

Supporting Information

Enantioselective Cobalt-Catalyzed Hydroboration of Fluoroalkyl-substituted Alkenes to Access Chiral Fluoroalkylboronates

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(A) General Remarks

All manipulations were performed in an Ar-filled glovebox, unless mentioned otherwise. THF, toluene, and hexane were purified by passing the degassed solvents (N₂) through a column of activated alumina (solvent purification system purchased from Innovative Technologies, Newburyport, MA). The following chemicals were purchased and used as received: Cobalt (II) acetylacetonate (99%, Sigma-Aldrich), pinacolborane (98%, Oakwood Chemical). All bisphosphine ligands were purchased from Sigma-Aldrich in high purity (Strem Chemicals). All other reagents and solvents were purchased from commercial sources and used without purification.

¹H and ¹³C{¹H} spectra were recorded using Bruker 400 MHz, or 500 MHz NMR spectrometers and done in CDCl₃ unless otherwise stated. ¹H NMR and ¹³C{¹H} NMR spectra were referenced to resonances of the residual signals of the deuterated solvents. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets and m = multiplet. GC analysis was acquired on Agilent 6850 gas chromatograph equipped with a flame-ionization detector. HR-MS analyses were performed using Agilent GC-QTOF. GC-MS analysis was performed on Shimadzu GC-2010 gas chromatograph coupled to a Shimadzu QP2010 mass selective detector. HR-MS analyses were performed at a Thermo Scientific Exactive (EI).

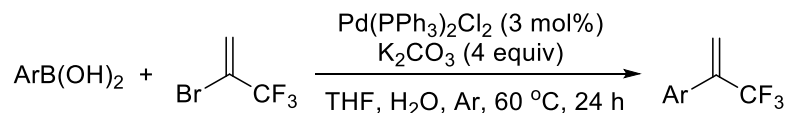
(B) General Experimental Procedures**(a) Preparation of Substrates Trifluoromethyl Alkenes:**

Trifluoromethyl alkene substrates were prepared according to literature procedures.¹

(i) Synthesis of trifluoromethyl aryl alkenes:

To a Schlenk tube equipped with a magnetic stir bar were added arylboronic acid (5 mmol), aqueous K₂CO₃ (2.0 M, 10 mL), THF (15 mL), PdCl₂(PPh₃)₂ (105 mg, 0.15 mmol) and 2-bromo-3,3,3-trifluoropropene (1399 mg, 8 mmol). The resulting solution was stirred at 40 °C or 60 °C for 24 h. After the reaction was finished, the reaction

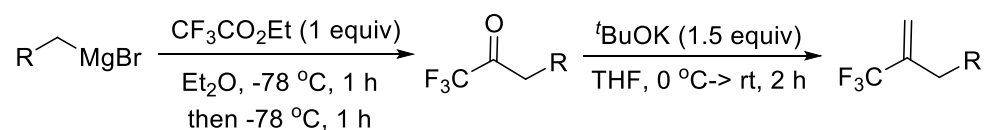
mixture was cooled to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl , and extracted with Et_2O ($3 \times 10 \text{ mL}$). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography silica gel (hexane as an eluent) to attain the trifluoromethyl alkenes.



(ii) Synthesis of alkyl substrates:

To a diethyl ether solution (25 mL) of ethyl trifluoroacetate (10 mmol) was added Grignard reagent (10 mmol), prepared from alkyl bromide (10 mmol) and magnesium turning (10 mmol), at -78°C over 30 min. After stirring for 1 h at the same temperature, the mixture was warmed to -50°C over 1 h, and saturated aqueous NH_4Cl was added. Organic materials were extracted with Et_2O ($3 \times 10 \text{ mL}$). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography silica gel (hexane as an eluent) to attain the trifluoromethyl alkyl ketones.

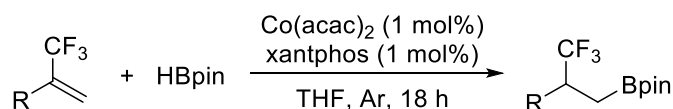
The ketone (5.0 mmol) was dissolved in THF (3 mL) and slowly added to a stirred mixture of methyltriphenylphosphonium bromide (1.5 equiv, 7.5 mmol) and potassium *tert*-butoxide (1.5 equiv, 7.5 mmol) in THF (10 mL) at 0°C . The mixture was warmed to room temperature and stirred for 2 hours. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was extracted with Et_2O ($3 \times 10 \text{ mL}$). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography silica gel (hexane as an eluent) to attain the trifluoromethyl aryl alkenes.



(b) General Procedures for Cobalt-Catalyzed Boration of Trifluoromethyl Alkenes:

(i) Cobalt-catalyzed hydroboration of trifluoromethyl alkenes:

In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with Co(acac)₂ (0.8 mg, 3.0 μmol), xantphos (1.3 mg, 3.0 μmol), trifluoromethyl alkene (0.300 mmol), THF (0.5 mL) and a magnetic stirring bar. The solution was stirred for 5 min and pinacolborane (46.0 mg, 0.360 mmol) was added to the vial. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The reaction was allowed to stir at room temperature for 18 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. Subsequently, the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 100:1) to afford the desired products **4**. The characterization data for these hydroboration products were listed in the following section.



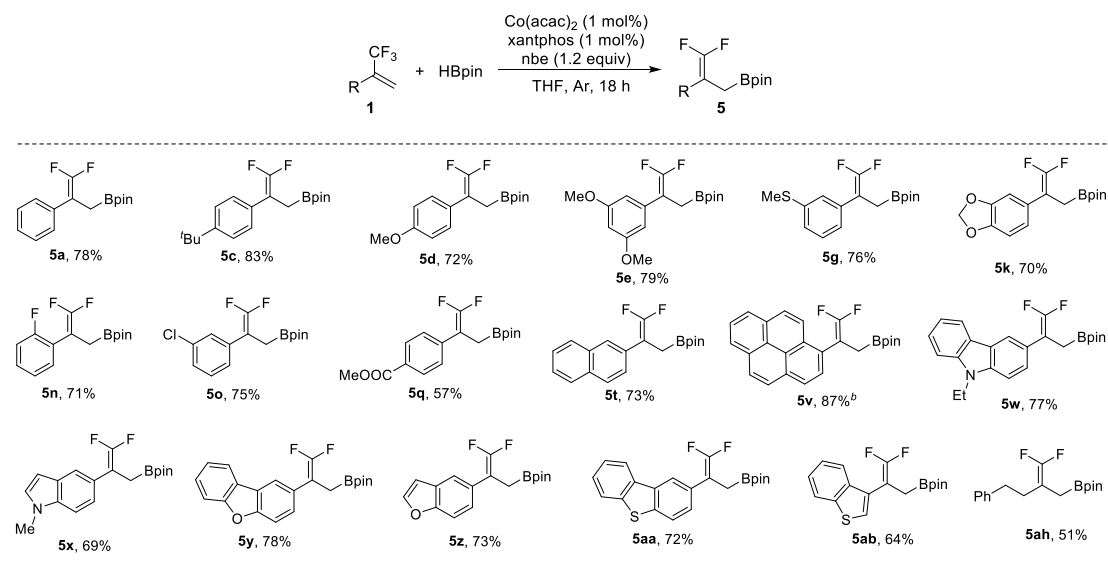
(ii) Enantioselective cobalt-catalyzed hydroboration of fluoroalkylated alkenes:

In an Ar-filled dry box, Co(acac)₂ (1.5 mg, 6.0 μmol), (*R*)-BTfM-Garphos (9.5 mg, 8.0 μmol), trifluoromethyl alkenes **1** (0.200 mmol), Me-THF (0.1 mL), and a magnetic stirring bar were added to a 4 mL screw-capped vial and stirred for 15 mins. Then Liacac (6.4 mg, 60 μmol) and HBpin (30.7 mg, 0.240 mmol) were added. The vial was sealed with a cap containing a PTFE septum and removed from the dry box. The reaction mixture was stirred at room temperature for 48 h and the resulting solution was concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate) to afford the desired products **4**. The characterization data of these chiral alkylboronates were listed below.

(iii) Cobalt-catalyzed defluoroborylation of trifluoromethyl alkenes:

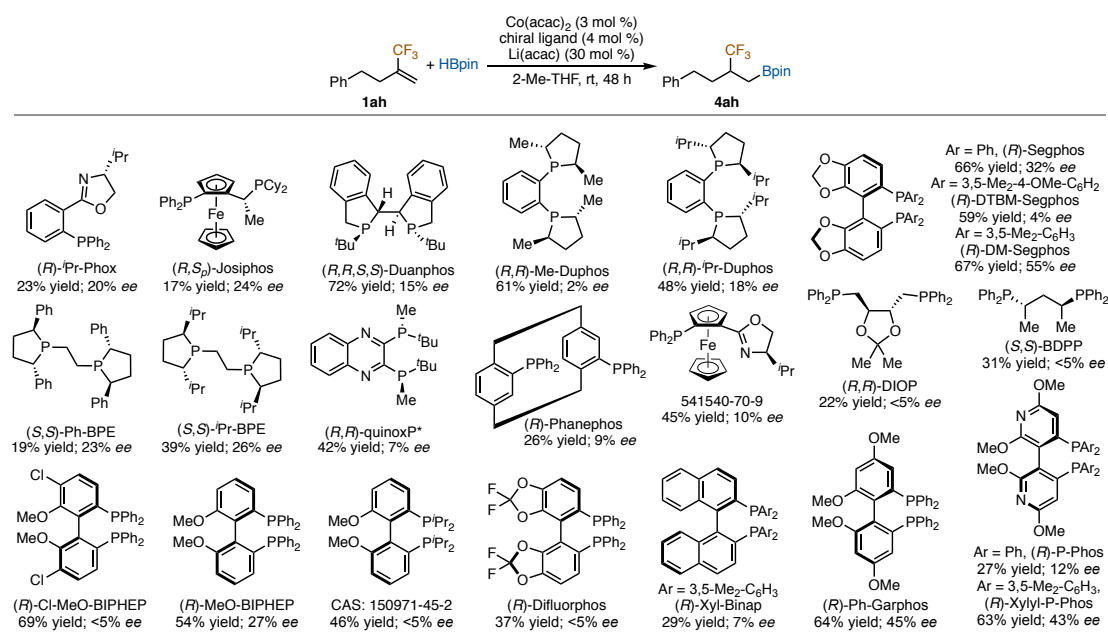
In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with Co(acac)₂ (0.8 mg, 3.0 μmol), xantphos (1.3 mg, 3.0 μmol), nbe (0.36 mmol), trifluoromethyl alkene (0.30 mmol), THF (0.5 mL) and a magnetic stirring bar. The solution was stirred for 5 min and pinacolborane (84.5 mg, 0.660 mmol) was then added to the vial. The vial was sealed with a cap containing a PTFE septum and removed from the

glovebox. The reaction was allowed to stir at room temperature for 18 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. Subsequently, the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 100:1) to afford the desired products **5**. The characterization data for these gem-difluoroallylic boronates were listed in the following section.

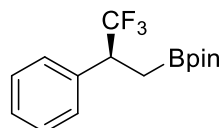


^aConditions: fluoroalkylated alkene (0.300 mmol), HBpin (2.1 equiv), Co(acac)₂ (1 mol%), xantphos (1 mol%), and norbornene (1.2 equiv), THF (1 mL), 18 h. ^b40 °C.

(c) Evaluation of Ligands for Asymmetric Hydroboration of Alkene **1ah**.



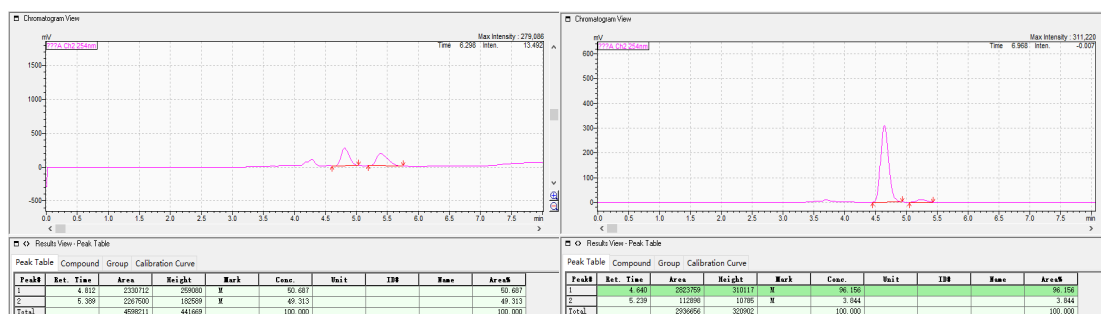
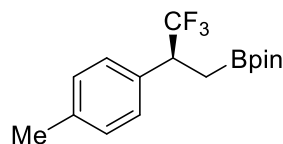
^aConditions: alkene **1h** (0.100 mmol), HBpin (0.120 mmol), Co(acac)₂ (3.0 μmol), ligand (4.0 μmol), 2-Me-THF (0.1 mL) at rt for 48 h.

(C) Characterization Data**(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-phenylpropyl)-1,3,2-dioxaborolane****(4a):**

Colorless oil (49.2 mg, 82% yield, 92% ee); ¹H NMR (400 MHz, CDCl₃) δ: 7.35-7.26 (m, 5H), 3.62-3.51 (m, 1H), 1.52-1.40 (m, 2H), 1.07 (s, 6H), 1.02 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 136.4, 129.0, 128.3, 127.9, 127.3 (q, *J* = 280 Hz), 83.5, 45.5 (q, *J* = 27.6 Hz), 24.6, 24.3, 11.7 (broad); ¹⁹F NMR (377 MHz, CDCl₃) δ: -71.7; HRMS *m/z* (EI) calcd for C₁₅H₂₀BF₃O₂: 300.1508; Found: 300.1506.

Optical rotation: [α]_D²⁵: 17.19 (*c* = 1.0, CHCl₃).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm, *t*_R = 4.6 min for the major isomer, *t*_R = 5.2 min for the minor isomer.

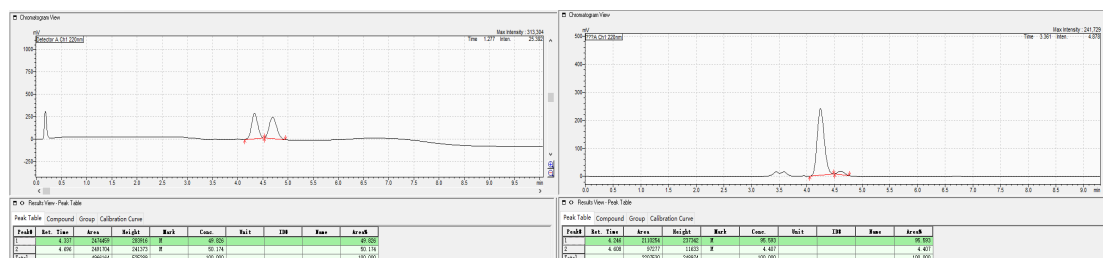
**(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(*p*-tolyl)propyl)-1,3,2-dioxaborolane****(4b):**

Colorless oil (45.8 mg, 73% yield, 91% ee); ¹H NMR (400 MHz, CDCl₃) δ: 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.59-3.48 (m, 1H), 2.32 (s, 3H), 1.51-1.36 (m, 2H), 1.08 (s, 6H), 1.04 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 137.5, 133.4, 129.0, 128.8, 127.4 (q, *J* = 280 Hz), 83.5, 45.1 (q, *J* = 27.5 Hz), 24.6, 24.4, 21.0; The boron-bound carbon was not detected due to quadrupolar relaxation, ¹⁹F NMR (377

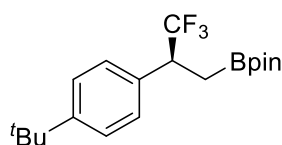
MHz, CDCl₃) δ : -71.8. HRMS m/z (EI) calcd for C₁₆H₂₂BF₃O₂: 314.1665; Found: 314.1663.

Optical rotation: $[\alpha]_D^{25}$: 26.11 ($c = 1.0$, CHCl₃).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_R = 4.2$ min for the major isomer, $t_R = 4.6$ min for the minor isomer.

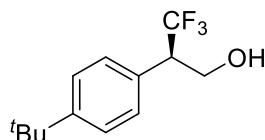


(S)-2-(2-(4-(*tert*-butyl)phenyl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c):



Colorless oil (54.1 mg, 76% yield, 88% ee); ¹H NMR (400 MHz, CDCl₃) δ : 7.34-7.32 (m, 2H), 7.26-7.24 (m, 2H), 3.60-3.49 (m, 1H), 1.51-1.39 (m, 2H), 1.05 (s, 6H), 1.01 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ : 150.8, 133.4 (two signals overlap), 128.7, 127.4 (q, $J = 280$ Hz), 125.1, 83.4, 45.0 (q, $J = 27.6$ Hz), 34.4, 31.2, 24.5, 24.3, 11.8 (broad); ¹⁹F NMR (377 MHz, CDCl₃) δ : -71.7; HRMS m/z (EI) calcd for C₁₉H₂₈BF₃O: 356.2135; Found: 356.2135.

(R)-2-(4-(*tert*-butyl)phenyl)-3,3,3-trifluoropropan-1-ol (4c'):

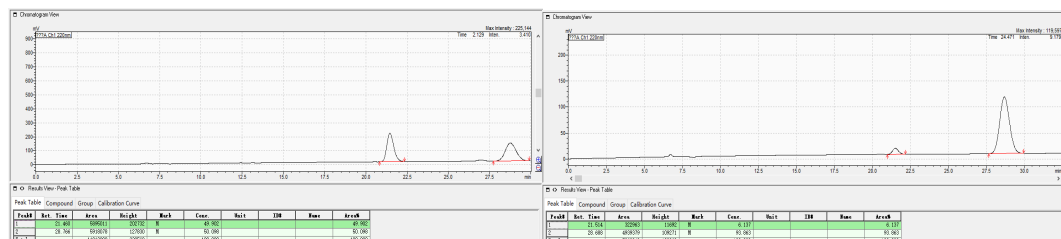


White solid; ¹H NMR (500 MHz, CDCl₃) δ : 7.43-7.40 (m, 2H), 7.26 (d, $J = 8.5$ Hz, 2H), 4.16 (dd, $J = 11.4, 5.7$ Hz, 1H), 4.01 (dd, $J = 11.4, 7.9$ Hz, 1H), 3.57-3.49 (m, 1H), 1.69 (s, 1H), 1.33 (s, 9H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ : 151.6, 129.2, 128.7, 126.1 (q, $J = 280$ Hz), 125.9, 61.3 (q, $J = 2.6$ Hz), 52.1 (q, $J = 25.5$ Hz), 31.2;

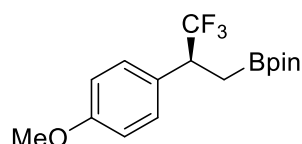
^{19}F NMR (471 MHz, CDCl_3) δ : -67.5, HRMS m/z (EI) calcd for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{O}$: 246.1232; Found: 246.1228.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: 28.32 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_{\text{R}} = 28.7$ min for the major isomer, $t_{\text{R}} = 21.5$ min for the minor isomer.



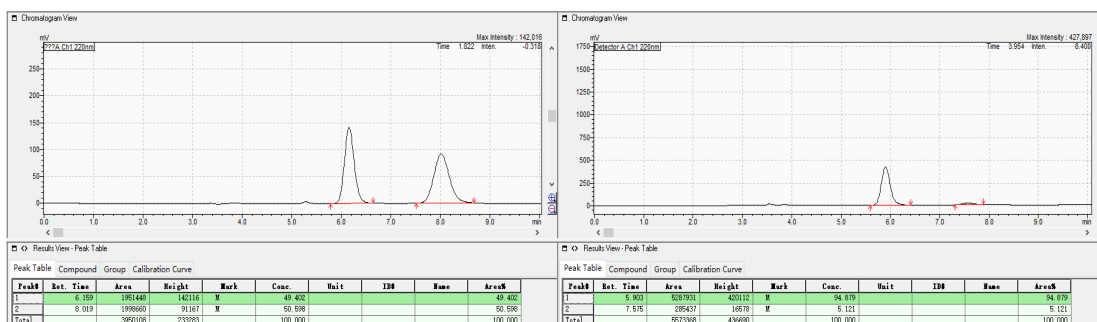
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(4-methoxyphenyl)propyl)-1,3,2-dioxaborolane (4d):



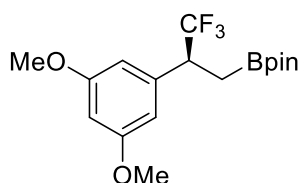
Colorless oil (51.5 mg, 78% yield, 90% ee); ^1H NMR (400 MHz, CDCl_3) δ : 7.24 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H), 3.57-3.46 (m, 1H), 1.49-1.36 (m, 2H), 1.08 (s, 6H), 1.03 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 159.3, 130.0, 127.4 (q, $J = 280$ Hz), 113.6 (two signals overlap), 83.4, 55.2, 44.7 (q, $J = 27.6$ Hz), 24.6, 24.3, 11.8 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -72.1; HRMS m/z (EI) calcd for $\text{C}_{16}\text{H}_{22}\text{BF}_3\text{O}_5$: 330.1614; Found: 330.1619.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: 36.13 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_{\text{R}} = 5.9$ min for the major isomer, $t_{\text{R}} = 7.6$ min for the minor isomer.



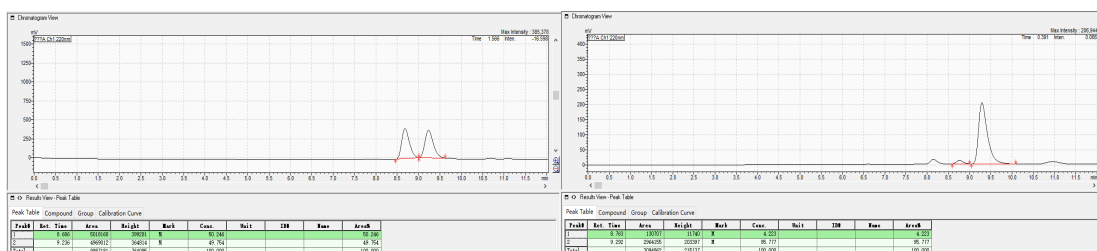
(S)-2-(2-(3,5-dimethoxyphenyl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e):



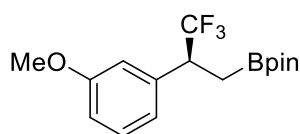
Light yellow oil (59.8 mg, 83% yield, 92% ee); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 6.46 (s, 2H), 6.37 (s, 1H), 3.76 (s, 6H), 3.53-3.44 (m, 1H), 1.46-1.35 (m, 2H), 1.09 (s, 6H), 1.05 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 160.5, 138.6, 127.2 (q, $J = 280$ Hz), 107.1, 99.9, 83.5, 55.2, 45.7 (q, $J = 27.7$ Hz), 24.6, 24.3, 11.8 (broad); $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ : -71.4, HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{24}\text{BF}_3\text{O}_4$: 360.1720; Found: 360.1723.

Optical rotation: $[\alpha]_D^{25}$: 11.31 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column IA, n-hexane/i-PrOH = 99:1, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_R = 9.3$ min for the major isomer, $t_R = 8.8$ min for the minor isomer.



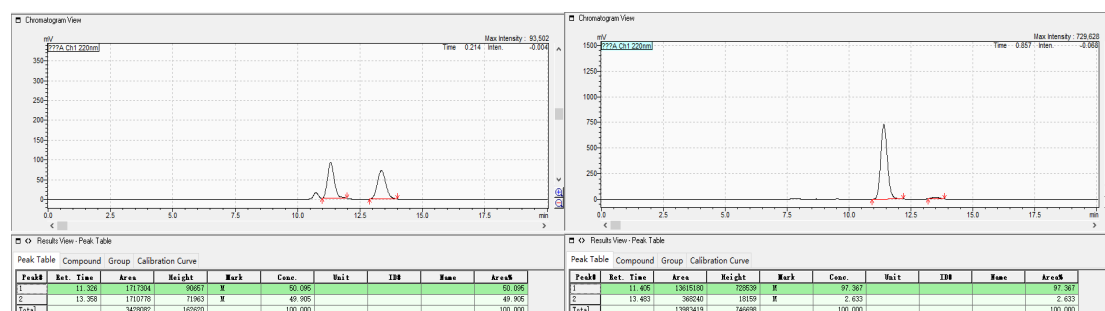
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(3-methoxyphenyl)propyl)-1,3,2-dioxaborolane (4f):



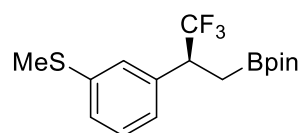
Colorless oil (48.2 mg, 73% yield, 95% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.22 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.86 (s, 1H), 6.83 (d, $J = 8.0$ Hz, 1H), 3.80 (s, 3H), 3.58-3.50 (m, 1H), 1.50-1.37 (m, 2H), 1.09 (s, 6H), 1.04 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 159.4, 137.9, 129.3, 127.2 (q, $J = 280$ Hz), 121.3, 114.8, 113.4, 83.5, 55.2, 45.5 (q, $J = 27.6$ Hz), 24.6, 24.4, 11.7 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.9; HRMS m/z (EI) calcd for $\text{C}_{10}\text{H}_{22}\text{BF}_3\text{O}_3$: 330.1614; Found: 330.1617.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: 7.28 ($c = 0.5$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 98:2, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_{\text{R}} = 11.4$ min for the major isomer, $t_{\text{R}} = 13.5$ min for the minor isomer.



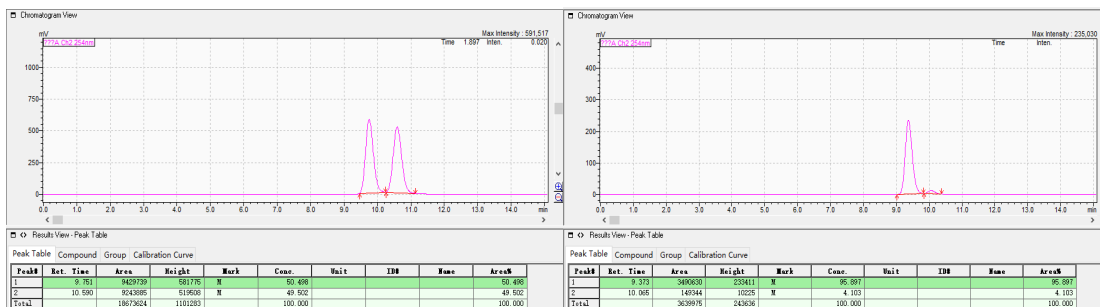
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(3-(methylthio)phenyl)propyl)-1,3,2-dioxaborolane (4g):



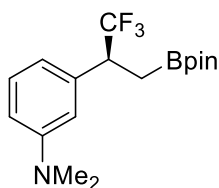
Colorless oil (51.9 mg, 75% yield, 92 % ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.25-7.16 (m, 3H), 7.09 (d, $J = 7.5$ Hz, 1H), 3.58-3.49 (m, 1H), 2.47 (s, 3H), 1.50-1.37 (m, 2H), 1.08 (s, 6H), 1.03 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 138.5, 137.2, 128.7, 127.3, 127.1 (q, $J = 280$ Hz), 126.1, 125.6, 83.5, 45.5 (q, $J = 27.7$ Hz), 24.6, 24.3, 15.8, 11.7 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.5; HRMS m/z (EI) calcd for $\text{C}_{16}\text{H}_{22}\text{BF}_3\text{O}_2\text{S}$: 346.1386; Found: 346.1386.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: 28.63 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 98:2, flow rate = 0.5 mL/min, wavelength = 254 nm, $t_{\text{R}} = 9.4$ min for the major isomer, $t_{\text{R}} = 10.1$ min for the minor isomer.



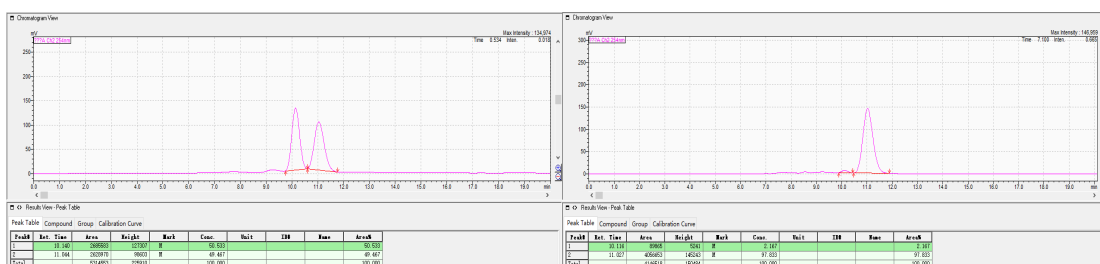
(S)-N,N-dimethyl-3-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)aniline (4h):



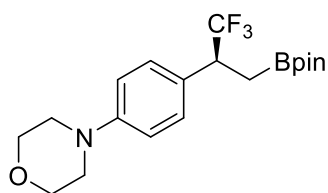
Light yellow oil (54.9 mg, 80% yield, 96% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.18-7.15 (m, 4H), 6.69-6.65 (m, 3H), 3.56-3.47 (m, 1H), 2.93 (s, 6H), 1.50-1.38 (m, 2H), 1.10 (s, 6H), 1.05 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 150.5, 137.2, 128.9, 127.5 (q, $J = 280$ Hz), 117.2, 113.5, 112.3, 83.4, 45.8 (q, $J = 27.3$ Hz), 40.6, 24.6, 24.4, 11.9 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.3. HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{BF}_3\text{NO}_2$: 343.1930; Found: 343.1932.

Optical rotation: $[\alpha]_D^{25}$: 20.08 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, wavelength = 254 nm, $t_R = 11.0$ min for the major isomer, $t_R = 10.1$ min for the minor isomer.



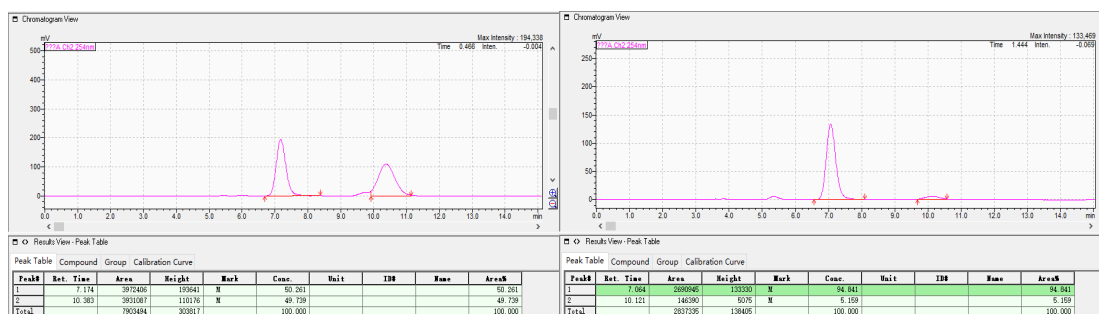
(S)-4-(4-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)phenyl)morpholine (4i):



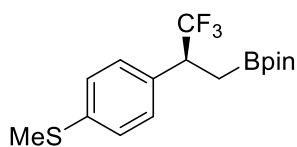
Light yellow oil (56.2 mg, 73% yield, 90% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.21 (d, $J = 8.5$ Hz, 2H), 6.85 (d, $J = 9.0$ Hz, 2H), 3.85 (t, $J = 5.0$ Hz, 2H), 3.54-3.45 (m, 1H), 3.13 (t, $J = 5.0$ Hz, 2H), 1.48-1.34 (m, 2H), 1.08 (s, 6H), 1.04 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 150.8, 129.7, 127.8, 127.4 (q, $J = 280$ Hz), 115.4, 83.4, 66.8, 49.3, 44.6 (q, $J = 27.6$ Hz), 24.6, 24.4, 11.8 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.9; HRMS m/z (EI) calcd for $\text{C}_{10}\text{H}_{17}\text{BF}_3\text{NO}$: 385.2036; Found: 385.2041.

Optical rotation: $[\alpha]_D^{25}$: 18.54 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 7.1$ min for the major isomer, $t_R = 10.1$ min for the minor isomer.



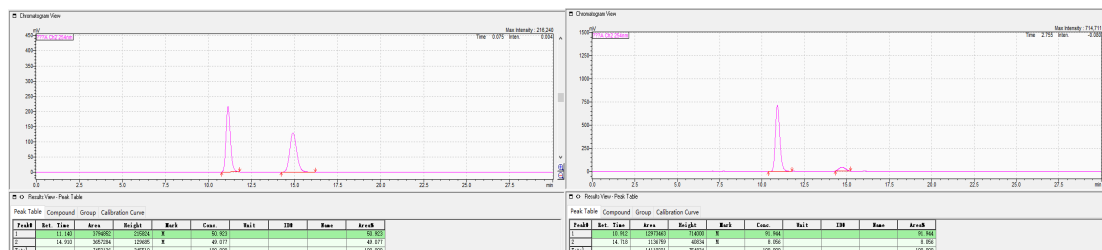
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(4-(methylthio)phenyl)propyl)-1,3,2-dioxaborolane (4j):



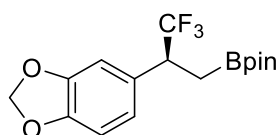
White solid (52.6 mg, 76% yield, 84% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.26-7.19 (m, 4H), 3.57-3.48 (m, 1H), 2.46 (s, 3H), 1.47 (dd, $J = 15.7, 5.7$ Hz, 1H), 1.38 (dd, $J = 15.6, 10.7$ Hz, 1H), 1.08 (s, 6H), 1.03 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 138.2, 130.1, 129.4, 127.2 (q, $J = 280$ Hz), 126.4, 83.5, 45.0 (q, $J = 27.5$ Hz), 24.6, 24.3, 15.8, 11.6 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.8; HRMS m/z (EI) calcd for $\text{C}_{16}\text{H}_{22}\text{BF}_3\text{O}_2\text{S}$: 346.1386; Found: 346.1392.

Optical rotation: $[\alpha]_D^{25}$: 31.12 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/i-PrOH = 95:5, flow rate = 0.5 mL/min, wavelength = 254 nm, $t_R = 14.7$ min for the major isomer, $t_R = 10.9$ min for the minor isomer.



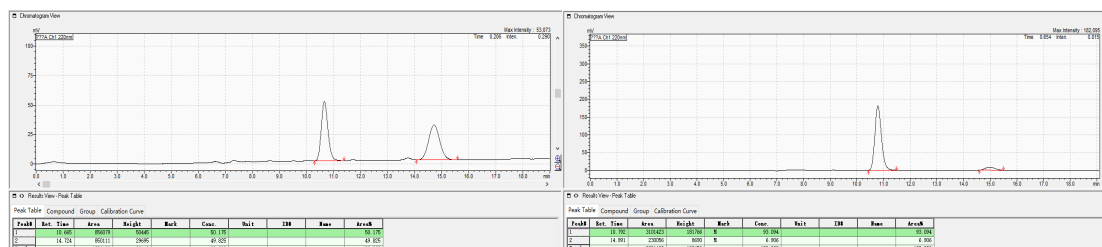
(S)-2-(2-(benzo[*d*][1,3]dioxol-5-yl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k):



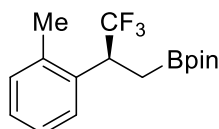
Colorless oil (49.5 mg, 72% yield, 86% ee); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 6.81-6.74 (m, 3H), 5.94 (s, 2H), 3.53-3.44 (m, 1H), 1.46-1.31 (m, 2H), 1.11 (s, 6H), 1.06 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 147.6, 147.2, 130.1, 127.2 (q, $J = 280$ Hz), 122.5, 109.2, 108.0, 101.0, 83.5, 45.2 (q, $J = 27.6$ Hz), 24.7, 24.4, 11.6 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -71.9. HRMS m/z (EI) calcd for $\text{C}_{16}\text{H}_{20}\text{BF}_3\text{O}_4$: 344.1407; Found: 344.1410.

Optical rotation: $[\alpha]_D^{25}$: 16.27 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/i-PrOH = 95:5, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_R = 10.8$ min for the major isomer, $t_R = 15.0$ min for the minor isomer.

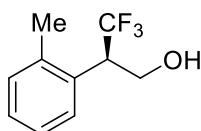


(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(*o*-tolyl)propyl)-1,3,2-dioxaborolane (4l):



Colorless oil (45.2 mg, 72% yield, 88% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.33 (d, $J = 7.0$ Hz, 1H), 7.20-7.13 (m, 3H), 3.94-3.85 (m, 1H), 2.42 (s, 3H), 1.53-1.44 (m, 2H), 1.02 (s, 6H), 0.95 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 137.6, 134.9, 130.1, 127.6 (q, $J = 280$ Hz), 127.6, 127.6, 126.1, 83.4, 40.0 (q, $J = 27.5$ Hz), 24.5, 24.2, 19.9, 11.8 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.6. HRMS m/z (EI) calcd for $\text{C}_{16}\text{H}_{22}\text{BF}_3\text{O}_2$: 314.1665; Found: 314.1646.

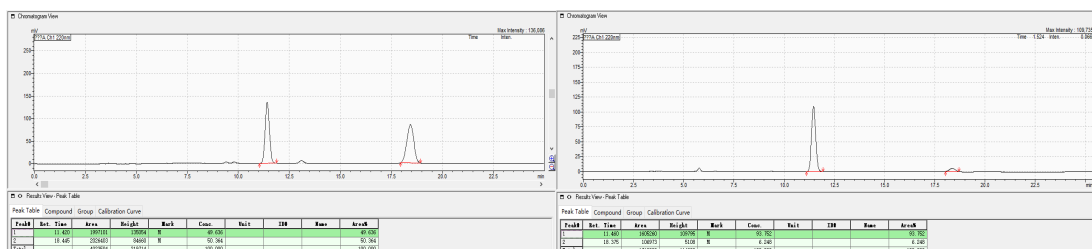
(R)-3,3,3-trifluoro-2-(o-tolyl)propan-1-ol (4l'):



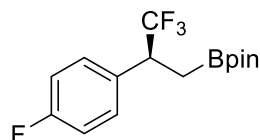
Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ : 7.35-7.34 (m, 1H), 7.26-7.25 (m, 3H), 4.24-4.21 (m, 1H), 4.04-4.00 (m, 1H), 3.99-3.91 (m, 1H), 3.74 (s, 1H), 2.40 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 138.1, 131.0, 130.9, 128.4, 127.0, 126.6, 126.3 (q, $J = 281$ Hz), 61.5 (q, $J = 2.7$ Hz), 47.2 (q, $J = 25.4$ Hz), 20.0; ^{19}F NMR (471 MHz, CDCl_3) δ : -67.2. HRMS m/z (EI) calcd for $\text{C}_{10}\text{H}_{11}\text{F}_3\text{O}$: 204.0762; Found: 204.0757.

Optical rotation: $[\alpha]_D^{25}$: 14.89 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_R = 11.5$ min for the major isomer, $t_R = 18.4$ min for the minor isomer.



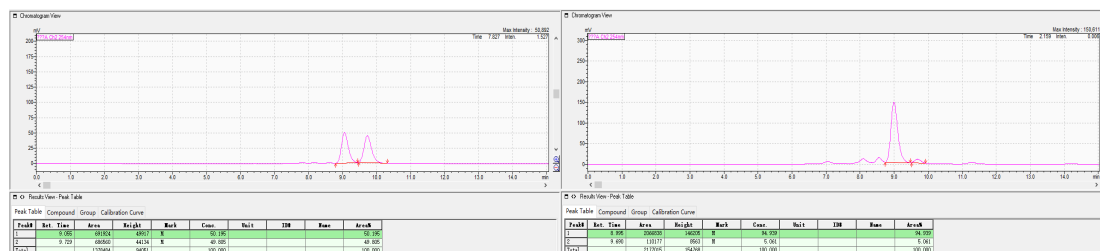
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(4-fluorophenyl)propyl)-1,3,2-dioxaborolane (4m):



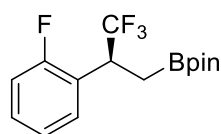
Colorless oil (45.2 mg, 71% yield, 90% ee); ^1H NMR (400 MHz, CDCl_3) δ : 7.31–7.28 (m, 2H), 7.04–6.98 (m, 2H), 3.61–3.50 (m, 1H), 1.51–1.35 (m, 2H), 1.08 (s, 6H), 1.02 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 162.5 (d, $J = 246$ Hz), 132.2 (dd, $J = 3.1, 1.9$ Hz), 130.6 (d, $J = 8.1$ Hz), 137.1 (q, $J = 279$ Hz), 115.2 (d, $J = 21.4$ Hz), 83.6, 44.9 (q, $J = 27.8$ Hz), 24.6, 24.3, 11.8 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -72.0, -114.5. HRMS m/z (EI) calcd for $\text{C}_{15}\text{H}_{19}\text{BF}_4\text{O}_2$: 318.1414; Found: 318.1414.

Optical rotation: $[\alpha]_D^{25}$: 28.35 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, wavelength = 254 nm, $t_R = 9.0$ min for the major isomer, $t_R = 9.7$ min for the minor isomer.



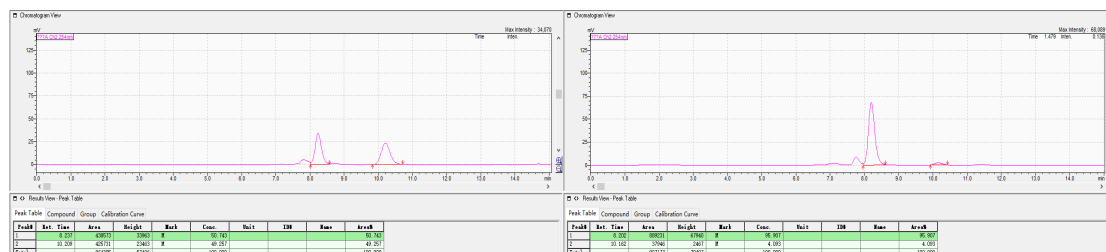
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(2-fluorophenyl)propyl)-1,3,2-dioxaborolane (4n):



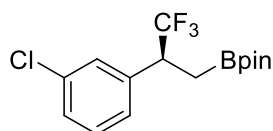
Colorless oil (42.6 mg, 67% yield, 92% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.36 (t, $J = 7.5$ Hz, 1H), 7.29–7.24 (m, 1H), 7.14–7.11 (m, 1H), 7.06–7.02 (m, 1H), 4.09–4.01 (m, 1H), 1.53–1.41 (m, 2H), 1.07 (s, 6H), 1.00 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 161.0 (d, $J = 28.5$ Hz), 129.5 (q, $J = 8.4$ Hz), 129.3 (q, $J = 2.7$ Hz), 127.0 (q, $J = 279$ Hz), 124.1 (q, $J = 3.7$ Hz), 123.7 (dq, $J = 14.3, 1.9$ Hz), 115.3 (q, $J = 22.9$ Hz), 83.5, 37.2 (qd, $J = 28.5, 3.3$ Hz), 24.6, 24.2, 11.1 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -71.9 (d, $J = 4.5$ Hz), -116.8 (q, $J = 4.3$ Hz); HRMS m/z (EI) calcd for $\text{C}_{15}\text{H}_{19}\text{BF}_4\text{O}_2$: 318.1414; Found: 318.1410.

Optical rotation: $[\alpha]_D^{25}$: 18.17 ($c = 0.5$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/i-PrOH = 95:5, flow rate = 0.5 mL/min, wavelength = 254 nm, $t_R = 8.2$ min for the major isomer, $t_R = 10.2$ min for the minor isomer.



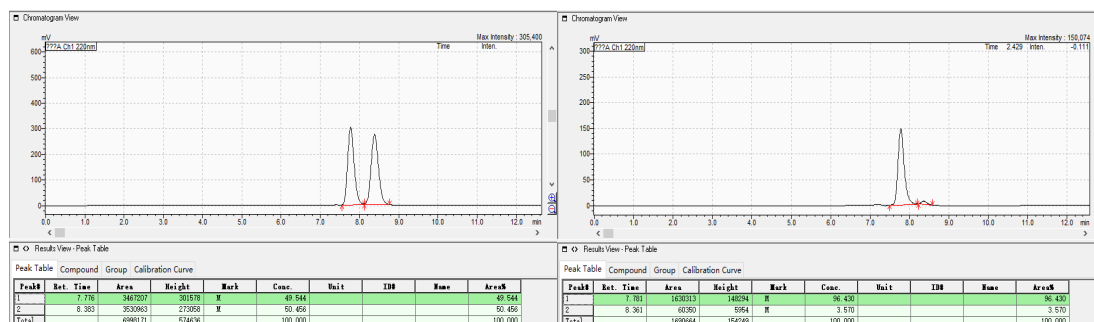
(S)-2-(2-(3-chlorophenyl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4o):



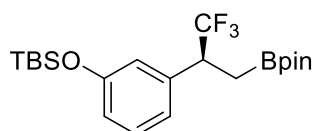
Colorless oil (38.7 mg, 58% yield, 93% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.32 (s, 1H), 7.28-7.21 (m, 3H), 3.59-3.50 (m, 1H), 1.50-1.35 (m, 2H), 1.09 (s, 6H), 1.03 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 138.5, 134.1, 129.6, 129.3, 128.1, 127.1, 124.7 (q, $J = 280$ Hz), 83.6, 45.3 (q, $J = 27.9$ Hz), 24.6, 24.3, 11.8 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -71.5; HRMS m/z (EI) calcd for $\text{C}_{15}\text{H}_{19}\text{BClF}_3\text{O}_2$: 334.1119, found 334.1115.

Optical rotation: $[\alpha]_D^{25}$: 28.35 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/i-PrOH = 98:2, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_R = 7.8$ min for the major isomer, $t_R = 8.4$ min for the minor isomer.

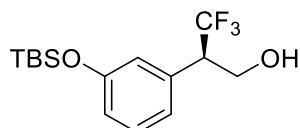


(S)-tert-butyl dimethyl(3-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)propan-2-yl)phenoxy)silane (4p):



Colorless oil (57.6 mg, 67% yield, 91% ee); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.16 (t, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.80 (s, 1H), 6.77-6.75 (m, 1H), 3.55-3.46 (m, 1H), 1.48-1.36 (m, 2H), 1.10 (s, 6H), 1.05 (s, 6H), 0.98 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 155.5, 137.8, 129.1, 127.2 (q, $J = 280$ Hz), 122.0, 120.9, 119.6, 83.5, 45.3 (q, $J = 27.6$ Hz), 25.7, 24.6, 24.4, 11.7 (broad), -4.5 (two signals overlap); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ : -71.6; HRMS m/z (EI) calcd for $\text{C}_{21}\text{H}_{34}\text{BF}_3\text{O}_3\text{Si}$: 430.2322; Found: 430.2330.

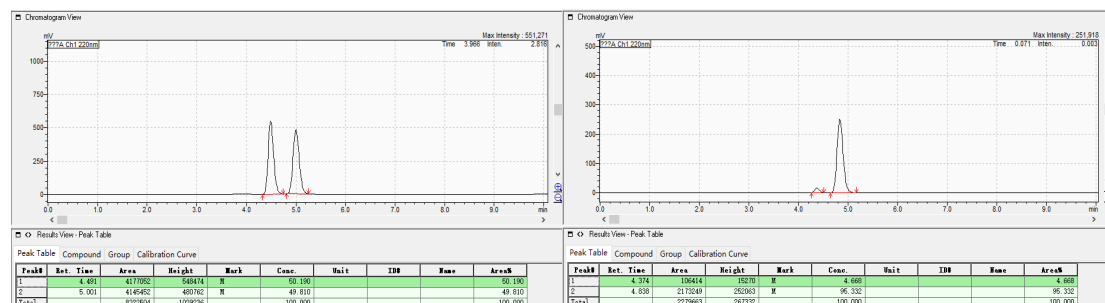
(R)-2-(3-((tert-butyldimethylsilyloxy)phenyl)-3,3,3-trifluoropropan-1-ol (4p'):

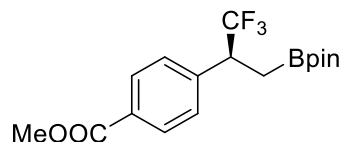


Colorless oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.24 (t, $J = 8.0$ Hz, 1H), 6.91 (t, $J = 8.0$ Hz, 1H), 6.86-6.83 (m, 1H), 6.82 (s, 1H), 4.16 (dd, $J = 11.5, 5.8$ Hz, 1H), 4.00 (dd, $J = 11.5, 7.8$ Hz, 1H), 3.54-3.45 (m, 1H), 1.59 (s, 1H), 0.98 (s, 9H), 0.20 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 156.1, 133.7, 129.9, 126.0 (q, $J = 280$ Hz), 122.0, 120.9, 120.3, 61.4 (d, $J = 2.6$ Hz), 52.4 (q, $J = 25.6$ Hz), 25.63, -4.47; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ : -67.4; HRMS m/z (EI) calcd for $\text{C}_{15}\text{H}_{23}\text{F}_3\text{O}_2\text{Si}$: 320.1419; Found: 320.1418.

Optical rotation: $[\alpha]_D^{25}$: 13.22 ($c = 0.5$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_R = 4.8$ min for the major isomer, $t_R = 4.4$ min for the minor isomer.

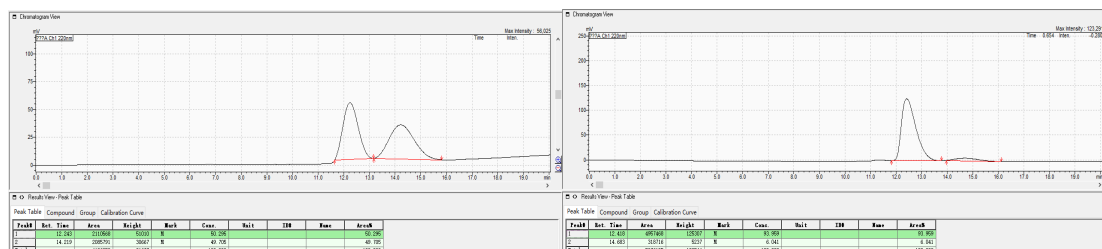
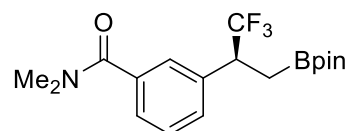


Methyl**(S)-4-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzoate (4q):**

Colorless oil (41.5 mg, 58% yield, 88% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.99 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 3.91 (s, 3H), 3.67-3.59 (m, 1H), 1.53-1.40 (m, 2H), 1.07 (s, 6H), 1.01 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 166.8, 141.6, 129.6, 129.1, 128.6, 126.9 (q, $J = 280$ Hz), 83.6, 52.1, 45.6 (q, $J = 27.9$ Hz), 24.6, 24.3, 11.6 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -71.4. HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{BF}_3\text{O}_4$: 358.1563; Found: 358.1557.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: 6.31 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/i-PrOH = 99.5:0.5, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_{\text{R}} = 12.4$ min for the major isomer, $t_{\text{R}} = 14.7$ min for the minor isomer.

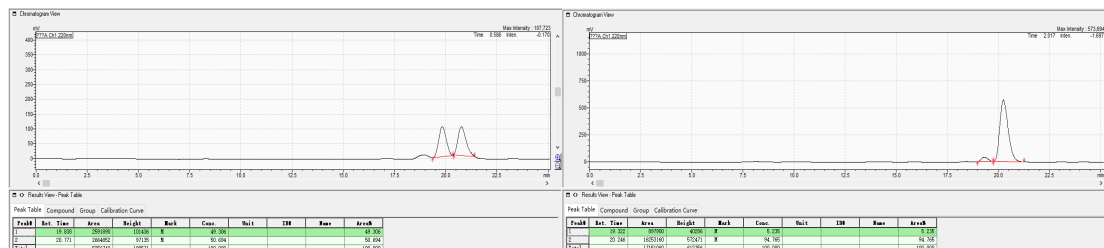
**(S)-N,N-dimethyl-3-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzamide (4r):**

Colorless oil (46.7 mg, 63% yield, 90% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.37 (s, 4H), 3.64-3.55 (m, 1H), 3.10 (s, 3H), 2.96 (s, 3H), 1.52-1.38 (m, 2H), 1.08 (s, 6H), 1.03 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 171.2, 136.6, 136.3, 130.2, 128.5, 127.8, 127.1 (d, $J = 280$ Hz), 126.9, 83.6, 45.4 (q, $J = 27.8$ Hz), 39.5, 35.4, 24.7, 24.4,

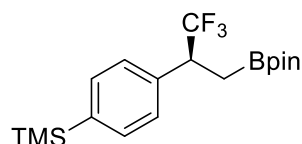
11.6 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.6; HRMS m/z (EI) calcd for $\text{C}_{18}\text{H}_{25}\text{BFNO}_3$; 371.1880; Found: 371.1876.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: 27.76 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OD-H, n-hexane/*i*-PrOH = 98:2, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_{\text{R}} = 20.2$ min for the major isomer, $t_{\text{R}} = 19.3$ min for the minor isomer.

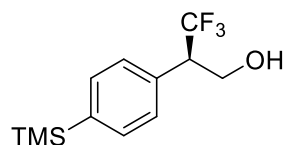


(S)-trimethyl(4-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (4s):



Colorless oil (47.6 mg, 64% yield, 89% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.48 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 7.5$ Hz, 2H), 3.61-3.53 (m, 1H), 1.51 (dd, $J = 15.6, 6.1$ Hz, 1H), 1.44 (dd, $J = 15.5, 10.4$ Hz, 1H), 1.06 (s, 6H), 1.02 (s, 6H), 0.26 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 140.1, 137.0, 133.2, 128.3, 127.3 (q, $J = 280$ Hz), 83.4, 45.5 (q, $J = 27.6$ Hz), 24.5, 24.3, 11.7 (broad), -1.3; ^{19}F NMR (471 MHz, CDCl_3) δ : -71.5, HRMS m/z (EI) calcd for $\text{C}_{18}\text{H}_{25}\text{BF}_3\text{O}_2\text{Si}$; 372.1904; Found: 372.1901.

(R)-3,3,3-trifluoro-2-(4-(trimethylsilyl)phenyl)propan-1-ol (4s')

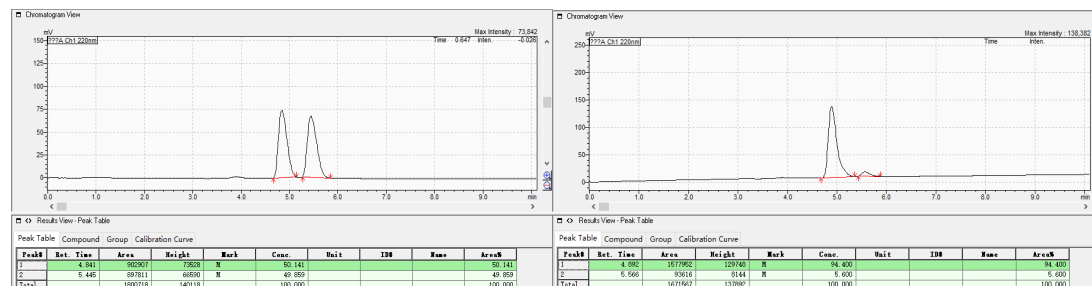


White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.57-7.55 (m, 2H), 7.33 (d, $J = 9.5$ Hz, 2H), 4.17 (dd, $J = 11.4, 5.8$ Hz, 1H), 4.02 (dd, $J = 11.4, 7.8$ Hz, 1H), 3.60-3.49 (m, 1H), 1.78 (s, 1H), 0.30 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 142.4, 135.2, 134.1 (q, $J = 1.9$ Hz), 127.3 (q, $J = 281$ Hz), 62.5 (q, $J = 2.8$ Hz), 53.8 (q, $J = 25.5$ Hz), 0; ^{19}F

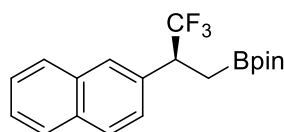
NMR (377 MHz, CDCl₃) δ : -67.3, HRMS m/z (EI) calcd for C₁₂H₁₇F₃OSi: 262.1001; Found: 262.0997.

Optical rotation: $[\alpha]_D^{25}$: 13.19 (c = 1.0, CHCl₃).

HPLC condition: Chiral column AD-H, n-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, t_R = 4.9 min for the major isomer, t_R = 5.6 min for the minor isomer.



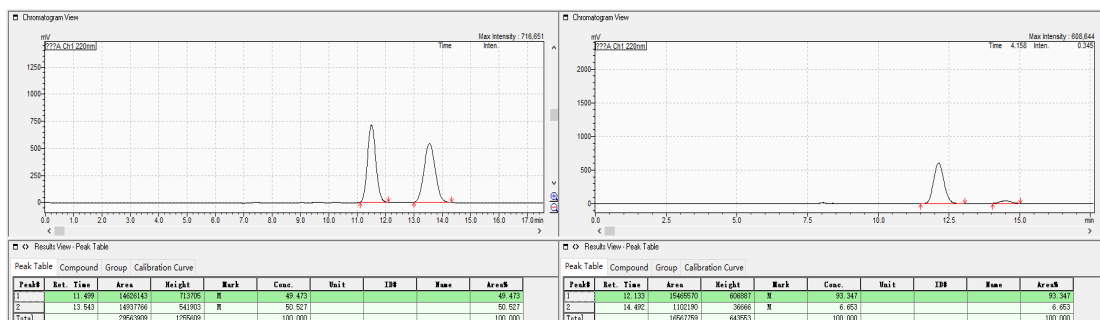
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane (4t):



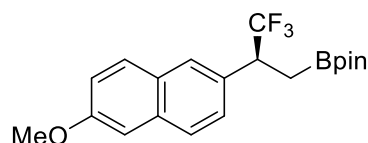
White solid (52.5 mg, 75% yield, 87% ee); ¹H NMR (400 MHz, CDCl₃) δ : 7.84-7.80 (m, 4H), 7.49-7.45 (m, 3H), 3.81-3.70 (m, 1H), 1.63-1.53 (m, 2H), 1.03 (s, 6H), 0.97 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ : 134.0, 133.1, 132.9, 128.2, 128.0, 127.9, 127.4 (q, J = 280 Hz), 126.6, 126.1 (two signals overlap), 83.5, 45.7 (q, J = 27.6 Hz), 24.6, 24.3; The boron-bound carbon was not detected due to quadrupolar relaxation, ¹⁹F NMR (377 MHz, CDCl₃) δ : -71.3; HRMS m/z (EI) calcd for C₁₉H₂₂BF₃O₂: 350.1665; Found: 350.1671.

Optical rotation: $[\alpha]_D^{25}$: 27.76 (c = 1.0, CHCl₃).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, wavelength = 220 nm, t_R = 12.1 min for the major isomer, t_R = 14.5 min for the minor isomer.



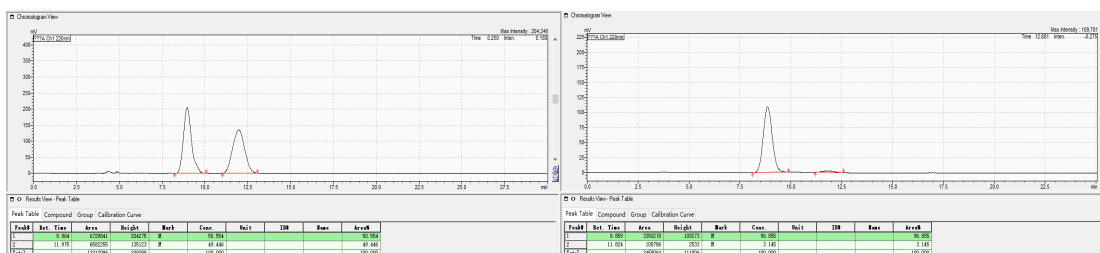
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(6-methoxynaphthalen-2-yl)propyl)-1,3,2-dioxaborolane (4u):



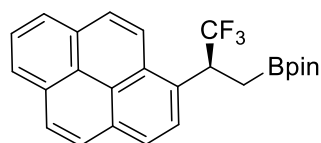
White solid (60.0 mg, 79% yield, 94% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.73 (t, $J = 9.0$ Hz, 3H), 7.43 (d, $J = 8.5$ Hz, 1H), 7.18-7.13 (m, 2H), 3.94 (s, 3H), 3.77-3.69 (m, 1H), 1.61-1.54 (m, 2H), 1.05 (s, 6H), 0.99 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 157.8, 134.1, 131.6, 129.4, 128.6, 128.0, 127.4 (q, $J = 280$ Hz), 127.1, 126.8, 119.0, 105.5, 83.5, 55.3, 45.4 (q, $J = 27.5$ Hz), 24.6, 24.3, 11.8 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.5; HRMS m/z (EI) calcd for $\text{C}_{20}\text{H}_{24}\text{BF}_3\text{O}$: 380.1771; Found: 380.1772.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: 41.62 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_{\text{R}} = 8.9$ min for the major isomer, $t_{\text{R}} = 11.8$ min for the minor isomer.



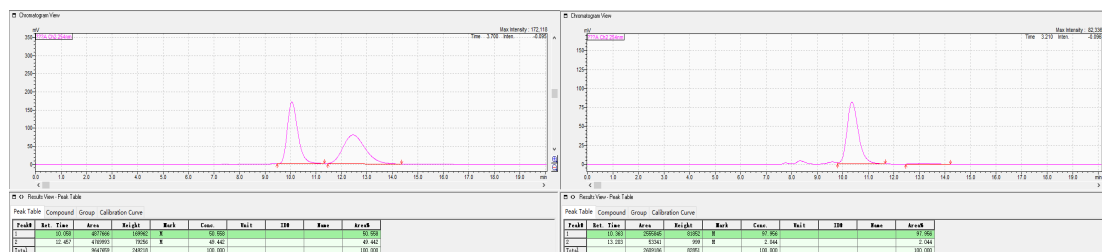
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(pyren-1-yl)propyl)-1,3,2-dioxaborolane (4v):



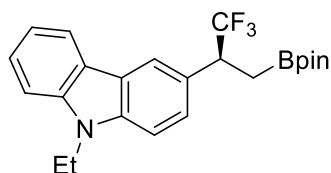
White solid (61.0 mg, 72% yield, 96% ee); ^1H NMR (500 MHz, CDCl_3) δ : 8.46 (d, J = 7.5 Hz, 1H), 8.22-8.15 (m, 5H), 8.09-8.01 (m, 3H), 4.97-4.88 (m, 1H), 1.88-1.81 (m, 2H), 0.90 (s, 6H), 0.73 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 131.3, 130.8, 130.6, 130.3, 130.0, 127.8, 127.7 (q, J = 280 Hz), 127.6, 127.4, 125.9, 125.4, 125.3, 125.0, 124.9, 124.8, 124.7, 122.9, 83.4, 39.5 (q, J = 27.8 Hz), 24.3, 24.1, 12.8 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -70.6, HRMS m/z (EI) calcd for $\text{C}_{25}\text{H}_{24}\text{BF}_3\text{O}_2$: 424.1822; Found: 424.1822.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: -48.39 (c = 1.0, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, wavelength = 254 nm, t_{R} = 10.4 min for the major isomer, t_{R} = 13.2 min for the minor isomer.



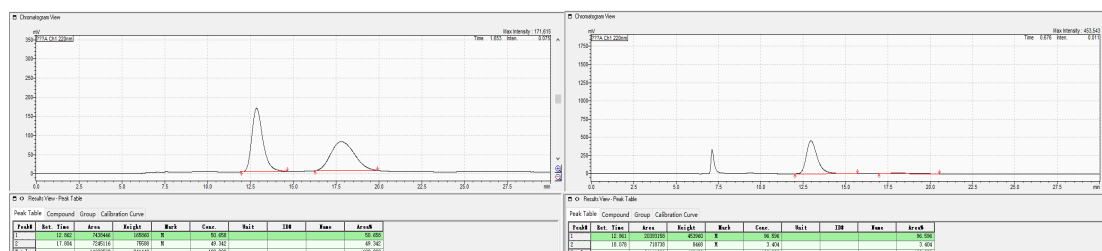
(*S*)-9-ethyl-3-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-9*H*-carbazole (4w):



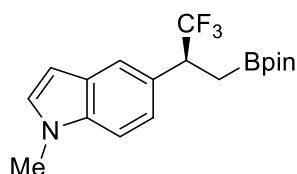
White solid (70.0 mg, 84% yield, 93% ee); ^1H NMR (500 MHz, CDCl_3) δ : 8.14 (d, J = 7.5 Hz, 1H), 8.11 (s, 1H), 7.51-7.48 (m, 2H), 7.41 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 7.28-7.25 (m, 1H), 4.37-4.33 (m, 2H), 3.86-3.81 (m, 1H), 1.69-1.60 (m, 2H), 1.43 (t, J = 7.5 Hz, 3H), 1.06 (s, 6H), 1.02 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 140.2, 139.6, 127.7 (q, J = 280 Hz), 126.7, 125.7, 122.8, 121.0, 120.4, 118.8, 108.4, 108.2, 83.4, 45.5 (q, J = 27.5 Hz), 37.5, 29.7, 24.6, 24.3, 13.7, 12.3 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.6; HRMS m/z (EI) calcd for $\text{C}_{23}\text{H}_{27}\text{BF}_3\text{NO}_2$: 417.2087; Found: 417.2090.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: 46.39 (c = 1.0, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/i-PrOH = 98:2, flow rate = 0.5 mL/min, wavelength = 220 nm, t_R = 13.0 min for the major isomer, t_R = 18.1 min for the minor isomer.



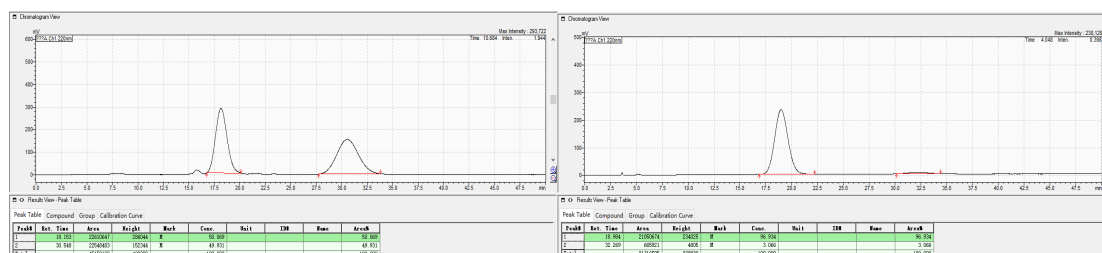
(S)-1-methyl-5-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2-yl)-1H-indole (4x):



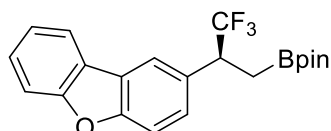
Reddish brown solid (57.2 mg, 81% yield, 94% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.59 (s, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.20 (d, J = 8.5 Hz, 1H), 7.03 (d, J = 3.0 Hz, 1H), 6.46 (d, J = 3.0 Hz, 1H), 3.76 (s, 3H), 3.73-3.66 (m, 1H), 1.60-1.49 (m, 2H), 1.06 (s, 6H), 1.02 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 136.3, 129.2, 127.7 (t, J = 280 Hz), 128.3, 127.2, 122.4, 121.3, 108.8, 100.9, 83.4, 45.5 (q, J = 27.3 Hz), 32.8, 24.6, 24.3, 12.3 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.6; HRMS m/z (EI) calcd for $\text{C}_{18}\text{H}_{23}\text{BFNO}_2$: 353.1774; Found: 353.1773.

Optical rotation: $[\alpha]_D^{25}$: 21.11 (c = 1.0, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, t_R = 19.0 min for the major isomer, t_R = 32.2 min for the minor isomer.



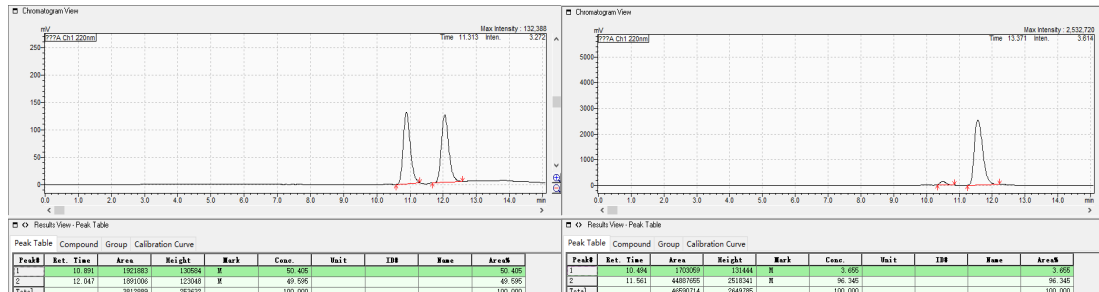
(S)-2-(2-(dibenzo[*b,d*]furan-2-yl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4y):



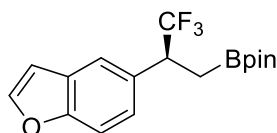
White solid (58.5 mg, 75% yield, 93% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.96 (d, $J = 7.5$ Hz, 1H), 7.92 (s, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.48-7.45 (m, 1H), 7.43 (d, $J = 8.5$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 3.80-3.71 (m, 1H), 1.61-1.51 (m, 2H), 1.03 (s, 6H), 0.98 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 156.5, 155.8, 131.0, 128.1, 127.4 (q, $J = 280$ Hz), 127.3, 124.2, 124.0, 122.8, 121.1, 120.7, 111.7, 111.4, 83.5, 45.5 (q, $J = 27.8$ Hz), 24.6, 24.3, 12.2 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.8; HRMS m/z (EI) calcd for $\text{C}_{21}\text{H}_{22}\text{BF}_3\text{O}_3$: 390.16141; Found: 390.1618.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: 26.32 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OD-H, n-hexane/*i*-PrOH = 99.5:0.5, flow rate = 0.3 mL/min, wavelength = 220 nm, $t_{\text{R}} = 10.5$ min for the major isomer, $t_{\text{R}} = 11.6$ min for the minor isomer.



(S)-2-(2-(benzofuran-5-yl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4z):

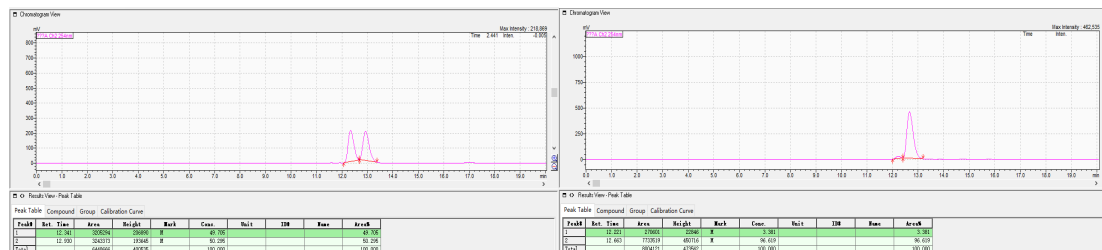


White solid (48.3 mg, 71% yield, 93% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.61 (d, $J = 2.0$ Hz, 1H), 7.57 (s, 1H), 7.45 (d, $J = 8.5$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 1H), 6.75 (d, $J = 2.0$ Hz, 1H), 3.72-3.64 (m, 1H), 1.57-1.46 (m, 2H), 1.04 (s, 6H), 0.98 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 154.5, 145.4, 131.0, 127.4, 127.4 (q, $J = 280$ Hz), 125.4, 121.6, 111.1, 106.6, 83.5, 45.4 (q, $J = 27.6$ Hz), 24.6, 24.3, 12.1 (broad); ^{19}F

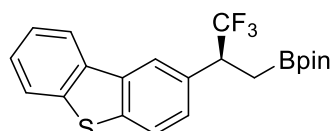
NMR (471 MHz, CDCl_3) δ : -71.8; HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{20}\text{BF}_3\text{O}_3$: 340.1458; Found: 340.1465.

Optical rotation: $[\alpha]_D^{25}$: 33.27 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OD-H, n-hexane/*i*-PrOH = 99.9:0.1, flow rate = 0.5 mL/min, wavelength = 254 nm, $t_R = 12.7$ min for the major isomer, $t_R = 12.2$ min for the minor isomer.



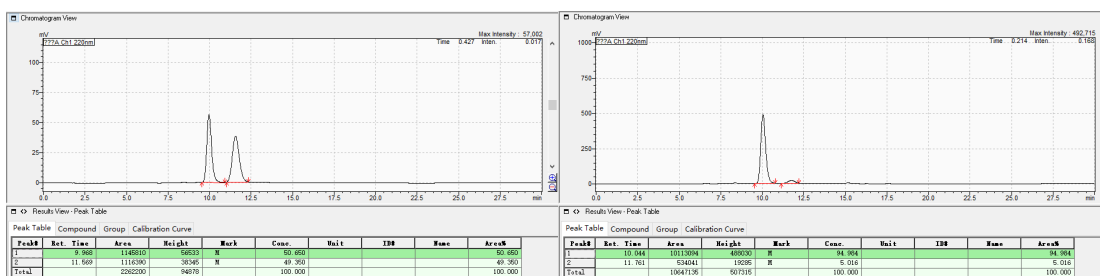
(S)-2-(2-(dibenzo[b,d]thiophen-2-yl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4aa):



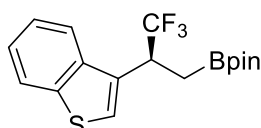
White solid (62.5 mg, 77% yield, 90% ee); ^1H NMR (500 MHz, CDCl_3) δ : 8.19-8.15 (m, 1H), 8.11 (s, 1H), 7.86-7.83 (m, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.49-7.43 (m, 3H), 3.82-3.73 (m, 1H), 1.63-1.52 (m, 2H), 1.04 (s, 6H), 0.99 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 139.8, 139.0, 135.6, 135.3, 130.7, 127.5, 127.3 (q, $J = 280$ Hz), 126.8, 124.4, 122.8, 122.7, 122.1, 121.6, 83.6, 45.6 (q, $J = 27.6$ Hz), 24.6, 24.3, 12.1 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.5; HRMS m/z (EI) calcd for $\text{C}_{21}\text{H}_{22}\text{BF}_3\text{O}_2\text{S}$: 406.1386; Found: 406.1387.

Optical rotation: $[\alpha]_D^{25}$: 10.71 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_R = 10.0$ min for the major isomer, $t_R = 11.8$ min for the minor isomer.



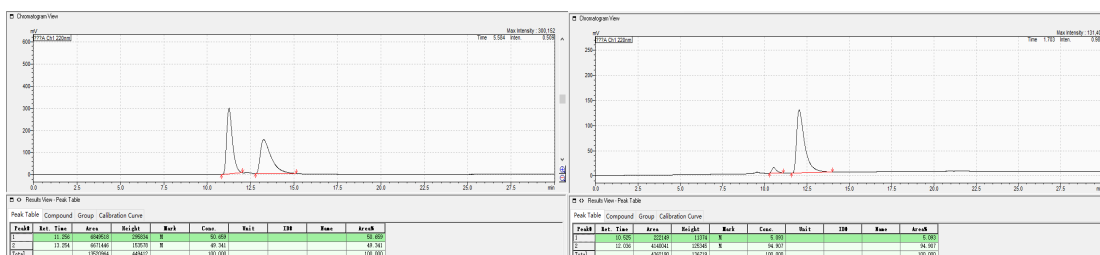
(S)-2-(2-(benzo[*b*]thiophen-3-yl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ab):



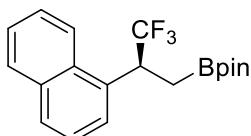
White solid (38.4 mg, 54% yield, 90% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.85 (t, $J = 9.0$ Hz, 2H), 7.43 (s, 1H), 7.42-7.40 (m, 1H), 7.37-7.34 (m, 1H), 4.14-4.05 (m, 1H), 1.59-1.57 (m, 2H), 1.02 (s, 6H), 0.87 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 139.8, 138.7, 131.9, 127.0 (q, $J = 280$ Hz), 125.0, 124.4, 124.1, 122.6, 122.0, 83.5, 38.5 (q, $J = 28.8$ Hz), 24.5, 24.2, 12.2 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -71.6, -113.2; HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{20}\text{BF}_3\text{O}_2\text{S}$: 356.1229; Found: 356.1229.

Optical rotation: $[\alpha]_D^{25}$: -5.45 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column IE, n -hexane/ i -PrOH = 99.9:0.1, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_R = 12.0$ min for the major isomer, $t_R = 10.5$ min for the minor isomer.



(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(naphthalen-1-yl)propyl)-1,3,2-dioxaborolane (4ac):

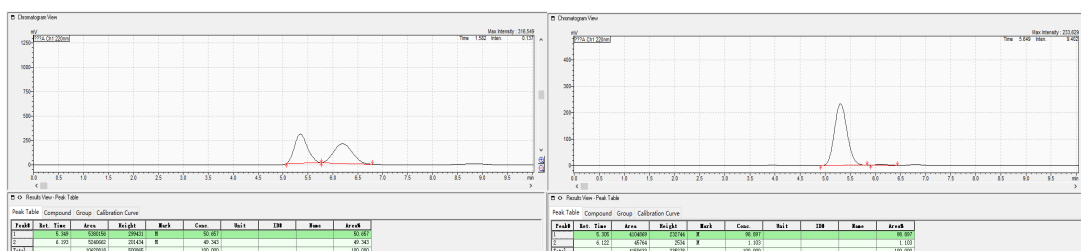


White solid (60.2 mg, 86% yield, 98% ee); ^1H NMR (400 MHz, CDCl_3) δ : 8.18 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 7.2$ Hz,

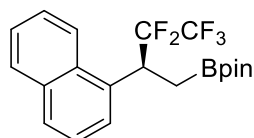
1H), 7.59-7.55 (m, 1H), 7.52-7.46 (m, 2H), 4.63-4.55 (m, 1H), 1.72-1.60 (m, 2H), 0.94 (s, 6H), 0.77 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 133.7, 133.0, 132.4, 128.7, 128.4, 127.6 (q, $J = 280$ Hz), 126.2, 125.8, 125.5, 125.1, 123.4, 83.4, 38.8 (q, $J = 28.0$ Hz), 24.4, 24.1, 12.5 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -70.9; HRMS m/z (EI) calcd for $\text{C}_{19}\text{H}_{22}\text{BF}_3\text{O}_2$: 350.1665; Found: 350.1669.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: -27.38 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_{\text{R}} = 5.3$ min for the major isomer, $t_{\text{R}} = 6.1$ min for the minor isomer.



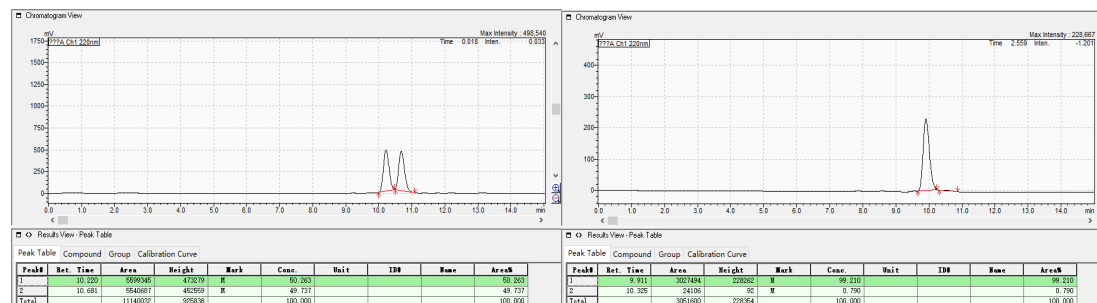
(S)-4,4,5,5-tetramethyl-2-(3,3,4,4,4-pentafluoro-2-(naphthalen-1-yl)butyl)-1,3,2-dioxaborolane (4ad):



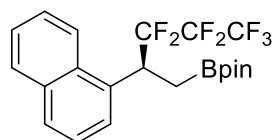
White solid (59.2 mg, 74% yield, 98% ee); ^1H NMR (500 MHz, CDCl_3) δ : 8.14 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 6.5$ Hz, 1H), 7.57-7.54 (m, 1H), 7.51-7.46 (m, 2H), 4.67-4.57 (m, 1H), 1.66 (d, $J = 8.0$ Hz, 2H), 0.84 (s, 6H), 0.63 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 133.6, 132.8 (d, $J = 4.4$ Hz), 132.3, 128.7, 128.4, 127.4 (q, $J = 258$ Hz), 126.6, 126.3, 125.5, 125.1, 123.3, 120.7 (t, $J = 37.2$ Hz), 118.4 (t, $J = 37.2$ Hz), 116.0 (q, $J = 36.2$ Hz), 83.3, 36.0 (t, $J = 21.7$ Hz), 24.2 24.0, 12.2 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -81.5, -117.0, -117.6, -119.5, -120.1; HRMS m/z (EI) calcd for $\text{C}_{20}\text{H}_{22}\text{BF}_5\text{O}_2$: 400.1633; Found: 400.1638.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: -26.32 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OD-H, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.5 mL/min, wavelength = 220 nm, t_R = 9.9 min for the major isomer, t_R = 10.3 min for the minor isomer.



