Supporting Information

Electrophilic Fluoroalkylthiolation Induced Diastereoselective and Stereospecific 1,2-Metalate Migration of Alkenylboronate Complexes

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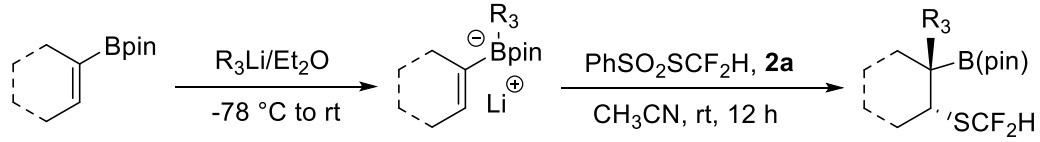
General information.

All solvents were purified by standard method. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on 300, 400, 500 MHz; 101, 126 MHz; 282, 376 MHz; 128 MHz spectrometer (300, 400, 500 MHz for ^{1}H; 101, 126 MHz for ^{13}C; 282, 376 MHz for ^{19}F; 128 MHz for ^{11}B). ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC or ^{19}F NMR. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure.

Materials. All reagents were received from commercial sources. Solvents were freshly dried and degassed according to the purification handbook *Purification of Laboratory Chemicals* before using.

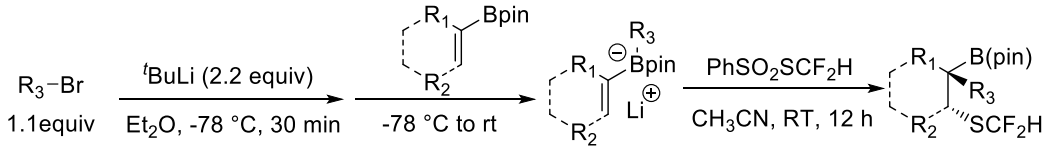
General Procedure for Reaction of Lithium aryl vinyl Boronate with Reagent 2a

***General Procedure 1a* (*GP1a*)**



An oven-dried, 25 mL Schlenk flask equipped with a stir bar, septum, and digital thermocouple probe was charged with Et_2O (2.0 mL) and vinyl pinacol boronate (47 mg, 0.30 mmol). The mixture was cooled to 0 °C. A solution of phenyl lithium in THF (195 μL, 2.0 M, 0.39 mmol, 1.3 equiv.) was added dropwise. The resulting solution was stirred at 0 °C for 15 min, then warmed to room temperature for additional 15 min. The solvent was carefully removed under reduced pressure, affording the lithium phenyl vinyl boronate complex as a white solid, which was used directly without further purification. To the solid was added CH_3CN (3.0 mL) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.). This mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, the residue was purified by silica gel chromatography (Eluent: ethyl acetate/petroleum ether = 1:50, R_f = 0.5) to give compound **3a** as a yellow oil (68 mg, 72% yield).

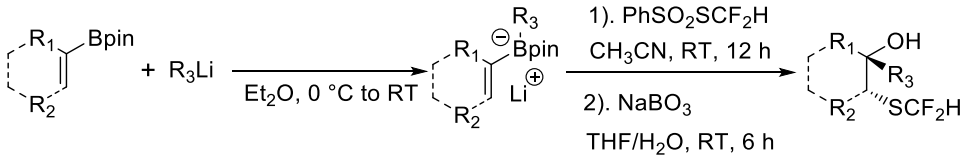
***General Procedure 1b* (*GP1b*)**



An oven-dried, 25-mL Schlenk flask equipped with a stir bar, septum, and digital thermocouple probe was charged with Et_2O (2.0 mL) and 4-bromoanisole (62 mg, 0.33 mmol, 1.1 equiv.). The resulting solution was cooled to -78 °C. A solution of ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.) was added dropwise. The mixture was stirred at -78 °C for 30 min. A solution of 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) in Et_2O (2.0 mL) was added dropwise. The mixture was stirred at -78 °C for 15 min, then warmed to room temperature for another 15 min. The solvent was carefully removed under reduced pressure, affording lithium aryl vinyl boronate complex as a white solid, which was used directly without further purification. To the solid was

added CH_3CN (3.0 mL) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.). This mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, the residue was purified by silica gel chromatography (Eluent: ethyl acetate/petroleum ether = 1:20, R_f = 0.4) to give compound **3c** as a yellow oil (61 mg, 51% yield).

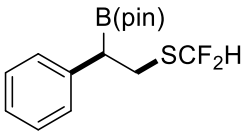
***General Procedure 1c* (*GP1c*)**



An oven-dried, 25 mL Schlenk flask equipped with a stir bar, septum, and digital thermocouple probe was charged with Et_2O (2.0 mL) and vinyl pinacol boronate (47 mg, 0.30 mmol). The mixture was cooled to 0 °C. A solution of phenyl lithium in THF (195 μL, 2.0 M, 0.39 mmol, 1.3 equiv.) was added dropwise. The resulting solution was stirred at 0 °C for 15 min, then warmed to room temperature for additional 15 min. The solvent was carefully removed under reduced pressure, affording the lithium phenyl vinyl boronate complex as a white solid, which was used directly without further purification. To the solid was added CH_3CN (3.0 mL) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.). This mixture was stirred at room temperature for 12 h.

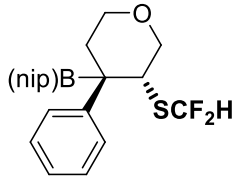
The solvent was removed under reduced pressure, then $NaBO_3$ (0.90 mmol, 3.0 equiv.) and THF/H_2O (v/v = 1:1, 6.0 mL) was added. The reaction was allowed to stir at room temperature for 6 h. Half of the solvent was removed under reduced pressure. The aqueous layer was extracted with ethyl acetate (10 mL × 3), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated. The residue was purified by silica gel chromatography (Eluent: ethyl acetate/petroleum ether = 1:5, R_f = 0.5) to give compound **4a** as a yellow oil (43 mg, 71%).

2-(2-(Difluoromethylthio)-1-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3a



Prepared according to ***GP1a*** using pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 µL, 2.0 M, 0.39 mmol, 1.3 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3a** as a yellow oil (68 mg, 72%). Eluent: ethyl acetate/petroleum ether (1:50, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 5 H), 6.74 (t, *J* = 56.6 Hz, 1 H), 3.31 – 3.19 (m, 1 H), 3.18 – 3.07 (m, 1 H), 2.67 (t, *J* = 8.1 Hz, 1 H), 1.24 (s, 6 H), 1.20 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.26 (dd, *J* = 233.4, 46.2 Hz), -93.03 (dd, *J* = 233.4, 46.5 Hz); **^{13}C NMR** (151 MHz, $CDCl_3$, signal of carbon adjacent to boron missing) δ 140.46, 128.63, 128.40, 120.98 (t, *J* = 272.2 Hz), 83.95, 30.41, 24.61, 24.56; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.58 (s) ppm. **IR** (KBr): ν_{max} = 3058, 3022, 2977, 2930, 1599, 1494, 1469, 1446, 1380, 1372, 1327, 1273, 1210, 1166, 1140, 1069, 1031, 979, 960, 909, 858, 775, 759, 737, 699, 672 cm^{-1}. **MS** (EI): m/z (%) 314, 279 (100). **HRMS**: Calcd for $C_{15}H_{21}F_2SO_2{}^{10}B$: 313.1360; Found: 313.1368.

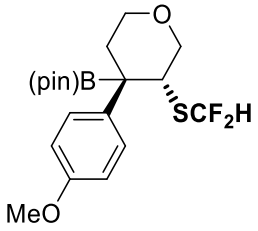
(±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-pyran-4-yl)-4,4,5,5 -tetramethyl-1,3,2-dioxaborolane 3b



Prepared according to ***GP1a*** using 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 µL, 2.0 M, 0.39 mmol, 1.3 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3b** as a yellow oil (80 mg, 72%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2 H), 7.45 – 7.30 (m, 3 H), 6.52 (t, *J* = 56.3 Hz, 1 H), 4.51 (dd, *J* = 11.4, 1.7 Hz, 1 H), 4.03 (td, *J* = 11.3, 2.3 Hz, 1 H), 3.77 – 3.65 (m, 2 H), 3.36 (d, *J* = 1.7 Hz, 1 H), 2.53 (ddd, *J* = 14.3, 11.5, 4.8 Hz, 1 H), 1.70

(dd, J = 14.1, 1.7 Hz, 1 H), 1.49 (s, 3 H), 1.33 (s, 3 H), 1.29 (s, 3 H), 1.19 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.03 (dd, J = 239.9, 55.8 Hz), -93.33 (dd, J = 239.8, 56.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron were missing) δ 134.08, 130.00, 127.34, 120.06 (dd, J = 275.0, 272.7 Hz), 79.97, 77.18, 68.82, 62.51, 43.53, 32.37, 26.34, 25.09, 25.05, 23.17; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.26 (s) ppm. **IR** (KBr): ν_{max} = 2977, 2867, 1465, 1434, 1390, 1375, 1337, 1302, 1213, 1158, 1143, 1108, 1057, 1030, 980, 949, 890, 862, 852, 775, 758, 731, 698 cm^{-1}. **MS** (ESI): 393 ($M+Na^+$). **HRMS** (ESI) for $C_{18}H_{29}{}^{10}BF_2O_3NS$ ($M+NH_4^+$): Calcd: 387.1960; Found: 387.1956.

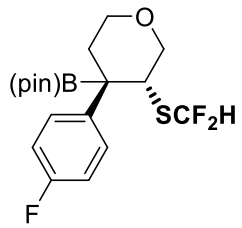
(±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-methoxyphenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3c



Prepared according to ***GP1b*** using 4-bromoanisole (62 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3c** as a yellow oil (61 mg, 51%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.4). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.7 Hz, 2 H), 6.89 (d, J = 8.8 Hz, 2 H), 6.49 (t, J = 56.3 Hz, 1 H), 4.56 (d, J = 11.2 Hz, 1 H), 4.05 (td, J = 11.7, 2.0 Hz, 1 H), 3.83 (s, 3 H), 3.77 (dd, J = 11.4, 1.8 Hz, 1 H), 3.71 (dd, J = 11.0, 3.3 Hz, 1 H), 3.35 (d, J = 1.8 Hz, 1 H), 2.55 (ddd, J = 14.2, 12.0, 4.9 Hz, 1 H), 1.65 (dd, J = 14.2, 1.7 Hz, 1 H), 1.47 (s, 3 H), 1.33 (s, 3 H), 1.27 (s, 3 H), 1.15 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.40 (dd, J = 240.7, 55.9 Hz), -93.45 (dd, J = 240.8, 57.2 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 161.49, 137.09, 120.08 (dd, J = 275.3, 272.5 Hz), 112.84, 79.77, 77.22, 68.77, 62.53, 55.02, 43.62, 32.38, 26.44, 25.07, 25.03, 23.03; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 43.25 (s) ppm. **IR** (KBr): ν_{max} = 2978, 1722, 1604, 1511, 1455, 1410, 1390, 1361, 1275, 1248,

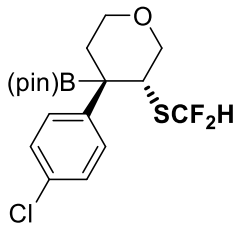
1179, 1143, 1091, 1066, 1031, 982, 963, 850, 829, 776, 734, 672 cm^{-1}. **MS** (ESI): 423 ($M+Na^+$). **HRMS** (ESI) for $C_{19}H_{31}{}^{10}BF_2O_4NS$ ($M+NH_4^+$): Calcd: 417.2066; Found: 417.2062.

(±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-fluorophenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3d



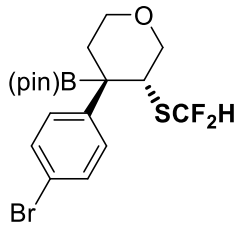
Prepared according to ***GP1b*** using 4-bromofluorobenzene (58 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3d** as a yellow oil (90 mg, 74%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.4, 6.3 Hz, 2 H), 7.03 (t, *J* = 8.7 Hz, 2 H), 6.51 (t, *J* = 56.1 Hz, 1 H), 4.54 (d, *J* = 11.4 Hz, 1 H), 4.05 (td, *J* = 11.5, 2.1 Hz, 1 H), 3.78 – 3.67 (m, 2 H), 3.36 (d, *J* = 1.8 Hz, 1 H), 2.49 (ddd, *J* = 14.2, 11.9, 4.9 Hz, 1 H), 1.67 (dd, *J* = 14.0, 1.7 Hz, 1 H), 1.48 (s, 3 H), 1.33 (s, 3 H), 1.29 (s, 3 H), 1.16 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.95 (dd, *J* = 239.6, 55.8 Hz, 1 F), -93.37 (dd, *J* = 239.6, 56.5 Hz, 1 F), -109.62 – -110.24 (m, 1 F); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 164.33 (d, *J* = 250.5 Hz), 136.97 (d, *J* = 7.9 Hz), 119.95 (t, *J* = 273.9 Hz), 114.37 (d, *J* = 19.8 Hz), 80.14, 77.34, 68.82, 62.42, 43.33, 32.21, 26.37, 25.06, 25.01, 23.07; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 43.98 (s) ppm. **IR** (KBr): ν_{max} = 2978, 2869, 1595, 1508, 1465, 1369, 1394, 1334, 1273, 1231, 1161, 1142, 1100, 1056, 1016, 912, 865, 832, 745 cm^{-1}. **MS** (ESI): 411 ($M+Na^+$). **HRMS** (ESI) for $C_{18}H_{28}{}^{10}BF_3O_3NS$ ($M+NH_4^+$): Calcd: 405.1866; Found: 405.1862.

(±)-2-((3*R*,4*R*)-4-(4-chlorophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3e



Prepared according to ***GP1b*** using 4-bromochlorobenzene (63 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3e** as a yellow oil (85 mg, 68%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.3 Hz, 2 H), 6.52 (t, *J* = 56.0 Hz, 1 H), 4.53 (dd, *J* = 11.4, 1.7 Hz, 1 H), 4.04 (td, *J* = 11.4, 2.1 Hz, 1 H), 3.71 (ddd, *J* = 7.9, 6.7, 2.0 Hz, 2 H), 3.36 (d, *J* = 1.9 Hz, 1 H), 2.47 (ddd, *J* = 14.1, 11.8, 4.9 Hz, 1 H), 1.67 (dd, *J* = 14.1, 1.8 Hz, 1 H), 1.48 (s, 3 H), 1.32 (s, 3 H), 1.29 (s, 3 H), 1.17 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.74 (dd, *J* = 239.0, 55.8 Hz), -93.36 (dd, *J* = 239.0, 56.1 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 136.43, 135.82, 127.58, 119.89 (dd, *J* = 274.5, 273.3 Hz), 80.24, 77.32, 68.81, 62.37, 43.18, 32.10, 26.32, 25.04, 24.99, 23.06; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 44.21 (s) ppm. **IR** (KBr): ν_{max} = 2978, 2868, 1586, 1489, 1463, 1391, 1360, 1334, 1302, 1235, 1143, 1092, 1055, 1015, 913, 890, 774, 744 cm^{-1}. **MS** (ESI): 427 ($M+Na^+$). **HRMS** (ESI) for $C_{18}H_{28}{}^{10}BF_2O_3NSCl$ ($M+NH_4^+$): Calcd: 421.1570; Found: 421.1567.

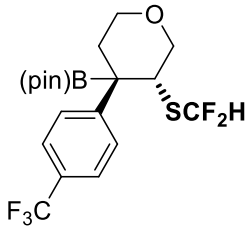
(±)-2-((3*R*,4*R*)-4-(4-bromophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3f



Prepared according to ***GP1b*** using 4-bromo-1,2,3,6-tetrahydropyran (54 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 4-bromophenylboronic acid pinacol ester (85 mg, 0.30 mmol, 1.0 equiv.) and reagent

2a (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3f** as a yellow oil (75 mg, 56%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2 H), 7.48 (d, *J* = 8.1 Hz, 2 H), 6.52 (t, *J* = 56.0 Hz, 1 H), 4.53 (d, *J* = 11.3 Hz, 1 H), 4.03 (t, *J* = 10.5 Hz, 1 H), 3.71 (t, *J* = 9.6 Hz, 2 H), 3.36 (s, 1 H), 2.46 (td, *J* = 14.2, 4.7 Hz, 1 H), 1.67 (d, *J* = 14.1 Hz, 1 H), 1.48 (s, 3 H), 1.32 (s, 3 H), 1.28 (s, 3 H), 1.16 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.69 (dd, *J* = 239.0, 55.8 Hz), -93.34 (dd, *J* = 239.1, 56.1 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 135.94, 130.52, 125.09, 119.85 (t, *J* = 273.5 Hz), 80.26, 77.32, 68.81, 62.35, 43.09, 32.05, 26.31, 25.02, 24.99, 23.05; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 45.69 (s) ppm. **IR** (KBr): ν_{max} = 2978, 2868, 1722, 1588, 1490, 1389, 1359, 1331, 1269, 1214, 1142, 1088, 1058, 1011, 950, 889, 857, 822, 776, 723, 650 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{28}{}^{10}BBrF_2O_3NS$ ($M+NH_4^+$): Calcd: 465.1065; Found: 465.1067.

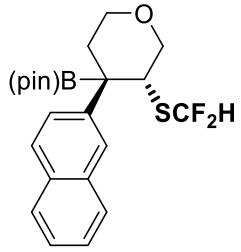
(±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-(trifluoromethyl)phenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3g



Prepared according to ***GP1b*** using 4-bromobenzotrifluoride (68 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3g** as a yellow oil (85 mg, 62%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 2 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 6.54 (t, *J* = 55.7 Hz, 1 H), 4.52 (d, *J* = 10.0 Hz, 1 H), 4.04 (td, *J* = 11.4, 1.9 Hz, 1 H), 3.77 – 3.67 (m, 2 H), 3.39 (d, *J* = 1.5 Hz, 1 H), 2.46 (ddd, *J* = 14.1, 11.7, 4.8 Hz, 1 H), 1.72 (d, *J* = 12.7 Hz, 1 H), 1.50 (s, 3 H), 1.33 (s, 3 H), 1.30 (s, 3 H), 1.20 (s, 3 H); **^{19}F NMR** (376 MHz, $cdcl_3$) δ -62.95 (s, 3 F), -91.56 (dd, *J* = 238.4, 55.8 Hz, 1 F), -93.33 (dd, *J* = 238.4, 55.7 Hz, 1 F); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2

carbon adjacent to boron was missing) δ 133.96, 131.42 (dd, *J* = 64.4, 32.3 Hz), 123.99 (q, *J* = 3.7 Hz), 119.86 (t, *J* = 273.9 Hz), 80.52, 77.38, 68.84, 62.32, 43.05, 32.01, 26.27, 25.07, 24.99, 23.13; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 44.71 (s) ppm. **IR** (KBr): ν_{max} = 2979, 2930, 2850, 1617, 1372, 1326, 1272, 1239, 1213, 1166, 1125, 1071, 1018, 851, 831, 782 cm^{-1}. **MS** (ESI): 456 ($M+NH_4^+$). **HRMS** (ESI) for $C_{19}H_{28}{}^{10}BF_5O_3NS$ ($M+NH_4^+$): Calcd: 455.1834; Found: 455.1828.

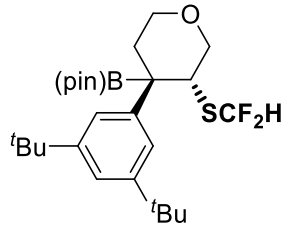
(±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(naphthalen-2-yl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3h



Prepared according to ***GP1b*** using 2-bromonaphthalene (68 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3h** as a yellow oil (79 mg, 63%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1 H), 7.94 (d, *J* = 8.3 Hz, 1 H), 7.91 – 7.85 (m, 1 H), 7.85 – 7.77 (m, 2 H), 7.48 (pd, *J* = 6.9, 3.5 Hz, 2 H), 6.49 (t, *J* = 56.2 Hz, 1 H), 4.54 (dd, *J* = 11.4, 1.9 Hz, 1 H), 4.07 (td, *J* = 11.3, 2.2 Hz, 1 H), 3.80 – 3.69 (m, 2 H), 3.44 (t, *J* = 11.1 Hz, 1 H), 2.67 (ddd, *J* = 14.1, 11.5, 4.7 Hz, 1 H), 1.78 (dd, *J* = 14.1, 1.8 Hz, 1 H), 1.53 (s, 3 H), 1.36 (s, 3 H), 1.31 (s, 3 H), 1.22 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.81 (dd, *J* = 239.1, 55.8 Hz), -93.36 (dd, *J* = 239.0, 56.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 135.39, 134.22, 132.60, 130.46, 128.86, 127.49, 126.82, 126.48, 125.68, 120.01 (dd, *J* = 275.0, 272.9 Hz), 80.16, 77.28, 68.88, 62.53, 43.50, 32.47, 26.41, 25.13, 25.08, 23.17; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 44.72 (s) ppm. **IR** (KBr): ν_{max} = 3055, 2977, 2867, 1466, 1369, 1351, 1319, 1301, 1277, 1236, 1193, 1142, 1132, 1104, 1056, 1017, 982, 962, 893, 877, 747 cm^{-1}. **MS** (ESI): 443 ($M+Na^+$). **HRMS** (ESI) for

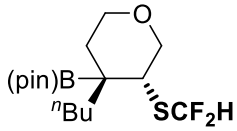
$C_{22}H_{31}{}^{10}BF_2O_3NS$ ($M+NH_4^+$): Calcd: 437.2117; Found: 437.2113.

(±)-2-((3*R*,4*R*)-4-(3,5-di-*tert*-butylphenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3i



Prepared according to ***GP1b*** using 3,5-di-*tert*-butylbromobenzene (89 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3i** as a yellow oil (69 mg, 48%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 2 H), 7.46 (d, *J* = 1.7 Hz, 1 H), 6.49 (t, *J* = 57.0 Hz, 1 H), 4.47 (d, *J* = 11.4 Hz, 1 H), 4.01 (t, *J* = 10.6 Hz, 1 H), 3.66 (dd, *J* = 16.4, 11.9 Hz, 2 H), 3.31 (s, 1 H), 2.57 – 2.45 (m, 1 H), 1.71 (d, *J* = 14.1 Hz, 1 H), 1.49 (s, 3 H), 1.34 – 1.28 (m, 24 H), 1.21 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.60 (dd, *J* = 218.7, 33.1 Hz), -93.34 (dd, *J* = 218.6, 34.0 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 149.30, 128.12, 124.08, 120.43 (t, *J* = 273.7 Hz), 79.82, 77.14, 69.02, 62.87, 44.47, 34.93, 33.05, 31.58, 26.39, 25.28, 25.24, 23.55; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 45.10 (s) ppm. **IR** (KBr): ν_{max} = 2964, 2868, 1595, 1467, 1426, 1391, 1369, 1306, 1266, 1248, 1216, 1144, 1057, 1027, 963, 852, 715 cm^{-1}. **MS** (ESI): 505 ($M+Na^+$). **HRMS** (ESI) for $C_{26}H_{45}{}^{10}BF_2O_3NS$ ($M+NH_4^+$): Calcd: 499.3212; Found: 499.3211.

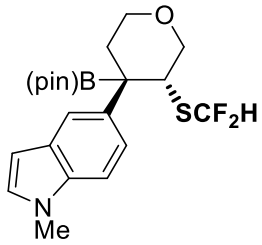
(±)-2-((3*R*,4*S*)-4-butyl-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3j



Prepared according to ***GP1a*** using 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.), n-butyl lithium in hexane (165 μL, 2.0 M, 0.330

mmol, 1.10 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3j** as a yellow oil (50 mg, 46%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.79 (t, *J* = 56.1 Hz, 1 H), 4.42 (d, *J* = 11.4 Hz, 1 H), 3.94 (t, *J* = 11.1 Hz, 1 H), 3.68 (d, *J* = 8.4 Hz, 2 H), 3.23 (s, 1 H), 2.12 – 2.00 (m, 1 H), 1.45 (d, *J* = 14.3 Hz, 1 H), 1.40 – 0.94 (m, 18 H), 0.89 (t, *J* = 6.8 Hz, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.07 (d, *J* = 55.9 Hz), -92.45 (d, *J* = 56.2 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon adjacent to boron was missing) δ 120.32 (t, *J* = 273.2 Hz), 78.47, 76.95, 68.84, 62.64, 43.45, 31.59, 26.15, 26.09, 25.55, 25.26, 25.13, 23.50, 14.06; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 49.53 (s) ppm. **IR** (KBr): ν_{max} = 2955, 2868, 1465, 1390, 1367, 1322, 1300, 1237, 1151, 1101, 1059, 1024, 913, 774, 745 cm^{-1}. **MS** (ESI): 373 ($M+Na^+$). **HRMS** (ESI) for $C_{16}H_{33}{}^{10}BF_2O_3NS$ ($M+NH_4^+$): Calcd: 367.2273; Found: 367.2269.

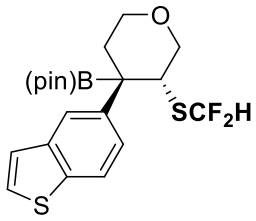
(±)-5-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)-1-methyl-1H-indole 3k



Prepared according to ***GP1b*** using 5-bromo-1-methyl-1*H*-indole (70 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3k** as a brown oil (63 mg, 48%). Eluent: ethyl acetate/petroleum ether (1:10, R_f = 0.3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1 H), 7.86 (d, *J* = 8.5 Hz, 1 H), 7.30 (d, *J* = 8.5 Hz, 1 H), 7.03 (d, *J* = 3.1 Hz, 1 H), 6.56 – 6.51 (m, 1 H), 6.47 (t, *J* = 56.1 Hz, 1 H), 4.56 (d, *J* = 11.3 Hz, 1 H), 4.06 (dd, *J* = 16.1, 6.6 Hz, 1 H), 3.83 – 3.67 (m, 5 H), 3.39 (s, 1 H), 2.72 (ddd, *J* = 14.4, 11.9, 4.8 Hz, 1 H), 1.71 (d, *J* = 14.2 Hz, 1 H), 1.50 (s, 3 H), 1.36 (s, 3 H), 1.28 (s, 3 H), 1.18 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.60 (dd, *J* = 241.2, 56.0 Hz), -93.50 (dd, *J* = 241.2, 57.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 138.02, 129.20, 128.87,

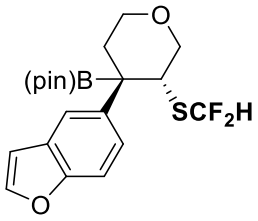
128.33, 127.87, 120.21 (dd, J = 275.5, 272.3 Hz), 108.12, 102.03, 79.72, 77.17, 68.80, 62.69, 43.97, 32.80, 32.72, 26.54, 25.11, 25.09, 23.08; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 44.54 (s) ppm. **IR** (KBr): ν_{max} = 2976, 2869, 1607, 1514, 1465, 1437, 1389, 1368, 1333, 1279, 1248, 1143, 1099, 1057, 1012, 981, 910, 959, 882, 852, 801, 772, 730 cm^{-1}. **MS** (ESI): 424 ($M+H^+$). **HRMS** (ESI) for $C_{21}H_{29}{}^{10}BF_2NO_3S$ ($M+H^+$): Calcd: 423.1960; Found: 423.1956.

(±)-2-((3*R*,4*R*)-4-(benzo[b]thiophen-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3l



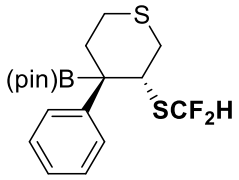
Prepared according to ***GP1b*** using 5-bromothianaphthene (70 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.5 equiv.) to give compound **3l** as a yellow oil (90 mg, 70%). Eluent: ethyl acetate/petroleum ether (1:10, R_f = 0.3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1 H), 7.86 (s, 2 H), 7.40 (d, J = 5.4 Hz, 1 H), 7.37 (d, J = 5.4 Hz, 1 H), 6.50 (t, J = 56.2 Hz, 1 H), 4.54 (dd, J = 11.4, 1.9 Hz, 1 H), 4.06 (td, J = 11.4, 2.2 Hz, 1 H), 3.82 – 3.69 (m, 2 H), 3.41 (d, J = 1.9 Hz, 1 H), 2.63 (ddd, J = 14.1, 11.6, 4.8 Hz, 1 H), 1.74 (dd, J = 14.1, 1.8 Hz, 1 H), 1.51 (s, 3 H), 1.35 (s, 3 H), 1.30 (s, 3 H), 1.20 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.90 (dd, J = 239.3, 55.8 Hz), -93.34 (dd, J = 239.4, 56.5 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 141.67, 138.93, 130.31, 129.84, 125.85, 124.41, 121.39, 120.00 (dd, J = 275.1, 272.9 Hz), 80.12, 77.26, 68.85, 62.53, 43.49, 32.52, 26.42, 25.08, 25.05, 23.11; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 45.34 (s) ppm. **IR** (KBr): ν_{max} = 2977, 2931, 1722, 1599, 1507, 1425, 1372, 1354, 1330, 1269, 1219, 1190, 1143, 1080, 1027, 981, 964, 851, 799, 775, 708 cm^{-1}. **MS** (ESI): 449 ($M+Na^+$). **HRMS** (ESI) for $C_{20}H_{29}{}^{10}BF_2O_3NS_2$ ($M+NH_4^+$): Calcd: 443.1681; Found: 443.1677.

(±)-2-((3*R*,4*R*)-4-(benzofuran-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3m



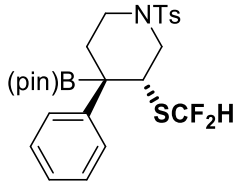
Prepared according to ***GP1b*** using 5-bromo-1-benzofuran (65 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give the product as a yellow oil (96 mg, 78%). Eluent: ethyl acetate/petroleum ether (1:10, R_f = 0.3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (s, 1 H), 7.88 (dd, *J* = 8.5, 1.2 Hz, 1 H), 7.60 (d, *J* = 2.2 Hz, 1 H), 7.48 (d, *J* = 8.5 Hz, 1 H), 6.79 (dd, *J* = 2.2, 0.9 Hz, 1 H), 6.49 (t, *J* = 56.4 Hz, 1 H), 4.55 (dd, *J* = 11.4, 1.7 Hz, 1 H), 4.06 (td, *J* = 11.4, 2.2 Hz, 1 H), 3.81 – 3.67 (m, 2 H), 3.39 (d, *J* = 1.9 Hz, 1 H), 2.62 (ddd, *J* = 14.2, 11.6, 4.8 Hz, 1 H), 1.72 (dd, *J* = 14.2, 1.8 Hz, 1 H), 1.50 (s, 3 H), 1.35 (s, 3 H), 1.29 (s, 3 H), 1.19 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.13 (dd, *J* = 240.1, 55.9 Hz), -93.35 (dd, *J* = 240.1, 56.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 156.25, 144.82, 130.91, 128.39, 126.73, 120.04 (dd, *J* = 275.2, 272.6 Hz), 110.43, 106.89, 80.03, 77.23, 68.82, 62.53, 43.60, 32.57, 26.43, 25.07, 25.03, 23.09; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 44.86 (s) ppm. **IR** (KBr): ν_{max} = 2977, 2868, 1723, 1609, 1537, 1430, 1371, 1354, 1337, 1261, 1230, 1143, 1131, 1110, 1057, 1028, 981, 963, 911, 899, 877, 849, 804, 773, 740, 685 cm^{-1}. **MS** (ESI): 428 ($M+NH_4^+$). **HRMS** (ESI) for $C_{18}H_{28}{}^{10}BF_2O_3NSCl$ ($M+NH_4^+$): Calcd: 428.1909; Found: 428.1905.

(±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-thiopyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3n



Prepared according to ***GP1a*** using 3,6-dihydro-2*H*-thiopyran-4-ylboronic acid pinacol ester (68 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3n** as a yellow oil (65 mg, 55%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 6.9 Hz, 2 H), 7.39 (d, *J* = 6.4 Hz, 1 H), 7.34 (t, *J* = 6.5 Hz, 2 H), 6.36 (t, *J* = 56.7 Hz, 1 H), 4.03 (d, *J* = 13.3 Hz, 1 H), 3.69 (s, 1 H), 3.33 (t, *J* = 12.7 Hz, 1 H), 2.54 (t, *J* = 13.3 Hz, 1 H), 2.39 (d, *J* = 12.9 Hz, 1 H), 2.18 (d, *J* = 12.7 Hz, 1 H), 2.09 (d, *J* = 14.1 Hz, 1 H), 1.48 (s, 3 H), 1.32 (s, 3 H), 1.29 (s, 3 H), 1.15 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.27 (dd, *J* = 240.2, 57.4 Hz), -93.26 (dd, *J* = 240.2, 55.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 134.94, 130.43, 127.27, 119.98 (dd, *J* = 276.0, 272.4 Hz), 80.03, 77.22, 42.17, 31.56, 31.12, 26.28, 25.02, 24.94, 23.16, 21.17; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 44.24 (s) ppm. **IR** (KBr): ν_{max} = 2978, 2927, 1597, 1434, 1375, 1367, 1338, 1275, 1261, 1219, 1145, 1072, 1054, 1019, 976, 932, 883, 861, 771, 698, 665 cm^{-1}. **MS** (ESI): 387 ($M+H^+$). **HRMS** (ESI) for $C_{18}H_{26}{}^{10}BF_2O_2S_2$ ($M+H^+$): Calcd: 386.1466; Found: 386.1464.

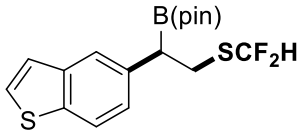
(±)-(3*R*,4*R*)-3-(difluoromethylthio)-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpiperidine 3o



Prepared according to ***GP1a*** using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -1-tosyl-1,2,3,6-tetrahydropyridine (109 mg, 0.300 mmol, 1.00 equiv.), phenyllithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3o** as a yellow oil (103 mg, 64%). Eluent: ethyl acetate/petroleum ether (1:10, R_f = 0.3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2 H), 7.68 (d, *J* = 8.2 Hz, 2 H), 7.44 – 7.29 (m, 5 H), 6.49 (t, *J* = 56.7 Hz, 1 H), 3.63 (d, *J* = 11.3 Hz, 1 H), 3.54 – 3.48 (m, 3 H), 2.89 (dd, *J* = 16.5, 6.8 Hz, 1 H), 2.54 – 2.40 (m, 4 H), 1.84 (d, *J* = 14.1 Hz, 1 H), 1.43 (s, 3 H), 1.29 (s, 3 H), 1.12 (s, 3 H),

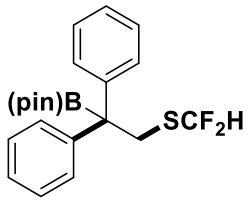
1.08 (s, 3 H); **^{19}F NMR** (376 MHz, cdcl$_3$) δ -92.53 (dd, *J* = 238.8, 55.9 Hz), -93.55 (dd, *J* = 238.8, 56.2 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 143.41, 134.49, 133.96, 130.33, 129.58, 127.70, 127.35, 119.70 (t, *J* = 274.5 Hz), 80.01, 77.35, 48.10, 42.32, 40.36, 31.24, 26.31, 24.97, 24.78, 23.00, 21.54; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 45.18 (s) ppm. **IR** (KBr): ν_{max} = 2981, 1462, 1434, 1391, 1343, 1280, 1238, 1155, 1090, 1045, 1018, 956, 913, 881, 773, 746, 709, 695 cm^{-1}. **MS** (ESI): 524 (M+H$^+$). **HRMS** (ESI) for $C_{25}H_{33}{}^{10}BF_2NO_4S_2$ (M+H$^+$): Calcd: 523.1943; Found: 523.1938.

2-(1-(Benzo[b]thiophen-5-yl)-2-(difluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3p



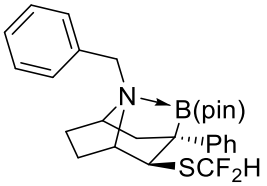
Prepared according to ***GP1b*** using 5-bromothianaphthene (1.2 g, 5.5 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), pinacol vinylboronate (0.77 g, 5.0 mmol, 1.0 equiv.) and reagent **2a** (1.7 g, 7.5 mmol, 1.5 equiv.) to give compound **3p** as a yellow solid (1.38 g, 75%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 1 H), 7.67 (d, *J* = 1.4 Hz, 1 H), 7.41 (d, *J* = 5.4 Hz, 1 H), 7.28 (d, *J* = 5.4 Hz, 1 H), 7.21 (dd, *J* = 8.3, 1.6 Hz, 1 H), 6.77 (t, *J* = 56.8 Hz, 1 H), 3.31 (dd, *J* = 13.0, 8.4 Hz, 1 H), 3.18 (dd, *J* = 13.1, 8.5 Hz, 1 H), 2.78 (t, *J* = 8.4 Hz, 1 H), 1.24 (s, 6 H), 1.20 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.20 (dd, *J* = 229.1, 42.0 Hz), -92.96 (dd, *J* = 229.1, 42.0 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon adjacent to boron was missing) δ 140.10, 137.74, 136.56, 126.59, 124.94, 123.74, 123.21, 122.58, 120.96 (t, *J* = 272.5 Hz), 84.01, 30.59 (t, *J* = 2.6 Hz), 24.60, 24.57 ppm. **IR** (KBr): ν_{max} = 2977, 1438, 1420, 1354, 1329, 1260, 1143, 1069, 818, 784, 713 cm^{-1}. **MS** (DART): 388 (M+NH$_4^+$). **HRMS** (DART) for $C_{17}H_{25}{}^{10}BF_2O_2NS_2$ (M+NH$_4^+$): Calcd: 387.1419; Found:387.1412.

2-(2-(Difluoromethylthio)-1,1-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3q



Prepared according to ***GP1a*** using 1-phenylvinylboronic acid, pinacol ester (69 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3q** as a yellow oil (73 mg, 62%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 4.2 Hz, 8 H), 7.21 (dq, *J* = 8.7, 4.3 Hz, 2 H), 6.16 (t, *J* = 58.4 Hz, 1 H), 3.59 (s, 2 H), 1.17 (s, 12 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -93.29 (d, *J* = 58.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ 143.72, 129.24, 128.1, 126.32, 121.27 (t, *J* = 272.0 Hz), 84.32, 36.58, 24.32; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.63 (s) ppm. **IR** (KBr): ν_{max} = 2954, 2924, 2852, 1495, 1462, 1444, 1377, 1027, 896, 772, 697 cm^{-1}. **MS** (ESI): 408 ($M+NH_4^+$). **HRMS** (ESI) for $C_{21}H_{29}{}^{10}BF_2NO_2S$ ($M+H^+$): Calcd: 407.2011; Found:407.2008.

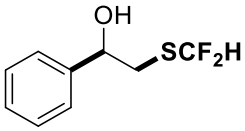
(±)-(1*S*,2*R*,3*R*,5*R*)-8-benzyl-2-(difluoromethylthio)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-azabicyclo[3.2.1]octane 3s



Prepared according to ***GP1a*** using 8-(phenylmethyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-azabicyclo[3.2.1]oct-2-ene (98 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) to give compound **3r** as a white solid (62 mg, 43%). Eluent: ethyl acetate/petroleum ether (1:5, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.3 Hz, 2 H), 7.41 – 7.26 (m, 7 H), 7.12 (d, *J* = 6.7 Hz, 1 H), 6.78 (t, *J* = 56.1 Hz, 1 H), 4.14 – 3.86 (m, 3 H), 3.61 (s, 1 H), 3.09 (s, 1 H), 2.95 – 2.82 (m, 1 H), 1.75 – 1.61 (m, 1 H), 1.55 – 1.41 (m, 1 H), 1.37 (s, 2 H), 1.24 (s, 6 H), 1.15 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.83 (d, *J* = 217.9 Hz), -94.28 (dd, *J* = 241.2, 61.7

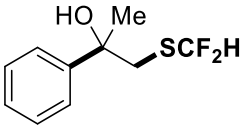
Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ 143.64, 135.31, 130.72, 128.76, 128.61, 128.50, 127.22, 124.70, 121.62 (t, *J* = 273.9 Hz), 80.66, 72.72, 60.41, 55.99, 55.16, 48.05, 31.65, 30.55, 27.72, 26.73; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 15.86 (s) ppm. **IR** (KBr): ν_{max} = 2971, 2928, 1495, 1456, 1385, 1372, 1325, 1191, 1179, 1134, 1100, 1076, 1042, 1001, 911, 861, 768, 758, 734, 704, 626 cm^{-1}. **MS** (ESI): 486 ($M+H^+$). **HRMS** (ESI) for $C_{27}H_{35}{}^{10}BF_2NO_2S$ ($M+H^+$): Calcd: 485.2480; Found: 485.2479.

2-(Difluoromethylthio)-1-phenylethanol 4a



Prepared according to ***GP1c*** pinacol vinylboronate (47 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.), reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) and $NaBO_3$ (74 mg, 0.90 mmol, 3.0 equiv.) to give compound **4a** as a yellow oil (43 mg, 71%). Eluent: ethyl acetate/petroleum ether (1:5, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.29 (m, 5 H), 6.86 (t, *J* = 56.6 Hz, 1 H), 5.00 – 4.84 (m, 1 H), 3.15 (dd, *J* = 14.2, 3.9 Hz, 1 H), 3.03 (dd, *J* = 14.2, 8.8 Hz, 1 H), 2.54 (d, *J* = 3.1 Hz, 1 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.98 (dd, *J* = 220.1, 33.8 Hz), -92.71 (dd, *J* = 220.2, 34.2 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.91, 128.69, 128.31, 125.77, 120.50 (t, *J* = 273.3 Hz), 73.65, 36.26 (t, *J* = 2.4 Hz) ppm. **IR** (KBr): ν_{max} = 3395, 2928, 1436, 1423, 1325, 1236, 1144, 1051, 1021, 897, 817, 765, 743, 703 cm^{-1}. **MS** (EI): m/z (%) 204, 107 (100), 79. **HRMS**: Calcd for $C_9H_{10}F_2SO$: 204.0420; Found:204.0423.

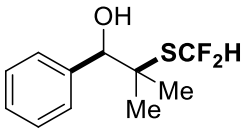
1-(Difluoromethylthio)-2-phenylpropan-2-ol 4b



Prepared according to ***GP1c*** using isopropenyl boronic acid pinacol ester (51 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.), reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) and $NaBO_3$ (74 mg, 0.90 mmol, 3.0

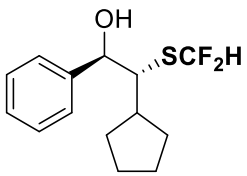
equiv.) to give the product as a yellow oil (40 mg, 61%). Eluent: ethyl acetate/petroleum ether (1:5, R_f = 0.6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.17 (m, 5 H), 6.70 (t, *J* = 57.0 Hz, 1 H), 3.31 (d, *J* = 13.9 Hz, 1 H), 3.16 (d, *J* = 13.9 Hz, 1 H), 2.44 (s, 1 H), 1.67 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.64 (dd, *J* = 242.9, 57.3 Hz), -92.50 (dd, *J* = 242.9, 56.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.71, 128.49, 127.47, 124.72, 120.30 (t, *J* = 273.3 Hz), 73.50, 41.36, 29.03 ppm. **IR** (KBr): ν_{max} = 3445, 2979, 1494, 1446, 1376, 1326, 1248, 1215, 1182, 1062, 1027, 943, 914, 767, 699 cm^{-1}. **MS** (EI): m/z (%) 218, 121 (100), 77. **HRMS**: Calcd for $C_{10}H_{12}F_2SO$: 218.0577; Found:218.0571.

2-(Difluoromethylthio)-2-methyl-1-phenylpropan-1-ol 4c



Prepared according to ***GP1c*** using 2,2-dimethylethenylboronic acid pinacol ester (55 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 µL, 2.0 M, 0.390 mmol, 1.30 equiv.), reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) and $NaBO_3$ (74 mg, 0.90 mmol, 3.0 equiv.) to give compound **4c** as a yellow oil (32 mg, 45%). Eluent: ethyl acetate/petroleum ether (1:5, R_f = 0.6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5 H), 7.14 (t, *J* = 56.9 Hz, 1 H), 4.79 (s, 1 H), 2.82 – 2.50 (m, 1 H), 1.42 (s, 3 H), 1.30 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.54 (dd, *J* = 254.5, 57.5 Hz), -91.25 (dd, *J* = 254.6, 56.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.32, 128.42, 128.12, 128.04, 121.46 (dd, *J* = 269.5, 268.5 Hz), 81.35, 27.37, 23.62 ppm. **IR** (KBr): ν_{max} = 3445, 2973, 1453, 1389, 1300, 1125, 1053, 1026, 912, 791, 748, 702 cm^{-1}. **MS** (EI): m/z (%) 232, 107 (100), 79. **HRMS**: Calcd for $C_{11}H_{14}F_2SO$: 232.0733; Found: 232.0735.

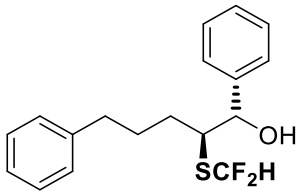
(±)-(1*R*,2*R*)-2-cyclopentyl-2-(difluoromethylthio)-1-phenylethanol 4d



Prepared according to ***GP1c*** using (E)-2-(2-cyclopentylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (67 mg, 0.30

mmol, 1.0 equiv.), phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.), reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) and $NaBO_3$ (74 mg, 0.90 mmol, 3.0 equiv.) to give compound **4d** as a yellow oil (32 mg, 45%). Eluent: ethyl acetate/petroleum ether (1:5, R_f = 0.6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5 H), 6.65 (dd, *J* = 60.3, 55.8 Hz, 1 H), 4.72 (d, *J* = 6.8 Hz, 1 H), 3.27 (t, *J* = 6.1 Hz, 1 H), 2.68 (s, 1 H), 2.03 – 1.88 (m, 1 H), 1.79 (d, *J* = 7.7 Hz, 1 H), 1.71 (dd, *J* = 16.5, 12.6 Hz, 1 H), 1.64 (s, 2 H), 1.54 (dd, *J* = 13.4, 6.7 Hz, 1 H), 1.53 – 1.41 (m, 2 H), 1.31 – 1.16 (m, 1 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -88.99 (dd, *J* = 245.0, 60.3 Hz), -92.88 (dd, *J* = 245.0, 55.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.59, 128.53, 128.16, 126.44, 120.85 (dd, *J* = 276.1, 269.8 Hz), 76.24, 58.02, 40.62, 31.11, 29.15, 25.49, 25.18 ppm. **IR** (KBr): ν_{max} = 3439, 2954, 2868, 1452, 1323, 1296, 1190, 1064, 1028, 771, 732, 700 cm^{-1}. **MS** (EI): m/z (%) 272, 107 (100), 79. **HRMS**: Calcd for $C_{14}H_{18}F_3SO$: 272.1046; Found: 272.1042.

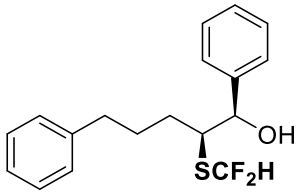
(±)-(1*S*,2*S*)-2-(difluoromethylthio)-1,5-diphenylpentan-1-ol 4e



Prepared according to ***GP1c*** using (E)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-enyl) -1,3,2-dioxaborolane (82 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.), reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv) and $NaBO_3$ (74 mg, 0.90 mmol, 3.0 equiv.) to give compound **4e** as a yellow oil (65 mg, 70%). Eluent: ethyl acetate/petroleum ether (1:5, R_f = 0.7). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5 H), 7.24 (dd, *J* = 10.1, 4.6 Hz, 2 H), 7.16 (t, *J* = 7.3 Hz, 1 H), 7.09 (d, *J* = 7.1 Hz, 2 H), 6.73 (dd, *J* = 59.5, 55.7 Hz, 1 H), 4.64 (dd, *J* = 7.2, 3.2 Hz, 1 H), 3.29 – 3.19 (m, 1 H), 2.67 – 2.54 (m, 2 H), 2.52 – 2.42 (m, 1 H), 1.96 – 1.81 (m, 1 H), 1.77 – 1.56 (m, 2 H), 1.52 – 1.39 (m, 1 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.41 (dd, *J* = 246.0, 59.6 Hz), -92.50 (dd, *J* = 246.0, 55.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.71, 141.09, 128.50, 128.31, 128.30, 128.27, 126.63, 125.80, 120.68 (dd, *J* = 275.6, 270.1 Hz), 76.88, 52.27, 35.18, 31.30, 28.40 ppm. **IR** (KBr): ν_{max} = 3434,

3061, 3026, 2930, 2859, 1494, 1452, 1324, 1189, 1059, 1027, 913, 794, 769, 750, 700 cm^{-1}. **MS** (ESI): 340 ($M+NH_4^+$). **HRMS** (ESI) for $C_{18}H_{28}{}^{10}BF_2O_3NSCl$ ($M+NH_4^+$): Calcd: 340.1541; Found: 340.1538.

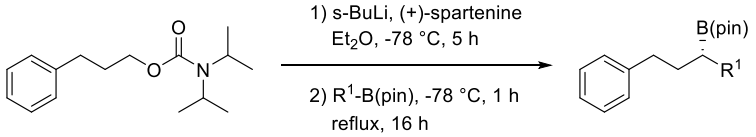
(±)-(1*R*,2*S*)-2-(difluoromethylthio)-1,5-diphenylpentan-1-ol 4f



Prepared according to ***GP1c*** using (Z)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-enyl) -1,3,2-dioxaborolane (82 mg, 0.30 mmol, 1.0 equiv.), phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.), reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.) and $NaBO_3$ (74 mg, 0.90 mmol, 3.0 equiv.) to give compound **4f** as a yellow oil (69 mg, 74%). Eluent: ethyl acetate/petroleum ether (1:5, R_f = 0.7). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5 H), 7.23 (t, *J* = 7.3 Hz, 2 H), 7.15 (t, *J* = 7.3 Hz, 1 H), 7.07 (d, *J* = 7.0 Hz, 2 H), 6.74 (dd, *J* = 57.4, 56.3 Hz, 1 H), 5.00 (t, *J* = 3.7 Hz, 1 H), 3.41 (dt, *J* = 10.4, 3.6 Hz, 1 H), 2.63 – 2.43 (m, 2 H), 2.40 (d, *J* = 4.0 Hz, 1 H), 1.96 – 1.81 (m, 1 H), 1.74 – 1.58 (m, 2 H), 1.52 – 1.38 (m, 1 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.16 (dd, *J* = 243.7, 57.6 Hz), -92.24 (dd, *J* = 243.7, 56.1 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.84, 140.62, 128.31, 128.30, 128.28, 127.93, 126.38, 125.75, 120.65 (t, *J* = 272.0 Hz), 76.66, 50.59, 35.21, 28.65, 28.27 ppm. **IR** (KBr): ν_{max} = 3445, 3207, 2938, 2860, 1495, 1452, 1342, 1054, 1027, 913, 792, 747, 700 cm^{-1}. **MS** (ESI): 340 ($M+NH_4^+$). **HRMS** (ESI) for $C_{18}H_{28}{}^{10}BF_2O_3NSCl$ ($M+NH_4^+$): Calcd: 340.1541; Found: 340.1538.

General Procedure for the Lithiation-Borylation of 2,4,6-Tri*iso*propylbenzoates[1]

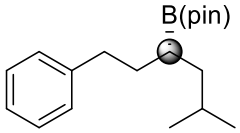
***General Procedure 2* (*GP2*)**



s-Butyl lithium (3.3 mL, 1.3 N, 4.2 mmol, 1.2 equiv.) was added dropwise to a solution of the benzoate (0.91 g, 3.5 mmol, 1.0 equiv) and (+)-sparteine (0.98 g, 4.2 mmol, 1.2 equiv.) in Et_2O (20.0 mL) at -78 °C. The resulting mixture was stirred at -78 °C for 5 h, followed by addition of 4,4,5,5-tetramethyl-2-(2-methylpropyl) -1,3,2-dioxaborolane (0.77 g, 4.2 mmol, 1.2 equiv.) dropwise. The mixture was further stirred at -78 °C for 1 h and was then allowed to warm up to room temperature and refluxed for 16 h. After cooling to room temperature, water (20.0 mL) was added, the organic layers were separated and the aqeous layer was extracted with Et_2O (20.0 mL × 3). The combined organic layers were washed with HCl (10 mL, 1.0 N), NaOH (10 mL, 1.0 N), water and brine, and dried over anhydrous $MgSO_4$. The solvente was removed in vacuo and the residue was purified by flash column chromatography to give the corresponding boronic piconal ester **5a**.

Racemic boronic esters were obtained by using TMEDA instead of (+)-sparteine.

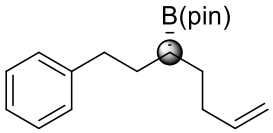
(*S*)-4,4,5,5-tetramethyl-2-(5-methyl-1-phenylhexan-3-yl)-1,3,2-dioxaborolane 5a



Prepared according to ***GP2*** using s-butyl lithium (3.3 mL, 1.3 N, 4.2 mmol, 1.2 equiv.) benzoate (0.91 g, 3.5 mmol, 1.0 equiv.), (+)-sparteine (0.98 g, 4.2 mmol, 1.2 equiv.) and 4,4,5,5-tetramethyl-2-(2-methylpropyl)-1,3,2-dioxaborolane (0.77 g, 4.2 mmol, 1.2 equiv.) to give the desired boronic ester **5a** as a colorless oil (225 mg, 21%). Eluent: ethyl acetate/petroleum ether (1:100, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.12 (m, 5 H), 2.68 – 2.52 (m, 2 H), 1.75 – 1.61 (m, 2 H), 1.44 – 1.33 (m, 1 H), 1.26 (s, 12 H), 1.18 – 1.07 (m, 1 H), 0.93 (d, *J* = 6.6 Hz, 2 H), 0.90 – 0.82 (m, 6 H); **^{13}C NMR** (151 MHz, $CDCl_3$, signal of sp^3 carbon adjacent to boron was missing) δ

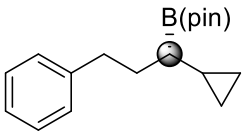
143.10, 128.35, 128.20, 125.51, 82.88, 40.49, 35.66, 33.75, 27.27, 24.86, 24.78, 23.05, 22.55; **^{11}B NMR** (193 MHz, $CDCl_3$) δ 33.75 (s) ppm. **IR** (KBr): ν_{max} = 2977, 2953, 2926, 2867, 1454, 1379, 1370, 1317, 1251, 1165, 1144, 698 cm^{-1}. **MS** (EI): m/z (%) 302, 174, 155, 91 (100). **HRMS**: Calcd for $C_{19}H_{31}{}^{10}BO_2$: 301.2453; Found:301.2451. **HPLC** (C1, 0.46 × 25 cm, 5 μm, carbon dioxide/isopropanol = 95/5 (v/v %), flow 2.0 mL/min, UV detection at 214 nm, 2000 psi, 40 °C), retion time = 6.06 min (major) and 7.32 min (minor). $[\alpha]_D^{20}$ = -16.46 (c = 0.130 g/100 mL, CH_3Cl). ee = 94%.

(*R*)-4,4,5,5-tetramethyl-2-(1-phenylhept-6-en-3-yl)-1,3,2-dioxaborolane 5b



Prepared according to ***GP2*** using s-butyl lithium (3.2 mL, 1.3 N, 4.1 mmol, 1.2 equiv.), the benzoate (0.90 g, 3.4 mmol, 1.0 equiv.), (+)-sparteine (0.96 g, 4.1 mmol, 1.2 equiv.) and 2-but-3-enyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.75 g, 4.1 mmol, 1.2 equiv.) to give the desired boronic ester **5b** as a colorless oil (150 mg, 15%). Eluent: ethyl acetate/petroleum ether (1:100, R_f = 0.5). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2 H), 7.27 – 7.25 (m, 3 H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1 H), 5.01 – 4.90 (m, 2 H), 2.67 – 2.54 (m, 2 H), 2.13 – 2.01 (m, 2 H), 1.78 – 1.72 (m, 1 H), 1.70 – 1.63 (m, 1 H), 1.60 – 1.54 (m, 1 H), 1.52 – 1.45 (m, 1 H), 1.26 (s, 12 H), 1.10 – 1.05 (m, 1 H); **^{13}C NMR** (151 MHz, $CDCl_3$, signal of sp^3 carbon adjacent to boron was missing) δ 142.99, 139.10, 128.36, 128.20, 125.54, 114.27, 82.96, 35.54, 33.36, 33.34, 30.50, 24.84, 24.81; **^{11}B NMR** (193 MHz, $CDCl_3$) δ 34.29 (s) ppm. **IR** (KBr): ν_{max} = 3025, 2977, 2925, 2855, 1496, 1454, 1409, 1380, 1371, 1317, 1263, 1233, 1214, 1165, 1144, 966, 908, 851, 747, 698 cm^{-1}. **MS** (EI): m/z (%) 300, 172, 155, 91 (100). **HRMS**: Calcd for $C_{19}H_{29}{}^{10}BO_2$: 299.2297; Found: 299.2301. **HPLC** (ODH, 0.46 × 25 cm, 5 μm, hexane/isopropanol = 9/1 (v/v %), flow 0.7 mL/min, UV detection at 214 nm), retion time = 8.71 min (major) and 10.98 min (minor). $[\alpha]_D^{20}$ = -7.73 (c = 0.150 g/100 mL, CH_3Cl). ee = 91%.

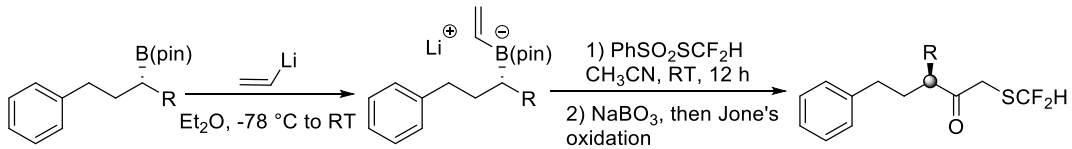
(*S*)-2-(1-cyclopropyl-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5c



Prepared according to ***GP2*** using s-butyl lithium (4.6 mL, 1.3 N, 6.0 mmol, 1.2 equiv.), the benzoate (1.3 g, 5.0 mmol, 1.0 equiv.), (+)-sparteine (1.4 g, 6.0 mmol, 1.2 equiv.) and cyclopropylboronic acid pinacol ester (1.0 g, 6.0 mmol, 1.2 equiv.) to give the desired boronic ester **5c** as a colorless oil (280 mg, 19%). Eluent: ethyl acetate/petroleum ether (1:100, R_f = 0.5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2 H), 7.20 – 7.14 (m, 3 H), 2.64 (td, *J* = 8.3, 4.0 Hz, 2 H), 1.90 – 1.75 (m, 2 H), 1.27 (s, 12 H), 0.71 (ddt, *J* = 9.6, 8.1, 4.8 Hz, 1 H), 0.49 – 0.36 (m, 3 H), 0.13 – 0.08 (m, 1 H), 0.04 (td, *J* = 9.0, 4.1 Hz, 1 H); **^{13}C NMR** (126 MHz, $CDCl_3$, signal of sp^3 carbon adjacent to boron was missing) δ 143.11, 128.36, 128.19, 125.51, 82.97, 35.78, 33.70, 24.84, 23.84, 12.45, 5.29, 3.49; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 33.49 (s) ppm. **IR** (KBr): ν_{max} = 33025, 2977, 2926, 2857, 1496, 1454, 1378, 1370, 1318, 1270, 1242, 1214, 1165, 1144, 1106, 1014, 967, 848, 747, 698 cm^{-1}. **MS** (EI): m/z (%) 286, 201, 158, 91 (100). **HRMS**: Calcd for $C_{18}H_{27}{}^{10}BO_2$: 285.2140; Found:285.2148. **HPLC** (C-1, 0.46 × 25 cm, 5 μm, carbon dioxide/isopropanol = 95/5 (v/v %), flow 2.0 mL/min, UV detection at 214 nm, 2000 psi, 40 °C), retion time = 7.66 min (major) and 9.40 min (minor). $[\alpha]_D^{20}$ = -8.75 (c = 0.160 g/100 mL, CH_3Cl). ee = 96%.

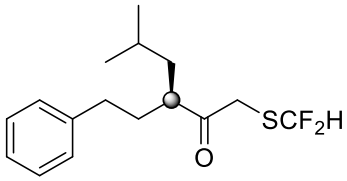
General Procedure for Synthesis of α-Chiral Ketones by Stereospecific 1,2-Migration.

***General Procedure 3* (*GP3*)**



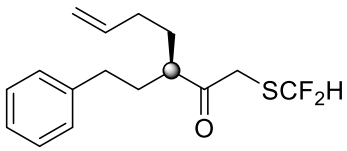
An oven-dried, 25-mL Schlenk flask equipped with a stir bar, septum, and digital thermocouple probe was charged with Et_2O (2.0 mL) and vinyl bromide (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.). The mixture was cooled to -78 °C. A solution of ^{t}BuLi (1.3 M in hexane, 0.55 mL, 0.72 mmol, 2.4 equiv.) was added dropwise. The mixture was stirred at -78 °C for 30 min. (S)-4,4,5,5-Tetramethyl-2-(5-methyl -1-phenylhexan-3-yl)-1,3,2-dioxaborolane (91 mg, 0.30 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred at -78 °C for 15 min, then warmed to room temperature for another 15 min. The solvent was carefully removed under reduced pressure to give the corresponding vinylboronate complex as a white solid, which was used directly without further purification. To the solid was added CH_3CN (3.0 mL) and reagent **2a** (100 mg, 0.45 mmol, 1.5 equiv.). This mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, then $NaBO_3$ (74 mg, 0.90 mmol, 3.0 equiv.) and THF/H_2O (v/v = 1:1, 6.0 mL) was added. The mixture was stirred at room temperature for 6 h. Half of the solvent was removed under reduced pressure. The aqueous layer was extracted with ethyl acetate (10 mL × 3), and the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated. To the residue was added acetone (5.0 mL) and Jone's reagent (3.0 N, 2.5 mL, 0.45 mmol, 1.5 equiv.) at 0 °C. The mixture was stirred at 0 °C for 1 h. The reaction was quenched by the addition of EtOH (2.0 mL). the solvente was removed in vacuo and the residue was purified by flash column chromatography (Eluent: ethyl acetate/petroleum ether = 1:10, R_f = 0.5) to give compound **6a** as a colorless oil (45 mg, 50%)..

(*S*)-1-(difluoromethylthio)-5-methyl-3-phenethylhexan-2-one 6a



Prepared according to ***GP3*** using vinyl bromide (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.), ^{t}BuLi (1.3 M in hexane, 0.55 mL, 0.72 mmol, 2.4 equiv.), (S)-4,4,5,5-tetramethyl-2-(5-methyl-1-phenylhexan-3-yl)-1,3,2-dioxaborolane (91 mg, 0.30 mmol, 1.0 equiv.), reagent **2a** (100 mg, 0.45 mmol, 1.5 equiv.), $NaBO_3$ (74 mg, 0.90 mmol, 3.0 equiv.) and Jone's reagent (3.0 N, 0.15 mL, 0.45 mmol, 1.5 equiv.) to give compound **6a** as a colorless oil (45 mg, 50%). Eluent: ethyl acetate/petroleum ether (1:10, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2 H), 7.20 (t, *J* = 7.1 Hz, 1 H), 7.15 (d, *J* = 7.5 Hz, 2 H), 6.86 (t, *J* = 56.5 Hz, 1 H), 3.74 – 3.61 (m, 2 H), 2.80 – 2.71 (m, 1 H), 2.65 – 2.50 (m, 2 H), 1.96 (dt, *J* = 14.7, 8.4 Hz, 1 H), 1.80 – 1.70 (m, 1 H), 1.59 – 1.48 (m, 2 H), 1.37 – 1.25 (m, 1 H), 0.89 (d, *J* = 6.3 Hz, 3 H), 0.87 (d, *J* = 6.2 Hz, 3 H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.07, 141.21, 128.49, 128.32, 126.13, 119.46 (t, *J* = 273.9 Hz), 48.55, 40.76, 36.50, 33.42, 33.27, 25.99, 22.66, 22.50; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -94.01 (d, *J* = 56.5 Hz) ppm. **IR** (KBr): ν_{max} = 2956, 2930, 2869, 1713, 1454, 1326, 1063, 1029, 749, 700 cm^{-1}. **MS** (EI): m/z (%) 300, 203, 196, 91 (100). **HRMS**: Calcd for $C_{16}H_{22}F_2SO$: 300.1359; Found: 300.1352. **HPLC** (AY3, 0.46 × 15 cm, 3 μm, hexane/isopropanol = 95/5 (v/v %), flow 0.7 mL/min, UV detection at 214 nm), retion time = 4.58 min (minor) and 4.84 min (major). $[\alpha]_D^{20}$ = -11.80 (c = 0.100 g/100 mL, CH_3Cl). ee = 95%.

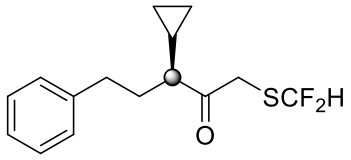
(*R*)-1-(difluoromethylthio)-3-phenethylhept-6-en-2-one 6b



Prepared according to ***GP3*** using vinyl bromide (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.), ^{t}BuLi (1.3 M in hexane, 0.55 mL, 0.72 mmol, 2.4 equiv.), (R)-4,4,5,5-tetramethyl-2-(1-phenylhept-6-en-3-yl)-1,3,2-dioxaborolane (90 mg, 0.30 mmol, 1.0 equiv.), reagent **2a** (100 mg, 0.45 mmol, 1.5 equiv.), $NaBO_3$ (74 mg, 0.90 mmol, 3.0 equiv.) and Jone's reagent (3.0 N, 0.15 mL, 0.45 mmol, 1.5 equiv.) to give

compound **6b** as a colorless oil (40 mg, 45%). Eluent: ethyl acetate/petroleum ether (1:10, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 5 H), 6.86 (t, *J* = 56.4 Hz, 1 H), 5.73 (ddt, *J* = 16.9, 10.3, 6.7 Hz, 1 H), 5.06 – 4.94 (m, 2 H), 3.73 – 3.60 (m, 2 H), 2.79 – 2.68 (m, 1 H), 2.66 – 2.51 (m, 2 H), 2.06 – 1.95 (m, 2 H), 1.84 – 1.73 (m, 2 H), 1.62 – 1.54 (m, 2 H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.79, 141.13, 137.46, 128.51, 128.32, 126.16, 119.44 (t, *J* = 274.1 Hz), 49.59, 36.88, 33.33, 32.94, 31.27, 30.57; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -93.94 (d, *J* = 56.4 Hz) ppm. **IR** (KBr): ν_{max} = 3063, 3027, 2928, 2859, 1712, 1641, 1496, 1454, 1392, 1326, 1205, 1062, 1029, 915, 750, 700 cm^{-1}. **MS** (EI): m/z (%) 298, 201, 131, 91 (100). **HRMS**: Calcd for $C_{16}H_{20}F_2SO$: 298.1203; Found: 298.1205. **HPLC** (ODH, 0.46 × 25 cm, 5 μm, hexane/isopropanol = 95/5 (v/v %), flow 0.7 mL/min, UV detection at 214 nm), retion time = 10.12 min (major) and 10.64 min (minor). $[\alpha]_D^{20}$ = -6.67 (c = 0.120 g/100 mL, CH_3Cl). ee = 91%.

(*S*)-3-cyclopropyl-1-(difluoromethylthio)-5-phenylpentan-2-one 6c

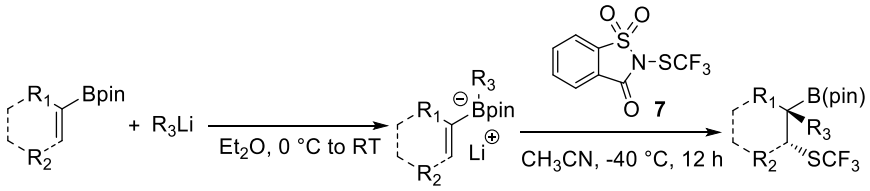


Prepared according to ***GP3*** using vinyl bromide (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.), ^{t}BuLi (1.3 M in hexane, 0.55 mL, 0.72 mmol, 2.4 equiv.), (S)-2-(1-cyclopropyl-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (86 mg, 0.30 mmol, 1.0 equiv), reagent **2a** (100 mg, 0.45 mmol, 1.5 equiv.), $NaBO_3$ (74 mg, 0.90 mmol, 3.0 equiv.) and Jone's reagent (3.0 N, 0.15 mL, 0.45 mmol, 1.5 equiv.) to give compound 6c as a colorless oil (46mg, 54%). Eluent: ethyl acetate/petroleum ether (1:10, R_f = 0.5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2 H), 7.22 – 7.14 (m, 3 H), 6.86 (t, *J* = 56.5 Hz, 1 H), 3.82 (d, *J* = 16.6 Hz, 1 H), 3.72 (d, *J* = 16.6 Hz, 1 H), 2.71 – 2.56 (m, 2 H), 2.20 – 2.09 (m, 1 H), 1.97 – 1.83 (m, 2 H), 0.88 – 0.81 (m, 1 H), 0.69 – 0.56 (m, 2 H), 0.27 (td, *J* = 9.4, 5.0 Hz, 1 H), 0.20 (td, *J* = 9.4, 5.0 Hz, 1 H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 205.98, 141.43, 128.45, 128.31, 126.04, 119.48 (t, *J* = 274.1 Hz), 55.32, 36.59, 33.41, 33.19, 13.70, 4.80, 4.38; **^{19}F NMR** (471 MHz, CDCl*3*) δ -93.94 (d, *J* = 56.0 Hz) ppm. **IR** (KBr): ν_{max} = 3082, 3026, 2925, 2861,

1713, 1496, 1454, 1394, 1326, 1175, 1062, 1027, 822, 751, 700 cm^{-1}. **MS** (EI): m/z (%) 284, 180 (100), 159, 117, 91. **HRMS**: Calcd for $C_{15}H_{18}F_2S$: 284.1046; Found: 284.1051. **HPLC** (ADH, 0.46 × 25 cm, 5 μm, hexane/isopropanol = 98/2 (v/v %), flow 0.7 mL/min, UV detection at 214 nm), retion time = 9.41 min (major) and 9.82 min (minor). $[\alpha]_D^{20}$ = 81.46 (c = 0.110 g/100 mL, CH_3Cl). ee = 97%.

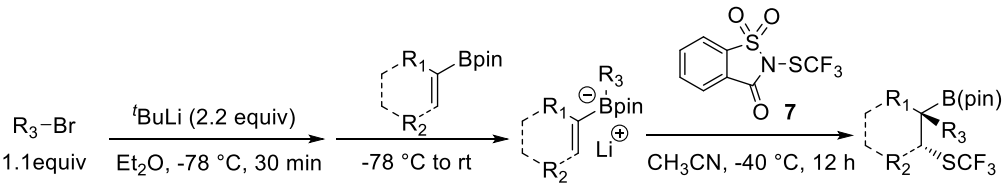
General Procedure for Reaction of Lithium vinyl Boronate with *N*-Trifluoromethylthiosaccharin 7

***General Procedure 4a* (*GP4a*)**



An oven-dried, 25-mL Schlenk flask equipped with a stir bar, septum, and digital thermocouple probe was charged with Et_2O (2.0 mL) and vinyl pinacol boranate (47 mg, 0.30 mmol, 1.0 equiv.). The resulting solution was cooled to 0 °C and a solution of phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.) was added dropwise. The mixture was stirred at 0 °C for 15 min, then warmed to room temperature for additional 15 min. The solvent was carefully removed under reduced pressure, affording lithium phenyl vinyl boronate complex as a white solid, which was used directly without further purification. To the solid was added CH_3CN (3.0 mL) and the mixture was cooled to -40 °C. *N*-Trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) was added. This reaction was stirred at -40 °C for 12 h. The solvent was removed under reduced pressure, the residue was purified by silica gel chromatography (Eluent: ethyl acetate/petroleum ether = 1:50, R_f = 0.6) to give compound **8a** as a yellow oil (76 mg, 76%).

