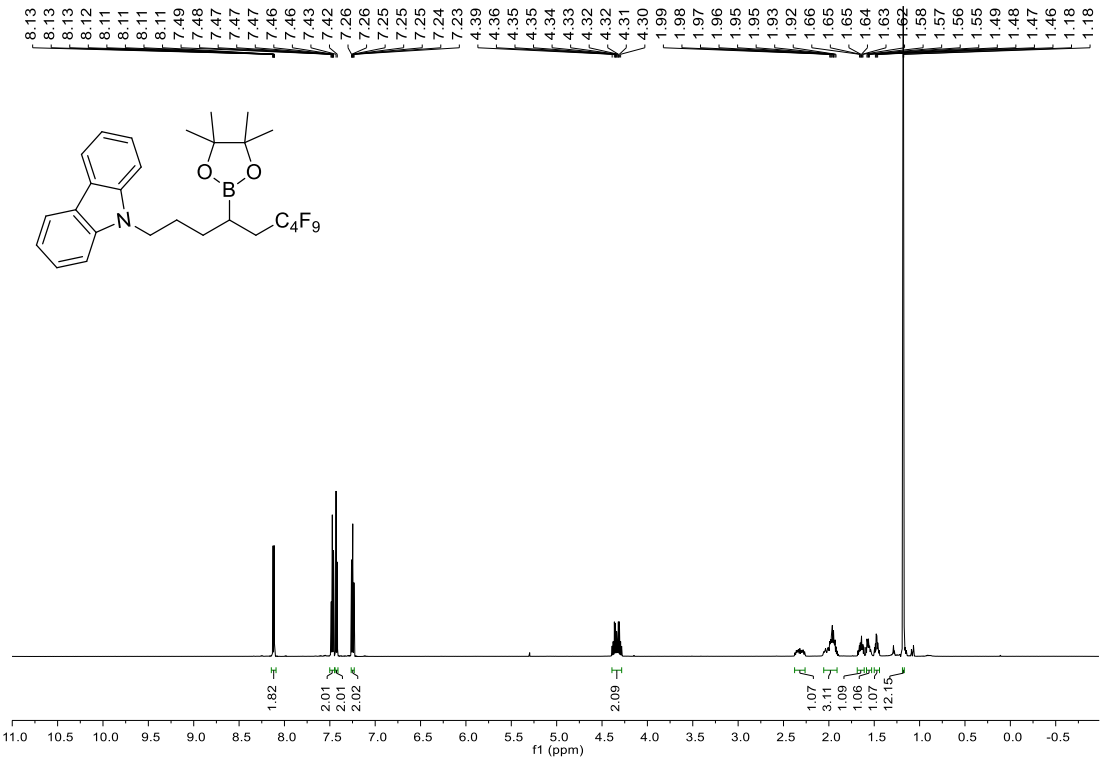


^{11}B NMR (96 MHz, $CDCl_3$)

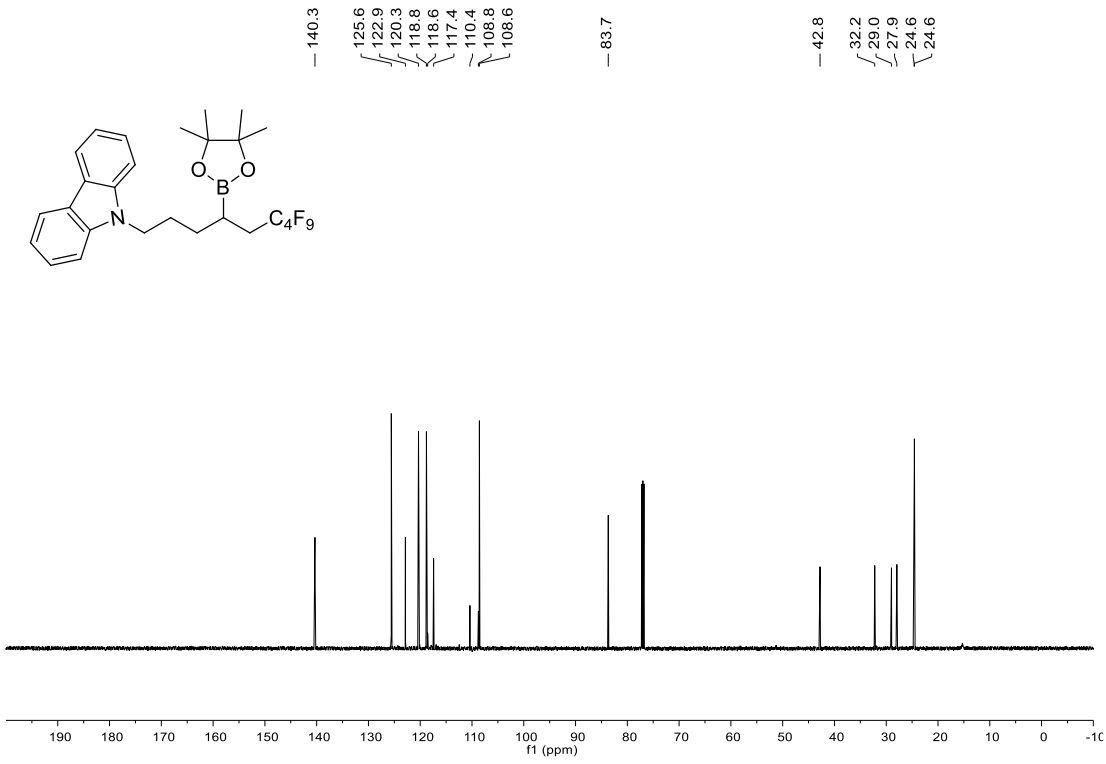


9-(6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)-9*H*-carbazole (4ab)

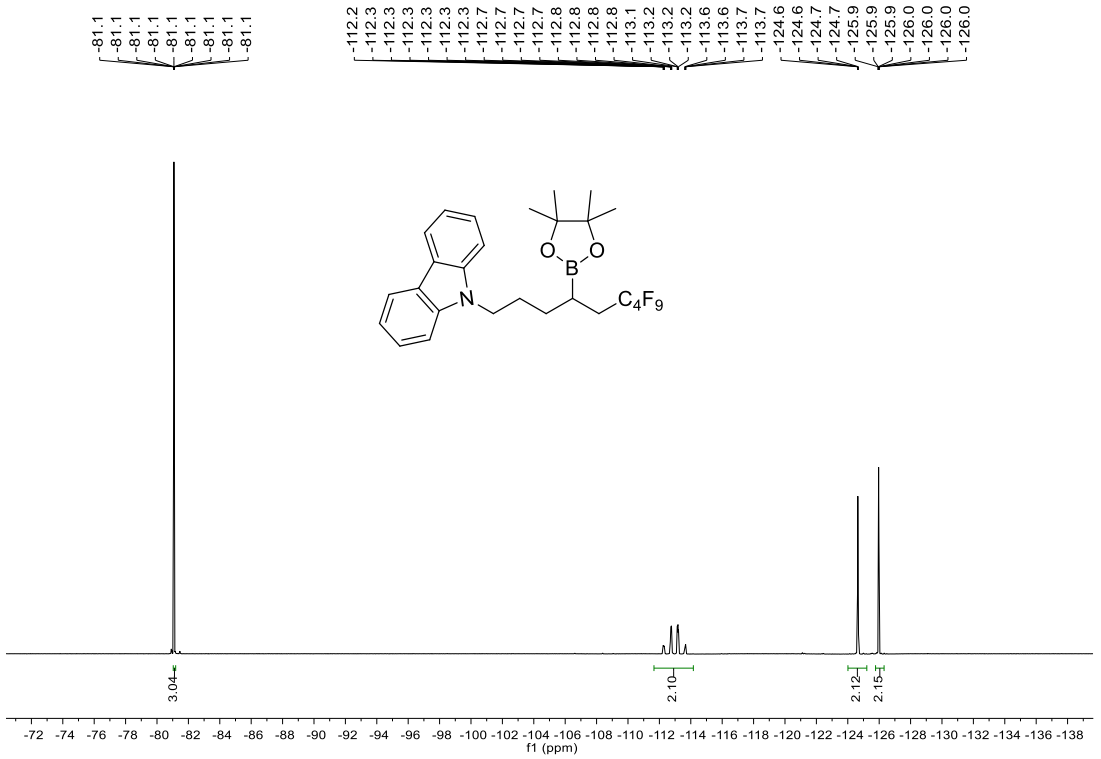
^{1}H NMR (600 MHz, $CDCl_3$)



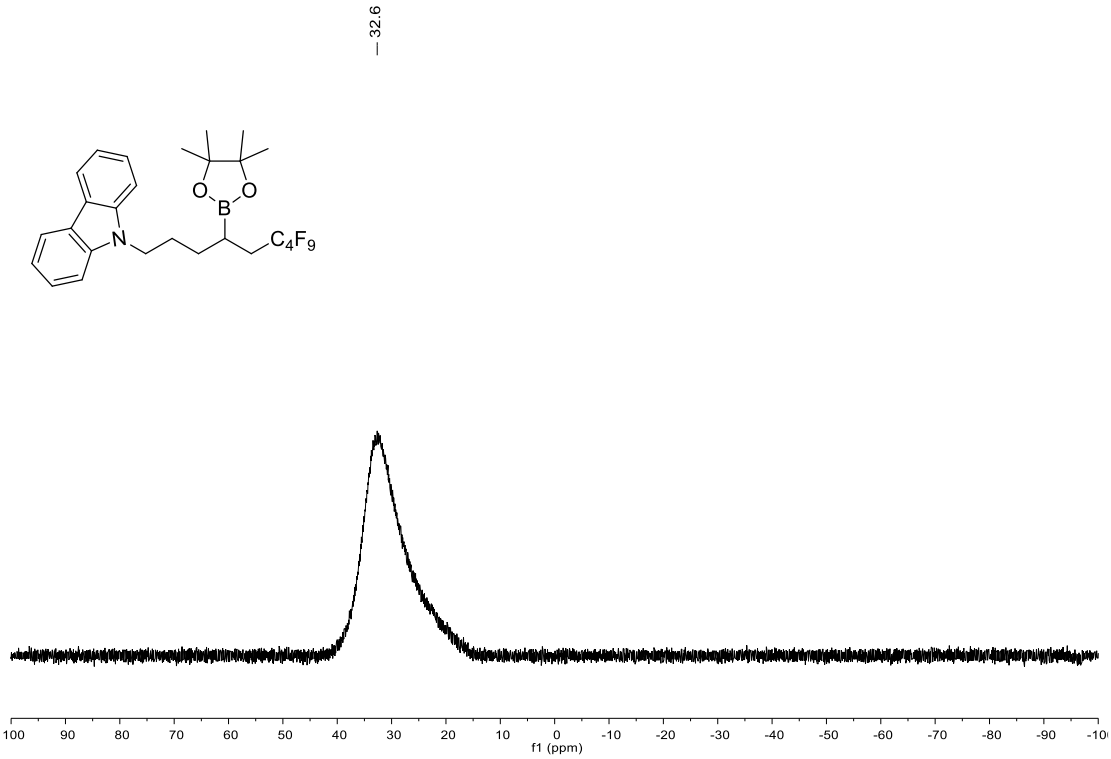
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

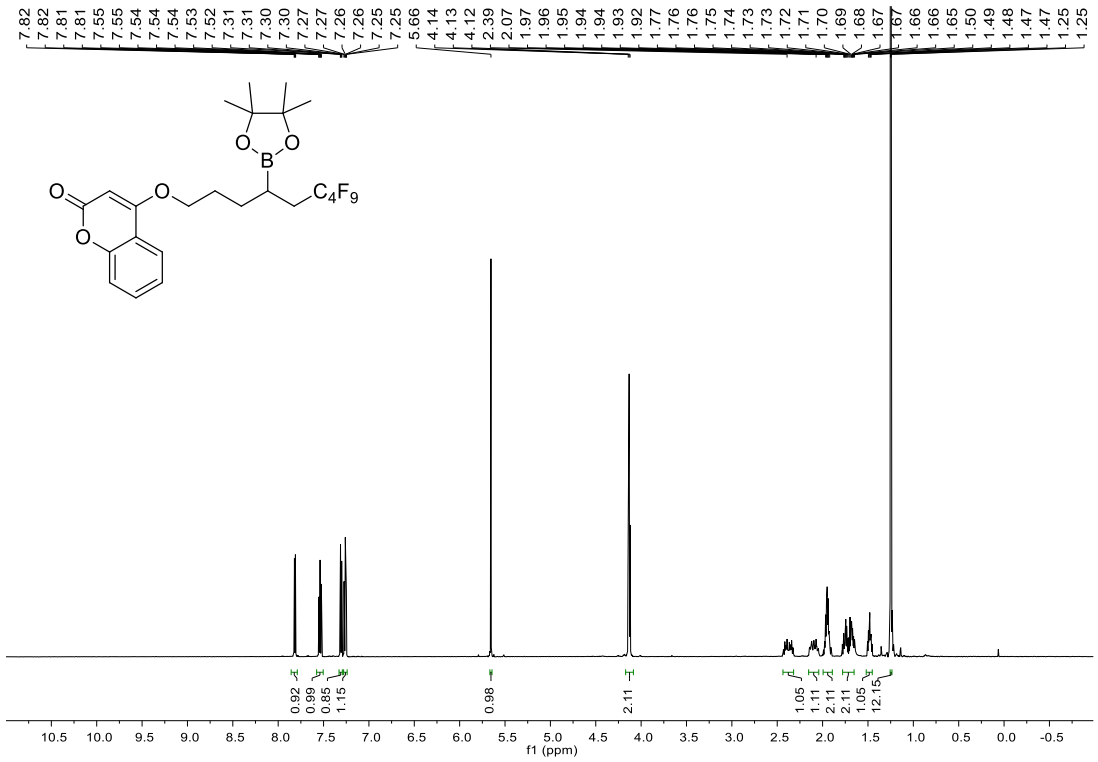


^{11}B NMR (96 MHz, $CDCl_3$)

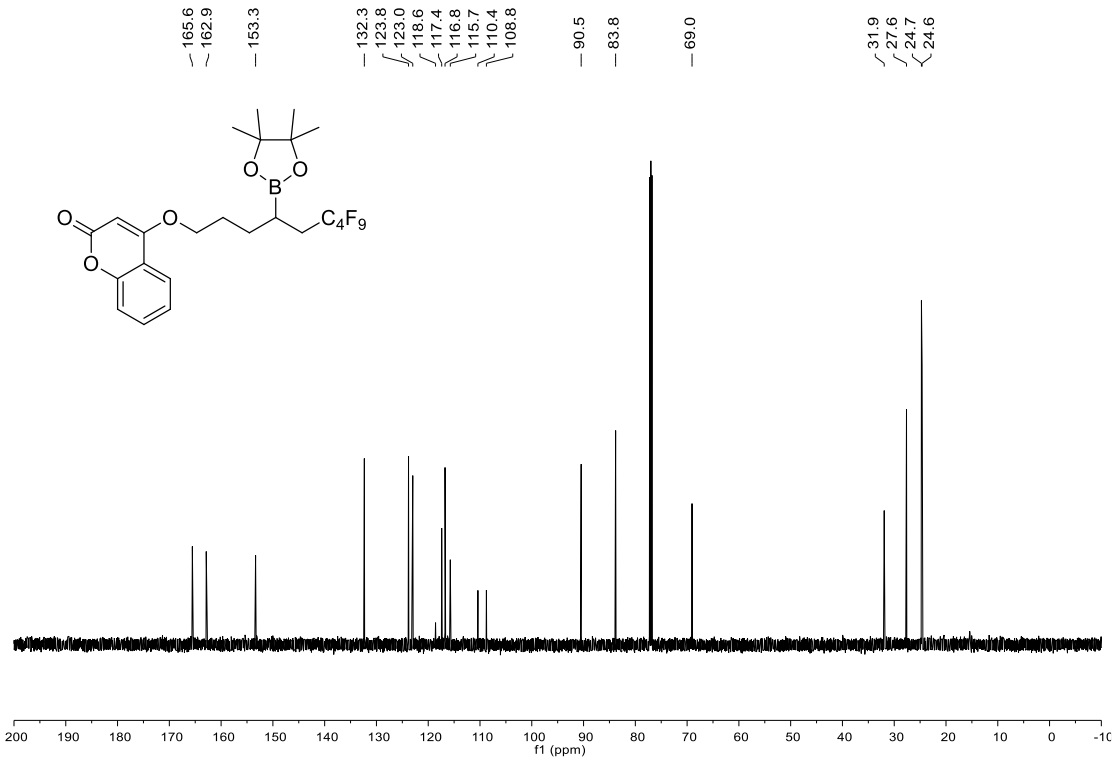


4-((6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)oxy)-2*H*-chromen-2-one (4ac)

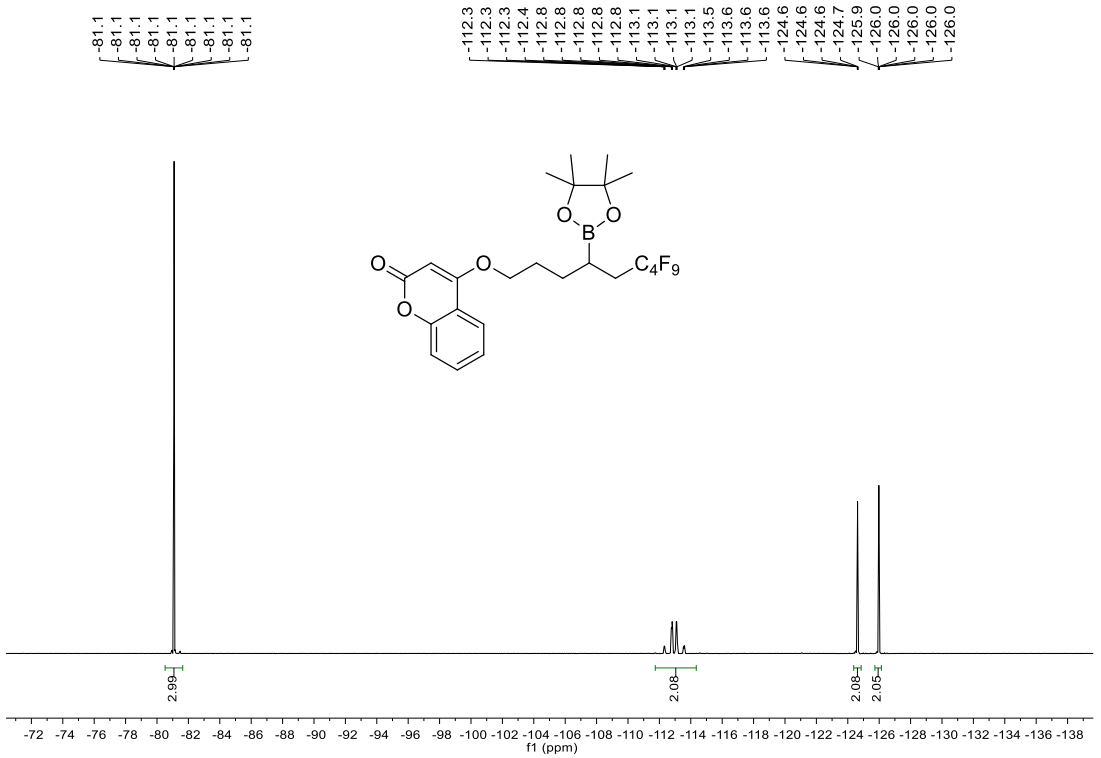
^{1}H NMR (600 MHz, $CDCl_3$)



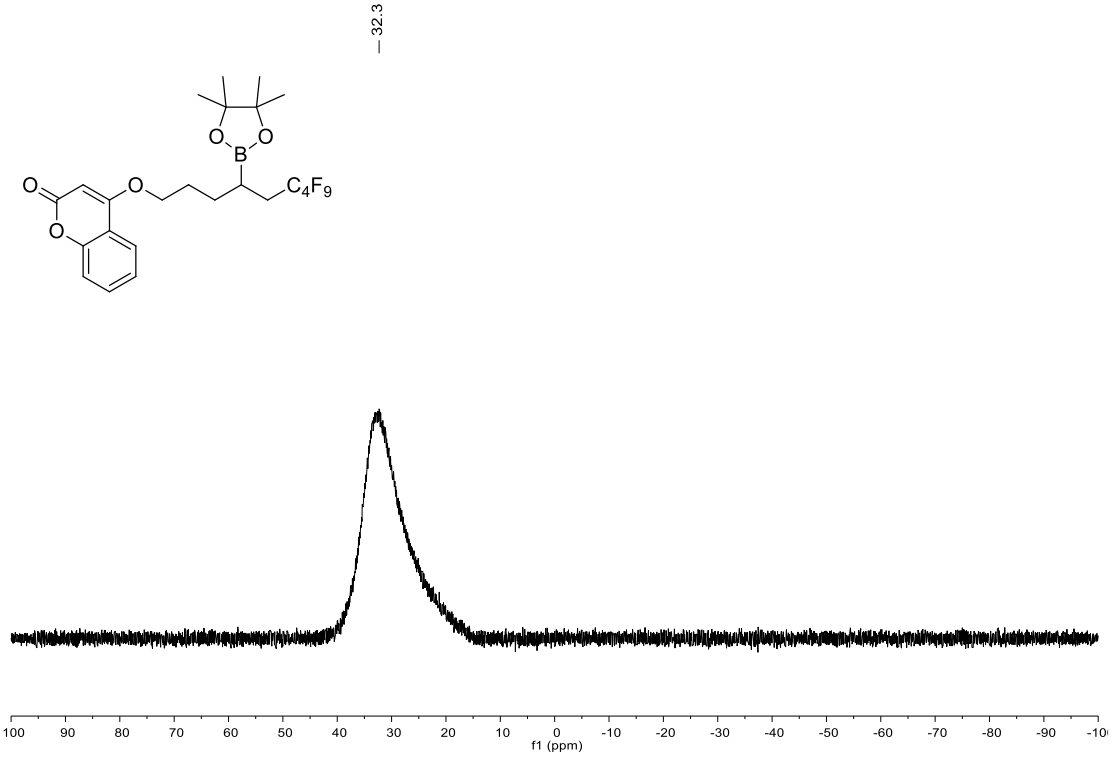
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

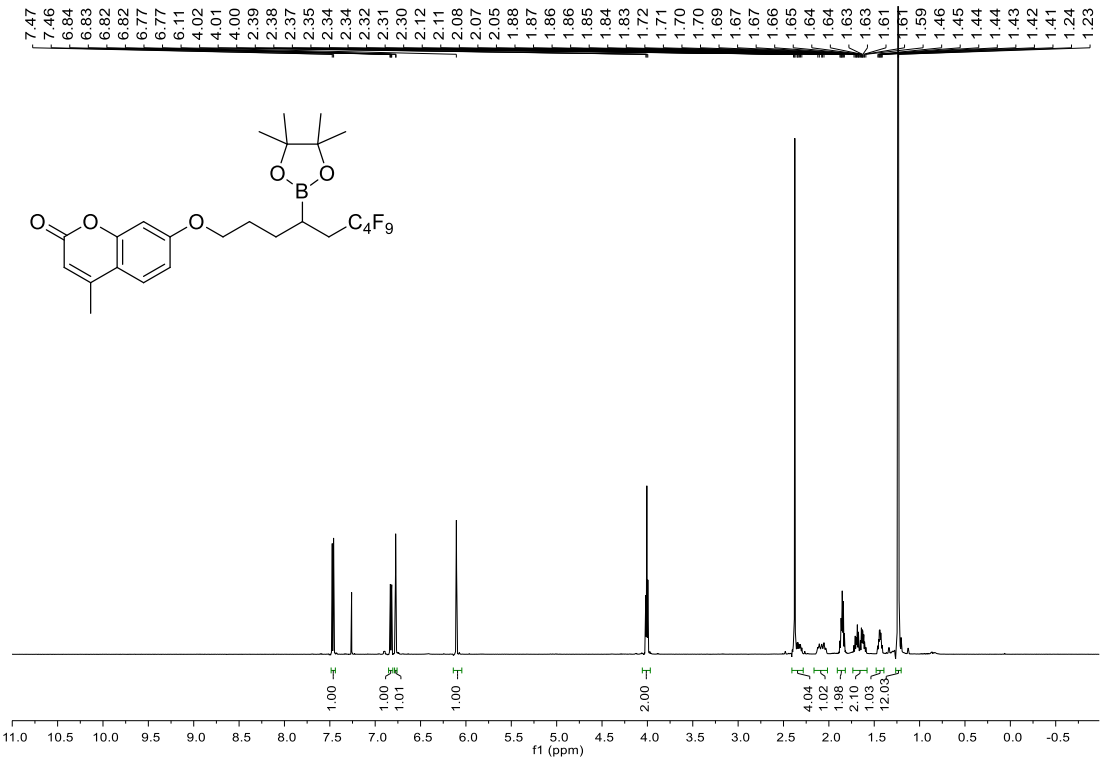


^{11}B NMR (96 MHz, $CDCl_3$)

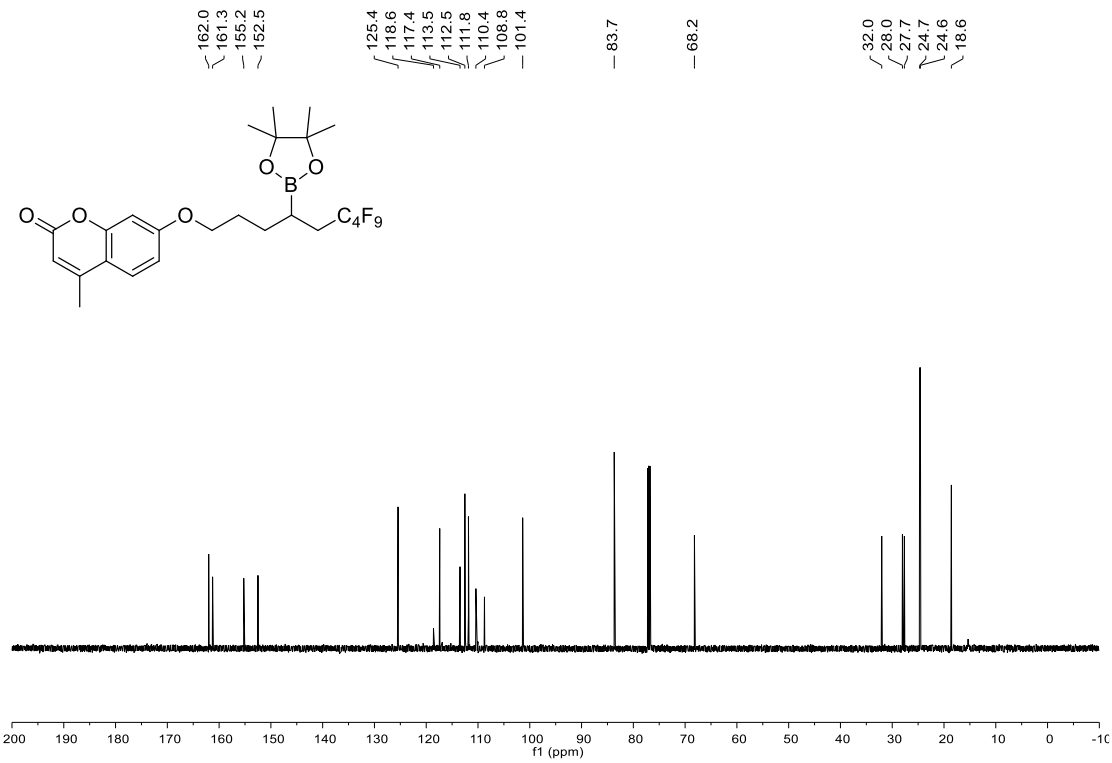


4-Methyl-7-((6,6,7,7,8,8,9,9,9-nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)oxy)-2*H*-chromen-2-one (4ad)

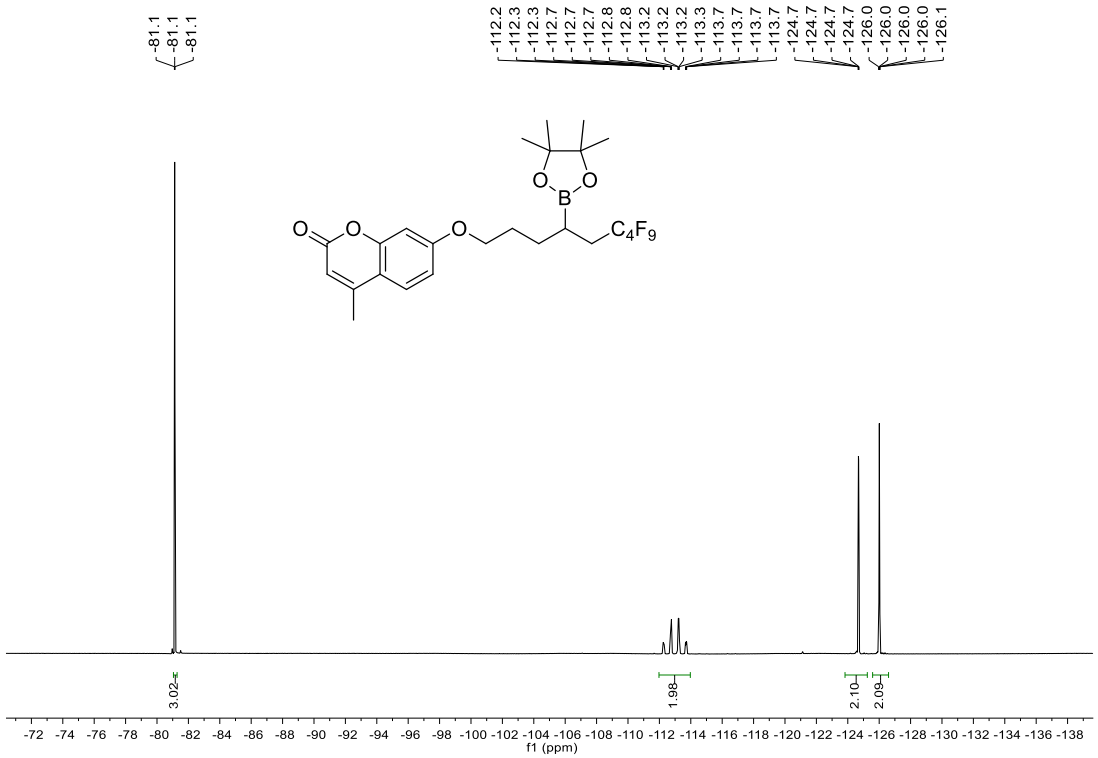
^{1}H NMR (600 MHz, $CDCl_3$)



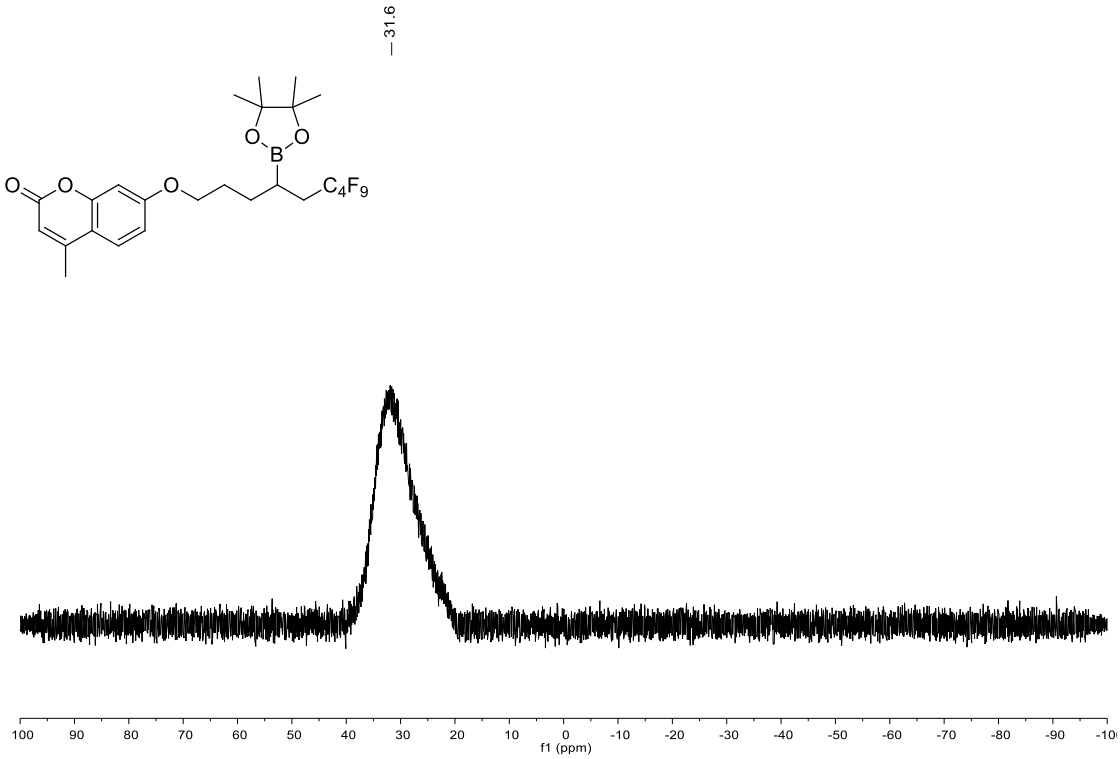
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

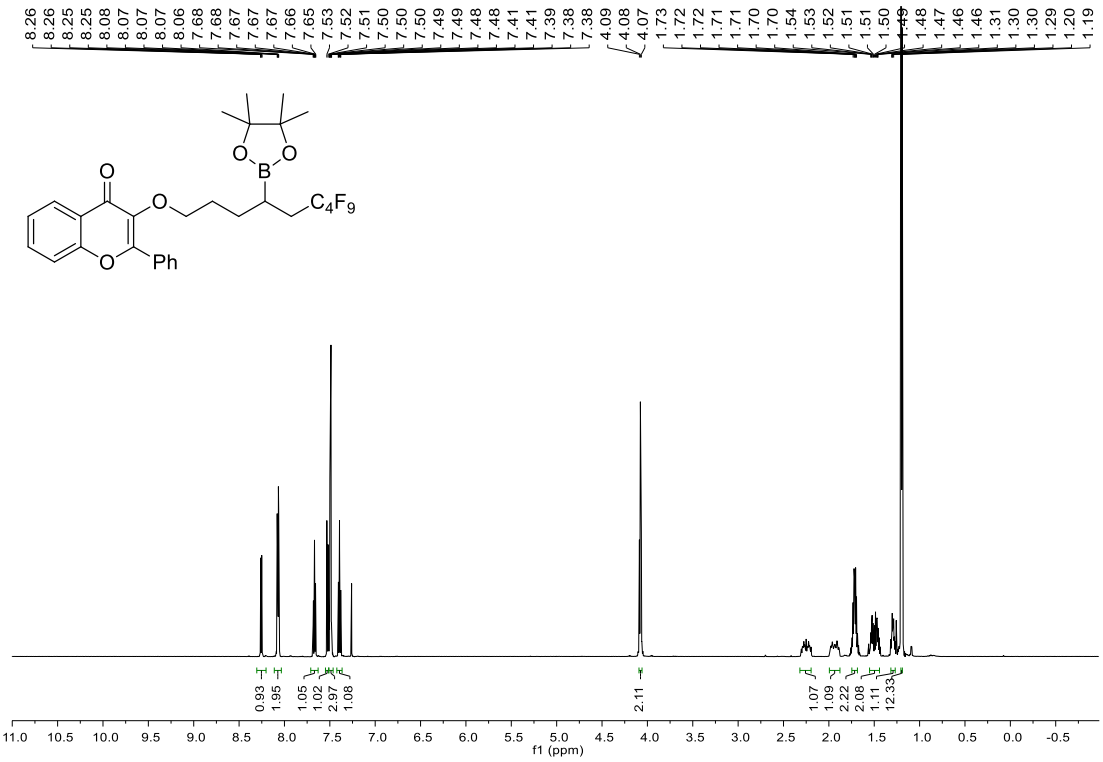


^{11}B NMR (96 MHz, $CDCl_3$)

