Supporting information

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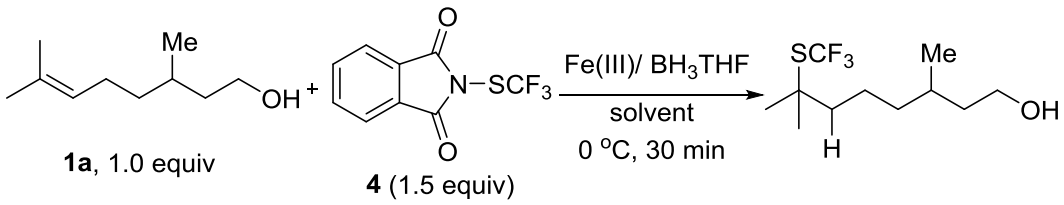
I. General information

All commercial reagents were used without further purification unless otherwise noted. All alkenes were commercially available or were synthesized by known procedures. All solvents were not purified and dried prior to use. ^{1}H NMR, ^{13}C NMR,^{19}FNMR spectra were recorded on a Agilent 400 M, Varian 300 M，400 M spectrometer. ^{1}H NMR and ^{13}C NMR spectra were internally referenced to tetramethylsilane signal or residual protio solvent signals. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), tt (triplet of triplet), dt (doublet of triplet), td (triplet of doublet); coupling constants (J) are in Hertz (Hz).

II. Optimization of reaction conditions for polysubstituted alkenes[a]

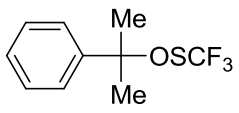


1a, 1.0 equiv

4 (1.5 equiv)

entry	Fe (x equiv)	solvent	yield[e]
1	$Fe(NO_3)_3{\cdot}9H_2O$ (1.5)	MeCN/H_2O = 1:1	18%
2	$Fe_2(ox)_3$ (1.5)	MeCN/H_2O = 1:1	Trace
3	$Fe_2(SO_4)_3$ (1.5)	MeCN/H_2O = 1:1	22%
4	$FeCl_3$ (1.5)	MeCN/H_2O = 1:1	5%
5	$Fe_2(SO_4)_3$ (1.5)	THF/H_2O = 1:1	Trace
6	$Fe_2(SO_4)_3$ (1.5)	EtOH/H_2O = 1:1	17%
7[b]	$Fe_2(SO_4)_3$ (3.0)	MeCN/H_2O = 1:1	46%
8[c]	$Fe_2(SO_4)_3$ (1.5)	MeCN/H_2O = 1:1	4%
9[d]	$Fe_2(SO_4)_3$ (1.5)	MeCN/H_2O = 1:1	5%

[a]Recation condition: **1a** (0.2 mmol), **4** (0.3 mmol), Fe salt (0.3 mmol), H source (1.0 mmol), solvent (10 mL) at 0 °C for 30 min; [b]Reagent **4** (0.6 mmol), Fe salt (0.6 mmol); [c]Reagent **2** was used as the trifluoromrthylthiolating reagent; [d]Reagent **9** was used as the trifluoromethylthiolating reagent; [e]Yields were determined by ^{19}F NMR spectroscopy in the presence of 1-fluoronaphthalene as an internal standard.



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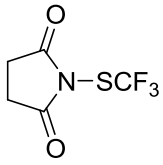

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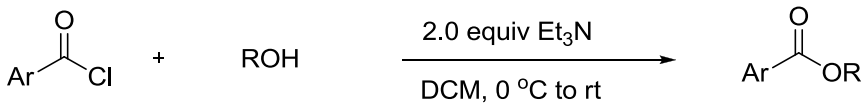
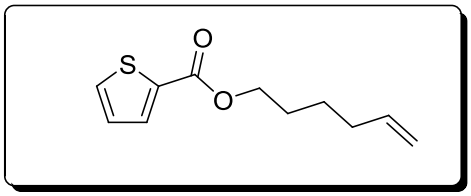
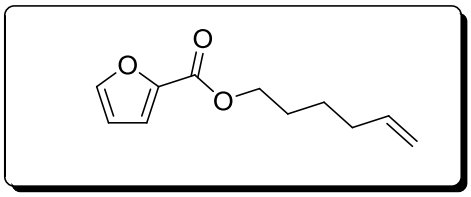
III. General procedure for preparation the alkenes.



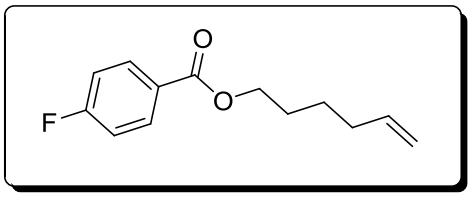
To a solution of alcohol (10 mmol), Et_3N (20 mmol), in CH_2Cl_2 (30 mL) was added dropwise with the corresponding acyl chloride (15 mmol) at 0 ^oC. The resulted mixture was vigorously stirred at room temperature. The reaction was monitored by TLC. After completed the reaction, the reaction mixture was treated with saturated aqueous $NaHCO_3$ (20 mL), and ethyl acetate (30 mL) was added. The organic layer was separated, and washed with water (3×20mL). The combined organic extracts were washed with brine (50 mL), and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by chromatography on silica gel to give the product.



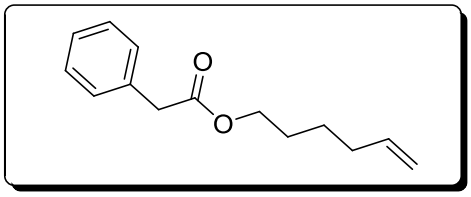
Hex-5-enyl thiophene-2-carboxylate (94% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.6, 0.9 Hz, 1 H), 7.54 (d, *J* = 4.8 Hz, 1 H), 7.09 (t, *J* = 4.8 Hz, 1 H), 5.81 (ddt, *J* =17.2, 10.4, 1.6 Hz, 1 H), 5.03 (dd, *J* = 17.2, 1.6 Hz, 1 H), 4.97 (dd, *J* = 10.4, 0.8 Hz, 1 H), 4.30 (t, *J* = 6.8 Hz, 2 H), 2.12 (m, 2 H), 1.76 (m, 2 H), 1.53 (m, 2 H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.26, 138.27, 134.00, 133.21, 132.15, 127.64, 114.83, 65.00, 33.22, 28.08, 25.18 ppm. IR (thin): ν_{max} 3077, 2937, 2859, 1710, 1640, 1525, 1419, 1358, 1279, 1259, 1096, 1076, 912, 860, 751, 719 cm^{-1}. MS (EI): m/z (%) 210, 129, 128, 111 (100%), 82, 67, 54, 41; HRMS for $C_{11}H_{14}O_2S$ Calcd: 210.0715; Found: 210.0713.



Hex-5-enyl furan-2-carboxylate[1] (96 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 1 H), 7.17 (m, 1 H), 6.50 (m, 1 H), 5.77-5.84 (m, 1 H), 5.02 (m, 1 H), 4.96 (m, 1 H), 4.31 (m, 2 H), 2.11 (m, 2 H), 1.76 (m, 2 H), 1.52 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.75, 146.13, 144.78, 138.18, 117.65, 114.82, 111.70, 64.77, 33.18, 28.04, 25.08 ppm.

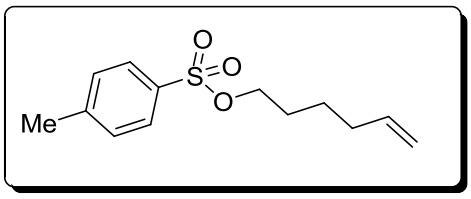


Hex-5-enyl 4-fluorobenzoate (98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.4, 2.8 Hz, 2 H), 7.13 (dd, *J* = 8.4, 8.4 Hz, 2 H), 5.81 (ddt, *J* = 17.2, 10.5, 1.2 Hz , 1 H), 5.03 (dd, *J* = 17.2, 1.2 Hz, 1 H), 4.98 (dd, *J* = 10.5, 0.8 Hz, 1 H), 4.32 (t, *J* = 6.4 Hz, 2 H), 2.13 (m, 2 H), 1.77 (m, 2 H), 1.55 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 252.1 Hz), 165.5, 138.2, 132.0 (d, *J* = 9.2 Hz), 126.7 (d, *J* = 3.1 Hz), 115.3 (d, *J* = 20.8 Hz), 114.7, 64.9, 33.2, 28.1, 25.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.1 (m, 1 F) ppm. IR (thin): ν_{max} 3078, 2938, 2861, 1720, 1603, 1508, 1411, 1274, 1238, 1153, 1114, 1090, 912, 854, 767 cm^{-1}. MS (EI): m/z (%) 222, 141, 124, 123 (100%); HRMS for $C_{13}H_{15}O_2F$ Calcd: 222.1056; Found: 222.1052.

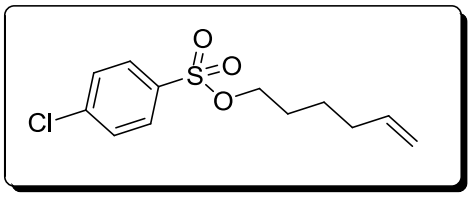


Hex-5-enyl 2-phenylacetate[2] (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 5 H), 5.75 (ddt, *J* = 17.6, 11.2, 1.4 Hz, 1 H), 5.04 (d, *J* = 17.6 Hz, 1 H), 4.95 (d, *J* = 11.2 Hz, 1 H), 4.08

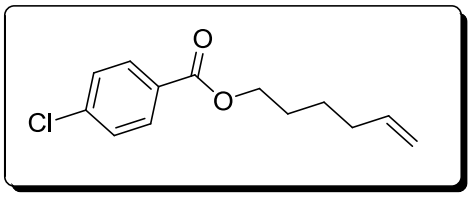
(t, *J* = 6.8 Hz, 2 H), 3.60 (s, 2 H), 2.03 (m, 2 H), 1.61 (m, 2 H), 1.39 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.58, 138.24, 134.10, 129.16, 128.40, 126.96, 114.73, 64.70, 41.39, 33.13, 27.92, 25.03 ppm.



Hex-5-enyl 4-methylbenzenesulfonate[3] (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 5.71 (m, 1 H), 4.92-4.97 (m, 2 H), 4.03 (t, *J* = 7.2 Hz, 2 H), 2.44 (s, 3 H), 2.00 (m, 2 H), 1.64 (m, 2 H), 1.40 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.63, 137.82, 133.10, 129.75, 127.78, 114.96, 70.37, 32.81, 28.11, 24.45, 21.52 ppm.

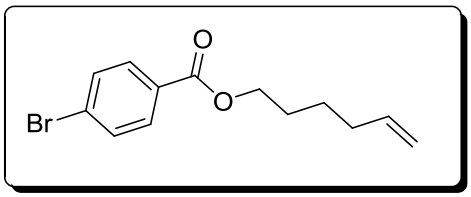


Hex-5-enyl 4-chlorobenzenesulfonate[3] (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.8, 1.2 Hz, 2 H), 7.53 (dd, *J* = 8.8, 1.2 Hz, 2 H), 5.72 (m, 1 H), 4.93-4.99 (m, 2 H), 4.07 (t, *J* = 6.4 Hz, 2 H), 2.01 (m, 2 H), 1.67 (m, 2 H), 1.41 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.28, 137.69, 134.66, 129.50, 129.20, 115.09, 70.89, 32.79, 28.10, 24.43 ppm.

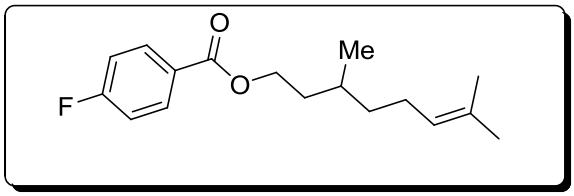


Hex-5-enyl 4-chlorobenzoate[4] (89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.40 (dd, *J* = 8.4, 1.2 Hz, 2 H), 5.81 (ddt, *J* = 16.8, 10.4, 1.2 Hz, 1 H), 5.03 (dd, *J* = 16.8, 1.6 Hz, 1 H), 4.98 (dd, *J* = 10.4, 1.2 Hz, 1 H), 4.32 (t, *J* = 6.8 Hz, 2 H), 2.12 (m, 2

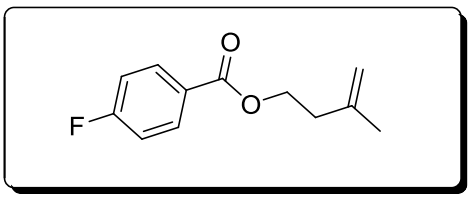
H), 1.78 (m, 2 H), 1.54 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 139.26, 138.25, 130.93, 128.92, 128.67, 114.94, 65.14, 33.29, 28.12, 25.28 ppm.



Hex-5-enyl 4-bromobenzoate[3] (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2 H), 7.57 (dd, *J* = 8.0, 1.2 Hz, 2 H), 5.81 (ddt, *J* = 17.2, 10.4, 1.6 Hz, 1 H), 5.03 (dd, *J* = 17.2, 1.6 Hz, 1 H), 4.98 (d, *J* = 10.4 Hz, 1 H), 4.31 (t, *J* = 6.4 Hz, 2 H), 2.12 (m, 2 H), 1.78 (m, 2 H), 1.54 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.86, 138.21, 131.64, 131.04, 129.33, 127.89, 114.9, 65.13, 33.24, 28.08, 25.24 ppm.

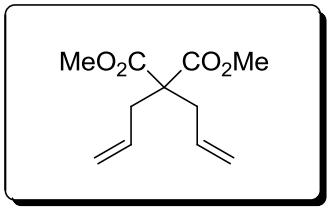


3,7-Dimethyloct-6-enyl 4-fluorobenzoate (92 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 2 H); 7.10 (dd, *J* = 8.8 Hz, 2 H), 5.09 (t, *J* = 7.2 Hz, 1 H), 4.35 (m, 2 H), 1.99 (m, 2 H), 1.82 (m, 1 H), 1.67 (s, 3 H), 1.60 (s, 3 H), 1.50-1.62 (m, 2 H), 1.40 (m, 1 H), 1.24 (m, 1 H), 0.97 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 252.4 Hz), 165.6, 132.0 (d, *J* = 9.2 Hz), 131.3, 126.7 (d, *J* = 3.0 Hz), 124.5, 115.4 (d, *J* = 21.8 Hz), 63.60, 36.92, 35.44, 29.51, 25.63, 25.34, 19.44, 17.58; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.0 (m, 1 F) ppm. IR (thin): ν_{max} 2963, 2926, 1720, 1604, 1508, 1458, 1411, 1379, 1274, 1238, 1153, 1113, 1090, 854, 767 cm^{-1}. MS (EI): m/z (%) 278, 138, 123 (100%), 95, 81, 75, 69, 55, 41; HRMS for $C_{17}H_{23}O_2F$ Calcd: 278.1682; Found: 278.1684.

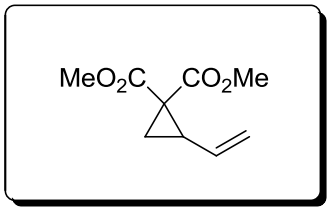


3-Methylbut-3-enyl 4-fluorobenzoate (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (m,

2 H), 7.09 (dd, *J* = 8.8, 8.8 Hz, 2 H), 4.82 (d, *J* = 14.0 Hz, 2 H), 4.49 (t, *J* = 6.8 Hz, 2 H), 2.48 (t, *J* = 6.8 Hz, 2 H), 1.81 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 252.1 Hz), 165.5, 141.6, 132.0 (d, *J* = 9.2 Hz), 126.6 (d, *J* = 3.0 Hz), 115.4 (d, *J* = 19.0 Hz), 112.4, 63.2, 36.7, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.9 (m, 1 F) ppm. IR (thin): ν_{max} 3078, 2969, 1720, 1650, 1604, 1508, 1455, 1411, 1376, 1274, 1238, 1153, 1115, 1090, 1014, 894, 854, 767 cm^{-1}. MS (EI): m/z (%) 208, 168, 140, 123 (100%), 95, 75, 68,59, 41. HRMS for $C_{12}H_{13}O_2F$ Calcd: 208.0900; Found: 208.0899.



