Supporting Information

Photo-Induced Weak Base-Catalyzed Synthesis of α-Haloboronates from Vinylboronates and Polyfluoroalkyl Halides

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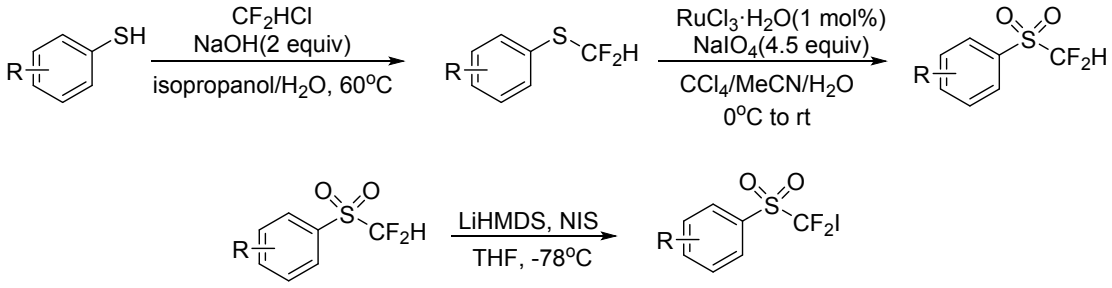
1. General methods

All experiments were conducted with a schlenk tube. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker Ascend^{TM} 400 (400 MHz) spectrometer, Bruker AVANCE NEO 600 (600 MHz) spectrometer or JEOL JNM-ECZ500R/S1 (500 MHz) spectrometer. Chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm), MeCN-d_3 (δ = 1.94 ppm) as internal standards. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.0 ppm), MeCN-d_3 (δ = 1.32 ppm). Data for 1H NMR are recorded as following abbreviations: multiplicity (s = singlet, d = doublet, t = triplet, q = quarter, m = multiplet), coupling constant (*J*, Hz). HRMS data were obtained on Thermo Scientific Orbitrap Elite Mass Spectrometer with an ESI source (Ion Trap) or Agilent 7250 GC/Q-TOF. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was accomplished by UV light (254 nm), or $KMnO_4$ staining solutions followed by heating, also by Gas chromatograph-Mass spectrometer analysis (GC-MS). No attempts were made to optimize yields for substrate synthesis. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation of the starting materials



The iodine difluoroaryl sulfone **1n-1u** were prepared according to the reference[1,2].

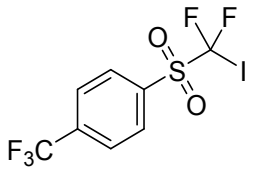
Step 1: Benzenethiol **6** (10 mmol) was dissolved in isopropanol (15 ml). The reaction mixture was warmed up to 60 °C, and solution of NaOH (800 mg, 20 mmol) in H_2O was added dropwise. A balloon was attached to the reaction vessel and CF_2HCl gas was bubbled into the stirred mixture from a cylinder for 4 h. When all of the starting material was converted into the product, the mixture was cooled down to room temperature, poured in water, and the aqueous layer was extracted with Et_2O, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was directly used in the next step without further purification.

Step 2: To a mixture of difluoromethyl aryl sulfide (9 mmol), CCl_4 (8 mml), CH_3CN (8 ml), H_2O (14 ml) and $RuCl_3·H_2O$ (10 mg, 0.04 mmol) at 0 °C, $NaIO_4$ was added (7.7 g, 36 mmol). After stirring at 0 °C to RT for 1.5 hours, the resulting reaction mixture was extracted with Et_2O. The combined organic phase was washed successively with saturated $NaHCO_3$ and saturated brine, and then dried over anhydrous Na_2SO_4. concentrated under reduced pressure. The crude product was directly used in the next step without further purification.

Step 3: Difluoromethyl aryl sulfone (5 mmol, 1.0 equiv) and NIS (15 mmol, 3.375 g, 3.0 equiv) were added to a dry Schlenk tube. The flask was evacuated and backfilled with pure Ar for 3 times. Then THF (20 mL) was added with syringe under Ar atmosphere. The mixture was cooled to –78 ℃. LiHMDS (1.0 M in THF, 15 mmol, 15 mL, 3.0 equiv) was added with syringe under Ar atmosphere in 15 min. The mixture was stirred at –78 ℃ for 3 h (monitored by GC-MS). After the reaction was complete, the mixture was quenched by saturated aqueous solution of NH_4Cl (10 mL). After the

mixture was warmed to room temperature, the aqueous layer was extracted with Et_2O for 3 times (30 mL × 3). Then the organic phase was combinated and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the desired product. The following compounds are synthesized according to this method.

1-((difluoroiodomethyl)sulfonyl)-4-(trifluoromethyl)benzene (1n)



White solid, mp: 91-92 ℃

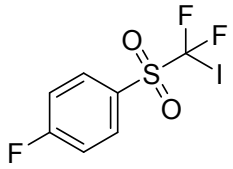
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -52.12, -63.37.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.5 (q, *J* = 33.4 Hz), 132.0, 126.8 (q, *J* = 3.7 Hz), 122.8 (q, *J* = 273.5 Hz), 101.8 (t, *J* = 355.1 Hz).

HRMS (ESI) calcd for $C_8H_5F_5IO_2S$ ($M+H^+$): 386.8970, found: 386.8986.

1-((difluoroiodomethyl)sulfonyl)-4-fluorobenzene (1o)



White solid, mp: 84-85 ℃

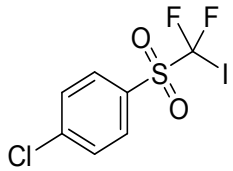
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 2H), 7.37 – 7.29 (m, 2H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -52.06, -98.36.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.5 (d, *J* = 260.8 Hz), 134.4 (d, *J* = 10.3 Hz), 123.8, 117.3 (d, *J* = 23.0 Hz), 102.0 (t, *J* = 354.7 Hz).

HRMS (EI) calcd for $C_7H_5F_3IO_2S$: 335.8929, found: 335.8930.

1-chloro-4-((difluoroiodomethyl)sulfonyl)benzene (1p)[3]



White solid, mp: 104-105 ℃

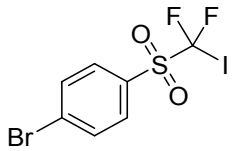
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -52.05.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.4, 132.7, 130.1, 126.4, 102.0 (t, *J* = 354.9 Hz).

HRMS (ESI) calcd for $C_7H_4ClF_2IO_2SNa$ ($M+Na^+$): 374.8525, found: 374.8521.

1-bromo-4-((difluoroiodomethyl)sulfonyl)benzene (1q)



White solid, mp: 132-133 ℃

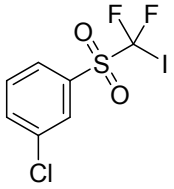
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 – 7.83 (m, 2H), 7.81 – 7.77 (m, 2H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -52.02.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 133.2, 132.7, 132.3, 127.0, 102.0 (t, *J* = 355.0 Hz).

HRMS (ESI) calcd for $C_7H_4BrF_2IO_2SNa$ ($M+Na^+$): 418.8020, found: 418.8020.

1-chloro-3-((difluoroiodomethyl)sulfonyl)benzene (1r)



White solid, mp: 66-67 ℃

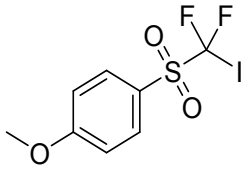
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (t, *J* = 2.0 Hz, 1H), 7.89 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.78 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -51.90.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.3, 136.0 131.1, 130.9, 129.9, 129.5, 101.9 (t, *J* = 355.2 Hz).

HRMS (ESI) calcd for $C_7H_5ClF_2IO_2S$ ($M+H^+$): 351.8633, found: 351.8630.

1-((difluoroiodomethyl)sulfonyl)-4-methoxybenzene (1s)



White solid, mp: 104-105 ℃

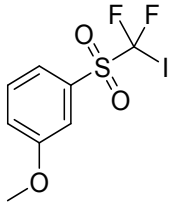
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -51.84.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.9, 133.7 118.4, 115.1, 102.7 (t, *J* = 354.9 Hz), 55.9.

HRMS (ESI) calcd for $C_8H_8F_2IO_3S$ ($M+H^+$): 348.9201, found: 348.9201.

1-((difluoroiodomethyl)sulfonyl)-3-methoxybenzene (1t)



White solid, mp: 76-77 ℃

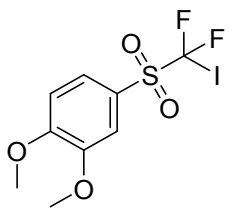
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 7.18 (ddd, *J* = 8.3, 2.5, 1.1 Hz, 1H), 3.74 (s, 3H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -51.91.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.2, 130.6, 129.1, 123.6, 122.9, 115.3, 102.6 (t, *J* = 355.5 Hz), 55.8.

HRMS (ESI) calcd for $C_8H_8F_2IO_3S$ ($M+H^+$): 348.9201, found: 348.9201.

4-((difluoroiodomethyl)sulfonyl)-1,2-dimethoxybenzene (1u)



White solid, mp: 120-121 ℃

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.5 Hz, 1H), 7.33 (s, 1H), 7.03 (d, *J*

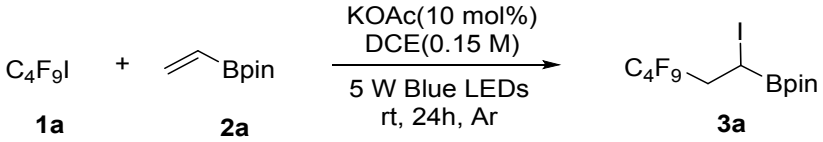
= 7.6 Hz, 1H), 3.97 (s, 3H), 3.92 (s, 3H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -51.65.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.6, 149.5, 126.4, 118.4, 112.5, 111.1, 102.6 (t, *J* = 354.9 Hz), 56.4, 56.3.

HRMS (ESI) calcd for $C_9H_{10}F_2IO_4S$ ($M+H^+$): 378.9307, found: 378.9306.

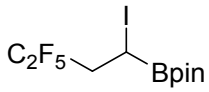
3. Typical procedure for the synthesis of *α*-haloboronates



1a **2a** **3a**

In air, a 25 mL schlenk tube was charged with KOAc (0.03 mmol, 3 mg, 10 mol%). The tube was evacuated and filled with Argon for three cycles. Then, 1,1-Dichloroethane (2 mL), Vinyl borate pinacol ester (**2a)** (0.3 mmol, 52 uL, 1.0 equiv), Perfluoroiodobutane (**1a**) (0.6 mmol, 105 uL, 2.0 equiv) were added to the tube at room temperature. The reaction was allowed to stir under Blue LEDs irradiation at room temperature. After 24 hours, the crude reaction mixture was concentrated in vacuo and purified by column chromatography (*n*-pentane: ethyl acetate = 30:1) to afford the desired product.

4,4,5,5-tetramethyl-2-(3,3,4,4,4-pentafluoro-1-iodobutyl)-1,3,2-dioxaborolane (3b)



Yellow liquid, Flash column chromatography conditions: n-pentane: ethyl acetate = 30:1; Yield: 100.7 mg (84%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.33 (dd, *J* = 11.8, 4.5 Hz, 1H), 2.93 – 2.77 (m, 1H), 2.66 – 2.52 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 12H).

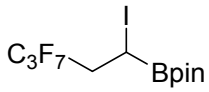
^{19}F NMR (471 MHz, Chloroform-*d*) δ -85.43, -117.79 – -118.30 (m).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 118.6 (qt, *J* = 286.0, 35.91 Hz), 115.2 (tq, *J* = 254.52, 37.8 Hz), 84.5, 37.0 (t, *J* = 21.3 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.4.

HRMS (ESI) calcd for $C_{10}H_{16}BF_5IO_2$ ($M+H^+$): 401.0203, found: 401.0203.

2-(3,3,4,4,5,5,5-heptafluoro-1-iodopentyl)-4,4,5,5-tetramethyl-1,3,2 dioxaborolane (3c)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 103.9 mg (77%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.36 (dd, *J* = 11.8, 4.4 Hz, 1H), 2.98 – 2.82 (m, 1H), 2.70 – 2.55 (m, 1H), 1.25 (d, *J* = 8.2 Hz, 12H).

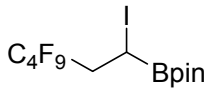
^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.45 (t, *J* = 10.0 Hz), -114.19 – -115.91 (m), -127.84.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 121.5 – 105.7 (m), 84.5, 37.1 (t, *J* = 21.4 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.4.

HRMS (ESI) calcd for $C_{11}H_{16}BF_7IO_2$ ($M+H^+$): 451.0171, found: 451.0181.

4,4,5,5-tetramethyl-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)-1,3,2-dioxaborolane (3a)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 114.1 mg (76%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.36 (dd, *J* = 11.9, 4.3 Hz, 1H), 2.99 – 2.83 (m, 1H), 2.71 – 2.56 (m, 1H), 1.25 (d, *J* = 8.6 Hz, 12H).

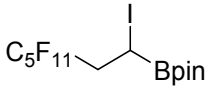
^{19}F NMR (471 MHz, Chloroform-*d*) δ -81.08 (t, *J* = 9.7 Hz), -113.51 – -115.14 (m), -124.47 – -124.65 (m), -125.95 – -126.04 (m).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 121.1 – 105.7 (m), 84.5, 37.3 (t, *J* = 21.4 Hz), 24.1, 23.9.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.3.

HRMS (ESI) calcd for $C_{12}H_{16}BF_9IO_2$ ($M+H^+$): 501.0139, found: 501.0136.

4,4,5,5-tetramethyl-2-(3,3,4,4,5,5,6,6,7,7,7-undecafluoro-1-iodoheptyl)-1,3,2-dioxaborolane (3d)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 118.7 mg (72%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.36 (dd, *J* = 11.9, 4.3 Hz, 1H), 3.00 – 2.84 (m, 1H), 2.71 – 2.56 (m, 1H), 1.25 (d, *J* = 8.6 Hz, 12H).

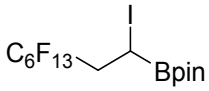
^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.89 (t, *J* = 10.0 Hz), -113.27 – -115.00 (m), -122.59 – -122.71 (m), -123.75 – -123.90 (m), -126.20 – -126.40 (m).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 121.3 – 105.7 (m), 84.5, 37.4 (t, *J* = 21.4 Hz), 24.1, 23.9.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.3.

HRMS (EI) calcd for $C_{13}H_{15}BF_{11}IO_2$: 500.0034, found: 500.0037.

4,4,5,5-tetramethyl-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctyl)-1,3,2-dioxaborolane (3e)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 133.3 mg (74%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.37 (dd, *J* = 11.9, 4.3 Hz, 1H), 3.00 – 2.84 (m, 1H), 2.71 – 2.57 (m, 1H), 1.26 (d, *J* = 8.6 Hz, 12H).

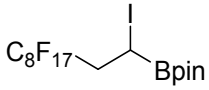
^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.86 (t, *J* = 9.9 Hz), -113.30 – -114.92 (m), -121.79 – -121.90 (m), -122.83 – -122.90 (m), -123.55 – -123.70 (m), -126.10 – -126.926 (m).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 124.7 – 105.0 (m), 84.5, 37.5 (t, *J* = 21.5 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.2.

HRMS (EI) calcd for $C_{14}H_{15}BF_{13}IO_2$: 600.0002, found: 600.0005.

2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 163.8 mg (78%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.36 (dd, *J* = 11.9, 4.3 Hz, 1H), 3.00 – 2.84 (m, 0H), 2.71 – 2.56 (m, 1H), 1.25 (d, *J* = 8.7 Hz, 12H).

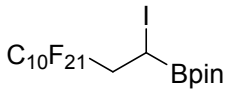
^{19}F NMR (471 MHz, Chloroform-*d*) δ -112.15 – -115.21 (m), -121.05 – -121.80 (m), -121.80 – -122.48 (m), -122.58 – -123.36 (m), -123.43 – -124.06 (m), -126.03 – -126.53 (m).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 125.2 – 105.0 (m), 84.5, 37.5 (t, *J* = 21.5 Hz), 24.1, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.2.

HRMS (EI) calcd for $C_{16}H_{15}BF_{17}IO_2$: 699.9938, found: 699.9947.

2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluoro-1-iodododecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 194.4 mg (81%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.37 (dd, *J* = 11.9, 4.4 Hz, 1H), 3.00 – 2.84 (m, 0H), 2.72 – 2.57 (m, 1H), 1.26 (d, *J* = 8.6 Hz, 12H).

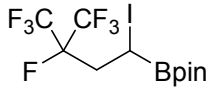
^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.82 (t, *J* = 9.9 Hz), -113.29 – -114.87 (m), -121.39 – -122.11 (m), -122.72, -123.58, -125.92 – -126.37 (m).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 121.1– 105.9 (m), 84.5, 37.4 (t, *J* = 21.4 Hz), 24.1, 23.9.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.1.

HRMS (EI) calcd for $C_{18}H_{15}BF_{21}IO_2$: 799.9874, found: 799.9878.

4,4,5,5-tetramethyl-2-(3,4,4,4-tetrafluoro-1-iodo-3-(trifluoromethyl)butyl)-1,3,2-dioxaborolane (3h)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 91.8 mg (68%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 12.6, 3.9 Hz, 1H), 6.90 – 6.78 (m, 1H), 6.55 – 6.43 (m, 1H), 5.11 (d, *J* = 7.9 Hz, 12H).

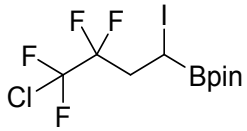
^{19}F NMR (471 MHz, Chloroform-*d*) δ -76.16 (m), -77.18 (m), -186.00 – -186.23 (m).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 124.6– 116.8 (m), 91.7 (dp, *J* = 204.9, 32.2 Hz), 84.4, 34.9(d, *J* = 19.4 Hz), 24.1, 24.0

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.6.

HRMS (ESI) calcd for $C_{11}H_{16}BF_7IO_2$ ($M+H^+$): 451.0171, found: 451.0175.

2-(4-chloro-3,3,4,4-tetrafluoro-1-iodobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 77.4 mg (62%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.35 (dd, *J* = 11.8, 4.4 Hz, 1H), 2.98 – 2.82 (m, 1H), 2.72 – 2.57 (m, 1H), 1.25 (d, *J* = 7.2 Hz, 12H).

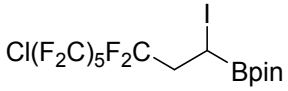
^{19}F NMR (471 MHz, Chloroform-*d*) δ -71.25, -112.99 – -114.67 (m).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 123.0 (tt, *J* = 298.7, 37.2 Hz), 116.8 (tt, *J* = 256.1, 33.7 Hz), 84.4, 37.1(t, *J* = 21.7 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.5.

HRMS (EI) calcd for $C_{10}H_{15}BClF_4IO_2$: 415.9834, found: 415.9843.

2-(8-chloro-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1-iodooctyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3*J*)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate =

30:1; Yield: 125.6 mg (68%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.36 (dd, *J* = 11.9, 4.3 Hz, 1H), 2.99 – 2.83 (m, 1H), 2.70 – 2.56 (m, 1H), 1.25 (d, *J* = 8.6 Hz, 12H).

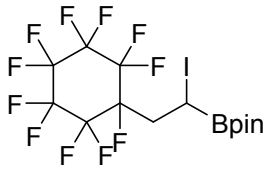
^{19}F NMR (471 MHz, Chloroform-*d*) δ -68.10 (t, *J* = 13.3 Hz), -113.32 – -114.96 (m), -120.22, -121.36, -121.74, -123.65.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 124.8 – 106.4 (m), 84.5, 37.5 (t, *J* = 21.4 Hz), 24.1, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.2.

HRMS (EI) calcd for $C_{14}H_{15}BClF_{12}IO_2$: 615.9707, found: 615.9710.

2-(1-iodo-2-(perfluorocyclohexyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 124.0 mg (76%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.46 (dd, *J* = 12.7, 2.5 Hz, 1H), 3.12 – 3.02 (m, 1H), 2.84 – 2.72 (m, 1H), 1.25 (d, *J* = 9.8 Hz, 12H).

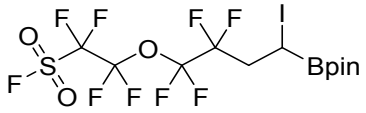
^{19}F NMR (471 MHz, Chloroform-*d*) δ -118.26 (dd, *J* = 497.9, 296.7 Hz), -121.60 – -124.80 (m), -132.58 (dd, *J* = 401.3, 295.9 Hz), -139.27 (d, *J* = 284.4 Hz), -142.12 (d, *J* = 286.3 Hz), -185.57.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 112.9 – 104.8 (m), 93.2 – 89.9 (m), 84.5, 32. (d, *J* = 19.5 Hz), 24.2 , 23.9.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.1.

HRMS (ESI) calcd for $C_{14}H_{16}BF_{11}IO_2$ ($M+H^+$): 563.0107, found: 563.0108.

1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-4-iodo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)ethane-1-sulfonyl fluoride (3l)



Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 114.8 mg (66%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.33 (dd, *J* = 11.7, 4.4 Hz, 2H), 2.93 – 2.77 (m, 1H), 2.65 – 2.50 (m, 1H), 1.25 (d, *J* = 8.5 Hz, 12H).

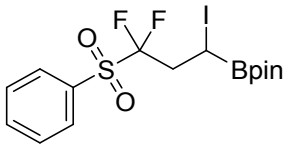
^{19}F NMR (471 MHz, Chloroform-*d*) -45.69 – -45.60 (m), -82.05 – -82.14 (m), -87.07 – -87.80 (m), -111.87 – -112.31 (m), -117.28 – -118.71 (m).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 120.0 – 109.5 (m), 84.5, 36.8 (t, *J* = 21.2 Hz), 24.1, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.3.

HRMS (EI) calcd for $C_{12}H_{15}BF_9IO_5S$: 579.9634, found: 579.9637.

2-(3,3-difluoro-1-iodo-3-(phenylsulfonyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)



White solid, mp: 94-95 ℃, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 113.3 mg (80%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 3.42 (dd, *J* = 11.0, 5.1 Hz, 1H), 3.23 – 3.07 (m, 1H), 3.00 – 2.85 (m, 1H), 1.24 (d, *J* = 6.3 Hz, 12H).

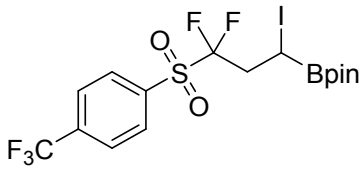
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.75 (d, *J* = 229.36 Hz), -103.80 (d, *J* = 229.36 Hz).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.5, 132.0, 130.8, 129.4, 123.4 (t, *J* = 287.9 Hz), 84.4, 35.5 (t, *J* = 19.7 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.8.

HRMS (ESI) calcd for $C_{15}H_{21}BF_2IO_4S$ ($M+H^+$): 473.0261, found: 473.0263.

2-(3,3-difluoro-1-iodo-3-((4-(trifluoromethyl)phenyl)sulfonyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)



White solid, mp: 93-94 ℃, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 103.6 mg (64%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 2H), 3.42 (dd, *J* = 10.9, 5.1 Hz, 1H), 3.24 – 3.09 (m, 1H), 3.02 – 2.87 (m, 1H), 1.24 (d, *J* = 6.6 Hz, 12H).

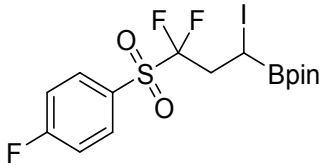
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.44, δ -102.56 (d, *J* = 229.36 Hz), -103.21 (d, *J* = 229.36 Hz).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.0 (q, *J* = 33.3 Hz), 135.7, 131.5, 126.5 (q, *J* = 3.7 Hz), 123.6.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.8.

HRMS (ESI) calcd for $C_{16}H_{20}BF_5IO_4S$ ($M+H^+$): 541.0135, found: 541.0132.

2-(3,3-difluoro-3-((4-fluorophenyl)sulfonyl)-1-iodopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)



White solid, mp: 77-78 ℃, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 104.4 mg (71%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.31 (t, *J* = 8.4 Hz, 2H), 3.42 (dd, *J* = 10.9, 5.1 Hz, 1H), 3.23 – 3.08 (m, 1H), 3.00 – 2.85 (m, 1H), 1.25 (d, *J* = 6.2 Hz, 12H).

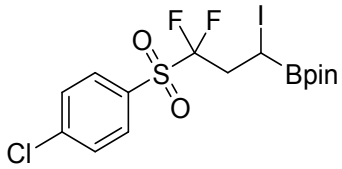
^{19}F NMR (376 MHz, Chloroform-*d*) δ -99.96, δ -103.10 (d, *J* = 229.36 Hz), -103.75 (d, *J* = 229.36 Hz).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.1 (d, *J* = 259.5 Hz), 133.8 (d, *J* = 10.1 Hz), 127.9, 123.3 (t, *J* = 287.8 Hz), 116.9 (d, *J* = 22.9 Hz), 84.4, 35.4 (t, *J* = 19.6 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.2.

HRMS (ESI) calcd for $C_{15}H_{20}BF_3IO_4S$ ($M+H^+$): 491.0167, found: 491.0169.

2-(3-((4-chlorophenyl)sulfonyl)-3,3-difluoro-1-iodopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)



White solid, mp: 109-110 ℃, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 115.4 mg (76%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 3.41 (dd, *J* = 10.9, 5.1 Hz, 1H), 3.22 – 3.07 (m, 1H), 2.99 – 2.85 (m, 1H), 1.25 (d, *J* = 6.5 Hz, 12H).

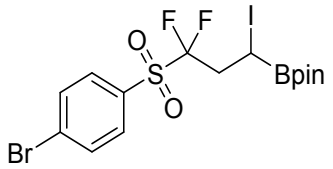
^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.98 (d, *J* = 229.36 Hz), -103.63 (d, *J* = 229.36 Hz).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.7, 132.2, 130.4, 129.8, 123.4 (t, *J* = 288.1 Hz), 84.5, 35.4 (t, *J* = 19.6 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.9.

HRMS (ESI) calcd for $C_{15}H_{20}BClF_2IO_4S$ ($M+H^+$): 506.9871, found: 506.9873.

2-(3-((4-bromophenyl)sulfonyl)-3,3-difluoro-1-iodopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q)



White solid, mp: 123-124 ℃, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 95.6 mg (58%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 3.41 (dd, *J* = 11.0, 5.1 Hz, 1H), 3.22 – 3.06 (m, 1H), 2.99 – 2.84 (m, 1H), 1.24 (d, *J* = 6.4 Hz, 12H).

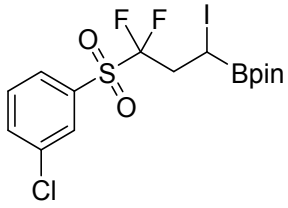
^{13}C NMR (126 MHz, Chloroform-*d*) δ 132.8, 132.2, 131.5 130.9, 123.4 (t, *J* = 288.1

Hz), 84.5, 35.4 (t, *J* = 19.6 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.8.

HRMS (ESI) calcd for $C_{15}H_{20}BBrF_2IO_4S$ ($M+H^+$): 550.9366, found: 550.9366.

2-(3-((3-chlorophenyl)sulfonyl)-3,3-difluoro-1-iodopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r)



White solid, mp: 66-67 ℃, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 106.3 mg (70%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (t, *J* = 2.0 Hz, 1H), 3.22 – 3.07 (m, 1H), 3.00 – 2.85 (m, 1H), 1.25 (d, *J* = 5.8 Hz, 12H).

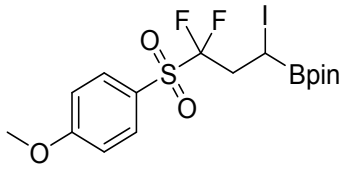
^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.74 (d, *J* = 229.36 Hz), -103.36 (d, *J* = 229.36 Hz).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.8, 135.7, 133.8, 130.6, 128.9, 123.5 (t, *J* = 288.4 Hz), 84.5, 35.4 (t, *J* = 19.5 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.2.

HRMS (ESI) calcd for $C_{15}H_{20}BClF_2IO_4S$ ($M+H^+$): 506.9871, found: 506.9869.

2-(3,3-difluoro-1-iodo-3-((4-methoxyphenyl)sulfonyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)



White solid, mp: 122-123 ℃, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 137.0 mg (91%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H), 3.40 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.19 – 3.04 (m, 1H), 2.96 – 2.81 (m, 1H), 1.23 (d, *J* = 6.1 Hz, 12H).

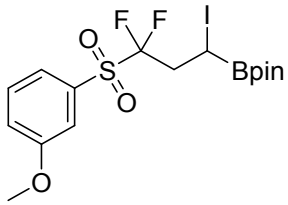
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.10 (d, *J* = 229.36 Hz), -103.75 (d, *J* = 229.36 Hz).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.3, 133.0, 123.2 (t, *J* = 287.1 Hz), 122.7, 114.7, 84.3, 55.8, 35.6 (t, *J* = 19.8 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.0.

HRMS (ESI) calcd for $C_{16}H_{23}BF_2IO_5S$ ($M+H^+$): 503.0367, found: 503.0367.

2-(3,3-difluoro-1-iodo-3-((3-methoxyphenyl)sulfonyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)



White solid, mp: 84-85 ℃, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 30:1; Yield: 122.2 mg (81%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.49 (m, 2H), 7.43 (t, *J* = 2.1 Hz, 1H), 7.28 (ddd, *J* = 8.2, 2.7, 1.2 Hz, 1H), 3.88 (s, 3H), 3.42 (dd, *J* = 10.9, 5.0 Hz, 1H), 3.22 – 3.07 (m, 1H), 2.99 – 2.84 (m, 1H), 1.25 (d, *J* = 6.3 Hz, 12H).

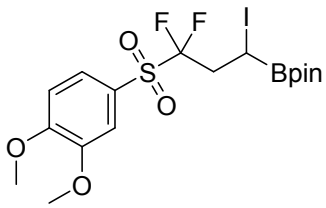
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.39 (d, *J* = 229.36 Hz), -104.04 (d, *J* = 229.36 Hz).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.0, 133.1, 130.4, 123.4 (t, *J* = 288.4 Hz), 123.1, 122.3, 114.8, 84.4, 55.8, 35.6 (t, *J* = 19.7 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.8.

HRMS (ESI) calcd for $C_{16}H_{23}BF_2IO_5S$ ($M+H^+$): 503.0367, found: 503.0367.

2-(3-((3,4-dimethoxyphenyl)sulfonyl)-3,3-difluoro-1-iodopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3u)



White solid, mp: 142-144 ℃, Flash column chromatography conditions: *n*-pentane:

ethyl acetate = 30:1; Yield: 110.1 mg (69%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.34 (s, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 3.41 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.21 – 3.05 (m, 1H), 2.97 – 2.82 (m, 1H), 1.24 (d, *J* = 6.5 Hz, 12H).

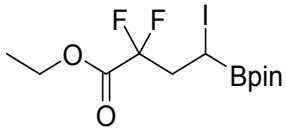
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.61 (d, *J* = 229.36 Hz), -104.19 (d, *J* = 229.36 Hz).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.1, 149.3, 125.6, 123.4 (t, *J* = 287.3 Hz), 122.9, 112.3, 110.9, 84.4, 56.3, 35.7 (t, *J* = 19.9 Hz), 24.2, 24.0.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.0.

HRMS (ESI) calcd for $C_{17}H_{25}BF_2IO_6S$ ($M+H^+$): 533.0472, found: 533.0472.

Ethyl 2,2-difluoro-4-iodo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) butanoate (3v)



Colourless liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 20:1; Yield: 89.7 mg (74%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.32 (q, *J* = 7.2, 6.7 Hz, 1H), 3.33 (dd, *J* = 11.2, 5.0 Hz, 1H), 2.89 – 2.77 (m, 1H), 2.74 – 2.62 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 1H), 1.26 (d, *J* = 5.3 Hz, 12H).

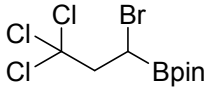
^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.17 (d, *J* = 262.3 Hz), -107.11 (d, *J* = 262.3 Hz).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3 (t, *J* = 32.4 Hz), 115.2 (t, *J* = 252.3 Hz), 84.3, 63.0, 40.5 (t, *J* = 23.3 Hz), 24.1, 24.1, 13.8.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.3.

HRMS (ESI) calcd for $C_{12}H_{21}BF_2IO_4$ ($M+H^+$): 405.0540, found: 405.0540.

2-(1-bromo-3,3,3-trichloropropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3w)



Colourless liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate =

80:1; Yield: 94.0 mg (89%);

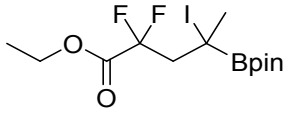
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 – 7.11 (m, 2H), 6.87 (dd, *J* = 14.2, 2.8 Hz, 1H), 4.92 (s, 12H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 97.8, 84.6, 58.4, 24.3, 24.3.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.4.

HRMS (EI) calcd for $C_9H_{15}BBrCl_3O_2$: 349.9414, found: 349.9411.

ethyl 2,2-difluoro-4-iodo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pentanoate (3x)



Colourless liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 20:1; Yield: 76.0 mg (61%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.31 (q, *J* = 7.2 Hz, 2H), 3.21 – 3.09 (m, 1H), 2.95 – 2.83 (m, 1H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.27 (d, *J* = 5.8 Hz, 12H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -101.28 (d, *J* = 264.8 Hz), -104.78 (d, *J* = 264.8 Hz).

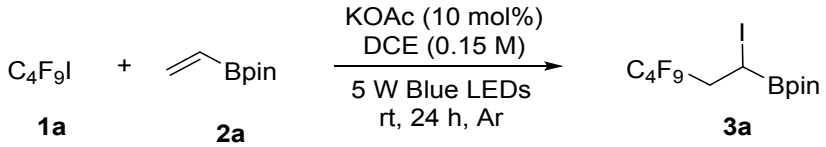
^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.5 (t, *J* = 32.5 Hz), δ 115.4 (t, *J* = 348.8 Hz), 84.4, 63.0, 47.8 (t, *J* = 22.0 Hz), 29.4, 24.1, 24.1, 13.9.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.1.

HRMS (ESI) calcd for $C_{13}H_{23}BF_2IO_4$ ($M+H^+$): 419.0697, found: 419.0696.

4. Synthetic applicability

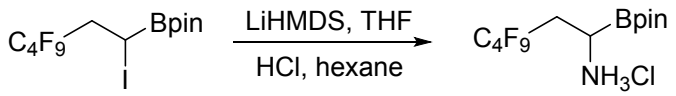
Gram scale study



1a **2a** **3a**

In air, a 200 mL schlenk tube was charged with KOAc (1 mmol, 99 mg, 10 mol%). The tube was evacuated and filled with Argon for three cycles. Then, 1,1-Dichloroethane (65 mL), Vinyl borate pinacol ester (**2a**) (10 mmol, 1.7 mL, 1.0 equiv), Perfluoroiodobutane (**2a**) (3.44 mL, 2.0 equiv) were added to the tube at room temperature. The reaction was allowed to stir under 5 W Blue LEDs irradiation at room

temperature. After 24 hours, the crude reaction mixture was concentrated in vacuo and purified by column chromatography (*n*-pentane: ethyl acetate = 30:1) to afford the desired product **3a** as a yellow liquid in 73% yield (3.69 g).

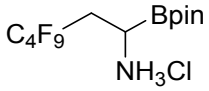


3a **4**

The amine hydrochloride **4** is prepared according to the reference[4].

α-haloboronates **3a** (500 mg, 1 mmol, 1 equiv) was dissolved in anhydrous THF (1.3 mL) and was added dropwise to a cool (-78 °C) solution consisting of lithium bis(trimethylsilyl)amide (1.2 mL, 1.2 mmol, 1.0 M in THF) and THF (1.3 mL). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. It was concentrated in vacuo, and hexane was added. The reaction mixture was cooled to -78 °C, and 4 N anhydrous hydrogen chloride in dioxane (0.75 mL, 3 mmol, 3 equiv) was added dropwise. The mixture was warmed to room temperature and stirred for 5 h. Solvent was removed by evaporation, and chloroform was added. Insoluble material was removed by filtration. The filtrate was evaporated almost to dryness, and hexanes were added. The desired product crystallized. It was isolated and washed with cold n-pentane to yield 250mg (59 %) of **4** as the amine hydrochloride.

3,3,4,4,5,5,6,6,6-nonafluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-amino hydrochloride (4)



Off-white solid, mp: 184-185 ℃

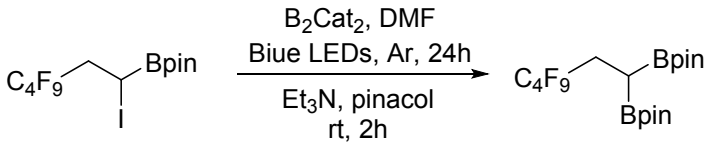
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (s, 3H), 3.59 (q, *J* = 5.8 Hz, 1H), 3.14 – 2.99 (m, 1H), 2.93 – 2.77 (m, 1H), 1.31 (s, 12H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.95 (t, *J* = 9.7 Hz), -110.16 – -111.64 (m)., -124.25 – -124.46 (m), -125.75 – -125.89 (m).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 86.5, 30.16 (t, *J* = 21.3 Hz), 24.9, 24.7.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.8.

HRMS (ESI) calcd for $C_{12}H_{18}BF_9NO_2$ ($M+H^+$): 390.1281, found: 390.1279.

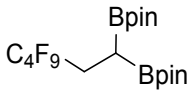


3a **5**

The *gem*-diboronate **5** is prepared according to the reference[5].

In air, a 25 mL schlenk tube was charged with bis(catecholato)diboron (190 mg, 0.800 mmol, 4 equiv). The tube was evacuated and filled with argon for three cycles. Then, Dimethylformamide (0.6 mL) and *α*-haloboronates **3a** (100 mg, 0.2 mmol, 1.0 equiv) was added. The reaction mixture was stirred under 5 W Blue LED irradiation at room temperature for 24 hours. A solution of pinacol (95 mg, 0.80 mmol, 4.0 equiv) in triethylamine (0.7 mL) was added to the mixture. After 2-hour, water (15 mL) was added and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified by flash column chromatography (*n*-pentane: ethyl acetate = 20:1) to afford the desired product **5** as a colorless oil in 61% yield (61.2 mg).

2,2'-(3,3,4,4,5,5,6,6,6-nonafluorohexane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5)



Known compound[6].

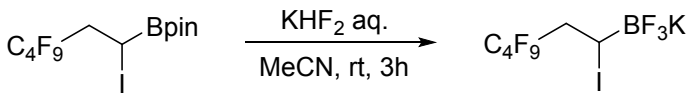
^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.42 – 2.29 (m, 2H), 1.22 (d, *J* = 6.1 Hz, 24H), 1.05 (t, *J* = 7.3 Hz, 1H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.98 (t, *J* = 9.9 Hz), -114.84 – -115.03 (m), -124.40 – -124.54 (m), -125.85 – -125.99 (m).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 83.7, 27.3 (t, *J* = 22.3 Hz), 24.8, 24.5.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.1.

HRMS (ESI) calcd for $C_{18}H_{28}B_2F_9O_4$ ($M+H^+$): 501.2025, found: 501.2021.

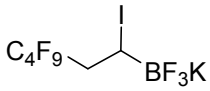


3a **6**

The potassium α-iodidetrifluoroborate **6** is prepared according to the reference[7].

α-haloboronates **3a** (400 mg, 0.8 mmol) was dissolved in acetonitrile (5 mL) and saturated aqueous potassium hydrogenfluoride solution (0.90 mL, 4.1 mmol, 4.5 M) was added. The reaction mixture was stirred at room temperature for 3 hours, concentrated, azeotroped with methanol and placed on the vacuum overnight. The crude product was dissolved in acetone, filtered and concentrated. The resulting crude product was washed with n-pentane several times to give the desired product **6** (375 mg, 98% yield) as a white solid.

potassium trifluoro(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)borate (6)



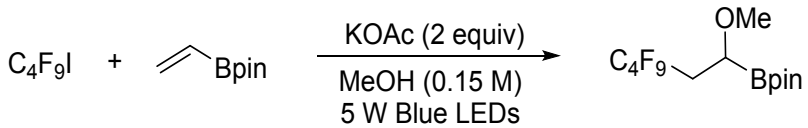
^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 2.92 (s, 1H), 2.81 – 2.63 (m, 5H), 2.50 – 2.30 (m, 1H).

^{19}F NMR (471 MHz, Acetonitrile-d_3) δ -81.82 (t, J = 10.4 Hz), -114.03 – -117.09 (m), -125.15. – -125.47 (m). -125.64 – -127.20 (m), -149.46 – -149.99 (m).

^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 36.7 (t, J = 21.1 Hz).

^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 3.0.

HRMS (ESI) calcd for $C_6H_3BF_{12}I$ $(M\text{-}K^+)^-$: 440.9186, found: 440.9184.

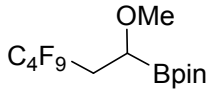


1a **2a** **7**

In air, a 25 mL Schlenk tube was charged with KOAc (0.6 mmol, 59 mg, 2.0 equiv). The tube was evacuated and filled with Argon for three cycles. Then, methanol (2 mL), Vinyl borate pinacol ester (**2a**) (0.3 mmol, 105 μL, 1.0 equiv), Perfluoroiodobutane (**1a**) (105 μL, 0.6 mmol, 2.0 equiv) were added to the tube at room temperature. The reaction was allowed to stir under Blue LEDs irradiation at room temperature. After 24 hours, the crude reaction mixture was concentrated in vacuo and purified by column

chromatography (*n*-pentane: ethyl acetate = 20:1) to afford the desired product **7** as a colorless oil in 79% yield (95.6 mg).

4,4,5,5-tetramethyl-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-methoxyhexyl)-1,3,2-dioxaborolane (7)



^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.45 (t, *J* = 5.9 Hz, 1H), 3.38 (s, 3H), 2.60 – 2.31 (m, 2H), 1.28 (s, 12H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.95 (t, *J* = 10.1 Hz), -111.32 – -113.57 (m), -124.49 – -124.67 (m), -125.75 – -125.93 (m).

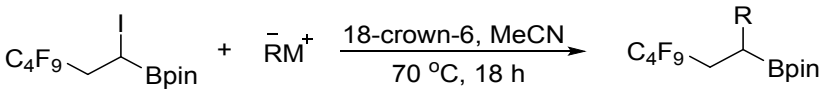
^{13}C NMR (126 MHz, Chloroform-*d*) δ 84.5, 58.3, 31.5 (t, *J* = 21.5 Hz), 24.7, 24.6.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.1.

HRMS (ESI) calcd for $C_{13}H_{19}BF_9O_3$ ($M+H^+$): 405.1278, found: 405.1278.

S_N2 reaction of *α*-haloboronates:

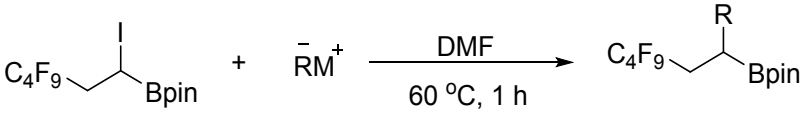
Method A



3a **8**

In air, a 25 mL schlenk tube was charged with potassium benzoate (0.4 mmol, 2.0 equiv), 18-crown-6 (0.2 mmol, 1.0 equiv). The tube was evacuated and filled with Argon for three cycles. Then, MeCN (2 mL), *α*-haloboronate **3a** was added to the tube at room temperature. The reaction mixture was vigorously stirred at 70 °C until the reaction was complete as monitored by TLC analysis (18 h). the crude reaction mixture was concentrated in vacuo and purified by column chromatography to afford the desired product.