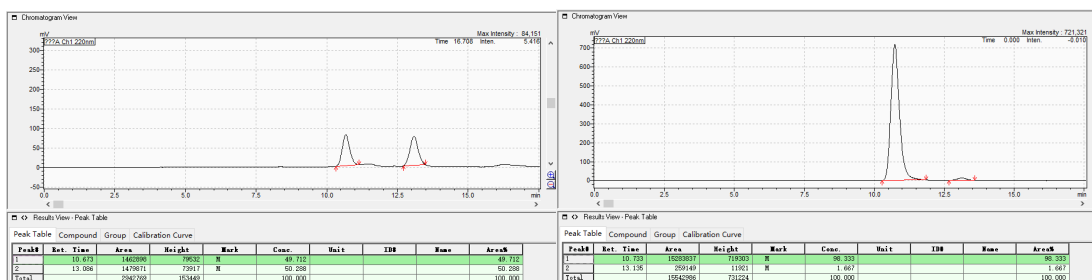
(S)-2-(3,3,4,4,5,5,5-heptafluoro-2-(naphthalen-1-yl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ae):



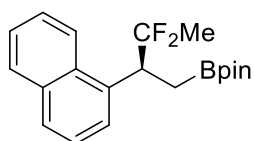
Colorless oil (45.9 mg, 51% yield, 97% ee); ^1H NMR (500 MHz, CDCl_3) δ : 8.15 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.57-7.54 (m, 1H), 7.50-7.46 (m, 2H), 4.75-4.66 (m, 1H), 1.66 (d, J = 8.5 Hz, 2H), 0.83 (s, 6H), 0.62 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 133.6, 132.8 (d, J = 3.6 Hz), 132.3, 128.6, 128.4, 126.0, 126.1, 125.5, 125.2, 123.5, 83.3, 36.2 (t, J = 21.8 Hz), 24.2, 24.0, 12.4 (broad); For the ^{13}C NMR (F coupled), peaks for the C of perfluoroalkyl chain and C adjacent to perfluoroalkyl chain (in most cases) are too broad to be assigned (not shown in the data); ^{19}F NMR (471 MHz, CDCl_3) δ : -80.6 (3F), -114.3 (3F), -116.0 (2F), -124.2 (2F); HRMS m/z (EI) calcd for $\text{C}_{21}\text{H}_{22}\text{BF}_7\text{O}_2$: 450.1601; Found: 450.1601.

Optical rotation: $[\alpha]_D^{25}$: -21.16 (c = 0.5, CHCl_3).

HPLC condition: Chiral column IF, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.5 mL/min, wavelength = 220 nm, t_R = 10.7 min for the major isomer, t_R = 13.1 min for the minor isomer.



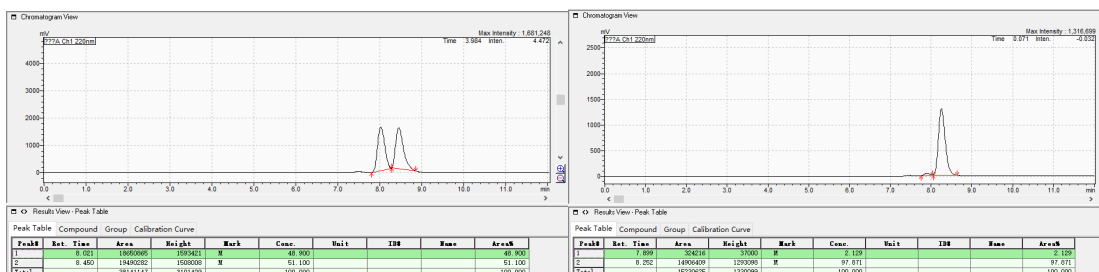
(S)-2-(3,3-difluoro-2-(naphthalen-1-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4af):



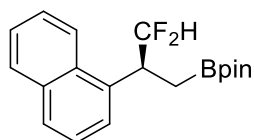
Colorless oil (46.4 mg, 67% yield, 96% ee); ^1H NMR (500 MHz, CDCl_3) δ : 8.23 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.56-7.52 (m, 1H), 7.48-7.45 (m, 2H), 4.37-4.29 (m, 1H), 1.67-1.50 (m, 2H), 1.45 (t, $J = 18.5$ Hz, 3H), 0.91 (s, 6H), 0.74 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 136.5 (two signals overlap), 133.7, 132.5, 128.7, 127.6, 125.9, 125.3 (two signals overlap), 125.1 (t, $J = 244$ Hz), 123.8, 83.1, 41.6 (t, $J = 24.8$ Hz), 24.4, 24.1, 22.1 (t, $J = 28.0$ Hz), 12.5 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -91.1 (d, $J = 237.2$ Hz, 1F), -98.6 (d, $J = 237.2$ Hz, 1F); HRMS m/z (EI) calcd for $\text{C}_{20}\text{H}_{25}\text{BF}_2\text{O}$: 346.1916; Found: 346.1917.

Optical rotation: $[\alpha]_D^{25}$: -18.54 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OD-H, n-hexane/*i*-PrOH = 98:2, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_R = 8.3$ min for the major isomer, $t_R = 7.9$ min for the minor isomer.



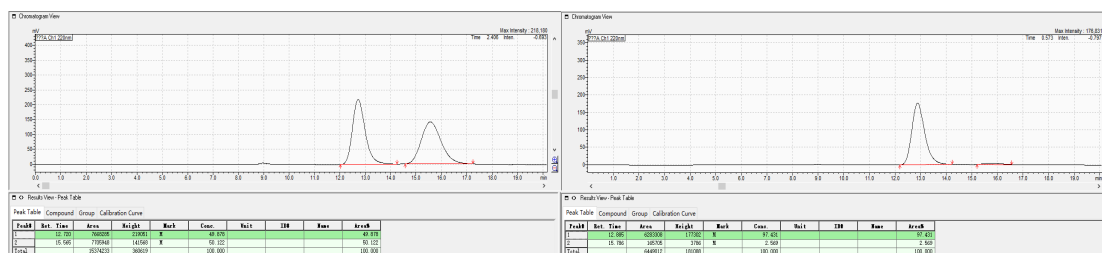
(S)-2-(3,3-difluoro-2-(naphthalen-1-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ag):



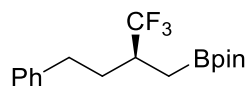
Colorless oil (46.5 mg, 70% yield, 95% ee); ^1H NMR (500 MHz, CDCl_3) δ : 8.18 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 7.5$ Hz, 1H), 7.57-7.54 (m, 1H), 7.51-7.45 (m, 3H), 6.10-5.86 (m, 1H), 4.33-4.24 (m, 1H), 1.57 (dd, $J = 15.7, 6.3$ Hz, 1H), 1.45 (dd, $J = 15.6, 9.4$ Hz, 1H), 1.02 (s, 6H), 0.90 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 135.0 (t, $J = 4.0$ Hz), 133.8, 132.1, 128.8, 127.9, 126.1, 125.5, 125.3, 123.3, 118.3 (t, $J = 245$ Hz), 83.3, 39.1 (t, $J = 17.8$ Hz), 24.5, 24.3, 11.3 (broad); ^{19}F NMR (471 MHz, CDCl_3) δ : -117.8 (d, $J = 273.7$ Hz, 1F), -122.3 (d, $J = 273.0$ Hz, 1F); HRMS m/z (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{BF}_2\text{O}_2$: 332.1759; Found: 332.1760.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: -2.92 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 99:1, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_{\text{R}} = 12.9$ min for the major isomer, $t_{\text{R}} = 15.8$ min for the minor isomer.

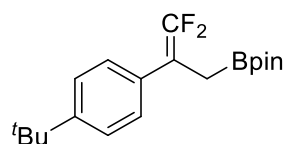


(S)-4,4,5,5-tetramethyl-2-(4-phenyl-2-(trifluoromethyl)butyl)-1,3,2-dioxaborolane (4ah):



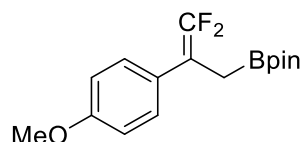
Colorless oil (51.2 mg, 78% yield, 52% ee); ^1H NMR (500 MHz, CDCl_3) δ : 7.32-7.29 (m, 2H), 7.22-7.20 (m, 3H), 2.77-2.66 (m, 2H), 2.50-2.39 (m, 1H), 2.02-1.95 (m, 1H), 1.78-1.70 (m, 1H), 1.27 (s, 12H), 1.15-1.11 (m, 1H), 1.02-0.97 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 141.6, 128.7 (q, $J = 280$ Hz), 128.4, 128.3, 126.0, 83.5, 39.0 (q, $J = 26.0$ Hz), 33.1, 32.1 (q, $J = 1.9$ Hz), 24.8, 24.7, 10.5 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -71.9. HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{24}\text{BF}_3\text{O}_2$: 328.1822; Found: 328.1820.

(R)-4-phenyl-2-(trifluoromethyl)butan-1-ol (4ah'):



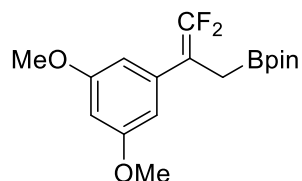
Colorless oil (83.7 mg, 83% yield); ^1H NMR (500 MHz, CDCl_3) δ : 7.37-7.36 (m, 2H), 7.32-7.30 (m, 2H), 1.95 (t, $J = 2.5$ Hz, 2H), 1.33 (s, 9H), 1.17 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 153.2 (dd, $J = 289, 284$ Hz), 149.8, 132.3 (t, $J = 3.4$ Hz), 127.5 (t, $J = 2.9$ Hz), 125.0, 88.5 (dd, $J = 23.3, 14.8$ Hz), 83.5, 34.4, 31.2, 24.5, 11.6 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -90.9 (d, $J = 46.3$ Hz, 1F), -92.4 (d, $J = 46.3$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{19}\text{H}_{27}\text{BF}_2\text{O}_2$: 336.2072; Found: 336.2077.

2-(3,3-Difluoro-2-(4-methoxyphenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d):



Colorless oil (66.9 mg, 72% yield); ^1H NMR (500 MHz, CDCl_3) δ : 7.30-7.27 (m, 2H), 6.88-6.85 (m, 2H), 3.79 (s, 3H), 1.92 (t, $J = 2.5$ Hz, 2H), 1.16 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 158.4, 153.0 (dd, $J = 288, 284$ Hz), 128.9 (t, $J = 3.7$ Hz), 127.5 (t, $J = 4.1$ Hz), 113.6, 88.2 (dd, $J = 23.5, 15.0$ Hz), 83.5, 55.1, 24.5, 11.7 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -91.9 (d, $J = 48.3$ Hz, 1F), -93.1 (d, $J = 48.3$ Hz, 1F); HRMS m/z (EI) calcd for $\text{C}_{16}\text{H}_{23}\text{BF}_2\text{O}_3$: 310.1552; Found: 310.1551.

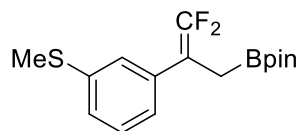
2-(2-(3,5-Dimethoxyphenyl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e):



Colorless oil (80.6 mg, 79% yield); ^1H NMR (400 MHz, CDCl_3) δ : 6.53 (dd, $J = 2.2, 1.0$ Hz, 2H), 6.35 (t, $J = 2.2$ Hz, 1H), 3.77 (s, 6H), 1.91 (t, $J = 2.8$ Hz, 2H), 1.17 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 160.5, 152.2 (dd, $J = 290, 285$ Hz), 137.2 (t, $J = 4.3$ Hz), 106.1 (t, $J = 3.8$ Hz), 99.3, 88.9 (dd, $J = 23.8, 14.4$ Hz), 83.6, 55.2, 24.5,

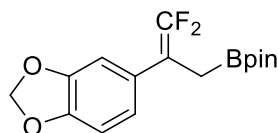
11.8 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -90.1 (d, $J = 44.2$ Hz, 1F), -90.7 (d, $J = 44.1$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{23}\text{BF}_2\text{O}_4$: 340.1658; Found: 340.1658.

2-(3,3-difluoro-2-(3-(methylthio)phenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5g):



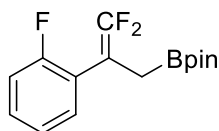
Colorless oil (74.3 mg, 76% yield); ^1H NMR (400 MHz, CDCl_3) δ : 7.18-7.14 (m, 2H), 7.06-7.04 (m, 2H), 2.39 (s, 3H), 1.85 (t, $J = 2.8$ Hz, 2H), 1.08 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 153.3 (dd, $J = 290, 285$ Hz), 138.3, 136.0 (d, $J = 4.2$ Hz), 128.5, 126.0 (t, $J = 3.8$ Hz), 125.2, 124.7 (dd, $J = 4.2, 3.2$ Hz), 88.6 (dd, $J = 23.8, 14.7$ Hz), 83.6, 24.5, 15.7, 11.6 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -90.1 (d, $J = 44.0$ Hz, 1F), -91.2 (d, $J = 44.1$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{16}\text{H}_{21}\text{BF}_2\text{O}_5\text{S}$: 326.1323; Found: 326.1326.

2-(2-(Benzo[*d*][1,3]dioxol-5-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5k):



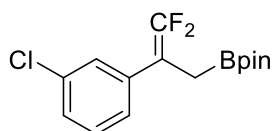
Colorless oil (68.0 mg, 70% yield); ^1H NMR (500 MHz, CDCl_3) δ : 6.88 (s, 1H), 6.82-6.76 (m, 2H), 5.94 (s, 2H), 1.89 (t, $J = 2.5$ Hz, 2H), 1.17 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 153.1 (dd, $J = 289, 284$ Hz), 147.4, 146.4, 131.9, 129.1 (t, $J = 3.9$ Hz), 121.4 (t, $J = 3.5$ Hz), 108.6 (dd, $J = 4.6, 3.2$ Hz), 108.0, 101.0, 88.6 (dd, $J = 24.0, 15.0$ Hz), 83.6, 24.6, 11.8 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -91.4 (d, $J = 47.1$ Hz, 1F), -92.4 (d, $J = 47.1$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{BF}_2\text{O}_4$: 324.1345; Found 324.1345.

2-(3,3-Difluoro-2-(2-fluorophenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5n):



Colorless oil (63.5 mg, 71% yield); ^1H NMR (500 MHz, CDCl_3) δ : 7.31-7.28 (m, 1H), 7.27-7.22 (m, 1H), 7.11-7.08 (m, 1H), 7.06-7.02 (m, 1H), 1.92 (s, 2H), 1.15 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 160.1 (dd, $J = 249$ Hz, 1.3 Hz), 152.8 (dd, $J = 287, 286$ Hz), 130.9 (dd, $J = 5.5, 2.8$ Hz), 129.2 (d, $J = 8.2$ Hz), 123.8 (d, $J = 3.6$ Hz), 123.0 (ddd, $J = 15.1, 5.3, 2.5$ Hz), 115.7, 115.5, 83.7 (dd, $J = 18.3, 17.2$ Hz), 83.6, 24.6, 11.8 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -90.0 (dd, $J = 41.9, 12.5$ Hz, 1F), -91.8 (dd, $J = 41.8, 1.7$ Hz, 1F), -113.4 (dd, $J = 12.5, 1.9$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{15}\text{H}_{18}\text{BF}_3\text{O}_2$: 298.1352; Found: 298.1350.

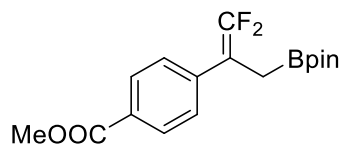
2-(2-(3-Chlorophenyl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5o):



Colorless oil (70.7 mg, 75% yield); ^1H NMR (500 MHz, CDCl_3) δ : 7.37-7.36 (m, 1H), 7.25-7.23 (m, 2H), 7.22-7.18 (m, 1H), 1.93 (t, $J = 2.5$ Hz, 2H), 1.16 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 153.4 (dd, $J = 291, 286$ Hz), 137.1 (t, $J = 4.4$ Hz), 134.1, 129.4, 128.0 (t, $J = 3.9$ Hz), 127.0, 126.0 (dd, $J = 4.5, 3.3$ Hz), 88.2 (dd, $J = 24.4, 14.5$ Hz), 83.7, 24.5, 11.6 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -89.4 (d, $J = 42.3$ Hz, 1F), -90.6 (d, $J = 42.4$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{15}\text{H}_{18}\text{BClF}_2\text{O}_2$: 314.1056; Found: 314.1058.

Methyl

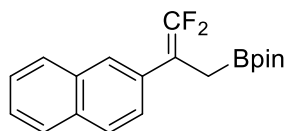
4-(1,1-Difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)benzoate (5q):



Colorless oil (57.8 mg, 57% yield); ^1H NMR (400 MHz, CDCl_3) δ : 7.98-7.95 (m, 2H), 7.42-7.40 (m, 2H), 3.88 (s, 3H), 1.95 (t, $J = 2.8$ Hz, 2H), 1.12 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 166.7, 153.5 (dd, $J = 292, 286$ Hz), 140.1 (t, $J = 4.6$ Hz), 129.4, 128.4, 127.6 (dd, $J = 4.6, 3.4$ Hz), 88.7 (dd, $J = 24.2, 13.8$ Hz), 83.7, 52.0, 24.5, 11.4

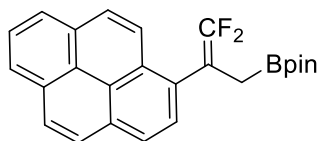
(broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -88.2 (d, $J = 39.8$ Hz, 1F), -89.6 (d, $J = 39.7$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{21}\text{BF}_2\text{O}_4$: 338.1501; Found: 338.1497.

2-(3,3-Difluoro-2-(naphthalen-2-yl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5t):



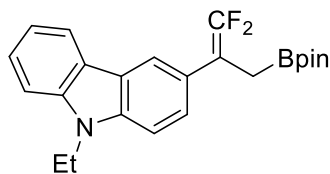
Colorless oil (72.3 mg, 73% yield); ^1H NMR (500 MHz, CDCl_3) δ : 7.88-7.80 (m, 4H), 7.56-7.46 (m, 3H), 2.08 (s, 2H), 1.15 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 153.5 (dd, $J = 290, 285$ Hz), 133.2, 132.7 (t, $J = 4.3$ Hz), 127.9, 127.7, 127.5, 126.7 (t, $J = 3.8$ Hz), 126.1, 125.9 (dd, $J = 5.2, 2.5$ Hz), 125.8, 89.0 (dd, $J = 23.6, 14.4$ Hz), 83.7, 24.6, 11.8 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -89.8 (d, $J = 44.2$ Hz, 1F), -91.3 (d, $J = 44.2$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{BF}_2\text{O}_2$: 330.1603; Found: 330.1599.

2-(3,3-Difluoro-2-(pyren-1-yl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5v):



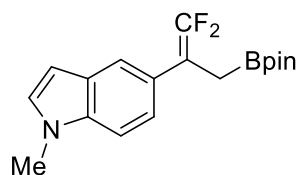
Gray solid (105.4 mg, 87% yield); ^1H NMR (500 MHz, CDCl_3) δ : 8.33 (d, $J = 8.0$ Hz, 1H), 8.22-8.19 (m, 3H), 8.15 (d, $J = 9.5$ Hz, 1H), 8.09-8.01 (m, 4H), 2.27 (s, 2H), 1.14 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 152.8 (dd, $J = 287, 285$ Hz), 131.2, 130.9, 130.8, 130.5 (d, $J = 5.0$ Hz), 128.9, 127.5 (d, $J = 4.1$ Hz), 127.3 (d, $J = 2.3$ Hz), 127.2, 125.9, 125.1, 125.0, 124.9, 124.8, 124.1, 124.6, 87.4 (dd, $J = 23.9, 20.0$ Hz), 83.6, 24.6, 14.0 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -90.1 (d, $J = 45.6$ Hz, 1F), -92.6 (d, $J = 45.5$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{23}\text{H}_{23}\text{BF}_2\text{O}_2$: 404.1759; Found: 404.1761.

3-(1,1-Difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-9-ethyl-9H-carbazole (5w):



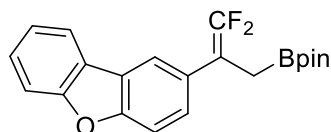
Colorless oil (91.7 mg, 77% yield); ^1H NMR (400 MHz, CDCl_3) δ : 8.17 (s, 1H), 7.74-8.13 (d, $J = 7.6$ Hz, 1H), 7.56-7.48 (m, 2H), 7.42-7.38 (m, 2H), 7.28 (d, $J = 7.6$ Hz, 1H), 4.35 (q, $J = 7.2$ Hz, 2H), 2.15 (s, 2H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.20 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 153.1 (dd, $J = 287, 284$ Hz), 140.2, 138.8, 125.8 (t, $J = 4.0$ Hz), 125.7 (t, $J = 3.6$ Hz), 125.6, 122.8, 122.7, 120.3, 119.8 (t, $J = 3.5$ Hz), 118.8, 108.4, 108.0, 89.2 (dd, $J = 23.0, 15.1$ Hz), 83.5, 37.4, 24.5, 13.6, 12.5 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -92.2 (d, $J = 49.4$ Hz, 1F), -93.5 (d, $J = 49.4$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{23}\text{H}_{26}\text{BF}_2\text{NO}_2$: 397.2025; Found: 397.2028.

5-(1,1-Difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-1-methyl-1H-indole (5x):



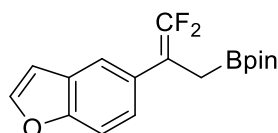
68.9 mg, 69% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.63 (s, 1H), 7.28 (s, 2H), 7.04 (d, $J = 3.2$ Hz, 1H), 6.47 (d, $J = 2.8$ Hz, 1H), 3.77 (s, 3H), 2.04 (s, 2H), 1.18 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 153.0 (dd, $J = 287, 283$ Hz), 135.7, 129.1, 128.3, 126.3 (t, $J = 3.8$ Hz), 121.8 (dd, $J = 4.0, 3.0$ Hz), 120.3 (t, $J = 3.5$ Hz), 108.8, 101.0, 89.3 (dd, $J = 22.7, 15.5$ Hz), 83.5, 32.7, 24.6, 12.4 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -92.6 (d, $J = 50.1$ Hz, 1F), -94.0 (d, $J = 50.0$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{18}\text{H}_{22}\text{BF}_2\text{NO}_2$: 333.1712; Found: 333.1715.

2-(2-(Dibenzo[*b,d*]furan-2-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5y):



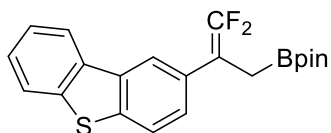
Colorless oil (86.6 mg, 78% yield); ^1H NMR (400 MHz, CDCl_3) δ : 7.97 (s, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.58-7.52 (m, 2H), 7.49-7.44 (m, 2H), 7.37-7.33 (m, 1H), 2.07 (t, $J = 2.4$ Hz, 2H), 1.16 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 156.5, 155.1, 153.2 (dd, $J = 288, 285$ Hz), 130.0 (dd, $J = 4.4, 3.9$ Hz), 127.2 (two signals overlap), 124.1 (two signals overlap), 122.7, 120.2 (t, $J = 3.6$ Hz), 120.1, 111.7, 111.3, 88.8 (dd, $J = 23.8, 15.3$ Hz), 83.6, 24.6, 12.2 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -91.4 (d, $J = 47.0$ Hz, 1F), -92.7 (d, $J = 47.0$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{21}\text{H}_{21}\text{BF}_2\text{O}_3$: 370.1552; Found: 370.1555.

2-(2-(Benzofuran-5-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5z):



Colorless oil (70.1 mg, 73% yield); ^1H NMR (400 MHz, CDCl_3) δ : 7.61-7.59 (m, 2H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.32-7.29 (m, 2H), 6.74 (dd, $J = 2.2, 0.9$ Hz, 1H), 2.01 (t, $J = 2.5$ Hz, 2H), 1.14 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 153.9, 153.1 (dd, $J = 288, 284$ Hz), 145.3, 130.1 (dd, $J = 4.5, 3.6$ Hz), 127.3, 124.5 (t, $J = 3.4$ Hz), 120.7 (t, $J = 3.6$ Hz), 111.0, 106.5, 88.9 (dd, $J = 23.6, 15.5$ Hz), 83.6, 24.5, 12.3 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -91.8 (d, $J = 47.9$ Hz, 1F), -93.2 (d, $J = 47.8$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{19}\text{BF}_2\text{O}_3$: 320.1395; Found: 320.1394.

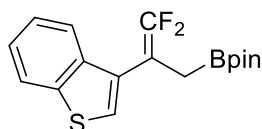
2-(2-(Dibenzo[*b,d*]thiophen-2-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5aa):



Colorless oil (83.4 mg, 72% yield); ^1H NMR (400 MHz, CDCl_3) δ : 8.05-8.02 (m, 2H), 7.74-7.71 (m, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.39-7.36 (m, 1H), 7.34-7.32 (m, 2H), 1.97 (t, $J = 2.4$ Hz, 2H), 1.04 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 153.3 (dd, $J = 289, 285$ Hz), 139.7, 138.0, 135.5, 135.4, 131.7 (t, $J = 4.3$ Hz), 126.7, 126.6 (dd, $J = 4.3, 3.2$ Hz), 124.3, 122.8, 122.4, 121.5, 120.9 (t, $J = 3.8$ Hz), 88.8 (dd, $J = 23.8,$

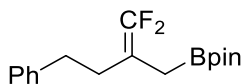
14.8 Hz), 83.7, 24.5, 11.9 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -90.3 (d, $J = 45.2$ Hz, 1F), -91.6 (d, $J = 45.2$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{21}\text{H}_{21}\text{BF}_2\text{O}_2\text{S}$: 386.1323; Found: 386.1326.

2-(2-(Benzo[*b*]thiophen-3-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ab):



Colorless oil (64.5 mg, 64% yield); ^1H NMR (400 MHz, CDCl_3) δ : 7.85 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.42-7.34 (m, 3H), 2.01 (t, $J = 2.2$ Hz, 2H), 1.12 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 153.1 (t, $J = 287$ Hz), 139.7, 137.7, 130.8 (dd, $J = 5.1, 2.0$ Hz), 125.0 (dd, $J = 4.4, 1.7$ Hz), 124.3, 124.0, 123.0 (d, $J = 2.2$ Hz), 122.6, 83.6, 83.4 (dd, $J = 18.8$ Hz, 17.2 Hz), 24.6, 12.6 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -88.5 (d, $J = 42.9$ Hz, 1F), -91.6 (d, $J = 42.9$ Hz, 1F). HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{19}\text{BF}_2\text{O}_2\text{S}$: 336.1167; Found: 336.1166.

2-(2-(Difluoromethylene)-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ah):



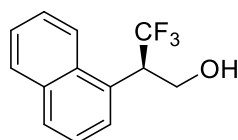
Colorless oil (47.1 mg, 51% yield); ^1H NMR (400 MHz, CDCl_3) δ : 7.29-7.22 (m, 2H), 7.19-7.16 (m, 3H), 2.72-2.67 (m, 2H), 2.33-2.28 (m, 2H), 1.57 (t, $J = 2.0$ Hz, 2H), 1.25 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 152.8 (t, $J = 283$ Hz), 141.5, 128.3 (two signals overlap), 125.9, 85.4 (dd, $J = 19.4, 18.5$ Hz), 83.5, 33.7 (dd, $J = 2.9, 2.4$ Hz), 30.3 (d, $J = 2.3$ Hz), 24.7, 9.8 (broad); ^{19}F NMR (377 MHz, CDCl_3) δ : -96.0 (d, $J = 58.1$ Hz, 1F), -96.6 (d, $J = 58.3$ Hz, 1F). GCMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{23}\text{BF}_2\text{O}_2$: 308.18; Found: 308.20.

(D) Procedures for Derivatization of 4ac

Gram-Scale Synthesis of 4ac:

In an Ar-filled dry box, Co(acac)₂ (20.6 mg, 2 mol %), (*R*)-BTFM-Garphos (142.4 mg, 3 mol %), 1-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene **1ac** (4 mmol), Me-THF (1 mL), and a magnetic stirring bar were added to a 10 mL screw-capped vial and stirred for 20 mins. Then Liacac (30 mol%) and HBpin (4.8 mmol) were added. The vial was sealed with a cap containing a PTFE septum and removed from the dry box. The reaction mixture was stirred at rt for 72 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash column chromatography with a mixture of hexane and ethyl acetate (100:1) as eluent, yielding the titled compound **4ac** (1.09 g, 78% yield, 96% ee) as a colorless oil.

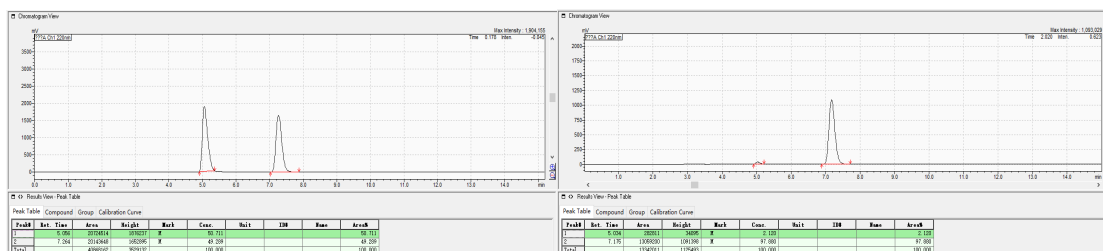
(*R*)-3,3,3-trifluoro-2-(naphthalen-1-yl)propan-1-ol (6**):²**



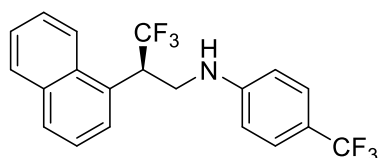
To a solution of **4ac** (70 mg, 0.20 mmol) in THF/H₂O (1:1, 2 mL) was added NaBO₃•4H₂O (1.8 mmol). The reaction mixture was stirred at room temperature for 6 h. After that the mixture was diluted with H₂O and extracted with diethyl ether. The combined organic phases were dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate (10:1) to afford the desired product **6** as colorless oil in 91% yield (43.7 mg, 96 % ee). ¹H NMR (500 MHz, CDCl₃) δ: 8.08 (d, *J* = 8.5 Hz, 1H), 7.92-7.88 (m, 2H), 7.62-7.59 (m, 2H), 7.56-7.50 (m, 2H), 4.61-4.52 (m, 1H), 4.36-4.33 (m, 1H), 4.15-4.12 (m, 1H), 1.80 (s, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ: 134.0, 132.5, 129.2, 129.1, 128.6, 127.8 (q, *J* = 286 Hz), 126.9, 126.0, 125.3, 125.2, 122.5, 61.8 (q, *J* = 2.4 Hz), 46.0 (q, *J* = 27.0 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ: -66.5; HRMS *m/z* (EI) calcd for C₁₃H₁₁F₃O: 240.0762; Found: 240.0761.

Optical rotation: [α]_D²⁵: -0.86 (c = 1.0, CHCl₃).

HPLC condition: Chiral column IE, n-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, *t*_R = 7.2 min for the major isomer, *t*_R = 5.0 min for the minor isomer.



(R)-N-(3,3,3-trifluoro-2-(naphthalen-1-yl)propyl)-4-(trifluoromethyl)aniline (7):³

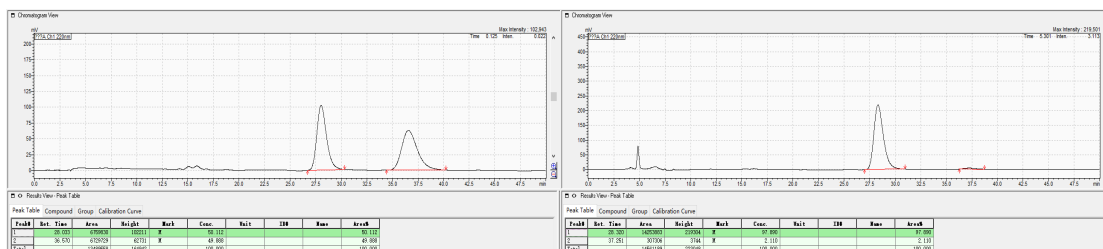


A mixture of alkylboronate **4ac** (70 mg, 0.20 mmol), 4-(trifluoromethyl)aniline (128.8 mg, 0.8 mmol), di-*tert*-butyl peroxide (116.8 mg, 0.40 mmol), Cu(OAc)₂ (4.0 mg, 10 mol%), and hexane (1.0 mL)

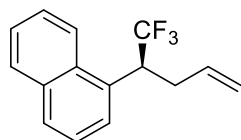
was stirred at 100 °C for 48 h in a sealed tube. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 100/1) to give **7** (54.4 mg, 71% yield, 96 % ee). Light yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.94-7.89 (m, 3H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.57-7.51 (m, 3H), 7.39 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 4.65-4.63 (m, 1H), 4.14-4.09 (m, 1H), 3.99 (s, 1H), 3.80-3.75 (m, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ: 149.3, 134.0, 132.5, 129.4, 129.2, 127.8 (q, *J* = 274.2 Hz), 127.0, 126.8 (three signals overlap), 126.7, 126.5 (q, *J* = 286 Hz), 126.1, 125.4, 122.3, 112.2, 43.6, 42.3 (q, *J* = 24.3 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ: -61.2 (two signals overlap); HRMS *m/z* (EI) calcd for C₂₀H₁₅F₆N: 383.1109; Found: 383.1112.

Optical rotation: [α]_D²⁵: -11.26 (c = 1.0, CHCl₃).

HPLC condition: Chiral column OJ-H, n-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, *t*_R = 28.3 min for the major isomer, *t*_R = 37.3 min for the minor isomer.



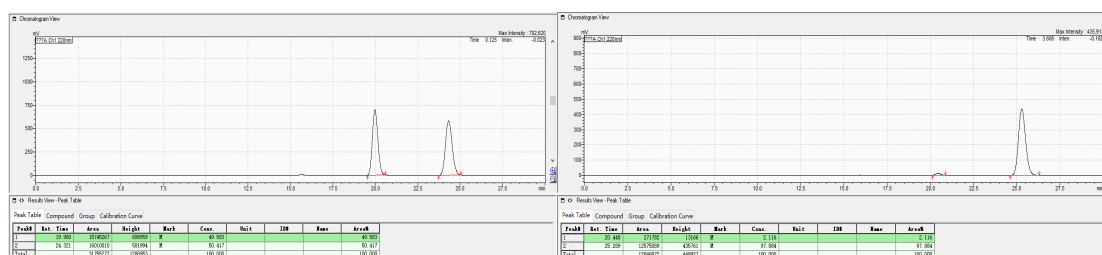
(S)-1-(1,1,1-trifluoropent-4-en-2-yl)naphthalene (8):⁴



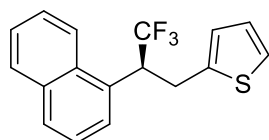
In an argon-filled glovebox, **4ac** (70 mg, 0.2 mmol) and anhydrous THF (2 mL) was added into a flask equipped with stir bar. The flask was then sealed with a rubber septum and removed from the glovebox. Vinylmagnesium bromide solution (0.8 mL, 1.0 M in THF, 0.8 mmol) was added dropwise using a syringe into the stirring mixture at 0 °C. The resulting solution was then stirred at 0 °C for 3 hours. Iodine crystals (203.0 mg, 0.8 mmol) dissolved in methanol (2.0 mL) was added dropwise using a syringe into the stirring mixture at 0 °C. The reaction was then stirred at 0 °C for another hour and warmed to room temperature. Saturated sodium thiosulfate (2 mL) was added to quench the reaction. Extraction was then performed using diethyl ether (3 x 10 mL). The combined organic phases were then combined and dried with sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography with hexane as eluent to afford the desired product **8** as colorless oil in 79% yield (39.5 mg, 96 % ee). ¹H NMR (500 MHz, CDCl₃) δ: 8.05 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 5.63-5.55 (m, 1H), 5.06 (d, *J* = 17.0 Hz, 1H), 4.91 (d, *J* = 10.0 Hz, 1H), 4.40-4.35 (m, 1H), 3.00-2.95 (m, 1H), 2.88-2.82 (m, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ: 133.9, 133.8, 132.6, 130.5, 129.1, 128.7, 127.0 (q, *J* = 281 Hz), 126.6, 125.7 (two signals overlap), 125.2, 122.6, 117.7, 43.0 (q, *J* = 25.7 Hz), 33.9; ¹⁹F NMR (471 MHz, CDCl₃) δ: -68.8; HRMS *m/z* (EI) calcd for C₁₅H₁₃F₃: 250.0969; Found: 250.0965.

Optical rotation: [α]_D²⁵: -13.31 (c = 1.0, CHCl₃).

HPLC condition: Chiral column OD-H, n-hexane/*i*-PrOH = 99.9:0.1, flow rate = 0.5 mL/min, wavelength = 220 nm, *t*_R = 25.3 min for the major isomer, *t*_R = 20.4 min for the minor isomer.



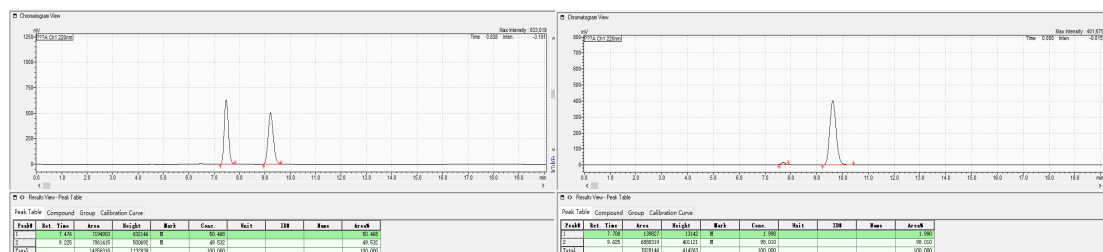
(S)-2-(3,3,3-trifluoro-2-(naphthalen-1-yl)propyl)thiophene (9):⁵



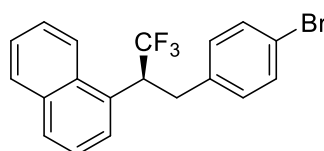
In an argon-filled glovebox, **4ac** (70 mg, 0.2 mmol) in anhydrous THF (2 mL) was added 2-thienyllithium (1.0 mmol) dropwise at $-78\text{ }^{\circ}\text{C}$ and stirred for 2 h before the solution was warmed to room temperature. *N*-Bromosuccinimide (0.24 mmol, 0.1 M in MeOH) was added dropwise. The reaction was stirred at room temperature for another 1 h, after which, a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ (5 mL) was added and the mixture was diluted with Et_2O (5 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O . The combined organic layers were washed with brine and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography with hexane as eluent to afford the desired product **9** as colorless oil in 73% yield (44.7 mg, 96 % ee). White solid; ^1H NMR (500 MHz, CDCl_3) δ : 7.95 (d, $J = 8.0$ Hz, 1H), 7.88-7.85 (m, 2H), 7.73 (d, $J = 7.0$ Hz, 1H), 7.55-7.47 (m, 3H), 6.93 (d, $J = 5.5$ Hz, 1H), 6.71-6.69 (m, 1H), 6.62 (d, $J = 3.0$ Hz, 1H), 4.68-4.60 (m, 1H), 3.78 (dd, $J = 15.1, 4.2$ Hz, 1H), 3.62 (dd, $J = 15.0, 10.8$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 139.5, 133.8, 132.9, 130.0, 129.0 (two signals overlap), 126.7 (q, $J = 281$ Hz), 126.6, 126.5, 126.0, 125.7, 125.6, 125.1, 124.0, 123.3, 122.4, 44.9 (q, $J = 26.3$ Hz), 30.0; ^{19}F NMR (471 MHz, CDCl_3) δ : -68.8; HRMS m/z (EI) calcd for $\text{C}_{17}\text{H}_{13}\text{F}_3\text{S}$: 306.0690; Found: 306.0692.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: -13.12 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OD-H, n-hexane/*i*-PrOH = 99.5:0.5, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_{\text{R}} = 9.6$ min for the major isomer, $t_{\text{R}} = 7.7$ min for the minor isomer.



(S)-1-(3-(4-bromophenyl)-1,1,1-trifluoropropan-2-yl)naphthalene (10):⁶

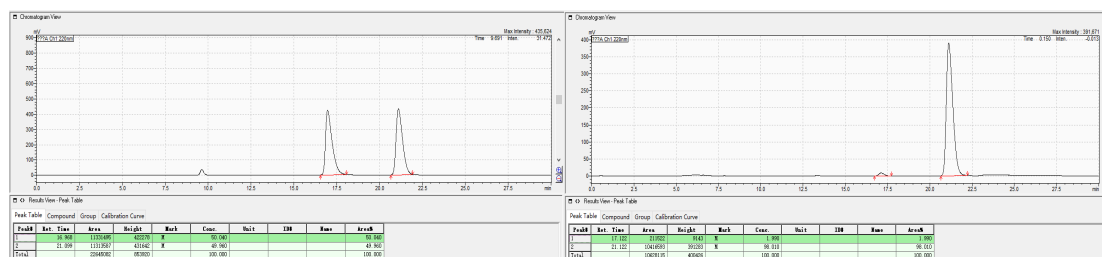


A mixture of alkylboronate **4ac** (0.2 mmol), 1-bromo-4-iodobenzene (0.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.02

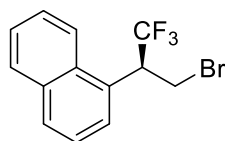
mmol), and NaOH (3M, 0.4 mmol) in dioxane (2 mL) was stirred at 80 °C under Ar atmosphere for 72 h. After that, the solvent was concentrated under reduced pressure and purified by flash column chromatography using hexane to afford the desired product **10** in 69% yield (52.2 mg, 96 % ee). ¹H NMR (500 MHz, CDCl₃) δ: 7.87-7.82 (m, 3H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.53-7.45 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.62-4.53 (m, 1H), 3.51 (dd, *J* = 14.3, 4.7 Hz, 1H), 3.30 (dd, *J* = 14.2, 10.2 Hz, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ: 136.5, 133.8, 132.5, 131.4, 130.4, 129.1, 129.0 (q, *J* = 264.1 Hz), 128.9, 126.7, 125.7, 125.6, 125.1, 122.1, 120.4, 44.5 (q, *J* = 26.4 Hz), 35.3; ¹⁹F NMR (471 MHz, CDCl₃) δ: -68.6; HRMS *m/z* (EI) calcd for C₁₉H₁₄BrF₃: 378.0231; Found: 378.0230.

Optical rotation: [α]_D²⁵: -26.03 (c = 1.0, CHCl₃).

HPLC condition: Chiral column IB, n-hexane/*i*-PrOH = 99.9:0.1, flow rate = 1.0 mL/min, wavelength = 220 nm, *t*_R = 21.1 min for the major isomer, *t*_R = 17.1 min for the minor isomer.



(*S*)-1-(3-bromo-1,1,1-trifluoropropan-2-yl)naphthalene (**11**):⁴

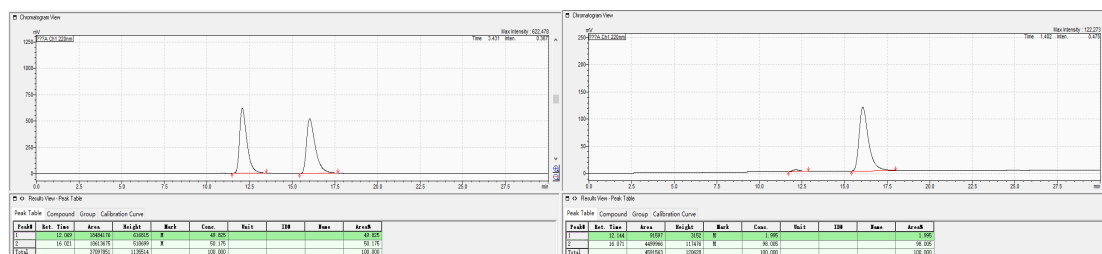


n-BuLi (0.30 mmol) was added dropwise to a solution of 1-bromo-3,5-bis(trifluoromethyl)benzene (0.3 mmol) in anhydrous THF (2.0 mL) at -78 °C. The mixture was stirred at -78 °C for 1 h, and then a solution of alkylboronate **4ac** (0.2 mmol) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 30 min. Next, N-bromosuccinimide (0.3 mmol) was added at -78 °C. The reaction mixture was stirred at -78 °C for 5 min, and then it was warmed to room temperature and stirred for 1 h. Na₂SO₃ (aq, 10.0 mL) was added, and the reaction mixture was extracted with Et₂O. The combined organic layers were washed with brine and dried over Na₂SO₄ and concentrated. The resulting residue was purified by silica gel flash column chromatography (hexane) to

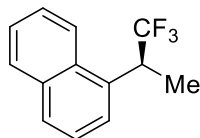
give **11** (51.3 mg, 85% yield, 96 % ee) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ : 8.03 (d, $J = 8.5$ Hz, 1H), 7.93-7.91 (m, 2H), 7.63-7.53 (m, 4H), 4.77-4.73 (m, 1H), 4.08 (dd, $J = 10.7, 5.3$ Hz, 1H), 3.84 (t, $J = 10.0$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 133.9, 132.4, 129.5, 129.2, 127.9 (q, $J = 278.0$ Hz), 127.0, 126.0, 125.2, 124.9, 124.6, 122.3, 46.0 (q, $J = 27.2$ Hz), 28.2; ^{19}F NMR (471 MHz, CDCl_3) δ : -67.7; HRMS m/z (EI) calcd for $\text{C}_{13}\text{H}_{10}\text{BrF}_3$: 301.9918; Found: 301.9917.

Optical rotation: $[\alpha]_{\text{D}}^{25}$: -2.89 ($c = 0.5$, CHCl_3).

HPLC condition: Chiral column OJ-H, n-hexane/i-PrOH = 99.8:0.2, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_{\text{R}} = 16.1$ min for the major isomer, $t_{\text{R}} = 12.1$ min for the minor isomer.



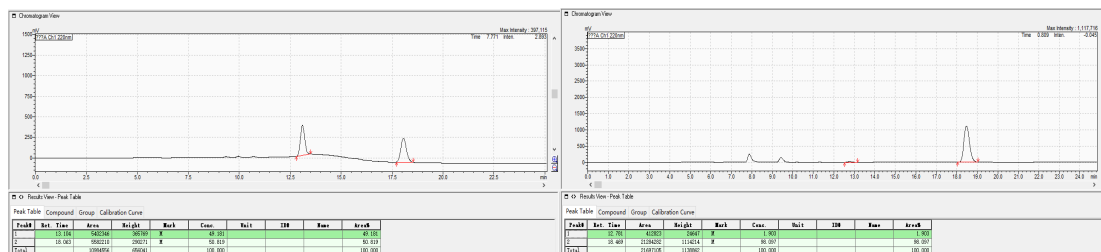
(S)-1-(1,1,1-trifluoropropan-2-yl)naphthalene (12**):**⁷



A solution of alkylboronate **4ac** (70 mg, 0.20 mmol) in anhydrous THF (2.0 mL) was cooled to -78 °C under argon atmosphere, *n*-BuLi (0.8 mmol) was added dropwise, the resulting complex was stirred for 1 h at -78 °C before THF was removed to dryness. To this ate complex was added $\text{Cu}(\text{OAc})_2$ (0.2 mmol), TBC (0.8 mmol), tridecane (0.3 mmol), flushed with Argon, and anhydrous DCE (2 mL). The resulting brown solution was refluxed at 80 °C for 24 h and the resulting crude was filtered through celite, washed with Et_2O and the solvent was removed in vacuo. The resulting residue was purified by silica gel flash column chromatography (hexane) to give **12** (28.2 mg, 63% yield, 96 % ee) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ : 8.06 (d, $J = 8.5$ Hz, 1H), 7.89 (d, $J = 7.5$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 7.5$ Hz, 1H), 7.59-7.56 (m, 1H), 7.53-7.49 (m, 2H), 4.46-4.36 (m, 1H), 1.65 (d, $J = 7.5$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 133.8, 132.7, 131.9, 129.1, 128.6, 127.5 (q, $J = 276.4$ Hz), 126.5, 125.7, 125.3 (two signals overlap), 122.6, 37.8 (q, $J = 25.9$ Hz), 29.7; ^{19}F NMR (471 MHz, CDCl_3) δ : -70.4; HRMS m/z (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{F}_3$: 224.0813; Found: 224.0807.

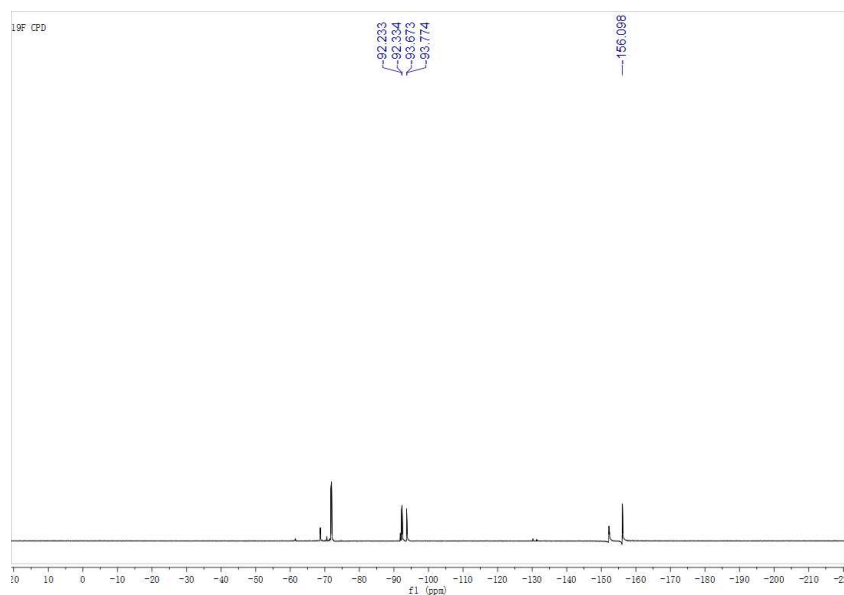
Optical rotation: $[\alpha]_D^{25}$: 0.39 ($c = 1.0$, CHCl_3).

HPLC condition: Chiral column OD-H, n-hexane/i-PrOH = 99:1, flow rate = 0.5 mL/min, wavelength = 220 nm, $t_R = 18.5$ min for the major isomer, $t_R = 12.8$ min for the minor isomer.



F-Bpin (v) detected by ^{19}F NMR:⁸

^{19}F NMR (471 MHz, CDCl_3) $\delta_{\text{F-Bpin}}$: -156.1



(E) Crystal structure of 4y:

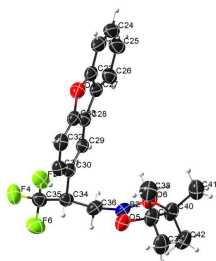


Table 1. Crystal data and structure refinement for **4y**.

Empirical formula

$\text{C}_{21}\text{H}_{22}\text{BF}_3\text{O}_3$

S45

Formula weight	390.19	
Temperature	223(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 6.5083(2) Å	a = 91.6750(10)°.
	b = 12.1996(4) Å	b = 101.8290(10)°.
	c = 13.2769(4) Å	g = 104.8840(10)°.
Volume	993.42(5) Å ³	
Z	2	
Density (calculated)	1.304 Mg/m ³	
Absorption coefficient	0.876 mm ⁻¹	
F(000)	408	
Crystal size	0.401 x 0.304 x 0.202 mm ³	
Theta range for data collection	3.763 to 70.114°.	
Index ranges	-7<=h<=7, -14<=k<=14, -15<=l<=16	
Reflections collected	31011	
Independent reflections	7233 [R(int) = 0.0264]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6701	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7233 / 557 / 667	
Goodness-of-fit on F ²	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1148	
R indices (all data)	R1 = 0.0402, wR2 = 0.1149	
Absolute structure parameter	-0.09(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.275 and -0.194 e.Å ⁻³	

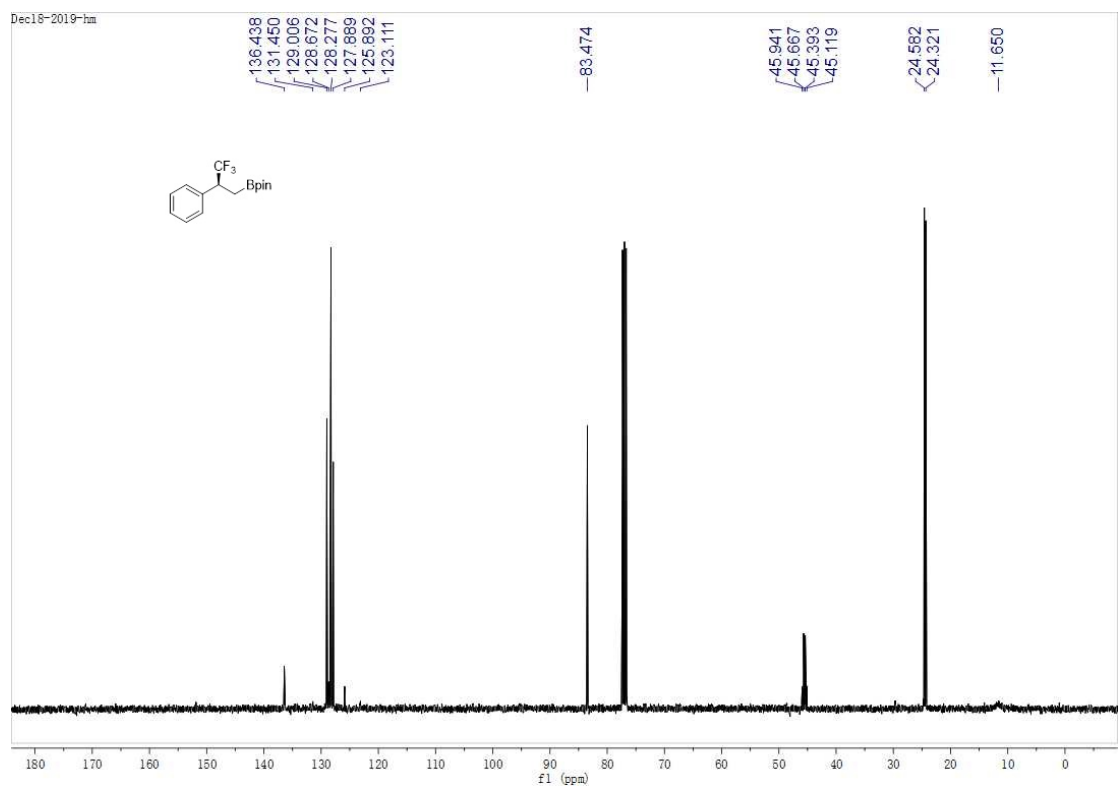
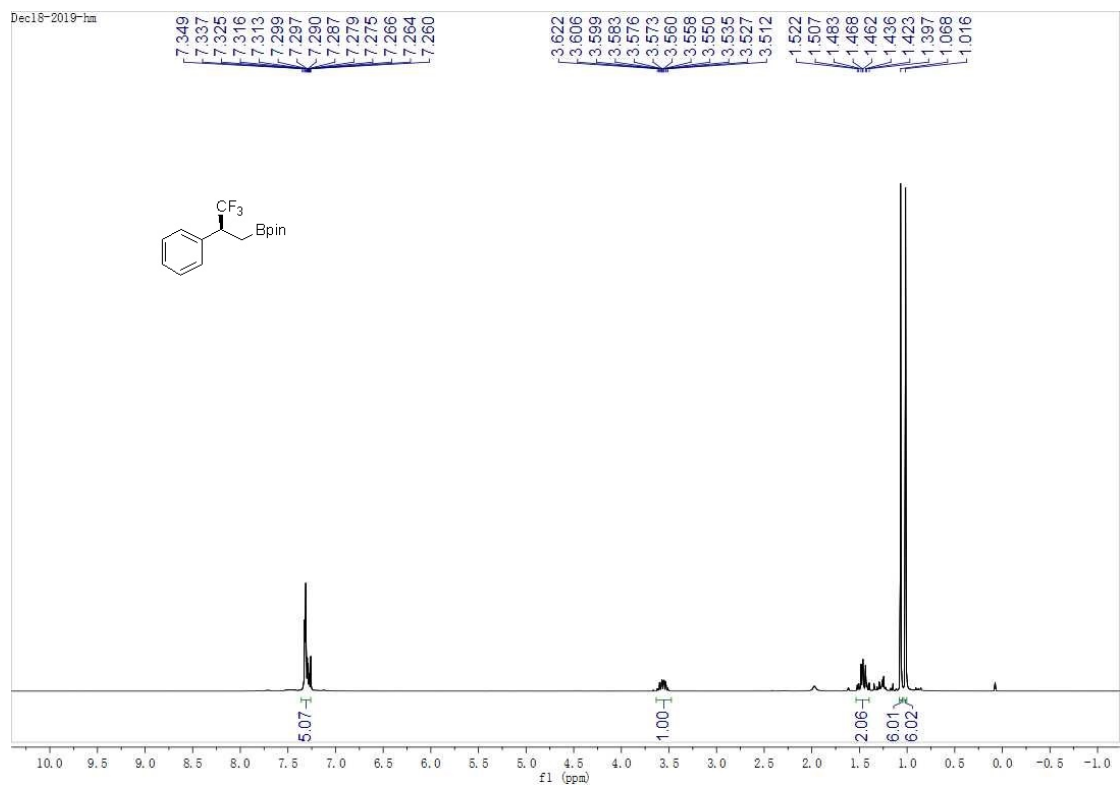
(F) Reference

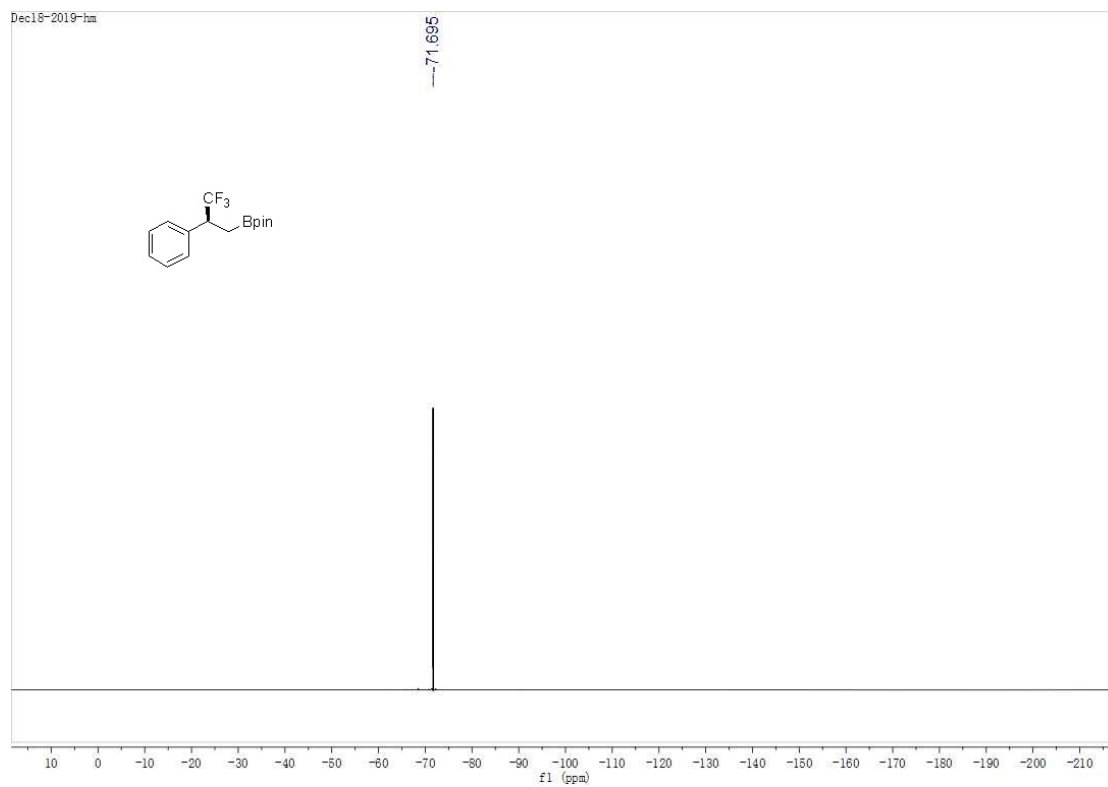
- (1) (a) Ichitsuka T.; Fujita T.; Ichikawa J. *ACS Catal.* **2015**, *5*, 5947. (b) Liu Y.; Zhou Y.; Zhao Y.; Qu J. *Org. Lett.* **2017**, *19*, 946. (c) Bos M.; Huang W.-S.; Poisson T.; Pannecoucke X.; Charette A. B.; Jubaul P. *Angew. Chem. Int. Ed.* **2017**, *56*, 13319. (d) Lin Z.; Lan Y.; Wang C. *Org. Lett.* **2019**, *21*, 8316. (e) Yao C.; Wang S.; Norton J.; Hammond M. *J. Am. Chem. Soc.* **2020**, *142*, 4793.
- (2) Kabalka G. W.; Shoup T. M.; Goudgaon N. M. *Tetrahedron Lett.* **1989**, *30*, 1483.
- (3) Sueki S.; Kuninobu Y. *Org. Lett.* **2013**, *15*, 1544.
- (4) Wu N.-Y.; Xu X.-H.; Qing F.-L. *ACS Catal.* **2019**, *9*, 5726.
- (5) Odachowski M.; Bonet A.; Essafi S.; Conti-Ramsden P.; Harvey J. N.; Leonori D.; Aggarwal V. K. *J. Am. Chem. Soc.* **2016**, *138*, 9521.
- (6) (a) Miyaura N.; Yamada K.; Suzuki A. *Tetrahedron Lett.* **1979**, *20*, 3437. (b) Miyaura N.; Suzuki A. *J. Chem. Soc., Chem. Commun.* **1979**, 866.
- (7) Bonet A.; Odachowski M.; Leonori D.; Essafi S.; Aggarwal V. *Nat. Chem.* **2014**, *6*, 584.
- (8) (a) Sakaguchi H.; Ohashi M.; Ogoshi S. *Angew. Chem. Int. Ed.* **2018**, *57*, 328. (b) Willcox D. R.; Nichol G. S.; Thomas S. P. *ACS Catal.* **2021**, *11*, 3190.

(G) Copies of NMR Spectra

(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-phenylpropyl)-1,3,2-dioxaborolane

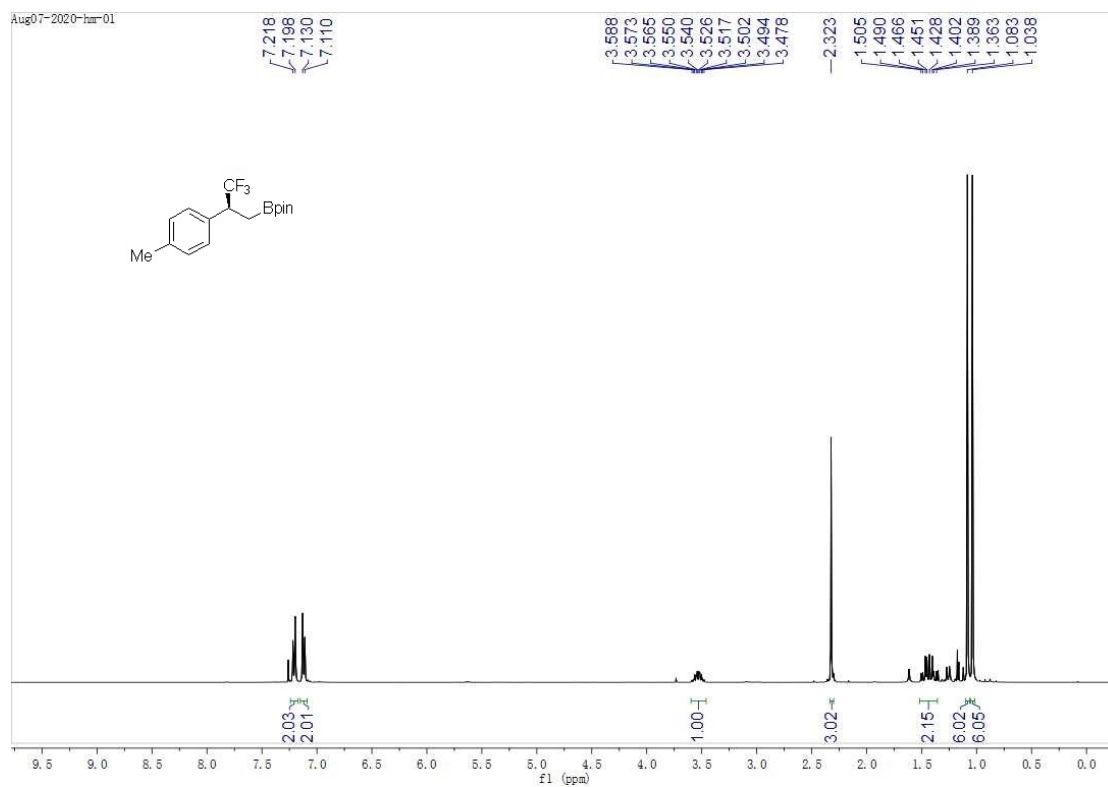
(4a):

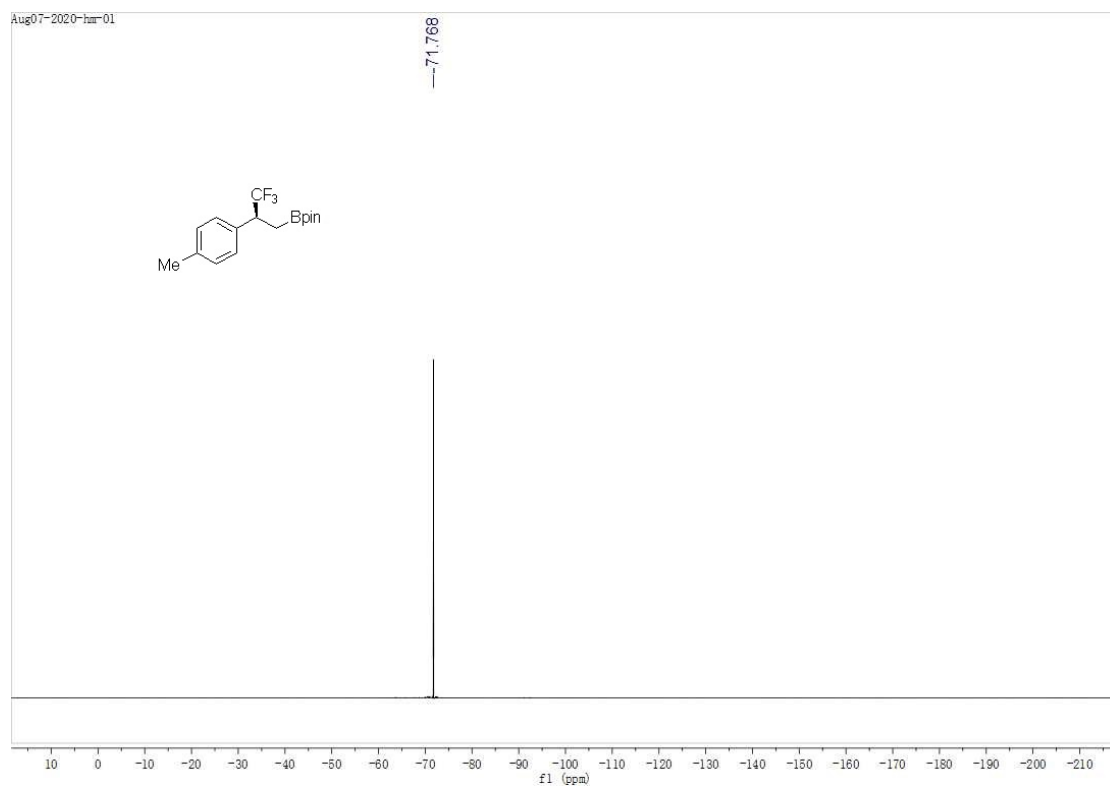
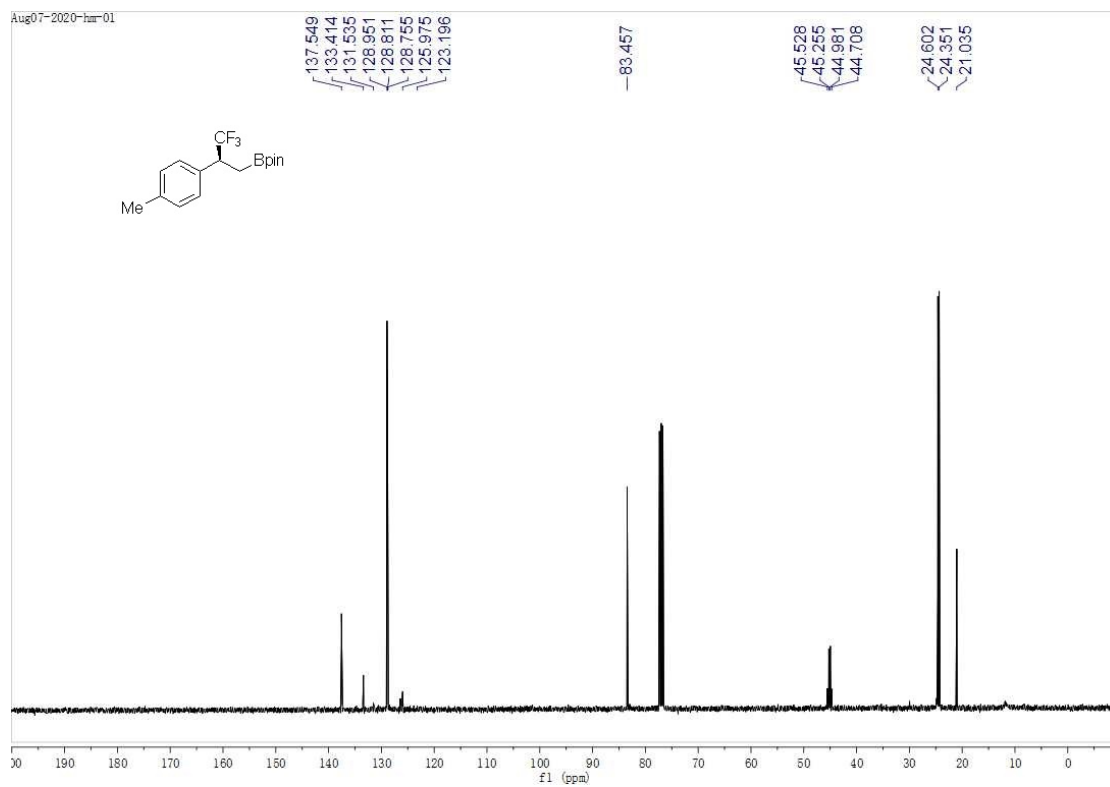


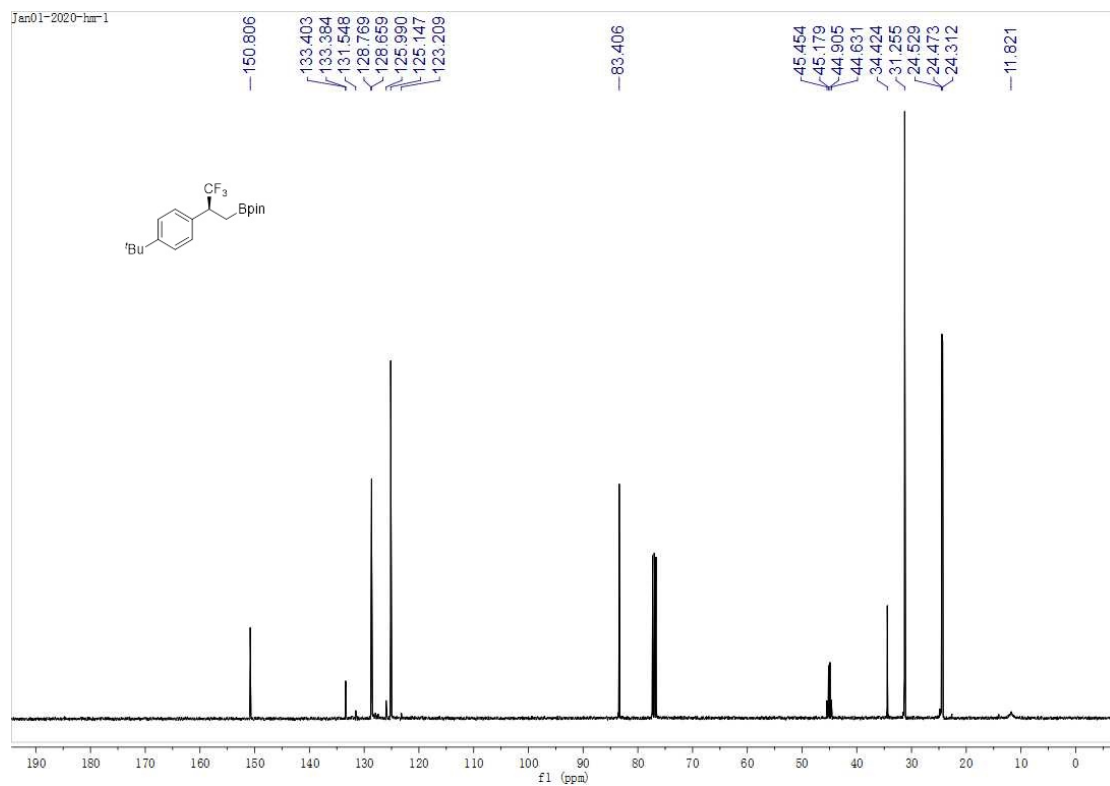
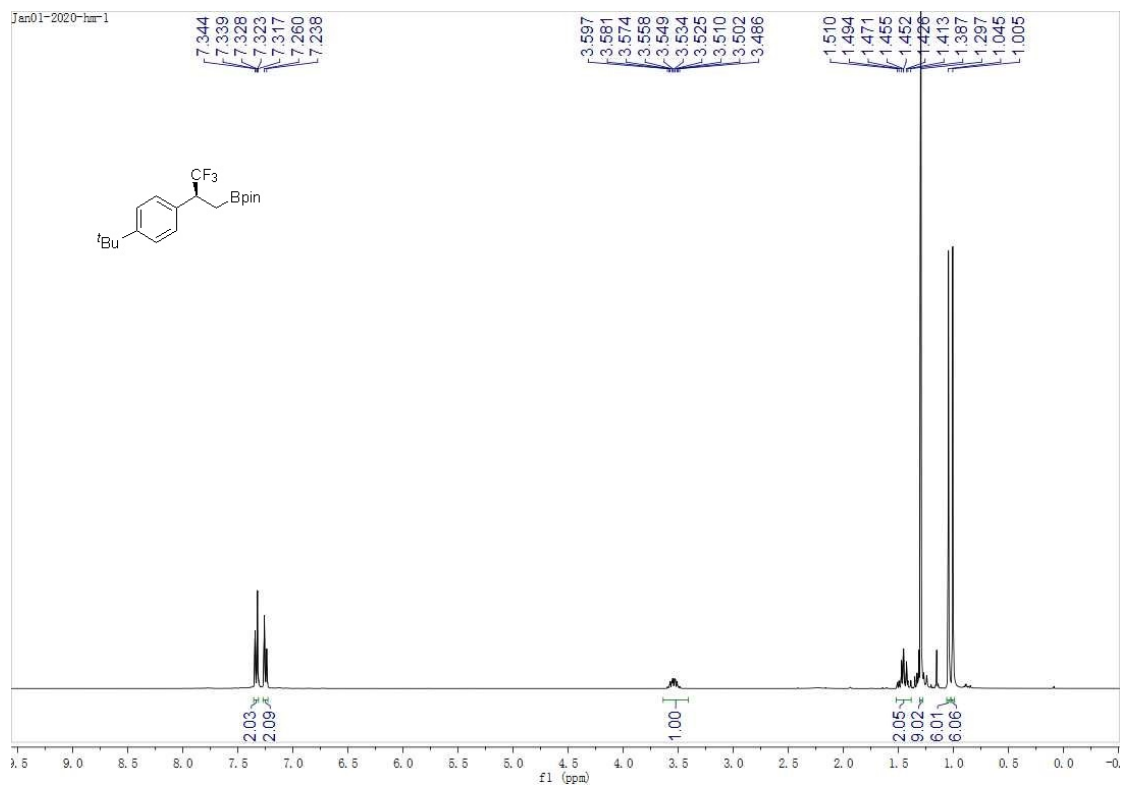


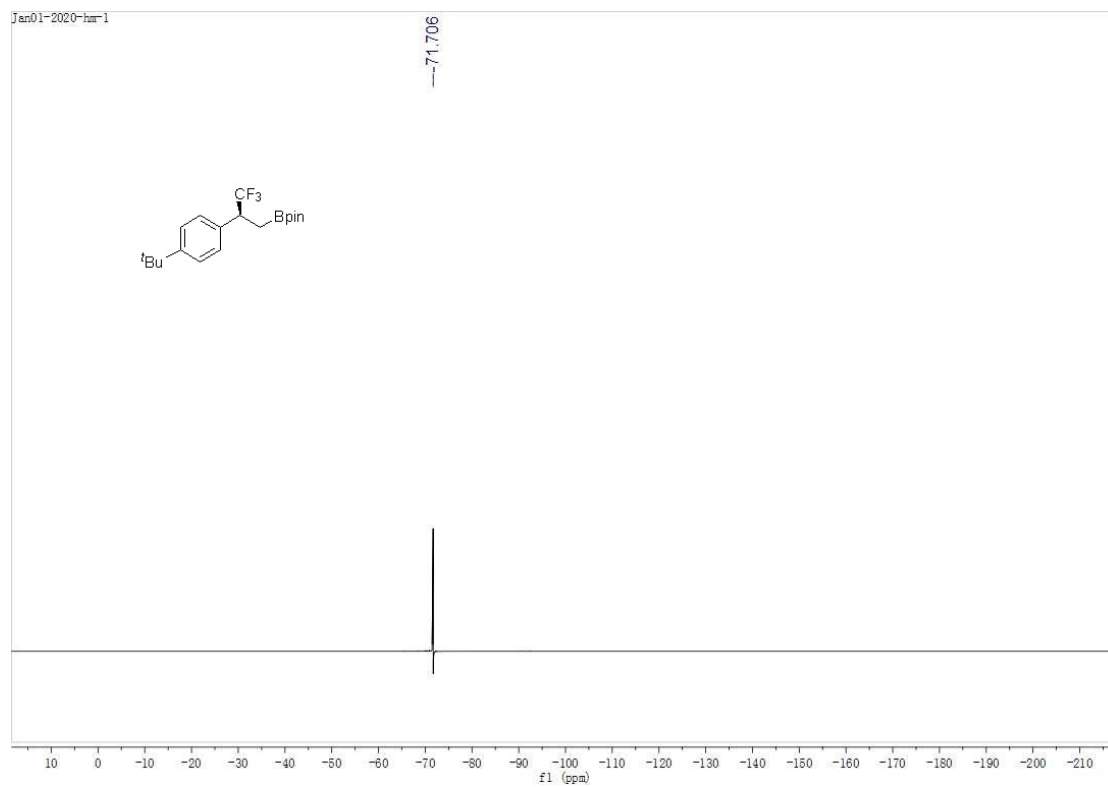
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(p-tolyl)propyl)-1,3,2-dioxaborolane

(4b):