Dimethyl 2,2-diallylmalonate[5] (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (m, 2 H), 5.11 (m, 2 H), 5.09 (m, 2 H), 3.72 (s, 6 H), 2.64 (d, *J* = 7.6 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.05, 132.21, 119.10, 57.56, 52.23, 36.87 ppm.



Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate[6] (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (m, 1 H), 5.30 (dd, *J* = 17.2, 1.2 Hz, 1 H), 5.15 (dd, *J* = 10.4, 1.2 Hz, 1 H), 3.75 (s, 6 H), 2.59 (dd, *J* = 16.8, 8.4 Hz, 1 H), 1.73 (dd, *J* = 7.6, 4.8 Hz, 1 H), 1.59 (dd, *J* = 8.4, 4.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.99, 167.76, 132.93, 118.67, 52.62, 35.71, 31.44, 20.57 ppm.

Reference

(1) A. T. Parsons, S. L. Buchwald, *Angew. Chem. Int. Ed*. 2011, **50**, 9120-9123.

(2) H. Kim, C. Lee, *Angew. Chem. Int. Ed*. 2012, **51**, 12303-12306.

(3) J. Xu, Y. Fu, D. Luo, Y. Jiang, B. Xiao, Z. Liu, T. Gong, L. Liu, *J. Am. Chem. Soc.* 2011, **133**, 15300-15303.

(4) X. Wu, L. Chu, F. Qing, *Angew. Chem. Int. Ed*. 2013, **52**, 2198-2202.

(5) C. Oliveira, E. Santo, J. Nunes, C. Correia *J. Org. Chem.* 2012, **77**, 8182 – 8190.

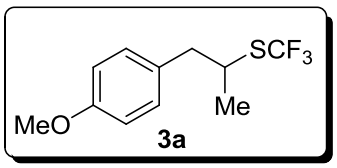
(6) A. P. Dieskau, M. S. Holzwarth, B. Plietker, *J. Am. Chem. Soc.* 2012, **134**, 5048.

IV. General procedure for Iron-mediated hydrotrifluoromethylthiotion of unactivated Alkenes

Procedure A: $Fe(NO_3)_3{\cdot}9H_2O$ (240 mg, 0.6 mmol) was dissolved in CH_3CN (10 mL) and H_2O (10 mL), The resulting solution was cooled to 0 ^oC and degassed for 10 min. The alkene (0.4 mmol) was added followed by the trifluoromethylthiolating reagent **2** (0.6 mmol). $BH_3{\cdot}THF$ (2.0 mL) was added dropwise via a syringe, The resulting mixture was stirred for 30 min, the mixture was extracted with dichloromethane (15 mL×3) and the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.

Procedure B: $Fe_2(SO_4)_3$ (240 mg, 0.6 mmol) was dissolved in CH_3CN (10 mL) and H_2O (10 mL). The resulting solution was cooled to 0 ^oC and degassed for 10 min. The alkene (0.4 mmol) was added followed by the trifluoromethylthiolating reagent **4** (0.6 mmol). $BH_3{\cdot}THF$ (2.0 mL) was added dropwise via a syringe. The resulting mixture was stirred for 30 min, the mixture was extracted with dichloromethane (15 mL×3) and the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.

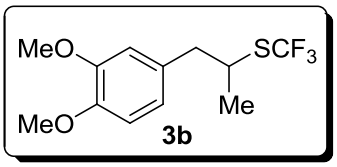
Procedure C: $Fe_2(SO_4)_3$ (480 mg, 0.6 mmol) was dissolved in CH_3CN (10 mL) and H_2O (10 mL). The resulting solution was cooled to 0 ^oC and degassed for 10 min. The alkene (0.4 mmol) was added followed by the trifluoromethylthiolating reagent **4** (1.2 mmol). $BH_3{\cdot}THF$ (2.0 mL) was added dropwise via a syringe. The resulting mixture was stirred for 30 min, the mixture was extracted with dichloromethane (15 mL×3) and the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.



3a

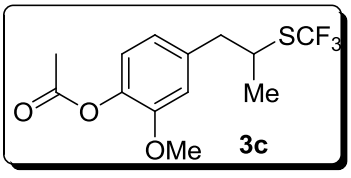
(1-(4-Methoxyphenyl)propan-2-yl)(trifluoromethyl)sulfane; Procedure A/B. petroleum ether/ethyl acetate = 100/1; 75% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 2 H), 6.85 (d, *J* = 8.0 Hz, 2 H), 3.80 (s, 3 H), 3.46-3.55 (m, 1 H), 3.02 (dd, *J* = 16.0, 8.0 Hz, 1

H), 2.74 (dd, *J* = 16.0, 8.0 Hz, 1 H), 1.35 (d, *J* = 4.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 131.1 (q, *J* = 304.0 Hz), 130.3, 129.8, 113.4, 55.23, 42.5, 42.2, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.01 (s, 3 F) ppm; IR (thin): ν_{max} 2960, 2925, 2853, 1512, 1437, 1260, 1183, 1117, 1015, 800, 721, 694 cm^{-1}. MS (EI): m/z (%) 250, 149, 122, 121 (100), 119, 91, 77; HRMS for $C_{11}H_{13}F_3OS$ Calcd: 250.0639; Found: 250.0641.



3b

(1-(3,4-Dimethoxyphenyl)propan-2-yl)(trifluoromethyl)sulfane; Procedure A/B. petroleum ether/ethyl acetate = 80/1; 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, *J* = 8.0 Hz, 1 H), 6.72 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.69 (d, *J* = 2.0 Hz, 1 H), 3.88 (s, 3 H), 3.87 (s, 3 H), 3.48-3.55 (m, 1 H), 3.02 (dd, *J* = 12.0, 8.0 Hz, 1 H), 2.75 (dd, *J* = 12.0, 8.0 Hz, 1 H), 1.36 (d, *J* = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 148.0, 131.1 (q, *J* = 305.0 Hz), 130.2, 121.4, 112.4, 111.2, 55.9, 55.8, 42.9, 42.1, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.98 (s, 3 F) ppm; IR (thin): ν_{max} 2998, 2935, 2836, 1591, 1516, 1465, 1418, 1246, 1239, 1191, 1114, 1029, 807, 767, 755 cm^{-1}. MS (EI): m/z (%) 280, 179, 152, 151 (100), 107, 105, 91, 77; HRMS for $C_{12}H_{15}F_3O_2S$ Calcd: 280.0745; Found: 280.0741.

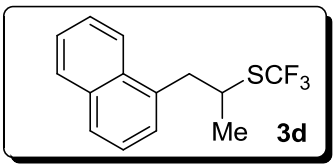


3c

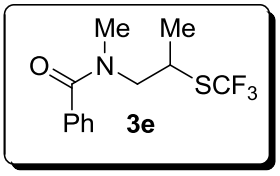
.

2-Methoxy-4-(2-(trifluoromethylthio)propyl)phenyl acetate; Procedure A/B. Petroleum ether/ethyl acetate = 50/1; 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.0 Hz, 1 H), 6.74- 6.77 (m, 2 H), 3.82 (s, 3 H), 3.50-3.58 (m, 1 H), 3.07 (dd, *J* = 16.0, 8.0 Hz, 1 H), 2.77 (dd, *J* = 16.0, 8.0 Hz, 1 H), 2.30 (s, 3 H), 1.37 (d, *J* = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 150.9, 138.7, 136.6, 131.0 (q, *J* = 305.0 Hz), 122.7, 121.4, 113.3, 55.8, 43.2, 41.7, 21.1, 20.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.02 (s, 3 F) ppm; IR (thin): ν_{max} 2967, 2938, 2874, 2848, 1766, 1605, 1511, 1465, 1420, 1370, 1282, 1201, 1114, 1035, 1012, 905,

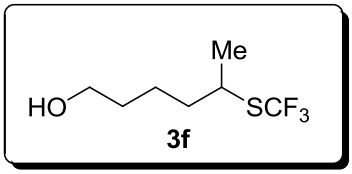
849, 755 cm^{-1}. MS (EI): m/z (%) 308, 266, 165, 138, 137 (100 %), 122, 105, 77, 43; HRMS for $C_{13}H_{15}F_3O_3S$ Calcd: 308.0694; Found: 308.0689.



(1-(Naphthalen-1-yl)propan-2-yl)(trifluoromethyl)sulfane; Procedure A/B . Petroleum; 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.54 (ddd, *J* = 8.0, 8.0, 4.0 Hz, 1 H), 7.48 (ddd, *J* = 8.0, 8.0, 4.0 Hz, 1 H), 7.40 (d, *J* = 8.0, 8.0 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 3.70-3.77 (m, 1 H), 3.65 (dd, *J* = 16.0, 8.0 Hz, 1 H), 3.12 (dd, *J* = 16.0, 8.0 Hz, 1 H), 1.34 (d, *J* = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 133.9, 131.8, 131.2 (q, *J* = 304.0 Hz), 129.0, 127.9, 127.8, 126.3, 125.7, 125.3, 123.3, 41.1, 40.9, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.69 (s, 3 F) ppm. IR (thin): ν_{max} 3063, 2969, 2929, 2871, 1510, 1458, 1395, 1380, 1149, 1114, 1016, 798, 790, 756 cm^{-1}. MS (EI): m/z (%) 270, 168, 167, 153, 152, 142, 141 (100), 115; HRMS for $C_{14}H_{13}F_3S$ Calcd: 270.0690; Found: 270.0691.

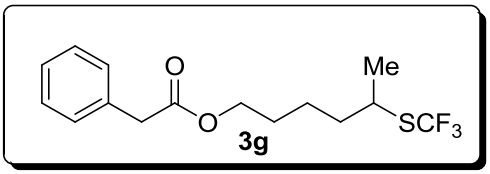


***N*-Methyl-N-(2-(trifluoromethylthio)propyl)benzamide; Procedure A/B.** Petroleum ether/ethyl acetate = 30/1; 42 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 5 H), 3.79 (br, 2 H), 3.57-3.64 (m, 1 H), 3.04 (s, 3 H), 1.50 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 135.9, 131.0 (q, *J* = 309.3 Hz), 129.2, 128.4, 126.9, 52.9, 39.2, 39.0, 20.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.01 (s, 3 F) ppm; IR (thin): ν_{max} 3061, 2967, 2930, 1637, 1622, 1499, 1448, 1400, 1287, 1114, 1096, 789, 700 cm^{-1}. MS (EI): m/z (%) 272, 208, 149, 148, 106, 105 (100 %), 77, 51, 42; HRMS for $C_{12}H_{14}F_3NOS$ Calcd: 277.0748; Found: 277.0743.



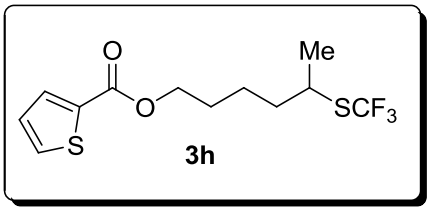
5-(Trifluoromethylthio)hexan-1-ol; Procedure A/B. Petroleum ether/ethyl acetate = 15/1 to

10/1; 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (d, *J* = 8.0 Hz, 2 H), 3.32 (m, 1 H), 1.62-1.69 (m, 3 H), 1.53-1.57 (m, 2 H), 1.49- 1.52 (m, 2 H), 1.43 (d, *J* = 4.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.2 (q, *J* = 305.0 Hz), 62.5, 41.1, 36.6, 32.2, 22.9, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.21 (s, 3 F) ppm; IR (thin): ν_{max} 3378, 2929, 2857, 1730, 1459, 1381, 1147, 1126, 756, 668 cm^{-1}. MS (EI): m/z (%) 202, 142, 133, 129, 115 (100), 99, 83, 67, 55; HRMS for $C_7H_{13}F_3OS$ Calcd: 202.0639; Found: 202.0642.



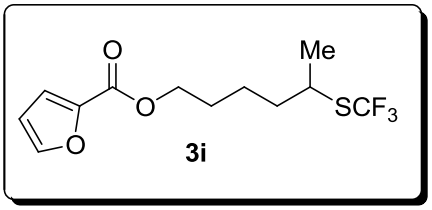
3g

5-(Trifluoromethylthio)hexyl 2-phenylacetate; Procedure A/B. Petroleum ether/ethyl acetate = 60/1; 75 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.43 (m, 5 H), 4.09 (t, *J* = 6.4 Hz, 2 H), 3.61 (s, 2 H), 3.21-3.29 (m, 1 H), 1.57-1.67 (m, 4 H), 1.41-1.48 (m, 2 H), 1.38 (d, *J* = 7.2 Hz, 3 H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 134.1, 131.2 (q, *J* = 304.2 Hz), 129.2, 128.5, 127.1, 64.4, 41.5, 40.9, 36.3, 28.1, 22.9, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.16 (s, 3 F) ppm; IR (thin): ν_{max} 2953, 2868, 1736, 1496, 1455, 1341, 1257, 1116, 1029, 756, 723 cm^{-1}. HRMS (ESI) for $C_{15}H_{19}F_3O_2S$ Na (M+Na^{+}) Calcd: 343.0956; Found: 343.0950.

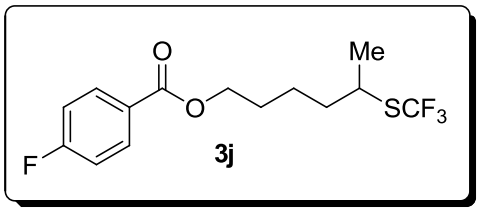


3h

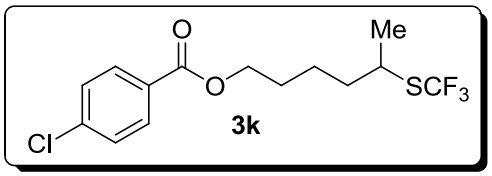
5-(Trifluoromethylthio)hexyl thiophene-2-carboxylate; Procedure A/B. Petroleum ether/ethyl acetate = 60/1; 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.6, 1.2 Hz, 1 H), 7.55 (dd, *J* = 4.8, 3.6 Hz, 1 H), 7.10 (dd, *J* = 4.8, 1.2 Hz, 1 H), 4.31 (t, *J* = 4.0 Hz, 2 H), 3.28-3.35 (m, 2 H), 1.74-.181 (m, 2 H), 1.65-1.70 (m, 2 H), 1.55-1.61 (m, 2 H), 1.43 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 133.9, 133.4, 132.3, 131.1 (q, *J* = 304.0 Hz), 127.7, 64.7, 41.0, 36.4, 28.3, 23.1, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.58 (s, 3 F) ppm; IR (thin): ν_{max} 2956, 2867, 1712, 1526, 1459, 1420, 1359, 1261, 1225, 1111, 1083, 860, 752 cm^{-1}. HRMS (ESI) for $C_{12}H_{15}F_3O_2S_2$ Na (M+Na^{+}) Calcd: 335.0363; Found: 335.0358.



5-(Trifluoromethylthio)hexyl furan-2-carboxylate; Procedure A/B. Petroleum ether/ethyl acetate = 60/1; 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 1 H), 7.17 (dd, *J* = 3.6, 0.8 Hz, 1 H), 6.51 (dd, *J* = 3.6, 1.6 Hz, 1 H), 4.32 (t, *J* = 6.4 Hz, 2 H), 3.28-3.36 (m, 1 H), 1.76-1.81 (m, 2 H), 1.64-1.73 (m, 2 H), 1.52-1.59 (m, 2 H), 1.43 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 146.2, 144.7, 131.1 (q, *J* = 304.0 Hz), 117.8, 111.8, 64.5, 40.9, 36.4, 28.3, 23.0, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.17 (s, 3 F) ppm; IR (thin): ν_{max} 2955, 2934, 2868, 1731, 1581, 1475, 1400, 1297, 1181, 1113, 1013, 763 cm^{-1}. HRMS (ESI) for $C_{12}H_{15}F_3O_3S$ Na (M+Na$^+$) Calcd: 319.0592; Found: 319.0586.

