Supporting Information

Light induced interrupted alkene diiodination with carbon atom insertion: Access to trifluoromethylated 1,3-diiodoalkanes

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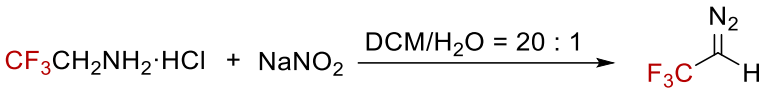
1. General information

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents and solvents were used without further purification. All reagents were purchased from commercial suppliers (Bidepharm and Energy Chemicals) or prepared as reported in the literature. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm. All products were purified by flash chromatography on silica gel (200−400 mesh) and the chemical yields referred are isolated products unless stated otherwise.

^{1}H NMR spectra were recorded on 400 MHz (AV400) or 600 MHz (AscendTM 600 MHz) Bruker spectrometers. ^{13}C NMR and ^{19}F NMR spectra were also recorded on the above spectrometers. Chemical shifts are reported in δ ppm relative to residual solvent of $CDCl_3$ (7.26 ppm for ^{1}H NMR and 77.1 ppm for ^{13}C NMR). The used abbreviations in chemical shifts are as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), td (triplet of doublets) dqd (doublet of quartet of doublets), m (multiplet) and brs (broad singlet). Data were reported as follows, chemical shift, multiplicity, coupling constants (Hz) and integration. High resolution mass spectra (HRMS) data were measured on a Bruker Daltonics SolariX 7T spectrometer (ESI) with a Fourier transform ion cyclotron resonace mass spectrometry (FT-ICR-MS) as the mass analyzer.

The photoreactor (RLH-18SH) used in this reaction was manufactured from Beijing Roger tech Ltd. Eight 10 W blue LED were equipped in this photoreactor. The reaction vessel is a borosilicate glass penicillin bottle and the distance between it and the lamp is 1.5 cm, no filter was used. Reaction temperature was kept at 25 °C with a water cooling system.

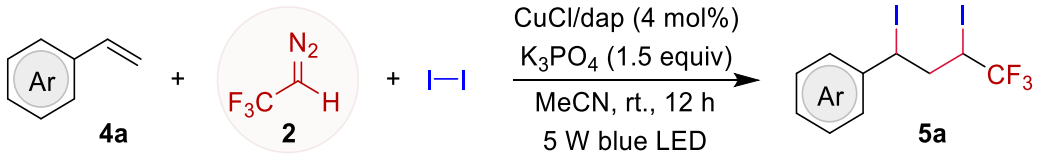
2. Preparation of substrate

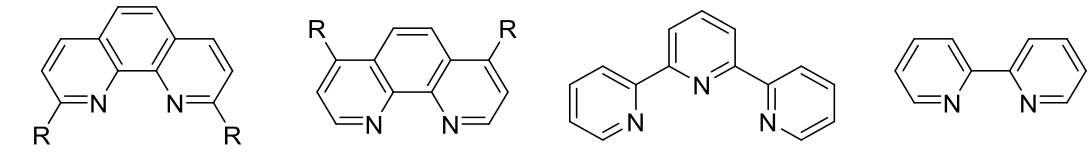


Trifluoroethylamine hydrochloride (2.76 g, 20 mmol) and sodium nitrite (1.66 g, 24 mmol, 1.2 equiv.) were added to a 50 mL round bottom flask, sealed the flask after add 25 mL of dichloromethane. The mixture was stirred in ice bath for 5 minutes and then added 1 mL of pure water to it. The solution turned yellow gradually, stired the reaction in an ice bath for 1 hour, and then stired at room temperature for 30 minutes. After that, the reaction solution was frozen in -20 ℃ overnight. Put the liquid in another bottle, dried it with anhydrous K_2CO_3, and stored the solution in a refrigerator at -20 ℃. Trifluorotoluene as the internal standard, calibrated the concentration of CF_3CHN_2 with ^{19}F NMR, which was 0.55 M.

3. Complete reaction optimization for aryl olefins

Table S1. Reaction optimization and control experiments[a].





L1, R = 4-(MeO)-Ph
L2, R = H **L3**, R = Me
L4, R = Cl **L5**, R = Ph

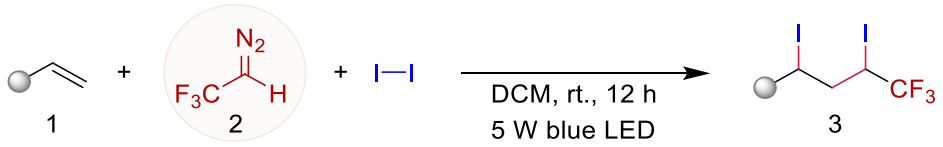
L6, R = Ph
L7, R = MeO

Entry	Deviation of standard condition	Yield (%)[b]
1	none	95 (90)
2	K_2CO_3 instead of K_3PO_4	76
3	2,6-Lutidine instead of K_3PO_4	trace
4	green LED instead of blue LED	81
5	DCM instead of MeCN	11
6	DMF instead of MeCN	0
7	MeCN (2 mL)	72
8	No light	0
9	In air	35
10	60 ℃, No light	0
11	CuCl/**L1** (3 mol%)	50 (47)
12[c]	**L2** instead of **L1**	32
13	**L3** instead of **L1**	41
14	**L4, L5** instead of **L1**	8
15	**L6**, **L7, L8, L9** instead of **L1**	0
16	$FeBr_2$ instead of CuCl	0
17	$NiBr_2$ instead of CuCl	0
18	No **L1**	7

[a] Reaction conditions: **4a** (0.2 mmol), **2** (0.53 mmol, 0.5 M in DCM), $\mathbf{I_2}$ (0.35 mmol), CuCl (4 mol%), **L1**(dap) (4 mol%), K_3PO_4 (0.3 mmol), additional MeCN (1.0 mL), N_2, blue LED, rt, 12 h. [b] The yield was determined by ^{19}F NMR. [c] 405 nm.

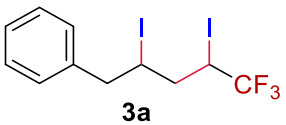
Notes: In the case of aryl alkenes, the actual catalyst is the in-situ formed Cu(dap)2Cl, which is generated more efficiently with MeCN due to the better solubility of the copper salt compared to DCM. In addition, the inorganic base K_3PO_4 is also more soluble in MeCN, which is important to prevent the catalyst poisoning[1]. This makes the significant difference in DCM and MeCN between aryl alkene and alkyl alkene.

4. General procedure and characterization data of products 3



I_2 (0.35 mmol) was dissolved in DCM (1.0 mL) under nitrogen atmosphere, then CF_3CHN_2 (1.05 ml, 0.525 mmol) and olefin (0.2 mmol) were added into the bottle. The mixture was stirred for 5 minutes and then irradiated under 5 W blue LED and stirred at room temperature for 12 hours. After the reaction, trace of the reaction supernatant was used for ^{19}F NMR spectroscopic analysis to determine the dr selectivity. Then, the other mixture was directly subjected to be concentrated in vacuo and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as an eluent to afford the desired product **3**.

(5,5,5-trifluoro-2,4-diiodopentyl)benzene (3a)



3a

The product **3a** was purified by column chromatography (petroleum ether) as a colourless oil (79.9 mg, 88 %, 3.7:1 dr).

TLC: R_f = 0.65 (Hexane).

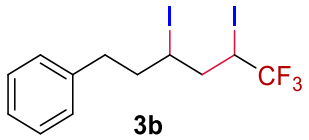
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 3H), 7.22 (dd, *J* = 6.8, 1.7 Hz, 2H), 4.57 – 4.53 (m, 0.8H, minor), 4.41 – 4.37 (m, 1.3H, major), 3.50 – 3.40 (m, 0.8H, major), 3.33 – 3.23 (m, 0.8H, major), 3.15 – 2.12 (m, 0.4H, minor), 2.71 – 2.51 (m, 0.5H, minor), 2.27 – 2.20 (m, 0.8H, major), 2.11 – 2.04 (m, 0.8H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.5, 129.1, 129.1, 128.9, 128.8, 127.4, 125.9, 124.6 (q, *J* = 276.8 Hz), 47.3, 45.9, 45.0, 41.5, 35.5, 32.5, 26.2 (q, *J* = 31.5 Hz), 21.1 (q, *J* = 31.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.69 (d, *J* = 7.8 Hz, 1F), -68.34 (d, *J* = 7.6 Hz, 3.7F).

HRMS (ESI, m/z): calcd for $C_{11}H_{11}F_3I_2Na^+$ $[M+Na]^+$: 476.8794, found: 476.8785.

(6,6,6-trifluoro-3,5-diiodohexyl)benzene (3b)



3b

The product **3b** was purified by column chromatography as a colourless oil (72.7 mg, 78%, 3.3:1 dr).

TLC: R_f = 0.65(Hexane).

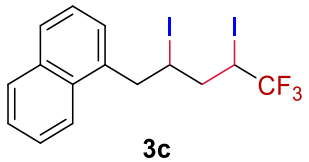
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.7, 6.5 Hz, 2H), 7.25 – 7.17 (m, 3H), 4.64 – 4.44 (m, 0.7H, major), 4.32 – 4.44 (m, 0.3H, minor), 4.16 – 4.06 (m, 1H), 2.91 – 2.85 (m, 1H), 2.80 – 2.70 (m, 1H), 2.70 – 2.45 (m, 0.5H, minor), 2.40 – 2.24 (m, 1.5H, major), 2.16 – 2.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 140.1, 128.8, 128.7, 128.6, 126.6, 124.6 (q, *J* = 276.8 Hz), 44.9, 42.4, 40.2, 36.2, 35.6, 32.3, 26.1 (q, *J* = 31.4 Hz), 20.9 (q, *J* = 31.3 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.03 (d, *J* = 7.8 Hz, 1F), -68.36 (d, *J* = 8.1 Hz, 3.3F).

HRMS (ESI, m/z): calcd for $C_{12}H_{13}F_3I_2Na^+$ $[M+Na]^+$: 490.8956, found: 490.8958.

1-(5,5,5-trifluoro-2,4-diiodopentyl)naphthalene (3c)



3c

The product **3c** was purified by column chromatography as a yellow oil (60.4 mg, 60 %, 1.5:1 dr).

TLC: R_f = 0.65 (Hexane).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.88 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.54 – 7.50 (m, 1H), 7.46 – 7.44 (m, 1H), 7.39 – 7.37 (m, 1H), 4.63 – 4.57 (m, 1H), 4.56 – 4.50 (m, 0.6H, major), 4.38 – 4.33 (m, 0.4H, minor), 3.97 – 3.93 (m, 0.6H, major), 3.72 – 3.68 (m, 0.6H, major), 3.67 – 3.62 (m, 0.4H, minor), 3.60 –

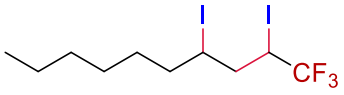
3.55 (m, 0.4H, minor), 2.78 – 2.73 (m, 0.4H, minor), 2.69 – 2.61 (m, 0.4H, minor), 2.40 – 2.35 (m, 0.6H, major), 2.15 – 2.10 (m, 0.6H, major).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7, 134.6, 134.2, 134.1, 131.62, 131.56, 129.3, 129.3, 128.41, 128.40, 127.9, 127.8, 126.7, 126.6, 126.4 (q, *J* = 276.5 Hz), 126.03, 126.01, 125.44, 125.41, 123.2, 123.1, 46.1, 44.8, 43.9, 42.1, 34.7, 31.5, 26.1 (q, *J* = 31.5 Hz), 20.9 (q, *J* = 31.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.80 (d, *J* = 7.4 Hz, 1F), -68.39 (d, *J* = 8.1 Hz, 1.5F).

HRMS (ESI, m/z): calcd for $C_{15}H_{14}F_3I_2^+$ $[M+H]^+$: 504.9132, found: 504.9136.

1,1,1-trifluoro-2,4-diiododecane (3d)



3d

The product **3d** was purified by column chromatography as a colourless oil (77.9 mg, 87%, 3.6:1 dr).

TLC: R_f = 0.70 (Hexane).

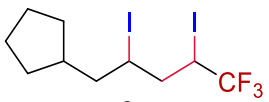
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 – 4.47 (m, 0.7H, major), 4.40 – 4.28 (m, 0.3H, minor), 4.22 – 4.06 (m, 1H), 2.65 – 2.41 (m, 0.5H, minor), 2.30 – 2.20 (m, 0.8H, major), 2.06 – 1.97 (m, 1.6H, major), 1.87 – 1.77 (m, 0.7H, minor), 1.70 – 1.37 (m, 3H), 1.35 – 1.26 (m, 6H), 0.93 – 0.87 (m, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 124.6 (q, *J* = 276.5 Hz), 45.1, 42.5, 42.4, 40.8, 38.5, 37.2, 33.3, 31.7, 29.5, 29.2, 28.6, 28.5, 26.4 (q, *J* = 31.4 Hz), 21.1 (q, *J* = 31.1 Hz), 22.7, 14.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.97 (d, *J* = 8.1 Hz, 1F), -68.41 (d, *J* = 8.0 Hz, 3.6F).

HRMS (ESI, m/z): calcd for $C_{10}H_{18}F_3I_2^+$ $[M+H]^+$: 448.9444, found: 448.9453.

(5,5,5-trifluoro-2,4-diiodopentyl)cyclopentane (3e)



3e

The product **3e** was purified by column chromatography as a colourless oil (66.1 mg, 74 %, 3.1:1 dr).

TLC: R_f = 0.71 (Hexane).

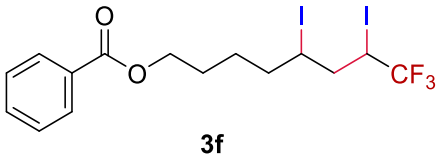
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.60 – 4.53 (m, 0.8H, major), 4.42 – 4.36 (m, 0.2H, minor), 4.20 – 4.10 (m, 1H), 2.66 – 2.57 (m, 0.3H, minor), 2.52 – 2.45 (m, 0.3H, minor), 2.26 – 2.17 (m, 1.7H, major), 2.14 – 2.01 (m, 2H), 1.88 – 1.78 (m, 2H), 1.78 – 1.72 (m, 0.9H, major), 1.67 – 1.60 (m, 2H), 1.59 – 1.55 (m, 1H), 1.21 – 1.12 (m,1H), 1.09 – 1.00 (m, 1H), 0.92 – 0.79 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 124.9 (q, J = 276.6 Hz), 47.4, 45.5, 45.2, 42.6, 40.3, 40.0, 36.3, 32.9, 32.7, 32.4, 32.0, 31.6, 26.4 (q, J = 31.4 Hz), 21.5 (q, J = 31.2 Hz), 25.2, 25.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.95 (d, J = 7.8 Hz, 1F), -68.42 (d, J = 8.1 Hz, 3.1F).

HRMS (ESI, m/z): calcd for $C_{10}H_{16}F_3I_2^+$ $[M+H]^+$: 446.9288, found: 446.9296.

8,8,8-trifluoro-5,7-diiodooctyl benzoate (3f)



3f

The product **3f** was purified by column chromatography as a colourless oil (90.7 mg, 84 %, 3.6:1 dr).

TLC: R_f = 0.6 (Hexane/EtOAc = 30:1).

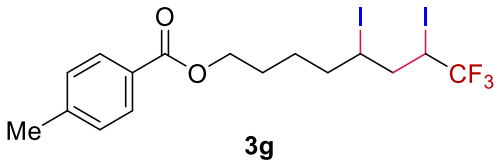
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.57– 7.53 (m, 1H), 7.46 – 7.42 (m, 2H), 4.58 – 4.50 (m, 0.7H, minor), 4.37 – 4.32 (m, 2H), 4.23 – 4.13 (m, 1.4H, major), 2.66 – 2.60 (m, 0.2H, minor), 2.53 – 2.44 (m, 0.2H, minor), 2.30 – 2.24 (m, 0.9H, major), 2.17 – 2.00 (m, 1.7H, major), 1.93 – 1.55 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 133.0, 130.3, 129.6, 128.4, 124.4 (q, J = 276.6 Hz), 64.5, 64.4, 44.9, 42.3, 40.1, 37.9, 36.4, 32.4, 27.9, 27.8, 26.2, 25.9, 26.1 (q, J = 31.4 Hz), 20.8 (q, J = 31.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.93 (d, *J* = 7.6 Hz, 1F), -68.33 (d, *J* = 7.8 Hz, 3.6F).

HRMS (ESI, m/z): calcd for $C_{15}H_{18}F_3I_2O_2^+[M+H]^+$: 540.9342, found: 540.9348.

8,8,8-trifluoro-5,7-diiodooctyl 4-methylbenzoate (3g)



3g

The product **3g** was purified by column chromatography as a colourless oil (88.8 mg, 80%, 3.7:1 dr).

TLC: R_f = 0.43 (Hexane/EtOAc = 30:1).

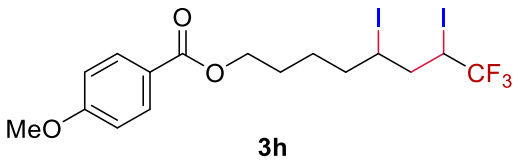
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.58 – 4.51 (m, 0.8H, minor), 4.33 (t, *J* = 6.4 Hz, 2H), 4.21 – 4.15 (m, 1.1H, major), 2.64 – 2.56 (m, 0.2H, minor), 2.52 – 2.46 (m, 0.2H, minor), 2.41 (s, 3H), 2.31 – 2.24 (m, 0.8H), 2.12 – 2.03 (m, 1.6H, major), 1.93 – 1.70 (m, 4H), 1.65 – 1.59 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 143.6, 129.6, 129.1, 127.6, 124.43 (q, *J* = 276.5 Hz), 64.3, 64.2, 44.8, 42.3, 40.1, 37.9, 36.4, 32.4, 27.9, 27.8, 26.2, 25.9, 25.9 (q, *J* = 31.3Hz), 20.8 (q, *J* = 31.2 Hz), 21.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.97 (d, *J* = 7.6 Hz, 1F), -68.38 (d, *J* = 7.9 Hz, 3.7F).

HRMS (ESI, m/z): calcd for $C_{16}H_{20}F_3I_2O_2^+$ $[M+H]^+$: 554.9499, found: 554.9495.

8,8,8-trifluoro-5,7-diiodooctyl 4-methoxybenzoate (3h)



3h

The product **3h** was purified by column chromatography as a colourless oil (96 mg, 84%, 3.5:1 dr).

TLC: R_f = 0.45 (Hexane/EtOAc = 30:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 6.93 – 6.90 (m, 2H), 4.57 – 4.50 (m, 0.8H, minor), 4.34 – 4.29 (m, 2H), 4.21 – 4.13 (m, 1H, major), 3.85 (s, 3H), 2.64 –

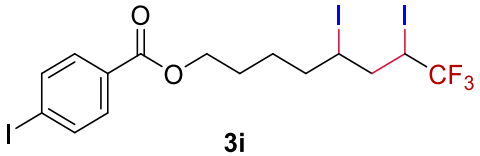
2.57 (m, 0.2H, minor), 2.52 – 2.44 (m, 0.2H, minor), 2.31 – 2.24 (m, 0.8H, major), 2.13 – 2.02 (m, 1.6H, major), 1.92 – 1.68 (m, 4H), 1.66 – 1.56 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 163.5, 131.7, 124.5 (q, J = 276.5 Hz), 122.79, 113.7, 64.2, 64.2, 55.5, 53.1, 44.9, 42.4, 40.2, 38.0, 36.5, 32.6, 28.0, 28.0, 26.3, 25.9, 26.2 (q, J = 31.4 Hz), 20.9 (q, J = 31.1 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.97 (d, J = 7.6 Hz, 1F), -68.38 (d, J = 7.9 Hz, 3.5F).

HRMS (ESI, m/z): calcd for $C_{17}H_{23}F_3I_2O_3^+$ $[M+H]^+$: 585.9689, found: 585.9688.

8,8,8-trifluoro-5,7-diiodooctyl 4-iodobenzoate (3i)



3i

The product **3i** was purified by column chromatography as a colourless oil (103.9 mg, 78%, 5.7:1 dr).

TLC: R_f = 0.44 (Hexane/EtOAc = 30:1).

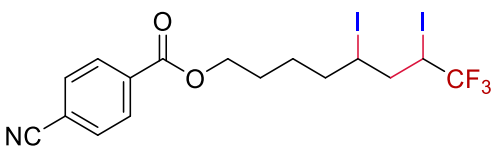
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.75 – 7.73 (m, 2H), 4.57 – 4.51 (m, 0.8H, minor), 4.35 – 4.33 (m, 2H), 4.18 – 4.14 (m, 1.2H, major), 2.64 – 2.56 (m, 0.2H, minor), 2.52 – 2.45 (m, 0.2H, minor), 2.33 – 2.20 (m, 0.9H, major), 2.14 – 2.02 (m, 1.7H, major), 1.90 – 1.70 (m, 4H), 1.64 – 1.58 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 137.9, 131.1, 129.8, 124.5 (q, J = 276.6 Hz), 100.9, 64.8, 64.7, 42.4, 40.2, 37.9, 36.4, 27.9, 26.2, 26.2 (q, J = 31.4 Hz), 20.2 (q, J = 31.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.94 (d, J = 7.8 Hz, 1F), -68.38 (d, J = 7.9 Hz, 5.7F).

HRMS (ESI, m/z): calcd for $C_{16}H_{17}F_3I_3O_2^+$ $[M+H]^+$: 666.8309, found: 666.8312.

8,8,8-trifluoro-5,7-diiodooctyl 4-cyanobenzoate (3j)



3j

The product **3j** was purified by column chromatography as a yellow oil (85.9 mg, 76%, 3.8:1 dr).

TLC: R_f = 0.43 (Hexane/EtOAc = 30:1).

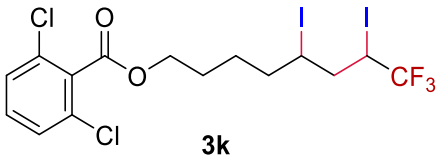
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.9 Hz, 2H), 7.75 – 7.73 (m, 2H), 4.56 – 0.76 (m, 0.8H, minor), 4.41 – 4.37 (m, 2H), 4.21 – 4.13 (m, 1H, major), 2.63 – 2.56 (m, 0.2H, minor), 2.52 – 2.45 (m, 0.2H, minor), 2.31 – 2.26 (m, 0.8H, major), 2.11 – 2.01 (m, 1.6H, major), 1.92 – 1.56 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 134.2, 134.1, 132.4, 130.2, 124.5 (q, *J* = 276.5 Hz), 118.1, 116.5, 65.4, 45.0, 42.4, 40.1, 37.9, 36.3, 32.3, 29.9, 27.9, 26.2 (q, *J* = 31.4 Hz), 20.77 (q, *J* = 31.3 Hz), 26.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.94 (d, *J* = 7.4 Hz, 1F), -68.39 (d, *J* = 7.7 Hz, 3.8F).

HRMS (ESI, m/z): calcd for $C_{16}H_{17}F_3I_2NO_2^+$ $[M+H]^+$: 565.9295, found: 565.9289.

8,8,8-trifluoro-5,7-diiodooctyl 2,6-dichlorobenzoate (3k)



3k

The product **3k** was purified by column chromatography as a colourless oil (103.3 mg, 84%, 3.8:1 dr).

TLC: R_f = 0.46 (Hexane/EtOAc = 30:1).

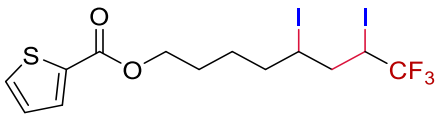
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 4.56 – 4.50 (m, 0.8H, minor), 4.44 – 4.42 (m, 2H), 4.18 – 4.14 (m, 1H, major), 2.74 – 2.55 (m, 0.3H, minor), 2.55 – 2.43 (m, 0.3H, minor), 2.30 – 2.21 (m, 0.8H, major), 2.10 – 1.97 (m, 0.1.7H, major, 1.92 – 1.72 (m, 4H), 1.71 – 1.60 (m, 1H,).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9, 133.8, 131.9, 131.0, 128.02, 124.5 (q, *J* = 276.5 Hz), 65.9, 65.9, 44.9, 42.4, 40.2, 38.0, 36.2, 32.3, 27.7, 26.2, 26.1, 26.0 (q, *J* = 110.6 Hz), 20.89 (q, *J* = 31.3 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.95 (d, *J* = 7.7 Hz, 1F), -68.38 (d, *J* = 8.1 Hz, 3.8F).

HRMS (ESI, m/z): calcd for $C_{15}H_{15}Cl_2F_3I_2O_2Na^+$ $[M+Na]^+$: 630.8382, found:630.8372.

8,8,8-trifluoro-5,7-diiodooctyl thiophene-2-carboxylate (3l)



3l

The product **3l** was purified by column chromatography as a colourless oil (77.3 mg, 71%, 3.6:1 dr).

TLC: R_f = 0.43 (Hexane/EtOAc = 30:1).

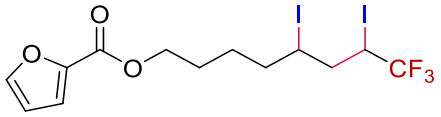
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.80 (m, 1H), 7.56 – 7.55 (m, 1H), 7.11 – 7.10 (m, 1H), 4.57 – 4.51 (m, 0.8H, minor), 4.33 – 4.31 (m, 2H), 4.20 – 4.13 (m, 1.1H, major), 2.73 – 2.58 (m, 0.3H, minor), 2.53 – 2.45 (m, 0.3H, minor), 2.30 – 2.23 (m, 0.8H, major), 2.10 – 2.03 (m, 1.7H, major), 1.93 – 1.70 (m, 4H), 1.66 – 1.23 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.31, 133.9, 133.9, 133.6, 133.6, 132.5, 127.9, 124.5 (q, J = 276.5 Hz), 64.7, 64.6, 44.9, 41.4, 40.2, 37.9, 36.5, 32.5, 28.0, 27.9, 26.2, 25.9, 26.2 (q, J = 31.4 Hz), 20.9 (q, J = 31.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.95 (d, J = 7.3 Hz, 1F), -68.36 (d, J = 8.4 Hz, 3.6F).

HRMS (ESI, m/z): calcd for $C_{13}H_{15}F_3I_2O_2SNa^+$ $[M+Na]^+$: 568.8735, found: 568.8737.

8,8,8-trifluoro-5,7-diiodooctyl furan-2-carboxylate (3m)



3m

The product **3m** was purified by column chromatography as a colourless oil (68.7 mg, 67%, 3.5:1 dr).

TLC: R_f = 0.43 (Hexane/EtOAc = 30:1).

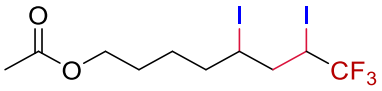
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 1H), 7.19 – 7.18 (m, 1H), 6.52 – 6.50 (m, 1H), 4.56 – 4.50 (m, 0.8H, minor), 4.34 – 4.30 (m, 2H), 4.20 – 4.12 (m, 1.1H, major), 2.68 – 2.54 (m, 0.3H, minor), 2.52 – 2.44 (m, 0.3H, major), 2.32 – 2.22 (m, 0.8H, major), 2.10 – 2.00 (m, 1.7H, major), 1.92 – 1.65 (m, 4H), 1.65 – 1.54 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 146.5, 144.8, 124.5 (q, *J* = 276.6 Hz), 118.1, 118.1, 112.0, 64.5, 64.5, 44.9, 42.4, 40.2, 37.9, 36.4, 32.4, 27.9, 27.8, 26.5, 26.2, 26.1 (q, *J* = 31.2 Hz), 20.9 (q, *J* = 31.1 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.99 (d, *J* = 8.0 Hz, 1F), -68.40 (d, *J* = 8.1 Hz, 3.5F).

HRMS (ESI, m/z): calcd for $C_{13}H_{15}F_3I_2O_2SNa^+$ $[M+Na]^+$: 552.8954, found: 552.8950.

8,8,8-trifluoro-5,7-diiodooctyl acetate (3n)



3n

The product **3n** was purified by column chromatography as a colourless oil (72 mg, 82%, 4.5:1 dr).

TLC: R_f = 0.43 (Hexane/EtOAc = 30:1).

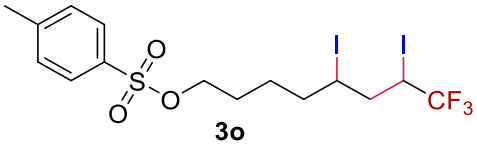
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.55 – 4.51 (m, 0.8H, major), 4.37 – 4.32 (m, 0.2H, minor), 4.19 – 4.11 (m, 1H), 4.07 (t, *J* = 6.3 Hz, 2H), 2.62 – 2.54 (m, 0.2H, minor), 2.52 – 2.42 (m, 0.2H, major), 2.30 – 2.22 (m, 0.8H, major), 2.05 (s, 3H), 2.04 – 1.09 (m, 1.3H, major), 1.76 – 1.57 (m, 4H), 1.56 – 1.44 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 124.5 (q, *J* = 276.5 Hz), 64.1, 45.0, 42.4, 40.2, 38.0, 36.4, 32.5, 27.9, 27.7, 26.2 (q, *J* = 31.4 Hz), 20.8 (q, *J* = 31.2 Hz), 26.1, 25.8, 21.1, 21.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.96 (d, *J* = 7.6 Hz, 1F), -68.41 (d, *J* = 8.0 Hz, 4.5F).

HRMS (ESI, m/z): calcd for $C_{10}H_{16}F_3I_2O_2^+$ $[M+H]^+$: 478.9186, found: 478.9177.

8,8,8-trifluoro-5,7-diiodooctyl 4-methylbenzenesulfonate (3o)



3o

The product **3o** was purified by column chromatography as a yellow solid (95.6 mg, 81%, 3.7:1 dr).

TLC: R_f = 0.45 (Hexane/EtOAc = 20:1).

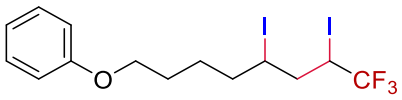
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.53 – 4.45 (m, 0.7H, major), 4.34 – 4.28 (m, 0.2H, minor), 4.08 – 4.02 (m, 3H), 2.59 – 2.53 (m, 0.24H, minor), 2.45 (s, 3H), 2.23 – 2.18 (m, 0.8H, major), 1.99 – 1.87 (m, 2H), 1.65 – 1.35 (m, 4H), 0.90 – 0.75 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.6, 136.9, 129.9, 127.2, 124.5 (q, *J* = 276.6 Hz), 44.8, 42.9, 42.9, 42.3, 40.0, 37.7, 36.4, 32.5, 28.8, 28.6, 26.6, 26.3, 26.1 (q, *J* = 31.5 Hz), 20.9 (q, *J* = 31.5), 21.7, 21.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.95 (d, *J* = 7.9 Hz, 1F), -68.36 (d, *J* = 8.1 Hz, 3.7F).

HRMS (ESI, m/z): calcd for $C_{15}H_{21}F_3I_2NO_2S^+$ $[M+H]^+$: 590.9175, found: 590.9178.

((7,7,7-trifluoro-4,6-diiodoheptyl)oxy)benzene (3p)



3p

The product **3p** was purified by column chromatography as a colourless oil (75.9 mg, 71 %, 3.6:1 dr).

TLC: R_f = 0.45 (Hexane).

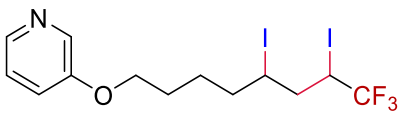
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.93 – 6.89 (m, 2H), 4.63 – 4.53 (m, 0.7H, major), 4.43 – 4.37 (m, 0.3H, minor), 4.30 – 4.22 (m, 1H), 4.05 – 3.98 (m, 2H), 2.67 – 2.61 (m, 0.2H, minor), 2.55 – 2.49 (m, 0.2H, minor), 2.36 – 2.28 (m, 0.7H, major), 2.23 – 2.16 (m, 0.7H, major), 2.15 – 2.01 (m, 3H), 2.00 – 1.85 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 129.6, 124.4 (q, *J* = 277.0 Hz), 120.9, 114.6, 66.8, 66.5, 44.9, 42.5, 37.6, 36.5, 35.1, 32.3, 29.5, 29.1, 26.2 (q, *J* = 31.5 Hz), 20.9 (q, *J* = 31.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.96 (d, *J* = 7.4 Hz, 1F), -68.34 (d, *J* = 8.2 Hz, 3.6F).

HRMS (ESI, m/z): calcd for $C_{13}H_{15}F_3I_2ONa^+$ $[M+Na]^+$: 520.9062, found: 520.9060.

3-((7,7,7-trifluoro-4,6-diiodoheptyl)oxy)pyridine (3q)



3q

The product **3q** was purified by column chromatography as a pale yellow liquid (84.7 mg, 84%, 3.5:1 dr).

TLC: R_f = 0.46 (Hexane/EtOAc = 10:1).

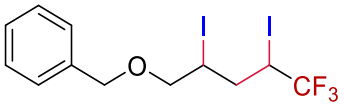
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (t, *J* = 2.6 Hz, 1H), 8.21 (dd, *J* = 4.5, 1.4 Hz, 1H), 7.23 – 7.14 (m, 2H), 4.56 – 4.48 (m, 0.8H, major), 4.41 – 4.33 (m, 0.2H, minor), 4.25 – 4.18 (m, 1H), 4.07 – 4.01 (m, 2H), 2.66 – 2.57 (m, 0.2H, minor), 2.53 – 2.47 (m, 0.2H, minor), 2.31 – 2.28 (m, 0.8H, major), 2.21 – 2.10 (m, 1.1H, major), 2.10 – 2.02 (m, 2H), 2.00 – 1.85 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 142.4, 138.0, 138.0, 124.5 (q, *J* = 276.6 Hz), 124.0, 121.2, 67.2, 67.0, 44.9, 42.4, 37.4, 36.2, 35.0, 31.9, 29.4, 29.1, 26.1 (q, *J* = 31.3 Hz), 20.7 (q, *J* = 31.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.95 (d, *J* = 7.7 Hz, 1F), -68.37 (d, *J* = 7.9 Hz, 3.5F).

HRMS (ESI, m/z): calcd for $C_{12}H_{14}F_3I_2NONa^+$ $[M+Na]^+$: 521.9015, found: 521.9014.

1,1,1-trifluoro-2,4-diiodo-5-methoxypentane (3r)



3r

The product **3r** was purified by column chromatography as a colourless oil (70.7 mg, 73%, 2.3:1 dr).

TLC: R_f = 0.5 (Hexane/EtOAc = 30:1).

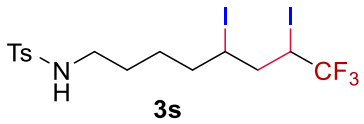
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 4.63 – 4.53 (m, 2H), 4.52 – 4.40 (m, 0.4H, minor), 4.40 – 4.36 (m, 0.6H, major), 4.36 – 4.27 (m, 1H), 3.85 – 3.64 (m, 2H), 2.71 – 2.61 (m, 0.6H, major), 2.56 – 2.49 (m, 0.6H, major), 2.35 – 2.27 (m, 0.4H, minor), 2.26 – 2.16 (m, 0.4H, minor).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.5, 128.7, 128.7, 128.2, 128.2, 127.9, 127.9, 124.6 (q, *J* = 276.2), 75.2, 74.8, 73.3, 73.3, 42.6, 39.1, 31.5, 29.8, 25.8 (q, *J* = 31.5 Hz), 21.6 (q, *J* = 31.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.36 (d, *J* = 7.7 Hz, 1F), -68.41 (d, *J* = 7.7 Hz, 2.3F).

HRMS (ESI, m/z): calcd for $C_{12}H_{14}F_3I_2O^+$ $[M+H]^+$: 484.9081, found: 484.9072.

4-methyl-N-(8,8,8-trifluoro-5,7-diiodooctyl)benzenesulfonamide (3s)



3s

The product **3s** was purified by column chromatography as a yellow solid (118.6 mg, 78%, 3.5:1 dr).

TLC: R_f = 0.45 (Hexane/EtOAc = 20:1).

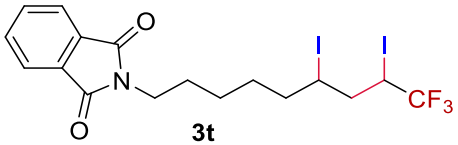
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.95 (t, *J* = 6.2 Hz, 1H), 4.55 – 4.45 (m, 0.7H, major), 4.35 – 4.29 (m, 0.3H, minor), 4.09 – 4.02 (m, 1H), 2.94 (q, *J* = 6.4 Hz, 2H), 2.57 – 2.50 (m, 0.2H, minor), 2.42 (s, 3H), 2.22 – 2.17 (m, 0.8H, major), 2.00 – 1.87 (m, 2H), 1.77 – 1.68 (m, 1H), 1.65 – 1.35 (m, 4H), 0.90 – 0.75 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.6, 136.9, 129.9, 127.2, 124.5 (q, *J* = 276.6 Hz), 44.8, 42.9, 42.9, 42.3, 40.0, 37.7, 36.4, 32.5, 28.8, 28.6, 26.6, 26.3, 26.1 (q, *J* = 31.5 Hz), 20.9 (q, 31.5), 21.7, 21.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.95 (d, *J* = 7.9 Hz, 1F), -68.36 (d, *J* = 8.1 Hz, 3.5F).

HRMS (ESI, m/z): calcd for $C_{15}H_{21}F_3I_2NO_2S^+$ $[M+H]^+$: 589.9329, found: 589.9332.

2-(9,9,9-trifluoro-6,8-diiodononyl)isoindoline-1,3-dione (3t)



3t

The product **3t** was purified by column chromatography as a white soild (71.2 mg, 61 %, 3.5:1 dr).

TLC: R_f = 0.30 (Hexane/EtOAc = 20:1).

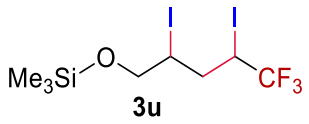
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.53 – 4.45 (m, 0.7H, major), 4.39 – 4.30 (m, 0.3H, minor), 4.16 – 4.08 (m, 1H), 3.68 (t, *J* = 7.2 Hz, 2H), 2.59 – 2.50 (m, 0.3H, minor), 2.47 – 2.31 (m, 0.3H, minor), 2.27 – 2.16 (m, 0.8H, major), 2.03 – 1.94 (m, 1.6H, major), 1.82 – 1.77 (m, 1H), 1.72 – 1.66 (m, 2H), 1.65 – 1.56 (m, 1H), 1.54 – 1.30 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 134.0, 132.2, 124.5 (q, *J* = 276.6 Hz), 123.3, 44.8, 42.3, 40.5, 38.1, 37.9, 37.8, 36.7, 32.7, 29.8, 29.0, 28.7, 28.4, 26.2 (q, *J* = 31.3 Hz), 21.03 (q, *J* = 31.1 Hz), 26.1, 26.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.00 (d, *J* = 8.0 Hz, 1F), -68.37 (d, *J* = 8.1 Hz, 3.5F).

HRMS (ESI, m/z): calcd for $C_{17}H_{18}F_3I_2NO_2Na^+$ $[M+Na]^+$: 601.9238, found: 601.9245.

trimethyl((5,5,5-trifluoro-2,4-diiodopentyl)oxy)silane (3u)



3u

The product **3u** was purified by column chromatography as a colourless oil (46.3 mg, 50 %, 2.4:1 dr).

TLC: R_f = 0.45(Hexane/EtOAc = 50:1).

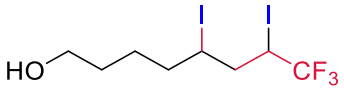
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.60 – 4.51 (m, 0.3H, minor), 4.51 – 4.43 (m, 0.7H, major), 4.26 – 4.13 (m, 1H), 3.99 – 3.93 (m, 0.7H, major), 3.92 – 3.87 (m, 0.3H, minor), 3.86 – 3.82 (m, 0.7H, major), 3.80 – 3.73 (m, 0.3H, minor), 2.74 – 2.61 (m, 0.3H, minor), 2.53 – 2.44 (m, 0.3H, minor), 2.37 – 2.30 (m, 0.7H, major), 2.16 – 2.08 (m, 0.7H, major), 0.15 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 125.1 (q, *J* = 276.5 Hz), 68.9, 68.7, 43.2, 39.1, 35.6, 30.2, 26.3 (q, *J* = 31.5 Hz), 22.7 (q, *J* = 31.2 Hz), 0.1, 0.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.42 (d, *J* = 8.2 Hz, 1F), -68.49 (d, *J* = 8.1 Hz, 2.4F).

HRMS (ESI, m/z): calcd for $C_8H_{16}F_3I_2OSi^+$ $[M+H]^+$: 466.9006, found: 466.8998.

8,8,8-trifluoro-5,7-diiodooctan-1-ol (3v)



3v

The product **3v** was purified by column chromatography as a colourless oil (63.7 mg, 73 %, 4.4:1 dr).

TLC: R_f = 0.57 (Hexane/EtOAc = 30:1).

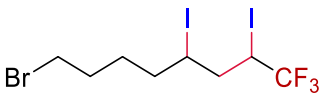
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.57 – 4.52 (m, 0.8H, major), 4.40 – 4.31 (m, 0.2H, minor), 4.20 – 4.12 (m, 1H), 3.68 (s, 2H), 2.65 – 2.50 (m, 0.2H, minor), 2.50 – 2.40 (m, 0.2H, minor), 2.33 – 2.10 (m, 0.8H, major), 2.00 – 1.94 (m, 1.7H, major), 1.80 – 1.76 (m, 1H), 1.68 – 1.42 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 124.4 (q, J = 276.7 Hz), 62.6, 45.0, 42.4, 40.5, 38.2, 36.8, 32.9, 31.9, 25.9, 26.2 (q, J = 31.6 Hz), 20.3 (q, J = 31.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.97 (d, J = 8.0 Hz, 1F), -68.40 (d, J = 8.2 Hz, 4.4F).

HRMS (ESI, m/z): calcd for $C_8H_{14}F_3I_2O^+$ $[M+H]^+$: 436.9086, found: 436.9085.

8-bromo-1,1,1-trifluoro-2,4-diiodooctane (3w)



3w

The product **3w** was purified by column chromatography as a colourless oil (71.0 mg, 86 %, 3.8:1 dr).

TLC: R_f = 0.57 (Hexane).

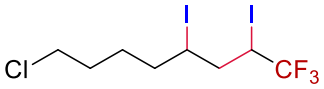
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.59 – 4.49 (m, 0.9H, major), 4.41 – 4.33 (m, 0.1H, minor), 4.22 – 4.09 (m, 1H), 3.48 – 3.38 (m, 2H), 2.70 – 2.57 (m, 0.1H, minor), 2.52 – 2.42 (m, 0.1H, minor), 2.33 – 2.23 (m, 0.9H, major), 2.09 – 1.99 (m, 1.9H, major), 1.98 – 1.81 (m, 3H), 1.78 – 1.67 (m, 1H), 1.6 – 1.58 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ124.4 (q, J = 276.5 Hz), 44.8, 42.3, 39.7, 39.2, 37.4, 36.0, 33.1, 32.1, 31.8, 31.6, 28.1, 27.8, 26.1 (q, J = 31.5 Hz), 20.8 (q, J = 31.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.97 (d, J = 8.0 Hz, 1F), -68.40 (d, J = 8.2 Hz, 3.8F).

HRMS (ESI, m/z): calcd for $C_8H_{13}BrF_3I_2^+$ $[M+H]^+$: 498.8242, found: 498.8238.

7-chloro-1,1,1-trifluoro-2,4-diiodoheptane (3x)



3x

The product **3x** was purified by column chromatography as a colourless oil (65.3 mg, 71 %, 3.7:1 dr).

TLC: R_f = 0.48 (Hexane).

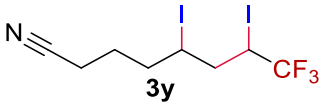
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.59 – 4.50 (m, 0.8H, major), 4.40 – 4.30 (m, 0.2H, minor), 4.20 – 4.09 (m, 1H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.67 – 2.52 (m, 0.2H, minor), 2.52 – 2.44 (m, 0.3H, minor), 2.31 – 2.21 (m, 0.8H, major), 2.09 – 1.97 (m, 1.6H, major), 1.93 – 1.61 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 124.5 (q, *J* = 276.6 Hz), 45.0, 44.6, 42.4, 42.4, 40.0, 37.7, 36.2, 32.3, 31.8, 31.6, 27.0, 26.7, 26.2 (q, *J* = 31.4 Hz), 20.8 (q, *J* = 31.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.93 (d, *J* = 7.6 Hz, 1F), -68.39 (d, *J* = 7.8 Hz, 3.7F).

HRMS (ESI, m/z): calcd for $C_8H_{13}ClF_3I_2^+$ $[M+H]^+$: 454.8747, found: 454.8745.

9,9,9-trifluoro-6,8-diiodononanenitrile (3y)



3y

The product **3y** was purified by column chromatography as a colourless oil (65 mg, 74 %, 3.6:1 dr)

TLC: R_f = 0.34 (Hexane/EtOAc = 30:1).

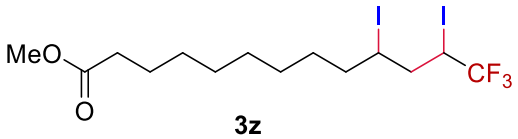
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.55 – 4.49 (m, 0.8H, major), 4.40 – 4.33 (m, 0.2H, minor), 4.17 – 4.10 (m, 1H), 2.66 – 2.54 (m, 0.2H, minor), 2.51 – 2.43 (m, 0.2H, minor), 2.39 (t, *J* = 6.6 Hz, 2H), 2.30 – 2.24 (m, 0.8H, major), 2.09 – 2.00 (m, 1.6H, major), 1.89 – 1.80 (m, 1H), 1.79 – 1.60 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 124.4 (q, *J* = 276.6 Hz), 119.3, 44.9, 42.3, 39.7, 37.6, 35.5, 31.7, 28.6, 28.6, 25.9 (q, *J* = 31.4 Hz), 20.6 (q, *J* = 31.3 Hz), 24.5, 24.5, 17.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.90 (d, *J* = 7.3 Hz, 1F), -68.40 (d, *J* = 8.0 Hz, 3.6F).

HRMS (ESI, m/z): calcd for $C_9H_{12}F_3I_2NNa^+$ $[M+Na]^+$: 467.8950, found: 467.8943.

methyl 13,13,13-trifluoro-10,12-diiodotridecanoate (3z)



3z

The product **3z** was purified by column chromatography as a colourless oil (106.1 mg, 73%, 3.8:1 dr).

TLC: R_f = 0.46 (Hexane/EtOAc = 30:1).

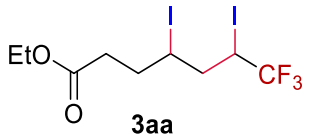
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 – 4.47 (m, 0.8H, major), 4.41 – 4.39 (m, 0.2H, minor), 4.17 – 4.09 (m, 1H), 3.65 (s, 3H), 2.63 – 2.53 (m, 0.2H, minor), 2.51 – 2.39 (m, 0.2H, minor), 2.30 (t, *J* = 7.6, 2H), 2.25 – 2.20 (m, 0.6H, major), 2.06 – 1.94 (m, 1.6H, major), 1.83 – 1.75(m, 1H), 1.67 – 1.36 (m, 5H), 1.30 (s, 8H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 124.4 (q, *J* = 276.5 Hz), 51.6, 44.9, 42.4, 40.7, 40.1, 38.4, 37.0, 34.1, 33.1, 29.4, 29.2, 29.1, 29.1, 29.0, 28.6, 28.5, 26.2 (q, *J* = 31.3 Hz), 20.9 (q, *J* = 31.1 Hz), 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.98 (d, *J* = 7.9 Hz, 1F), -68.40 (d, *J* = 7.8 Hz, 3.8F).

HRMS (ESI, m/z): calcd for $C_{14}H_{23}F_3I_2O_2Na^+$[M+Na]$^+$: 556.9631, found: 556.9621.

ethyl 7,7,7-trifluoro-4,6-diiodoheptanoate (3aa)



3aa

The product **3aa** was purified by column chromatography as a colourless oil (74.0 mg, 80 %, 3.3:1 dr).

TLC: R_f = 0.48 (Hexane/EtOAc = 30:1).

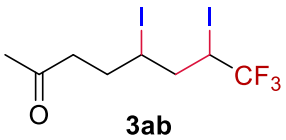
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.53 – 4.35 (m, 0.8H, major), 4.42 – 4.36 (m, 0.2H, minor), 4.23 – 4.17 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.80 – 2.55 (m, 1.4H, major), 2.55 – 2.44 (m, 1.4H, minor), 2.35 – 2.20 (m, 2H), 2.10 – 2.10 (m, 0.9H, minor), 2.10 – 1.90 (m, 1.3H, major), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 124.6 (q, J = 276.6 Hz), 124.2 (q, J = 276.6 Hz), 60.9, 60.9, 45.1, 42.5, 35.6, 35.5, 34.3, 34.2, 33.6, 31.2, 25.8 (q, J = 31.4 Hz), 20.6 (q, J = 31.2 Hz), 14.4, 14.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.09 (d, J = 7.8 Hz, 1F), -68.44 (d, J = 7.9 Hz, 3.3F).

HRMS (ESI, m/z): calcd for $C_9H_{13}F_3I_2O_2Na^+$ $[M+Na]^+$: 486.8849, found: 486.8842.

8,8,8-trifluoro-5,7-diiodooctan-2-one (3ab)



3ab

The product **3ab** was purified by column chromatography as a colourless oil (49.2 mg, 63%, 3.5:1 dr).

TLC: R_f = 0.43 (Hexane/EtOAc = 30:1).

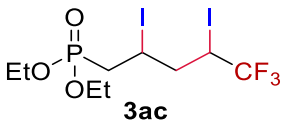
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.54 – 4.47 (m, 0.7H, major), 4.41 – 4.37 (m, 0.3H, minor), 4.18 – 4.14 (m, 1H), 2.77 – 2.59 (m, 2.4H, major), 2.49 – 2.45 (m, 0.3H, minor), 2.30 – 2.26 (m, 0.8H, major), 2.19 (s, 3H), 2.17 – 2.10 (m, 2.5H, major), 2.00 – 1.82 (m, 0.5H, minor).

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.8, 206.8, 124.38 (q, J = 276.5 Hz), 45.2, 43.4, 43.4, 42.6, 36.4, 34.1, 32.1 31.9, 30.3, 25.7 (q, J = 31.5 Hz), 20.6 (q, J = 31.1 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.15 (d, J = 7.6 Hz, 1F), -68.42 (d, J = 7.9 Hz, 3.5F).

HRMS (ESI, m/z): calcd for $C_8H_{12}F_3I_2O^+$ $[M+H]^+$: 434.8916, found: 434.8924.

diethyl (5,5,5-trifluoro-2,4-diiodopentyl)phosphonate (3ac)



3ac

The product **3ac** was purified by column chromatography as a colourless oil (74.4 mg, 73 %, 5.2:1 dr).

TLC: R_f = 0.2 (Hexane/EtOAc = 10:1).

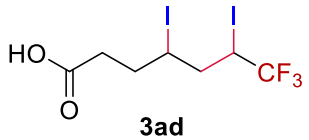
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.54 – 4.45 (m, 2H), 4.18 – 4.03 (m, 4H), 4.20 – 4.12 (m, 1H), 2.85 – 2.71 (m, 1H), 2.63 – 2.56 (m, 1H), 2.45 – 2.37 (m,1H), 2.20 – 2.12 (m, 1H), 1.37 – 1.29 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 124.4 (q, *J* = 276.6 Hz), 62.5 (d, *J* = 6.6 Hz), 62.4 (d, *J* = 6.6 Hz),42.4, 38.9, 26.2 (q, *J* = 31.2 Hz), 23.7, 20.2 (q, *J* = 31.2 Hz), 16.6 (d, *J* = 6.0 Hz), 16.5 (d, *J* = 6.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.29 (d, *J* = 8.1 Hz, 1F), -68.39 (d, *J* = 8.0 Hz, 5.2F).

HRMS (ESI, m/z): calcd for $C_9H_{17}F_3I_2O_3P^+$ $[M+H]^+$: 514.8951, found: 514.8954.

7,7,7-trifluoro-4,6-diiodoheptanoic acid (3ad)



3ad

The product **3ad** was purified by column chromatography as a colourless oil (65.0 mg, 63 %, 3.0:1 dr).

TLC: R_f = 0.21 (Hexane/EtOAc = 7:1).

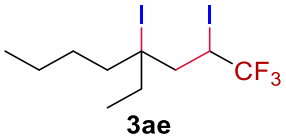
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.76 – 4.68 (m, 0.3H, minor), 4.68 – 4.63 (m, 0.7H, major), 4.56 – 4.38 (m, 0.2H, minor), 4.34 – 4.18 (m, 0.7H, major), 2.64 – 2.54 (m, 2H), 2.51 – 2.31 (m, 2H), 2.17 – 2.05 (m, 0.6H, major), 2.03 – 1.87 (m, 0.3H, minor) , 1.87 – 1.77 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 124.5 (q, *J* = 276.6 Hz), 78.8, 78.4, 40.1, 39.0, 28.6, 28.3, 27.5, 27.4, 20.1 (q, *J* = 31.9 Hz), 15.0 (q, *J* = 32.3 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.19 (d, *J* = 7.2 Hz, 3F), -69.48 (d, *J* = 8.2 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_7H_{10}F_3I_2O_2^+$ $[M+H]^+$: 436.8722, found: 436.8724.

4-ethyl-1,1,1-trifluoro-2,4-diiodooctane (3ae)



3ae

The product **3ae** was purified by column chromatography as a colourless oil (64.9 mg,

71 %, 1:1 dr)

TLC: R_f = 0.52 (Hexane).

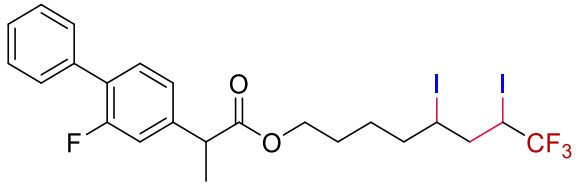
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.44 (m, 1H), 2.75 (m, 1H), 2.36 (m, 1H), 2.12 – 1.99 (m, 1H), 1.96 – 1.74 (m, 3H), 1.52 – 1.26 (m, 5H), 1.03 (m, 3H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 125.93 (q, *J* = 276.6 Hz), 65.1, 65.0, 47.9, 47.6, 44.6，43.9, 38.1, 37.4, 29.1, 28.9, 22.6, 22.5, 18.8 (q, *J* = 30.29), 18.6 (q, *J* = 30.30), 14.1, 11.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.99 (d, *J* = 8.7 Hz, 1F), 69.01 (d, *J* = 8.7 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{10}H_{18}F_3I_2^+$ $[M+H]^+$: 448.9450, found: 448.9455.

8,8,8-trifluoro-5,7-diiodooctyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (3af)



3af

The product **3af** was purified by column chromatography as a colourless oil (118.1 mg, 89%, 3.8:1 dr).

TLC: R_f = 0.34 (Hexane/EtOAc = 100:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.33 (m, 4H), 7.21 – 7.11 (m, 2H), 4.60 – 4.44 (m, 0.8H, major), 4.39 – 4.27 (m, 0.2H, minor), 4.24 – 4.04 (m, 5H), 3.82 – 3.73 (m, 1H), 2.71 – 2.5 (m, 0.2H, minor), 2.50 – 2.31 (m, 0.2H, minor), 2.31 – 4.17 (m, 0.8H, major), 2.14 – 1.92 (m, 2H), 1.87 – 1.57 (m, 1.8H, major), 1.56 (d, *J* = 7.3 Hz, 3H), 1.51 – 1.38 (m, 1H).

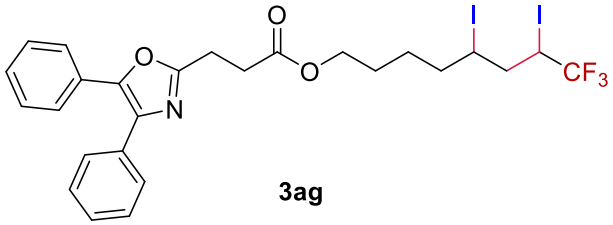
^{13}C NMR (151 MHz, $CDCl_3$) δ 174.0, 160.5, 158.9, 141.9, 141.8, 135.5, 130.9, 130.8, 129.0, 128.5, 127.7, 124.43 (q, *J* = 276.5 Hz), 123.6, 115.4, 115.2, 65.5 64.4, 45.1, 45.1, 42.3, 40.0, 37.8, 36.3, 36.3, 27.7, 27.7, 26.3, 26.1, 25.98 (q, *J* = 31.4 Hz), 20.73 (q, *J* = 31.4 Hz), 18.4, 18.4

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.92 (d, *J* = 7.4 Hz, 1F), -68.37 (d, *J* = 7.7 Hz, 3.8F),

-117.42 (t, J = 9.8 Hz, 2.2F).

HRMS (ESI, m/z): calcd for $C_{23}H_{25}F_4I_2O_2^+$ $[M+H]^+$: 662.9880, found: 662.9882.

8,8,8-trifluoro-5,7-diiodooctyl 2-(4,5-diphenyloxazol-2-yl)acetate



3ag

The product **3ag** was purified by column chromatography as a clear yellow liquid (118.5 mg, 85%, 3.5:1 dr).

TLC: R_f = 0.37 (Hexane/EtOAc = 20:1).

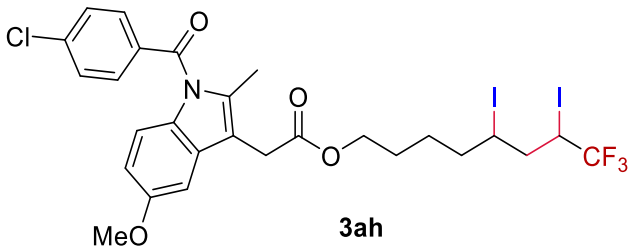
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.60 – 7.54 (m, 2H), 7.39 – 7.29 (m, 6H), 4.59 – 4.44 (m, 0.8H, major), 4.39 – 4.29 (m, 0.2H, minor), 4.16 (t, J = 6.2 Hz, 2H), 4.14 – 4.07 (m, 1H), 3.20 (t, J = 7.5 Hz, 2H), 2.93 (t, J = 7.7 Hz, 2H), 2.62 – 2.51 (m, 0.2H, minor), 2.50 – 2.40 (m, 0.2H, minor), 2.30 – 2.20 (m, 0.7H, major), 2.05 – 1.95 (m, 1H), 1.82 – 1.59 (m, 3H), 1.56 – 1.45 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 161.8, 145.4, 135.1, 132.5, 129.0, 128.7, 128.6, 128.5, 128.1, 127.9, 126.5, 124.4 (q, J = 276.7 Hz), 64.3, 64.2, 44.9, 42.3, 40.1, 37.8, 36.3, 32.4, 31.2, 27.8, 27.7, 26.0 (q, J = 31.6 Hz), 20.8 (q, J = 31.2 Hz), 26.0, 23.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.94 (d, J = 7.8 Hz, 1F), -68.38 (d, J = 8.0 Hz, 3.5F).

HRMS (ESI, m/z): calcd for $C_{25}H_{25}F_3I_2NO_3^+$ $[M+H]^+$: 697.9876, found: 697.9875.

8,8,8-trifluoro-5,7-diiodooctyl 2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)acetate (3ah)



3ah

The product **3ah** was purified by column chromatography as a colourless oil (134.9 mg,

87%, 3.0:1 dr).

TLC: R_f = 0.34 (Hexane/EtOAc = 30:1).

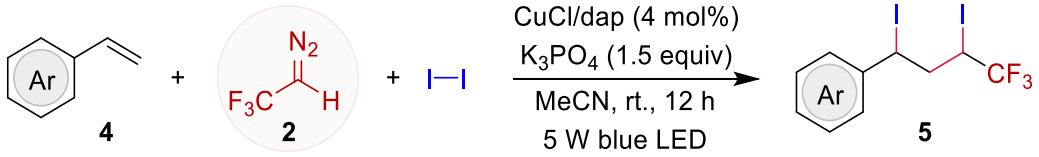
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 2H), 7.53 – 7.47 (m, 2H), 7.00 (d, *J* = 2.6 Hz, 1H), 6.89 (d, *J* = 9.1 Hz, 1H), 6.72 – 6.68 (m, 1H), 4.58 – 4.47 (m, 0.7H, major), 4.41 – 4.31 (m, 0.2H, minor), 4.20 – 4.14 (m, 3H), 4.15 – 4.06 (m, 1H), 3.86 (s, 3H), 3.70 (d, *J* = 1.6 Hz, 2H), 2.62 – 2.55 (m, 0.2H, minor), 2.50 – 2.42 (m, 0.3H, minor), 2.43 (s, 3H), 2.30 – 2.20 (m, 0.6H, major), 2.06 – 1.92 (m, 1.5H, major), 1.83 – 1.72 (m, 0.7H, major), 1.75 – 1.56 (m, 2H), 1.53 – 1.42 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 168.3, 156.1, 139.3, 136.0, 133.9, 131.2, 130.8, 130.7, 129.6, 124.4 (q, *J* = 277.1 Hz), 115.0, 112.6, 111.6, 101.5, 101.5, 64.5, 55.8, 44.8, 42.3, 40.1, 37.8, 36.3, 32.4, 30.4, 27.7, 26.1, 26.0 (q, *J* = 31.4 Hz), 25.8, 20.7 (q, *J* = 31.7 Hz), 13.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.91 (d, *J* = 7.3 Hz, 1F), -68.35 (d, *J* = 7.6 Hz, 3F).

HRMS (ESI, m/z): calcd for $C_{27}H_{28}ClF_3I_2NO_4^+$ $[M+H]^+$: 775.9748, found: 775.9750.

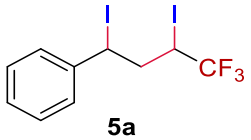
5. General procedure and characterization data of products 5.



I_2 (0.35 mmol), CuCl (4 mol%) and dap (4 mol%) were dissolved in MeCN (1.0 mL), with the nitrogen atmosphere being maintained throughout the process. It is important to ensure that the solids are completely dissolved before adding CF_3CHN_2 (0.52 mmol) and alkene **4** (0.2 mmol). Subsequently, the reaction mixture is irradiated with a 455 nm LED while being magnetically stirred at room temperature (25 °C) for 12 hours. After the reaction, trace of the reaction supernatant was used for ^{19}F NMR spectroscopic analysis to determine the dr selectivity. Then, the other mixture was directly subjected to be concentrated in vacuo and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as an eluent to afford the desired product

5.

(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5a)



5a

The product **5a** was purified by column chromatography as a colourless oil (79.2 mg, 90 %, 1.2:1 dr).

TLC: R_f = 0.67 (Hexane).

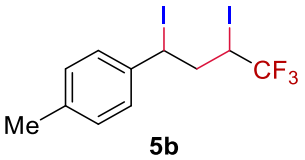
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.27 (m, 3H), 5.28 (dd, *J* = 11.6, 4.7 Hz, 1H), 4.61 – 4.53 (m, 0.5H, major), 3.70 – 3.60 (m, 0.4H, minor), 2.89 – 2.77 (m, 0.5H, minor), 2.87 – 2.77 (m, 1H), 2.19 (m, 0.6H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 140.4, 129.5, 129.2, 129.0, 128.8, 127.4, 127.4, 124.6 (q, *J* = 277.0 Hz), 123.8 (q, *J* = 277.0 Hz), 44.7, 43.1, 33.0, 25.7, 25.22 (q, *J* = 31.4 Hz), 21.95 (q, *J* = 31.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.97 (d, *J* = 7.9 Hz, 1.2F), -68.85 (d, *J* = 7.8 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{10}H_{10}F_3I_2^+$ $[M+H]^+$: 440.8824, found: 440.8819.

1-methyl-4-(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5b)



5b

The product **5b** was purified by column chromatography as a colourless oil (54.2 mg, 60%, 1.2:1 dr).

TLC: R_f = 0.70 (Hexane).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.08 (m, 4H), 5.30 – 5.19 (m, 1H), 4.64 – 4.52 (m, 0.5H, major), 3.71 – 3.61 (m, 0.4H, minor), 3.00 – 2.94 (m, 0.43H, minor), 2.86 – 2.76 (m, 1H), 2.36 (d, *J* = 3.3 Hz, 3H), 2.20 – 2.13 (m, 0.5H, major).

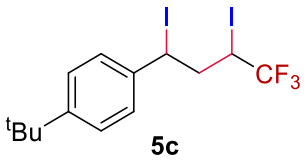
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 140.2, 139.1, 138.9, 129.8, 129.5, 129.2, 129.0, 127.9, 127.9, 124.5 (q, *J* = 276.9 Hz), 124.4, 124.3, 44.5, 43.1, 33.1, 25.9, 25.1 (q, *J* =

31.4 Hz), 21.8 (q, J = 31.4 Hz), 21.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.98 (d, J = 8.0 Hz, 1.2F), -68.85 (d, J = 8.0 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{11}H_{12}F_3I_2^+$ $[M+H]^+$: 454.8981, found: 454.8978.

1-(tert-butyl)-4-(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5c)



5c

The product **5c** was purified by column chromatography as a colourless oil (78.4 mg, 79%, 1.9:1 dr).

TLC: R_f = 0.67 (Hexane).

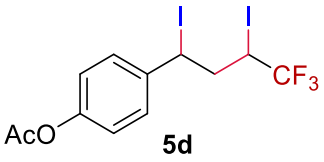
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.35 – 7.30 (m, 2H), 4.87 (d, J = 10.0 Hz, 1H), 4.70 – 4.61 (m, 0.6H, major), 3.88 – 3.77 (m, 0.3H, minor), 2.52 – 2.43 (m, 0.4H, major), 2.40 – 2.33 (m, 0.4H, minor), 2.22 – 2.15 (m, 0.4H, minor), 2.11 – 2.04 (m, 0.5H, major), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 151.4, 140.1, 138.7, 126.0, 125.9, 125.7, 125.5, 124.5 (q, J = 276.9 Hz), 73.6, 72.4, 41.7, 41.6, 34.7, 34.6, 31.3, 25.1 (q, J = 31.4 Hz), 21.83 (q, J = 31.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.66 (d, J = 7.6 Hz, 1F), -68.96 (d, J = 8.2 Hz, 1.9F).

HRMS (ESI, m/z): calcd for $C_{14}H_{18}F_3I_2^+$ $[M+H]^+$: 496.9450, found: 496.9454.

4-(4,4,4-trifluoro-1,3-diiodobutyl)phenyl acetate (5d)



5d

The product **5d** was purified by column chromatography as a colourless oil (67 mg, 60%, 1.4:1 dr).

TLC: R_f = 0.58 (Hexane/EtOAc = 30:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.52 – 7.45 (m, 2H), 5.31 – 5.22

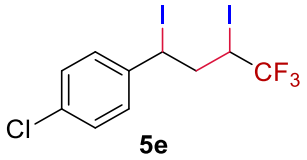
(m, 1H), 4.60 – 4.49 (m, 0.5H, major), 3.65 – 3.62 (m, 0.5H, minor), 3.00 – 2.90 (m, 0.5H, minor), 2.84 – 2.70 (m, 1H), 2.30 (s, 3H), 2.24 – 2.12 (m, 0.6H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ169.1, 150.6 (d, J = 25.0 Hz), 140.0, 137.8, 128.5, 128.4, 124.6 (q, J = 276.6 Hz), 122.5, 122.2, 44.6, 43.1, 31.7, 24.60, 25.0 (q, J = 31.8 Hz), 21.8 (q, J = 31.6 Hz), 21.2 (d, J = 4.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.02 (d, J = 8.0 Hz, 1.4F), -68.80 (d, J = 7.8 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{12}H_{12}F_3I_2O_2^+$ $[M+H]^+$: 498.8879, found: 498.8877.

1-chloro-4-(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5e)



5e

The product **5e** was purified by column chromatography as a colourless oil (84 mg, 88%, dr 1.2:1 dr).

TLC: R_f = 0.70 (Hexane).

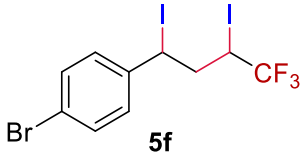
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 5.26 – 5.18 (m, 1H), 4.57 – 4.50 (m, 0.6H, major), 3.67 – 3.58 (m, 0.5H, minor), 2.96 – 2.89 (m, 0.5H, minor), 2.85 – 2.72 (m, 1H), 2.16 – 2.13 (m, 0.6H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 139.1, 134.8, 134.5, 129.8, 129.4, 128.8, 128.7, 122.7 (q, J = 276.7), 44.6, 43.1, 31.3, 24.1, 24.9 (q, J = 31.6), 21.7 (q, J = 31.6).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.01 (d, J = 7.7 Hz, 1.2F), -68.86 (d, J = 7.7 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{10}H_9ClF_3I_2^+$ $[M+H]^+$: 474.8434, found: 474.8428.

1-bromo-4-(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5f)



5f

The product **5f** was purified by column chromatography as a colourless oil (89 mg, 86%, 1.2:1 dr).

TLC: R_f = 0.71 (Hexane).

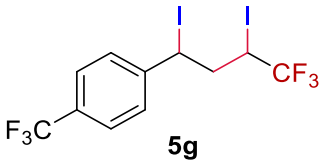
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (t, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 8.5, 3.3 Hz, 2H), 5.27 – 5.17 (m, 1H), 4.57 – 4.48 (m, 0.6H, major), 3.66 – 3.57 (m, 0.5H, minor), 2.95 – 2.88 (m, 0.4H, minor),2.85 – 2.72 (m, 1H), 2.19 – 2.11 (m, 0.6H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 139.1, 134.8, 134.5, 129.8, 129.4, 128.8, 128.7, 124.6 (q, *J* = 276.7), 123.6 (q, *J* = 276.9), 44.6, 43.1, 31.3, 24.1, 24.9 (q, *J* = 31.6), 21.7 (q, *J* = 31.6).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.98 (d, *J* = 8.1 Hz, 1.2F), -68.83 (d, *J* = 8.1 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{10}H_9BrF_3I_2^+$ $[M+H]^+$: 518.7929, found: 518.7923.

1-(4,4,4-trifluoro-1,3-diiodobutyl)-4-(trifluoromethyl)benzene (5g)



5g

The product **5g** was purified by column chromatography as a colourless oil (72.1 mg, 70%, 1.4:1).

TLC: R_f = 0.66 (Hexane).

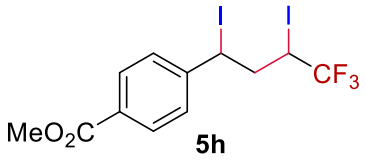
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.51 (m, 4H), 5.32 – 5.21 (m, 1H), 4.60 – 4.50 (m, 0.6H, major), 3.68 – 3.57 (m, 0.4H, minor), 3.04 – 2.90 (m, 0.4H, minor), 2.88 – 2.73 (m, 1H), 2.23 – 2.13 (m, 0.6H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 144.4, 130.7 (q, *J* = 32 Hz), 127.8, 127.7, 126.4 (q, *J* = 3.9 Hz), 126.1 (q, *J* = 3.9 Hz), 123.9 (q, *J* = 276.7), 44.1, 42.7, 30.3, 24.7 (q, *J* = 31.9 Hz), 21.4 (q, *J* = 31.9 Hz), 23.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.81 (s, 1F), -62.85 (s, 0.8F), -68.06 (d, *J* = 7.7 Hz, 1.4F), -68.88 (d, *J* = 7.6 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{11}H_9F_6I_2^+$ $[M+H]^+$: 508.8698, found: 508.8693.

methyl 4-(4,4,4-trifluoro-1,3-diiodobutyl)benzoate (5h)



5h

The product **5h** was purified by column chromatography as a colourless oil (67 mg, 66%, 1.2:1 dr).

TLC: R_f = 0.61 (Hexane/EtOAc = 30:1).

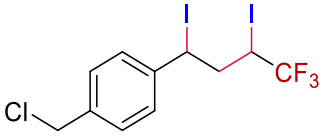
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.52 – 7.45 (m, 2H), 5.31 – 5.22 (m, 1H), 4.60 – 4.49 (m, 0.5H, major), 3.92 (s, 3H), 3.65 – 3.55 (m, 0.4H, minor), 3.00 – 2.92 (m, 0.5H, minor), 2.88 – 2.74 (m, 1H), 2.24 – 2.12 (m, 0.6H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ166.4 (d, J = 4.3 Hz), 147.2, 145.4, 130.8, 130.5, 127.5, 127.4, 124.6 (q, J = 276.6 Hz), 52.4, 44.3, 42.7, 31.1, 24.9 (q, J = 31.4 Hz), 24.0, 21.5 (q, J = 31.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.02 (d, J = 8.0 Hz, 1.2F), -68.90 (d, J = 7.9 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{12}H_{12}F_3I_2O_2^+$ $[M+H]^+$: 498.8879, found: 498.8876.

1-(chloromethyl)-4-(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5i)



5i

The product **5i** was purified by column chromatography as as a colourless oil (90.1 mg, 92%, 1.5:1 dr).

TLC: R_f = 0.63 (Hexane).

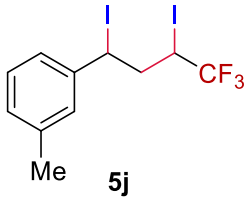
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, J = 7.8 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.30 – 7.21 (m, 1H), 5.32 – 5.20 (m, 1.13H, major), 4.57 (s, 2H), 4.56 – 4.36 (m, 0.5H, minor), 3.71 – 3.60 (m, 0.5H, major), 3.00 – 2.91 (m, 0.5H, minor), 2.88 – 2.75 (m, 1.3H, major), 2.22 – 2.13 (m, 0.6H, minor).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 140.6, 138.2, 138.0, 129.6, 129.3, 127.7, 127.6, 123.5 (q, J = 274.7 Hz), 45.5, 44.3, 42.8, 31.9, 25.0 (q, J = 31.6 Hz), 24.8, 21.8 (q, J = 31.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.97 (d, J = 7.9 Hz, 1.5F), -68.82 (d, J = 7.5 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{11}H_{11}ClF_3I_2^+$ $[M+H]^+$: 488.8591, found: 488.8587.

1-methyl-3-(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5j)



5j

The product **5j** was purified by column chromatography as a colourless oil (63.4 mg, 68%, 1.2:1 dr).

TLC: R_f = 0.68 (Hexane).

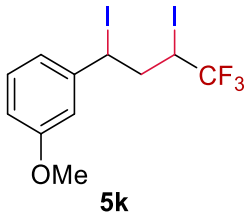
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, J = 7.5 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.17 – 7.08 (m, 1H), 5.31 – 5.20 (m, 1H), 4.57 – 4.65 (m, 0.5H, major), 3.66 – 3.57 (m, 0.5H, minor), 2.97 – 2.95 (m, 0.5H, minor), 2.86 – 2.76 (m, 1H), 2.40 – 2.31 (m, 3H), 2.21 – 2.12 (m, 0.5H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 140.3, 139.7, 139.3, 139.1, 139.0, 138.9, 137.4, 130.2, 129.9, 129.6, 129.4, 129.1, 128.1, 127.3, 124.6 (q, J = 275.1 Hz), 44.6, 43.2, 33.3, 26.1, 25.3 (q, J = 31.4 Hz), 22.0 (q, J = 31.4 Hz), 21.5, 21.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.99 (d, J = 8.0 Hz, 1.2F), -68.87 (d, J = 8.1 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{11}H_{12}F_3I_2^+$ $[M+H]^+$: 454.8981, found: 454.8978.

1-methoxy-3-(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5k)



5k

The product **5k** was purified by column chromatography as a colourless oil (73 mg, 77%, 1.7:1 dr).

TLC: R_f = 0.67 (Hexane).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.96 –

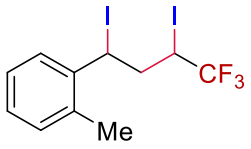
6.92 (m, 1H), 6.87 – 6.80 (m, 1H), 5.28 – 5.17 (m, 1H), 4.58 – 4.48 (m, 0.7H, major), 3.87 – 3.79 (m, 3H), 3.72 – 3.62 (m, 0.5H, minor), 3.00 – 2.91 (m, 0.4H, minor), 2.84 – 2.74 (m, 1H), 2.24 – 2.13 (m, 0.7H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 159.9, 143.8, 141.7, 130.4, 130.1, 124.5 (q, J = 276.6 Hz), 119.5 (d, J = 6.3 Hz), 114.1, 114.1, 113.2, 113.0, 55.3 (d, J = 3.1 Hz), 44.5, 43.1, 32.5, 24.9 (q, J = 32.0 Hz), 21.7 (q, J = 31.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.99 (d, J = 8.2 Hz, 1.7F), -68.90 (d, J = 7.8 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{11}H_{12}F_3I_2O^+$ $[M+H]^+$: 470.8930, found: 470.8926.

1-methyl-2-(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5l)



5l

The product **5l** was purified by column chromatography as a colourless oil (59 mg, 65%, 1.3:1 dr).

TLC: R_f = 0.70 (Hexane).

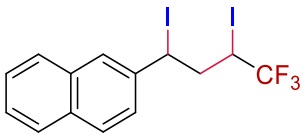
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.39 (m, 1H), 7.24 – 7.12 (m, 3H), 5.57 – 5.40 (m, 1H), 4.70 – 4.55 (m, 0.5H, major), 3.92 – 3.79 (m, 0.4H, minor), 3.28 – 3.06 (m, 0.5H, minor), 2.92 – 2.80 (m, 1H), 2.41 (s, 1.3H, major), 2.37 (s, 1.7H, major), 2.27 – 2.17 (m, 0.59H, minor).

^{13}C NMR (101 MHz, $CDCl_3$) δ140.3, 135.7, 134.5, 131.6, 131.0, 128.7, 128.6, 127.4, 127.3, 127.2, 124.6 (q, J = 275.1 Hz), 43.1, 42.5, 29.7, 25.2 (q, J = 31.4 Hz), 21.6 (q, J = 31.4 Hz), 19.4, 19.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.01 (d, J = 7.8 Hz, 1.3F), -69.00 (d, J = 7.7 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{11}H_{12}F_3I_2^+$ $[M+H]^+$: 454.8981, found: 454.8979.

2-(4,4,4-trifluoro-1,3-diiodobutyl)naphthalene (5m)



5m

The product **5m** was purified by column chromatography as a colourless oil (67.6 mg, 68%, 1.1:1 dr).

TLC: R_f = 0.65 (Hexane).

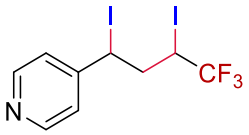
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 4H), 7.57 – 7.48 (m, 3H), 5.47 (dd, *J* = 11.5, 3.6 Hz, 1H), 4.65 – 4.56 (m, 0.5H, major), 3.68 – 3.60 (m, 0.5H, minor), 3.13 – 3.05 (m, 0.4H, minor), 2.99 – 2.87 (m, 1H), 2.32 – 2.23 (m, 0.5H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 137.4, 133.3, 133.2, 133.1, 129.8, 129.2, 128.07 (d, *J* = 2.5 Hz), 127.80 (d, *J* = 6.5 Hz), 126.95 (d, *J* = 1.9 Hz), 126.8, 125.6, 125.4, 124.6, 124.5 (q, *J* = 276.6 Hz), 44.3, 43.0, 33.4, 26.3, 24.9 (q, *J* = 31.5 Hz), 21.9 (q, *J* = 31.5 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.94 (d, *J* = 7.4 Hz, 1.1F), -68.90 (d, *J* = 8.0 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{14}H_{12}F_3I_2^+$ $[M+H]^+$: 490.8981, found: 490.8978.

4-(4,4,4-trifluoro-1,3-diiodobutyl)pyridine (5n)



5n

The product **5n** was purified by column chromatography as a yellow oil (83.8 mg, 95%, 1.4:1 dr).

TLC: R_f = 0.27 (Hexane/EtOAc = 5:1).

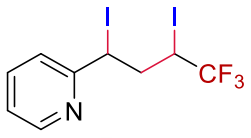
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 – 8.57 (m, 2H), 7.33 – 7.30 (m, 2H), 5.15 – 5.09 (m, 1H), 4.57 – 4.47 (m, 0.6H, major), 3.67 – 3.58 (m, 0.5H, minor), 2.95 – 2.86 (m, 0.4H, minor), 2.84 – 2.69 (m, 1H), 2.20 – 2.12 (m, 0.6H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 150.7, 149.1, 124.4 (q, *J* = 276.9 Hz), 122.0, 121.8, 43.5, 41.9, 28.7, 21.7, 24.6 (q, *J* = 31.7 Hz), 21.1 (q, *J* = 32.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.08 (d, *J* = 7.4 Hz, 1.4F), -68.87 (d, *J* = 7.7 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_9H_9F_3I_2N^+$ $[M+H]^+$: 441.8776, found: 441.8772.

2-(4,4,4-trifluoro-1,3-diiodobutyl)pyridine (5o)



5o

The product **5o** was purified by column chromatography as a yellow oil (84.7 mg, 96%, 1.2:1 dr).

TLC: R_f = 0.29 (Hexane/EtOAc = 5:1).

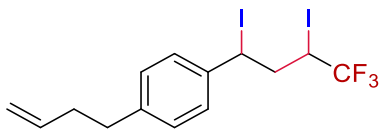
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 17.2, 4.8 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.20 (q, *J* = 6.4 Hz, 1H), 5.40 – 5.31 (m, 1H), 4.62 – 4.52 (m, 0.6H, major), 3.90 – 3.81 (m, 0.5H, minor), 3.36 – 3.28 (m, 0.5H, minor), 3.09 – 3.01 (m, 0.6H, major), 2.79 – 2.71 (m, 0.5H, minor), 2.33 – 2.25 (m, 0.6H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 158.6, 150.4, 150.0, 137.3 (d, *J* = 8.2 Hz), 123.7 (q, *J* = 277.0 Hz), 123.4 (d, *J* = 2.3 Hz), 122.7, 122.0, 41.8, 40.6, 33.2, 26.6, 25.4 (q, *J* = 31.6 Hz), 22.7 (q, *J* = 31.5 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.91 (d, *J* = 7.4 Hz, 1.2F), -68.89 (d, *J* = 7.7 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_9H_9F_3I_2N^+$ $[M+H]^+$: 441.8776, found: 441.8773.

1-(but-3-en-1-yl)-4-(4,4,4-trifluoro-1,3-diiodobutyl)benzene (5p)



5p

The product **5p** was purified by column chromatography as a colourless oil (81 mg, 80%, 1.2:1 dr).

TLC: R_f = 0.63 (Hexane).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 5.91 – 5.81 (m, 1H), 5.27 (d, *J* = 11.0 Hz, 1H), 5.10 – 4.95 (m, 2H), 4.60 – 4.52 (m, 0.6H, major), 4.60 – 4.52 (m, 0.4H, minor), 3.00 – 2.93 (m, 0.4H, minor), 2.87 – 2.76 (m,

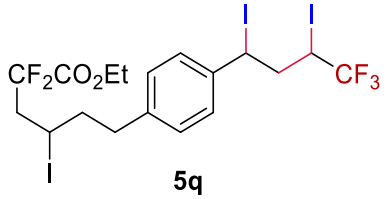
1H), 2.74 – 2.66 (m, 2H), 2.42 – 2.33 (m, 2H), 2.22 – 2.10 (m, 0.6H, major).

^{13}C NMR (101 MHz, $CDCl_3$) δ142.9, 142.7, 140.0, 137.8, 129.4, 129.1, 127.3, 127.2, 124.5 (q, J = 276.2 Hz), 115.2, 44.5, 43.1, 35.2, 35.1, 35.1, 33.2, 26.0, 25.2 (q, J = 31.6 Hz), 21.9 (q, J = 31.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.97 (d, J = 7.8 Hz, 1.2F), -68.83 (d, J = 8.1 Hz,1F).

HRMS (ESI, m/z): calcd for $C_{14}H_{16}F_3I_2^+$ $[M+H]^+$: 494.9294, found: 494.9296.

ethyl 2,2-difluoro-4-iodo-6-(4-(4,4,4-trifluoro-1,3-diiodobutyl)phenyl)hexanoate (5q)



5q

The product **5q** was purified by column chromatography as a colorless liquid (105.6 mg, 71%, 1.2:1 dr).

TLC: R_f = 0.42 (Hexane/EtOAc = 50:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.18 (dd, J = 8.2, 2.9 Hz, 2H), 5.30 – 5.22 (m, 1H), 4.59 – 4.50 (m, 0.5H, minor), 4.35 – 4.27 (m, 2H), 4.21 – 4.11 (m, 0.7H, major), 3.71 – 3.59 (m, 0.4H, minor), 3.02 – 2.93 (m, 1.2H, major), 2.92 – 2.84 (m, 1H), 2.84 – 2.74 (m, 2H), 2.74 – 2.66 (m, 1H), 2.20 – 1.99 (m, 2H), 1.37 – 1.31 (m, 3H).

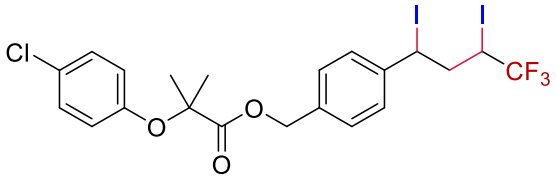
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3 (t, J = 32.2 Hz), 141.1, 140.9, 140.5, 138.3, 129.5, 129.2, 127.5, 127.4, 125.4 (q, J = 277.6 Hz), 115.9 (t, J = 252.4 Hz), 63.3, 45.3 (t, J = 23.1 Hz), 44.5, 43.0, 41.4 (d, J = 5.1 Hz), 35.3 (d, J = 9.2 Hz), 32.8, 25.7 (d, J = 4.2 Hz), 25.1 (q, J = 34.9 Hz), 22.2 (d, J = 4.3 Hz), 21.8 (q, J = 29.2 Hz), 13.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.00 (d, J = 7.9 Hz, 1.2F), -68.86 (dd, J = 13.1, 8.0 Hz, 1F), -101.41 to -102.08 (m, 0.9F), -106.23 (tt, J = 15.6, 7.5 Hz), -106.69 (tt, J = 15.7, 7.4 Hz).

HRMS (ESI, m/z): calcd for $C_{18}H_{21}F_5I_3O_2$ $[M+H]^+$: 744.8596, found: 744.8599.

4-(4,4,4-trifluoro-1,3-diiodobutyl)benzyl 2-(4-chlorophenoxy)-2-

methylpropanoate (5r)



5r

The product **5r** was purified by column chromatography as a colorless liquid (94.6 mg, 71%, 1.5:1 dr).

TLC: R_f = 0.38 (Hexane/EtOAc = 20:1).

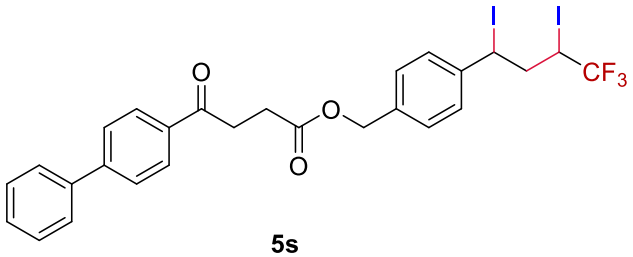
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.25 – 7.21 (m, 2H), 7.17 – 7.09 (m, 2H), 6.74 – 6.66 (m, 2H), 5.30 – 5.23 (m, 1H), 5.16 (s, 2H), 4.60 – 4.50 (m, 0.6H, major), 3.68 – 3.60 (m, 0.4H, minor), 2.99 – 2.91 (m, 0.4H, minor), 2.87 – 2.75 (m, 1H), 2.21 – 2.10 (m, 0.6H, major), 1.61 (s, 2H), 1.60 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 173.7, 154.0, 142.8, 140.56, 136.0, 135.8, 129.2, 129.1, 129.1, 127.5, 127.5, 123.6 (q, J = 276.3 Hz), 120.4, 120.3, 79.6, 79.5, 66.5, 44.3, 42.8, 32.0, 25.4, 24.9, 25.0 (q, J = 31.6 Hz), 21.7 (q, J = 31.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.95 (d, J = 7.8 Hz, 1.5F), -68.78 (d, J = 7.6 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{21}H_{21}ClF_3I_2O^+$ $[M+H]^+$: 666.9221, found: 666.9225.

4-(4,4,4-trifluoro-1,3-diiodobutyl)benzyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (5s)



5s

The product **5s** was purified by column chromatography as a colorless liquid (79.1 mg, 56%, 1.4:1 dr).

TLC: R_f = 0.26 (Hexane/EtOAc = 15:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.3, 2.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.37 – 7.33 (m,

2H), 5.31 – 5.24 (m, 1H), 5.14 (s, 2H), 4.60 – 4.51 (m, 0.6H, major), 3.68 – 3.59 (m, 0.4H, minor), 3.38 (m, 2H), 3.03 – 2.91 (m, 0.4H, minor), 2.90 – 2.84 (m, 2H), 2.24 – 2.13 (m, 0.8H, major), 2.83 – 2.77(m, 0.5H, minor).

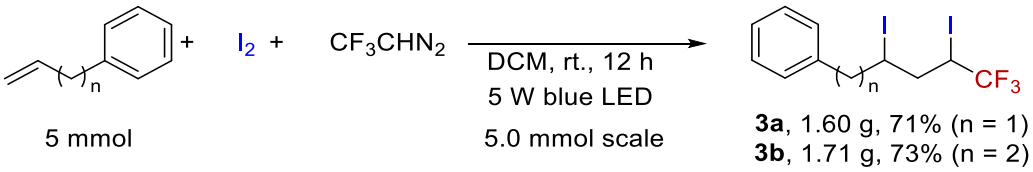
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 172.7, 172.7, 146.0, 142.3, 140.2, 139.8, 136.8, 136.6, 135.2, 129.0, 129.0, 128.8, 128.7, 128.3, 127.5, 127.5, 127.3, 123.5 (q, J = 276.9 Hz), 65.8, 65.8, 44.33, 42.96, 33.4, 33.4, 32.2, 28.3, 25.0 (q, J = 31.6 Hz), 21.8 (q, J = 31.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.96 (d, J = 7.5 Hz, 1.4F), -68.81 (d, J = 8.1 Hz, 1F).

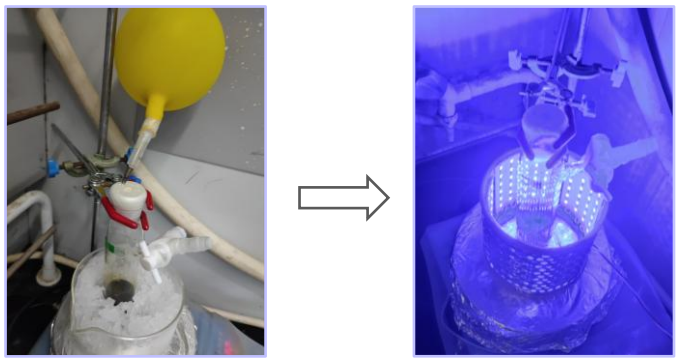
HRMS (ESI, m/z): calcd for $C_{27}H_{24}F_3I_2O_3^+$ $[M+H]^+$: 706.9767, found: 706.9770.

6. Follow-up chemistry

6.1 Gram scale preparation of product 3a, 3b



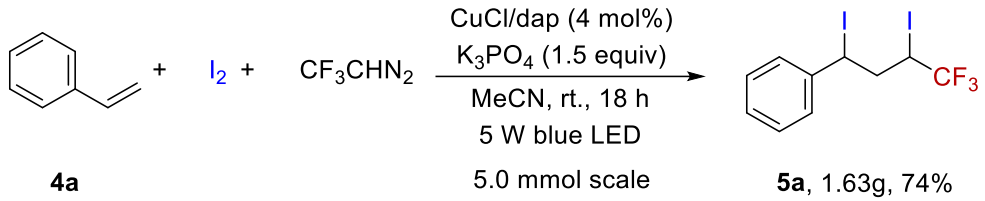
3a, 1.60 g, 71% (n = 1)
3b, 1.71 g, 73% (n = 2)



To a 250-mL Schlenk flask equipped with a magnetic stir bar were added corresponding olefin (5.0 mmol), I_2 (2.28 g, 9 mmol) were dissolved in DCM (20 mL) under N_2 atmosphere. Then CF_3CHN_2 (16.7 mL, 10 mmol) were added with syringe at 0 °C. The mixture was stirred at 0 °C for 30 minutes and then irradiated under 30 W blue LED for 24 hours. Upon the completion of reaction, the mixture was directly subjected to be concentrated in vacuo and purified by flash chromatography on silica gel with petroleum ether as an eluent to give the product (**3a**, 1.60g, 71%; **3b**, 1.71g,

73%).