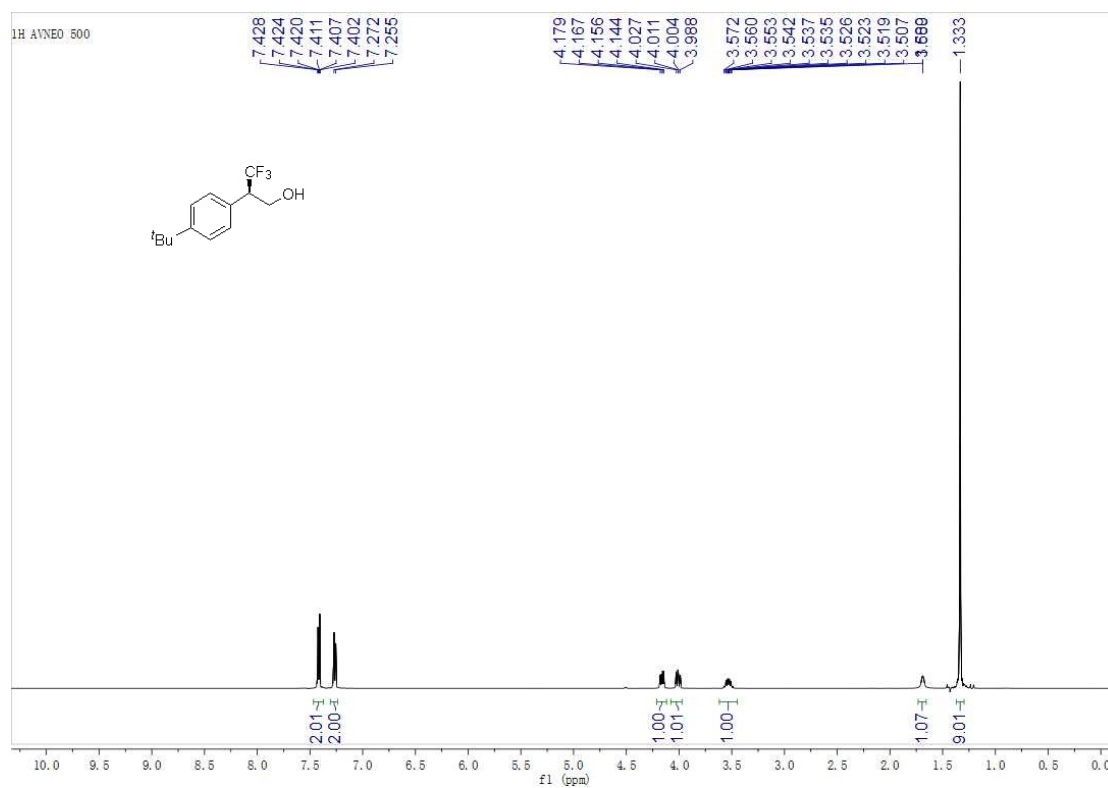


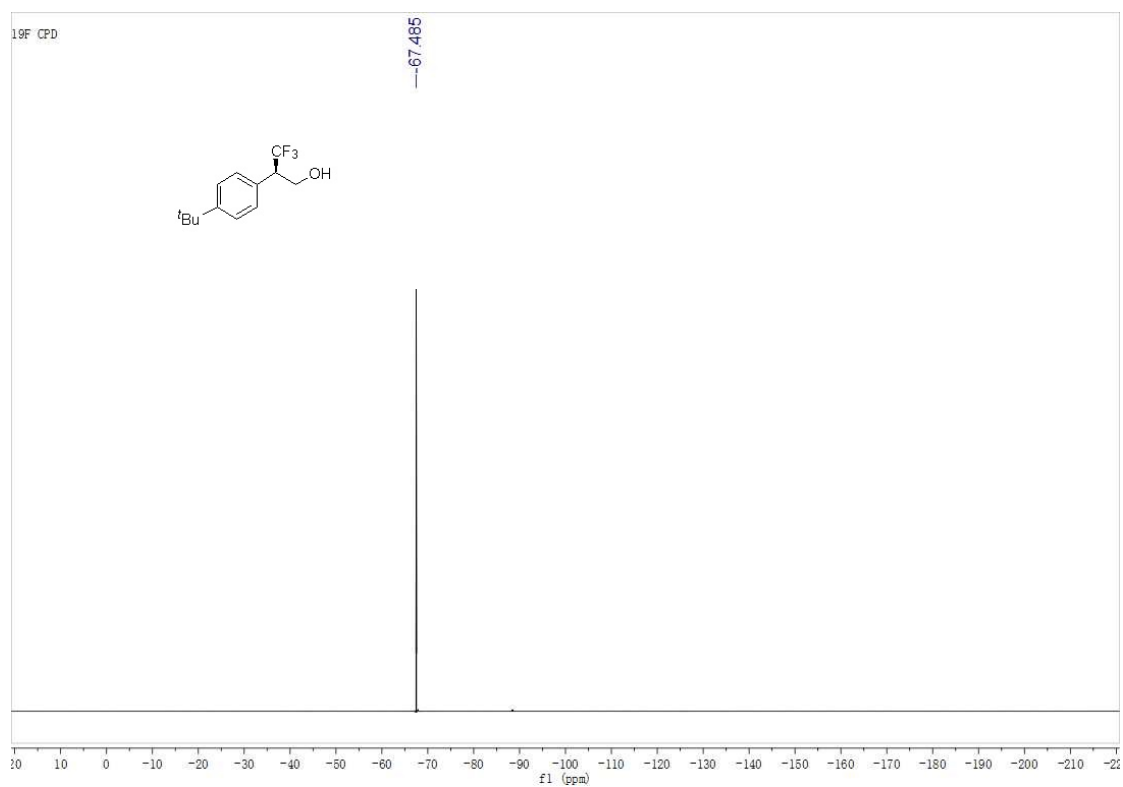
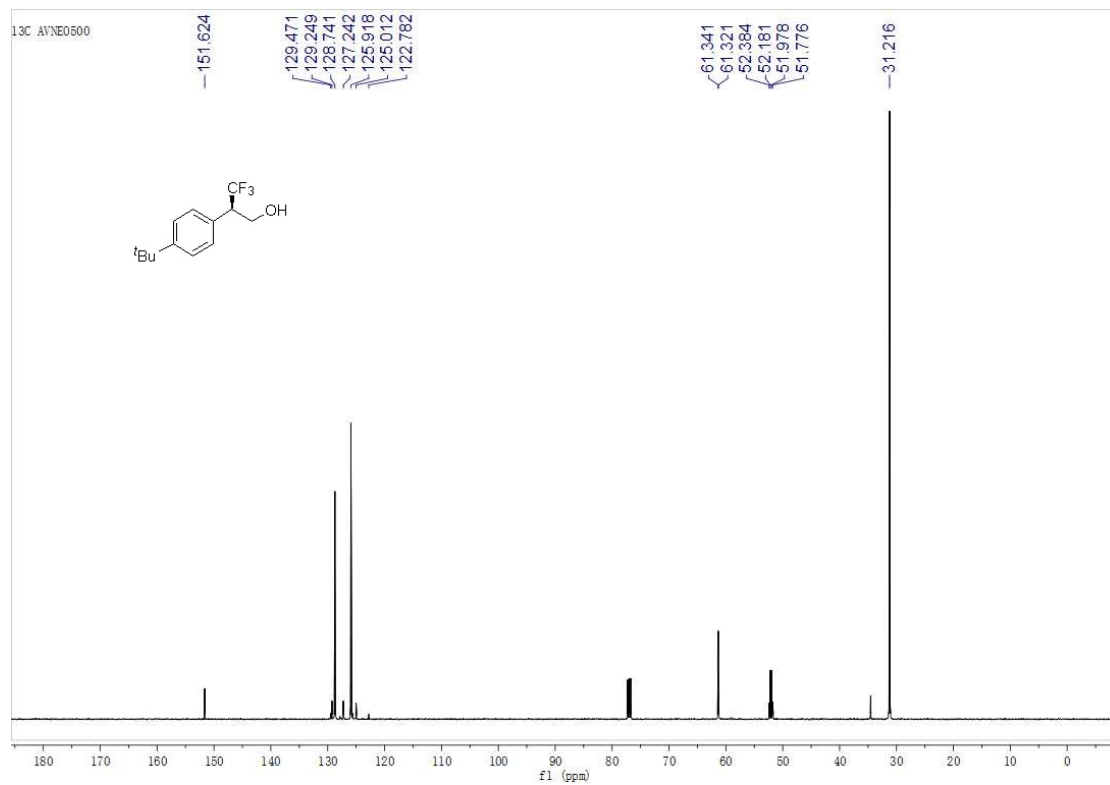


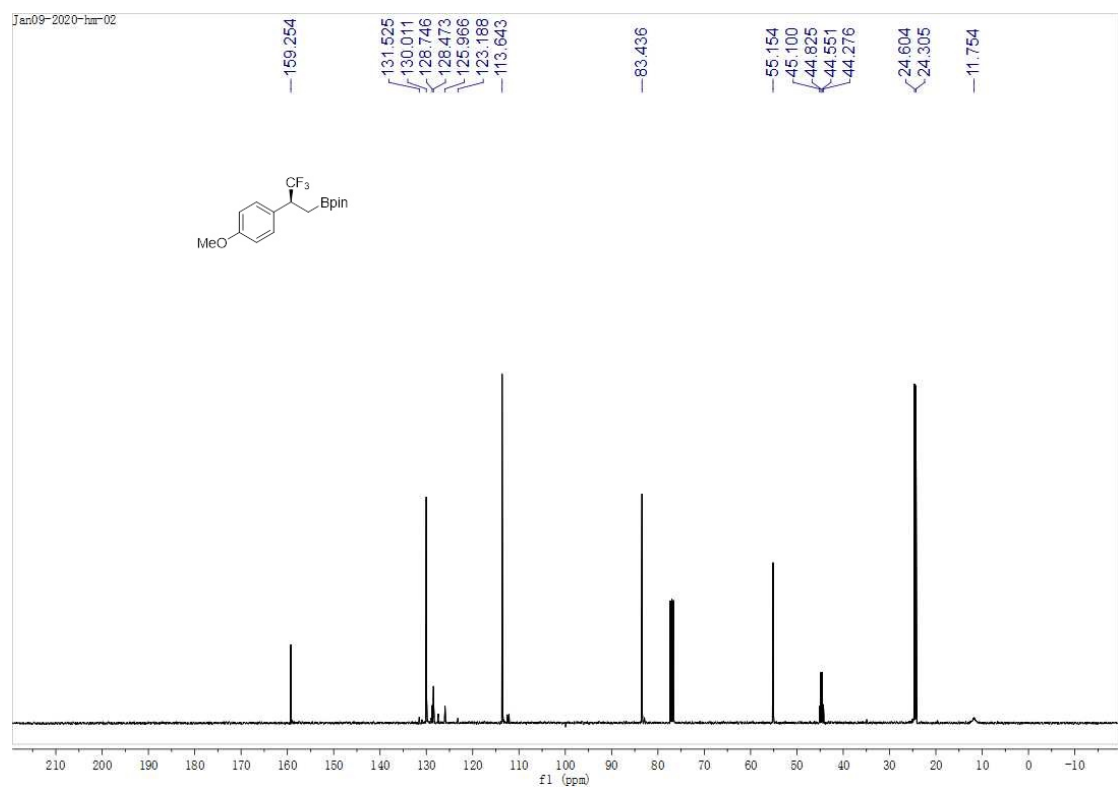
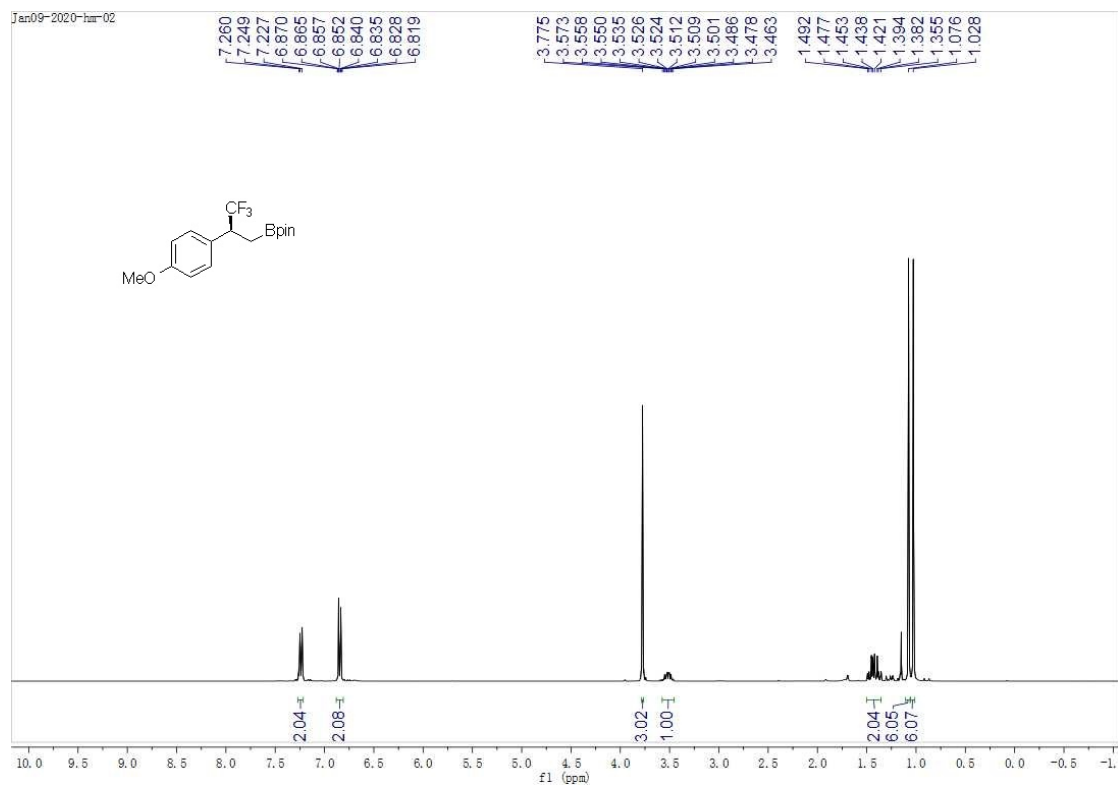
(S)-2-(2-(4-(tert-butyl)phenyl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c):

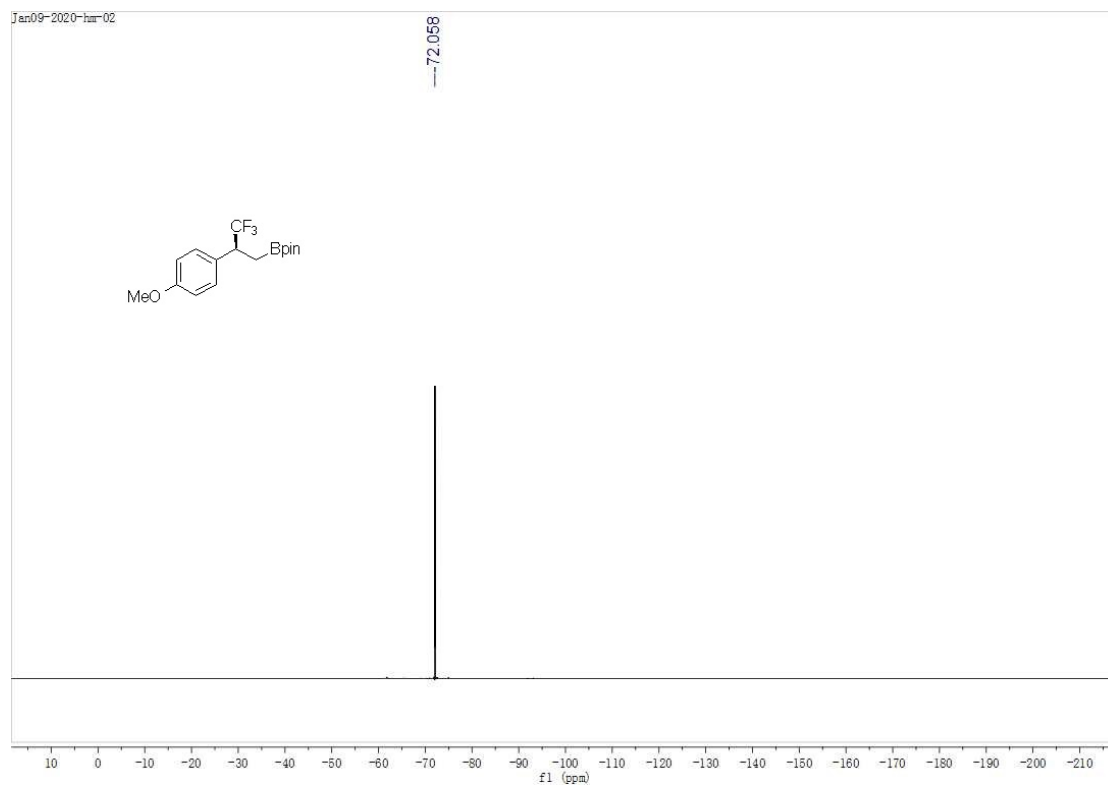


(R)-2-(4-(tert-butyl)phenyl)-3,3,3-trifluoropropan-1-ol (4c'):

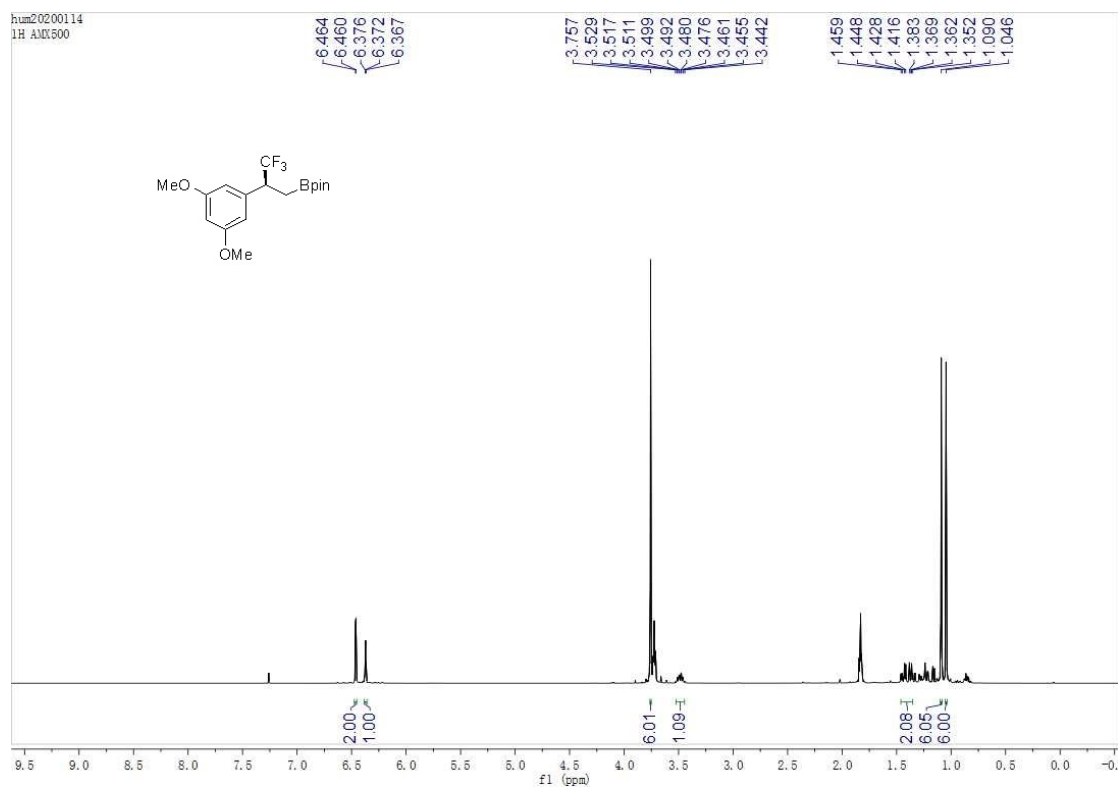


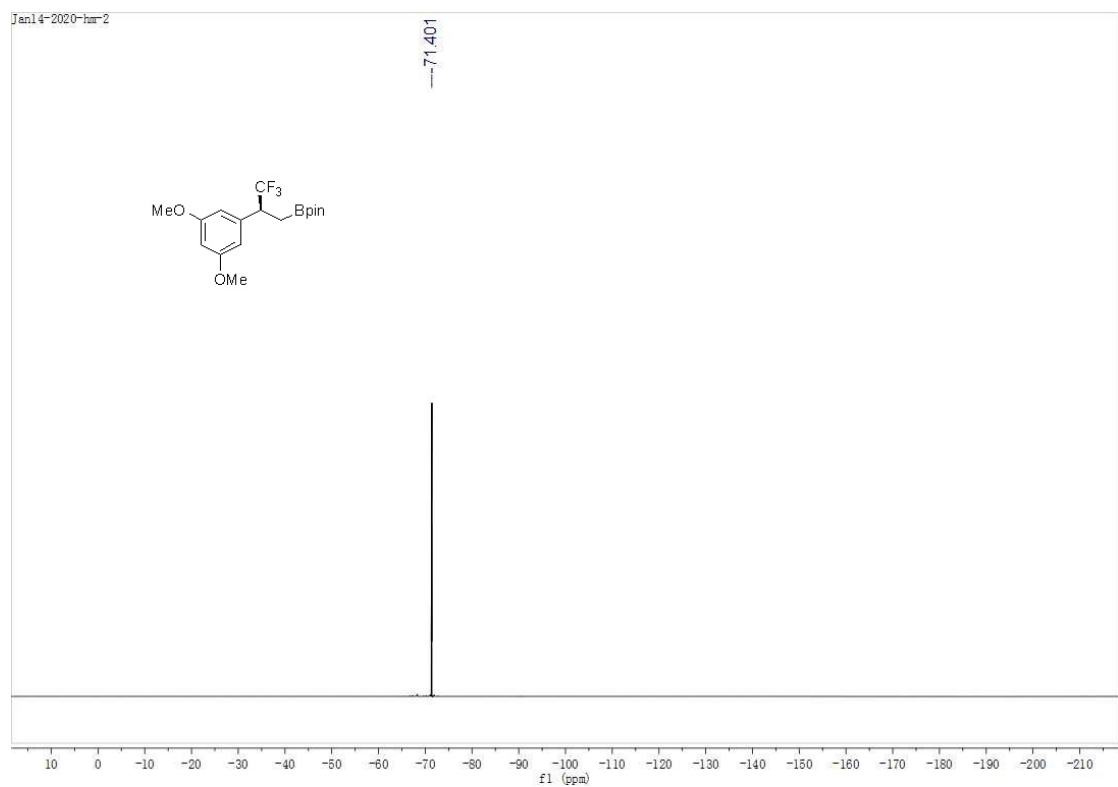
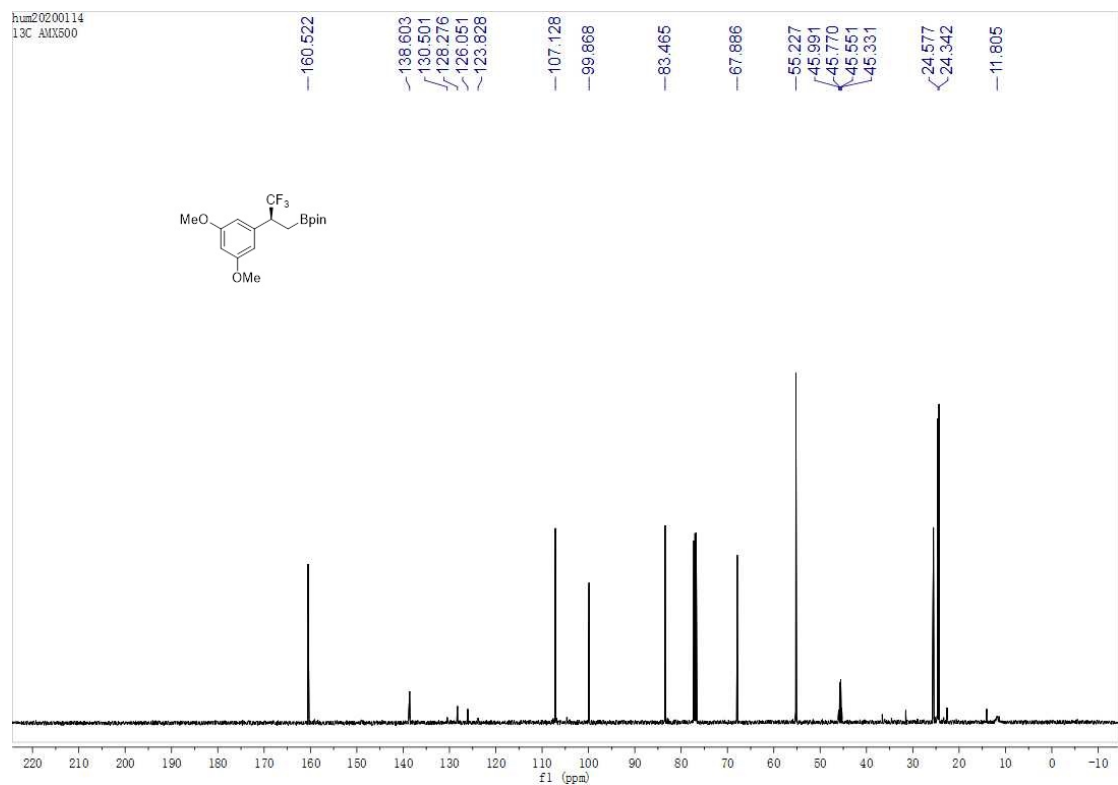


4,4,5,5-Tetramethyl-2-(3,3,3-trifluoro-2-(4-methoxyphenyl)propyl)-1,3,2-dioxaborolane (4d):

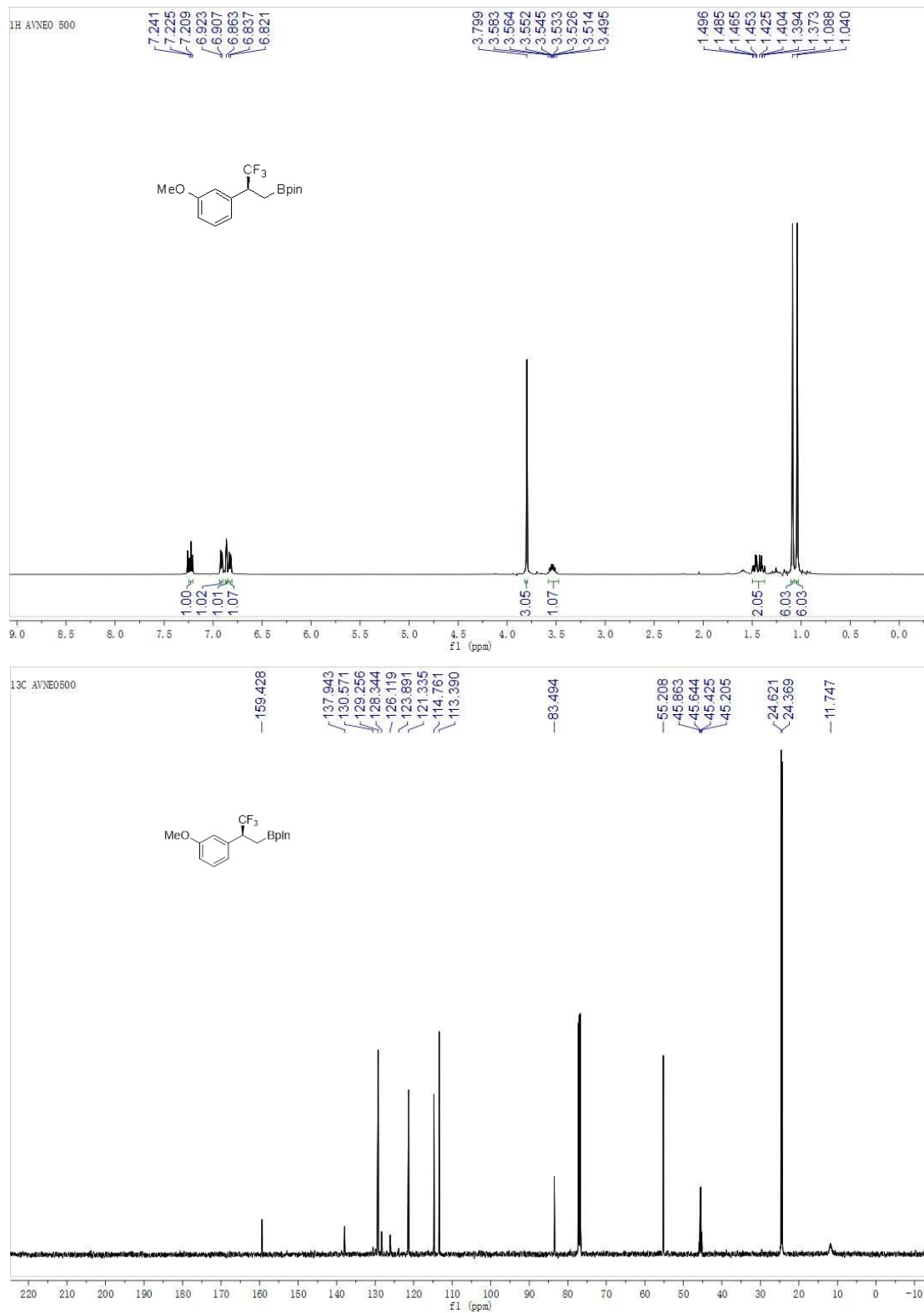


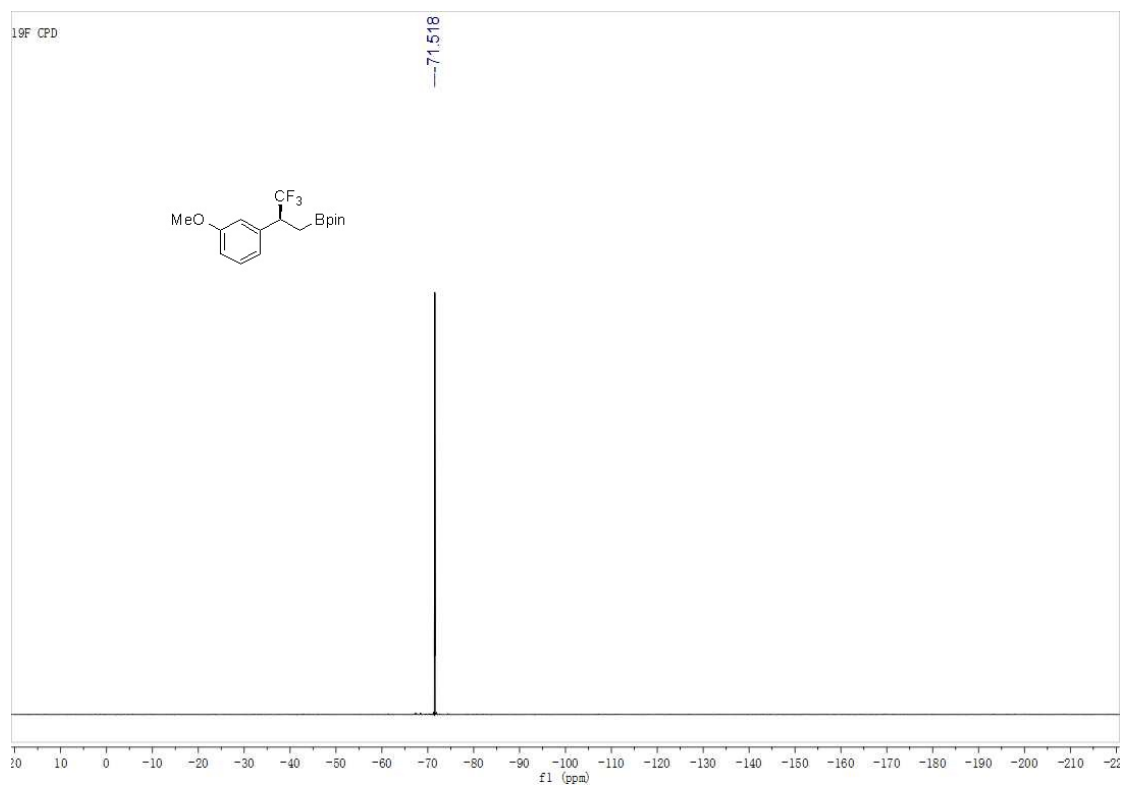
(S)-2-(2-(3,5-dimethoxyphenyl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e):



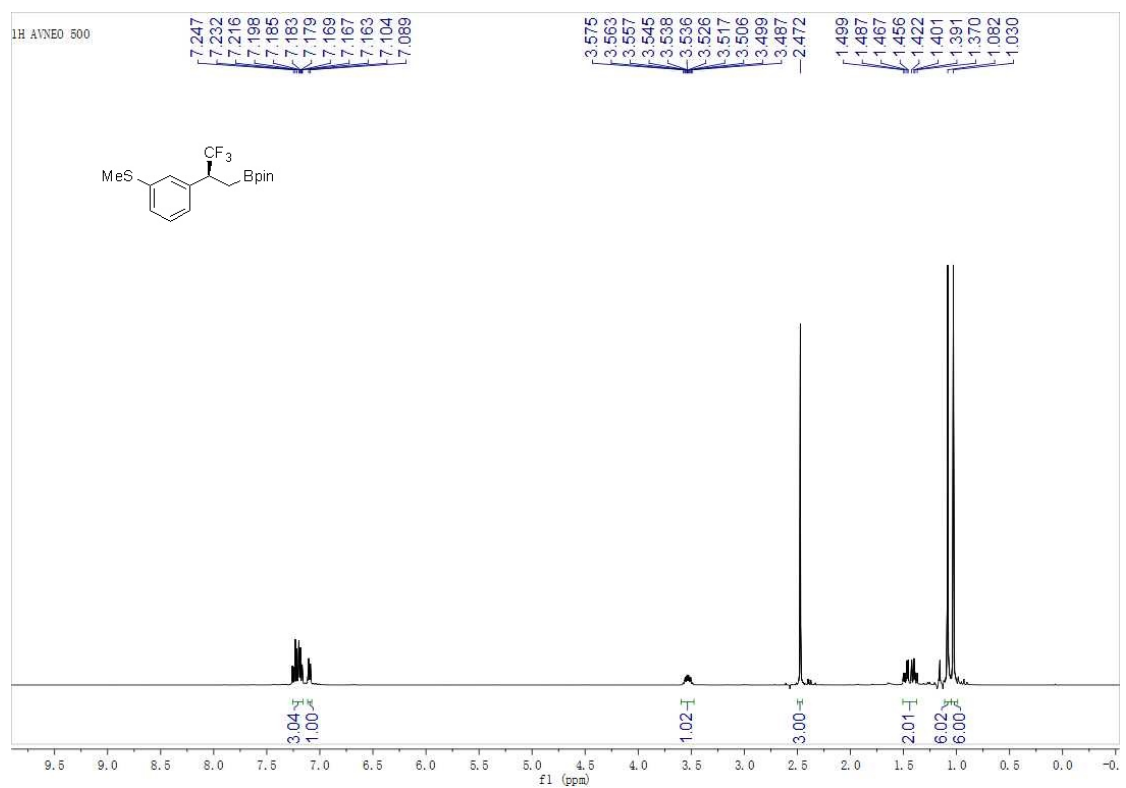


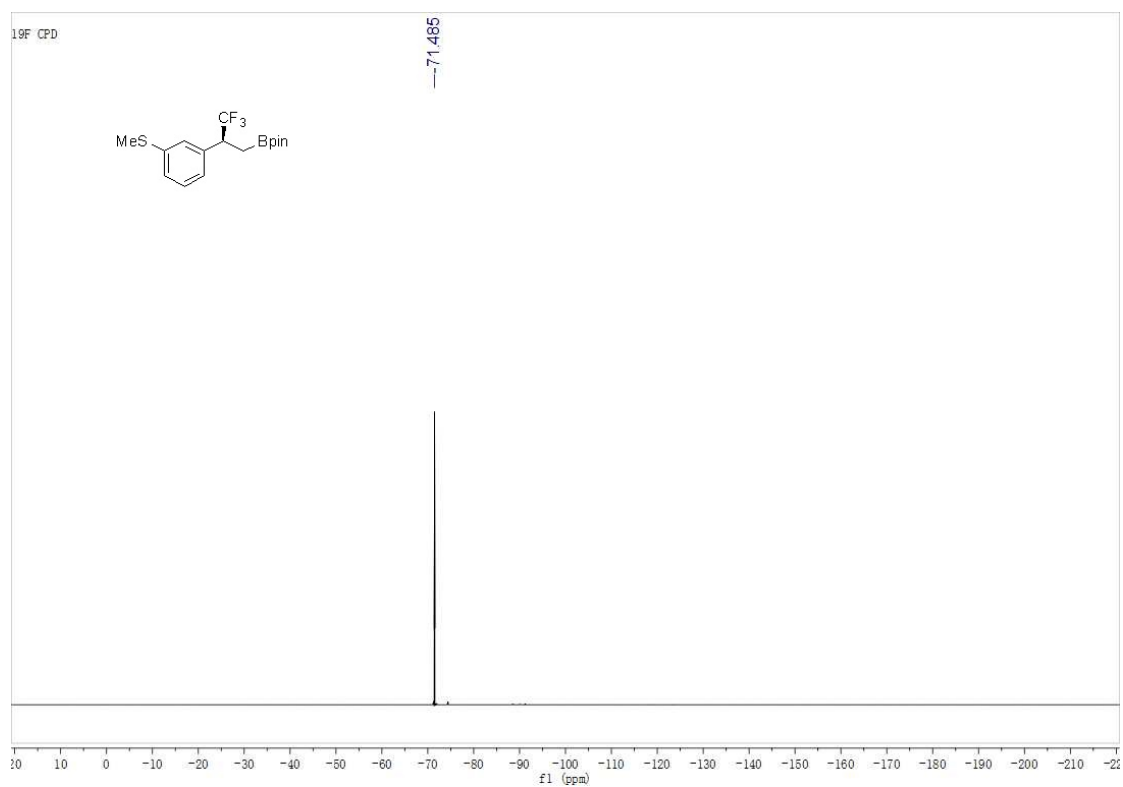
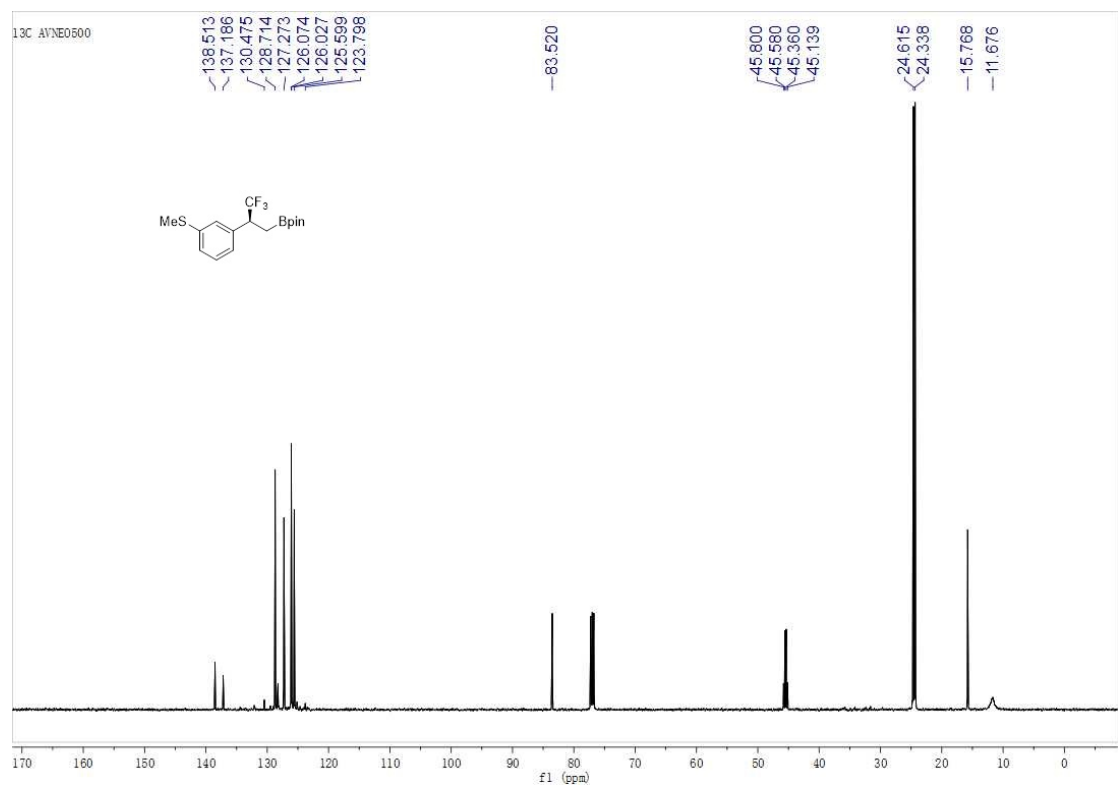
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(3-methoxyphenyl)propyl)-1,3,2-dioxaborolane (4f):



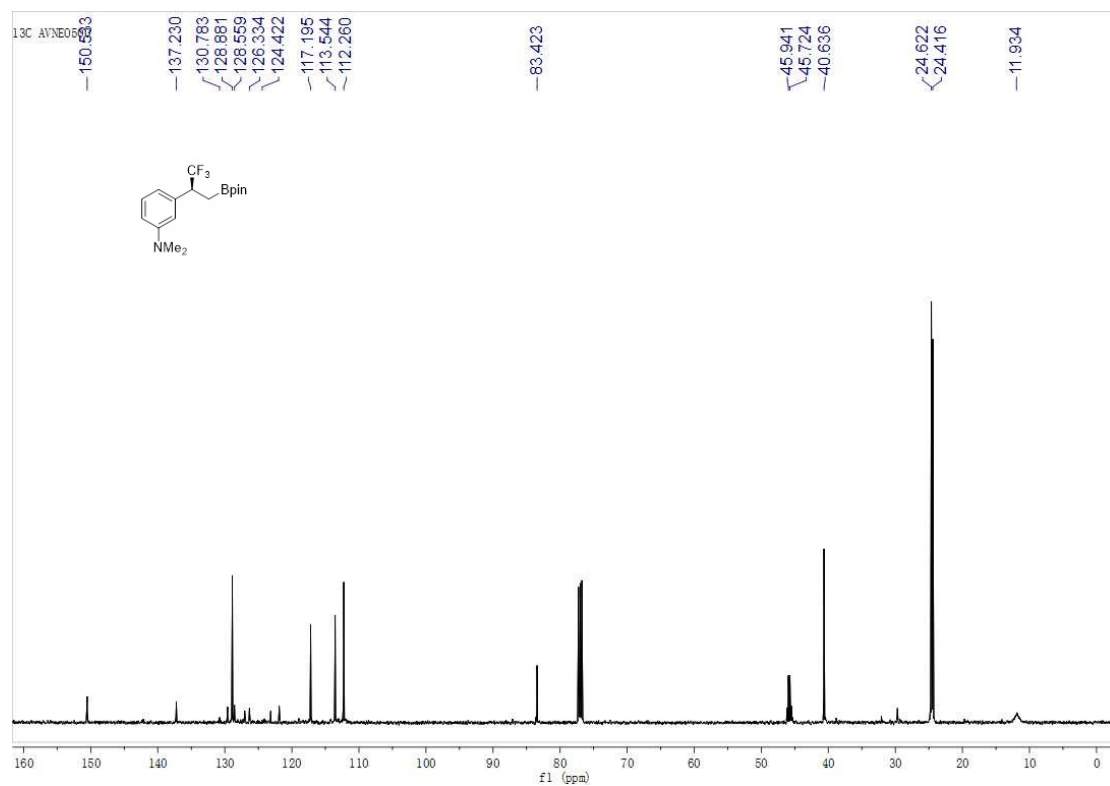
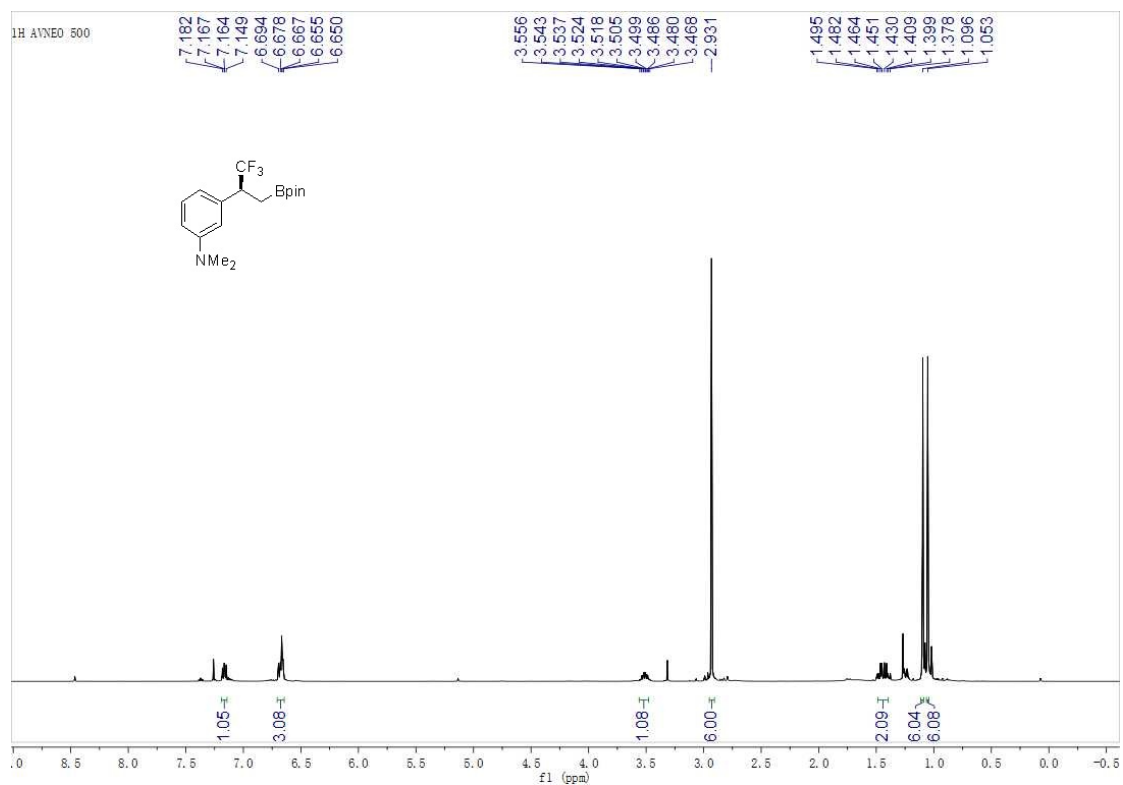


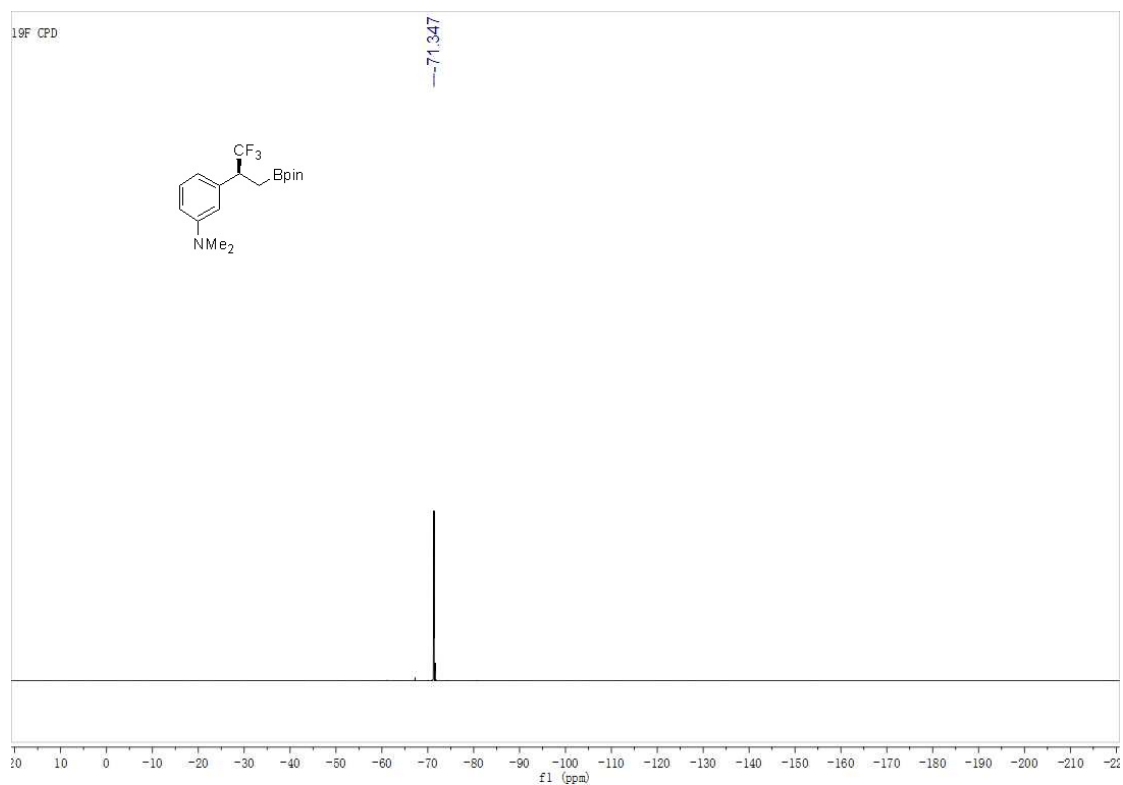
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(3-(methylthio)phenyl)propyl)-1,3,2-dioxaborolane (4g):



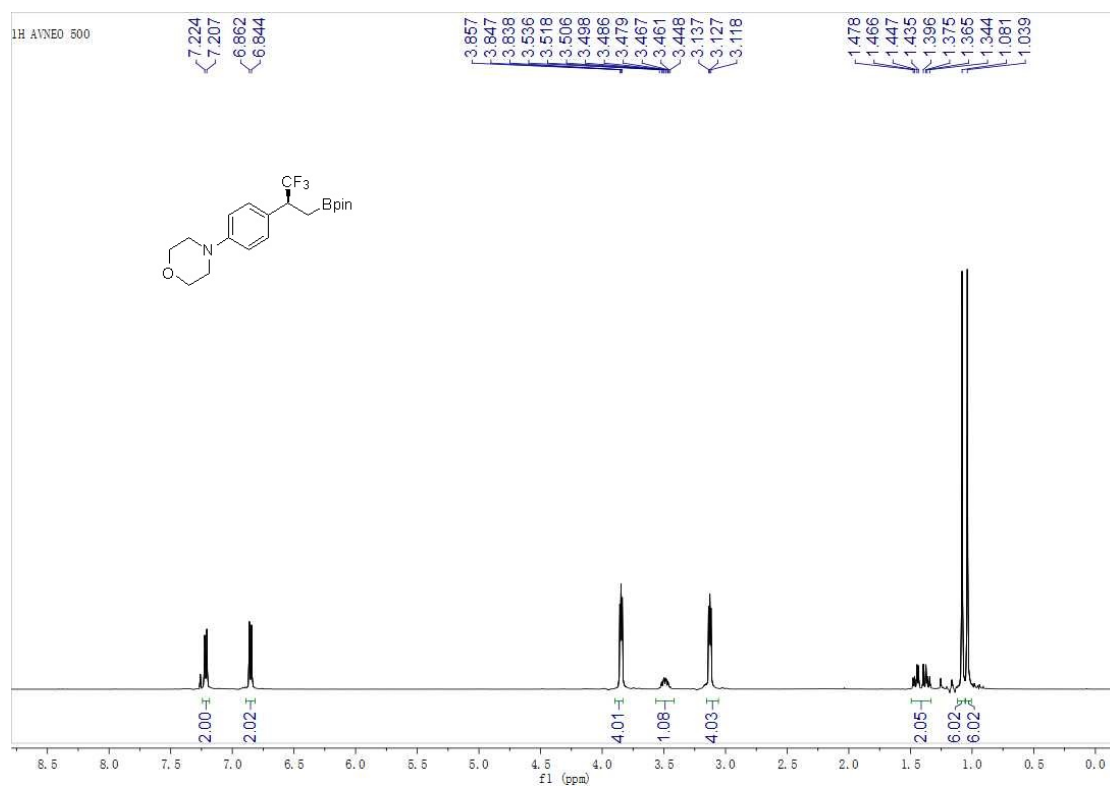


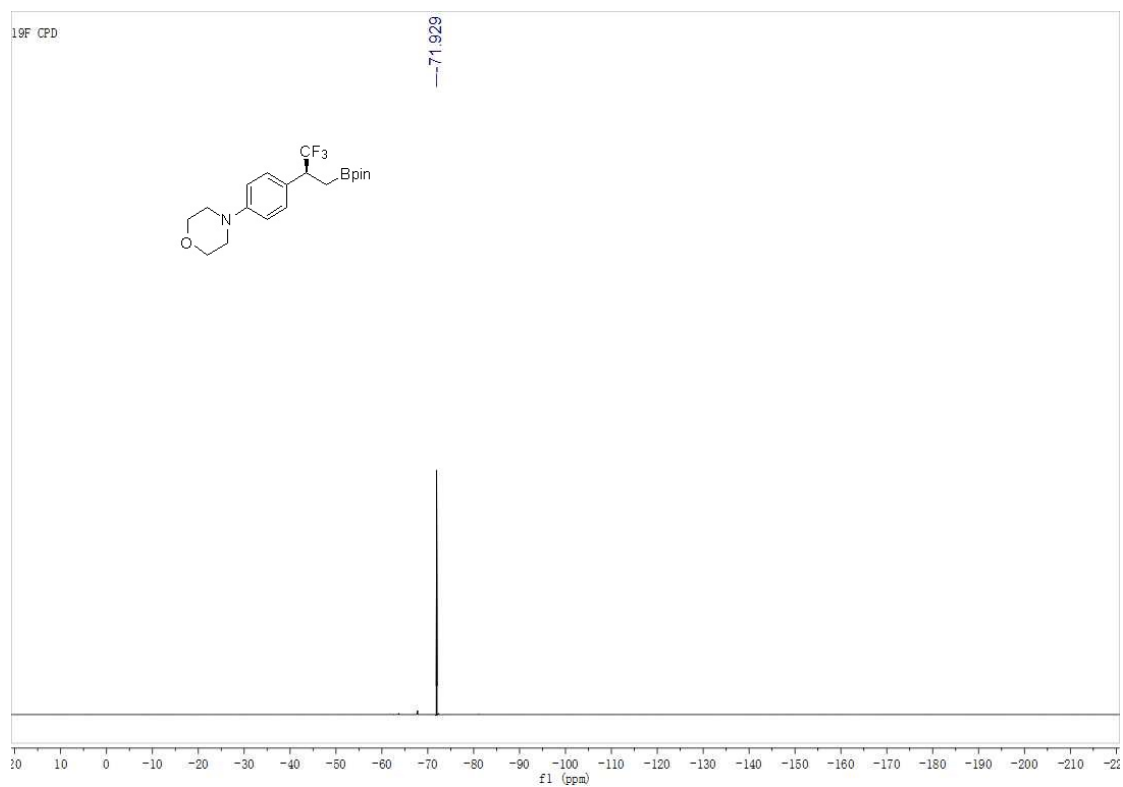
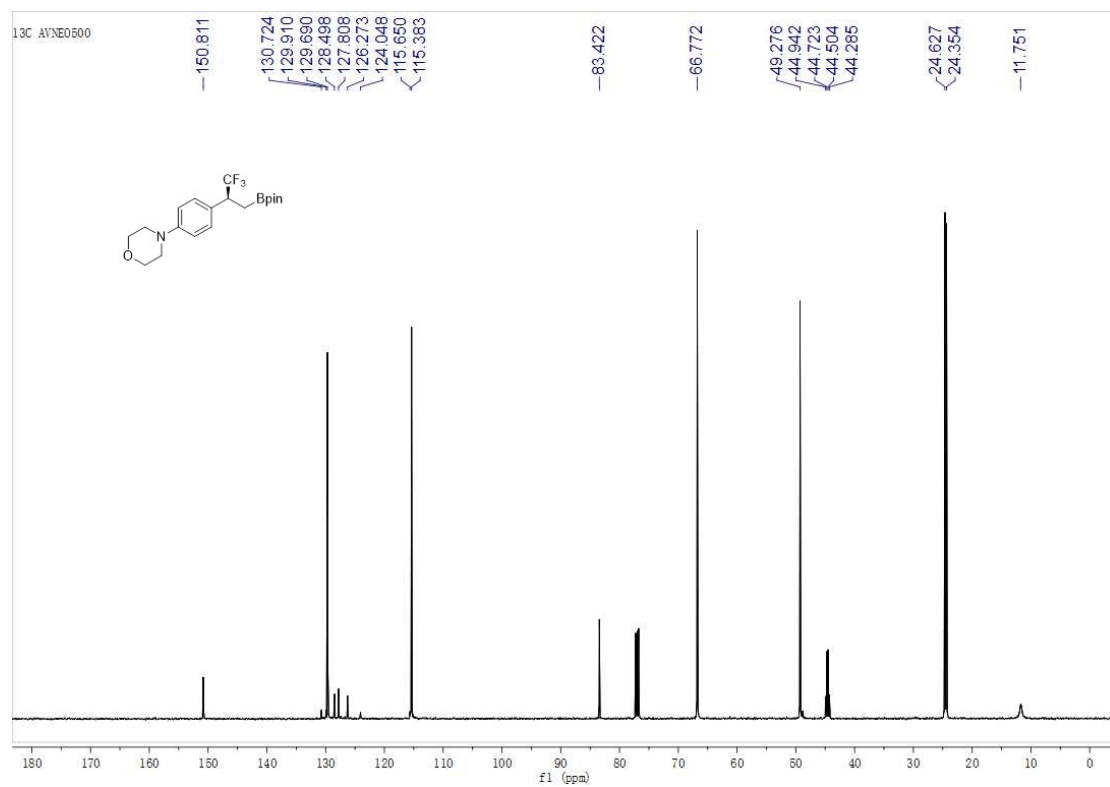
(S)-N,N-dimethyl-3-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)aniline (4h):



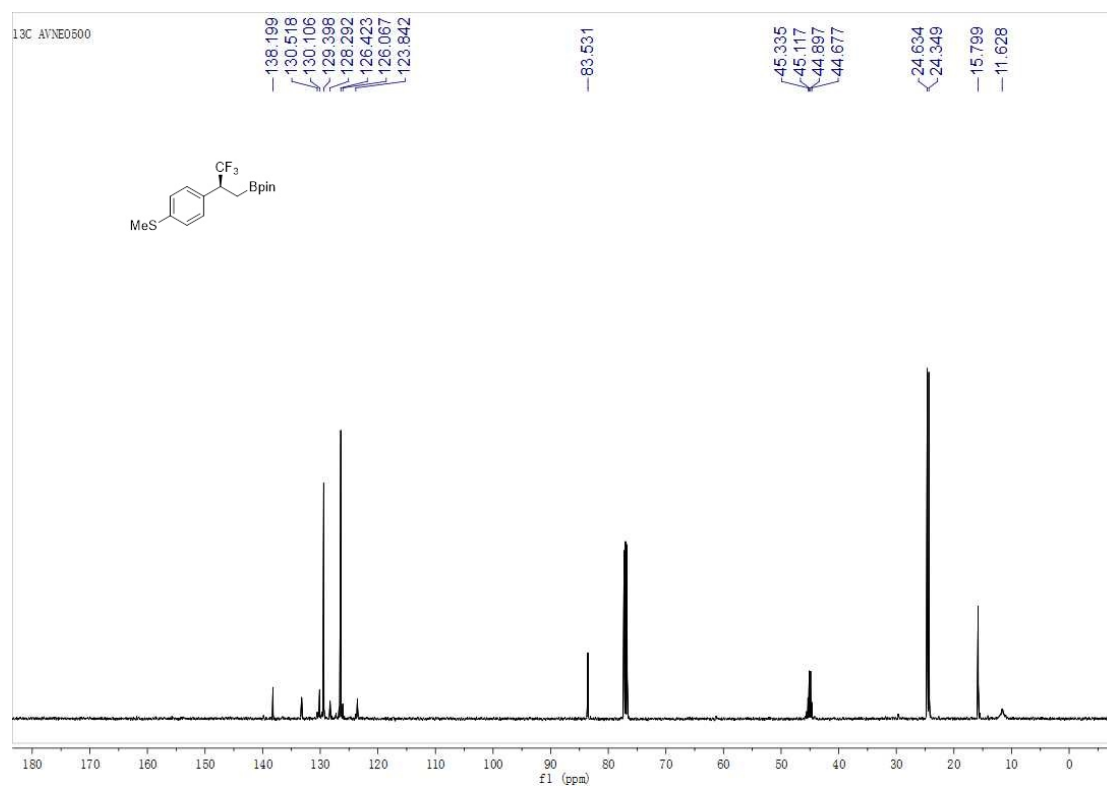
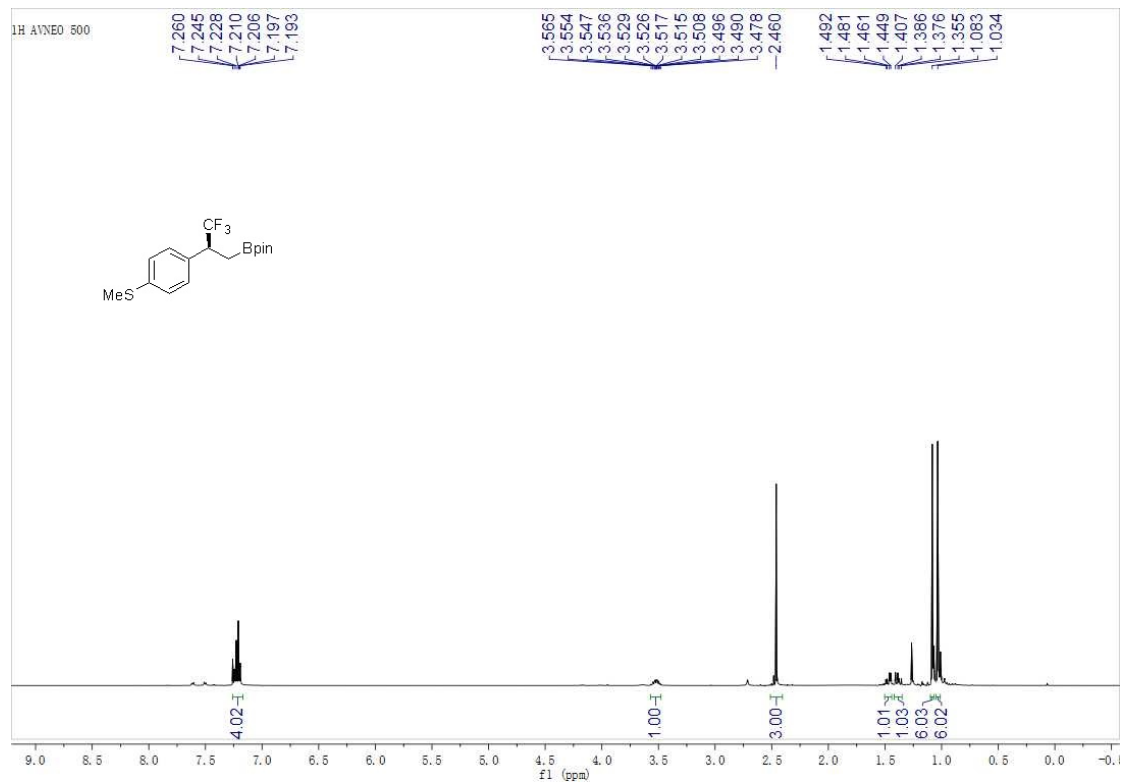


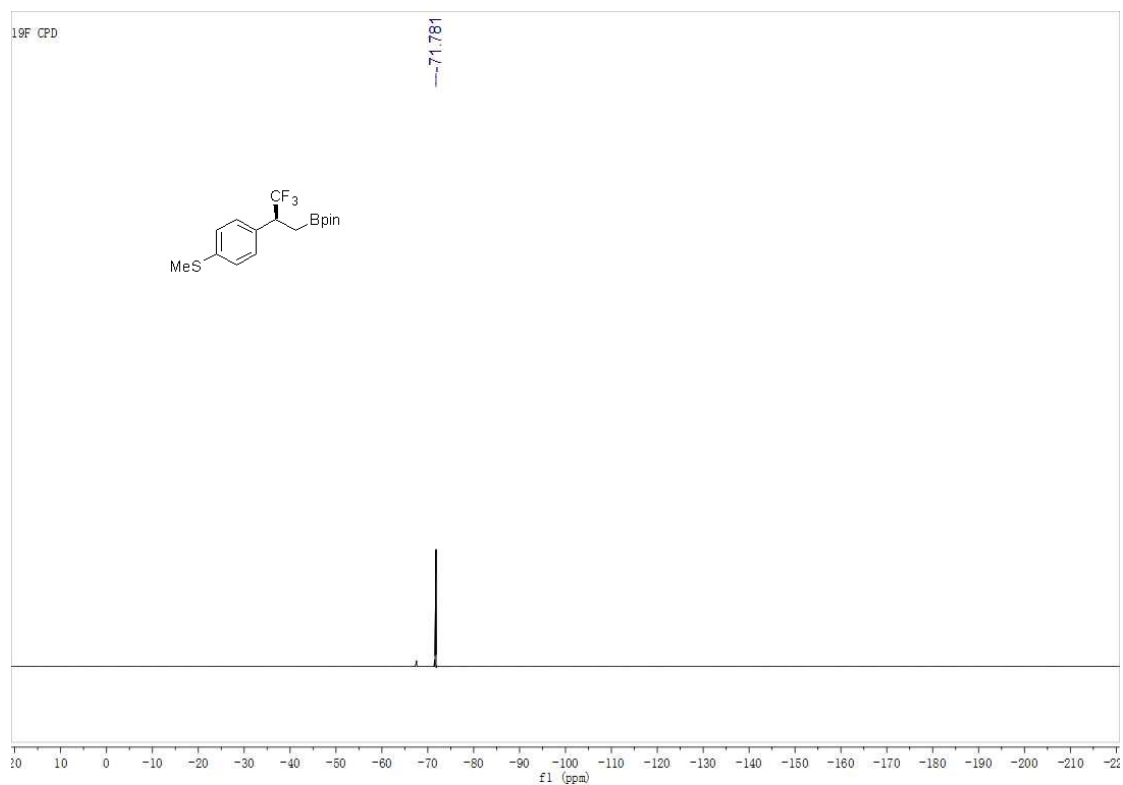
(S)-4-(4-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)phenyl)morpholine (4i):



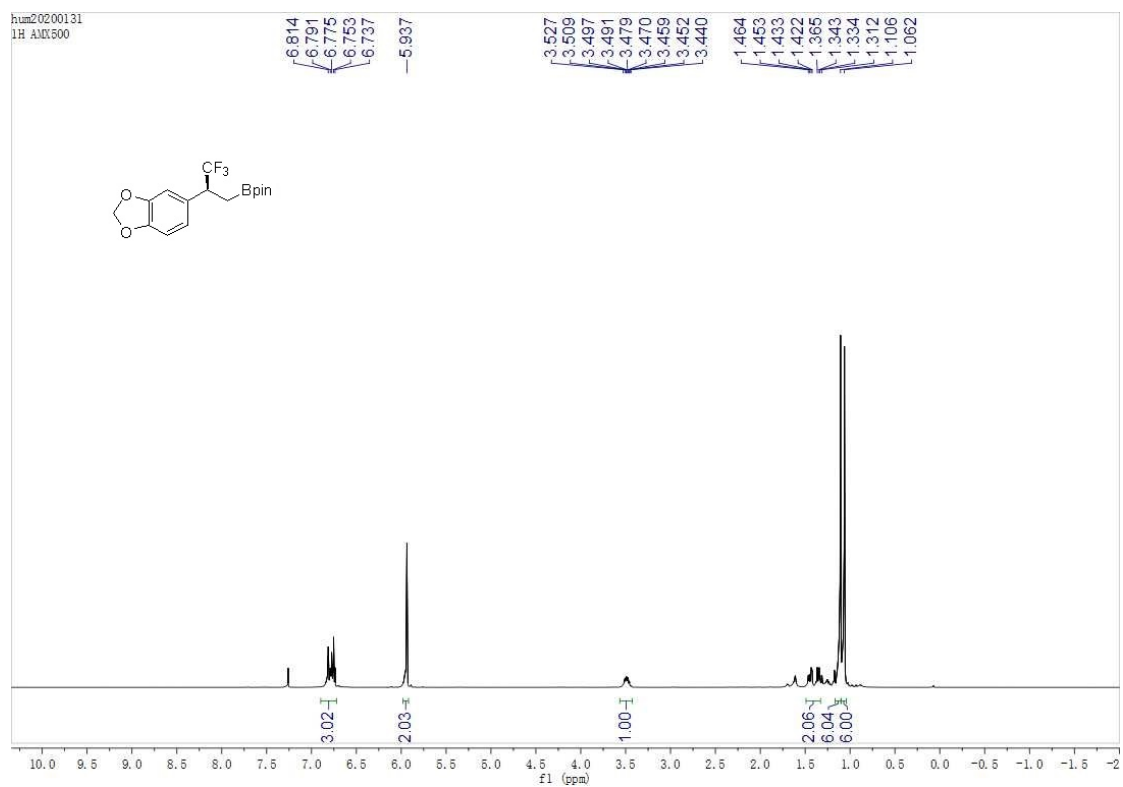


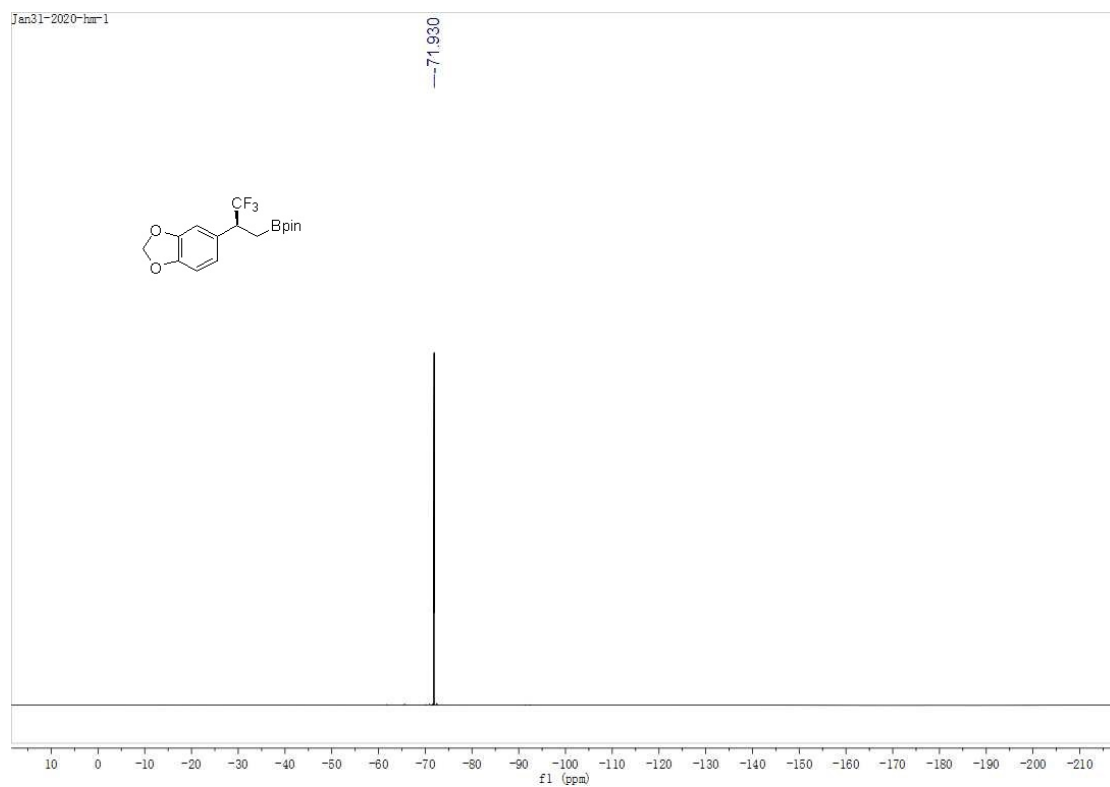
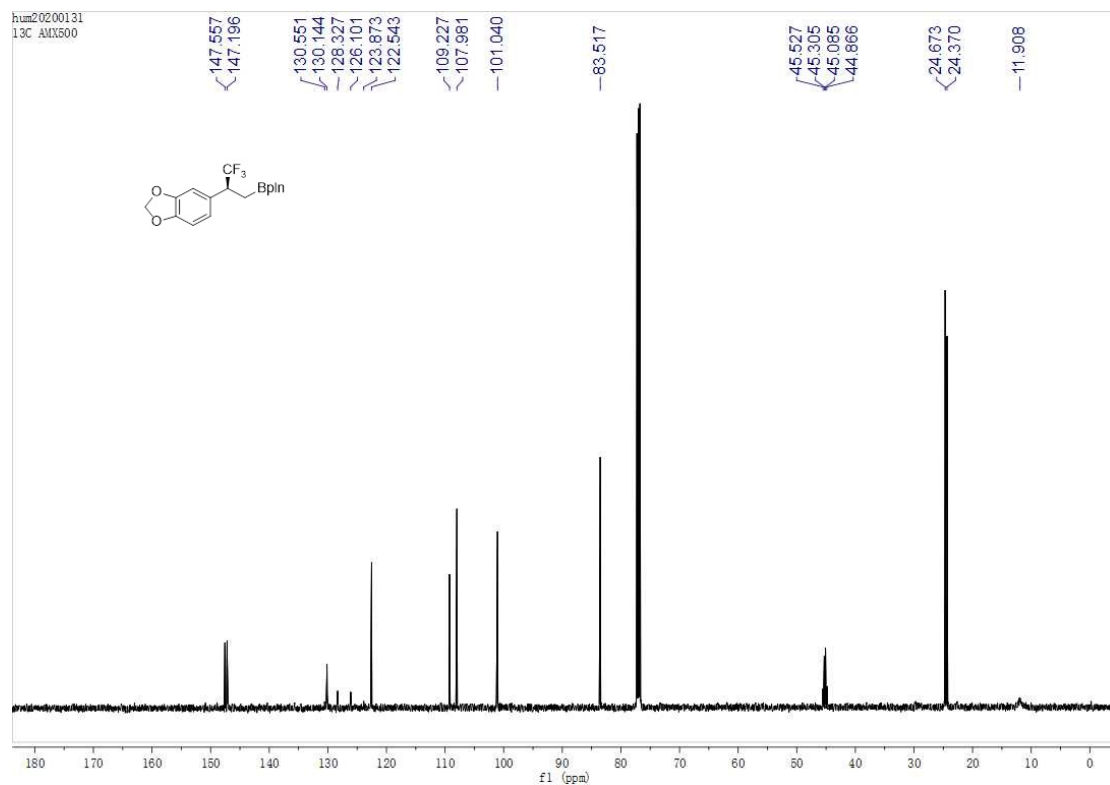
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(4-(methylthio)phenyl)propyl)-1,3,2-dioxaborolane (4j):

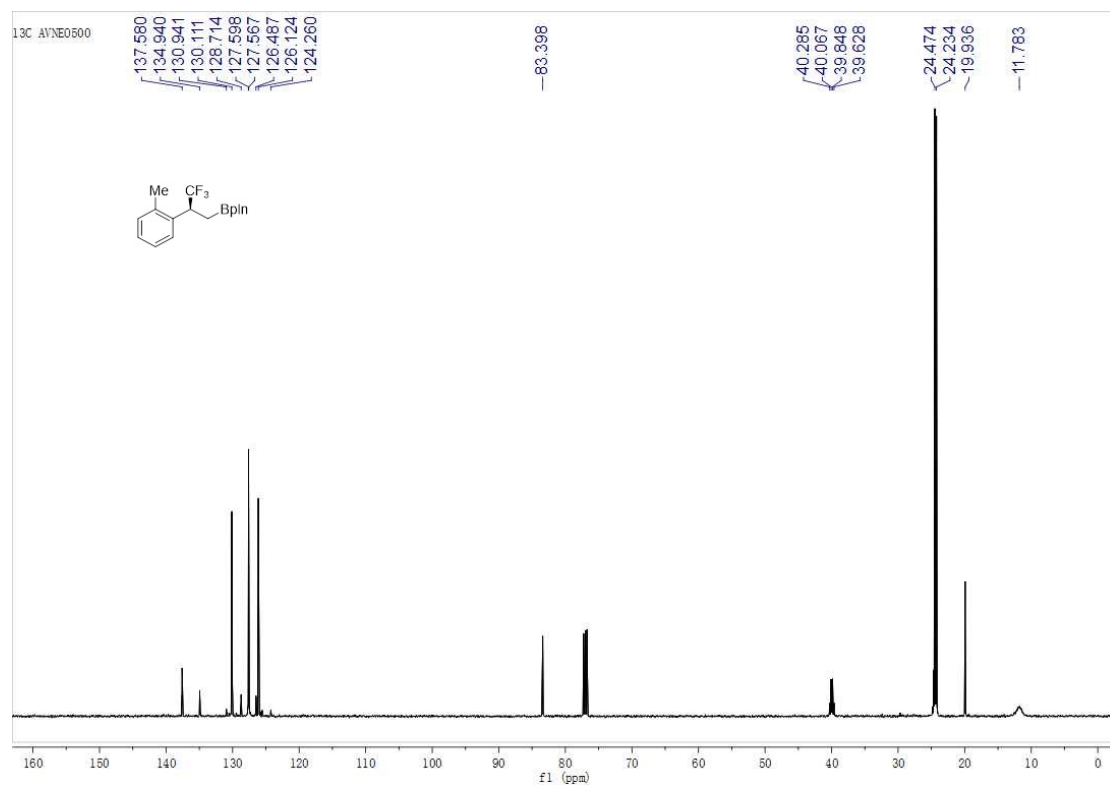
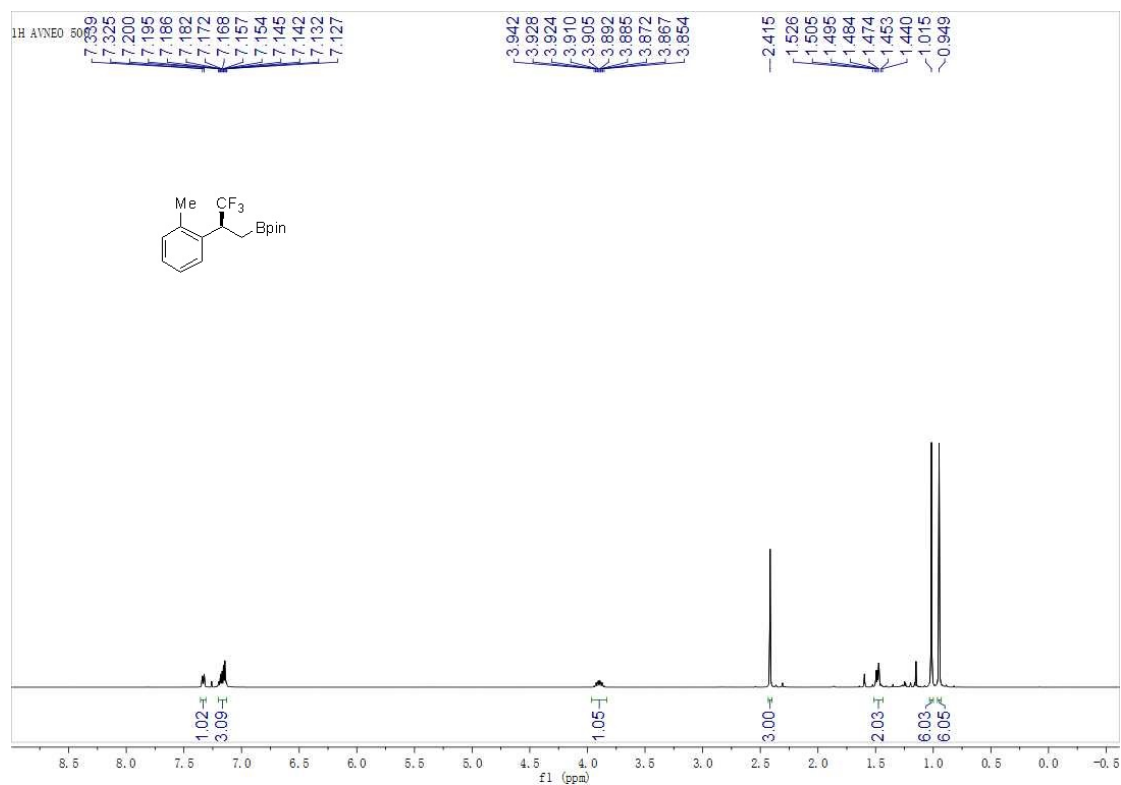