Method B

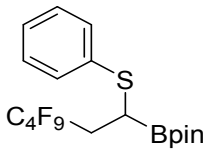


3a **8**

In air, a 25 mL schlenk tube was charged with sodiumthiophenate (0.24 mmol, 1.2

equiv), The tube was evacuated and filled with Argon for three cycles. Then, DMF (2 mL), *α*-haloboronate **3a** was added to the tube at room temperature. The reaction mixture was vigorously stirred at 60 °C until the reaction was complete as monitored by TLC analysis (1 h). The reaction mixture was quenched with water and extracted with EtOAc. The combined organic layers were concentrated in vacuo and purified by column chromatography to afford the desired product.

4,4,5,5-tetramethyl-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-(phenylthio)hexyl)-1,3,2-dioxaborolane (8a)



This compound was synthesized according to the Method B, Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 50:1; Yield: 63.5 mg (66%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 6H), 7.33 – 7.28 (m, 6H), 7.26 – 7.22 (m, 3H), 3.01 (dd, *J* = 11.5, 3.3 Hz, 3H), 2.73 – 2.57 (m, 1H), 2.46 – 2.32 (m, 1H), 1.23 (d, *J* = 10.4 Hz, 38H).

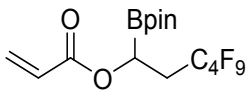
^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.4, 130.6, 129.1, 127.1, 84.5, 33.3 (t, *J* = 21.4 Hz), 24.5, 24.4.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.95 (t, *J* = 10.8 Hz), -111.73 – -114.16 (m), -124.33 – -124.50 (m), -125.83 – -125.99 (m).

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.1.

HRMS (ESI) calcd for $C_{18}H_{21}BF_9O_2S$ ($M+H^+$): 483.1206, found: 483.1201.

3,3,4,4,5,5,6,6,6-nonafluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl acrylate (8b)



This compound was synthesized according to the Method A, Colourless liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 50:1; Yield: 71.6 mg (81%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.48 (d, *J* = 17.3 Hz, 1H), 6.15 (ddd, *J* = 17.4, 10.5, 1.8 Hz, 1H), 5.93 (d, *J* = 10.4 Hz, 1H), 4.38 (dt, *J* = 9.7, 2.6 Hz, 1H), 2.69 – 2.36 (m, 2H), 1.26 (s, 12H).

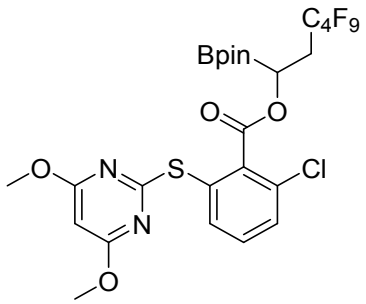
^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.03 (t, *J* = 9.8 Hz), -111.68 – -115.03 (m), -124.33 – -124.60 (m), -125.85 – -126.07 (m).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.3, 132.8, 126.7, 84.1, 31.5 (t, *J* = 21.3 Hz), 24.7, 24.6.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.9.

HRMS (ESI) calcd for $C_{15}H_{19}BF_9O_4$ ($M+H^+$): 445.1227, found: 445.1222.

3,3,4,4,5,5,6,6,6-nonafluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl 2-chloro-6-((4,6-dimethoxypyrimidin-2-yl)thio)benzoate (8c)



This compound was synthesized according to the Method A, Yellow liquid, Flash column chromatography conditions: *n*-pentane: ethyl acetate = 50:1; Yield: 66.2 mg (49%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.46 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 5.69 (s, 1H), 4.57 (dd, *J* = 8.0, 4.7 Hz, 1H), 3.69 (s, 6H), 2.66 – 2.44 (m, 2H), 1.25 (d, *J* = 5.1 Hz, 12H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.96 (t, *J* = 9.7 Hz), -112.48 – -114.39 (m), -124.34 – -124.49 (m), -125.85 – -125.99 (m),

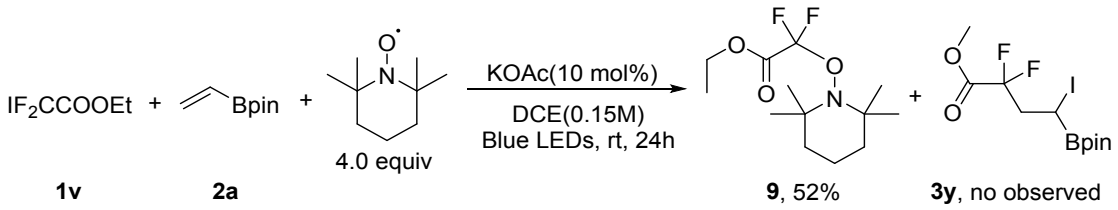
^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.8, 169.2, 166.5, 138.1, 136.1, 131.4, 130.4, 130.2, 129.3, 86.4, 84.6, 53.9, 31.5 (t, *J* = 21.7 Hz), 24.6.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.4.

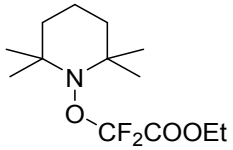
HRMS (ESI) calcd for $C_{25}H_{26}BClF_9N_2O_6S$ ($M+H^+$): 699.1144, found: 699.1140.

5. Mechanism studies

5.1. Radical inhibition experiment with TEMPO



In air, a 25 mL schlenk tube was charged with KOAc (3 mg, 0.03 mmol, 10 mol%) and TEMPO (188 mg, 1.2 mmol, 4.0 equiv). The tube was evacuated and filled with Argon for three cycles. Then, 1,1-Dichloroethane (2 mL), Vinyl borate pinacol ester (**2a**) (52 μL, 0.3 mmol, 1.0 equiv), Ethyl iododifluoroacetate (**1v**) (88 μL, 0.6 mmol, 2.0 equiv) were added to the tube at room temperature. The reaction was allowed to stir under Blue LEDs irradiation at room temperature. After 24 hours, the crude reaction mixture was concentrated in vacuo and purified by column chromatography (*n*-pentane: ethyl acetate = 30:1) to afford the TEMPO-CF_2COOEt Adduct **9** (44 mg, 52% yield). as colorless liquid.



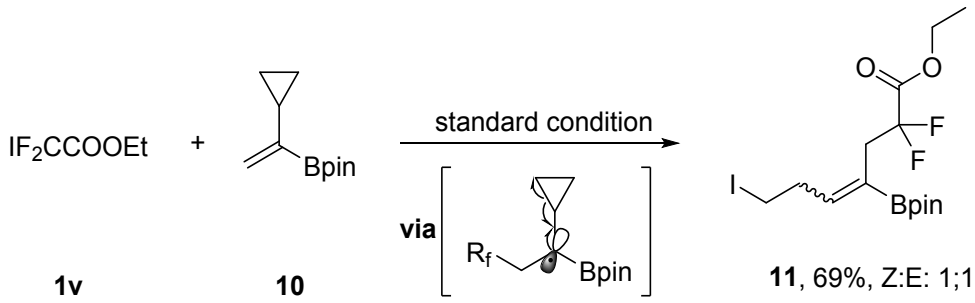
known compound[8].

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.35 (q, *J* = 7.1 Hz, 2H), 1.64 – 1.50 (m, 5H), 1.37 (t, *J* = 7.2 Hz, 4H), 1.21 – 1.13 (m, 12H).

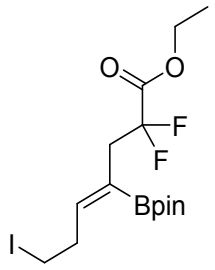
^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.45.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.7 (t, *J* = 42.6 Hz), 115.5 (t, *J* = 271.5 Hz), 63.0, 61.4, 40.2, 33.4 (t, *J* = 4.4 Hz), 20.7, 16.9, 13.9.

5.2. Radical clock experiments



In air, a 25 mL schlenk tube was charged with KOAc (3 mg, 0.03 mmol, 10 mol%). The tube was evacuated and filled with Argon for three cycles. Then, 1,1-Dichloroethane (2 mL), Alkenyl borate 10 (0.3 mmol, 1.0 equiv), Ethyl iododifluoroacetate (**1v**) (88 μL, 0.6 mmol, 2.0 equiv) were added to the tube at room temperature. The reaction was allowed to stir under 5 W Blue LEDs irradiation at room temperature. After 24 hours, the crude reaction mixture was concentrated in vacuo and purified by column chromatography (*n*-pentane: ethyl acetate = 30:1) to afford the open ring product **11** (92 mg, 69% yield) as colorless liquid, no unopened products are detected.



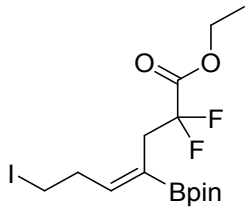
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.45 (t, *J* = 7.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 7.3 Hz, 2H), 2.94 (t, *J* = 17.3 Hz, 2H), 2.79 (q, *J* = 7.3 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 12H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -104.28.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.1 (t, *J* = 32.8 Hz), 149.3, 115.3 (t, *J* = 251.4 Hz), 83.8, 62.7, 33.4 (t, *J* = 23.8 Hz), 33.4, 24.6, 13.9, 2.7.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.7.

HRMS (ESI) calcd for $C_{15}H_{25}BF_2IO_4$ ($M+H^+$): 445.0853, found: 445.0852.



^{1}H NMR (500 MHz, Chloroform-d) δ 6.15 (t, *J* = 7.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.14 (t, *J* = 7.1 Hz, 2H), 3.00 – 2.81 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.25 (s, 12H).

^{13}C NMR (126 MHz, Chloroform-d) δ 164.1 (t, *J* = 32.9 Hz), 150.8, 115.6 (t, *J* = 251.3 Hz), 83.6, 62.6, 40.6 (t, *J* = 23.0 Hz), 34.7, 24.7, 14.0, 5.27.

^{19}F NMR (471 MHz, Chloroform-d) δ -104.54.

^{11}B NMR (128 MHz, Chloroform-d) δ 29.69.

HRMS (ESI) calcd for $C_{15}H_{25}BF_2IO_4$ ($M+H^+$): 445.0853, found: 445.0852.

5.3. UV-vis spectroscopic measurement

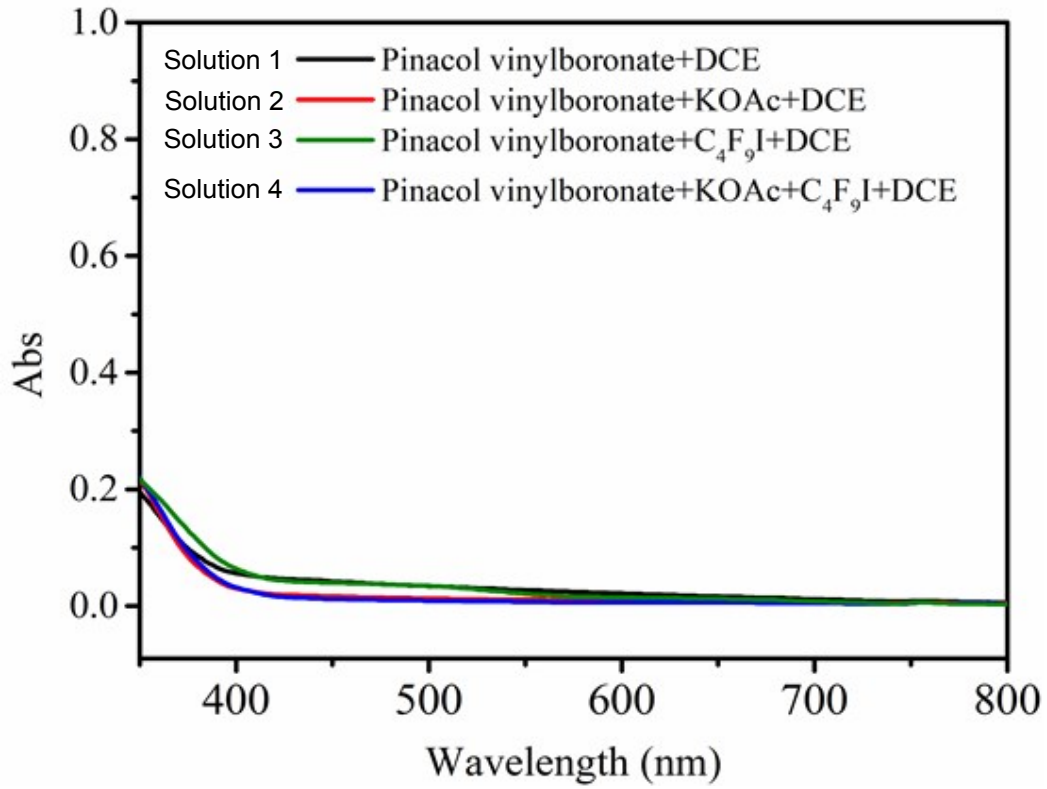
UV/vis absorption spectra were recorded in 1 cm path quartz cuvettes using Hitachi UH4150 UV/Vis spectrometer, pure DCE as blank sample.

Solution 1: Vinyl borate pinacol ester (53 μL, 0.3 mmol) was dissolved in DCE (2.0 mL).

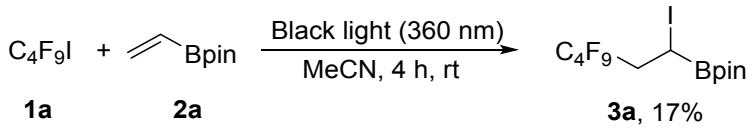
Solution 2: Vinyl borate pinacol ester (53 μL, 0.3 mmol) and KOAc (3 mg, 0.03 mmol) was dissolved in DCE (2.0 mL). The mixtures were stirred for two minutes, filtered before use.

Solution 3: Vinyl borate pinacol ester (53 μL, 0.3 mmol) and perfluoroiodobutane (0.6 mmol, 105 μL, 2.0 equiv) was dissolved in DCE (2.0 mL). The mixtures were stirred for two minutes, filtered before use.

Solution 4: Vinyl borate pinacol ester (53 μL, 0.3 mmol), perfluoroiodobutane (0.6 mmol, 105 μL, 2.0 equiv) and KOAc (3 mg, 0.03 mmol) was dissolved in DCE (2.0 mL). The mixtures were stirred for two minutes, filtered before use.

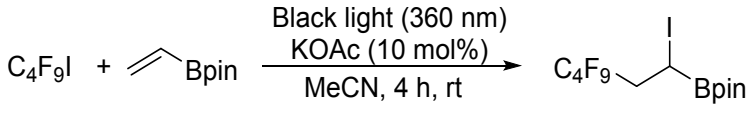


5.4. Comparative Experiment



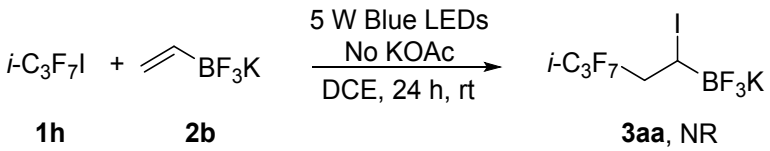
1a **2a** **3a**, 17%

In air, a 25 mL schlenk tube was evacuated and filled with argon for three cycles. Then, MeCN (0.5 mL), vinyl borate pinacol ester (**2a**) (0.5 mmol, 86 μL, 1.0 equiv), perfluoroiodobutane (**1a**) (0.75 mmol, 129 μL, 1.5 equiv) were added to the tube at room temperature. The reaction was allowed to stir under Black light (360 nm) irradiation at room temperature. After 4 hours, the yield is 17% after GC detection (dodecane as internal standard).



1a **2a** **3a**, 47%

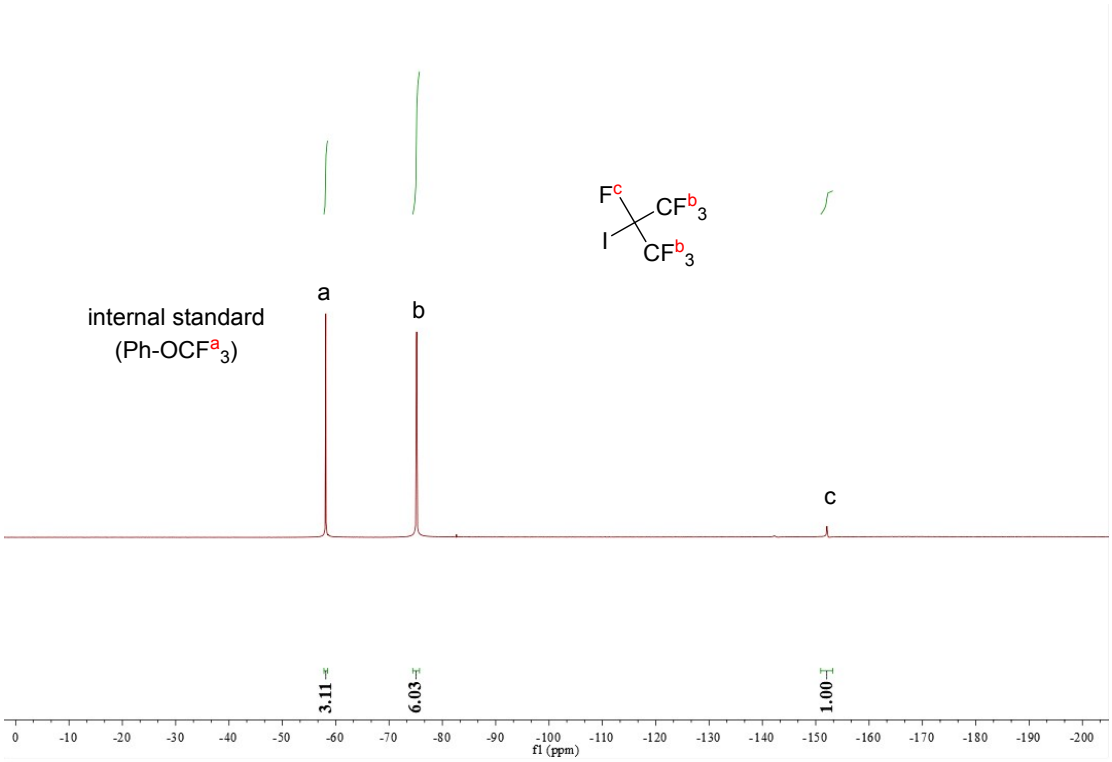
In air, a 25 mL schlenk tube was charged with KOAc (0.05 mmol, 5 mg, 10 mol%). The tube was evacuated and filled with Argon for three cycles. Then, MeCN (2 mL), vinyl borate pinacol ester (**2a**) (0.5 mmol, 86 μL, 1.0 equiv) and perfluoroiodobutane (**1a)** (0.75 mmol, 129 μL, 1.5 equiv) were added to the tube at room temperature. The reaction was allowed to stir under Black light (360 nm) irradiation at room temperature. After 4 hours, the yield is 47% after GC detection (dodecane as internal standard).

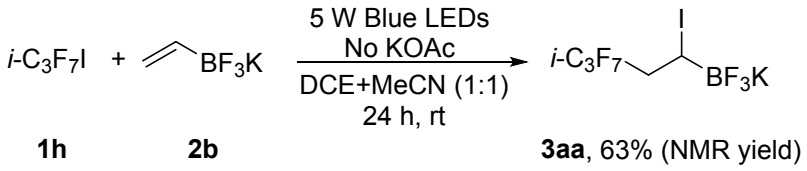


1h **2b** **3aa**, NR

In air, a 25 mL schlenk tube was charged with Potassium vinyl trifluoroborate (**2b**) (0.03 mmol, 40 mg, 1.0 equiv). The tube was evacuated and filled with argon for three cycles. Then, DCE (2 mL) and *i*-C_3F_7I (**1h**) (0.6 mmol, 81 μL, 2.0 equiv) were added to the tube at room temperature. The reaction was allowed to stir under 5 W Blue LEDs

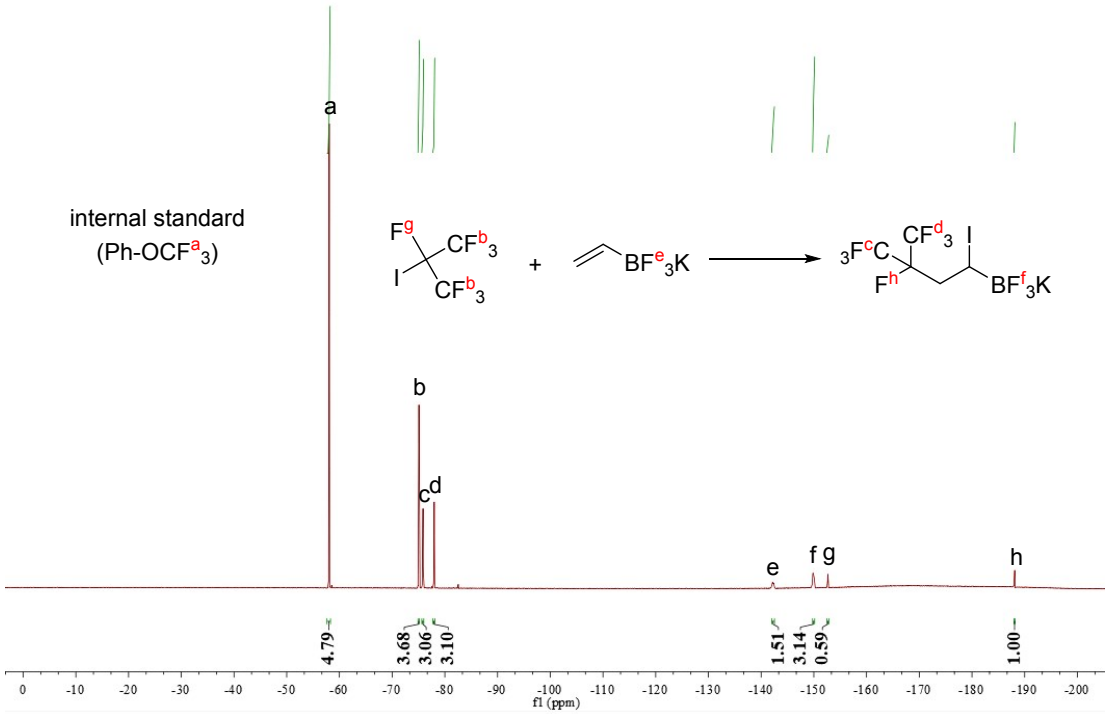
irradiation at room temperature. After 24 hours, trifluoromethoxybenzene (0.3 mmol, 40 μL, 1.0 equiv) was added as an internal standard, and the NMR spectrum was measured, but the target product was not obtained.





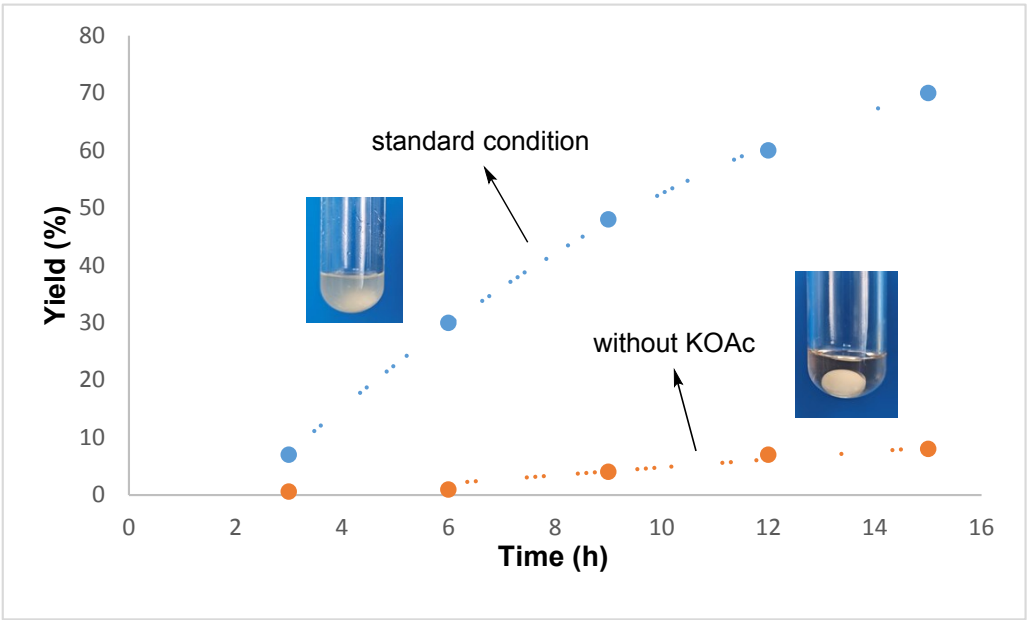
1h **2b** **3aa**, 63% (NMR yield)

In air, a 25 mL schlenk tube was charged with potassium vinyl trifluoroborate (**2b)** (0.03 mmol, 40 mg, 1.0 equiv). The tube was evacuated and filled with argon for three cycles. Then, DCE (1 mL), MeCN (1 ml) and *i*-C_3F_7I (**1h**) (0.6 mmol, 81 μL, 2.0 equiv) were added to the tube at room temperature. The reaction was allowed to stir under 5 W Blue LEDs irradiation at room temperature. After 24 hours, trifluoromethoxybenzene (0.3 mmol, 40 μL, 1.0 equiv) was added as an internal standard, and the NMR spectrum yield is 63%.

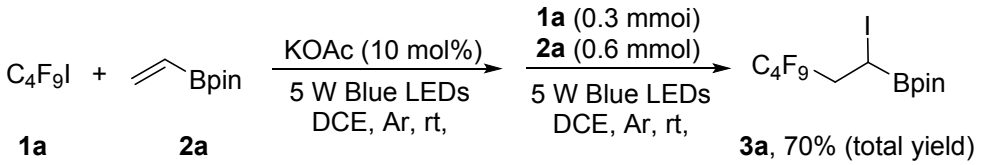


5.5. Comparison with or without KOAc

Yields were determined by GC using dodecane as internal standard.

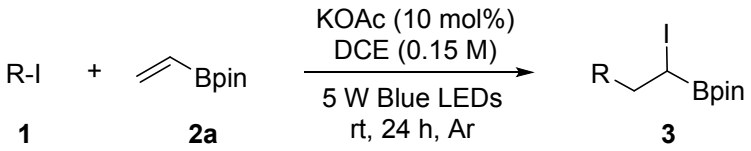


5.6. Catalyst cycle experiment

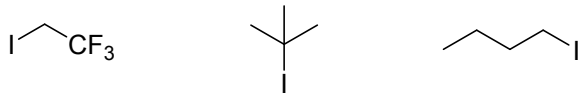


In air, a 25 mL schlenk tube was charged with KOAc (0.03 mmol, 3 mg, 10 mol%). The tube was evacuated and filled with Argon for three cycles. Then, DCE (2 mL), vinyl borate pinacol ester (**2a**) (0.3 mmol, 52 μL, 1.0 equiv) and perfluoroiodobutane (**1a**) (105 μL, 2.0 equiv) were added to the tube at room temperature. The reaction was allowed to stir under 5 W Blue LEDs irradiation at room temperature. After 24 hours, under argon atmosphere, add the same proportions of vinyl borate pinacol ester (**2a**) (0.3 mmol, 52 μL, 1.0 equiv), perfluoroiodobutane (**1a**) (105 μL, 2.0 equiv) and DCE (2 ml). After continuing the reaction for 24 hours, the total yield is 70% after GC detection.

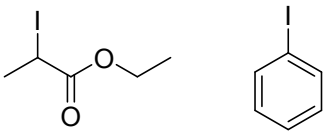
6. Unsuccessful examples



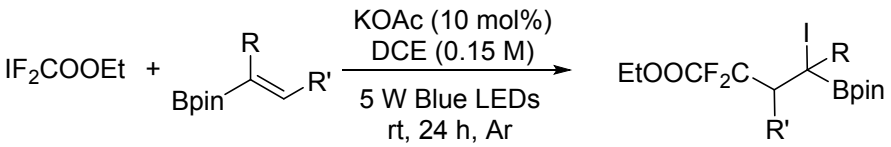
1 **2a** **3**



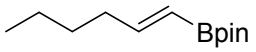
1z, N.D. **1aa**, N.D. **1ab**, N.D.



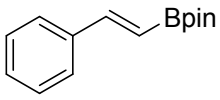
1ac, N.D. **1ad**, N.D.



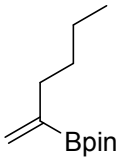
1v **2** **3**



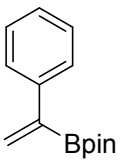
2c, <10%
Low regioselectivity



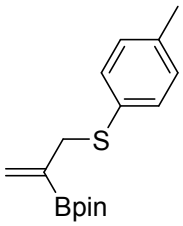
2d, N.D.



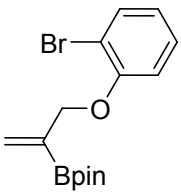
2e, <10%



2f, N.D.



2g, N.D.



2y, trace

7. References

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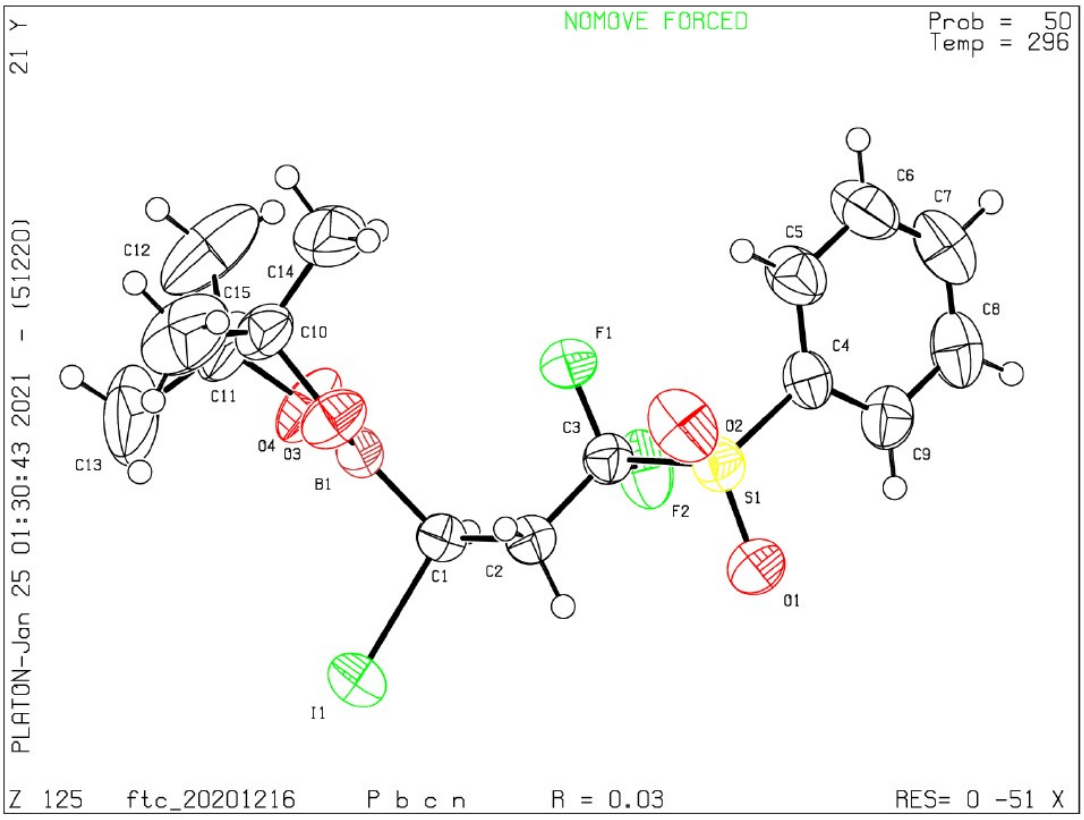
8. Nie, X.; Cheng, C.; Zhu, G. *Angew. Chem., Int. Ed*. 2017, **56**, 1898.

8. Crystal data and structure refinement for 3m (CCDC 2058412)



Bond precision: C-C = 0.0060 A Wavelength=0.71073

Cell: a=21.746(5) b=10.386(3) c=17.254(4)

alpha=90 beta=90 gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	3896.9(17)	3896.9(17)
Space group	P b c n	P b c n
Hall group	-P 2n 2ab	-P 2n 2ab
Moiety formula	C15 H20 B F2 I O4 S	C15 H20 B F2 I O4 S
Sum formula	C15 H20 B F2 I O4 S	C15 H20 B F2 I O4 S
Mr	472.08	472.08
Dx,g cm-3	1.609	1.609
Z	8	8
Mu (mm-1)	1.783	1.783
F000	1872.0	1872.0
F000’	1870.15	
h,k,lmax	24,11,19	24,11,19
Nref	2995	2994
Tmin,Tmax	0.807,0.899	0.654,0.745
Tmin’	0.807	

Correction method= # Reported T Limits: Tmin=0.654 Tmax=0.745

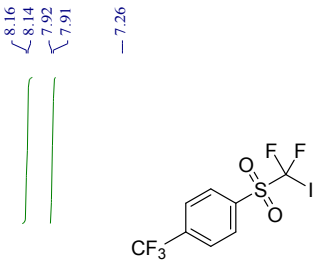
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 23.814

R(reflections)= 0.0276(2446) wR2(reflections)= 0.0699(2994)

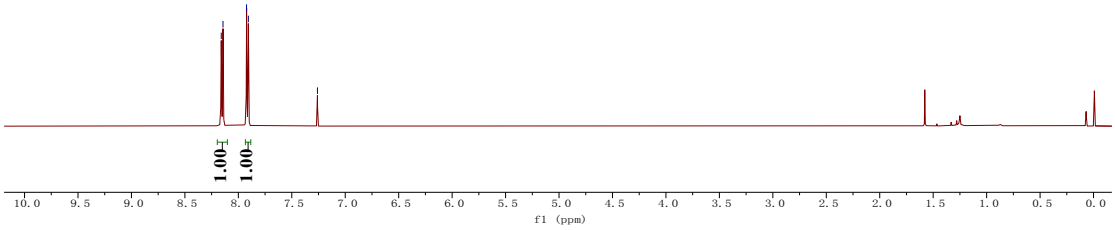
S = 1.025 Npar= 221

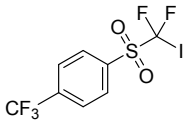
9. Copies of NMR spectra of all new compounds



1n

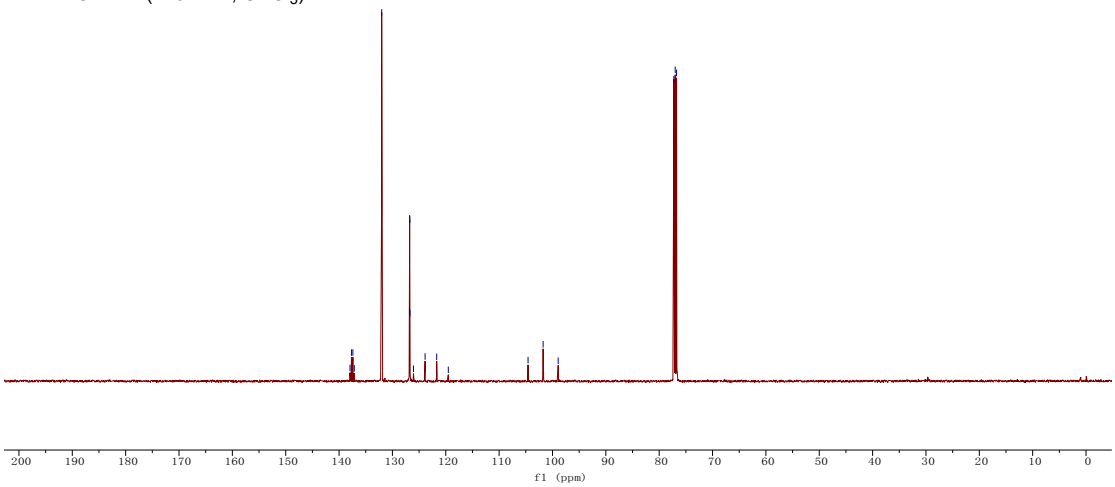
^{1}H NMR (500 MHz, $CDCl_3$)

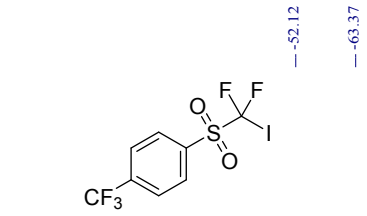




1n

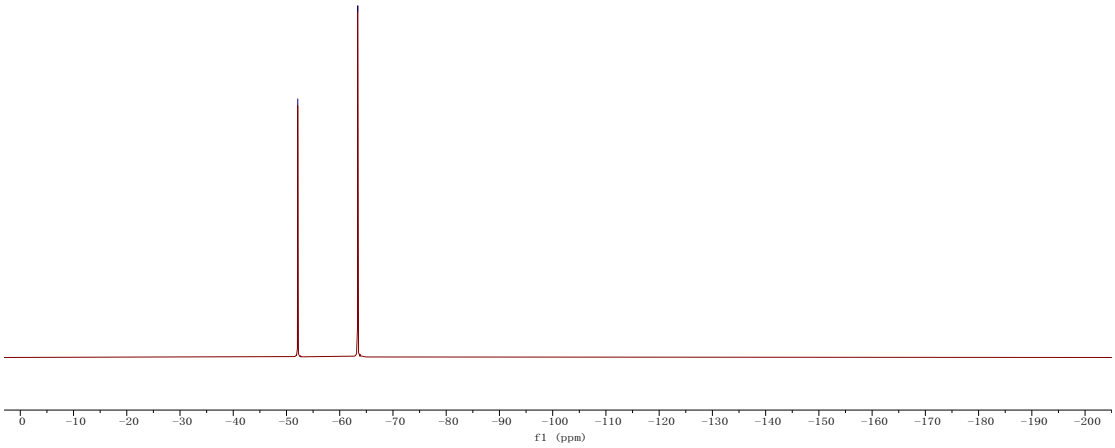
^{13}C NMR (126 MHz, $CDCl_3$)

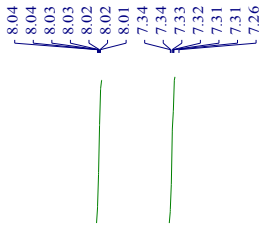


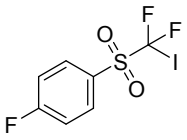


1n

^{19}F NMR (471 MHz, $CDCl_3$)

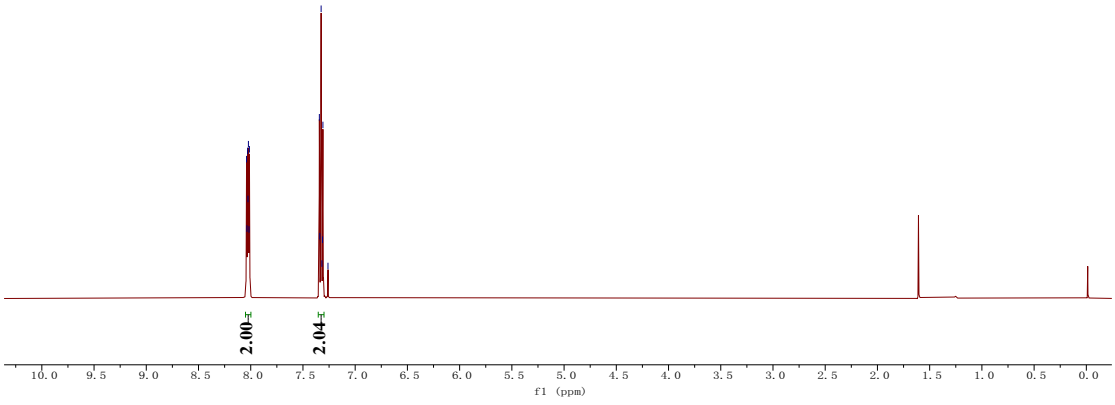


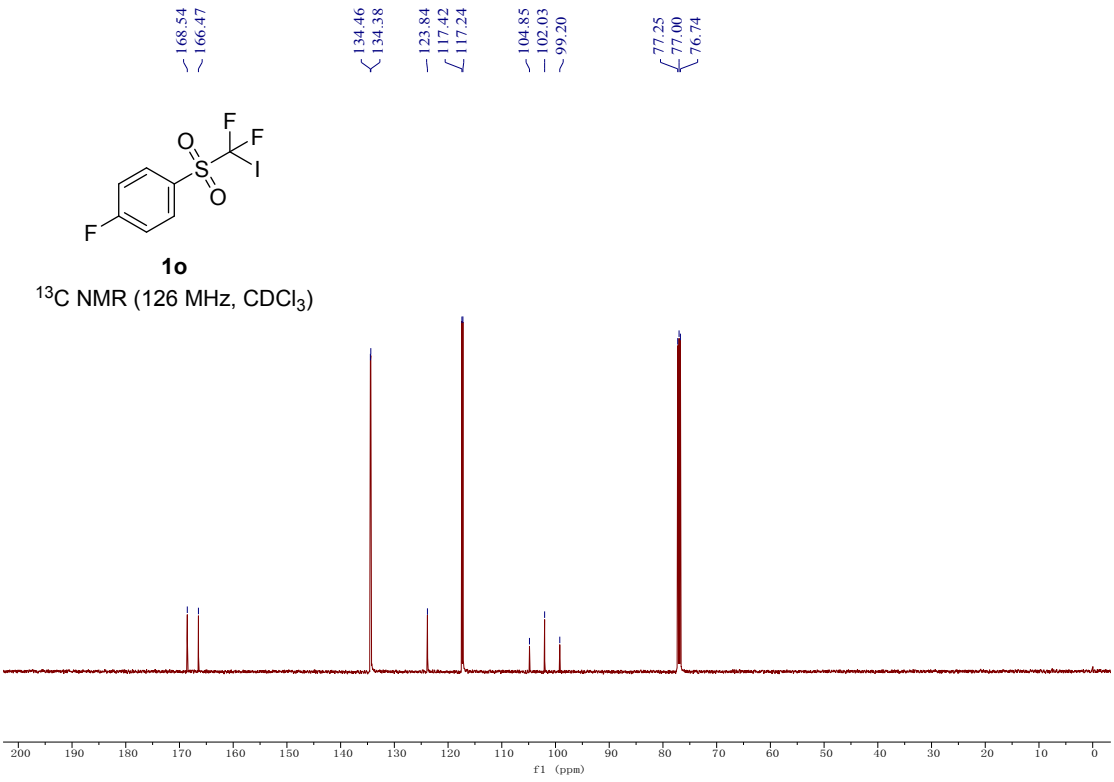




1o

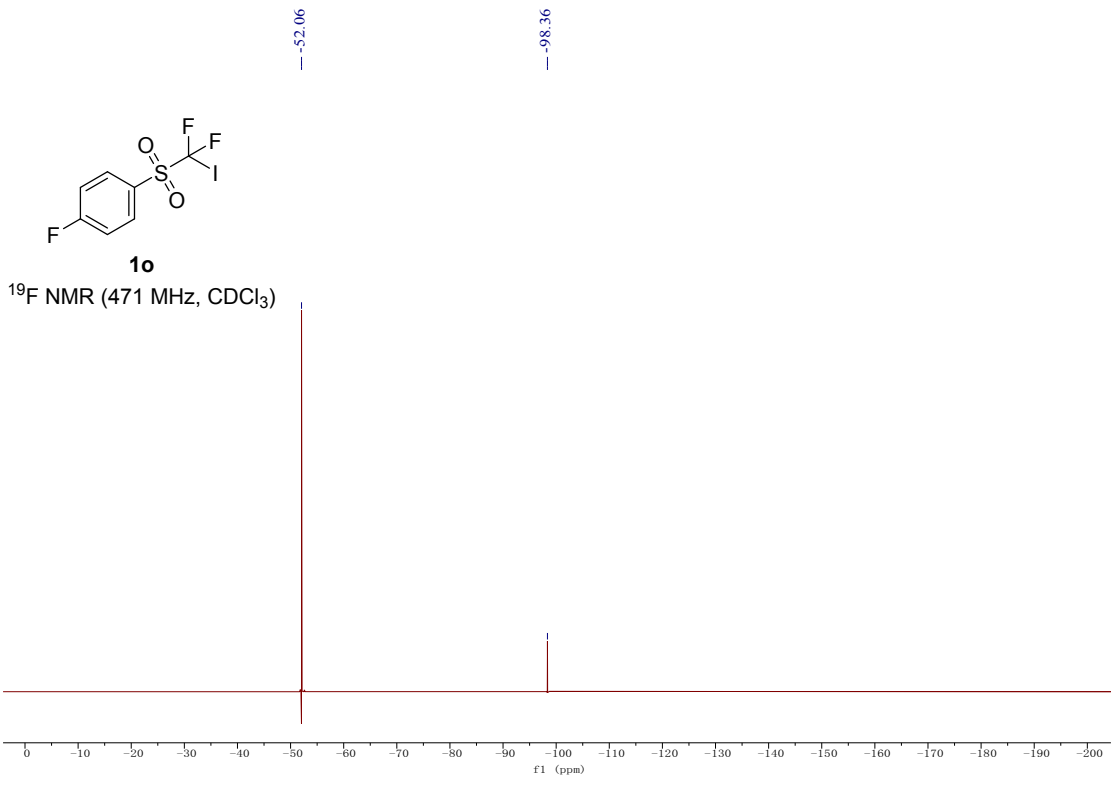
^{1}H NMR (500 MHz, $CDCl_3$))