6.2 Gram scale preparation of product 5a



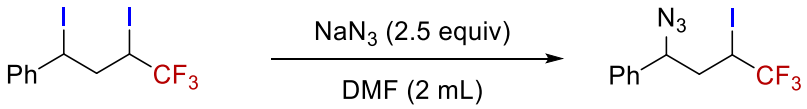
4a 5.0 mmol scale **5a**, 1.63g, 74%

To a 250-mL Schlenk flask equipped with a magnetic stir bar were added corresponding I_2 (2.28 g, 9 mmol), CuCl (4 mol%), dap (4 mol%) were dissolved in MeCN (20 mL) under N_2 atmosphere (Note: solids should be completely dissolved). Then olefin (5.0 mmol) and CF_3CHN_2 (16.7 mL, 10 mmol) were added with syringe at 0 °C. The mixture was stirred at 0 °C for 30 minutes and then irradiated under 30 W blue LED for 24 hours. Upon the completion of reaction, the mixture was directly subjected to be concentrated in vacuo and purified by flash chromatography on silica gel with petroleum ether as an eluent to give the product **5a** (1.63g, 74%).

6.3 Synthetic transformations of the product 3a or 3b or 5a.

6.3.1 Nucleophilic substitution reaction

(1-azido-4,4,4-trifluoro-3-iodobutyl)benzene (6a)



5a 0.2 mmol **6a** 56.8 mg, 80%

5a (89.2 mg, 0.2 mmol) was dissolved in 2.0 mL DMF in a penicillin bottle. The reactants, NaN_3 (40.5 mg, 0.50 mmol) were added separately, and the reaction was allowed to proceed for 24 hours. The mixture was then partitioned between water and EtOAc, the organic layer was collected, dried over Na_2SO_4 evaporated under vacuum and purified by flash chromatography with Pe/EA (10:1) to furnish 56.8 mg (80%, 12.4:1 dr) of **6a** as a colorless oil.

TLC: R_f = 0.34 (PE/EA = 30:1).

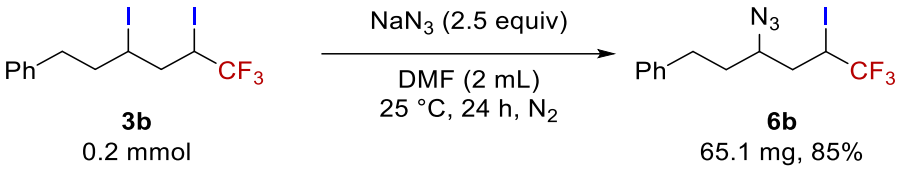
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 5H), 4.69 (dd, *J* = 9.5, 5.8 Hz, 1H), 3.77 – 3.67 (m, 1H), 2.43 – 2.29 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.5, 129.5, 127.2, 124.3 (q, *J* = 276.5 Hz), 65.2, 39.1, 18.7 (q, *J* = 32.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.78 (d, *J* = 7.7 Hz, 12.4F), -68.91 (d, *J* = 7.6 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{10}H_{10}F_3IN_3^+$ $[M+H]^+$: 355.9872, found: 355.9877.

(3-azido-6,6,6-trifluoro-5-iodohexyl)benzene (6b)



3b
0.2 mmol

6b
65.1 mg, 85%

3b (94.3 mg, 0.2 mmol) was dissolved in 2.0 mL DMF in a penicillin bottle. The reactants, NaN_3 (40.5 mg, 0.50 mmol) were added separately, and the reaction was allowed to proceed for 24 hours. The mixture was then partitioned between water and EtOAc, the organic layer was collected, dried over Na_2SO_4 evaporated under vacuum and purified by flash chromatography with Hexane/EtOAc (10:1) to furnish 65.1 mg (85%) of **6b** as a colorless oil.

TLC: R_f = 0.24 (Hexane/EtOAc = 10:1).

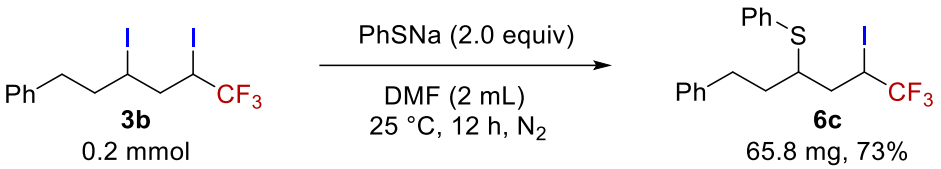
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.22 (dd, *J* = 18.4, 7.4 Hz, 3H), 4.23 (h, *J* = 7.6 Hz, 1H), 3.55 – 3.48 (m, 1H), 2.95 – 2.60 (m, 2H), 2.22 (t, *J* = 7.2 Hz, 2H), 1.88 – 1.73 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 128.8, 128.5, 126.5, 124.7 (q, *J* = 276.6 Hz), 61.5, 38.9, 35.5, 32.0, 17.2 (q, *J* = 31.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.17 (d, *J* = 7.8 Hz).

HRMS (ESI, m/z): calcd for $C_{12}H_{14}F_3IN_3^+$ $[M+H]^+$: 384.0185, found: 384.0180.

phenyl(6,6,6-trifluoro-5-iodo-1-phenylhexan-3-yl)sulfane (6c)



Sodium thiophenolate (53.1 mg, 0.4 mmol), **3b** (94.1 mg, 0.2 mmol) were added to 2.0 mL dry DMF. The resulting mixture was stirred at room temperature for 24 hours. The mixture was then partitioned between water and EtOAc, the organic layer was collected, dried over Na_2SO_4 evaporated under vacuum and purified by flash chromatography with PE/EA (100:1) to furnish 65.8 mg (73%, 3.5:1 dr) of **6c** as a colorless oil.

TLC: R_f = 0.55 (PE/EA = 100:1).

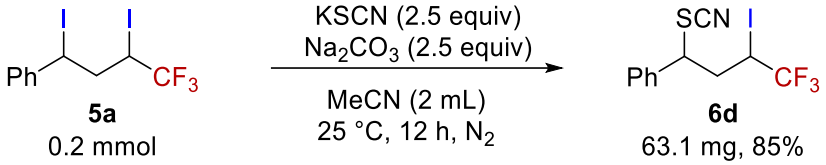
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.34 – 7.24 (m, 5H), 7.23 – 7.12 (m, 3H), 4.88 – 4.74 (m, 0H), 4.37 – 4.27 (m, 1H), 3.26 – 3.11 (m, 1H), 2.99 – 2.76 (m, 2H), 2.27 – 1.72 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 134.2, 132.1, 129.3, 128.6, 128.6, 128.3, 126.3, 48.5, 37.5 (d, J = 14.9 Hz), 33.1, 23.3 (q, J = 31.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.35 (d, J = 7.4 Hz, 3.5F), -68.53 (d, J = 8.2 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{18}H_{19}F_3IS^+$ $[M+H]^+$: 451.0204, found: 451.0209.

(4,4,4-trifluoro-3-iodo-1-thiocyanatobutyl)benzene (6d)



A flame-dried Schlenk flask was charged with **5a** (89.2mg, 0.20 mmol), NaSCN (40.5 mg, 0.50 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol), dissolved in anhydrous MeCN (2.0 mL, 0.1 M) and magnetically stirred at room temperature (25 °C) for 12 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes to hexanes / EtOAc 10:1) to yield 63.1 mg (85%, 1:4.2 dr) of **6d** as a colorless oil

TLC: R_f = 0.49 (PE/EA = 10:1).

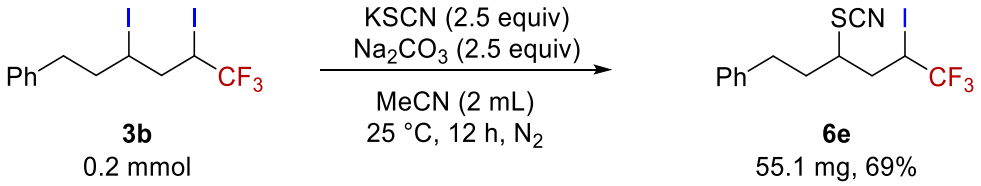
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 5H), 4.63 (dd, *J* = 11.7, 4.1 Hz, 1H), 4.51 – 4.39 (m, 1H), 3.66 (m, 1H), 2.85 – 2.56 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.4, 134.4, 130.1, 129.9, 129.6, 129.5, 127.6, 127.3, 124.0 (q, *J* = 276.7 Hz), 110.5, 109.5, 38.4, 38.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.10 (d, *J* = 7.8 Hz, 1F), -69.01 (d, *J* = 7.8 Hz, 4.2F).

HRMS (ESI, m/z): calcd for $C_{11}H_{10}F_3INS^+[M+H]^+$: 371.9531, found:371.9533.

(6,6,6-trifluoro-5-iodo-3-thiocyanatohexyl)benzene (6e)



3b
0.2 mmol

6e
55.1 mg, 69%

A flame-dried Schlenk flask was charged with **3b** (93.2 mg, 0.20 mmol), NaSCN (40.5 mg, 0.50 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol), dissolved in anhydrous MeCN (2.0 mL, 0.1 M) and then magnetically stirred at room temperature (25 °C) for 12 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (Hexanes to Hexanes / EtOAc 10:1) to yield 55.1 mg (69%, dr 9.6:1) of **6e** as a colorless oil

TLC: R_f = 0.47 (Hexanes / EtOAc = 10:1).

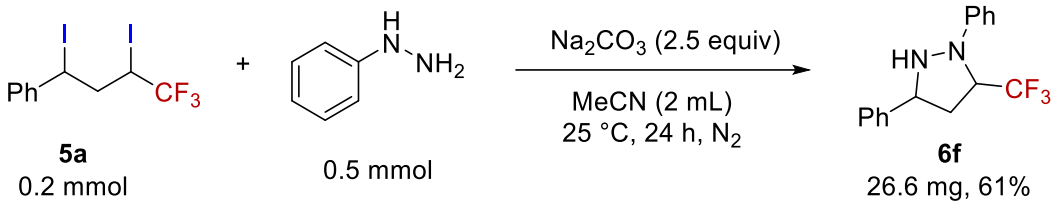
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.23 (dd, *J* = 22.6, 7.4 Hz, 3H), 4.29 – 4.20 (m, 1H), 3.17 – 3.09 (m, 1H), 3.04 – 2.90 (m, 1H), 2.81 – 2.72 (m, 1H), 2.53 – 2.36 (m, 2H), 2.11 – 1.92 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.3, 128.9, 128.5, 125.9 (q, *J* = 276.6 Hz), 109.5, 48.7, 39.8, 34.7, 32.6, 18.2 (q, *J* = 31.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.21 (d, *J* = 7.6 Hz, 9.6F), -68.76 (d, *J* = 7.7 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{13}H_{14}F_3ISN^+$ $[M+H]^+$: 399.9844, found: 399.9846.

1,3-diphenyl-5-(trifluoromethyl)pyrazolidine (6f)



A flame-dried Schlenk flask was charged with **5a** (89.2 mg, 0.20 mmol), phenylhydrazine (49.3 μL, 54.1 mg, 0.5 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol), dissolved in anhydrous MeCN (2.0 mL, 0.1 M) and magnetically stirred at room temperature (25 °C) for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (Hexanes to Hexanes / EtOAc 30:1) to yield 26.6 mg (61%) of **6f** as a colorless oil.

TLC: R_f = 0.21 (PE/EA = 30:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 4H), 7.34 – 7.30 (m, 1H), 7.23 – 7.19 (m, 2H), 7.08 – 7.04 (m, 2H), 6.85 – 6.81 (m, 1H), 4.90 (t, J = 7.2 Hz, 1H), 4.59 (d, J = 7.5 Hz, 1H), 3.91 – 3.80 (m, 1H), 2.92 – 2.84 (m, 1H), 2.50 – 2.40 (m, 1H).

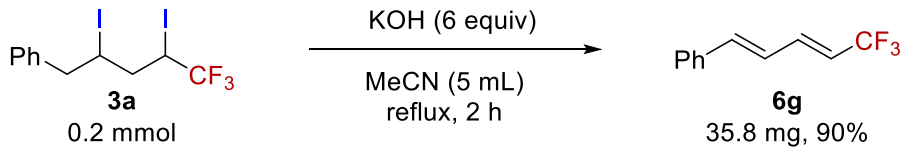
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.6, 142.6, 129.2, 128.8, 127.6, 125.8, 119.5, 114.1, 67.2, 59.4 (q, J = 31.4 Hz), 38.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -74.84 (d, J = 8.2 Hz).

HRMS (ESI, m/z): calcd for $C_{16}H_{16}F_3N_2^+$ $[M+H]^+$: 293.1266, found: 293.1264.

6.3.2 Elimination reaction

(5,5,5-trifluoropenta-1,3-dien-1-yl)benzene (6g)



A Schlenk flask was charged with **3a** (90.3 mg, 0.20 mmol), KOH (67.3 mg, 1.20 mmol), dissolved in MeCN (5 mL) and magnetically stirred under reflux for 2 h. The reaction was monitored by TLC. Afterwards the reaction mixture was allowed to cool down to room temperature, acidified with HCl (1.0 M), subsequently neutralized with

saturated aqueous $NaHCO_3$ and extracted three times with EtOAc. The combined organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexanes) to yield 42.2 mg (35.8 mg, 90%) of **6g** as a colorless oil.

TLC: R_f = 0.8 (Hexanes).

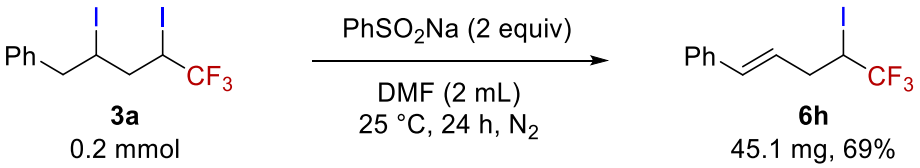
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.39 – 7.35 (m, 2H), 7.33 – 7.30 (m, 1H), 6.94 – 6.88 (m, 1H), 6.85 – 6.74 (m, 2H), 5.85 – 5.77 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.5, 137.7 (d, J = 6.9 Hz), 137.6 (d, J = 7.1 Hz), 136.0, 129.1, 129.0, 127.2, 125.0, 118.5 (q, J = 33.6 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.20 (d, J = 6.9 Hz).

HRMS (ESI, m/z): calcd for $C_{11}H_{10}F_3^+$ $[M+H]^+$: 199.0735, found: 199.0731.

(5,5,5-trifluoro-4-iodopent-1-en-1-yl)benzene (6h)



A flame-dried Schlenk flask was charged with **3a** (90.3 mg, 0.20 mmol), sodium benzenesulfinate (65.7 mg, 0.40 mmol), dissolved in anhydrous DMF (2.0 mL, 0.1 M) and magnetically stirred at room temperature (25 °C) for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (Hexanes) to yield 45.1 mg (69%) of **6h** as a colorless oil.

TLC: R_f = 0.65 (Hexane).

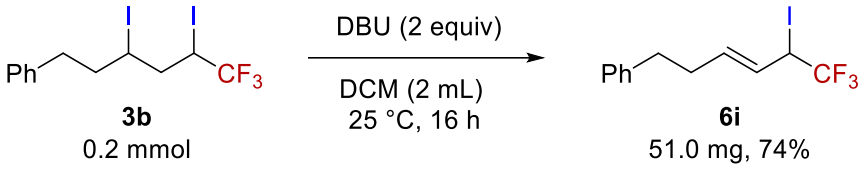
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 6.54 (dd, J = 15.7, 1.5 Hz, 1H), 6.12 (m, 1H), 4.30 – 4.20 (m, 1H), 3.00 – 2.92 (m, 1H), 2.85 – 2.76 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.6, 134.3, 128.7, 127.8, 126.4, 125.3 (q, J = 276.2 Hz), 125.2, 36.6, 23.5 (q, J = 30.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.57 (d, J = 7.3 Hz).

HRMS (ESI, m/z): calcd for $C_{11}H_{11}F_3I^+$ $[M+H]^+$: 326.9858, found: 326.9859

(E)-(6,6,6-trifluoro-5-iodohex-3-en-1-yl)benzene (6i)



3b
0.2 mmol

6i
51.0 mg, 74%

3b (93.3 mg, 0.2 mmol) was dissolved in 2.0 mL DCM in a reaction tube, 0.4 mmol of 1,8-diazabicyclo[5.4.0]undecane-7-ene (DBU, 2equiv) was added and the mixture was stirred at 25 °C (**Note:** The reaction must be protected from light). The mixture was then evaporated under vacuum and purified by flash chromatography with petroleum ether to furnish 51.0 mg (74%) of **6i** as a colorless oil.

TLC: R_f = 0.70 (Hexane).

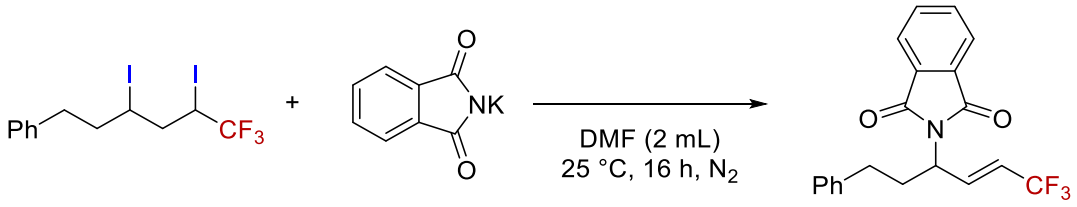
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, J = 7.5 Hz, 2H), 7.18 (dd, J = 29.4, 7.3 Hz, 3H), 5.86 (dt, J = 14.1, 6.8 Hz, 1H), 5.69 (dd, J = 15.2, 10.3 Hz, 1H), 4.84 (dt, J = 15.5, 7.8 Hz, 1H), 2.72 (t, J = 7.6 Hz, 2H), 2.41 (dt, J = 12.7, 6.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8, 137.3, 133.3, 128.5, 126.1, 124.8, 123.5 (q, J = 276.2 Hz), 34.8, 33.7, 21.9 (q, J = 33.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.11 (d, J = 7.8 Hz).

HRMS (ESI, m/z): calcd for $C_{12}H_{13}F_3I^+$ $[M+H]^+$: 341.0014, found: 341.0010.

2-(6,6,6-trifluoro-1-phenylhex-4-en-3-yl)isoindoline-1,3-dione (6j)



3b
0.2 mmol

0.4 mmol

6j
65.8 mg, 74%

Sodium thiophenolate (53.1 mg, 0.4 mmol), **3b** (94.1 mg, 0.2 mmol) were added to 1.0 mL dry DMF. The resulting mixture was stirred at room temperature for 24 hours. The mixture was then partitioned between water and EtOAc, the organic layer was collected, dried over Na_2SO_4 evaporated under vacuum and purified by flash

chromatography with Hexane/EtOAc (20:1) to furnish 65.8 mg (74%) of **6j** as a colorless oil.

TLC: R_f = 0.35 (Hexane/EtOAc = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H), 7.75 – 7.67 (m, 2H), 7.22 – 7.03 (m, 2H), 5.84 – 5.75 (m, 1H), 4.88 (m, 1H), 2.72 – 2.50 (m, 3H), 2.26 – 2.15 (m, 1H).

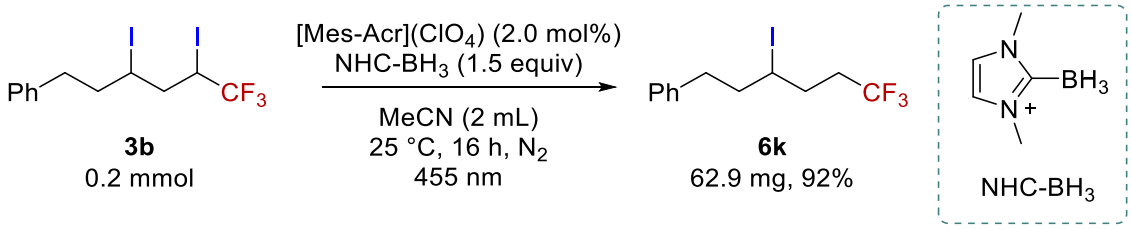
^{13}C NMR (151 MHz, $CDCl_3$) δ 167.7, 140.0, 137.0 (q, J = 6.4 Hz), 134.2, 131.6, 128.5, 128.3, 126.2, 123.4 121.0 (q, J = 34.1 Hz), 51.2, 32.7, 32.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -64.37 (d, J = 6.2 Hz).

HRMS (ESI, m/z): calcd for $C_{20}H_{17}F_3NO_2^+$ $[M+H]^+$: 360.1211, found: 360.1206.

6.3.3 Radical reactions

(6,6,6-trifluoro-3-iodohexyl)benzene (6k)



A flame-dried Schlenk flask was charged with **3b** (93.2 mg, 0.20 mmol), NHC-BH_3 (25.1 mg, 0.3 mmol), [Mes-Acr](ClO_4) (2 mol%), dissolved in anhydrous MeCN (2.0 mL, 0.1 M) under N_2. The reaction mixture was stirred at room temperature (25 °C) under blue LED irradiation. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (Hexanes) to yield 62.9 mg (92%) of **6k** as a colorless oil.

TLC: R_f = 0.65 (Hexanes).

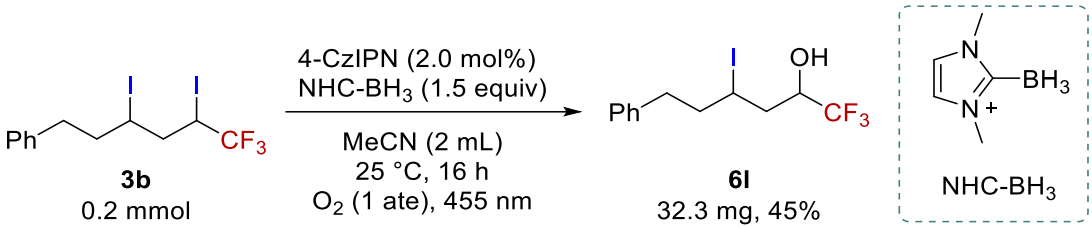
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 2H), 7.24 – 7.21 (m, 3H), 3.99 – 3.97 (m, 1H), 2.93 – 2.88 (m, 1H), 2.76 – 2.73 (m, 1H), 2.43 – 2.40 (m, 1H), 2.24 – 2.17 (m, 2H), 2.08 – 1.96 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 129.6, 128.7, 128.6, 126.8 (q, J = 276.5 Hz), 42.3, 35.6, 35.0, 34.3 (q, J = 28.6 Hz), 33.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -65.82 (t, J = 10.7 Hz).

HRMS (ESI, m/z): calcd for $C_{12}H_{15}F_3I^+$ $[M+H]^+$: 343.0171, found: 343.0175.

1,1,1-trifluoro-4-iodo-6-phenylhexan-2-ol (6l)



A flame-dried Schlenk flask was charged with **3b** (93.2 mg, 0.20 mmol), NHC-BH_3 (25.1 mg, 0.3 mmol), 4-CzIPN (2 mol%), dissolved in anhydrous MeCN (2.0 mL, 0.1 M) under O_2. The reaction mixture was stirred at room temperature (25 °C) under blue LED irradiation. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (Hexanes to Hexanes/EtOAc = 10:1) to yield 32.3 mg (45%, 4.3:1 dr) of **6l** as a white solid.

TLC: R_f = 0.31 (Hexanes/EtOAc = 15:1).

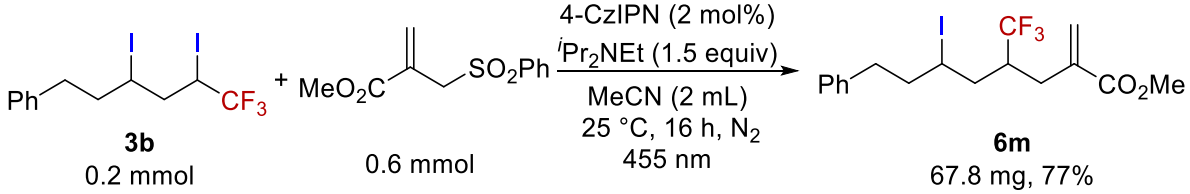
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 6.6 Hz, 3H), 4.36 – 4.29 (m, 1H), 4.28 – 4.16 (m, 1H), 2.92 (m, 1H), 2.81 – 2.68 (m, 1H), 2.40 – 2.22 (m, 2H), 2.20 – 2.12 (m, 1H), 2.10 – 1.83 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 141.2, 128.8, 128.7, 128.5, 126.3, 126.3, 124.6 (q, J = 276.5 Hz), 71.4, 68.1, 71.1 (q, J = 31.4 Hz), 68.0 (q, J = 31.4 Hz), 39.7, 39.3, 35.8, 35.5, 32.1, 31.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -79.46 (d, J = 6.6 Hz, 4.3F), -79.71 (d, J = 6.5 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{12}H_{15}F_3IO^+$ $[M+H]^+$: 359.0120, found: 359.0127.

methyl 6-iodo-2-methylene-8-phenyl-4-(trifluoromethyl)octanoate (6m)



3b (0.2 mmol), methyl 2-((phenylsulfonyl)methyl)acrylate (0.6 mmol), ^{i}Pr$_2$NEt (0.3 mmol) and 4-CzIPN (2 mol%) were dissolved in 2.0 mL MeCN in a penicillin

bottle under N_2. The reaction mixture was then stirred overnight under blue LED irradiation. The mixture was then evaporated under vacuum and purified by flash chromatography with Hexane/EtOAc (10:1) to furnish 67.8 mg (77%, 1.1:1 dr) of **6m** as a colorless oil.

TLC: R_f = 0.40 (Hexane/EtOAc = 10:1).

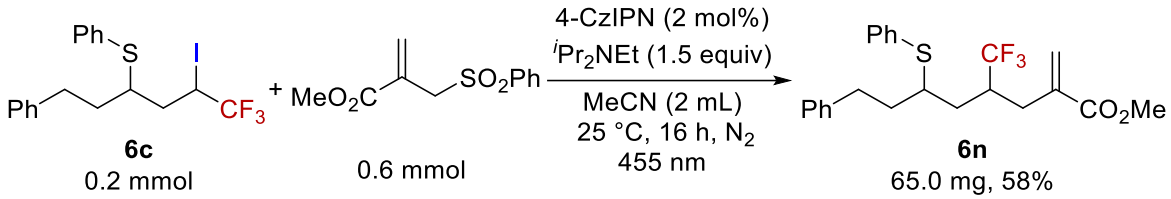
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.23 – 2.19 (m, 3H), 6.25 (d, J = 82.7 Hz, 1H), 5.63 (d, J = 50.1 Hz, 1H), 4.12– 4.08 (m, 1H), 3.77 (d, J = 20.8 Hz, 3H), 2.96 – 2.78 (m, 2H), 2.77 – 2.58 (m, 2H), 2.36 – 2.23 (m, 1H), 2.19 – 2.10 (m, 1H), 2.04 – 1.93 (m, 2H), 1.77 – 1.70 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.72, 140.48, 140.38, 136.61, 136.15, 128.8, 128.6, 128.5, 128.5, 127.75 (q, J = 277.1 Hz), 126.3, 126.2, 52.2, 52.2, 42.2 (q, J = 25.3 Hz), 42.2, 39.8, 39.2, 35.6, 35.4, 35.3, 33.8, 31.8 (q, J = 3.3 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.15 (d, J = 8.5 Hz, 1.1F), -70.34 (d, J = 8.9 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{17}H_{21}F_3IO_2^+$ $[M+H]^+$: 441.0538, found: 441.0540.

methyl 2-methylene-8-phenyl-6-(phenylthio)-4-(trifluoromethyl)octanoate (6n)



6c (0.2 mmol), methyl 2-((phenylsulfonyl)methyl)acrylate (0.6 mmol), ^{i}Pr$_2$NEt (0.3 mmol) and 4-CzIPN (2 mol%) were dissolved in 2.0 mL MeCN in a penicillin bottle under N_2. The reaction mixture was then stirred overnight under blue LED irradiation. The mixture was then evaporated under vacuum and purified by flash chromatography with Hexane/EtOAc (10:1) to furnish 65.0 mg (58%, 1:1.3 dr) of **6n** as a colorless oil.

TLC: R_f = 0.43 (Hexane/EtOAc = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 1H), 7.39 – 7.35 (m, 1H), 7.31 (dd, J = 14.2, 7.2 Hz, 5H), 7.24 – 7.19 (m, 1H), 7.16 (d, J = 7.5 Hz, 2H), 6.25 (d, J = 29.3 Hz,

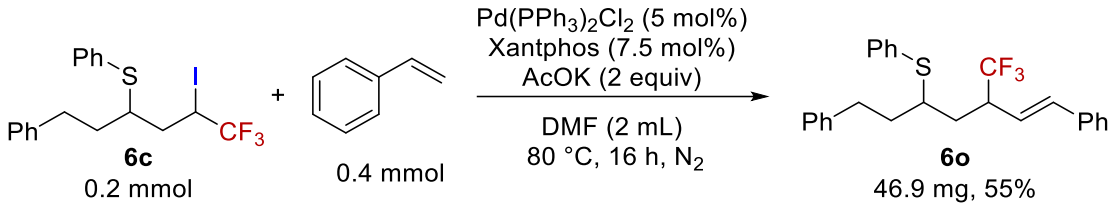
1H), 5.62 (d, J = 8.3 Hz, 1H), 3.79 (s, 1H), 3.74 (s, 2H), 3.23 – 3.13 (m, 1H), 2.99 – 2.87 (m, 1H), 2.86 – 2.77 (m, 2H), 2.72 – 2.65 (m, 1H), 2.43 – 2.26 (m, 1H), 2.01 – 1.81 (m, 3H), 1.70 – 1.59 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 141.4, 136.9, 136.5, 134.2, 132.9, 133.4, 132.6, 129.0, 128.5, 128.4, 128.3, 127.4, 127.3, 126.0, 126.0, 52.1, 52.0, 46.9, 45.5, 39.6 (q, J = 25.3 Hz), 37.0, 36.4, 33.5, 32.8, 32.7, 32.2, 32.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.07 (d, J = 9.0 Hz, 1F), -70.20 (d, J = 9.1 Hz, 1.3F).

HRMS (ESI, m/z): calcd for $C_{23}H_{26}F_3O_2S^+$ $[M+H]^+$: 423.1606, found: 423.1610.

(1,7-diphenyl-5-(trifluoromethyl)hept-6-en-3-yl)(phenyl)sulfane (6o)



6c (0.2 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), Xantphos (7.5 mol%) and AcOK (2 equiv) were dissolved in 2.0 mL DMF in a penicillin bottle under N_2. The resulting mixture was stirred at 80 °C for 16 hours. The mixture was then partitioned between water and EtOAc, the organic layer was collected, dried over Na_2SO_4 evaporated under vacuum and purified by flash chromatography with hexane to furnish 46.9 mg (55%, 1.5:1 dr) of **6o** as a colorless oil.

TLC: R_f = 0.32 (Hexane).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.07 (m, 15H), 6.45 (d, J = 15.9 Hz, 0.6H, major), 6.26 (d, J = 15.9 Hz, 0.4H, minor), 5.90 – 5.85 (m, 0.6H, major), 5.78 – 5.74 (m, 0.4H, minor), 3.52 (m, 0.6H, major), 3.08 (m, 0.4H, minor), 3.02 – 2.73 (m, 3H), 2.03 (m, 0.6H), 1.99 – 1.91 (m, 1.6H), 1.86 (m, 2H).

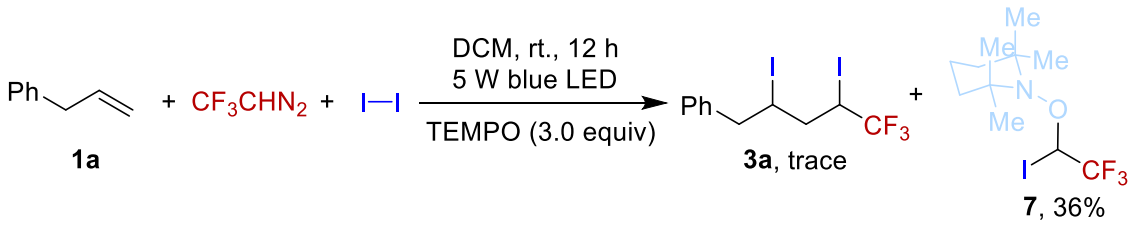
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 141.2, 137.1, 136.1, 136.1, 136.0, 134.1, 133.5, 133.1, 132.3, 129.0, 128.6, 128.6, 128.5, 128.4, 128.2, 127.5, 127.2, 126.6, 126.6, 126.2, 126.0, 122.1 (q, J = 2.6 Hz), 121.7 (q, J = 2.6 Hz), 45.7 (q, J = 27.2 Hz), 45.5, 44.5, 37.8, 35.0, 33.9, 33.0, 32.9, 32.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.47 (d, J = 9.0 Hz, 1.5F), -70.53 (d, J = 8.8 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{18}H_{18}F_3S^+$ $[M+H]^+$: 427.1707, found: 427.1711.

7. Investigation of the reaction mechanism

7.1 Radical trapping experiments with TEMPO.



1a **3a**, trace **7**, 36%

To a penicillin bottle equipped with magnetic stir bar, I_2 (51.8 mg, 0.2 mmol), CF_3CHN_2 (0.5 or 0.3 mmol), **1a** (0.6 mmol), TEMPO (96.6 mg, 0.6 mmol) were added under N_2, and the resulting mixture was irradiated under 5 W blue LED. Upon the completion of reaction, the mixture was directly subjected to be concentrated in vacuo and purified by flash chromatography on silica gel with petroleum ether as an eluent to afford the product **7**[1] as a colorless oil (26.3 mg, 36%).

TLC: R_f = 0.55 (Hexane).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.75 (q, J = 6.2 Hz, 1H), 1.55 – 1.48 (m, 6H), 1.24 – 1.20 (m, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 121.3 (q, J = 278.5 Hz), 68.2 (q, J = 33.7 Hz), 53.6, 40.8, 29.9, 16.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.97 (d, J = 5.8 Hz)

7.2 Radical clock experiment.

8 **9**

I_2 (0.35 mmol) were added into a 10 mL penicillin bottle with magneton under N_2, then CF_3CHN_2 (1.05 ml, 0.525 mmol) and olefin (0.2 mmol) were added into the bottle.

The mixture was stirred for 5 minutes and then irradiated under 5 W blue LED and stirred at room temperature for 12 hours. After the reaction, trace of the reaction supernatant was used for ^{19}F NMR spectroscopic analysis to determine the dr selectivity. Then, the other mixture was directly subjected to be concentrated in vacuo and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as an eluent to afford the desired product **9** as a yellow liquid (82.2 mg, 70%, 1.2:1 dr).

TLC: R_f = 0.29 (Hexane/EtOAc = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 10.7, 8.1 Hz, 2H), 7.35 (t, *J* = 6.7 Hz, 2H), 4.14 – 3.90 (m, 1H), 3.58 – 3.50 (m, 0.5H, major), 3.19 – 3.13 (m, 0.5H, minor), 3.48 (dt, *J* = 12.2, 6.7 Hz, 1H), 3.40 – 3.31 (m, 1H), 3.13 – 3.07 (m, 0.5H, major), 2.86 – 2.81 (m, 0.5H, minor), 3.07 – 3.01 (m, 1H), 3.01 – 2.91 (m, 1H), 2.61 (t, *J* = 10.1 Hz, 1H), 2.53 – 2.46 (m, 0.4H, minor), 2.40 – 2.32 (m, 0.6H, major), 2.44 (d, *J* = 3.1 Hz, 3H), 1.99 – 1.89 (m, 0.6H, major), 1.76 – 1.68 (m, 0.5H, minor), 1.76 – 1.68 (m, 0.6H, major), 1.53 – 1.46 (m, 0.4H, minor).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.1, 133.4, 130.0, 127.4, 124.3 (q, *J* = 277.3 Hz), 53.0, 52.5, 50.6, 50.2, 44.8, 43.9, 41.5, 31.2, 29.4, 22.0 (q, *J* = 31.4 Hz), 20.0 (q, *J* = 31.5 Hz), 21.6.

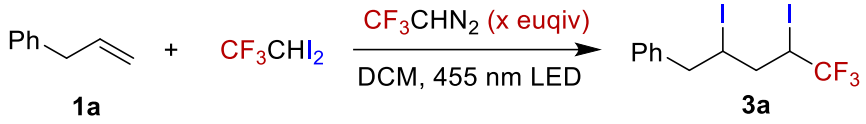
^{19}F NMR (565 MHz, $CDCl_3$) δ -68.50 (d, *J* = 8.0 Hz, 1.2F), -69.05 (d, *J* = 7.3 Hz, 1F).

HRMS (ESI, m/z): calcd for $C_{15}H_{19}F_3I_2N$ $[M+H]^+$: 587.9178, found: 587.9180.

7.3 Control experiments

CF_3CHN_2 (0 equiv, 0.2 equiv, 0.4 equiv, 0.8 equiv, 1.0 equiv) was added to a series of 10 mL penicillin vials containing magnets under N_2, then CF_3CHI_2[2] (0.35 mmol) and olefin (0.2 mmol) were added into the bottle. The mixture was stirred for 5 minutes and then irradiated under 5 W blue LED and stirred at room temperature for 12 hours. After the reaction, trace of the reaction supernatant was used for ^{19}F NMR spectroscopic analysis with $PhCF_3$ (0.1 mmol) as the internal standard to determine the yield. As shown in the table below, when the amount of CF_3CHN_2 added is 0 equiv, the reaction does not react. However, as the amount of CF_3CHN_2 increases, the yield of the reaction

gradually increases. Therefore, CF_3CHN_2 has an important role in the occurrence of this reaction.



x (equiv)	yield (%)
0	0
0.2	44
0.4	62
0.8	77
1.0	89

7.4 Light ON/OFF experiments and reaction monitoring.

7.4.1 Light ON/OFF experiments

According to standard procedure, the mixture was irradiated under blue LED for 1 hour at which point a reaction aliquot (20 μL) was taken via syringe for ^{19}F NMR analysis using $PhCF_3$ (0.1 mmol) as an internal standard. The light was switched off and the mixture was then stirred in the dark for another hour at which point a reaction aliquot (20 μL) was taken for ^{19}F NMR analysis. The blue LED was then switched ON and OFF and ON and OFF alternatively and ^{19}F NMR yields were calculated. (**Note:** When the reaction reached the 6^{th} hour, reaction aliquot (20 μL) was taken every two hours, and the light was kept on in 10 hours before the last sample was taken.) As shown in Figure S1, the yield increased faster at the beginning under light conditions, and in the absence of light, the yield still increased, albeit in a quite slow rate. The results suggest that a chain propagation involved in the reaction.

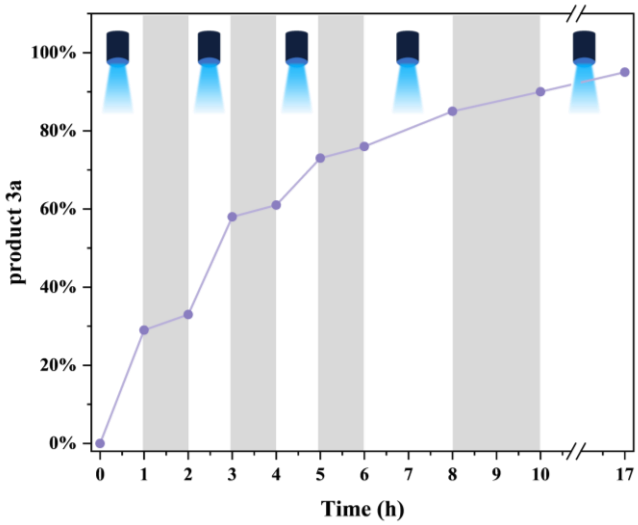


Figure S1 Light ON/OFF experiments

7.4.2 Reaction Monitoring

In accordance with established protocols, the mixture was exposed to blue LED irradiation for a duration of 1 h, 2 h, 3 h and so forth. Subsequently, an equivalent volume of the reaction (20 μL) was meticulously transferred via a syringe for ^{19}F NMR analysis with $PhCF_3$ (0.1 mmol) as the internal standard to determine the yield of the product and the consumption of CF_3CHN_2. (**Note:** The ratio of CF_3CHN_2 expresses the ratio of the amount of CF_3CHN_2 remaining in the reaction system over time to the amount of CF_3CHN_2 remaining after the initial CF_3CHN_2 has fully reacted with iodine; The ratio of product **3a** is the proportion of product **3a** that has been present over a given period to the total amount of the initial substrate.) As demonstrated in Figure S2, the product **3a** initially increases rapidly at the beginning, along with the consumption of CF_3CHN_2. The observation further supported that CF_3CHN_2 has a promoting effect in the reaction. Furthermore, an attempt was made to irradiate CF_3CHN_2 in the DCM; however, after a period of three hours, it was ascertained that there was only a minimal depletion of CF_3CHN_2, amounting to a mere 5%.

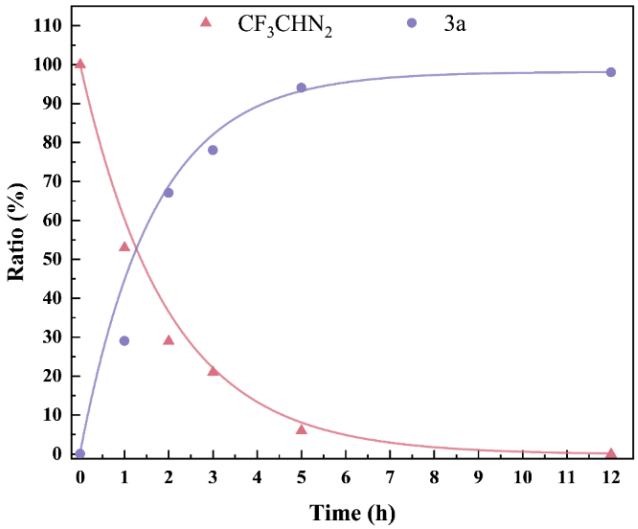


Figure S2 The distribution of product **3a** and CF_3CHN_2 content over time.

7.6 ^{19}F NMR at the start of the reaction of alkyl olefin 1a and aryl olefin 4a

I_2 (0.35 mmol) was added into a 10 mL penicillin bottle with magneton under N_2 (In the case of **1a)** or I_2 (0.35 mmol), CuCl (4 mol%) and dap (4 mol%) dissolved in MeCN (0.5 mL, 0.40 M), under N_2 (in the case of **4a**), then CF_3CHN_2 (1.05 ml, 0.525 mmol) and olefin **1a** or **4a** (0.2 mmol) were added into the bottle. The mixture was stirred for a period of five minutes, after which the internal standard ($PhCF_3$, 0.1 mmol) was added. The mixture was then analyzed by ^{19}F NMR spectroscopy using a micro reaction mixture to determine the amount of CF_3CHN_2 at the reaction's inception. The results demonstrate that in the alkyl olefin system, a significant quantity of CF_3CHN_2 persists prior to blue light irradiation (Figure S3, a), whereas in the aryl olefin system, no CF_3CHN_2 remains before blue light irradiation (Figure S3, b).

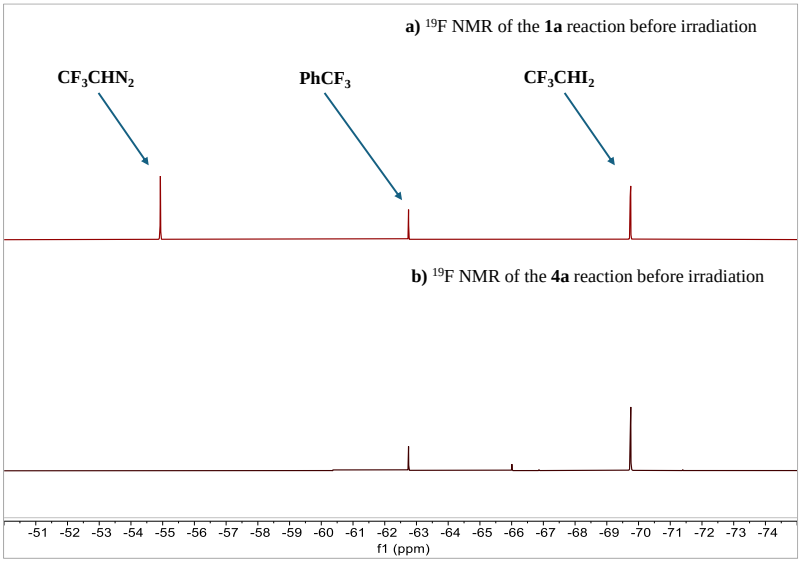
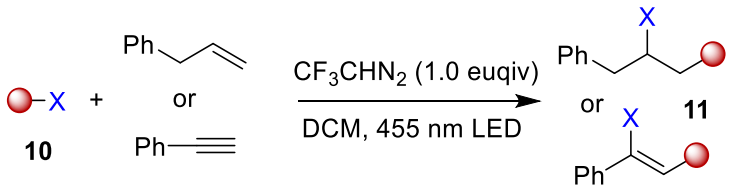


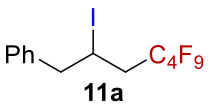
Figure S3 ^{19}F NMR of alkyl olefin **1a** and aryl olefin **4a** before blue light irradiation

7.7 General procedure and characterization data of products 11



Compound **10** (0.35 mmol) were added into a 10 mL penicillin bottle with magneton under N_2, then CF_3CHN_2 (1.05 ml, 0.525 mmol) and olefins or alkynes (0.2 mmol) were added into the bottle. The mixture was stirred for 5 minutes and then irradiated under 5 W blue LED and stirred at room temperature for 12 hours. Then, the mixture was directly subjected to be concentrated in vacuo and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as an eluent to afford the desired product **11**.

(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene (11a)[3]



11a

The product **11a** was purified by column chromatography as a colorless liquid (55.7 mg, 60%).

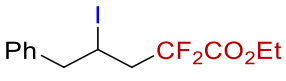
TLC: R_f = 0.43 (Hexane).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 3H), 7.26 – 7.21 (m, 2H), 4.55 – 4.46 (m, 1H), 3.37 – 3.30 (m, 1H), 3.28 – 3.20 (m, 1H), 3.02 – 2.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 129.0, 128.7, 127.4, 47.1 (d, J = 1.9 Hz), 40.8 (t, J = 20.8 Hz), 19.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -81.06 (t, J = 9.4 Hz), -111.98 (dt, J = 27.3, 12.8 Hz), -112.37 to -112.57 (m), -113.62 to -113.86 (m), -114.15 to -114.34 (m), -124.57 (q, J = 9.3 Hz), -125.92 (tt, J = 11.9, 6.0 Hz).

ethyl 2,2-difluoro-4-iodo-5-phenylpentanoate (11b)[3]



11b

The product **11b** was purified by column chromatography as a colorless liquid (53.7 mg, 73%).

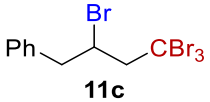
TLC: R_f = 0.43 (Hexane/EtOAc = 30:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 1H), 7.22 – 7.17 (m, 2H), 4.41 – 4.30 (m, 3H), 3.30 – 3.17 (m, 2H), 2.99 – 2.73 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4 (t, J = 32.2 Hz), 138.8, 129.0, 128.6, 127.2, 115.2 (t, J = 252.7 Hz), 63.3, 47.2, 44.4 (t, J = 23.4 Hz), 21.9 (t, J = 3.9 Hz), 13.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -101.53 (dd, J = 17.2, 13.2 Hz), -102.00 (dd, J = 17.2, 13.2 Hz), -106.12 (t, J = 16.8 Hz), -106.59 (t, J = 16.8 Hz).

(2,4,4,4-tetrabromobutyl)benzene (11c)[4]



11c

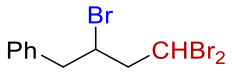
The product **11c** was purified by column chromatography as a colorless liquid (65.1 mg, 71%).

TLC: R_f = 0.53 (Hexane).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.29 (m, 3H), 4.37 (m, 1H), 3.85 (dd, *J* = 16.2, 4.7 Hz, 1H), 3.67 (dd, *J* = 16.2, 4.5 Hz, 1H), 3.53 (dd, *J* = 14.4, 5.2 Hz, 1H), 3.23 (dd, *J* = 14.4, 9.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 129.5, 128.6, 127.3, 65.8, 51.5, 46.0, 36.0.

(2,4,4-tribromobutyl)benzene (11d)



11d

The product **11d** was purified by column chromatography as a colorless liquid (53.9 mg, 73%).

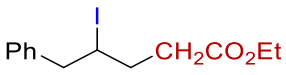
TLC: R_f = 0.57 (Hexane).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.27 – 7.23 (m, 2H), 5.95 – 5.87 (m, 1H), 4.42 – 4.32 (m, 1H), 3.35 – 3.18 (m, 2H), 2.89 – 2.77 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.0, 129.2, 128.7, 127.3, 53.4, 52.5, 44.9, 43.4.

HRMS (ESI, m/z): calcd for $C_{10}H_{12}Br_3^+$ $[M+H]^+$: 370.8469, found:370.8473.

ethyl 4-iodo-5-phenylpentanoate (11e)



11e

The product **11e** was purified by column chromatography as a colorless liquid (45.1 mg, 68%).

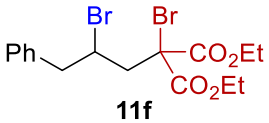
TLC: R_f = 0.52 (Hexane/EtOAc = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.19 (m, 5H), 4.74 – 4.61 (m, 1H), 4.46 – 4.16 (m, 2H), 3.35 (m, 2H), 2.40 – 1.97 (m, 4H), 1.31 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 138.8, 129.0, 128.6, 127.2, 62.0, 47.1, 43.8, 36.2, 23.8, 13.8.

HRMS (ESI, m/z): calcd for $C_{13}H_{18}IO_2^+$ $[M+H]^+$: 333.0352, found:333.035.

diethyl 2-bromo-2-(2-bromo-3-phenylpropyl)malonate (11f)



11f

The product **11f** was purified by column chromatography as a colorless liquid (61.9 mg, 71%).

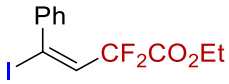
TLC: R_f = 0.35 (Hexane/EtOAc = 50:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.27 – 7.23 (m, 2H), 5.95 – 5.87 (m, 1H), 4.42 – 4.32 (m, 1H), 3.35 – 3.18 (m, 2H), 2.89 – 2.77 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 165.8, 137.6, 129.3, 128.5, 127.1, 63.5, 63.3, 61.7, 50.8, 46.1, 45.5, 13.8, 13.7.

HRMS (ESI, m/z): calcd for $C_{16}H_{21}Br_2O_4^+$ $[M+H]^+$: 436.9786, found: 436.9789.

ethyl 2,2-difluoro-4-iodo-4-phenylbut-3-enoate (11g)[5]



11g

The product **11g** was purified by column chromatography as a colorless liquid (57.7 mg, 82%, E/Z = 7.5:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 6.75 (t, *J* = 10.9 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6 (t, *J* = 33.3 Hz), 140.7, 133.1 (t, *J* = 28.4 Hz), 129.5, 128.1, 127.8 (t, *J* = 2.2 Hz), 110.9 (t, *J* = 250.1 Hz), 108.7 (t, *J* = 10.1 Hz), 63.1, 13.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -93.82 (d, *J* = 10.9 Hz, 7.5F) -98.09 (d, *J* = 11.5, 1F).

7.8 ^{19}F NMR analysis of the crude reaction with 11e

Compound **10** (0.35 mmol) was added into a 10 mL penicillin bottle with

magneton under N_2, then CF_3CHN_2 (0.45 ml, 0.2 mmol) and olefin **1a** (0.2 mmol) were added into the bottle. The mixture was stirred for 5 minutes and then irradiated under 5 W blue LED and stirred at room temperature for 12 hours. The mixture was stirred for 5 minutes, then illuminated under a 5 W blue LED light and stirred for 12 hours at room temperature. The internal standard ($PhCF_3$, 0.1 mmol) was added after completion of the reaction. The mixture was then analyzed by ^{19}F NMR spectroscopy using a micro reaction mixture to determine the amount of CF_3CHI_2.

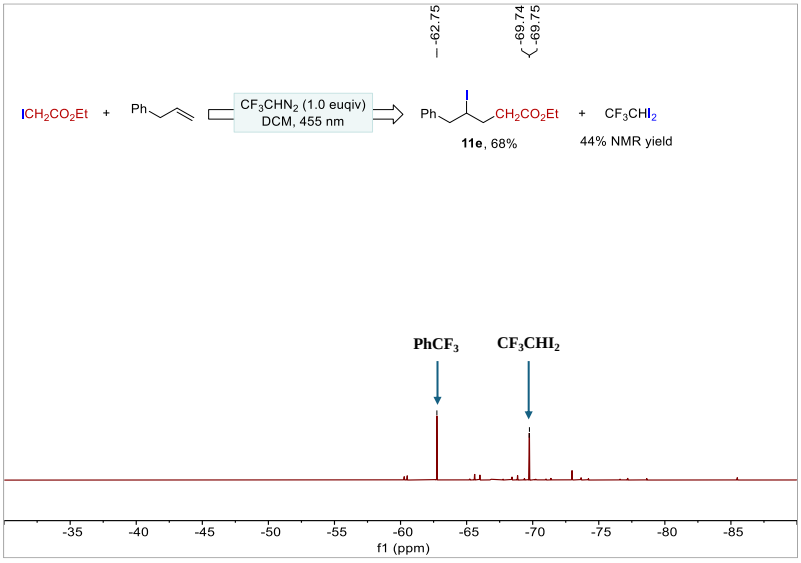
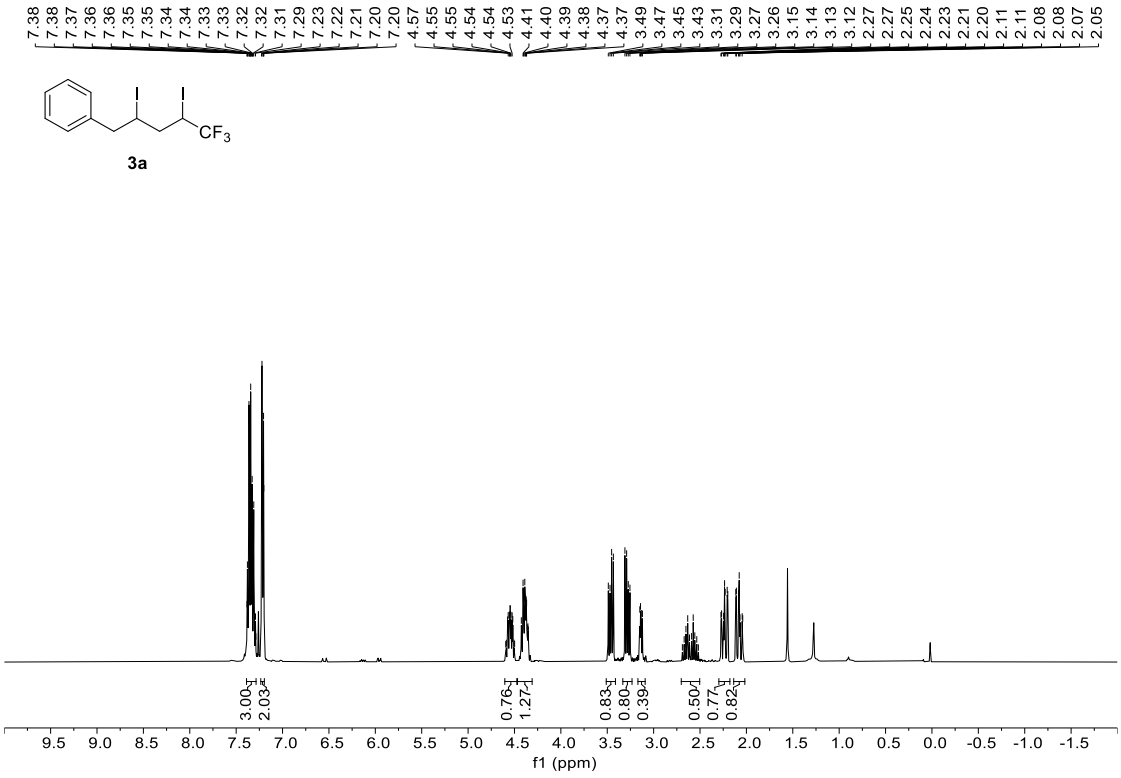


Figure S4 ^{19}F NMR analysis of the crude reaction with **11e**

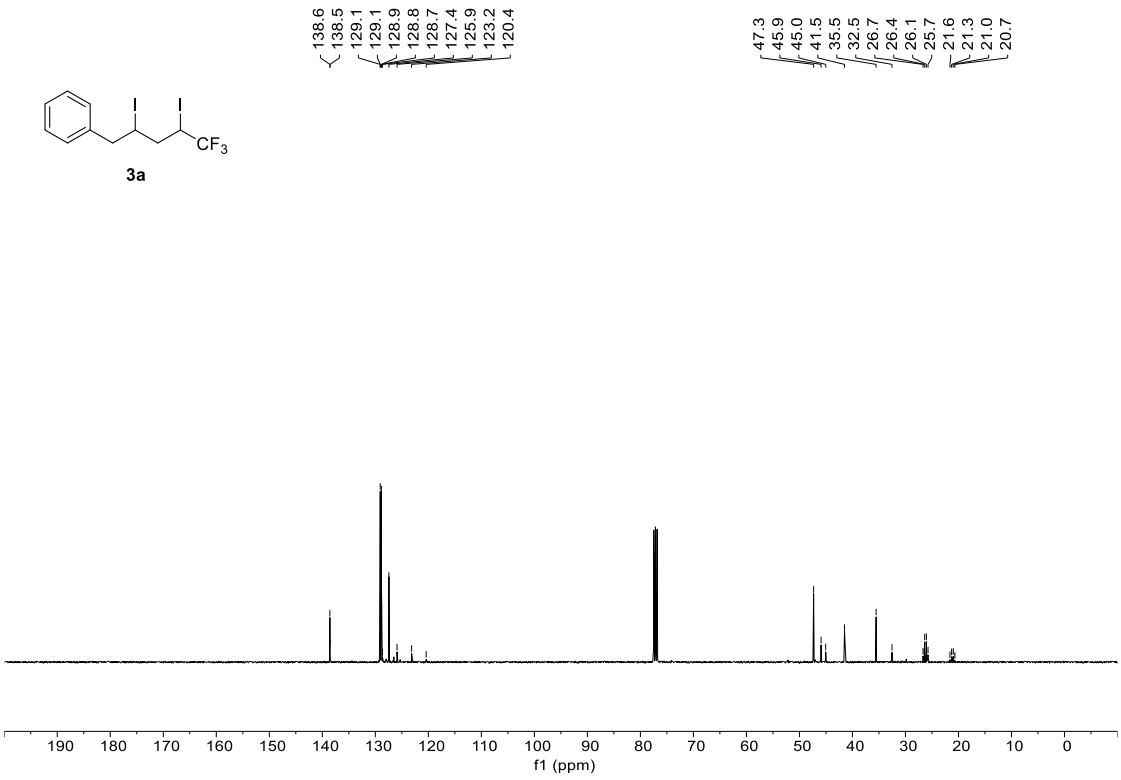
8. References

1. A. Hossian, S. Engl, E. Lutsker, O. Reiser, *ACS Catal*. 2019, **9**, 1103-1109
2. Y. Liu, T. Pang, W. Yao, F. Zhong and G. Wu, *Org. Lett.*, 2023, **25**, 1958-1962.
3. T. Tasnim, C. Ryan, M. L. Christensen, C. J. Fennell and S. P. Pitre, *Org. Lett.*, 2022, **24**, 446-450.
4. P. Bianchi, J. D. Williams and C. O. Kappe, *Green Chem.*, 2021, **23**, 2685-2693.
5. X. Li, S. He and Q. Song, *Org. Lett.*, 2021, **23**, 2994-2999.

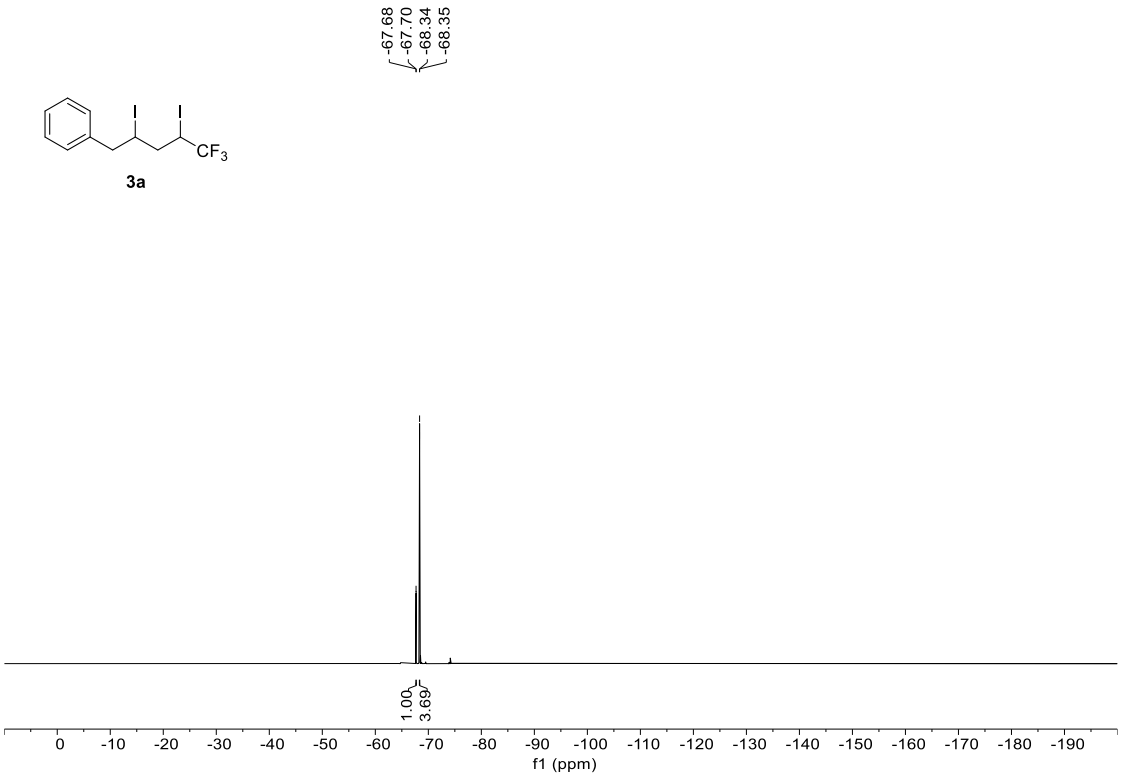
9. Copies of ^{1}H, ^{13}C, ^{19}F NMR spectra



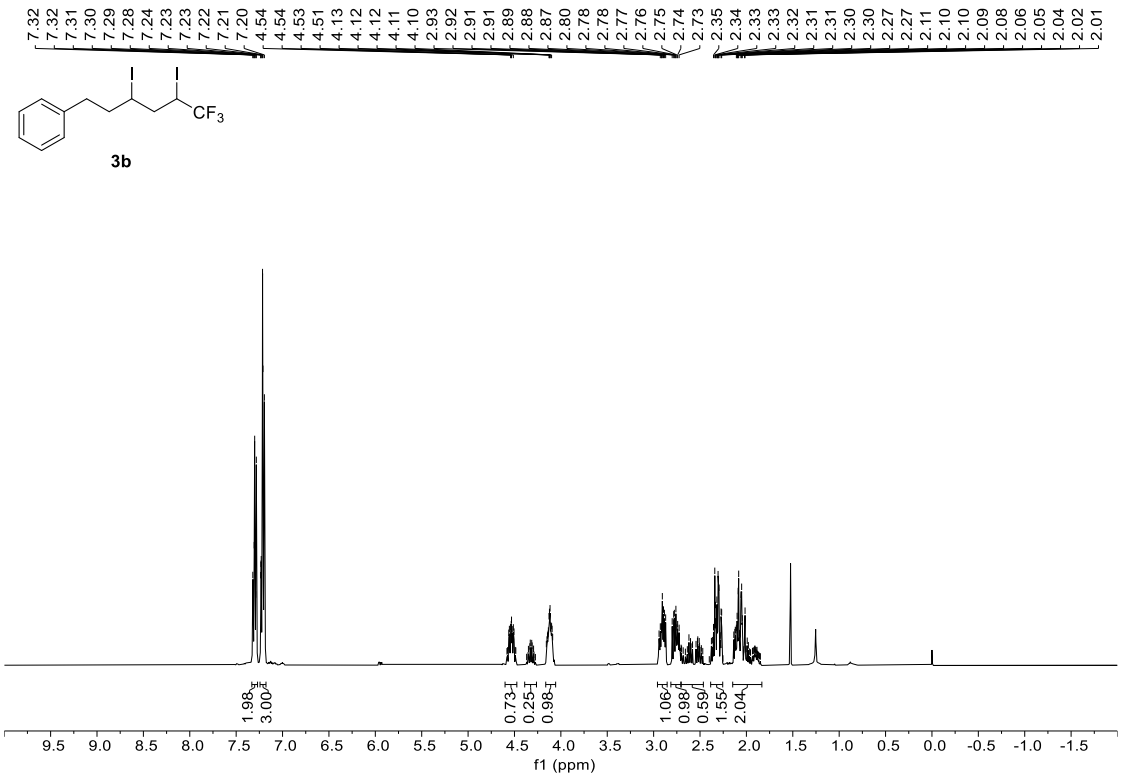
^{1}H NMR (400 MHz, $CDCl_3$) for **3a**



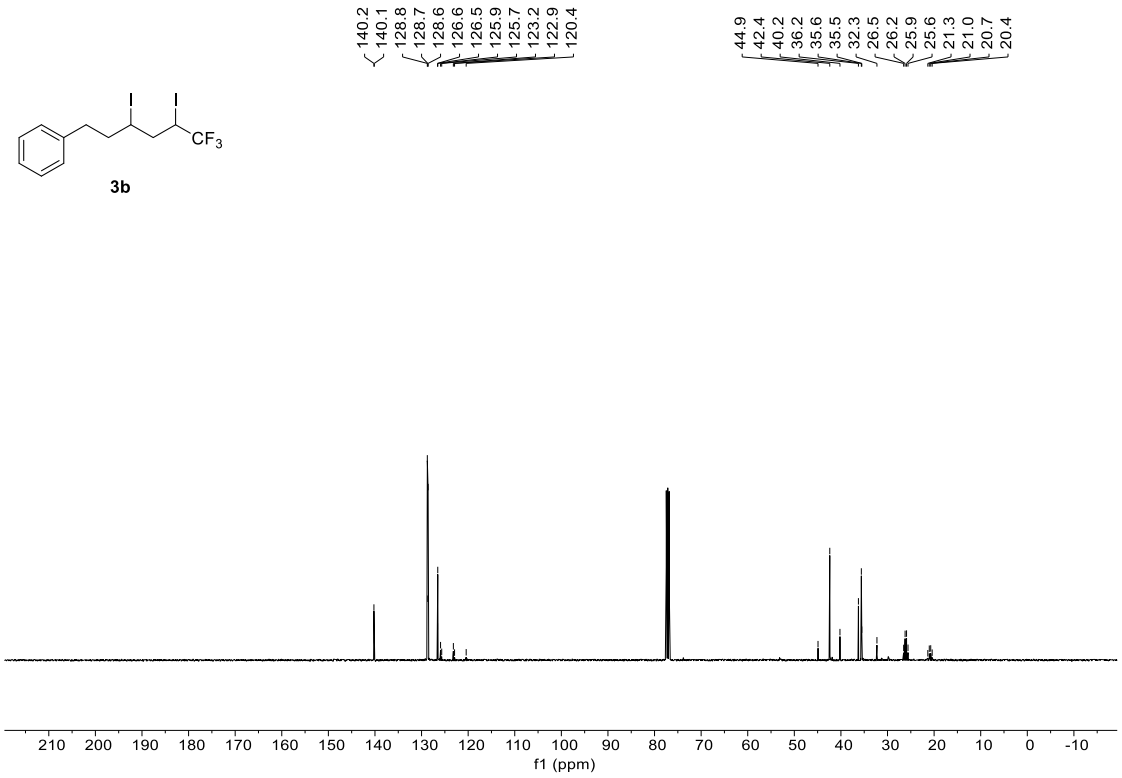
^{13}C NMR (101 MHz, $CDCl_3$) for **3a**



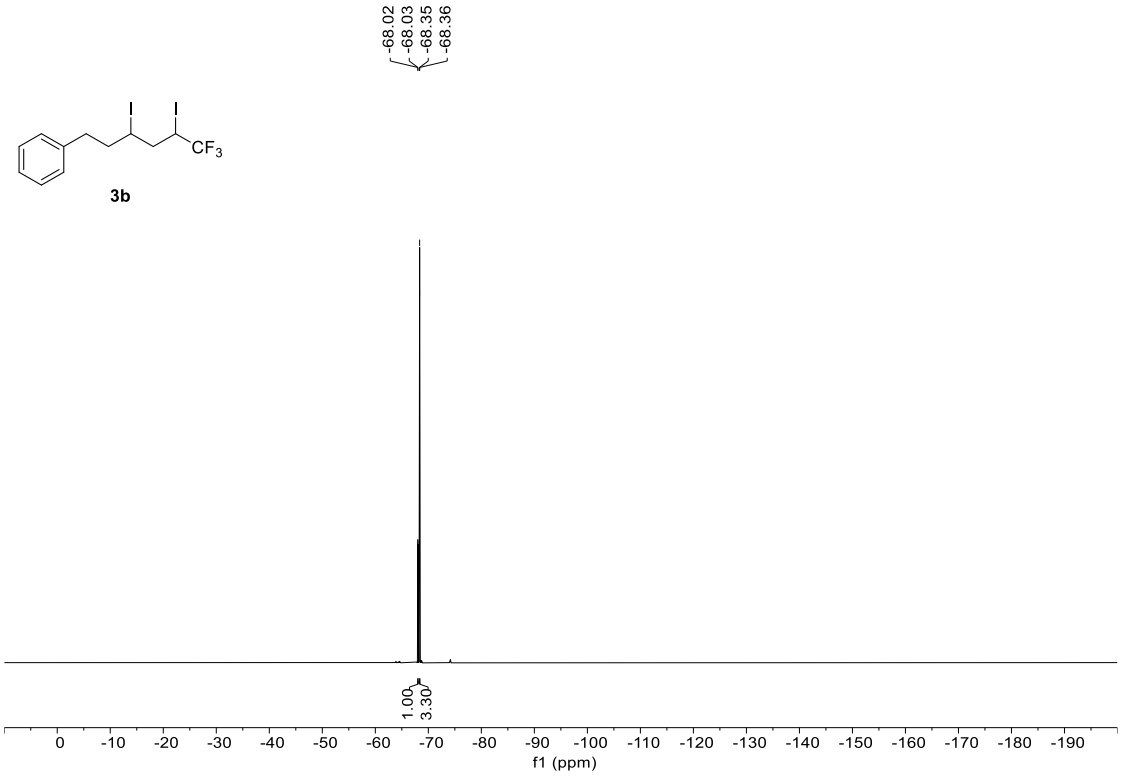
^{19}F NMR (565MHz, $CDCl_3$) for **3a**



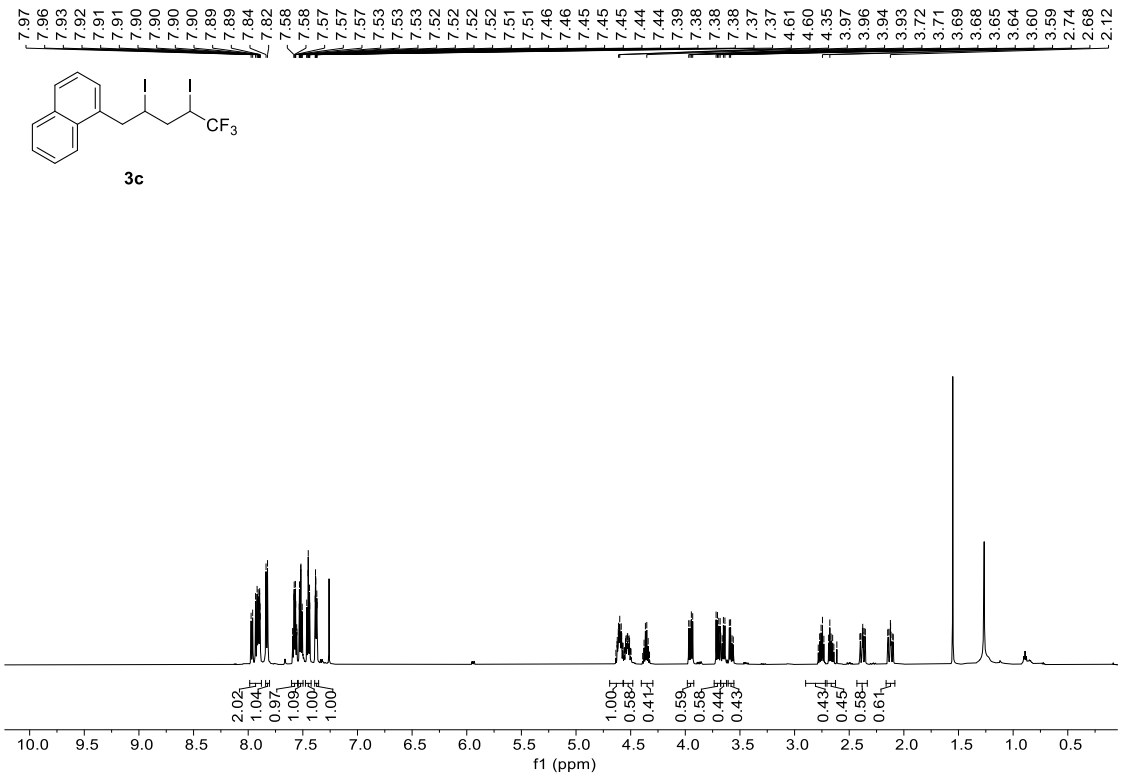
^{1}H NMR (400 MHz, $CDCl_3$) for **3b**



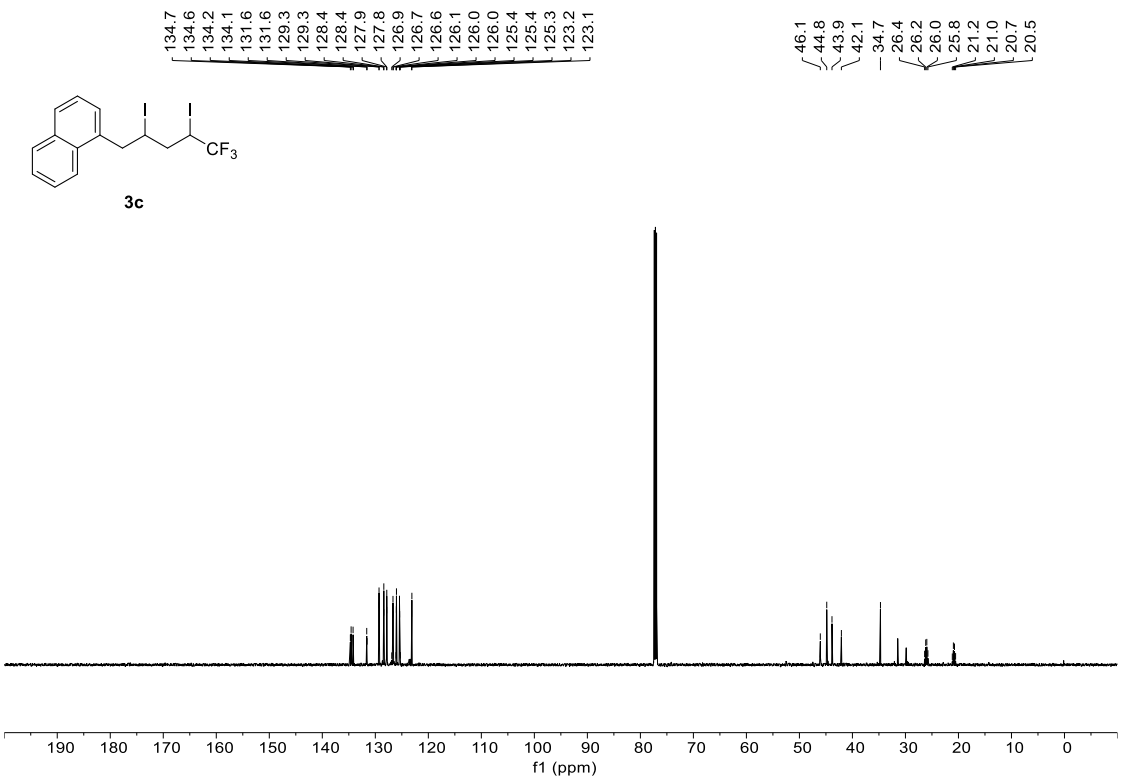
^{13}C NMR (101 MHz, $CDCl_3$) for **3b**



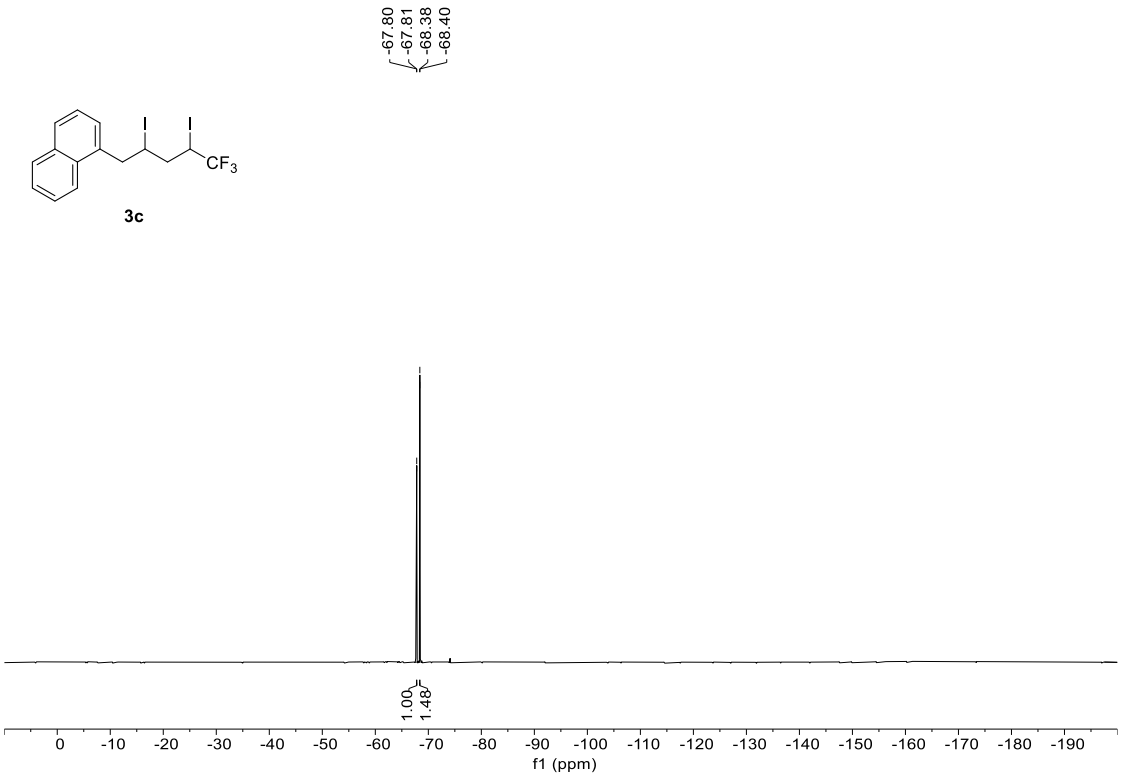
^{19}F NMR (565 MHz, $CDCl_3$) for **3b**



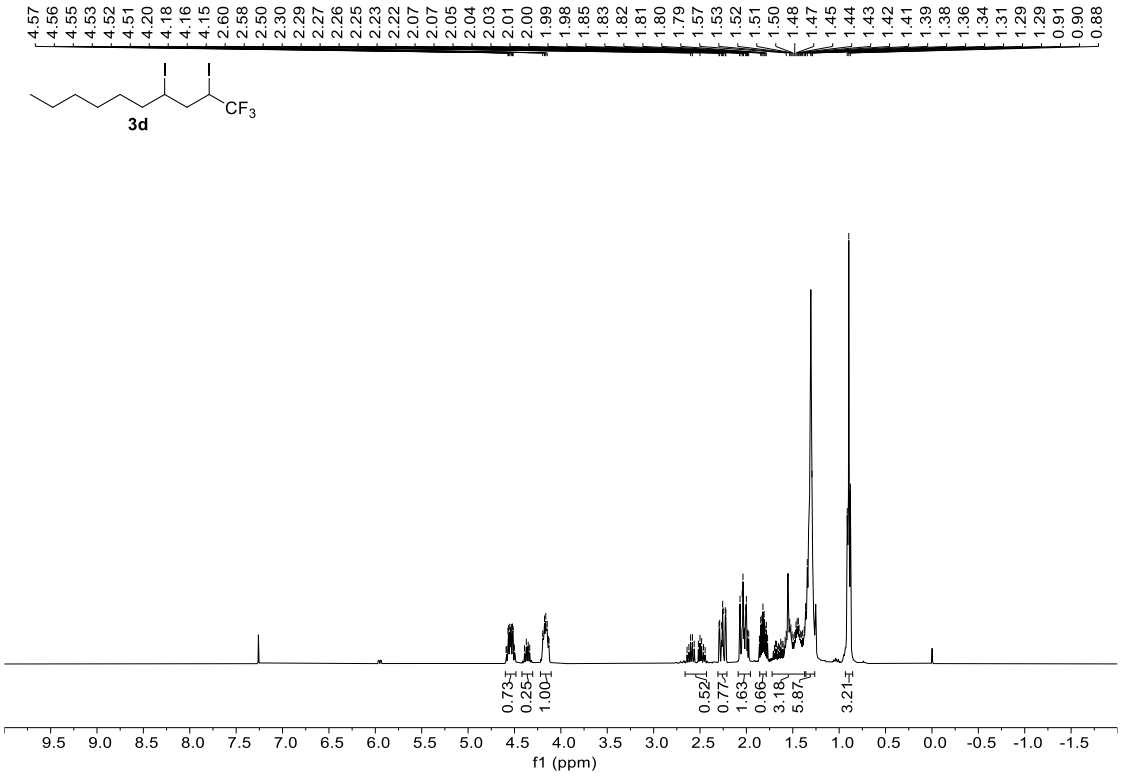
^{1}H NMR (600 MHz, $CDCl_3$) for **3c**



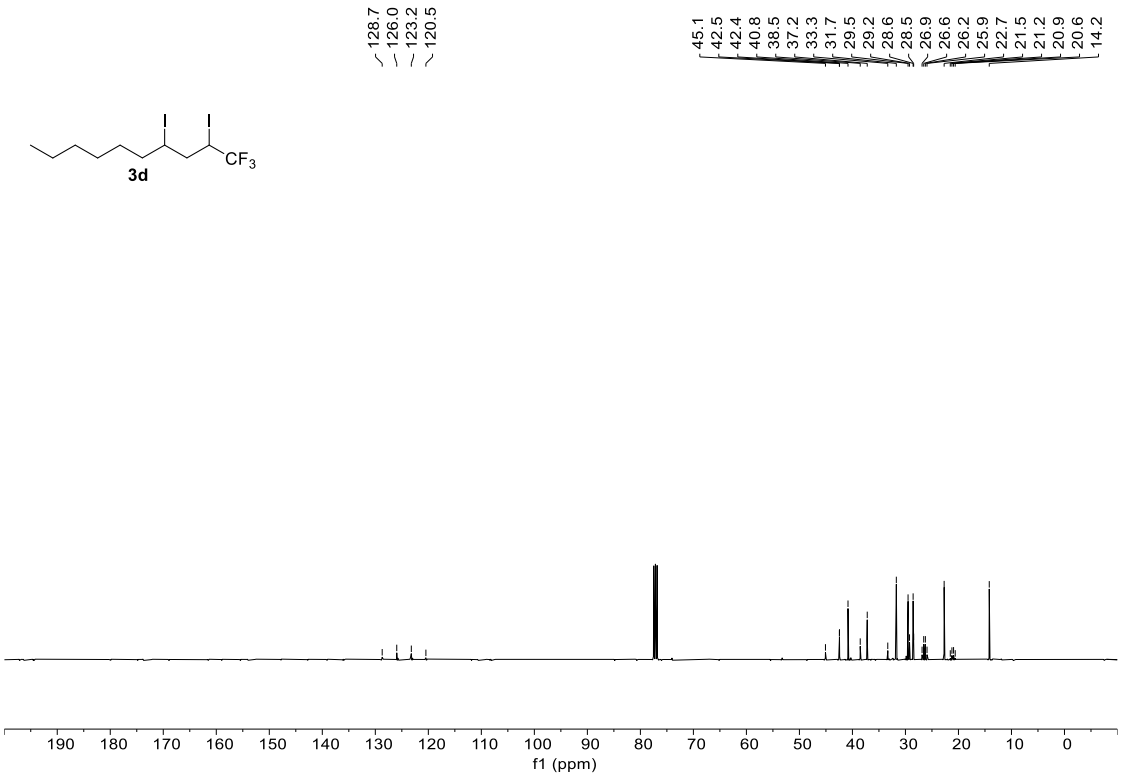
^{13}C NMR (151 MHz, $CDCl_3$) for **3c**



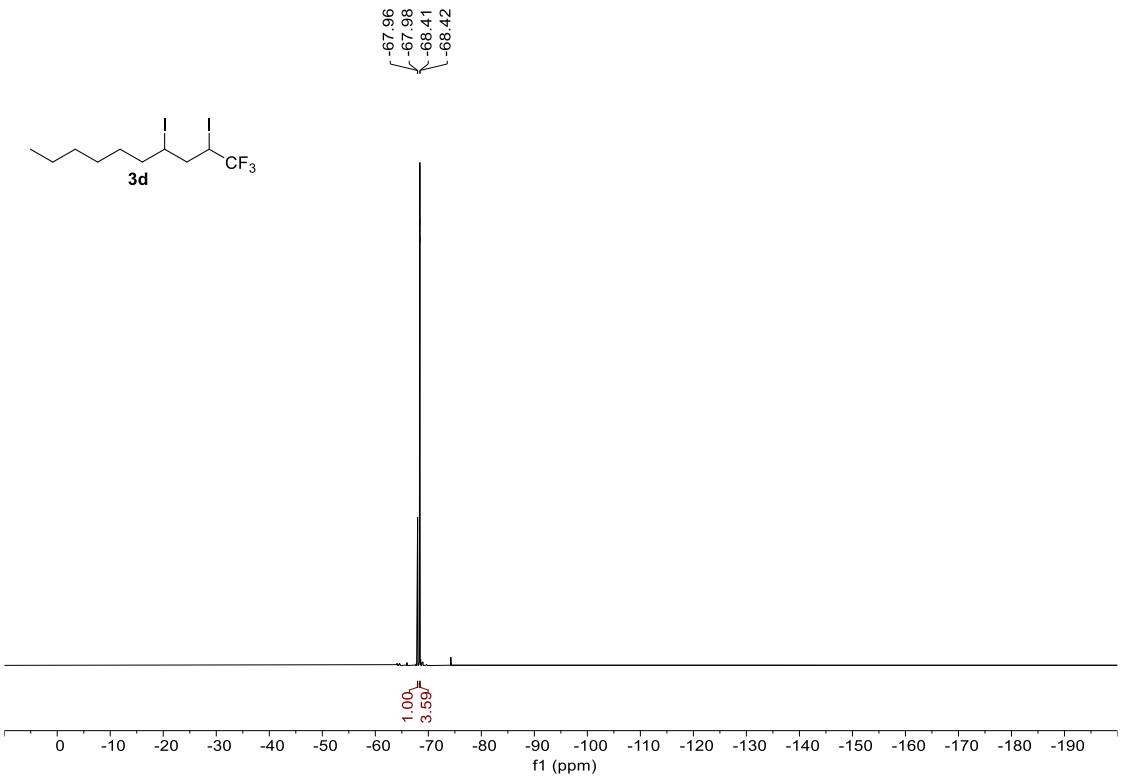
^{19}F NMR (565 MHz, $CDCl_3$) for **3c**



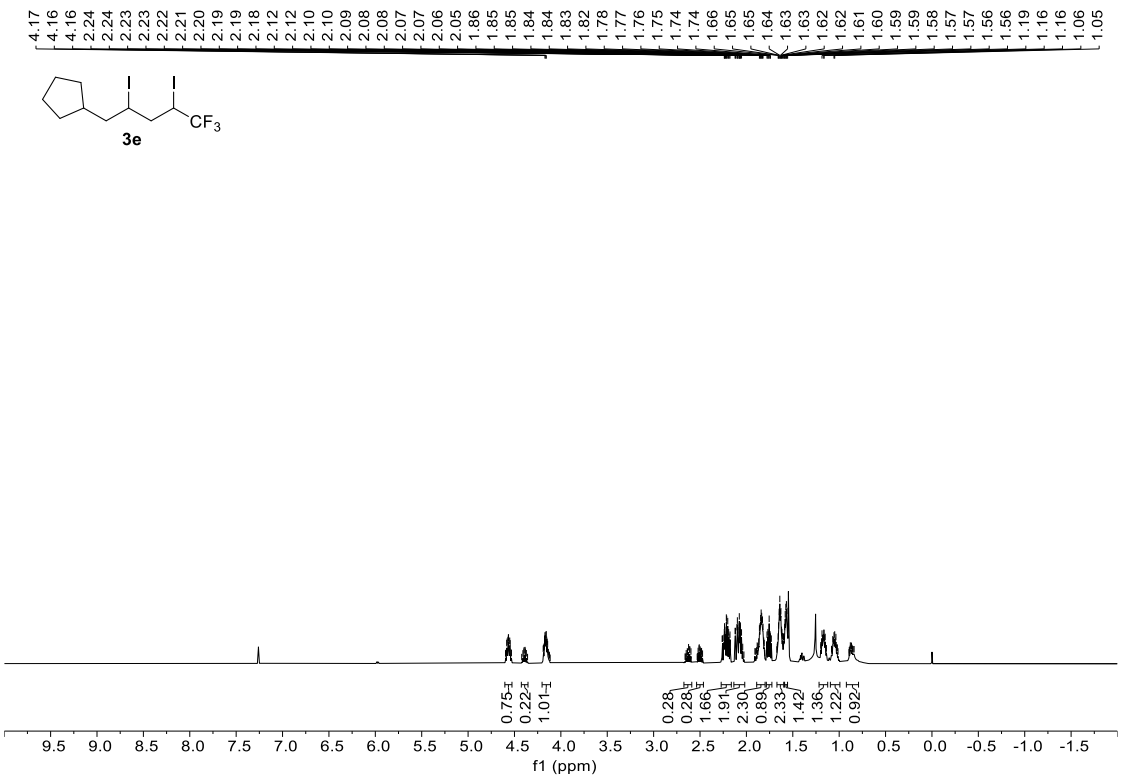
^{1}H NMR (400 MHz, $CDCl_3$) for **3d**



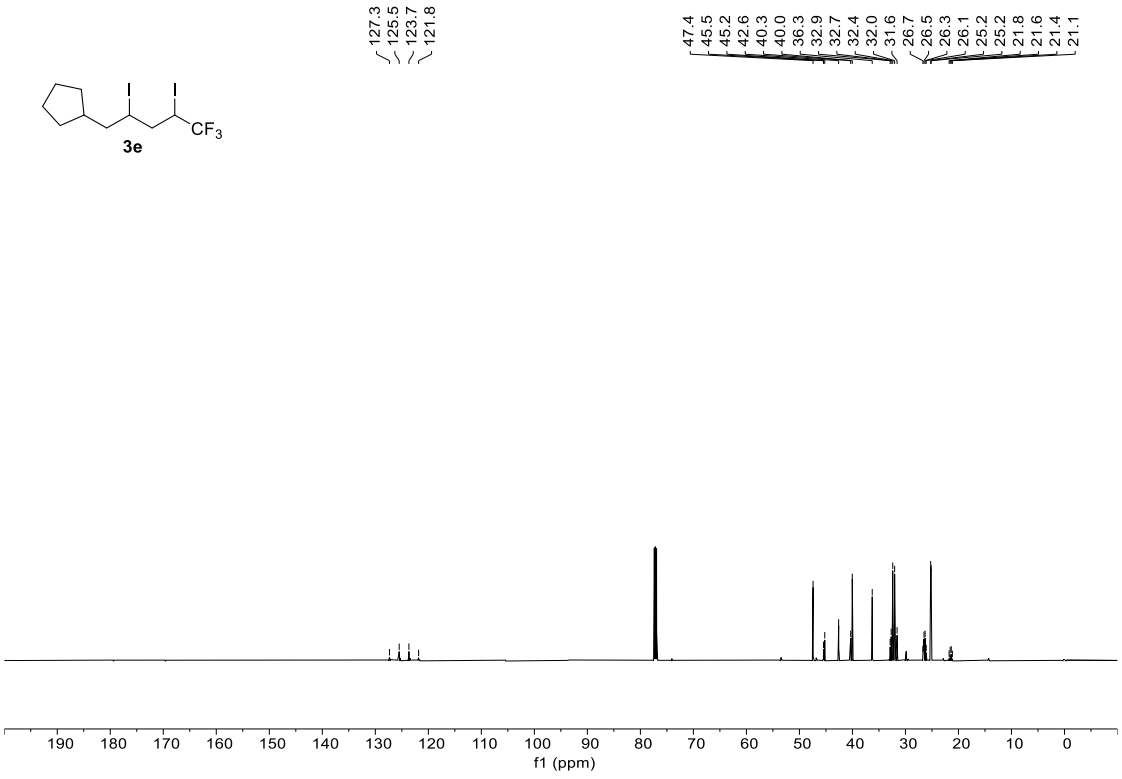
^{13}C NMR (101 MHz, $CDCl_3$) for **3d**