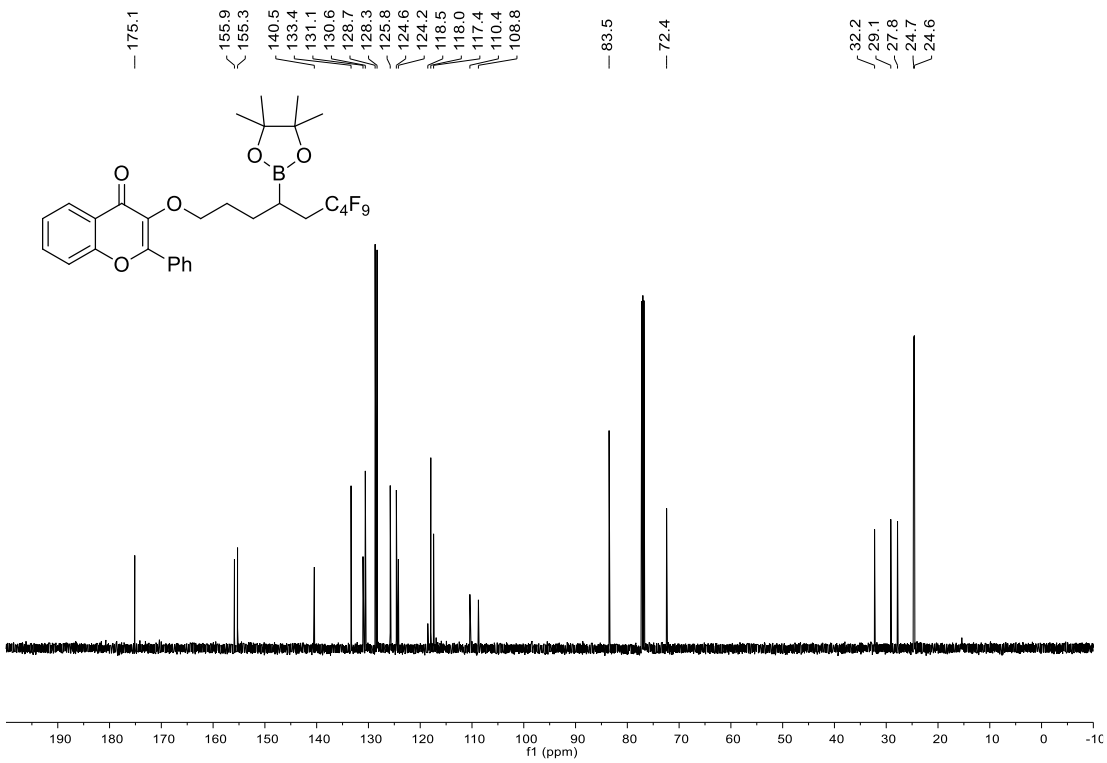


3-((6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)oxy)-2-phenyl-4*H*-chromen-4-one (4ae)

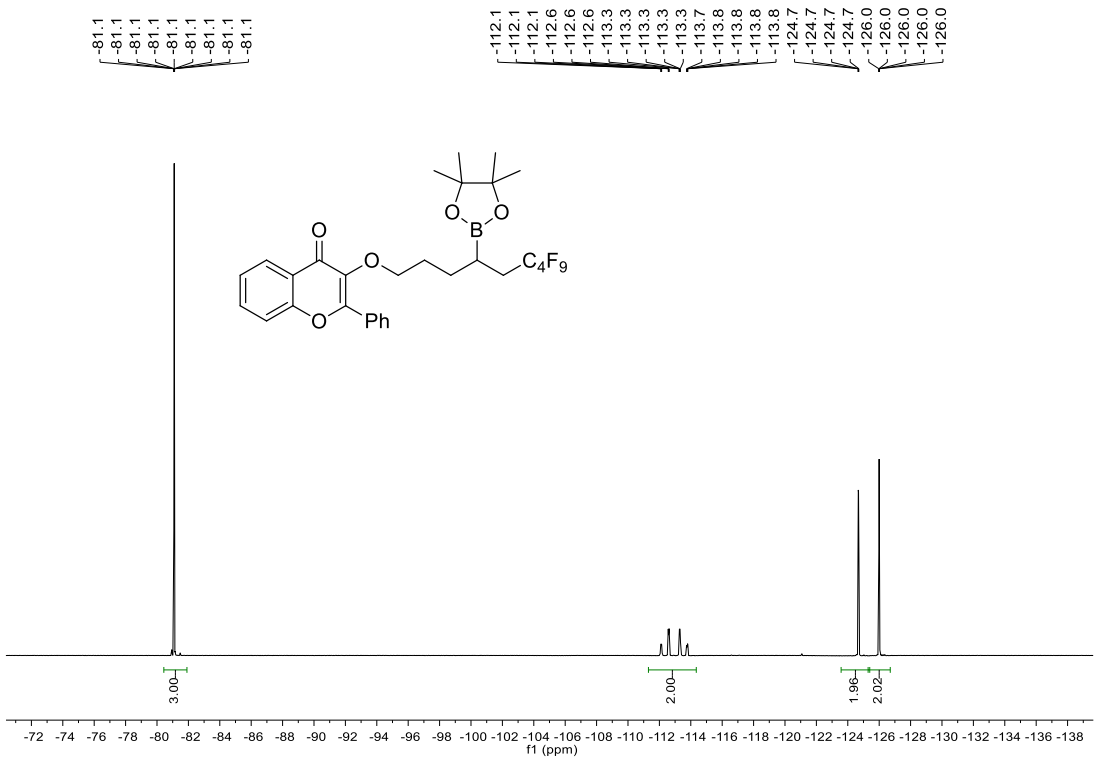
^{1}H NMR (600 MHz, $CDCl_3$)



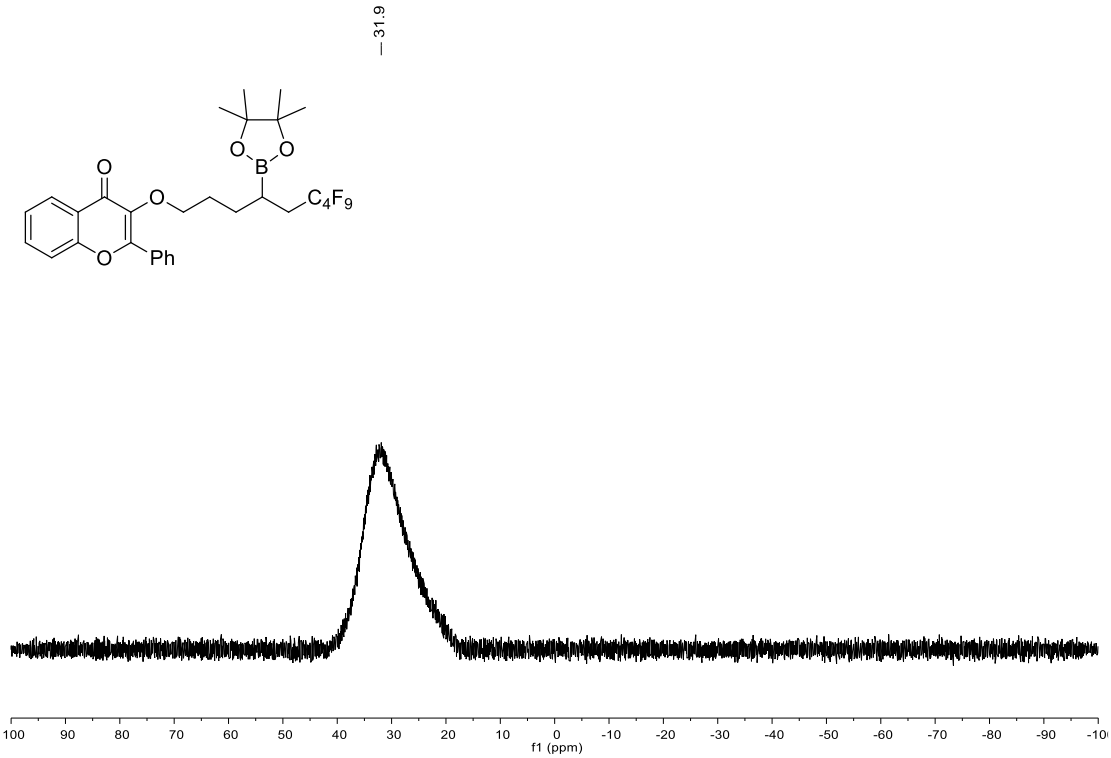
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

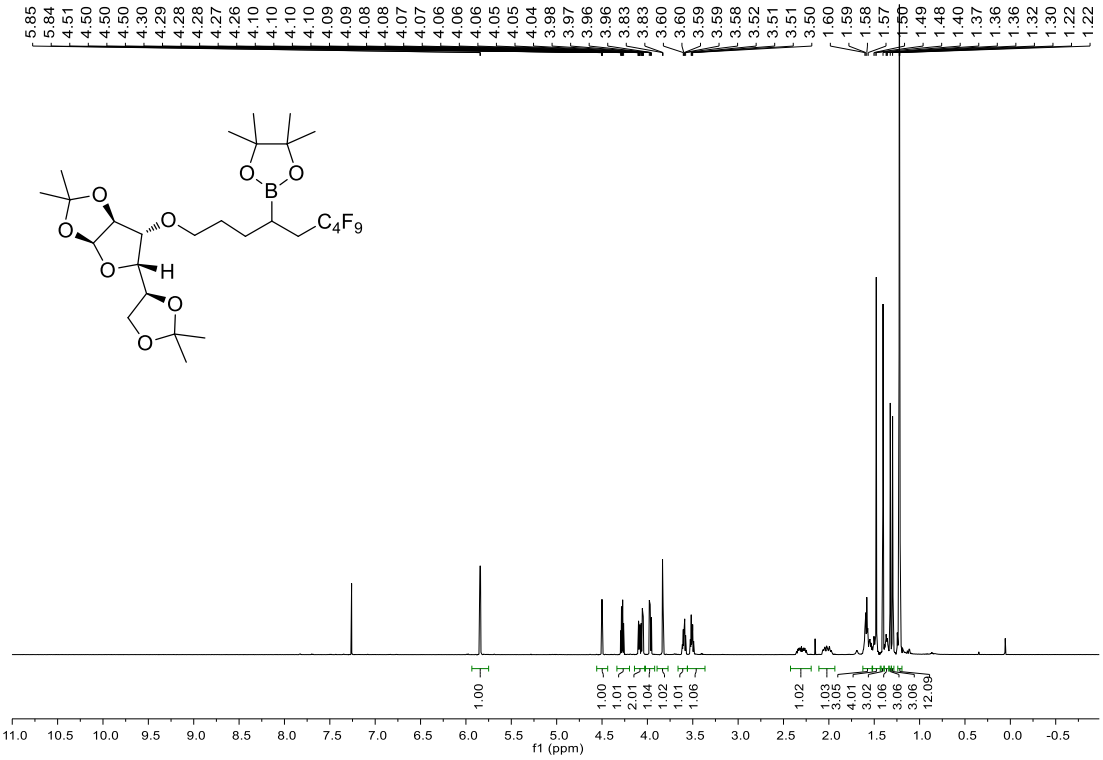


^{11}B NMR (96 MHz, $CDCl_3$)

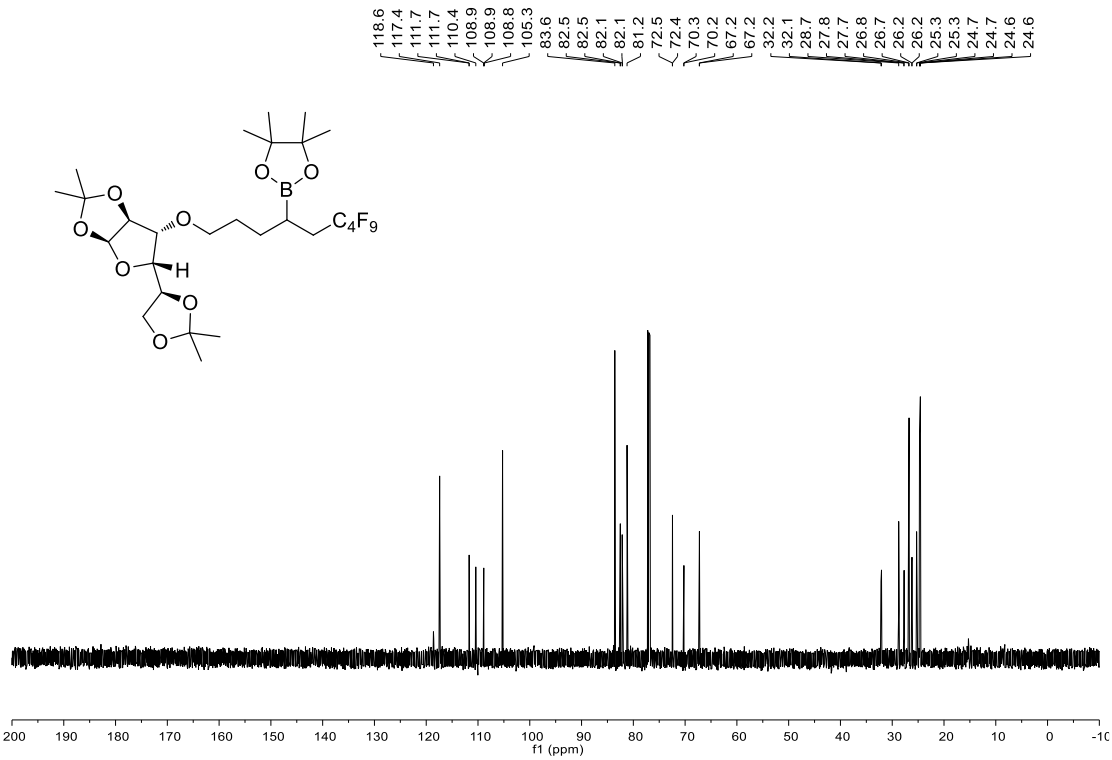


2-(1-(((3a*S*,5*S*,6*R*,6a*S*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)-6,6,7,7,8,8,9,9,9-nonafluorononan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4af)

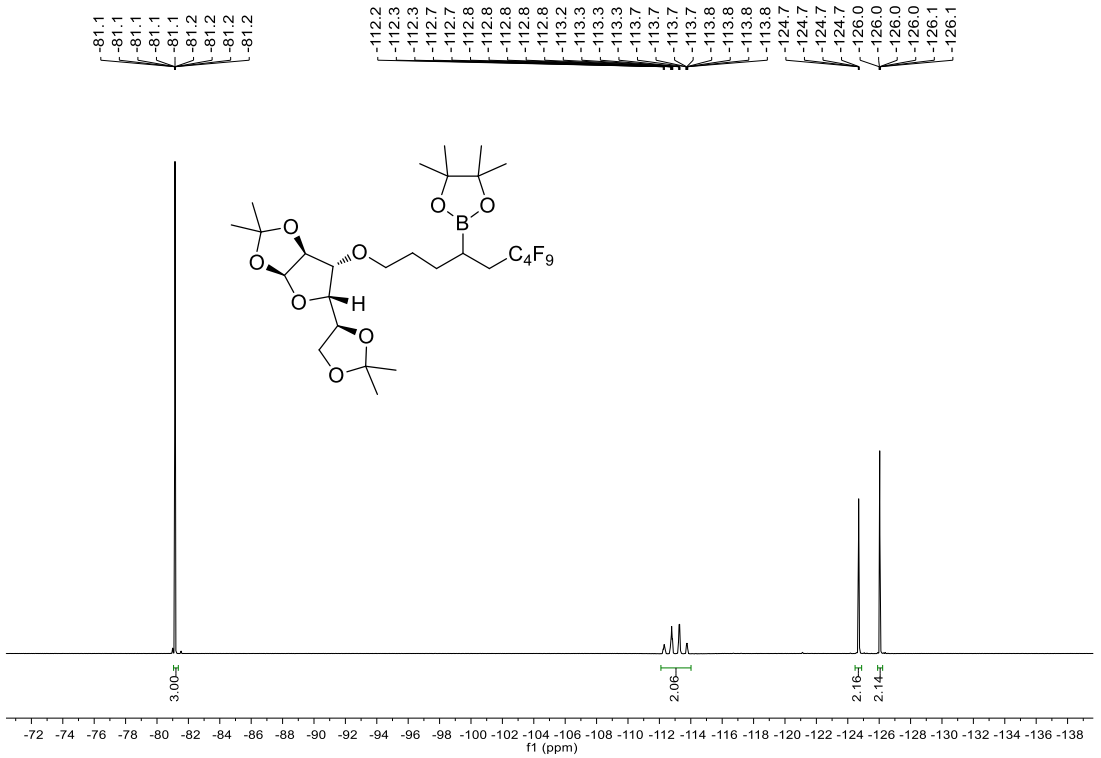
^{1}H NMR (600 MHz, $CDCl_3$)



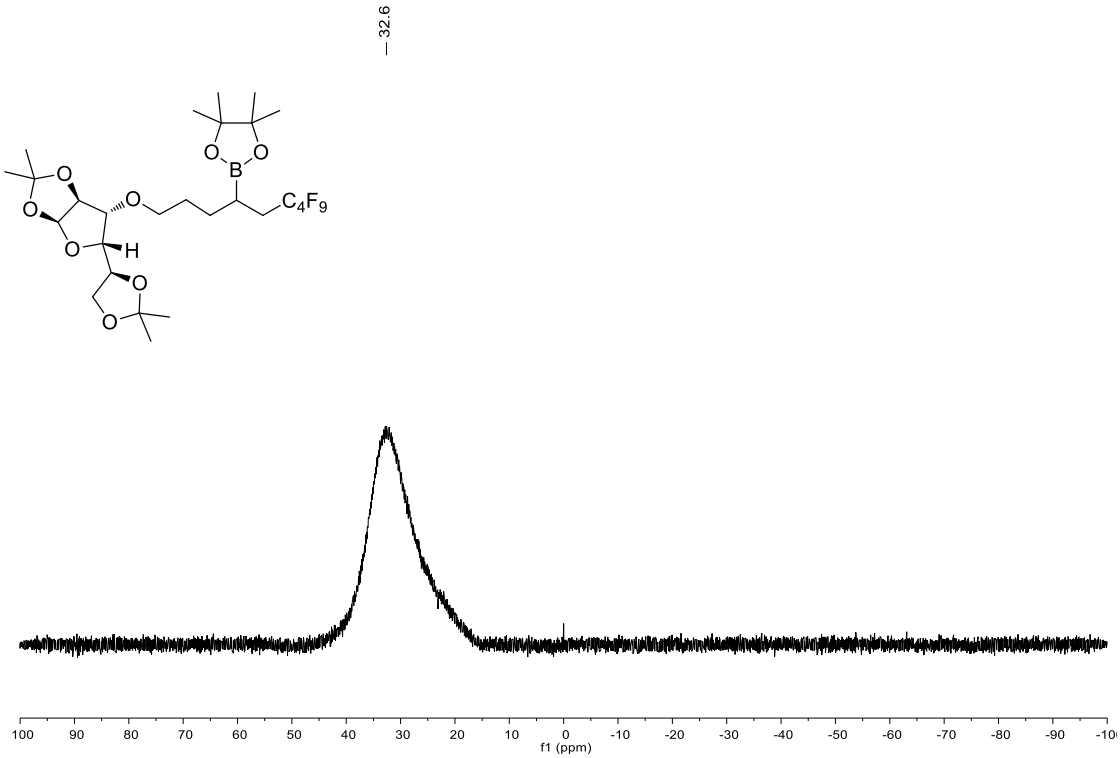
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

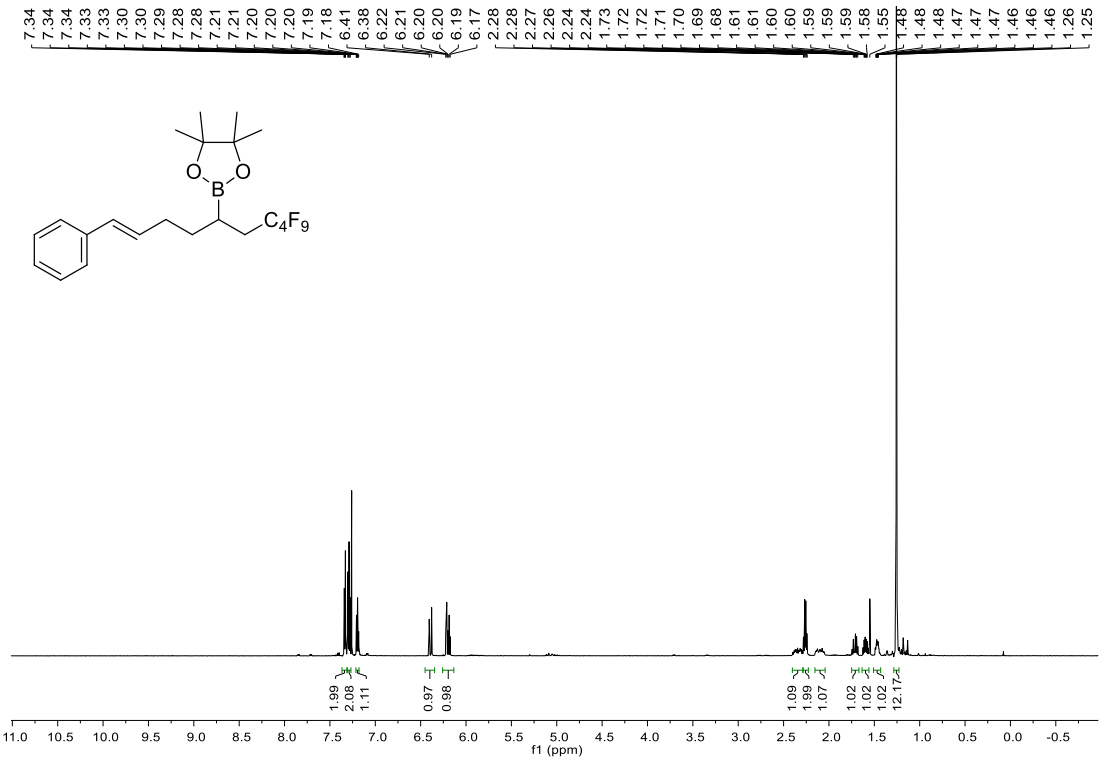


^{11}B NMR (96 MHz, $CDCl_3$)

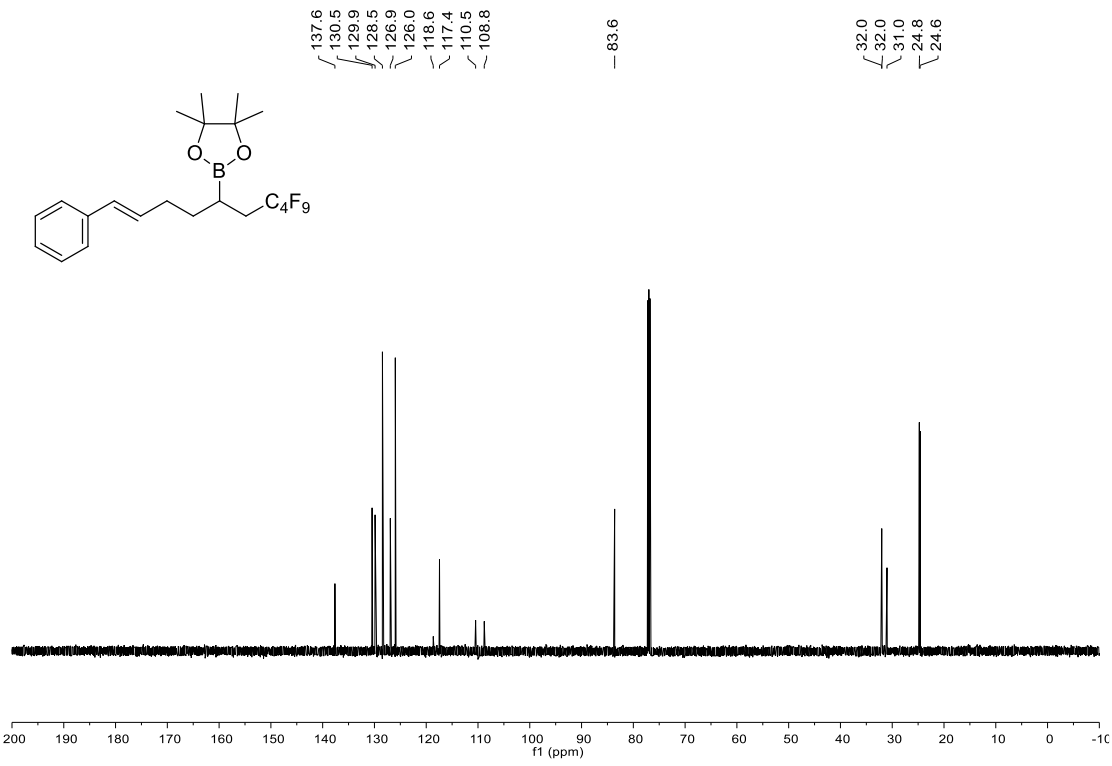


(*E*)-4,4,5,5-Tetramethyl-2-(7,7,8,8,9,9,10,10,10-nonafluoro-1-phenyldec-1-en-5-yl)-1,3,2-dioxaborolane (4ag)

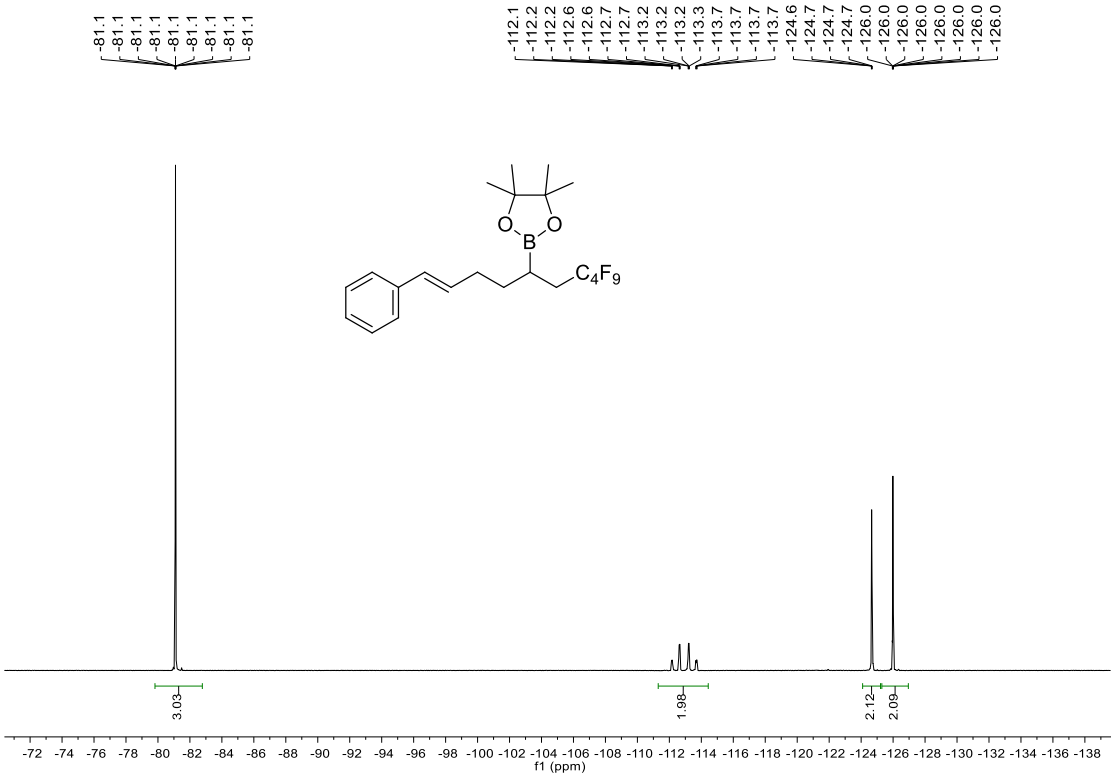
^{1}H NMR (600 MHz, $CDCl_3$)



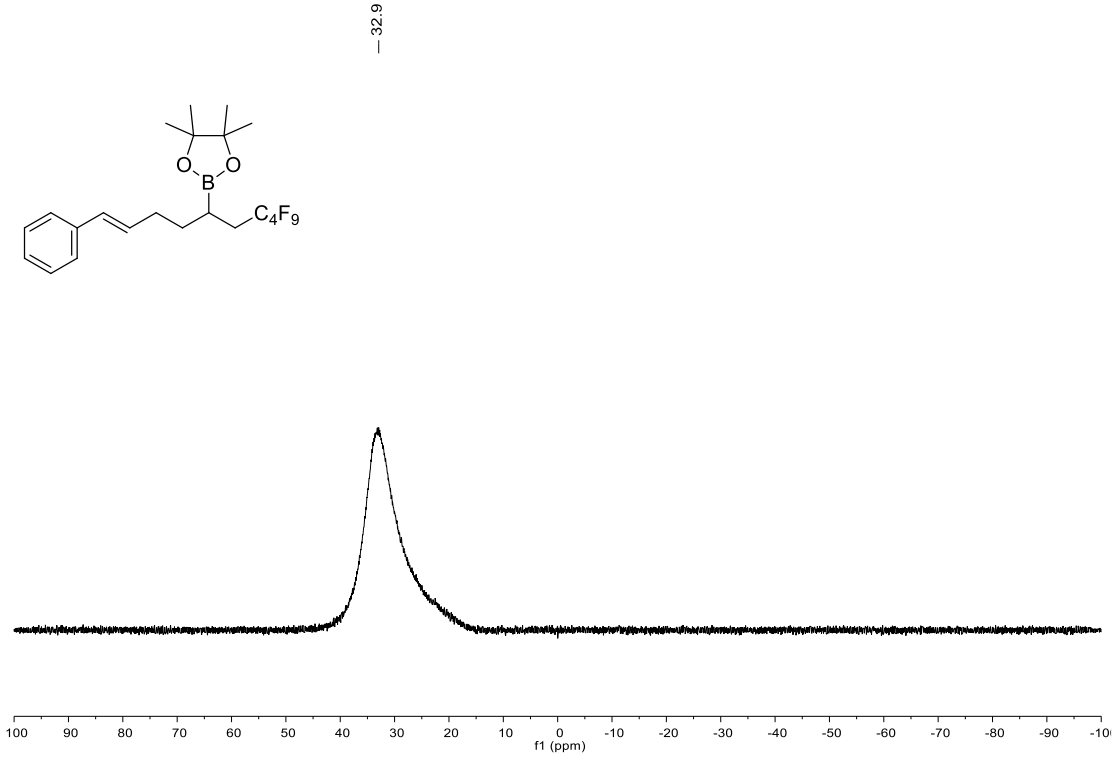
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

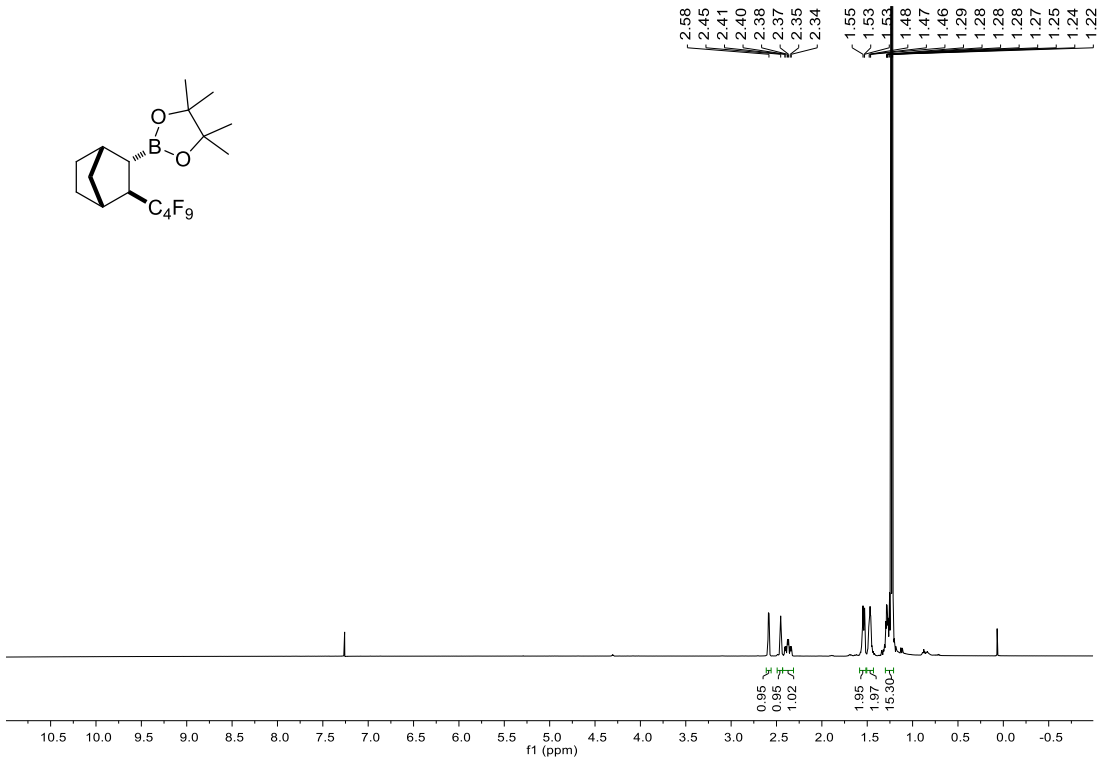


^{11}B NMR (96 MHz, $CDCl_3$)

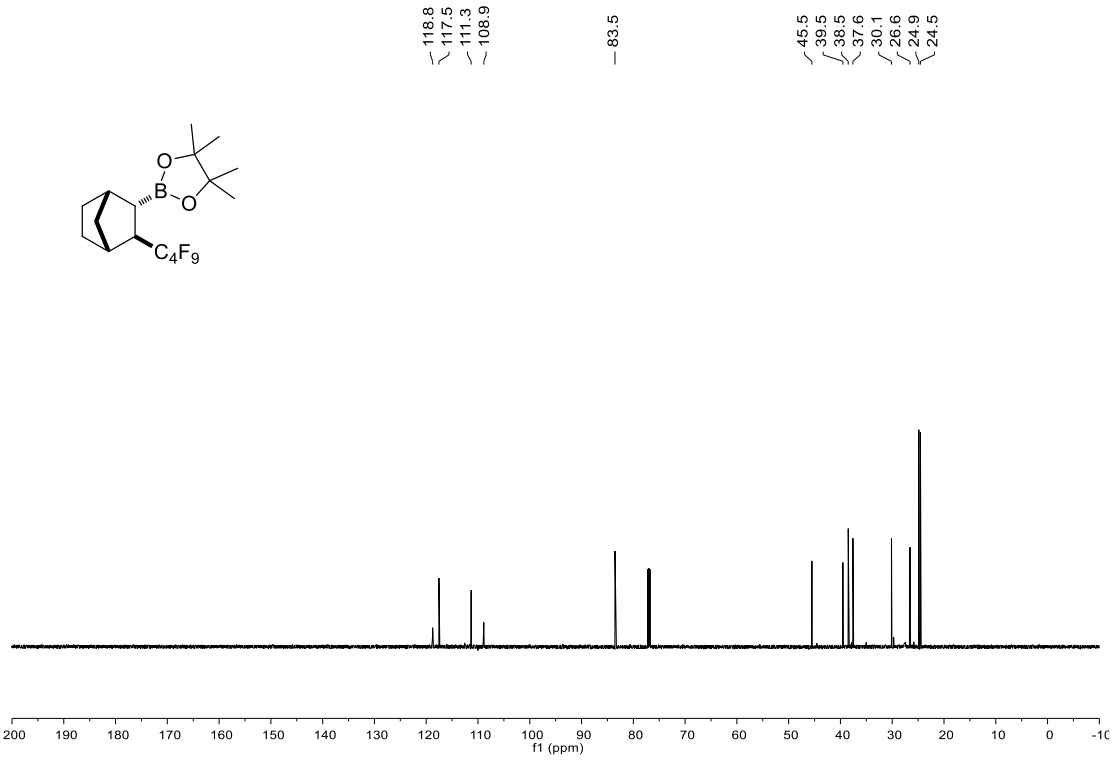


***trans*-4,4,5,5-Tetramethyl-2-(3-(perfluorobutyl)bicyclo[2.2.1]heptan-2-yl)-1,3,2-dioxaborolane (4ah)**

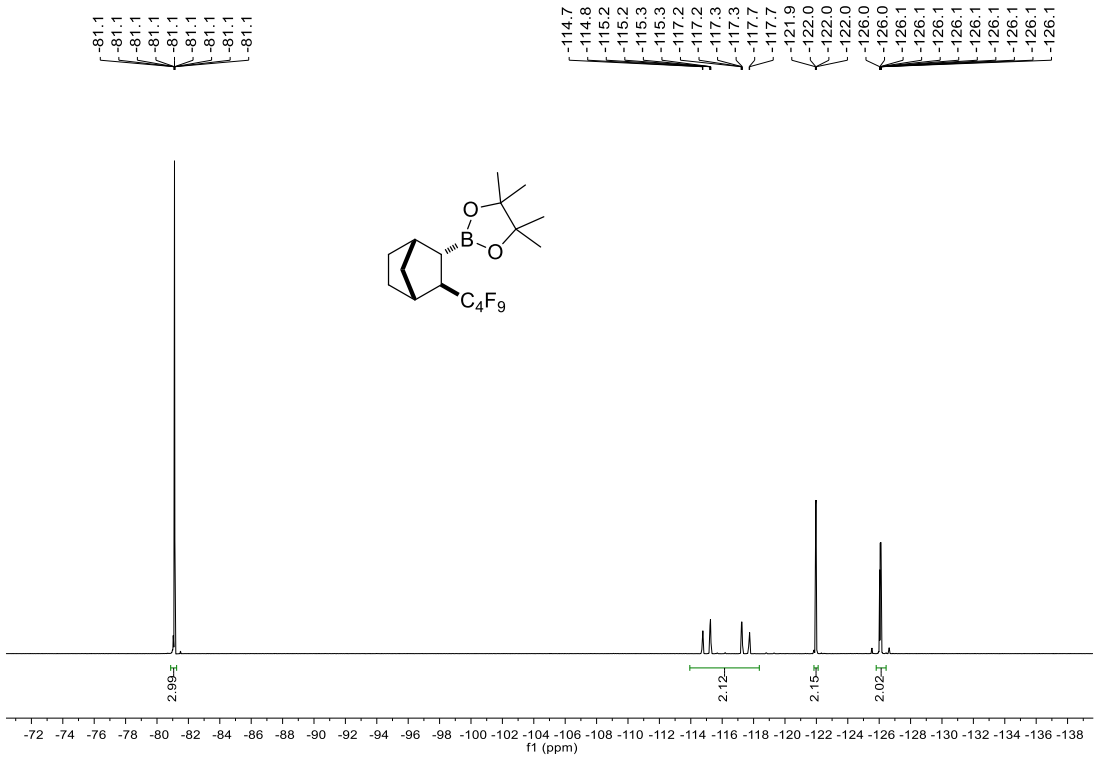
^{1}H NMR (600 MHz, $CDCl_3$)