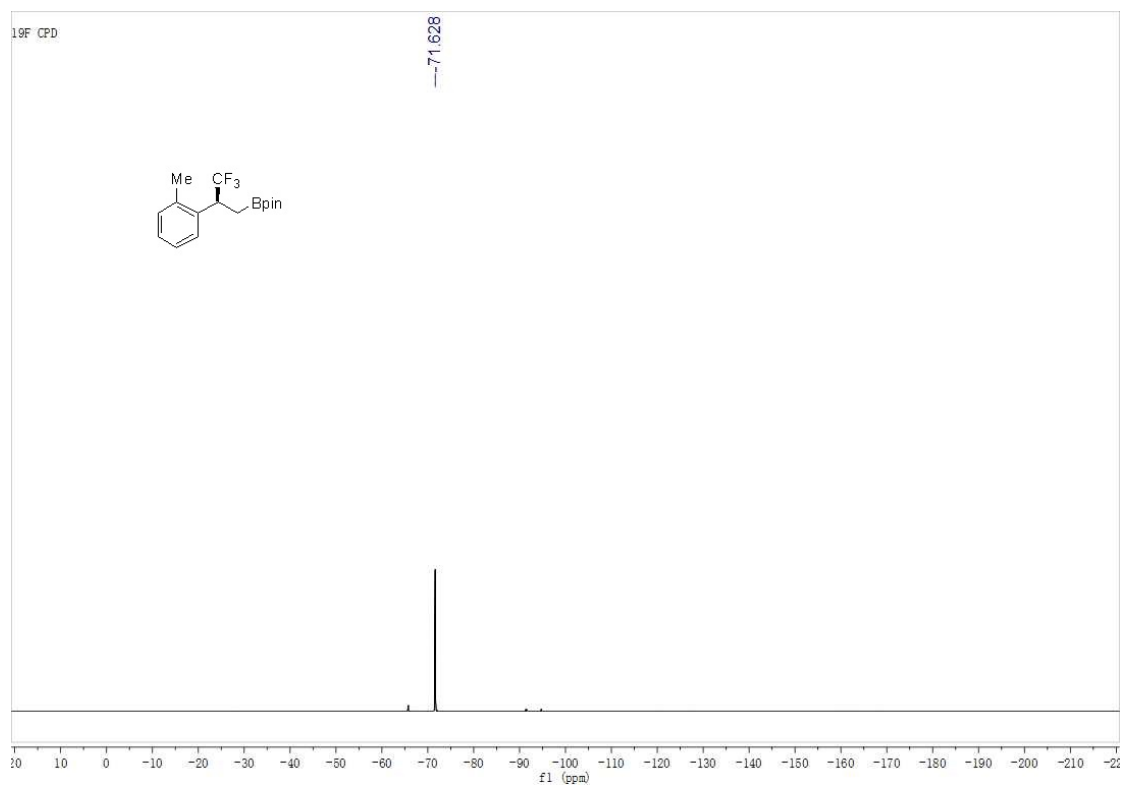


(S)-2-(2-(benzo[d][1,3]dioxol-5-yl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane (4k):

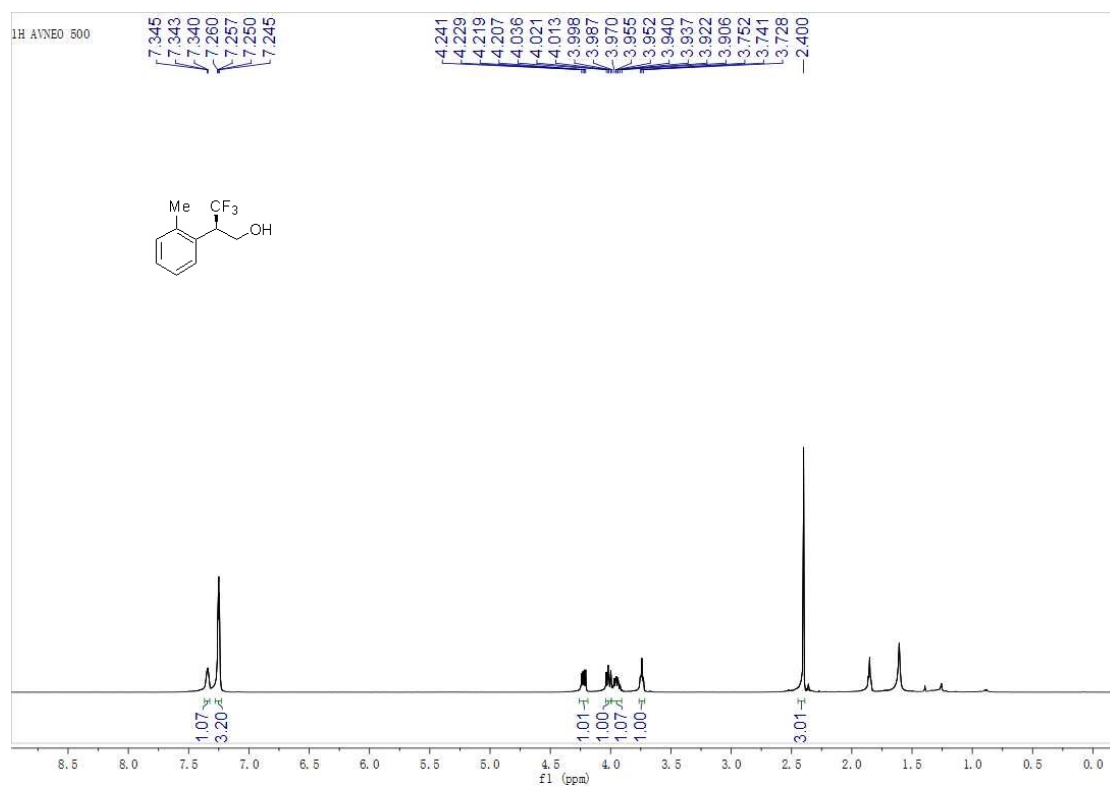


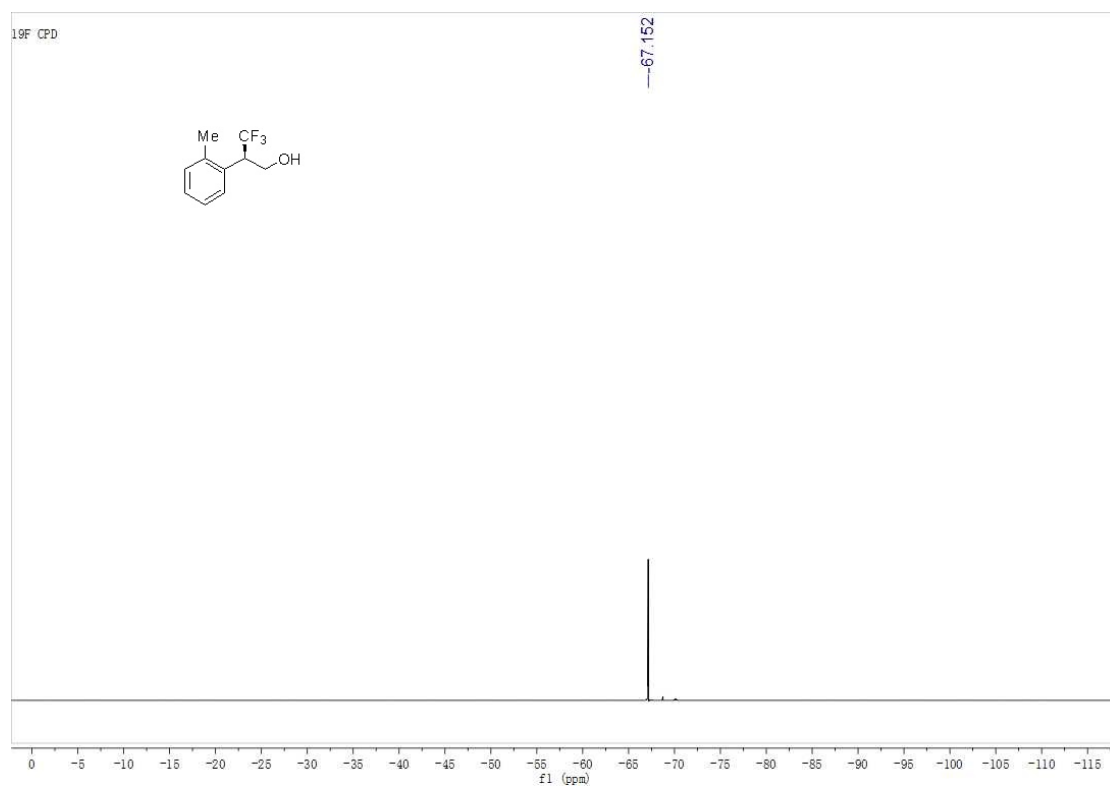
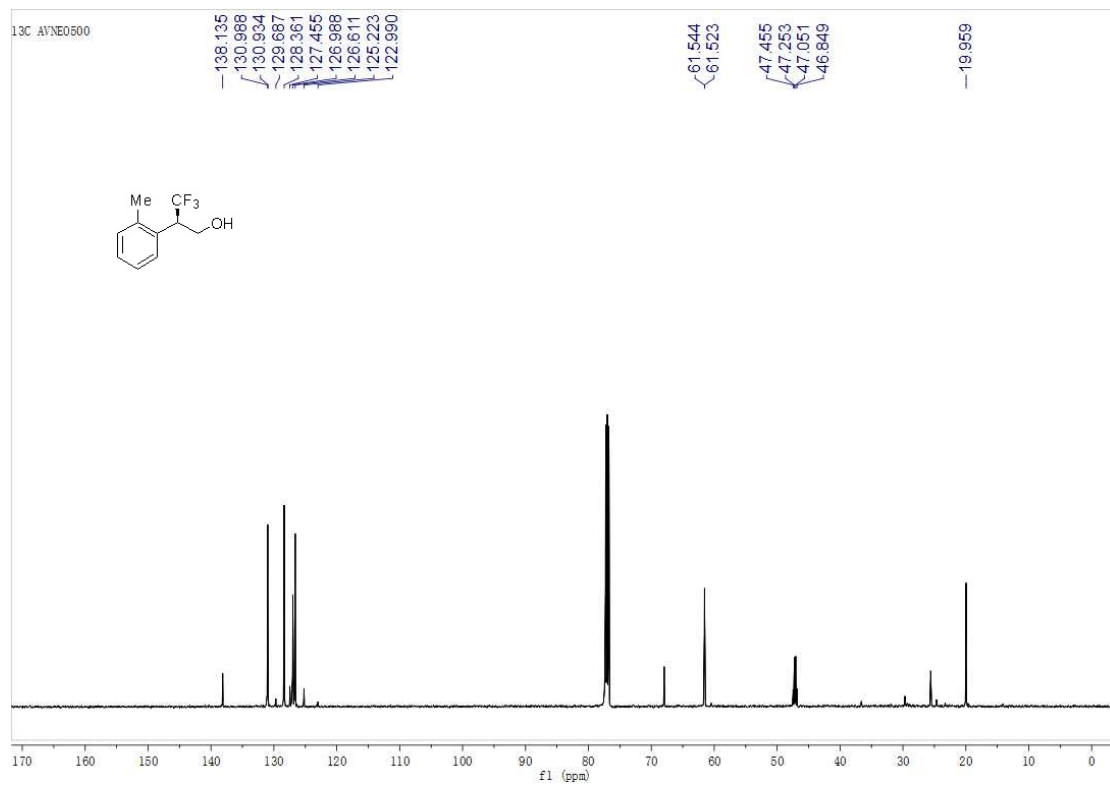


(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(o-tolyl)propyl)-1,3,2-dioxaborolane**(41):**

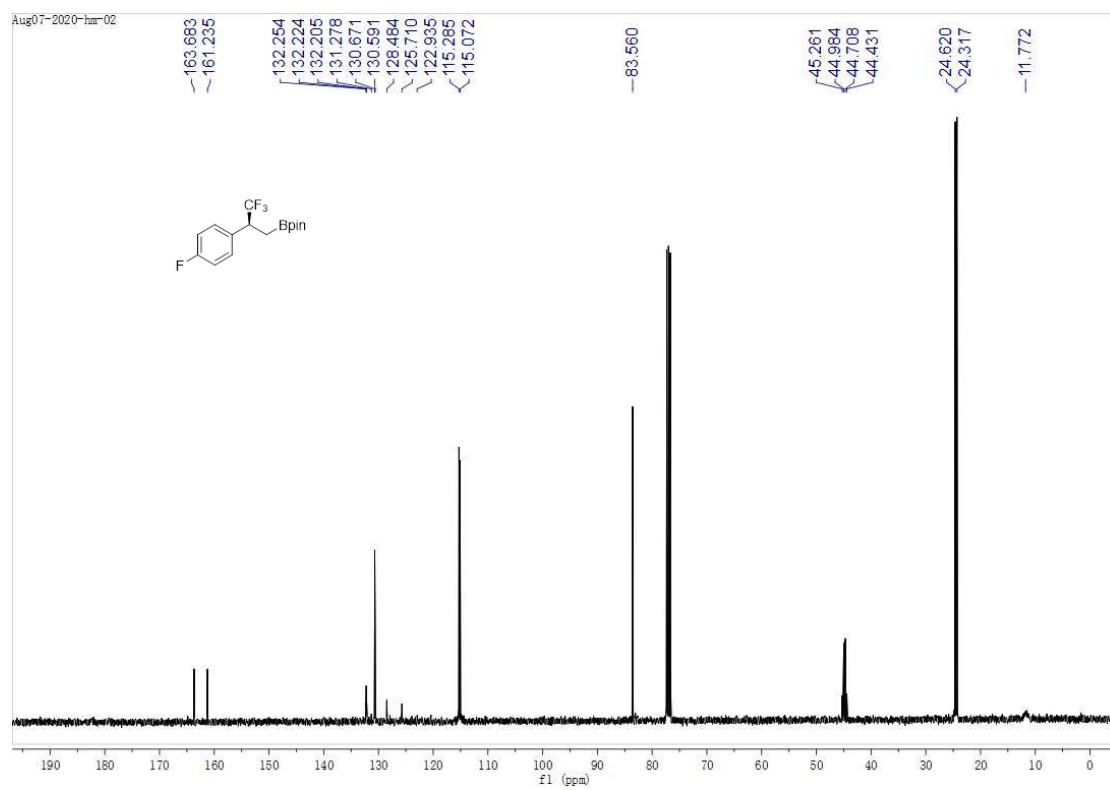
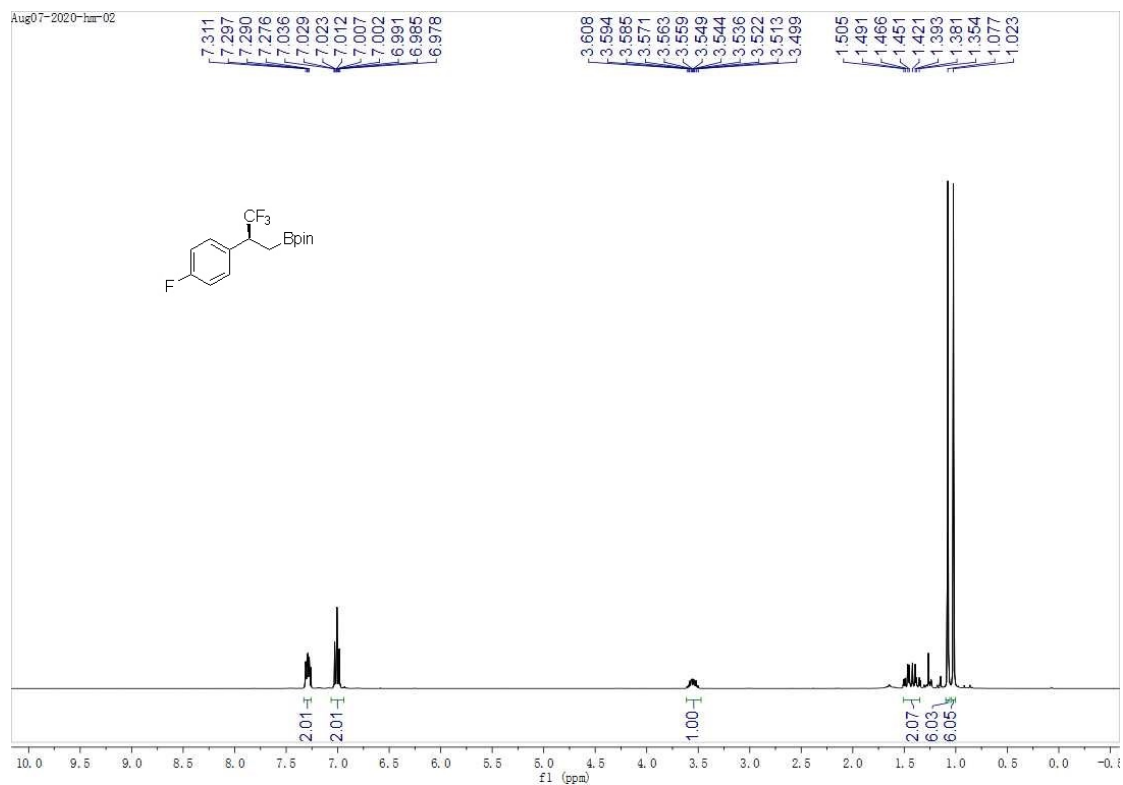


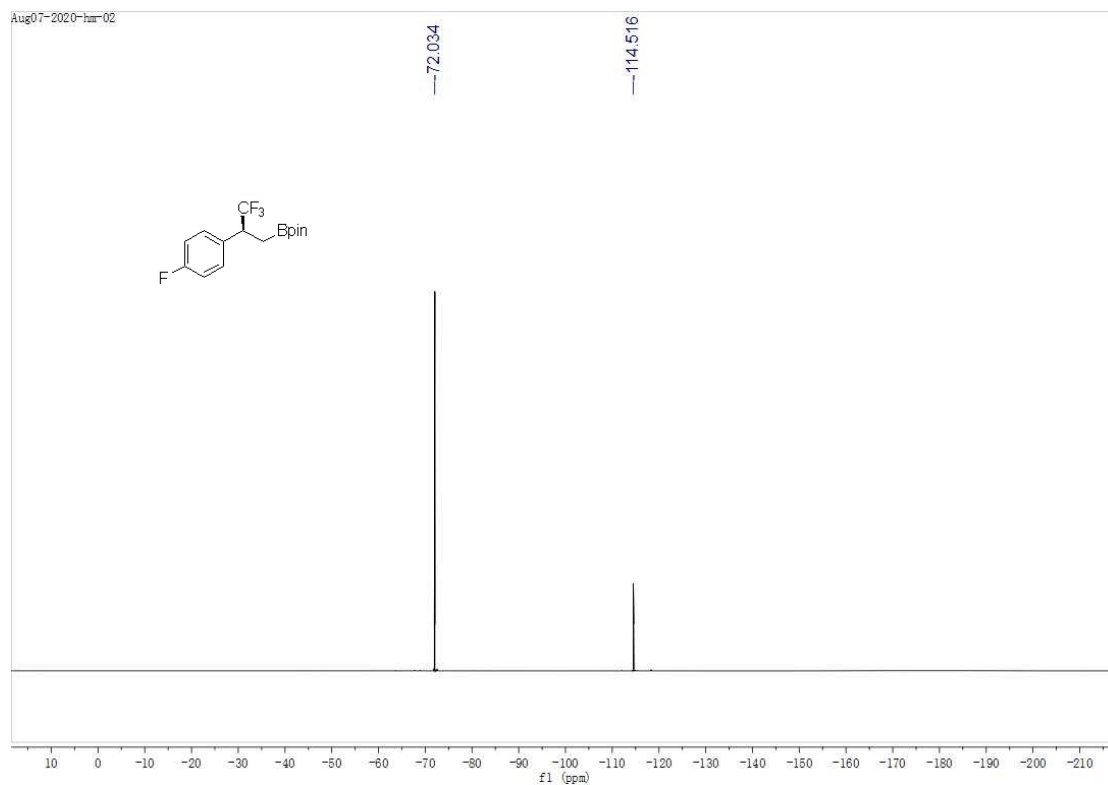
(R)-3,3,3-trifluoro-2-(o-tolyl)propan-1-ol (4I')



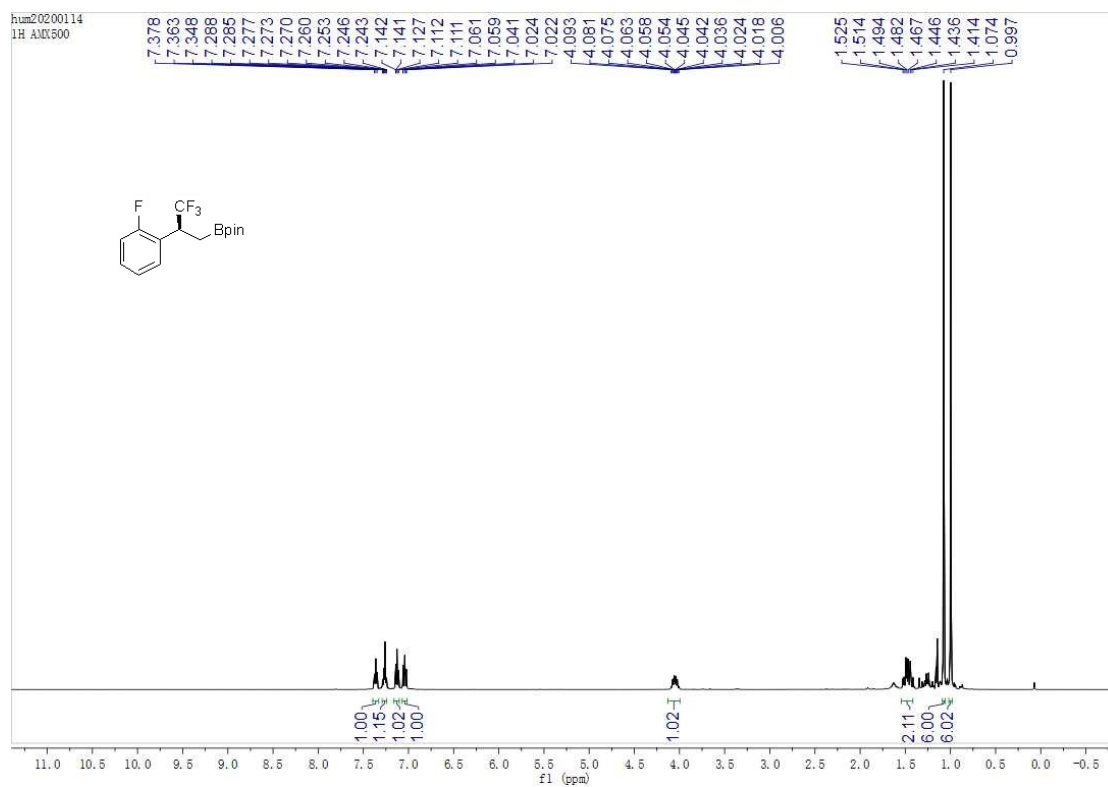


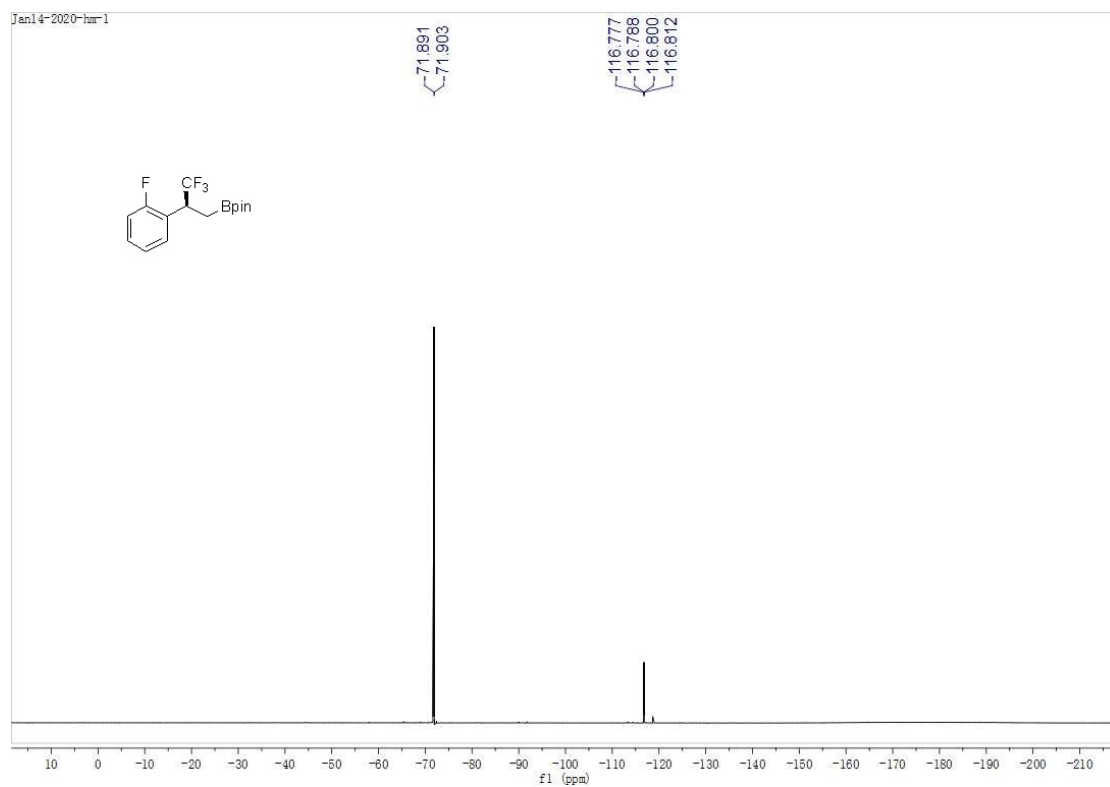
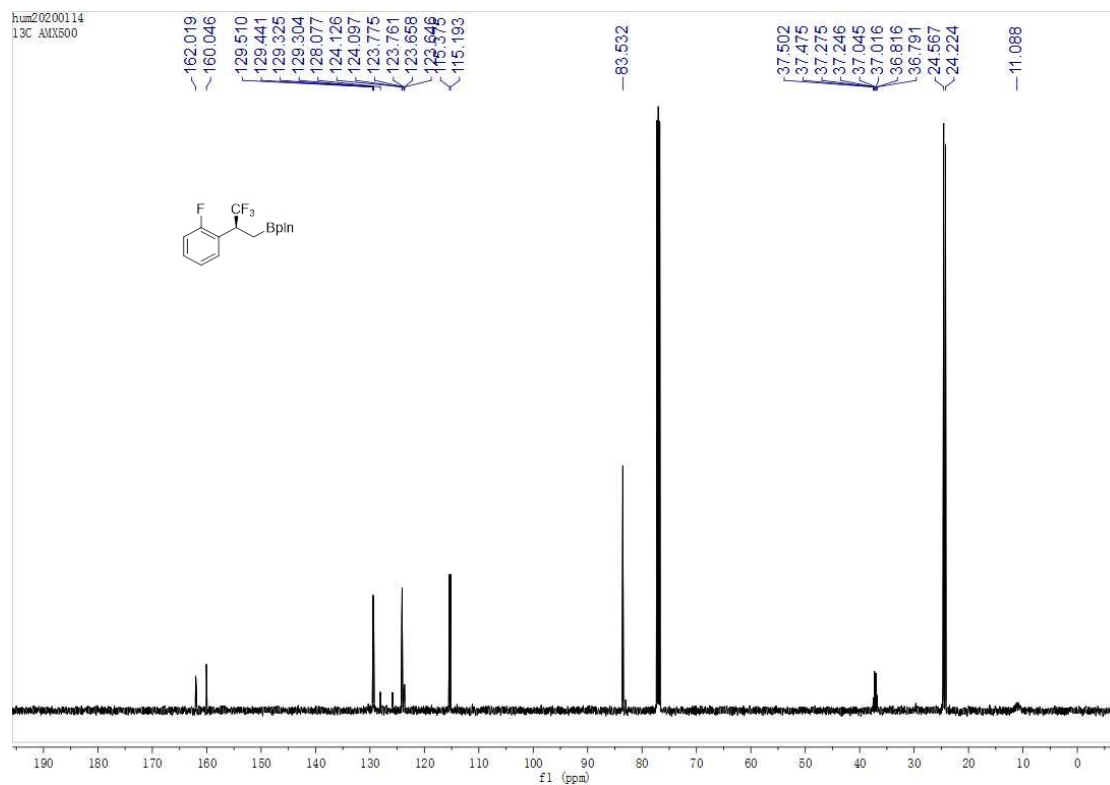
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(4-fluorophenyl)propyl)-1,3,2-dioxaborolane (4m):



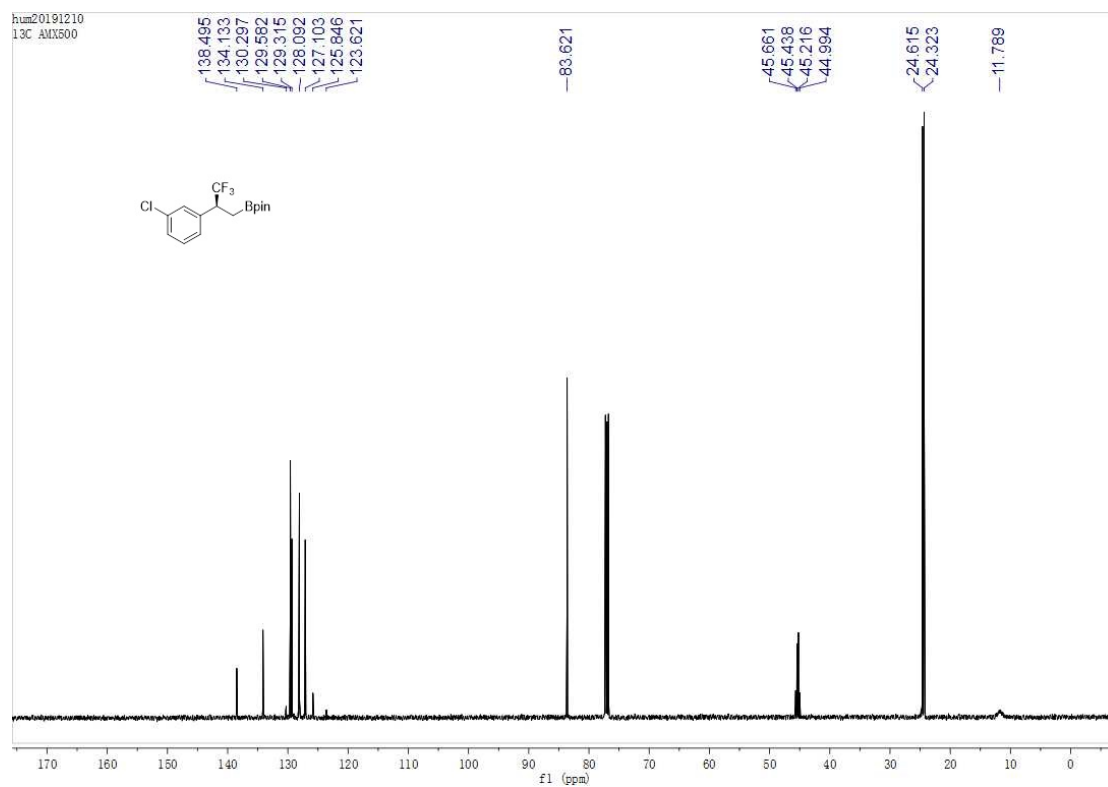
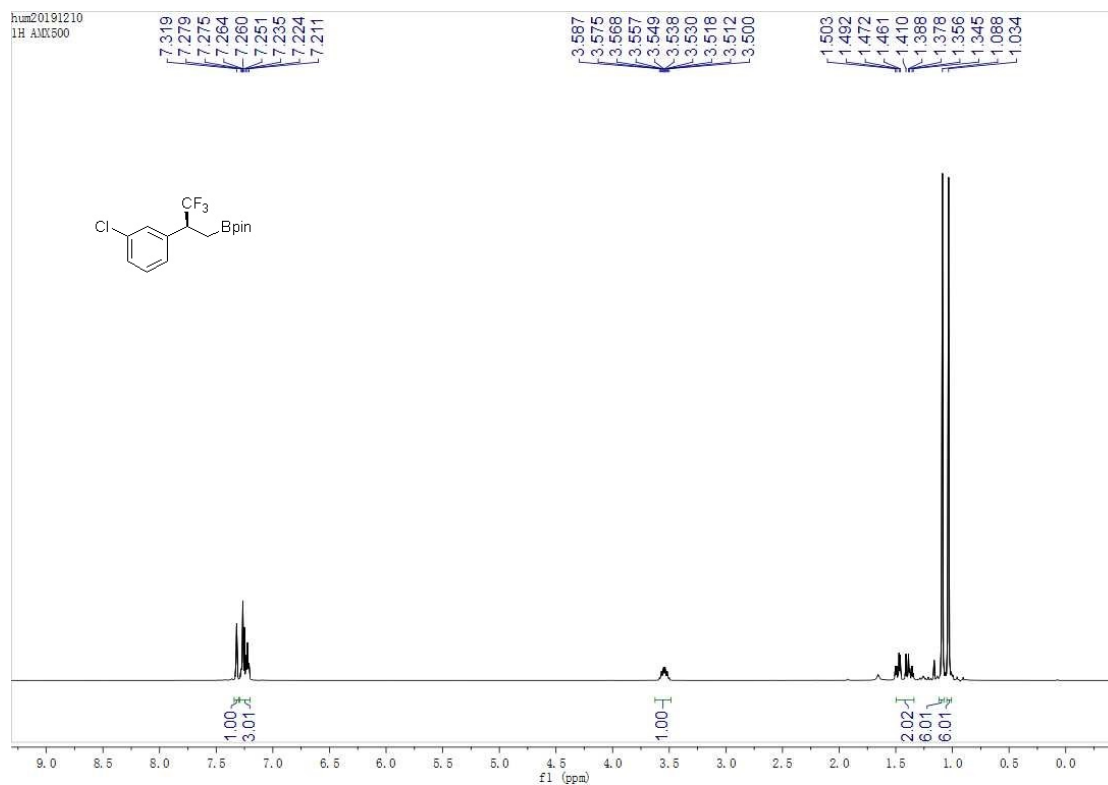


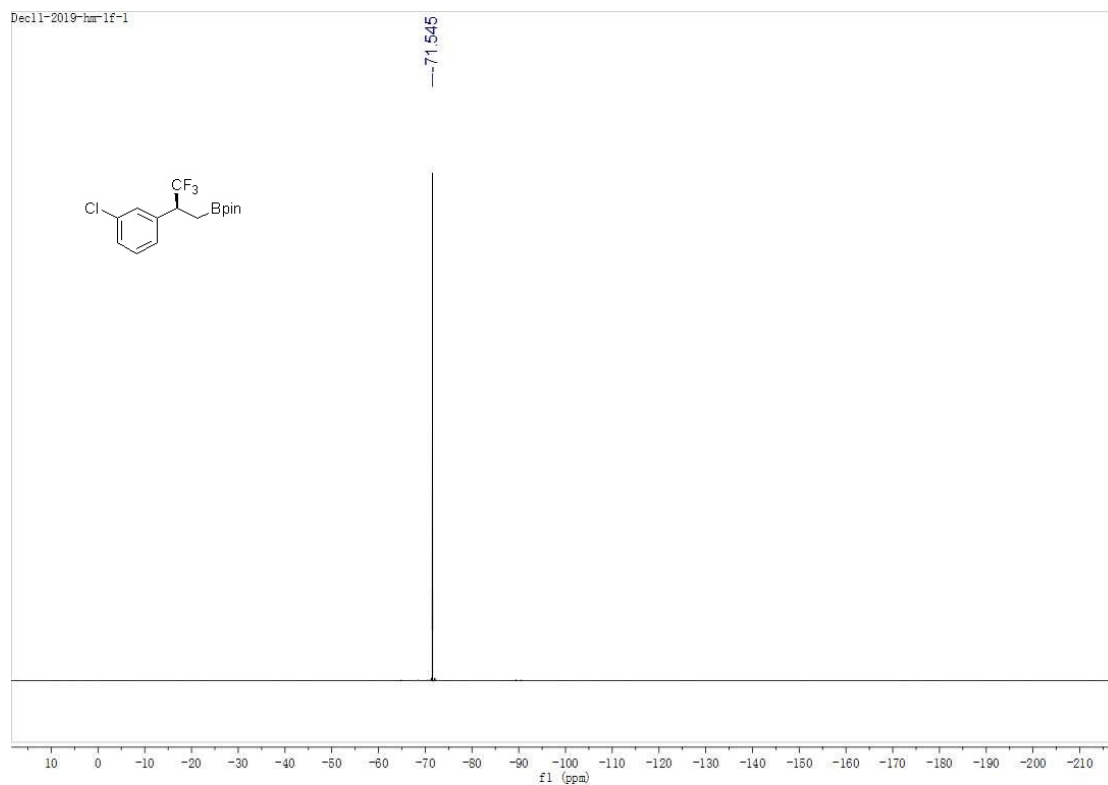
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(2-fluorophenyl)propyl)-1,3,2-dioxaborolane (4n):



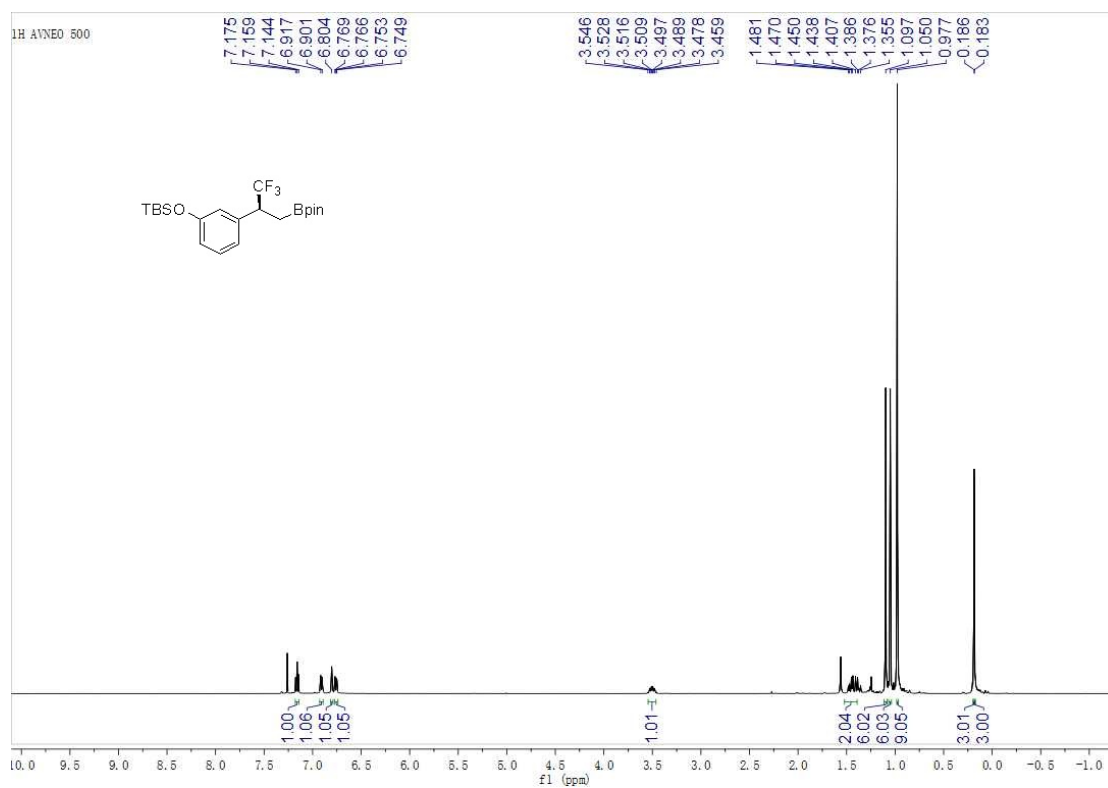


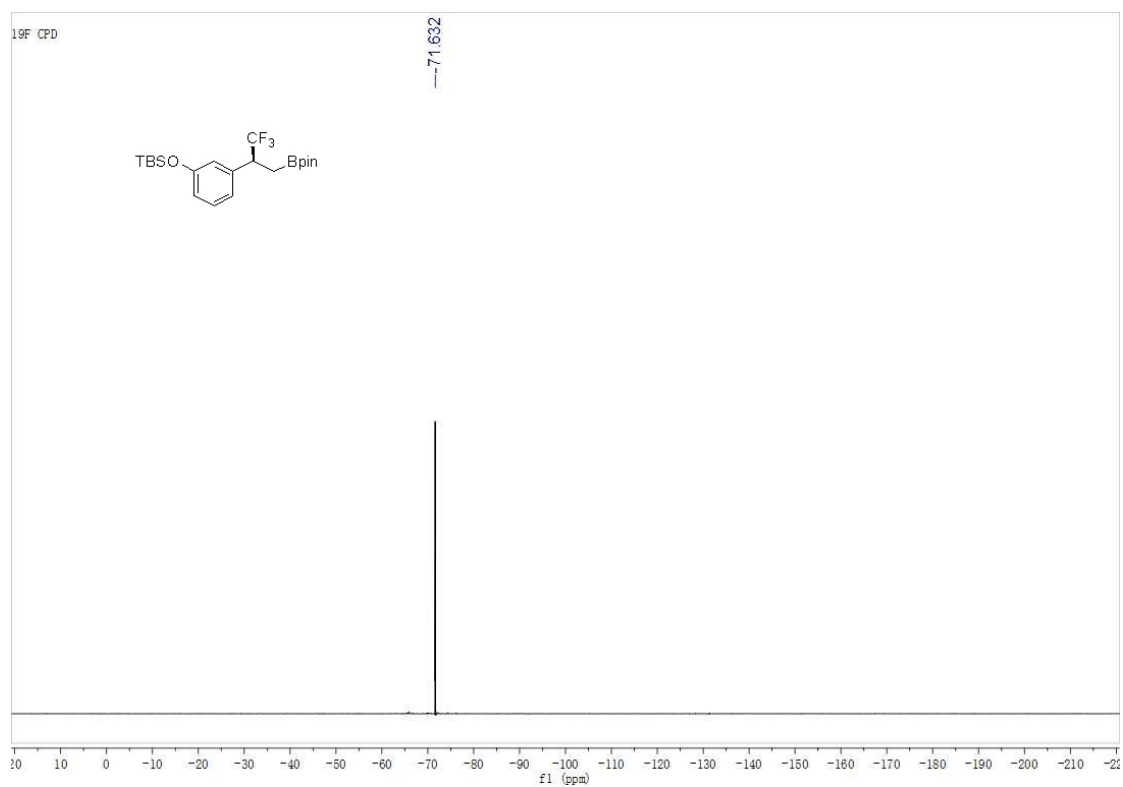
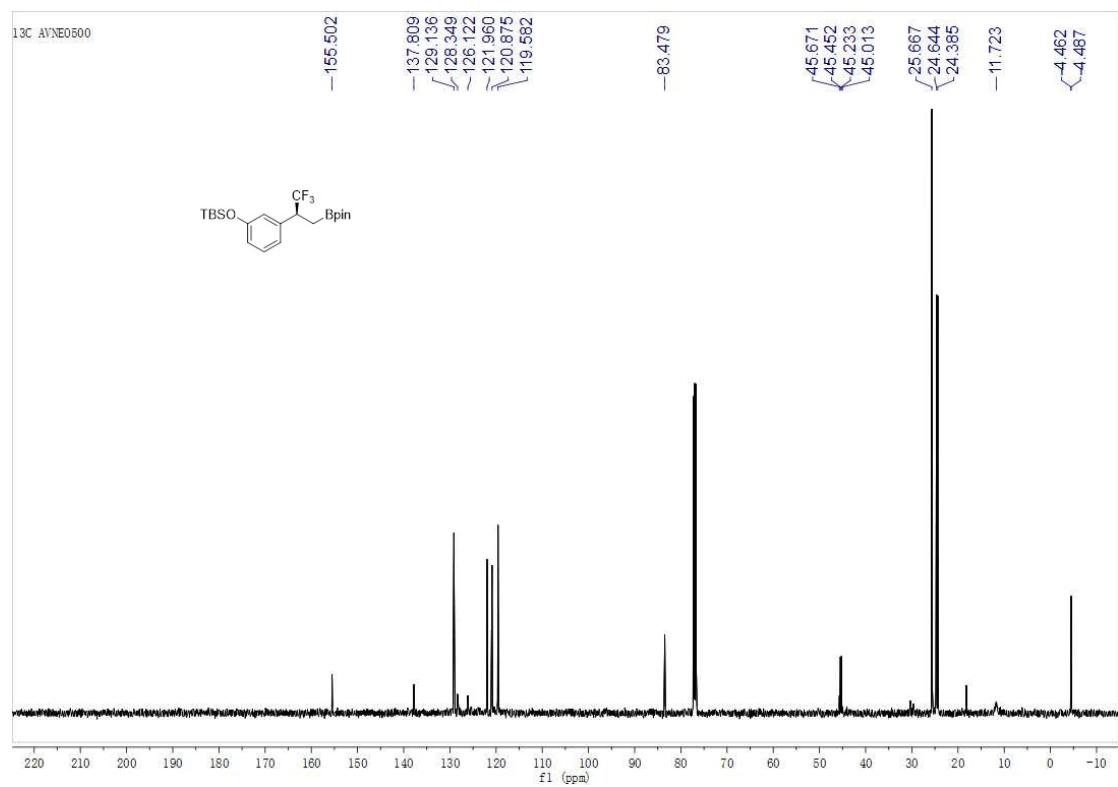
(S)-2-(2-(3-chlorophenyl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4o):

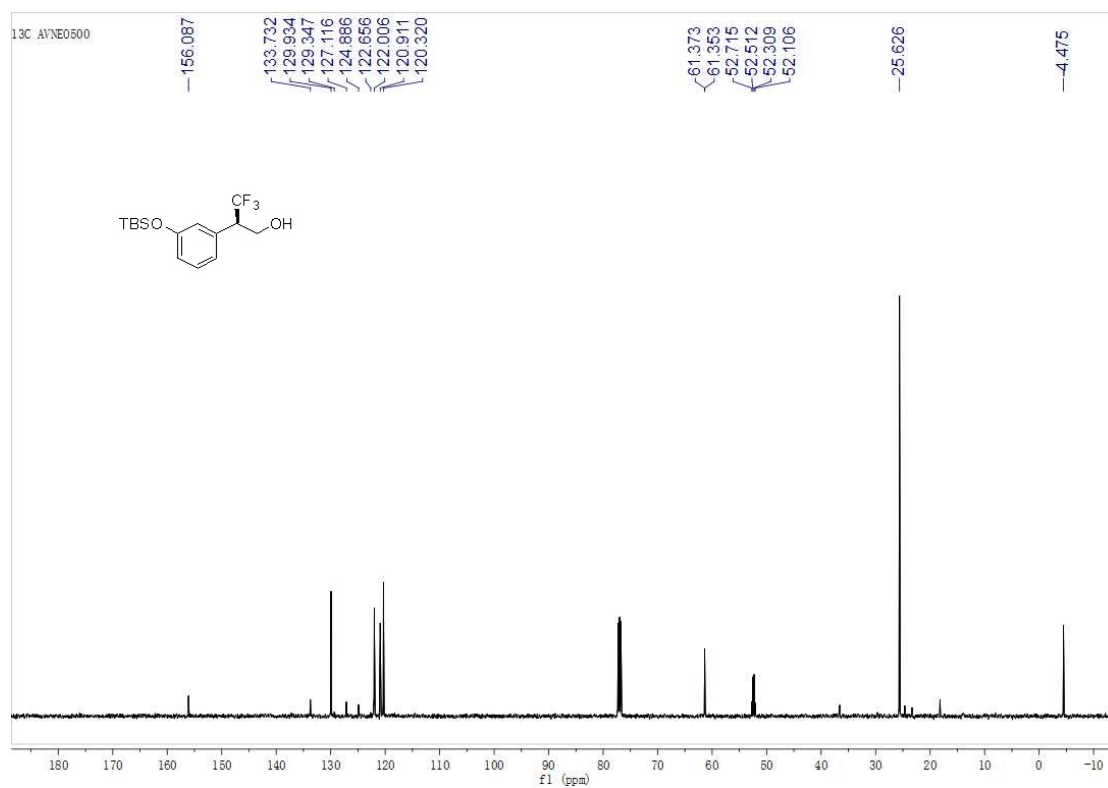
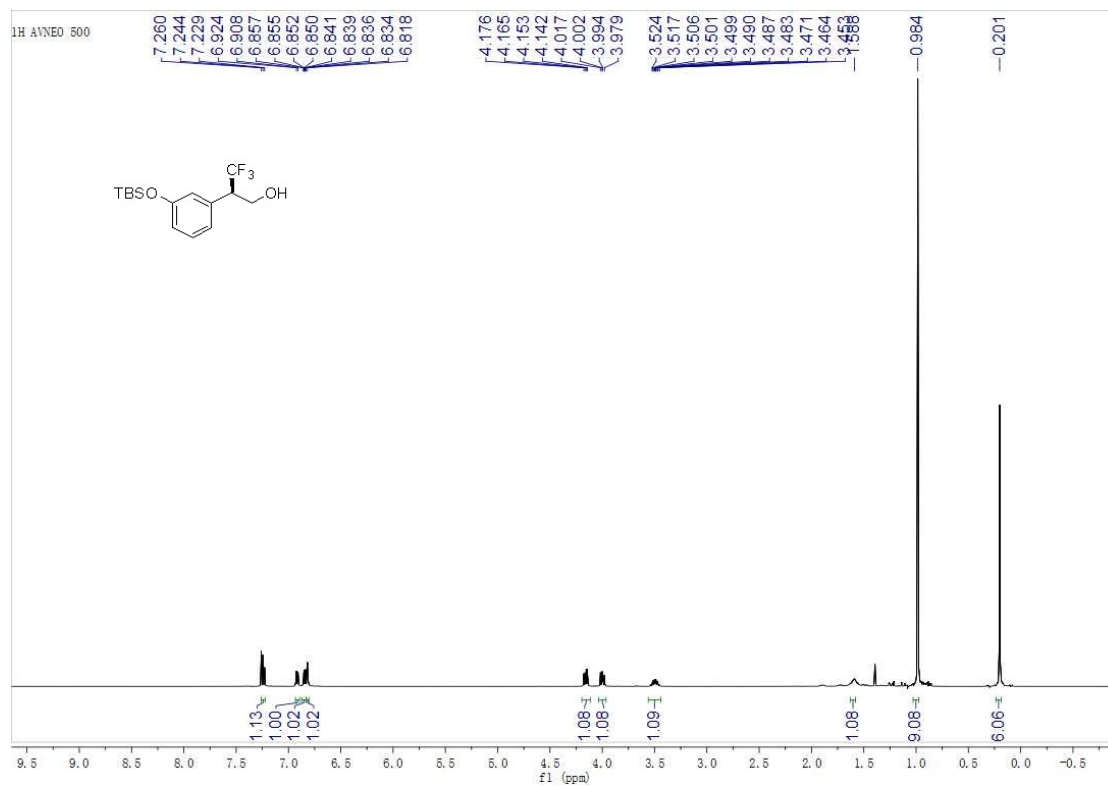


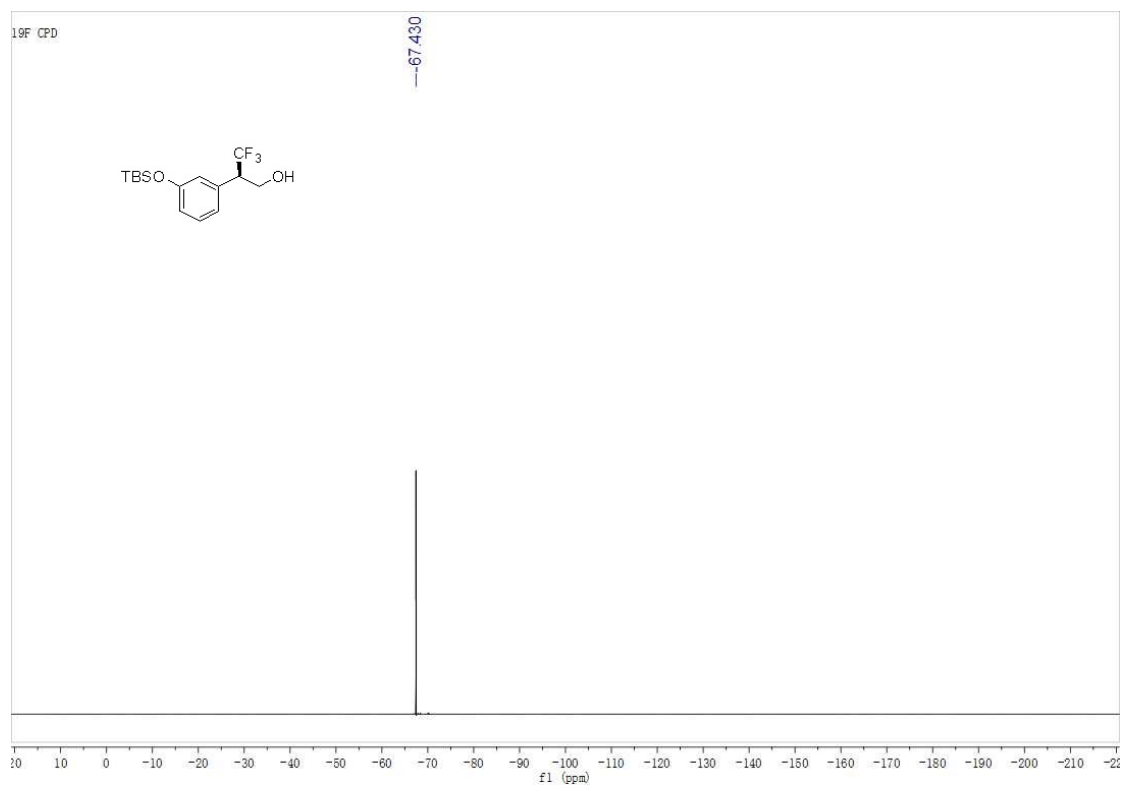


(S)-tert-butyl(2-(4-chlorophenyl)propan-2-yl)boronic acid pinacol ester
n-2-yl)propan-2-yl)phenoxy)silane (4p):



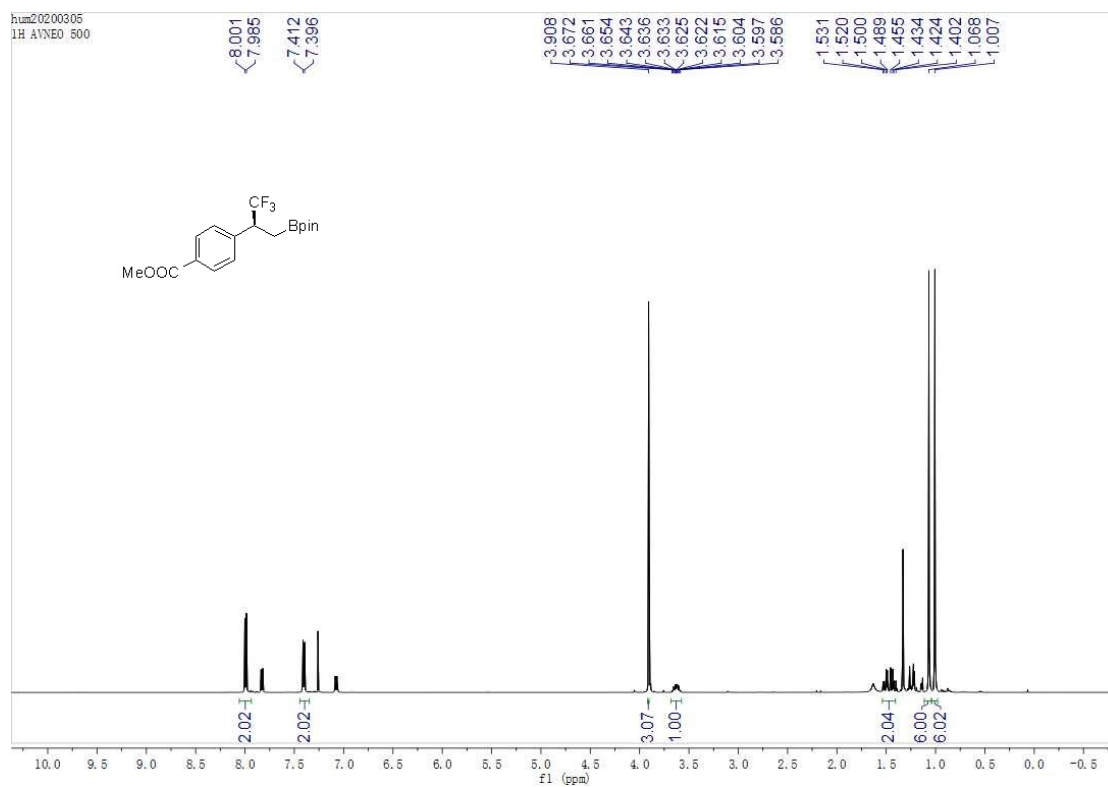


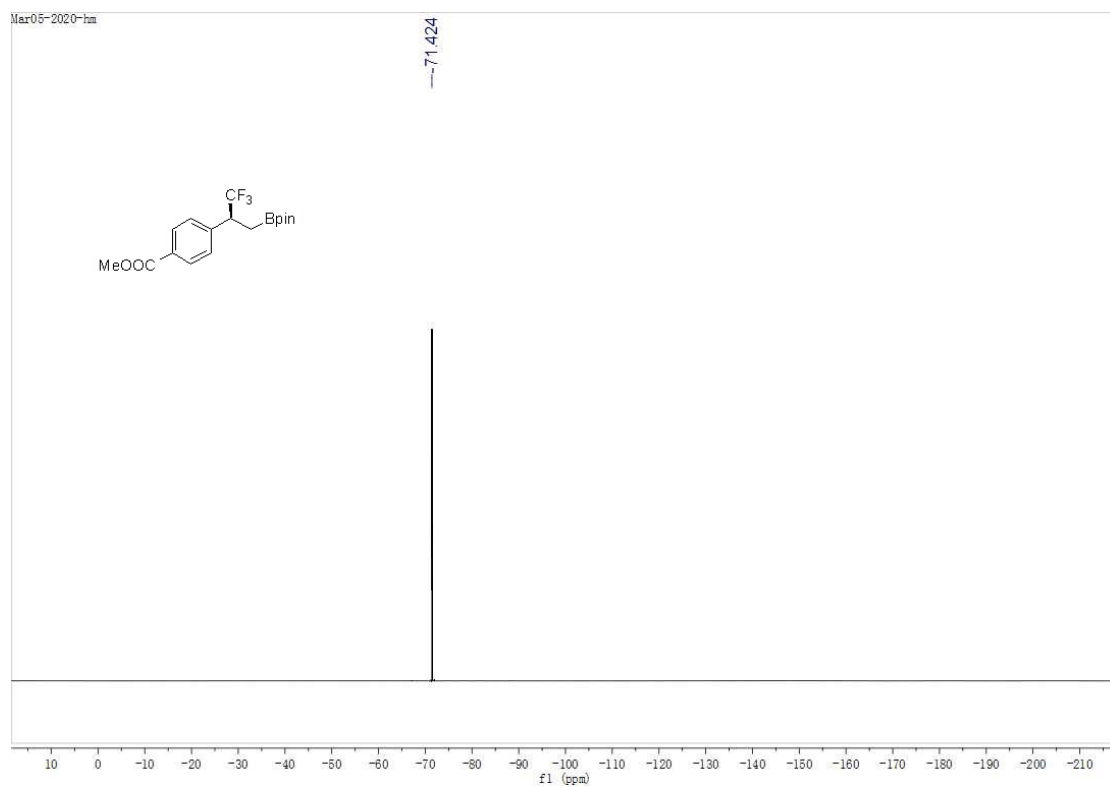
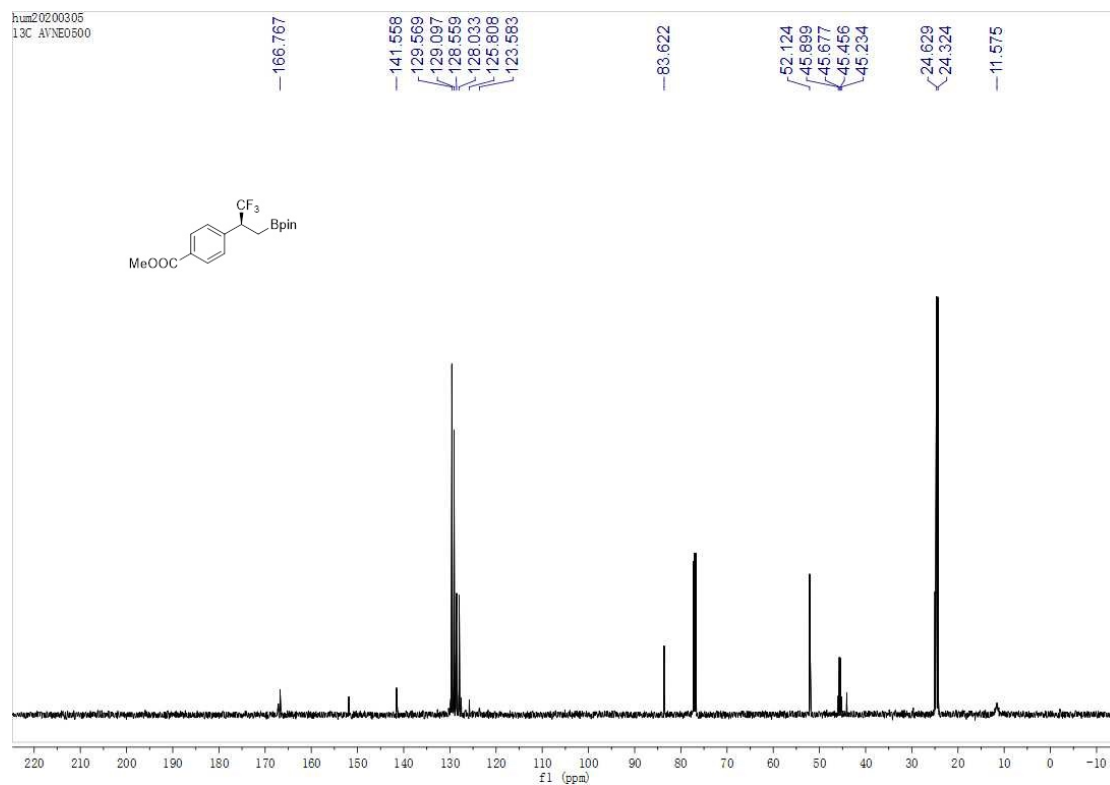
(R)-2-(3-((tert-butyldimethylsilyloxy)phenyl)-3,3,3-trifluoropropan-1-ol (4p')



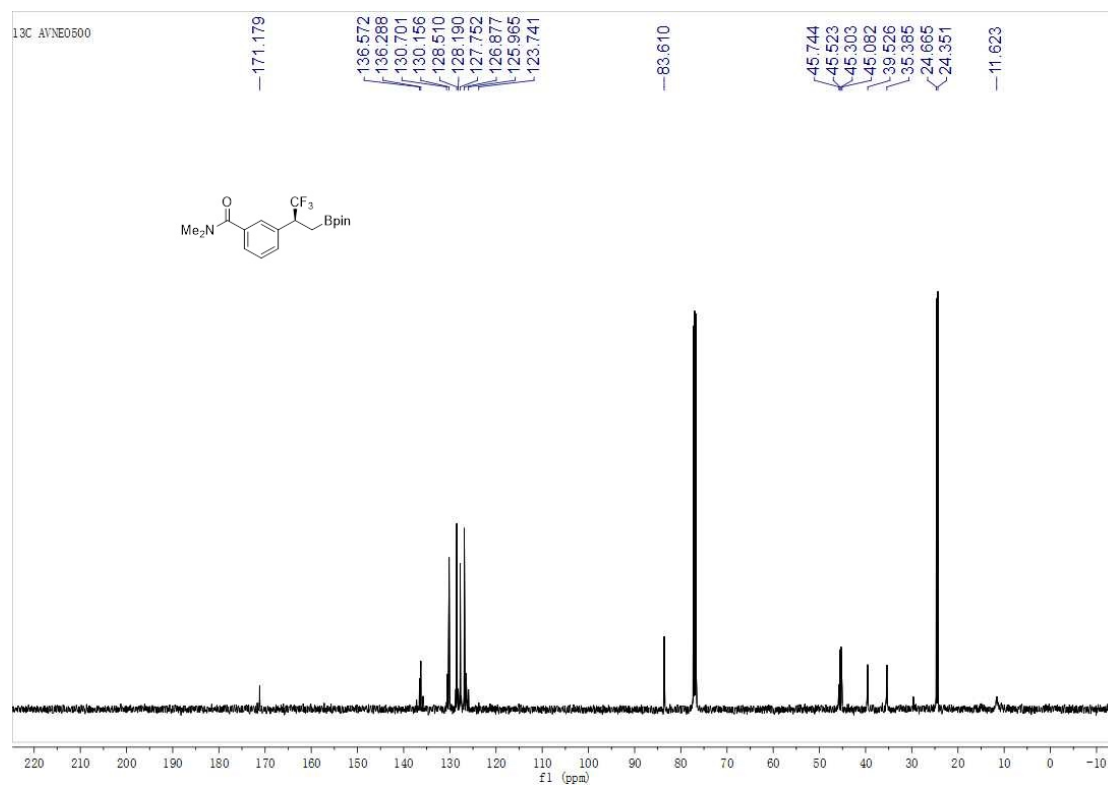
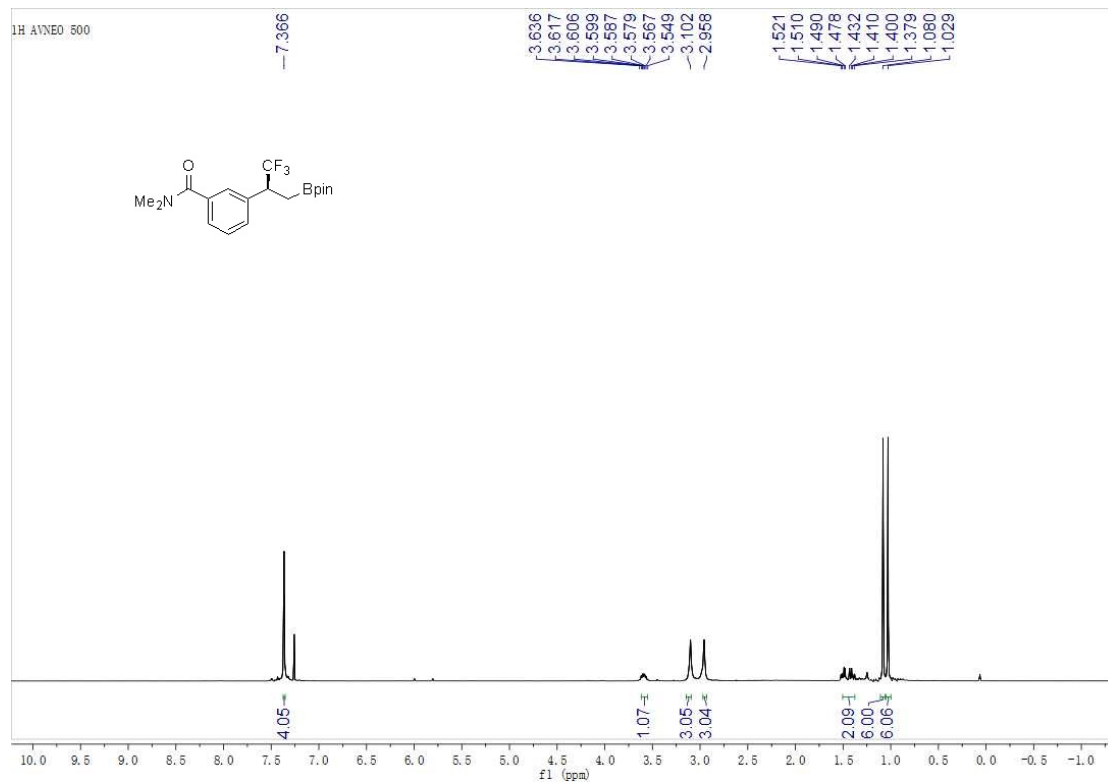
Methyl

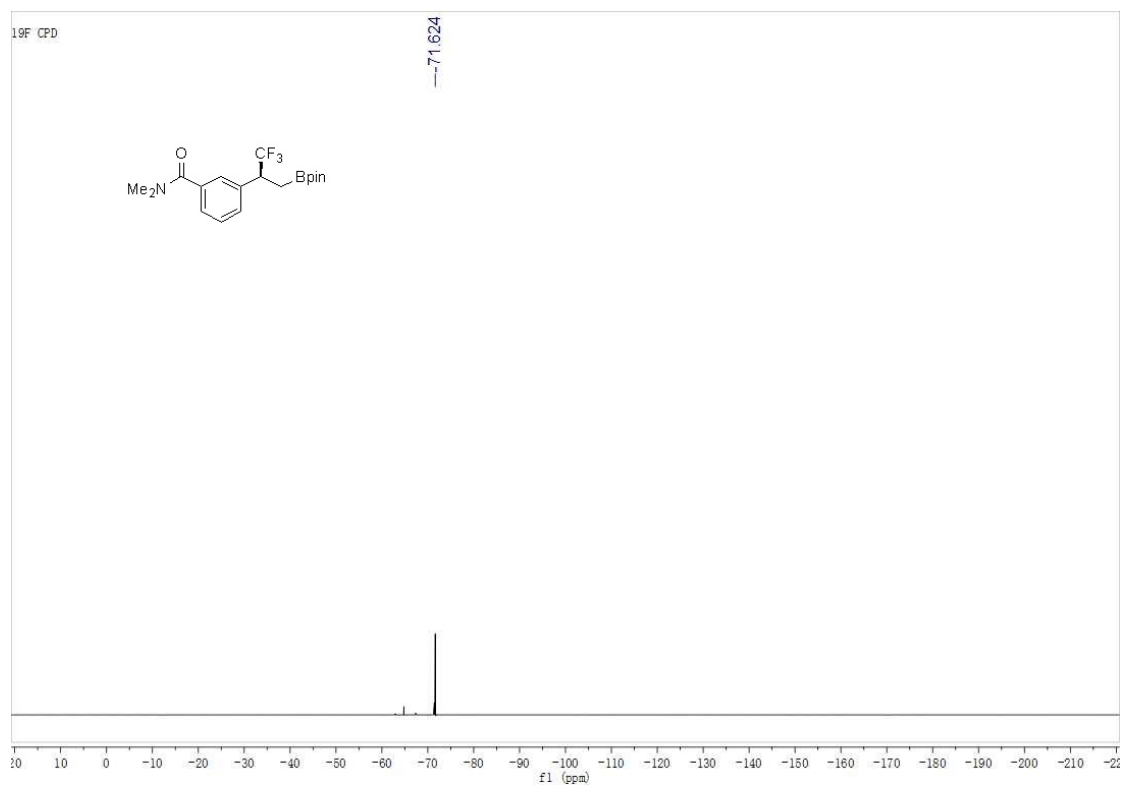
(S)-4-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzoate (4q):



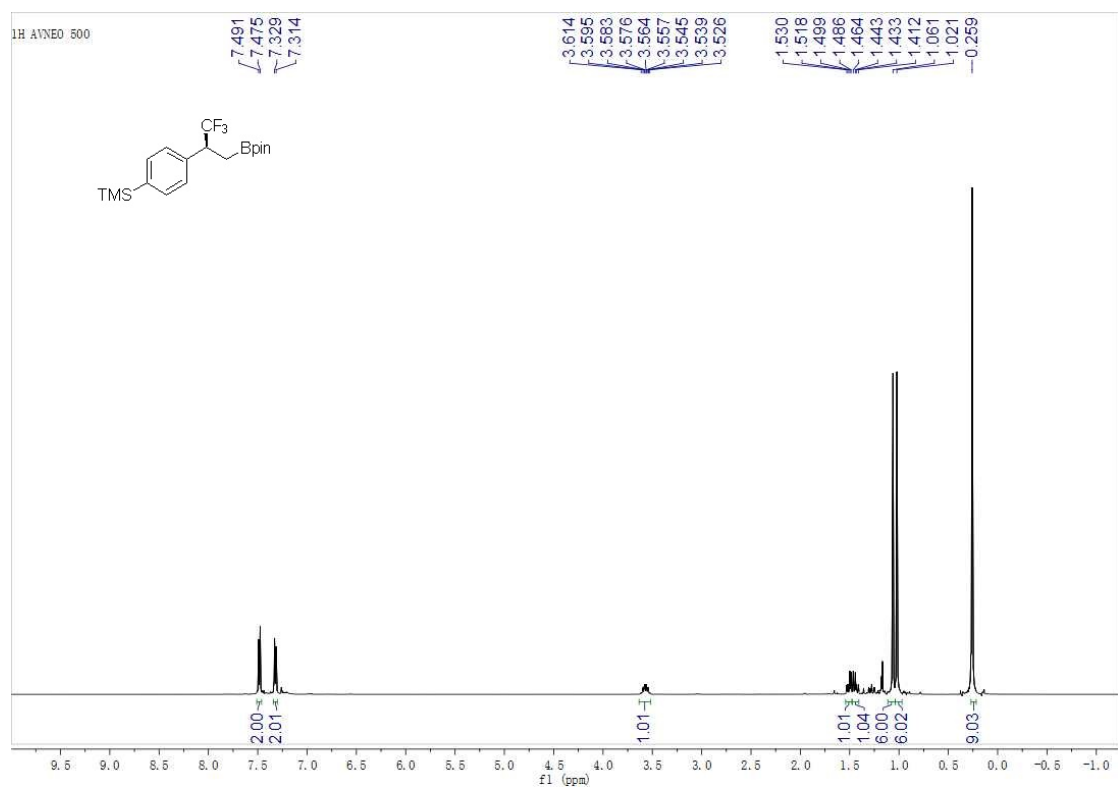


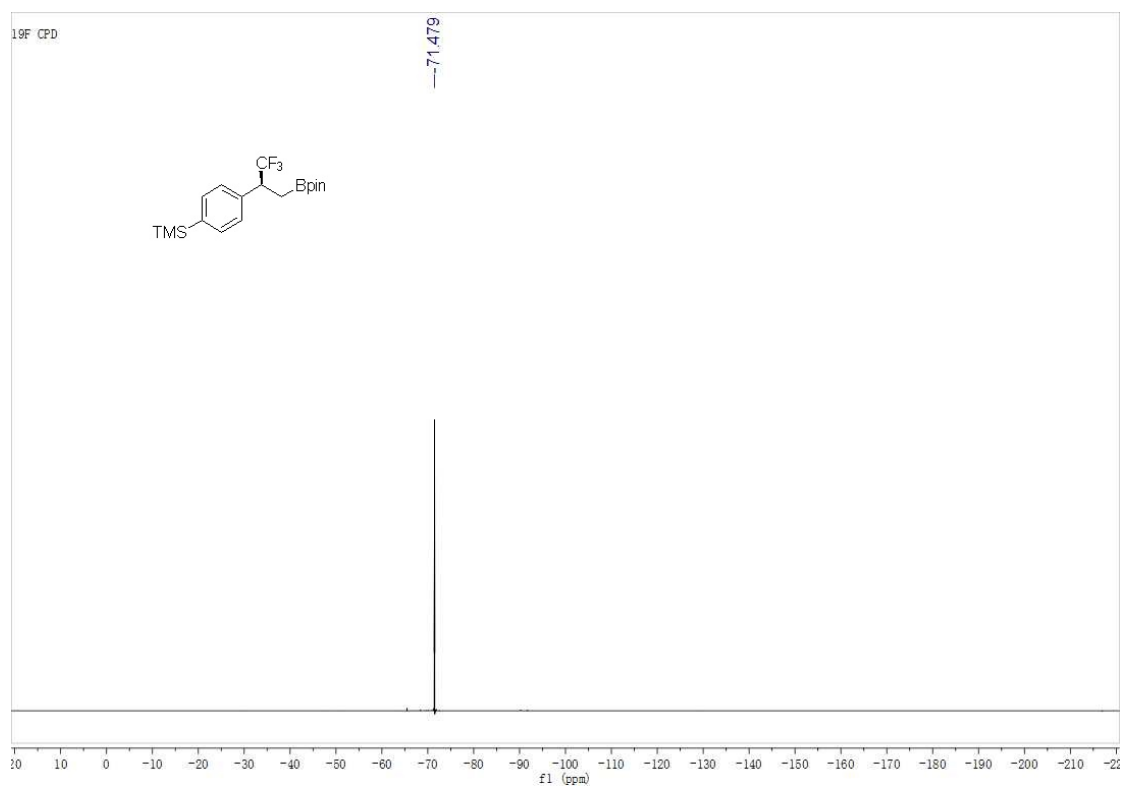
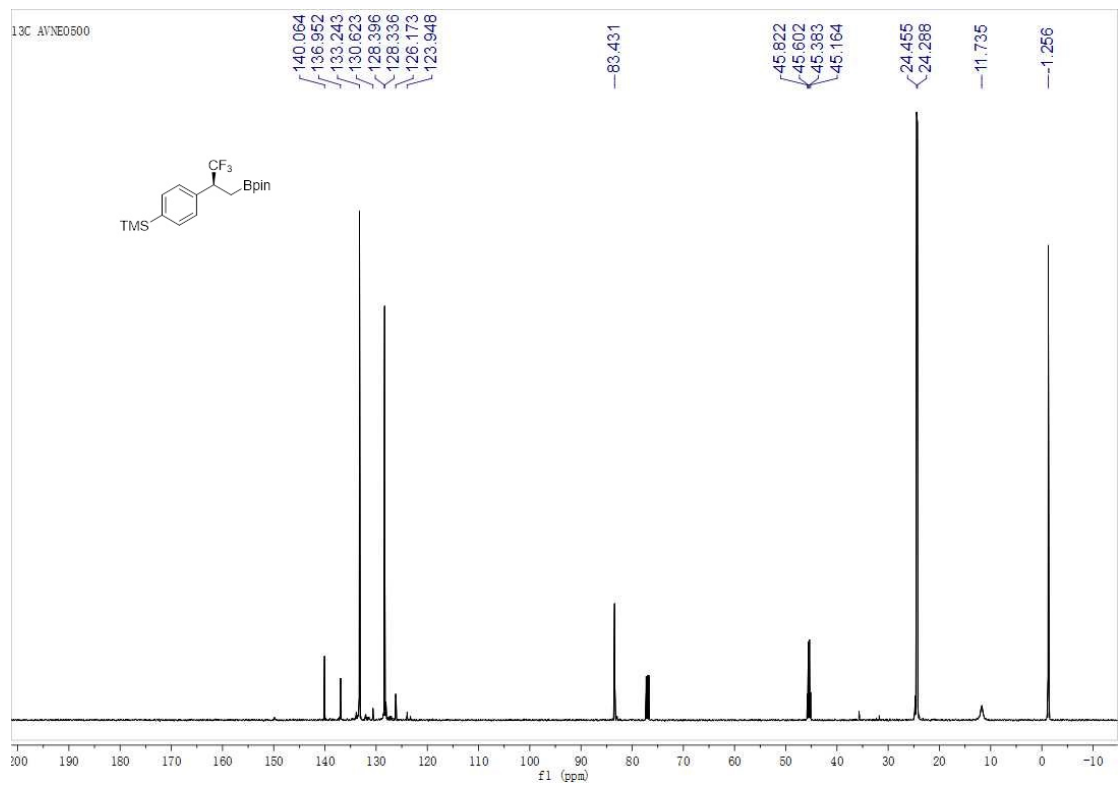
(S)-N,N-dimethyl-3-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzamide (4r):