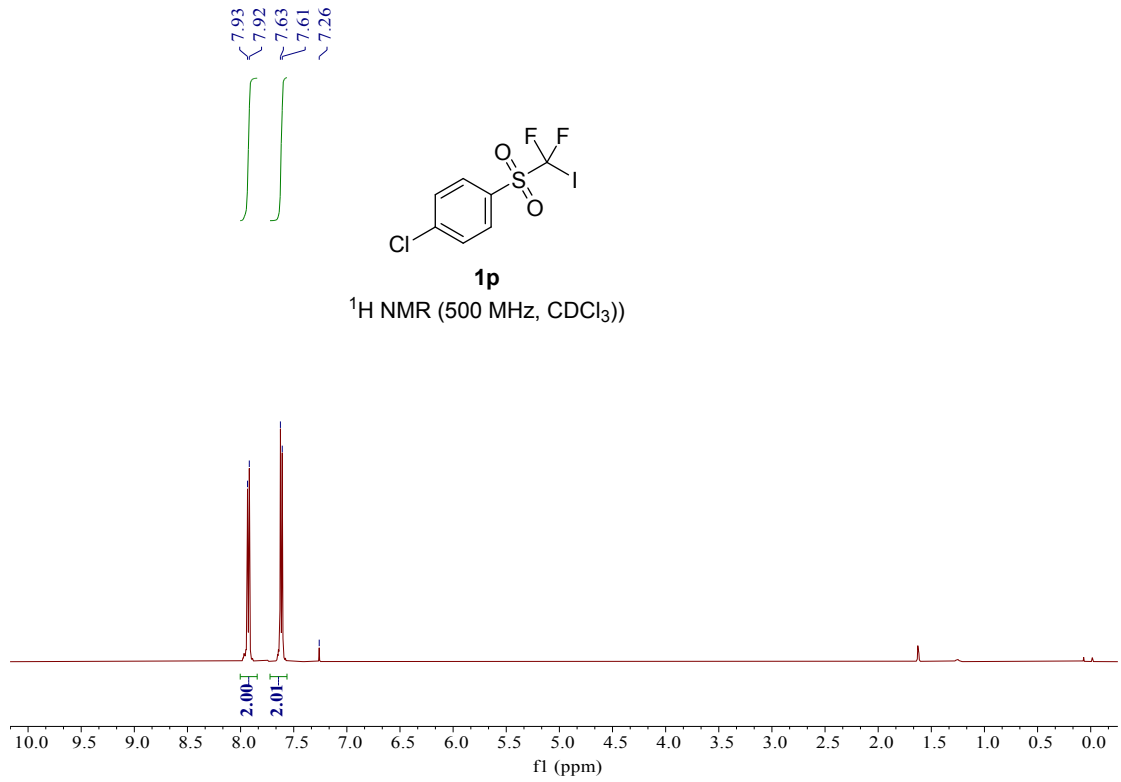
1o

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



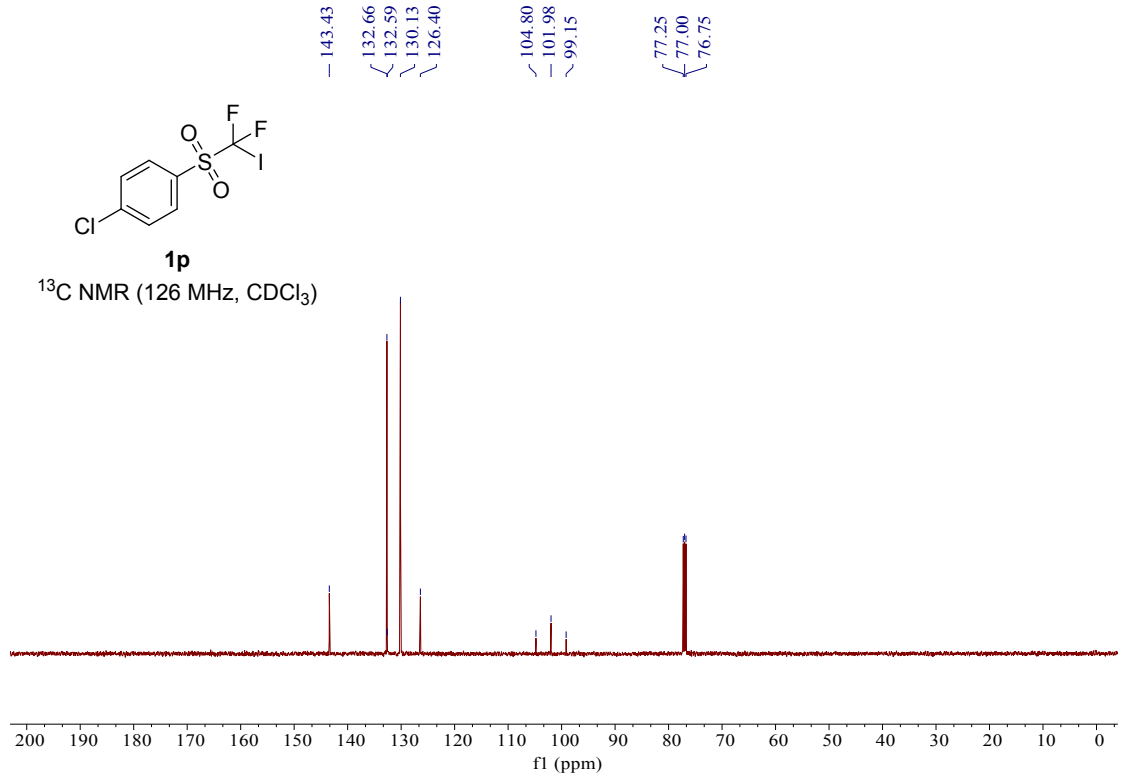
1o

^{19}F NMR (471 MHz, $CDCl_3$)



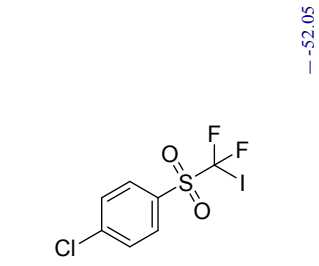
1p

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



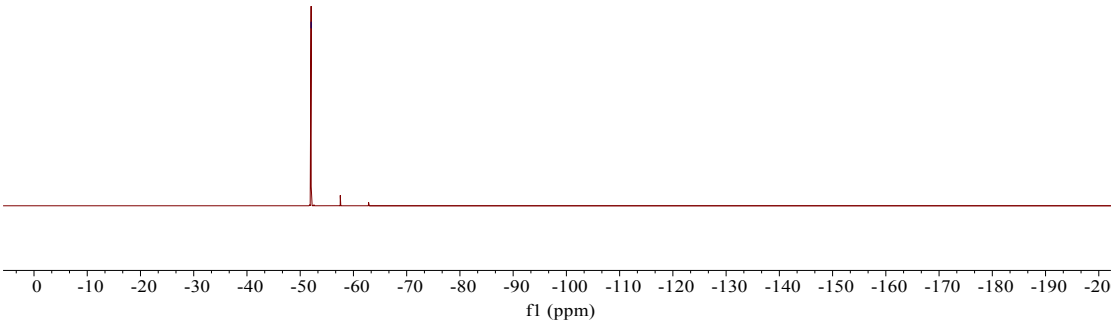
1p

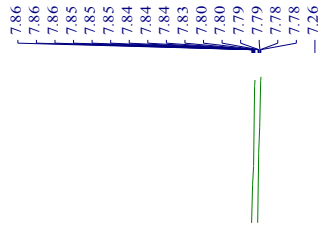
^{13}C NMR (126 MHz, $CDCl_3$)

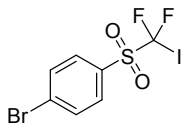


1p

^{19}F NMR (471 MHz, $CDCl_3$)

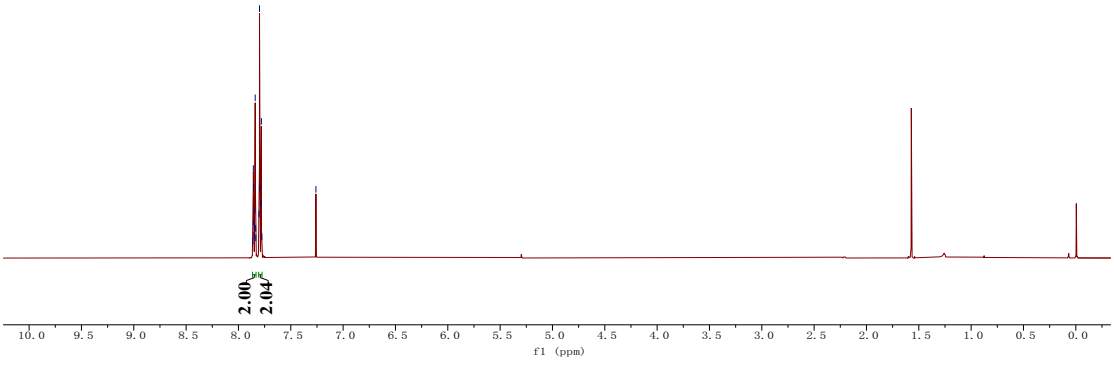


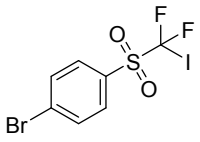




1q

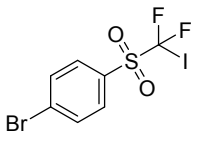
^{1}H NMR (500 MHz, $CDCl_3$))





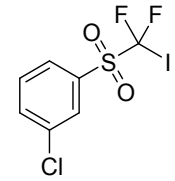
1q

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



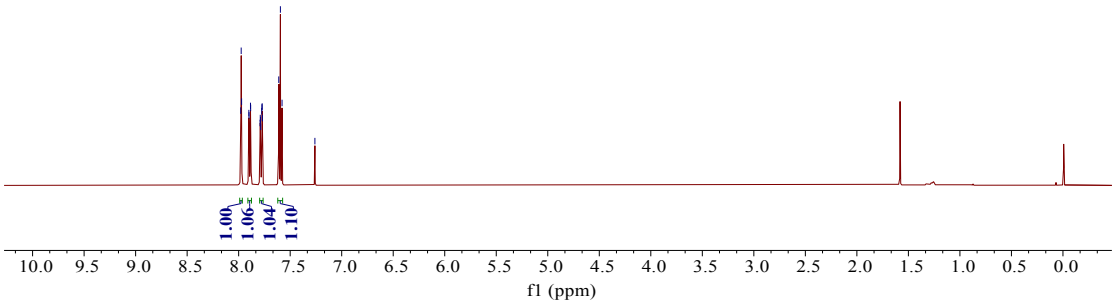
1q

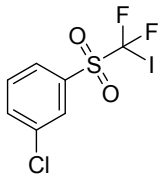
^{19}F NMR (471 MHz, $CDCl_3$)



1r

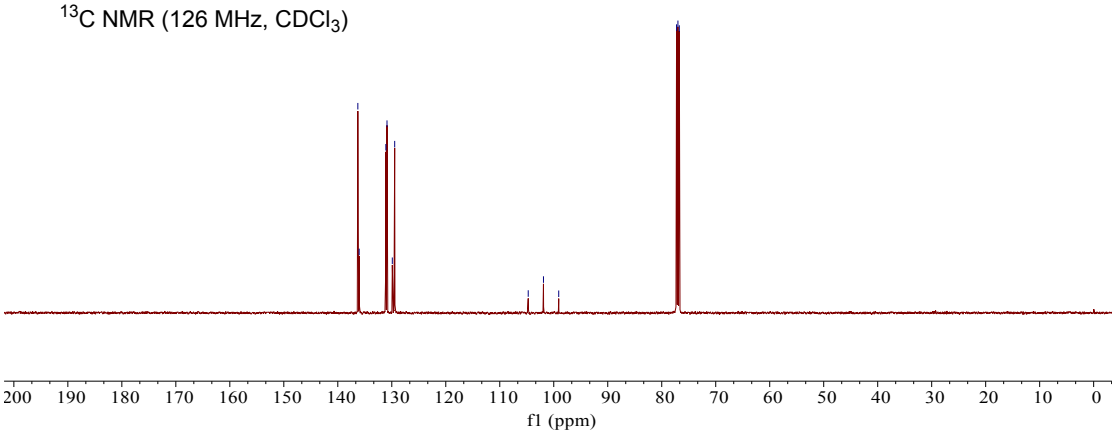
^{1}H NMR (500 MHz, $CDCl_3$))

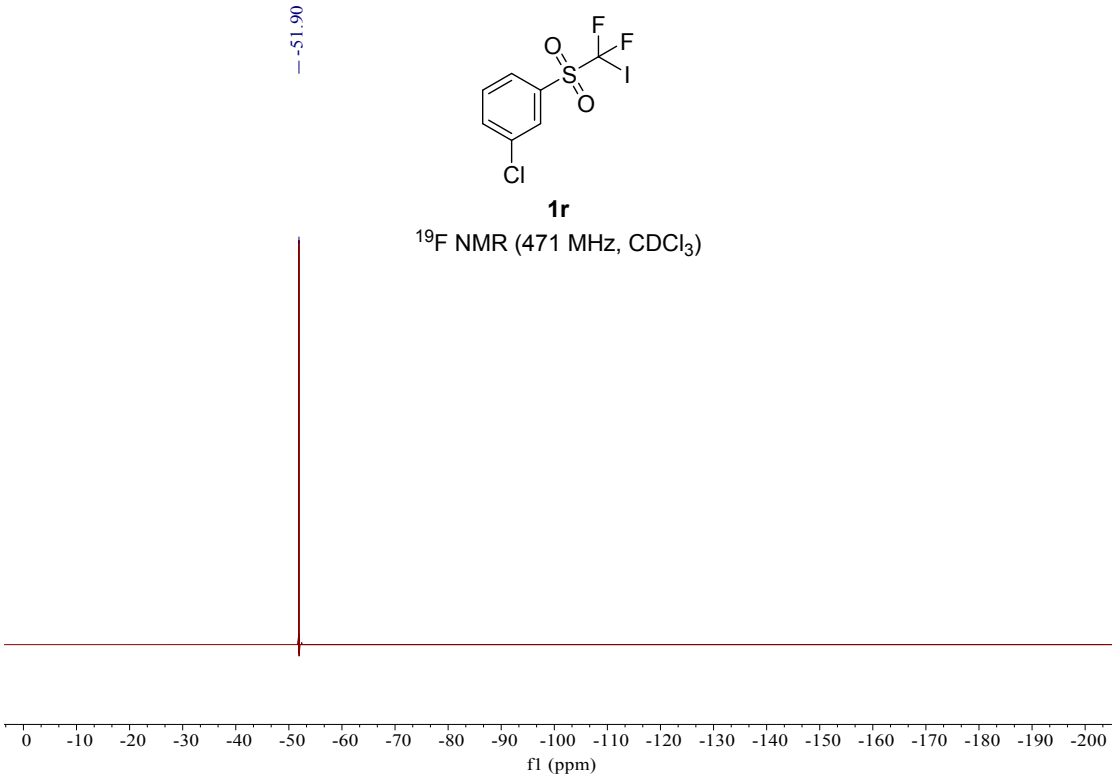




1r

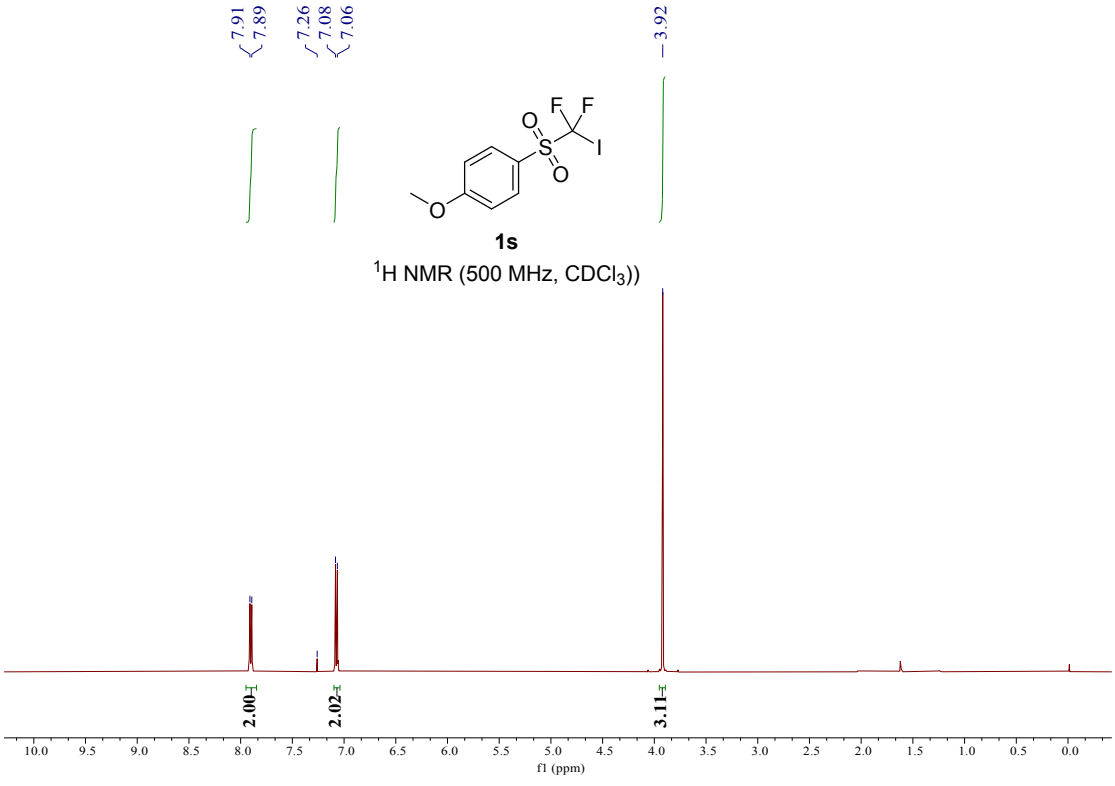
^{13}C NMR (126 MHz, $CDCl_3$)





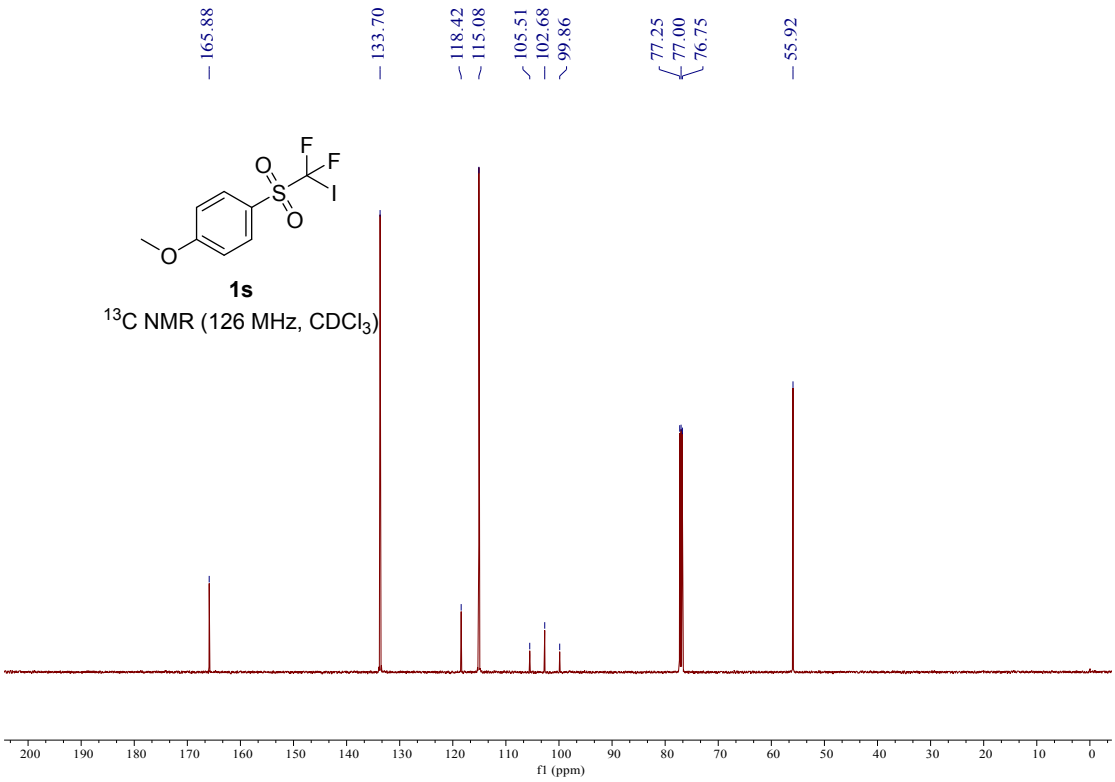
1r

^{19}F NMR (471 MHz, $CDCl_3$)



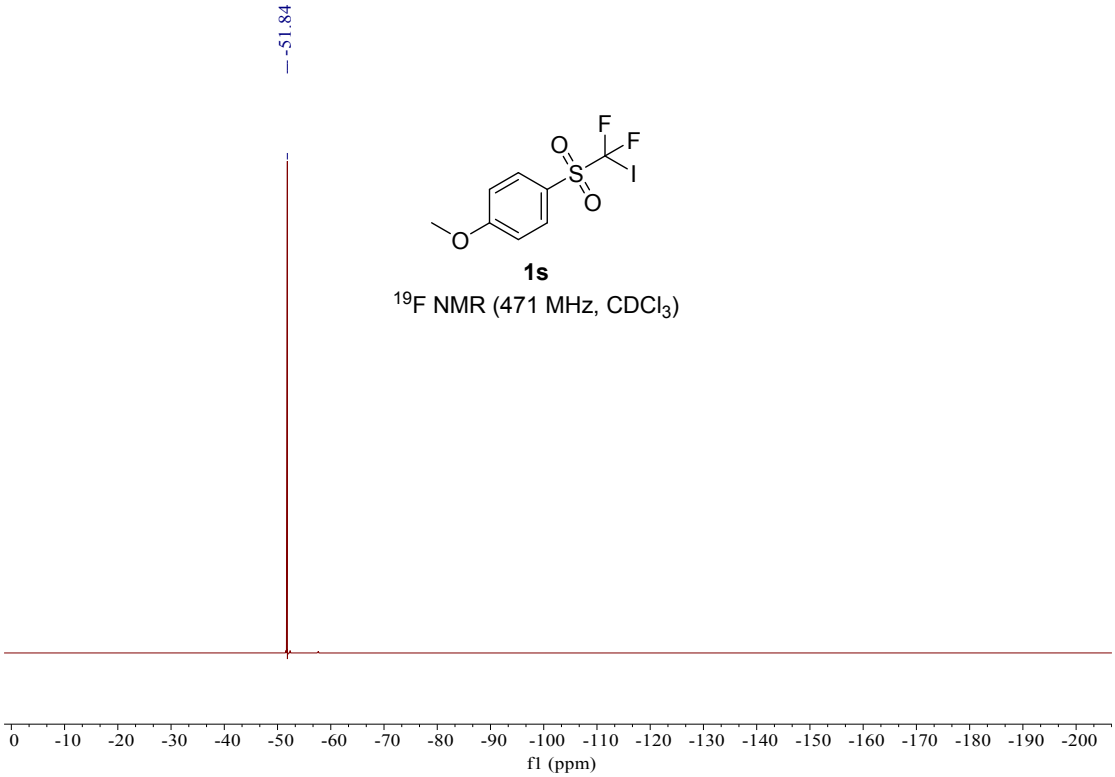
1s

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



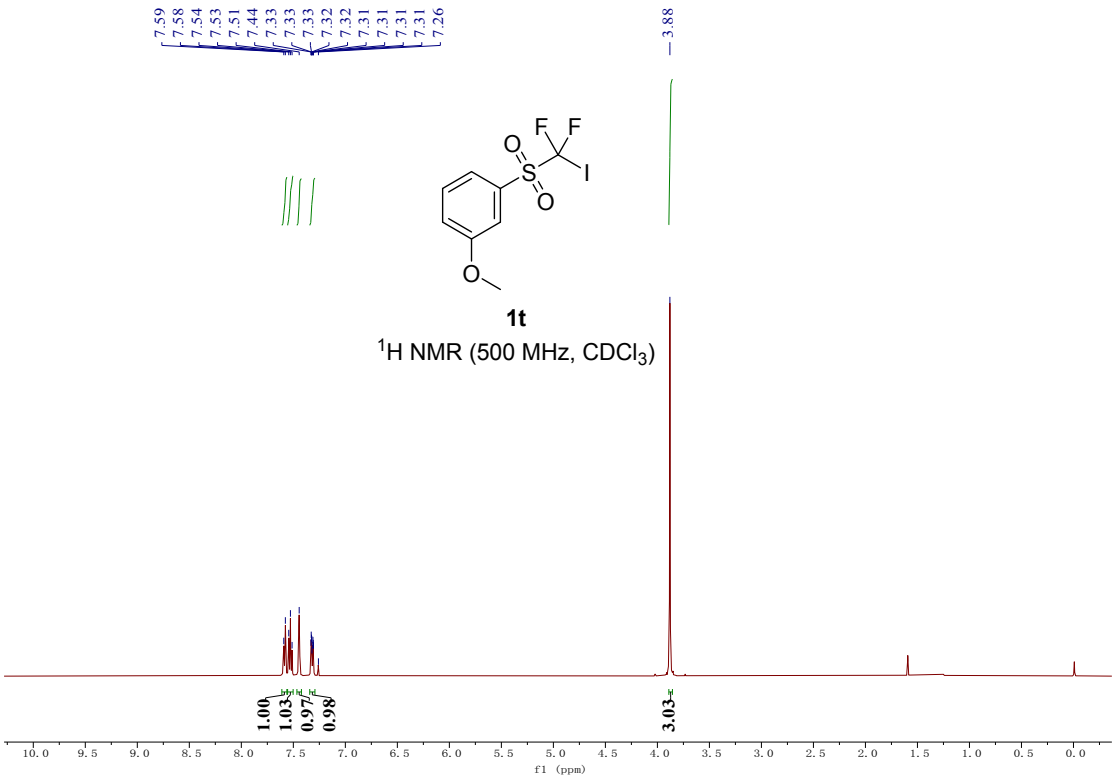
1s

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



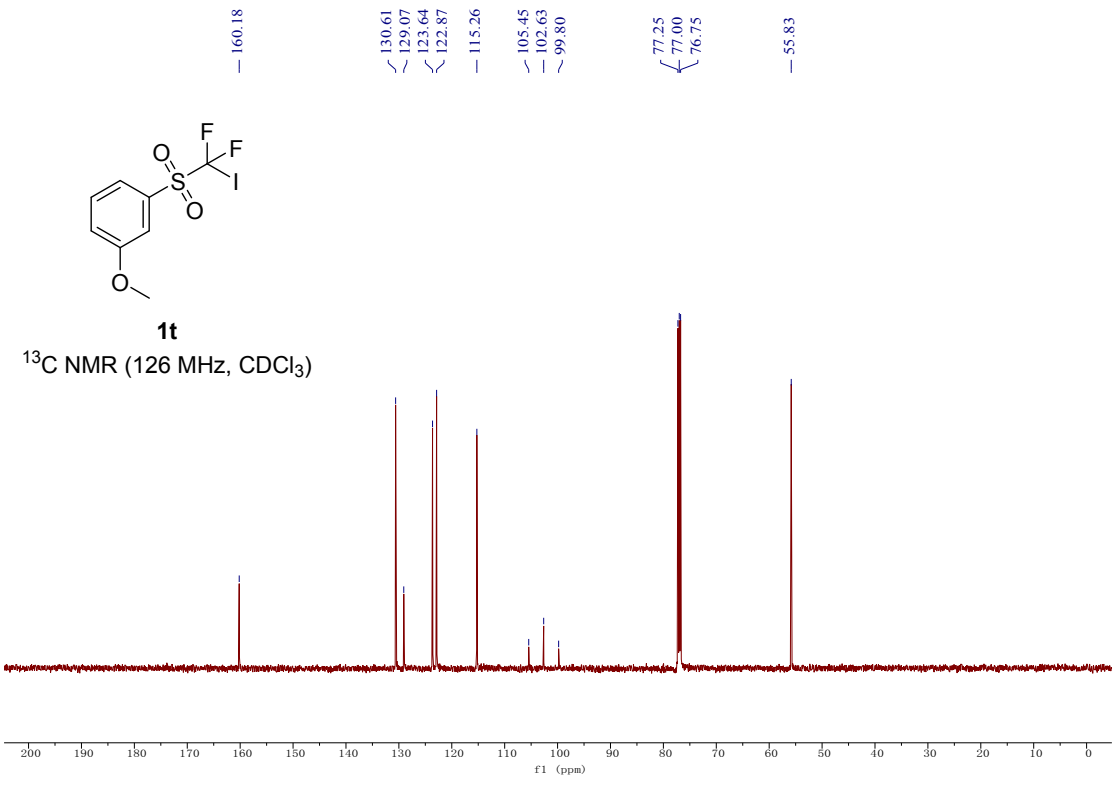
1s

^{19}F NMR (471 MHz, $CDCl_3$)



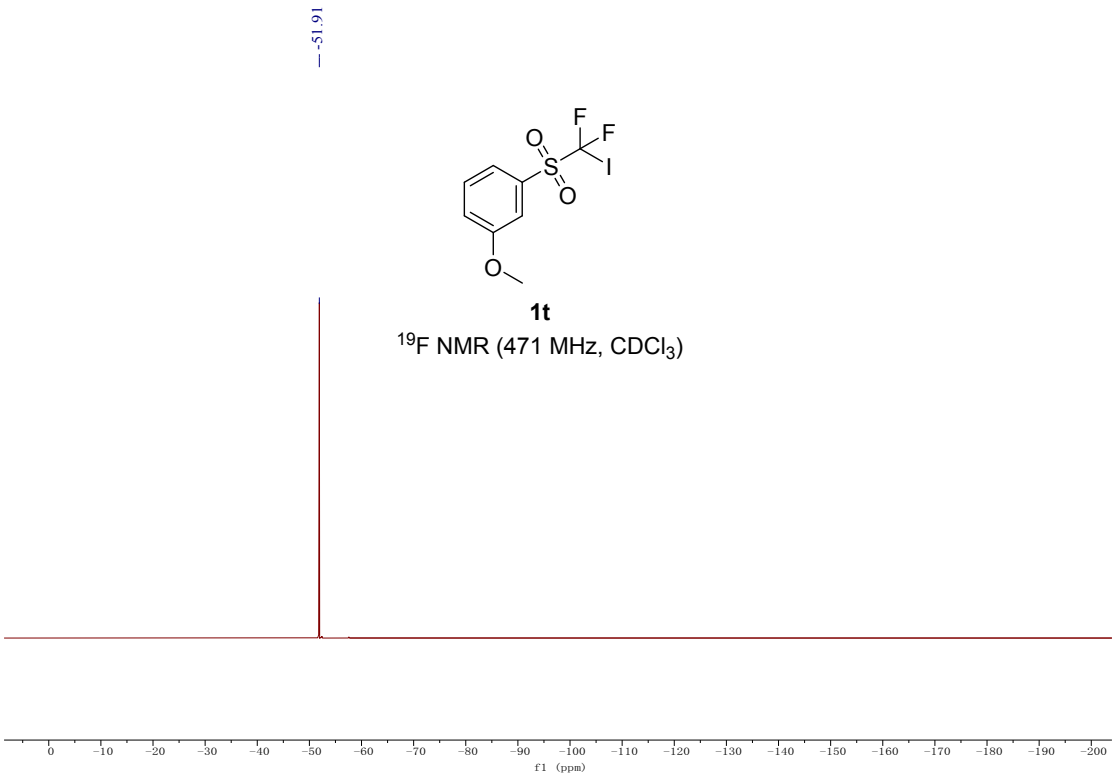
1t

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



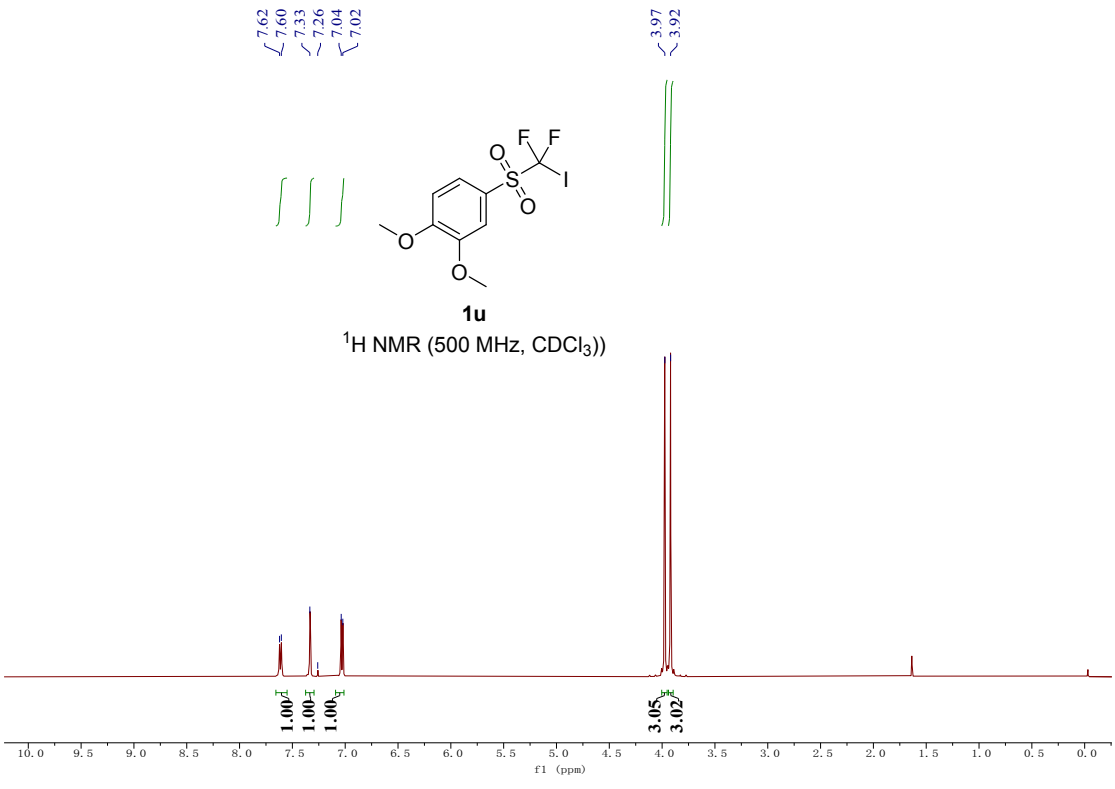
1t

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



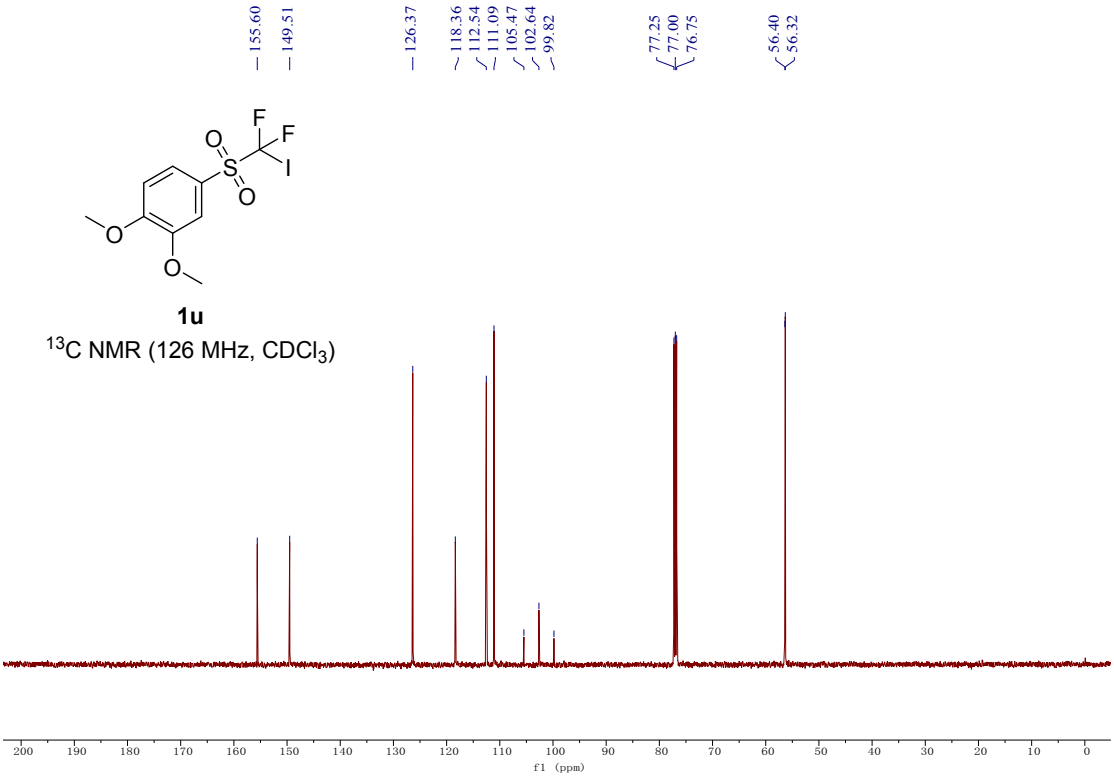
1t

^{19}F NMR (471 MHz, $CDCl_3$)



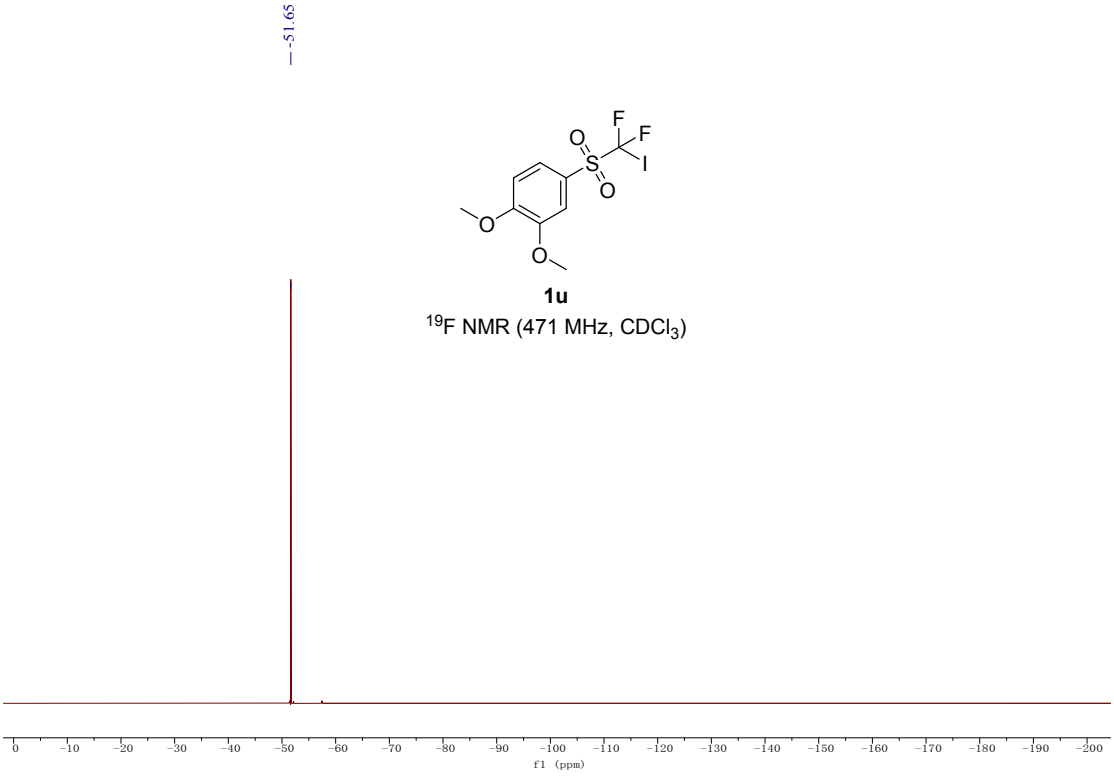
1u

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



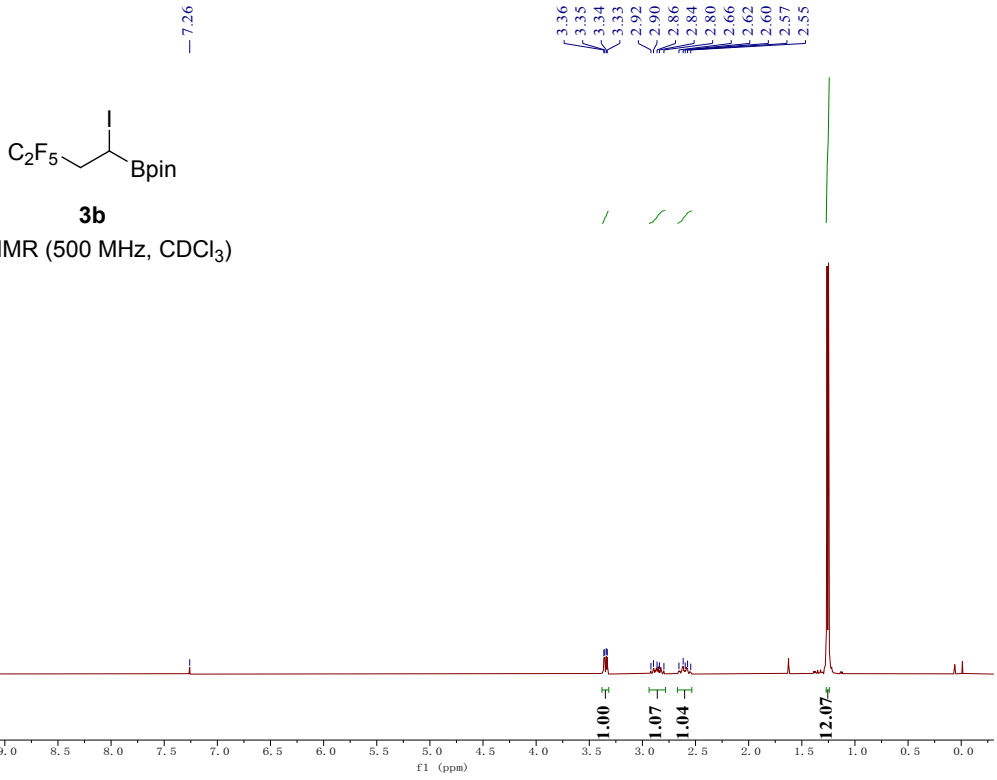
1u

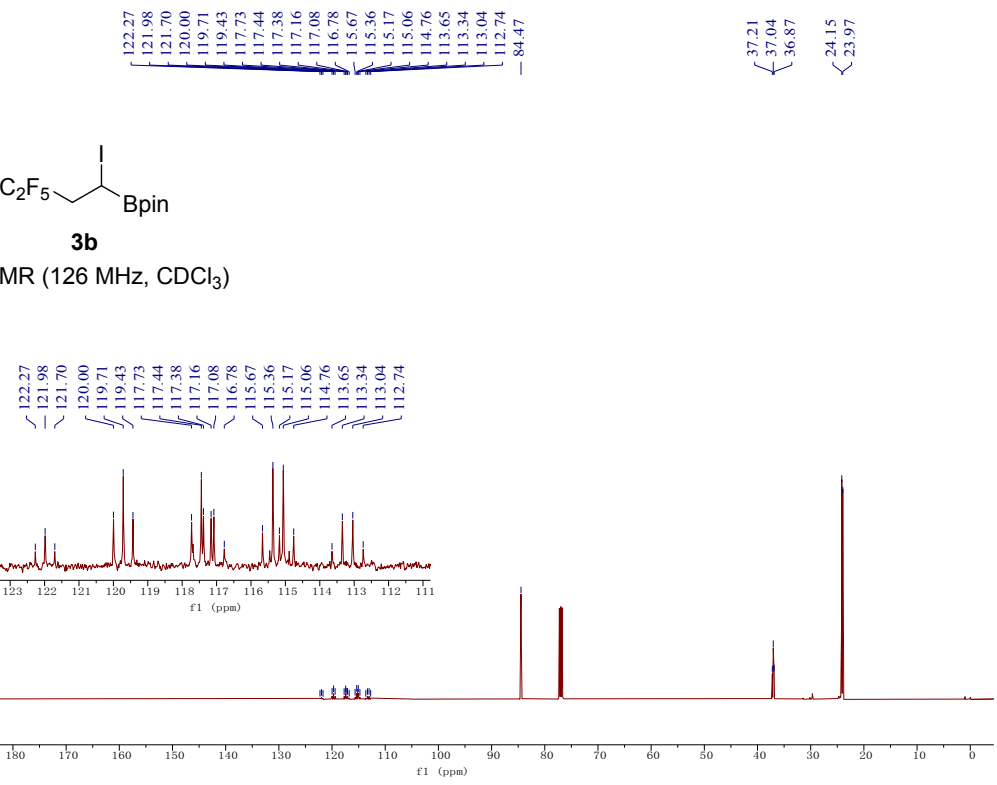
^{13}C NMR (126 MHz, $CDCl_3$)