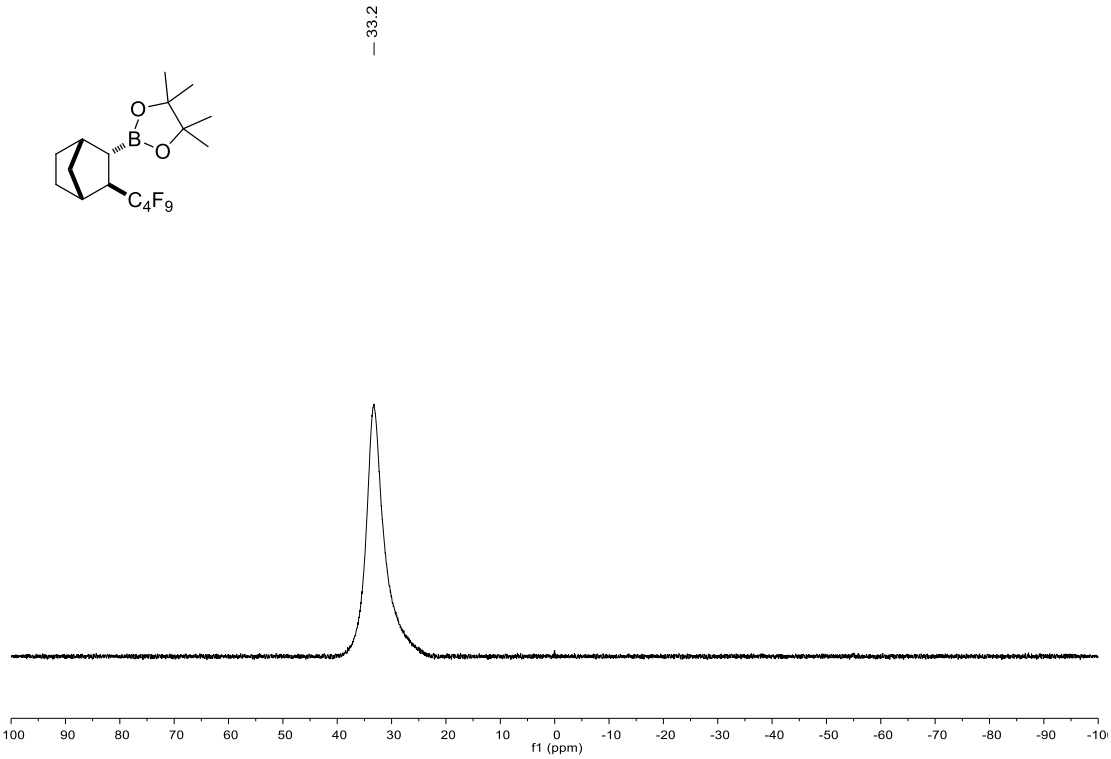
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

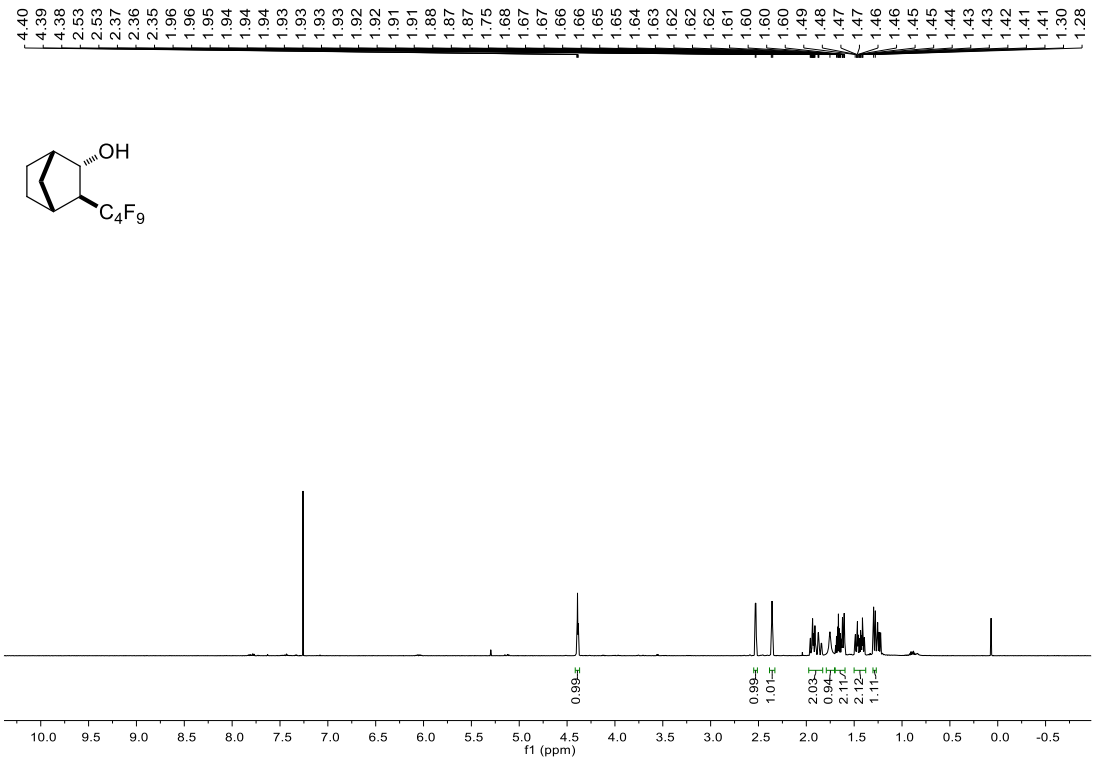


^{11}B NMR (96 MHz, $CDCl_3$)

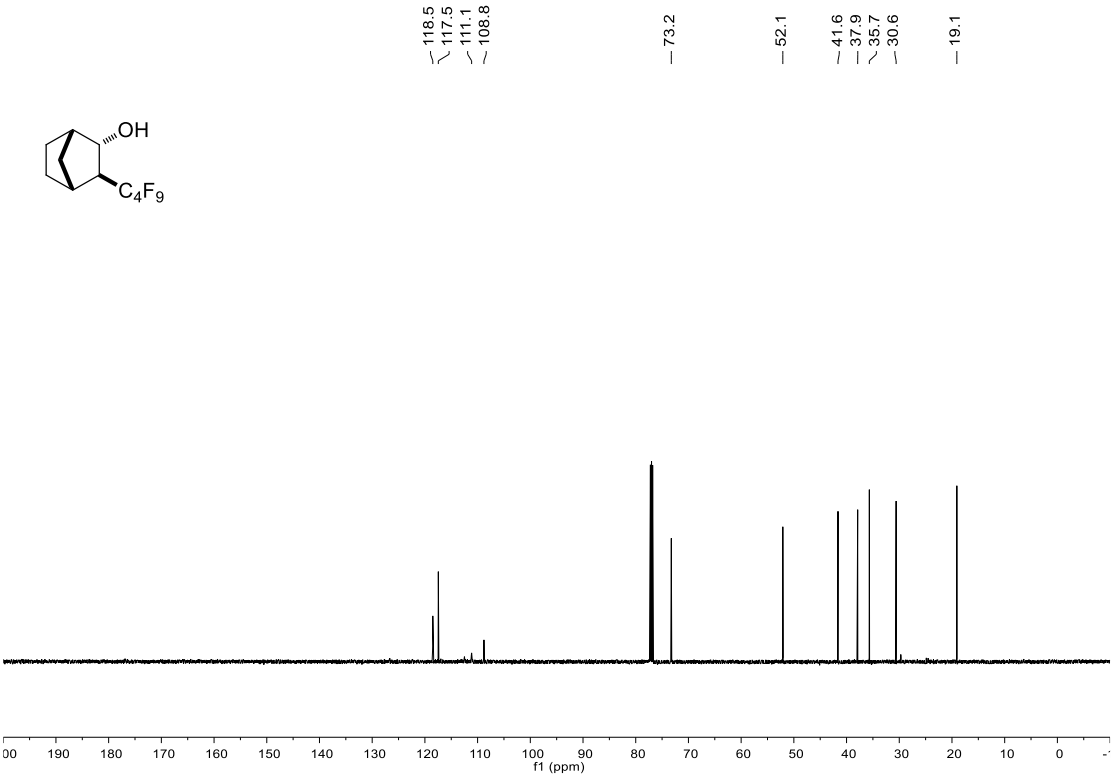


trans-3-(Perfluorobutyl)bicyclo[2.2.1]heptan-2-ol (S1)

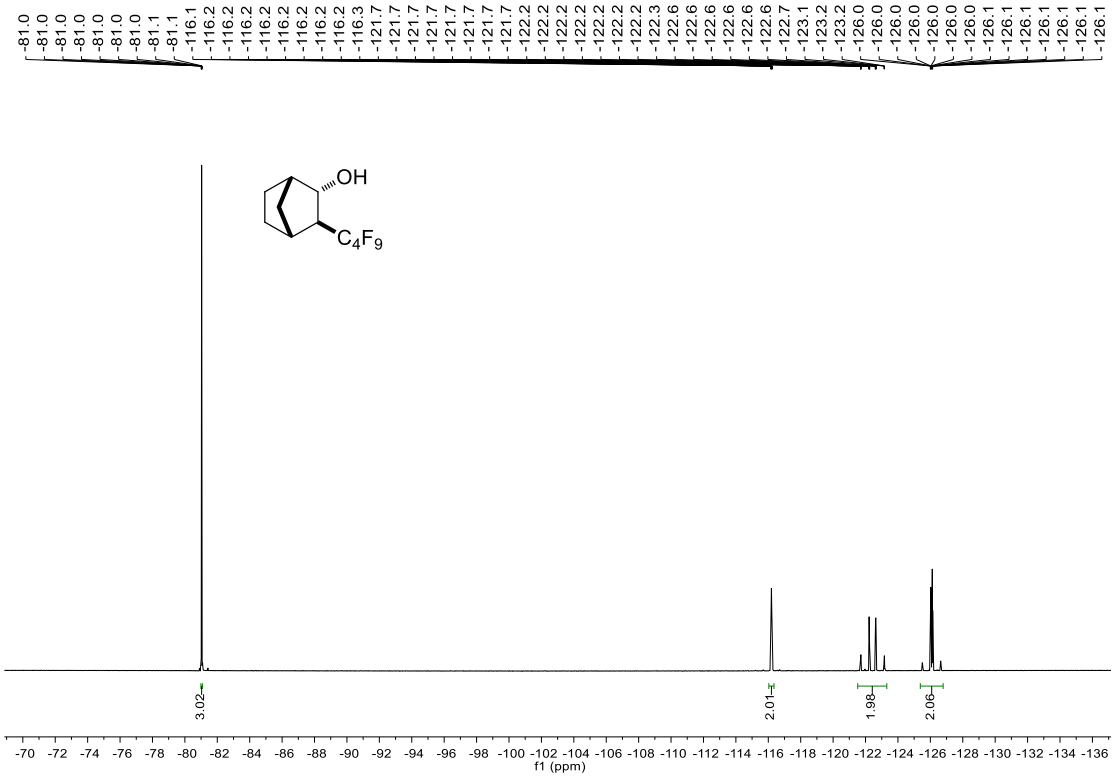
^{1}H NMR (600 MHz, $CDCl_3$)



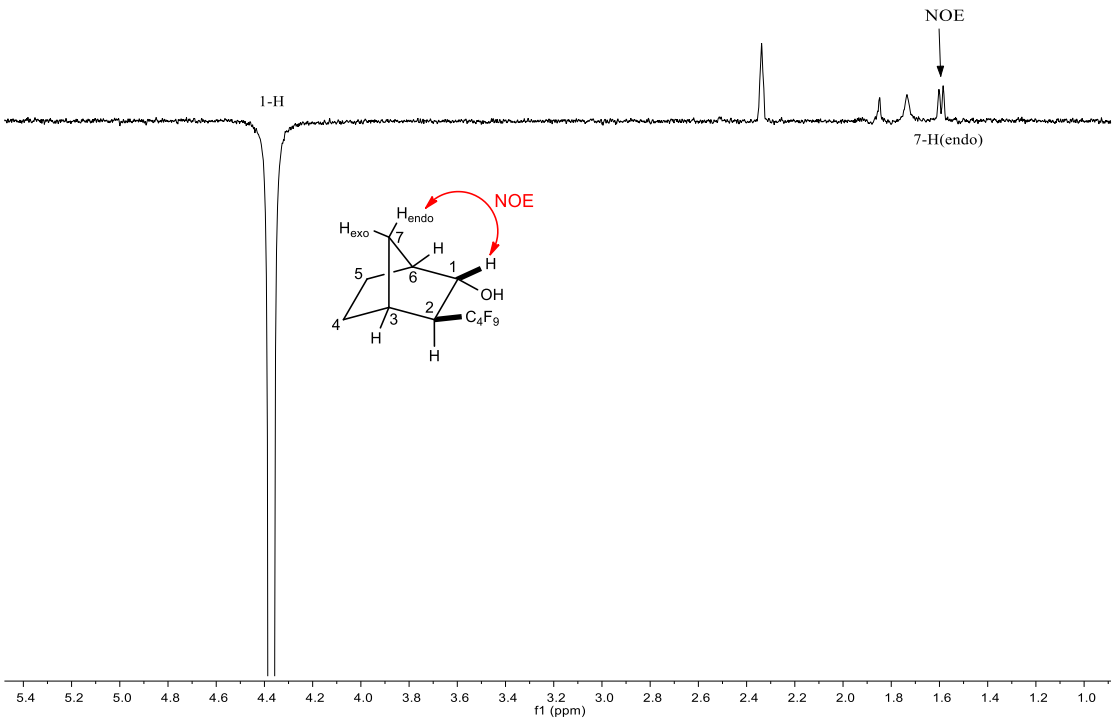
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



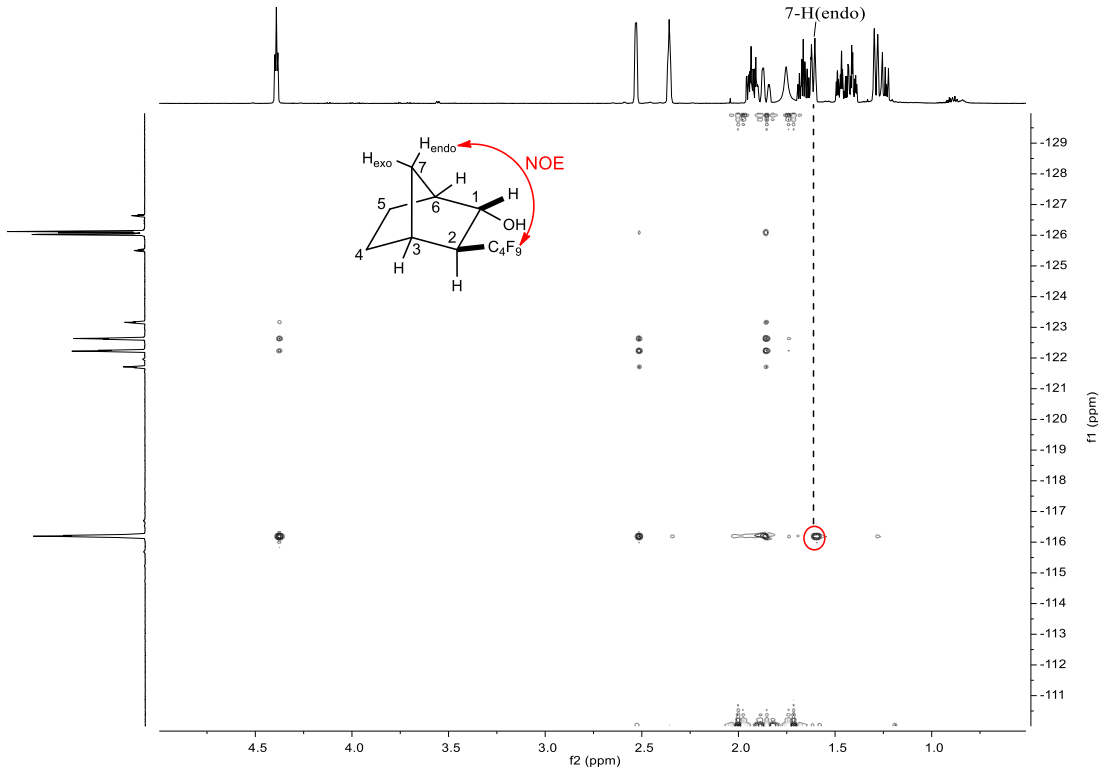
^{19}F NMR (564 MHz, $CDCl_3$)



1D NOESY {^{19}F} (600 MHz, $CDCl_3$)

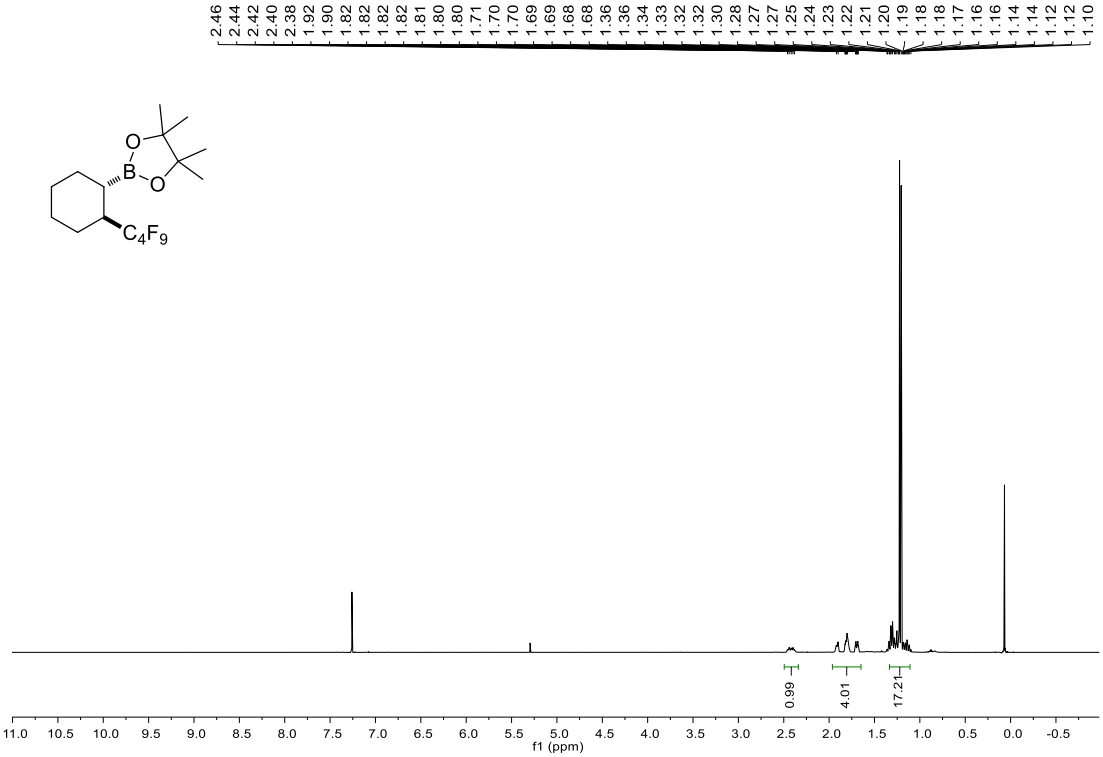


^{1}H-^{19}F HOESY

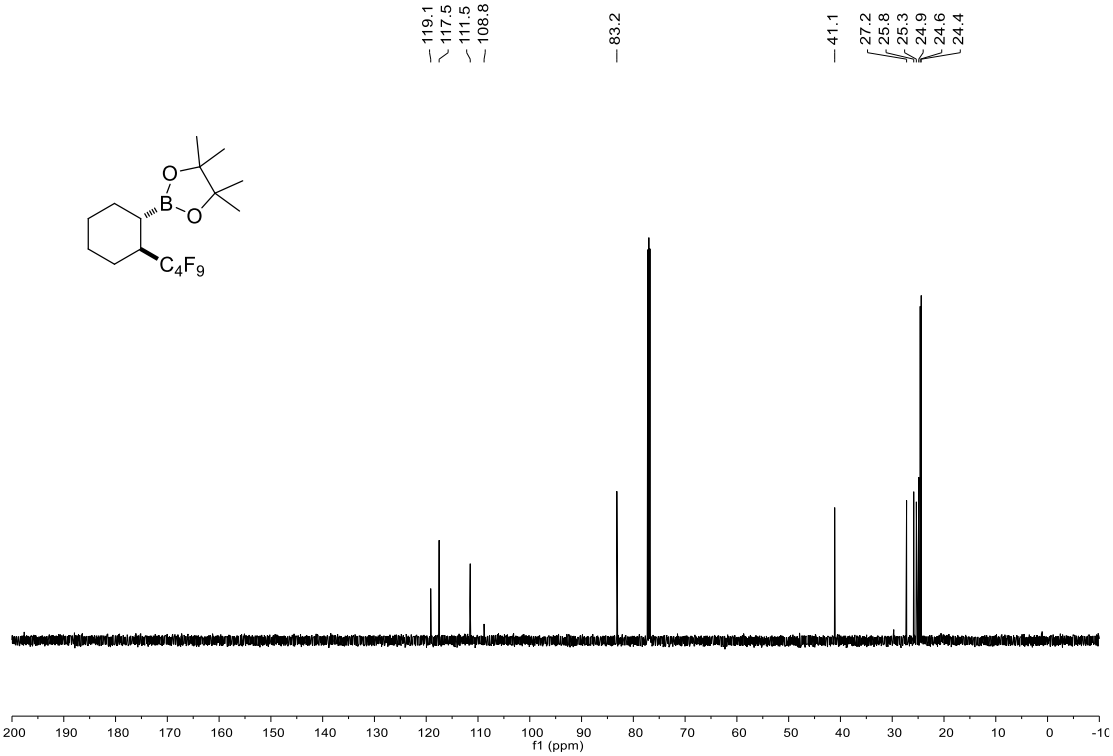


***trans*-4,4,5,5-Tetramethyl-2-(2-(perfluorobutyl)cyclohexyl)-1,3,2-dioxaborolane (4ai)**

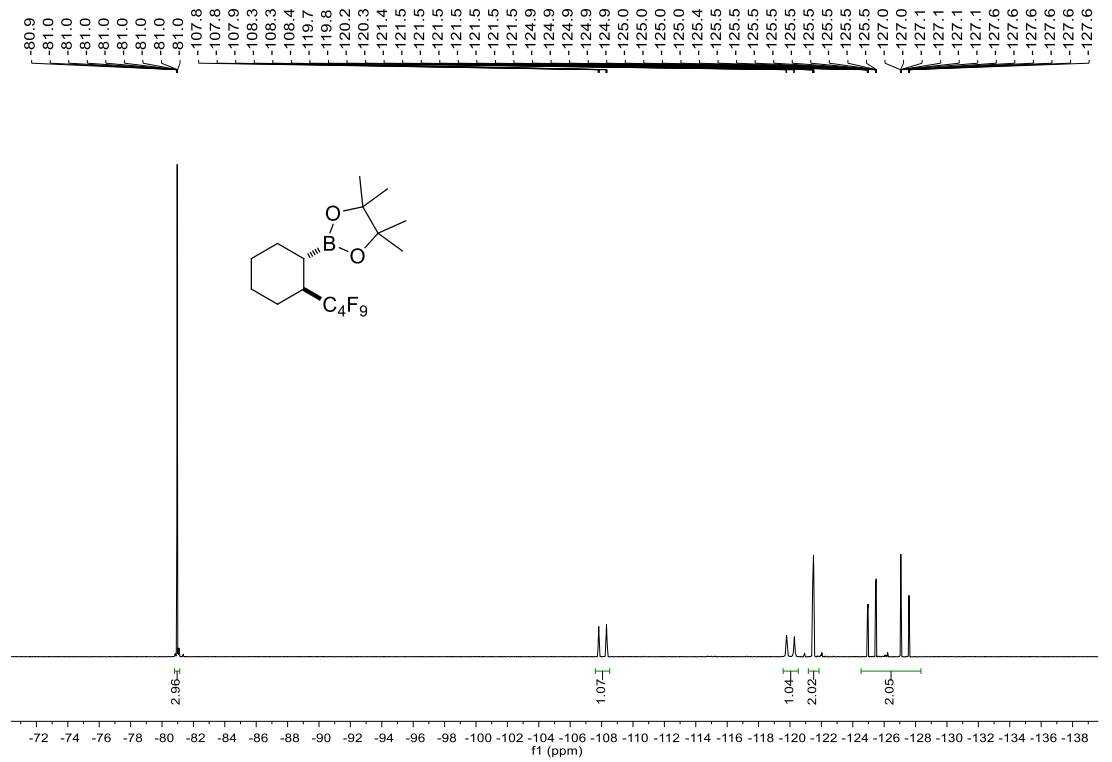
^{1}H NMR (600 MHz, $CDCl_3$)



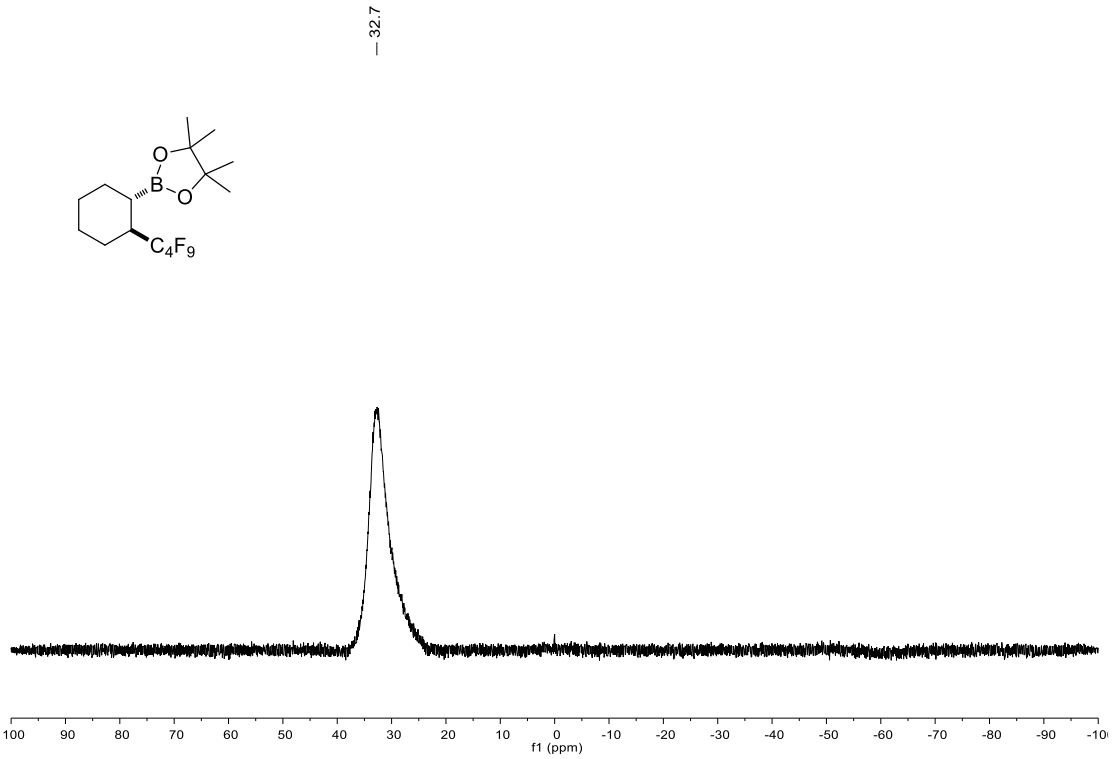
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

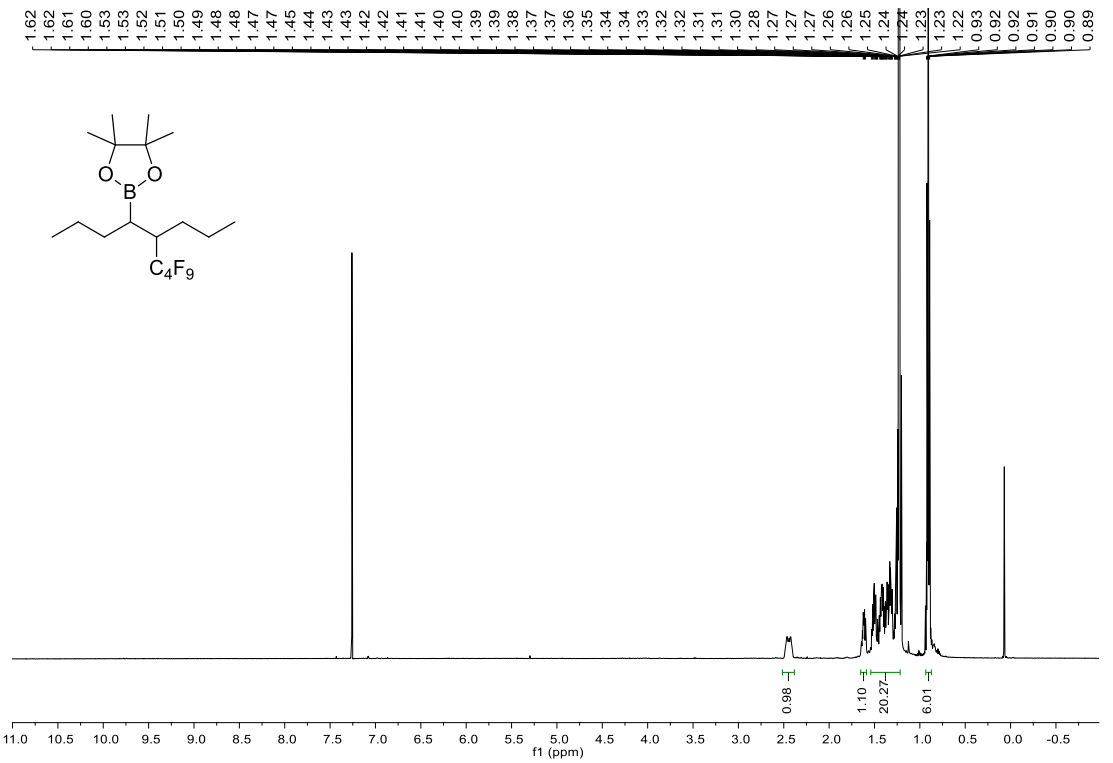


^{11}B NMR (96 MHz, $CDCl_3$)

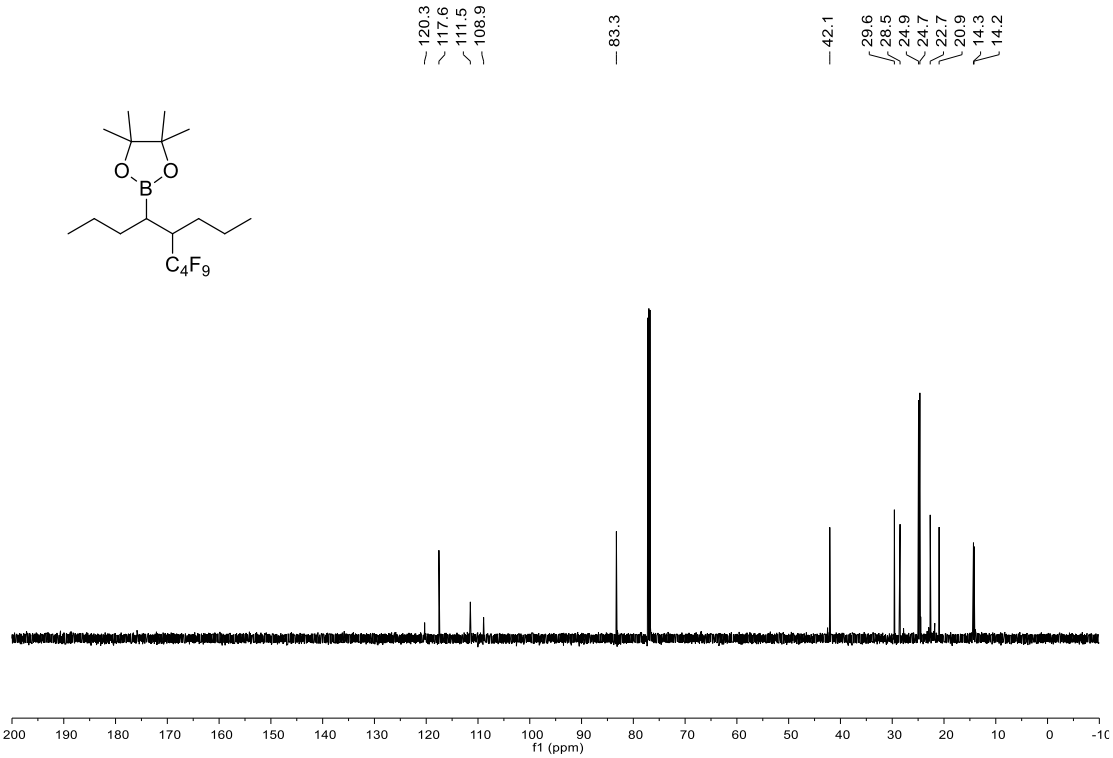


4,4,5,5-Tetramethyl-2-(6,6,7,7,8,8,9,9,9-nonafluoro-5-propylnonan-4-yl)-1,3,2-dioxaborolane (4aj)

