Intermolecular oxidative radical fluoroalkylfluorosulfonylation of unactivated alkenes with (fluoroalkyl)trimethylsilane, silver fluoride, sulfur dioxide and *N*-fluorobenzenesulfonimide

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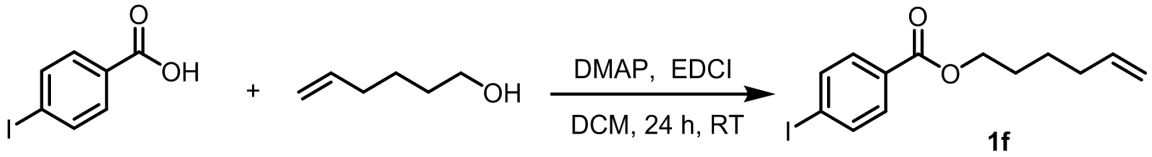
1. General information

^{1}H, ^{13}C and ^{19}F NMR spectra were measured on a 400 MHz NMR spectrometer. ^{1}H and ^{13}C spectra chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0. ^{19}F NMR spectra chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Chemical shifts (δ) are reported in ppm and coupling constants are in hertz (Hz). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). The NMR yield was determined by ^{19}F NMR using 1-methoxy-4-(trifluoromethoxy)benzene (^{19}F NMR: δ -59.0 ppm) as an internal standard before working up the reaction. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode. Unless otherwise noted, solvents were freshly dried and degassed according to the purification handbook Purification of Laboratory Chemicals before using. Flash column chromatography was carried out using 300-400 mesh silica gel.

2. Preparation of various alkene starting materials

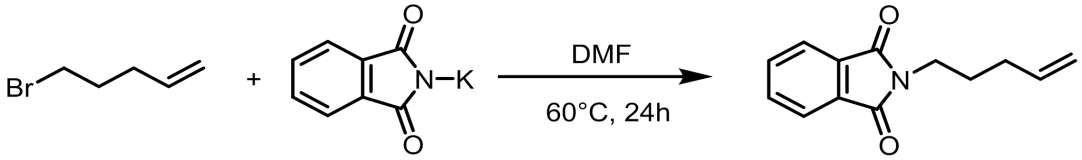
1a, 1k, 1p, 1q, 1w were purchased from commercial source and used without further purification. **1b**,[1] **1c**,[1] **1d**,[1] **1e**,[1] **1g**,[1] **1h**[1] and **1i**[1] were prepared according to the literature.

Synthesis of hex-5-en-1-yl 4-iodobenzoate (1f)



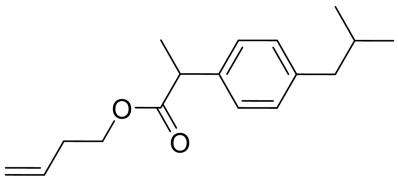
The method was adapted from a procedure reported previously for similar compound.[2] 4-iodobenzoic acid (1.49 g, 6 mmol), DMAP (122 mg, 1 mmol) and EDCI (1.92 g, 10 mmol) were added into 100 mL three-neck flask containing a magnetic stir bar at 0 ℃. Then anhydrous DCM (10 mL) and 1-hexen-6-ol (0.46 mL, 5 mmol) were added in turn. The mixture was warmed to room temperature and stirred for 24 hours. The reaction mixture was purified by silica gel chromatography eluted with PE:EA = 30:1 to give a colorless liquid (2.17 g, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07 – 4.94 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.82 – 1.73 (m, 2H), 1.59 – 1.48 (m, 2H). **GC-MS** (EI): *m/z* = 330.0 (M^+). The analytical data are consistent with literature values.[3]

Synthesis of 2-(pent-4-en-1-yl)isoindoline-1,3-dione (1j)

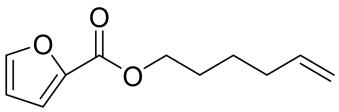


To a flame-dried 100 mL three-neck flask containing a magnetic stir bar was added potassium 1,3-dioxoisoindolin-2-ide (3.26 g, 17.6 mmol), then distilled DMF (32 mL) and 5-bromopent-1-ene (1.9 mL, 16 mmol) were added to the three-neck flask in turn. The mixture was heated to 60 ℃ for 24 hours. After filtration, the mixture was diluted with H_2O (100 mL) and extracted with DCM (100 mL). The organic layer was washed with brine (80 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting

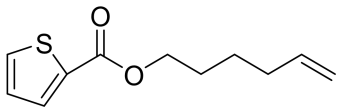
residue was purified by silica gel column chromatography (PE/EA = 15:1 v/v) to give a white solid (3.13 g, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 – 7.82 (m, 2H), 7.73 – 7.68 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.08 – 4.96 (m, 2H), 3.70 (t, *J* = 7.2 Hz, 2H), 2.14 – 2.09 (m, 2H), 1.82 – 1.75 (m, 2H). **GC-MS (EI)**: *m/z* = 215.1 (M^+). The analytical data are consistent with literature values.[2]



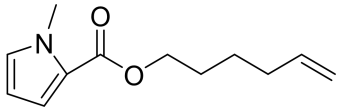
but-3-en-1-yl 2-(4-isobutylphenyl)propanoate (1l): According to the procedure given for the synthesis of **1f**, **1l** was obtained as a colorless liquid in 89% yield by silica gel column chromatography (PE/EA = 40:1 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.70 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.04 – 4.99 (m, 2H), 4.12 (t, *J* = 6.7 Hz, 2H), 3.69 (q, *J* = 7.1 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 2.33 (qd, *J* = 6.7, 1.1 Hz, 2H), 1.85 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.8, 140.6, 137.9, 134.0, 129.4, 127.3, 117.3, 63.8, 45.3, 45.2, 33.2, 30.3, 22.5, 18.6. **HRMS** (EI): calcd for $C_{17}H_{24}O_2$ (M^+) 260.1776, found 260.1787. **IR** (film) ν_{max}: 3447, 3080, 2955, 2932 2869, 1735, 1653, 1559, 1512, 1420, 1383, 1367, 1242, 1200, 1167, 1093, 1072 cm^{-1}.



hex-5-en-1-yl furan-2-carboxylate (1m): According to the procedure given for the synthesis of **1f**, **1m** was obtained as a colorless liquid in 99% yield by silica gel column chromatography (PE/EA = 15:1 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 0.8 Hz, 1H), 7.16 (d, *J* = 2.9 Hz, 1H), 6.49 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 – 4.93 (m, 2H), 4.29 (t, *J* = 6.7 Hz, 2H), 2.10 (q, *J* = 7.2 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.56 – 1.46 (m, 2H). **GC-MS** (EI): *m/z* = 195.2 (M^+). The analytical data are consistent with literature values.[4]

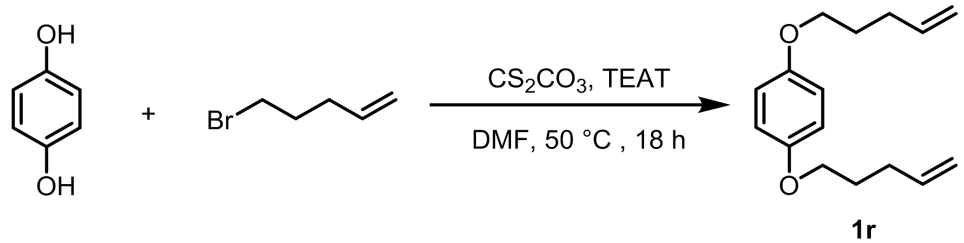


hex-5-en-1-yl thiophene-2-carboxylate (1n): According to the procedure given for the synthesis of **1f**, **1n** was obtained as a colorless liquid in 99% yield by silica gel column chromatography (PE/EA = 30:1 v/v).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.54 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.09 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07 – 4.94 (m, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 2.12 (dd, *J* = 14.3, 7.2 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.58 – 1.49 (m, 2H). **GC-MS** (EI): *m/z* = 210.0 (M^+). The analytical data are consistent with literature values.[4]



hex-5-en-1-yl 1-methyl-1H-pyrrole-2-carboxylate (1o): According to the procedure given for the synthesis of **1f**, **1o** was obtained as a yellow liquid in 86% yield by silica gel column chromatography (PE/EA = 10:1 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.94 (dd, *J* = 3.9, 1.8 Hz, 1H), 6.78 (t, *J* = 2.0 Hz, 1H), 6.11 (q, *J* = 3.9 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09 – 4.94 (m, 2H), 4.22 (t, *J* = 6.6 Hz, 2H), 3.92 (s, 3H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.56 – 1.49 (m, 2H). **GC-MS** (EI): *m/z* = 207.2 (M^+). The analytical data are consistent with literature values.[5]

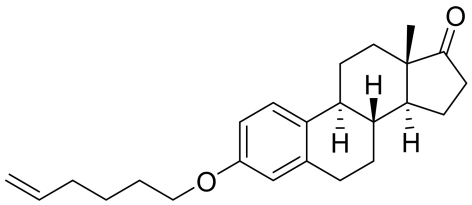
Synthesis of 1,4-bis(pent-4-en-1-yloxy)benzene (1r)



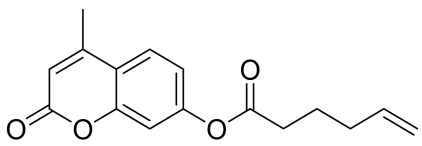
1r

The method was adapted from a procedure reported previously for similar compound.[2] Hydroquinone (550.6 mg, 5 mmol), cesium carbonate (2.12 g, 6.5 mmol) and tetraethylammonium iodide (128.6 mg, 0.5 mmol) were added into a 100 mL three-neck dried flask. The mixture was evacuated and backfilled with Ar (3 times). Then

anhydrous DMF (25 mL) and 5-bromopent-1-ene (1.8 mL, 15 mmol) were added via syringe subsequently. The reaction was stirred at 50 ℃ for 18 hours. After filtration, the mixture was washed with H_2O (50 mL×3) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel chromatography eluted with PE: EA = 12:1 v/v to give a white solid (423.3 mg, 34% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.82 (s, 4H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 2H), 5.08 (d, *J* = 1.7 Hz, 1H), 5.04 (d, *J* = 1.7 Hz, 1H), 5.01 (s, 1H), 4.99 (s, 1H), 3.92 (t, *J* = 6.5 Hz, 4H), 2.23 (q, *J* = 7.3 Hz, 4H), 1.93 – 1.78 (m, 4H). **LRMS** (EI): *m/z* = 246.0 (M^+). The analytical data are consistent with literature values.[6]



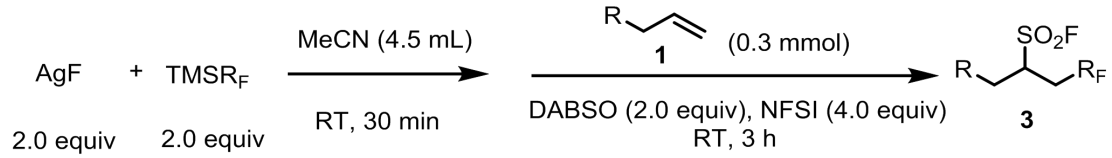
(8R,9S,13S,14S)-3-(hex-5-en-1-yloxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro -17H-cyclopenta[a]phenanthren-17-one (1s): According to the procedure given for the synthesis of **1r**, **1s** was obtained as a white solid in 70% yield by silica gel column chromatography (PE/DCM = 12:1 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 1H), 5.88 – 5.78 (m, 1H), 5.00 (ddd, *J* = 13.7, 11.1, 1.1 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.91 – 2.88 (m, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.42 – 2.38 (m, 1H), 2.27 – 2.17 (m, 1H), 2.14 – 2.07 (m, 3H), 2.06 – 1.94 (m, 2H), 1.86 – 1.75 (m, 2H), 1.68 – 1.54 (m, 5H), 1.52 – 1.37 (m, 4H), 0.91 (s, 3H). **GC-MS** (EI): *m/z* = 352.2 (M^+). The analytical data are consistent with literature values.[1]

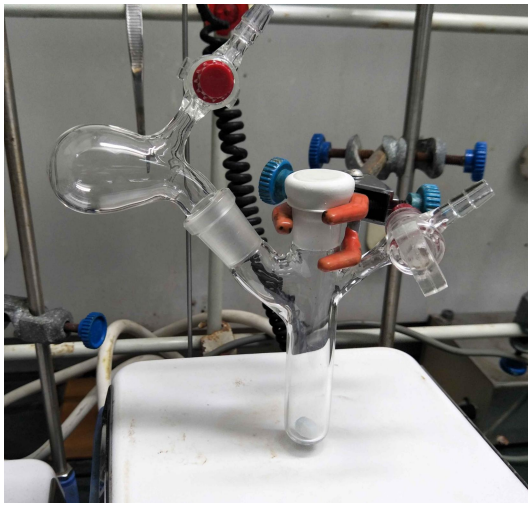


4-methyl-2-oxo-2H-chromen-7-yl hex-5-enoate (1u): According to the procedure given for the synthesis of **1f**, **1u** was obtained as a white solid in 84% yield by silica gel column chromatography (PE/DCM = 4:1 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.6

Hz, 1H), 7.10 (d, *J* = 2.2 Hz, 1H), 7.06 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.27 (d, *J* = 1.1 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.12 – 5.02 (m, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.43 (d, *J* = 1.1 Hz, 3H), 2.19 (q, *J* = 7.1 Hz, 2H), 1.87 (p, *J* = 7.4 Hz, 2H). **GC-MS (EI)**: *m/z* = 272.1 (M^+). The analytical data are consistent with literature values.[1]

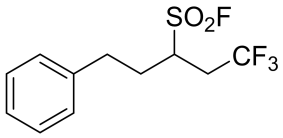
3. General procedures for fluoroalkylfluorosulfonylation of various unactivated alkenes



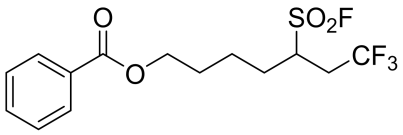


As shown in the figure, to a dry solid feeder were added NFSI (378 mg, 1.2 mmol) and DABSO (144 mg, 0.6 mmol). AgF (76.2 mg, 0.6 mmol) was added to an oven-dried two-neck schlenk tube equipped with the solid feeder. The system was then evacuated and backfilled with Ar (3 times). Freshly-distilled CH_3CN (4.5 mL) and $TMSR_F$ (0.6 mmol) were added to the schlenk tube in turn. The reaction mixture was stirred under Ar atmosphere at room temperature for 30 minutes to generate the [AgR_F] species. Alkene substrate (0.3 mmol) was then added via syringe to the schlenk tube. Then NFSI (378 mg, 1.2 mmol) and DABSO (144 mg, 0.6 mmol) stored in the solid feeder was added into the schlenk tube. The resulting reaction mixture was further stirred at room temperature for 3 hours. 1-methoxy-4-(trifluoromethoxy)benzene (45.3 uL, 0.3 mmol) was added into the reaction mixture as an internal standard and the yield of the desired product was measured by ^{19}F NMR before working up. Then the reaction mixture was filtered through a pad of celite. After removal of the solvent under reduced pressure with a rotary evaporator, the crude product was purified by silica gel chromatography to give the desired fluoroalkylfluorosulfonylation product.

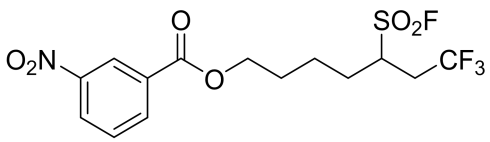
4. Characterization data



1,1,1-trifluoro-5-phenylpentane-3-sulfonyl fluoride (3a): Obtained as a colorless liquid in 72% yield (60.9 mg) by silica gel flash column chromatography eluted with pentane/EA = 40:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 3.69 – 3.62 (m, 1H), 3.00 – 2.93 (m, 1H), 2.89 (t, *J* = 8.1 Hz, 2H), 2.68 – 2.54 (m, 1H), 2.48 – 2.38 (m, 1H), 2.36 – 2.25 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.3 (s, 1F), -63.8 (td, *J* = 10.2, 2.1 Hz, 3F). **GC-MS** (EI): *m/z* = 284.1 (M^+). The analytical data are consistent with literature values.[1]

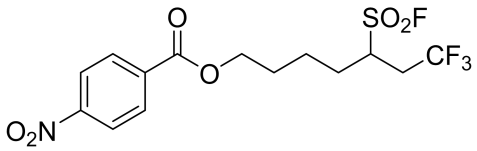


7,7,7-trifluoro-5-(fluorosulfonyl)heptyl benzoate (3b): Obtained as a yellow liquid in 45% yield (48.2 mg) by silica gel flash column chromatography eluted with PE/EA = 20:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.35 (t, *J* = 6.2 Hz, 2H), 3.72 – 3.63 (m, 1H), 3.05 – 2.85 (m, 1H), 2.68 – 2.51 (m, 1H), 2.27 – 2.00 (m, 2H), 1.91 – 1.79 (m, 2H), 1.79 – 1.65 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.2 (s, 1F), -64.1 (td, *J* = 10.2, 2.2 Hz, 3F). **GC-MS** (EI): *m/z* = 356.1 (M^+). The analytical data are consistent with literature values.[1]

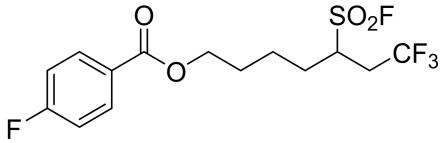


7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 3-nitrobenzoate (3c): Obtained as a yellow liquid in 81% yield (97.5 mg) by silica gel flash column chromatography eluted with PE/EA = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.82 (t, *J* = 4.0 Hz, 1H), 8.41 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 4.41 (t, *J* = 6.4 Hz,

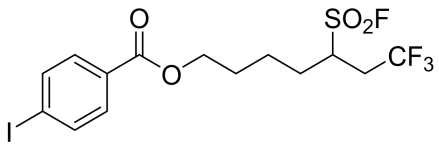
2H), 3.75 – 3.66 (m, 1H), 3.01 – 2.88 (m, 1H), 2.73 – 2.53 (m, 1H), 2.24 – 2.03 (m, 2H), 1.95 – 1.82 (m, 2H), 1.82 – 1.64 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.3 (s, 1F), -64.0 (td, *J* = 10.2, 1.8 Hz, 3F). **GC-MS** (EI): *m/z* = 402.0 (M^+). The analytical data are consistent with literature values.[1]



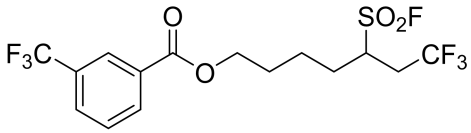
7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-nitrobenzoate (3d): Obtained as a yellow liquid in 57% yield (69 mg) by silica gel flash column chromatography eluted with PE/EA = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.9 Hz, 2H), 8.19 (d, *J* = 9.0 Hz, 2H), 4.40 (t, *J* = 6.3 Hz, 2H), 3.74 – 3.65 (m, 1H), 3.04 – 2.85 (m, 1H), 2.71 – 2.50 (m, 1H), 2.23 – 2.04 (m, 2H), 1.92 – 1.84 (m, 2H), 1.80 – 1.70 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.3 (s, 1F), -64.0 (td, *J* = 10.4, 1.8 Hz, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.7, 150.7, 135.6, 130.8, 125.0 (q, *J* = 277.2 Hz), 123.6, 65.0, 56.9 (dd, *J* = 14.6, 2.6 Hz), 33.8 (q, *J* = 31.0 Hz), 29.1, 28.2, 22.4. **HRMS** (ESI): calcd for $[M + NH_4]^+$ 419.0905, found 419.0895. **IR** (film) ν_{max}: 3363, 2975, 2897, 1632, 1519, 1412, 1264, 1206, 1149, 1089, 1049 cm^{-1}.



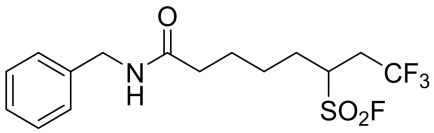
7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-fluorobenzoate (3e): Obtained as a yellow liquid in 85% yield (95.2 mg) by silica gel flash column chromatography eluted with PE/EA = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 – 7.99 (m, 2H), 7.11 (t, *J* = 8.7 Hz, 2H), 4.34 (t, *J* = 6.2 Hz, 2H), 3.72 – 3.62 (m, 1H), 3.00 – 2.88 (m, 1H), 2.66 – 2.51 (m, 1H), 2.24 – 2.00 (m, 2H), 1.90 – 1.65 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.2 (s, 1F), -64.1 (td, *J* = 10.2, 1.8 Hz, 3F), -105.6 (m, 1F). **GC-MS** (EI): *m/z* = 374.1 (M^+). The analytical data are consistent with literature values.[1]



7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-iodobenzoate (3f): Obtained as a yellow liquid in 71% yield (102.9 mg) by silica gel flash column chromatography eluted with PE/EA = 20:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 4.33 (t, *J* = 6.2 Hz, 2H), 3.68 (d, *J* = 2.6 Hz, 1H), 3.02 – 2.85 (m, 1H), 2.67 – 2.48 (m, 1H), 2.24 – 1.97 (m, 2H), 1.89 – 1.78 (m, 2H), 1.76 – 1.62 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.3 (s, 1F), -64.0 (t, *J* = 9.7 Hz, 3F). **GC-MS** (EI): *m/z* = 482.2 (M^+). The analytical data are consistent with literature values.[1]

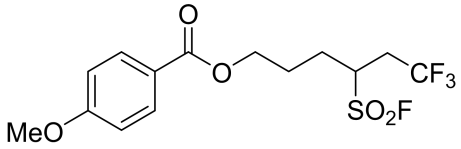


7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 3-(trifluoromethyl)benzoate (3g): Obtained as a yellow liquid in 82% yield (104.4 mg) by silica gel flash column chromatography eluted with PE/EA = 30:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 4.38 (t, *J* = 6.3 Hz, 2H), 3.76 – 3.62 (m, 1H), 3.04 – 2.84 (m, 1H), 2.70 – 2.48 (m, 1H), 2.27 – 1.97 (m, 2H), 1.96 – 1.83 (m, 2H), 1.79 – 1.62 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.1 (s, 1F), -63.0 (s, 3F), -64.2 (t, *J* = 9.5 Hz, 3F). **GC-MS** (EI): *m/z* = 424.2 (M^+). The analytical data are consistent with literature values.[1]

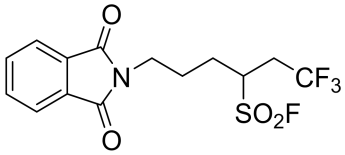


8-(benzylamino)-1,1,1-trifluoro-8-oxooctane-3-sulfonyl fluoride (3h): Obtained as a yellow liquid in 79% yield (87.1 mg) by silica gel flash column chromatography eluted with PE/EA = 1:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 2H), 7.24 (dd, *J* = 11.3, 7.5 Hz, 3H), 6.13 (s, 1H), 4.37 (d, *J* = 5.6 Hz, 2H), 3.61 (s, 1H), 3.00 – 2.75 (m, 1H), 2.65 – 2.38 (m, 1H), 2.20 (t, *J* = 7.2 Hz, 2H), 2.07 – 1.91 (m, 2H), 1.67 (dt, *J* = 14.6,

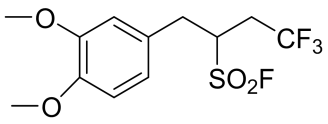
7.1 Hz, 2H), 1.58 – 1.47 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.4 (s, 1F), -64.0 (td, *J* = 10.2, 1.8 Hz, 3F). **GC-MS** (EI): *m/z* = 369.1 (M^+). The analytical data are consistent with literature values.[1]



7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-methoxybenzoate (3i): Obtained as a yellow liquid in 85% yield (95.5 mg) by silica gel flash column chromatography eluted with PE/EA = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.34 (t, *J* = 5.9 Hz, 2H), 3.86 (s, 3H), 3.81 – 3.71 (m, 1H), 3.06 – 2.85 (m, 1H), 2.73 – 2.49 (m, 1H), 2.37 – 2.13 (m, 2H), 2.13 – 1.94 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.3 (s, 1F), -64.0 (t, *J* = 9.8 Hz, 3F). **GC-MS** (EI): *m/z* = 372.1 (M^+). The analytical data are consistent with literature values.[1]

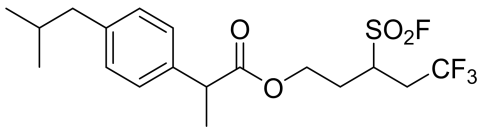


6-(1,3-dioxoisoindolin-2-yl)-1,1,1-trifluorohexane-3-sulfonyl fluoride (3j): Obtained as a white solid in 95% yield (104.6 mg) by silica gel flash column chromatography eluted with PE/EA = 6:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.74 (t, *J* = 6.6 Hz, 3H), 2.97 – 2.85 (m, 1H), 2.64 – 2.47 (m, 1H), 2.19 – 2.02 (m, 2H), 2.01 – 1.88 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.4 (s, 1F), -64.0 (td, *J* = 10.2, 2.2 Hz, 3F). **GC-MS** (EI): *m/z* = 367.0 (M^+). The analytical data are consistent with literature values.[1]

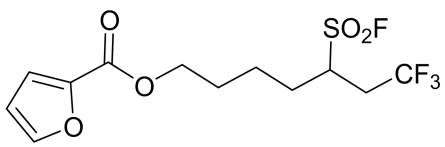


1-(3,4-dimethoxyphenyl)-4,4,4-trifluorobutane-2-sulfonyl fluoride (3k): Obtained as a yellow liquid in 58% yield (57.3 mg) by silica gel flash column chromatography eluted

with PE/EA = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.84 (d, *J* = 8.2 Hz, 1H), 6.78 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.73 (d, *J* = 1.8 Hz, 1H), 3.87 (s, 6H), 3.92 – 3.85 (m, 1H), 3.40 (dd, *J* = 14.7, 5.7 Hz, 1H), 3.14 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.91 – 2.75 (m, 1H), 2.70 – 2.46 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 49.8 (d, *J* = 3.9 Hz, 1F), -63.8 (td, *J* = 10.1, 4.4 Hz, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.5, 149.0, 125.9, 124.9 (q, *J* = 277.3 Hz), 122.0, 112.4, 111.6, 58.3 (dd, *J* = 12.8, 2.1 Hz), 56.1, 56.0, 34.9, 32.9 (q, *J* = 31.4 Hz). **HRMS** (ESI): calcd for $[M + H]^+$ 331.0622, found 331.0624. **IR** (film) ν_{max}: 3115, 3083, 2958, 2874, 1725, 1609, 1530, 1466, 1410, 1351, 1278, 1205, 1152, 1027 cm^{-1}.

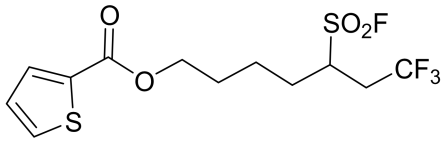


5,5,5-trifluoro-3-(fluorosulfonyl)pentyl 2-(4-isobutylphenyl)propanoate (3l): Obtained as a yellow liquid in 69% yield (85.7 mg) by silica gel flash column chromatography eluted with PE/EA = 15:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.37 – 4.20 (m, 2H), 3.71 (q, *J* = 7.1 Hz, 1H), 3.66 – 3.52 (m, 1H), 2.95 – 2.71 (m, 1H), 2.58 – 2.48 (m, 1H), 2.45 (d, *J* = 7.1 Hz, 2H), 2.43 – 2.33 (m, 1H), 2.28 – 2.17 (m, 1H), 1.92 – 1.79 (m, 1H), 1.51 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 47.4 (d, *J* = 81.3 Hz, 1F), -63.9 – -64.0 (m, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.3 (d, *J* = 3.0 Hz), 141.0, 137.3 (d, *J* = 5.5 Hz), 129.6, 127.2 (d, *J* = 1.1 Hz), 124.8 (qd, *J* = 277.4, 2.9 Hz), 60.1 (d, *J* = 8.1 Hz), 53.8 (ddd, *J* = 28.4, 16.2, 2.6 Hz), 45.2, 45.1, 34.0 (qd, *J* = 31.1, 9.8 Hz), 30.3, 28.9 (d, *J* = 8.3 Hz), 22.4, 18.1 (d, *J* = 6.9 Hz). **HRMS** (EI): calcd for $C_{18}H_{24}O_4F_4S$ (M^+) 412.1331, found 412.1336. **IR** (film) ν_{max}: 2958, 2871, 1740, 1513, 1465, 1415, 1320, 1262, 1206, 1158, 1096 cm^{-1}.

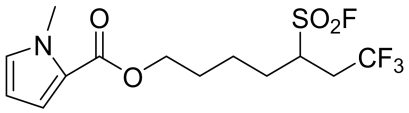


7,7,7-trifluoro-5-(fluorosulfonyl)heptyl furan-2-carboxylate (3m): Obtained as a

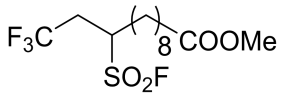
yellow liquid in 53% yield (54.9 mg) by silica gel flash column chromatography eluted with PE/EA = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (t, *J* = 12.0 Hz, 1H), 7.17 (d, *J* = 3.5 Hz, 1H), 6.51 (dd, *J* = 3.2, 1.5 Hz, 1H), 4.32 (t, *J*= 6.3 Hz, 2H), 3.72 – 3.63 (m, 1H), 3.03 – 2.85 (m, 1H), 2.67 – 2.51 (m, 1H), 2.24 – 1.97 (m, 2H), 1.87 – 1.76 (m, 2H), 1.75 – 1.62 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.2 (s, 1F), -64.1 (td, *J* = 10.2, 2.1 Hz, 3F). **GC-MS** (EI): *m/z* = 346.1 (M^+). The analytical data are consistent with literature values.[1]



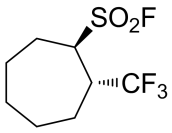
7,7,7-trifluoro-5-(fluorosulfonyl)heptyl thiophene-2-carboxylate (3n): Obtained as a yellow liquid in 53% yield (58 mg) by silica gel flash column chromatography eluted with PE/EA = 20:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 3.1 Hz, 1H), 7.56 (d, *J* = 4.6 Hz, 1H), 7.10 (t, *J* = 4.2 Hz, 1H), 4.32 (t, *J* = 6.1 Hz, 2H), 3.68 (s, 1H), 3.03 – 2.84 (m, 1H), 2.68 – 2.50 (m, 1H), 2.24 – 1.99 (m, 2H), 1.88 – 1.79 (m, 2H), 1.76 – 1.63 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.2 (s, 1F), -64.1 (t, *J* = 9.7 Hz, 3F). **GC-MS** (EI): *m/z* = 362.2 (M^+). The analytical data are consistent with literature values.[1]



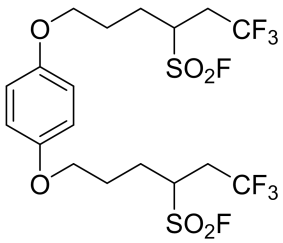
7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 1-methyl-1H-pyrrole-2-carboxylate (3o): Obtained as a yellow liquid in 45% yield (48.5 mg) by silica gel flash column chromatography eluted with PE/EA = 18:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.93 (dd, *J* = 3.9, 1.8 Hz, 1H), 6.79 (t, *J* = 1.8 Hz, 1H), 6.12 (dd, *J* = 3.9, 2.5 Hz, 1H), 4.25 (t, *J* = 6.1 Hz, 2H), 3.92 (s, 3H), 3.69 – 3.63 (m, 1H), 3.00 – 2.88(m, 1H), 2.66 – 2.52 (m, 1H), 2.23 – 1.97 (m, 2H), 1.84 – 1.66 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.3 (s, 1F), -64.1 (td, *J* = 10.2, 2.0 Hz, 3F). **GC-MS** (EI): *m/z* = 359.2 (M^+). The analytical data are consistent with literature values.[1]



Methyl 12,12,12-trifluoro-10-(fluorosulfonyl)dodecanoate (3p): Obtained as a yellow liquid in 59% yield (62.2 mg) by silica gel flash column chromatography eluted with PE/EA = 30:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): 3.65 (d, *J* = 0.6 Hz, 4H), 3.02 – 2.77 (m, 1H), 2.67 – 2.46 (m, 1H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.12 – 1.87 (m, 2H), 1.66 – 1.56 (m, 2H), 1.56 – 1.46 (m, 2H), 1.29 (s, 8H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.1 (s, 1F), -64.0 (td, *J* = 10.0, 2.2 Hz, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.3, 125.0 (q, *J* = 277.2 Hz), 57.1 (dd, *J* = 14.2, 2.6 Hz), 51.6, 34.2, 33.9 (q, *J* = 31.0 Hz), 29.5, 29.3, 29.2, 29.1, 29.0, 25.7, 25.0. **HRMS** (ESI): calcd for $[M + H]^+$ 351.1248, found 351.1249. **IR** (film) ν_{max}: 2934, 2859, 1737, 1438, 1411, 1263, 1205, 1156, 1090 cm^{-1}. The analytical data are consistent with literature values.[1]

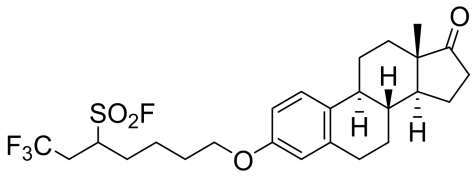


2-(trifluoromethyl)cycloheptane-1-sulfonyl fluoride (3q): ^{19}F NMR spectroscopic analysis showed that 50% yield of target product was detected. **Crude ^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.97 – 3.90 (m, 1H), 3.25 – 3.14 (m, 1H), 2.41 – 2.25 (m, 1H), 2.26 – 2.13 (m, 1H), 2.14 – 2.01 (m, 1H), 1.94 – 1.77 (m, 3H), 1.67 (m, 3H), 1.58 – 1.45 (m, 1H). **Crude ^{19}F NMR** (376 MHz, $CDCl_3$): δ 51.0 (t, *J* = 12.0 Hz, 1F), -70.3 (dd, *J* = 9.1, 6.6 Hz, 3F). **GC-MS** (EI): *m/z* = 247.0 (M^+). The analytical data are consistent with literature values.[5]

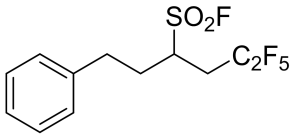


6,6'-(1,4-phenylenebis(oxy))bis(1,1,1-trifluorohexane-3-sulfonyl fluoride) (3r): Obtained as a white solid in 54% yield (45.7 mg) by silica gel flash column

chromatography eluted with PE/EA = 9:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.82 (s, 4H), 3.97 (t, *J* = 5.7 Hz, 4H), 3.84 – 3.75 (m, 2H), 3.04 – 2.87 (m, 2H), 2.69 – 2.51 (m, 2H), 2.37 – 2.16 (m, 4H), 2.09 – 1.97 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.0 (s, 2F), -64.0 (td, *J* = 10.2. 1.8 Hz, 6F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.1, 125.0 (q, *J* = 277.3 Hz), 115.6, 67.3, 56.8 (dq, *J* = 14.7, 2.5 Hz), 34.0 (q, *J* = 31.1 Hz), 26.8, 25.7. **HRMS** (ESI): calcd for $[M + NH_4]^+$ 568.1068, found 568.1064. **IR** (film) ν_{max}: 2957, 1509, 1474, 1410, 1263, 1232, 1157, 1062 cm^{-2}. m.p.: 58 – 60 ℃.