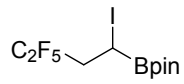


1u

^{19}F NMR (471 MHz, $CDCl_3$)

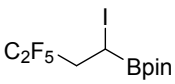

7.26
3.36
3.35
3.34
3.33
2.92
2.90
2.86
2.84
2.80
2.66
2.62
2.60
2.57
2.55
1.00
1.07
1.04
12.07
f1 (ppm)


122.27
121.98
121.70
120.00
119.71
119.43
117.73
117.44
117.38
117.16
117.08
116.78
115.67
115.36
115.17
115.06
114.76
113.65
113.34
113.04
112.74
84.47
37.21
37.04
36.87
24.15
23.97
f1 (ppm)



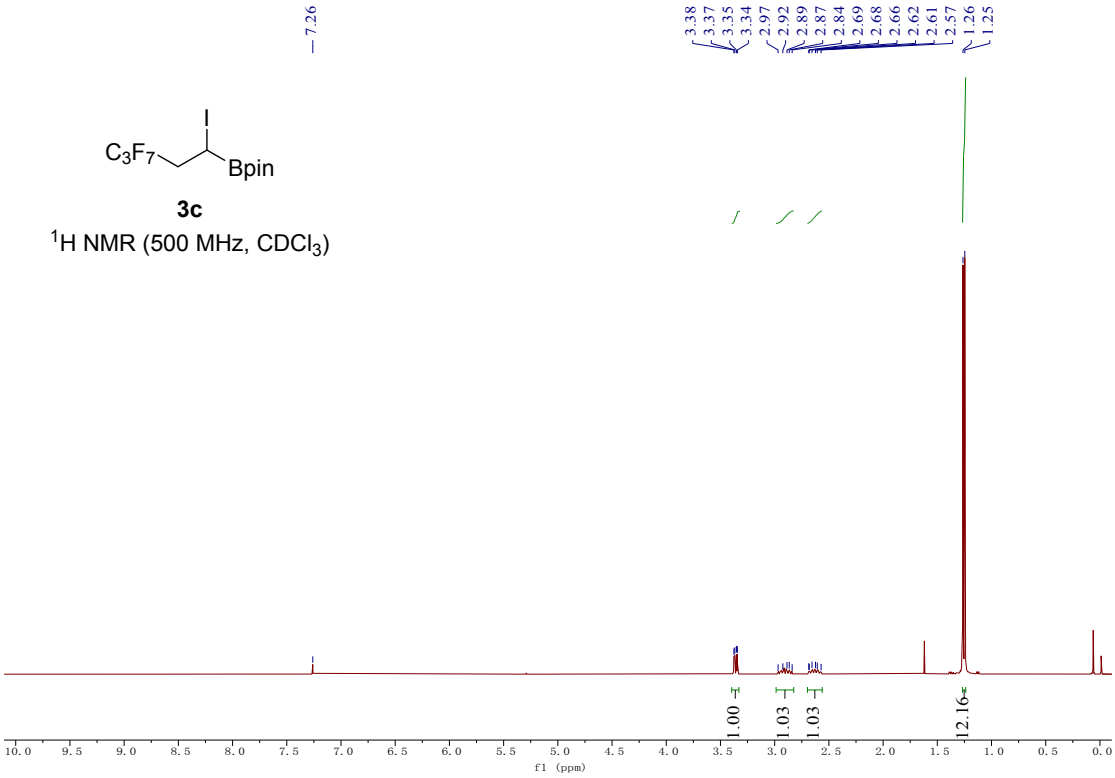
3b

^{19}F NMR (471 MHz, $CDCl_3$)



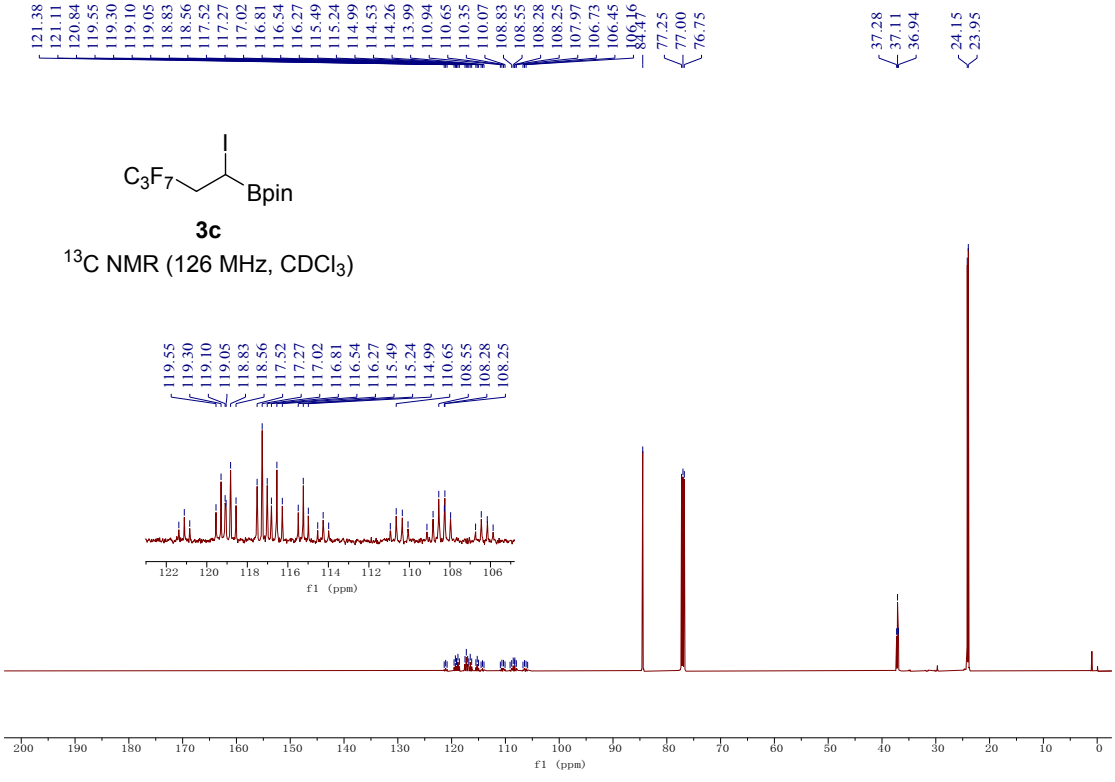
3b

^{11}B NMR (128 MHz, $CDCl_3$)



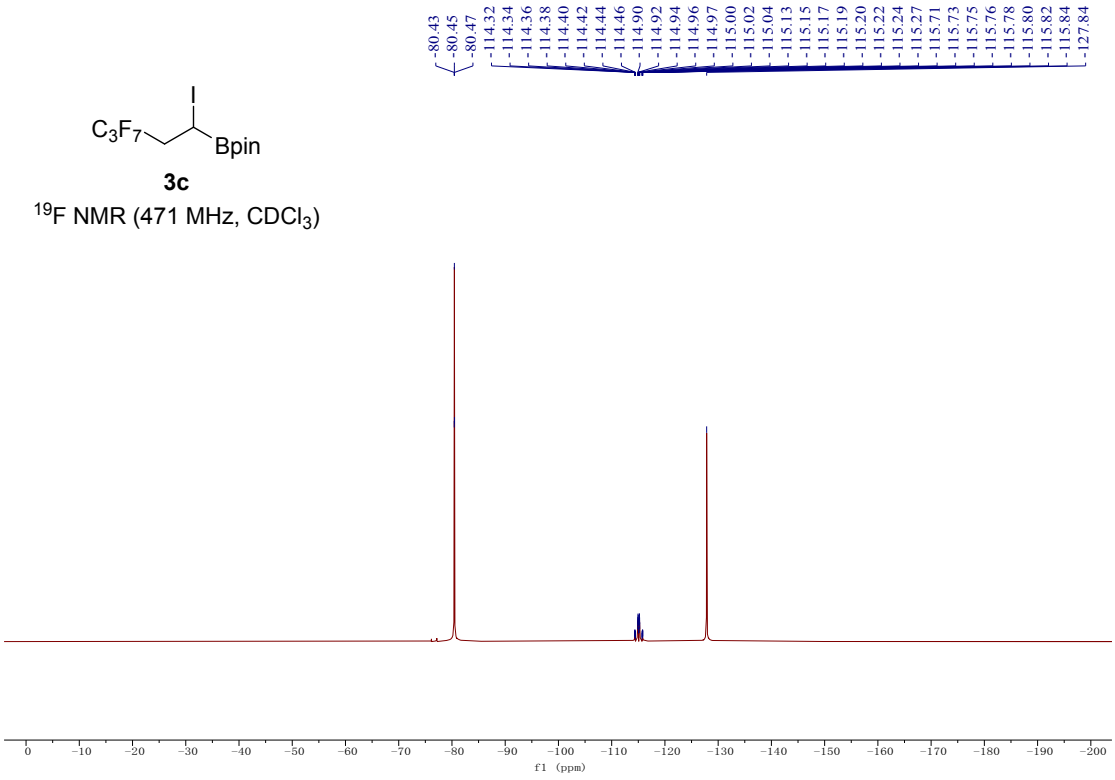
3c

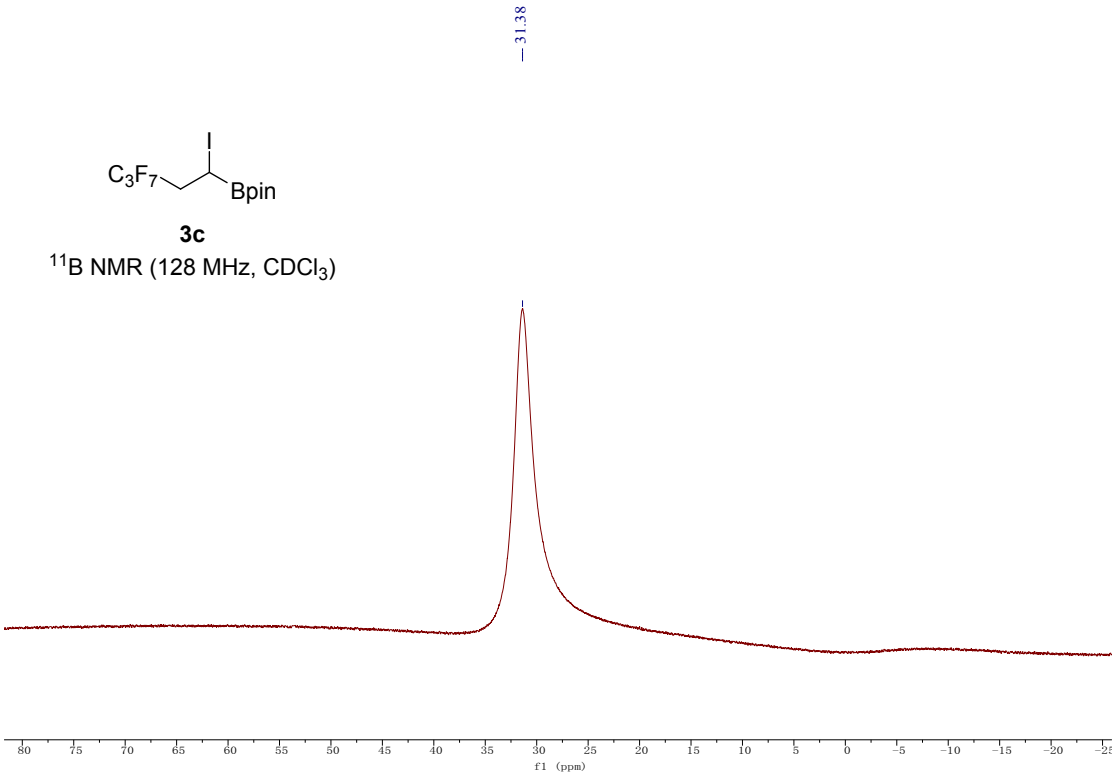
^{1}H NMR (500 MHz, $CDCl_3$)

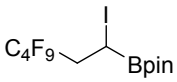


3c

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

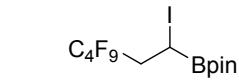

-80.43
-80.45
-80.47
-114.32
-114.34
-114.36
-114.38
-114.40
-114.42
-114.44
-114.46
-114.90
-114.92
-114.94
-114.96
-114.97
-115.00
-115.02
-115.04
-115.13
-115.15
-115.17
-115.19
-115.20
-115.22
-115.24
-115.27
-115.71
-115.73
-115.75
-115.76
-115.78
-115.80
-115.82
-115.84
-127.84
I
C3F7
Bpin
3c
19F NMR (471 MHz, CDCl3)
0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)


31.38
I
C3F7
Bpin
3c
11B NMR (128 MHz, CDCl3)
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20
f1 (ppm)



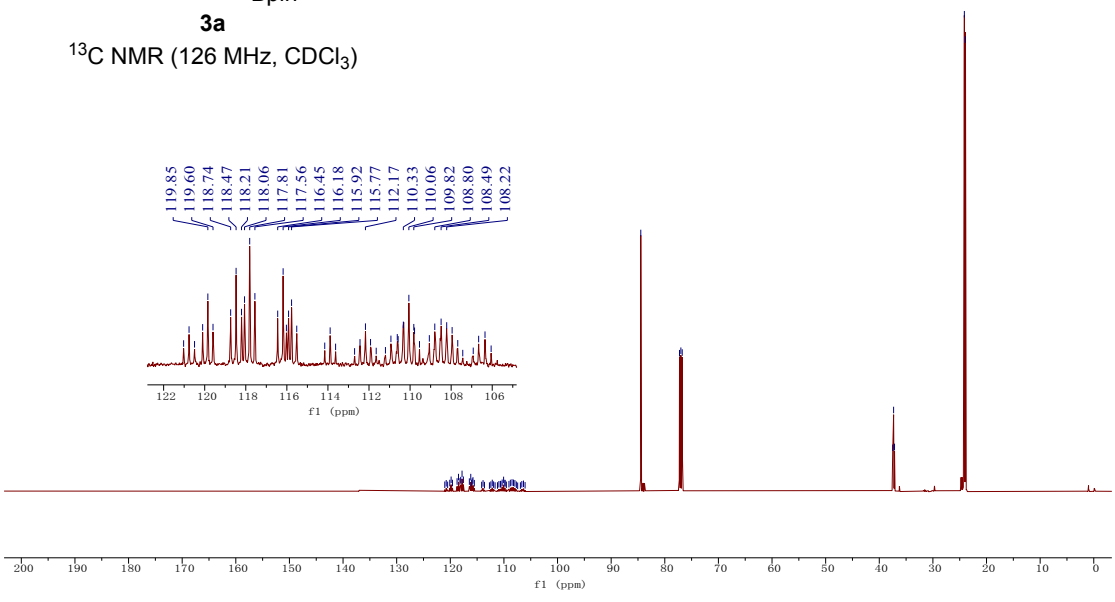
3a

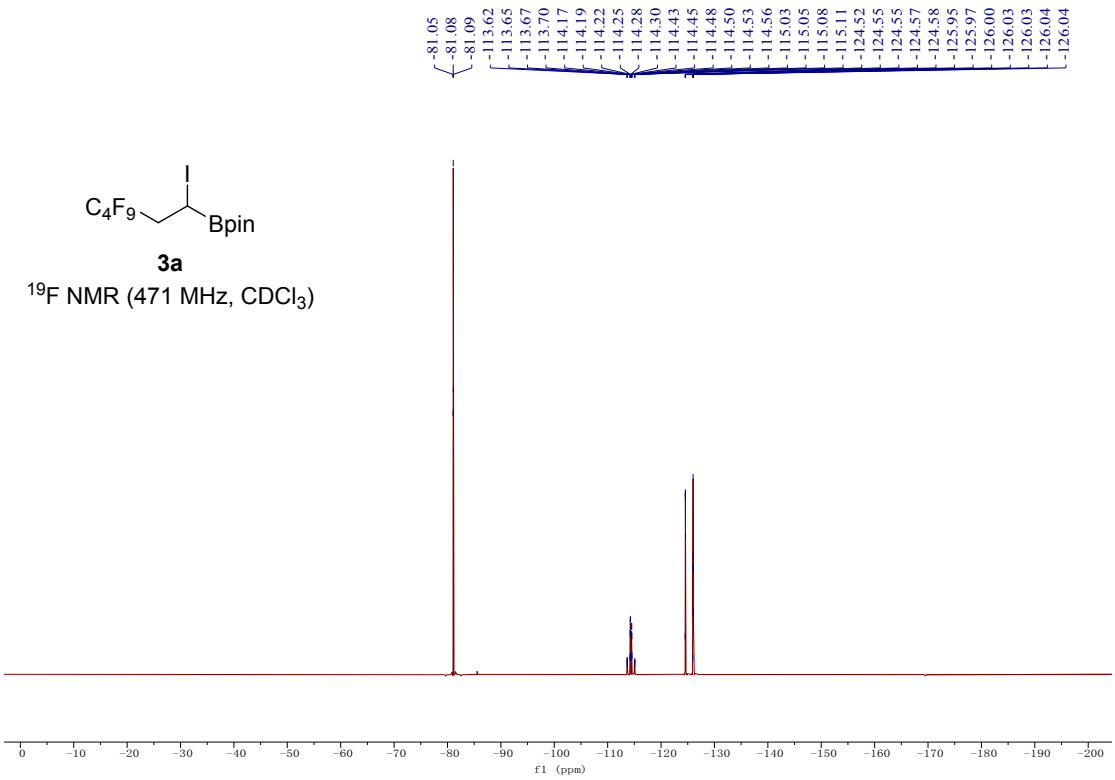
^{1}H NMR (500 MHz, $CDCl_3$)

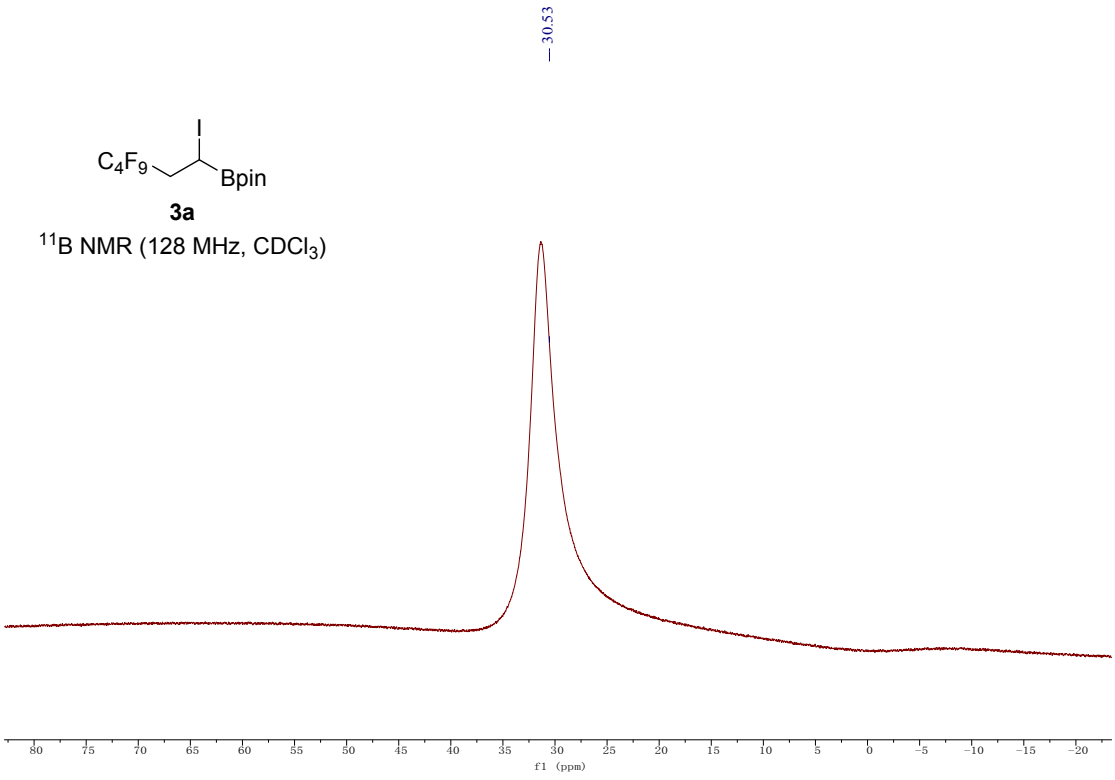


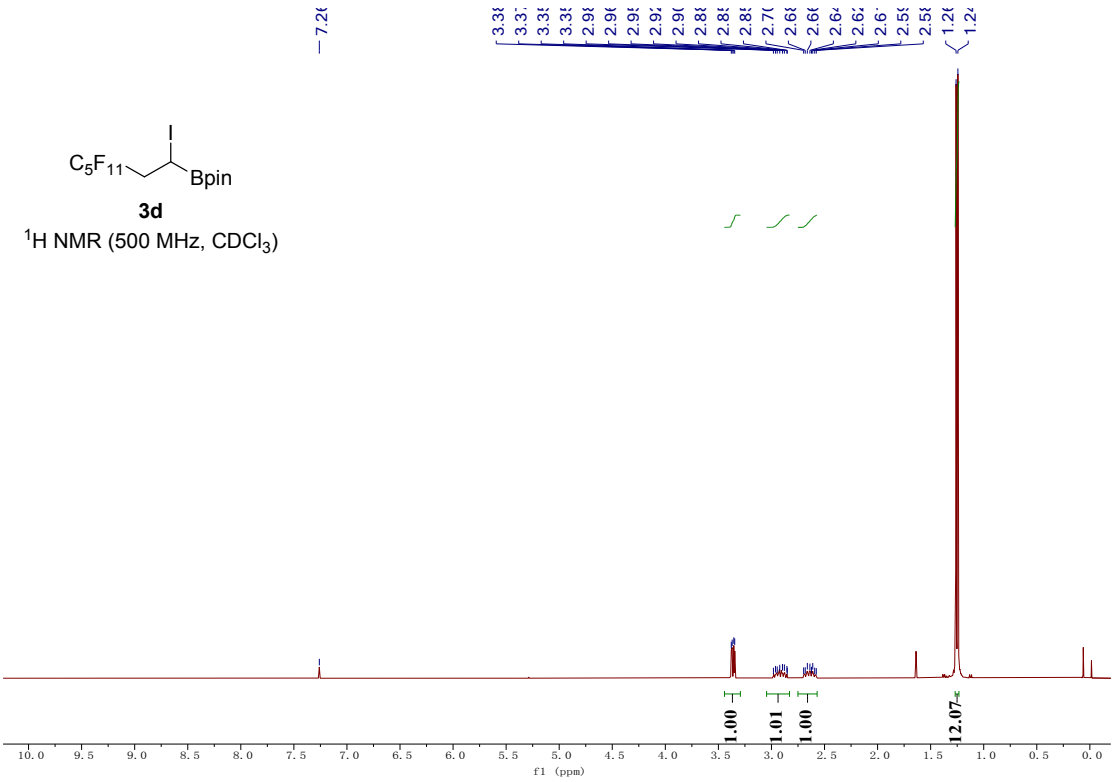
3a

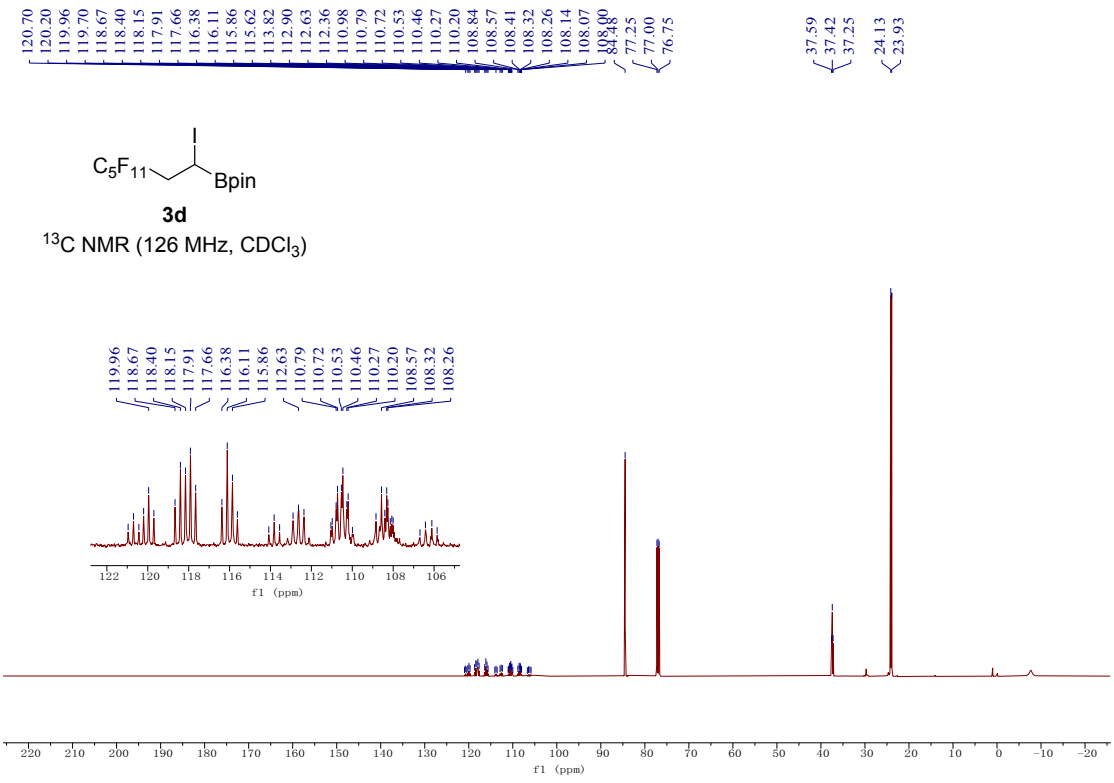
^{13}C NMR (126 MHz, $CDCl_3$)

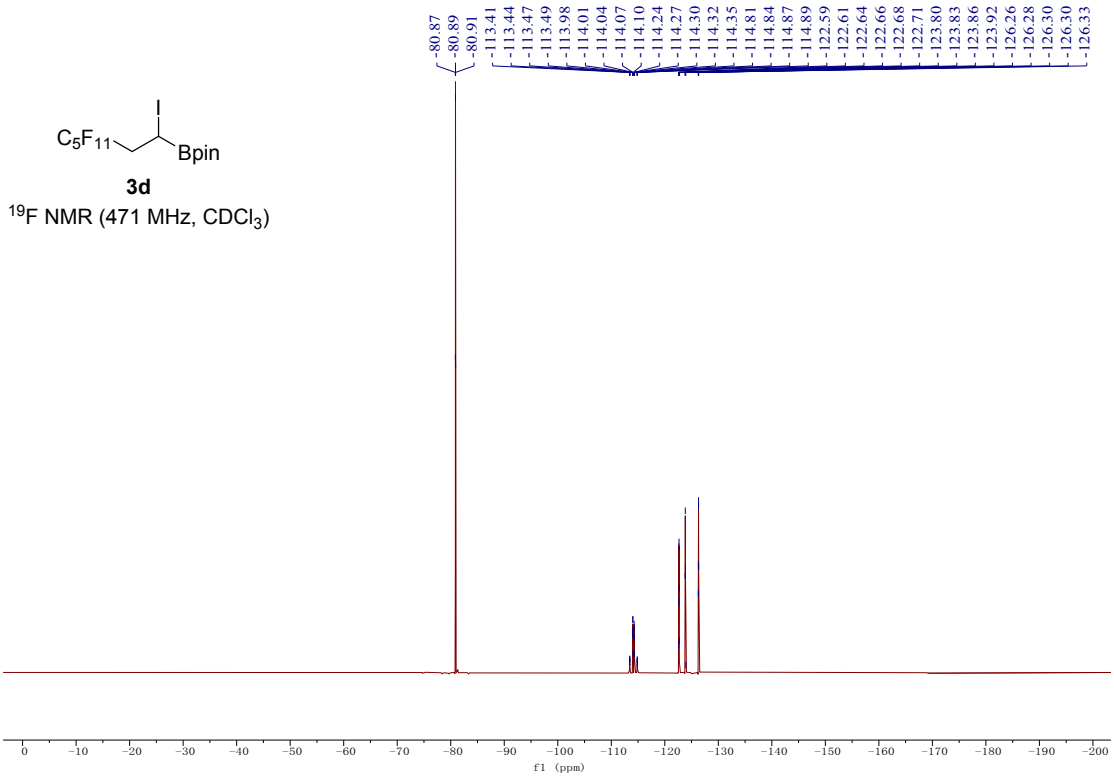



-81.05
-81.08
-81.09
-113.62
-113.65
-113.67
-113.70
-114.17
-114.19
-114.22
-114.25
-114.28
-114.30
-114.43
-114.45
-114.48
-114.50
-114.53
-114.56
-115.03
-115.05
-115.08
-115.11
-124.52
-124.55
-124.55
-124.57
-124.58
-125.95
-125.97
-126.00
-126.03
-126.03
-126.04
-126.04
I
C4F9
Bpin
3a
19F NMR (471 MHz, CDCl3)
0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)


30.53
I
C4F9
Bpin
3a
11B NMR (128 MHz, CDCl3)
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20
f1 (ppm)


C5F11
I
Bpin
3d
1H NMR (500 MHz, CDCl3)
1.00
1.01
1.00
12.07
f1 (ppm)

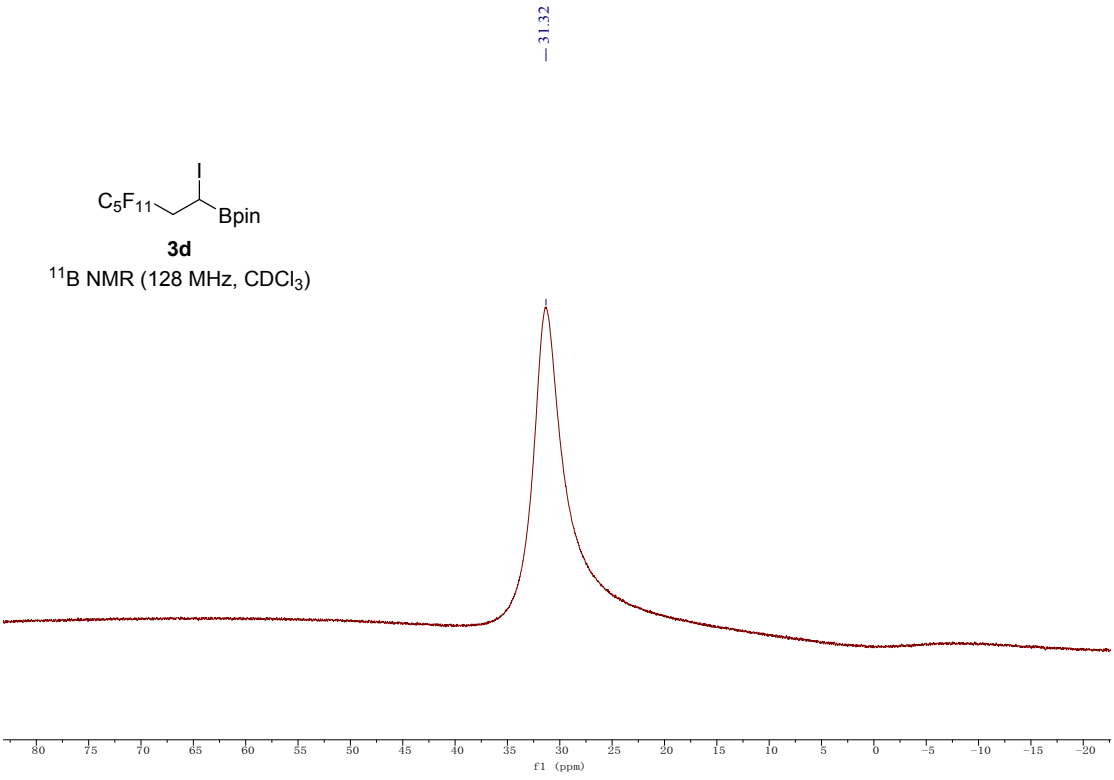

C5F11
I
Bpin
3d
13C NMR (126 MHz, CDCl3)
f1 (ppm)



C_5F_{11} I Bpin

3d

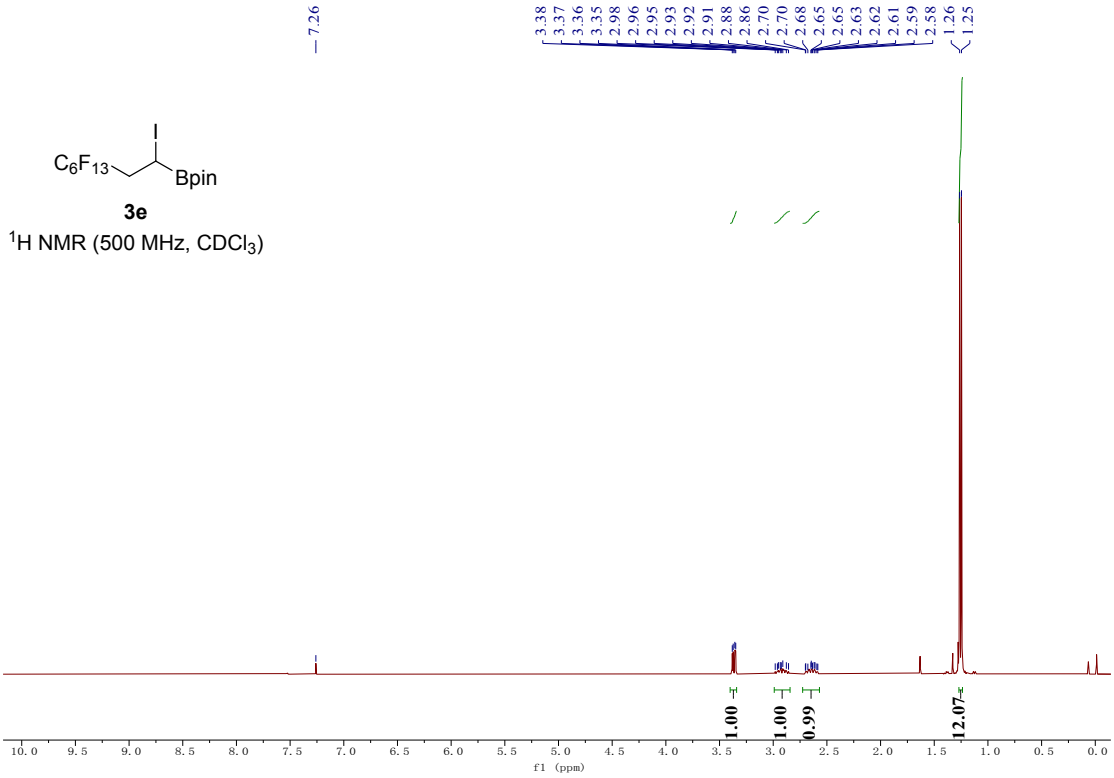
^{19}F NMR (471 MHz, $CDCl_3$)



C_5F_{11} I Bpin

3d

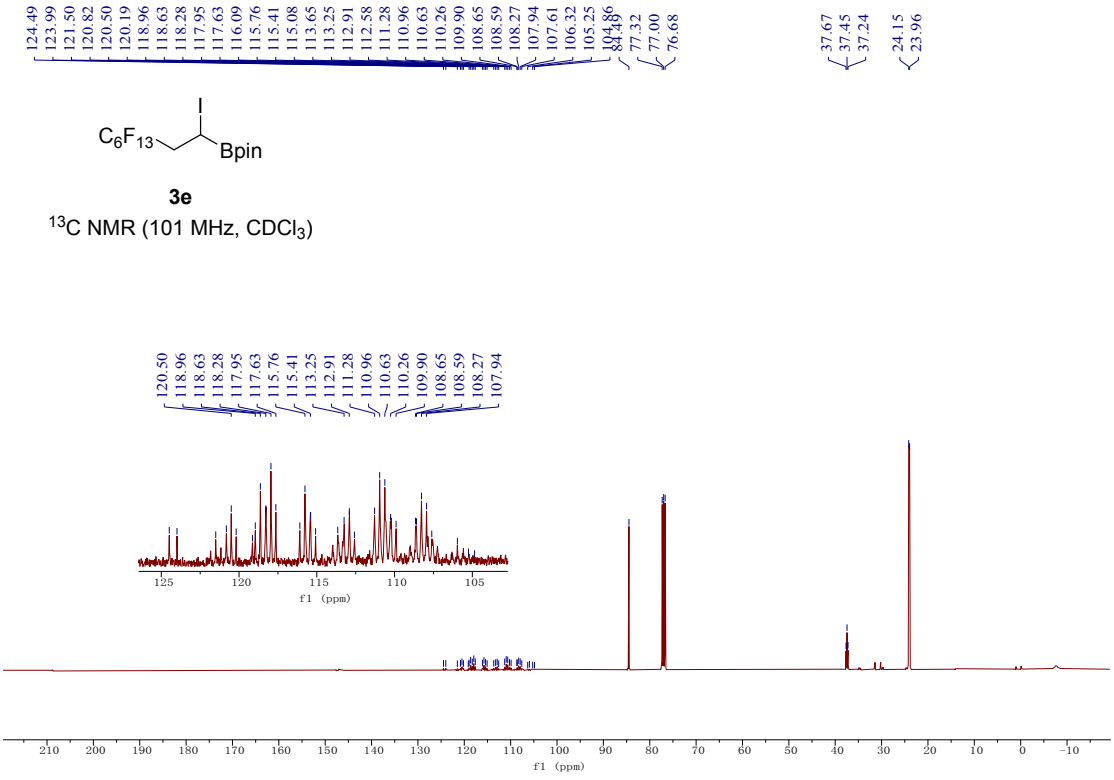
^{11}B NMR (128 MHz, $CDCl_3$)



C_6F_{13}, I, Bpin

3e

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



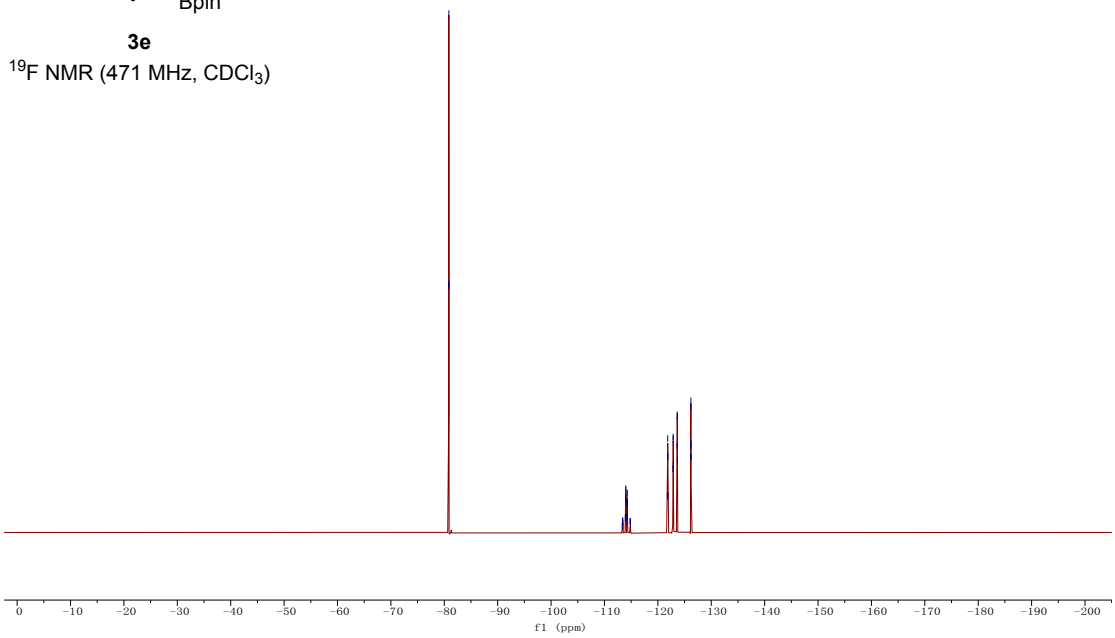
C_6F_{13}, I, Bpin

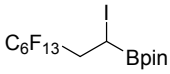
3e

^{13}C NMR (101 MHz, $CDCl_3$)

3e

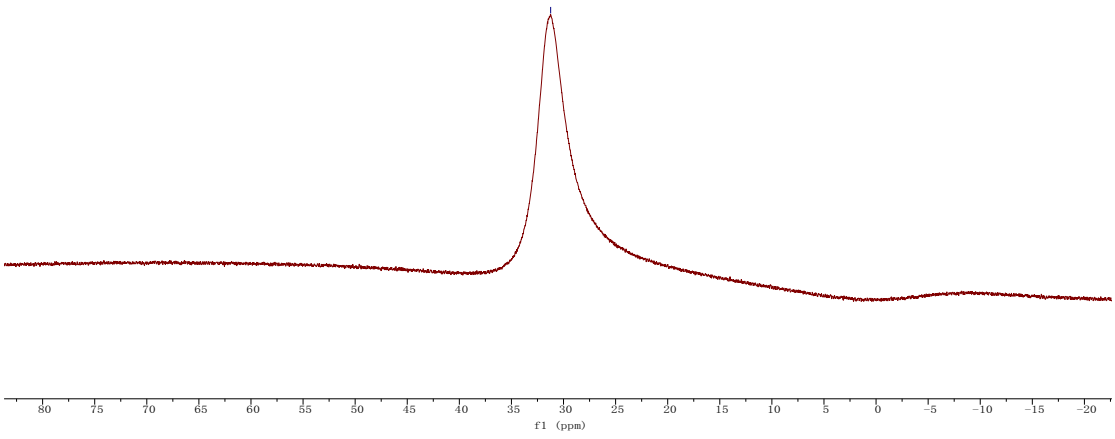
^{19}F NMR (471 MHz, $CDCl_3$)