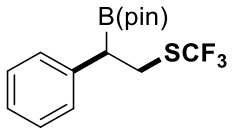
***General Procedure 4b* (*GP4b*)**



An oven-dried, 25-mL Schlenk flask equipped with a stir bar, septum, and digital thermocouple probe was charged with Et_2O (2.0 mL) and 4-bromochlorobenzene (63 mg, 0.33 mmol, 1.1 equiv.). The resulting solution was cooled to -78 °C. A solution of ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.) was added dropwise. The mixture was stirred at -78 °C for 30 min. A solution of pinacol vinylboronate (47 mg, 0.30 mmol, 1.0 equiv.) in Et_2O (2.0 mL) was added dropwise. The mixture was stirred

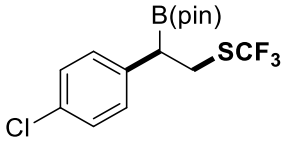
at -78 °C for 15 min, then warmed to room temperature for another 15 min. The solvent was carefully removed under reduced pressure, affording the corresponding lithium phenyl vinylboronate complex as a white solid, which was used directly without further purification. To the solid was added CH_3CN (3.0 mL) and cooled to -40 °C. *N*-Trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) was added and the mixture was stirred for at -40 °C 12 h. The solvent was removed under reduced pressure, the residue was purified by silica gel chromatography to give compound **8b**.

4,4,5,5-Tetramethyl-2-(1-phenyl-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8a



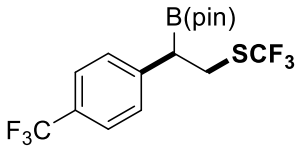
Prepared according to ***GP4a*** using pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.) phenyl lithium in THF (195 μL, 2.0 M, 0.390 mmol, 1.30 equiv.) and *N*-trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) to give compound **8a** as a yellow oil (76 mg, 76%). Eluent: ethyl acetate/petroleum ether (1:50, R_f = 0.6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2 H), 7.20 (dd, *J* = 7.6, 5.8 Hz, 3 H), 3.34 (dd, *J* = 12.9, 8.4 Hz, 1 H), 3.21 (dd, *J* = 12.9, 8.6 Hz, 1 H), 2.68 (t, *J* = 8.5 Hz, 1 H), 1.23 (s, 6 H), 1.20 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.14 (s); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ 139.91, 131.26 (q, *J* = 306.0 HZ), 128.71, 128.34, 126.40, 84.07, 32.82, 24.62, 24.52; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.86 (s) ppm. **IR** (KBr): ν_{max} = 2980, 1372, 1329, 1141, 1112, 966, 848, 700 cm^{-1}. **HRMS** (ESI) for $C_{15}H_{24}{}^{10}BF_3NO_2S$ ($M+NH_4^+$): Calcd: 349.1604; Found: 349.1601.

2-(1-(4-Chlorophenyl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8b



Prepared according to ***GP4b*** using 4-bromochlorobenzene (63 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.) and *N*-trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) to give compound **8b** as a yellow oil (93 mg, 83%). Eluent: ethyl acetate/petroleum ether (1:50, R_f = 0.6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.1 Hz, 2 H), 7.13 (d, *J* = 8.3 Hz, 2 H), 3.33 (dd, *J* = 12.9, 8.0 Hz, 1 H), 3.30 – 3.11 (m, 1 H), 2.66 (t, *J* = 8.4 Hz, 1 H), 1.23 (s, 6 H), 1.20 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.11 (s); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ 138.37, 132.22, 131.13 (q, *J* = 306.1 Hz), 129.67, 128.84, 84.21, 32.59, 24.60, 24.50; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.31 (s) ppm. **IR** (KBr): ν_{max} = 2980, 2934, 1491, 1469, 1410, 1372, 1333, 1294, 1271, 1236, 1214, 1115, 1015, 966, 849, 828, 755 cm^{-1}. **MS** (EI): m/z (%) 366, 251, 138 (100). **HRMS**: Calcd for $C_{15}H_{19}F_3SO_2{}^{10}BCl$: 365.0876; Found:365.0874.

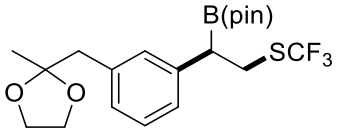
4,4,5,5-Tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8c



Prepared according to ***GP4b*** using 4-bromobenzotrifluoride (68 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.) and *N*-trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) to give compound **8c** as a yellow oil (100 mg, 83%). Eluent: ethyl acetate/petroleum ether (1:50, R_f = 0.6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 3.40 (dd, *J* = 13.1, 7.9 Hz, 1 H), 3.23 (dd, *J* = 13.1, 9.0 Hz, 1 H), 2.78 (t, *J* = 8.4 Hz, 1 H), 1.25 (s, 6 H), 1.22 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.14 (s, 3 F), -62.48 (s, 3 F); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ 144.11, 131.08 (q, *J* = 306.1 Hz), 128.73 (q, *J* = 32.4 Hz), 128.65, 125.64 (dd, *J* = 7.6, 3.8 Hz), 84.38, 32.34, 24.60, 24.51; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.21 (s) ppm. **IR** (KBr): ν_{max} = 2981, 2935, 1618, 1373, 1325, 1272, 1237, 1214, 1113, 1069, 1018, 966, 850, 756

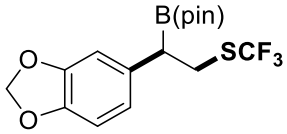
cm^{-1}. **MS** (DART): 418 (M+NH_4^+). **HRMS** (DART) for $C_{16}H_{23}{}^{10}BF_6O_2NS$ (M+NH_4^+): Calcd: 417.1478; Found: 417.1474.

4,4,5,5-Tetramethyl-2-(1-(3-((2-methyl-1,3-dioxolan-2-yl)methyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8d



Prepared according to ***GP4b*** using 2-(3-bromobenzyl)-2-methyl-1,3-dioxolane (85 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.) and *N*-trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) to give compound **8d** as a yellow oil (100 mg, 77%). Eluent: ethyl acetate/petroleum ether (1:10, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.4 Hz, 1 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 7.5 Hz, 1 H), 3.86 (d, *J* = 10.0 Hz, 2 H), 3.80 – 3.63 (m, 2 H), 3.35 (dd, *J* = 12.7, 8.1 Hz, 1 H), 3.22 (dd, *J* = 12.6, 9.1 Hz, 1 H), 2.89 (s, 2 H), 2.66 (t, *J* = 8.4 Hz, 1 H), 1.30 (s, 3 H), 1.23 (s, 6 H), 1.19 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.13 (s); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ 139.35, 137.29, 131.26 (q, *J* = 305.8 Hz), 130.54, 128.66, 128.24, 126.43, 109.66, 83.98, 64.84, 64.82, 45.34, 32.86, 24.62, 24.50; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.99 (s) ppm. **IR** (KBr): ν_{max} = 2980, 2934, 2883, 1443, 1372, 1332, 1270, 1214, 1114, 1049, 969, 848, 833, 709 cm^{-1}. **HRMS** (ESI) for $C_{20}H_{29}{}^{10}BF_3O_4S$ (M+H^+): Calcd: 432.1863; Found: 432.1863.

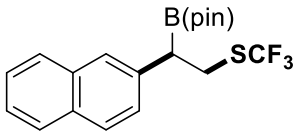
2-(1-(Benzo[d][1,3]dioxol-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8e



Prepared according to ***GP4b*** using 4-bromo-1,2-(methylenedioxy)benzene (67 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.) and

N-trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) to give compound **8e** as a yellow oil (87 mg, 77%). Eluent: ethyl acetate/petroleum ether (1:10, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.79 – 6.69 (m, 2 H), 6.65 (d, *J* = 7.9 Hz, 1 H), 5.93 (s, 2 H), 3.28 (dd, *J* = 12.8, 8.1 Hz, 1 H), 3.15 (dd, *J* = 12.8, 9.0 Hz, 1 H), 2.59 (t, *J* = 8.4 Hz, 1 H), 1.24 (s, 6 H), 1.21 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.11 (s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.85, 146.15, 133.58, 131.25 (d, *J* = 306.0 Hz), 121.45, 108.75, 108.48, 100.91, 84.09, 33.18, 24.63, 24.54; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.62 (s) ppm. **IR** (KBr): ν_{max} = 2978, 2932, 1489, 1436, 1372, 1247, 1116, 1041, 967, 935, 854, 811, 756, 673 cm^{-1}. **MS** (DART): 394 ($M+NH_4^+$). **HRMS** (DART) for $C_{16}H_{24}{}^{10}BF_3O_4NS$ ($M+NH_4^+$): Calcd: 393.1502; Found: 393.1496.

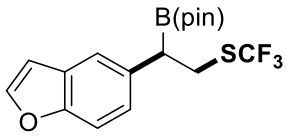
4,4,5,5-Tetramethyl-2-(1-(naphthalen-2-yl)-2-(trifluoromethylthio)ethyl)-1,3,2-di oxaborolane 8f



Prepared according to ***GP4b*** using 2-bromonaphthalene (68 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.) and *N*-trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) to give compound **8f** as a yellow oil (98 mg, 85%). Eluent: ethyl acetate/petroleum ether (1:50, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.86 – 7.77 (m, 3 H), 7.64 (s, 1 H), 7.54 – 7.29 (m, 3 H), 3.43 (d, *J* = 8.1 Hz, 1 H), 3.39 – 3.24 (m, 1 H), 2.86 (s, 1 H), 1.23 (s, 6 H), 1.19 (s, 6 H); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ 137.36, 133.68, 132.20, 131.26 (d, *J* = 306.0 Hz), 130.39, 128.38, 127.60, 126.79, 126.60, 126.05, 125.47, 84.15, 32.61, 24.63, 24.54; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.06 (s); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.09 (s) ppm. **IR** (KBr): ν_{max} = 2978, 2931, 1477, 1439, 1381, 1372, 1333, 1271, 1326, 1213, 1141, 1112, 967, 855, 819, 746, 687 cm^{-1}. **MS** (DART): 400 ($M+NH_4^+$). **HRMS** (DART) for $C_{19}H_{26}{}^{10}BF_3O_2NS$ ($M+NH_4^+$): Calcd: 399.1760; Found:399.1754.

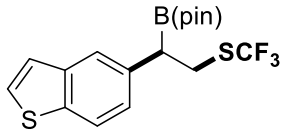
2-(1-(Benzofuran-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dio

xaborolane 8g



Prepared according to ***GP4b*** using 5-bromo-1-benzofuran (65 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.) and *N*-trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) to give compound **8g** as a yellow oil (92 mg, 82%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (s, 1 H), 7.42 (dd, *J* = 4.7, 3.0 Hz, 2 H), 7.13 (d, *J* = 8.6 Hz, 1 H), 6.71 (d, *J* = 2.0 Hz, 1 H), 3.38 (dd, *J* = 12.8, 8.2 Hz, 1 H), 3.24 (dd, *J* = 12.8, 8.8 Hz, 1 H), 2.77 (t, *J* = 8.4 Hz, 1 H), 1.24 (s, 6 H), 1.20 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.07 (s); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ 153.84, 145.23, 134.35, 131.30 (q, *J* = 306.0 Hz), 127.87, 124.63, 120.77, 111.50, 106.50, 84.06, 33.36 (q, *J* = 1.2 Hz), 24.61, 24.52; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.97 (s) ppm. **IR** (KBr): ν_{max} = 2979, 2933, 1536, 1467, 1445, 1372, 1329, 1263, 1214, 1111, 1032, 968, 883, 849, 813, 768, 755, 741, 698, 671, 642 cm^{-1}. **MS** (ESI): 373 (M+H$^+$). **HRMS** (ESI) for $C_{17}H_{21}{}^{10}BF_3O_3NS$ (M+NH_4^+): Calcd: 372.1287; Found: 372.1284.

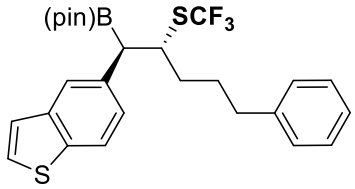
2-(1-(Benzo[b]thiophen-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1, 3,2-dioxaborolane 8h



Prepared according to ***GP4b*** using 5-bromothianaphthene (70 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.) and *N*-trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) to give compound **8h** as a yellow oil (102 mg, 88%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 1 H), 7.65 (s, 1 H), 7.41 (d, *J* = 5.4 Hz, 1 H), 7.27 (d, *J* = 5.4 Hz,

1 H), 7.19 (dd, *J* = 8.3, 1.3 Hz, 1 H), 3.41 (dd, *J* = 12.9, 8.2 Hz, 1 H), 3.27 (dd, *J* = 12.9, 8.8 Hz, 1 H), 2.80 (t, *J* = 8.5 Hz, 1 H), 1.23 (s, 6 H), 1.19 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$)) δ -41.05 (s); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ 140.16, 137.93, 136.02, 131.28 (q, *J* = 306.0 Hz), 126.72, 124.82, 123.72, 123.21, 122.70, 84.12, 33.07, 24.61, 24.53; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.06 (s) ppm. **IR** (KBr): ν_{max} = 2978, 1597, 1437, 1328, 1144, 1112, 1051, 897, 812, 755, 700 cm^{-1}. **MS** (DART): 406 ($M+NH_4^+$). **HRMS** (DART) for $C_{17}H_{24}{}^{10}BF_3O_2NS_2$ ($M+NH_4^+$): Calcd: 405.1324; Found: 405.1319.

(±)-2-((1*R*,2*R*)-1-(benzo[b]thiophen-5-yl)-5-phenyl-2-(trifluoromethylthio)pentyl) -4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8i

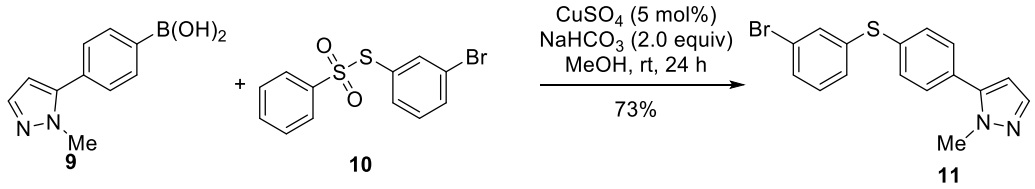


Prepared according to ***GP4b*** using 5-bromothianaphthene (70 mg, 0.33 mmol, 1.1 equiv.), ^{t}BuLi in hexane (0.50 mL, 1.3 M, 0.66 mmol, 2.2 equiv.), pinacol vinyl boronate (47 mg, 0.30 mmol, 1.0 equiv.) and *N*-trifluoromethylthiosaccharin **7** (128 mg, 0.450 mmol, 1.50 equiv.) to give compound **8i** as a yellow oil (97 mg, 72%). Eluent: ethyl acetate/petroleum ether (1:20, R_f = 0.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 1 H), 7.67 (s, 1 H), 7.42 (d, *J* = 5.4 Hz, 1 H), 7.28 (d, *J* = 5.4 Hz, 1 H), 7.25 – 7.20 (m, 1 H), 7.15 (t, *J* = 7.2 Hz, 2 H), 7.10 (d, *J* = 7.0 Hz, 1 H), 7.01 (d, *J* = 7.0 Hz, 2 H), 3.75 (ddd, *J* = 11.0, 7.6, 3.5 Hz, 1 H), 2.75 (d, *J* = 10.9 Hz, 1 H), 2.51 (ddd, *J* = 14.6, 8.7, 6.2 Hz, 1 H), 2.46 – 2.34 (m, 1 H), 1.83 – 1.61 (m, 3 H), 1.49 (dt, *J* = 14.3, 8.4 Hz, 1 H), 1.20 (s, 6 H), 1.17 (s, 6 H); **^{19}F NMR** (376 MHz, $CDCl_3$, signal of sp^3 carbon and adjacent to boron was missing) δ -38.51 (s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.87, 140.02, 137.89, 134.91, 131.12 (q, *J* = 306.8 Hz), 128.20, 128.15, 126.52, 125.79, 125.65, 124.21, 123.81, 122.42, 83.94, 49.09, 35.19, 33.10, 26.87, 24.62, 24.42; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.57 (s) ppm. **IR** (KBr): ν_{max} = 2978, 2933, 1438, 1421, 1361, 1271, 1214, 1143, 1112, 1051, 968, 848, 754, 733, 712, 698 cm^{-1}. **MS** (ESI): 524 ($M+NH_4^+$). **HRMS** (ESI) for $C_{26}H_{34}{}^{10}BF_3O_2NS_2$ ($M+NH_4^+$):

Calcd: 523.2107; Found: 523.2103.

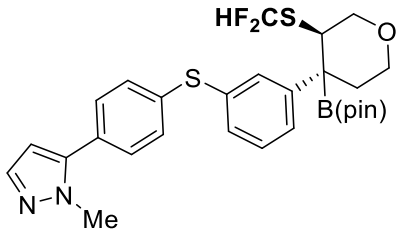
Preparation of difluoromethylthiolated derivative of PF-4191834 by Conjunctive Cross-Coupling

5-(4-(3-Bromophenylthio)phenyl)-1-methyl-1*H*-pyrazole 11[2]



Aryl boronic acids **9** (0.49 g, 2.4 mmol, 1.2 equiv), $CuSO_4$ (16 mg, 0.10 mmol, 5.0 mol%), $NaHCO_3$ (0.25 g, 3.0 mmol, 1.5 equiv.) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under an atmosphere of argon. 15 mL of Absolute methanol and S-3-bromophenyl benzenesulfonothioate **10** (0.66 g, 2.0 mmol, 1.0 equiv.) was added. The mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, the residue was purified by silica gel chromatography (Eluent: ethyl acetate/petroleum ether = 1:5, R_f = 0.3) to give compound **11** as a colorless oil (504 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2 H), 7.42 – 7.36 (m, 5 H), 7.31 (d, *J* = 7.9 Hz, 1 H), 7.20 (t, *J* = 7.9 Hz, 1 H), 6.32 (d, *J* = 1.8 Hz, 1 H), 3.90 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.54, 138.54, 137.40, 135.48, 133.54, 131.02, 130.54, 130.40, 129.73, 129.63, 129.43, 123.04, 106.14, 37.51 ppm. **IR** (KBr): ν_{max} = 3051, 2945, 1602, 1573, 1558, 1481, 1458, 1422, 1396, 1334, 1274, 1251, 1177, 1091, 1081, 1067, 1015, 992, 978, 927, 871, 835, 777, 751, 702, 679, 647 cm^{-1}. **HRMS**: Calcd for $C_{16}H_{13}N_2SBr$: 343.9983; Found: 343.9989.

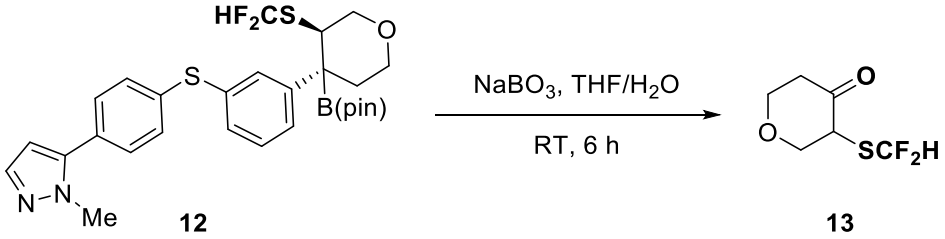
(±)-5-(4-(3-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)phenylthio)phenyl)-1-methyl-1*H*-pyrazole 12



Prepared according to ***GP1b*** using 5-(4-(3-bromophenylthio)phenyl) -1-methyl-1*H*-pyrazole **11** (114 mg, 0.33 mmol, 1.1 equiv.) ^{t}BuLi (1.3 M in hexane,

0.50 mL, 0.66 mmol, 2.2 equiv.), 3,6-dihydro-2*H*-pyran-4-boronic acid pinacol ester (63 mg, 0.30 mmol, 1.0 equiv.) and reagent **2a** (100 mg, 0.450 mmol, 1.50 equiv.). to give compound **12** as a yellow oil (195 mg, 70%). Eluent: ethyl acetate/petroleum ether (1:5, R_f = 0.2). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.91 (s, 1 H), 7.79 (d, *J* = 7.4 Hz, 1 H), 7.48 (d, *J* = 6.8 Hz, 2 H), 7.38 – 7.27 (m, 5 H), 6.49 (t, *J* = 56.3 Hz, 1 H), 6.28 (d, *J* = 1.7 Hz, 1 H), 4.50 (d, *J* = 11.3 Hz, 1 H), 4.01 (t, *J* = 10.5 Hz, 1 H), 3.88 (s, 3 H), 3.66 (t, *J* = 11.0 Hz, 2 H), 3.32 (s, 1 H), 2.48 – 2.33 (m, 1 H), 1.66 (d, *J* = 13.6 Hz, 1 H), 1.47 (s, 3 H), 1.31 (s, 3 H), 1.28 (s, 3 H), 1.18 (s, 3 H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.82 (dd, *J* = 240.3, 56.0 Hz), -93.19 (dd, *J* = 240.3, 56.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$, signal of sp^3 carbon and sp^2 carbon adjacent to boron was missing) δ 142.76, 138.42, 138.02, 137.68, 133.75, 133.35, 132.95, 129.65, 129.13, 128.65, 128.45, 119.94 (t, *J* = 274 Hz), 105.95, 80.21, 77.17, 68.62, 62.24, 43.40, 37.39, 31.96, 26.17, 24.98, 24.90, 23.06; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 45.39 (s) ppm. **IR** (KBr): ν_{max} = 2977, 1722, 1586, 1477, 1401, 1372, 1353, 1325, 1271, 1223, 1142, 1113, 1089, 1067, 1026, 979, 963, 911, 862, 851, 837, 780, 732, 703 cm^{-1}. **MS** (ESI): 559 ($M+H^+$). **HRMS** (ESI) for $C_{28}H_{34}{}^{10}BF_2N_2O_3S_2$ ($M+H^+$): Calcd: 558.2103; Found: 558.2096.

3-(Difluoromethylthio)dihydro-2*H*-pyran-4(3*H*)-one 13



An 25-mL Schlenk flask equipped with a stir bar, septum, and digital thermocouple probe was charged with **12** (55.7 mg, 0.100 mmol), $NaBO_3$ (24.5 mg, 0.300 mmol, 3.00 equiv.) and THF/H_2O (v/v = 1:1, 3.0 mL) was added. The reaction was allowed to stir at room temperature for 6 h. Half of the solvent was removed under reduced pressure. The aqueous layer was extracted with ethyl acetate (5 mL × 3), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated. The residue was purified by silica gel chromatography (Eluent: ethyl acetate/petroleum ether = 1:5, R_f = 0.5) to give compound **13** as a yellow oil (15.5 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.90 (t, *J* = 56.1 Hz, 1 H), 4.40 (dd, *J* = 11.6,

5.7 Hz, 1 H), 4.26 – 4.13 (m, 1 H), 4.14 – 4.05 (m, 1 H), 3.87 (ddd, *J* = 11.5, 9.4, 4.1 Hz, 1 H), 3.78 (dd, *J* = 11.6, 8.8 Hz, 1 H), 2.80 (dt, *J* = 14.4, 4.2 Hz, 1 H), 2.76 – 2.62 (m, 1 H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.24, 119.38 (dd, *J* = 275.6, 273.8 Hz), 73.38, 68.40, 50.41, 41.95; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.34 (dd, *J* = 242.3, 55.7 Hz), -92.80 (dd, *J* = 242.3, 56.4 Hz). **IR** (KBr): ν_{max} = 2976, 2920, 2864, 1715, 1473, 1416, 1316, 1222, 113, 863, 776 cm^{-1}. **MS** (EI): m/z (%) 182, 124, 110 (100), 88. **HRMS**: Calcd for $C_6H_8F_2SO_2$: 182.0208; Found: 182.0207.

References

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2. S. Yoshida, Y. Sugimura, Y. Hazama, Y. Nishiyama, T. Yano, S. Shimizu, T. Hosoya, *Chem. Commun. 2015*, **51**, 16613.

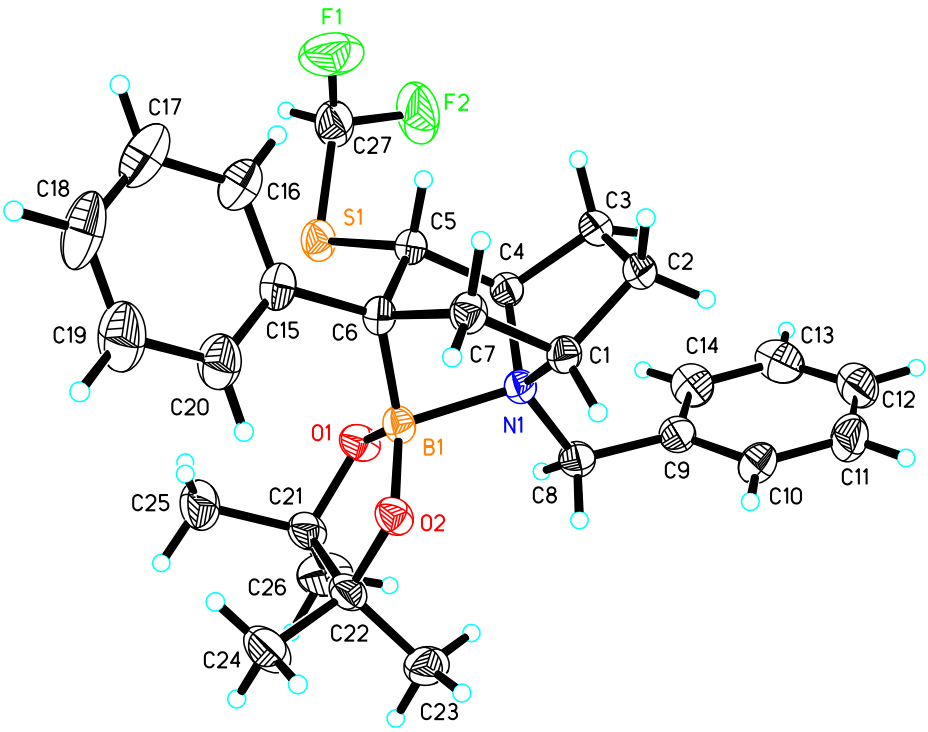


Figure S1. X-ray Structure of 3s

Table S1. Crystal data and structure refinement for mo_d8v18370_0m.

Identification code	mo_d8v18370_0m	
Empirical formula	C27 H34 B F2 N O2 S	
Formula weight	485.42	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 29.1214(7) Å	α = 90°.
	b = 10.5552(2) Å.	β = 104.0720(10)°.
	c = 17.3216(4) Å	γ = 90°.
Volume	5164.6(2) $Å^3$	
Z	8	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	0.164 mm^{-1}	
F(000)	2064	
Crystal size	0.20 x 0.16 x 0.11 mm^3	
Theta range for data collection	2.477 to 25.994°.	
Index ranges	-35<=h<=35, -13<=k<=13, -21<=l<=21	
Reflections collected	37446	
Independent reflections	5055 [R(int) = 0.0692]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5651	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5055 / 0 / 312	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1292	
R indices (all data)	R1 = 0.0631, wR2 = 0.1459	
Extinction coefficient	0.0034(6)	
Largest diff. peak and hole	0.243 and -0.208 $e.Å^{-3}$	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for mo_d8v18370_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4484(1)	5258(1)	5459(1)	54(1)
F(1)	4500(1)	7118(2)	4466(1)	114(1)
F(2)	4443(1)	7700(2)	5622(2)	128(1)
N(1)	3264(1)	4439(1)	5624(1)	37(1)
O(1)	4021(1)	3186(1)	6109(1)	48(1)
O(2)	3401(1)	2022(1)	5357(1)	43(1)
B(1)	3630(1)	3225(2)	5435(1)	40(1)
C(1)	2881(1)	4550(2)	4871(1)	41(1)
C(2)	2733(1)	5943(2)	4816(1)	48(1)
C(3)	3179(1)	6656(2)	5257(1)	48(1)
C(4)	3544(1)	5624(2)	5580(1)	40(1)
C(5)	3848(1)	5290(2)	4987(1)	41(1)
C(6)	3668(1)	3993(2)	4632(1)	40(1)
C(7)	3136(1)	4165(2)	4222(1)	44(1)
C(8)	3102(1)	4255(2)	6370(1)	48(1)
C(9)	2787(1)	5250(2)	6597(1)	48(1)
C(10)	2300(1)	5121(2)	6368(1)	59(1)
C(11)	2007(1)	6048(3)	6551(2)	75(1)
C(12)	2197(1)	7108(3)	6958(2)	79(1)
C(13)	2679(1)	7234(2)	7209(1)	75(1)
C(14)	2974(1)	6308(2)	7036(1)	61(1)
C(15)	3917(1)	3464(2)	4028(1)	49(1)
C(16)	4134(1)	4233(3)	3570(1)	66(1)
C(17)	4333(1)	3728(3)	2985(2)	86(1)
C(18)	4320(1)	2464(4)	2849(2)	99(1)
C(19)	4102(1)	1682(3)	3289(2)	93(1)
C(20)	3902(1)	2183(2)	3867(1)	67(1)
C(21)	4126(1)	1902(2)	6345(1)	51(1)
C(22)	3651(1)	1177(2)	5977(1)	49(1)
C(23)	3345(1)	958(2)	6563(1)	63(1)
C(24)	3713(1)	-84(2)	5594(2)	74(1)
C(25)	4538(1)	1488(2)	6000(2)	83(1)
C(26)	4281(1)	1875(3)	7246(2)	82(1)

C(27)	4644(1)	6808(2)	5245(2)	74(1)

Table S3. Bond lengths [Å] and angles [°] for mo_d8v18370_0m.

S(1)-C(27)	1.764(2)
S(1)-C(5)	1.8337(17)
F(1)-C(27)	1.354(3)
F(2)-C(27)	1.356(3)
N(1)-C(8)	1.492(2)
N(1)-C(1)	1.500(2)
N(1)-C(4)	1.507(2)
N(1)-B(1)	1.748(2)
O(1)-B(1)	1.420(2)
O(1)-C(21)	1.427(2)
O(2)-B(1)	1.425(2)
O(2)-C(22)	1.449(2)
B(1)-C(6)	1.636(3)
C(1)-C(2)	1.529(2)
C(1)-C(7)	1.545(2)
C(1)-H(1)	0.9800
C(2)-C(3)	1.535(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.529(2)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.551(2)
C(4)-H(4)	0.9800
C(5)-C(6)	1.541(2)
C(5)-H(5)	0.9800
C(6)-C(15)	1.518(2)
C(6)-C(7)	1.549(2)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.509(3)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.383(3)
C(9)-C(14)	1.386(3)
C(10)-C(11)	1.383(3)

C(10)-H(10)	0.9300
C(11)-C(12)	1.366(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.373(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.380(3)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(15)-C(20)	1.380(3)
C(15)-C(16)	1.390(3)
C(16)-C(17)	1.390(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.354(5)
C(17)-H(17)	0.9300
C(18)-C(19)	1.378(5)
C(18)-H(18)	0.9300
C(19)-C(20)	1.380(3)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(21)-C(26)	1.515(3)
C(21)-C(25)	1.531(3)
C(21)-C(22)	1.574(3)
C(22)-C(24)	1.517(3)
C(22)-C(23)	1.522(3)
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-H(27)	0.9800

C(27)-S(1)-C(5)	100.28(11)
C(8)-N(1)-C(1)	116.04(14)
C(8)-N(1)-C(4)	116.19(14)
C(1)-N(1)-C(4)	100.84(12)
C(8)-N(1)-B(1)	113.76(13)
C(1)-N(1)-B(1)	104.62(12)
C(4)-N(1)-B(1)	103.66(12)
B(1)-O(1)-C(21)	109.58(14)
B(1)-O(2)-C(22)	109.85(13)
O(1)-B(1)-O(2)	108.43(15)
O(1)-B(1)-C(6)	120.42(15)
O(2)-B(1)-C(6)	119.16(15)
O(1)-B(1)-N(1)	105.73(14)
O(2)-B(1)-N(1)	112.23(14)
C(6)-B(1)-N(1)	88.07(12)
N(1)-C(1)-C(2)	105.57(14)
N(1)-C(1)-C(7)	103.05(13)
C(2)-C(1)-C(7)	112.67(15)
N(1)-C(1)-H(1)	111.7
C(2)-C(1)-H(1)	111.7
C(7)-C(1)-H(1)	111.7
C(1)-C(2)-C(3)	104.39(14)
C(1)-C(2)-H(2A)	110.9
C(3)-C(2)-H(2A)	110.9
C(1)-C(2)-H(2B)	110.9
C(3)-C(2)-H(2B)	110.9
H(2A)-C(2)-H(2B)	108.9
C(4)-C(3)-C(2)	105.21(15)
C(4)-C(3)-H(3A)	110.7
C(2)-C(3)-H(3A)	110.7
C(4)-C(3)-H(3B)	110.7
C(2)-C(3)-H(3B)	110.7
H(3A)-C(3)-H(3B)	108.8
N(1)-C(4)-C(3)	105.81(14)
N(1)-C(4)-C(5)	104.40(13)
C(3)-C(4)-C(5)	112.20(15)
N(1)-C(4)-H(4)	111.4
C(3)-C(4)-H(4)	111.4

C(5)-C(4)-H(4)	111.4
C(6)-C(5)-C(4)	105.77(13)
C(6)-C(5)-S(1)	111.84(11)
C(4)-C(5)-S(1)	112.72(12)
C(6)-C(5)-H(5)	108.8
C(4)-C(5)-H(5)	108.8
S(1)-C(5)-H(5)	108.8
C(15)-C(6)-C(5)	115.31(14)
C(15)-C(6)-C(7)	108.58(14)
C(5)-C(6)-C(7)	106.60(14)
C(15)-C(6)-B(1)	123.11(15)
C(5)-C(6)-B(1)	100.85(14)
C(7)-C(6)-B(1)	100.49(13)
C(1)-C(7)-C(6)	107.44(13)
C(1)-C(7)-H(7A)	110.2
C(6)-C(7)-H(7A)	110.2
C(1)-C(7)-H(7B)	110.2
C(6)-C(7)-H(7B)	110.2
H(7A)-C(7)-H(7B)	108.5
N(1)-C(8)-C(9)	118.38(15)
N(1)-C(8)-H(8A)	107.7
C(9)-C(8)-H(8A)	107.7
N(1)-C(8)-H(8B)	107.7
C(9)-C(8)-H(8B)	107.7
H(8A)-C(8)-H(8B)	107.1
C(10)-C(9)-C(14)	118.38(19)
C(10)-C(9)-C(8)	120.23(19)
C(14)-C(9)-C(8)	121.39(19)
C(9)-C(10)-C(11)	120.7(2)
C(9)-C(10)-H(10)	119.7
C(11)-C(10)-H(10)	119.7
C(12)-C(11)-C(10)	120.3(2)
C(12)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8
C(11)-C(12)-C(13)	119.7(2)
C(11)-C(12)-H(12)	120.1
C(13)-C(12)-H(12)	120.1
C(12)-C(13)-C(14)	120.3(2)

C(12)-C(13)-H(13)	119.8
C(14)-C(13)-H(13)	119.8
C(13)-C(14)-C(9)	120.5(2)
C(13)-C(14)-H(14)	119.7
C(9)-C(14)-H(14)	119.7
C(20)-C(15)-C(16)	116.9(2)
C(20)-C(15)-C(6)	120.21(18)
C(16)-C(15)-C(6)	122.65(19)
C(15)-C(16)-C(17)	121.4(3)
C(15)-C(16)-H(16)	119.3
C(17)-C(16)-H(16)	119.3
C(18)-C(17)-C(16)	120.4(3)
C(18)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
C(17)-C(18)-C(19)	119.5(2)
C(17)-C(18)-H(18)	120.3
C(19)-C(18)-H(18)	120.3
C(18)-C(19)-C(20)	120.2(3)
C(18)-C(19)-H(19)	119.9
C(20)-C(19)-H(19)	119.9
C(19)-C(20)-C(15)	121.6(3)
C(19)-C(20)-H(20)	119.2
C(15)-C(20)-H(20)	119.2
O(1)-C(21)-C(26)	107.62(18)
O(1)-C(21)-C(25)	106.90(17)
C(26)-C(21)-C(25)	109.3(2)
O(1)-C(21)-C(22)	103.96(14)
C(26)-C(21)-C(22)	114.94(18)
C(25)-C(21)-C(22)	113.52(19)
O(2)-C(22)-C(24)	107.98(17)
O(2)-C(22)-C(23)	108.62(15)
C(24)-C(22)-C(23)	108.09(18)
O(2)-C(22)-C(21)	103.54(14)
C(24)-C(22)-C(21)	114.60(17)
C(23)-C(22)-C(21)	113.68(17)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5

C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(21)-C(25)-H(25A)	109.5
C(21)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(21)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(21)-C(26)-H(26A)	109.5
C(21)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(21)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
F(1)-C(27)-F(2)	104.3(2)
F(1)-C(27)-S(1)	113.59(18)
F(2)-C(27)-S(1)	112.11(18)
F(1)-C(27)-H(27)	108.9
F(2)-C(27)-H(27)	108.9
S(1)-C(27)-H(27)	108.9

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for mo_d8v18370_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	35(1)	49(1)	77(1)	-5(1)	13(1)	-2(1)
F(1)	90(1)	107(1)	144(2)	46(1)	26(1)	-28(1)
F(2)	112(1)	57(1)	237(2)	-33(1)	81(2)	2(1)
N(1)	36(1)	39(1)	38(1)	4(1)	10(1)	4(1)
O(1)	40(1)	44(1)	54(1)	5(1)	-4(1)	-2(1)
O(2)	37(1)	39(1)	50(1)	2(1)	2(1)	2(1)
B(1)	33(1)	39(1)	45(1)	-2(1)	6(1)	3(1)
C(1)	32(1)	47(1)	44(1)	6(1)	7(1)	2(1)
C(2)	42(1)	50(1)	54(1)	16(1)	17(1)	12(1)
C(3)	51(1)	39(1)	60(1)	6(1)	22(1)	9(1)
C(4)	39(1)	37(1)	46(1)	-1(1)	12(1)	1(1)
C(5)	36(1)	41(1)	47(1)	3(1)	13(1)	3(1)
C(6)	35(1)	42(1)	43(1)	-2(1)	11(1)	3(1)
C(7)	39(1)	52(1)	41(1)	1(1)	7(1)	4(1)
C(8)	54(1)	49(1)	44(1)	8(1)	18(1)	7(1)
C(9)	58(1)	52(1)	39(1)	7(1)	20(1)	9(1)
C(10)	58(1)	67(1)	61(1)	5(1)	30(1)	3(1)
C(11)	68(2)	94(2)	76(2)	17(2)	41(1)	23(1)
C(12)	110(2)	78(2)	67(2)	18(1)	54(2)	40(2)
C(13)	121(2)	62(2)	49(1)	-4(1)	34(1)	15(1)
C(14)	77(2)	68(1)	39(1)	-4(1)	15(1)	7(1)
C(15)	38(1)	61(1)	47(1)	-7(1)	11(1)	4(1)
C(16)	62(1)	83(2)	60(1)	-7(1)	27(1)	-3(1)
C(17)	69(2)	132(3)	66(2)	-17(2)	35(1)	-11(2)
C(18)	81(2)	144(3)	83(2)	-48(2)	41(2)	3(2)
C(19)	97(2)	96(2)	92(2)	-42(2)	36(2)	6(2)
C(20)	70(2)	69(2)	66(1)	-21(1)	24(1)	2(1)
C(21)	37(1)	47(1)	64(1)	11(1)	2(1)	5(1)
C(22)	41(1)	38(1)	63(1)	9(1)	6(1)	6(1)
C(23)	51(1)	64(1)	72(1)	22(1)	11(1)	0(1)
C(24)	72(2)	42(1)	106(2)	-1(1)	15(1)	9(1)
C(25)	46(1)	75(2)	130(2)	7(2)	25(1)	13(1)
C(26)	66(2)	96(2)	69(2)	28(1)	-12(1)	-10(1)

C(27)	51(1)	55(1)	122(2)	-5(1)	30(1)	-5(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for mo_d8v18370_0m.

	x	y	z	U(eq)
H(1)	2614	3988	4876	49
H(2A)	2475	6083	5070	57
H(2B)	2635	6214	4265	57
H(3A)	3291	7212	4896	58
H(3B)	3116	7158	5688	58
H(4)	3743	5854	6103	48
H(5)	3789	5921	4560	49
H(7A)	3096	4818	3817	53
H(7B)	3005	3380	3970	53
H(8A)	3381	4178	6807	58
H(8B)	2936	3452	6328	58
H(10)	2168	4403	6090	71
H(11)	1681	5948	6396	90
H(12)	1999	7743	7065	95
H(13)	2808	7946	7497	90
H(14)	3300	6394	7216	73
H(16)	4147	5103	3657	79
H(17)	4477	4262	2686	103
H(18)	4456	2126	2462	119
H(19)	4089	813	3195	111
H(20)	3754	1643	4155	81
H(23A)	3322	1731	6843	95
H(23B)	3486	313	6937	95
H(23C)	3035	692	6280	95
H(24A)	3409	-429	5345	112
H(24B)	3879	-660	5995	112
H(24C)	3892	40	5202	112
H(25A)	4442	1518	5429	124
H(25B)	4630	639	6168	124
H(25C)	4802	2048	6185	124
H(26A)	4558	2392	7421	123
H(26B)	4353	1019	7423	123

H(26C)	4031	2196	7464	123
H(27)	4989	6891	5415	89

Table S6. Torsion angles [°] for mo_d8v18370_0m.

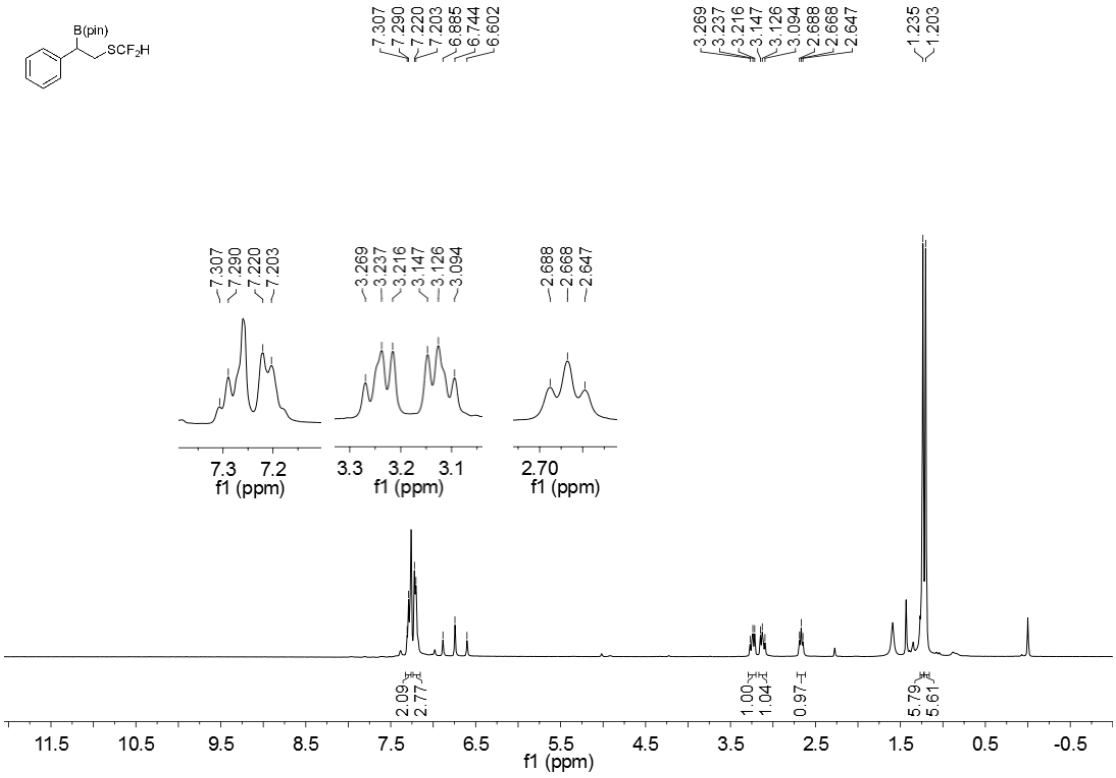
C(21)-O(1)-B(1)-O(2)	15.1(2)
C(21)-O(1)-B(1)-C(6)	-127.23(17)
C(21)-O(1)-B(1)-N(1)	135.61(14)
C(22)-O(2)-B(1)-O(1)	-1.14(19)
C(22)-O(2)-B(1)-C(6)	141.72(15)
C(22)-O(2)-B(1)-N(1)	-117.55(15)
C(8)-N(1)-B(1)-O(1)	-58.11(18)
C(1)-N(1)-B(1)-O(1)	174.27(13)
C(4)-N(1)-B(1)-O(1)	68.99(16)
C(8)-N(1)-B(1)-O(2)	59.91(19)
C(1)-N(1)-B(1)-O(2)	-67.70(17)
C(4)-N(1)-B(1)-O(2)	-172.98(14)
C(8)-N(1)-B(1)-C(6)	-179.23(14)
C(1)-N(1)-B(1)-C(6)	53.15(14)
C(4)-N(1)-B(1)-C(6)	-52.13(13)
C(8)-N(1)-C(1)-C(2)	84.54(17)
C(4)-N(1)-C(1)-C(2)	-41.88(16)
B(1)-N(1)-C(1)-C(2)	-149.25(13)
C(8)-N(1)-C(1)-C(7)	-157.08(14)
C(4)-N(1)-C(1)-C(7)	76.50(15)
B(1)-N(1)-C(1)-C(7)	-30.87(16)
N(1)-C(1)-C(2)-C(3)	28.36(18)
C(7)-C(1)-C(2)-C(3)	-83.38(18)
C(1)-C(2)-C(3)-C(4)	-3.39(19)
C(8)-N(1)-C(4)-C(3)	-86.77(17)
C(1)-N(1)-C(4)-C(3)	39.55(16)
B(1)-N(1)-C(4)-C(3)	147.67(14)
C(8)-N(1)-C(4)-C(5)	154.67(14)
C(1)-N(1)-C(4)-C(5)	-79.01(14)
B(1)-N(1)-C(4)-C(5)	29.11(15)
C(2)-C(3)-C(4)-N(1)	-22.55(18)
C(2)-C(3)-C(4)-C(5)	90.69(17)
N(1)-C(4)-C(5)-C(6)	8.22(17)
C(3)-C(4)-C(5)-C(6)	-105.88(16)
N(1)-C(4)-C(5)-S(1)	-114.28(12)
C(3)-C(4)-C(5)-S(1)	131.61(14)

C(27)-S(1)-C(5)-C(6)	145.84(15)
C(27)-S(1)-C(5)-C(4)	-95.13(15)
C(4)-C(5)-C(6)-C(15)	-179.93(14)
S(1)-C(5)-C(6)-C(15)	-56.87(18)
C(4)-C(5)-C(6)-C(7)	59.49(17)
S(1)-C(5)-C(6)-C(7)	-177.46(11)
C(4)-C(5)-C(6)-B(1)	-45.03(16)
S(1)-C(5)-C(6)-B(1)	78.03(14)
O(1)-B(1)-C(6)-C(15)	78.6(2)
O(2)-B(1)-C(6)-C(15)	-59.8(2)
N(1)-B(1)-C(6)-C(15)	-174.29(15)
O(1)-B(1)-C(6)-C(5)	-51.57(19)
O(2)-B(1)-C(6)-C(5)	170.06(14)
N(1)-B(1)-C(6)-C(5)	55.57(13)
O(1)-B(1)-C(6)-C(7)	-160.92(15)
O(2)-B(1)-C(6)-C(7)	60.71(18)
N(1)-B(1)-C(6)-C(7)	-53.78(13)
N(1)-C(1)-C(7)-C(6)	-6.04(18)
C(2)-C(1)-C(7)-C(6)	107.25(17)
C(15)-C(6)-C(7)-C(1)	173.39(15)
C(5)-C(6)-C(7)-C(1)	-61.80(17)
B(1)-C(6)-C(7)-C(1)	42.97(17)
C(1)-N(1)-C(8)-C(9)	-59.0(2)
C(4)-N(1)-C(8)-C(9)	59.3(2)
B(1)-N(1)-C(8)-C(9)	179.59(16)
N(1)-C(8)-C(9)-C(10)	93.3(2)
N(1)-C(8)-C(9)-C(14)	-86.9(2)
C(14)-C(9)-C(10)-C(11)	2.3(3)
C(8)-C(9)-C(10)-C(11)	-177.90(19)
C(9)-C(10)-C(11)-C(12)	0.2(3)
C(10)-C(11)-C(12)-C(13)	-2.1(4)
C(11)-C(12)-C(13)-C(14)	1.5(4)
C(12)-C(13)-C(14)-C(9)	1.0(3)
C(10)-C(9)-C(14)-C(13)	-2.9(3)
C(8)-C(9)-C(14)-C(13)	177.29(19)
C(5)-C(6)-C(15)-C(20)	158.70(18)
C(7)-C(6)-C(15)-C(20)	-81.8(2)
B(1)-C(6)-C(15)-C(20)	34.8(3)

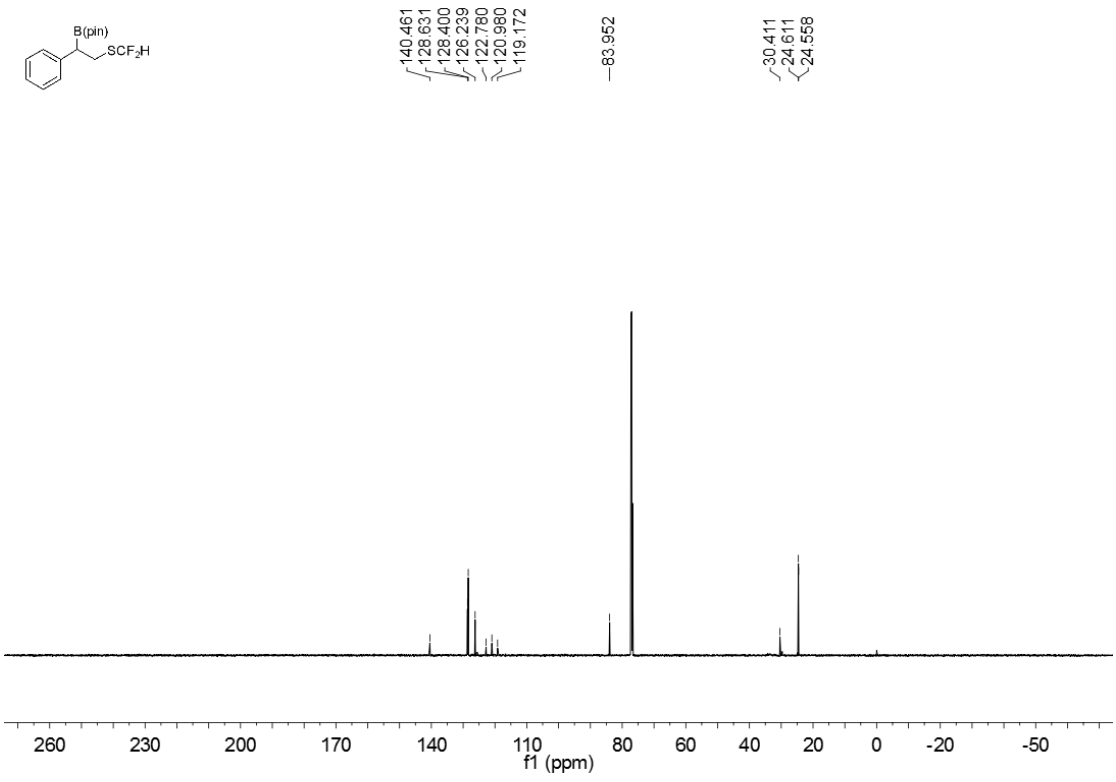
C(5)-C(6)-C(15)-C(16)	-26.6(3)
C(7)-C(6)-C(15)-C(16)	92.9(2)
B(1)-C(6)-C(15)-C(16)	-150.42(19)
C(20)-C(15)-C(16)-C(17)	-0.9(3)
C(6)-C(15)-C(16)-C(17)	-175.8(2)
C(15)-C(16)-C(17)-C(18)	-0.1(4)
C(16)-C(17)-C(18)-C(19)	0.8(5)
C(17)-C(18)-C(19)-C(20)	-0.4(5)
C(18)-C(19)-C(20)-C(15)	-0.6(4)
C(16)-C(15)-C(20)-C(19)	1.2(3)
C(6)-C(15)-C(20)-C(19)	176.3(2)
B(1)-O(1)-C(21)-C(26)	-143.79(18)
B(1)-O(1)-C(21)-C(25)	98.9(2)
B(1)-O(1)-C(21)-C(22)	-21.5(2)
B(1)-O(2)-C(22)-C(24)	-133.41(17)
B(1)-O(2)-C(22)-C(23)	109.61(18)
B(1)-O(2)-C(22)-C(21)	-11.52(19)
O(1)-C(21)-C(22)-O(2)	19.82(19)
C(26)-C(21)-C(22)-O(2)	137.18(19)
C(25)-C(21)-C(22)-O(2)	-95.95(19)
O(1)-C(21)-C(22)-C(24)	137.17(19)
C(26)-C(21)-C(22)-C(24)	-105.5(2)
C(25)-C(21)-C(22)-C(24)	21.4(3)
O(1)-C(21)-C(22)-C(23)	-97.83(18)
C(26)-C(21)-C(22)-C(23)	19.5(2)
C(25)-C(21)-C(22)-C(23)	146.39(19)
C(5)-S(1)-C(27)-F(1)	-51.99(19)
C(5)-S(1)-C(27)-F(2)	65.9(2)

Symmetry transformations used to generate equivalent atoms:

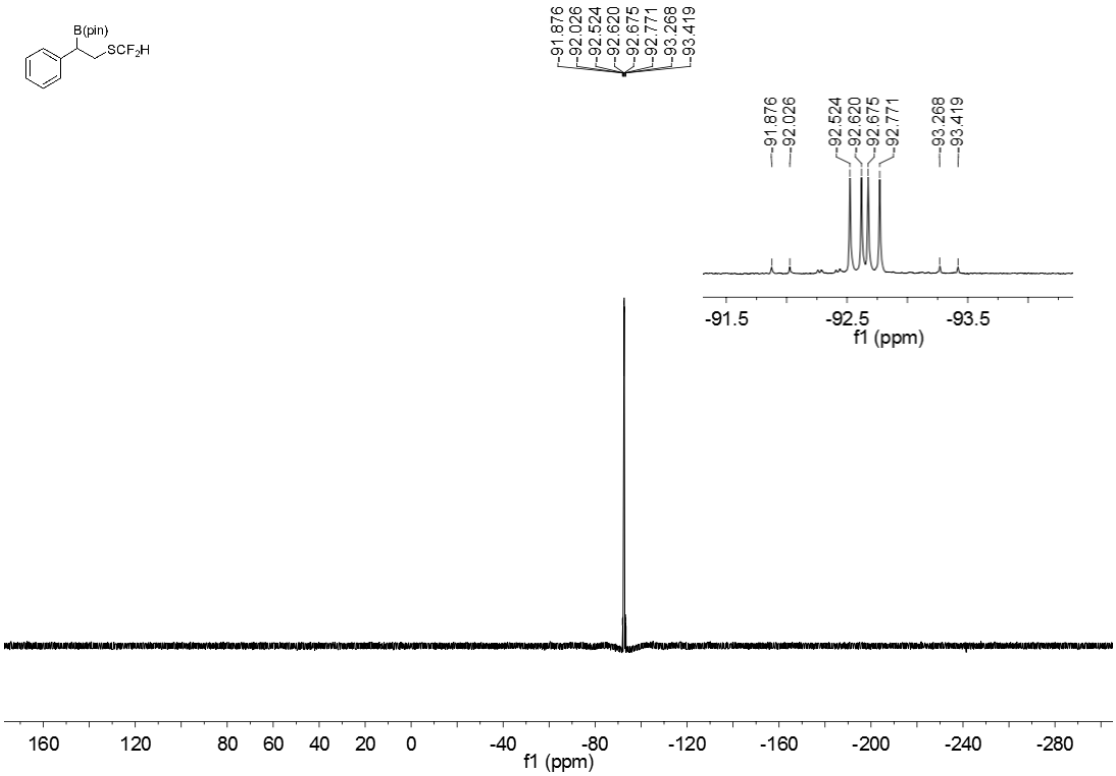
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(2-(difluoromethylthio)-1-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3a



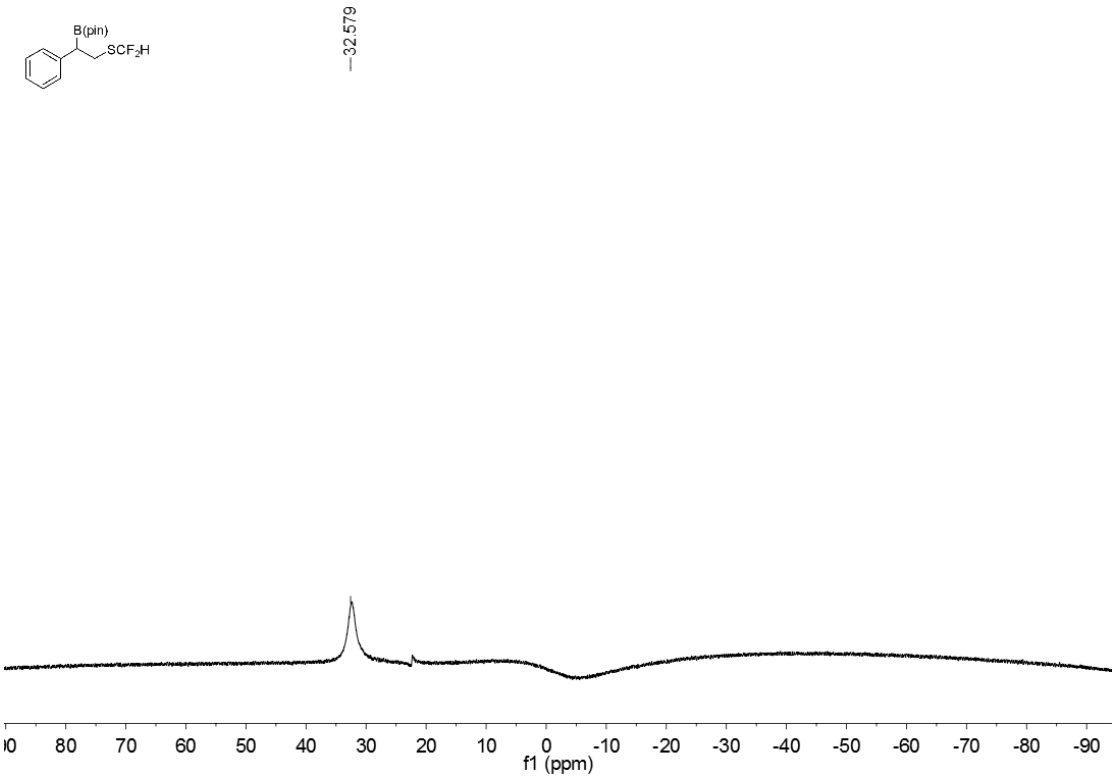
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 2-(2-(difluoromethylthio)-1-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3a



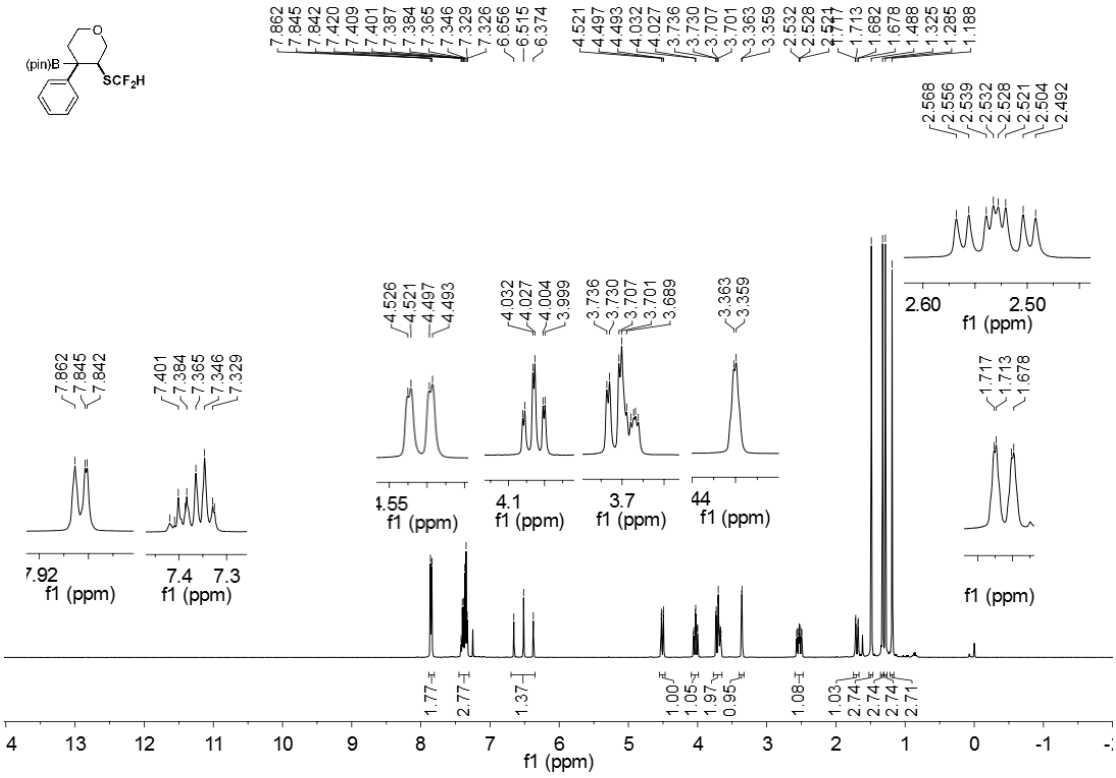
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(2-(difluoromethylthio)-1-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3a



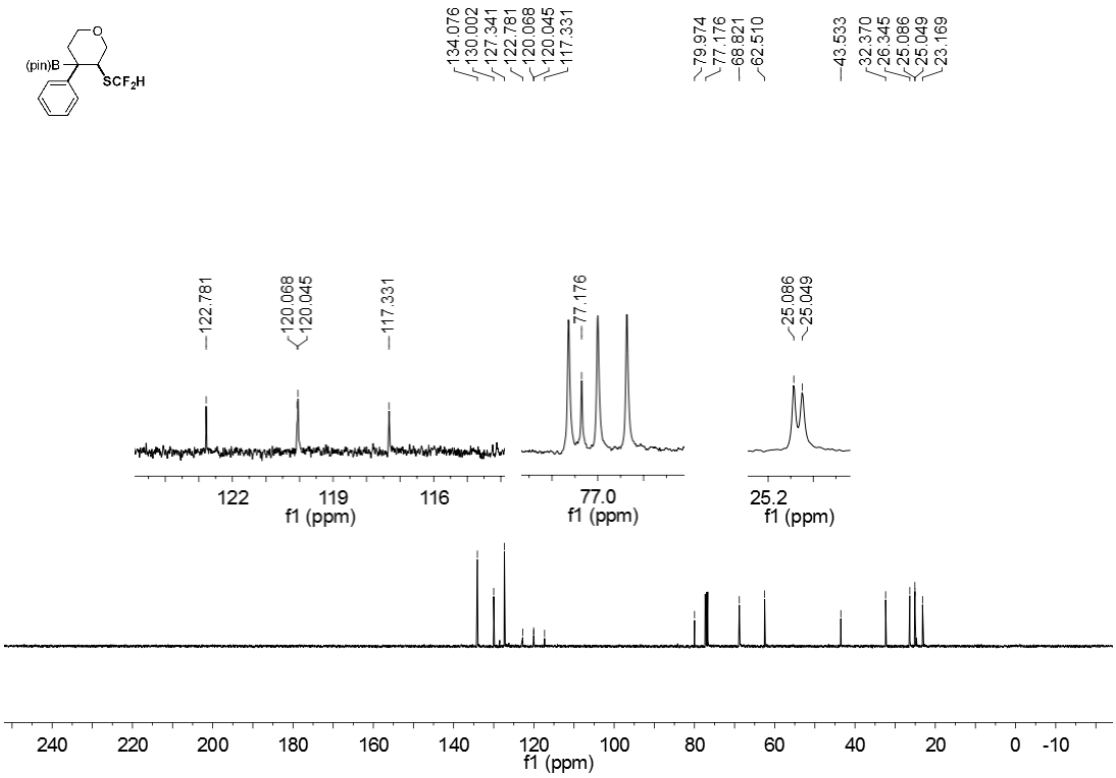
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 2-(2-(difluoromethylthio)-1-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3a



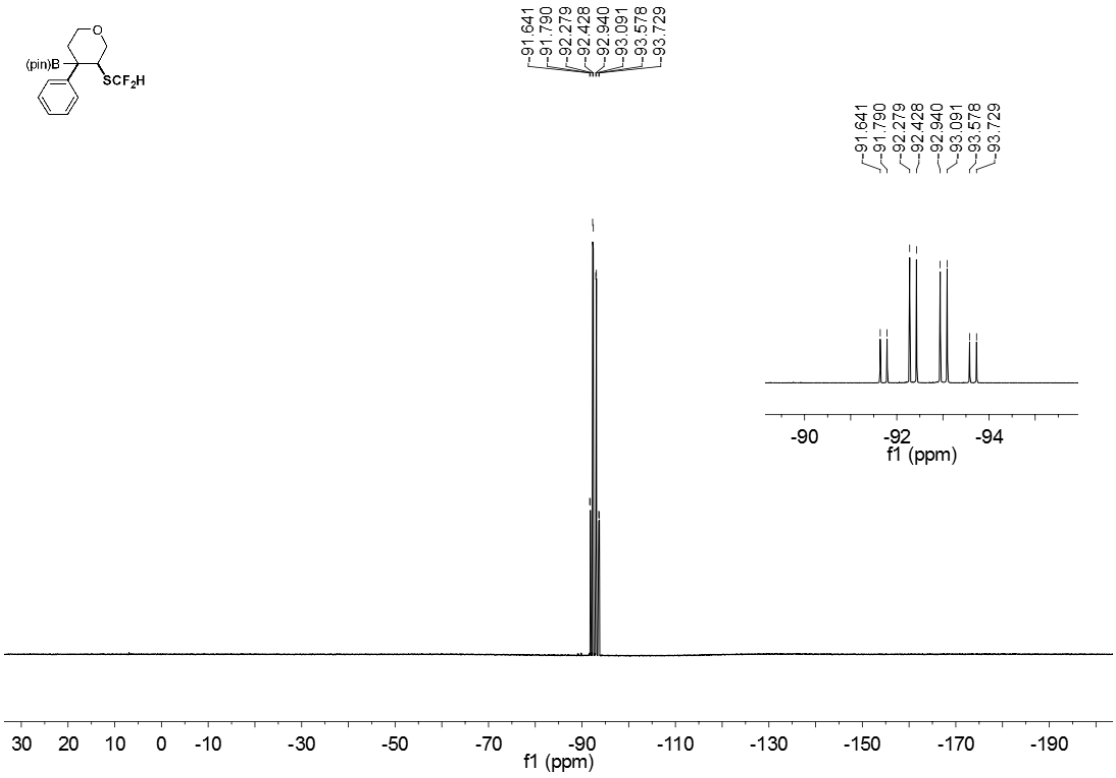
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3b



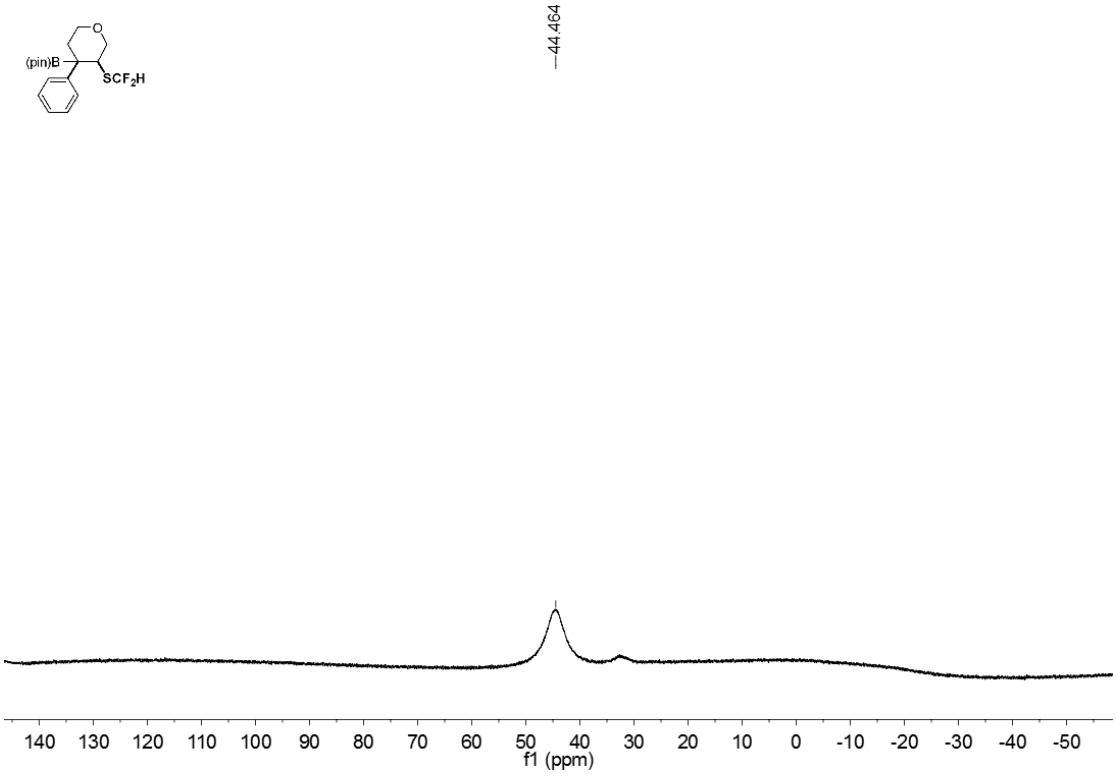
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3b



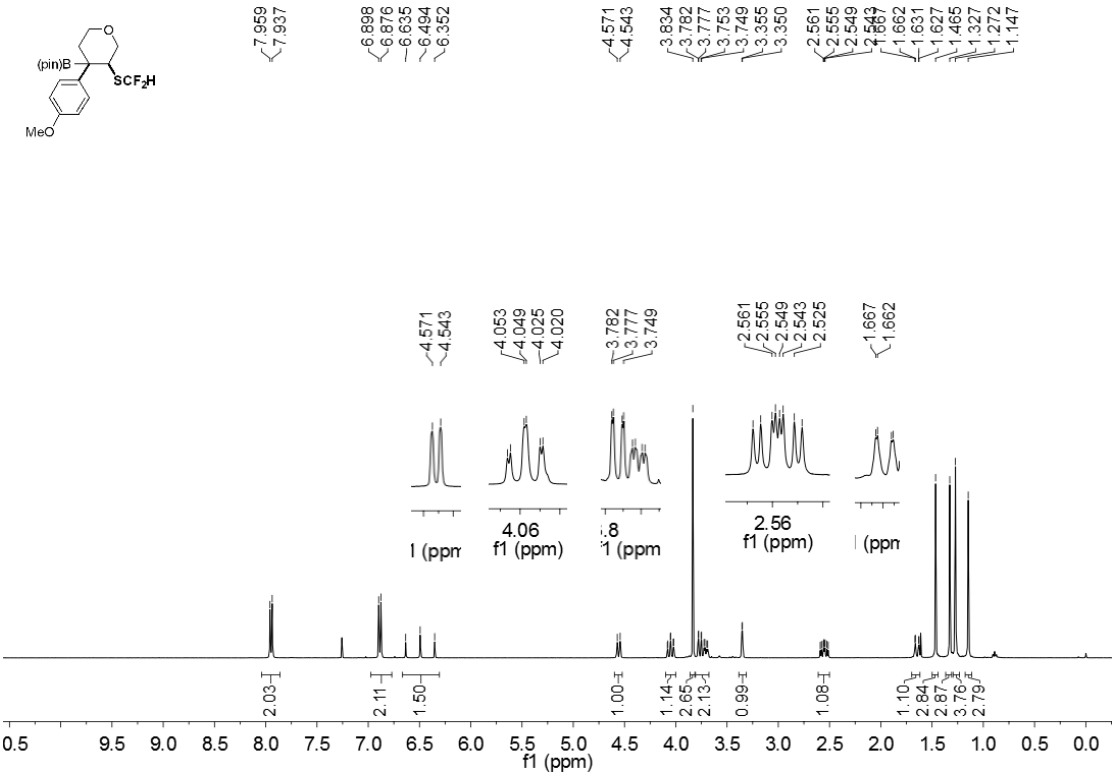
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3b