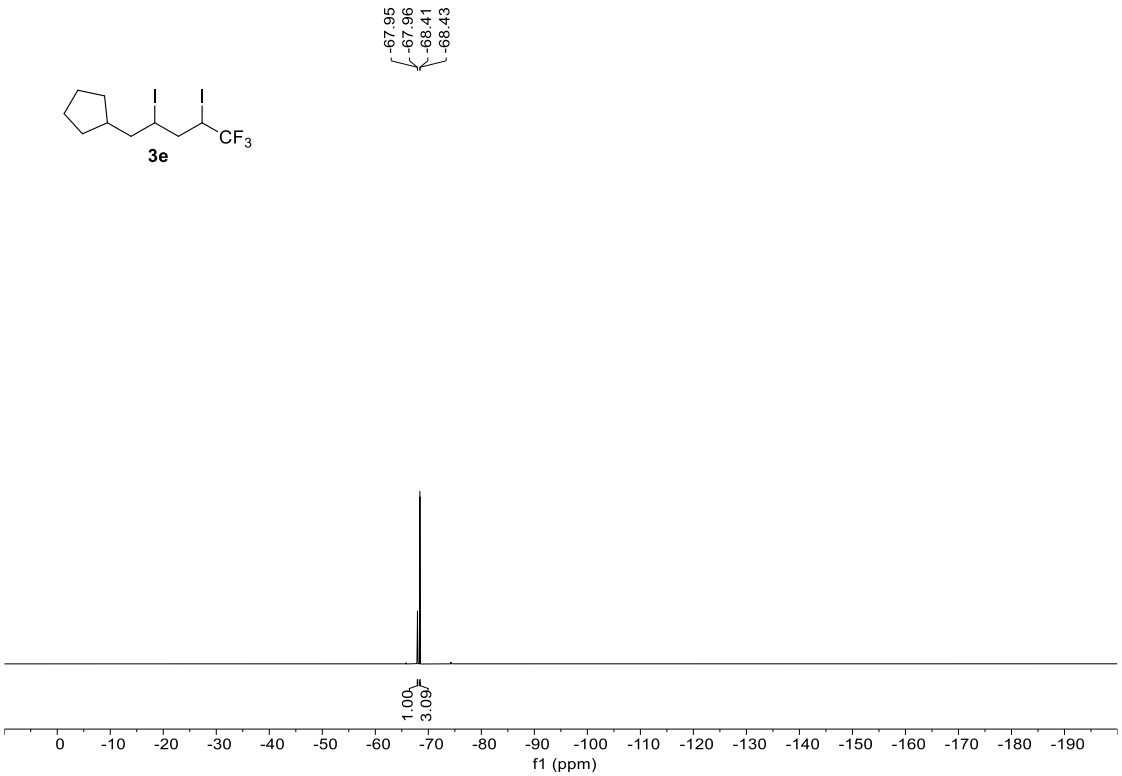
^{19}F NMR (565 MHz, $CDCl_3$) for **3d**



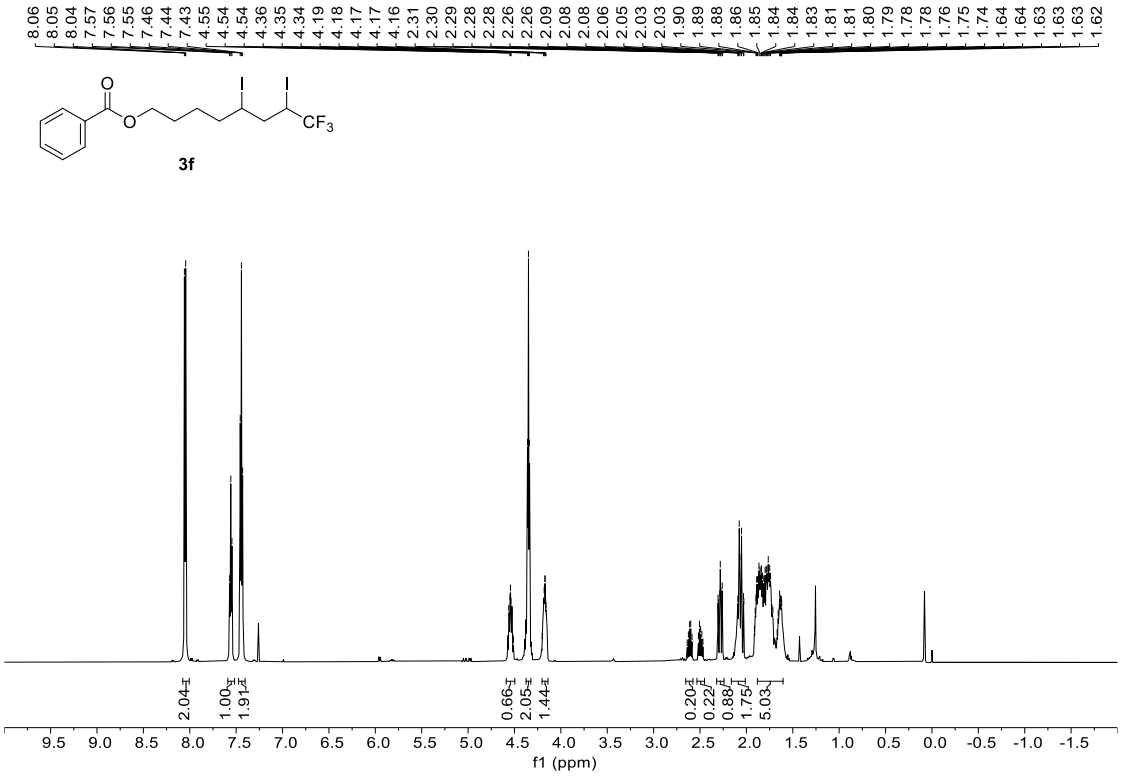
^{1}H NMR (600 MHz, $CDCl_3$) for **3e**



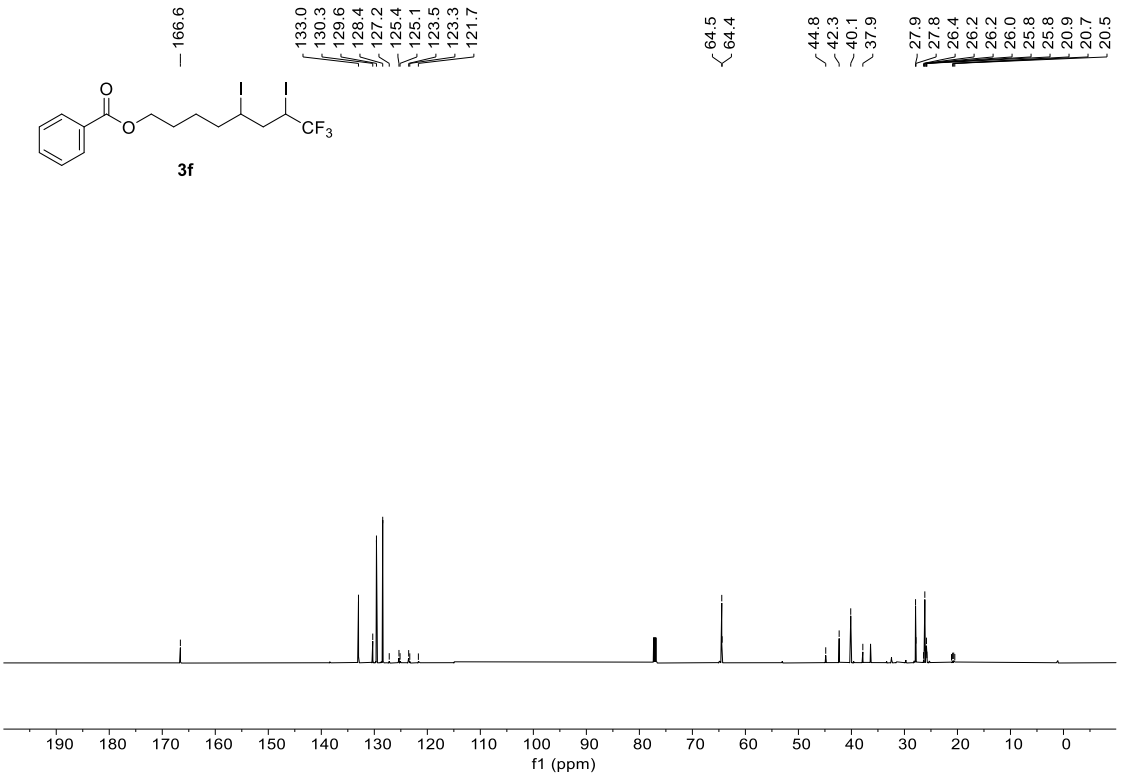
^{13}C NMR (151 MHz, $CDCl_3$) for **3e**



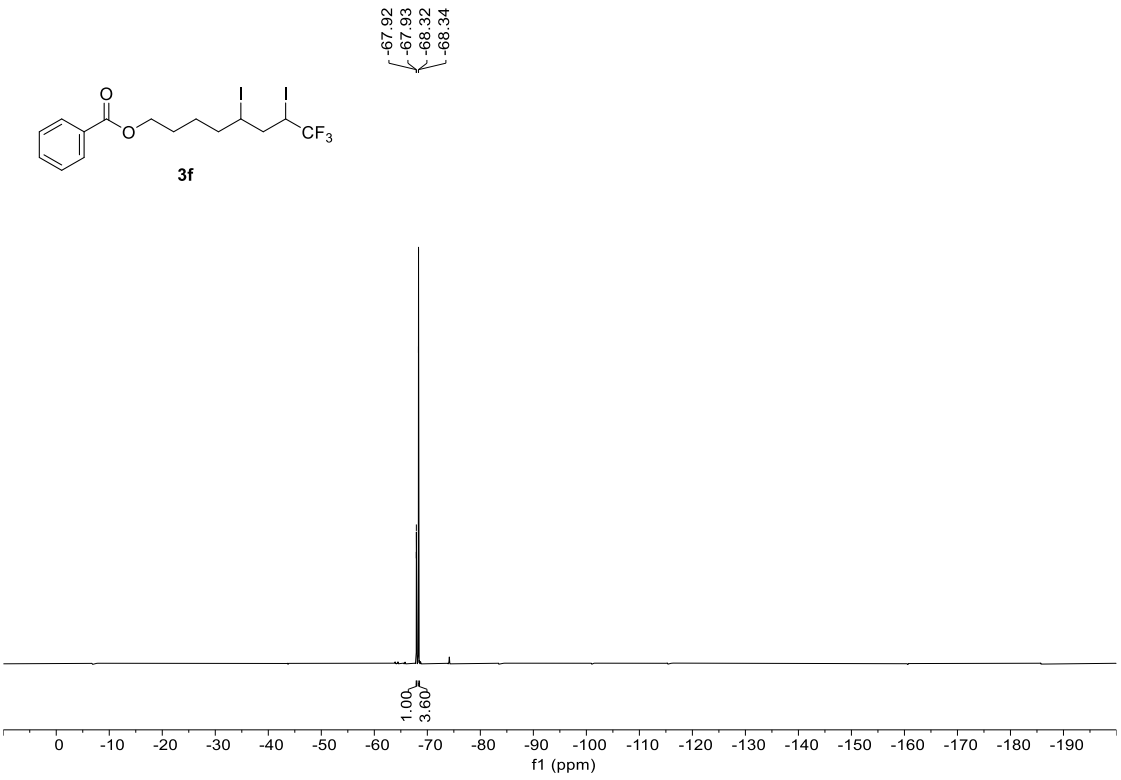
^{19}F NMR (565 MHz, $CDCl_3$) for **3e**



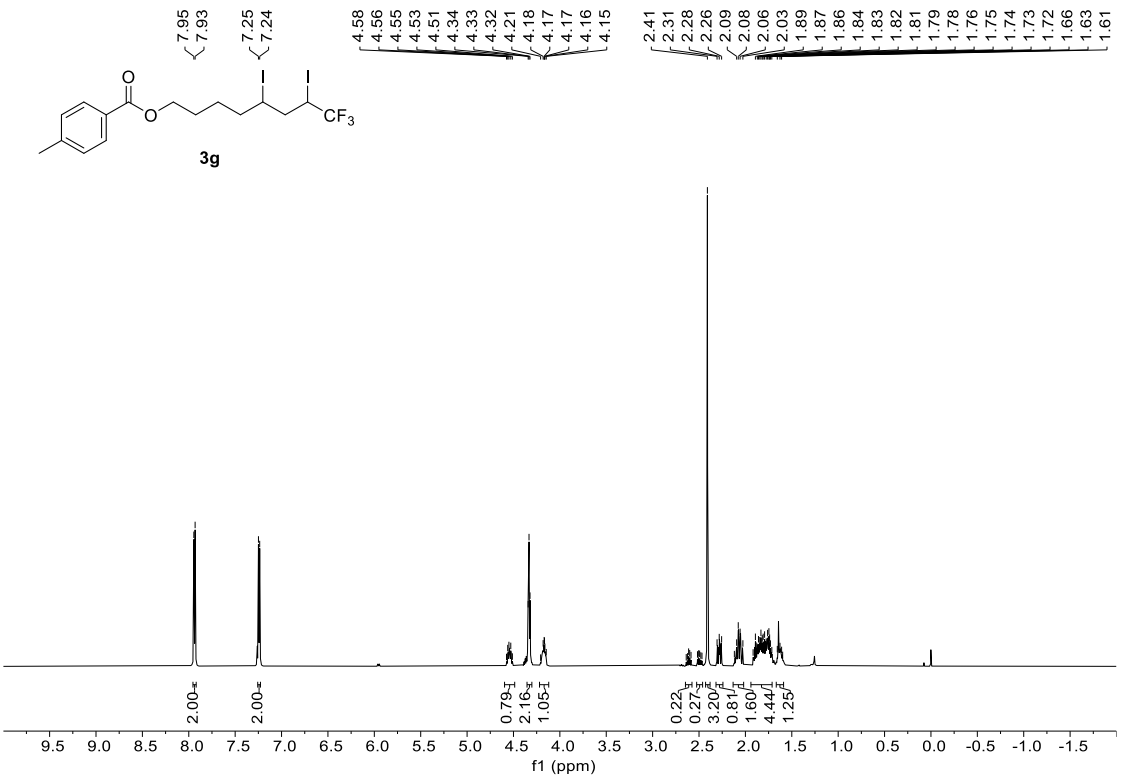
^{1}H NMR (600 MHz, $CDCl_3$) for **3f**



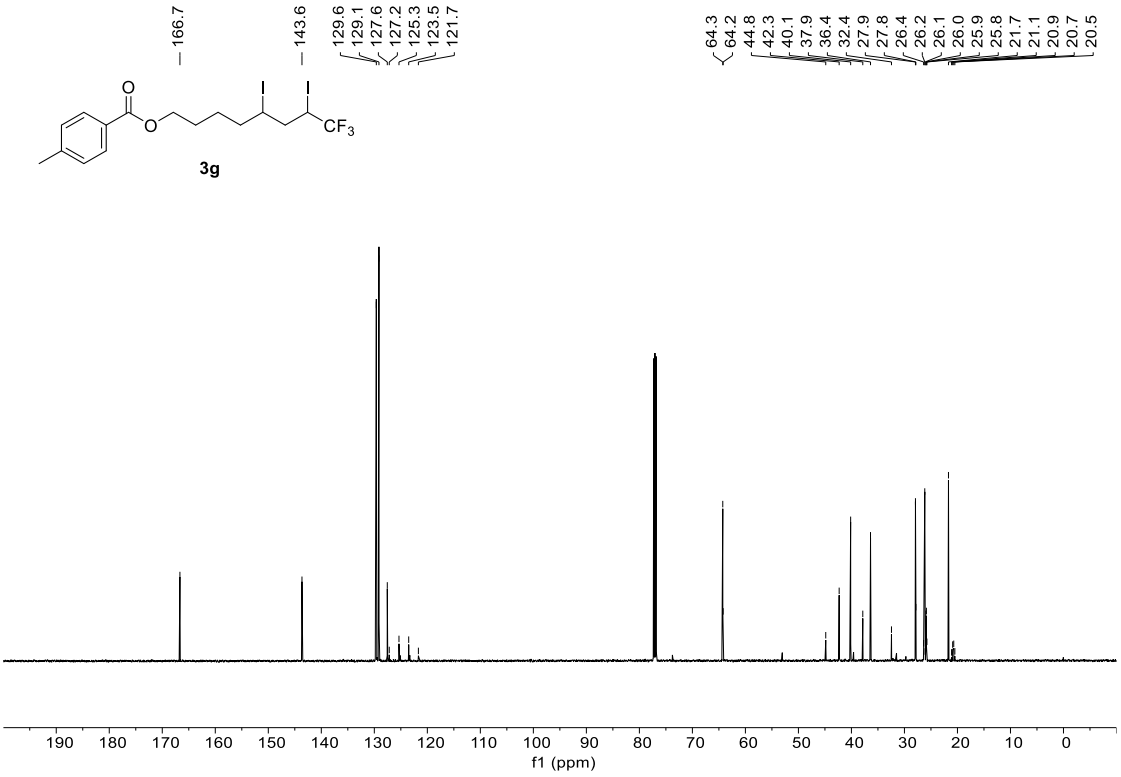
^{13}C NMR (151 MHz, $CDCl_3$) for **3f**



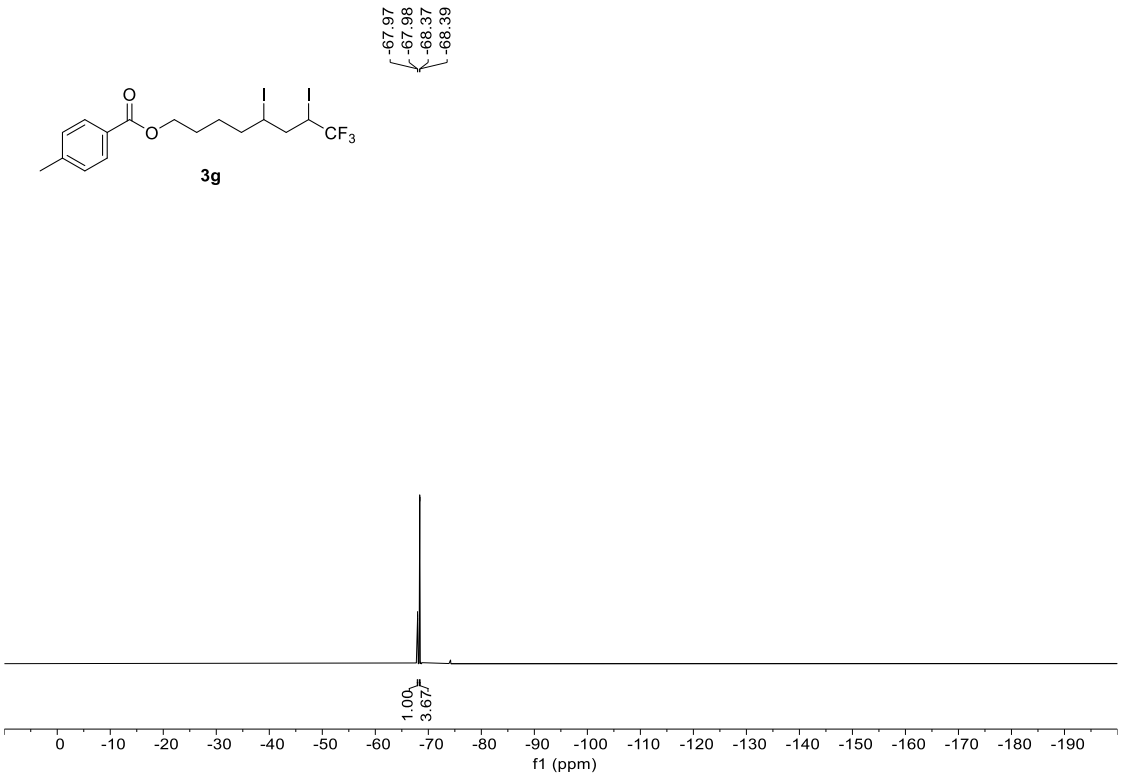
^{19}F NMR (565 MHz, $CDCl_3$) for **3f**



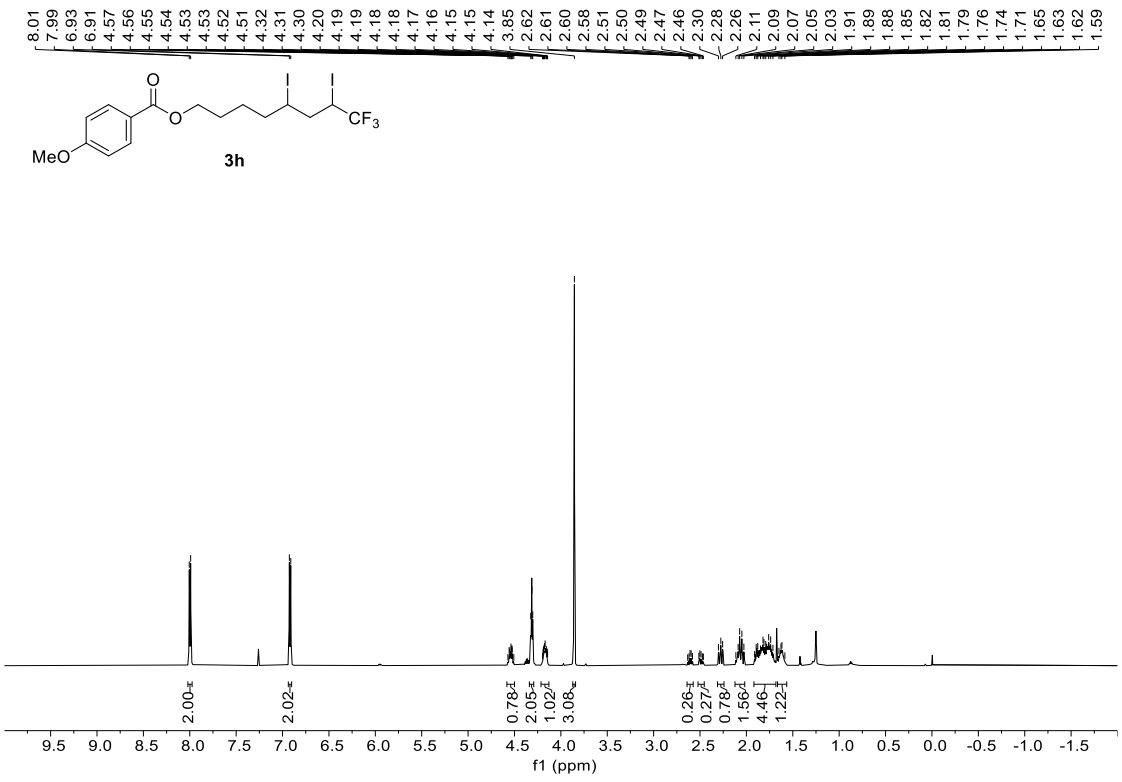
^{1}H NMR (600 MHz, $CDCl_3$) for **3g**



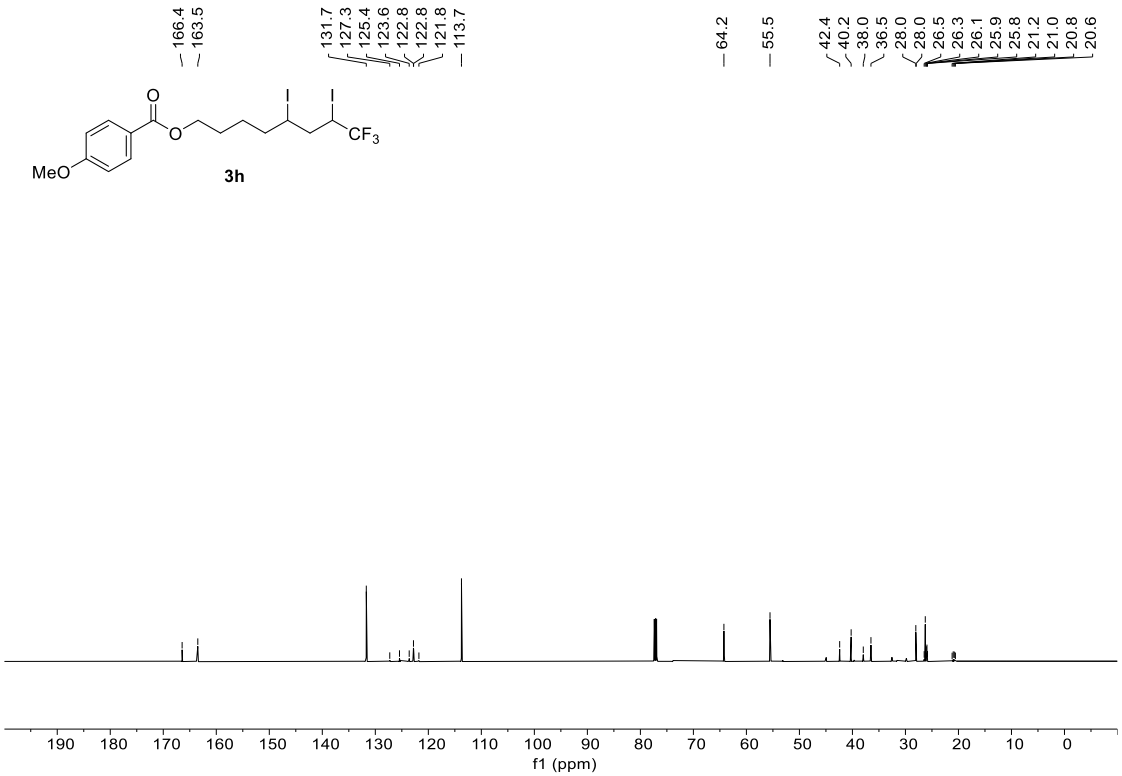
^{13}C NMR (151 MHz, $CDCl_3$) for **3g**



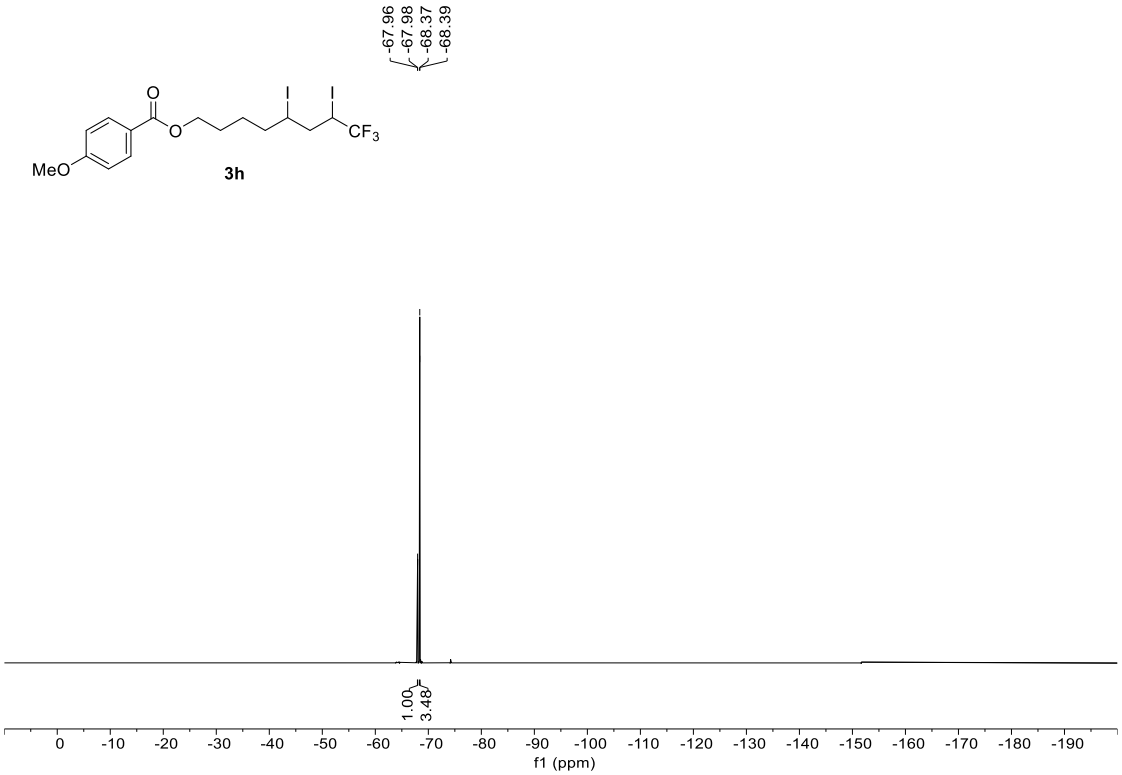
^{19}F NMR (565 MHz, $CDCl_3$) for **3g**



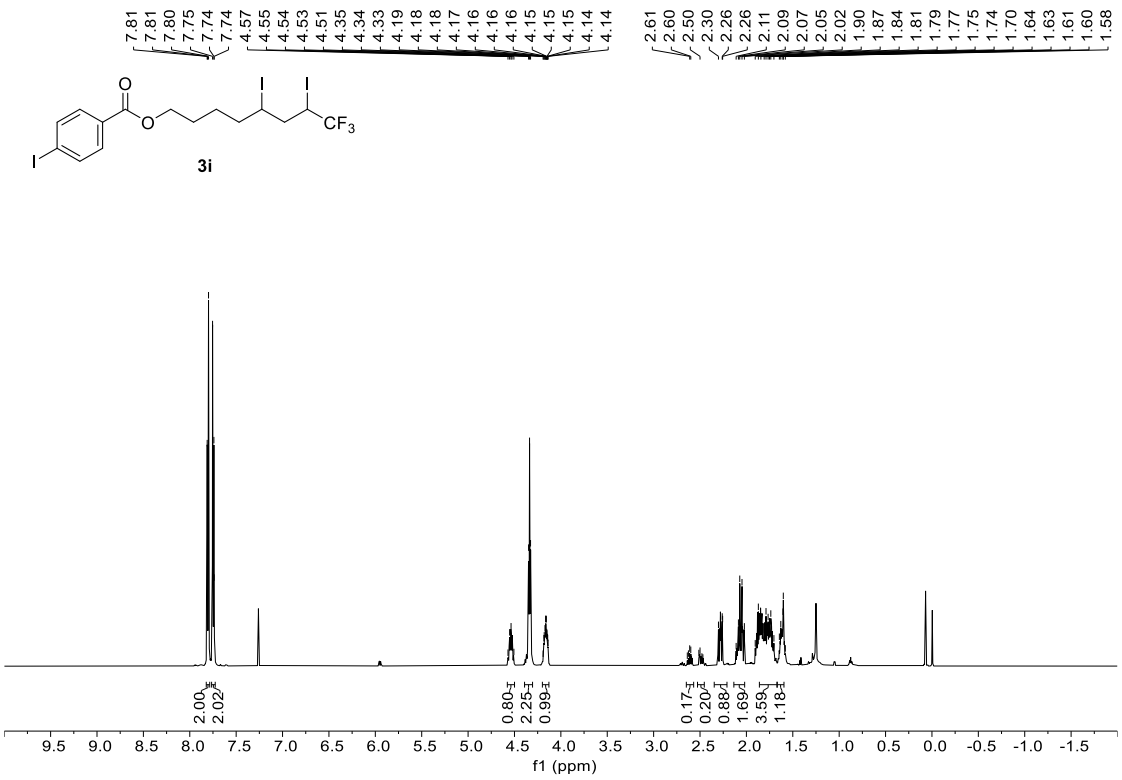
^{1}H NMR (600 MHz, $CDCl_3$) for **3h**



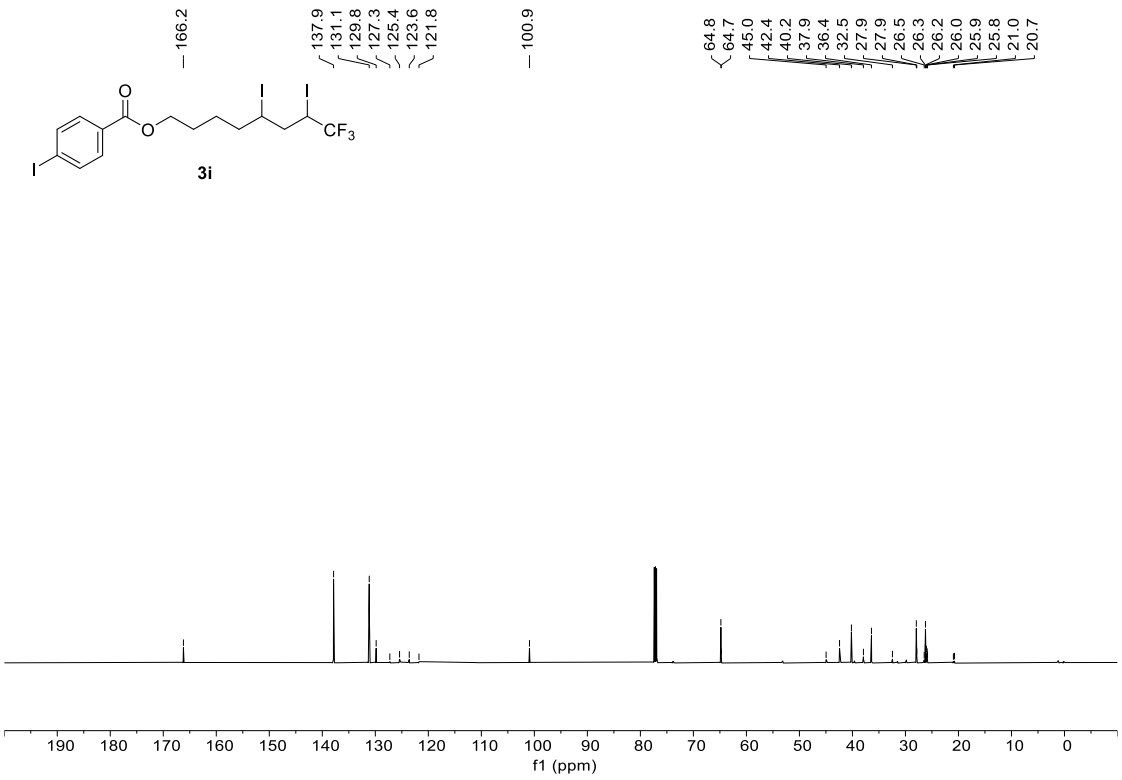
^{13}C NMR (151 MHz, $CDCl_3$) for **3h**



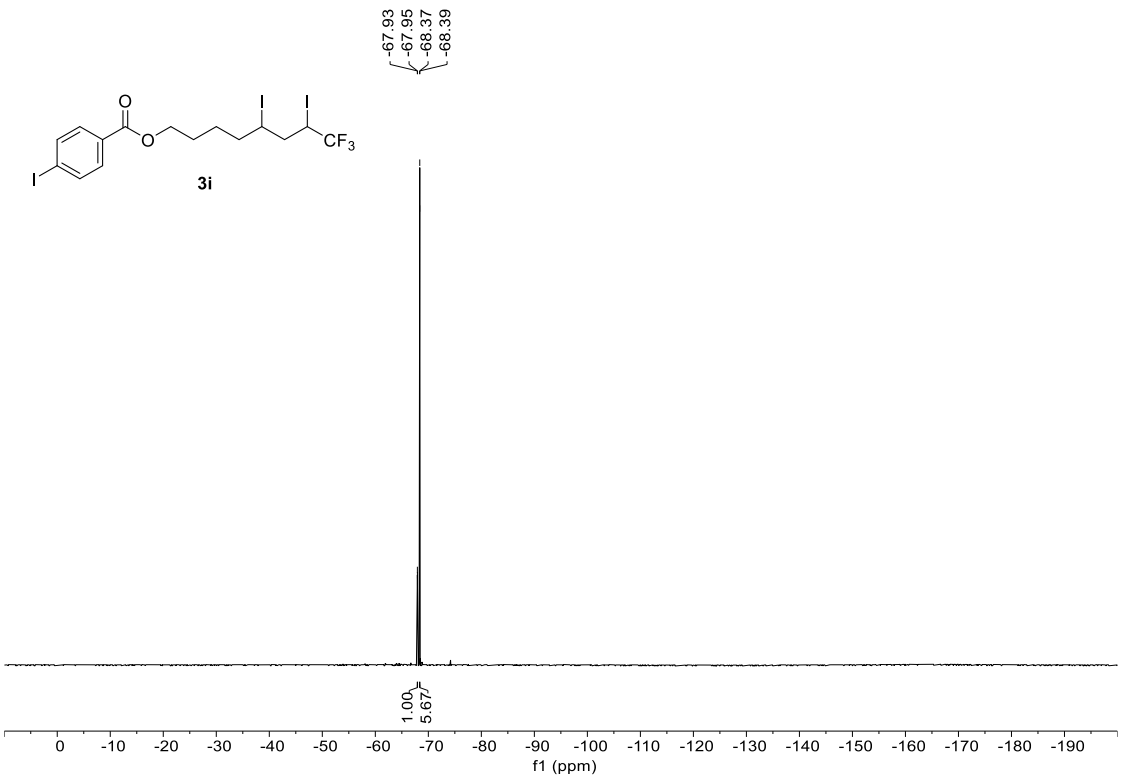
^{19}F NMR (565 MHz, $CDCl_3$) for **3h**



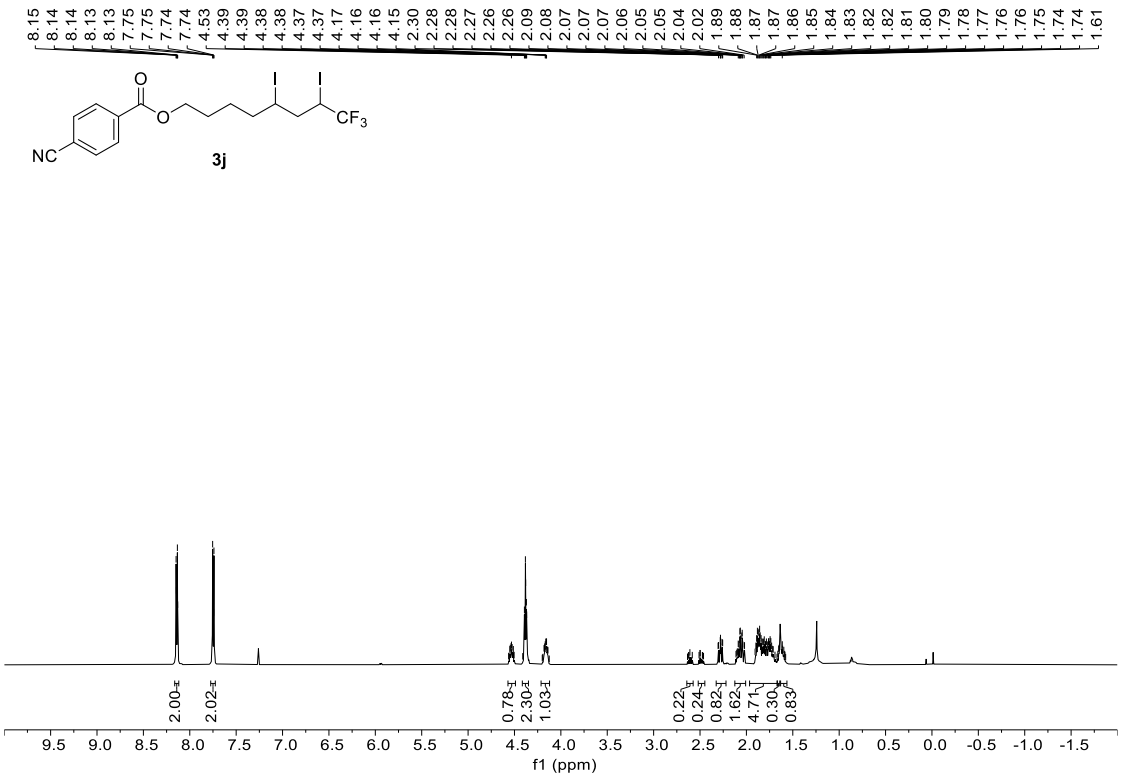
^{1}H NMR (600 MHz, $CDCl_3$) for **3i**



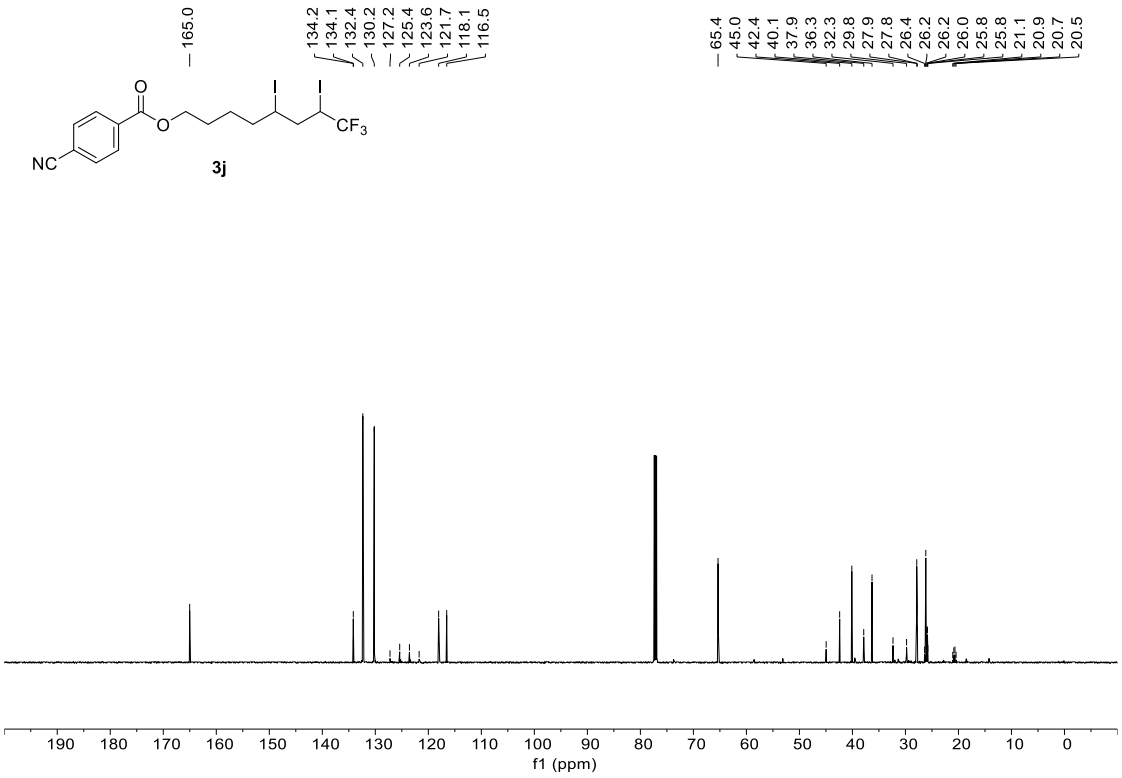
^{13}C NMR (151 MHz, $CDCl_3$) for **3i**



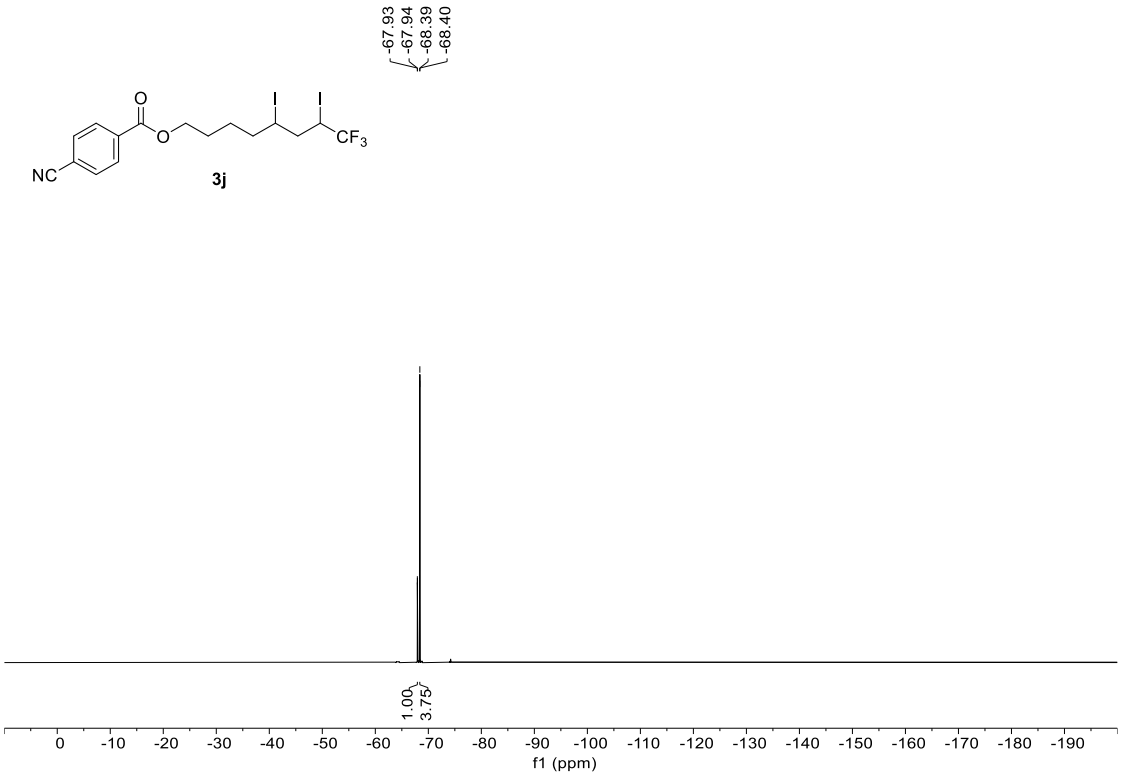
^{19}F NMR (565 MHz, $CDCl_3$) for **3i**



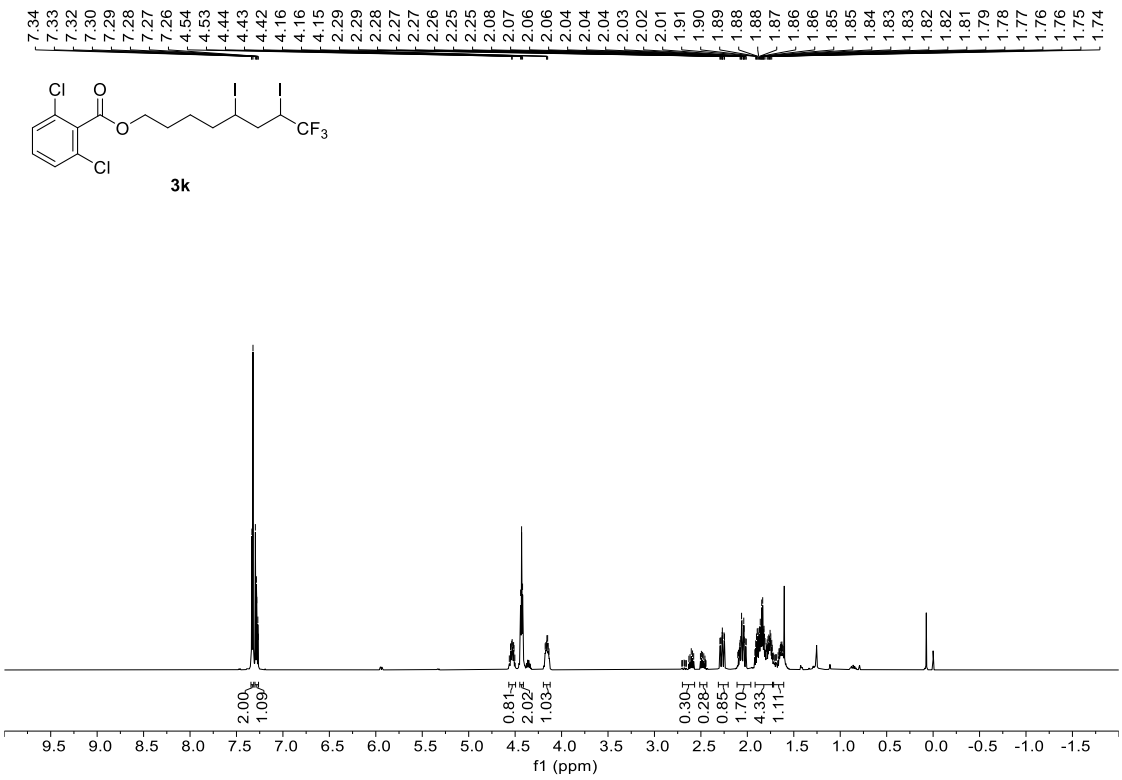
^{1}H NMR (600 MHz, $CDCl_3$) for **3j**



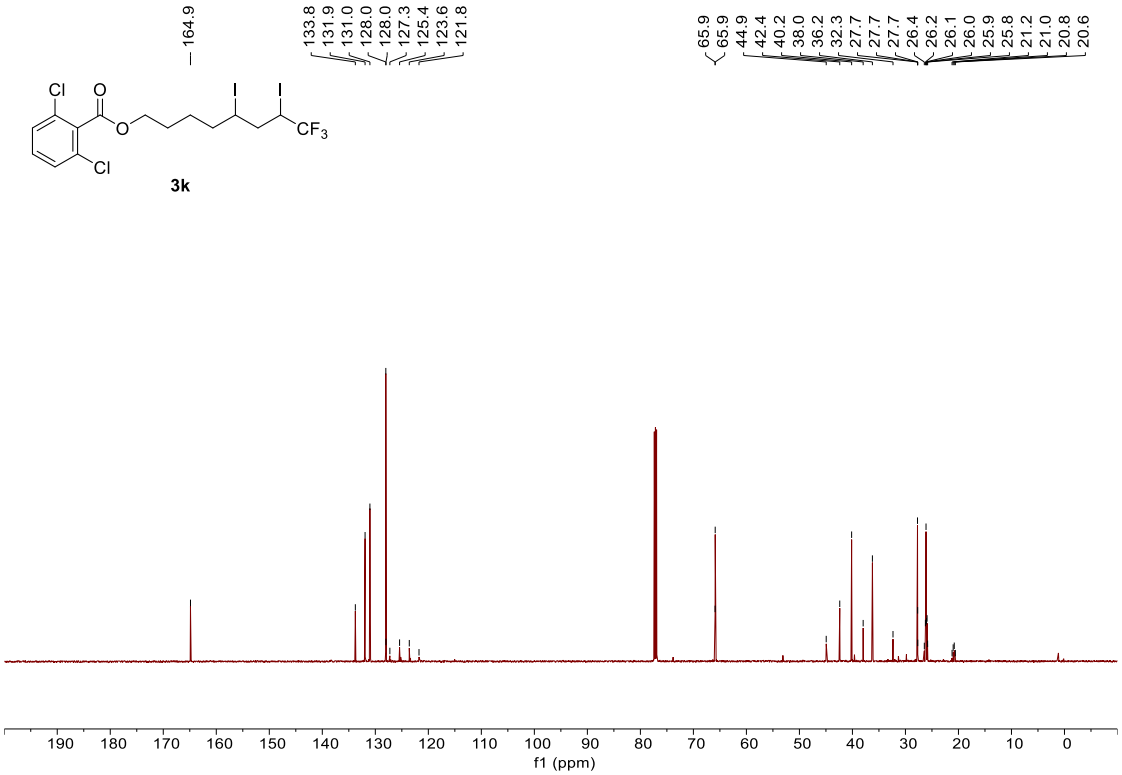
^{13}C NMR (151 MHz, $CDCl_3$) for **3j**



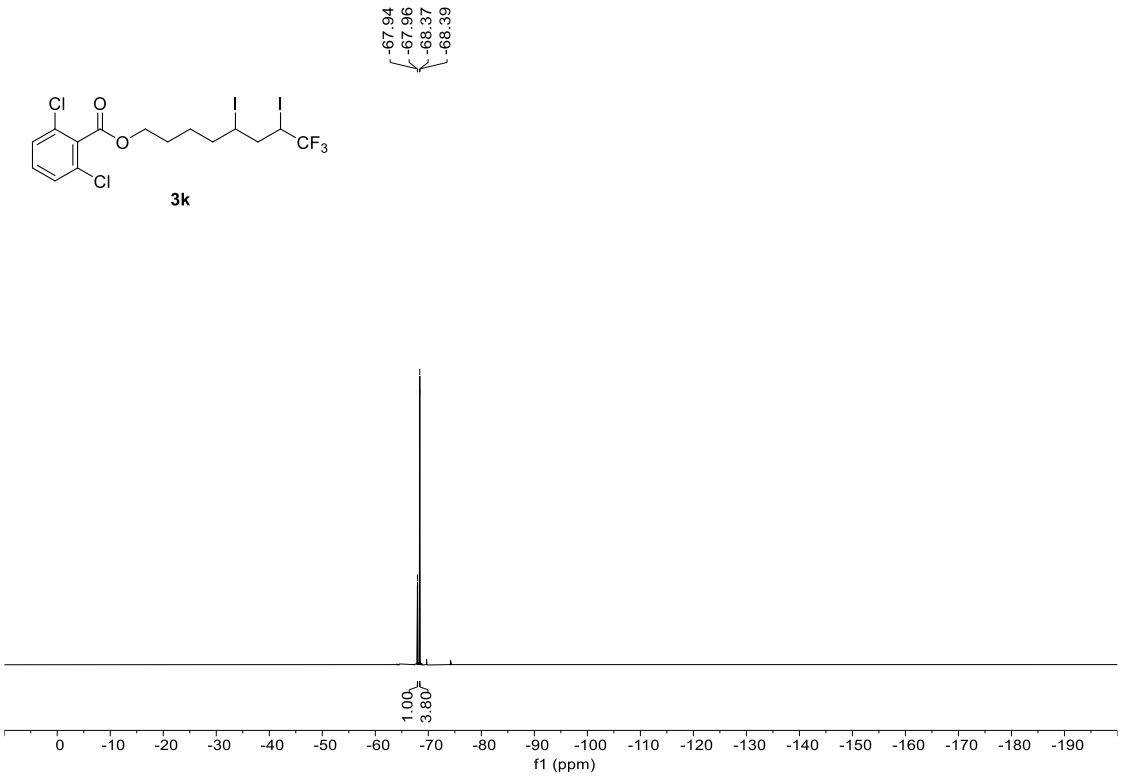
^{19}F NMR (565 MHz, $CDCl_3$) for **3j**



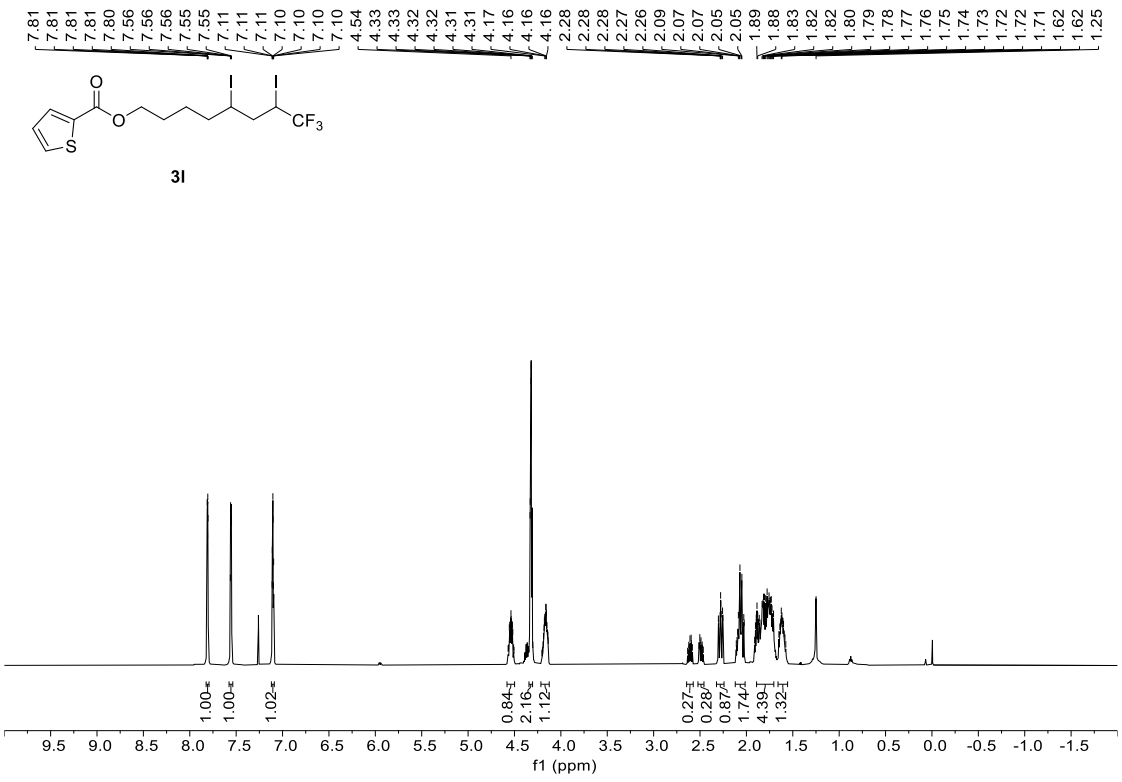
^{1}H NMR (600 MHz, $CDCl_3$) for **3k**



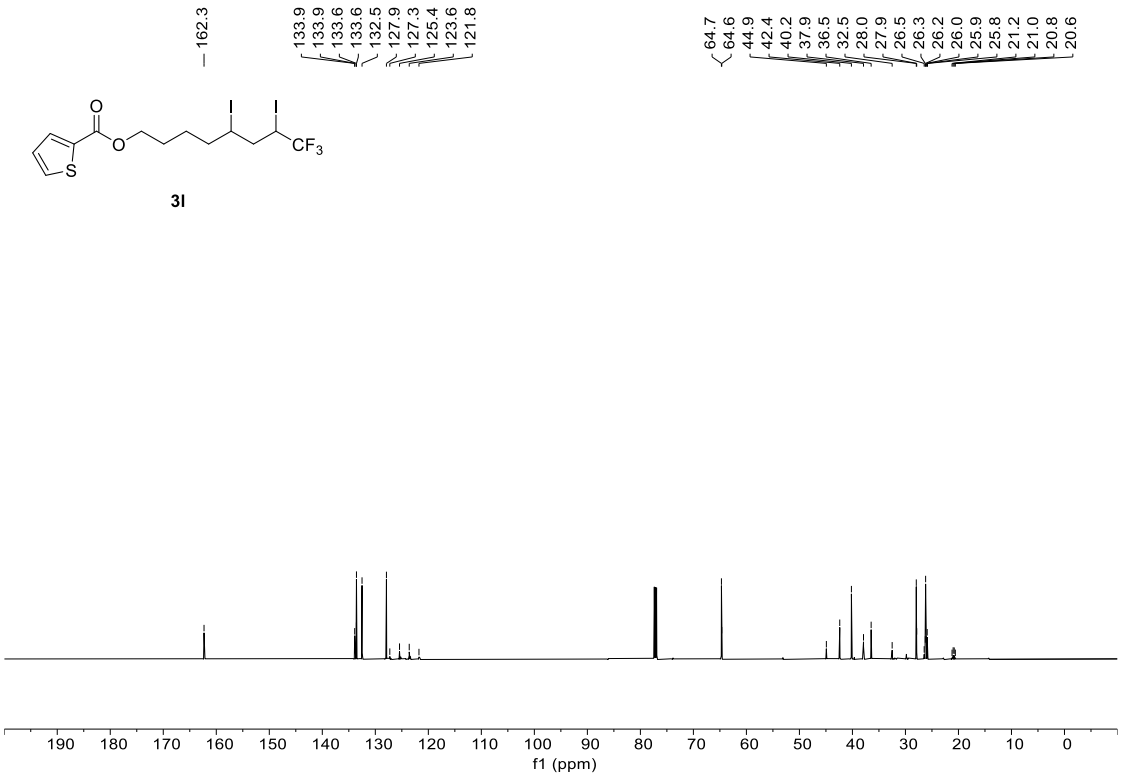
^{13}C NMR (151 MHz, $CDCl_3$) for **3k**



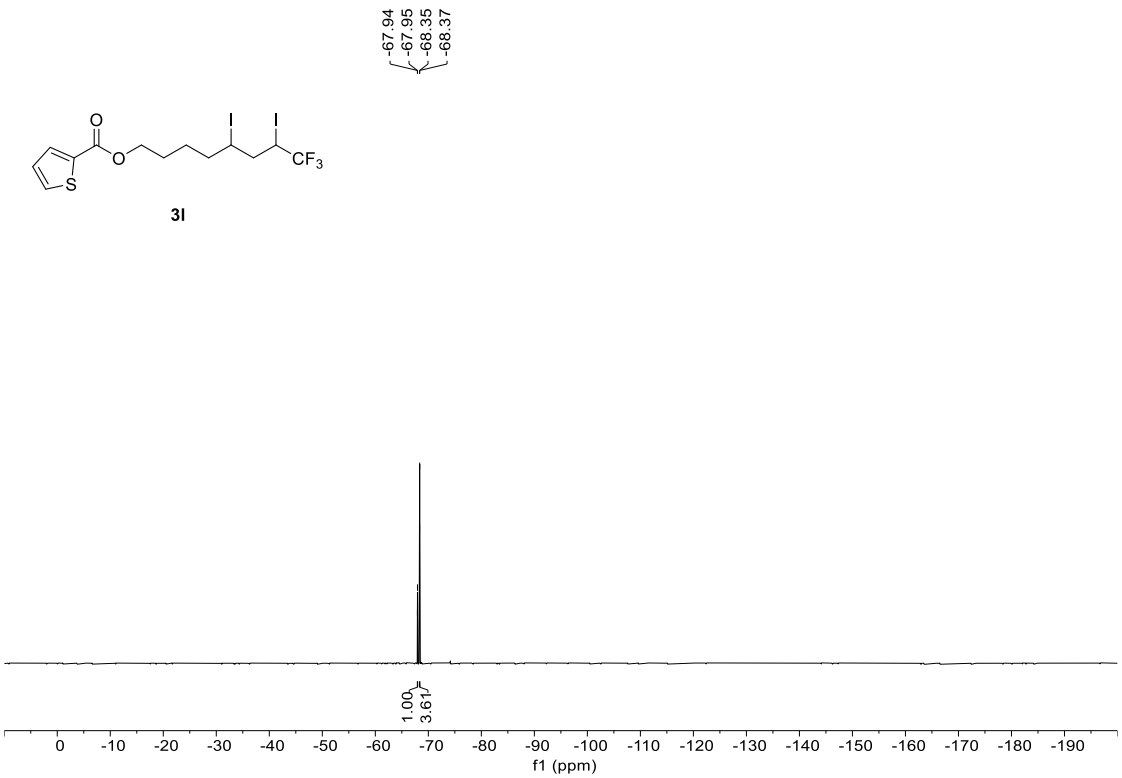
^{19}F NMR (565 MHz, $CDCl_3$) for **3k**



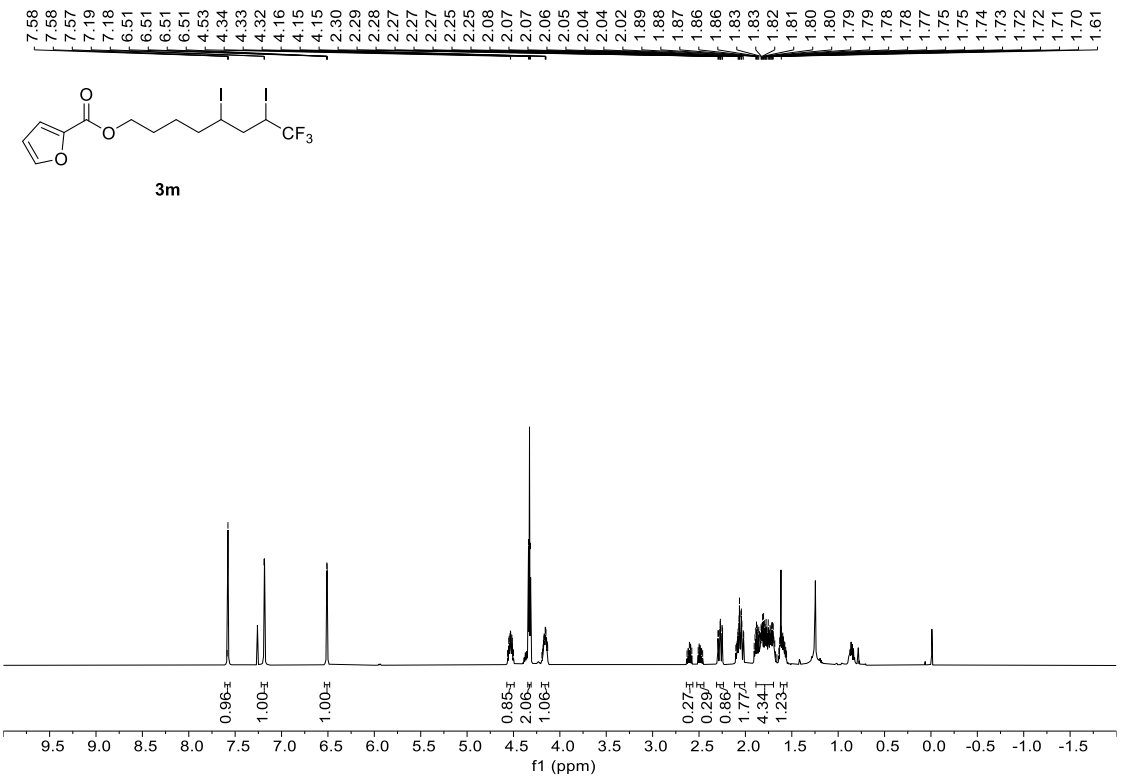
^{1}H NMR (600 MHz, $CDCl_3$) for **3l**



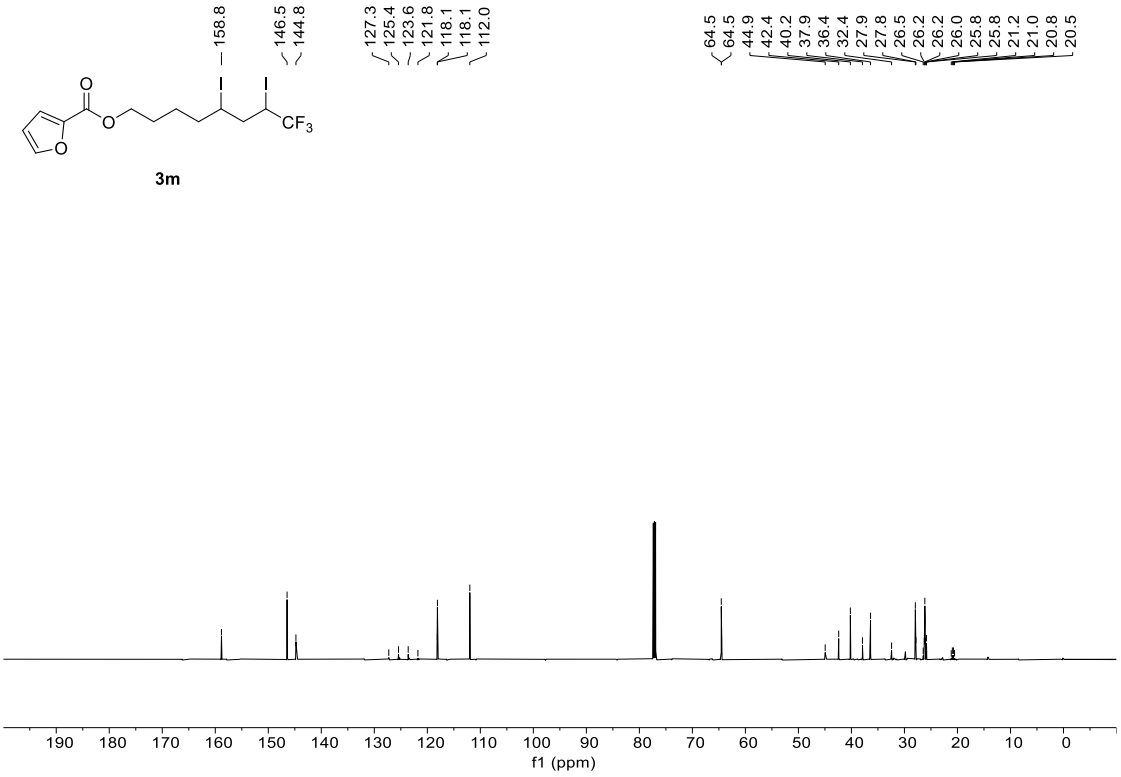
^{13}C NMR (151 MHz, $CDCl_3$) for **3l**



^{19}F NMR (565 MHz, $CDCl_3$) for **3l**

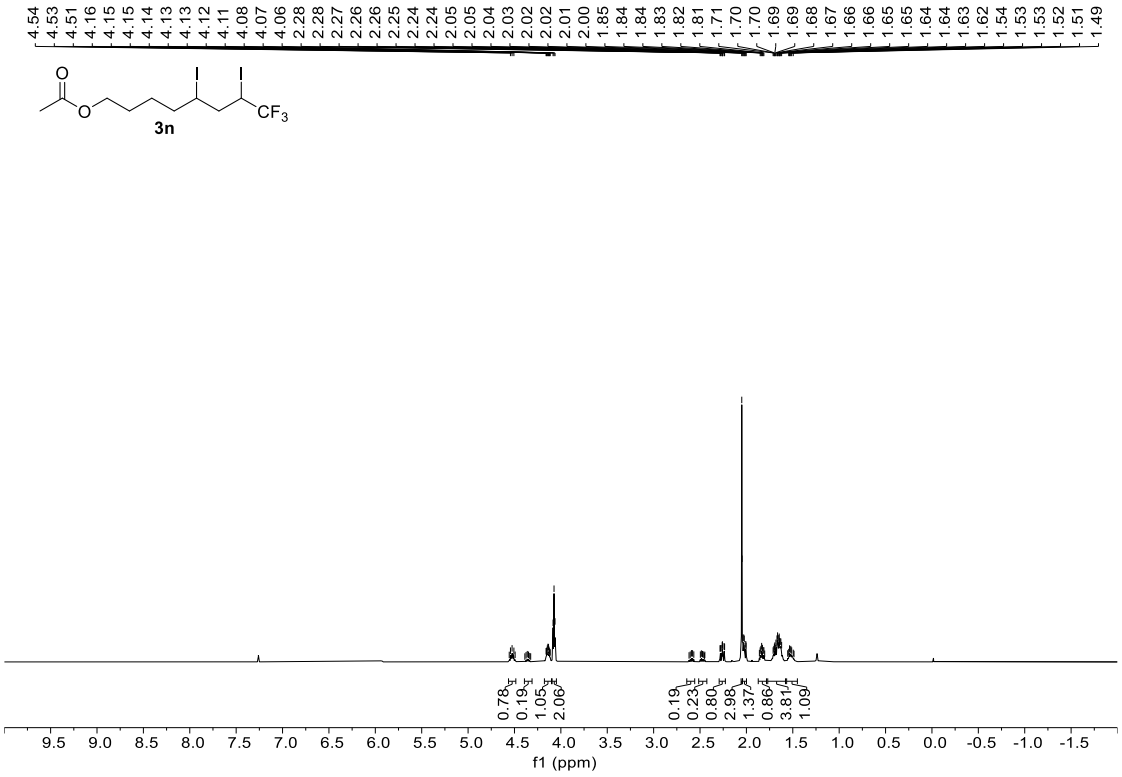


^{1}H NMR (600 MHz, $CDCl_3$) for **3m**

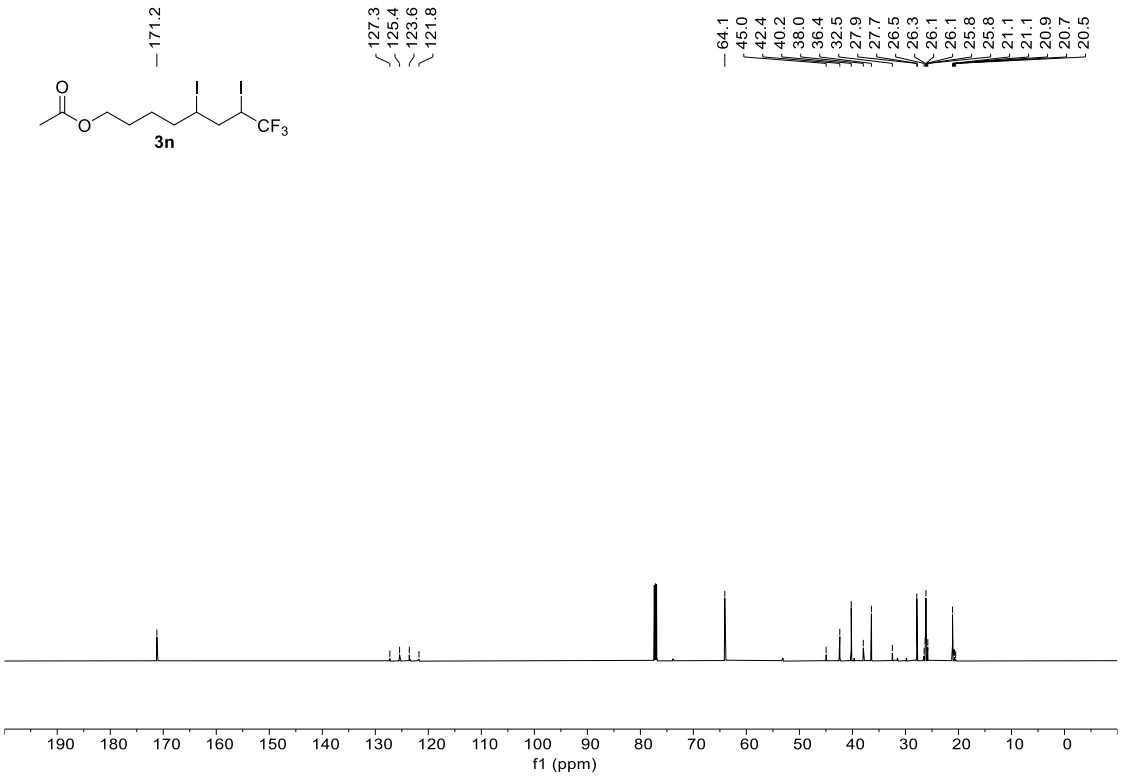


^{13}C NMR (151 MHz, $CDCl_3$) for **3m**

^{19}F NMR (565 MHz, $CDCl_3$) for **3m**

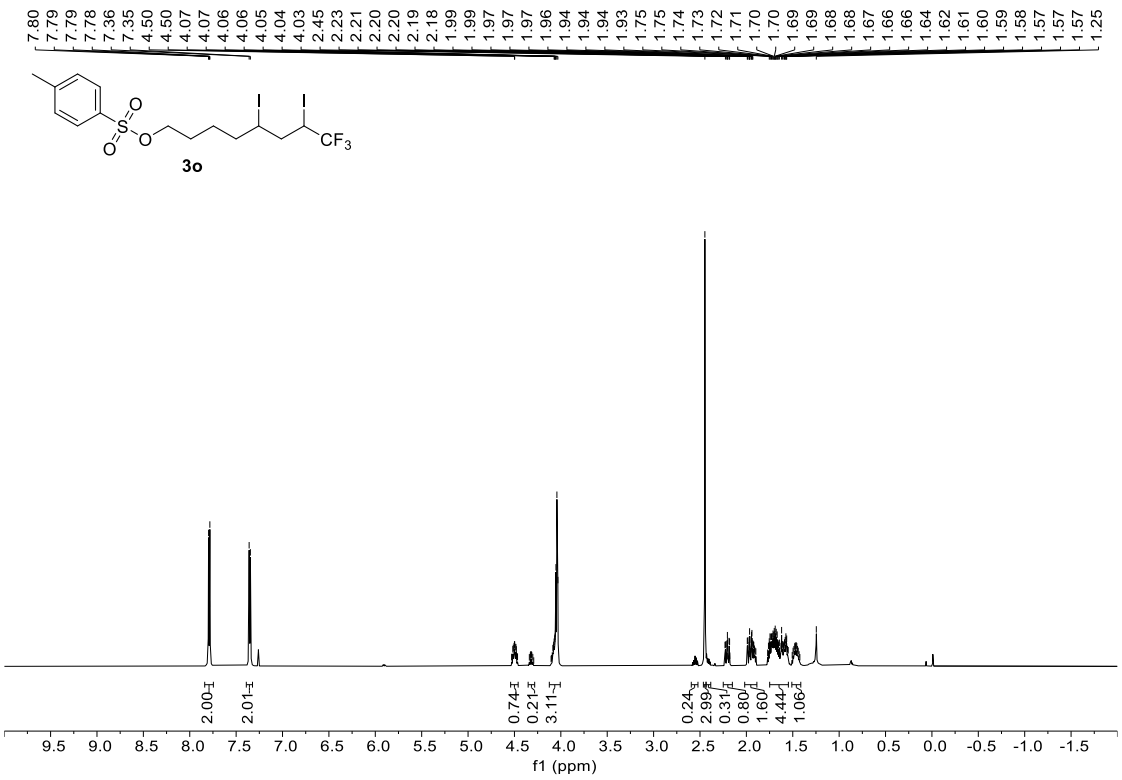


^{1}H NMR (600 MHz, $CDCl_3$) for **3n**

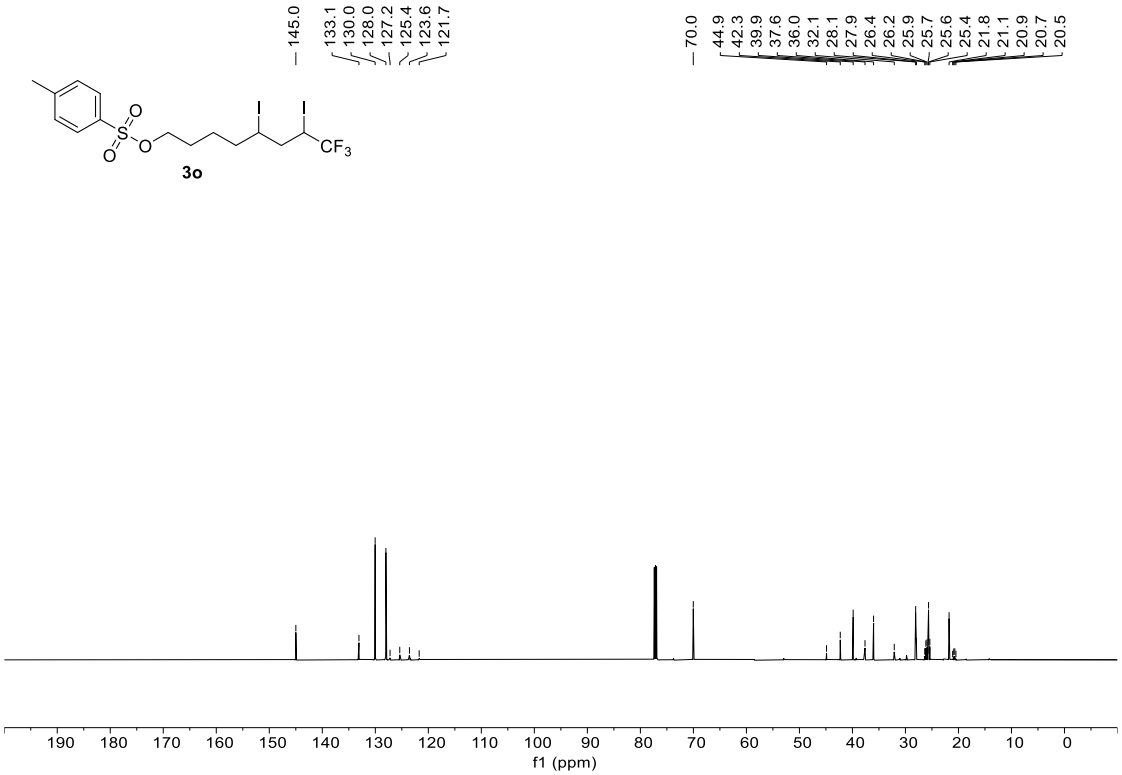


^{13}C NMR (151 MHz, $CDCl_3$) for **3n**

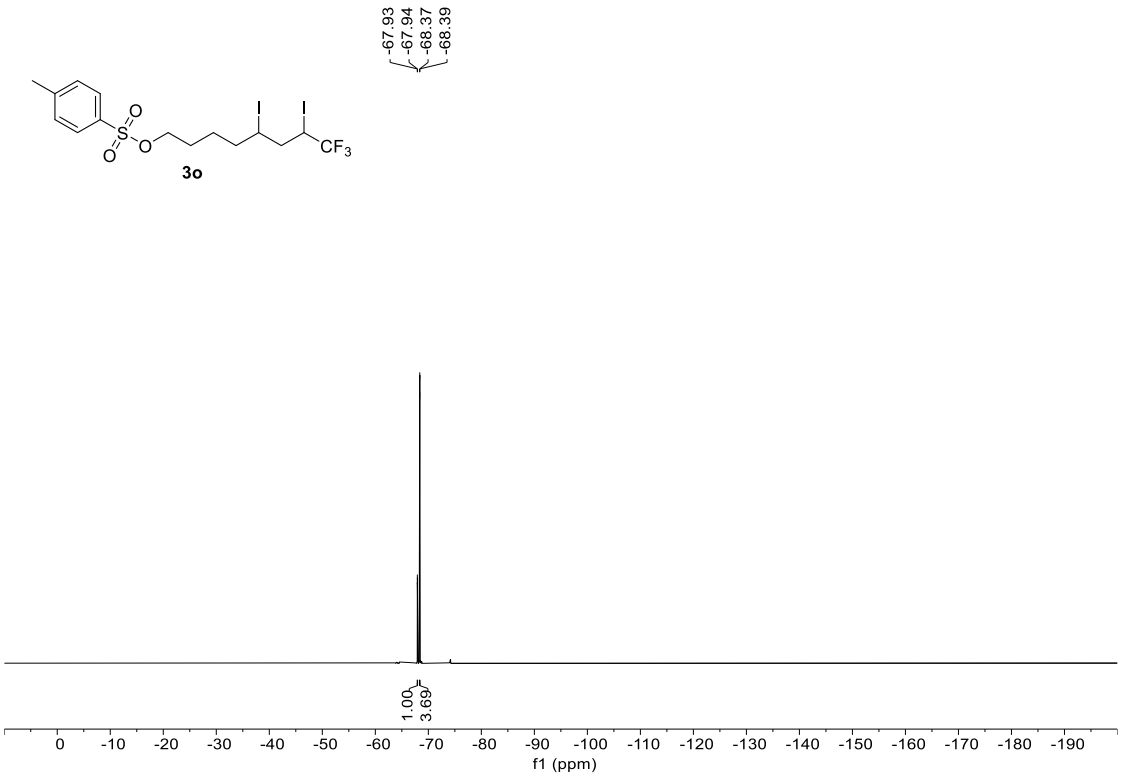
^{19}F NMR (565 MHz, $CDCl_3$) for **3n**



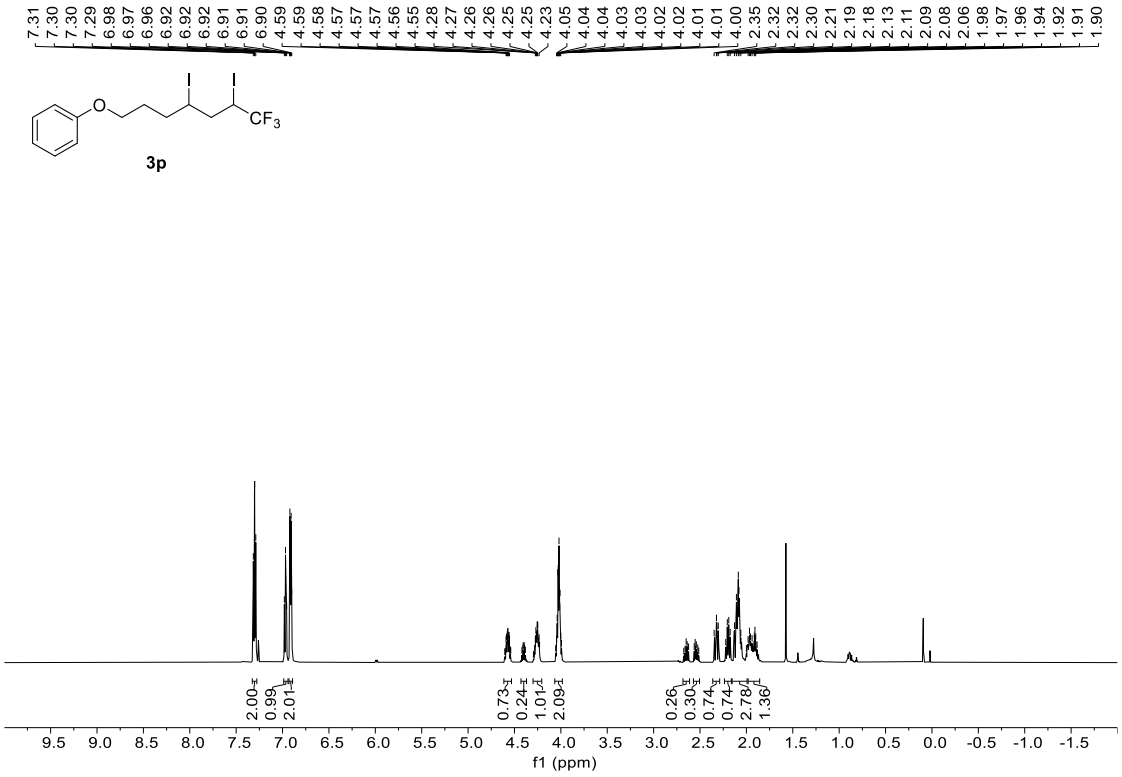
^{1}H NMR (600 MHz, $CDCl_3$) for **3o**



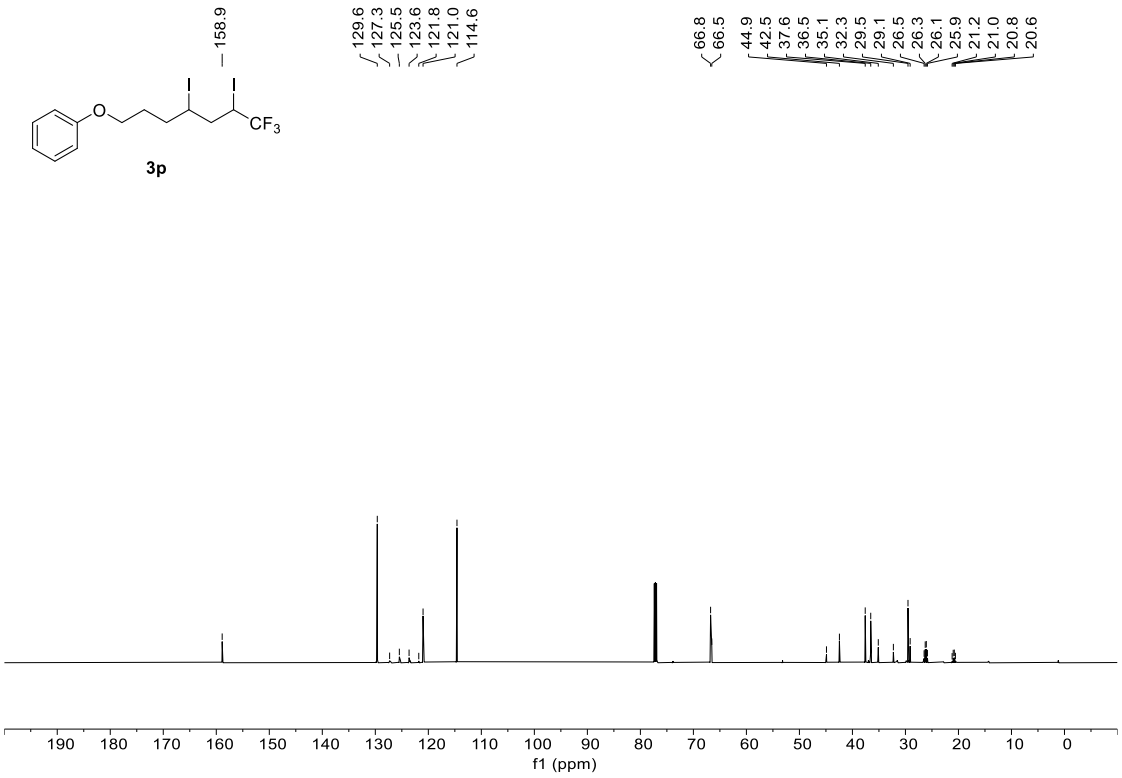
^{13}C NMR (151 MHz, $CDCl_3$) for **3o**



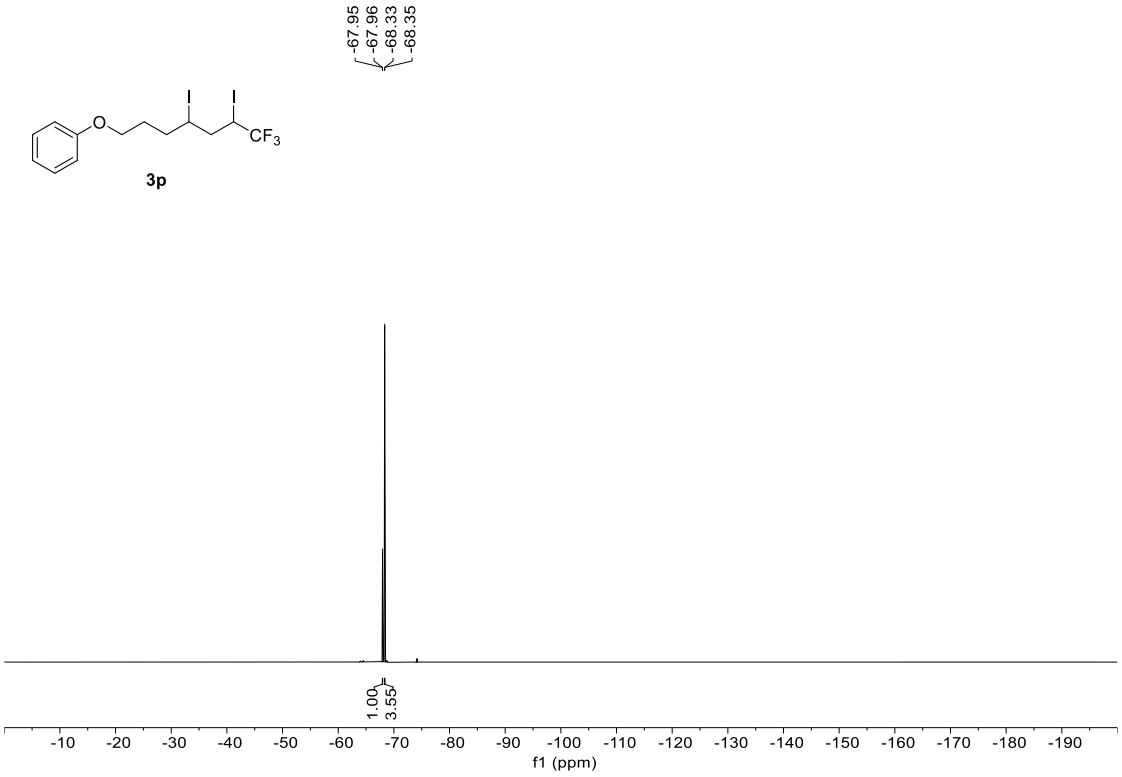
^{19}F NMR (565 MHz, $CDCl_3$) for **3o**