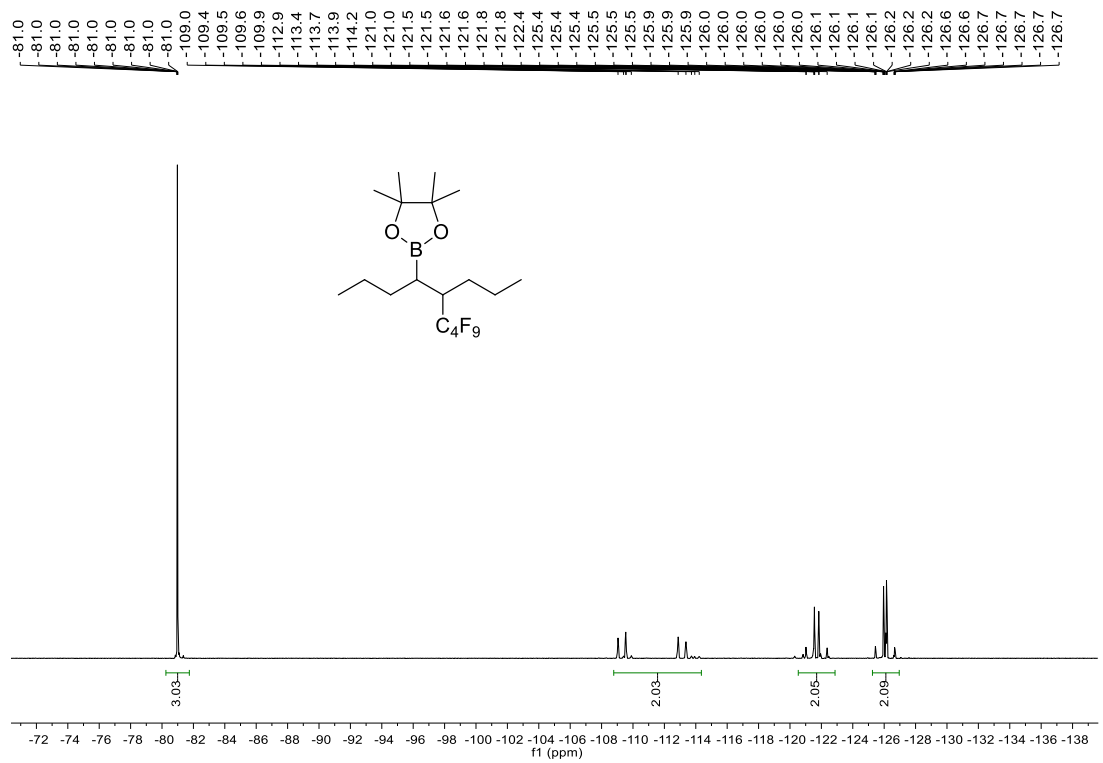
^{1}H NMR (600 MHz, $CDCl_3$)



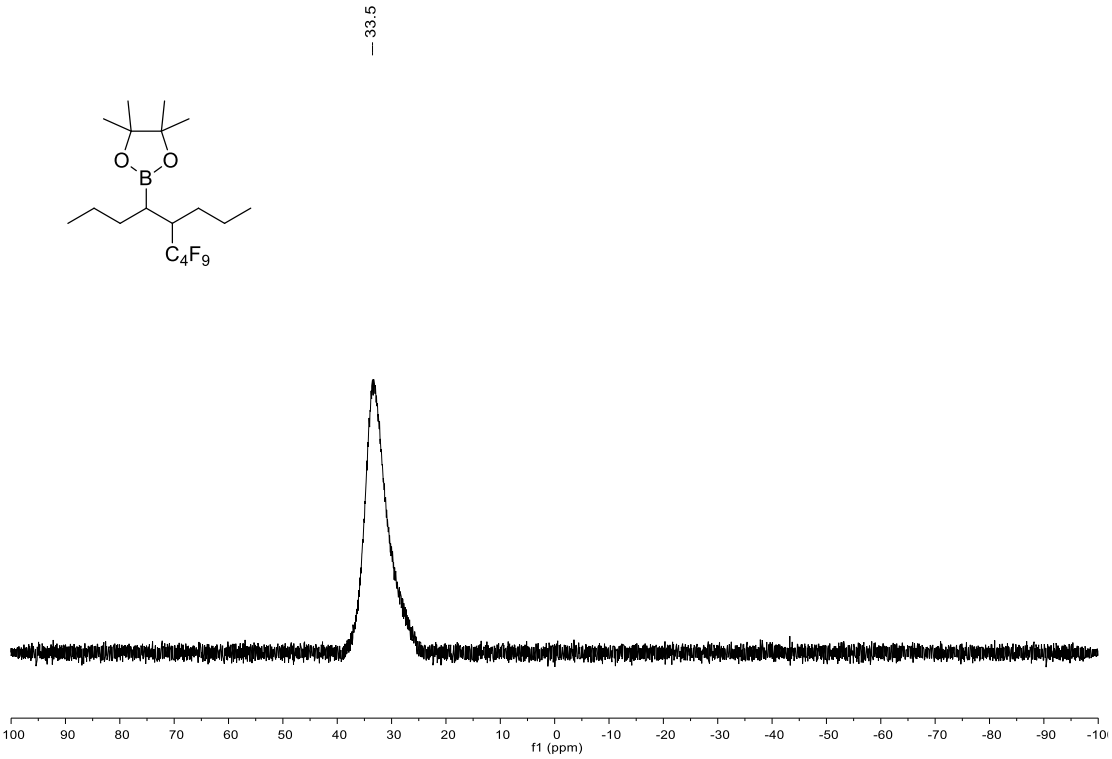
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

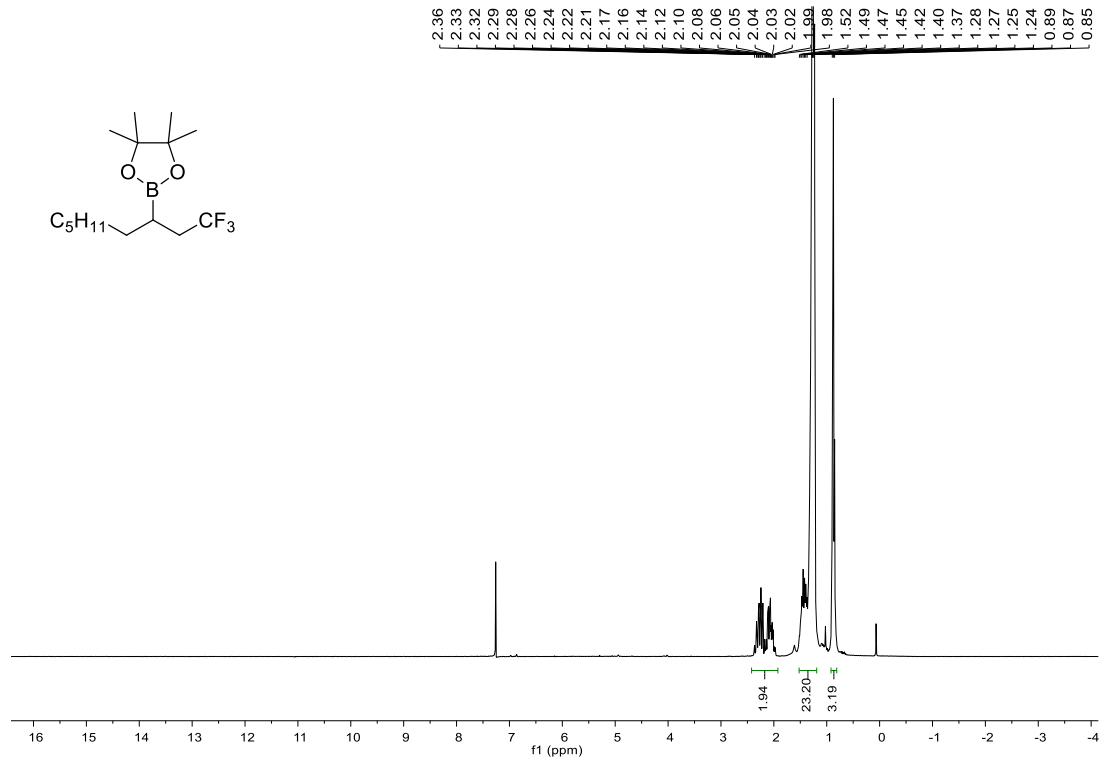


^{11}B NMR (96 MHz, $CDCl_3$)

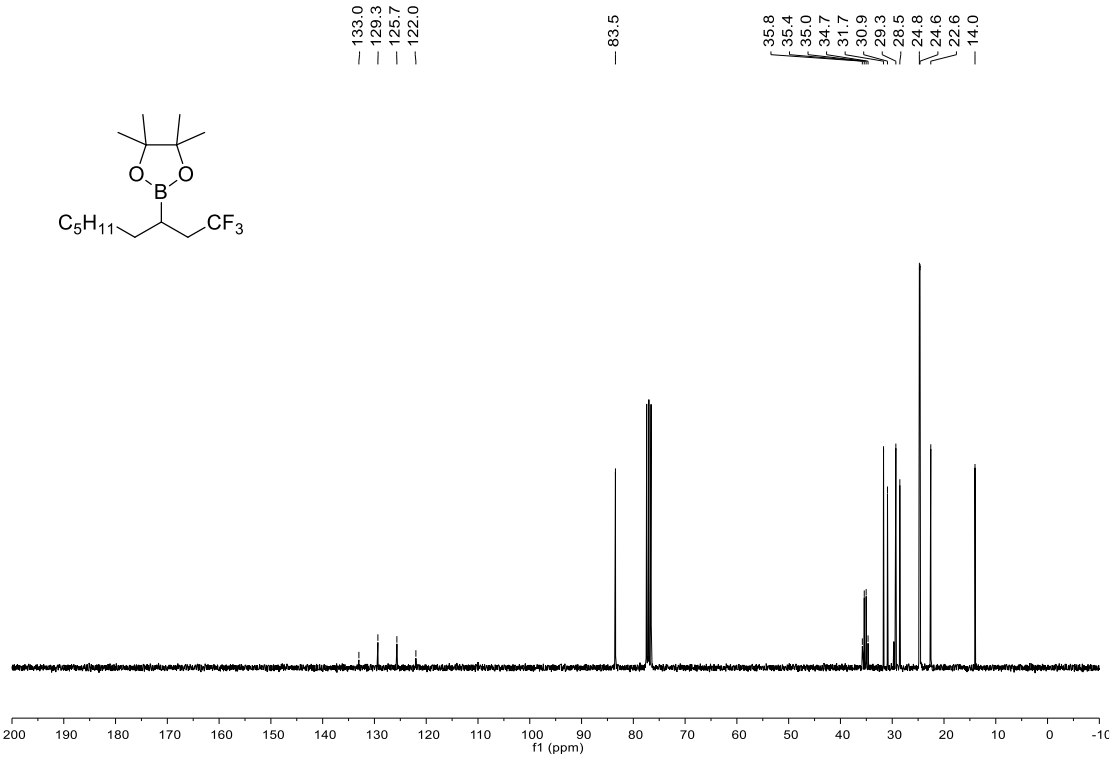


4,4,5,5-Tetramethyl-2-(1,1,1-trifluorononan-3-yl)-1,3,2-dioxaborolane (5a)

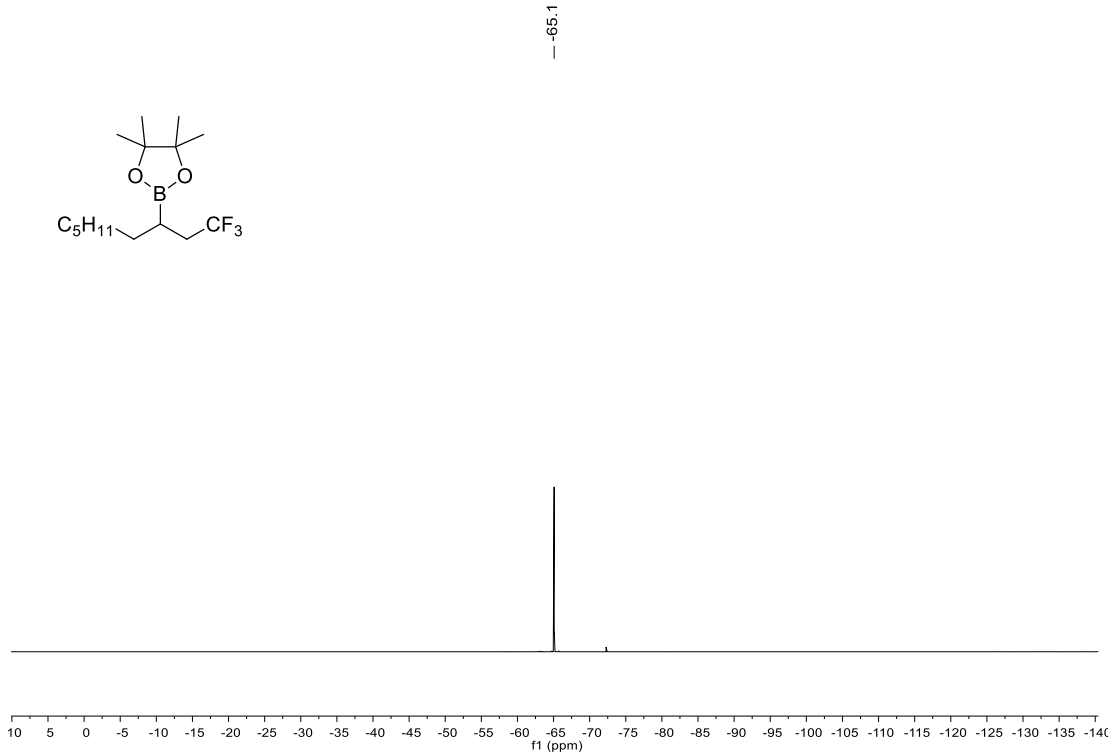
^{1}H NMR (300 MHz, $CDCl_3$)



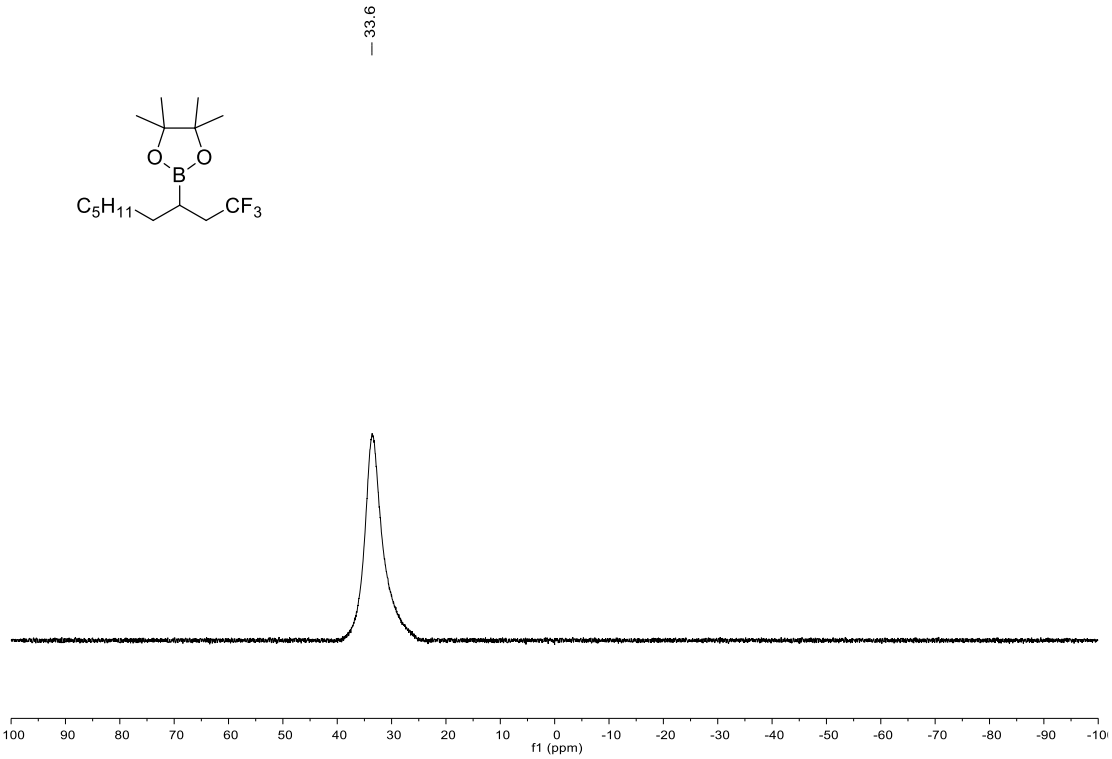
^{13}C NMR (75 MHz, $CDCl_3$)



^{19}F NMR (282 MHz, $CDCl_3$)

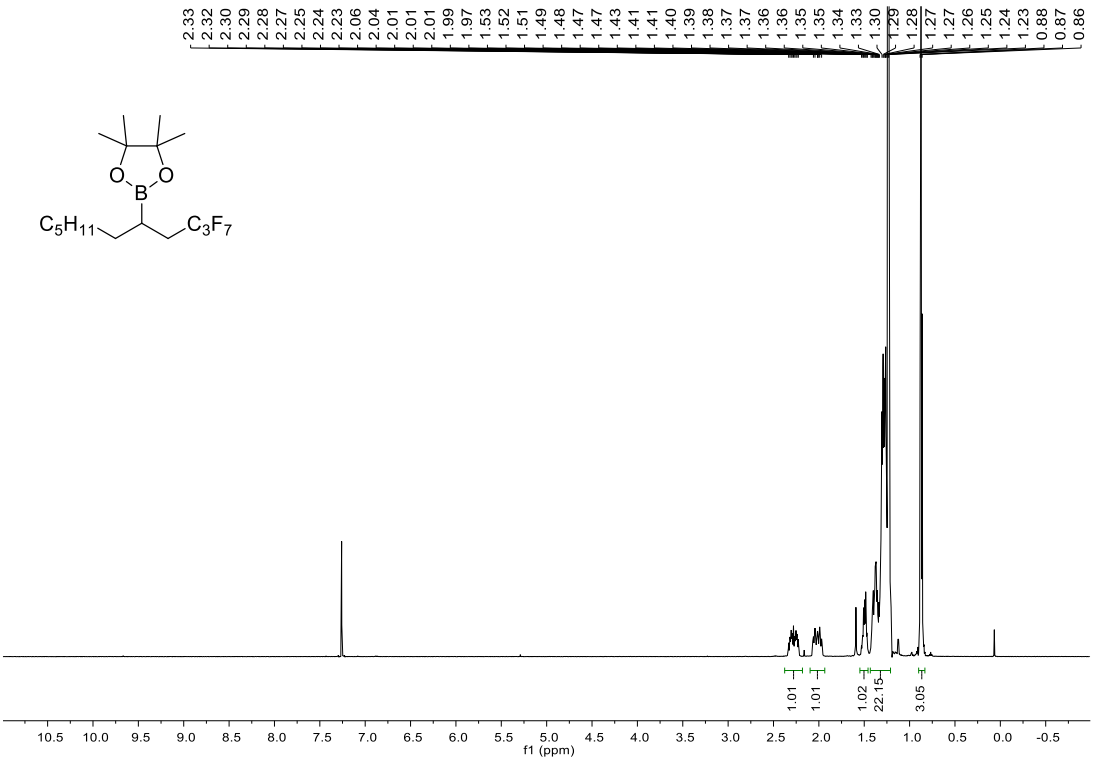


^{11}B NMR (96 MHz, $CDCl_3$)

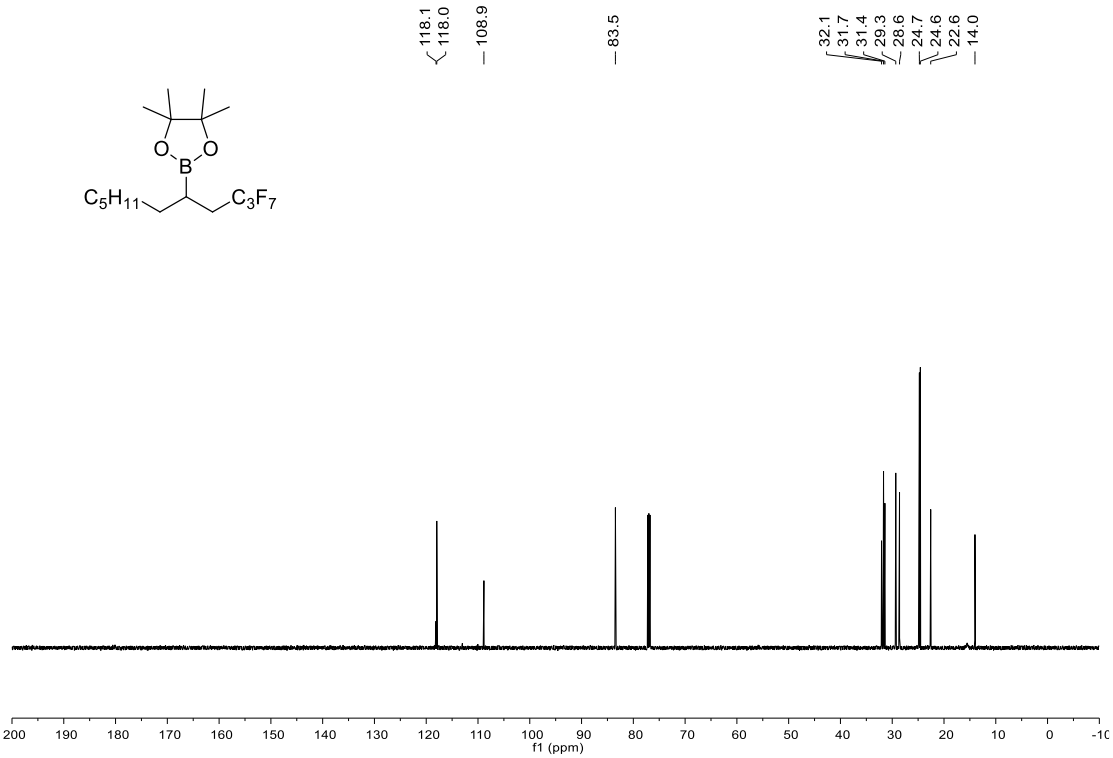


2-(1,1,1,2,2,3,3-Heptafluoroundecan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)

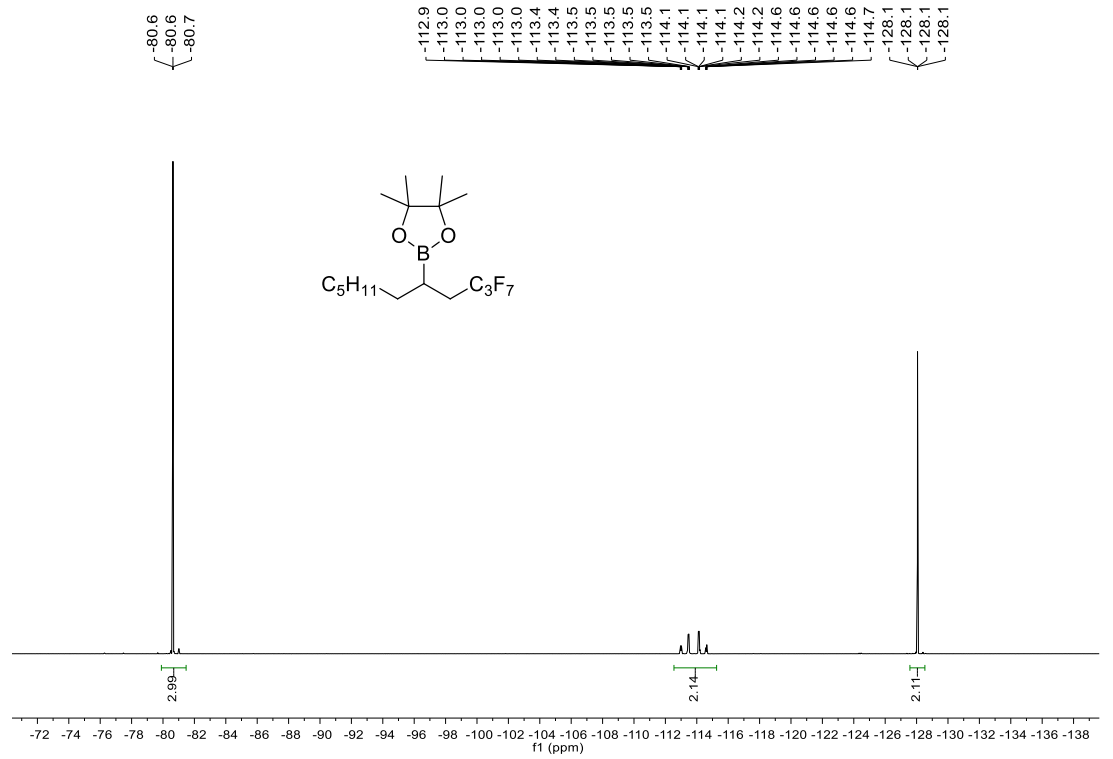
^{1}H NMR (600 MHz, $CDCl_3$)



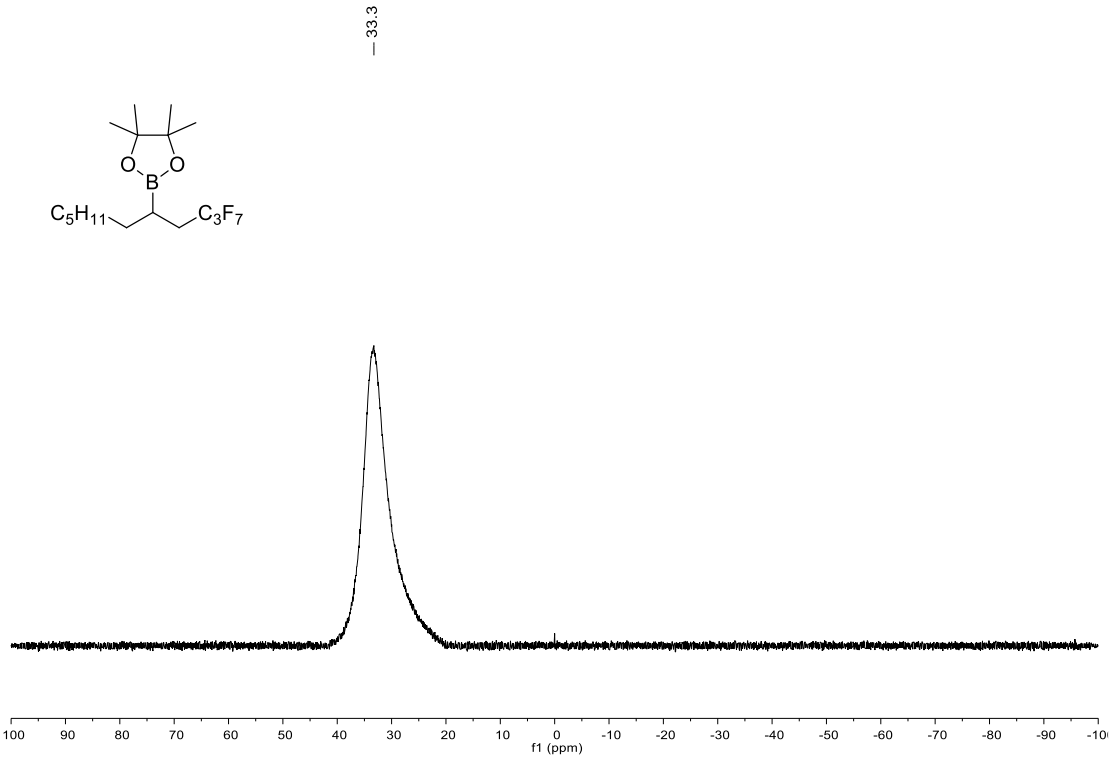
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

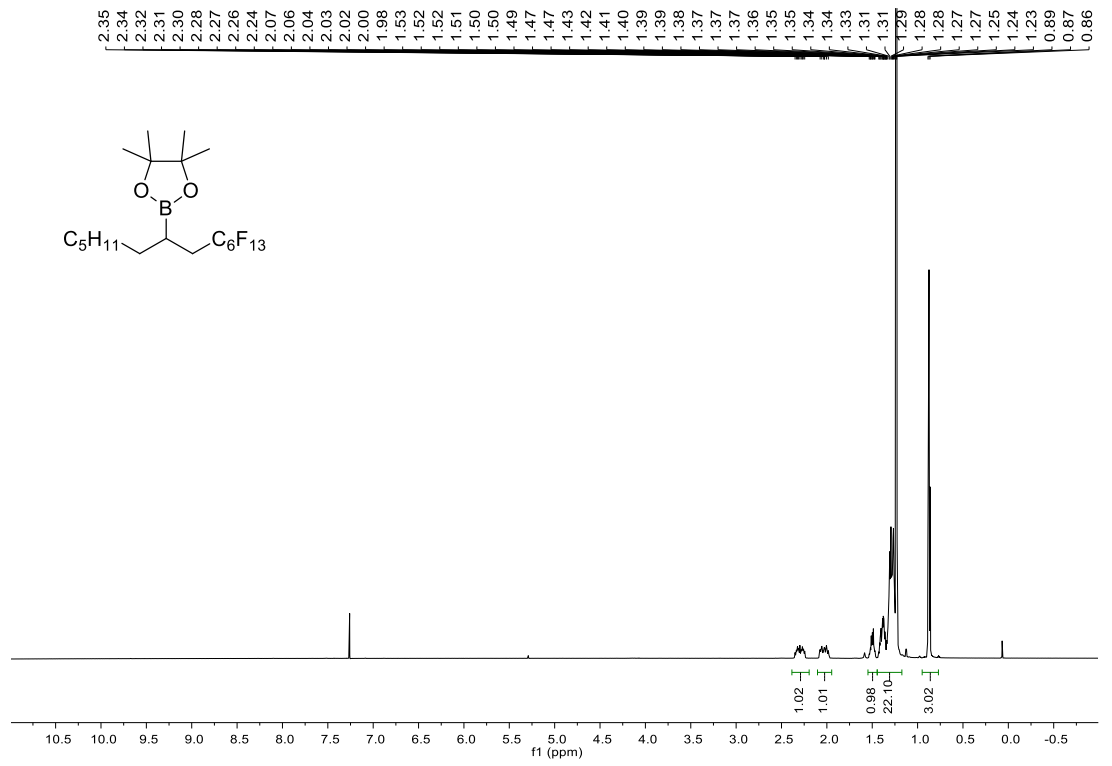


^{11}B NMR (96 MHz, $CDCl_3$)

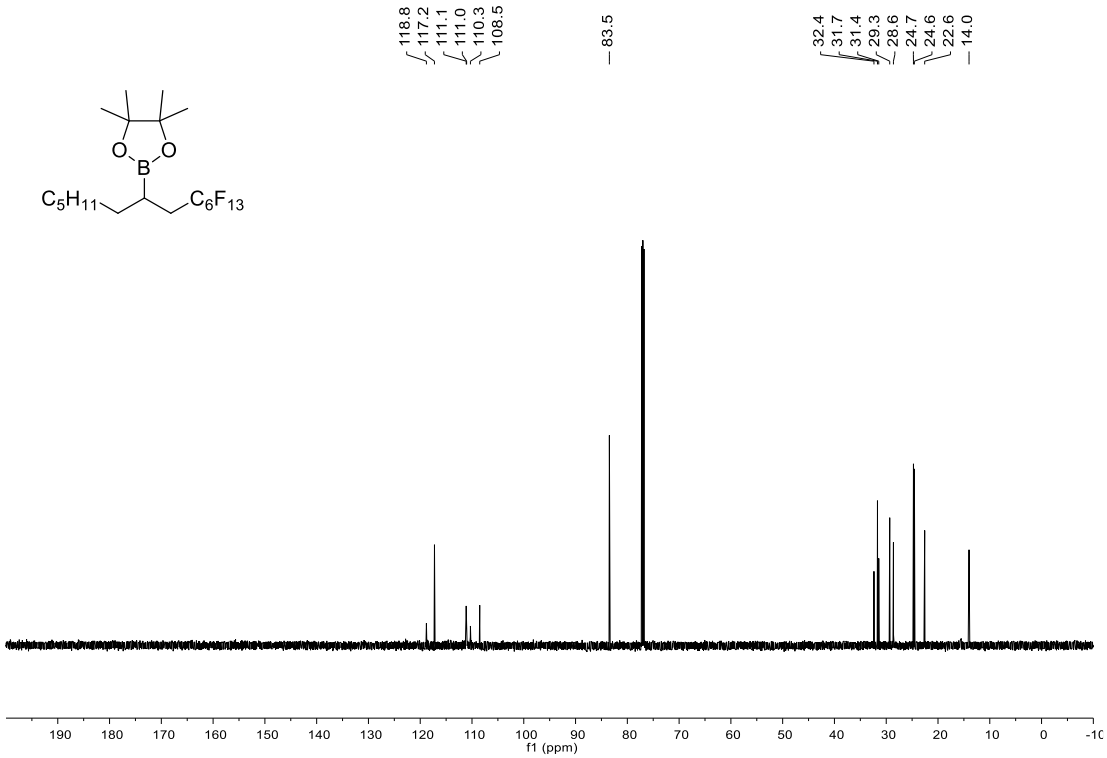


4,4,5,5-Tetramethyl-2-(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecan-7-yl)-1,3,2-dioxaborolane (5c)

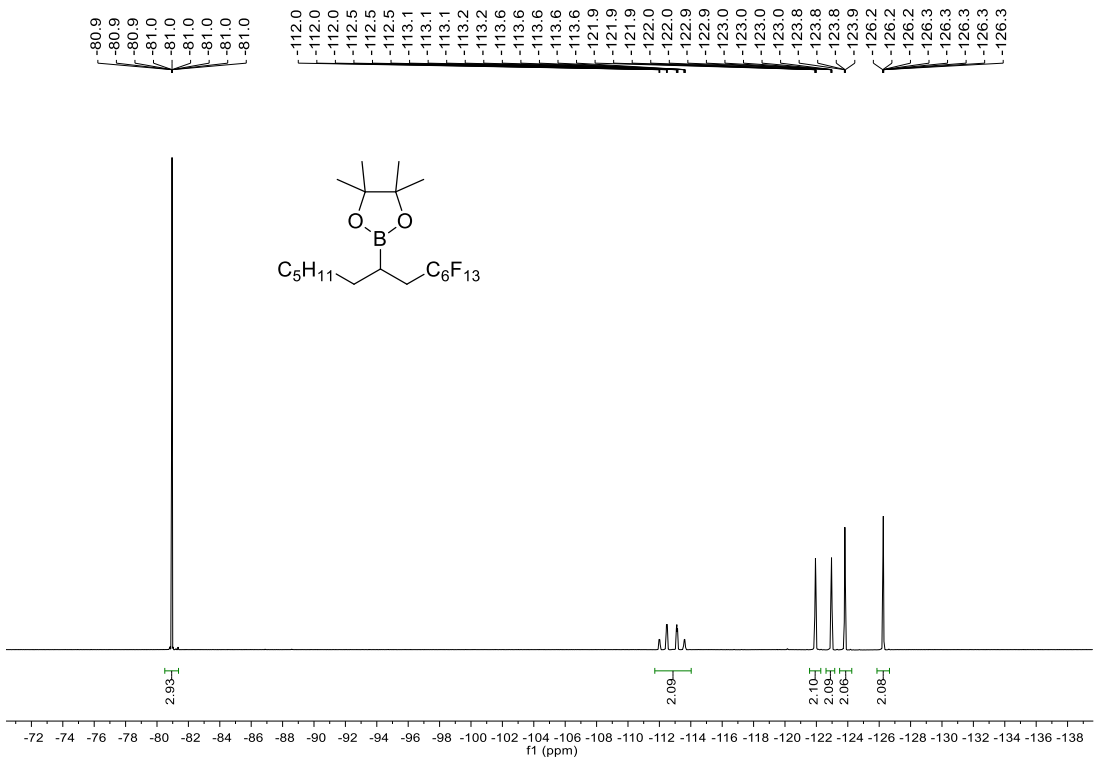
^{1}H NMR (600 MHz, $CDCl_3$)