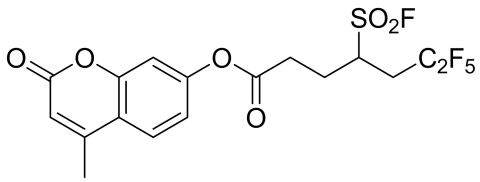


1,1,1-trifluoro-7-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)heptane-3-sulfonyl fluoride (3s): Obtained as a white solid in 60% yield (89.2 mg) by silica gel flash column chromatography eluted with PE/EA = 8:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.64 (d, *J* = 2.2 Hz, 1H), 3.97 (t, *J* = 5.8 Hz, 2H), 3.69 (s, 1H), 3.02 – 2.81 (m, 3H), 2.67 – 2.57 (m, 1H), 2.57 – 2.46 (m, 1H), 2.40 (d, *J* = 9.8 Hz, 1H), 2.29 – 2.13 (m, 3H), 2.12 – 1.91 (m, 4H), 1.89 – 1.70 (m, 4H), 1.70 – 1.35 (m, 6H), 0.91 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.3 (s, 1F), -64.1 (td, *J* = 10.2, 2.2 Hz, 3F). **GC-MS** (EI): *m/z* = 504.0 (M^+). The analytical data are consistent with literature values.[1]

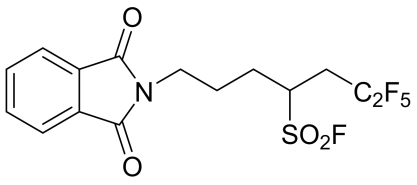


5,5,6,6,6-pentafluoro-1-phenylhexane-3-sulfonyl fluoride (3t): Obtained as a colorless liquid in 64% yield (43 mg) by silica gel flash column chromatography eluted with PE/EA = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.0 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 3.84 – 3.67 (m, 1H), 2.95 – 2.77 (m, 3H), 2.63 – 2.38 (m, 2H), 2.37 – 2.24 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.1 (s, 1F), -85.7 (s,

3F), -115.7 (ddd, J = 265.9, 29.4, 7.2 Hz, 1F), -117.8 (ddt, J = 265.8, 27.2, 6.6 Hz, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.9, 129.0, 128.5, 127.1, 118.0 (qt, J = 255.8, 38.6 Hz), 114.5 (tq, J = 283.0, 35.0 Hz), 55.3 (d, J = 14.8 Hz), 32.0, 31.9, 30.8 (t, J = 21.5 Hz). **HRMS** (ESI): calcd for $[M + NH_4]^+$ 352.0800, found 352.0800. **IR** (film) ν_{max}: 2936, 1498, 1414, 1345, 1201, 1122, 1075, 1046 cm^{-1}.

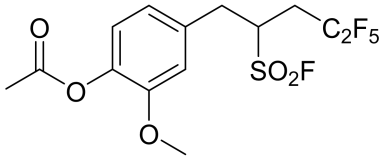


4-methyl-2-oxo-2H-chromen-7-yl 6,6,7,7,7-pentafluoro-4-(fluorosulfonyl)heptanoate (3u): Obtained as a white solid in 68% yield (94 mg) by silica gel flash column chromatography eluted with PE/EA = 4:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.7 Hz, 1H), 7.12 (d, J = 1.9 Hz, 1H), 7.07 (dd, J = 8.6, 2.0 Hz, 1H), 6.27 (s, 1H), 4.13 – 3.98 (m, 1H), 3.08 – 2.84 (m, 3H), 2.60 – 2.47 (m, 3H), 2.43 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 47.7 (s, 1F), -85.5 (s, 3F), -115.5 (ddd, J = 266.1, 29.7, 6.8 Hz, 1F), -117.9 (ddt, J = 266.5, 28.7, 7.0 Hz, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.5, 160.3, 154.5, 152.8, 151.8, 125.6, 118.3, 118.1 (qt, J= 283.0, 35.0 Hz), 117.9, 115.0, 114.5 (tq, J= 229.0, 26.0 Hz), 110.5, 55.0 (dd, J = 15.9, 2.4 Hz), 31.3 (t, J = 21.8 Hz), 30.6, 25.5 (d, J = 2.3 Hz), 18.7. **HRMS** (ESI): calcd for $[M + H]^+$ 461.0488, found 461.0487. **IR** (film) ν_{max}: 2971, 1754, 1733, 1614, 1412, 1326, 1303, 1195, 1160, 1122, 1054, 1018 cm^{-1}. m. p.: 81 - 83 ℃。

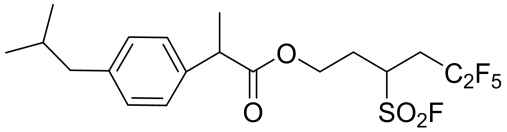


7-(1,3-dioxoisoindolin-2-yl)-1,1,1,2,2-pentafluoroheptane-4-sulfonyl fluoride (3v): Obtained as a white solid in 80% yield (101 mg) by silica gel flash column chromatography eluted with PE/DCM = 1:2 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (dd, J = 5.3, 3.1 Hz, 2H), 7.72 (dd, J = 5.2, 3.1 Hz, 2H), 3.84 (s, 1H), 3.75 (t, J = 6.5 Hz, 2H),

2.97 – 2.75 (m, 1H), 2.57 – 2.36 (m, 1H), 2.27 – 2.12 (m, 1H), 2.10 – 1.91 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 48.1 (d, *J* = 3.8 Hz, 1F), -85.6 (s, 3F), -116.0 (ddd, *J* = 265.8, 29.5, 7.3 Hz, 1F), -117.8 (ddt, *J* = 265.9, 27.3, 6.9 Hz, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.2, 134.1, 131.8, 122.9, 118.4 (qt, *J* = 283.0, 35.0 Hz), 114.0 (tq, *J* = 253.0, 38.0 Hz), 55.3 (dd, *J* = 15.1, 2.0 Hz), 36.7, 30.3 (t, *J* = 21.6 Hz), 27.3 (d, *J* = 1.8 Hz), 24.5. **HRMS** (ESI): calcd for $[M + H]^+$ 418.0542, found 418.0542. **IR** (film) ν_{max}: 2939, 1716, 1617, 1466, 1400, 1337, 1200, 1111, 1059 cm^{-1}. m. p.: 145 - 147 ℃。

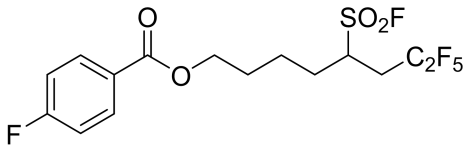


2-methoxy-4-(4,4,5,5,5-pentafluoro-2-(fluorosulfonyl)pentyl)phenyl acetate (3w): Obtained as a white solid in 83% yield (102 mg) by silica gel flash column chromatography eluted with PE/EA = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.02 (d, *J* = 7.9 Hz, 1H), 6.89 – 6.75 (m, 2H), 4.03 (s, 1H), 3.81 (s, 3H), 3.43 (dd, *J* = 14.8, 6.1 Hz, 1H), 3.24 (dd, *J* = 14.8, 6.5 Hz, 1H), 2.91 – 2.71 (m, 1H), 2.65 – 2.45 (m, 1H), 2.30 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 49.3 (s, 1F), -85.7 (s, 3F), -116.3 (dddd, *J* = 22.9, 19.3, 11.8, 4.8 Hz, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.0, 152.6, 139.7, 132.6, 123.4, 121.8, 117.4 (qt, *J* = 284.0, 35 Hz), 113.9 (tq, *J* = 265.0, 38.0 Hz), 113.6, 57.1 (d, *J* = 13.4 Hz), 56.0, 35.6, 29.7 (t, *J* = 21.6 Hz), 20.7. **HRMS** (ESI): calcd for $[M + H]^+$ 409.0539, found 409.0538. **IR** (film) ν_{max}: 3411, 2943, 1763, 1713, 1608, 1516, 1411, 1367, 1285, 1204, 1157, 1125, 1036 cm^{-1}. m. p.: 68 – 71 ℃。

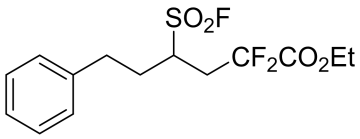


5,5,6,6,6-pentafluoro-3-(fluorosulfonyl)hexyl 2-(4-isobutylphenyl)propanoate (3x): Obtained as a colorless liquid in 55% yield (76.2 mg) by silica gel flash column chromatography eluted with PE/EA = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 6.7 Hz, 2H), 4.38 – 4.19 (m, 2H), 3.71 (dd, *J* = 14.1, 7.0 Hz,

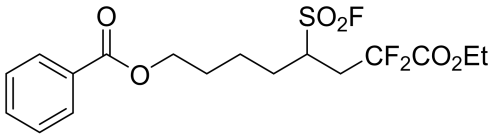
2H), 2.90 – 2.69 (m, 1H), 2.52 – 2.36 (m, 4H), 2.32 – 2.19 (m, 1H), 1.90 – 1.78 (m, 1H), 1.50 (d, J = 7.2 Hz, 3H), 0.90 (d, J = 6.6 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 47.1 (d, J = 35.8 Hz, 1F), -85.64 (s, 3F), -116.02 (ddd, J = 266.0, 29.1, 7.0 Hz, 1F), -117.82 (dddd, J = 266.0, 27.1, 14.1, 8.0 Hz, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.3 (d, J = 2.7 Hz), 141.1, 137.3 (d, J = 9.5 Hz), 129.6 (d, J = 2.2 Hz), 127.2, 118.9 (qt, J = 416.8, 34.0 Hz), 114.1 (tq, J = 257.5, 23.7 Hz), 60.0 (d, J = 11.0 Hz), 52.8 (ddd, J = 31.5, 16.3, 2.1 Hz), 45.2, 45.1, 30.8 (td, J = 21.6, 8.1 Hz), 30.3, 29.6 (dd, J = 7.7, 1.8 Hz), 22.4, 18.2 (d, J = 5.9 Hz). **HRMS** (EI): calcd for $C_{19}H_{24}O_4F_6S$ (M^+) 462.1300, found 462.1298. **IR** (film) ν_{max}: 2959, 1740, 1513, 1465, 1417, 1343, 1201, 1070 cm^{-1}.



7,7,8,8,8-pentafluoro-5-(fluorosulfonyl)octyl 4-fluorobenzoate (3y): Obtained as a colorless liquid in 83% yield (106 mg) by silica gel flash column chromatography eluted with PE/EA = 15:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (dd, J = 8.4, 5.6 Hz, 2H), 7.09 (t, J = 8.6 Hz, 2H), 4.34 (t, J = 6.2 Hz, 2H), 3.79 (d, J = 2.8 Hz, 1H), 2.96 – 2.75 (m, 1H), 2.59 – 2.40 (m, 1H), 2.30 – 2.15 (m, 1H), 2.14 – 2.00 (m, 1H), 1.94 – 1.77 (m, 2H), 1.77 – 1.67 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 47.8 (d, J = 2.9 Hz, 1F), -85.7 (s, 3F), -105.0 – -107.1 (m, 1F), -116.1 (ddd, J = 265.8, 29.4, 7.3 Hz, 1F), -117.9 (ddt, J = 265.8, 27.3, 6.9 Hz, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.9 (d, J = 253.9 Hz), 165.7, 132.2 (d, J = 9.3 Hz), 126.5 (d, J = 3.0 Hz), 118.6 (qt, J = 285.5, 35.3 Hz), 115.7 (d, J = 22.1 Hz), 114.3 (tq, J = 254.9, 38.6 Hz), 64.1, 55.8 (dd, J = 14.7, 2.0 Hz), 30.5(t, J = 21.6 Hz), 29.8 (d, J = 1.8 Hz), 28.3, 22.5. **HRMS** (EI): calcd for $C_{15}H_{15}O_4F_7S$ (M^+) 424.0579, found 424.0574. **IR** (film) ν_{max}: 2962, 1717, 1605, 1508, 1413, 1278, 1200, 1119, 1039 cm^{-1}.



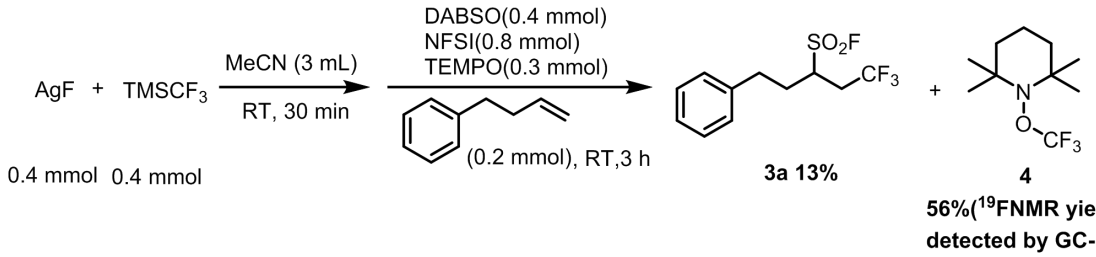
ethyl 2,2-difluoro-4-(fluorosulfonyl)-6-phenylhexanoate (3aa): According to the general procedure, AgF (76.2 mg, 0.6 mmol) and $TMSCF_2COOEt$ (117.8 mg, 0.6 mmol) in freshly-distilled CH_3CN (4.5 mL) were stirred under Ar atmosphere at 0 °C for 15 minutes to generate the $AgCF_2COOEt$ species. The following procedure was similar to the general procedure. The desired product **3aa** was obtained as a colorless liquid in 65% yield (66.1 mg) by silica gel flash column chromatography eluted with PE/EA = 55:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.84 – 3.68 (m, 1H), 3.02 – 2.89 (m, 1H), 2.90 – 2.82 (m, 2H), 2.63 – 2.47 (m, 1H), 2.47 – 2.34 (m, 1H), 2.33 – 2.20 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 47.5 (s, 1F), -103.0 (ddd, *J* = 266.1, 22.4, 9.4 Hz, 1F), -106.1 (dddd, *J* = 266.0, 21.6, 13.1, 3.7 Hz, 1F). **GC-MS** (EI): *m/z* = 338.1 (M^+). The analytical data are consistent with literature values.[7]



[8-]**ethoxy-7,7-difluoro-5-(fluorosulfonyl)-8-oxooctyl benzoate (3bb):** According to the procedure given for **3aa**, **3bb** was obtained as a colorless liquid in 62% yield (76.3 mg) by silica gel flash column chromatography eluted with PE/EA = 12:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.42 – 4.29 (m, 4H), 3.81 – 3.71 (m, 1H), 3.03 – 2.81 (m, 1H), 2.62 – 2.42 (m, 1H), 2.24 – 2.13 (m, 1H), 2.12 – 2.00 (m, 1H), 1.90 – 1.79 (m, 2H), 1.78 – 1.67 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ 47.30 (s, 1F), -103.50 (ddd, *J* = 265.1, 22.5, 9.4 Hz, 1F), -106.41 (dddd, J = 265.1, 21.7, 13.1, 3.8 Hz, 1F). **GC-MS** (EI): *m/z* = 410.0 (M^+). The analytical data are consistent with literature values.[7]

5. Control experiments

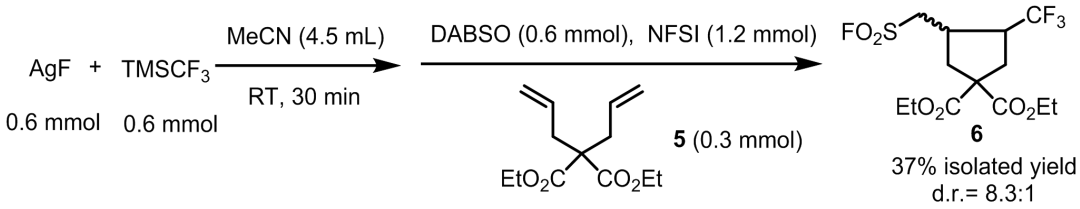
(a) Inhibition experiments



To an oven-dried sealed tube equipped with a magnetic stir bar were added AgF (50.8 mg, 0.4 mmol), freshly-distilled CH_3CN (3 mL) and $TMSCF_3$ (59 μL, 0.4 mmol) under argon atmosphere. The reaction mixture was stirred at room temperature for 30 minutes. Then 4-phenyl-1-butene (26.4 mg, 0.2 mmol), TEMPO (46.9 mg, 0.3 mmol), NFSI (252 mg, 0.8 mmol) and DABSO (96 mg, 0.4 mmol) were added to the sealed tube under argon atmosphere. The mixture was further stirred at room temperature for 3 hours. 1-methoxy-4-(trifluoromethoxy)benzene (30.2 uL, 0.2 mmol) was added as an internal standard. The crude reaction mixture was then analyzed by ^{19}F NMR spectroscopy and GC-MS. ^{19}F NMR spectroscopic analysis showed 56% yield TEMPO-CF_3 adducts and 13% yield of the desired product **3a** was detected.

TEMPO-CF_3 (4): GC-MS (EI): *m/z* = 225.1 (M^+). **^{19}F NMR** (376 MHz, MeCN, unlocked): δ -56.0 (s, 3F). The analytical data are consistent with literature values.[8]

(b) Radical clock experiment



To an oven-dried sealed tube equipped with a magnetic stir bar were added AgF (76.2 mg, 0.6 mmol), freshly-distilled CH_3CN (4.5 mL) and $TMSCF_3$ (85.2 mg, 0.6 mmol) under argon atmosphere. The reaction mixture was stirred at room temperature for 30 minutes. Then diethyl 2,2-diallylmalonate (72.1 mg, 0.3 mmol), NFSI (378 mg, 1.2 mmol) and DABSO (144 mg, 0.6 mmol) were added to the sealed tube under argon

atmosphere. The mixture was further stirred at room temperature for 3 hours. 1-methoxy-4-(trifluoromethoxy)benzene (45.3 uL, 0.3 mmol) was added into the reaction mixture as an internal standard and the yield of the desired product was measured by ^{19}F NMR before working up. The resulting mixture was filtered through a pad of celite. After removal of the solvent under reduced pressure with a rotary evaporator, the crude product was purified by silica gel chromatography to give the desired product **6**.

diethyl-3-((fluorosulfonyl)methyl)-4-(trifluoromethyl)cyclopentane-1,1-dicarboxylate (6): ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.25 – 4.14 (m, 4H), 3.50 – 3.29 (m, 2H), 2.85 – 2.76 (m, 1H), 2.62 – 2.48 (m, 4H), 2.19 – 2.10 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ57.7 (s, 1F), 56.7 (s, 1F), -64.4 (t, *J* = 10.5 Hz, 3F), -64.5 (t, *J* = 10.7 Hz, 3F). **GC-MS** (EI): *m/z* = 365.1 (M^+). The analytical data are consistent with literature values.[1]

6. Reference:

[1] Y. Liu, H. Wu, Y. Guo, J.-C. Xiao, Q.-Y. Chen and C. Liu, *Angew. Chem. Int. Ed.*, 2017, **56,** 15432.

[2] J. Xu, Y. Fu, D. F. Luo, Y. Y. Jiang, B. Xiao, Z. J. Liu, T. J. Gong and L. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 15300.

[3] M. Huang, L. Li, Z.-G. Zhao, Q.-Y. Chen and Y. Guo, *Synthesis*, 2015, **47,** 3891.

[4] T. Yang, L. Lu and Q. Shen, *Chem. Commun.*, 2015, **51,** 5479.

[5] X. Wu, L. Chu and F.-L. Qing, *Angew. Chem. Int. Ed.*, 2013, **52,** 2198.

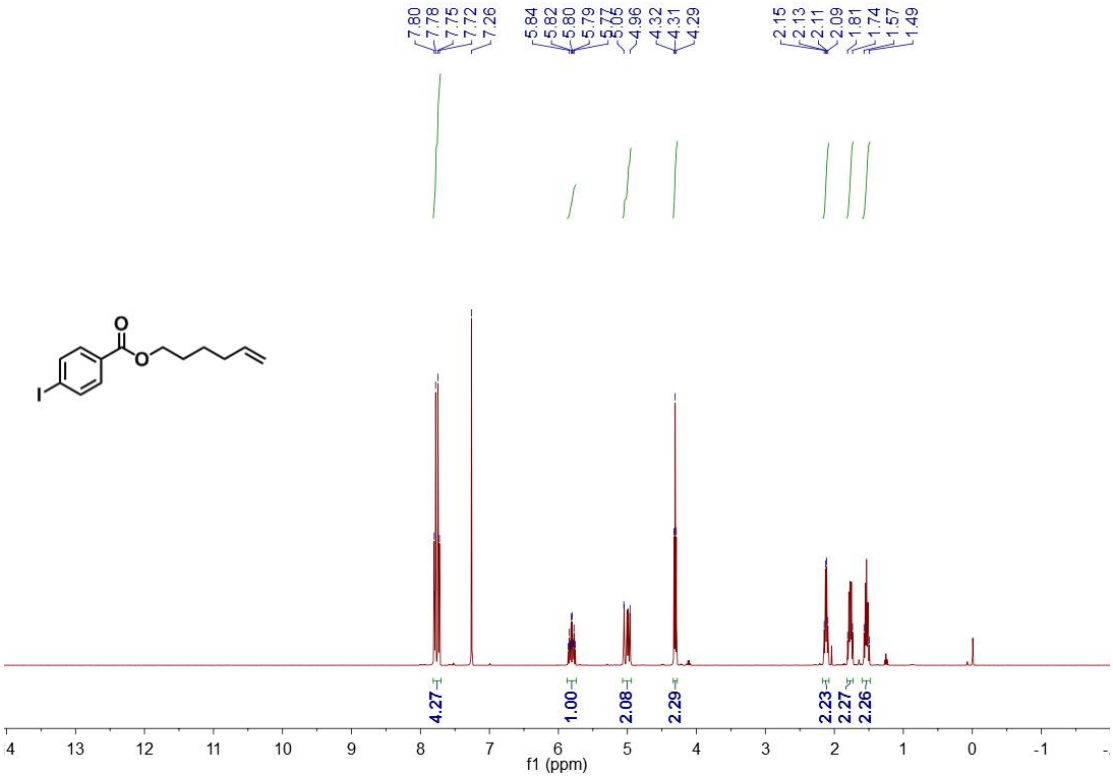
[6] L. Zhu, D. R. Mootoo, *J. Org. Chem.*, 2004, **69,** 3154.

[7] Y. Liu, Q. Lin, Z. Xiao, C.-G. Zheng, Y. Guo, Q.-Y. Chen and C. Liu, *Chem. Eur. J.*, 2019, **25**, 10.1002/chem.201805526.

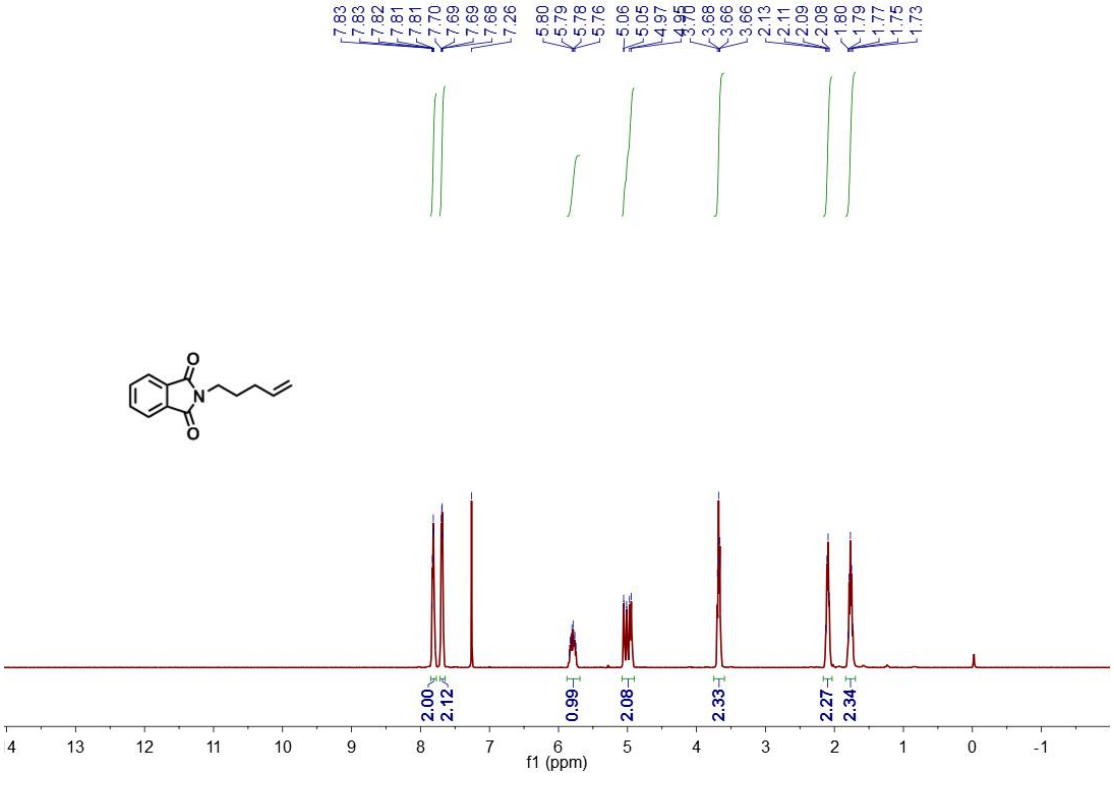
[8] X. Wang, Y. Ye, S. Zhang, J. Feng, Y. Xu, Y. Zhang and J. Wang, *J. Am. Chem. Soc.*, 2011, **133,** 16410.

7. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

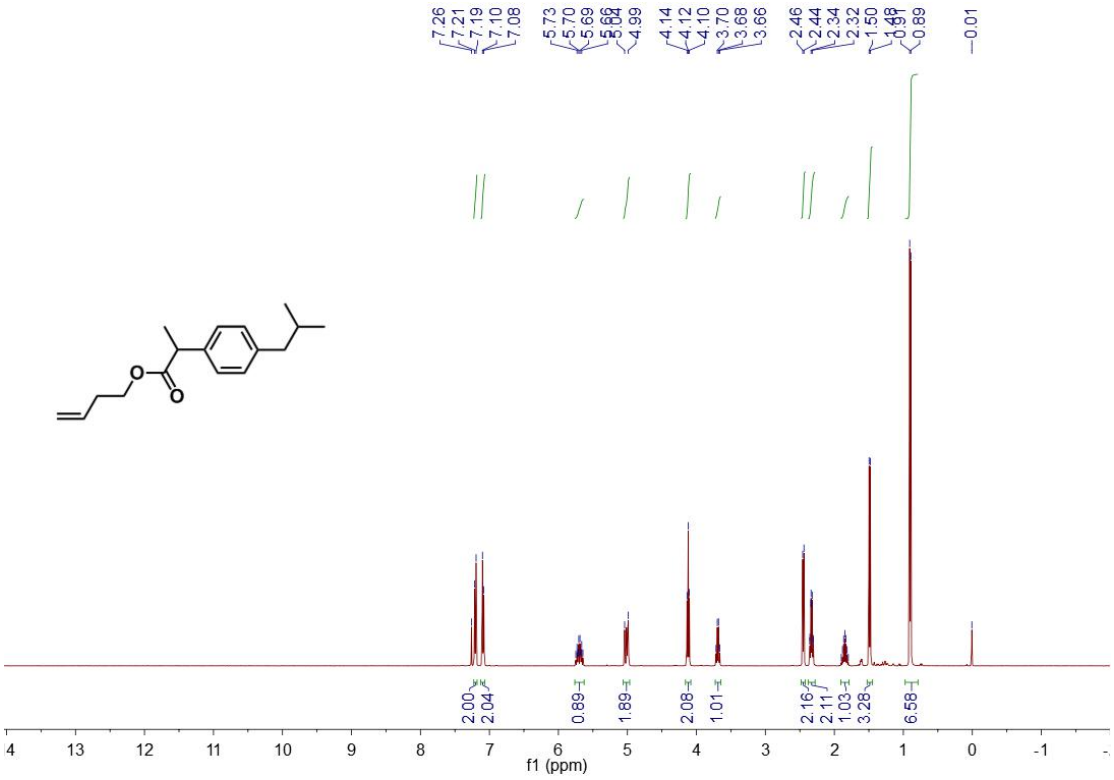
^{1}H NMR spectrum of hex-5-en-1-yl 4-iodobenzoate (1f)



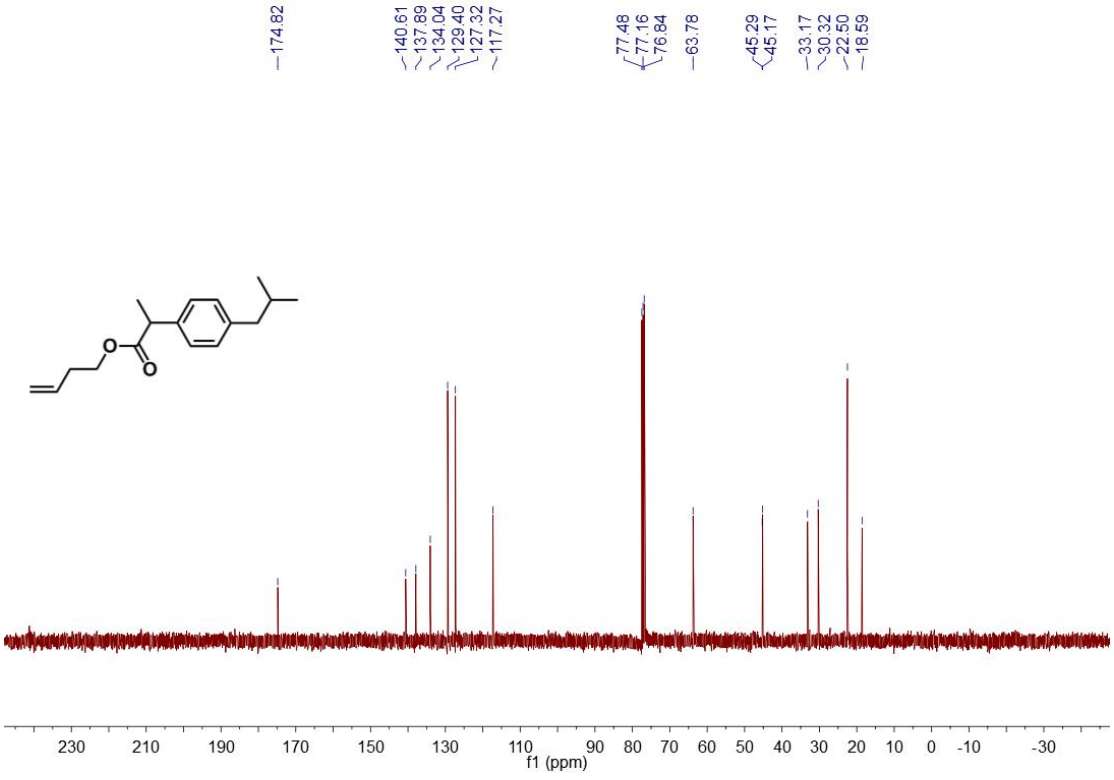
^{1}H NMR spectrum of 2-(pent-4-en-1-yl)isoindoline-1,3-dione (1j)



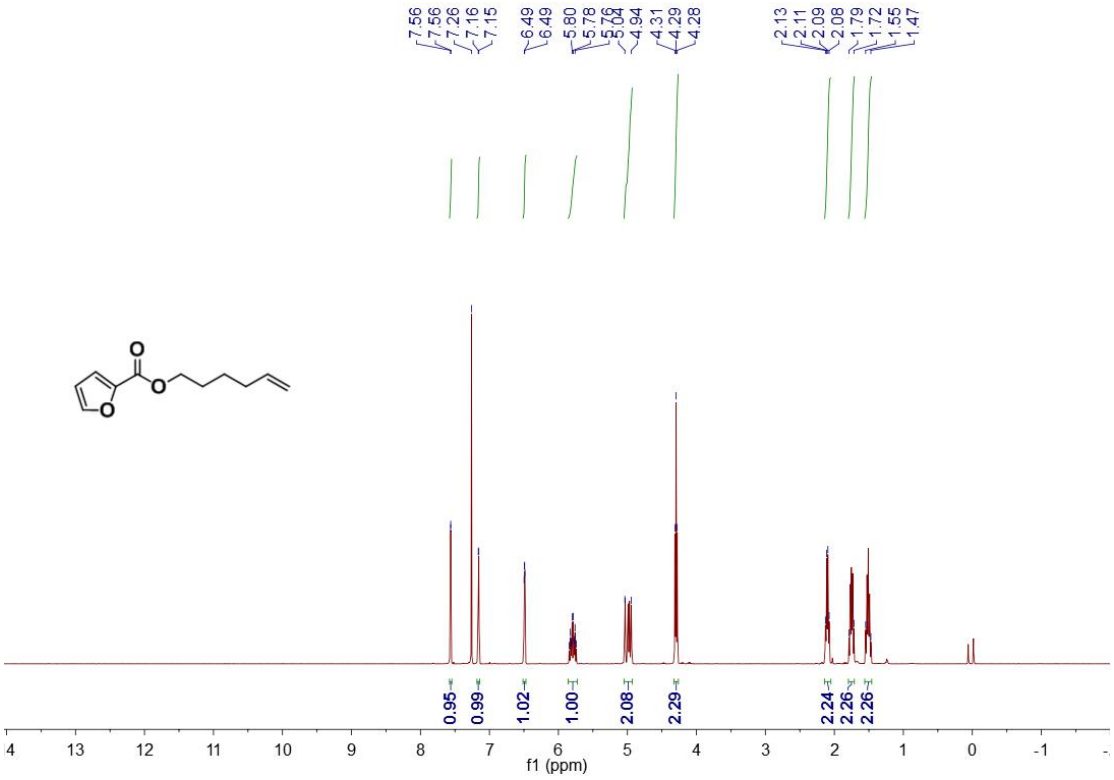
^{1}H NMR spectrum of but-3-en-1-yl 2-(4-isobutylphenyl)propanoate(1l)