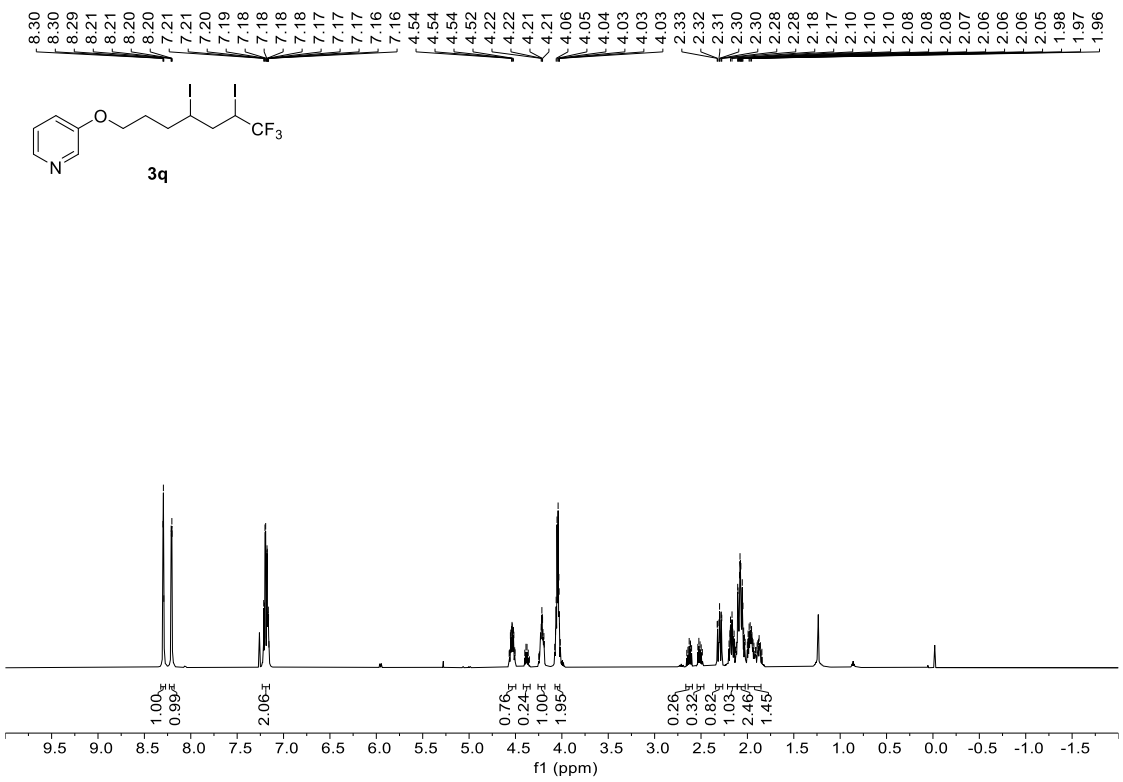
^{1}H NMR (600 MHz, $CDCl_3$) for **3p**



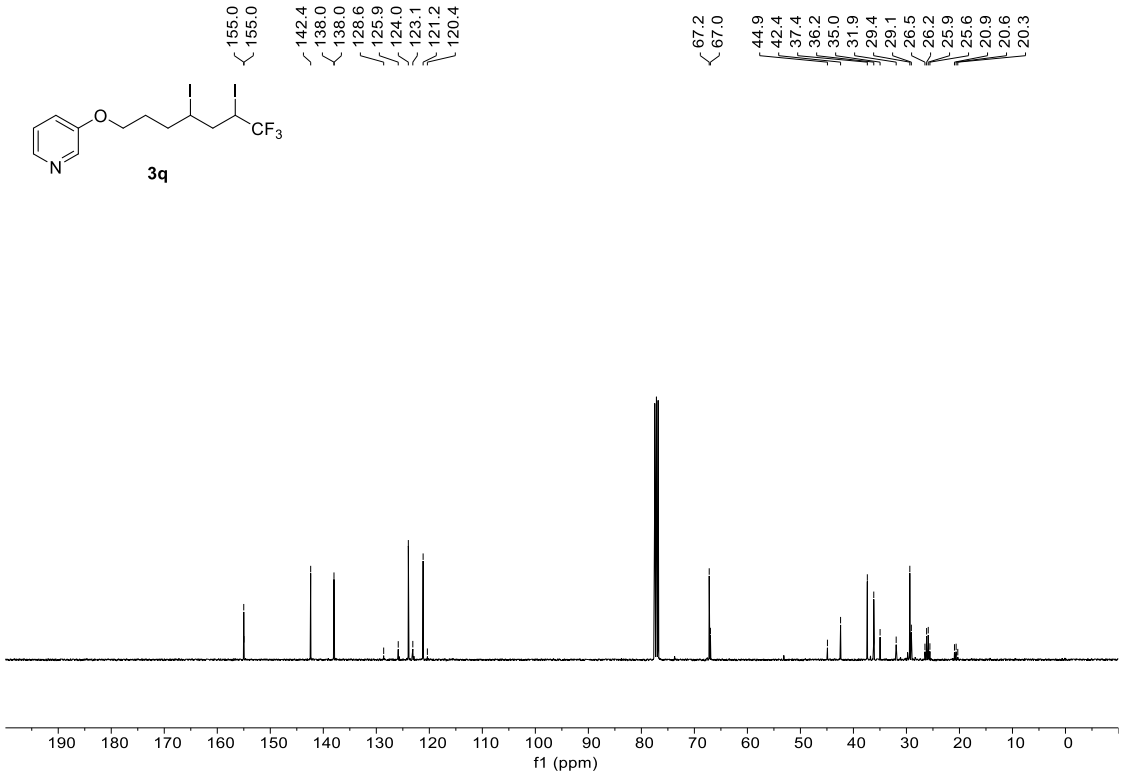
^{13}C NMR (151 MHz, $CDCl_3$) for **3p**



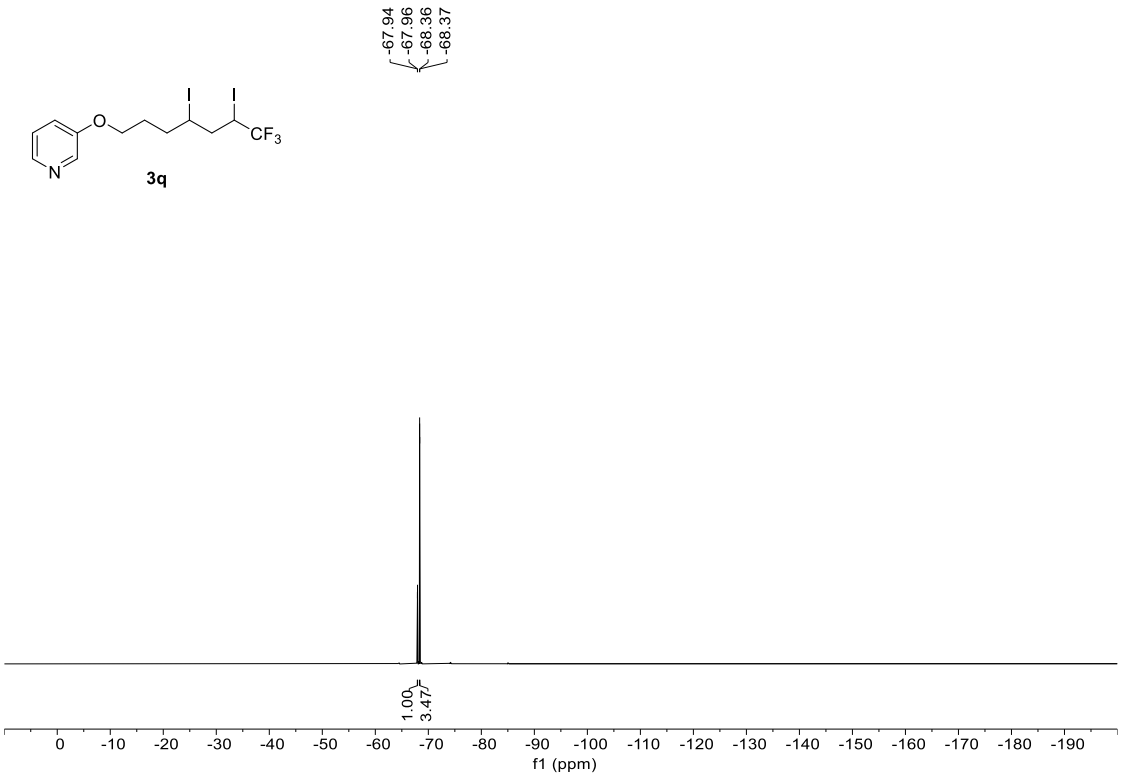
^{19}F NMR (565 MHz, $CDCl_3$) for **3p**



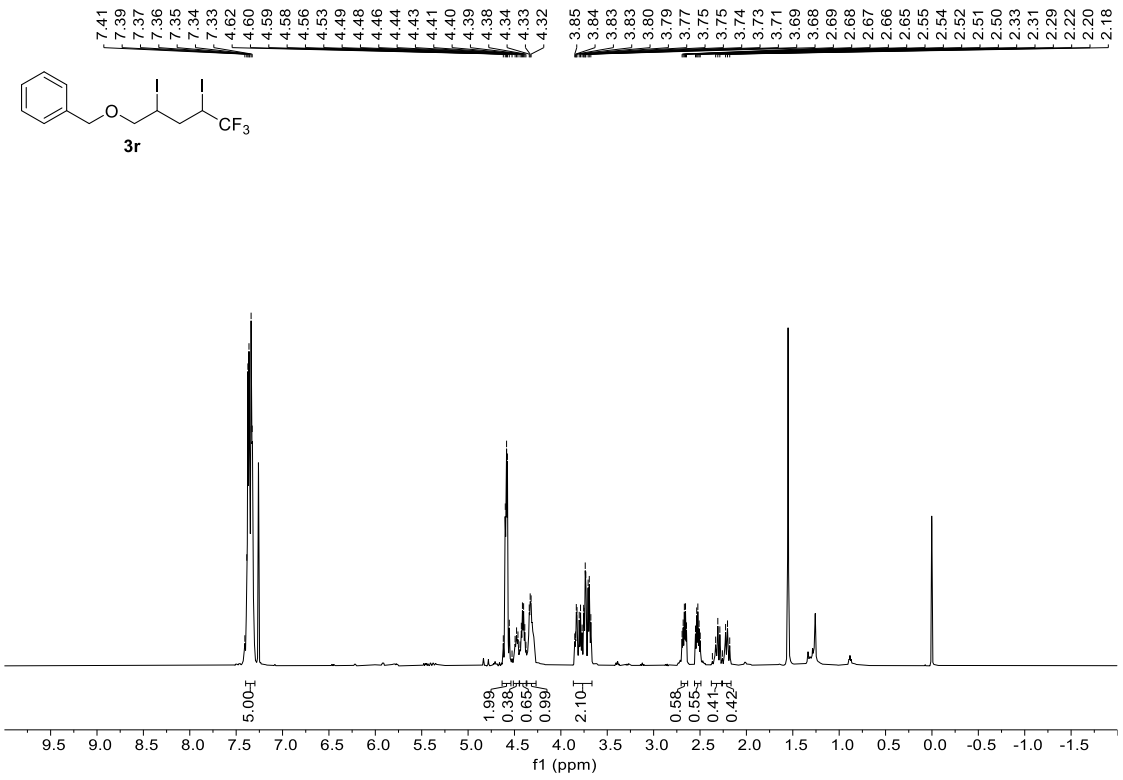
^{1}H NMR (600 MHz, $CDCl_3$) for **3q**



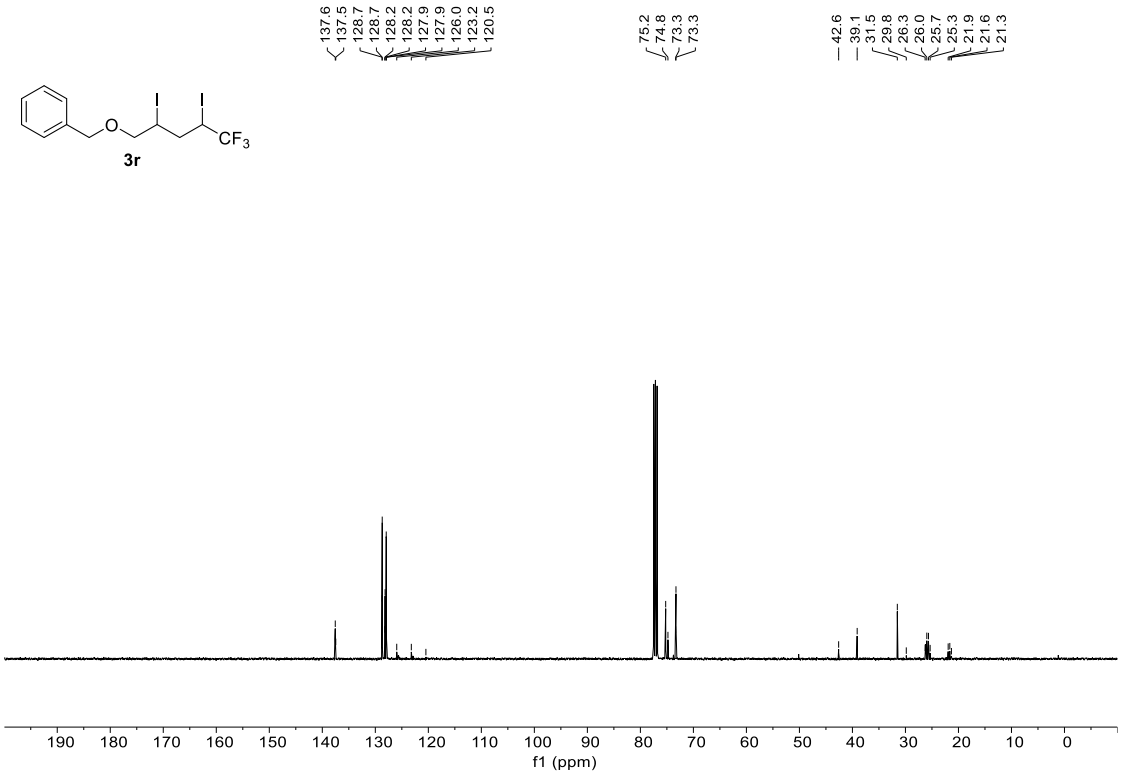
^{13}C NMR (101 MHz, $CDCl_3$) for **3q**



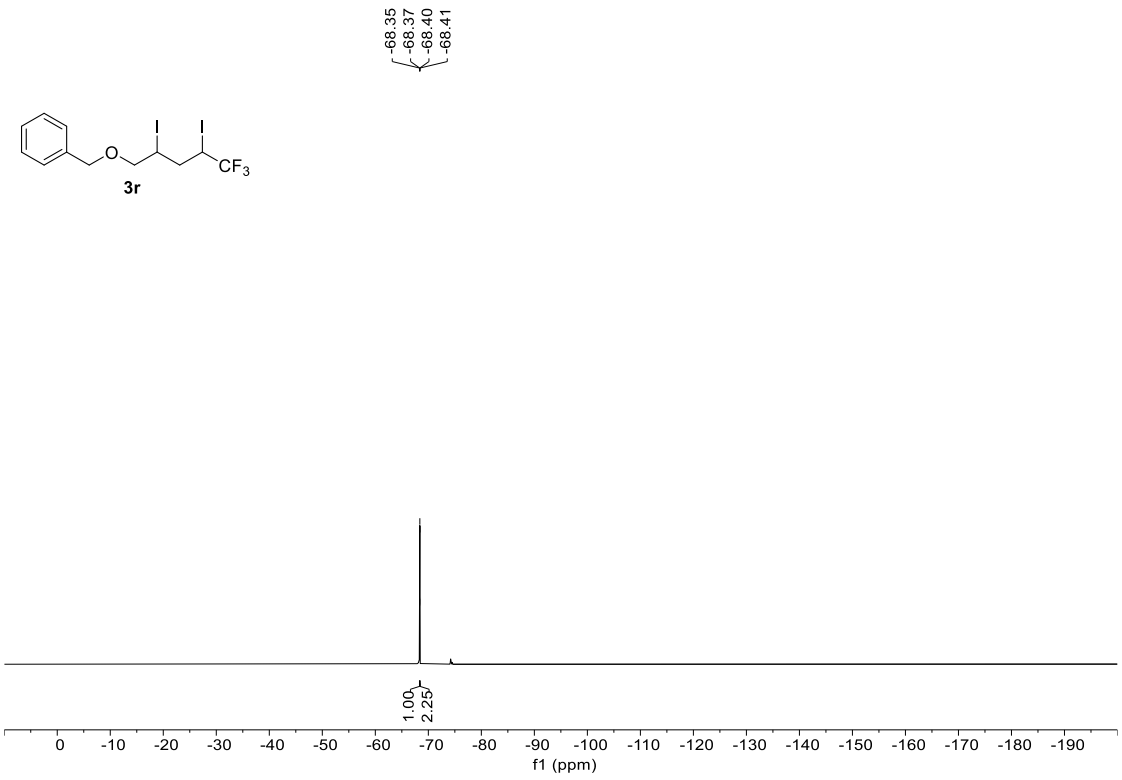
^{19}F NMR (565 MHz, $CDCl_3$) for **3q**



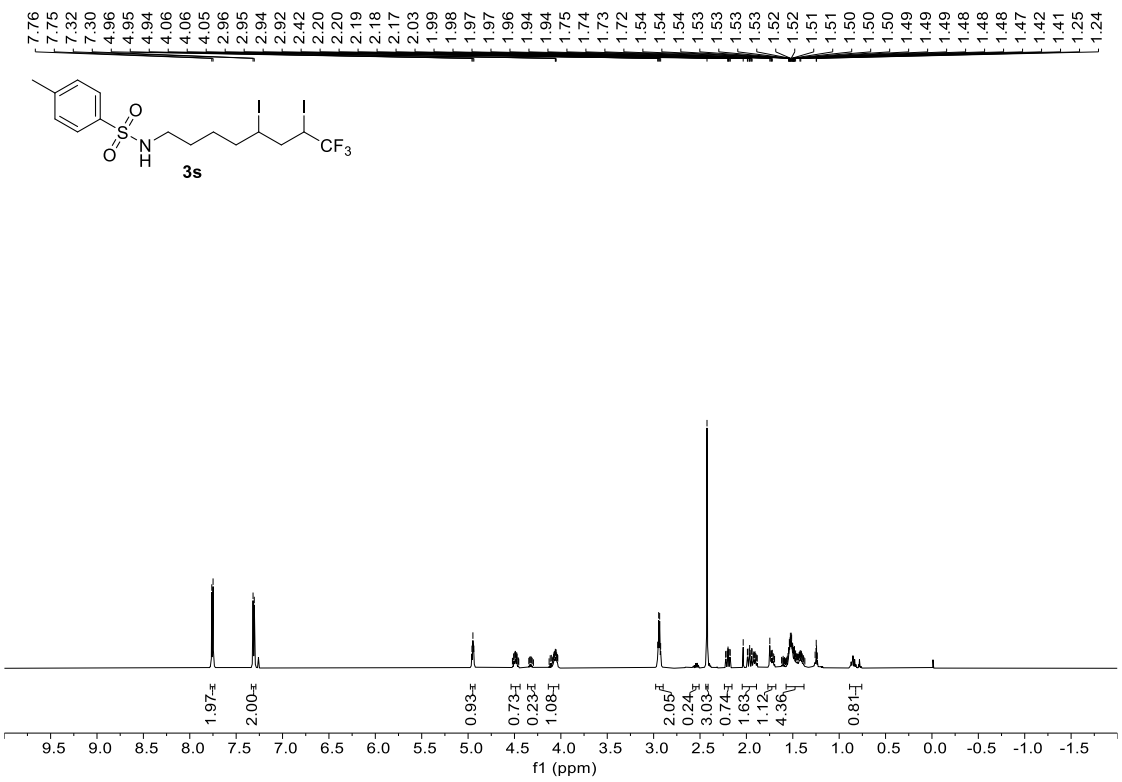
^{1}H NMR (600 MHz, $CDCl_3$) for **3r**



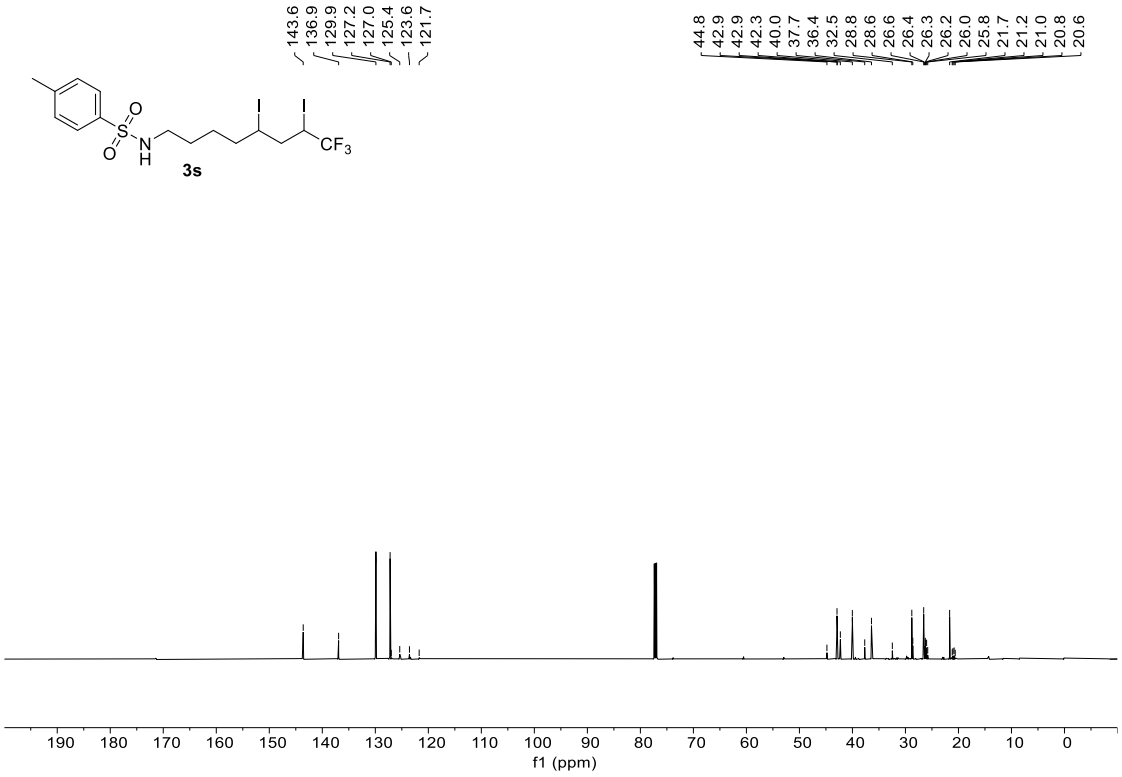
^{13}C NMR (101 MHz, $CDCl_3$) for **3r**



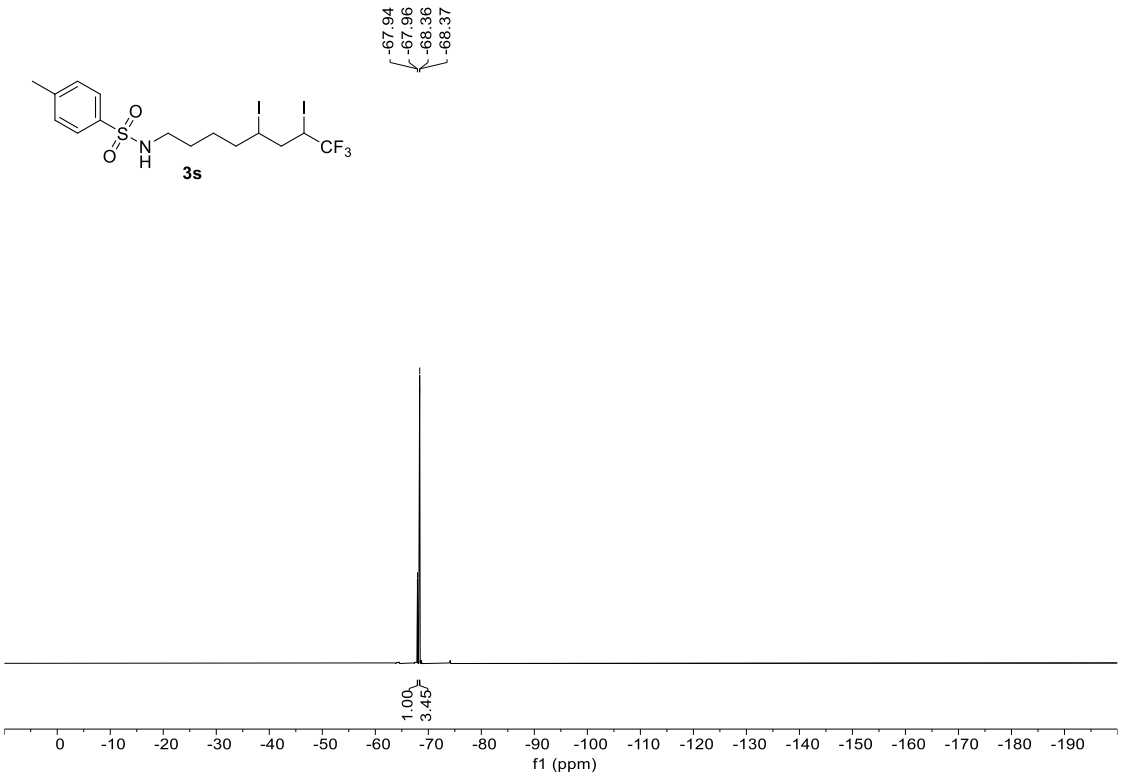
^{19}F NMR (565 MHz, $CDCl_3$) for **3r**



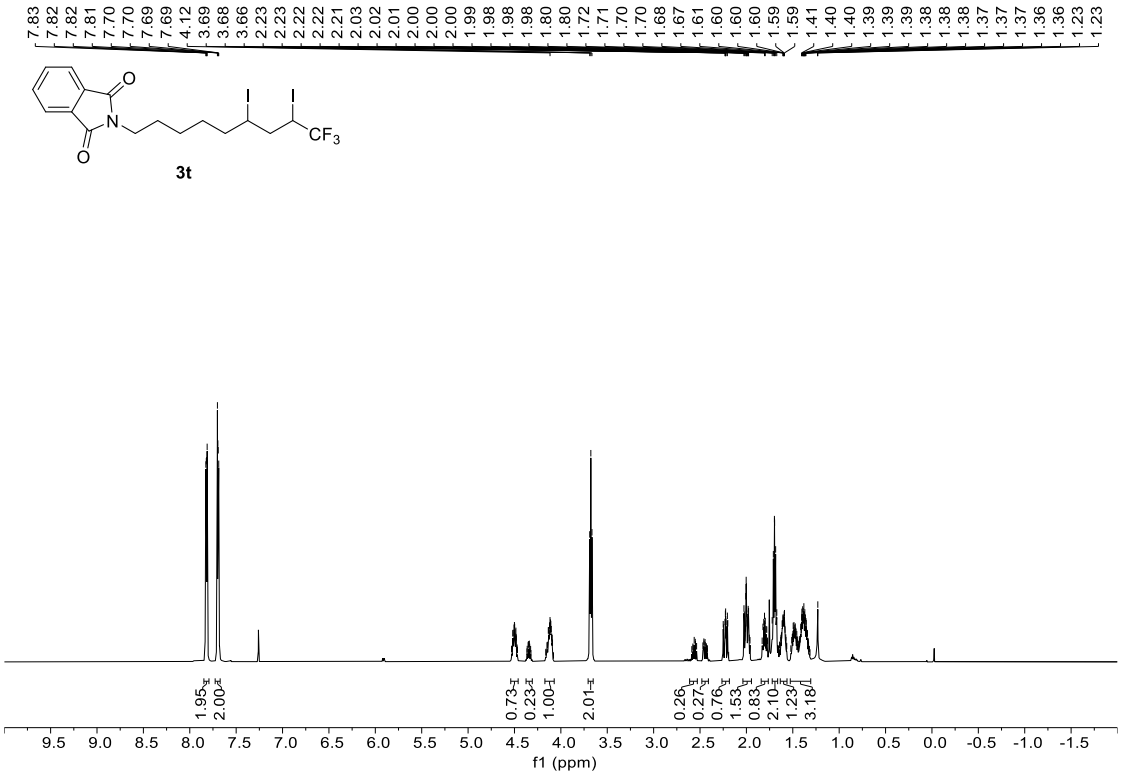
^{1}H NMR (600 MHz, $CDCl_3$) for **3s**



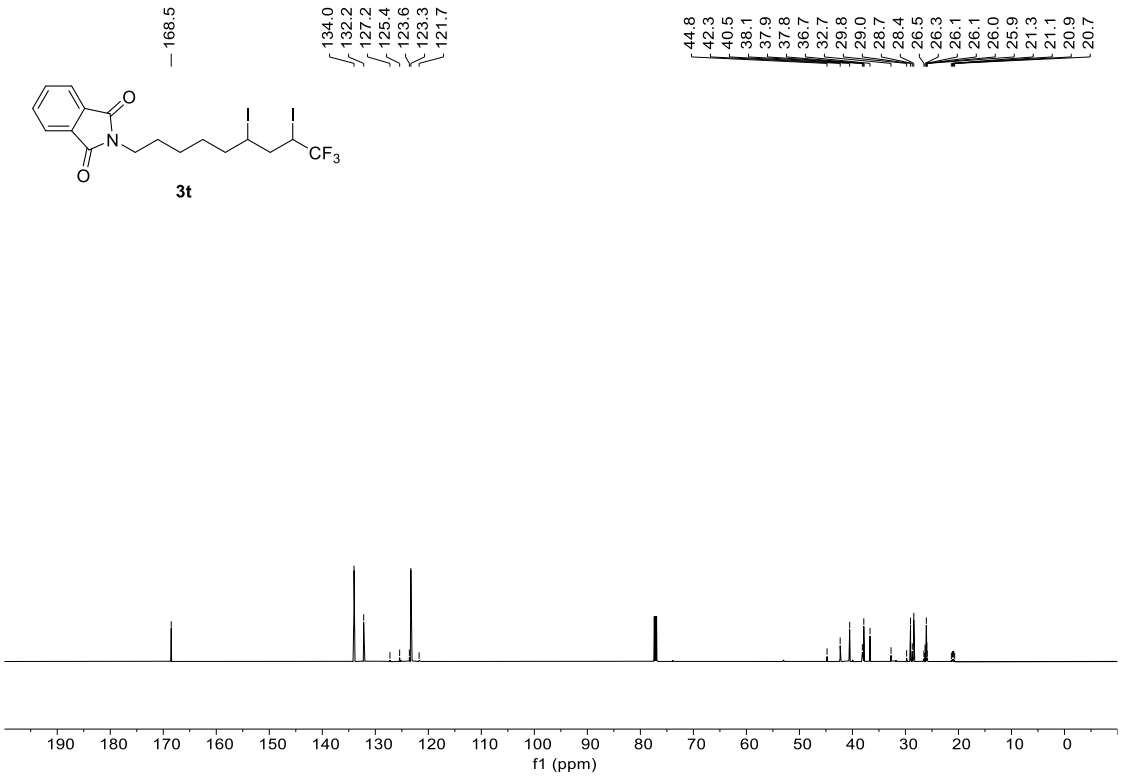
^{13}C NMR (151 MHz, $CDCl_3$) for **3s**



^{19}F NMR (565 MHz, $CDCl_3$) for **3s**

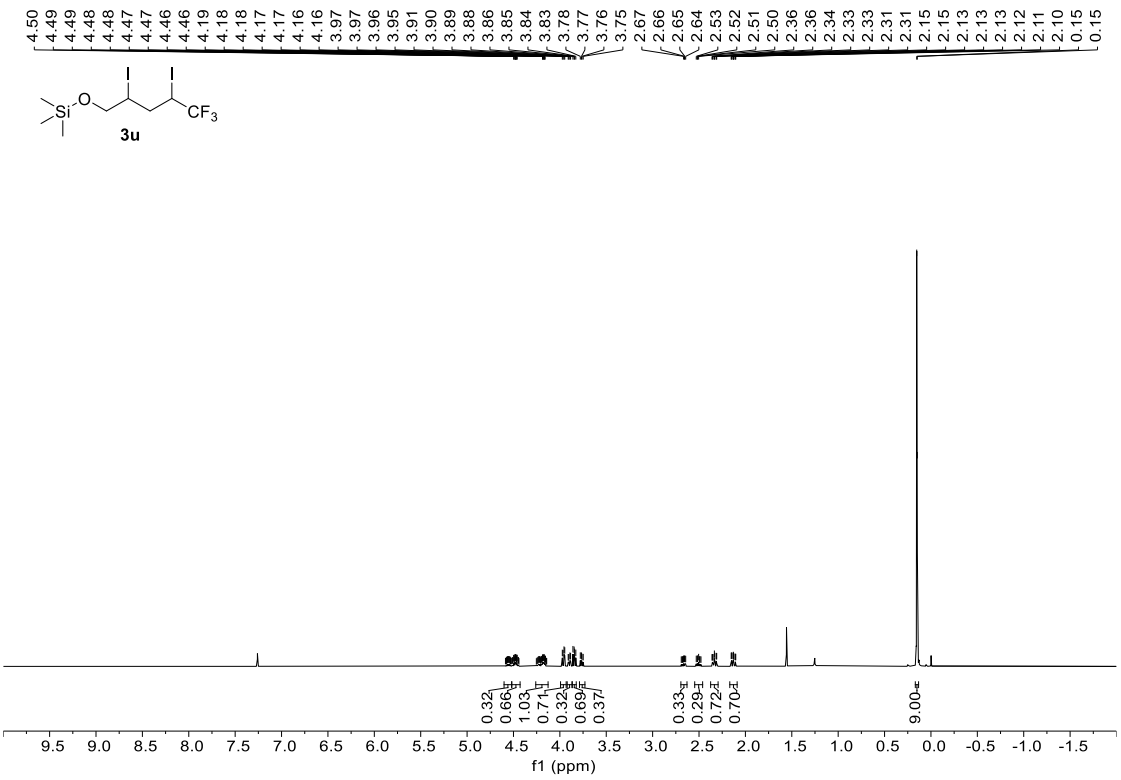


^{1}H NMR (600 MHz, $CDCl_3$) for **3t**

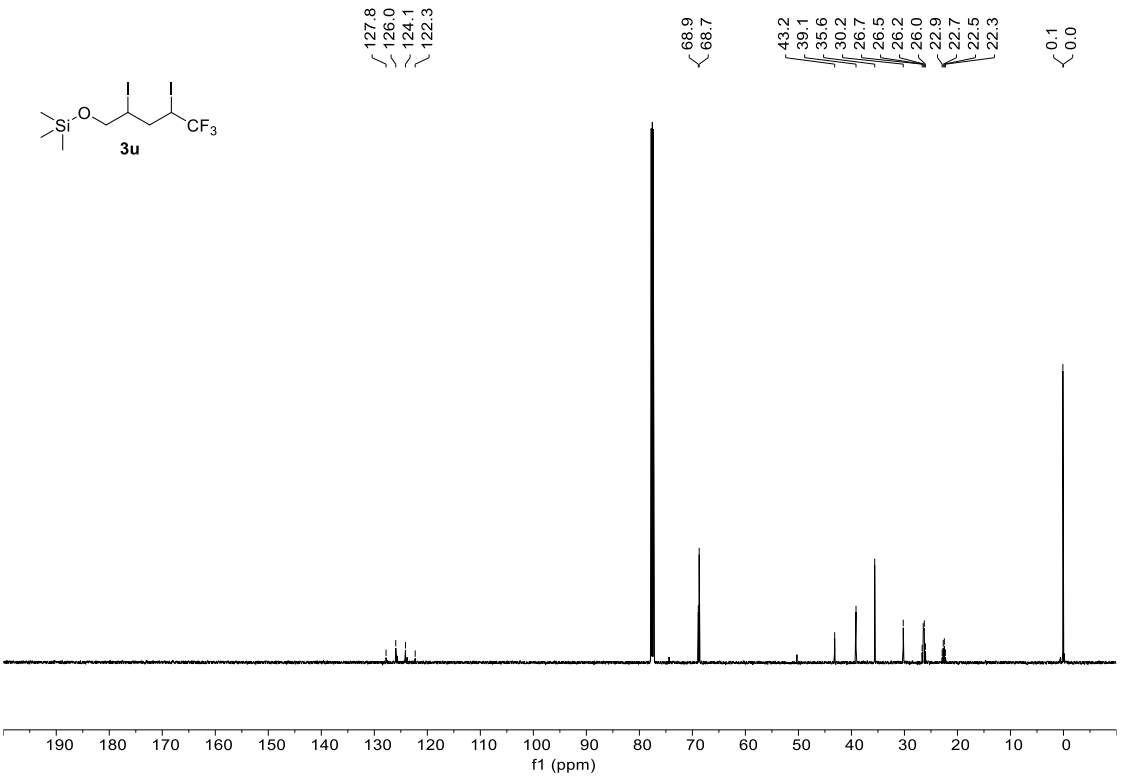


^{13}C NMR (151 MHz, $CDCl_3$) for **3t**

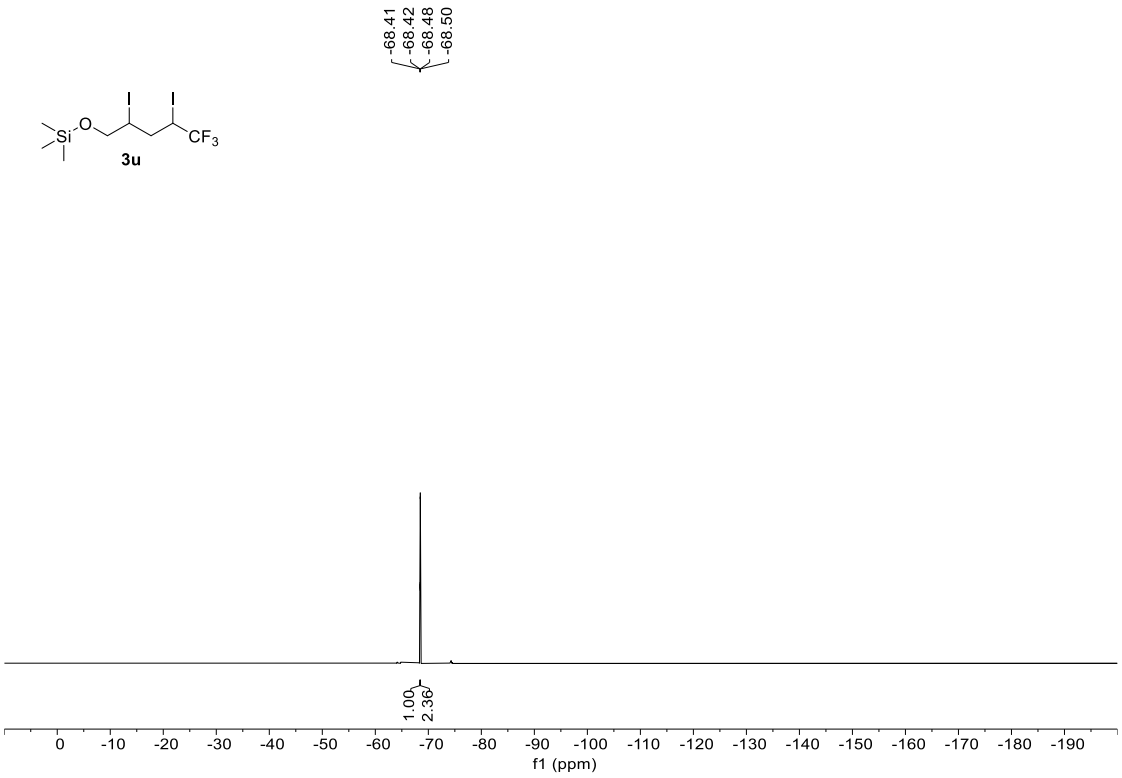
^{19}F NMR (565 MHz, $CDCl_3$) for **3t**



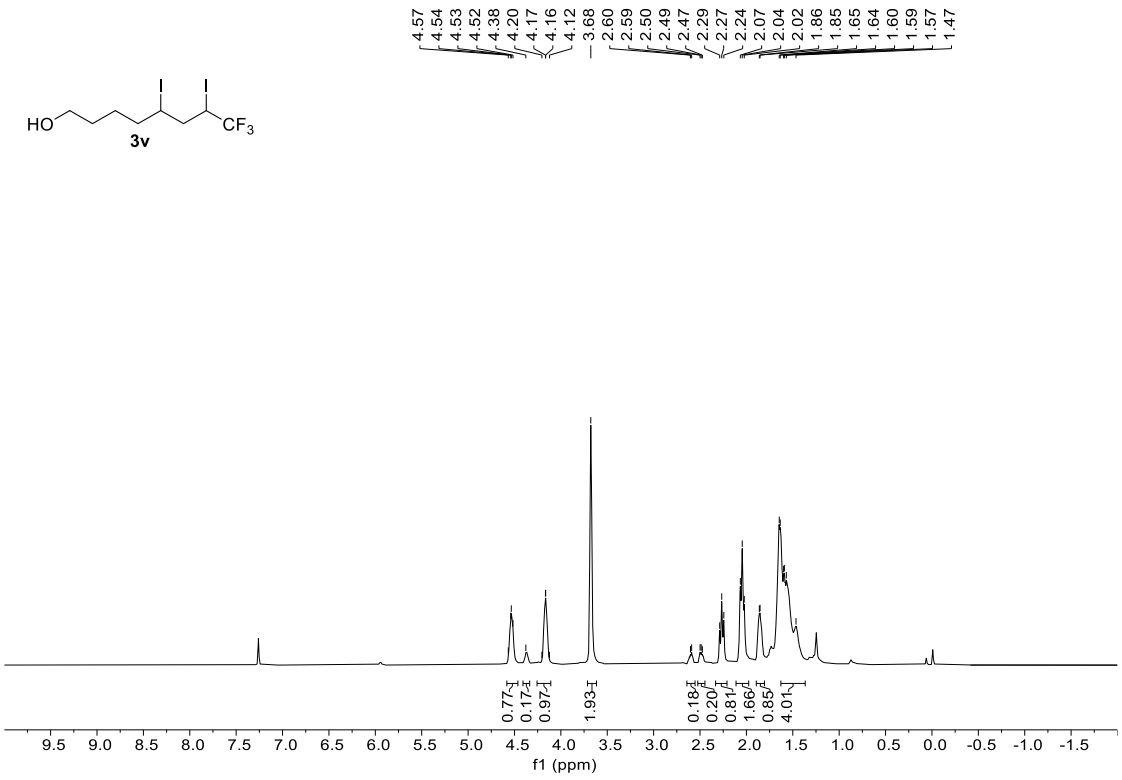
^{1}H NMR (600 MHz, $CDCl_3$) for **3u**



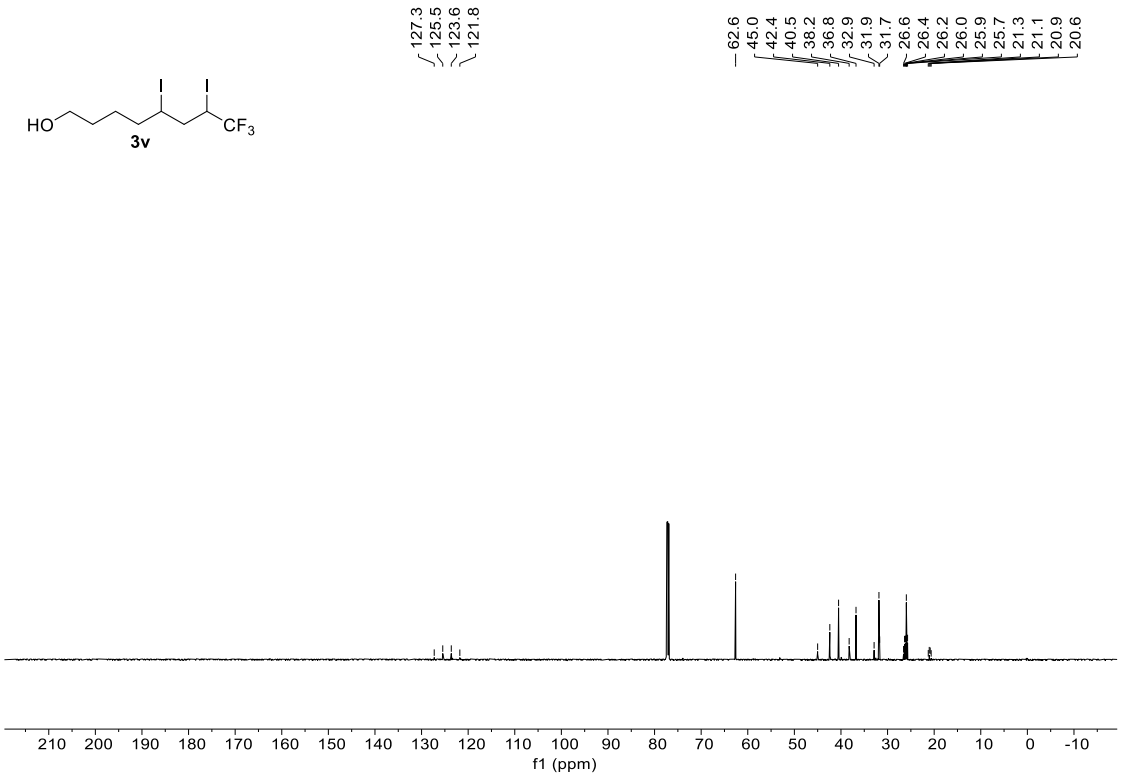
^{13}C NMR (151 MHz, $CDCl_3$) for **3u**



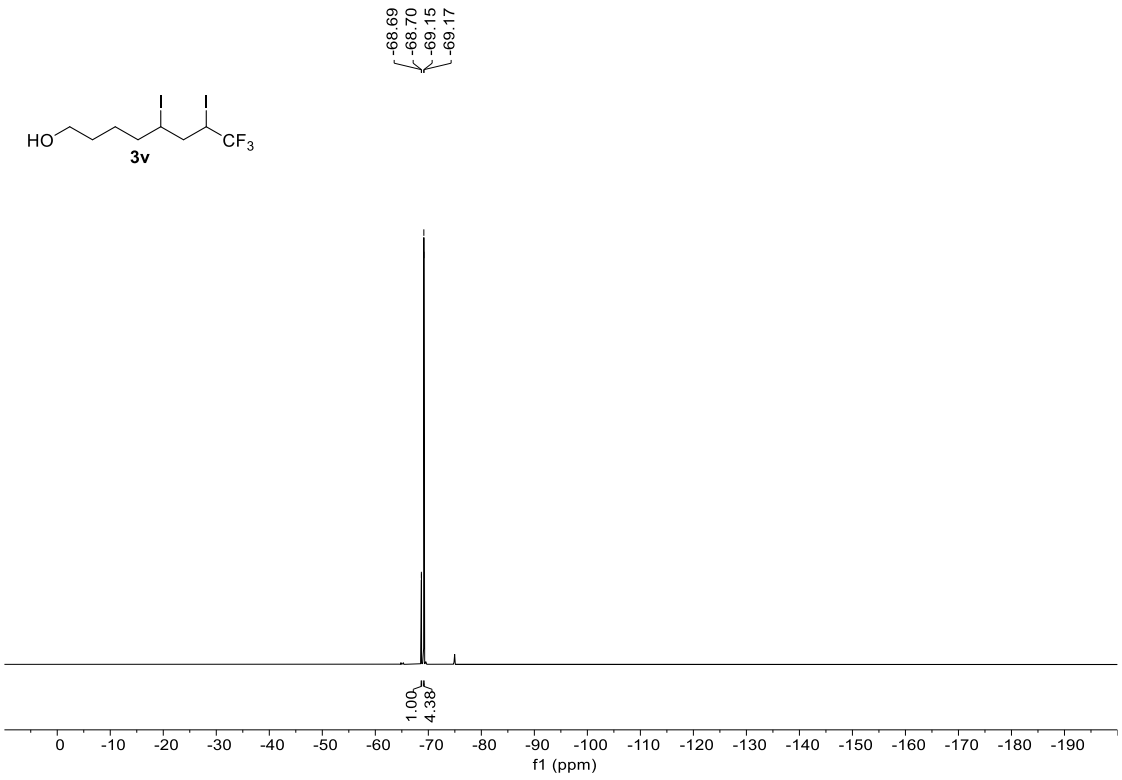
^{19}F NMR (565 MHz, $CDCl_3$) for **3u**



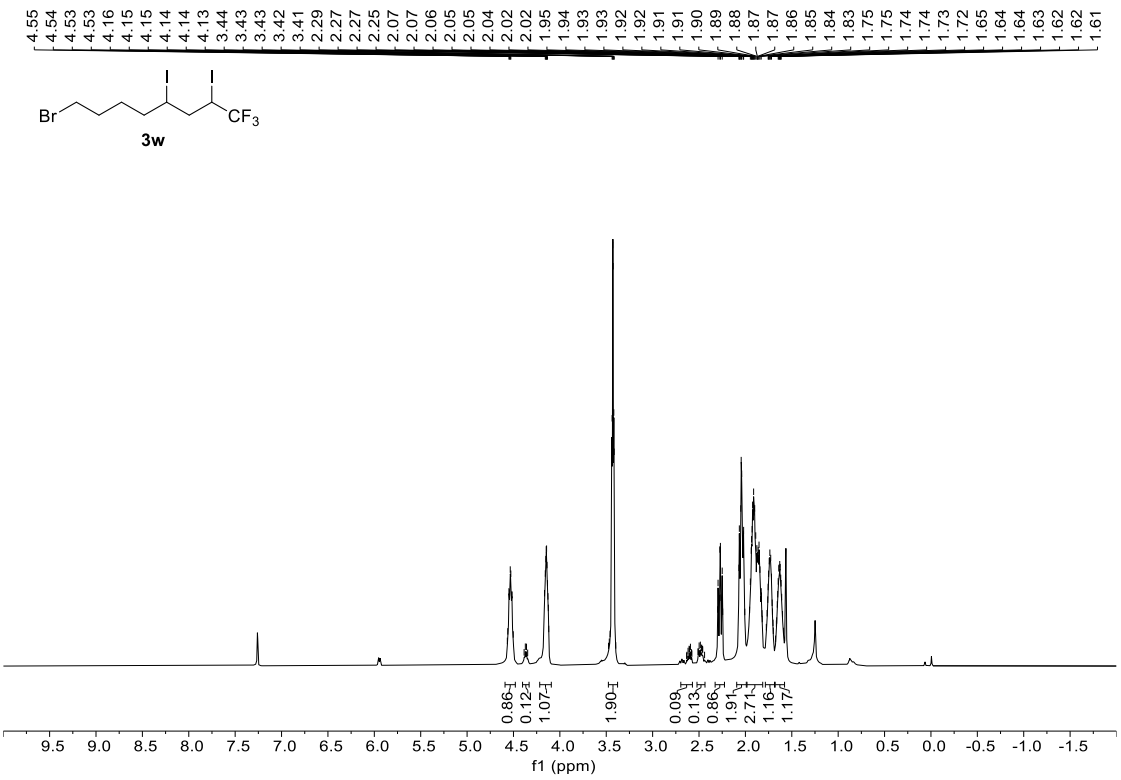
^{1}H NMR (600 MHz, $CDCl_3$) for **3v**



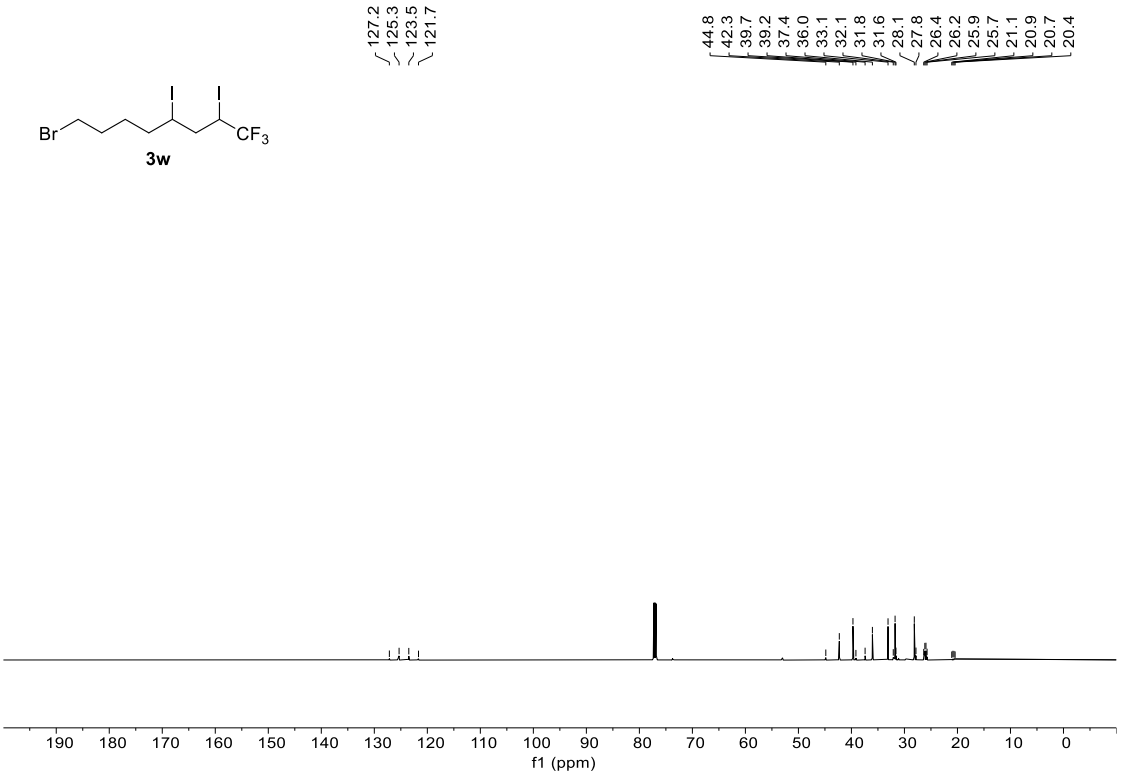
^{13}C NMR (151 MHz, $CDCl_3$) for **3v**



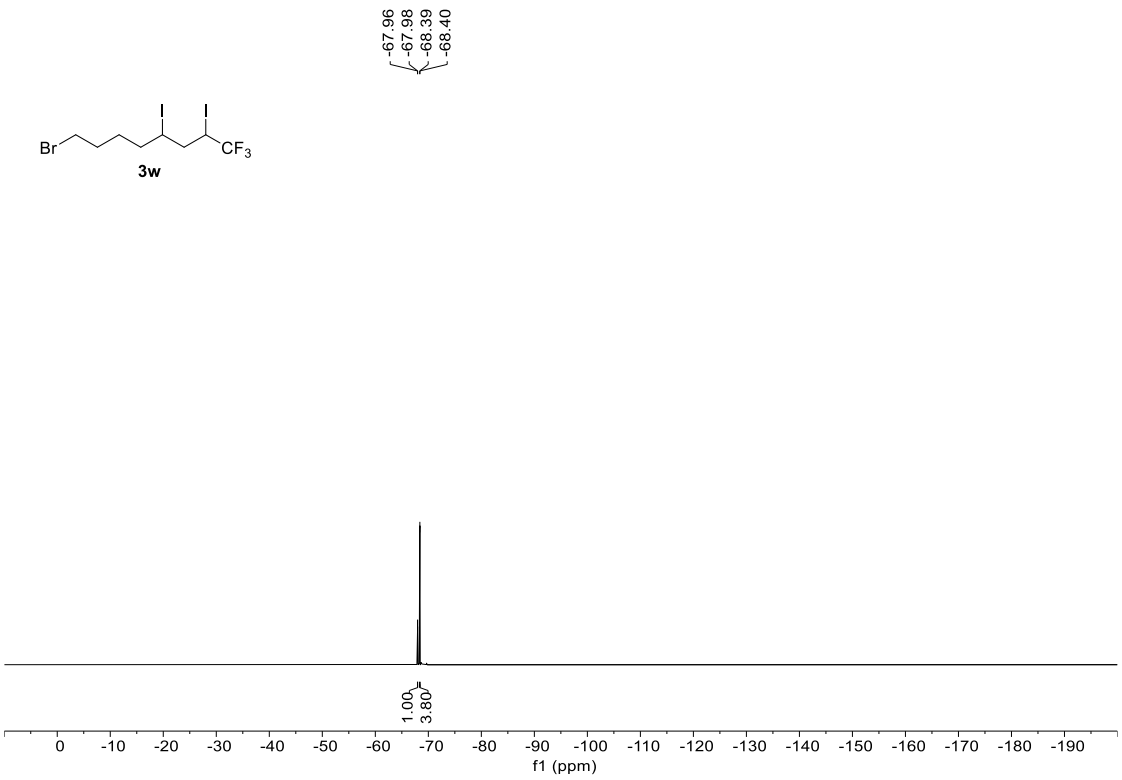
^{19}F NMR (565 MHz, $CDCl_3$) for **3v**



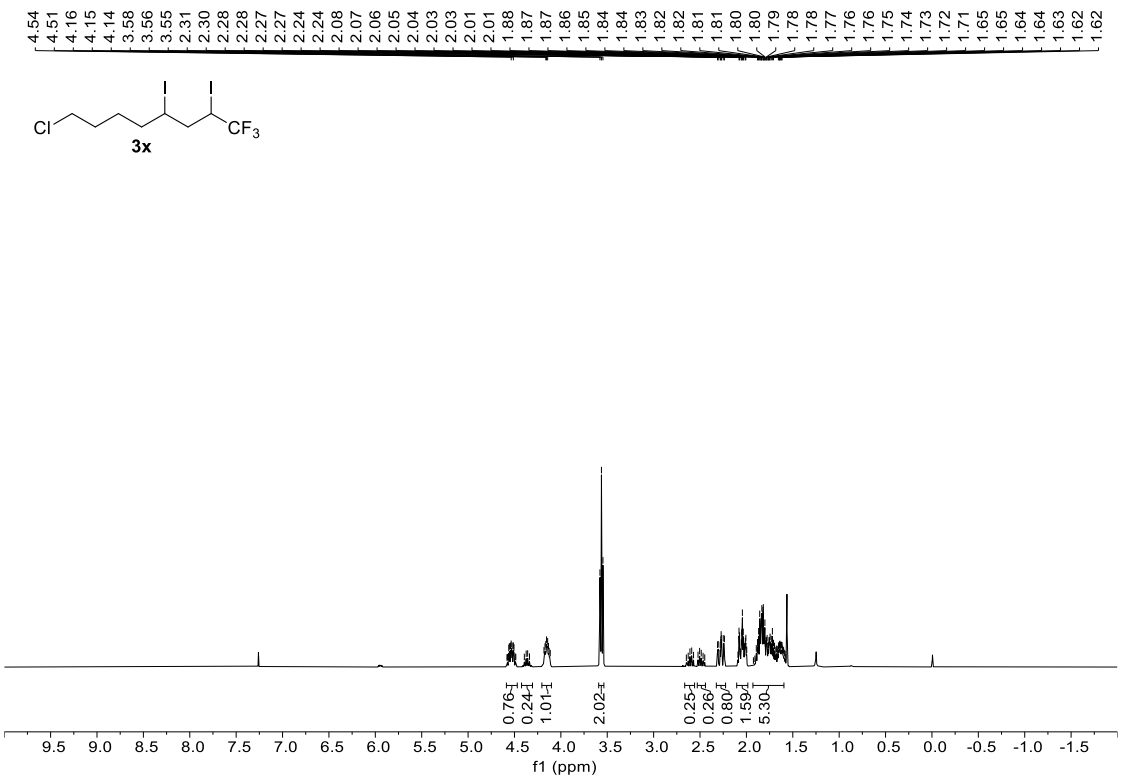
^{1}H NMR (600 MHz, $CDCl_3$) for **3w**



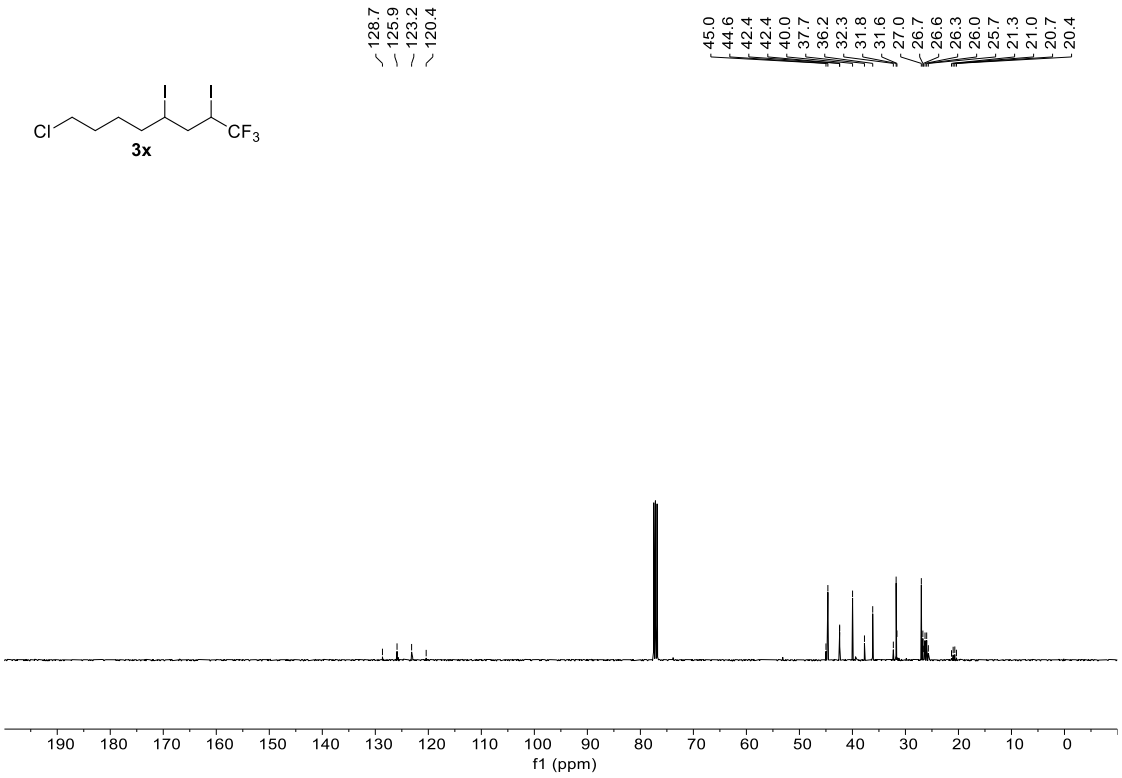
^{13}C NMR (151 MHz, $CDCl_3$) for **3w**



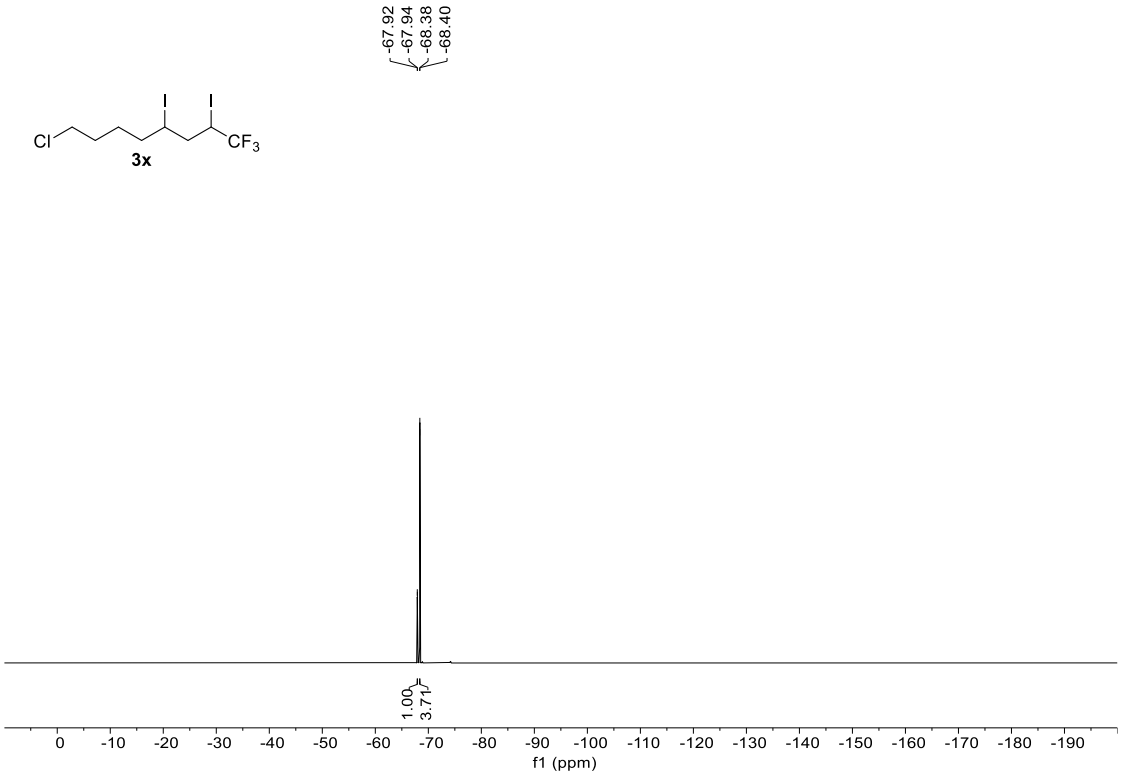
^{19}F NMR (565 MHz, $CDCl_3$) for **3w**



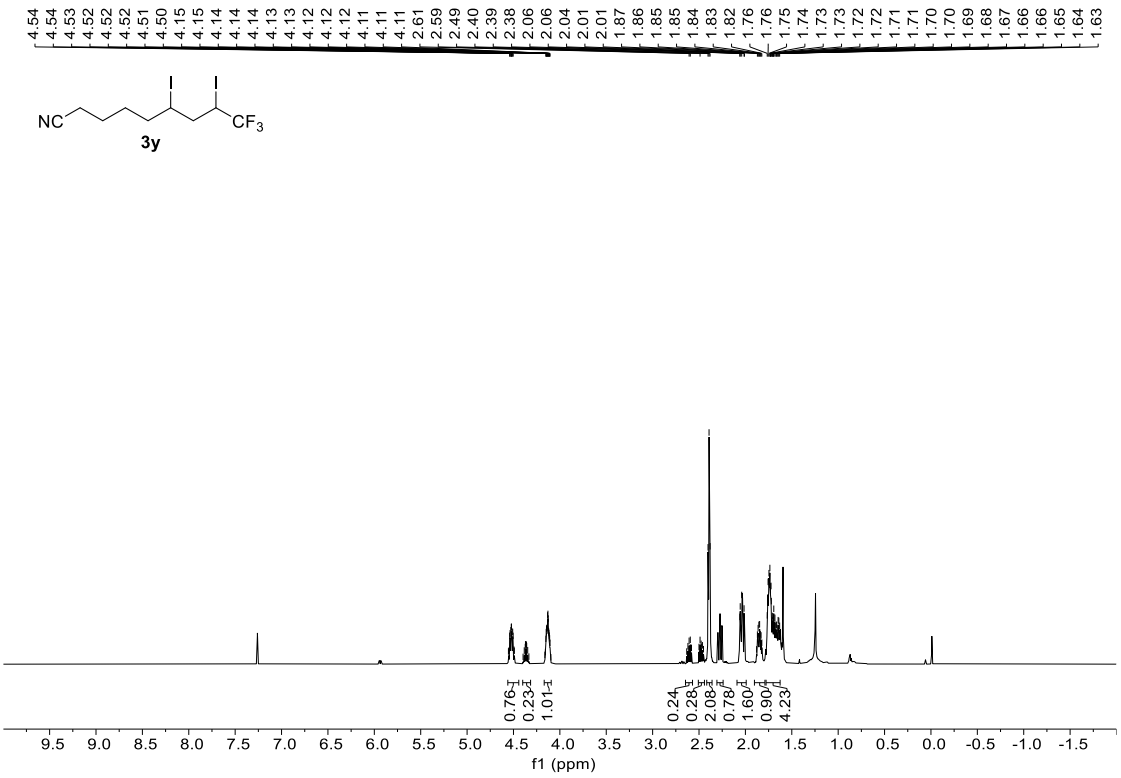
^{1}H NMR (400 MHz, $CDCl_3$) for **3x**



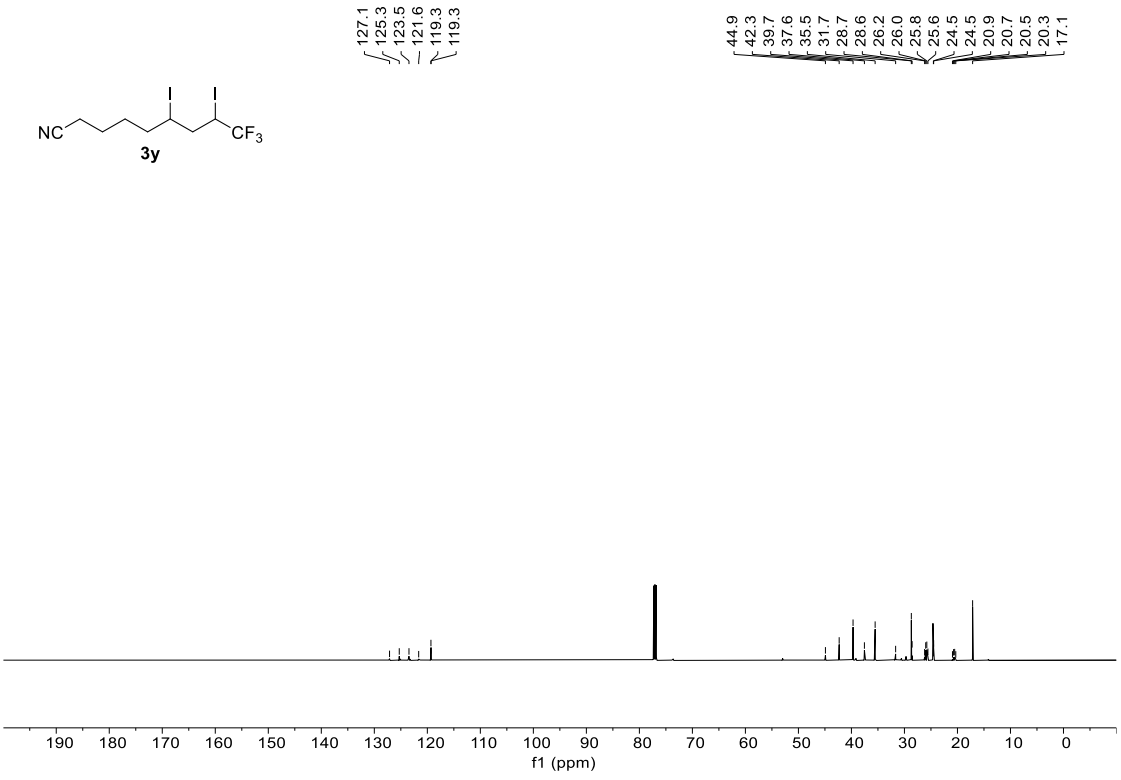
^{13}C NMR (101 MHz, $CDCl_3$) for **3x**



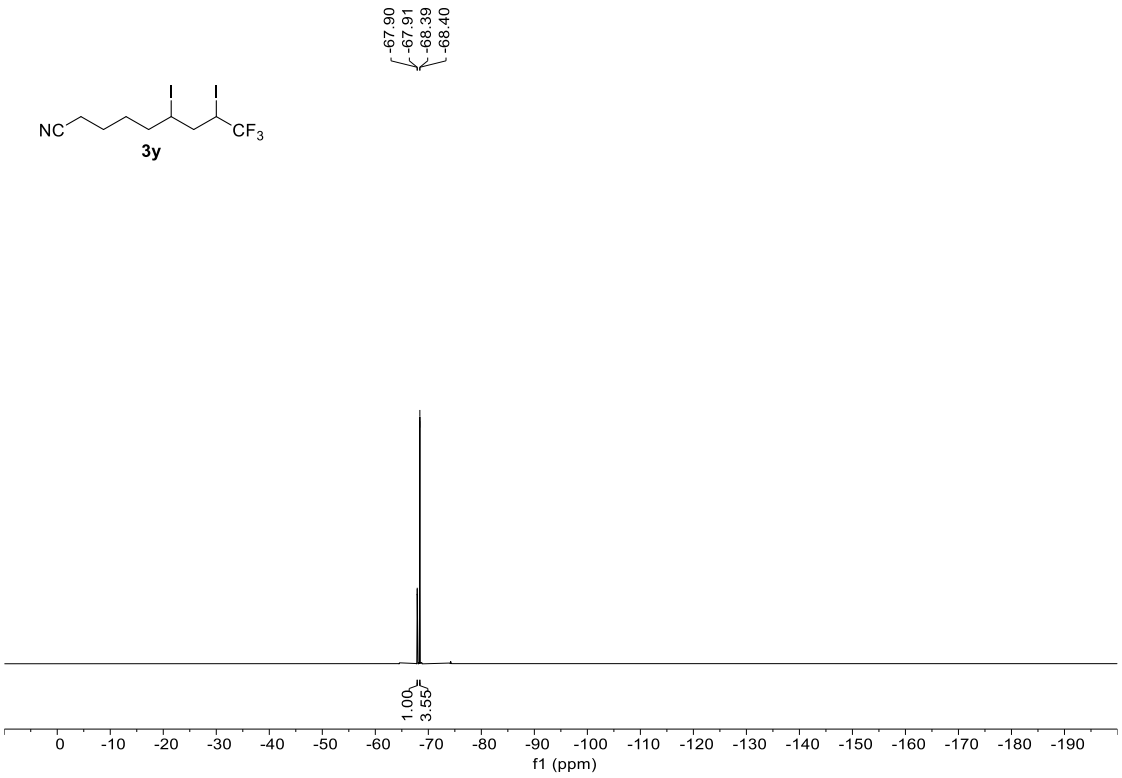
^{19}F NMR (376 MHz, $CDCl_3$) for **3x**



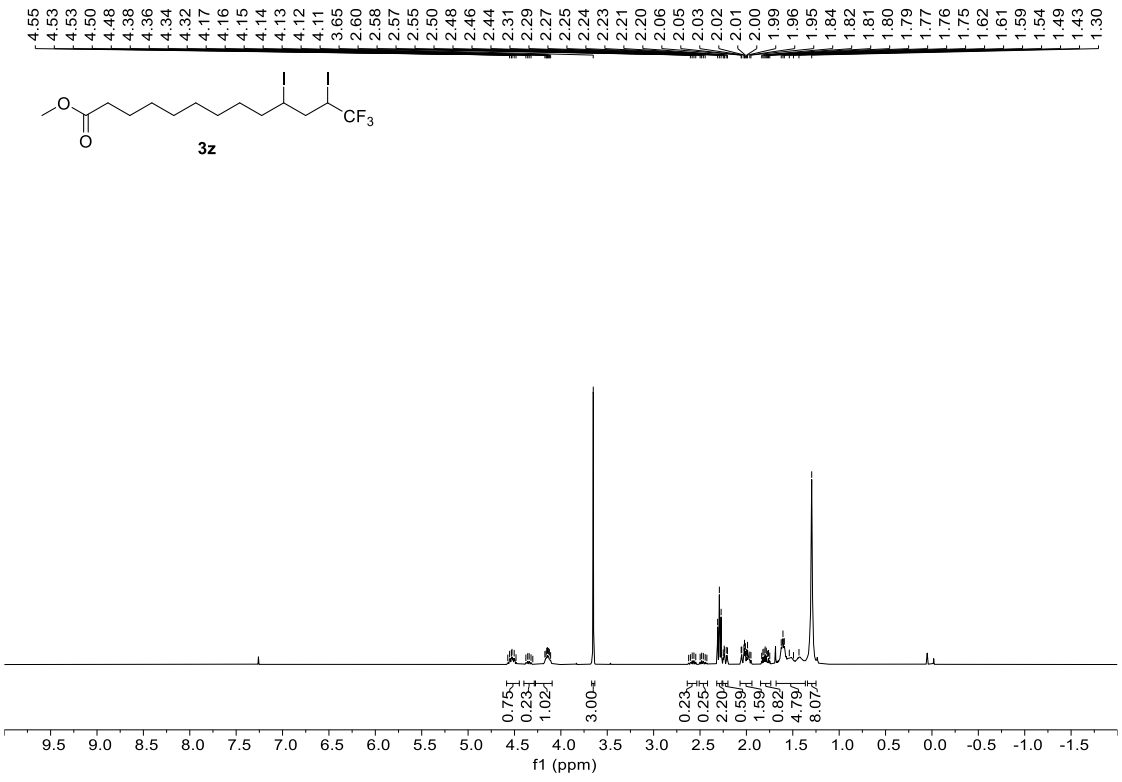
^{1}H NMR (600 MHz, $CDCl_3$) for **3y**



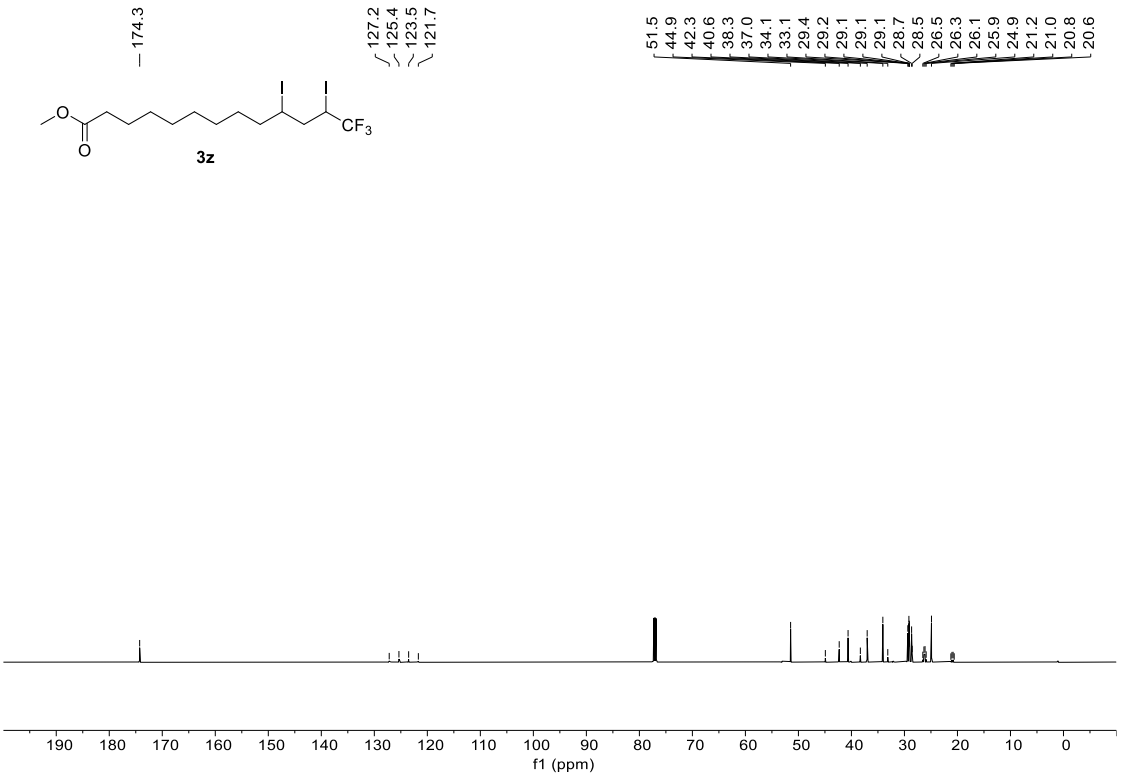
^{13}C NMR (151 MHz, $CDCl_3$) for **3y**



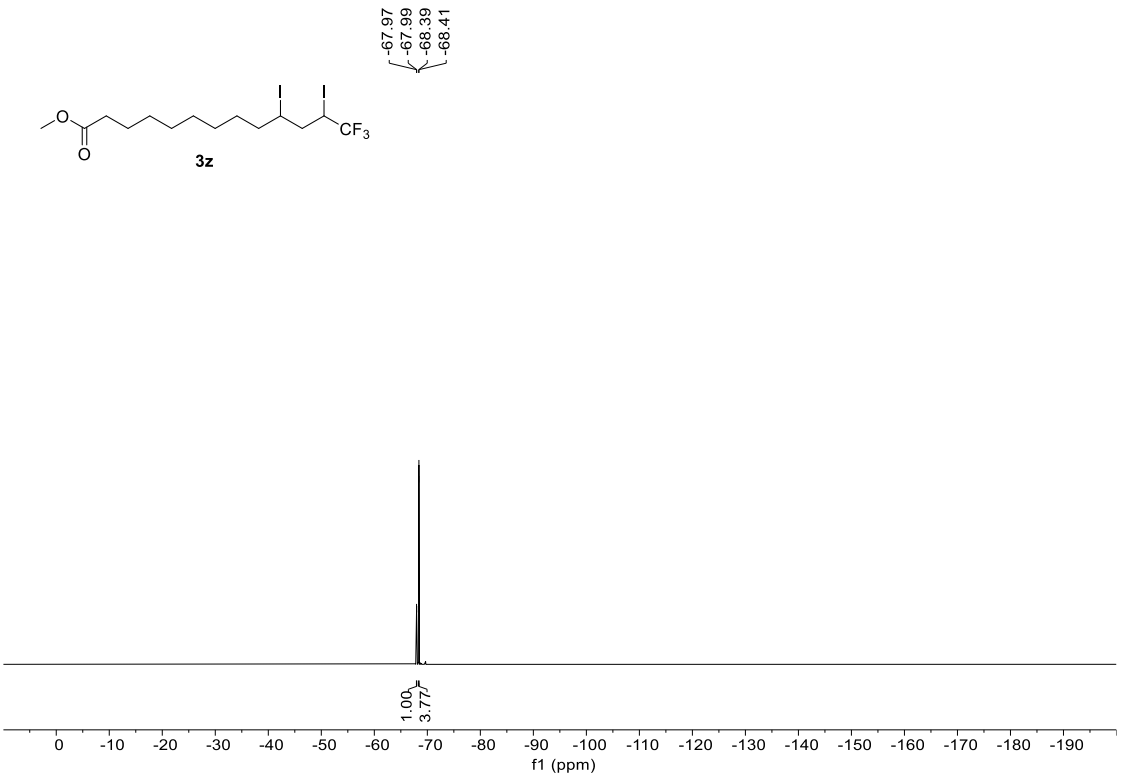
^{19}F NMR (565 MHz, $CDCl_3$) for **3y**



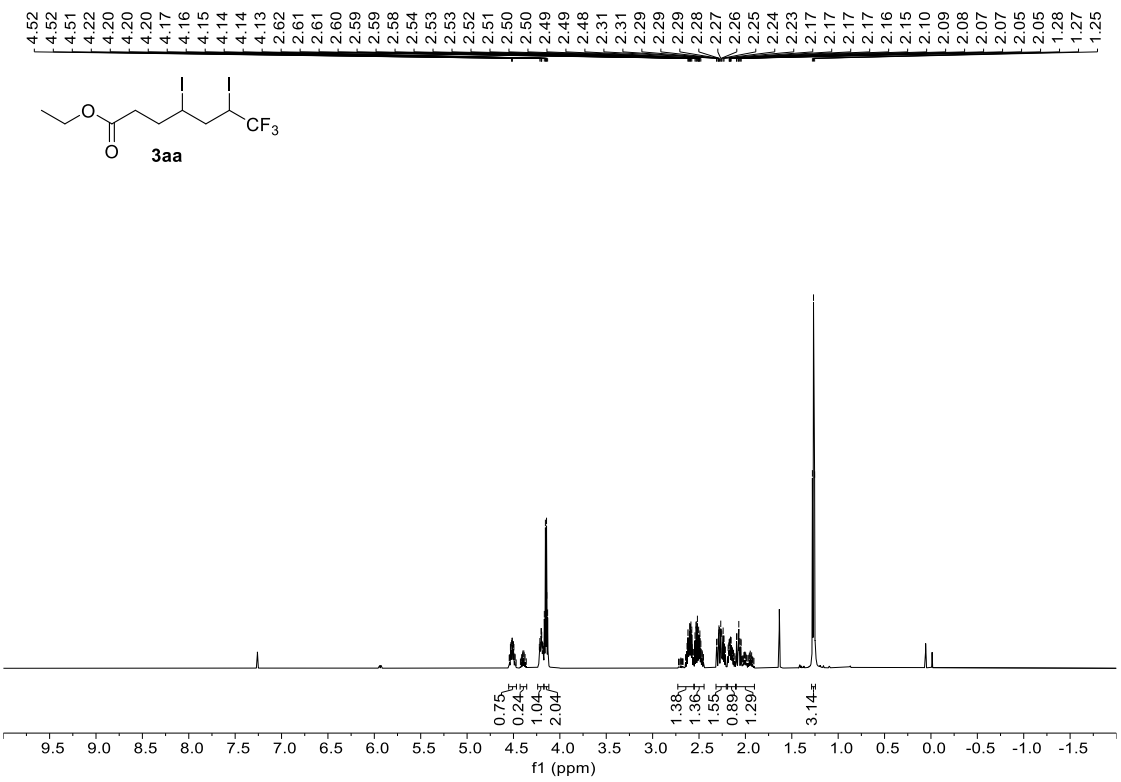
^{19}H NMR (400 MHz, $CDCl_3$) for **3z**



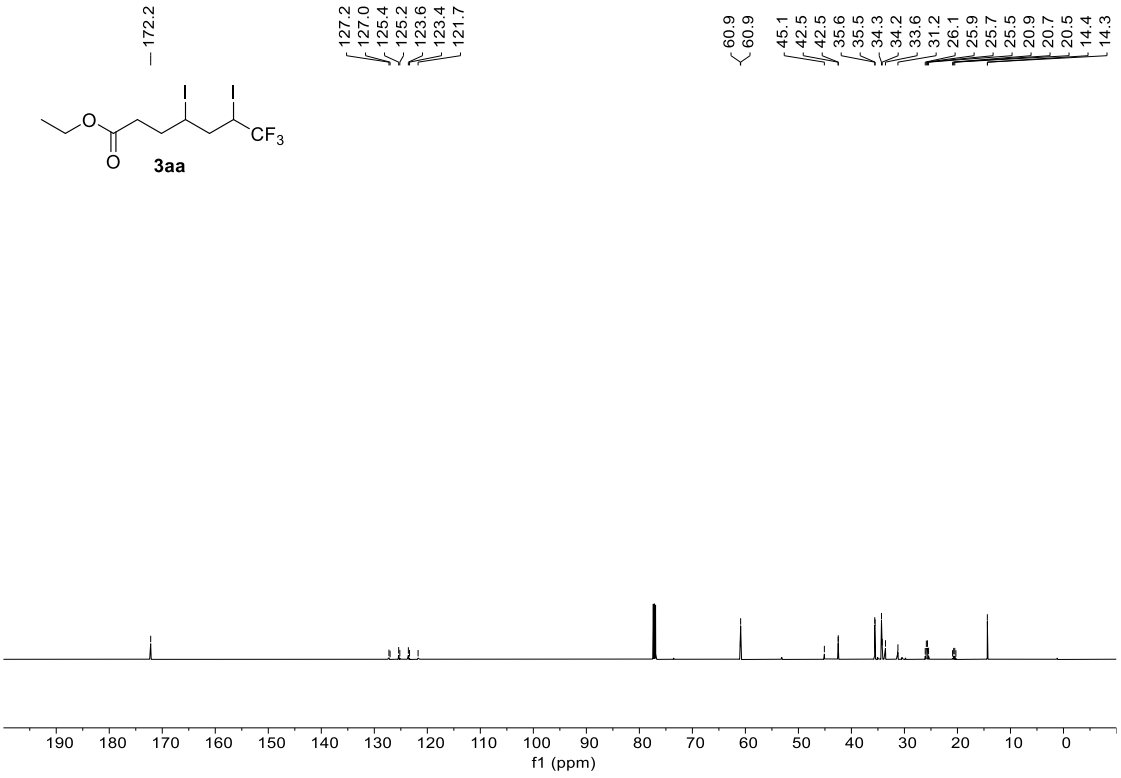
^{13}C NMR (151 MHz, $CDCl_3$) for **3z**



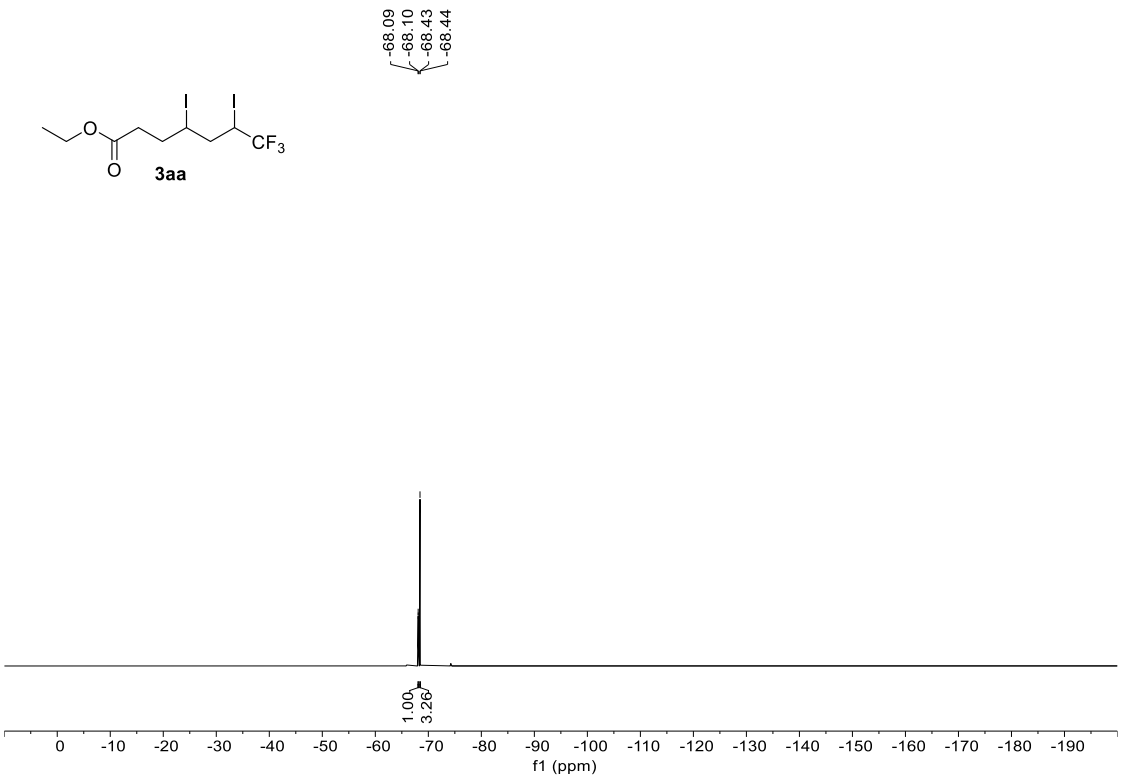
^{13}F NMR (376 MHz, $CDCl_3$) for **3z**



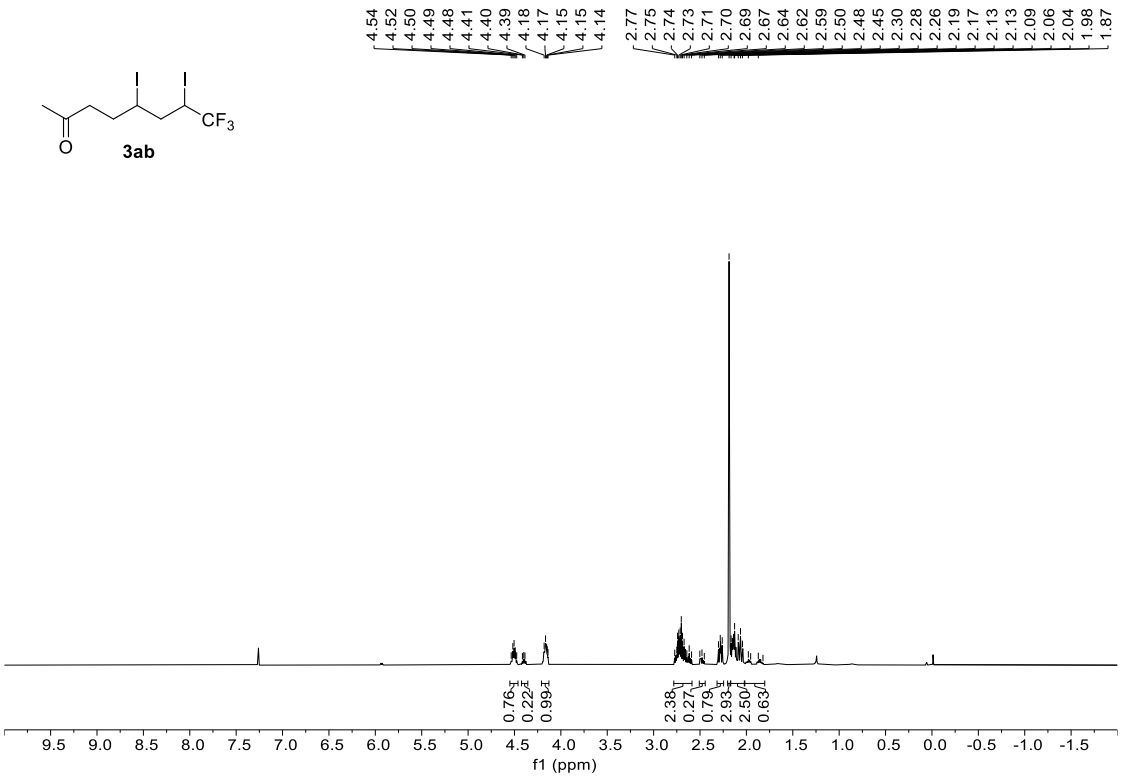
^{1}H NMR (600 MHz, $CDCl_3$) for **3aa**