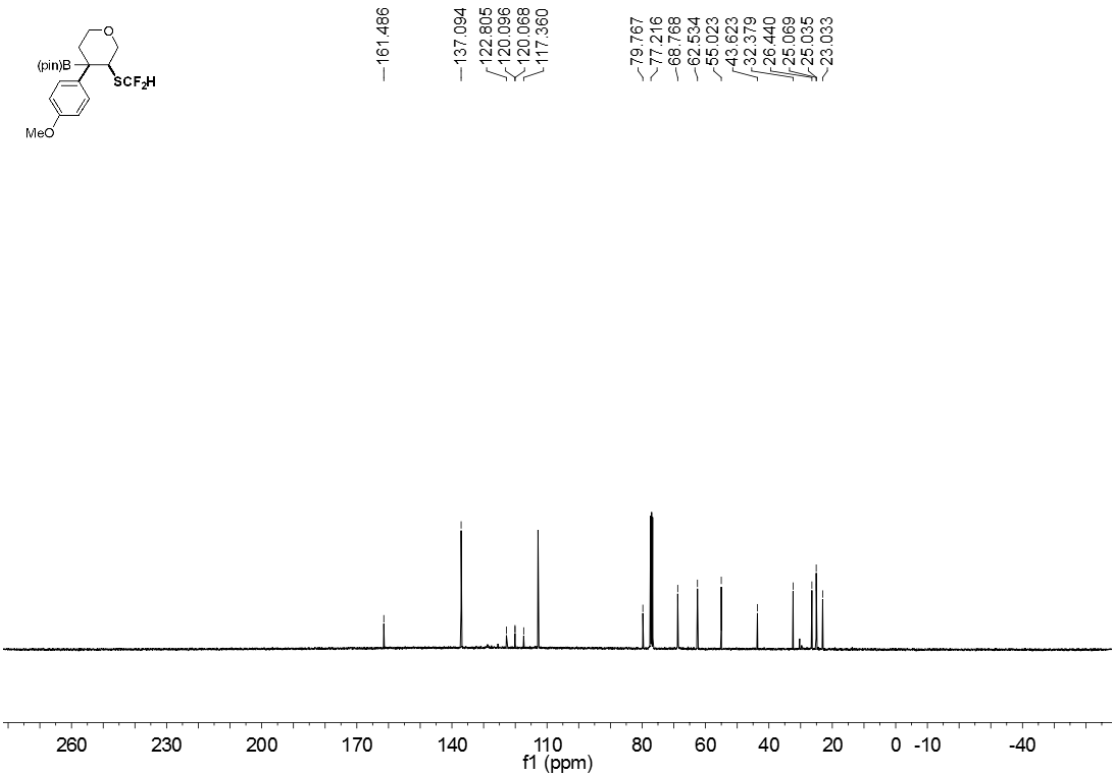
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3b



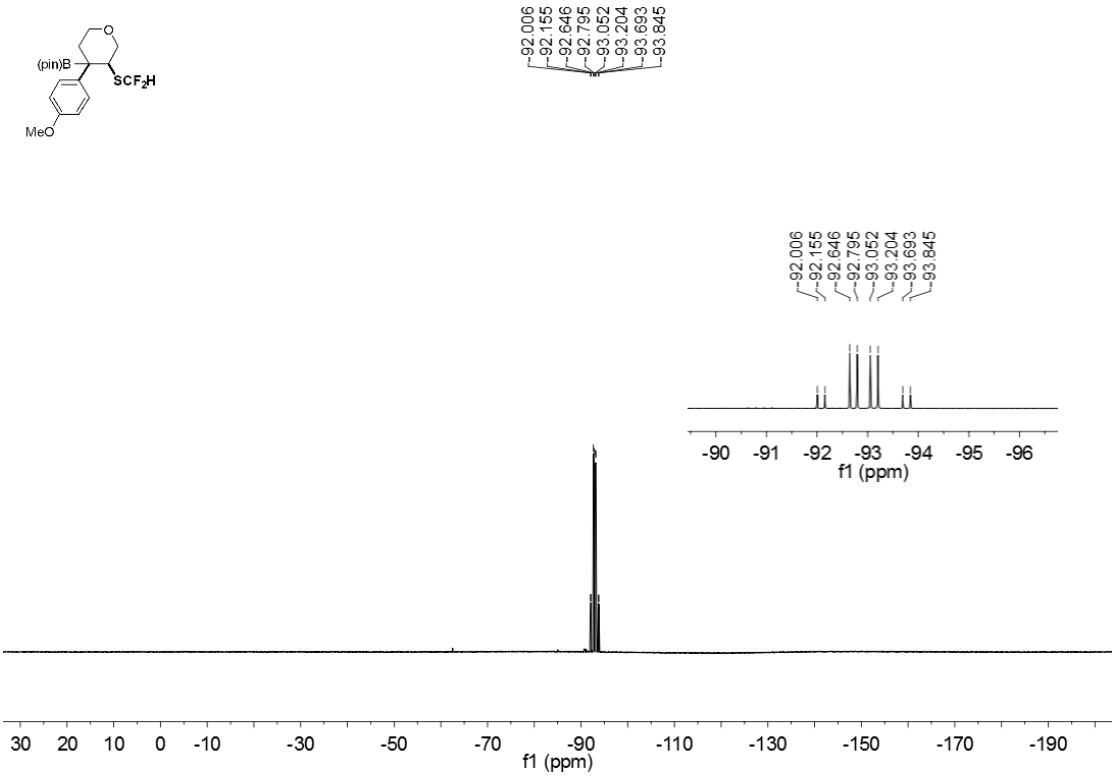
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-methoxyphenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3c



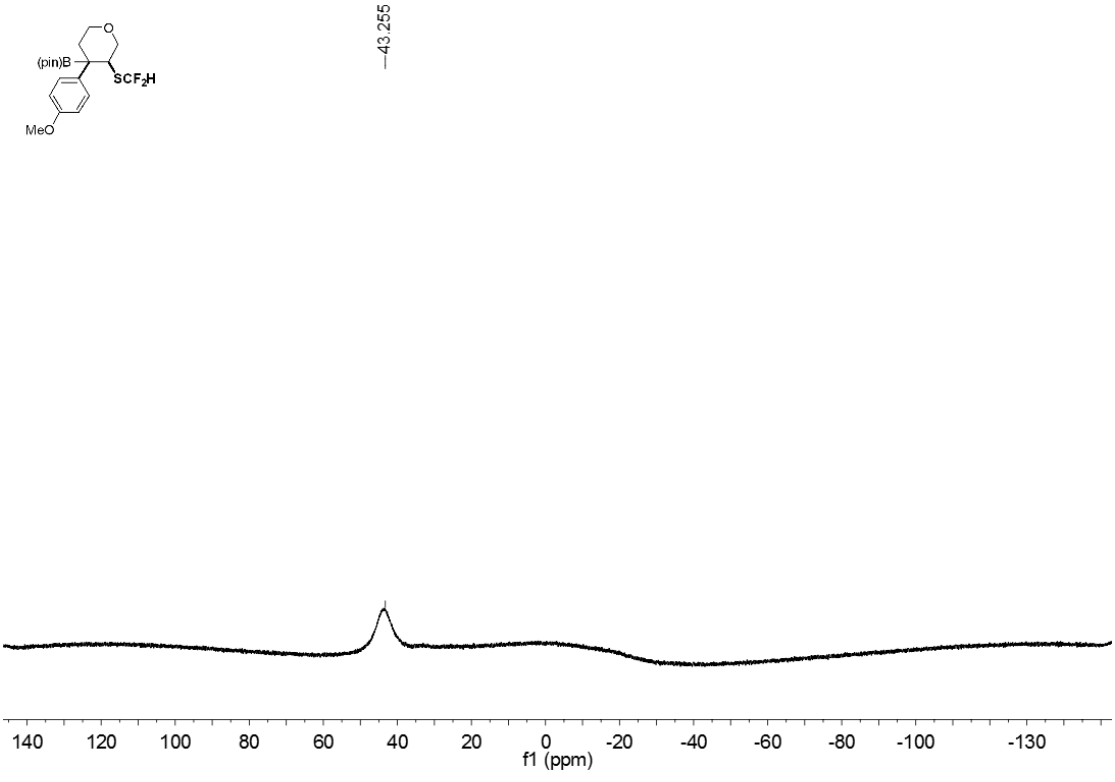
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-methoxyphenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3c



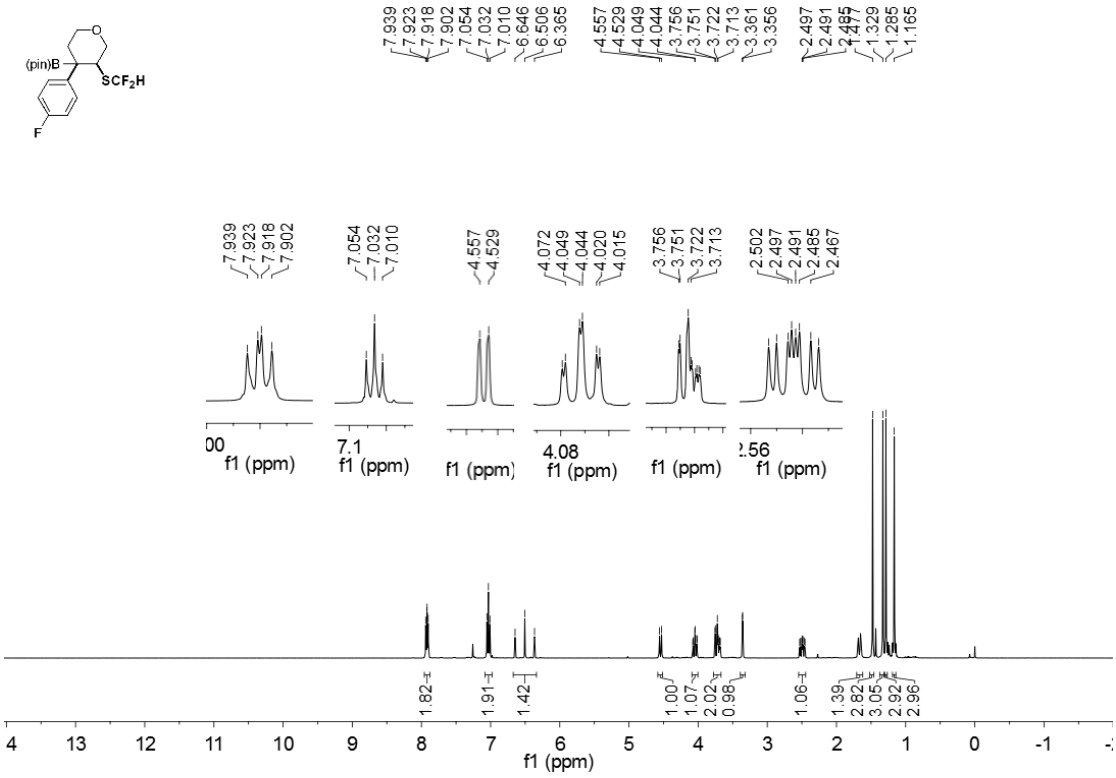
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-methoxyphenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3c



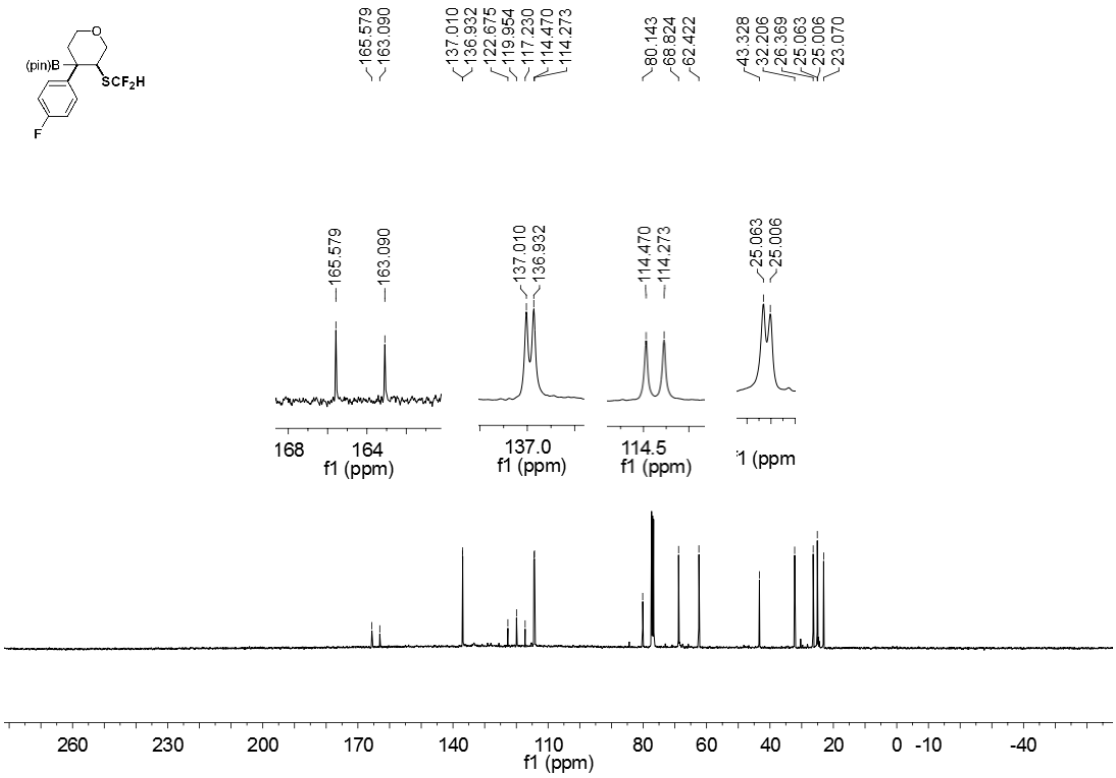
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-methoxyphenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3c



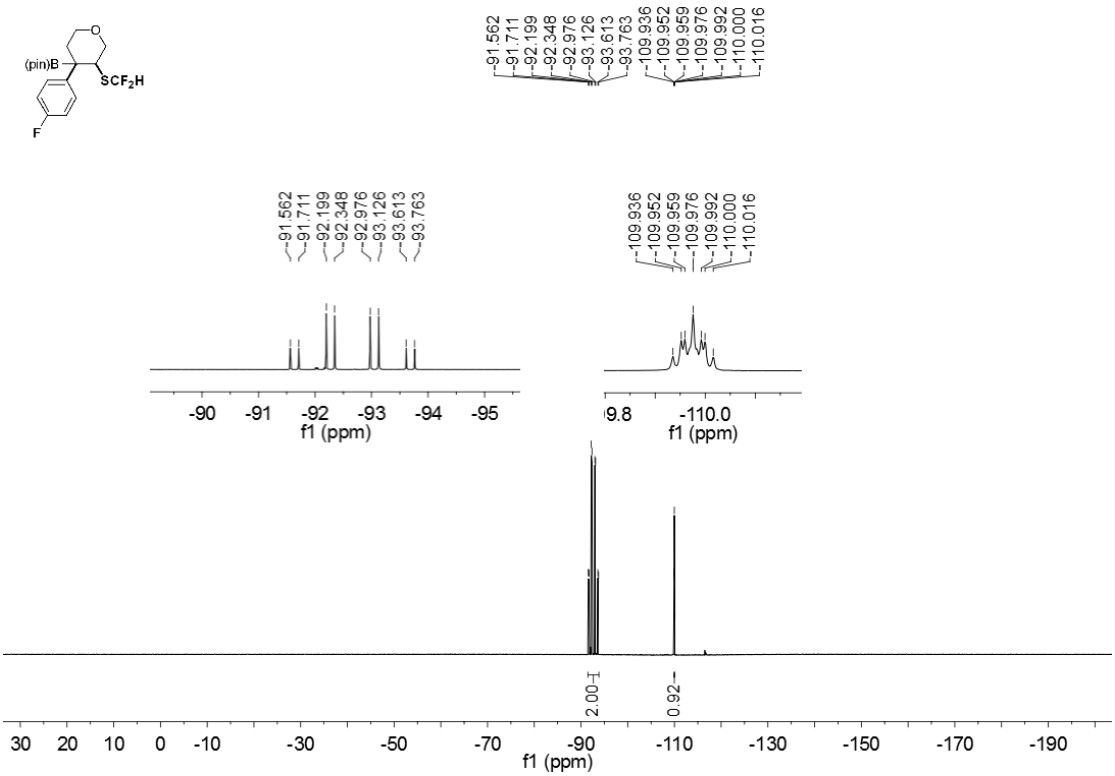
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-fluorophenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3d



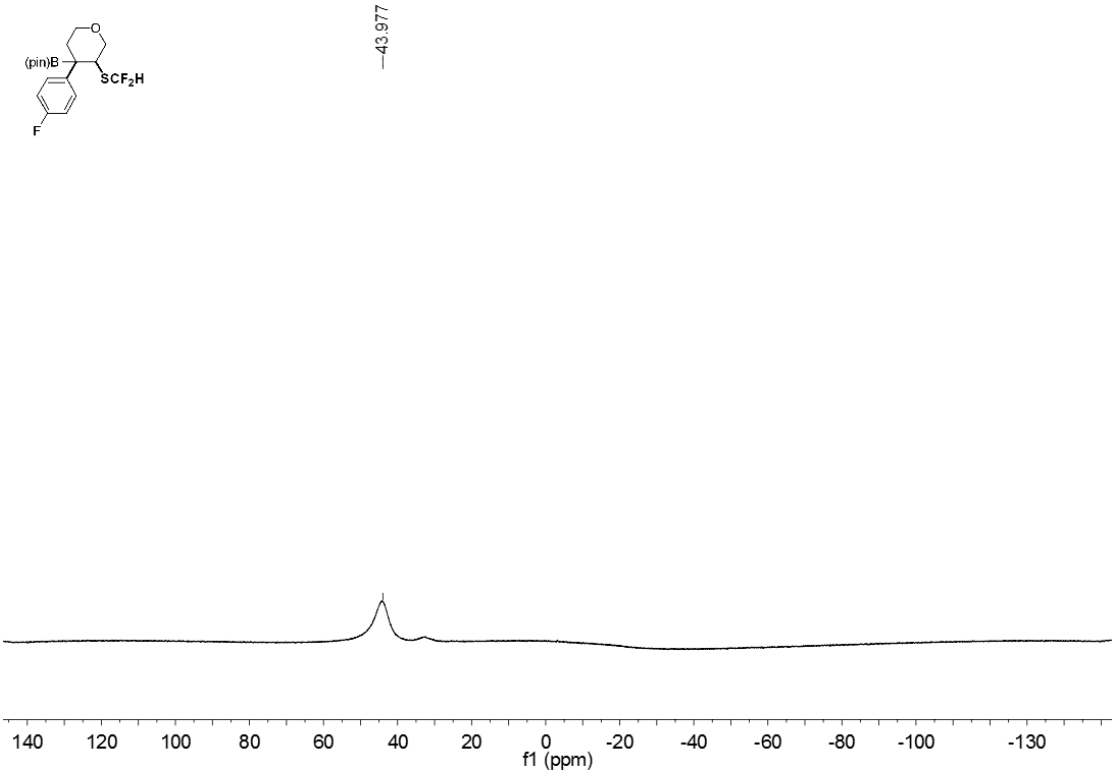
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-fluorophenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3d



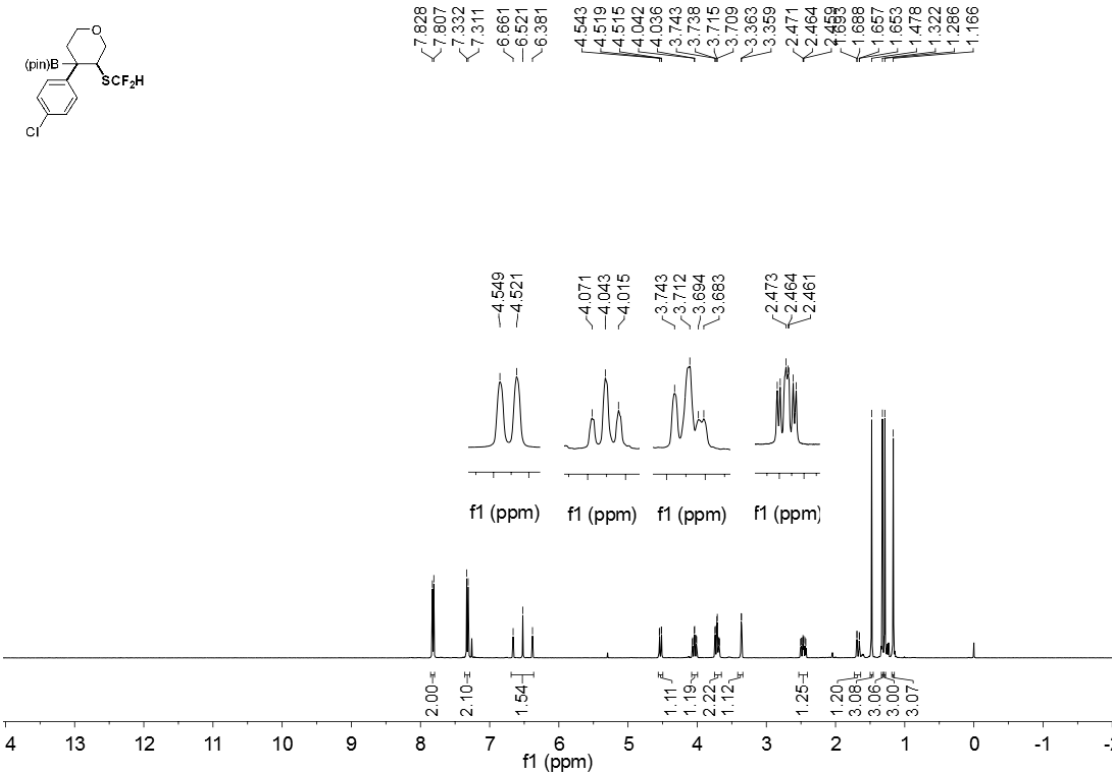
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-fluorophenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3d



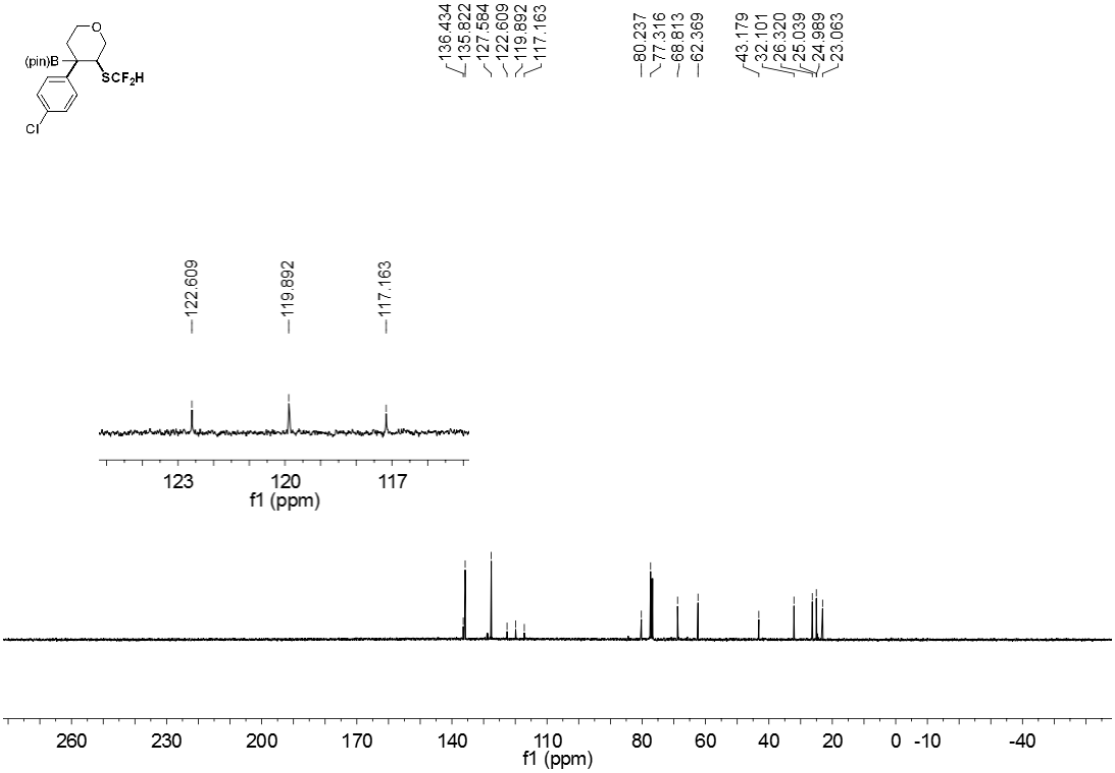
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-fluorophenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3d



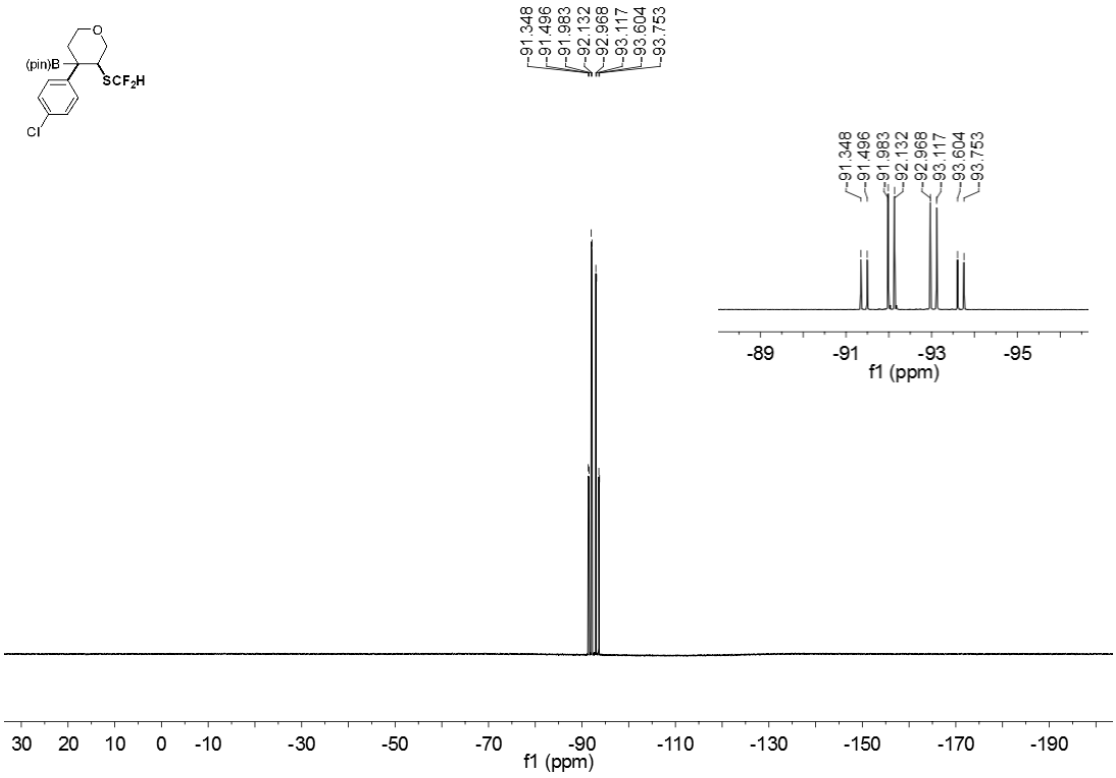
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(4-chlorophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3e



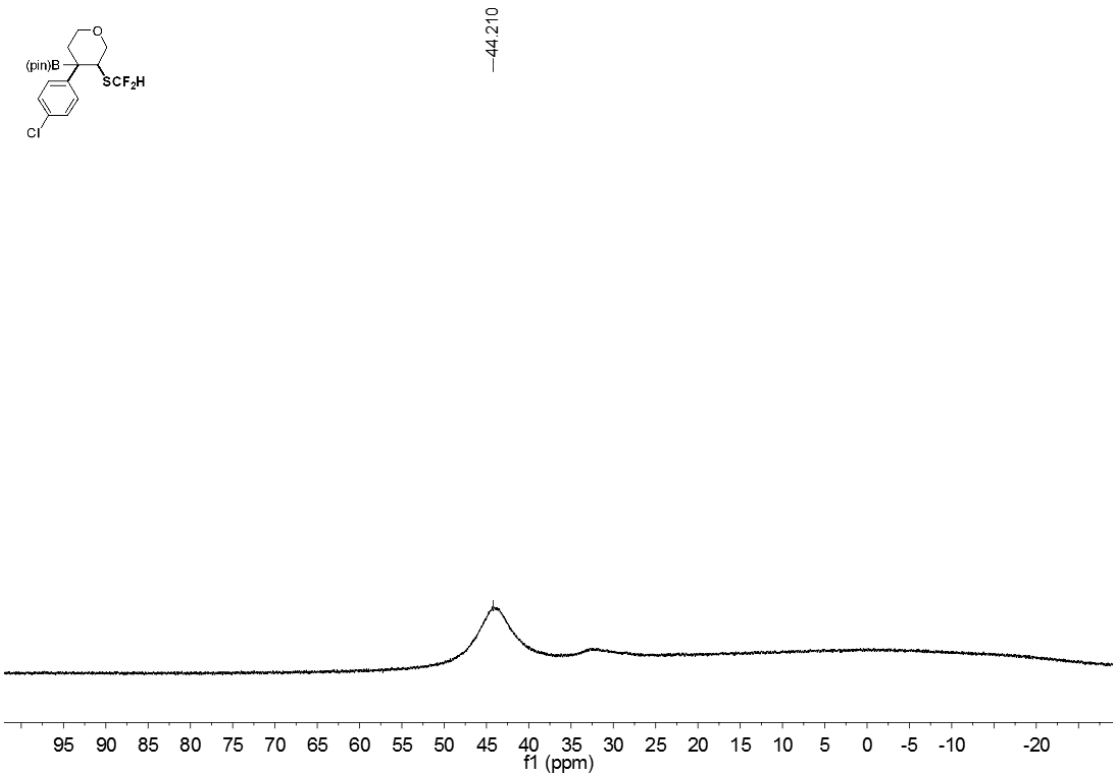
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(4-chlorophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3e



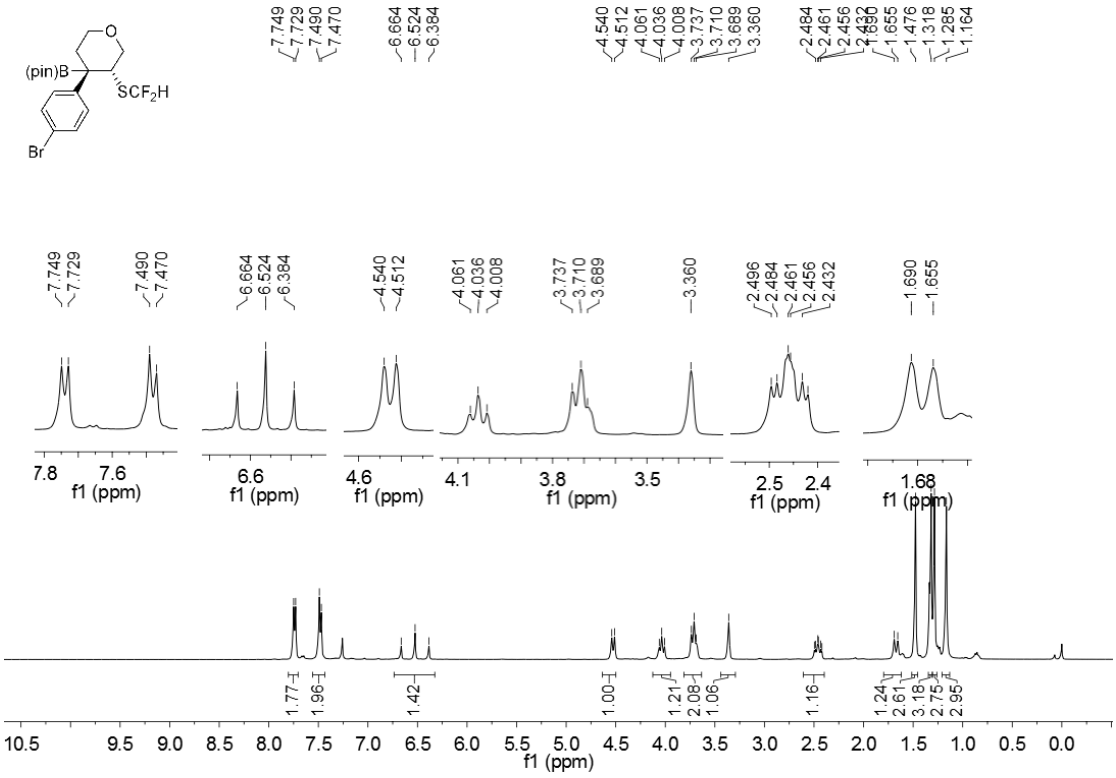
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(4-chlorophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3e



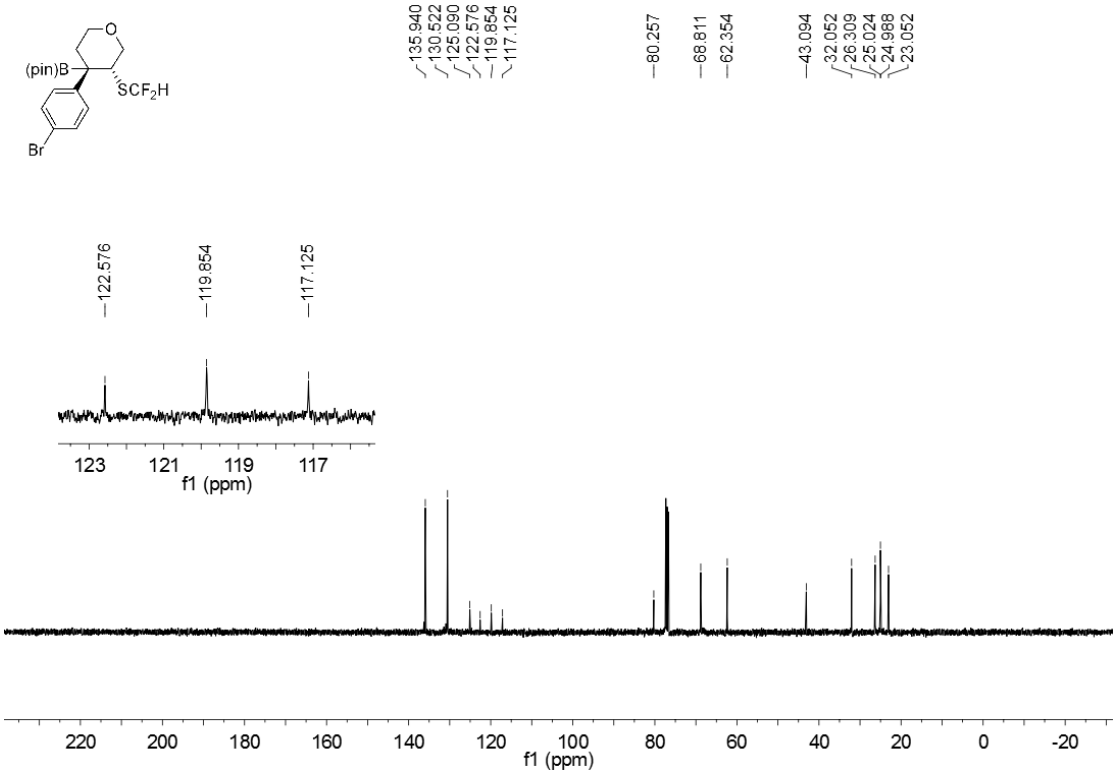
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-4-(4-chlorophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3e



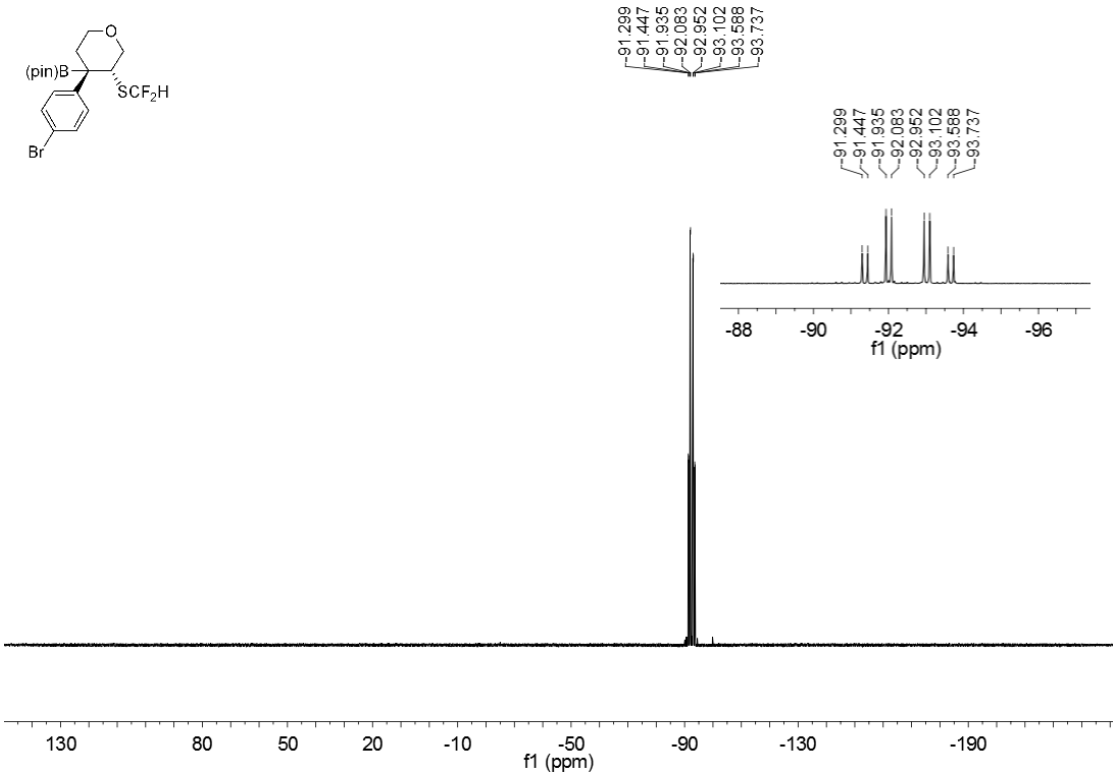
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(4-bromophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3f



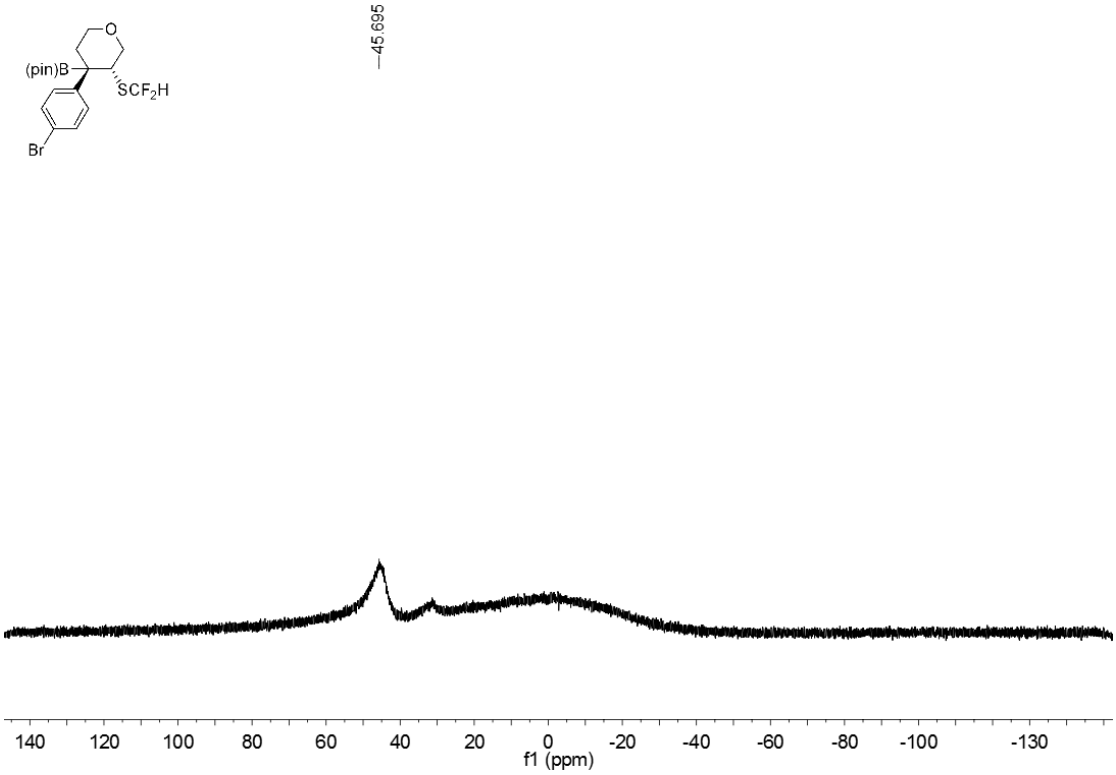
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(4-bromophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3f



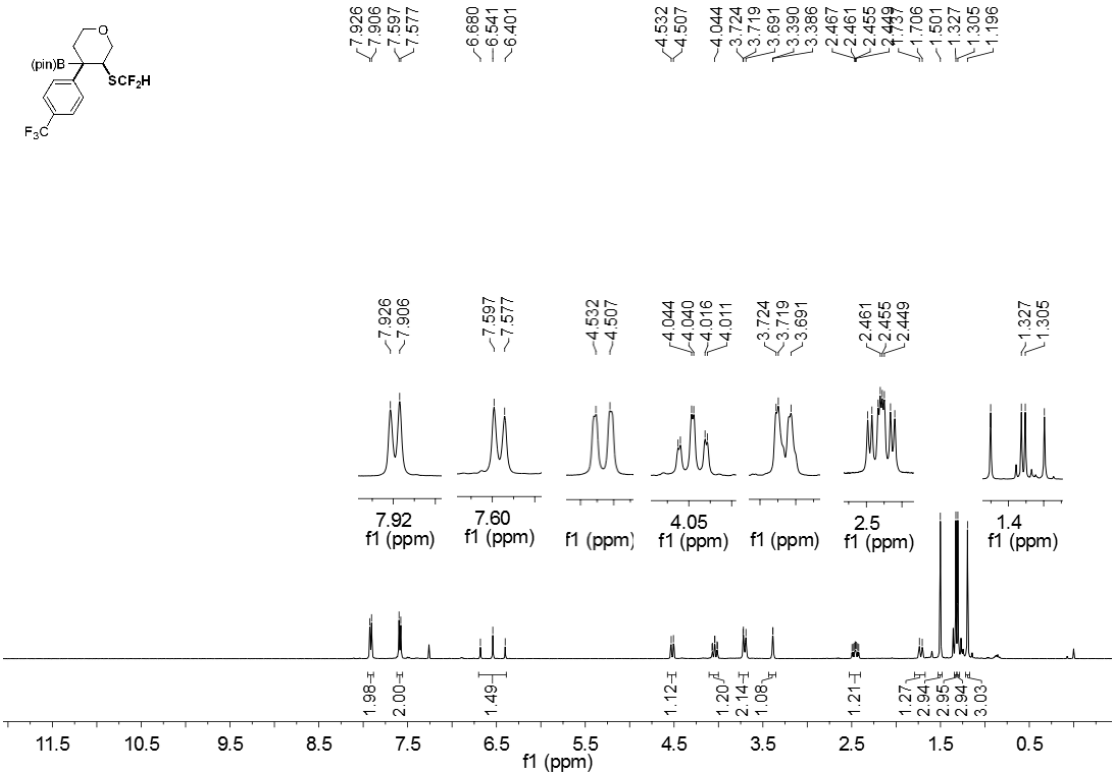
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(4-bromophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3f



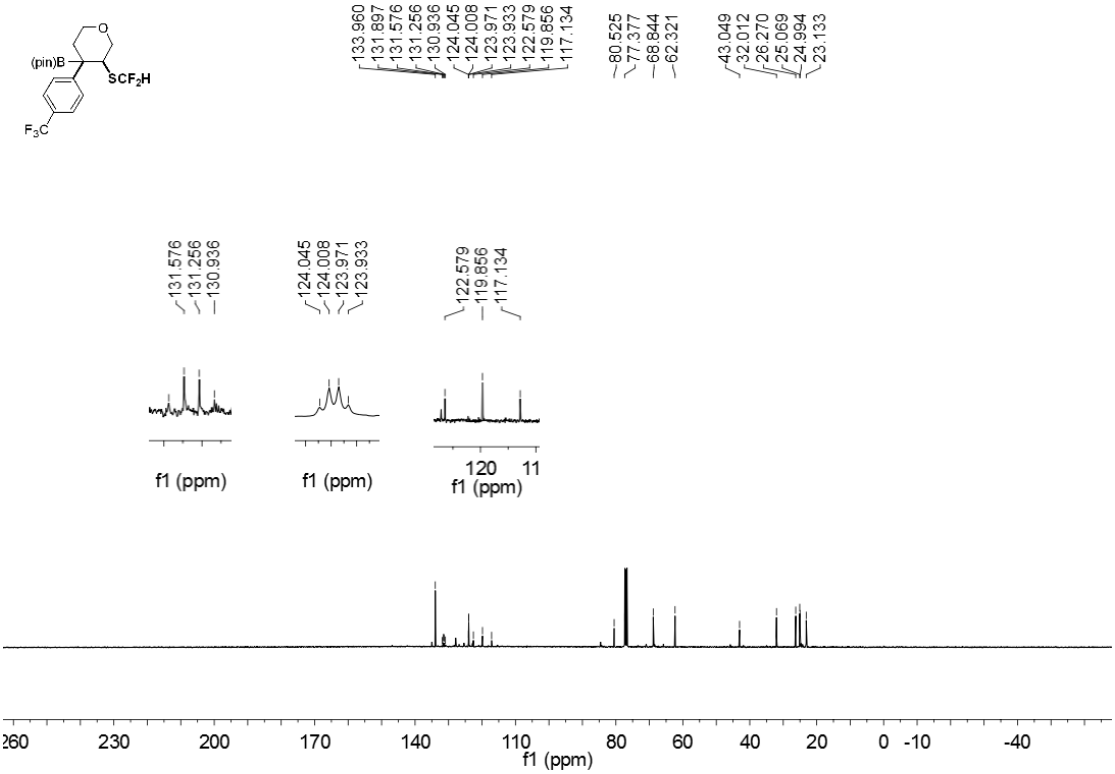
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-4-(4-bromophenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3f



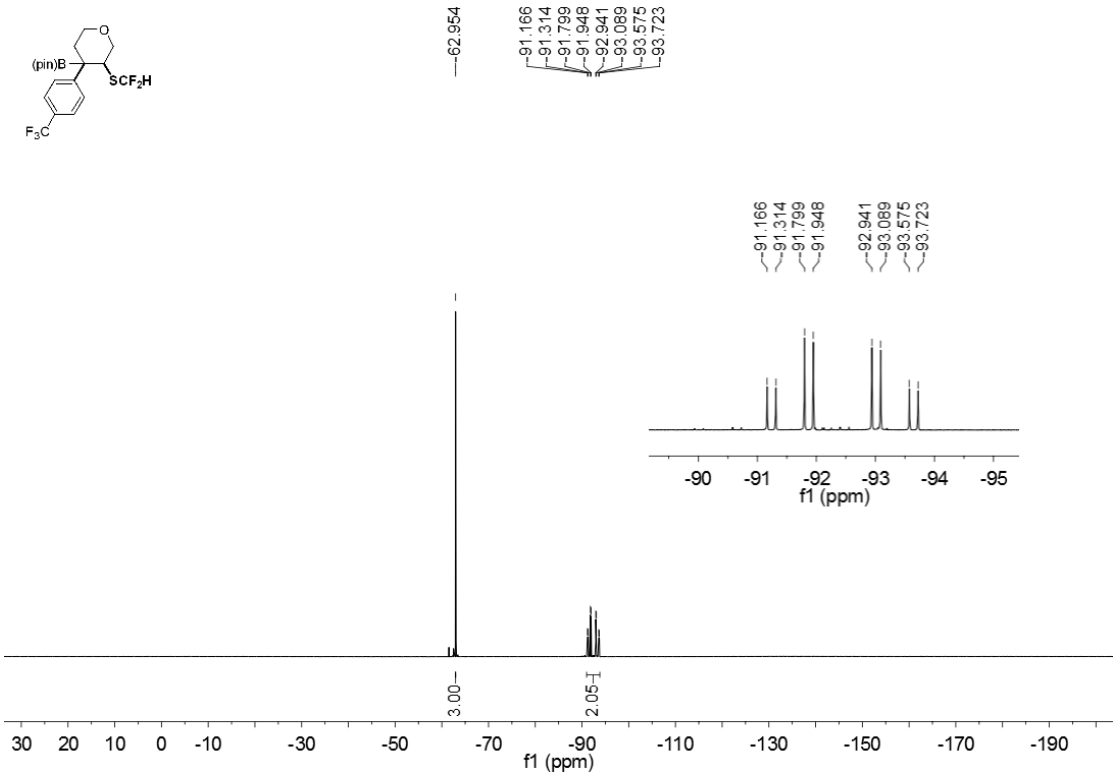
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-(trifluoromethyl)phenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3g



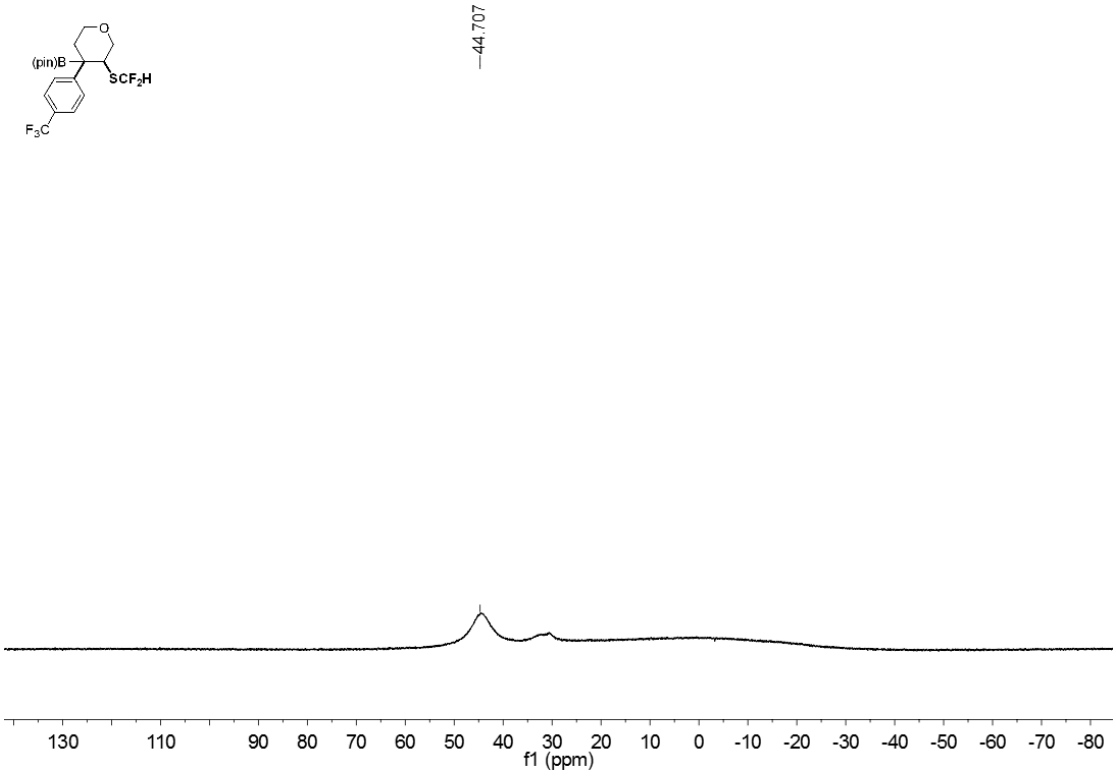
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-(trifluoromethyl)phenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3g



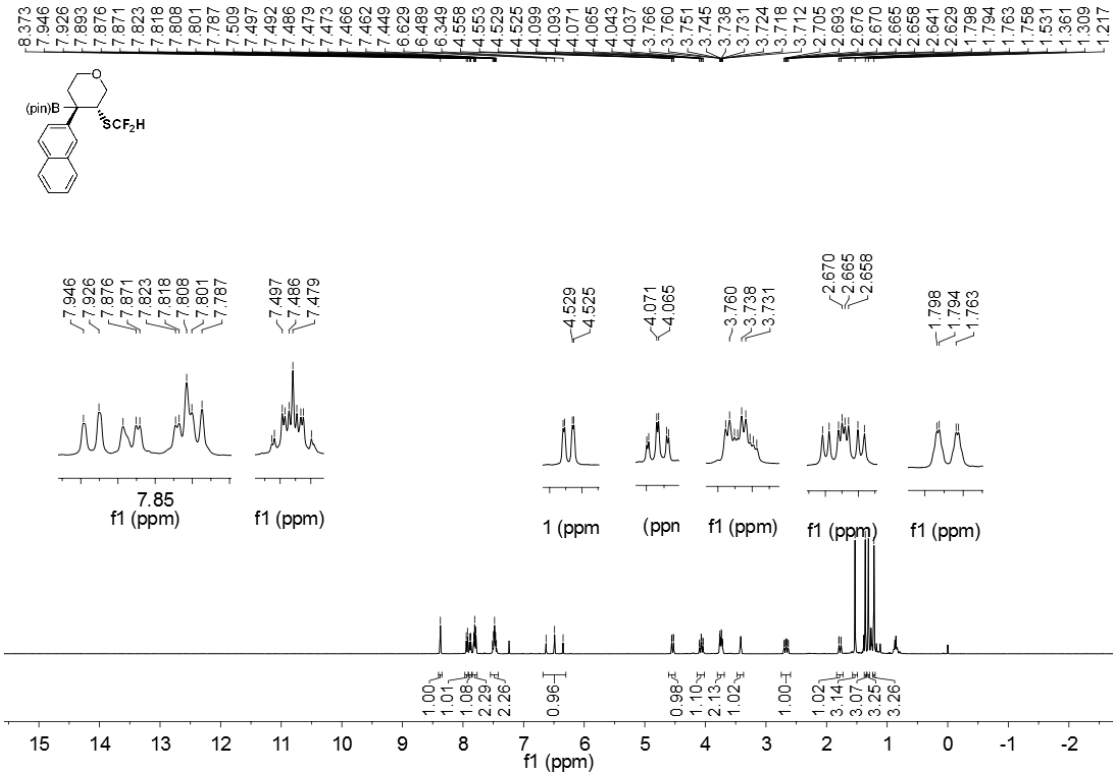
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-(trifluoromethyl)phenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3g



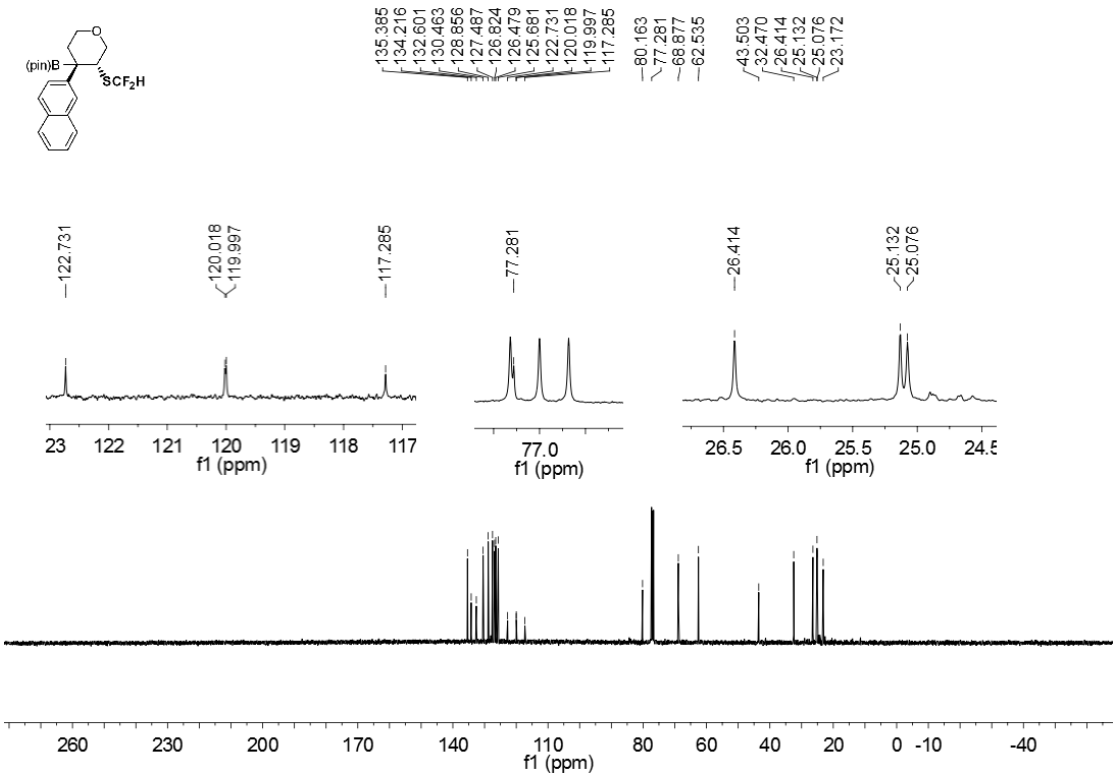
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4-(trifluoromethyl)phenyl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3g



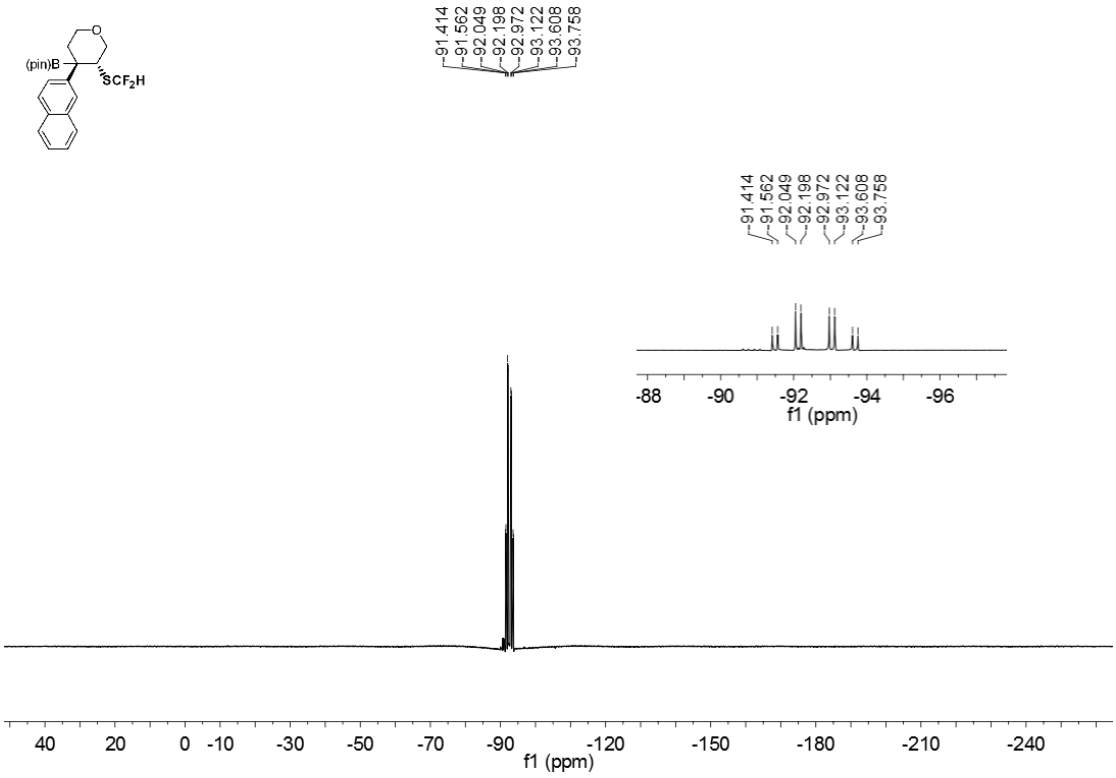
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(naphthalen-2-yl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3h



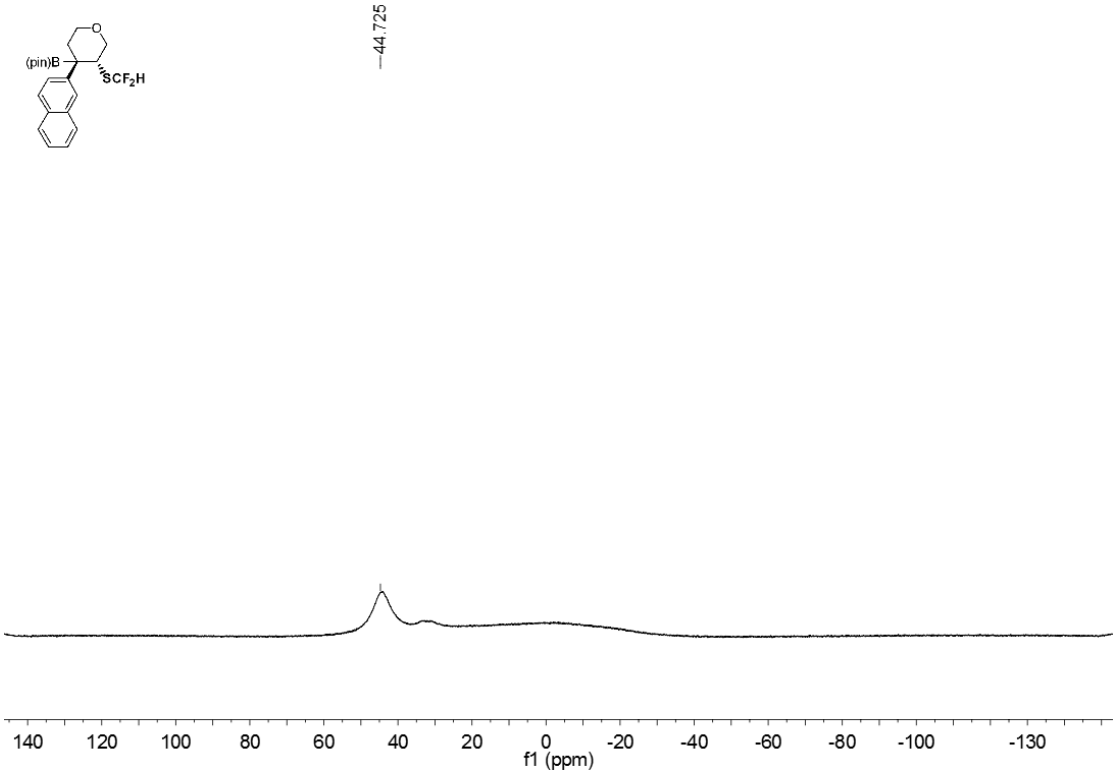
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(naphthalen-2-yl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3h



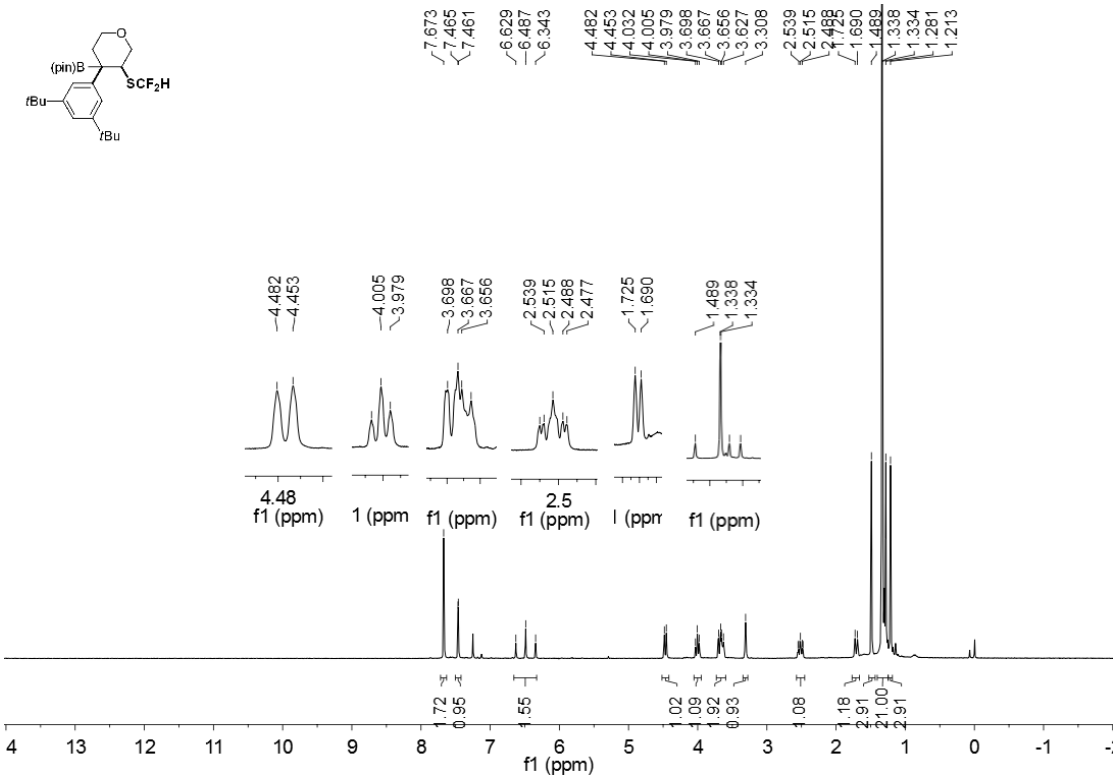
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(naphthalen-2-yl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3h



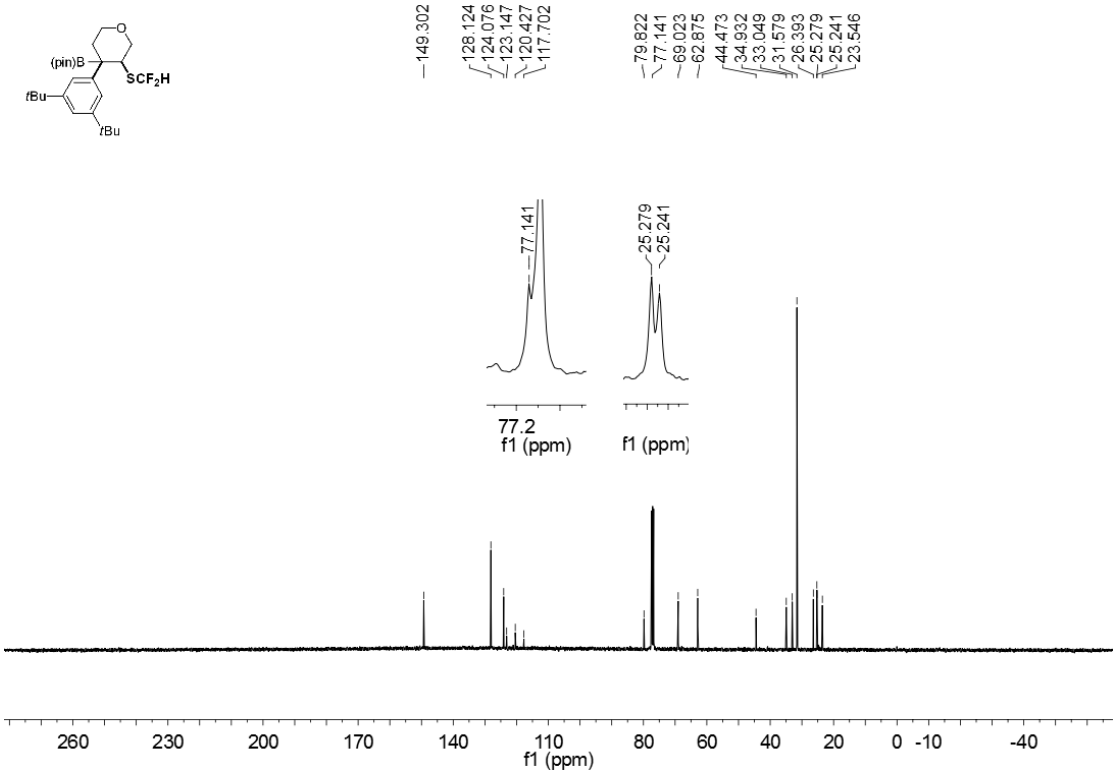
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-(naphthalen-2-yl)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3h



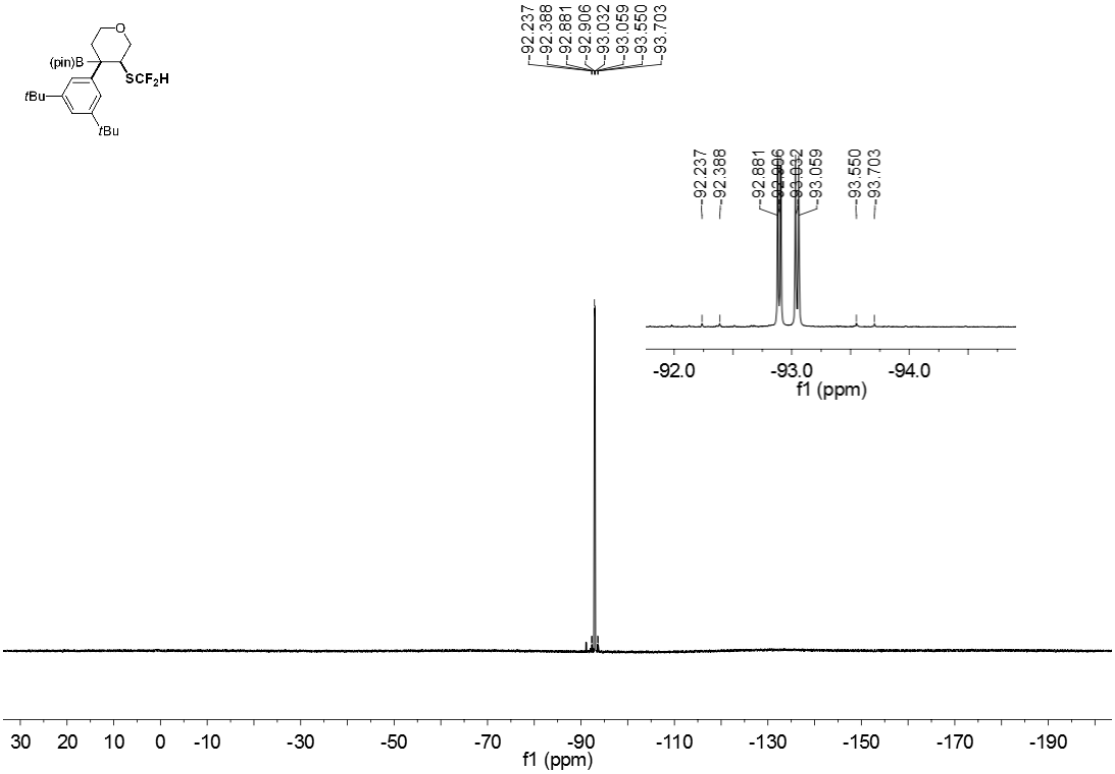
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(3,5-di-tert-butylphenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3i