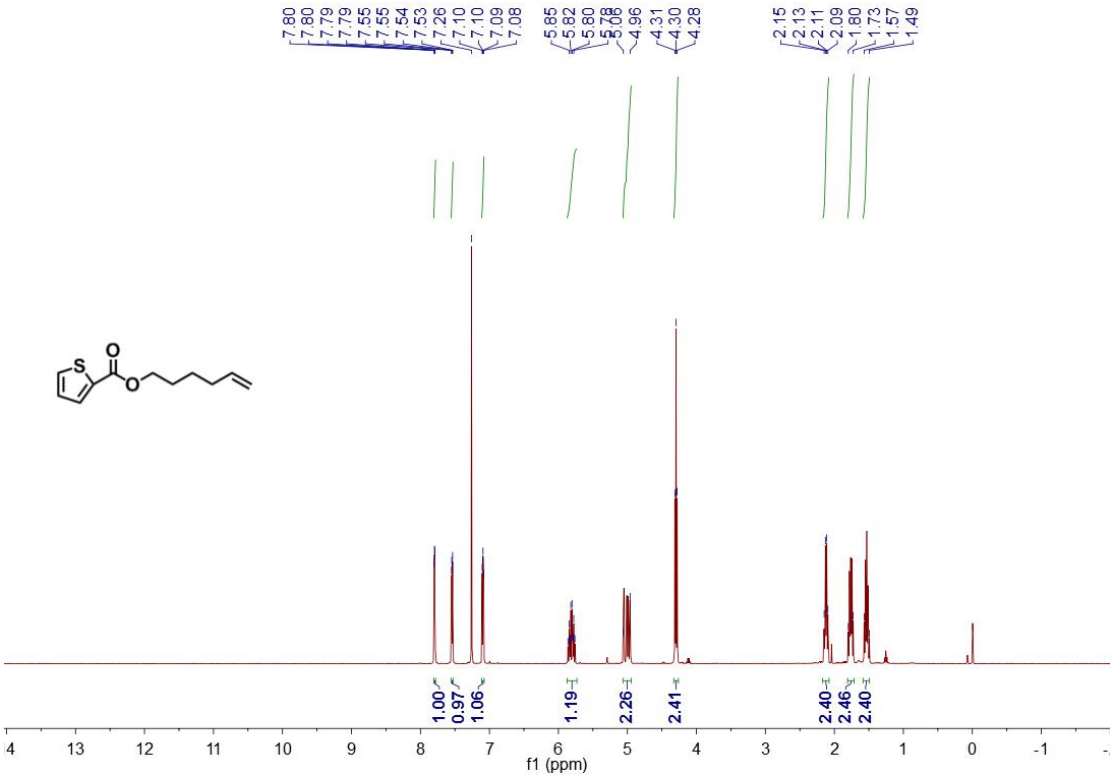
^{13}C NMR spectrum of but-3-en-1-yl 2-(4-isobutylphenyl)propanoate(1l)



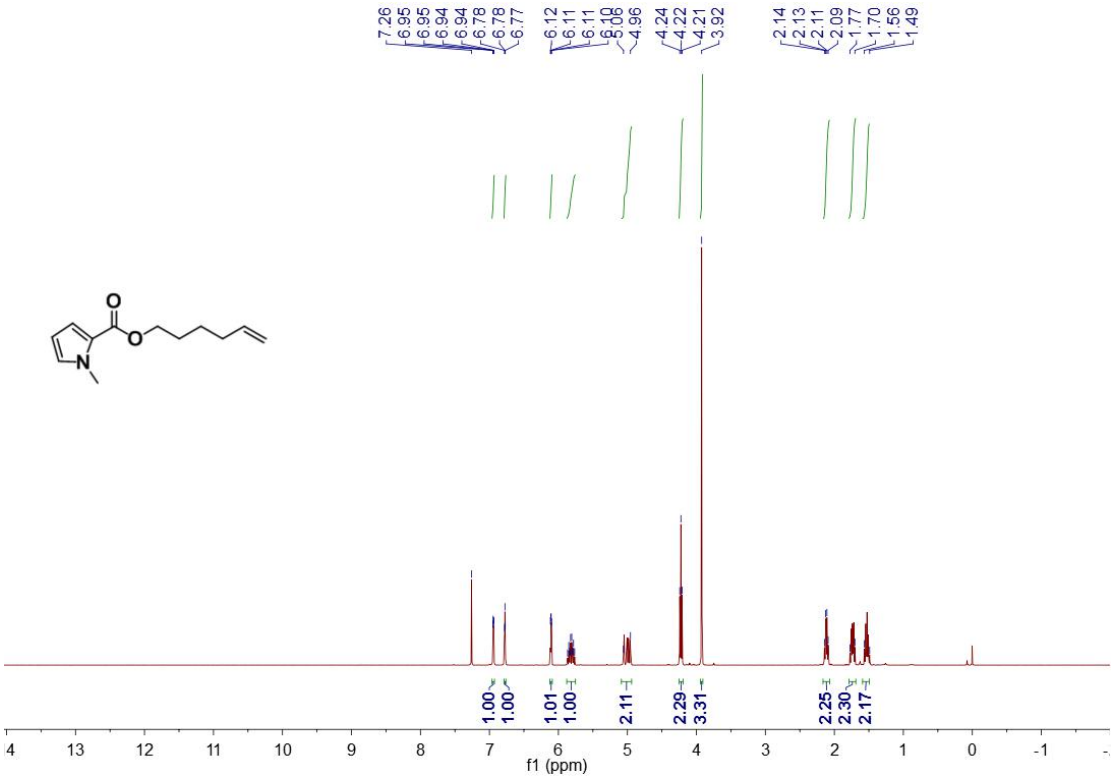
^{1}H NMR spectrum of hex-5-en-1-yl furan-2-carboxylate (1m)



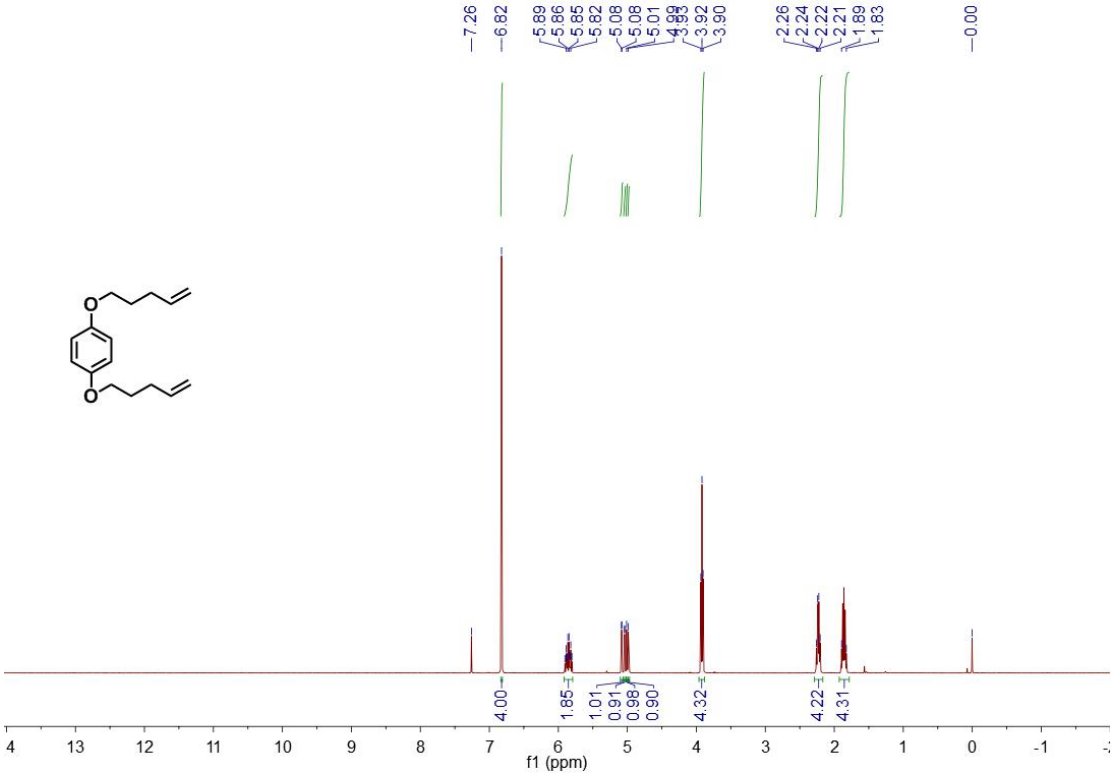
^{1}H NMR spectrum of hex-5-en-1-yl thiophene-2-carboxylate (1n)



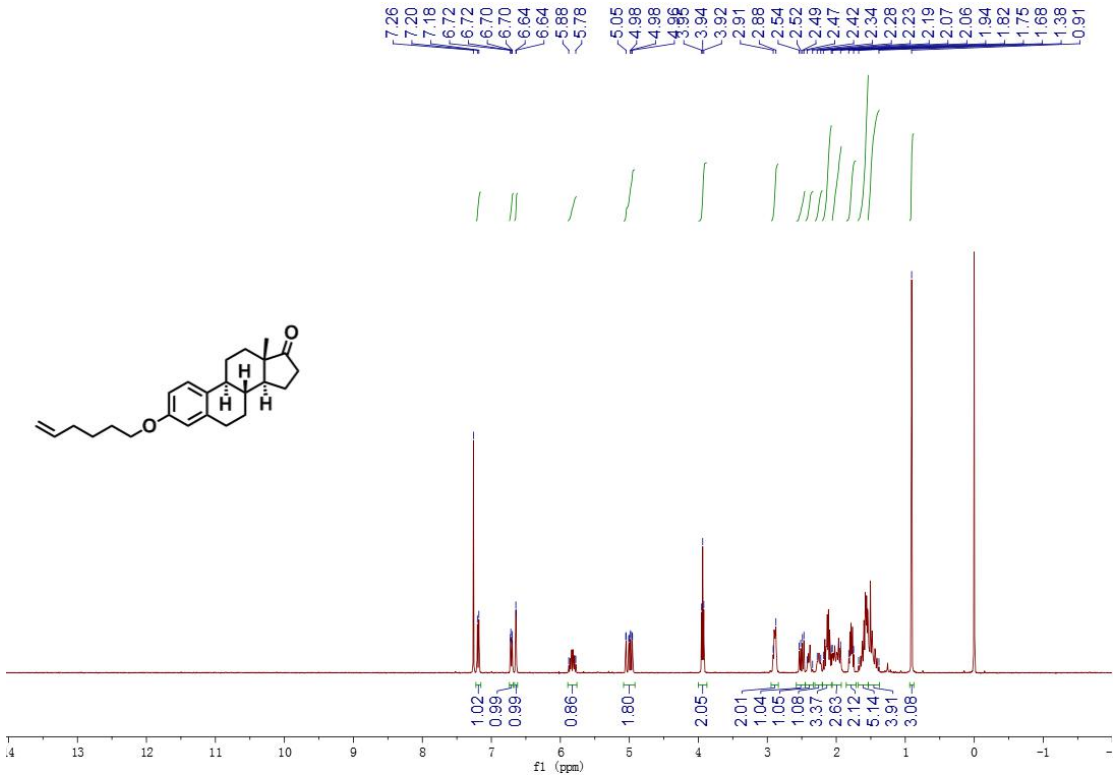
^{1}H NMR spectrum of hex-5-en-1-yl 1-methyl-1H-pyrrole-2-carboxylate (1o)



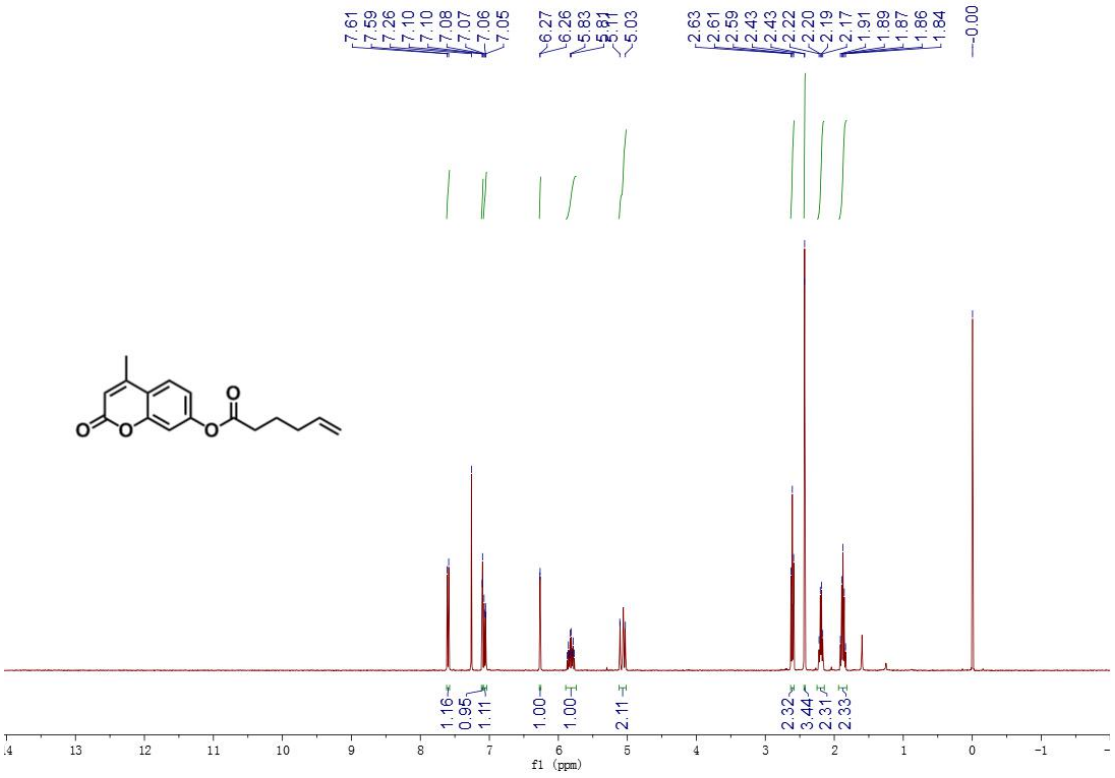
^{1}H NMR spectrum of 1,4-bis(pent-4-en-1-yloxy)benzene(1r)



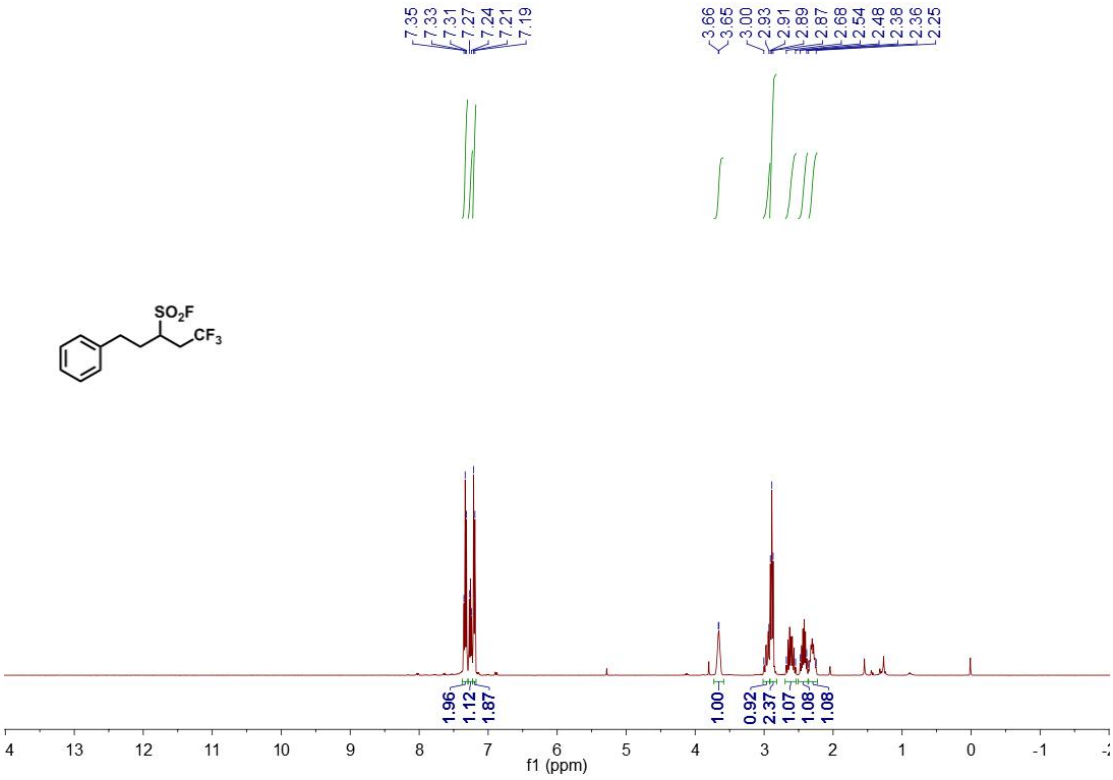
^{1}H NMR spectrum of (8R,9S,13S,14S)-3-(hex-5-en-1-yloxy)-13-Methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one(1s)



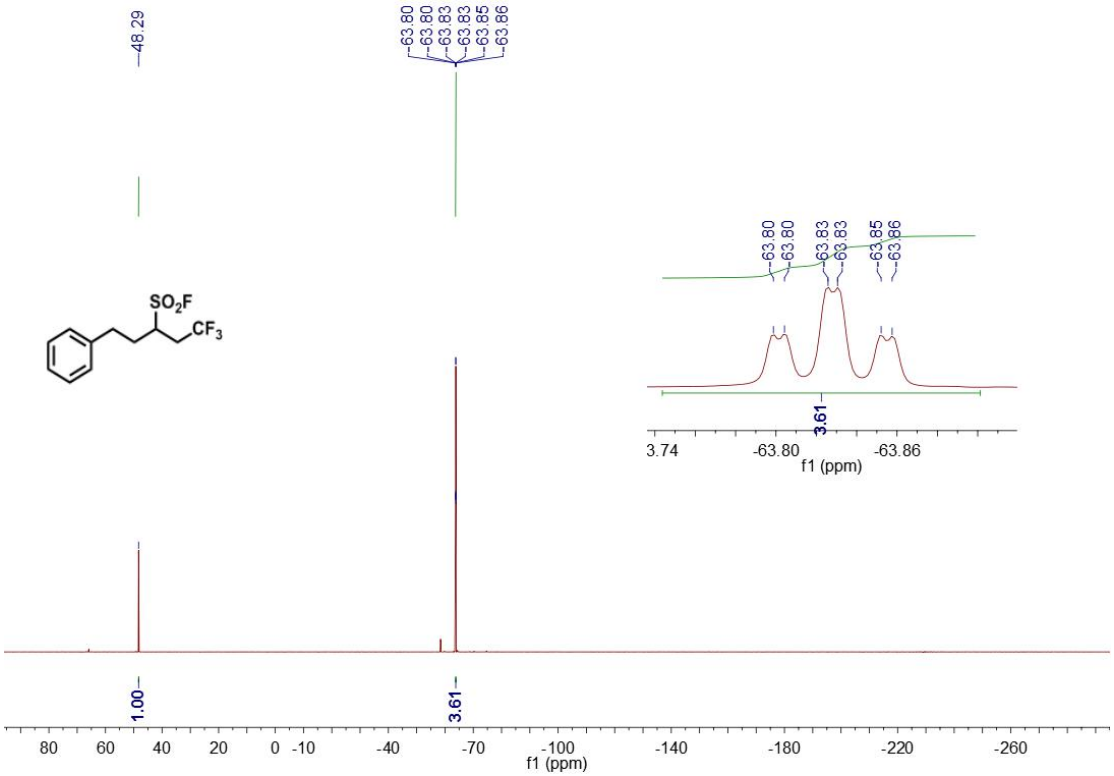
^{1}H NMR spectrum of 4-methyl-2-oxo-2H-chromen-7-yl hex-5-enoate(1u)



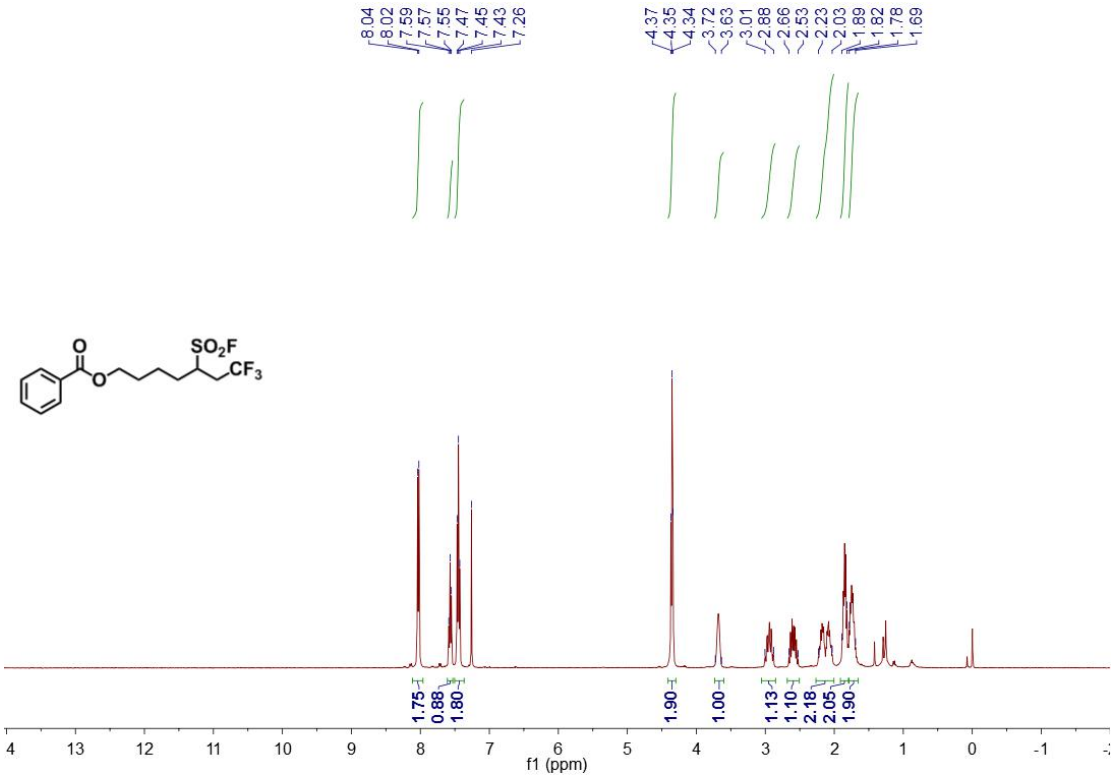
^{1}H NMR spectrum of 1,1,1-trifluoro-5-phenylpentane-3-sulfonyl fluoride (3a)



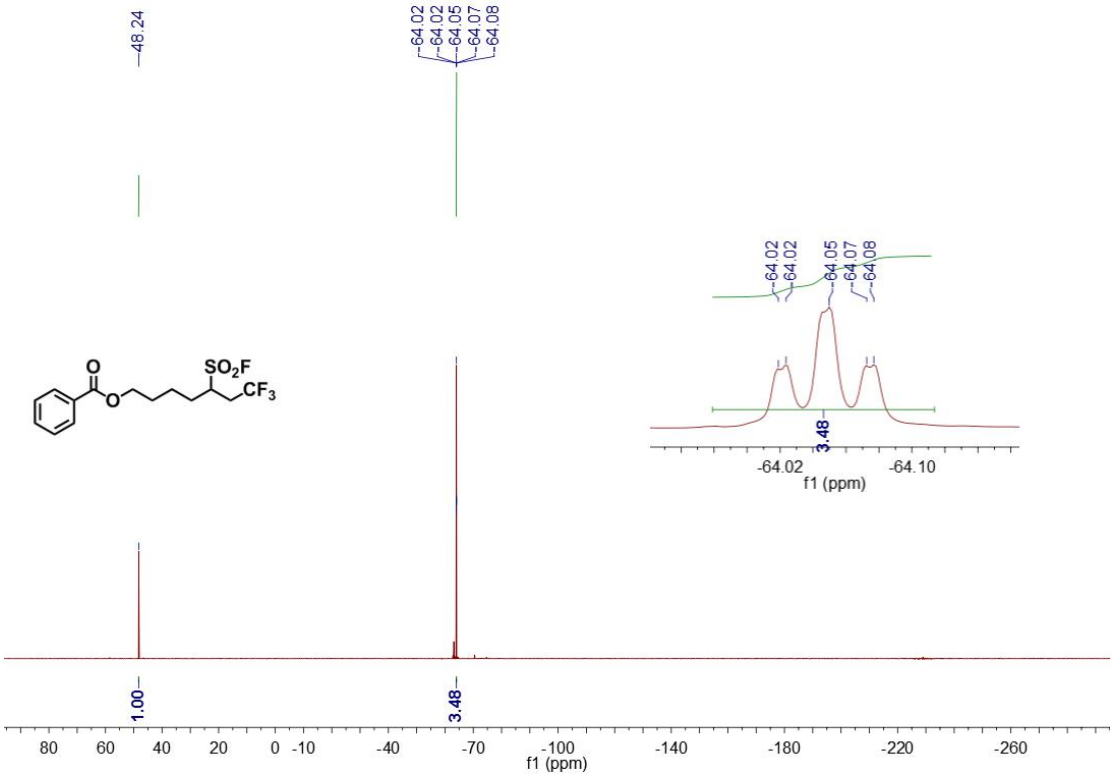
^{19}F NMR spectrum of 1,1,1-trifluoro-5-phenylpentane-3-sulfonyl fluoride (3a)



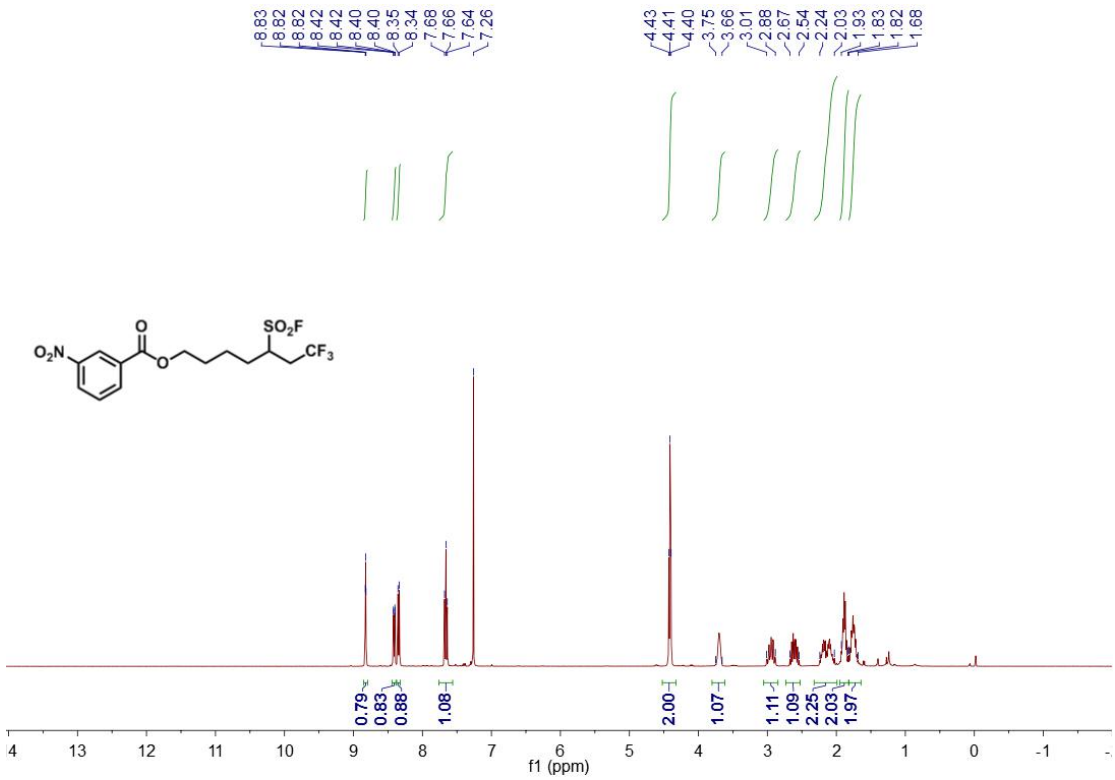
^{1}H NMR spectrum of 7-7,7,7-trifluoro-5-(fluorosulfonyl)heptyl benzoate (3b)



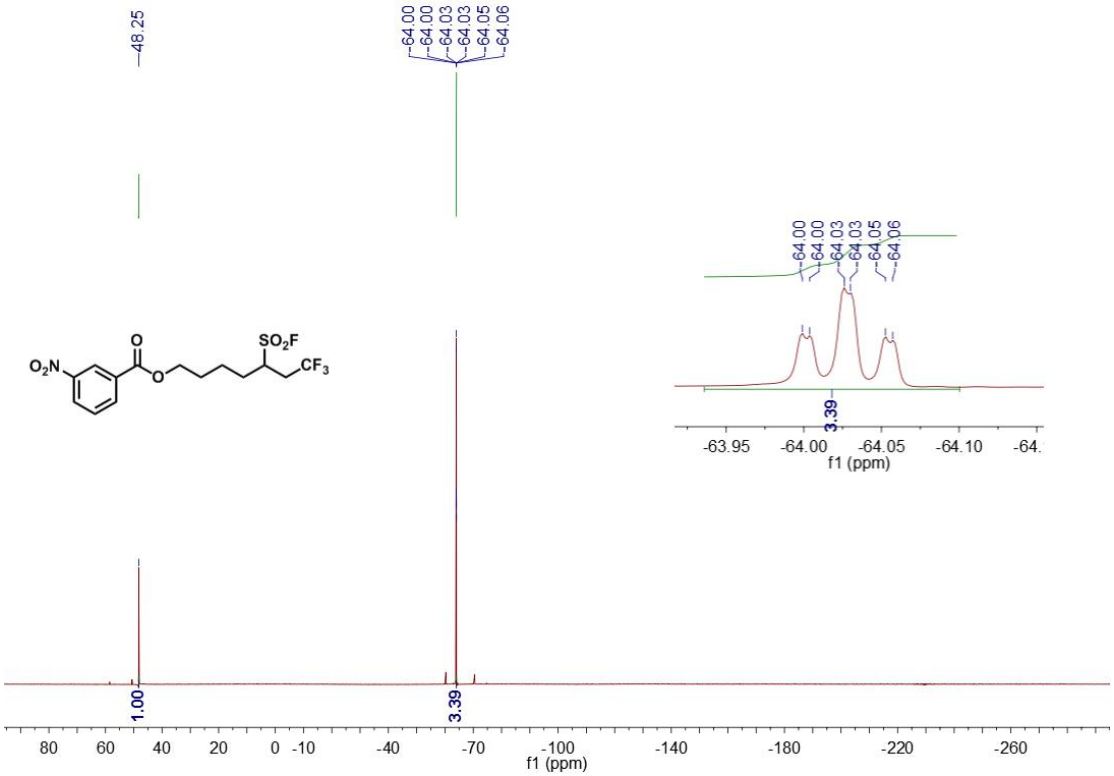
^{19}F NMR spectrum of 7-7,7,7-trifluoro-5-(fluorosulfonyl)heptyl benzoate (3b)



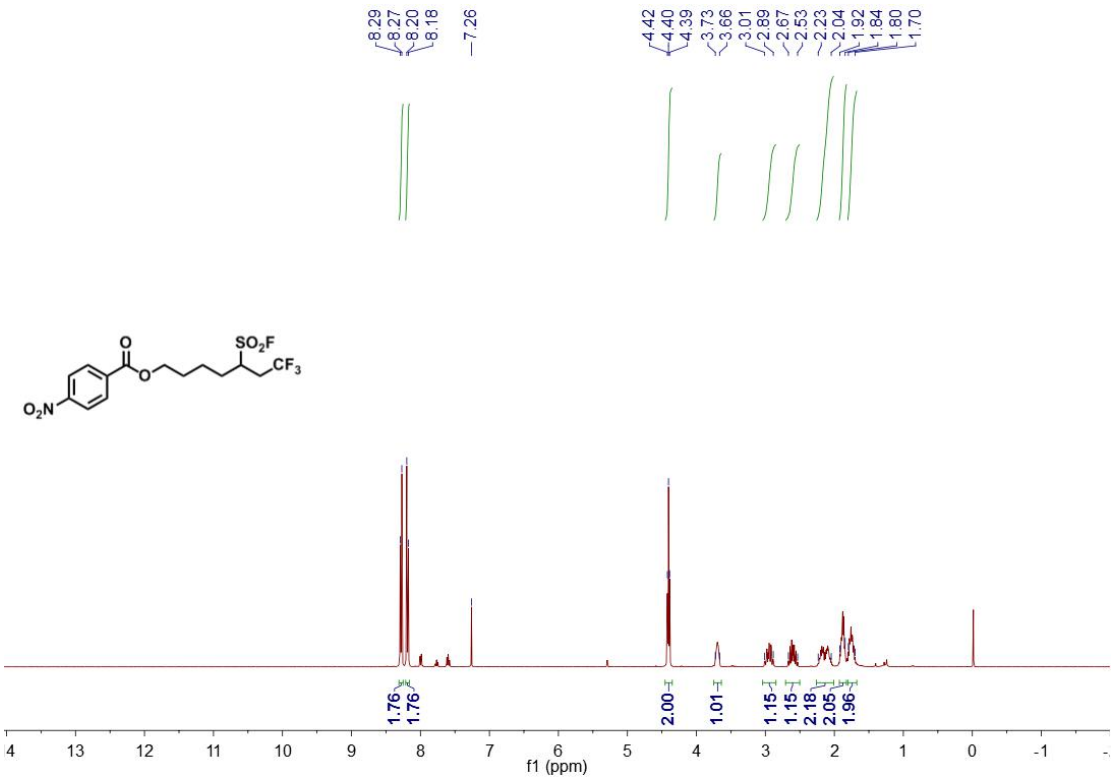
^{1}H NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 3-nitrobenzoate (3c)