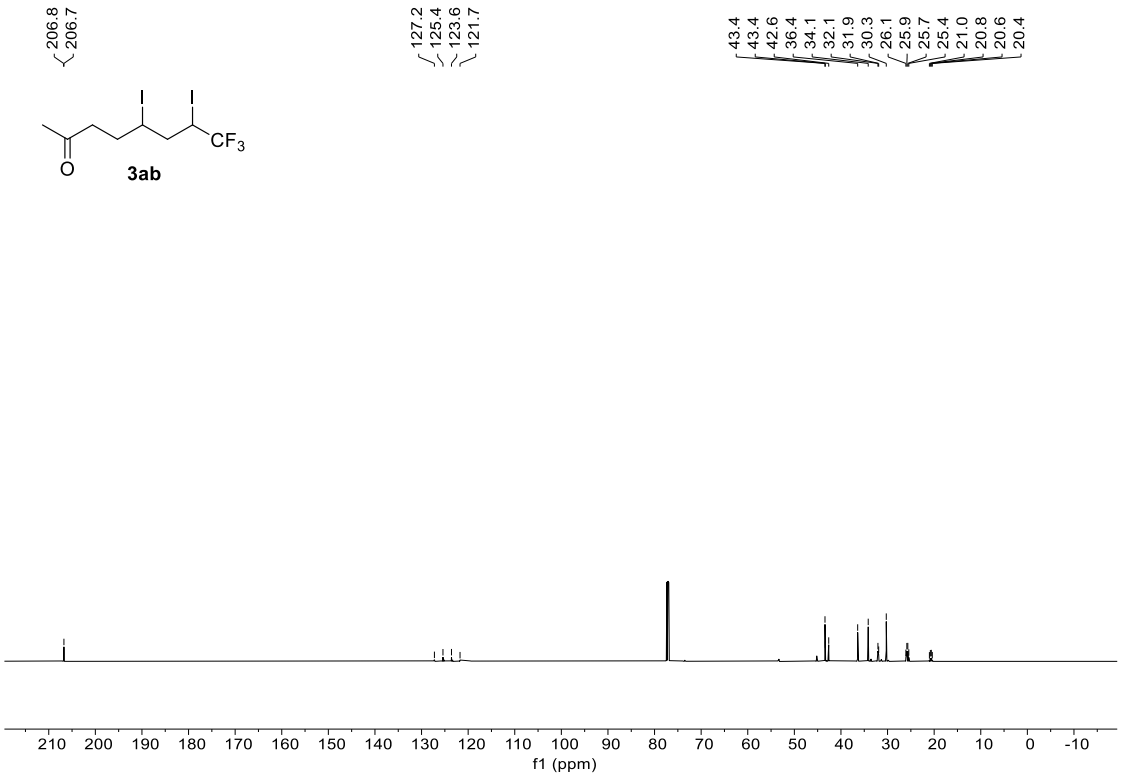
^{13}C NMR (151 MHz, $CDCl_3$) for **3aa**



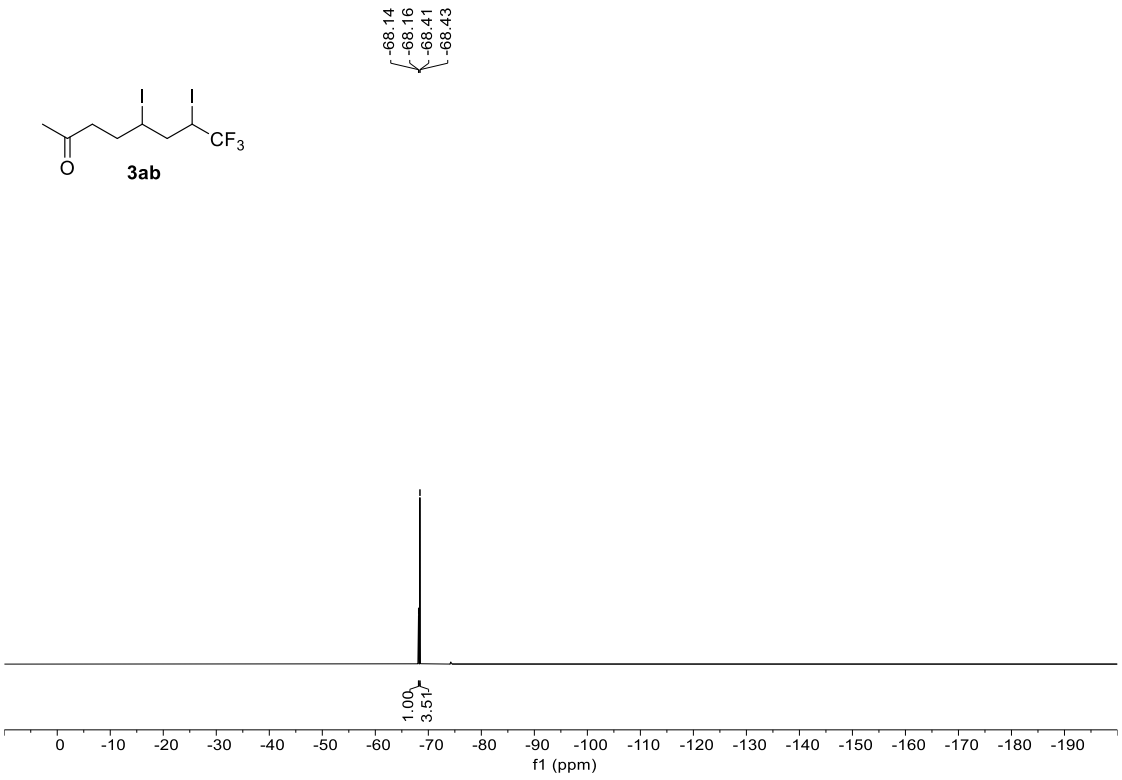
^{19}F NMR (565 MHz, $CDCl_3$) for **3aa**



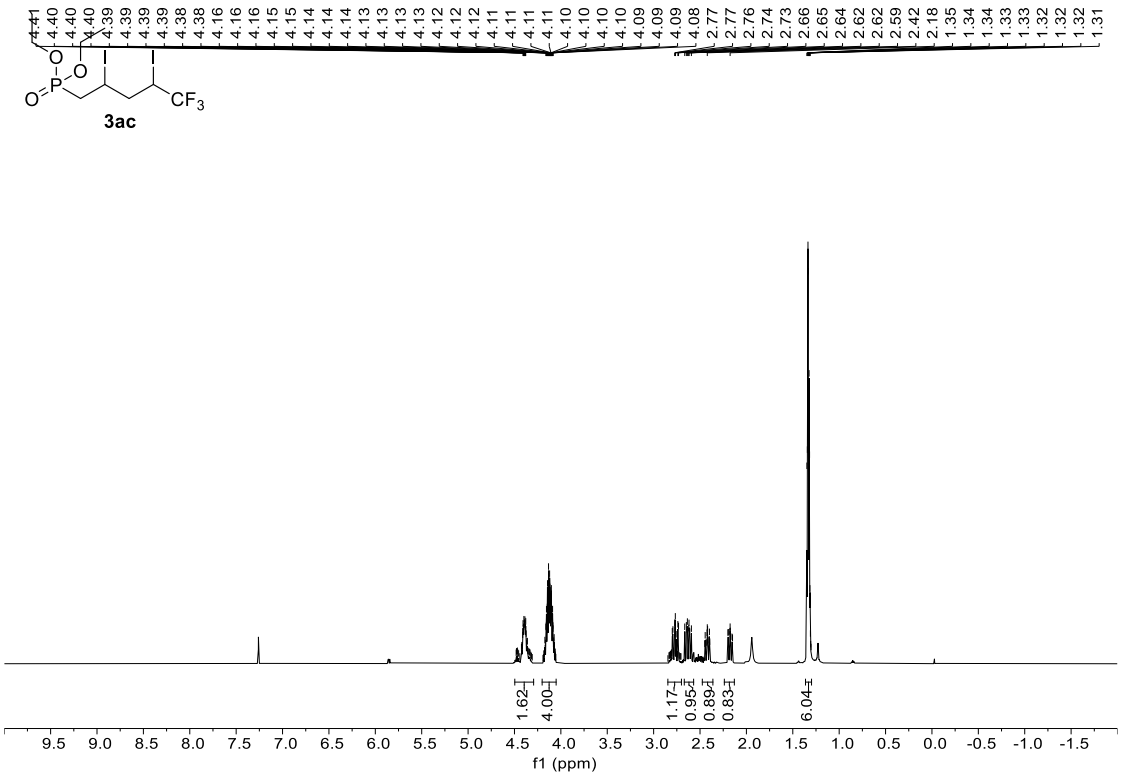
^{1}H NMR (600 MHz, $CDCl_3$) for **3ab**



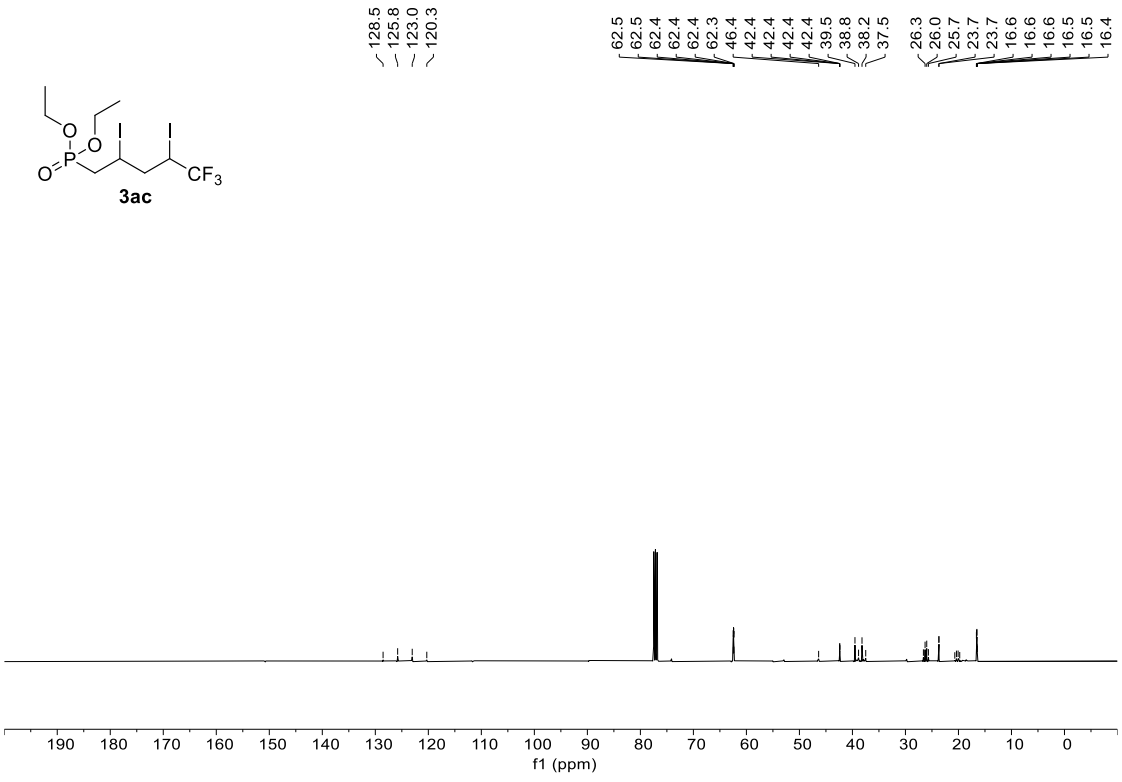
^{13}C NMR (151 MHz, $CDCl_3$) for **3ab**



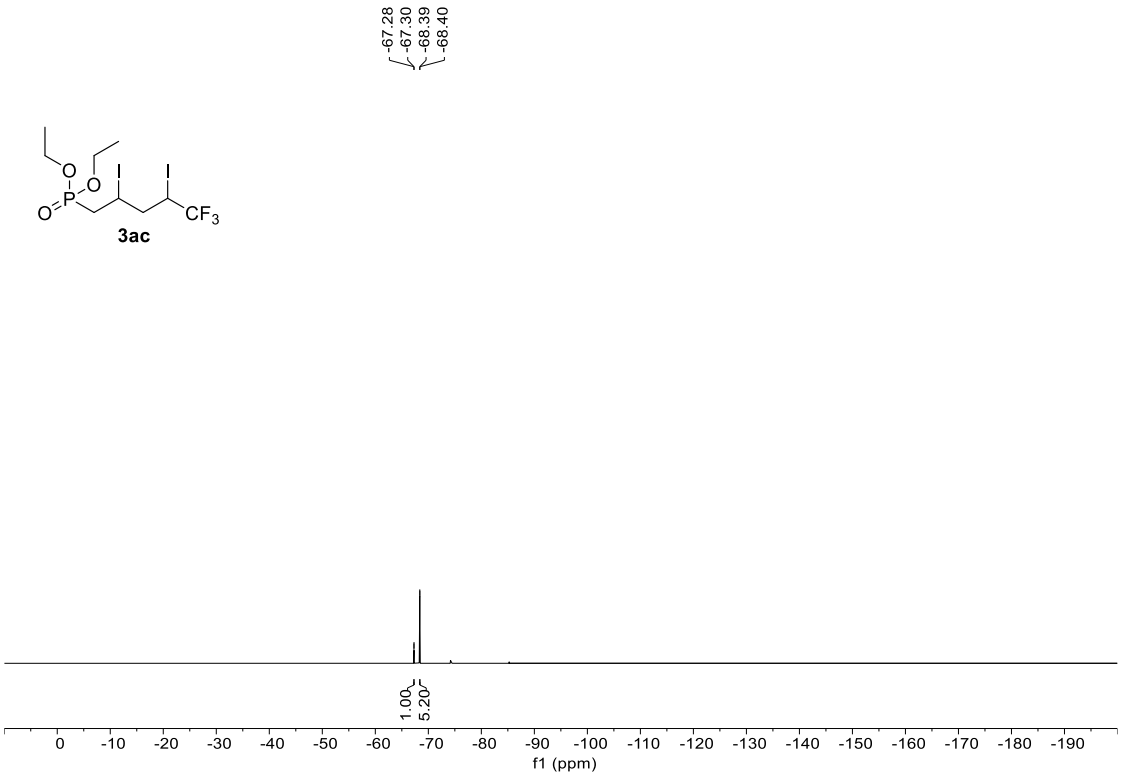
^{19}F NMR (565 MHz, $CDCl_3$) for **3ab**



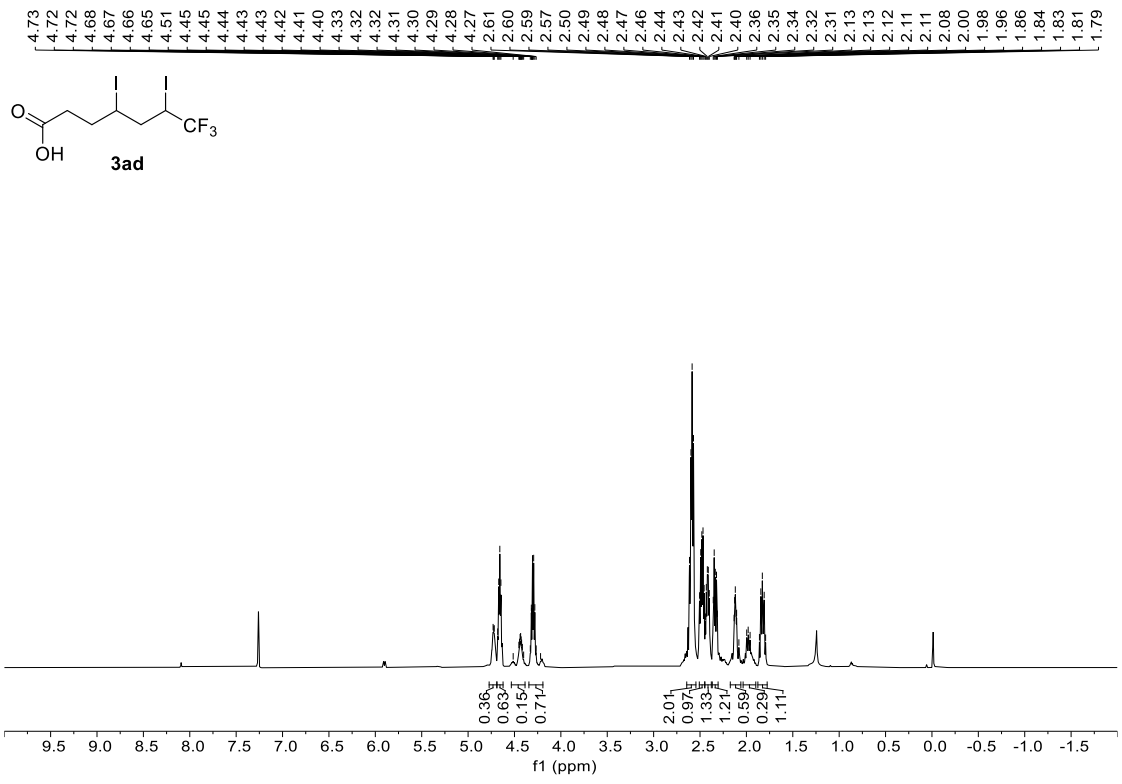
^{1}H NMR (600 MHz, $CDCl_3$) for **3ac**



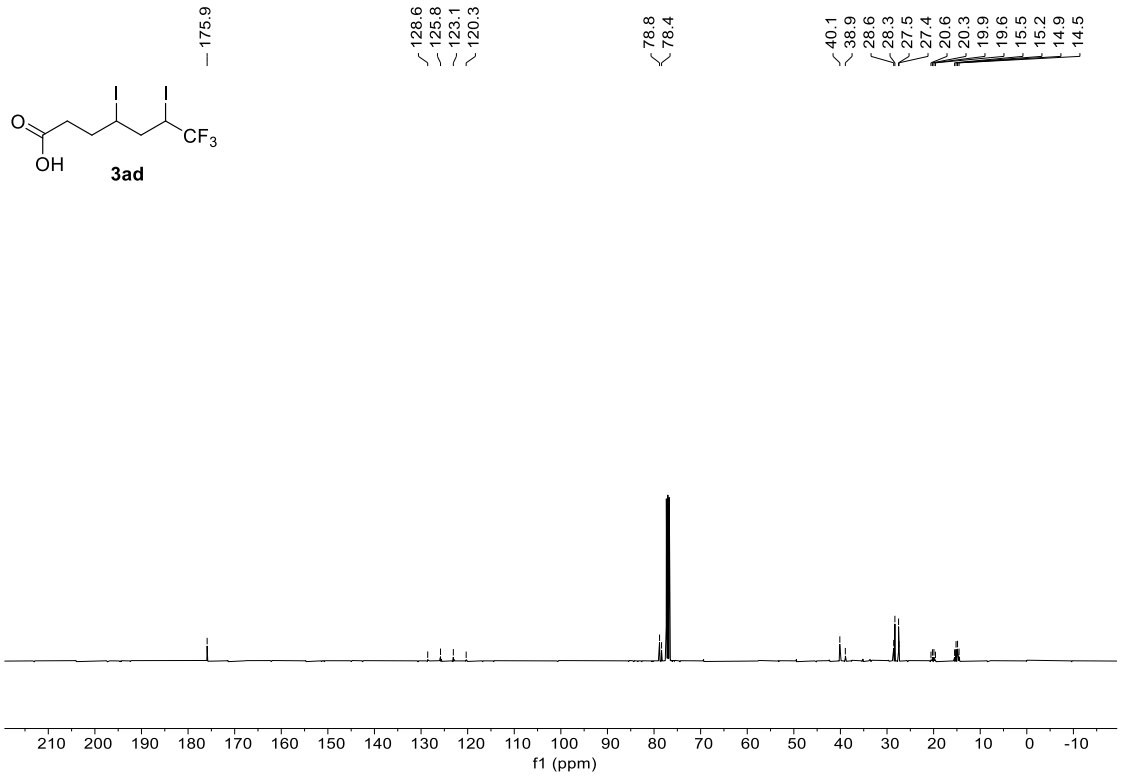
^{13}C NMR (101 MHz, $CDCl_3$) for **3ac**



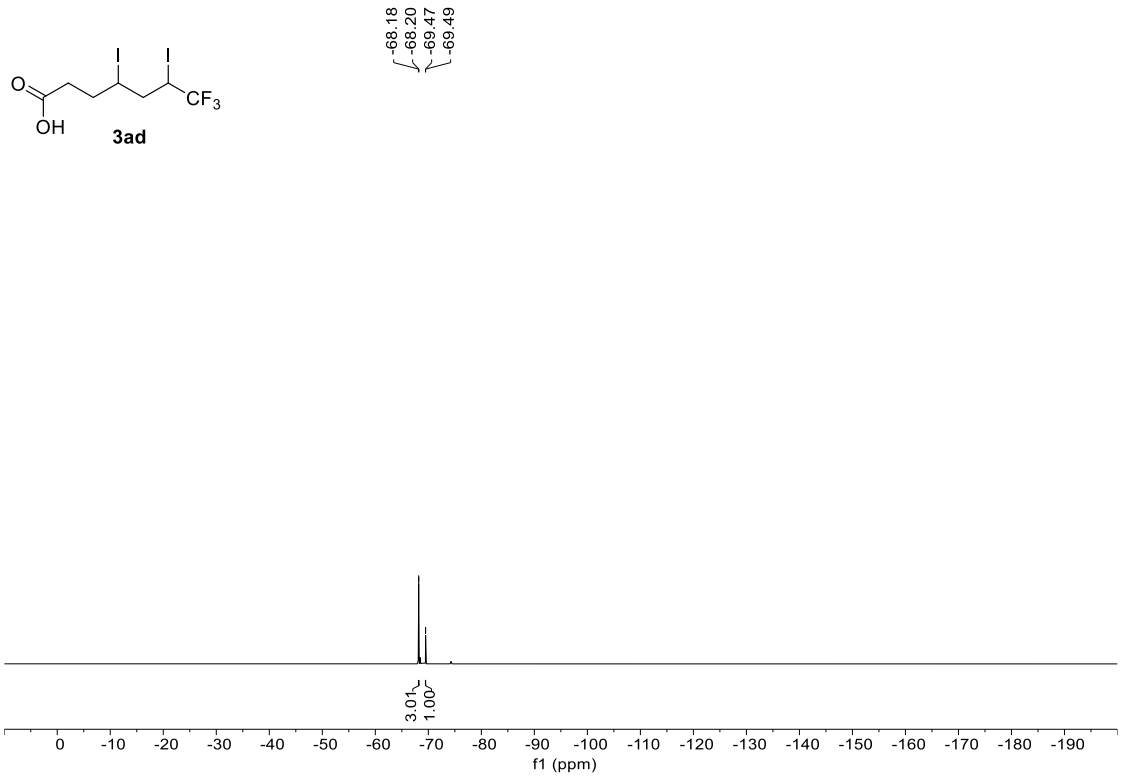
^{19}F NMR (565 MHz, $CDCl_3$) for **3ac**



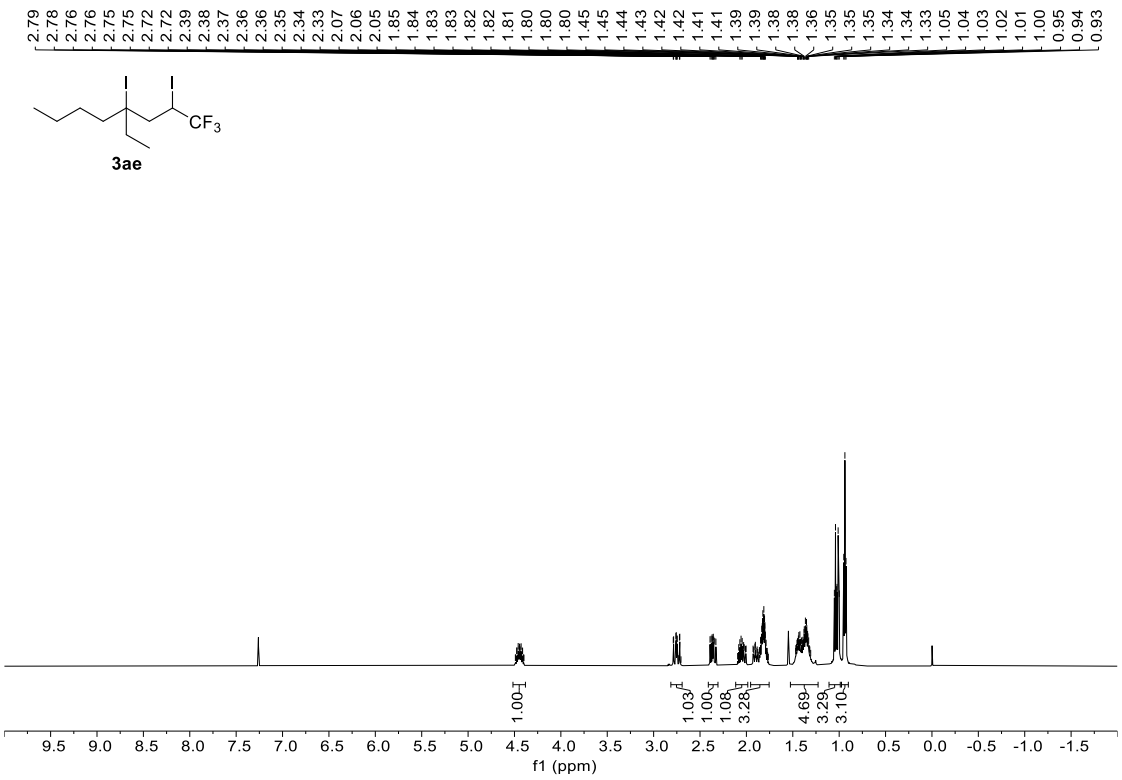
^{1}H NMR (600 MHz, $CDCl_3$) for **3ad**



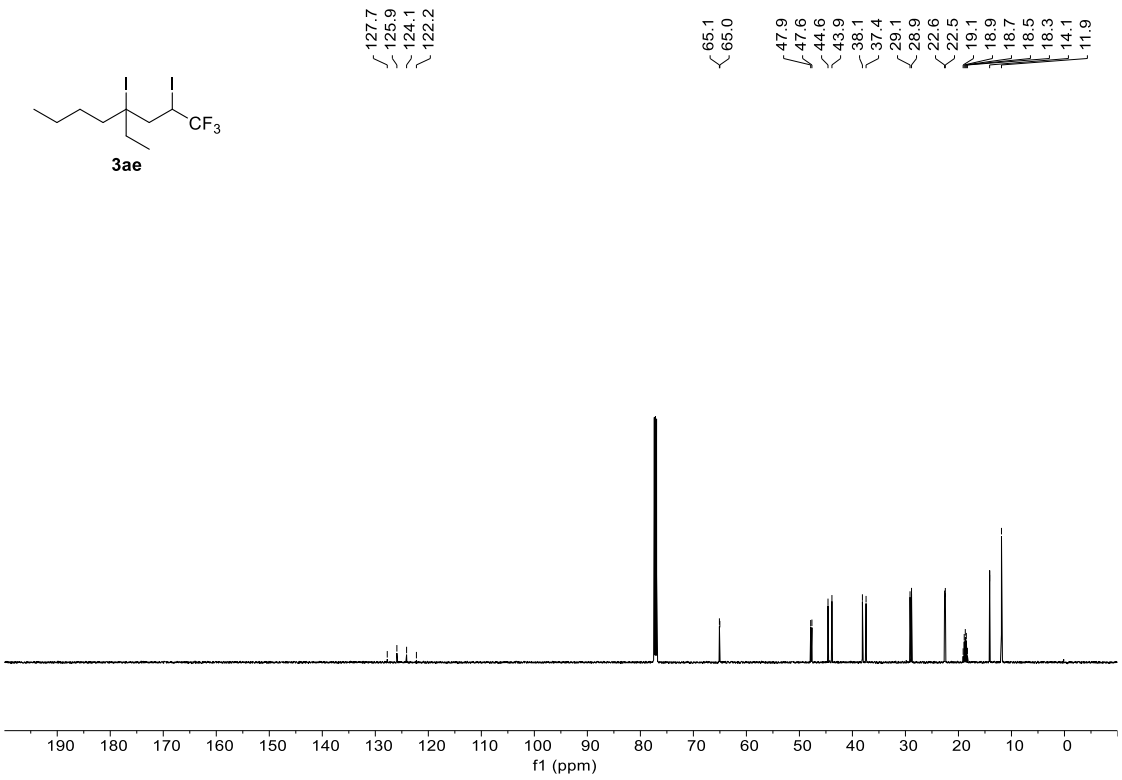
^{13}C NMR (101 MHz, $CDCl_3$) for **3ad**



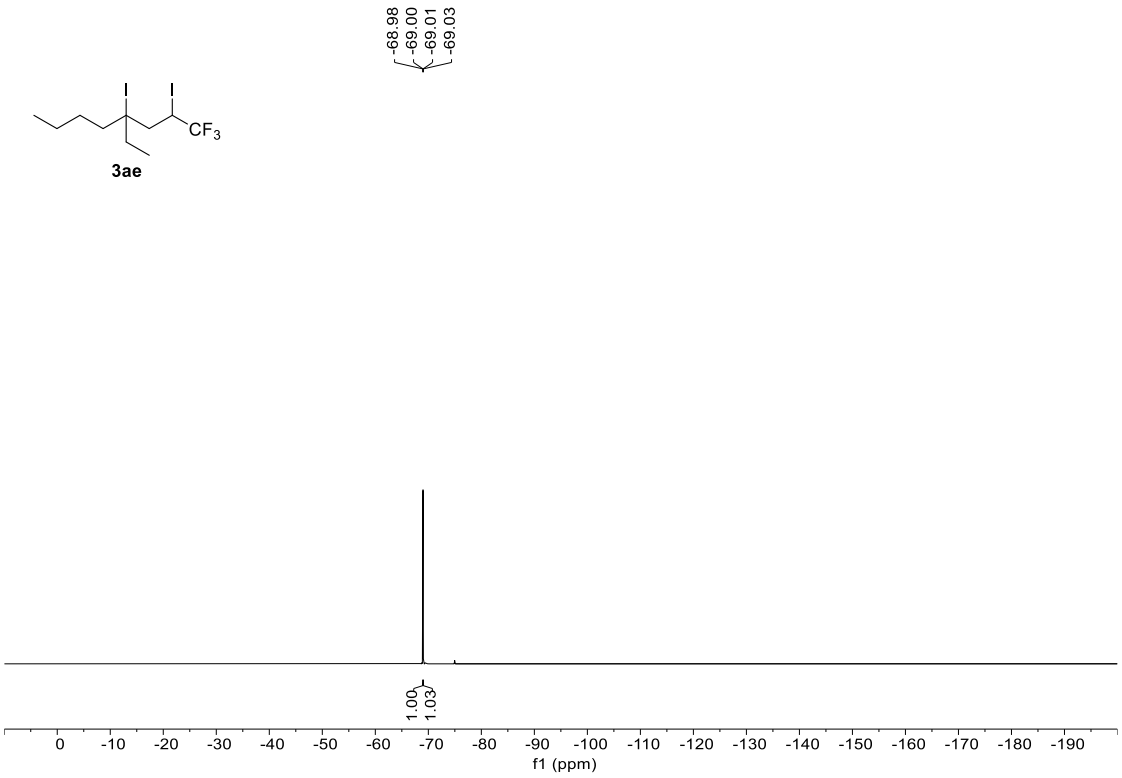
^{19}F NMR (565 MHz, $CDCl_3$) for **3ad**



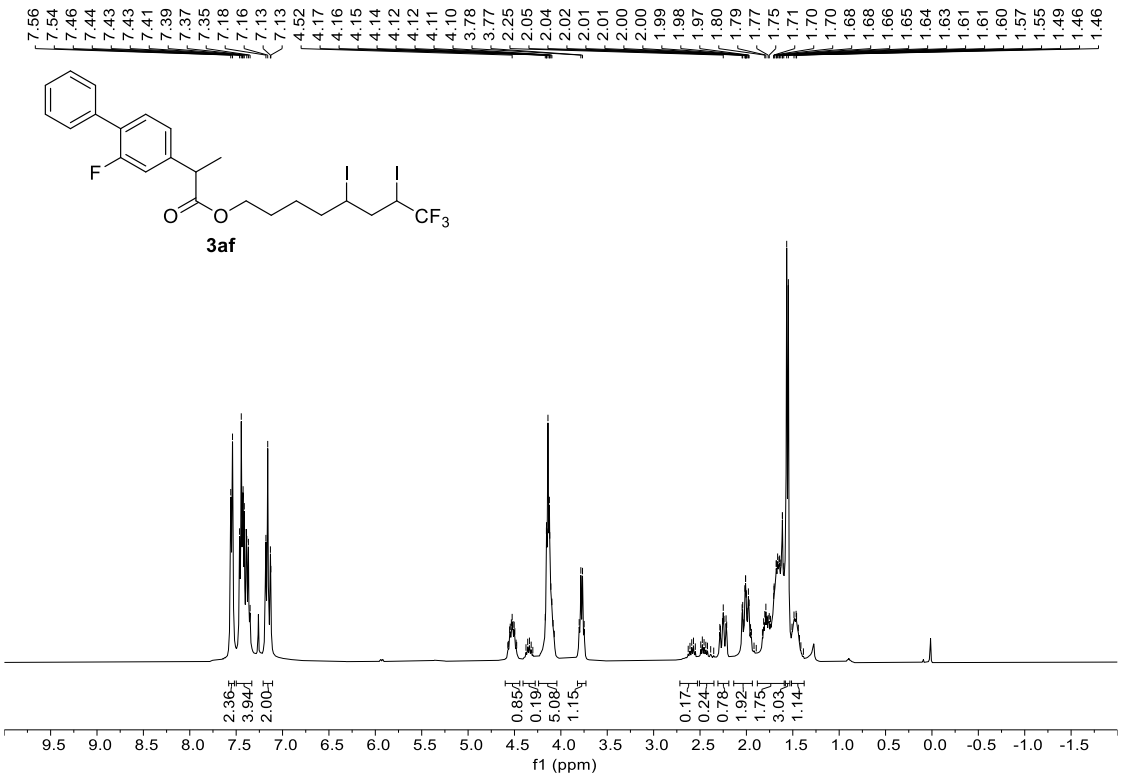
^{1}H NMR (600 MHz, $CDCl_3$) for **3ae**



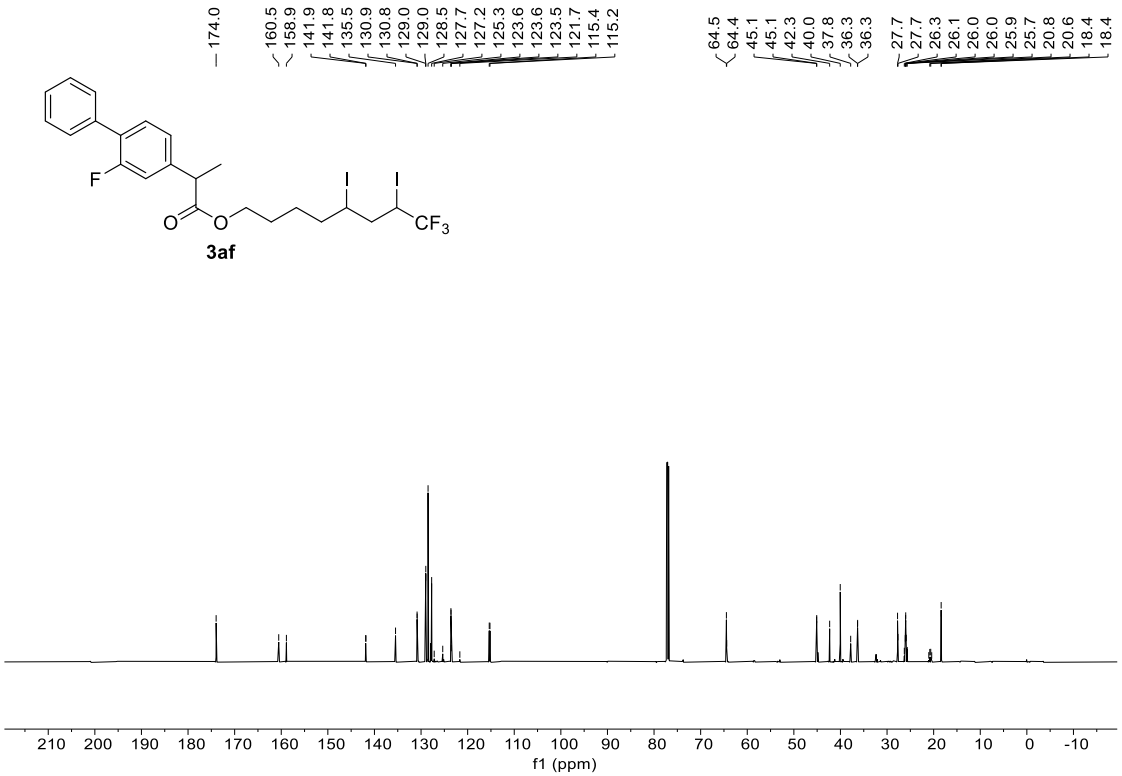
^{13}C NMR (151 MHz, $CDCl_3$) for **3ae**



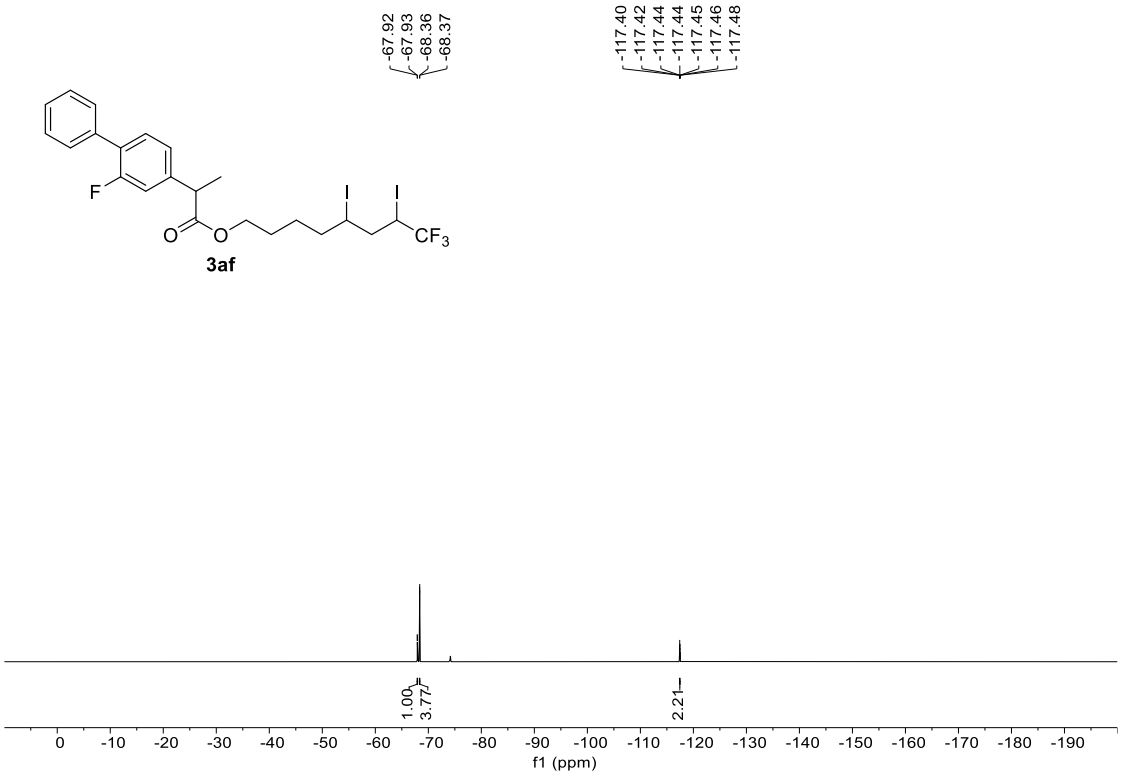
^{19}F NMR (565 MHz, $CDCl_3$) for **3ae**



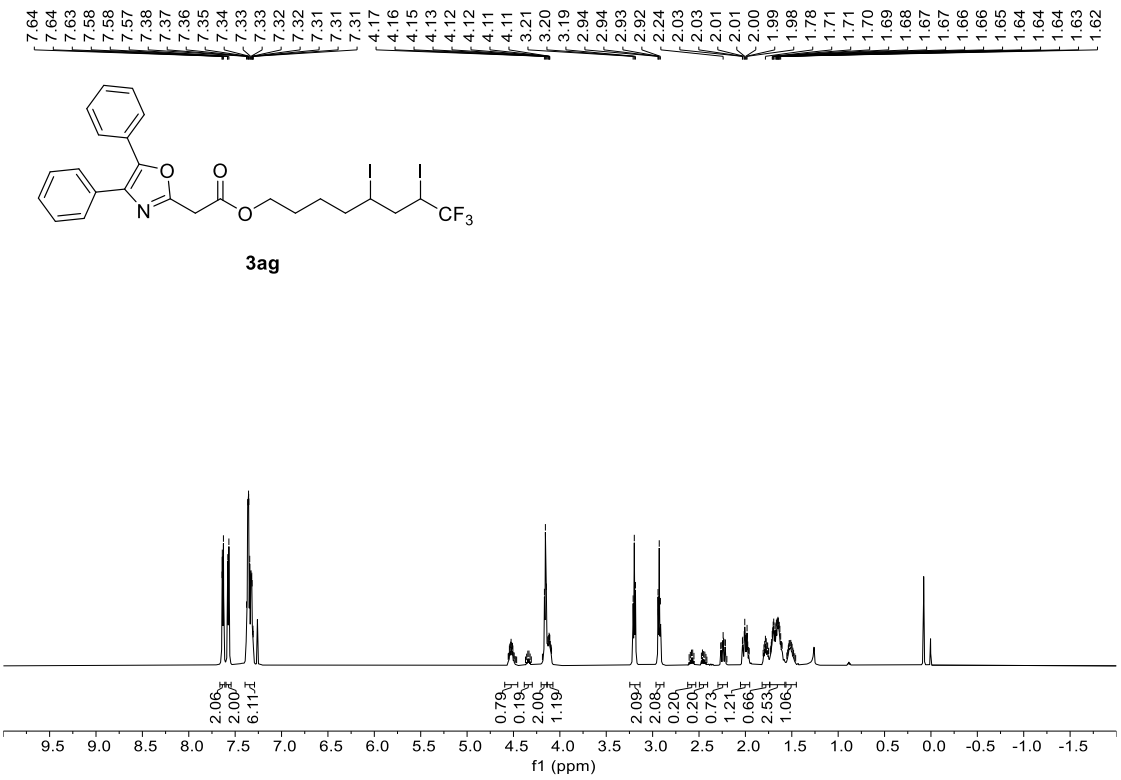
^{1}H NMR (400 MHz, $CDCl_3$) for **3af**



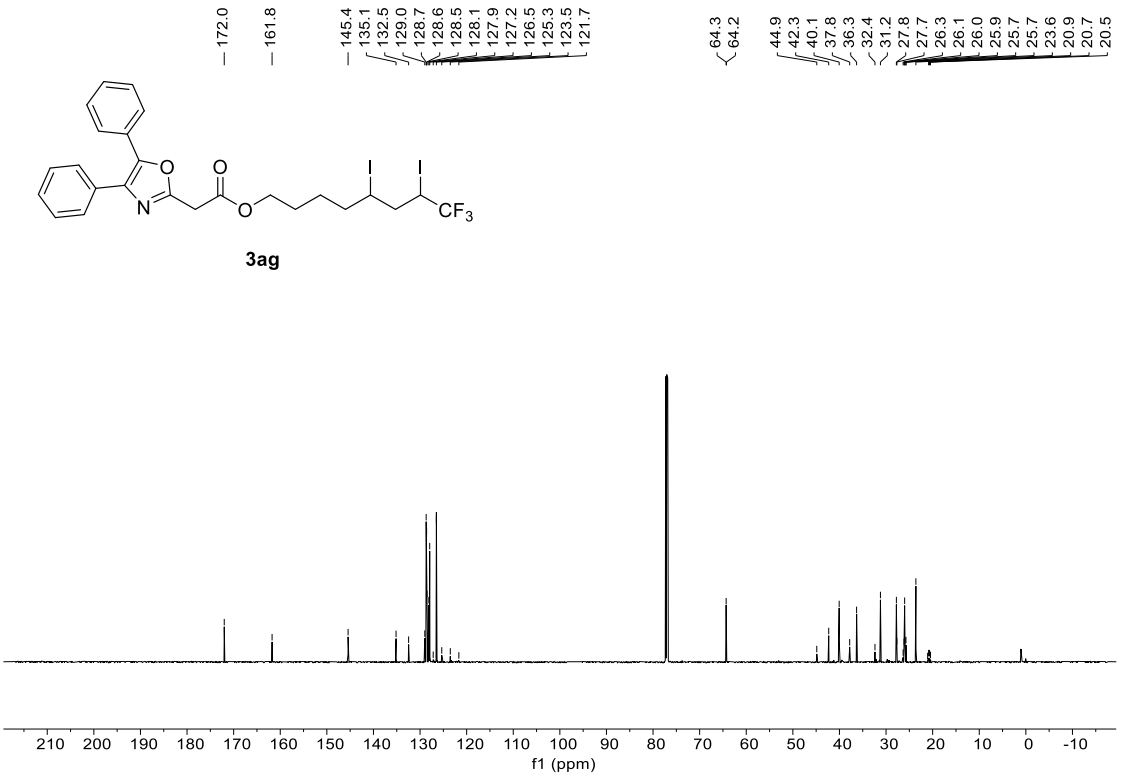
^{13}C NMR (151 MHz, $CDCl_3$) for **3af**



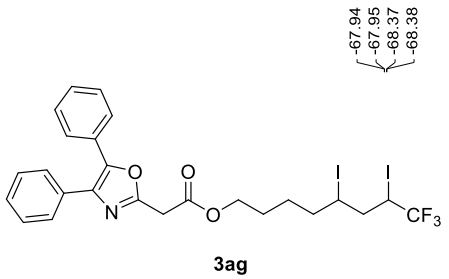
^{1}H NMR (565 MHz, $CDCl_3$) for **3af**



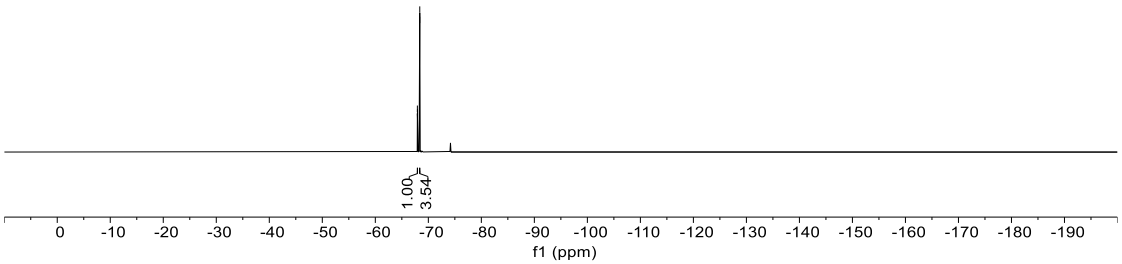
^{1}H NMR (600 MHz, $CDCl_3$) for **3ag**



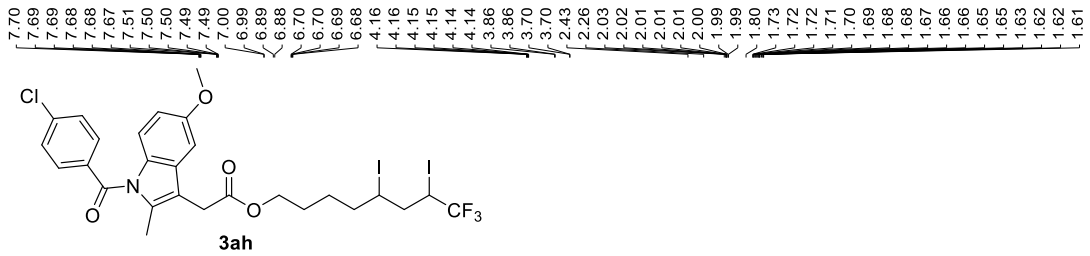
^{13}C NMR (151 MHz, $CDCl_3$) for 3**ag**



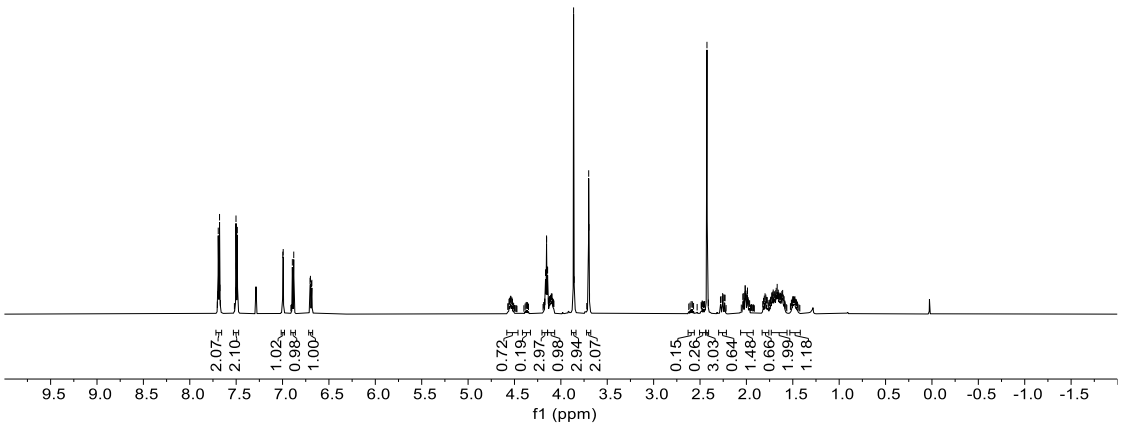
3ag



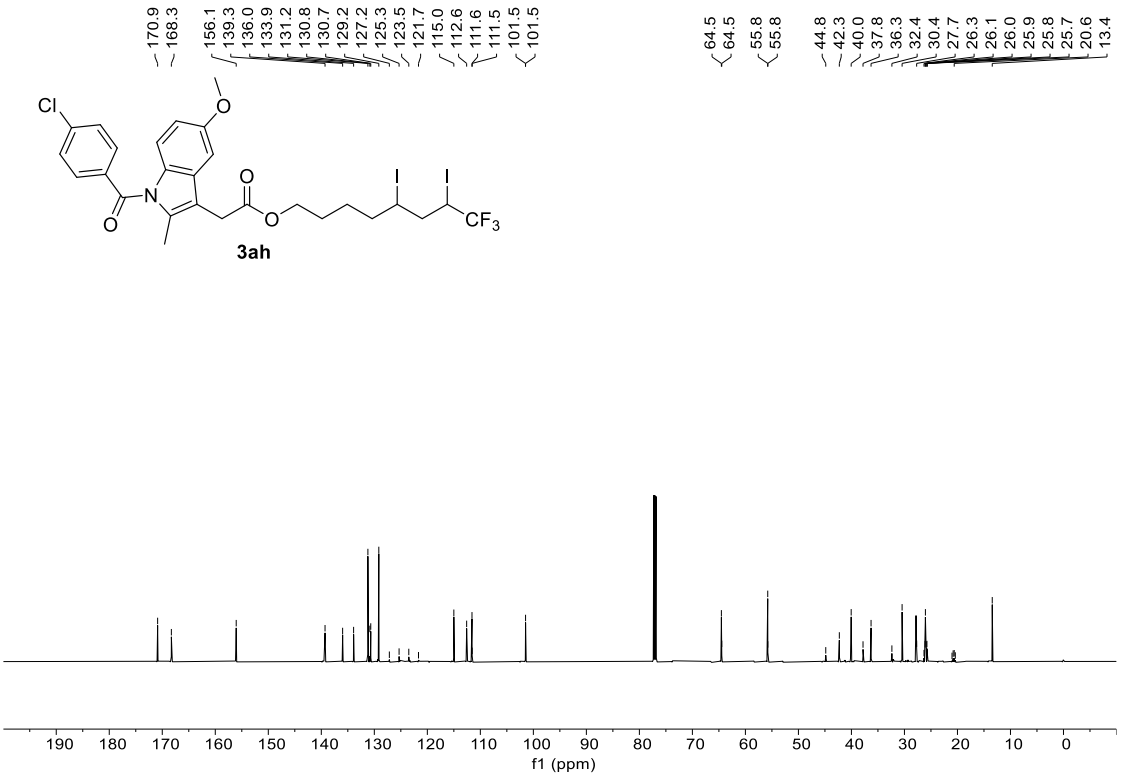
^{19}F NMR (565 MHz, $CDCl_3$) for **3ag**



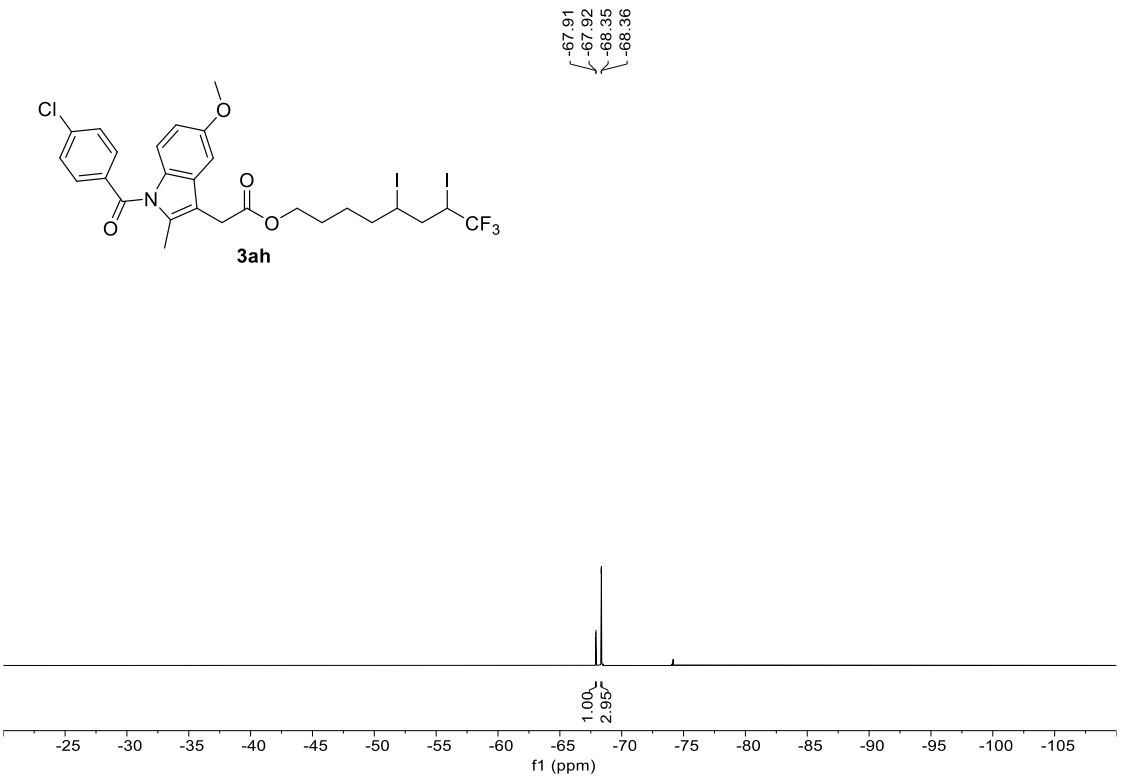
3ah



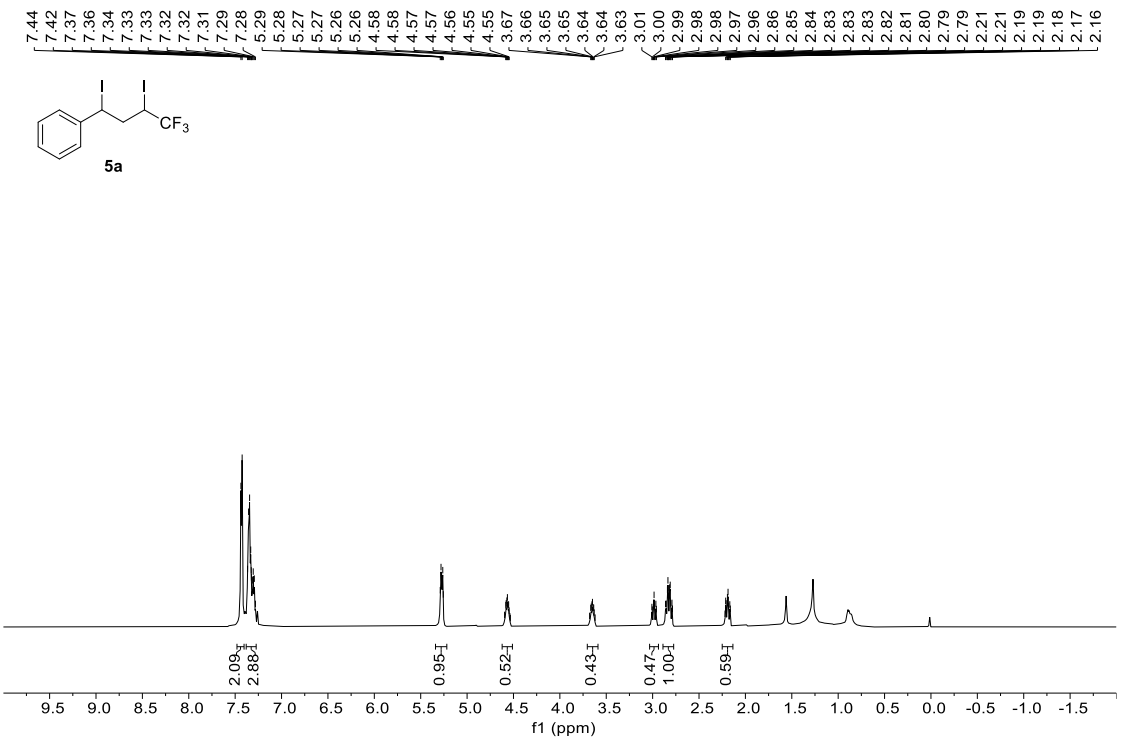
^{1}H NMR (600 MHz, $CDCl_3$) for **3ah**



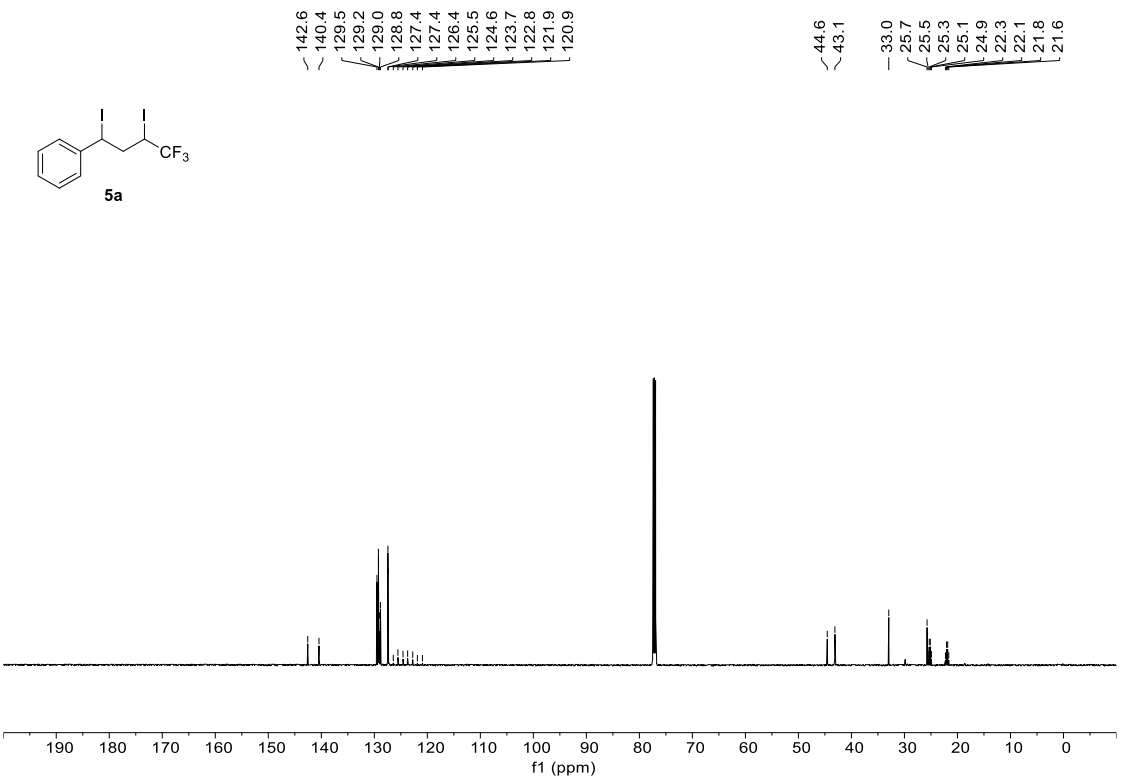
^{13}C NMR (151 MHz, $CDCl_3$) for **3ah**



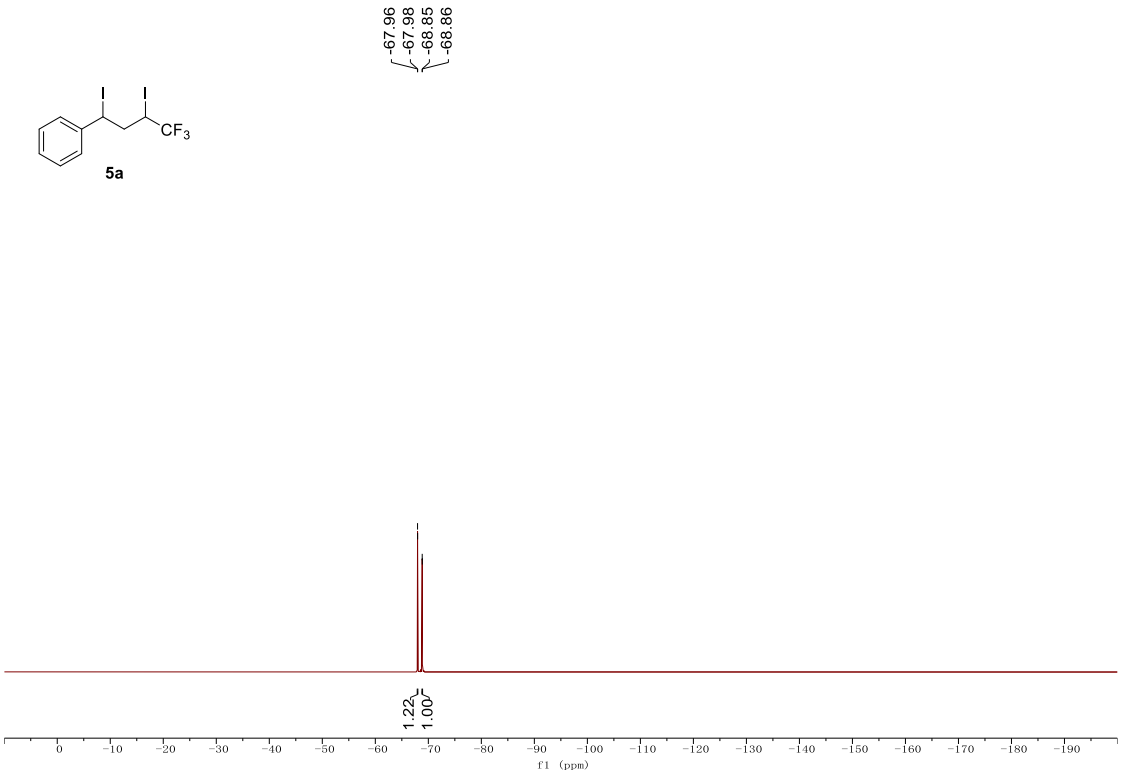
^{19}F NMR (565 MHz, $CDCl_3$) for **3ah**



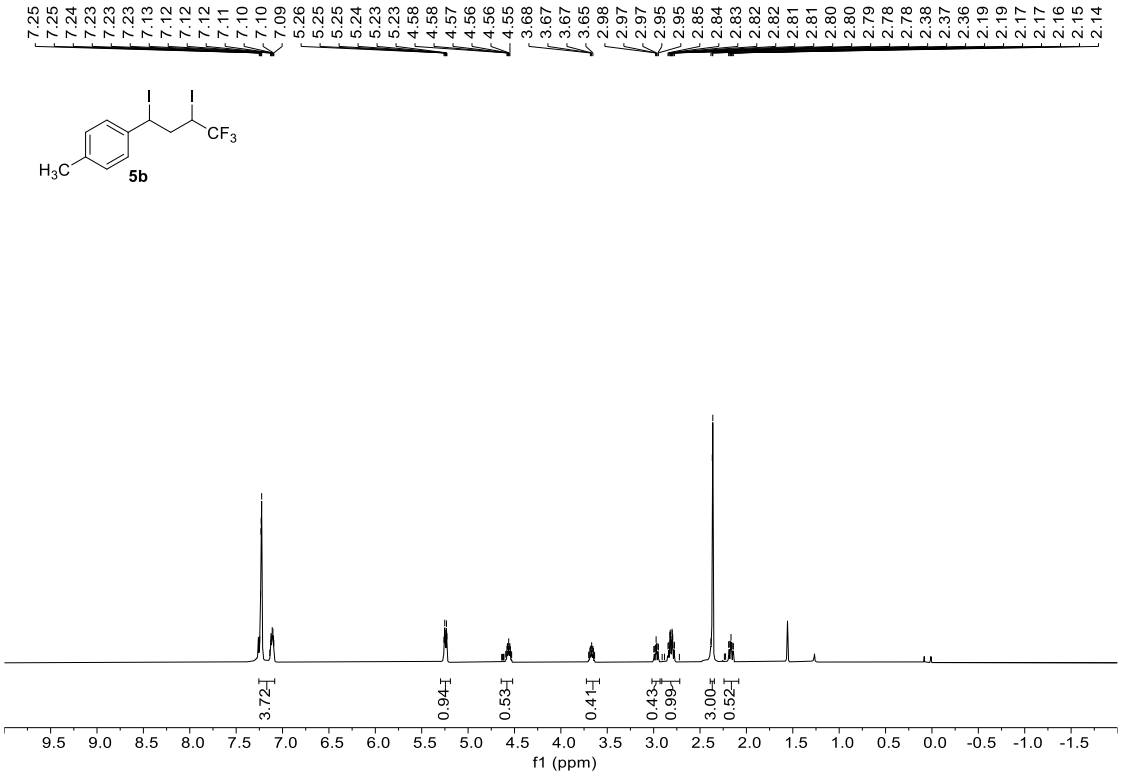
^{1}H NMR (600 MHz, $CDCl_3$) for **5a**



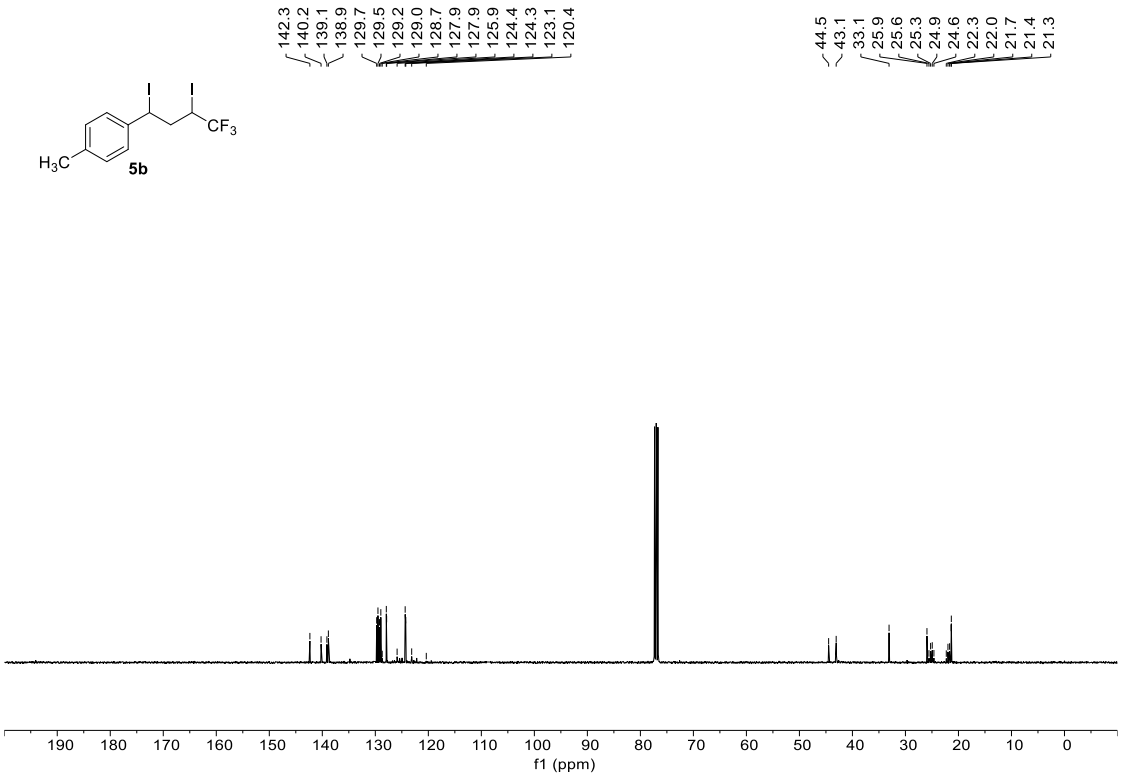
^{13}C NMR (101 MHz, $CDCl_3$) for **5a**



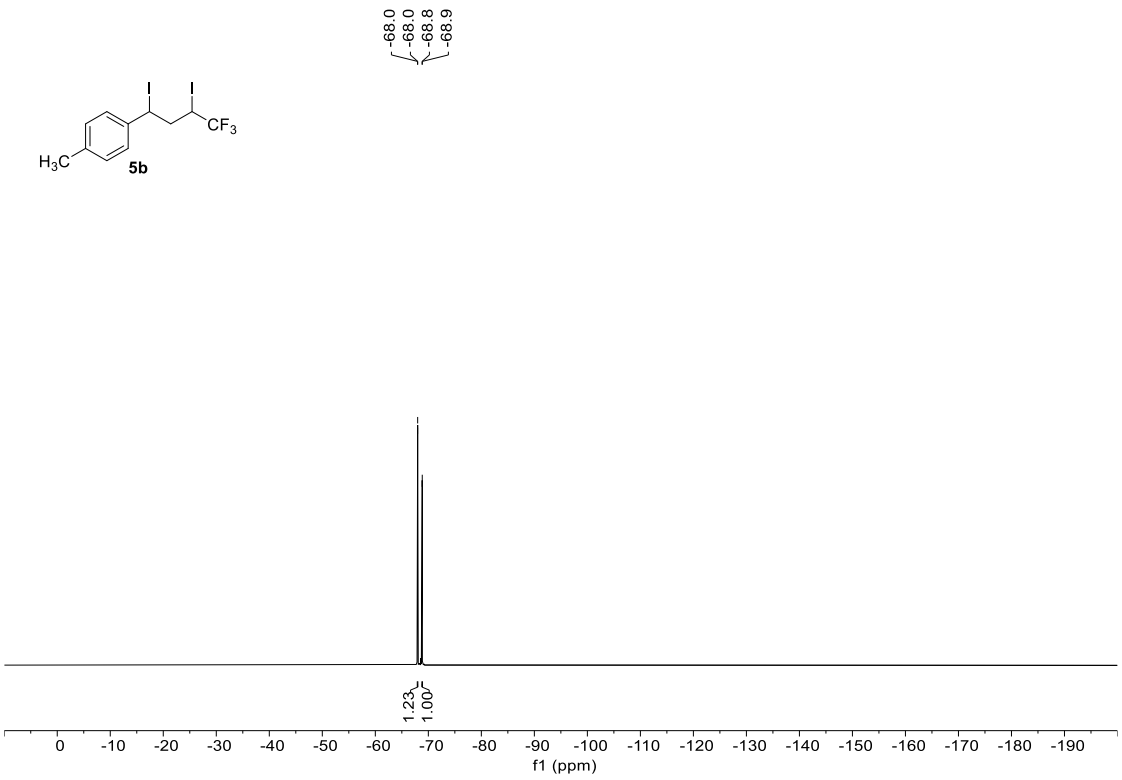
^{19}F NMR (565 MHz, $CDCl_3$) for **5a**



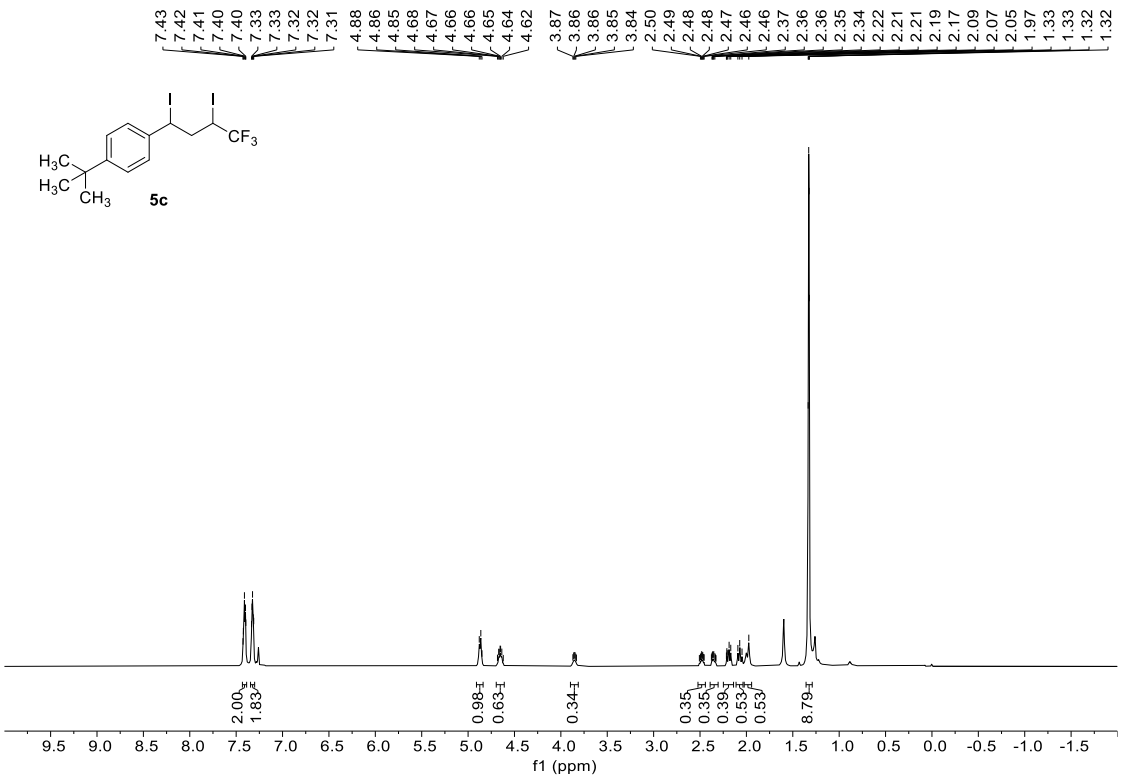
^{1}H NMR (600 MHz, $CDCl_3$) for **5b**



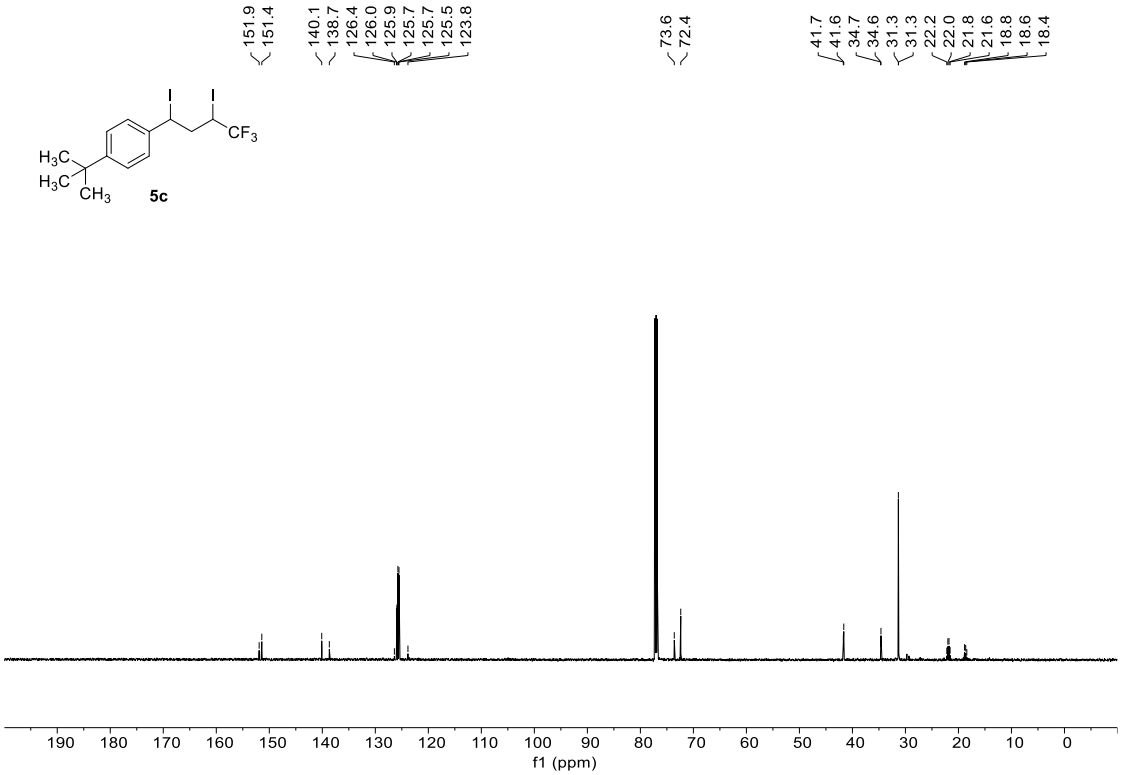
^{13}C NMR (101 MHz, $CDCl_3$) for **5b**



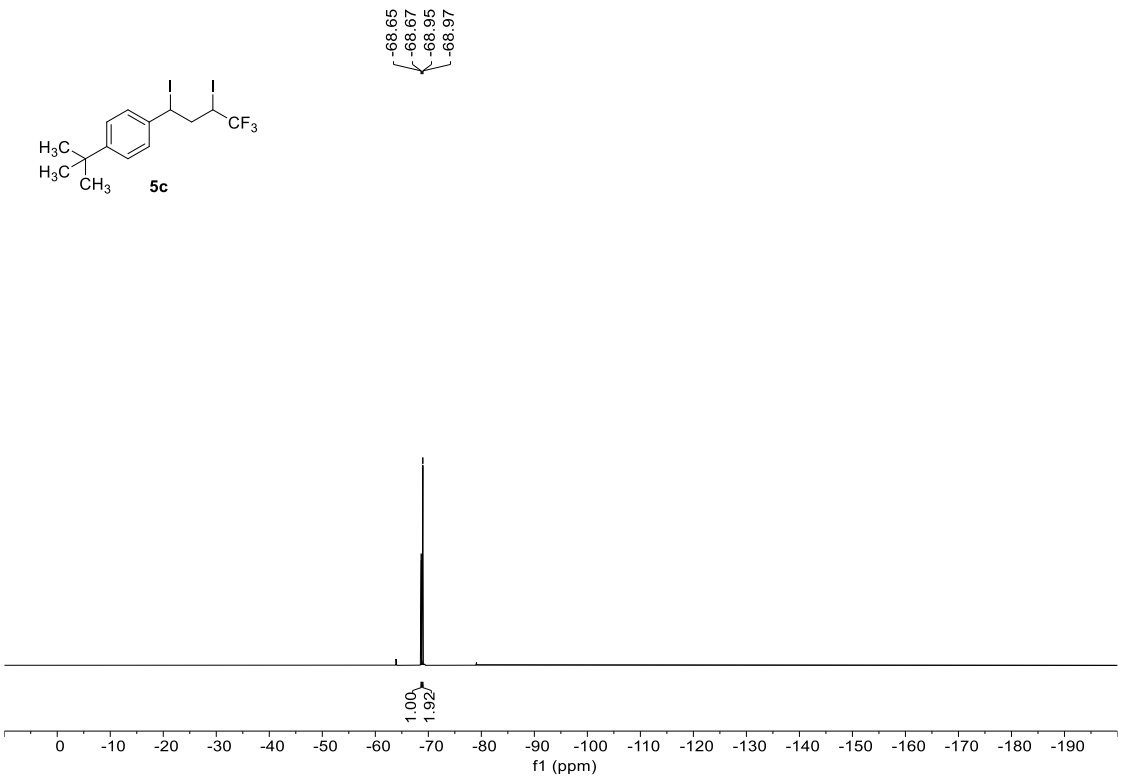
^{13}F NMR (565 MHz, $CDCl_3$) for **5b**



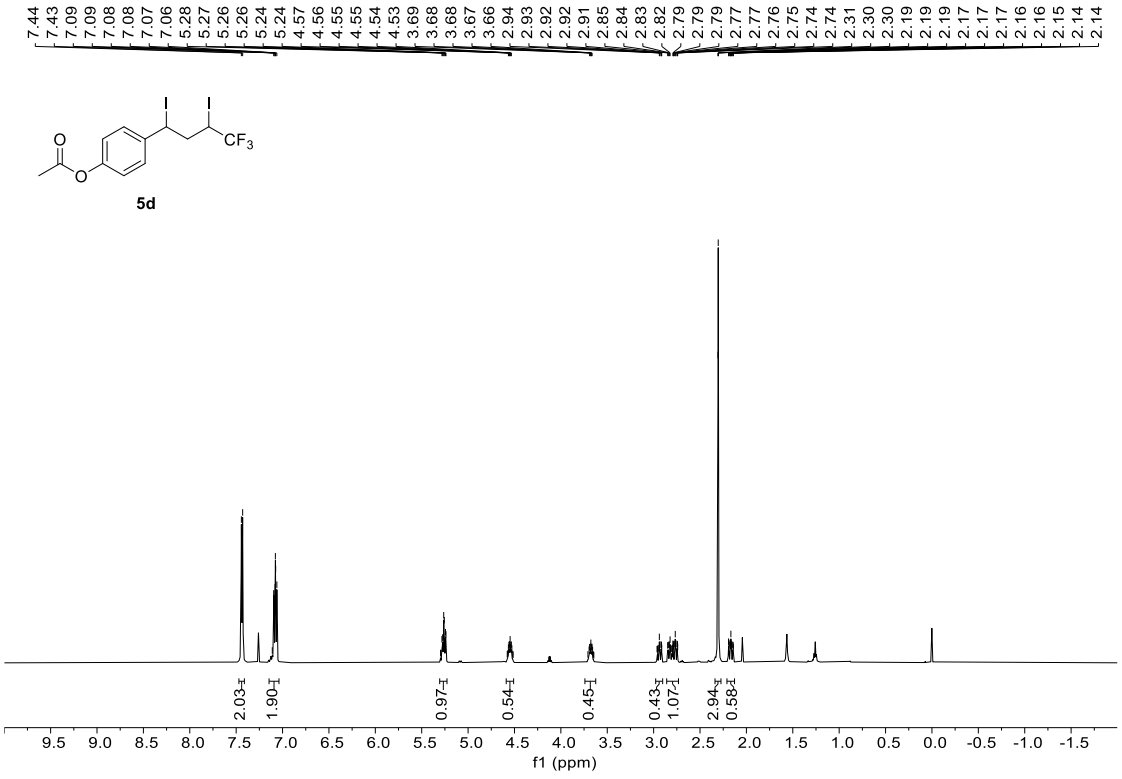
^{1}H NMR (600 MHz, $CDCl_3$) for **5c**



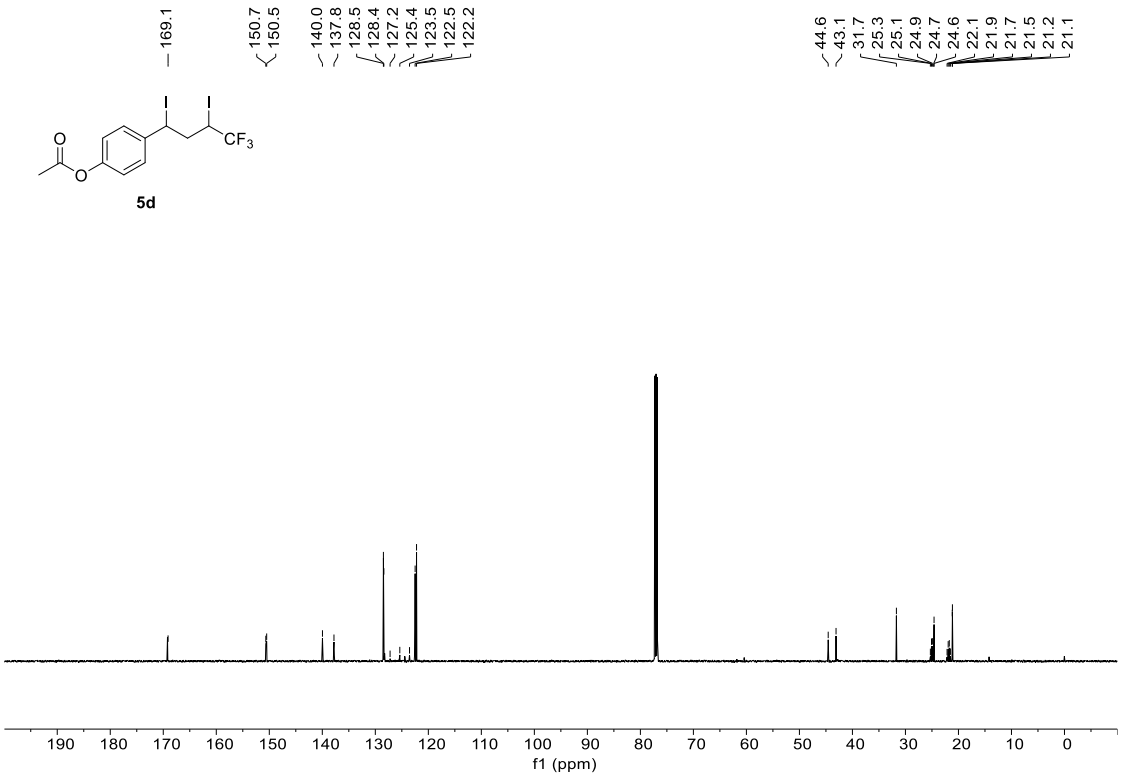
^{13}C NMR (101 MHz, $CDCl_3$) for **5c**



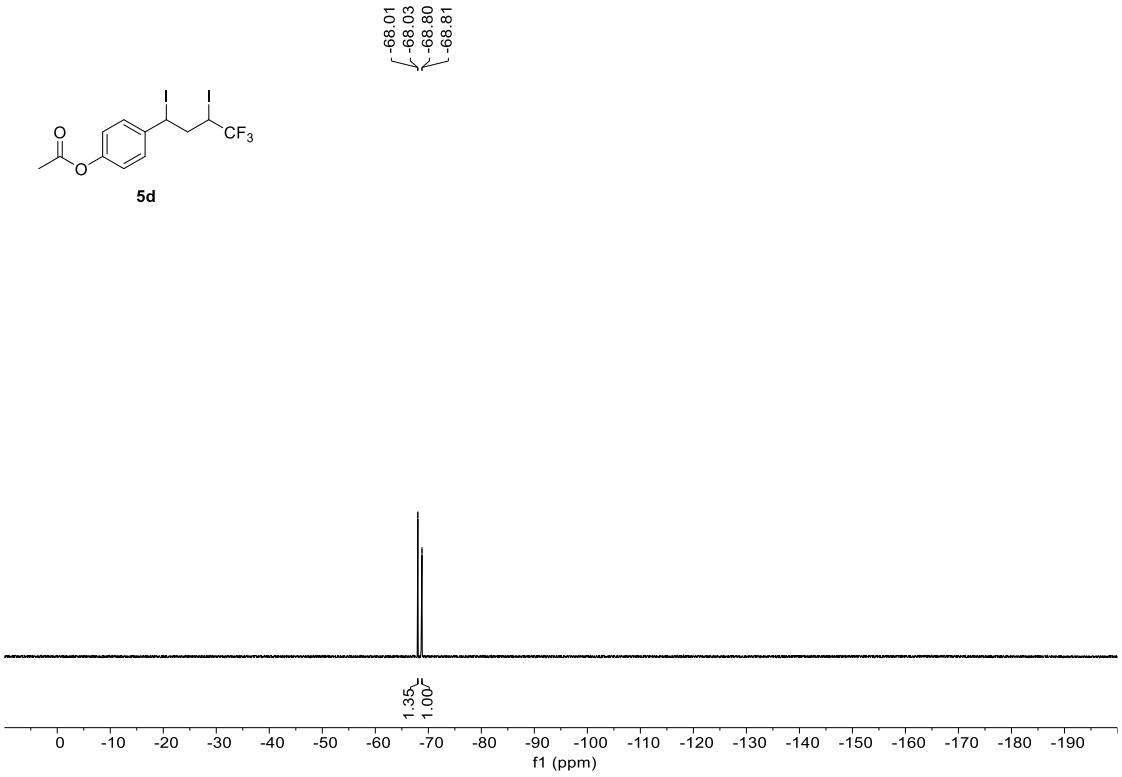
^{19}F NMR (565 MHz, $CDCl_3$) for **5c**



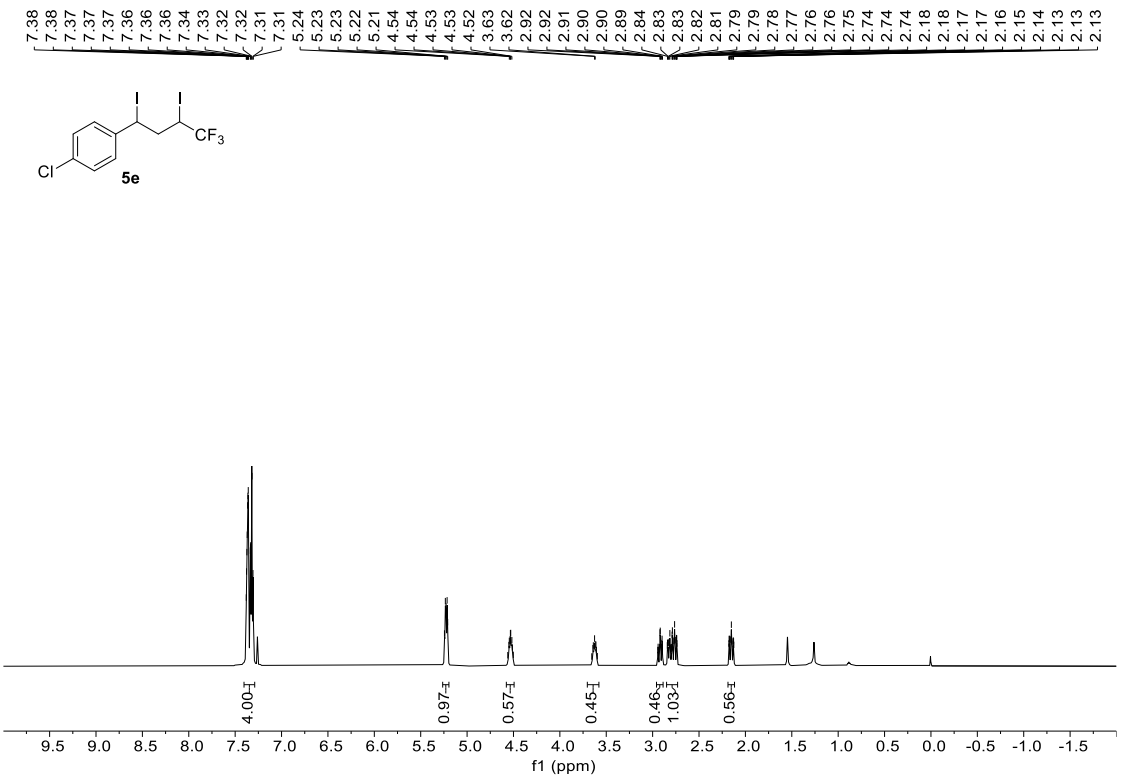
^{1}H NMR (600 MHz, $CDCl_3$) for **5d**