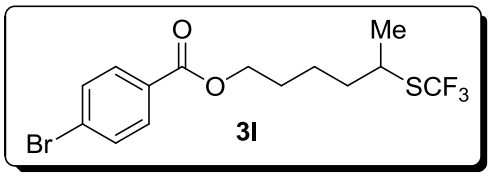


5-(Trifluoromethylthio)hexyl 4-fluorobenzoate; Procedure A/B. Petroleum ether/ethyl acetate = 60/1; 64 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.8 Hz, 2 H), 7.11 (dd, *J* = 8.8, 8.8 Hz, 2 H), 4.32 (t, *J* = 6.4 Hz, 2 H), 3.29-3.37 (m, 1 H), 1.76-1.83 (m, 2 H), 1.63-1.74 (m, 2 H), 1.58- 1.63 (m, 2 H), 1.43 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 252.0 Hz), 165.5, 132.1 (d, *J* = 9.2 Hz), 131.1 (q, *J* = 304.0 Hz), 126.5 (d, *J* = 3.0 Hz), 115.5 (d, *J* = 21.8 Hz), 64.7, 41.0, 36.5, 28.3, 23.2, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.15 (s, 3 F), -105.9 (m, 1 F) ppm; IR (thin): ν_{max} 2956, 2868, 1721, 1604, 1508, 1276, 1152, 1111, 854, 768 cm^{-1}. HRMS (ESI) for $C_{14}H_{16}F_4O_2S$ Na (M+Na$^+$) Calcd: 347.0705; Found: 347.0699.

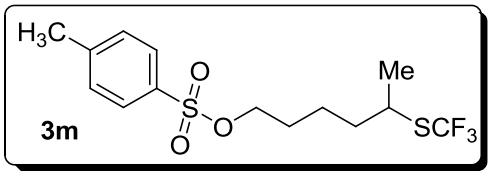


5-(Trifluoromethylthio)hexyl 4-chlorobenzoate; Procedure A/B. Petroleum ether/ethyl

acetate = 60/1; 61 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 4.33 (t, *J* = 6.8 Hz, 2 H), 3.28-3.37 (m, 1 H), 1.76-1.83 (m, 2 H), 1.66-1.74 (m, 2 H), 1.54-1.62 (m, 2 H), 1.43 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 139.4, 131.1 (q, *J* = 304.2 Hz), 130.9, 128.8, 128.7, 64.8, 40.9, 36.4, 28.3, 23.1, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.14 (s, 3 F) ppm; IR (thin): ν_{max} 2962, 2925, 1721, 1477, 1396, 1363, 1261, 1186, 1098, 1016, 933, 798, 623 cm^{-1}. MS (EI): m/z (%) 340, 156, 139 (100%), 111, 82, 67, 54. HRMS for $C_{14}H_{16}ClF_3O_2S$ Calcd: 340.0512; Found: 340.0511.

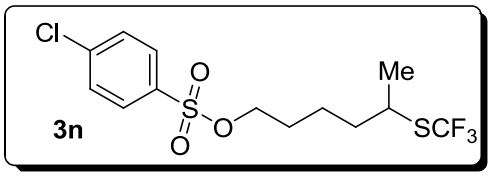


5-(Trifluoromethylthio)hexyl 4-bromobenzoate; Procedure A/B. Petroleum ether/ethyl acetate = 60/1; 62 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 4.32 (t, *J* = 6.4 Hz, 2 H), 3.28-3.37 (m, 1 H), 1.76-1.83 (m, 2 H), 1.67-1.74 (m, 2 H), 1.56-1.64 (m, 2 H), 1.43 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 131.7, 131.1 (q, *J* = 305.0 Hz), 130.0, 129.2, 128.0, 64.8, 41.0, 36.4, 28.3, 23.1, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.14 (s, 3 F) ppm; IR (thin): ν_{max} 2956, 2868, 1723 1591, 1483, 1459, 1398, 1271, 1105, 1069, 1012, 848, 756 cm^{-1}. MS (EI): m/z (%) 384,185(100%), 183 (100%), 157, 155, 115, 83, 82, 55. HRMS for $C_{14}H_{16}BrF_3O_2S$ Calcd: 384.0006; Found: 384.0011.

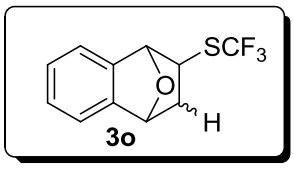


5-(Trifluoromethylthio)hexyl 4-methylbenzenesulfonate; Procedure A/B. Petroleum ether/ethyl acetate = 50/1; 81 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 4.03 (t, *J* = 8.0 Hz, 2 H), 3.19- 3.27 (m, 1 H), 2.45 (s, 3 H), 1.62-1.69 (m, 2 H), 1.53- 1.60 (m, 2 H), 1.41-1.48 (m, 2 H), 1.37 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 133.0, 131.0 (q, *J* = 304.0 Hz), 129.8, 127.8, 70.0, 40.8, 36.0, 28.4, 22.5, 22.1, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.20 (s, 3 F) ppm; IR (thin): ν_{max} 2952, 2931, 2870, 1598, 1458, 1362, 1291, 1189, 1177, 1115, 934, 815, 664 cm^{-1}. HRMS

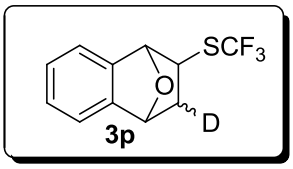
(ESI) for $C_{14}H_{19}F_3O_3S_2$ Na ($M+Na^+$) Calcd: 379.0625; Found: 379.0620.



5-(Trifluoromethylthio)hexyl 4-chlorobenzenesulfonate; Procedure A/B. Petroleum ether/ethyl acetate = 50/1; 75 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 4.07 (t, *J* = 6.4 Hz, 2 H), 3.20-3.29 (m, 1 H), 1.65-1.72 (m, 2 H), 1.56-1.63 (m, 2 H), 1.43-1.50 (m, 2 H), 1.39 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 134.6, 131.0 (q, *J* = 304.2 Hz), 129.6, 129.2, 70.5, 40.8, 36.0, 28.4, 22.5, 22.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.18 (s, 3 F) ppm; IR (thin): ν_{max} 3092, 2935, 2870, 1589, 1478, 1396, 1366, 1187, 1117, 934, 829, 754, 624 cm^{-1}. HRMS (ESI) for $C_{13}H_{16}ClF_3O_3S_2$ Na ($M+Na^+$) Calcd: 399.0079; Found: 399.0074.

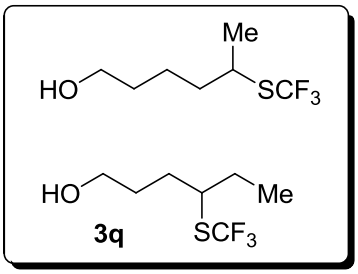


1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-(2-Trifluoromethyl) sulfane; **Procedure A** Petroleum ether/ethyl acetate = 100/1; 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.33 (m, 1 H), 7.23-7.27 (m, 1 H), 7.19-7.22 (m, 2 H), 5.46 (d, *J* = 4.0 Hz, 1 H), 5.38 (s, 1 H), 3.30 (dd, *J* = 8.0, 4.0 Hz, 1 H), 2.09 (dd, *J* = 12.0, 4.0 Hz, 1 H), 1.93 (dt, *J* = 12.0, 4.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 142.7, 130.7 (q, *J* = 304.7 Hz), 127.7, 127.3, 119.8, 119.2, 84.1, 78.7, 42.9 (q, *J* = 2.0 Hz), 35.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.99 (s, 3 F) ppm; IR (thin): ν_{max} 3070, 2961, 1428, 1261, 1092, 1024, 802, 728, 698 cm^{-1}. TOFMS (EI): m/z (%) 246, 228, 159, 118, 115. HRMS for $C_{11}H_9F_3OS$ [M] Calcd: 246.0326; Found: 246.0322.



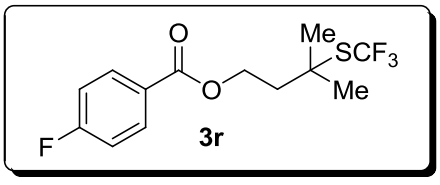
1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-(3-deuterium)-(2-Trifluoromethyl) sulfane; **Procedure A.** Petroleum ether/ethyl acetate = 100/1; 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.30-7.33 (m, 1 H); 7.23-7.27 (m, 1 H), 7.19-7.22 (m, 2 H), 5.46 (s, 1 H), 5.38 (s, 1 H), 3.29 (d, *J* = 4.0 Hz, 1 H), 2.07 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 142.7, 130.7 (q, *J* = 304.7 Hz), 127.7, 127.3, 119.8, 119.2, 84.1, 78.7, 42.9 (q, *J* = 2.0 Hz), 35.8 (t, *J* = 20.9 Hz); ^{2}H NMR (61 MHz, $CDCl_3$) δ 7.24 (s, 1 D); ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.9 (s, 3 F) ppm; IR (thin): ν_{max} 3446, 1635, 1153, 1115, 855, 756, 628 cm^{-1}. TOF MS (EI): m/z (%) 247, 146, 118 (100%), 116, 104, 90, 77, 63, 51. HRMS for $C_{11}H_8DF_3OS$ Calcd: 247.0389; Found: 247.0392.



3q

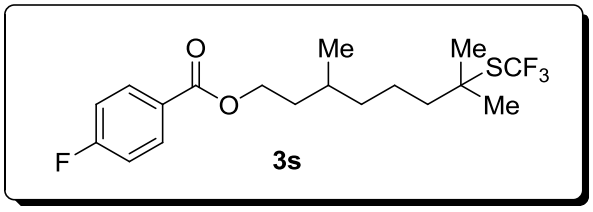
4-(Trifluoromethylthio)hexan-1-ol and 5-(Trifluoromethylthio)hexan-1-ol; Procedure A/B . Petroleum ether/ethyl acetate = 15/1 to 10/1; 82% yield (1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65-3.69 (m, 4 H), 3.27-3.36 (m, 1 H), 3.11-3.17 (m, 1 H), 1.47-1.80 (m, 14 H), 1.43 (d, *J* = 8.0 Hz, 3 H), 1.03 (d, *J* = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.3 (q, *J* = 304.0 Hz), 131.2 (d, *J* = 304.0 Hz), 62.6, 62.4, 48.0, 41.1, 36.6, 32.2, 30.9, 29.5, 28.2, 22.9, 22.2, 10.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.14 (s, 3 F), -39.20 (s, 3 F) ppm; IR (thin): ν_{max} 3375, 2927, 2856, 1727, 1459, 1380, 1149, 1122, 756, 668 cm^{-1}. MS (EI): m/z (%) 202, 149, 142, 133, 129, 115, 99, 83, 67, 55 (100%), 41; HRMS for $C_7H_{13}F_3OS$ Calcd: 202.0639; Found: 202.0636.



3r

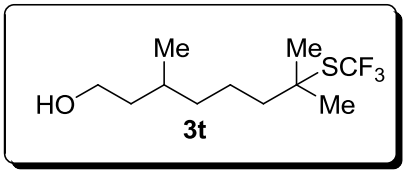
3-Methyl-3-(trifluoromethylthio)butyl 4-fluorobenzoate; Procedure C. Petroleum ether/ethyl acetate = 80/1; 30 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 6.6, 1.5 Hz, 2 H), 7.10 (t, *J* = 8.4 Hz, 2 H), 4.50 (t, *J* = 6.9 Hz, 2 H), 2.20 (t, *J* = 6.9 Hz, 2 H), 1.56 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (d, *J* = 252.6 Hz), 165.4, 132.1 (d, *J* = 9.2 Hz), 131.1 (q, *J* = 306.5 Hz), 126.2 (d, *J* = 3.2 Hz), 115.5 (d, *J* = 21.9 Hz), 61.7, 50.2, 41.2 (q, *J* = 0.8 Hz), 29.7 (q, *J* = 1.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.18 (s, 3 F); -105.9 (m, 1 F)

ppm. IR (thin): ν_{max} 2959, 2925, 2854, 1725, 1604, 1508, 1465, 1273, 1153, 1103, 1015, 767 cm^{-1}. MS (EI): m/z (%) 310, 209, 123, 95, 75, 69 (100%), 41; HRMS for $C_{13}H_{14}F_4O_2S$ Calcd: 310.0651; Found: 310.0649.



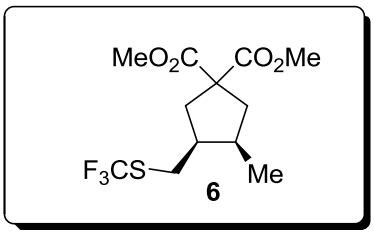
3s

3,7-Dimethyl-7-(trifluoromethylthio)octyl 4-fluorobenzoate; Procedure C. Petroleum ether/ethyl acetate = 80/1; 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 5.6, 2.8 Hz, 2 H), 7.10 (t, *J* = 8.4 Hz, 2 H), 4.30-4.40 (m, 2 H), 1.77-1.85 (m, 1 H), 1.59-1.68 (m, 4 H), 1.42-1.52 (m, 3 H), 1.45 (s, 6 H), 1.16-1.26 (m, 1 H), 0.97 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 228.7 Hz), 165.6, 132.0 (d, *J* = 9.2 Hz), 131.1 (q, *J* = 305.6 Hz), 126.7 (d, *J* = 3.0 Hz), 115.4 (d, *J* = 22.1 Hz), 63.5, 52.1, 43.4 (d, *J* = 1.2 Hz), 36.9, 35.5, 29.8, 29.4, 21.9, 19.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.68 (s, 3F); -105.5 (m, 1 F); IR (thin): ν_{max} 2961, 2872, 1720, 1604, 1508, 1463, 1275, 1239, 1153, 1113,854, 767 cm^{-1}. HRMS (ESI) for $C_{18}H_{28}NF_4O_2S$ Na ($M+NH_4^+$) Calcd: 398.1777; Found: 398.1771.

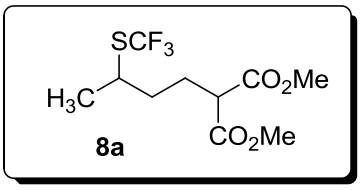


3t

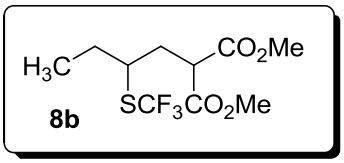
3,7-Dimethyl-7-(trifluoromethylthio)octan-1-ol; Procedure C. Petroleum ether/ethyl acetate = 15/1; 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26-3.73 (m, 2 H), 1.54-1.67 (m, 4 H), 1.44 (s, 6 H), 1.27-1.41 (m, 4 H), 1.10-1.21 (m, 2 H), 0.90 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.1 (q, *J* = 306.0 Hz); 61.0, 52.1, 43.4 (q, *J* = 2.4 Hz), 39.8, 37.2, 29.5 (q, *J* = 1.5 Hz), 29.4 (q, *J* = 1.5 Hz), 29.3, 21.9, 19.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.7 (s, 3 F); IR (thin): ν_{max} 3449, 2930, 2872, 1726, 1464, 1371, 1262, 1111, 802 cm^{-1}. TOF MS (EI): m/z (%) 240, 189, 171, 157, 143, 97, 83 (100%), 69, 55, 41. HRMS for $C_{11}H_{19}F_3OS$ [$M-H_2O$] Calcd: 240.1159; Found: 240.1155.



