Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Iodoperfluoroalkylation of Unactivated Alkenes via Pyridine-Boryl Radical Initiated Atom-Transfer Radical Addition

Jia Cao[ab], Guoao Li[a], Guoqiang Wang*[a], Liuzhou Gao[a], and Shuhua Li*[a]

[a]Key Laboratory of Mesoscopic Chemistry of Ministry of Education, Institute of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China

[b]School of Chemistry and Chemical Engineering, Yan'an University, Yan'an 716000, P. R. China

Corresponding Author: shuhua@nju.edu.cn; wangguoqiang710@nju.edu.cn

Table of Contents

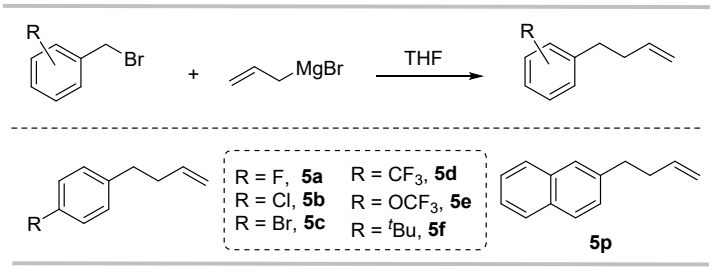
1. General Information

All reactions were carried out with standard Schlenk techniques under argon. Bis(pinacolato)diboron (B_2pin_2), bis(catecholato)diboron (B_2cat_2), pyridines, perfluoroalkyl iodides and alkenes (**1a**, **1b**, **1d, 5g-5l**) were purchased from commercial source and used without further purification. Commercial chemicals were purchased from Acros, Sigma-Aldrich, J&K, and Alfa Aesar Chemical Companies and used as received. Other alkenes were synthesized according to the reported procedure. Other Anhydrous CH_3CN, CH_2Cl_2, methyl tert-butyl ether (MTBE) and THF were purchased from J&K and used as received (water < 30 ppm, J&KSeal). Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum sheets from Qingdao Haiyang Chemical Co., Ltd. Flash chromatography was performed on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd).

^1H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE Avance III 400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm for ^1H NMR, and 77.16 ppm for $^{13}C\{^1H$ NMR). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet), coupling constants (Hz) and integration. Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using a neat thin-film technique. High-resolution mass spectra (HRMS) were recorded on the Thermo Quest Finnigan LCQDECA system equipped with an ESI or APCI ionization source and a TOF detector mass spectrometer.

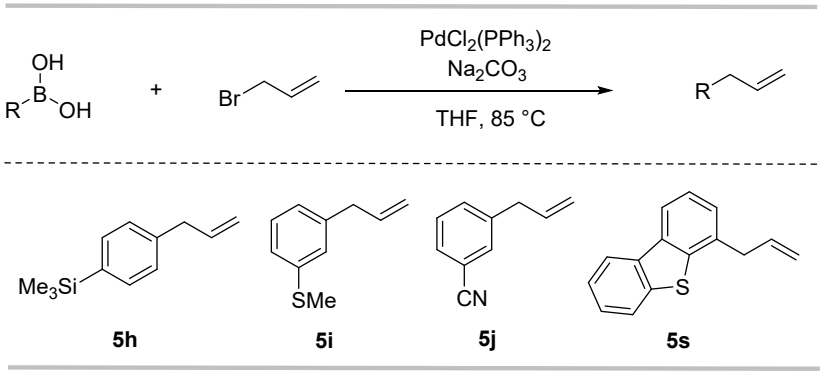
2. Experimental Details for the iodoperfluoroalkylation of unactivated Alkenes

2.1 Synthesis of alkenes

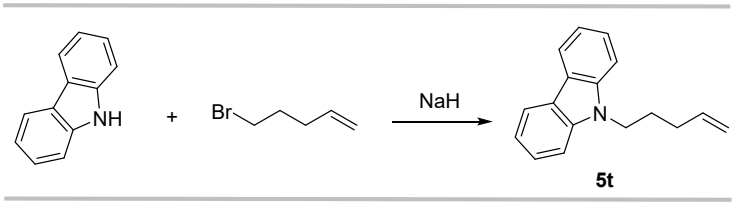


For preparation of alkenes (**5a**-**5f**, **5p**) according to the literature procedure,[1a] under argon atmosphere, benzyl bromide (1.0 equiv) and 20 mL anhydrous THF were added to a flame dried 100 mL round-bottom flash assembled with a constant pressure funnel which had been previously flame dried. Allylmagnesium bromide (2.0 equiv) in the constant pressure funnel were added dropwise. The

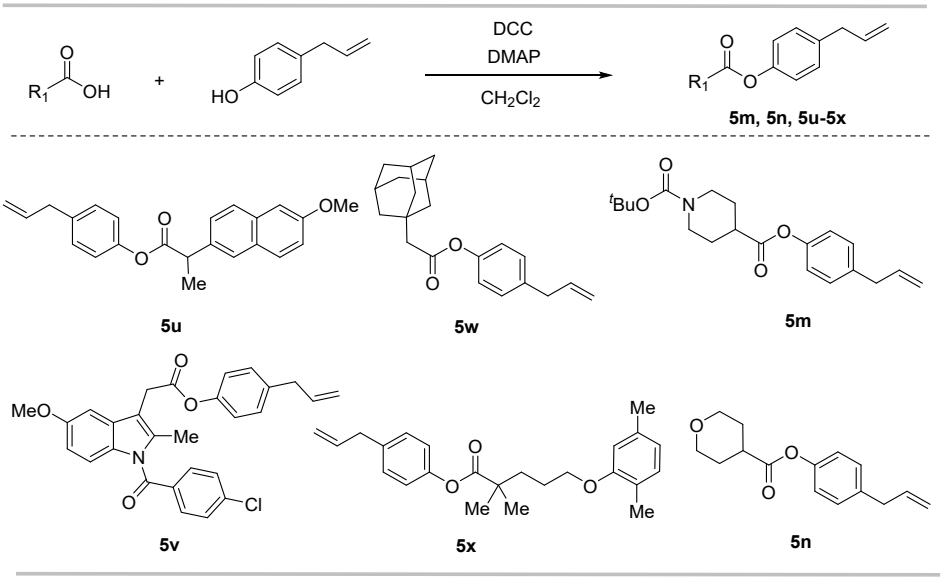
reaction was stirred for 8 h at room temperature and then quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with CH_2Cl_2 and the combined organics were dried over $MgSO_4$, filtered through celite and concentrated under reduced pressure. The crude product was purified by flash chromatography, affording to the corresponding products.[1]



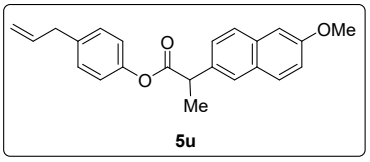
For the preparation of alkenes (**5h**, **5i**, **5j**, **5s**) according to the literature procedure,[2a] under argon atmosphere, to a solution of substituted boronic acid (1 equiv) and allyl halide (1.5 equiv) in THF (0.2 M) in a round bottom flask were added $PdCl_2(PPh_3)_2$ (2.5 mol %). The reaction mixture was heated to 50 ^oC, then aq Na_2CO_3 (1 M, 2 equiv) solution was added dropwise and then heating continued in reflux for 3-4 h. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuum. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired products.[2]



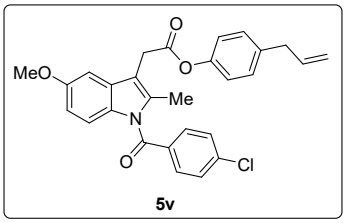
For the preparation of alkene **5t** according to the literature procedure:[3] A 100 mL round-bottom flask equipped with a Teflon-coated magnetic stirring bar was charged with 9H-carbazole (6.0 mmol) and 15 mL of DMF. Sodium hydride (6.0 mmol) was added and the reaction was stirred at room temperature for 1 h. 5-Bromo-1-pentene (9.0 mmol) was added, and the reaction was allowed to stir for an additional 2 h at 80˚C. Water was added and the mixture extracted with CH_2Cl_2. The organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography with silica gel using a mixture of hexane/EtOAc (20:1) as an eluent to afford the desired compound (**5t**).



For preparation of alkenes **5m, 5n**, **5u-5x**:[4] At first, a sealed reaction bottle charged with a magnetic stir bar, carboxylic acid (10.0 mmol, 1.0 equiv), DCC (dicyclohexylcarbodiimide) (12.0 mmol, 1.2 equiv), DMAP (4-dimethylaminepyridine) (1.5 mmol, 0.15 equiv) and 4-hydroxyacetophenone (12.0 mmol, 1.2 equiv) in CH_2Cl_2 (20 mL). The reaction mixtures were stirred at room temperature for 24 h. Then it was filtered through a plug of silica gel (washed with EA/ethyl acetate). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel (PE/EA=50: 1~5:1) to afford the corresponding product.

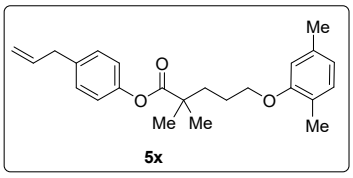


Characterization Data of 4-allylphenyl 2-(6-methoxynaphthalen-2-yl)propanoate (**5u**) as a white solid in 45% yield, mp 82-84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 3H), 7.61 – 7.54 (m, 1H), 7.26 – 7.15 (m, 4H), 7.03 – 6.93 (m, 2H), 6.05 – 5.89 (m, 1H), 5.30 – 4.89 (m, 2H), 4.20 – 4.08 (m, 1H), 3.94 (s, 3H), 3.45 – 3.30 (m, 2H), 1.82 – 1.65 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.3, 157.7, 149.1, 137.5, 137.1, 135.2, 133.8, 129.4, 129.3, 129.0, 127.4, 126.1, 121.2, 119.1, 116.0, 116.0, 105.6, 55.2, 45.6, 39.5, 18.6. **IR** (film): 2976, 2935, 1749, 1634, 1504, 1263, 1163, 1130, 993, 850; **HRMS** (ESI) exact mass calculated for $[M+H]^+$: 347.1642, measured: 347.1647.



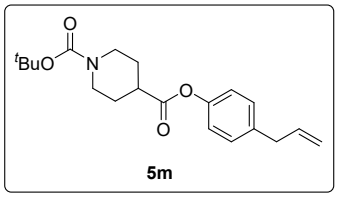
Characterization Data of 4-allylphenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**5v**) as a white solid in 40% yield, mp 107-108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.67 (m, 2H), 7.49 – 7.46 (m, 2H), 7.20 – 7.17 (m, 2H), 7.08 (d, *J* = 2.5 Hz, 1H), 7.01 – 6.98 (m, 2H), 6.92 (d, *J* = 9.0 Hz, 1H), 6.72 – 6.70 (m, 1H), 6.00 – 5.87 (m, 1H), 5.11 – 5.03 (m, 2H), 3.90 (s, 2H), 3.84 (s, 3H), 3.39 – 3.36 (m, 2H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 168.4, 156.2, 149.0, 139.4, 137.8, 137.1, 136.2, 133.9, 131.3, 130.9, 130.6, 129.6, 129.2, 121.3, 116.1, 115.1, 112.2, 111.9, 101.3, 55.8, 39.6, 30.6, 13.5. **IR** (film): 3075, 2929, 2833, 1753,

1671, 1590, 1435, 1195, 1164, 1064, 1035, 924, 832; **HRMS** (ESI) exact mass calculated for $[M+H]^+$: 474.1467, measured: 474.1464.



5x

Characterization Data of 4-allylphenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**5x**) as a colorless oil in 38% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.06 – 7.03 (m, 2H), 6.75 (d, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 1.6 Hz, 1H), 6.08 – 5.97 (m, 1H), 5.19 – 5.14 (m, 2H), 4.07 – 4.03 (m, 2H), 3.47 – 3.44 (m, 2H), 2.40 (s, 3H), 2.28 (s, 3H), 1.98 – 1.94 (m, 4H), 1.46 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.4, 156.9, 149.3, 137.4, 137.2, 136.4, 130.4, 129.5, 123.6, 121.4, 120.8, 116.0, 111.9, 67.8, 42.4, 39.6, 37.2, 25.3, 25.2, 25.2, 21.4, 15.8. **IR** (film): 2923, 2873, 2117, 1748, 1506, 1472, 1263, 1163, 1045, 914, 802; **HRMS** (ESI) exact mass calculated for $[M+H]^+$: 367.2268, measured: 367.2269.



5m

Characterization Data of 4-(4-allylphenyl) 1-(tert-butyl) piperidine-1,4-dicarboxylate **(5m)** as a colorless oil in 42% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.3 Hz, 2H), 6.98 – 6.95 (m, 2H), 5.98 – 5.86 (m, 1H), 5.09 – 5.02 (m, 2H), 4.11 – 4.02 (m, 2H), 3.36 (d, *J* = 6.7 Hz, 2H), 2.93 – 2.86 (m, 2H), 2.73 – 2.62 (m, 1H), 2.04 – 1.98 (m, 2H), 1.79 – 1.73 (m, 2H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 154.6, 148.9, 137.6, 137.0, 129.5, 121.2, 116.0, 79.6, 42.6, 41.1, 39.5, 28.4, 27.9. **IR** (film): 2975, 2929, 1751, 1689, 1506, 1419, 1365, 1237, 1196, 1140, 1026, 915, 869; **HRMS** (ESI) exact mass calculated for $[M+Na]^+$: 368.1832, measured: 368.1837.

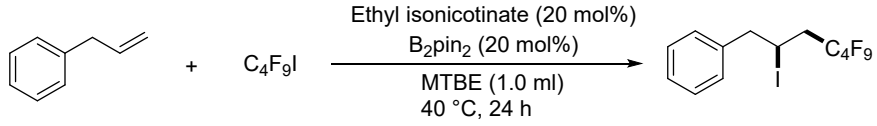
2.2 Optimization Studies

General procedure. Under argon atmosphere, a sealed reaction tube was charged with a magnetic stir bar, alkene (1.0 equiv, 0.2 mmol), perfluoroalkyl iodides (2.0 equiv, 0.4 mmol), B_2pin_2 (0.04 mmol, 20 mol%), ethyl isonicotinate (0.04 mmol, 20 mol%) and MTBE (1 mL). The reaction mixture was stirred at 40 °C for 24 h. Then, the reaction mixture was concentrated under reduced pressure, and the resulting crude product was purified by preparative TLC on silca gel to afford the desired product. The results are tabulated in Table S1.

In the presence of catalytic amount of B_2pin_2 (20 mol%) and ethyl isonicotinate (20 mol%), the reaction proceeded in tert-Butyl methyl ether (MTBE) at 40 °C and the desired product **3a** was obtained in 77% yield (Table S1, entry 1). When using 4-cyanopyridine as the initiator, the model reaction could furnish iodoperfluoroalkylation product **3a** at 40 °C in 61% (entry 2). Using the 0.1 and 0.1 equivalent of ethyl isonicotinate/B_2pin_2 combination respectively, the corresponding product **3a** was formed in 72% yield (entry 3). The reaction was performed at elevated temperature of 60 °C and 80 °C, a good yields of **3a** were obtained (entry 4 and 5). Lowering the reaction temperature to room temperature led to a slightly diminished yield (entry 6). The reaction could be reacted well in the dark, and the corresponding iodoperfluoroalkylated product **3a** was also obtained in 78% yield, indicating

light have no effect on the reaction outcome (entry 7). The use of Ethyl acetate (EA) and $PhCF_3$ as the solvent shown good reactivity (entries 8 and 9). However, the product was also produced in reduced yield when performing the reactions in the hexane and CH_3CN (entries 10 and 11). Further experiments revealed that the B_2pin_2 and ethyl isonicotinate are essential for obtaining the target product (entries 12-14).

Table S1. optimization of reaction conditions.[a]



1a (0.2 mmol) **2a** (0.4 mmol) **3a**

entry	Variation from standard conditions	Yield of **3a**[b]
1	none	77%
2	4-cyanopyridine instead of ethyl isonicotinate	61%
3	ethyl isonicotinate (10 mol%)，$B_2(pin)_2$ (10 mol%)	72%
4	60 °C instead of 40 °C	82%
5	80 °C instead of 40 °C	79%
6	rt	75%
7	rt, in the dark	78%
8	EA instead of MTBE	74%
9	$PhCF_3$ instead of MTBE	73%
10	hexane instead of $PhCF_3$	61%
11	CH_3CN instead of $PhCF_3$	55%
12	no ethyl isonicotinate	ND
13	no B_2pin_2	ND
14	no ethyl isonicotinate and B_2pin_2	ND

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $B_2(pin)_2$ (20 mol%), ethyl isonicotinate (20 mol%), MTBE (1.0 mL), 24 h, 40 °C. [b]Isolated yield. ND = not detected. EA = Ethyl acetate, MTBE = tert-Butyl methyl ether, $PhCF_3$ = trifluorotoluene, rt = room temperature.

2.3 Experimental Studies on the Reaction Mechanism

2.3.1 Detect the reaction mixtures by GC-MS analysis

1a **2a**

1.0 equiv 2.0 equiv 1.2 equiv 1.2 equiv

3a, 42%, isolated yield **3a'**, trace

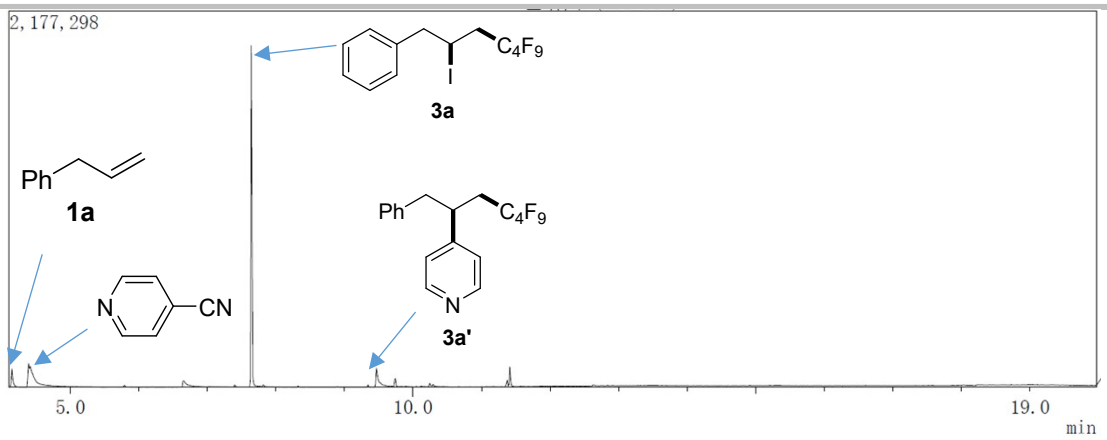
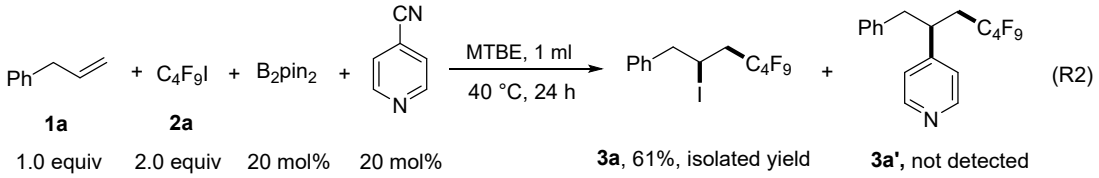


Figure S1. GC-MS analysis of the crude reaction mixture of reaction (R1)

The crude reaction mixture of allylbenzene **1a** and C_4F_9I in the presence of 1.2 equivalent of 4-cyanopyridine/B_2pin_2 combination under standard conditions (R1) was detected by GC-MS analysis. As shown in Figure S1, we detected the formations of iodoperfluoroalkylation product **3a** and the trace amount of perfluoroalkylative pyridinylation product **3a′** and **1a** were detected by GC-MS analysis. The residue crude reaction mixture was further purified by preparative TLC on silica gel to give the product **3a** in 42% isolated yield. This result indicated the iodoperfluoroalkylation pathway is much easier than perfluoroalkylative pyridinylation pathway for the unactivated alkenes.



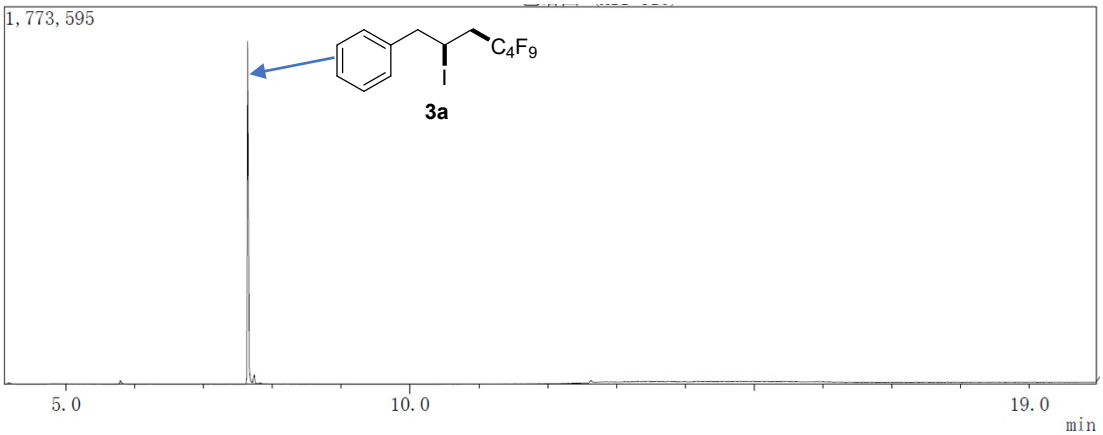
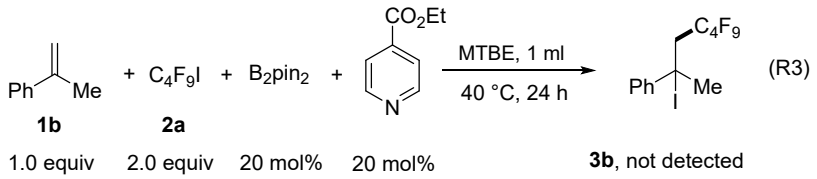


Figure S1. GC-MS analysis of the crude reaction mixture of reaction (R2)

The crude reaction mixture of allylbenzene **1a** and C_4F_9I using 4-canopyridine and B_2pin_2 as the initiator under standard conditions was detected by GC-MS analysis (R2). As shown in Figure S2, the targeted compounds **3a** were detected by GC-MS analysis. The perfluoroalkylative pyridinylation product **3a′** was not detected. The crude reaction mixture was further purified by preparative TLC on

silica gel to give the product **3a** in 61% isolated yield. This results indicated the atom transfer radical addition pathway is favorable for alkyl-substituted alkenes.



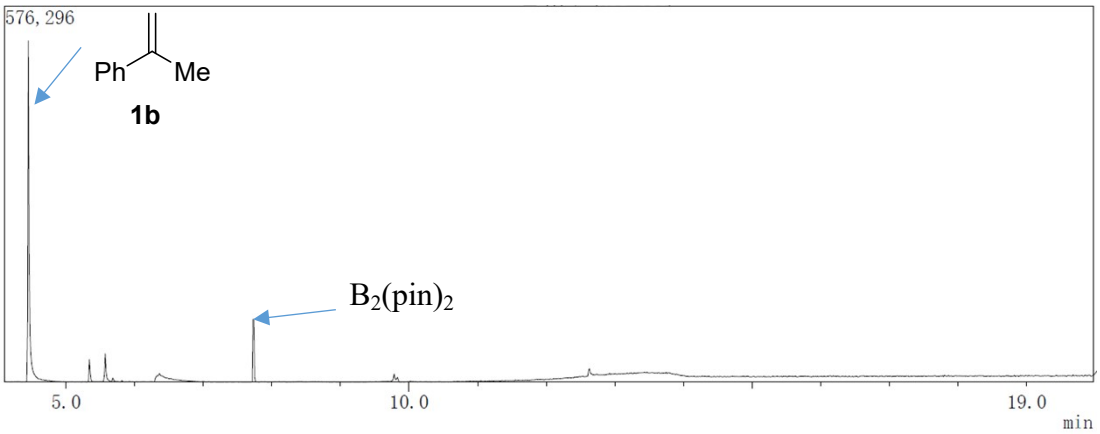


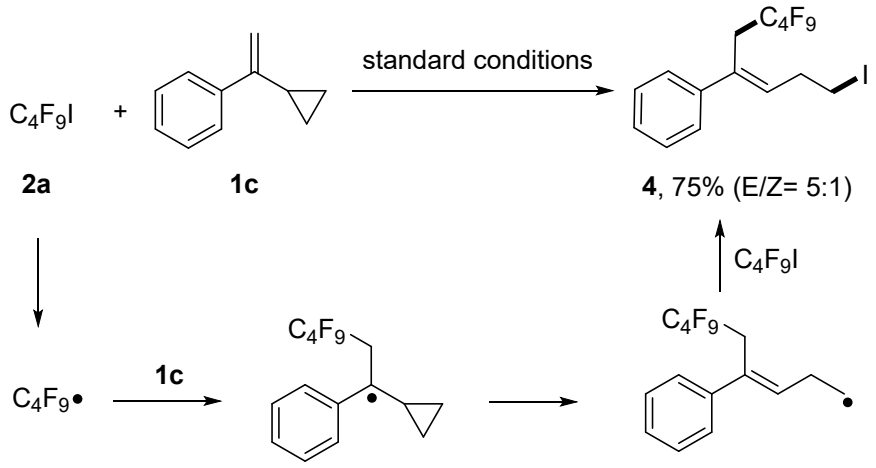
Figure S3. GC-MS analysis of the crude reaction mixture of reaction (R3)

The crude reaction mixture of α-methylstyrene **1b** and C_4F_9I using 20 mol% ethyl isonicotinate and 20 mol% B_2pin_2 under standard conditions was detected by GC-MS analysis (R3). As shown in Figure S3, the expected iodoperfluoroalkylation product **3b** was not detected by GC-MS analysis. The raw material **1b** was not transformed by GC-MS analysis. This results indicated the atom transfer radical addition pathway may be not sutiable for aryl-substituted alkenes.

Experimental procedure: A sealed reaction tube charged with a magnetic stir bar, prepared by general procedure using allylbenzene **1a,** α-methylstyrene **1b** or 1,1-Diphenylethylene (1.0 equiv, 0.2 mmol), ethyl isonicotinate or 4-CN pyridine, B_2pin_2, **2a** (0.4 mmol) and MTBE (1 mL) at 40 °C. After 24 h, the crude reaction mixture was detected by GC-MS analysis. The residue reaction mixture was concentrated under reduced pressure, and isolated with the preparative TLC on silica (PE/EA) to afford the corresponding product.

2.3.2 Radical clock experiments

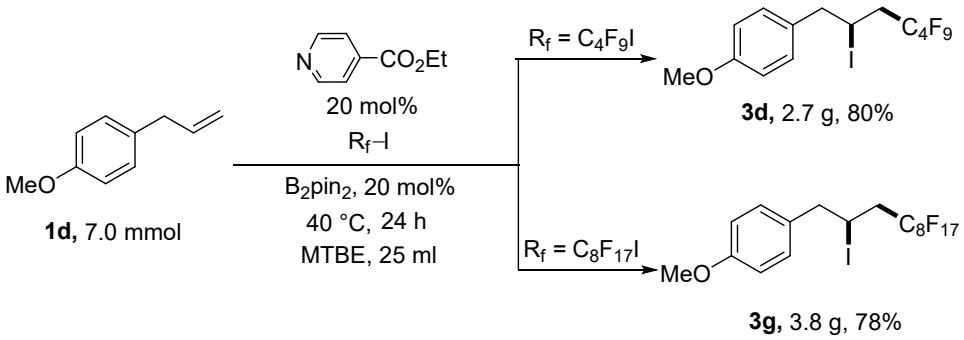
We performed a radical-clock experiment using *α*-cyclopropylstyrene **1c** as the substrate. After the generation of C_4F_9 radical, which adds to the alkene at the terminal position, and simultaneously the resulting alkyl radical proceed *via* ring-opening isomerization to form the new alkyl radical. Finally, the new alkyl radical abstracts the indine atom of the other molecule C_4F_9I to give the corresponding product **4**.



Experimental procedure: a sealed reaction tube charged with a magnetic stir bar, prepared following general procedure using **1c** (28.8 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at room temperature. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **4** as colorless oil (73.5 mg, 75% yield of only *E* isomer). The *E/Z* (5: 1) ratio was determined by ^{1}H NMR analysis of the crude mixture. The *E/Z* ratio was determined by ^{1}H NMR at the vinylic proton of the product.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.98 (t, *J* = 7.3 Hz, 1H), 3.38 – 3.24 (m, 4H), 2.84 (q, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 135.0, 130.8, 128.6, 127.7, 126.5, 120.7 – 112.2 (m, 4C, -C_4F_9), 33.1, 31.5 (t, J_{C-F} = 22.1 Hz), 4.1, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.8 – -81.1 (m, 3F), -111.3 – -111.6 (m, 2F), -123.9 – -124.2 (m, 2F), -125.7 – -125.9 (m, 2F). **IR** (film): 3059, 3028, 2962, 1494, 1446, 1344, 1235, 1133, 1103, 1028, 879. **HRMS** (APCI) exact mass calculated for $[M-I]^+$: 369.0790, measured: 363.0782. Spectra are consistent with literature data.[8a]

3. Synthetic applicability

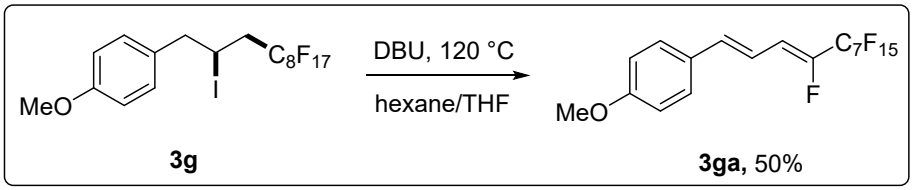
3.1 Gram scale experiments



A sealed reaction tube charged with a magnetic stir bar, prepared following general procedure using **1d** (7.0 mmol, 1.0 equiv), ethyl isonicotinate (1.4 mmol, 20 mol%), B_2pin_2 (1.4 mmol, 20 mol%),

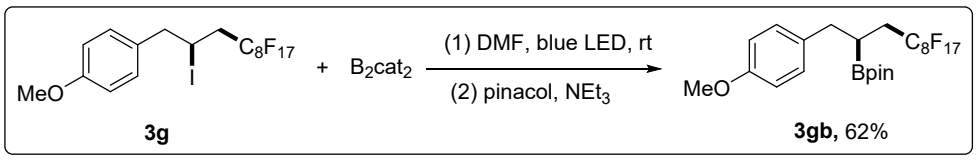
perfluoroalkyl iodides (14.0 mmol, 2.0 equiv) and MTBE (15 mL) at 40 °C. After 24 h, the reaction mixture was isolated with by flash chromatography on silica (PE/EA = 50:1) to afford the product **3d** in 80% yield or **3g** in 78% yield.

3.2 Product transformations



3g **3ga,** 50%

Experimental procedure: According to the literature procedure,[6] under argon atmosphere, a sealed reaction tube was charged with a magnetic stir bar, **3g** (0.2 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.6 mmol) and anhydrous *n*-hexane/THF (4:1, 1 mL) were added. The solution was stirred at 120 °C for 12 h. Then solvent was removed and the residue was purified by preparative TLC on silica gel (hexane/ethyl acetate = 50:1) to give product **3ga** as white solid in 50% yield. mp 77-78 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 6.92 – 6.88 (m, 2H), 6.88 – 6.72 (m, 2H), 6.33 – 6.19 (m, 1H), 3.83 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.1 – -81.8 (m, 3F), -116.2 – -118.1 (m, 2F), -118.8 – -125.2 (m, 8F), -125.6 – -127.0 (m, 2F), -131.1 – -132.8 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 145.4 (t, *J* = 29.1 Hz), 142.8 (t, *J* = 29.1 Hz), 13.84 – 138.2 (m), 128.7, 115.8 – 115.5 (m), 114.9, 114.4, 120.5 – 109.7 (m, 7C, -C_7F_{15}), 55.4. **IR** (film): 3044, 2970, 2939, 2842, 1678, 1621, 1604, 1513, 1371, 1307, 1251, 1199, 1143, 1104, 1023, 969, 814, **HRMS** (ESI-TOF) exact mass calculated for $[M]^+$: 546.0471, measured: 546.0461.



3g **3gb,** 62%

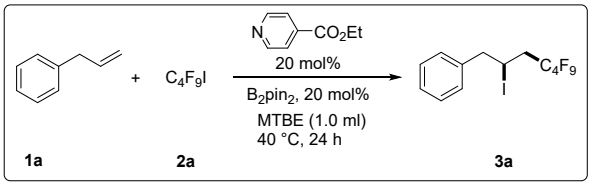
Experimental procedure: According to the literature procedure,[7] to a Schlenk tube were added the **3g** (0.2 mmol) and bis(catecholato)diboron (B_2cat_2), 0.8 mmol). The reaction vessel was evacuated and backfilled with Argon for three times. Dimethylformamide (0.6 mL) was added. The reaction mixture was stirred under blue LED irradiation at room temperature for 24 hours. A solution of pinacol (95 mg, 0.80 mmol) in triethylamine (0.7 mL) was added to the mixture. After 1 hour, water (15 mL) was added and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified by preparative TLC on silica gel (hexane/ethyl acetate = 50:1) to give the corresponding product **3gb** in 62% yield.

Experimental procedure for one-pot operation: (step 1) A sealed reaction tube charged with a magnetic stir bar, prepared following general procedure using **1d** (0.2 mmol, 1.0 equiv), ethyl

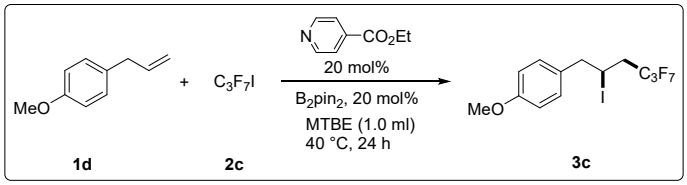
isonicotinate (20 mol%), B_2pin_2 (20 mol%), perfluoroalkyl iodides (2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture cooling to room temperature. The crude reaction solution was concentrated under reduced pressure, which was applied to the next step reaction. **(step 2)** To a schlenk tube was added the resulting crude reaction mixture of step 1, and bis(catecholato)diboron (B_2cat_2, 0.8 mmol). The reaction vessel was evacuated and backfilled with argon for three times. Dimethylformamide (0.6 mL) was added. The reaction mixture was stirred under blue LED irradiation at room temperature for 24 hours. A solution of pinacol (95 mg, 0.80 mmol) in triethylamine (0.7 mL) was added to the mixture. After 1 hour, water (15 mL) was added and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified by preparative TLC on silica gel (hexane/ethyl acetate = 50:1) to give the corresponding product **3gb** in 57% yield.

3gb: Colorless viscous oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 2H), 6.86 – 6.78 (m, 2H), 3.77 (s, 3H), 2.81 – 2.73 (m, 1H), 2.69 – 2.60 (m, 1H), 2.33 – 1.99 (m, 2H), 1.79 – 1.69 (m, 1H), 1.18 (s, 6H), 1.12 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3, 132.2, 129.9, 113.9, 122.4 – 106.3 (m, 4C, - C_4F_9), 83.7, 55.3, 36.0, 31.8 (t, J_{C-F} = 21.8 Hz), 24.8, 17.7, ^{13}C-NMR for C_4F_9 could not be assigned. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 – -81.1 (m, 3F), -111.1 – -113.6 (m, 2F), -121.71 – -122.10 (m, 6F), -122.7 – -122.9 (m, 2F), -123.6 – -123.8 (m, 2F), -126.2 – -126.4 (m, 2F). **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.6. **IR** (film): 2982, 2937, 2839, 1613, 1548, 1514, 1468, 1390, 1331, 1245, 1209, 1145, 1114, 1039, 966, 863. **HRMS** (ESI-TOF) exact mass calculated for $[M]^+$: 694.1542, measured: 694.1527.

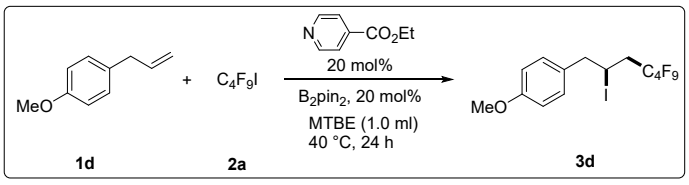
4. Spectroscopic Characterization of the Products



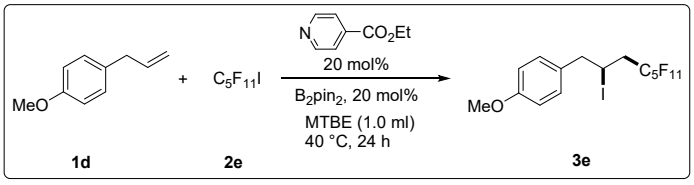
3a: Prepared following *general procedure* using **1a** (26.5 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **3a** as colorless oil (71.5 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 3H), 7.24 – 7.18 (m, 2H), 4.52 – 4.43 (m, 1H), 3.34 – 3.20 (m, 2H), 2.98 – 2.83 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 129.1, 128.8, 127.5, 122.0 – 113.9 (m, 3C, - C_3F_7), 47.2, 40.8 (t, J_{C-F} = 20.9 Hz), 19.4, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – -81.1 (m, 3F), -111.9 – -114.4 (m, 2F), -124.4 – -124.6 (m, 2F), -125.8 – -125.9 (m, 2F). **IR (film)**: 3031, 2927, 1603, 1497, 1349, 1221, 1134, 1019, 728. **HRMS** (APCI) exact mass calculated for $[M-I]^+$: 337.0633, measured: 337.0625. Spectra are consistent with literature data.[8b]



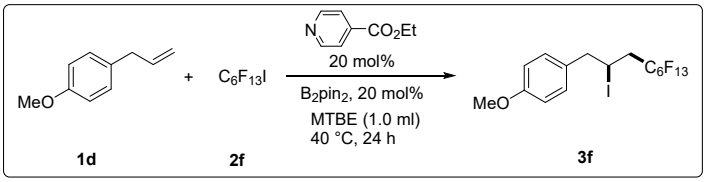
3c: Prepared following *general procedure* using **1d** (30.7 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2c** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **3c** as colorless oil (71.0 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.09 (m, 2H), 6.91 – 6.84 (m, 2H), 4.47 – 4.38 (m, 1H), 3.82 (s, 3H), 3.25 – 3.12 (m, 2H), 2.94 – 2.80 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 130.7, 130.1, 120.4 – 112.6 (m, 3C, - C_3F_7), 114.1, 55.3, 46.3, 40.4 (t, $J_{C\text{-}F}$ = 20.8 Hz), 20.2, ^{13}C-NMR for C_3F_7 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.3 – -180.4 (m, 3F), -112.6 – -115.0 (m, 2F), -127.7 – -127.9 (m, 2F). **IR** (film): 3002, 2921, 2838, 1612, 1513, 1353, 1250, 1226, 1178, 732. **HRMS** (ESI-TOF) exact mass calculated for $[M\text{-}I]^+$: 317.0771, measured: 317.0762.



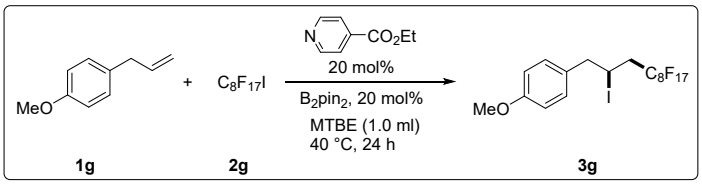
3d: Prepared following *general procedure* using **1d** (30.7 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **3d** as colorless oil (77.1 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) 7.16 – 7.07 (m, 2H), 6.93 – 6.85 (m, 2H), 4.46 – 4.38 (m, 1H), 3.81 (s, 3H), 3.25 – 3.13 (m, 2H), 2.94 – 2.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 130.8, 130.1, 121.0 – 109.2 (m, 4C, -C_4F_9), 114.1, 55.3, 46.3, 40.6 (t, $J_{C\text{-}F}$ = 20.9 Hz), 20.2, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.7 – -81.6 (m, 3F), -111.9 – -114.3 (m, 2F), -124.4 – -124.7 (m, 2F), -125.8 – -126.0 (m, 2F). **IR** (film): 3003, 2956, 2937, 1613, 1514, 1301, 1320, 1133, 736. **HRMS** (ESI-TOF) exact mass calculated for $[M\text{-}I]^+$: 367.0739, measured: 367.0738. Spectra are consistent with literature data.[8b]



3e: Prepared following *general procedure* using **1d** (30.7 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2e** (76.5 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **3e** as colorless oil (89.2 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 2H), 6.94 – 6.81 (m, 2H), 4.47 – 4.38 (m, 1H), 3.82 (s, 3H), 3.26 – 3.12 (m, 2H), 2.96 – 2.80 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) -80.8 – -81.04 (m, 3F), -111.6 – -114.2 (m, 2F), -122.4 – -122.8 (m, 2F), -123.7 – -123.9 (m, 2F), -126.2 – -126.4 (m, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 130.8, 130.1, 122.0 – 107.2 (m, 5C, $-C_5F_{11}$), 114.1, 55.3, 46.3, 40.7 (t, $J_{C\text{-}F}$ = 20.9 Hz), 20.3, ^{13}C-NMR for C_5F_{11} could not be assigned. **IR** (film): 3003, 2936, 2838, 1613, 1514, 1240, 1140, 1112, 871. **HRMS** (ESI-TOF) exact mass calculated for $[M\text{-}Na]^+$: 566.9649, measured: 566.9646. Spectra are consistent with literature data.[9b]

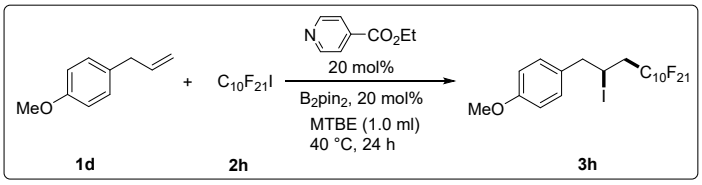


3f: Prepared following *general procedure* using **1d** (30.7 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2f** (86.5 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **3f** as colorless oil (99.8 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 2H), 6.93 – 6.82 (m, 2H), 4.47 – 4.38 (m, 1H), 3.81 (s, 3H), 3.25 – 3.11 (m, 2H), 2.95 – 2.77 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ158.9, 130.8, 130.1, 122.2 – 105.3 (m, 6C, $-C_6F_{13}$), 114.1, 55.3, 46.3, 40.7 (t, $J_{C\text{-}F}$ = 20.9 Hz), 20.3, ^{13}C-NMR for C_6F_{13} could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.6 – -81.5 (m, 3F), -111.7 – -114.0 (m, 2F), -121.7 – -121.9 (m, 2F), -122.7 – -123.0 (m, 2F), -123.6 – -123.7 (m, 2F), -126.1 – -126.4 (m, 2F). **IR** (film): 3002, 2958, 2838, 1613, 1301, 1248, 1114, 810. **HRMS** (ESI-TOF) exact mass calculated for $[M\text{-}I]^+$: 467.0675, measured: 467.0677. Spectra are consistent with literature data.[9a]

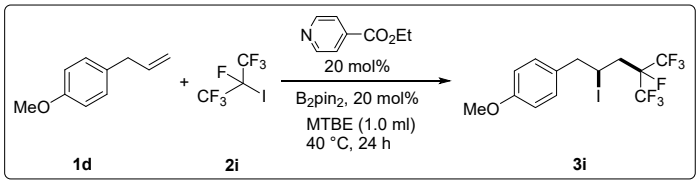


3g: Prepared following *general procedure* using **1d** (30.7 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2g** (105.7 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **3g** as white solid (119.4 mg, 86% yield).

mp 50-52 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 2H), 6.93 – 6.85 (m, 2H), 4.47 – 4.39 (m, 1H), 3.81 (s, 3H), 3.26 – 3.12 (m, 2H), 2.96 – 2.80 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 130.8, 130.2, 121.5 – 107.1 (m, 8C, -C_8F_{17}), 114.1, 55.3, 46.3, 40.8 (t, $J_{C\text{-}F}$ = 20.8 Hz), 20.4, ^{13}C-NMR for C_8F_{17} could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.8 – -81.2 (m, 3F), -111.70– -114.1 (m, 2F), -121.5 – -121.7 (m, 2F), -121.8 – -122.2 (m, 4F), -122.7 – -123.0 (m, 2F), -123.6 – -123.7 (m, 2F), -126.2 – -126.5 (m, 2F). **IR** (film): 3003, 2937, 2838, 1613, 1513, 1247, 1115, 1037, 807. **HRMS** (ESI-TOF) exact mass calculated for [M-I]$^+$: 567.0611, measured: 567.0612. Spectra are consistent with literature data.[9b]

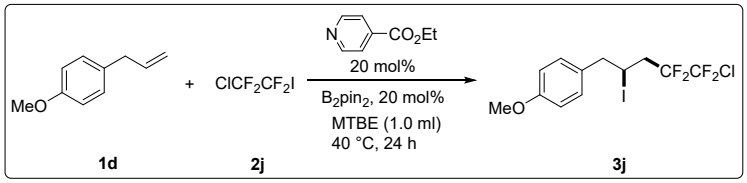


3h: Prepared following *general procedure* using **1d** (30.7 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2h** (258.4 mg, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **3h** as white solid (112.7 mg, 71% yield). mp 73-75 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 6.91 – 6.82 (m, 2H), 4.45 – 4.38 (m, 1H), 3.81 (s, 3H), 3.26 – 3.11 (m, 2H), 2.97 – 2.78 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 130.8, 130.1, 121.7 – 107.1 (m, 10C, -$C_{10}F_{21}$), 118.3, 118.0, 115.8, 115.4, 114.1, 55.3, 46.3, δ 40.79 (t, $J_{C\text{-}F}$ = 20.8 Hz), 20.4, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.8 – -81.2 (3m, F), -111.72 – -114.17 (m, 2F), -121.5 – -122.3 (m, 10F), -122.7 – -123.0 (m, 2F), -123.5 – -123.8 (m, 2F), -126. 1 – -126.4 (m, 2F). **IR** (film): 2936, 2839, 1613, 1514, 1210, 1150, 741. **HRMS** (ESI-TOF) exact mass calculated for [M-I]$^+$: 667.0547, measured: 667.0544.

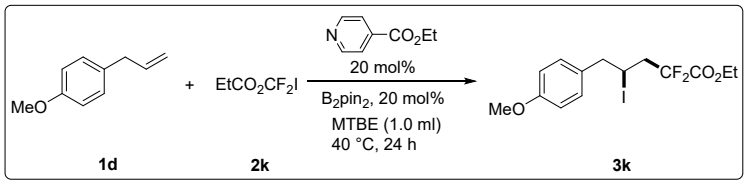


3i: Prepared following *general procedure* using **1d** (30.7 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2i** (118.4 mg, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **3i** as colorless oil (71.0 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 6.94 – 6.83 (m, 2H), 4.46 – 4.37 (m, 1H), 3.81 (s, 3H), 3.25 – 3.17 (m, 1H), 3.14 – 3.06 (m, 1H), 3.00 – 2.86 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 130.9, 13.14, 125.5 – 126.0 (m, 1C, -CF), 114.0, 93.6 – 90.3 (m, 2C, -2CF_3), 55.3, 46.7, 38.8 (d, $J_{C\text{-}F}$ =

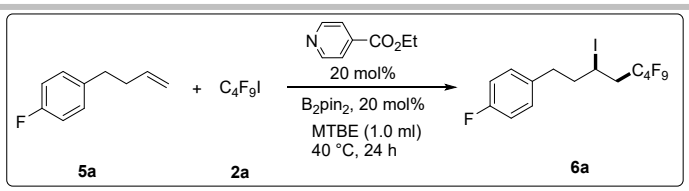
18.5 Hz), 22.7. ^{3}C-NMR for CF_3 and CF could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.4 – -76.6 (m, 3F), -76.7 – -78.1 (m, 3F), -185.0 – -185.6 (m, 1F). **IR** (film): 3001, 2935, 2838, 1613, 1514, 1301, 1222, 1611, 807. **HRMS** (ESI-TOF) exact mass calculated for $[M-I]^+$: 317.0771, measured: 317.0772. Spectra are consistent with literature data.[9c]



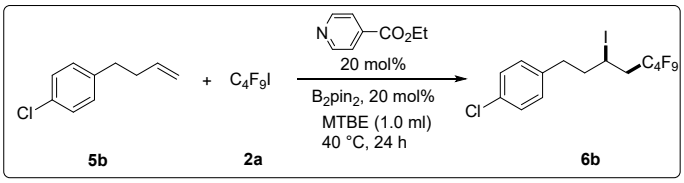
3j: Prepared following *general procedure* using **1d** (30.7 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2j** (105.0 mg, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **3j** as colorless oil (61.5 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) 7.16 – 7.11 (m, 2H), 6.92 – 6.84 (m, 2H), 4.47 – 4.38 (m, 1H), 3.81 (s, 3H), 3.26 – 3.12 (m, 2H), 2.95 – 2.82 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 130.8, 130.2, 124.7 – 115.3 (m, 2C, $-CF_2CF_2$), 114.0, 55.3, 46.2, 40.5 (t, J_{C-F} = 21.1 Hz), 21.1, ^{13}C-NMR for CF_2CF_2 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.5 – -71.6 (m, 2F), -111.29 – -113.89 (m, 2F). **IR** (film): 2962, 2837, 1688, 1620, 1614, 1259, 1086, 1032, 802. **HRMS** (ESI-TOF) exact mass calculated for $[M-Na]^+$: 432.9450, measured: 432.9446.



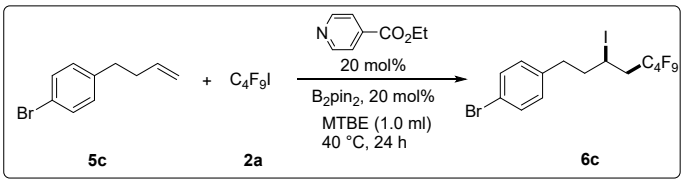
3k: Prepared following *general procedure* using **1d** (30.7 μL, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2k** (81.2 mg, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **3k** as colorless oil (63.7 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.09 (m, 2H), 6.90 – 6.82 (m, 2H), 4.36 – 4.28 (m, 2H), 3.80 (s, 3H), 3.19 – 3.12 (m, 2H), 2.92 – 2.74 (m, 2H), 1.36 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5 (t, J_{C-F} = 32.3 Hz), 158.8, 131.0, 130.1, 115.3 (t, J_{C-F} = 252.4 Hz, CF_2), 114.0, 63.3, 55.3, 46.5, 44.2 (t, J_{C-F} = 23.4 Hz), 22.8, 14.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.3 – -101.2 (m, 2F), -105.9 – -106.7 (m, 2F). **IR** (film): 2936, 2838, 1769, 1613, 1515, 1455, 1338, 1248, 1177, 1080, 838. **HRMS** (ESI-TOF) exact mass calculated for $[M-Na]^+$: 421.0083, measured: 421.0084. Spectra are consistent with literature data.[9a]



6a: Prepared following *general procedure* using **5a** (30.0 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6a** as colorless oil (79.4 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$). 7.21 – 7.16 (m, 2H), 7.05 – 6.94 (m, 2H), 4.28 – 4.21 (m, 1H), 3.00 – 2.88 (m, 2H), 2.85 – 2.65 (m, 2H), 2.15 – 2.06 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 244.3 Hz), 135.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.0 (d, $J_{C\text{-}F}$ = 7.9 Hz), 122.2 – 105.0 (m, 4C, - C_4F_9), 115.5 (d, $J_{C\text{-}F}$ = 21.3 Hz), 41.9, 41.8 (t, $J_{C\text{-}F}$ = 20.9 Hz), 35.0, 19.9, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.1 – -81.1 (m, 3F), -111.8 – -114.5 (m, 2F), -116.7 – -116.8 (m, 1F), -124.5 – -124.7 (m, 2F), -125.9 – -126.0 (m, 2F). **IR** (film): 3040, 2917, 2858, 1888, 1601, 1510, 1493, 1351, 1221, 1134, 1093, 880. **HRMS** (APCI) exact mass calculated for [M-I]$^+$: 369.0696, measured: 369.0692.

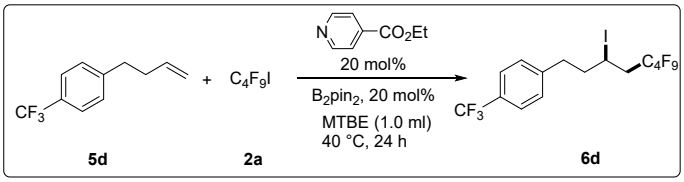


6b: Prepared following *general procedure* using **5b** (33.2 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **6b** as colorless oil (82.9 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 132.3, 129.9, 128.9, 122.8 – 105.4 (m, 4C, - C_4F_9), 41.7 (t, $J_{C\text{-}F}$ = 20.8 Hz), 41.6, 41.5, 35.2, 19.8. ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.17 – 7.13 (m, 2H), 4.28 – 4.19 (m, 1H), 2.99 – 2.71 (m, 4H), 2.17 – 2.01 (m, 2H). **IR** (film): 3028, 2927, 2857, 1895, 1598, 1493, 1351, 1234, 1134, 1093, 1016, 818. **HRMS** (APCI) exact mass calculated for [M-I]$^+$: 385.0400, measured: 385.0396.

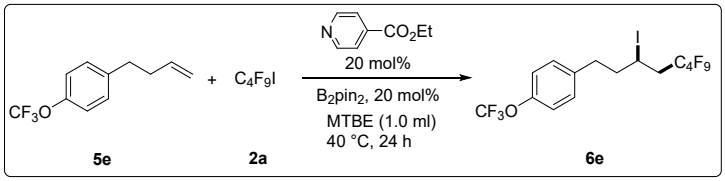


6c: Prepared following *general procedure* using **5c** (42.0 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4

mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **6c** as colorless oil (93.4 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.11 – 7.08 (m, 2H), 4.28 – 4.19 (m, 1H), 2.98 – 2.69 (m, 4H), 2.19 – 1.99 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.9, 131.8, 130.3, 120.3, 119.6 – 108.1 (m, 4C, - C_4F_9), 41.6 (d, $J_{C\text{-}F}$ = 20.0 Hz), 41.5, 35.2, 19.8, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ. -81.9 – -81.1 (m, 3F), -111.10 – -115.16 (m, 2F), -124.4 – -124.7 (m, 2F), -125.86 – -125.99 (m, 2F). **IR** (film): 3024, 2927, 2858, 1898, 1591, 1488, 1233, 1134, 1012, 842, 736. **HRMS** (APCI) exact mass calculated for $[M\text{-}I]^+$: 428.9895, measured: 428.9897. Spectra are consistent with literature data.[9d]

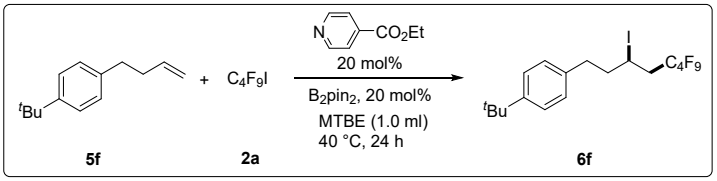


6d: Prepared following *general procedure* using **5d** (40.0 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **6d** as colorless oil (93.4 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$). δ 7.57 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 4.29 – 4.21 (m, 1H), 3.06 – 2.91 (m, 2H), 2.88 – 2.74 (m, 2H), 2.20 – 2.07 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) 144.1, 129.1 (d, $J_{C\text{-}F}$ = 32.4 Hz), 129.0, 125.7 (d, $J_{C\text{-}F}$ = 3.7 Hz), 123.0, 122.2 – 105.4 (m, 4C, - C_4F_9), 41.8 (t, $J_{C\text{-}F}$ = 20.8 Hz), 41.4, 35.7, 19.6, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.4 – -62.5 (m, 3F), -81.0 – -81.2 (m, 3F), -111.0 – -115.2 (m, 2F), -124.5 – -124.7 (m, 2F), -125.8 – -126.0 (m, 2F). **IR** (film): 2927, 2856, 1620, 1434, 1326, 1130, 1067, 1019, 822. **HRMS** (APCI) exact mass calculated for $[M\text{-}H_2I]^{\cdot-}$: 417.0518, measured: 417.0512.

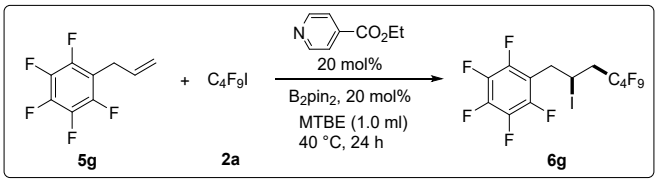


6e: Prepared following *general procedure* using **5e** (43.2 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **6e** as colorless oil (78.7 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 4.33 – 4.26 (m, 1H), 3.05 – 2.68 (m, 4H), 2.19 – 2.02 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 138.7, 129.9, 131.4 – 108.1 (m, 5C, OCF_3 and C_4F_9), 121.3, 41.7 (d, $J_{C\text{-}F}$ = 20.9 Hz), 41.7, 35.2, 19.7, ^{13}C-NMR for OCF_3 and

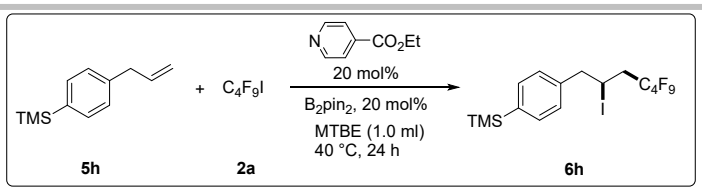
C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.0 – -58.1 (m, 3F), -81.1 – -81.2 (m, 3F), -111.0 – -115.3 (m, 2F), -124.5 – -124.7 (m, 2F), -125.96 – -126.07 (m, 2F). **IR** (film): 3042, 2930, 2862, 1510, 1434, 1351, 1224, 1134, 845. **HRMS** (APCI) exact mass calculated for $[M-I]^+$: 435.0613, measured: 435.0612.