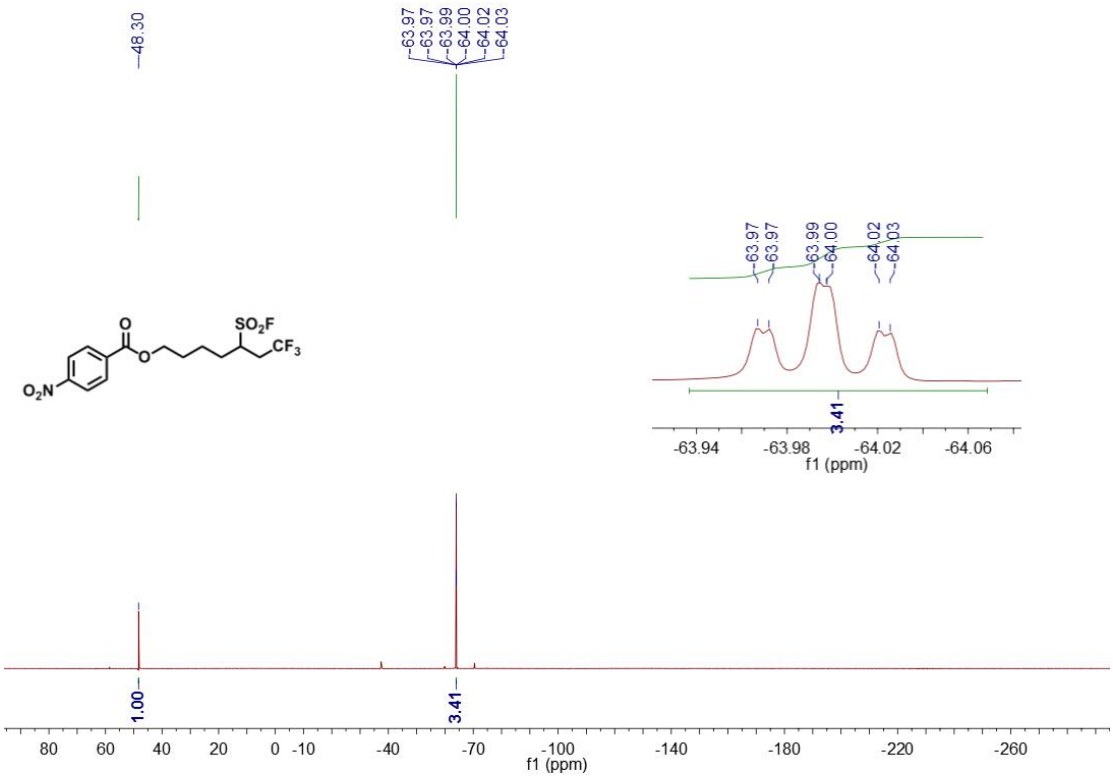
^{19}F NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 3-nitrobenzoate (3c)



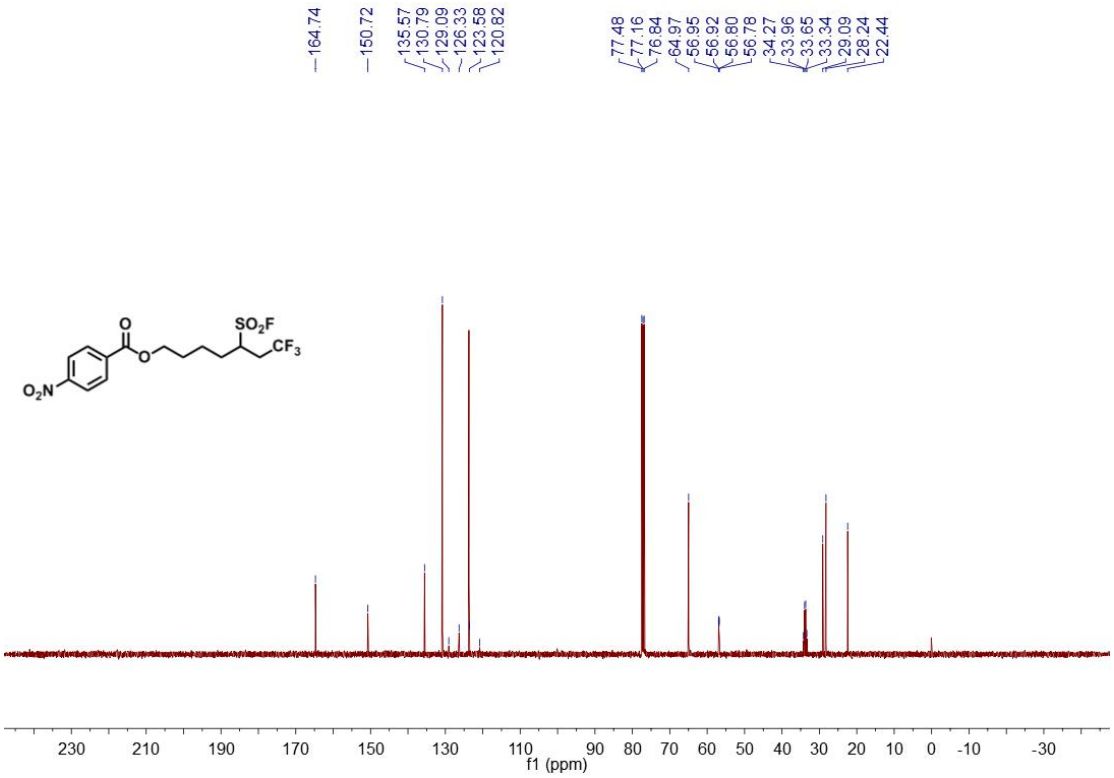
^{1}H NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-nitrobenzoate (3d)



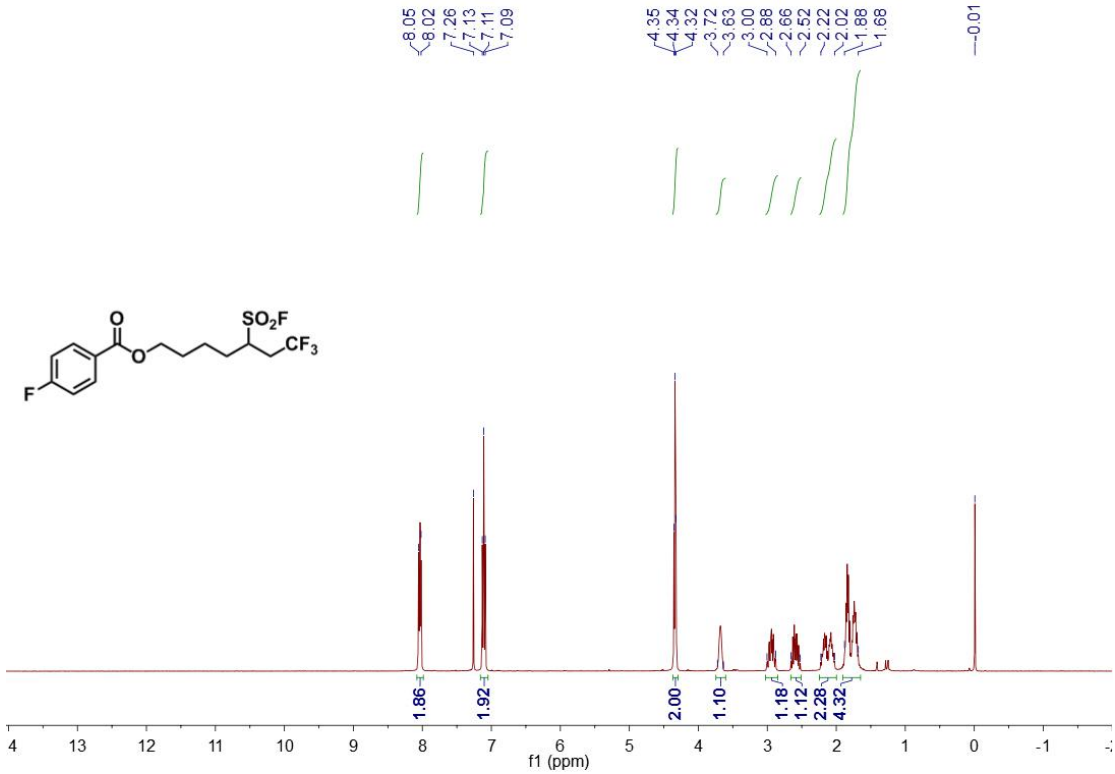
^{19}F NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 3-nitrobenzoate (3d)



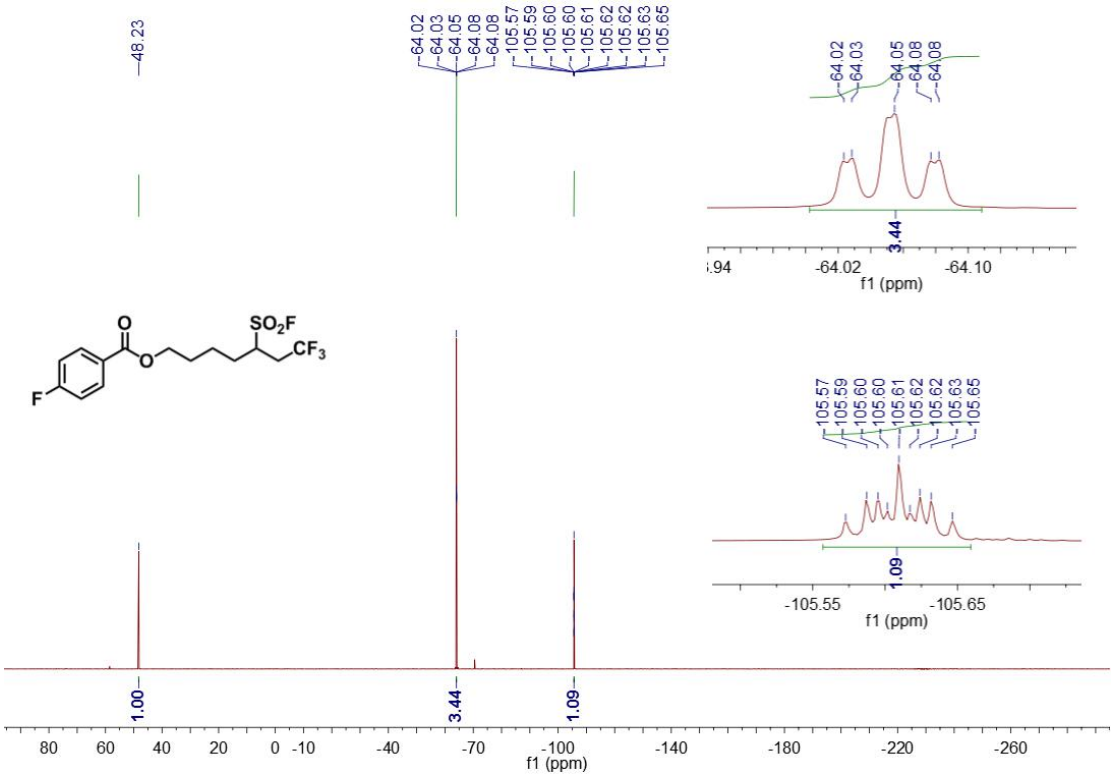
^{13}C NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-nitrobenzoate (3d)



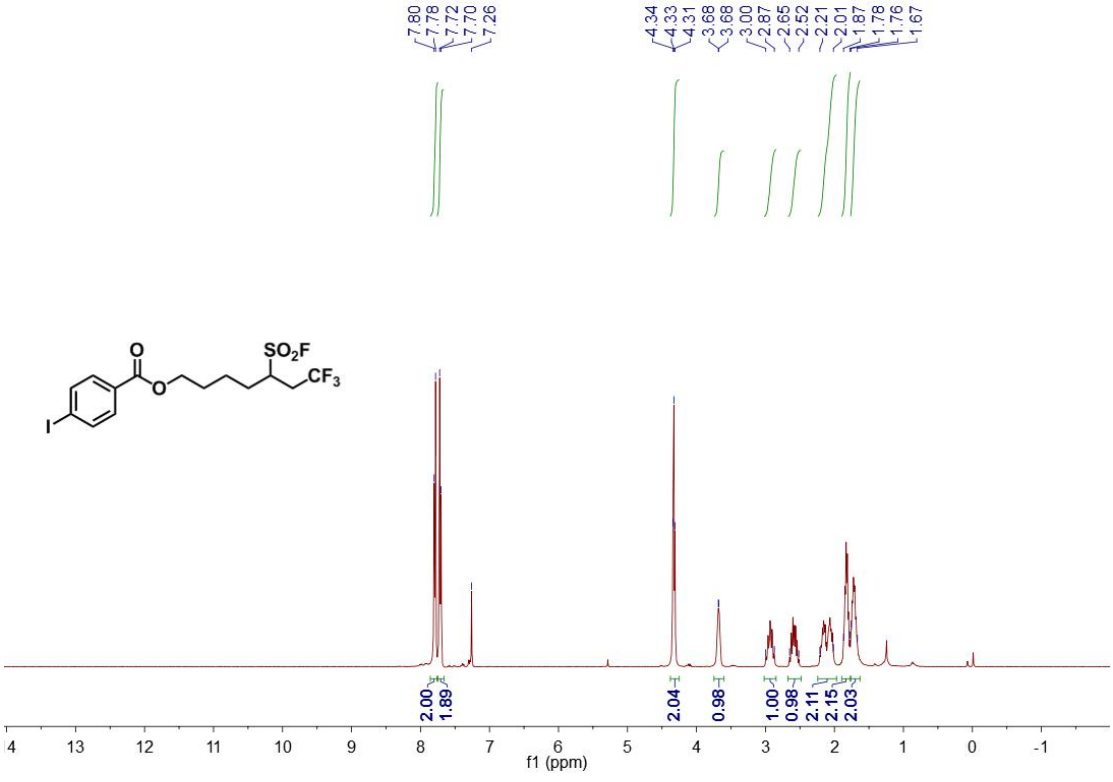
^{1}H NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-fluorobenzoate (3e)



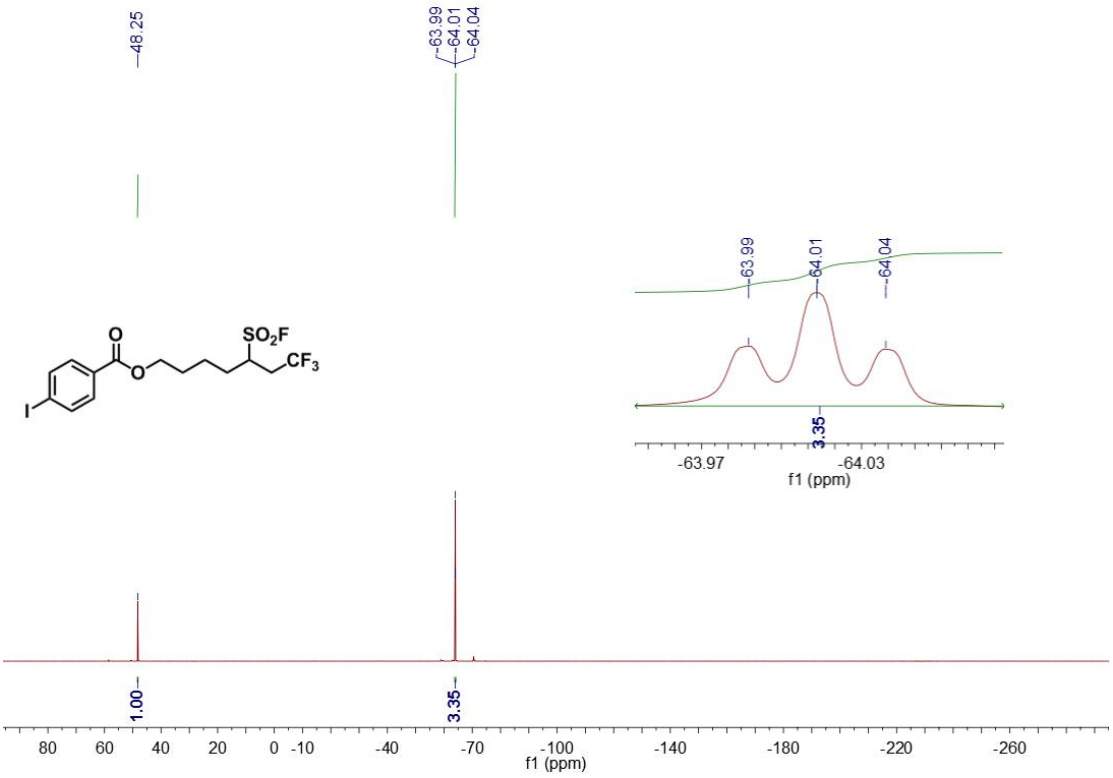
^{19}F NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-fluorobenzoate (3e)



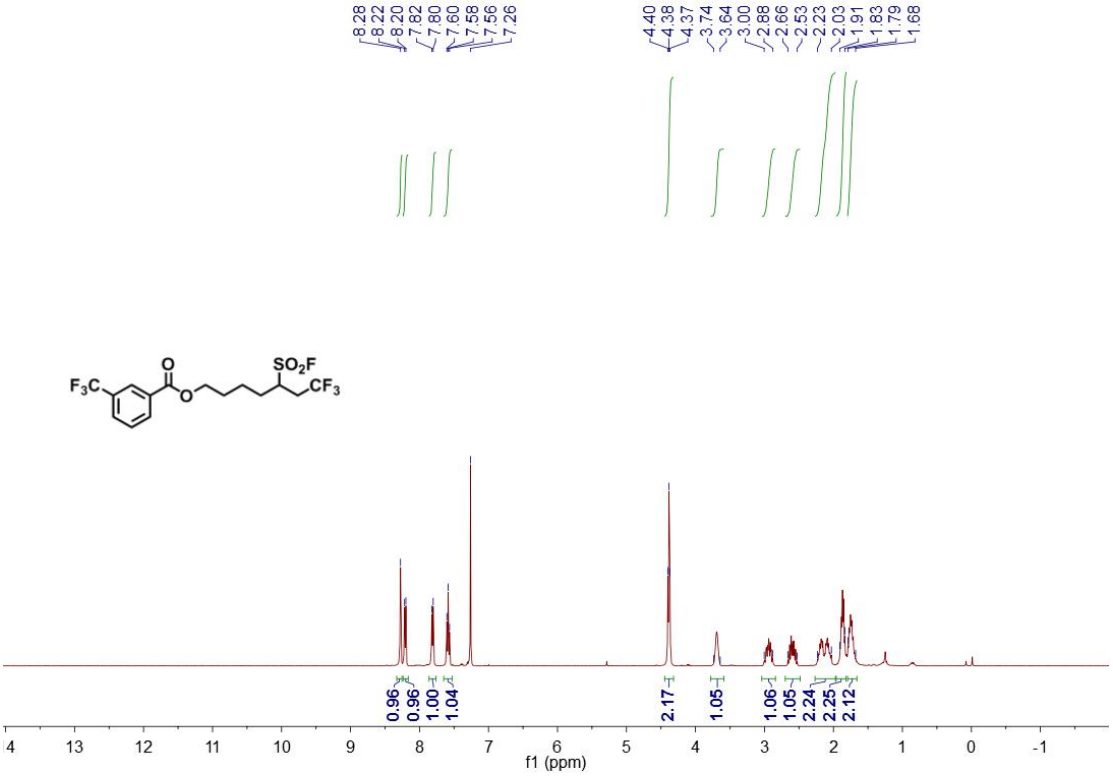
^{1}H NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-iodobenzoate (3f)



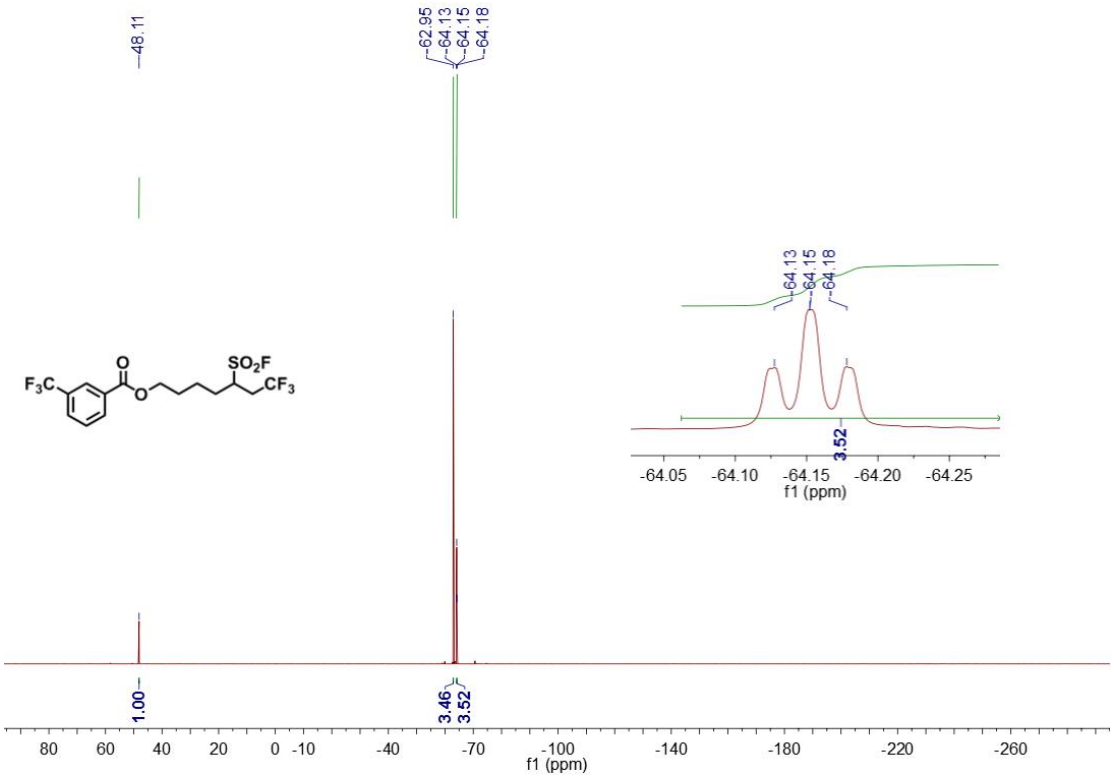
^{19}F NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-iodobenzoate (3f)



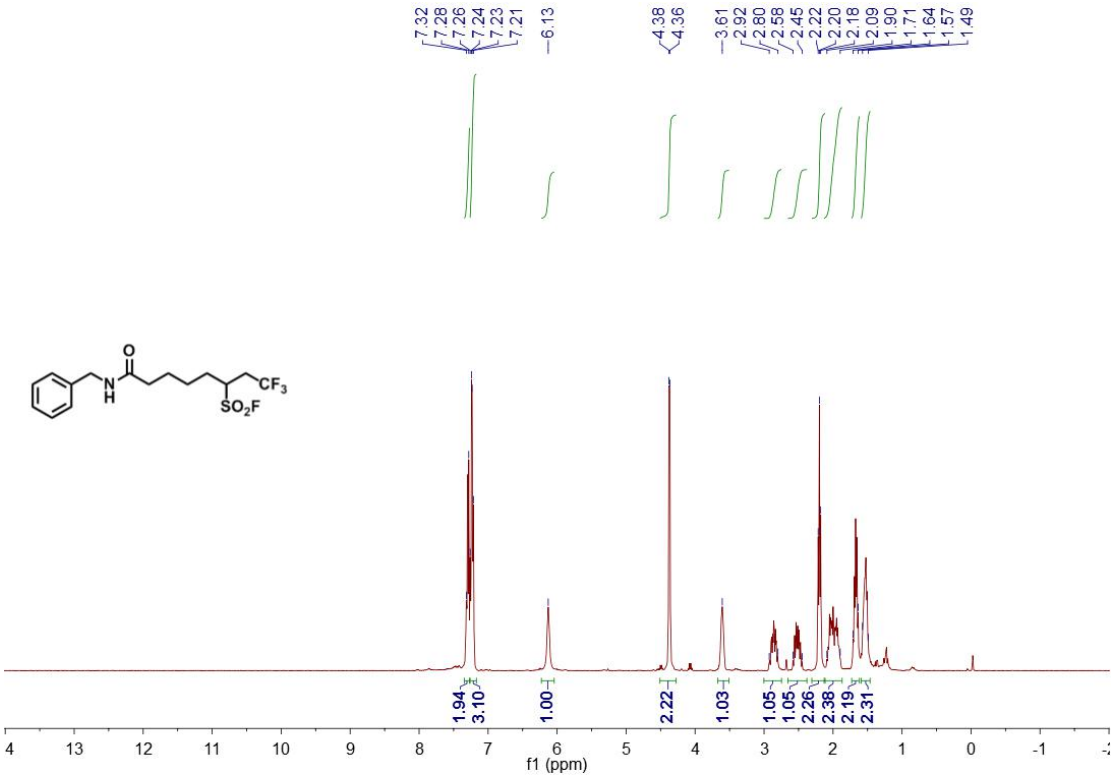
^{1}H NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-(trifluoromethyl)benzoate (3g)



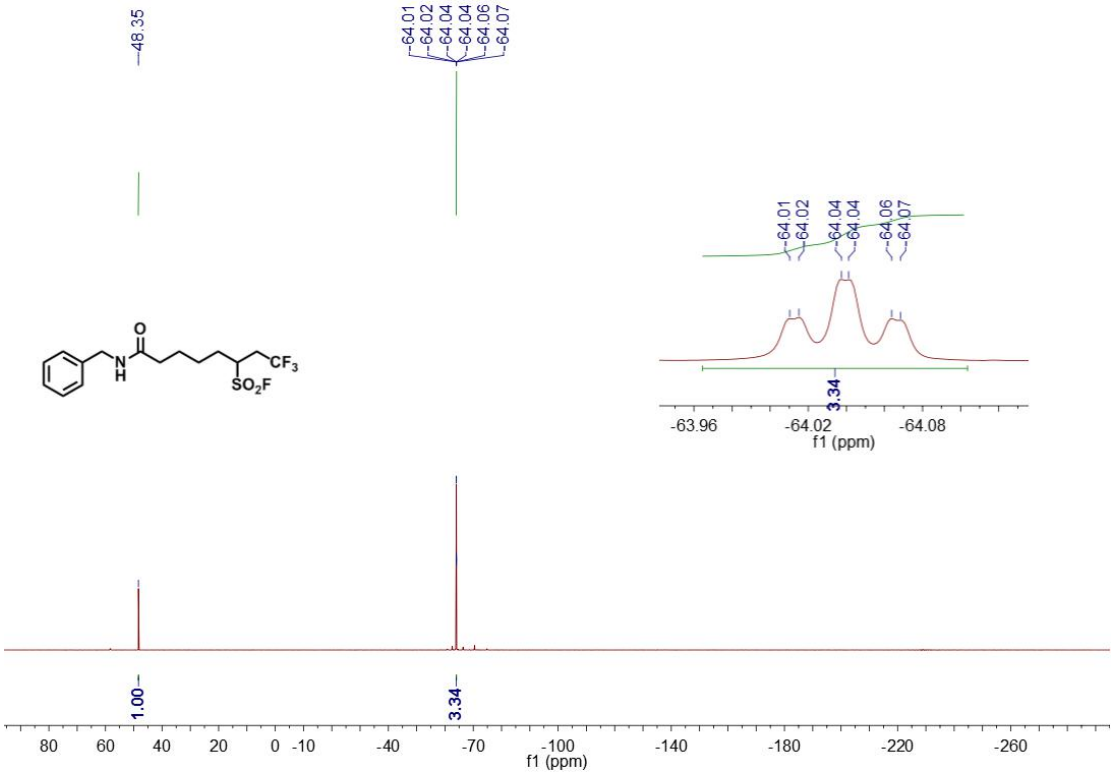
^{19}F NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 4-(trifluoromethyl)benzoate (3g)



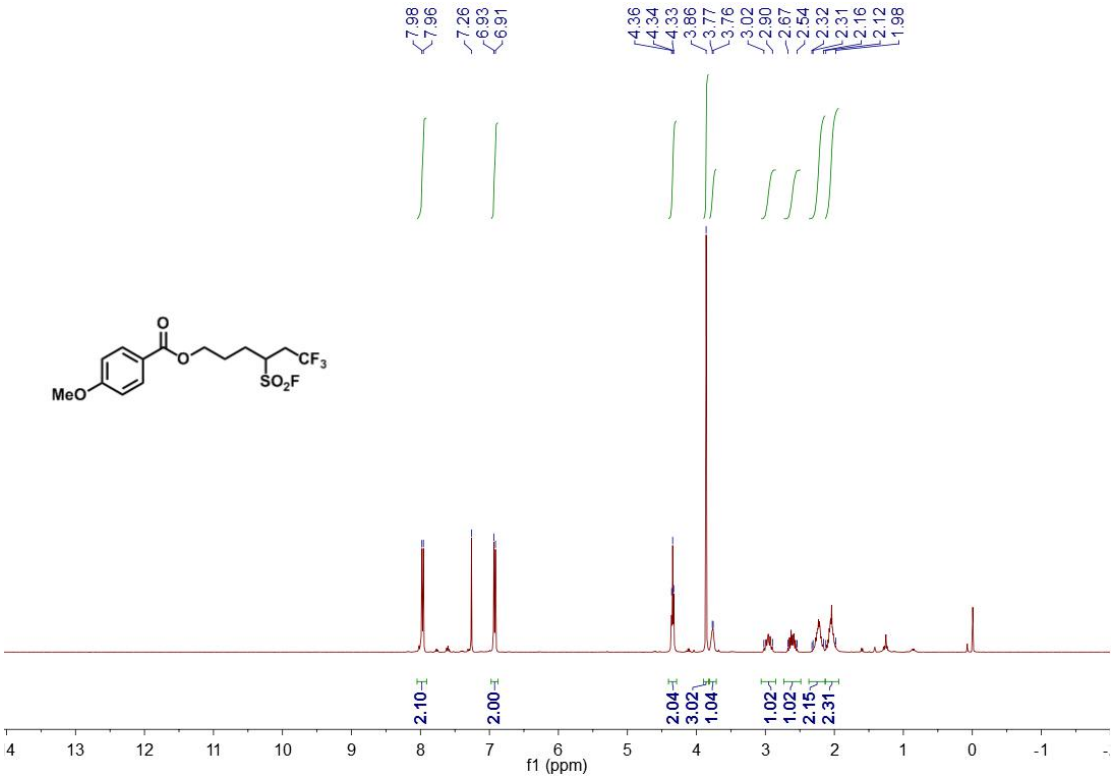
^{1}H NMR spectrum of 8-(benzylamino)-1,1,1-trifluoro-8-oxooctane-1-sulfonyl fluoride(3h)



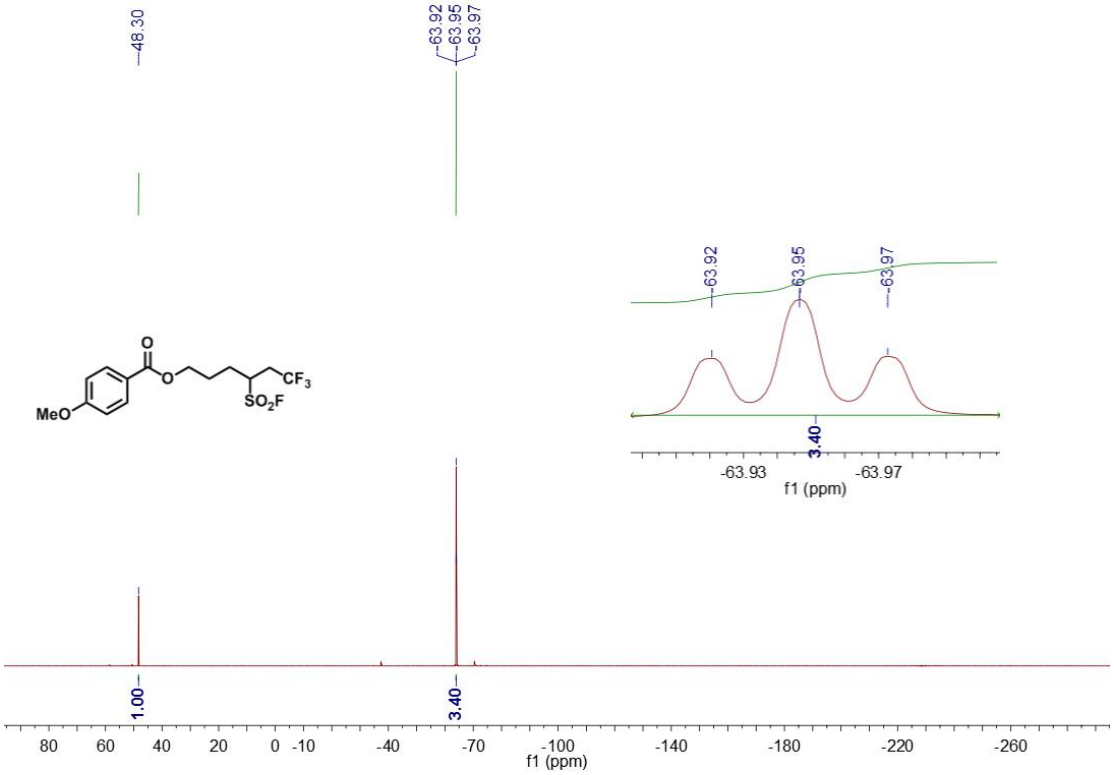
^{19}F NMR spectrum of 8-(benzylamino)-1,1,1-trifluoro-8-oxooctane-4-sulfonyl fluoride(3h)