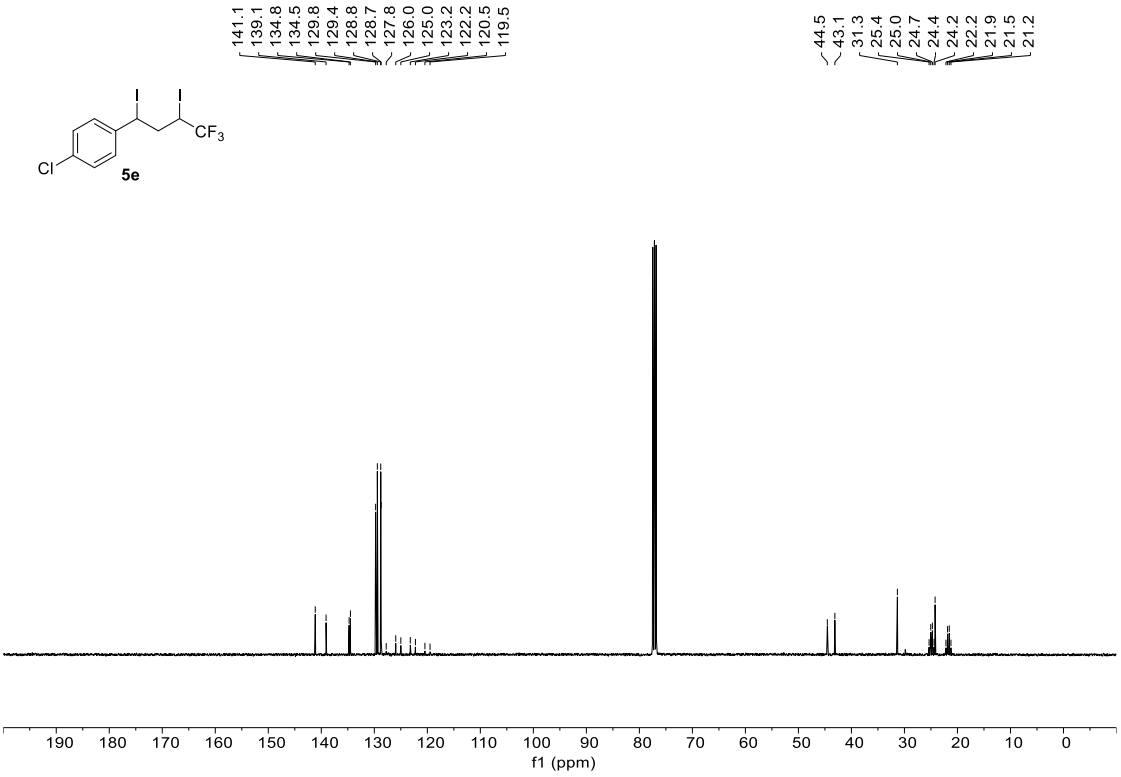
^{13}C NMR (101 MHz, $CDCl_3$) for **5d**



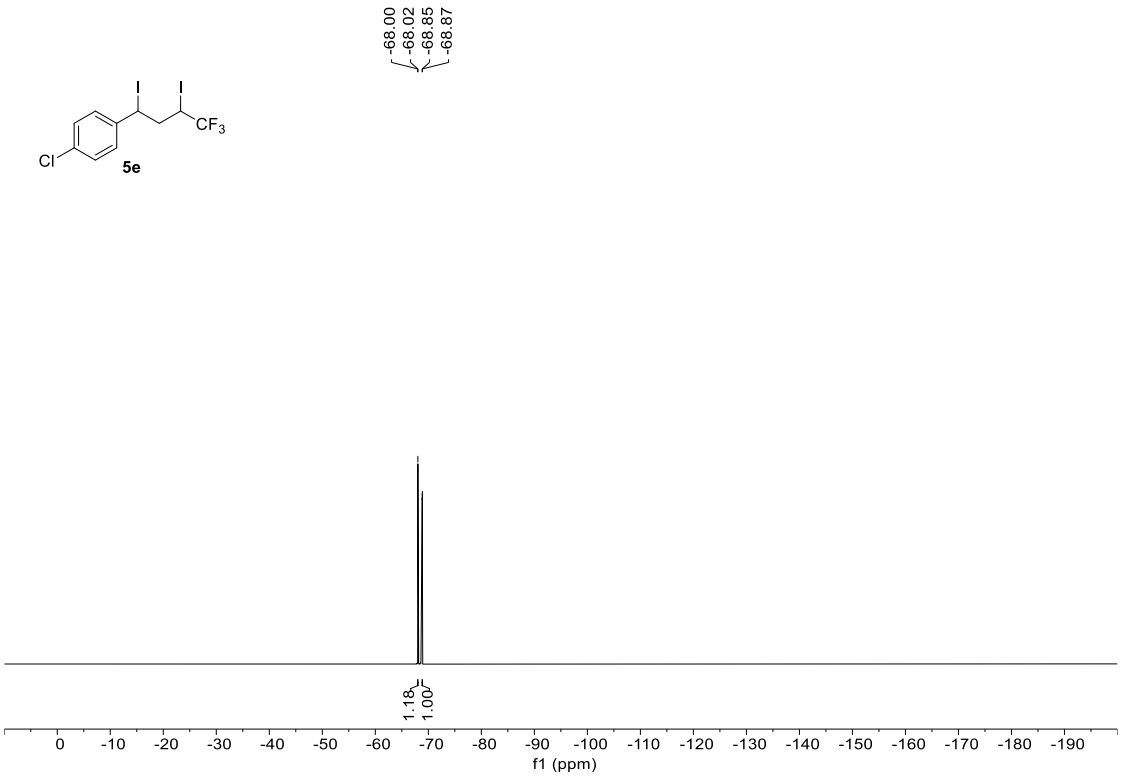
^{19}F NMR (565 MHz, $CDCl_3$) for **5d**



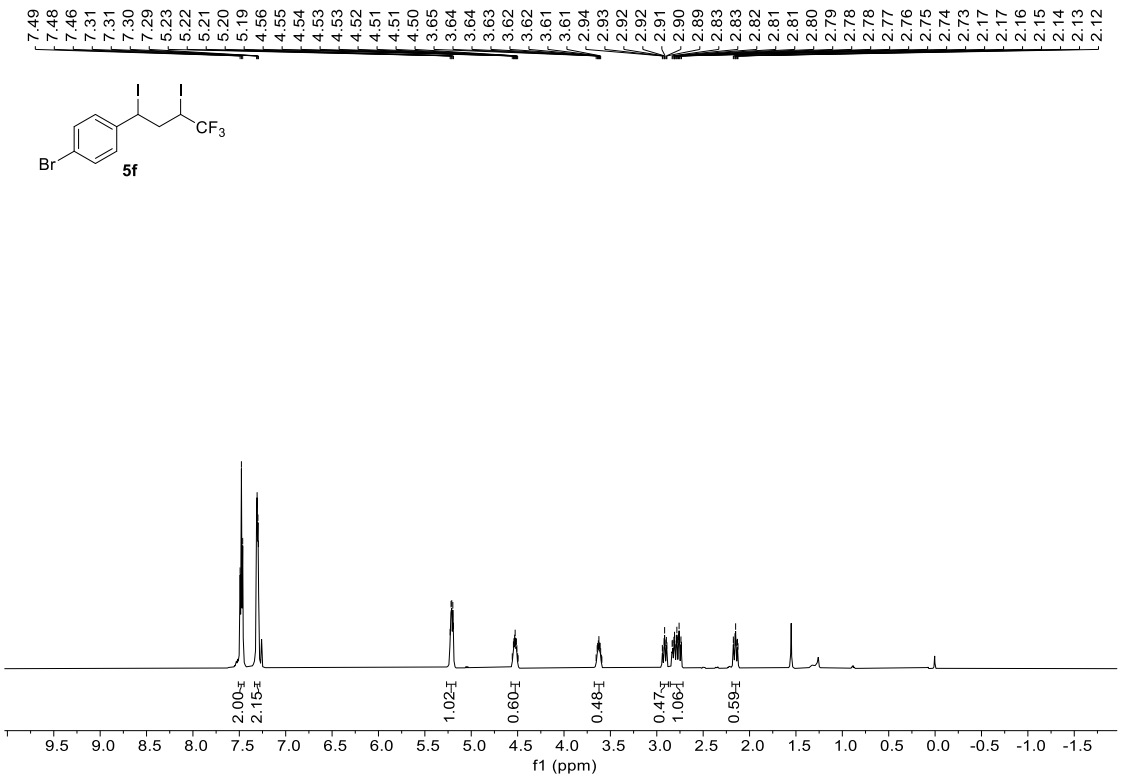
^{1}H NMR (600 MHz, $CDCl_3$) for **5e**



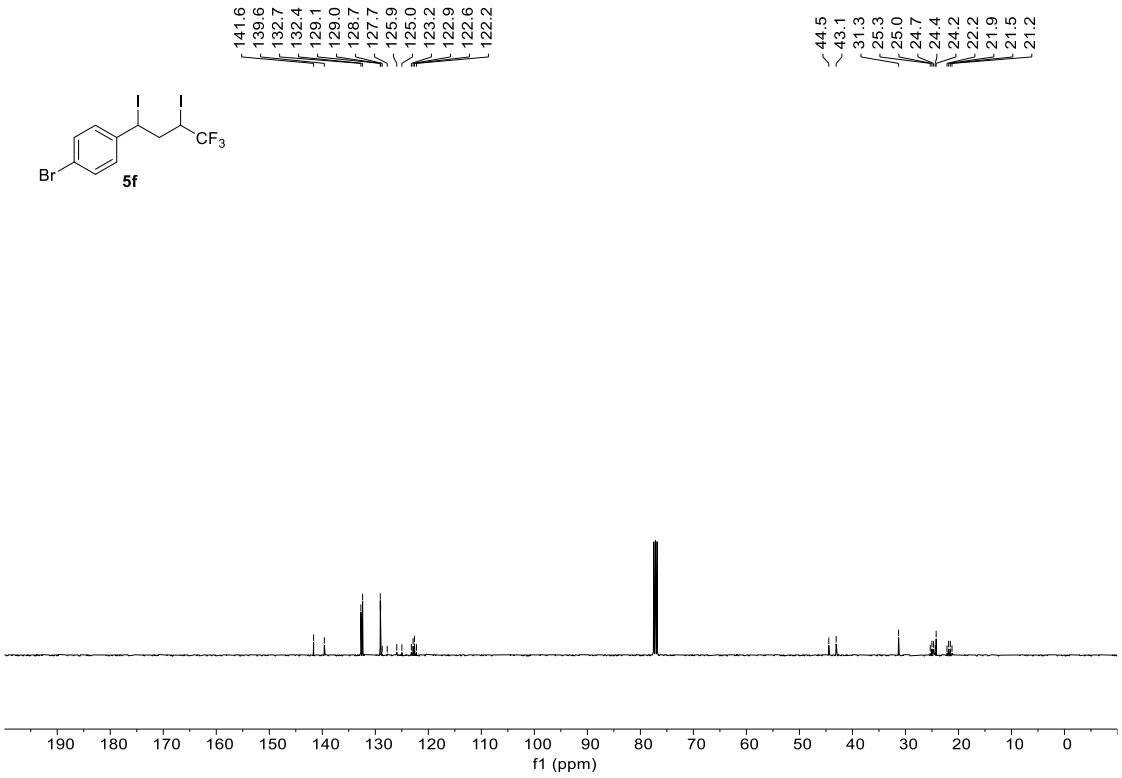
^{13}C NMR (101 MHz, $CDCl_3$) for **5e**



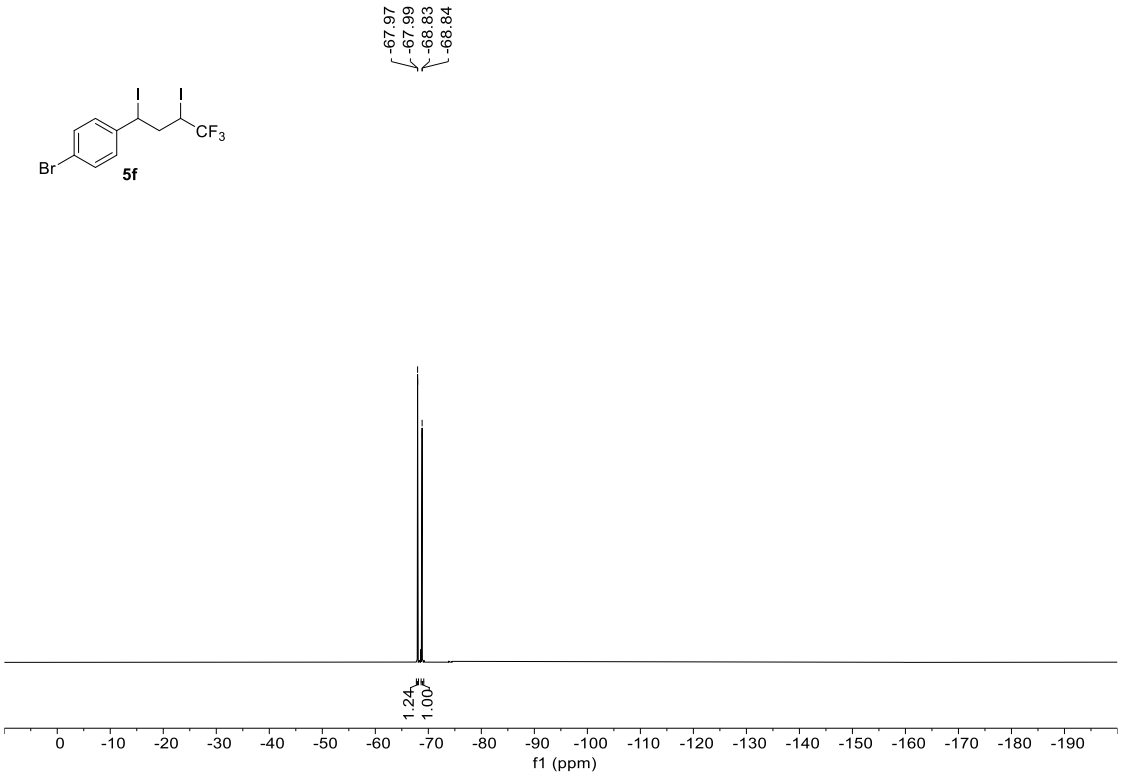
^{19}F NMR (565 MHz, $CDCl_3$) for **5e**



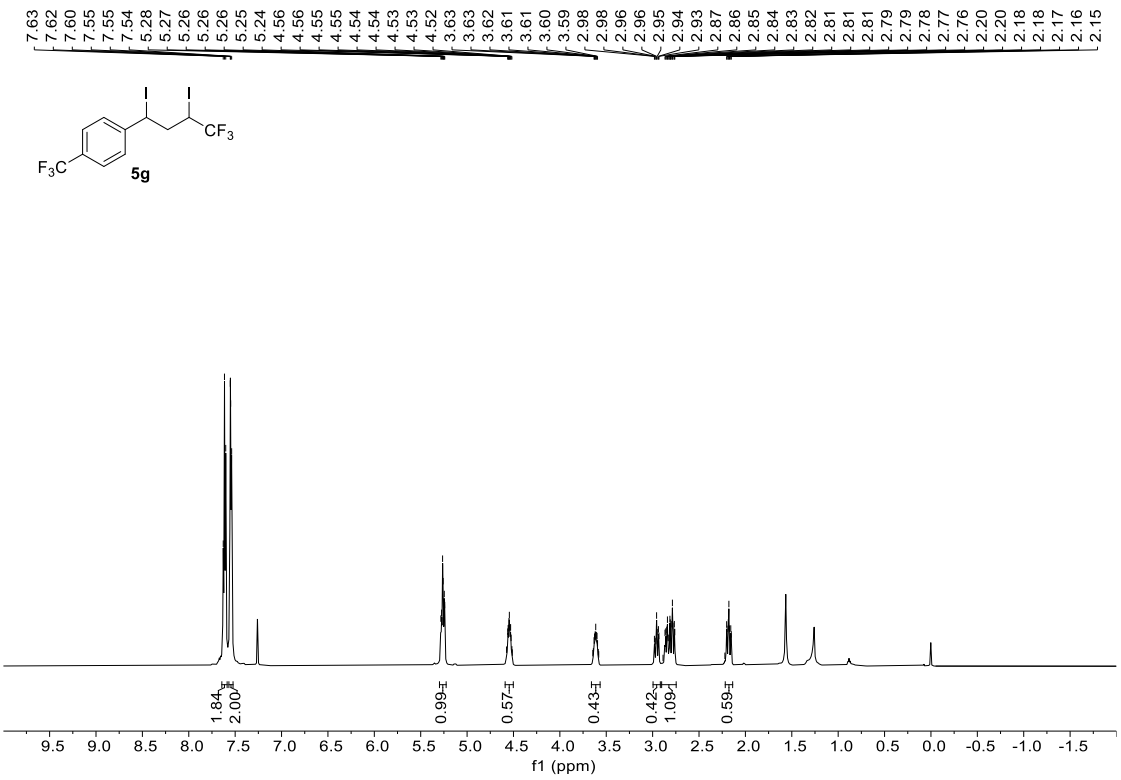
^{1}H NMR (600 MHz, $CDCl_3$) for **5f**



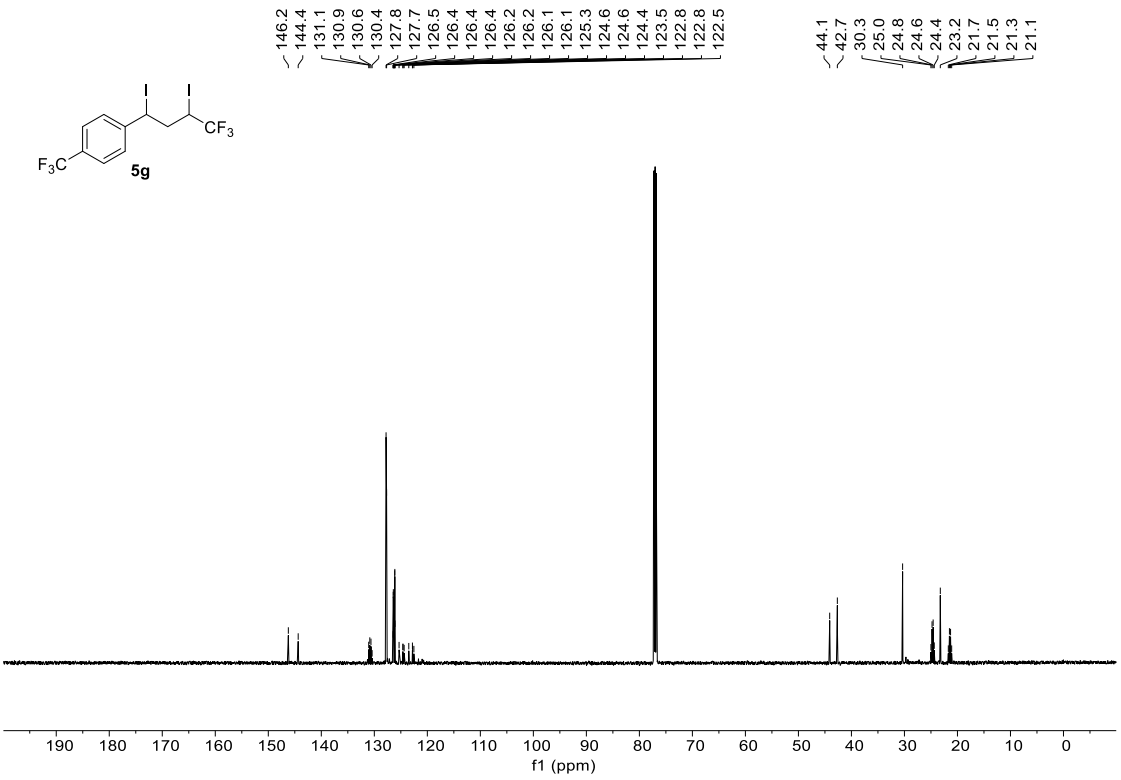
^{13}C NMR (101 MHz, $CDCl_3$) for **5f**



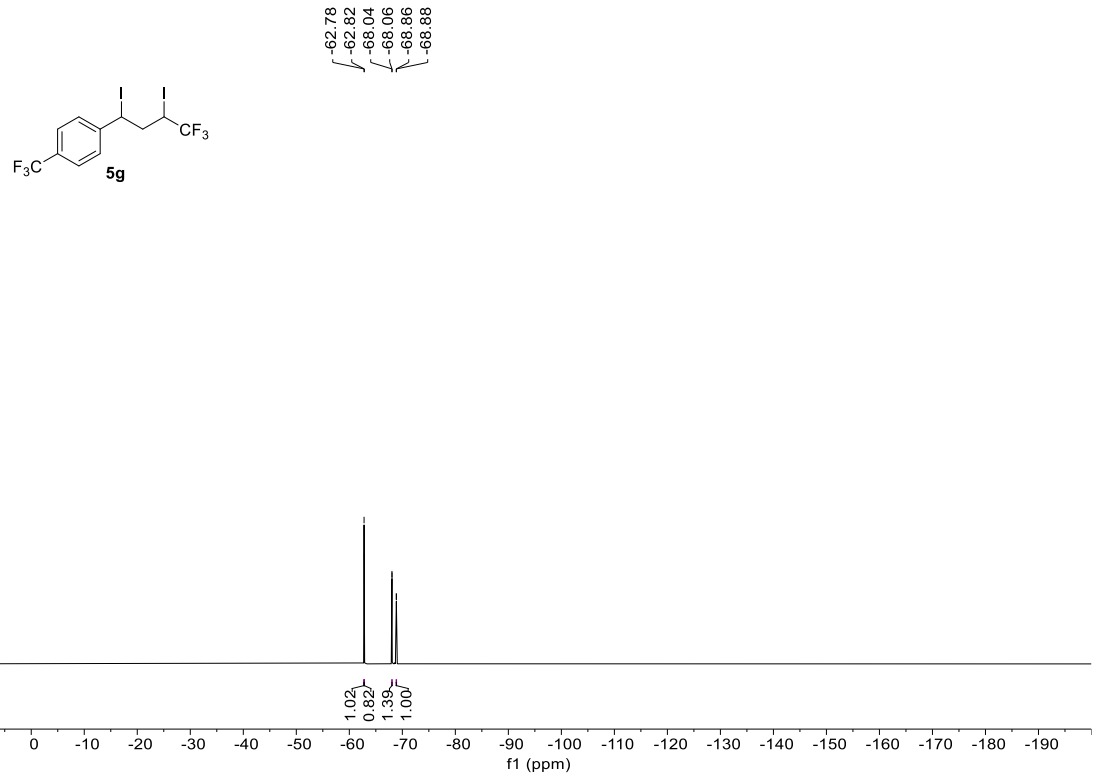
^{19}F NMR (565 MHz, $CDCl_3$) for **5f**



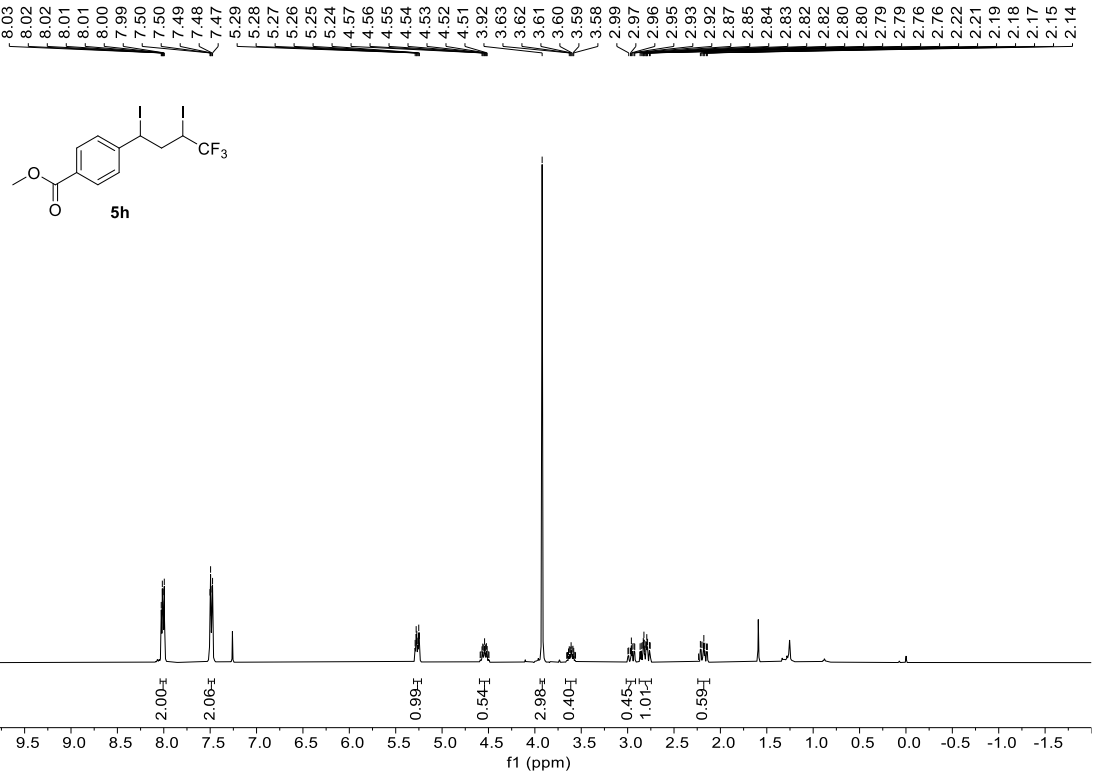
^{1}H NMR (600 MHz, $CDCl_3$) for **5g**



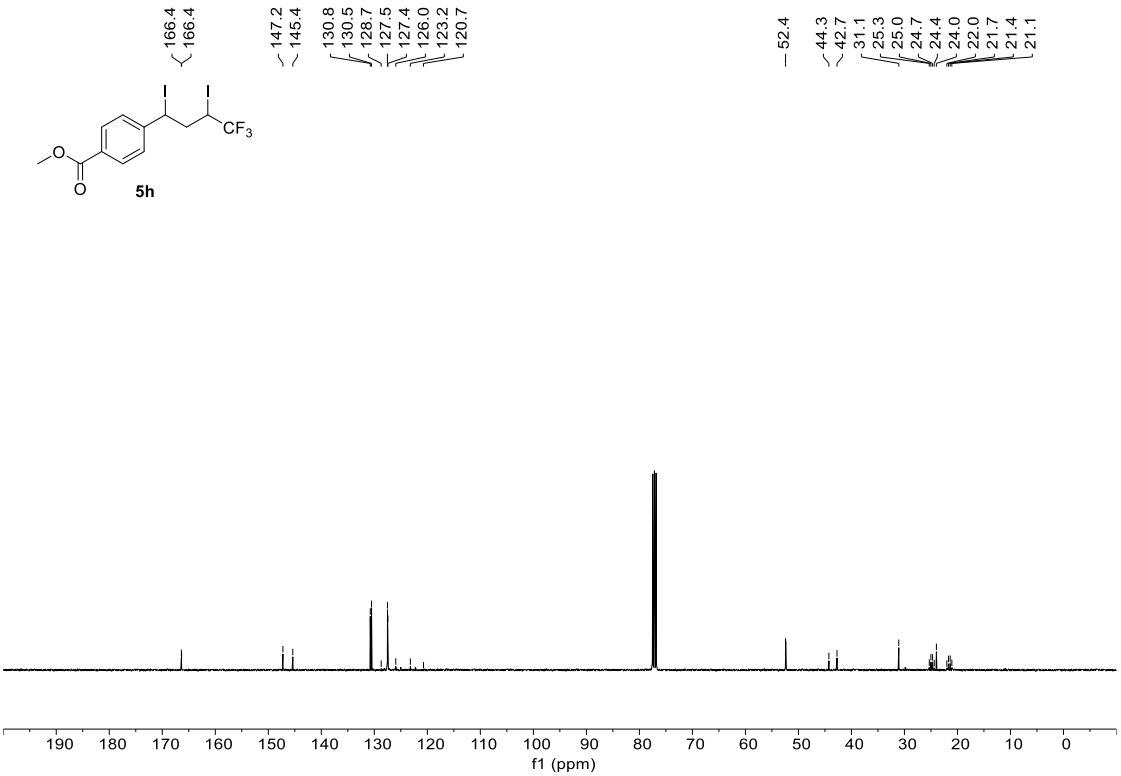
^{13}C NMR (101 MHz, $CDCl_3$) for **5g**



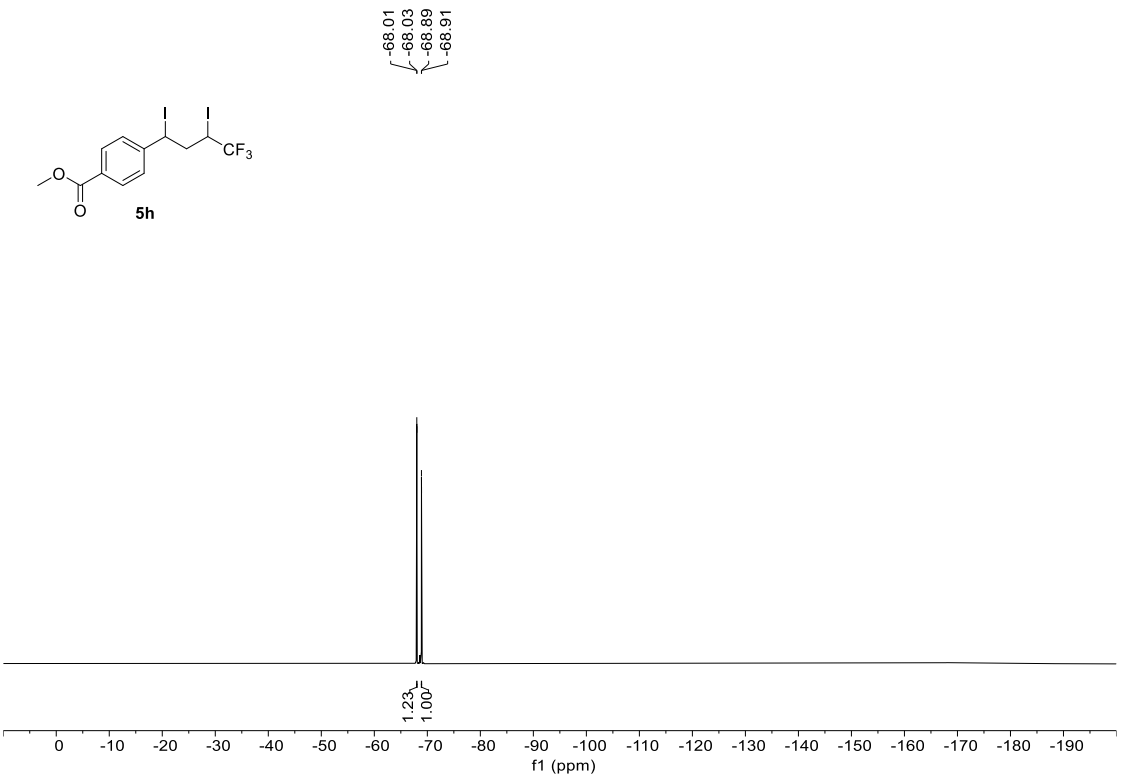
^{19}F NMR (565 MHz, $CDCl_3$) for **5g**



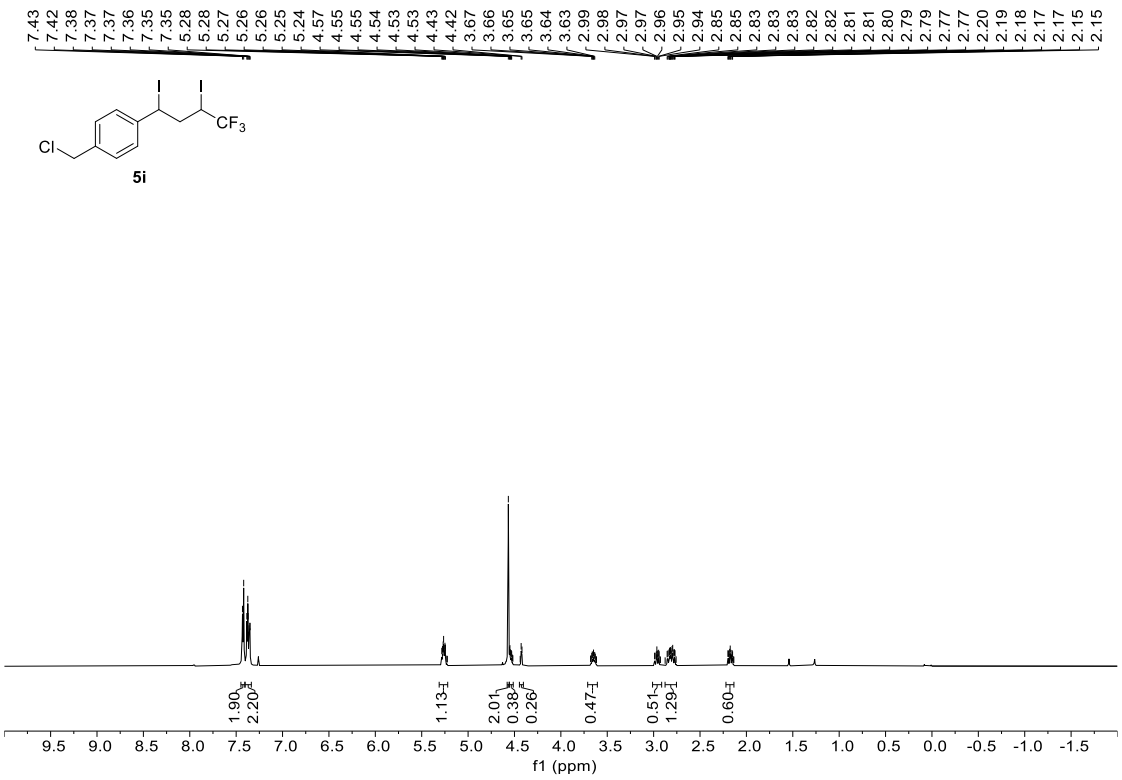
^{1}H NMR (600 MHz, $CDCl_3$) for **5h**



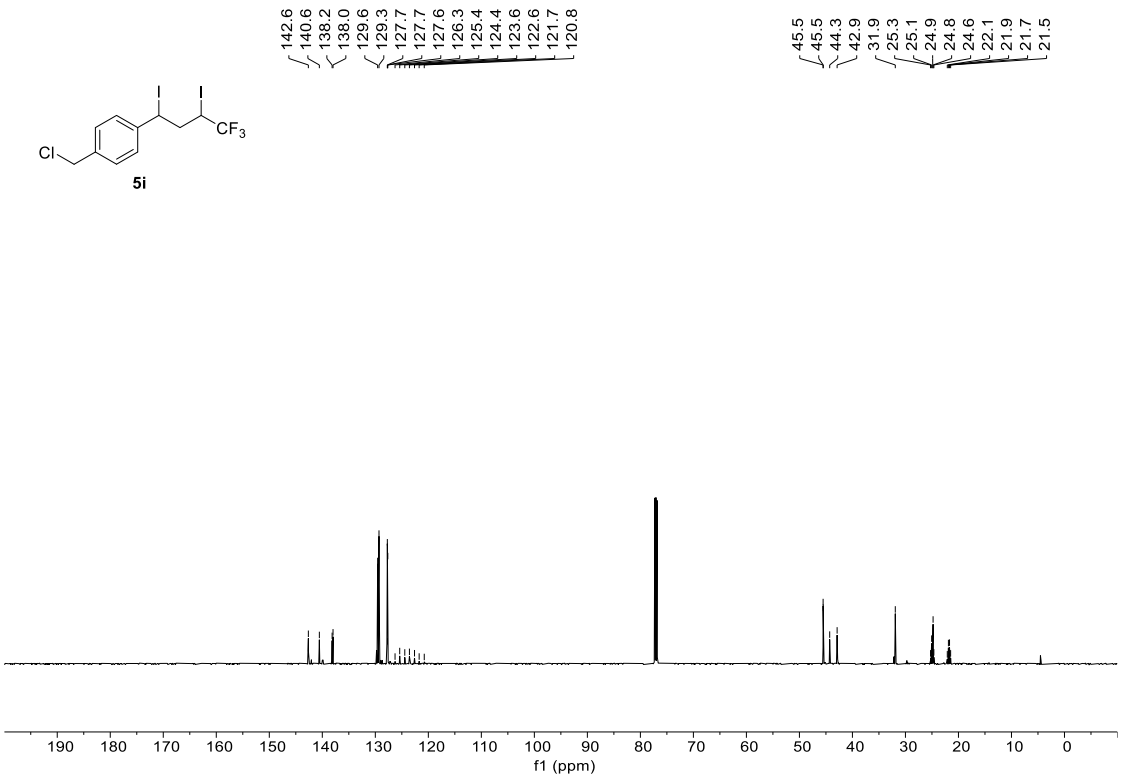
^{13}C NMR (101 MHz, $CDCl_3$) for **5h**



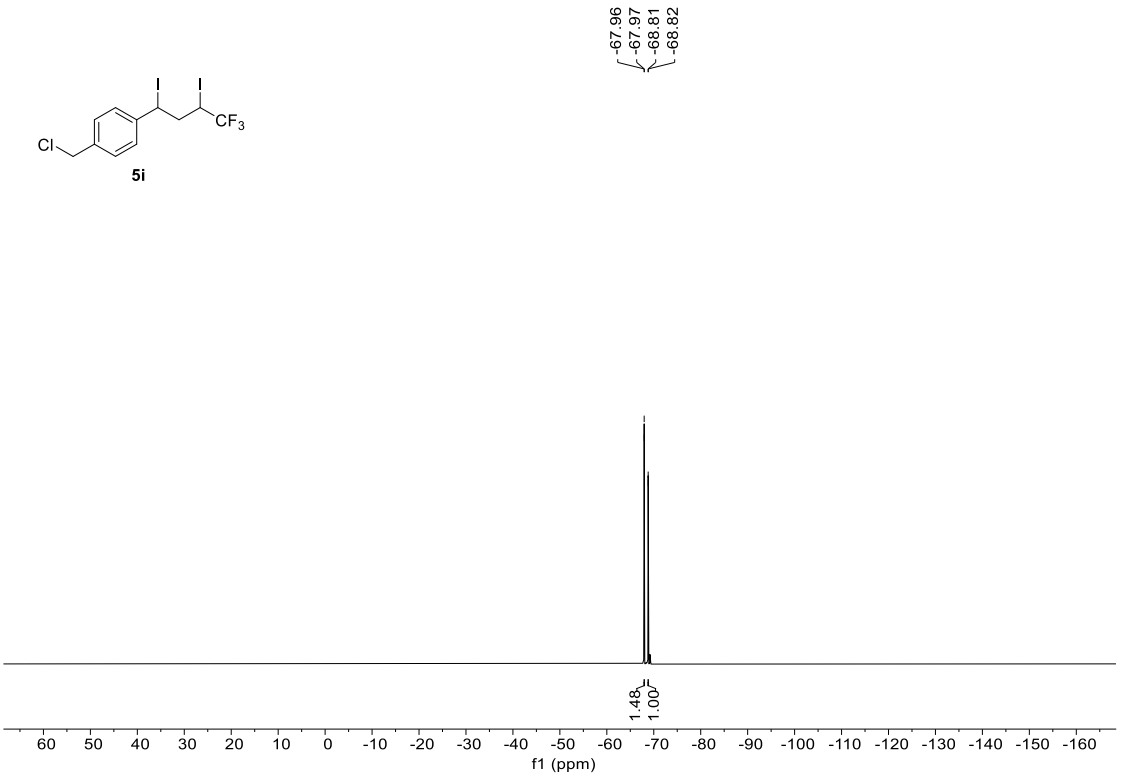
^{19}F NMR (565 MHz, $CDCl_3$) for **5h**



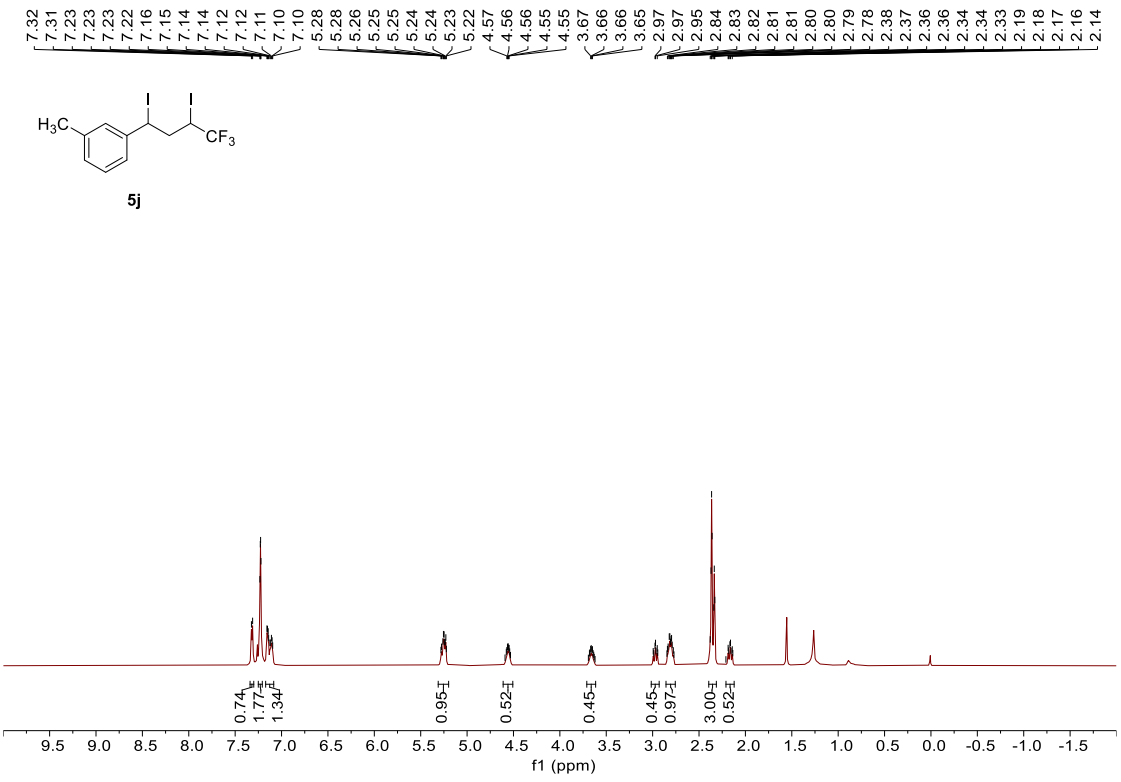
^{1}H NMR (600 MHz, $CDCl_3$) for **5i**



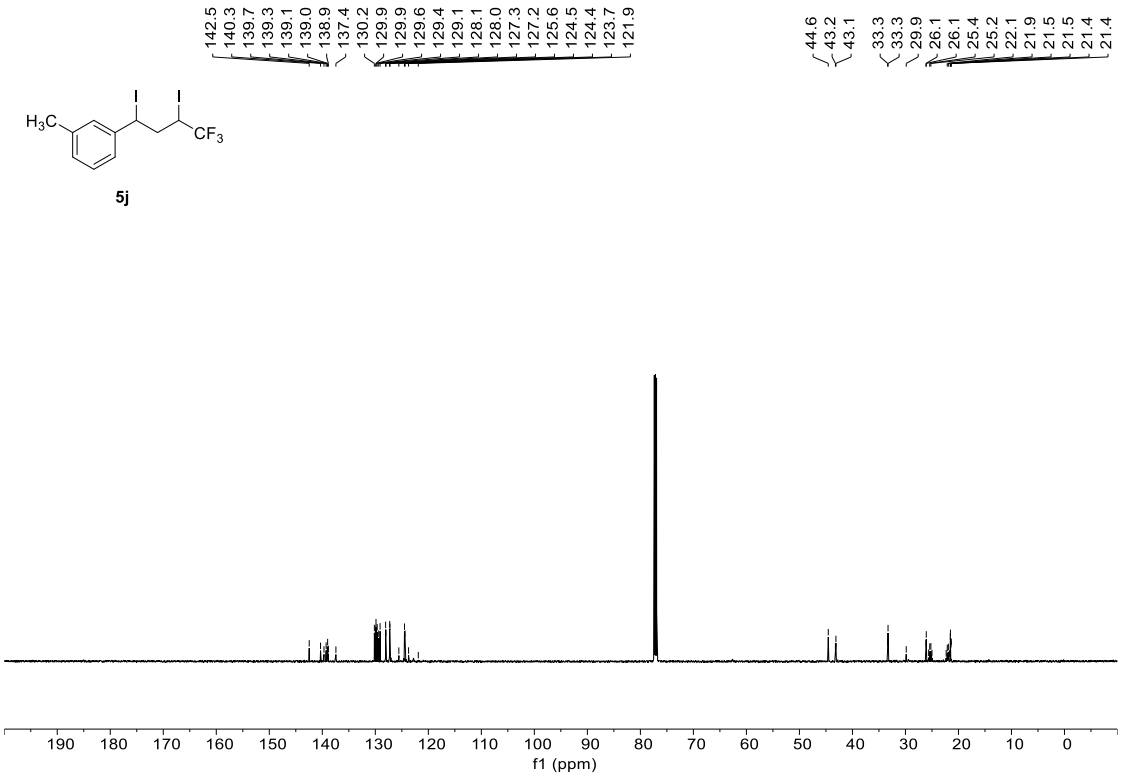
^{13}C NMR (101 MHz, $CDCl_3$) for **5i**



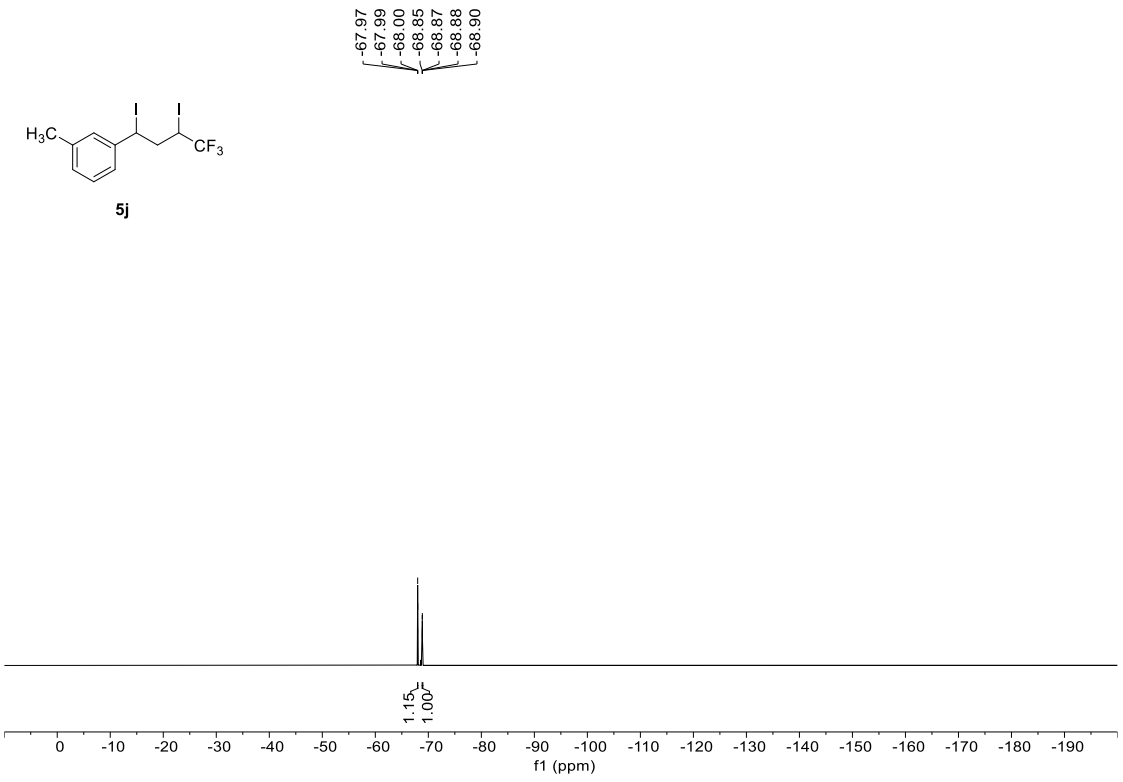
^{19}F NMR (565 MHz, $CDCl_3$) for **5i**



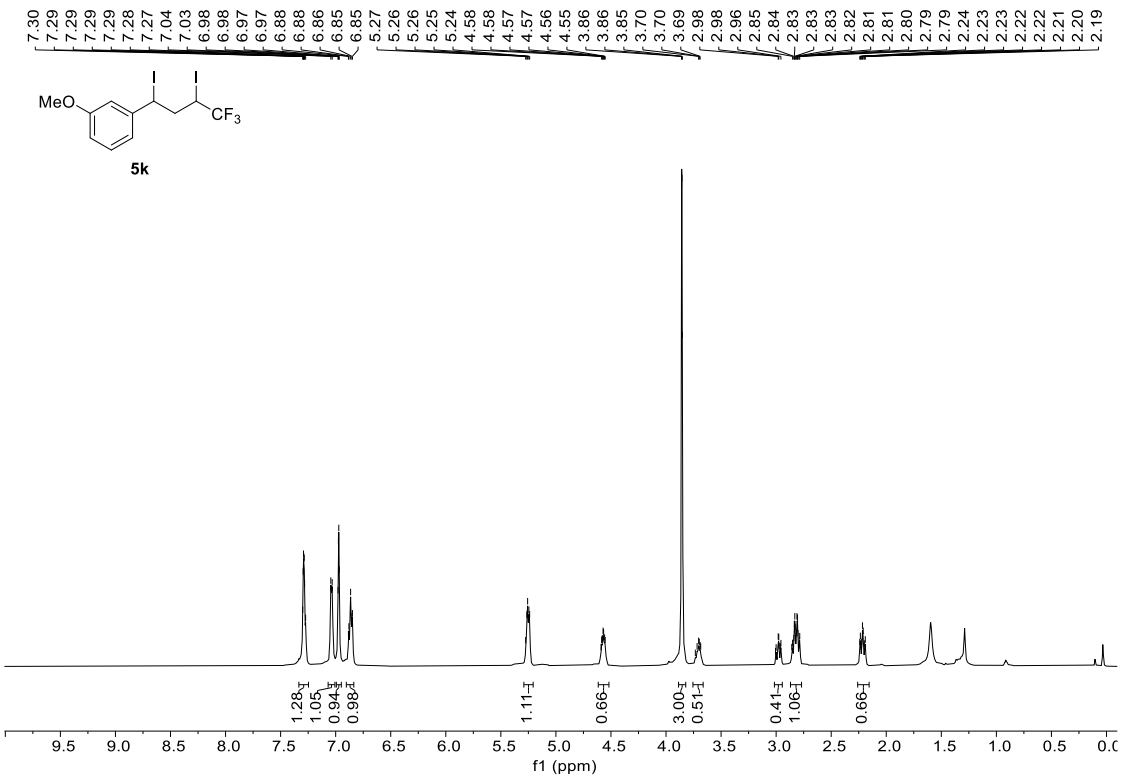
^{1}H NMR (600 MHz, $CDCl_3$) for **5j**



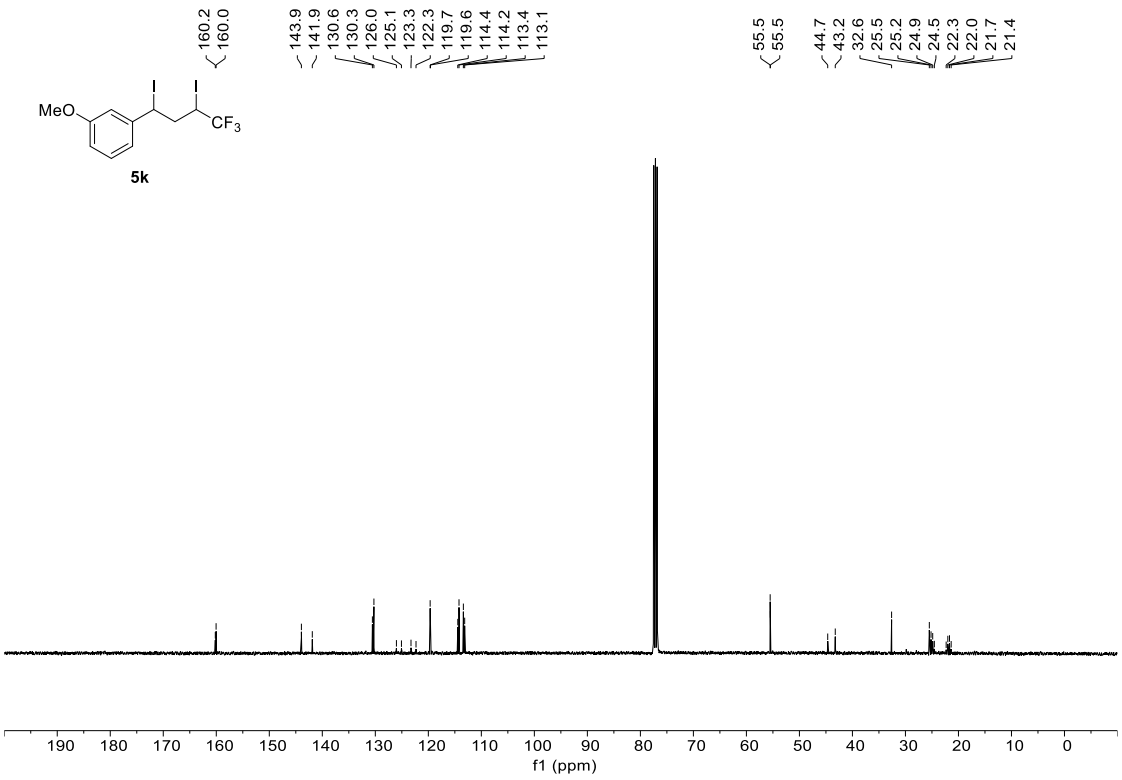
^{13}C NMR (101 MHz, $CDCl_3$) for **5j**



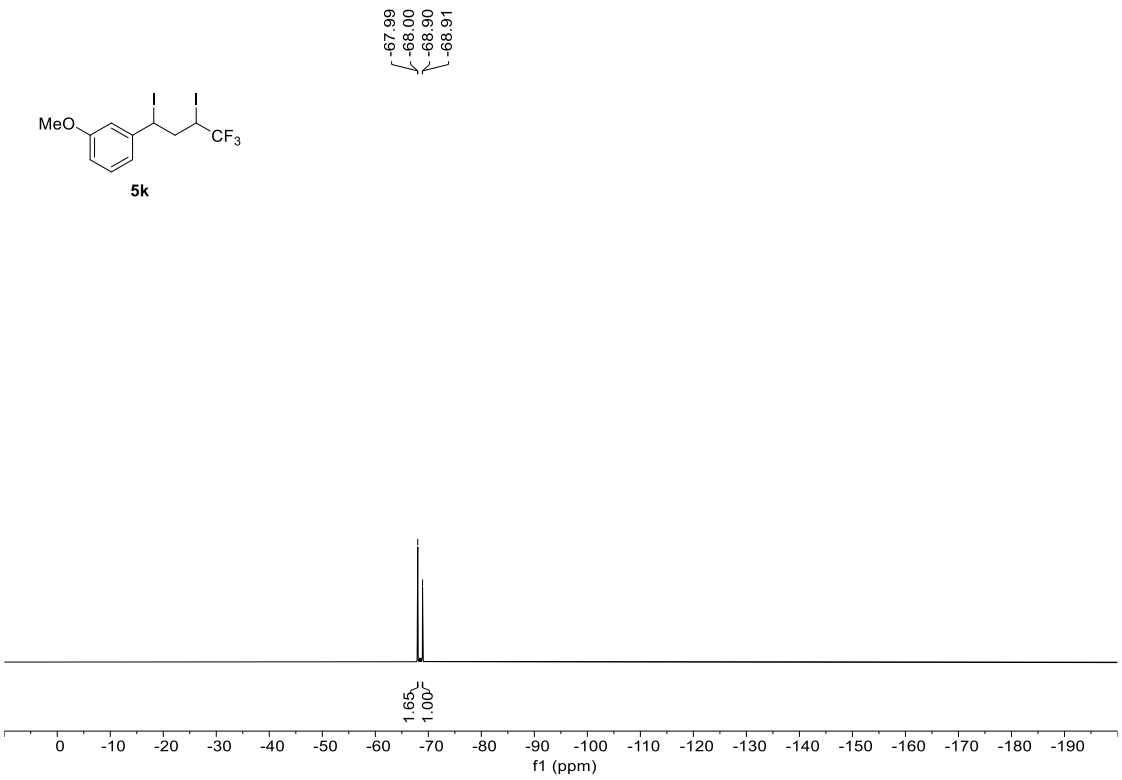
^{19}F NMR (565 MHz, $CDCl_3$) for **5j**



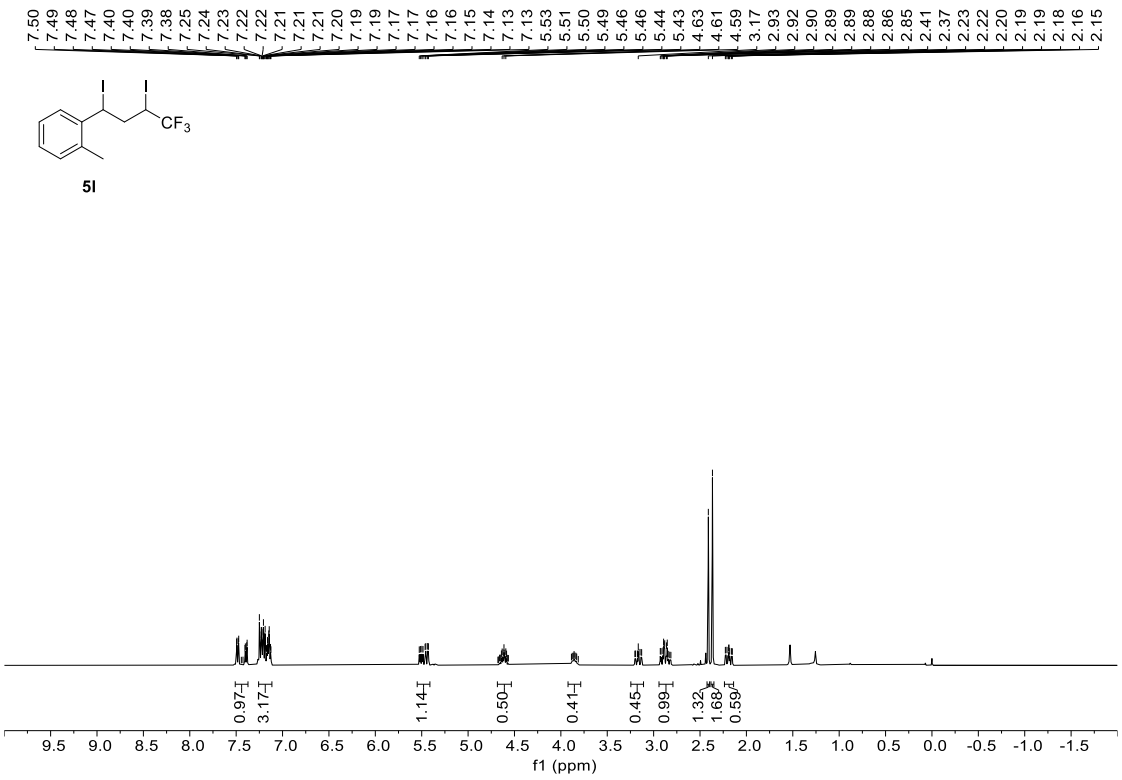
^{1}H NMR (600 MHz, $CDCl_3$) for **5k**



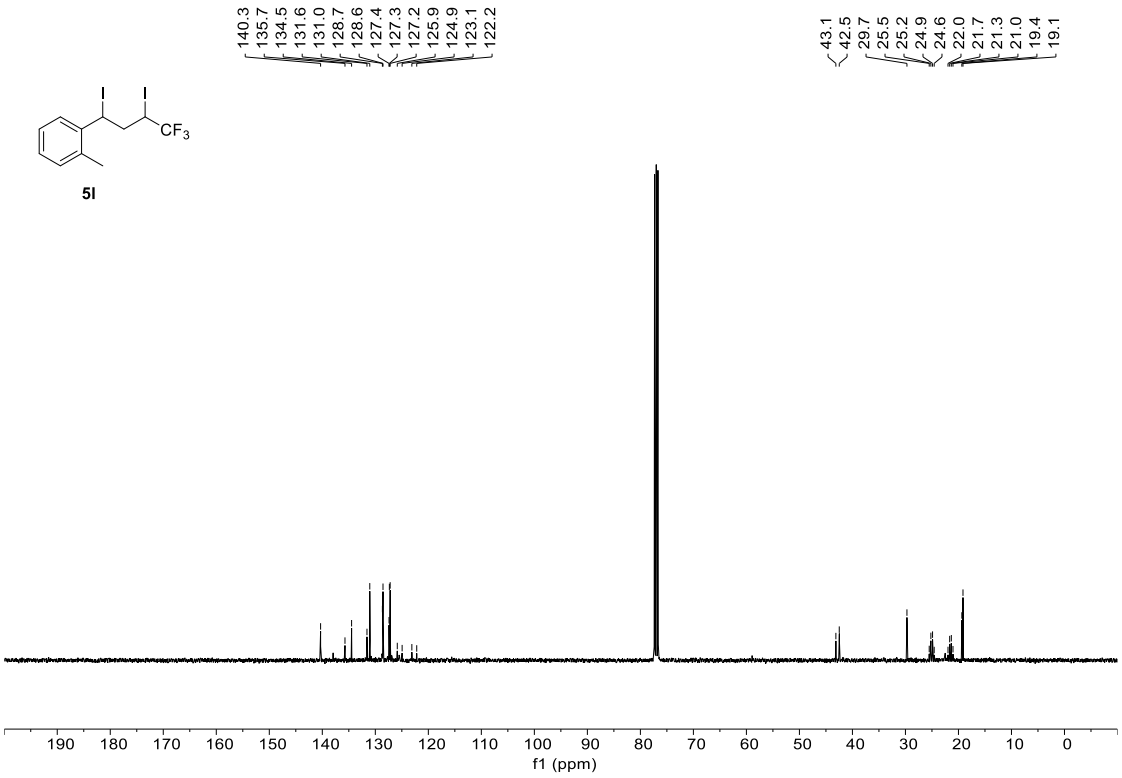
^{13}C NMR (101 MHz, $CDCl_3$) for **5k**



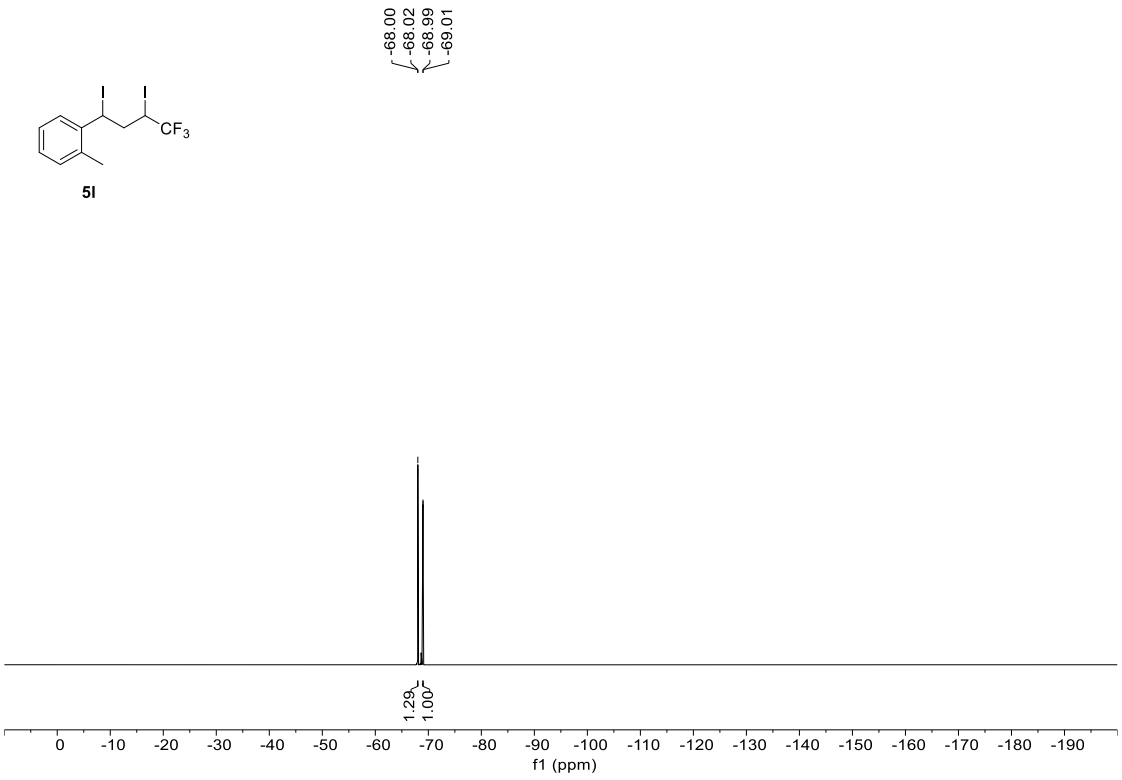
^{19}F NMR (565 MHz, $CDCl_3$) for **5k**



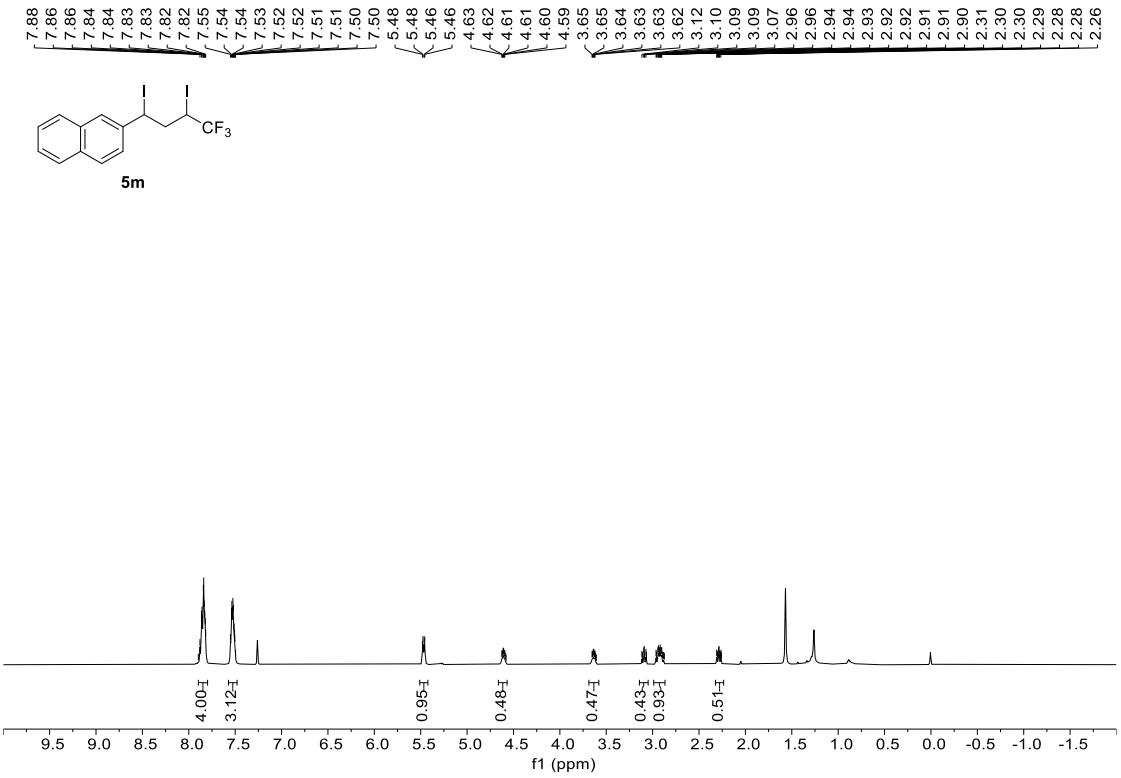
^{1}H NMR (600 MHz, $CDCl_3$) for **5l**



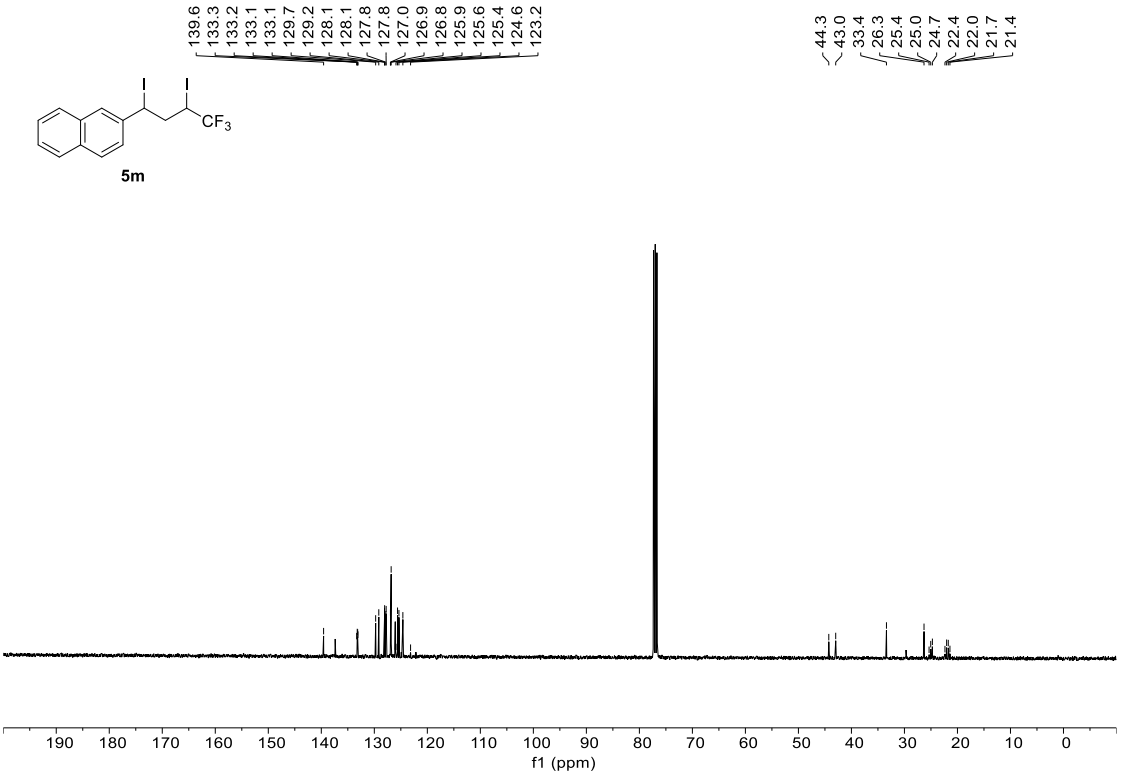
^{13}C NMR (101 MHz, $CDCl_3$) for **5l**



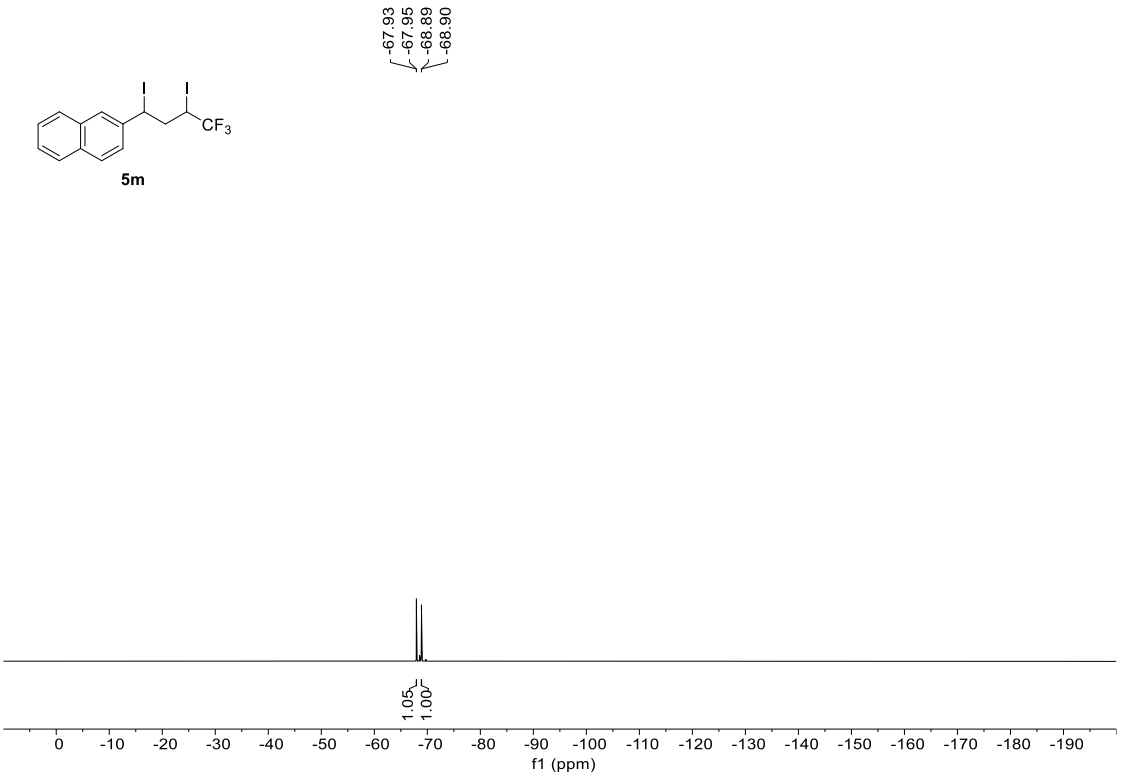
^{19}F NMR (565 MHz, $CDCl_3$) for **5l**



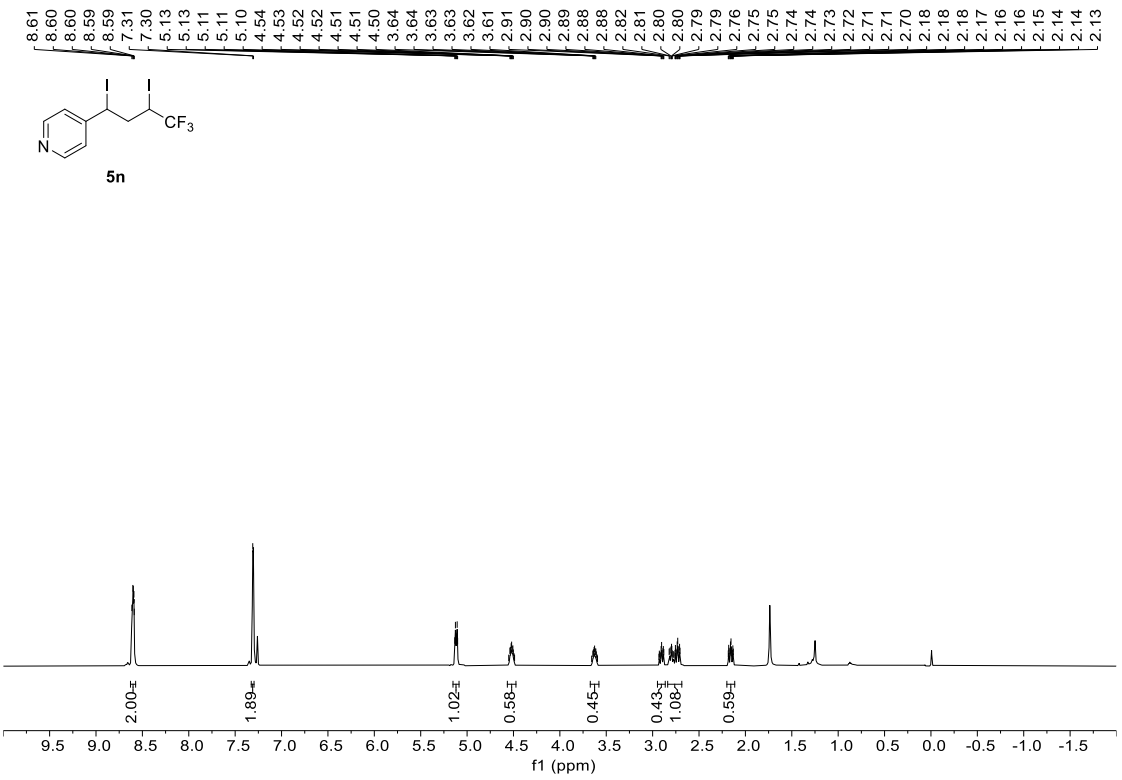
^{1}H NMR (600 MHz, $CDCl_3$) for **5m**



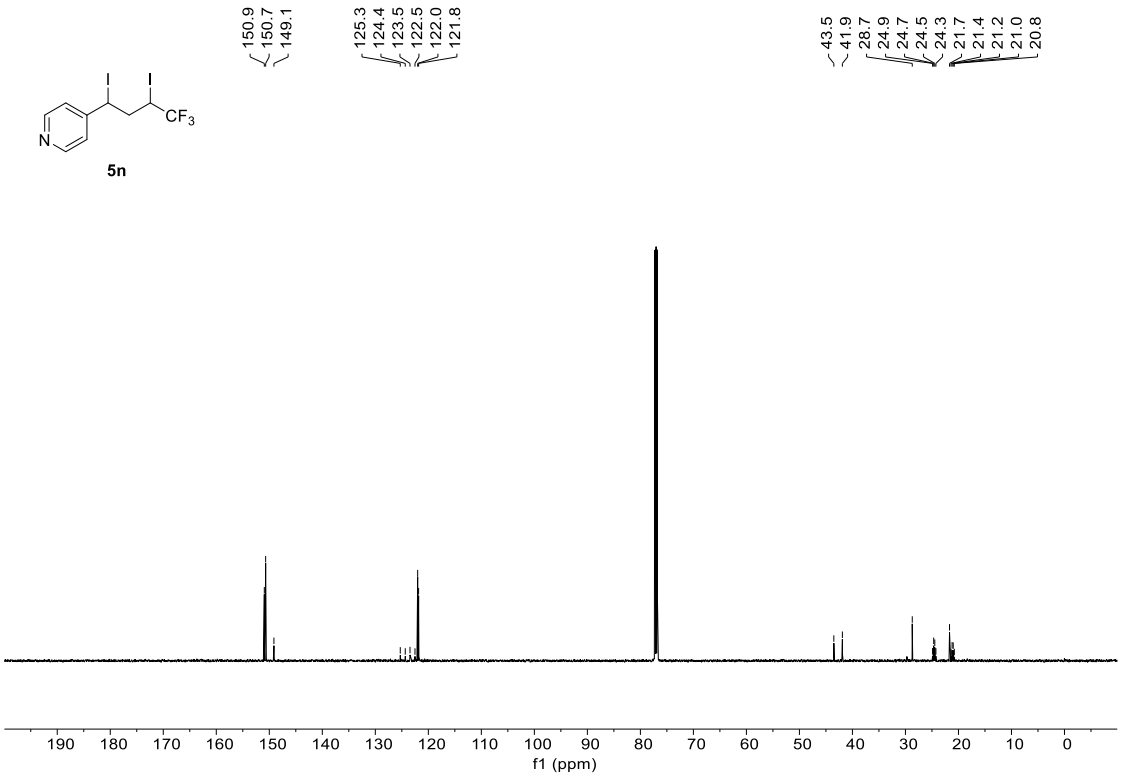
^{13}C NMR (101 MHz, $CDCl_3$) for **5m**



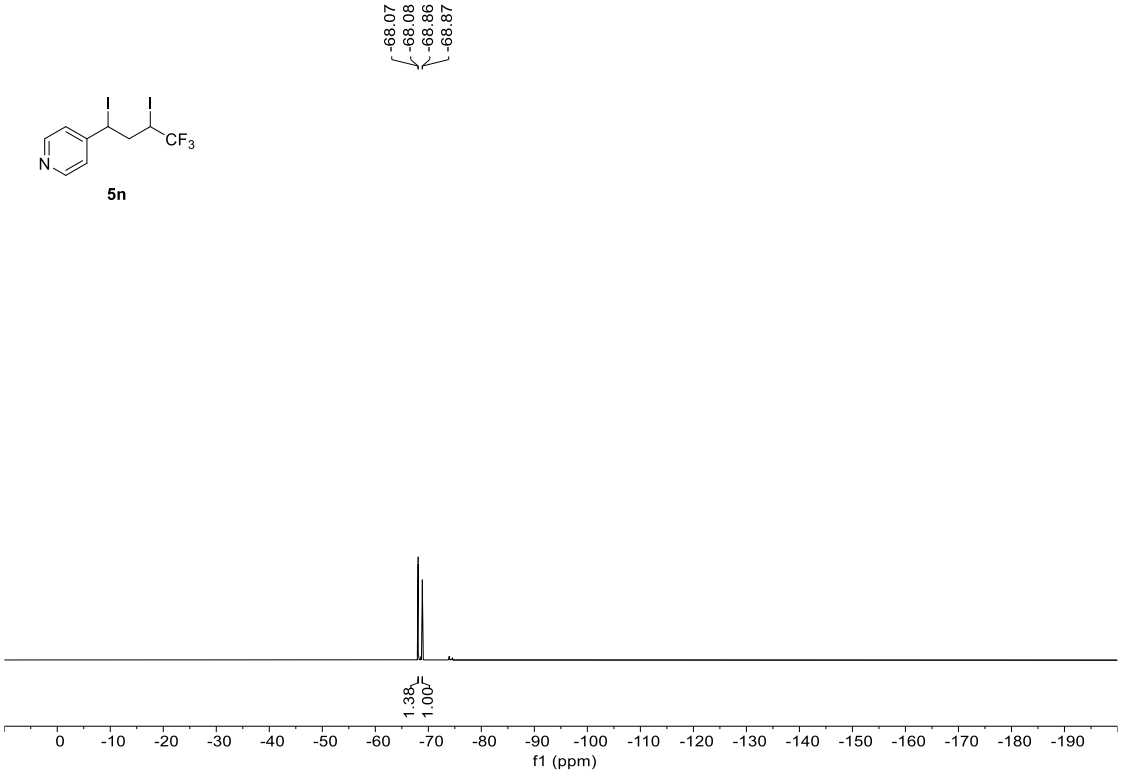
^{19}F NMR (565 MHz, $CDCl_3$) for **5m**



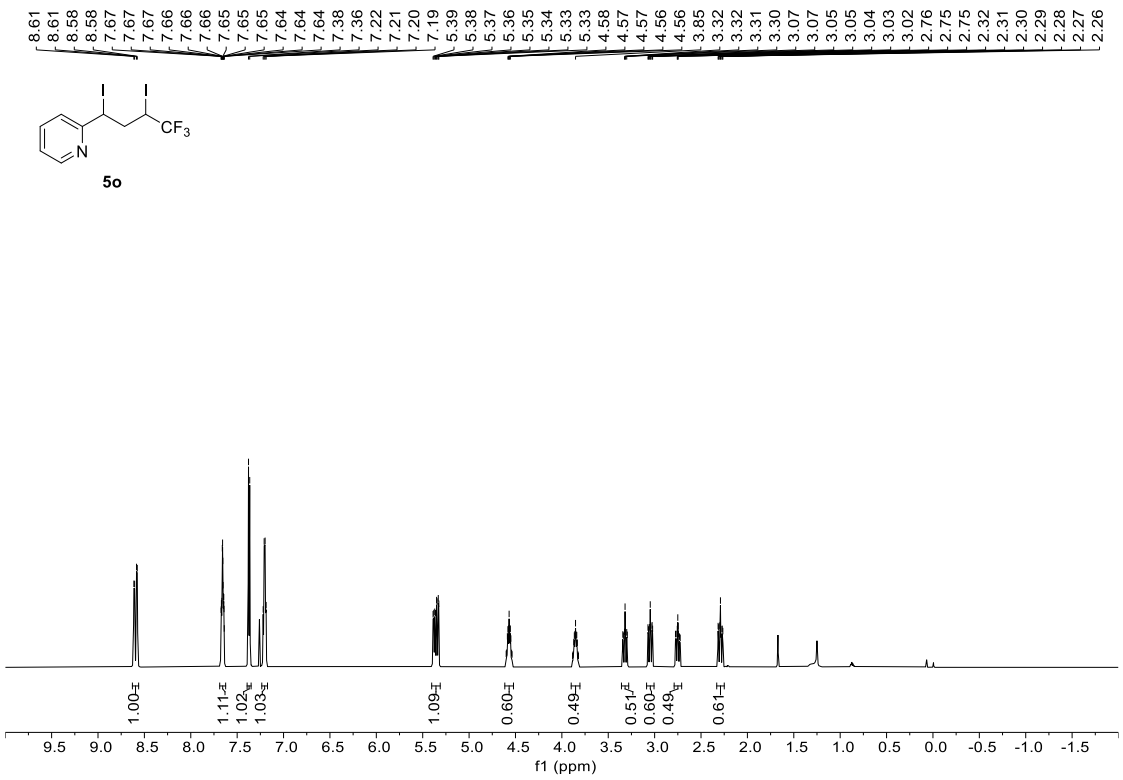
^{1}H NMR (600 MHz, $CDCl_3$) for **5n**



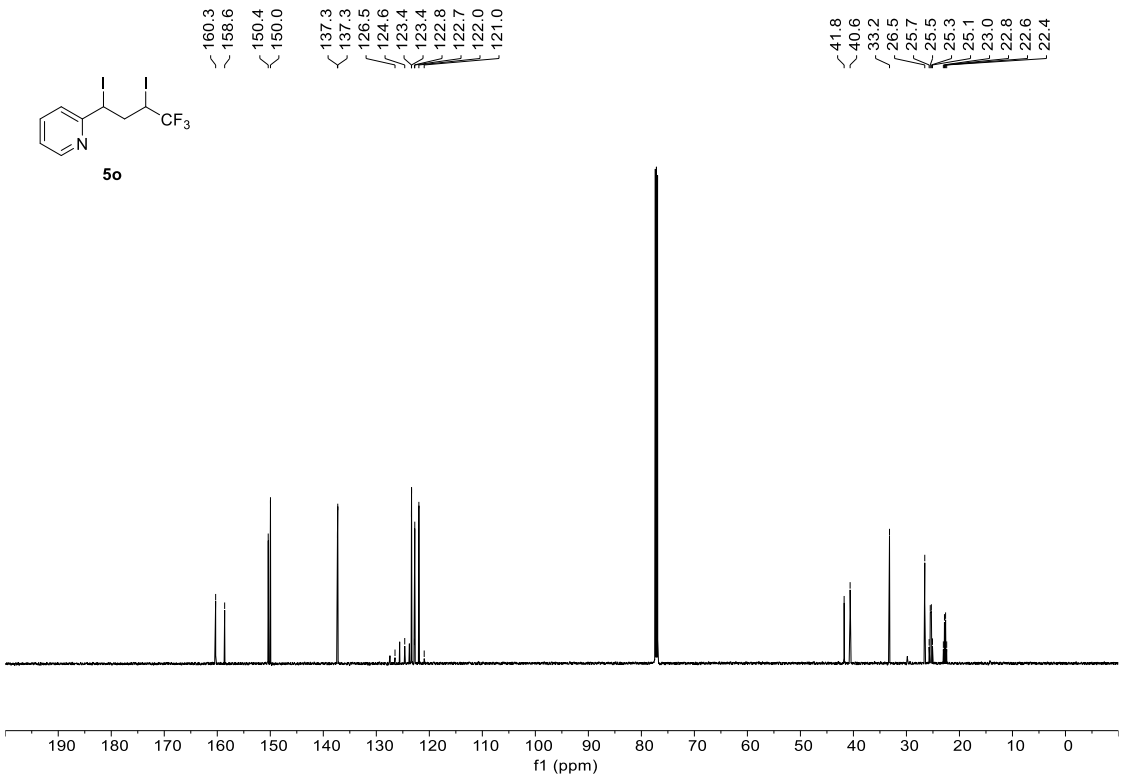
^{13}C NMR (101 MHz, $CDCl_3$) for **5n**



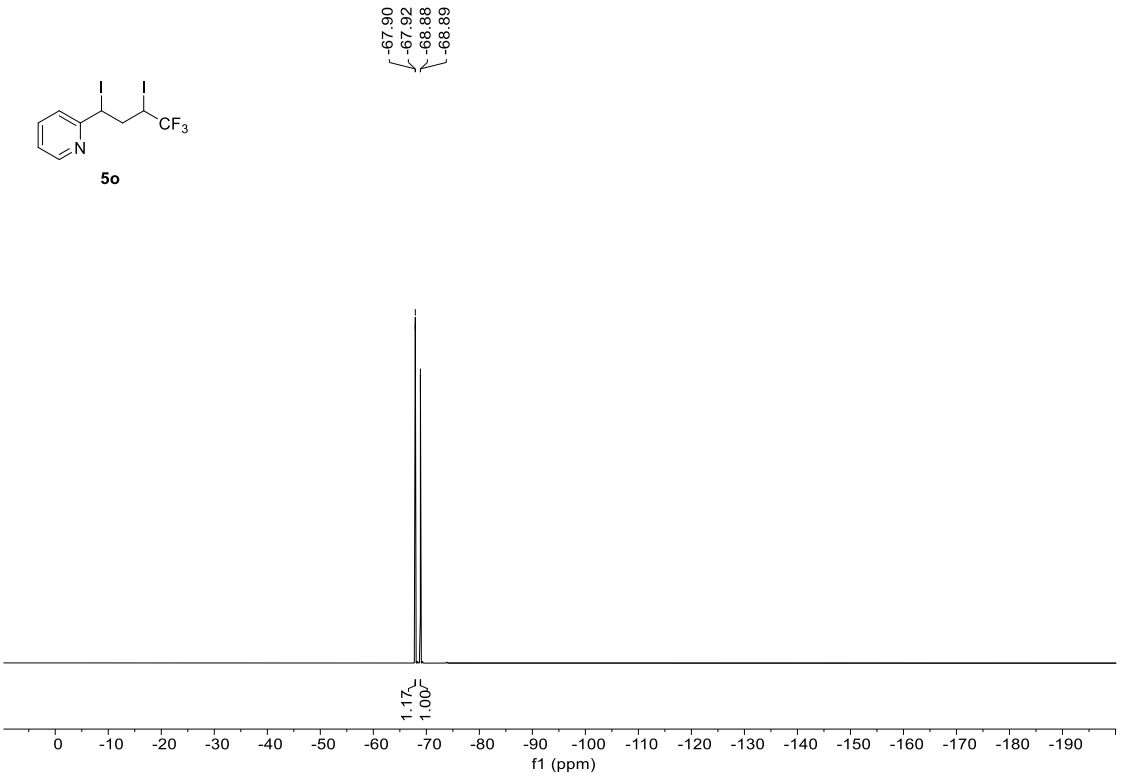
^{19}F NMR (565 MHz, $CDCl_3$) for **5n**



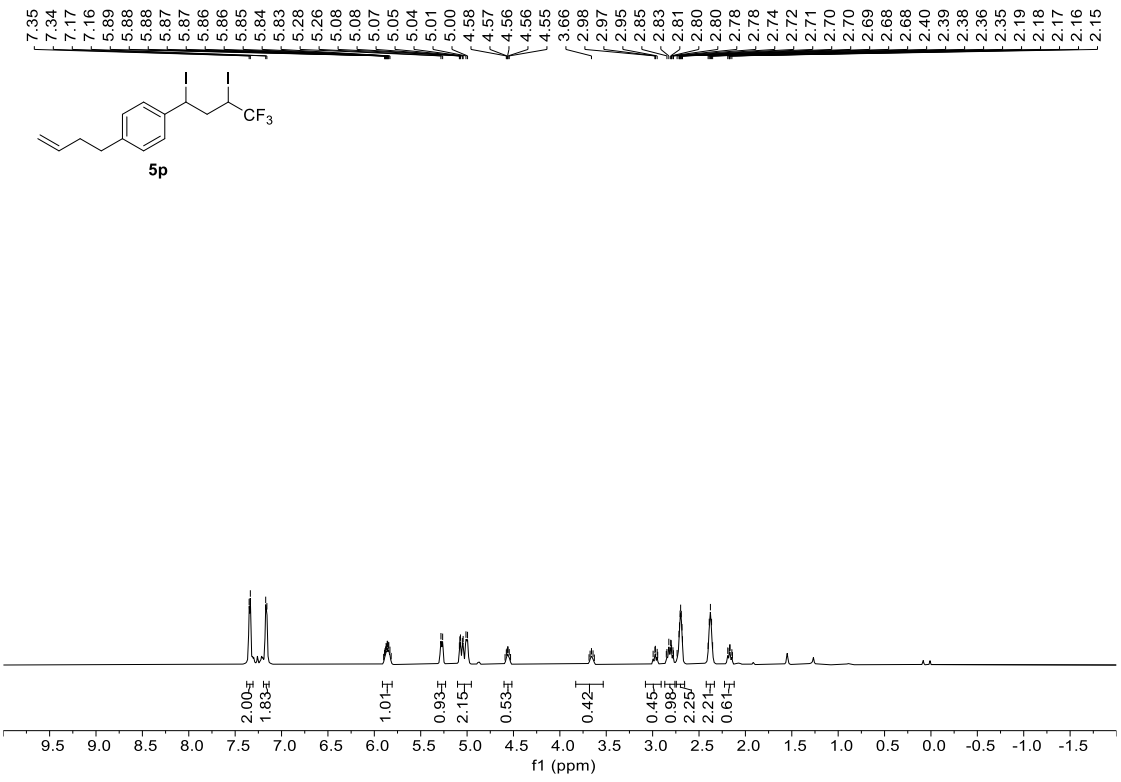
^{1}H NMR (600 MHz, $CDCl_3$) for **5o**