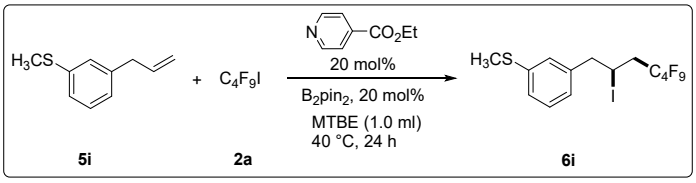
6f: Prepared following *general procedure* using **5f** (37.6 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **6f** as colorless oil (79.0 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.21 – 7.15 (m, 2H), 4.36 – 4.28 (m, 1H), 3.01 – 2.71 (m, 4H), 2.23 – 2.06 (m, 2H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 136.9, 128.2, 125.6, 121.1 – 108.1 (m, 4C, -C_4F_9), 41.9, 41.7 (t, J_{C-F} = 20.9 Hz), 35.3, 34.5, 31.5, 20.2, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – 81.1 (m, 3F), -111.28 – -115.01 (m, 2F), -124.56 (m, 2F), -125.86 – -125.98 (m, 2F). **IR** (film): 2964, 2868, 1697, 1515, 1463, 1351, 1235, 1134, 880. **HRMS** (ESI-TOF) exact mass calculated for $[M-Na]^+$: 557.0358, measured: 557.0367.



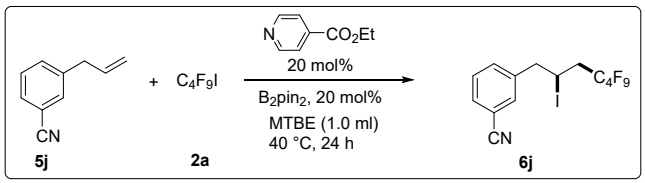
6g: Prepared following *general procedure* using **5g** (41.6 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **6g** as colorless oil (66.5 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) 4.57 – 4.47 (m, 1H), 3.44 – 3.28 (m, 2H), 3.11 – 2.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.3 (dm, J = 247.2 Hz), 140.8 (dm, J = 252.0 Hz), 137.8 (dm, J = 253.1 Hz), 122.2 – 114.5 (m, 4C, -C_4F_9), 113.6 – 112.7 (m), 42.0 (t, J = 21.1 Hz), 33.9, 14.6, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.1 – 81.2 (m, 3F), -111.18 – -115.14 (m, 2F), -124.4 – -124.6 (m, 2F), -126.8 – -126.2 (m, 2F), -142.30 – -142.39 (m, 2F), -154.6 – -154.7 (m, 1F), -161.72 – -161.86 (m, 2F). **IR** (film): 1657, 1523, 1506, 1433, 1236, 1134, 1041, 1010, 880. **HRMS** (APCI) exact mass calculated for $[M-I]^+$: 427.0162, measured: 427.0180.



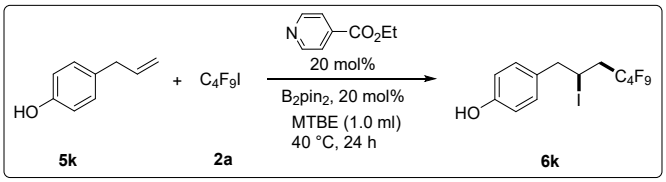
6h: Prepared following *general procedure* using **5h** (38.0 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **6h** as colorless oil (75.0 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.21 – 7.18 (m, 2H), 4.51 – 4.44 (m, 1H), 3.32 – 3.18 (m, 2H), 2.96 – 2.83 (m, 2H), 0.28 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.6, 139.0, 133.8, 128.4, 121.3 – 114. (m, 4C, -C_4F_9), 47.1, 40.8 (t, J_{C-F} = 20.9 Hz), 19.1, 1.0, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – -81.1 (m, 3F), -111.87 – -114.31 (m, 2F), -124.4 – -124.6 (m, 2F), -125.8 – -125.9 (m, 2F). **IR** (film): 3014, 2956, 2898, 1601, 1350, 1235, 1135, 1109, 840. **HRMS** (APCI) exact mass calculated for $[M-I]^+$: 409.1029, measured: 409.1024.



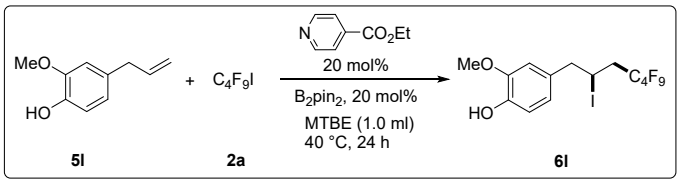
6i: Prepared following *general procedure* using **5i** (32.8 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 50:1) to afford the product **6i** as Colorless oil (58.1 mg, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 7.24 – 7.20 (m, 1H), 7.13 – 7.10 (m, 1H), 7.01 – 6.97 (m, 1H), 4.52 – 4.42 (m, 1H), 3.33 – 3.17 (m, 2H), 3.00 – 2.84 (m, 2H), 2.52 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.3, 139.1, 129.1, 127.2, 125.7, 125.5, 124.5 – 110.2 (m, 4C, -C_4F_9), 46.8, 40.9 (t, J_{C-F} = 20.9 Hz), 19.1, 15.8, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – -81.2 (m, 3F), -111.6 – -114.5 (m, 2F), -124.3 – -124.6 (m, 2F), -125.7 – -126.7 (m, 2F). **IR** (film): 2984, 2923, 2853, 1592, 1476, 1429, 1349, 1235, 1134, 1095, 877. **HRMS** (APCI) exact mass calculated for $[M-H]^-$: 508.9488, measured: 508.9469.



6j: Prepared following *general procedure* using **5j** (28.6 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 10:1) to afford the product **6j** as colorless oil (68.4 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 1H), 7.51 (s, 1H), 7.47 – 7.45 (m, 2H), 4.43 – 4.38 (m, 1H), 3.42 – 3.34 (m, 1H), 3.17 – 3.10 (m, 1H), 3.03 – 2.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 133.5, 132.6, 131.2, 129.5, 121.2 – 106.3 (m, 4C, -C_4F_9), 118.6, 112.8, 45.9, 41.3 (t, J_{C-F} = 20.9 Hz), 18.8, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.9 – -81.1 (m, 3F), -110.97 – -114.60 (m, 2F), -124.3 – -124.6 (m, 2F), -125.8 – -126.0 (m, 2F). **IR** (film): 3066, 2931, 2231, 1602, 1485, 1431, 1350, 1221, 1134, 1019, 879. **HRMS** (APCI) exact mass calculated for [M-I]$^+$: 362.0586, measured: 362.0581.

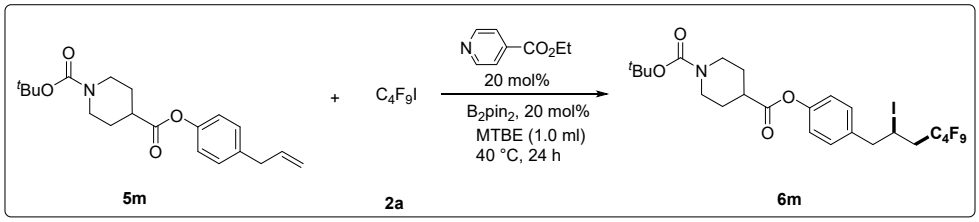


6k: Prepared following *general procedure* using **5k** (26.8 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 10:1) to afford the product **6k** as colorless oil (57.6 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 – 7.05 (m, 2H), 6.87 – 6.75 (m, 2H), 5.38 (s, 1H), 4.45 – 4.38 (m, 1H), 3.22 – 3.10 (m, 2H), 2.94 – 2.79 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 131.0, 130.4, 126.6 – 108.9 (m, 4C, -C_4F_9), 115.6, 46.3, 40.6 (t, J_{C-F} = 20.9 Hz), 20.3, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – 81.1 (m, 3F), -111.89 – -114.32 (m, 2F), -124.4 – -124.6 (m, 2F), -125.8 – -126.0 (m, 2F). **IR** (film): 3375, 3024, 2928, 2692, 1715, 1613, 1515, 1444, 1351, 1233, 1134, 1094, 881. **HRMS** (APCI) exact mass calculated for [M-I]$^+$: 353.0582, measured: 353.0574.

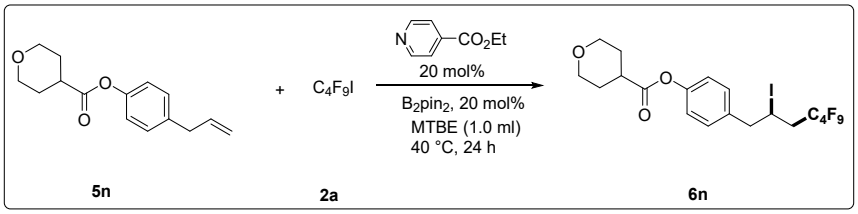


6l: Prepared following *general procedure* using **5l** (32.8 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 10:1) to afford the product **6l** ac colorless oil (61.2 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.90 – 6.87 (m, 1H), 6.71 – 6.68 (m, 2H), 5.63 (br, 1H), 4.46 – 4.40 (m,

1H), 3.90 (s, 3H), 3.23 – 3.10 (m, 2H), 2.95 – 2.78 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.6, 145.0, 130.5, 122.0, 121.2 – 108.3 (m, 4C, -C_4F_9), 114.6, 111.5, 56.0, 46.9, 40.5 (t, J_{C-F} = 20.9 Hz), 19.9, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.1 – -82.2 (m, 3F), -110.99 – -115.59 (m, 2F), -124.07 – -124.99 (m 2F), -125.49 – -126.44 (m, 2F). **IR** (film): 3513, 3007, 2940, 2846, 1613, 1517, 1432, 1353, 1271, 1237, 1134, 1035, 880. **HRMS** (APCI) exact mass calculated for [M-I]$^+$: 383.0688, measured: 383.0682.

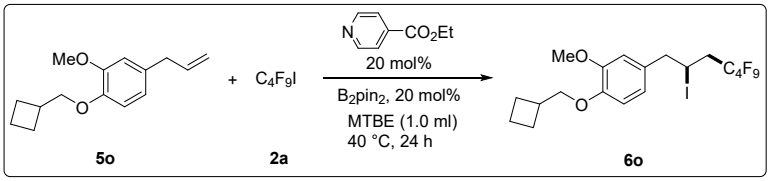


6m: Prepared following *general procedure* using **5m** (69.0 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6m** as colorless viscous oil (55.3 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.08 – 7.01 (m, 2H), 4.47 – 4.39 (m, 1H), 4.07 (s, 2H), 3.32 – 3.13 (m, 2H), 2.98 – 2.80 (m, 4H), 2.75 – 2.65 (m, 1H), 2.06 – 1.99 (m, 2H), 1.83 – 1.70 (m, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 154.8, 149.9, 136.2, 130.1, 121.7, 121.0 – 113.7 (m, 4C, -C_4F_9), 79.8, 46.2, 42.8, 41.3, 40.9 (t, J_{C-F} = 20.9 Hz), 28.5, 28.0, 19.3, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – -91.1 (m, 3F), -111.62 – -114.43 (m, 2F), -124.3 – -12.6 (m, 2F), -125.7 – -126.0 (m, 2F). **IR** (film): 3478, 2978, 2933, 2862, 1757, 1696, 1508, 1450, 1426, 1367, 1236, 1167, 1030, 879. **HRMS** (APCI) exact mass calculated for [M-H_2I]$^+$: 562.1645, measured: 562.1635.

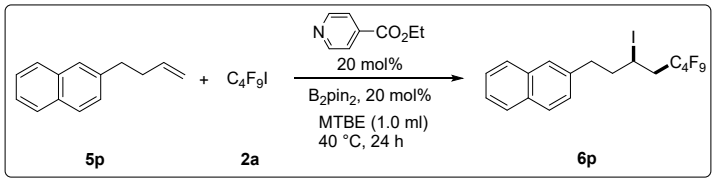


6n: Prepared following *general procedure* using **5n** (49.2 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6n** as colorless viscous oil (69.2 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.08 – 7.03 (m, 2H), 4.47 – 4.37 (m, 1H), 4.07 – 3.98 (m, 2H), 3.55 – 3.46 (m, 2H), 3.33 – 3.25 (m, 1H), 3.20 – 3.13 (m, 1H), 2.97 – 2.76 (m, 3H), 2.03 – 1.88 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 149.9, 136.2, 130.1, 121.7, 120.9 – 106.9 (m, 4C,

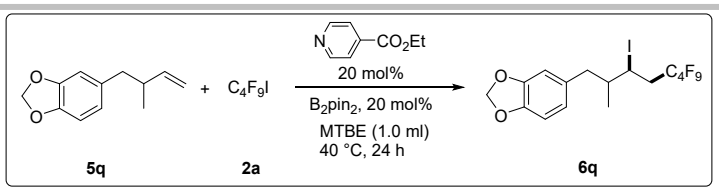
-C_4F_9), 67.1, 46.2, 40.9 (t, J = 20.9 Hz), 40.3, 28.6, 19.4. ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – -81.1 (m, 3F), -111.60 – -114.43 (m, 2F), -124.4 – -124.6 (m, 2F), -125.8 – -126.0 (m, 2F). **IR** (film): 3036, 2960, 2931, 2850, 1754, 1508, 1350, 1221, 1134. 1093, 880. **HRMS** (ESI-TOF) exact mass calculated for $[M+H]^+$: 593.0230, measured: 593.0219.



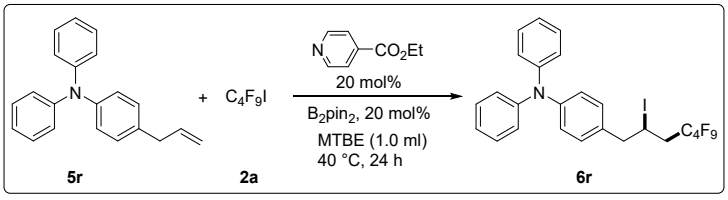
6o: Prepared following *general procedure* using **5o** (46.4 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 10:1) to afford the product **6o** as white solid (98.3 mg, 85% yield). mp 66-67 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.86 – 6.82 (m, 1H), 6.75 – 6.67 (m, 2H), 4.48 – 4.39 (m, 1H), 4.01 – 3.95 (m, 2H), 3.86 (s, 3H), 3.24 – 3.13 (m, 2H), 2.95 – 2.75 (m, 3H), 2.22 – 2.10 (m, 2H), 2.01 – 1.81 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.6, 148.2, 131.2, 121.4, 121.0 – 106.8 (m, 4C, -C_4F_9), 113.5, 113.0, 73.5, 56.2, 46.8, 40.4 (t, J_{C-F} = 20.8 Hz), 34.7, 25.2, 19.6, 18.7, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.00 – -81.19 (m, 3F), -112.11 – -114.28 (m, 2F), -124.57 – -124.64 (m, 2F), -125.8 – -126.0 (m, 2F). **IR** (film): 2937, 2862, 1606, 1515, 1465, 1420, 1352, 1235, 1134, 1038, 879. **HRMS** (APCI) exact mass calculated for $[M-I]^+$: 451.1314, measured: 451.1308.



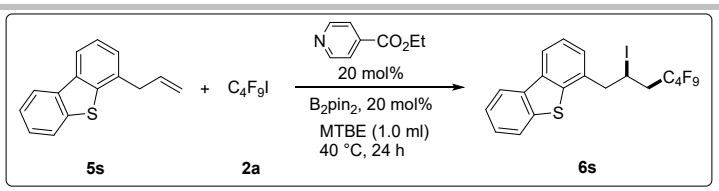
6p: Prepared following *general procedure* using **5p** (36.4 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 10:1) to afford the product **6p** as colorless oil (68.6 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 3H), 7.70 – 7.66 (m, 1H), 7.51 – 7.45 (m, 2H), 7.37 – 7.32 (m, 1H), 4.35 – 4.26 (m, 1H), 3.14 – 2.99 (m, 2H), 2.94 – 2.88 (m, 2H), 2.25 – 2.20 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.4, 133.7, 132.3, 128.4, 127.8, 127.6, 127.0, 126.9, 126.2, 125.6, 122.7 – 114.8 (m, 4C, -C_4F_9), 41.7 (t, J_{C-F} = 20.8 Hz), 41.7, 36.0, 20.1, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.8 – -81.1 (m, 3F), -111.14 – -115.05 (m, 2F), -124.4 – -124.6 (m, 2F), -125.7 – - 125.9 (m, 2F). **IR** (film): 3054, 2927, 2856, 1908, 1634, 1601, 1508, 1232, 1133, 1019, 816. **HRMS** (ESI-TOF) exact mass calculated for $[M-I]^+$: 401.0946, measured: 401.0945.



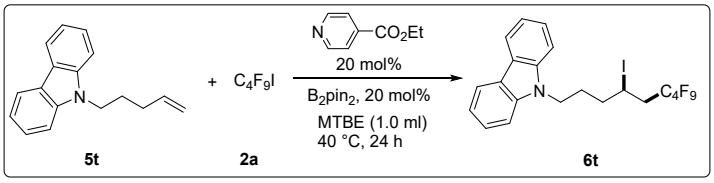
6q: Prepared following *general procedure* using **5q** (38.4 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 10:1) to afford the product **6q** as colorless oil (76.4 mg, 70% yield, d. r. = 1: 1.9). The two diastereomers were not separated by preparative TLC. Reported as a mixture of diastereomers. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.78 – 6.54 (m, 3H), 5.95 – 5.92 (m, 2H), 4.49 – 4.43 (m, 0.34H), 4.36 – 4.29 (m, 0.66H), 2.93 – 2.76 (m, 2H), 2.62 – 2.22 (m, 2H), 1.49 – 1.39 (m, 0.34H), 1.15 – 1.04 (m, 0.66H), 1.01 – 0.89 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 146.3, 146.2, 132.9, 132.7, 122.2, 122.1, 121.4 – 114.7 (m, 4C, -C_4F_9), 109.5, 109.4, 108.4, 108.3, 101.1, 101.0, 43.9, 41.8, 41.8, 40.6, 40.5, 40.0, 39.7 (t, $J_{C\text{-}F}$ = 20.4 Hz), 38.8 (t, $J_{C\text{-}F}$ = 20.9 Hz), 31.3, 29.5, 20.1, 17.1, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.6 – -81.5 (m, 3F), -110.2 – -116.7 (m, 2F), -123.1 –125.0 (m, 2F), -125.5 – -126.7 (m, 2F). **IR** (film): 2968, 2931, 2894, 1609, 1504, 1490, 1441, 1347, 1244, 1135, 1042, 941, 844. **HRMS** (APCI) exact mass calculated for $[M\text{-}I]^+$: 409.0845, measured: 409.0838.



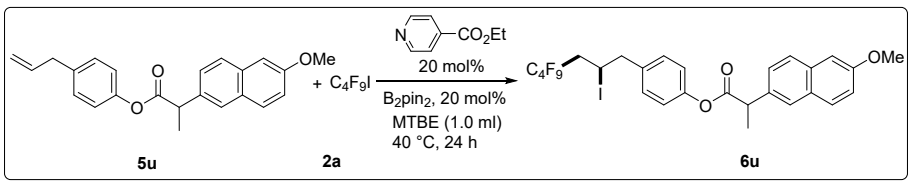
6r: Prepared following *general procedure* using **5r** (57.0 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6r** as colorless oil (75.7 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.06 (m, 4H), 7.00 – 6.86 (m, 10H), 4.36 – 4.26 (m, 1H), 3.14 – 3.01 (m, 2H), 2.88 – 2.66 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 147.0, 132.5, 130.2, 129.8, 129.2, 124.3, 123.8, 122.9, 120.6 –114.3 (m, 4C, -C_4F_9), 46.5, 40.5 (t, $J_{C\text{-}F}$ = 20.9 Hz), 19.4, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – -81.1 (m, 3F), -112.1 – -113.8 (m, 2F), -124.4 – -124.7 (m, 2F), -125.7 – -125.9 (m, 2F). **IR** (film): 3062, 3034, 2926, 1941, 1791, 1593, 1510, 1494, 1236, 1133, 1028, 880. **HRMS** (ESI-TOF) exact mass calculated for $[M\text{-}I]^+$: 504.1368, measured: 504.1364.



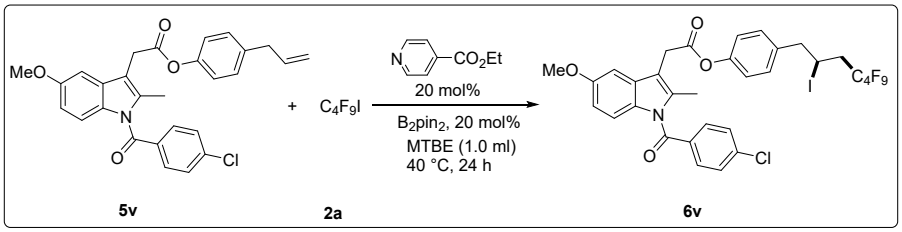
6s: Prepared following *general procedure* using **5s** (44.8 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6s** as white solid (62.7 mg, 55% yield). mp 54-57 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 – 8.10 (m, 2H), 7.93 – 7.84 (m, 1H), 7.50 – 7.46 (m, 3H), 7.52 – 7.44 (m, 1H), 4.91 – 4.80 (m, 1H), 3.63 – 3.47 (m, 2H), 3.12 – 2.91 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.3, 138.8, 136.3, 136.0, 133.4, 127.5, 127.1, 124.9, 124.7, 123.0, 121.9, 120.9, 120.6 – 107.8 (m, 4C, -C_4F_9), 46.7, 41.4 (t, J_{C-F} = 20.9 Hz), 16.3, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.8 – -81.0 (m, 3F), -111.6 – -114.4 (m, 2F), -124.4 (m, 2F), -125.7 – -125.9 (m, 2F). **IR** (film): 3066, 2932, 1585, 1441, 1403, 1349, 1221, 1134, 1090, 879. **HRMS** (APCI) exact mass calculated for $[M-I]^+$: 443.0511, measured: 443.0504.



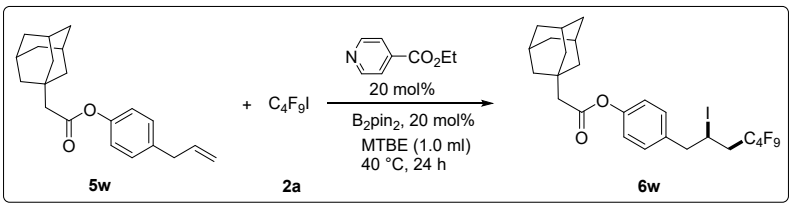
6t: Prepared following *general procedure* using **5t** (47.0 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6t** as colorless oil (75.5 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 – 8.11 (m, 2H), 7.56 – 7.48 (m, 2H), 7.46 – 7.39 (m, 2H), 7.33 – 7.24 (m, 2H), 4.41 – 4.17 (m, 3H), 2.97 – 2.69 (m, 2H), 2.24 – 2.16 (m, 1H), 2.09 – 2.02 (m, 1H), 1.94 – 1.84 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.3, 125.9, 123.1, 120.6, 120.3 – 111.5 (m, 4C, -C_4F_9), 119.2, 108.6, 41.9, 41.4 (t, J_{C-F} = 20.8 Hz), 37.7, 29.1, 19.2, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – -81.0 (m, 3F), -111.73 – -115.01 (m, 2F), -124.4 – -124.6 (m, 2F), -125.7 – -125.9 (m, 2F). **IR** (film): 3052, 2936, 2879, 1627, 1485, 1349, 1235, 1134, 880. **HRMS** (APCI) exact mass calculated for $[M-I]^+$: 454.1212, measured: 454.1203.



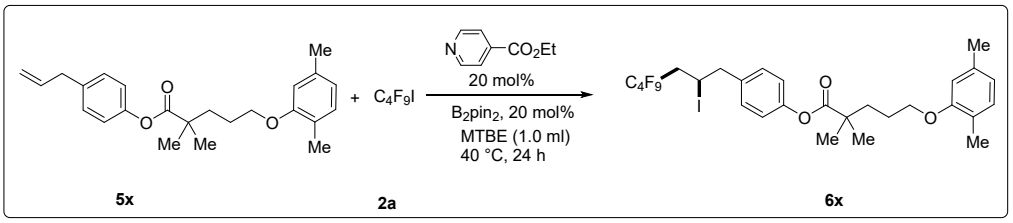
6u: Prepared following *general procedure* using **5u** (69.2 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6u** as colorless viscous oil (96.9 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 3H), 7.54 – 7.48 (m, 1H), 7.20 – 7.12 (m, 4H), 7.01 – 6.93 (m, 2H), 4.45 – 4.35 (m, 1H), 4.14 – 4.08 (m, 1H), 3.93 (s, 3H), 3.29 – 3.12 (m, 2H), 2.99 – 1.75 (m, 2H), 1.73 – 1.67 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 157.9, 150.1, 136.1, 135.2, 133.9, 130.0, 129.4, 129.1, 127.5, 126.3, 121.7, 121.3, 121.2 – 108.6 (m, 4C, -C_4F_9), 119.2, 105.7, 55.4, 46.2, 45.7, 40.8 (t, J_{C-F} = 20.9 Hz), 19.3, 18.5, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.8 – -81.1 (m. 3F), -111.59 – -114.45 (m, 2F), -124.4 – -124.6 (m, 2F), -125.7 – -125.9 (m, 2F). **IR** (film): 2978, 2937, 2841, 1754, 1606, 1507, 1222, 1167, 1134, 1071, 1033, 853. **HRMS** (APCI) exact mass calculated for $[M+H]^+$: 693.0543, measured: 693.0526.



6v: Prepared following *general procedure* using **5v** (94.6 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6v** as white solid (81.9 mg, 50% yield). mp 55-56 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.50 – 7.44 (m, 2H), 7.21 – 7.17 (m, 2H), 7.07 – 7.03 (m, 3H), 6.90 – 6.87 (m, 1H), 6.71 – 6.67 (m, 1H), 4.43 – 4.39 (m, 1H), 3.90 (s, 2H), 3.84 (s, 3H), 3.31 – 3.23 (m, 1H), 3.18 – 3.09 (m, 1H), 2.98 – 2.79 (m, 2H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 168.4, 156.2, 150.6, 150.0, 139.5, 136.3, 133.9, 131.3, 130.9, 130.6, 130.1, 129.2, 121.6, 120.7 – 107.0 (m, 4C, -C_4F_9), 115.1, 112.0, 111.9, 101.3, 55.8, 46.2, 40.9 (t, J_{C-F} = 20.9 Hz), 30.7, 19.4, 13.5, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.8 – -81.1 (m, 3F), -111.53 – -114.44 (m, 2F), -124.3 – -124.5 (m, 2F), -125.7 – -125.9 (m, 2F). **IR** (film): 3486, 3052, 2946, 2846, 1751, 1674, 1616, 1595, 1507, 1440, 1358, 1324, 1231, 1108, 1071, 878. **HRMS** (APCI) exact mass calculated for $[M+H]^+$: 820.0368, measured: 820.0367.



6w: Prepared following *general procedure* using **5w** (62.0 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6w** as colorless viscous oil (91.8 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 7.10 – 7.04 (m, 2H), 4.47 – 4.39 (m, 1H), 3.32 – 3.14 (m, 2H), 2.98 – 2.80 (m, 2H), 2.30 (s, 2H), 2.02 (t, *J* = 3.1 Hz, 3H), 1.76 – 1.66 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 150.0, 135.9, 130.0, 122.0, 120.8 – 109.4 (m, 4C, -C_4F_9), 48.8, 46.3, 42.6, 40.91 (t, J_{C-F} = 20.9 Hz), 36.8, 33.3, 28.7, 19.4, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – -81.1 (m, 3F), -111.6 – -114.3 (m, 3F), -124.4 – -124.6 (m, 2F), -125.8 – -125.9 (m, 2F). **IR** (film): 2905, 2849, 1754, 1508, 1452, 1349, 1235, 1134, 1098, 881. **HRMS** (APCI) exact mass calculated for $[M-I]^+$: 529.1784, measured: 529.1773.



6x: Prepared following *general procedure* using **5x** (73.2 mg, 0.2 mmol, 1.0 equiv), ethyl isonicotinate (6.0 μL, 0.04 mmol, 20 mol%), B_2pin_2 (10.2 mg, 0.04 mmol, 20 mol%), **2a** (68.9 μL, 0.4 mmol, 2.0 equiv) and MTBE (1 mL) at 40 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **6x** as colorless viscous oil (111.1 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 7.07 – 6.99 (m, 3H), 6.72 – 6.63 (m, 2H), 4.48 – 4.41 (m, 1H), 4.05 – 3.95 (m, 2H), 3.31 – 3.24 (m, 1H), 3.21 – 3.12 (m, 1H), 3.00 – 2.80 (m, 2H), 2.33 (s, 3H), 2.20 (s, 3H), 1.93 – 1.84 (m, 4H), 1.39 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ. 176.3, 156.9, 150.3, 136.5, 135.9, 130.4, 130.0, 123.7, 121.8, 120.8, 112.0, 121.4 – 108.0 (m, 4C, -C_4F_9), 67.8, 46.2, 42.5, 40.8 (t, J_{C-F} = 20.8 Hz), 37.2, 25.3, 25.2, 25.2, 21.4, 19.3, 15.8, ^{13}C-NMR for C_4F_9 could not be assigned. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.9 – -81.1 (m, 3F), -111.61 – -114.37 (m, 2F), -124.4 – -124.5 (m, 2F), -125.7 – -125.9 (m, 2F). **IR** (film): 2951, 2871, 1750, 1614, 1508, 1474, 1235, 1132, 1066, 881. **HRMS** (APCI) exact mass calculated for $[M+H]^+$: 713.1169, measured: 713.1150.

5. Computational Investigations

5.1 Computational methods

All calculations were performed with the Gaussian 16 package.[10] A “broken-symmetry” guess was used for calculations on open-shell systems. Geometry structures of all the stationary points were optimized by using the M06-2X[11] method. The LANL2DZ basis set is employed for the iodine atom, and the 6-31G(d,p) basis set is used for all the other atoms. At the same level of theory, vibrational

frequencies of all the stationary points were further calculated to check the nature of the minima and the transition states. To confirm that each transition state connects the desired reactants and products along the reaction path, we performed intrinsic reaction coordinate (IRC)[12] calculations at the same level. To obtain reliable energies, single point energies (Esol) were computed using M06-2X method with a larger basis set. The cc-PVTZ basis set is used for all the other atoms (the LANL2DZ basis set for the iodine atom). The solvent effect was treated with the polarizable continuum model (PCM) with benzene as the solvent.[13] The 3D structures were generated with CLY view.[14]

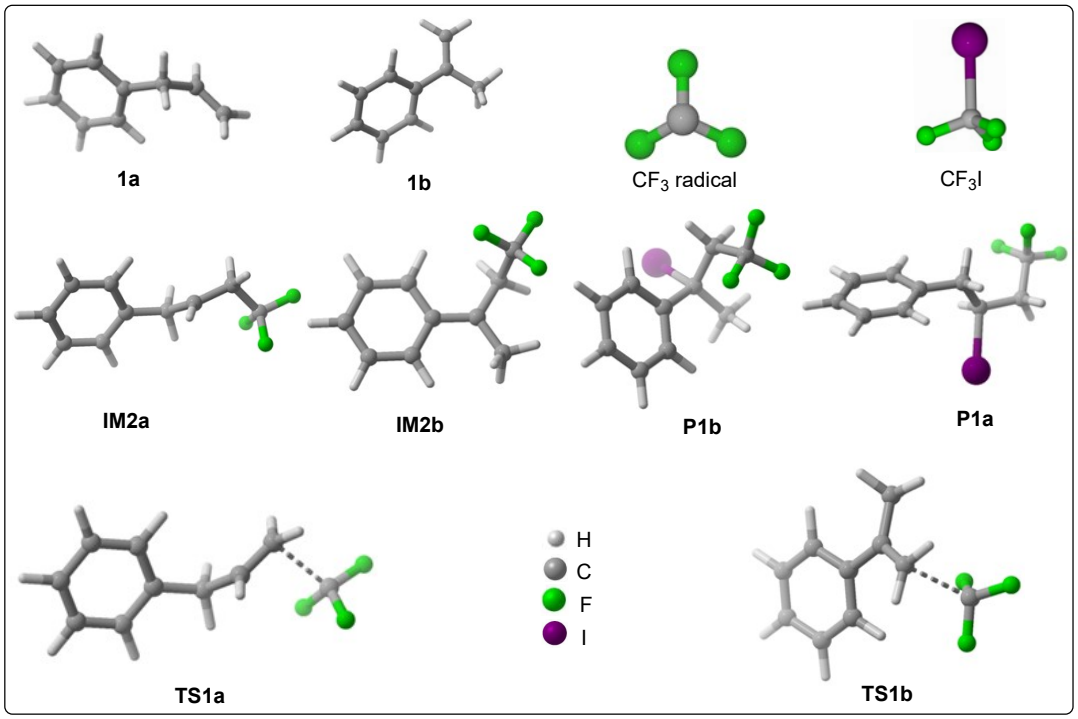


Figure S4. Optimized structures of reactants, product and intermediates for the atom transfer radical addition process with allylbenzene **1a** and α-methylstyrene **1b**

5.2 Computational mechanism studies on the reaction of alpha-cyclopropylstyrene **1c** and CF_3 radical.

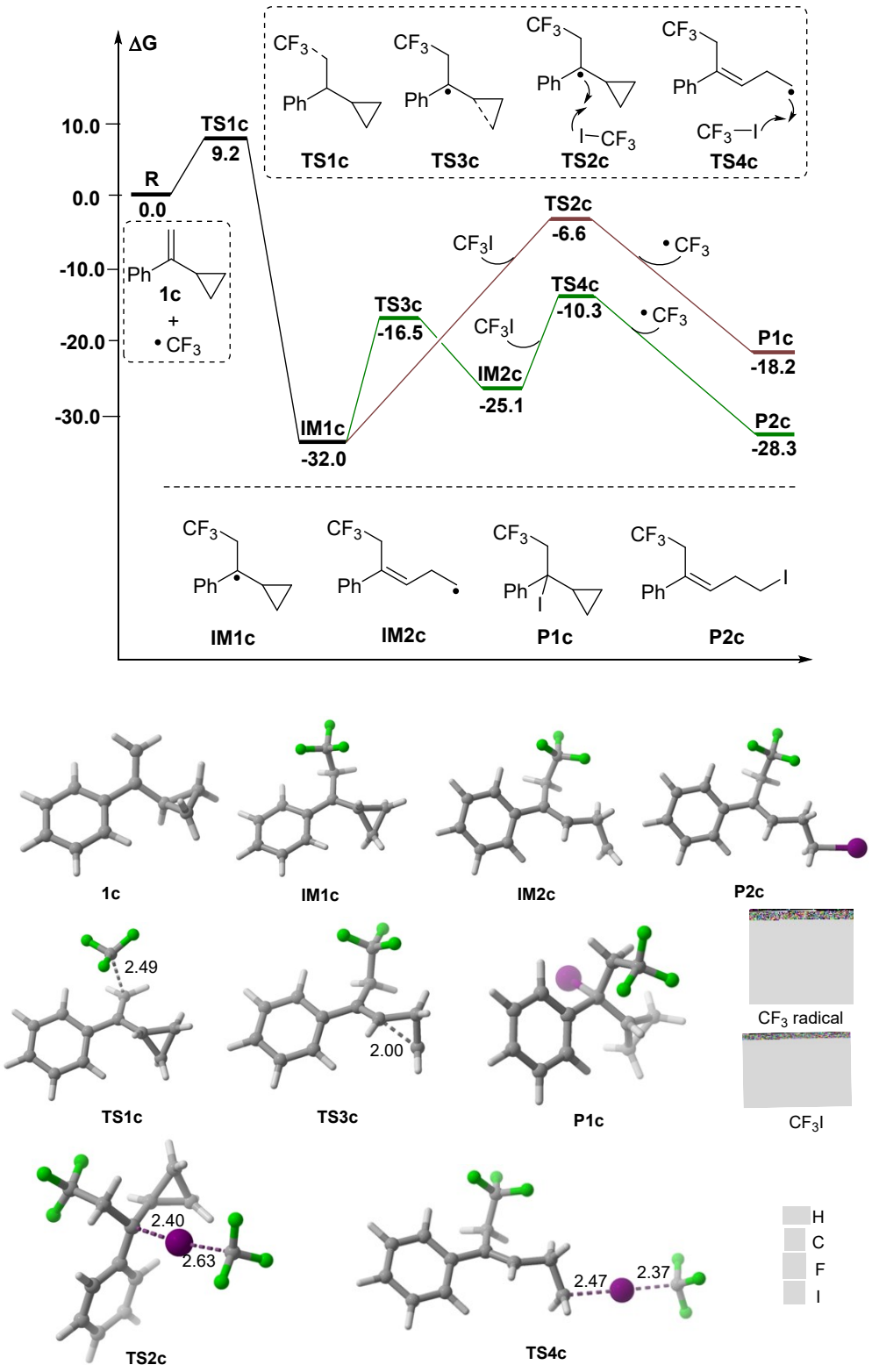


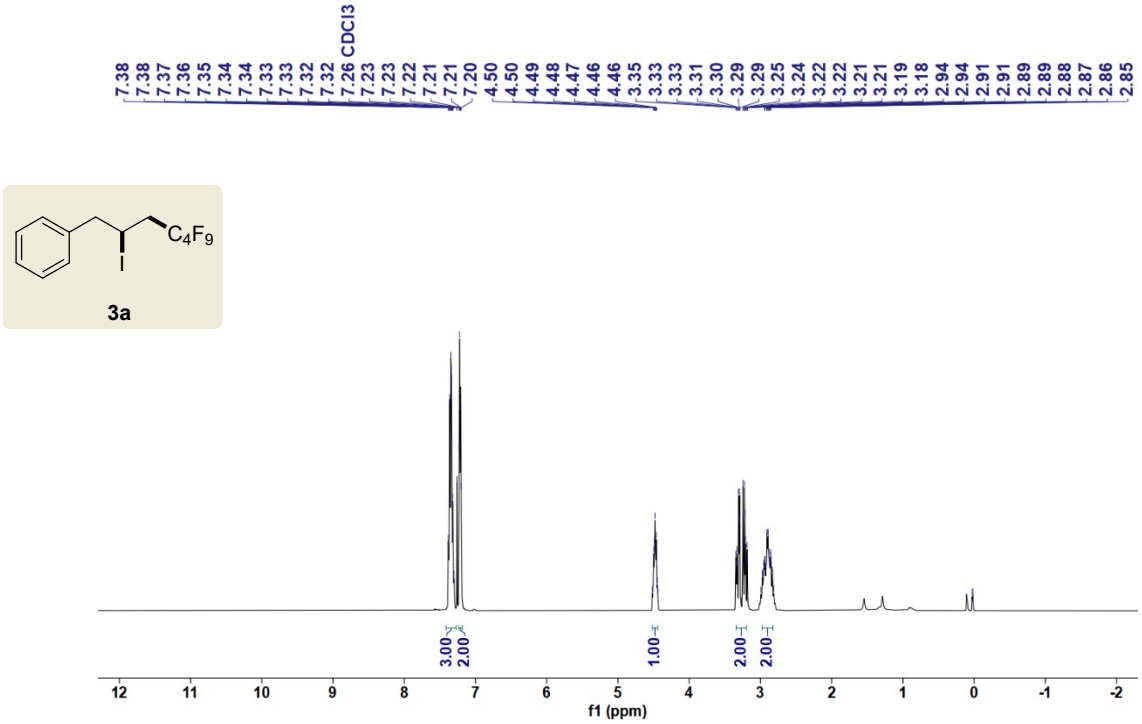
Figure S5. Computational Gibbs free energies for the atom transfer radical addition process for the reaction of alpha-cyclopropylstyrene **1c** and CF_3I. Energies in kcal/mol, interatomic distances are in Å.

The calculated free energy profile for the reaction of alpha-cyclopropylstyrene **1c** and CF_3 radical are listed in Figure S2. First, the addition between **1c** and CF_3 radical forms an intermediate (**IM1c**),

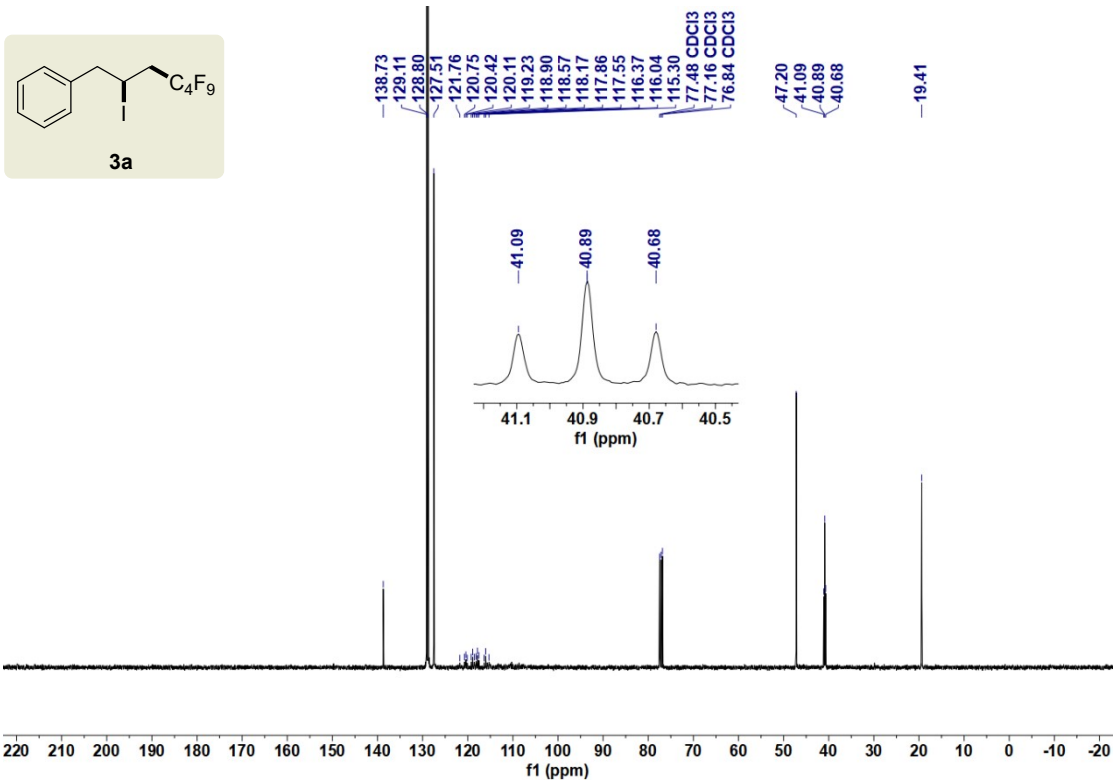
which is exothermic by 32.0 kcal/mol. Then, the **IM1c** abstracts the iodine atom of the other CF_3I molecule to regenerate the CF_3 radical and product **P1c** *via* transition state **TS2c**. The barrier height of **TS2c** is 25.4 kcal/mol (relative to the **IM1c**), this reaction is endergonic by 13.8 kcal/mol. Alternatively, **IM1c** can isomeric to the intermediate **IM2c** *via* ring-opening transition state **TS3c** with a barrier of 15.5 kcal/mol (relative to the **IM1c**). The resulting **IM2c** further proceeds iodine atom transfer to generate the product **P2c**. Overall, the formation of product **P2c** is the major path.

6. NMR Spectra

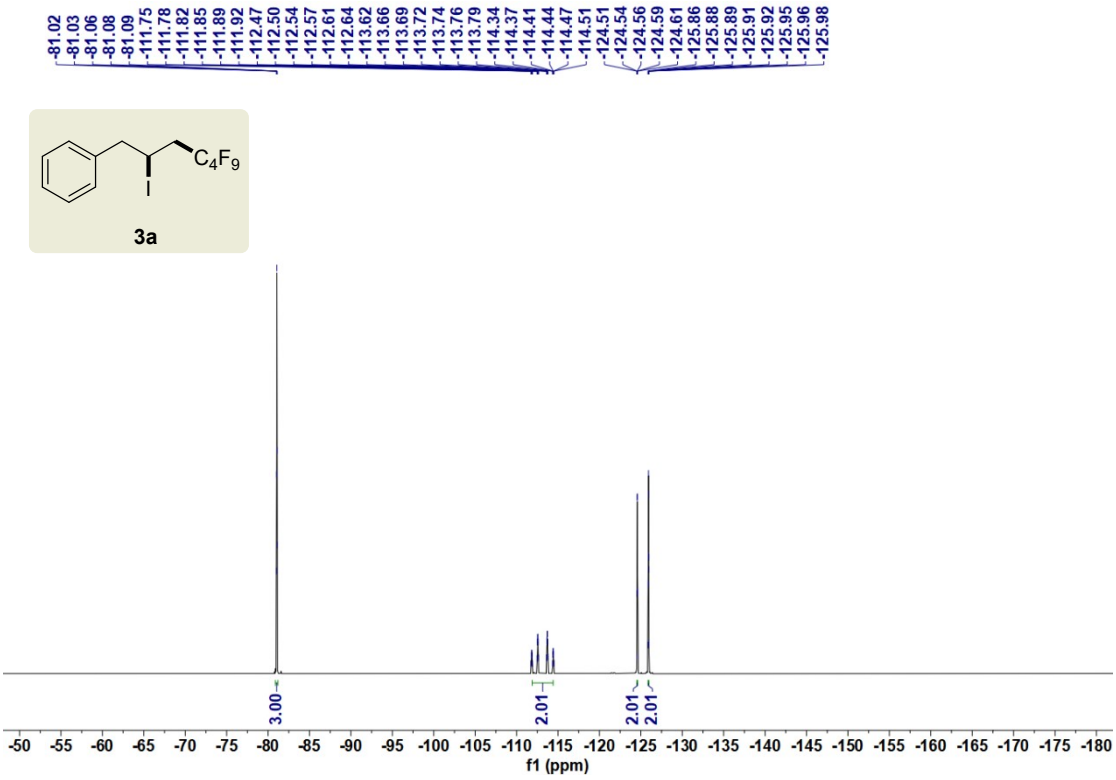
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**:



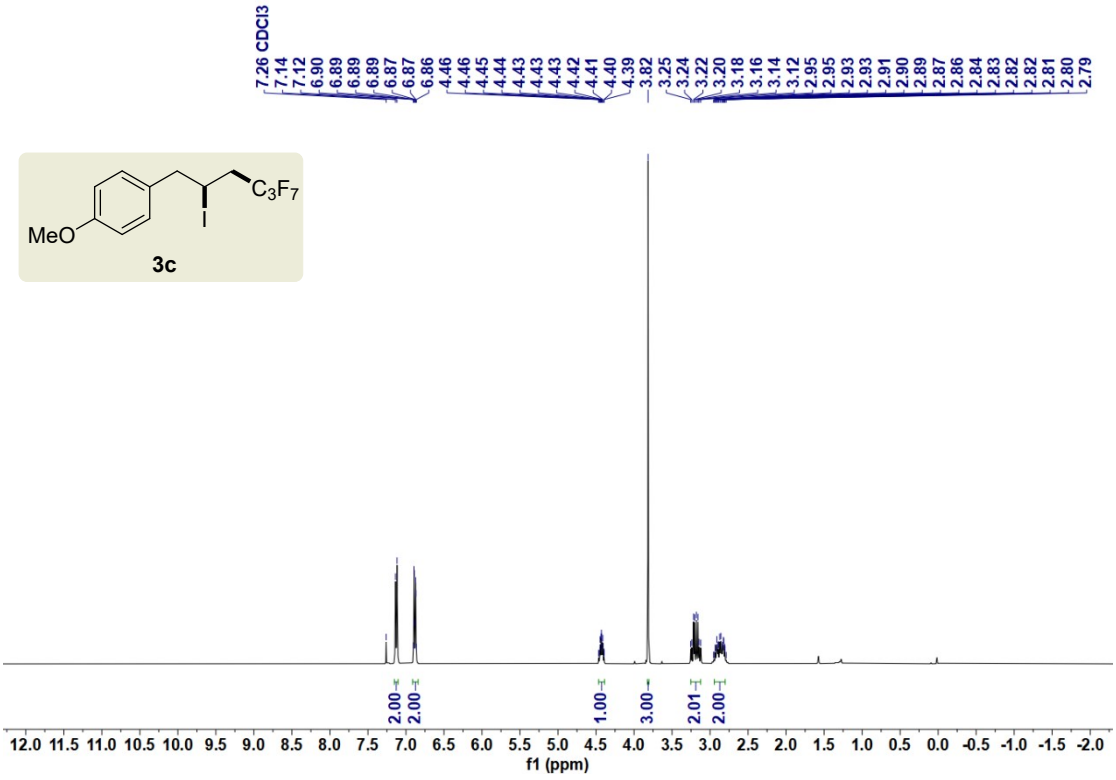
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**:



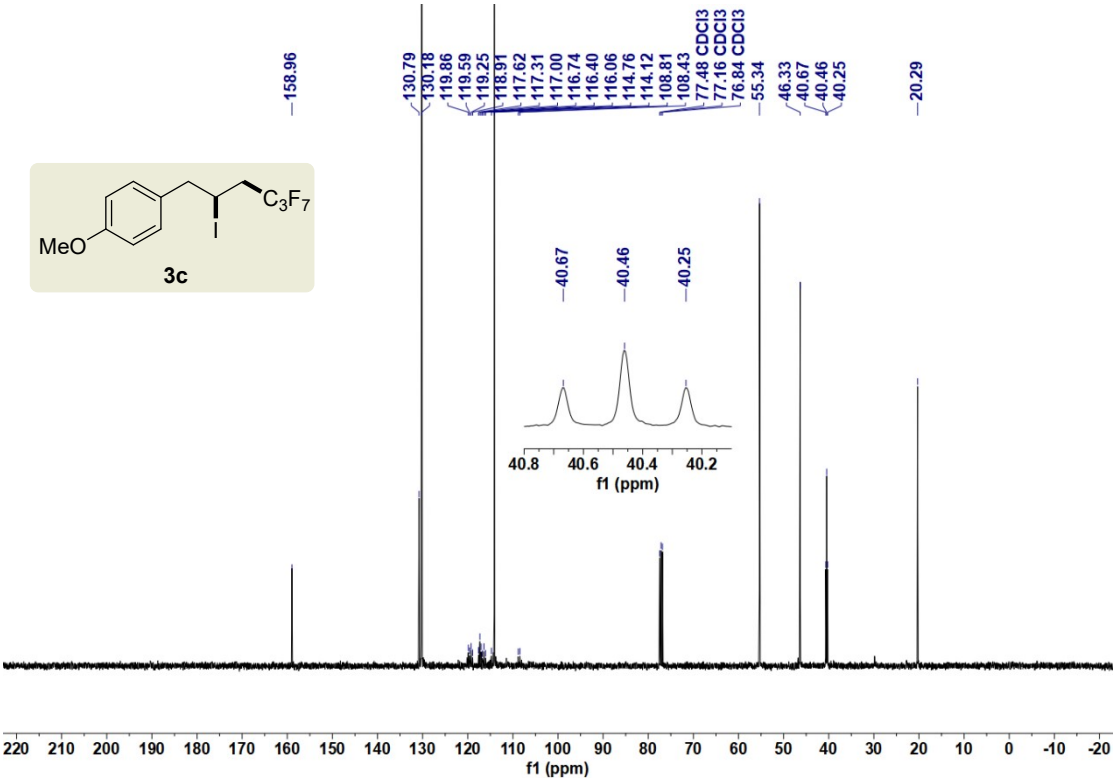
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3a**:



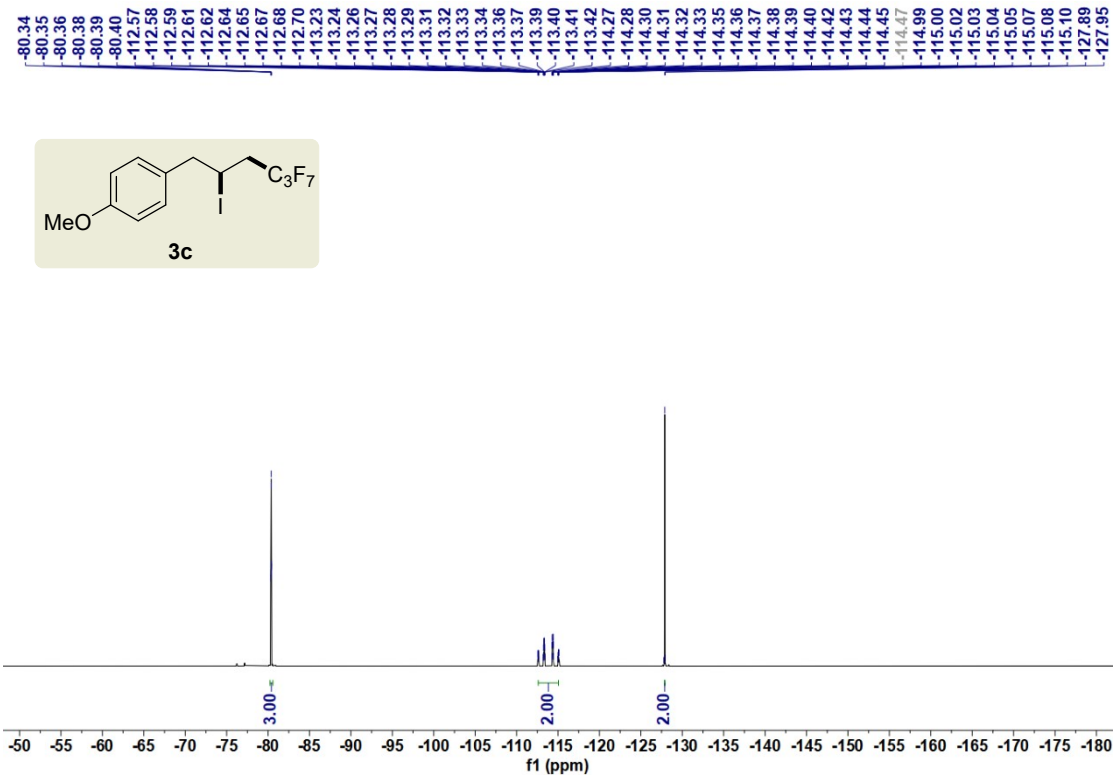
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**:



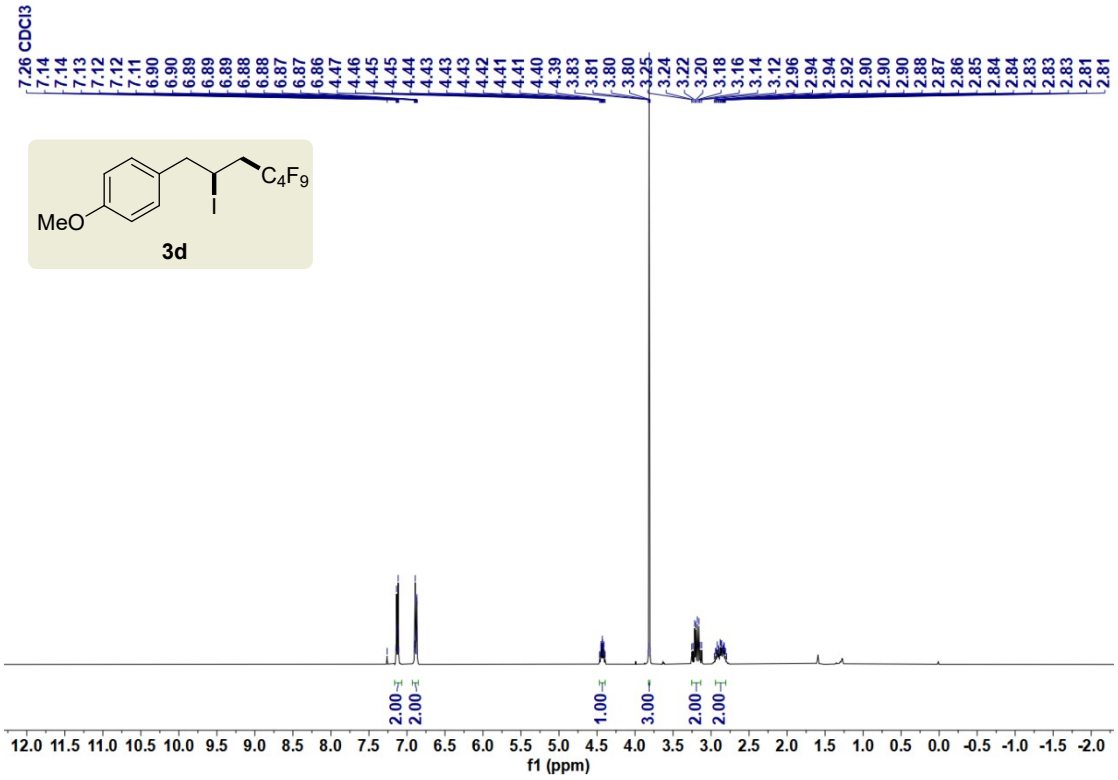
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3c**:



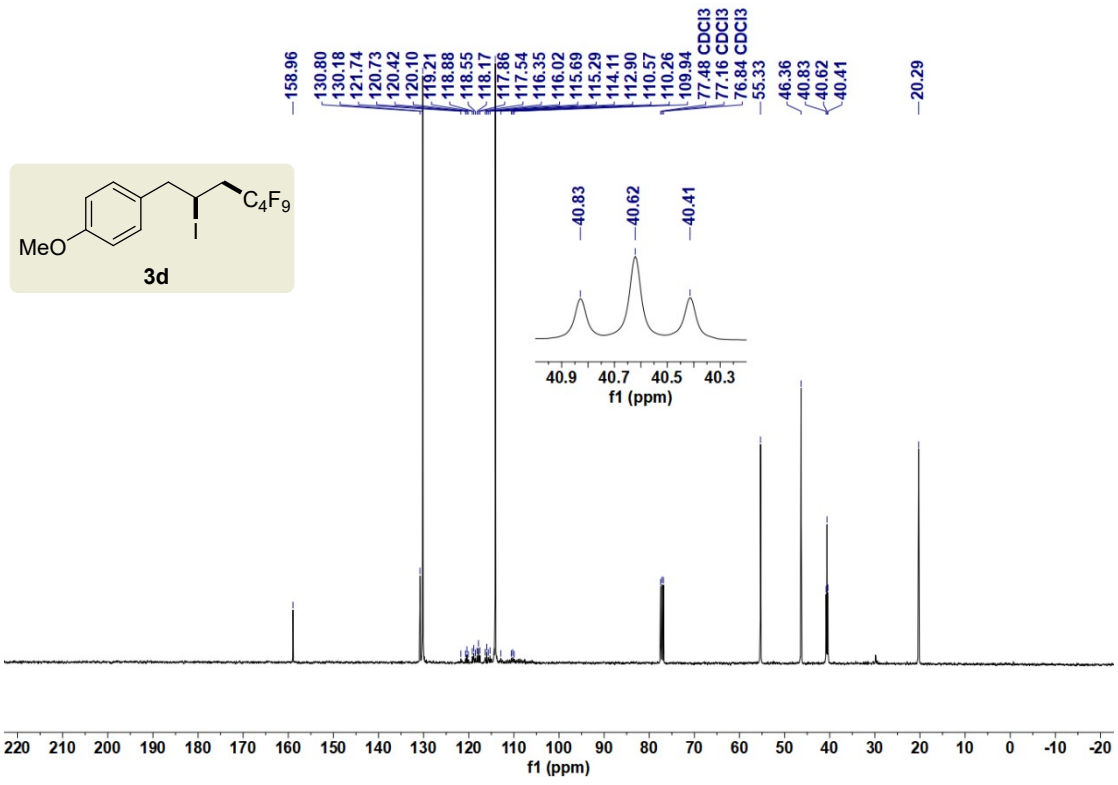
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3c**:



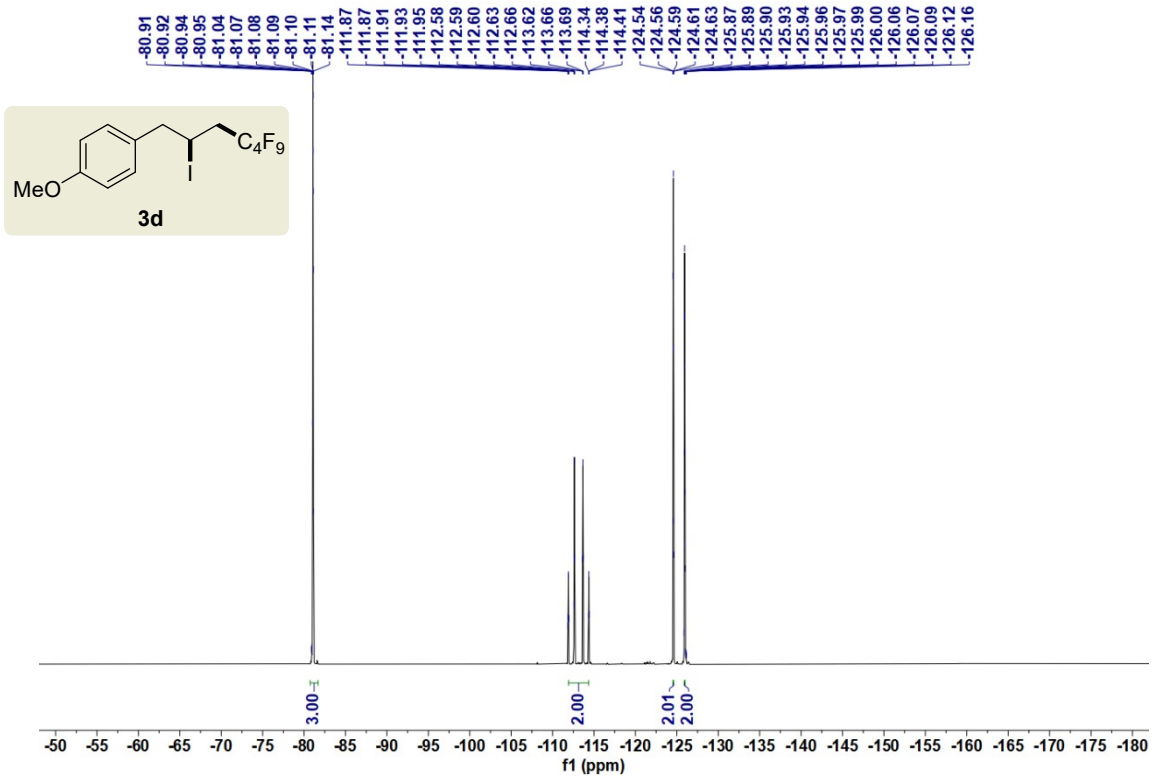
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**:



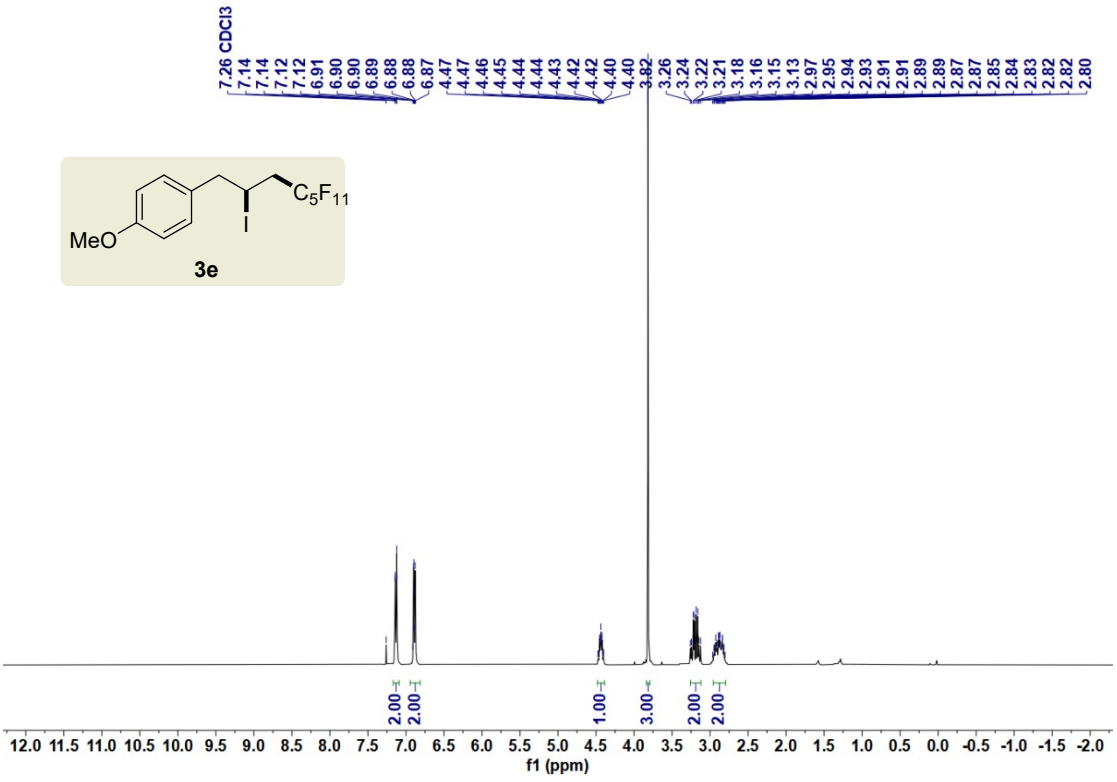
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3d**:



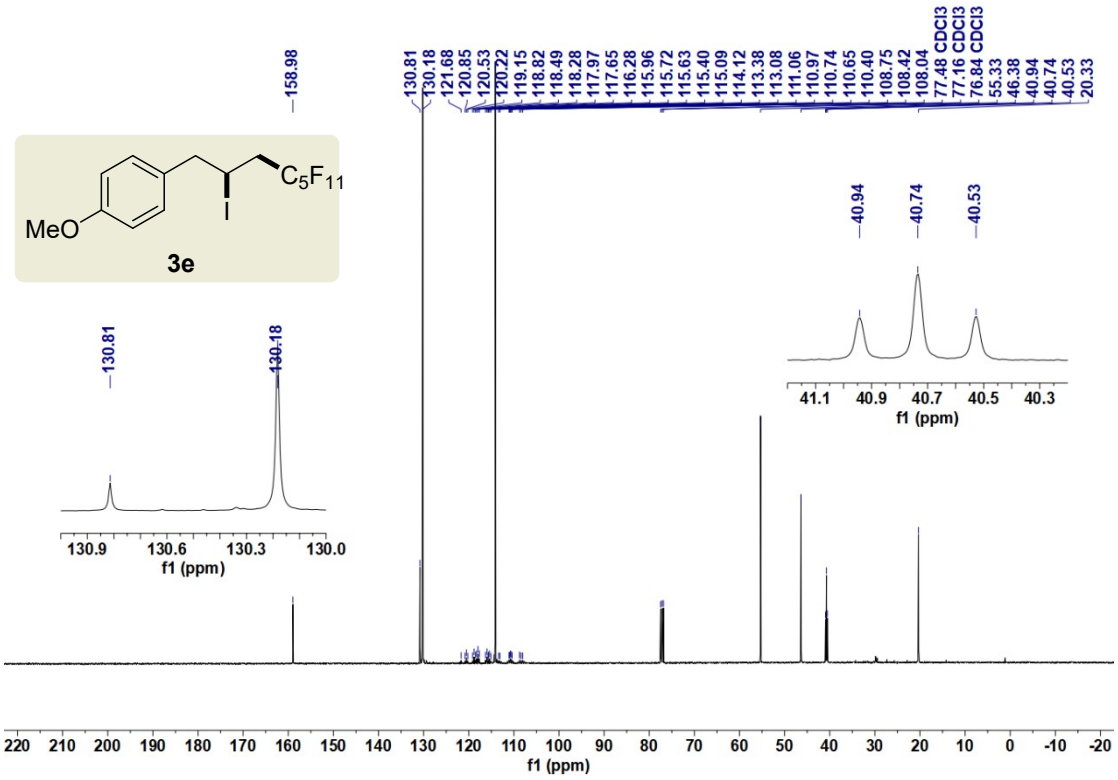
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3d**:



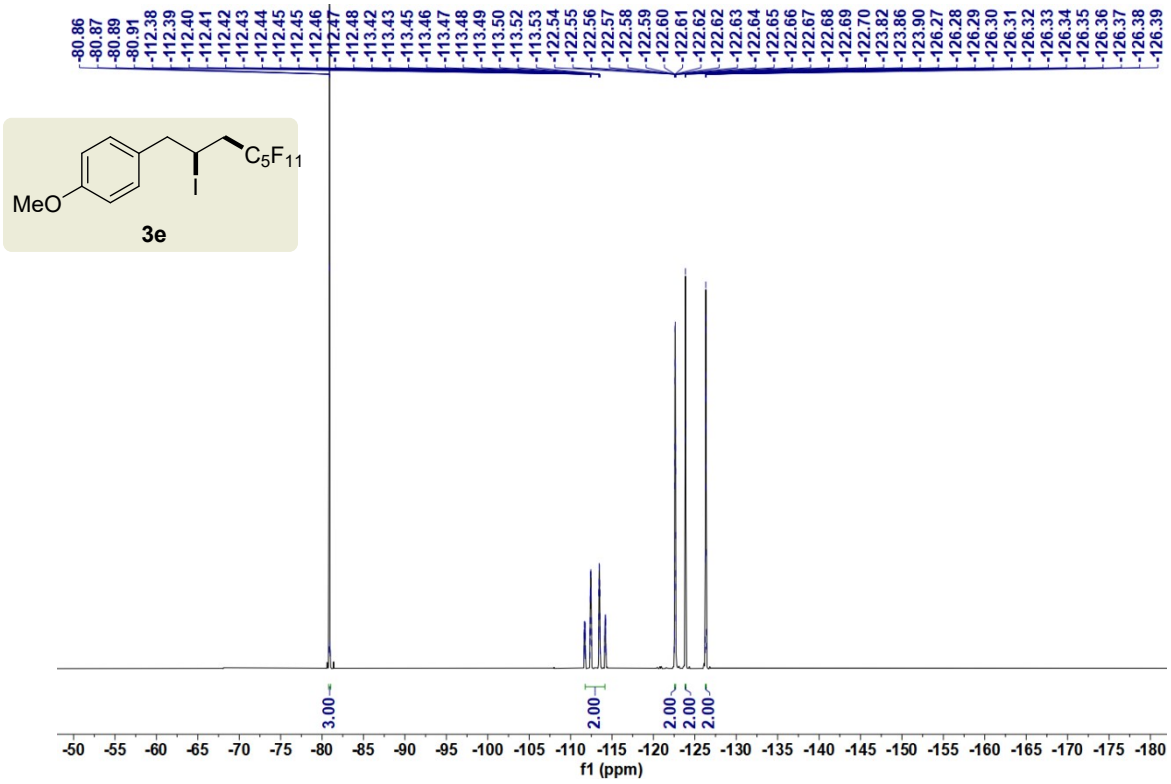
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**:



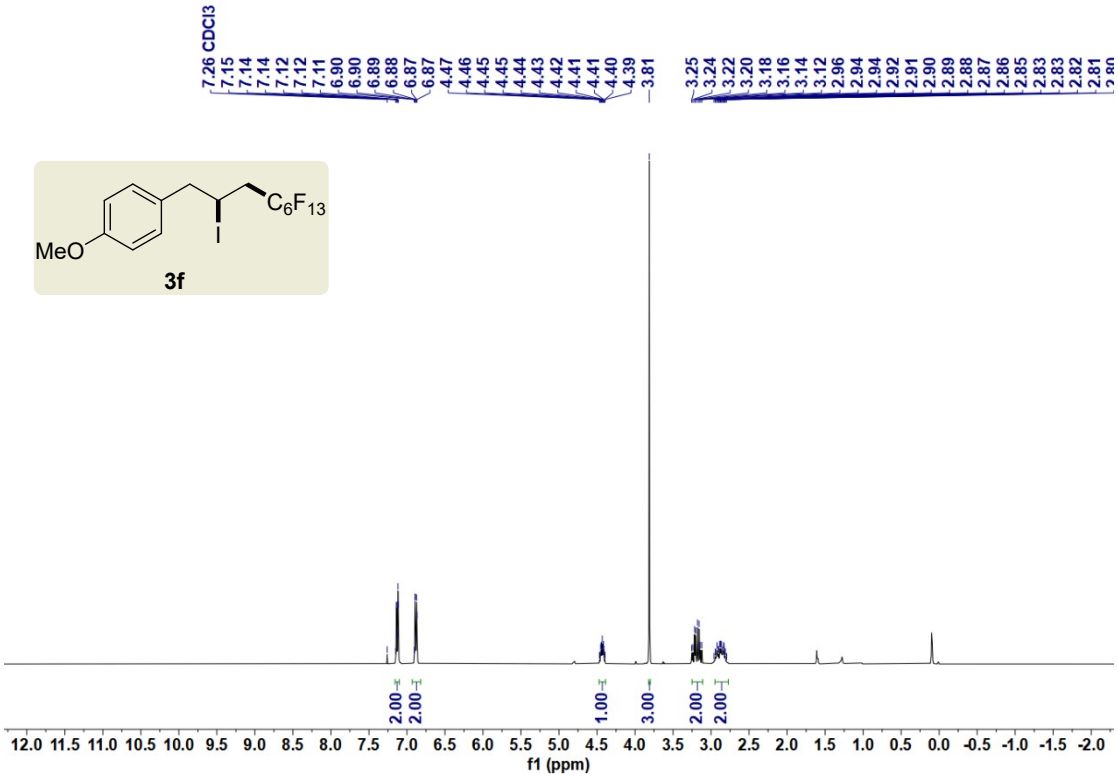
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3e**:



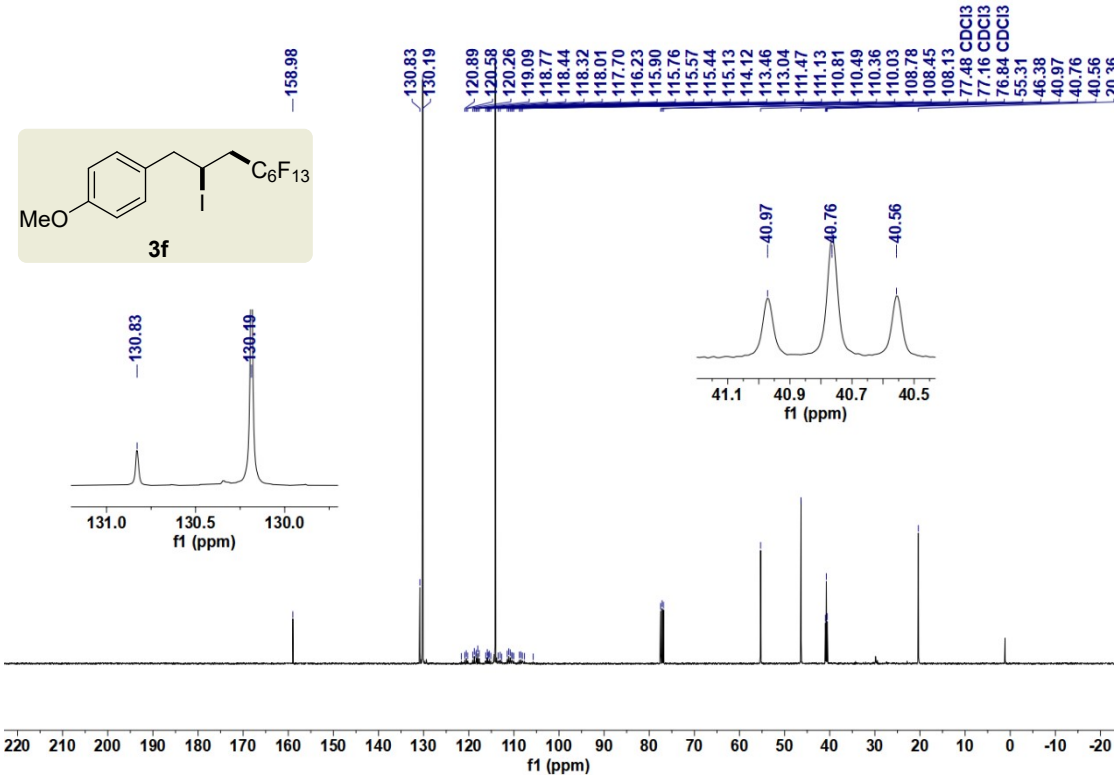
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3e**:



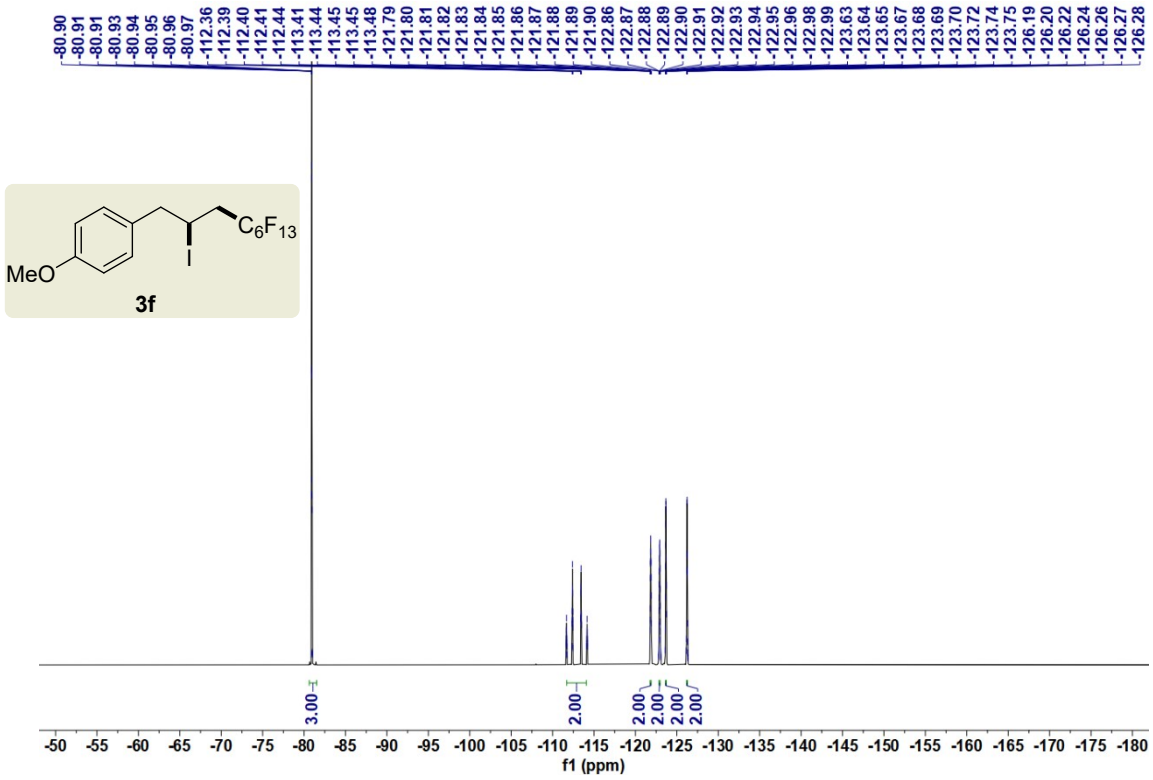
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**:



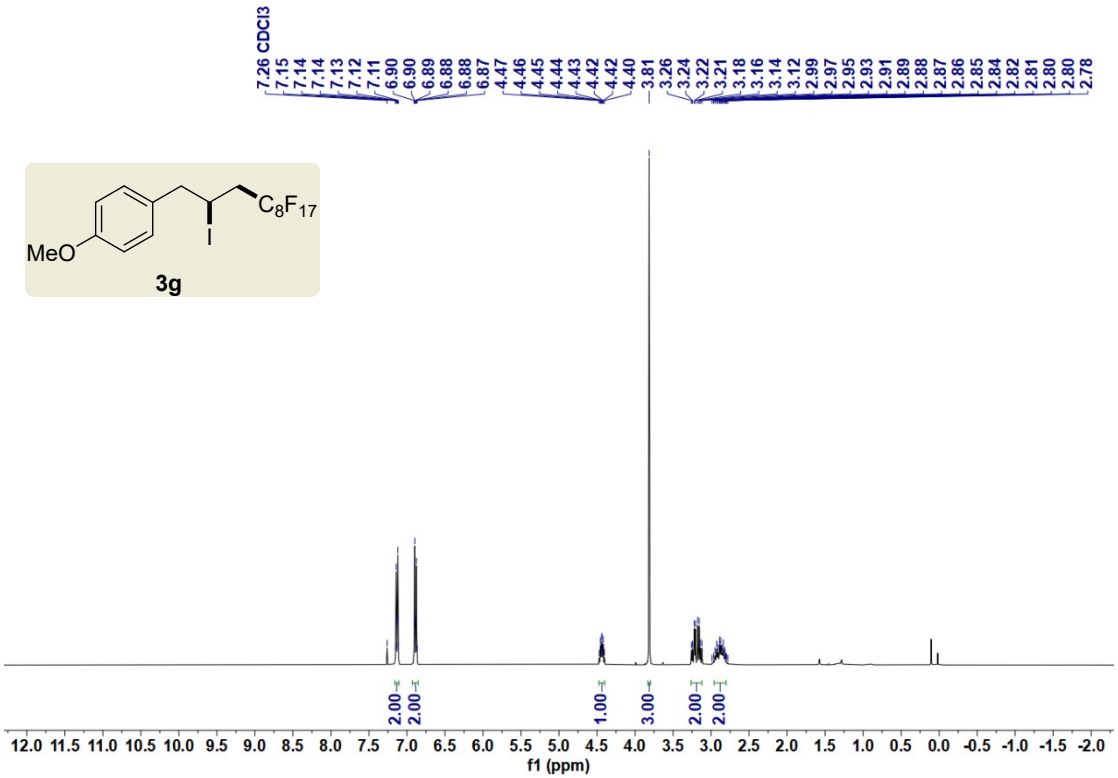
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3f**:



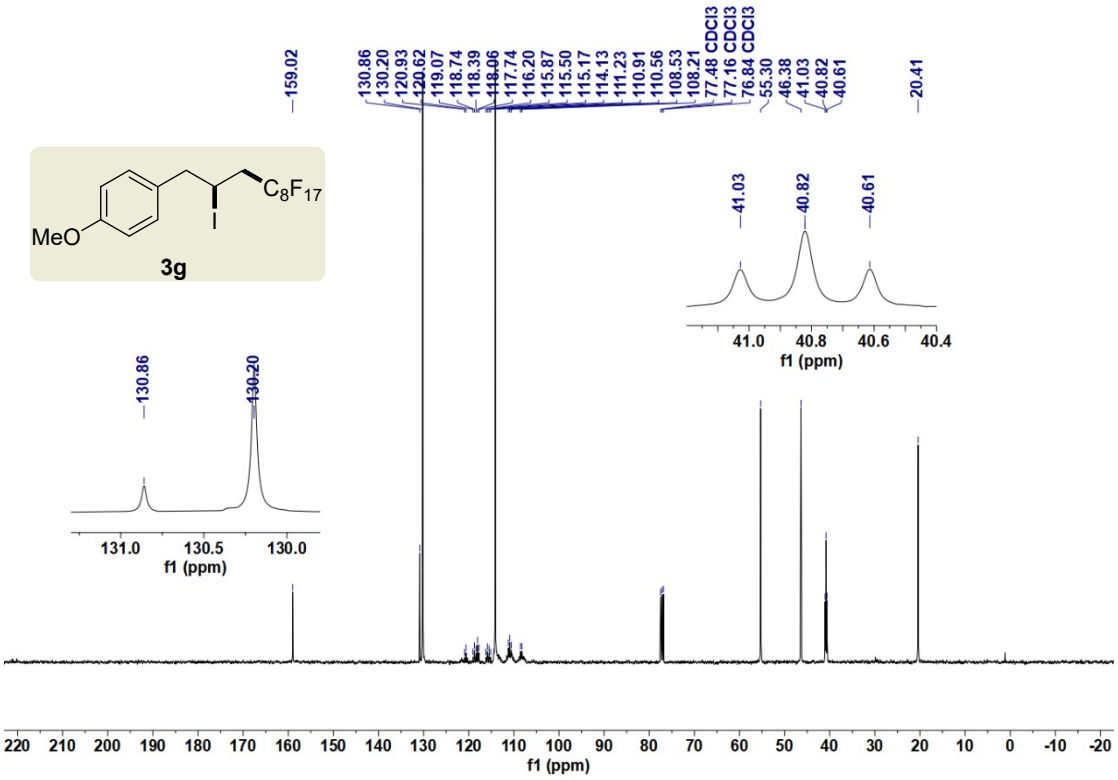
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3f**:



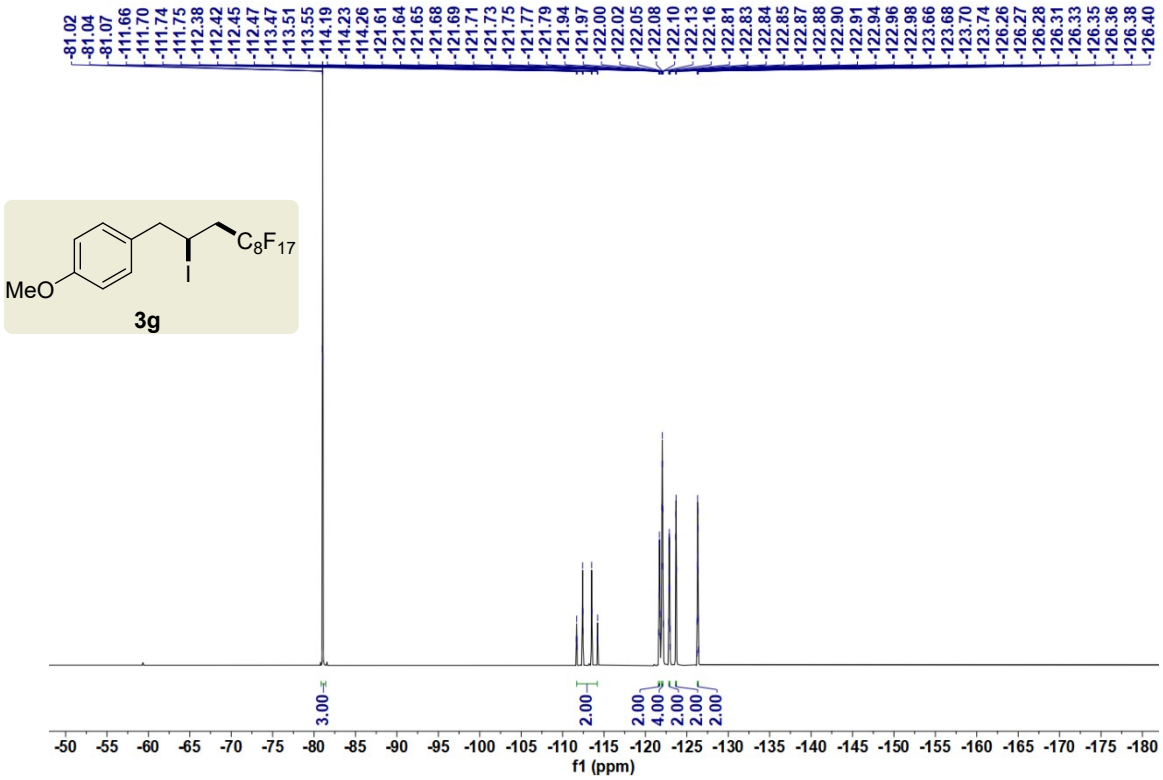
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**:



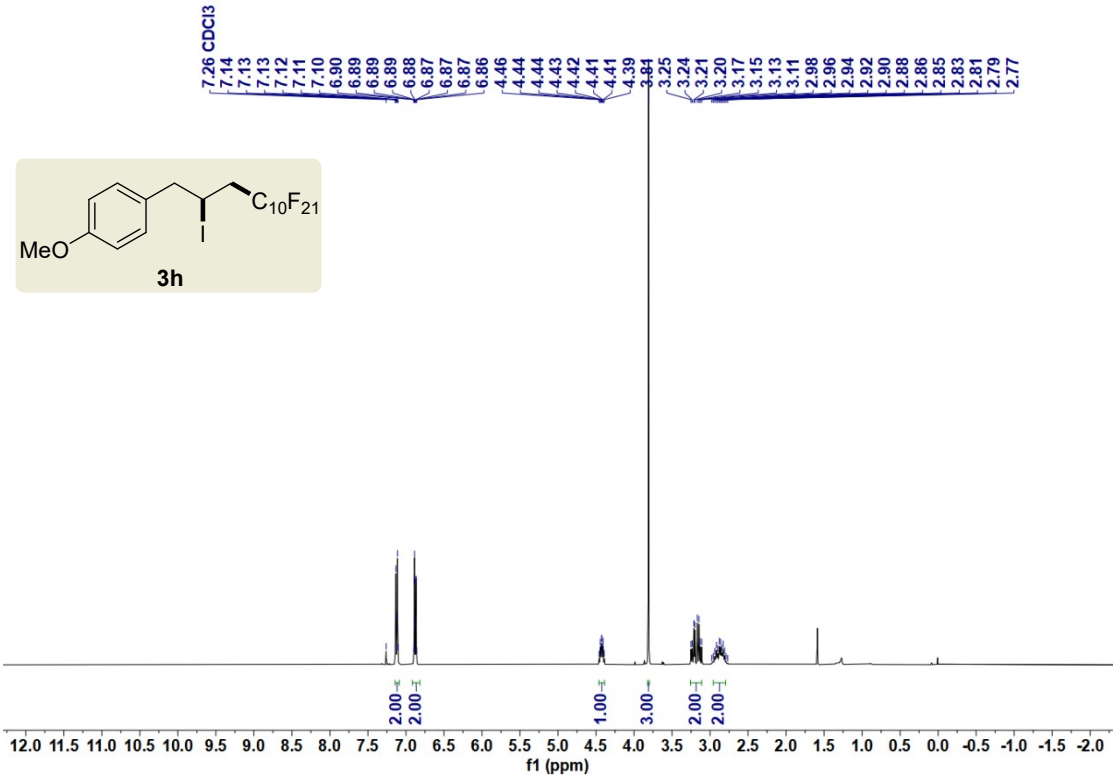
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3g**:



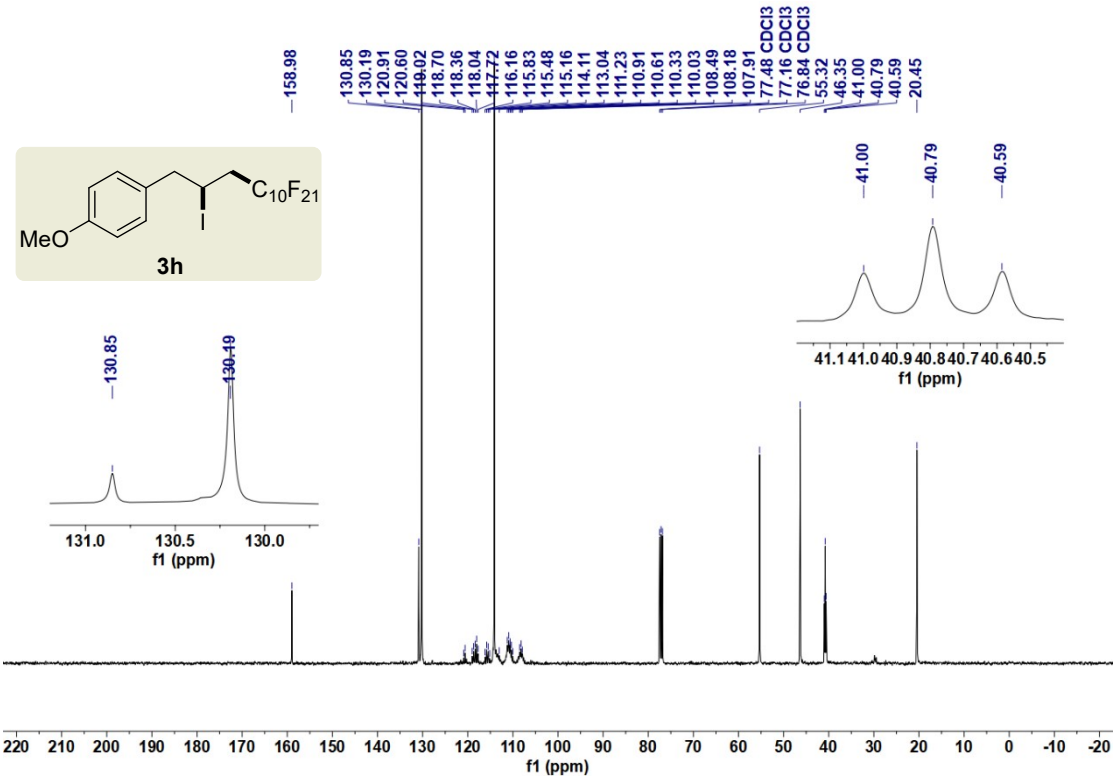
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3g**:



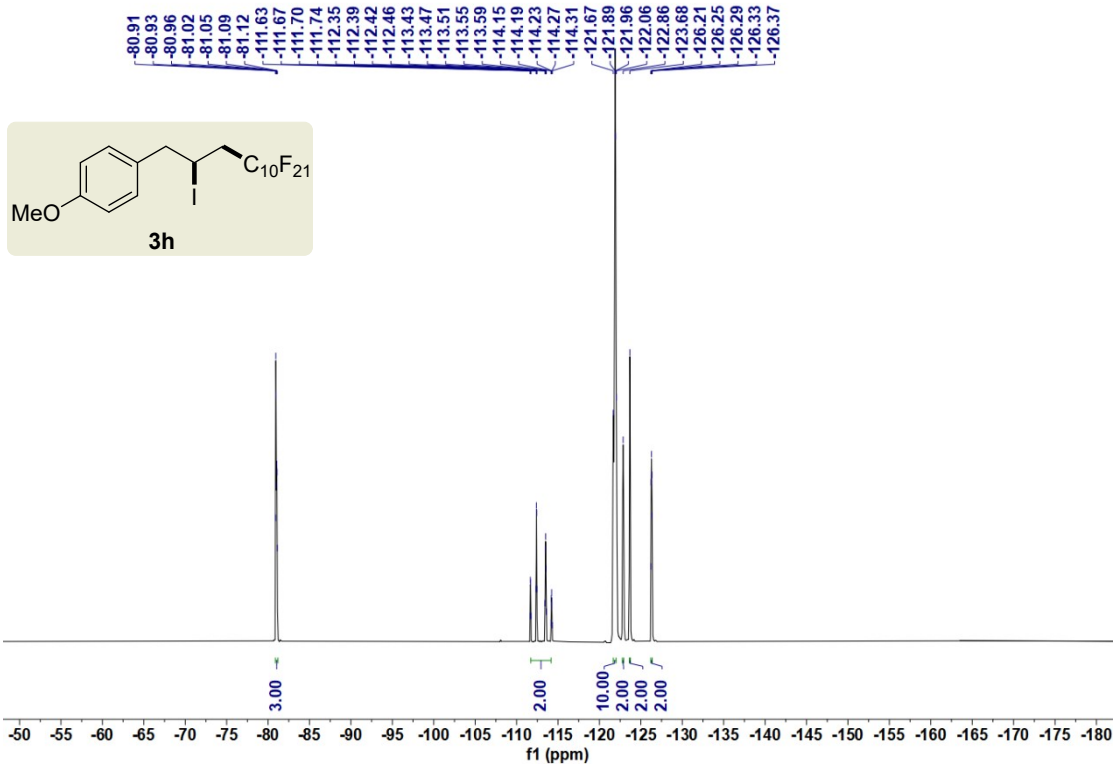
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**:



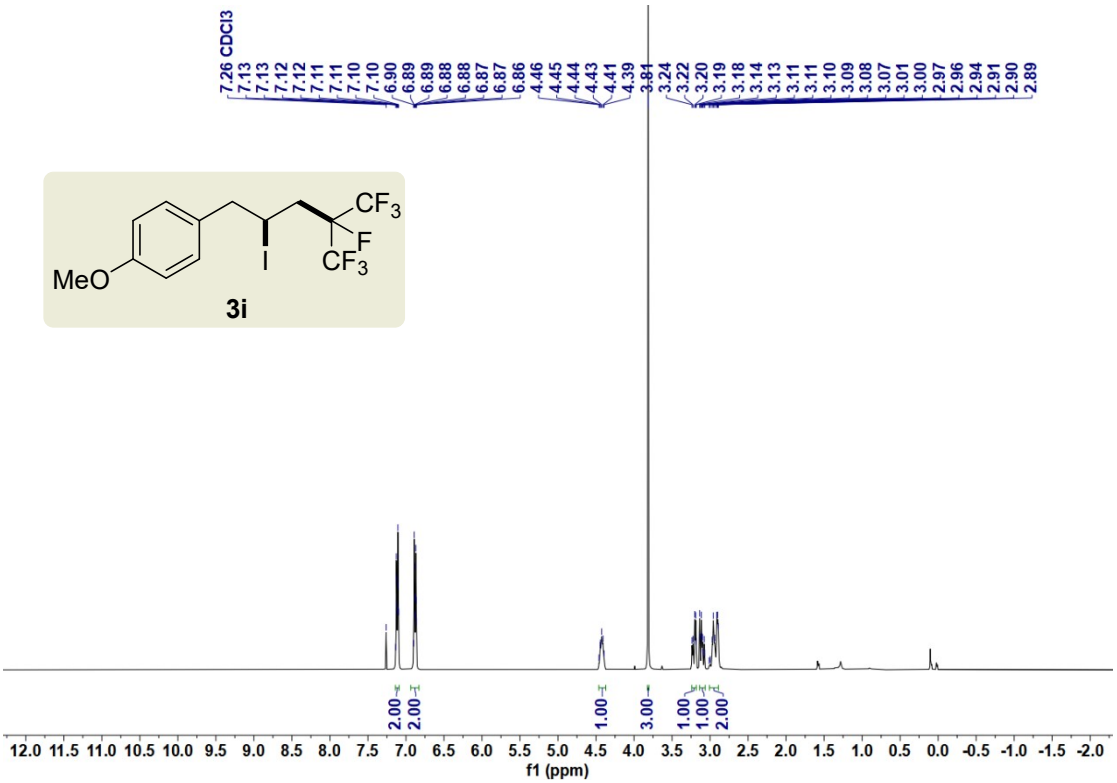
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3h**:



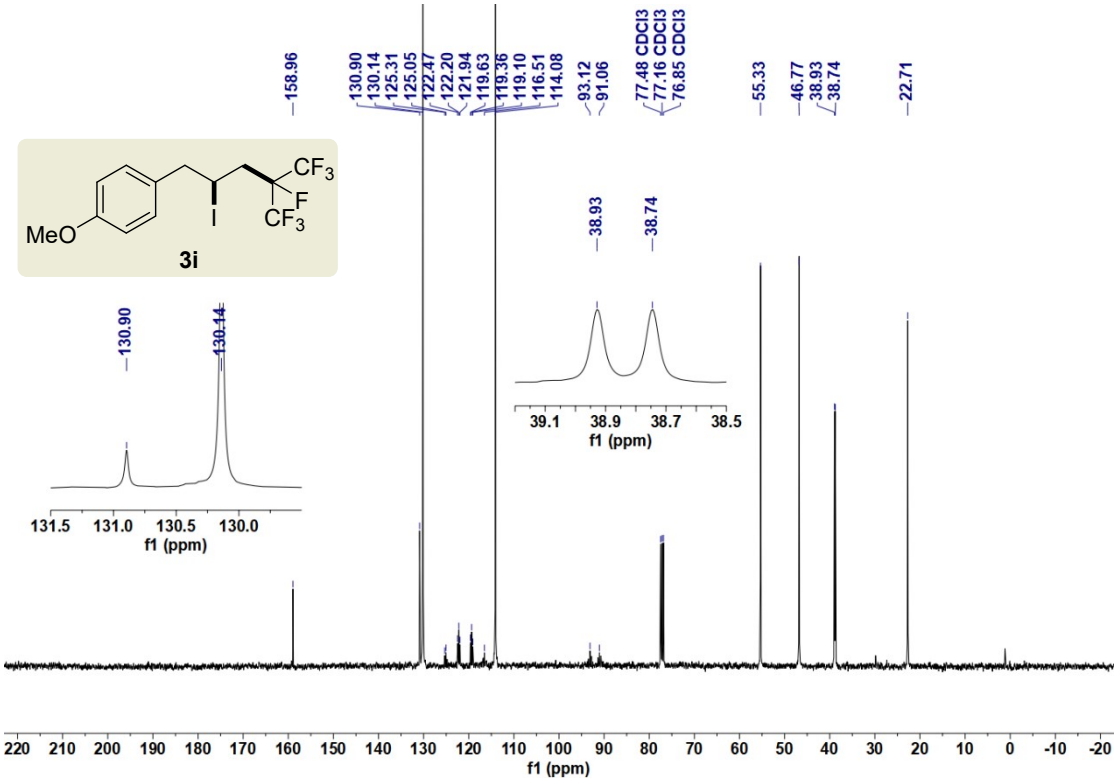
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3h**:



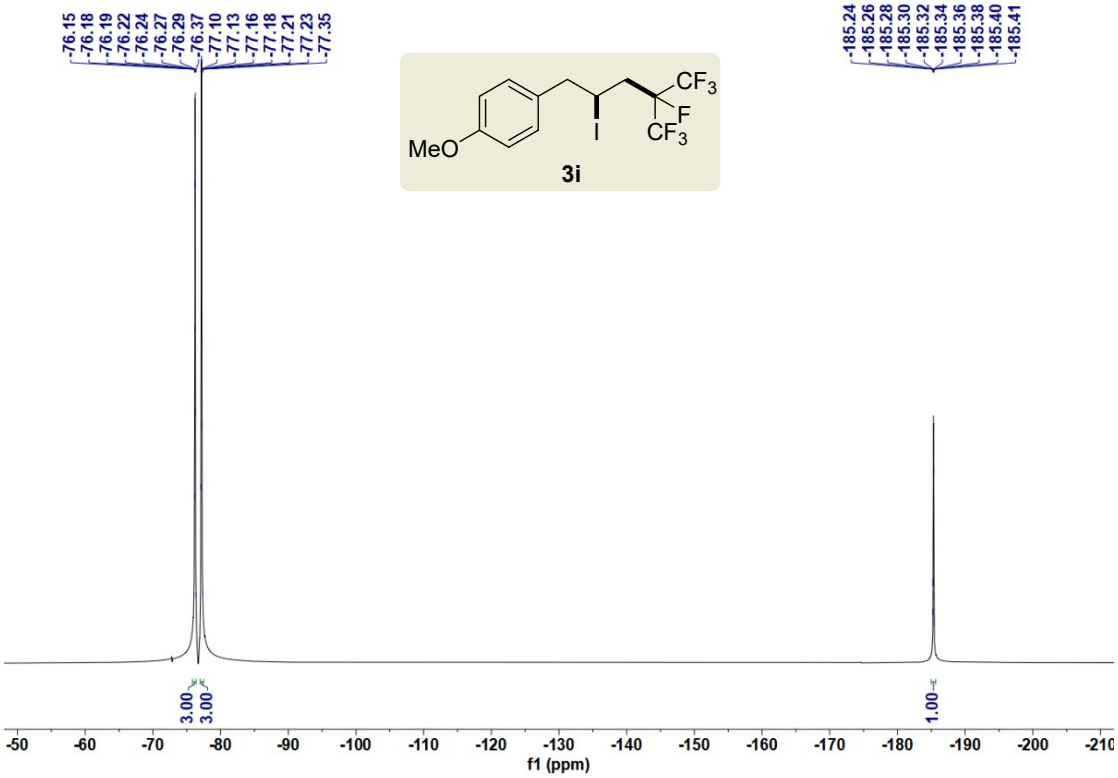
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**:



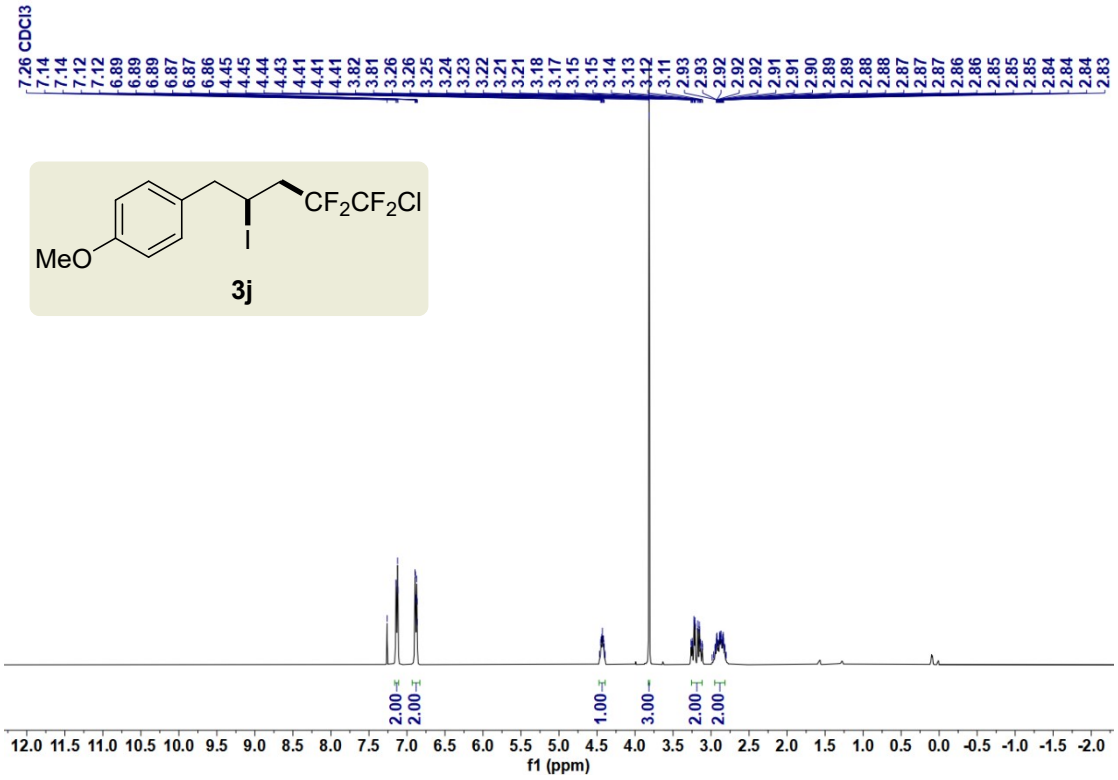
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3i**:



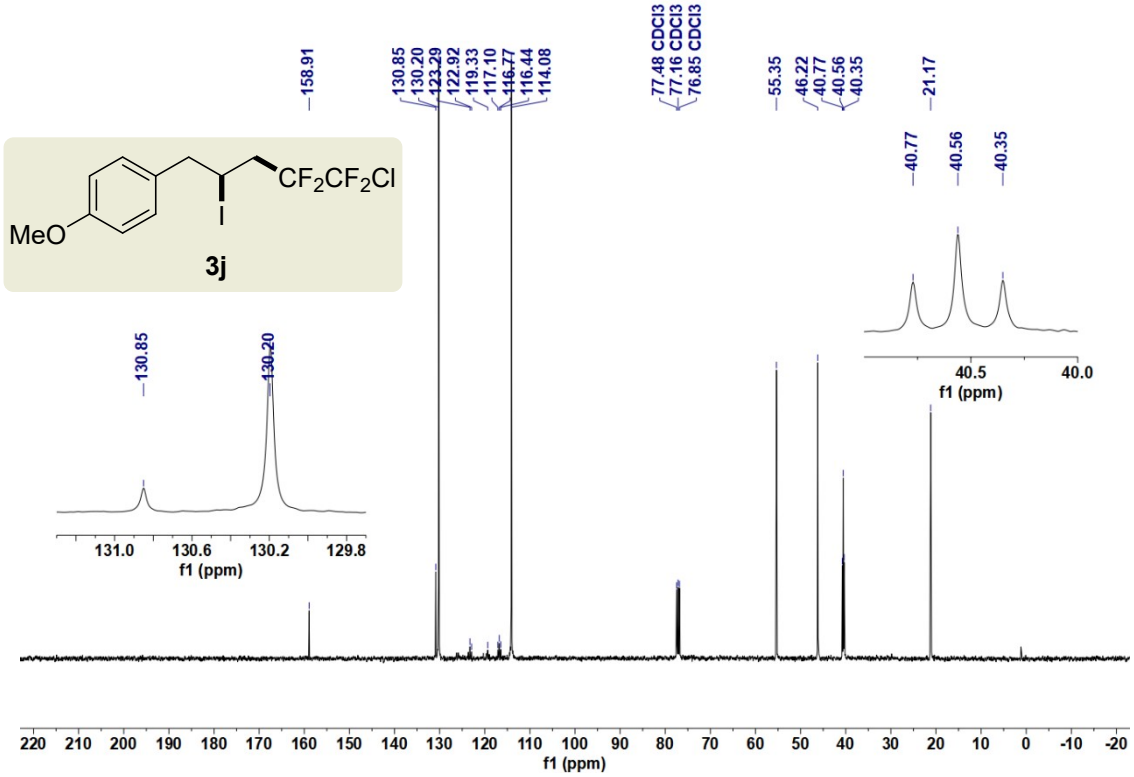
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3i**:



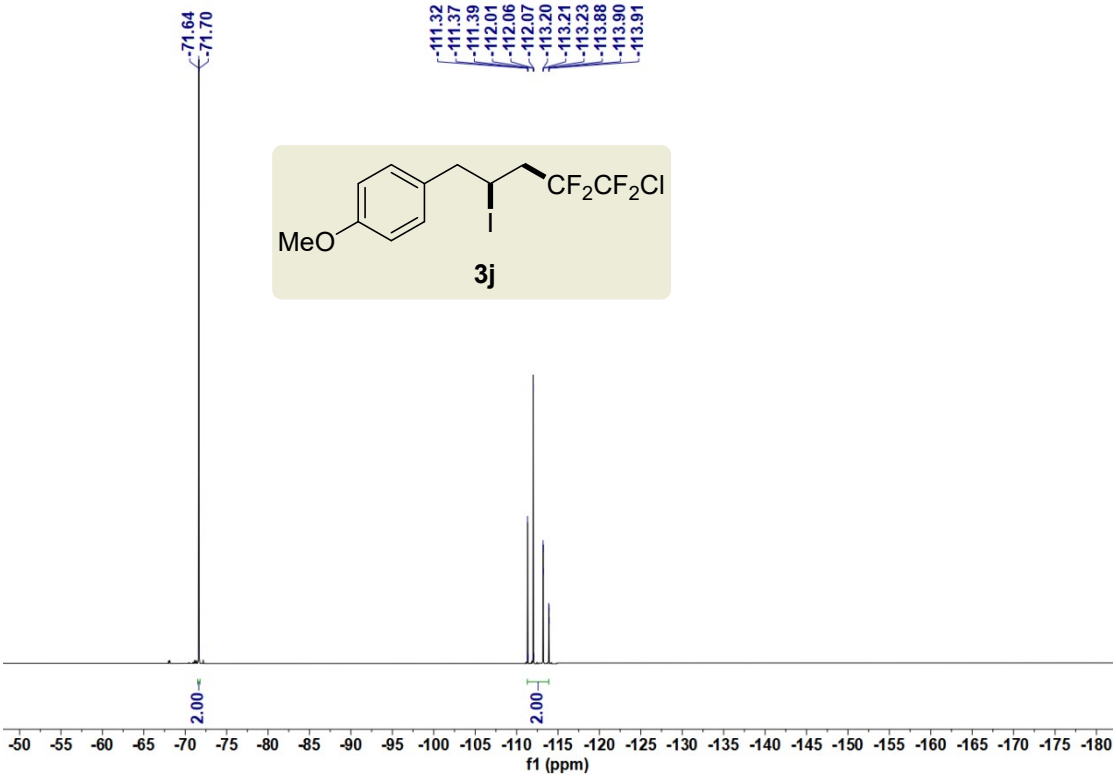
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**:



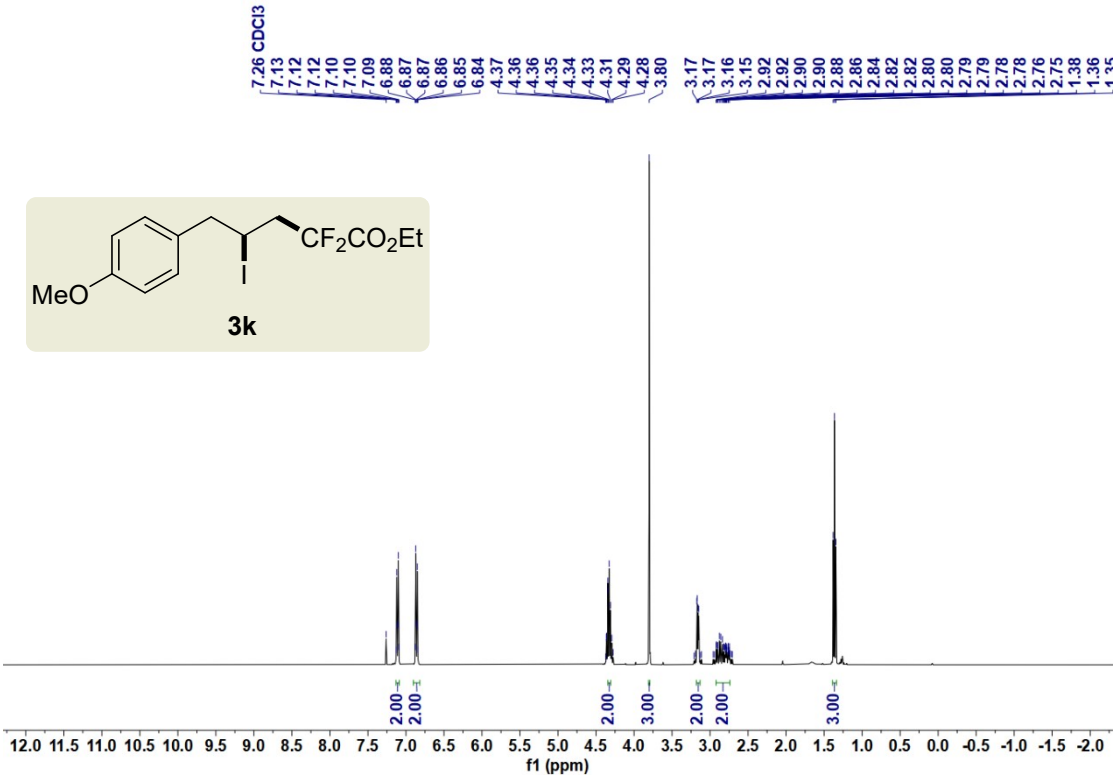
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3j**:



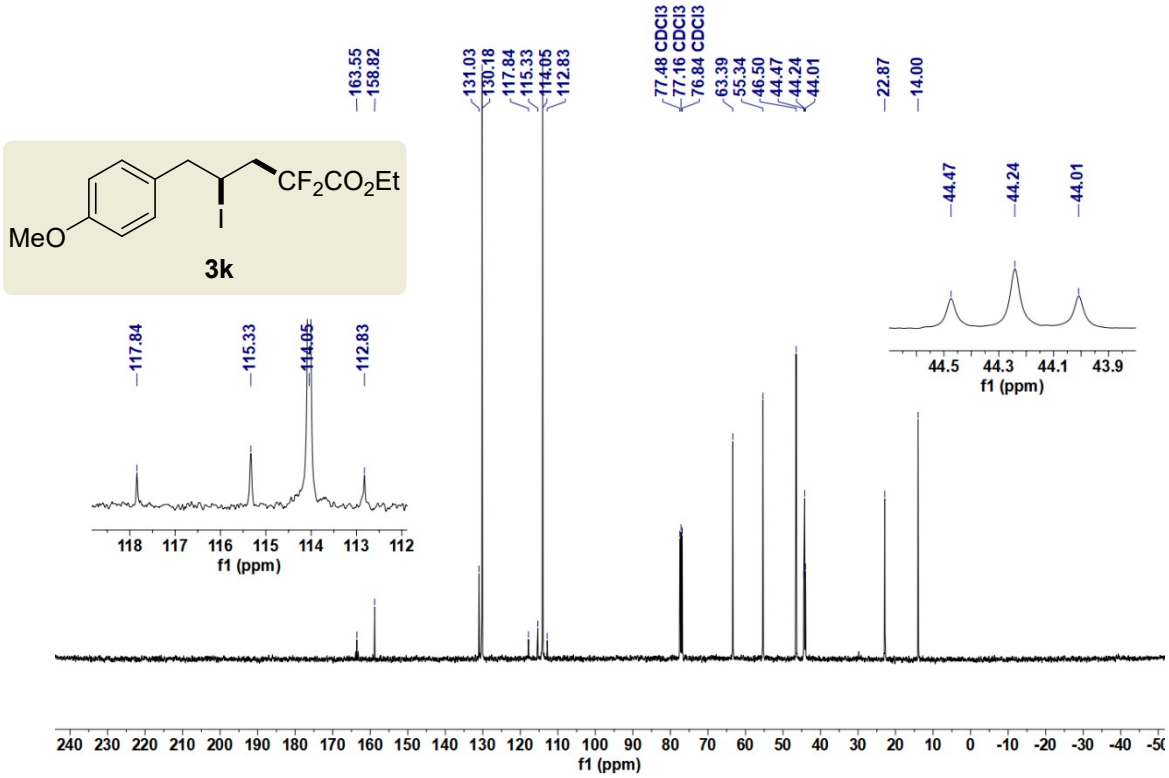
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3j**:



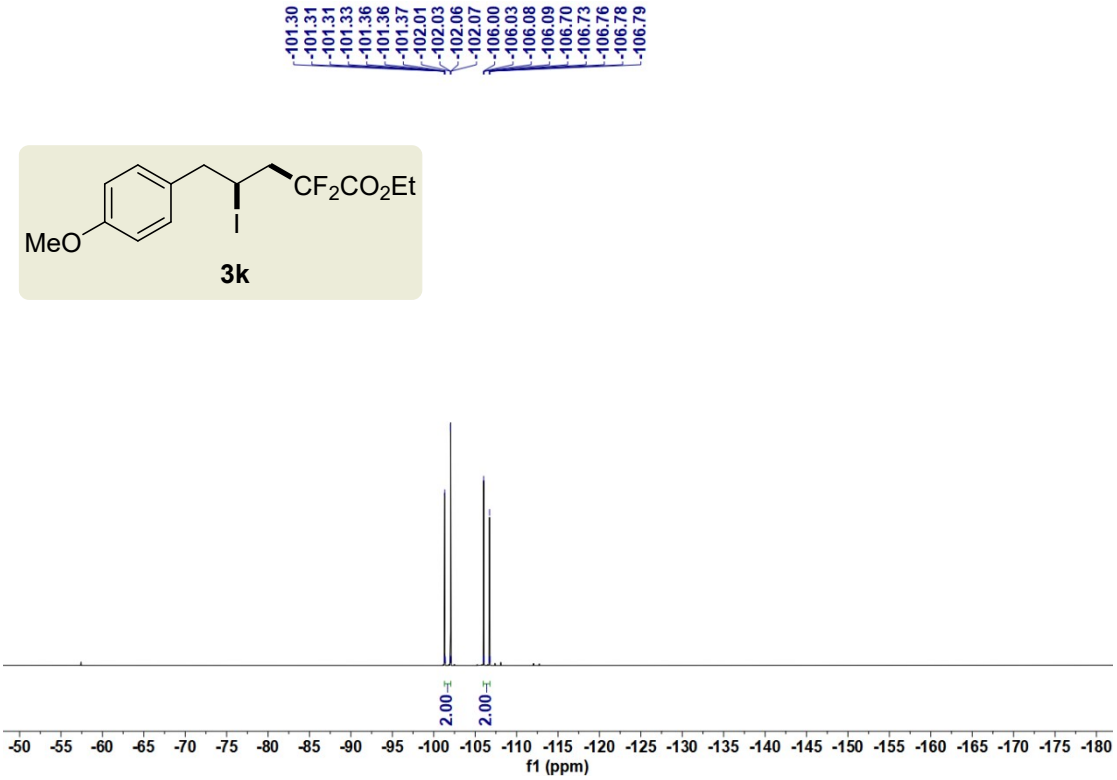
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**:



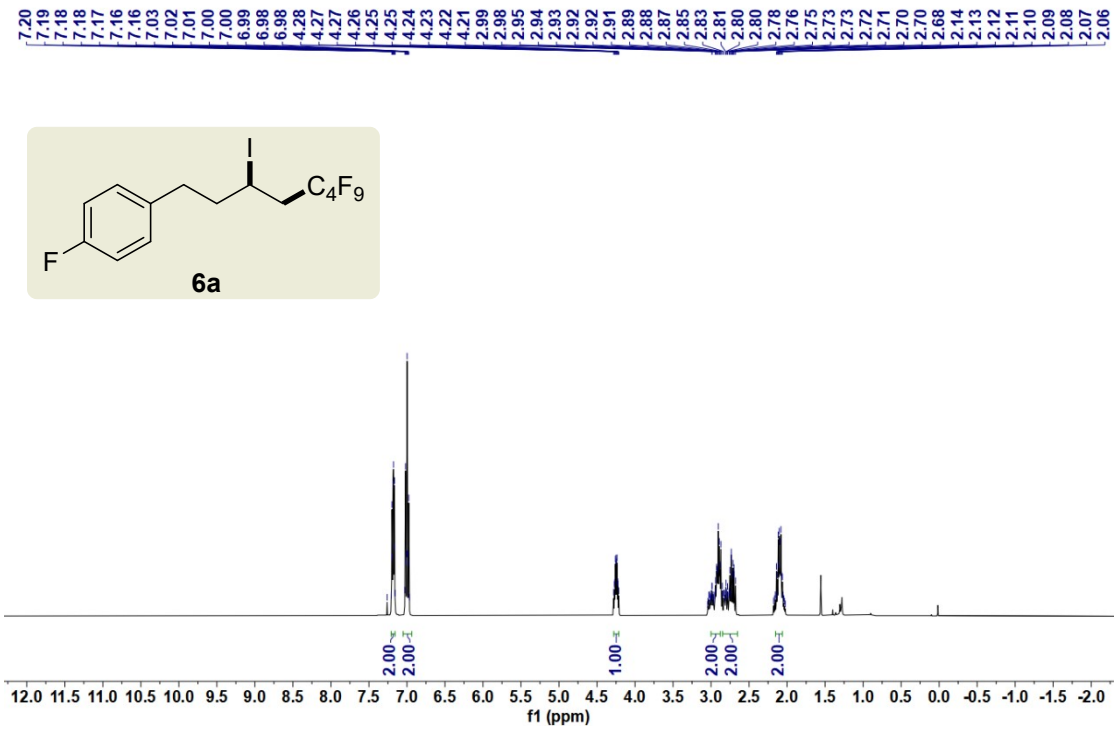
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3k**:



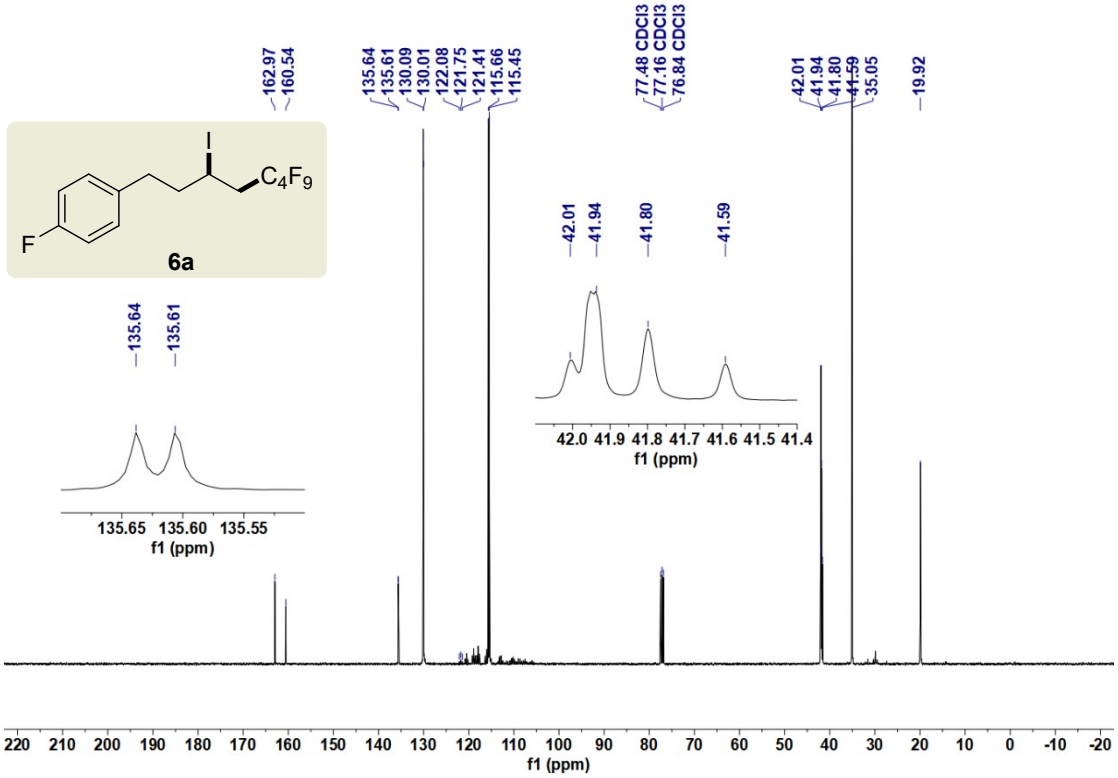
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3k**:



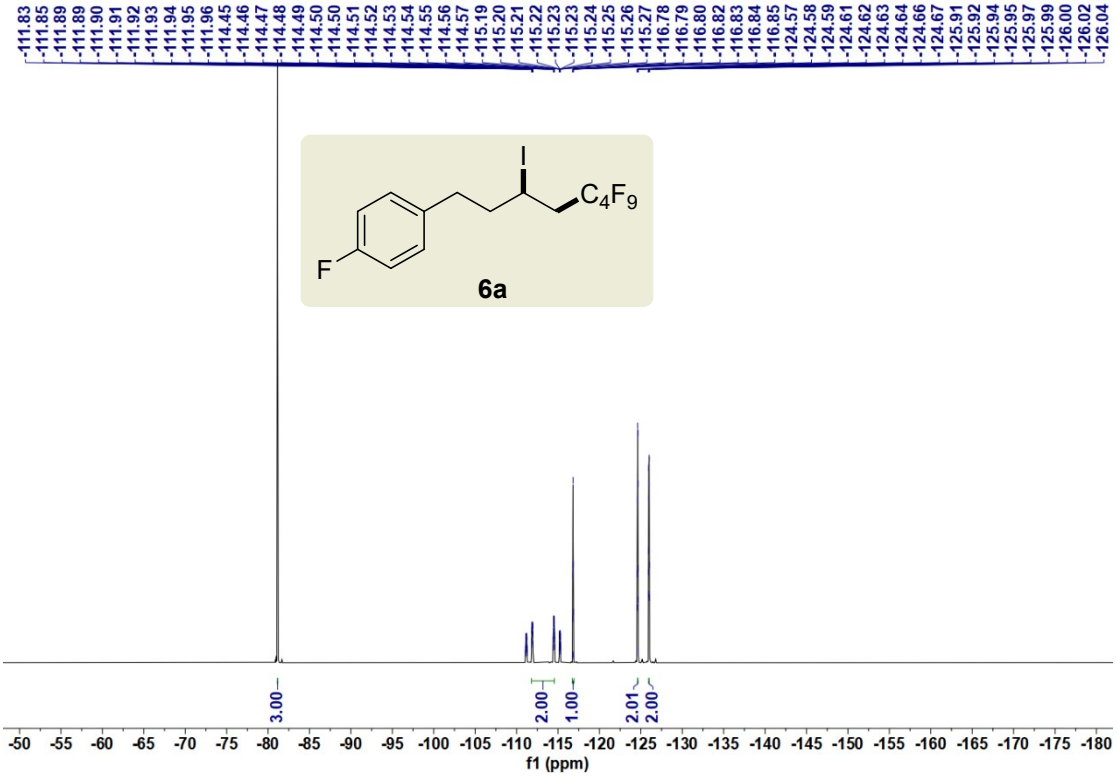
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6a**:



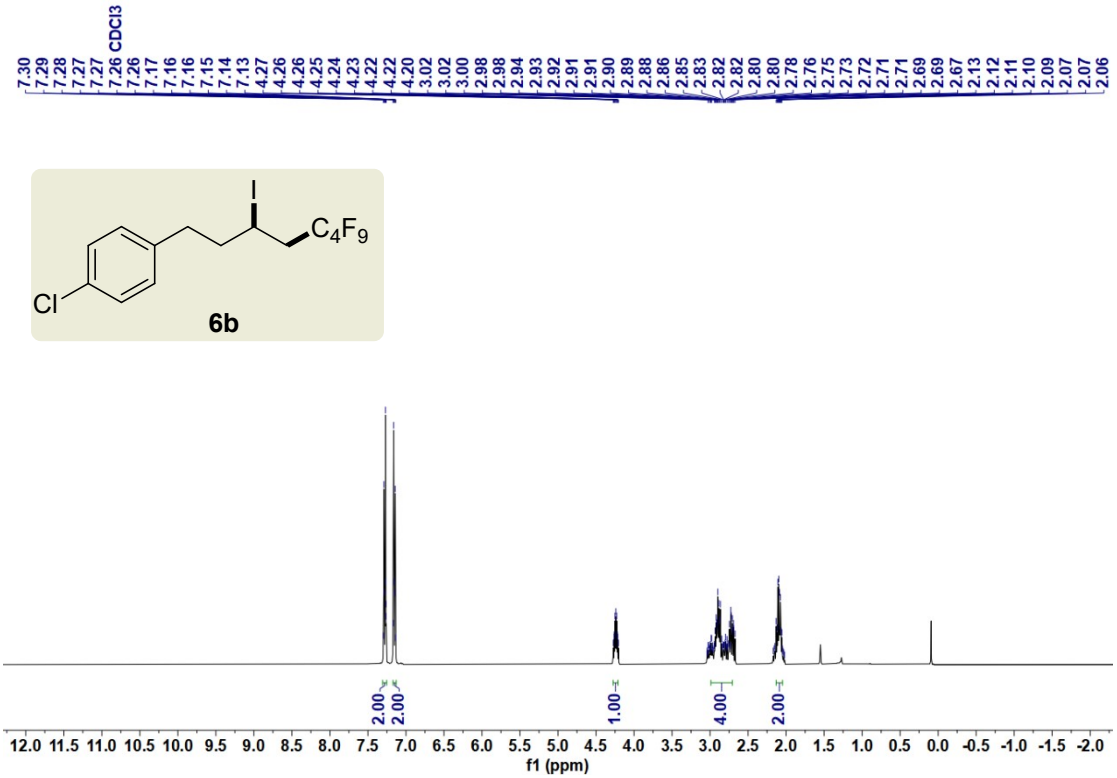
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6a**:



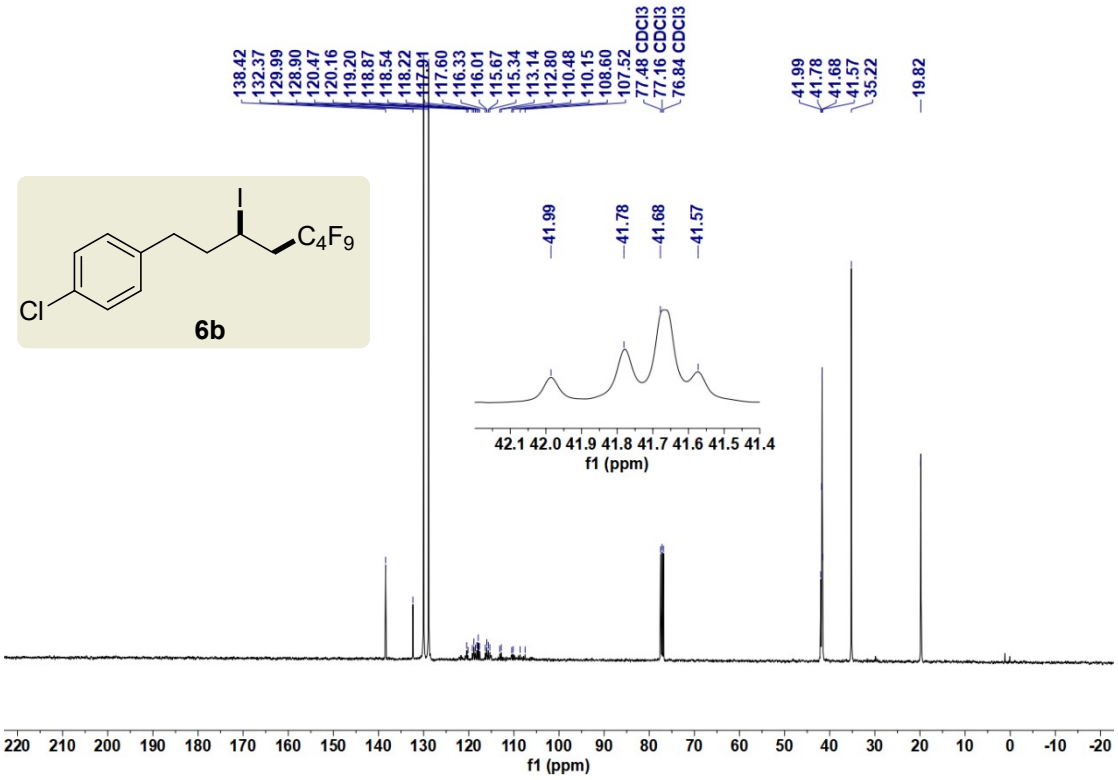
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6a**:



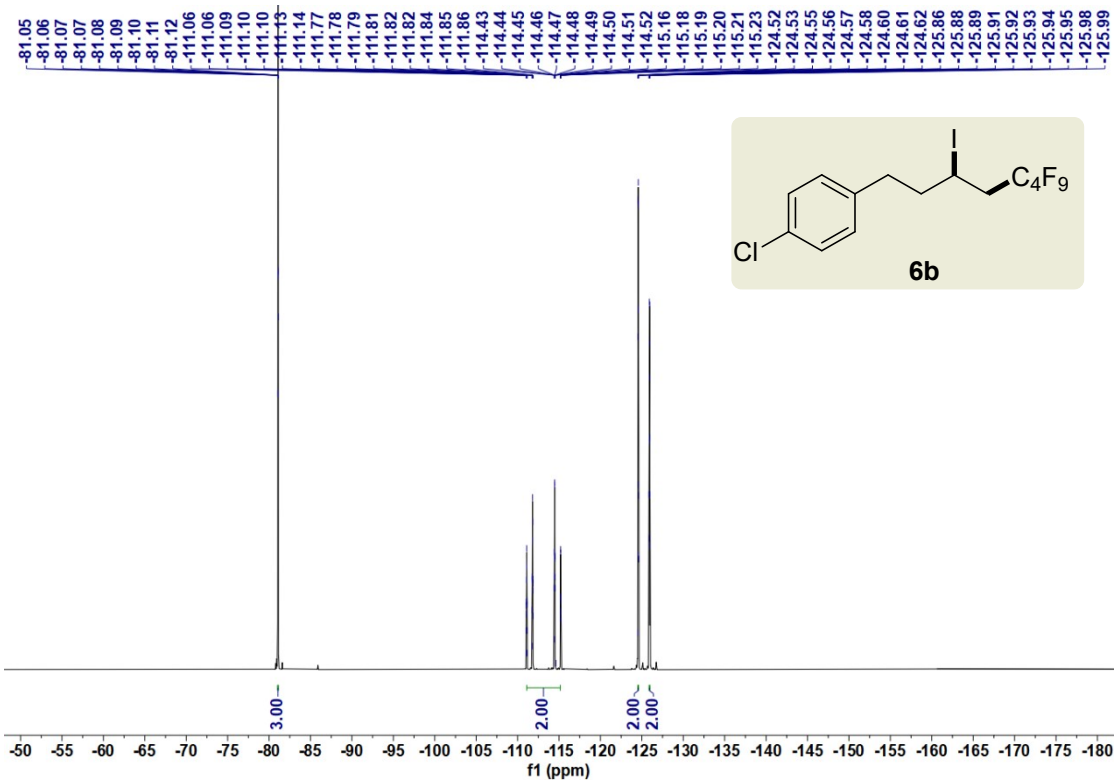
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6b**:



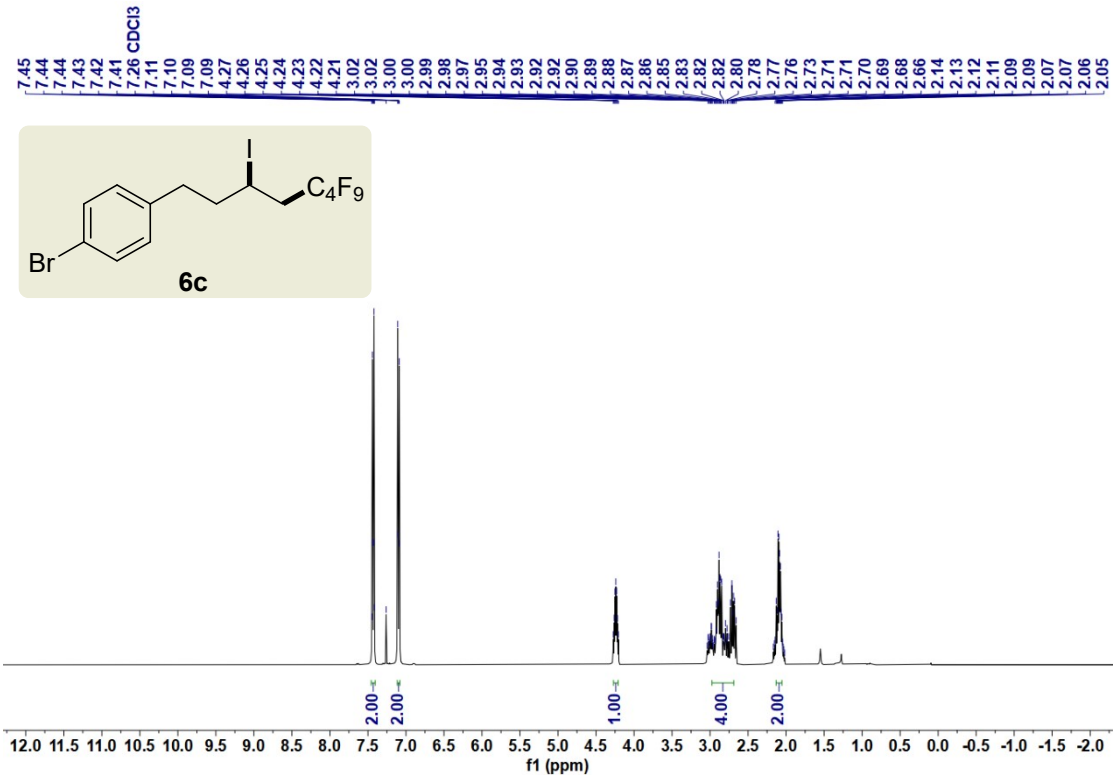
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6b**:



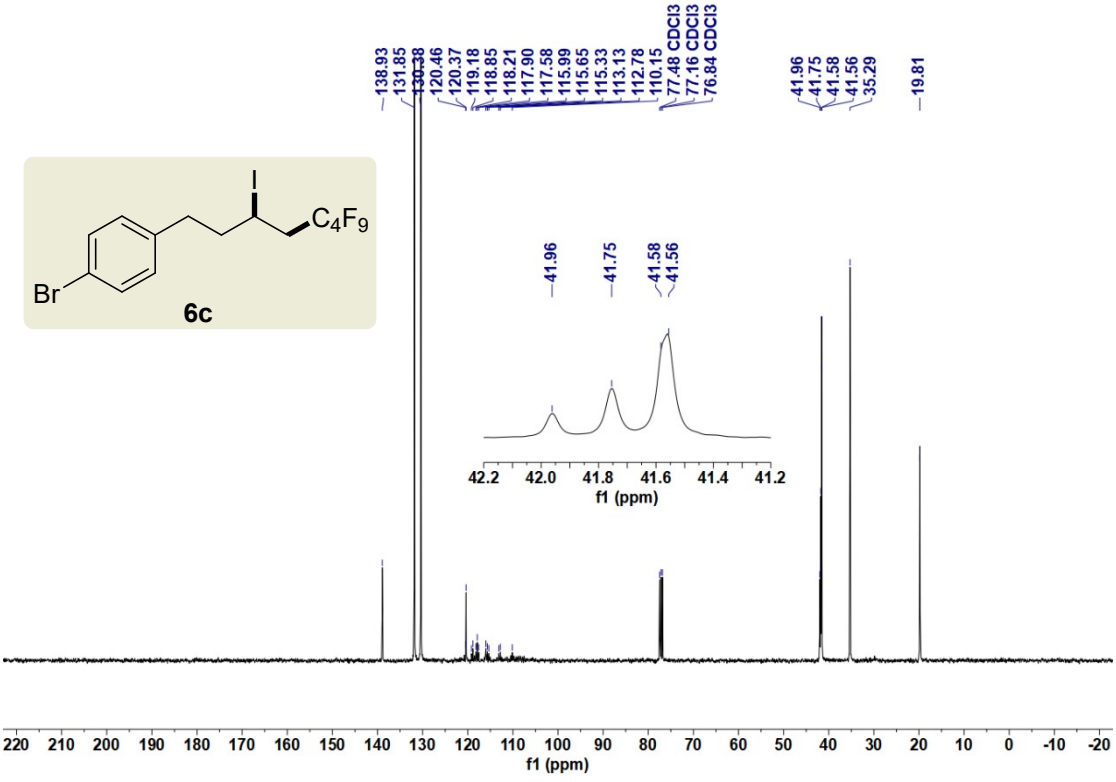
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6b**:



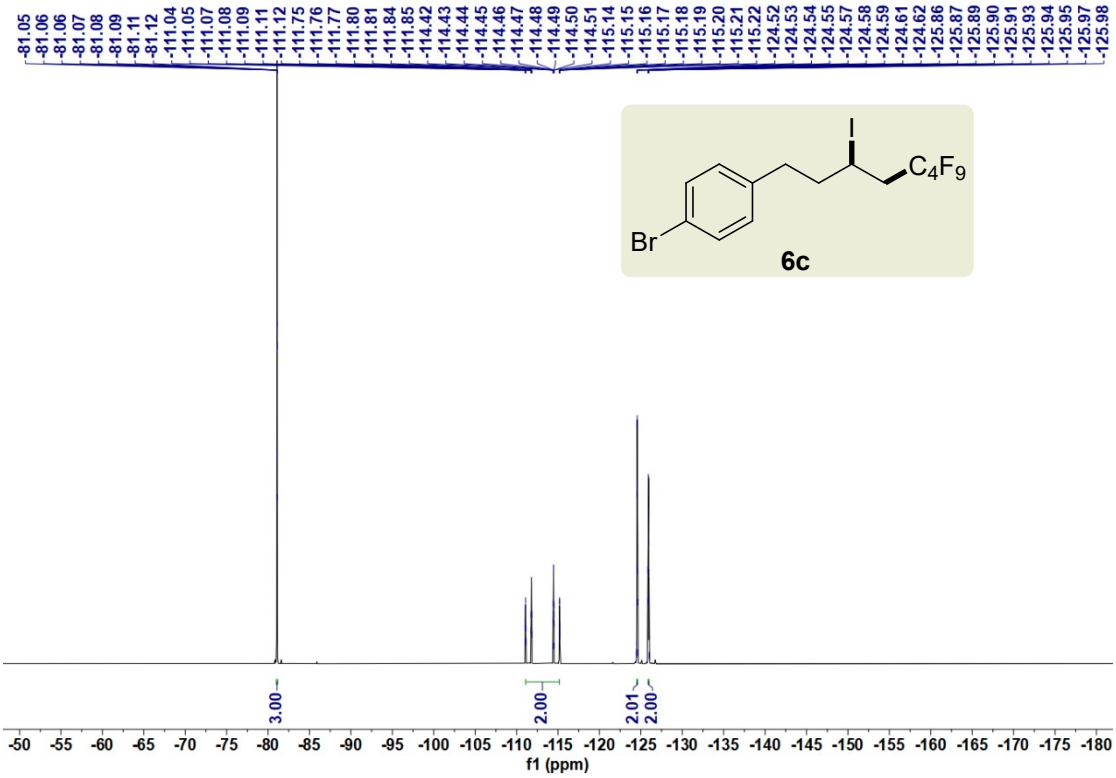
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6c**:



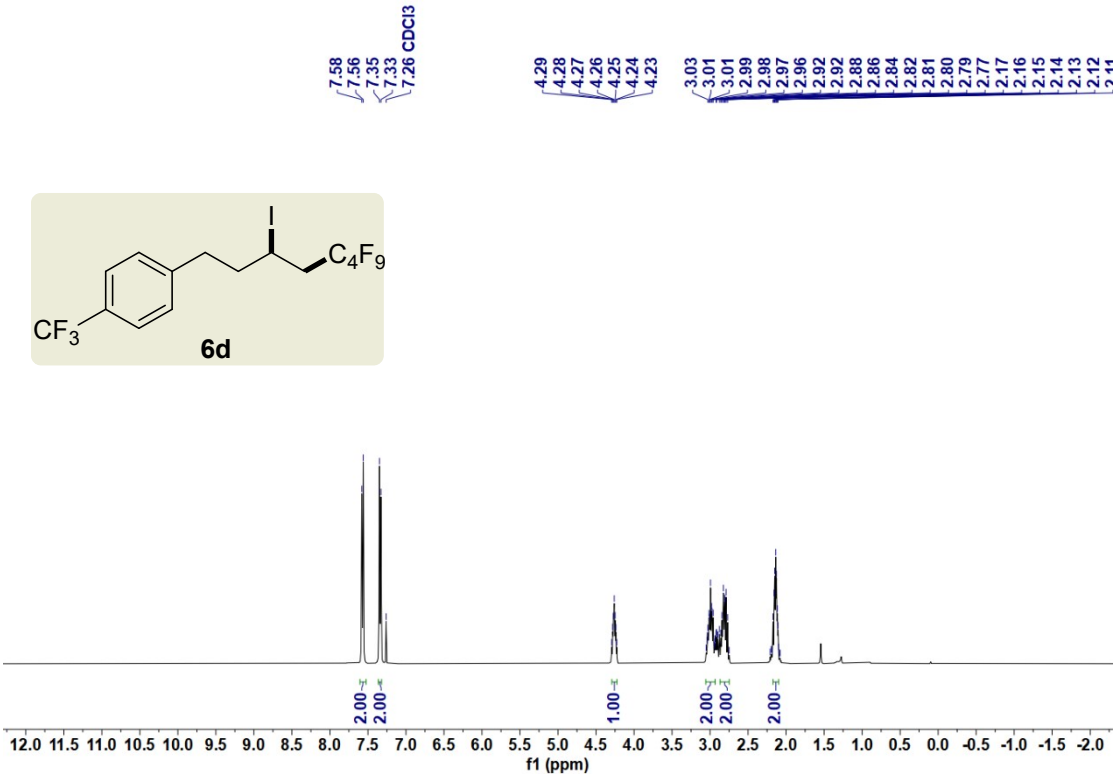
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6c**:



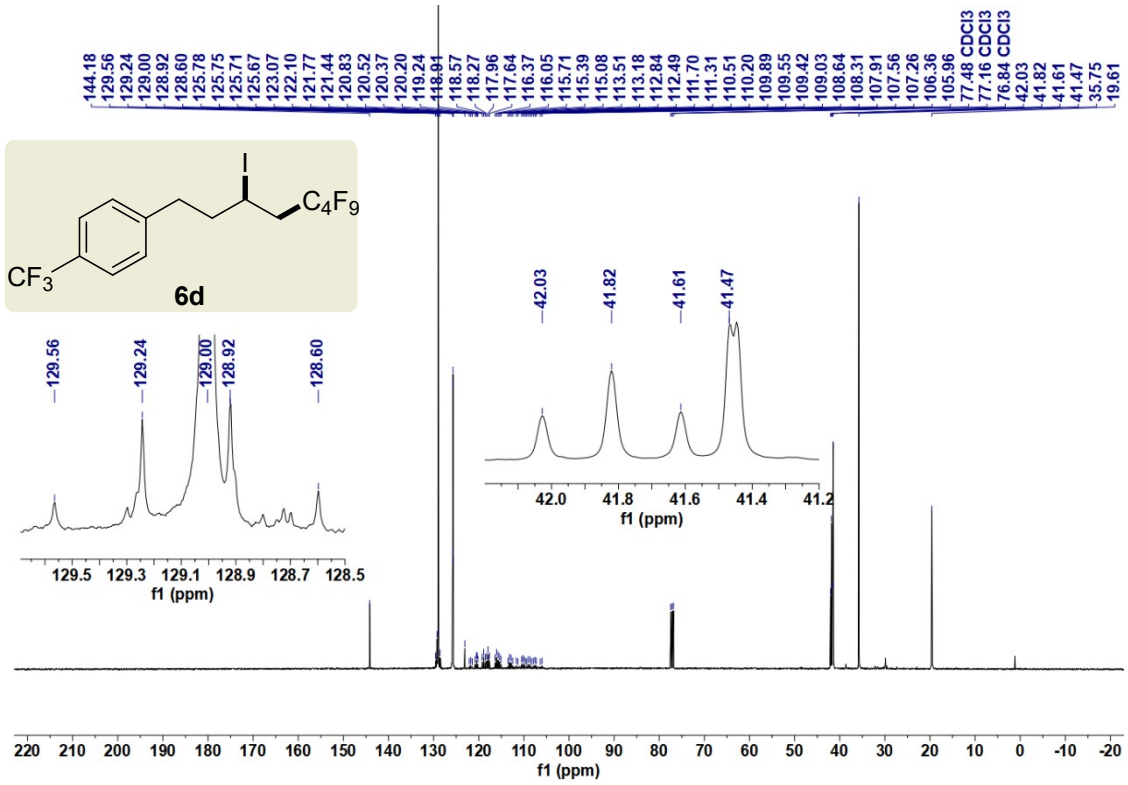
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6c**:



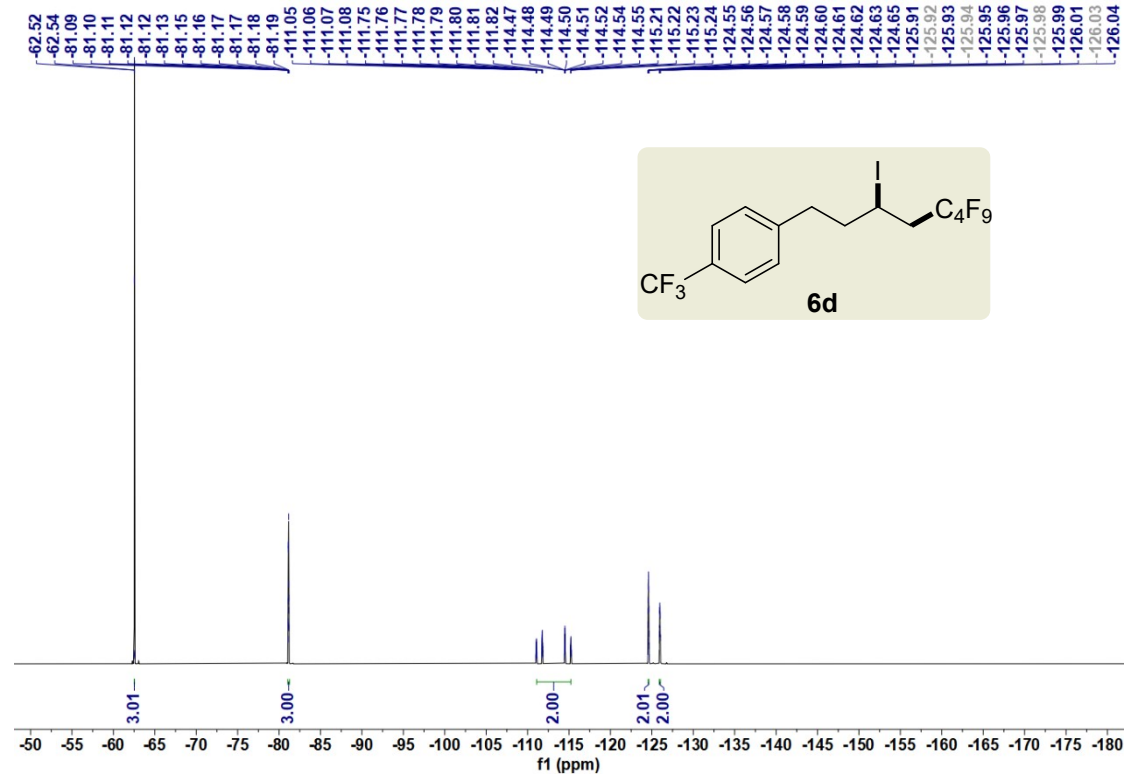
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6d**:



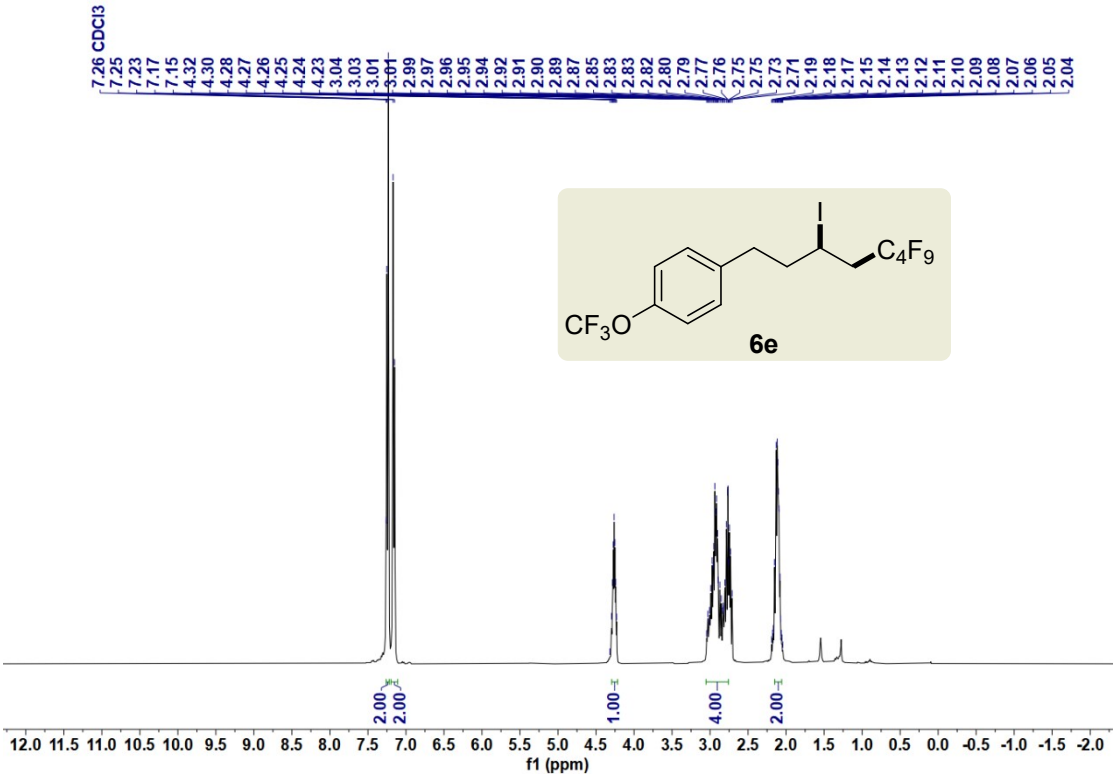
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6d**:



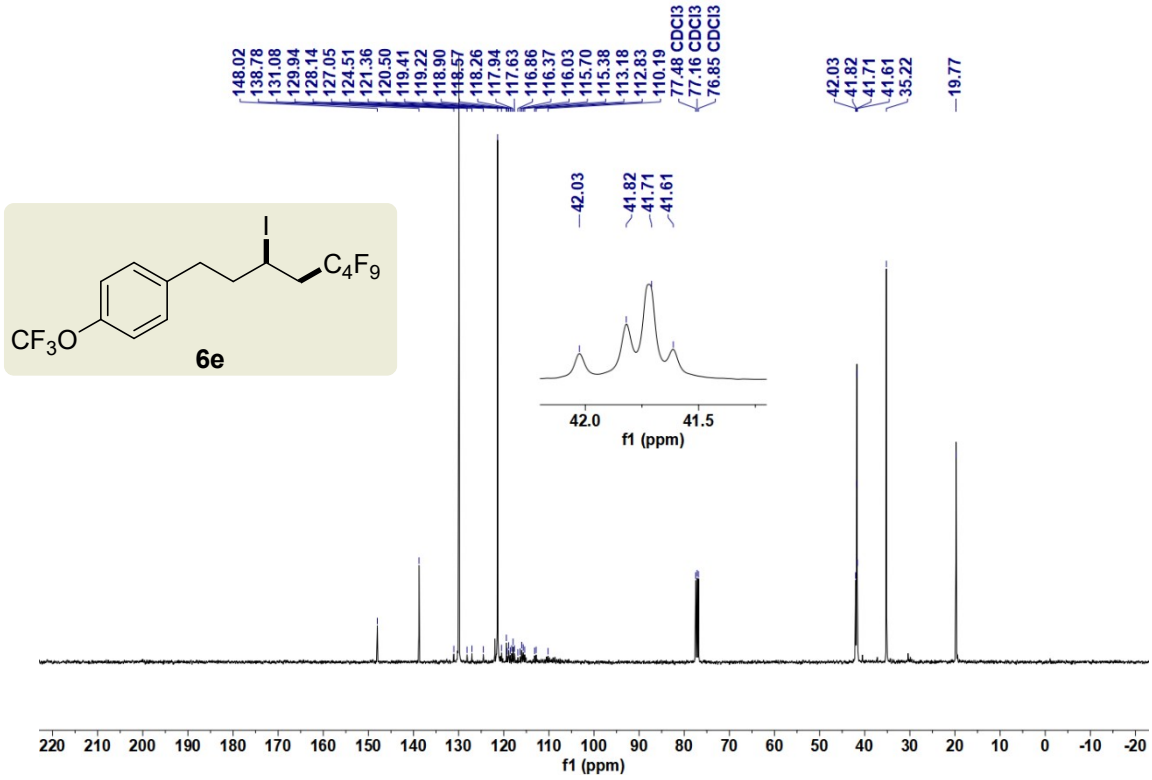
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6d**:



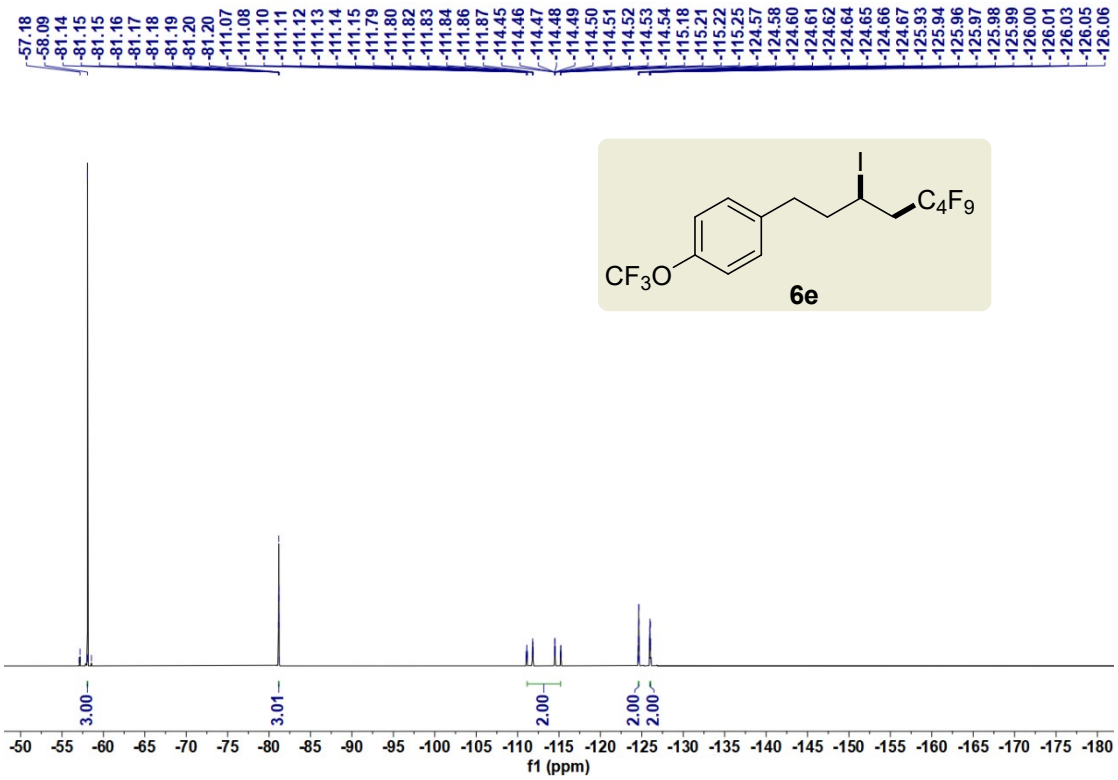
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6e**:



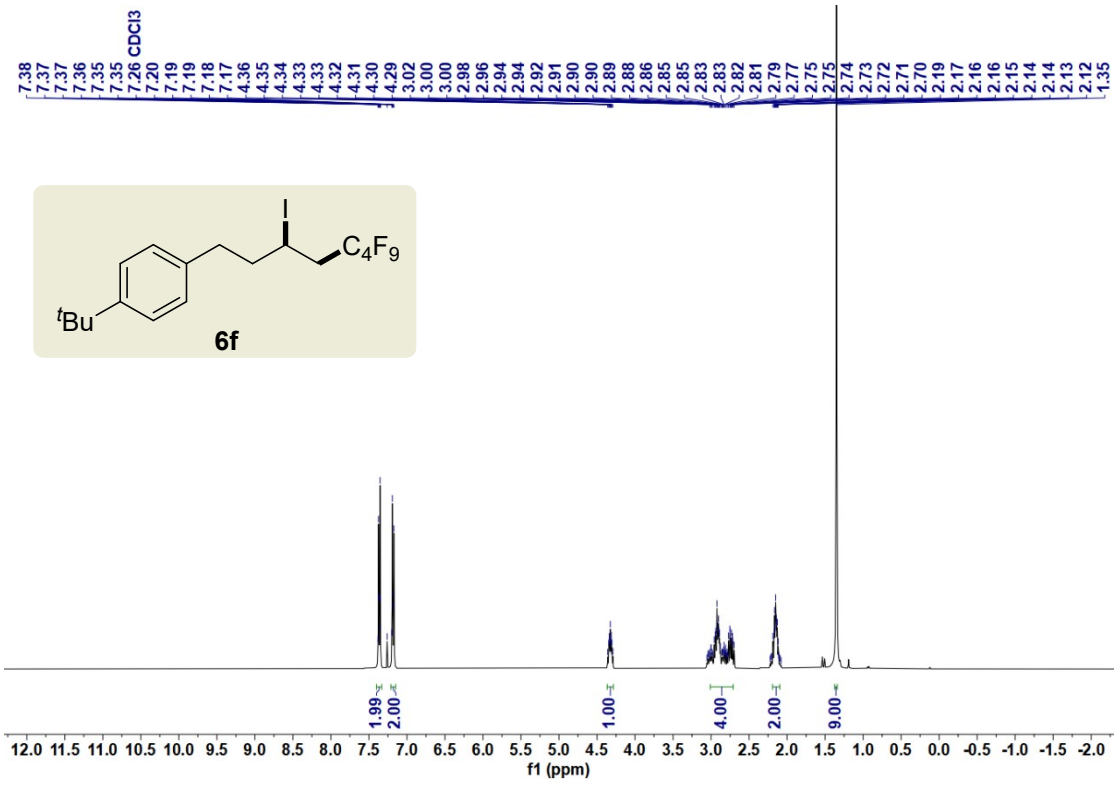
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6e**:



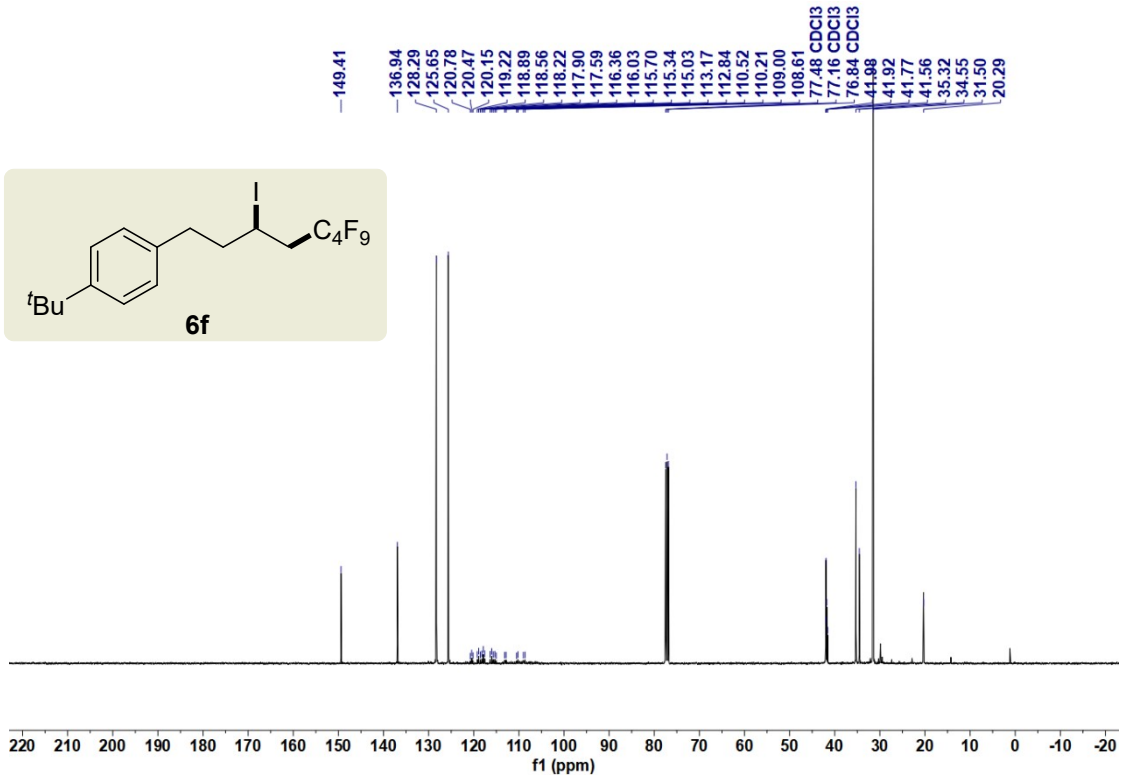
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6e**:



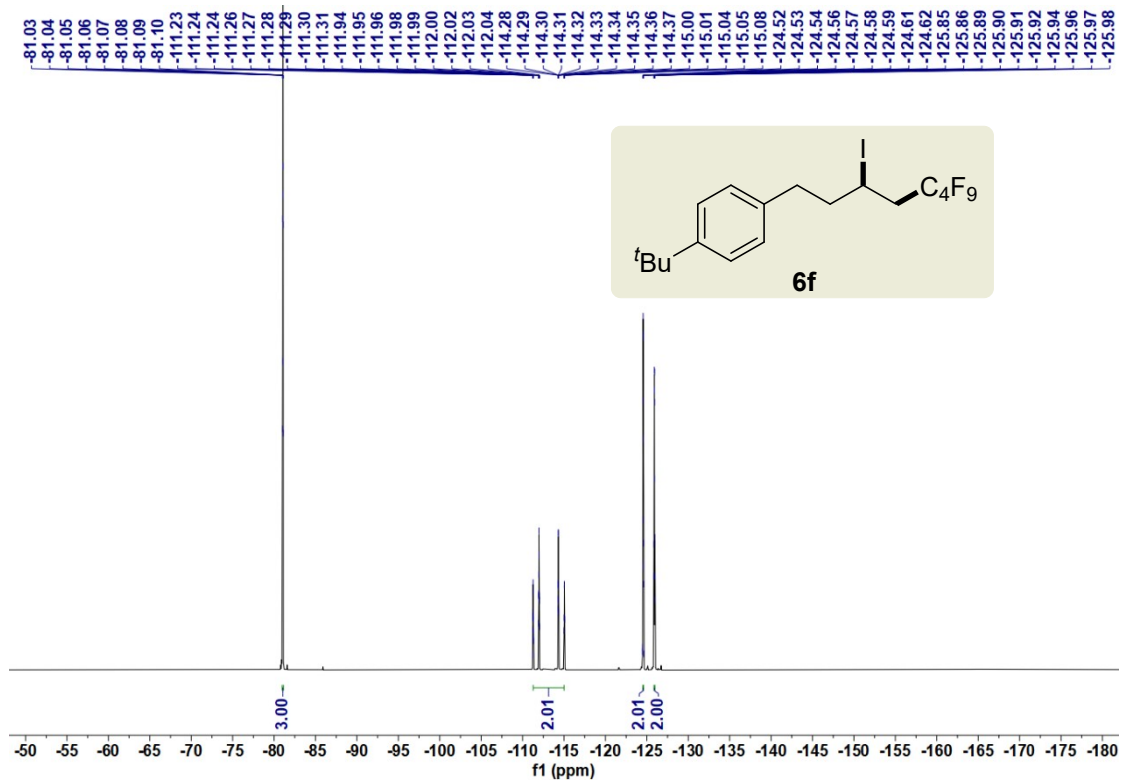
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6f**:



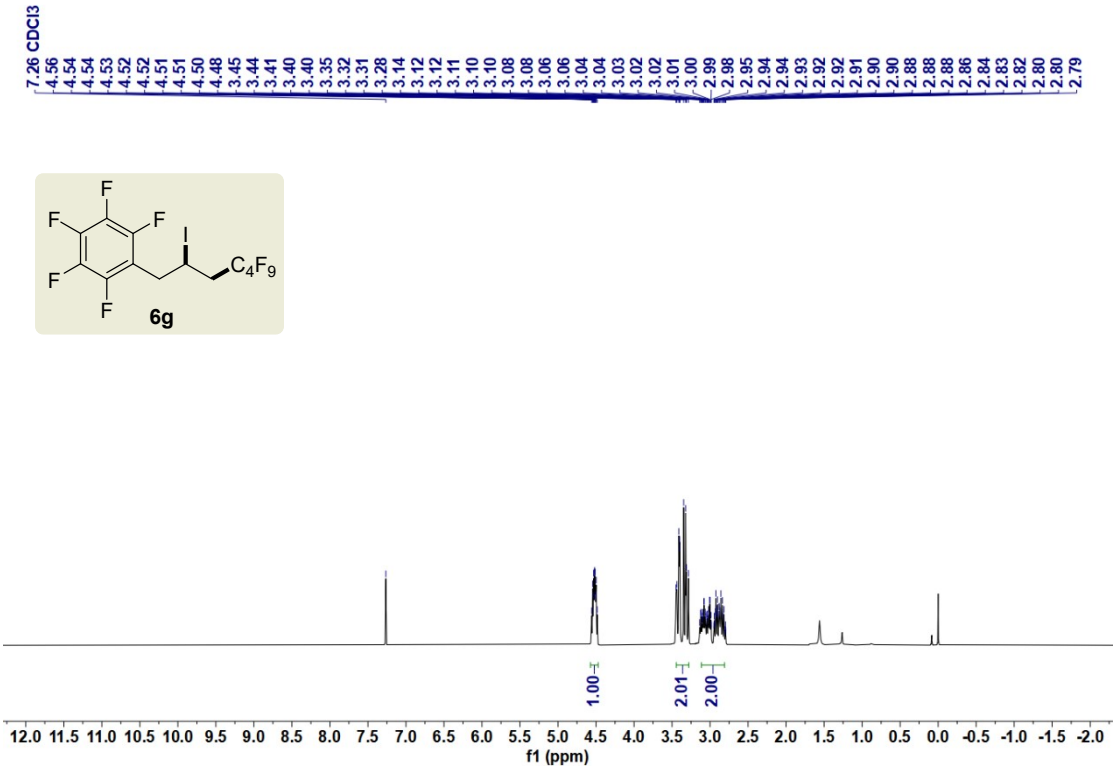
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6f**:



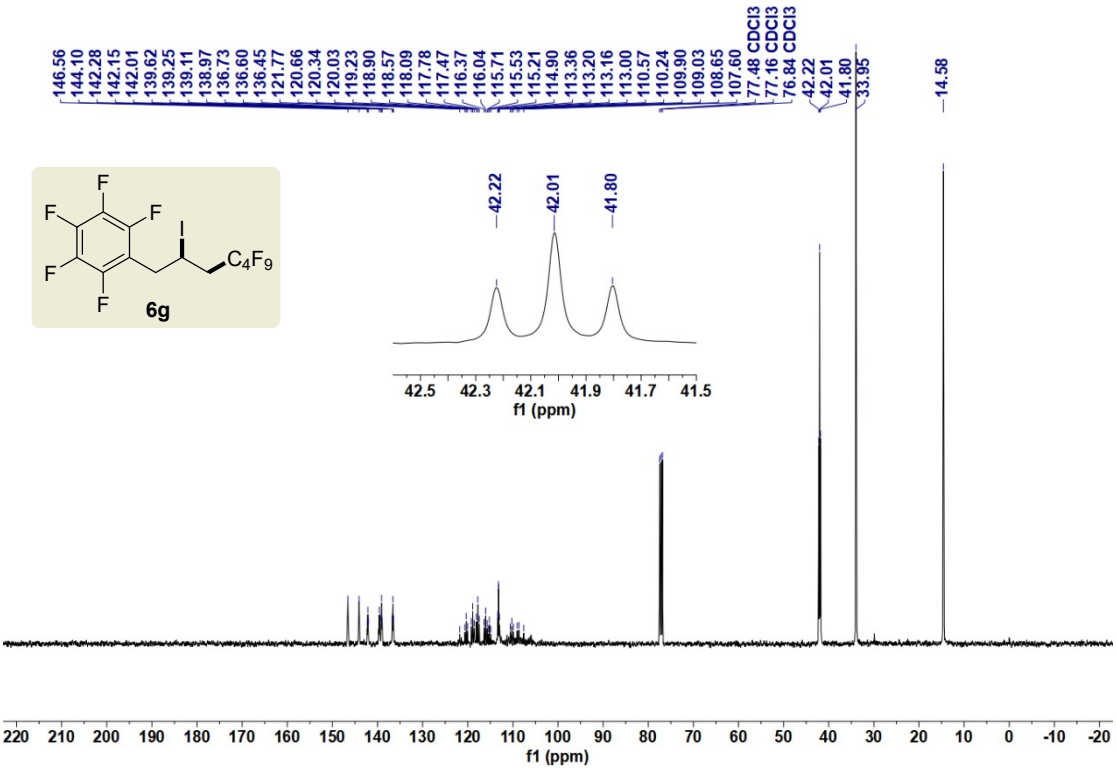
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6f**:



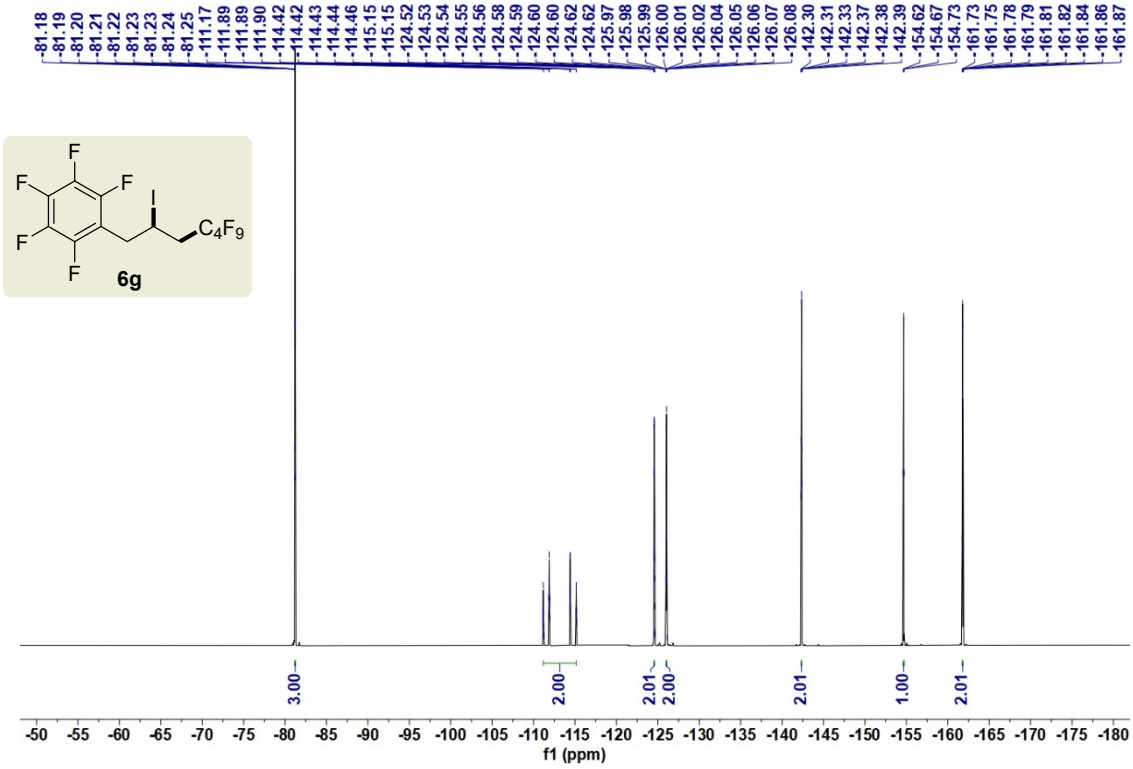
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6g**:



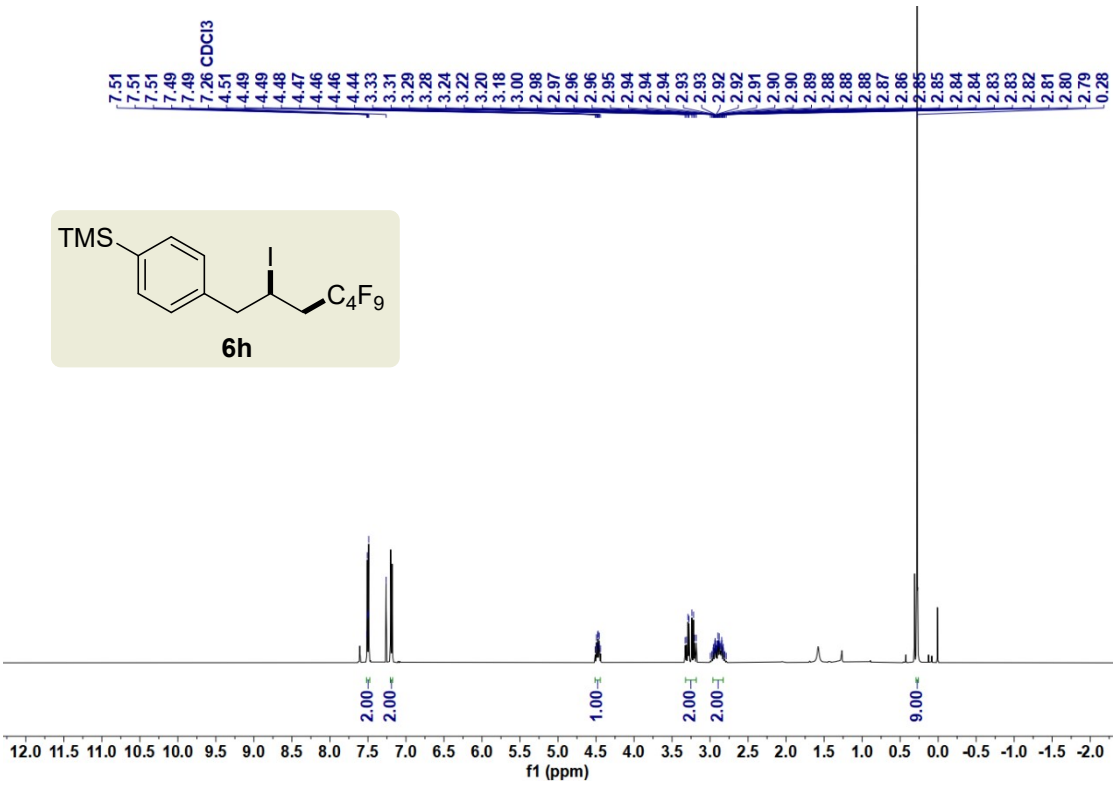
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6g**:



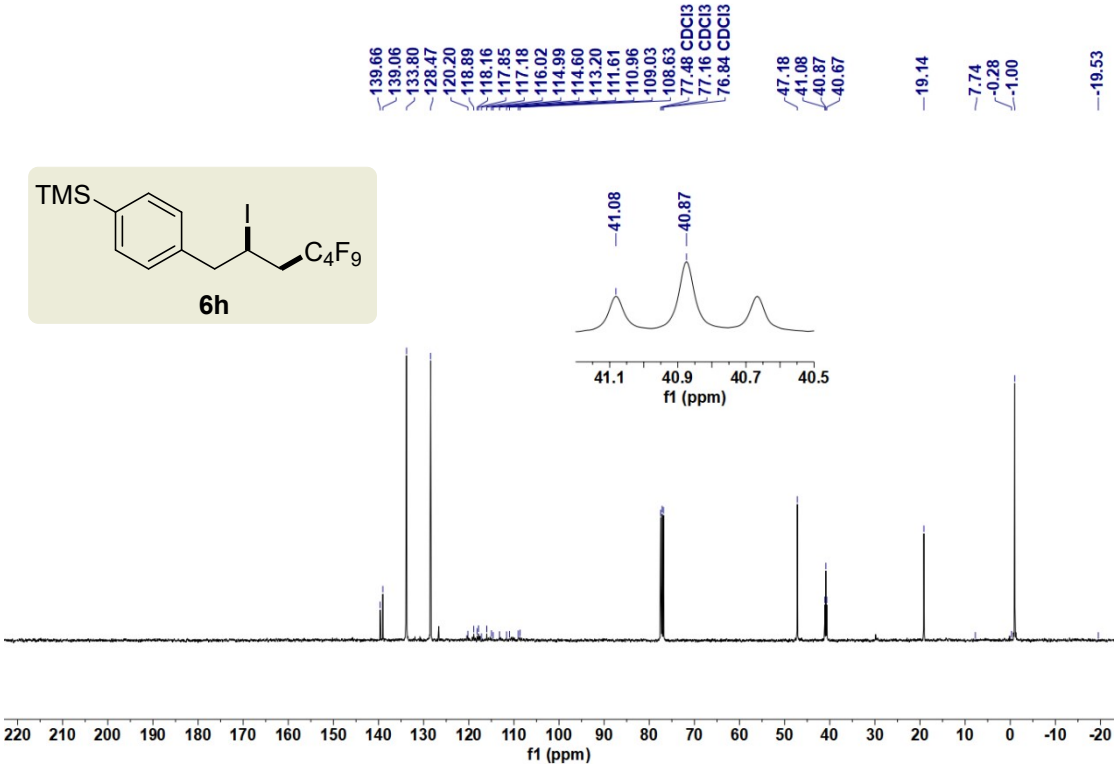
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6g**:



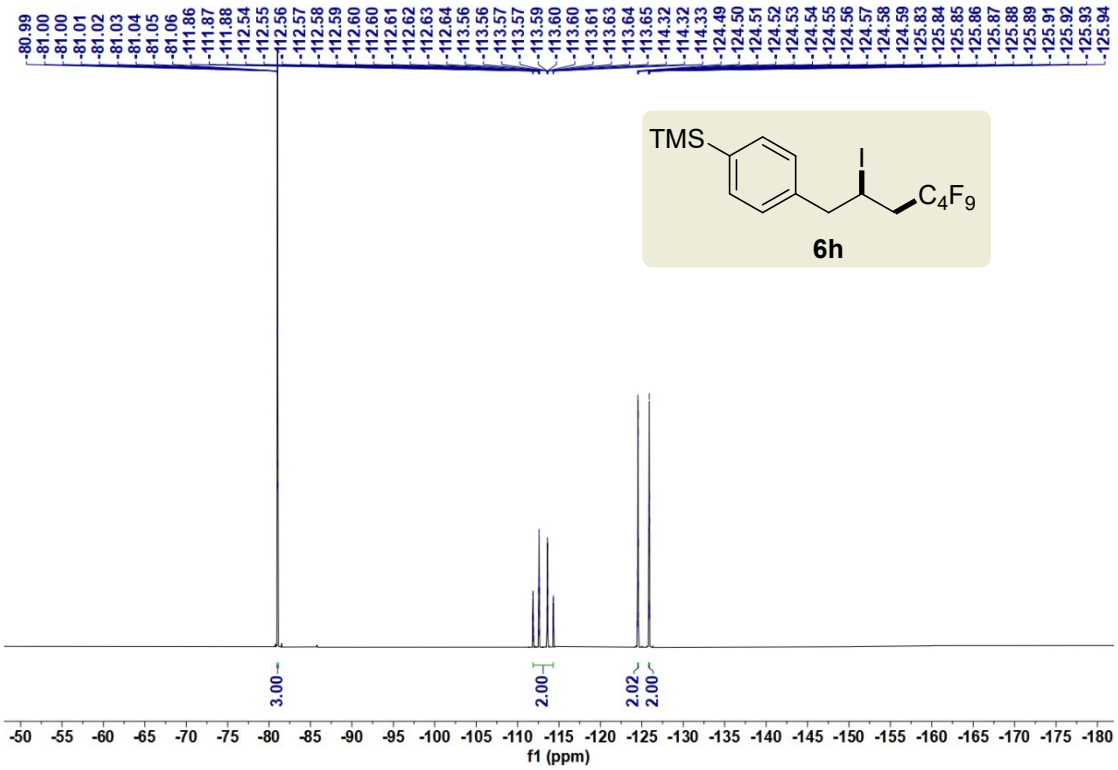
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6h**:



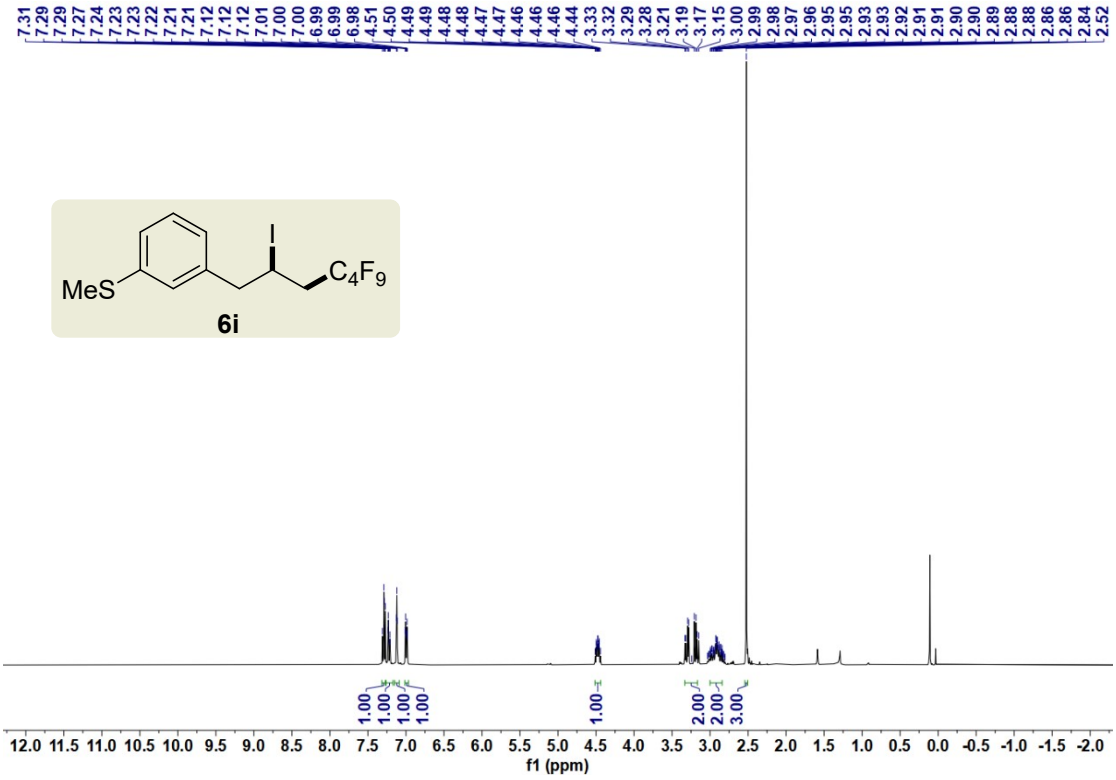
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6h**:



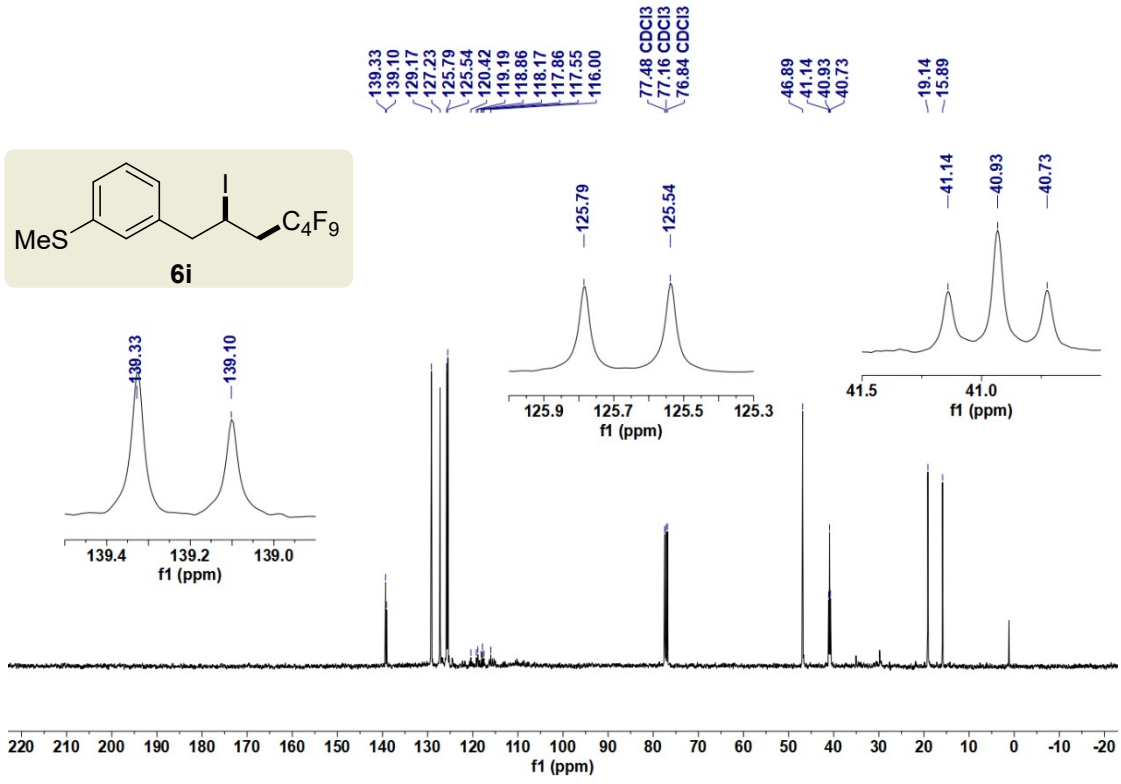
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6h**:



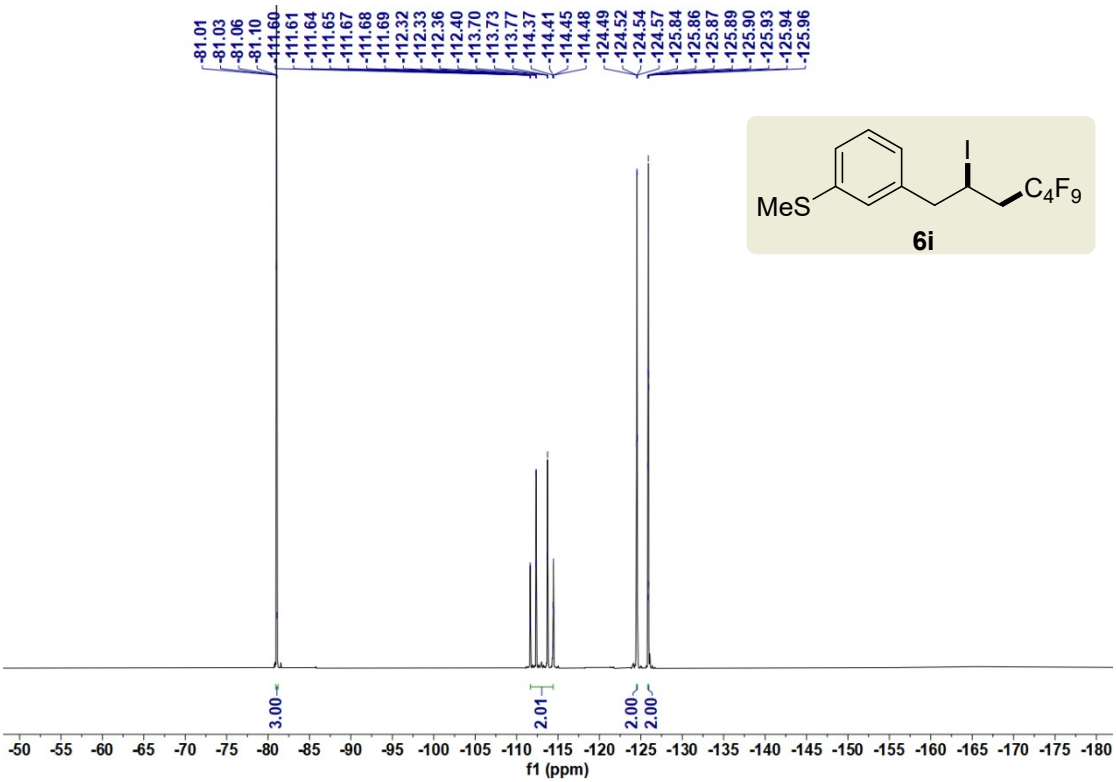
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6i**:



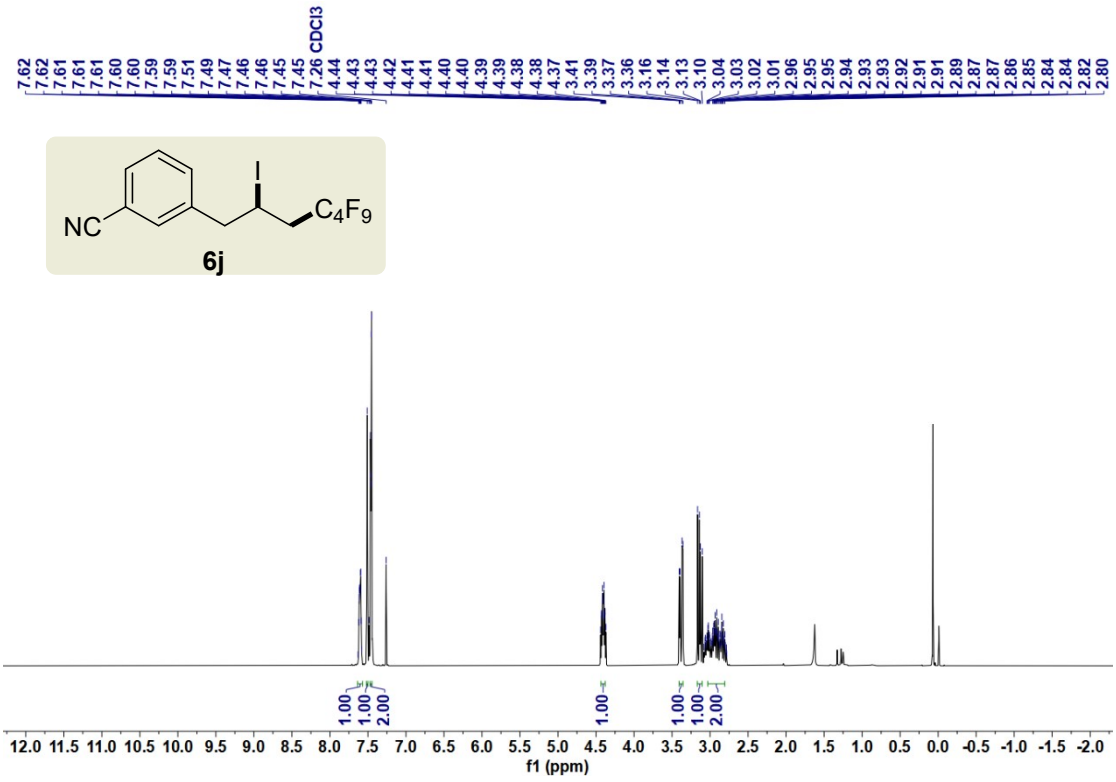
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6i**:



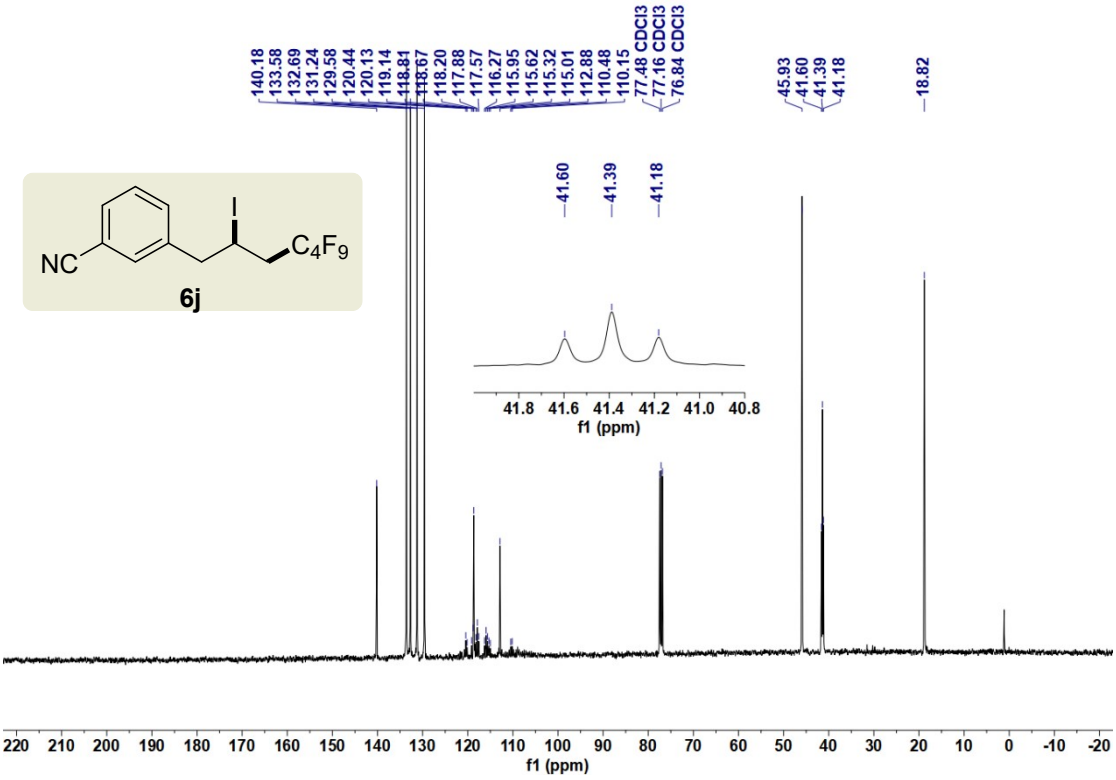
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6i**:



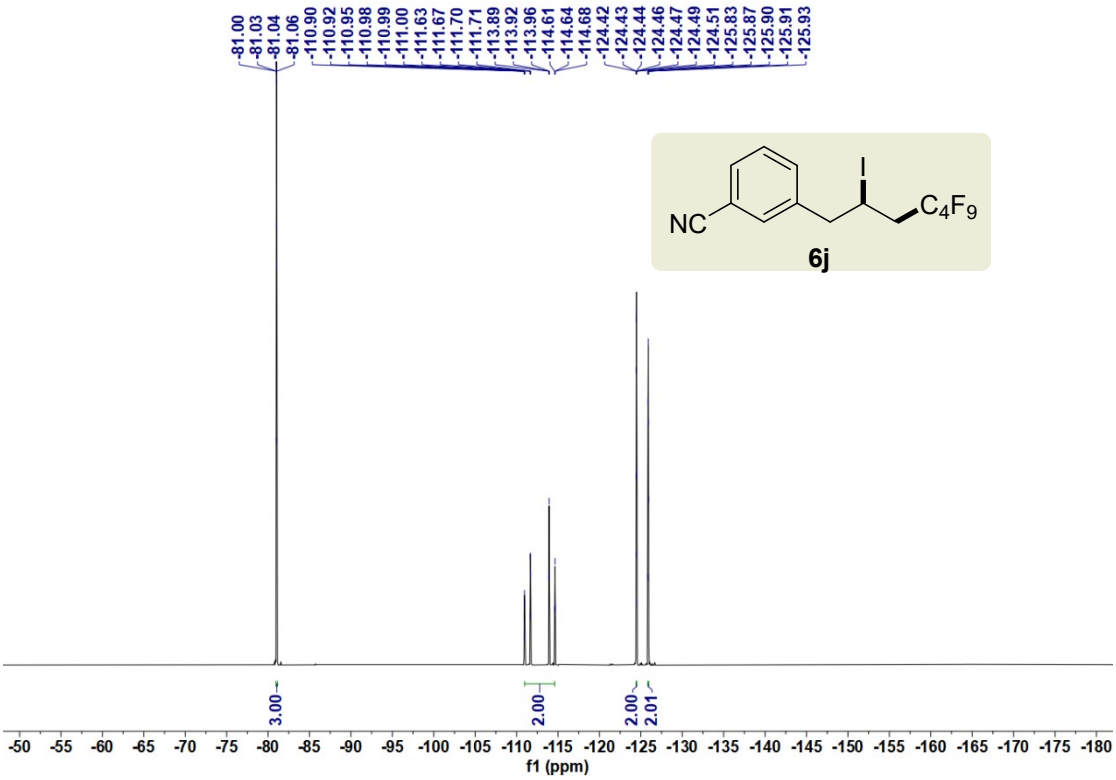
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6j**:



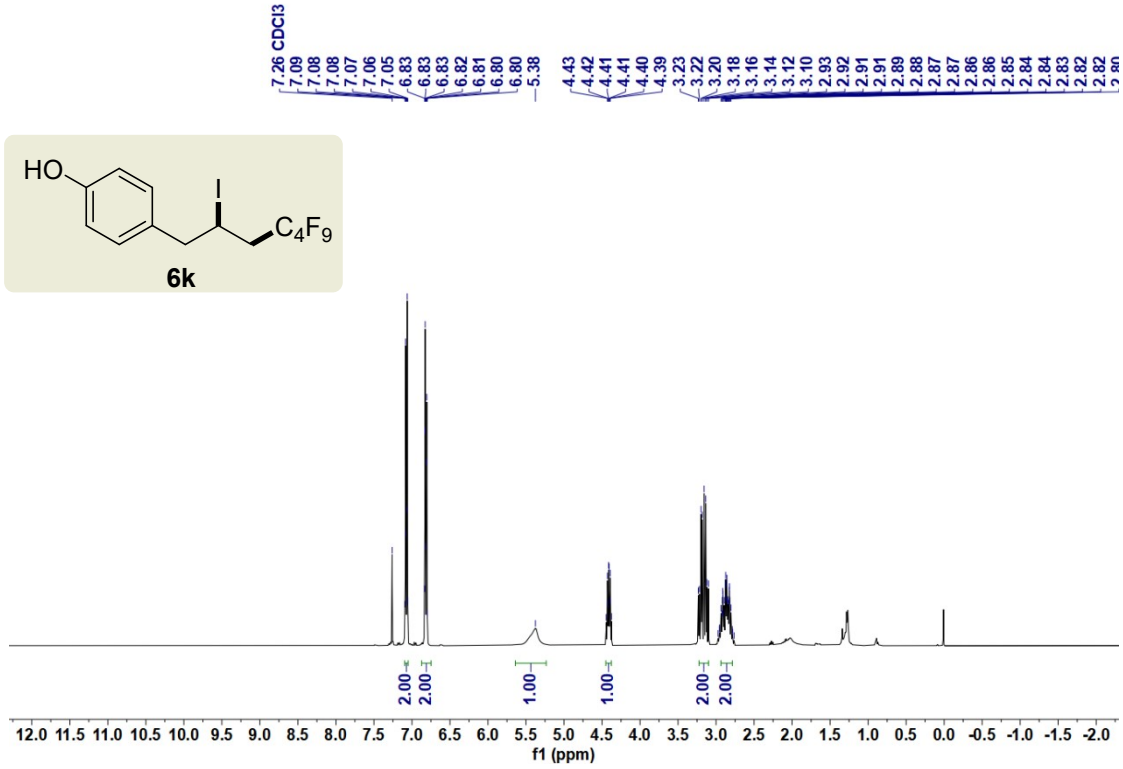
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6j**:



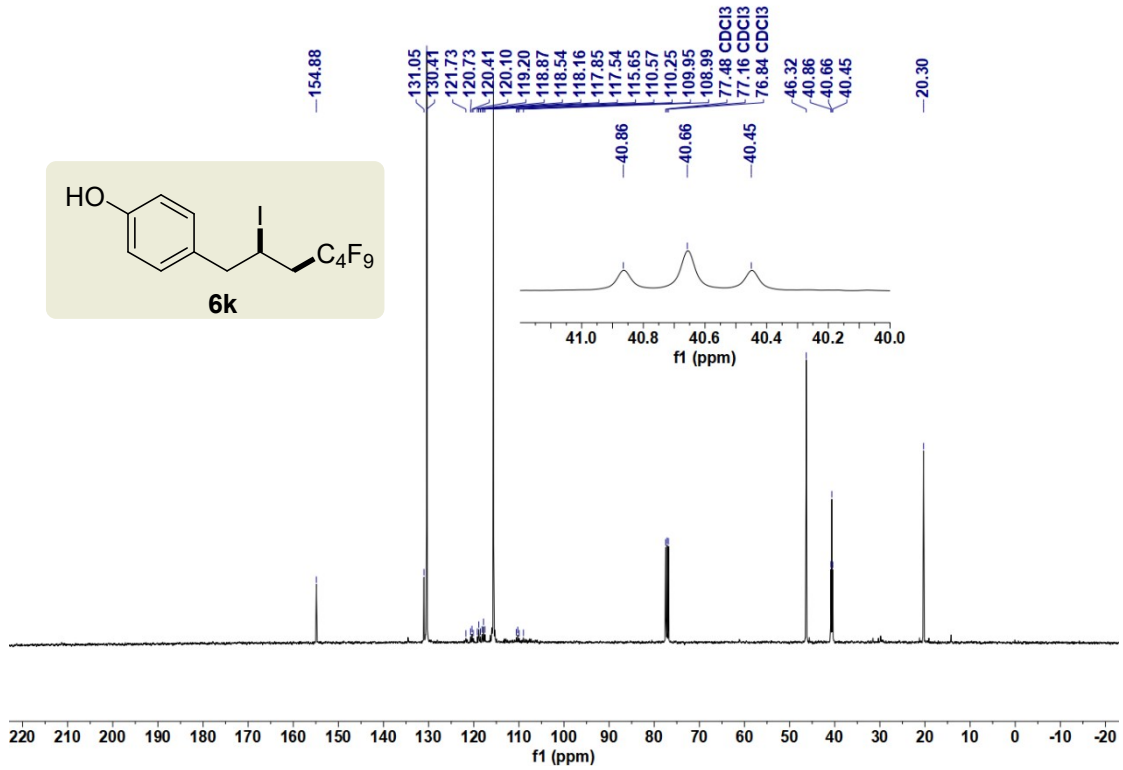
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6j**:



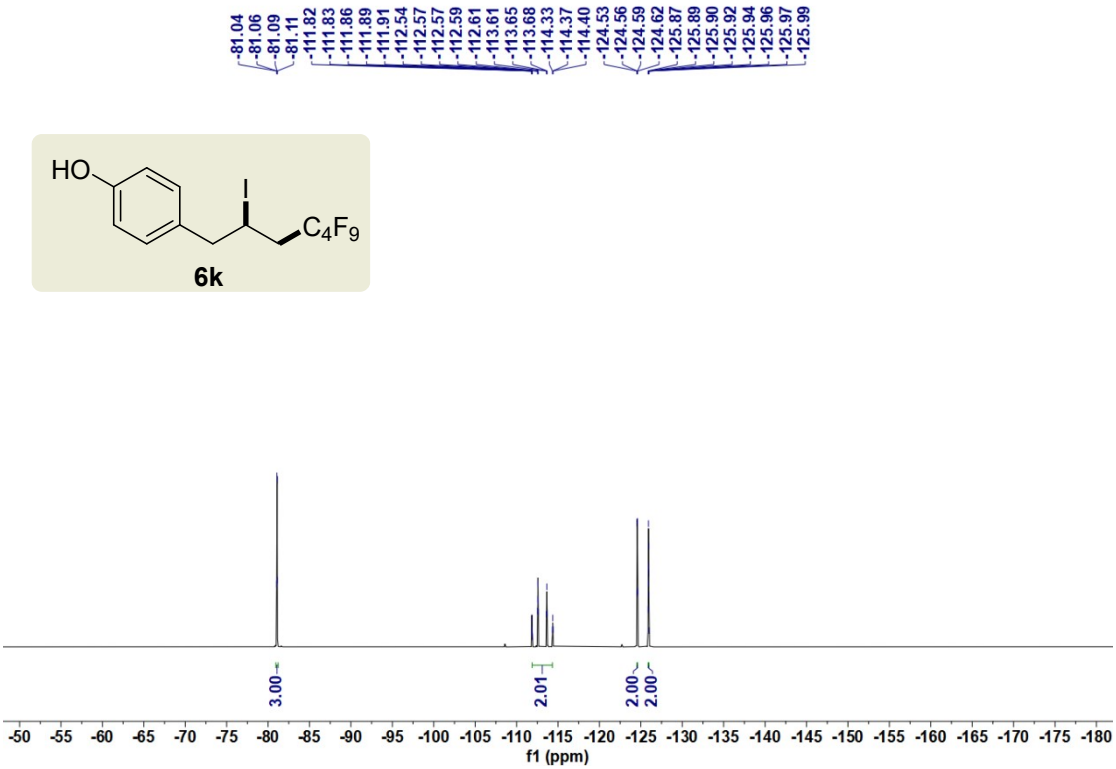
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6k**:



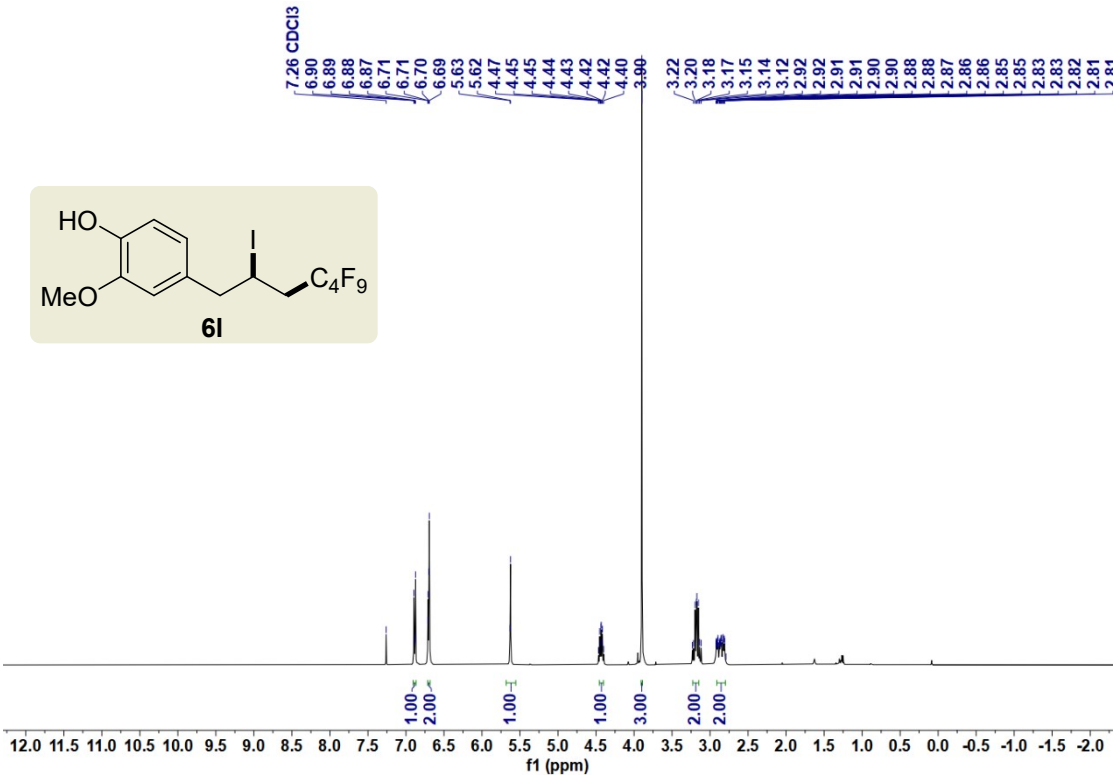
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6k**:



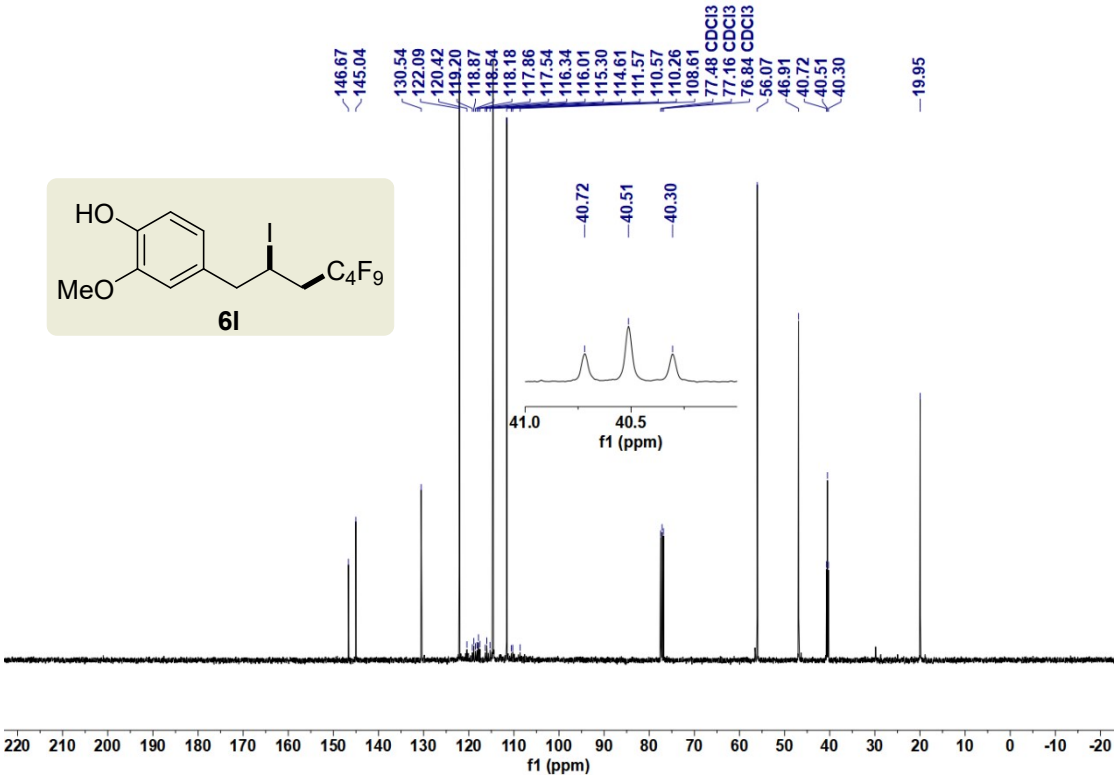
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6k**:



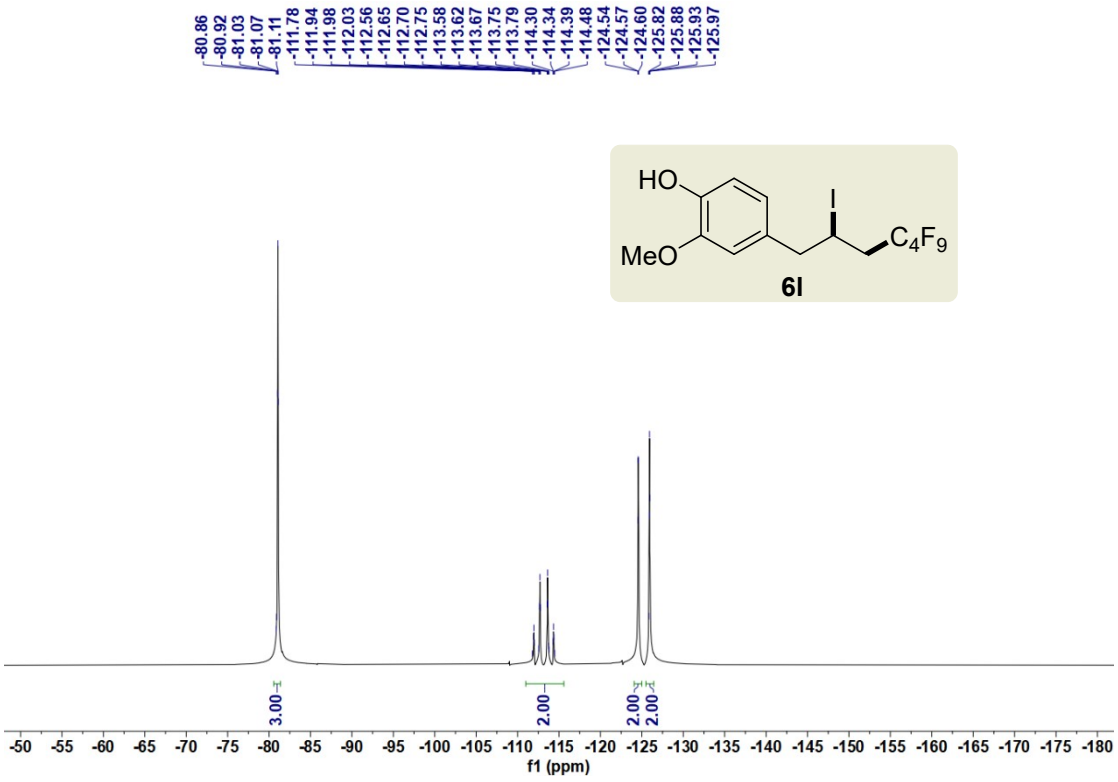
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6l**:



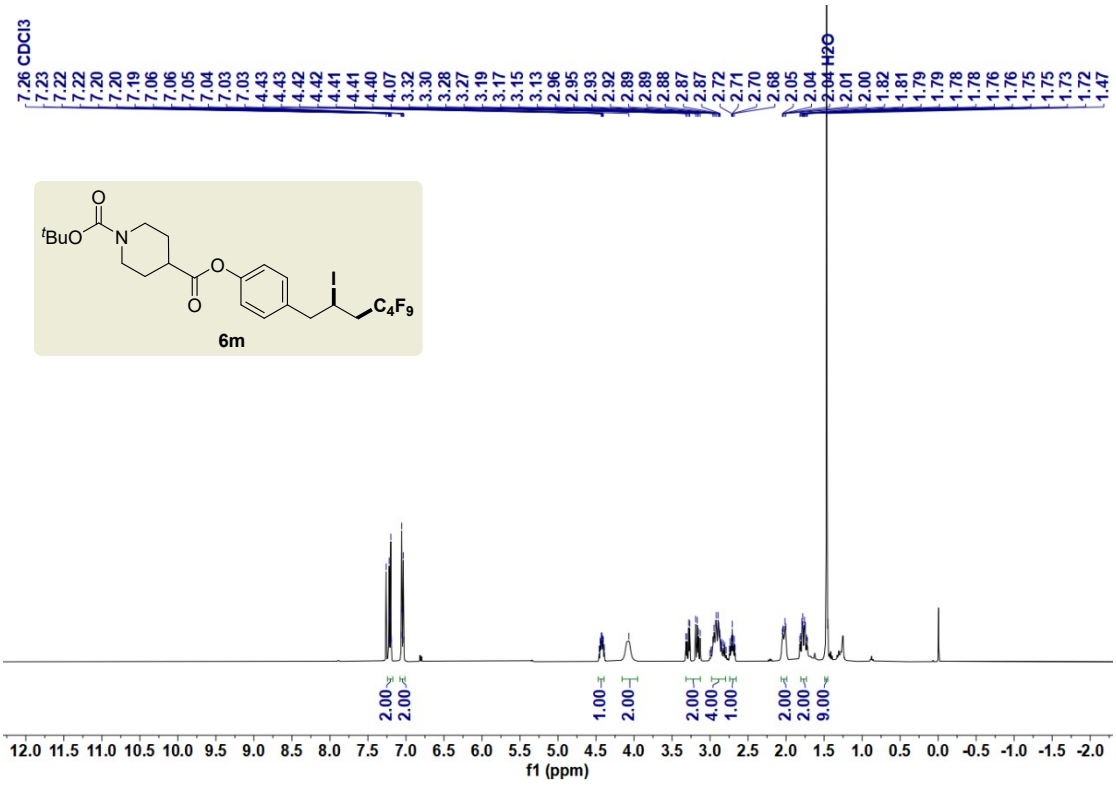
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6l**:



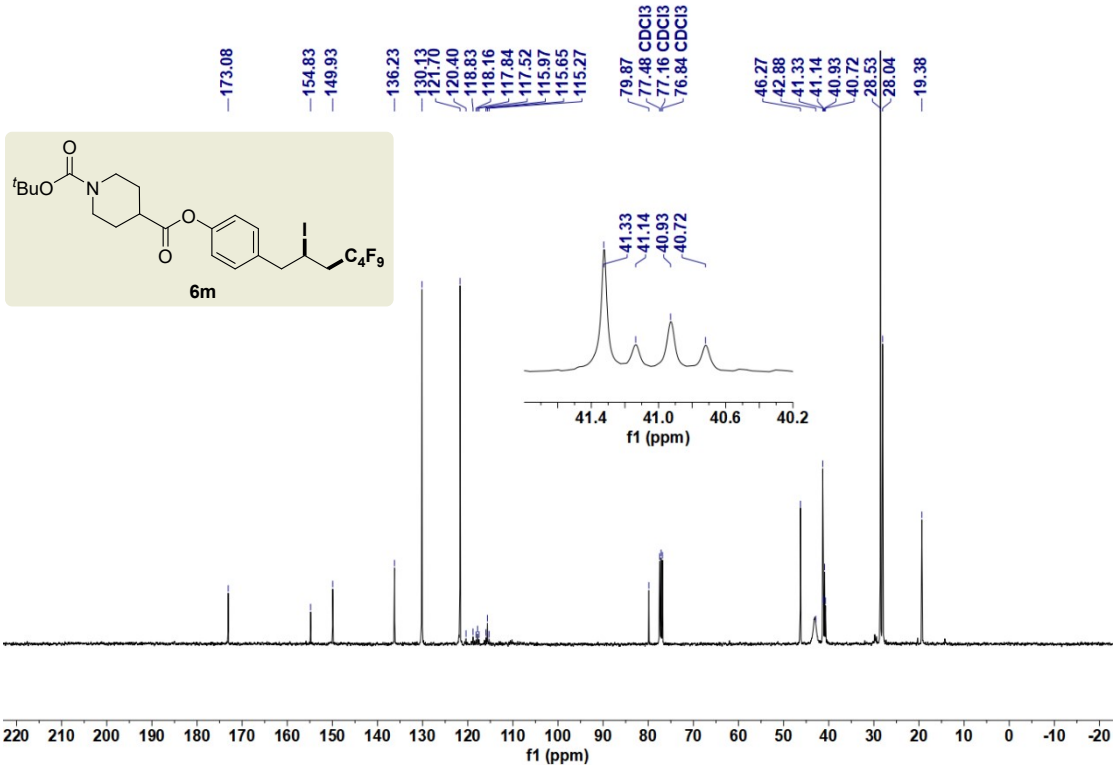
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6l**:



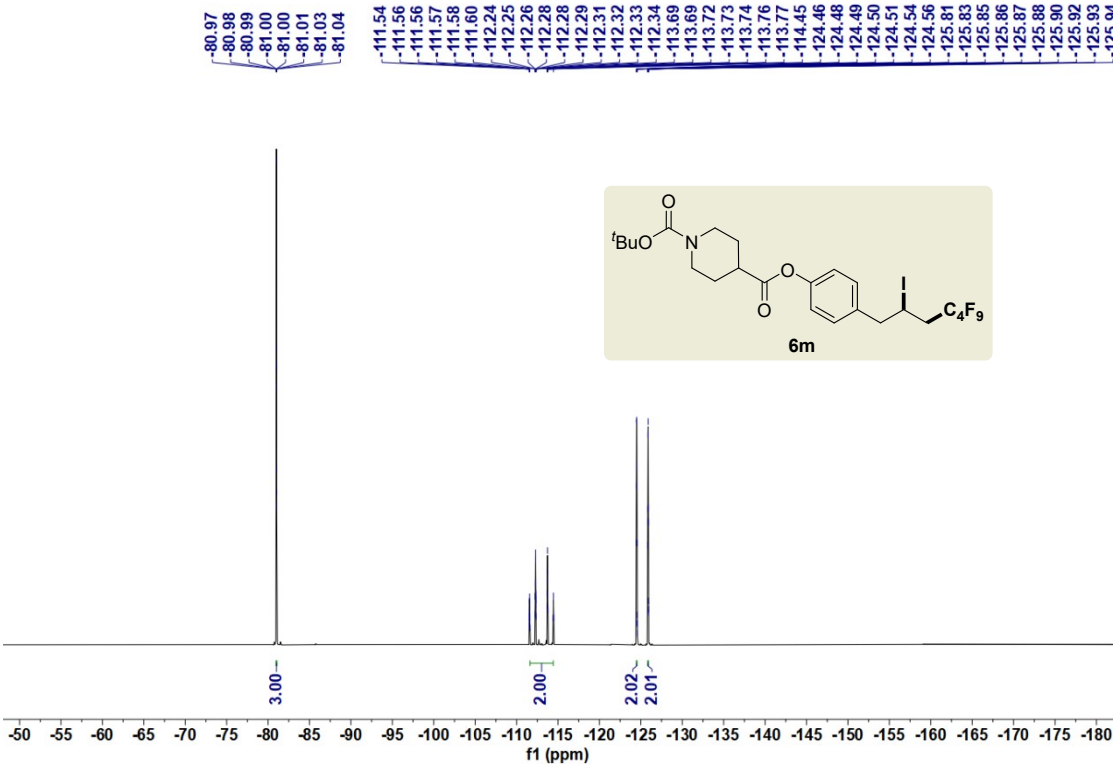
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6m**:



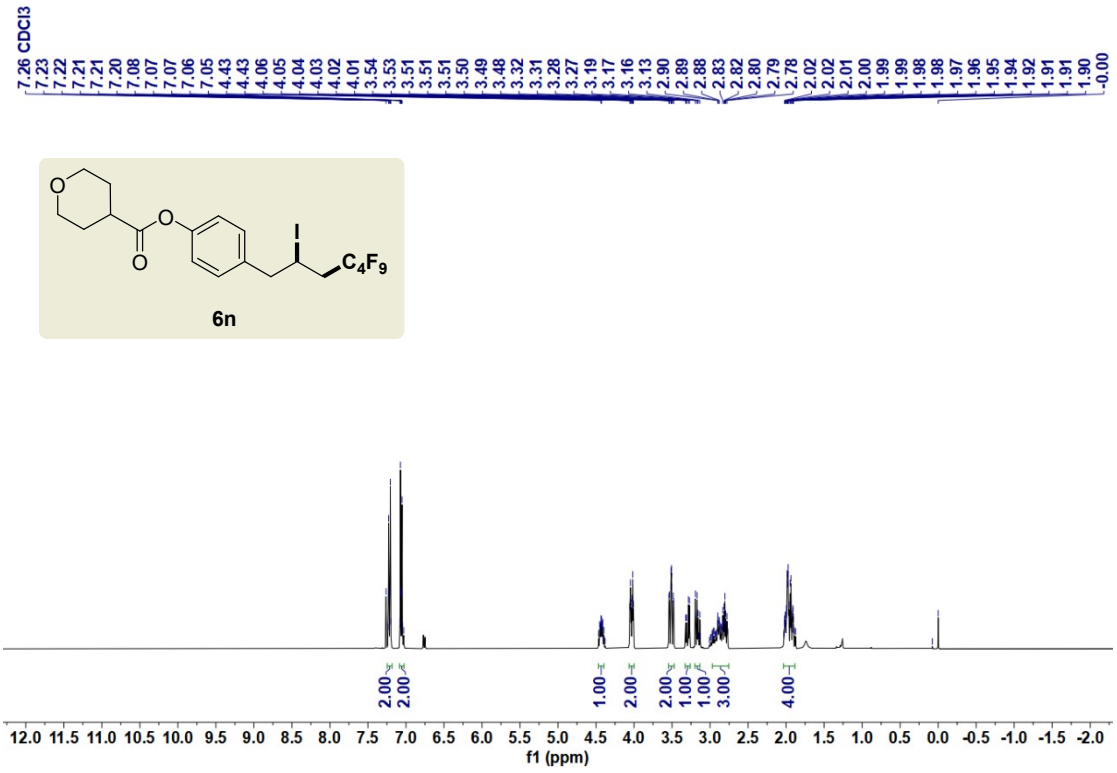
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6m**:



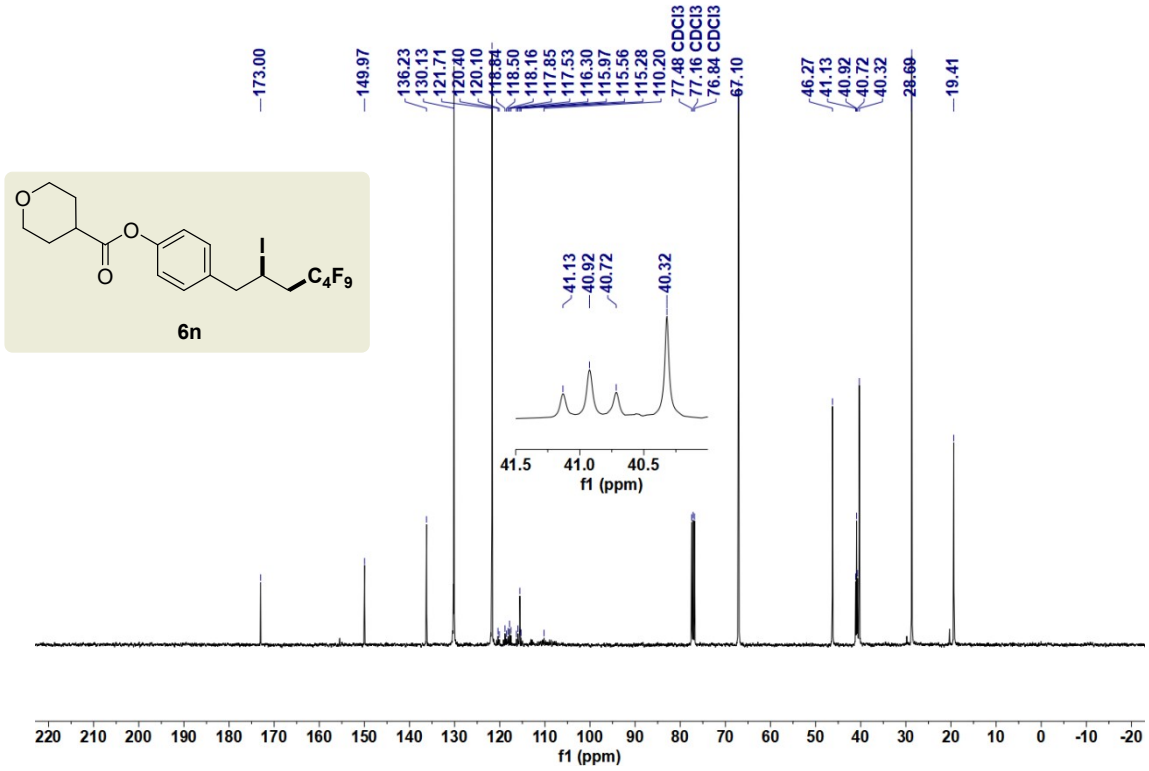
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6m**:



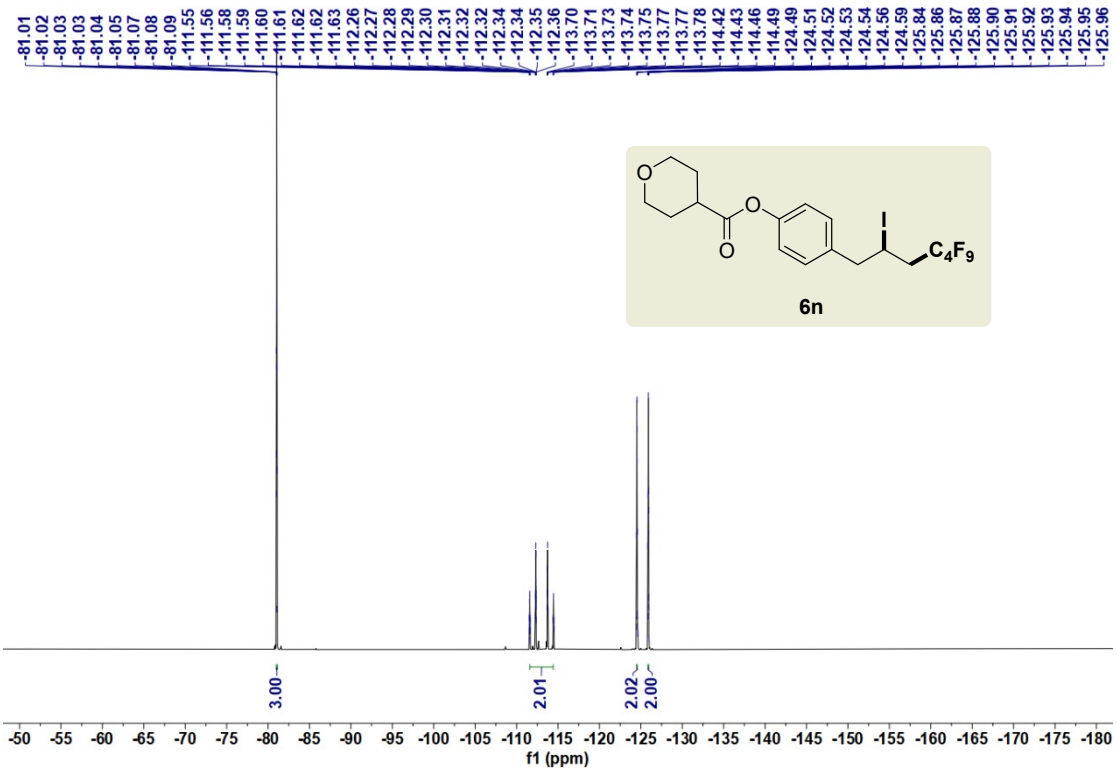
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6n**:



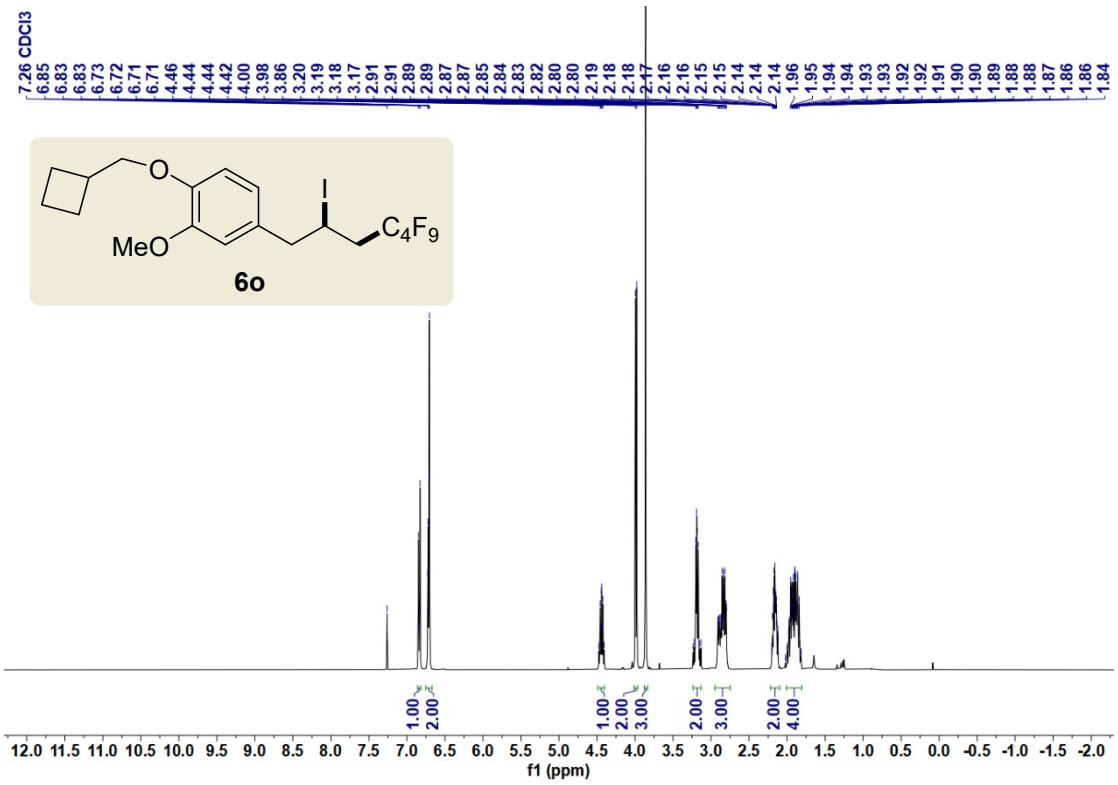
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6n**:



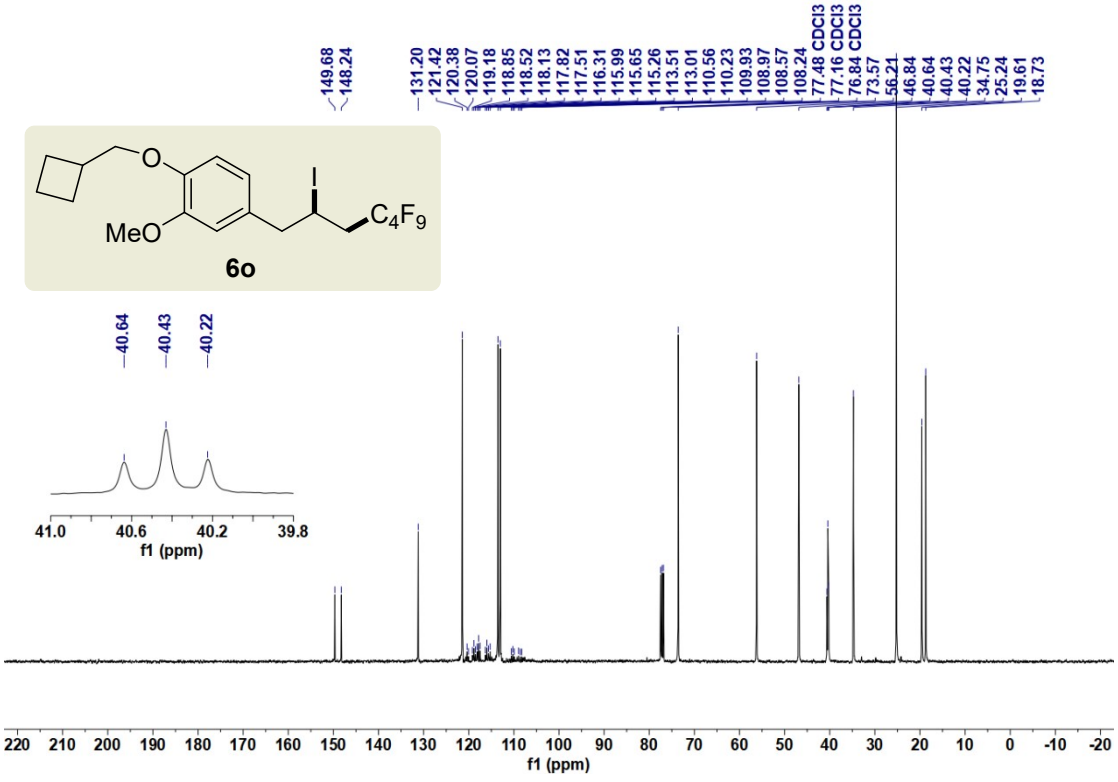
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6n**:



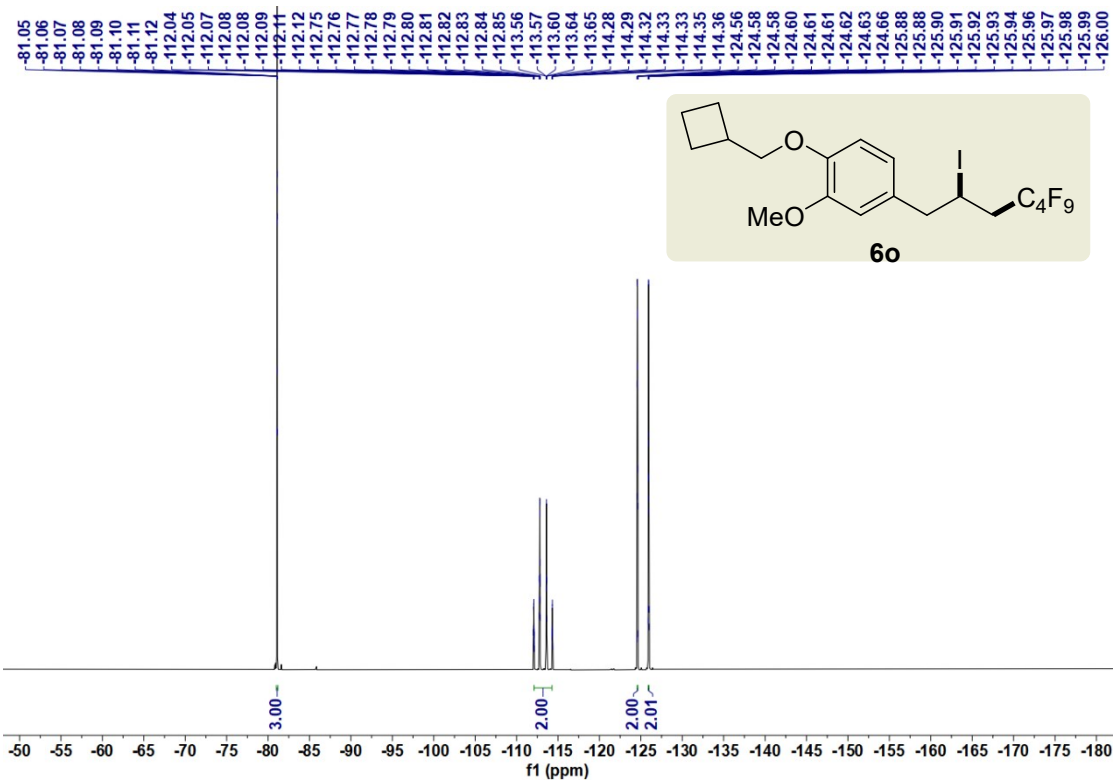
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6o**:



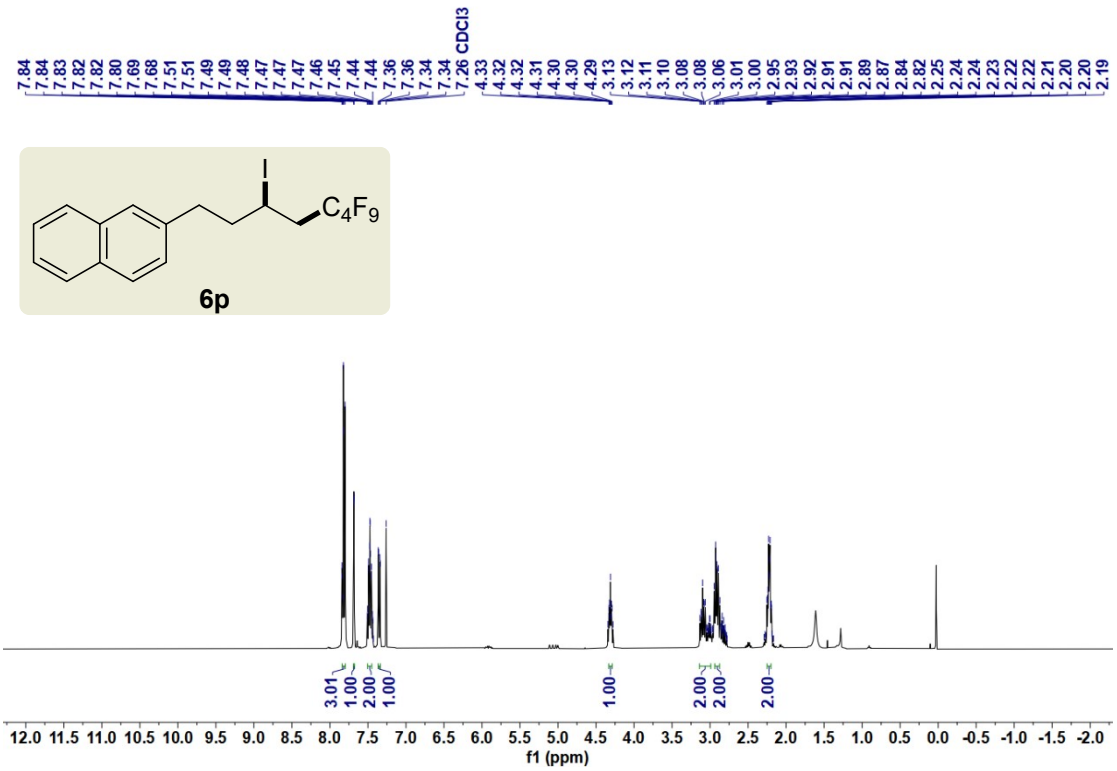
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6o**:



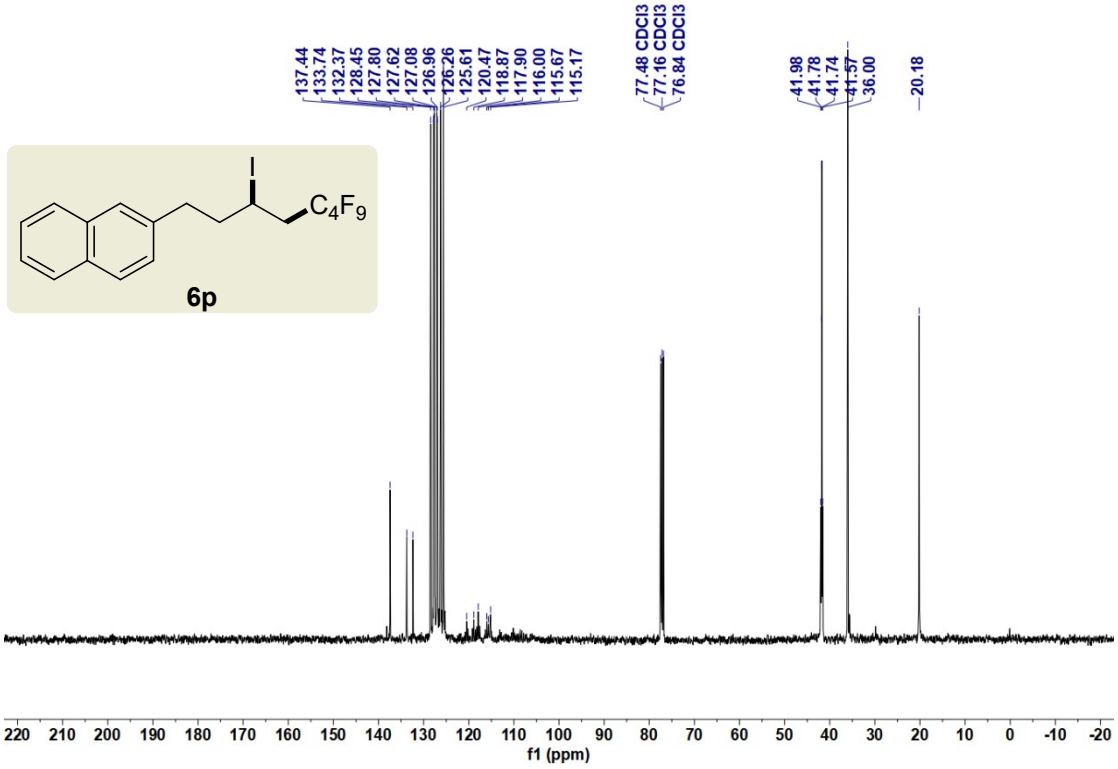
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6o**:



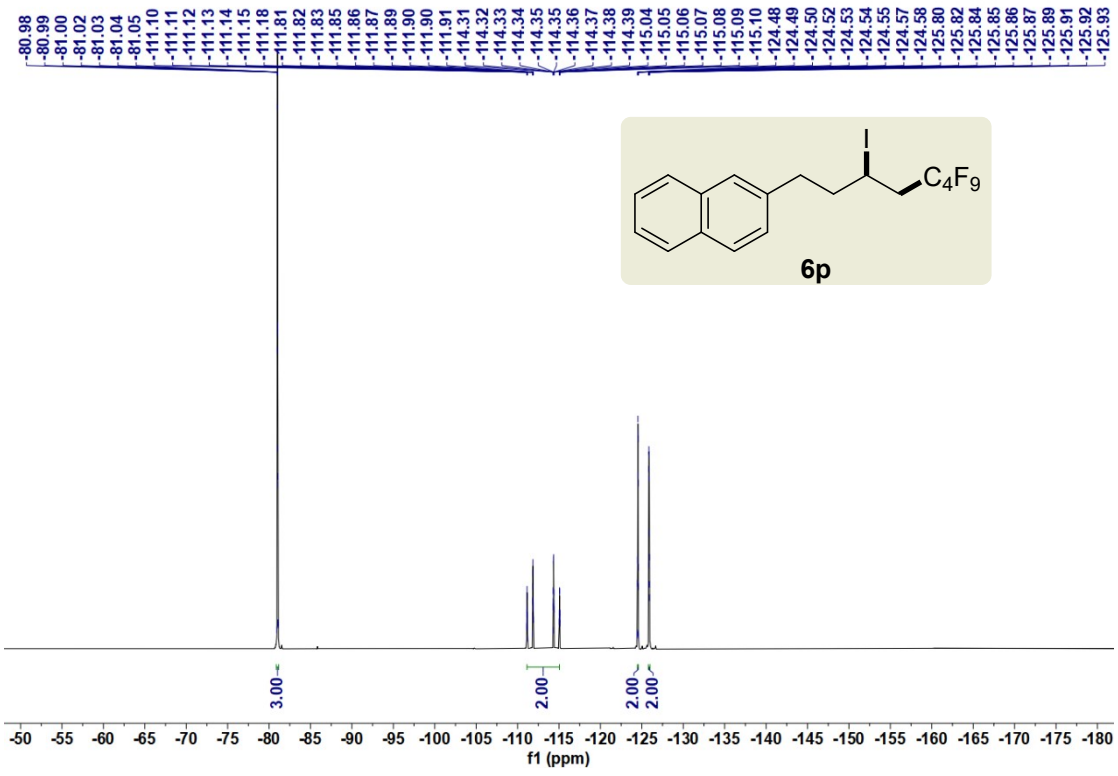
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6p**:



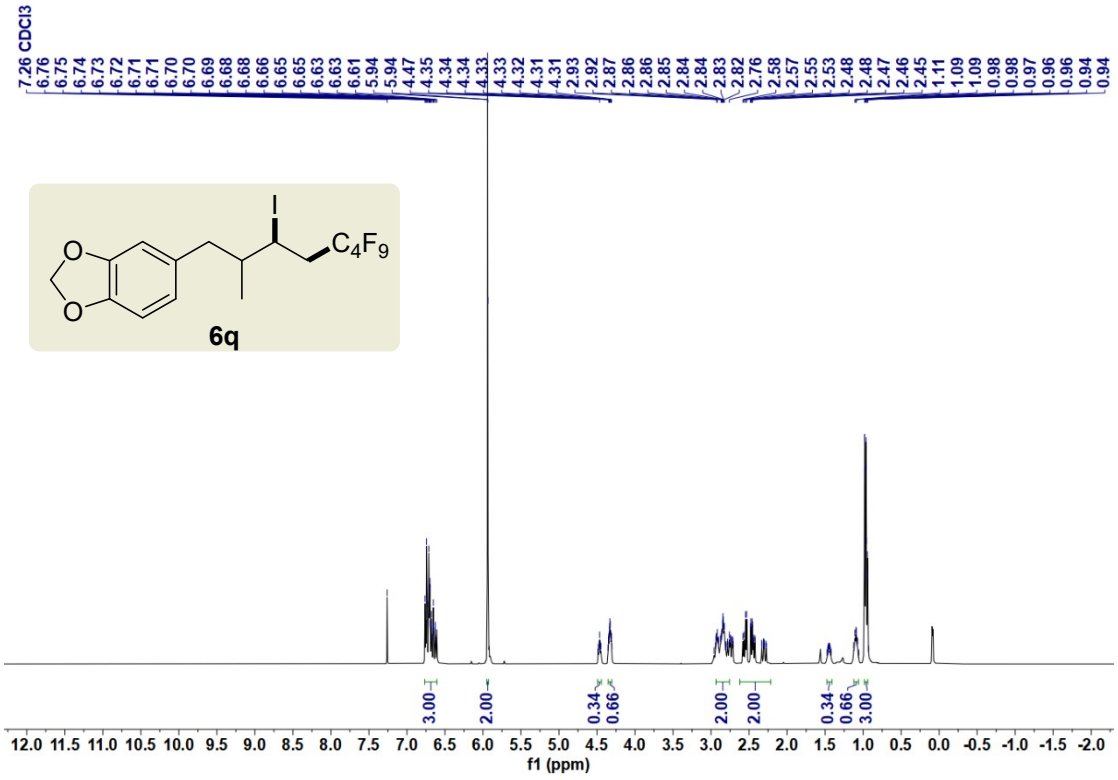
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6p**:



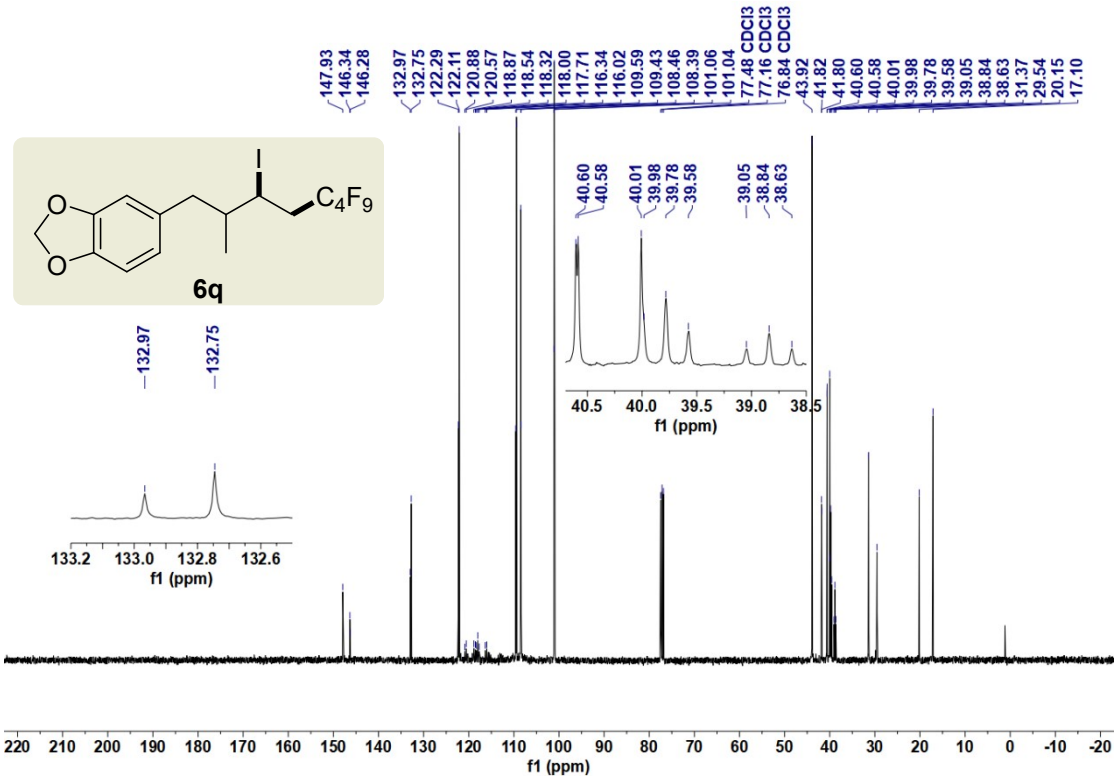
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6p**:



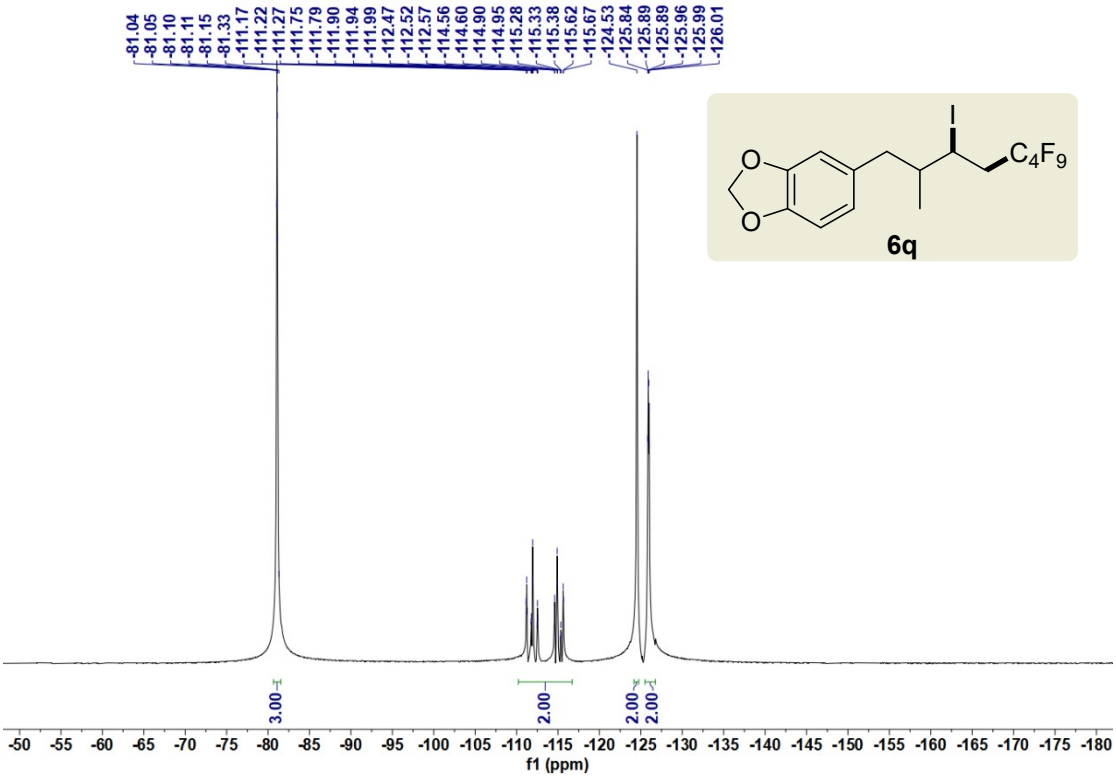
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6q**:



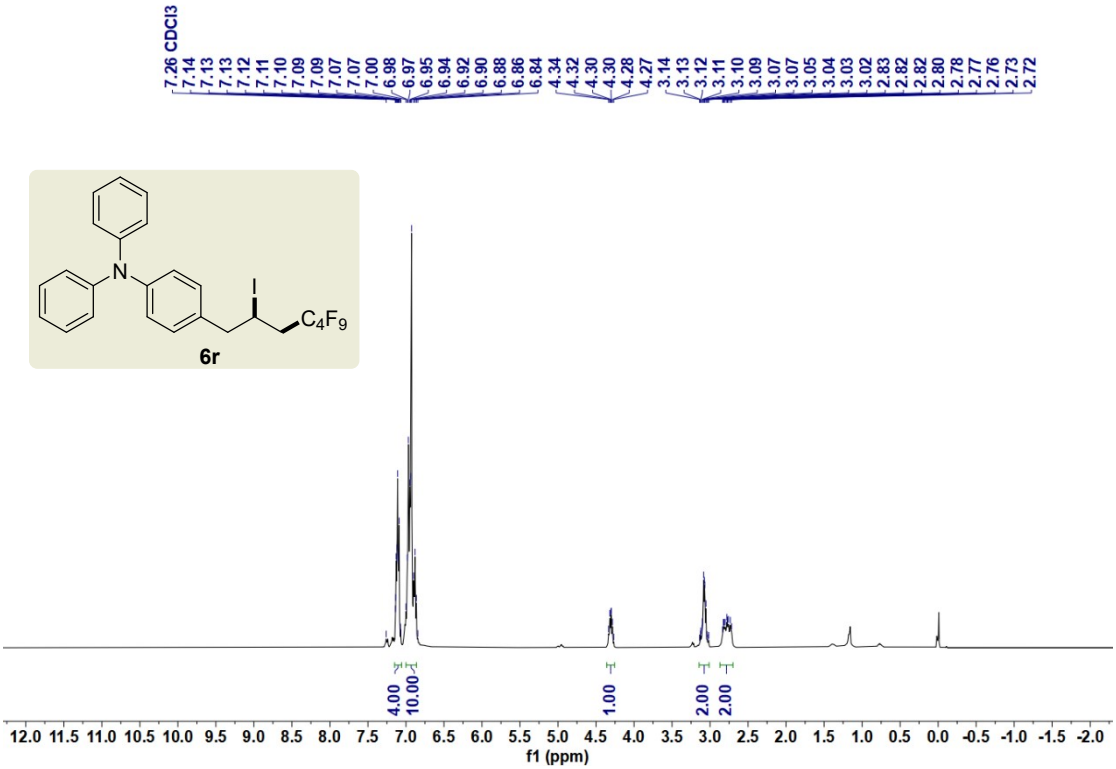
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6q**:



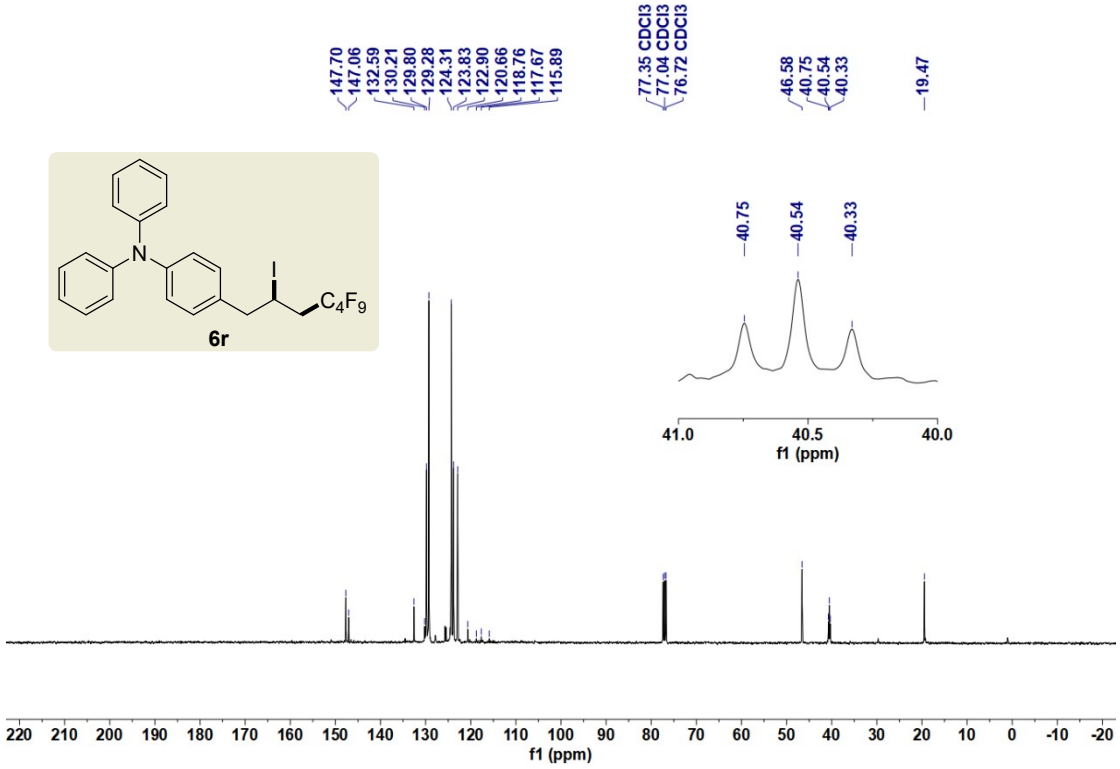
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6q**:



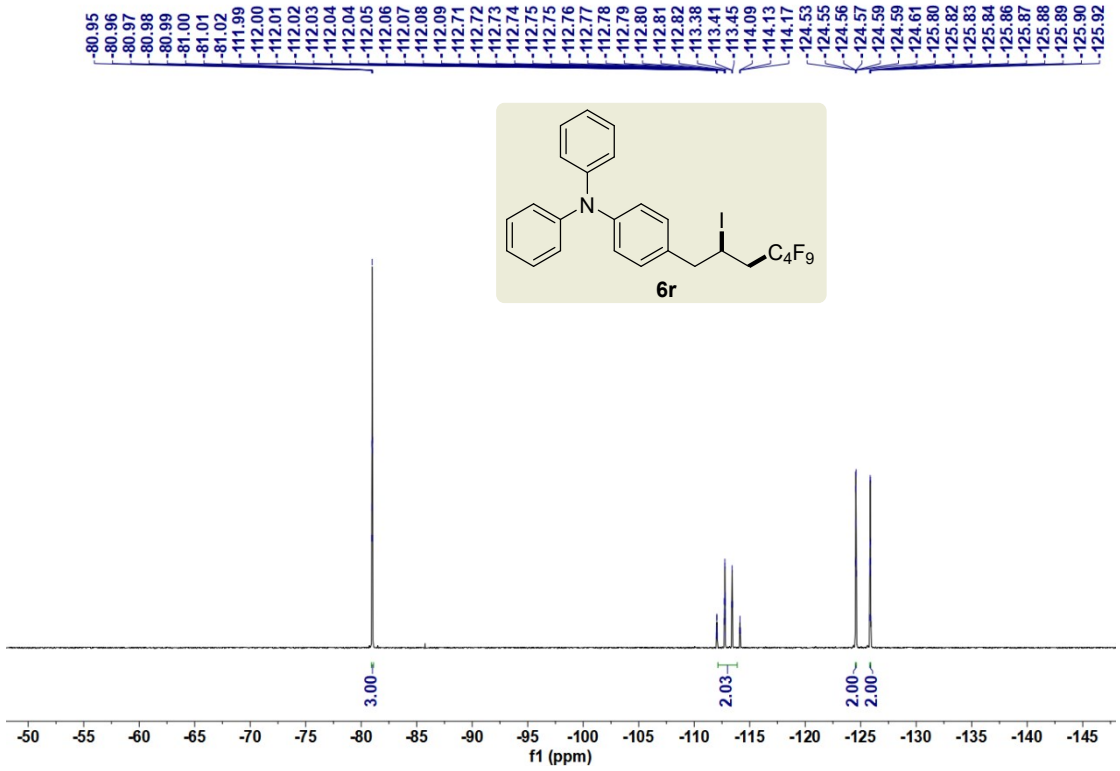
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6r**:



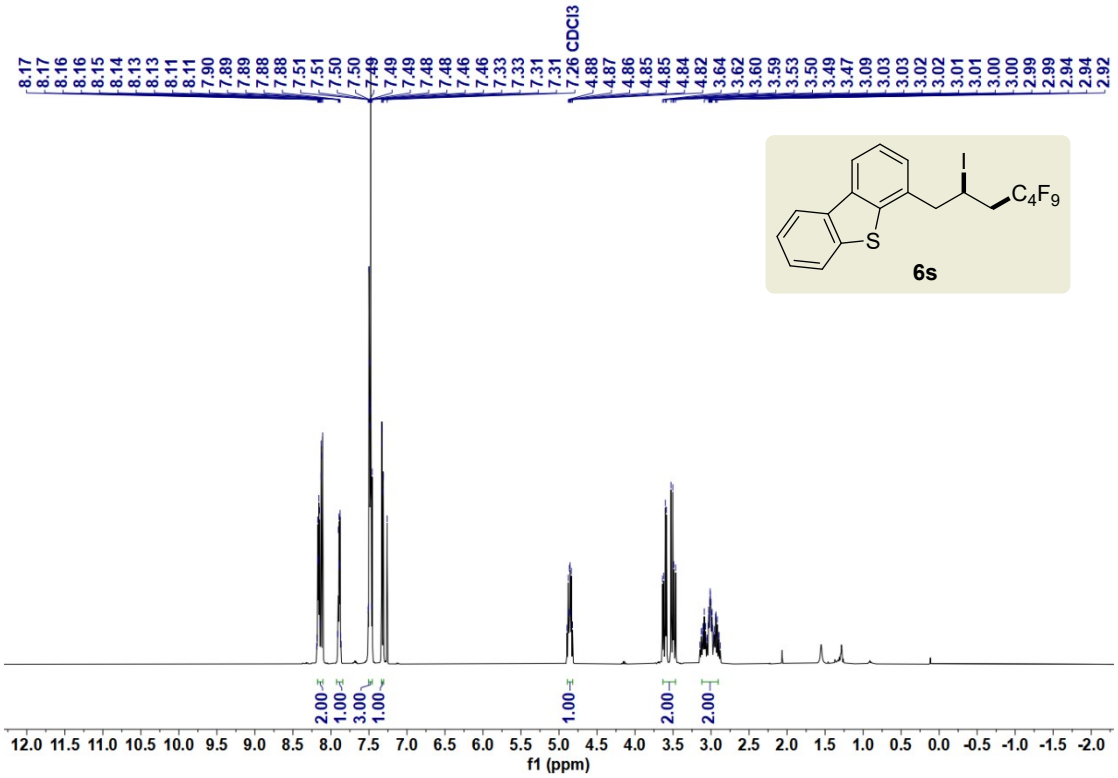
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6r**:



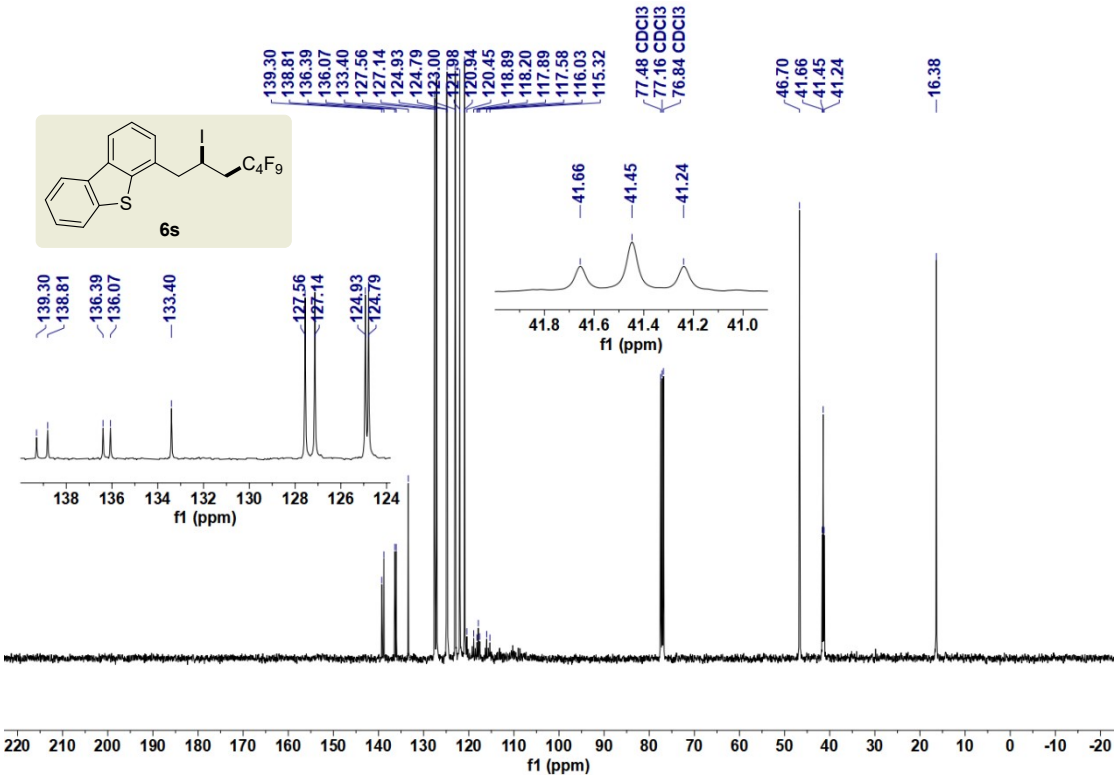
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6r**:



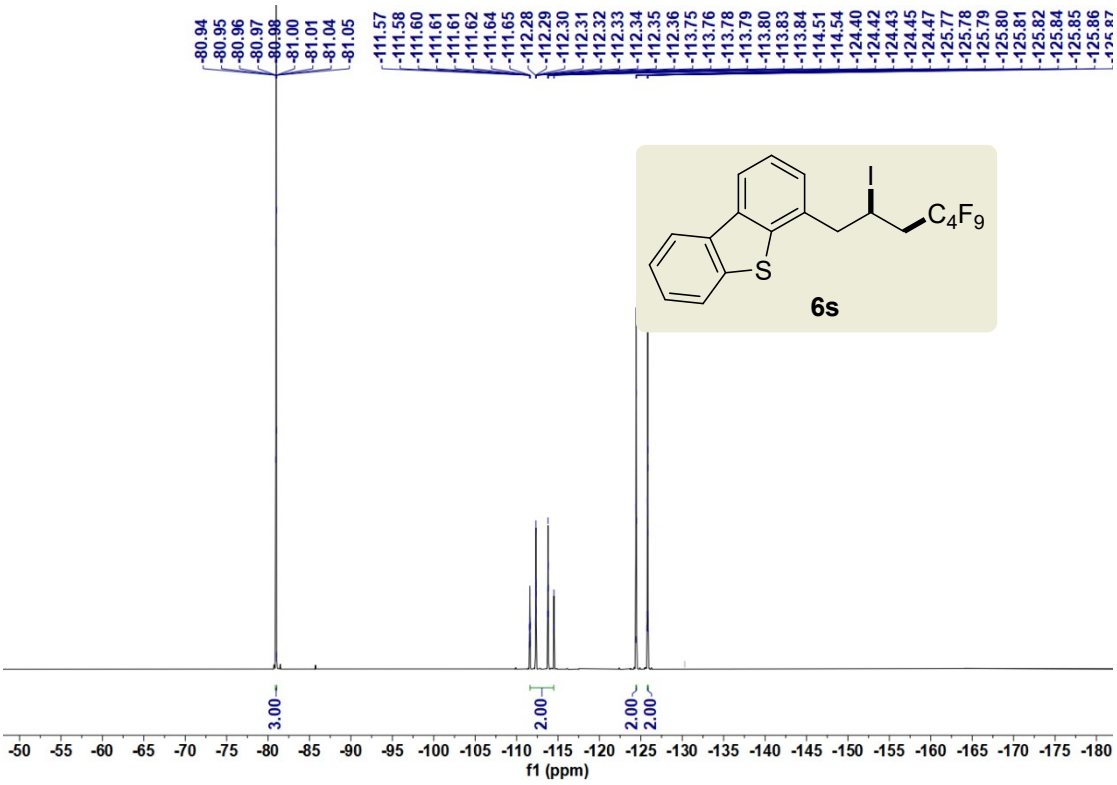
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6s**:



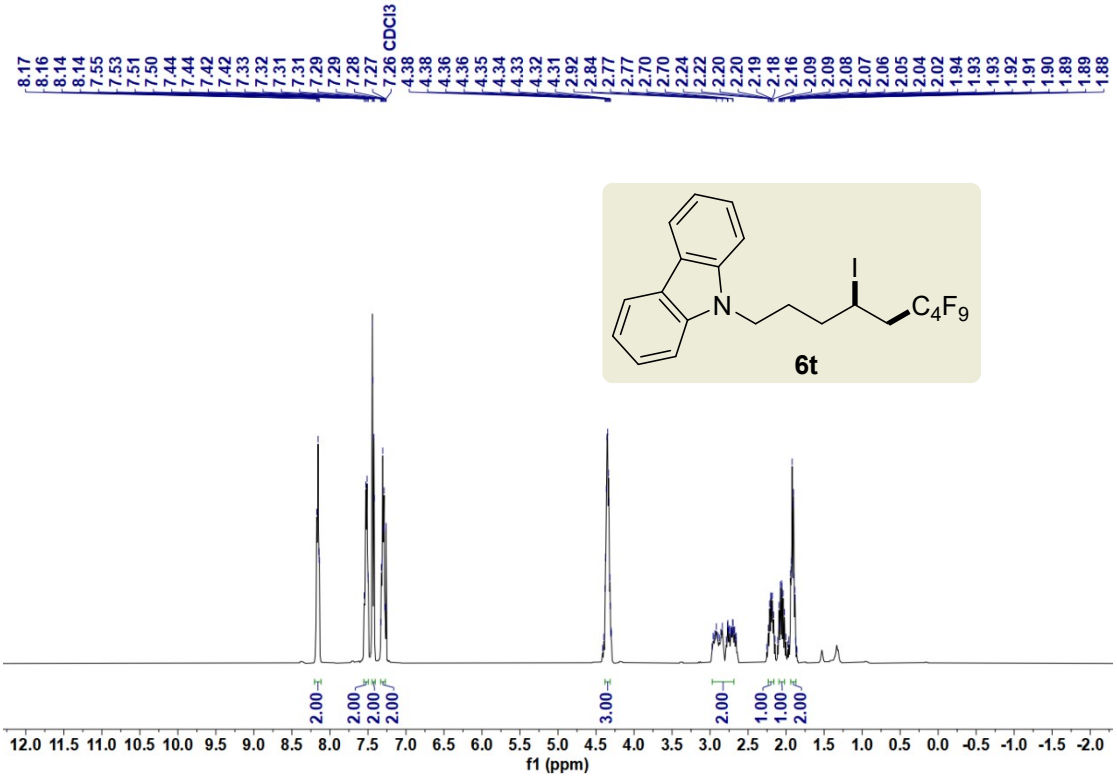
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6s**:



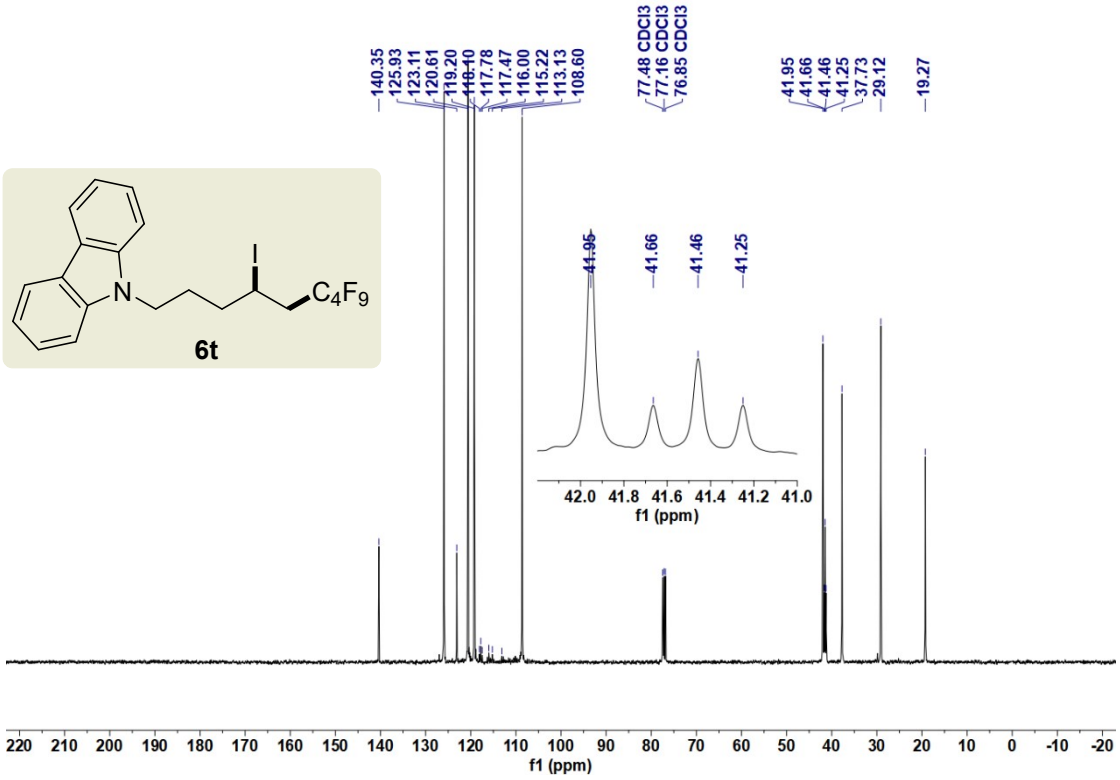
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6s**:



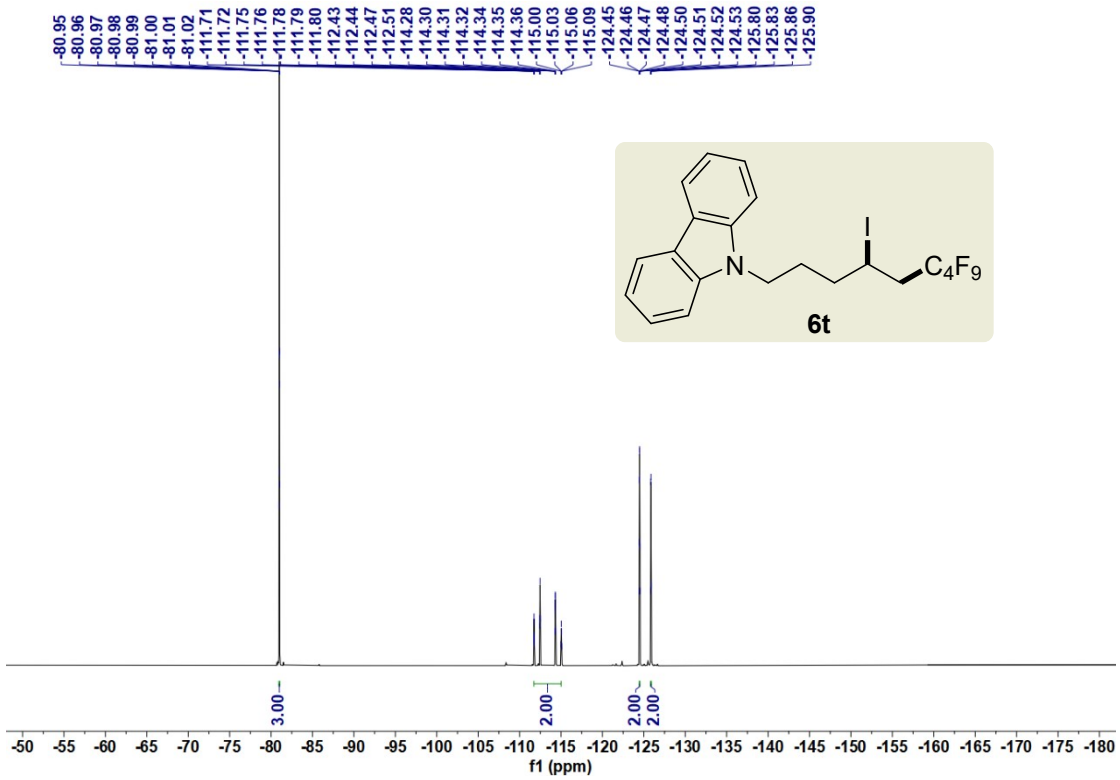
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6t**:



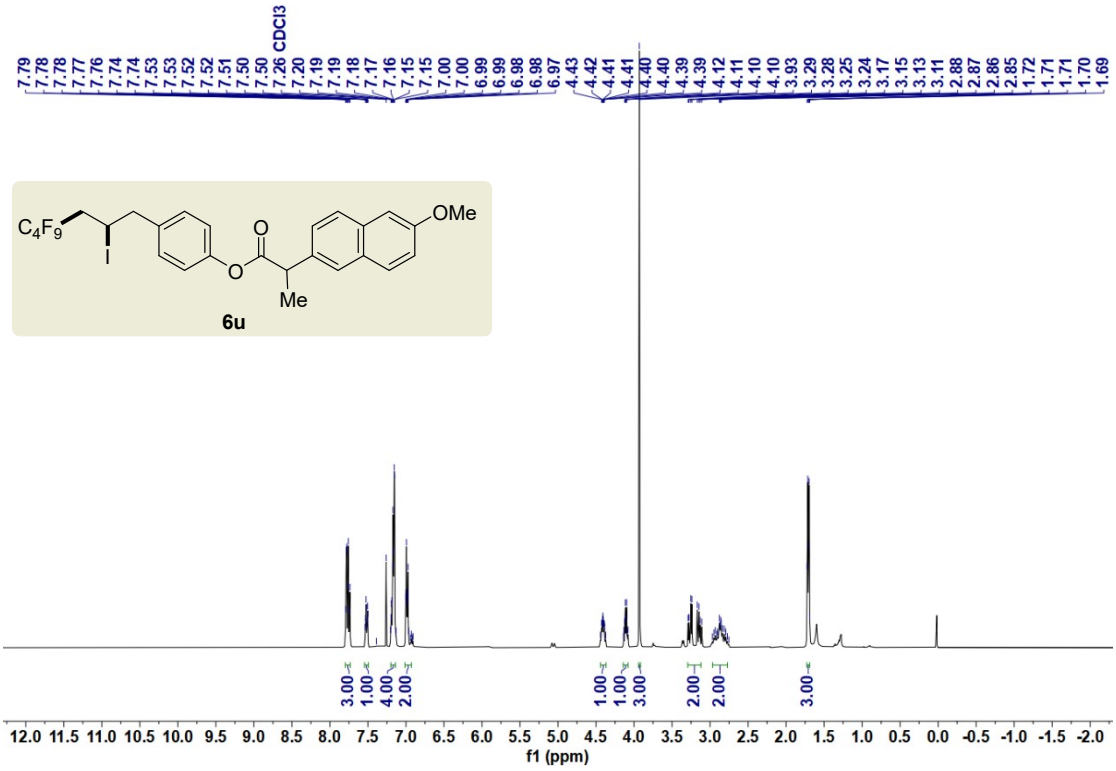
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6t**:



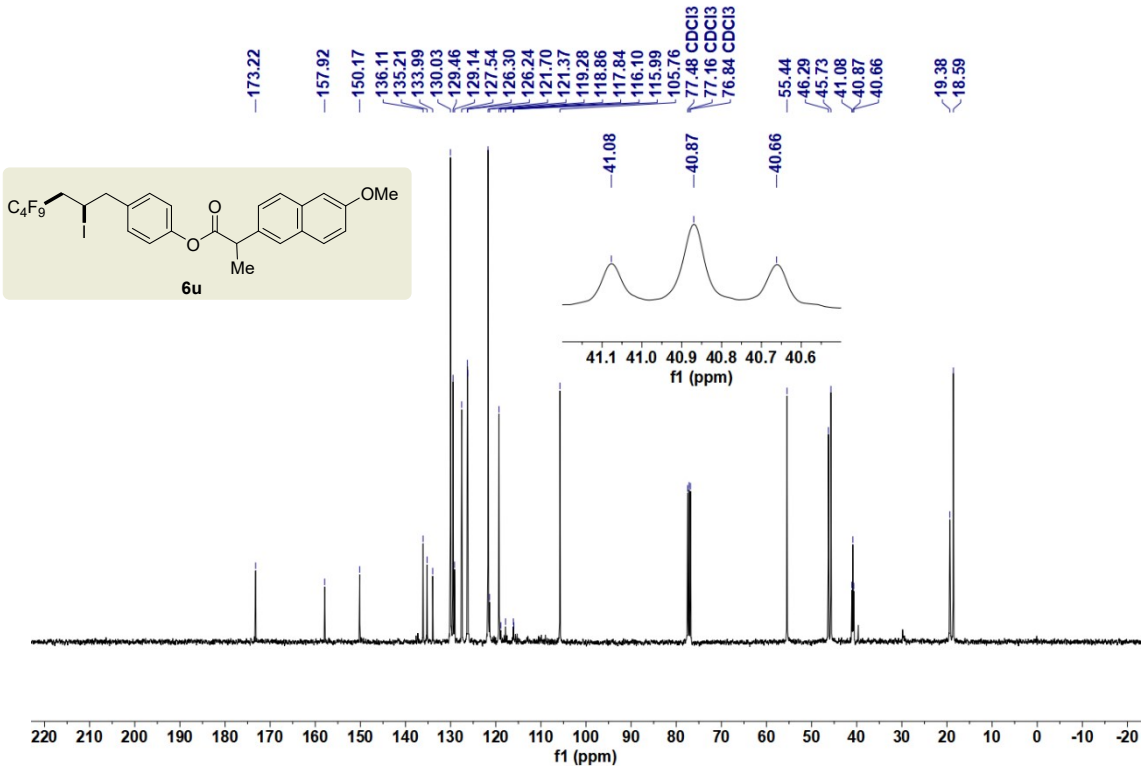
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6t**:



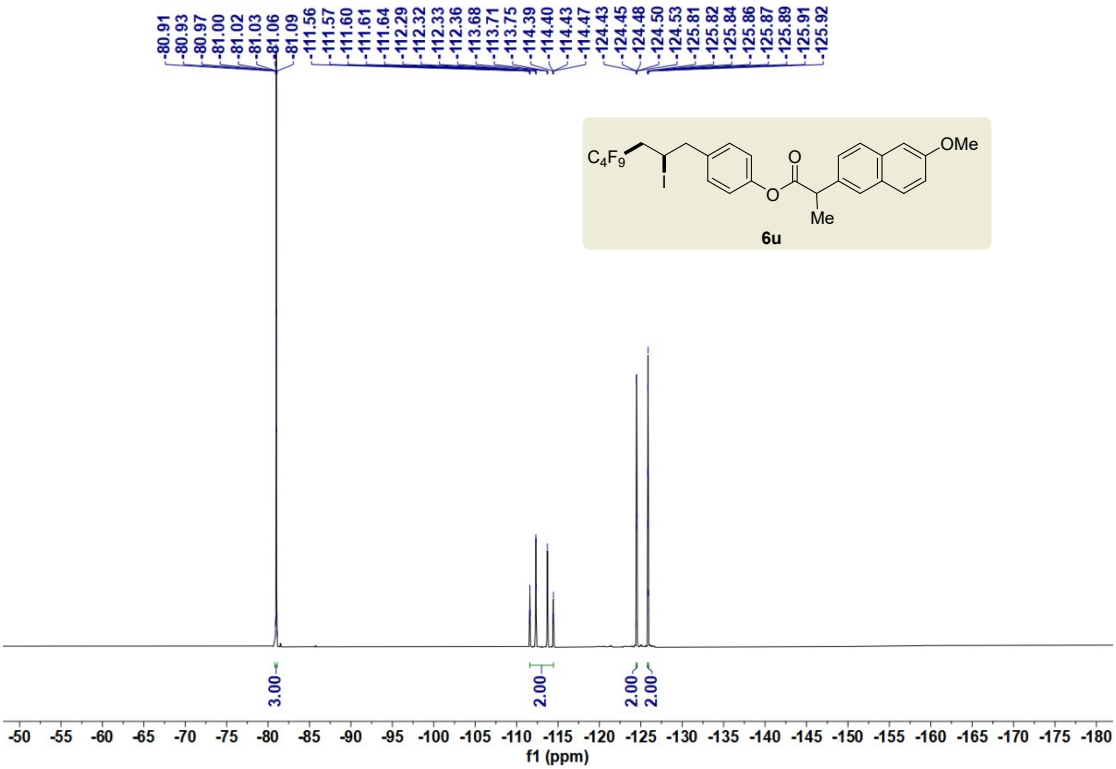
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6u**:



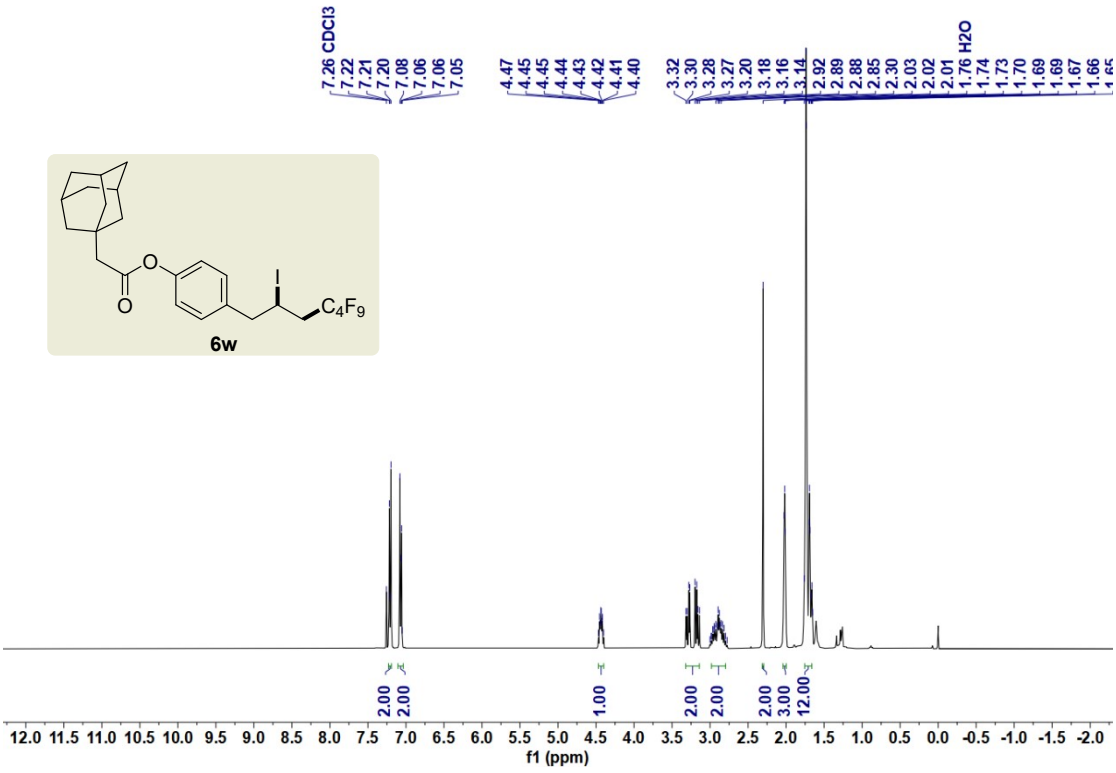
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6u**:



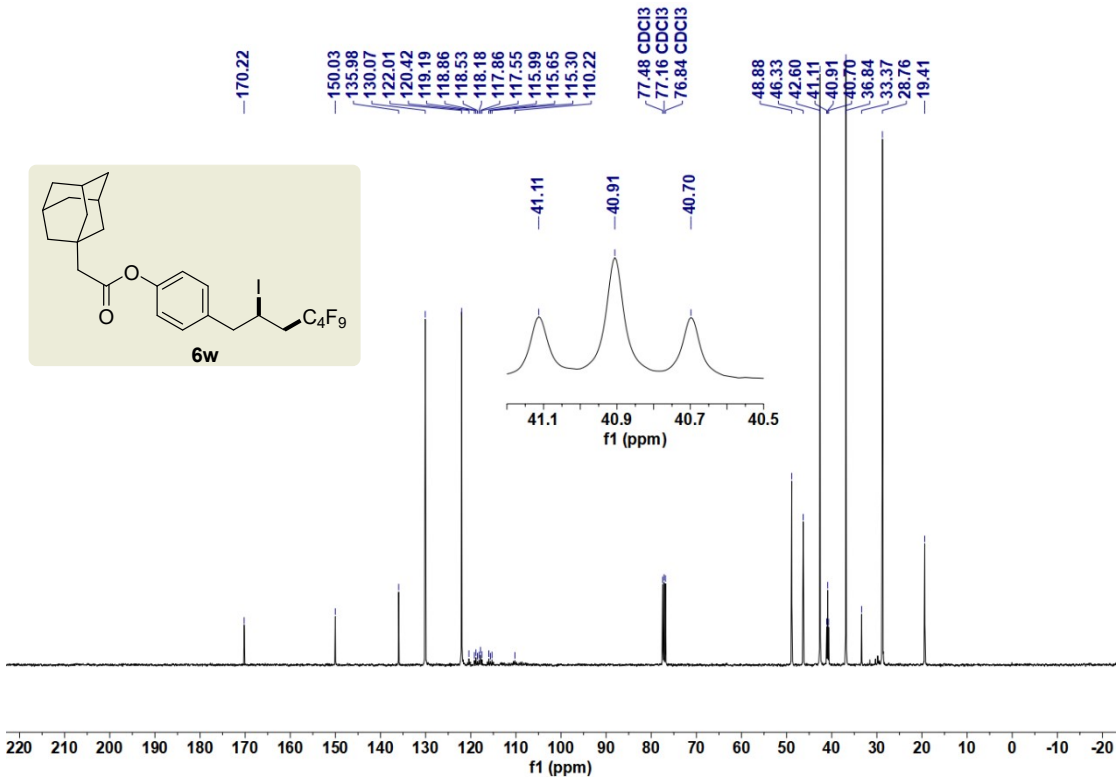
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6u**:



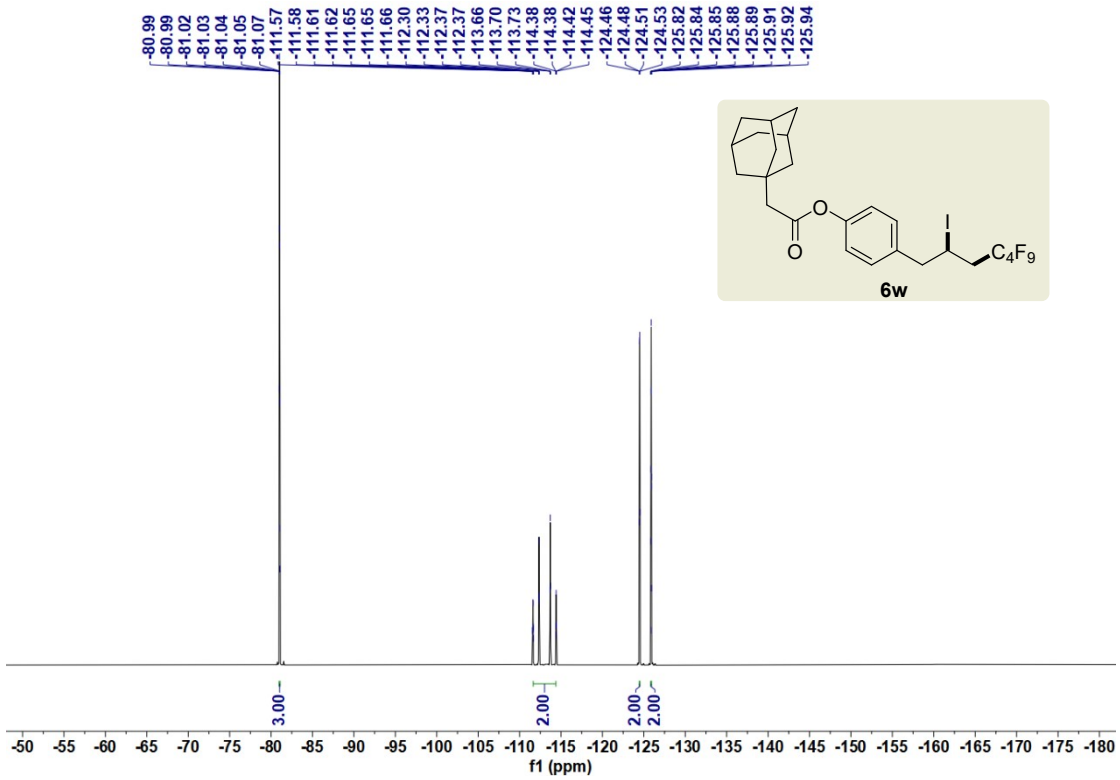
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6w**:



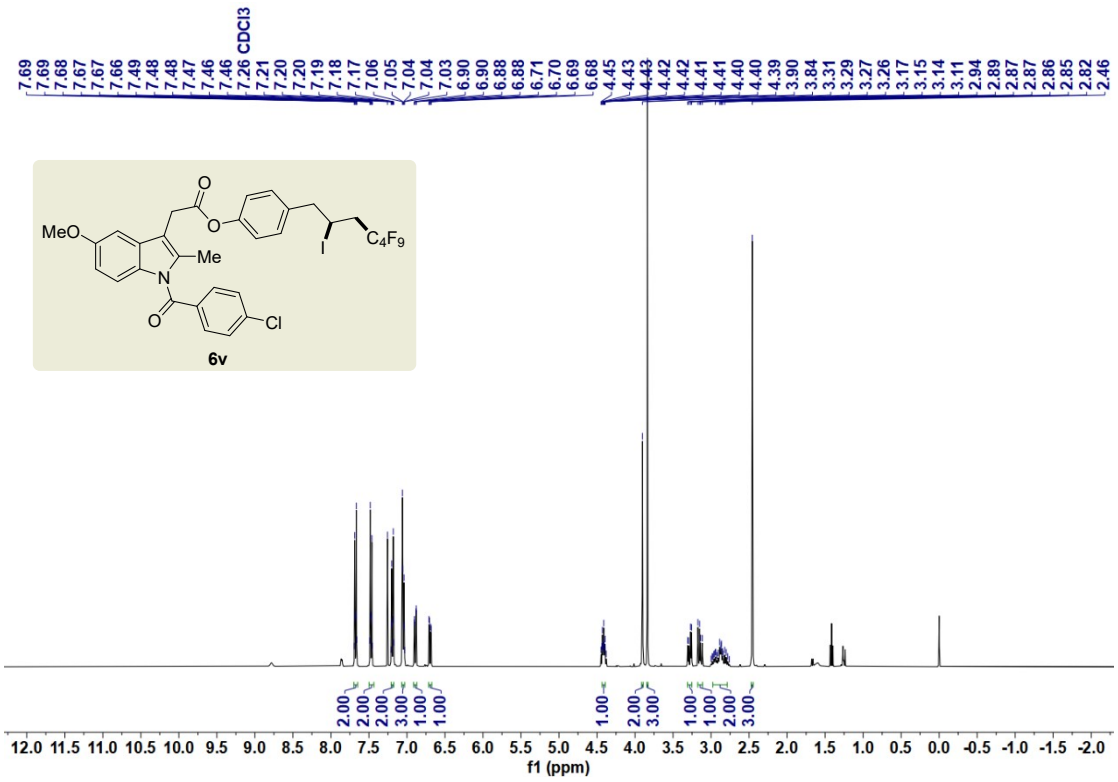
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6w**:



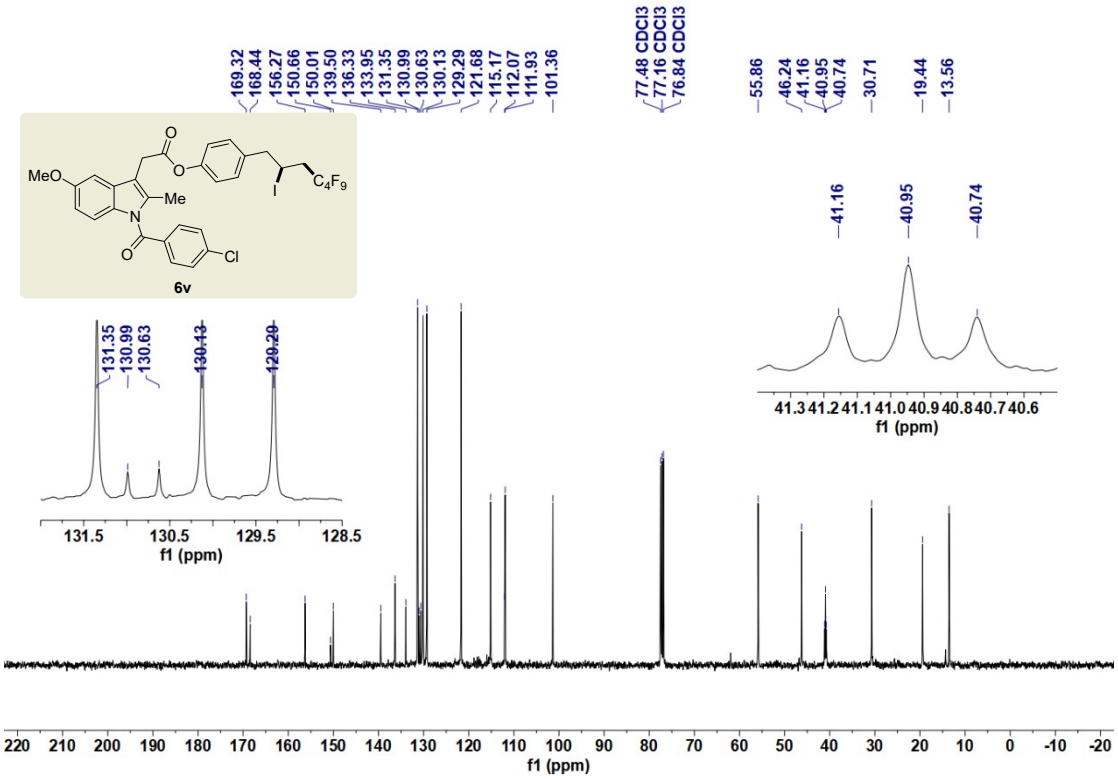
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6w**:



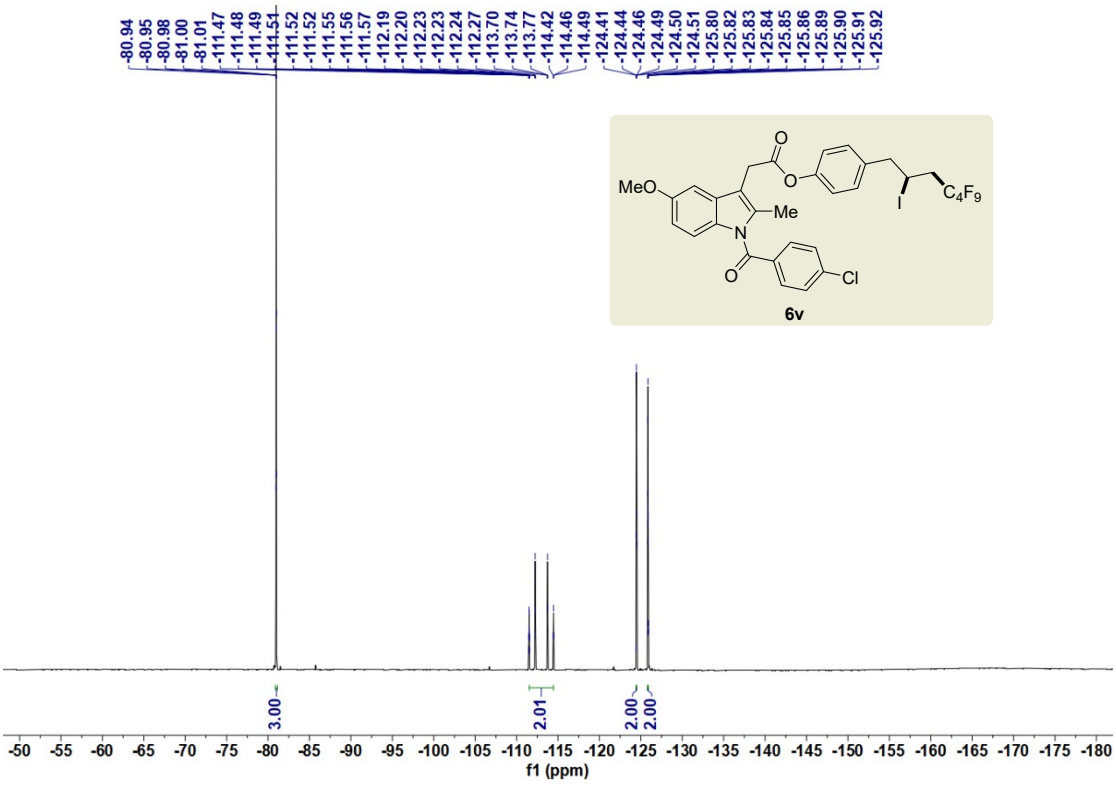
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6v**:



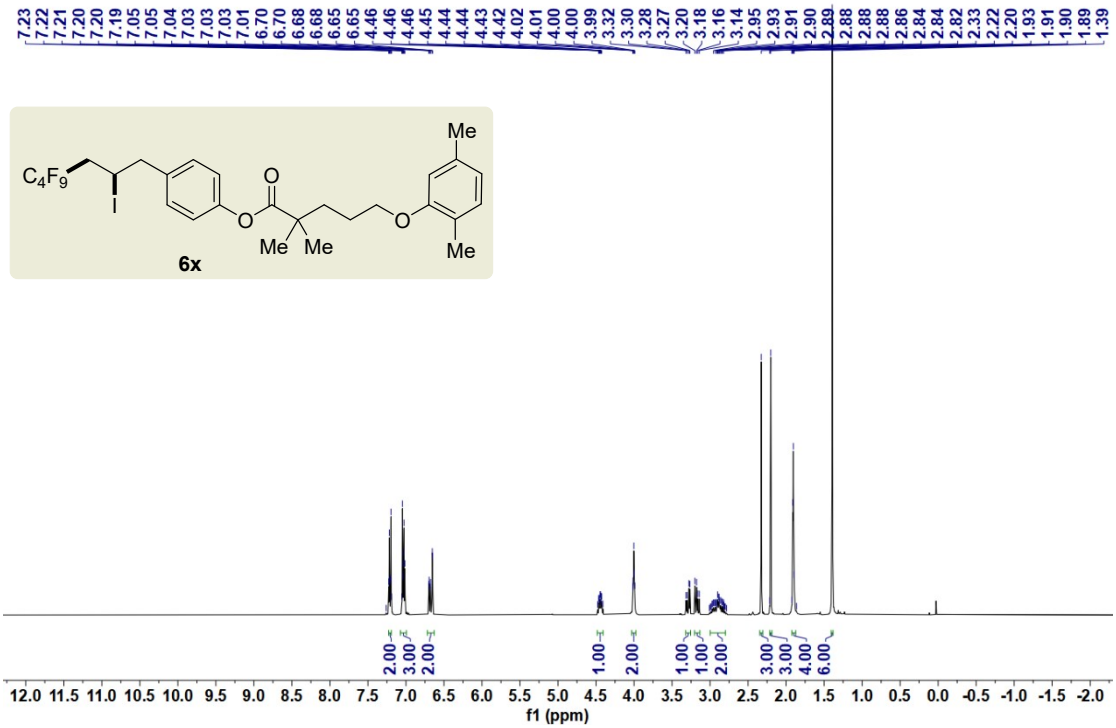
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6v**:



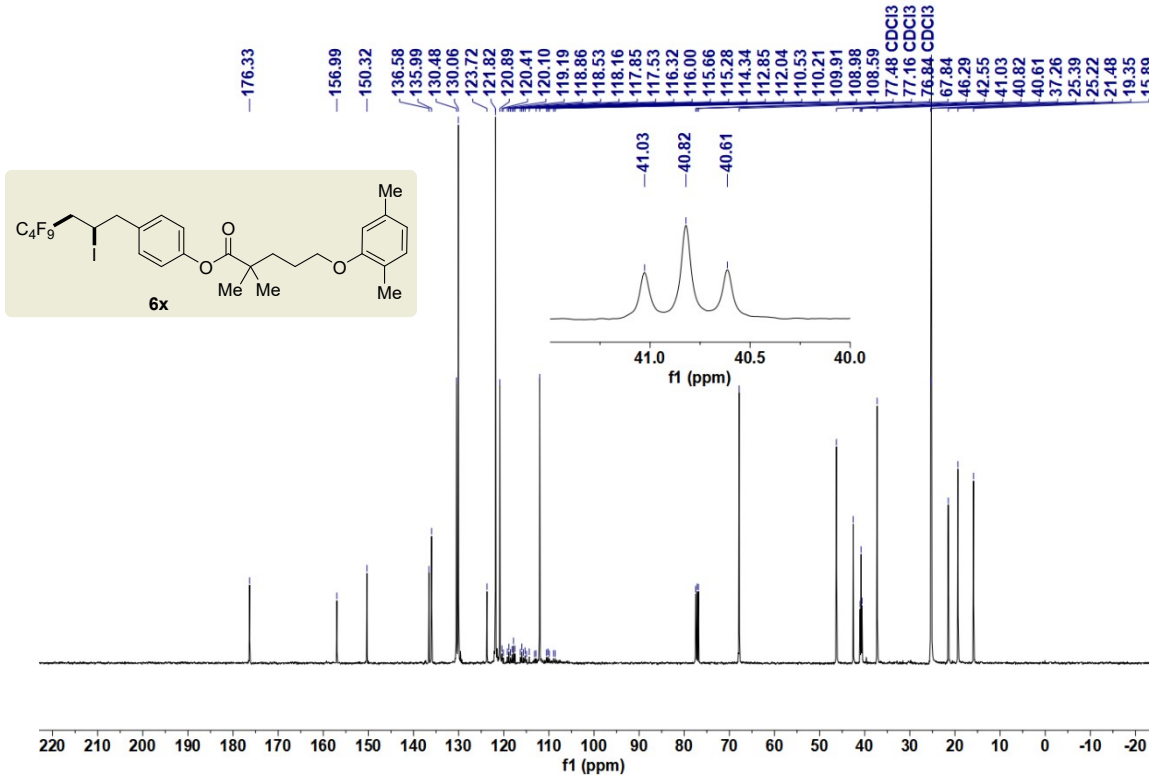
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6v**:



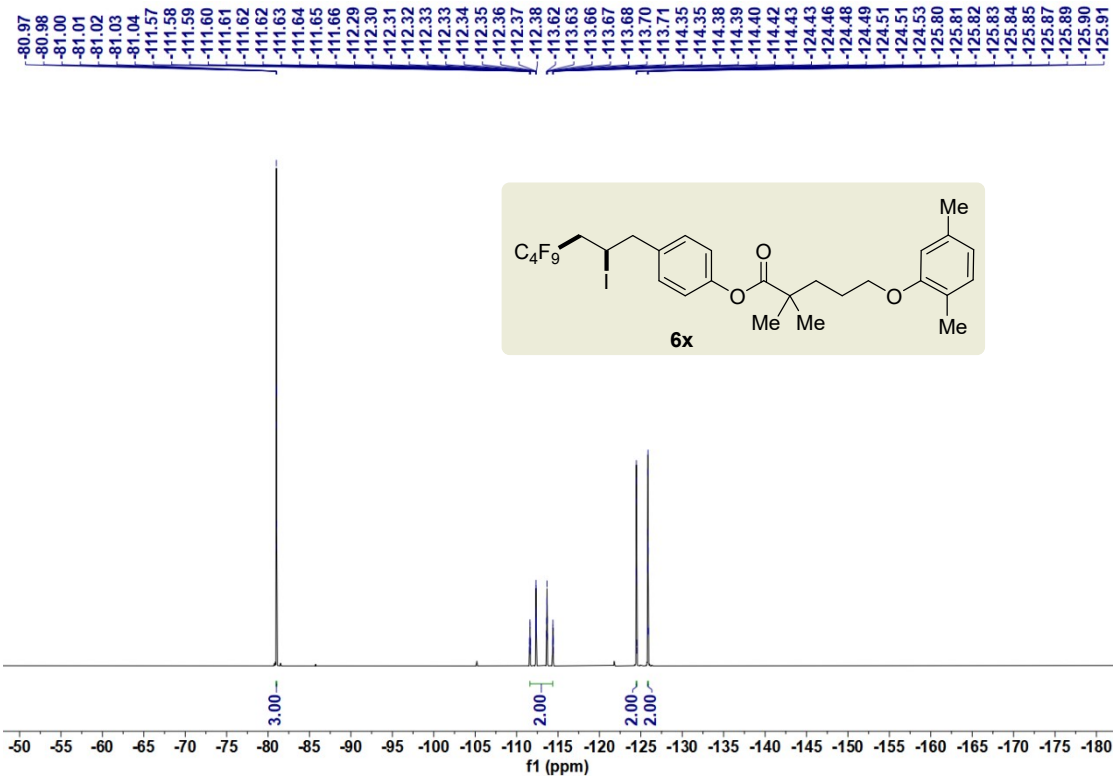
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6x**:



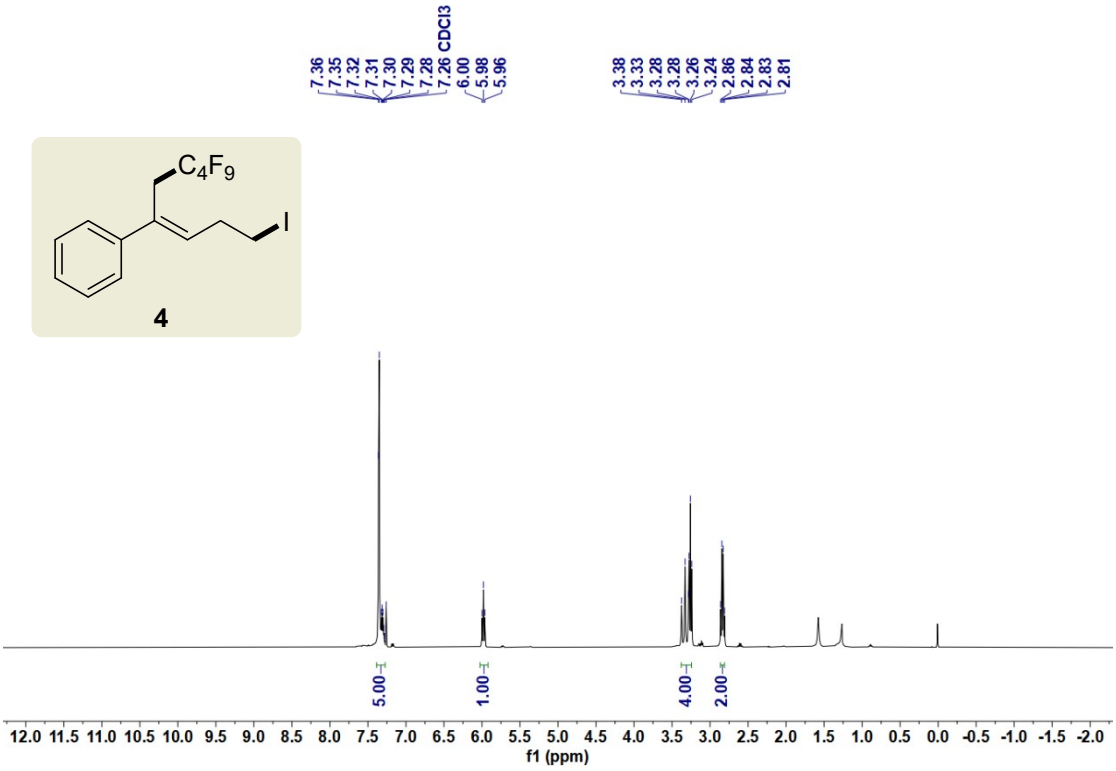
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6x**:



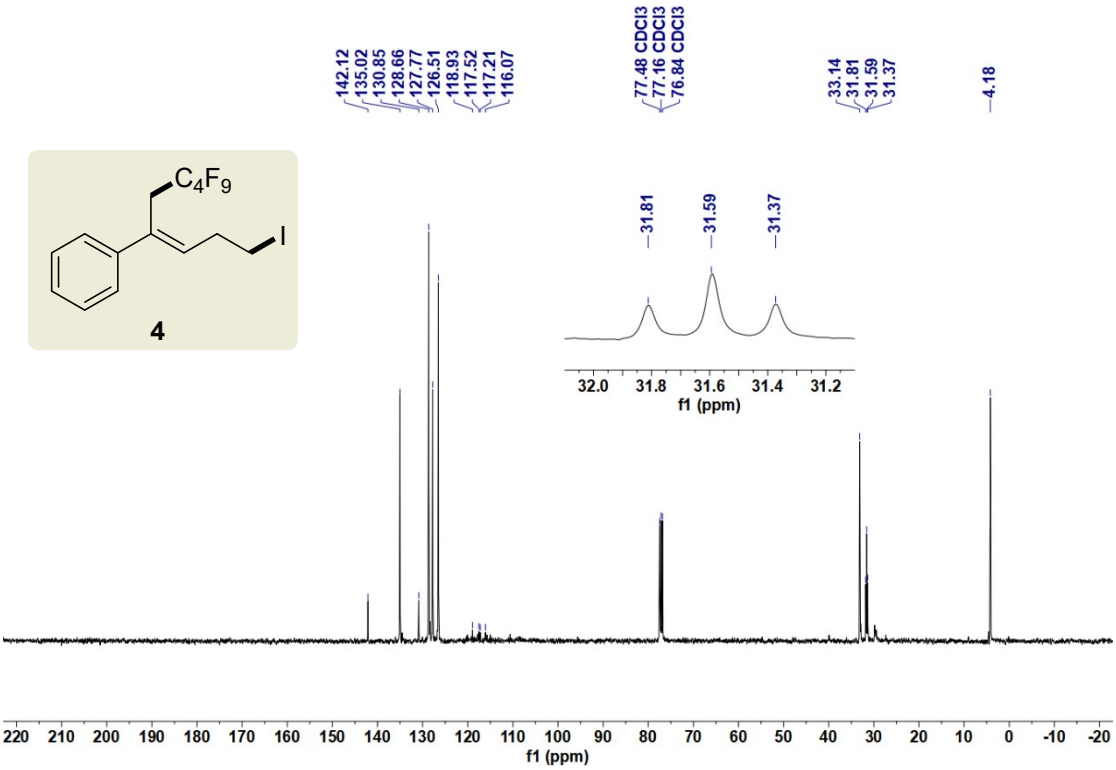
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6x**:



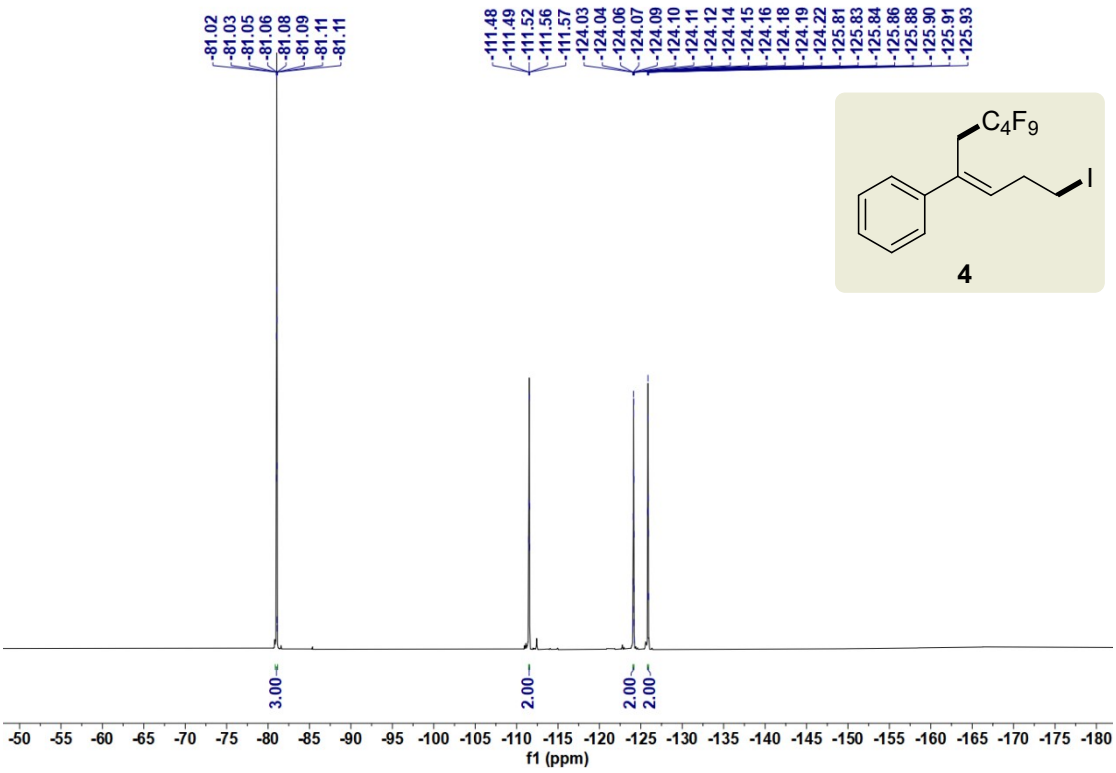
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4**:



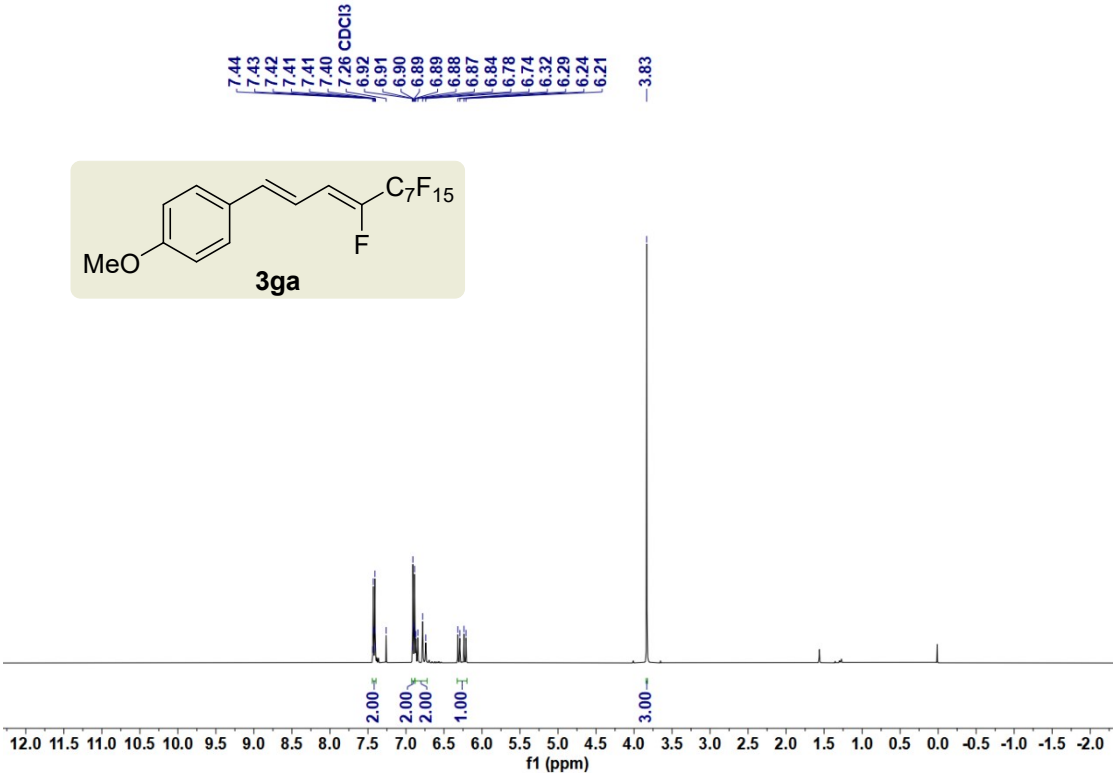
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4**:



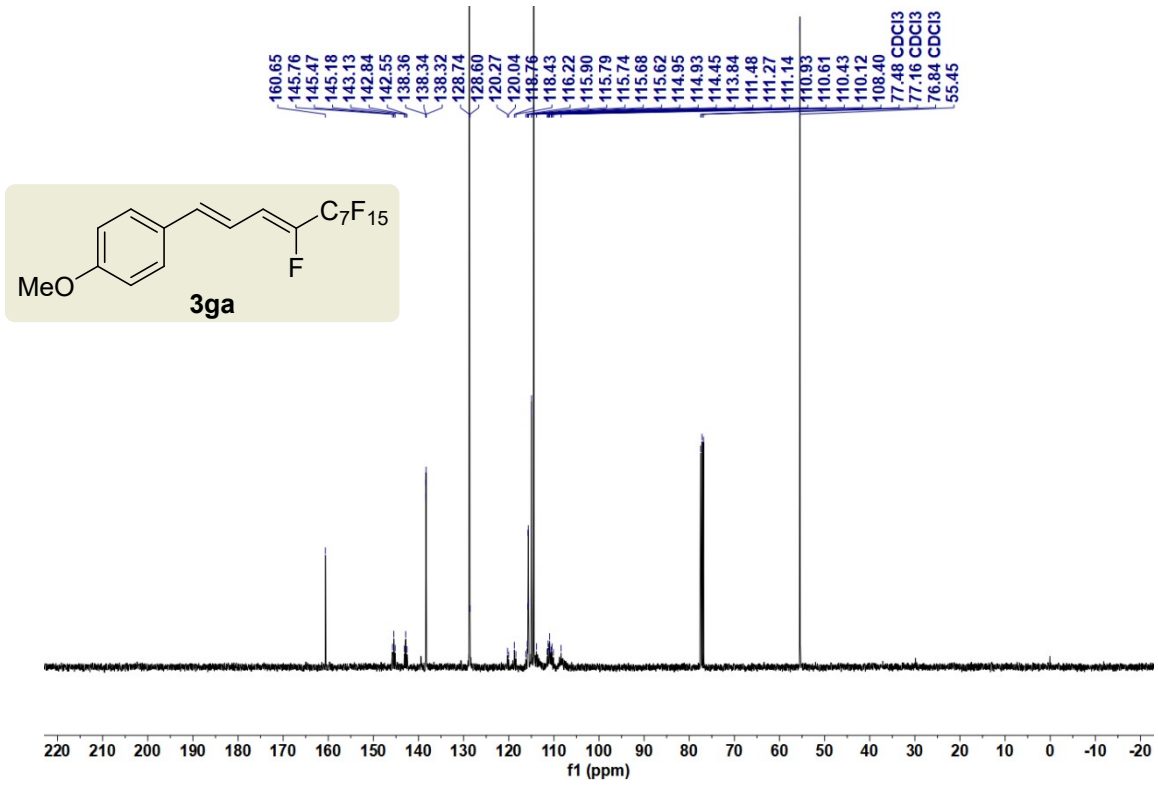
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4**:



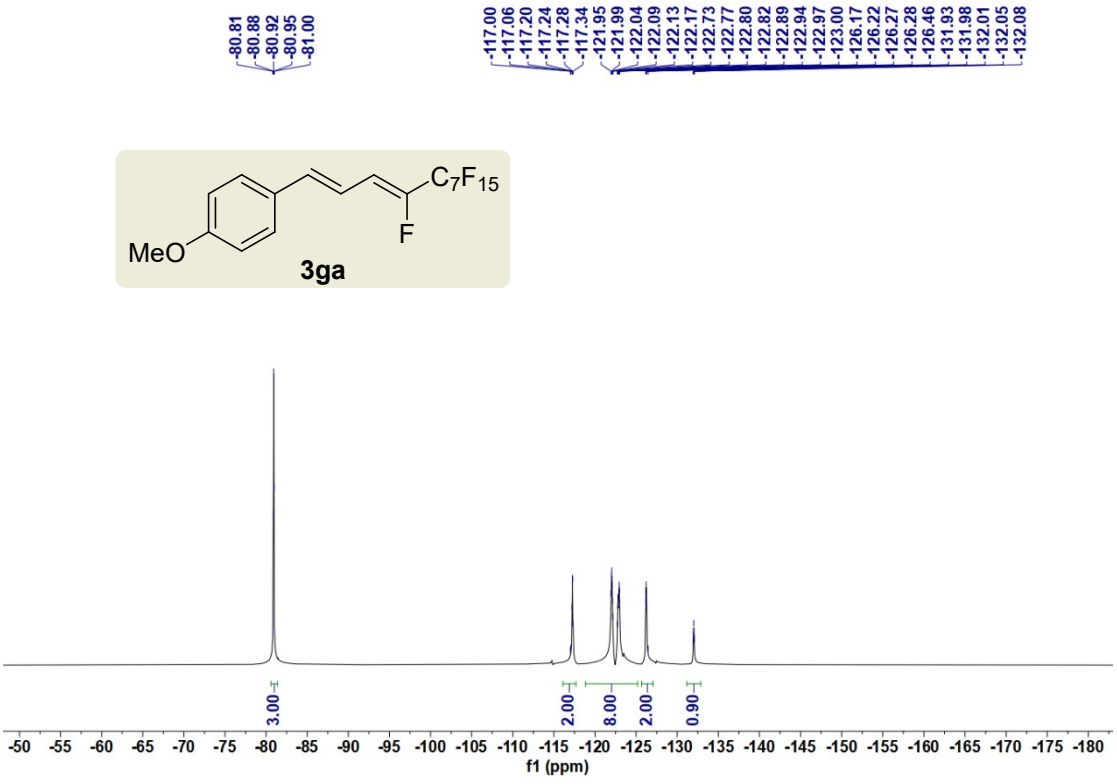
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ga**:



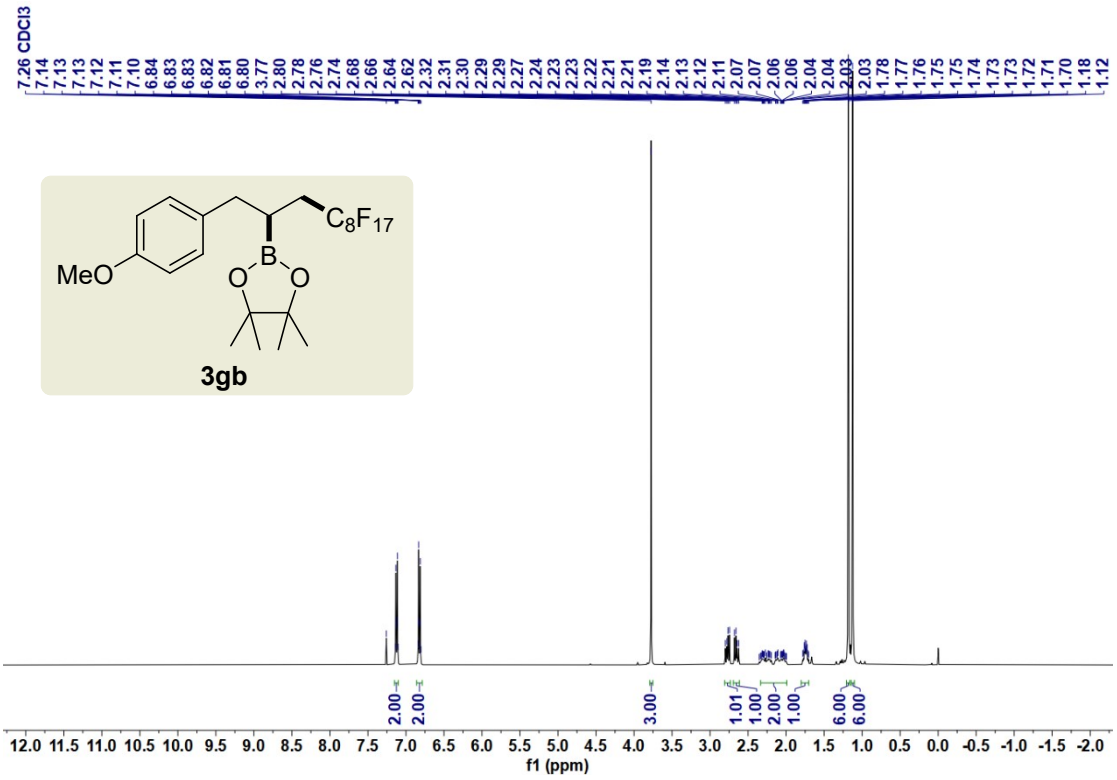
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ga**:



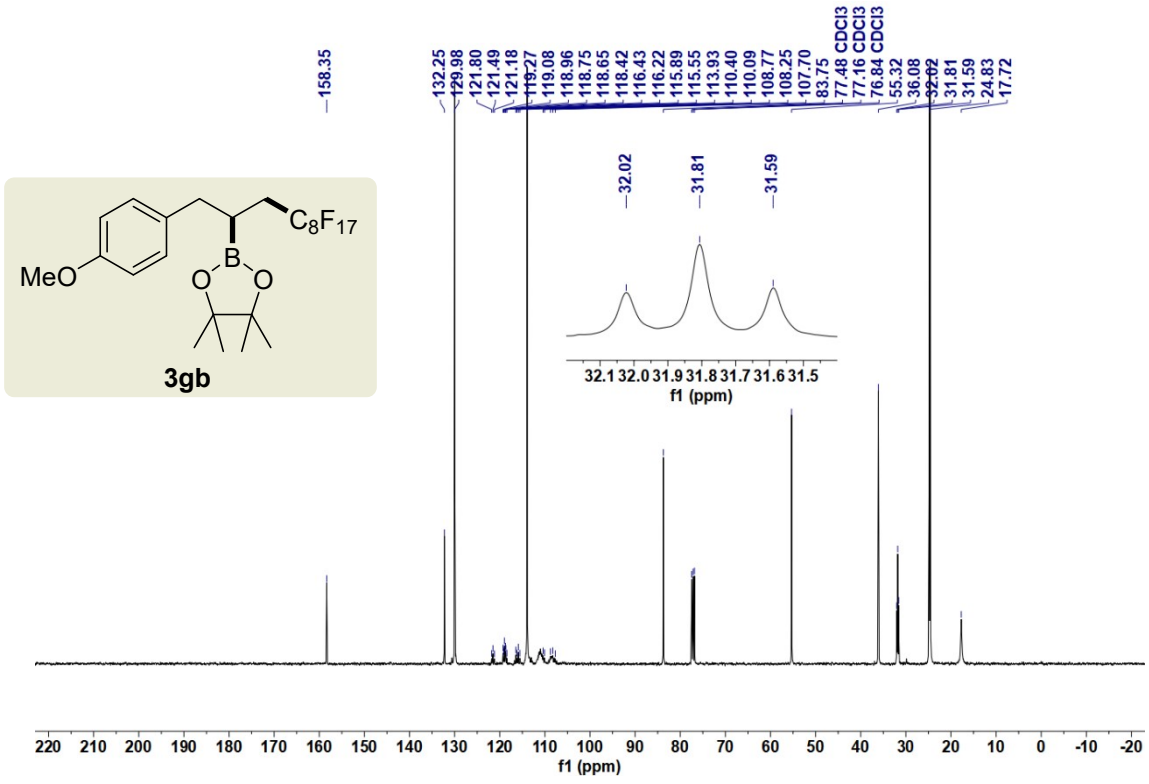
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3ga**:



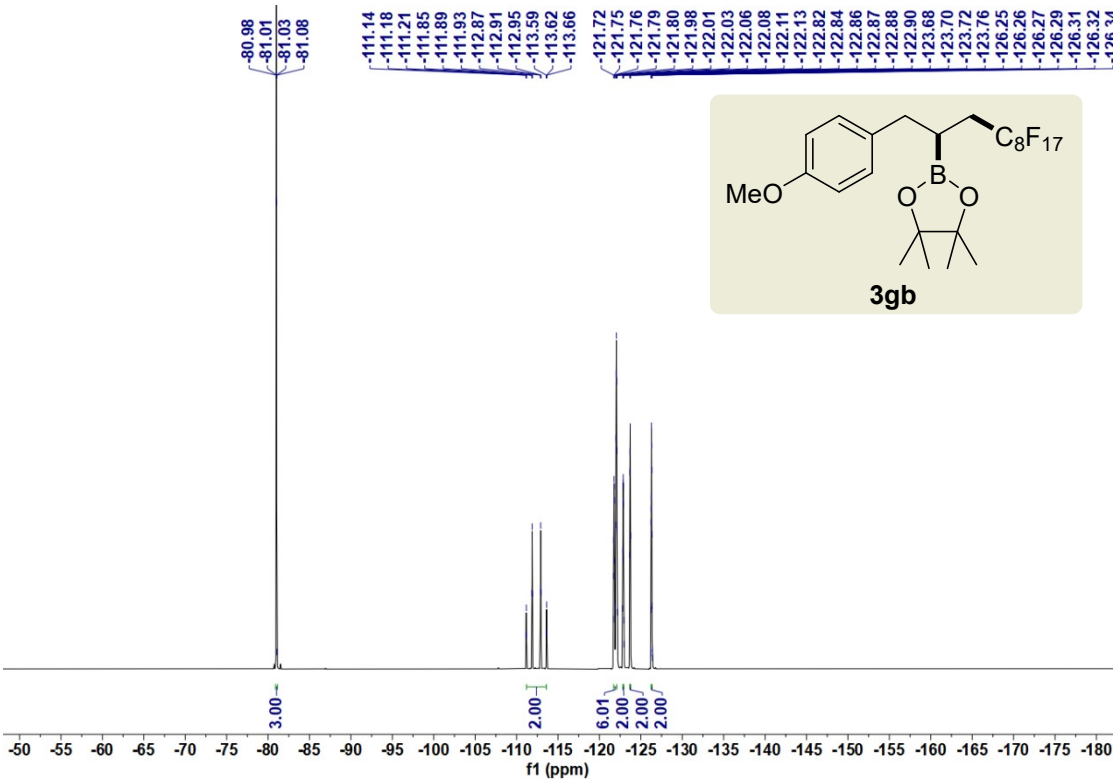
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3gb**:



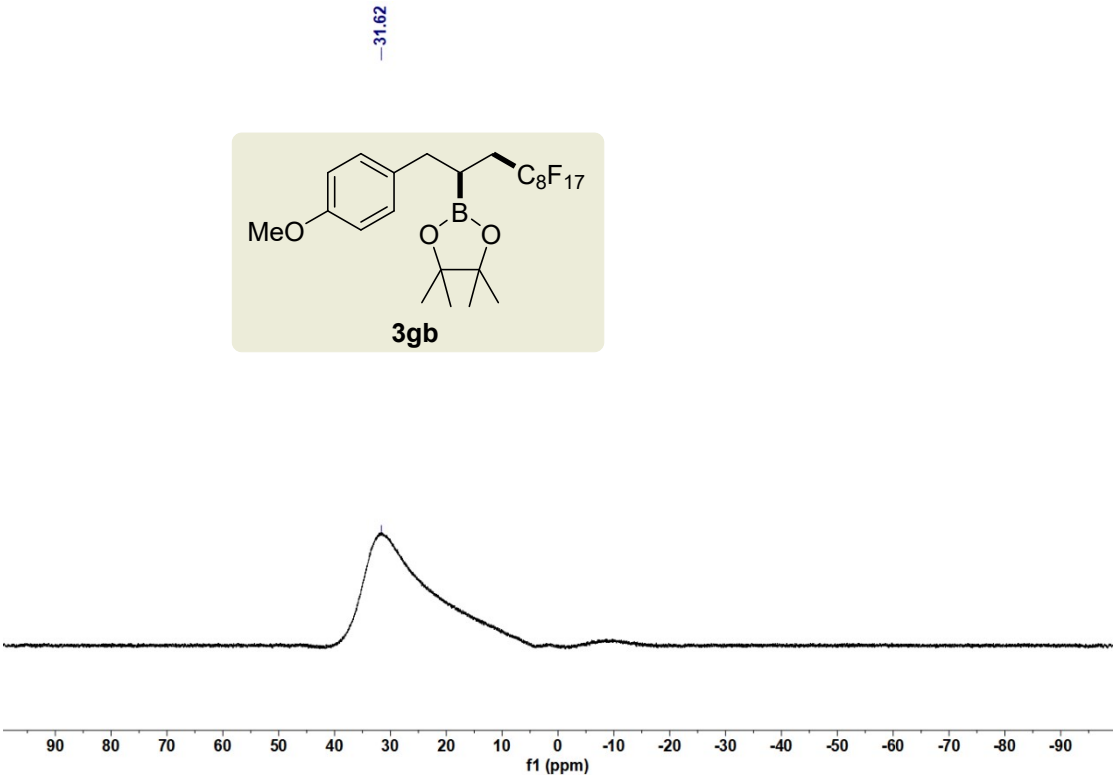
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3gb**:



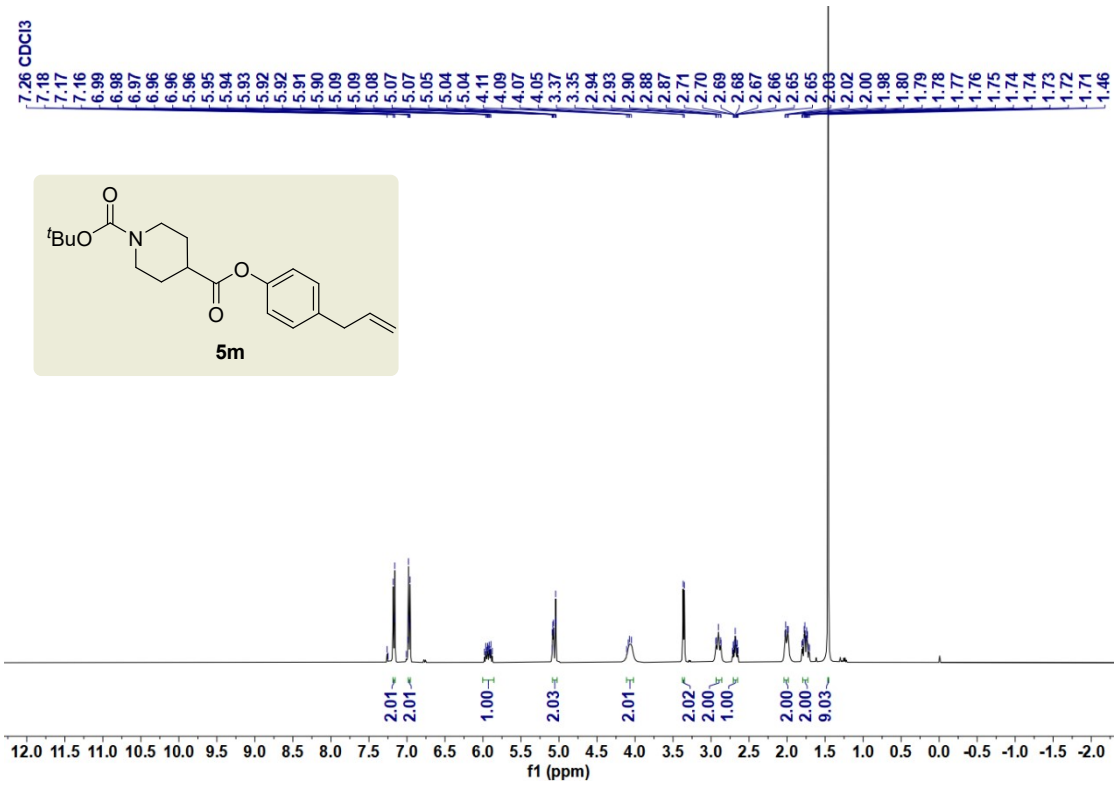
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3gb**:



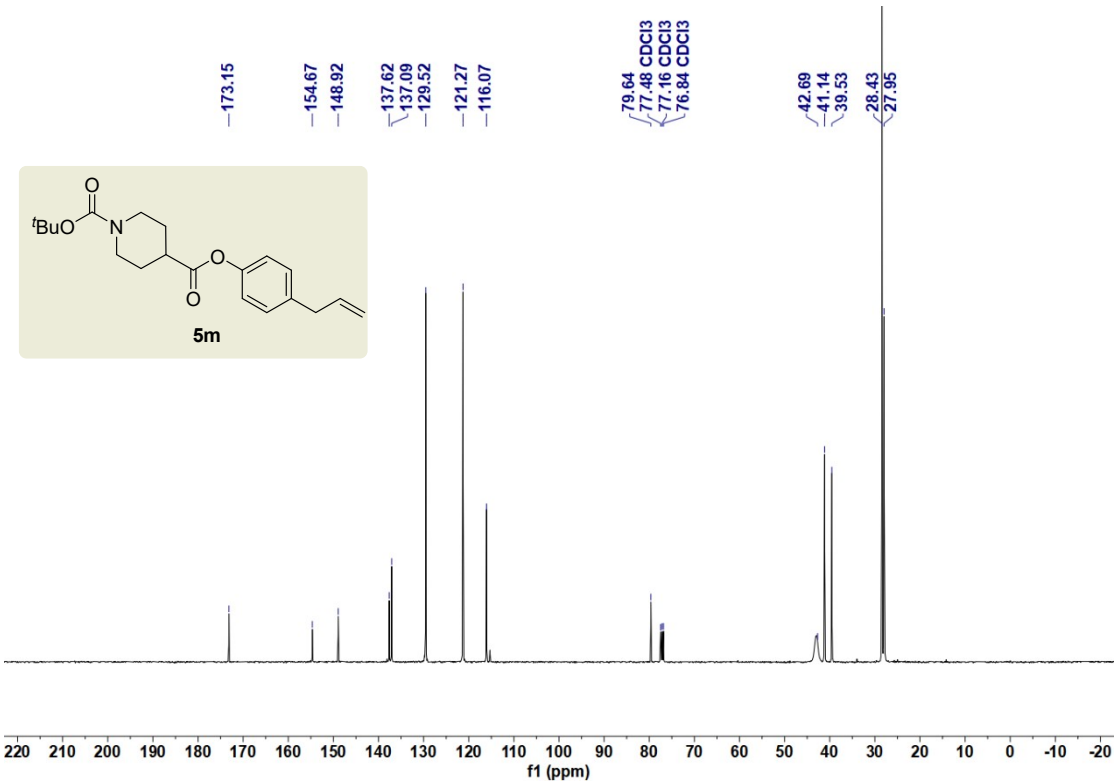
^{11}B NMR (128 MHz, $CDCl_3$) of compound **3gb:**