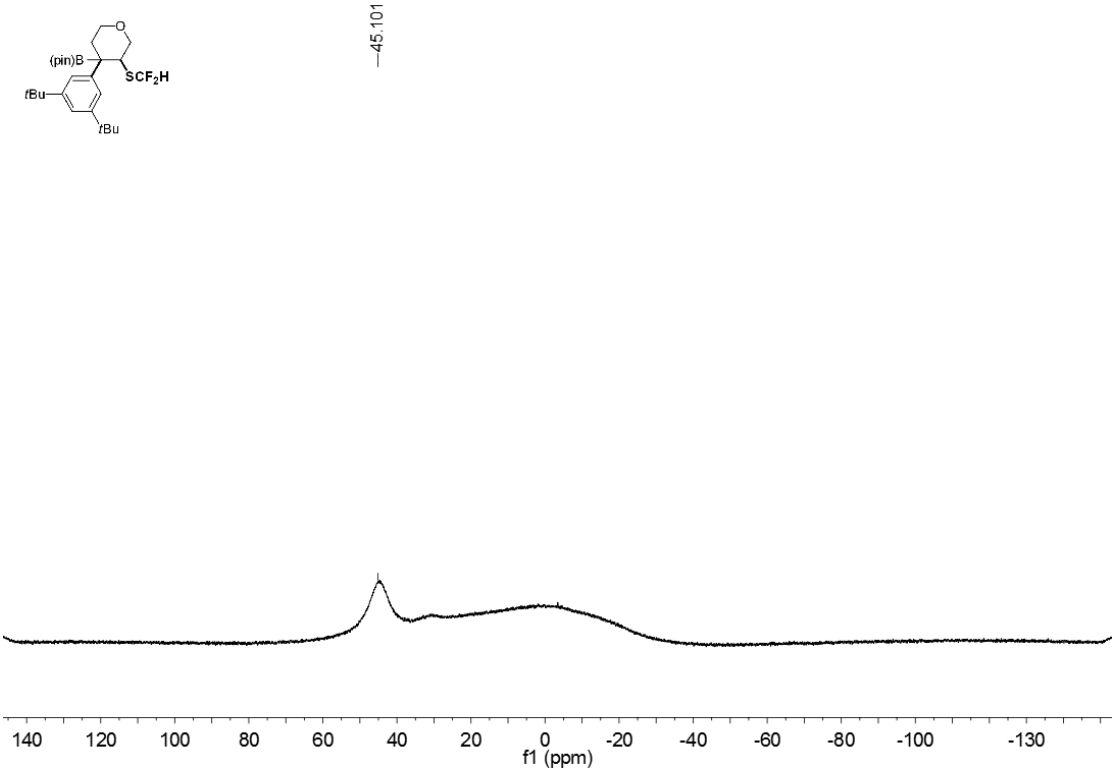
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(3,5-di-tert-butylphenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3i



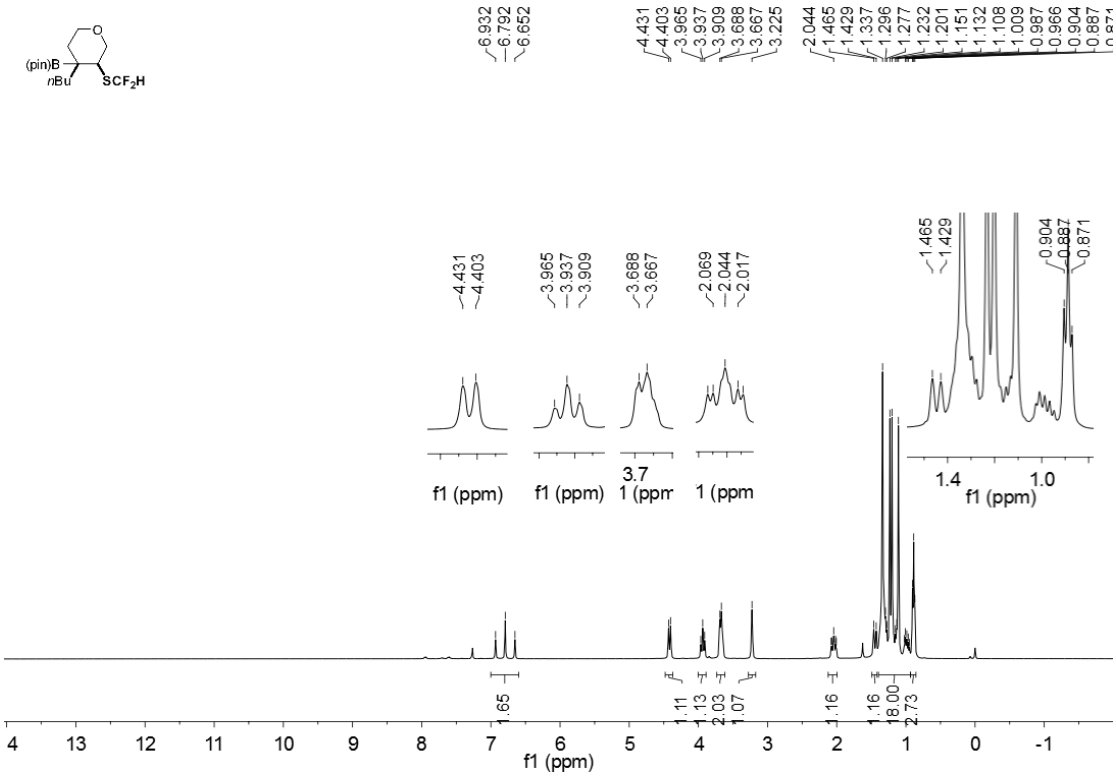
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(3,5-di-tert-butylphenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3i



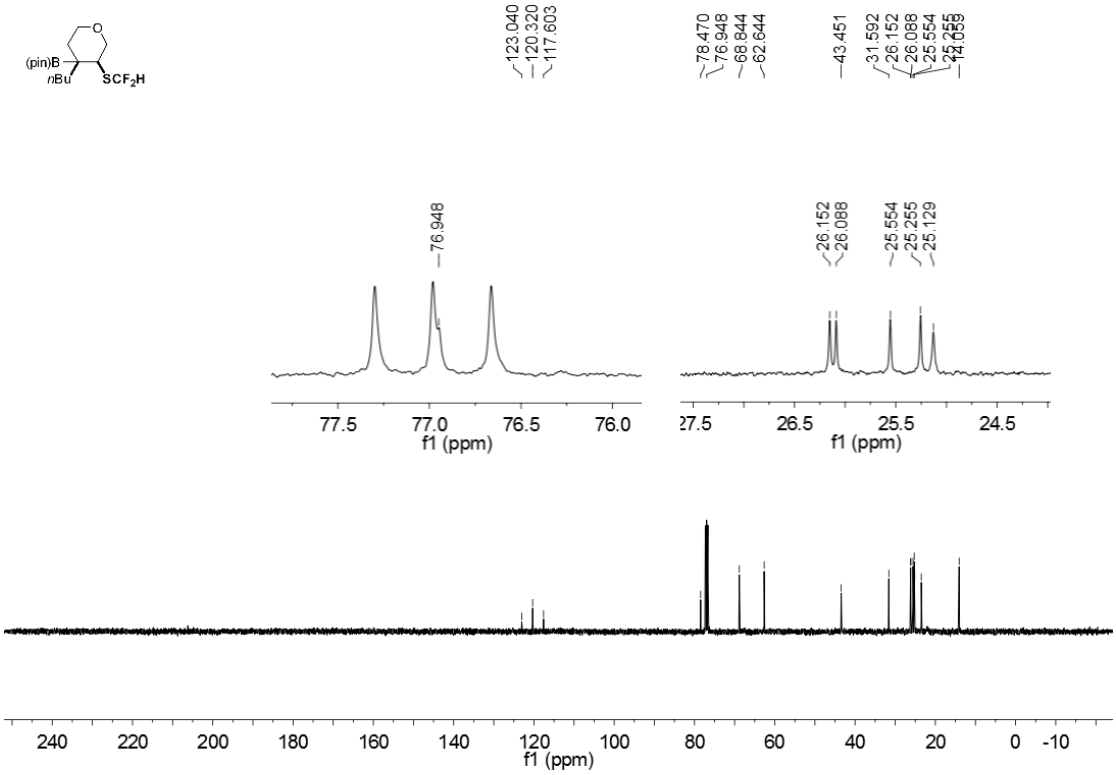
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-4-(3,5-di-tert-butylphenyl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3i



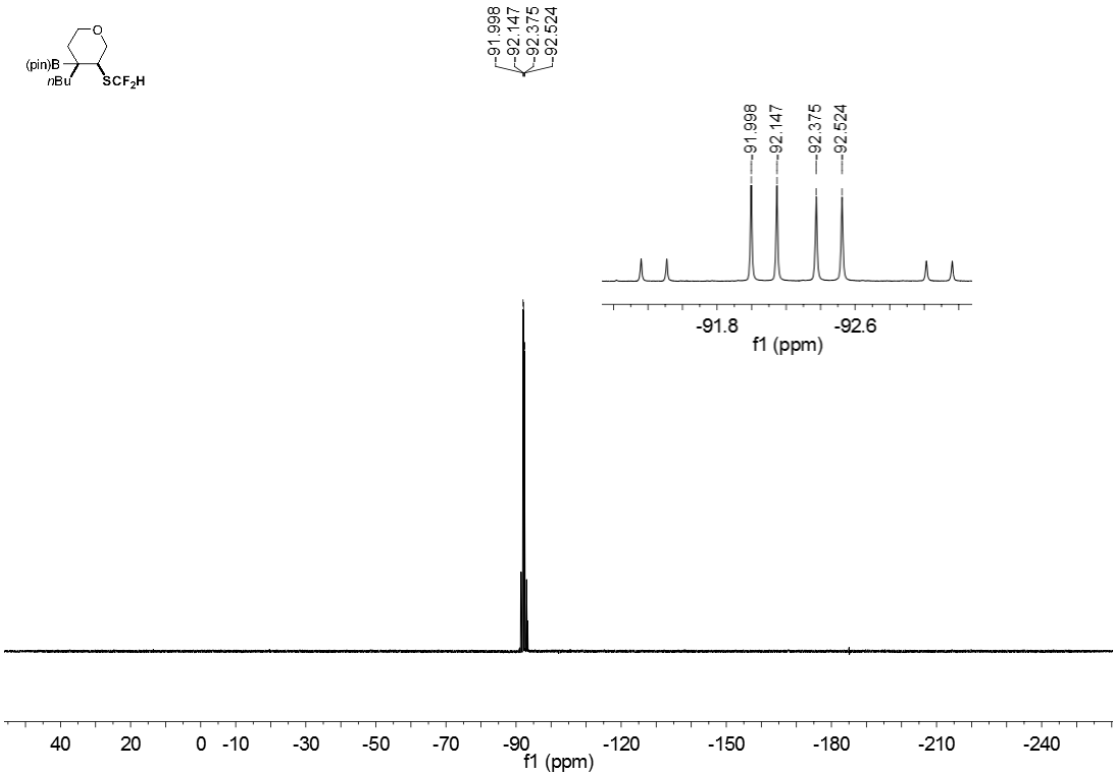
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*S*)-4-butyl-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3j



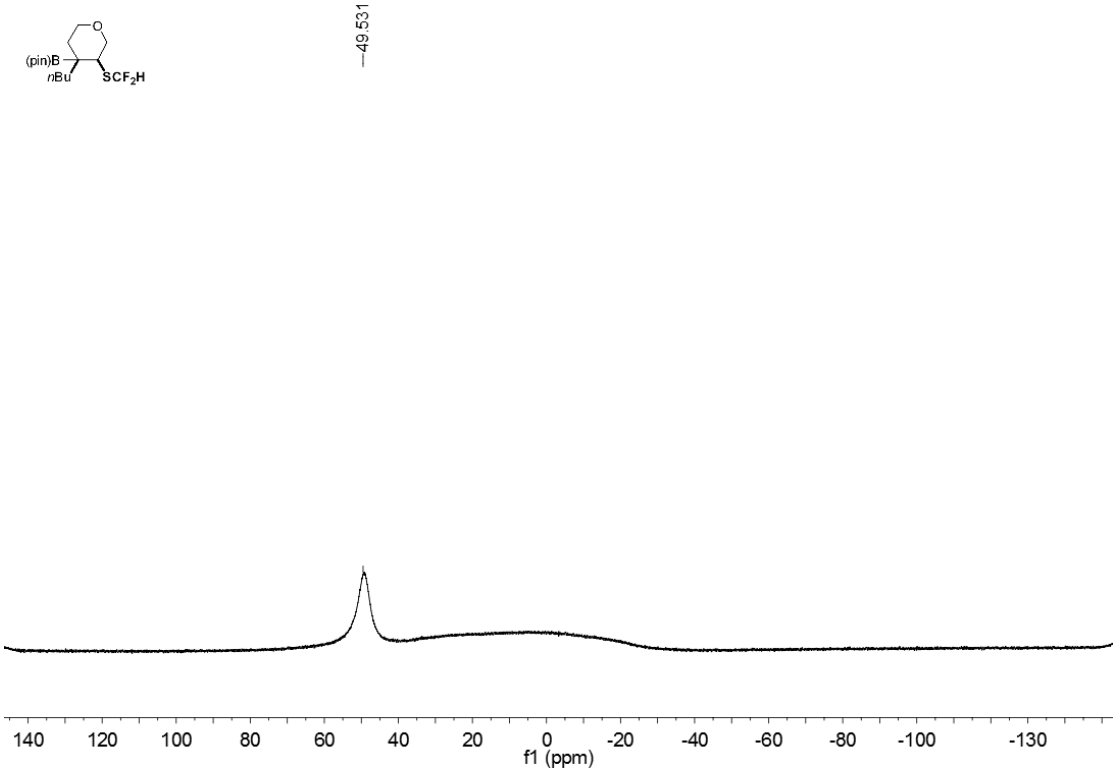
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*S*)-4-butyl-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3j



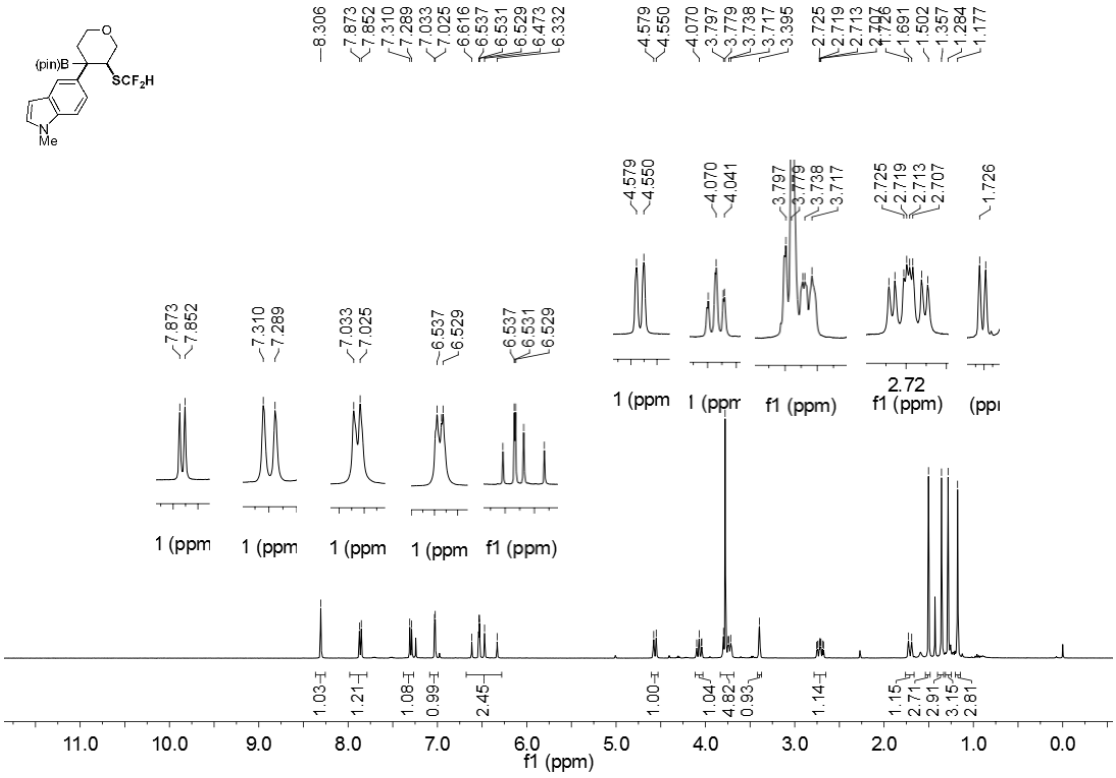
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*S*)-4-butyl-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3j



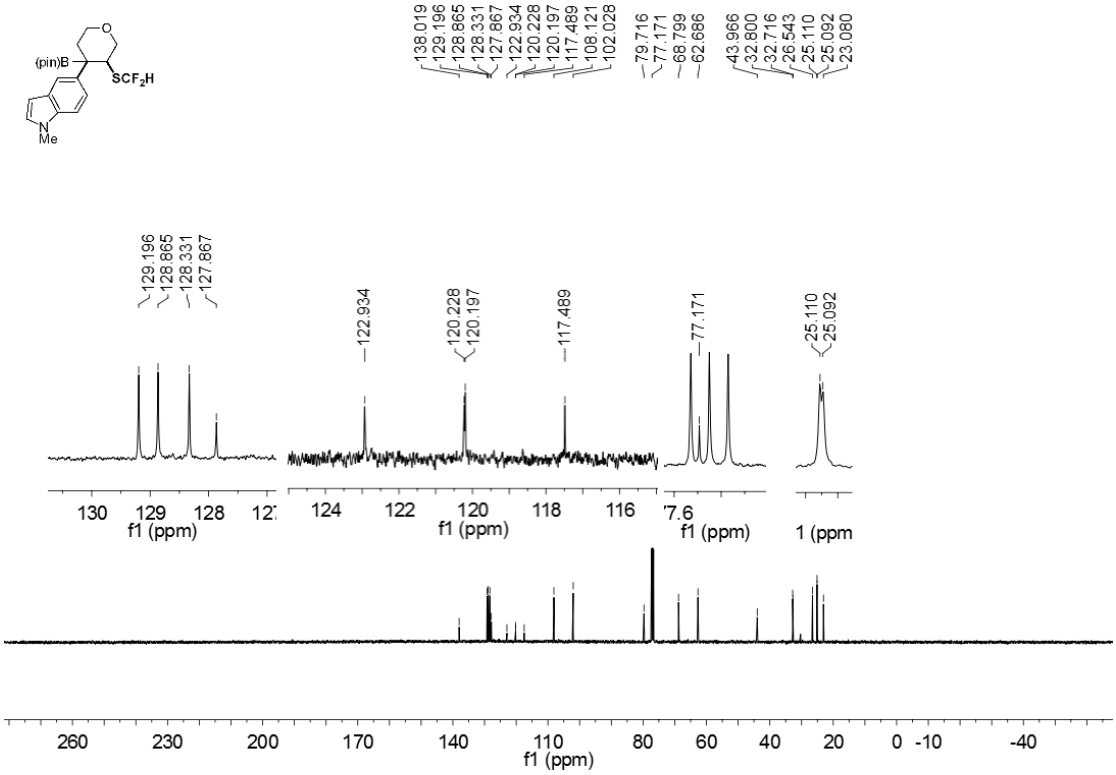
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*S*)-4-butyl-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3j



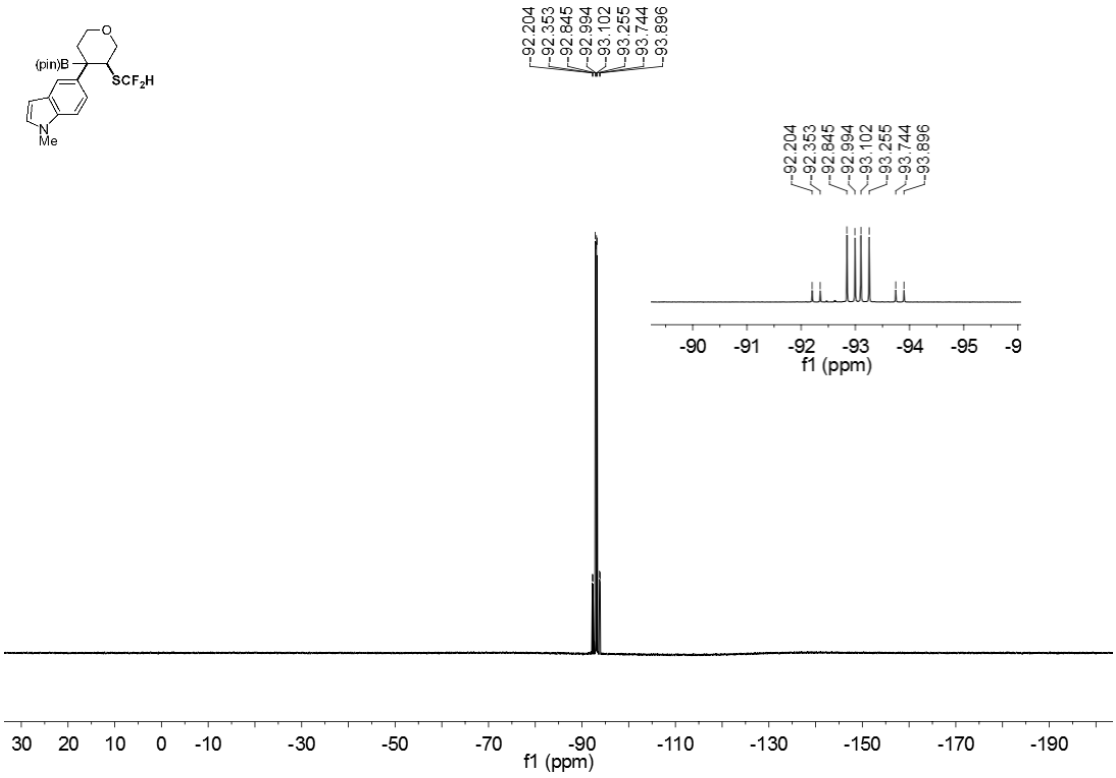
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-5-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)-1-methyl-1H-indole 3k



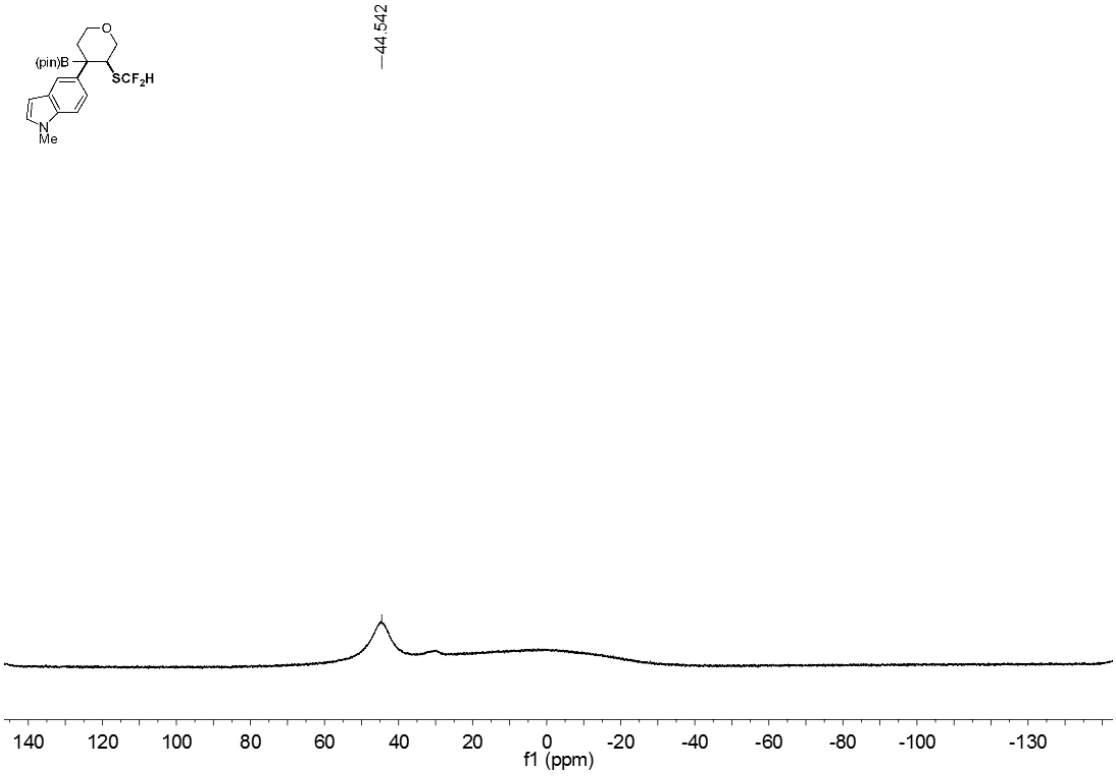
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-5-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)-1-methyl-1H-indole 3k



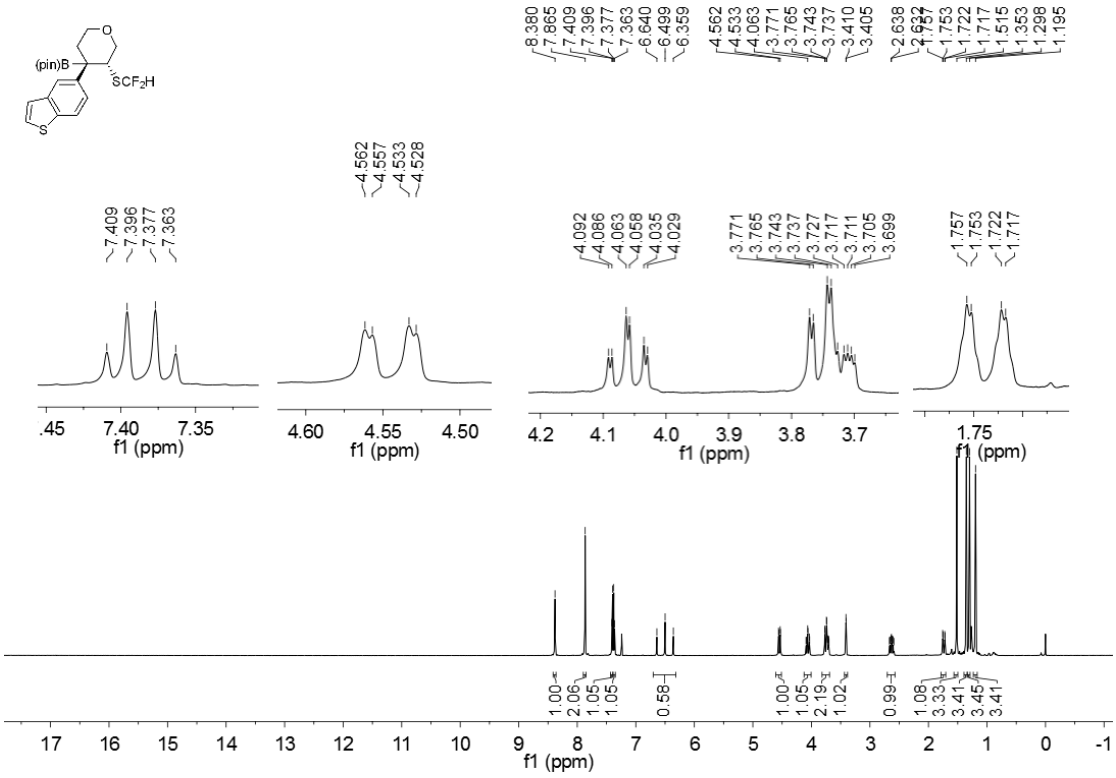
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-5-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)-1-methyl-1H-indole 3k



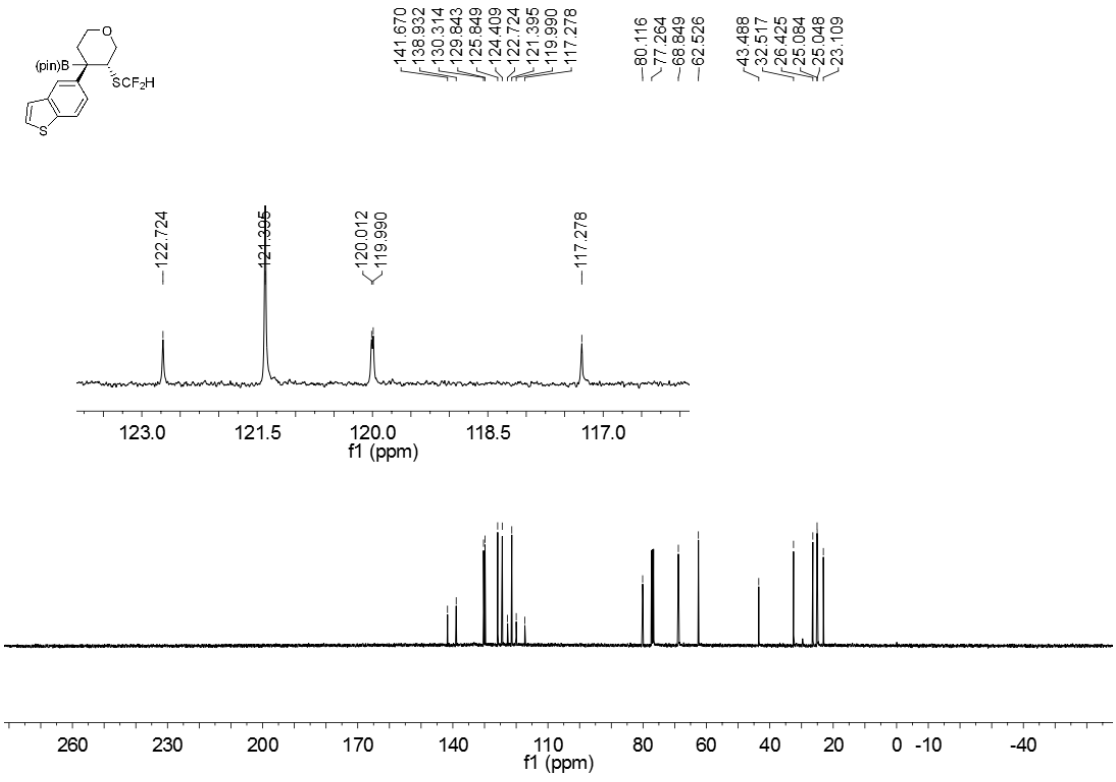
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-5-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)-1-methyl-1H-indole 3k



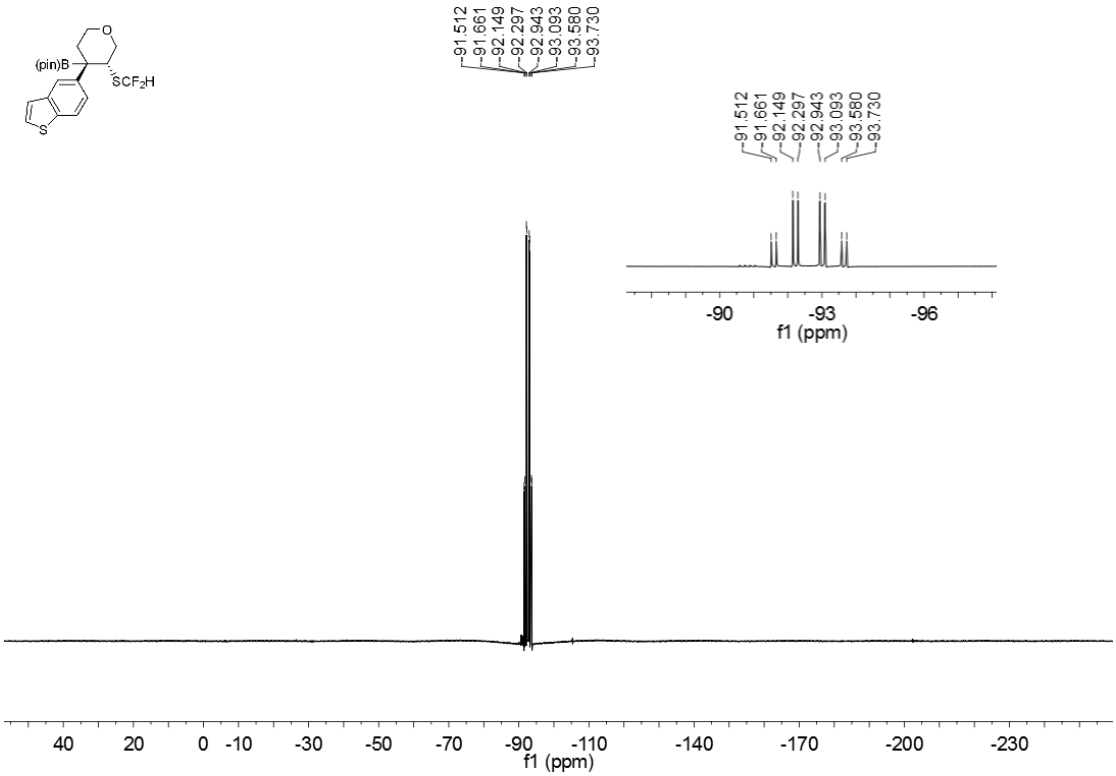
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(benzo[b]thiophen-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3l



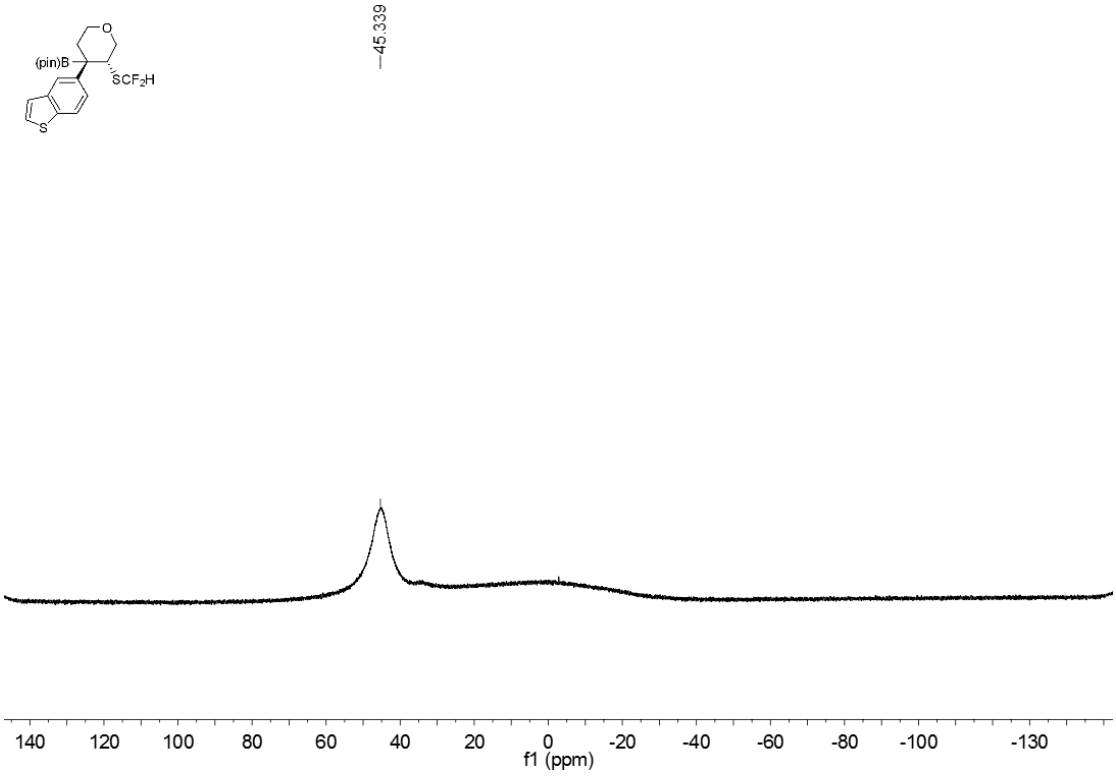
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(benzo[b]thiophen-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3l



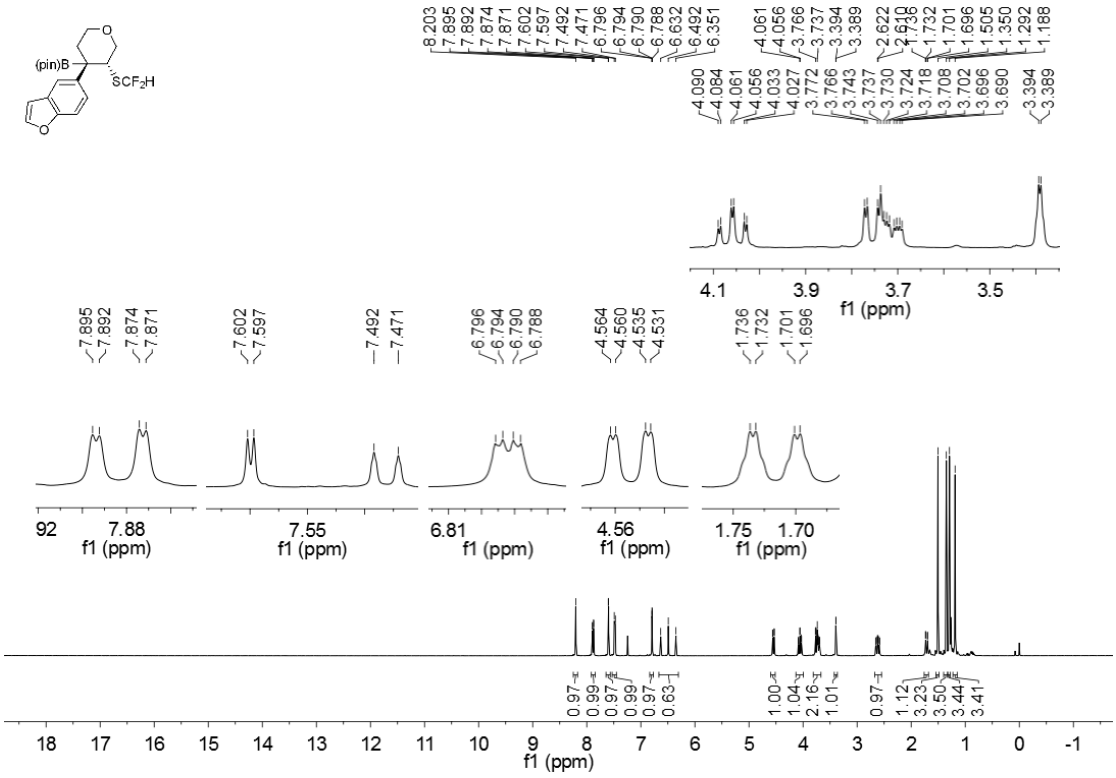
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(benzo[b]thiophen-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3l



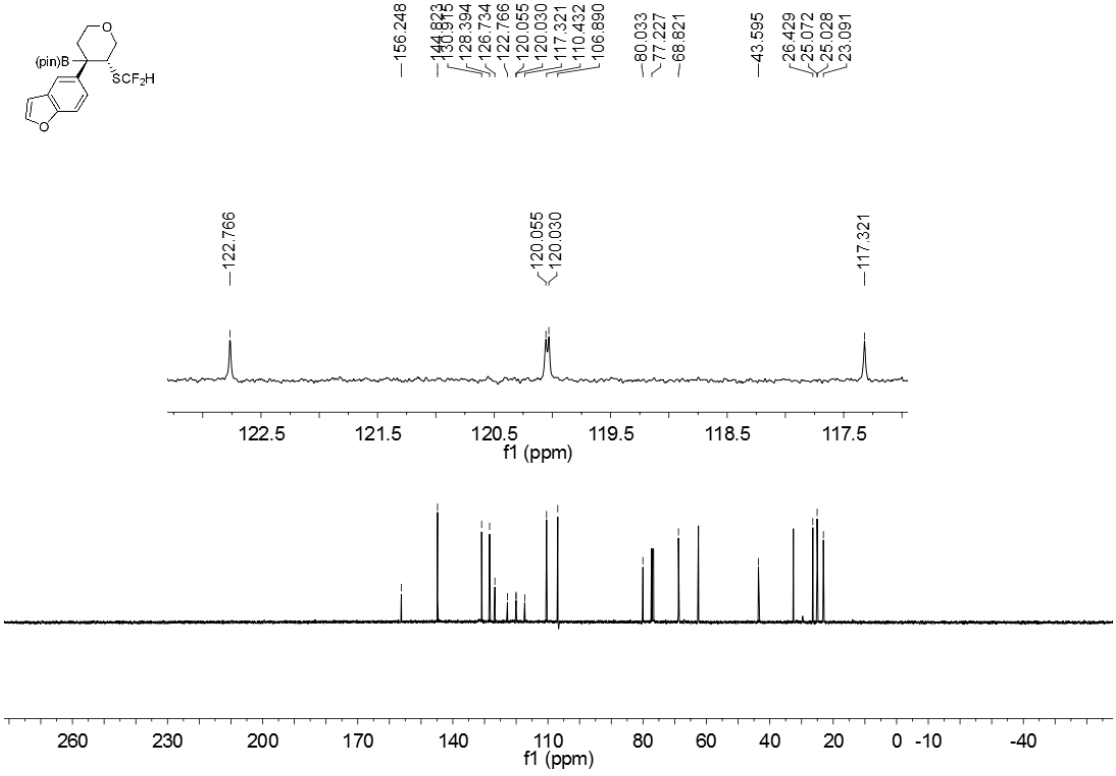
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-4-(benzo[b]thiophen-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3l



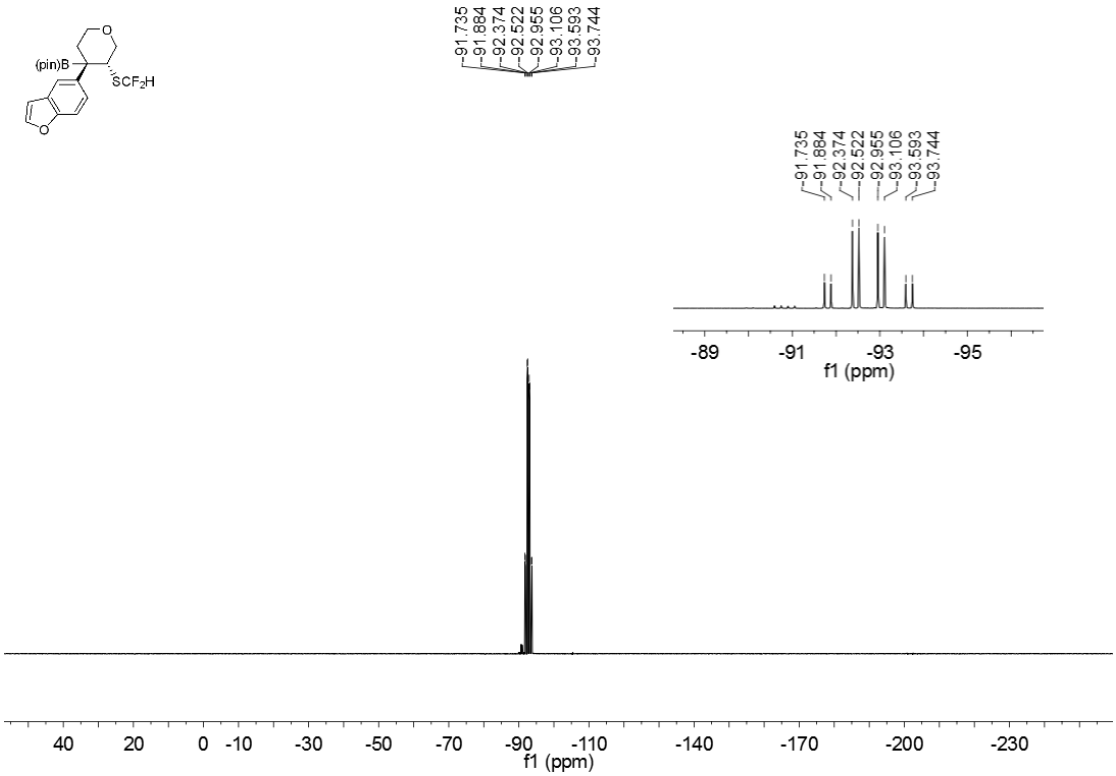
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(benzofuran-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3m



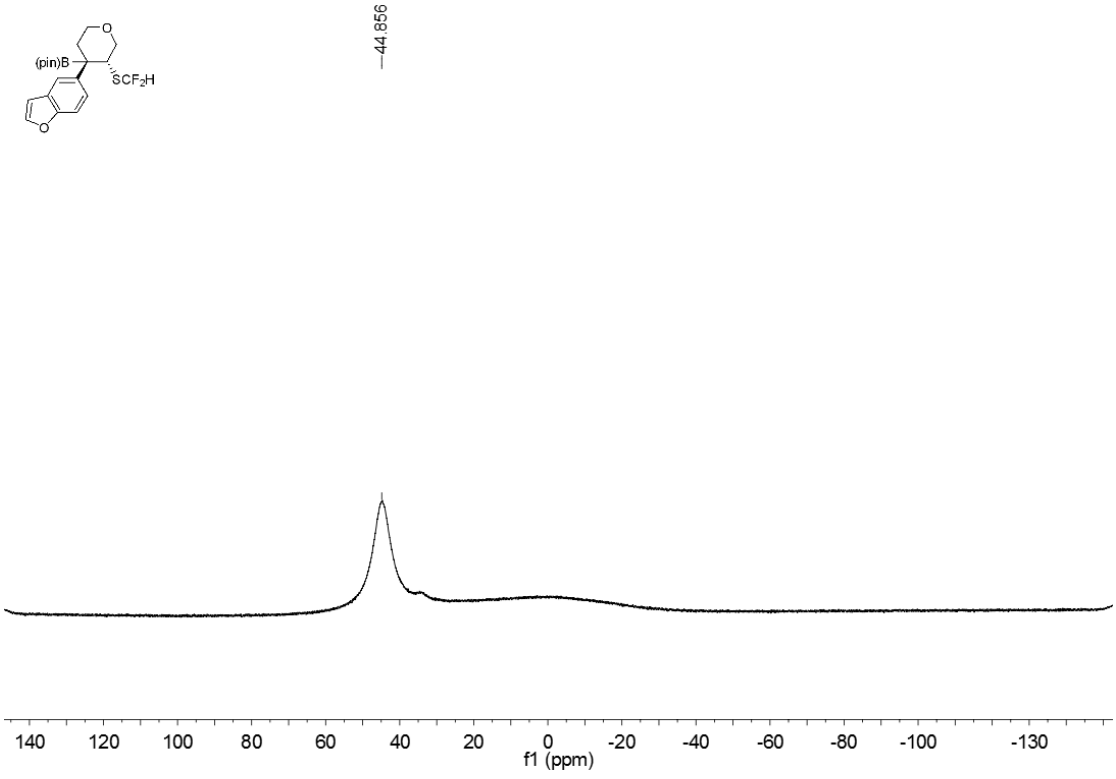
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(benzofuran-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3m



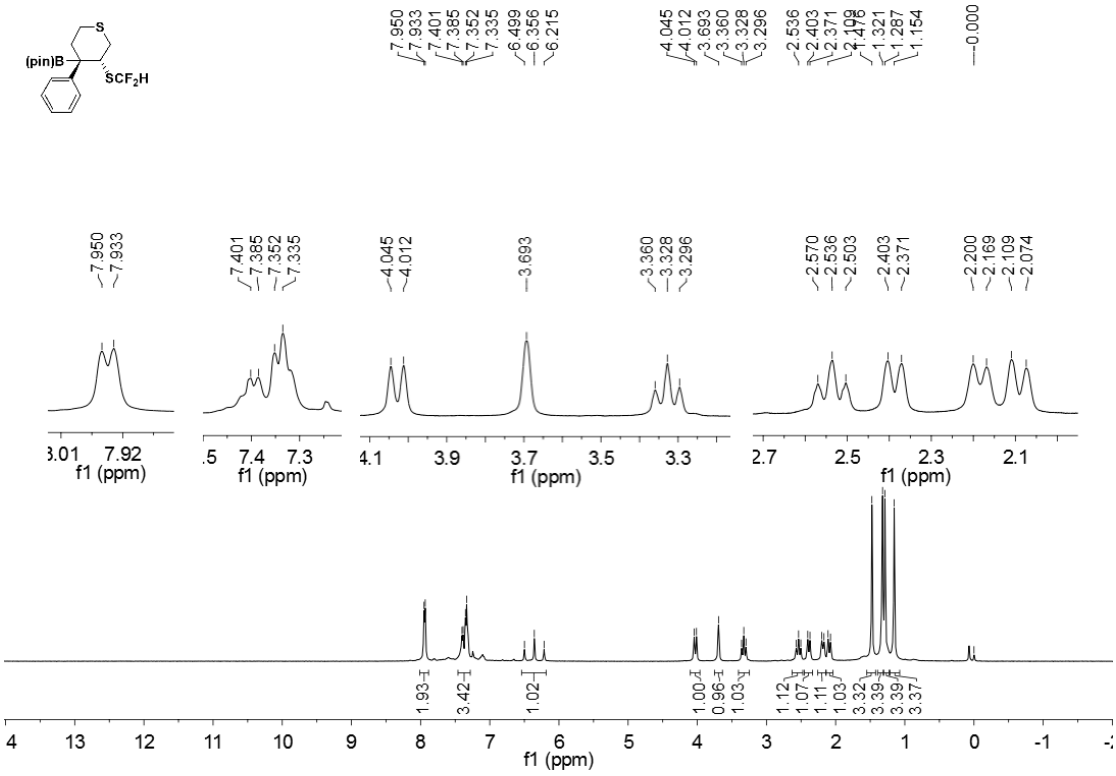
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-4-(benzofuran-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3m



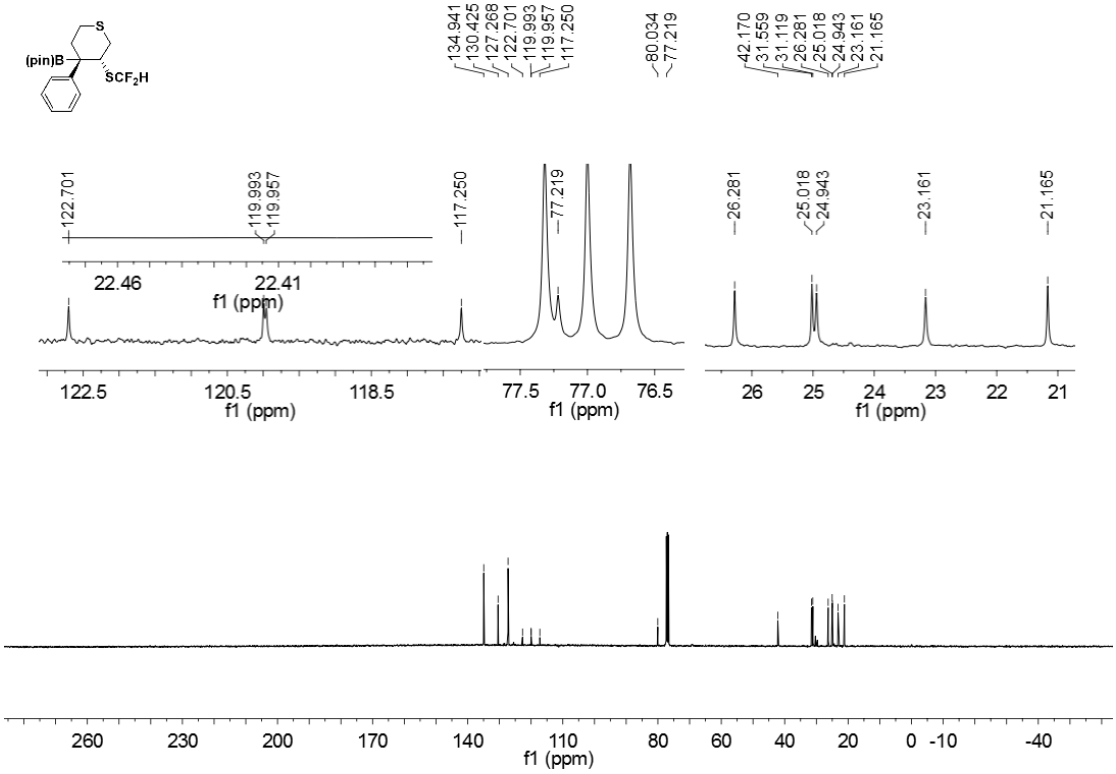
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-4-(benzofuran-5-yl)-3-(difluoromethylthio)tetrahydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3m



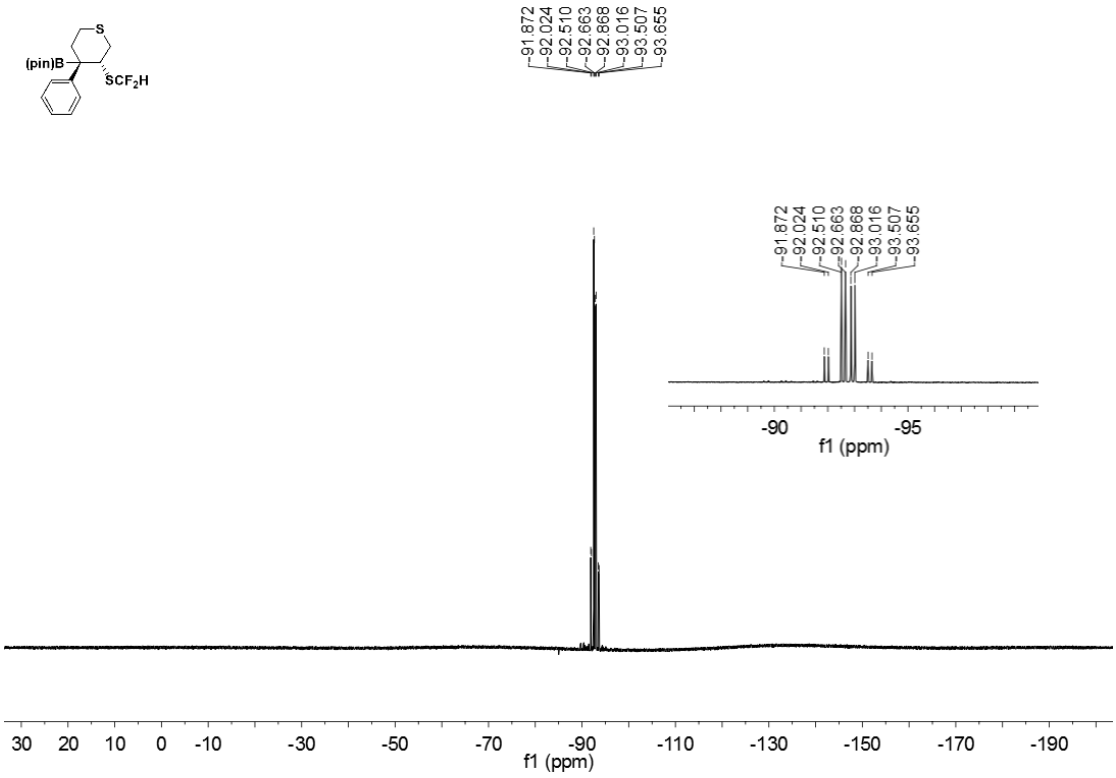
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-thiopyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3n



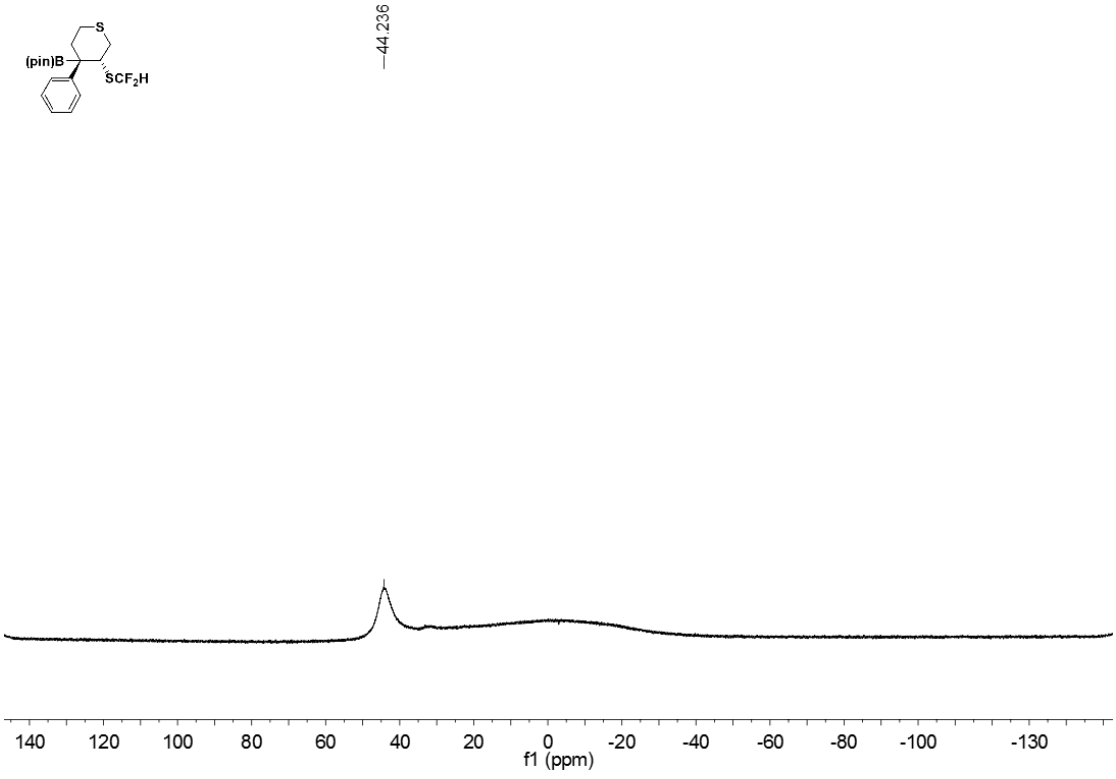
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-thiopyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3n



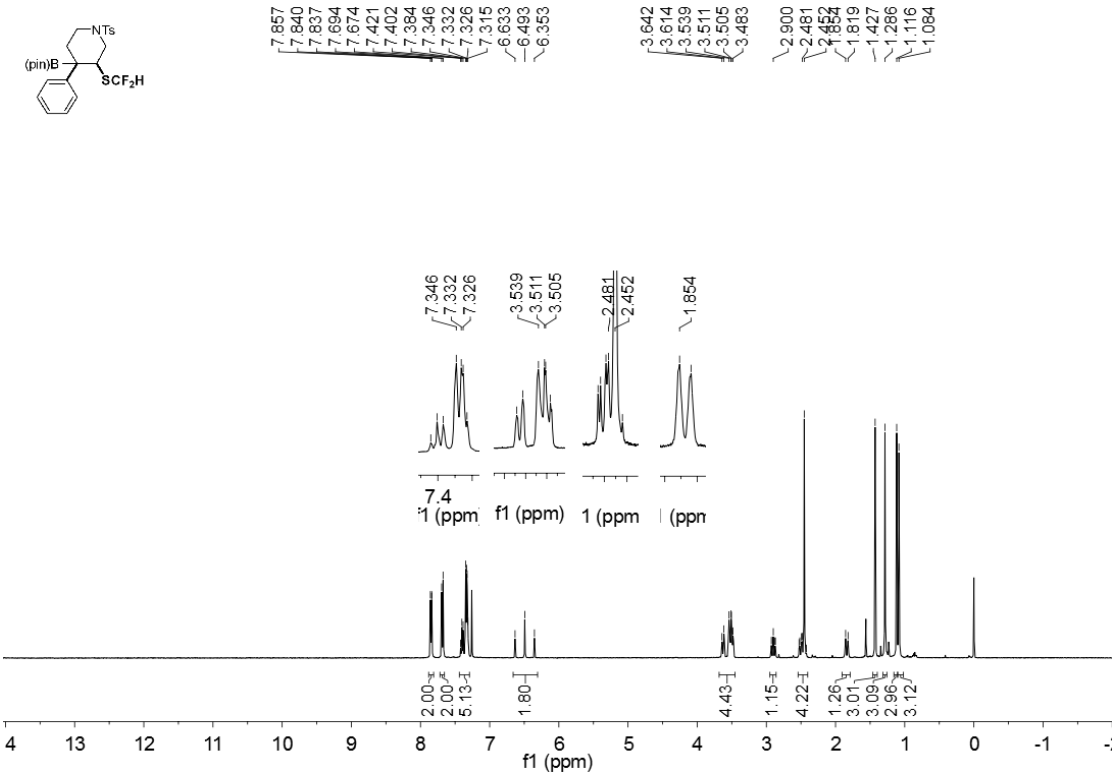
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-thiopyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3n



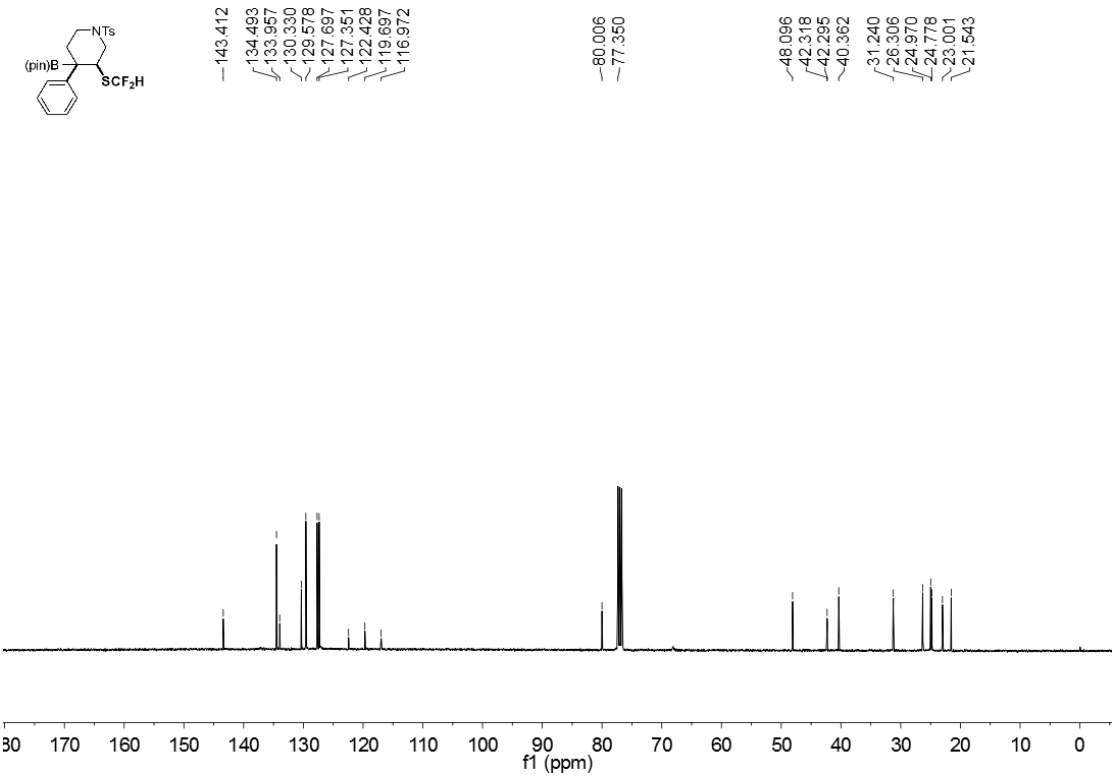
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-2-((3*R*,4*R*)-3-(difluoromethylthio)-4-phenyltetrahydro-2*H*-thiopyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3n



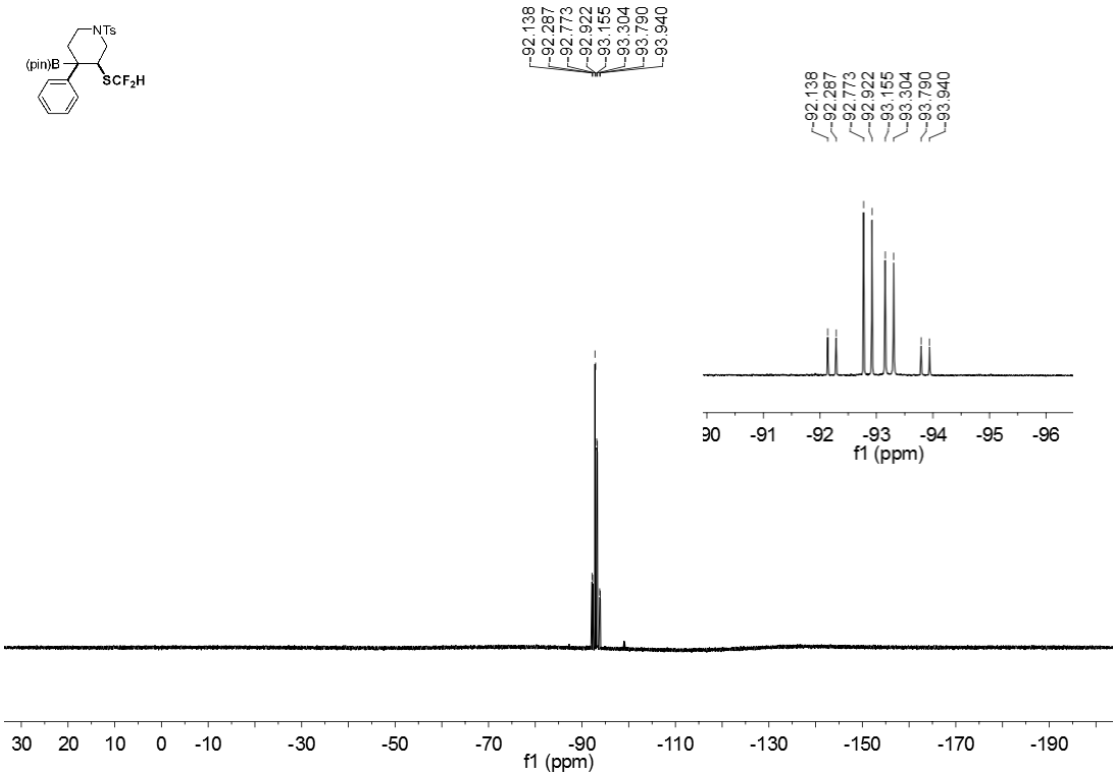
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-(3*R*,4*R*)-3-(difluoromethylthio)-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpiperidine 3o



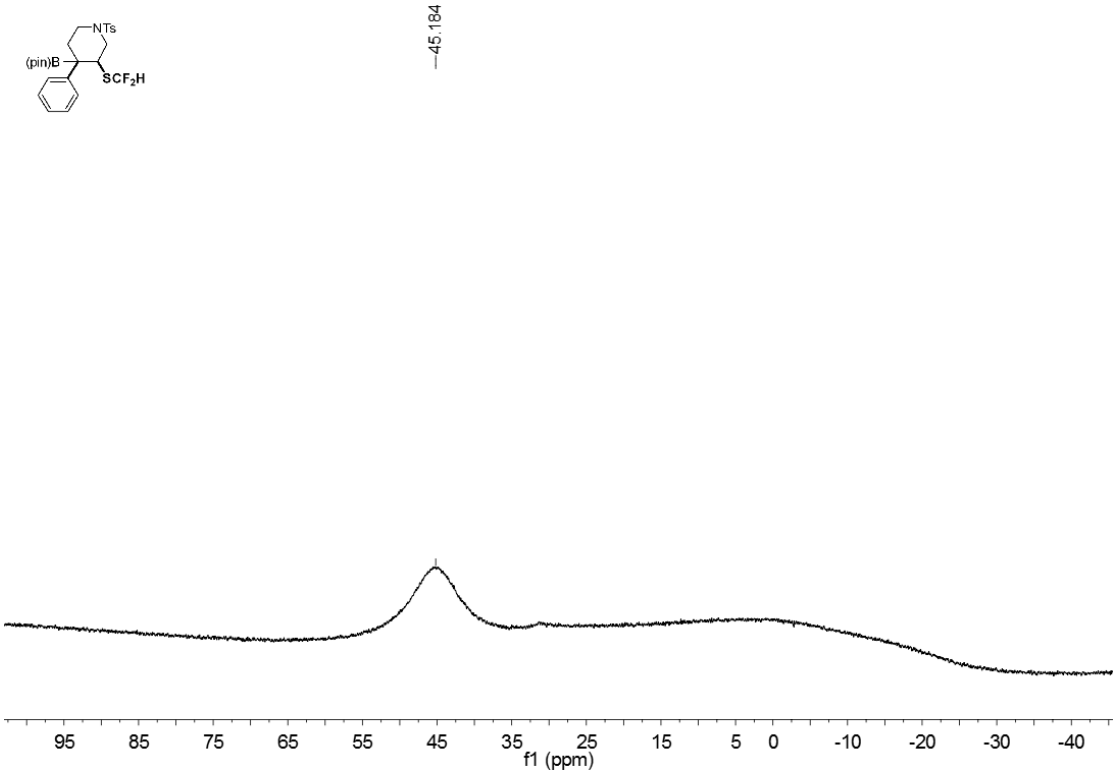
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-(3*R*,4*R*)-3-(difluoromethylthio)-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpiperidine 3o



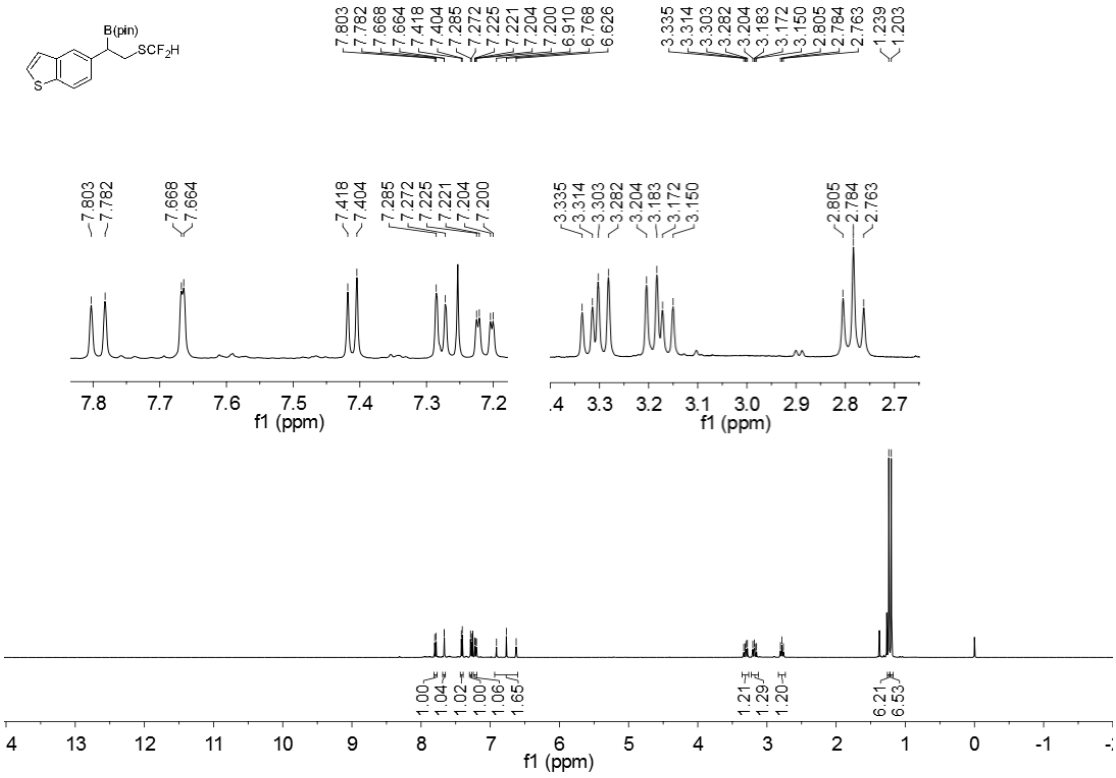
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-(3*R*,4*R*)-3-(difluoromethylthio)-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpiperidine 3o