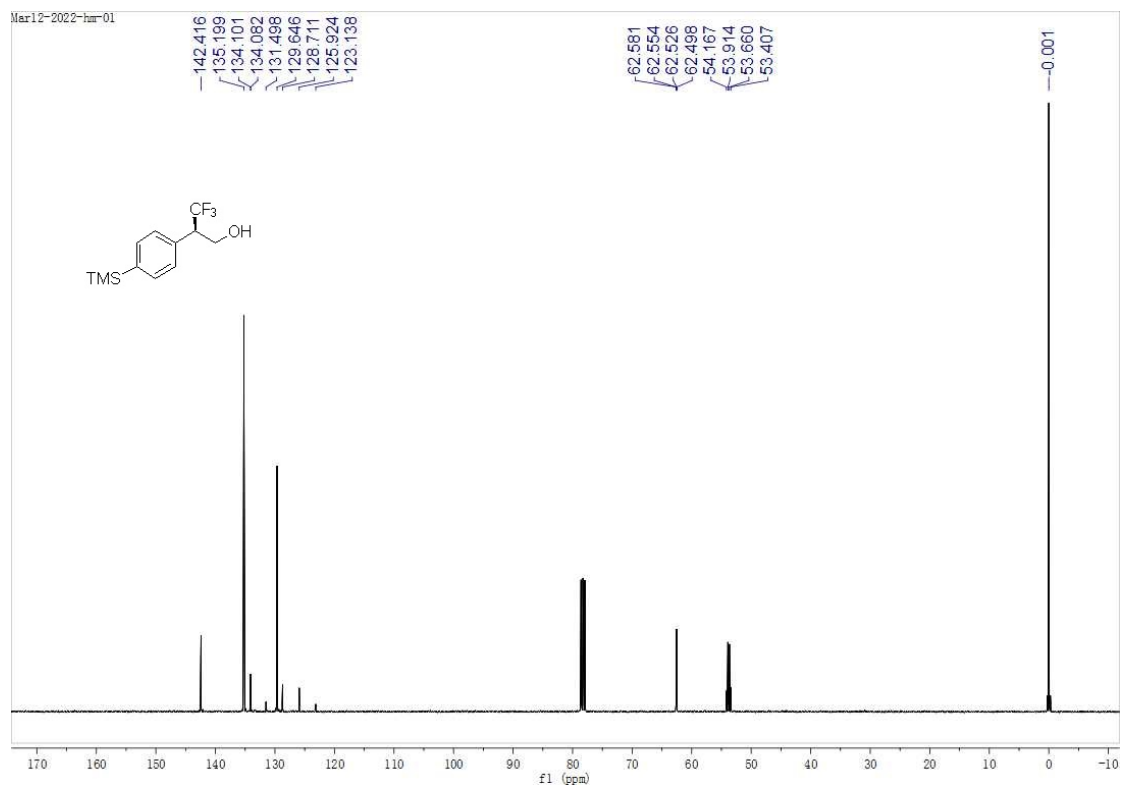
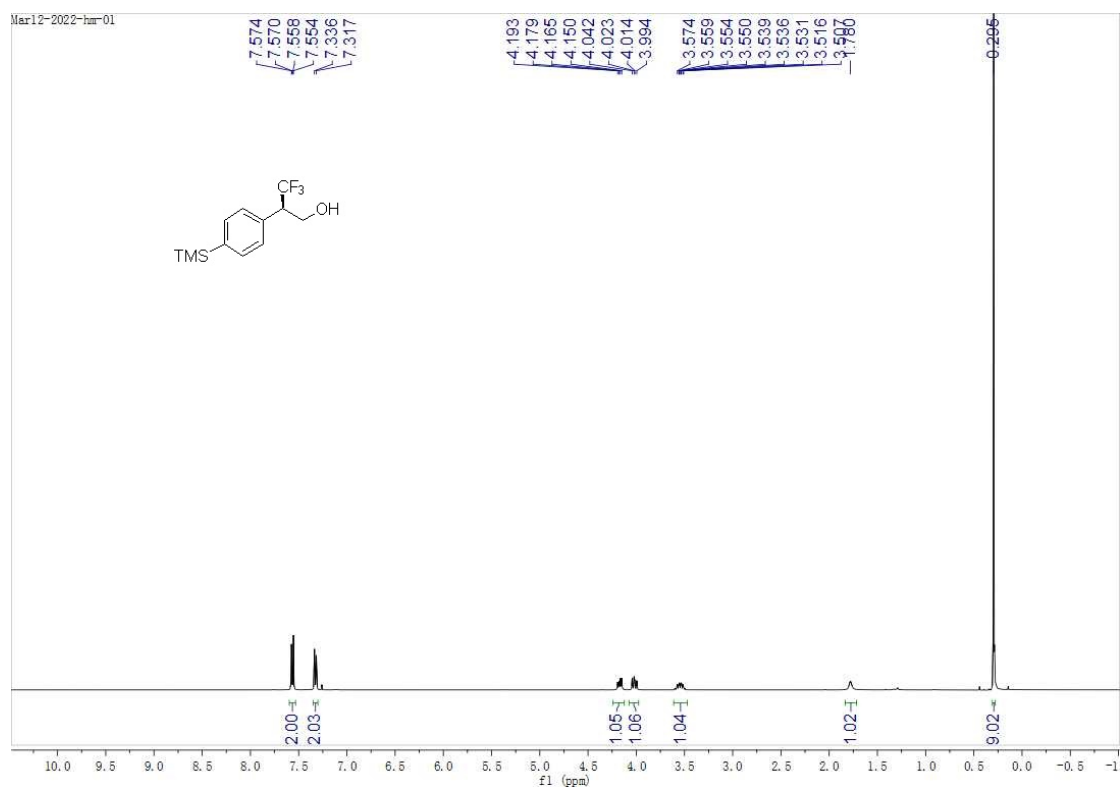


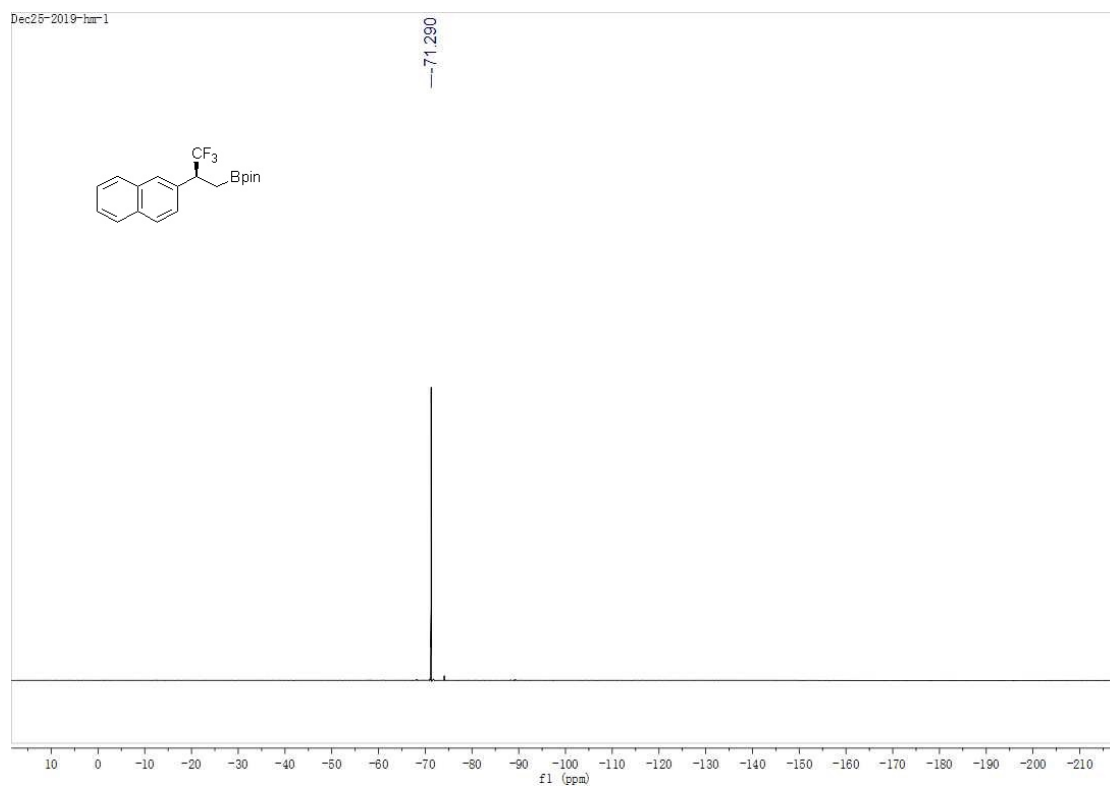
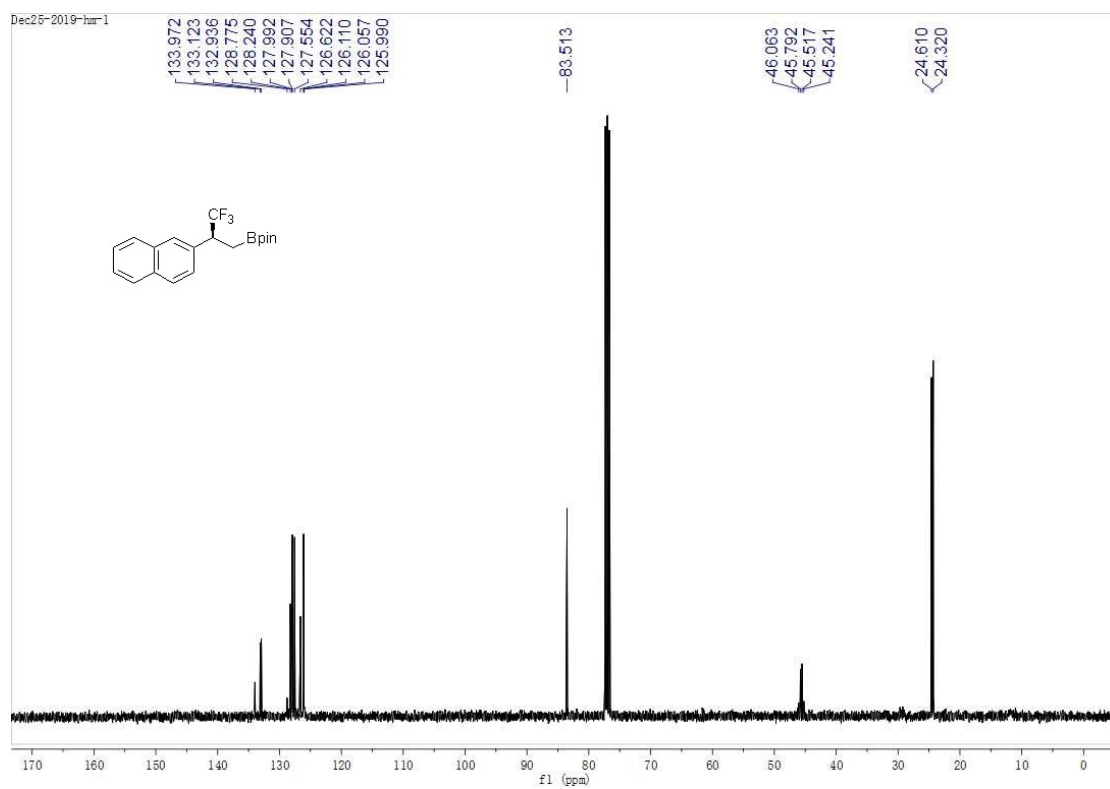


(S)-trimethyl(4-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)phenyl)silane (4s):

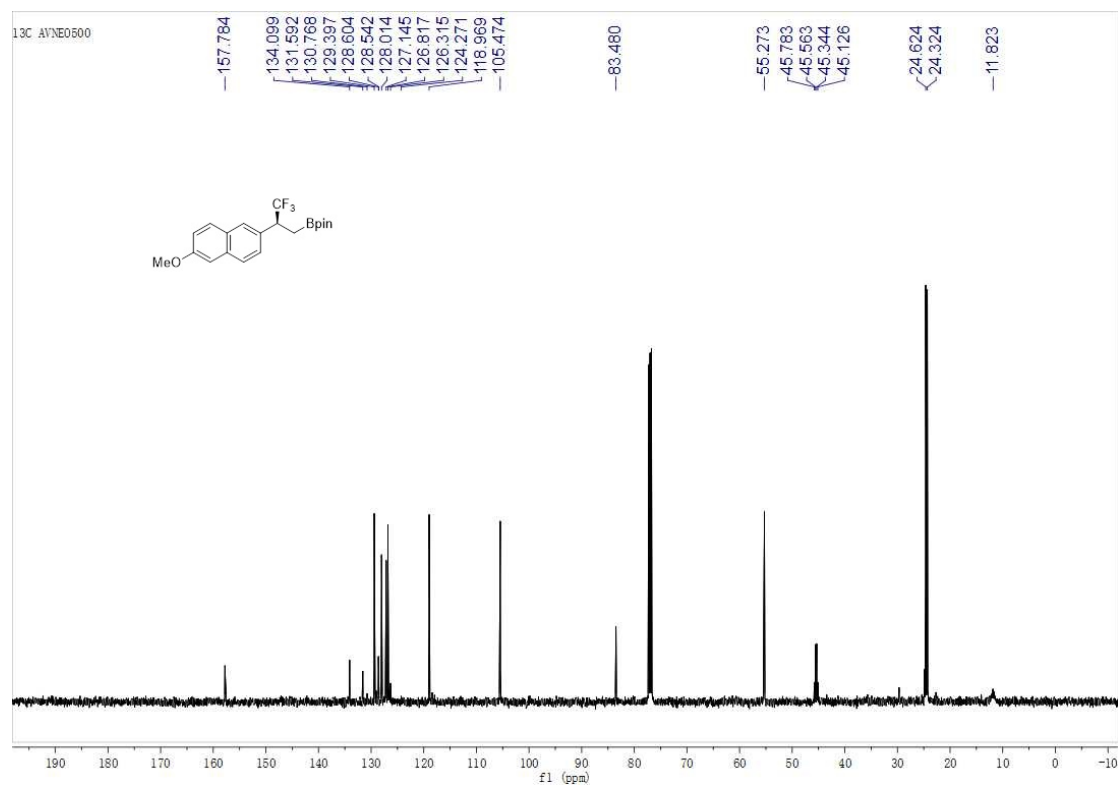
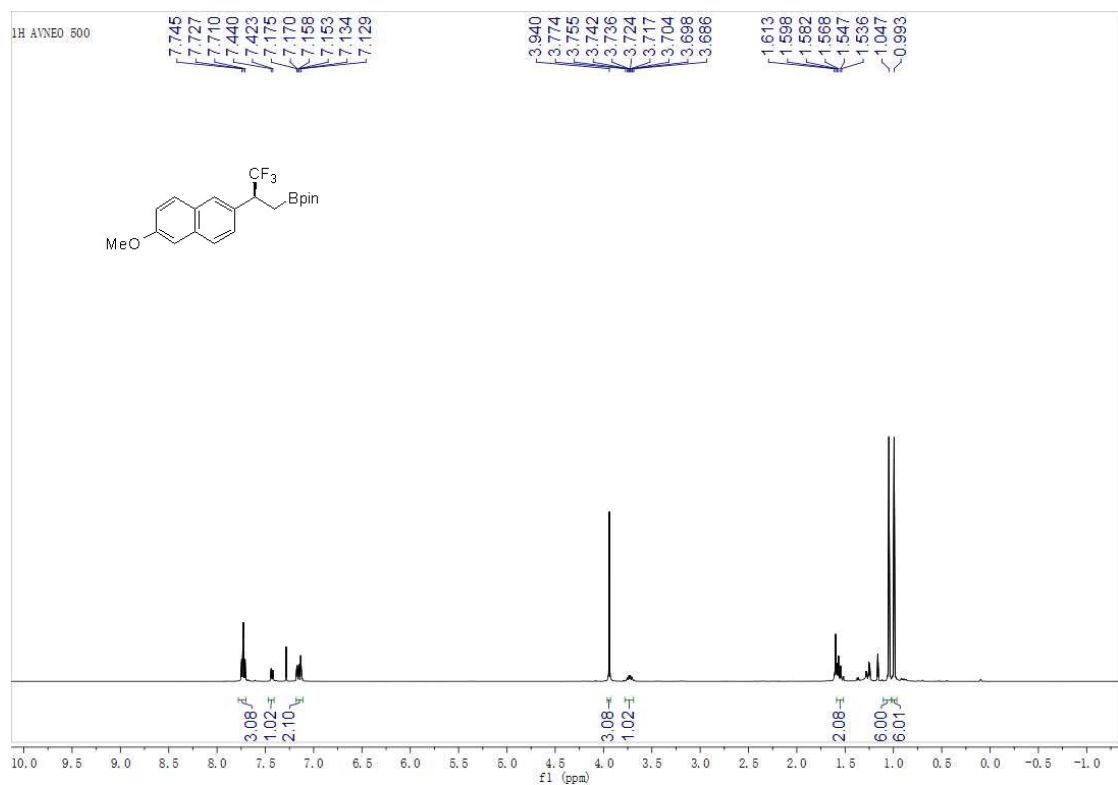


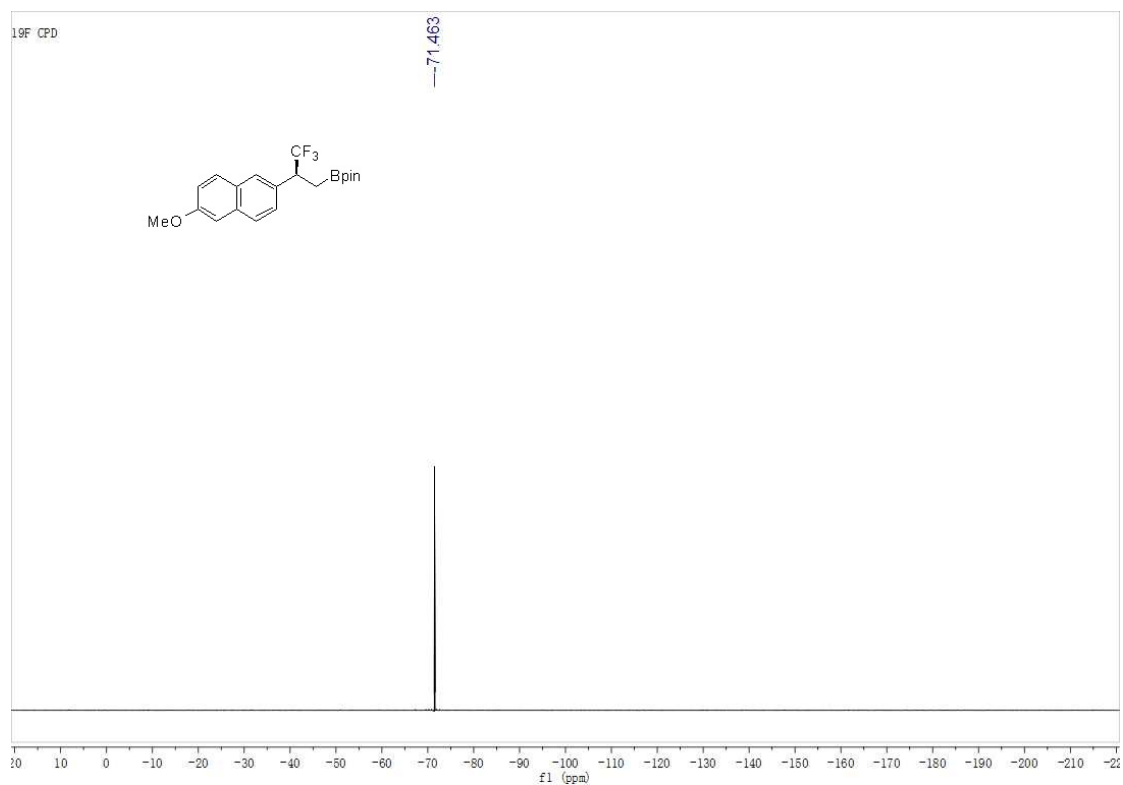


(R)-3,3,3-trifluoro-2-(4-(trimethylsilyl)phenyl)propan-1-ol (4s')

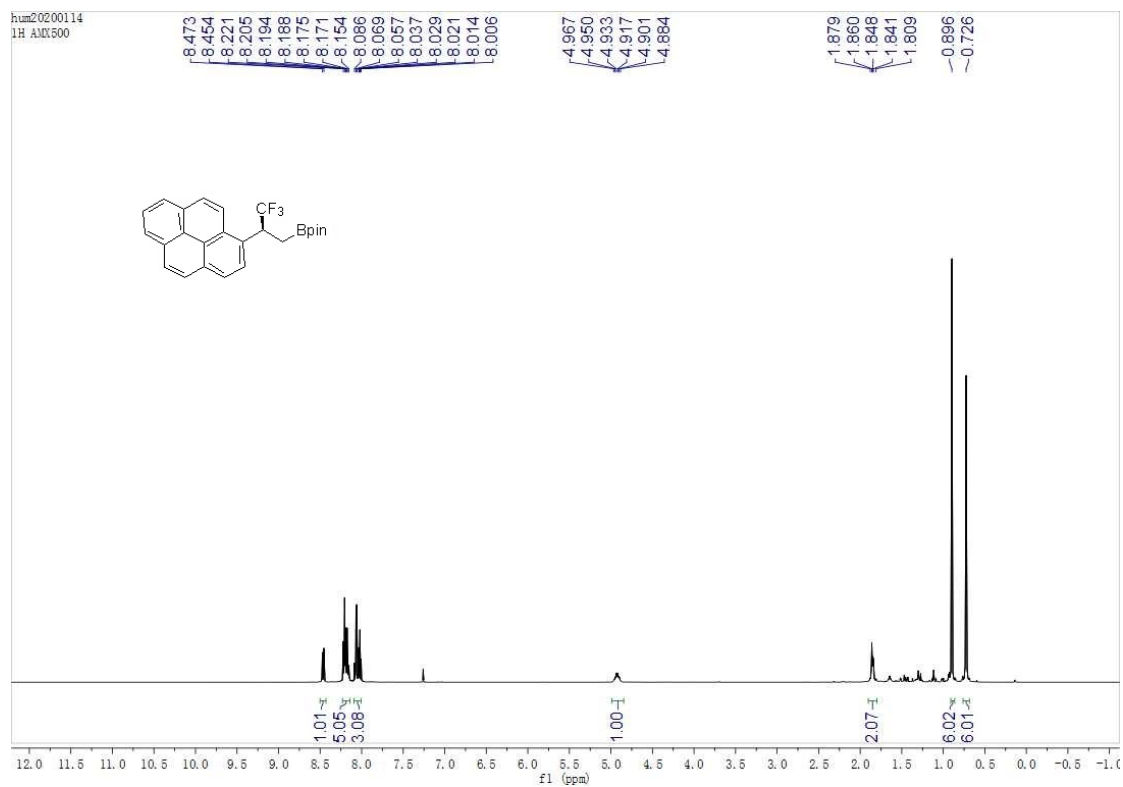


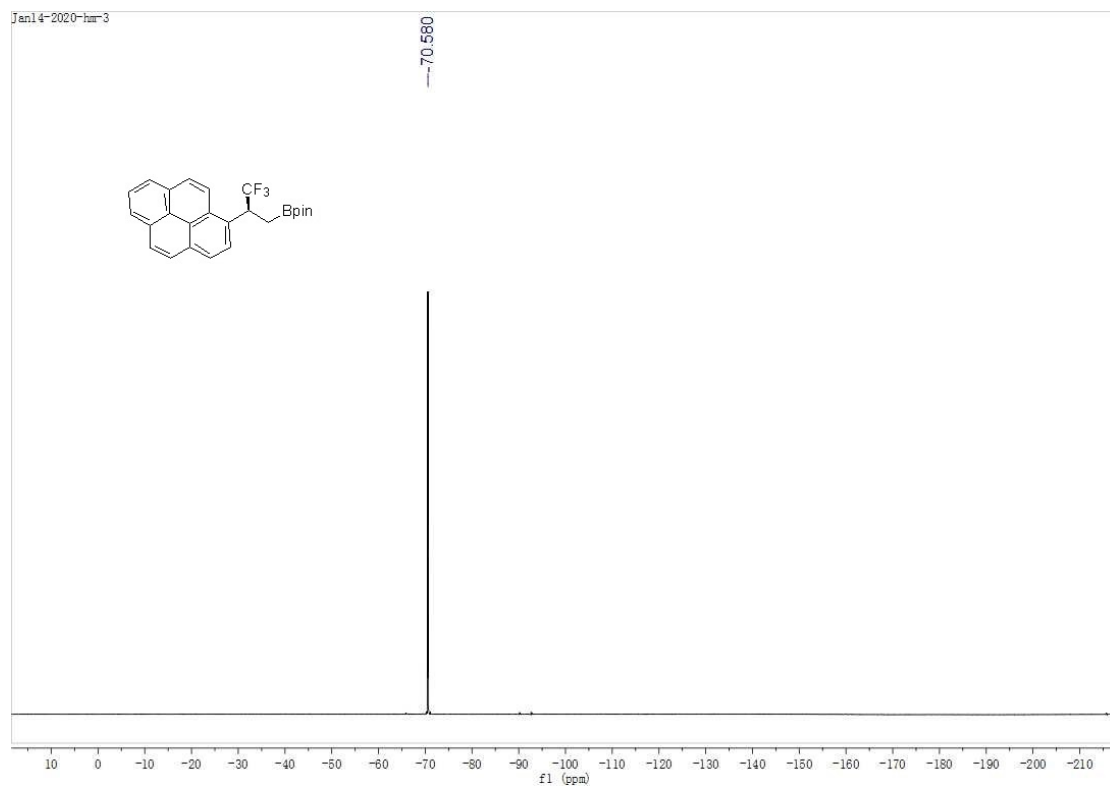
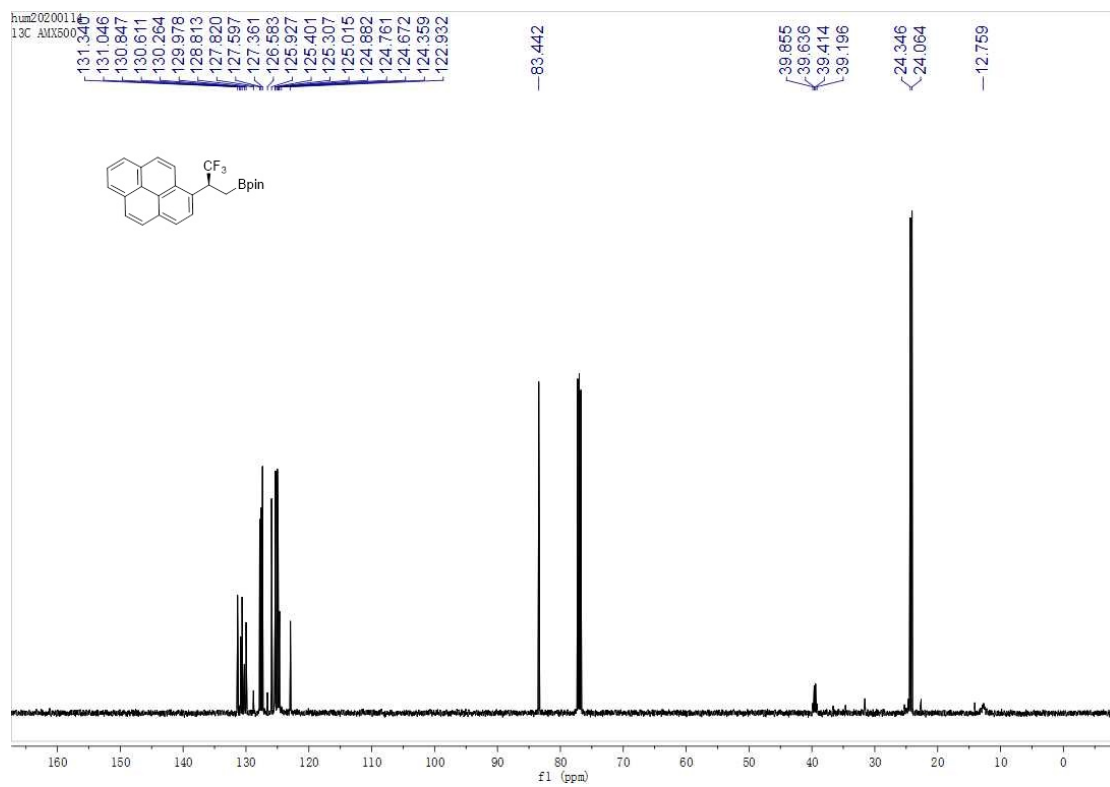
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(6-methoxynaphthalen-2-yl)propyl)-1,3,2-dioxaborolane (4u):



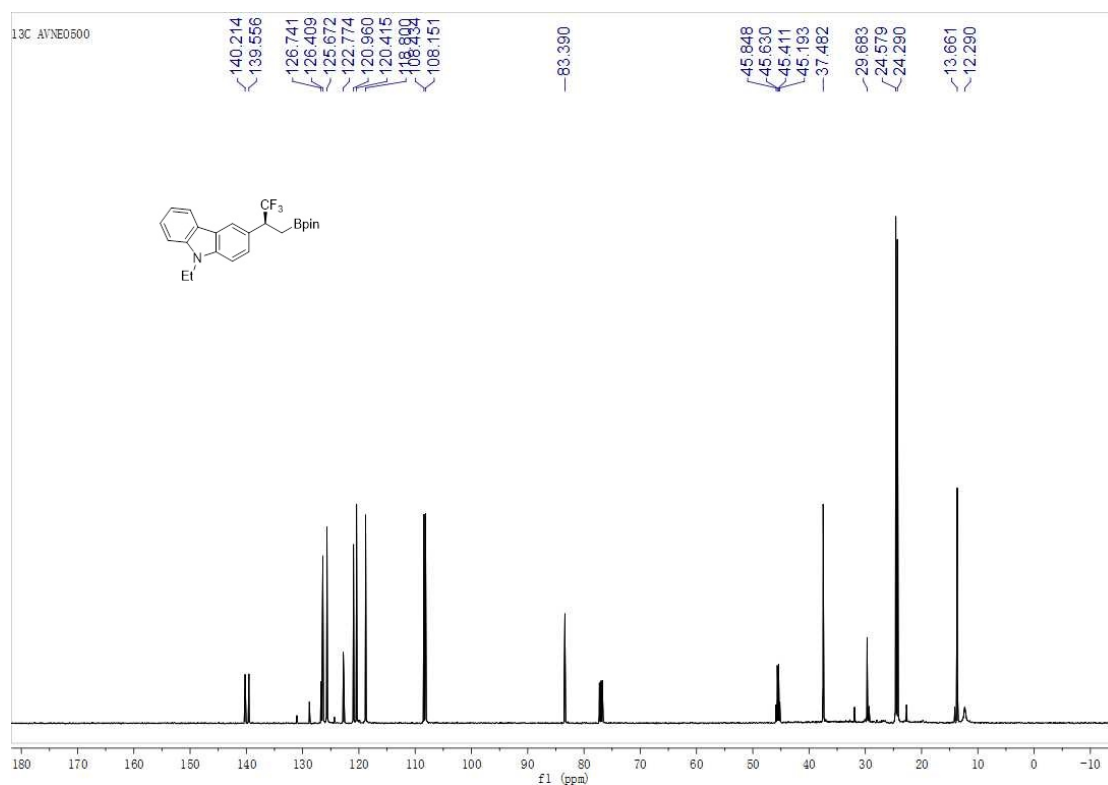
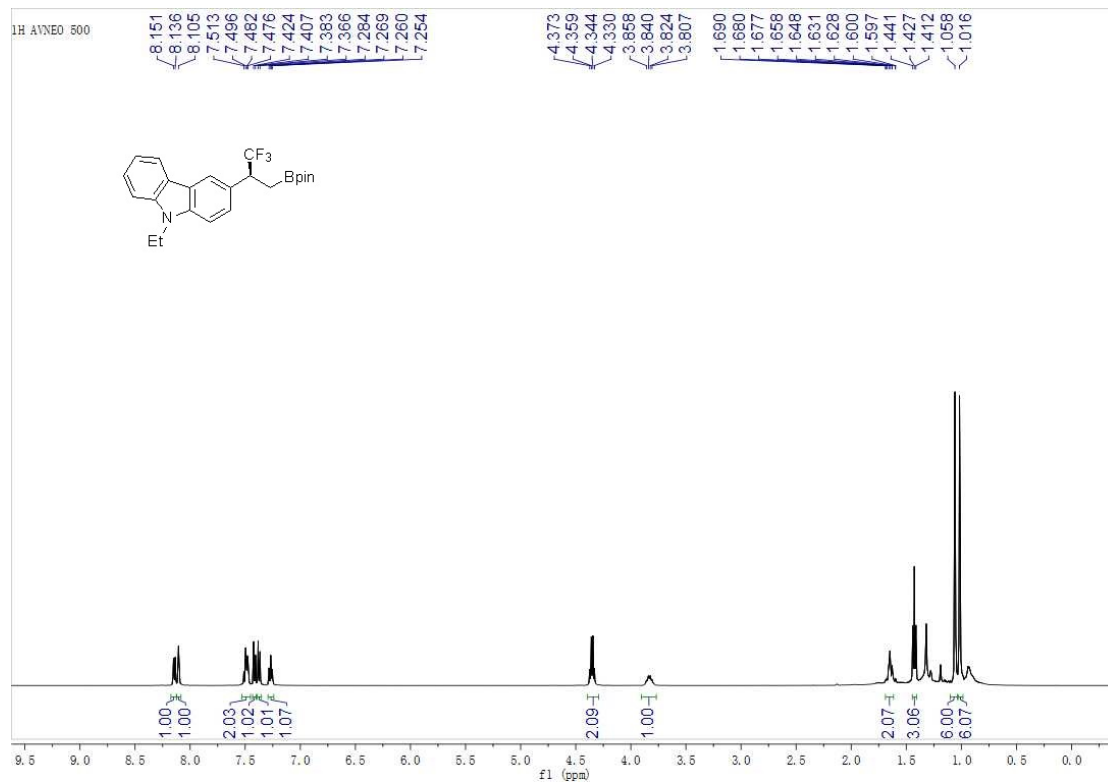


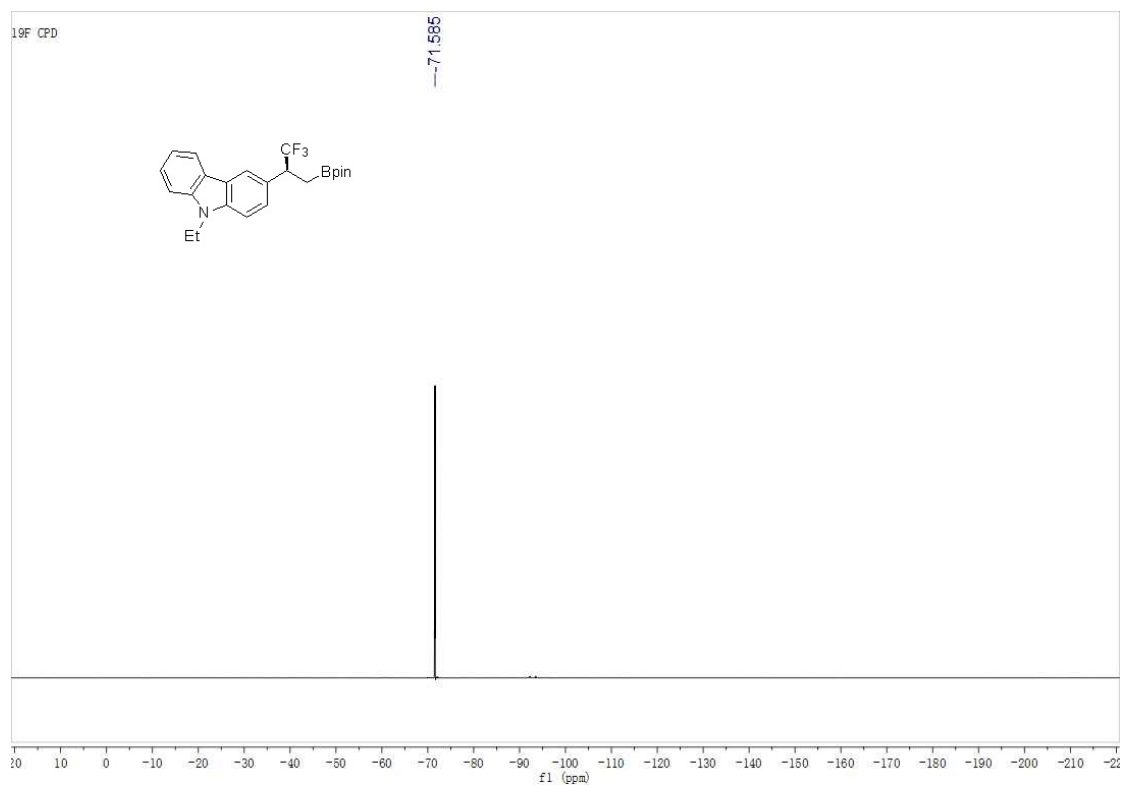
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(pyren-1-yl)propyl)-1,3,2-dioxaborolane (4v):



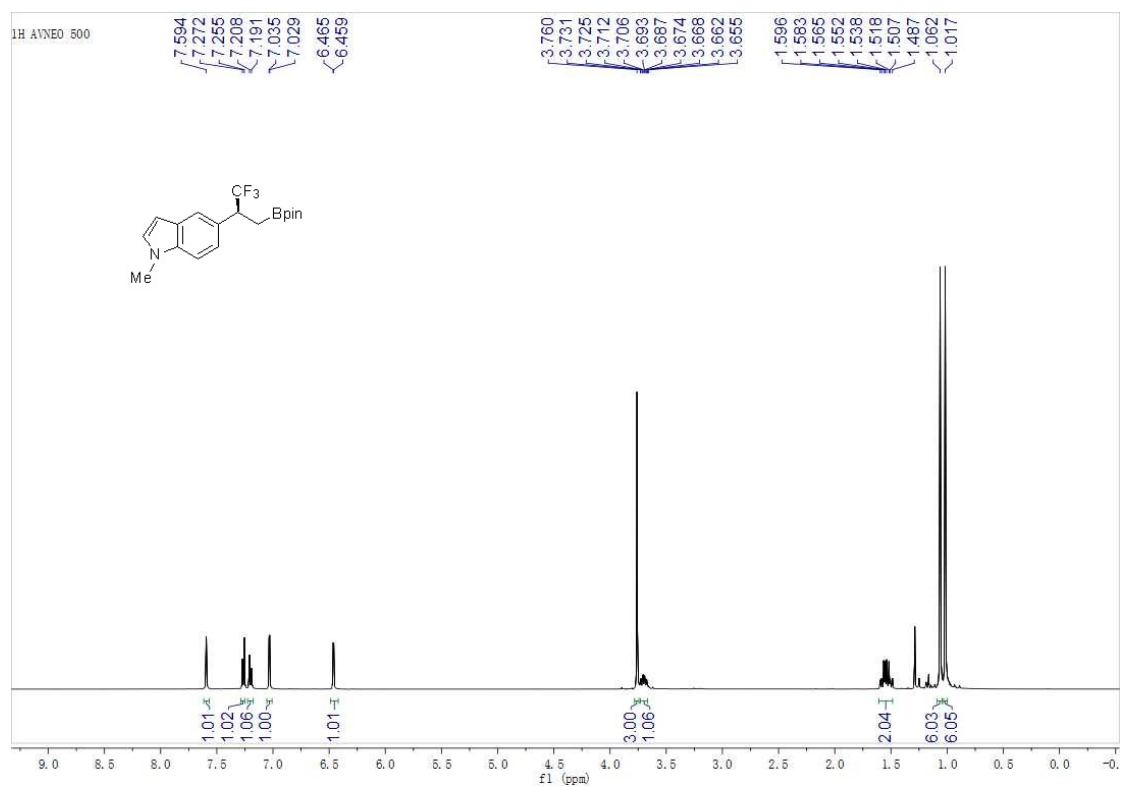


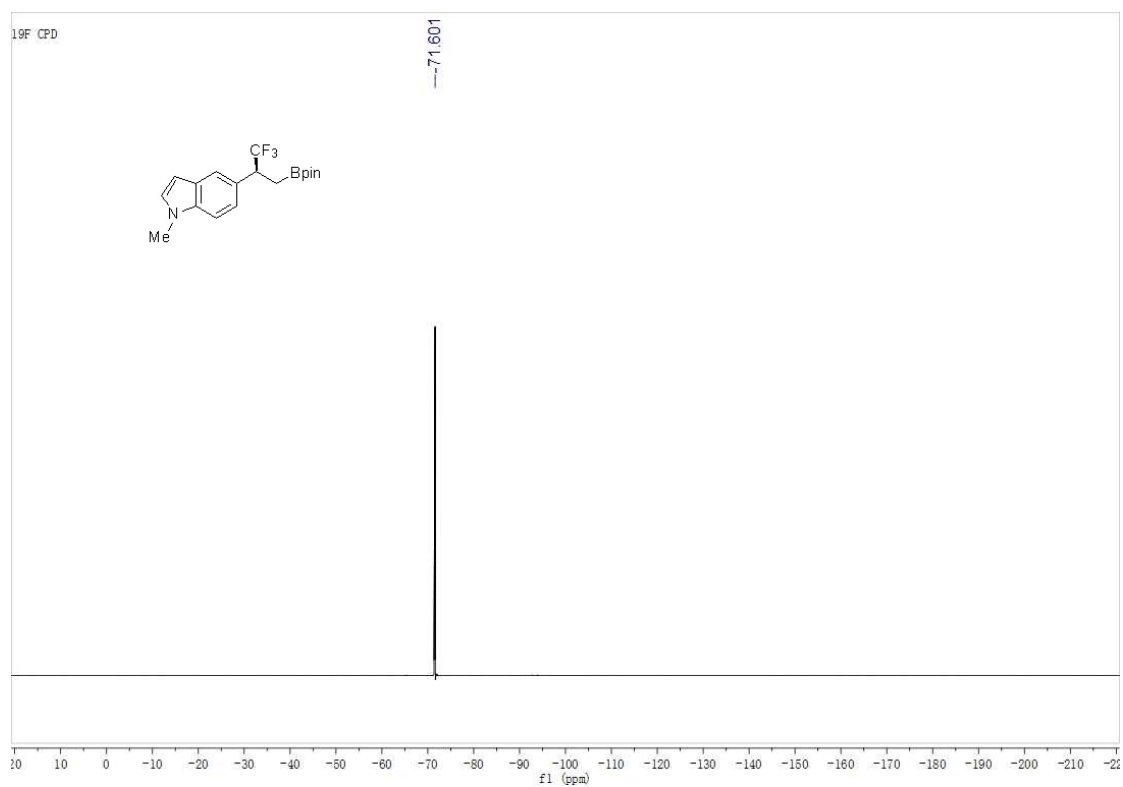
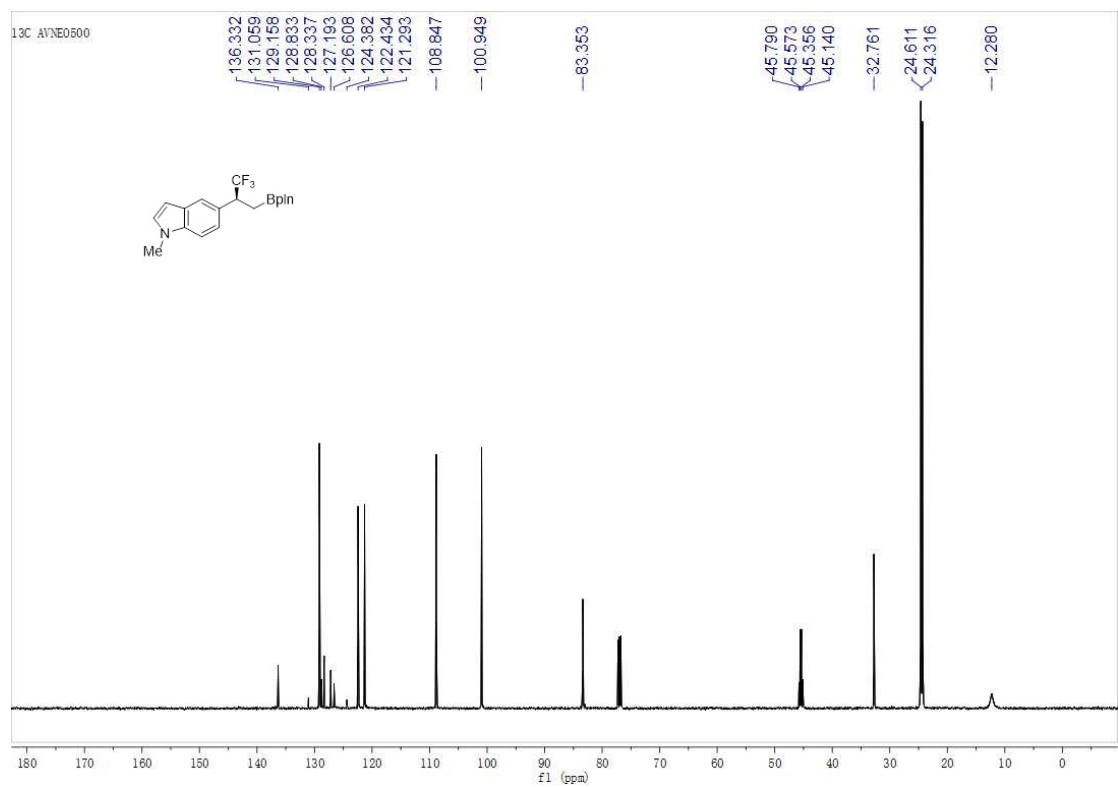
(S)-9-ethyl-3-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop
an-2-yl)-9H-carbazole (4w):

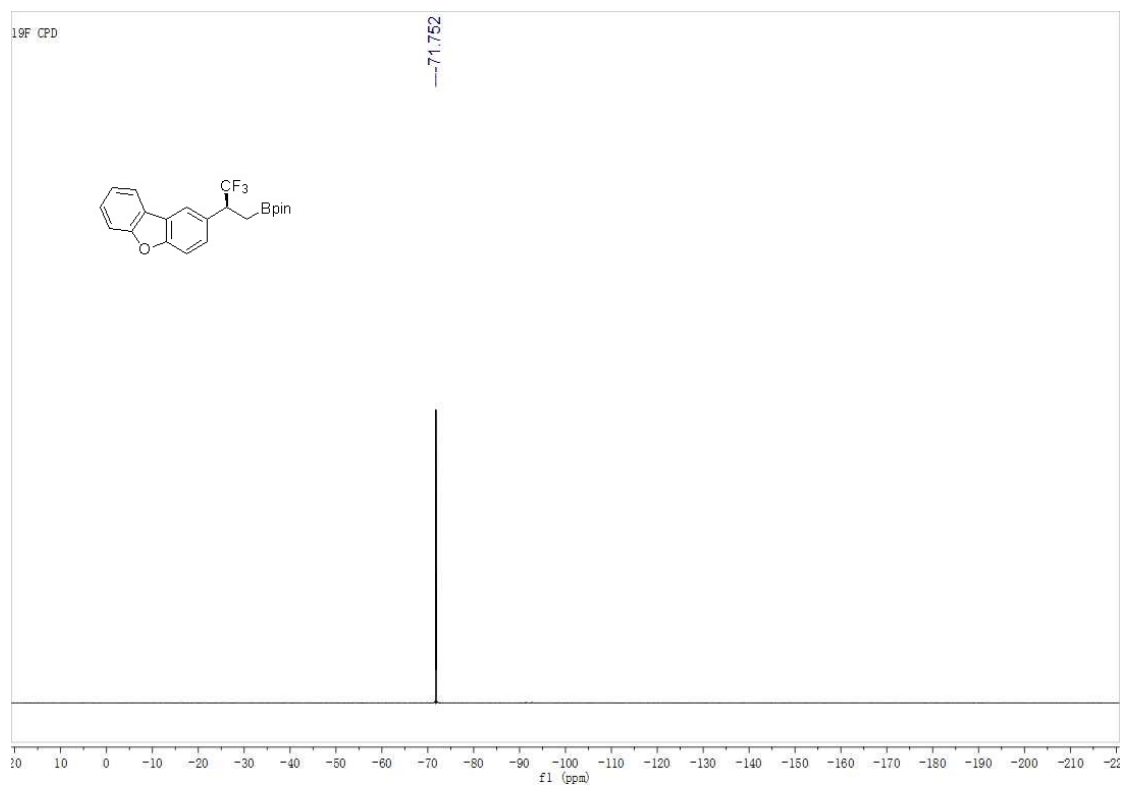




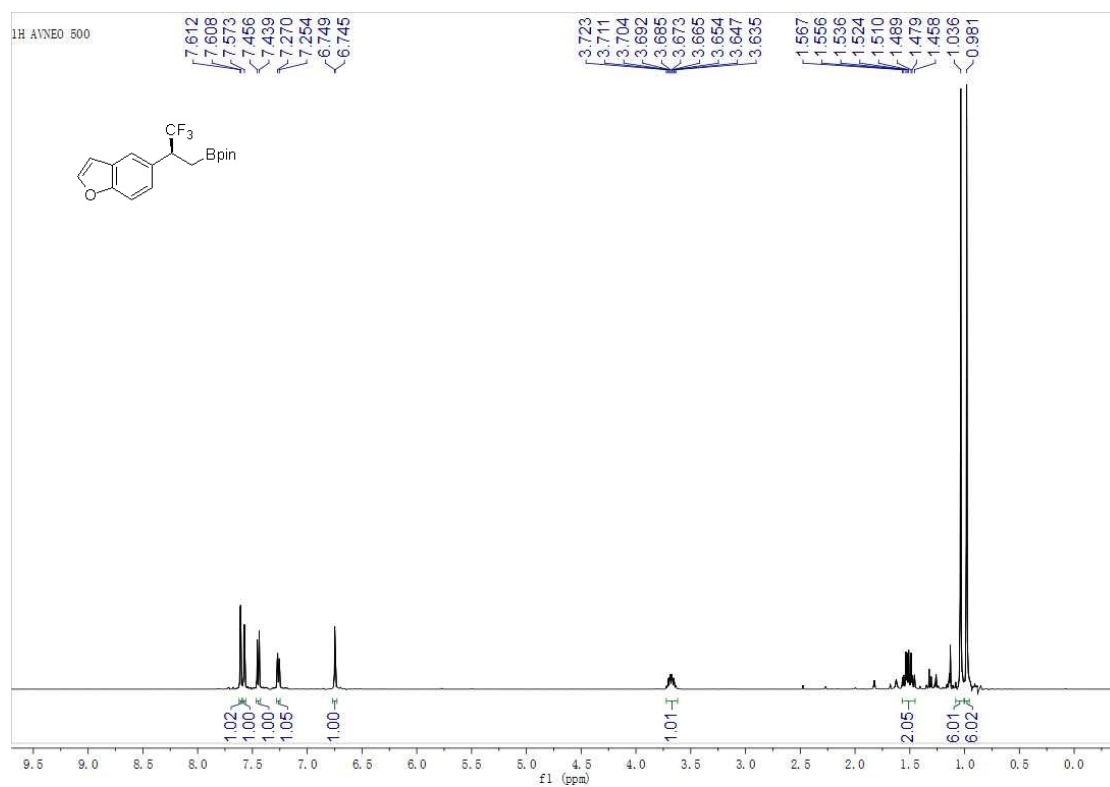
(S)-1-methyl-5-(1,1,1-trifluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)-1H-indole (4x):

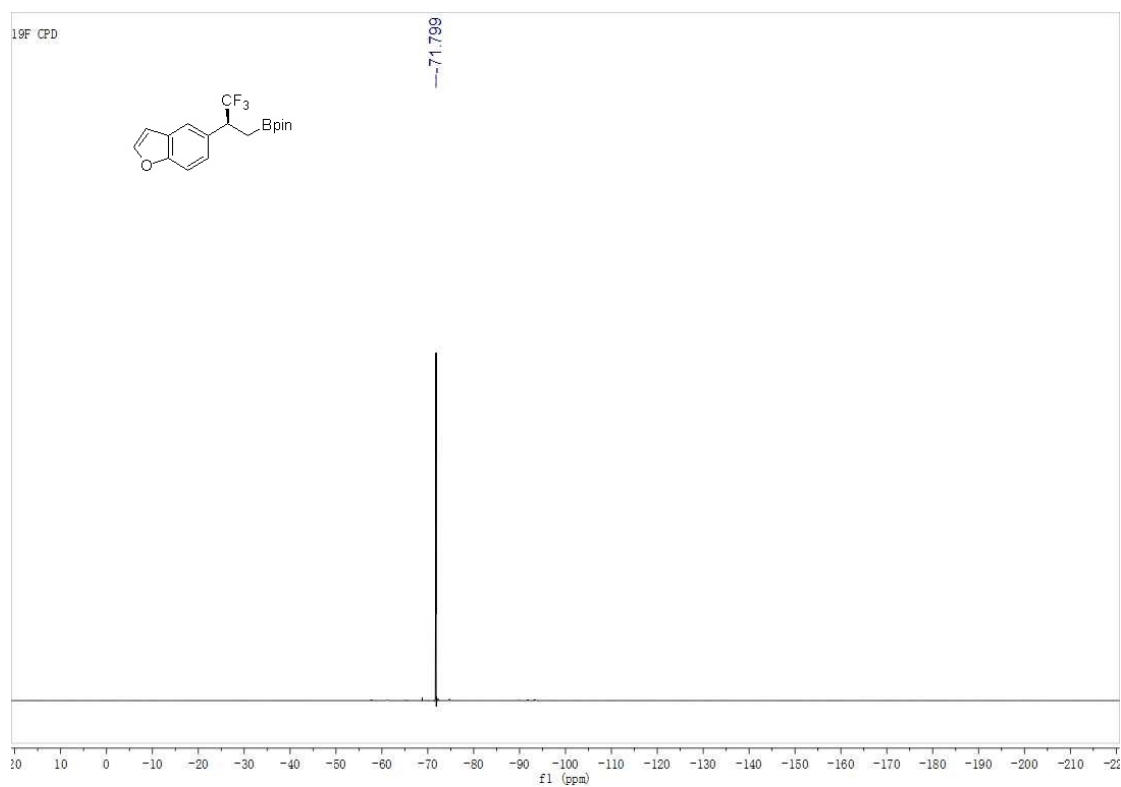
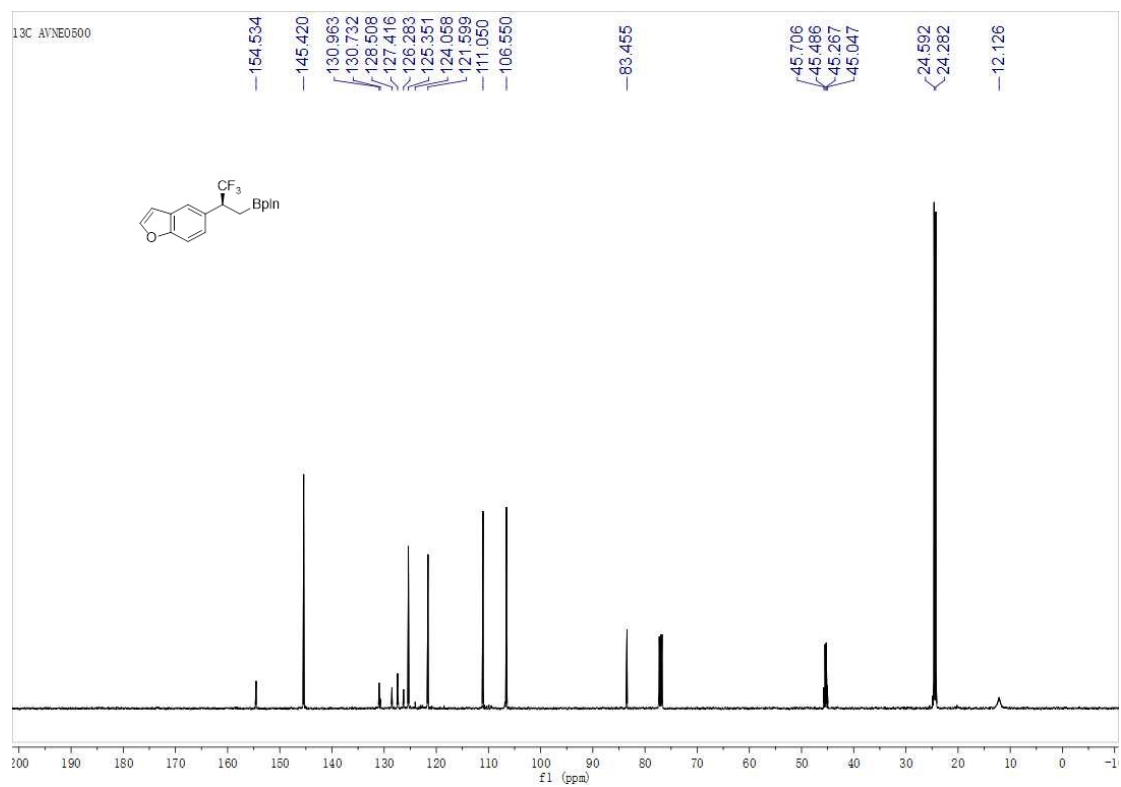




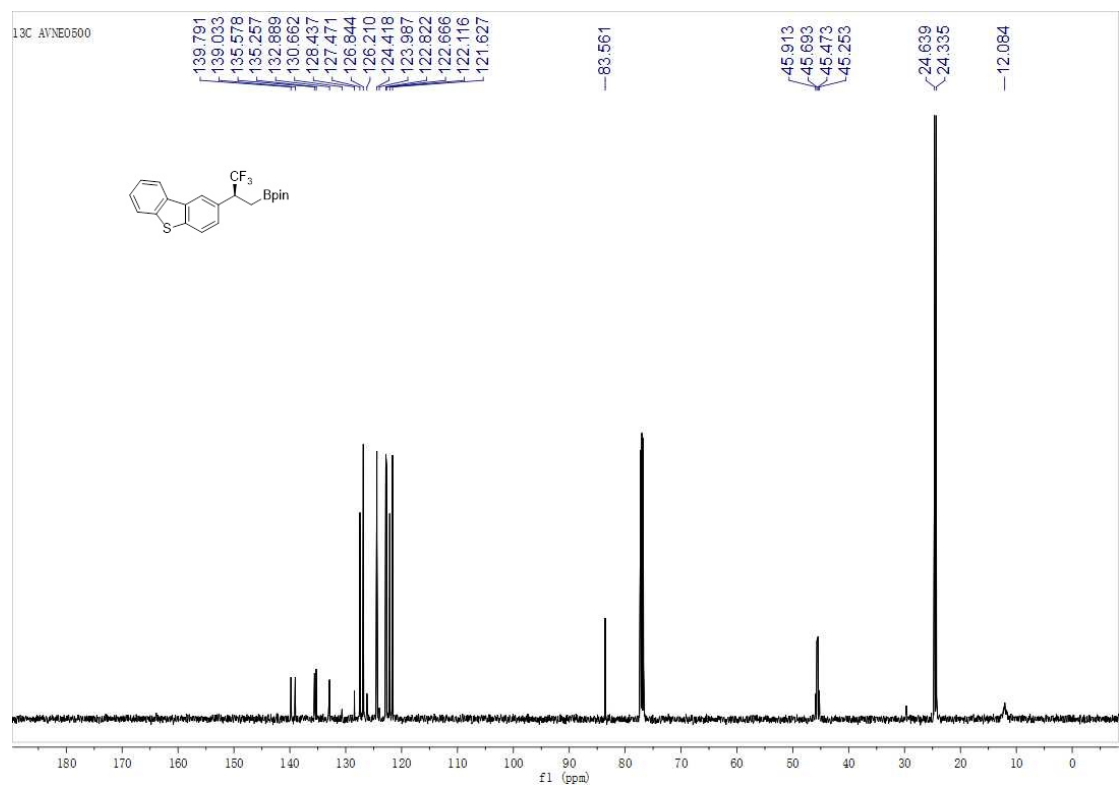
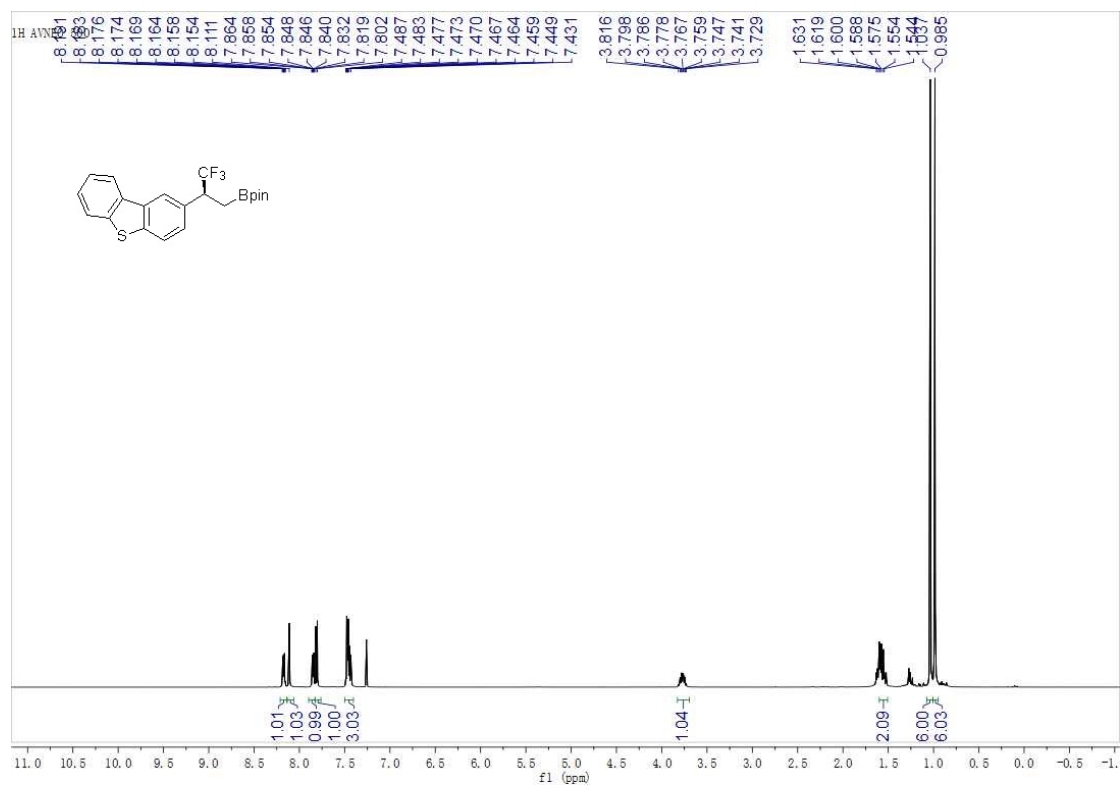


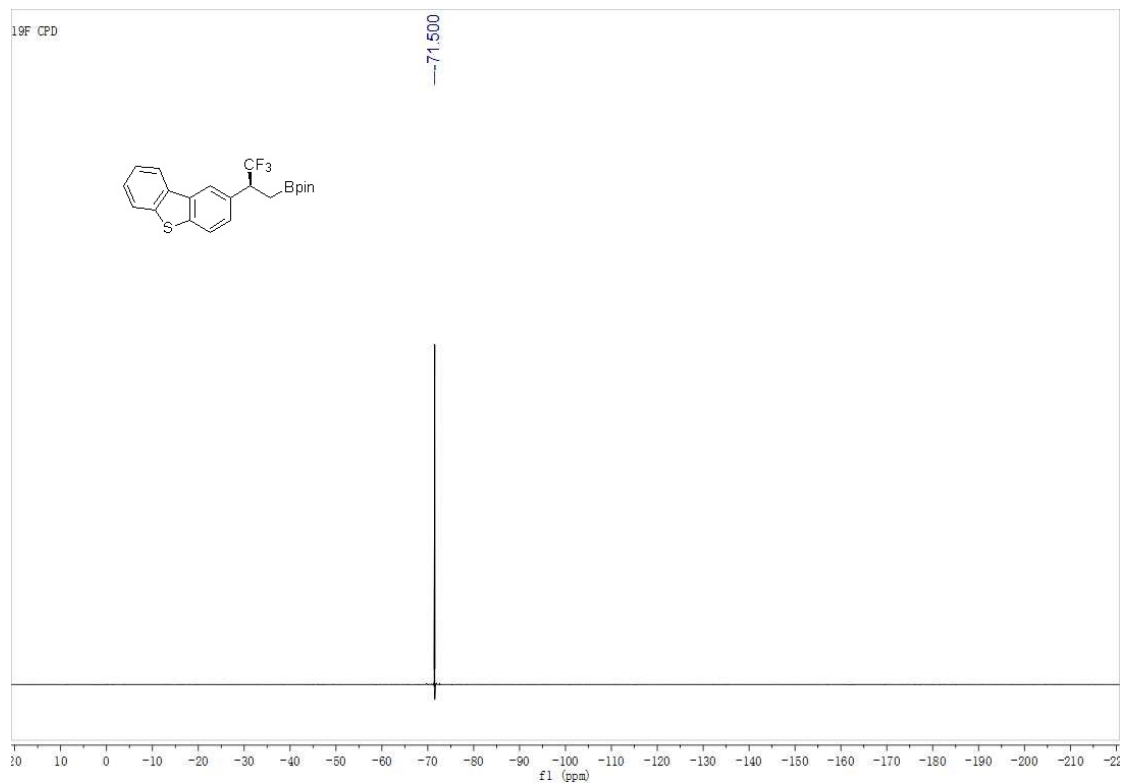
(S)-2-(2-(benzofuran-5-yl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4z):



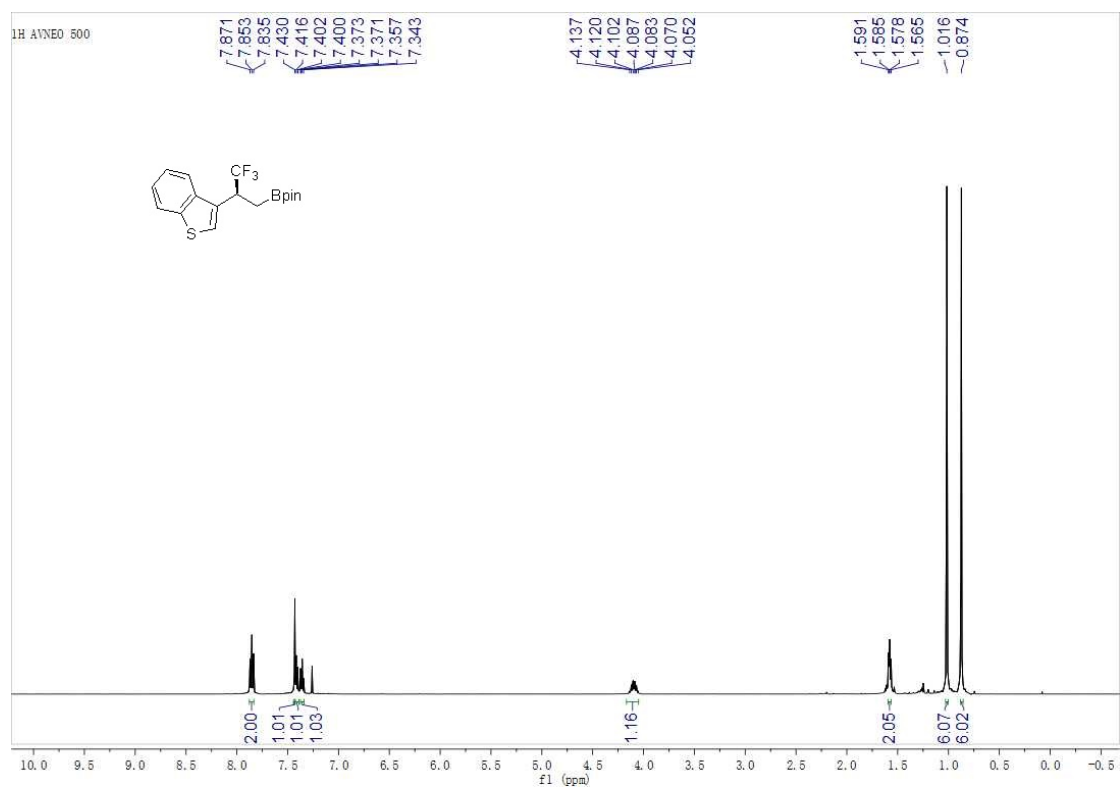


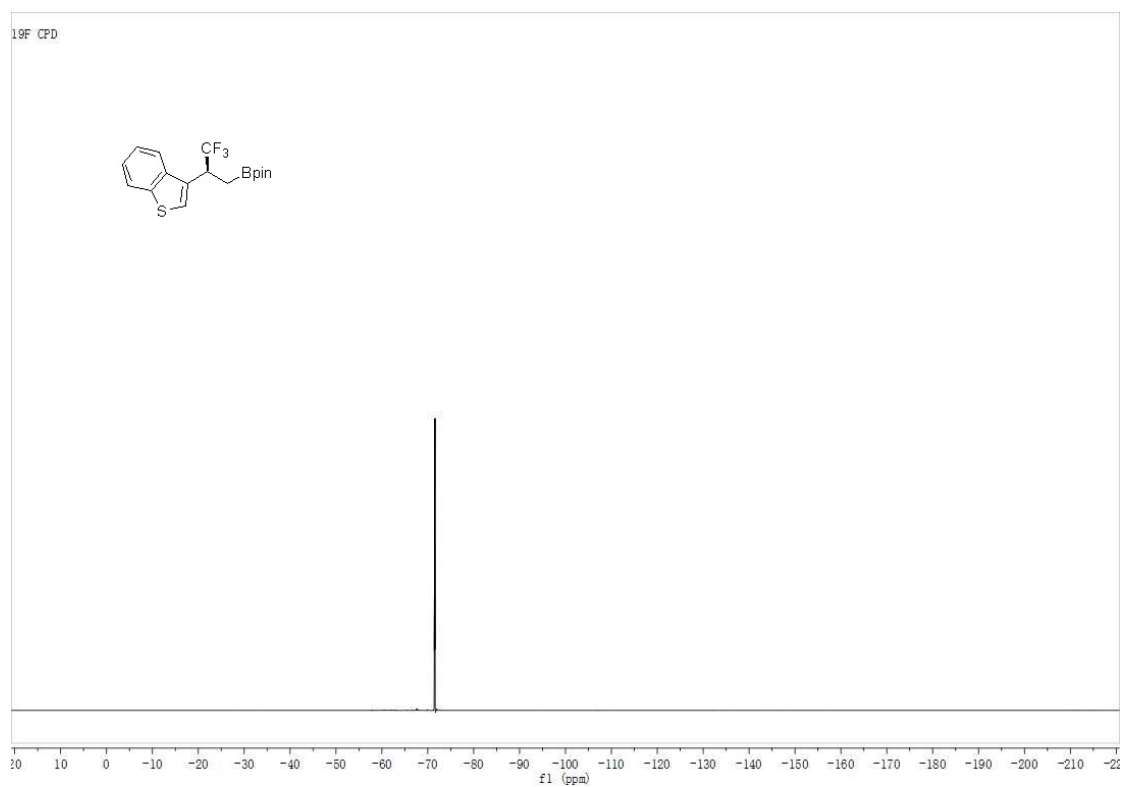
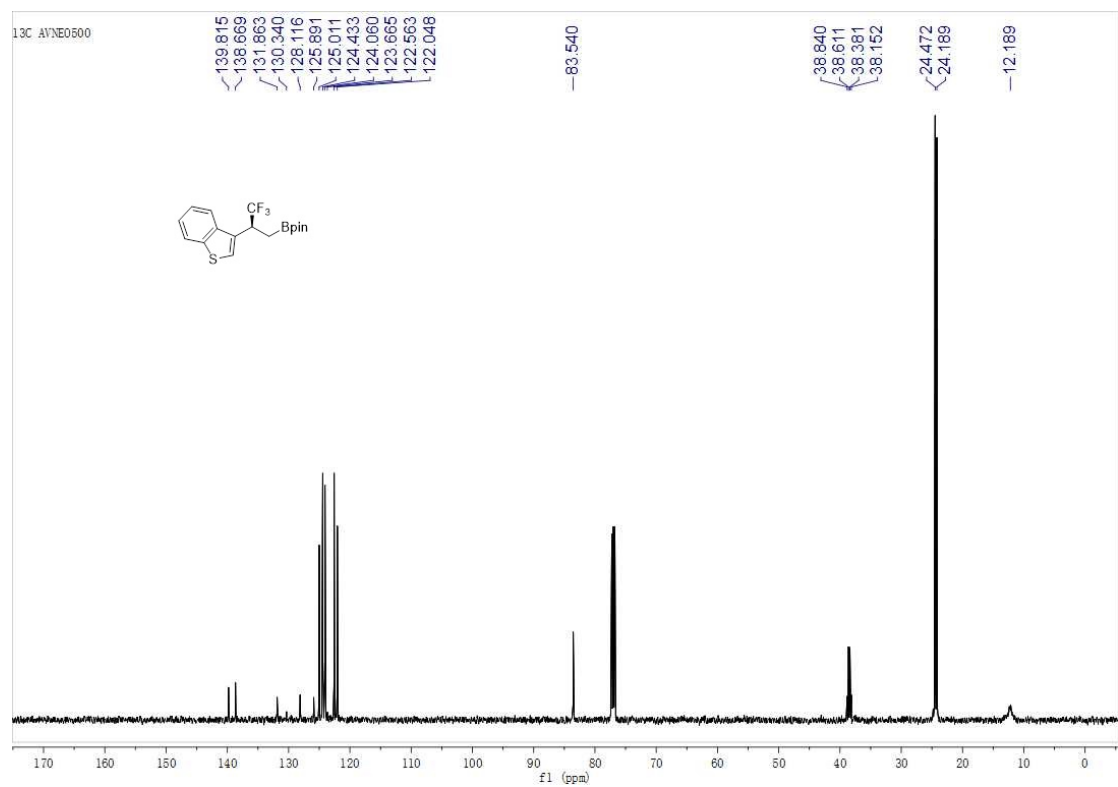
(S)-2-(2-(dibenzo[b,d]thiophen-2-yl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4aa):



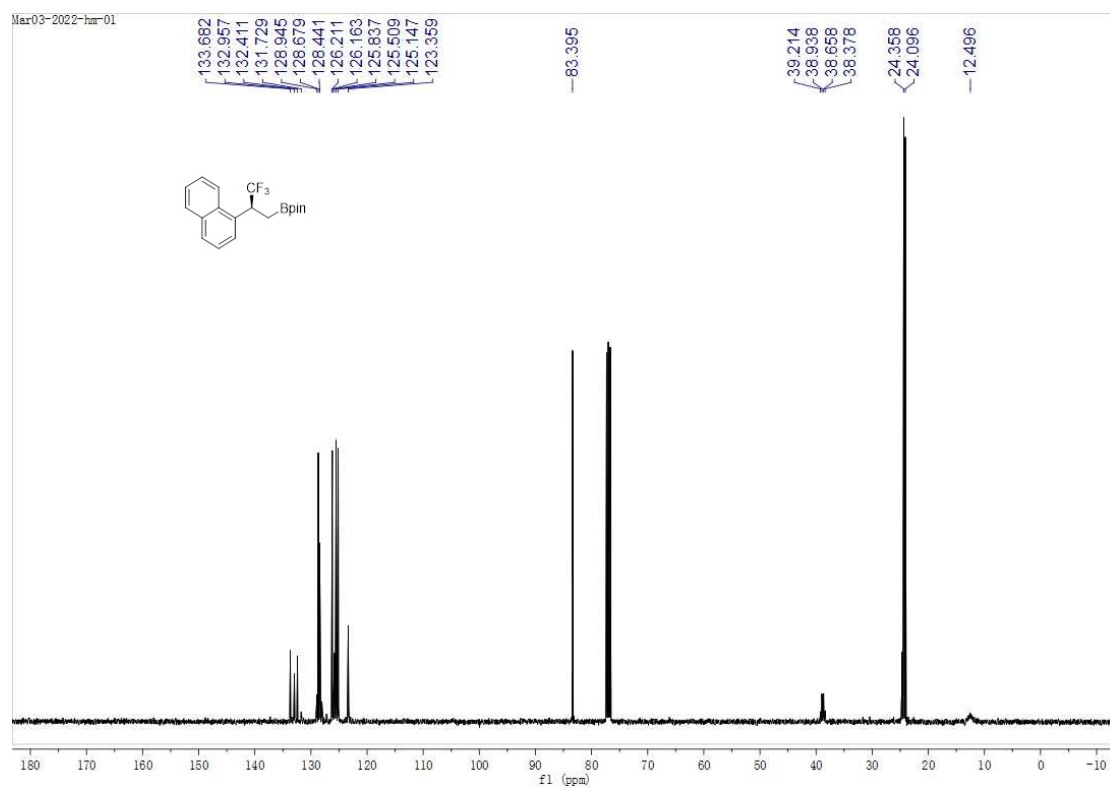
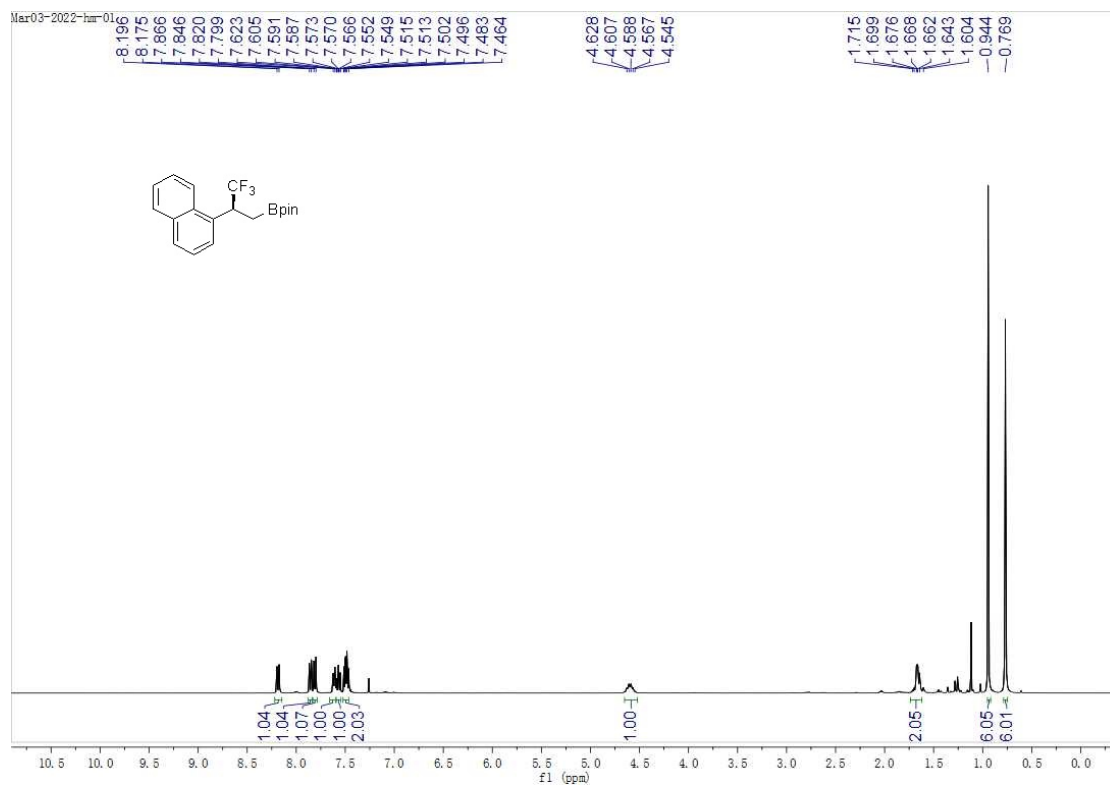


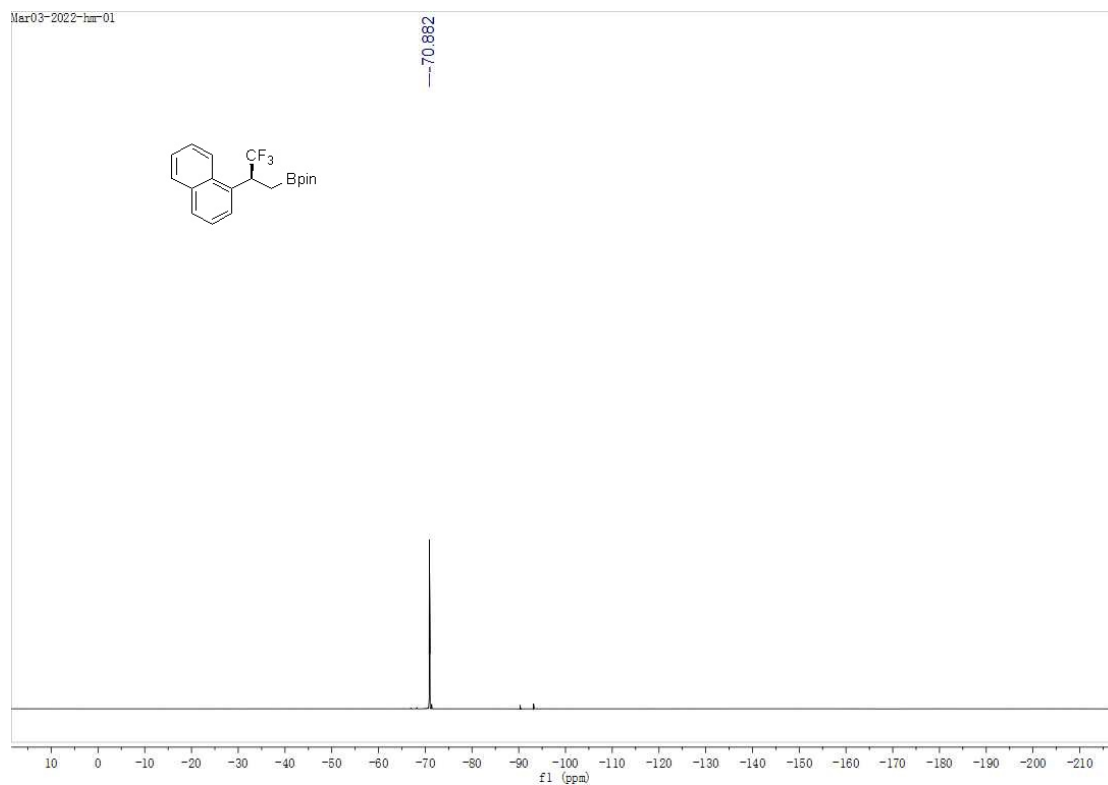
(S)-2-(2-(benzo[b]thiophen-3-yl)-3,3,3-trifluoropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ab):