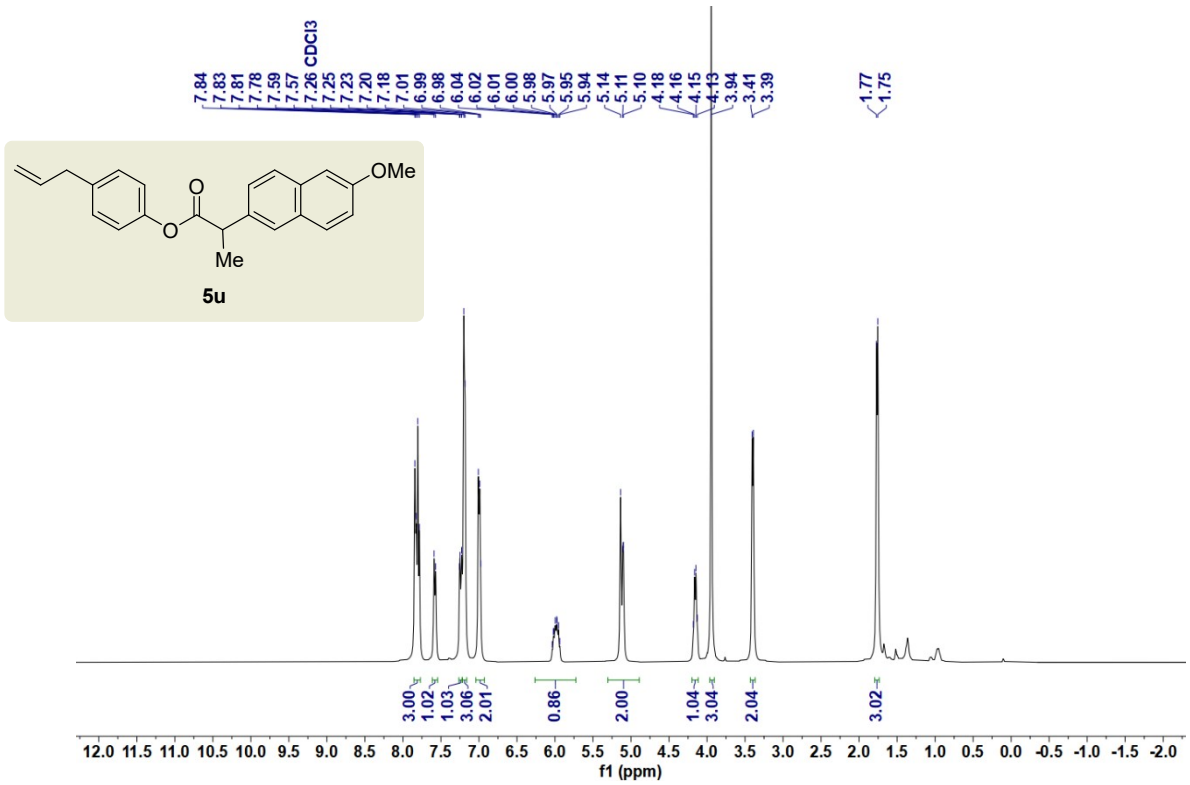
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5m**:



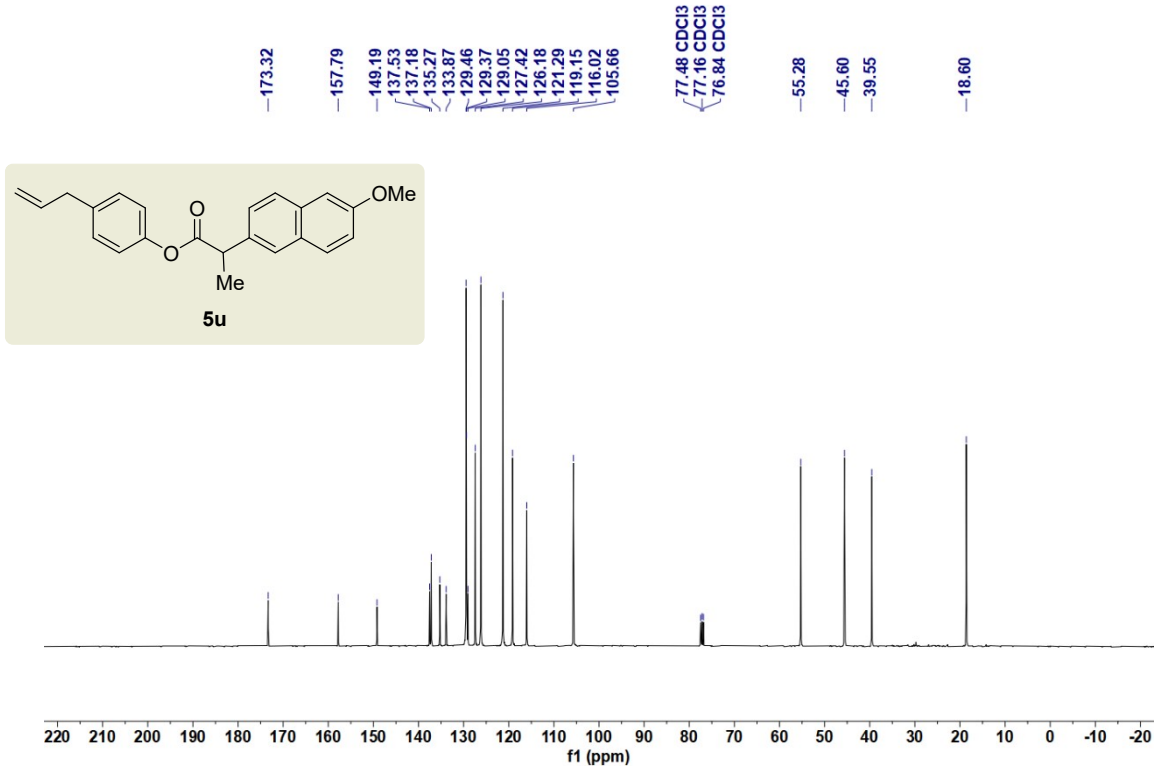
^{13}C NMR (100 MHz, $CDCl_3$) of compound **5m**:



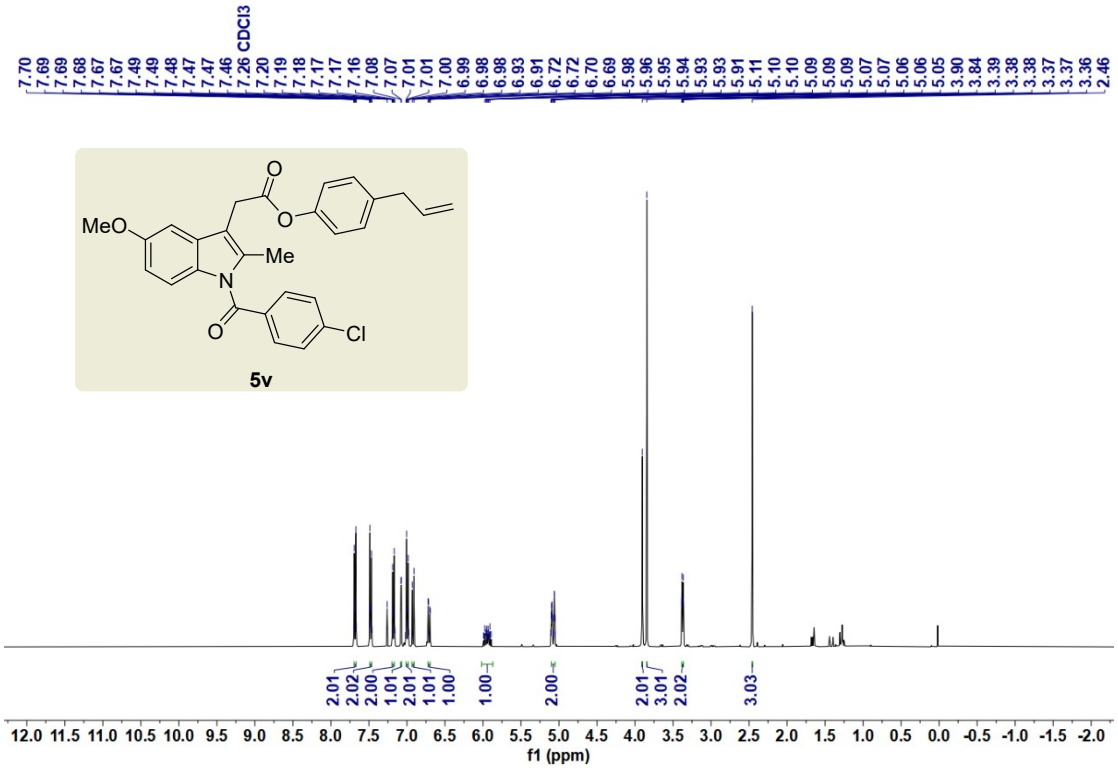
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5u**:



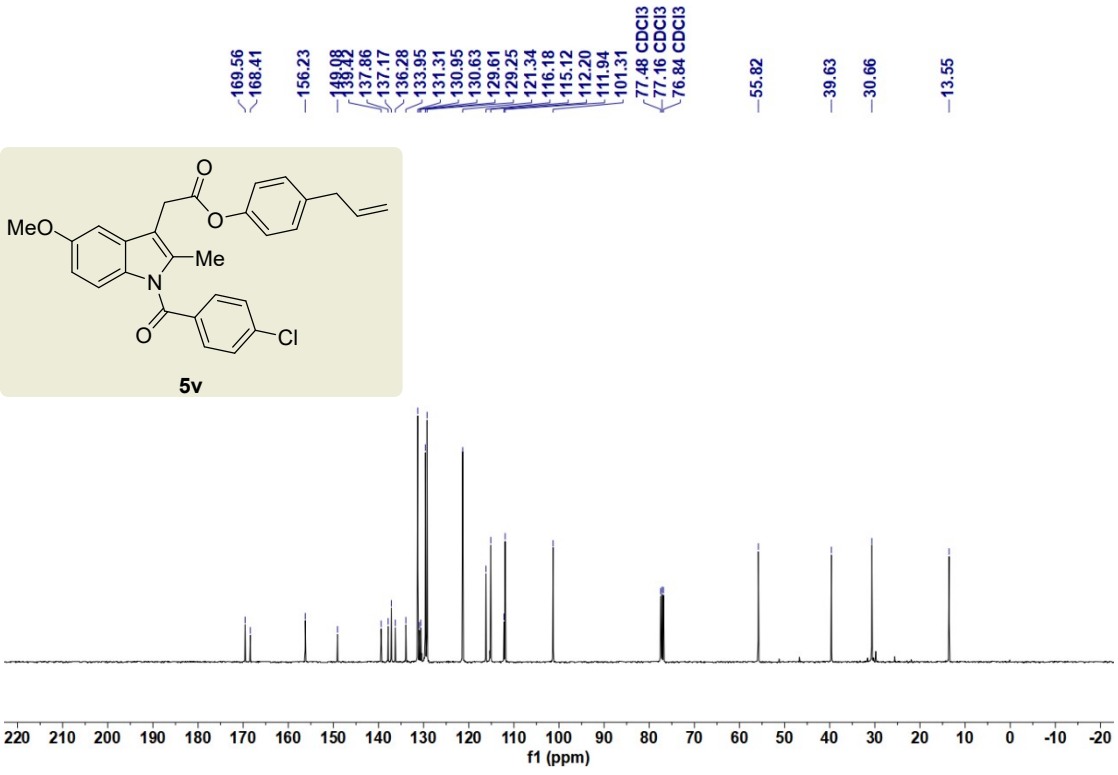
^{13}C NMR (100 MHz, $CDCl_3$) of compound **5u**:



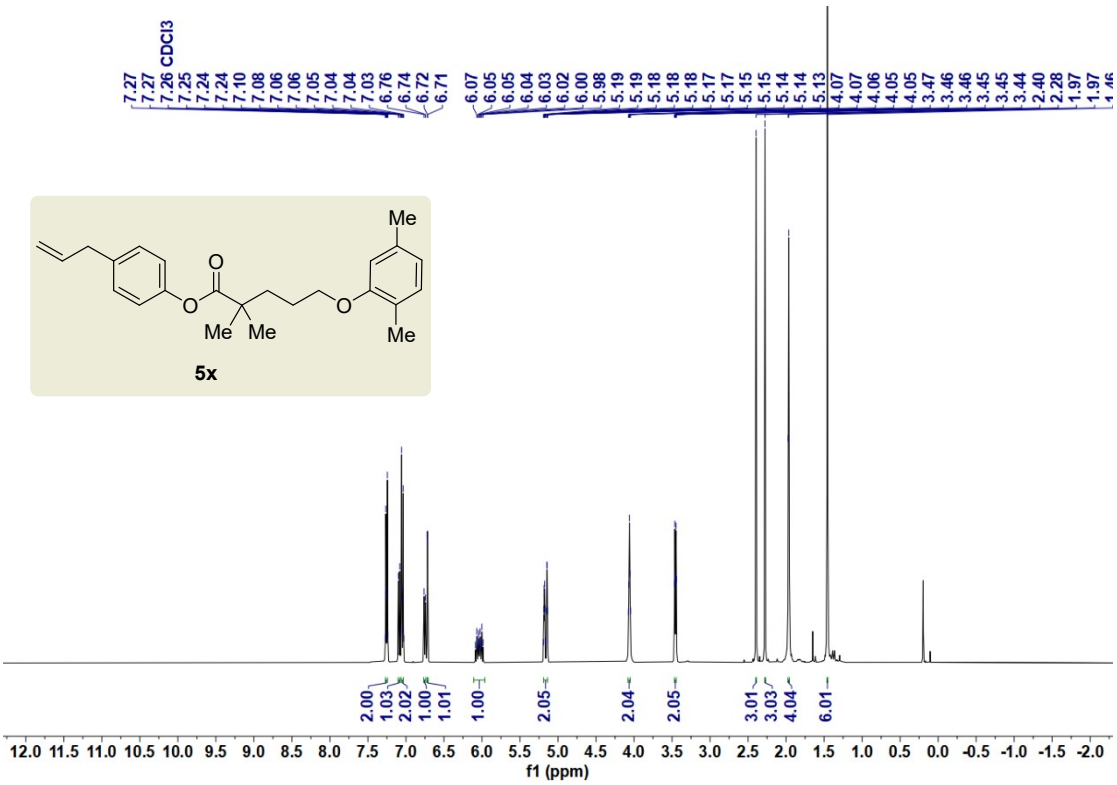
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5v**:



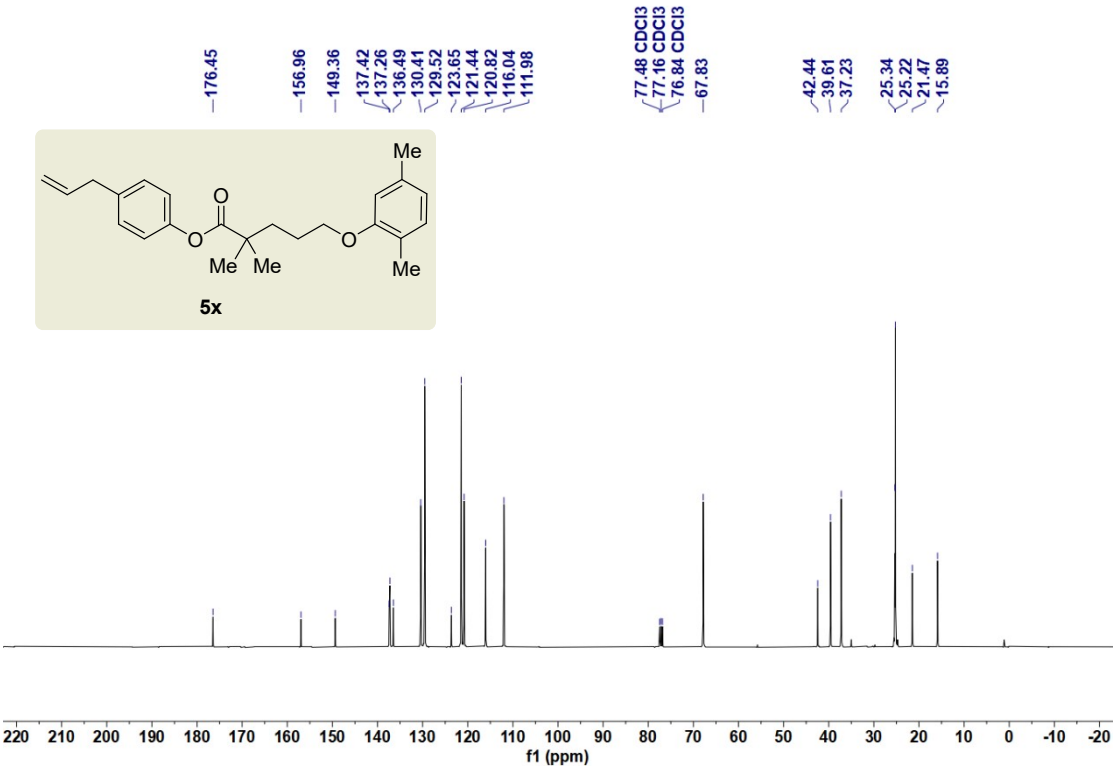
^{13}C NMR (100 MHz, $CDCl_3$) of compound **5v**:



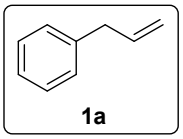
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5x**:



^{13}C NMR (100 MHz, $CDCl_3$) of compound **5x**:



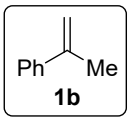
7. Cartesian Coordinates of the Optimized Structures



Zero-point correction= 0.163278(Hartree/Particle)
Thermal correction to Energy= 0.171342
Thermal correction to Enthalpy= 0.172287
Thermal correction to Gibbs Free Energy= 0.129613
Sum of electronic and zero-point Energies= -348.638067
Sum of electronic and thermal Energies= -348.630002
Sum of electronic and thermal Enthalpies= -348.629058
Sum of electronic and thermal Free Energies= -348.671732

Esol= -348.9191033

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.005662	-0.384479	0.187689
2	6	0	1.593754	1.441117	0.058208
3	6	0	2.635702	0.535190	-0.129829
4	6	0	2.362865	-0.828697	-0.161509
5	6	0	1.055342	-1.282753	-0.004762
6	1	0	1.798181	2.506991	0.081483
7	1	0	3.653231	0.891548	-0.253663
8	1	0	3.167411	-1.541845	-0.311265
9	1	0	0.846132	-2.349101	-0.031467
10	6	0	-2.399845	-0.153377	-0.504423
11	1	0	-2.217576	-0.226972	-1.575884
12	6	0	-3.428235	0.561169	-0.058523
13	1	0	-4.107812	1.067342	-0.735807
14	1	0	-3.627245	0.658250	1.005747
15	6	0	0.289639	0.983701	0.213225
16	1	0	-0.525817	1.689184	0.349739
17	6	0	-1.417728	-0.872571	0.378926
18	1	0	-1.716786	-0.742517	1.426178
19	1	0	-1.452657	-1.948682	0.170927



Zero-point correction= 0.163146(Hartree/Particle)
Thermal correction to Energy= 0.171223
Thermal correction to Enthalpy= 0.172167
Thermal correction to Gibbs Free Energy= 0.130057

Sum of electronic and zero-point Energies= -348.645420
Sum of electronic and thermal Energies= -348.637344
Sum of electronic and thermal Enthalpies= -348.636400
Sum of electronic and thermal Free Energies= -348.678510

Esol= -348.9255457

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.943340	1.137060	0.275522
2	6	0	-0.554173	1.184981	0.265145
3	6	0	0.204908	0.042843	-0.020547
4	6	0	-0.473157	-1.155843	-0.271650
5	6	0	-1.863674	-1.205001	-0.264515
6	6	0	-2.604748	-0.058925	0.007798
7	1	0	-2.510943	2.033388	0.504897
8	1	0	-0.041560	2.112054	0.502647
9	1	0	0.087752	-2.058119	-0.493413
10	1	0	-2.368991	-2.142753	-0.472902
11	6	0	1.691580	0.110445	-0.048155
12	6	0	2.323207	1.188349	-0.520684
13	1	0	3.406823	1.248876	-0.520840
14	1	0	1.779429	2.029840	-0.937428
15	6	0	2.452399	-1.072835	0.492649
16	1	0	2.213306	-1.990226	-0.053923
17	1	0	3.529065	-0.910472	0.416120
18	1	0	2.196208	-1.250218	1.542037
19	1	0	-3.689106	-0.098812	0.019429

CF_3 radical

Zero-point correction= 0.012690(Hartree/Particle)
Thermal correction to Energy= 0.016102
Thermal correction to Enthalpy= 0.017046
Thermal correction to Gibbs Free Energy= -0.013995
Sum of electronic and zero-point Energies= -337.425185
Sum of electronic and thermal Energies= -337.421773
Sum of electronic and thermal Enthalpies= -337.420829
Sum of electronic and thermal Free Energies= -337.451870

Esol= -337.5898162

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.477950	-0.276754	0.025720

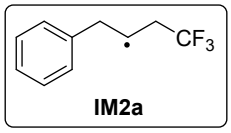
2	9	0	0.935391	0.369695	1.078557
3	9	0	0.935457	-1.511919	-0.007741
4	9	0	-0.838805	-0.257324	-0.007879

CF_3I

Zero-point correction= 0.014644(Hartree/Particle)
Thermal correction to Energy= 0.019359
Thermal correction to Enthalpy= 0.020303
Thermal correction to Gibbs Free Energy= -0.015577
Sum of electronic and zero-point Energies= -348.816993
Sum of electronic and thermal Energies= -348.812278
Sum of electronic and thermal Enthalpies= -348.811333
Sum of electronic and thermal Free Energies= -348.847214

Esol= -348.9903869

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	1.658316	0.877559	-0.878940
2	9	0	1.657939	-1.200239	-0.320286
3	9	0	1.657858	0.322573	1.199425
4	6	0	1.204004	-0.000016	-0.000065
5	53	0	-0.980963	0.000020	-0.000026



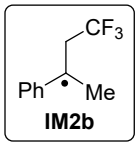
IM2a

Zero-point correction= 0.178985(Hartree/Particle)
Thermal correction to Energy= 0.190864
Thermal correction to Enthalpy= 0.191808
Thermal correction to Gibbs Free Energy= 0.137628
Sum of electronic and zero-point Energies= -686.128050
Sum of electronic and thermal Energies= -686.116171
Sum of electronic and thermal Enthalpies= -686.115227
Sum of electronic and thermal Free Energies= -686.169407

Esol= -686.5714789

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.676626	0.155699	-0.225886
2	6	0	3.644472	-1.240982	0.005696
3	6	0	4.436160	-0.110678	0.197438

4	6	0	3.849060	1.150686	0.179387
5	6	0	2.478165	1.280268	-0.029735
6	1	0	4.094253	-2.228802	0.019688
7	1	0	5.503741	-0.213720	0.362395
8	1	0	4.457216	2.036592	0.332462
9	1	0	2.022900	2.267134	-0.039185
10	6	0	-0.630040	-0.646525	0.356341
11	1	0	-0.349668	-0.792670	1.393792
12	6	0	-1.988334	-1.080391	-0.083981
13	1	0	-1.990271	-1.380677	-1.138431
14	1	0	-2.357355	-1.920729	0.509995
15	6	0	-3.015920	0.026011	0.041077
16	9	0	-3.106700	0.475377	1.300475
17	9	0	-2.699729	1.077463	-0.734822
18	9	0	-4.236049	-0.389129	-0.328734
19	6	0	2.276078	-1.106656	-0.202759
20	1	0	1.656922	-1.988642	-0.347441
21	6	0	0.188686	0.289643	-0.471779
22	1	0	-0.114549	1.331669	-0.285584
23	1	0	-0.030607	0.114003	-1.534747



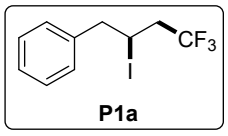
IM2b

Zero-point correction= 0.179520(Hartree/Particle)
Thermal correction to Energy= 0.191298
Thermal correction to Enthalpy= 0.192242
Thermal correction to Gibbs Free Energy= 0.139897
Sum of electronic and zero-point Energies= -686.147436
Sum of electronic and thermal Energies= -686.135659
Sum of electronic and thermal Enthalpies= -686.134715
Sum of electronic and thermal Free Energies= -686.187059

Esol= -686.5907939

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.342742	-1.802007	1.252969
2	6	0	0.730078	-1.269914	0.557291
3	6	0	0.660299	0.021072	-0.022974
4	6	0	-0.556653	0.731540	0.127513
5	6	0	-1.623267	0.191535	0.827212
6	6	0	-1.526406	-1.077349	1.398595
7	1	0	-0.260437	-2.796590	1.679701
8	1	0	1.621378	-1.872756	0.426344
9	1	0	-0.652069	1.724446	-0.298600

10	1	0	-2.539257	0.764578	0.931281
11	6	0	1.758553	0.601595	-0.734138
12	6	0	3.119907	-0.029274	-0.729520
13	1	0	3.897280	0.740632	-0.774478
14	1	0	3.303829	-0.628478	0.165763
15	6	0	1.597677	1.882871	-1.495026
16	1	0	1.488959	2.745056	-0.822186
17	1	0	2.461940	2.066596	-2.135442
18	1	0	0.708857	1.862023	-2.134183
19	6	0	3.350736	-0.930935	-1.923327
20	9	0	2.505636	-1.971987	-1.931636
21	9	0	3.180705	-0.269775	-3.079258
22	9	0	4.597280	-1.427095	-1.925923
23	1	0	-2.363483	-1.498468	1.944863



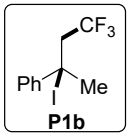
P1a

Zero-point correction= 0.183347(Hartree/Particle)
Thermal correction to Energy= 0.196436
Thermal correction to Enthalpy= 0.197380
Thermal correction to Gibbs Free Energy= 0.139570
Sum of electronic and zero-point Energies= -697.520842
Sum of electronic and thermal Energies= -697.507753
Sum of electronic and thermal Enthalpies= -697.506809
Sum of electronic and thermal Free Energies= -697.564619

Esol= -697.9755704

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.478966	-1.117431	-0.436289
2	6	0	-3.079561	-2.155208	1.056804
3	6	0	-4.127583	-1.577874	0.343202
4	6	0	-3.852500	-0.774179	-0.759285
5	6	0	-2.534478	-0.545019	-1.145249
6	1	0	-3.287319	-2.787775	1.913787
7	1	0	-5.154596	-1.756693	0.644333
8	1	0	-4.664567	-0.322662	-1.319895
9	1	0	-2.320054	0.089805	-2.000684
10	6	0	0.697862	0.045695	0.154064
11	1	0	0.537115	-0.290609	1.179166
12	6	0	2.191416	0.194046	-0.118171
13	1	0	2.375710	0.609271	-1.113008
14	1	0	2.642438	0.864827	0.616267
15	6	0	2.935853	-1.121753	-0.026288

16	9	0	2.528973	-1.847301	1.028370
17	9	0	2.763573	-1.884651	-1.118556
18	9	0	4.251450	-0.915992	0.104554
19	53	0	-0.174805	2.059621	0.149484
20	6	0	-1.764555	-1.927208	0.665812
21	1	0	-0.945986	-2.387800	1.215419
22	6	0	-0.042939	-0.865978	-0.821963
23	1	0	0.491381	-1.823345	-0.828890
24	1	0	0.027281	-0.453976	-1.834297



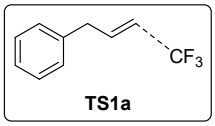
P1b

Zero-point correction= 0.183160(Hartree/Particle)
Thermal correction to Energy= 0.196101
Thermal correction to Enthalpy= 0.197045
Thermal correction to Gibbs Free Energy= 0.141384
Sum of electronic and zero-point Energies= -697.519338
Sum of electronic and thermal Energies= -697.506397
Sum of electronic and thermal Enthalpies= -697.505453
Sum of electronic and thermal Free Energies= -697.561114

Esol= -697.9726406

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.230860	-1.568864	1.859706
2	6	0	1.261589	-0.887241	1.230457
3	6	0	0.996001	0.138806	0.314034
4	6	0	-0.336114	0.468019	0.058355
5	6	0	-1.373522	-0.215086	0.691476
6	1	0	0.462764	-2.357198	2.568175
7	1	0	2.289722	-1.134849	1.479863
8	1	0	-0.583514	1.255195	-0.643744
9	1	0	-2.401173	0.057081	0.474197
10	6	0	3.116450	-0.142387	-1.051781
11	1	0	4.004894	0.385648	-1.407143
12	1	0	3.443321	-0.897383	-0.334896
13	6	0	2.557791	-0.889007	-2.247608
14	9	0	1.368212	-1.449297	-2.005153
15	9	0	2.409122	-0.088344	-3.317349
16	9	0	3.402516	-1.866431	-2.606447
17	6	0	-1.096455	-1.236198	1.590400
18	6	0	2.131423	0.841818	-0.402487
19	53	0	3.357779	1.901374	1.154337
20	6	0	1.686957	1.923297	-1.380049

21	1	0	2.553768	2.376624	-1.864140
22	1	0	1.056692	1.481269	-2.157572
23	1	0	1.123885	2.706626	-0.870820
24	1	0	-1.903993	-1.767331	2.083080

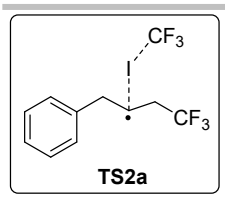


TS1a

Zero-point correction= 0.176224(Hartree/Particle)
Thermal correction to Energy= 0.188720
Thermal correction to Enthalpy= 0.189664
Thermal correction to Gibbs Free Energy= 0.132612
Sum of electronic and zero-point Energies= -686.064497
Sum of electronic and thermal Energies= -686.052001
Sum of electronic and thermal Enthalpies= -686.051056
Sum of electronic and thermal Free Energies= -686.108108

Esol= -686.5086464

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.907655	1.784296	-0.261631
2	6	0	-0.108445	3.398487	-0.089315
3	6	0	-1.034653	4.434959	0.007208
4	6	0	-2.395332	4.146590	-0.028529
5	6	0	-2.826514	2.828760	-0.160585
6	1	0	0.954796	3.615110	-0.059888
7	1	0	-0.696559	5.460748	0.112288
8	1	0	-3.124031	4.947237	0.049726
9	1	0	-3.890276	2.607206	-0.186060
10	6	0	-1.693695	-0.588868	0.534961
11	1	0	-1.786566	-0.351662	1.593085
12	6	0	-1.058199	-1.714691	0.158149
13	1	0	-0.867195	-1.918916	-0.892906
14	1	0	-0.546699	-2.343903	0.879604
15	6	0	-2.874662	-3.205886	-0.012636
16	9	0	-3.383675	-3.344523	1.200167
17	9	0	-3.723621	-2.542884	-0.786087
18	9	0	-2.617459	-4.394399	-0.539017
19	6	0	-0.543227	2.084065	-0.220781
20	1	0	0.178391	1.273839	-0.288529
21	6	0	-2.368527	0.348968	-0.422183
22	1	0	-2.186373	0.007045	-1.448411
23	1	0	-3.454295	0.302394	-0.268676

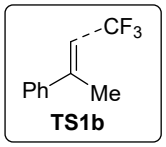


TS2a

Zero-point correction= 0.195009(Hartree/Particle)
Thermal correction to Energy= 0.212992
Thermal correction to Enthalpy= 0.213936
Thermal correction to Gibbs Free Energy= 0.140593
Sum of electronic and zero-point Energies= -1034.934480
Sum of electronic and thermal Energies= -1034.916497
Sum of electronic and thermal Enthalpies= -1034.915553
Sum of electronic and thermal Free Energies= -1034.988896

Esol= -1035.5549763

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.957551	1.542274	0.464003
2	6	0	2.850331	3.217347	-1.040857
3	6	0	2.098614	4.200674	-0.401594
4	6	0	1.279834	3.856369	0.669845
5	6	0	1.209874	2.533520	1.098677
6	1	0	3.495133	3.479586	-1.873406
7	1	0	2.153249	5.231302	-0.736516
8	1	0	0.691980	4.617476	1.172534
9	1	0	0.562932	2.264278	1.929201
10	6	0	1.199061	-0.803873	-0.098386
11	1	0	1.456848	-0.591343	-1.136117
12	6	0	1.142512	-2.280291	0.218635
13	1	0	0.761150	-2.457819	1.228639
14	1	0	0.491110	-2.802154	-0.486543
15	6	0	2.500815	-2.945756	0.122074
16	9	0	3.105680	-2.658975	-1.040214
17	9	0	3.328802	-2.556016	1.105973
18	9	0	2.386667	-4.276156	0.205270
19	6	0	2.780704	1.897618	-0.607336
20	1	0	3.377049	1.132505	-1.100060
21	9	0	-4.217389	-0.658248	-0.034732
22	9	0	-3.809983	0.994778	-1.366335
23	9	0	-3.749533	1.290527	0.774000
24	6	0	-3.505412	0.440986	-0.207447
25	53	0	-1.149415	-0.129259	-0.193332
26	6	0	1.879617	0.100475	0.902163
27	1	0	2.900399	-0.287190	1.037705
28	1	0	1.387047	0.011583	1.877226

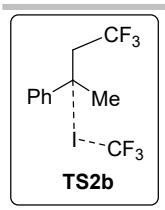


TS1b

Zero-point correction= 0.176115(Hartree/Particle)
Thermal correction to Energy= 0.188696
Thermal correction to Enthalpy= 0.189641
Thermal correction to Gibbs Free Energy= 0.133917
Sum of electronic and zero-point Energies= -686.075978
Sum of electronic and thermal Energies= -686.063396
Sum of electronic and thermal Enthalpies= -686.062452
Sum of electronic and thermal Free Energies= -686.118175

Esol= -686.5187649

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.200412	-1.749248	0.210918
2	6	0	-1.083375	-0.954180	0.434078
3	6	0	-1.143529	0.436820	0.261040
4	6	0	-2.352422	0.997376	-0.172767
5	6	0	-3.471840	0.201602	-0.391668
6	6	0	-3.401975	-1.174712	-0.197684
7	1	0	-2.128795	-2.823997	0.343820
8	1	0	-0.143846	-1.419983	0.714439
9	1	0	-2.425303	2.068939	-0.328089
10	1	0	-4.400833	0.659158	-0.716549
11	6	0	0.043202	1.286841	0.506183
12	6	0	1.016243	0.906524	1.361154
13	1	0	1.870841	1.549236	1.548942
14	1	0	0.902640	0.042463	2.007883
15	6	0	0.167000	2.566565	-0.275772
16	1	0	-0.596791	3.292742	0.022824
17	1	0	1.143138	3.027454	-0.113967
18	1	0	0.038447	2.380720	-1.346882
19	6	0	2.391722	-0.468647	-0.140091
20	9	0	2.316037	-1.736067	0.247925
21	9	0	1.830231	-0.323777	-1.327233
22	9	0	3.656631	-0.081660	-0.179656
23	1	0	-4.273271	-1.796840	-0.374091

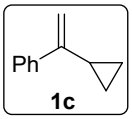


TS2b

Zero-point correction= 0.195423(Hartree/Particle)
Thermal correction to Energy= 0.213381
Thermal correction to Enthalpy= 0.214325
Thermal correction to Gibbs Free Energy= 0.141929
Sum of electronic and zero-point Energies= -1034.939524
Sum of electronic and thermal Energies= -1034.921566
Sum of electronic and thermal Enthalpies= -1034.920622
Sum of electronic and thermal Free Energies= -1034.993018

Esol= -1035.5590176

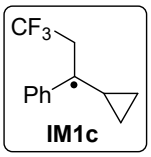
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.952096	-0.344699	0.527234
2	6	0	-1.292888	-1.471818	-0.444301
3	1	0	-1.113448	-1.183081	-1.480998
4	1	0	-0.679171	-2.352031	-0.236817
5	6	0	-2.738221	-1.925008	-0.365148
6	9	0	-3.018937	-2.509566	0.811965
7	9	0	-3.603413	-0.918207	-0.524530
8	9	0	-2.986636	-2.829384	-1.322937
9	9	0	4.247804	0.797511	-1.221085
10	9	0	4.395402	-1.240539	-0.503489
11	9	0	4.556415	0.411471	0.887744
12	6	0	3.986621	-0.019652	-0.219883
13	53	0	1.396203	-0.064334	0.148653
14	6	0	-1.561422	0.979291	0.200224
15	6	0	-1.612506	1.443712	-1.124332
16	6	0	-2.104053	1.790813	1.203988
17	6	0	-2.196894	2.661754	-1.433047
18	1	0	-1.162470	0.859598	-1.921249
19	6	0	-2.693501	3.013230	0.893411
20	1	0	-2.083915	1.468217	2.238195
21	6	0	-2.744668	3.453583	-0.423581
22	1	0	-2.220668	2.999483	-2.463763
23	1	0	-3.114436	3.620100	1.688249
24	6	0	-1.022671	-0.772633	1.981224
25	1	0	-0.536604	-1.740341	2.118018
26	1	0	-0.536959	-0.048144	2.636293
27	1	0	-2.070676	-0.874211	2.284668
28	1	0	-3.202326	4.407121	-0.664966



Zero-point correction= 0.198592(Hartree/Particle)
Thermal correction to Energy= 0.208047
Thermal correction to Enthalpy= 0.208991
Thermal correction to Gibbs Free Energy= 0.163382
Sum of electronic and zero-point Energies= -425.963515
Sum of electronic and thermal Energies= -425.954060
Sum of electronic and thermal Enthalpies= -425.953116
Sum of electronic and thermal Free Energies= -425.998725

Esol= -426.3087399

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.929514	0.704771	0.022720
2	6	0	-1.296222	1.903855	-0.440576
3	1	0	-2.326142	2.238852	-0.396327
4	1	0	-0.576999	2.581845	-0.887370
5	6	0	0.495931	0.275039	0.020455
6	6	0	1.530546	1.207400	0.170936
7	6	0	0.835638	-1.076323	-0.118162
8	6	0	2.861138	0.806614	0.153932
9	1	0	1.283345	2.252542	0.329090
10	6	0	2.167696	-1.478500	-0.135584
11	1	0	0.047220	-1.814159	-0.226910
12	6	0	3.185966	-0.539073	-0.002935
13	1	0	3.647061	1.545089	0.277099
14	1	0	2.409989	-2.529988	-0.253598
15	1	0	4.224672	-0.853100	-0.011760
16	6	0	-1.911931	-0.291905	0.545825
17	6	0	-3.383252	-0.183022	0.284252
18	6	0	-2.587104	-1.241678	-0.418297
19	1	0	-1.628863	-0.734740	1.497993
20	1	0	-3.744895	0.646470	-0.311570
21	1	0	-4.053173	-0.490542	1.078422
22	1	0	-2.714377	-2.275975	-0.118119
23	1	0	-2.381191	-1.089370	-1.472355

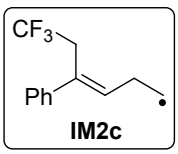


Zero-point correction= 0.214767(Hartree/Particle)

Thermal correction to Energy= 0.228025
Thermal correction to Enthalpy= 0.228970
Thermal correction to Gibbs Free Energy= 0.172585
Sum of electronic and zero-point Energies= -763.462739
Sum of electronic and thermal Energies= -763.449481
Sum of electronic and thermal Enthalpies= -763.448537
Sum of electronic and thermal Free Energies= -763.504921

Esol= -763.9726054

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.055738	-1.810689	1.572716
2	6	0	1.041644	-1.252929	0.775784
3	6	0	0.891123	0.040831	0.216197
4	6	0	-0.320127	0.724515	0.492820
5	6	0	-1.301697	0.156391	1.287703
6	1	0	0.202222	-2.804282	1.984187
7	1	0	1.929238	-1.836528	0.561966
8	1	0	-0.477681	1.710127	0.070841
9	1	0	-2.217727	0.706258	1.479548
10	6	0	1.905036	0.646943	-0.596833
11	6	0	3.166934	-0.084237	-0.953093
12	1	0	3.963791	0.625088	-1.191200
13	1	0	3.528676	-0.733774	-0.151776
14	6	0	2.998574	-0.946273	-2.186236
15	9	0	2.113385	-1.934214	-1.993281
16	9	0	2.567847	-0.222980	-3.231477
17	9	0	4.160357	-1.515300	-2.543282
18	6	0	-1.122208	-1.112342	1.839932
19	1	0	-1.892179	-1.553845	2.463562
20	6	0	1.669468	1.959680	-1.258307
21	6	0	1.535371	3.221969	-0.443556
22	6	0	2.749242	3.003887	-1.296528
23	1	0	1.037055	1.915613	-2.145722
24	1	0	1.656249	3.127021	0.630308
25	1	0	0.805449	3.960135	-0.757398
26	1	0	2.860149	3.590911	-2.200521
27	1	0	3.679875	2.790005	-0.780346



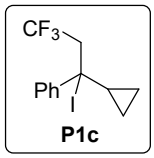
IM2c

Zero-point correction= 0.212162(Hartree/Particle)
Thermal correction to Energy= 0.226448

Thermal correction to Enthalpy= 0.227392
Thermal correction to Gibbs Free Energy= 0.169211
Sum of electronic and zero-point Energies= -763.449243
Sum of electronic and thermal Energies= -763.434956
Sum of electronic and thermal Enthalpies= -763.434012
Sum of electronic and thermal Free Energies= -763.492193

Esol= -763.9573374

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.122338	-2.517987	0.778292
2	6	0	0.836993	-1.817498	0.053835
3	6	0	0.751604	-0.426923	-0.091349
4	6	0	-0.311198	0.240287	0.532433
5	6	0	-1.270778	-0.460097	1.254227
6	1	0	-0.042173	-3.596547	0.868959
7	1	0	1.644600	-2.360467	-0.424670
8	1	0	-0.364983	1.322878	0.471873
9	1	0	-2.081542	0.079001	1.733882
10	6	0	1.764305	0.336377	-0.869791
11	6	0	3.203649	-0.131380	-0.794938
12	1	0	3.888544	0.712403	-0.673071
13	1	0	3.354230	-0.796123	0.059126
14	6	0	3.668749	-0.881247	-2.022065
15	9	0	2.936930	-1.983280	-2.254236
16	9	0	3.604334	-0.130344	-3.131519
17	9	0	4.943862	-1.275165	-1.882305
18	6	0	-1.181694	-1.844190	1.378954
19	1	0	-1.926761	-2.391428	1.947076
20	6	0	1.401022	1.404937	-1.594853
21	6	0	2.014885	3.769858	-1.935866
22	6	0	2.290494	2.360685	-2.355043
23	1	0	0.340573	1.649143	-1.634546
24	1	0	2.359475	4.120352	-0.970859
25	1	0	1.288604	4.375447	-2.462676
26	1	0	2.104335	2.240894	-3.428667
27	1	0	3.344373	2.112635	-2.199531



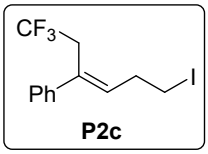
P1c

Zero-point correction= 0.217589(Hartree/Particle)
Thermal correction to Energy= 0.232322
Thermal correction to Enthalpy= 0.233266

Thermal correction to Gibbs Free Energy= 0.173264
Sum of electronic and zero-point Energies= -774.840750
Sum of electronic and thermal Energies= -774.826017
Sum of electronic and thermal Enthalpies= -774.825073
Sum of electronic and thermal Free Energies= -774.885075

Esol= -775.3536981

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.167382	-1.720401	1.703898
2	6	0	1.221076	-1.047279	1.102028
3	6	0	1.000767	0.122584	0.364186
4	6	0	-0.305149	0.608430	0.267195
5	6	0	-1.363213	-0.066200	0.872031
6	1	0	0.363259	-2.625212	2.269774
7	1	0	2.228908	-1.428391	1.234954
8	1	0	-0.501446	1.522565	-0.280468
9	1	0	-2.369838	0.328572	0.780373
10	6	0	3.178516	-0.082986	-0.964013
11	1	0	4.054190	0.491458	-1.274569
12	1	0	3.516199	-0.853948	-0.270966
13	6	0	2.676594	-0.793884	-2.207337
14	9	0	1.453603	-1.315624	-2.053177
15	9	0	2.625318	0.022782	-3.272768
16	9	0	3.509113	-1.796053	-2.525178
17	6	0	-1.133843	-1.234388	1.588030
18	6	0	2.147553	0.852062	-0.309377
19	53	0	3.314969	1.834653	1.346849
20	1	0	-1.957963	-1.760363	2.058424
21	6	0	1.680576	1.883082	-1.320172
22	6	0	1.328497	3.311314	-1.037825
23	6	0	2.549314	2.978409	-1.852414
24	1	0	1.050485	1.398415	-2.064329
25	1	0	1.485625	3.687264	-0.033267
26	1	0	0.464294	3.720719	-1.549294
27	1	0	2.528107	3.157741	-2.920772
28	1	0	3.512905	3.139476	-1.379889



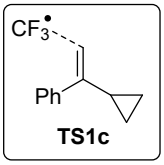
P2c

Zero-point correction= 0.217693(Hartree/Particle)
Thermal correction to Energy= 0.232864
Thermal correction to Enthalpy= 0.233808

Thermal correction to Gibbs Free Energy= 0.171315
Sum of electronic and zero-point Energies= -774.853278
Sum of electronic and thermal Energies= -774.838108
Sum of electronic and thermal Enthalpies= -774.837164
Sum of electronic and thermal Free Energies= -774.899656

Esol= -775.3679157

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.296595	-1.824228	1.062293
2	6	0	0.711305	-1.260724	0.286326
3	6	0	0.775877	0.125017	0.094005
4	6	0	-0.184514	0.928531	0.722724
5	6	0	-1.191827	0.365044	1.497195
6	1	0	-0.334952	-2.901302	1.189383
7	1	0	1.437299	-1.906537	-0.194969
8	1	0	-0.119728	2.007820	0.624899
9	1	0	-1.921018	1.007345	1.980443
10	6	0	3.222876	0.122014	-0.687302
11	1	0	3.999587	0.888537	-0.617539
12	1	0	3.326146	-0.524084	0.187571
13	6	0	3.561160	-0.717920	-1.898389
14	9	0	2.702529	-1.736739	-2.066346
15	9	0	3.543012	-0.002242	-3.032159
16	9	0	4.787079	-1.246952	-1.779487
17	6	0	-1.253464	-1.015531	1.668517
18	6	0	1.841707	0.743471	-0.740051
19	1	0	-2.035901	-1.456306	2.277386
20	6	0	1.574828	1.818205	-1.496960
21	6	0	2.535945	2.623078	-2.326136
22	1	0	0.543532	2.169198	-1.520421
23	1	0	2.307342	2.496176	-3.390458
24	1	0	3.568049	2.294326	-2.191972
25	6	0	2.403037	4.092243	-1.946995
26	1	0	1.399569	4.476755	-2.126779
27	1	0	2.681339	4.274676	-0.909904
28	53	0	3.720165	5.358621	-3.131836

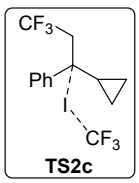


Zero-point correction= 0.176115(Hartree/Particle)
Thermal correction to Energy= 0.188696
Thermal correction to Enthalpy= 0.189641

Thermal correction to Gibbs Free Energy= 0.133917
Sum of electronic and zero-point Energies= -686.075978
Sum of electronic and thermal Energies= -686.063396
Sum of electronic and thermal Enthalpies= -686.062452
Sum of electronic and thermal Free Energies= -686.118175

Esol= -686.5187649

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.047078	-1.266422	0.350447
2	6	0	-0.815120	-0.646921	0.518388
3	6	0	-0.664383	0.729334	0.291141
4	6	0	-1.783379	1.454724	-0.139544
5	6	0	-3.017683	0.835050	-0.303154
6	6	0	-3.156003	-0.527455	-0.055771
7	1	0	-2.138737	-2.333712	0.524711
8	1	0	0.048372	-1.242505	0.797587
9	1	0	-1.694059	2.518251	-0.336053
10	1	0	-3.873232	1.419240	-0.626716
11	6	0	0.645480	1.393059	0.477398
12	6	0	1.570616	0.897518	1.326508
13	1	0	2.518908	1.406089	1.470656
14	1	0	1.342279	0.085635	2.009497
15	6	0	0.944452	2.608792	-0.357516
16	1	0	0.310194	3.455136	-0.072408
17	1	0	1.984016	2.918048	-0.234576
18	1	0	0.760185	2.406415	-1.417436
19	6	0	2.676681	-0.728165	-0.146770
20	9	0	2.416605	-1.953523	0.293114
21	9	0	2.112786	-0.541032	-1.326843
22	9	0	3.984659	-0.544023	-0.228036
23	1	0	-4.117304	-1.012700	-0.189025

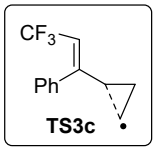


TS2c

Zero-point correction= 0.229991(Hartree/Particle)
Thermal correction to Energy= 0.249654
Thermal correction to Enthalpy= 0.250598
Thermal correction to Gibbs Free Energy= 0.174326
Sum of electronic and zero-point Energies= -1112.261057
Sum of electronic and thermal Energies= -1112.241394
Sum of electronic and thermal Enthalpies= -1112.240449
Sum of electronic and thermal Free Energies= -1112.316722

Esol= -1112.9401383

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.970257	-0.283082	0.247008
2	6	0	-1.280275	-1.151819	-0.971813
3	1	0	-1.029471	-0.652527	-1.908435
4	1	0	-0.693093	-2.071931	-0.924472
5	6	0	-2.731134	-1.584150	-1.074956
6	9	0	-3.069643	-2.459385	-0.114709
7	9	0	-3.586862	-0.558039	-0.993264
8	9	0	-2.940069	-2.192488	-2.251808
9	9	0	4.573279	0.405848	0.751830
10	9	0	4.274252	0.967126	-1.319170
11	9	0	4.400190	-1.124663	-0.770993
12	6	0	4.002541	0.072948	-0.389046
13	53	0	1.395974	0.031260	-0.038653
14	6	0	-1.506344	1.110902	0.228749
15	6	0	-1.746460	1.797088	-0.971905
16	6	0	-1.761475	1.779844	1.434433
17	6	0	-2.237622	3.094592	-0.965750
18	1	0	-1.543930	1.322395	-1.925674
19	6	0	-2.254380	3.079531	1.439350
20	1	0	-1.568210	1.277279	2.375101
21	6	0	-2.496272	3.742987	0.240495
22	1	0	-2.418806	3.602660	-1.907091
23	1	0	-2.447803	3.575113	2.385049
24	1	0	-2.879685	4.757920	0.243776
25	6	0	-1.218789	-1.035035	1.533569
26	6	0	-0.460928	-2.262661	1.930969
27	6	0	-0.363648	-1.015821	2.766539
28	1	0	-2.290052	-1.074430	1.731442
29	1	0	0.414143	-2.528565	1.346429
30	1	0	-1.028454	-3.102984	2.312745
31	1	0	-0.875188	-0.997730	3.722595
32	1	0	0.568280	-0.463211	2.735374

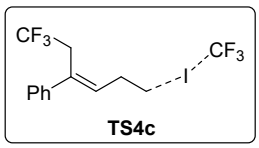


Zero-point correction= 0.212306(Hartree/Particle)
Thermal correction to Energy= 0.225491
Thermal correction to Enthalpy= 0.226435
Thermal correction to Gibbs Free Energy= 0.171174

Sum of electronic and zero-point Energies= -763.445327
Sum of electronic and thermal Energies= -763.432141
Sum of electronic and thermal Enthalpies= -763.431197
Sum of electronic and thermal Free Energies= -763.486458

Esol= -763.9467537

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.002315	-1.582522	0.061317
2	6	0	-1.663207	-1.213430	0.109969
3	6	0	-1.283298	0.137869	0.050607
4	6	0	-2.302925	1.101661	-0.039564
5	6	0	-3.639675	0.729737	-0.092911
6	1	0	-3.267703	-2.634383	0.098830
7	1	0	-0.901611	-1.983896	0.160510
8	1	0	-2.038697	2.154579	-0.026823
9	1	0	-4.406805	1.495365	-0.154418
10	6	0	1.104840	-0.307492	0.874860
11	1	0	1.795071	0.309529	1.460988
12	1	0	0.582138	-0.957916	1.580740
13	6	0	1.968283	-1.203117	0.014208
14	9	0	1.238322	-2.050487	-0.727523
15	9	0	2.738494	-0.503981	-0.834393
16	9	0	2.790403	-1.946616	0.772196
17	6	0	-3.998586	-0.615604	-0.044596
18	6	0	0.130048	0.543577	0.097570
19	1	0	-5.043310	-0.906009	-0.080734
20	6	0	0.542323	1.707042	-0.509910
21	6	0	1.228779	3.203769	0.635227
22	6	0	1.881134	2.362823	-0.392333
23	1	0	-0.165636	2.219060	-1.154140
24	1	0	1.211776	2.887038	1.669348
25	1	0	0.717165	4.118492	0.368823
26	1	0	2.191456	2.889671	-1.293693
27	1	0	2.679653	1.717575	-0.034033



TS4c

Zero-point correction= 0.229173(Hartree/Particle)
Thermal correction to Energy= 0.249224
Thermal correction to Enthalpy= 0.250168
Thermal correction to Gibbs Free Energy= 0.172212

Sum of electronic and zero-point Energies= -1112.264259
Sum of electronic and thermal Energies= -1112.244208
Sum of electronic and thermal Enthalpies= -1112.243264
Sum of electronic and thermal Free Energies= -1112.321220

Esol= -1112.9440127

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.384055	-0.700044	-0.058792
2	6	0	5.149768	-0.063496	-0.140980
3	6	0	3.964398	-0.765918	0.110955
4	6	0	4.057079	-2.116812	0.472571
5	6	0	5.290381	-2.752452	0.553439
6	1	0	7.289532	-0.139964	-0.268738
7	1	0	5.107681	0.980979	-0.428775
8	1	0	3.152490	-2.662796	0.721914
9	1	0	5.338294	-3.797518	0.842054
10	6	0	2.536179	1.341334	0.463405
11	1	0	1.638236	1.512353	1.063399
12	1	0	3.394018	1.618710	1.080406
13	6	0	2.479112	2.329155	-0.681013
14	9	0	3.564491	2.258948	-1.468421
15	9	0	1.412937	2.130688	-1.469832
16	9	0	2.404595	3.584550	-0.217207
17	6	0	6.460350	-2.046529	0.285211
18	6	0	2.634907	-0.104872	0.020986
19	1	0	7.424311	-2.539805	0.353376
20	6	0	1.568123	-0.784695	-0.428230
21	6	0	0.133742	-0.322809	-0.472529
22	1	0	1.729561	-1.803957	-0.775294
23	1	0	-0.248396	-0.391601	-1.496665
24	1	0	0.030492	0.718534	-0.165937
25	6	0	-0.656675	-1.224171	0.441038
26	1	0	-0.763672	-2.260754	0.128554
27	1	0	-0.467042	-1.109971	1.505927
28	53	0	-3.022094	-0.509055	0.347784
29	6	0	-5.285550	0.211284	0.230740
30	9	0	-5.326766	1.532194	0.258513
31	9	0	-5.829519	-0.225112	-0.892133
32	9	0	-5.952790	-0.274136	1.263671

8 References

[1].(a) R. Liu, Z. Lu, X. H. Hu, J. L. Li and X. Yang, *Org. Lett*., **2015**, *17*, 1489; (b) Q. Y. Meng, T. E. Schirmer, K. Katou, and B. Kçnig, *Angew. Chem. Int. Ed*., **2019**, *58*, 5723–5728; (c) Z. Li, D. Wu, C. Ding, G. Yin, *CCS Chem*., **2020**, *2*, 576–582.

[2].(a) S. Fang, X. Wang, F. Yin, P. Cai, H. Yang and L. Kong, *Org. Lett*., **2019**, *21*, 841; (b) M. O. Akram, P. S. Mali, and N. T. Patil, *Org. Lett*., **2017**, *19*, 3075−3078; (c) Z. Shu, Y. Zhou, Y. Zhang and J. Wang, *Org. Chem. Front*., **2014**, *1*, 1123–1127.

[3].I. Buslov, S. C. Keller and X. Hu, *Org. Lett*., **2016**, *18*, 1928−1931.

[4].X. Qi, P. Chen, and G. Liu, *Angew. Chem. Int. Ed*., **2017**, *56*, 9517–9521.

[5].K. Tsuchii, M. Imura, N. Kamada, T. Hirao and A. Ogawa., *J. Org. Chem*., **2004**, *69*, 6658–6665.

[6].(a) Y. Chen, L. Li, X. He, Z. Li, *ACS Catal*., **2019**, *9*, 9098-9102; (b) W. Li, X. Zhou, T. Xiao, Z. Ke and L. Zhou, *CCS Chem*., **2021**, *3*, 794–805; (c) J. Ignatowska, W. Dmowski, Journal of Fluorine Chemistry., **2007**, *128*, 997–1006.

[7].Y. Cheng, C. Mgck-Lichtenfeld and A. Studer, *Angew. Chem. Int. Ed*., **2018**, *57*, 16832–16836.

[8].(a) L. Tang, F. Yang, Z. Yang, H. Chen, H. Cheng, S. Zhang, Q. Zhou, and W. Rao, Org. Lett. 2021, 23, 519−524; (b) L. Helmecke, M. Spittler, K. Baumgarten, and C. Czekelius, *Org. Lett*., **2019**, *21*, 7823−7827.

[9].(a) E. Zhu, X. Liu, A. Wang, T. Mao, L. Zhao, X. Zhang and C. He, *Chem. Commun*., **2019**, *55*, 12259–12262; (b) T. Mao, M. J. Ma, L. Zhao, D. P. Xue, Y. B. Yu, J. G, and C. Y. He, *Chem. Commun*., 2020,56, 1815-1818; (c) J. Ignatowska, W. Dmowski, Journal of Fluorine Chemistry, 2007, 128, 997–1006; (d) O. F. Aebischer, D. T. Muñoz, P. Tondo, J. L. Débieux, T. A. Jenny, Synthesis, 2010, 7, 1123-1140.

[10].Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[11].a) Y. Zhao, N. E Schultz, D. G.Truhlar, *J. Chem. Theory. Comput*., **2006**, *2*, 364; b) Y. Zhao, D. G.Truhlar, *J. Chem. Phys*. **2006**, *125*, 194101; c) Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2006**,*110*, 13126.

[12].C. Gonzalez, H. B.Schlegel, *J. Chem. Phys*.,**1989**, *90*, 2154.

[13].J. Tomasi, M. Persico, *Chem. Rev*.,**1994**, *94*, 2027.

[14].CYLview, 1.0 b; C. Y. Legault, Université de Sherbrooke, 2009 (http://www.cylview.org).