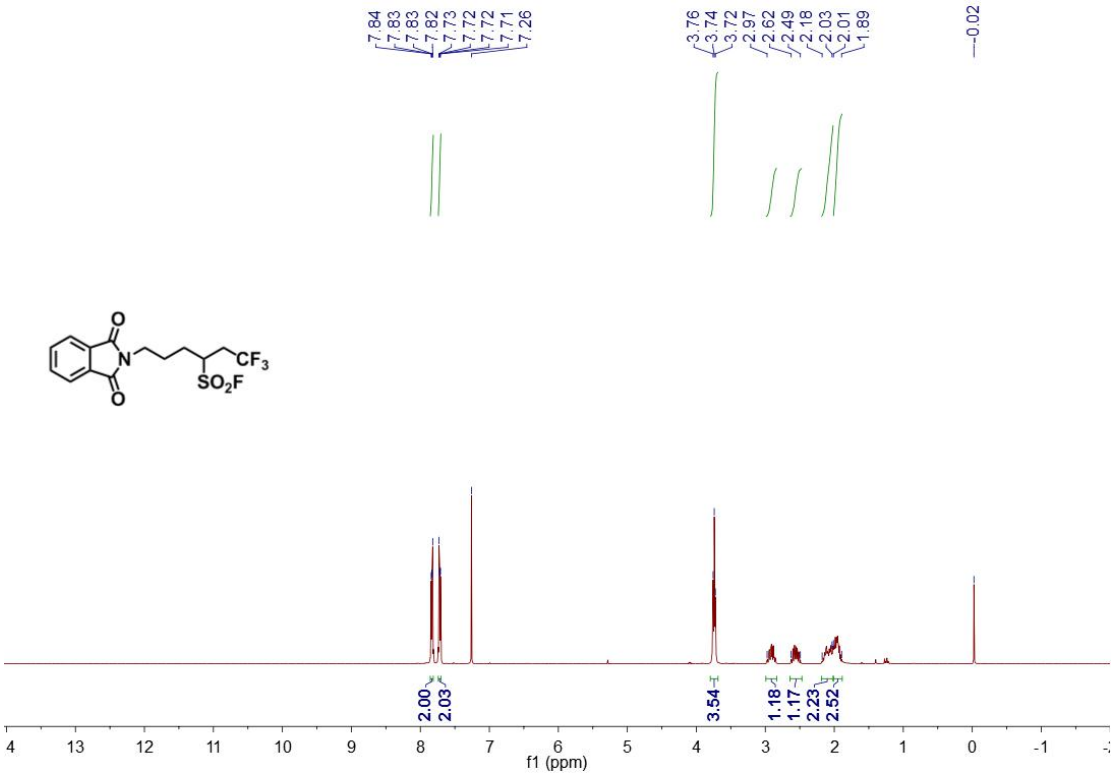
^{1}H NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl) heptyl 4-methoxybenzoate(3i)



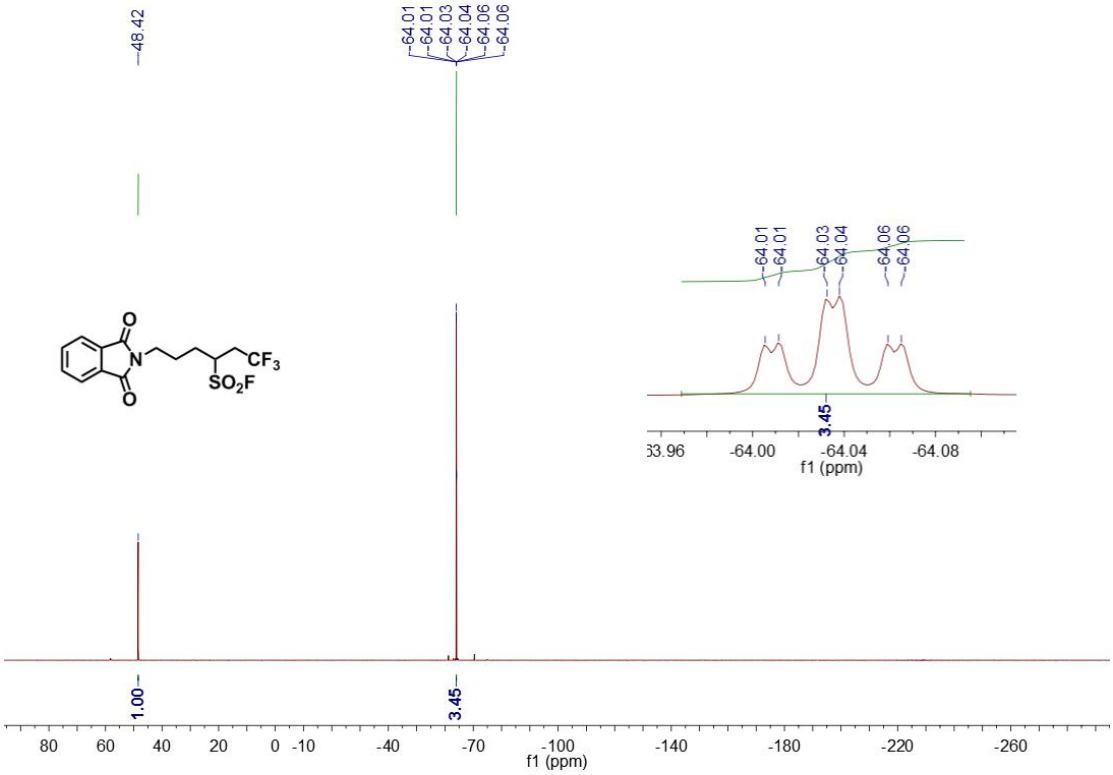
^{19}F NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl) heptyl 4-methoxybenzoate(3i)



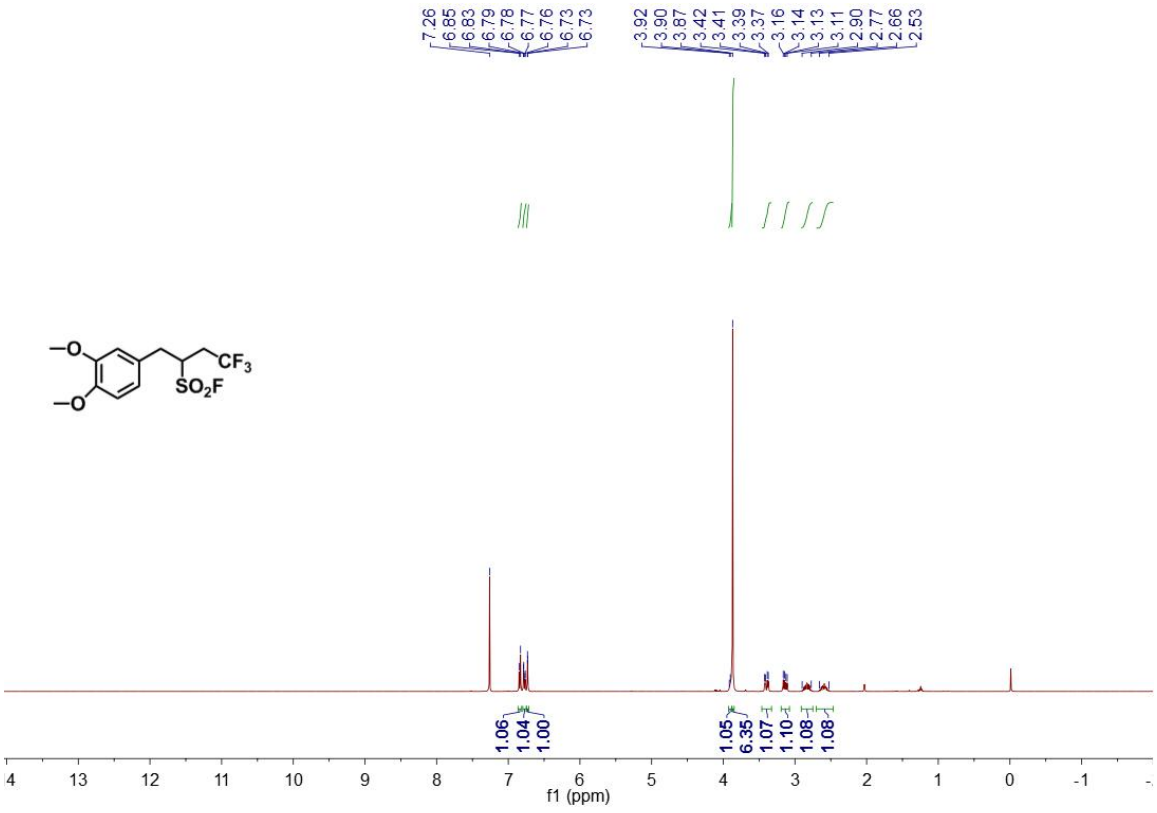
^{1}H NMR spectrum of 6-(1,3-dioxoisoindolin-2-yl)-1,1,1-trifluorohexane-3-sulfonyl fluoride (3j)



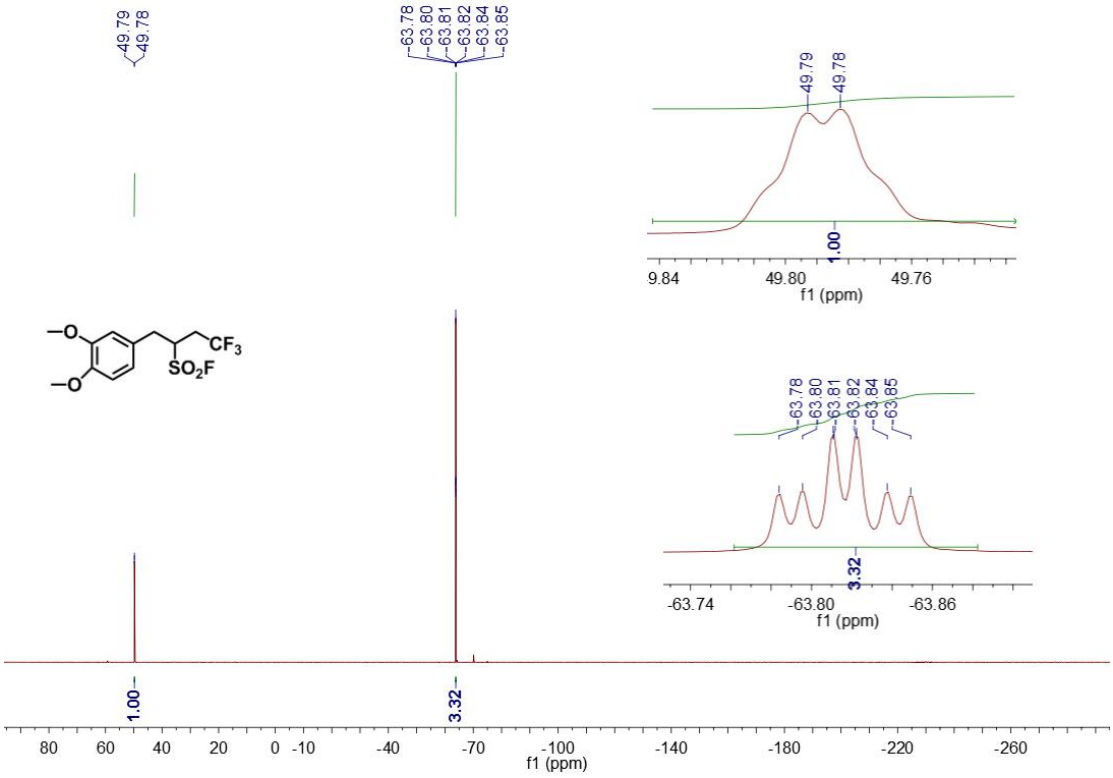
^{19}F NMR spectrum of 6-(1,3-dioxoisoindolin-2-yl)-1,1,1-trifluorohexane-3-sulfonyl fluoride (3j)



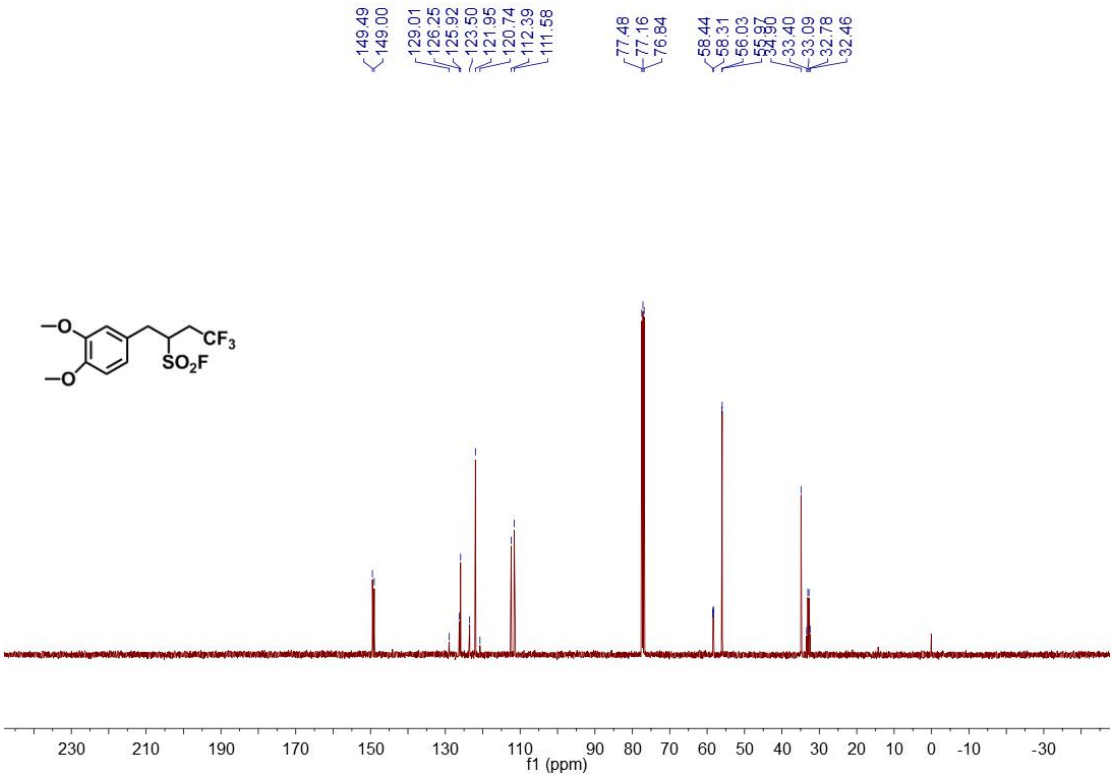
^{1}H NMR spectrum of 1-(3,4-dimethoxyphenyl)-4,4,4-trifluorobutane-2-sulfonyl fluoride (3k)



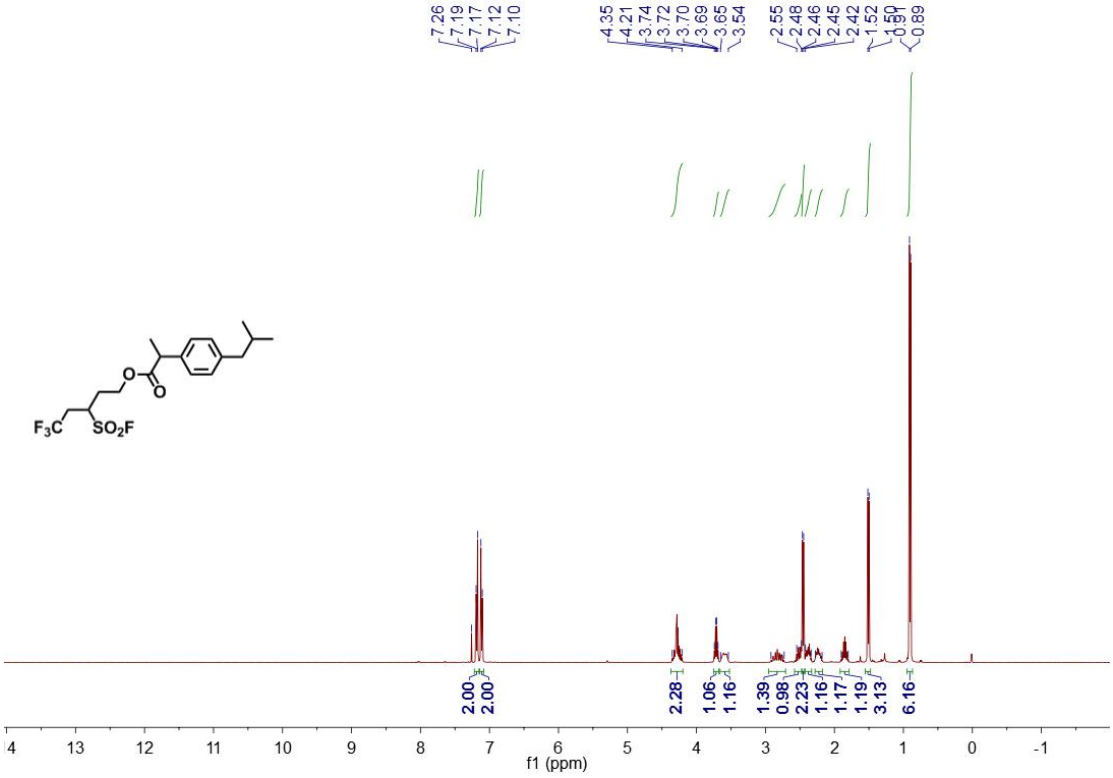
^{19}F NMR spectrum of 1-(3,4-dimethoxyphenyl)-4,4,4-trifluorobutane-2-sulfonyl fluoride (3k)



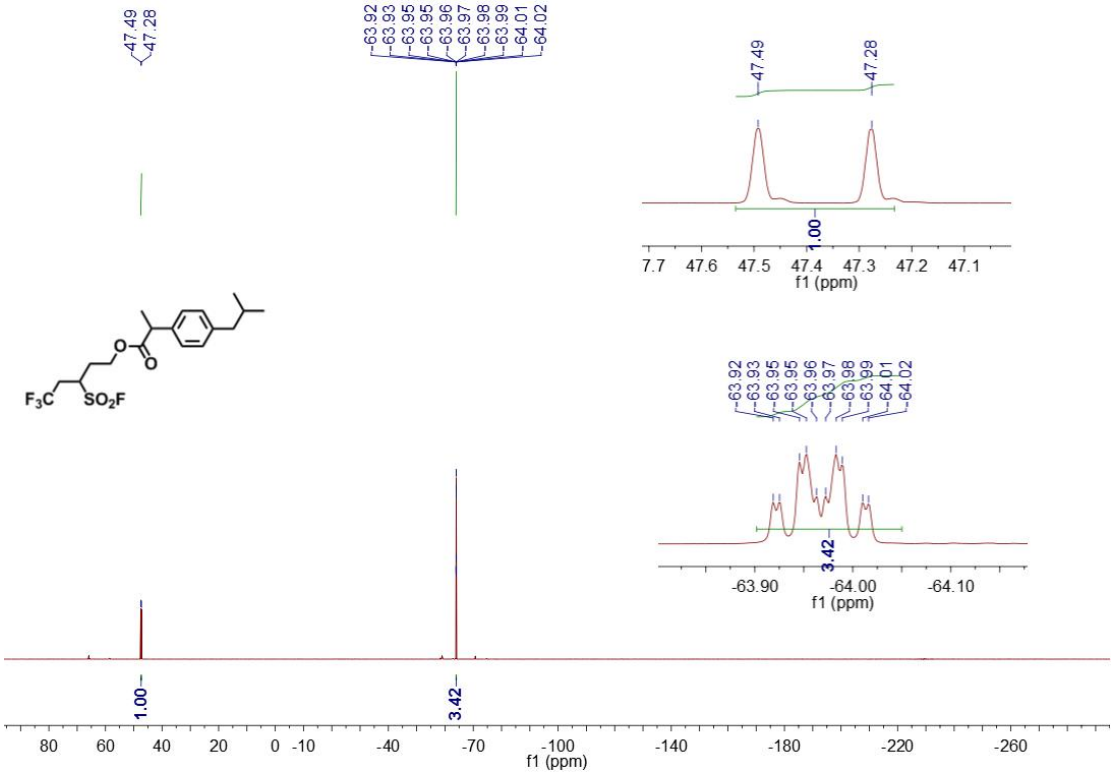
^{13}C NMR spectrum of 1-(3,4-dimethoxyphenyl)-4,4,4-trifluorobutane-2-sulfonyl fluoride (3k)



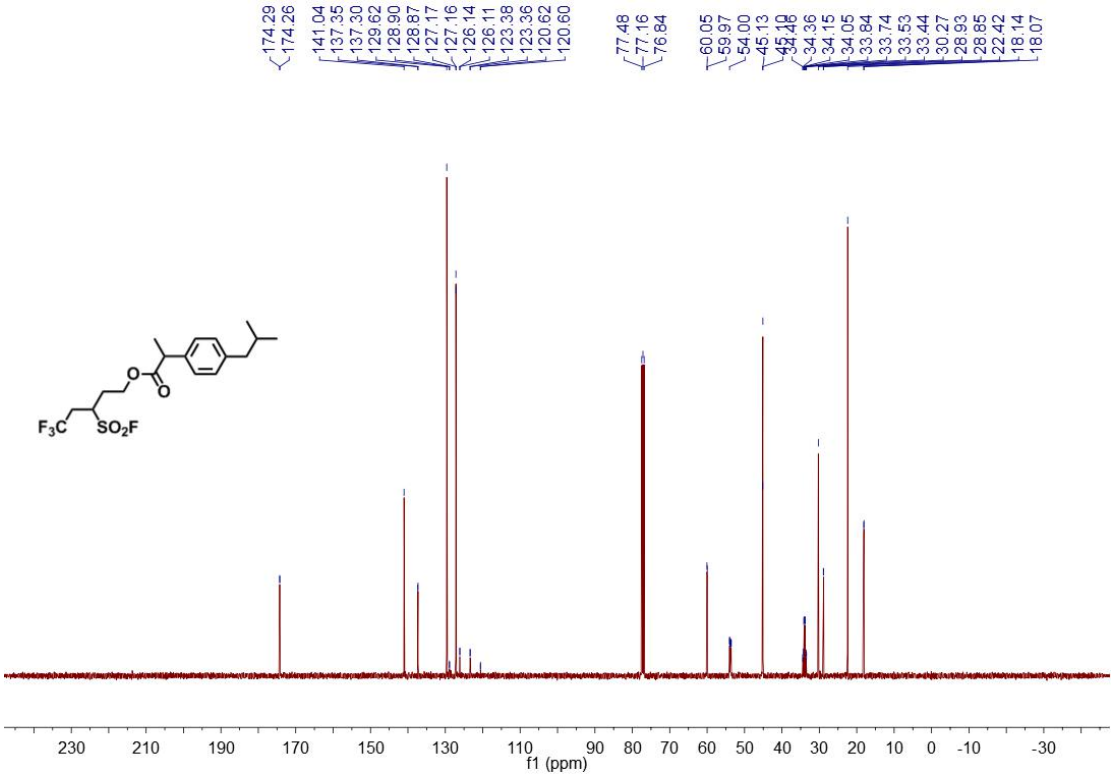
^{1}H NMR spectrum of 5,5,5-trifluoro-3-(fluorosulfonyl)pentyl 2-(4-isobutylphenyl)propanoate (3l)



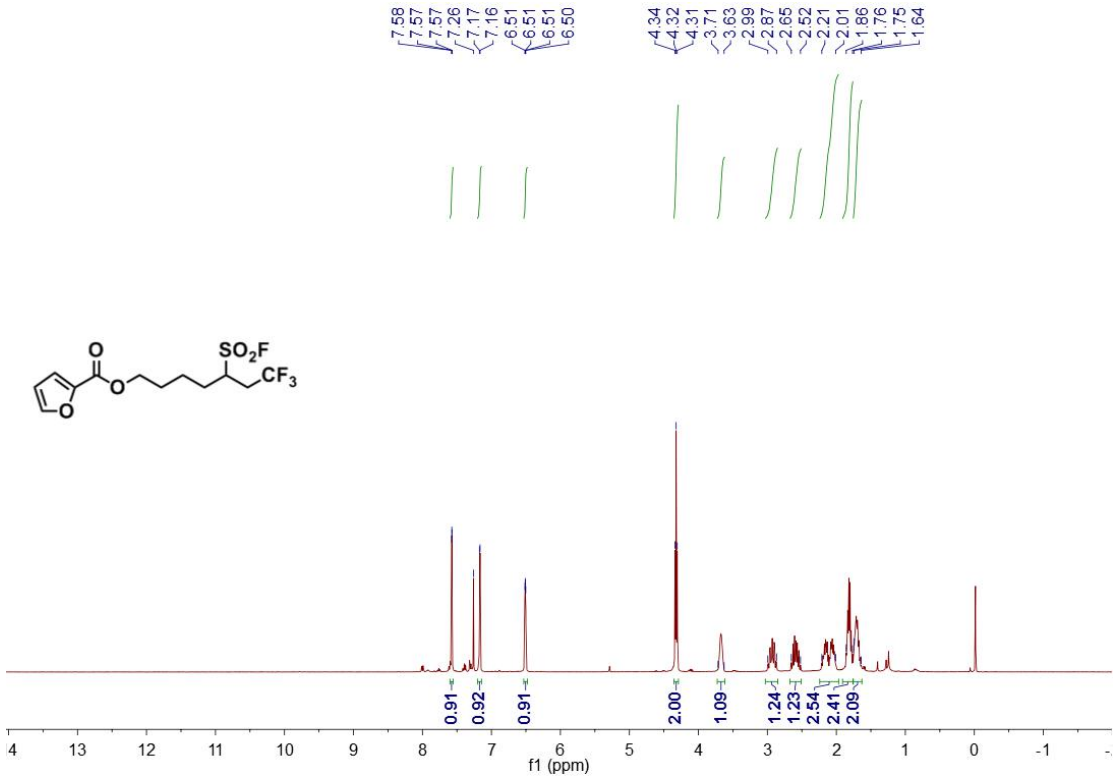
^{19}F NMR spectrum of 5,5,5-trifluoro-3-(fluorosulfonyl)pentyl 2-(4-isobutylphenyl)propanoate (3l)



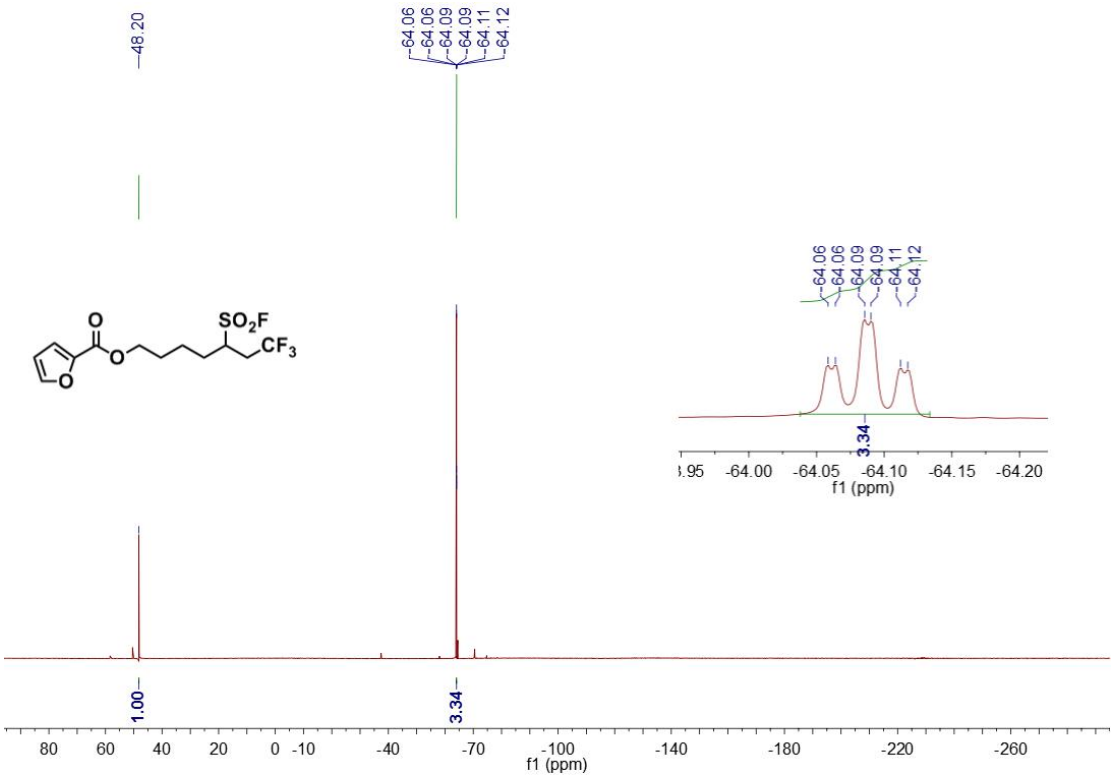
^{13}C NMR spectrum of 5,5,5-trifluoro-3-(fluorosulfonyl)pentyl 2-(4-isobutylphenyl)propanoate (3l)



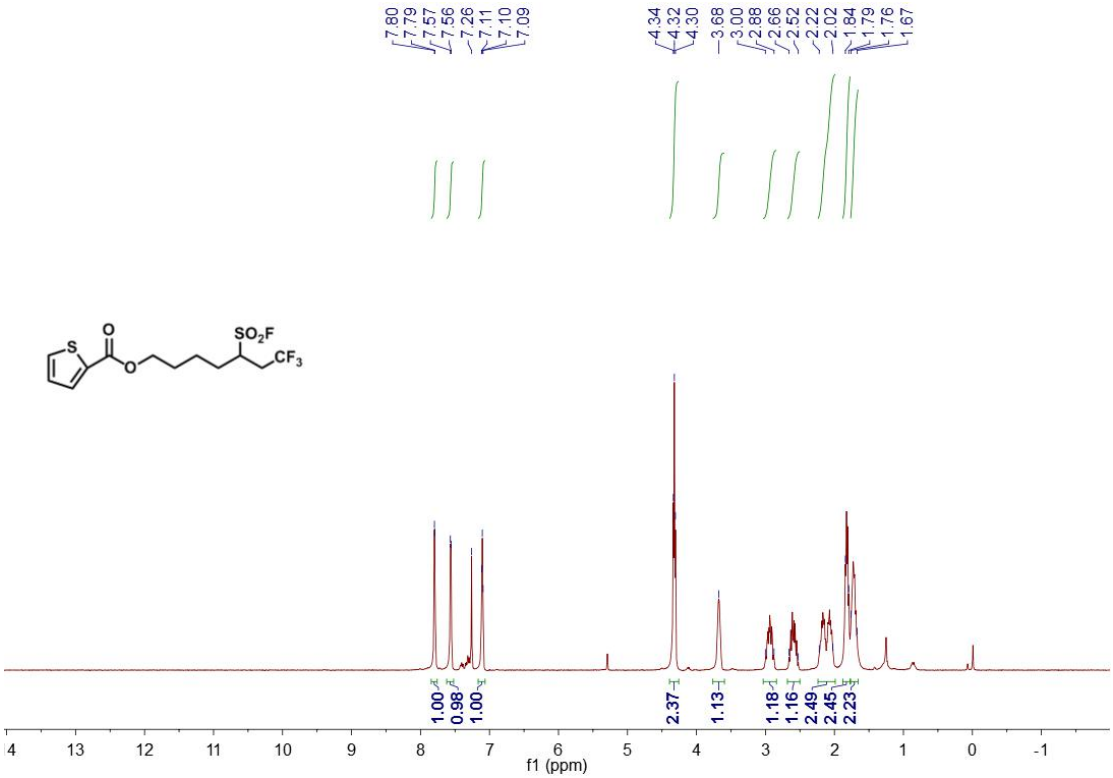
^{1}H NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl furan-2-carboxylate (3m)



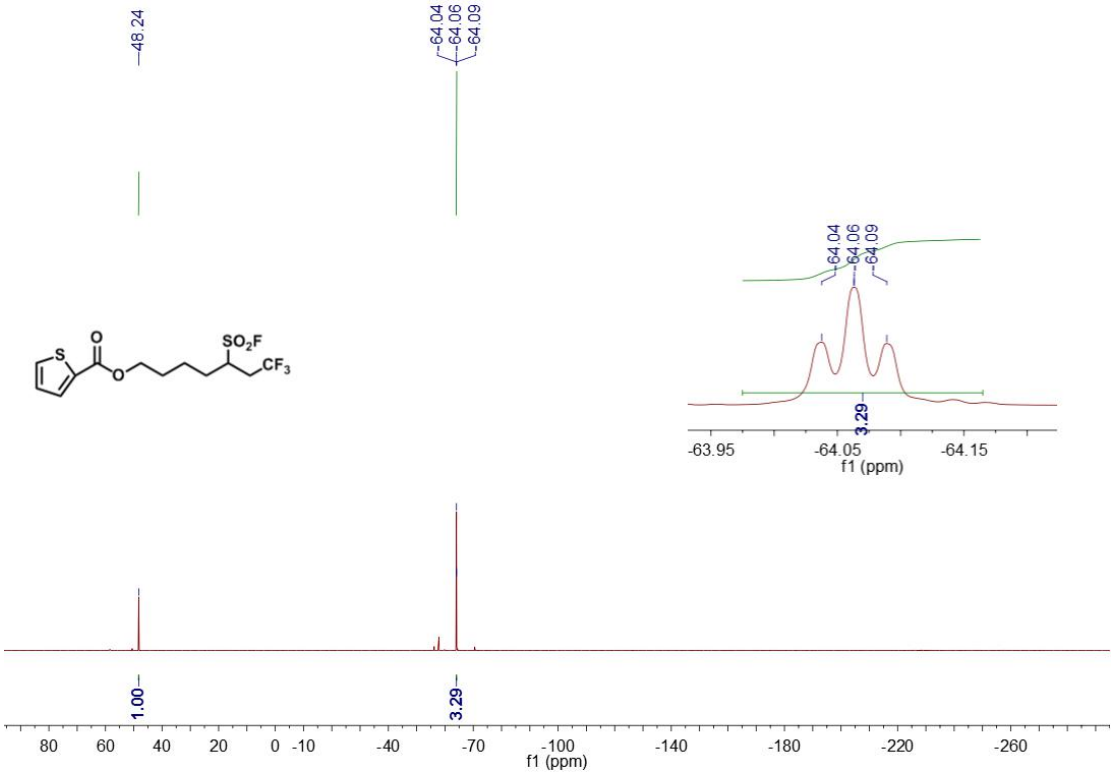
^{19}F NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl furan-2-carboxylate (3m)