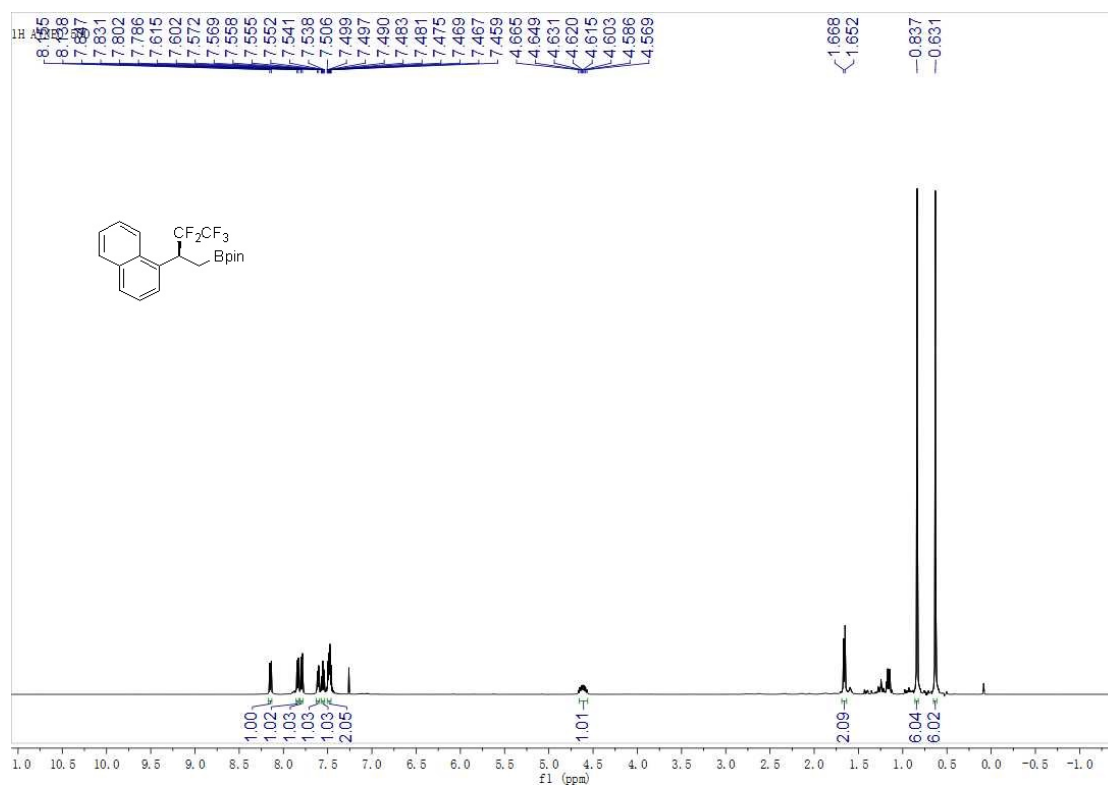


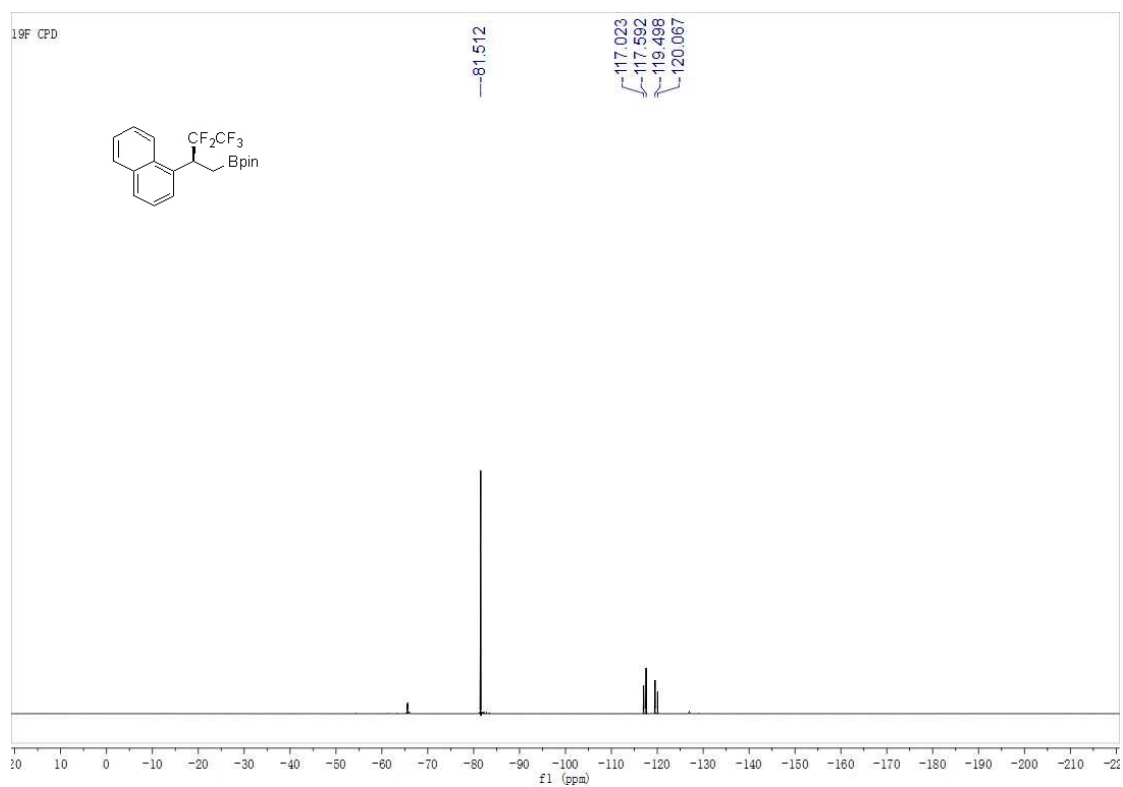
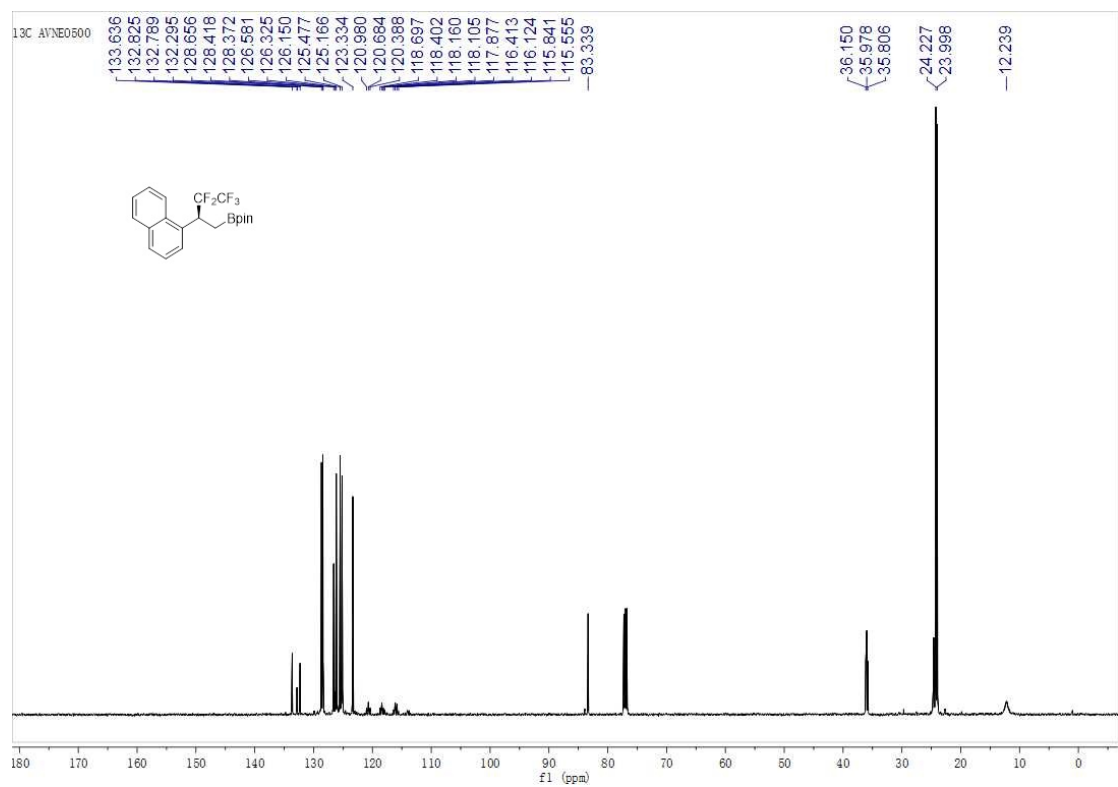
(S)-4,4,5,5-tetramethyl-2-(3,3,3-trifluoro-2-(naphthalen-1-yl)propyl)-1,3,2-dioxaborolane (4ac):



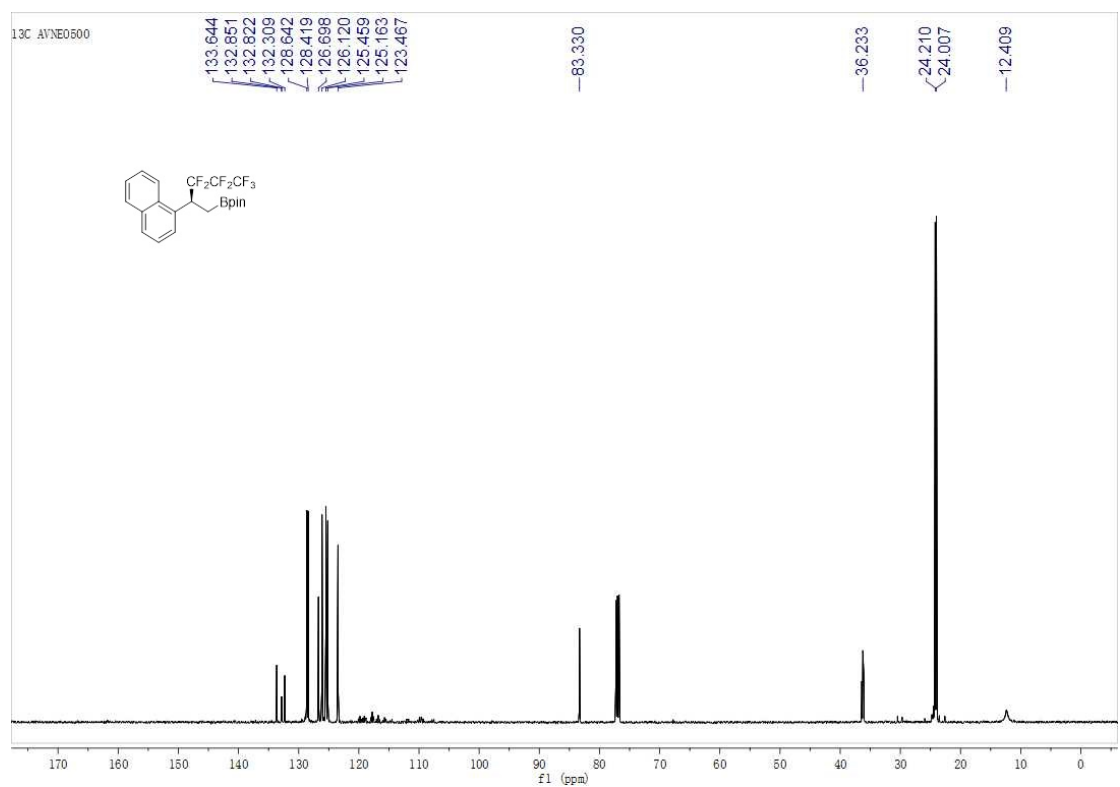
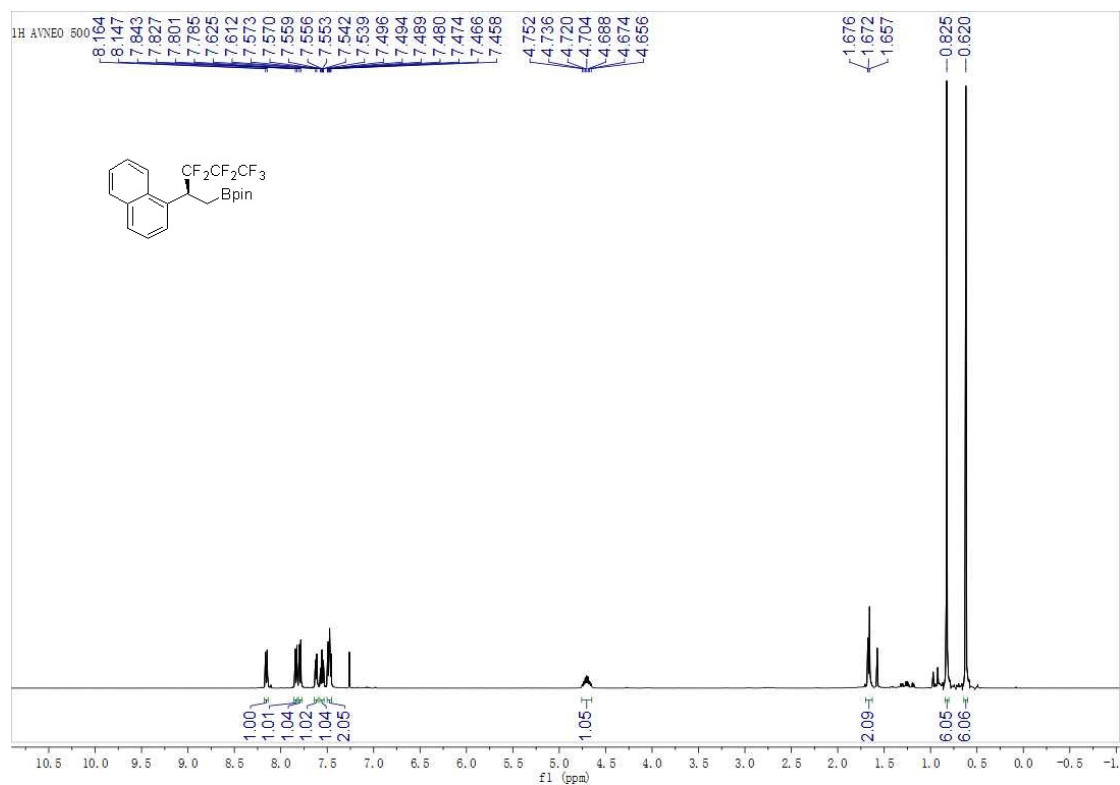


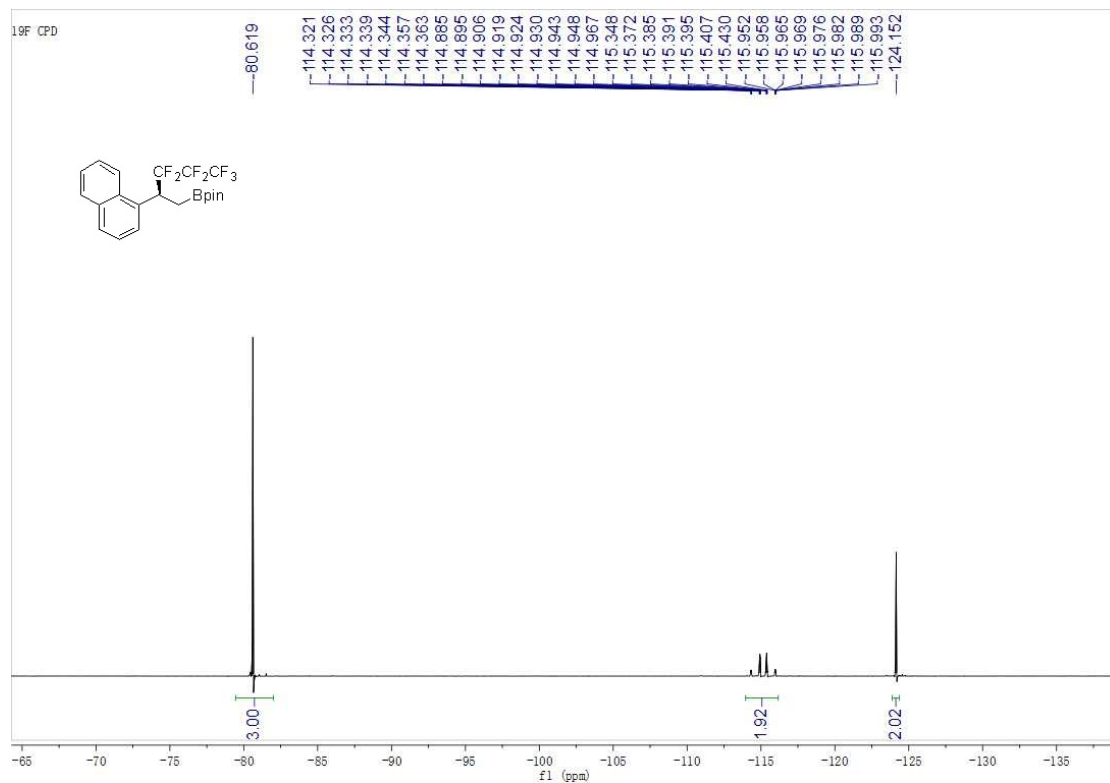
(S)-4,4,5,5-tetramethyl-2-(3,3,4,4,4-pentafluoro-2-(naphthalen-1-yl)butyl)-1,3,2-dioxaborolane (4ad):



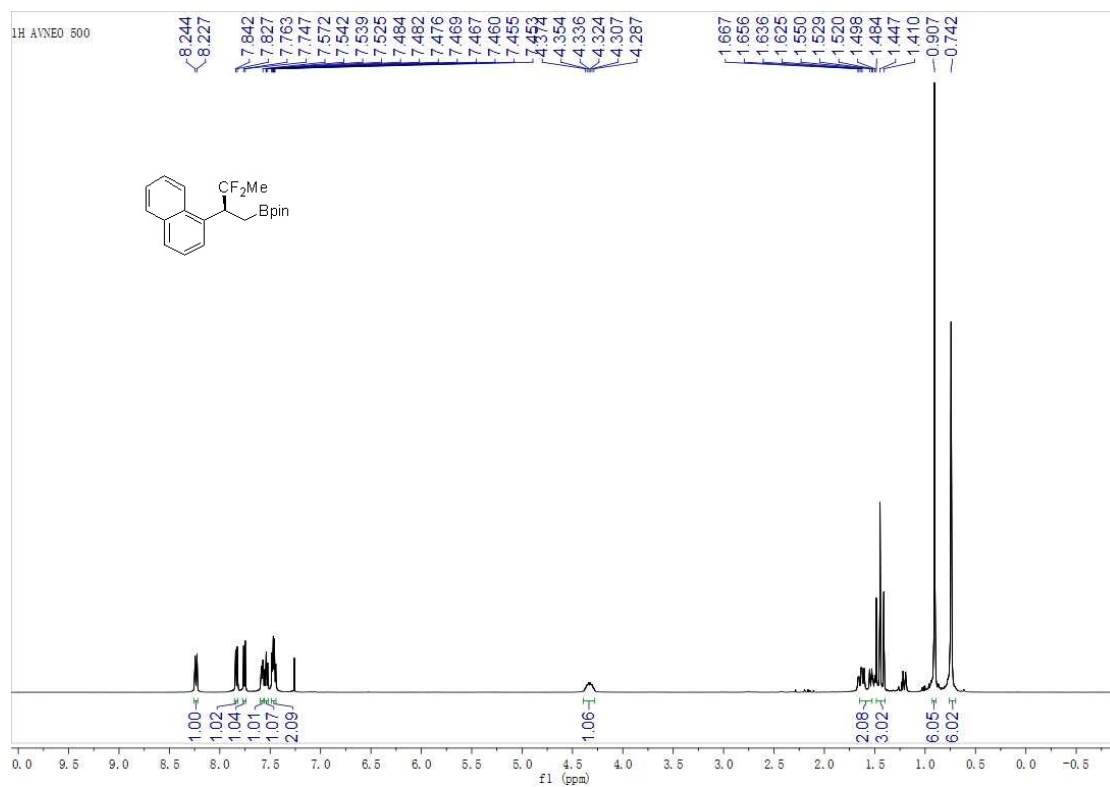


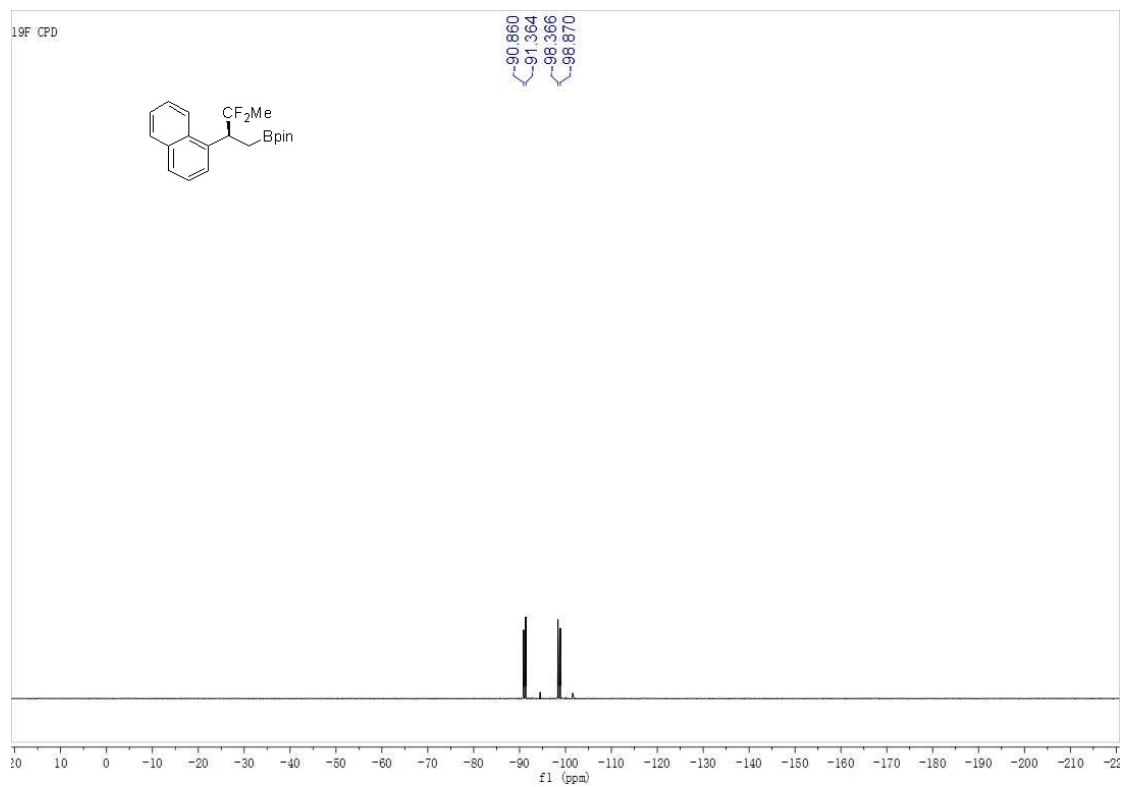
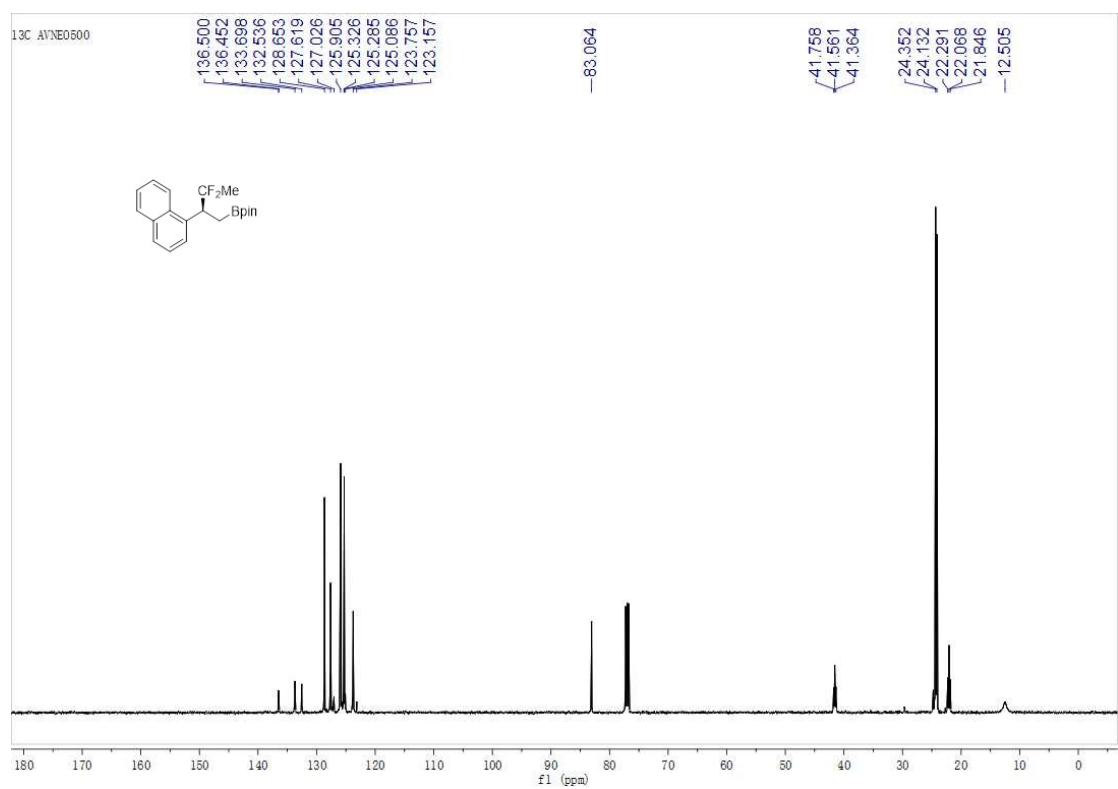
(S)-2-(3,3,4,4,5,5,5-heptafluoro-2-(naphthalen-1-yl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ae):



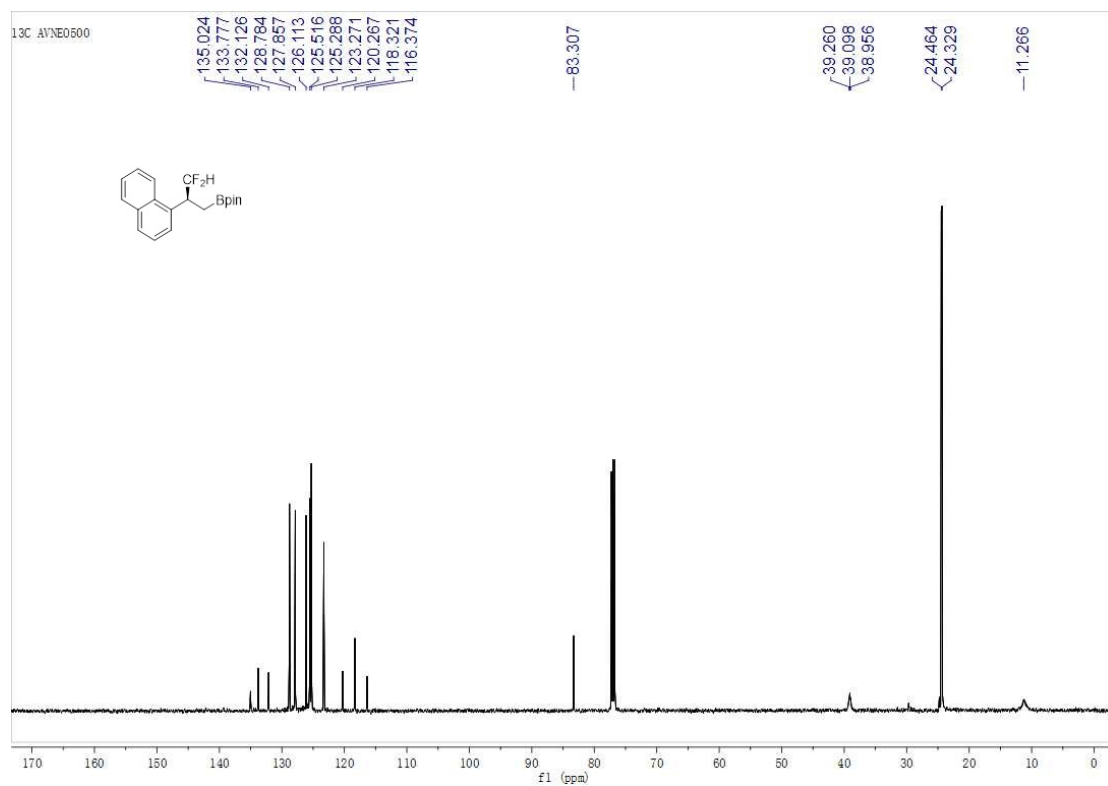
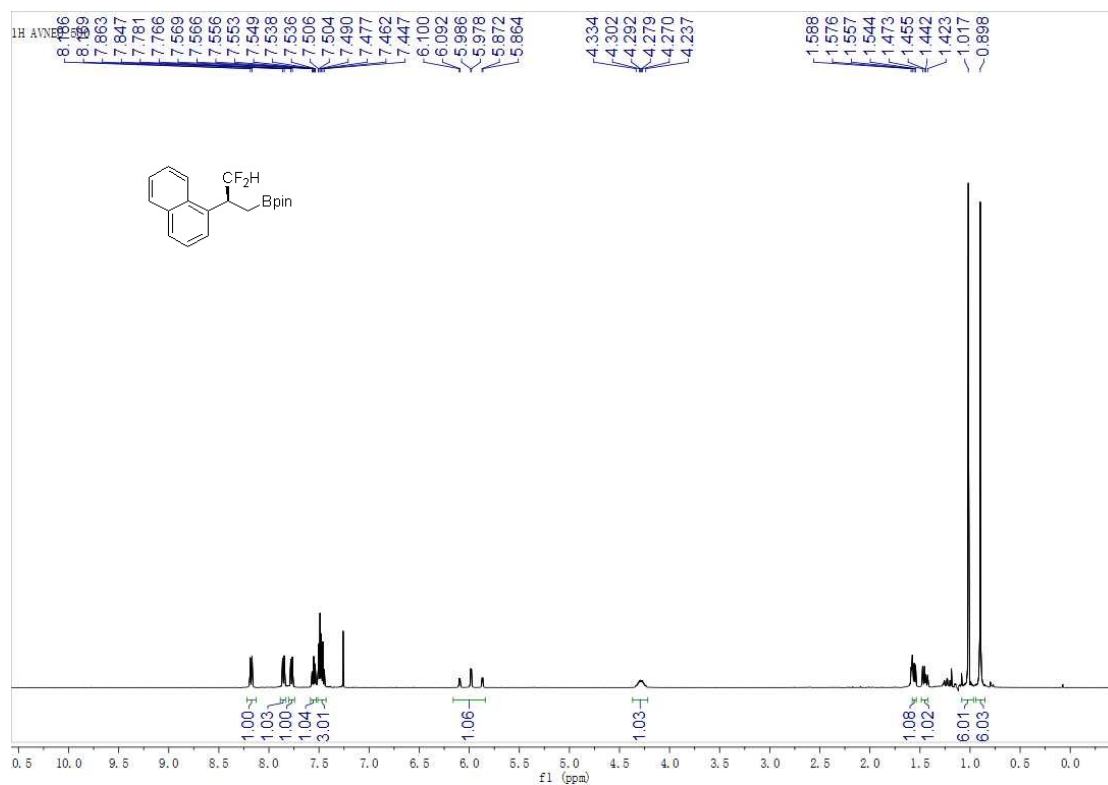


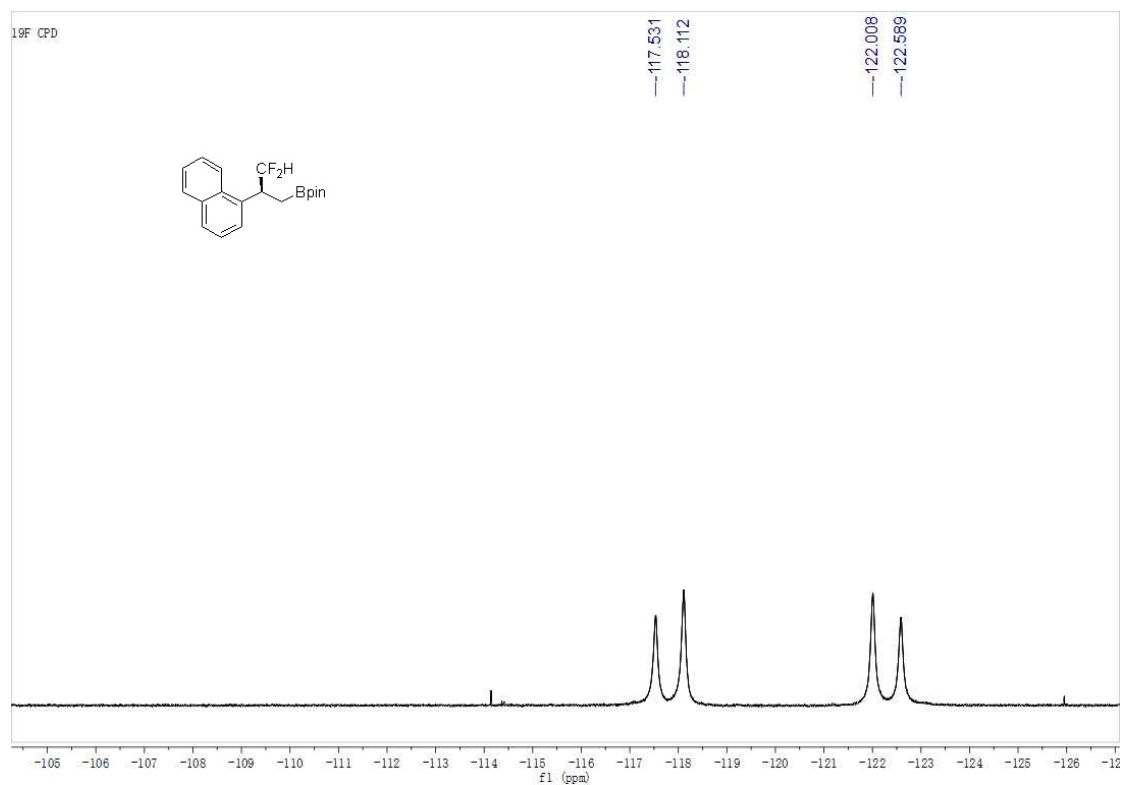
(S)-2-(3,3-difluoro-2-(naphthalen-1-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4af):



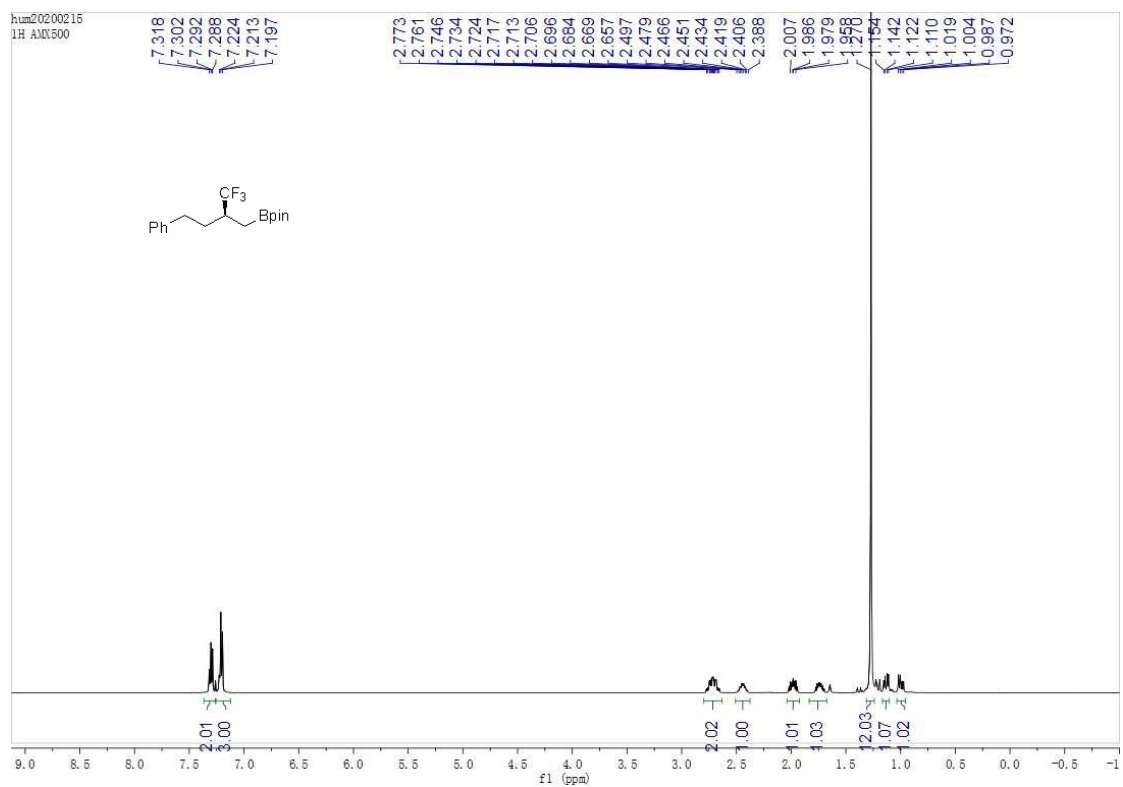


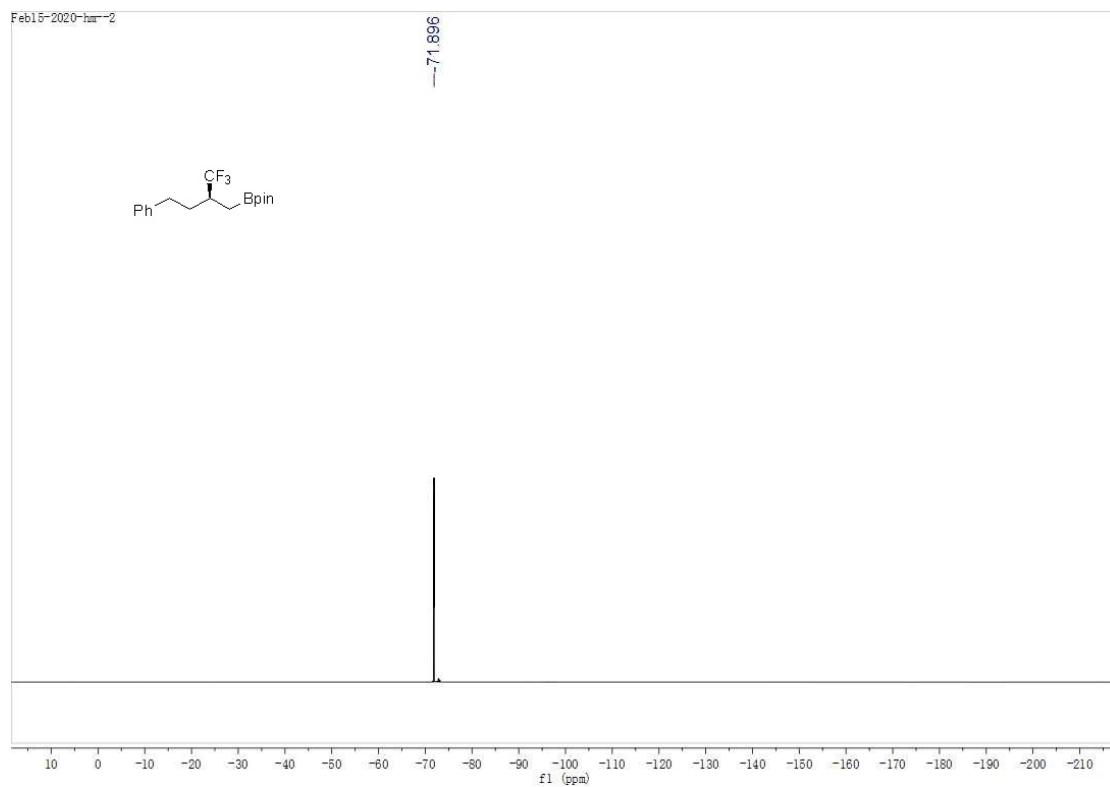
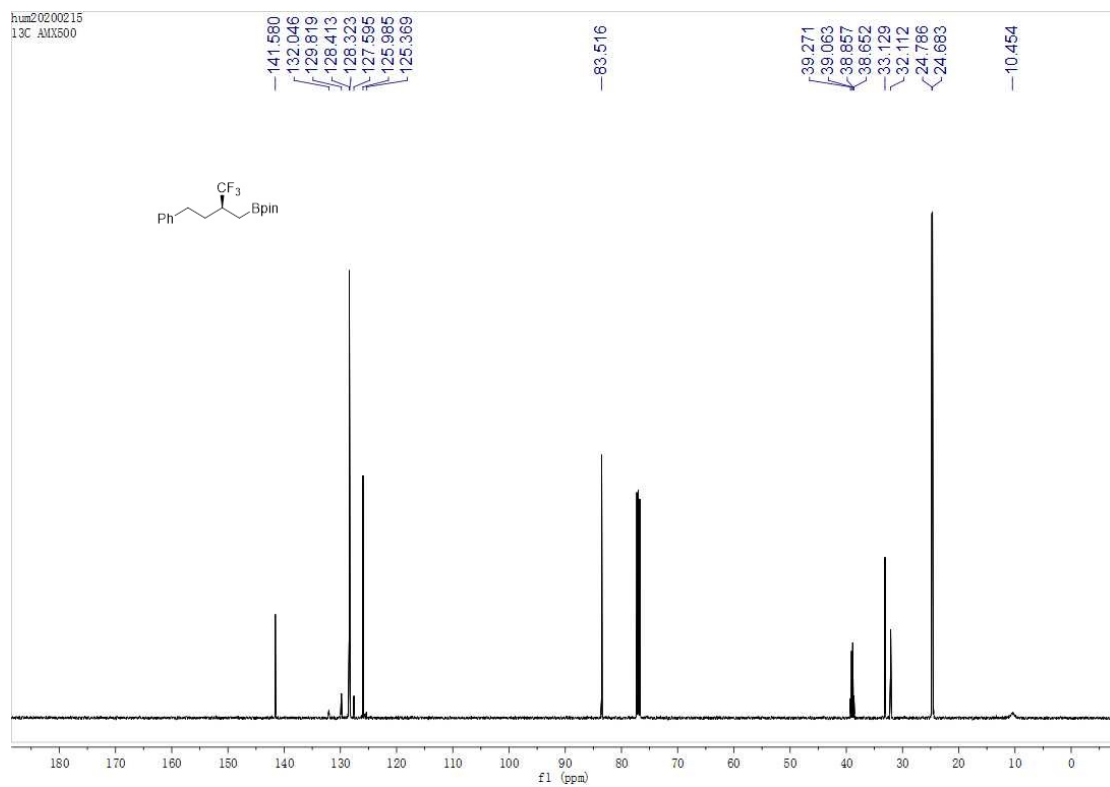
(S)-2-(3,3-difluoro-2-(naphthalen-1-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ag):

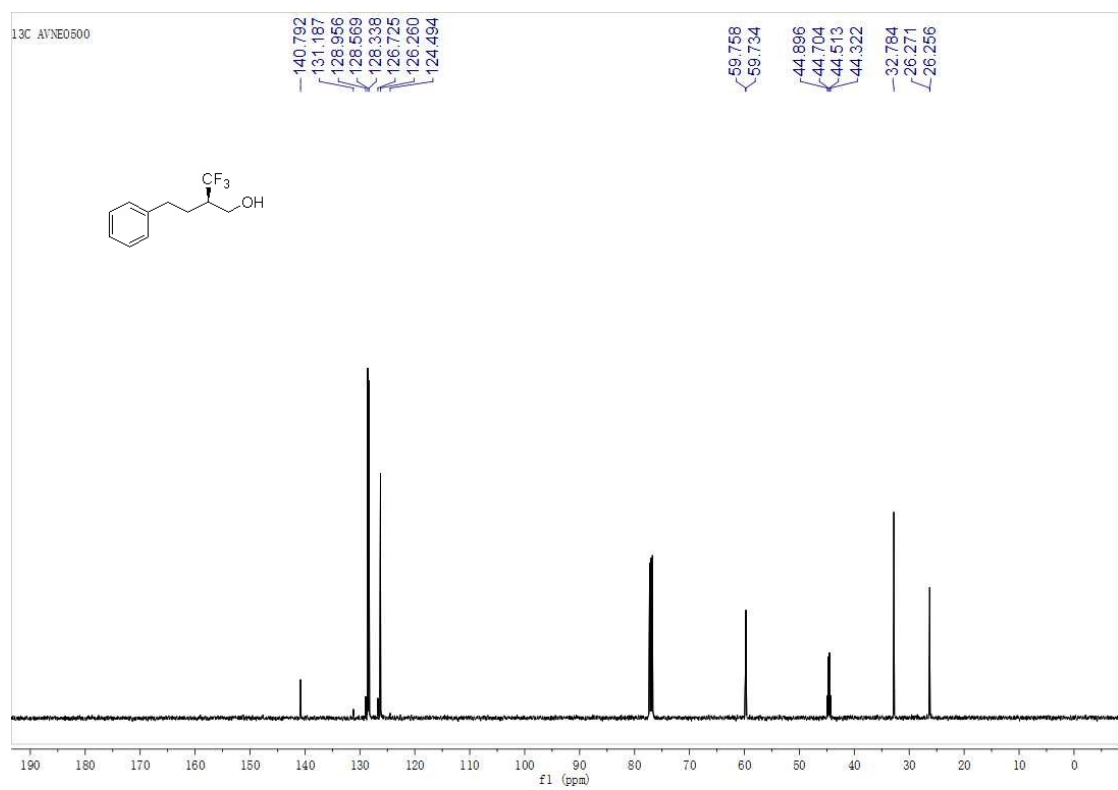
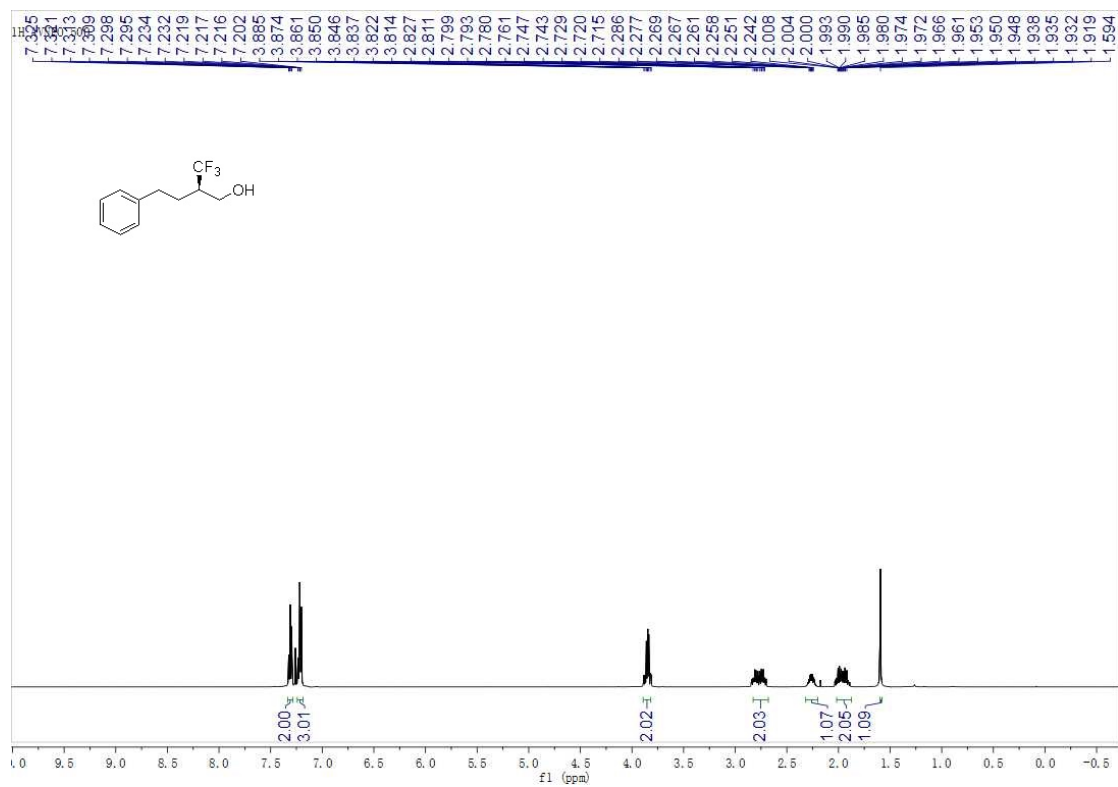


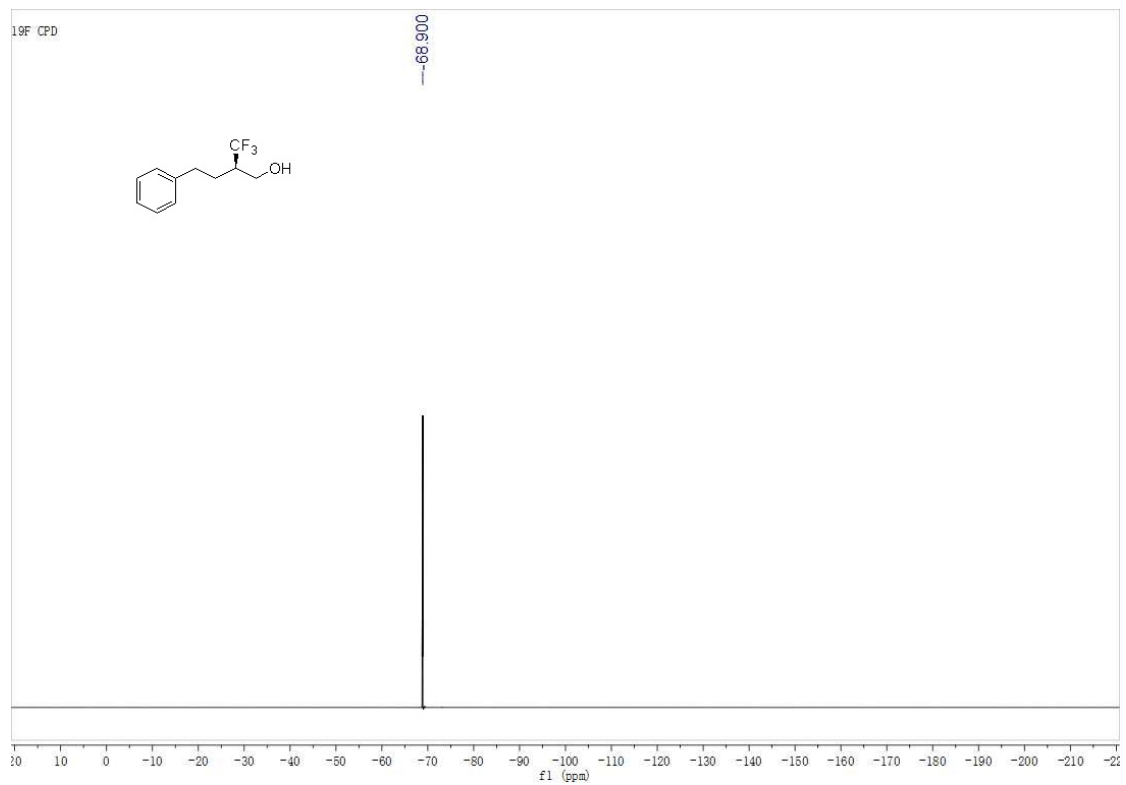


(S)-4,4,5,5-tetramethyl-2-(4-phenyl-2-(trifluoromethyl)butyl)-1,3,2-dioxaborolan
e (4ah):

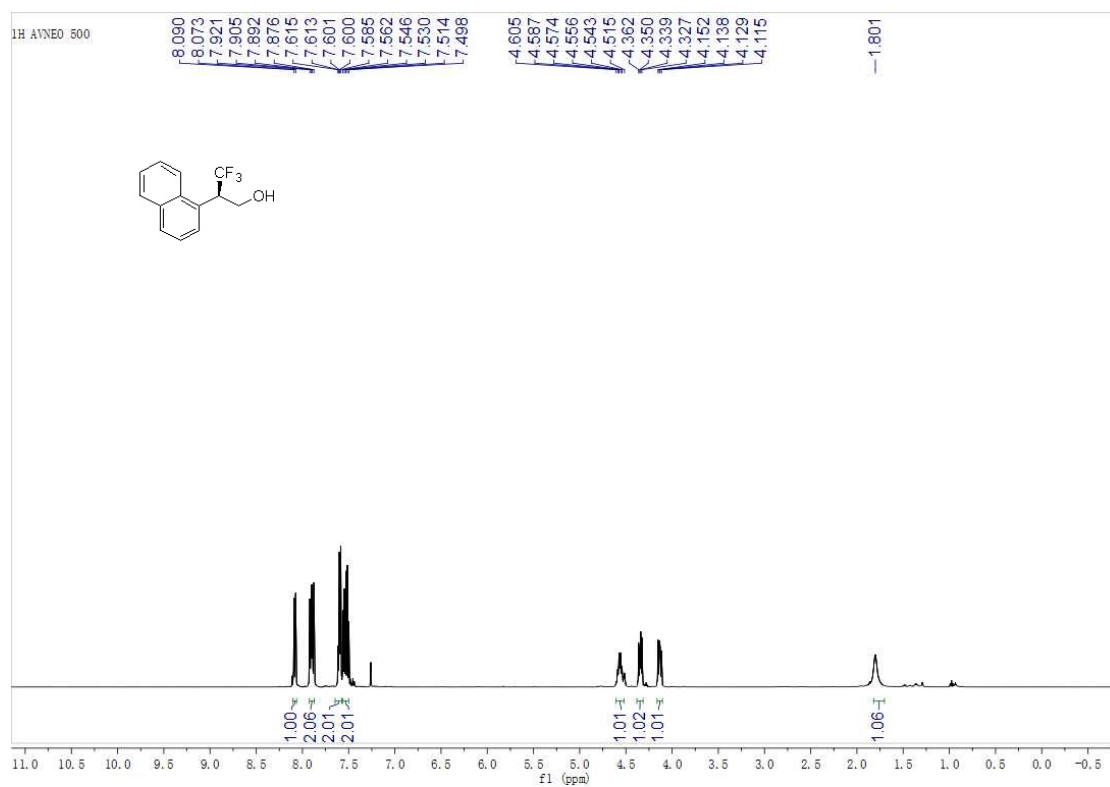


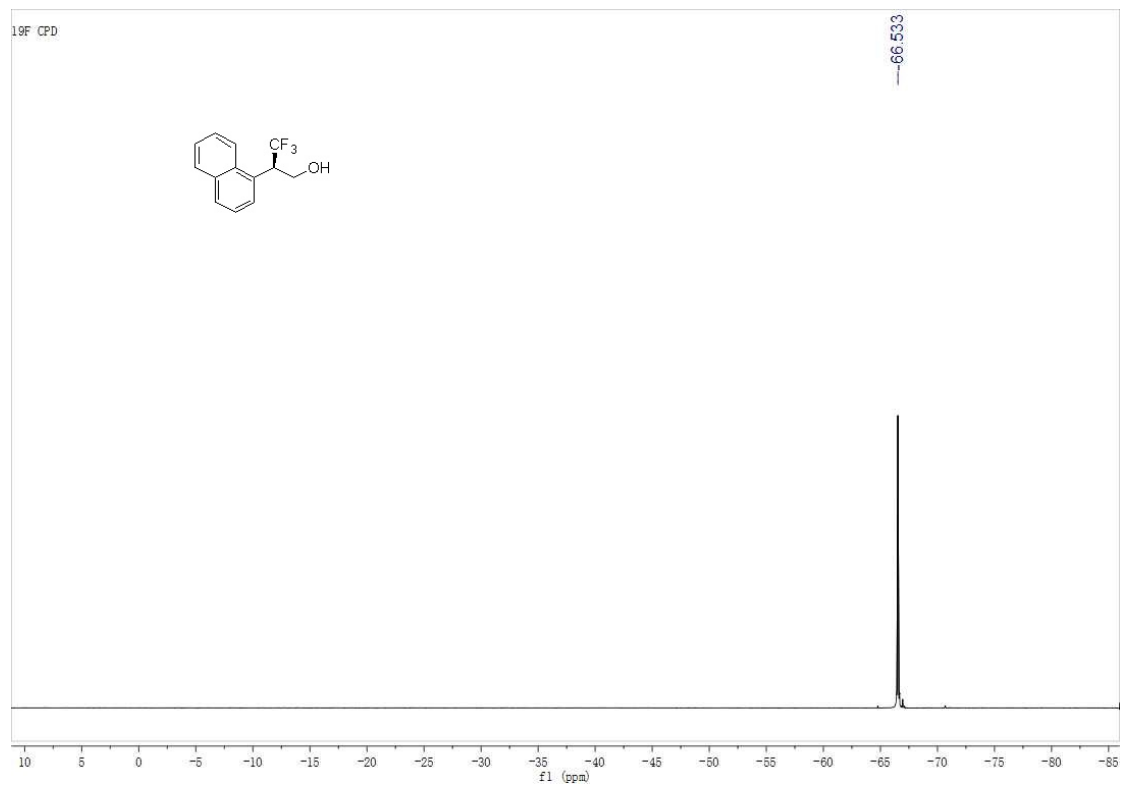
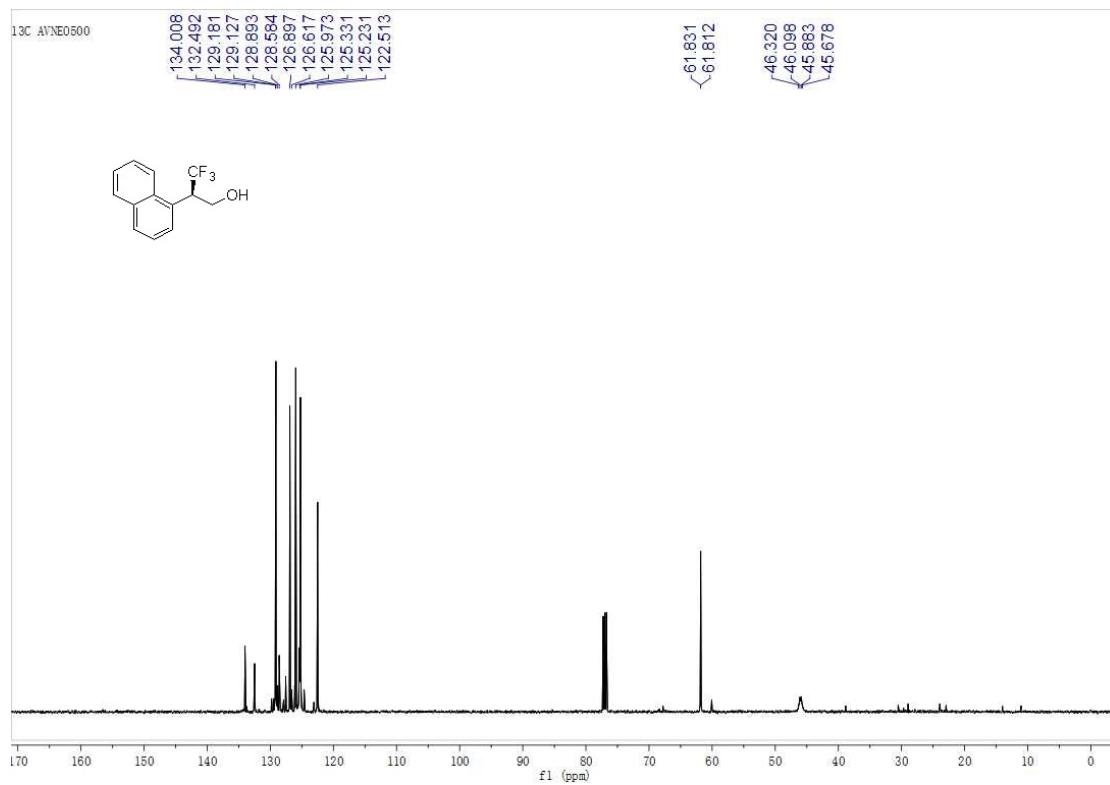


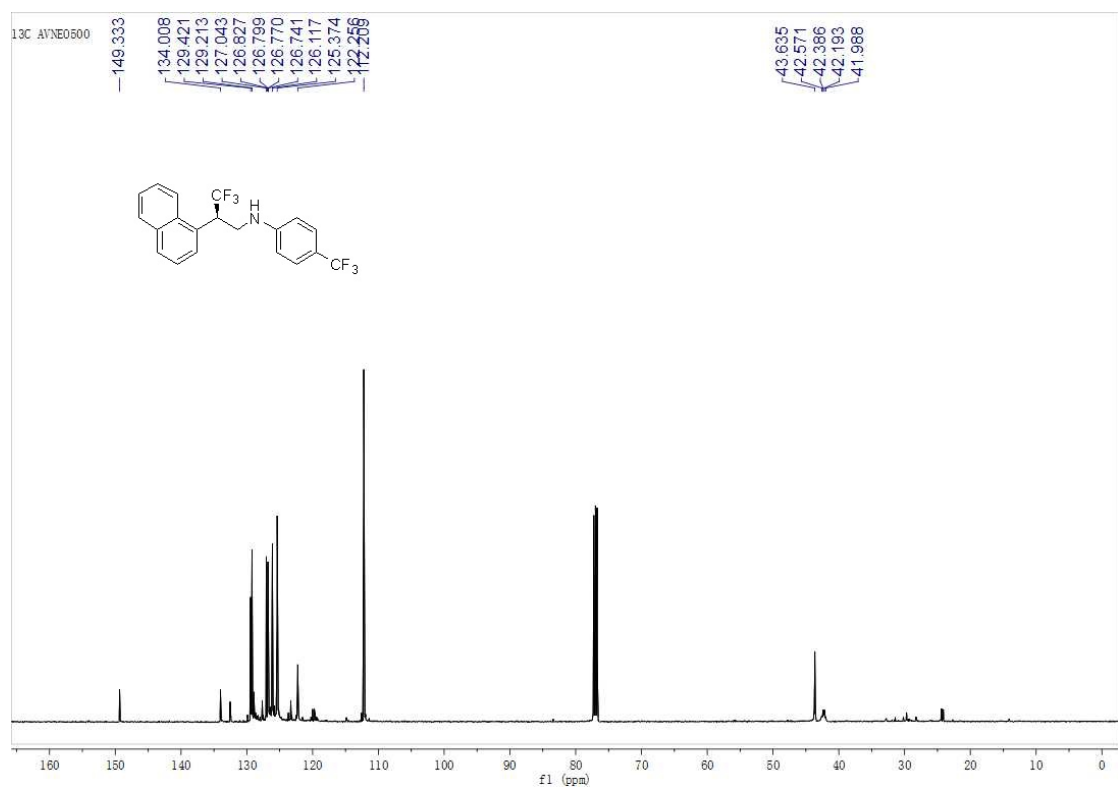
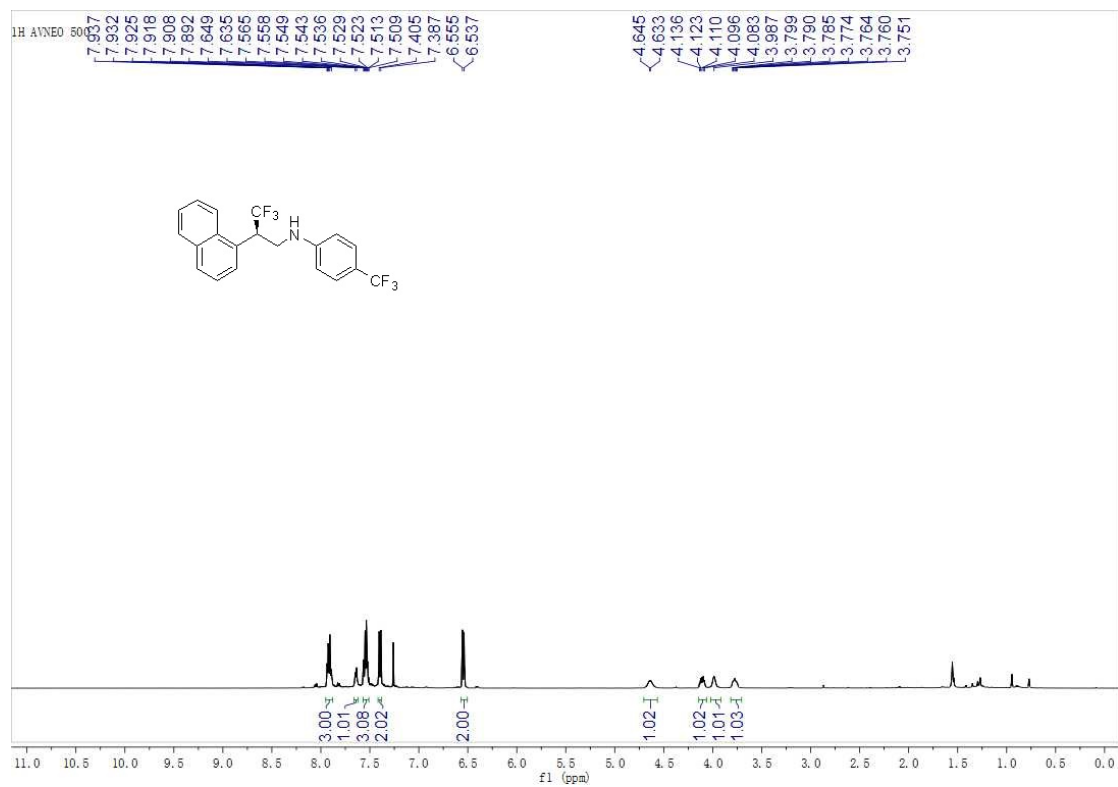
(R)-4-phenyl-2-(trifluoromethyl)butan-1-ol (4ah')

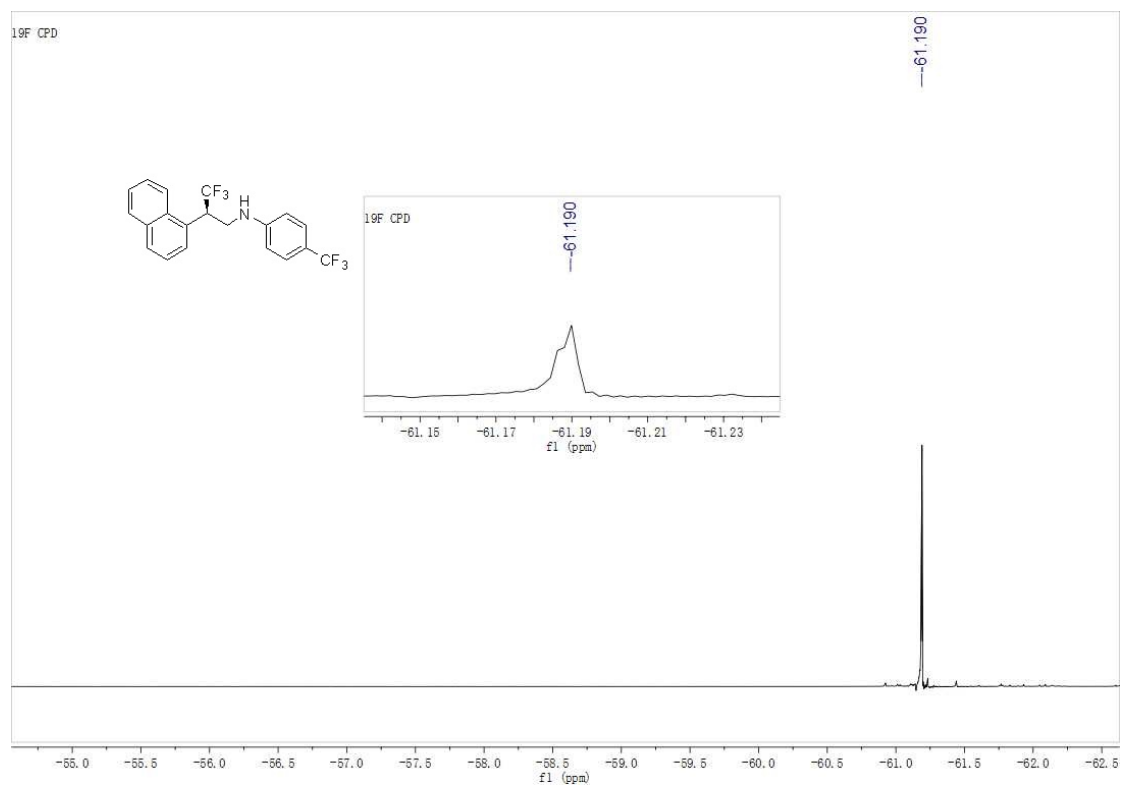


(R)-3,3,3-trifluoro-2-(naphthalen-1-yl)propan-1-ol (6):

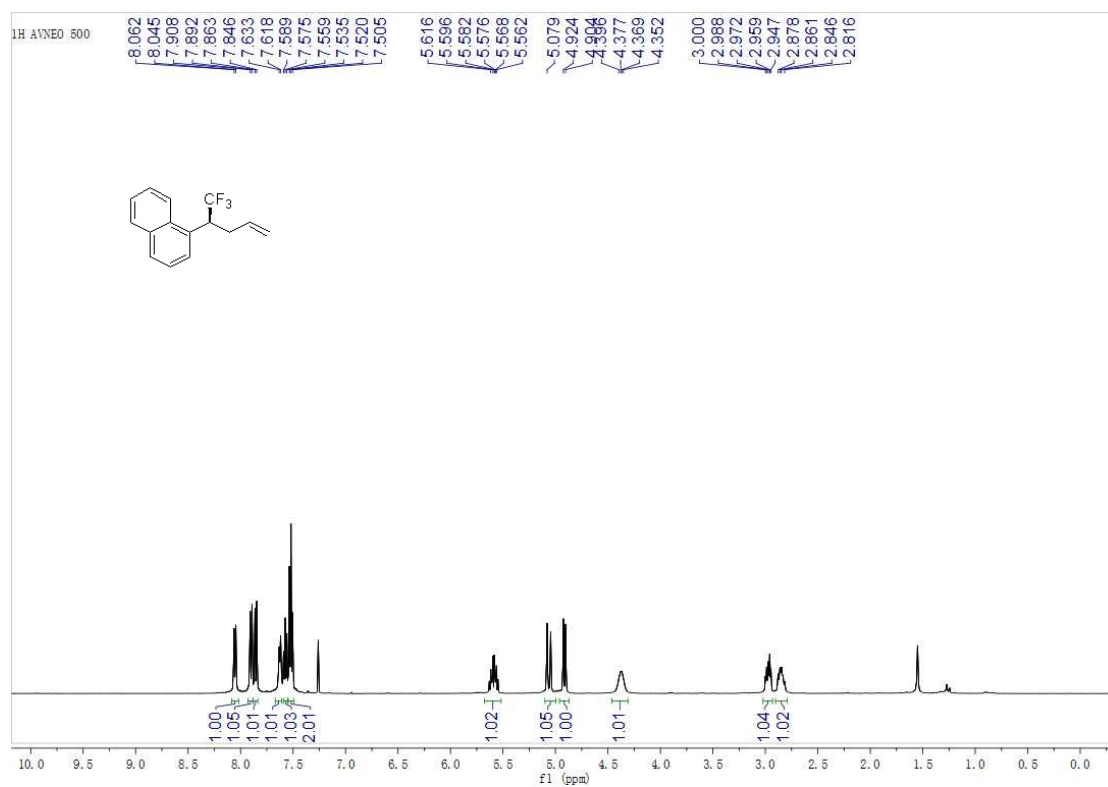


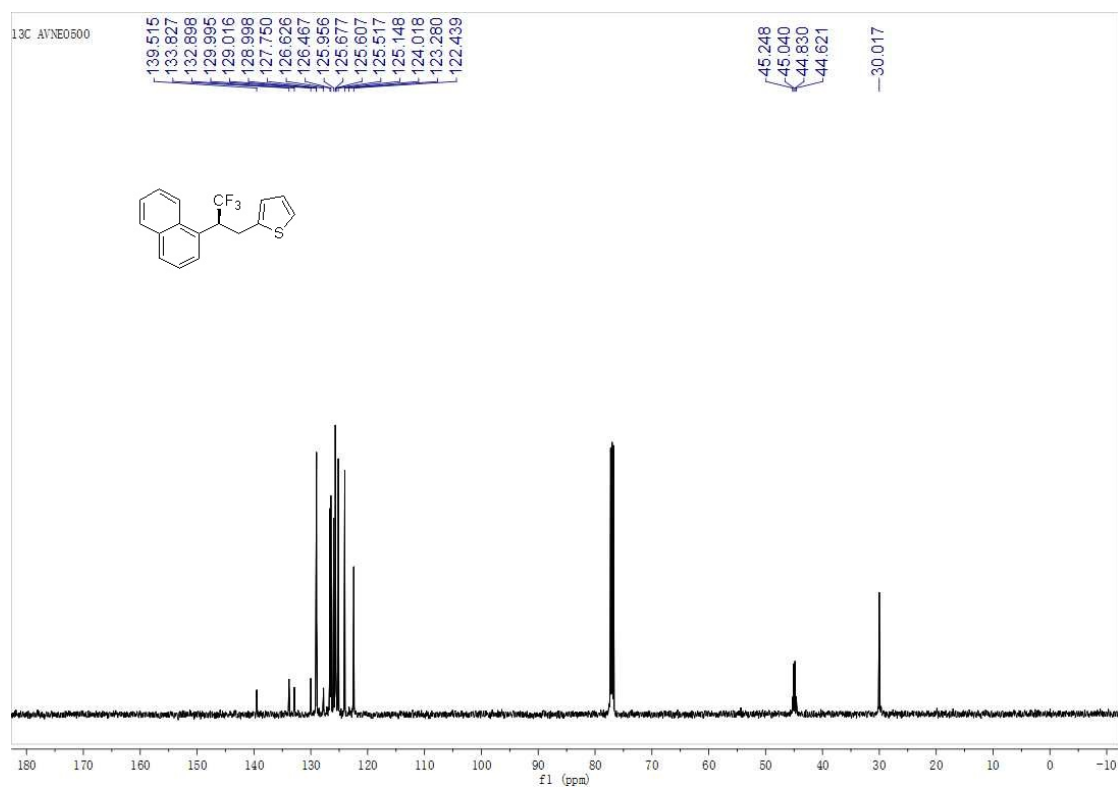
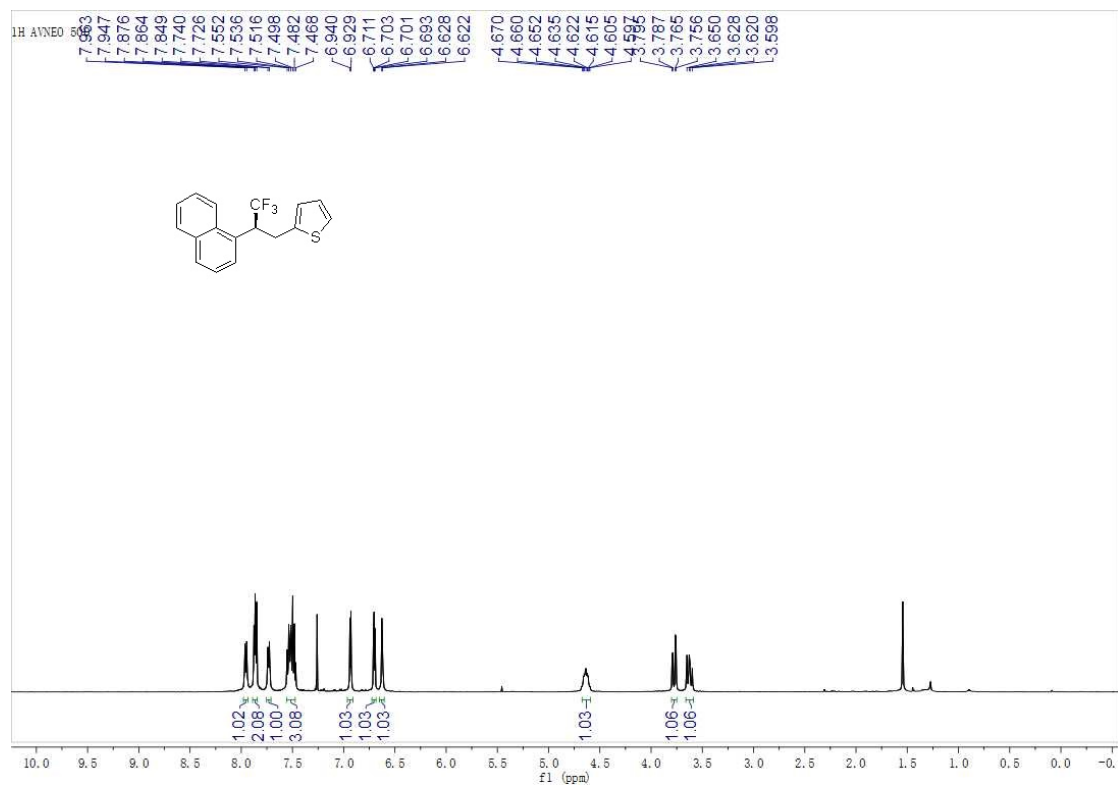


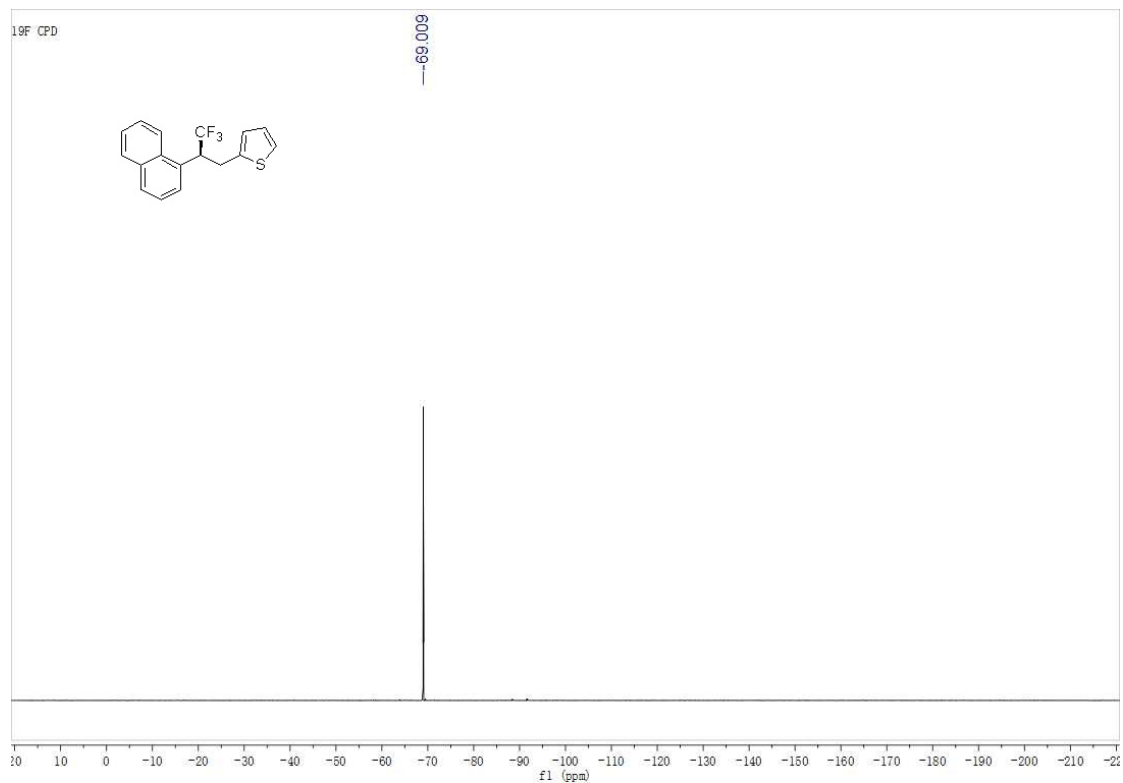
(R)-N-(3,3,3-trifluoro-2-(naphthalen-1-yl)propyl)-4-(trifluoromethyl)aniline (7):