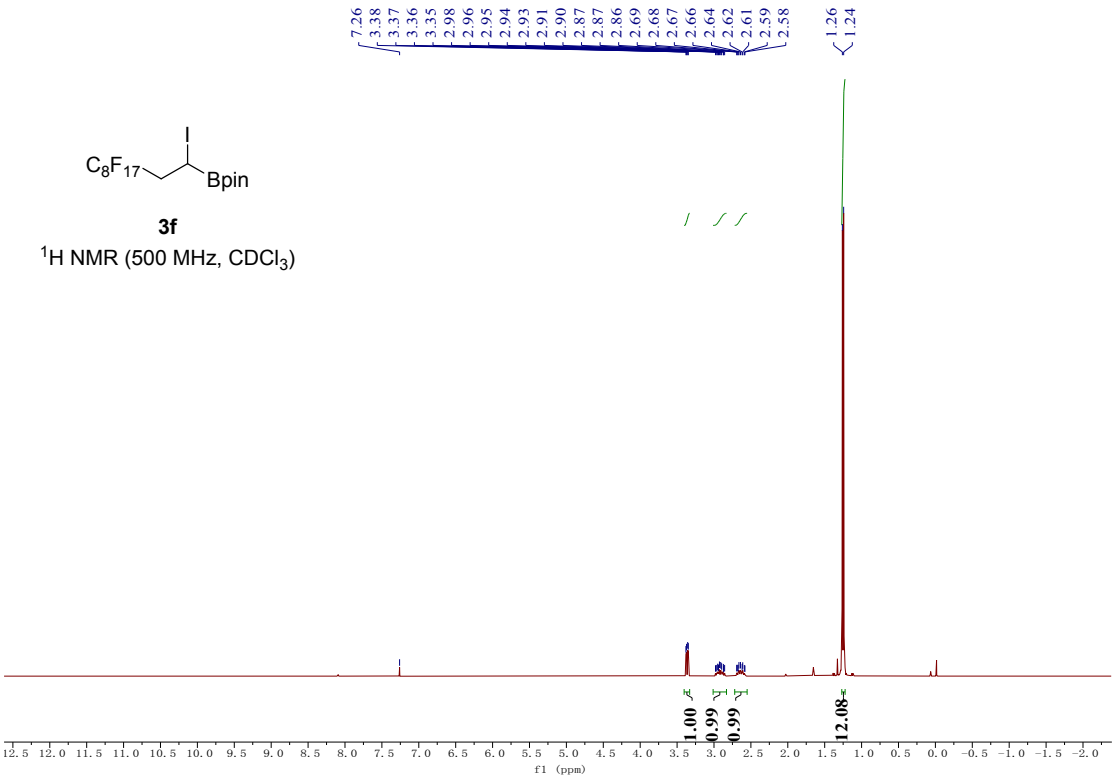




3e

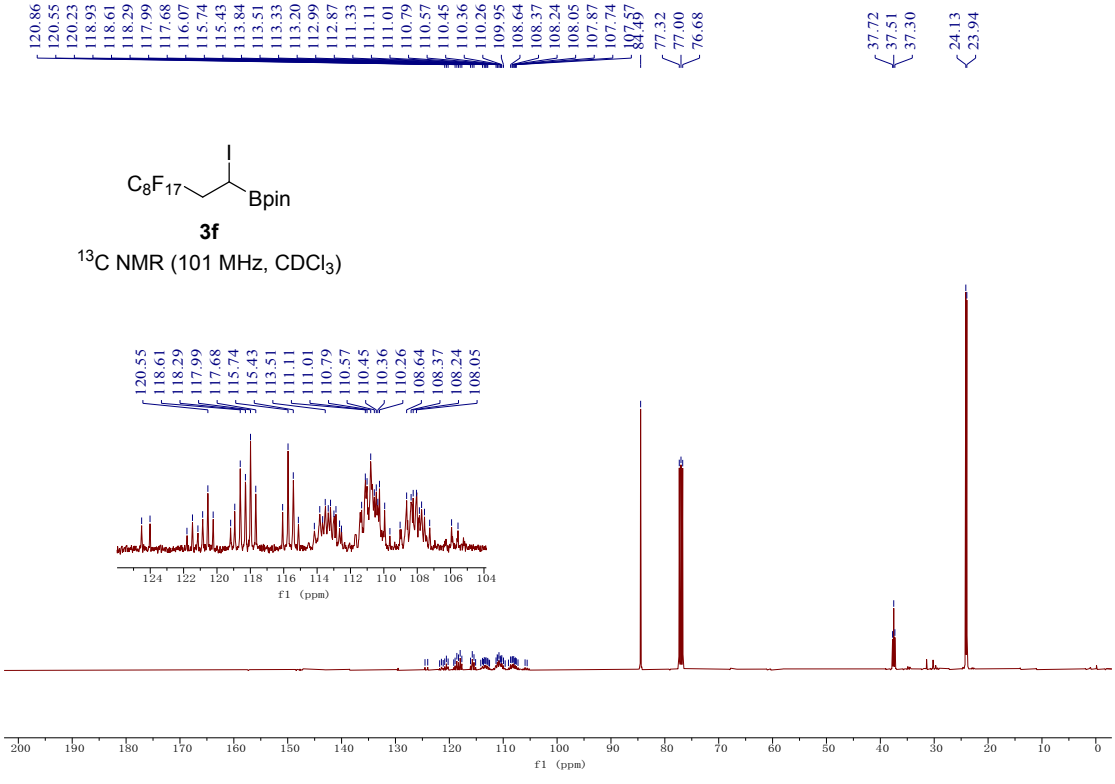
^{11}B NMR (128 MHz, $CDCl_3$)





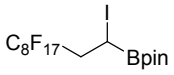
3f

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



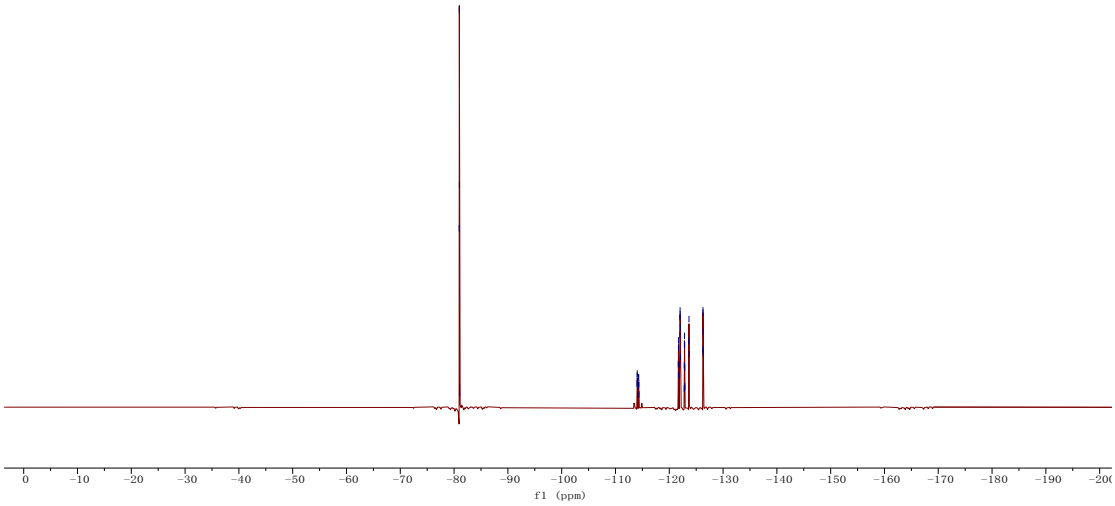
3f

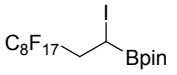
^{13}C NMR (101 MHz, $CDCl_3$)



3f

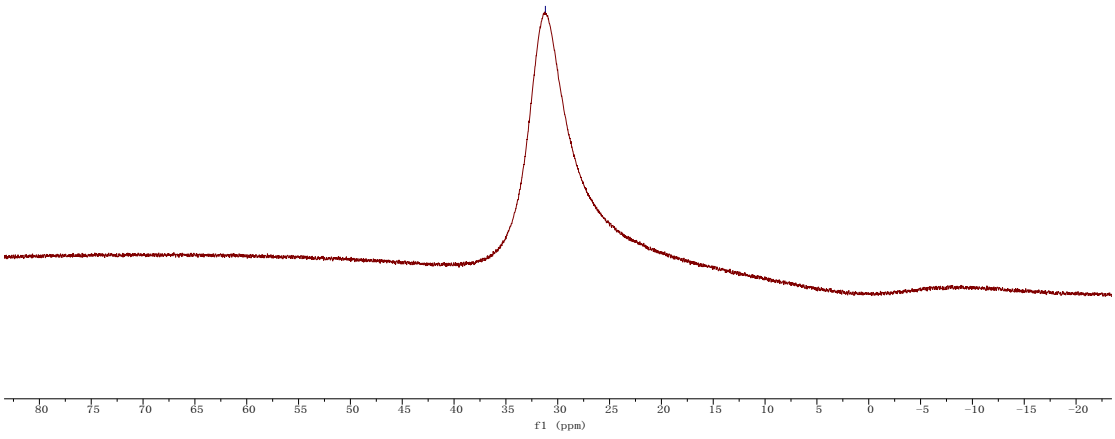
^{19}F NMR (471 MHz, $CDCl_3$)

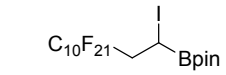




3f

^{11}B NMR (128 MHz, $CDCl_3$)



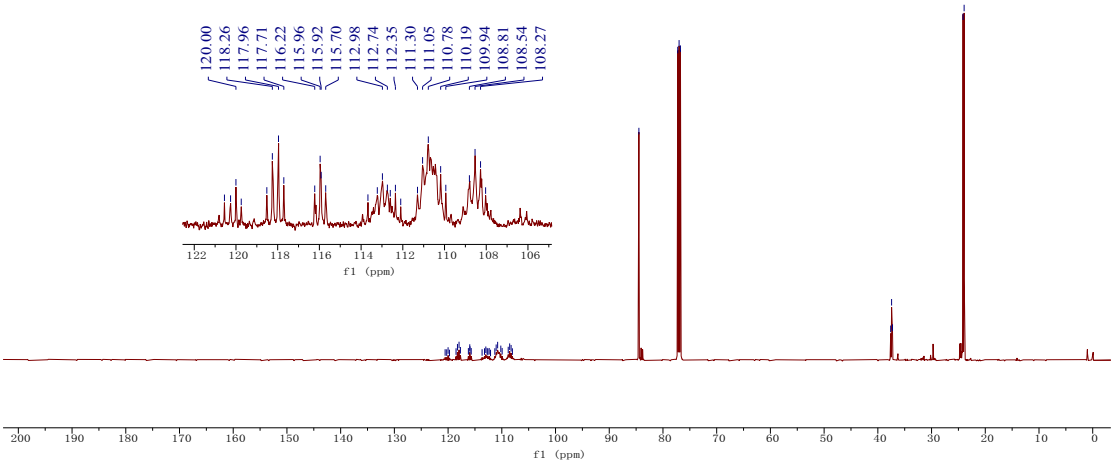


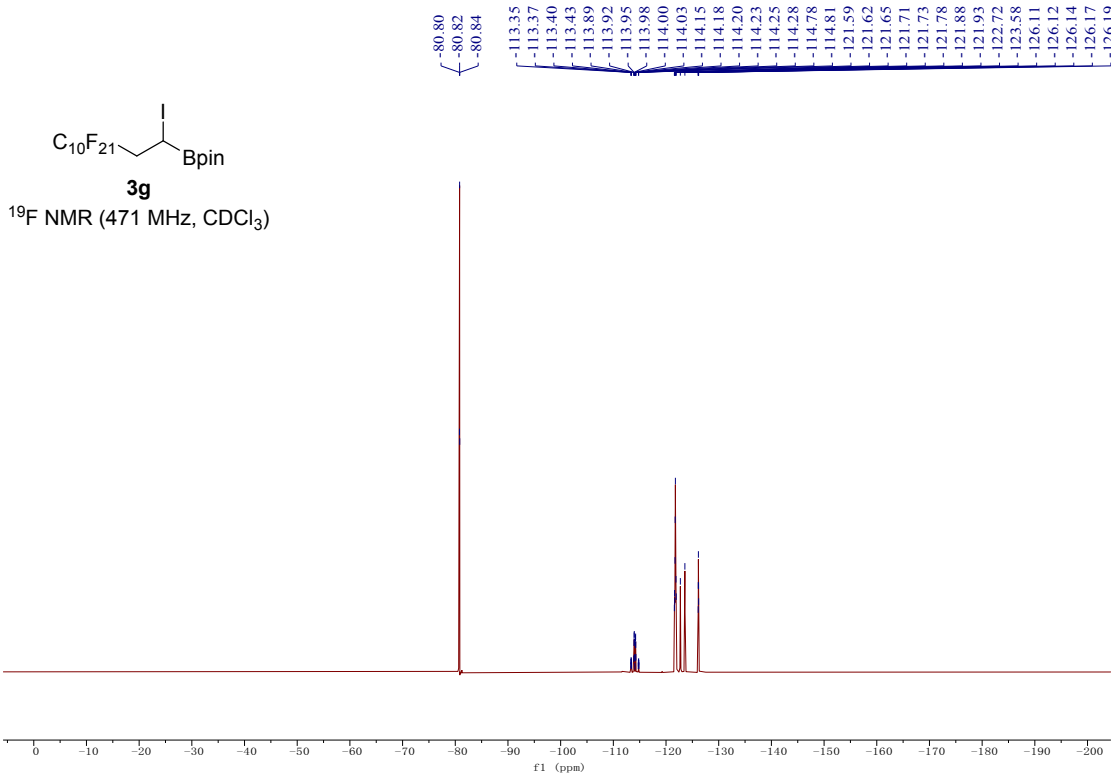
3g

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

3g

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

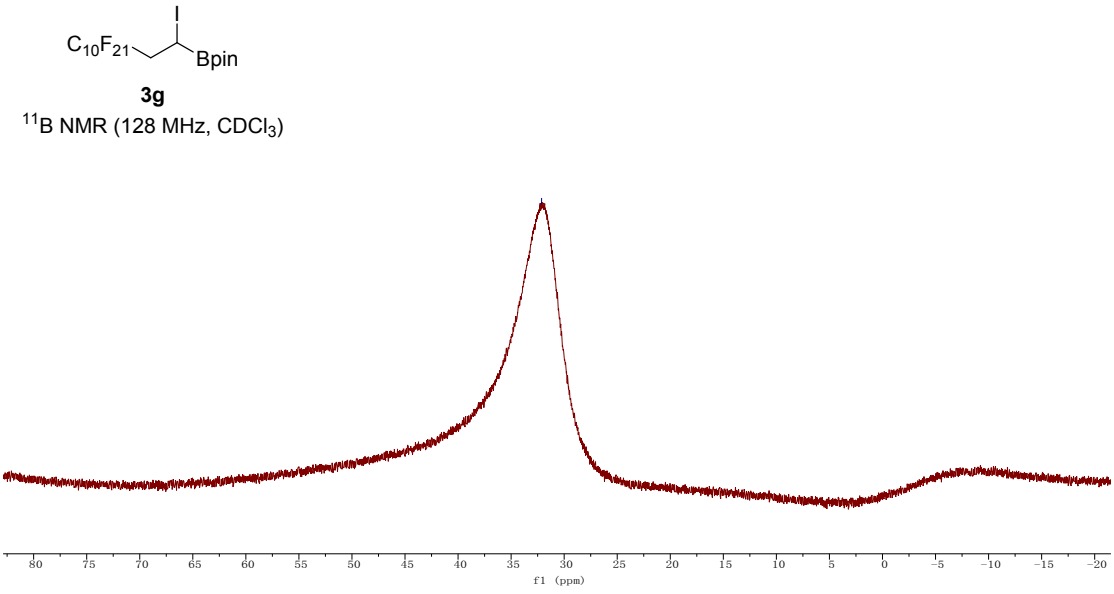




$C_{10}F_{21}$ I Bpin

3g

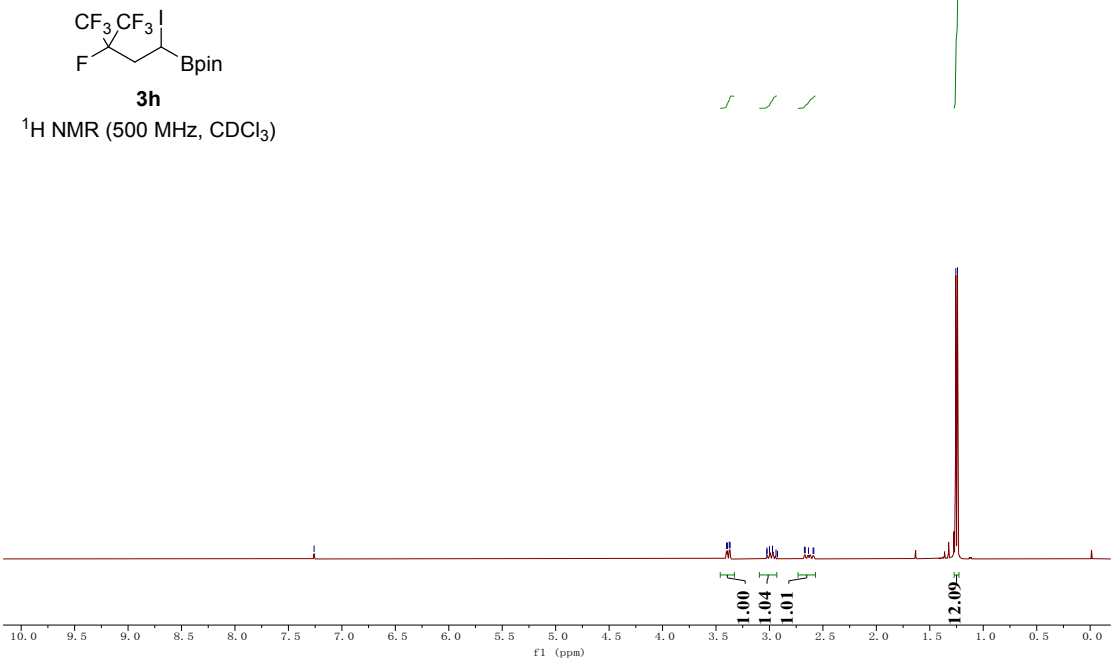
^{19}F NMR (471 MHz, $CDCl_3$)



$C_{10}F_{21}$ I Bpin

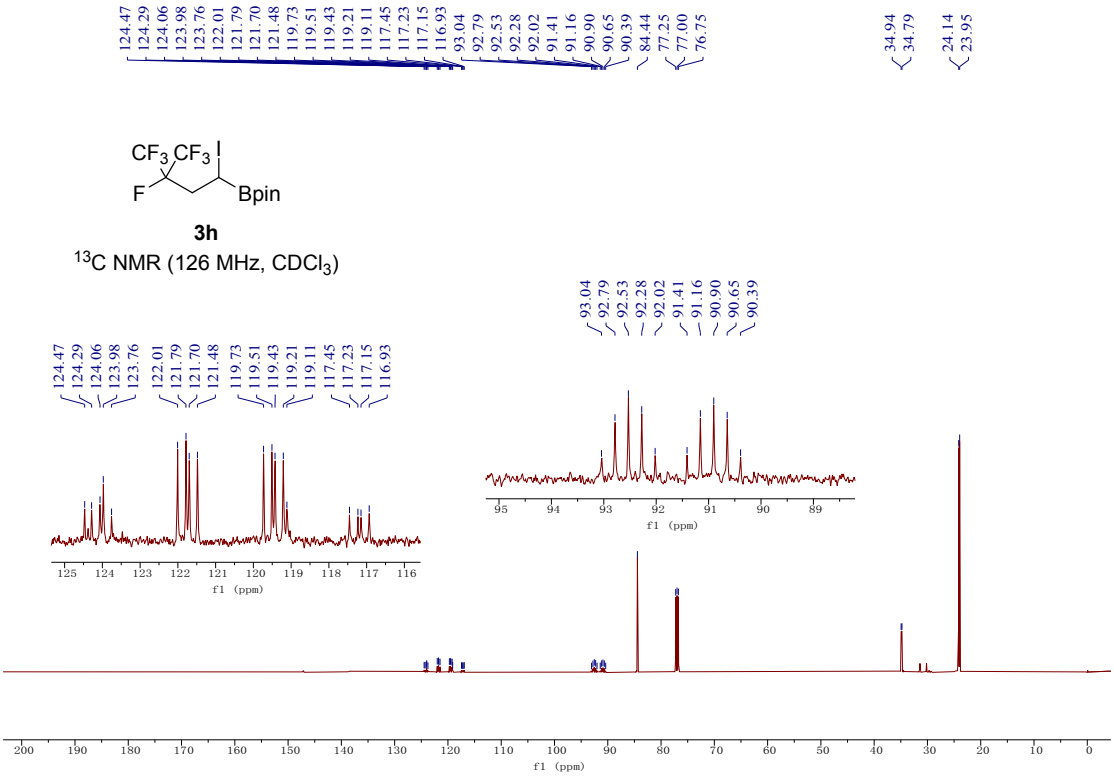
3g

^{11}B NMR (128 MHz, $CDCl_3$)



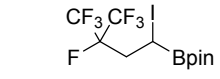
3h

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



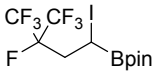
3h

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



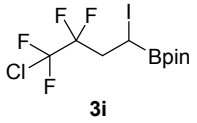
3h

^{19}F NMR (471 MHz, $CDCl_3$)



3h

^{11}B NMR (128 MHz, $CDCl_3$)

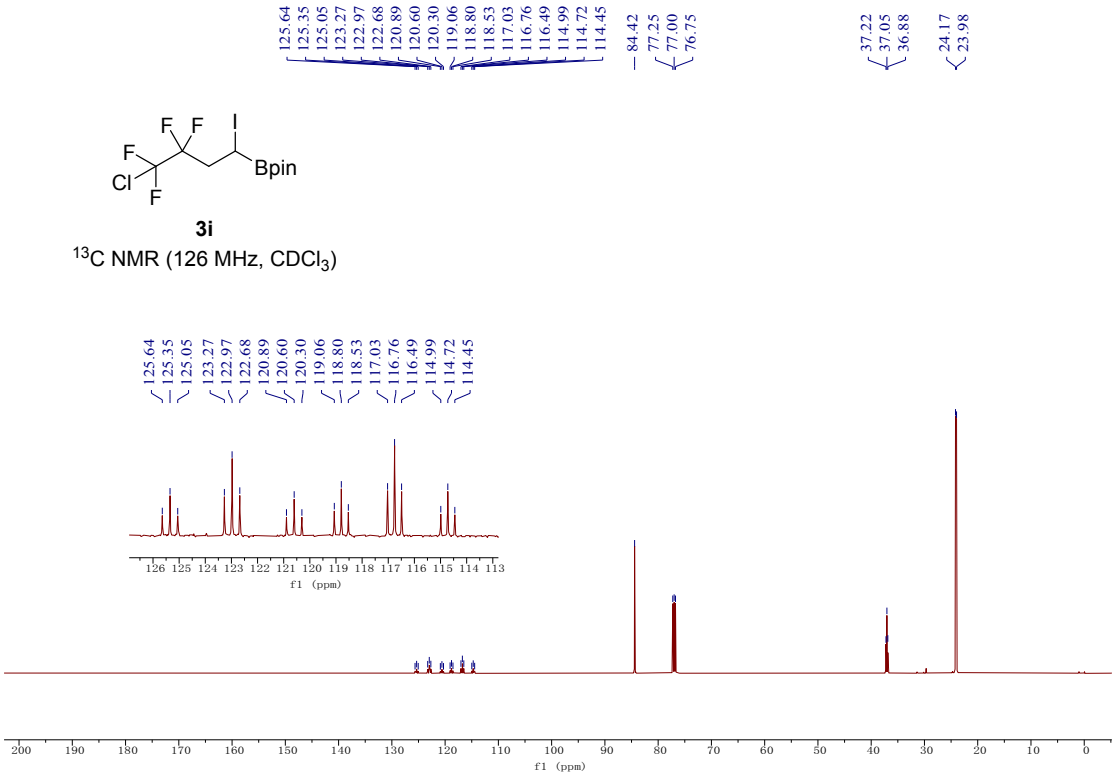


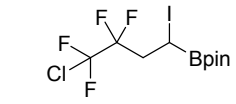
3i

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

3i

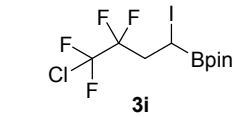
^{13}C NMR (126 MHz, $CDCl_3$)





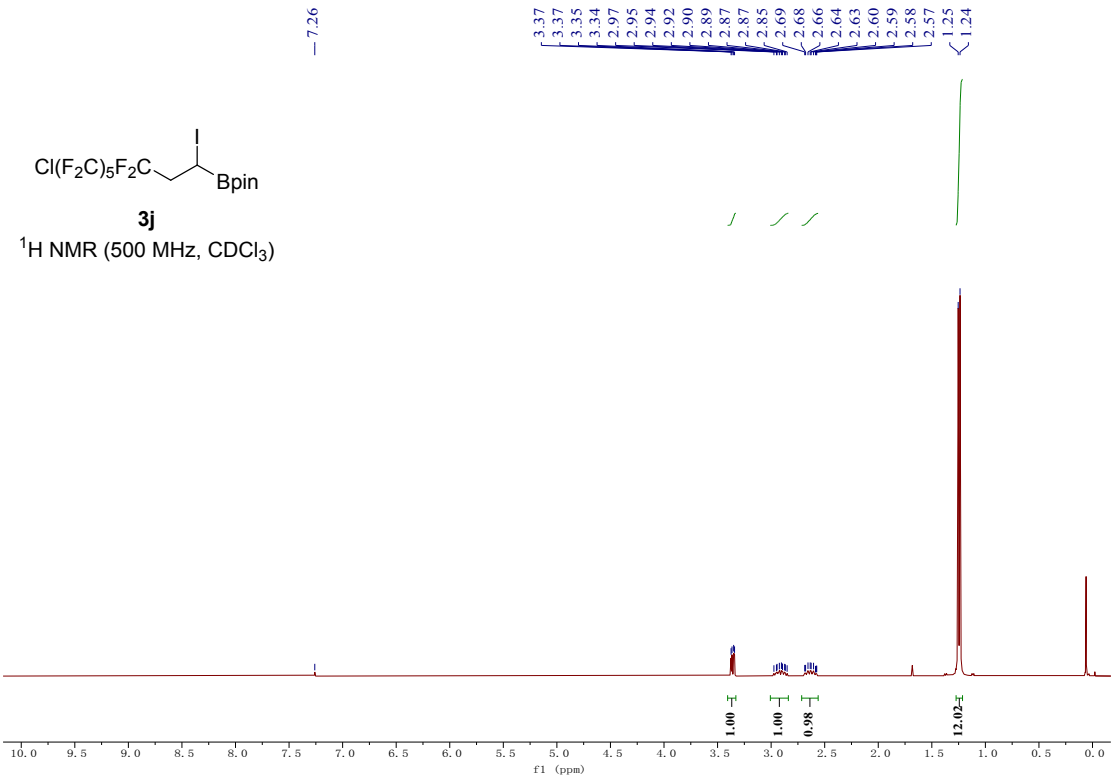
3i

^{19}F NMR (471 MHz, $CDCl_3$)



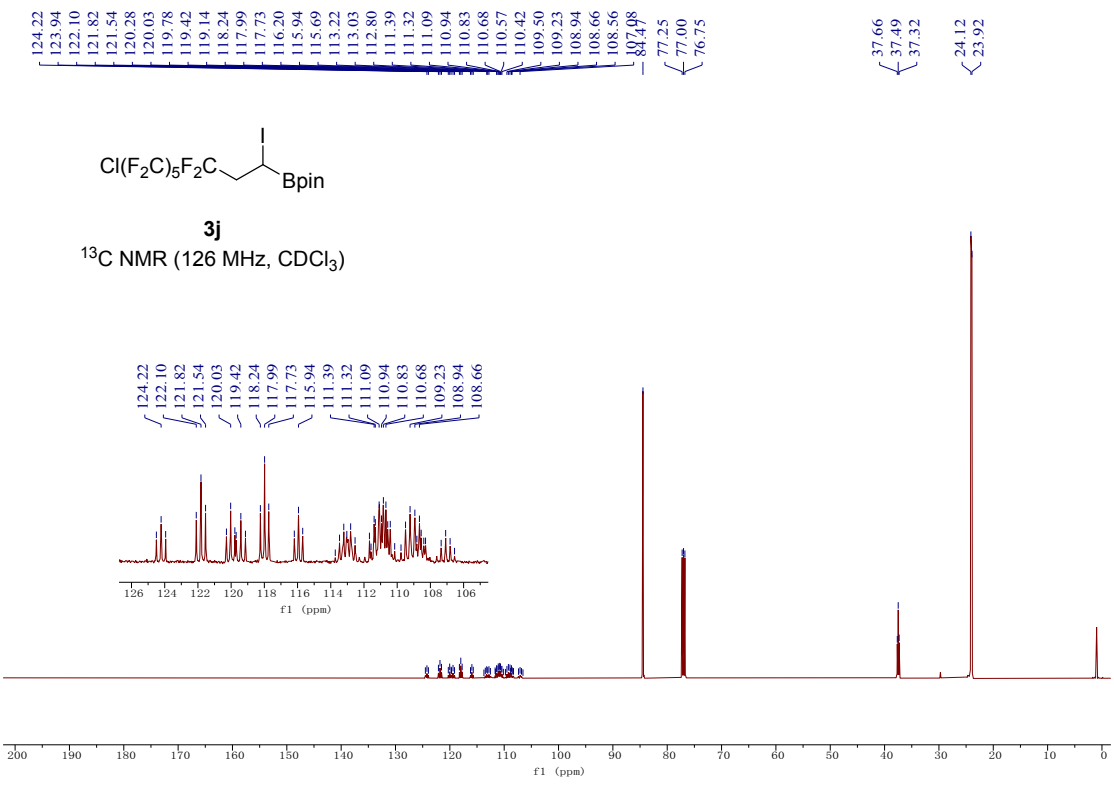
3i

^{11}B NMR (128 MHz, $CDCl_3$)



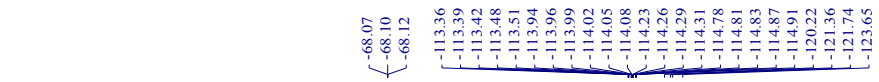
3j

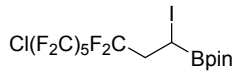
^{1}H NMR (500 MHz, $CDCl_3$)



3j

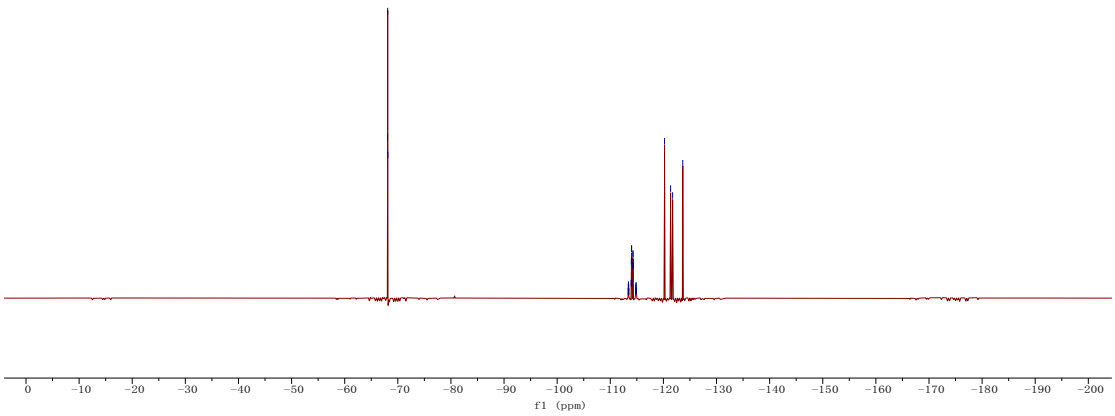
^{13}C NMR (126 MHz, $CDCl_3$)

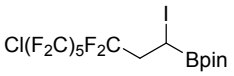




3j

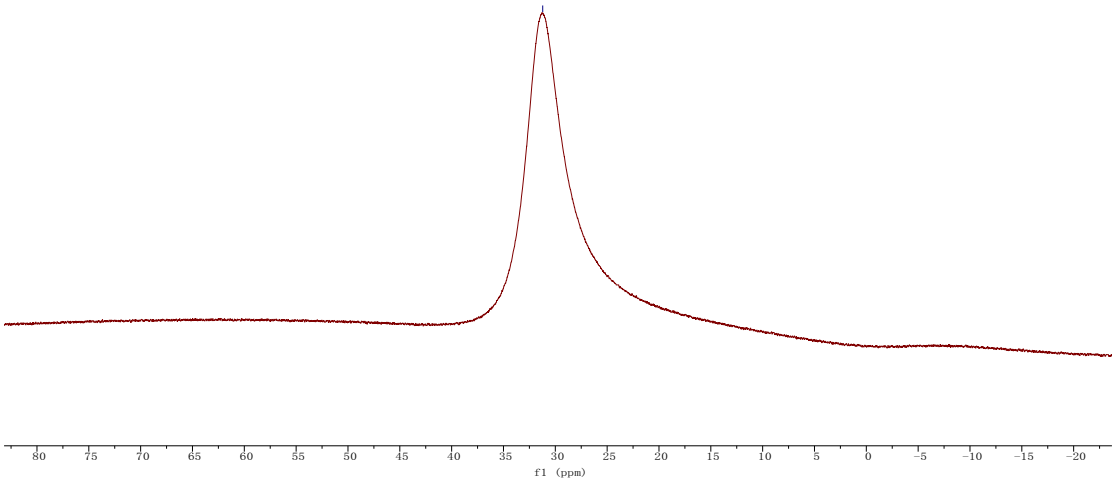
^{19}F NMR (471 MHz, $CDCl_3$)

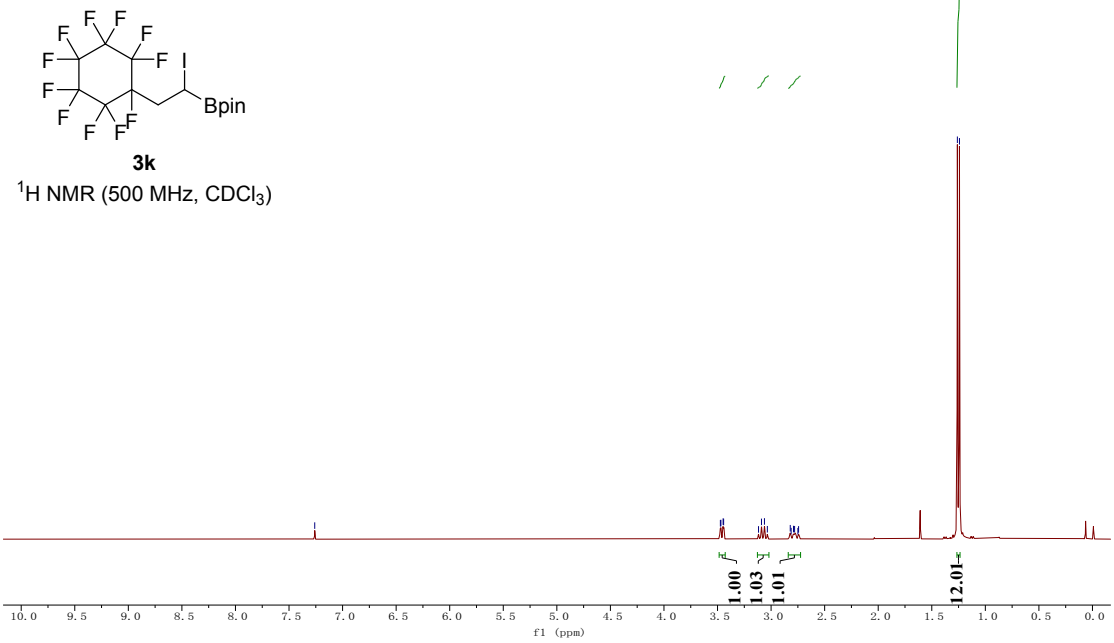




3j

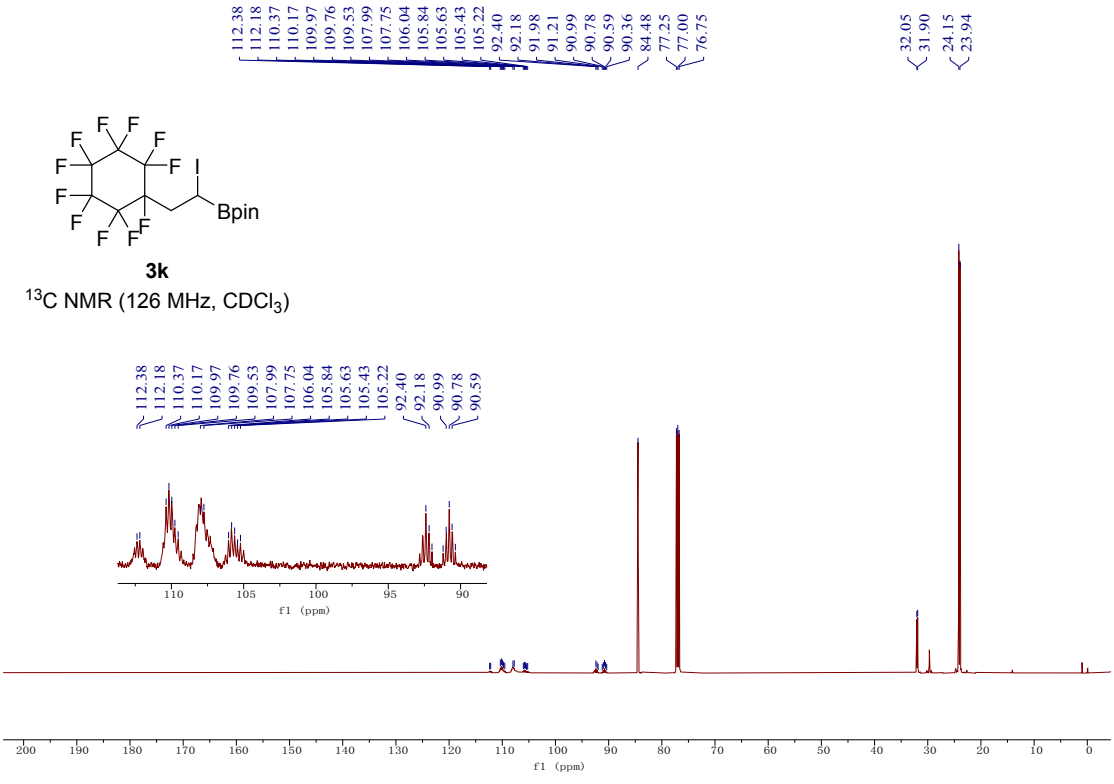
^{11}B NMR (128 MHz, $CDCl_3$)





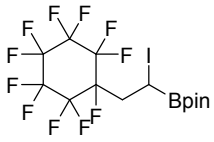
3k

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



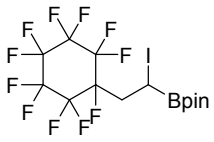
3k

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



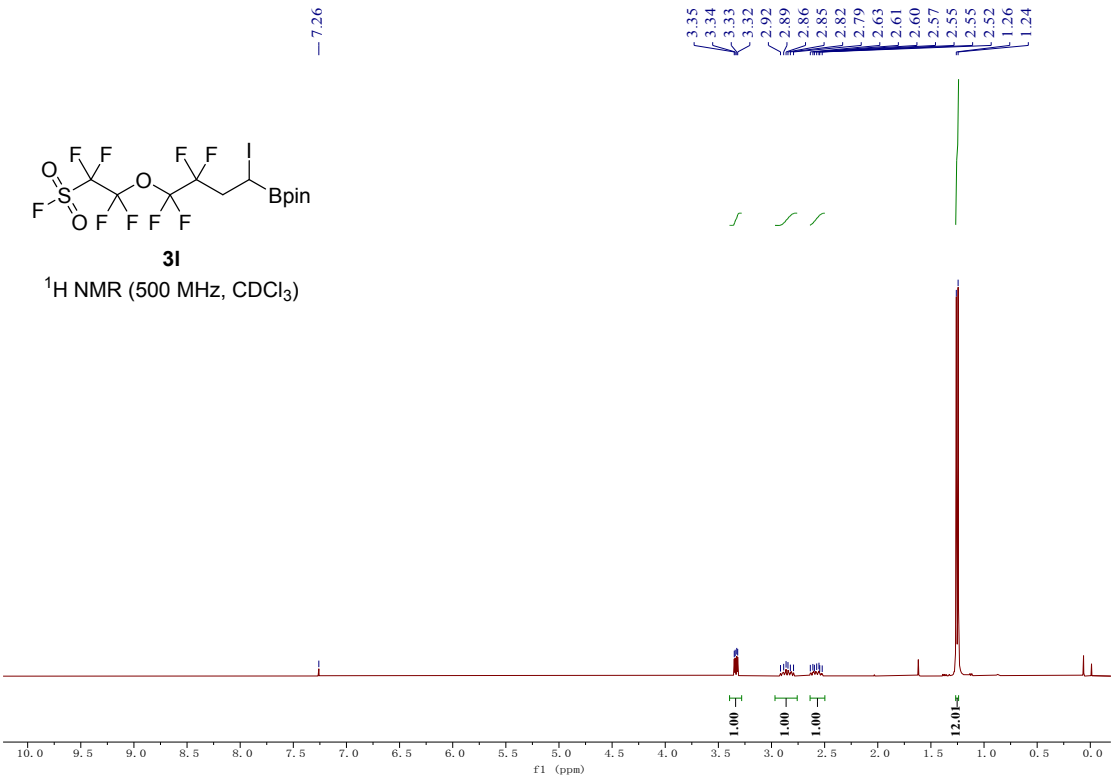
3k

^{19}F NMR (471 MHz, $CDCl_3$)



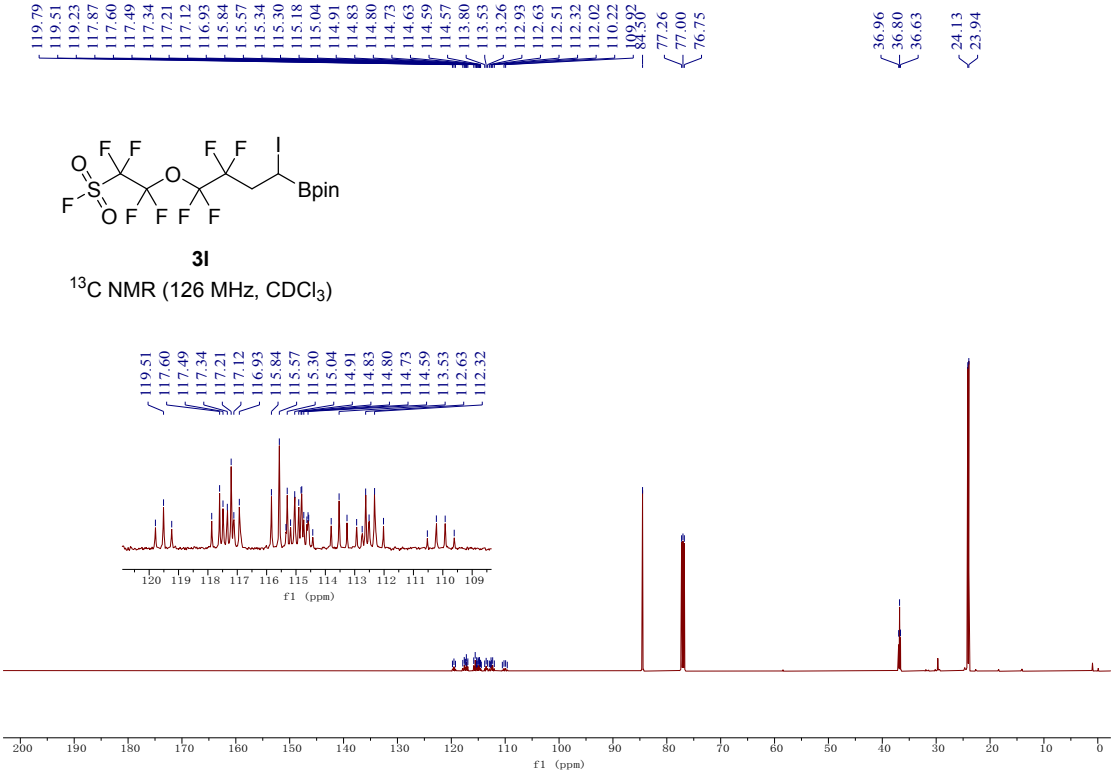
3k

^{11}B NMR (128 MHz, $CDCl_3$)