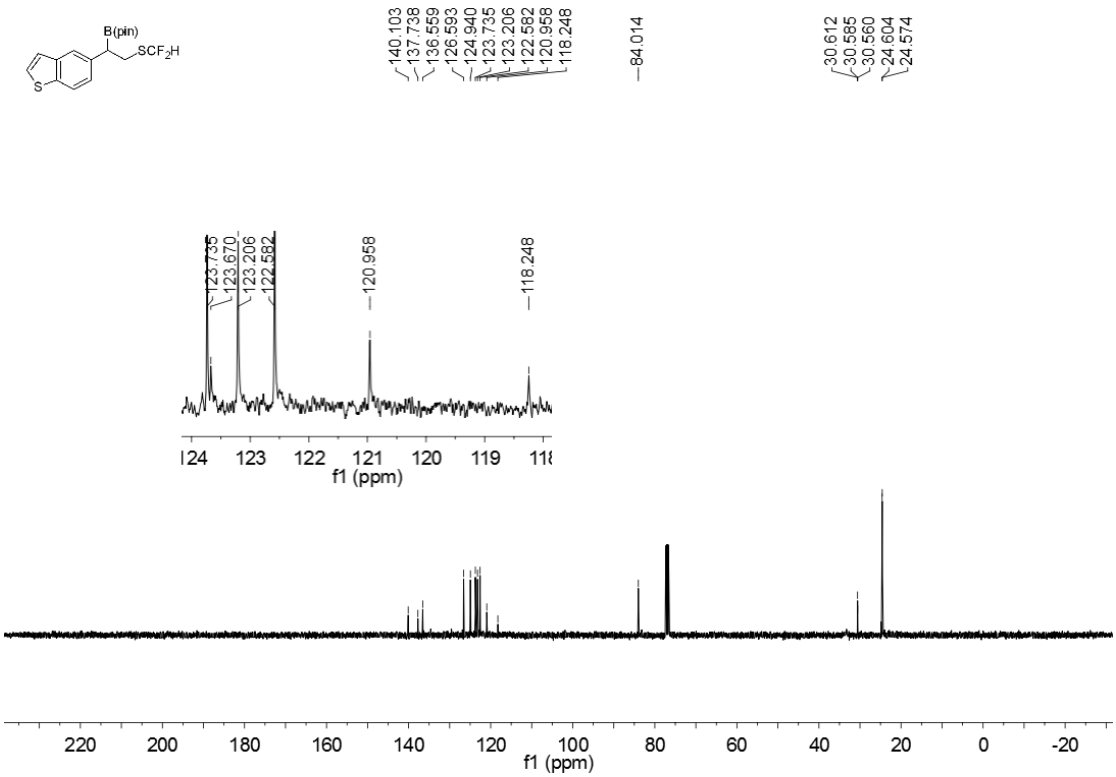
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-(3*R*,4*R*)-3-(difluoromethylthio)-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpiperidine 3o



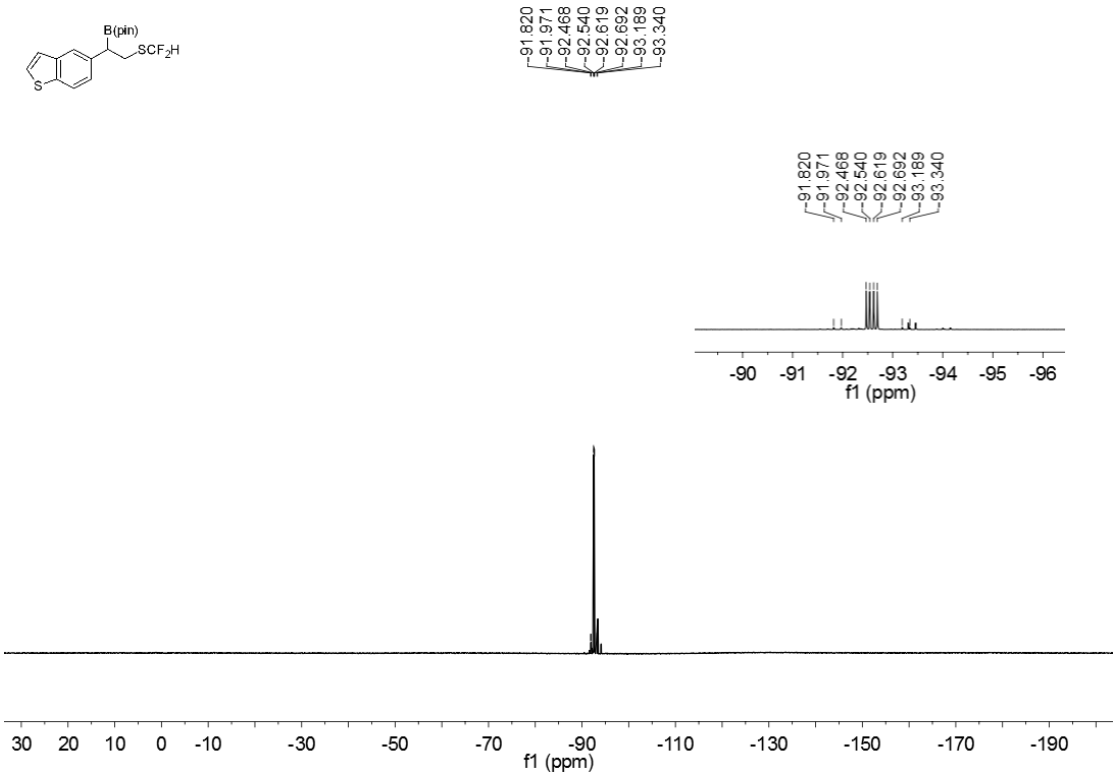
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(1-(benzo[b]thiophen-5-yl)-2-(difluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3p



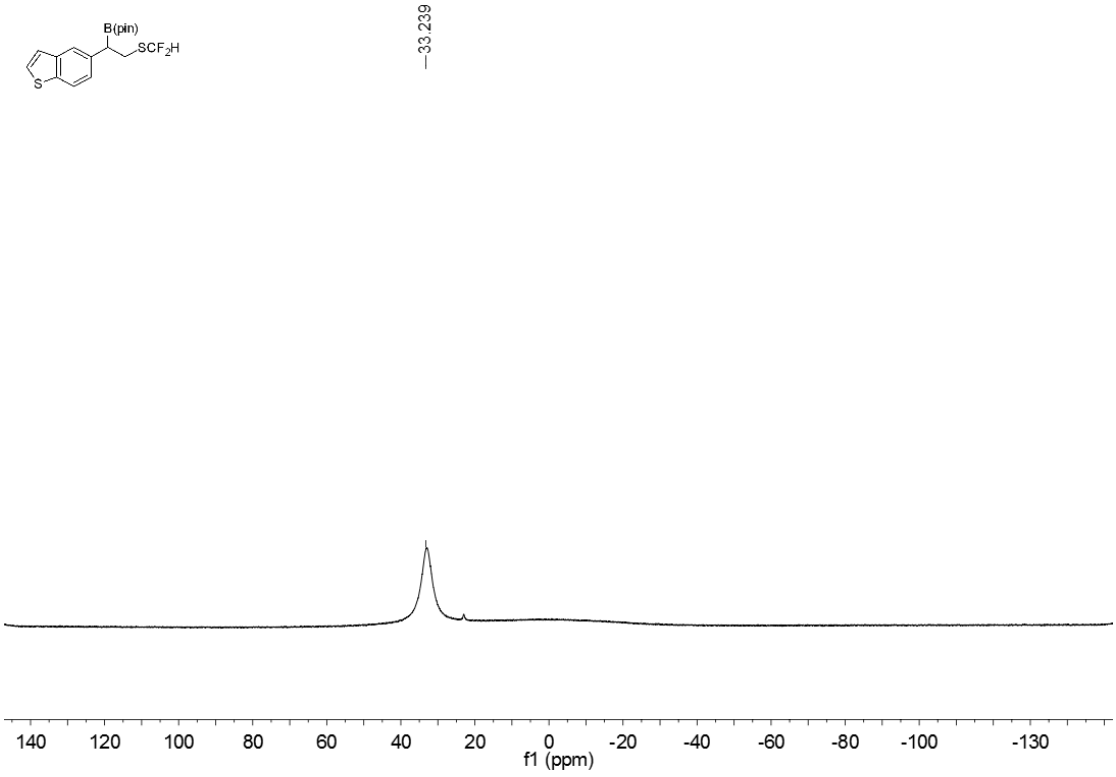
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-(1-(benzo[b]thiophen-5-yl)-2-(difluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3p



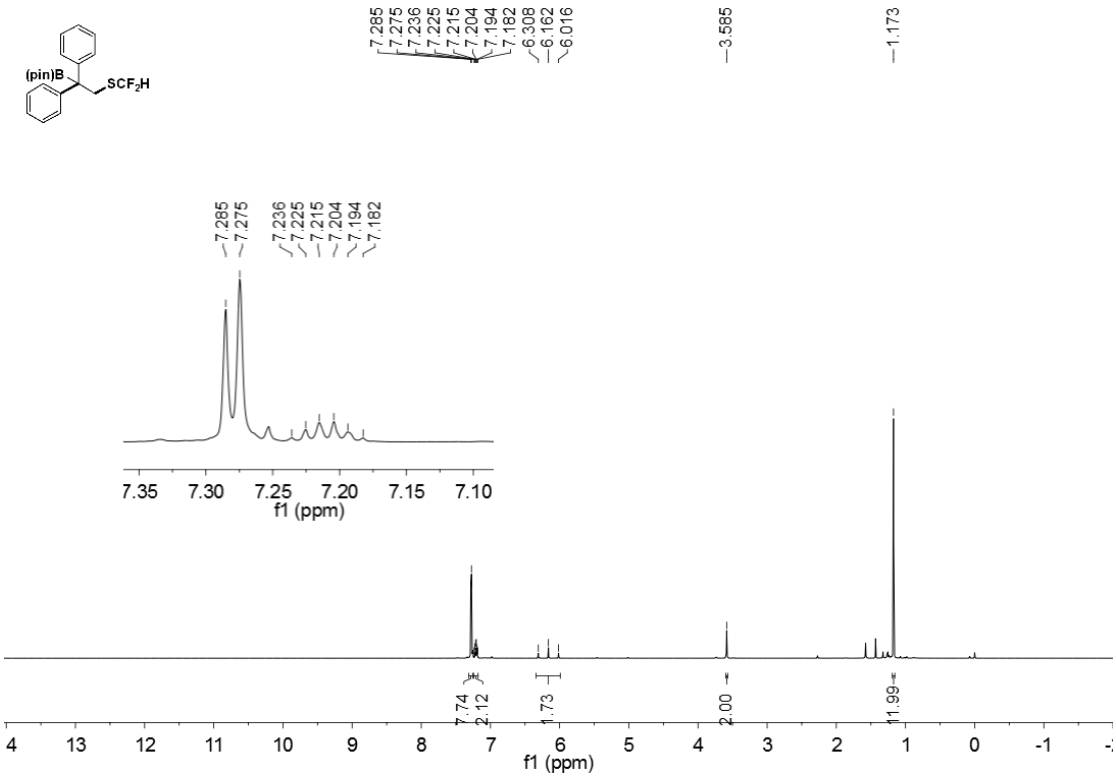
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(1-(benzo[b]thiophen-5-yl)-2-(difluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3p



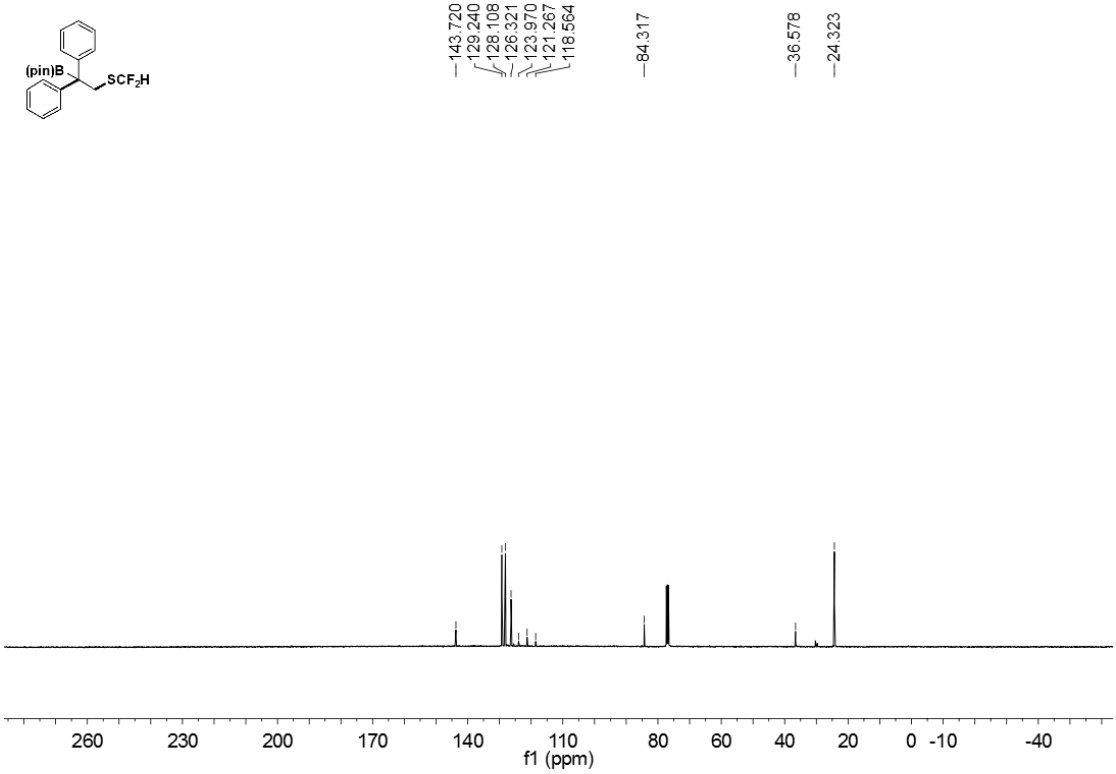
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 2-(1-(benzo[b]thiophen-5-yl)-2-(difluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3p



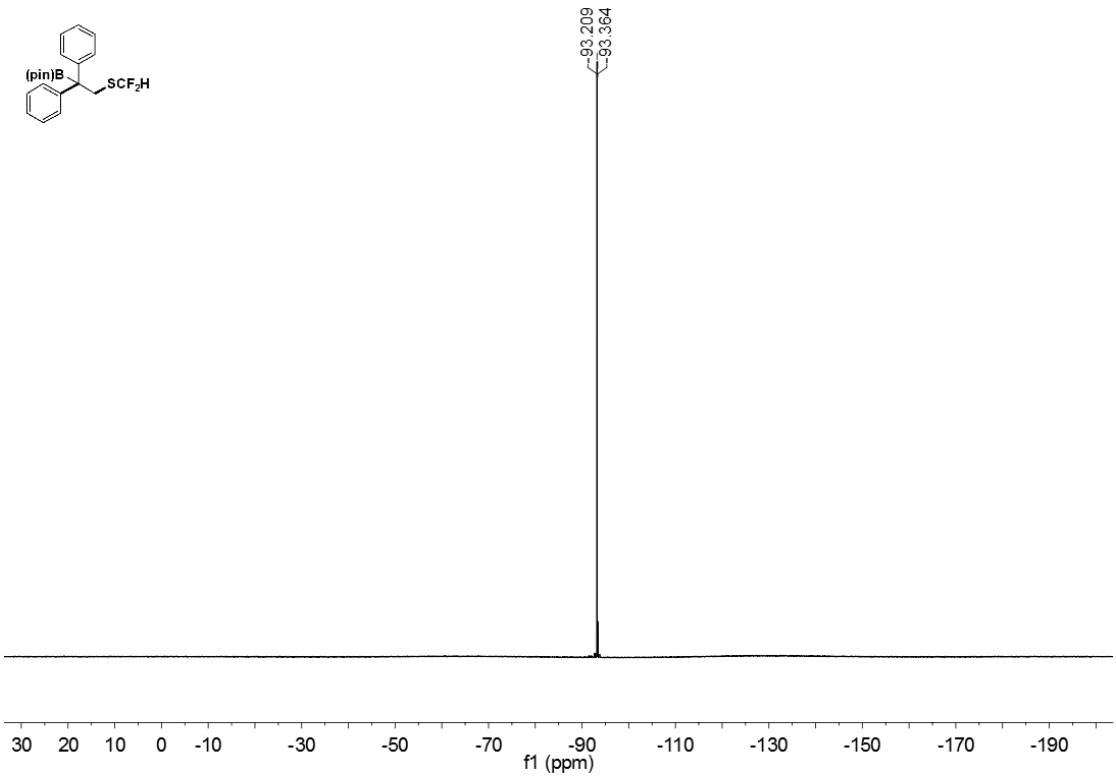
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(2-(difluoromethylthio)-1,1-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3q



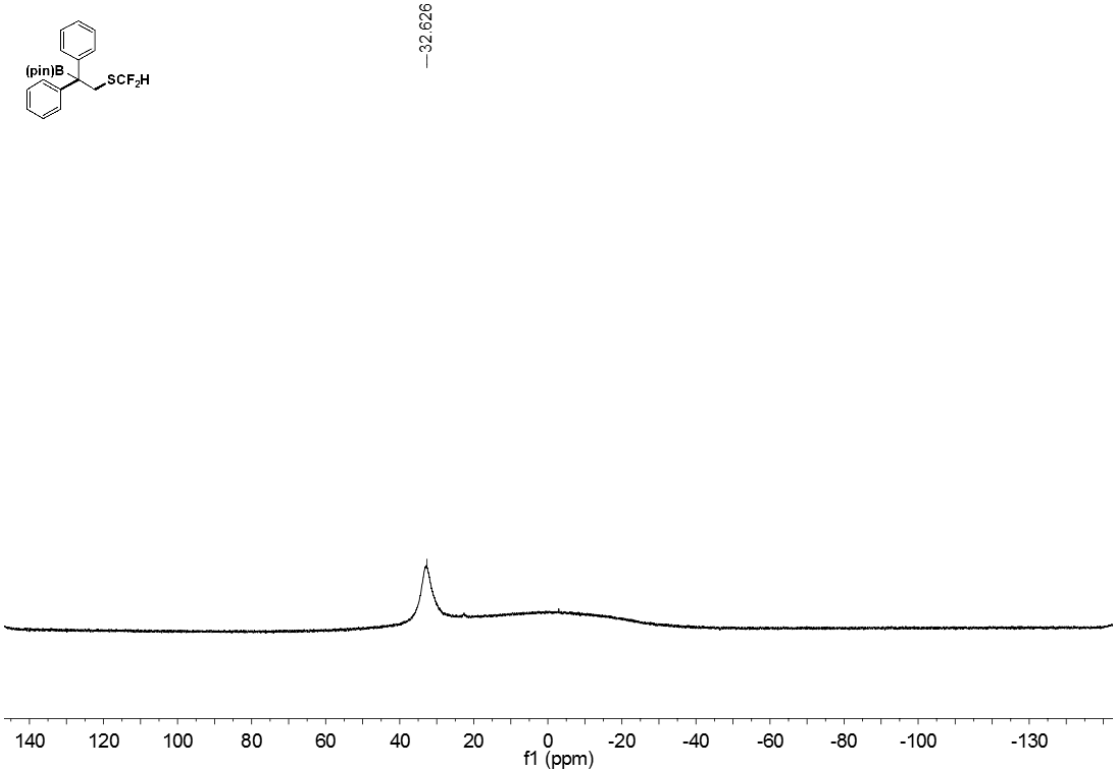
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of x2-(2-(difluoromethylthio)-1,1-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3q



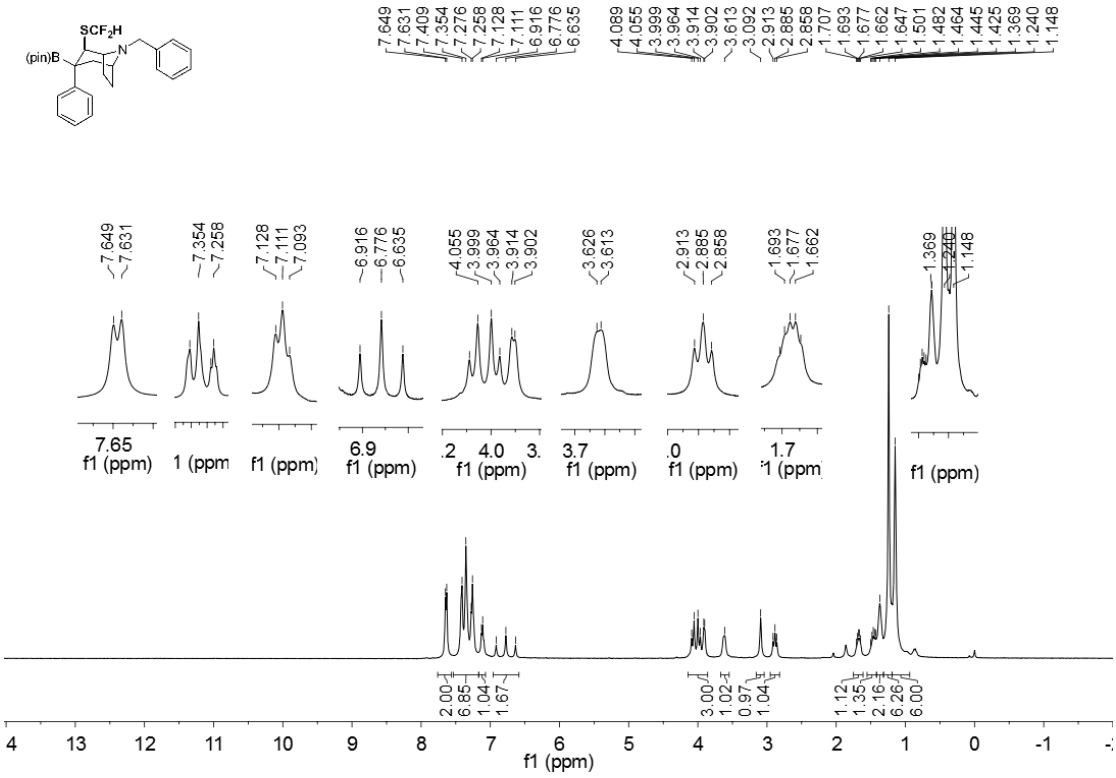
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(2-(difluoromethylthio)-1,1-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3q



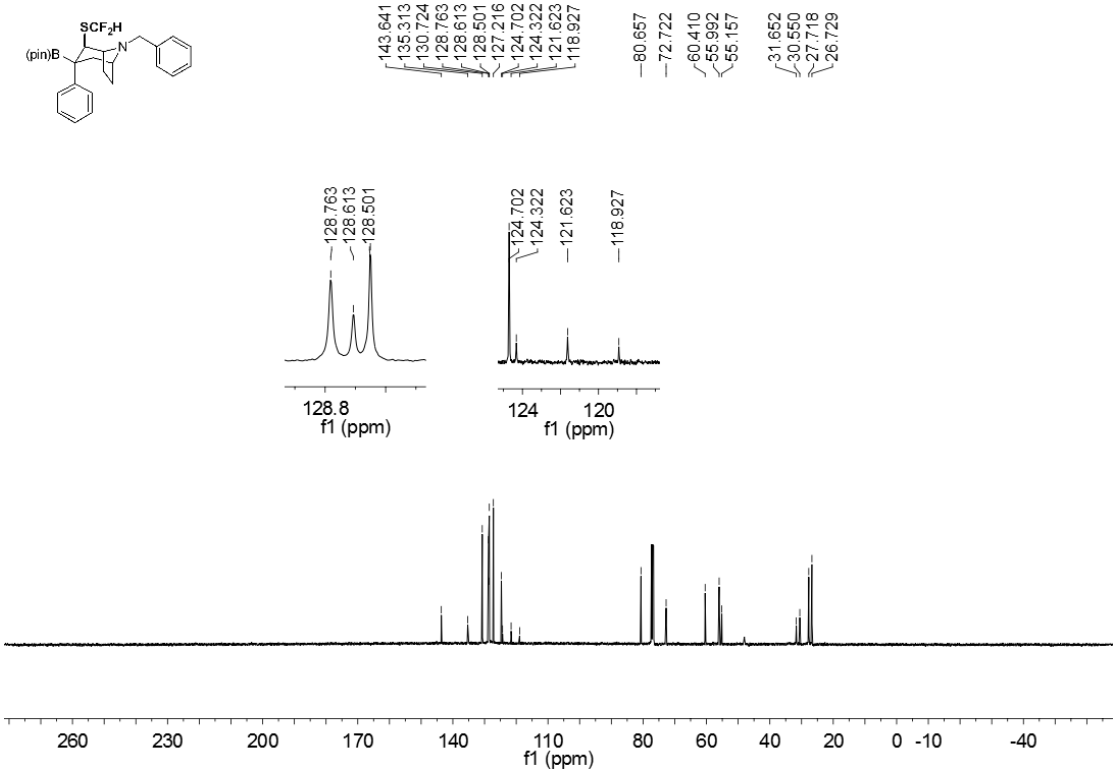
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 2-(2-(difluoromethylthio)-1,1-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3q



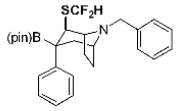
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-(1*S*,2*R*,3*R*,5*R*)-8-benzyl-2-(difluoromethylthio)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-azabicyclo[3.2.1]octane 3s

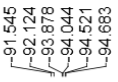


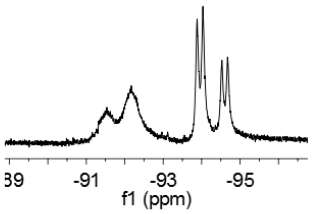
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-(1*S*,2*R*,3*R*,5*R*)-8-benzyl-2-(difluoromethylthio)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-azabicyclo[3.2.1]octane 3s

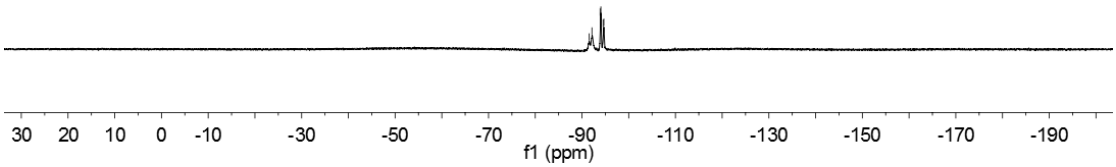


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-(1*S*,2*R*,3*R*,5*R*)-8-benzyl-2-(difluoromethylthio)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-azabicyclo[3.2.1]octane 3s

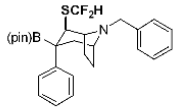


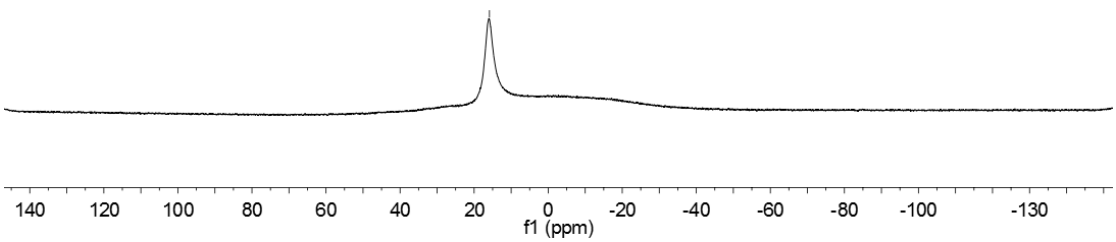




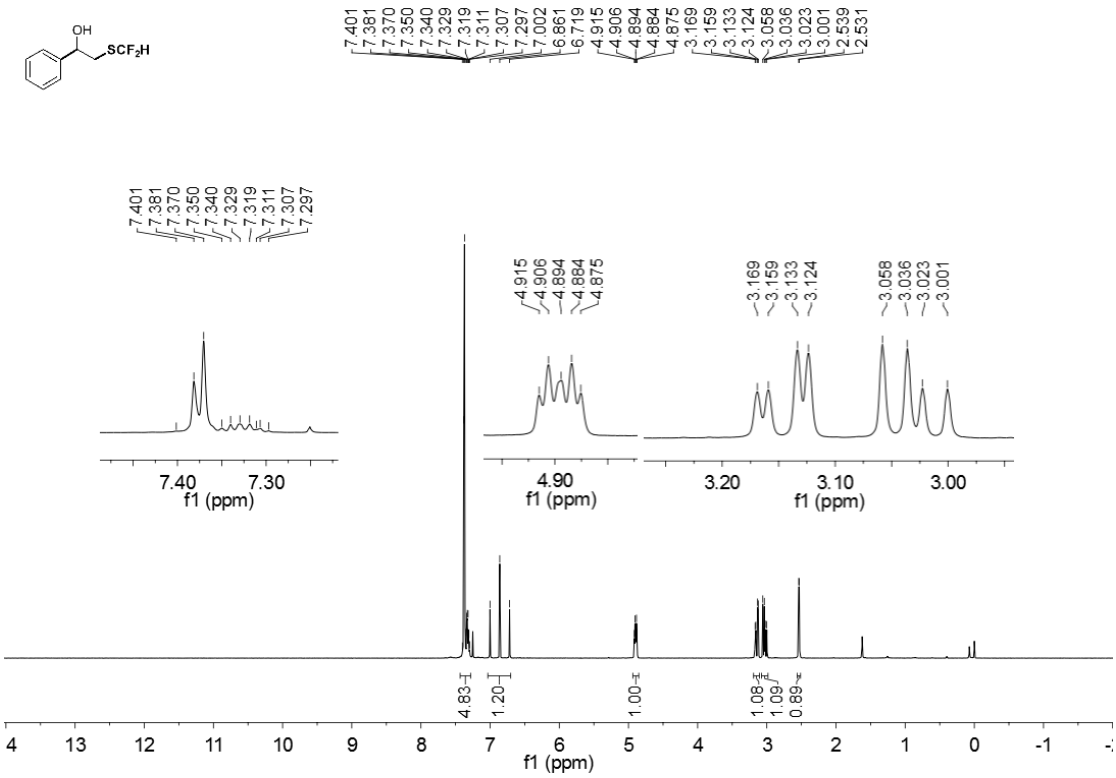


^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-(1*S*,2*R*,3*R*,5*R*)-8-benzyl-2-(difluoromethylthio)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-azabicyclo[3.2.1]octane 3s

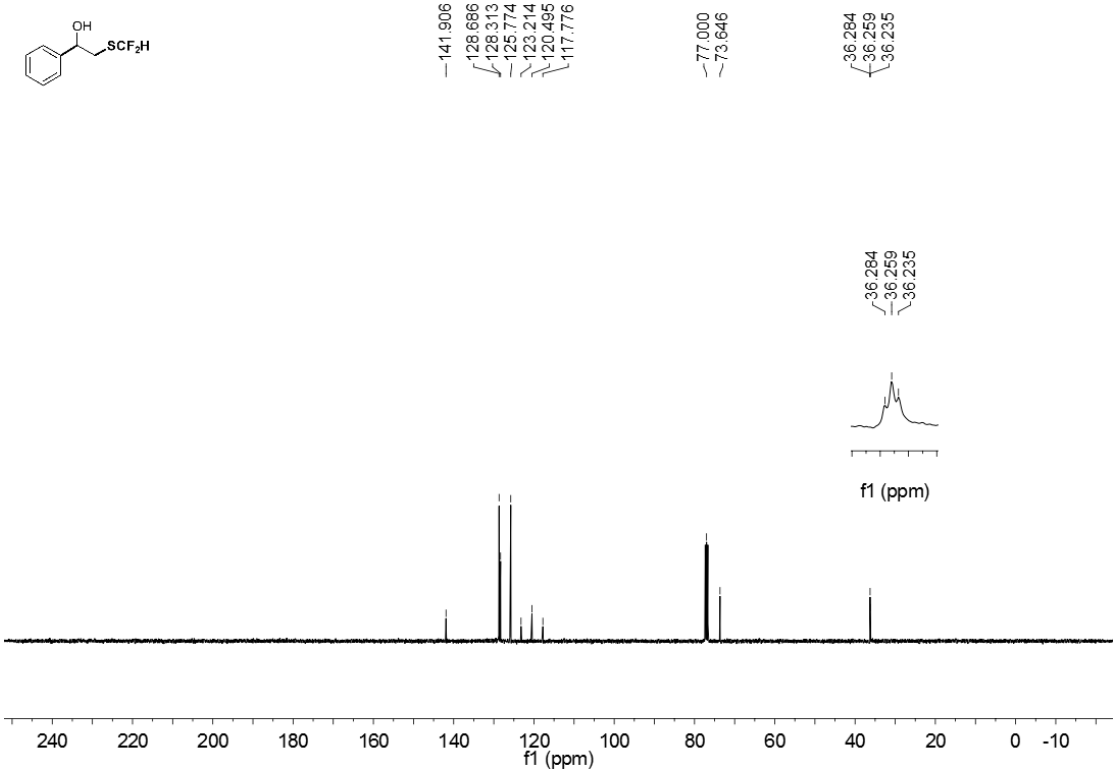




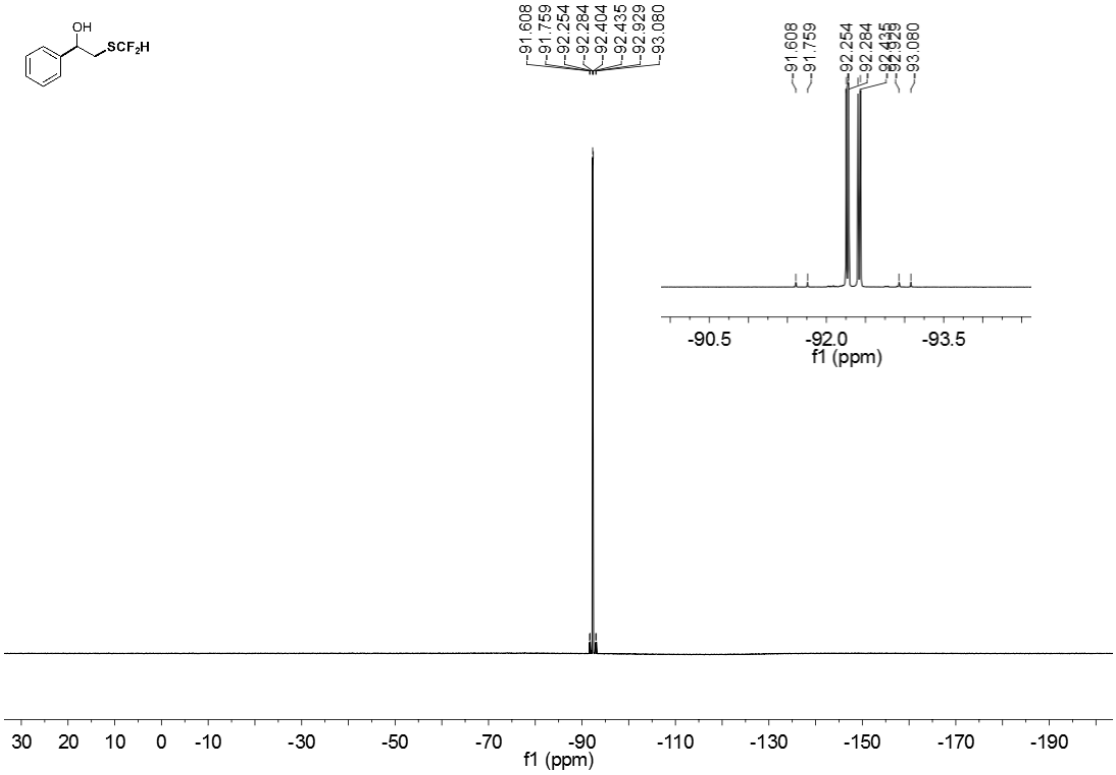
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(difluoromethylthio)-1-phenylethanol 4a



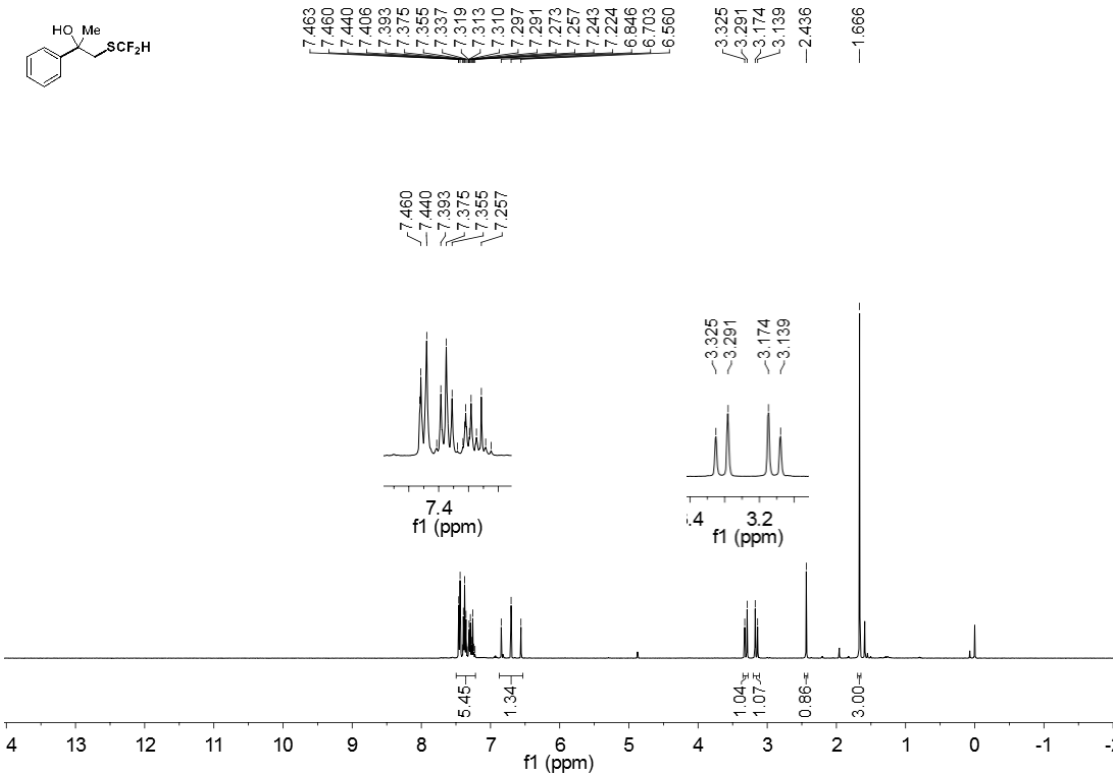
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-(difluoromethylthio)-1-phenylethanol 4a



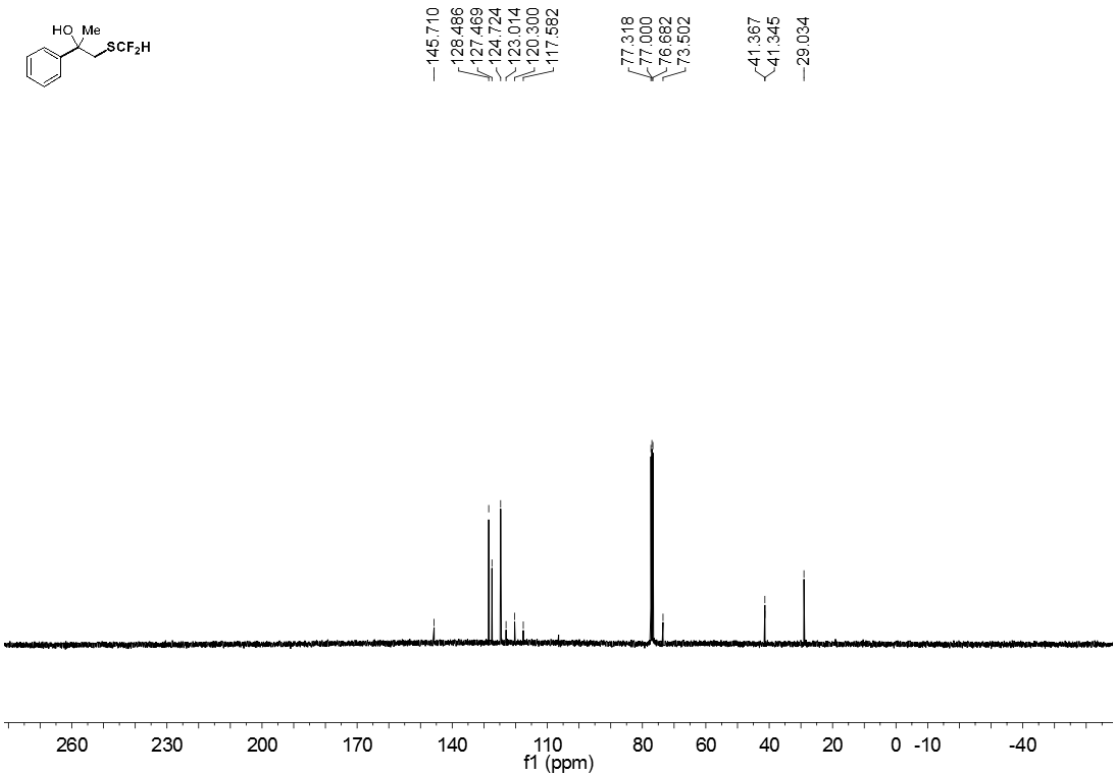
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(difluoromethylthio)-1-phenylethanol 4a



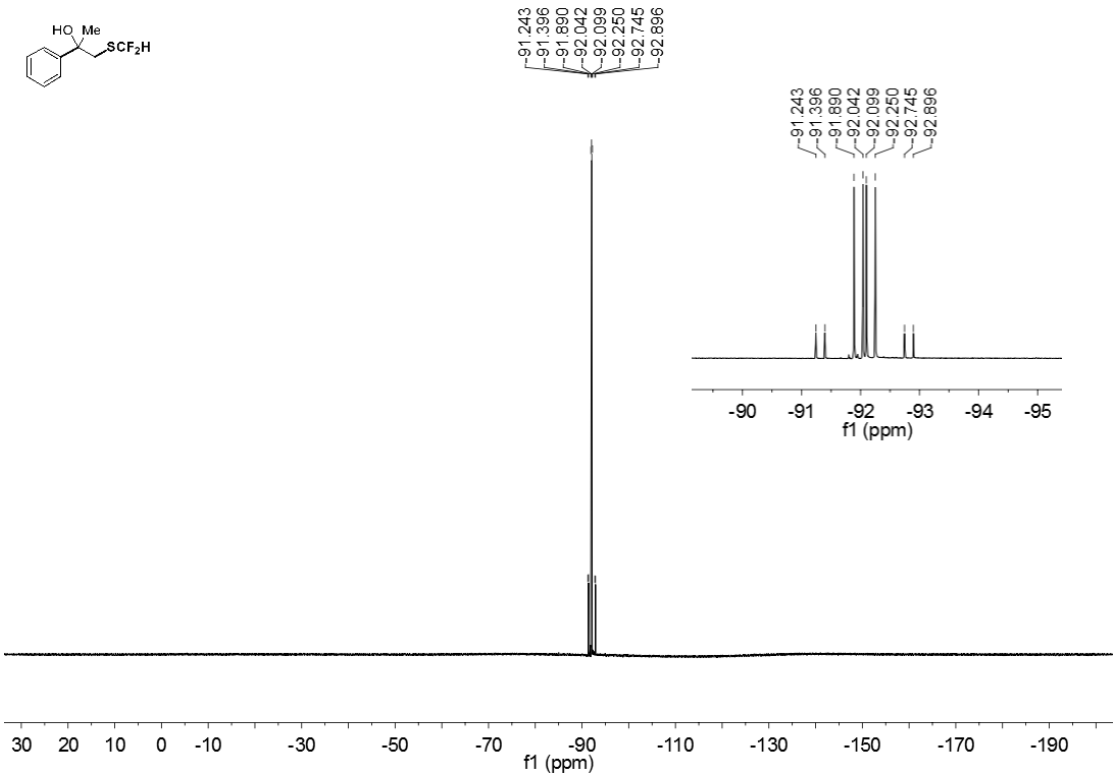
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(difluoromethylthio)-2-phenylpropan-2-ol 4b



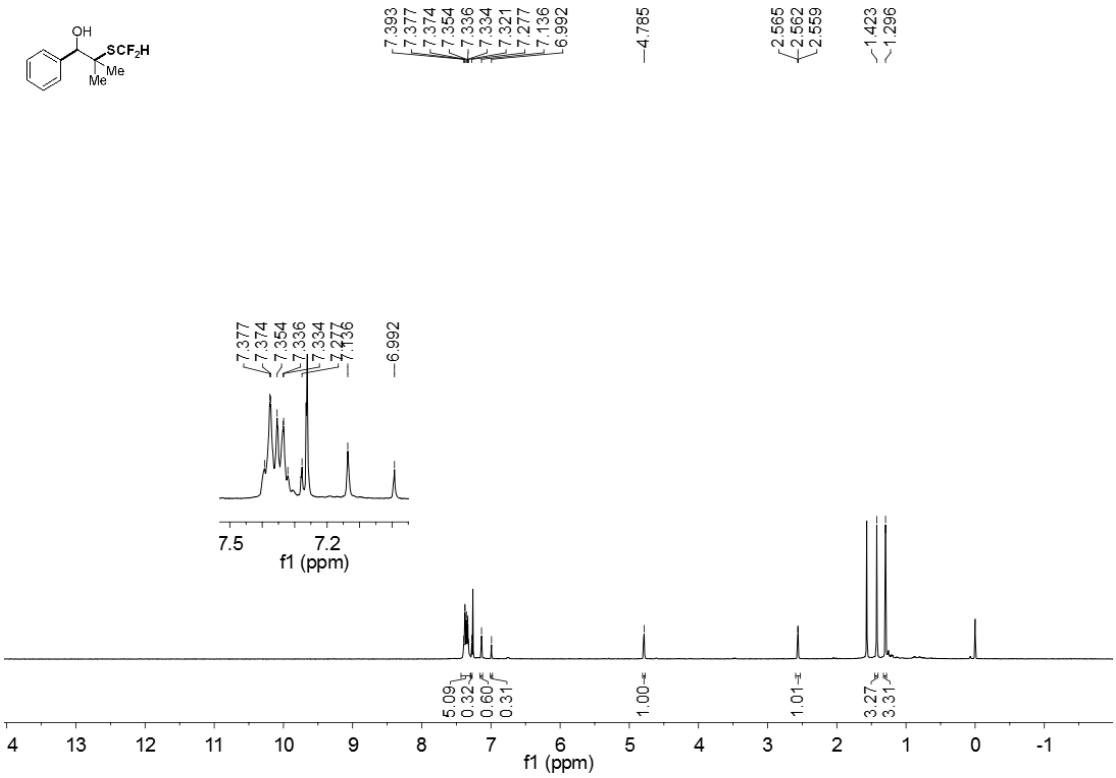
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-(difluoromethylthio)-2-phenylpropan-2-ol 4b



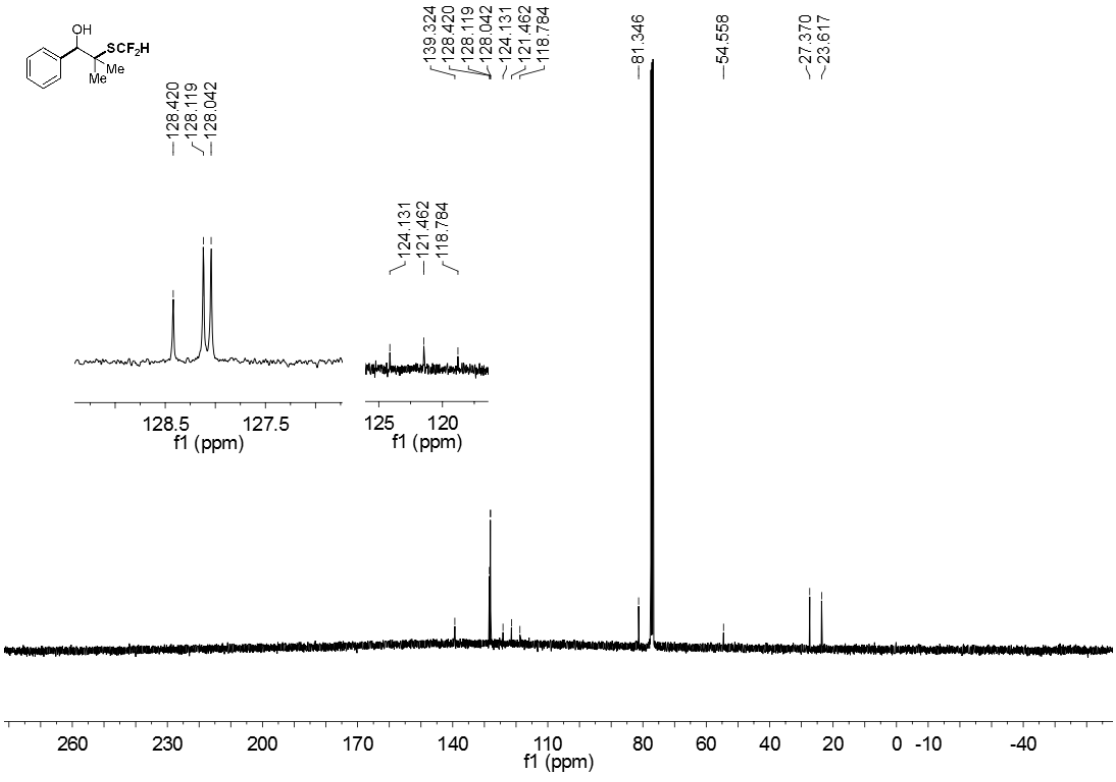
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(difluoromethylthio)-2-phenylpropan-2-ol 4b



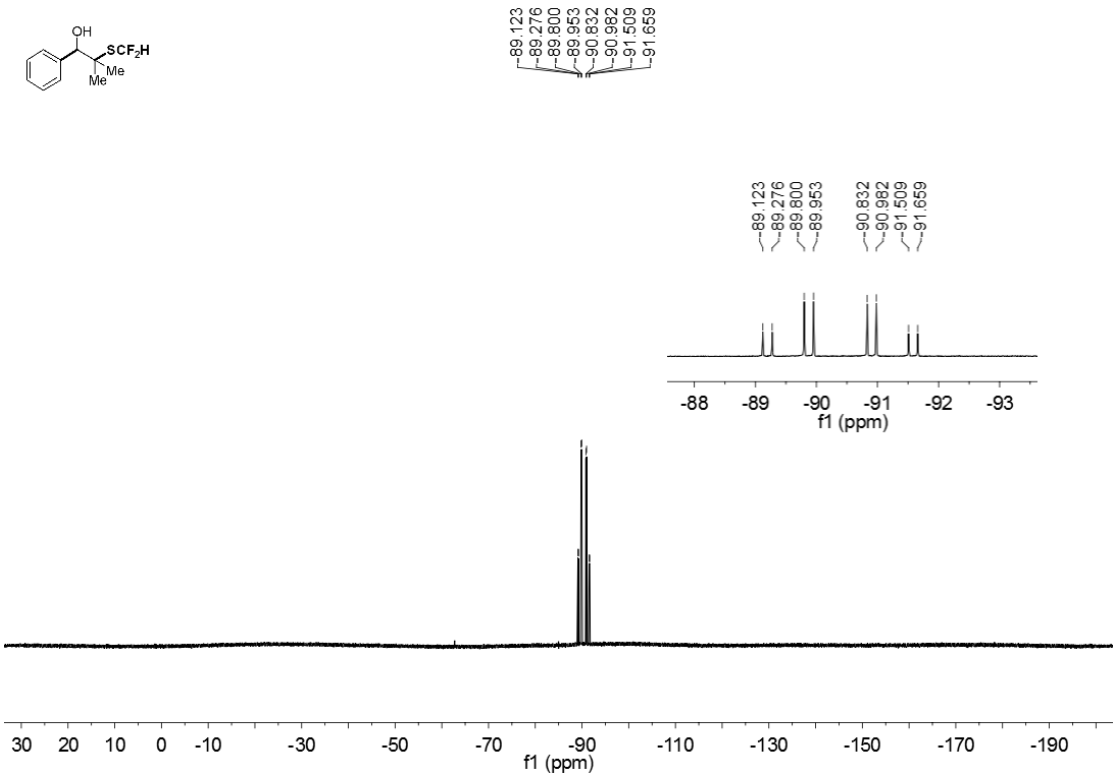
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(difluoromethylthio)-2-methyl-1-phenylpropan-1-ol 4c



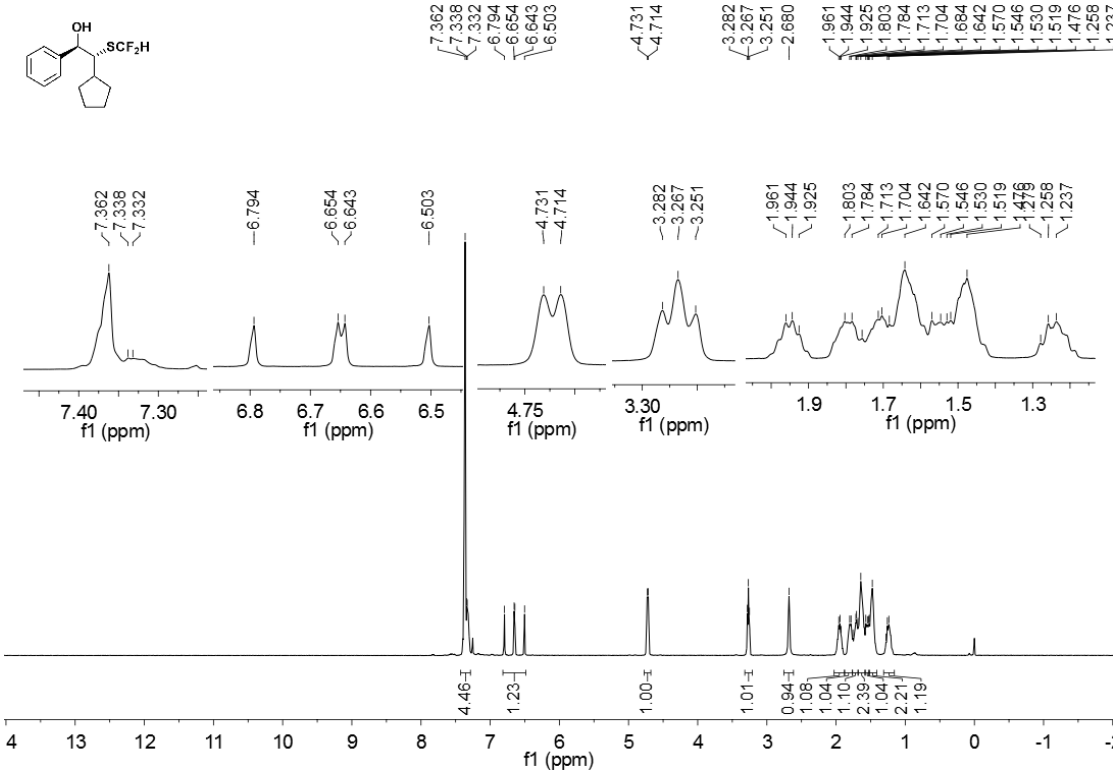
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-(difluoromethylthio)-2-methyl-1-phenylpropan-1-ol 4c



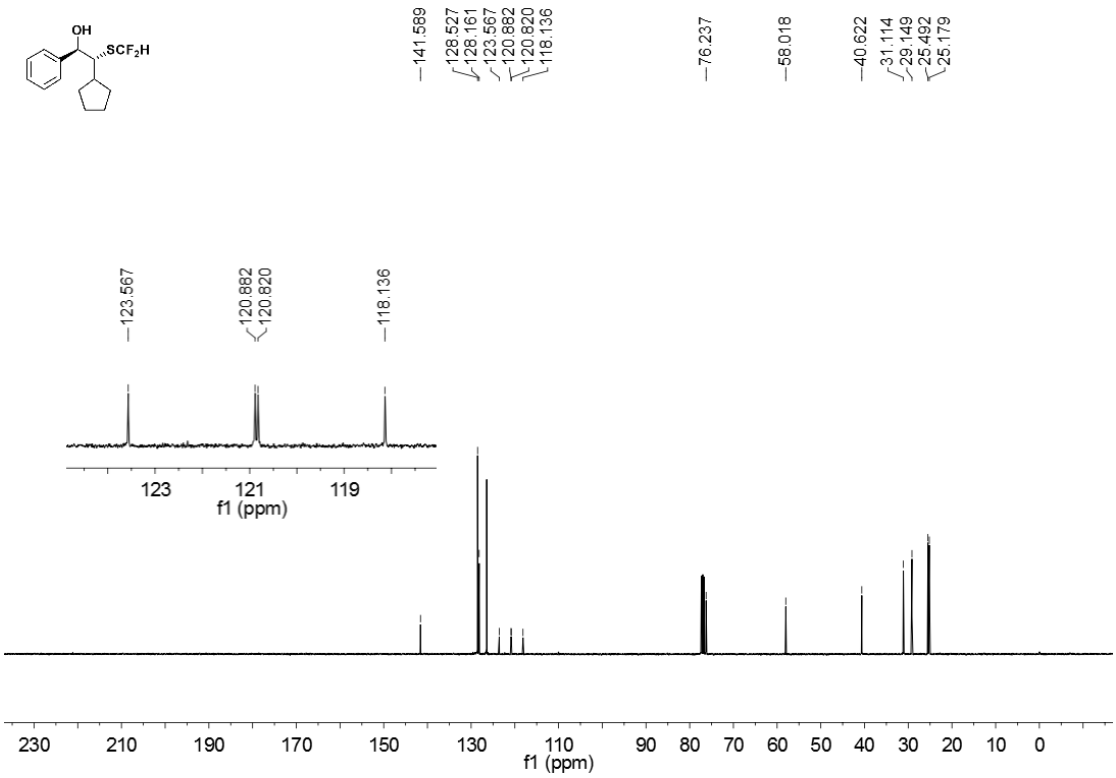
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(difluoromethylthio)-2-methyl-1-phenylpropan-1-ol 4c



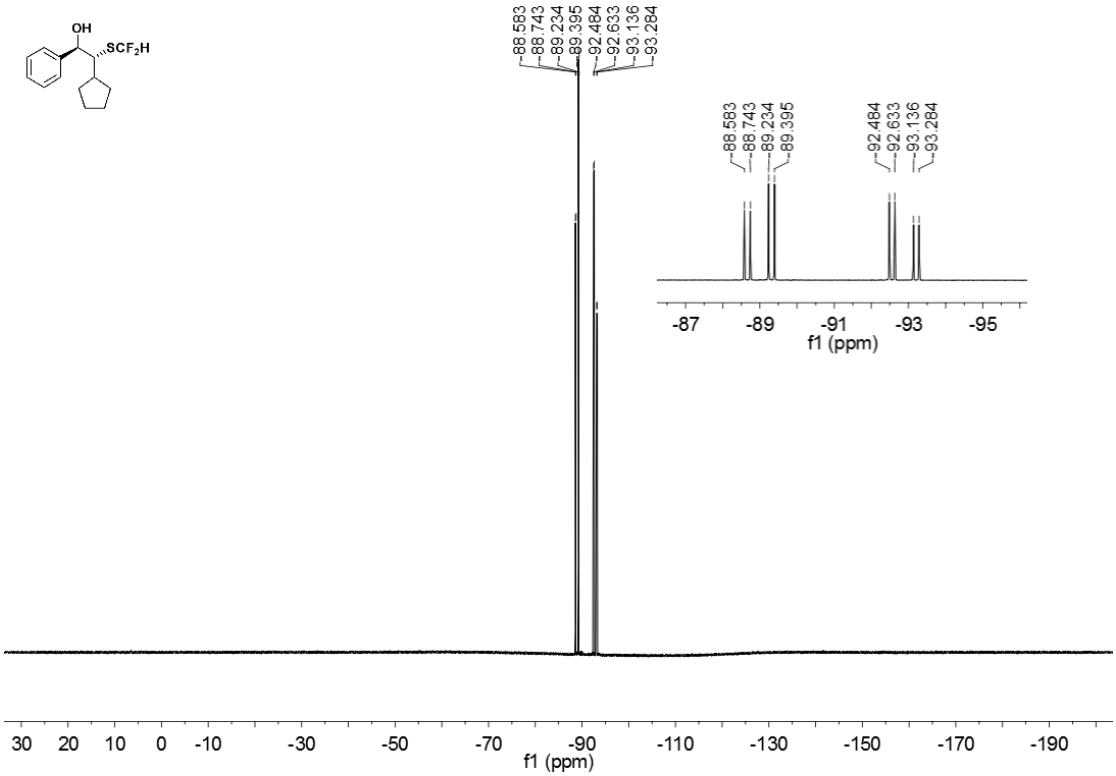
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-(1*R*,2*R*)-2-cyclopentyl-2-(difluoromethylthio)-1-phenylethanol 4d



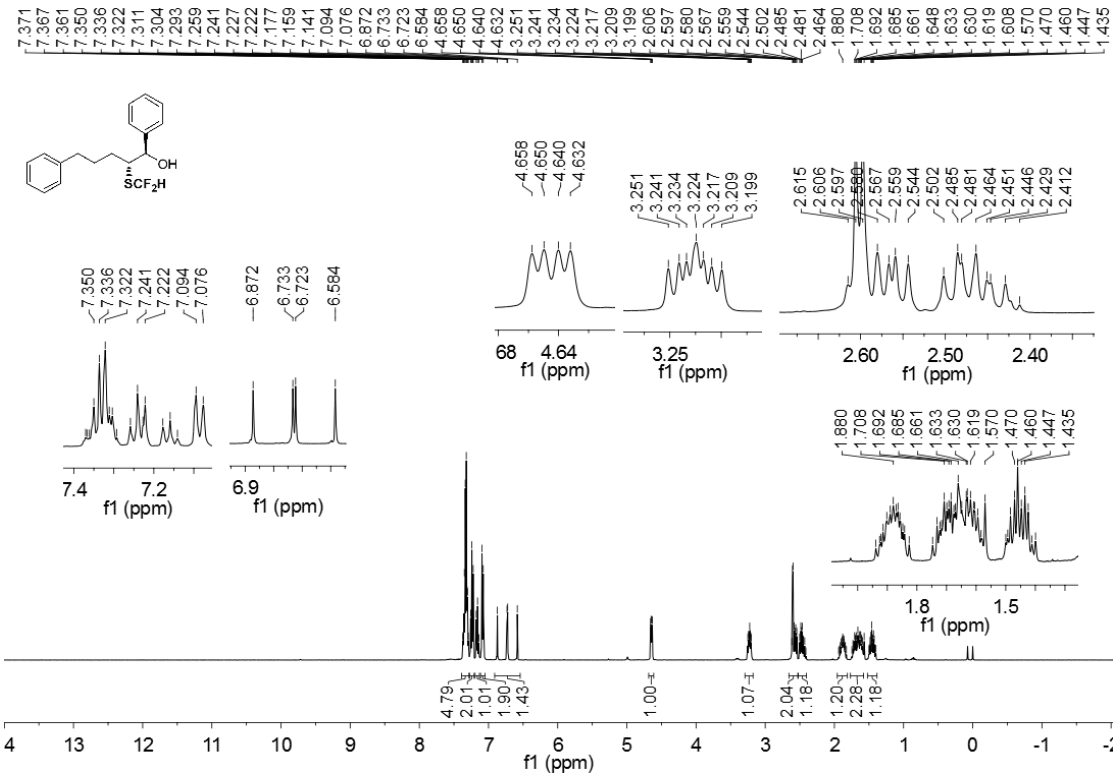
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-(1*R*,2*R*)-2-cyclopentyl-2-(difluoromethylthio)-1-phenylethanol 4d



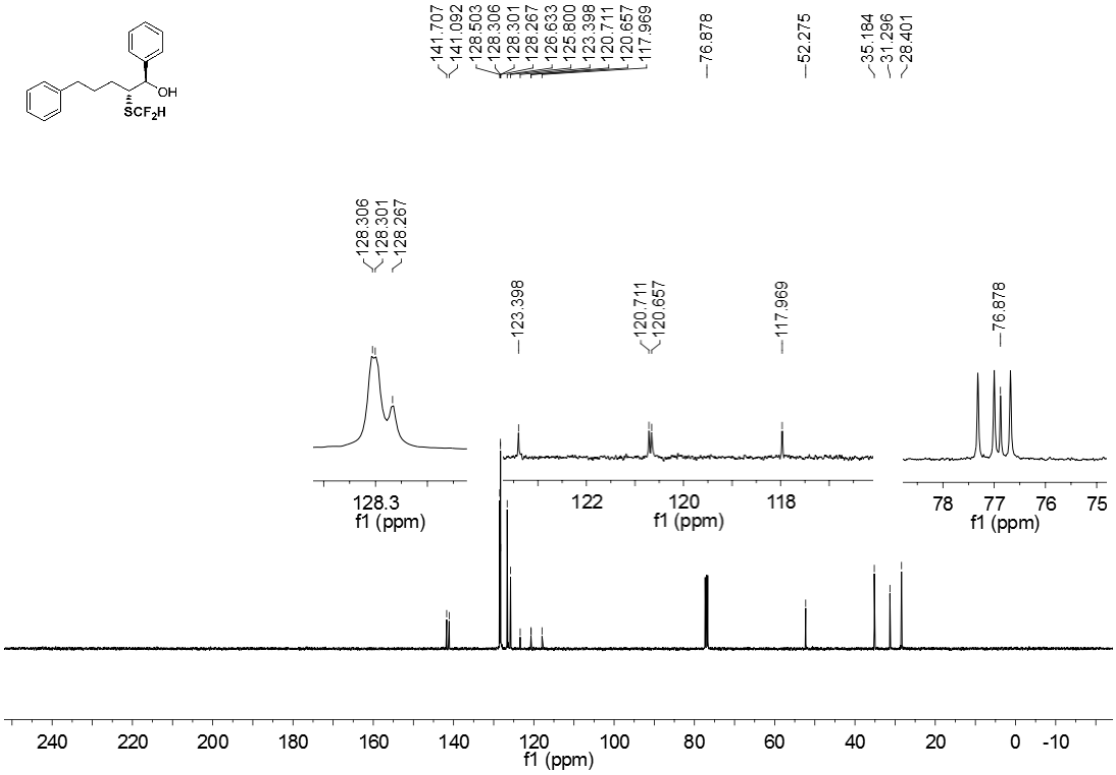
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-(1*R*,2*R*)-2-cyclopentyl-2-(difluoromethylthio)-1-phenylethanol 4d



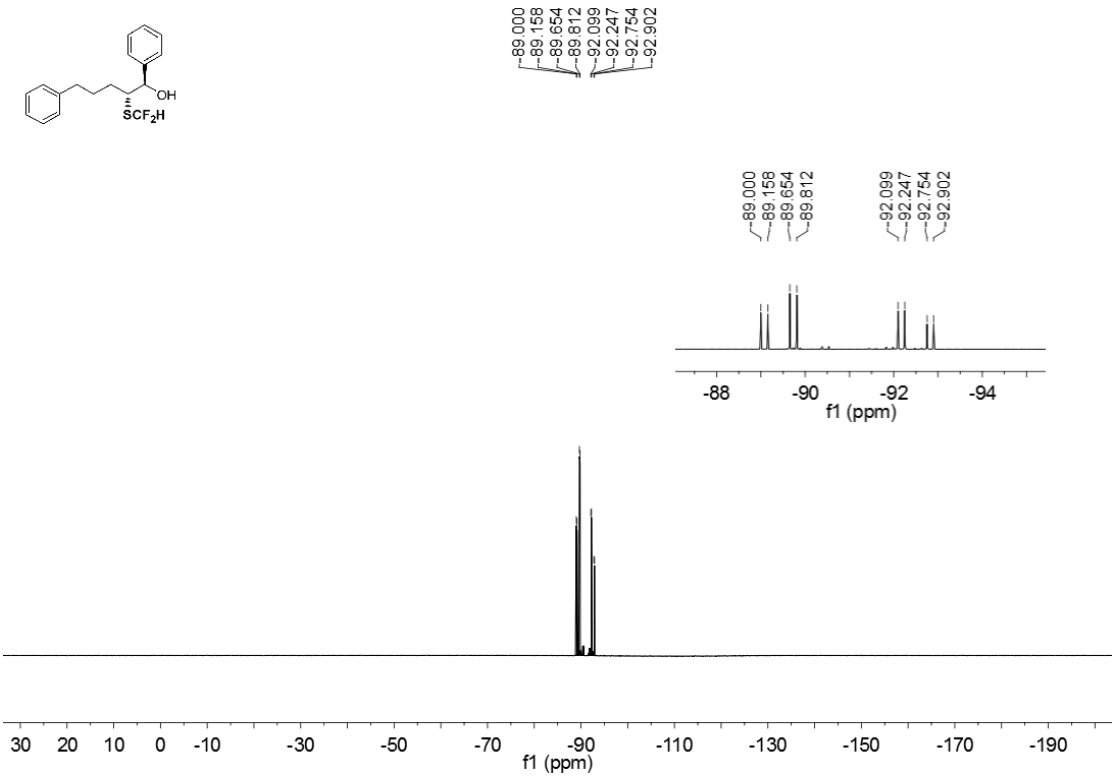
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of
(±)-(1*S*,2*S*)-2-(difluoromethylthio)-1,5-diphenylpentan-1-ol 4e



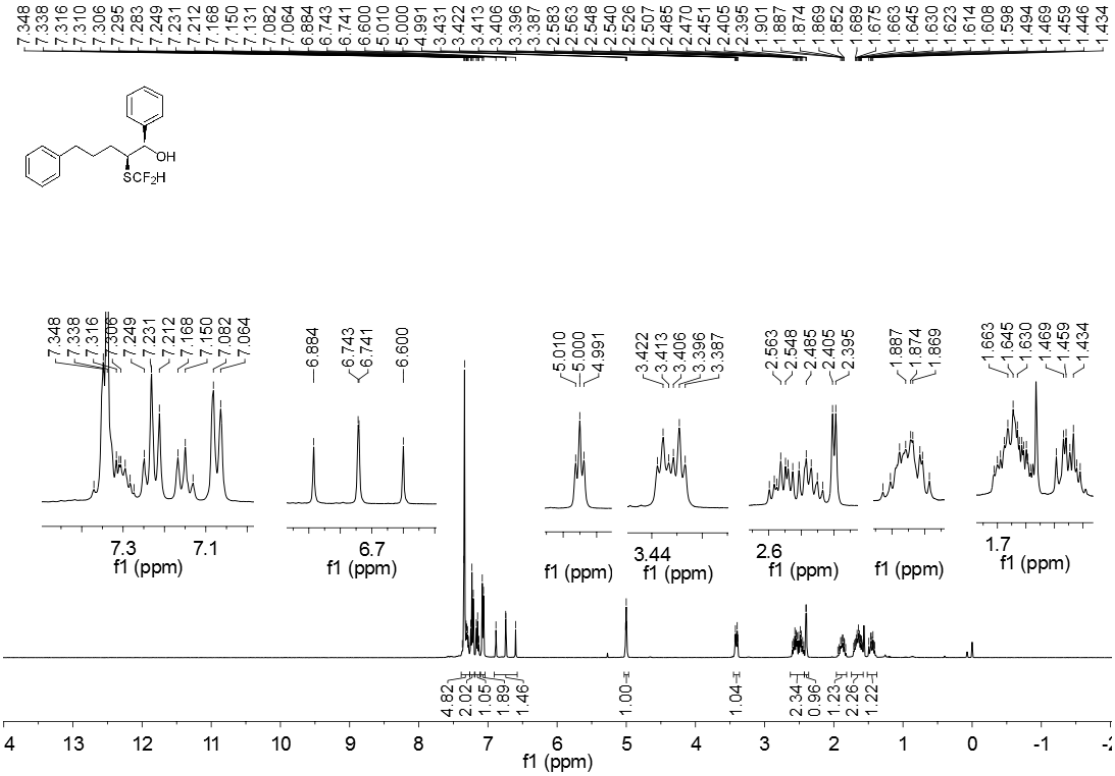
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of
(±)-(1*S*,2*S*)-2-(difluoromethylthio)-1,5-diphenylpentan-1-ol 4e