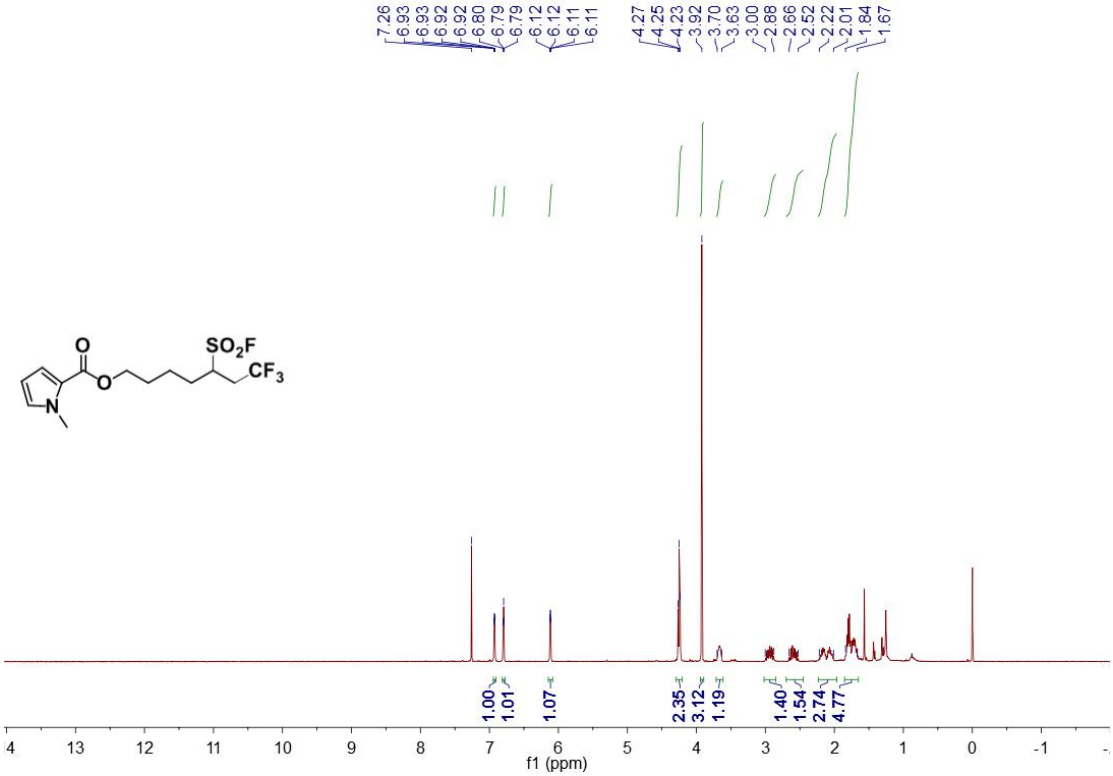
^{1}H NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl thiophene-2-carboxylate (3n)



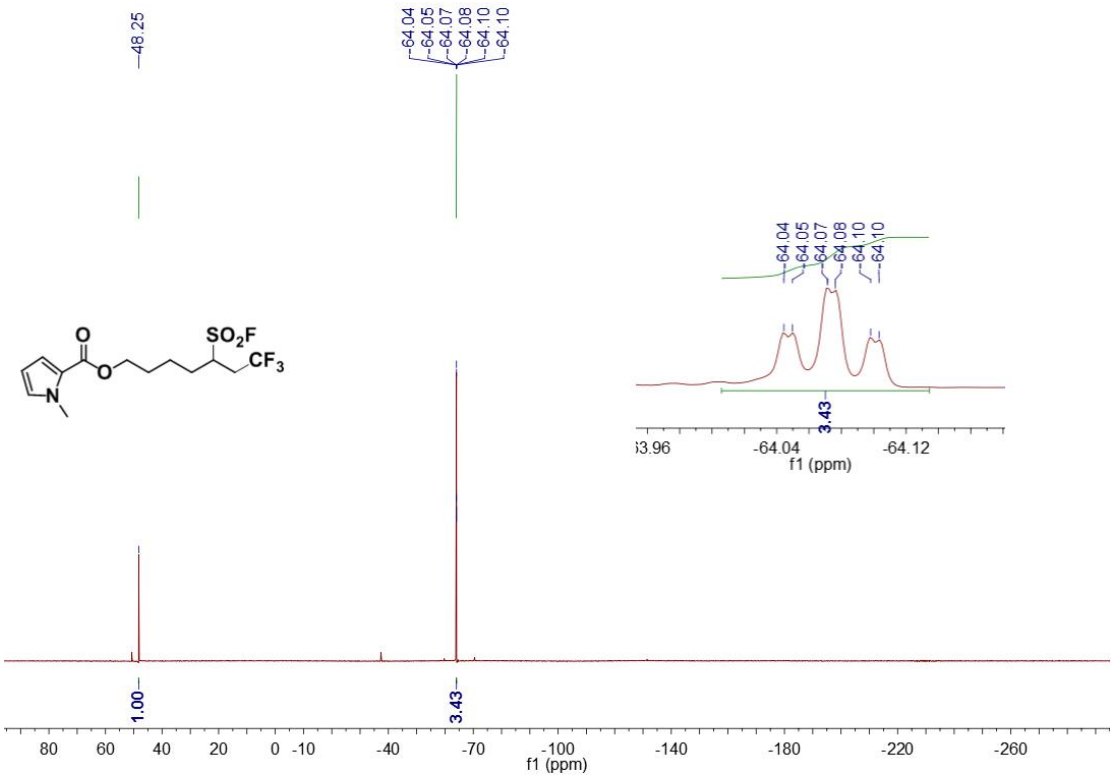
^{19}F NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl thiophene-2-carboxylate (3n)



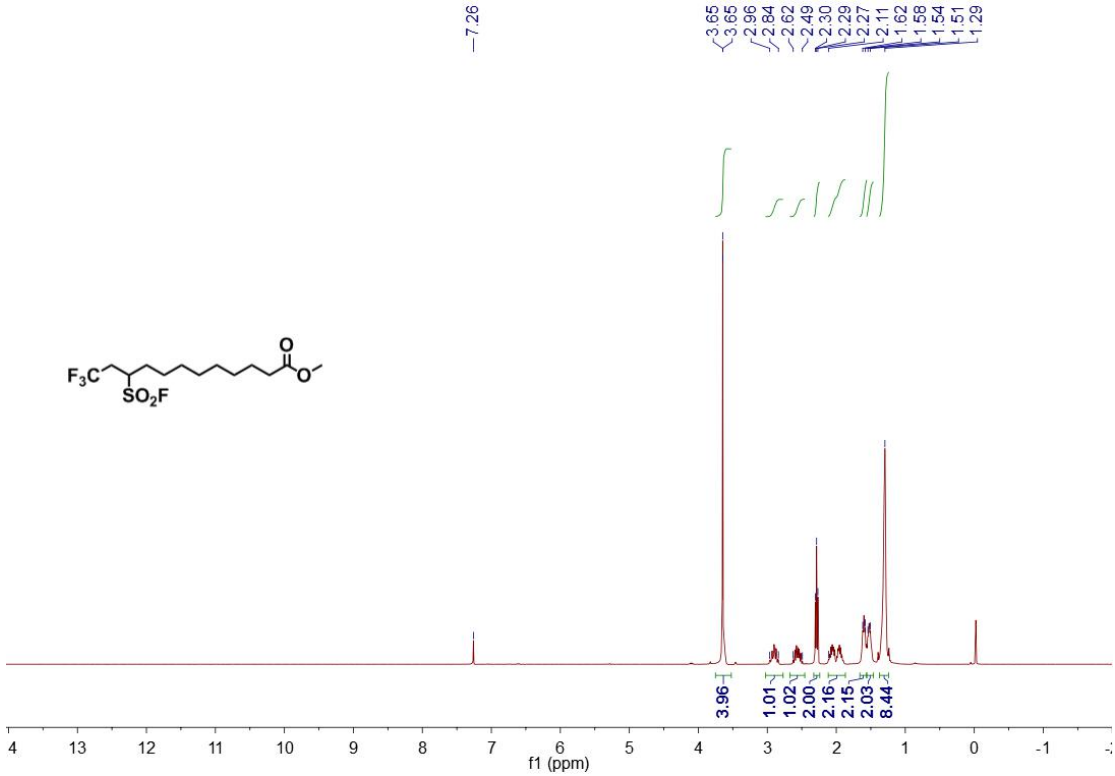
^{1}H NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 1-methyl-1H-pyrrole-2-carboxylate (3o)



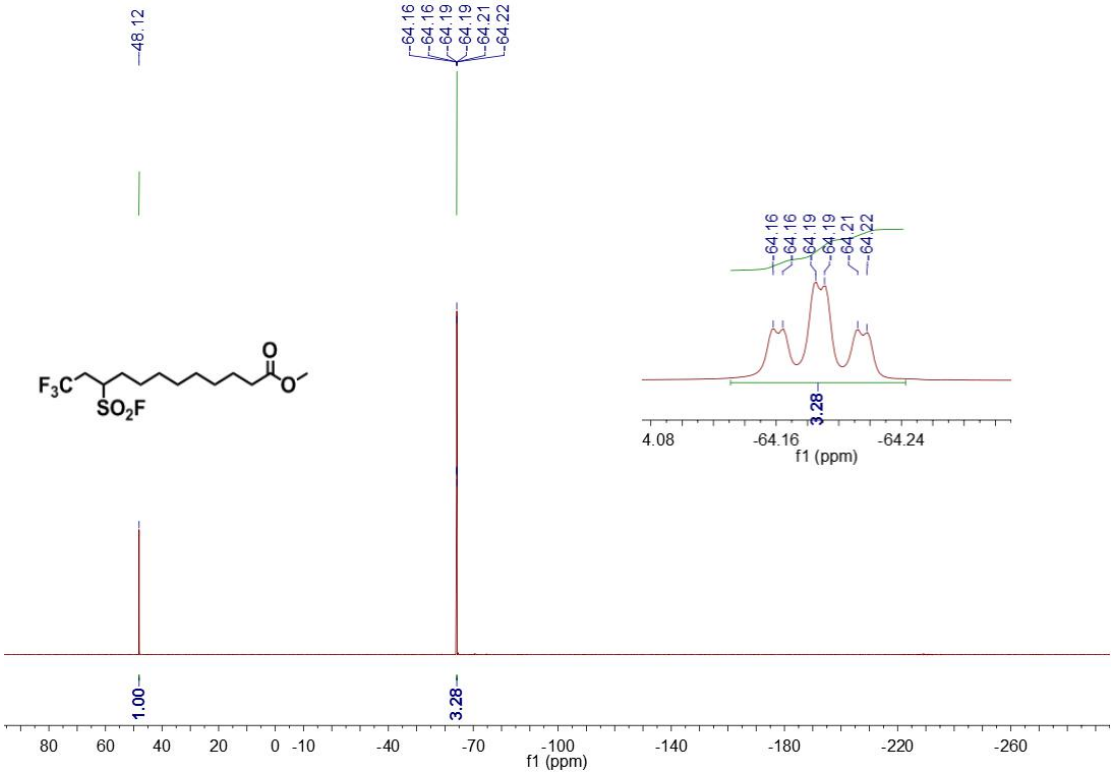
^{19}F NMR spectrum of 7,7,7-trifluoro-5-(fluorosulfonyl)heptyl 1-methyl-1H-pyrrole-2-carboxylate (3o)



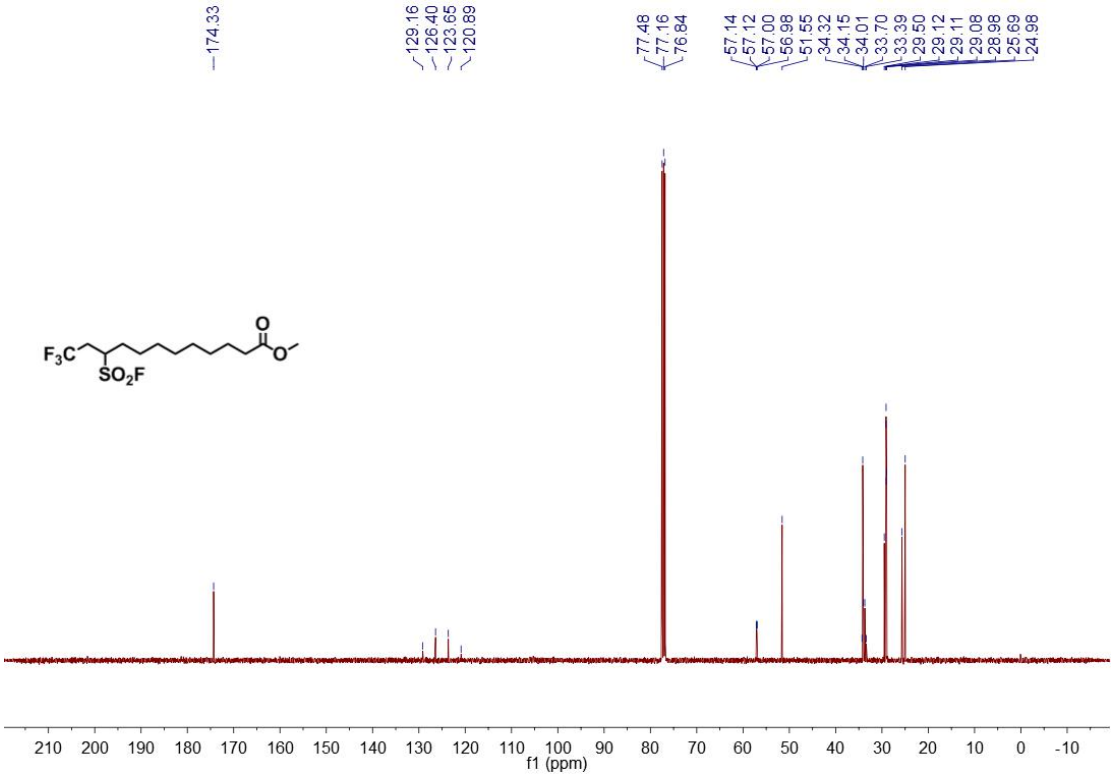
^{1}H NMR spectrum of methyl 12,12,12-trifluoro-10-(fluorosulfonyl) dodecanoate (3p)



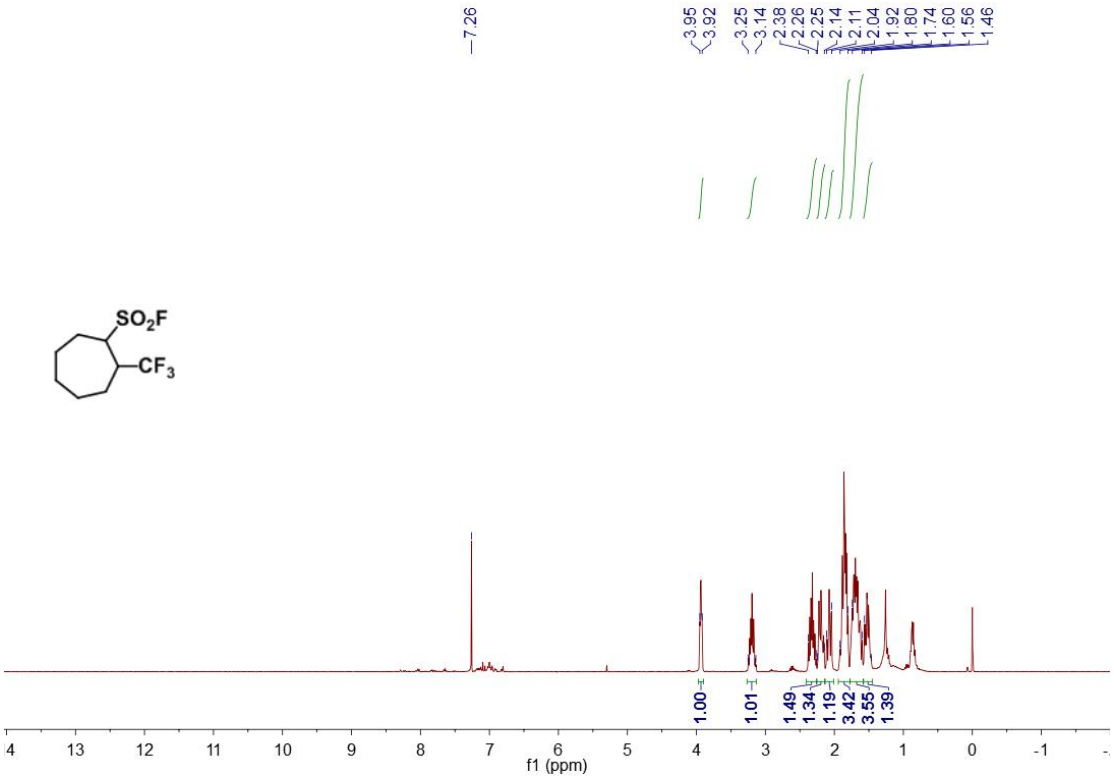
^{19}F NMR spectrum of methyl 12,12,12-trifluoro-10-(fluorosulfonyl) dodecanoate (3p)



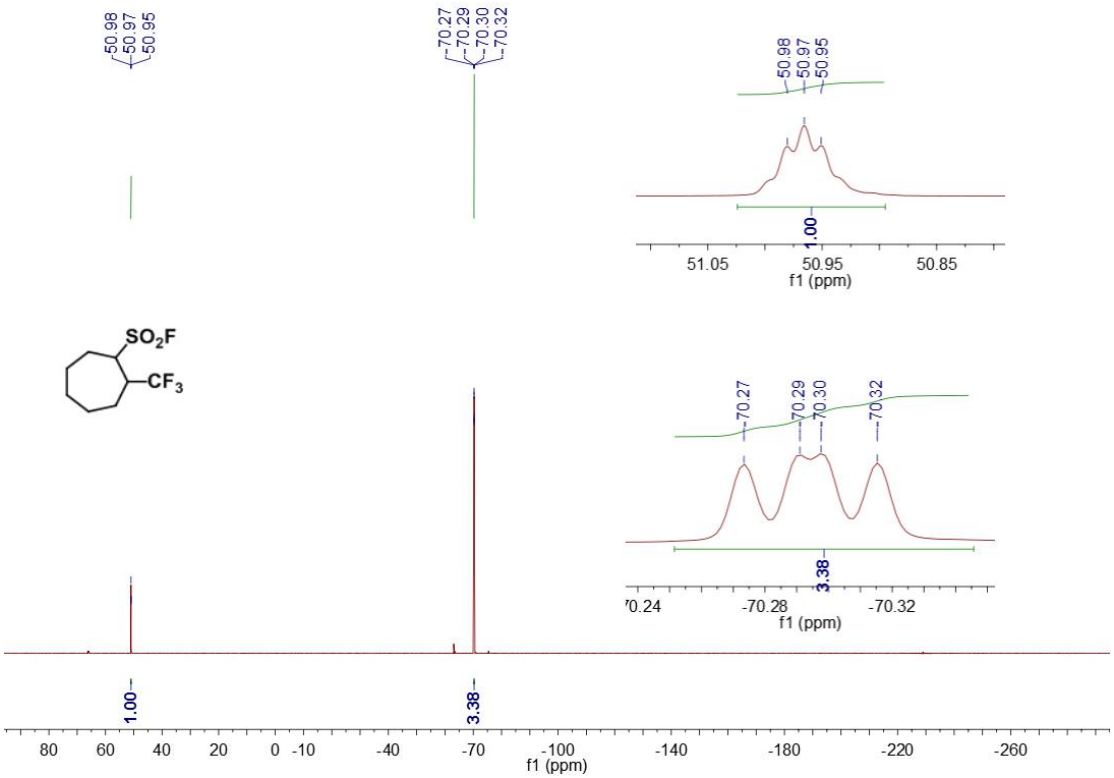
^{13}C NMR spectrum of methyl 12,12,12-trifluoro-10-(fluorosulfonyl) dodecanoate (3p)



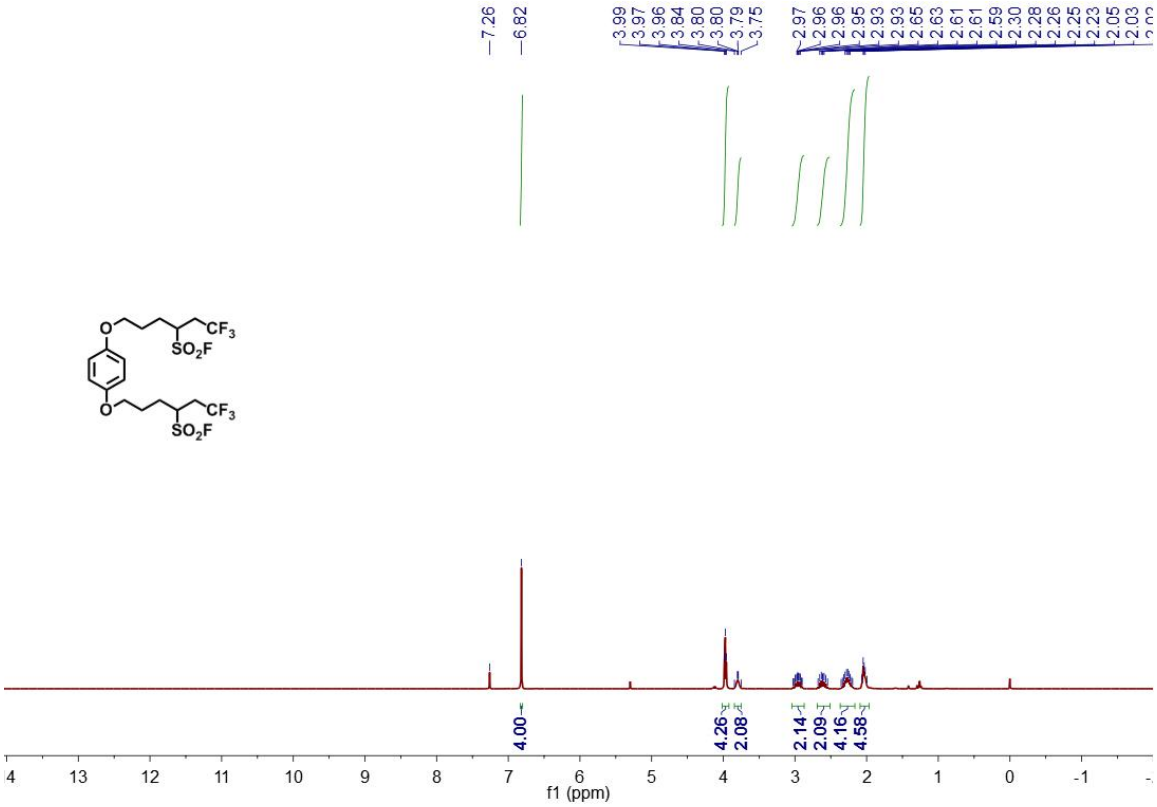
^{1}H NMR spectrum of 2-(trifluoromethyl)cycloheptane-1-sulfonyl fluoride (3q)



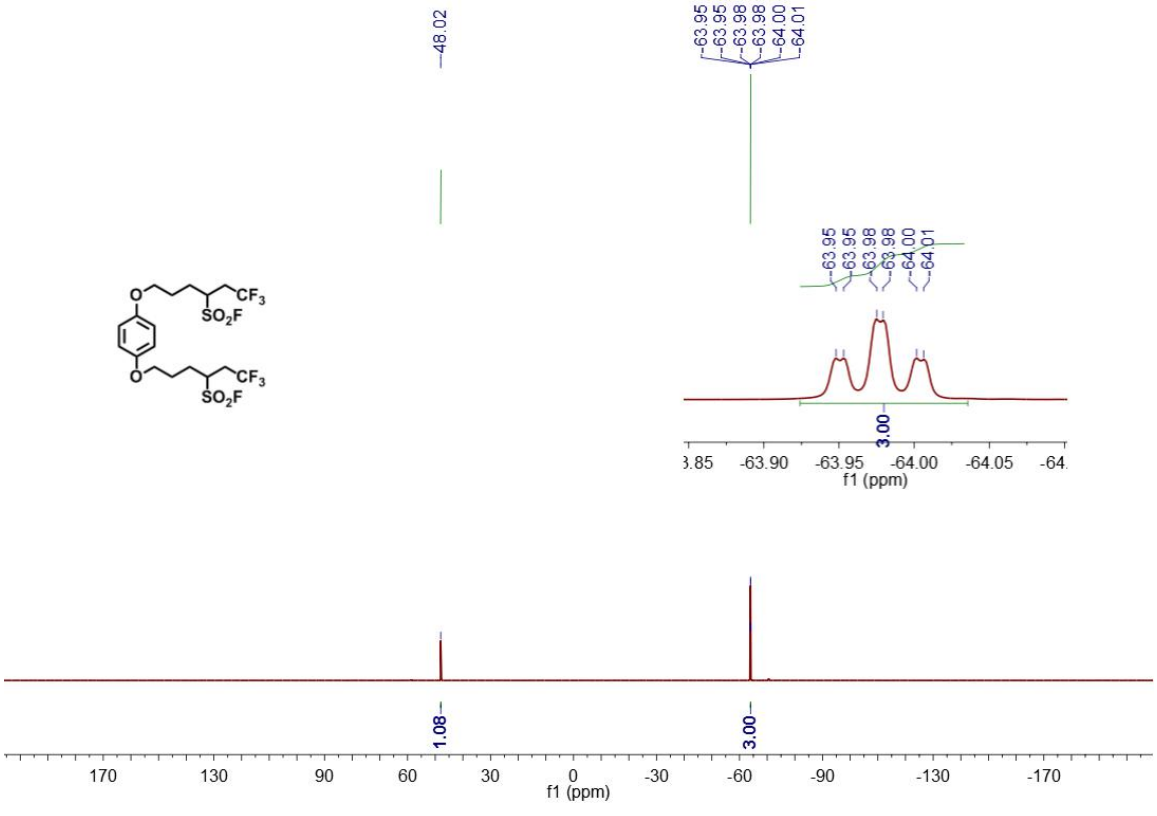
^{19}F NMR spectrum of 2-(trifluoromethyl)cycloheptane-1-sulfonyl fluoride (3q)



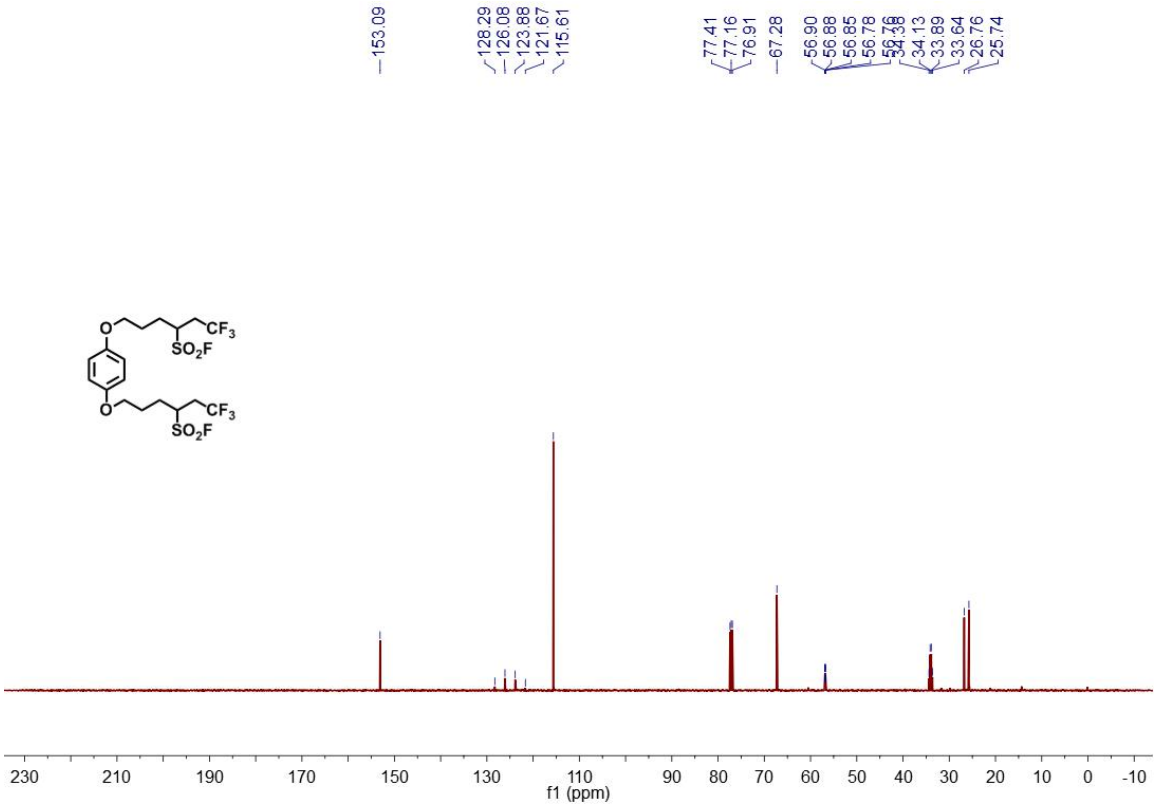
^{1}H NMR spectrum of 6,6'-(1,4-phenylenebis(oxy))bis(1,1,1-trifluorohexane-3-sulfonyl fluoride) (3r)



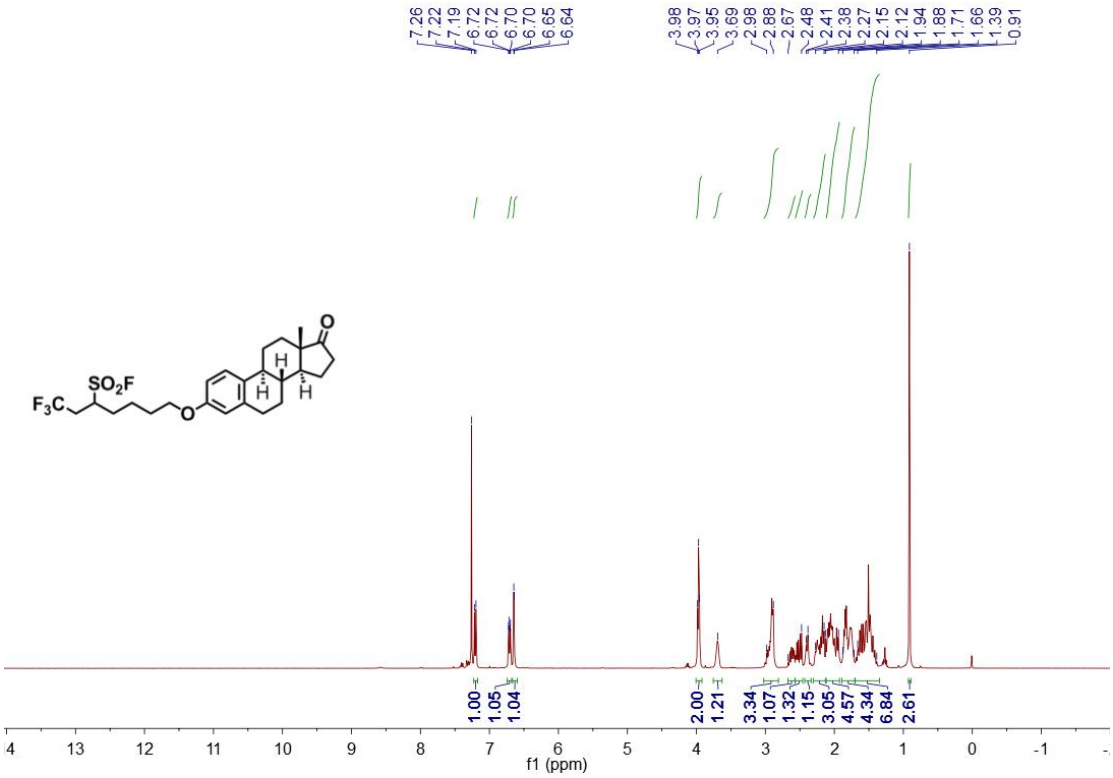
^{19}F NMR spectrum of 6,6'-(1,4-phenylenebis(oxy))bis(1,1,1-trifluorohexane-3-sulfonylfluoride) (3r)



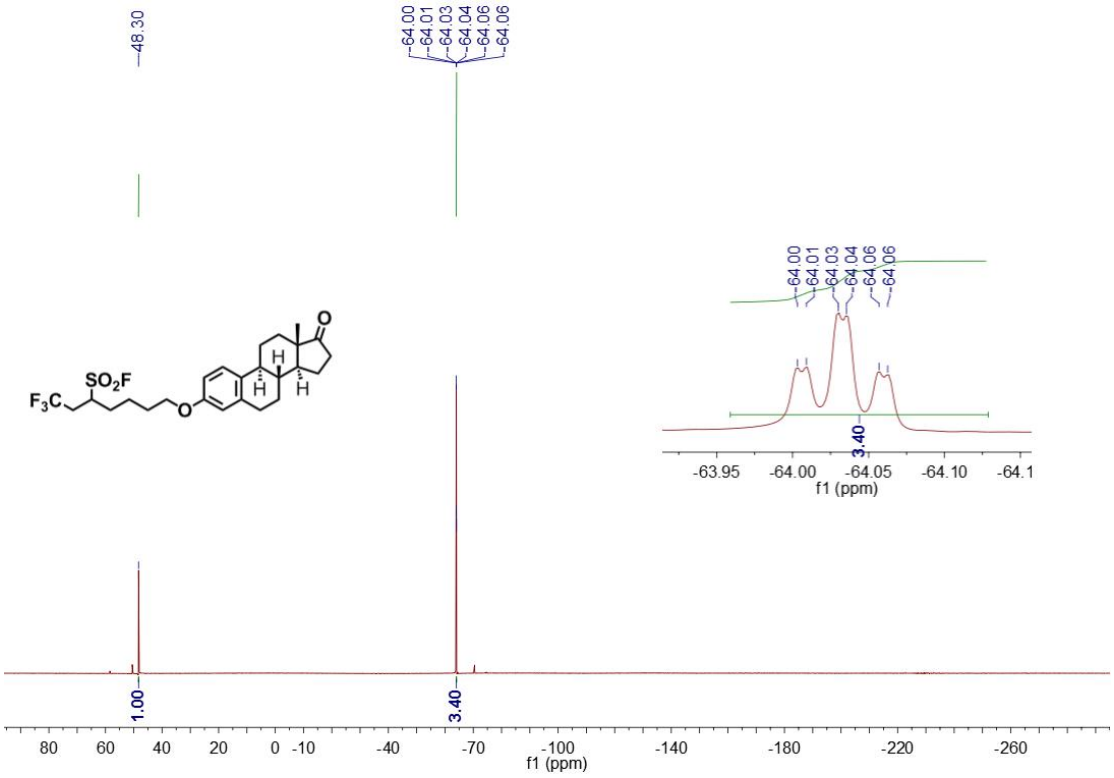
^{13}C NMR spectrum of 6,6'-(1,4-phenylenebis(oxy))bis(1,1,1-trifluorohexane-3-sulfonylfluoride) (3r)