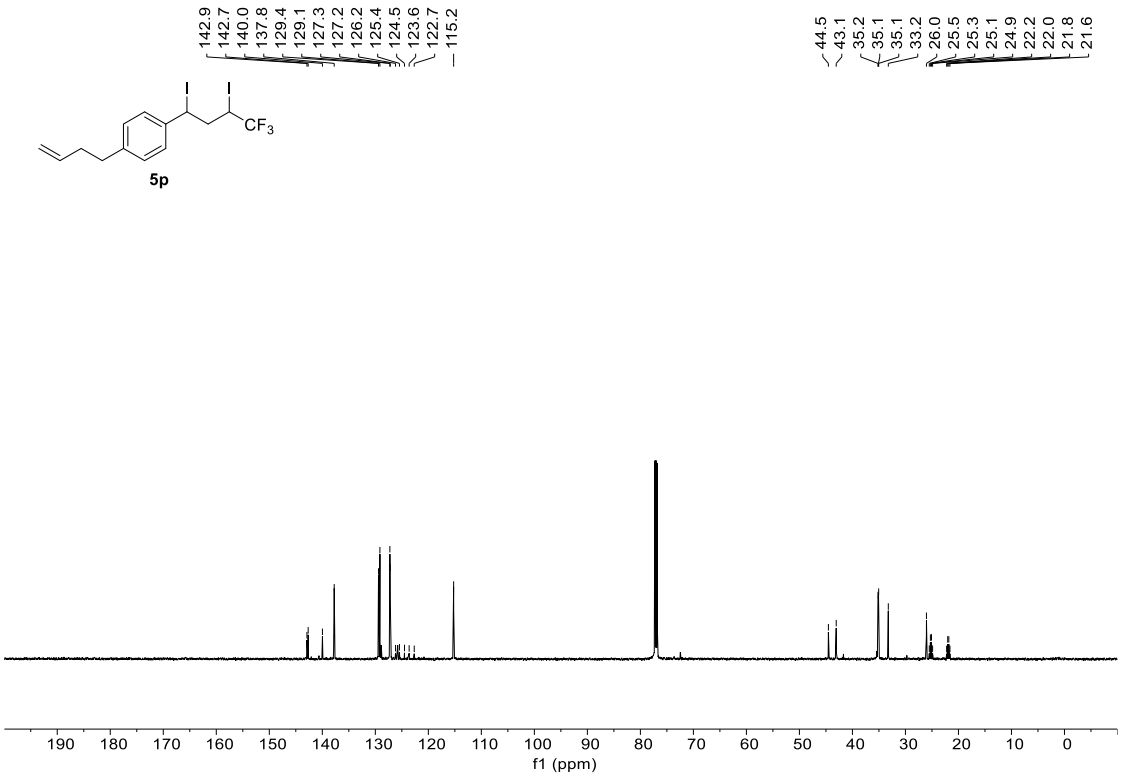
^{13}C NMR (101 MHz, $CDCl_3$) for **5o**



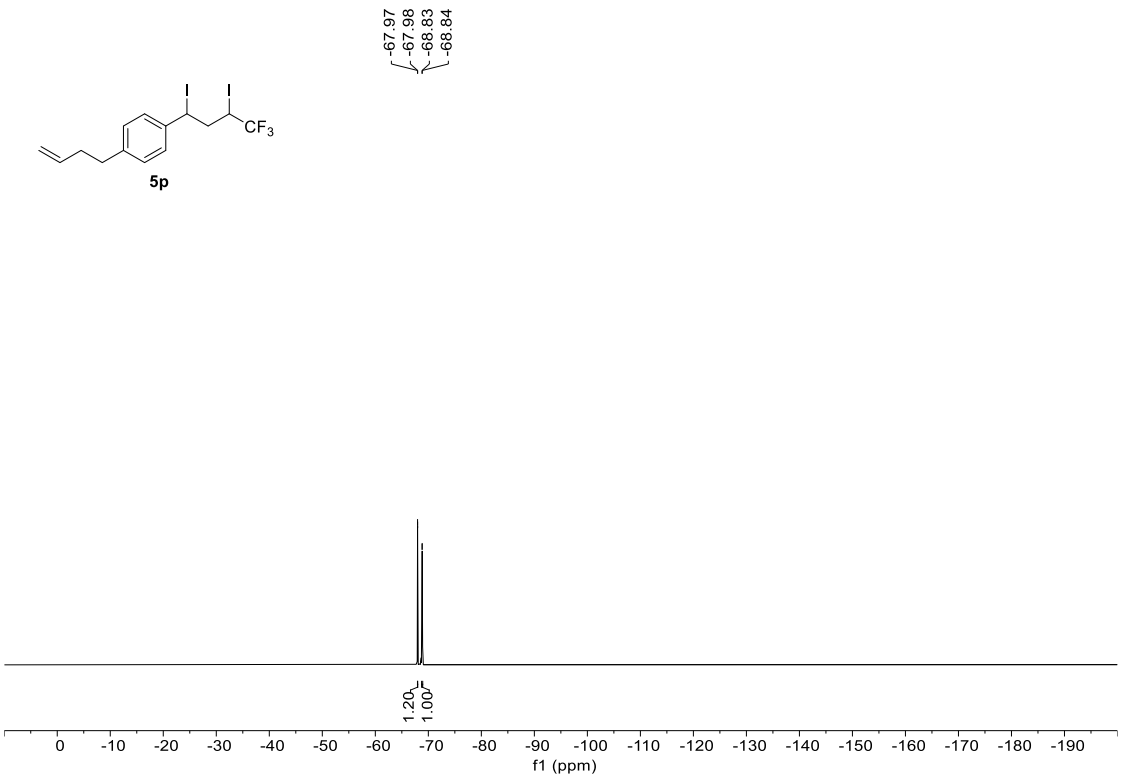
^{19}F NMR (565 MHz, $CDCl_3$) for **5o**



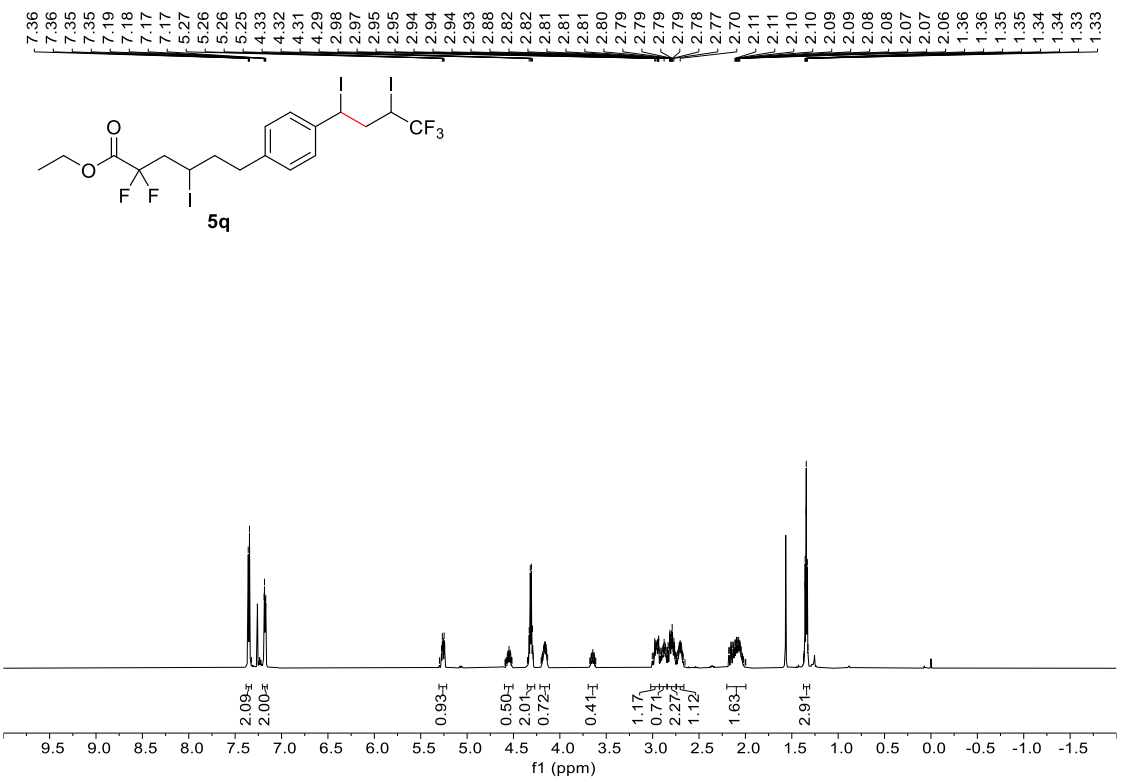
^{1}H NMR (600 MHz, $CDCl_3$) for **5p**



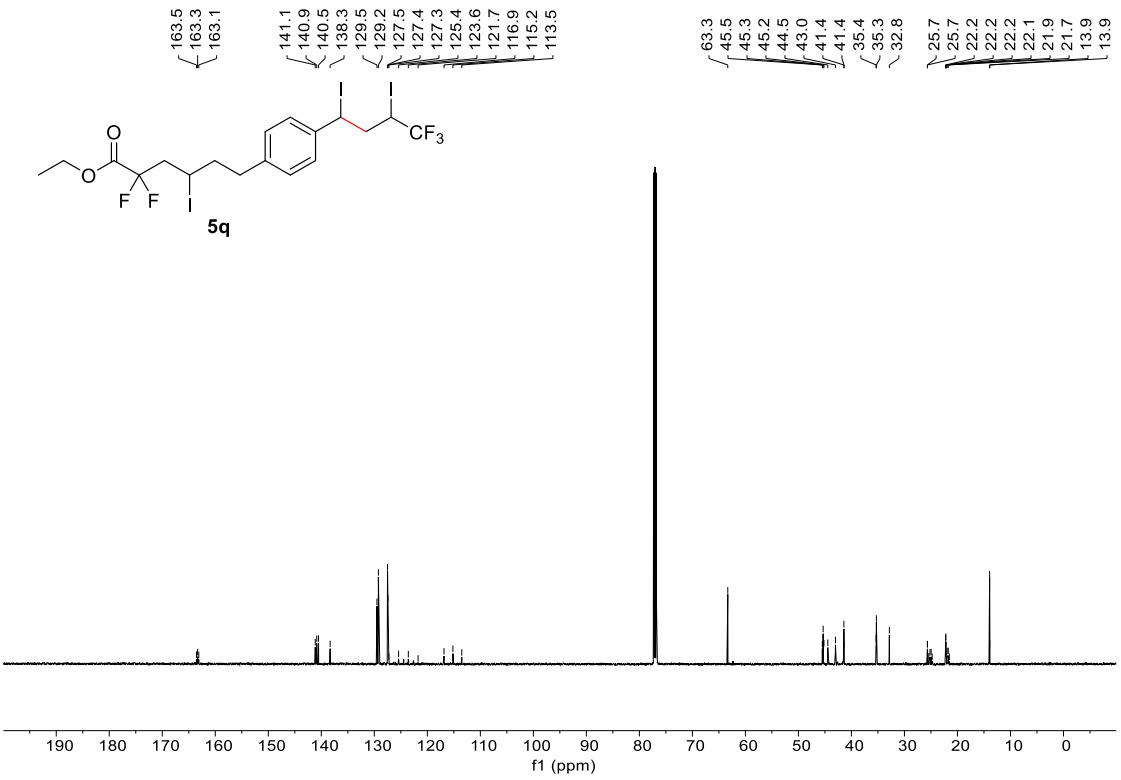
^{13}C NMR (101 MHz, $CDCl_3$) for **5p**



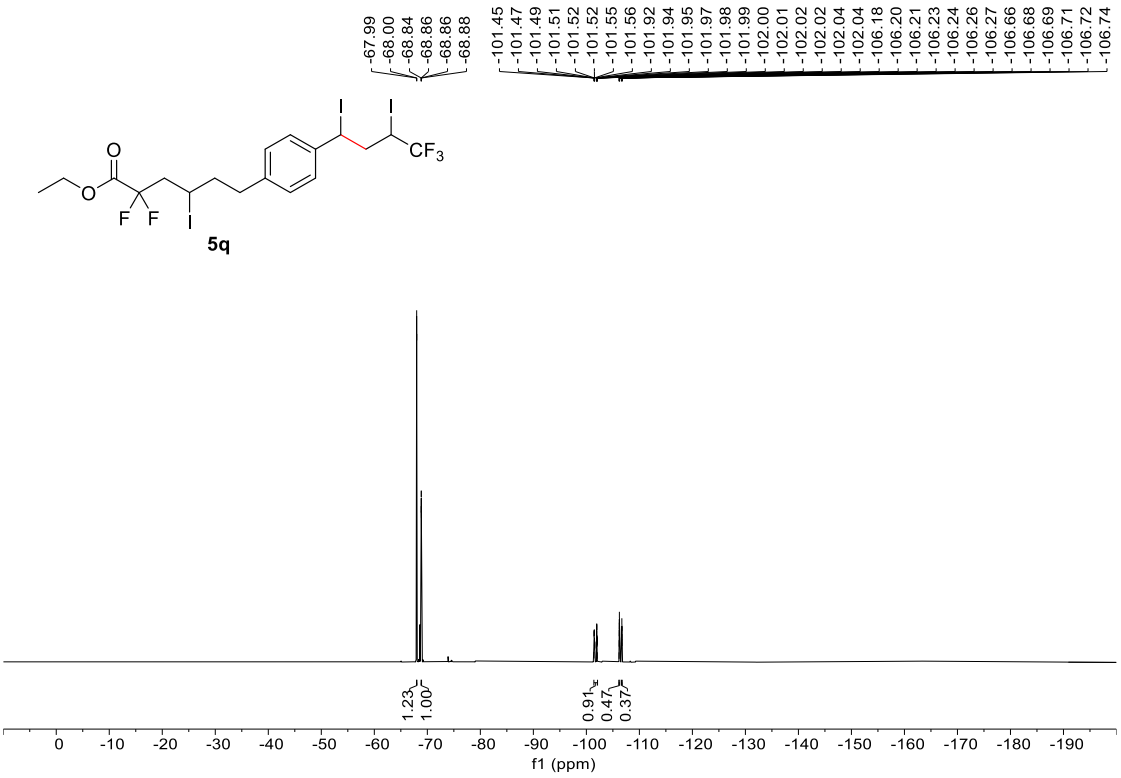
^{19}F NMR (565 MHz, $CDCl_3$) for **5p**



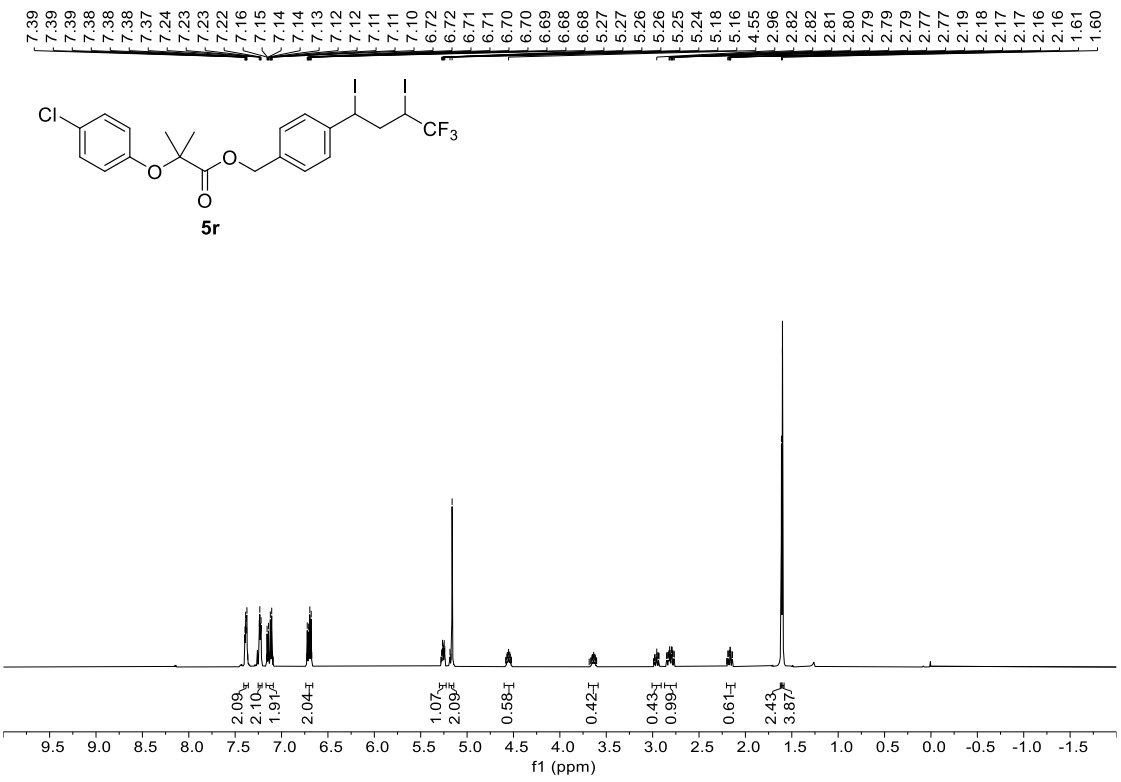
^{1}H NMR (600 MHz, $CDCl_3$) for **5q**



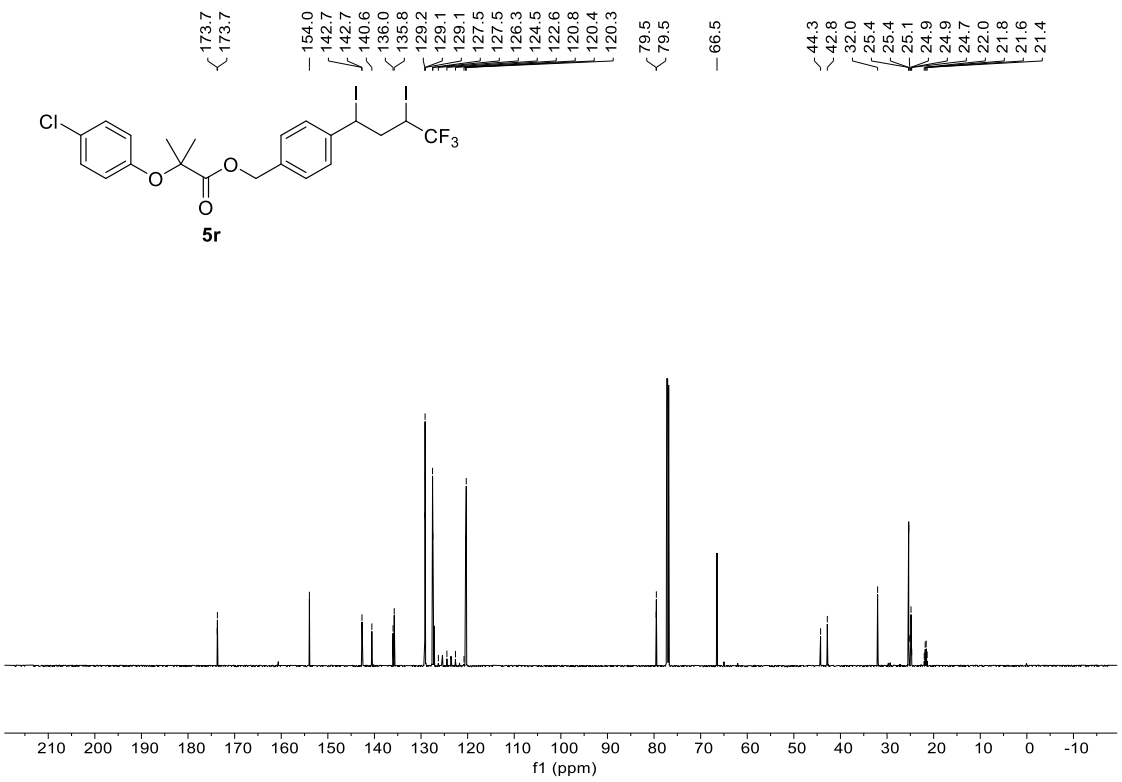
^{13}C NMR (151 MHz, $CDCl_3$) for **5q**



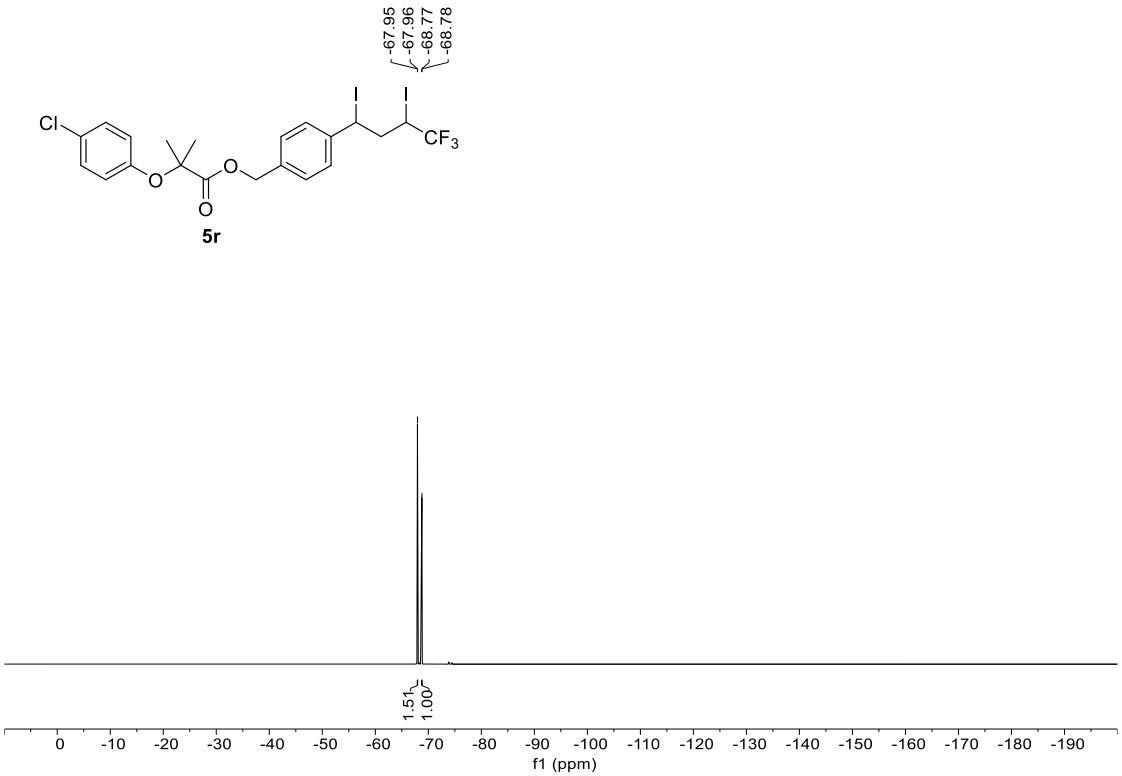
^{19}F NMR (565 MHz, $CDCl_3$) for **5q**



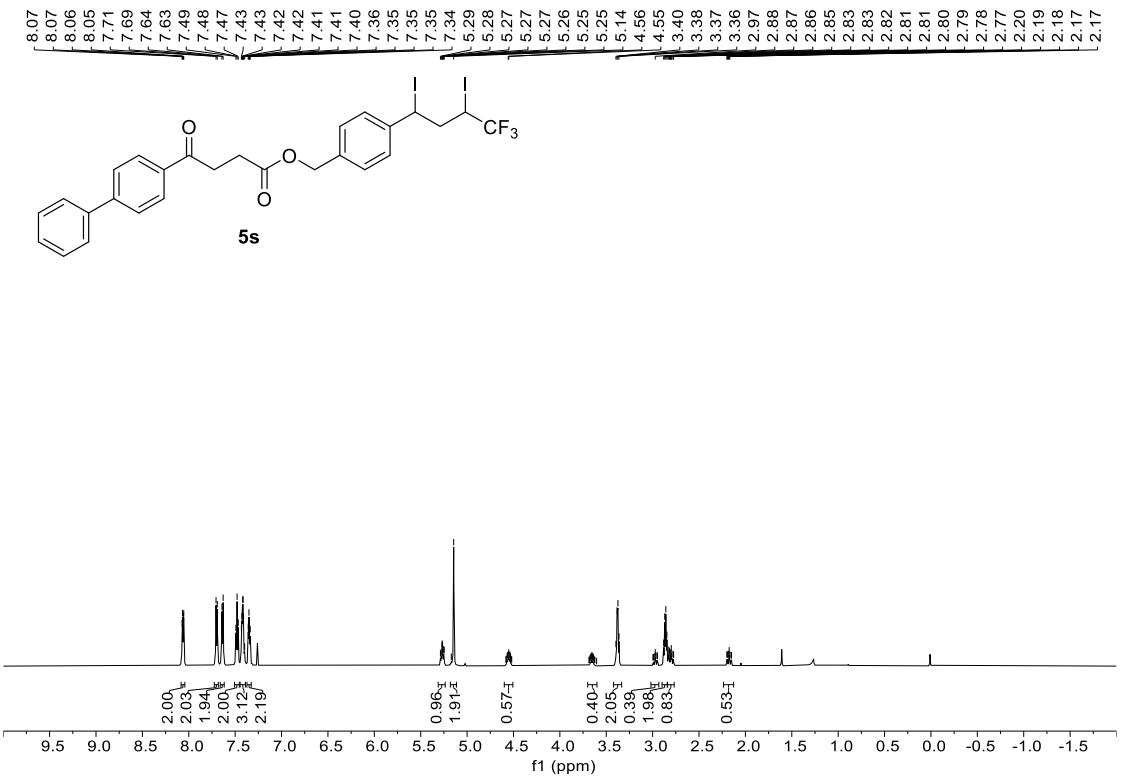
^{1}H NMR (600 MHz, $CDCl_3$) for **5r**



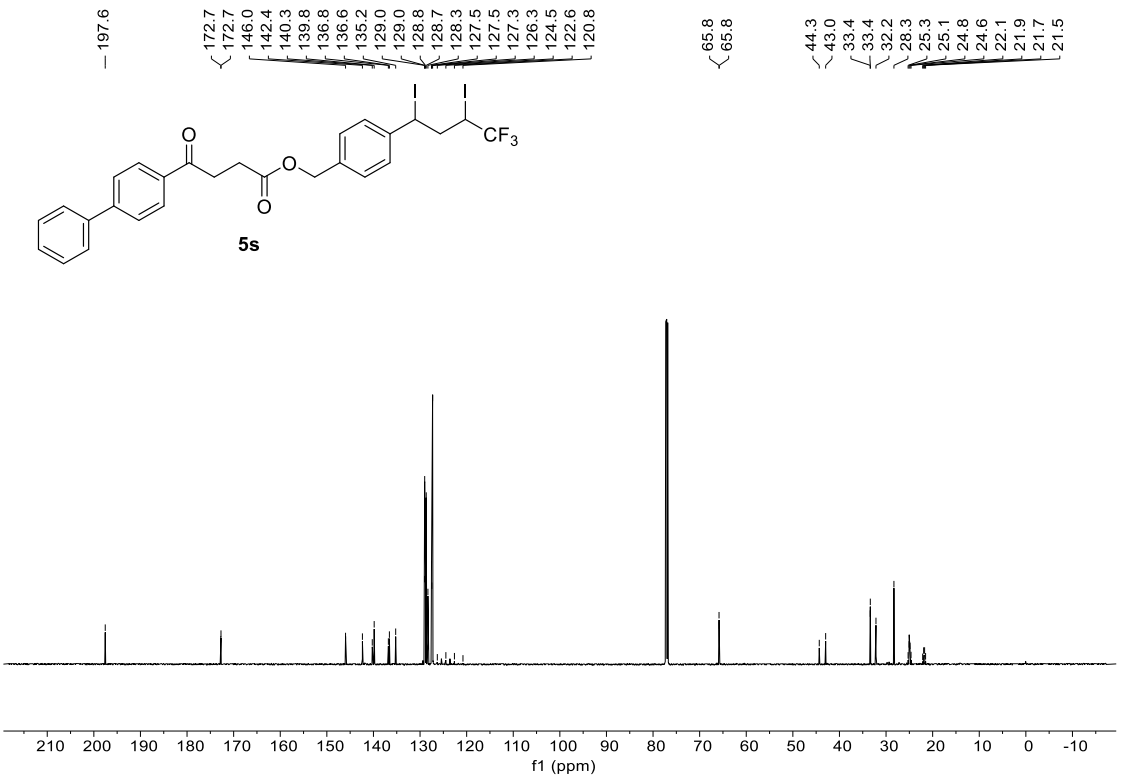
^{13}C NMR (151 MHz, $CDCl_3$) for **5r**



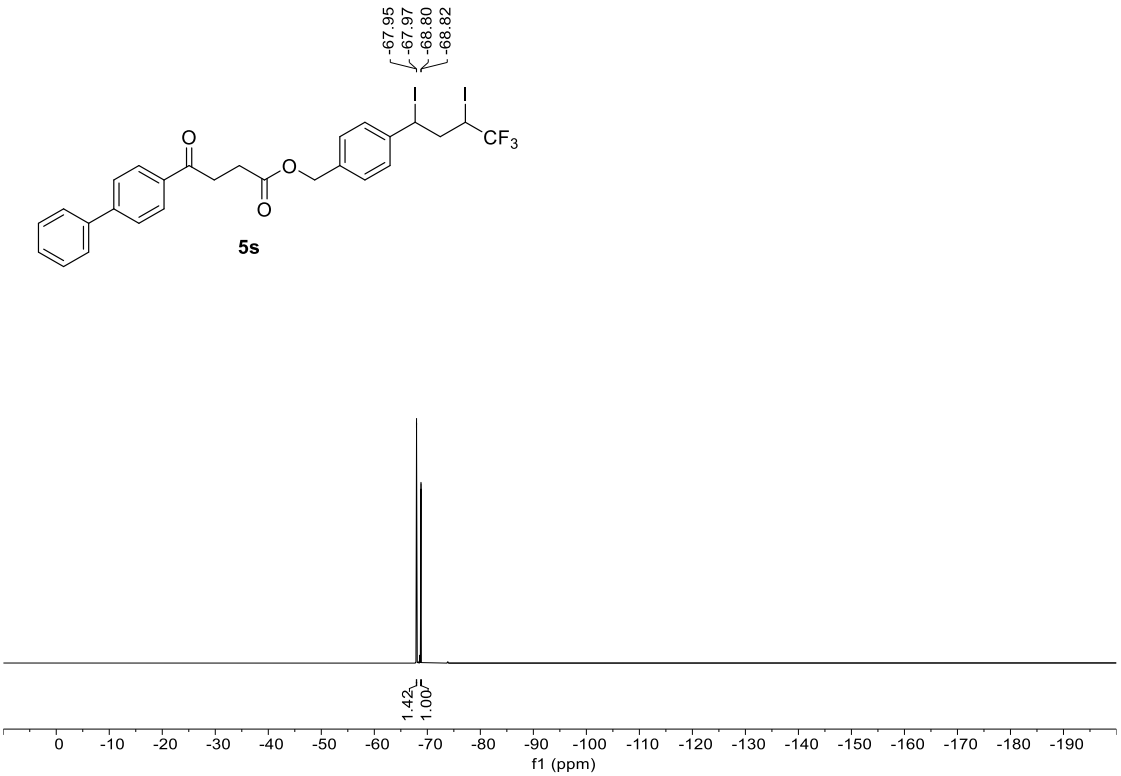
^{19}F NMR (565 MHz, $CDCl_3$) for **5r**



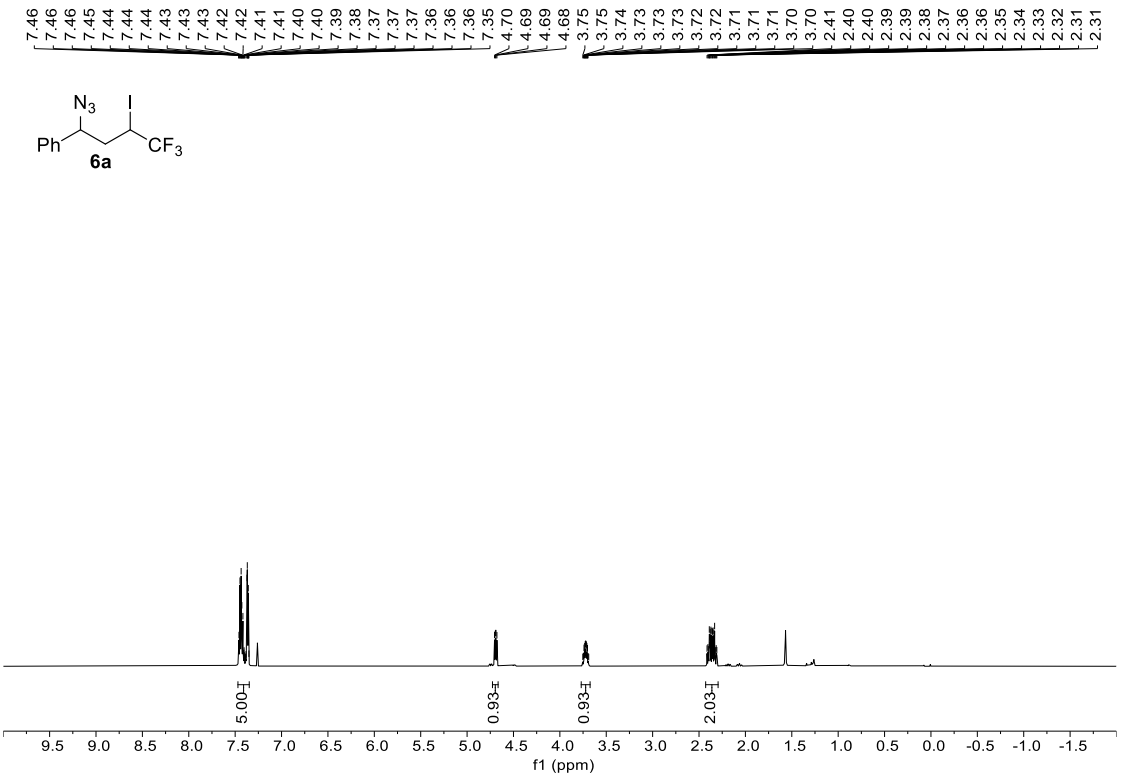
^{1}H NMR (600 MHz, $CDCl_3$) for **5s**



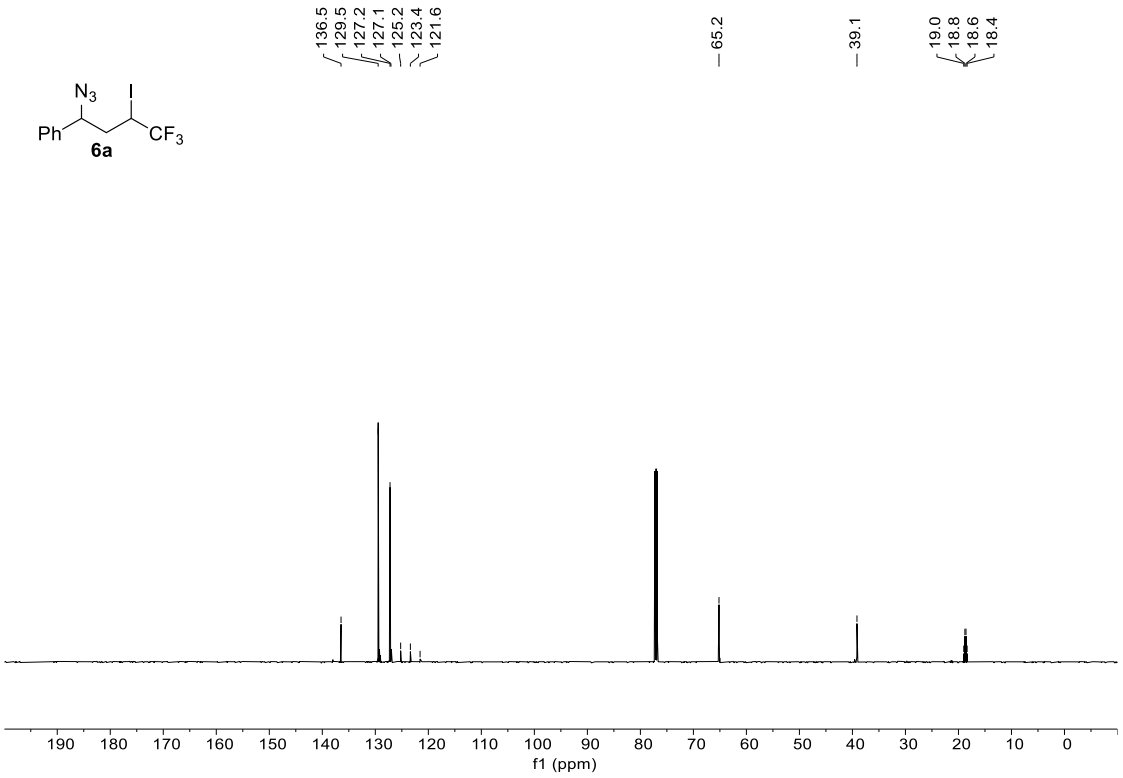
^{13}C NMR (151 MHz, $CDCl_3$) for **5s**



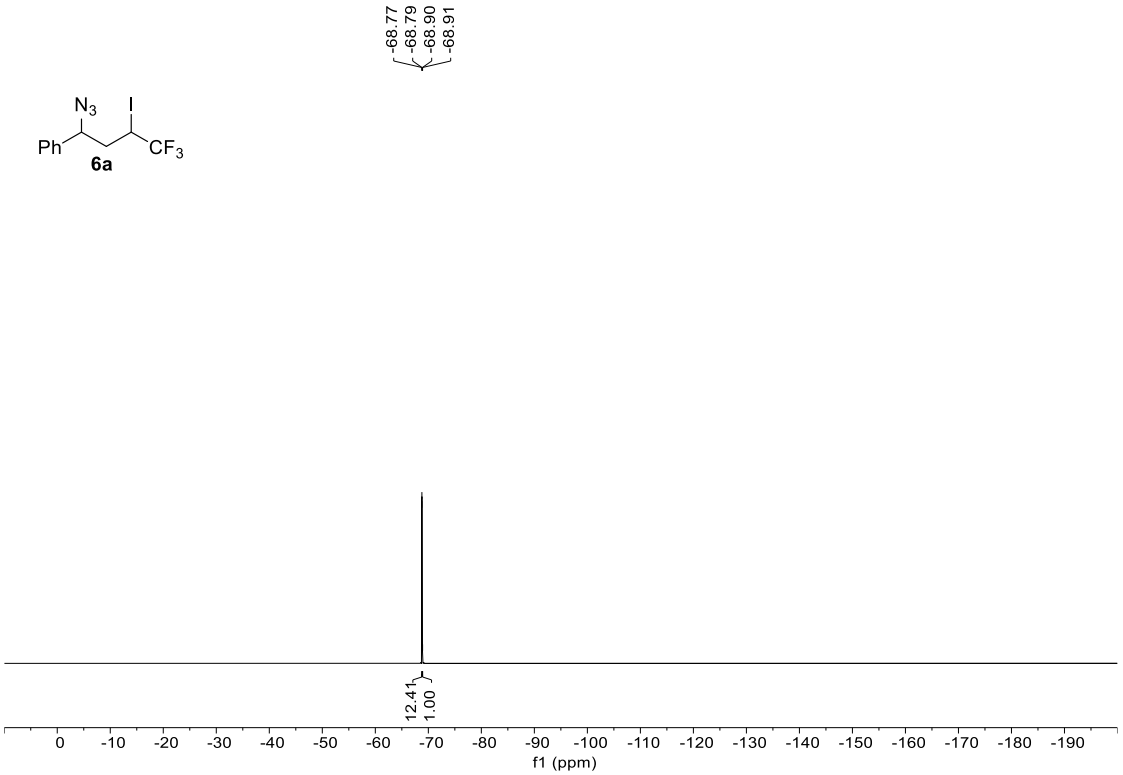
^{19}F NMR (565 MHz, $CDCl_3$) for **5s**



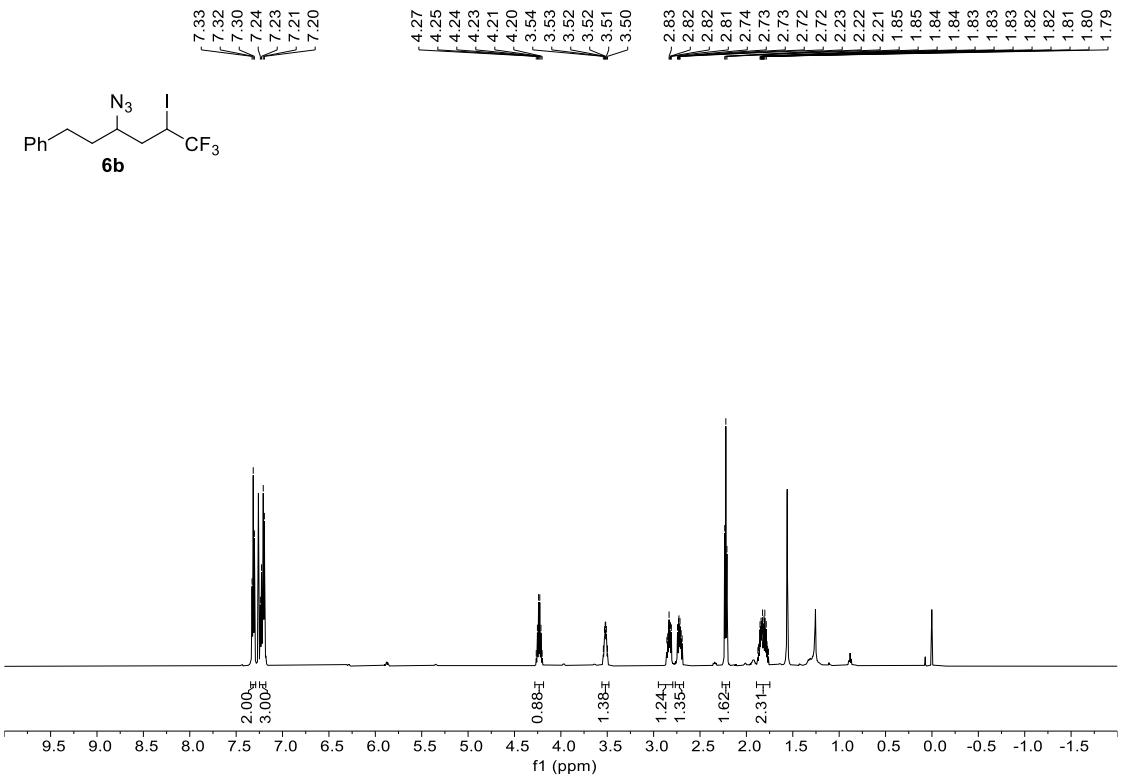
^{1}H NMR (600 MHz, $CDCl_3$) for **6a**



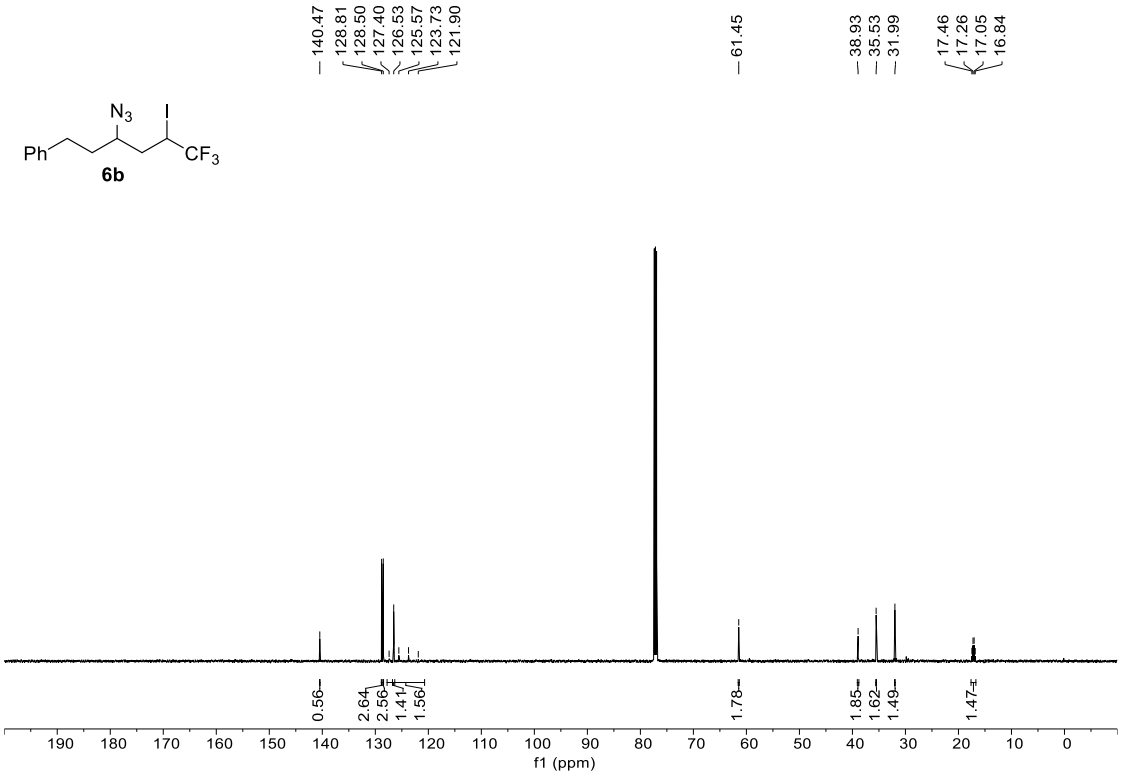
^{13}C NMR (151 MHz, $CDCl_3$) for **6a**



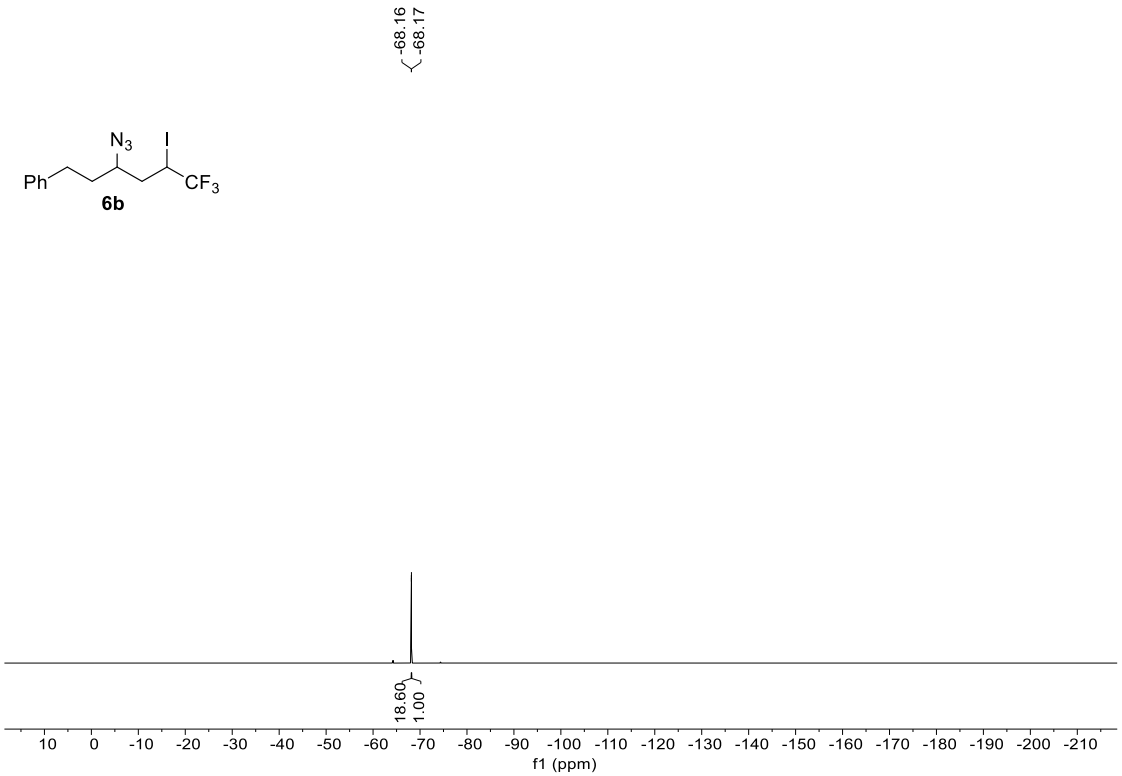
^{19}F NMR (565 MHz, $CDCl_3$) for **6a**



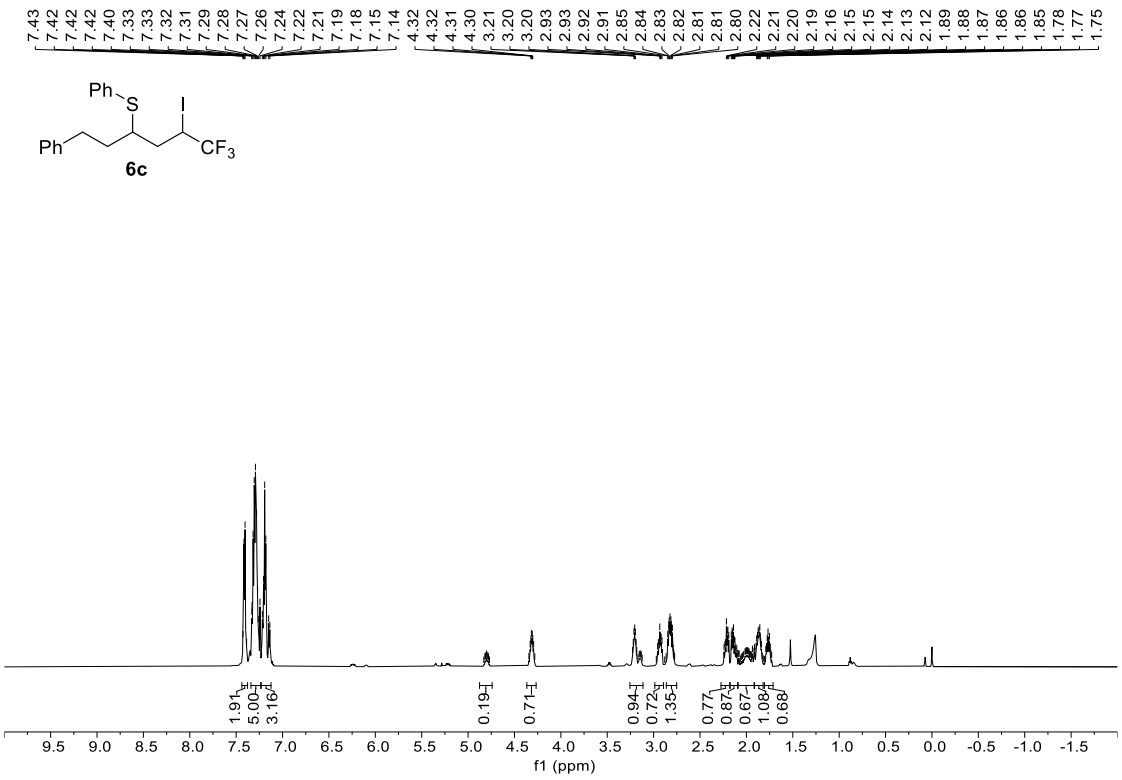
^{1}H NMR (600 MHz, $CDCl_3$) for **6b**



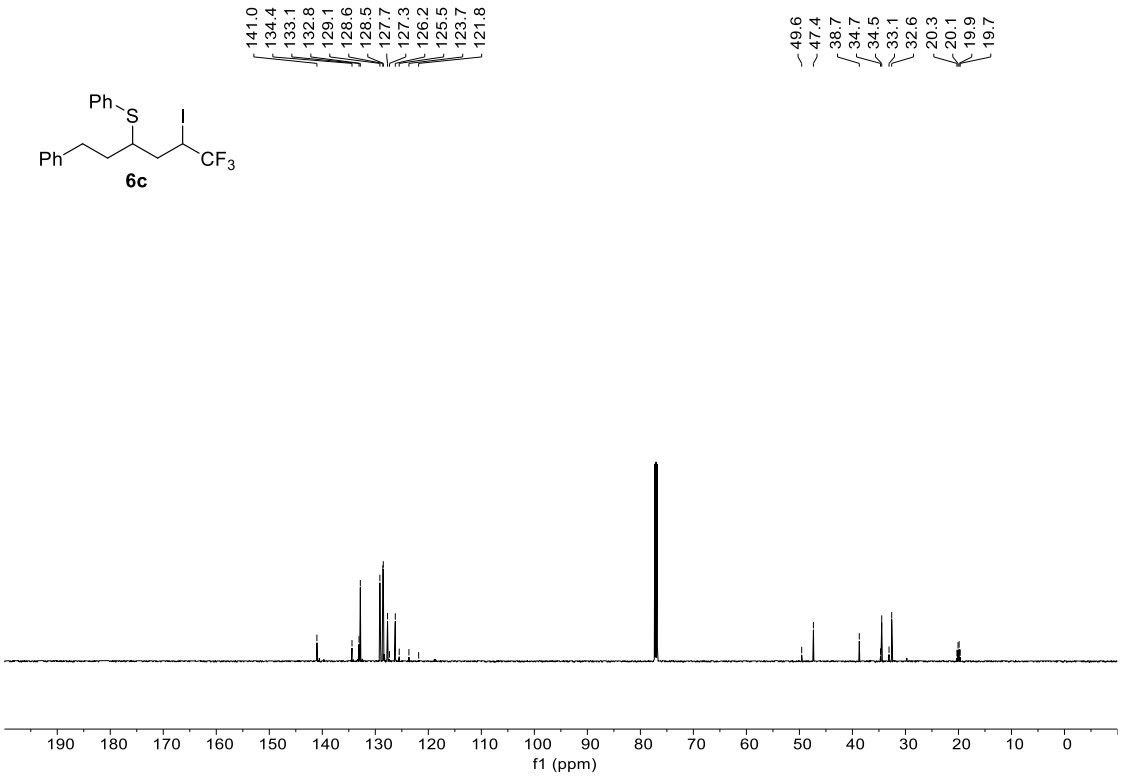
^{13}C NMR (151 MHz, $CDCl_3$) for **6b**



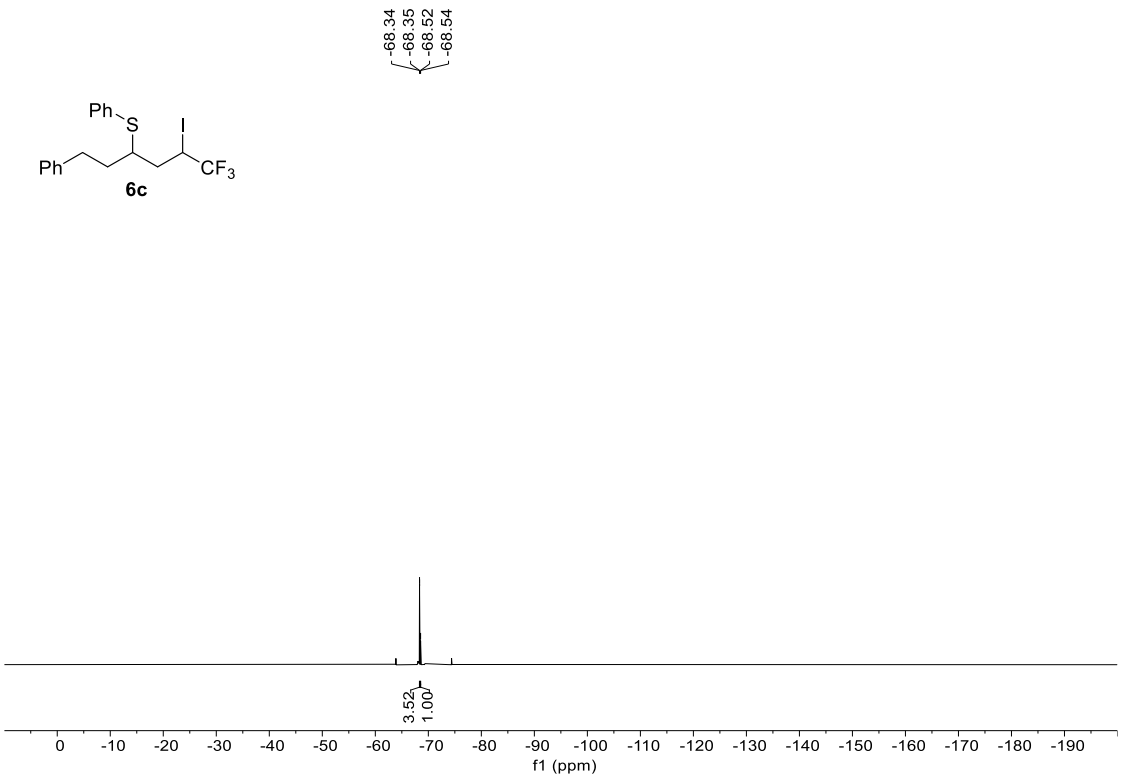
^{19}F NMR (565 MHz, $CDCl_3$) for **6b**



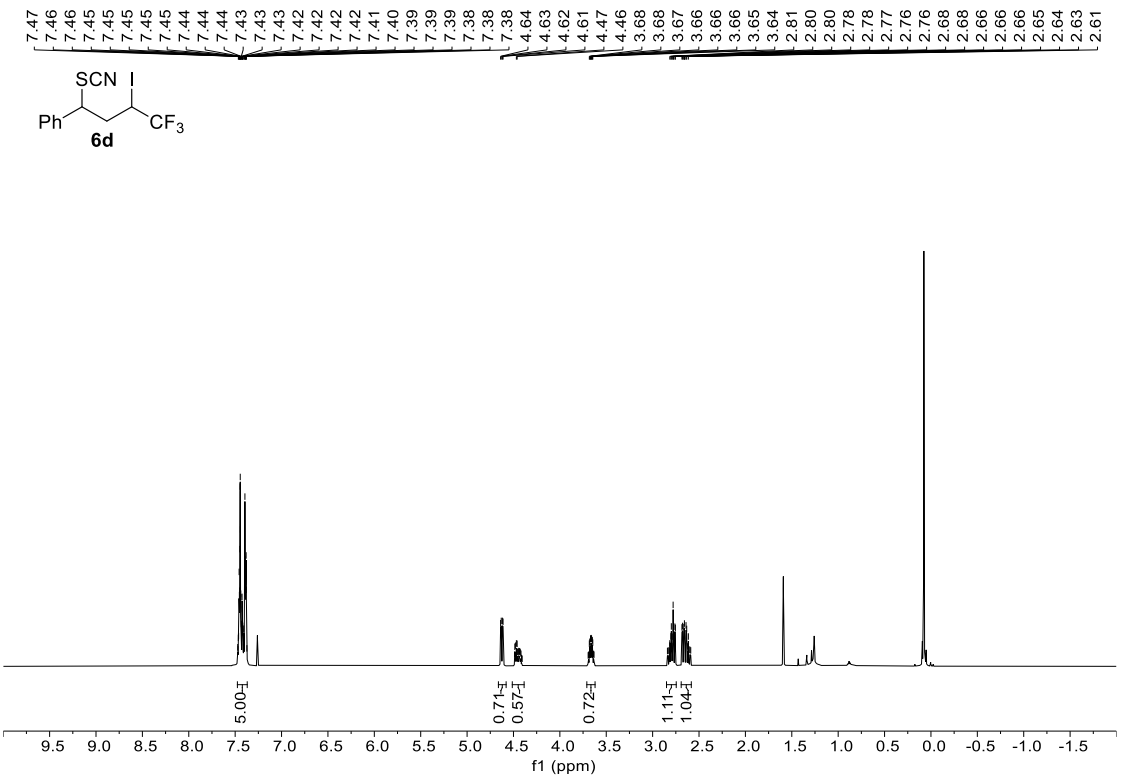
^{1}H NMR (600 MHz, $CDCl_3$) for **6c**



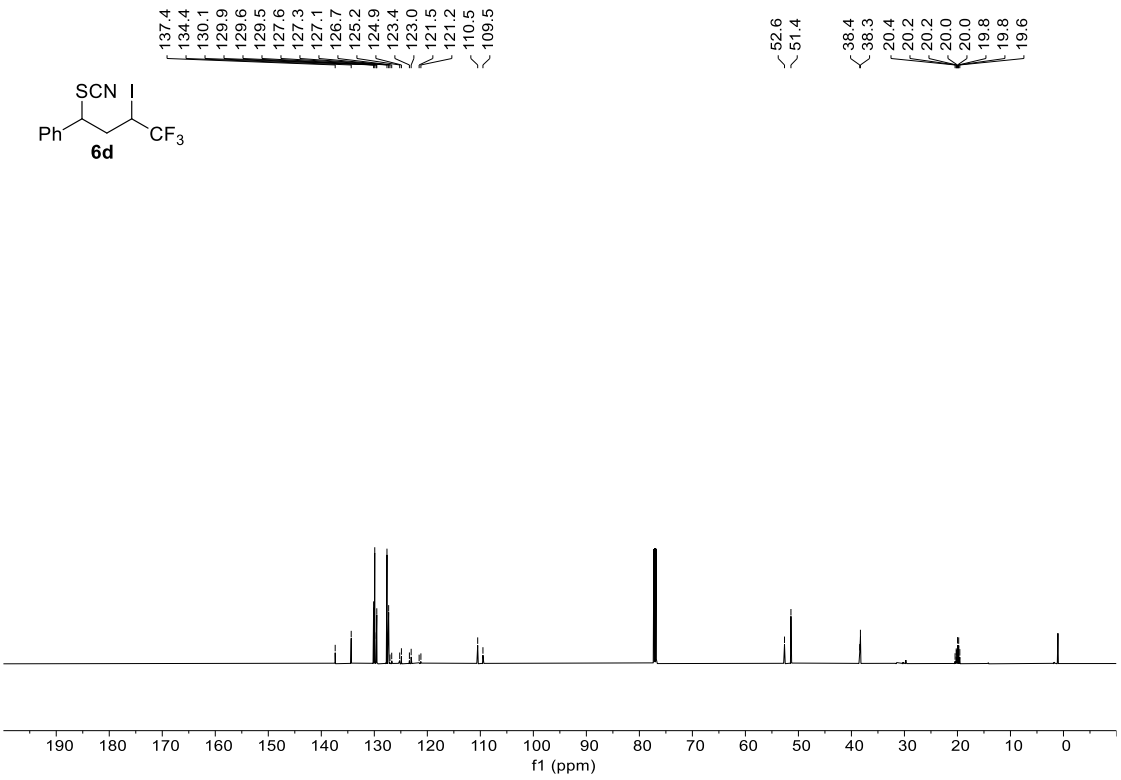
^{13}C NMR (151 MHz, $CDCl_3$) for **6c**



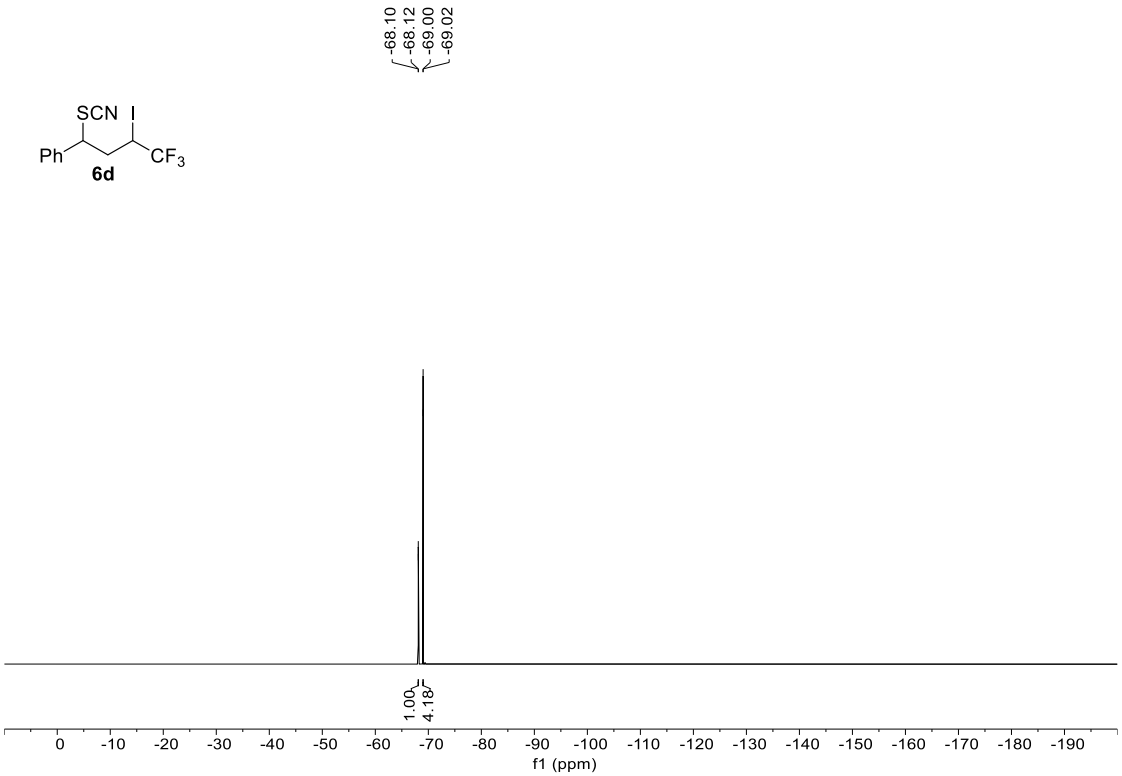
^{19}F NMR (565 MHz, $CDCl_3$) for **6c**



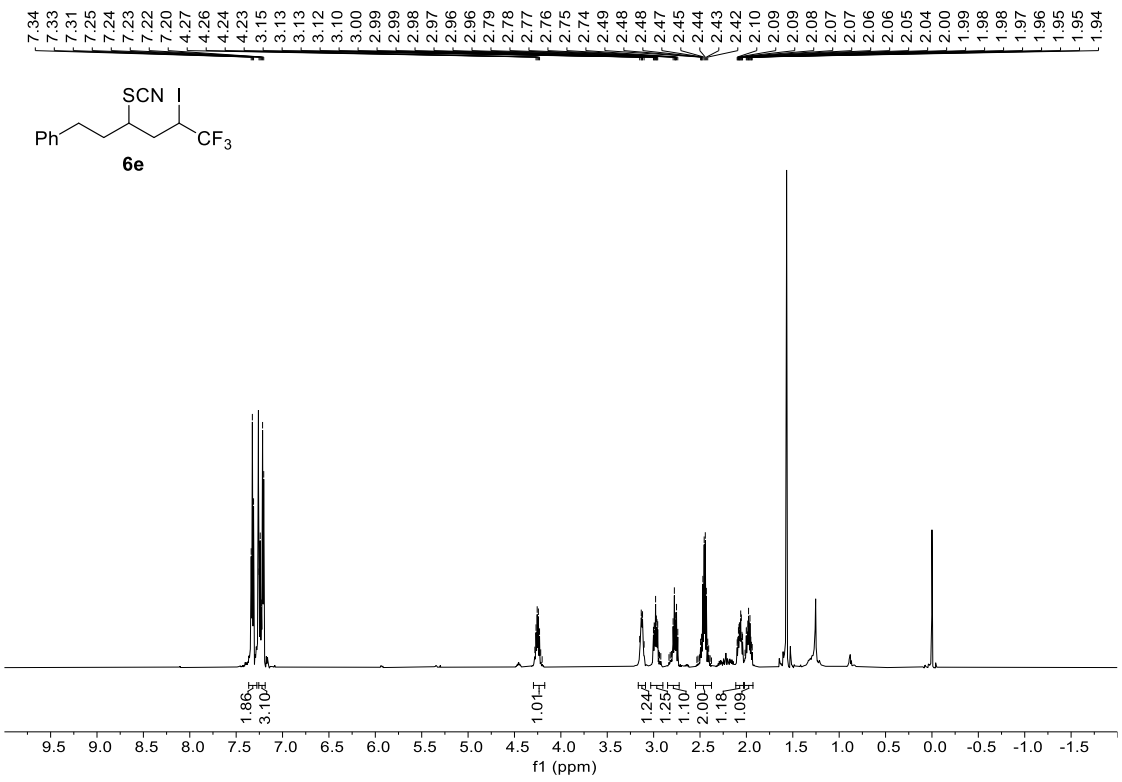
^{1}H NMR (600 MHz, $CDCl_3$) for **6d**



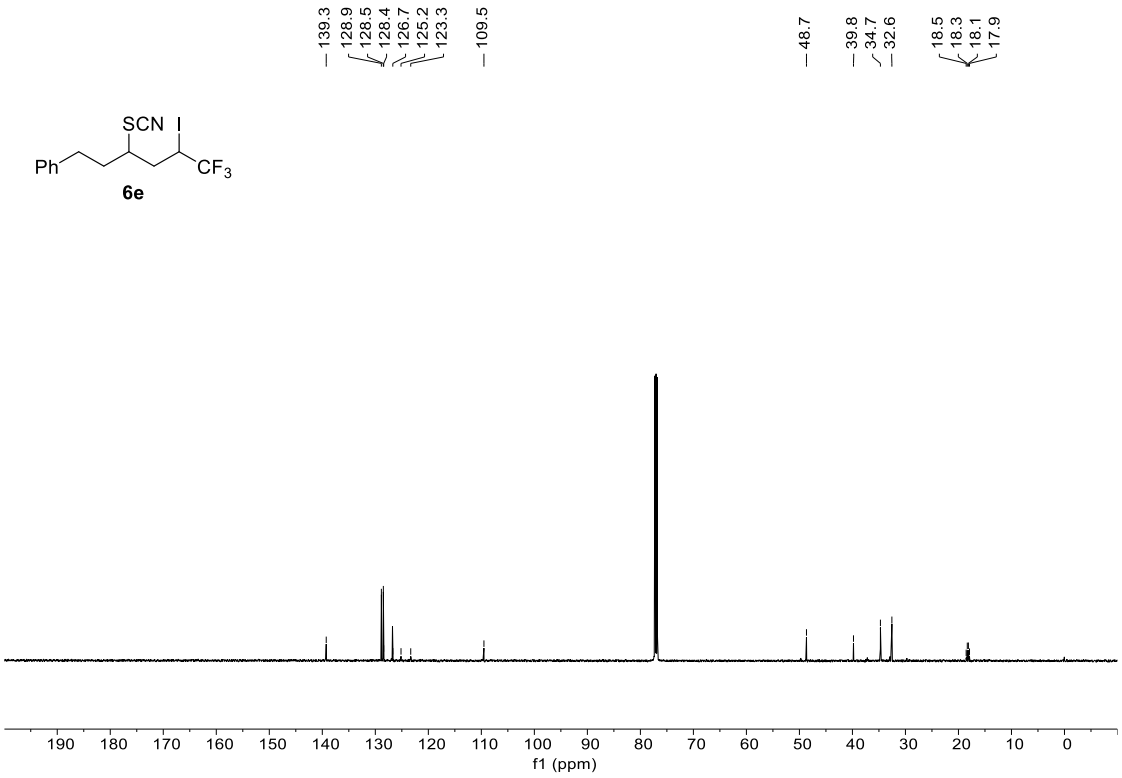
^{13}C NMR (151 MHz, $CDCl_3$) for **6d**



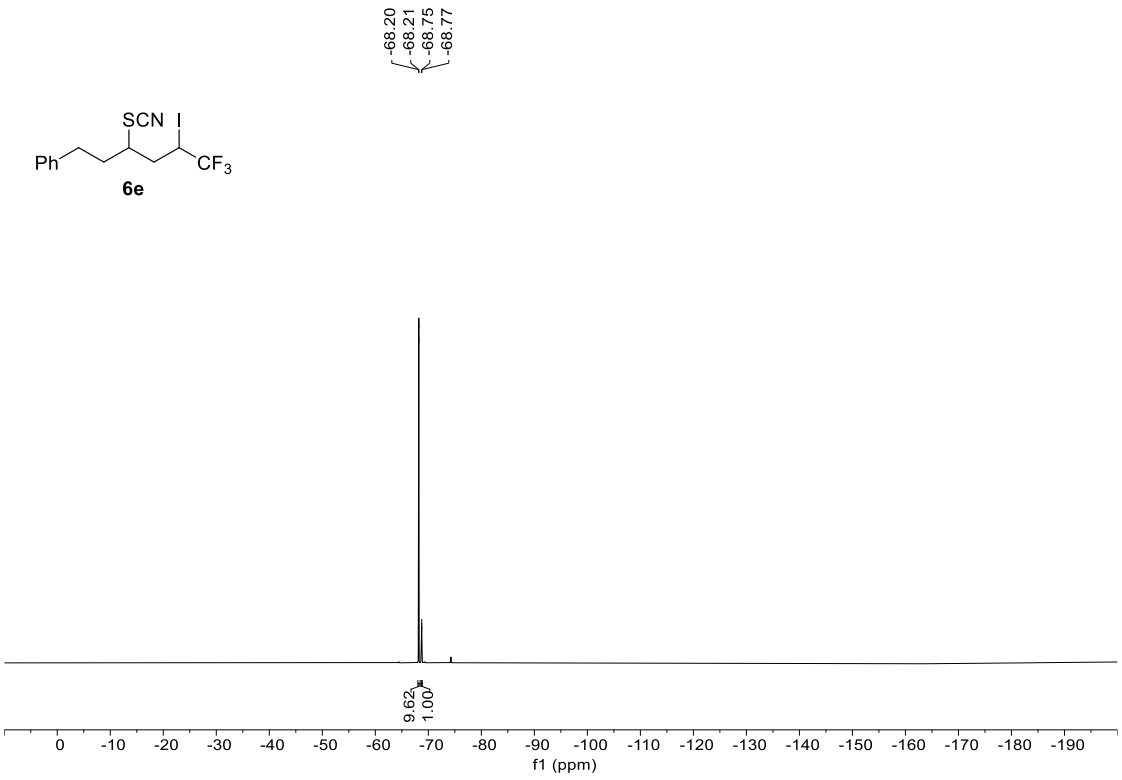
^{19}F NMR (565 MHz, $CDCl_3$) for **6d**



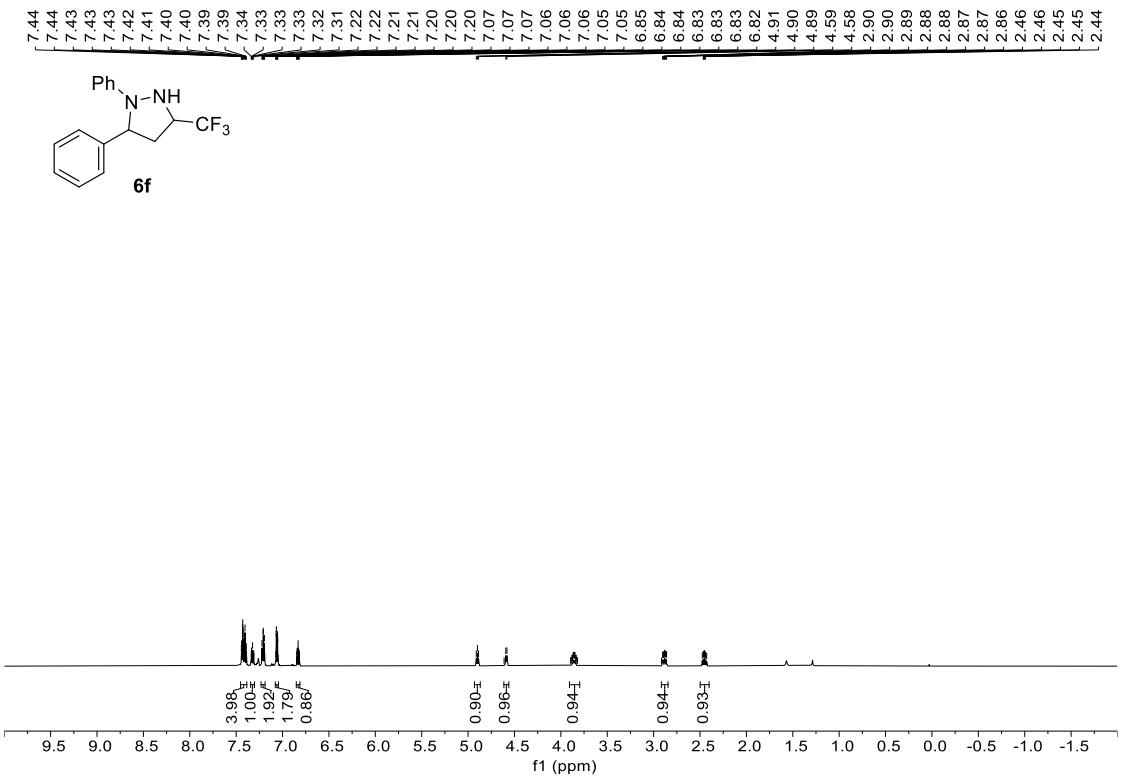
^{1}H NMR (600 MHz, $CDCl_3$) for **6e**



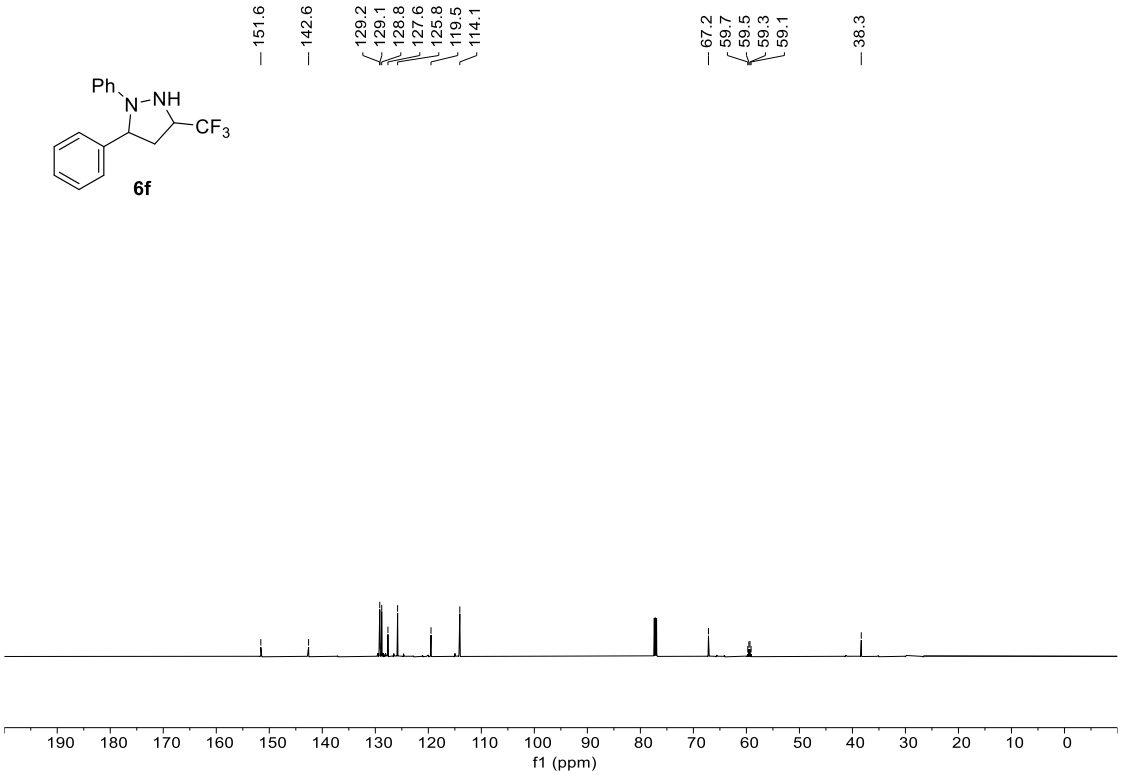
^{13}C NMR (151 MHz, $CDCl_3$) for **6e**



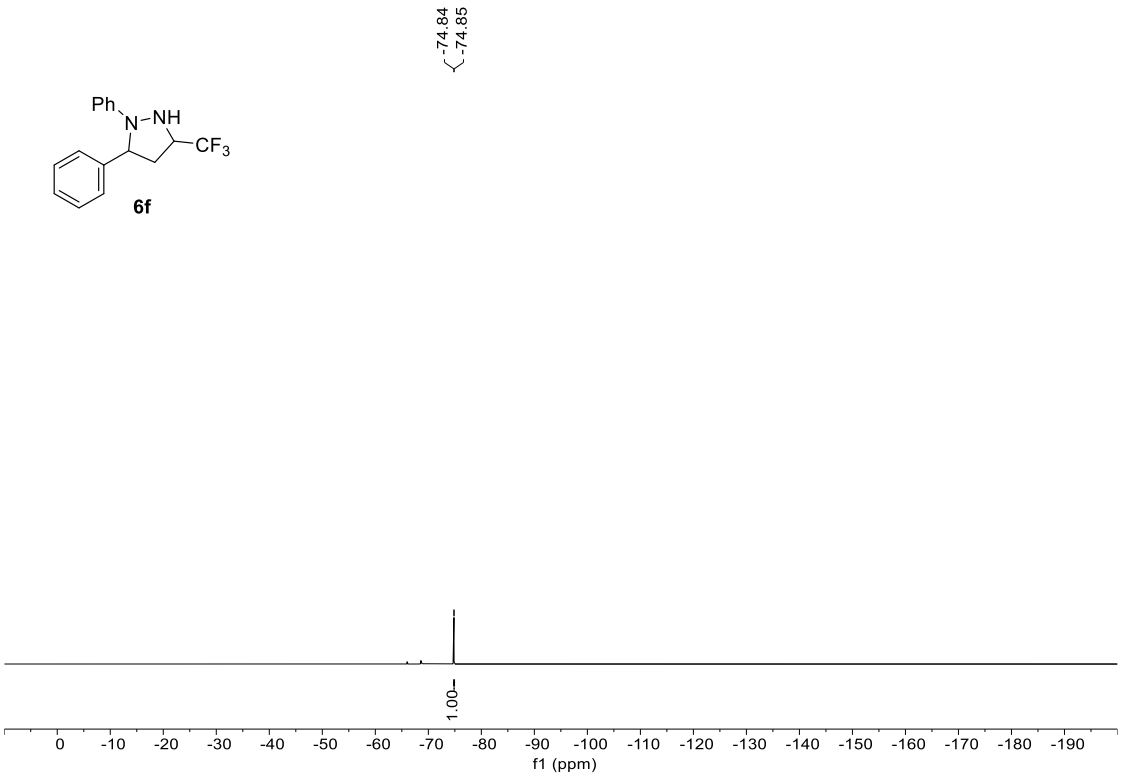
^{19}F NMR (565 MHz, $CDCl_3$) for **6e**



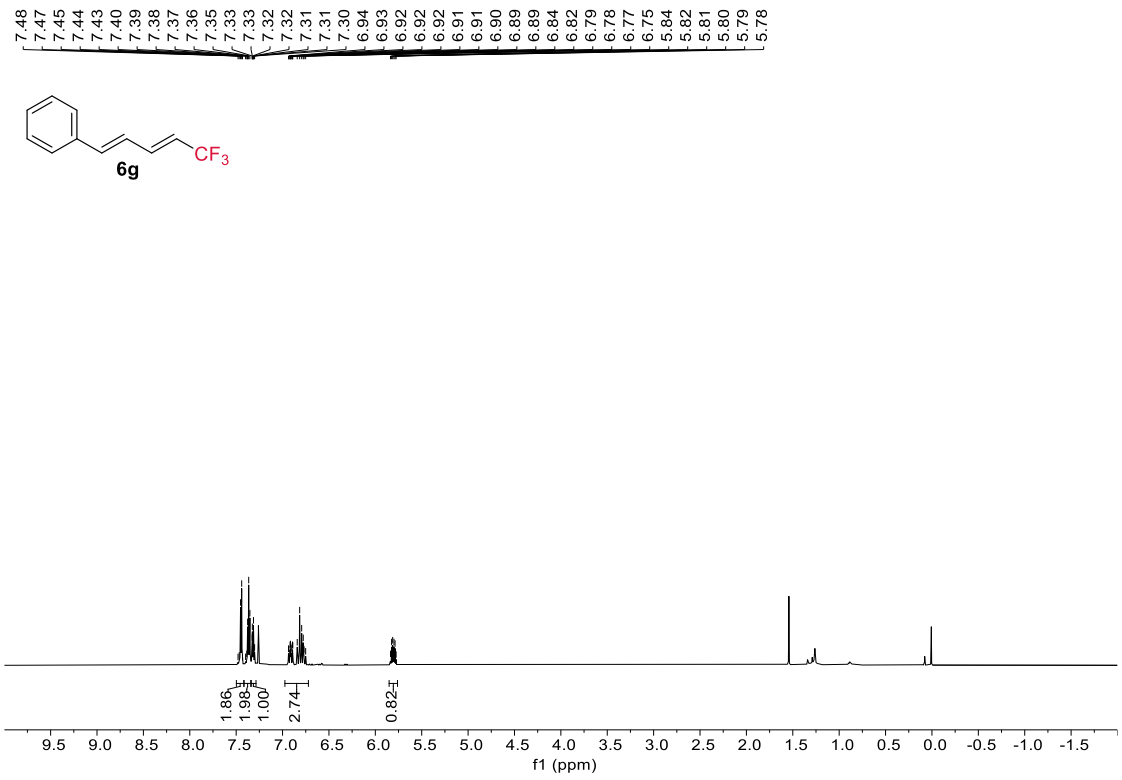
^{1}H NMR (600 MHz, $CDCl_3$) for **6f**



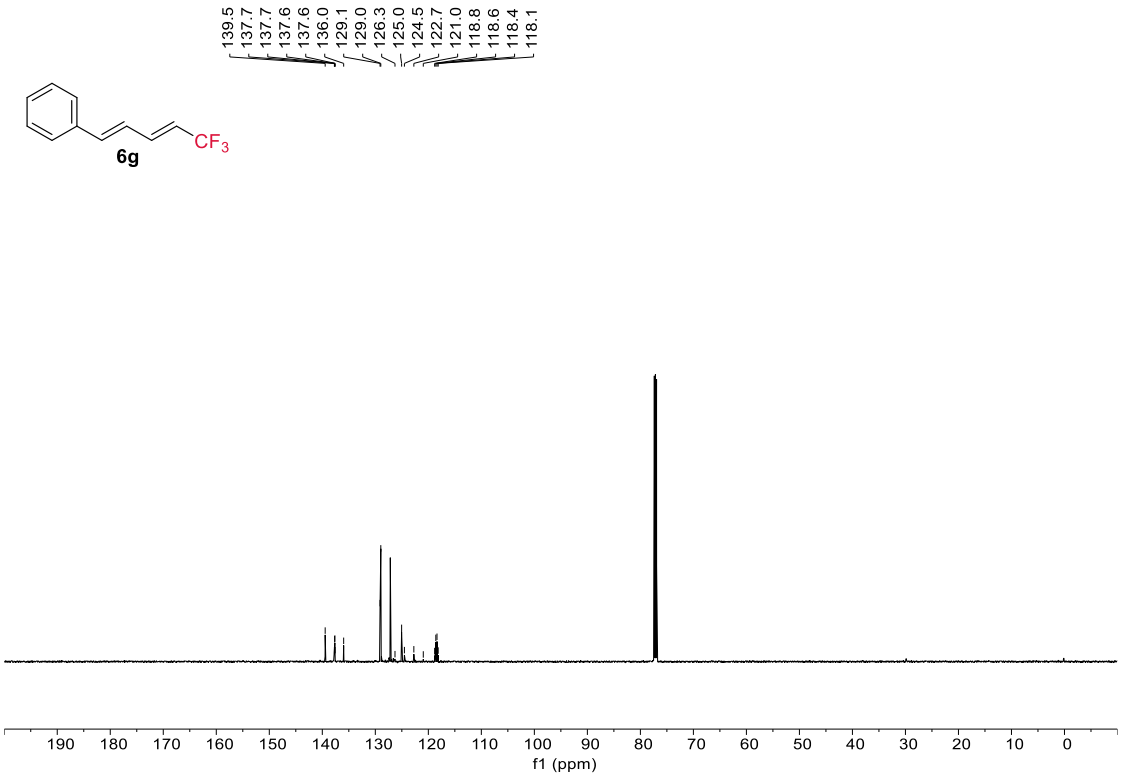
^{13}C NMR (151 MHz, $CDCl_3$) for **6f**



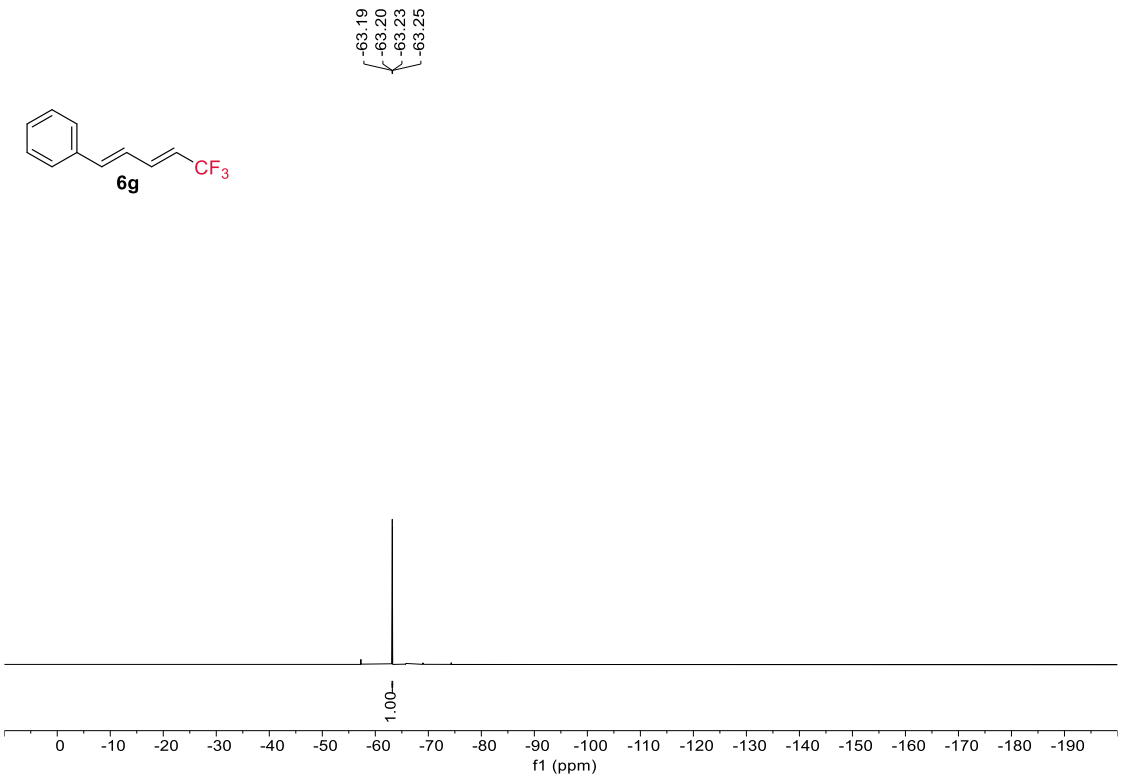
^{19}F NMR (565 MHz, $CDCl_3$) for **6f**