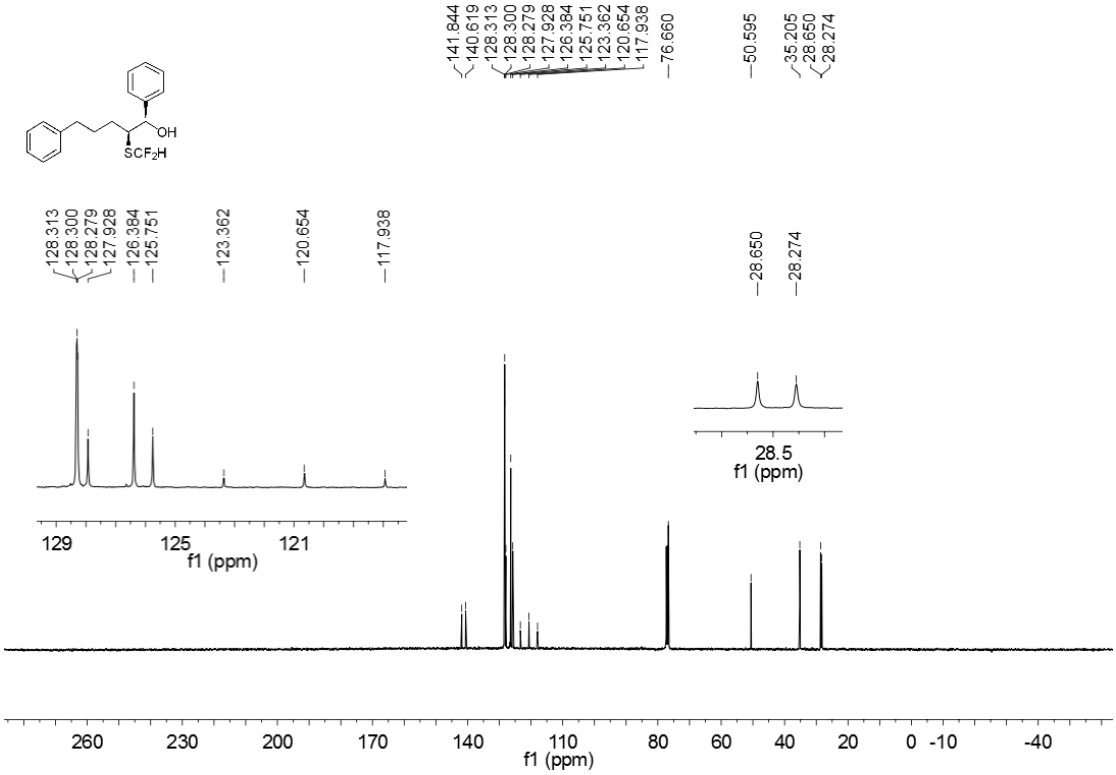
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-(1*S*,2*S*)-2-(difluoromethylthio)-1,5-diphenylpentan-1-ol 4e



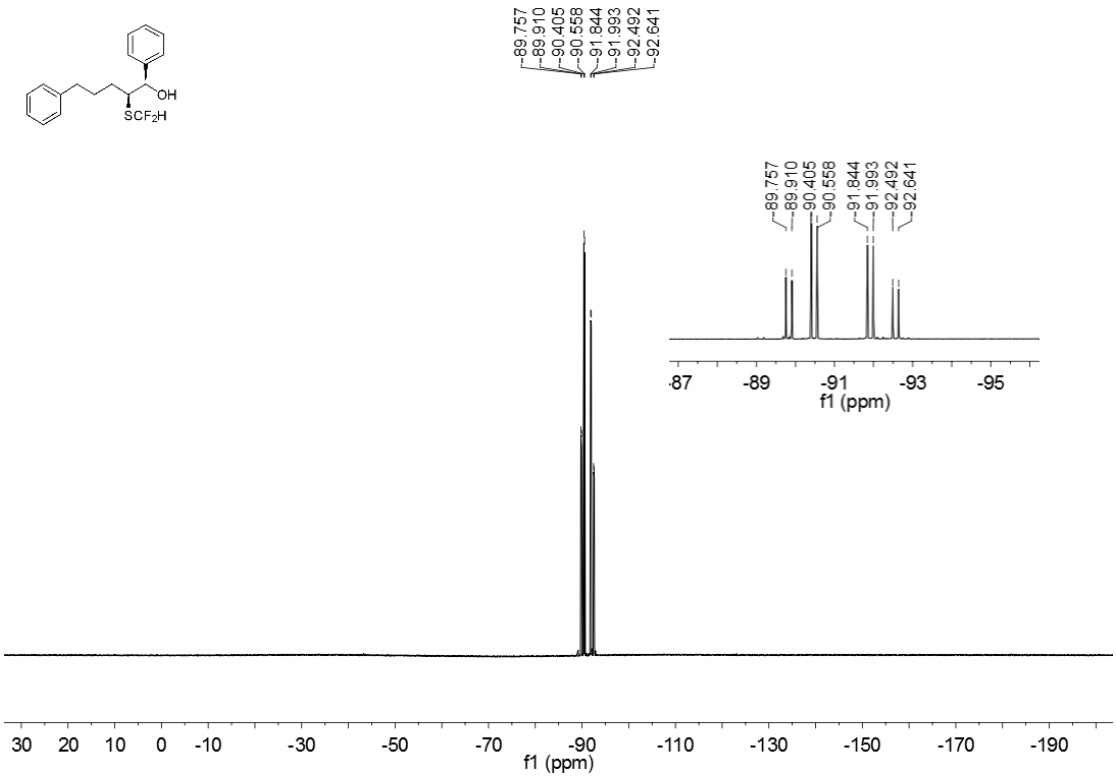
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-(1*R*,2*S*)-2-(difluoromethylthio)-1,5-diphenylpentan-1-ol 4f



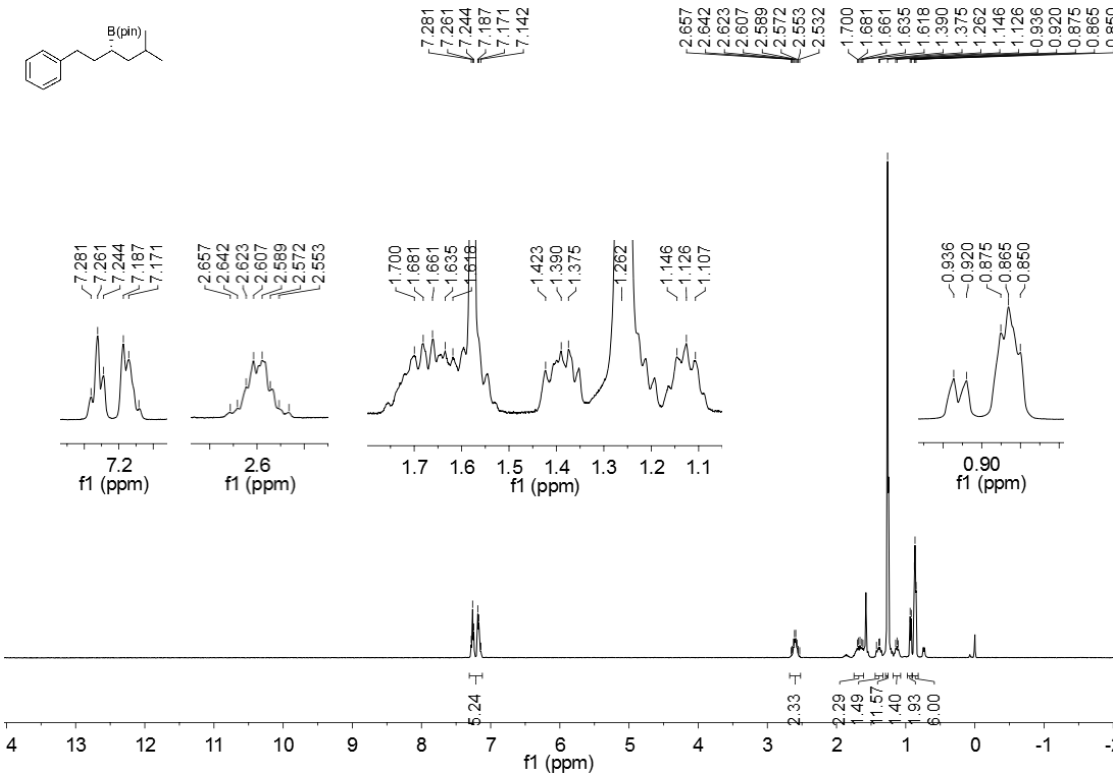
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-(1*R*,2*S*)-2-(difluoromethylthio)-1,5-diphenylpentan-1-ol 4f



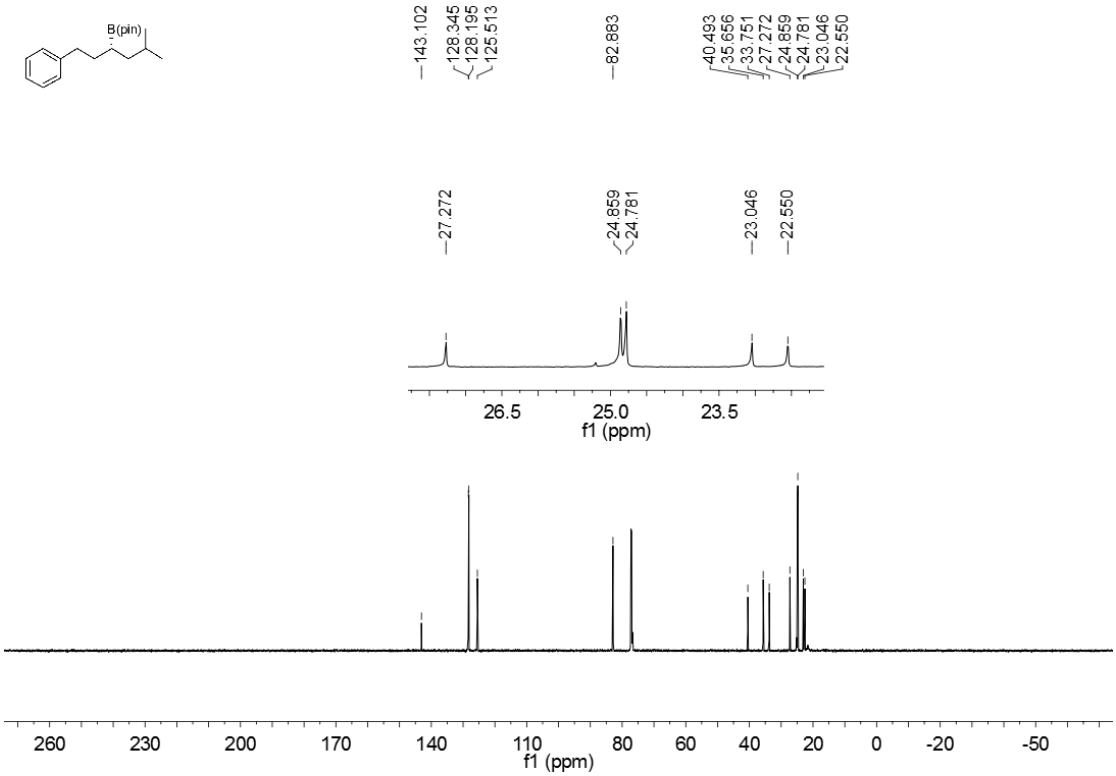
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-(1*R*,2*S*)-2-(difluoromethylthio)-1,5-diphenylpentan-1-ol 4f



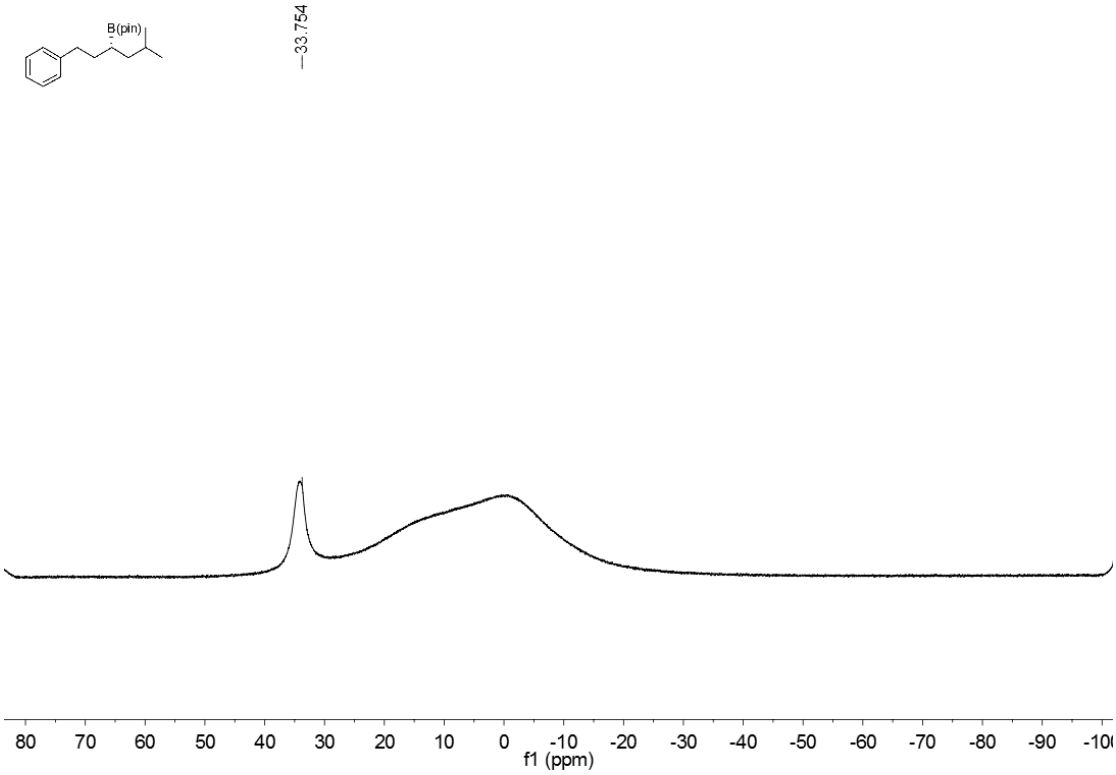
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of
(*S*)-4,4,5,5-tetramethyl-2-(5-methyl-1-phenylhexan-3-yl)-1,3,2-dioxaborolane 5a



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
(*S*)-4,4,5,5-tetramethyl-2-(5-methyl-1-phenylhexan-3-yl)-1,3,2-dioxaborolane 5a

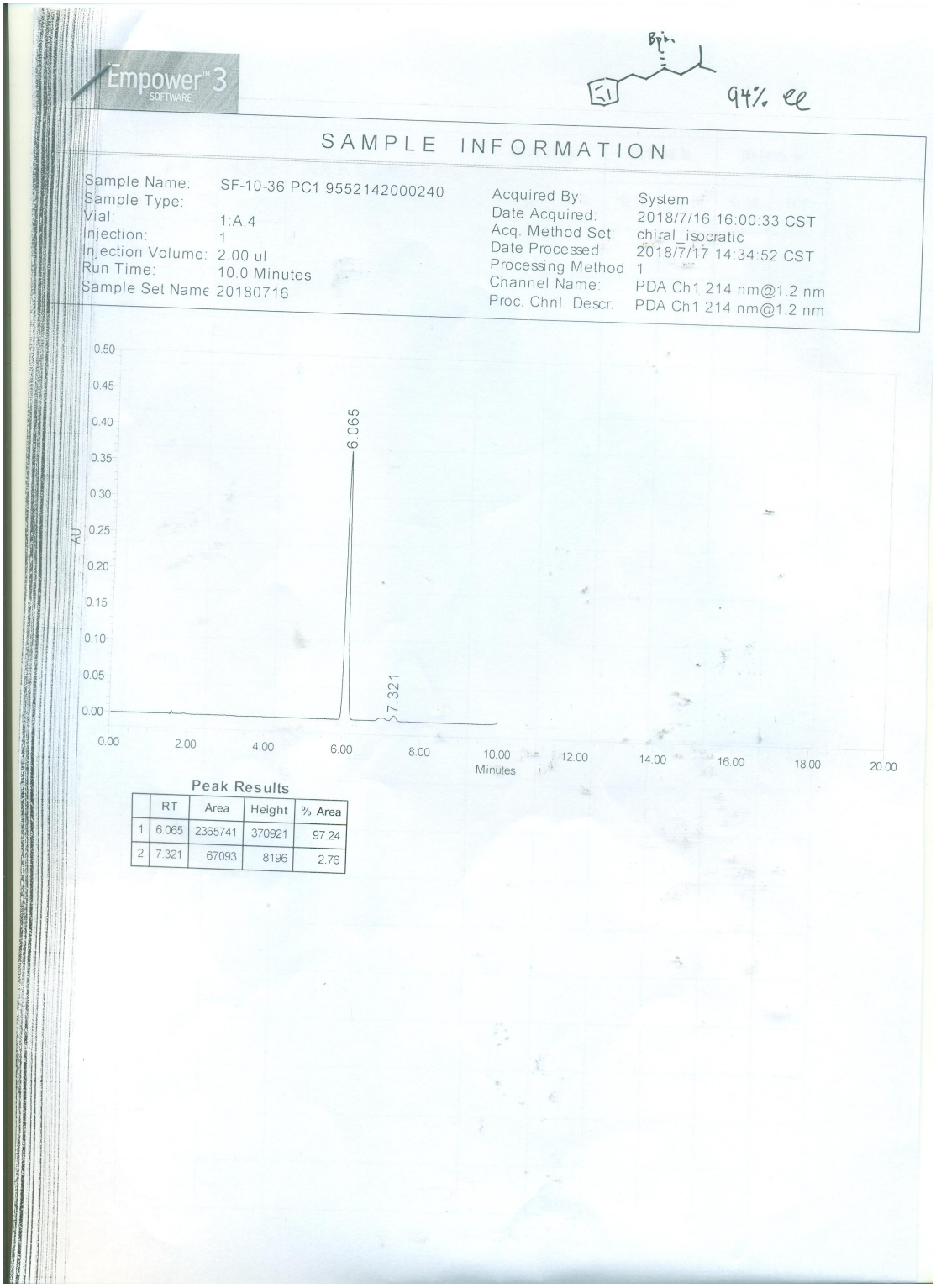


^{11}B NMR (193 MHz, CD_3Cl_3) spectrum of (*S*)-4,4,5,5-tetramethyl-2-(5-methyl-1-phenylhexan-3-yl)-1,3,2-dioxaborolane 5a



HPLC spectrum of
(*S*)-4,4,5,5-tetramethyl-2-(5-methyl-1-phenylhexan-3-yl)-1,3,2-dioxaborolane 5a

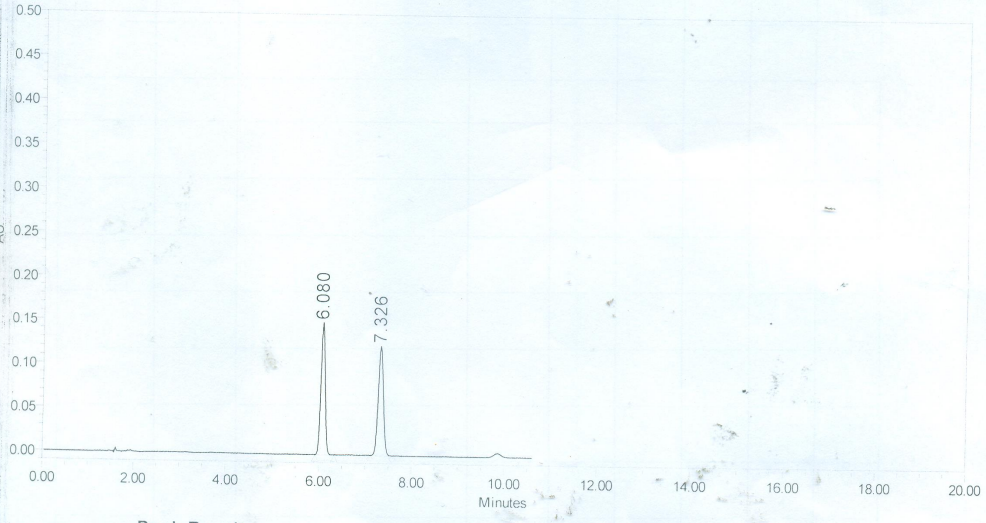
HPLC (C1, 0.46 × 25 cm, 5 μm, carbon dioxide/isopropanol = 95/5 (v/v %), flow 2.0 mL/min, UV detection at 214 nm, 2000 psi, 40 °C)



Empower 3 SOFTWARE

SAMPLE INFORMATION

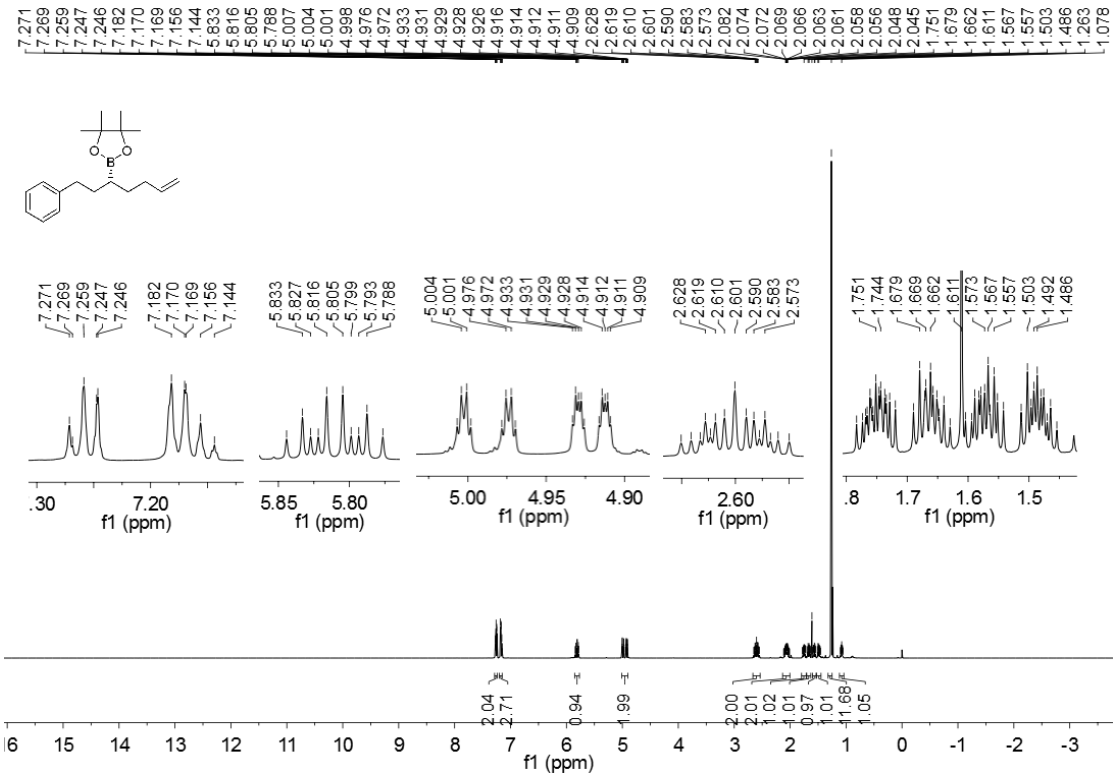
Sample Name:	SF-10-36+- PC1 9552142000240	Acquired By:	System
Sample Type:		Date Acquired:	2018/7/16 15:48:37 CST
Vial:	1:A,3	Acq. Method Set:	chiral_isocratic
Injection:	1	Date Processed:	2018/7/17 14:34:01 CST
Injection Volume:	2.00 ul	Processing Method	1
Run Time:	30.0 Minutes	Channel Name:	PDA Ch1 214 nm@1.2 nm
Sample Set Name	20180716	Proc. Chnl. Descr:	PDA Ch1 214 nm@1.2 nm



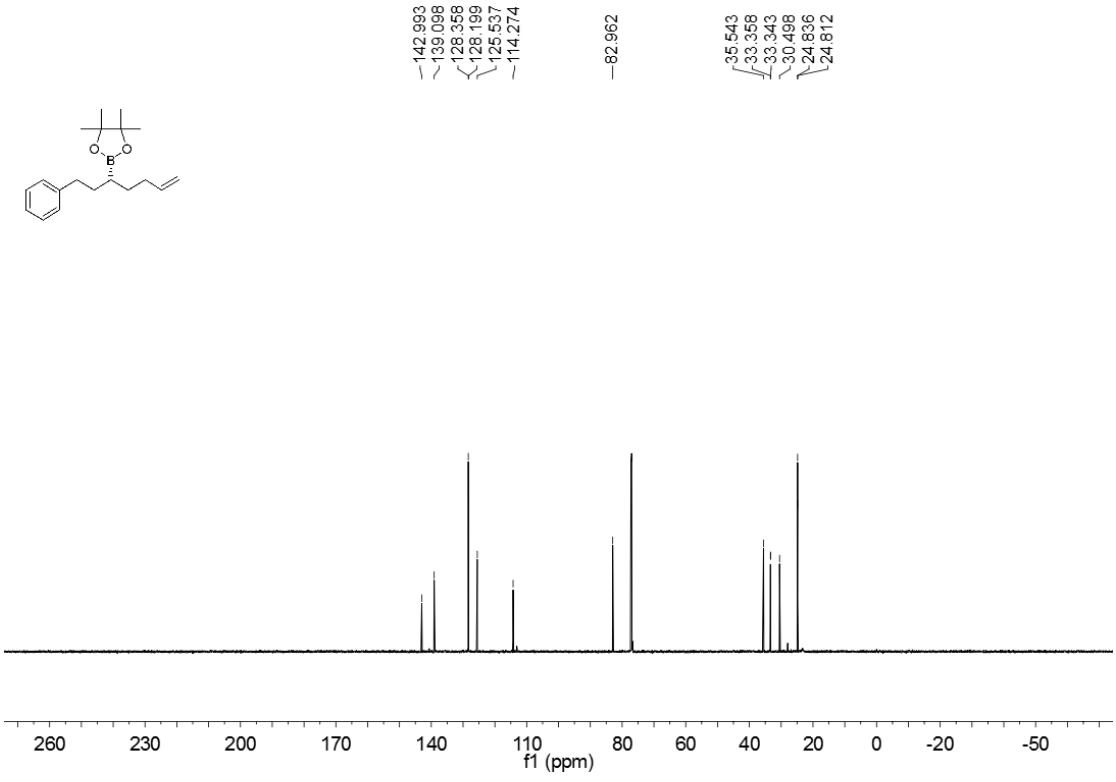
Peak Results

	RT	Area	Height	% Area
1	6.080	961772	150838	49.80
2	7.326	969632	124815	50.20

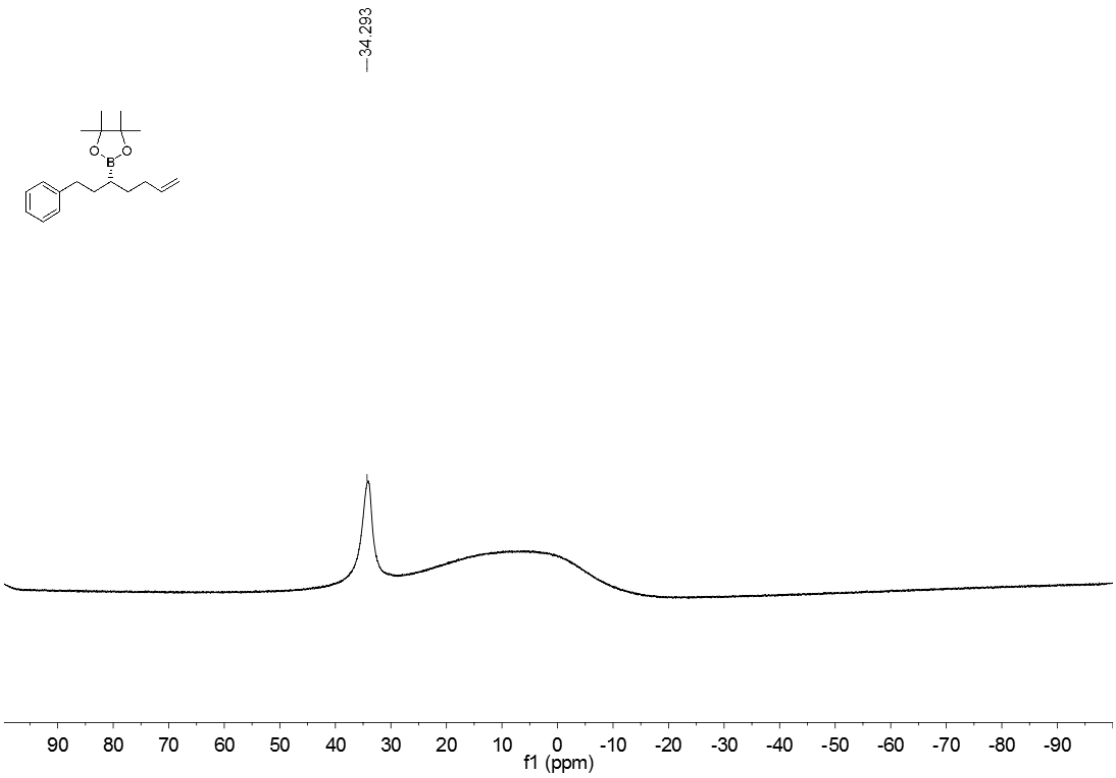
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
(*R*)-4,4,5,5-tetramethyl-2-(1-phenylhept-6-en-3-yl)-1,3,2-dioxaborolane 5b



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
(*R*)-4,4,5,5-tetramethyl-2-(1-phenylhept-6-en-3-yl)-1,3,2-dioxaborolane 5b

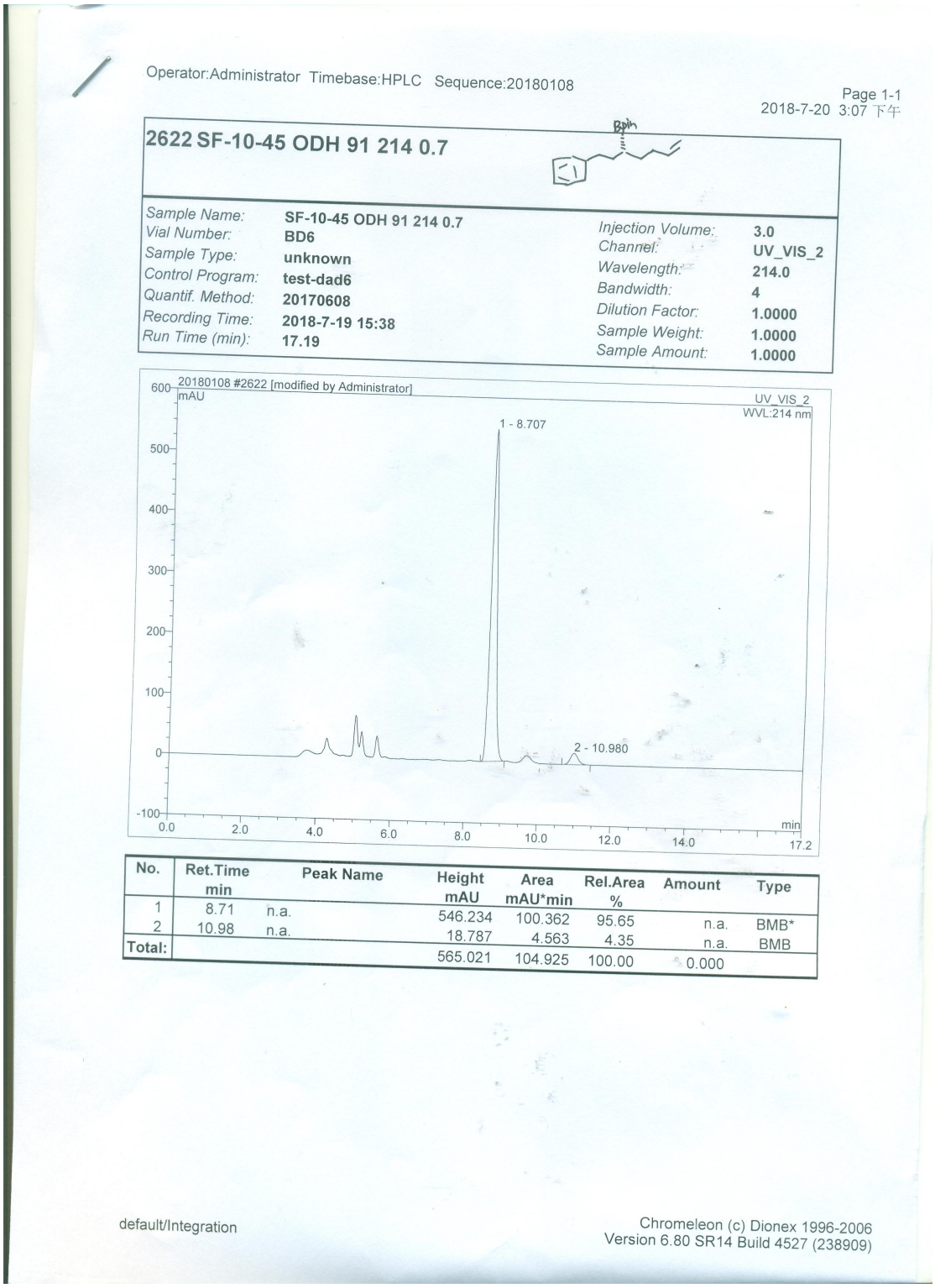


^{11}B NMR (193 MHz, CD_3Cl_3) spectrum of (*R*)-4,4,5,5-tetramethyl-2-(1-phenylhept-6-en-3-yl)-1,3,2-dioxaborolane 5b



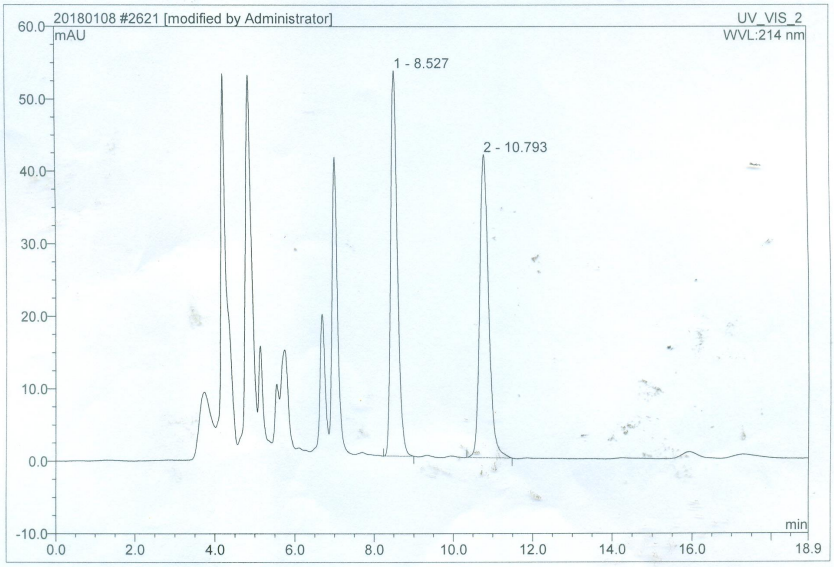
HPLC spectrum of
(*R*)-4,4,5,5-tetramethyl-2-(1-phenylhept-6-en-3-yl)-1,3,2-dioxaborolane 5b

HPLC (ODH, 0.46 × 25 cm, 5 μm, hexane/isopropanol = 9/1 (v/v %), flow 0.7 mL/min, UV detection at 214 nm)



2621 SF-10-45+- ODH 91 214 0.7

Sample Name:	**SF-10-45+- ODH 91 214 0.7**	*Injection Volume:*	**3.0**
Vial Number:	**BC6**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**214.0**
Control Program:	**test-dad6**	*Bandwidth:*	**4**
Quantif. Method:	**20170608**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018-7-19 15:18**	*Sample Weight:*	**1.0000**
Run Time (min):	**18.95**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.53	n.a.	53.234	10.495	48.95	n.a.	BMB
2	10.79	n.a.	41.825	10.945	51.05	n.a.	BMB
Total:			95.059	21.440	100.00	0.000	

default/Integration

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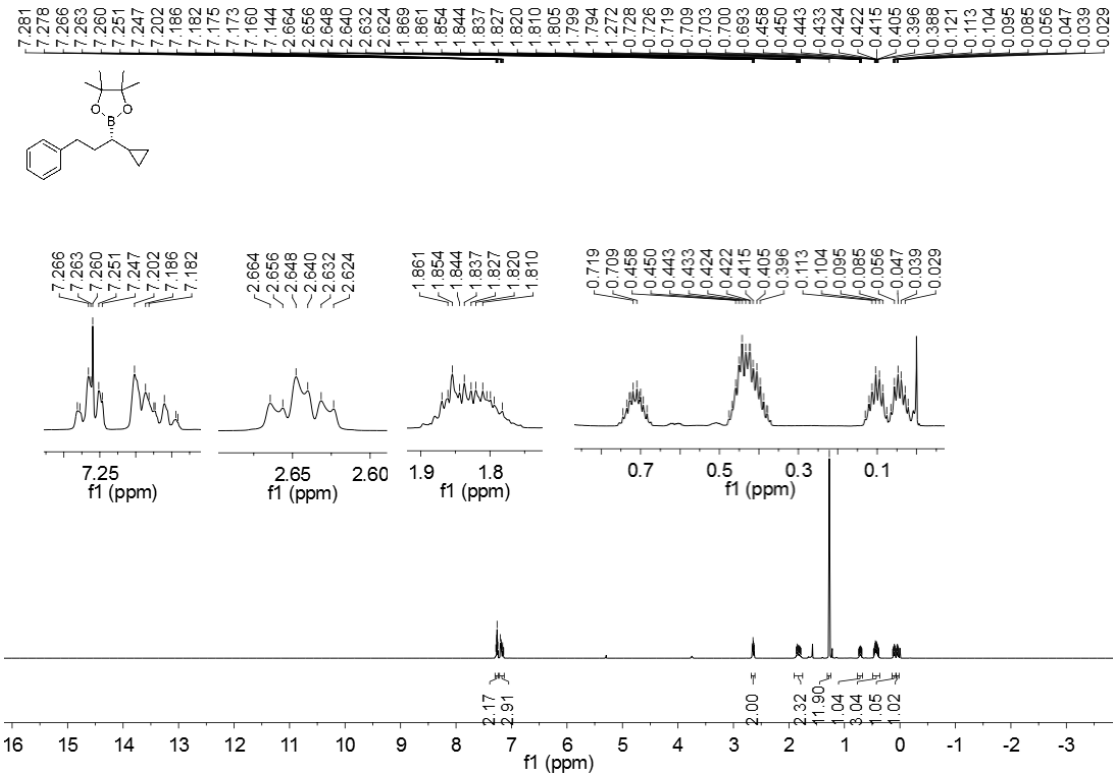
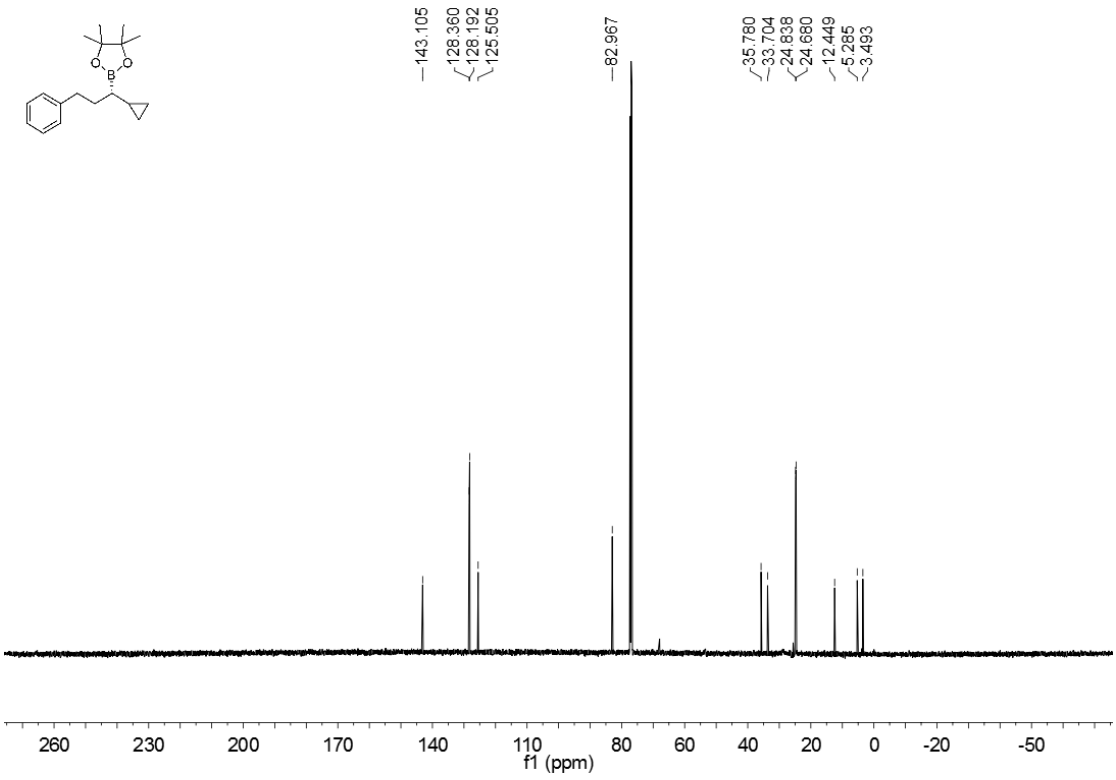
Version 6.80 SR14 Build 4527 (238909)

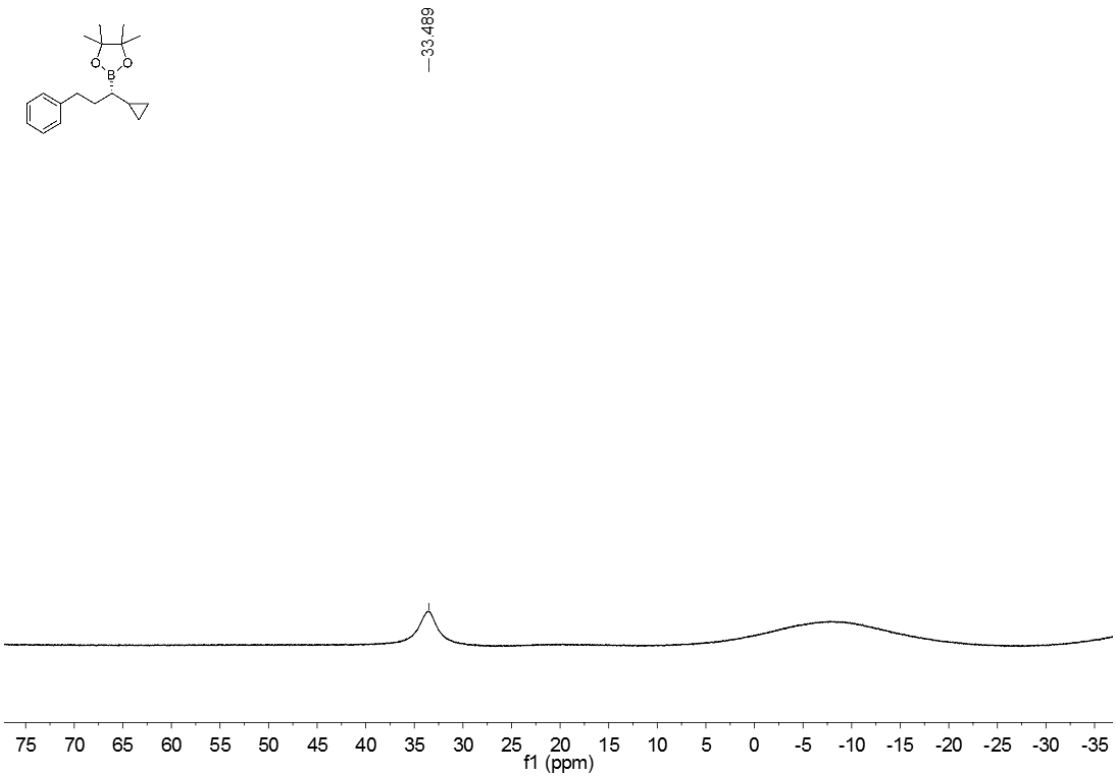
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of
(*S*)-2-(1-cyclopropyl-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5c



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of
(*S*)-2-(1-cyclopropyl-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5c

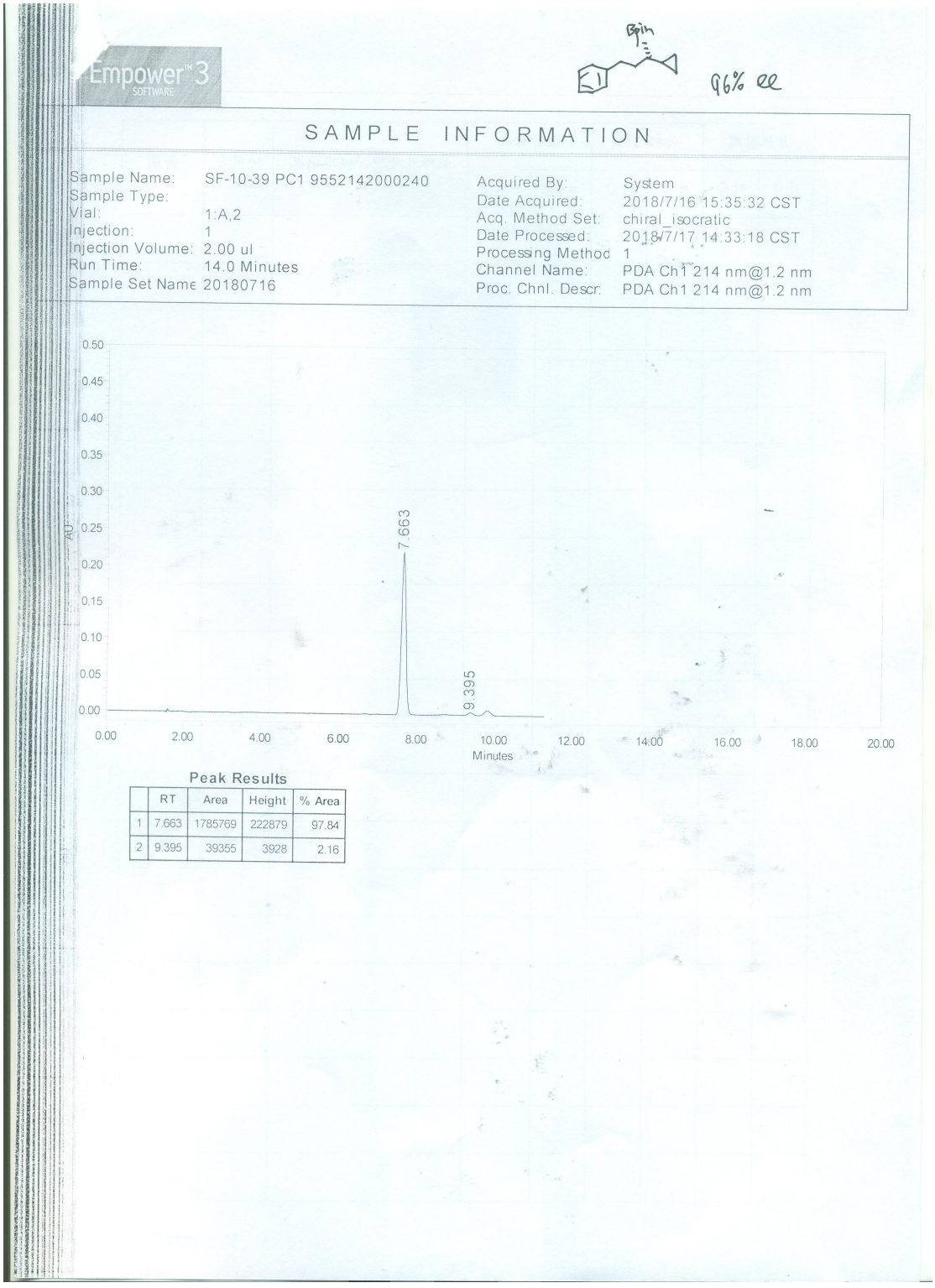


^{11}B NMR (160 MHz, CD_3Cl_3) spectrum of (*S*)-2-(1-cyclopropyl-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5c



HPLC spectrum of
(*S*)-2-(1-cyclopropyl-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5c

HPLC (C1, 0.46 × 25 cm, 5 μm, carbon dioxide/isopropanol = 95/5 (v/v %), flow 2.0 mL/min, UV detection at 214 nm, 2000 psi, 40 °C)



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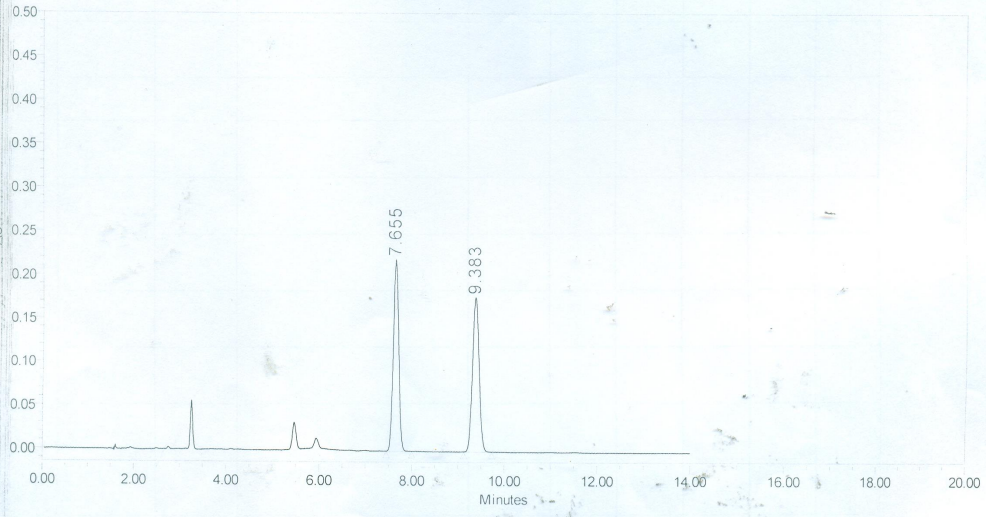
SAMPLE INFORMATION

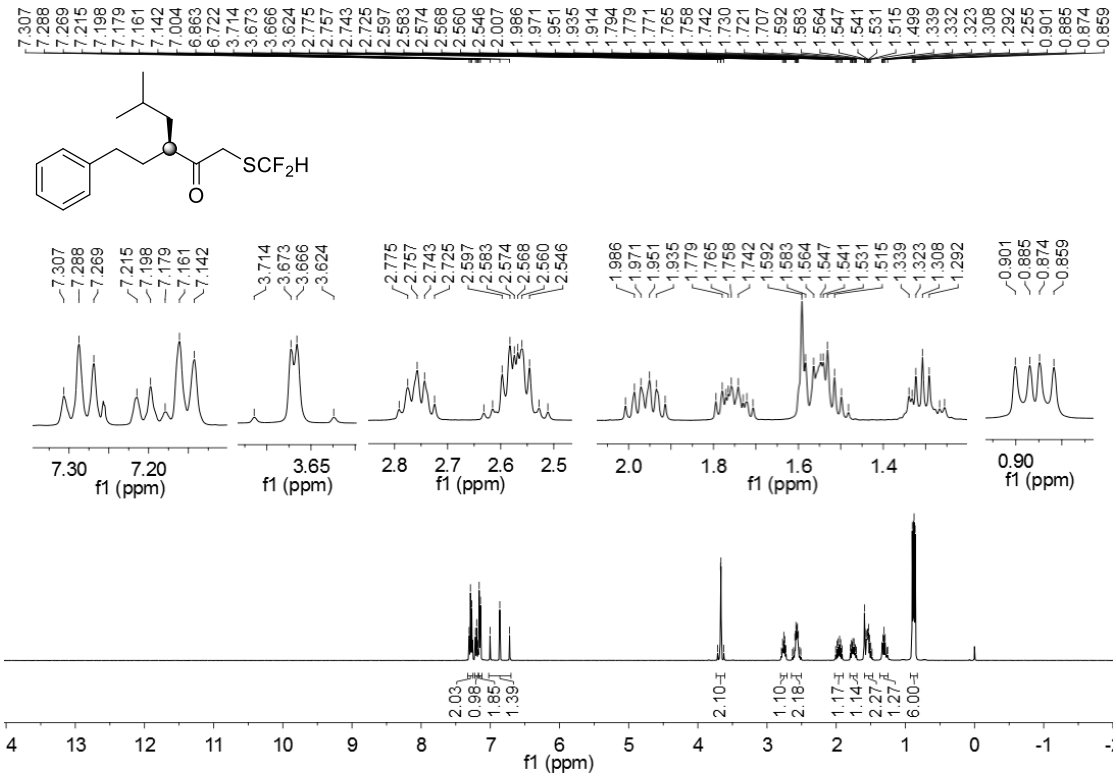
Sample Name:	SF-10-39+- PC1 9552142000240	Acquired By:	System
Sample Type:		Date Acquired:	2018/7/16 15:20:40 CST
Vial:	1:A,1	Acq. Method Set:	chiral_isocratic
Injection:	1	Date Processed:	2018/7/17 14:32:52 CST
Injection Volume:	2.00 ul	Processing Method	1
Run Time:	14.0 Minutes	Channel Name:	PDA Ch1 214 nm@1.2 nm
Sample Set Name	20180716	Proc. Chnl. Descr:	PDA Ch1 214 nm@1.2 nm



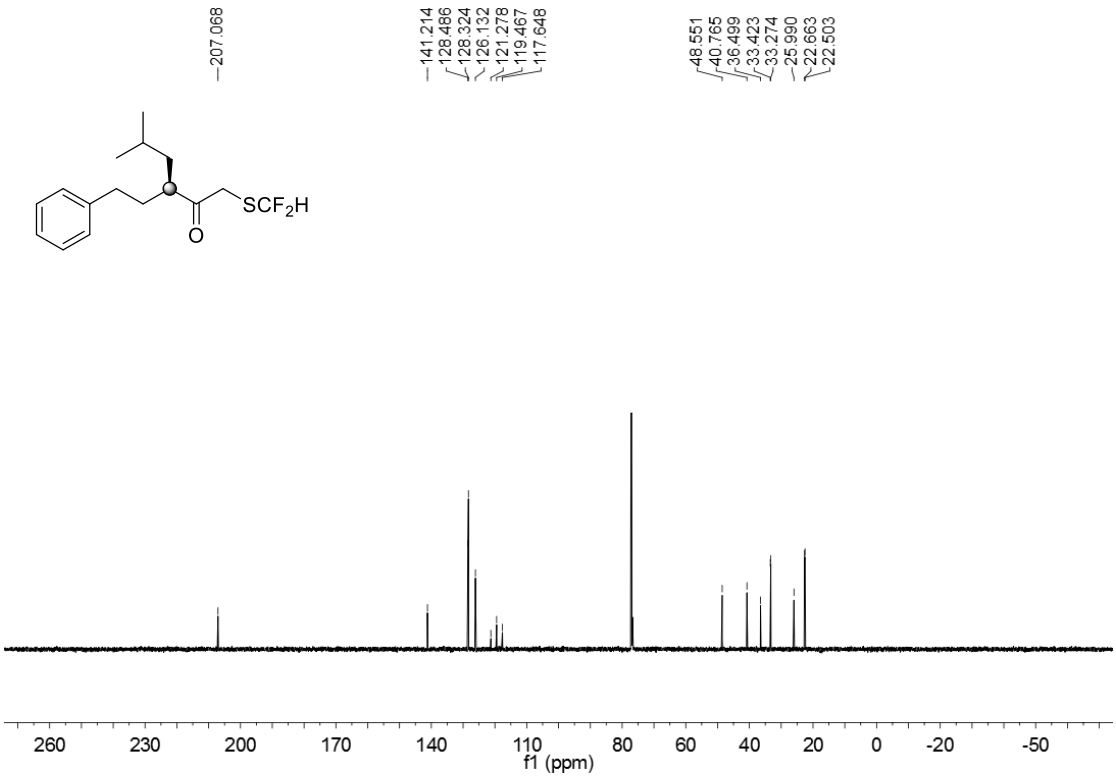
Peak Results

	RT	Area	Height	% Area
1	7.655	1779014	220537	50.05
2	9.383	1775747	177741	49.95

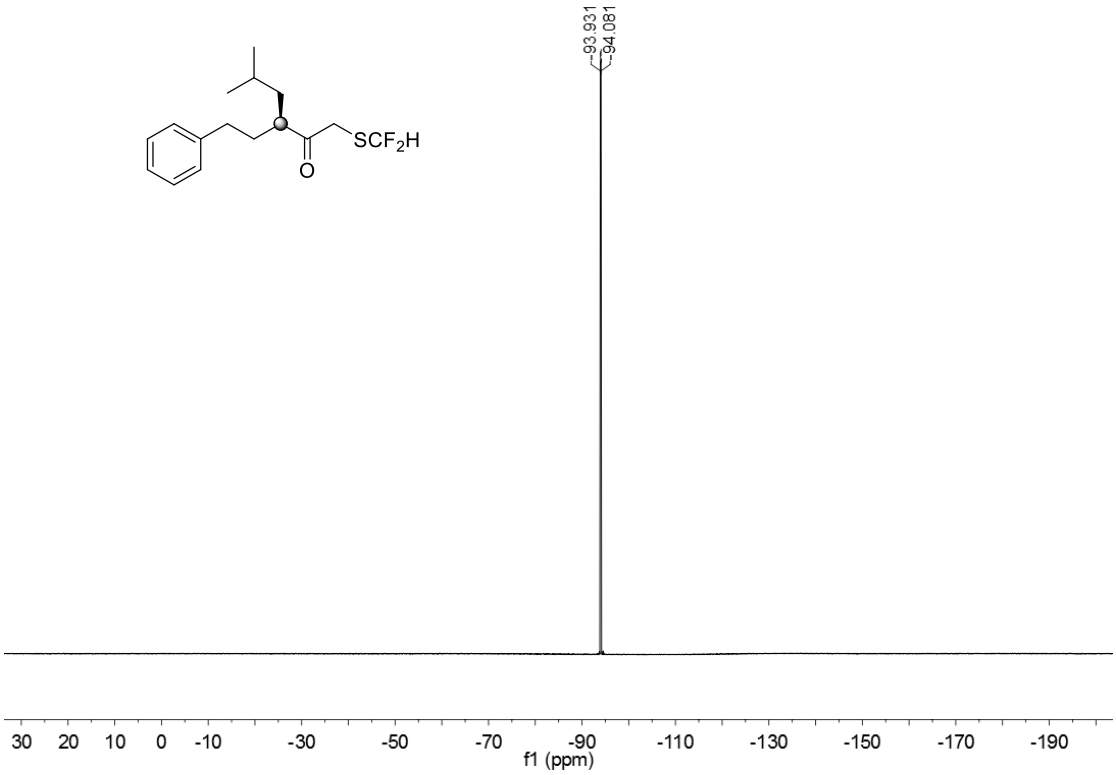
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of
(*S*)-1-(difluoromethylthio)-5-methyl-3-phenethylhexan-2-one 6a



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
(*S*)-1-(difluoromethylthio)-5-methyl-3-phenethylhexan-2-one 6a

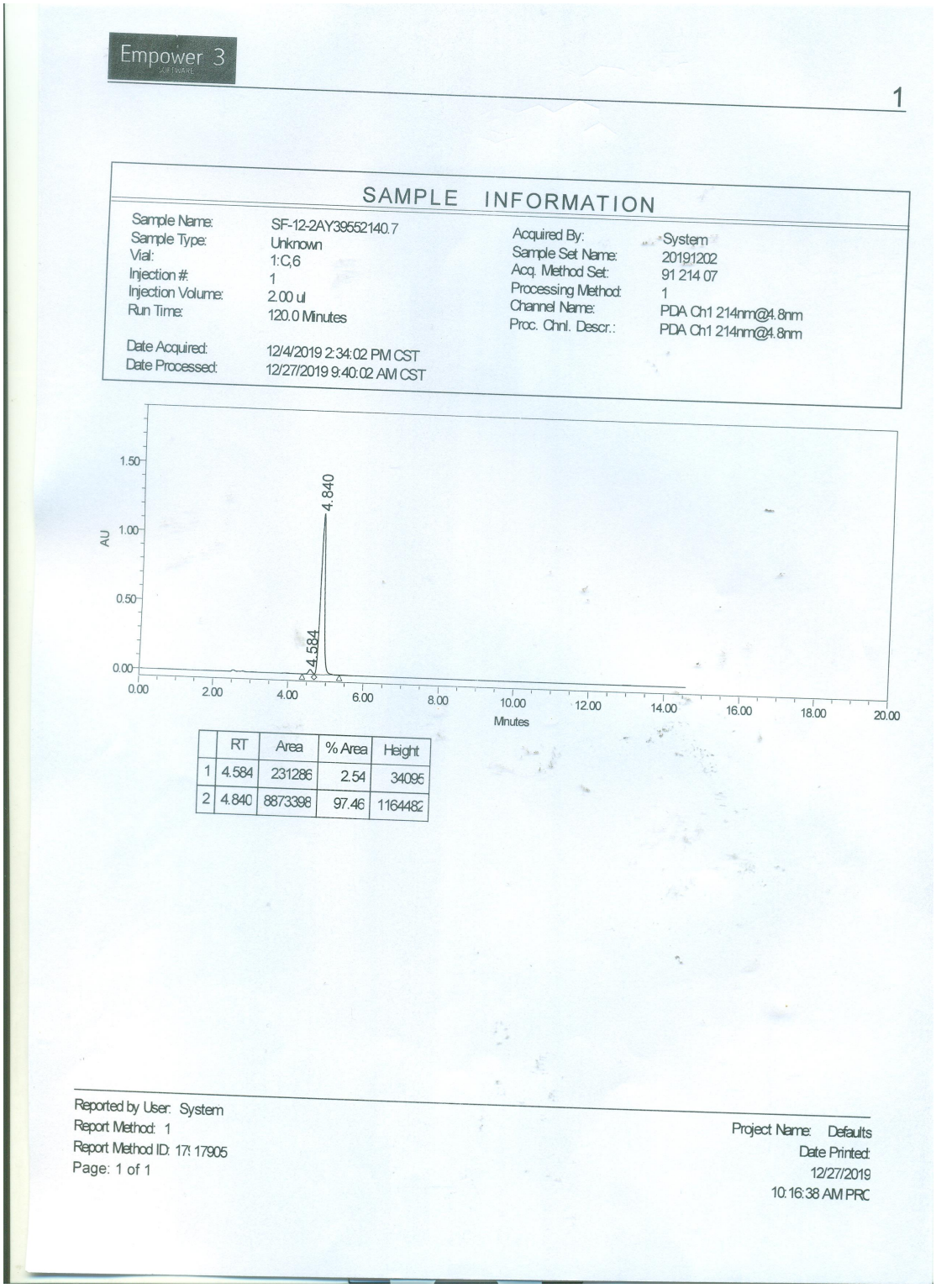


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of
(*S*)-1-(difluoromethylthio)-5-methyl-3-phenethylhexan-2-one 6a

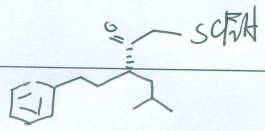


HPLC spectrum of
(*S*)-1-(difluoromethylthio)-5-methyl-3-phenethylhexan-2-one 6a

HPLC (AY3, 0.46 × 15 cm, 3 μm, hexane/isopropanol = 95/5 (v/v %), flow 0.7 mL/min, UV detection at 214 nm)

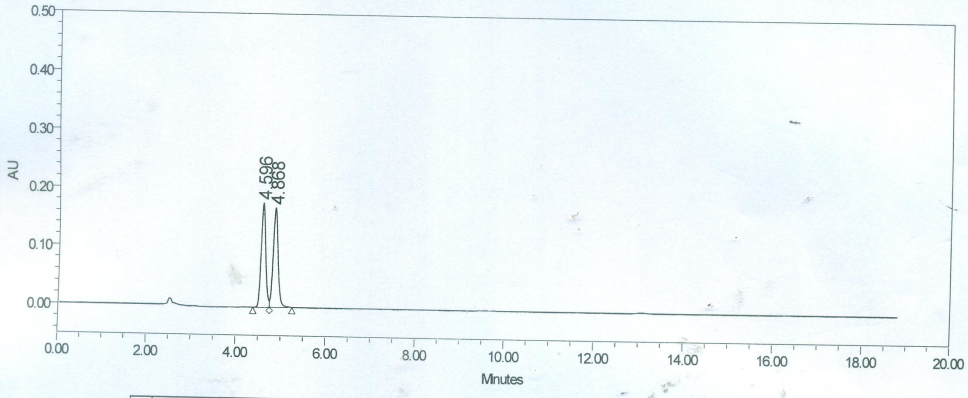


Empower 3
SOFTWARE



SAMPLE INFORMATION

Sample Name:	SF-12-2+-AY39552140.7	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	20191202
Vial:	1:C,5	Acq. Method Set:	91 214 07
Injection #:	1	Processing Method:	1
Injection Volume:	2.00 ul	Channel Name:	PDA Ch1 214nm@4.8nm
Run Time:	120.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 214nm@4.8nm
Date Acquired:	12/4/2019 2:14:28 PM CST		
Date Processed:	12/27/2019 9:39:37 AM CST		

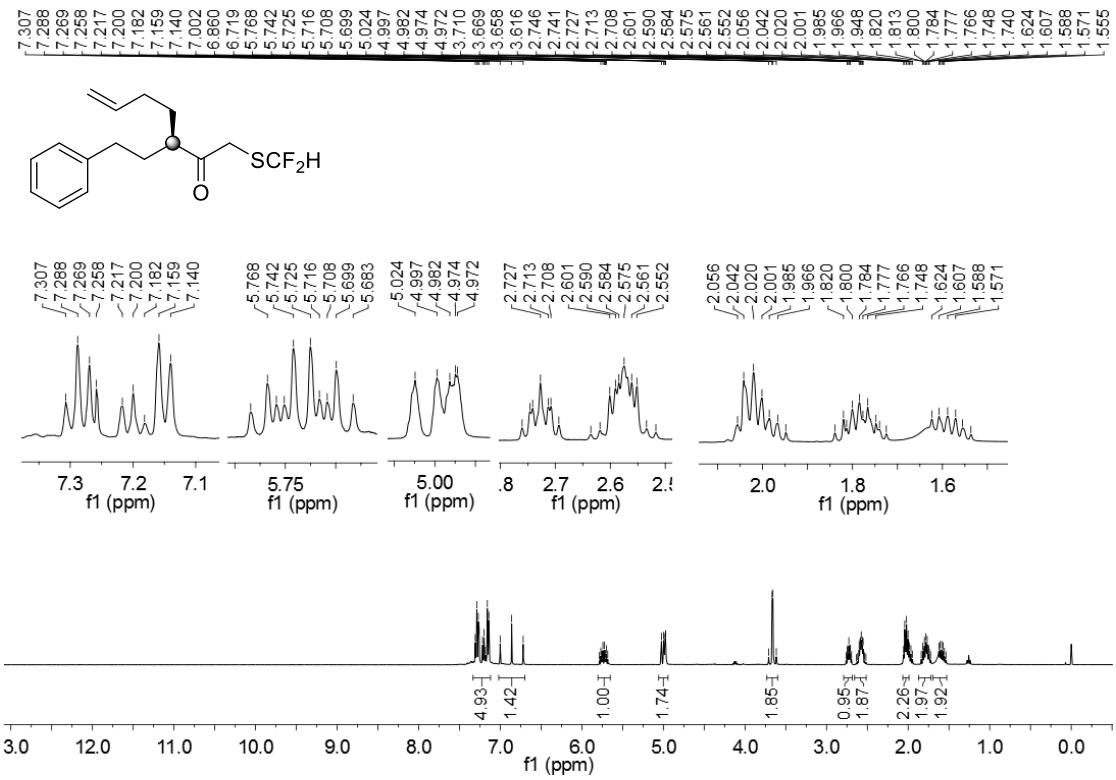


	RT	Area	% Area	Height
1	4.596	1249816	49.13	178795
2	4.868	1293888	50.87	170215

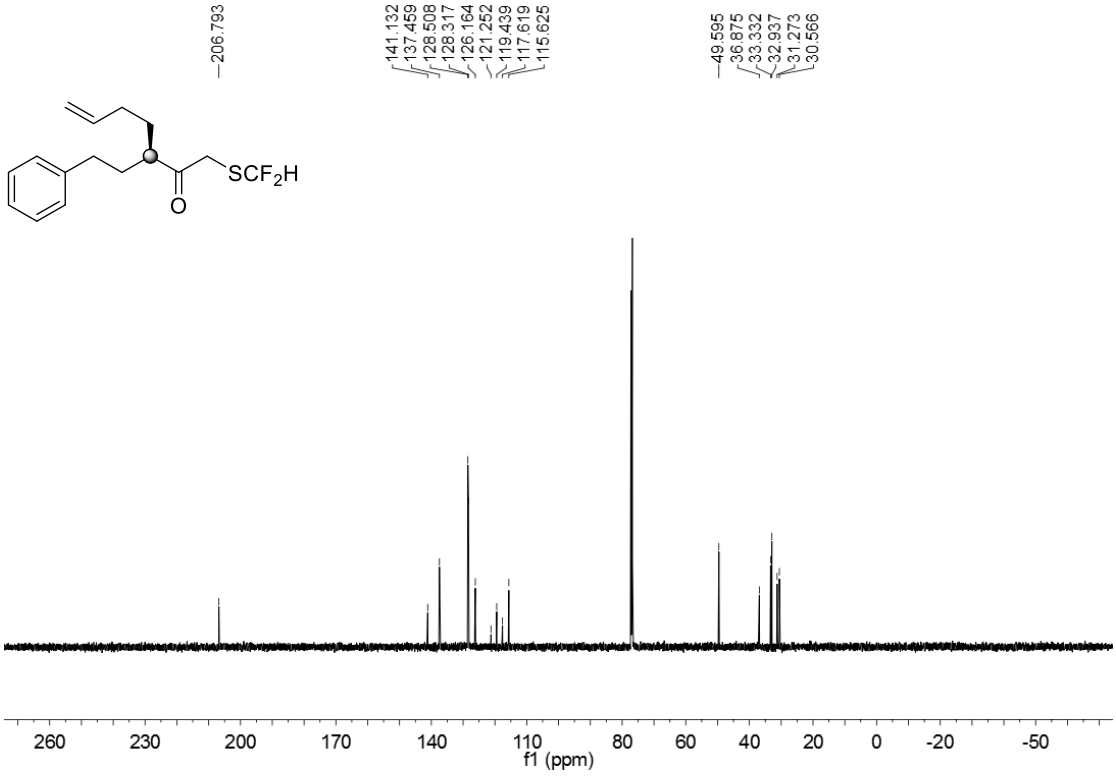
Reported by User: System
Report Method: 1
Report Method ID: 17! 17904
Page: 1 of 1

Project Name: Defaults
Date Printed:
12/27/2019
10:14:20 AM PRC

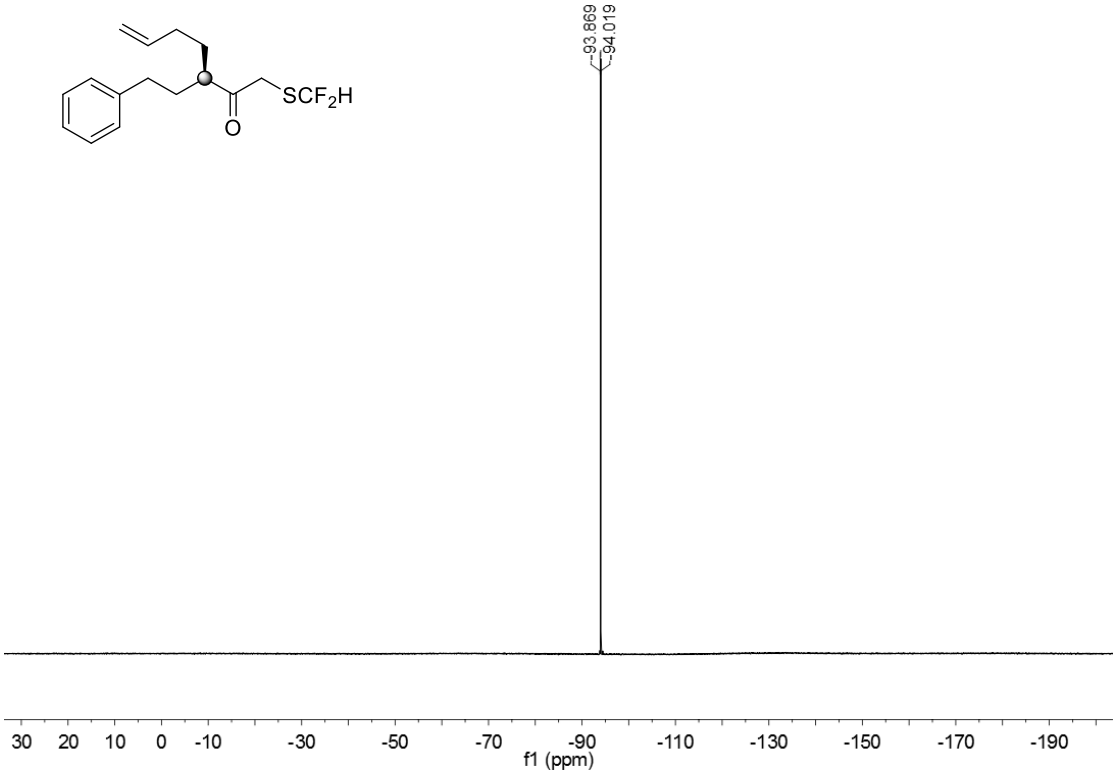
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-1-(difluoromethylthio)-3-phenethylhept-6-en-2-one 6b