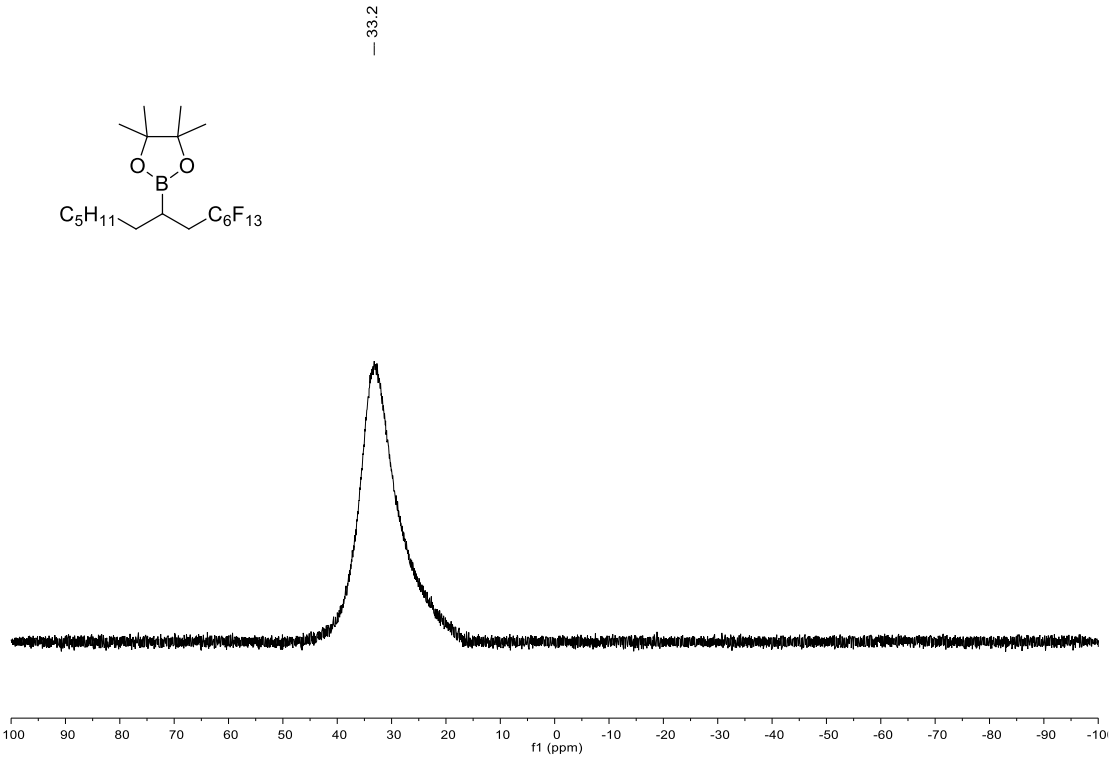
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

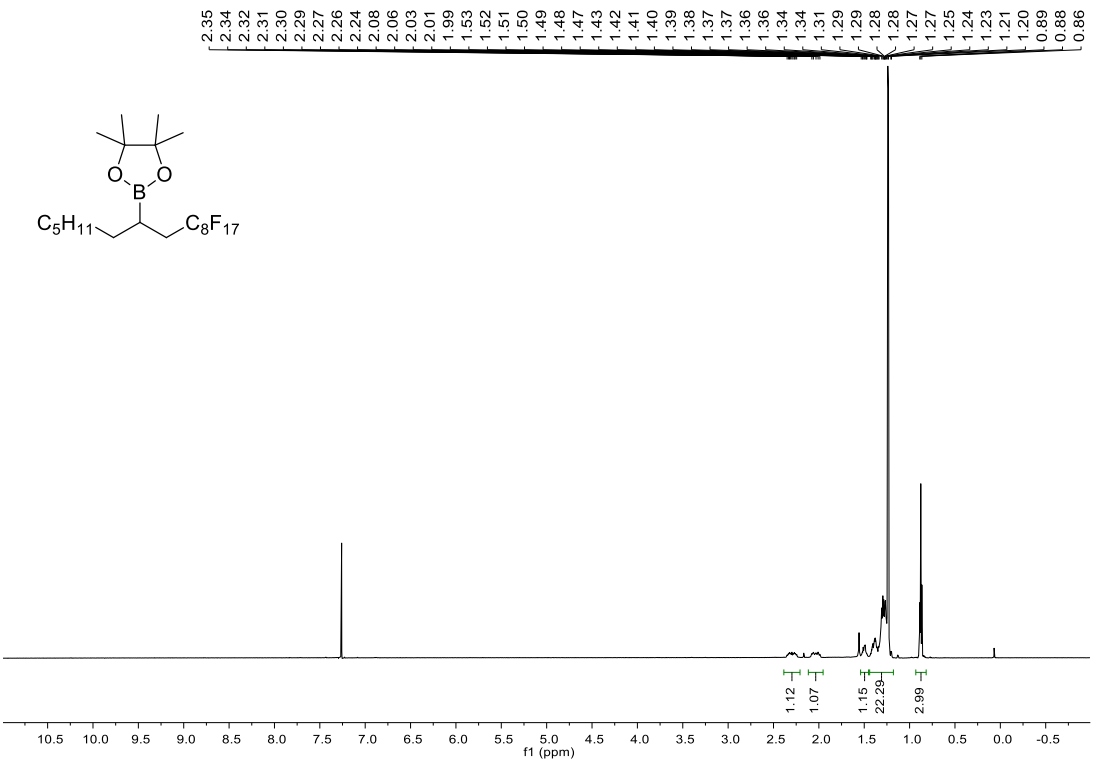


^{11}B NMR (96 MHz, $CDCl_3$)

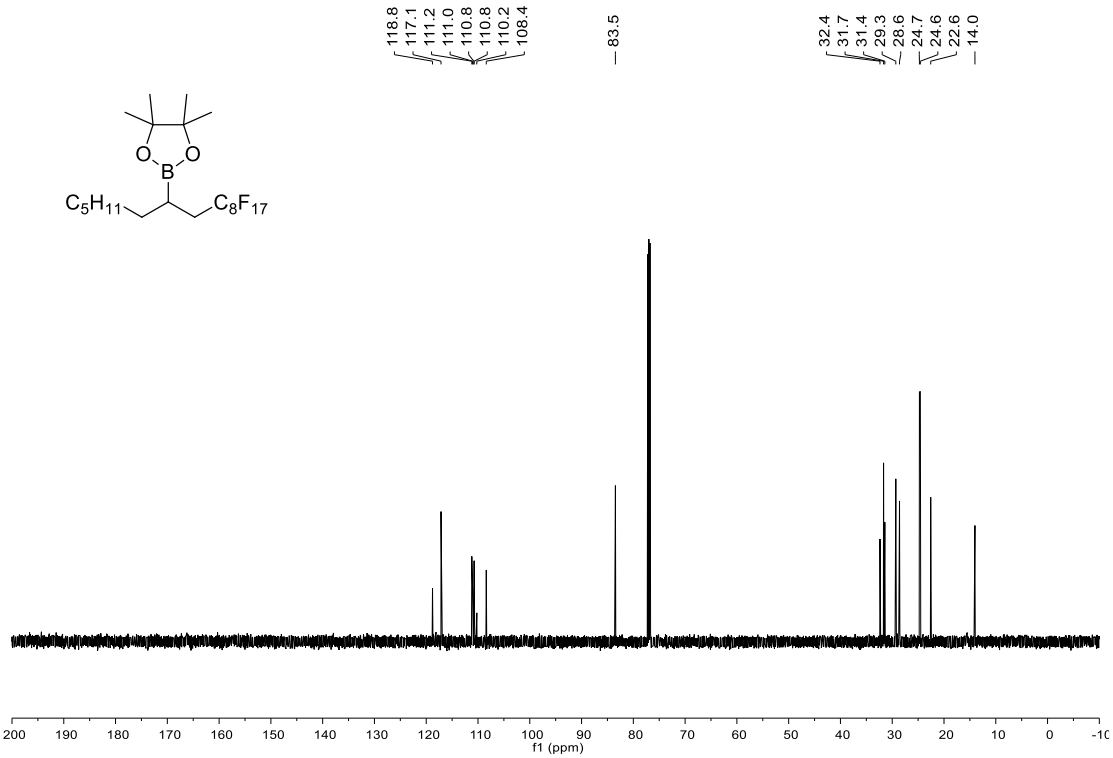


2-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluorohexadecan-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d)

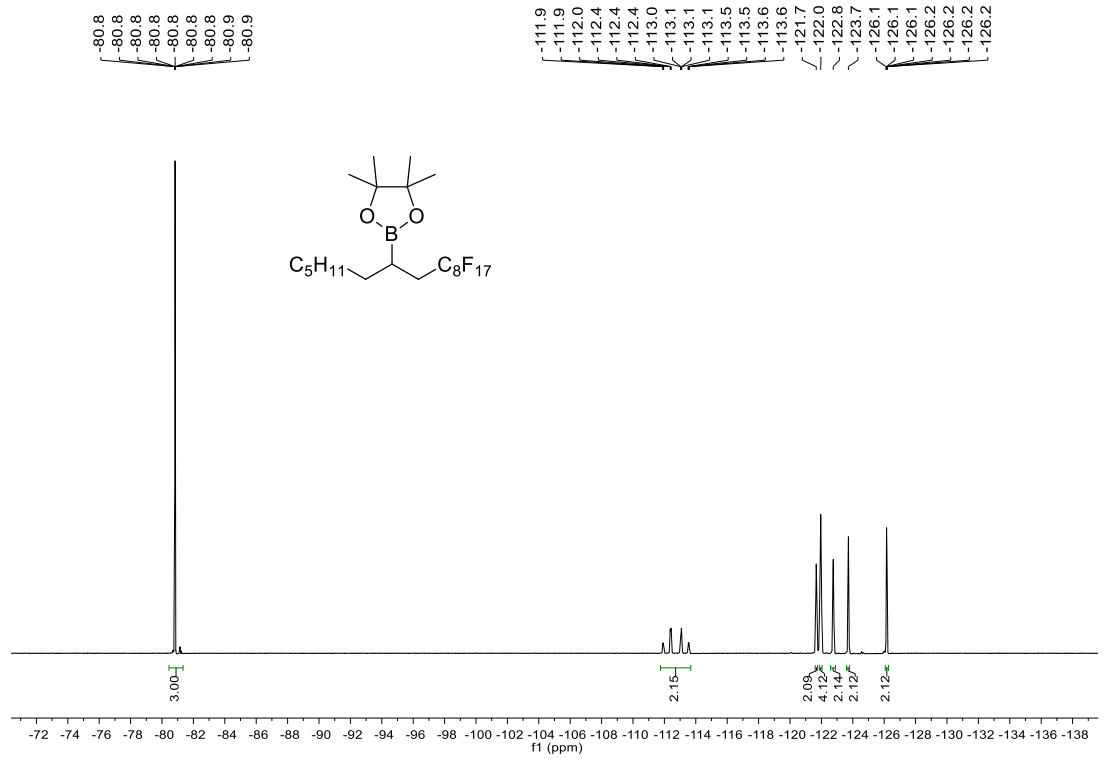
^{1}H NMR (600 MHz, $CDCl_3$)



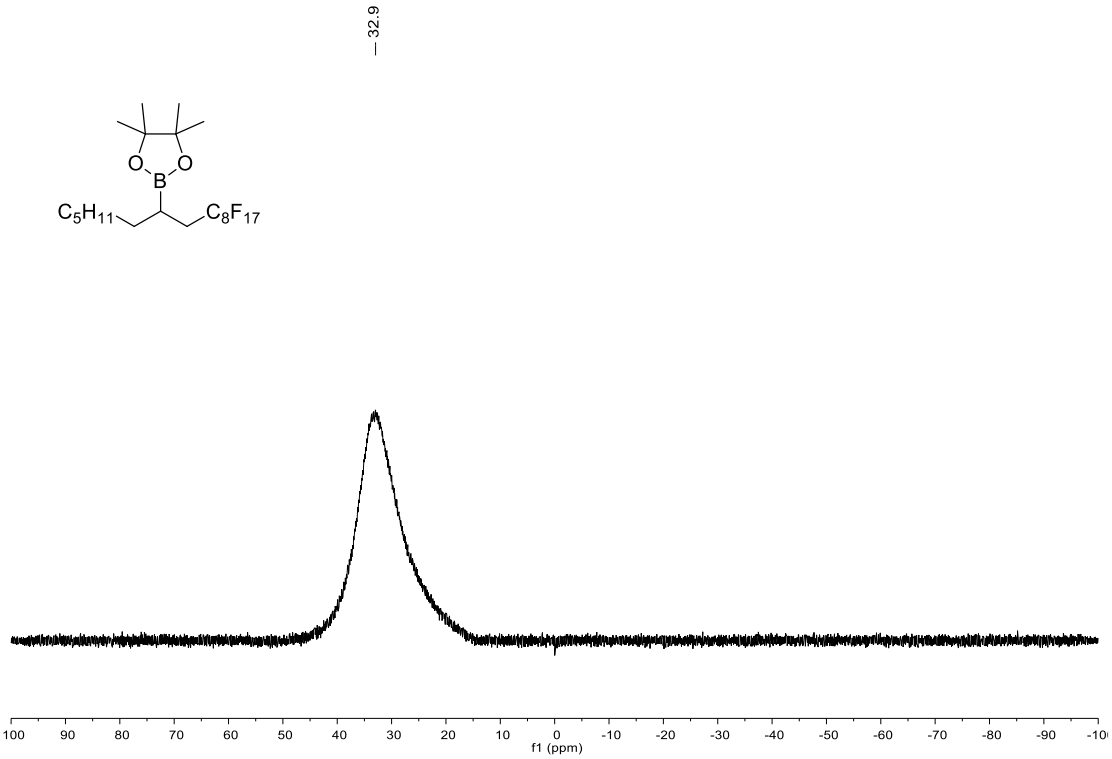
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

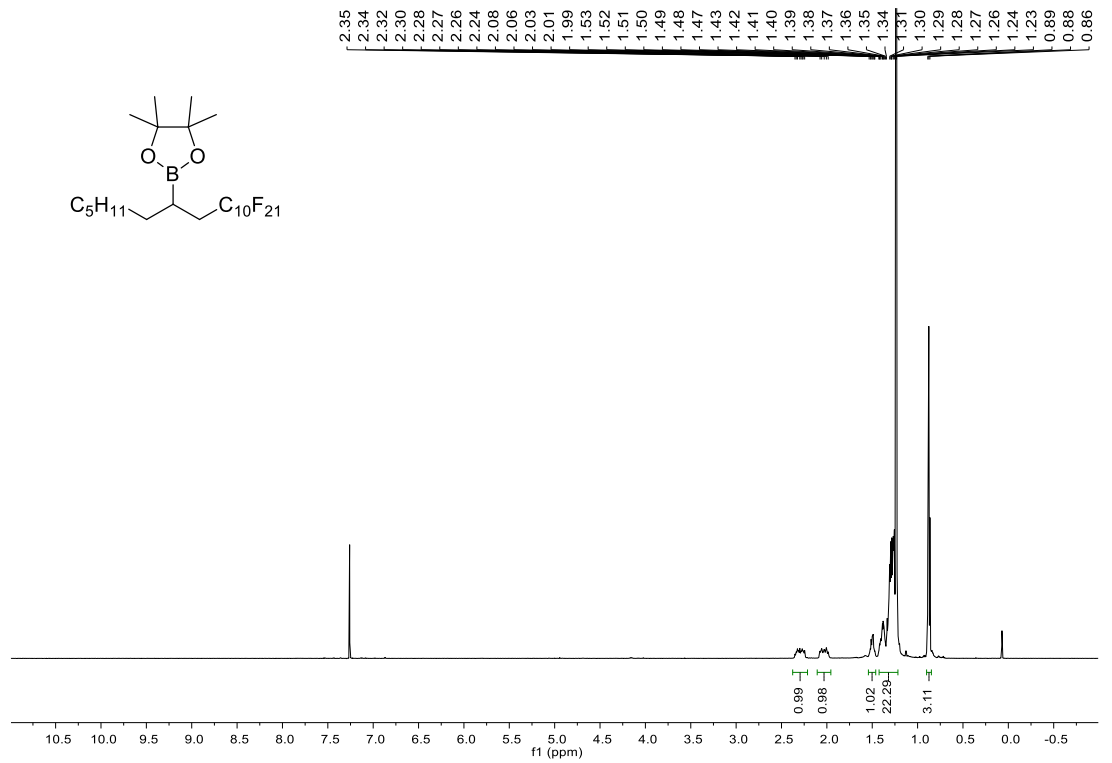


^{11}B NMR (96 MHz, $CDCl_3$)

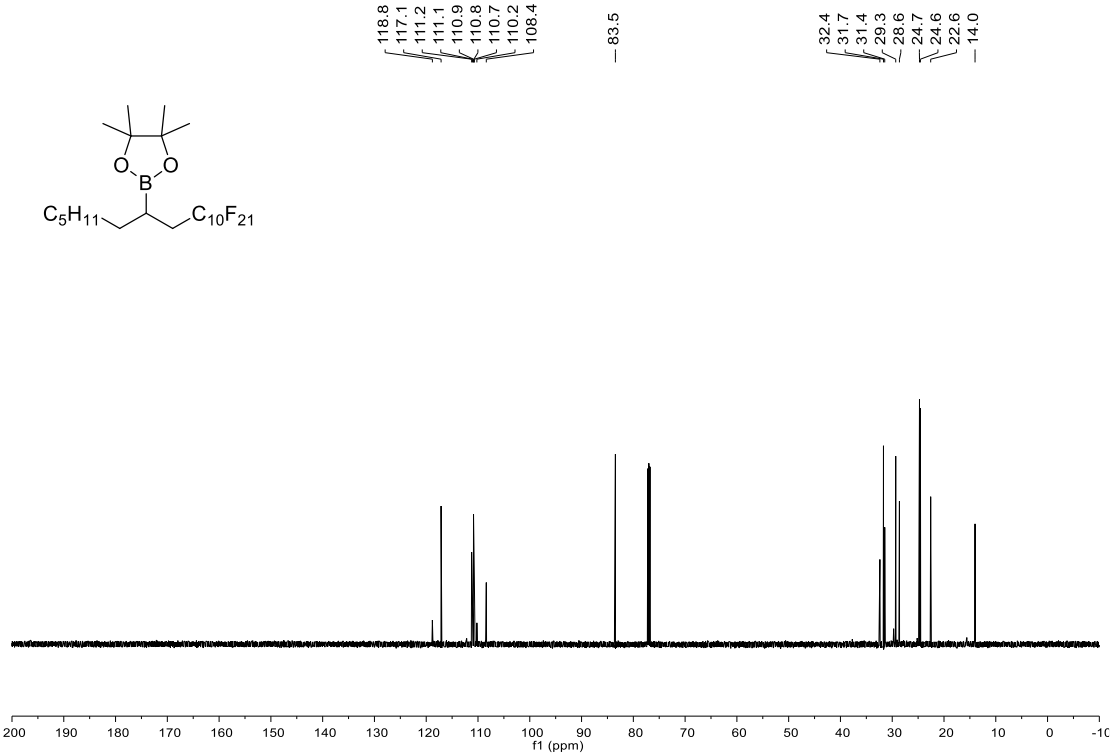


2-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-Henicosafluorooctadecan-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e)

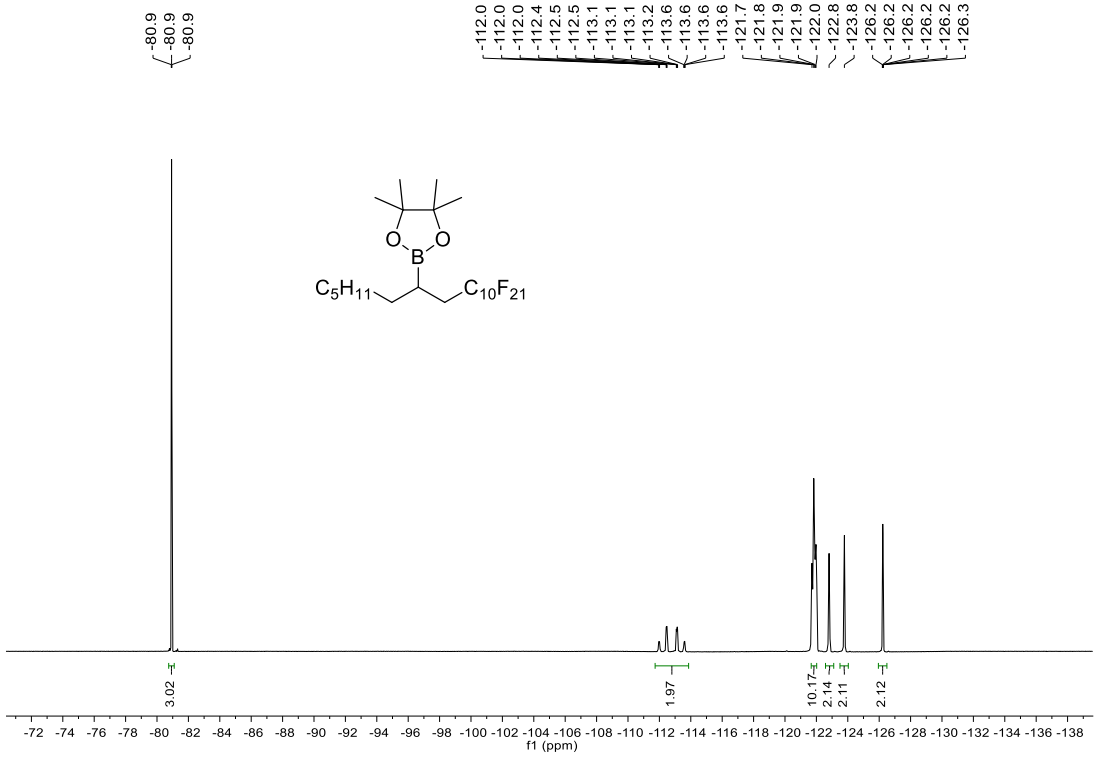
^{1}H NMR (600 MHz, $CDCl_3$)



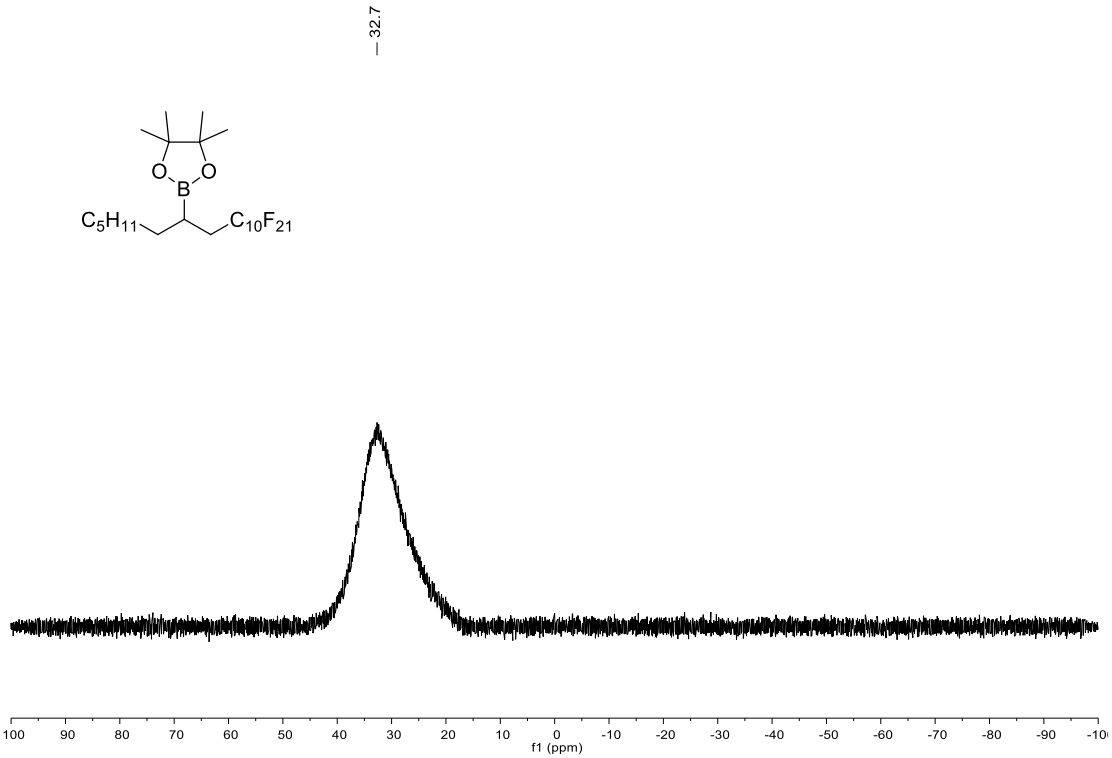
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

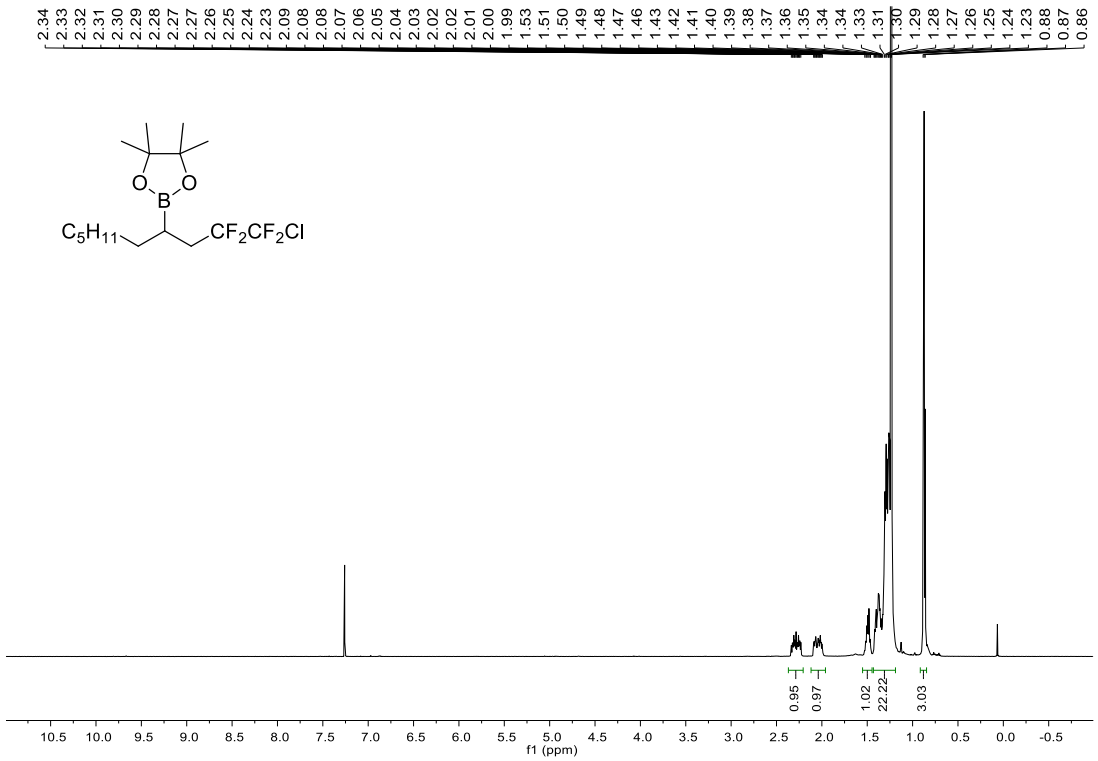


^{11}B NMR (96 MHz, $CDCl_3$)

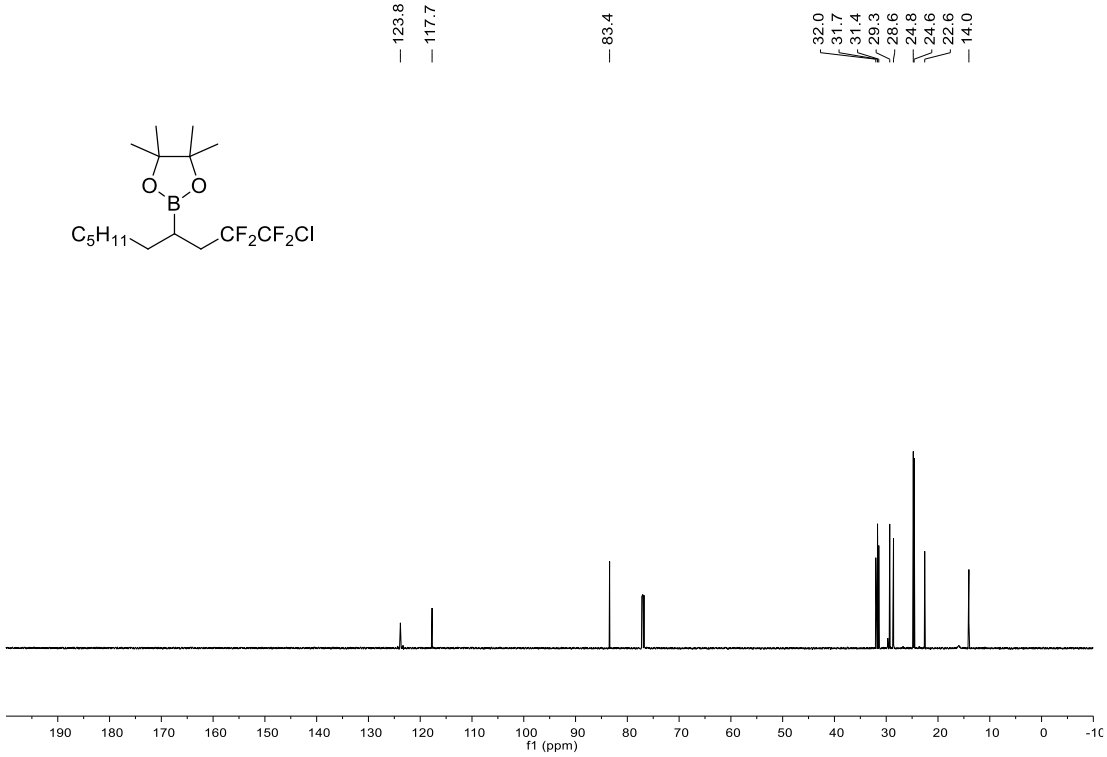


2-(1-Chloro-1,1,2,2-tetrafluorodecan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f)

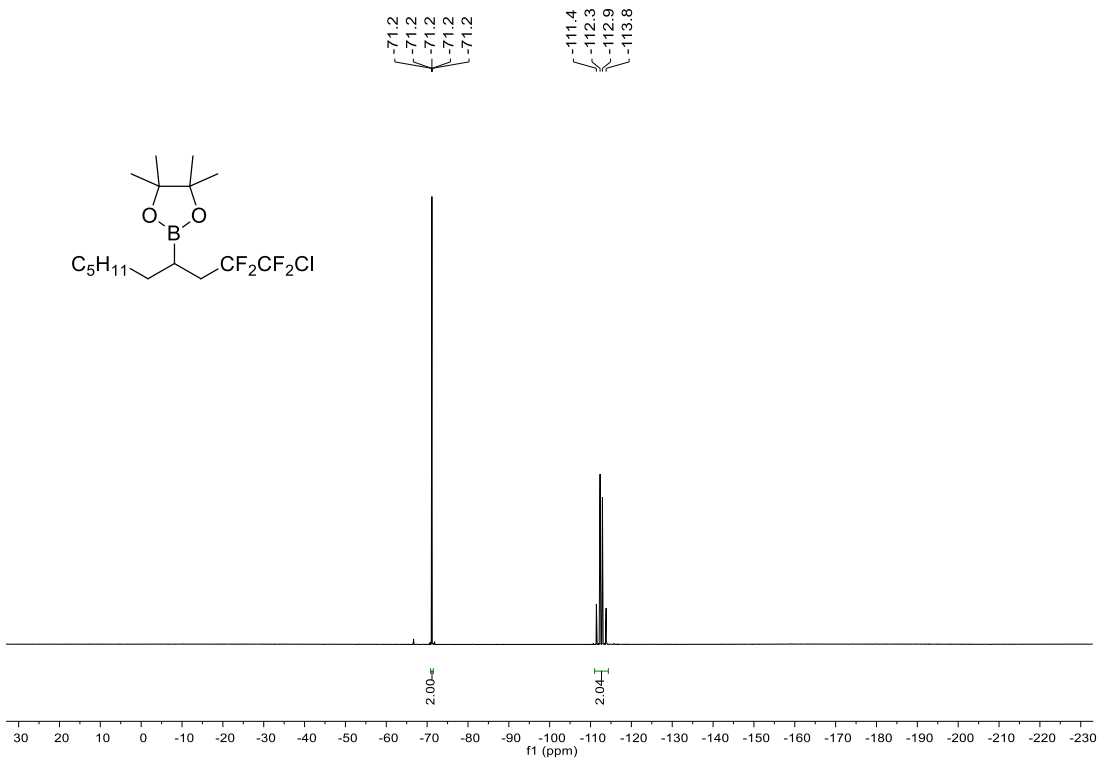
^{1}H NMR (600 MHz, $CDCl_3$)



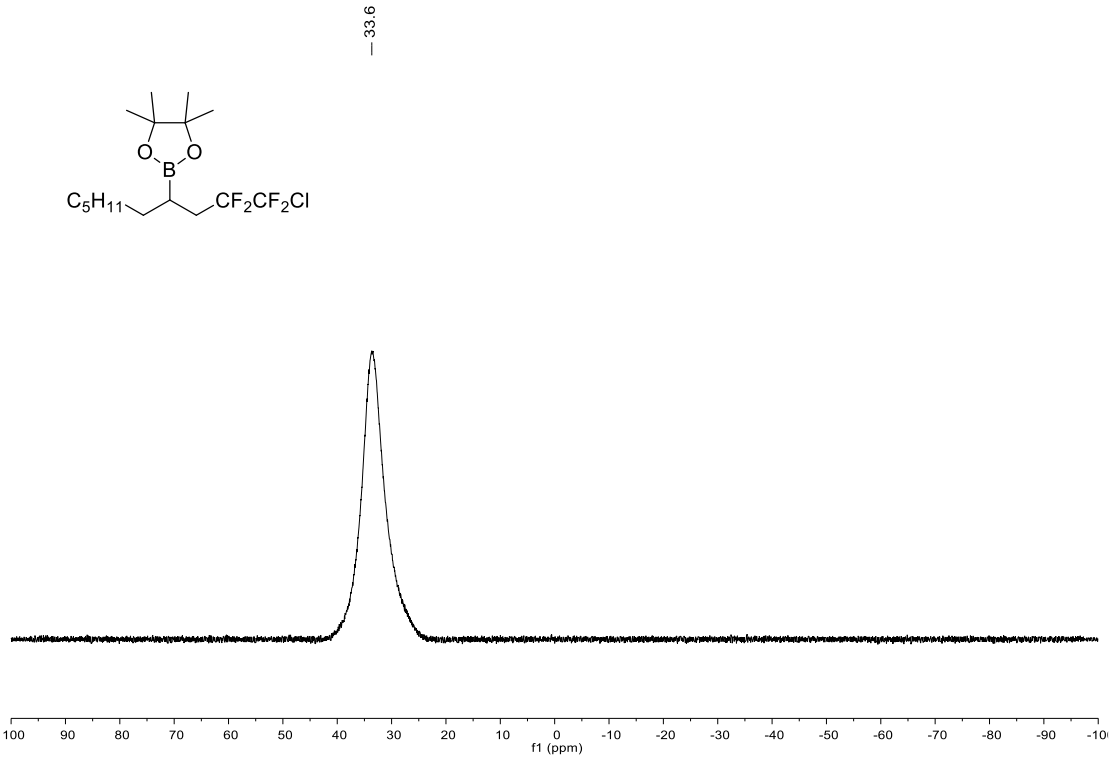
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (282 MHz, $CDCl_3$)