Dimethyl 3-methyl-4-((trifluoromethylthio)methyl)cyclopentane-1,1-dicarboxylate; Procedure A/B. Petroleum ether/ethyl acetate = 100/1; 70% yield (dr = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 6 H), 2.94 (dd, *J* = 16.0, 8.0 Hz, 1 H), 2.79 (dd, *J* = 12.0, 8.0 Hz, 1 H), 2.45-2.52 (m, 2 H), 2.29 (m, 2 H), 2.14 (dd, *J* = 12.0, 8.0 Hz, 1 H), 2.00 (dd, *J* = 12.0, 8.0 Hz, 1 H), 0.92 (d, *J* = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 172.8, 131.0 (q, *J* = 304 Hz), 58.6, 58.2, 58.1, 41.9, 41.2, 38.0, 35.8, 30.3, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.38 (s, 3 F), -41.42 (s, 0.3 F) ppm; IR (thin): ν_{max} 2957, 1735, 1435, 1270, 1199, 1149, 1116 cm^{-1}. MS (EI): m/z (%) 314, 282, 213, 153, 93 (100%), 79, 59, 41. HRMS for $C_{12}H_{17}F_3O_4S$ Calcd: 314.0800; Found: 314.0798



Dimethyl 2-(3-(trifluoromethylthio)butyl)malonate; Procedure A/B. Petroleum ether/ethyl acetate = 50/1; 34% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 6 H), 3.37 (t, *J* = 7.2 Hz, 1 H), 3.31 (m, 1 H), 3.29 (m, 1 H), 1.99-2.09 (m, 2 H), 1.67 (m, 2 H), 1.43 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 130.9 (q, *J* = 304.7 Hz), 52.6, 51.1, 40.6, 34.3, 25.8, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.22 (s, 3F). IR (thin): ν_{max} 2959, 1756, 1739, 1437, 1262, 1155, 1112, 1021, 997 cm^{-1}. MS (EI): m/z (%) 288, 219, 187, 155, 145 (100%), 123, 113, 87, 69, 55, 41; HRMS for $C_{10}H_{15}F_3O_4S$ Calcd: 288.0643; Found: 288.0645.

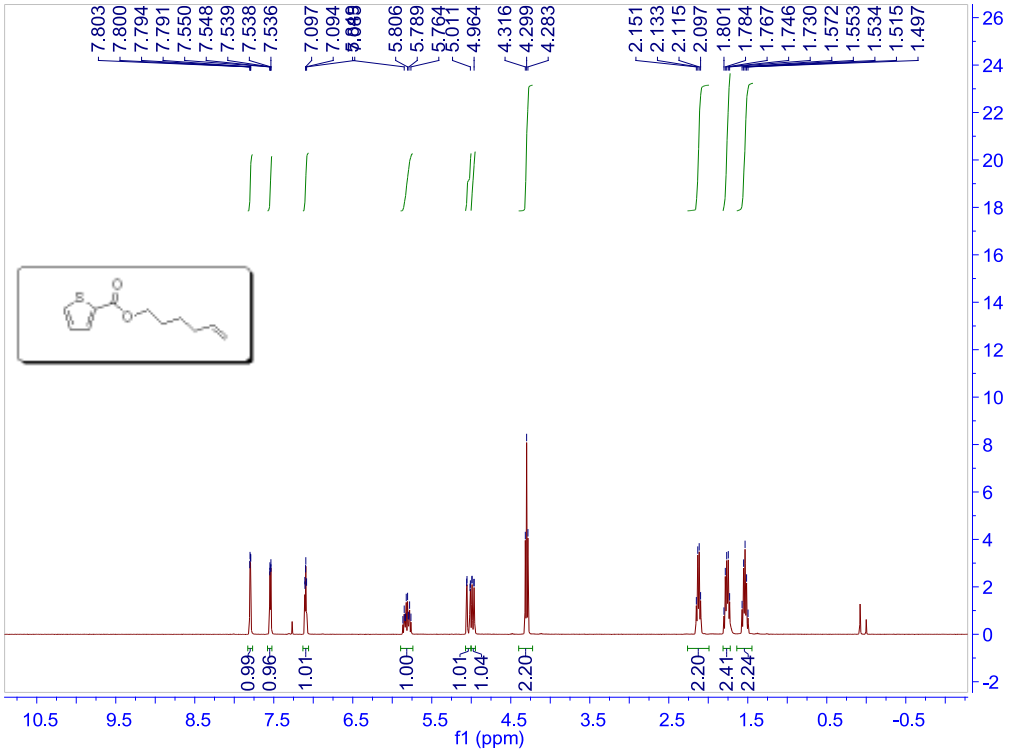


Dimethyl 2-(2-(trifluoromethylthio)butyl)malonate; Procedure A/B. Petroleum ether/ethyl acetate = 50/1; 23% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3 H), 3.75 (s, 3 H),

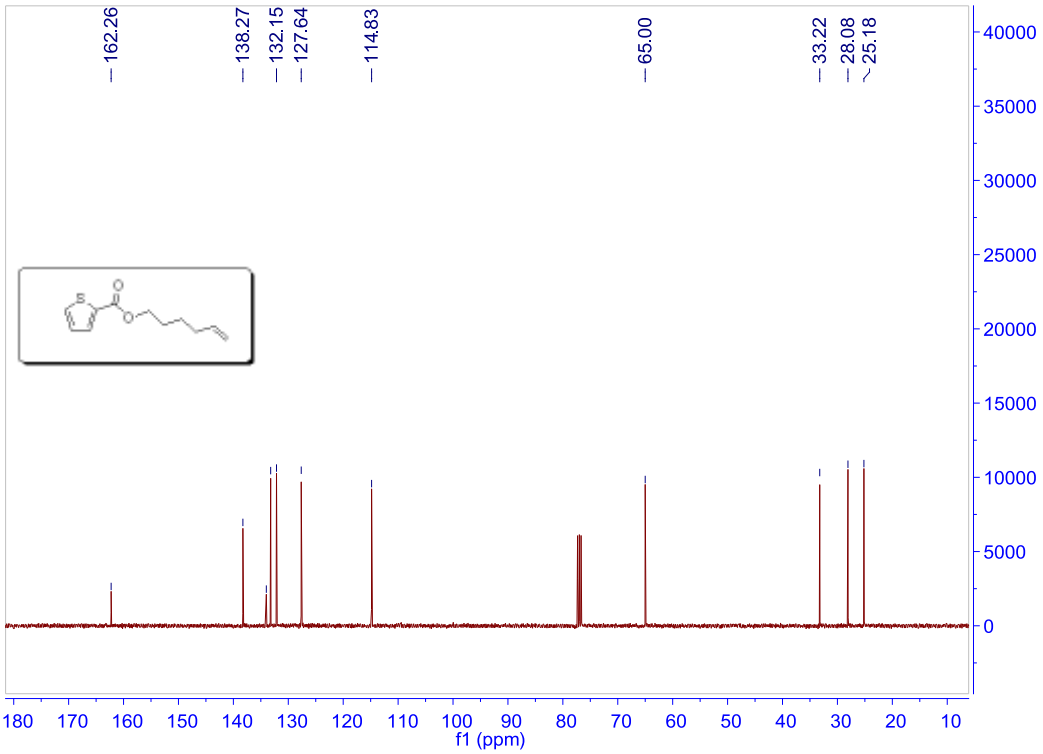
3.74-3.78 (m, 1 H), 306-3.12 (m, 1 H), 2.33-2.40 (m, 1 H), 2.00-2.08 (m, 1 H), 1.69-1.84 (m, 2 H), 1.05 (t, J = 8.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 169.1, 130.85 (q, J = 304.7 Hz); 52. 8, 52.7, 49.2, 46.2, 33.7, 29.2, 10.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.14 (s, 3 F) ppm. IR (thin): ν_{max} 2957, 1753, 1738, 1437, 1346, 1219, 1151, 1114, 1017 cm^{-1}. TOF MS (EI): m/z (%) 288, 257, 225, 155, 132 (100%), 123, 113, 100, 87, 69, 55, 41. HRMS for $C_{10}H_{15}F_3O_4S$ Calcd: 288.0643; Found: 288.0640

V: NMR spectra for new compounds

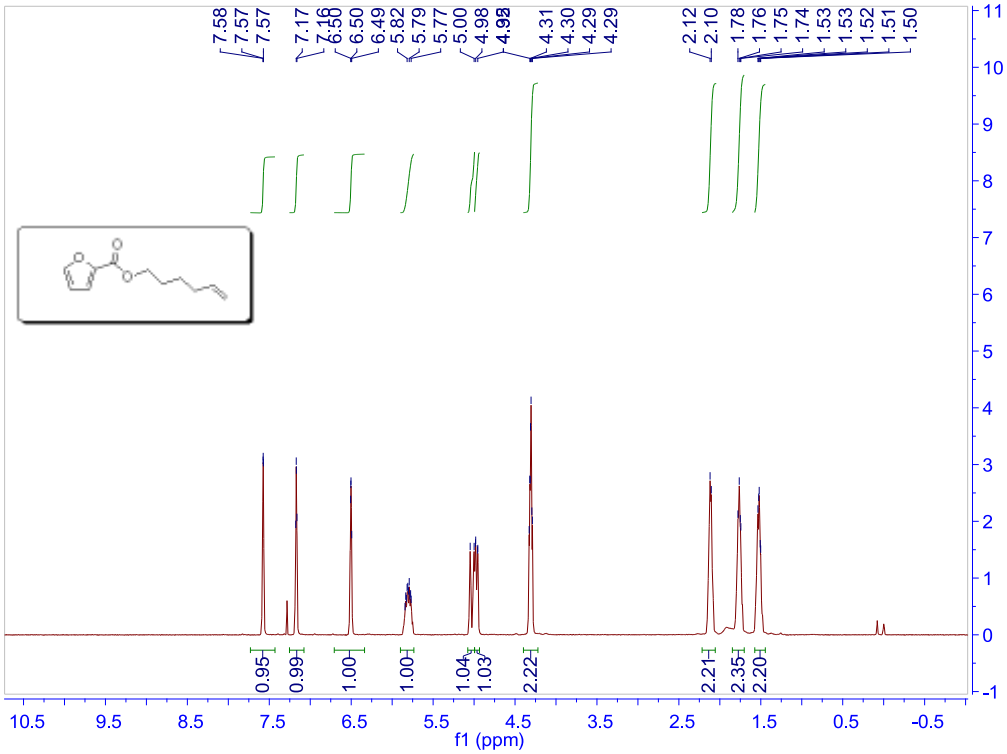
^{1}H NMR spectrum for hex-5-enyl thiophene-2-carboxylate



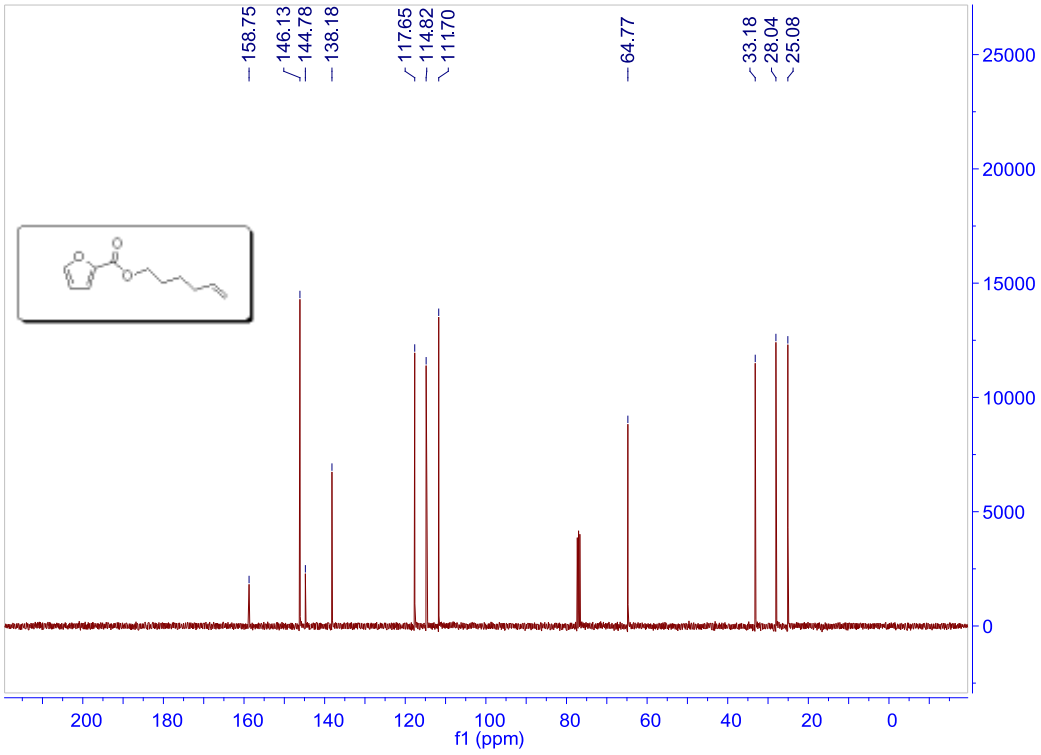
^{13}C NMR spectrum for hex-5-enyl thiophene-2-carboxylate



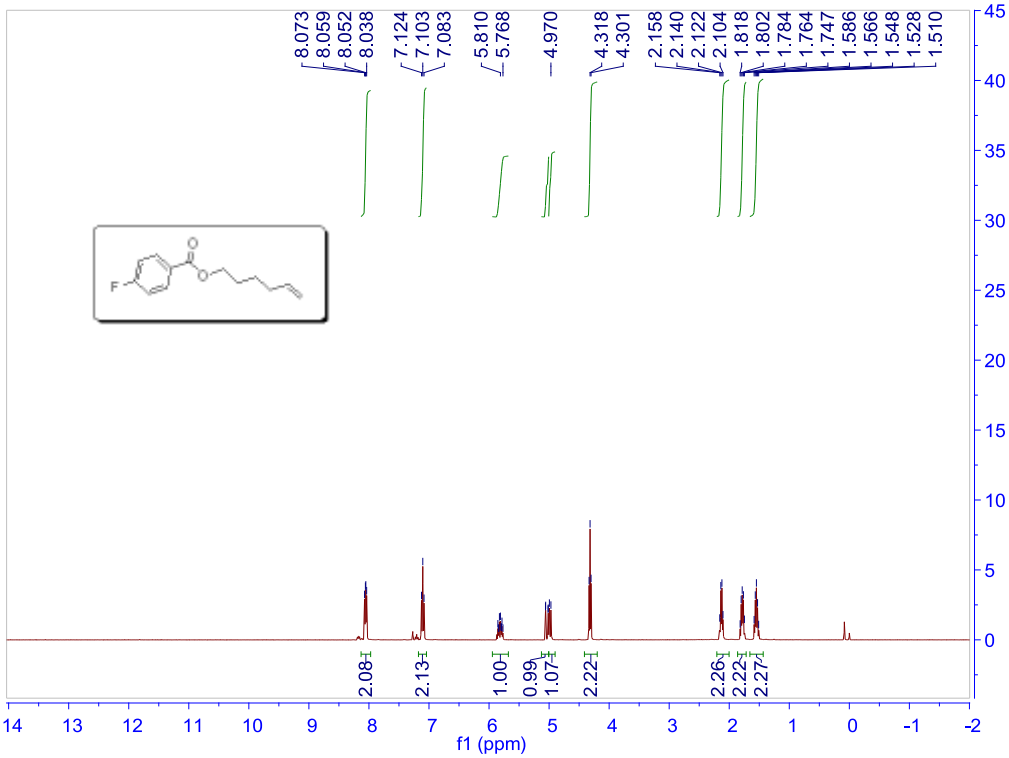
^{1}H NMR spectrum for hex-5-enyl furan-2-carboxylate