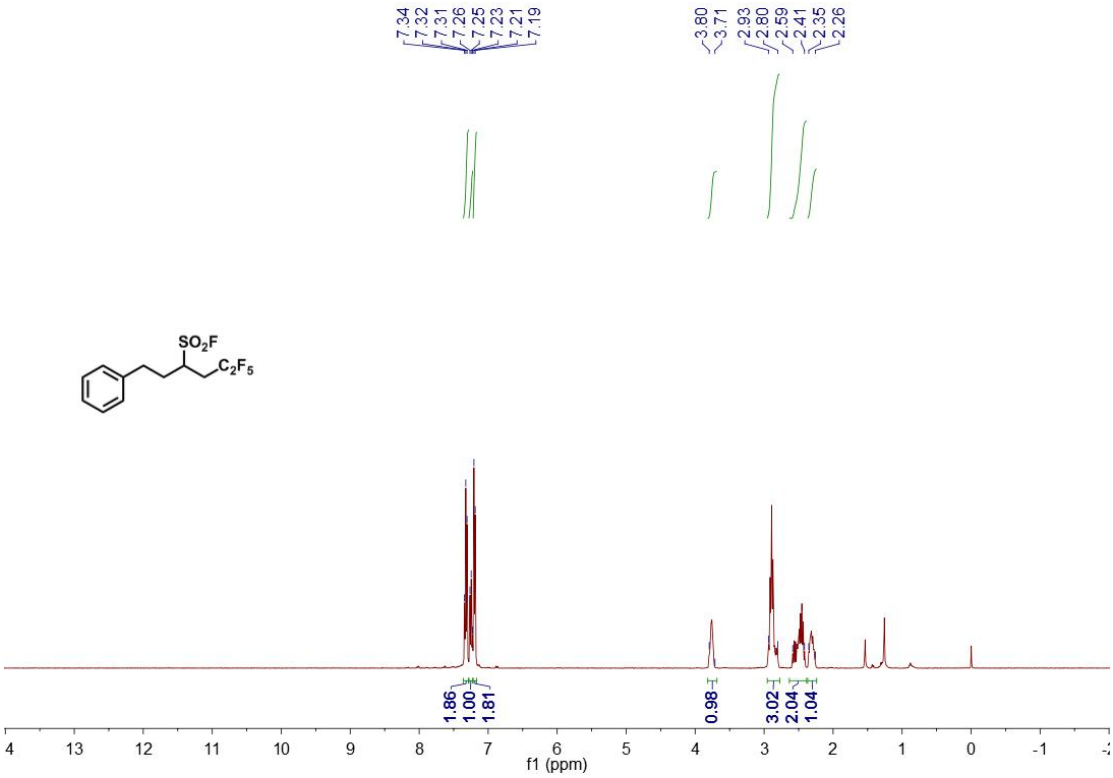
^{1}H NMR spectrum of 1,1,1-trifluoro-7-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy) heptane-3-sulfonyl fluoride (3s)



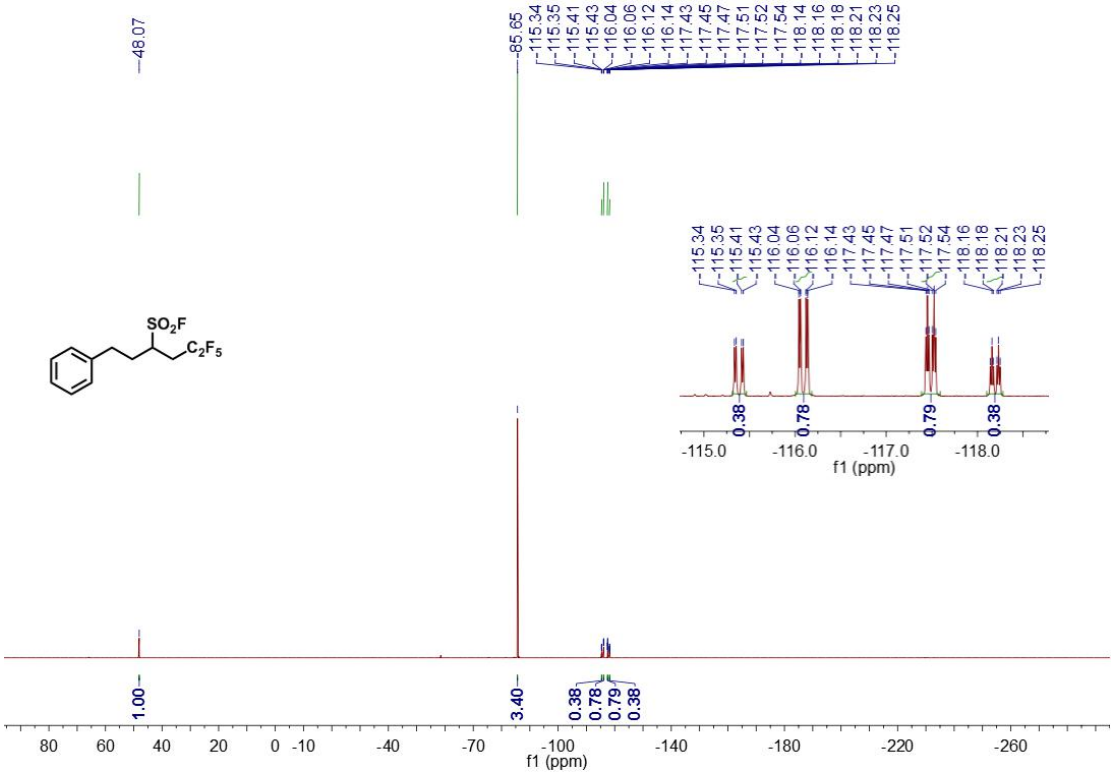
^{19}F NMR spectrum of 1,1,1-trifluoro-7-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy) heptane-3-sulfonyl fluoride (3s)



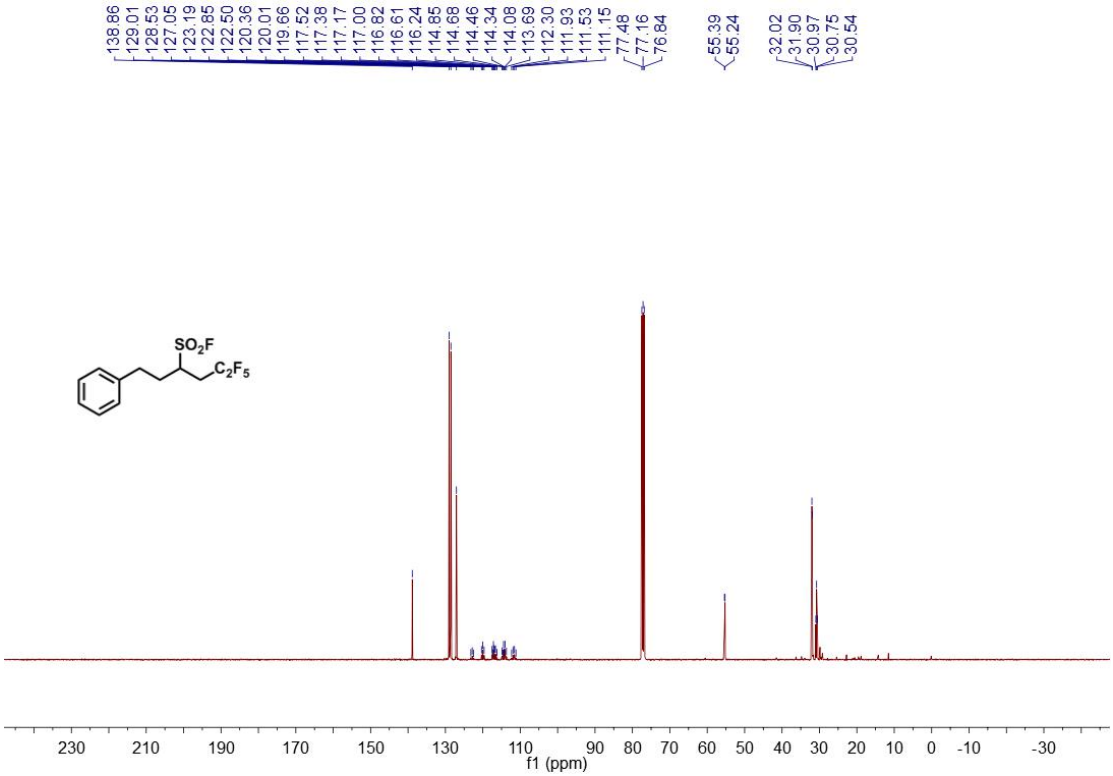
^{1}H NMR spectrum of 5,5,6,6,6-pentafluoro-1-phenylhexane-3-sulfonyl fluoride (3t)



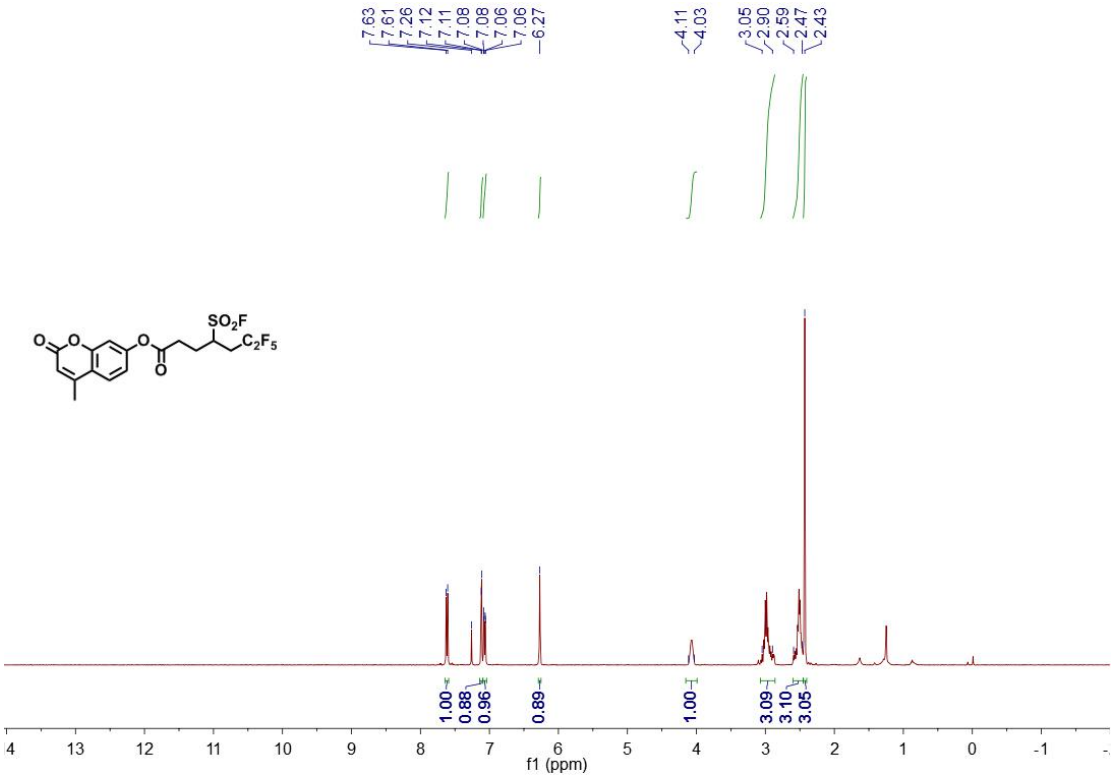
^{19}F NMR spectrum of 5,5,6,6,6-pentafluoro-1-phenylhexane-3-sulfonyl fluoride (3t)



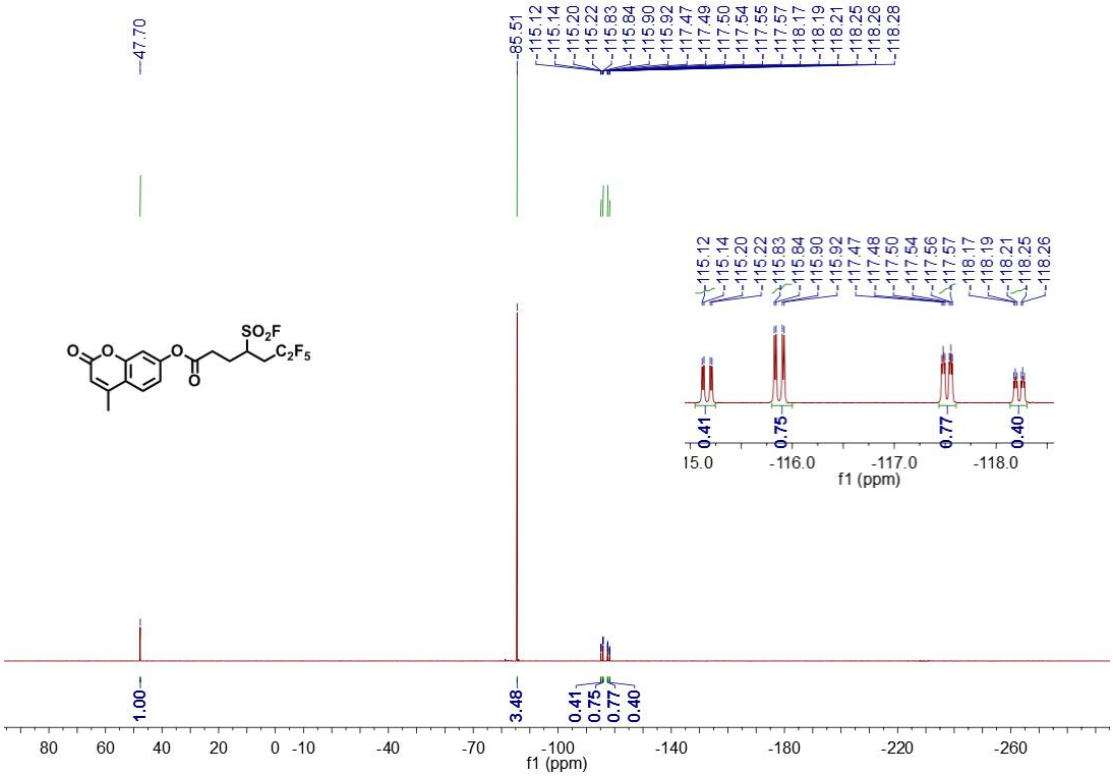
^{13}C NMR spectrum of 5,5,6,6,6-pentafluoro-1-phenylhexane-3-sulfonyl fluoride (3t)



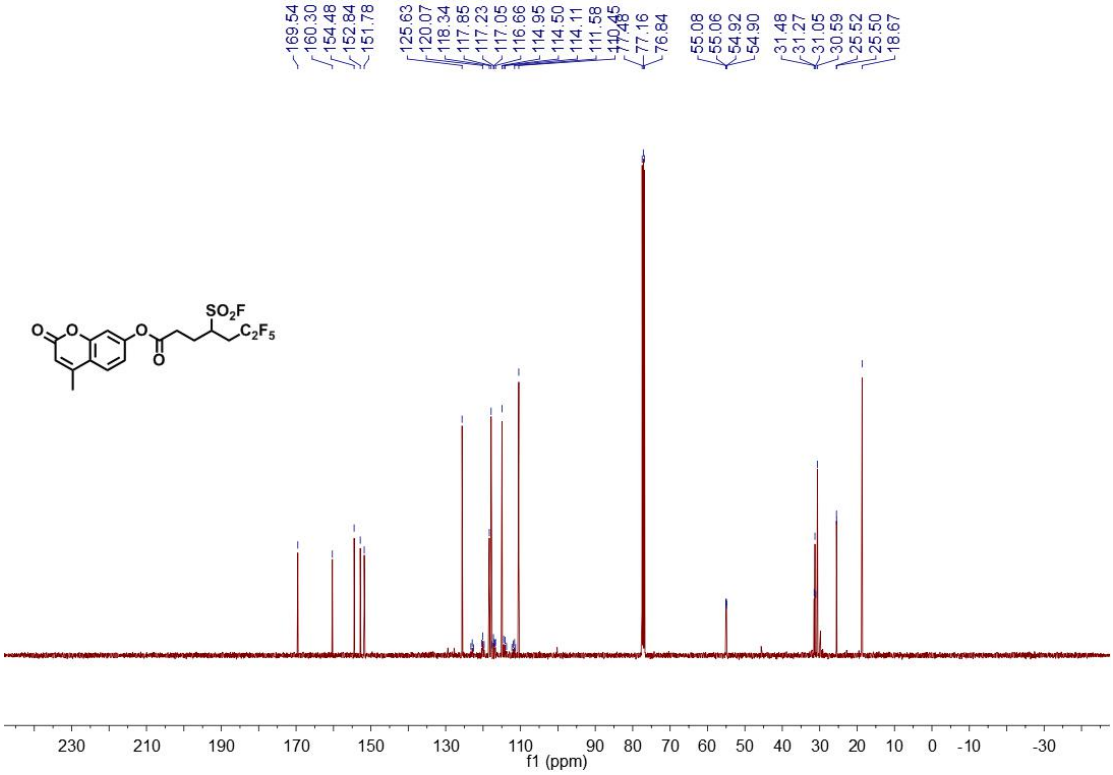
^{1}H NMR spectrum of 4-methyl-2-oxo-2H-chromen-7-yl 6,6,7,7,7-pentafluoro-4-(fluorosulfonyl)heptanoate (3u)



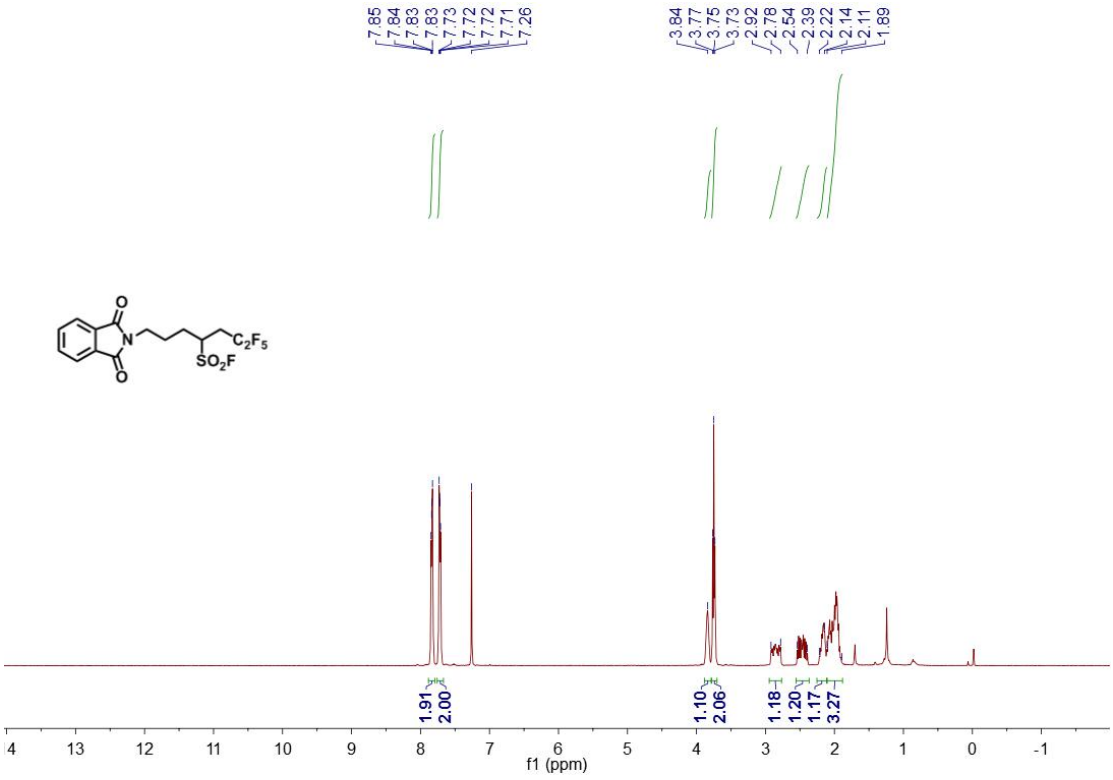
^{19}F NMR spectrum of 4-methyl-2-oxo-2H-chromen-7-yl 6,6,7,7,7-pentafluoro-4-(fluorosulfonyl)heptanoate (3u)



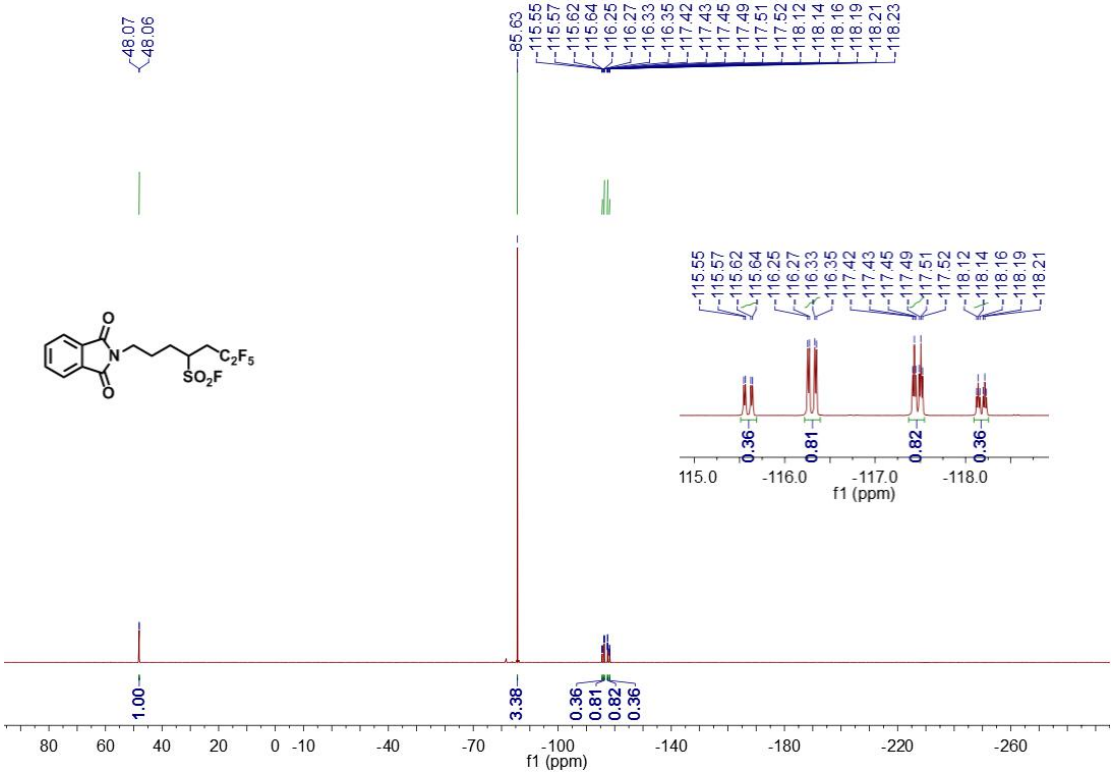
^{13}C NMR spectrum of 4-methyl-2-oxo-2H-chromen-7-yl 6,6,7,7,7-pentafluoro-4-(fluorosulfonyl)heptanoate (3u)



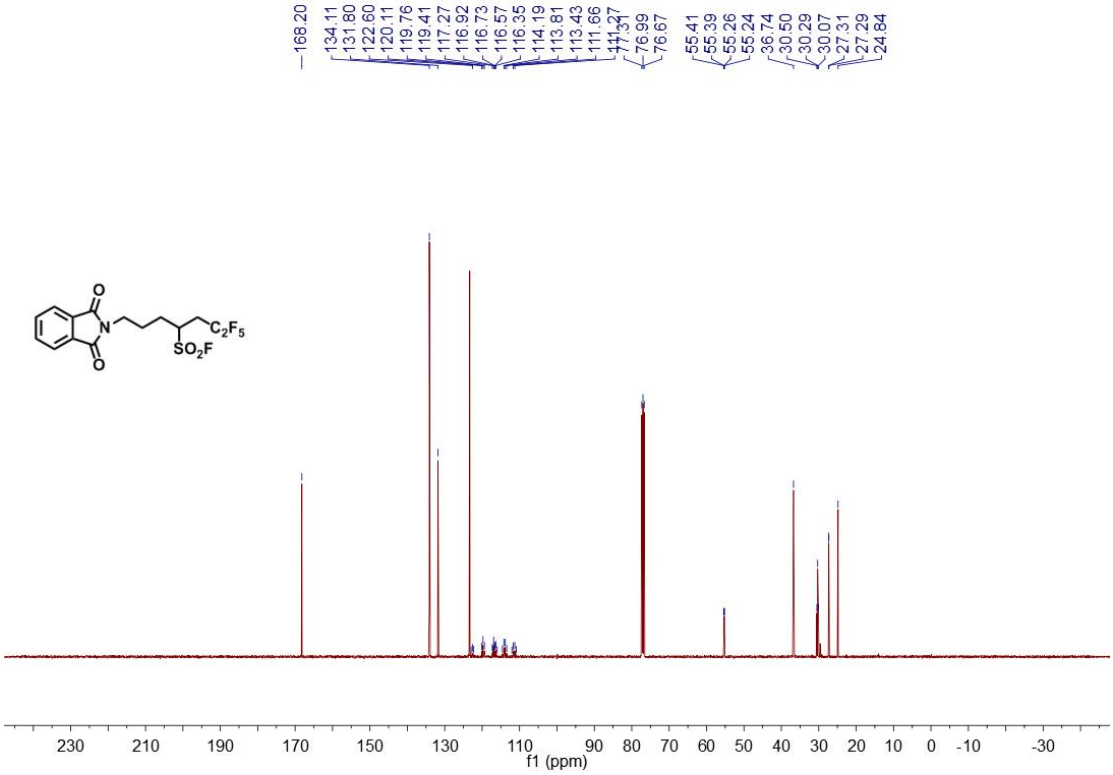
^{1}H NMR spectrum of 7-(1,3-dioxoisoindolin-2-yl)-1,1,1,2,2-pentafluoroheptane-4-sulfonyl fluoride (3v)



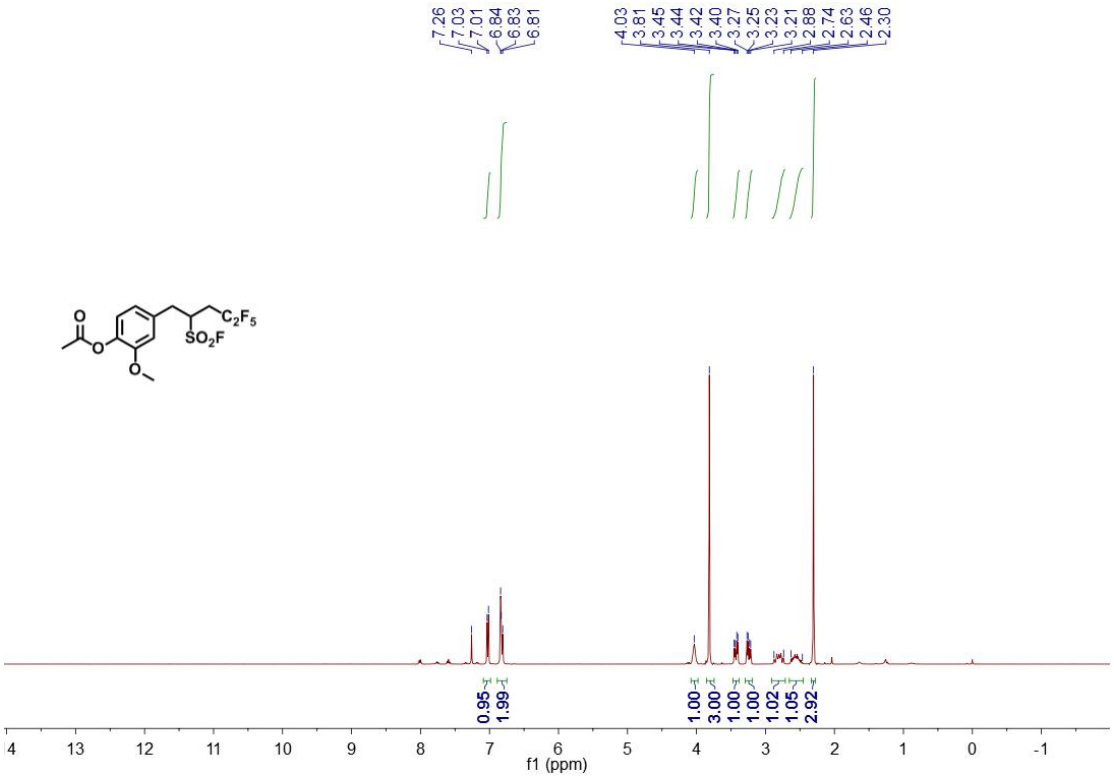
^{19}F NMR spectrum of
7-(1,3-dioxoisoindolin-2-yl)-1,1,1,2,2-pentafluoroheptane-4-sulfonyl fluoride (3v)



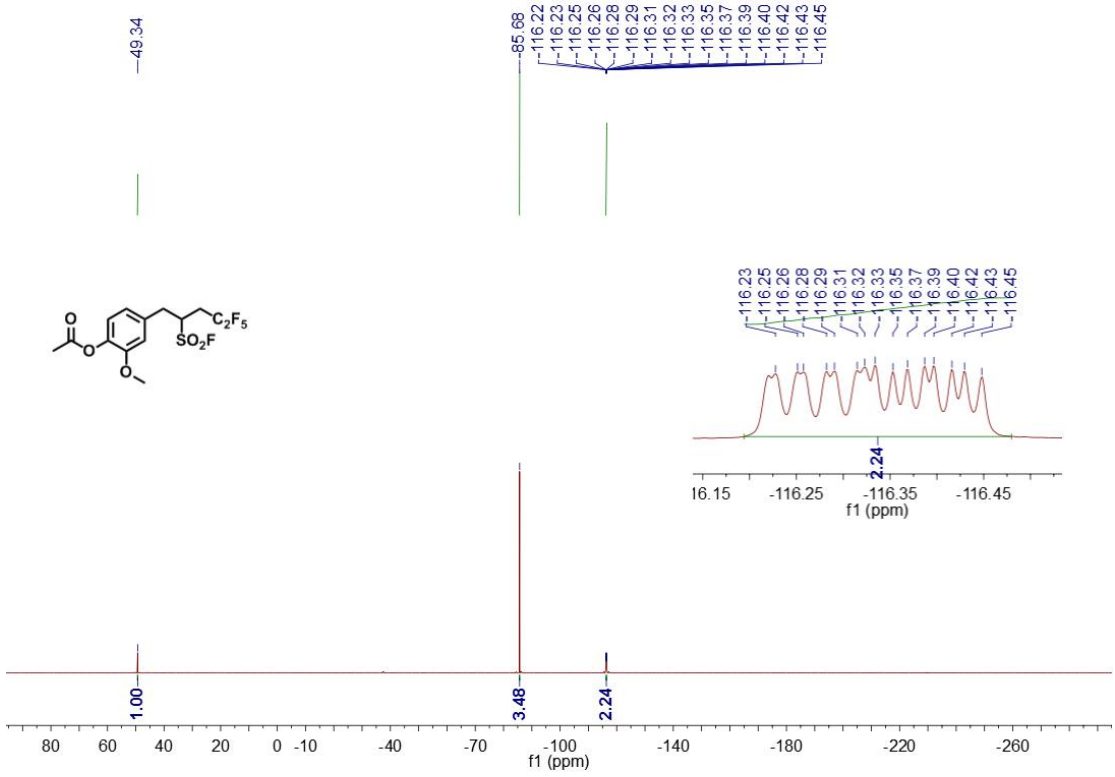
^{13}C NMR spectrum of
7-(1,3-dioxoisoindolin-2-yl)-1,1,1,2,2-pentafluoroheptane-4-sulfonyl fluoride (3v)



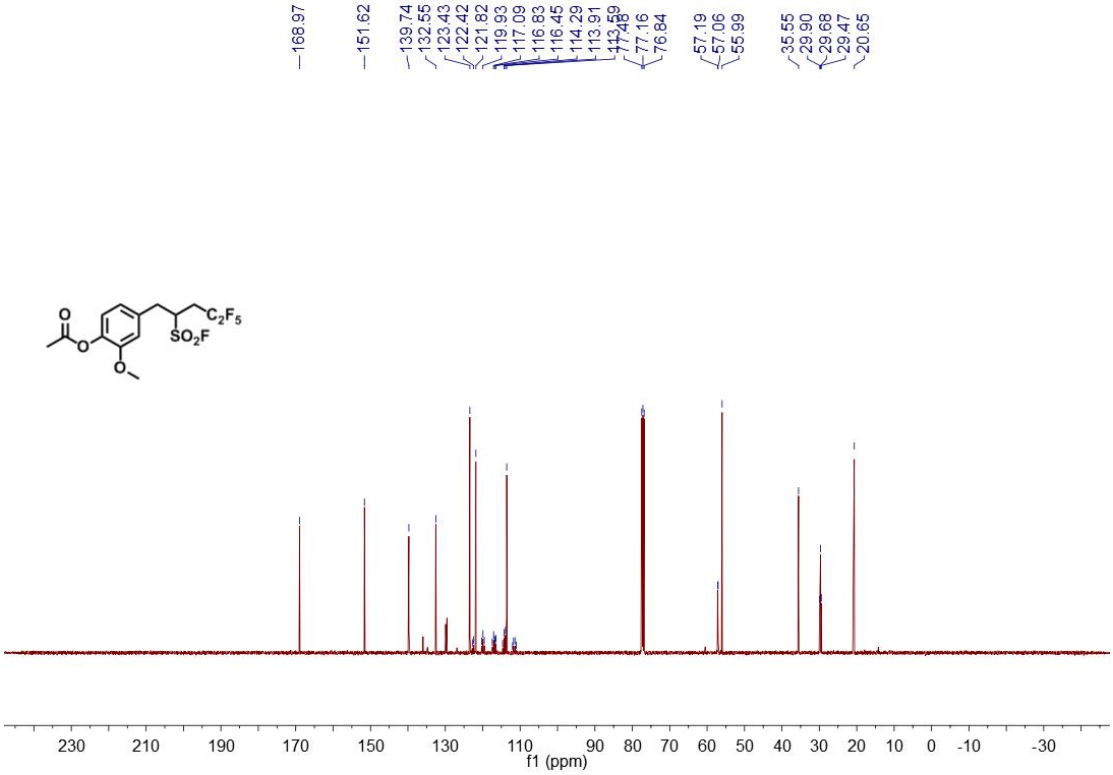
^{1}H NMR spectrum of
2-methoxy-4-(4,4,5,5,5-pentafluoro-2-(fluorosulfonyl)pentyl)phenyl acetate (3w)