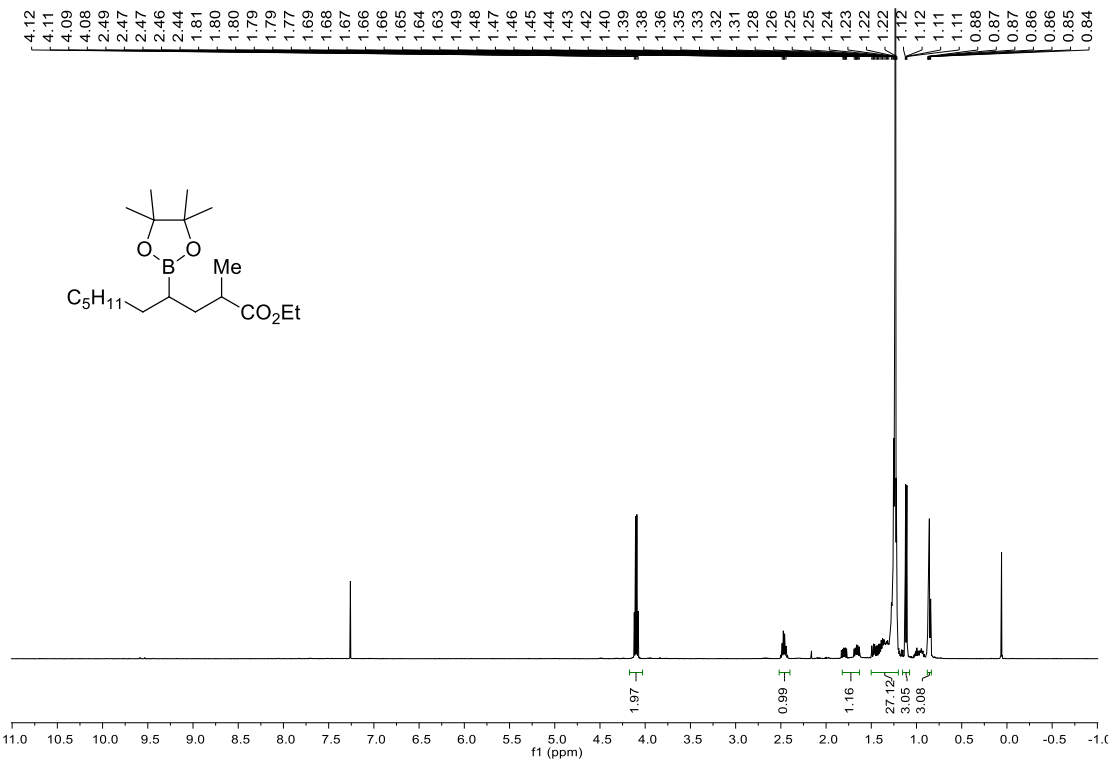


^{11}B NMR (96 MHz, $CDCl_3$)

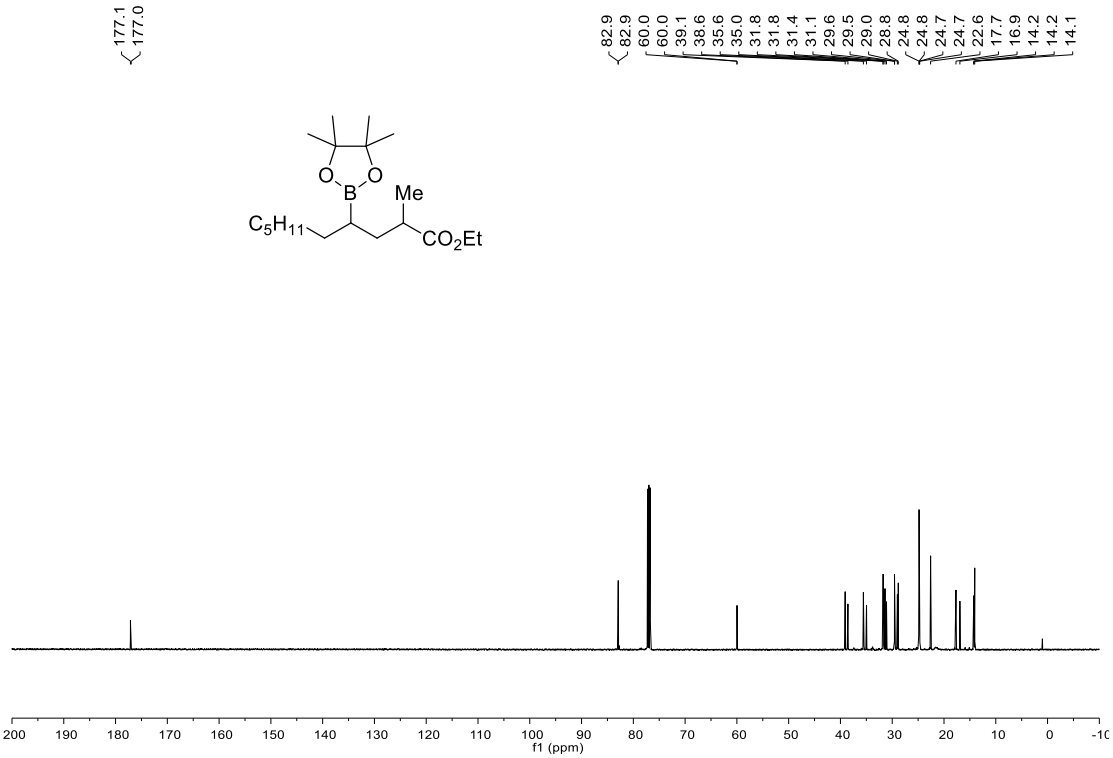


Ethyl 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decanoate (5g)

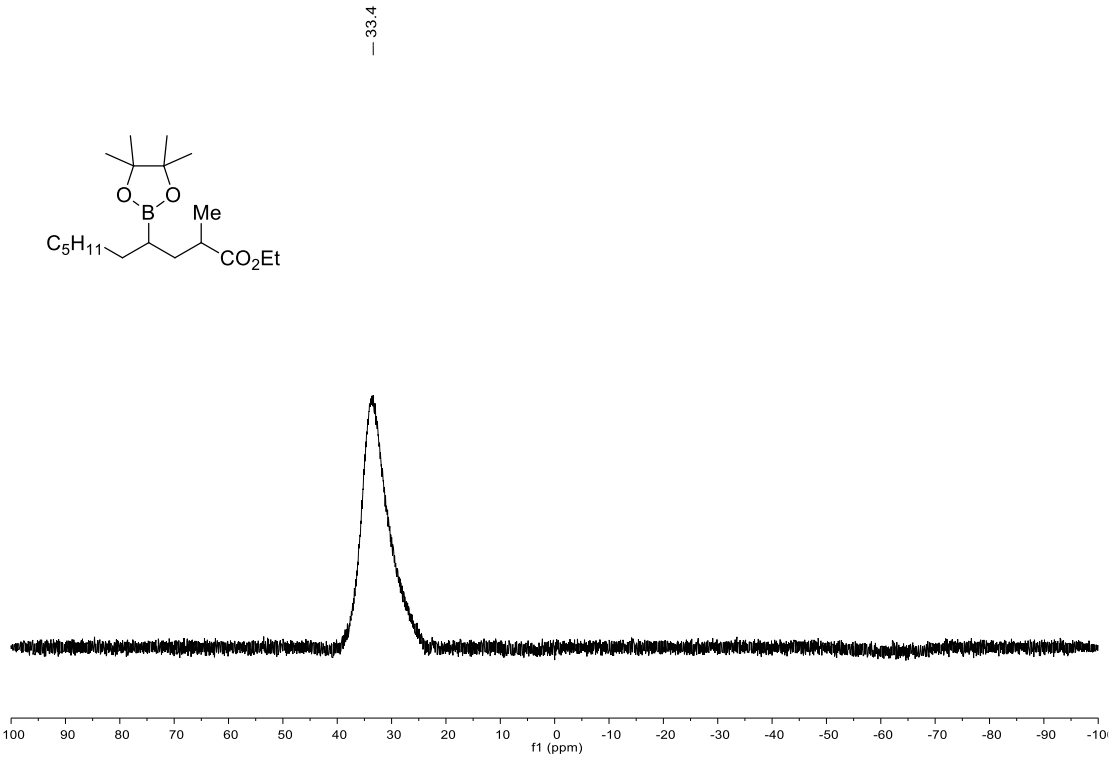
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

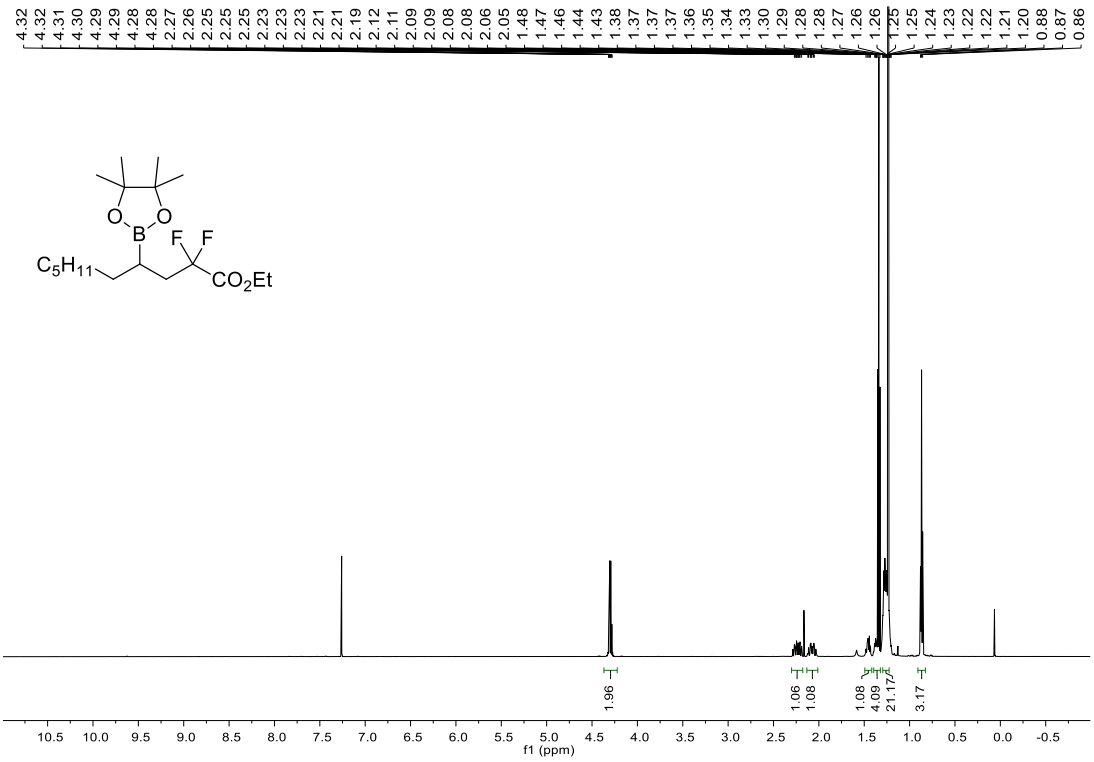


^{11}B NMR (96 MHz, $CDCl_3$)

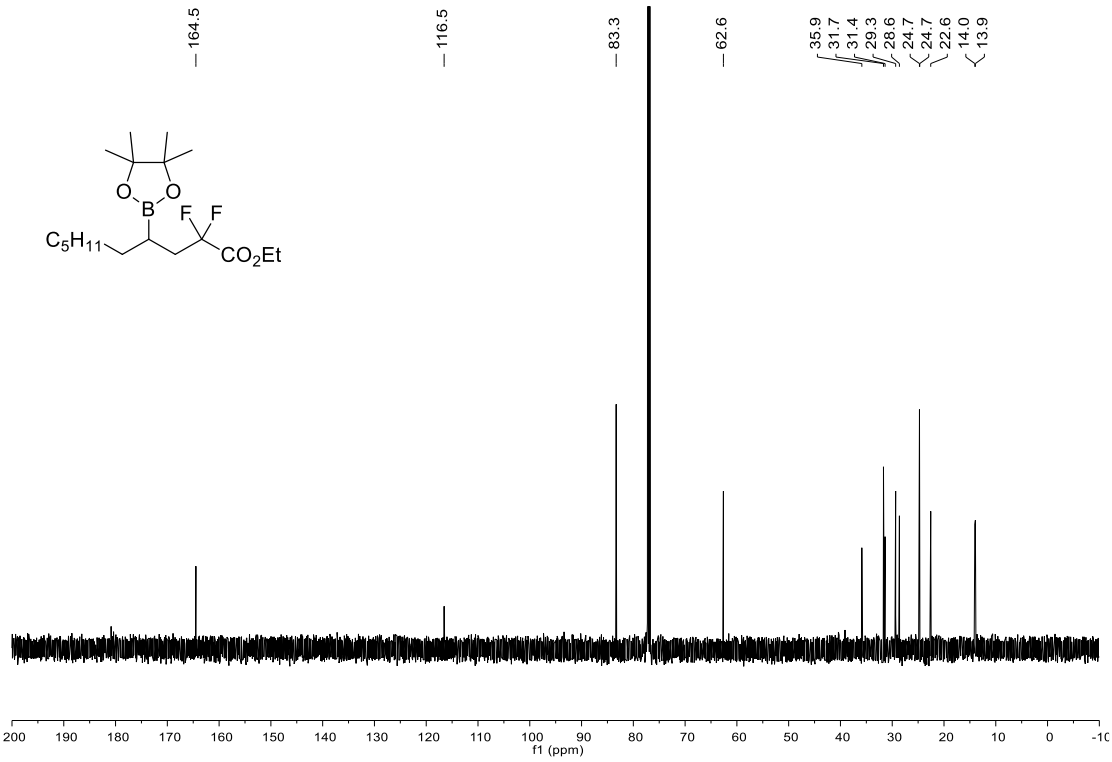


Ethyl 2,2-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decanoate (5h)

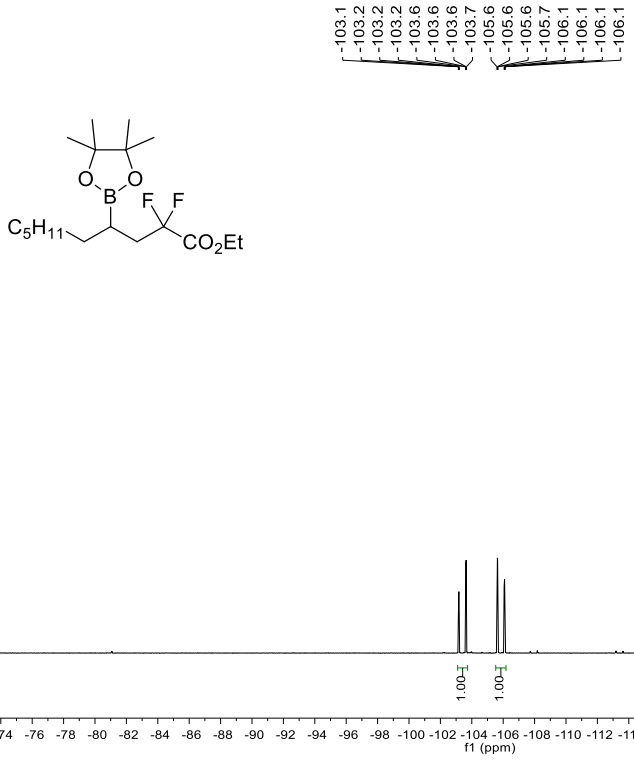
^{1}H NMR (600 MHz, $CDCl_3$)



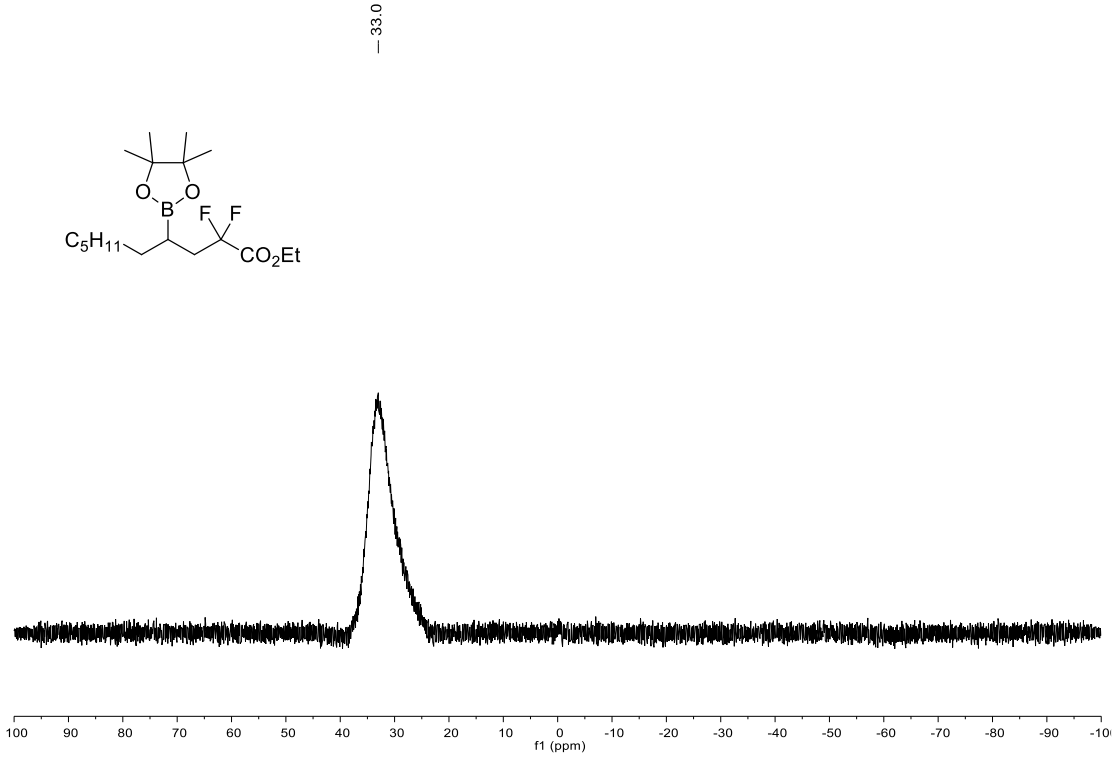
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

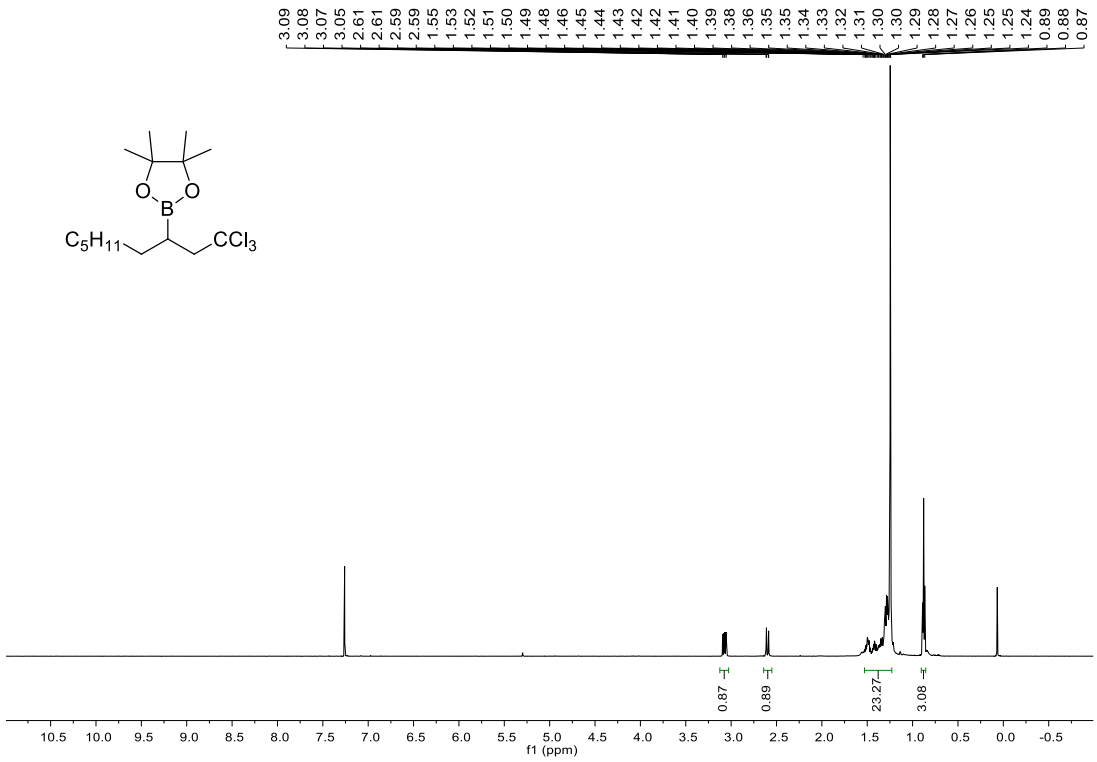


^{11}B NMR (96 MHz, $CDCl_3$)

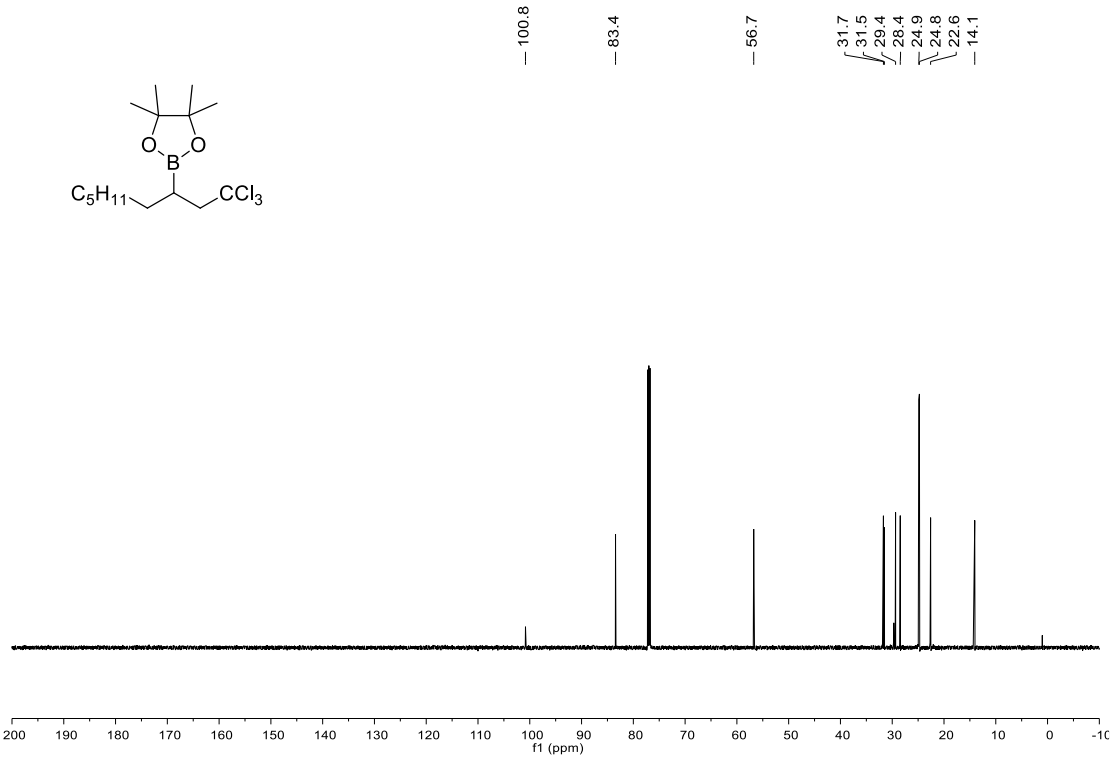


4,4,5,5-Tetramethyl-2-(1,1,1-trichlorononan-3-yl)-1,3,2-dioxaborolane (5i)

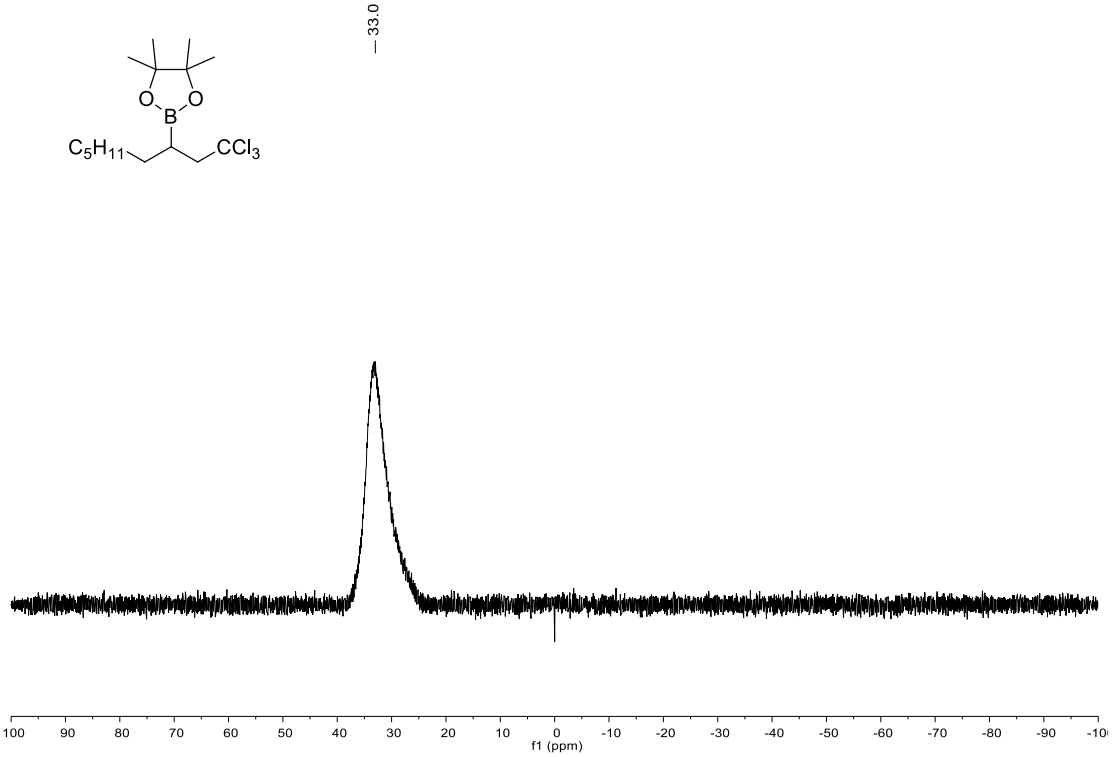
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

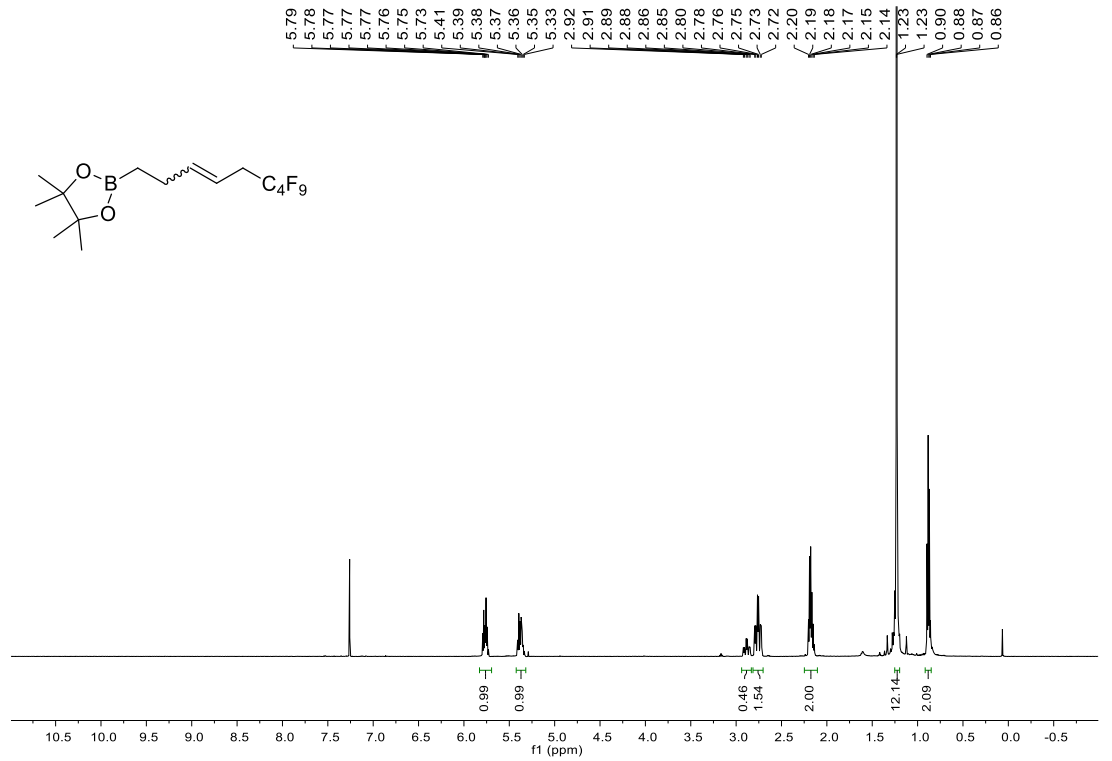


^{11}B NMR (96 MHz, $CDCl_3$)

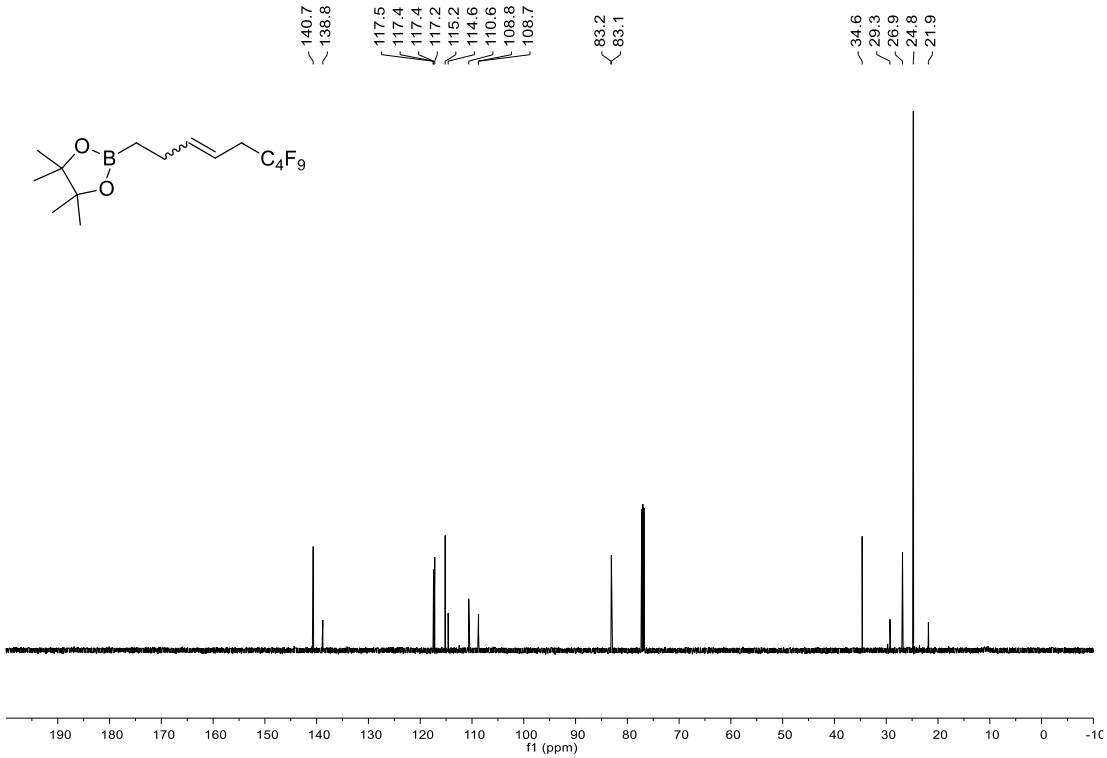


4,4,5,5-Tetramethyl-2-(6,6,7,7,8,8,9,9,9-nonafluoronon-3-en-1-yl)-1,3,2-dioxaborolane (6)

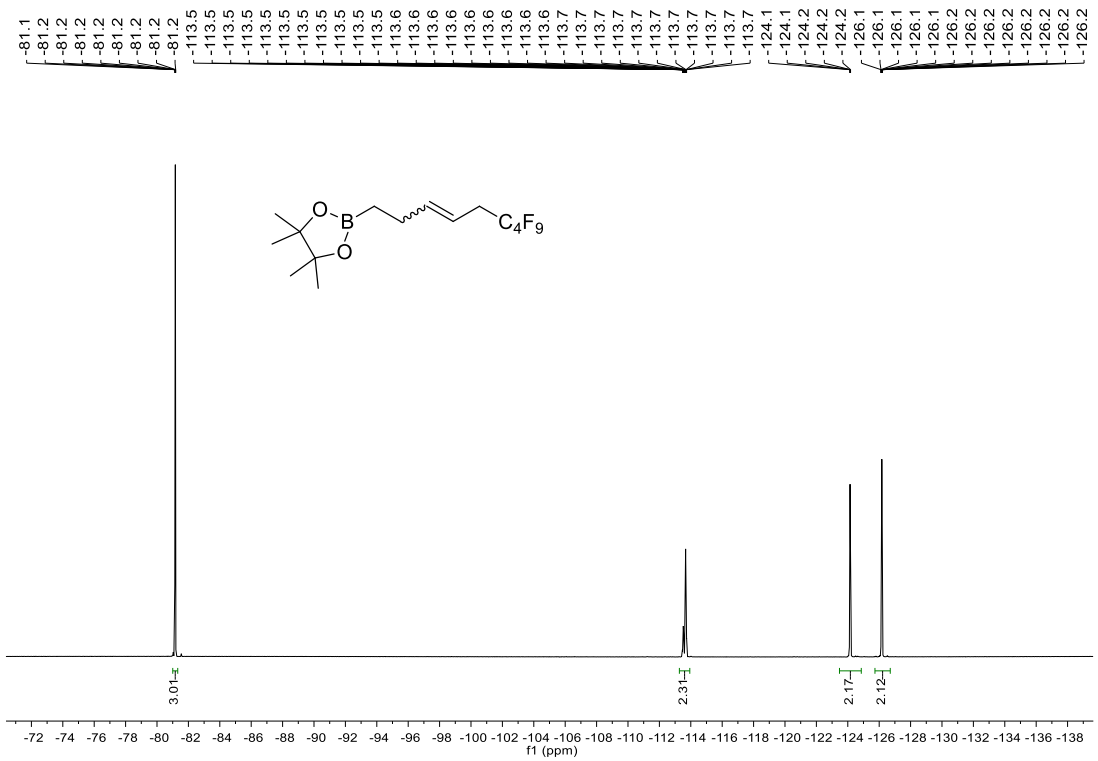
^{1}H NMR (600 MHz, $CDCl_3$)



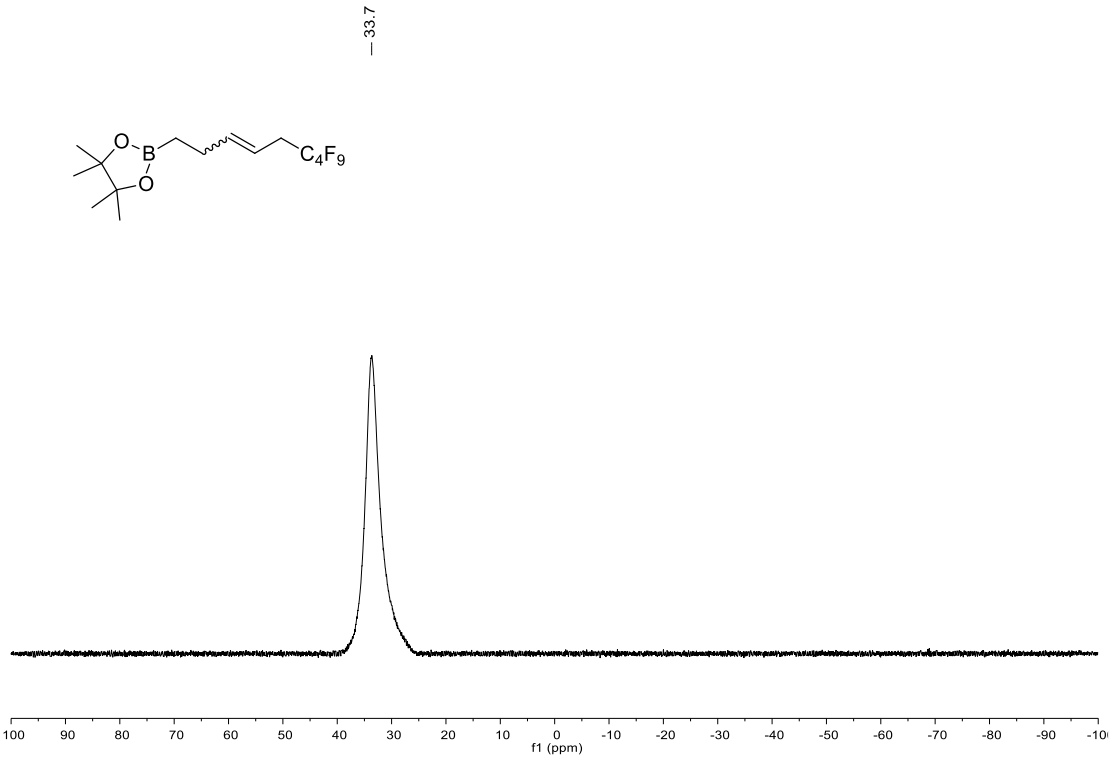
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