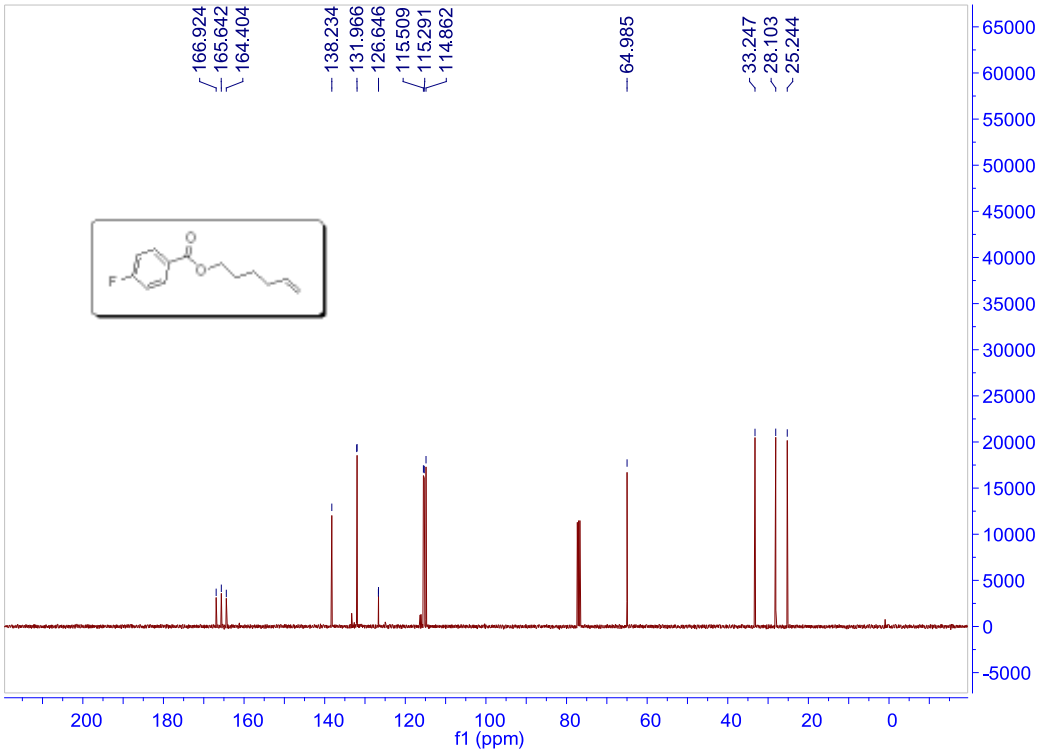
^{13}C NMR spectrum for hex-5-enyl thiophene-2-carboxylate



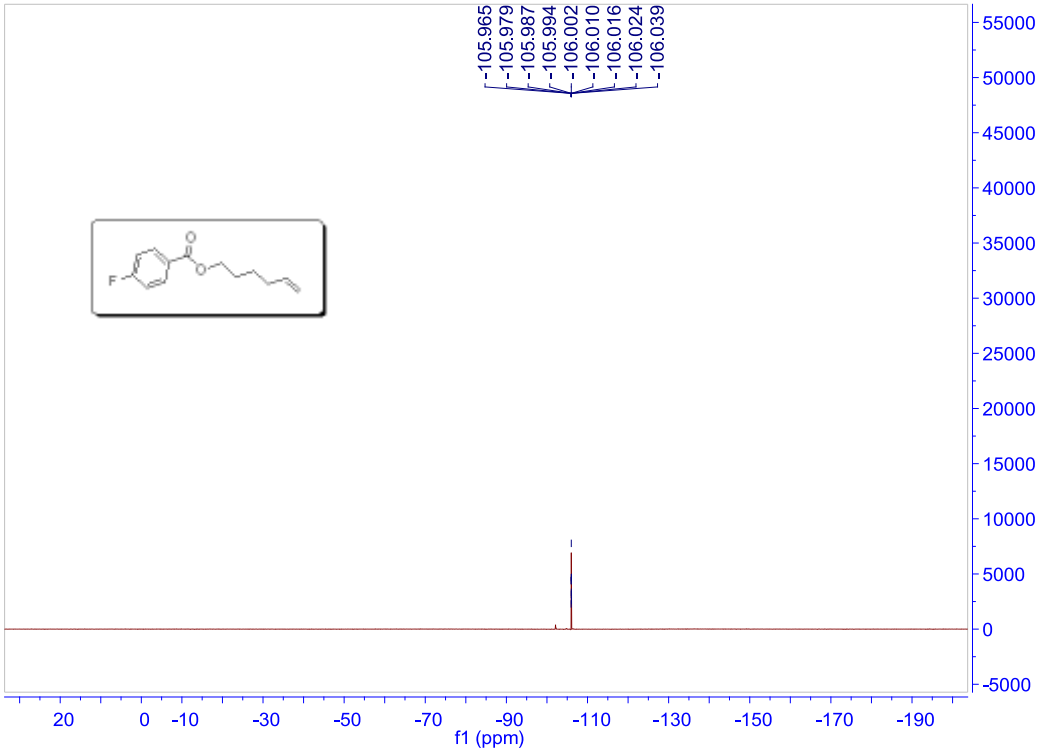
^{1}H NMR spectrum for hex-5-enyl 4-fluorobenzoate



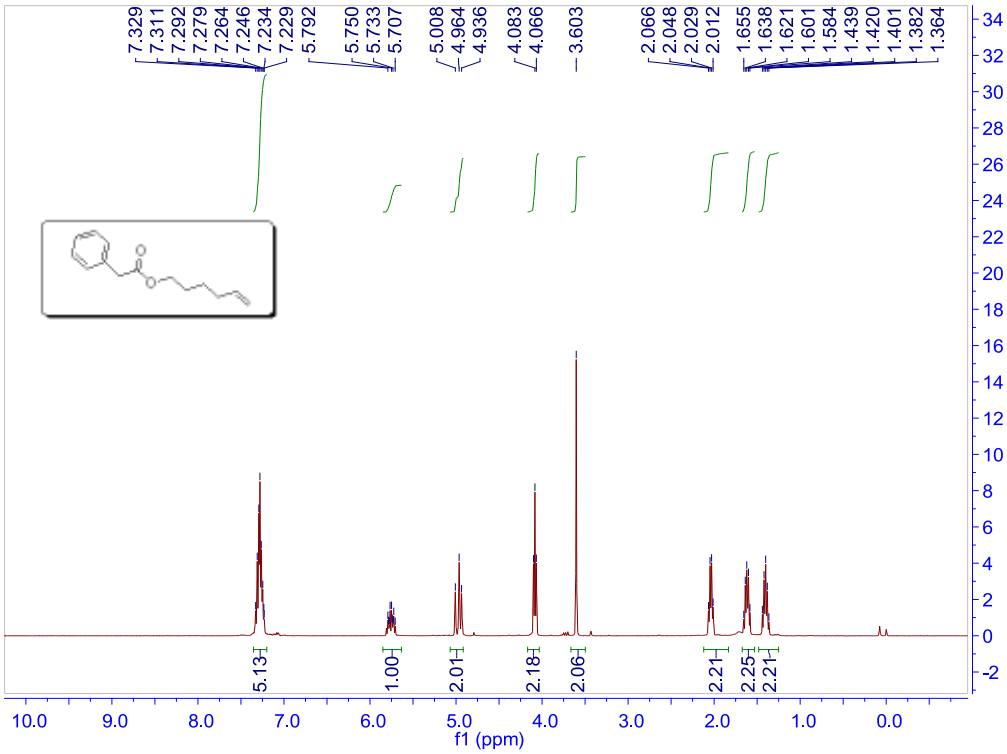
^{13}C NMR spectrum for hex-5-enyl 4-fluorobenzoate



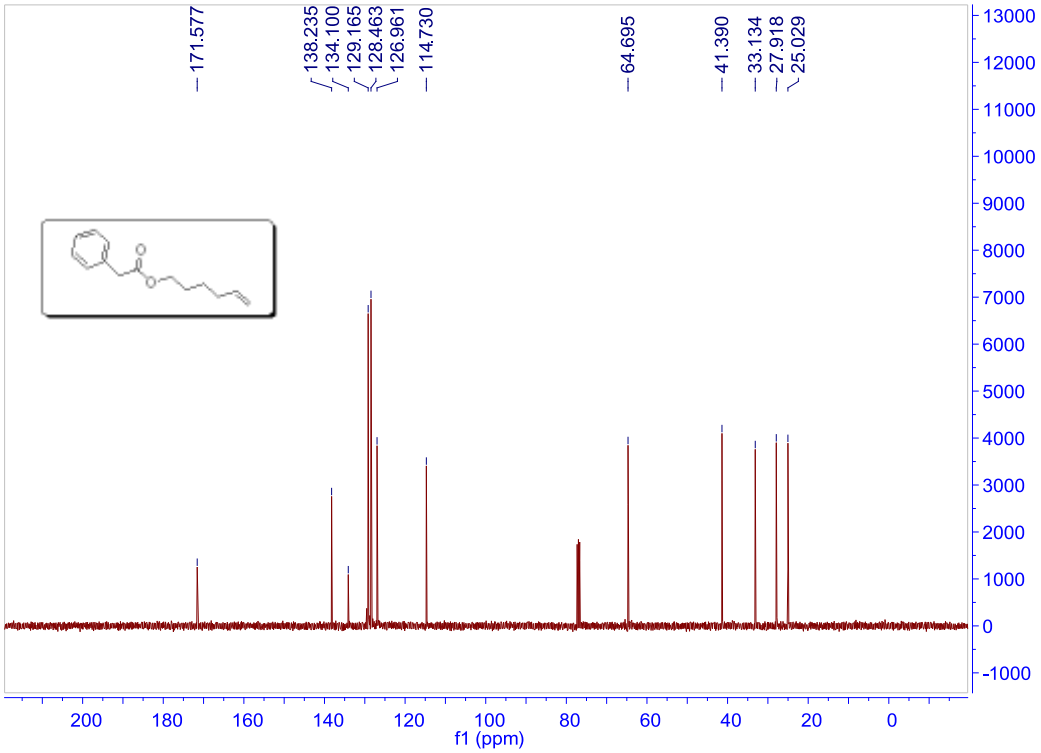
^{19}F NMR spectrum for hex-5-enyl 4-fluorobenzoate



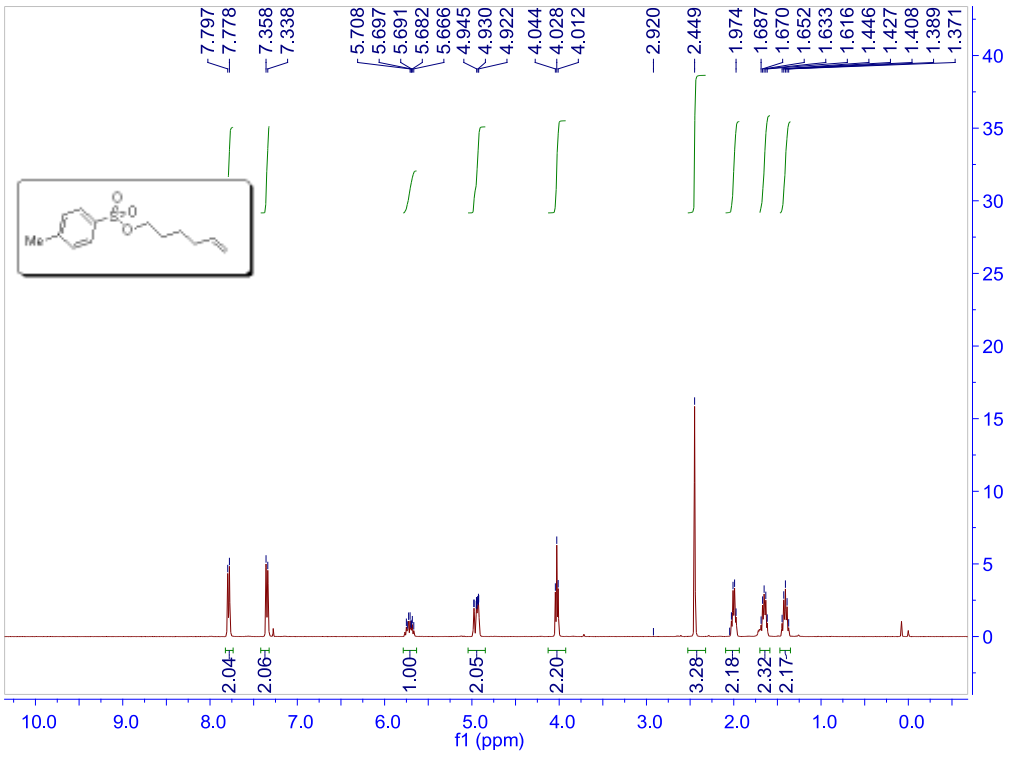
^{1}H NMR spectrum for hex-5-enyl 2-phenylacetate



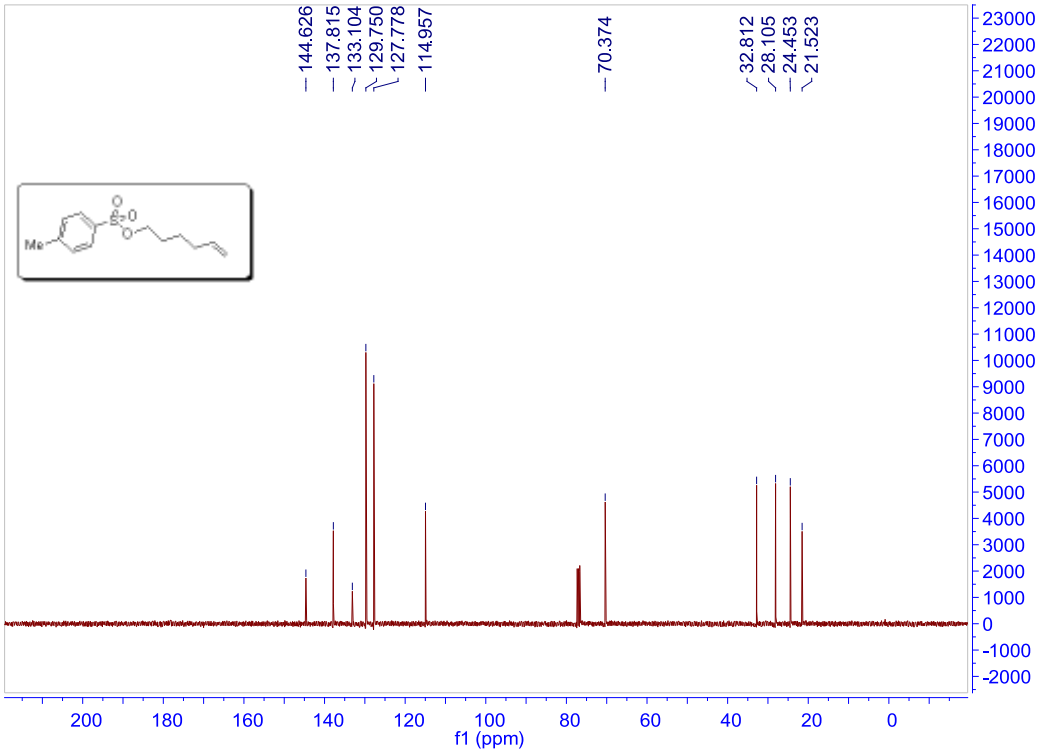
^{13}C NMR spectrum for hex-5-enyl 2-phenylacetate