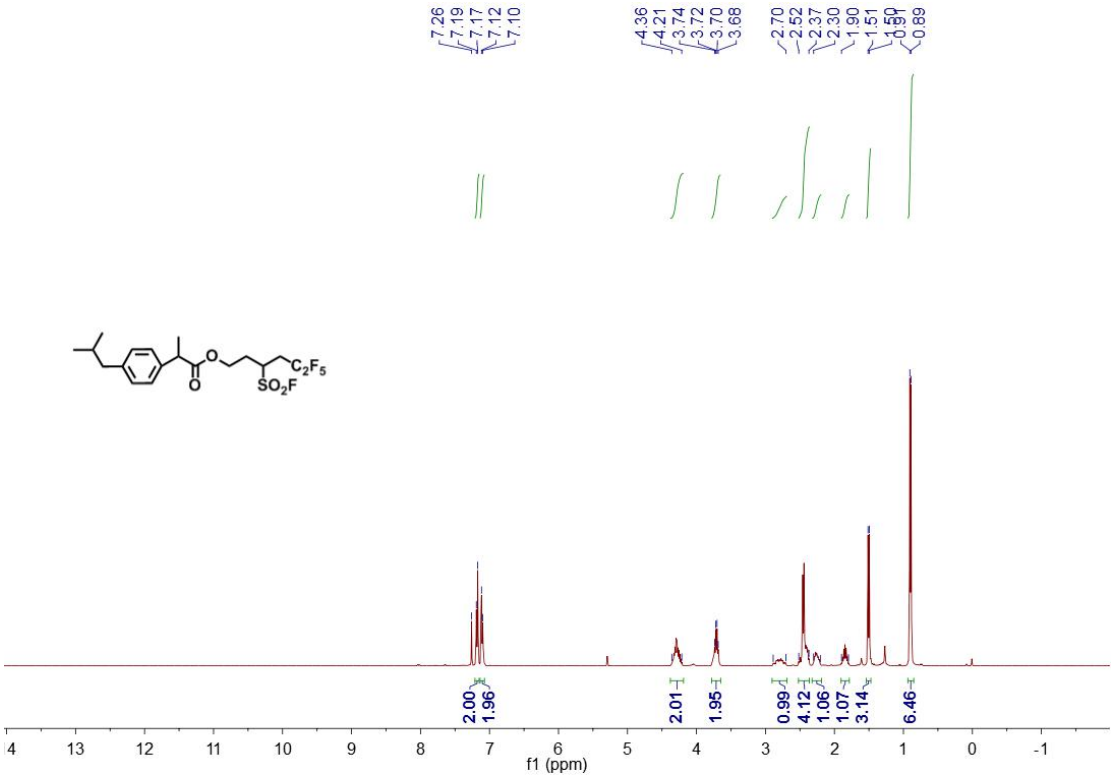
^{19}F NMR spectrum of
2-methoxy-4-(4,4,5,5,5-pentafluoro-2-(fluorosulfonyl)pentyl)phenyl acetate (3w)



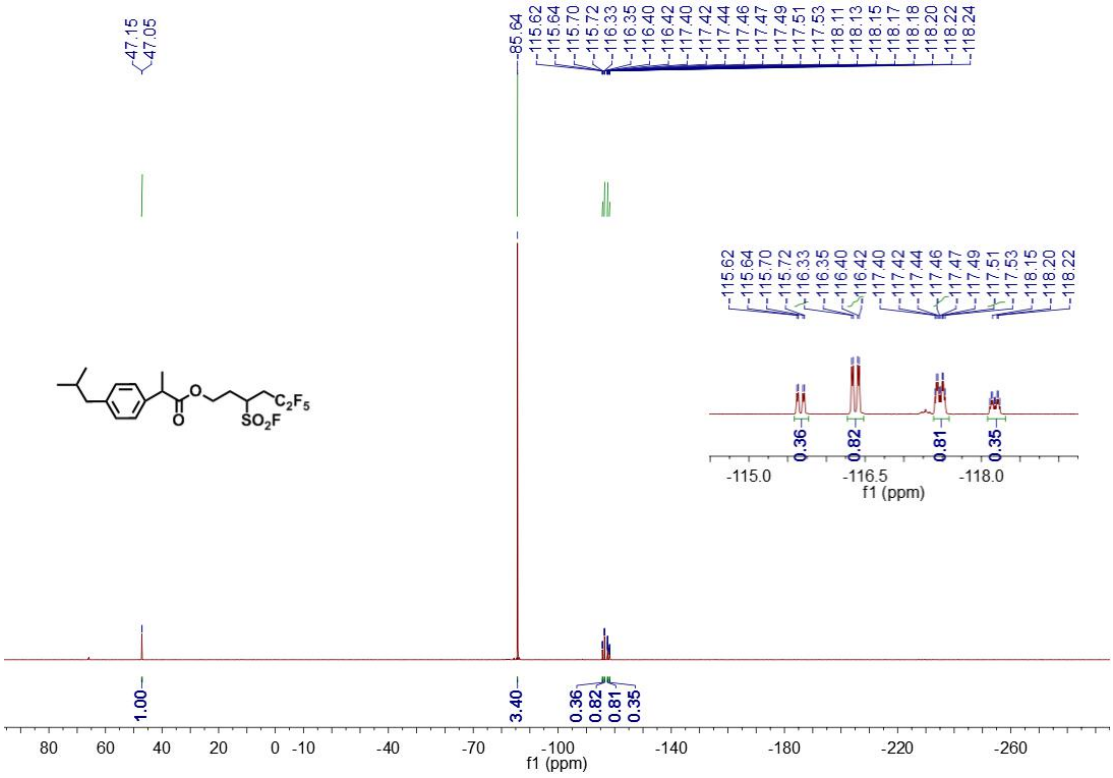
^{13}C NMR spectrum of
2-methoxy-4-(4,4,5,5,5-pentafluoro-2-(fluorosulfonyl)pentyl)phenyl acetate (3w)



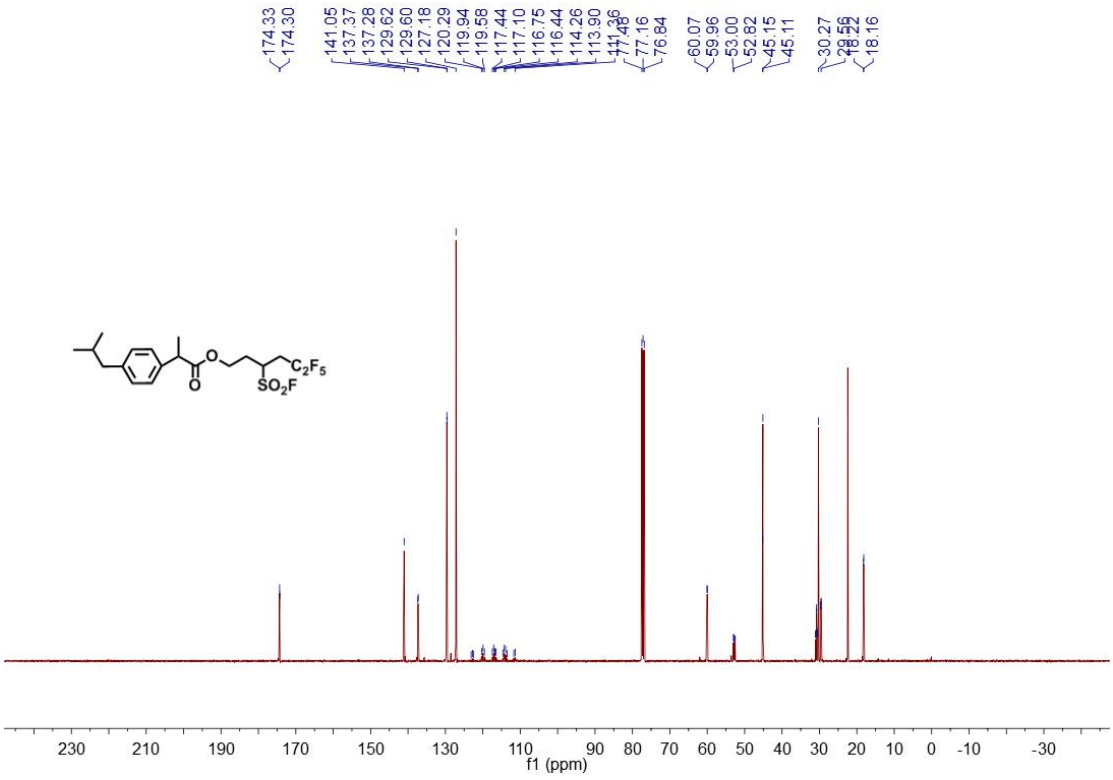
^{1}H NMR spectrum of 5,5,6,6,6-pentafluoro-3-(fluorosulfonyl)hexyl
2-(4-isobutylphenyl)propanoate (3x)



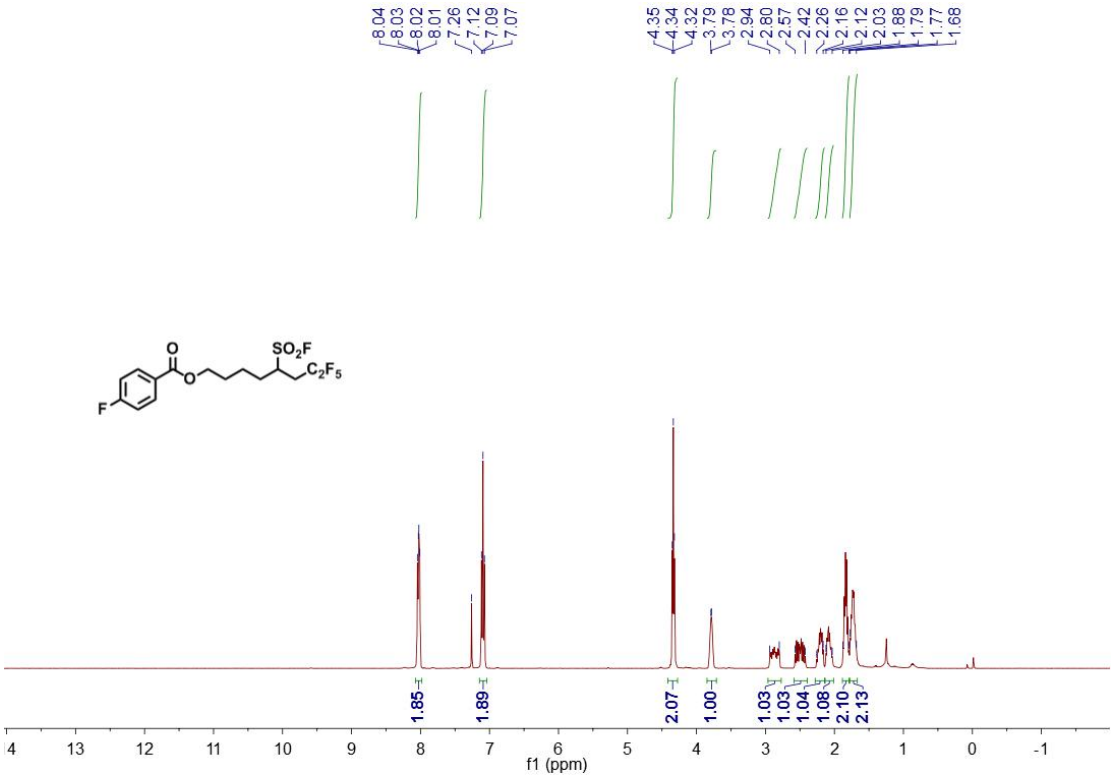
^{19}F NMR spectrum of 5,5,6,6,6-pentafluoro-3-(fluorosulfonyl)hexyl 2-(4-isobutylphenyl)propanoate (3x)



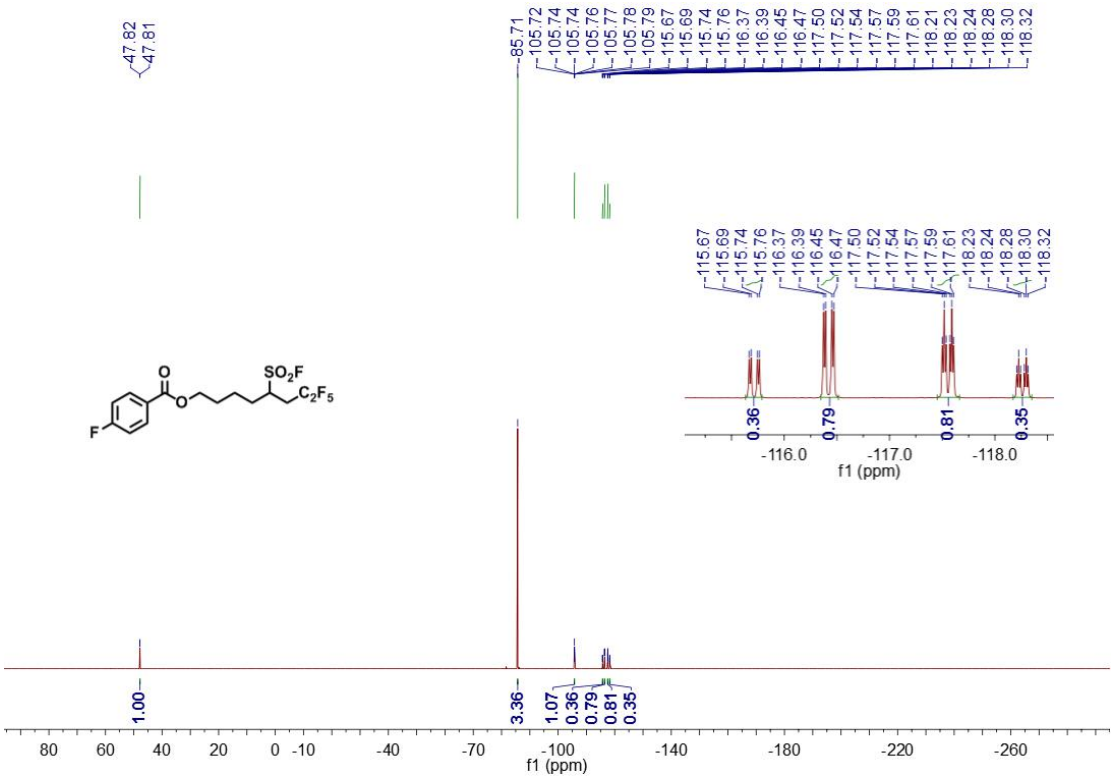
^{13}C NMR spectrum of 5,5,6,6,6-pentafluoro-3-(fluorosulfonyl)hexyl 2-(4-isobutylphenyl)propanoate (3x)



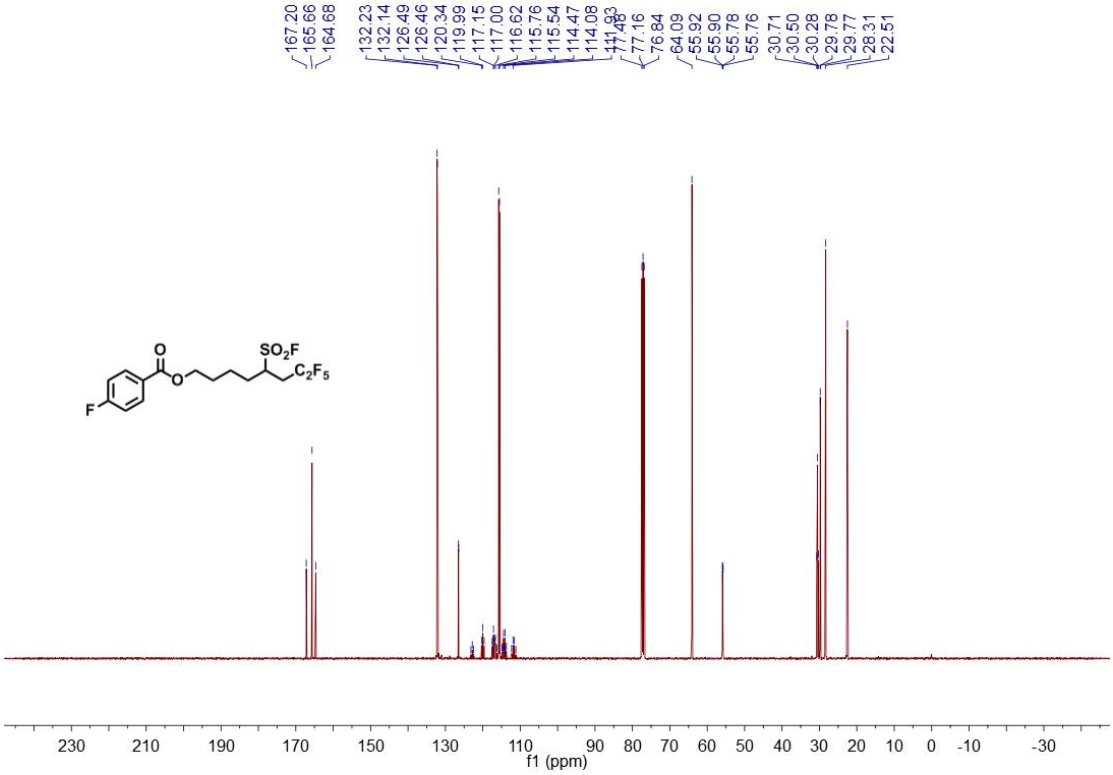
^{1}H NMR spectrum of
7,7,8,8,8-pentafluoro-5-(fluorosulfonyl)octyl 4-fluorobenzoate (3y)



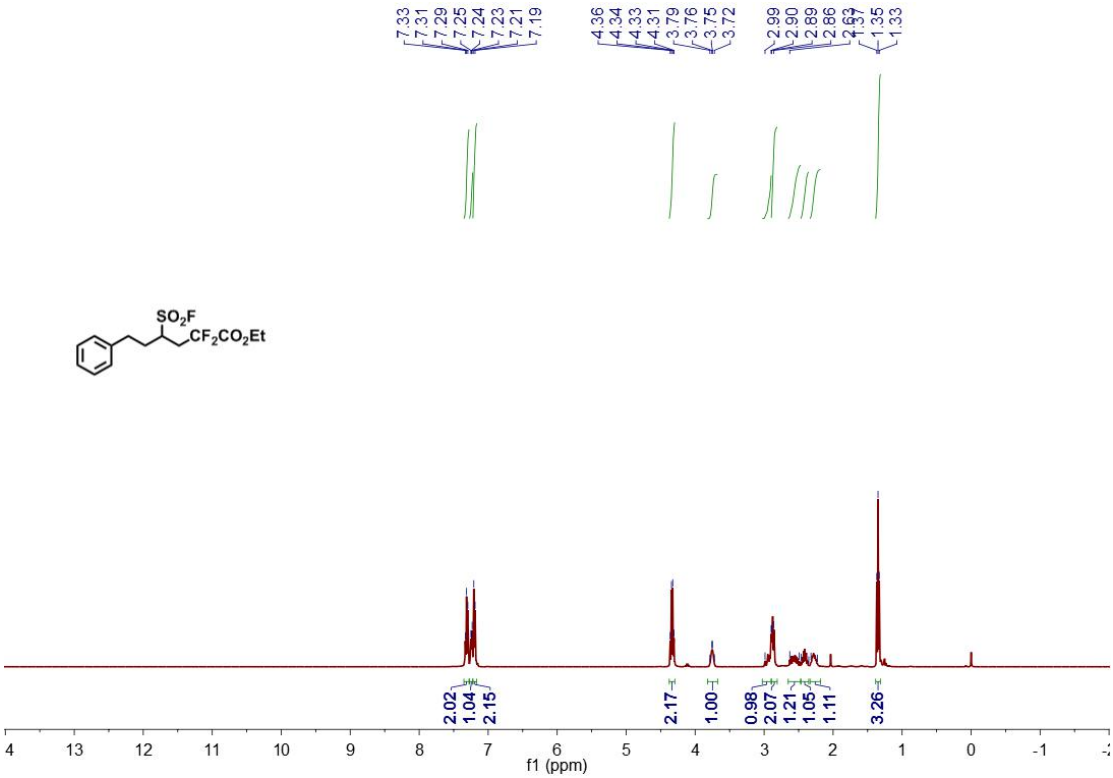
^{19}F NMR spectrum of
7,7,8,8,8-pentafluoro-5-(fluorosulfonyl)octyl 4-fluorobenzoate (3y)



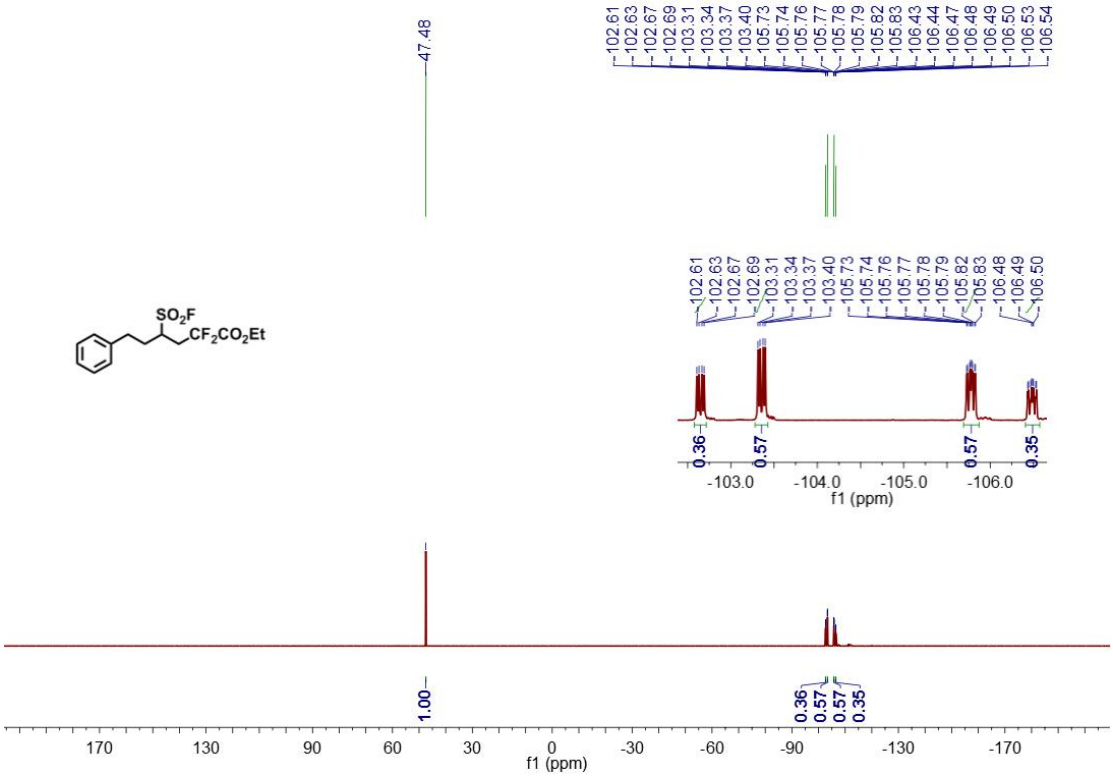
^{13}C NMR spectrum of
7,7,8,8,8-pentafluoro-5-(fluorosulfonyl)octyl 4-fluorobenzoate (3y)



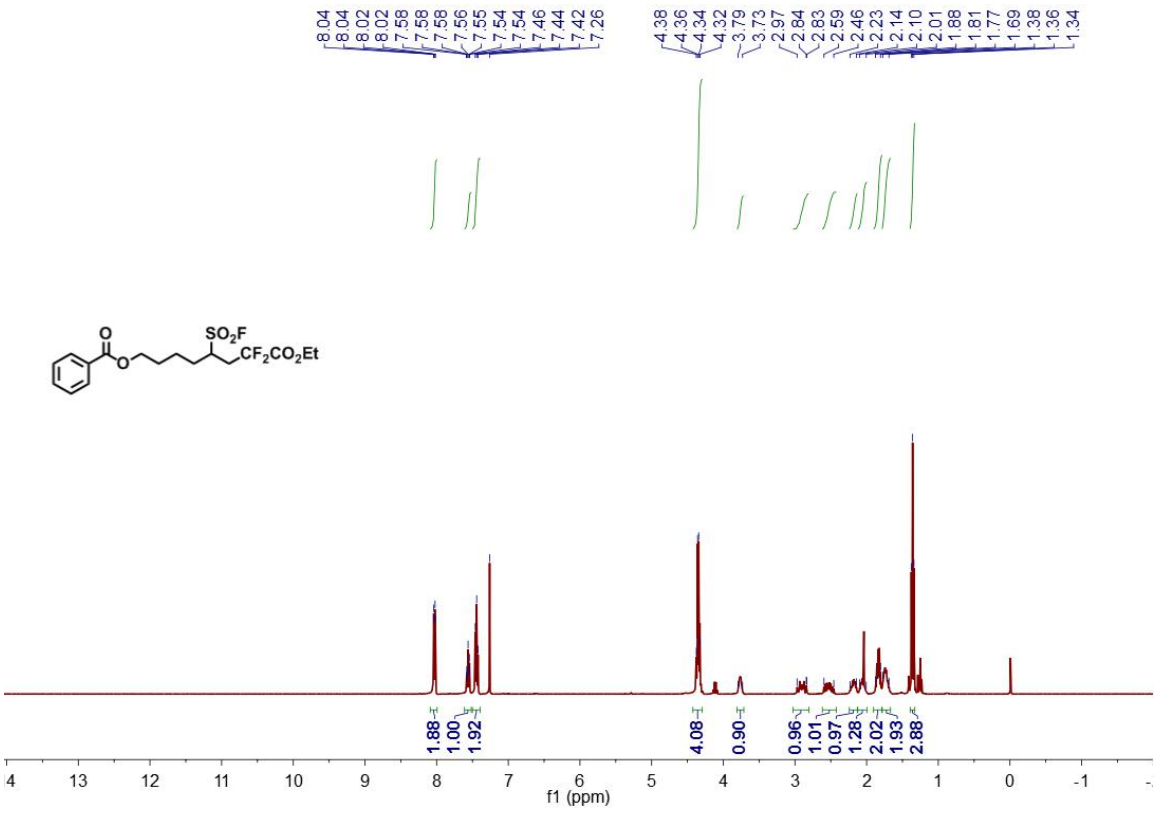
^{1}H NMR spectrum of ethyl 2,2-difluoro-4-(fluorosulfonyl)
-6-phenylhexanoate (3aa)



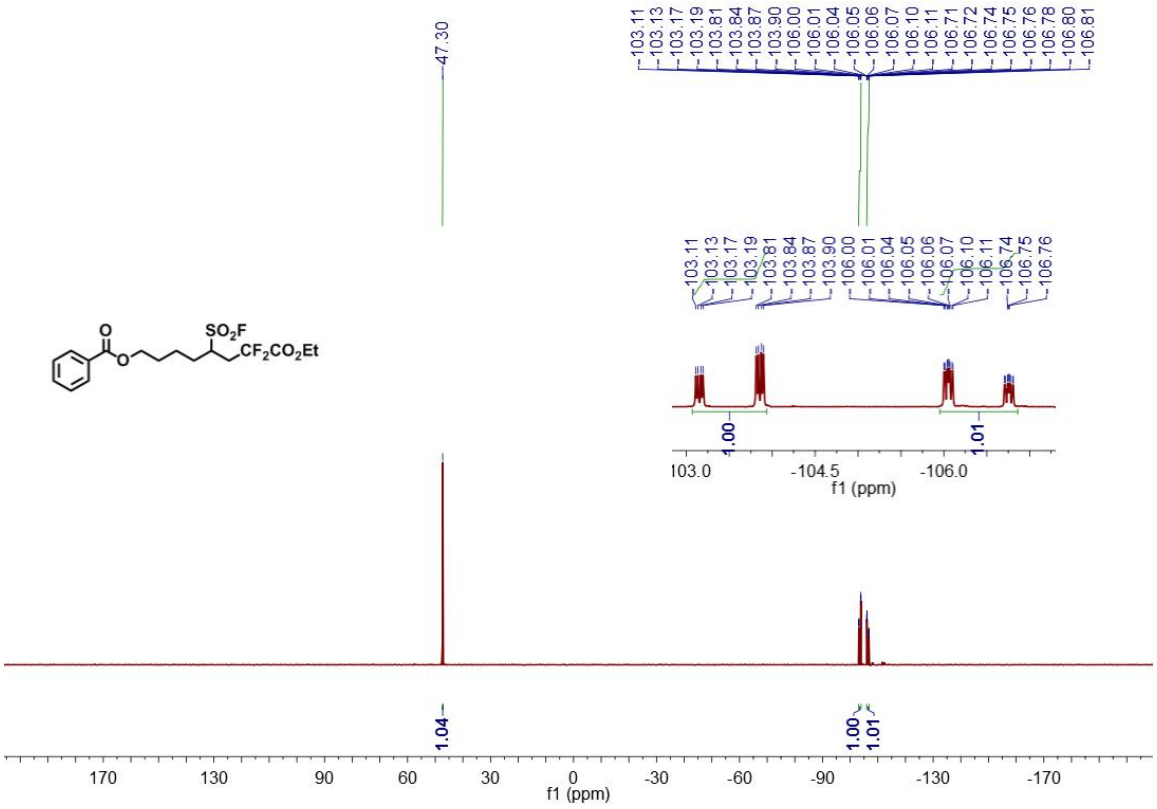
^{19}F NMR spectrum of ethyl 2,2-difluoro-4-(fluorosulfonyl) -6-phenylhexanoate (3aa)



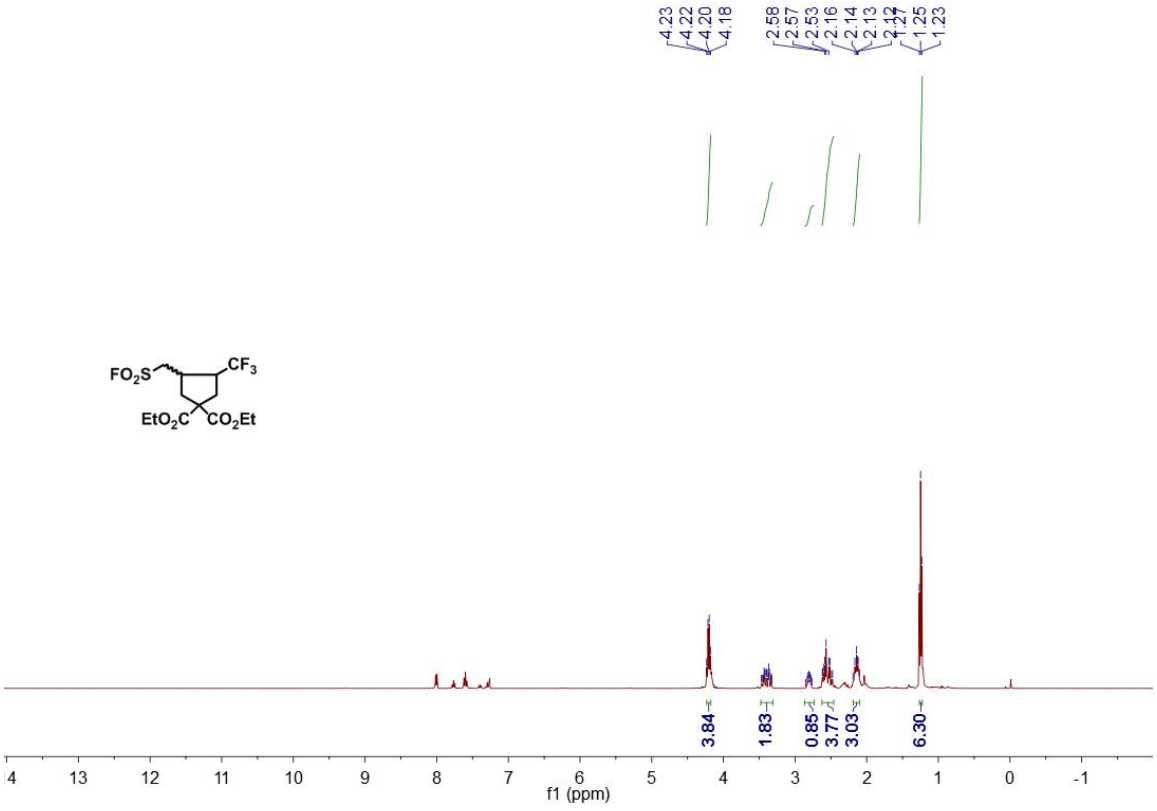
^{1}H NMR spectrum of 8-ethoxy-7,7-difluoro-5-(fluorosulfonyl)-8-oxooctyl benzoate (3bb)



^{19}F NMR spectrum of 8-ethoxy-7,7-difluoro-5-(fluorosulfonyl)-8-oxooctyl benzoate (3bb)



^{1}H NMR spectrum of diethyl3-((fluorosulfonyl)methyl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (6)



^{19}F NMR spectrum of diethyl 3-((fluorosulfonyl)methyl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (6)