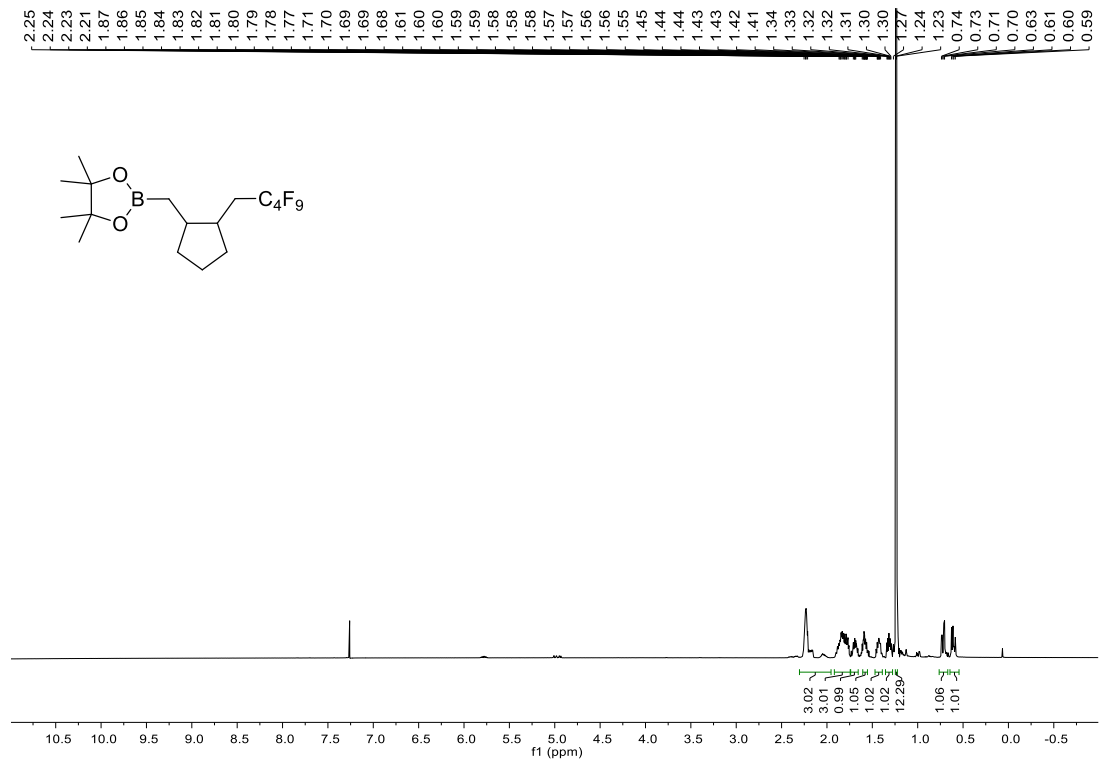


^{11}B NMR (96 MHz, $CDCl_3$)

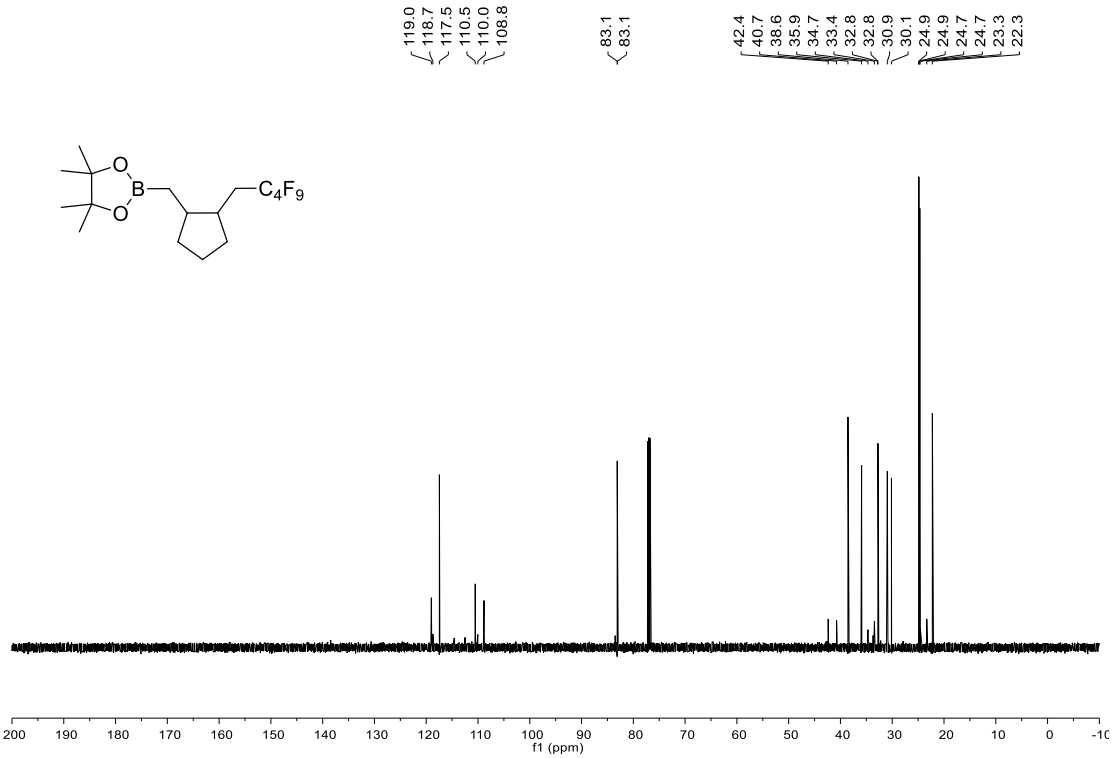


4,4,5,5-Tetramethyl-2-((2-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)cyclopentyl)methyl)-1,3,2-dioxaborolane (7)

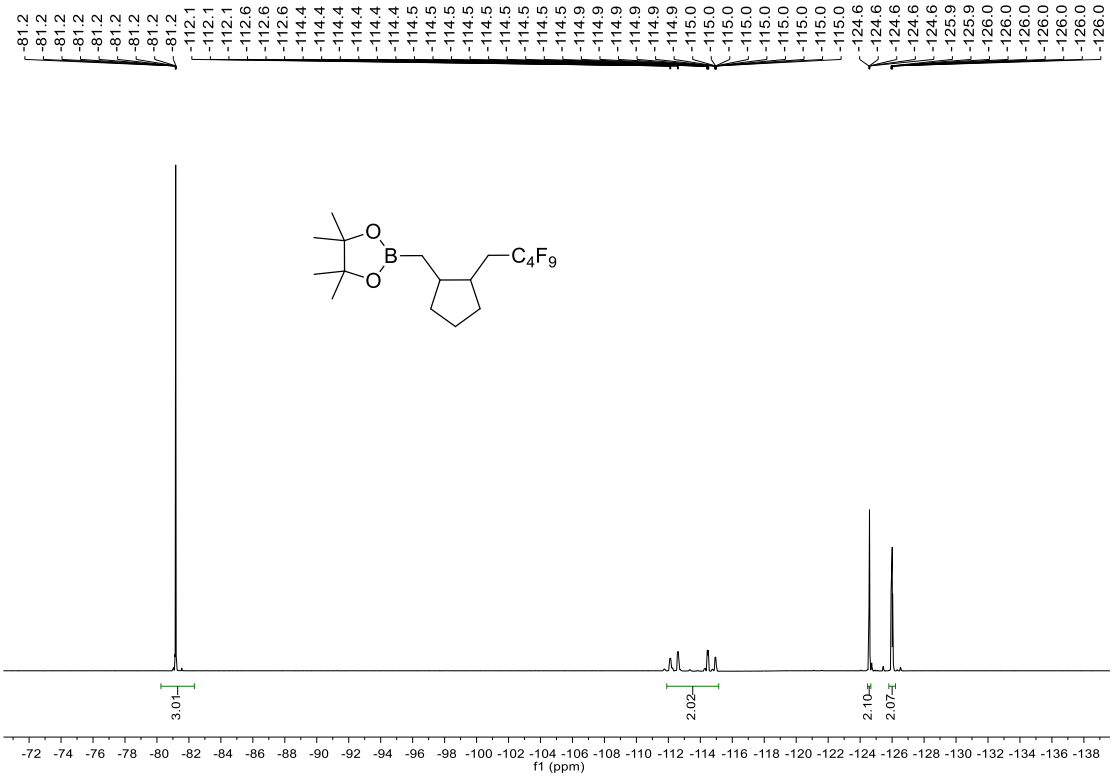
^{1}H NMR (600 MHz, $CDCl_3$)



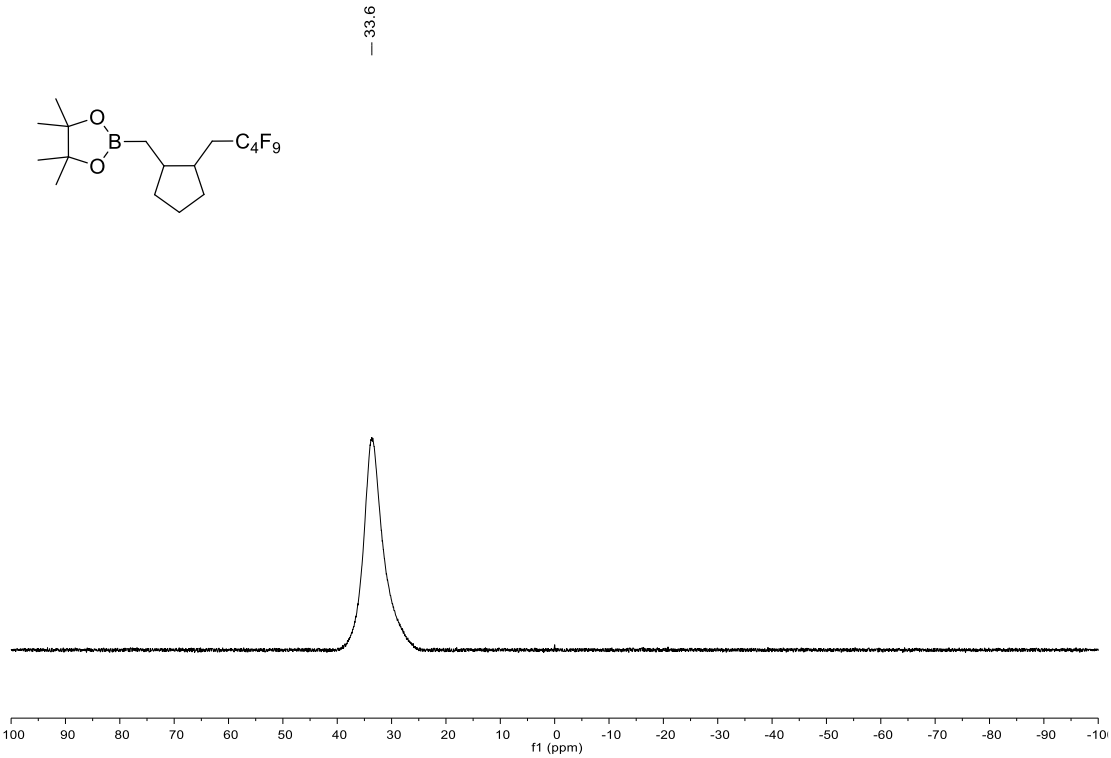
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

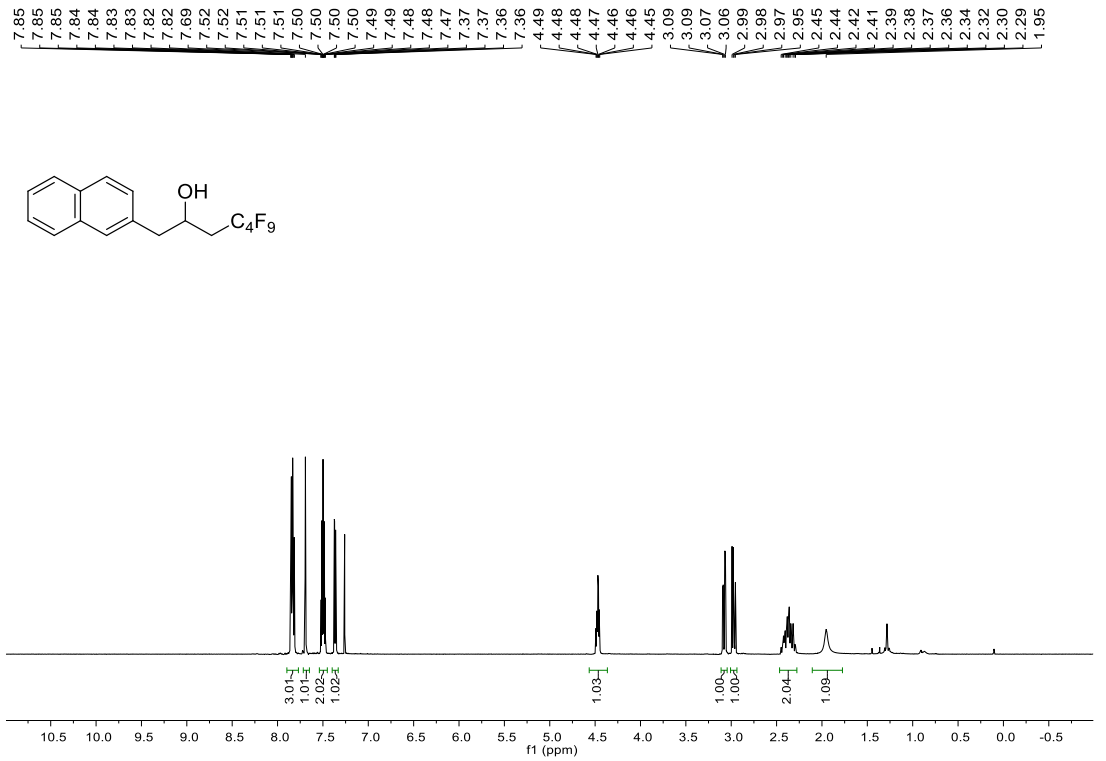


^{11}B NMR (96 MHz, $CDCl_3$)

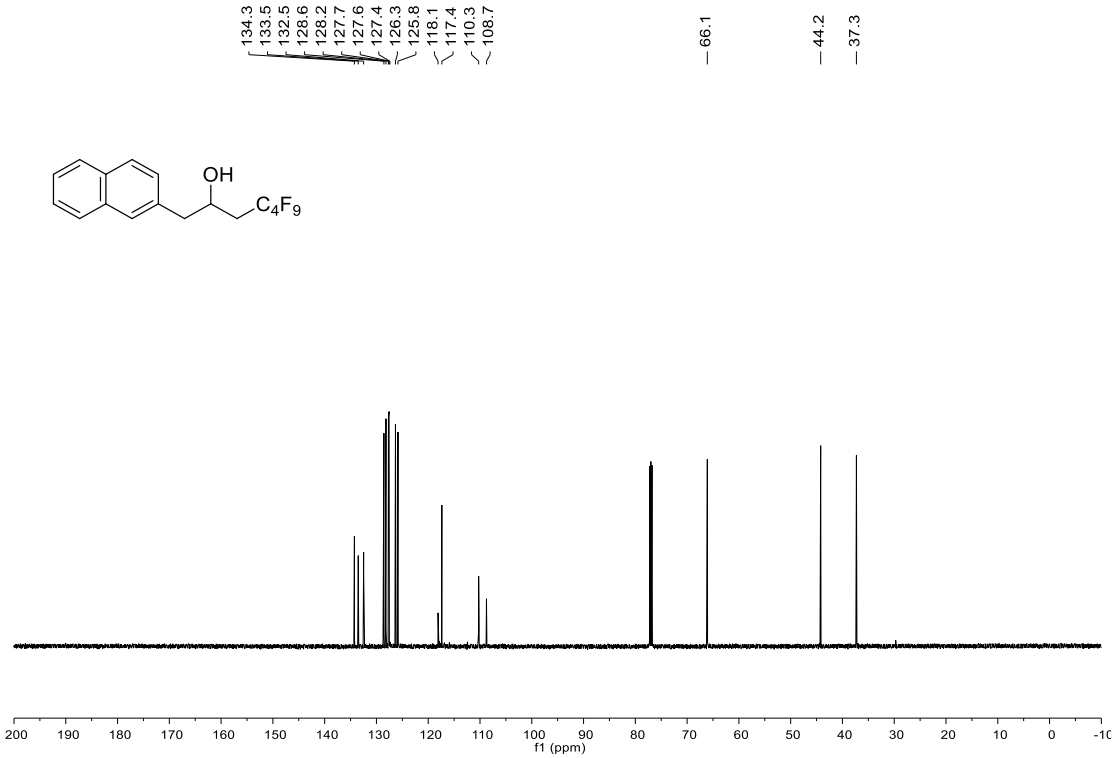


4,4,5,5,6,6,7,7,7-Nonafluoro-1-(naphthalen-2-yl)heptan-2-ol (8)

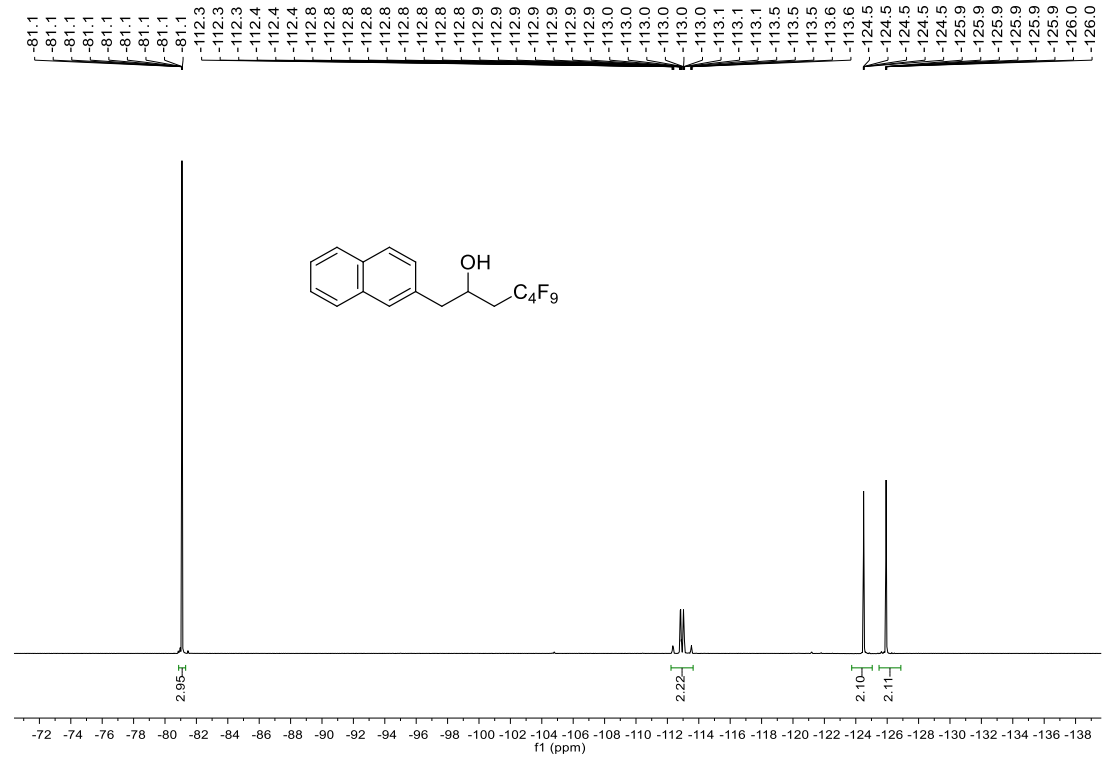
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)

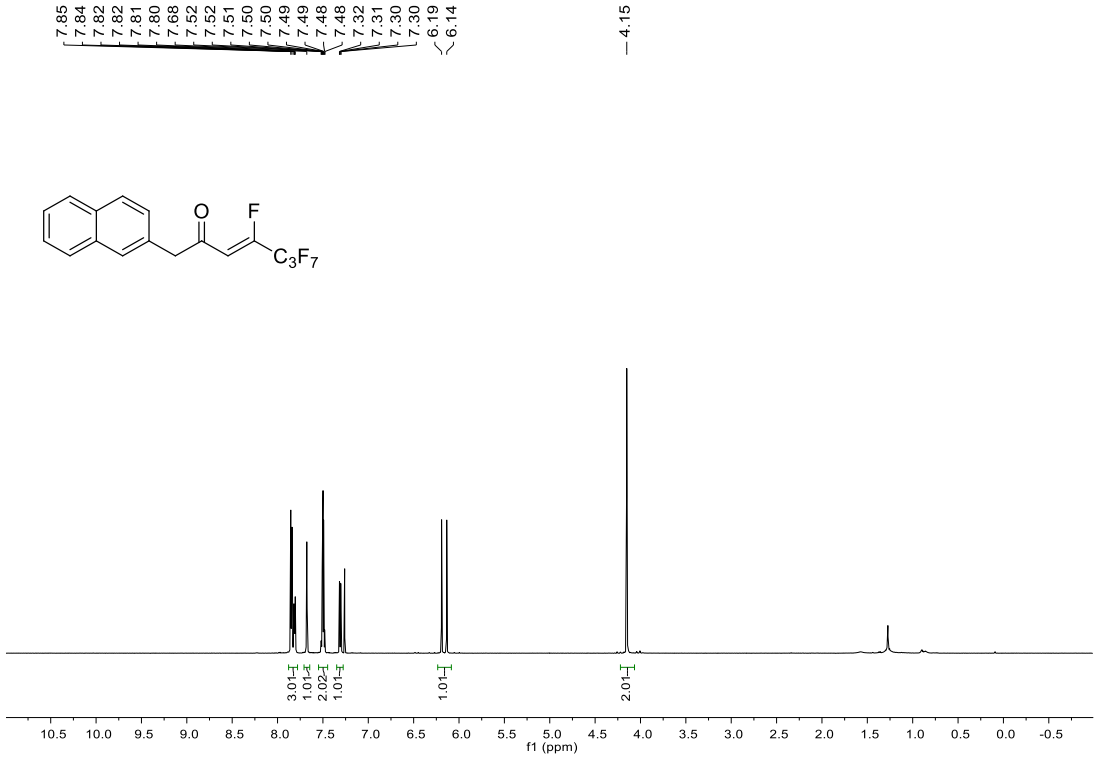


^{19}F NMR (564 MHz, $CDCl_3$)

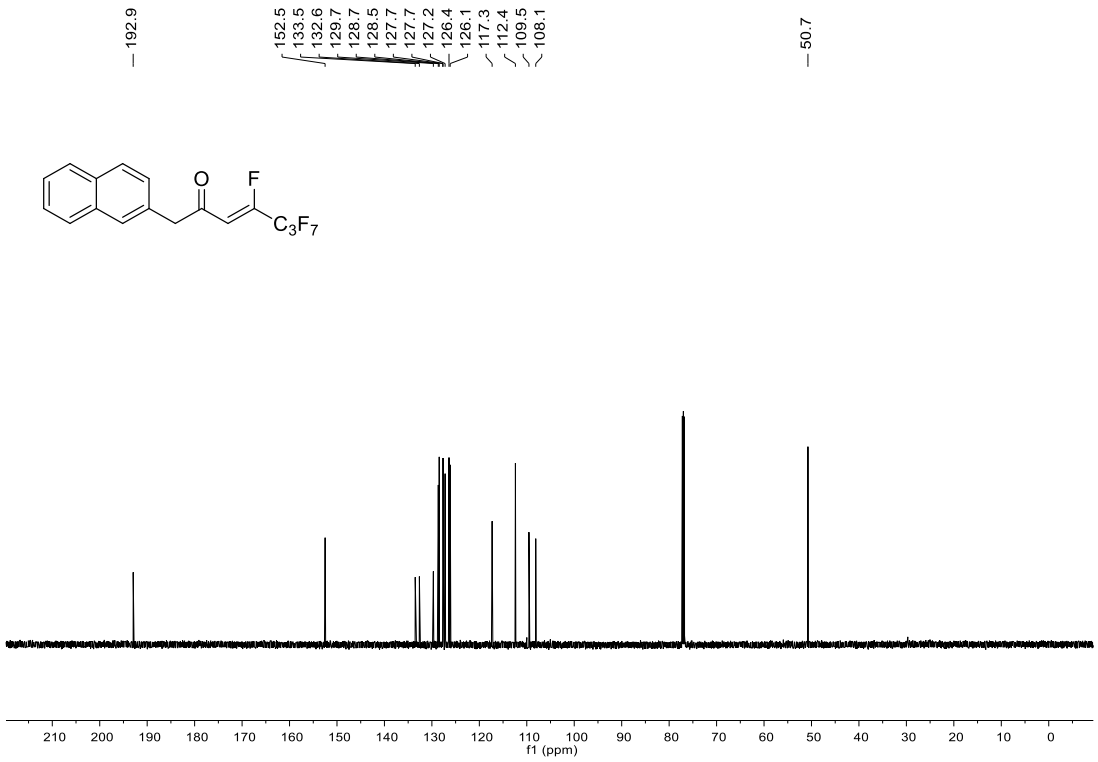


(*Z*)-4,5,5,6,6,7,7,7-Octafluoro-1-(naphthalen-2-yl)hept-3-en-2-one (9)

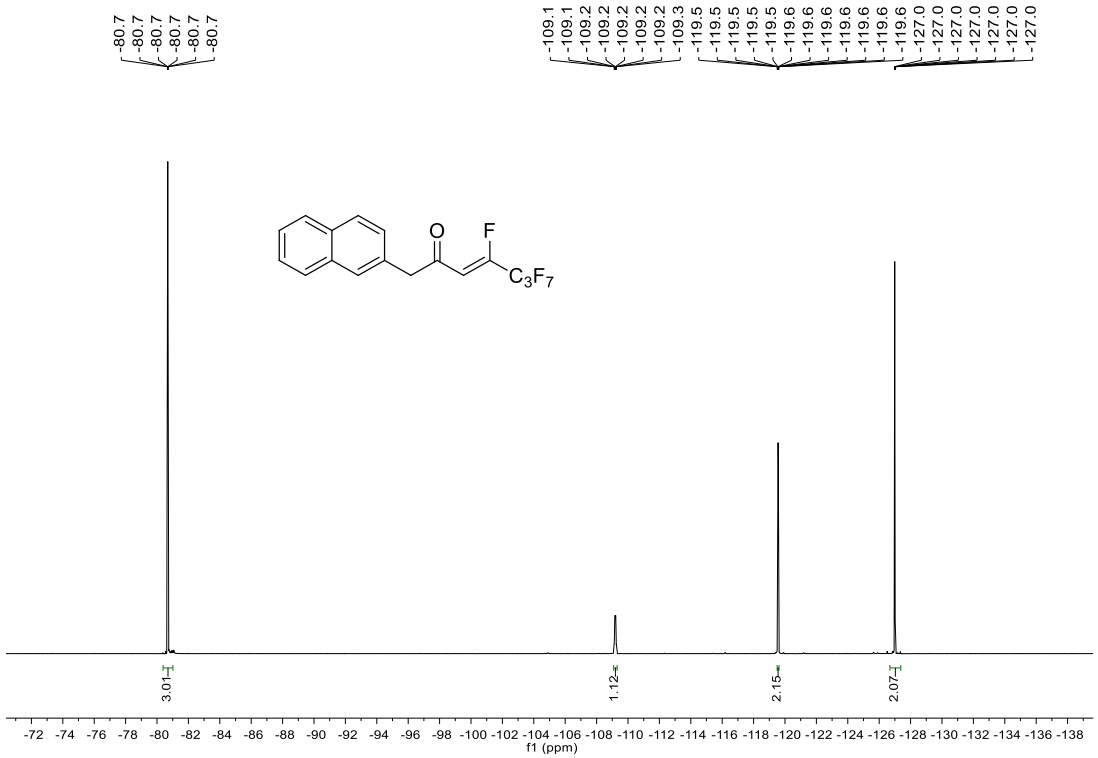
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)

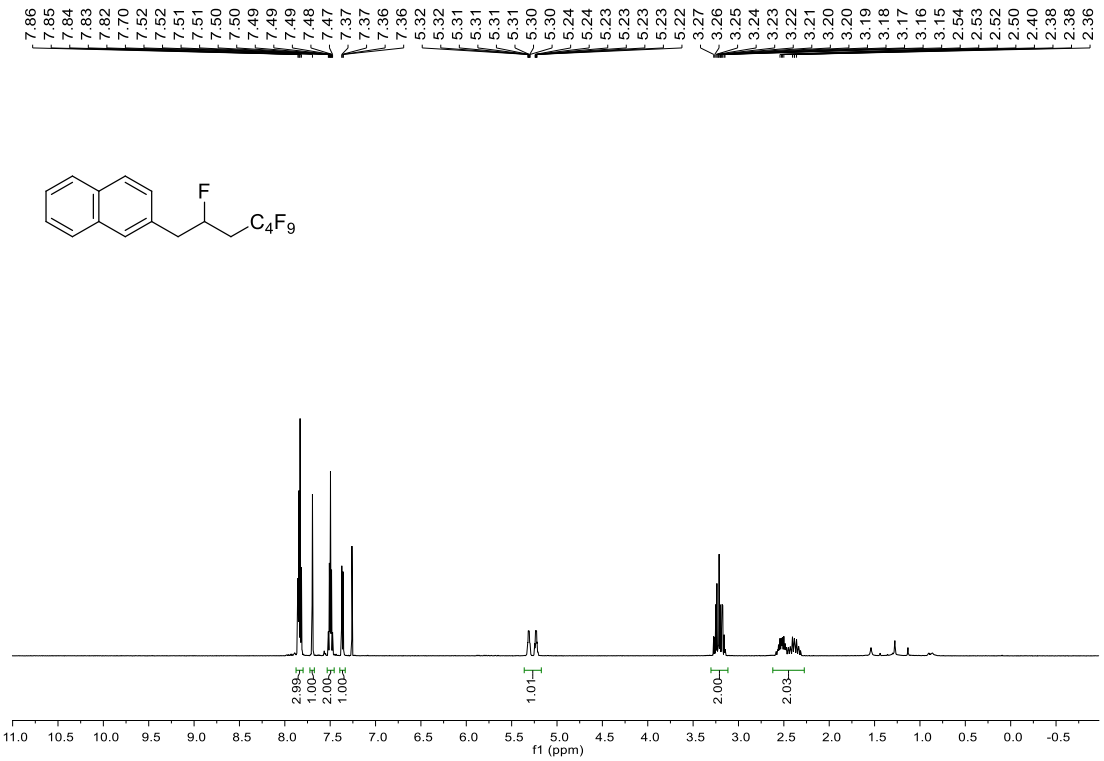


^{19}F NMR (564 MHz, $CDCl_3$)

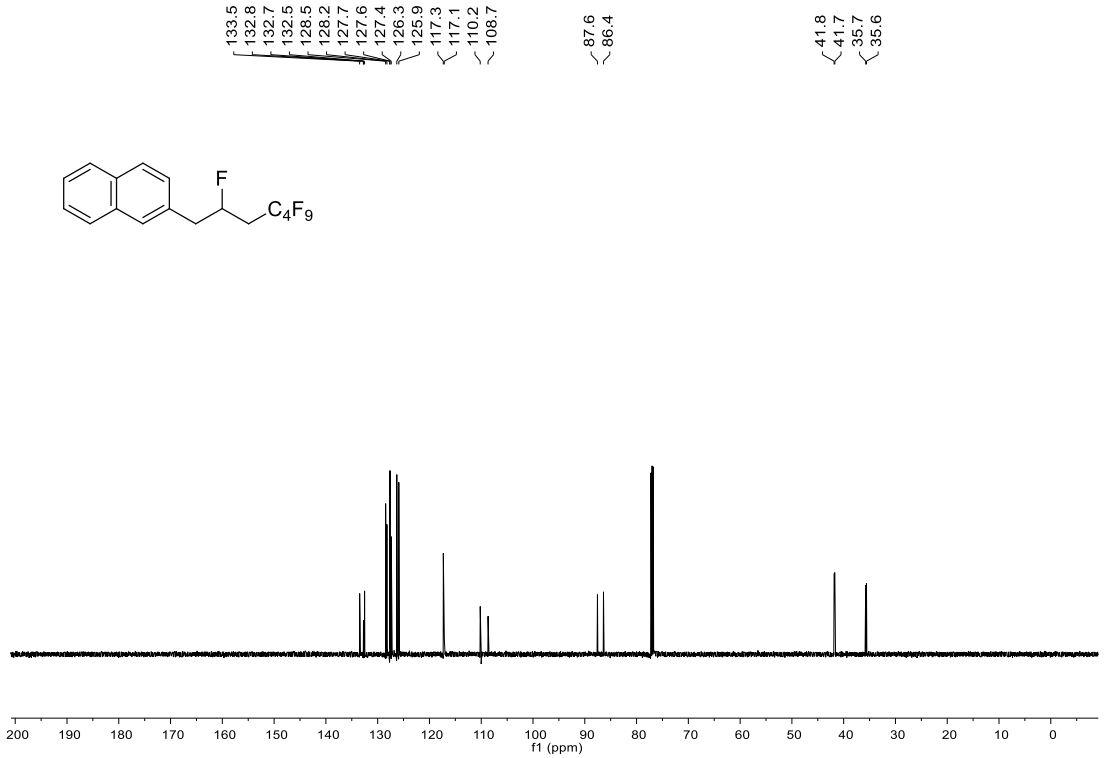


2-(2,4,4,5,5,6,6,7,7,7-Decafluoroheptyl)naphthalene (10)

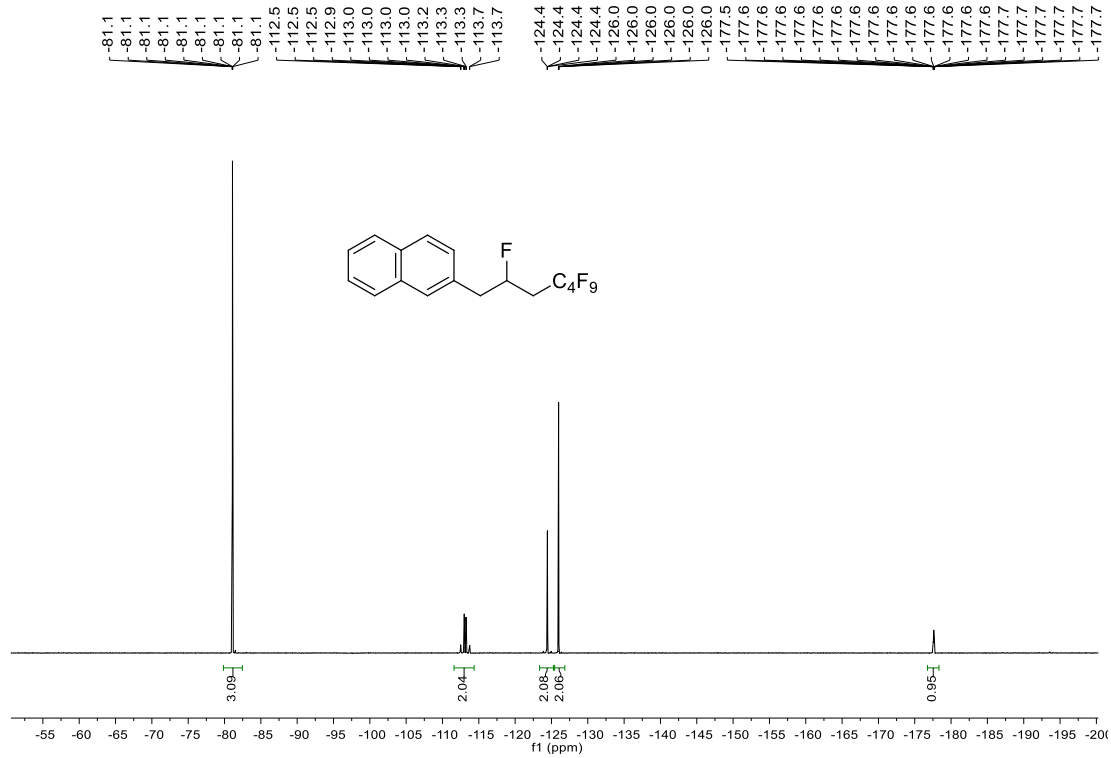
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)