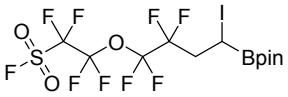
3l

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



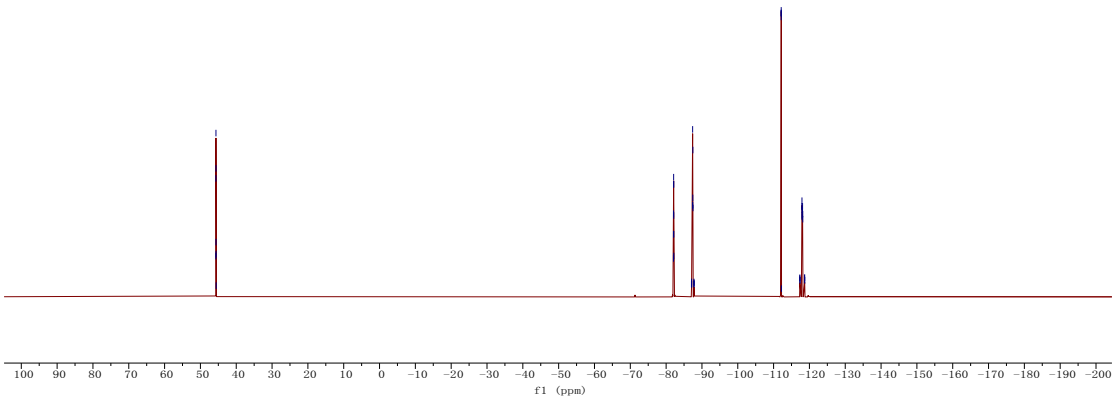
3l

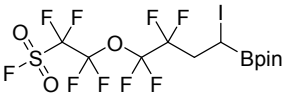
^{13}C NMR (126 MHz, $CDCl_3$)



3l

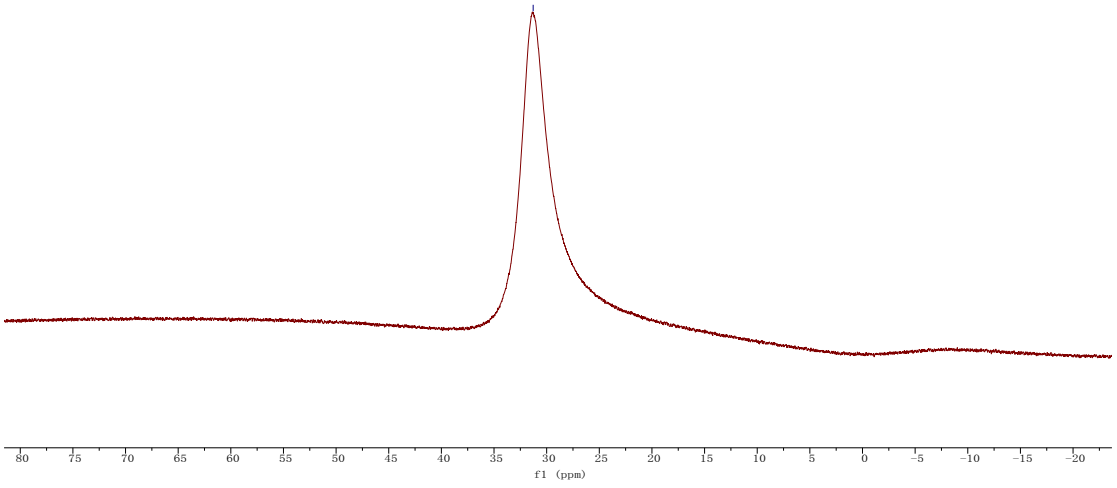
^{19}F NMR (471 MHz, $CDCl_3$)

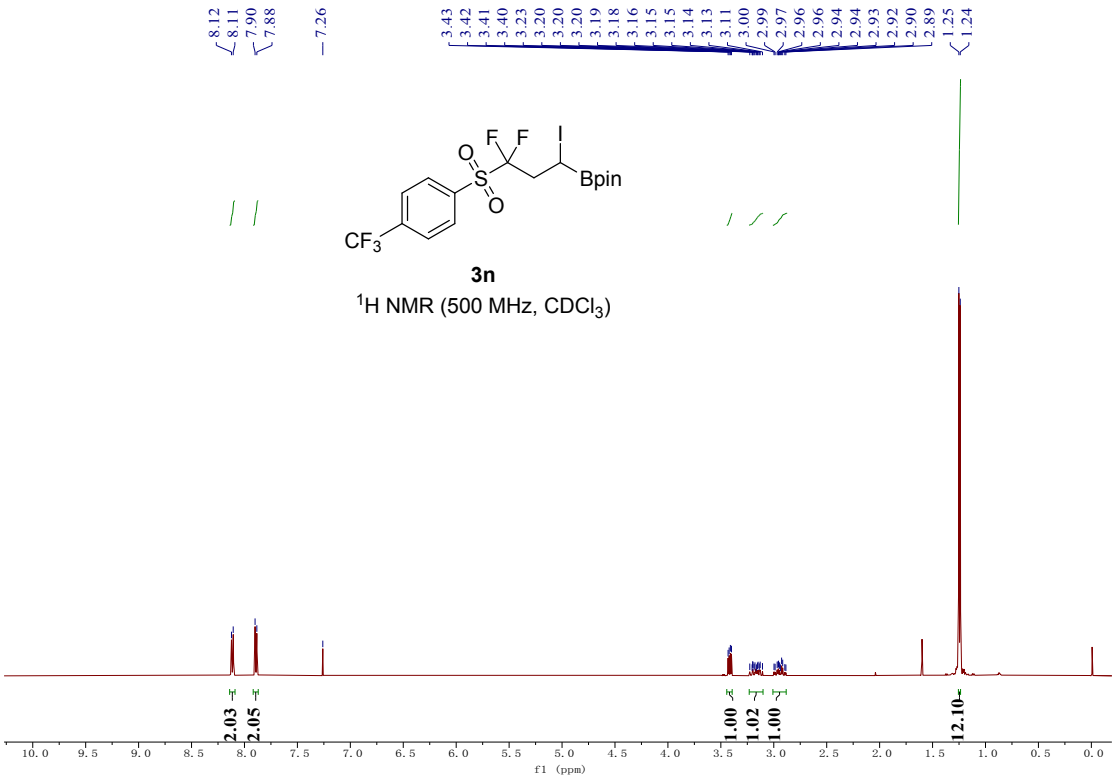




3l

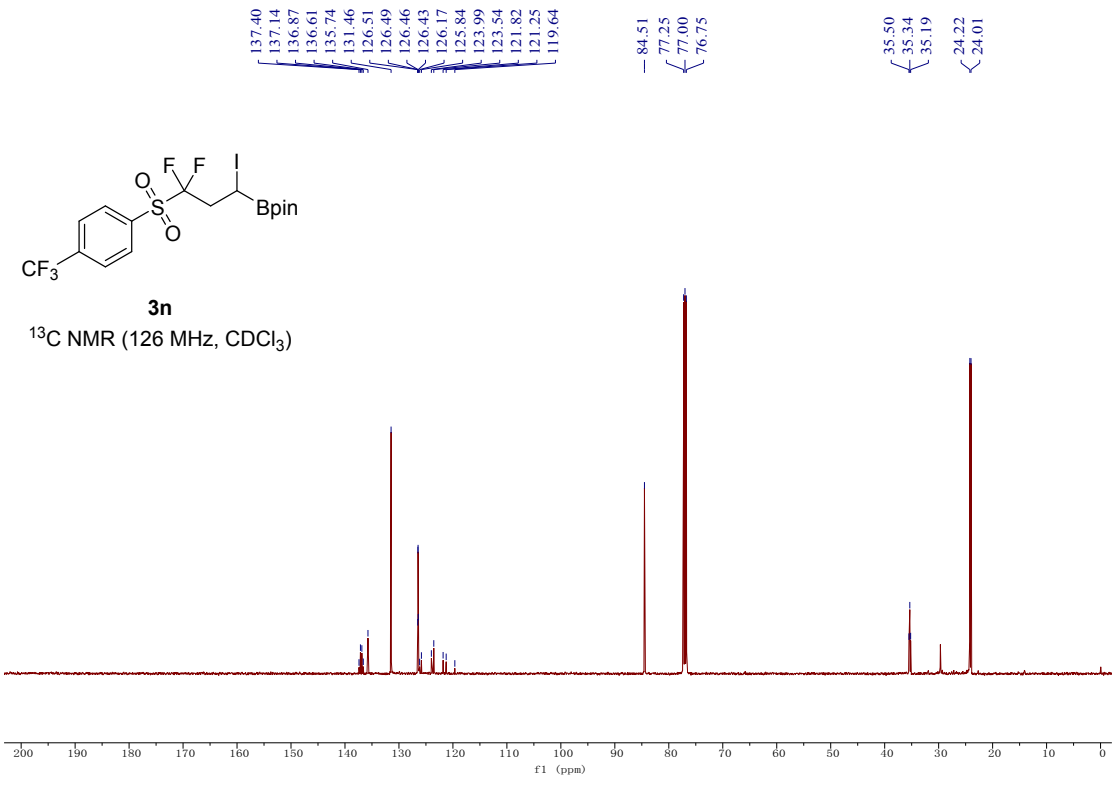
^{11}B NMR (128 MHz, $CDCl_3$)





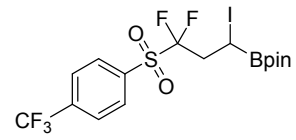
3n

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



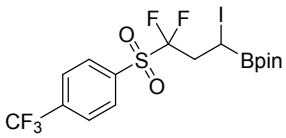
3n

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



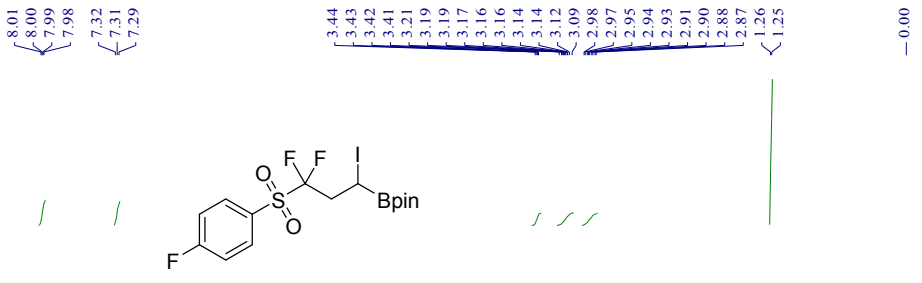
3n

^{19}F NMR (376 MHz, $CDCl_3$)



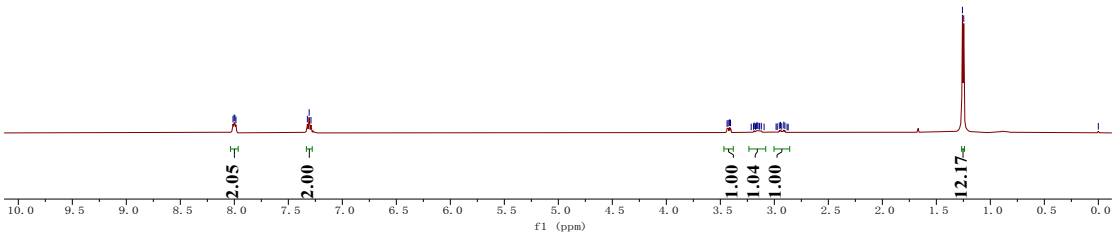
3n

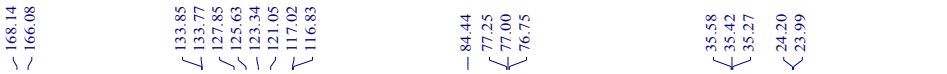
^{11}B NMR (128 MHz, $CDCl_3$)

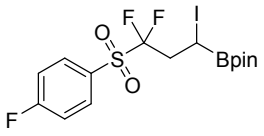


3o

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

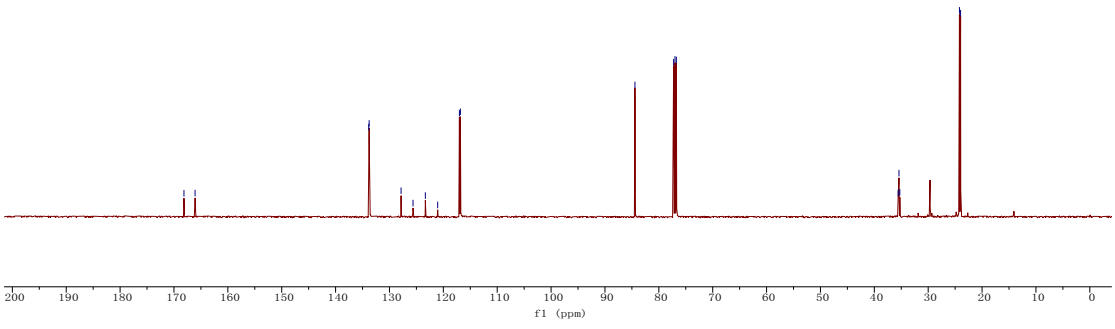


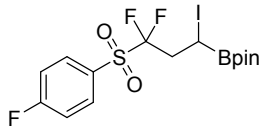




3o

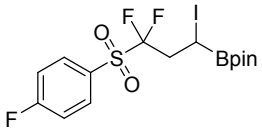
^{13}C NMR (126 MHz, $CDCl_3$)





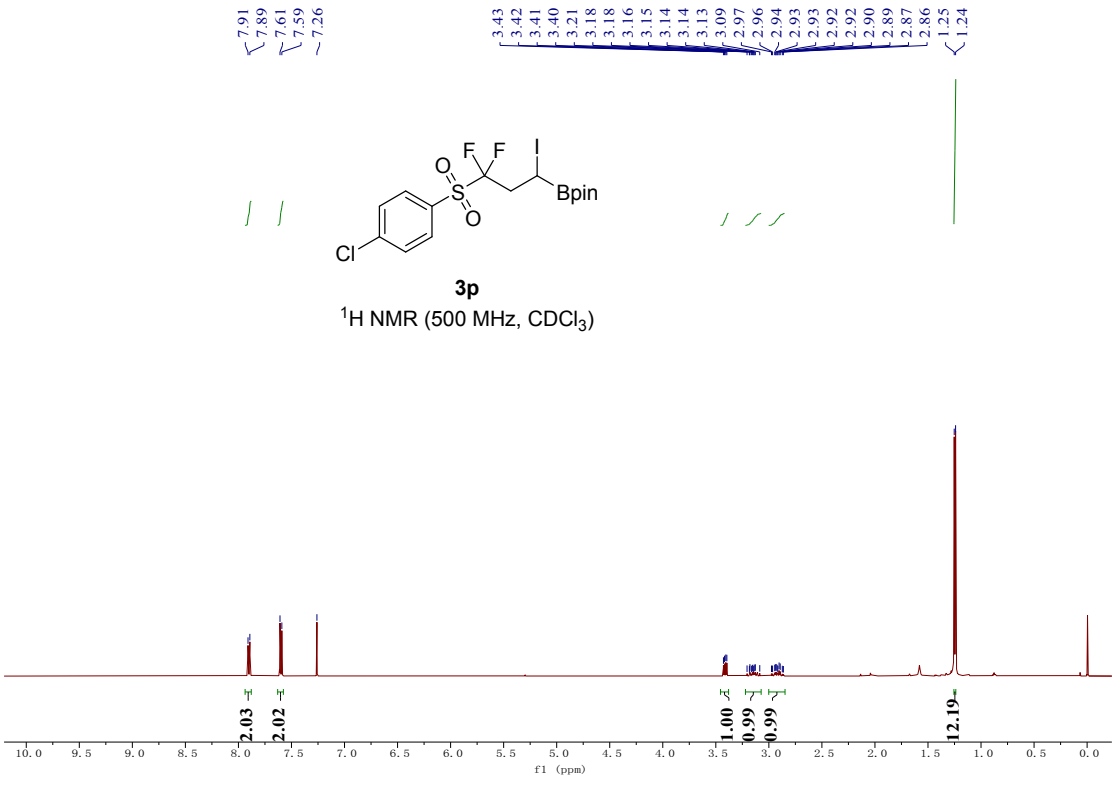
3o

^{19}F NMR (376 MHz, $CDCl_3$)



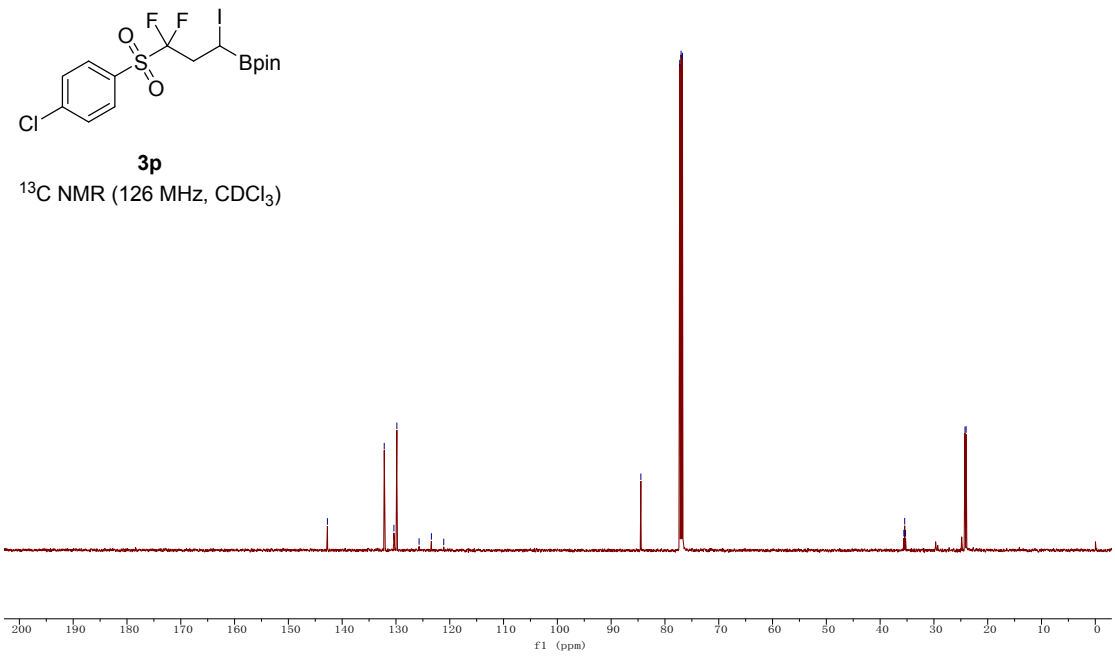
3o

^{11}B NMR (128 MHz, $CDCl_3$)



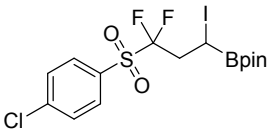
3p

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



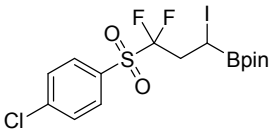
3p

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



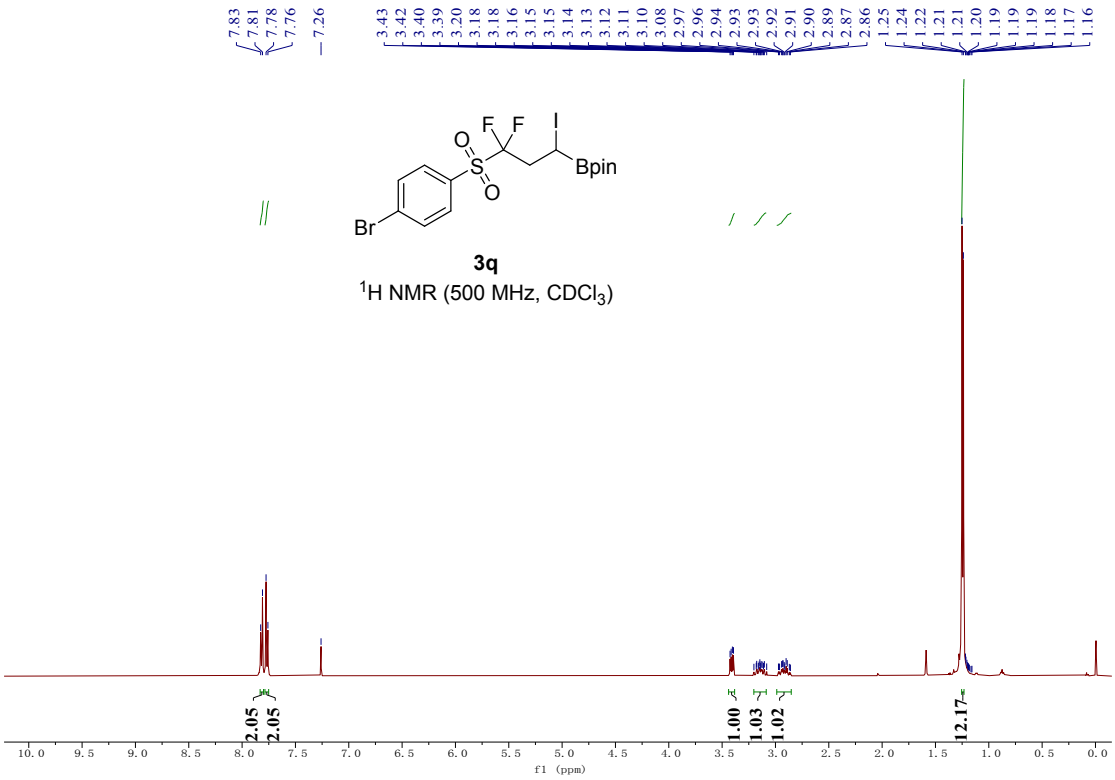
3p

^{19}F NMR (376 MHz, $CDCl_3$)



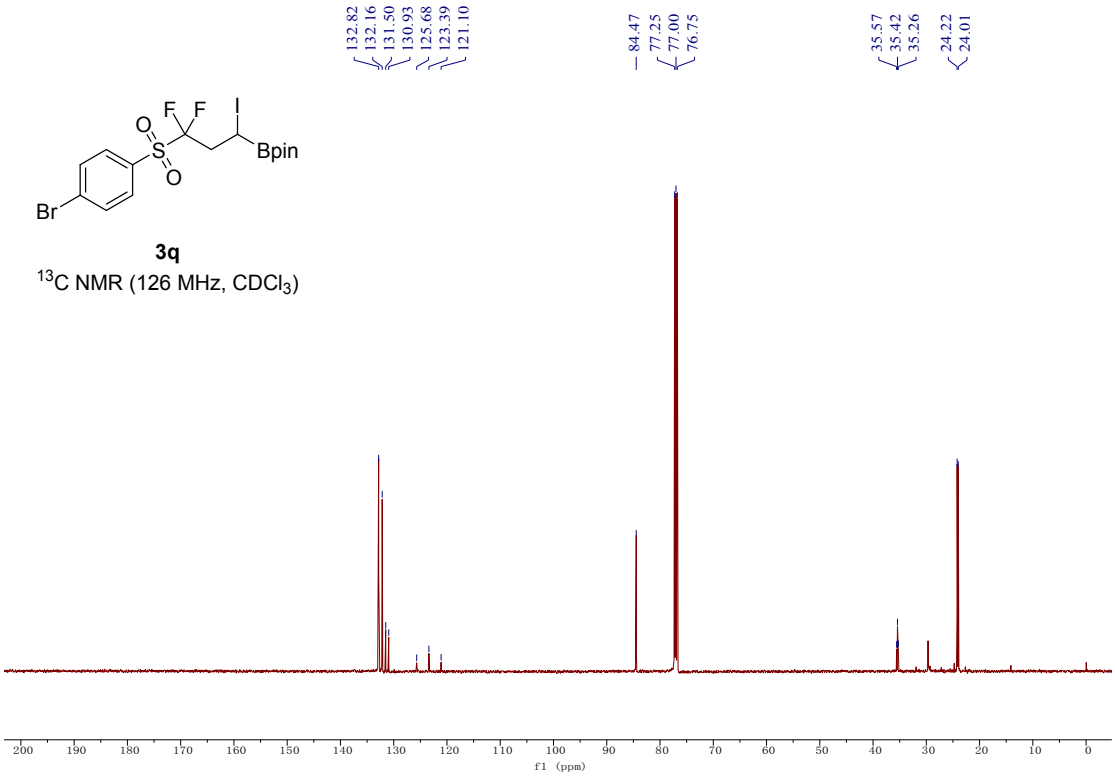
3p

^{11}B NMR (128 MHz, $CDCl_3$)



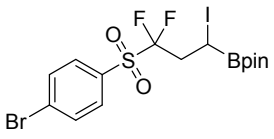
3q

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



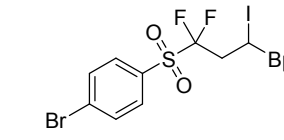
3q

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



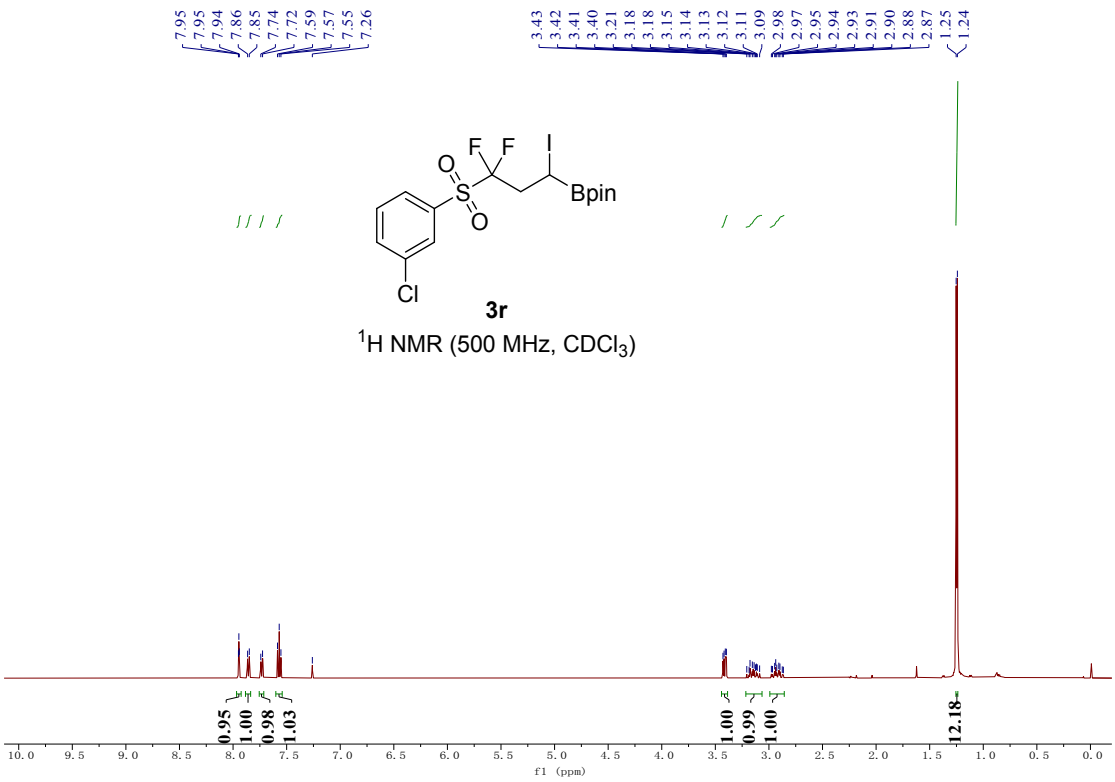
3q

^{19}F NMR (376 MHz, $CDCl_3$)



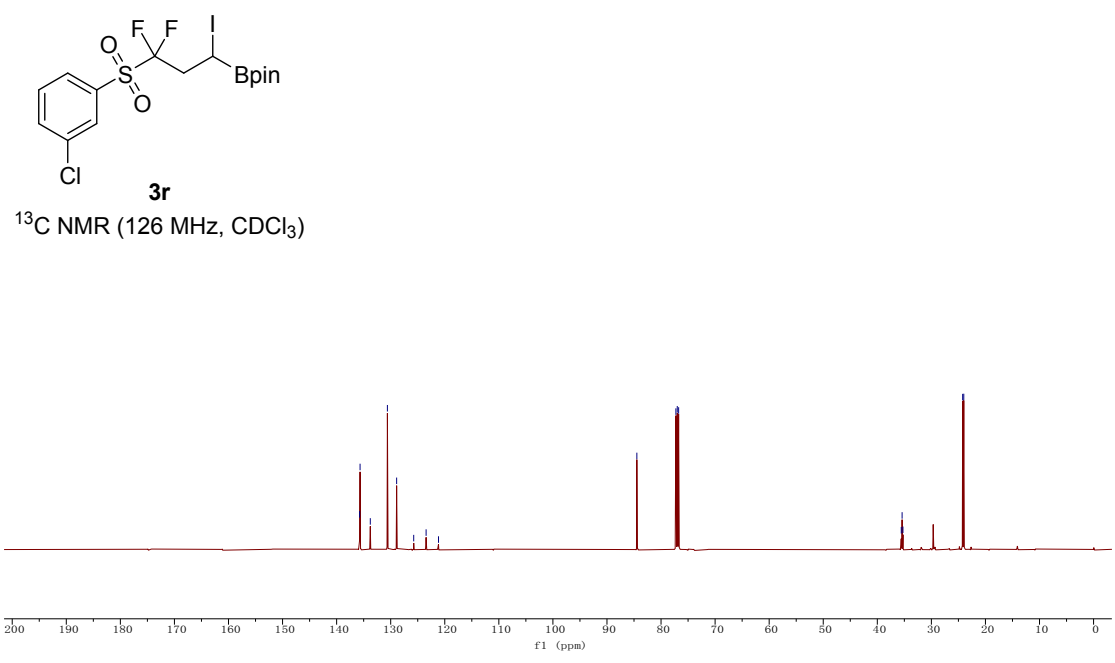
3q

^{11}B NMR (128 MHz, $CDCl_3$)



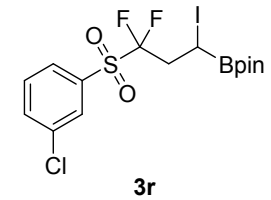
3r

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



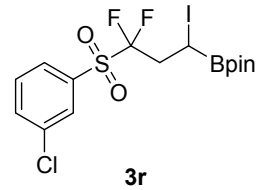
3r

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



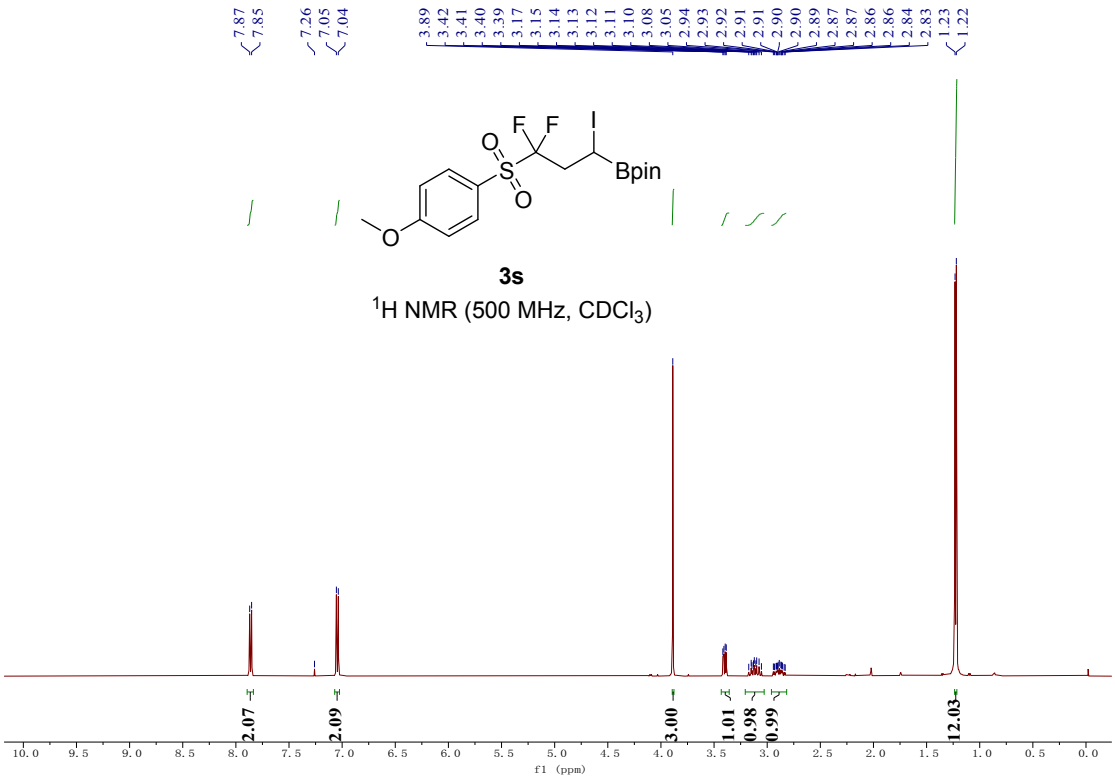
3r

^{19}F NMR (376 MHz, $CDCl_3$)



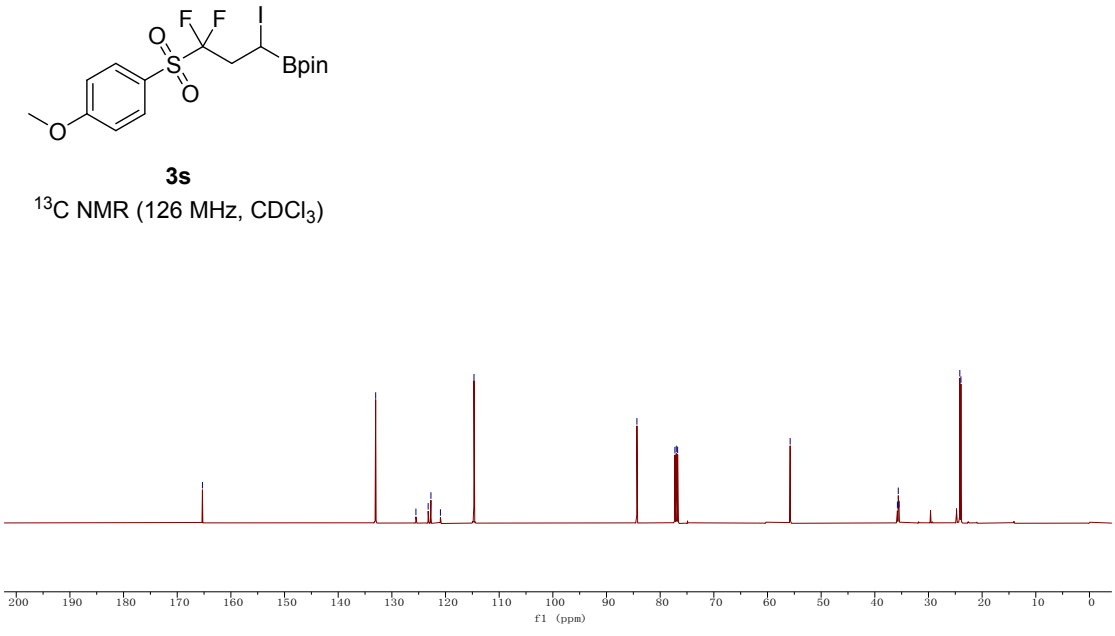
3r

^{11}B NMR (128 MHz, $CDCl_3$)



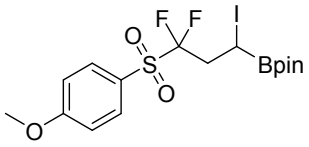
3s

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



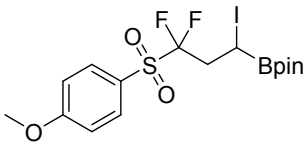
3s

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



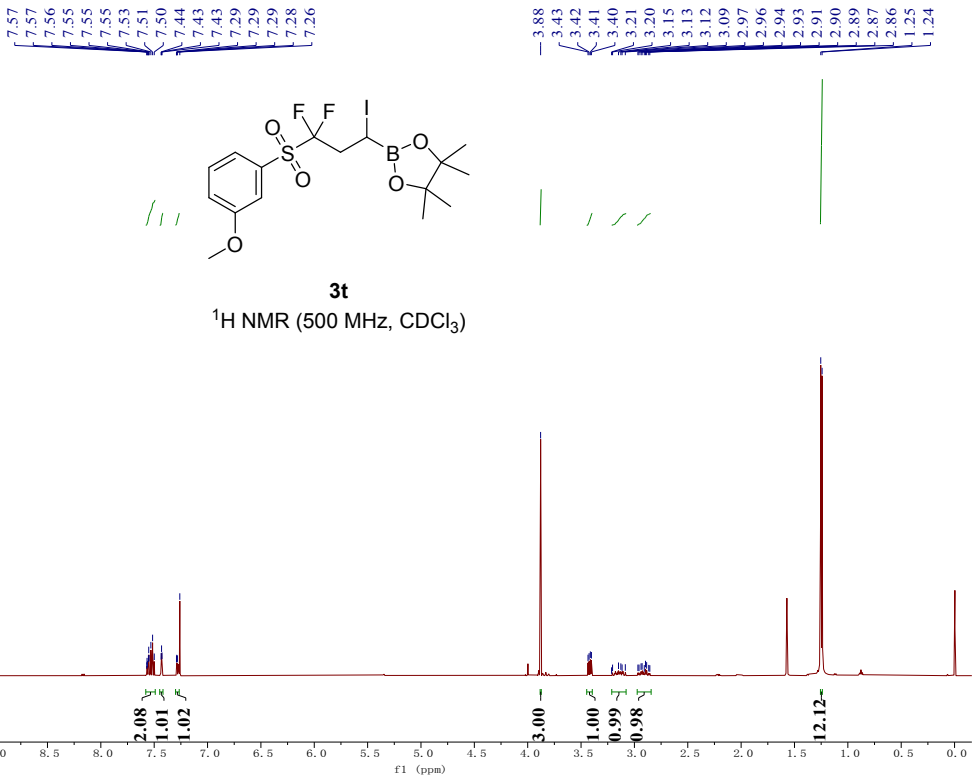
3s

^{19}F NMR (376 MHz, $CDCl_3$)



3s

^{11}B NMR (128 MHz, $CDCl_3$)

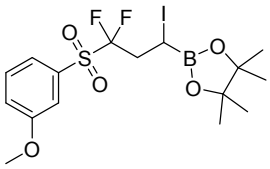


3t

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

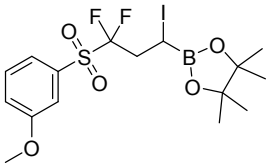
3t

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



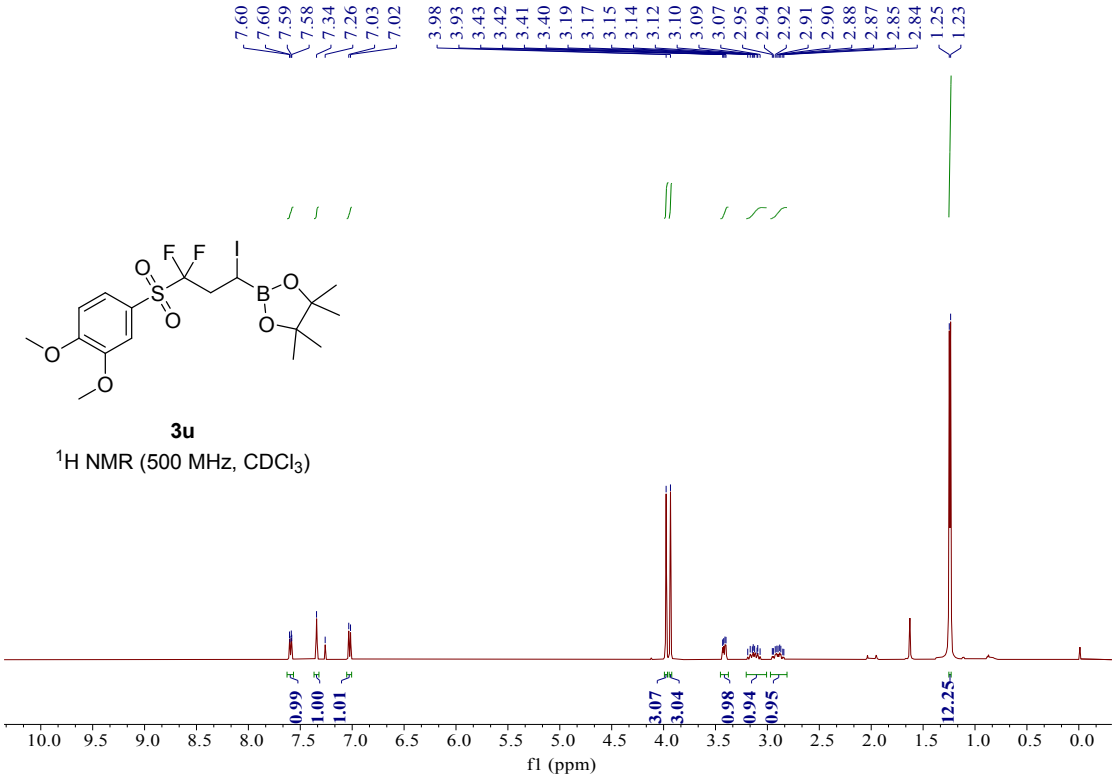
3t

^{19}F NMR (376 MHz, $CDCl_3$)