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (*R*)-1-(difluoromethylthio)-3-phenethylhept-6-en-2-one 6b



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of
(*R*)-1-(difluoromethylthio)-3-phenethylhept-6-en-2-one 6b



HPLC spectrum of
(*R*)-1-(difluoromethylthio)-3-phenethylhept-6-en-2-one 6b

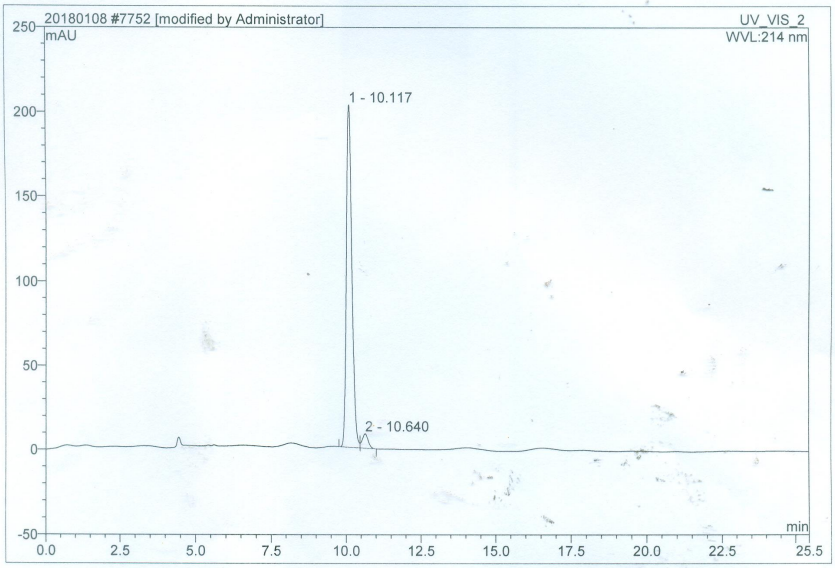
HPLC (ODH, 0.46 × 25 cm, 5 μm, hexane/isopropanol = 95/5 (v/v %), flow 0.7 mL/min, UV detection at 214 nm)

Operator:Administrator Timebase:HPLC Sequence:20180108

Page 1-1
2019-12-27 9:49 上午

7752 SF-12-6 ODH 955 214 0.7

Sample Name:	**SF-12-6 ODH 955 214 0.7**	*Injection Volume:*	**3.0**
Vial Number:	**RD7**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**214.0**
Control Program:	**test-dad4**	*Bandwidth:*	**4**
Quantif. Method:	**20170608**	*Dilution Factor:*	**1.0000**
Recording Time:	**2019-12-9 12:13**	*Sample Weight:*	**1.0000**
Run Time (min):	**25.46**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.12	n.a.	202.781	43.308	95.61	n.a.	BM
2	10.64	n.a.	8.623	1.991	4.39	n.a.	MB
Total:			211.403	45.298	100.00	0.000	

default/Integration

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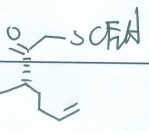
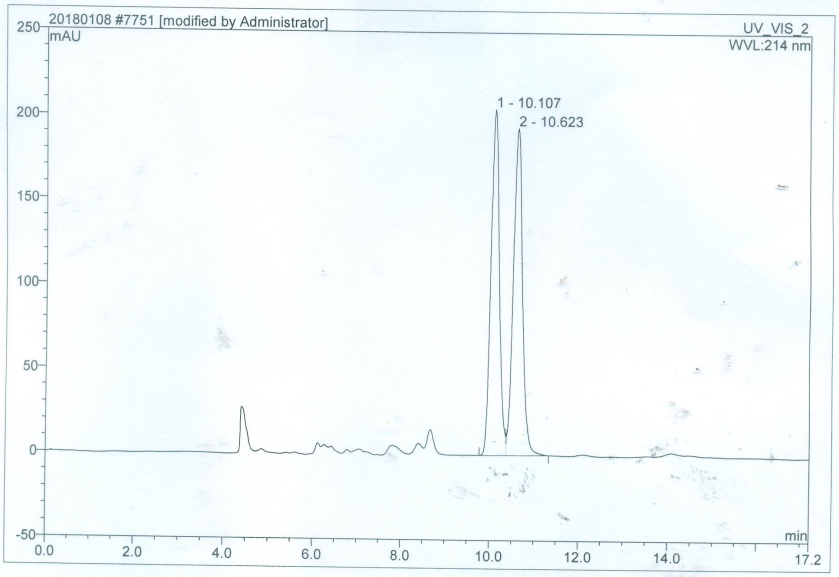
Version 6.80 SR14 Build 4527 (238909)



7751 SF-12-6+- ODH 955 214 0.7

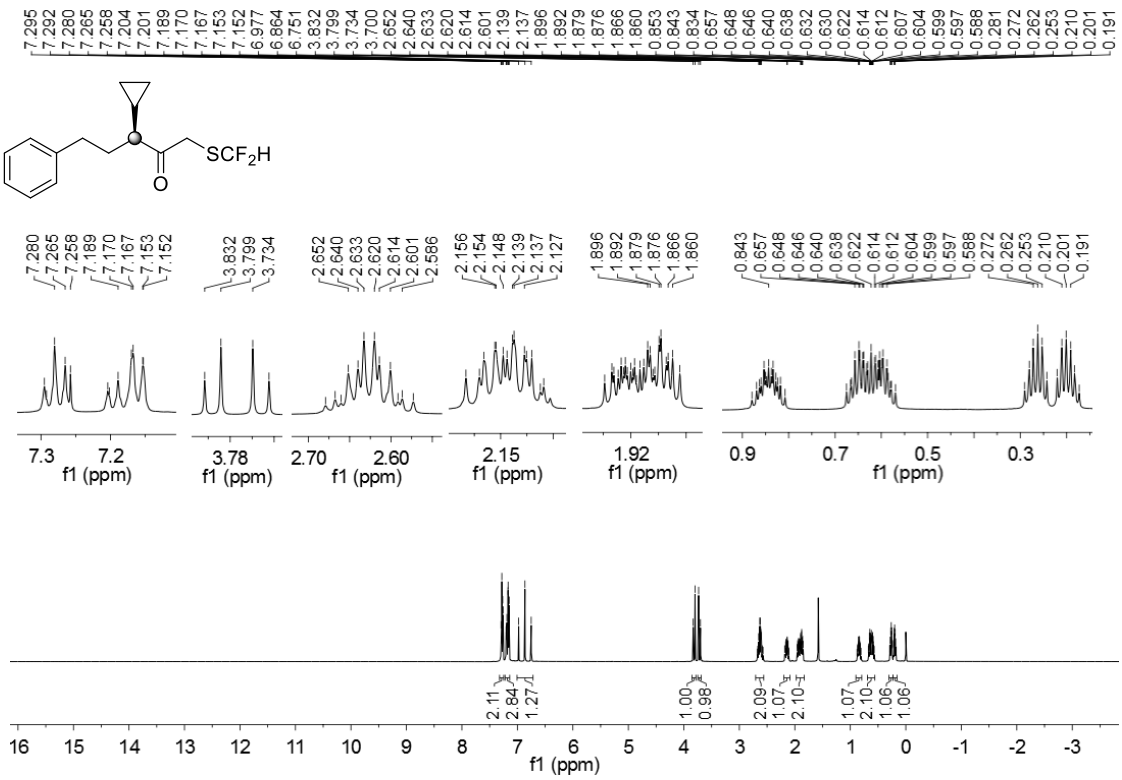
Sample Name:	**SF-12-6+- ODH 955 214 0.7**	*Injection Volume:*	**3.0**
Vial Number:	**RD6**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**214.0**
Control Program:	**test-dad4**	*Bandwidth:*	**4**
Quantif. Method:	**20170608**	*Dilution Factor:*	**1.0000**
Recording Time:	**2019-12-9 11:54**	*Sample Weight:*	**1.0000**
Run Time (min):	**17.20**	*Sample Amount:*	**1.0000**



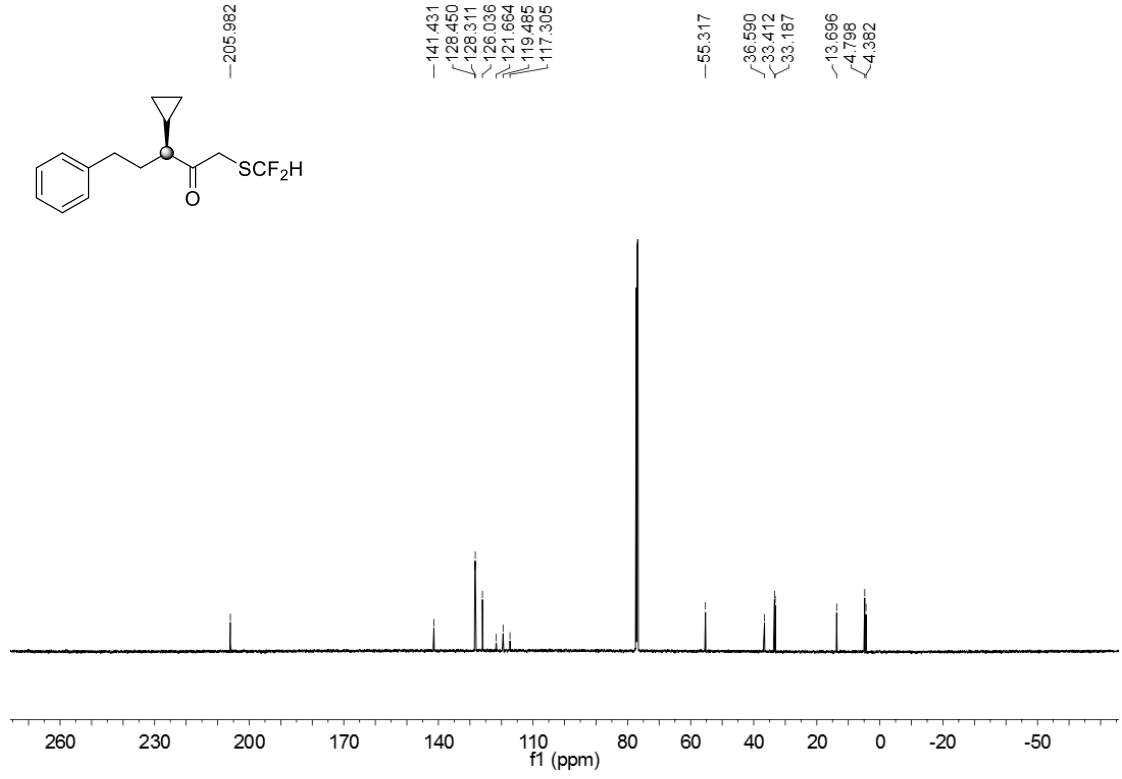
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.11	n.a.	204.681	45.129	49.33	n.a.	BM
2	10.62	n.a.	193.563	46.351	50.67	n.a.	MB
Total:			398.244	91.480	100.00	0.000	

default/Integration

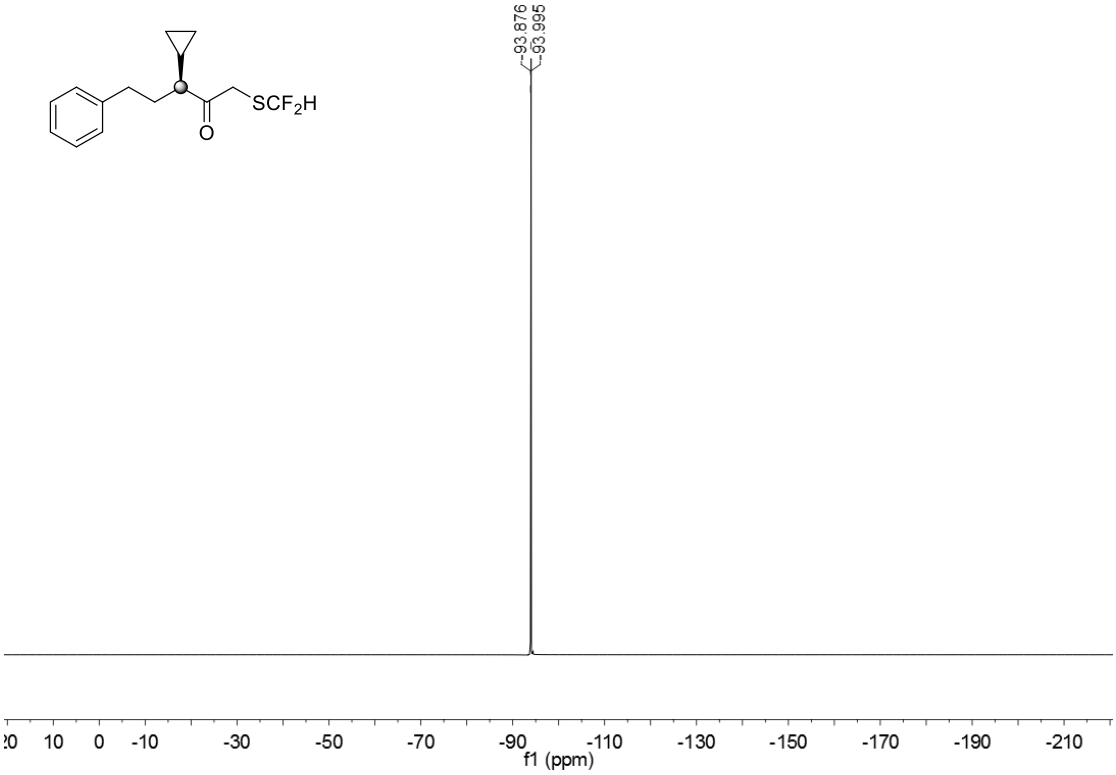
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (*S*)-3-cyclopropyl-1-(difluoromethylthio)-5-phenylpentan-2-one 6c



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (*S*)-3-cyclopropyl-1-(difluoromethylthio)-5-phenylpentan-2-one 6c

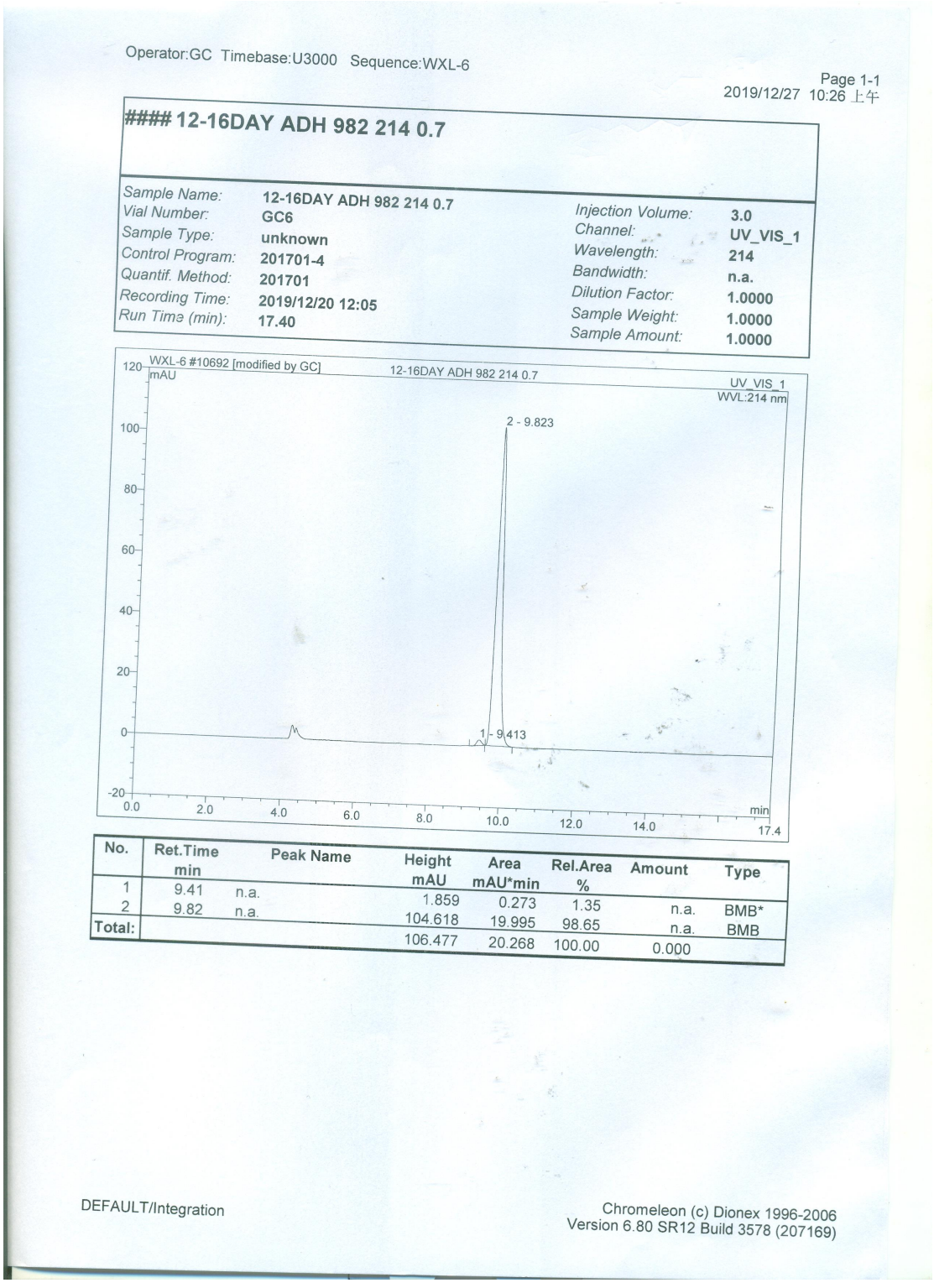


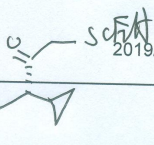
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of
(*S*)-3-cyclopropyl-1-(difluoromethylthio)-5-phenylpentan-2-one 6c



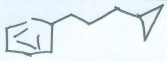
HPLC spectrum of
(*S*)-3-cyclopropyl-1-(difluoromethylthio)-5-phenylpentan-2-one 6c

HPLC (ADH, 0.46 × 25 cm, 5 μm, hexane/isopropanol = 98/2 (v/v %), flow 0.7 mL/min, UV detection at 214 nm)

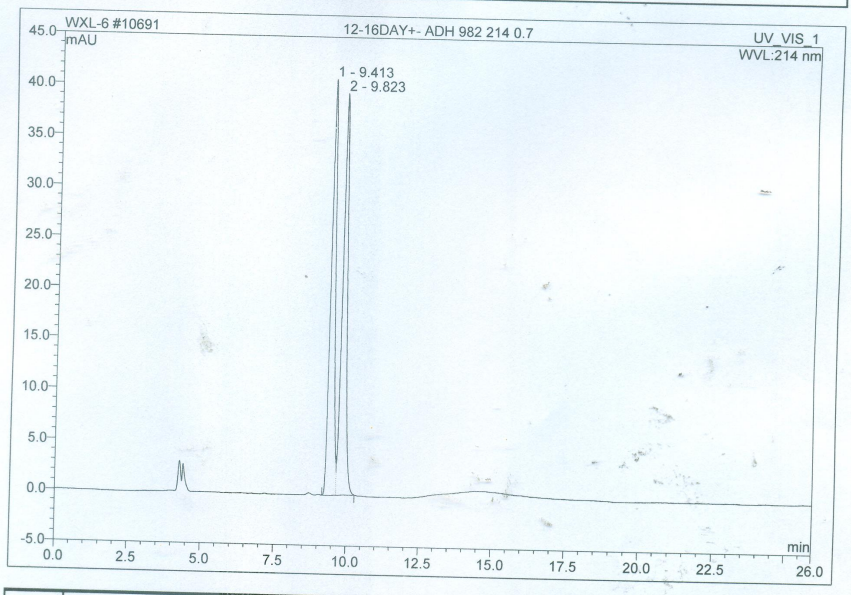




12-16DAY+- ADH 982 214 0.7

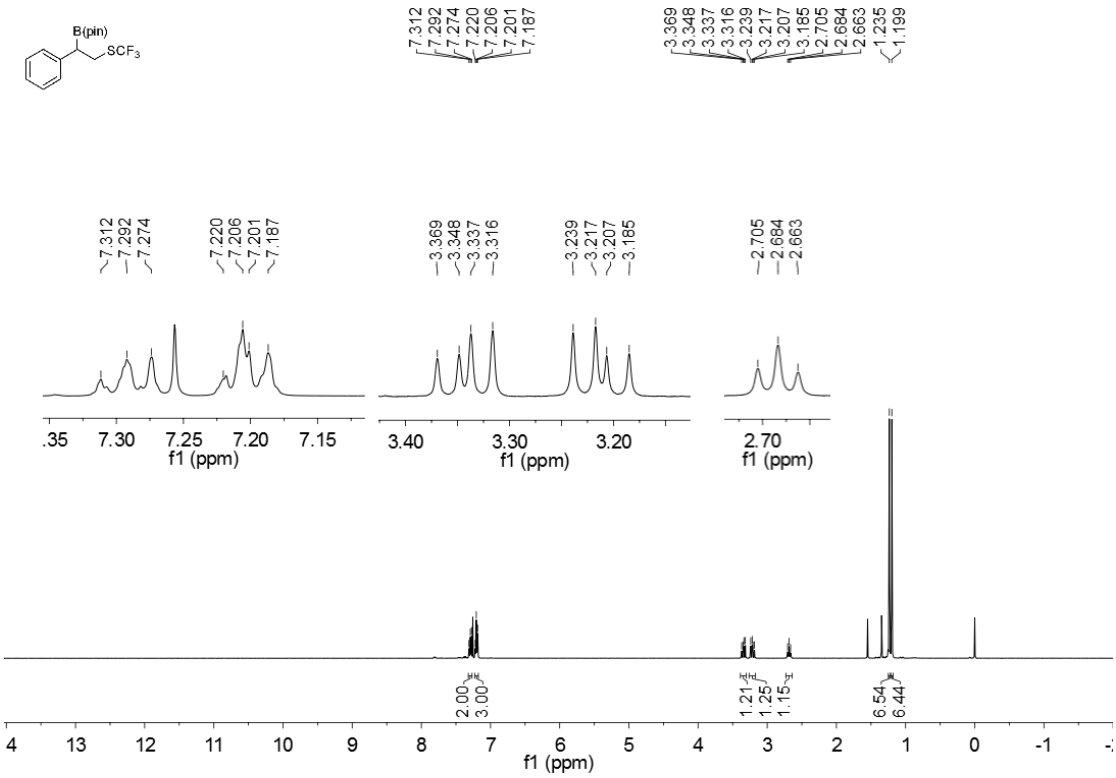


Sample Name:	**12-16DAY+- ADH 982 214 0.7**	*Injection Volume:*	**3.0**
Vial Number:	**GD6**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**201701-4**	*Bandwidth:*	**n.a.**
Quantif. Method:	**201701**	*Dilution Factor:*	**1.0000**
Recording Time:	**2019/12/20 12:26**	*Sample Weight:*	**1.0000**
Run Time (min):	**25.96**	*Sample Amount:*	**1.0000**

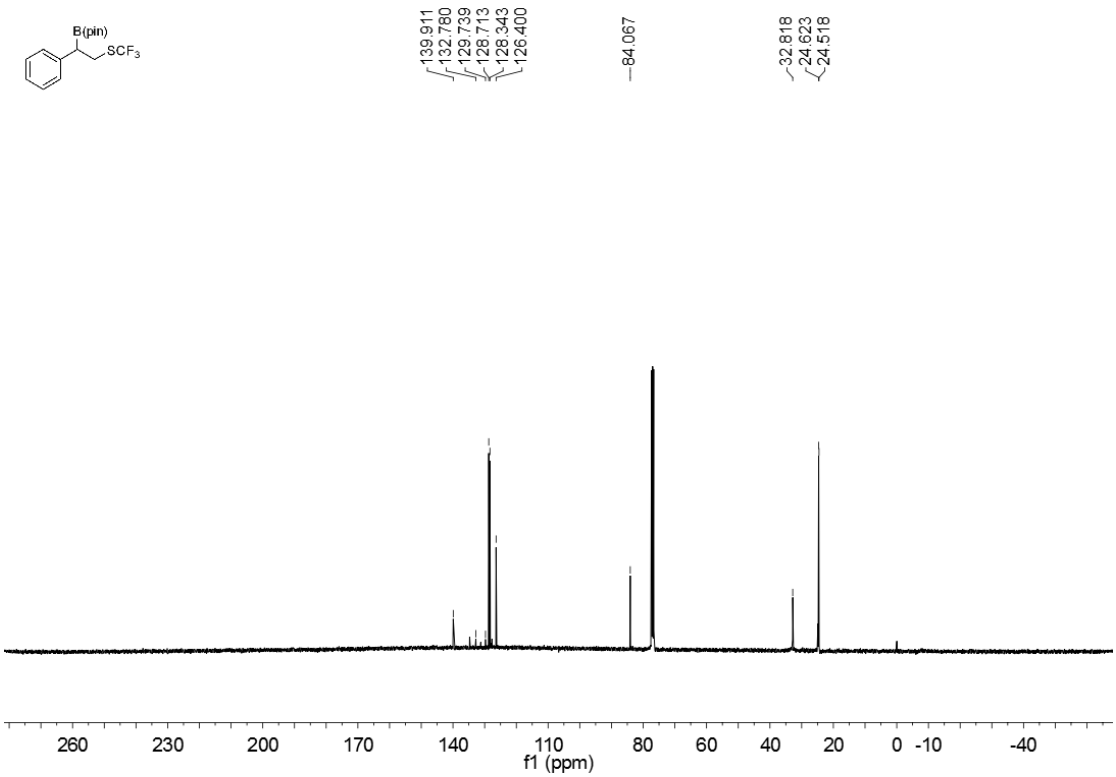


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.41	n.a.	40.925	7.365	49.20	n.a.	BM
2	9.82	n.a.	39.522	7.605	50.80	n.a.	MB
Total:			80.447	14.970	100.00	0.000	

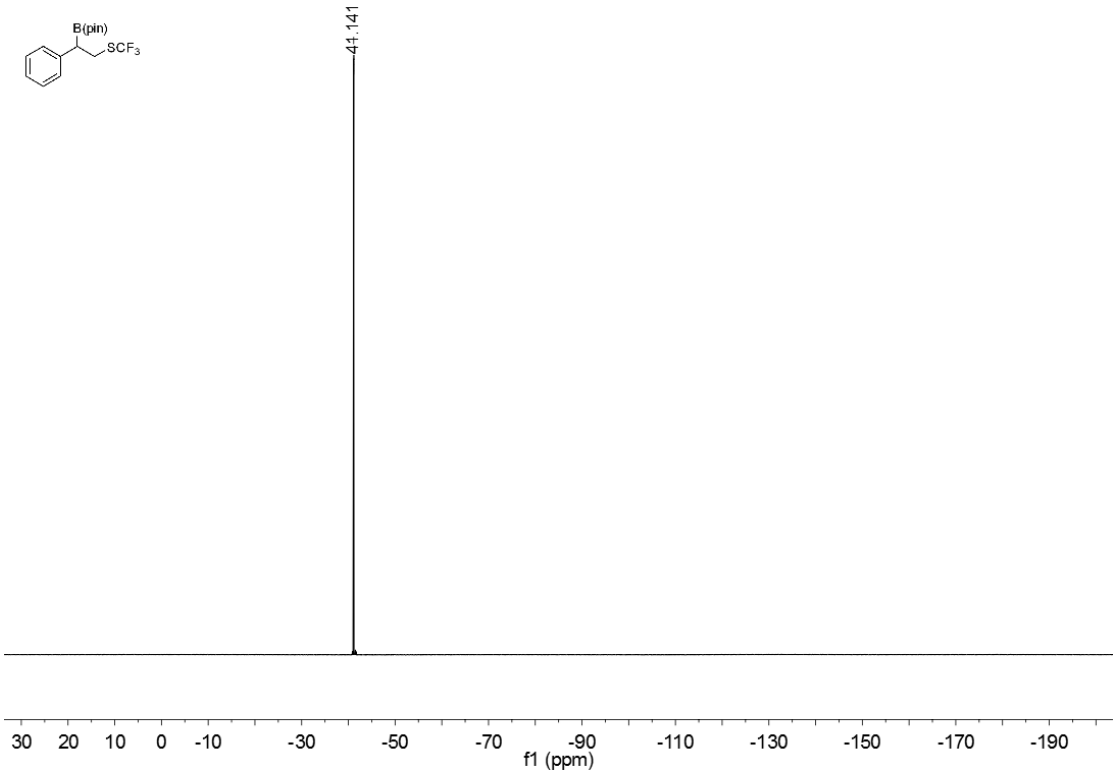
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-phenyl-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8a



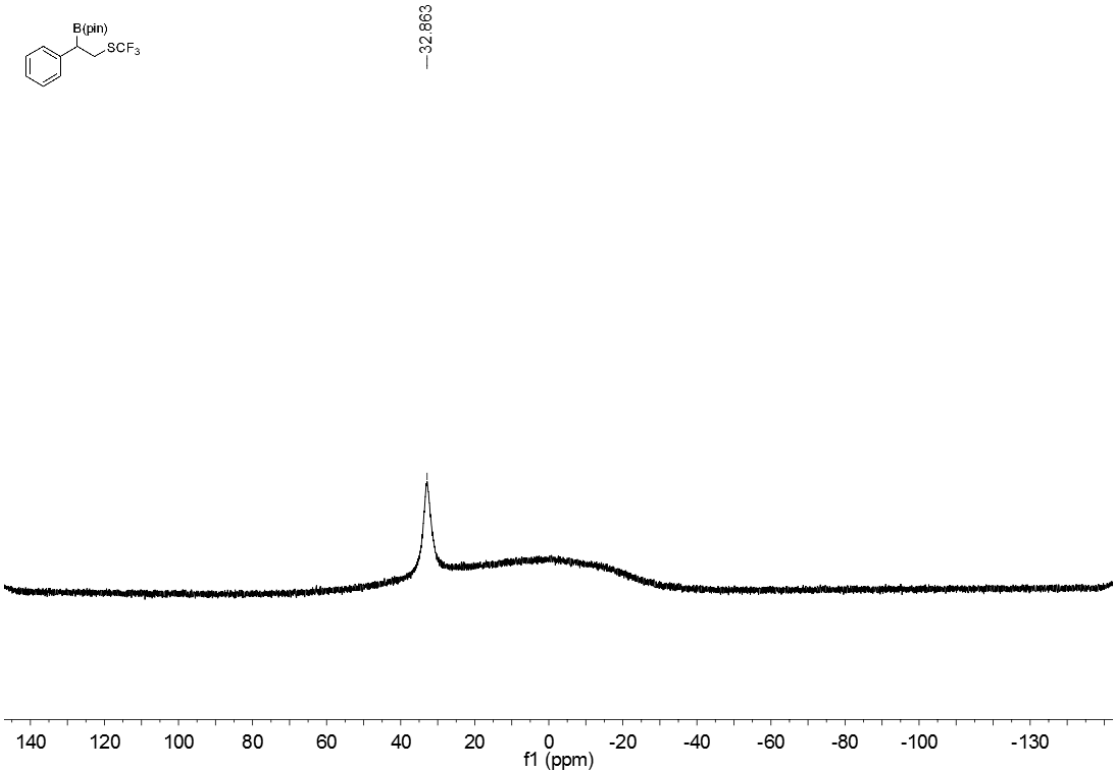
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-phenyl-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8a



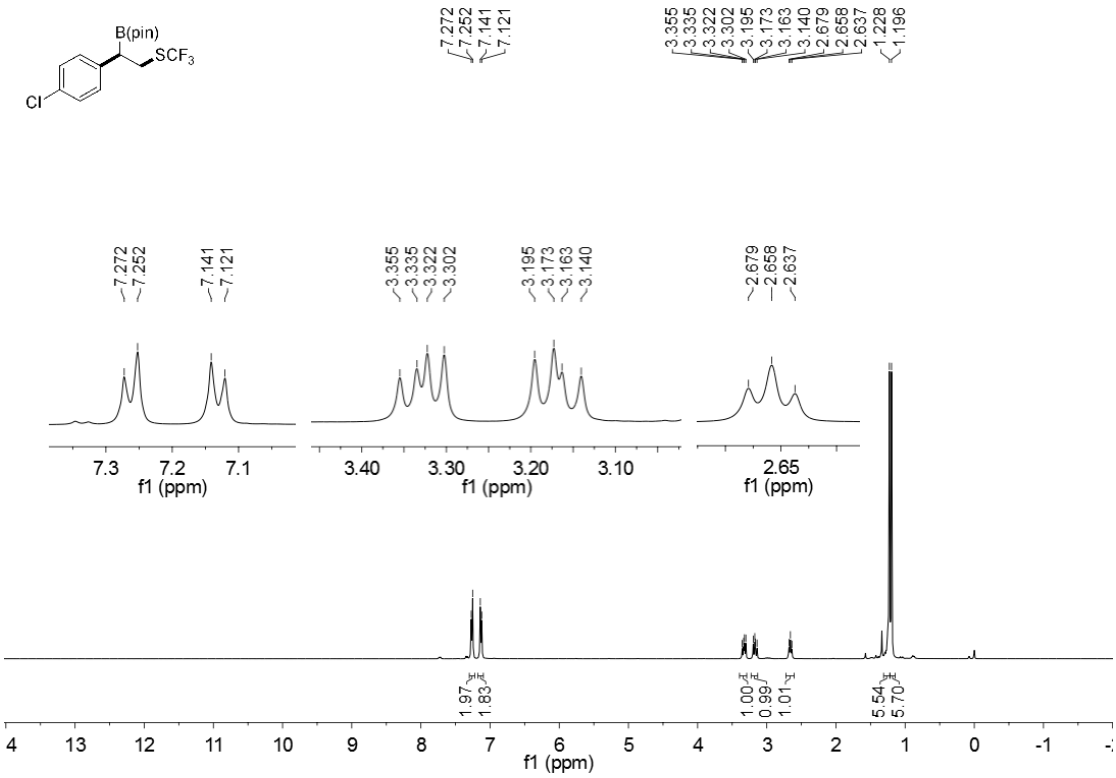
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-phenyl-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8a



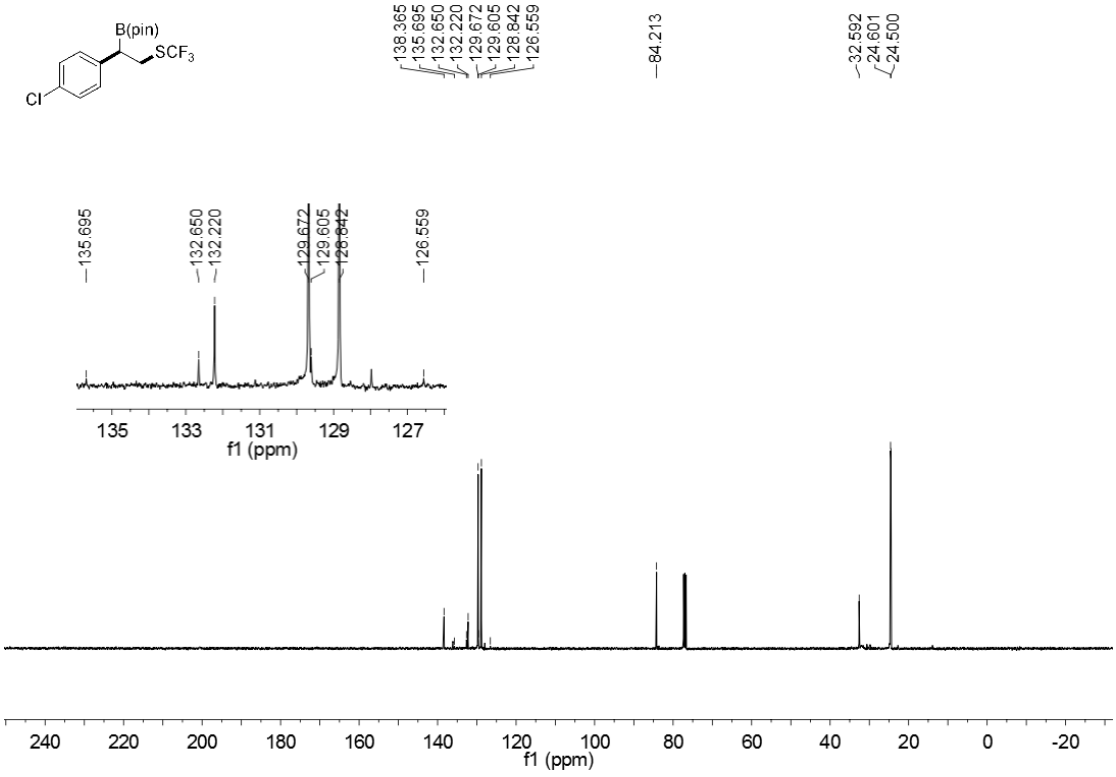
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 4,4,5,5-tetramethyl-2-(1-phenyl-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8a



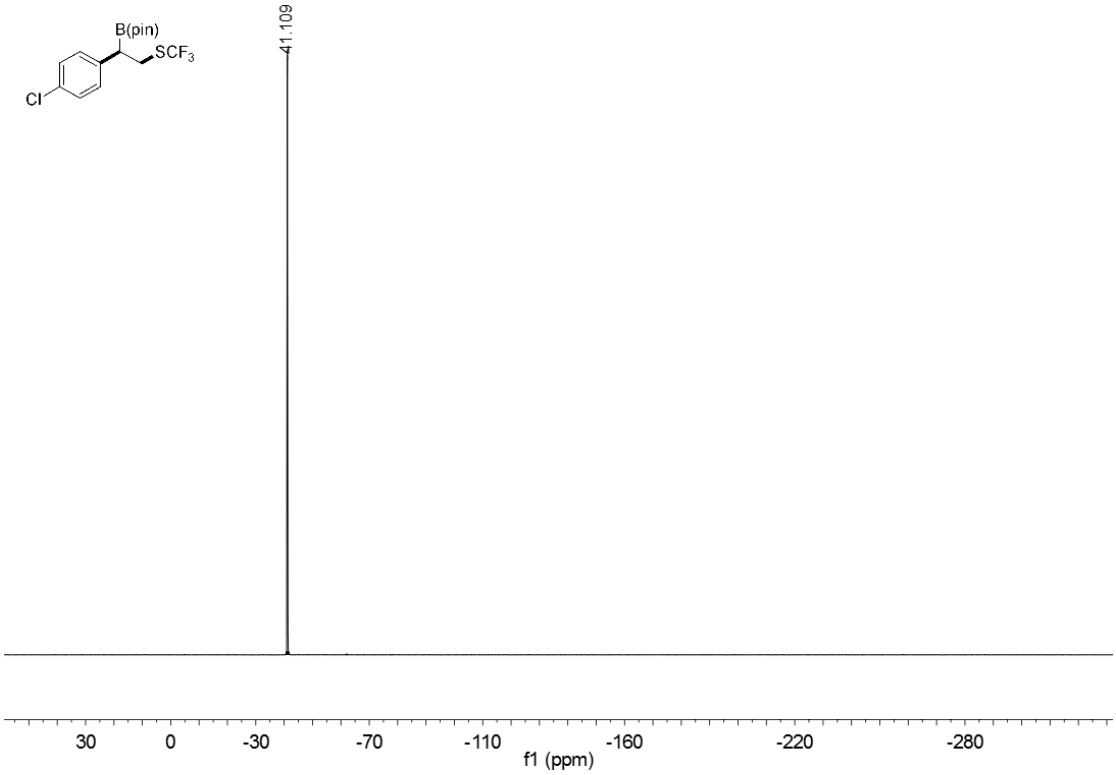
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(1-(4-chlorophenyl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8b



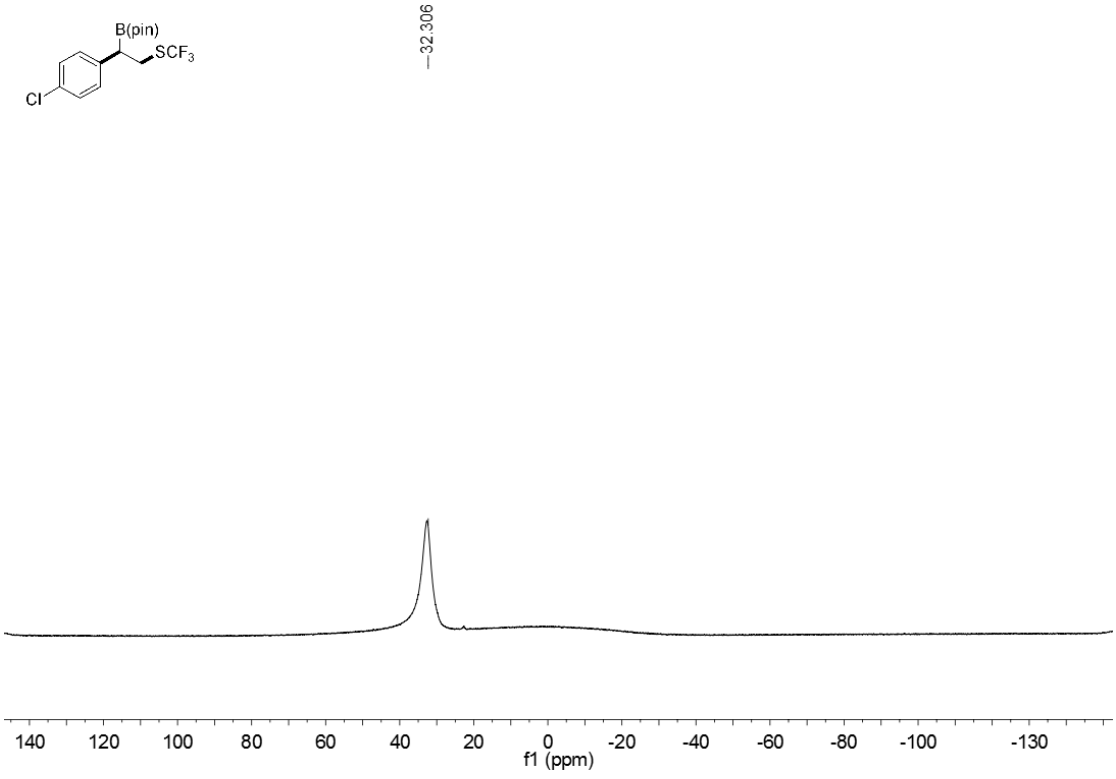
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-(1-(4-chlorophenyl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8b



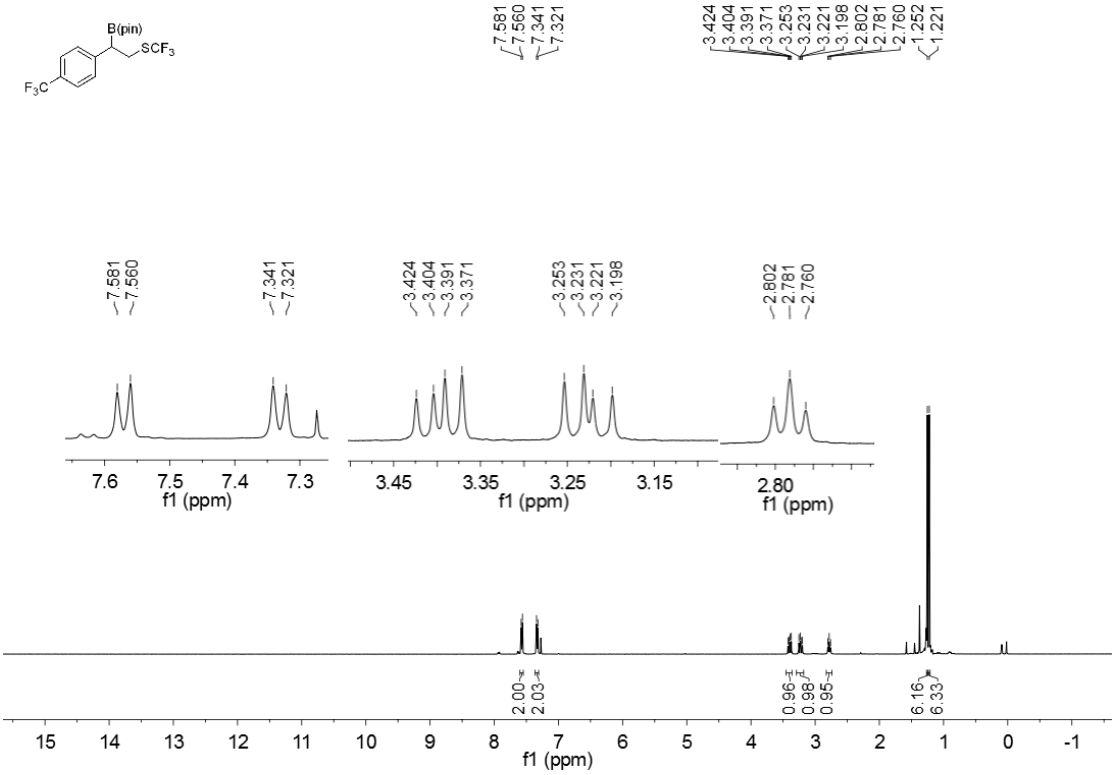
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(1-(4-chlorophenyl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8b



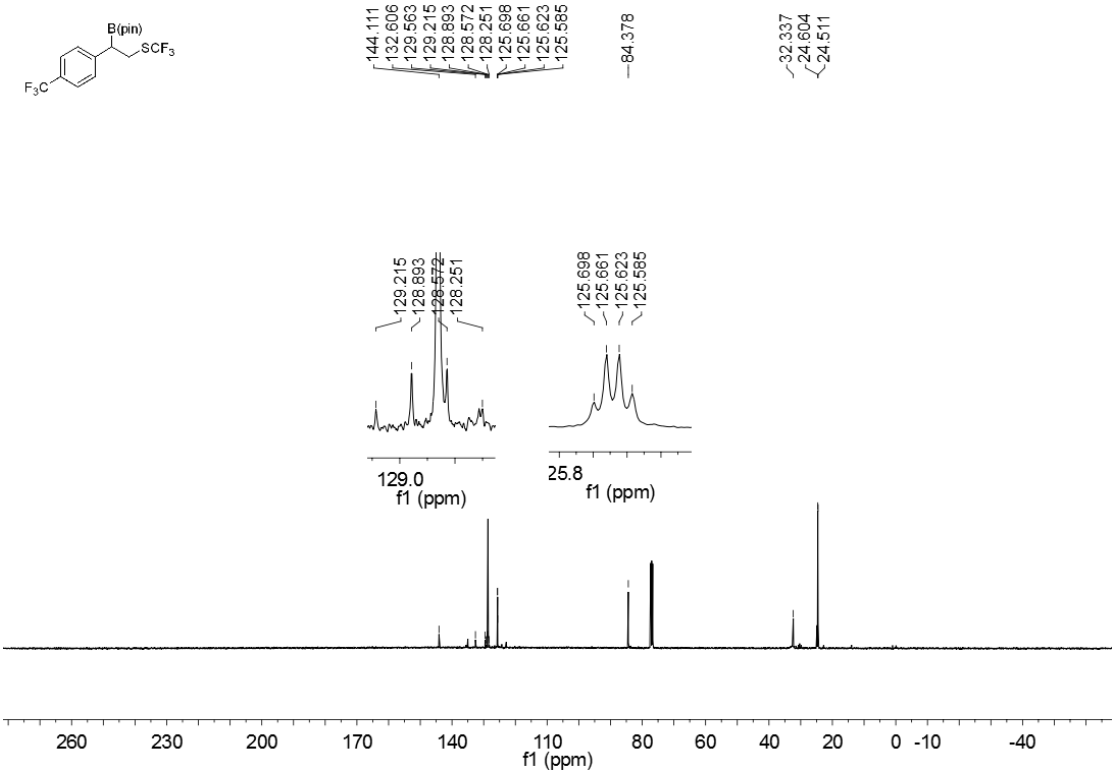
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 2-(1-(4-chlorophenyl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8b



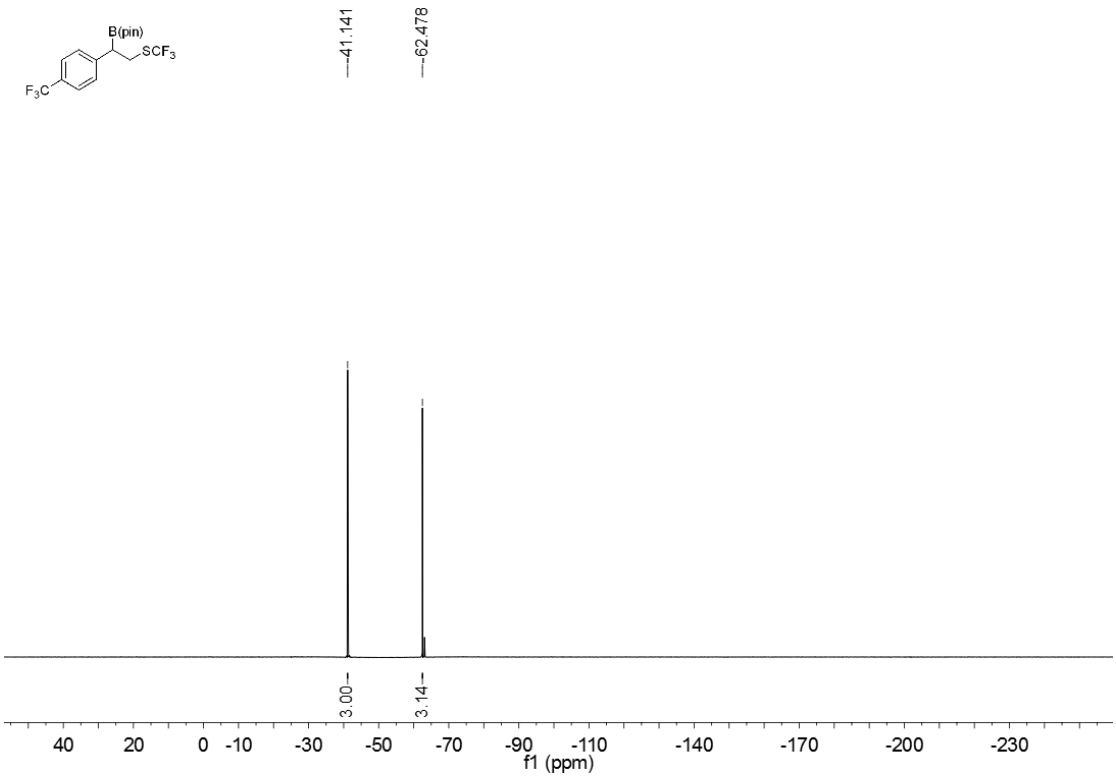
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8c



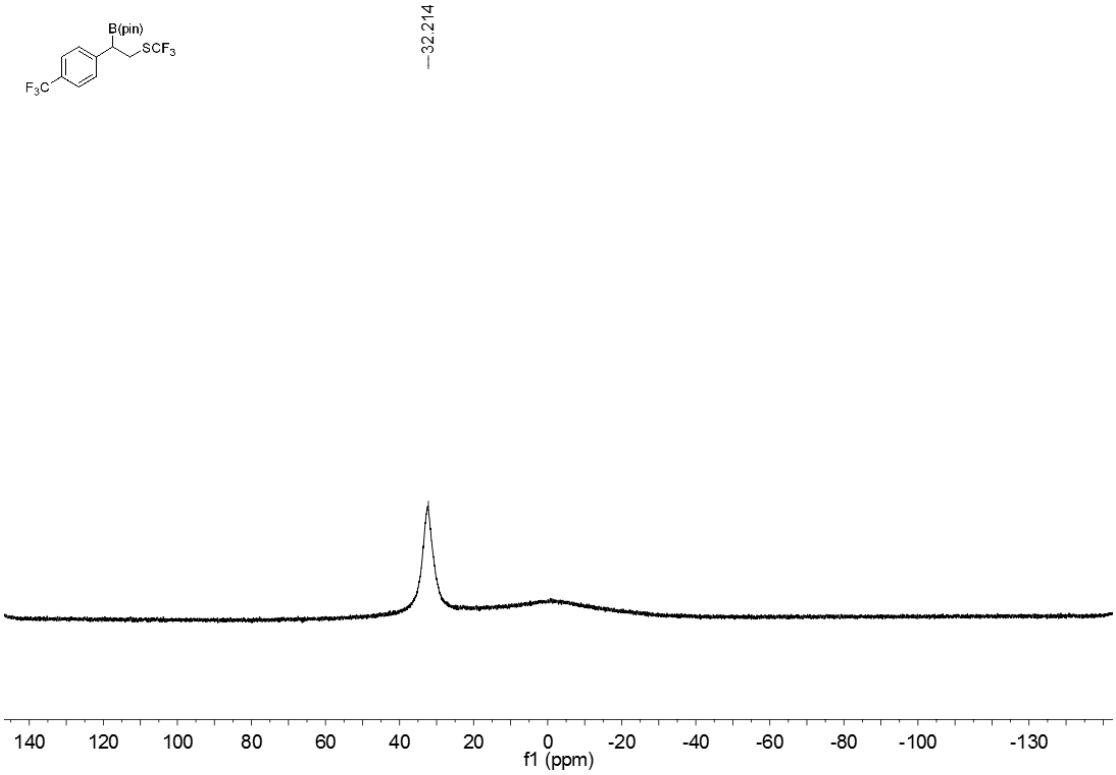
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8c



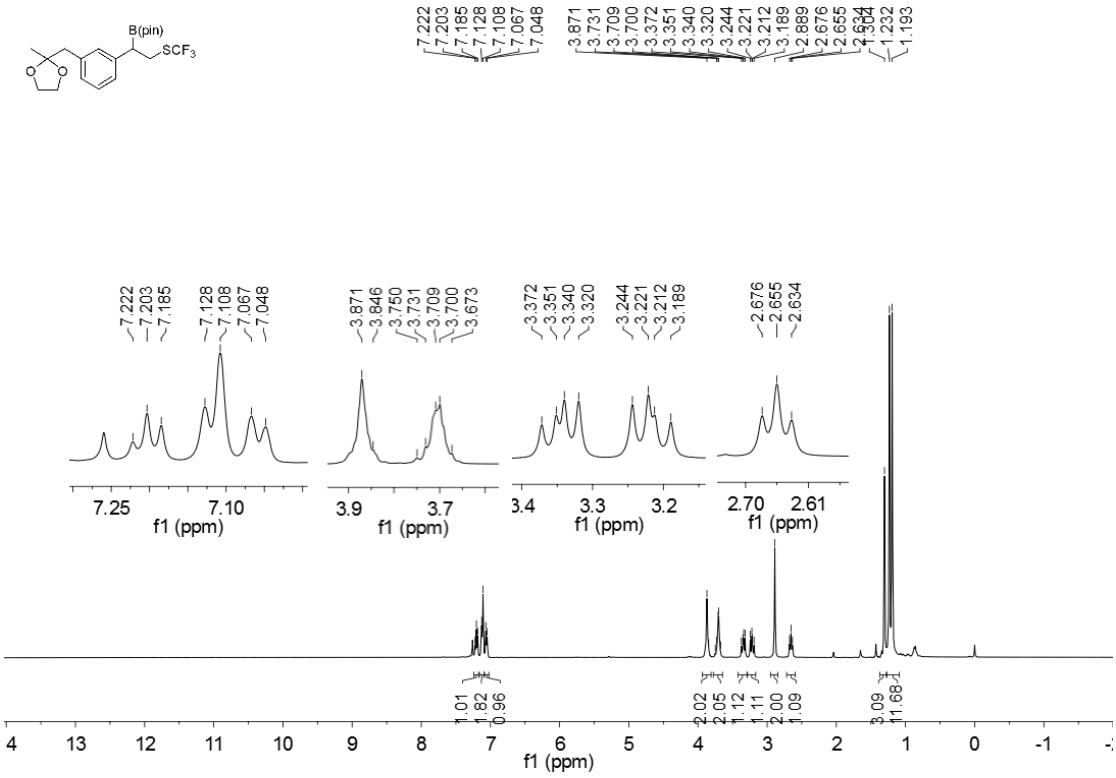
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8c



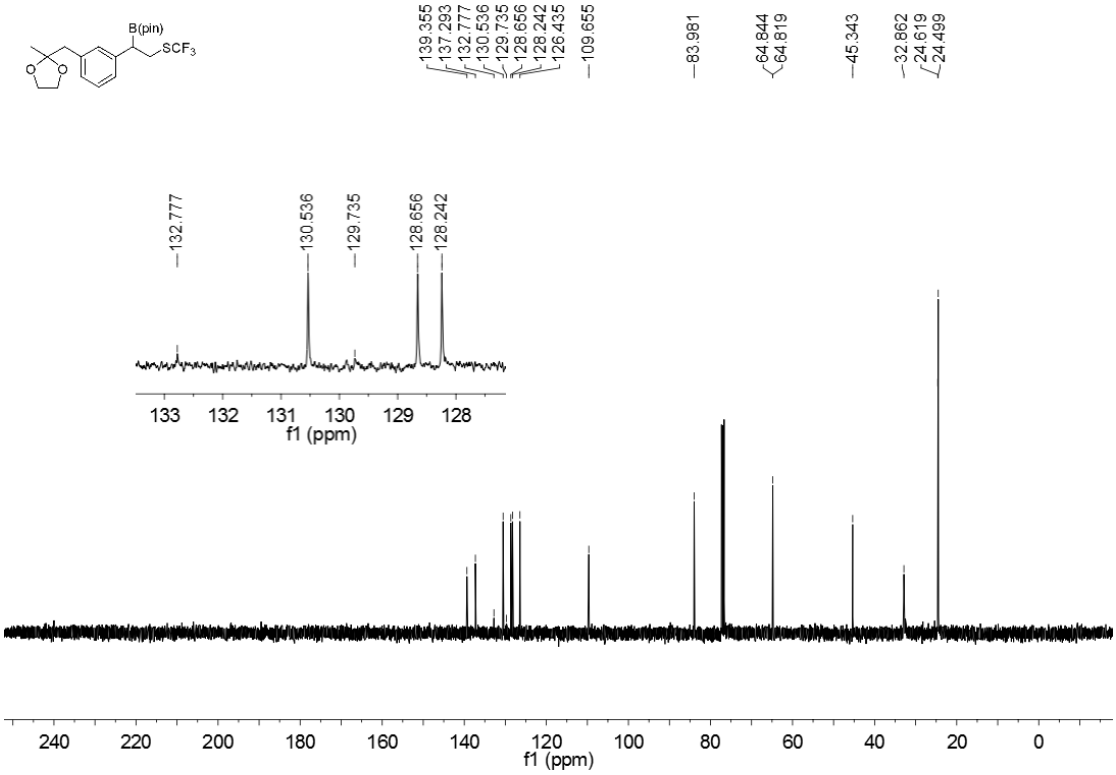
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8c



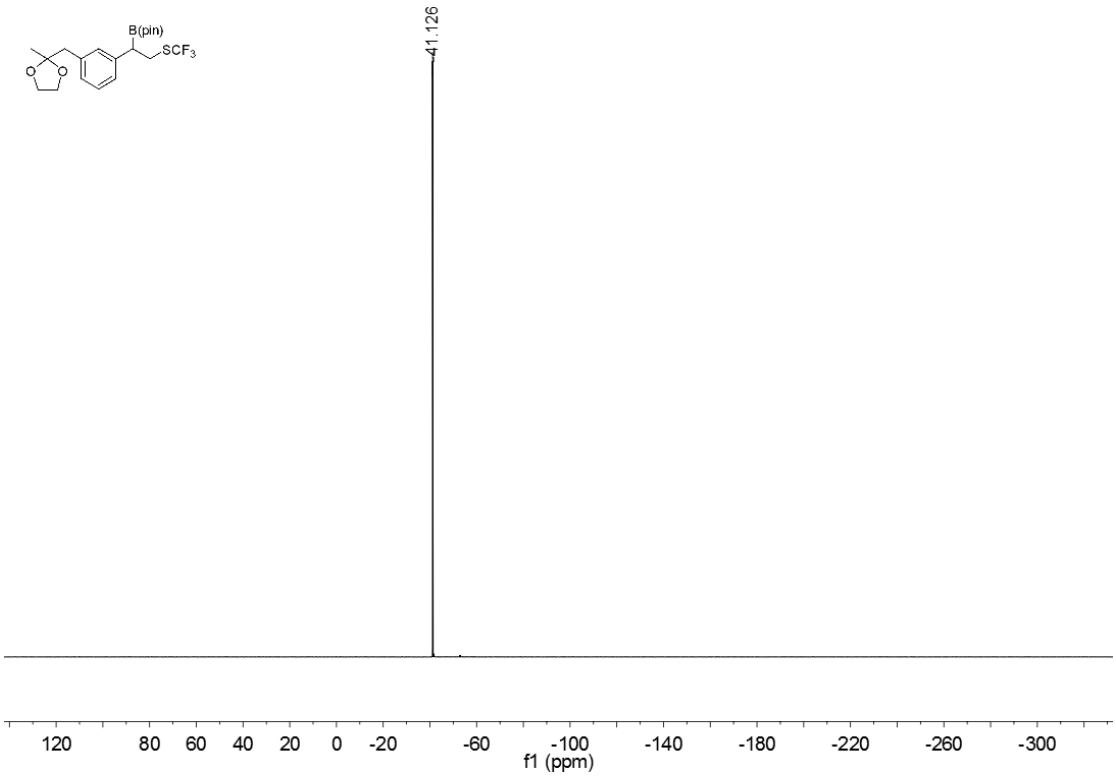
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-(3-((2-methyl-1,3-dioxolan-2-yl)methyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8d



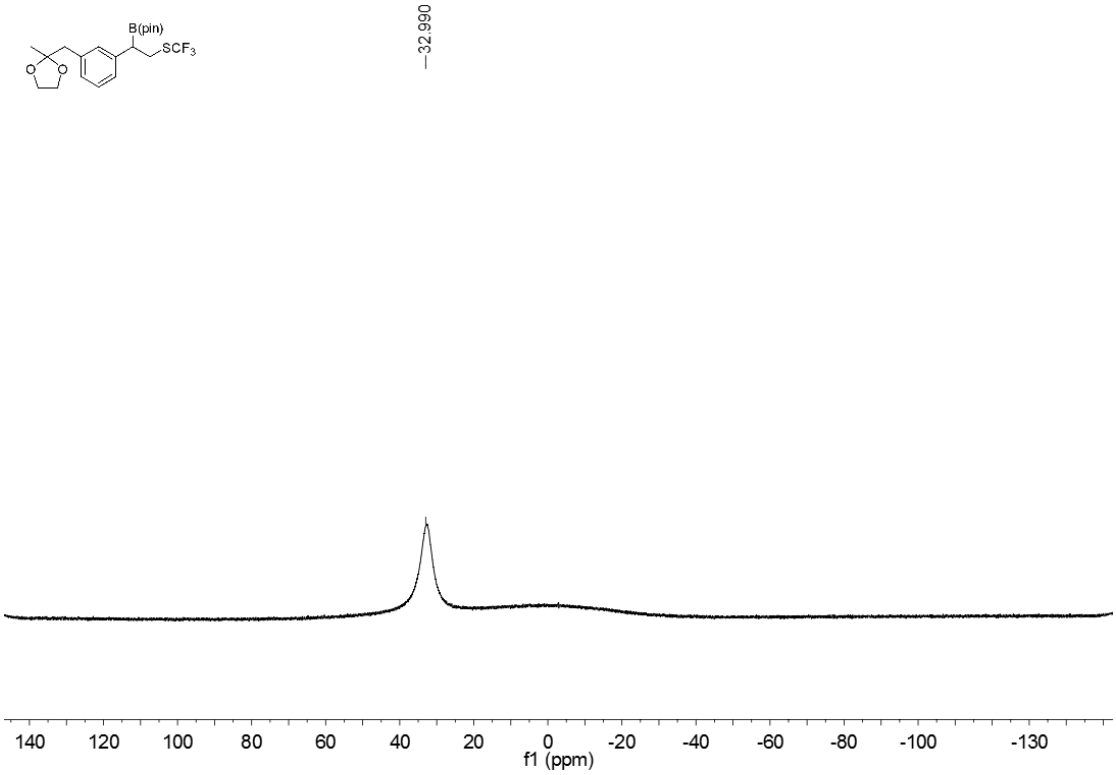
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-(3-((2-methyl-1,3-dioxolan-2-yl)methyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8d



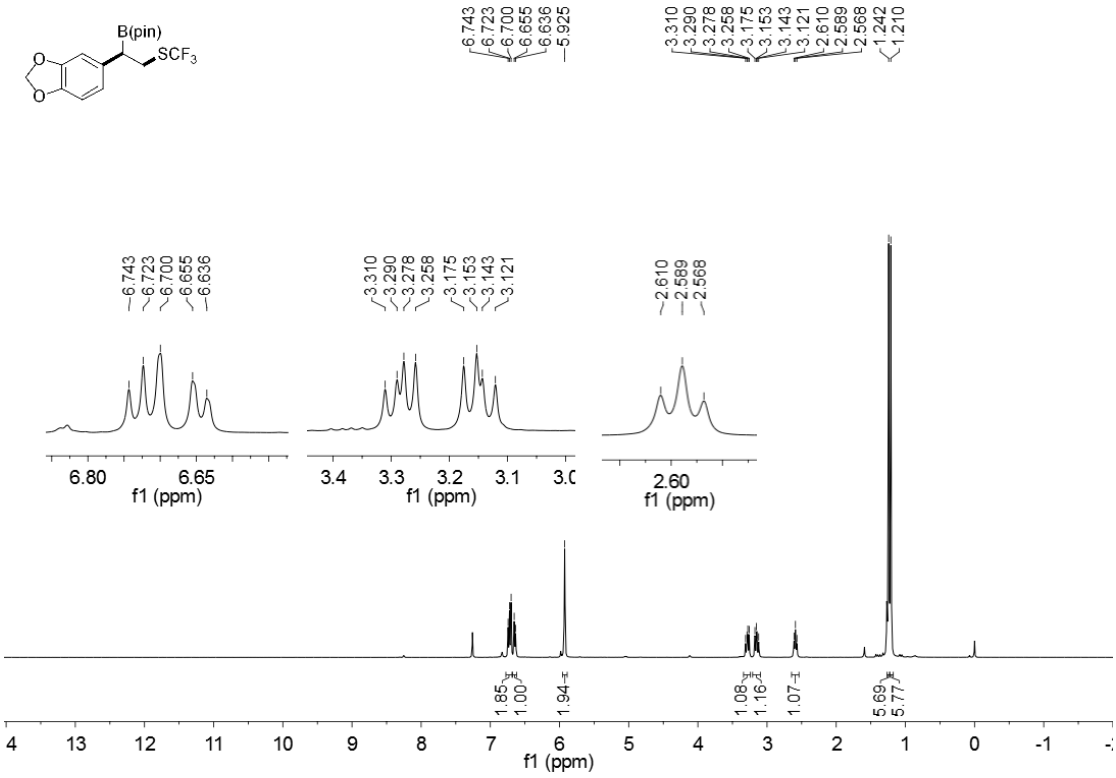
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-(3-((2-methyl-1,3-dioxolan-2-yl)methyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8d



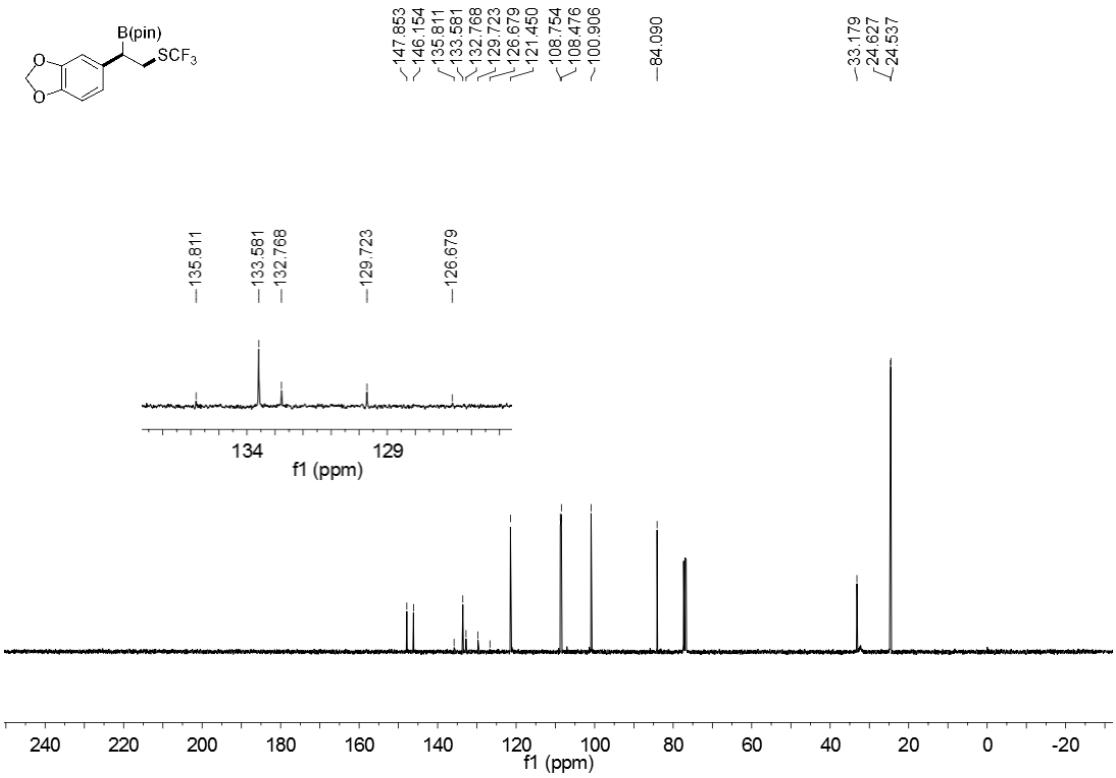
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 4,4,5,5-tetramethyl-2-(1-(3-((2-methyl-1,3-dioxolan-2-yl)methyl)phenyl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8d