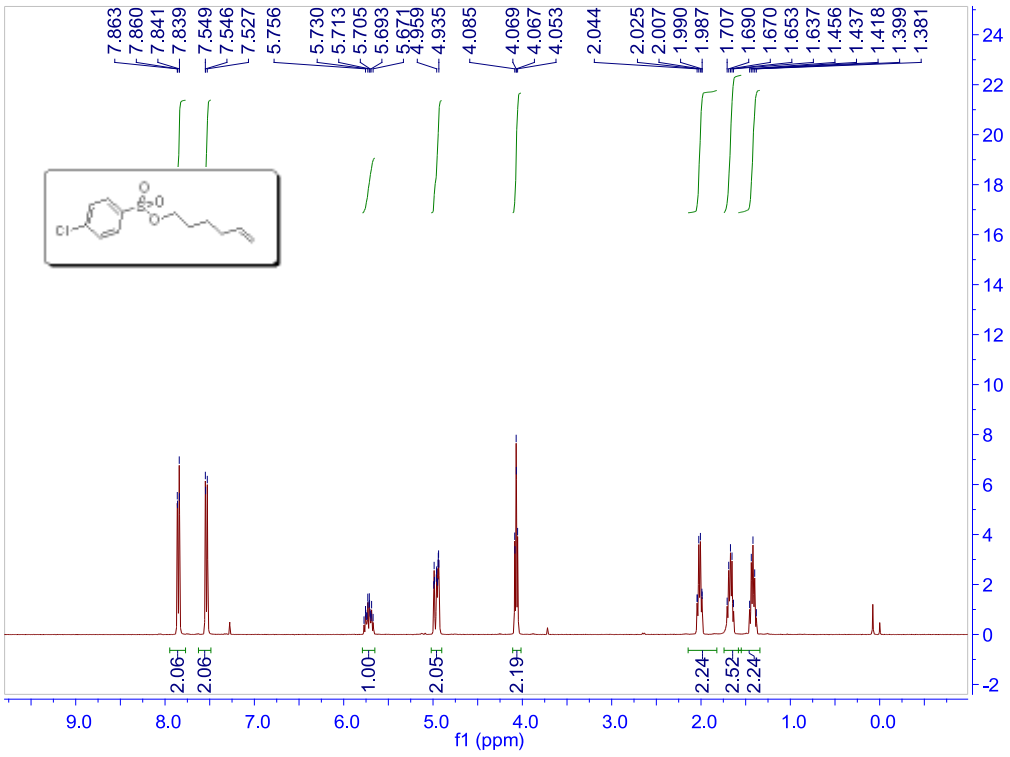
^{1}H NMR spectrum for hex-5-enyl 4-methylbenzenesulfonate



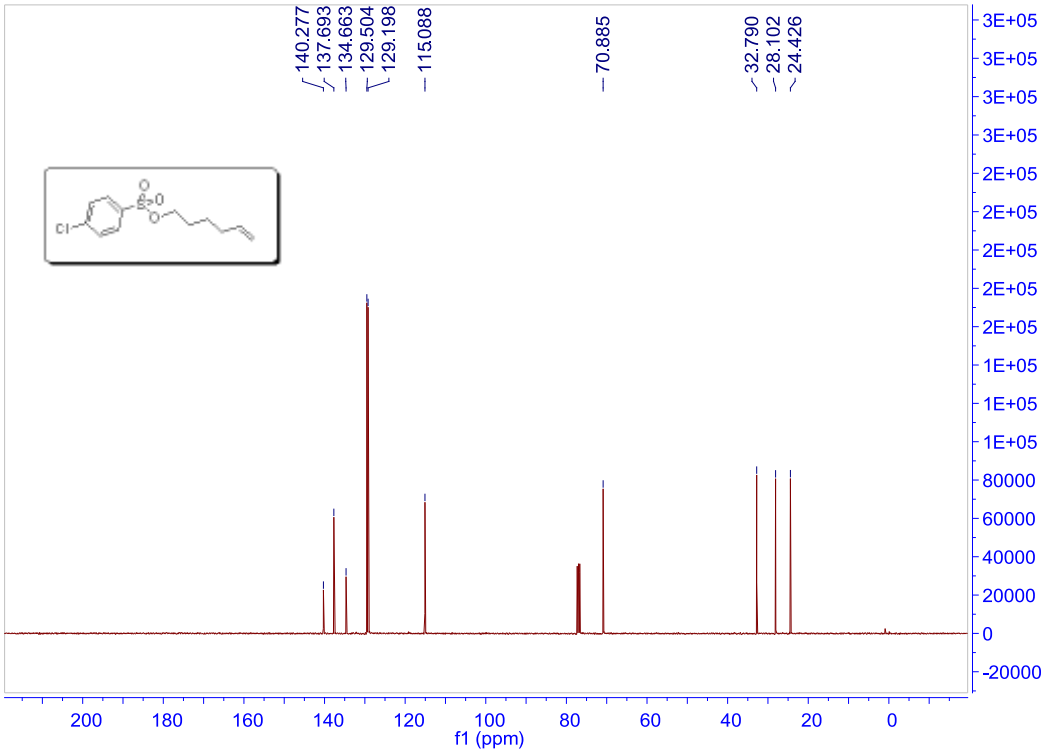
^{13}C NMR spectrum for hex-5-enyl 4-methylbenzenesulfonate



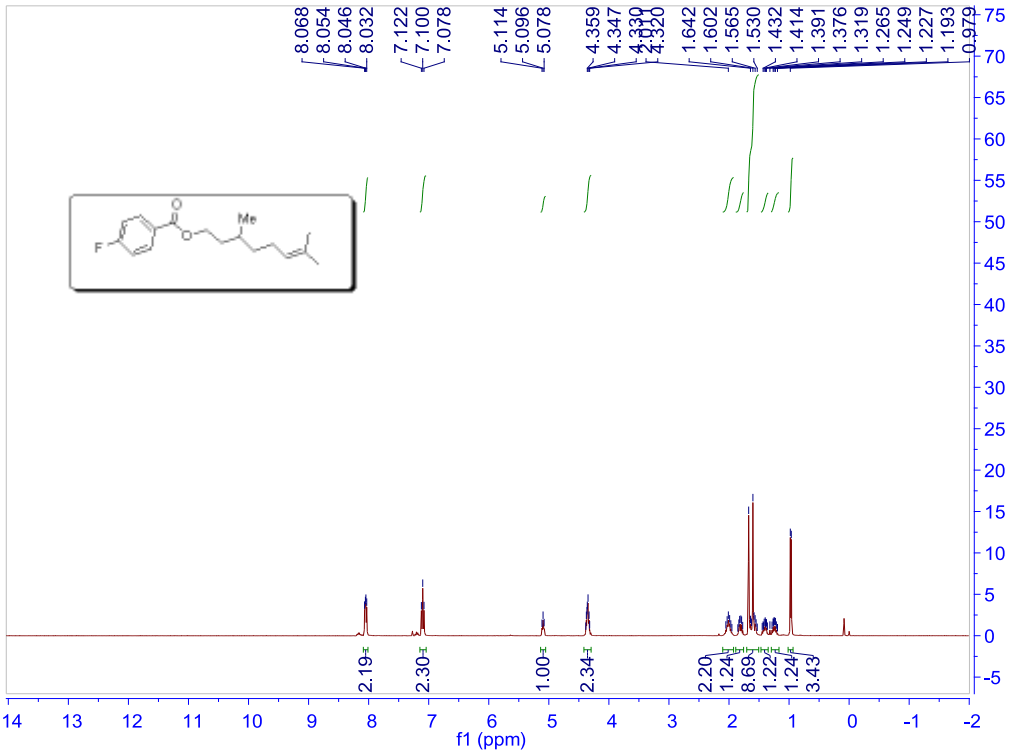
^{1}H NMR spectrum for hex-5-enyl 4chlorobenzenesulfonate



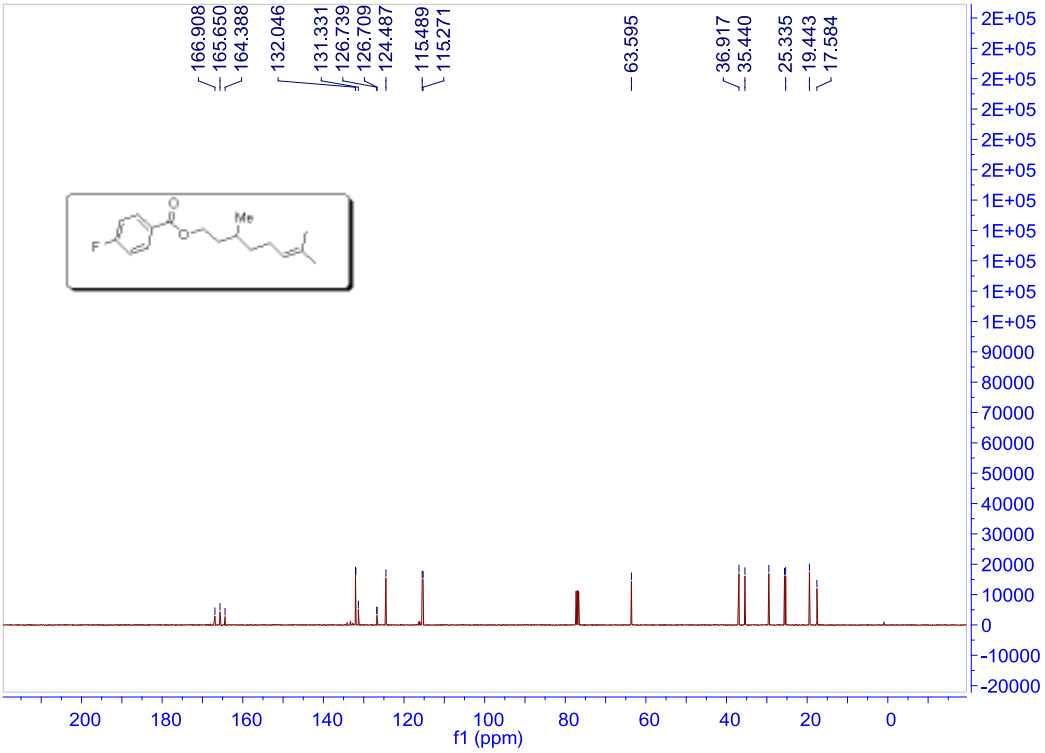
^{13}C NMR spectrum for hex-5-enyl 4chlorobenzenesulfonate



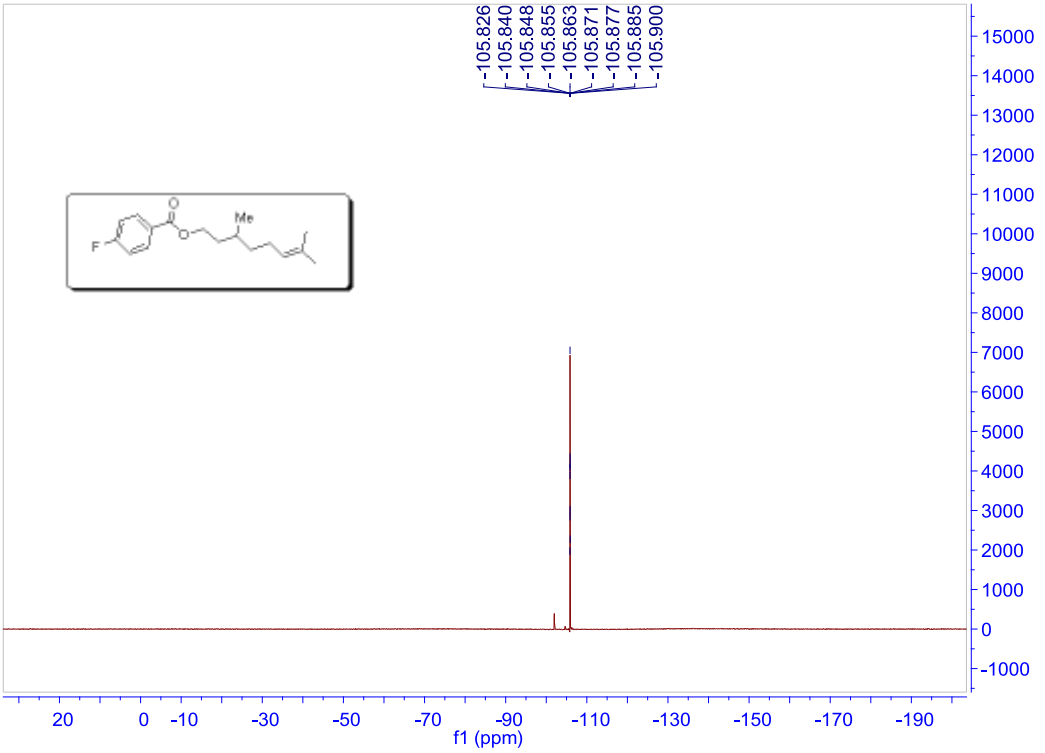
^{1}H NMR spectrum for 3,7-dimethyloct-6-enyl 4-fluorobenzoate



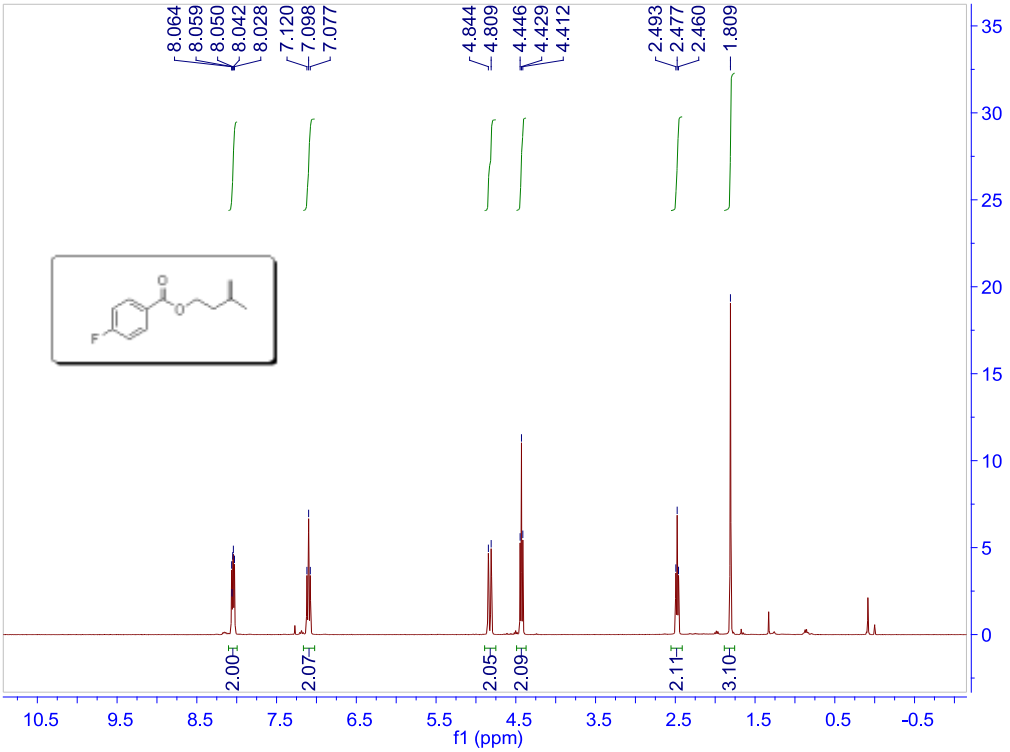
^{13}C NMR spectrum for 3,7-dimethyloct-6-enyl 4-fluorobenzoate



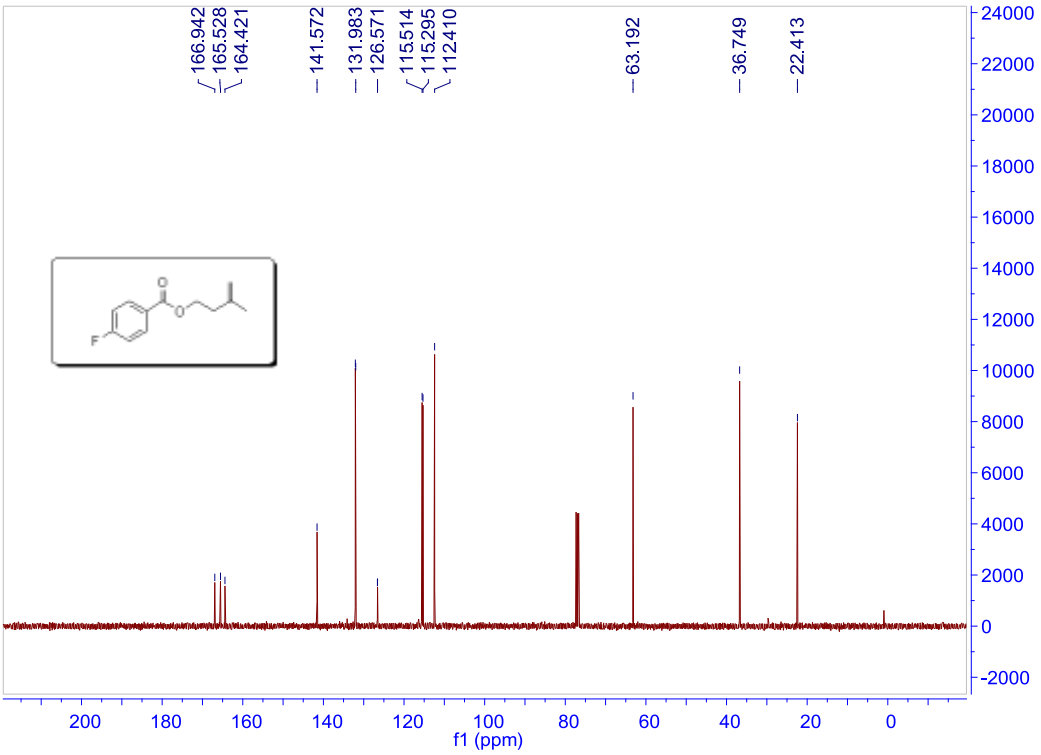
^{19}F NMR spectrum for 3,7-dimethyloct-6-enyl 4-fluorobenzoate