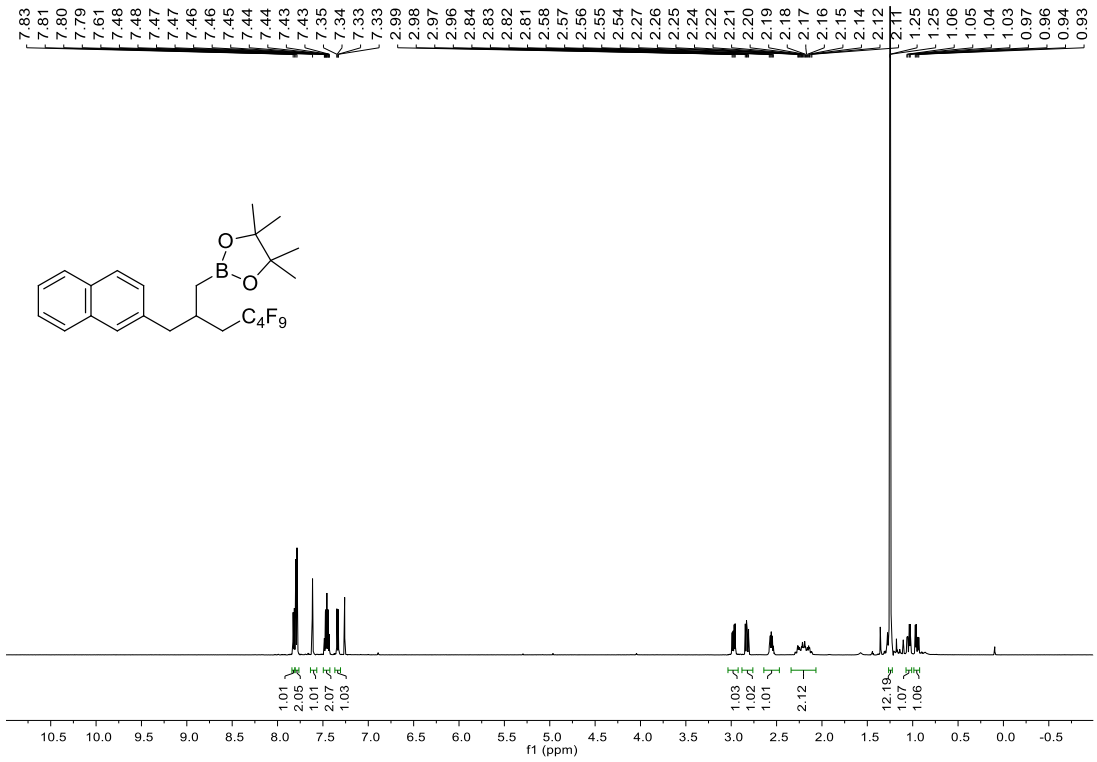


^{19}F NMR (564 MHz, $CDCl_3$)

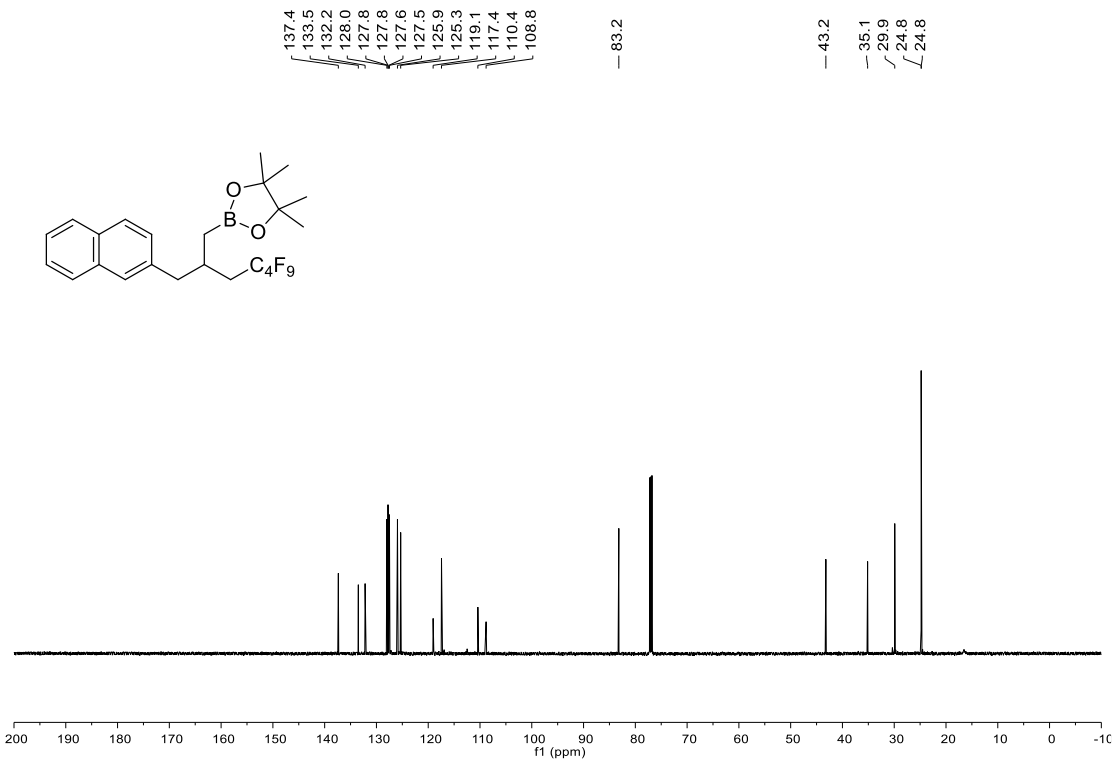


4,4,5,5-Tetramethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-2-(naphthalen-2-ylmethyl)heptyl)-1,3,2-dioxaborolane (11)

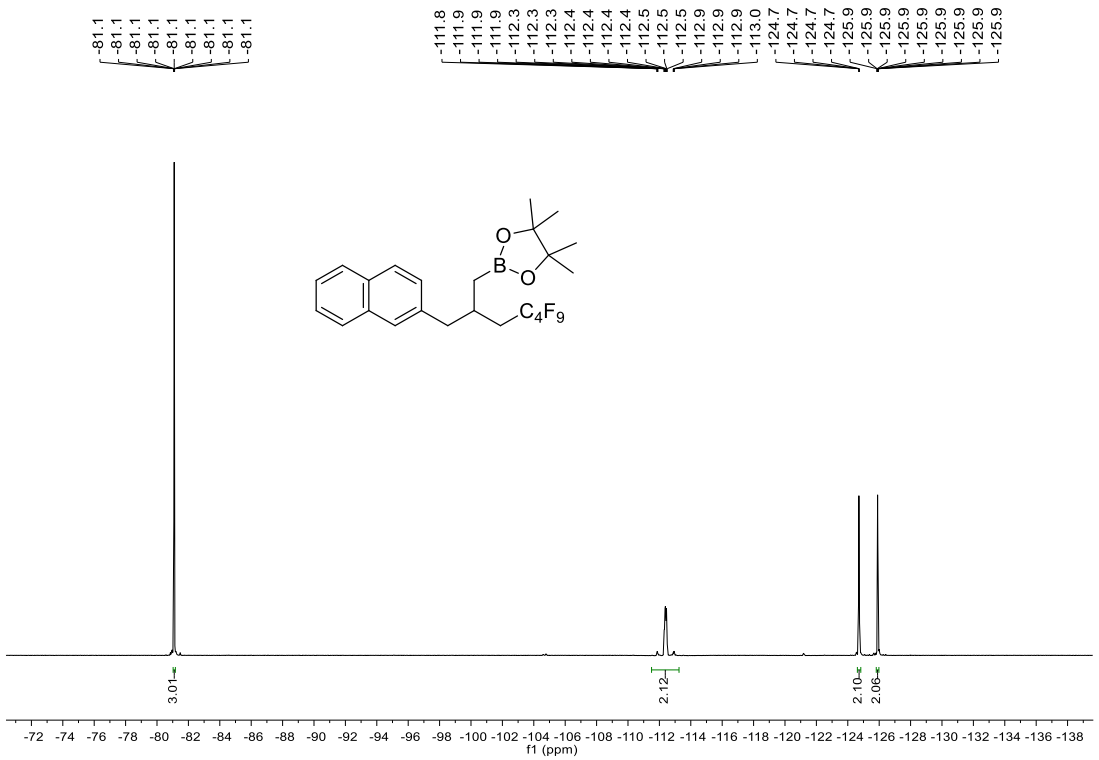
^{1}H NMR (600 MHz, $CDCl_3$)



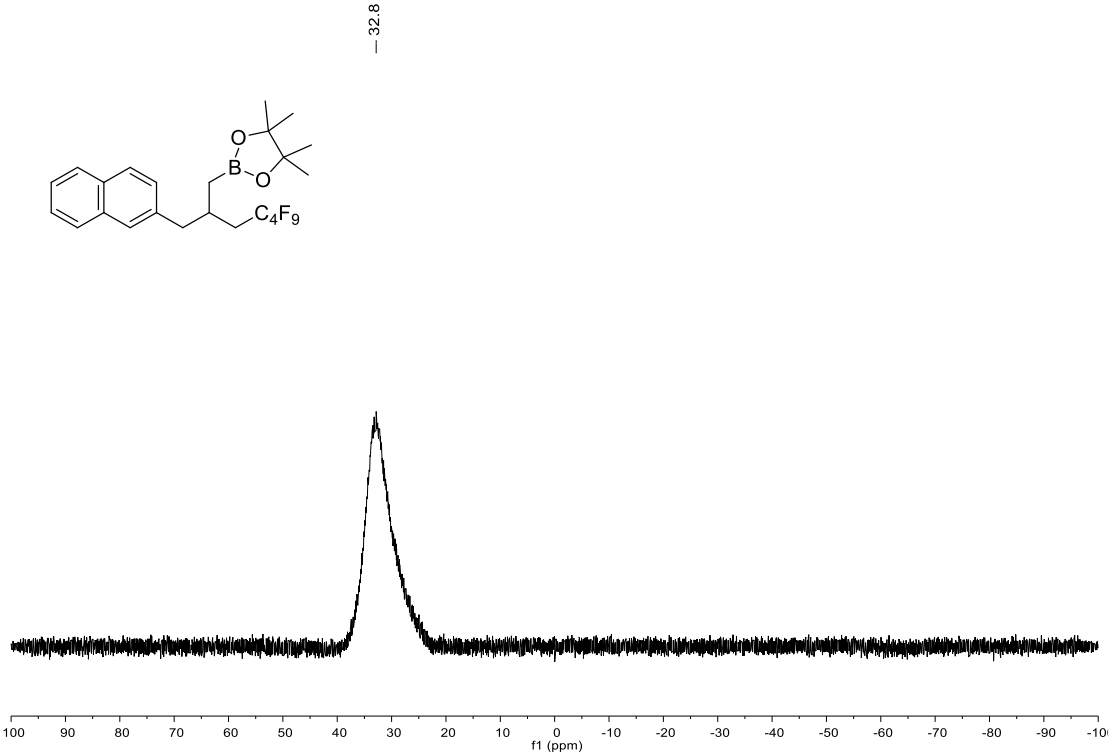
^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)

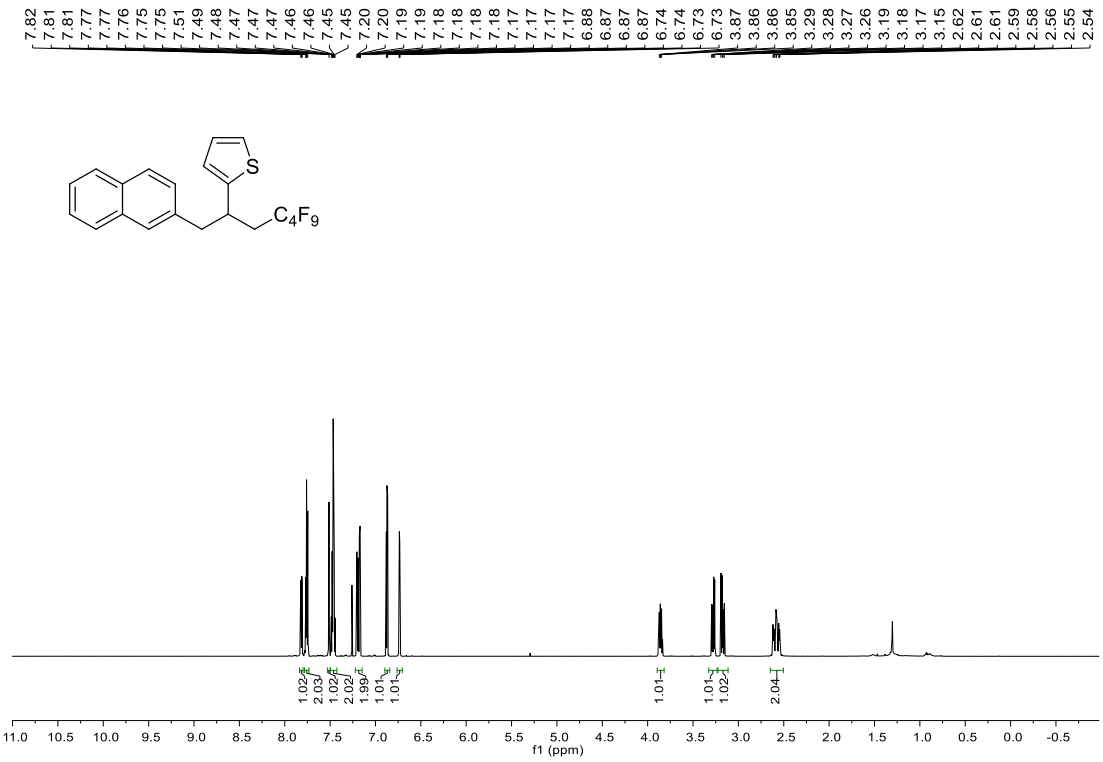


^{11}B NMR (96 MHz, $CDCl_3$)

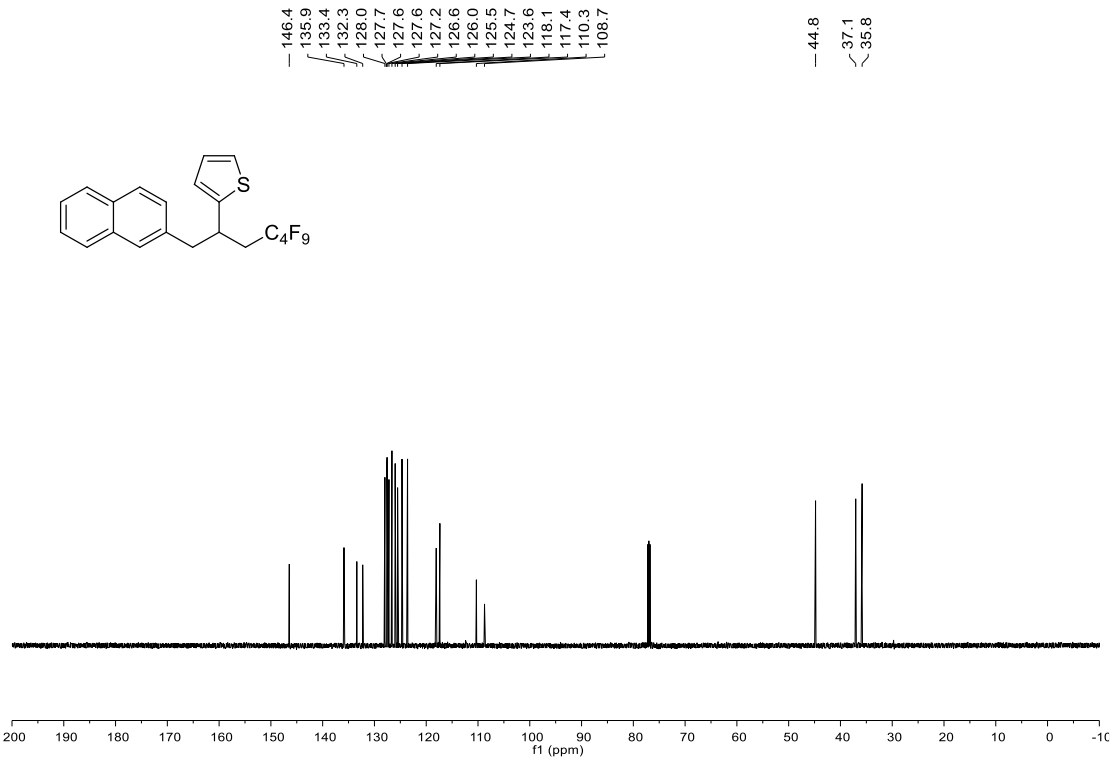


2-(4,4,5,5,6,6,7,7,7-Nonafluoro-1-(naphthalen-2-yl)heptan-2-yl)thiophene (12)

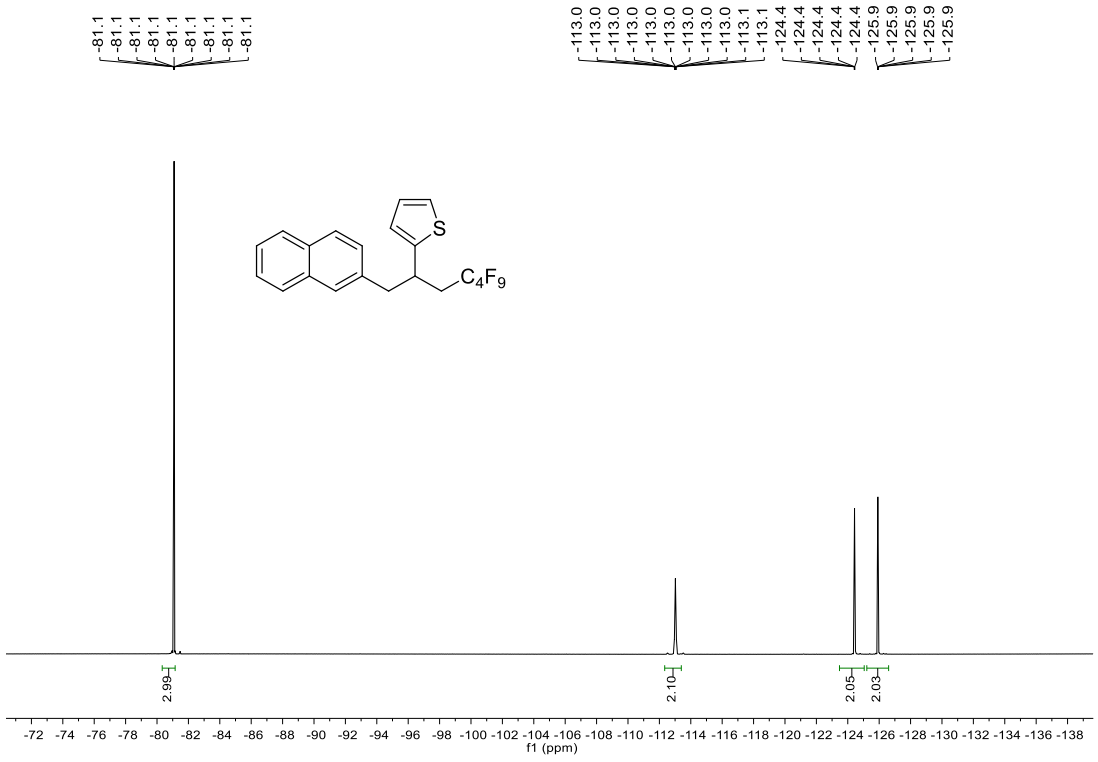
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)

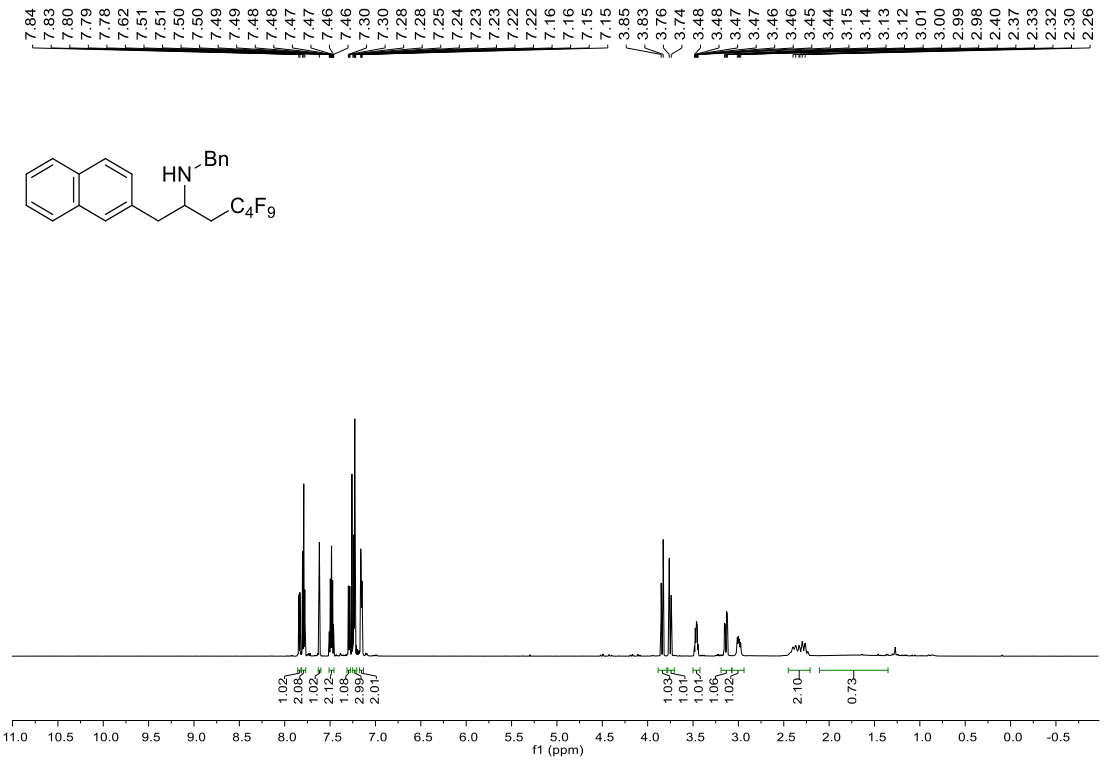


^{19}F NMR (564 MHz, $CDCl_3$)

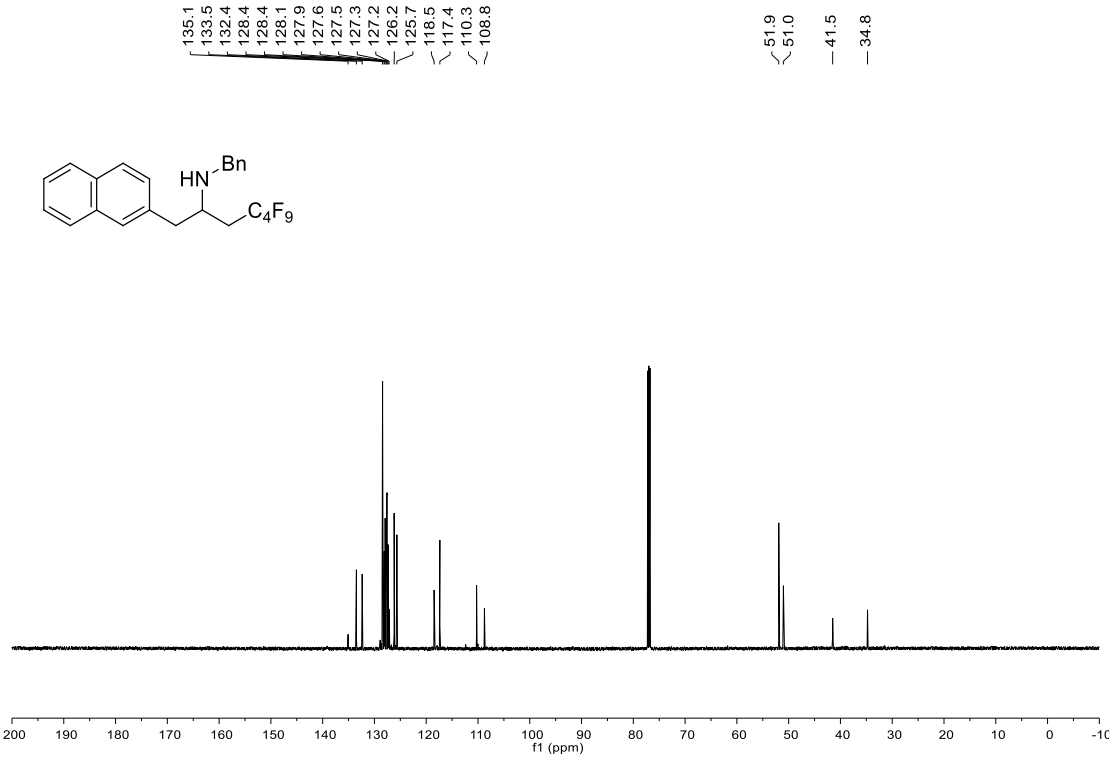


N-Benzyl-4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-2-yl)heptan-2-amine (13)

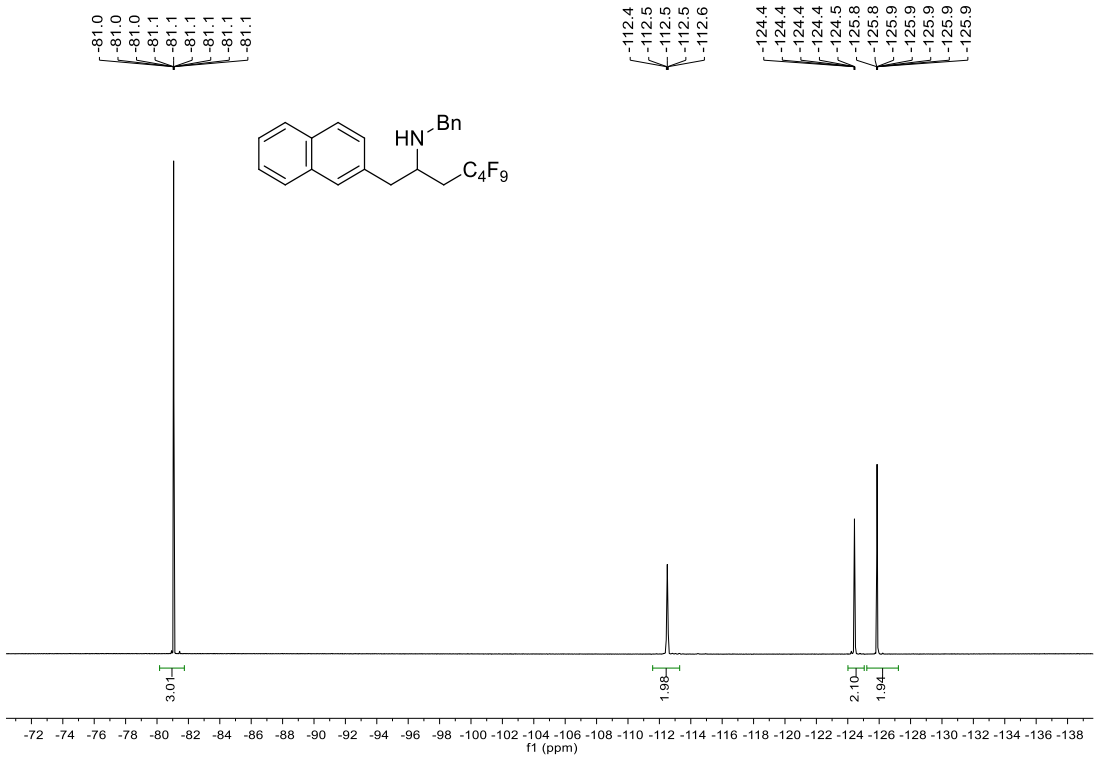
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR {^{19}F} (150 MHz, $CDCl_3$)

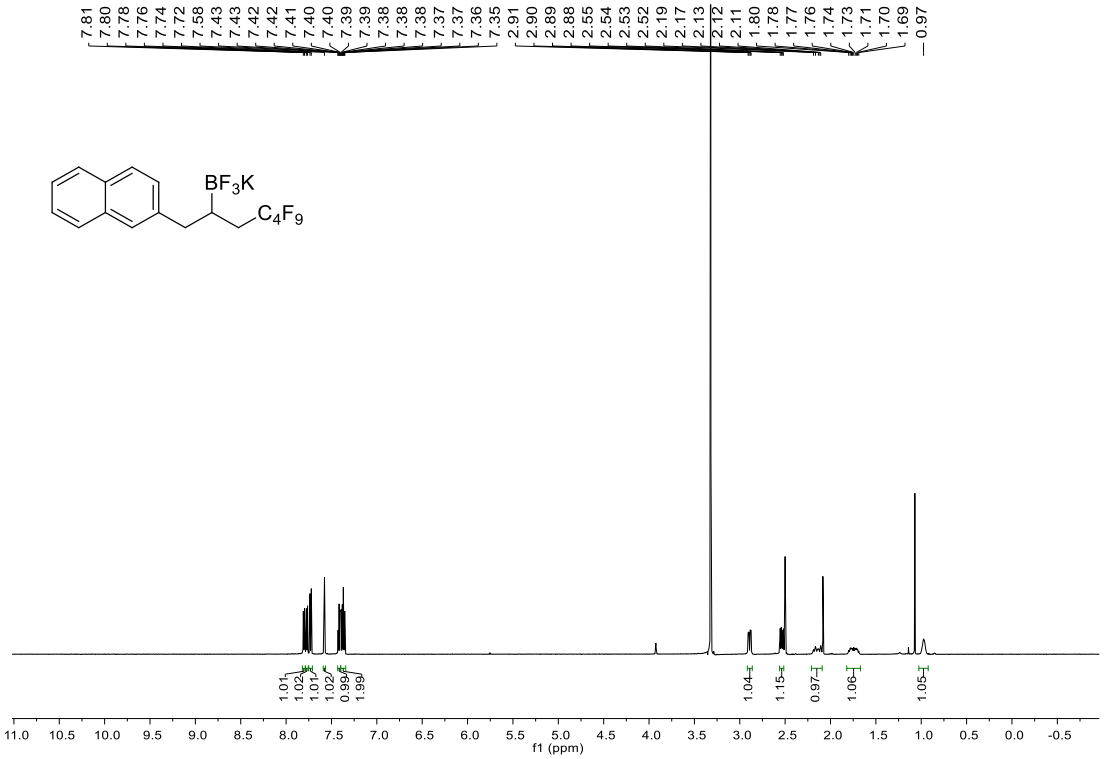


^{19}F NMR (564 MHz, $CDCl_3$)

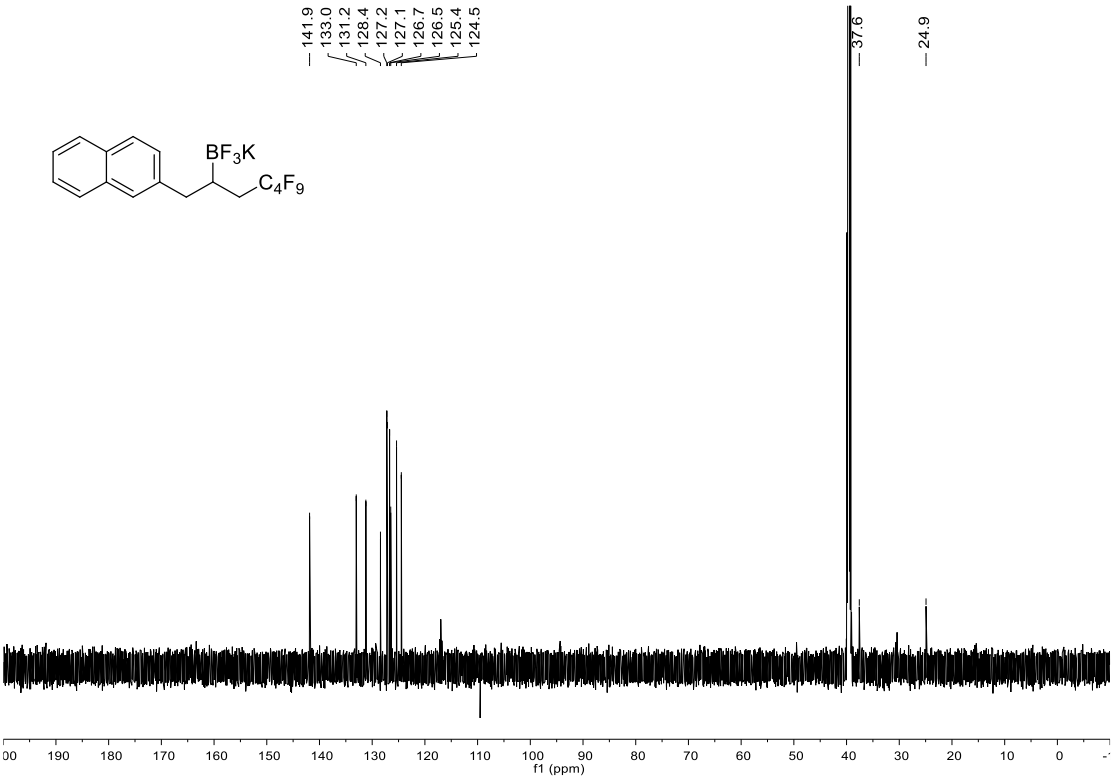


Potassium trifluoro(4,4,5,5,6,6,7,7,7-nonafluoro-1-(naphthalen-2-yl)heptan-2-yl)borate (14)

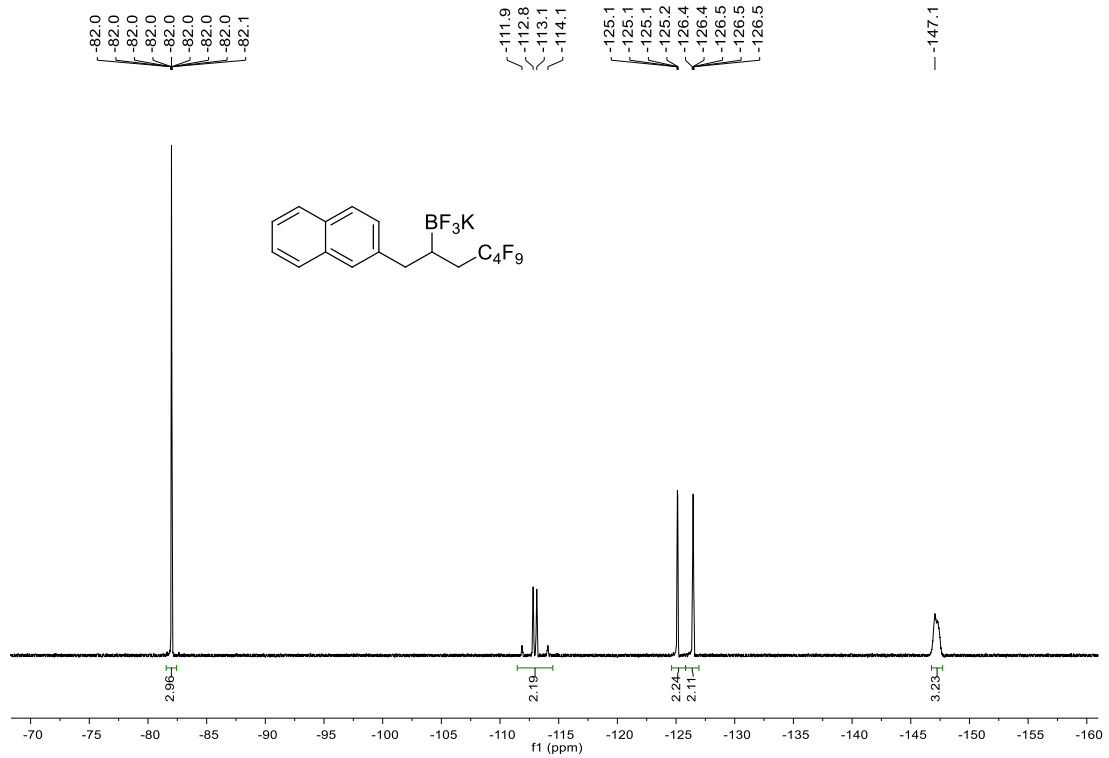
^{1}H NMR (600 MHz, dmso-d6)



^{13}C NMR (150 MHz, dmso-d6)



^{19}F NMR (282 MHz, acetone-d6)



^{11}B NMR (96 MHz, acetone-d6)