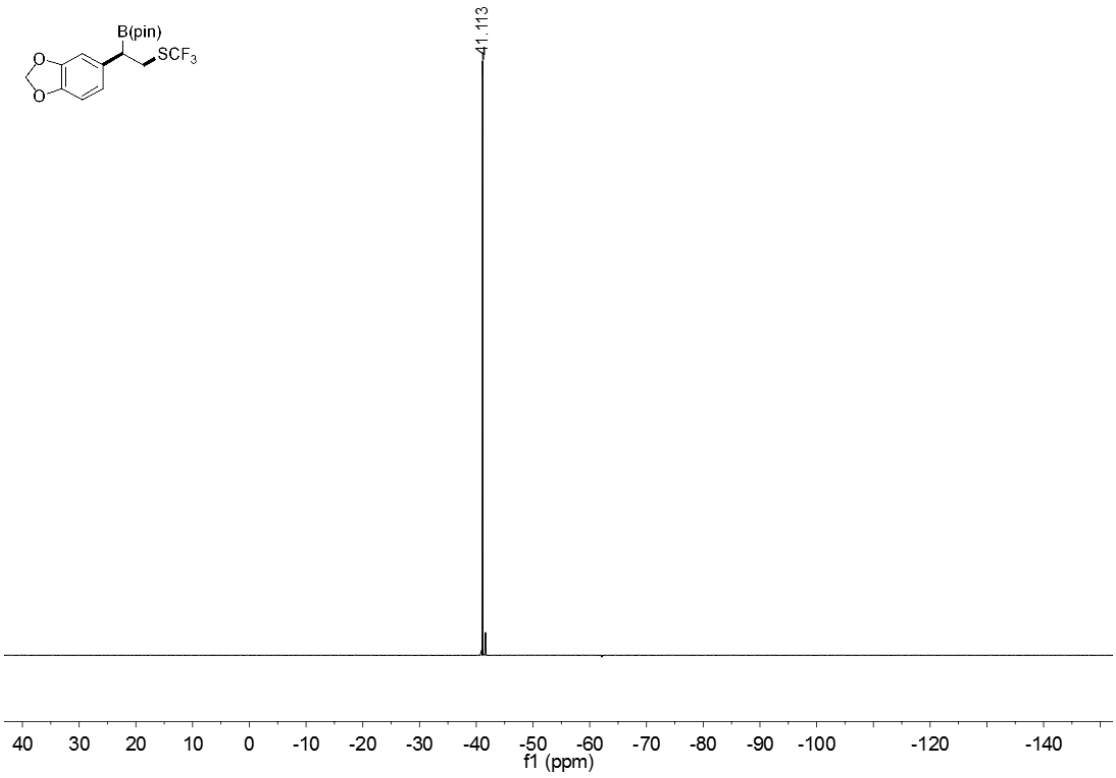
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(1-(benzo[d][1,3]dioxol-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8e



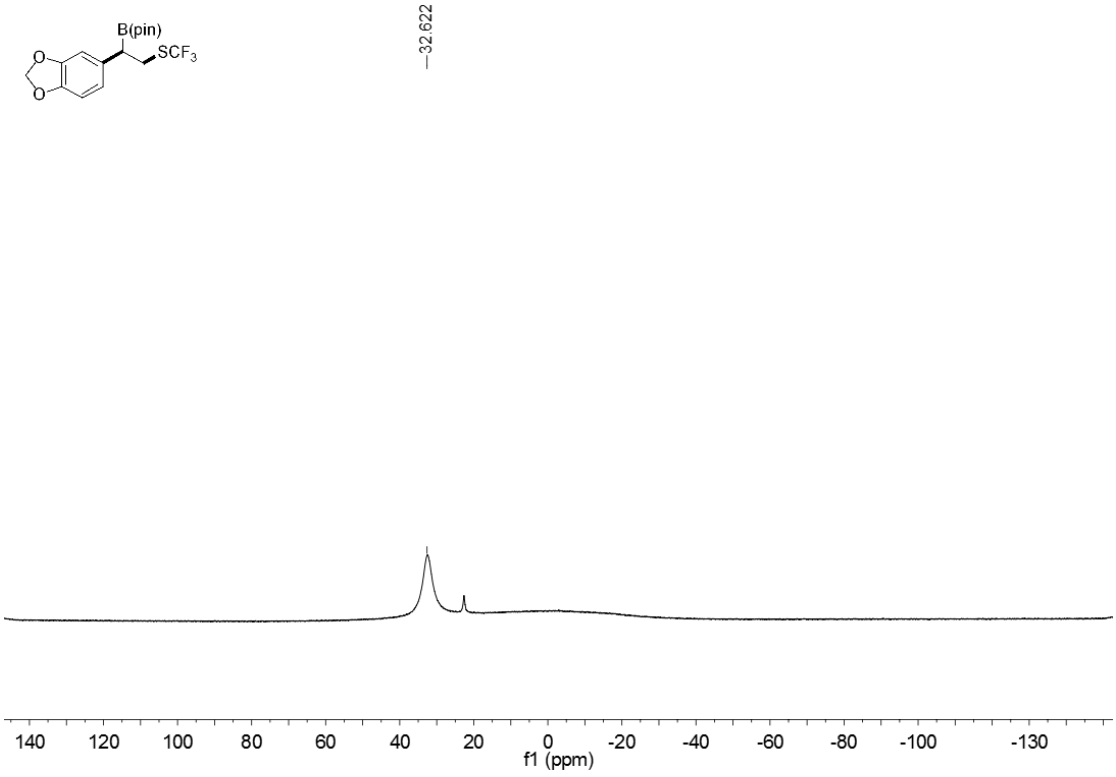
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-(1-(benzo[d][1,3]dioxol-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8e



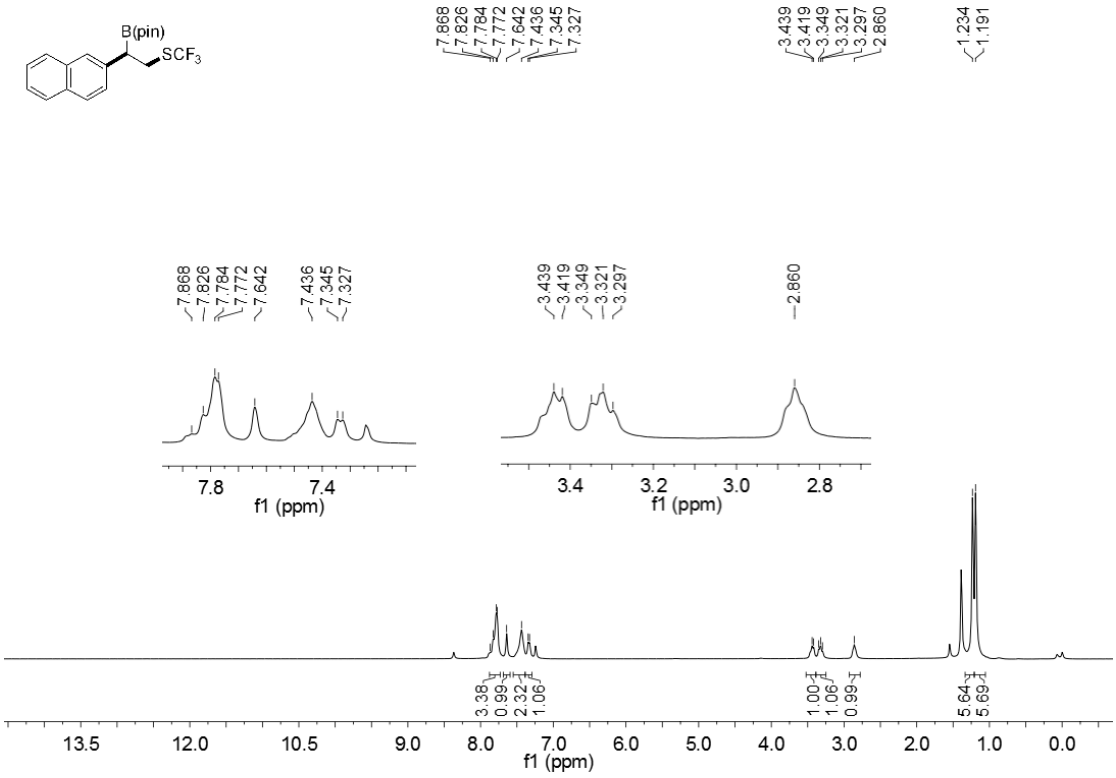
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(1-(benzo[d][1,3]dioxol-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8e



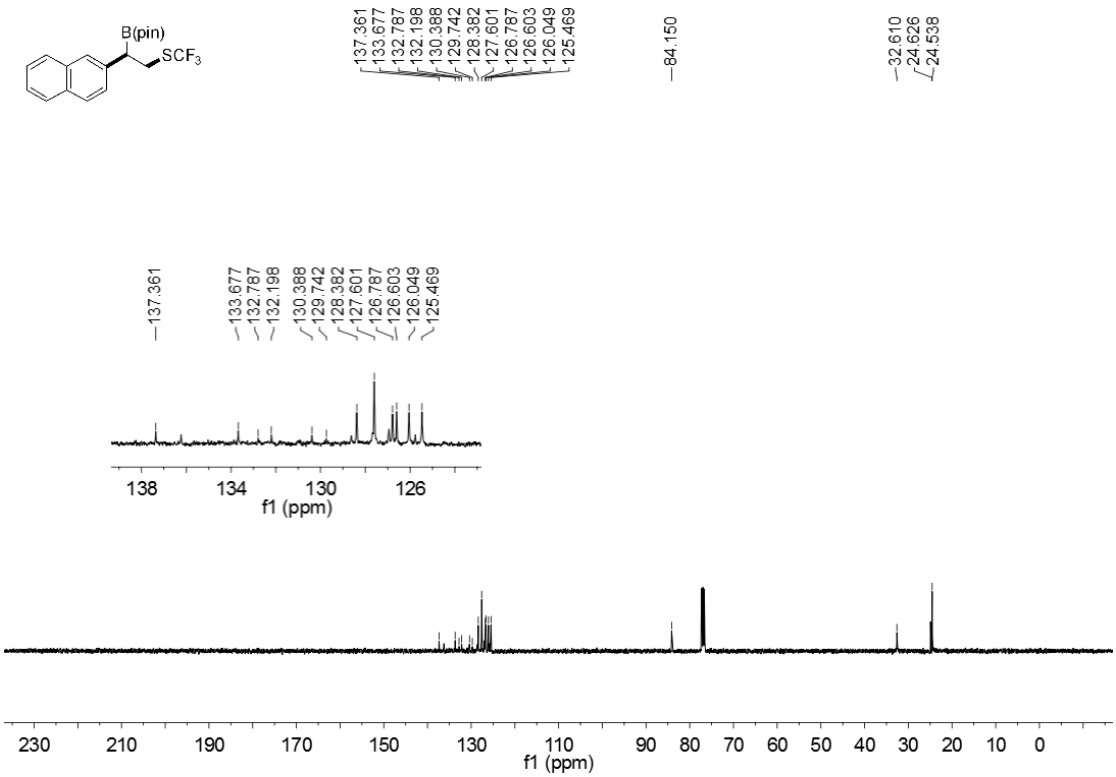
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 2-(1-(benzo[d][1,3]dioxol-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8e



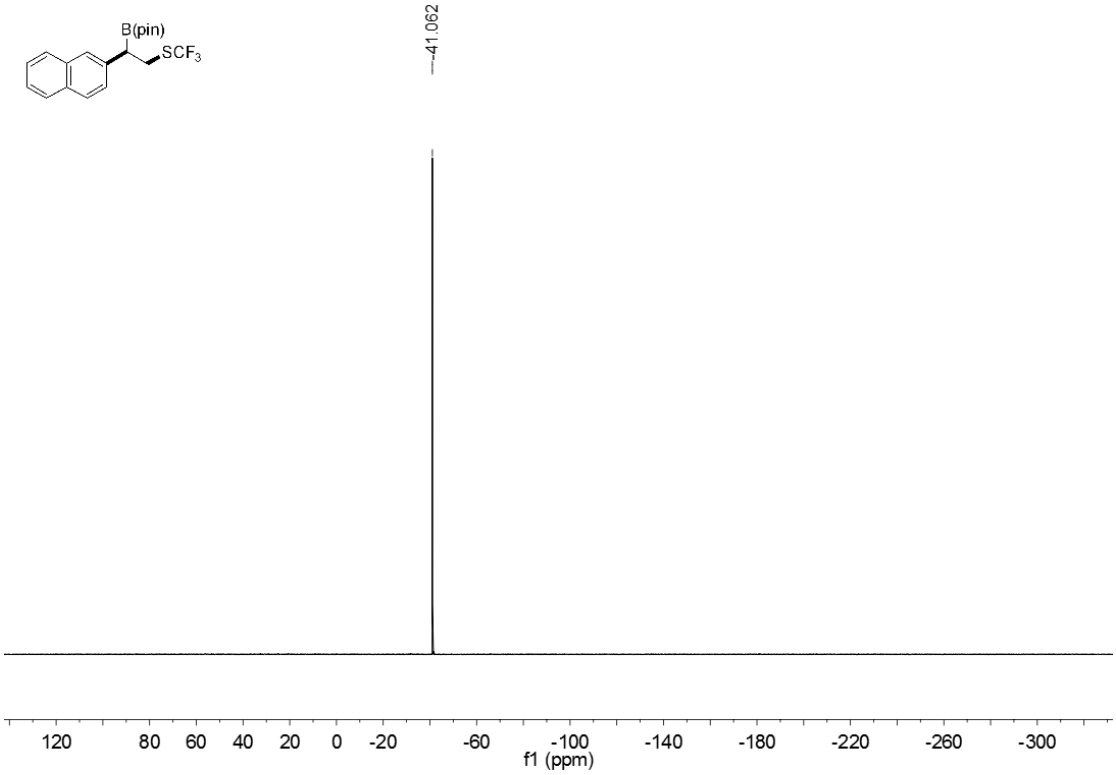
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8f



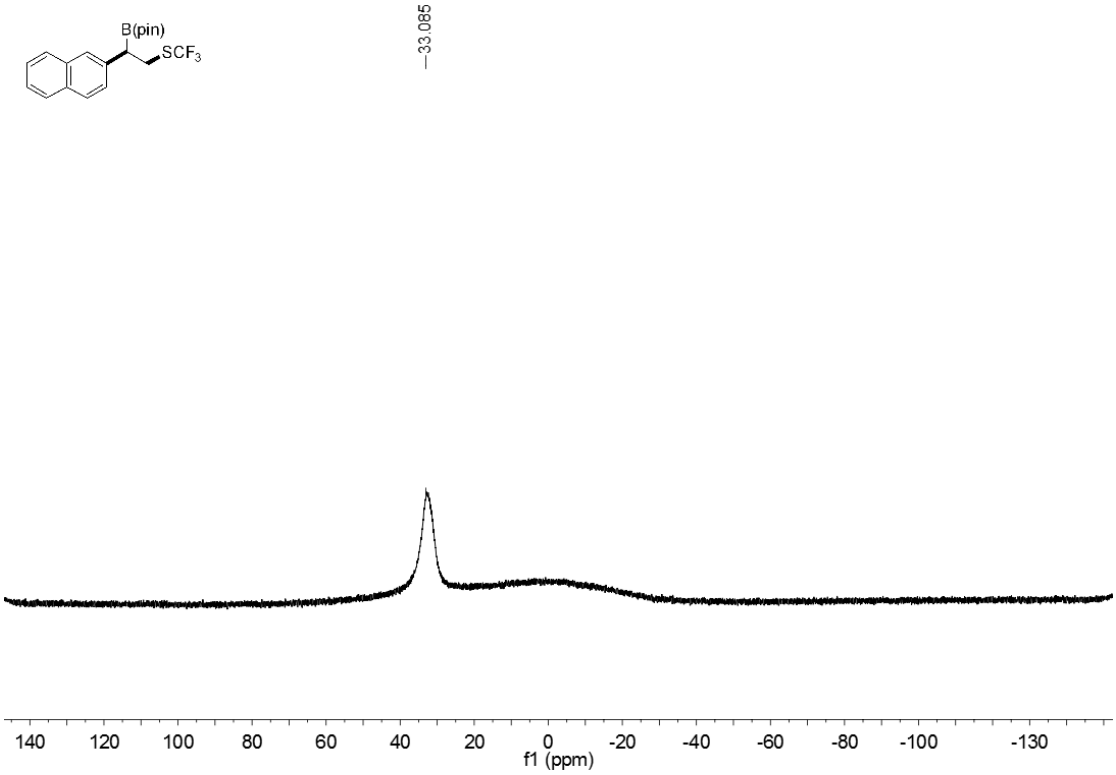
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8f



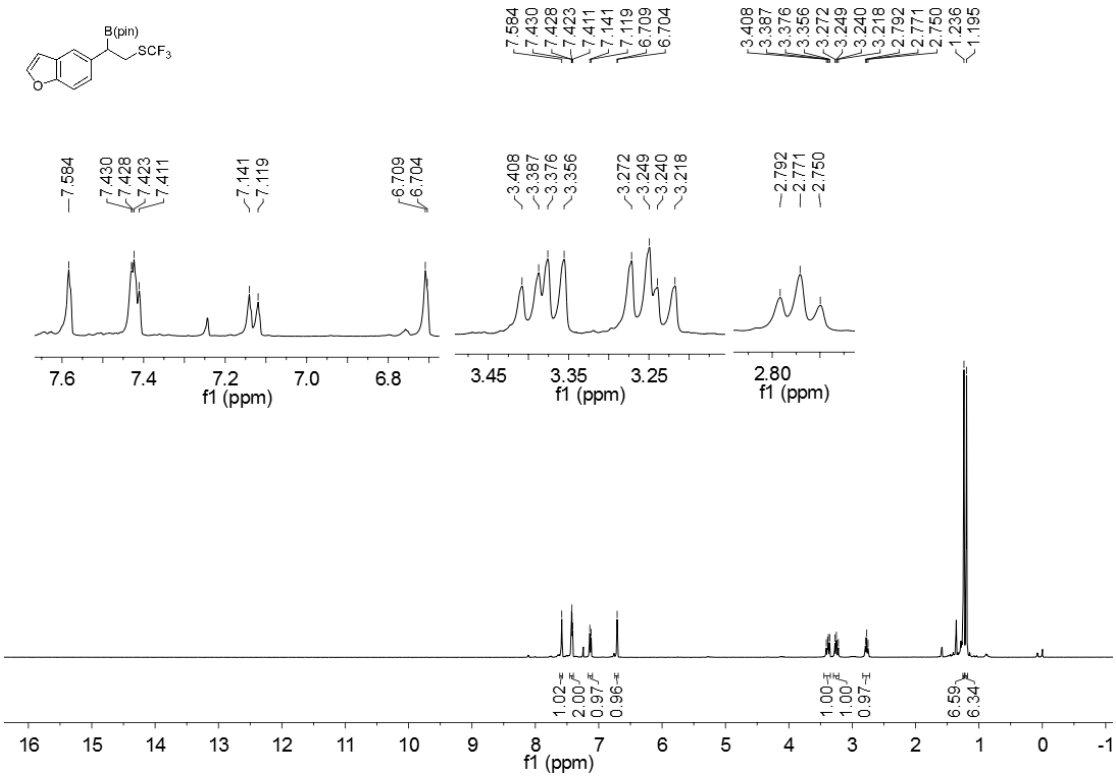
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8f



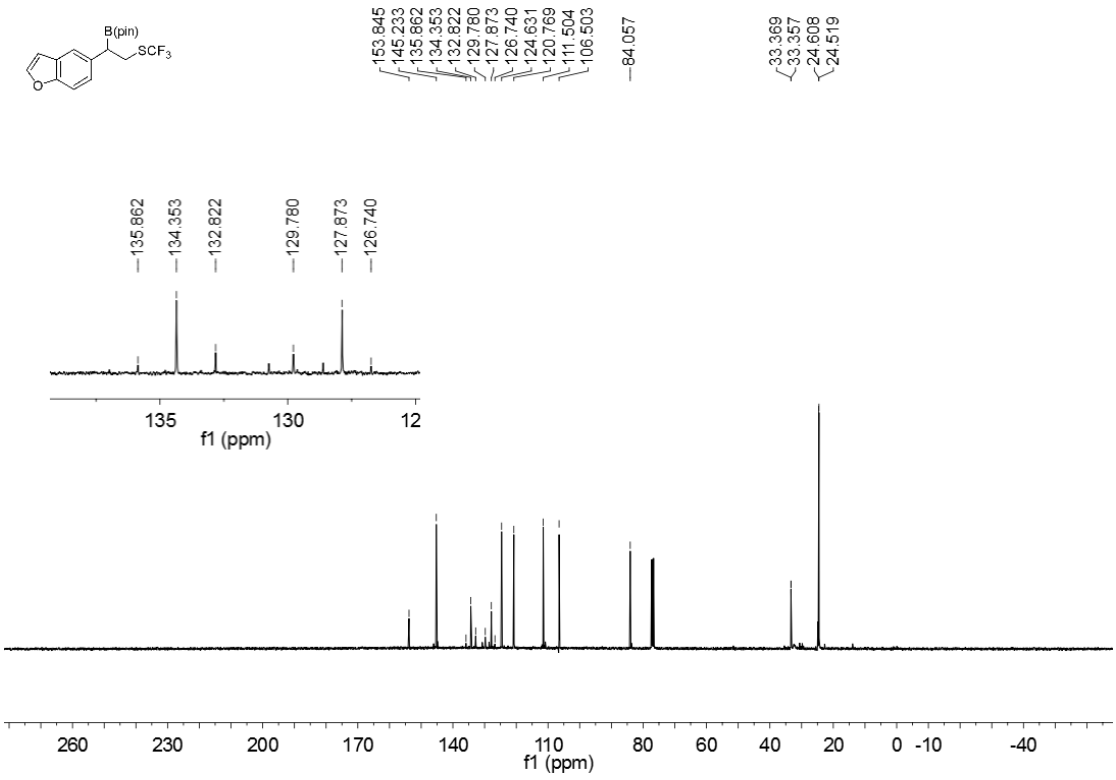
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)-2-(trifluoromethylthio)ethyl)-1,3,2-dioxaborolane 8f



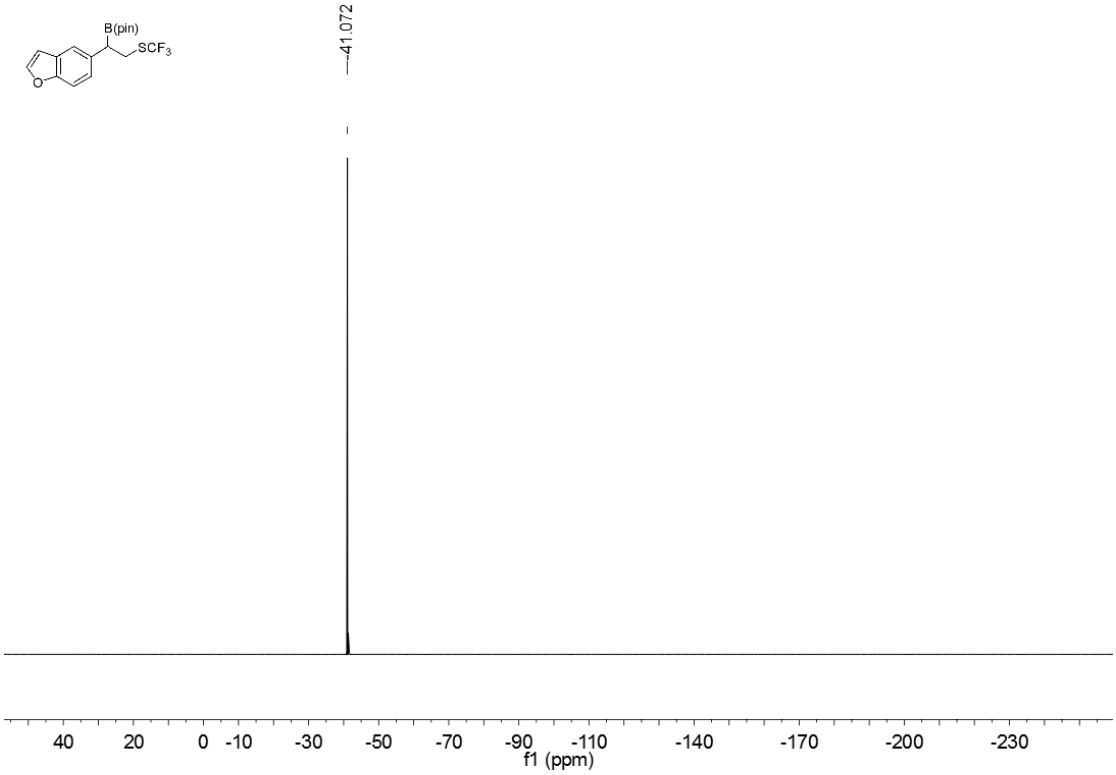
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(1-(benzofuran-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8g



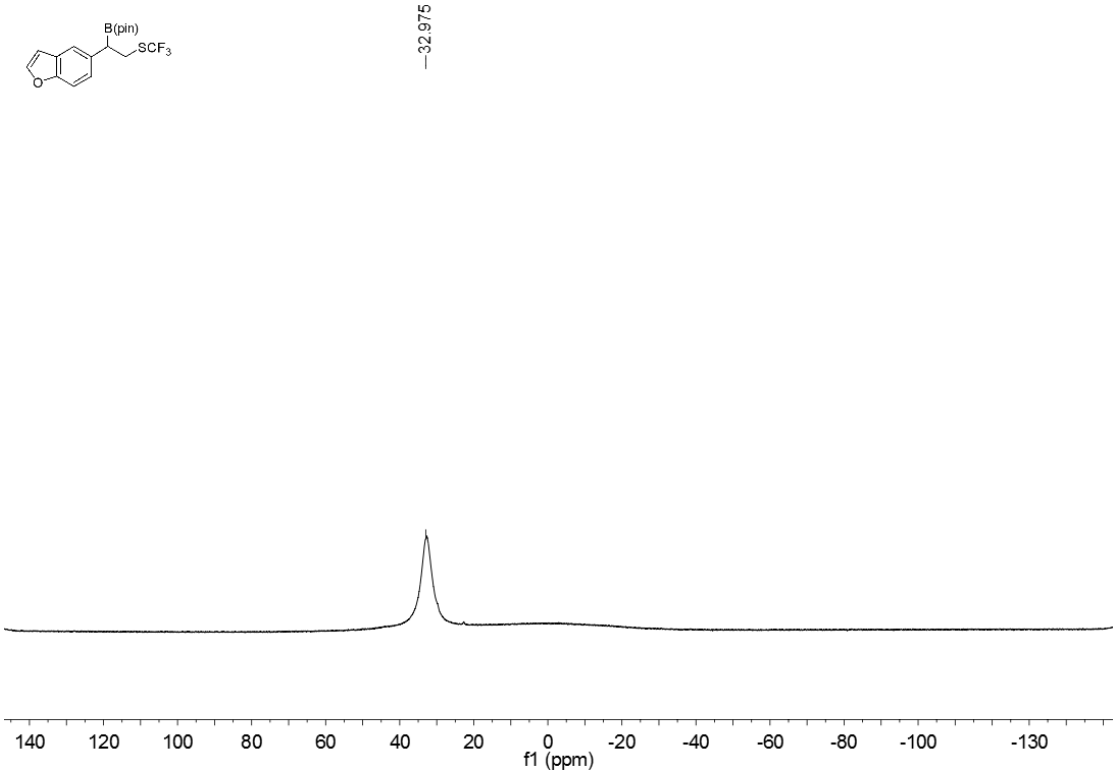
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-(1-(benzofuran-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8g



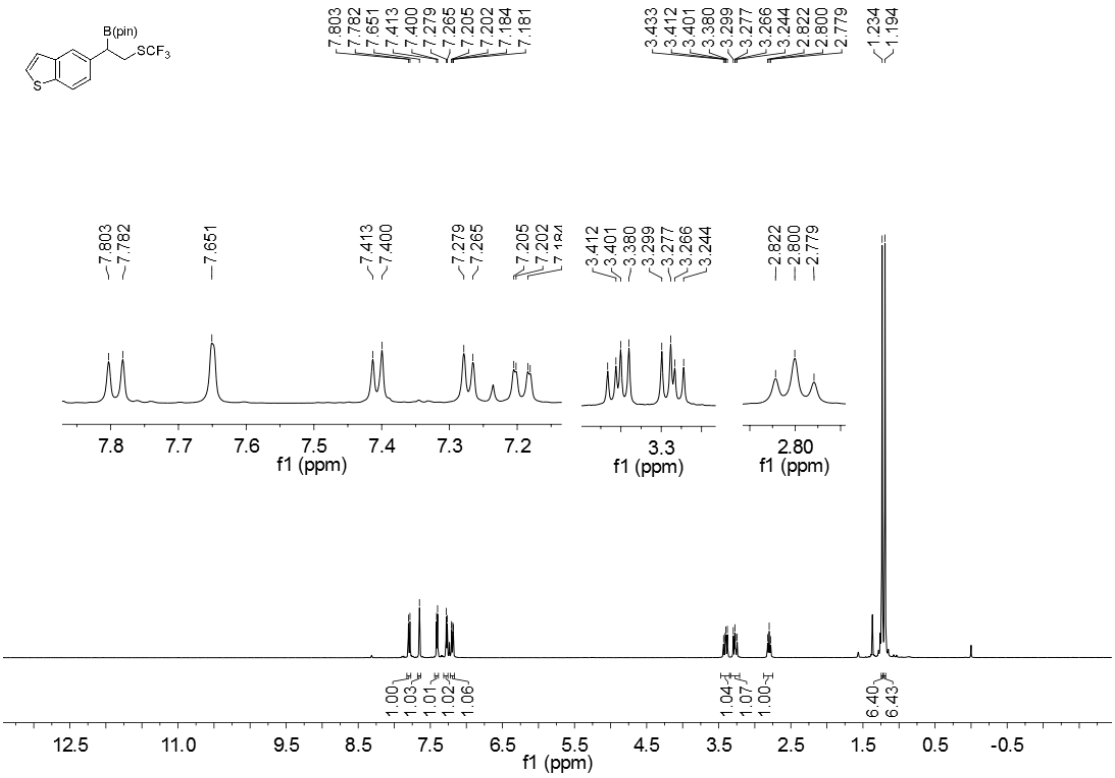
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(1-(benzofuran-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8g



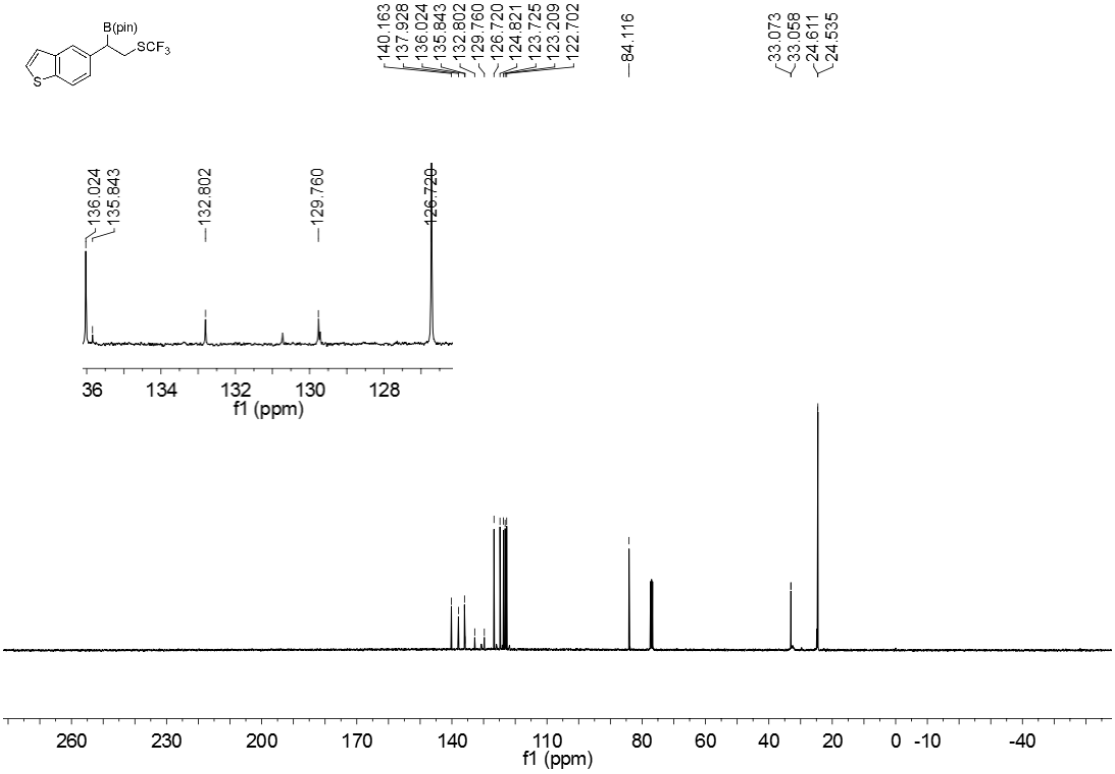
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 2-(1-(benzofuran-5-yl)-2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8g



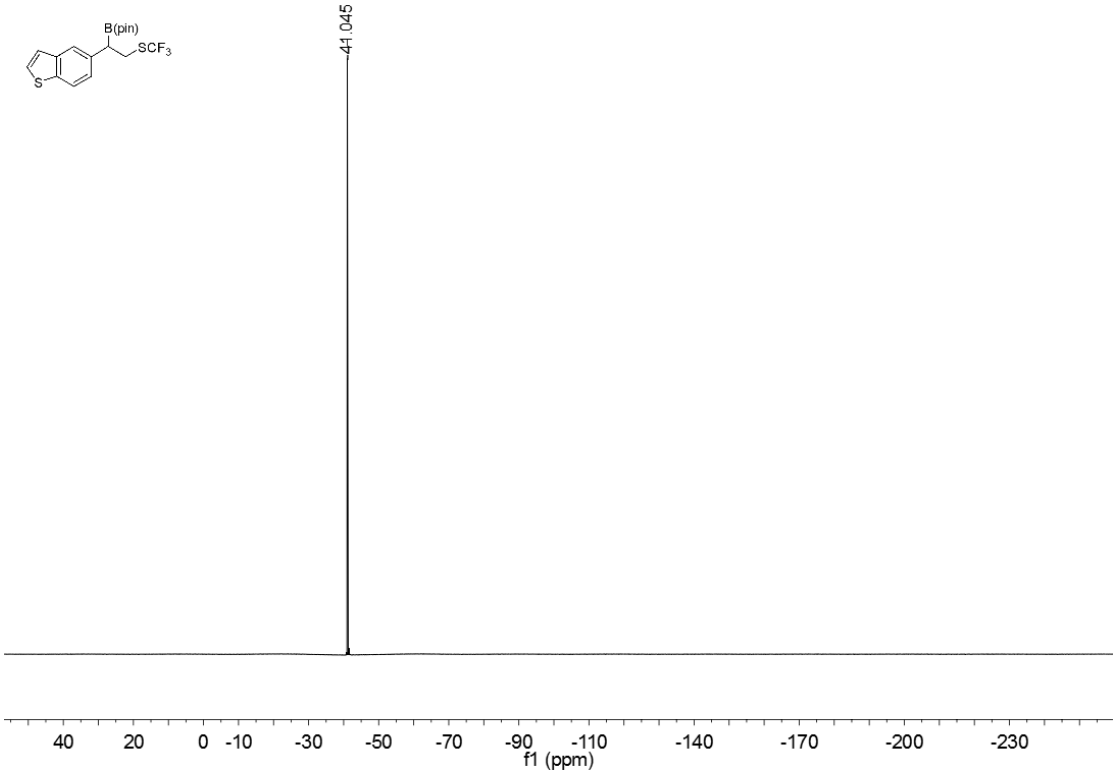
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(1-(benzo[b]thiophen-5-yl) -2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8h



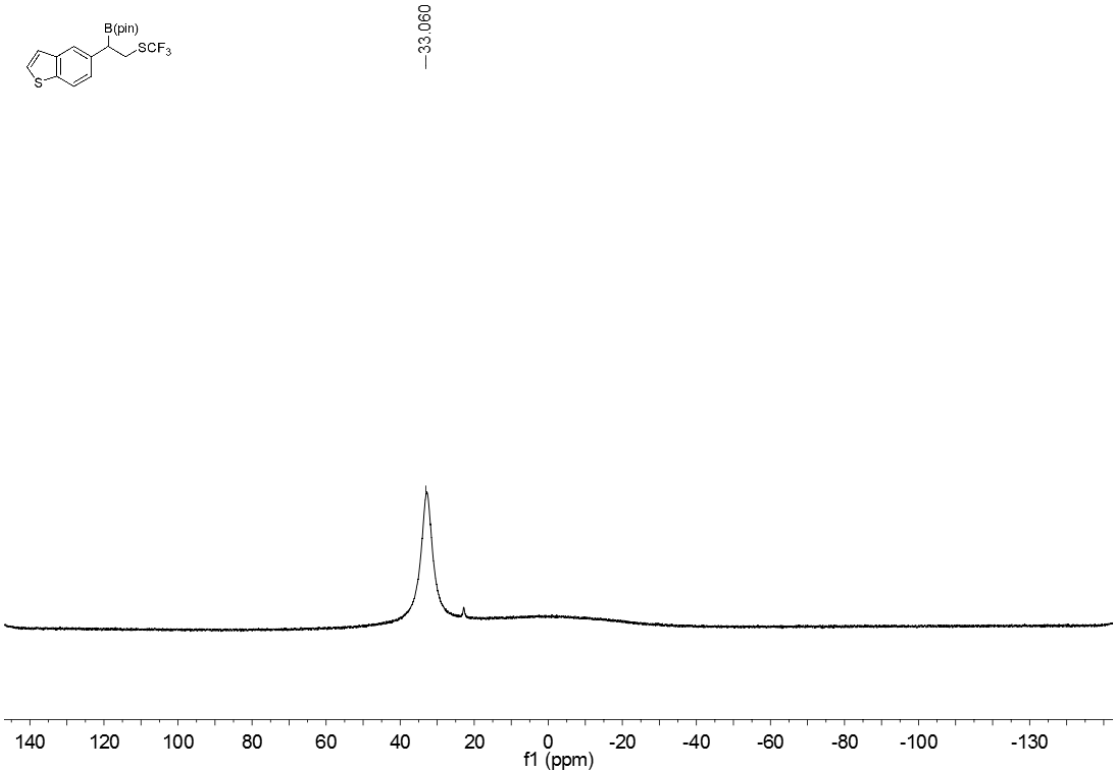
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-(1-(benzo[b]thiophen-5-yl) -2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8h



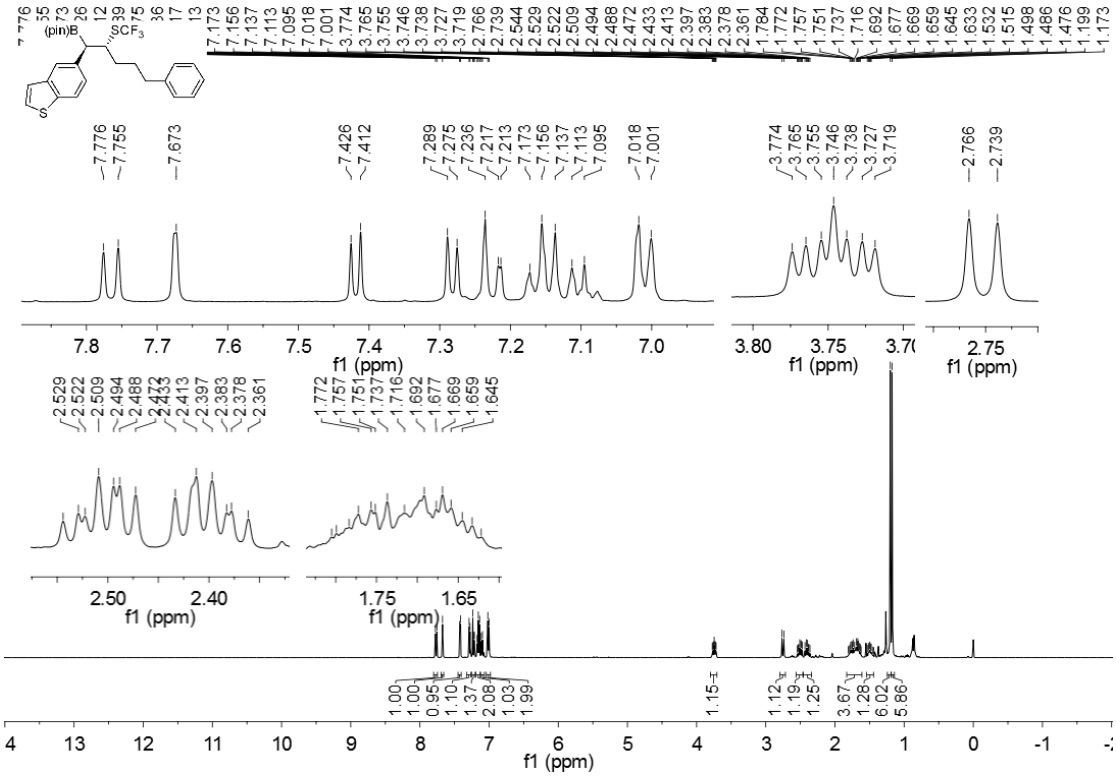
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(1-(benzo[b]thiophen-5-yl) -2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8h



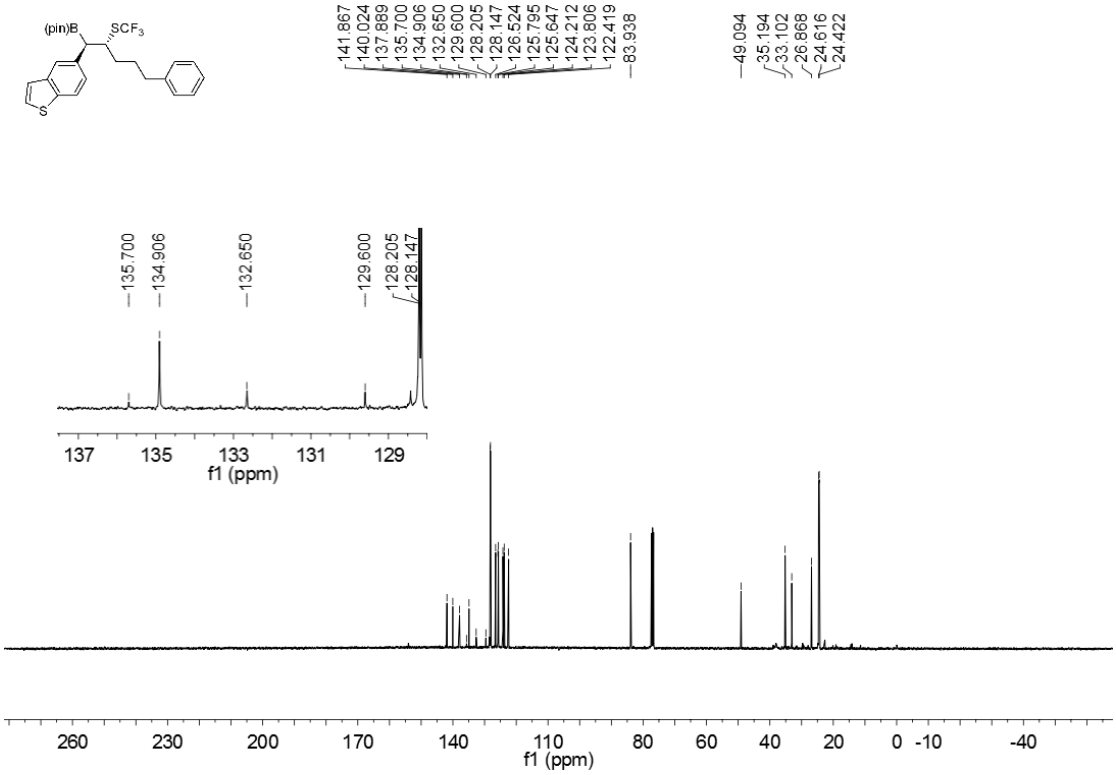
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of 2-(1-(benzo[b]thiophen-5-yl) -2-(trifluoromethylthio)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8h



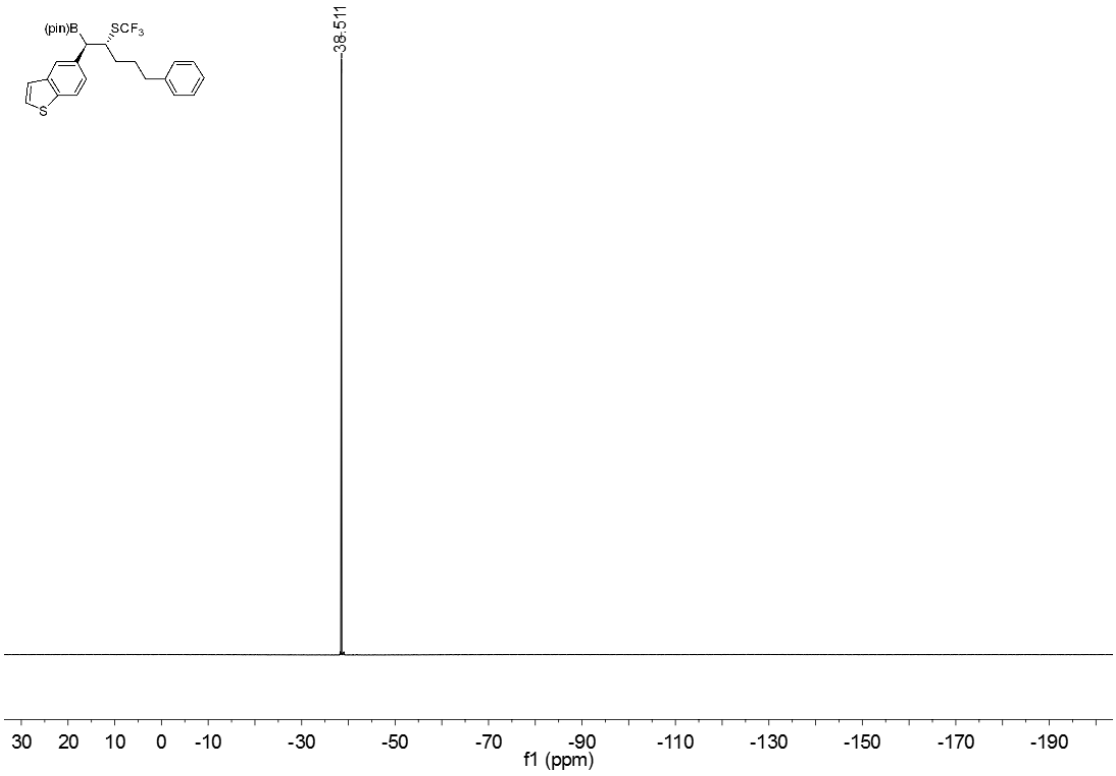
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (±)-2-((1*R*,2*R*)-1-(benzo[b]thiophen-5-yl)-5-phenyl-2-(trifluoromethylthio)pentyl) -4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8i



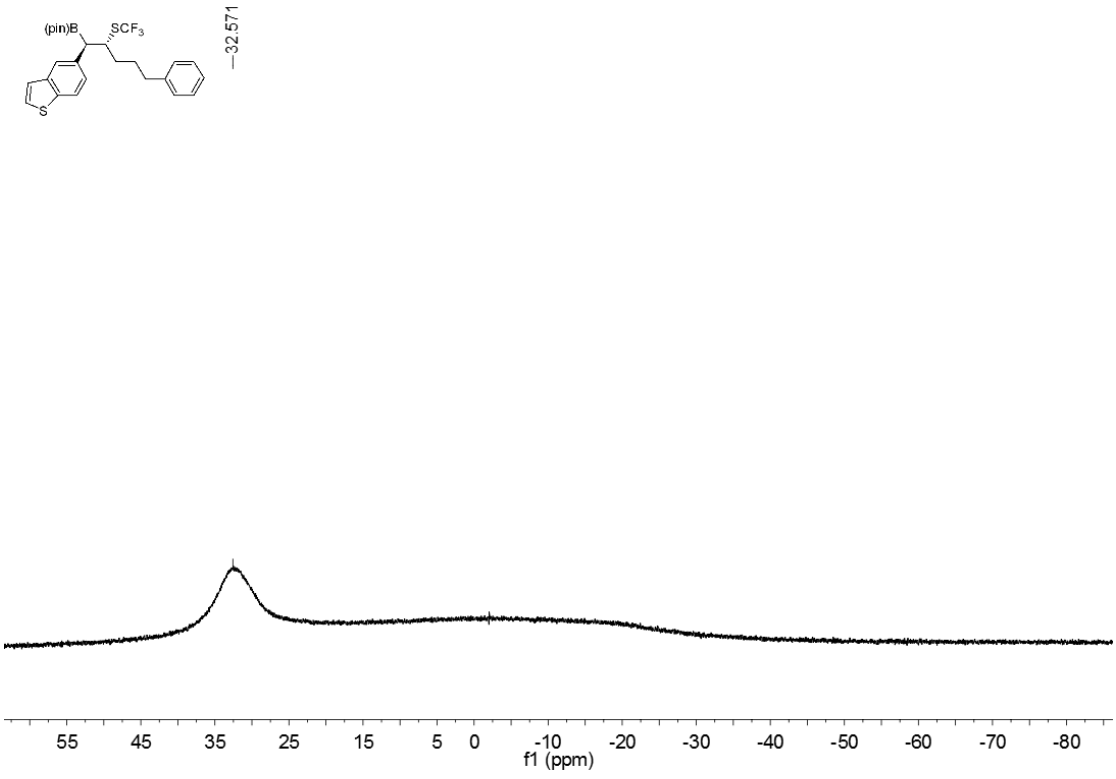
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-2-((1*R*,2*R*)-1-(benzo[b]thiophen-5-yl)-5-phenyl-2-(trifluoromethylthio)pentyl) -4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8i



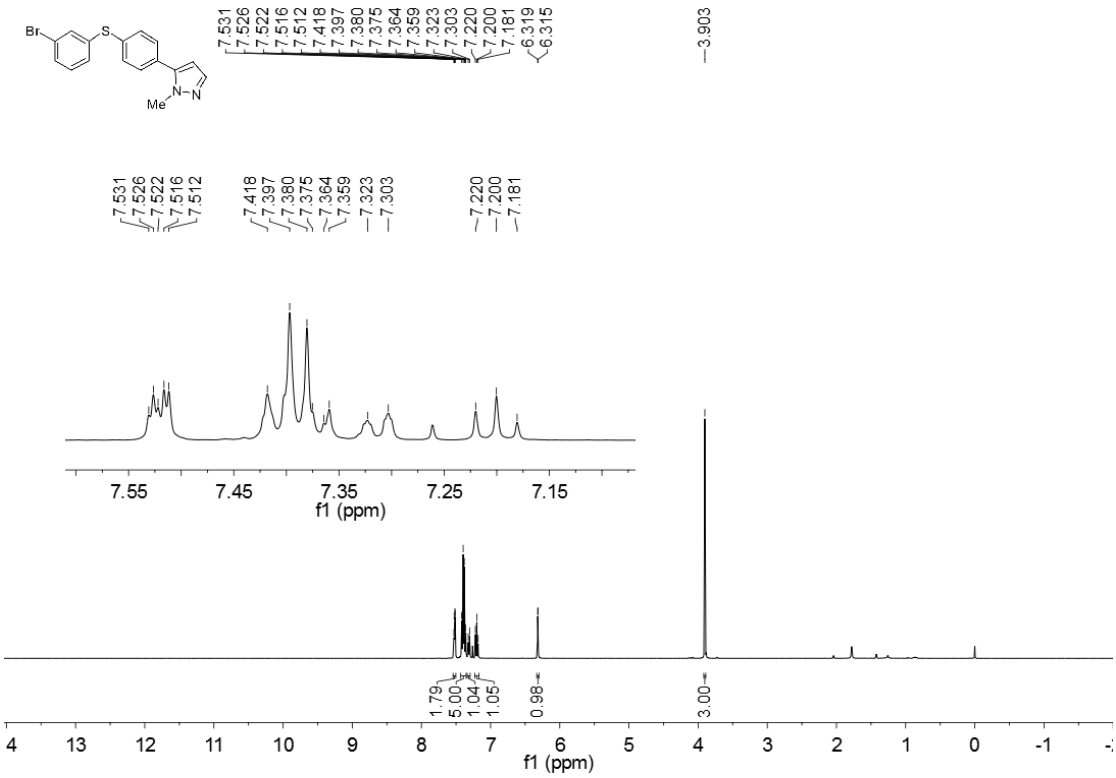
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of ((±)-2-((1*R*,2*R*)-1-(benzo[b]thiophen-5-yl)-5-phenyl-2-(trifluoromethylthio)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8i



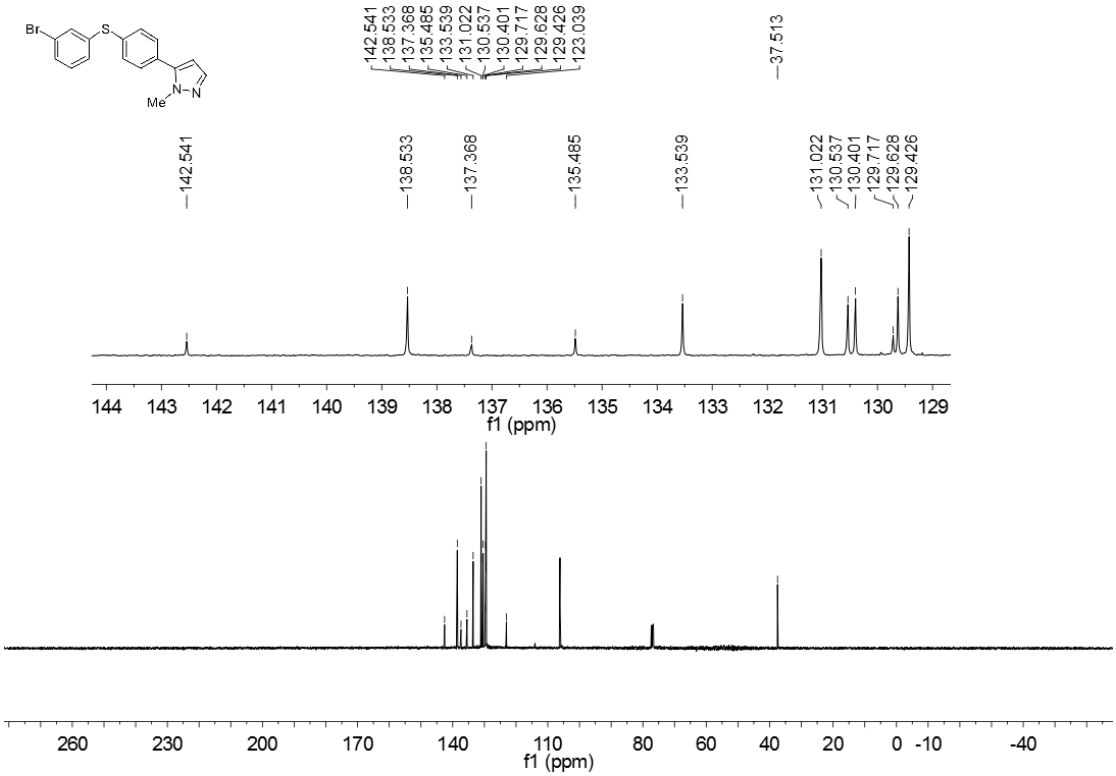
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of l(±)-2-((1*R*,2*R*)-1-(benzo[b]thiophen-5-yl)-5-phenyl-2-(trifluoromethylthio)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8i



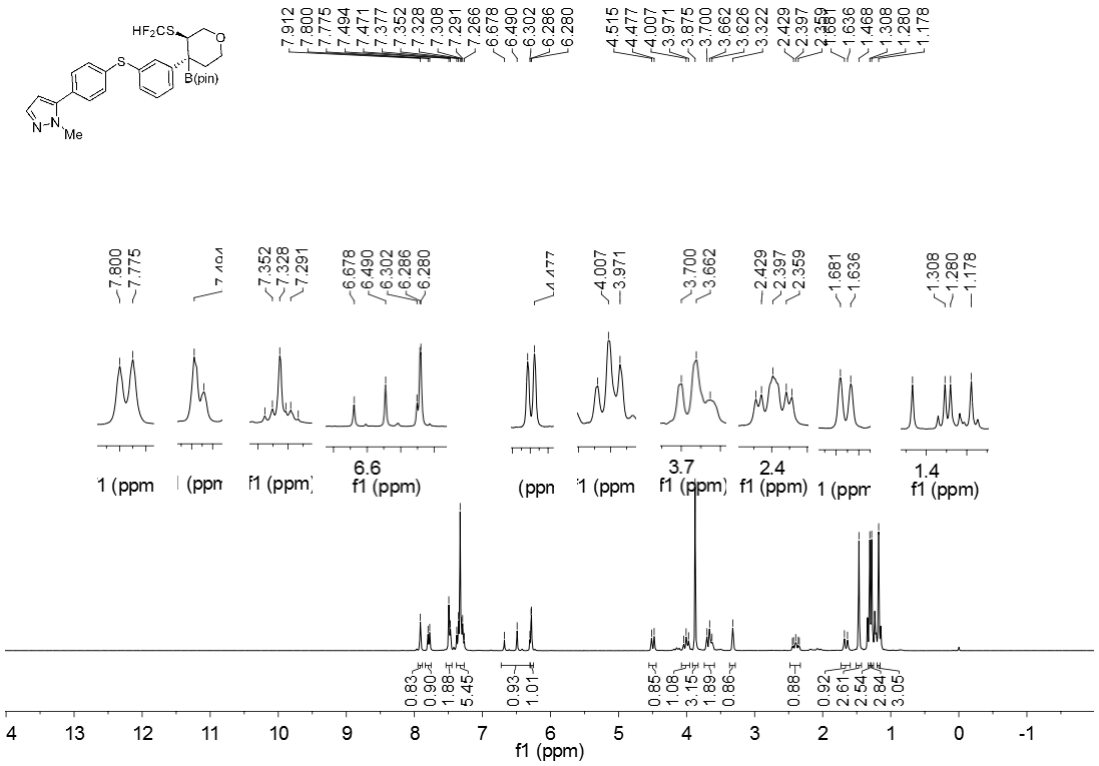
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5-(4-(3-bromophenylthio)phenyl)-1-methyl-1*H*-pyrazole 11



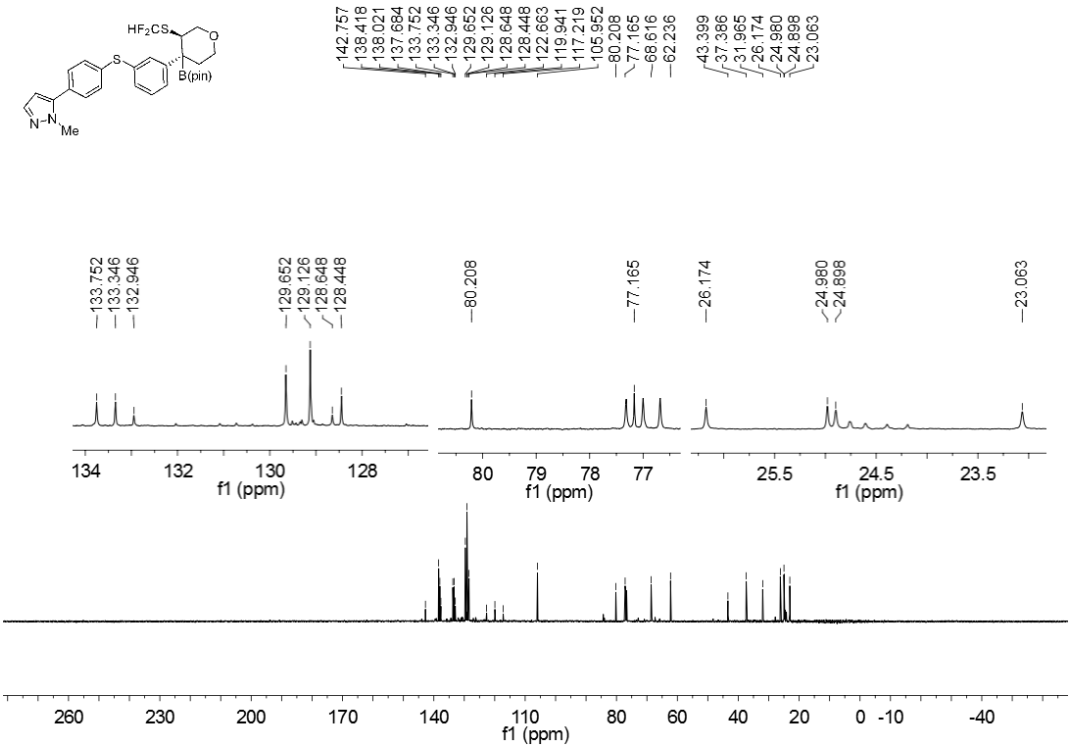
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5-(4-(3-bromophenylthio)phenyl)-1-methyl-1*H*-pyrazole 11



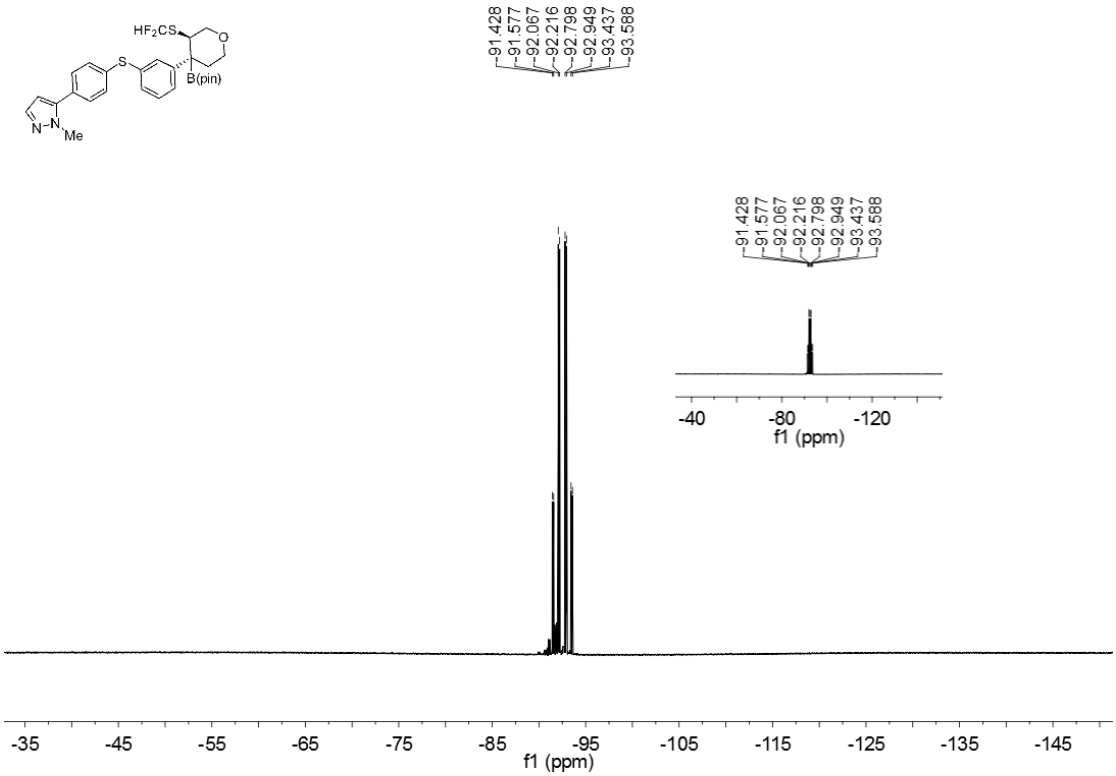
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of (±)-5-(4-(3-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)phenylthio)phenyl)-1-methyl-1*H*-pyrazole 12



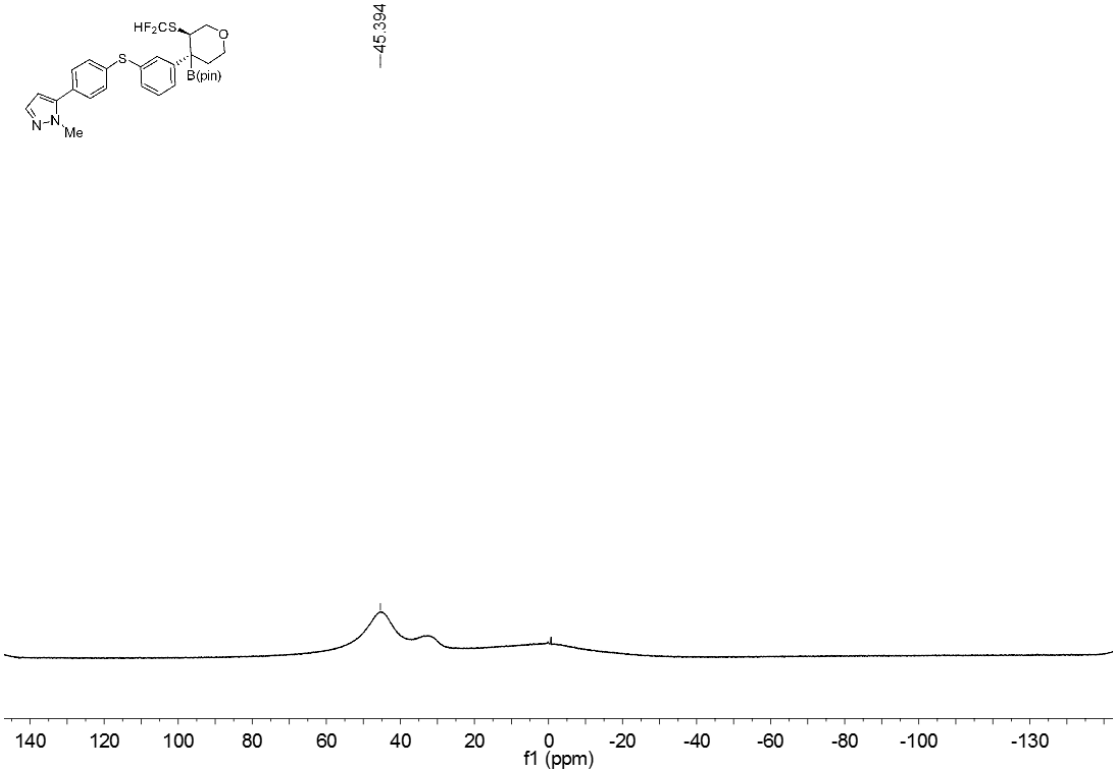
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (±)-5-(4-(3-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)phenylthio)phenyl)-1-methyl-1*H*-pyrazole 12



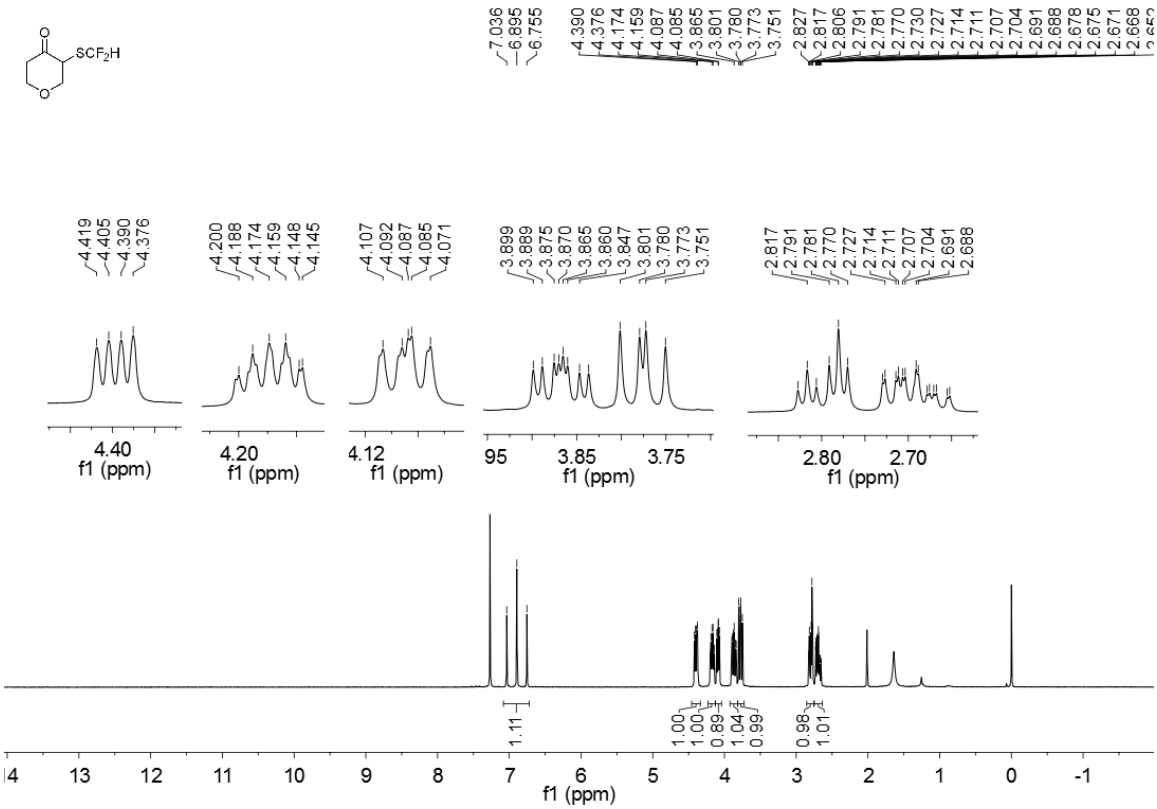
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (±)-5-(4-(3-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)phenylthio)phenyl)-1-methyl-1*H*-pyrazole 12



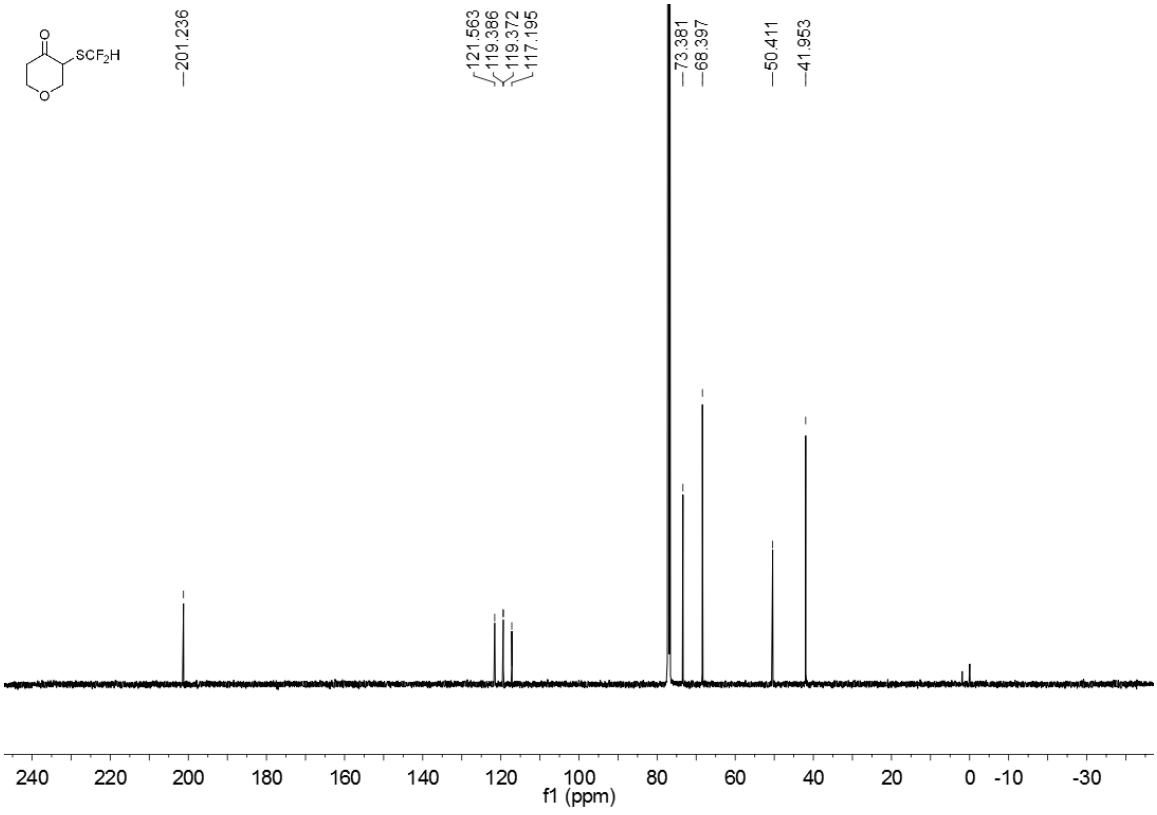
^{11}B NMR (128 MHz, CD_3Cl_3) spectrum of (±)-5-(4-(3-((3*R*,4*R*)-3-(difluoromethylthio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2*H*-pyran-4-yl)phenylthio)phenyl)-1-methyl-1*H*-pyrazole 12



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(difluoromethylthio)dihydro-2*H*-pyran-4(3*H*)-one 13



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3-(difluoromethylthio)dihydro-2*H*-pyran-4(3*H*)-one 13



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of
3-(difluoromethylthio)dihydro-2*H*-pyran-4(3*H*)-one 13