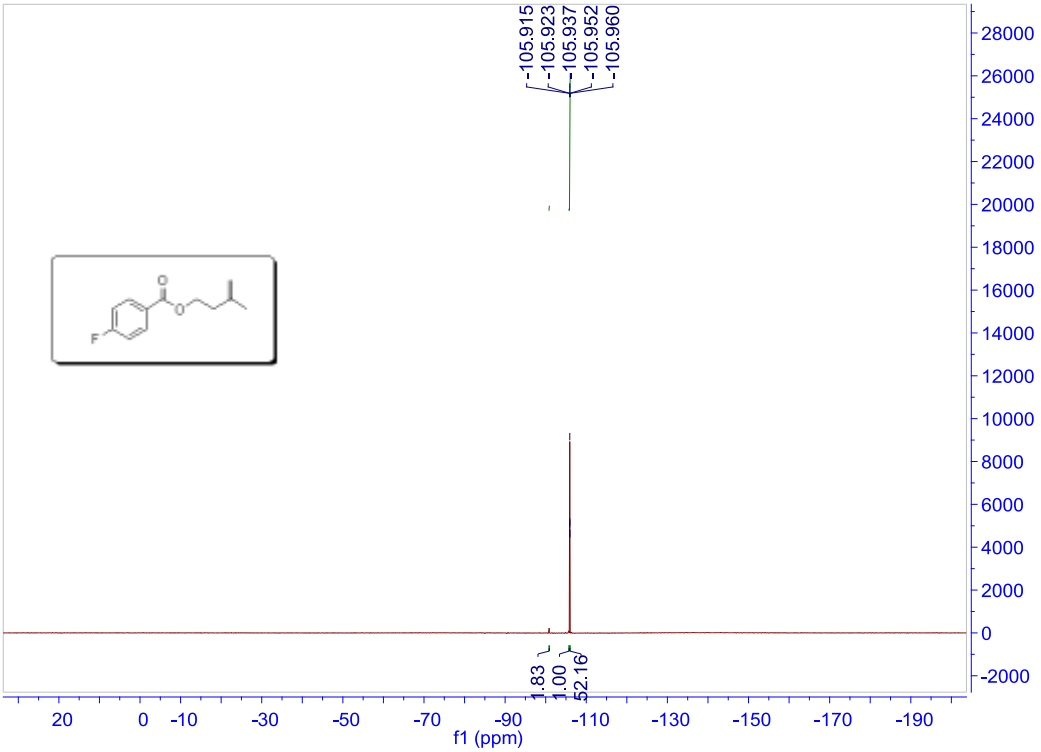
^{1}H NMR spectrum for 3-methylbut-3-enyl 4-fluorobenzoate



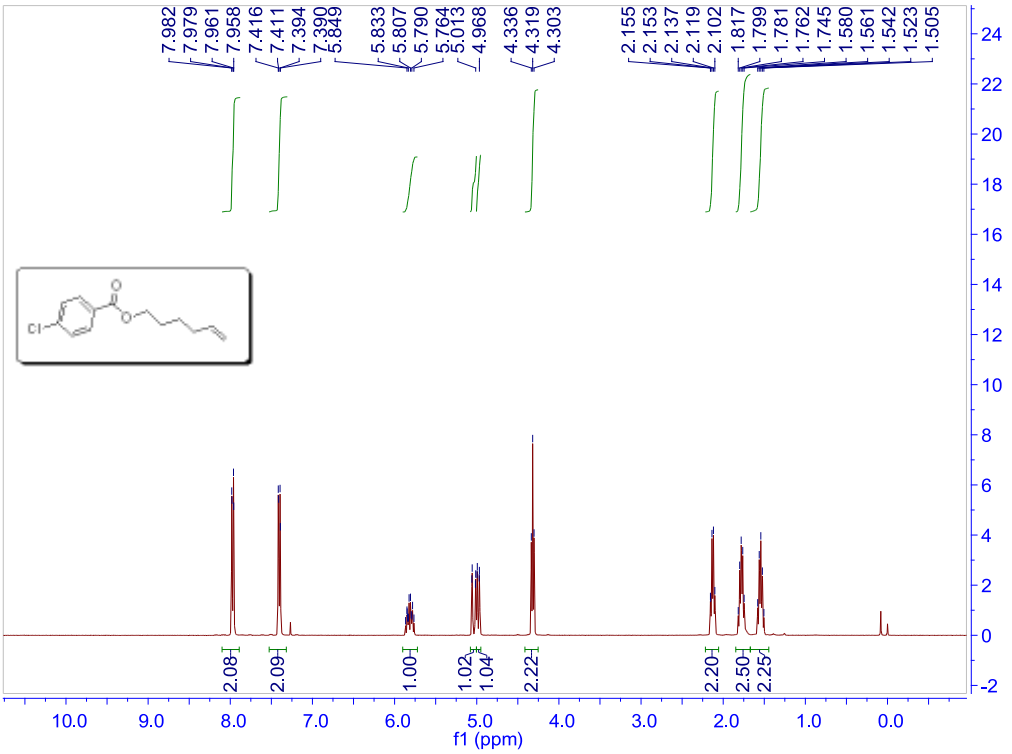
^{13}C NMR spectrum for 3-methylbut-3-enyl 4-fluorobenzoate



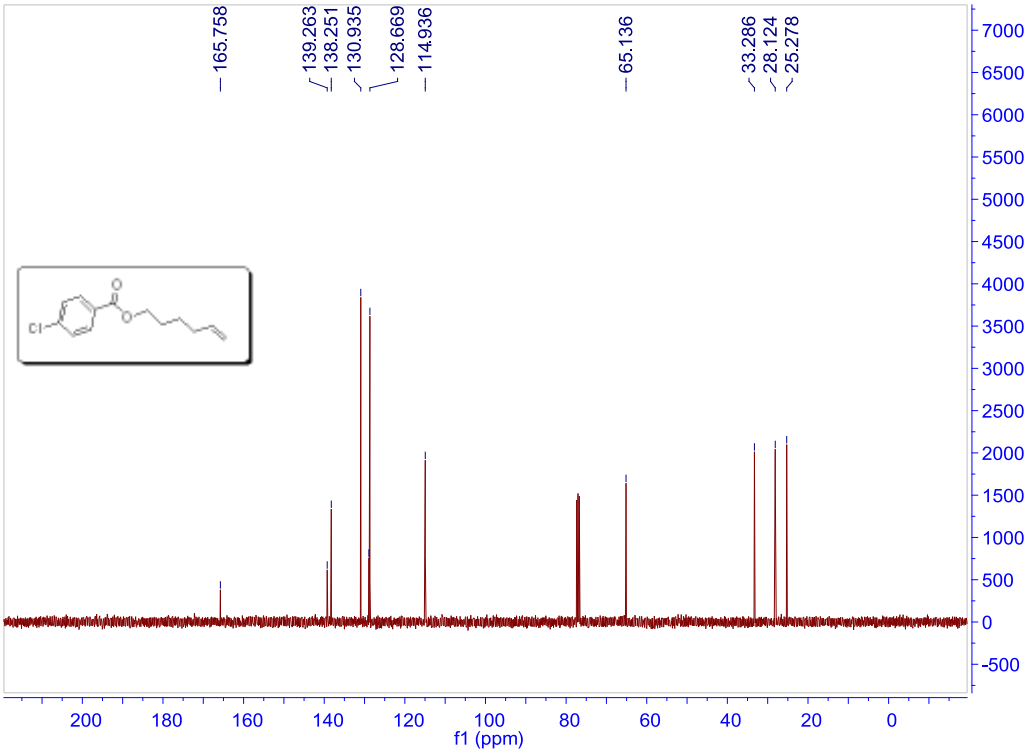
^{19}F NMR spectrum for 3-methylbut-3-enyl 4-fluorobenzoate



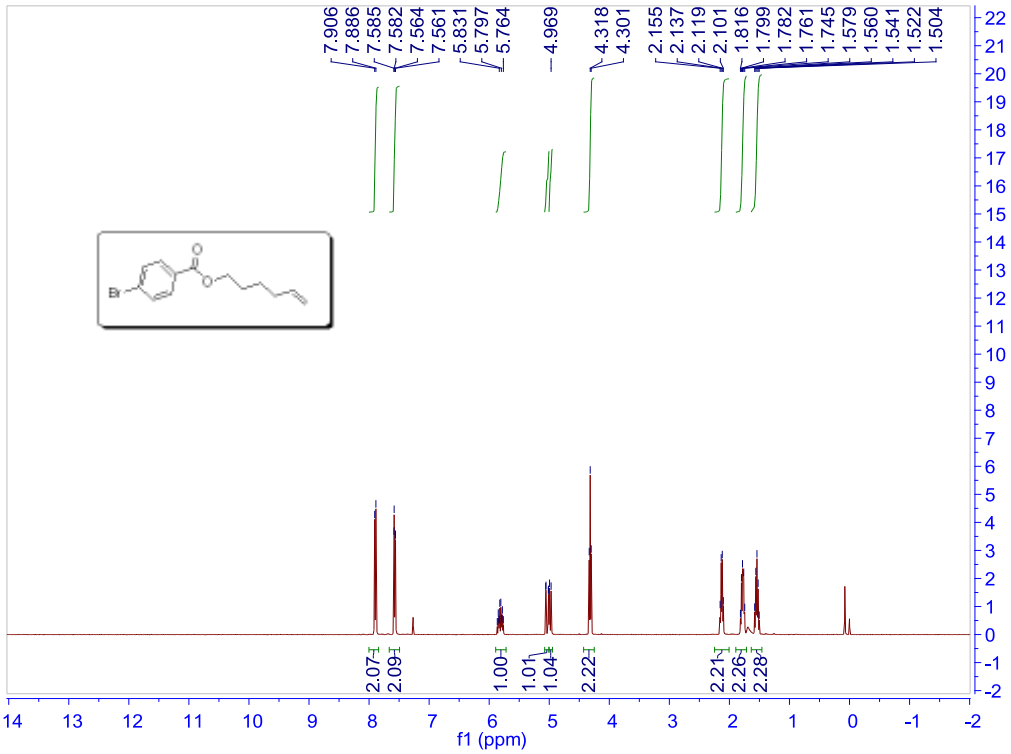
^{1}H NMR spectrum for hex-5-enyl 4-chlorobenzoate



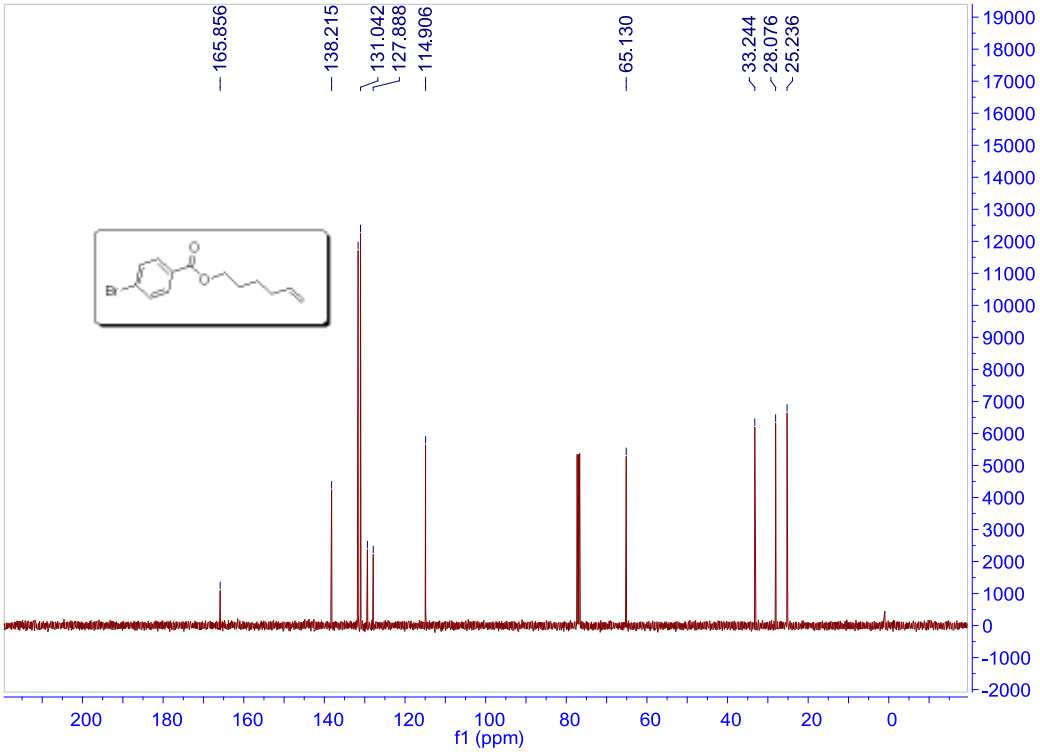
^{13}C NMR spectrum for hex-5-enyl 4-chlorobenzoate



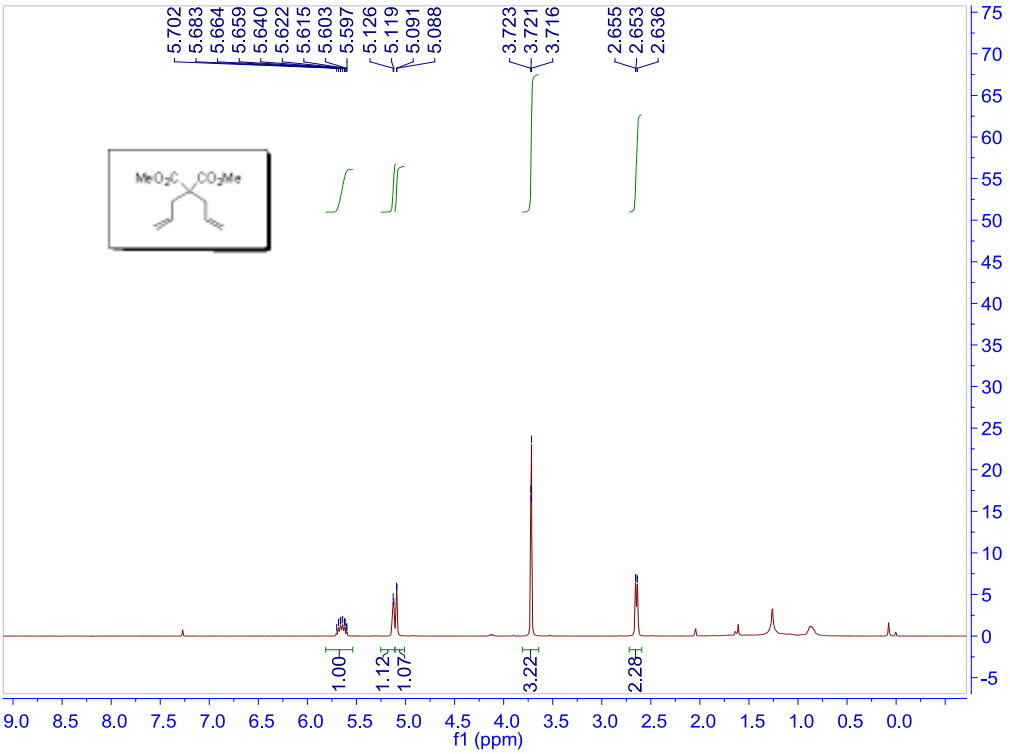
^{1}H NMR spectrum for hex-5-enyl 4-bromobenzoate