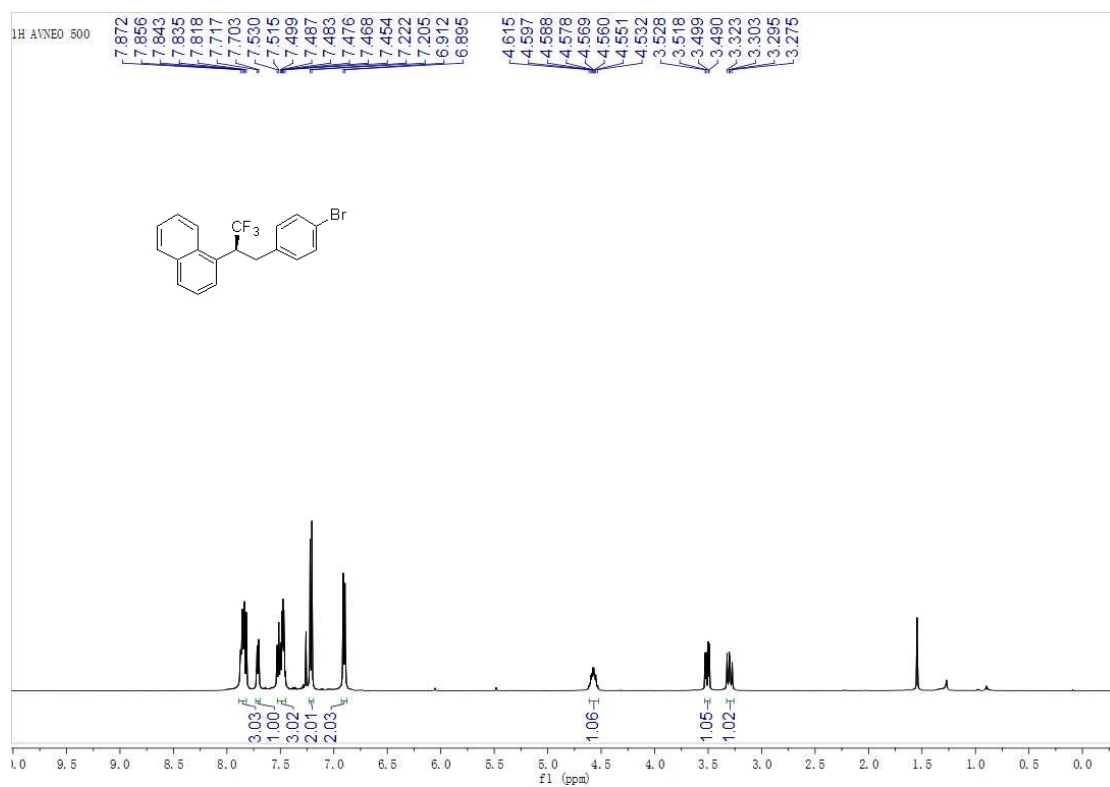
(S)-1-(1,1,1-trifluoropent-4-en-2-yl)naphthalene (8):

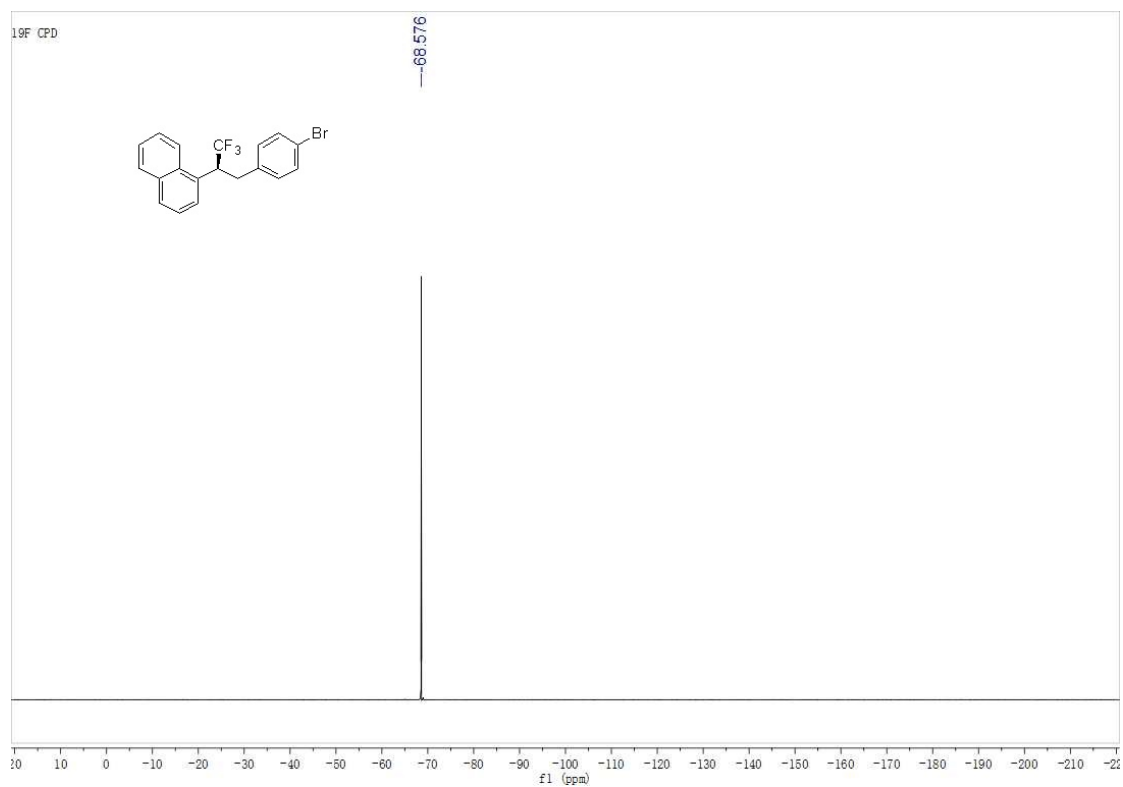
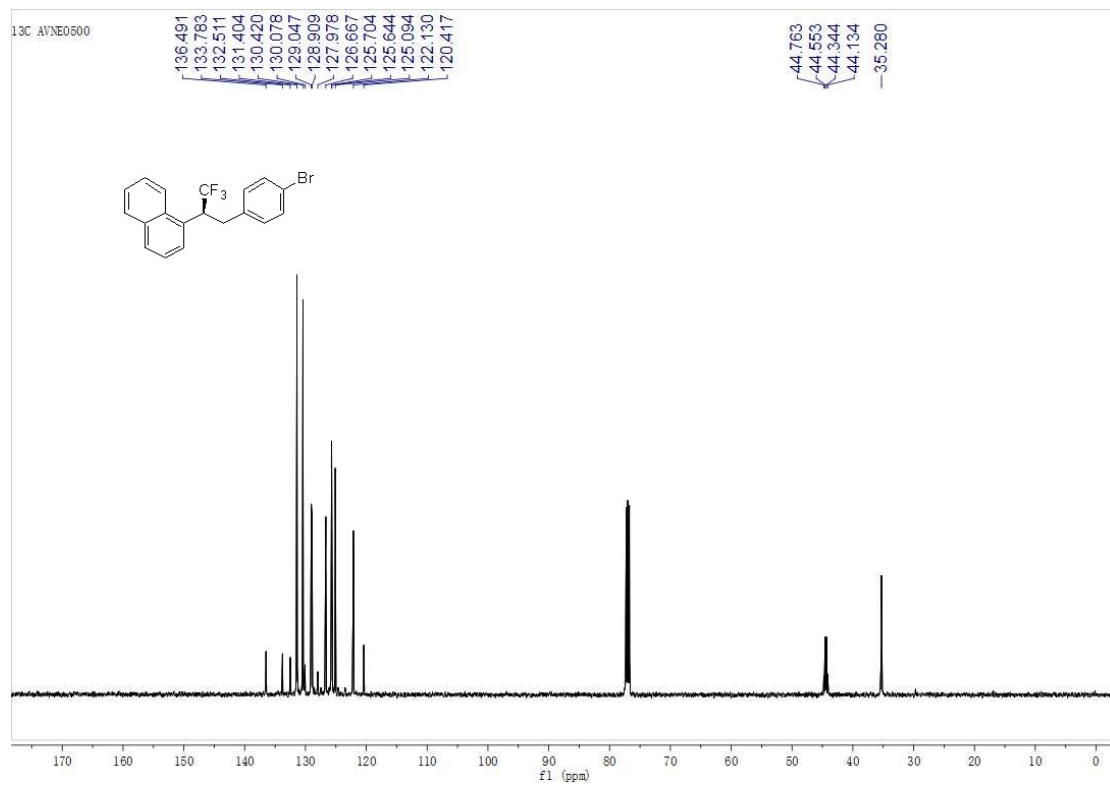


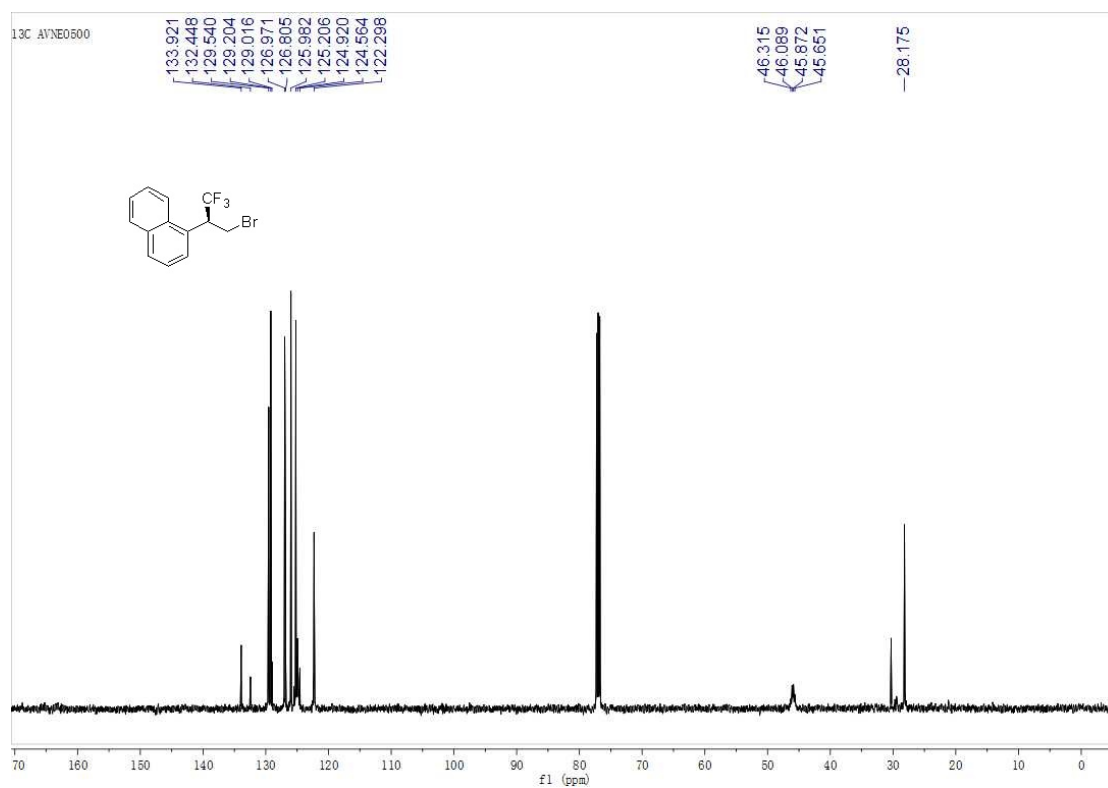
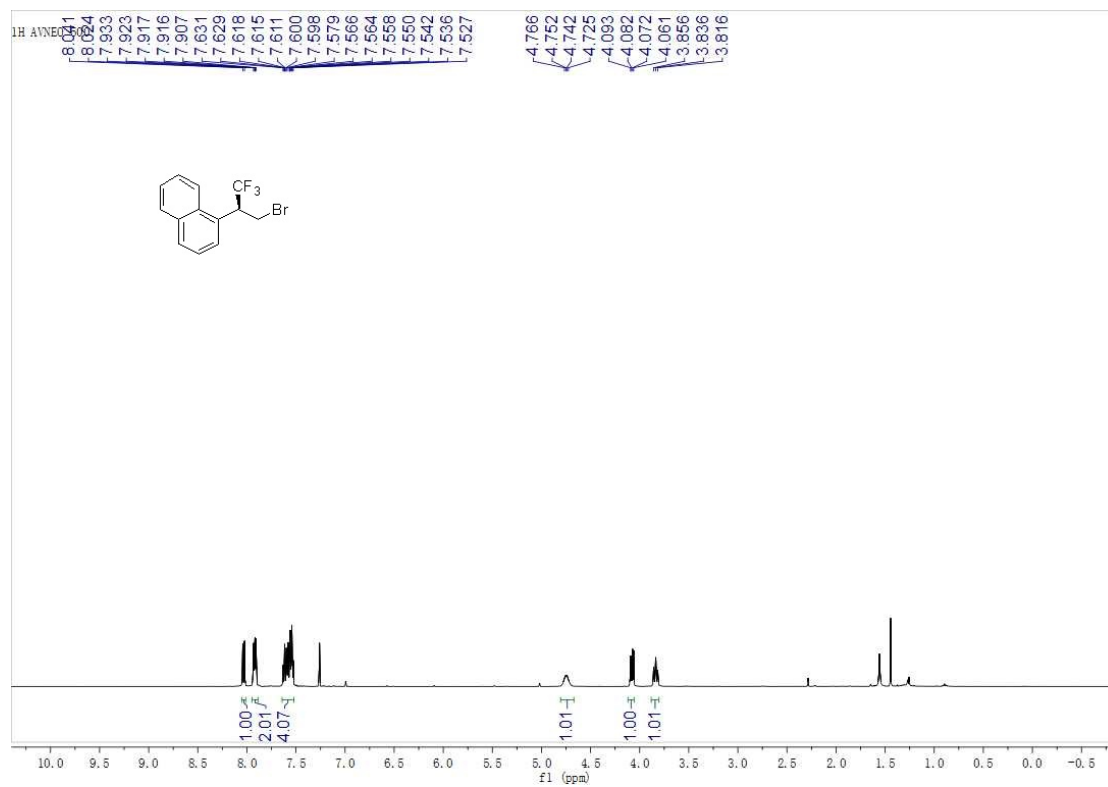
(S)-2-(3,3,3-trifluoro-2-(naphthalen-1-yl)propyl)thiophene (9):

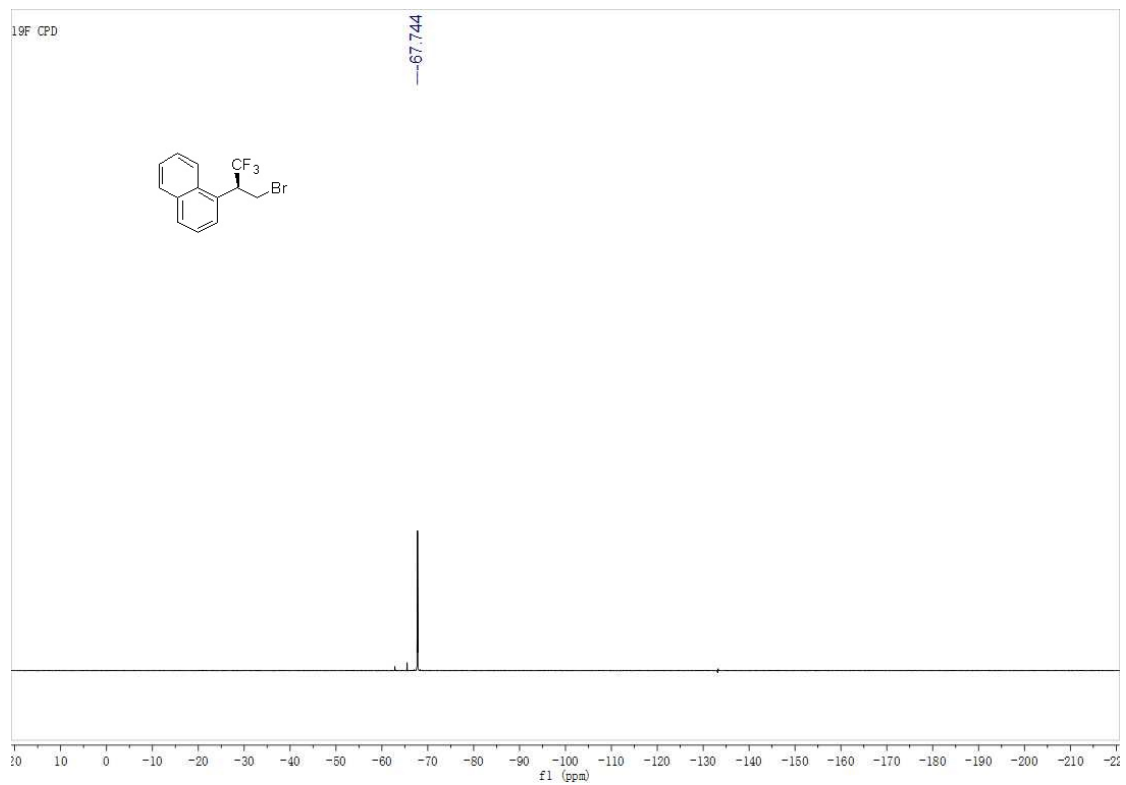


(S)-1-(3-(4-bromophenyl)-1,1,1-trifluoropropan-2-yl)naphthalene (10):

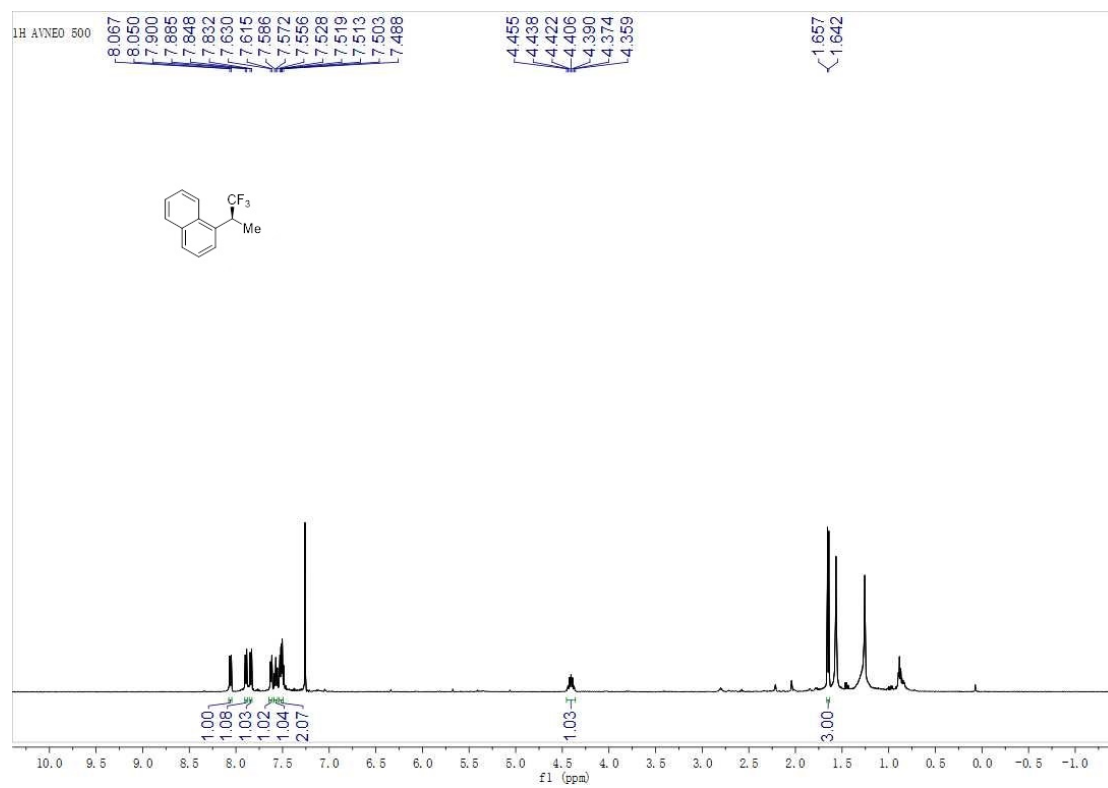


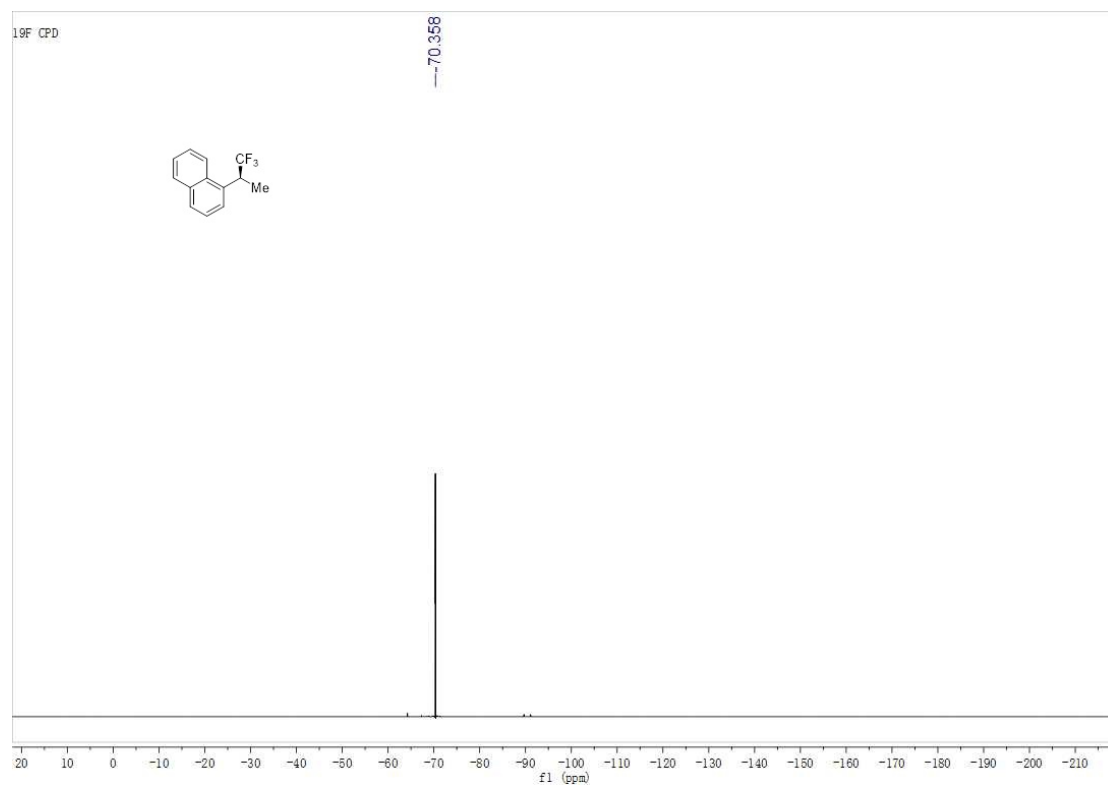
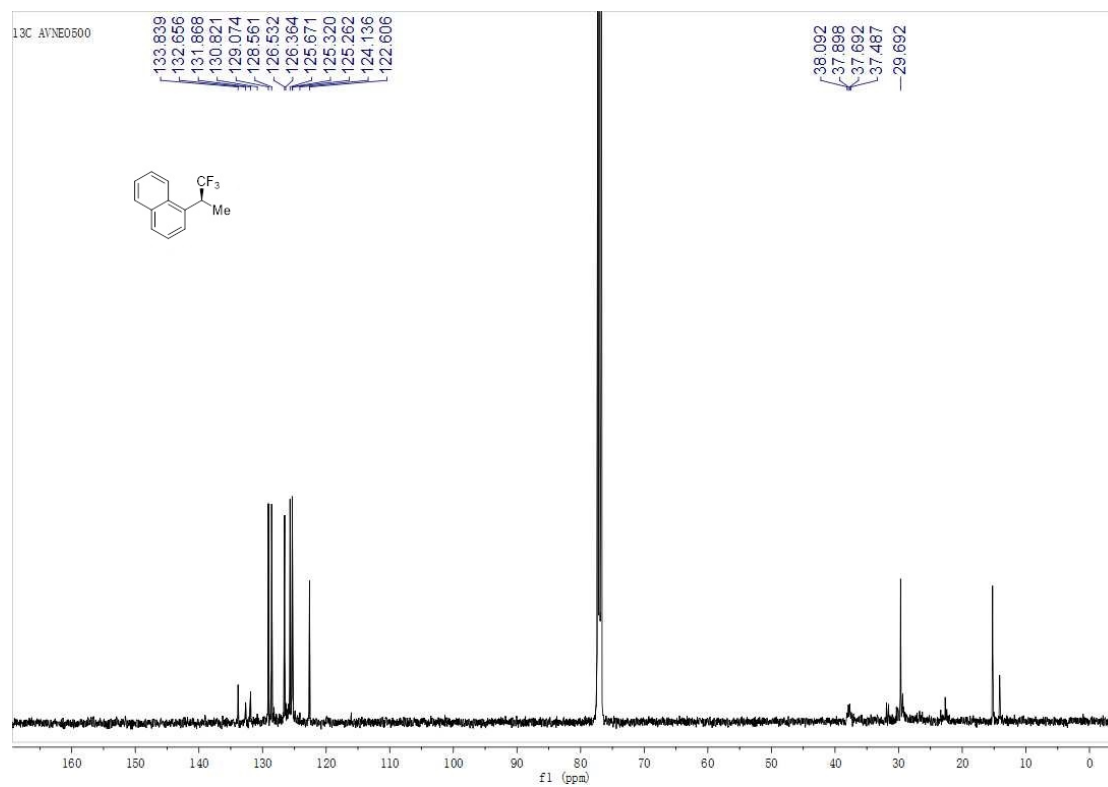


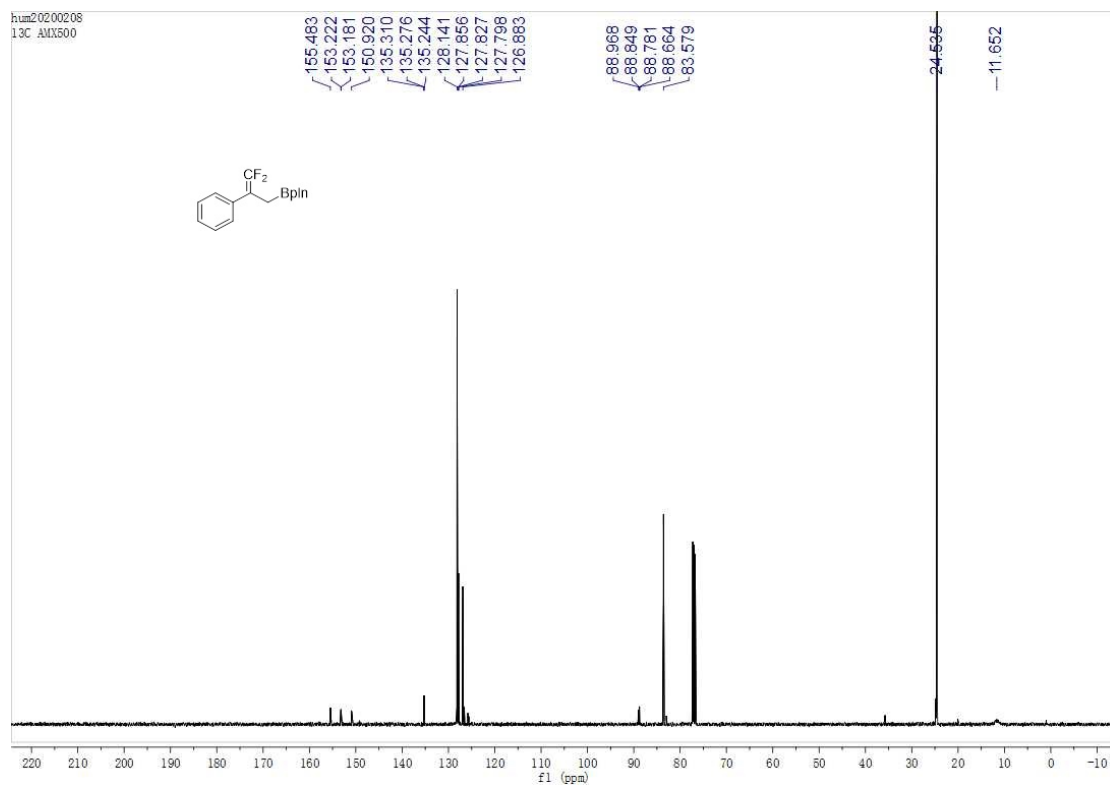
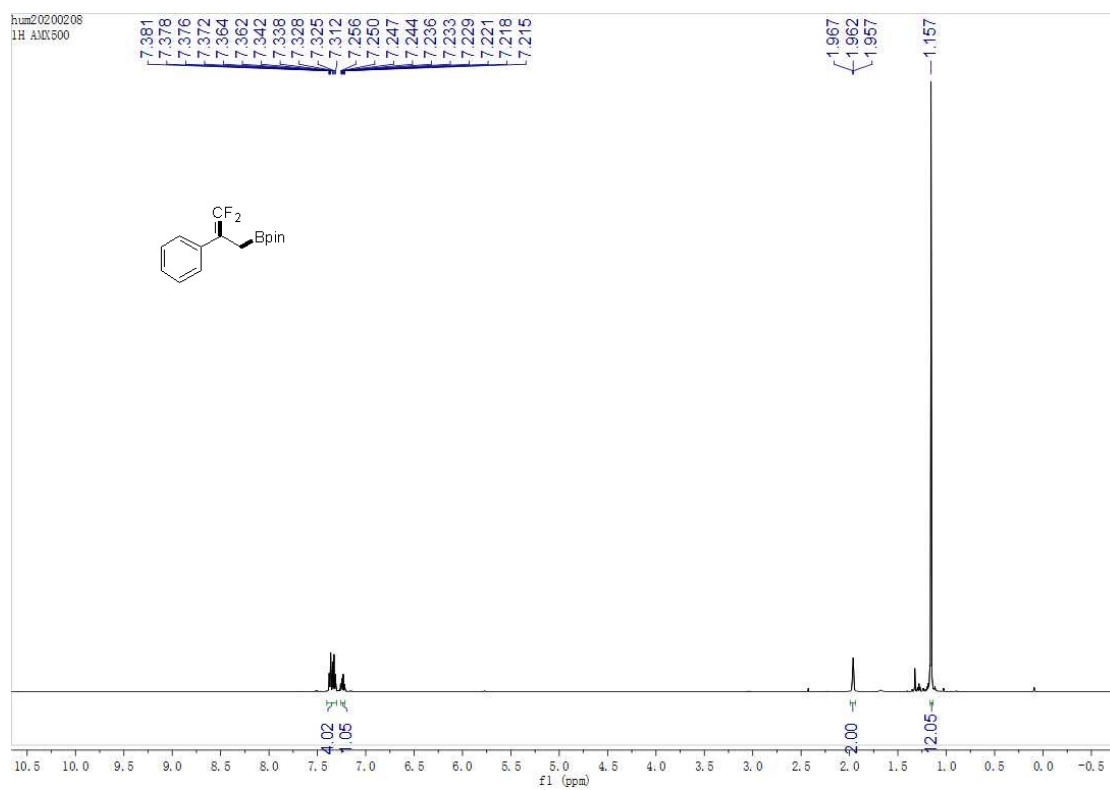
(S)-1-(3-bromo-1,1,1-trifluoropropan-2-yl)naphthalene (11):

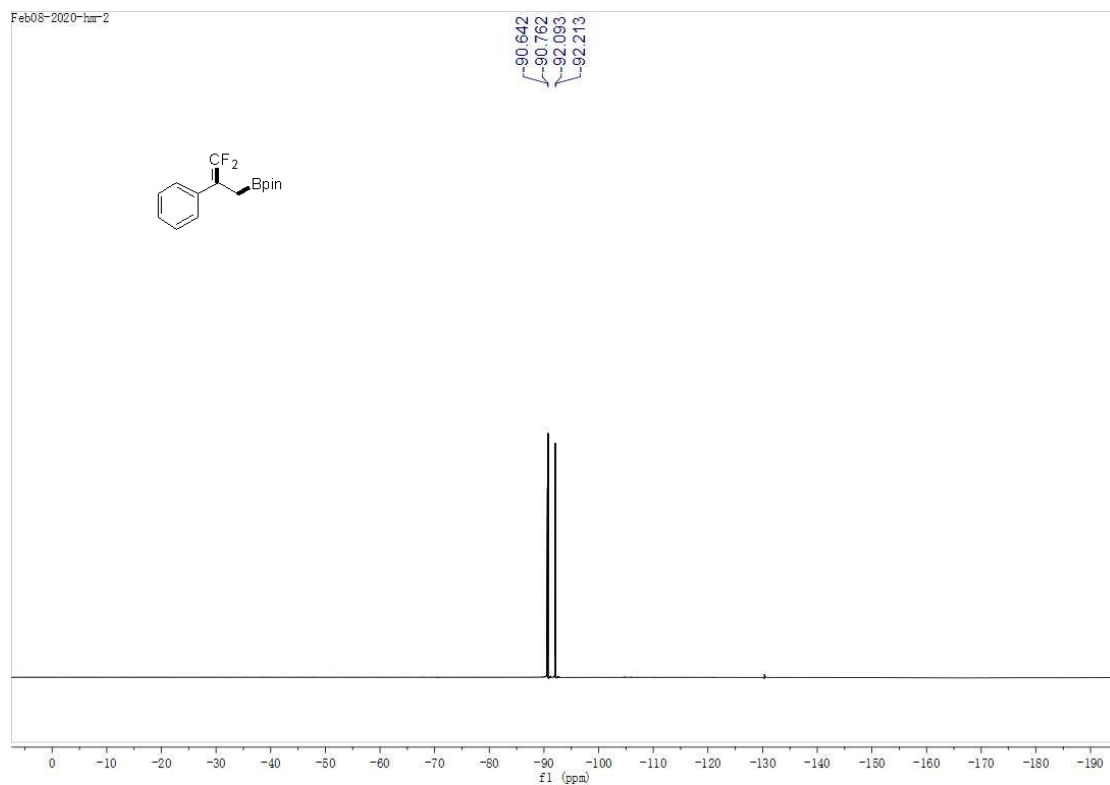


(S)-1-(1,1,1-trifluoropropan-2-yl)naphthalene (12):

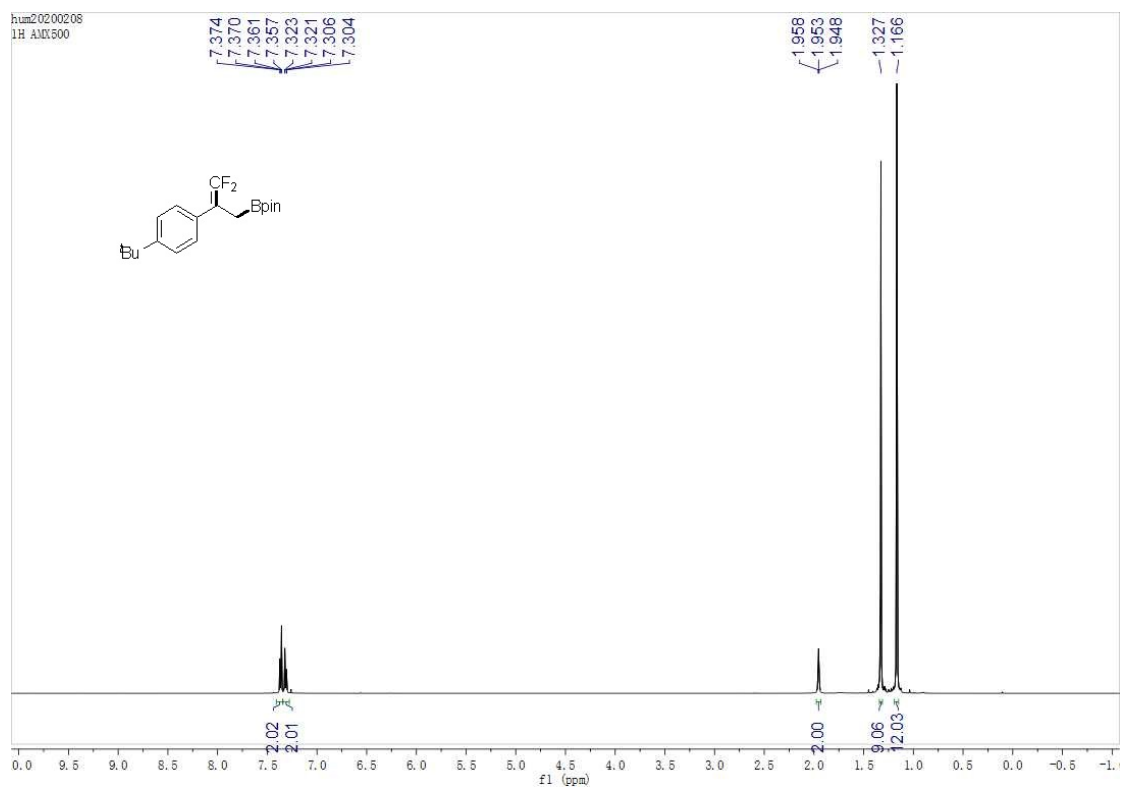


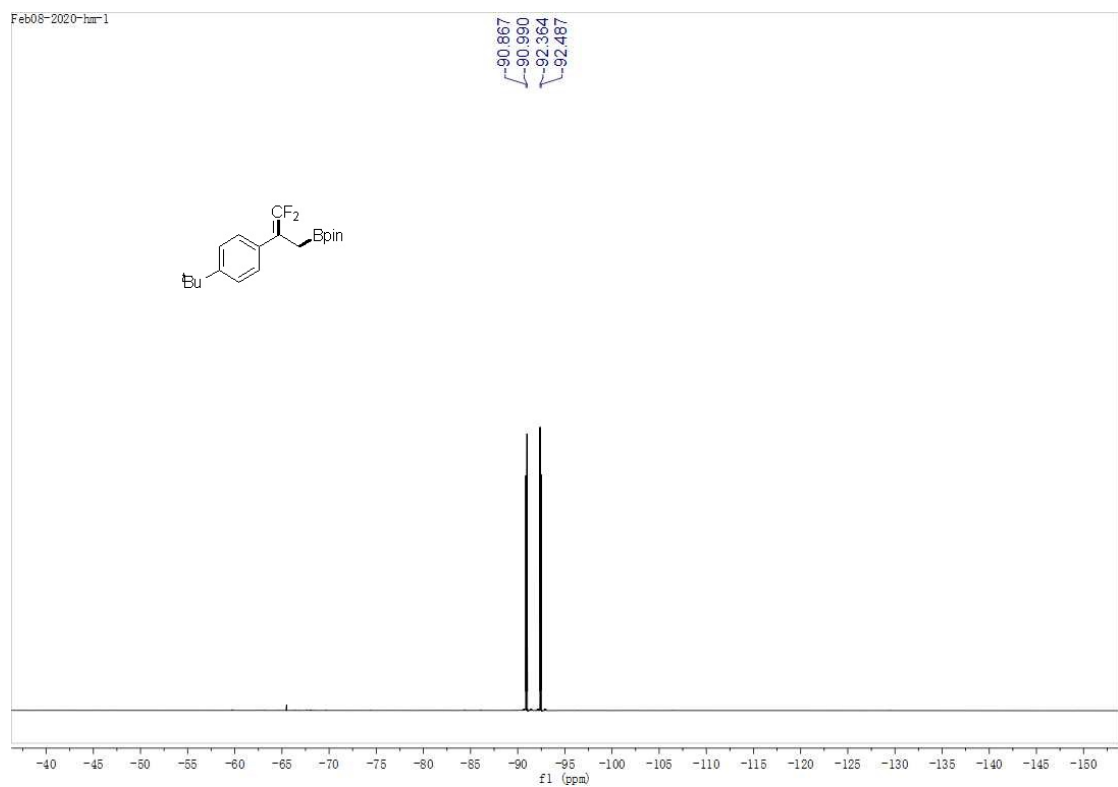
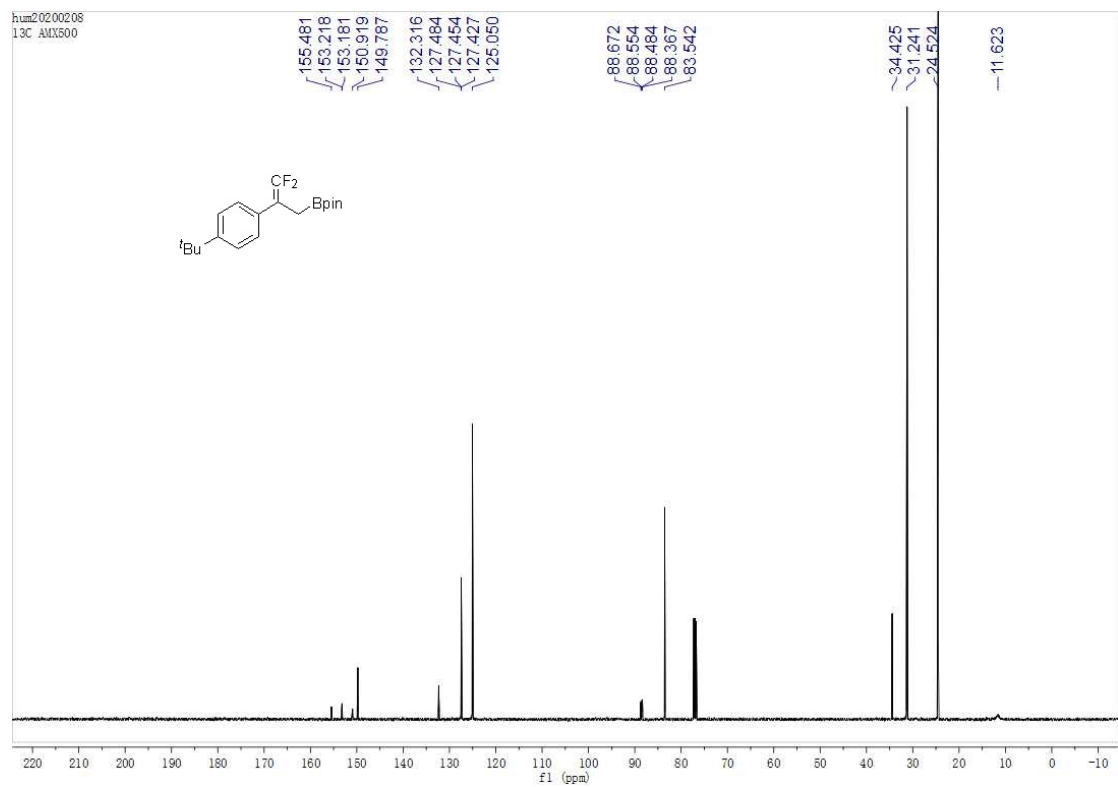


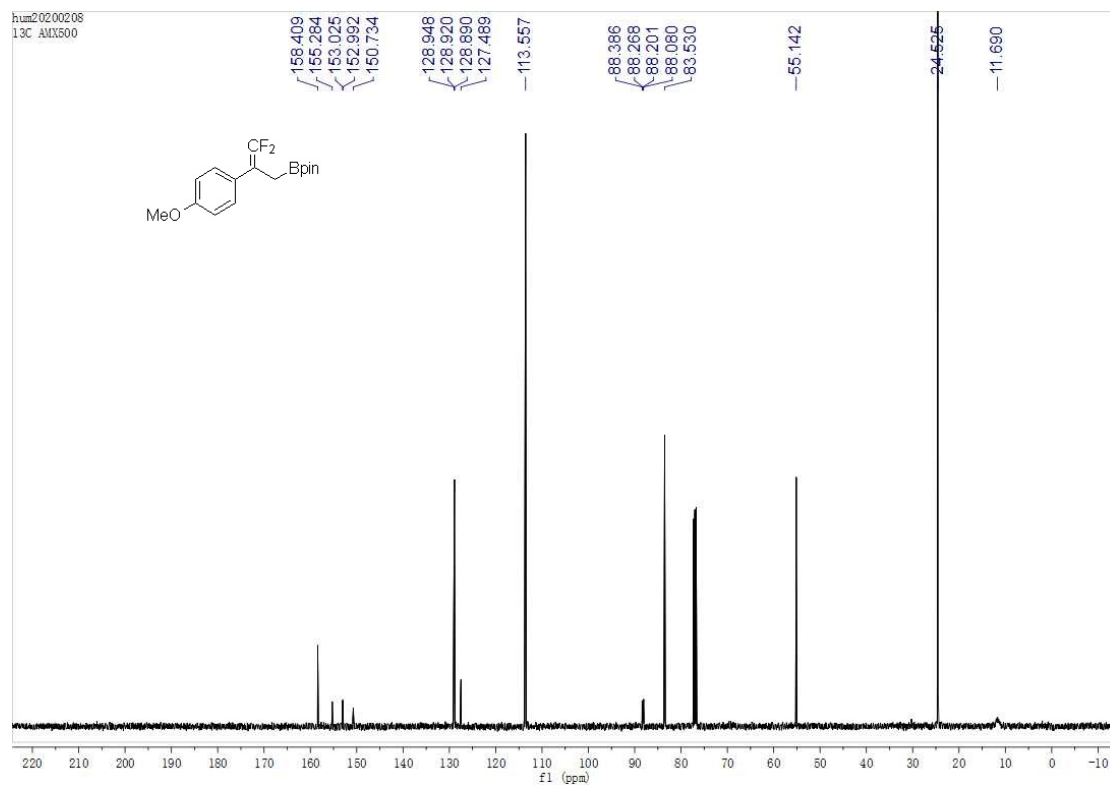
2-(3,3-Difluoro-2-phenylallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a):

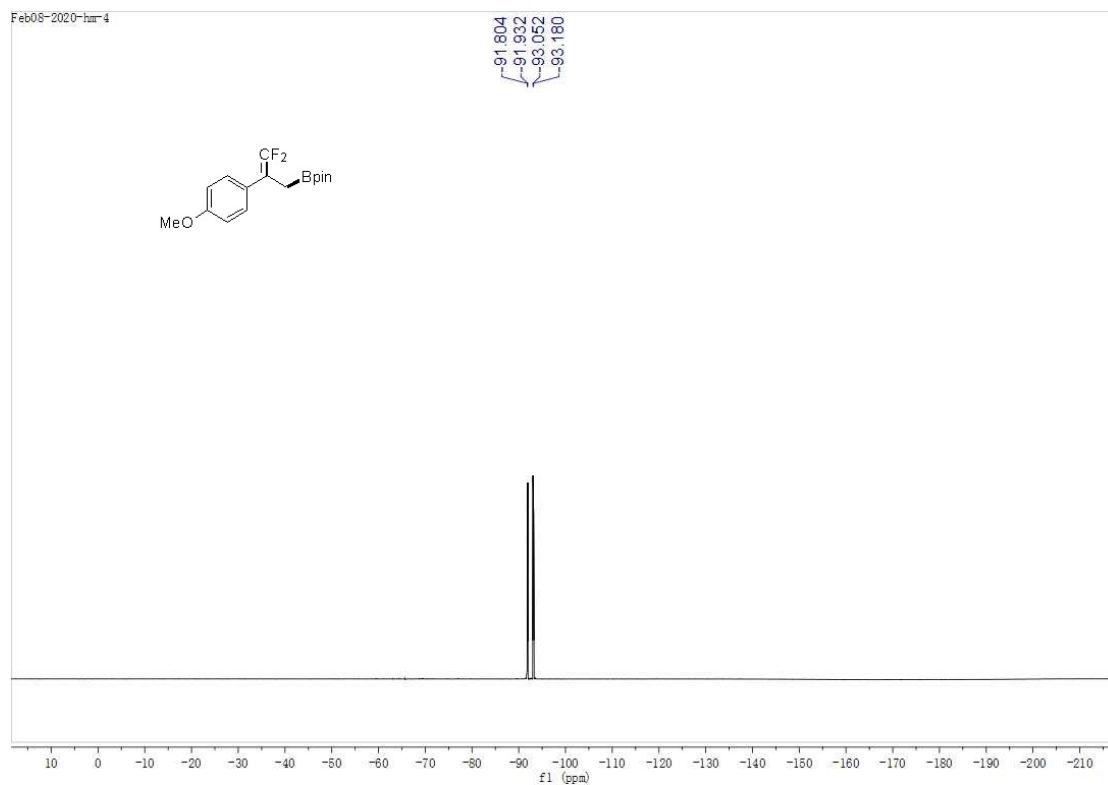


2-(2-(4-(*tert*-Butyl)phenyl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c):

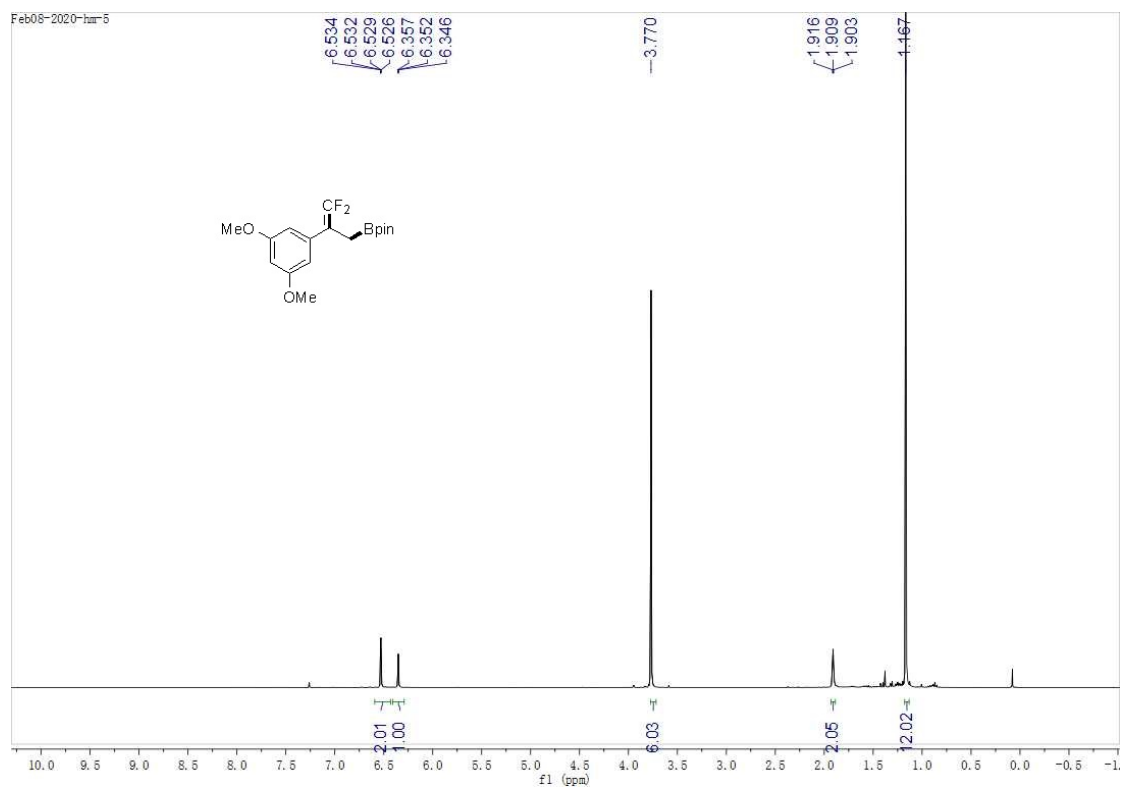


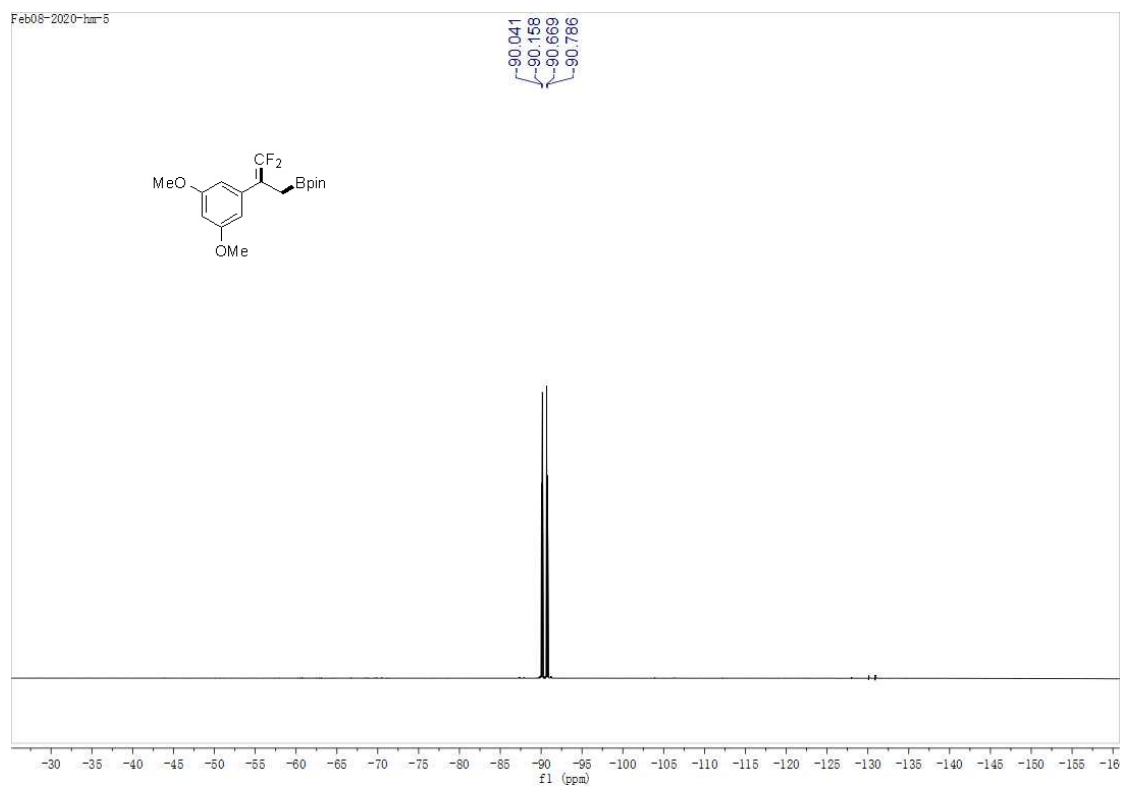
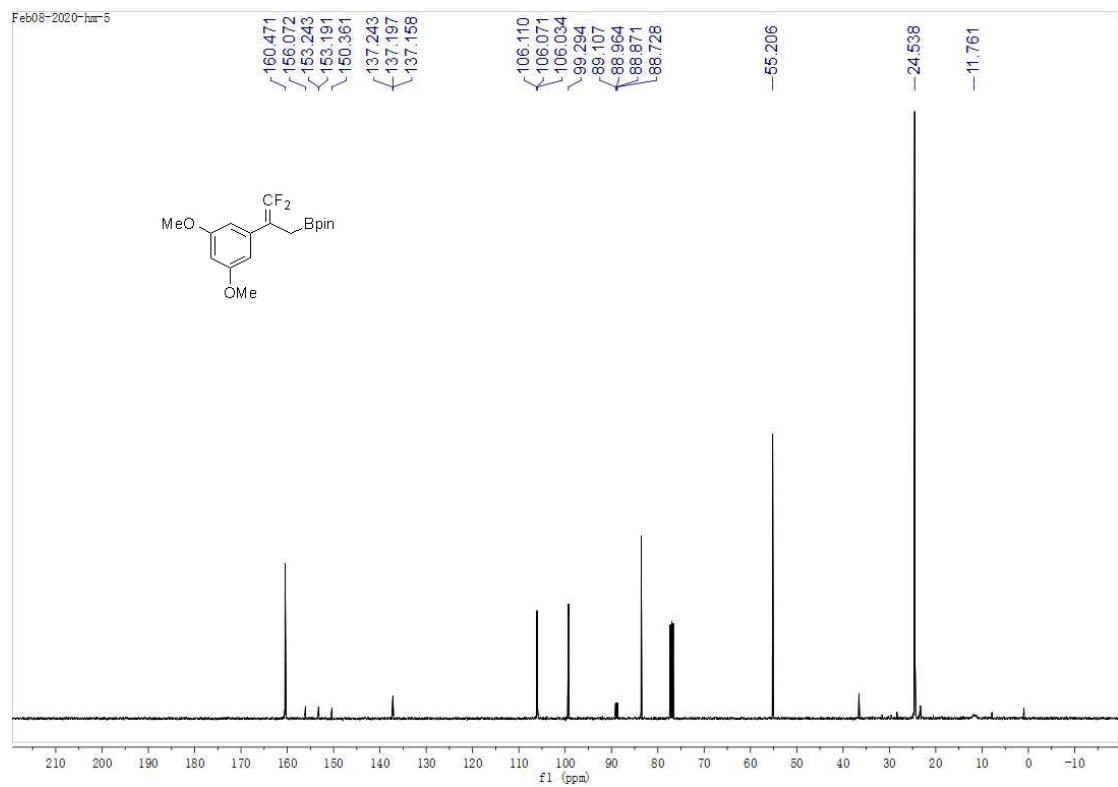


2-(3,3-Difluoro-2-(4-methoxyphenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan
e (5d):

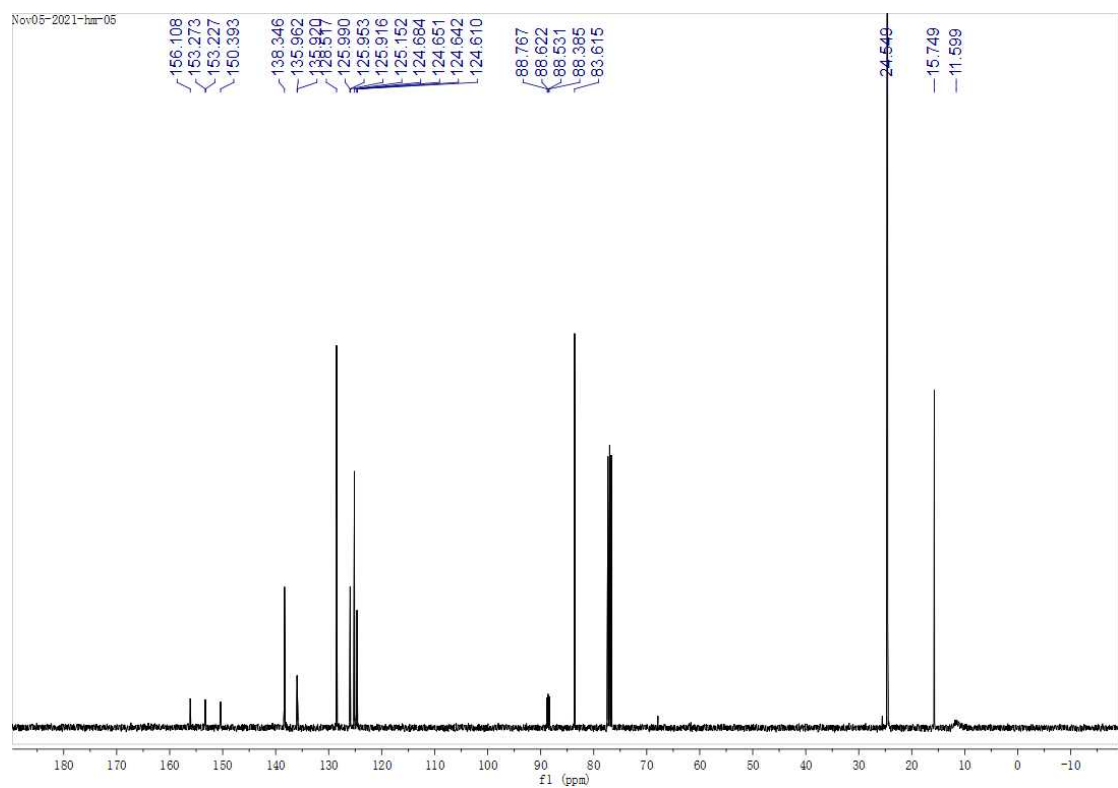
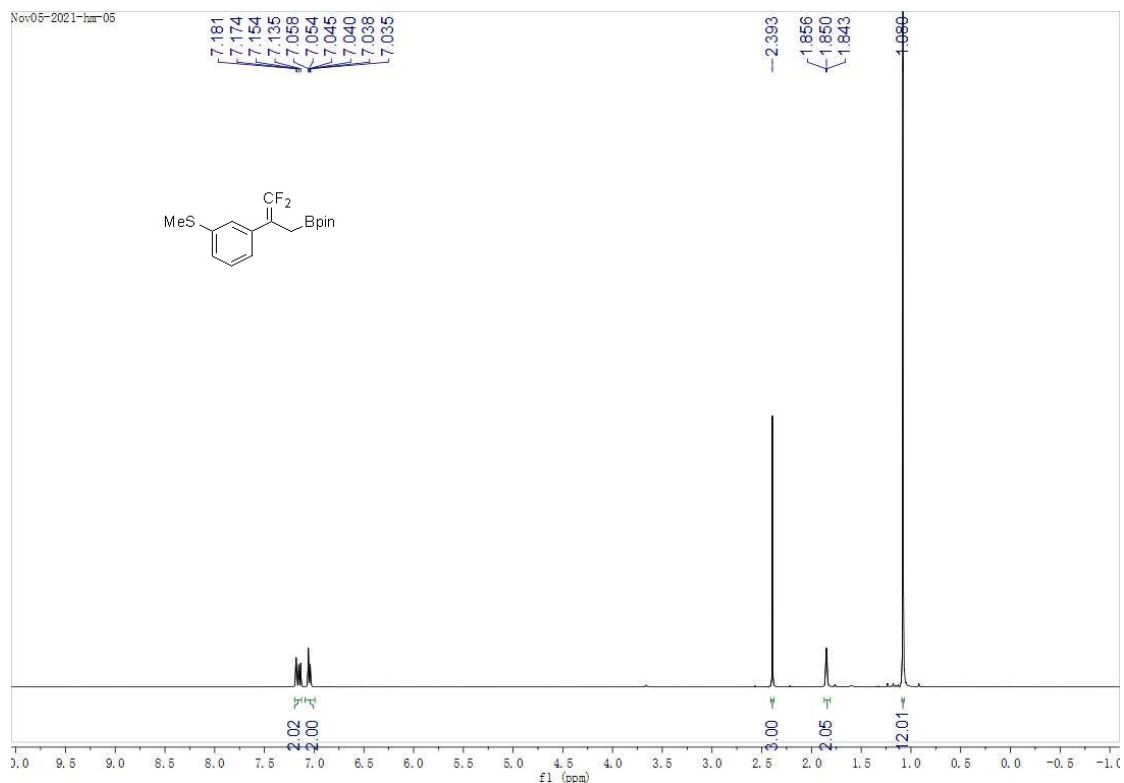


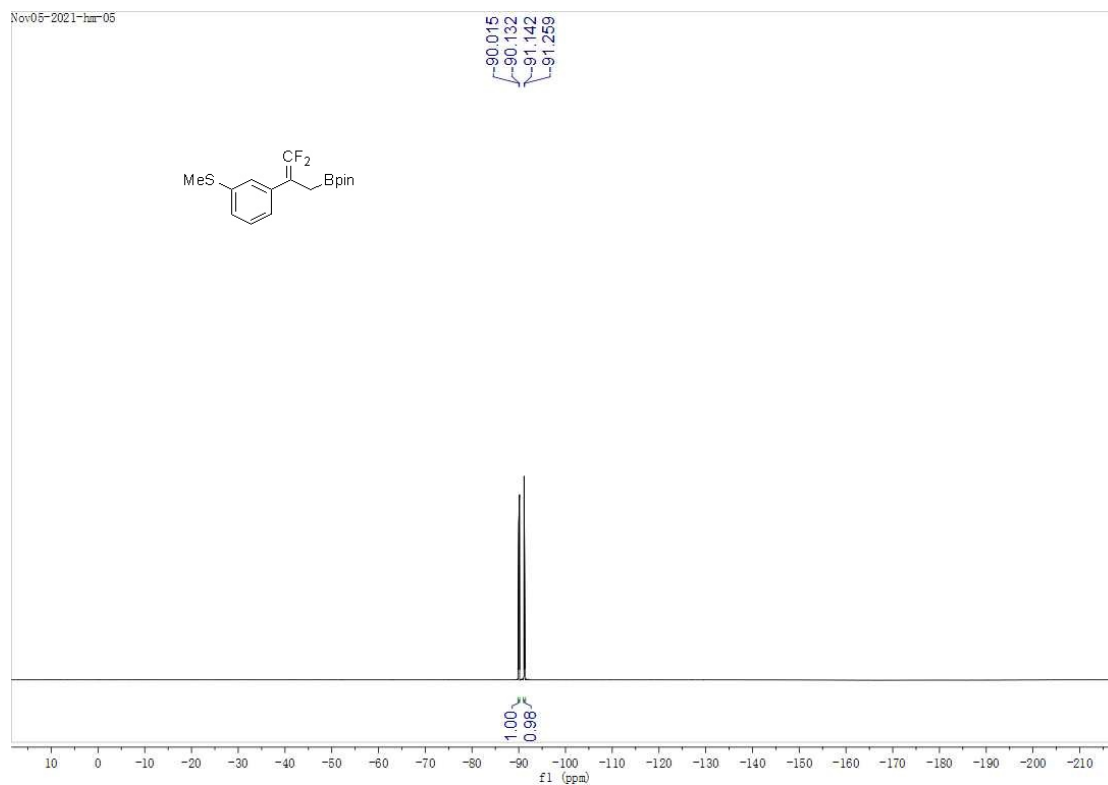
2-(2-(3,5-Dimethoxyphenyl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e):



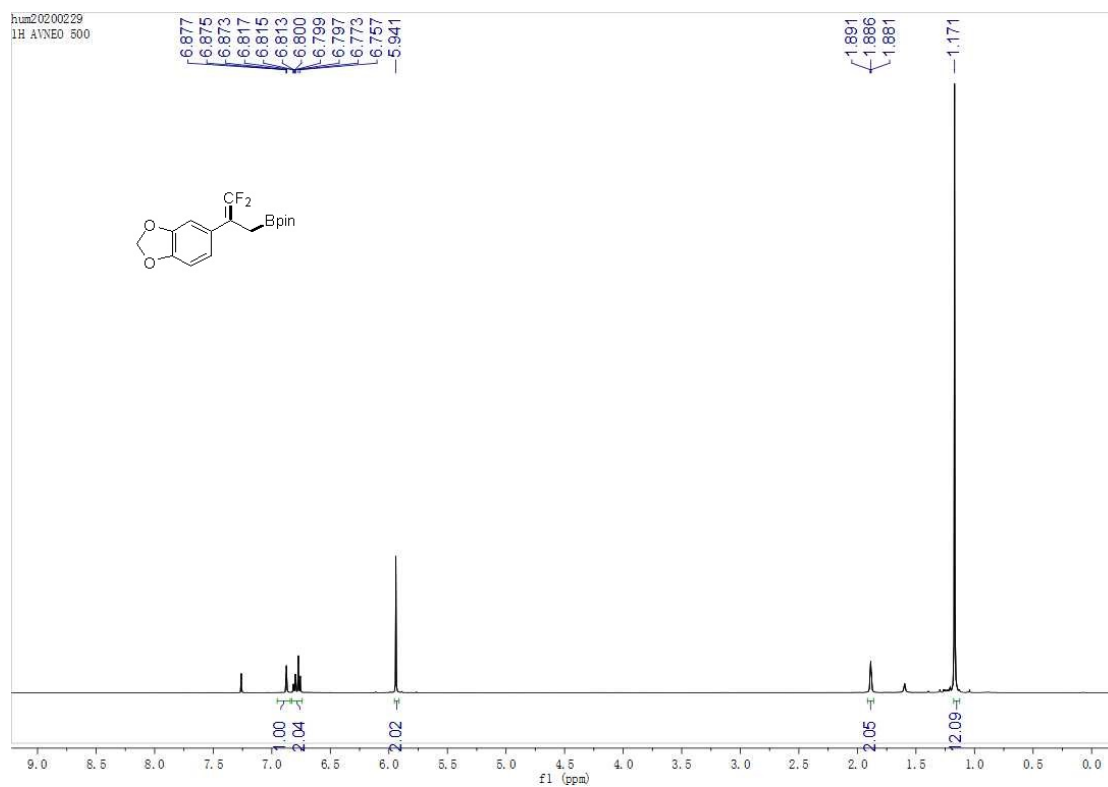


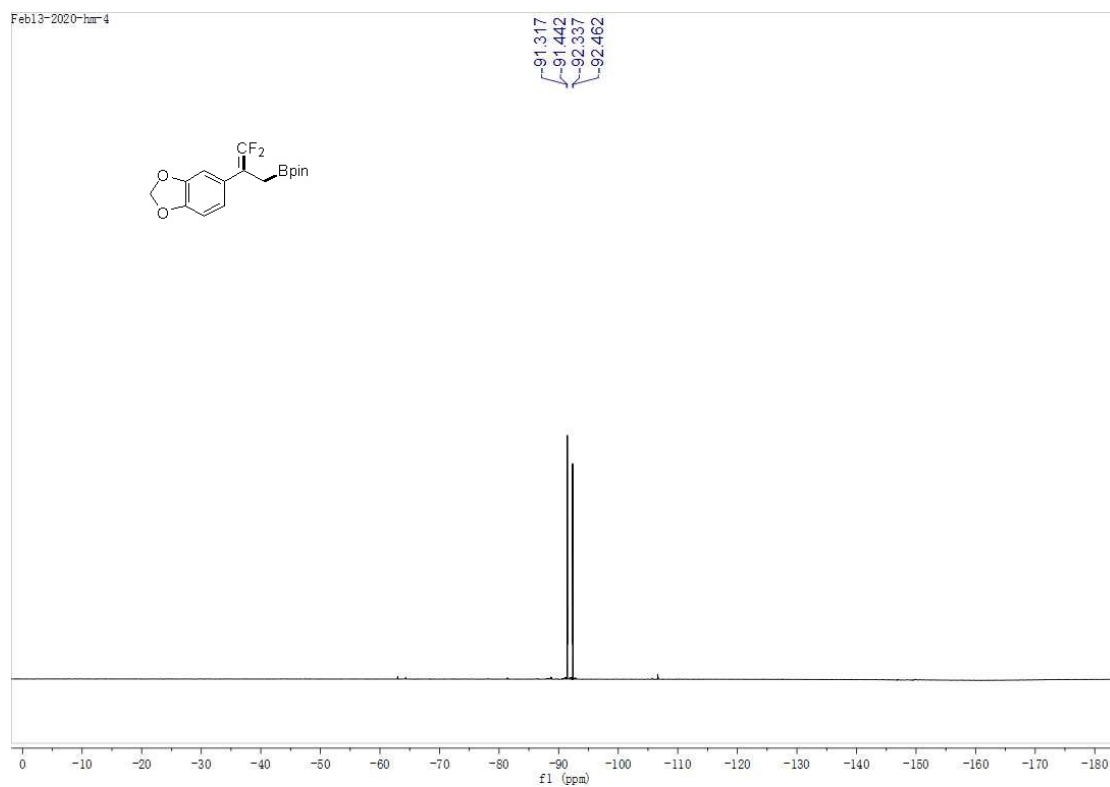
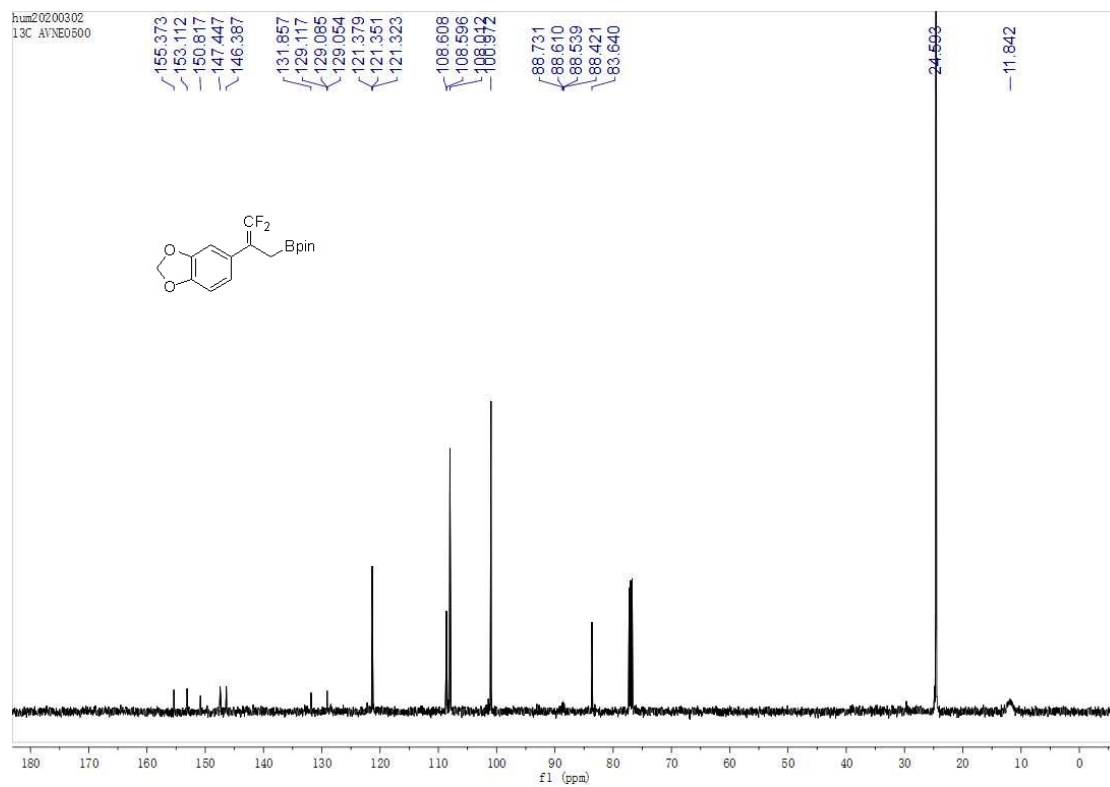
2-(3,3-difluoro-2-(3-(methylthio)phenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5g):

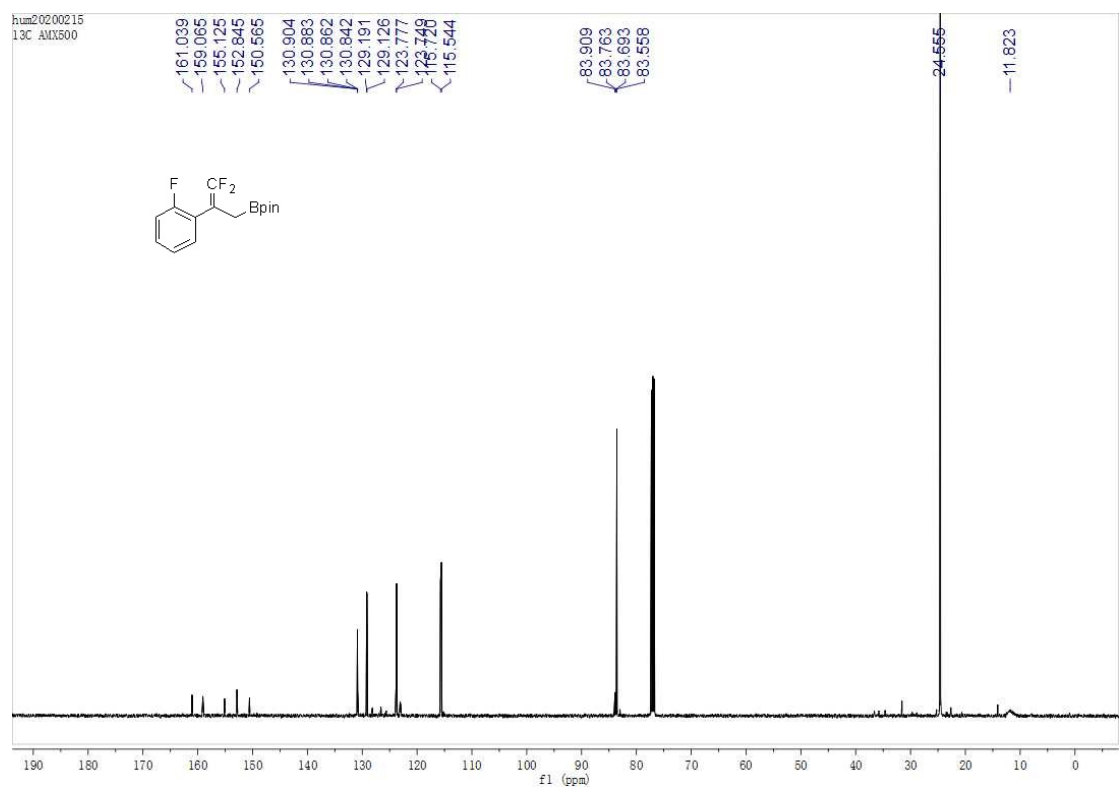
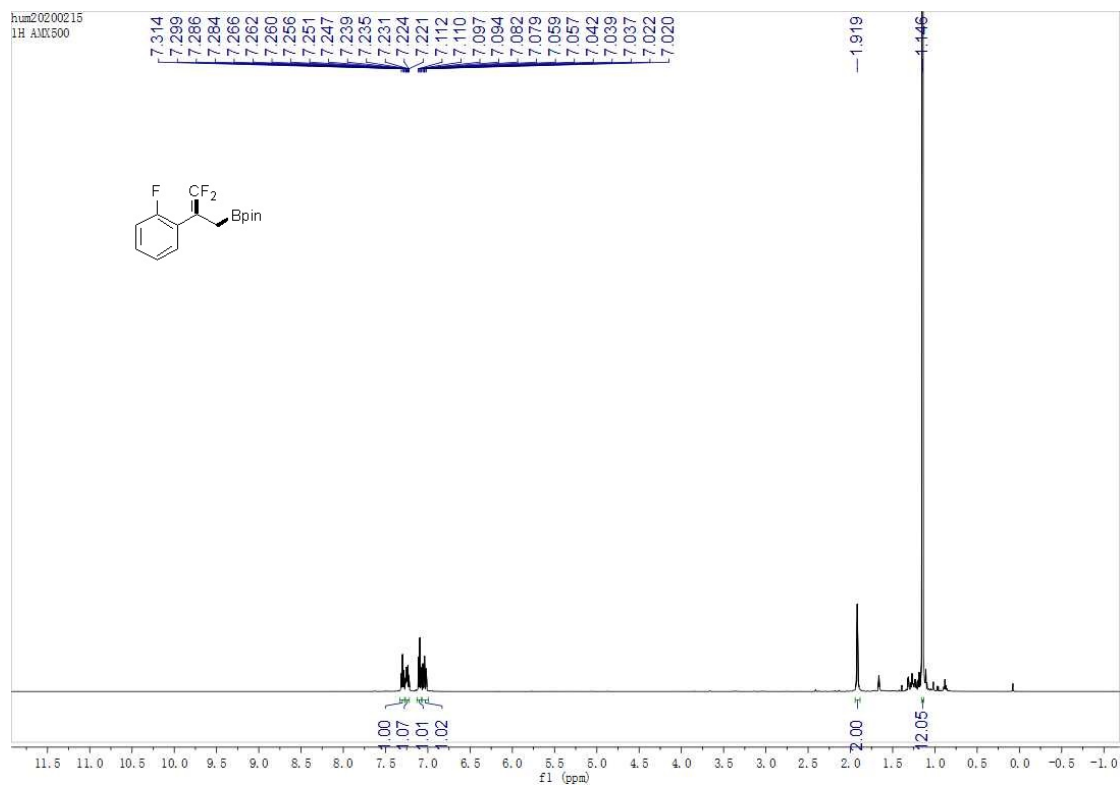