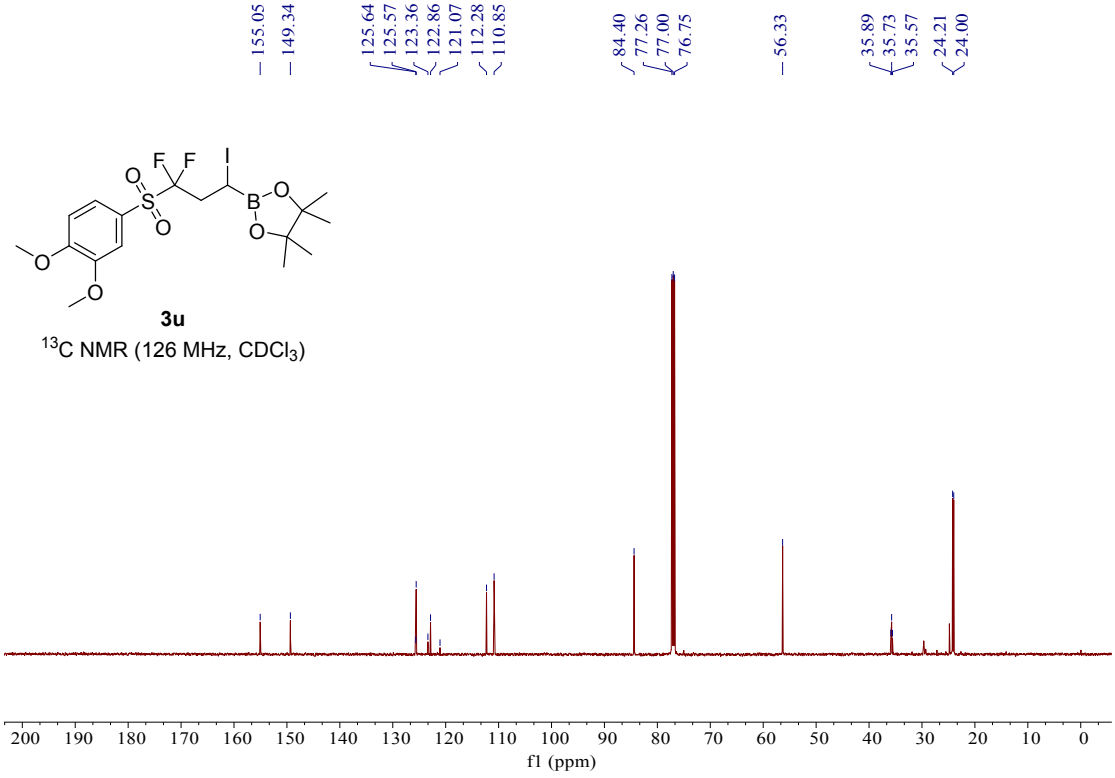
3t

^{11}B NMR (128 MHz, $CDCl_3$)



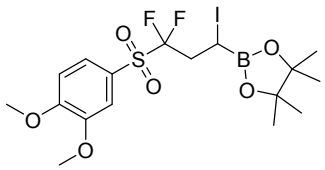
3u

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



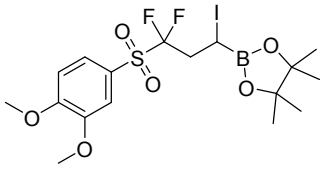
3u

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



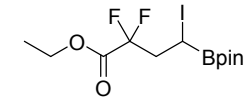
3u

^{19}F NMR (376 MHz, $CDCl_3$)



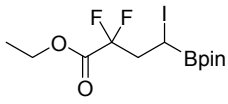
3u

^{11}B NMR (128 MHz, $CDCl_3$)



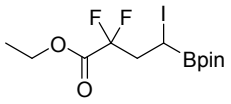
3v

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



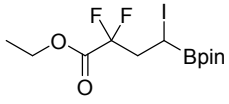
3v

^{13}C NMR (101 MHz, $CDCl_3$)



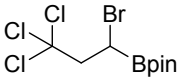
3v

^{19}F NMR (376 MHz, $CDCl_3$)



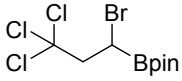
3v

^{11}B NMR (128 MHz, $CDCl_3$)



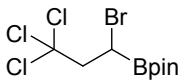
3w

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



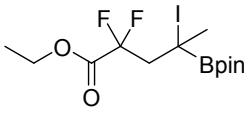
3w

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



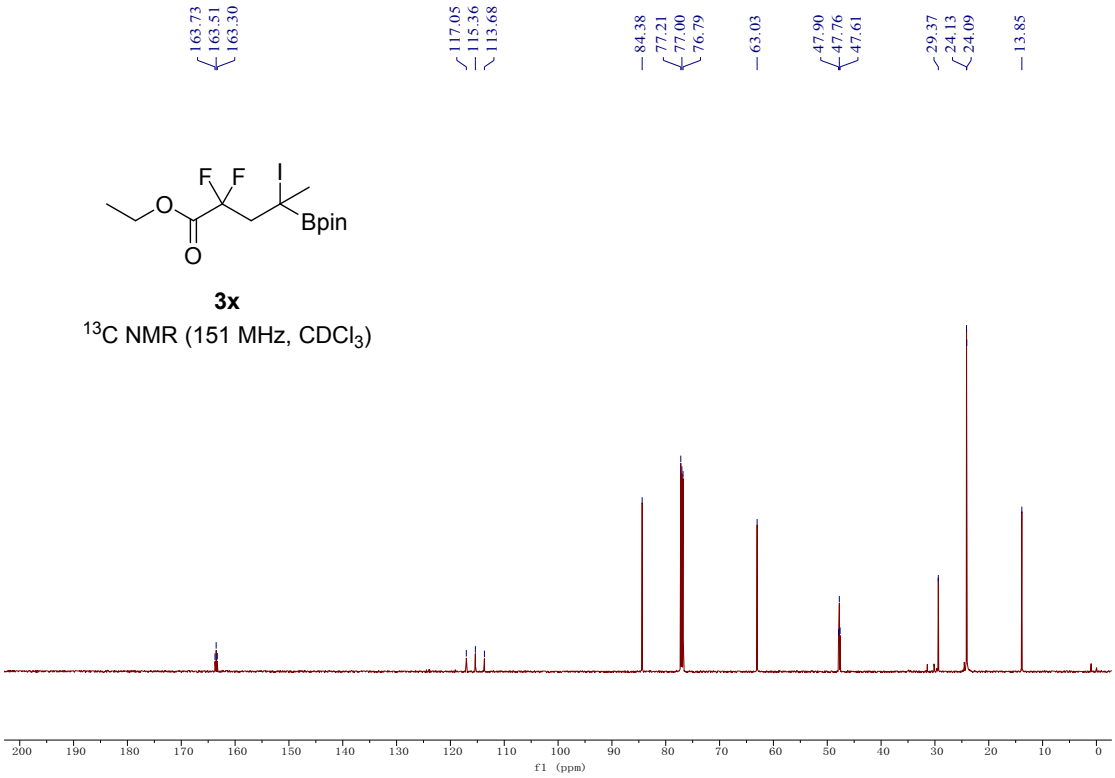
3w

^{11}B NMR (128 MHz, $CDCl_3$)



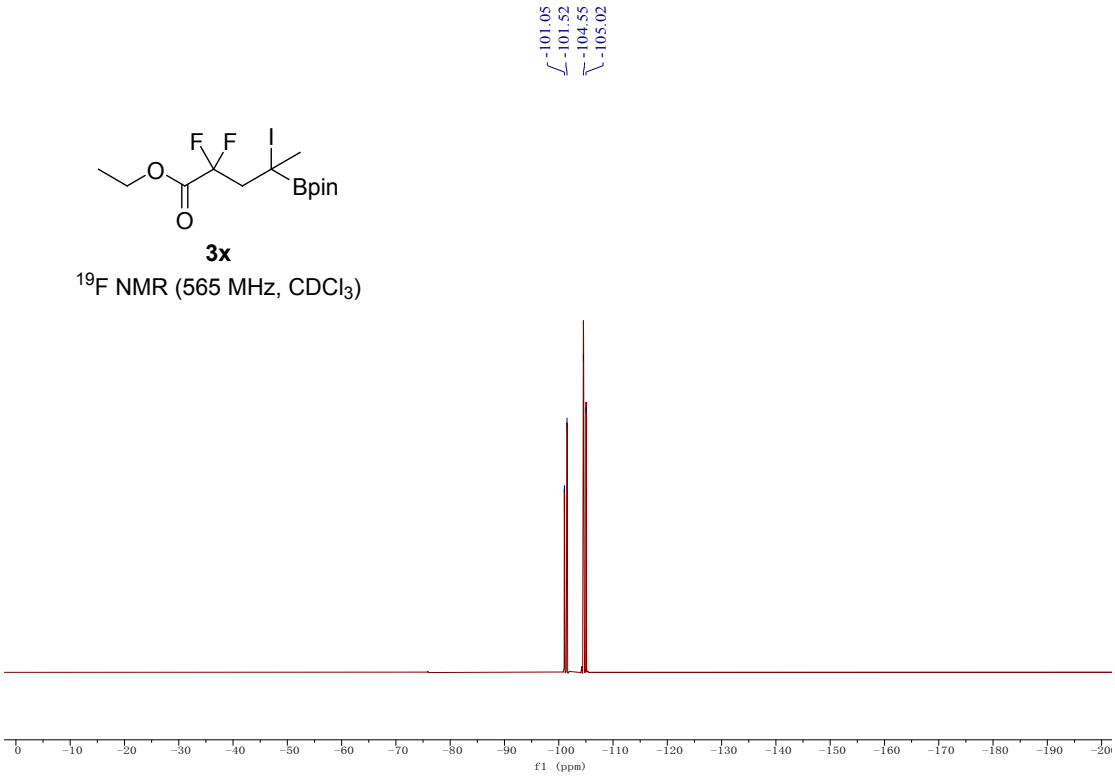
3x

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



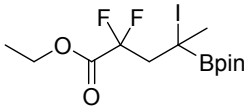
3x

^{13}C NMR (151 MHz, $CDCl_3$)



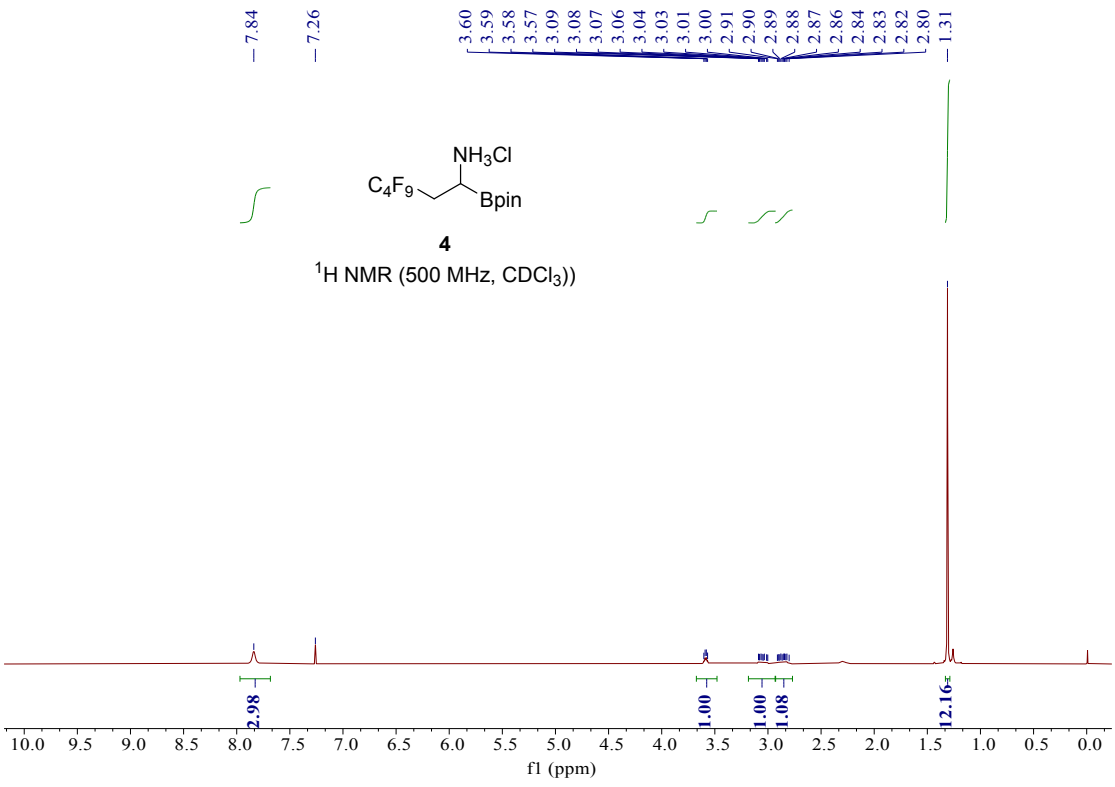
3x

^{19}F NMR (565 MHz, $CDCl_3$)



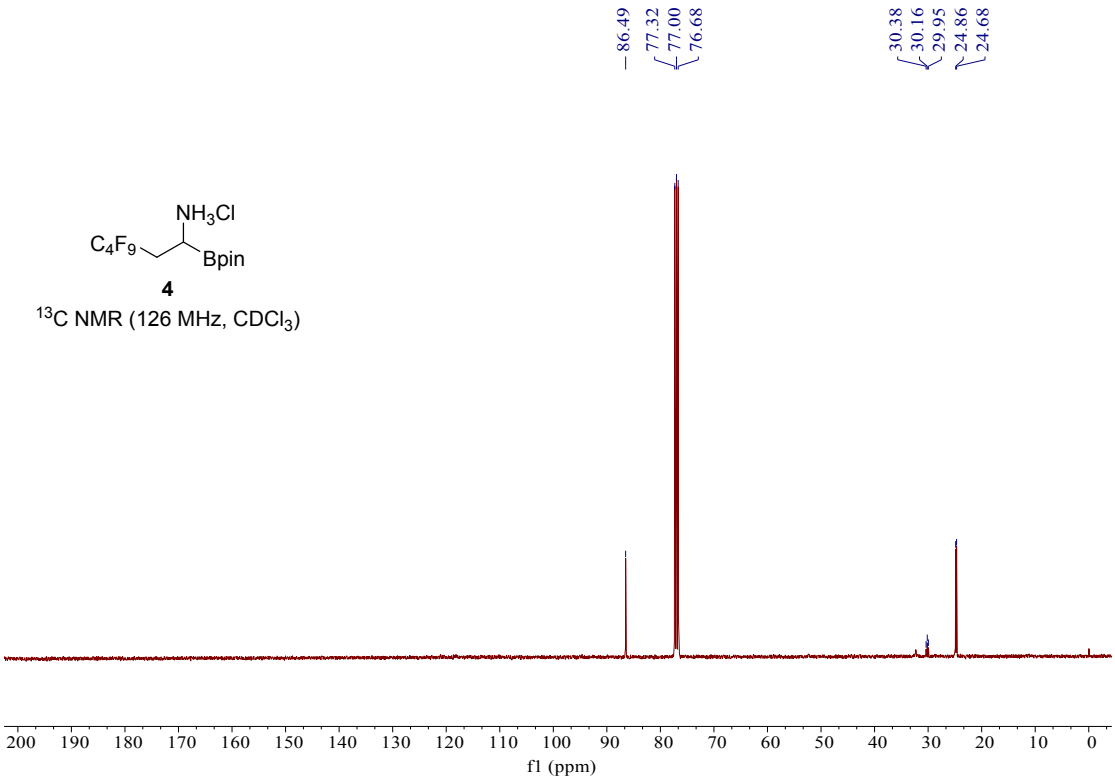
3x

^{11}B NMR (128 MHz, $CDCl_3$)



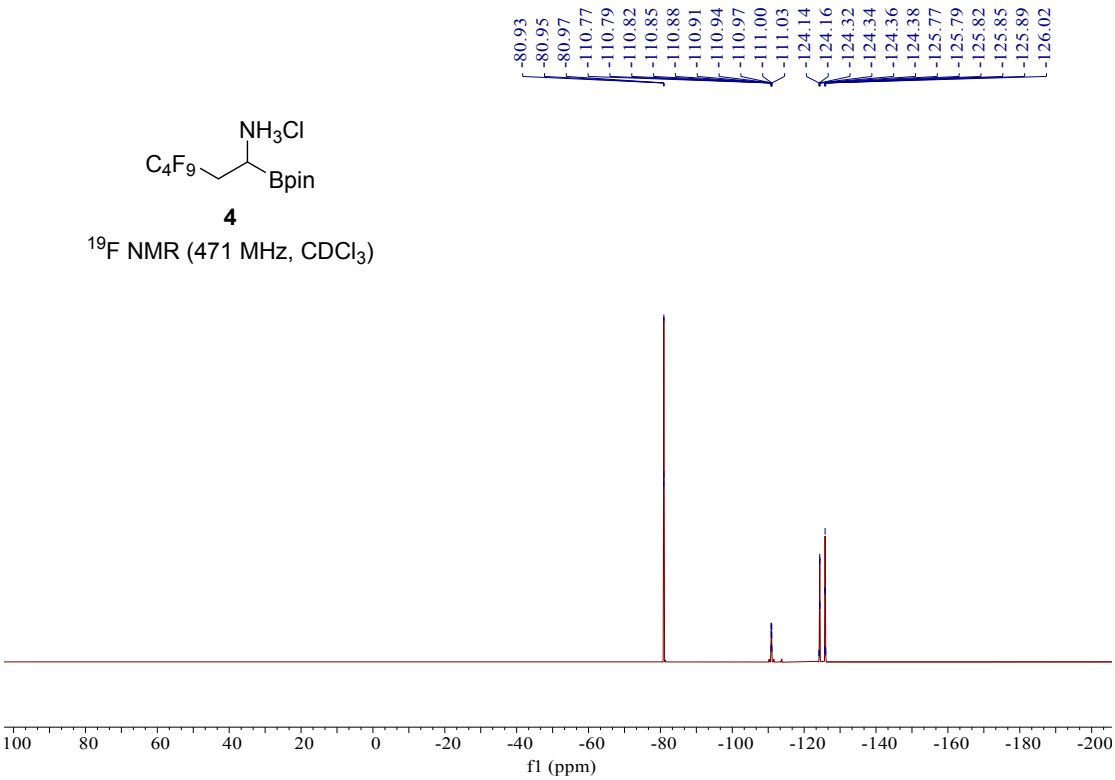
4

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



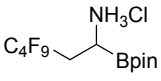
4

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



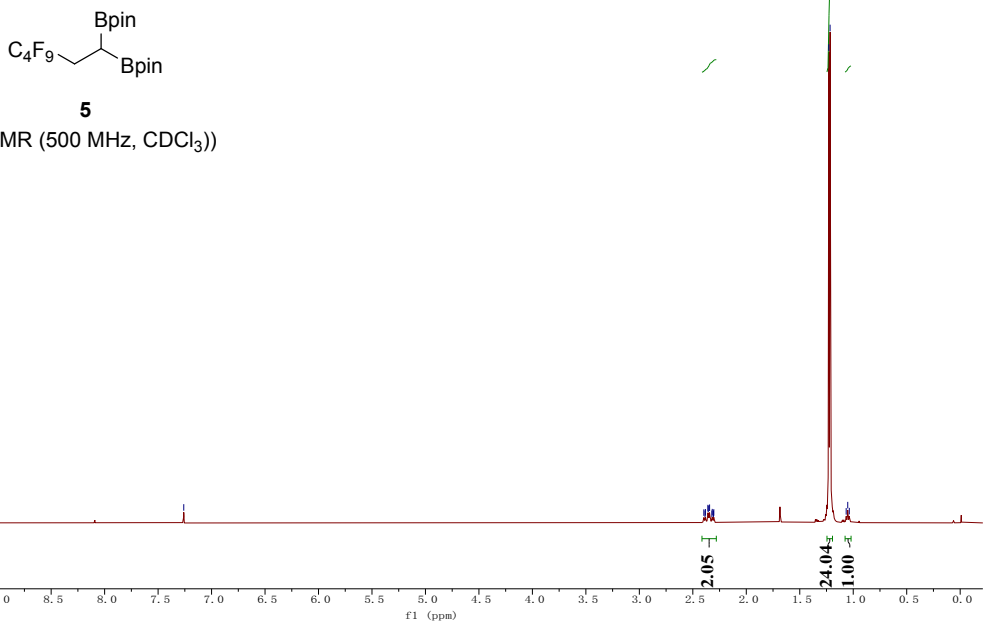
4

^{19}F NMR (471 MHz, $CDCl_3$)



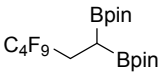
4

^{11}B NMR (128 MHz, $CDCl_3$)



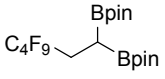
5

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



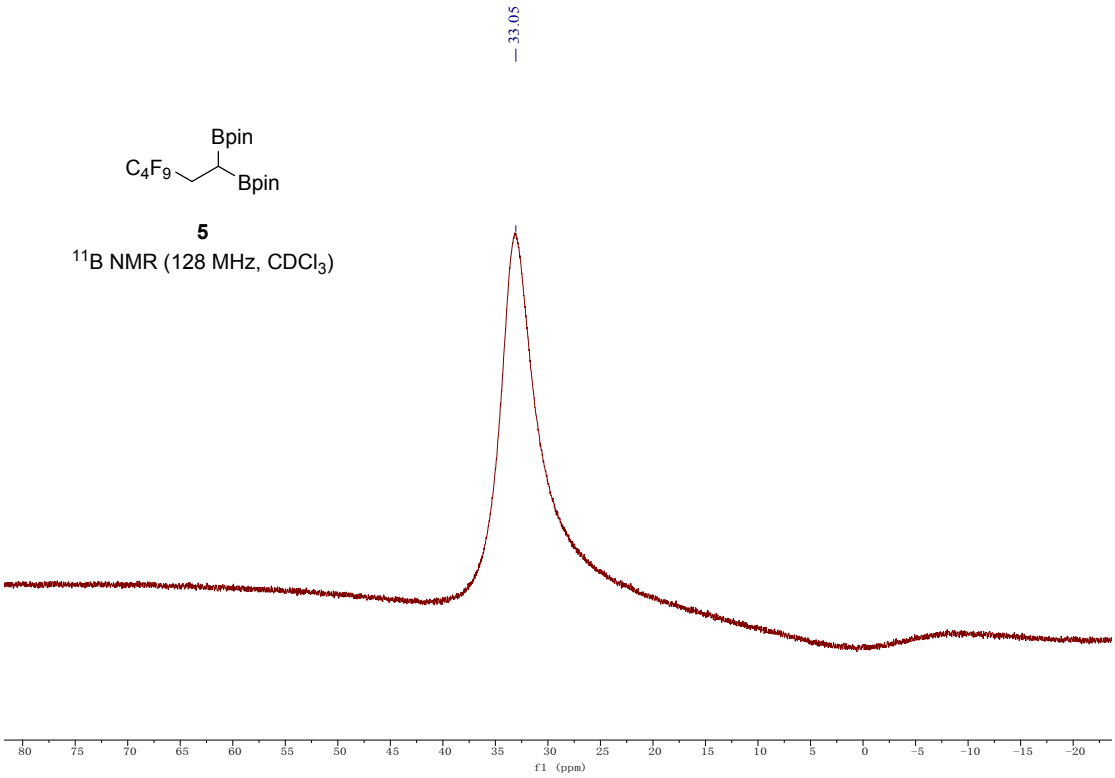
5

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



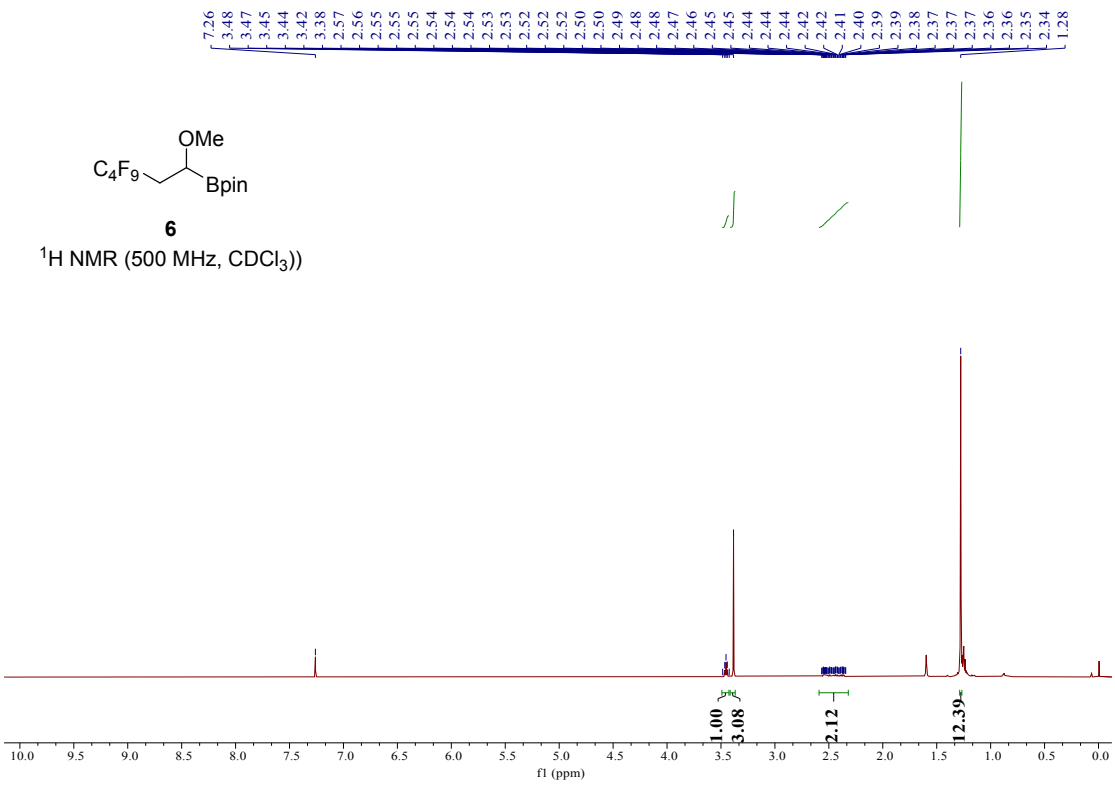
5

^{19}F NMR (471 MHz, $CDCl_3$)



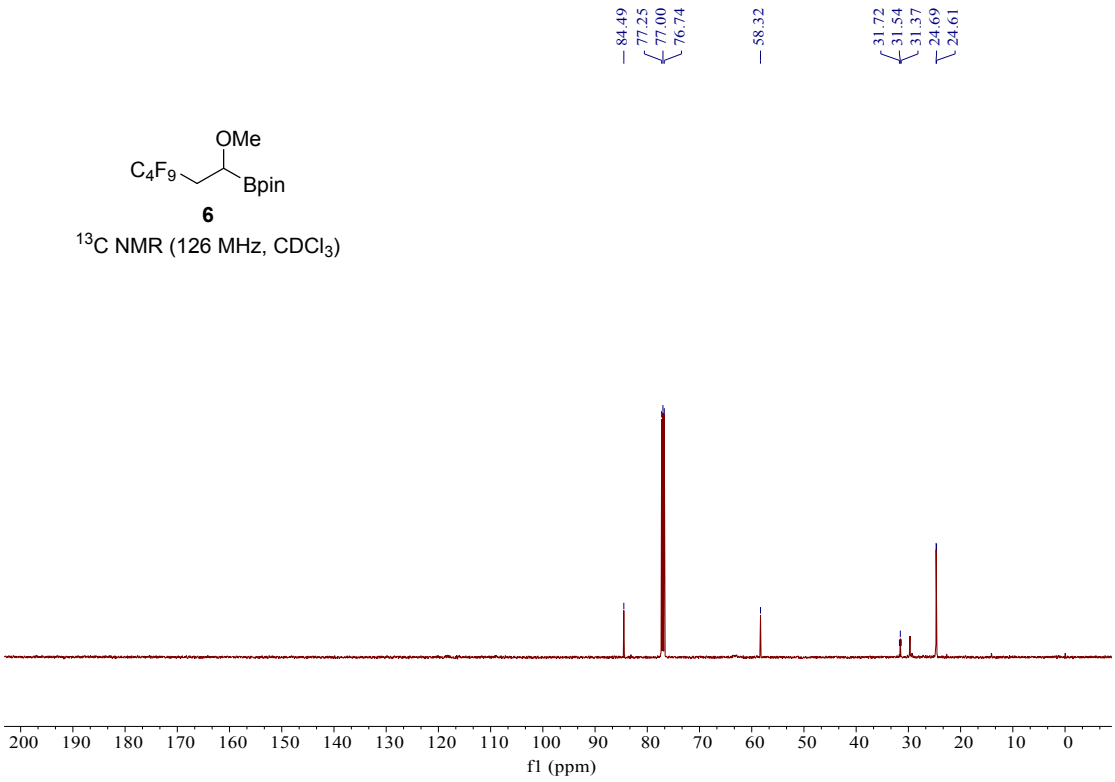
5

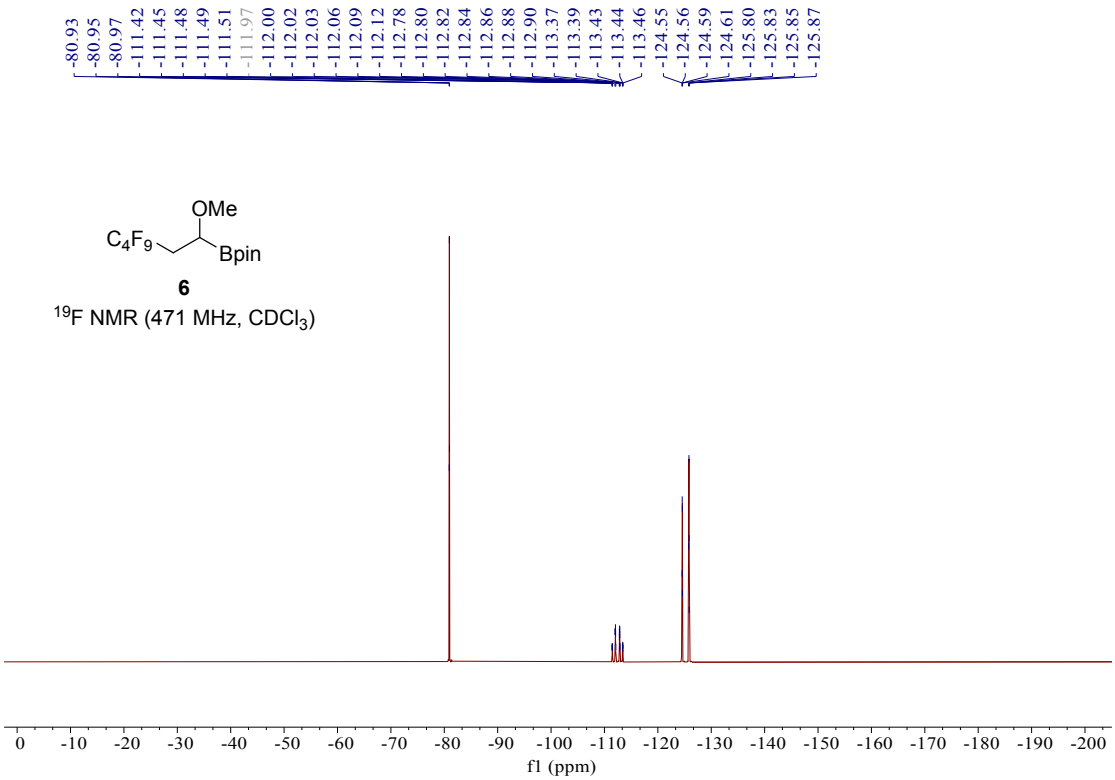
^{11}B NMR (128 MHz, $CDCl_3$)

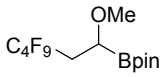


6

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

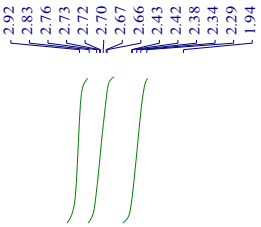

84.49
77.25
77.00
76.74
58.32
31.72
31.54
31.37
24.69
24.61
OMe
C4F9
Bpin
6
13C NMR (126 MHz, CDCl3)
f1 (ppm)

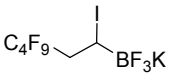

-80.93
-80.95
-80.97
-111.42
-111.45
-111.48
-111.49
-111.51
-111.97
-112.00
-112.02
-112.03
-112.06
-112.09
-112.12
-112.78
-112.80
-112.82
-112.84
-112.86
-112.88
-112.90
-113.37
-113.39
-113.43
-113.44
-113.46
-124.55
-124.56
-124.59
-124.61
-125.80
-125.83
-125.85
-125.87
OMe
C4F9
Bpin
6
19F NMR (471 MHz, CDCl3)
f1 (ppm)



6

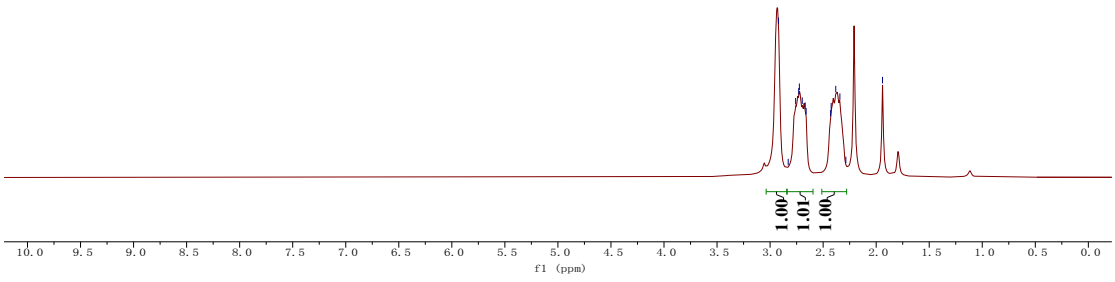
^{11}B NMR (128 MHz, $CDCl_3$)

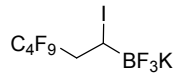




7

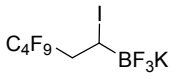
^{1}H NMR (500 MHz, CD_3CN)





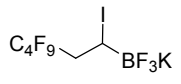
7

^{13}C NMR (126 MHz, CD_3CN)



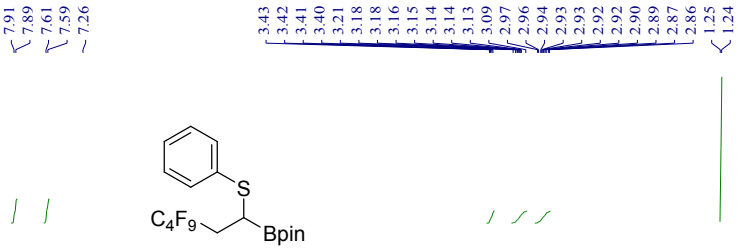
7

^{19}F NMR (471 MHz, CD_3CN)



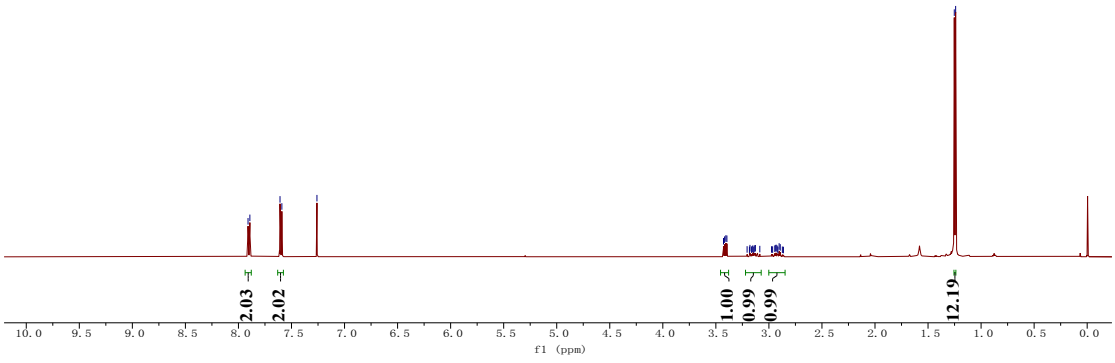
7

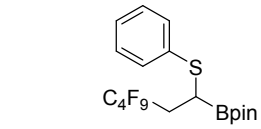
^{11}B NMR (128 MHz, CD_3CN)



8a

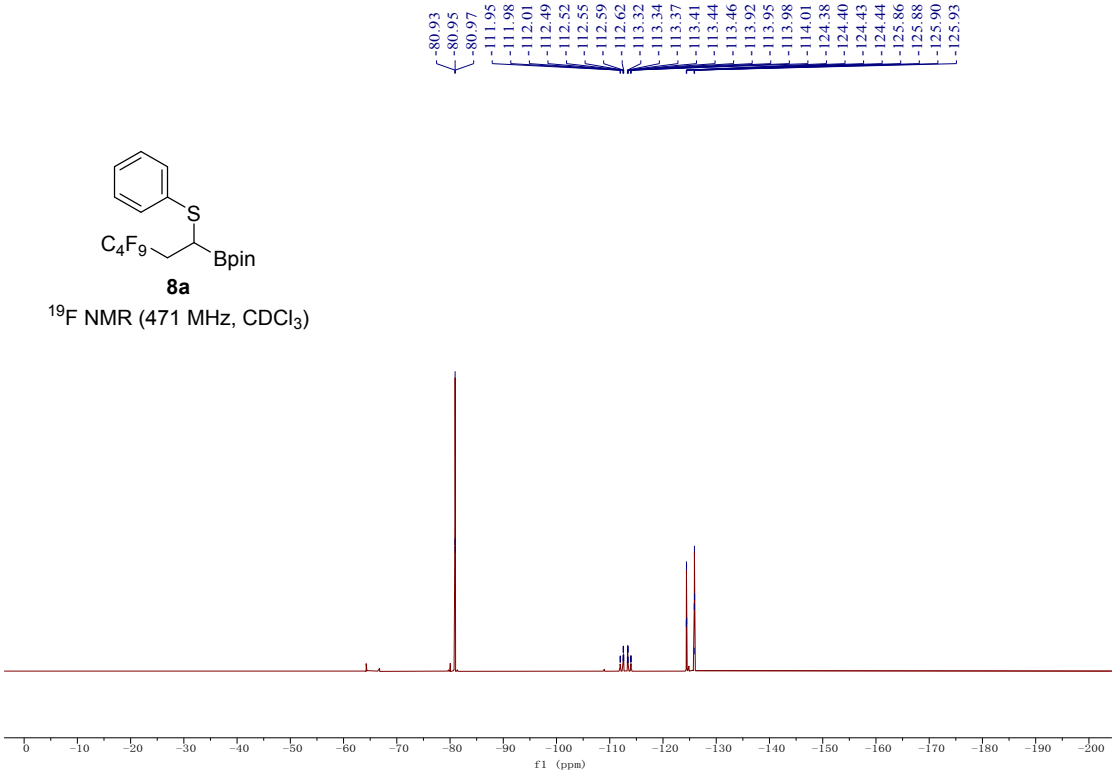
^{1}H NMR (500 MHz, $CDCl_3$))





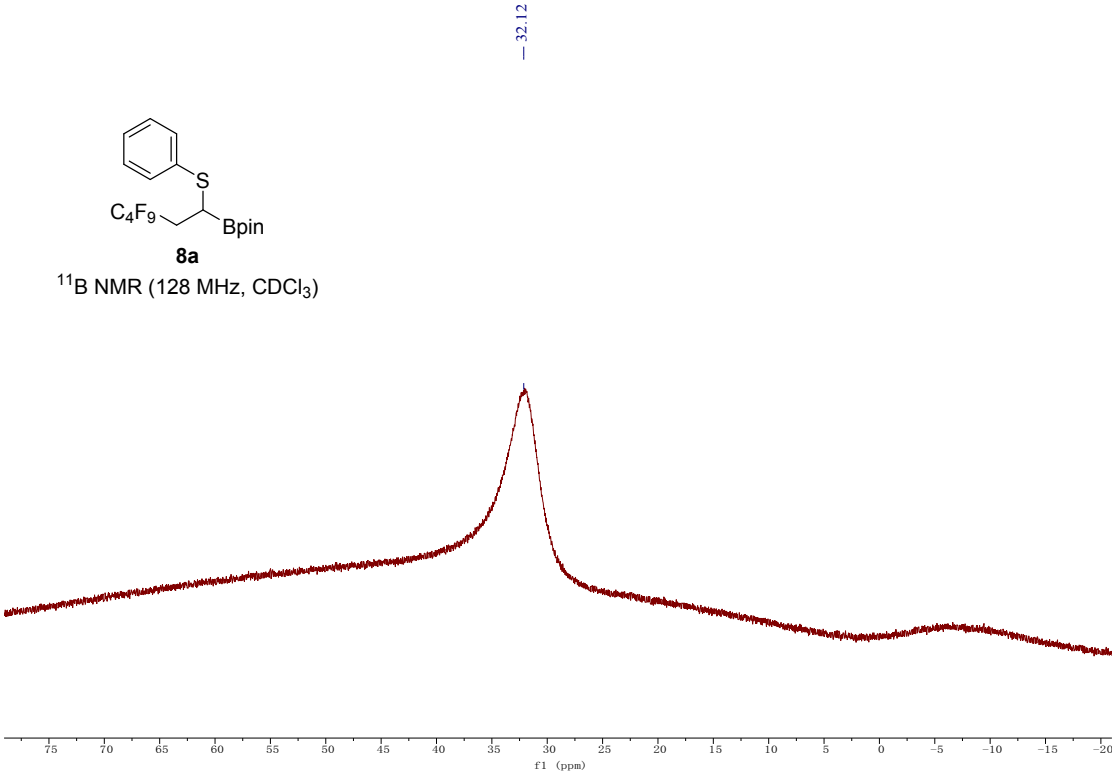
8a

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



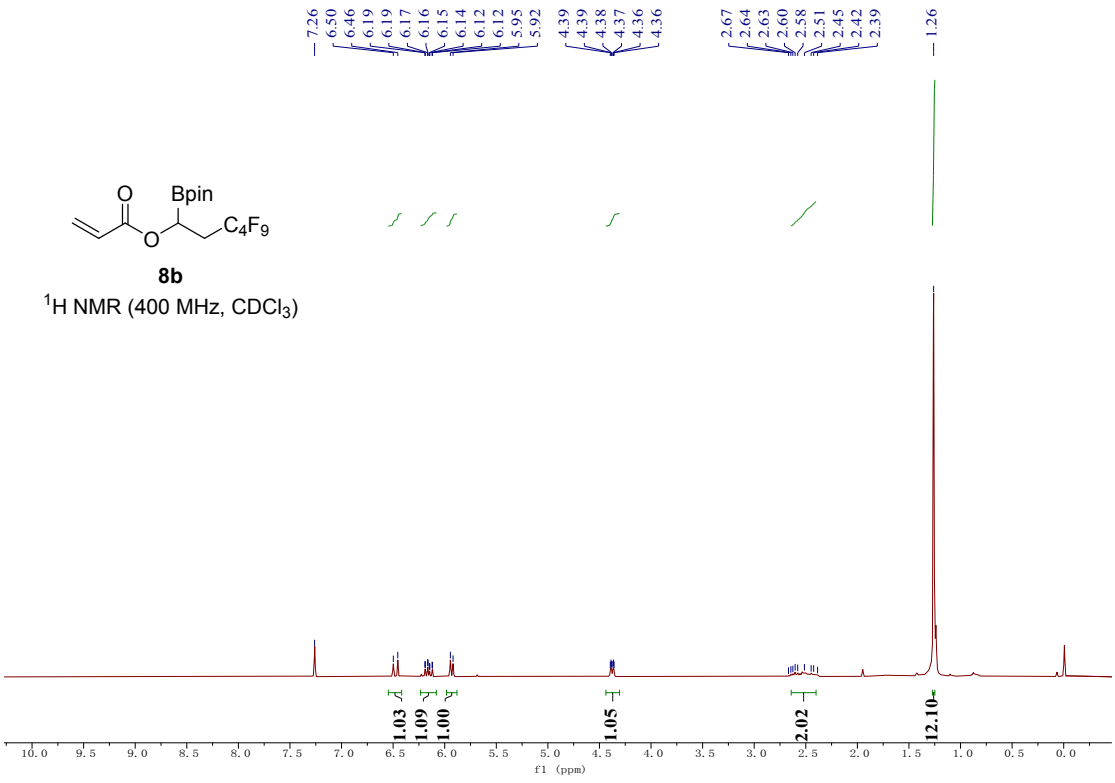
8a

^{19}F NMR (471 MHz, $CDCl_3$)