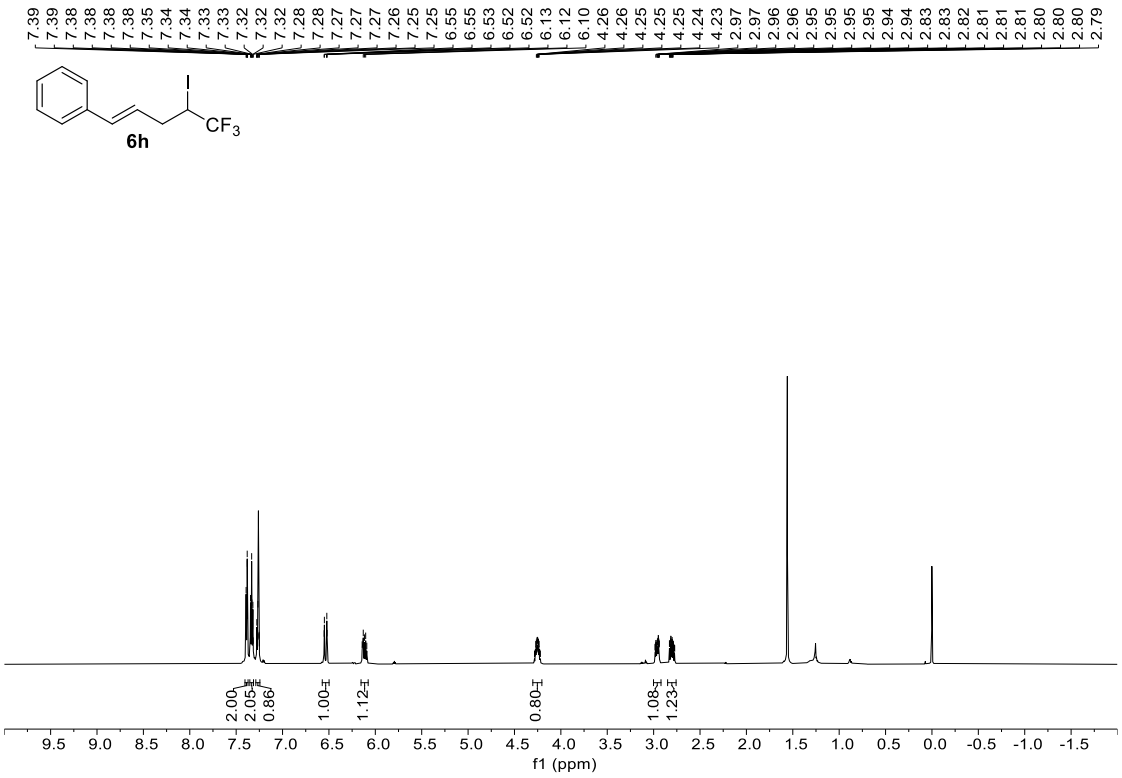
^{1}H NMR (600 MHz, $CDCl_3$) for **6g**



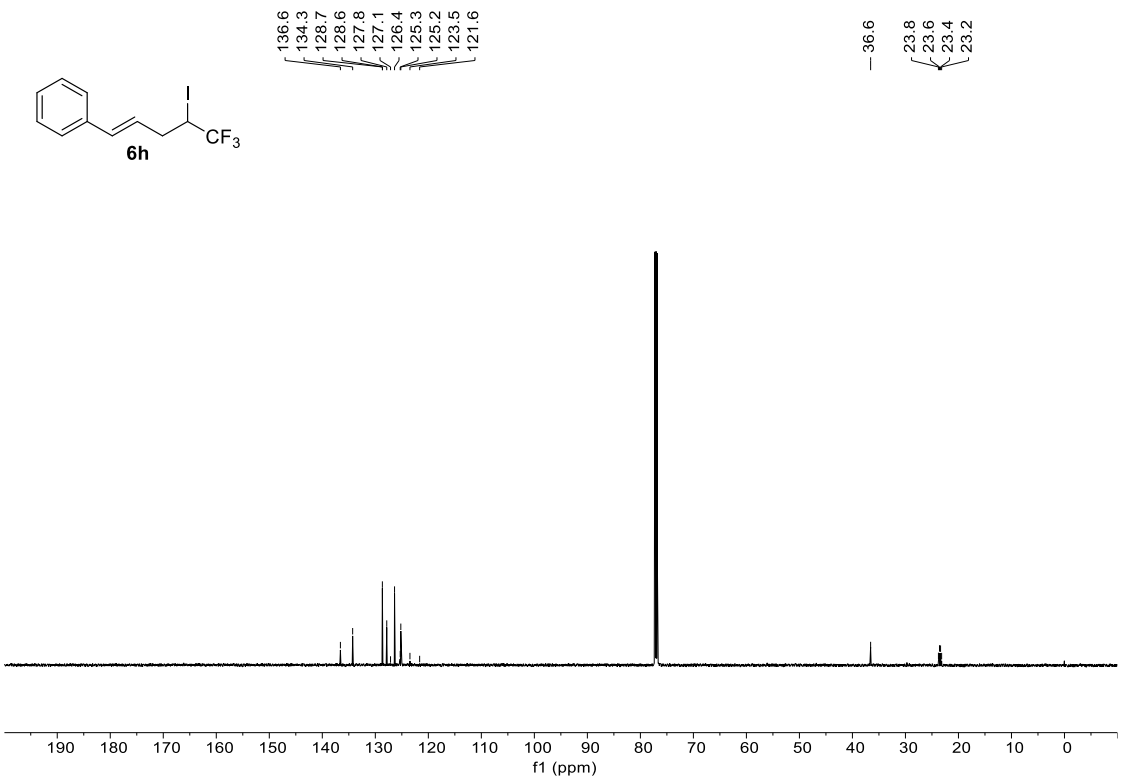
^{13}C NMR (151 MHz, $CDCl_3$) for **6g**



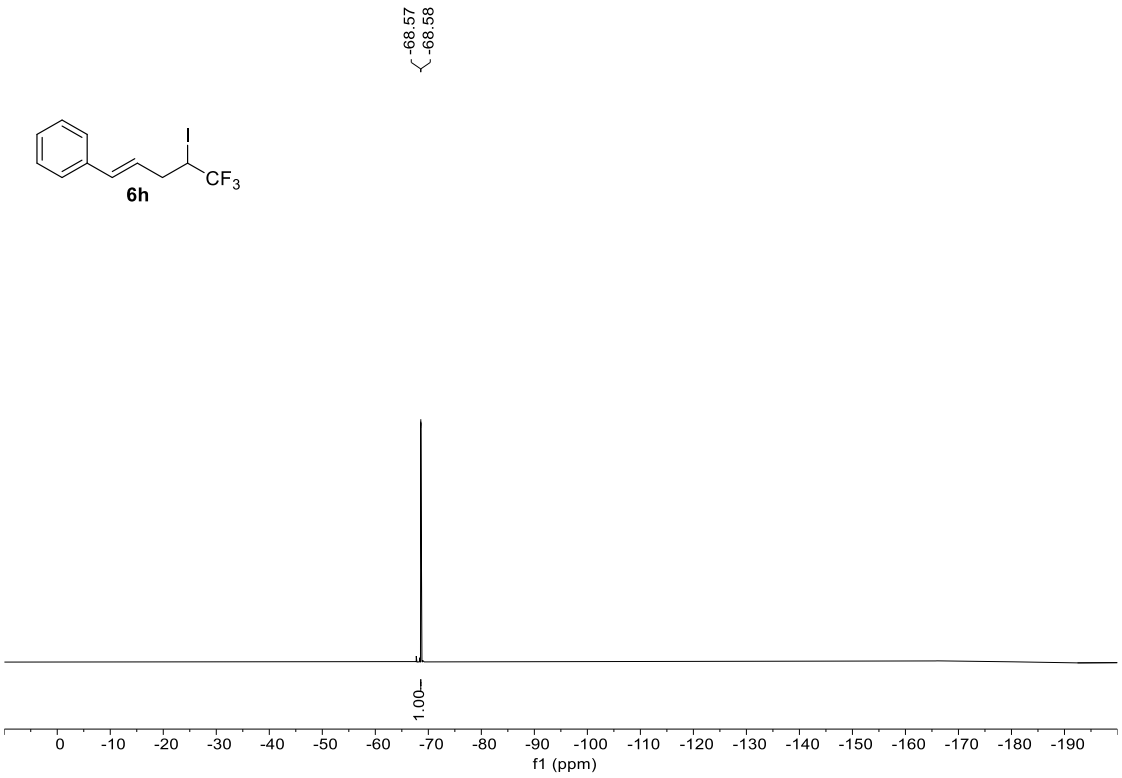
^{19}F NMR (565 MHz, $CDCl_3$) for **6g**



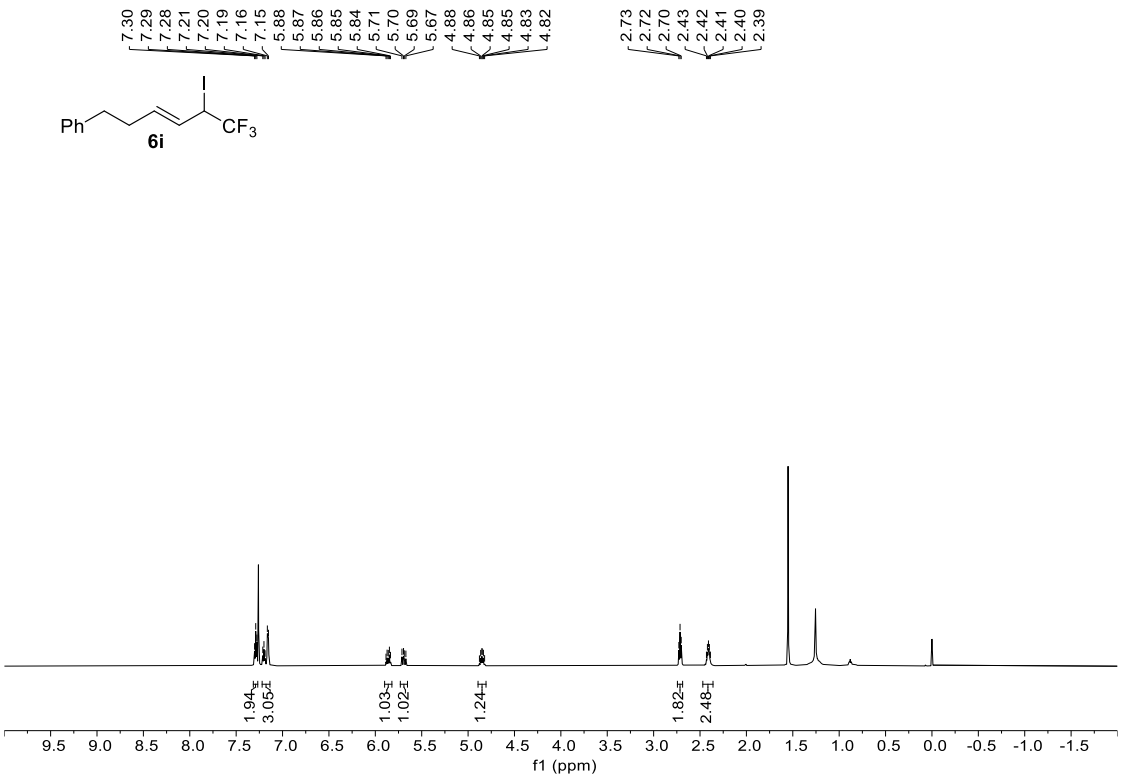
^{1}H NMR (600 MHz, $CDCl_3$) for **6h**



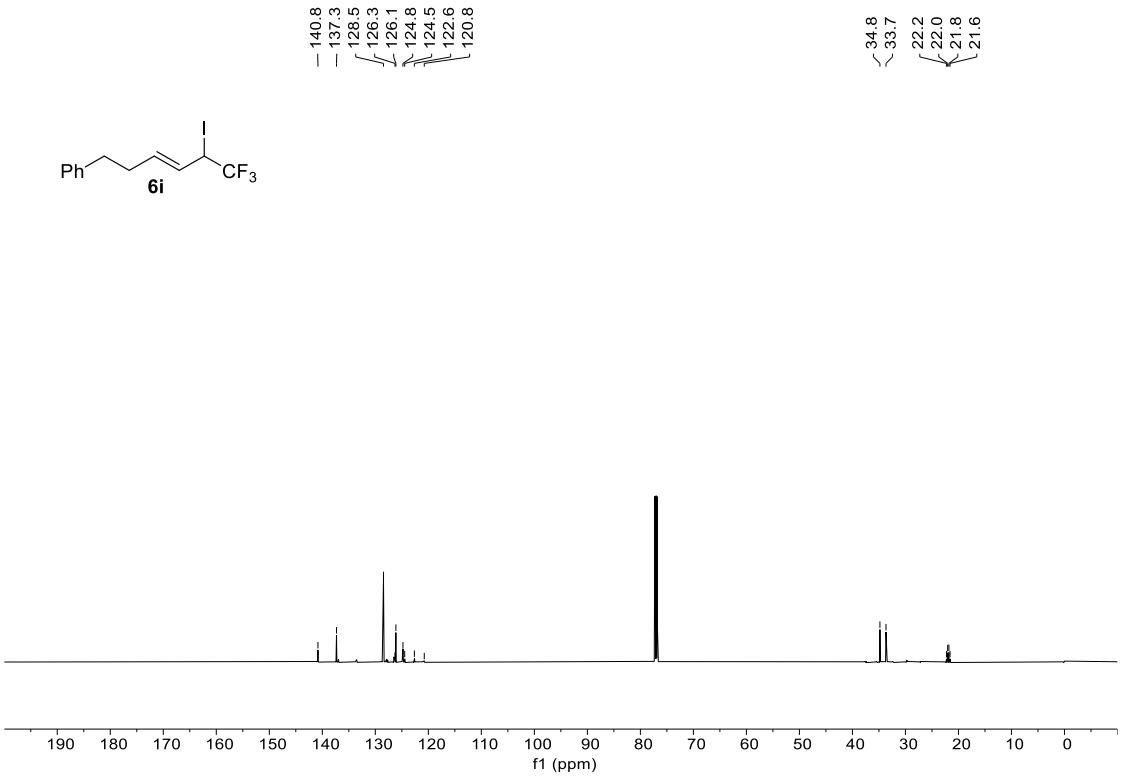
^{13}C NMR (151 MHz, $CDCl_3$) for **6h**



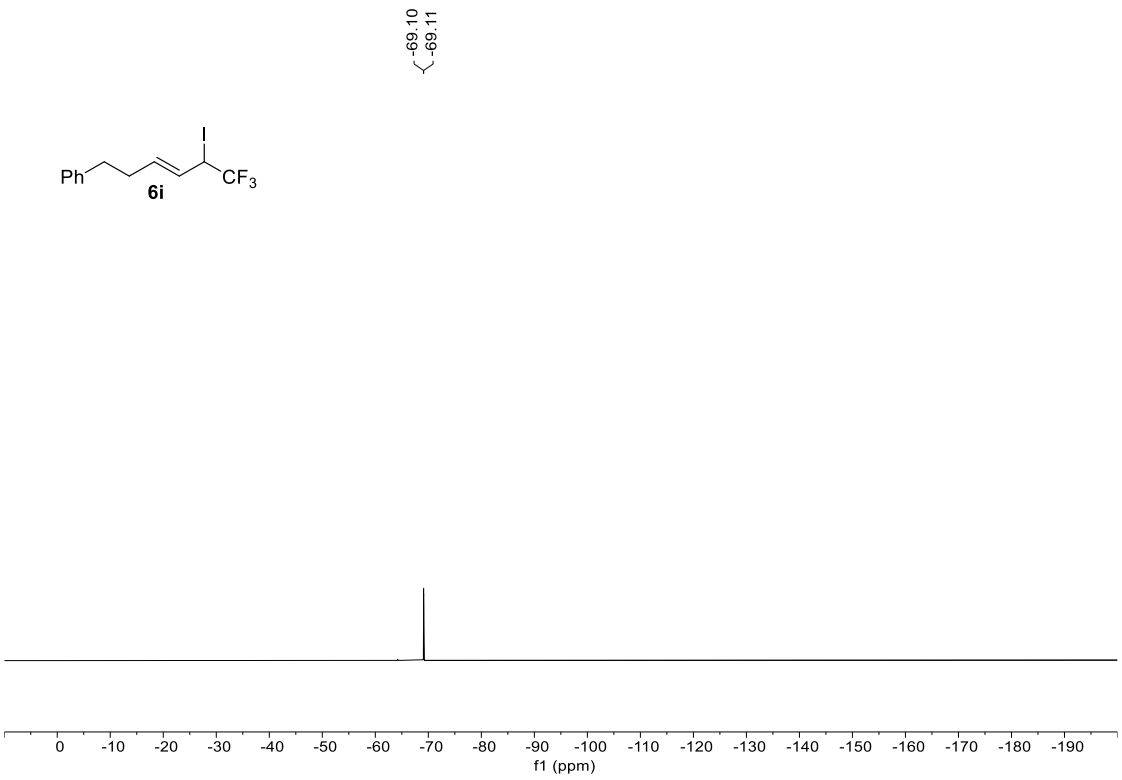
^{19}F NMR (565 MHz, $CDCl_3$) for **6h**



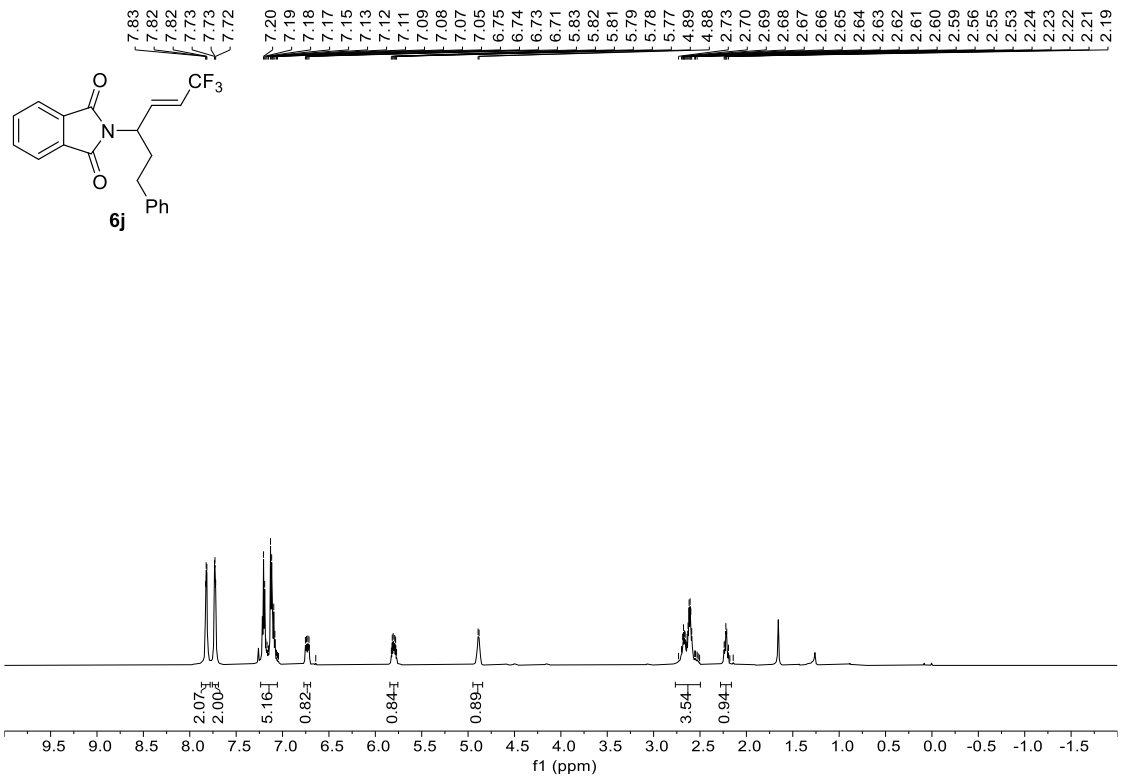
^{1}H NMR (600 MHz, $CDCl_3$) for **6i**



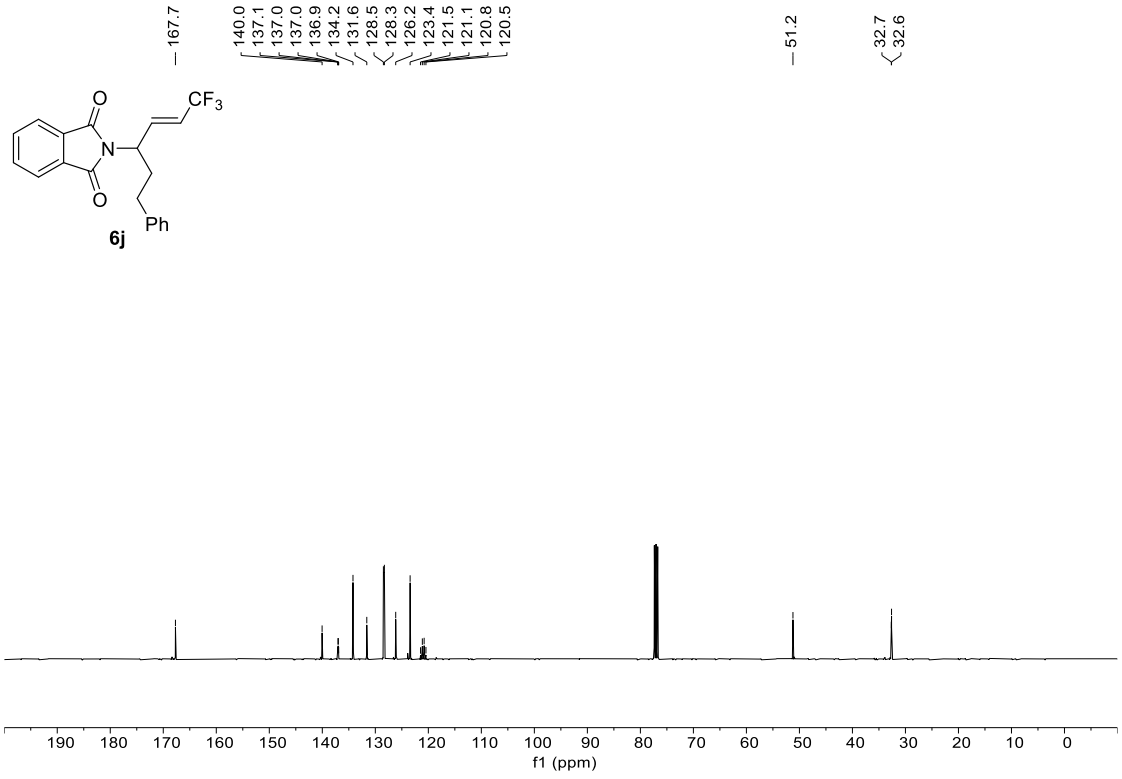
^{13}C NMR (151 MHz, $CDCl_3$) for **6i**



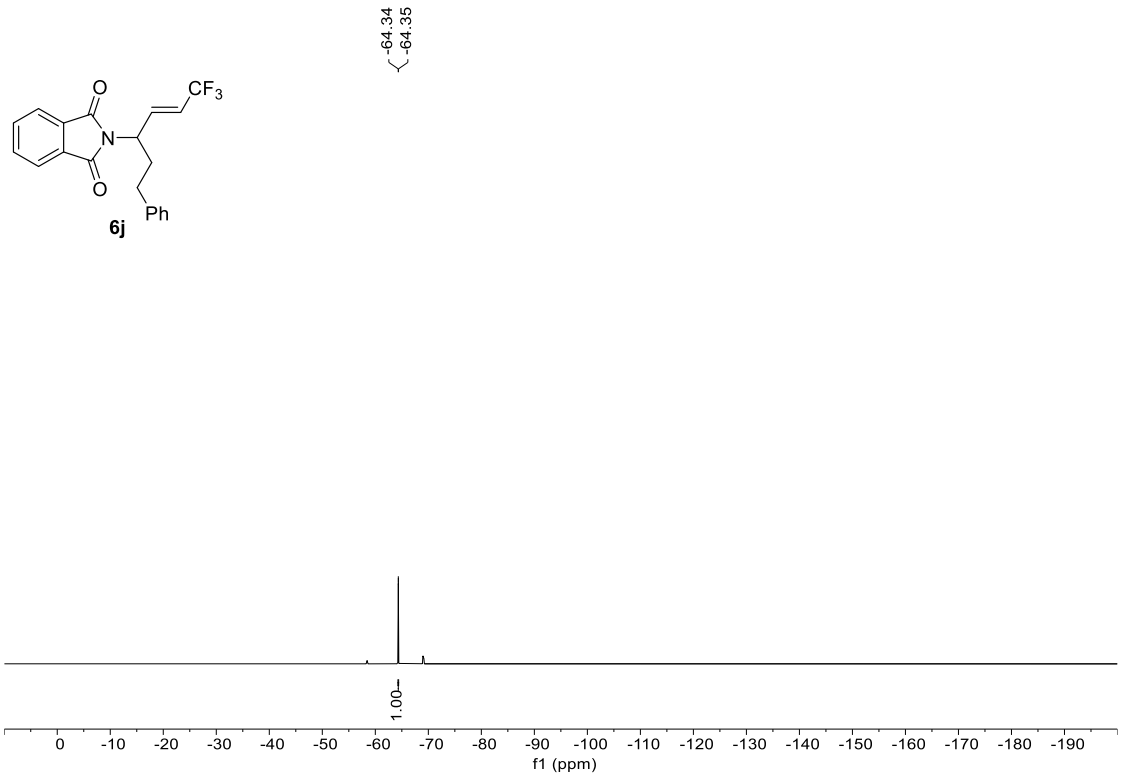
^{19}F NMR (565 MHz, $CDCl_3$) for **6i**



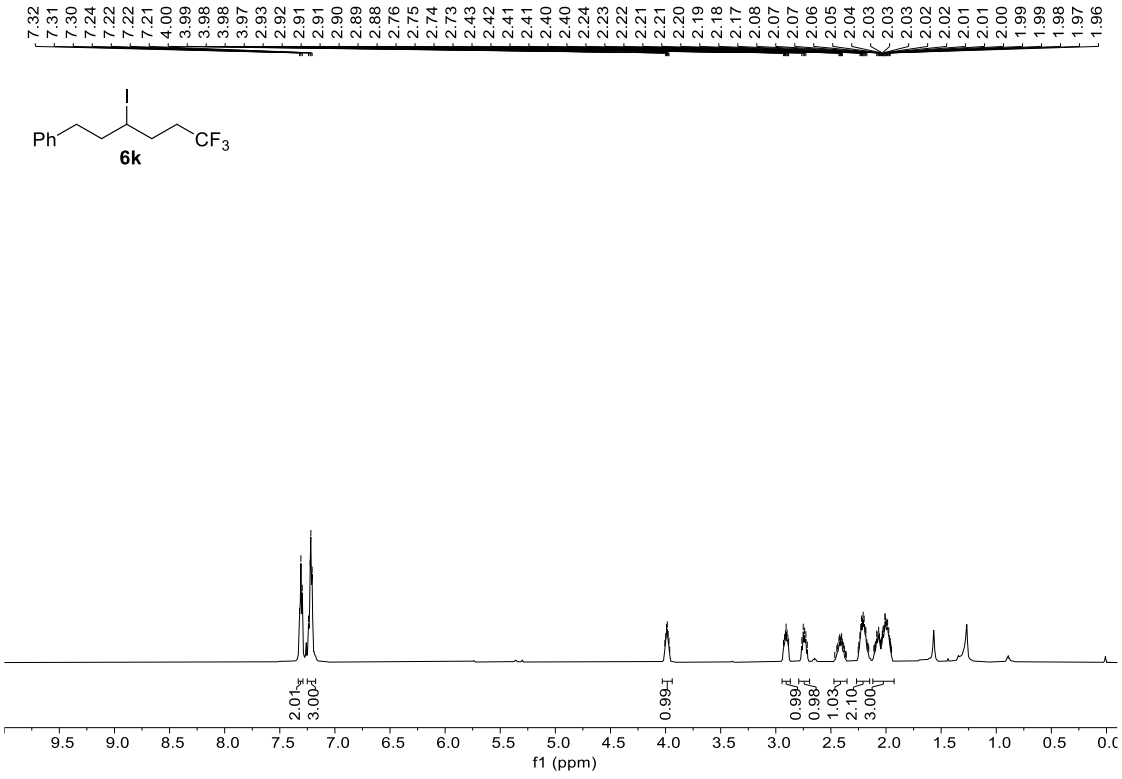
^{1}H NMR (600 MHz, $CDCl_3$) for **6j**



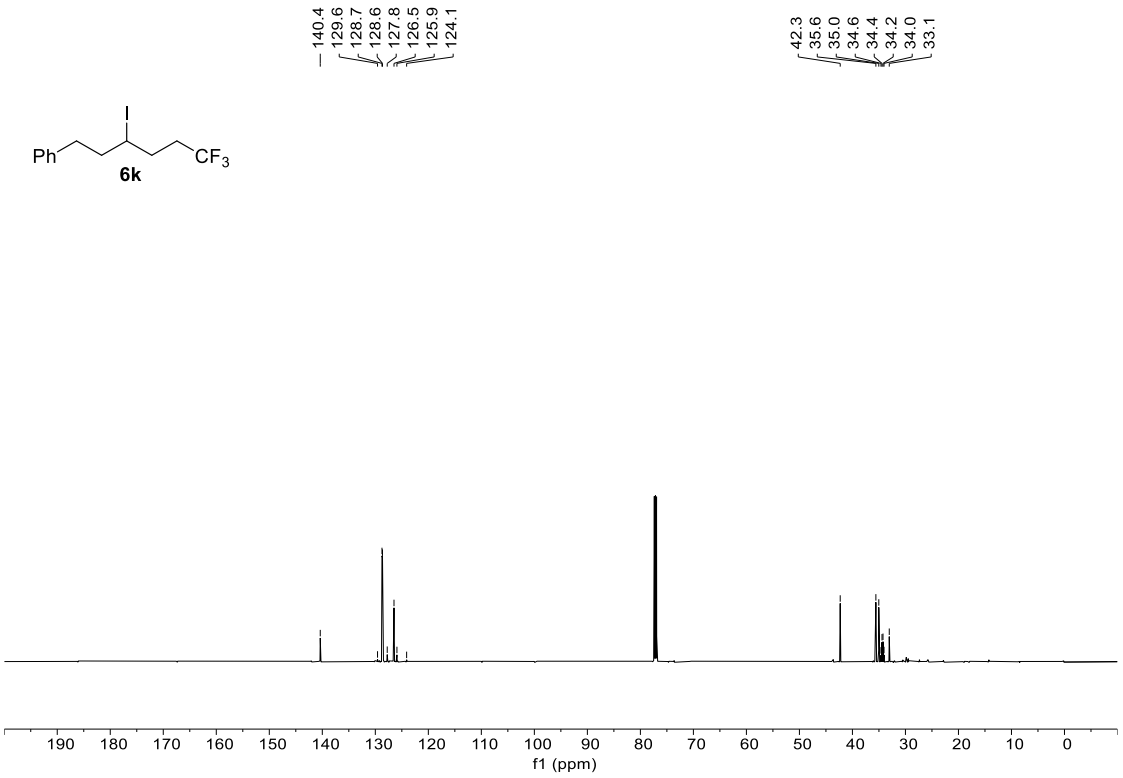
^{13}C NMR (151 MHz, $CDCl_3$) for **6j**



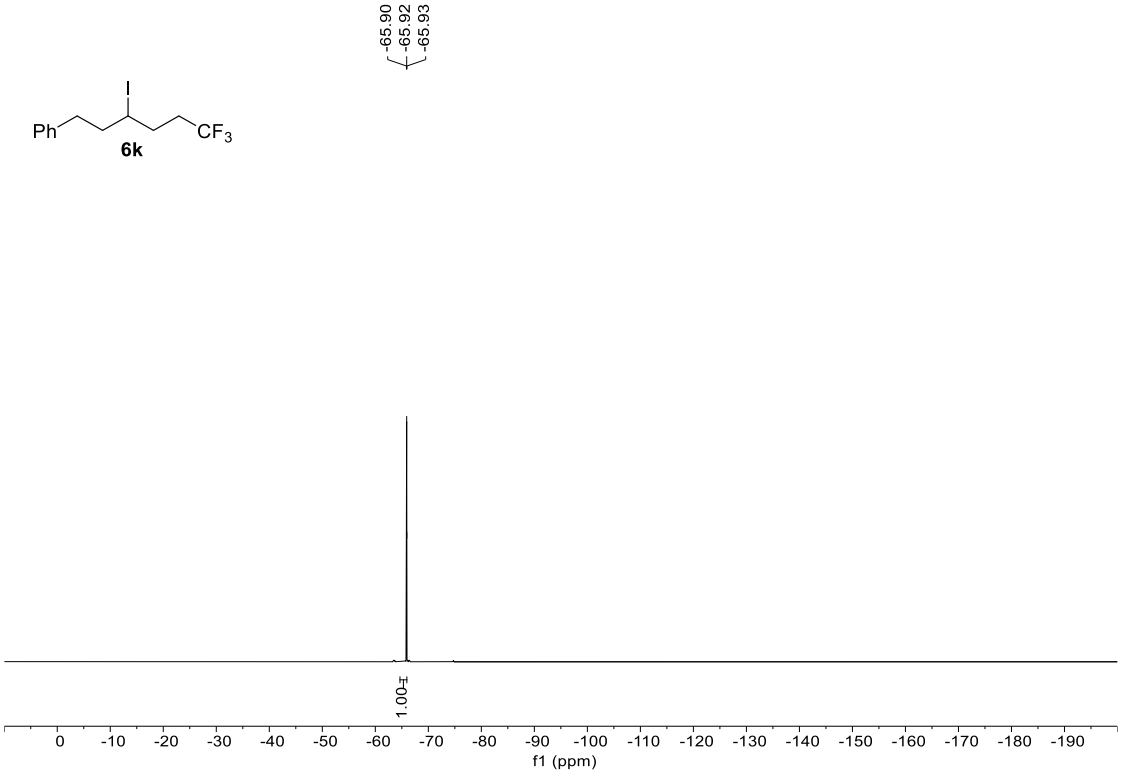
^{19}F NMR (565 MHz, $CDCl_3$) for **6j**



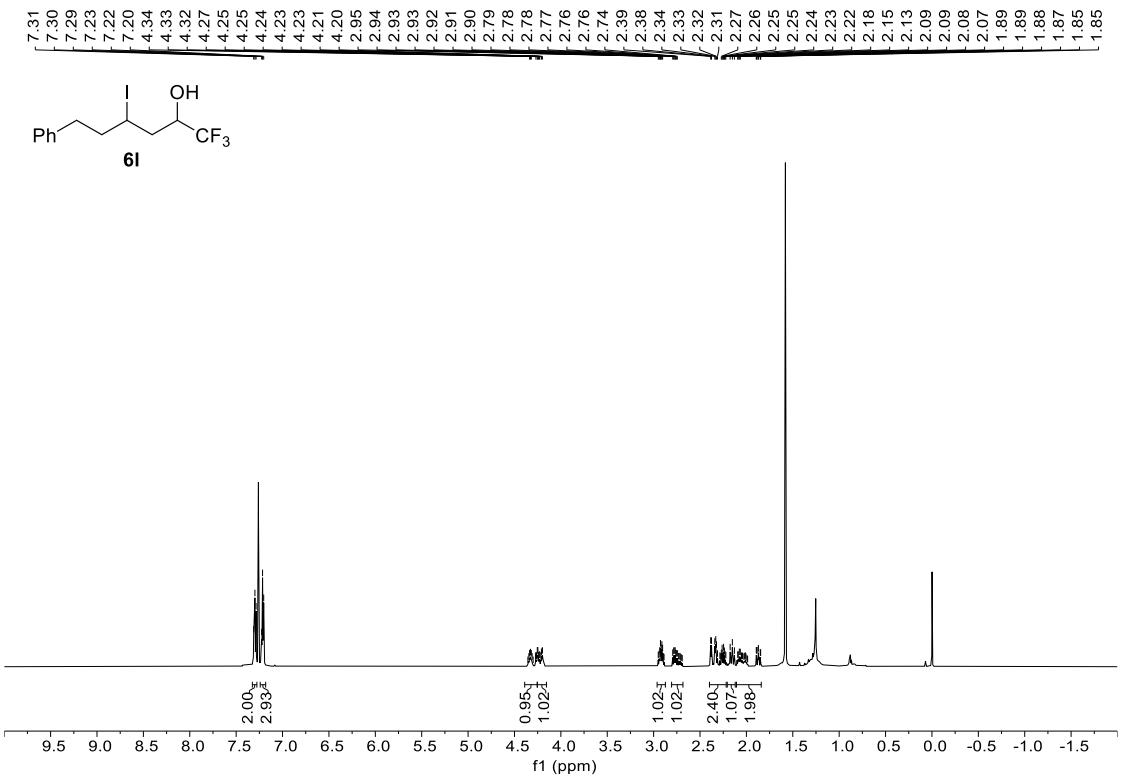
^{1}H NMR (600 MHz, $CDCl_3$) for **6k**



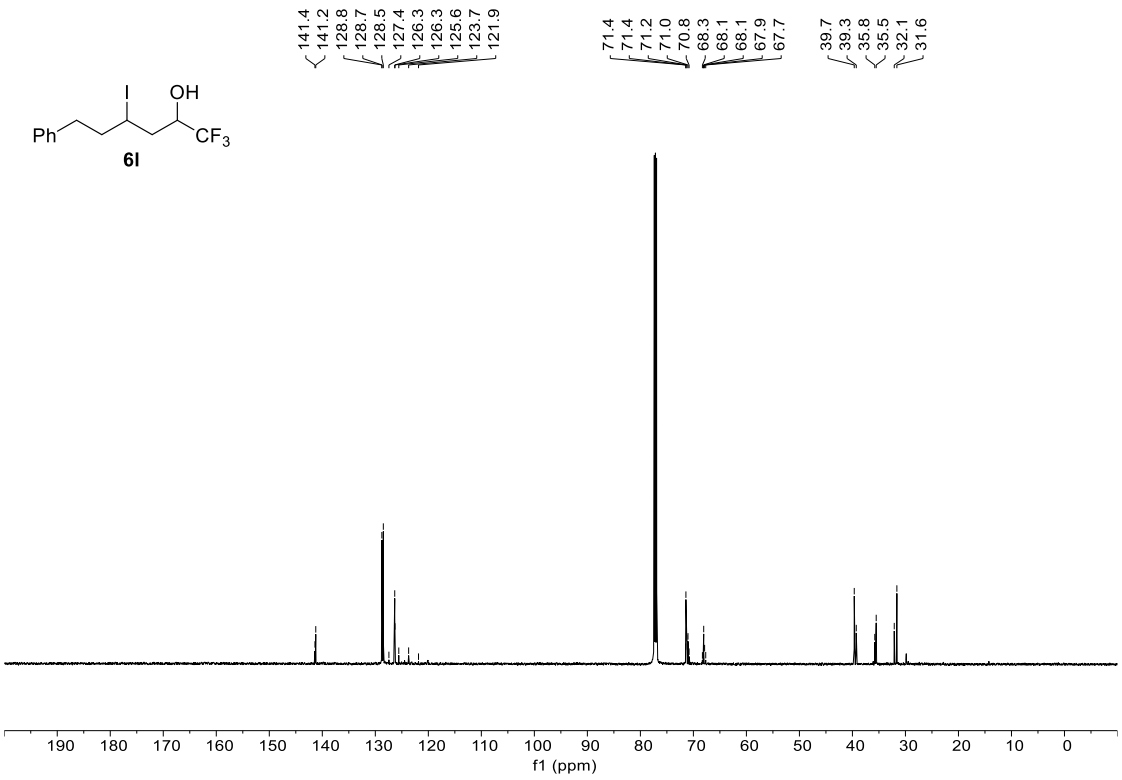
^{13}C NMR (151 MHz, $CDCl_3$) for **6k**



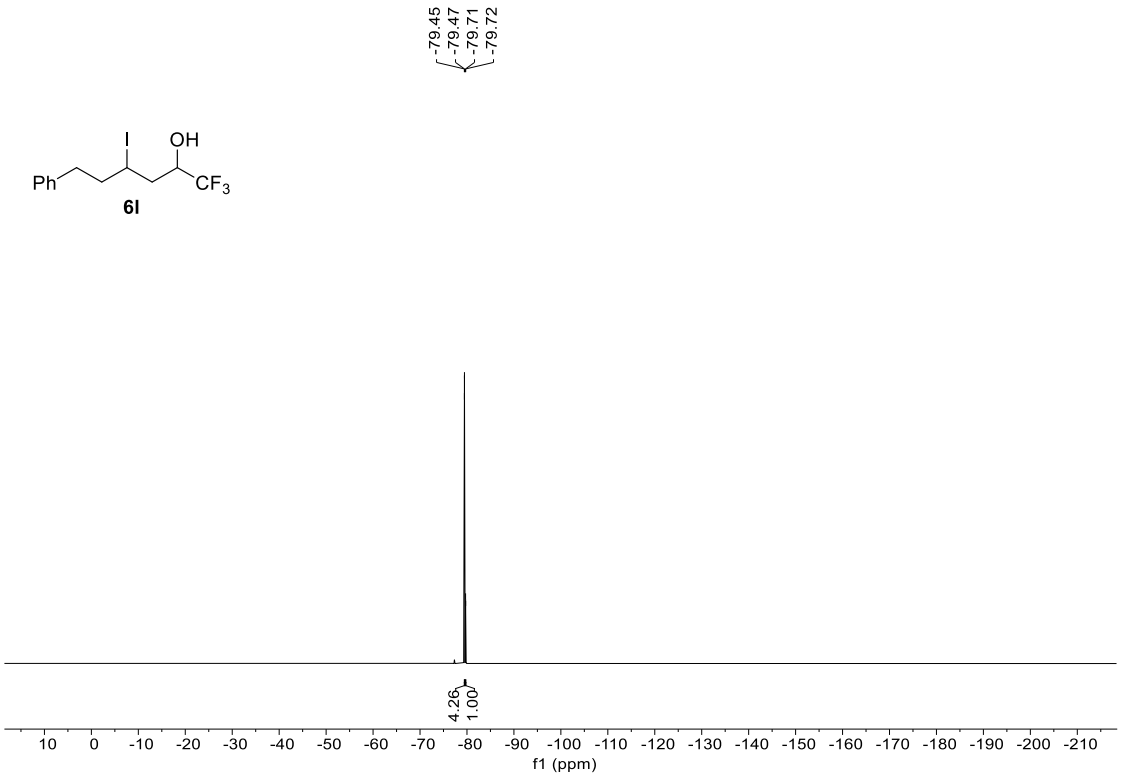
^{19}F NMR (565 MHz, $CDCl_3$) for **6k**



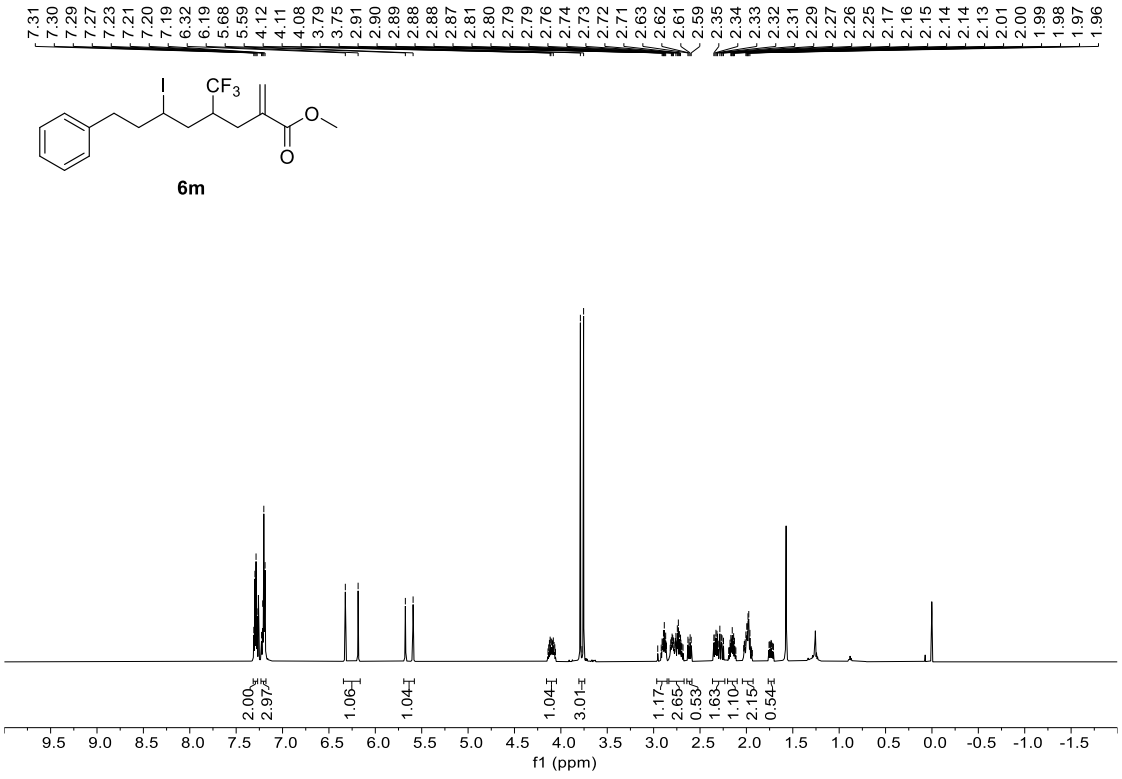
^{1}H NMR (600 MHz, $CDCl_3$) for **6l**



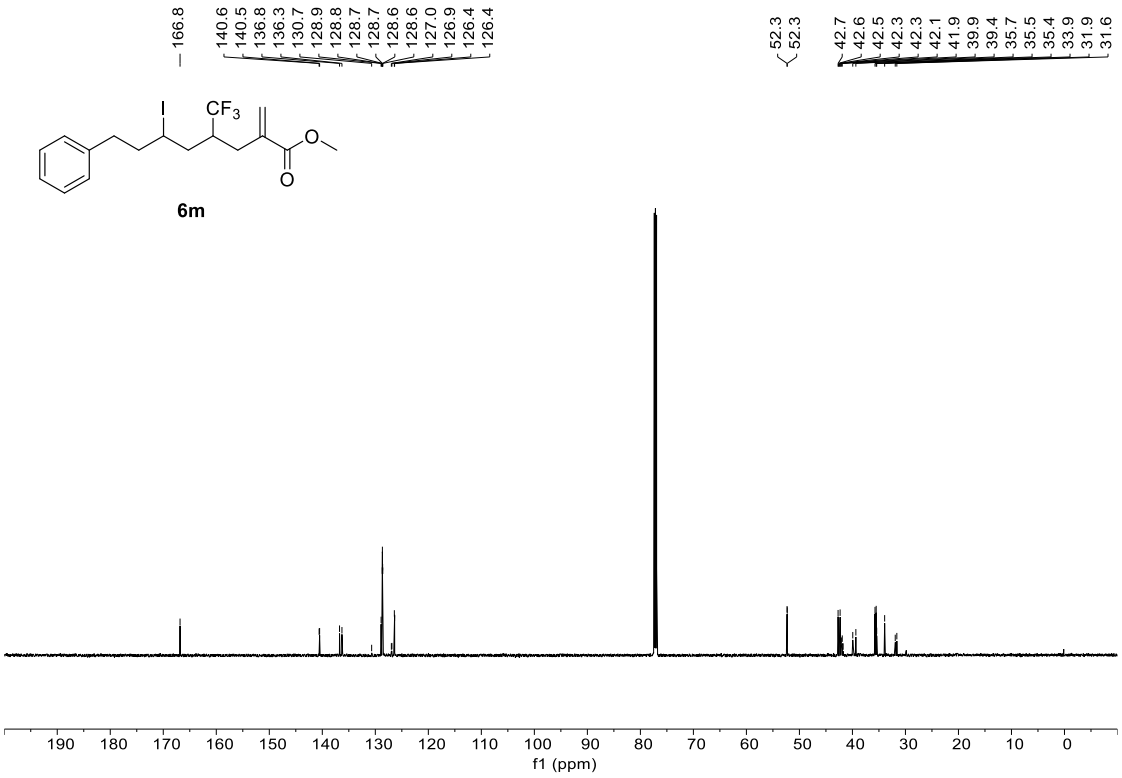
^{13}C NMR (151 MHz, $CDCl_3$) for **6l**



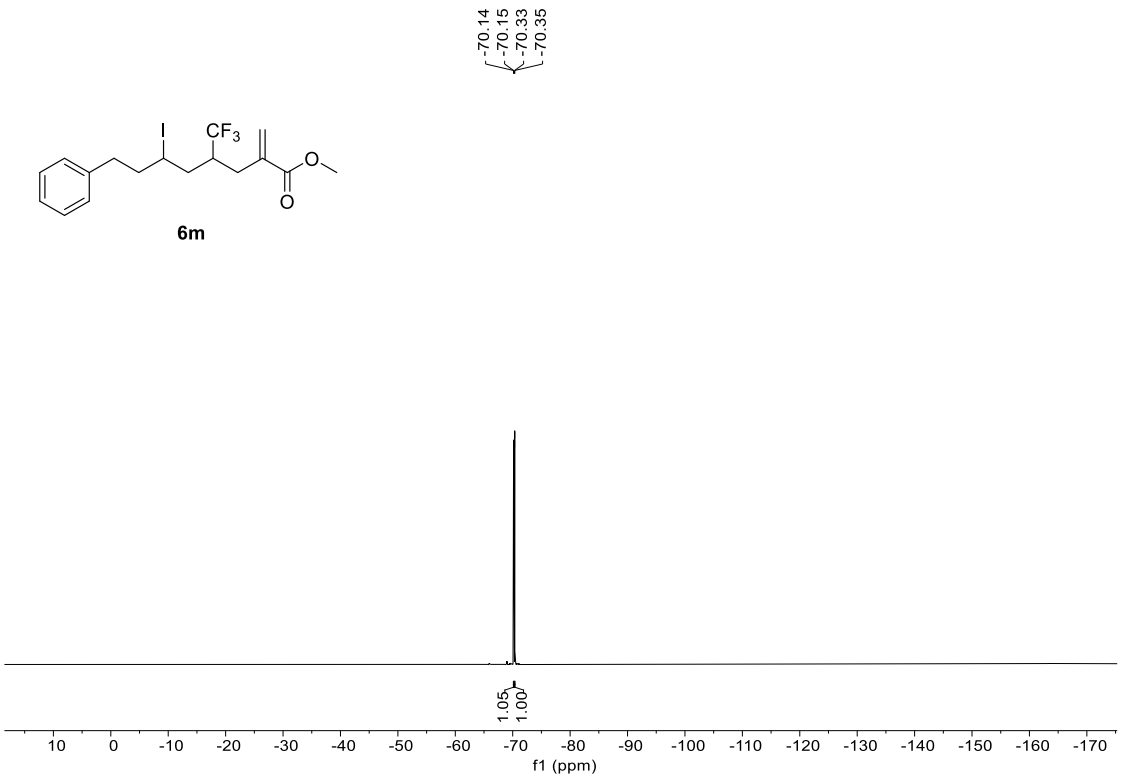
^{19}F NMR (565 MHz, $CDCl_3$) for **6l**



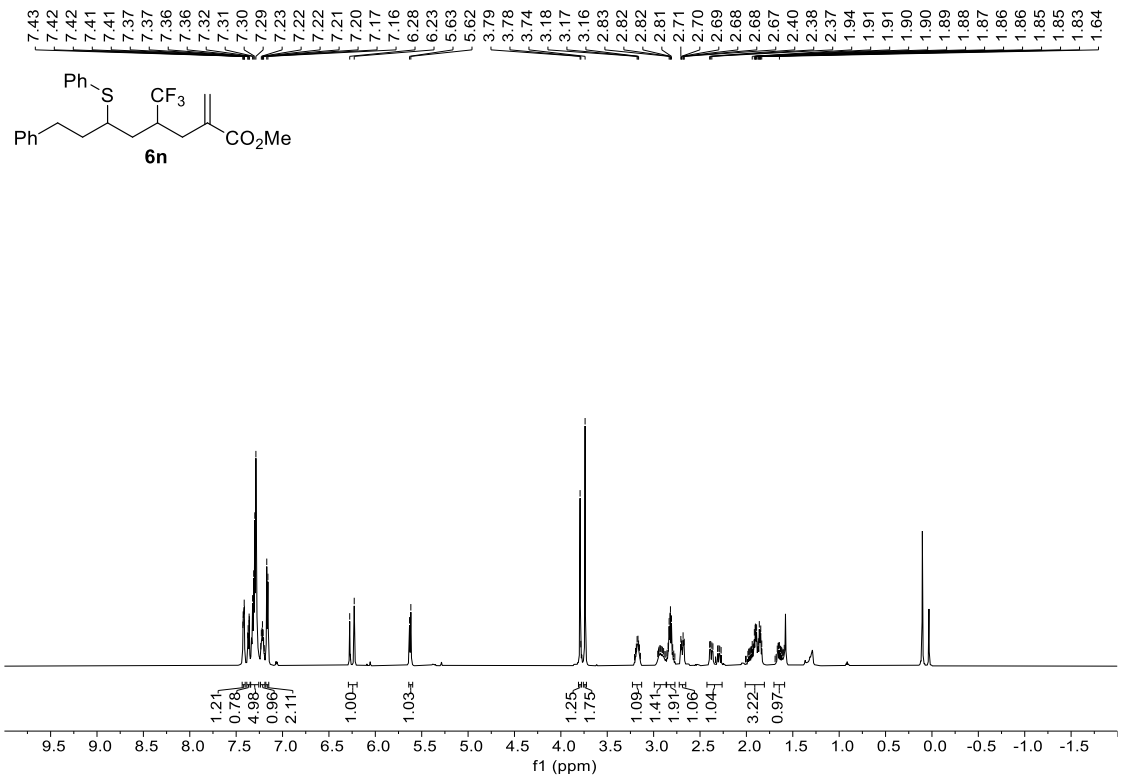
^{1}H NMR (600 MHz, $CDCl_3$) for **6m**



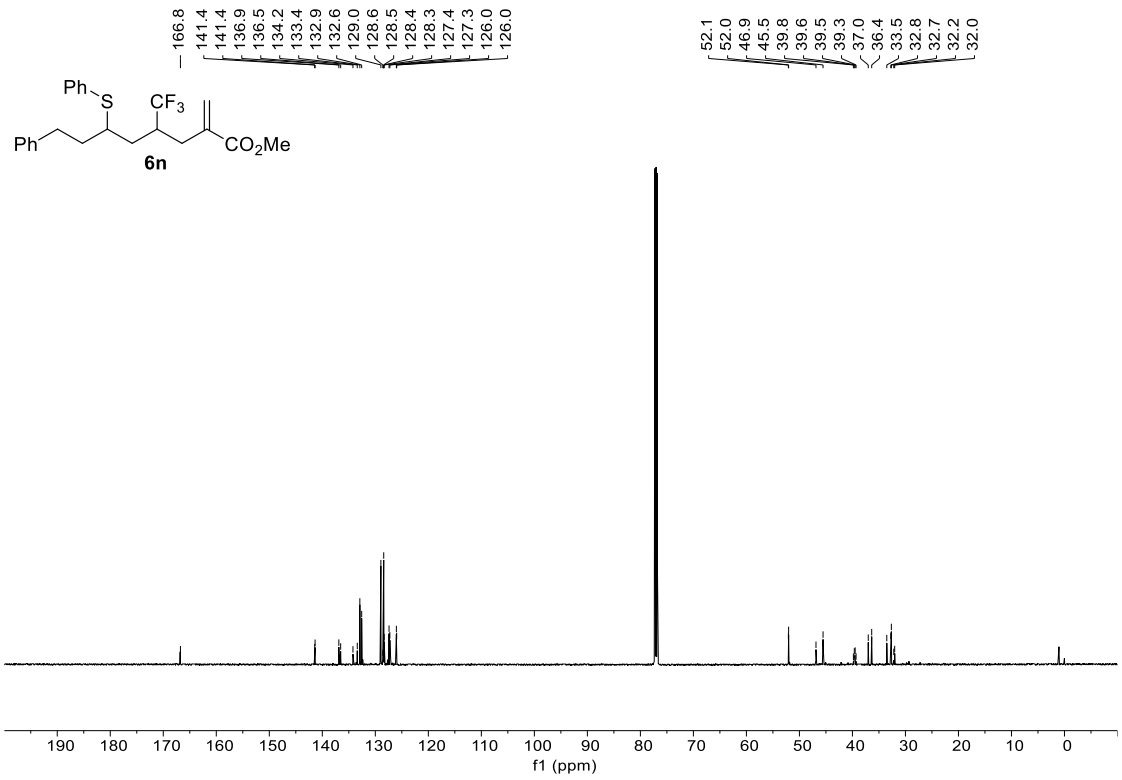
^{13}C NMR (151 MHz, $CDCl_3$) for **6m**



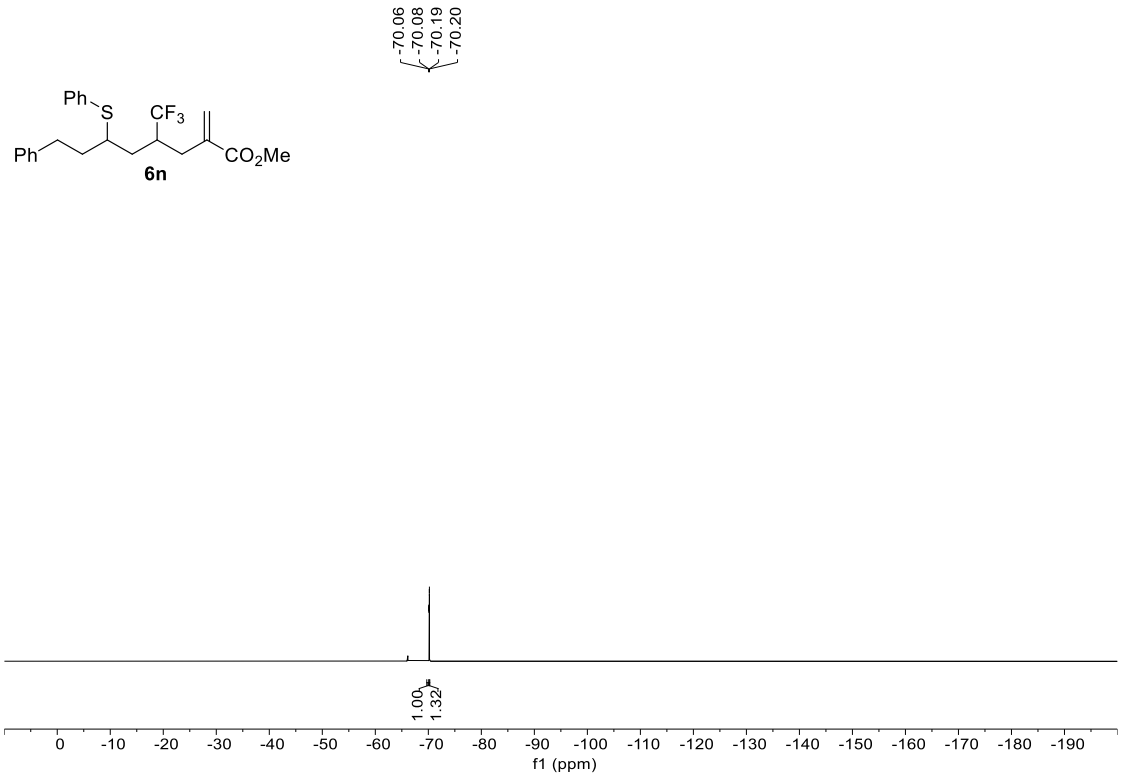
^{19}F NMR (565 MHz, $CDCl_3$) for **6m**



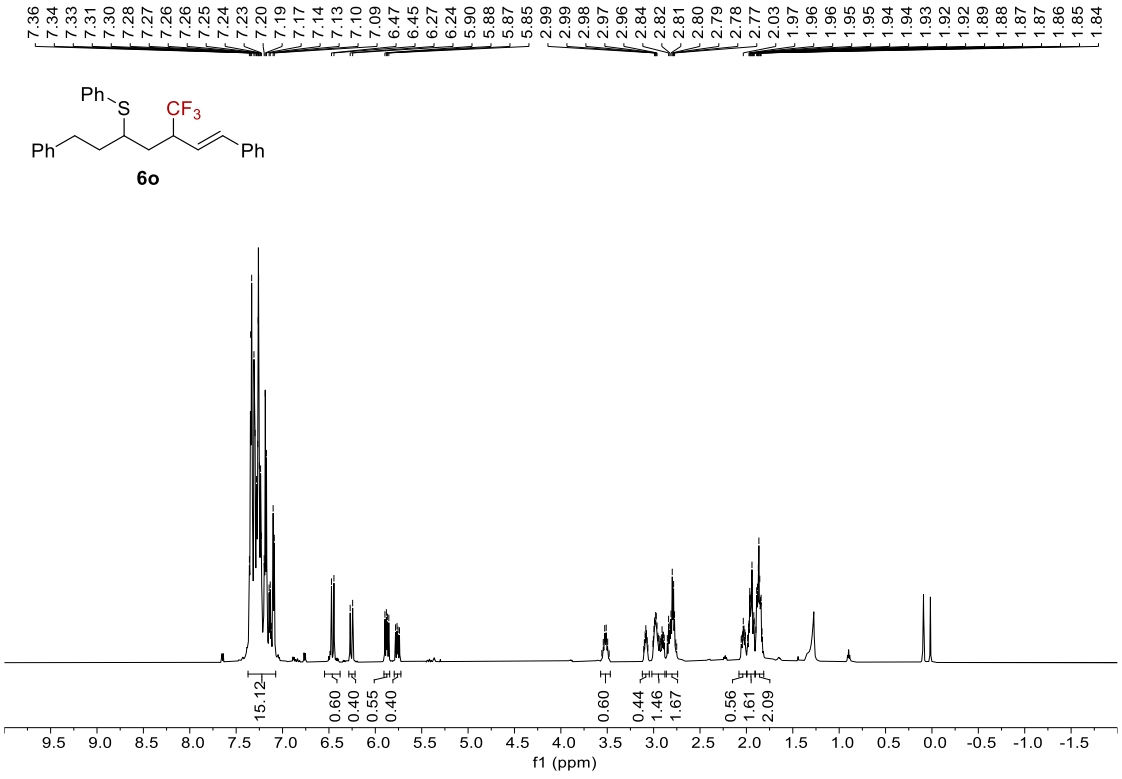
^{1}H NMR (600 MHz, $CDCl_3$) for **6n**



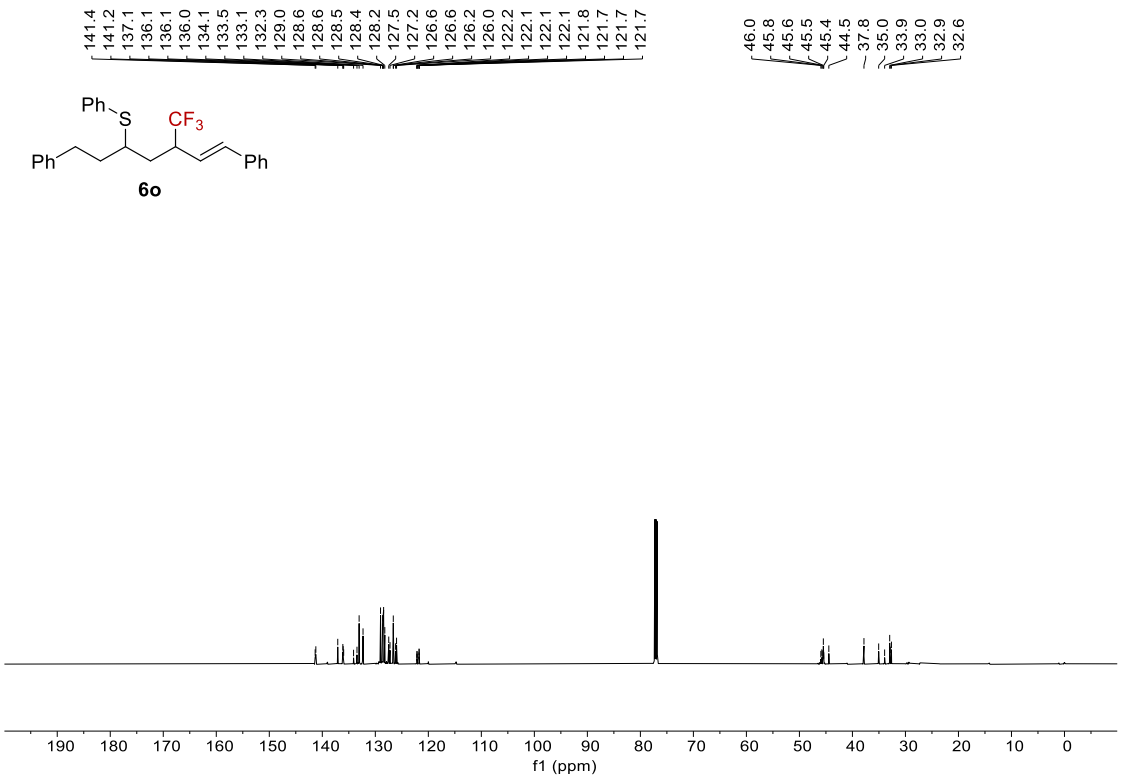
^{13}C NMR (151 MHz, $CDCl_3$) for **6n**



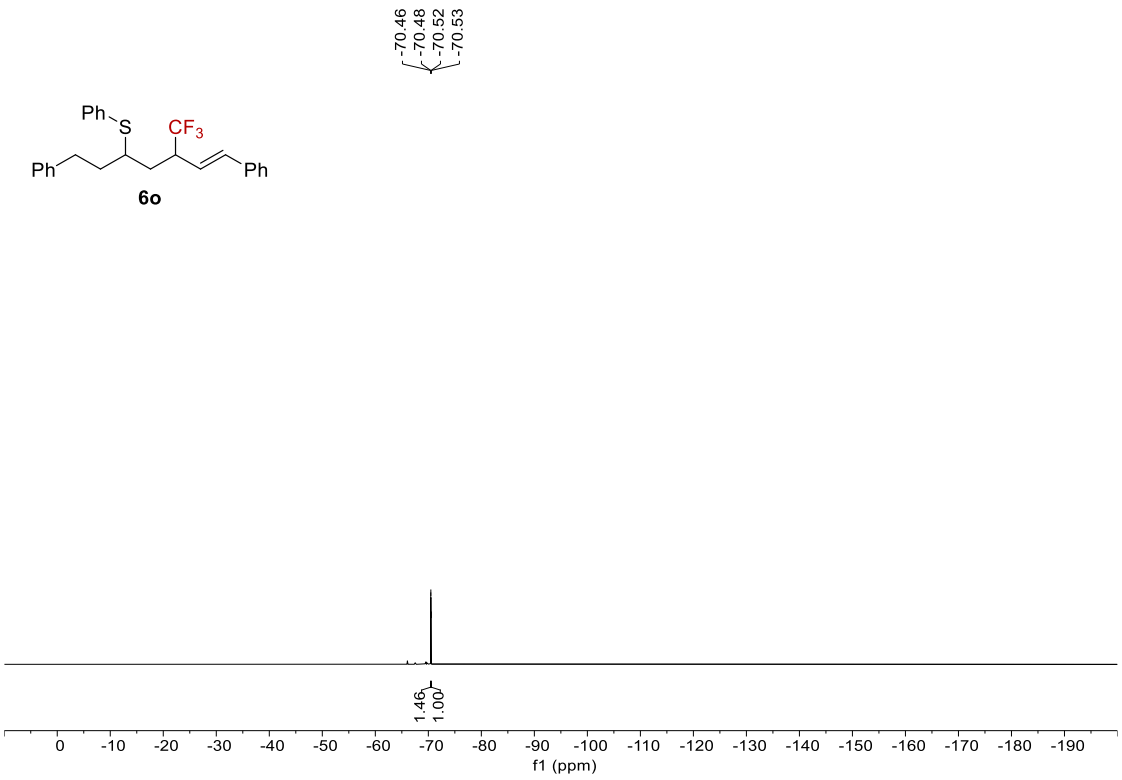
^{19}F NMR (565 MHz, $CDCl_3$) for **6n**



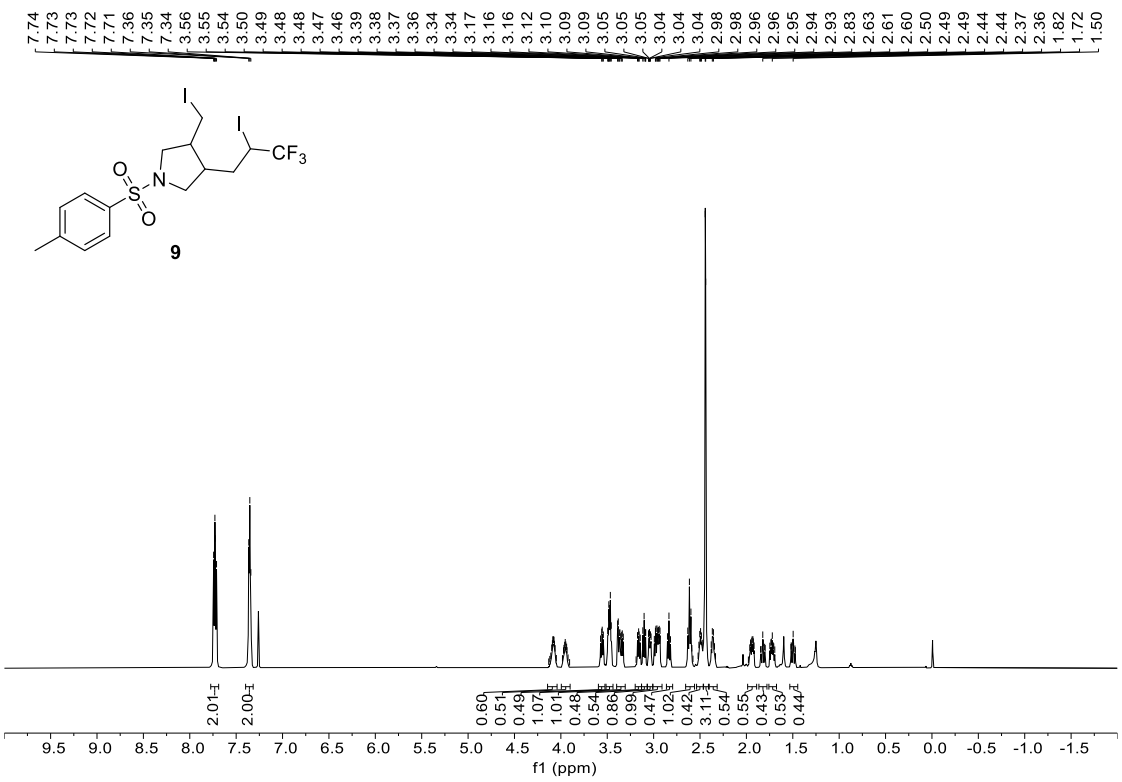
^{1}H NMR (600 MHz, $CDCl_3$) for **6o**



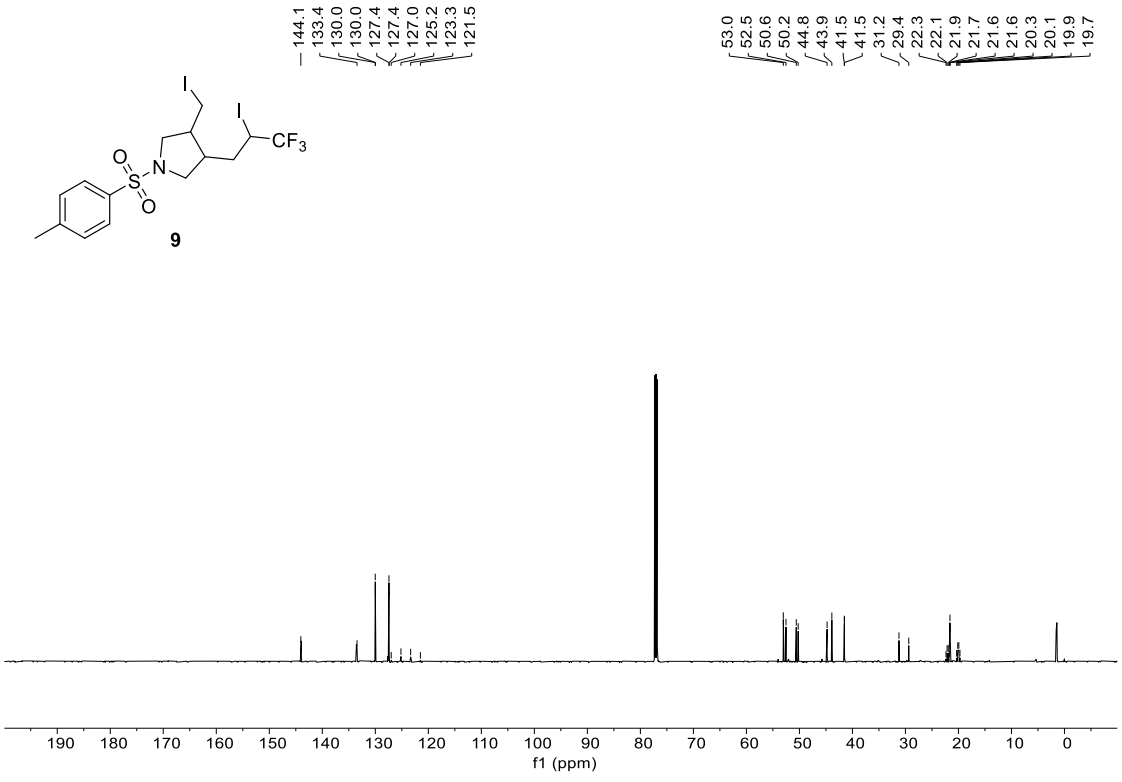
^{13}C NMR (151 MHz, $CDCl_3$) for **6o**



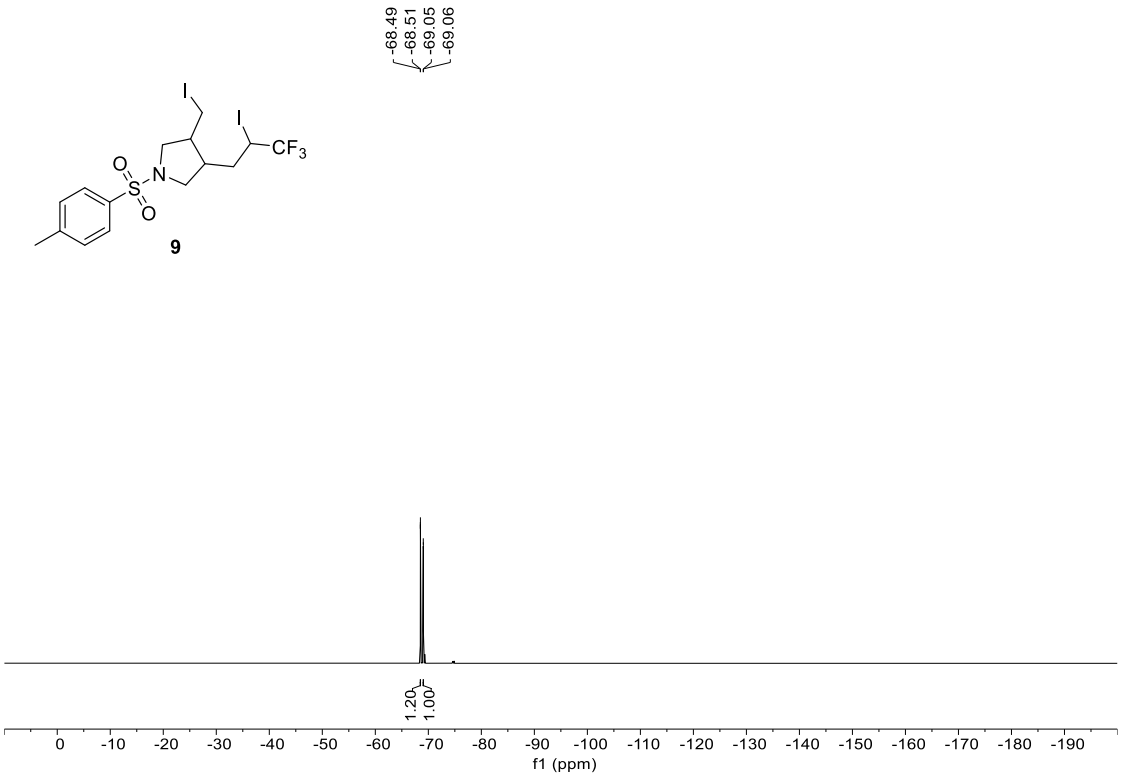
^{19}F NMR (565 MHz, $CDCl_3$) for **6o**



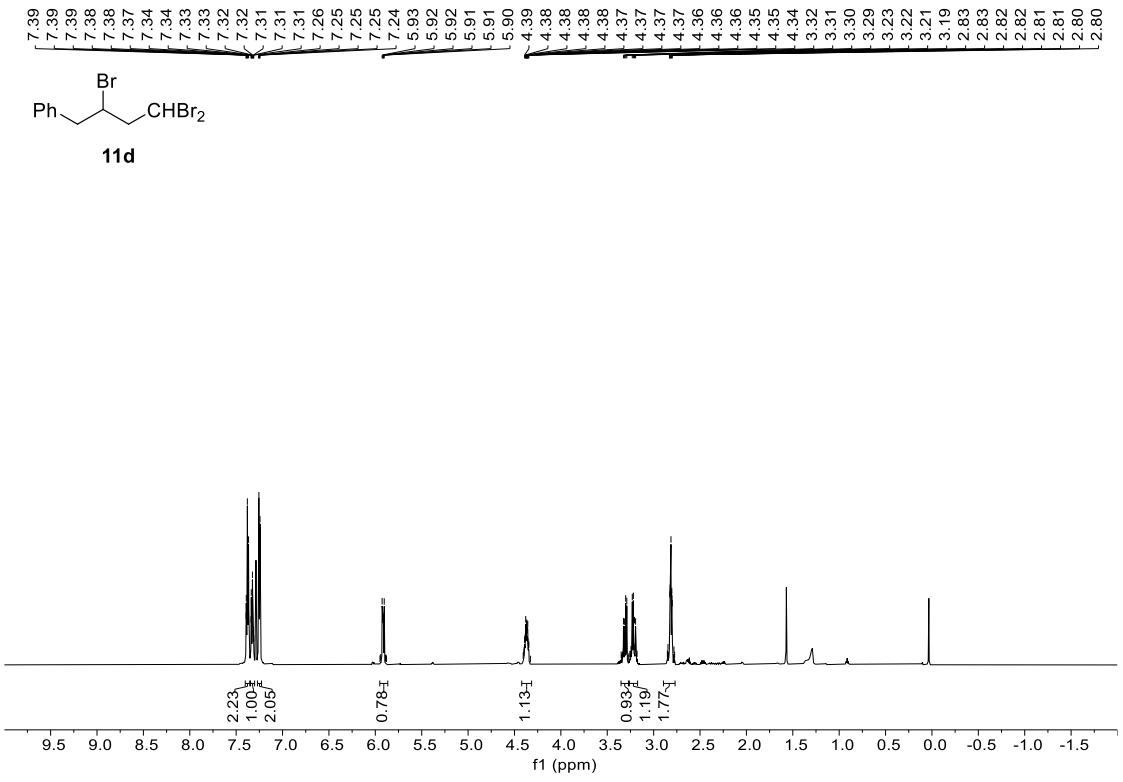
^{1}H NMR (600 MHz, $CDCl_3$) for **9**



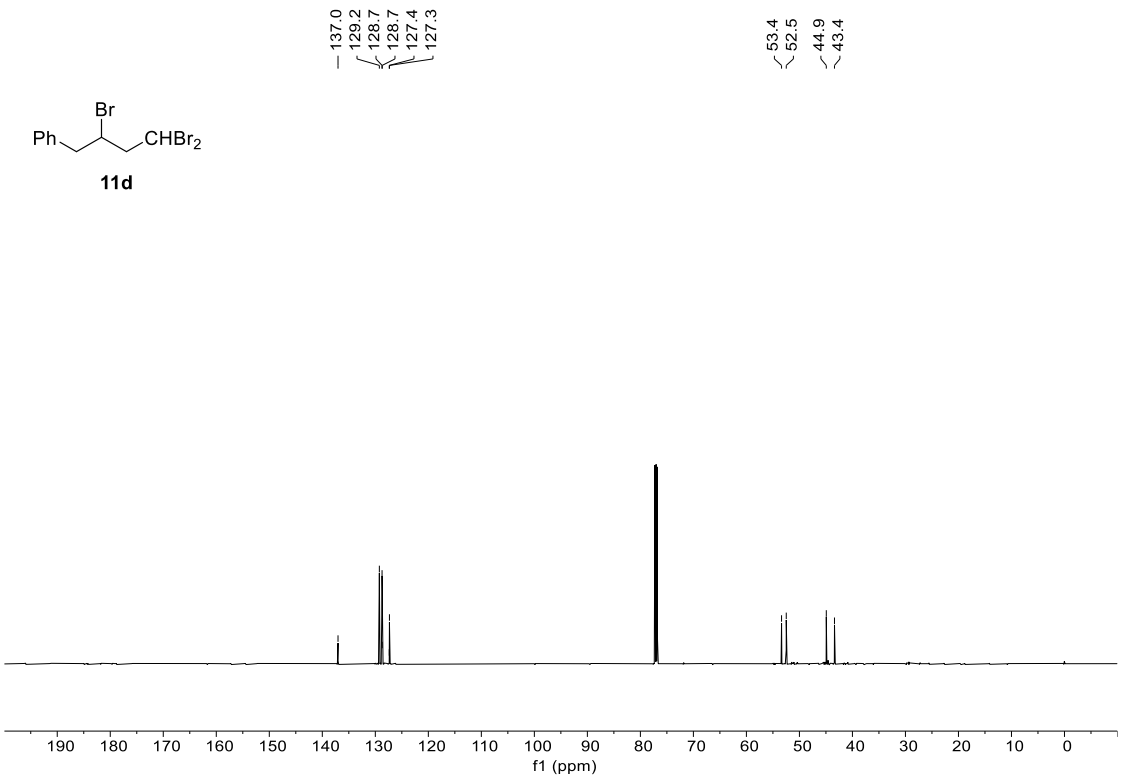
^{13}C NMR (151 MHz, $CDCl_3$) for **9**



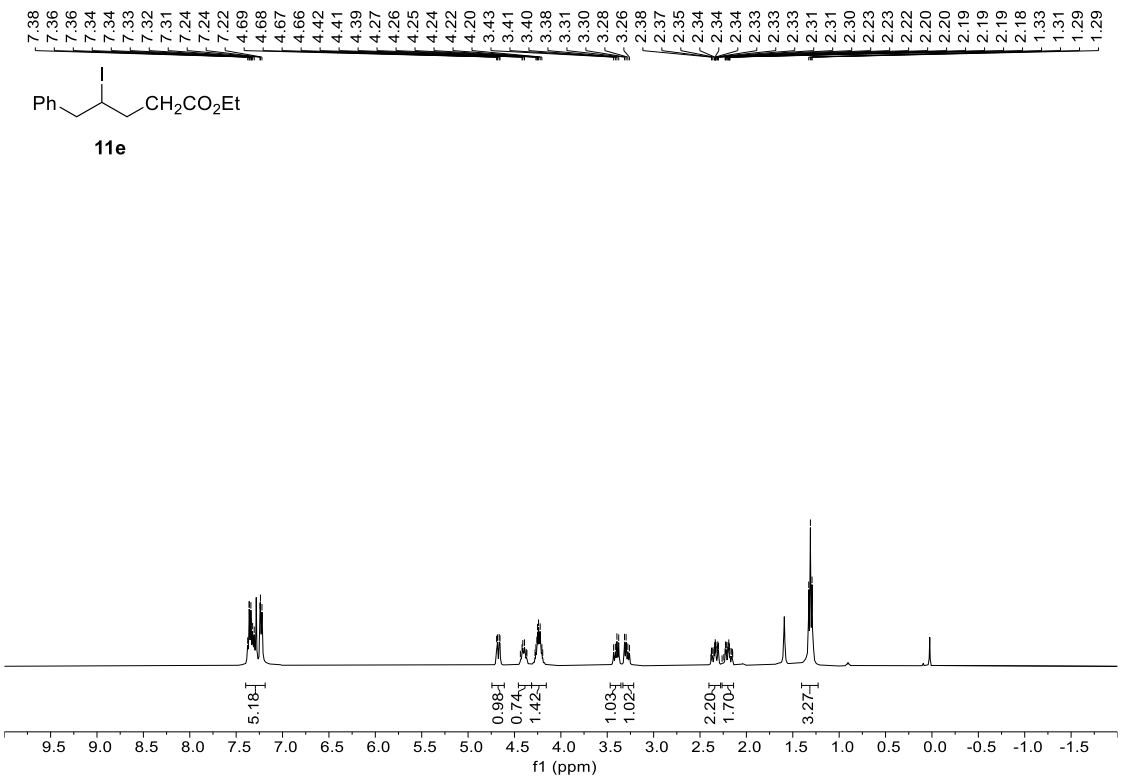
^{19}F NMR (565 MHz, $CDCl_3$) for **9**



^{1}H NMR (600 MHz, $CDCl_3$) for **11d**



^{13}C NMR (151 MHz, $CDCl_3$) for **11d**



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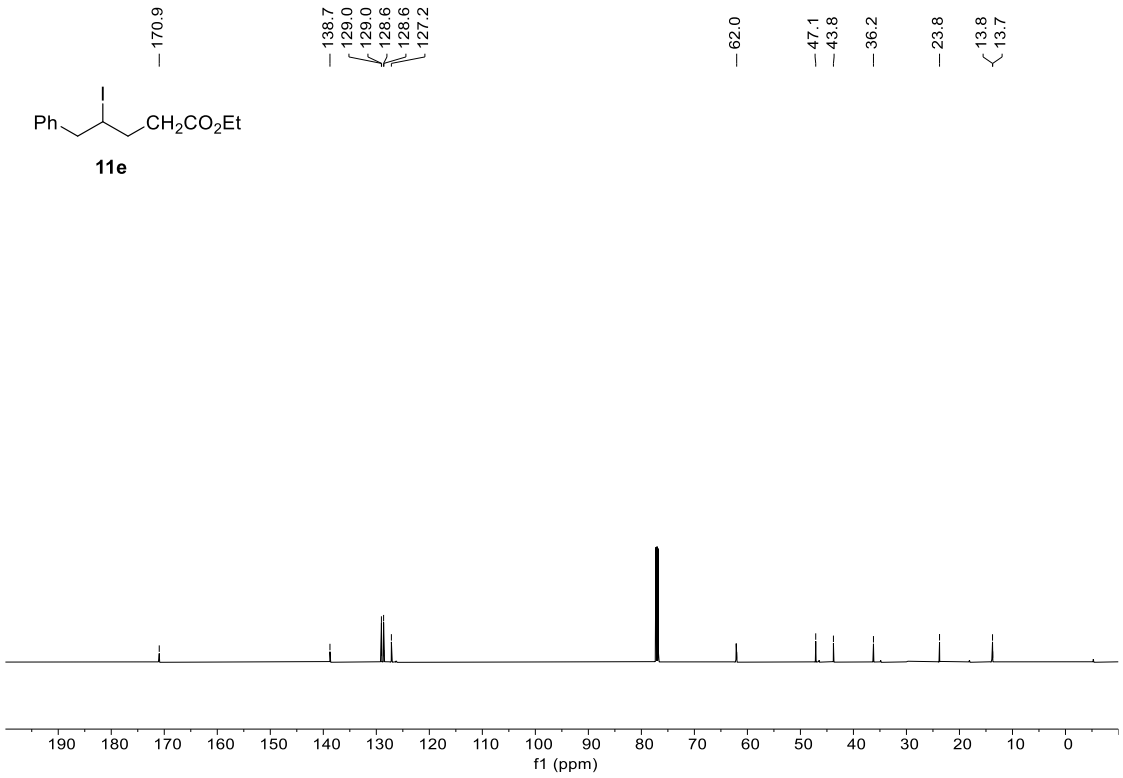
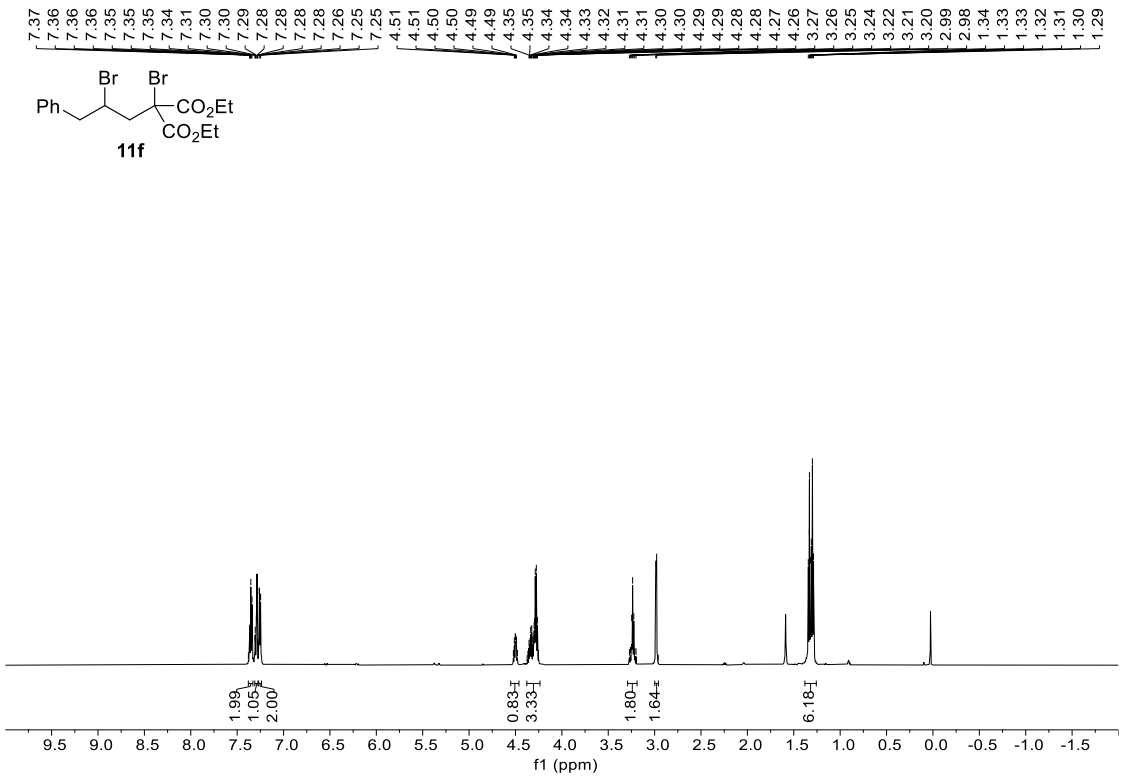
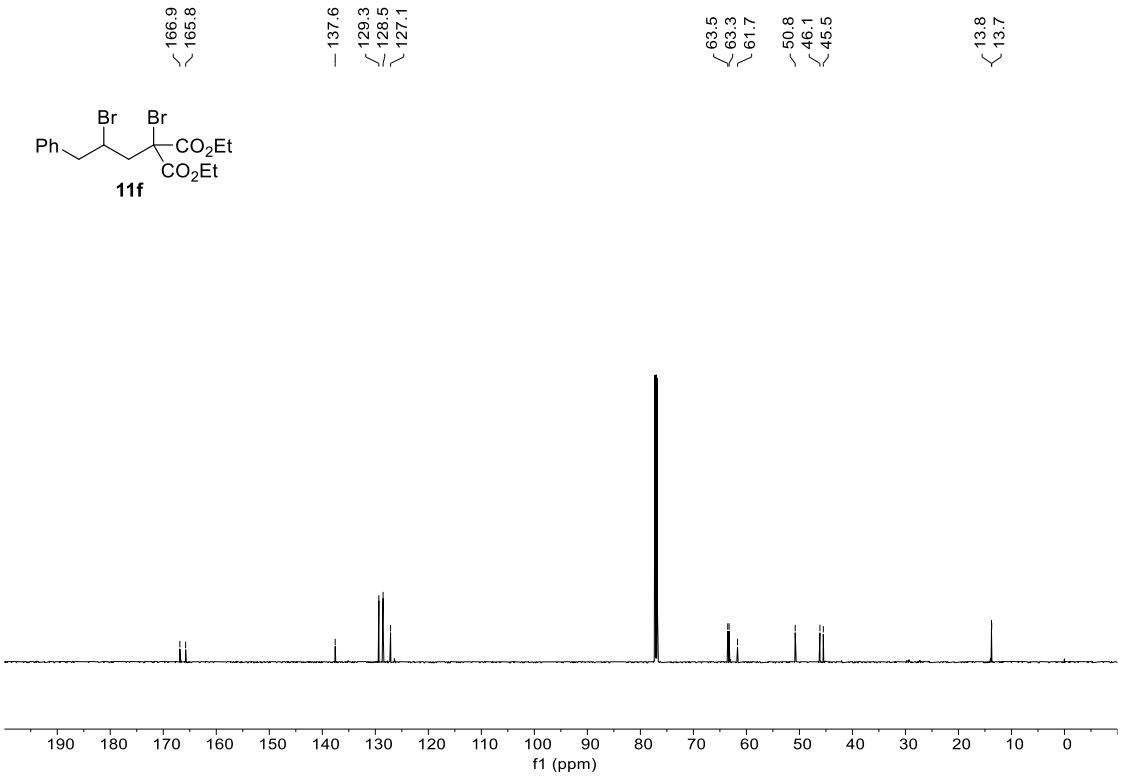


^{13}C NMR (151 MHz, $CDCl_3$) for **11e**



^{1}H NMR (600 MHz, $CDCl_3$) for **11f**



^{13}C NMR (151 MHz, $CDCl_3$) for **11f**