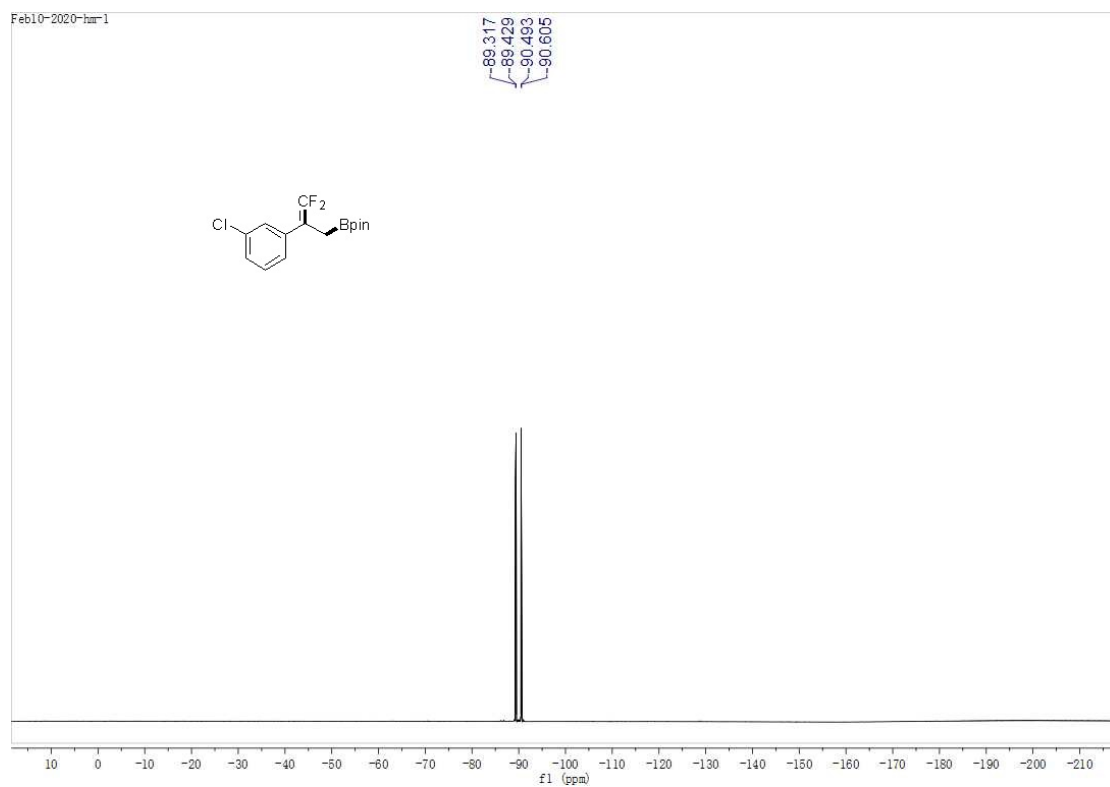
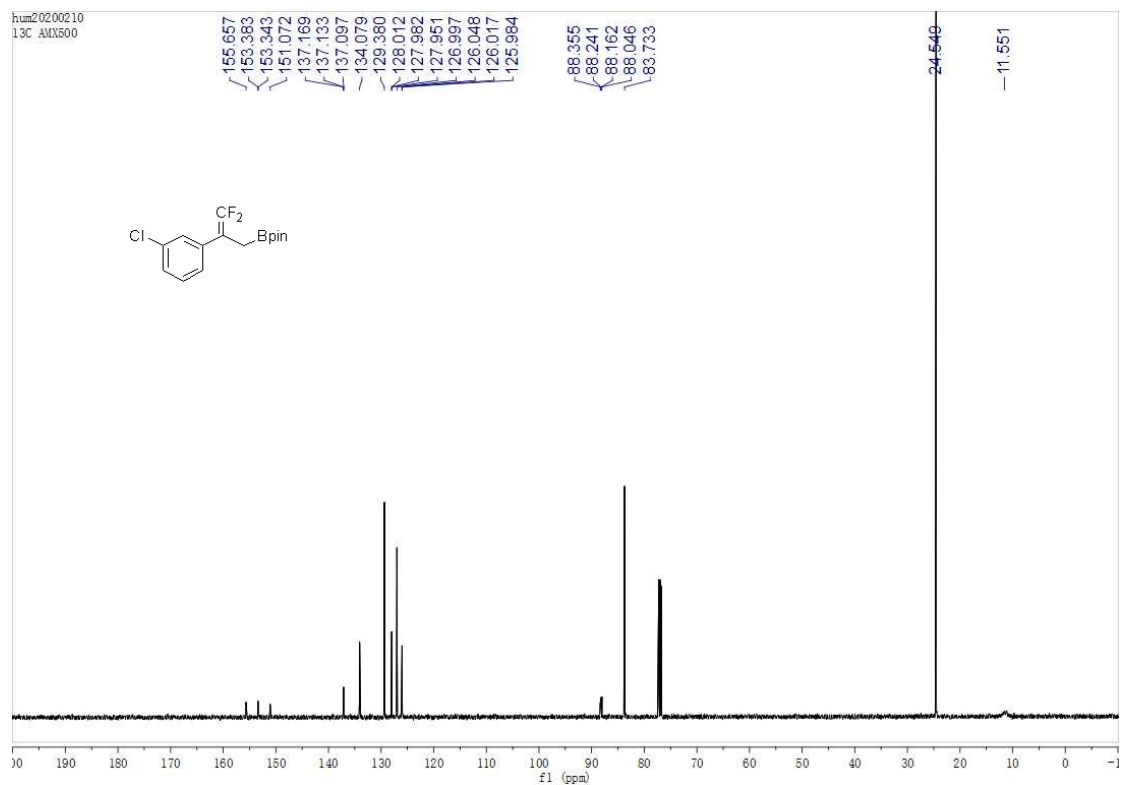


**2-(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxab
orolane (5k):**

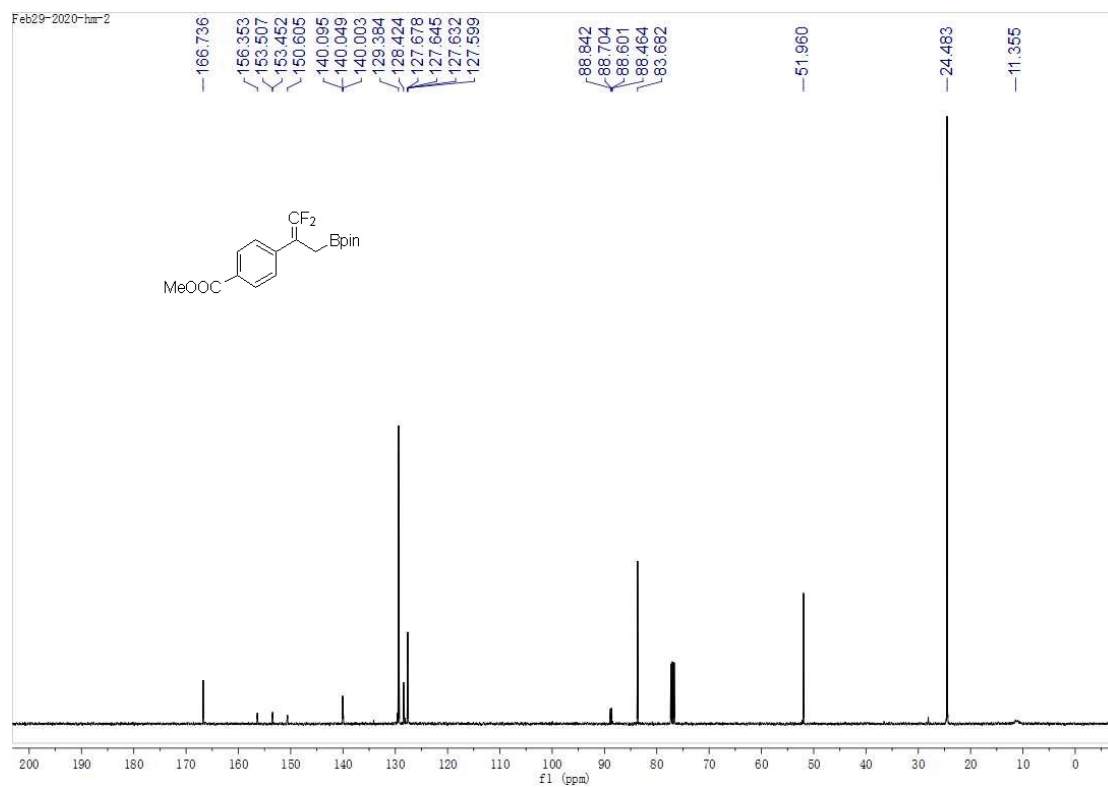
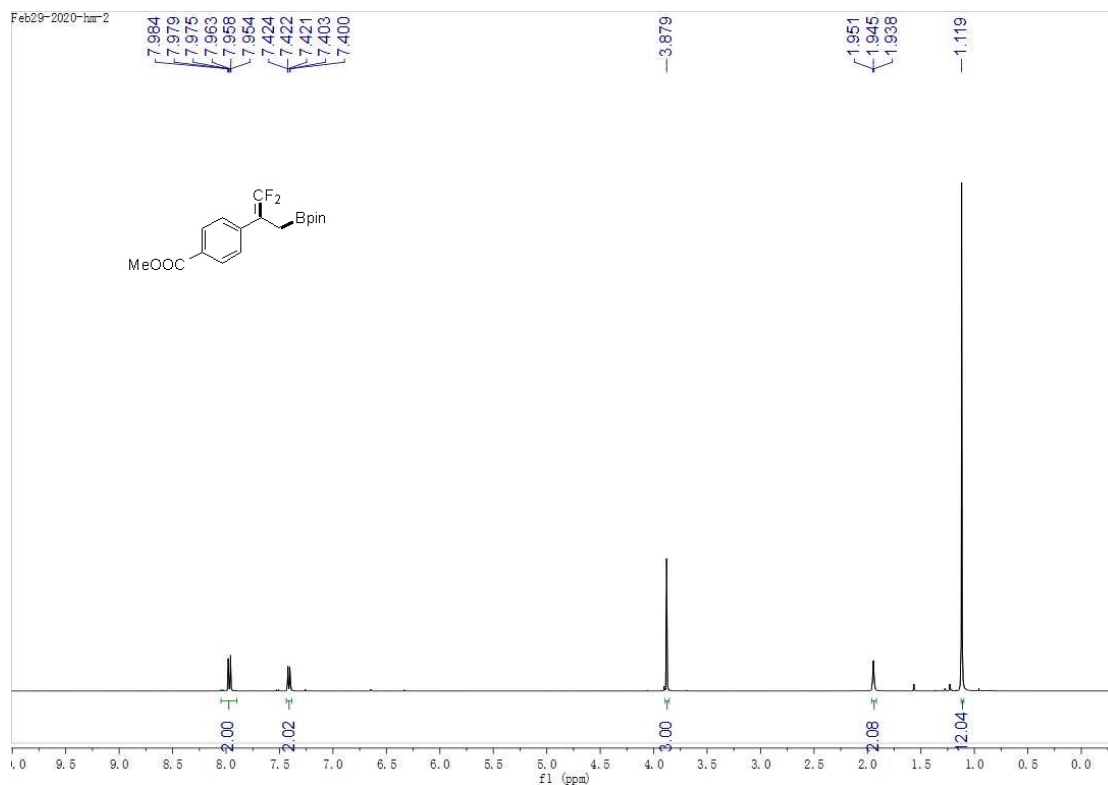


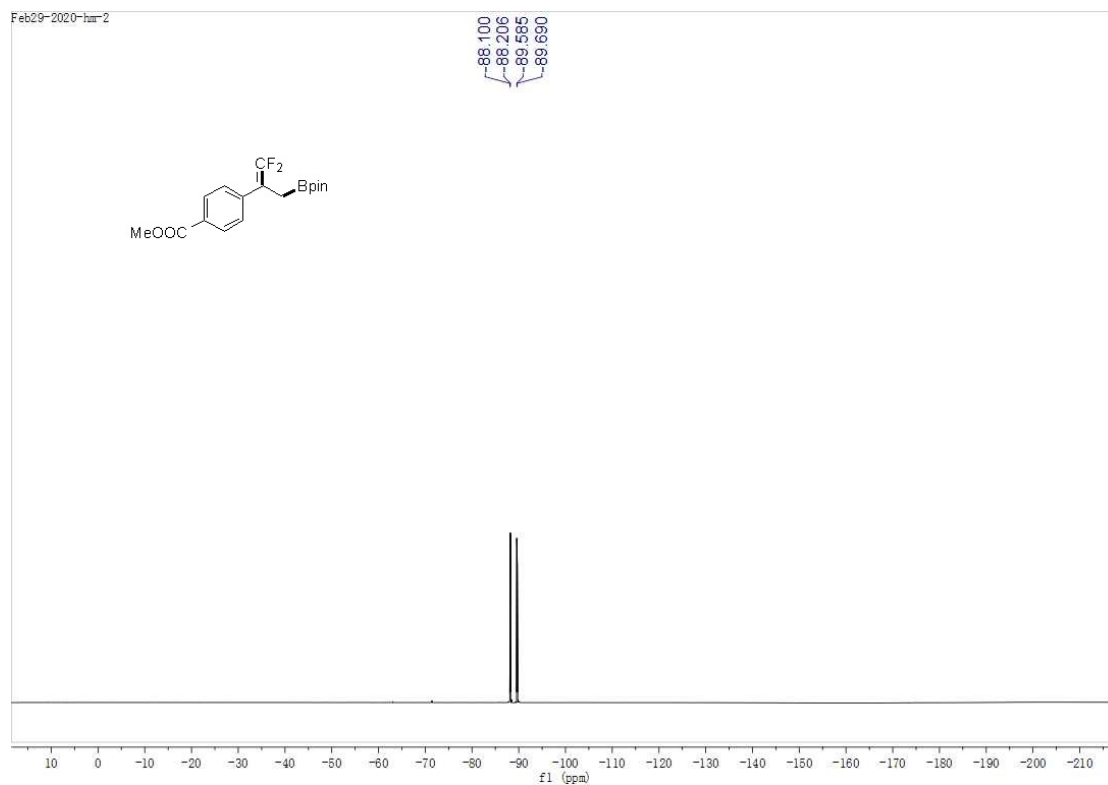
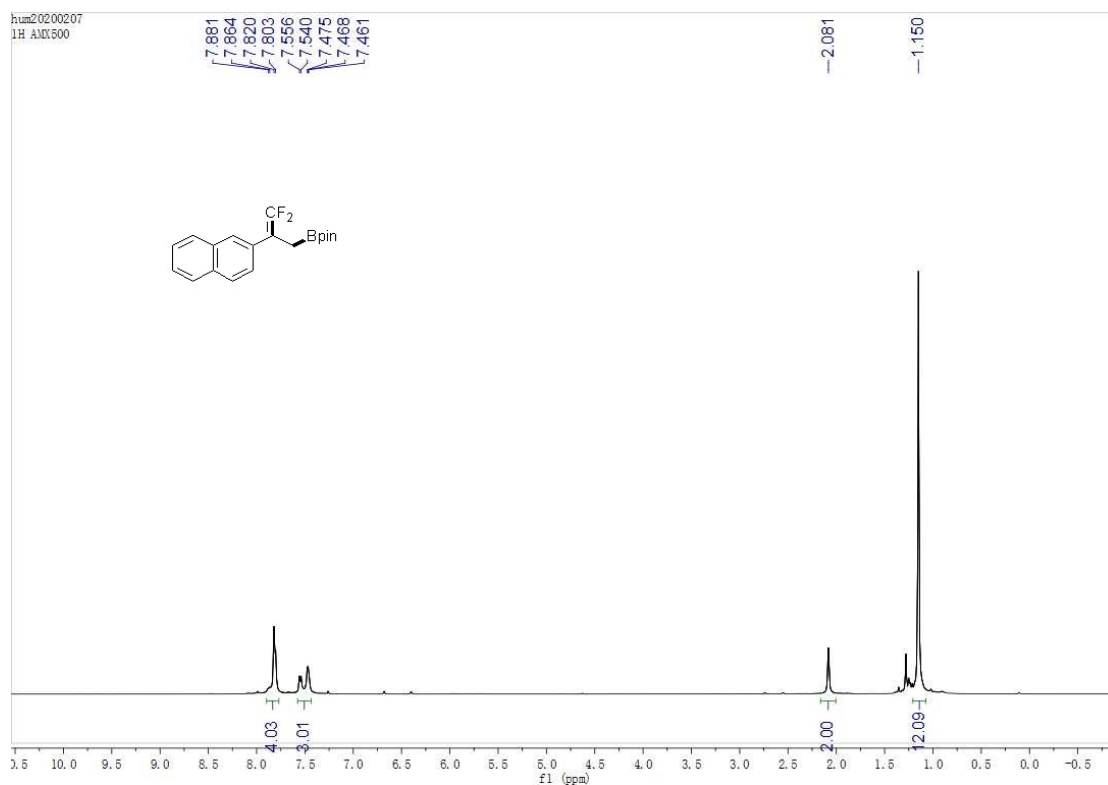


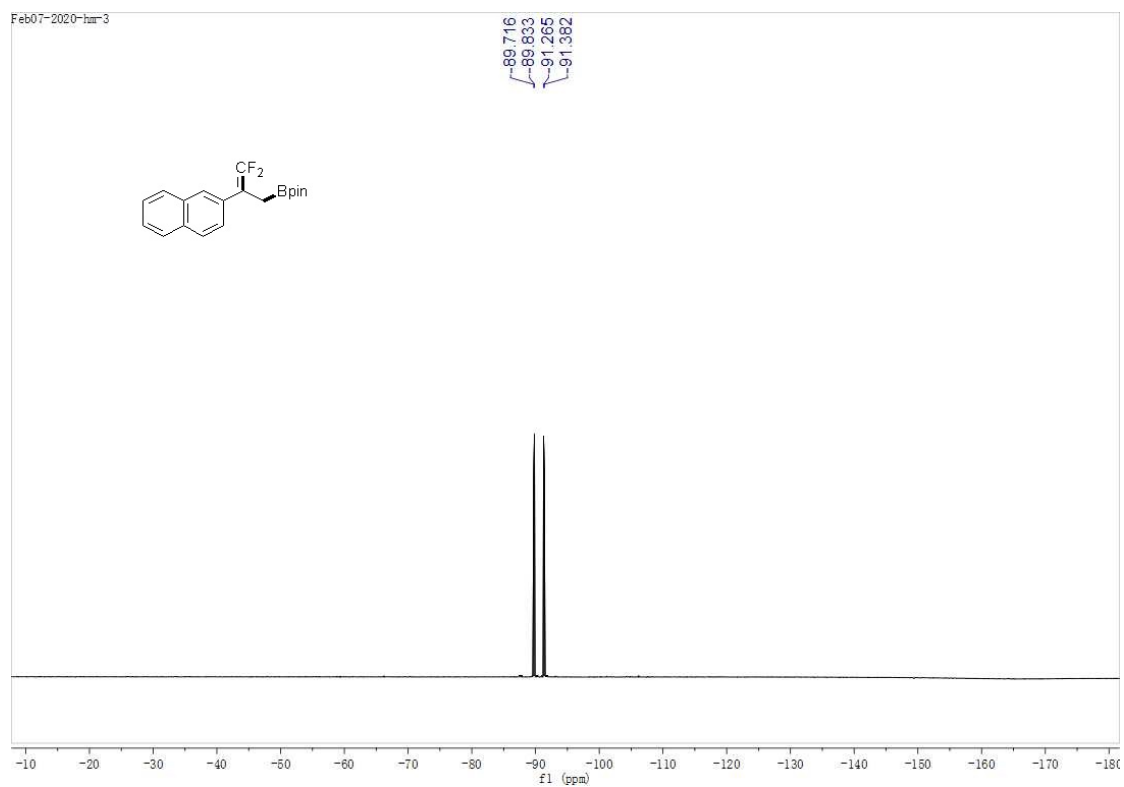
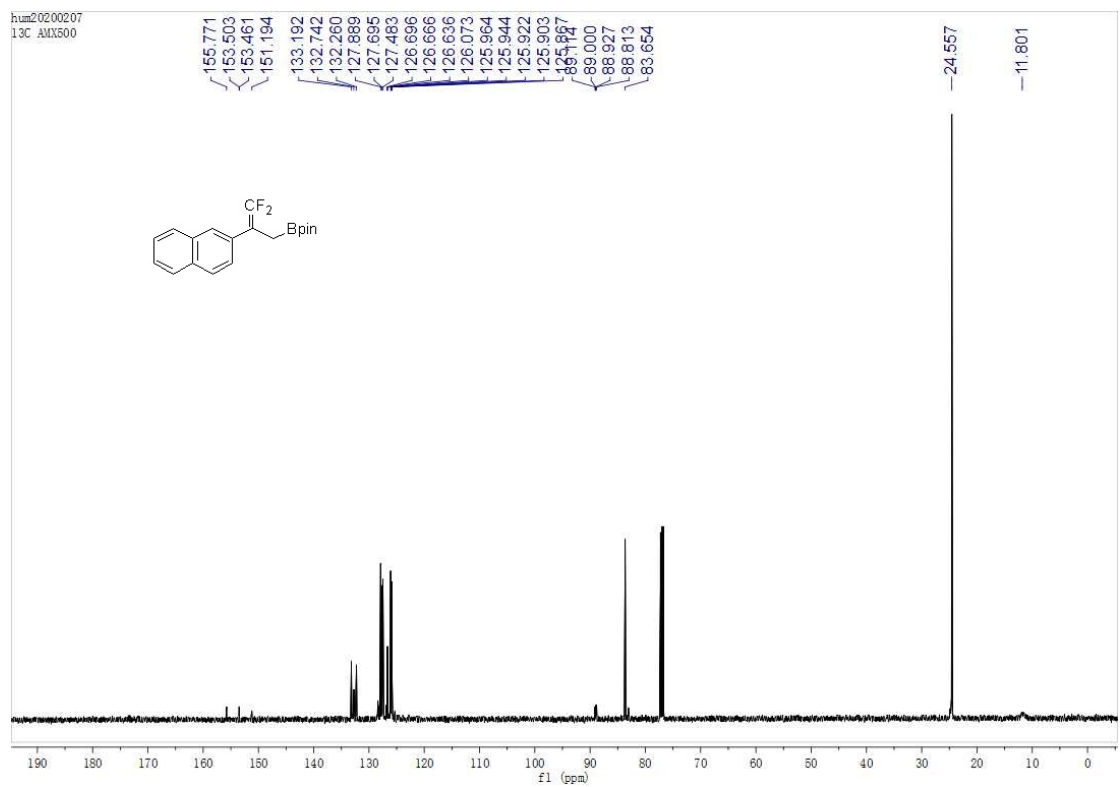
2-(3,3-Difluoro-2-(2-fluorophenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**(5n):**

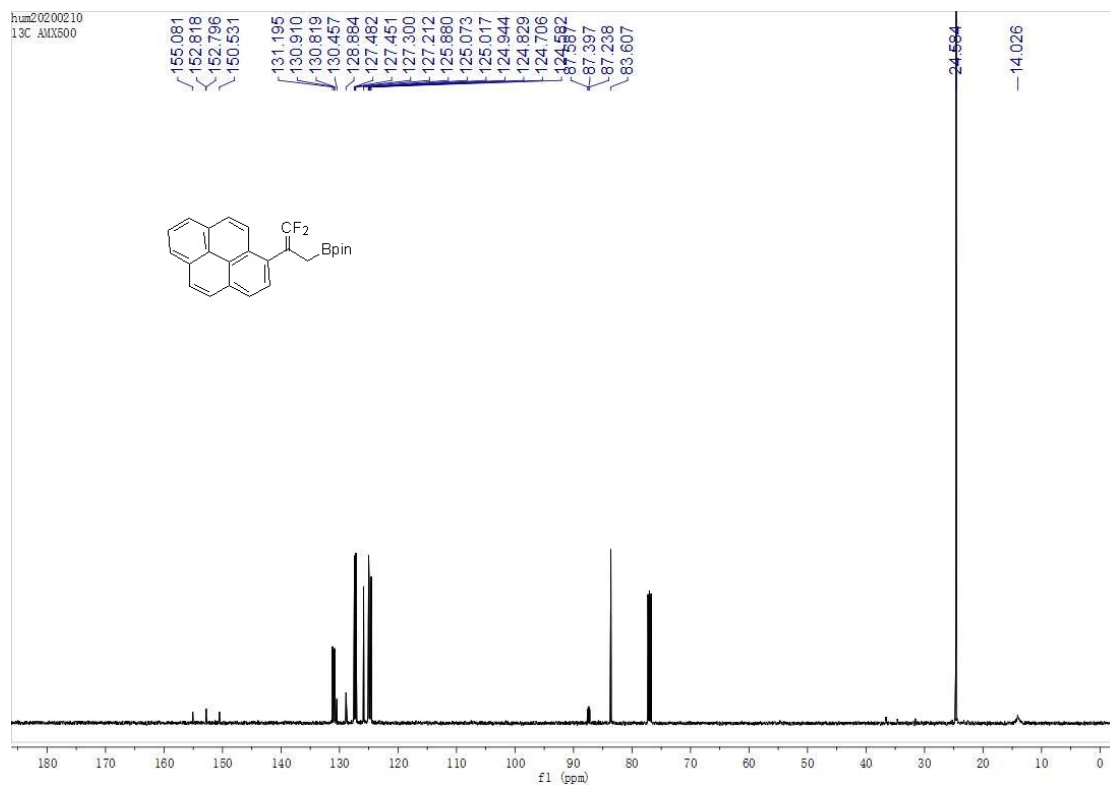
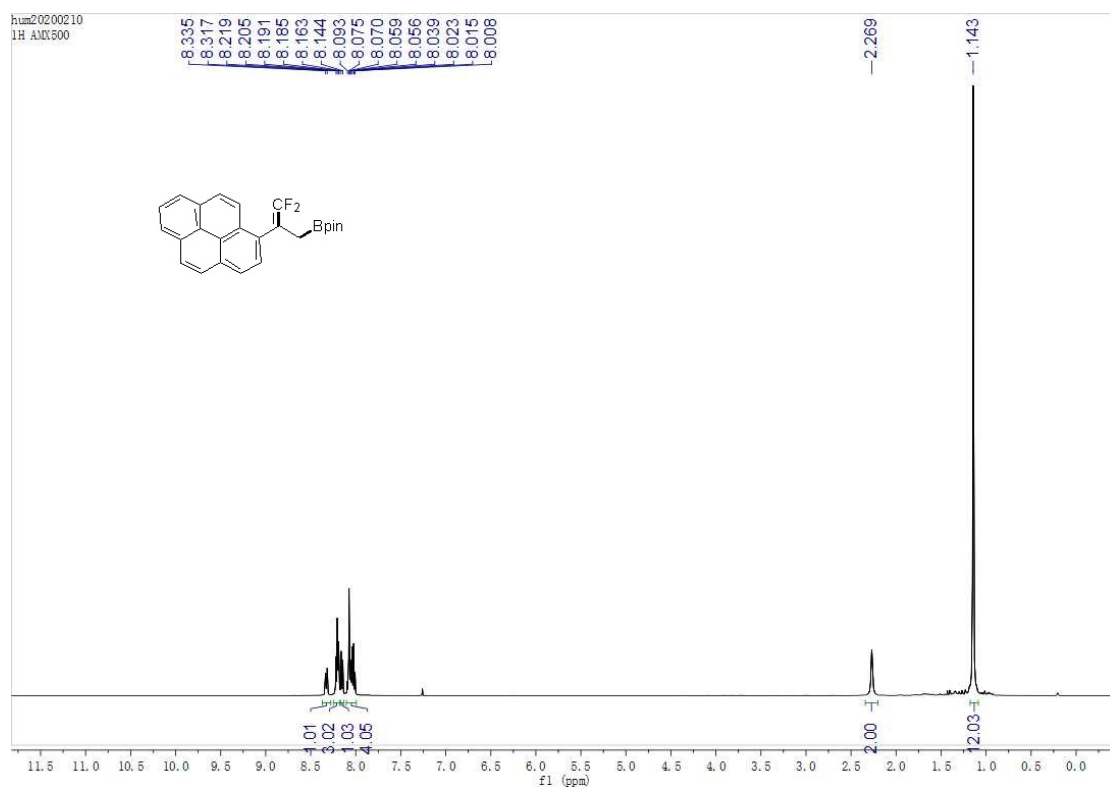


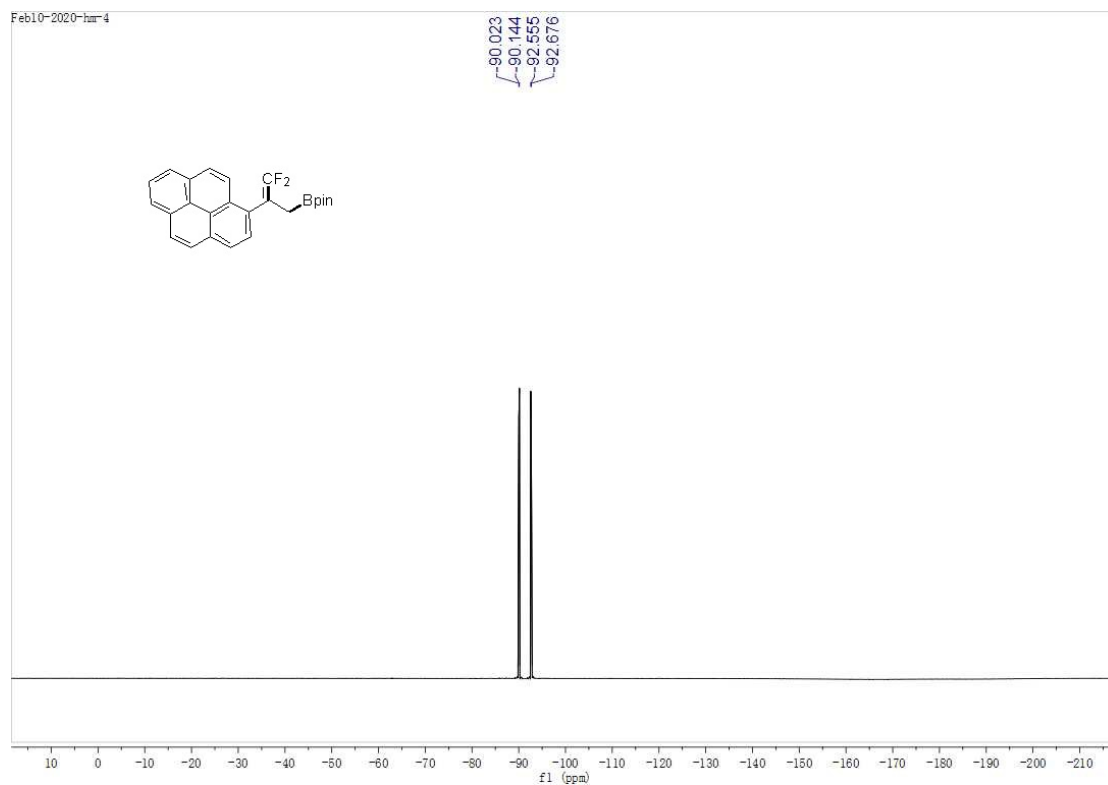
Methyl
4-(1,1-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)benzoate (5q):



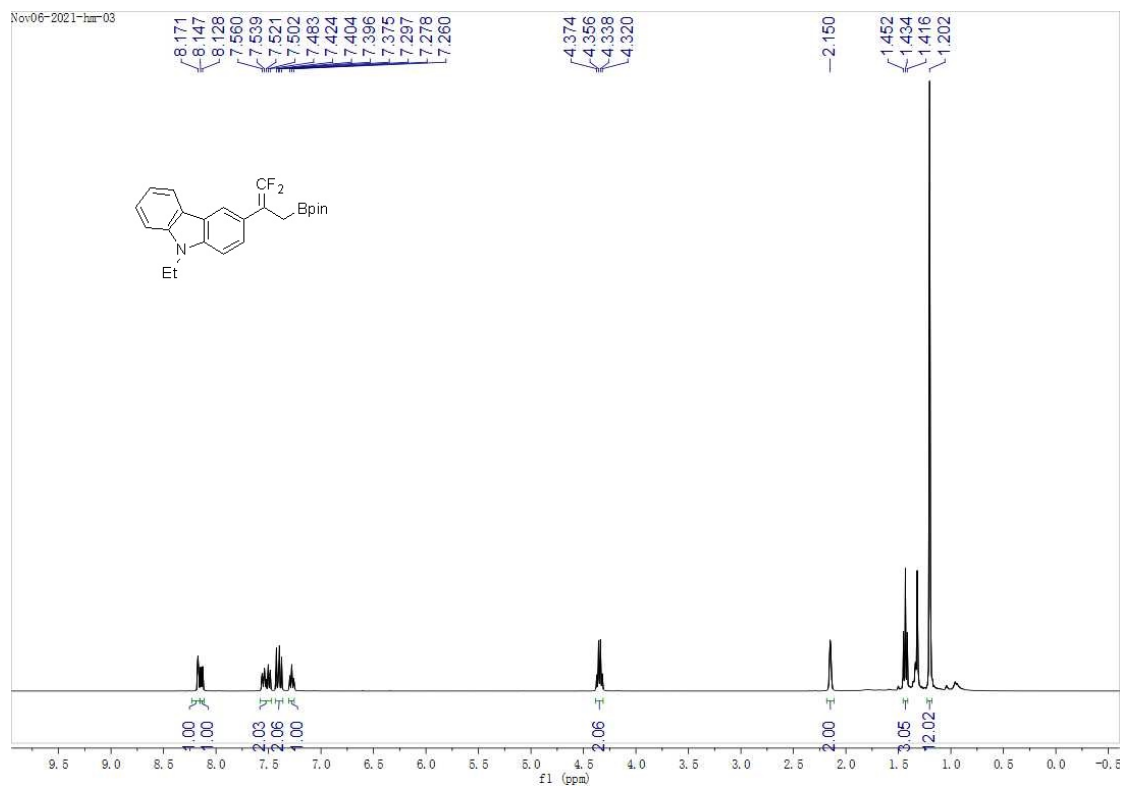
**2-(3,3-Difluoro-2-(naphthalen-2-yl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane****(5t):**

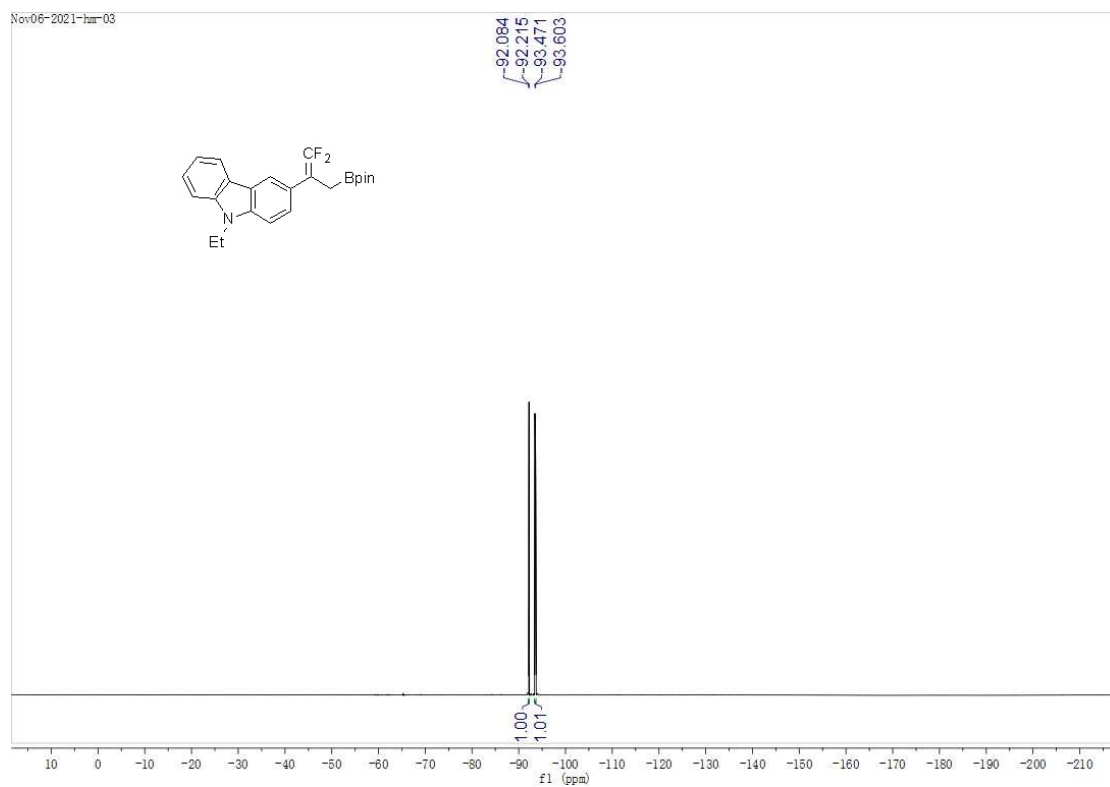
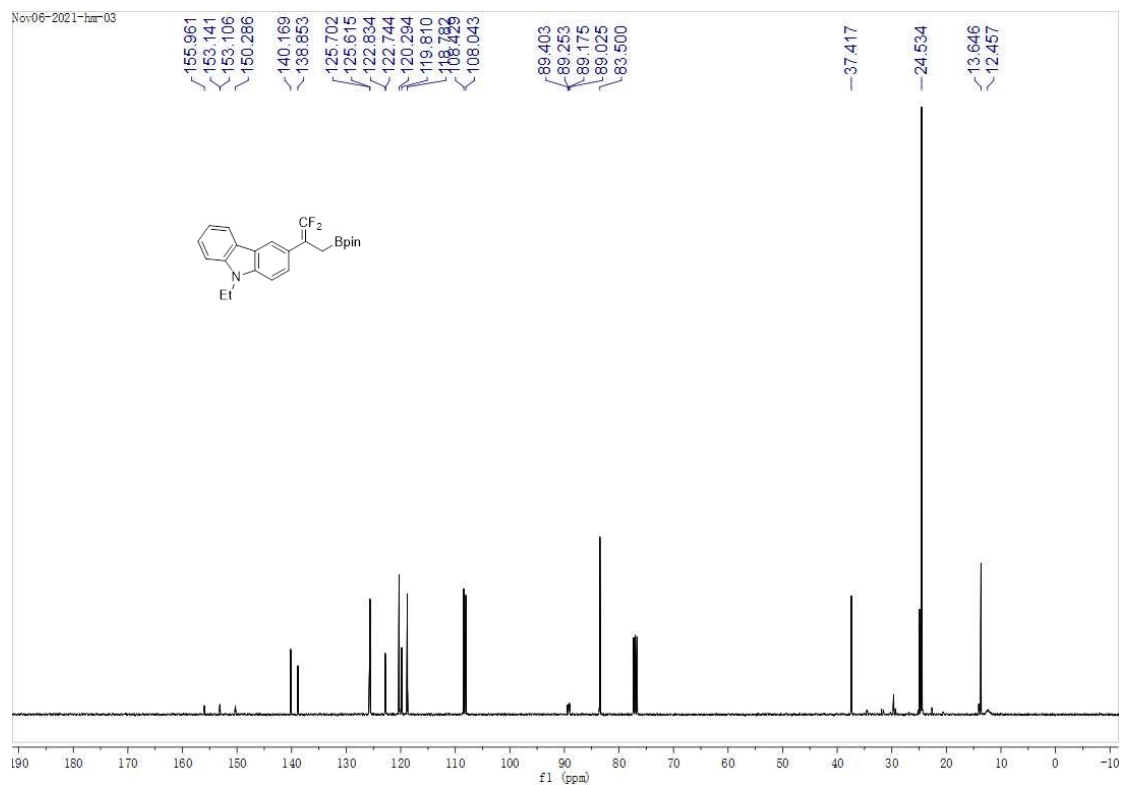


2-(3,3-Difluoro-2-(pyren-1-yl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5v):

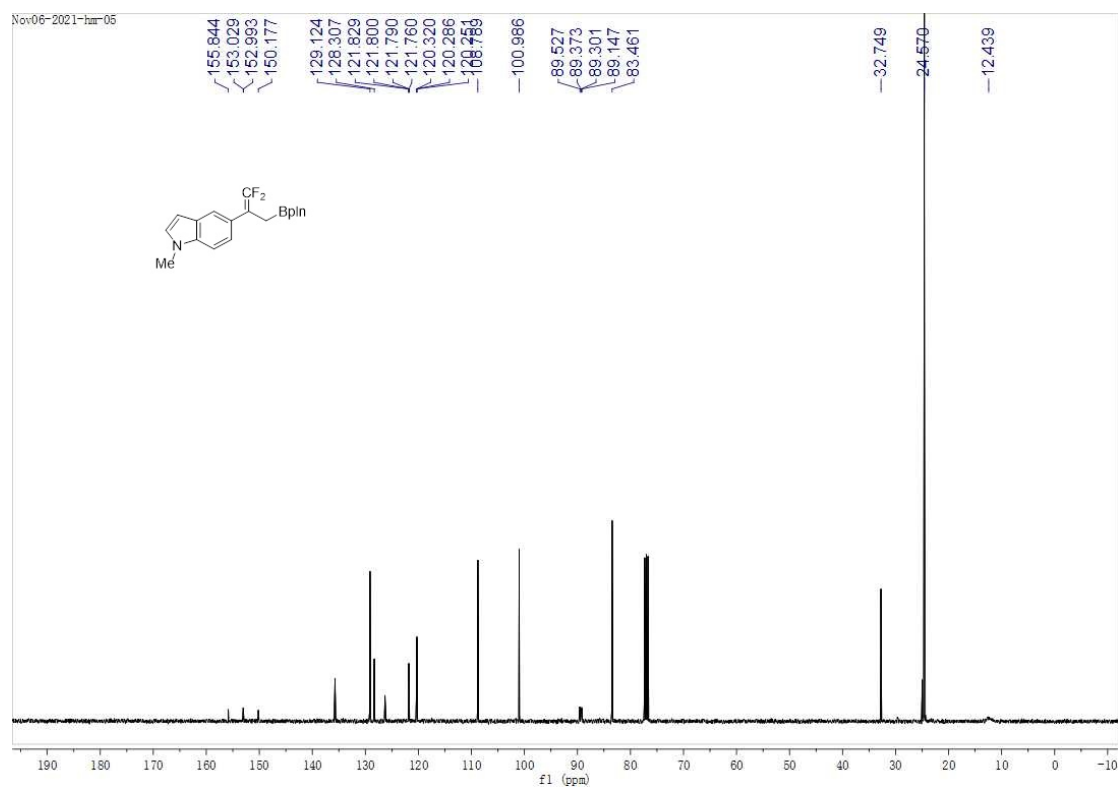
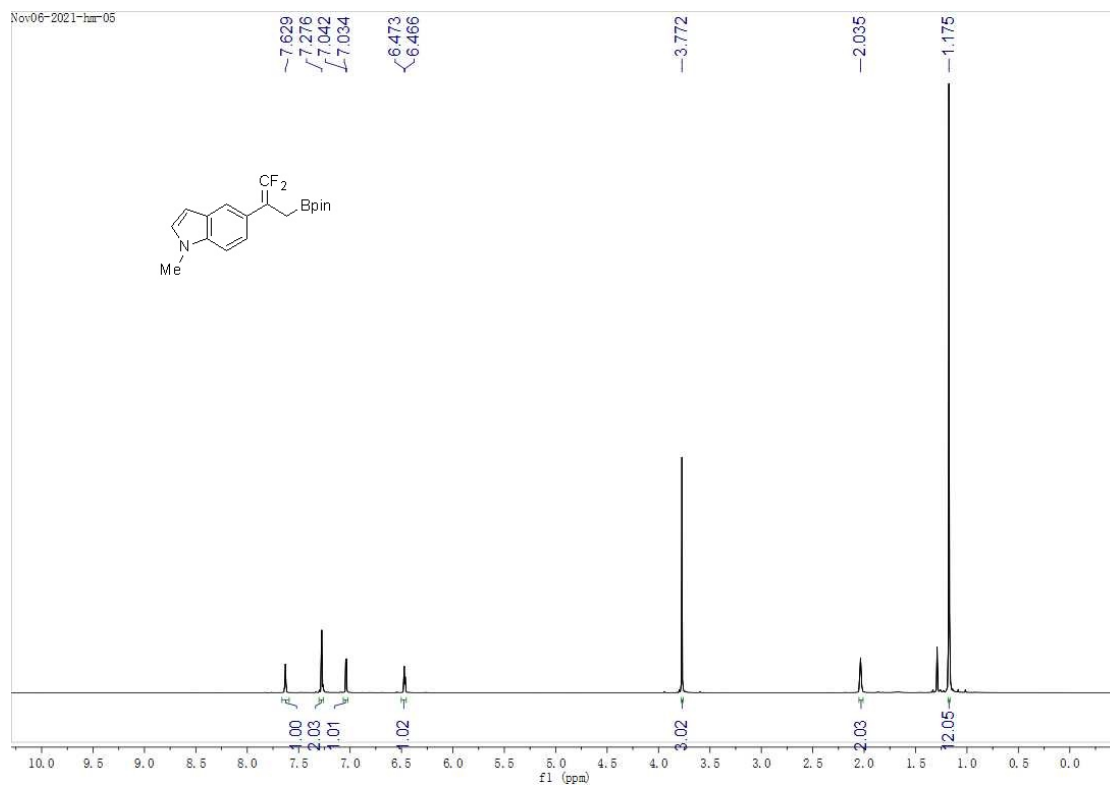


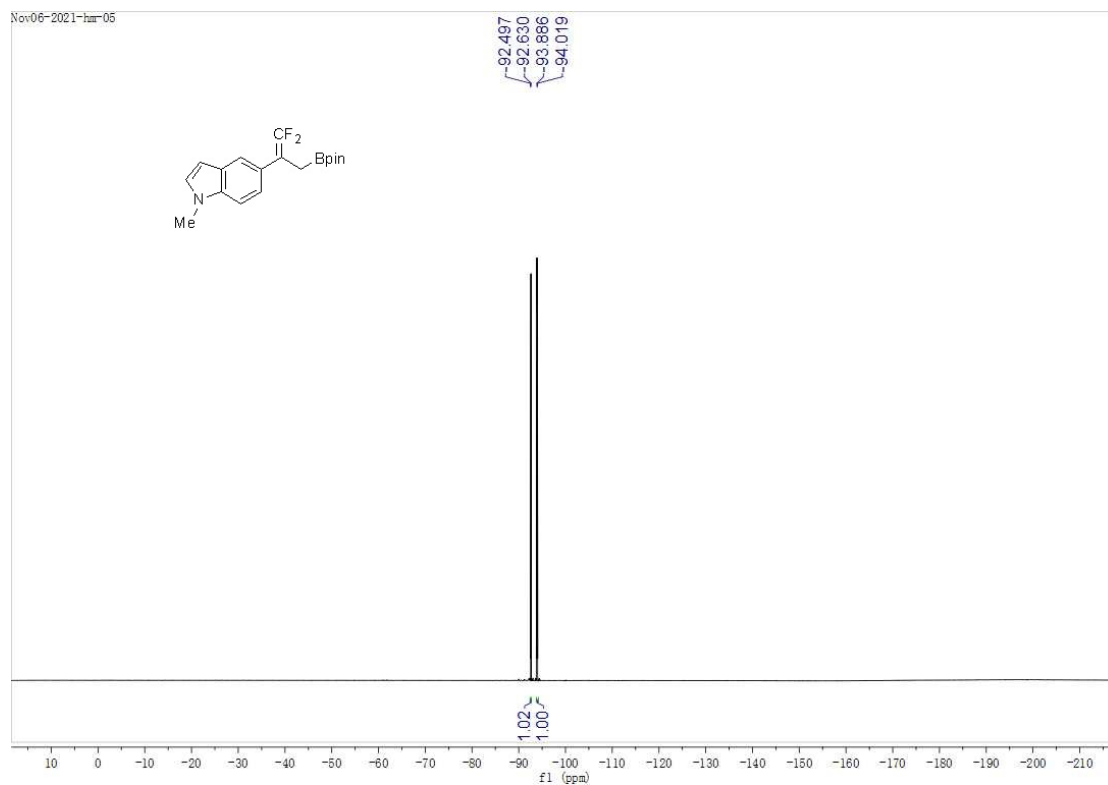
3-(1,1-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-9-ethyl-9H-carbazole (5w):



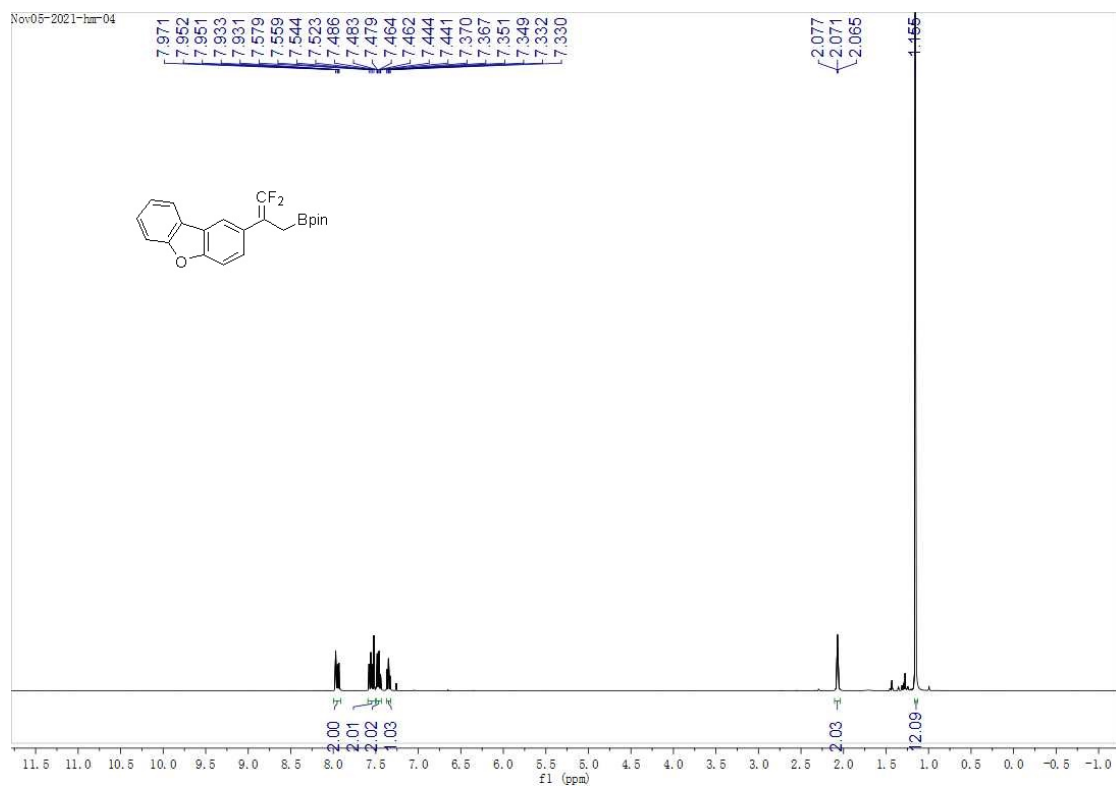


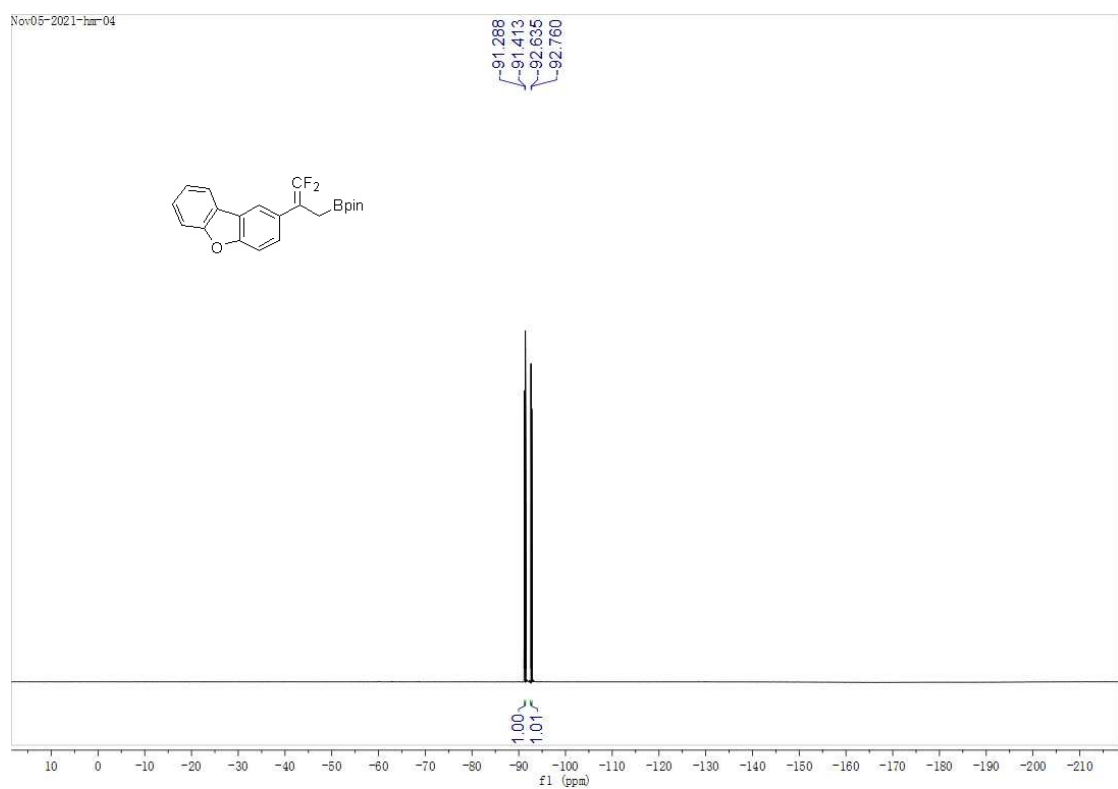
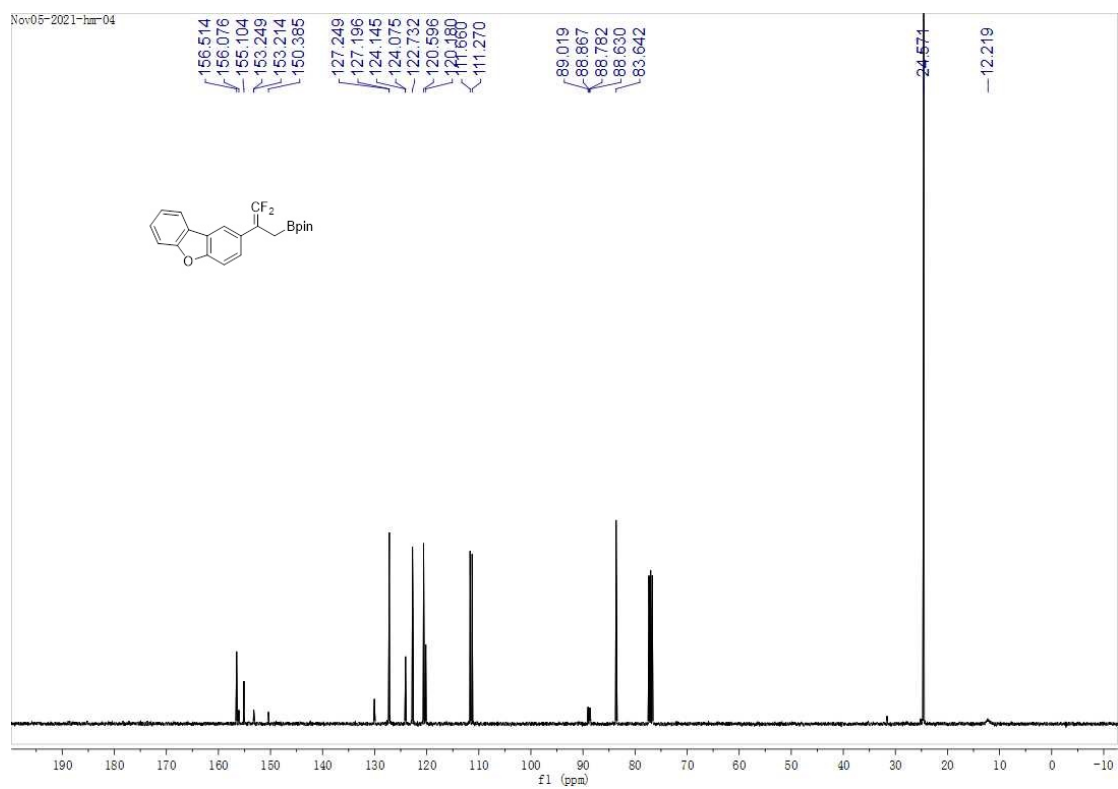
5-(1,1-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-1-methyl-1H-indole (5x):

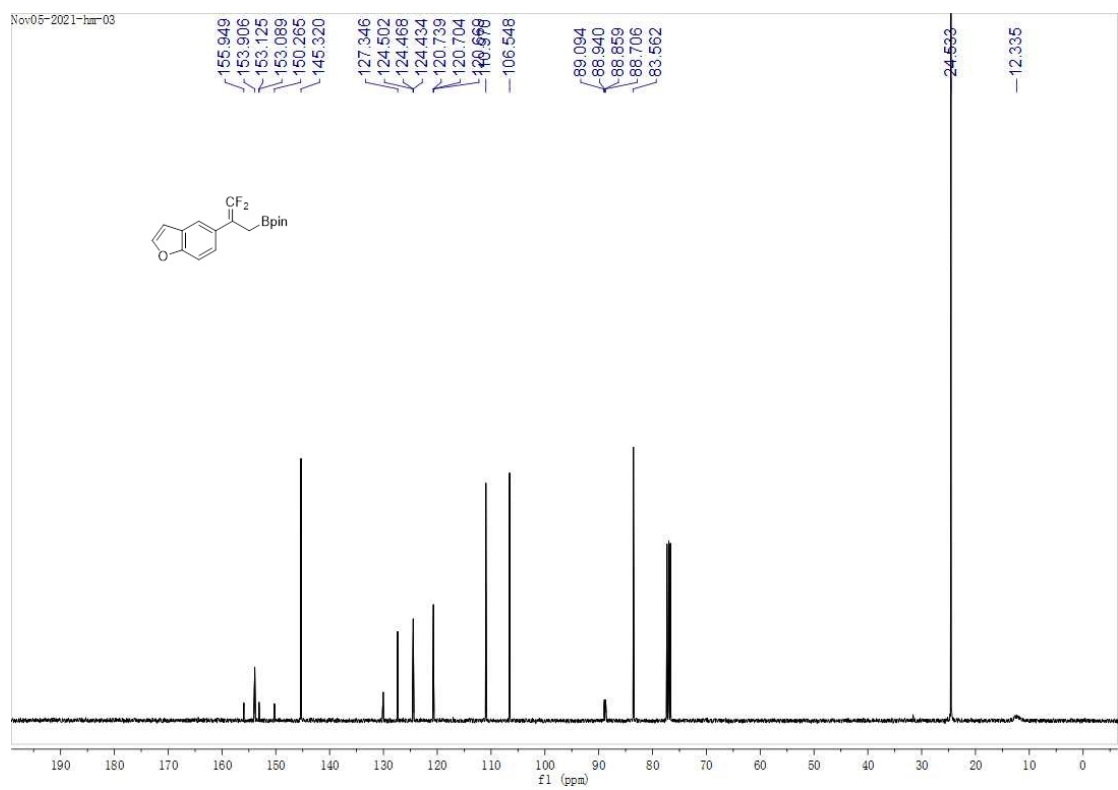
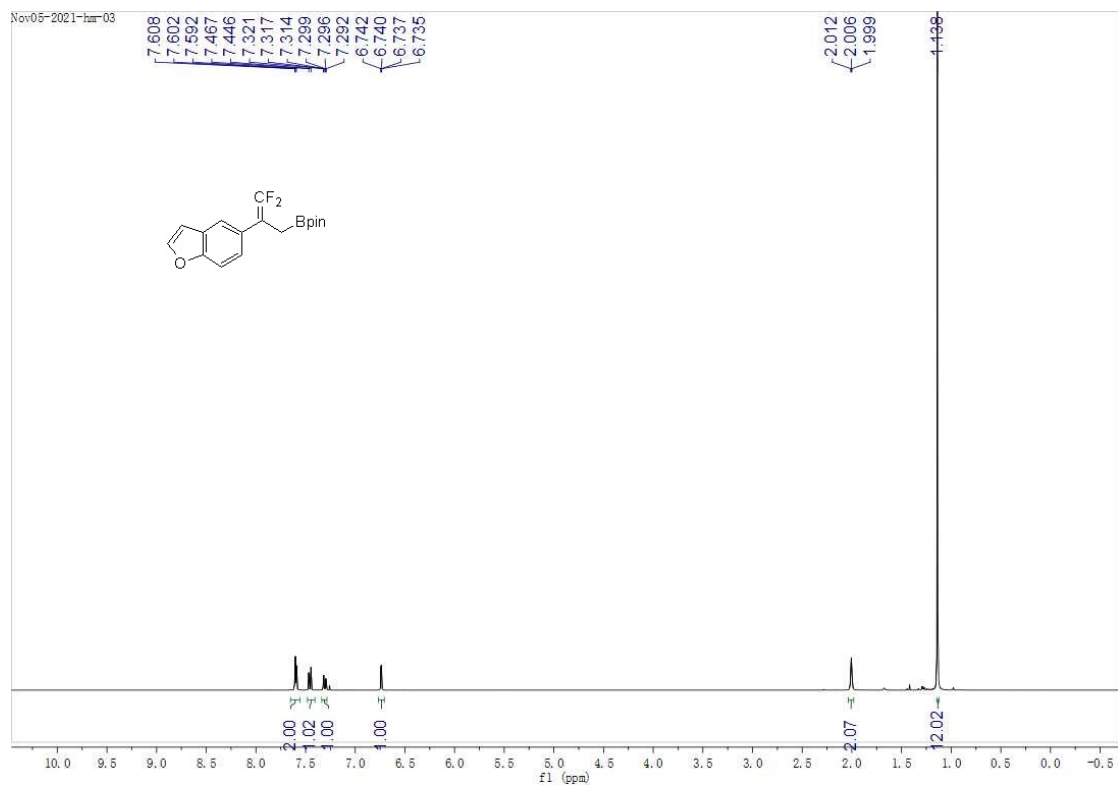


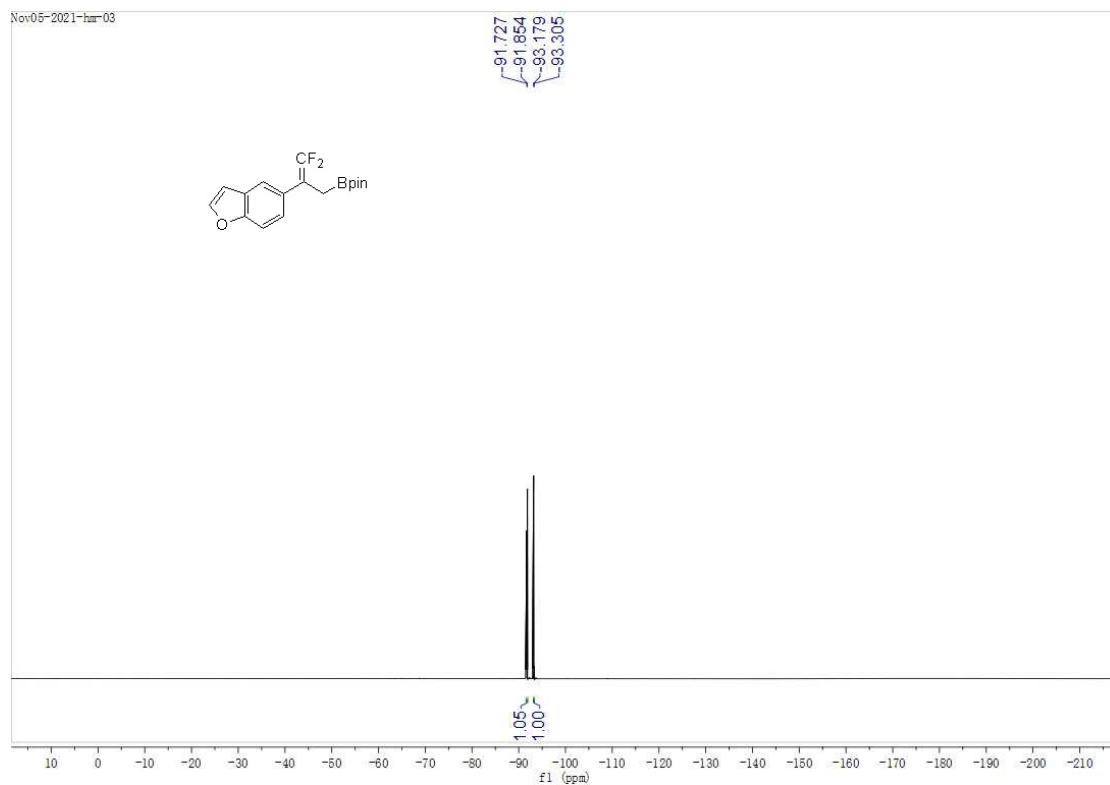


2-(2-(dibenzo[*b,d*]furan-2-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5y):

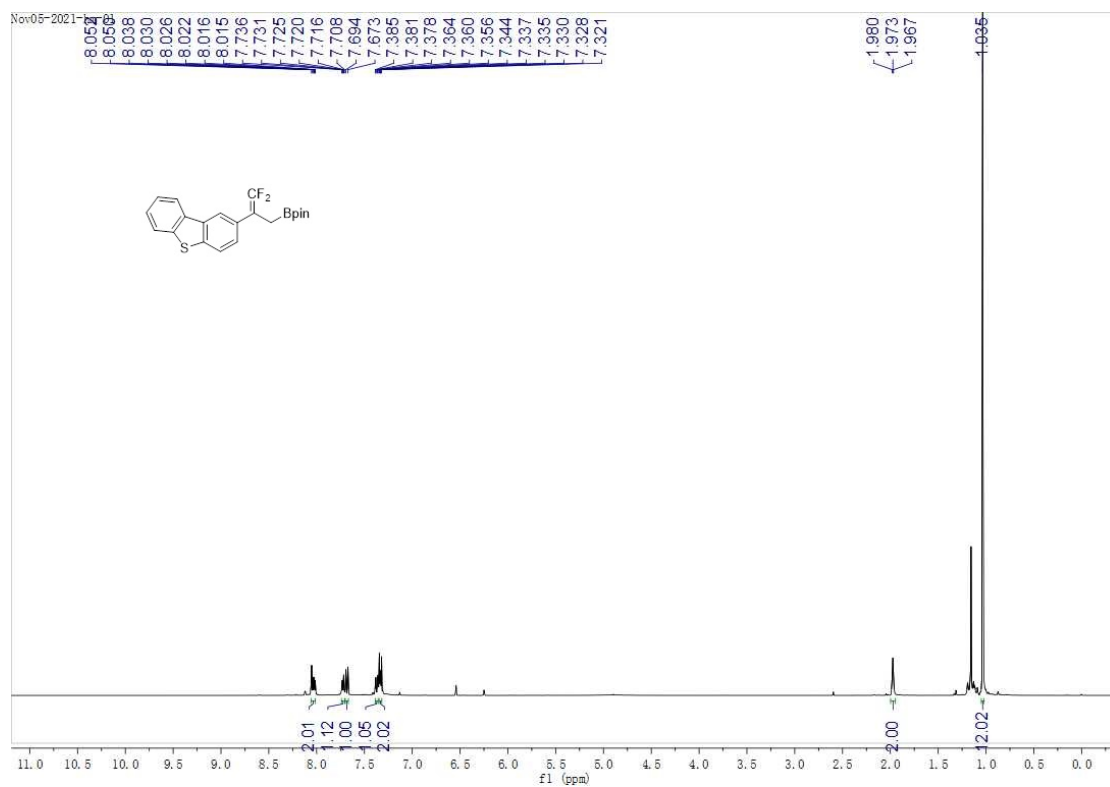


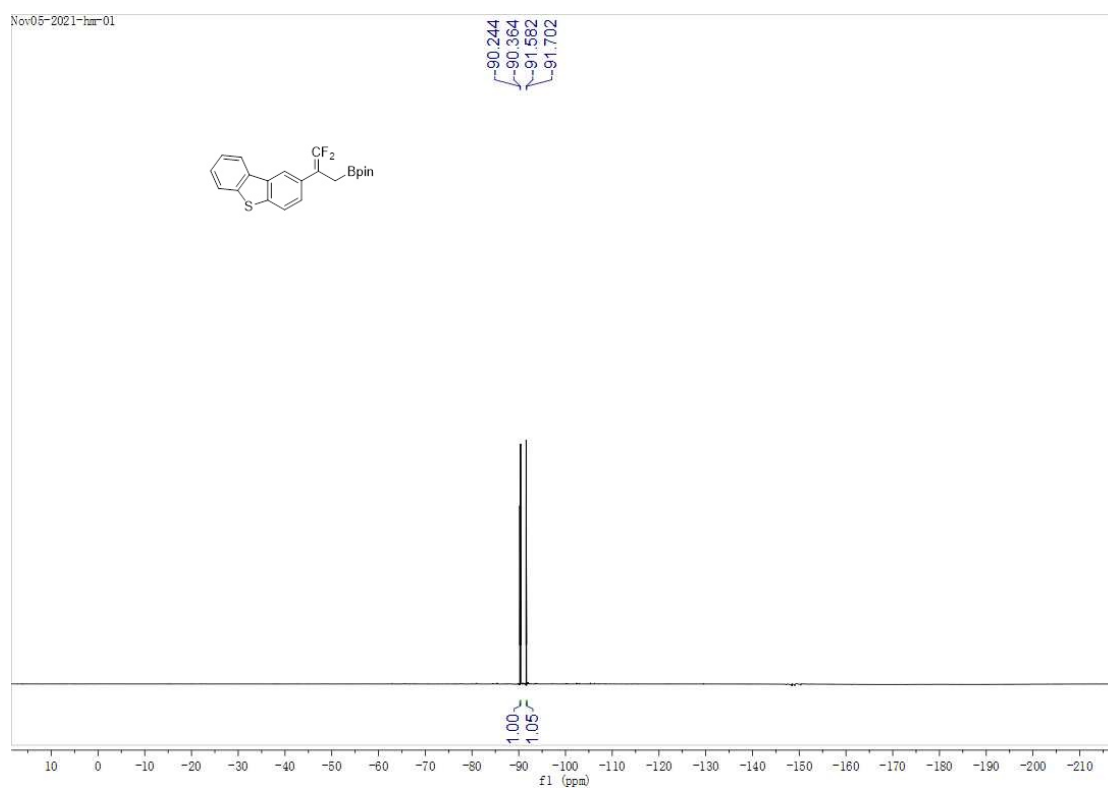
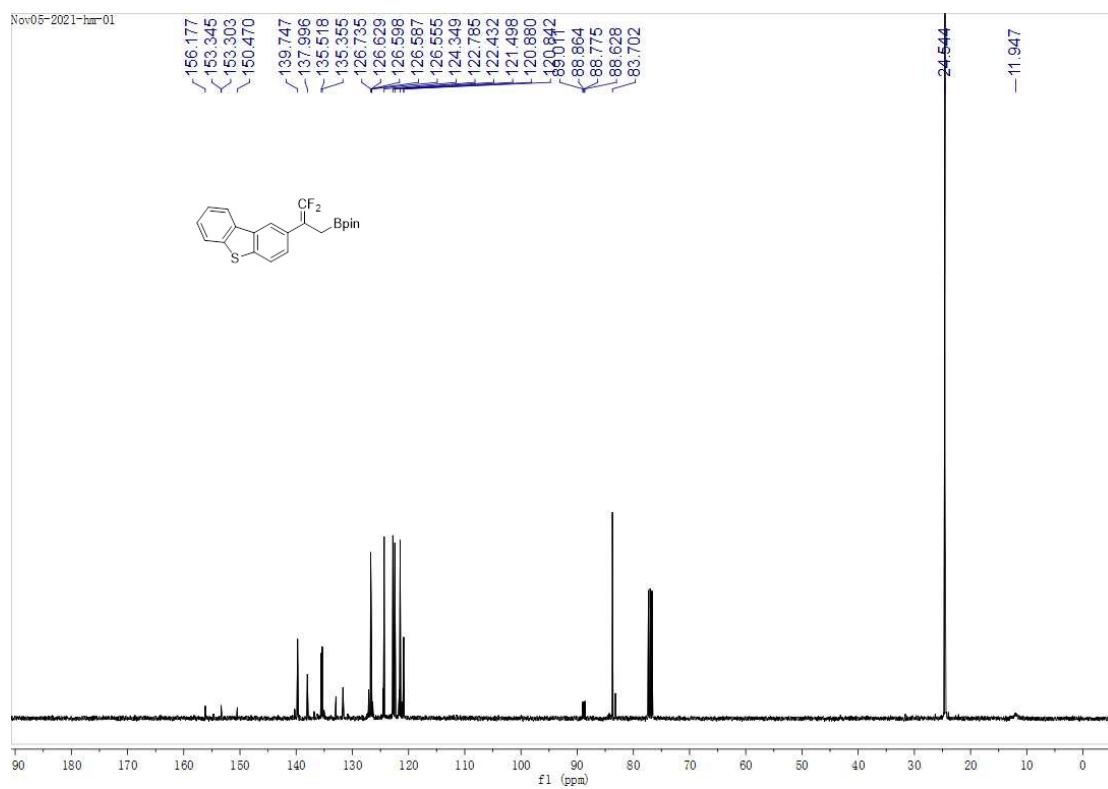


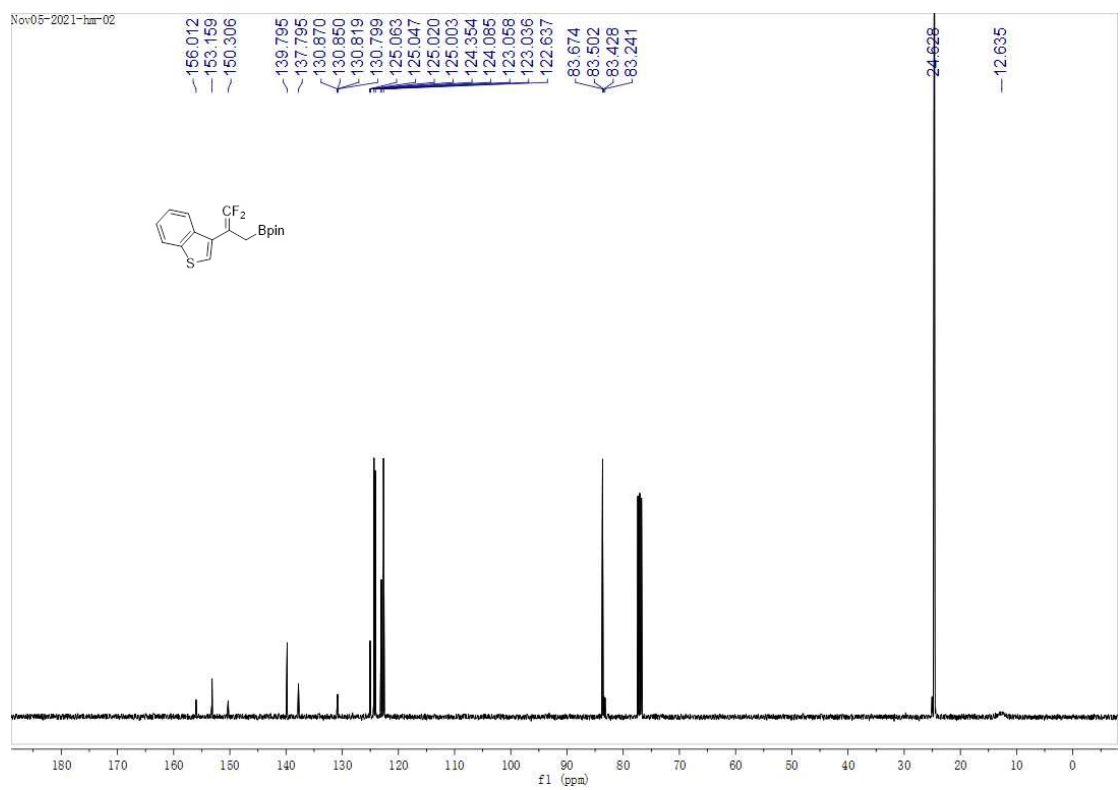
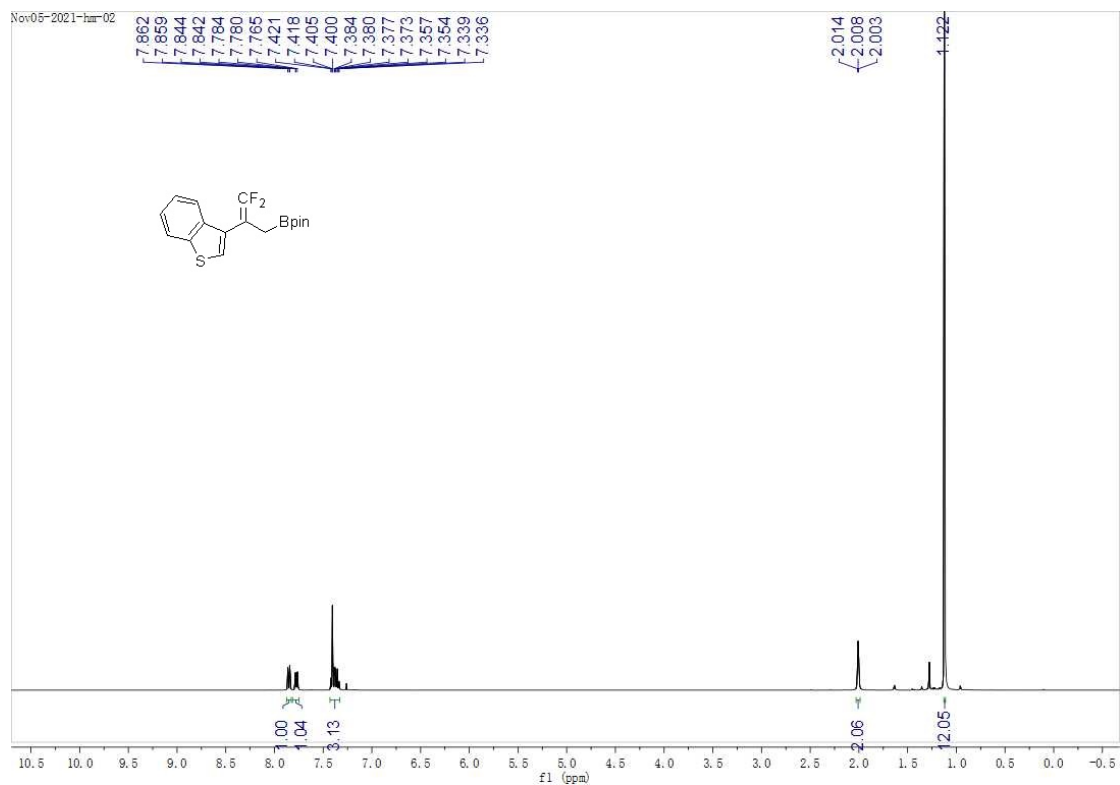
2-(2-(benzofuran-5-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**(5z):**

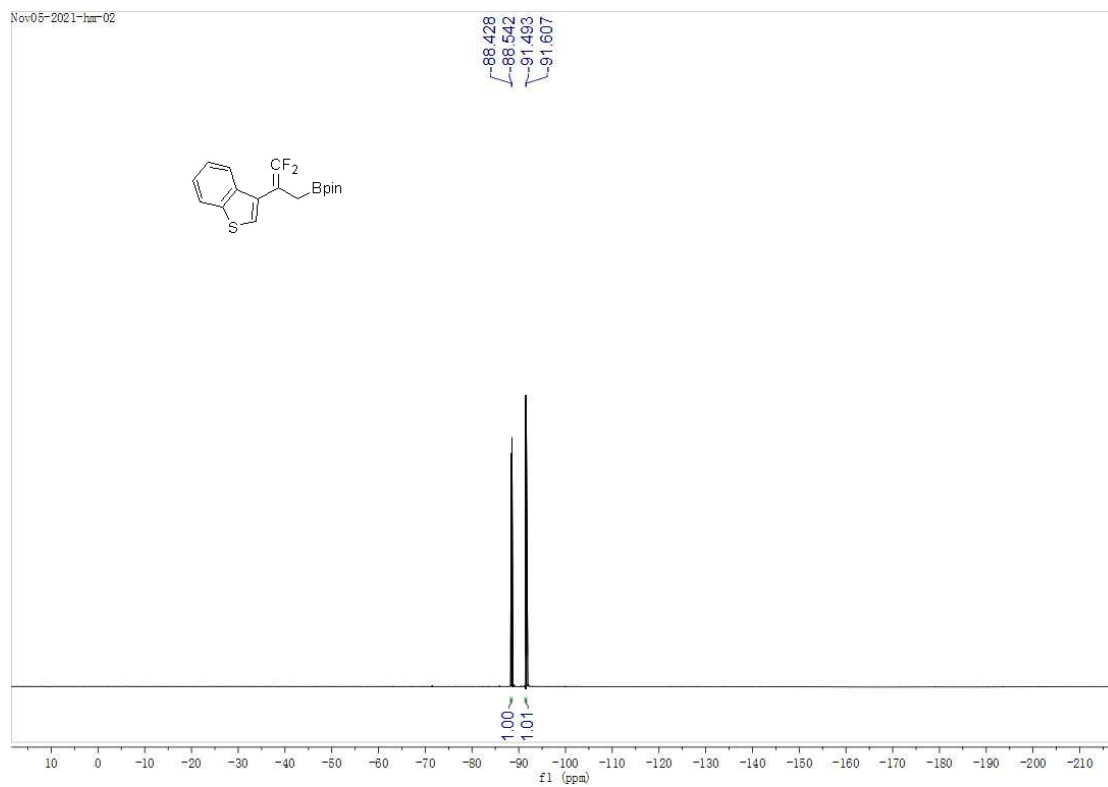


2-(2-(dibenzo[*b,d*]thiophen-2-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5aa):





2-(2-(benzo[*b*]thiophen-3-yl)-3,3-difluoroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5ab):

**2-(2-(Difluoromethylene)-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane****(5ah):**