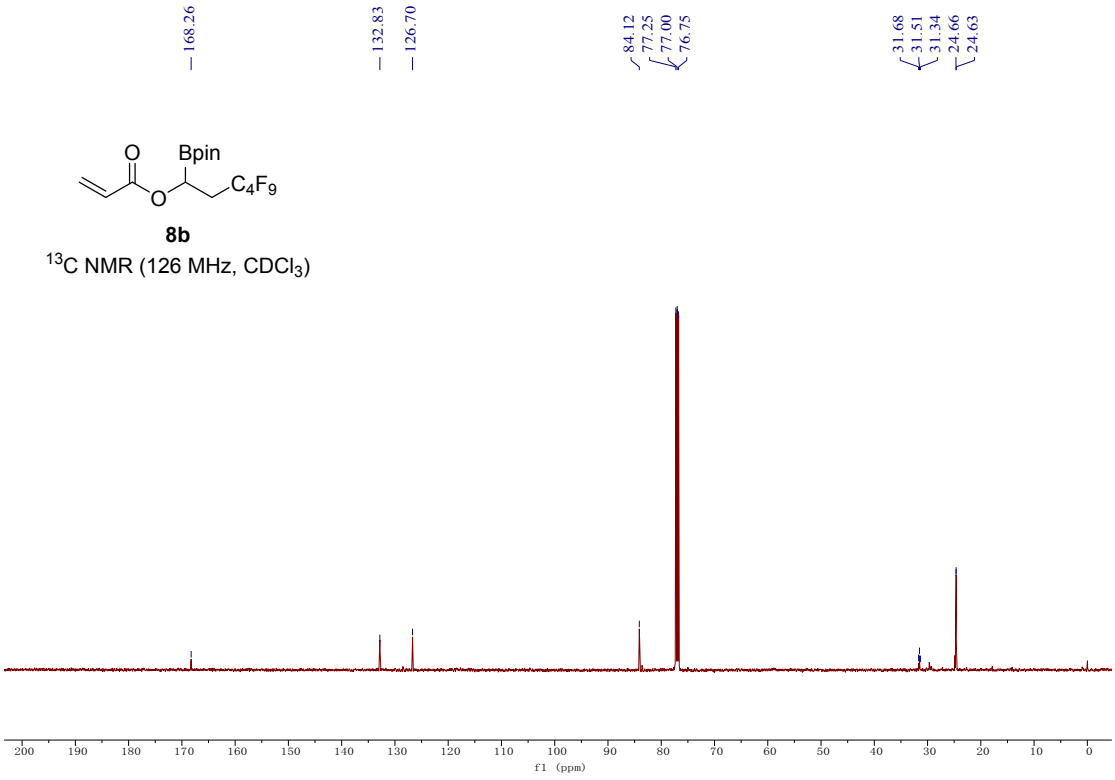
8a

^{11}B NMR (128 MHz, $CDCl_3$)



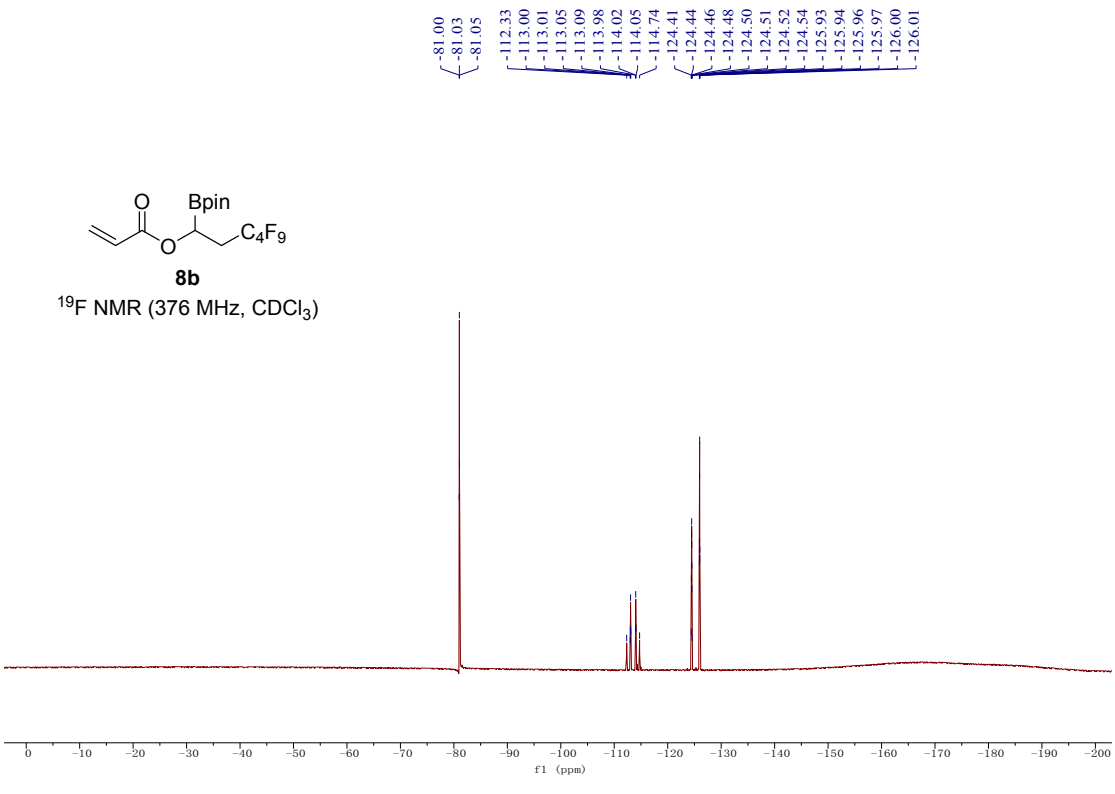
8b

^{1}H NMR (400 MHz, $CDCl_3$)



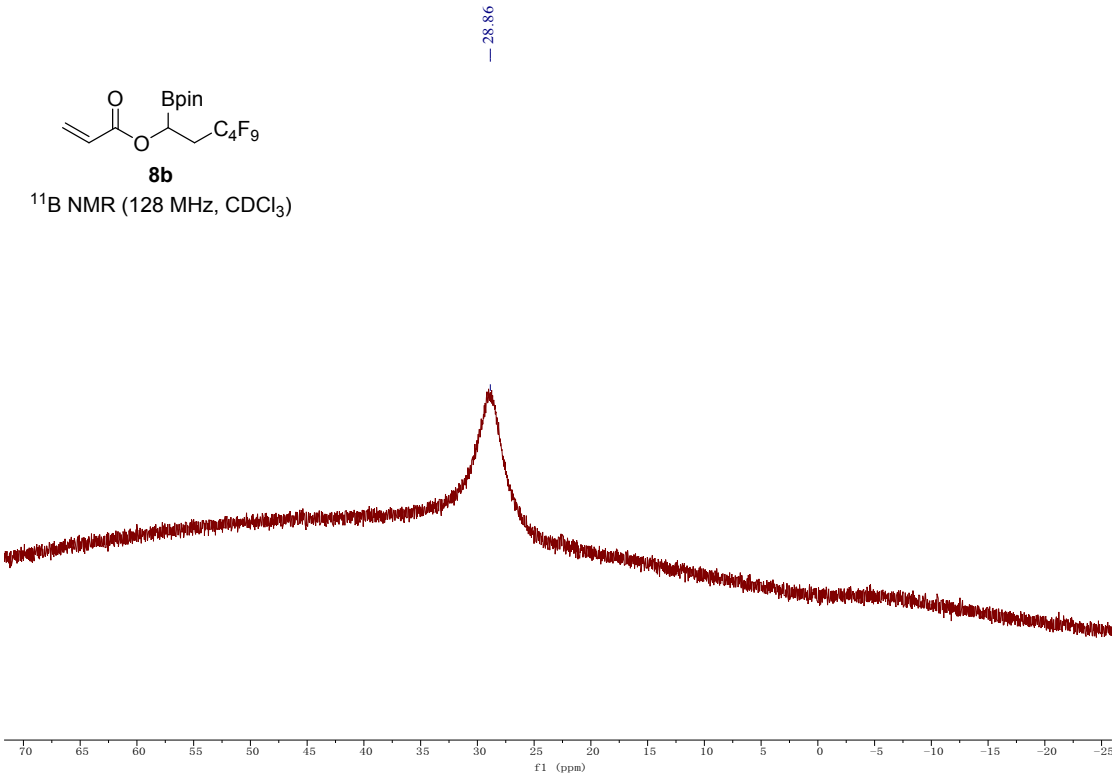
8b

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



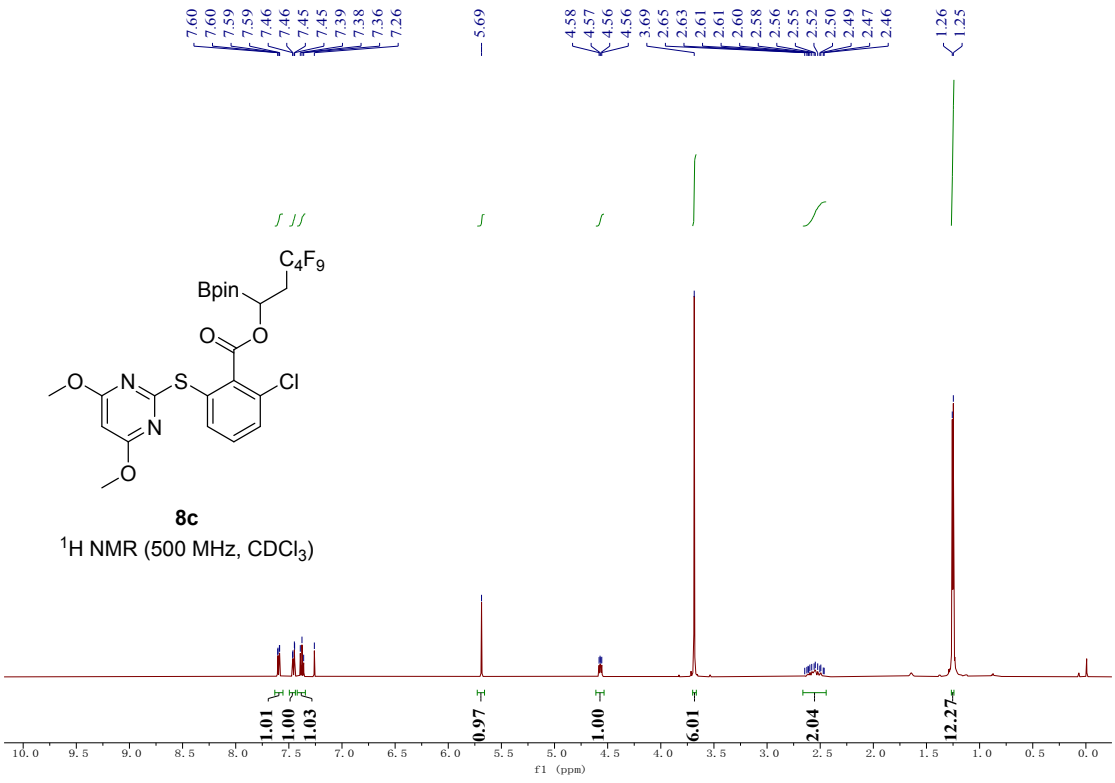
8b

^{19}F NMR (376 MHz, $CDCl_3$)



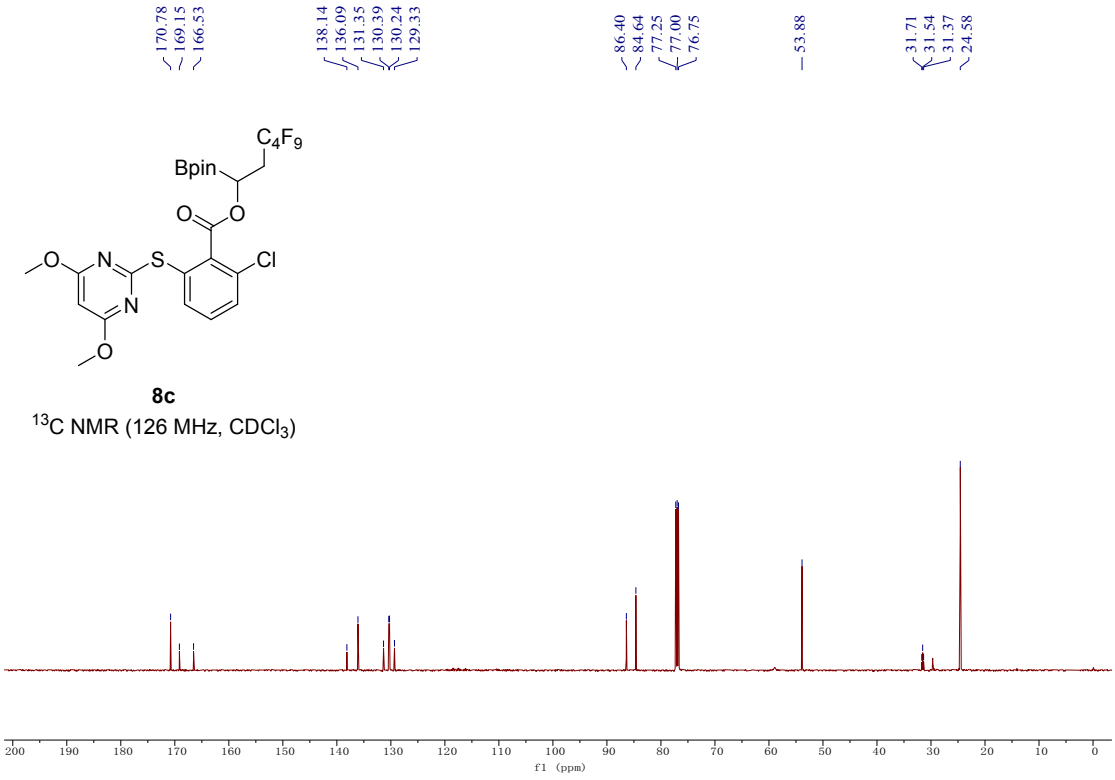
8b

^{11}B NMR (128 MHz, $CDCl_3$)



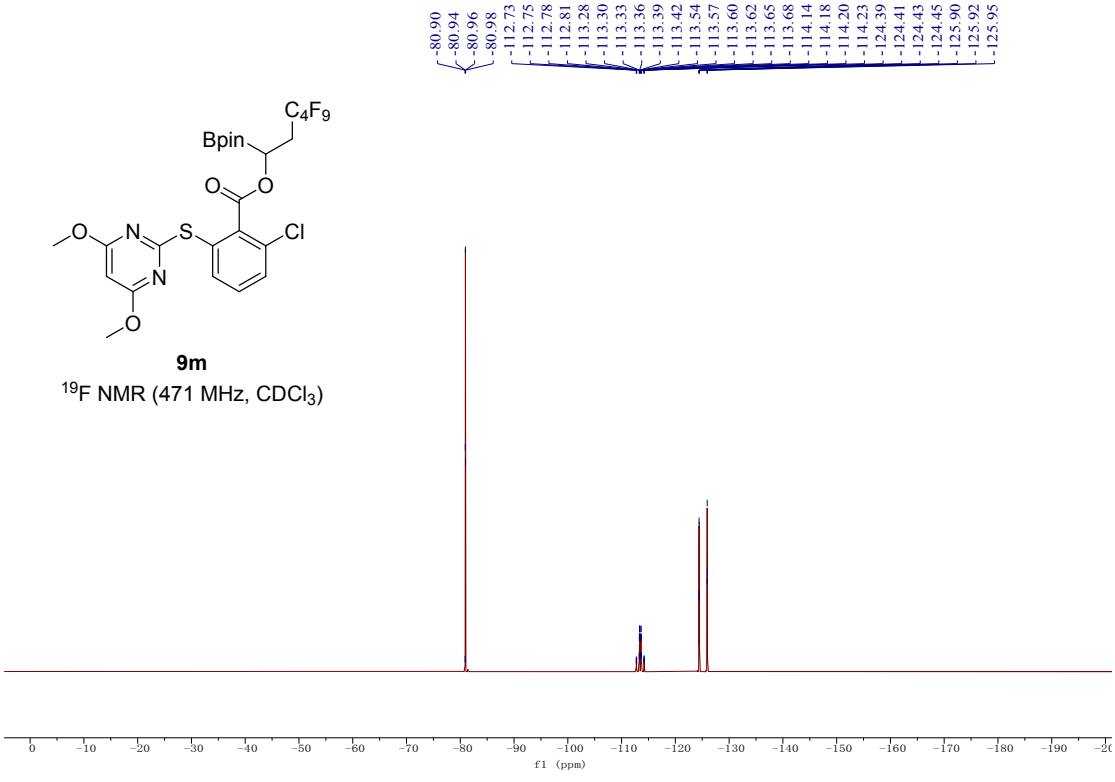
8c

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



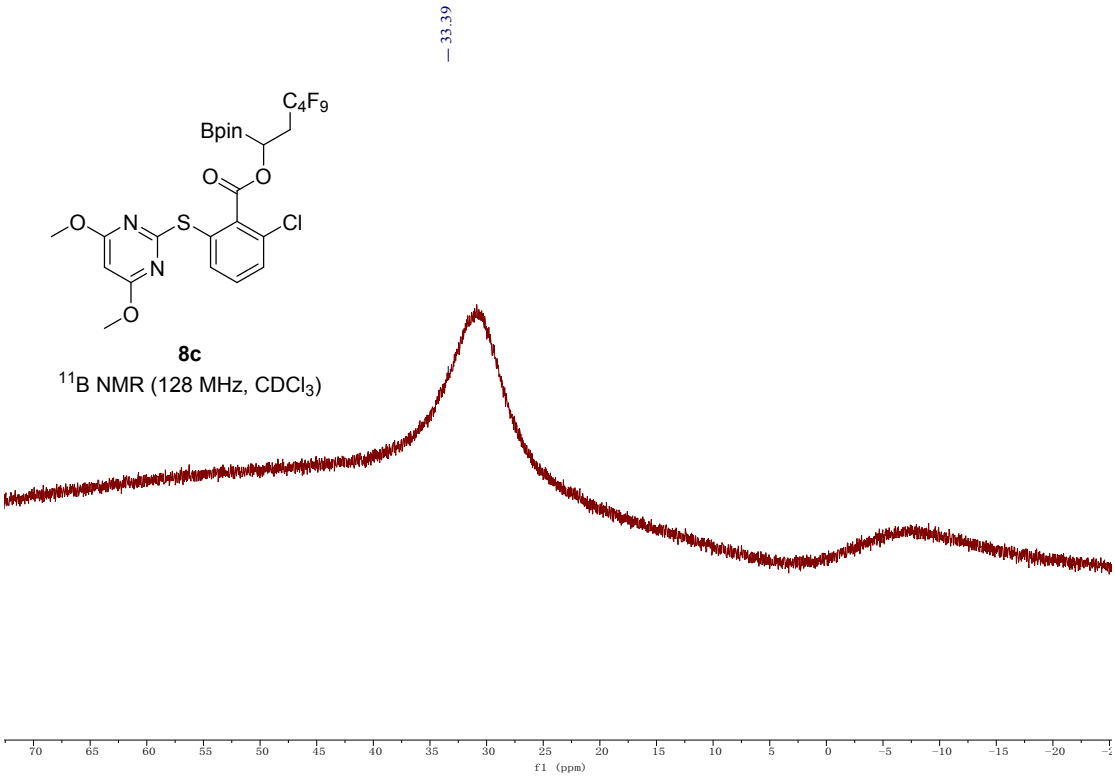
8c

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



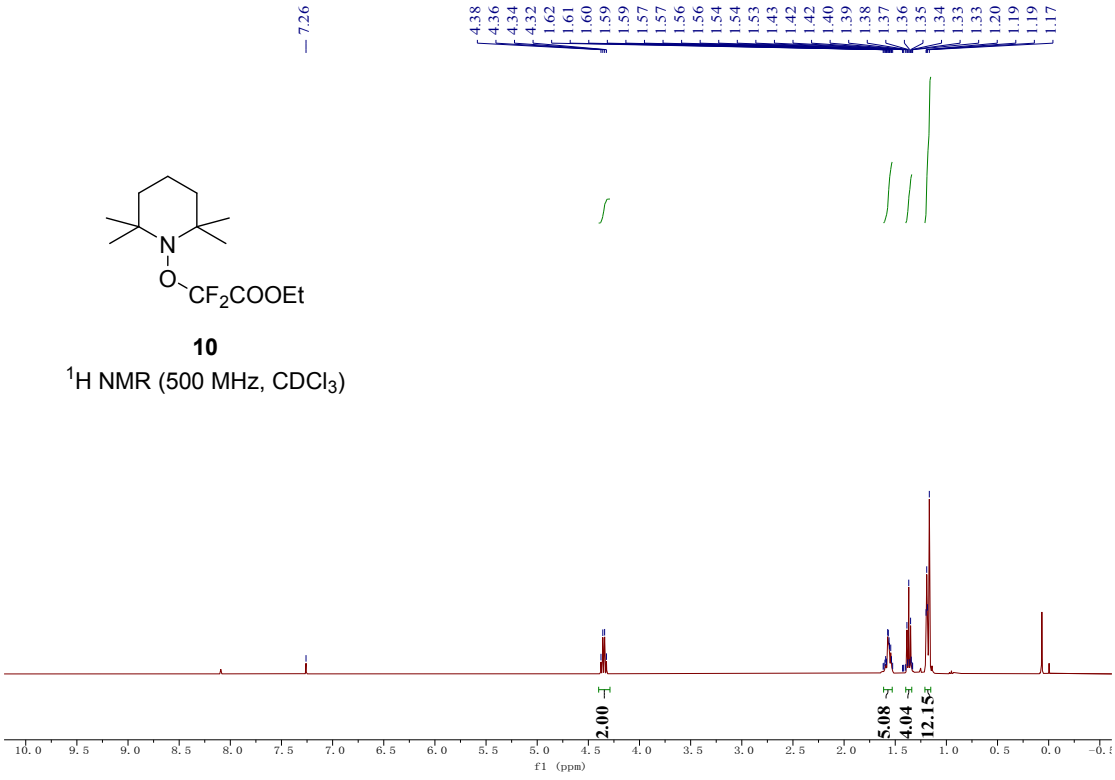
9m

^{19}F NMR (471 MHz, $CDCl_3$)



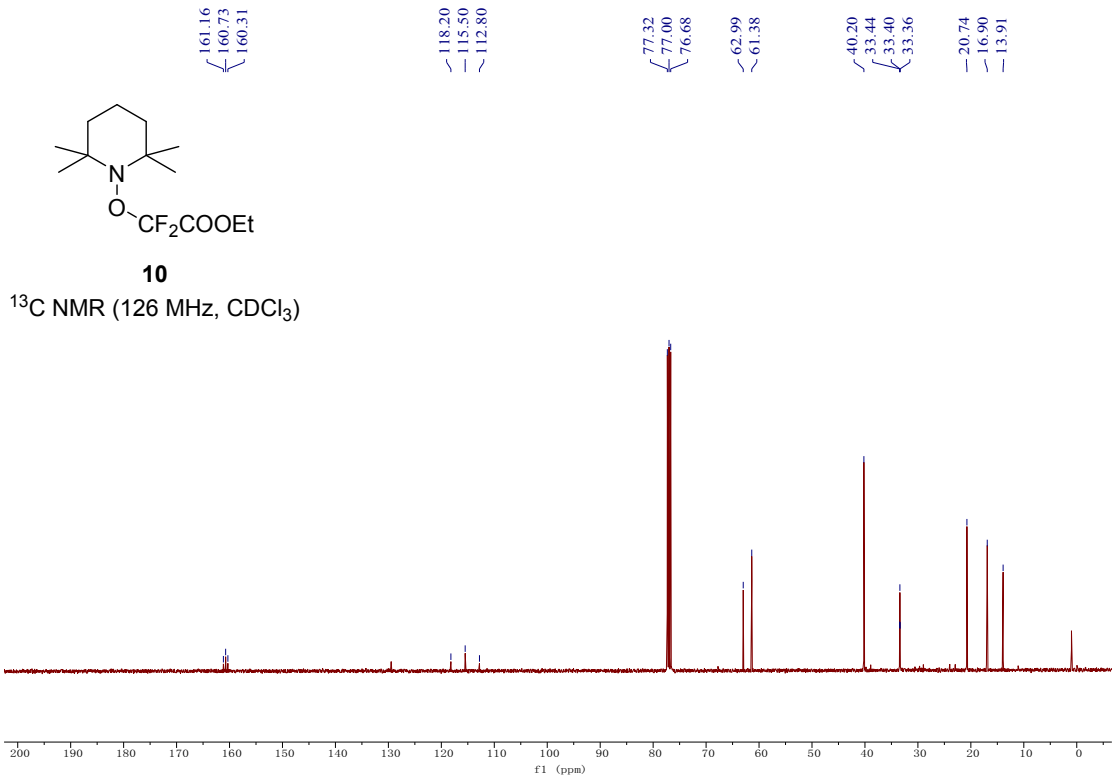
8c

^{11}B NMR (128 MHz, $CDCl_3$)



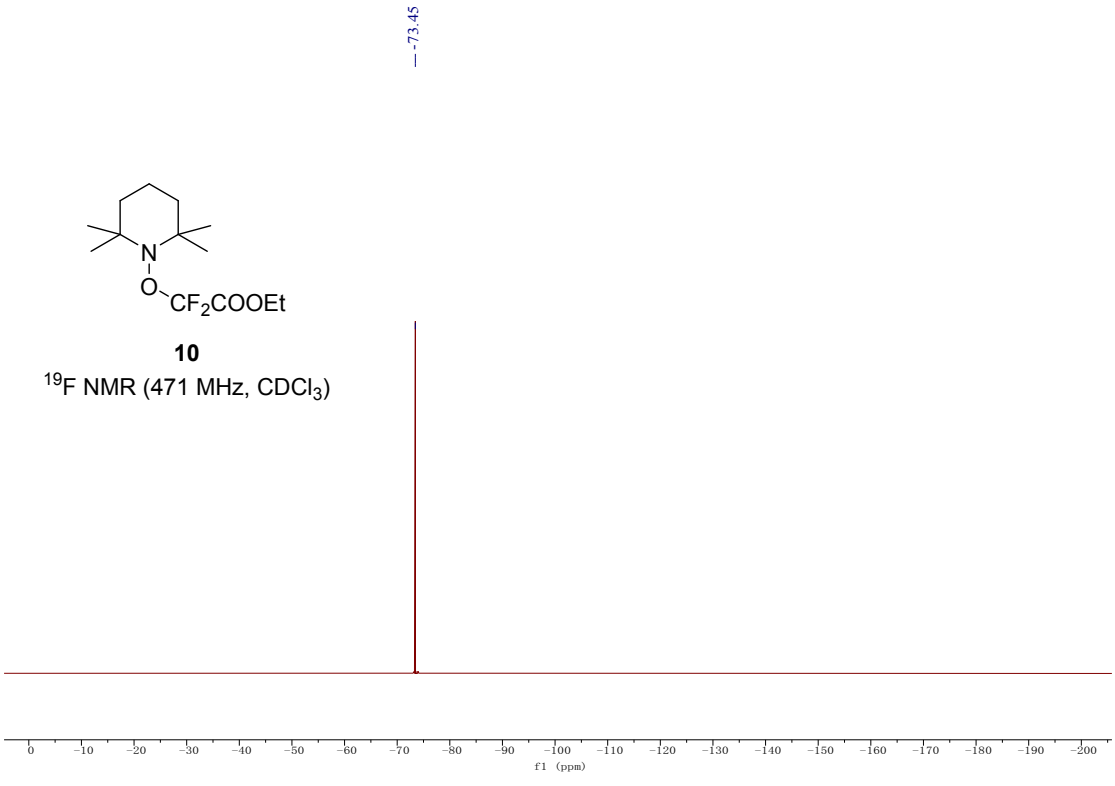
10

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



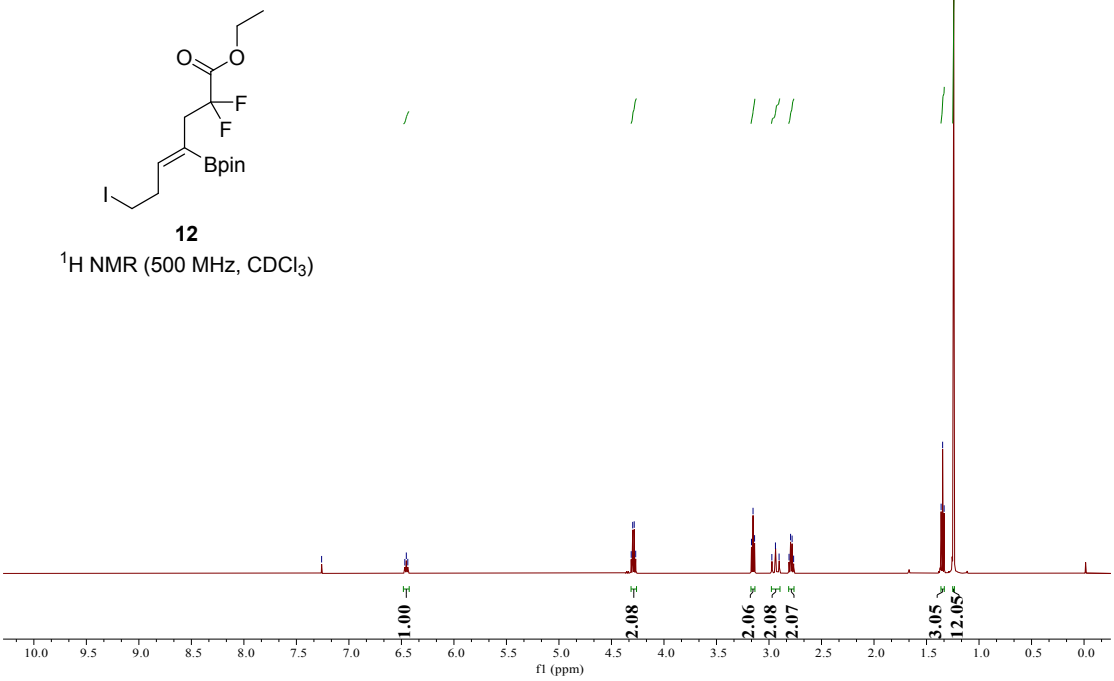
10

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



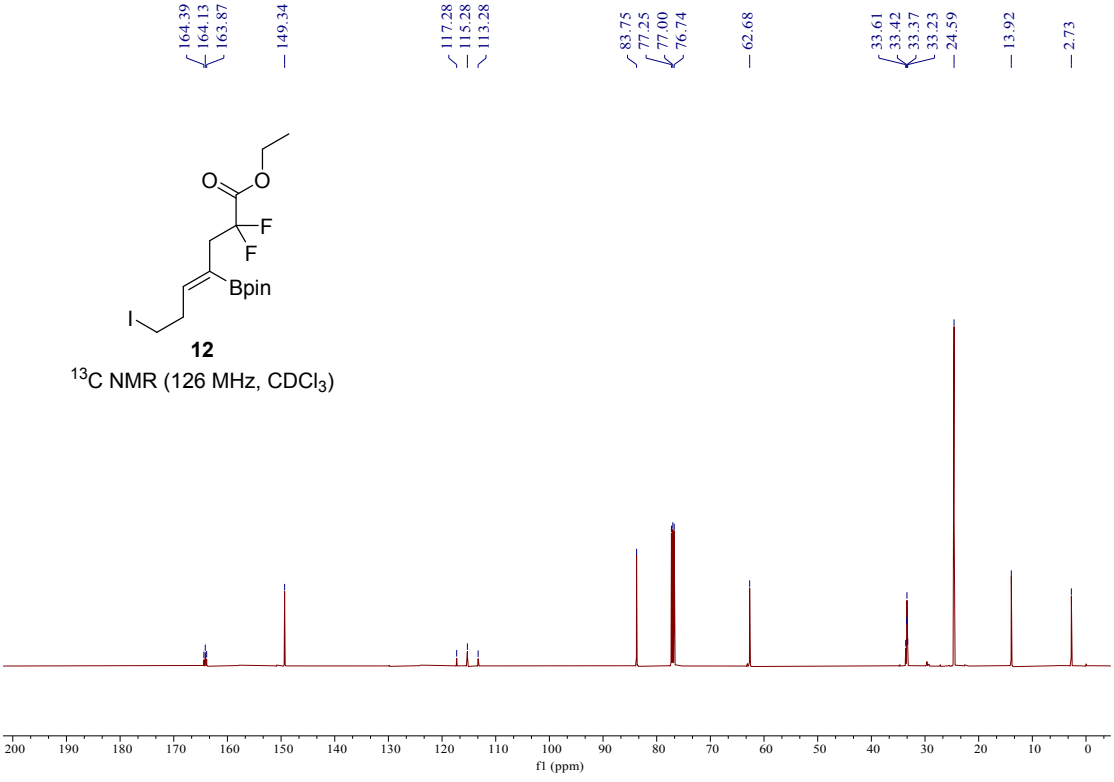
10

^{19}F NMR (471 MHz, $CDCl_3$)



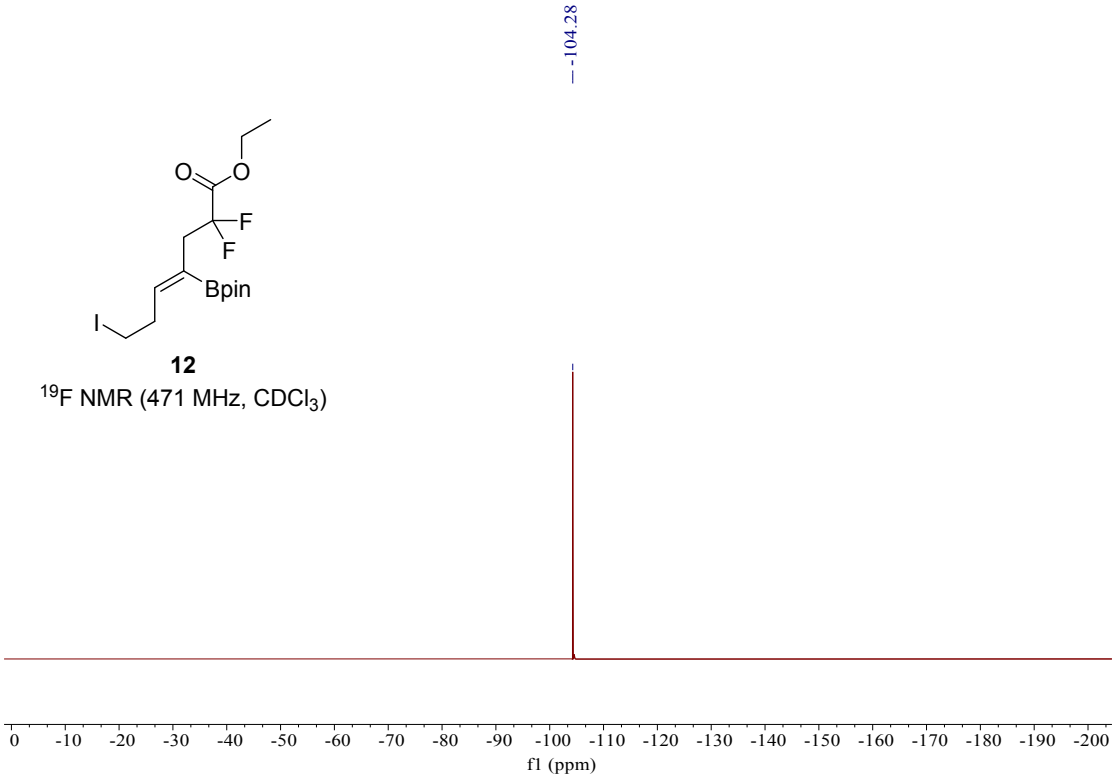
12

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



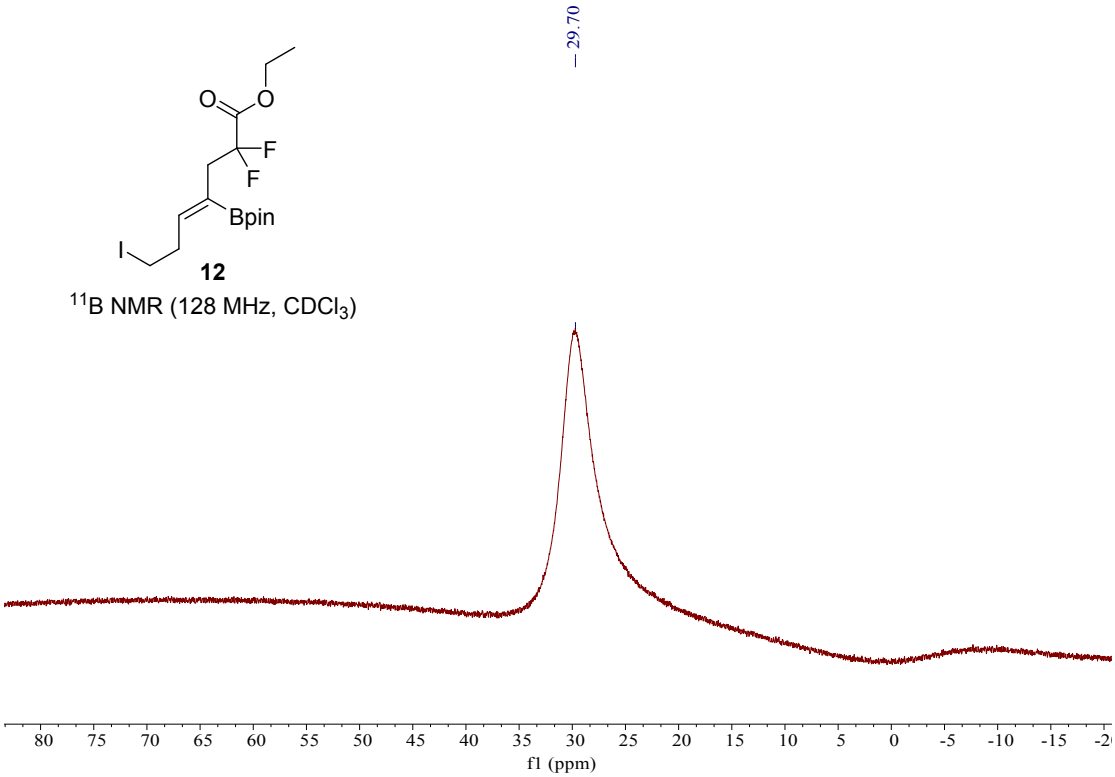
12

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



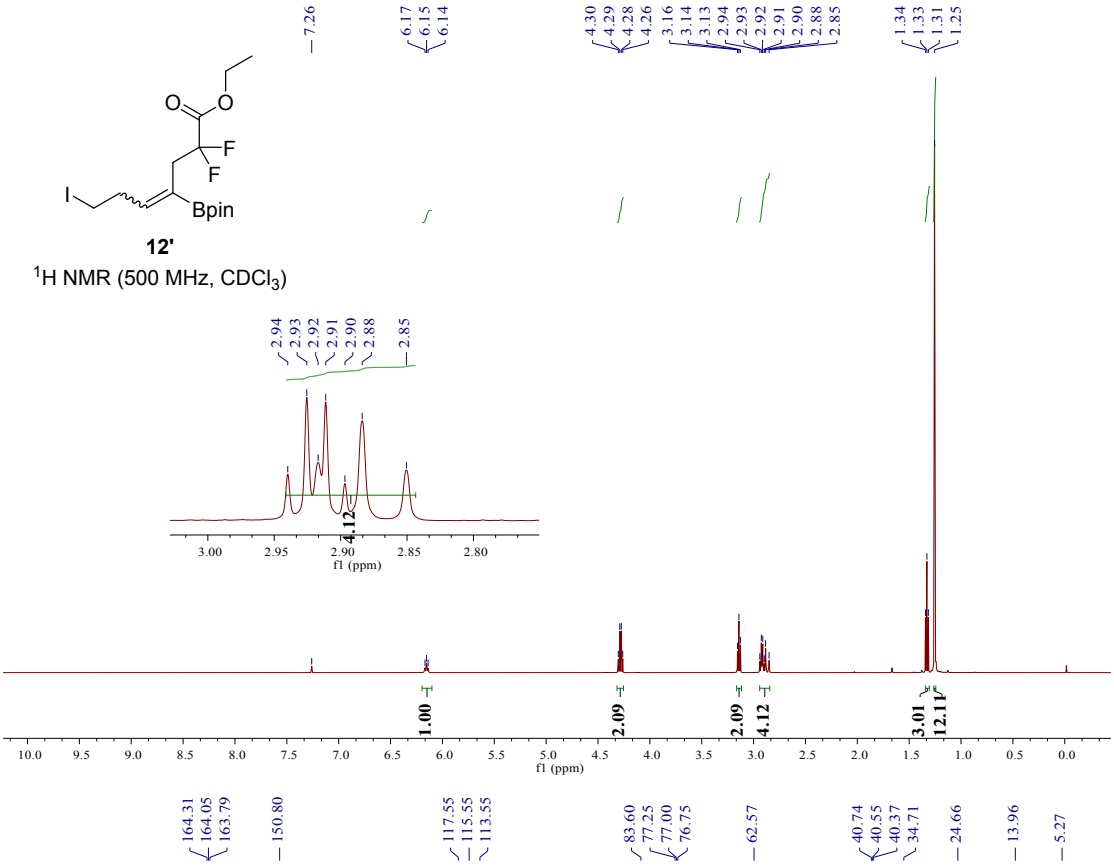
12

^{19}F NMR (471 MHz, $CDCl_3$)



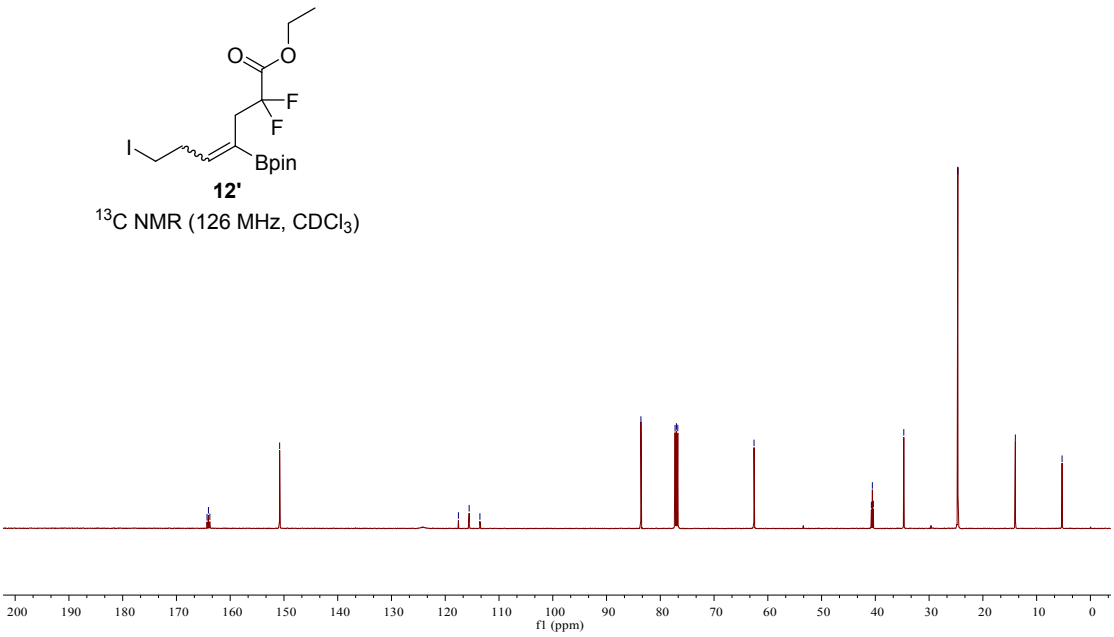
12

^{11}B NMR (128 MHz, $CDCl_3$)



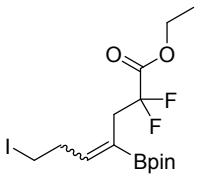
12'

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



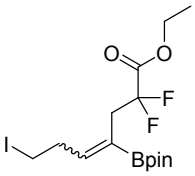
12'

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



12'

^{19}F NMR (471 MHz, $CDCl_3$)



12'

^{11}B NMR (128 MHz, $CDCl_3$)