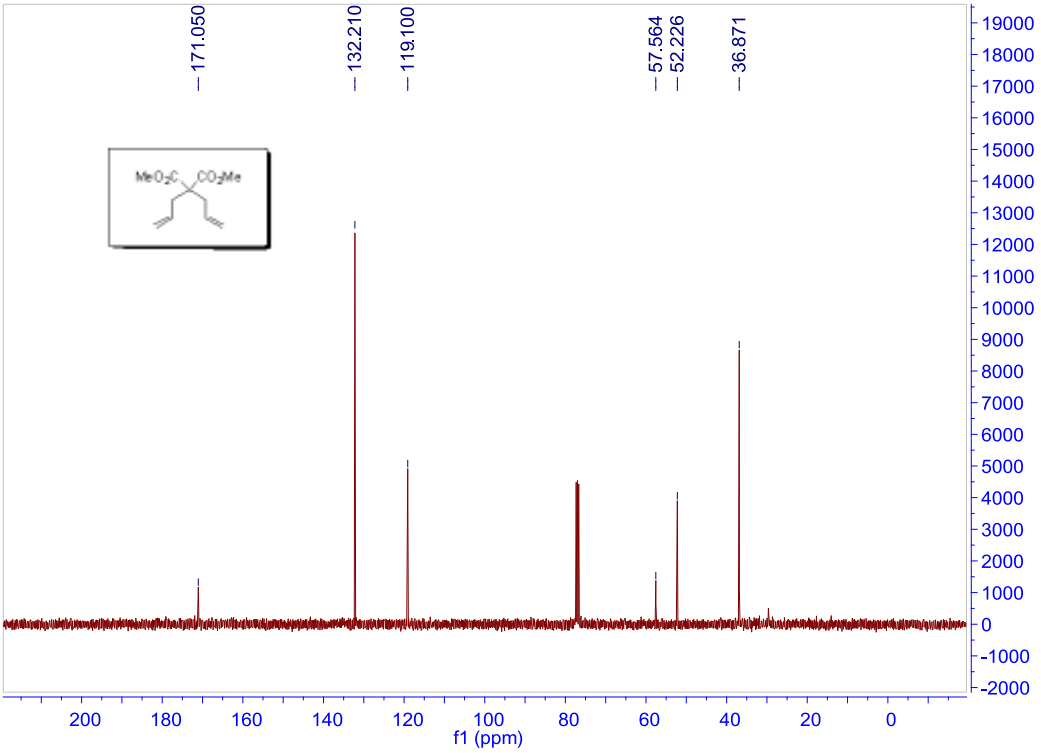
^{13}C NMR spectrum for hex-5-enyl 4-bromobenzoate



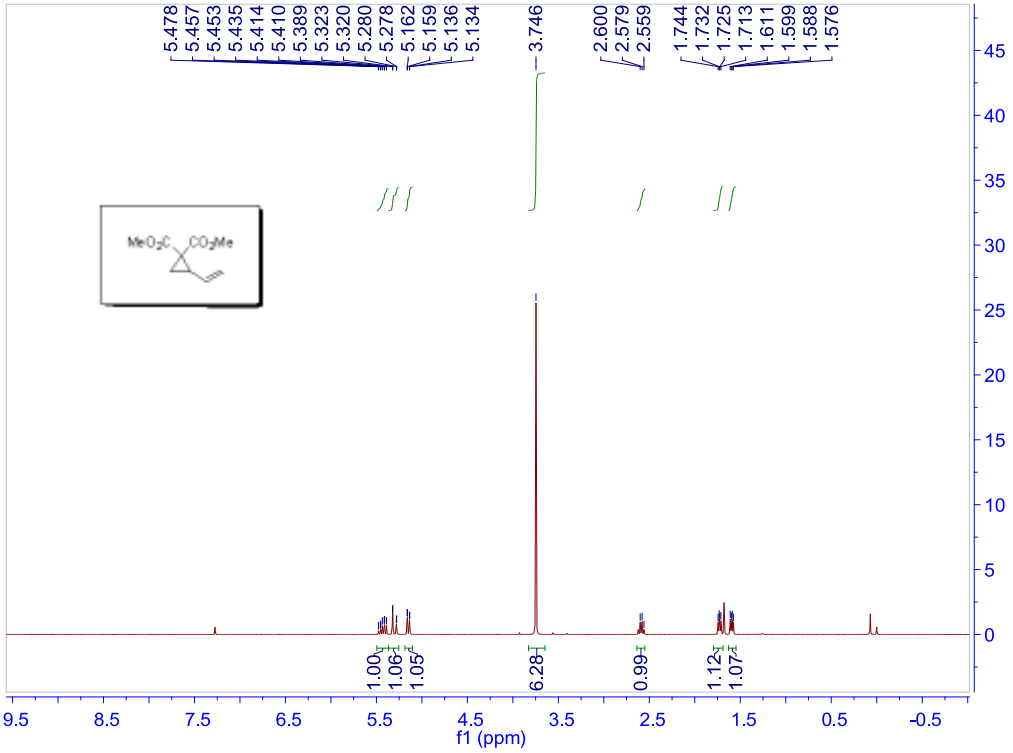
^{1}H NMR spectrum for dimethyl 2,2-diallylmalonate



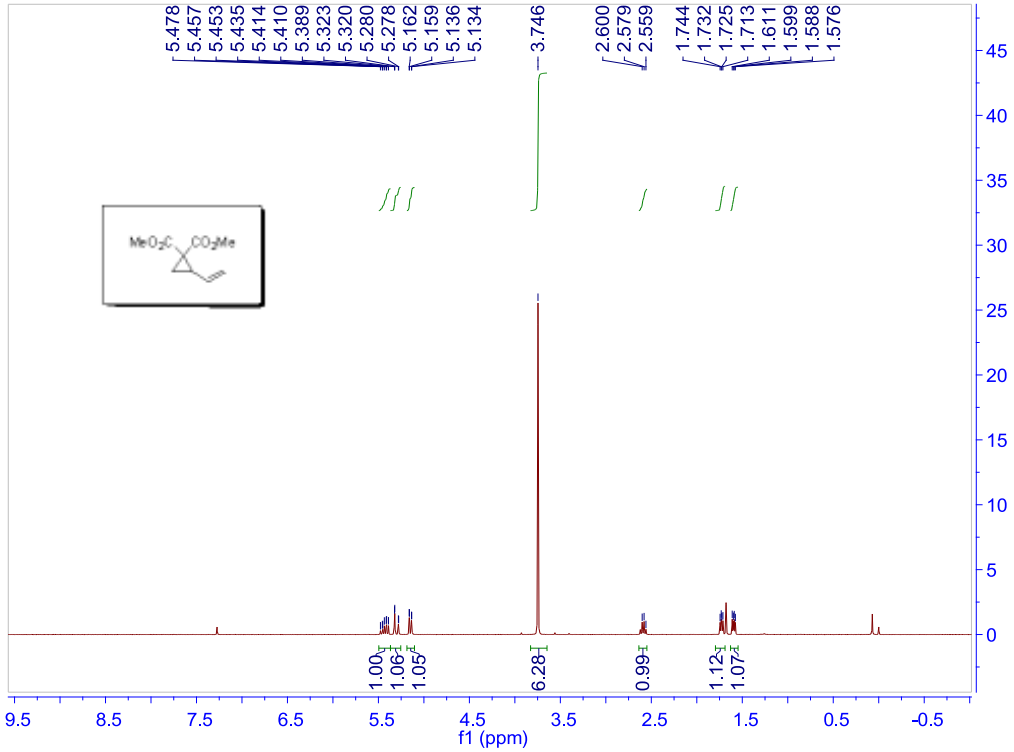
^{13}C NMR spectrum for dimethyl 2,2-diallylmalonate



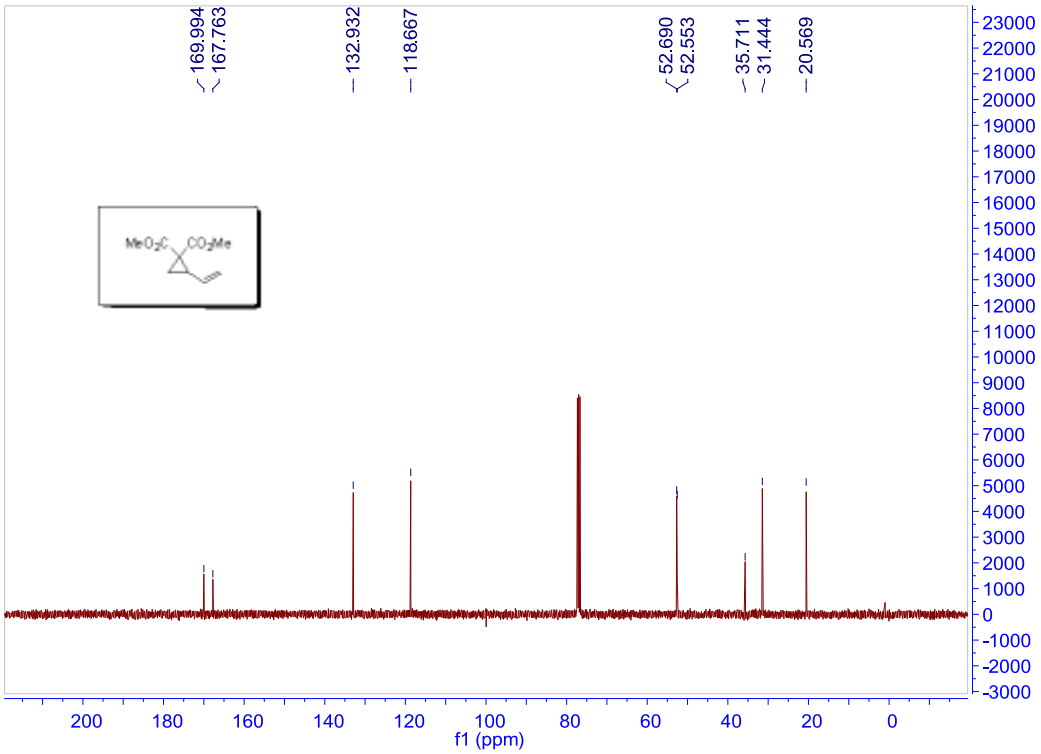
^{1}H NMR spectrum for dimethyl 2-vinylcyclopropane-1,1-dicarboxylate



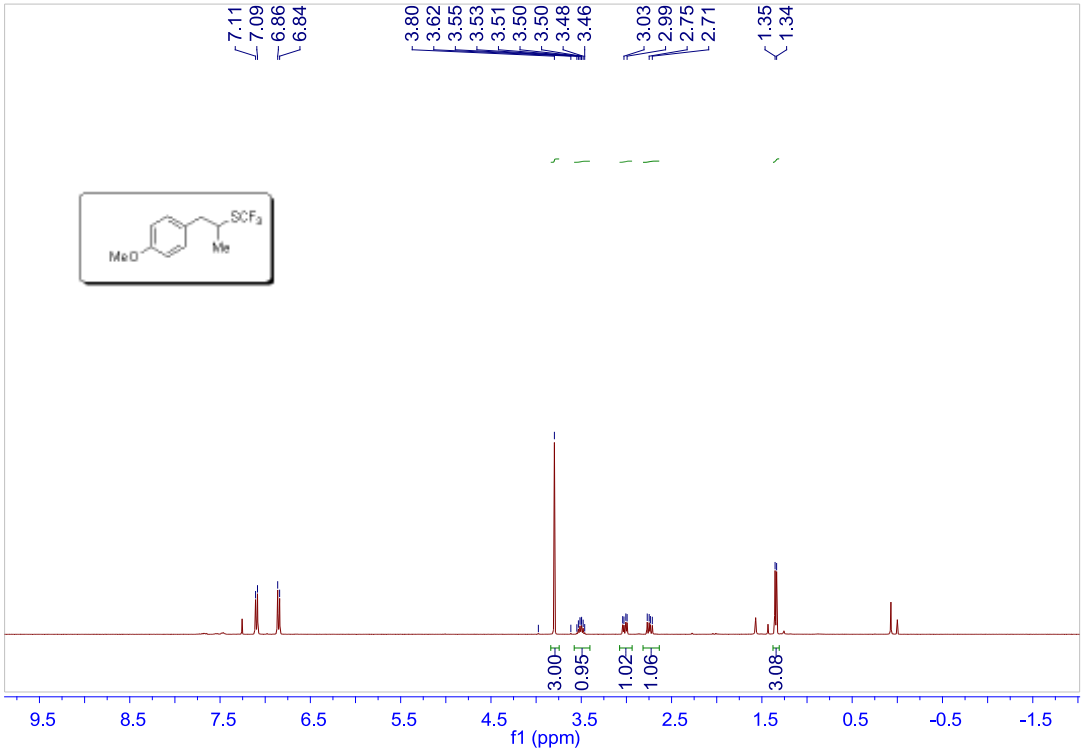
^{1}H NMR spectrum for dimethyl 2-vinylcyclopropane-1,1-dicarboxylate



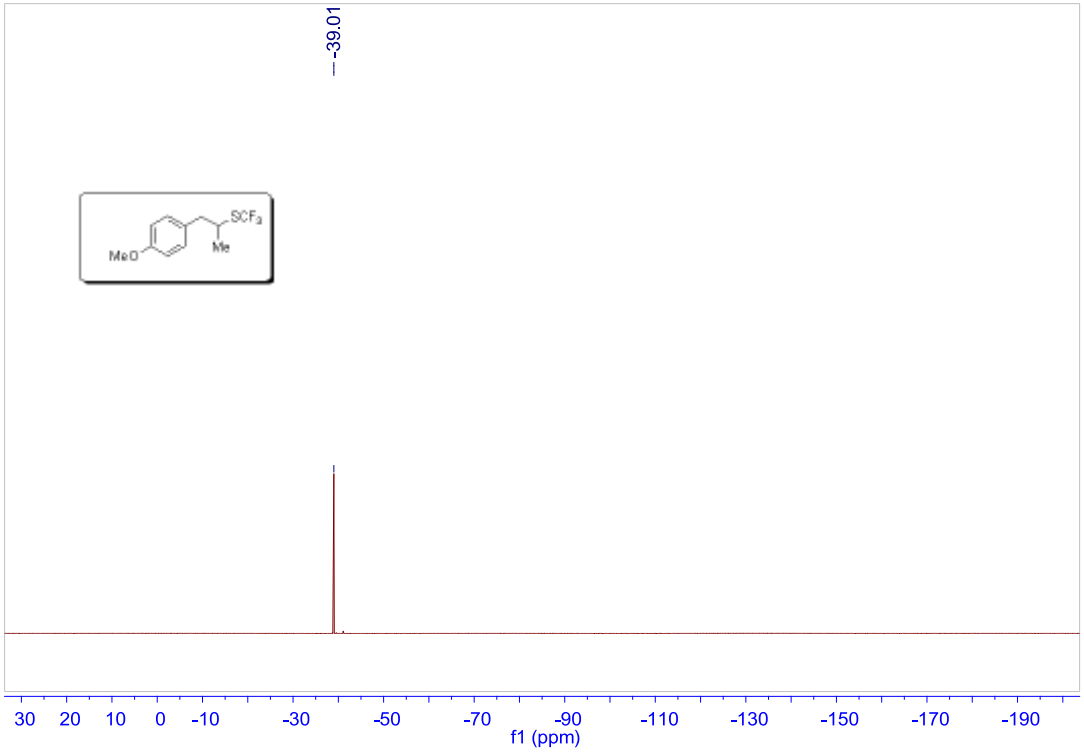
^{13}C NMR spectrum for dimethyl 2-vinylcyclopropane-1,1-dicarboxylate



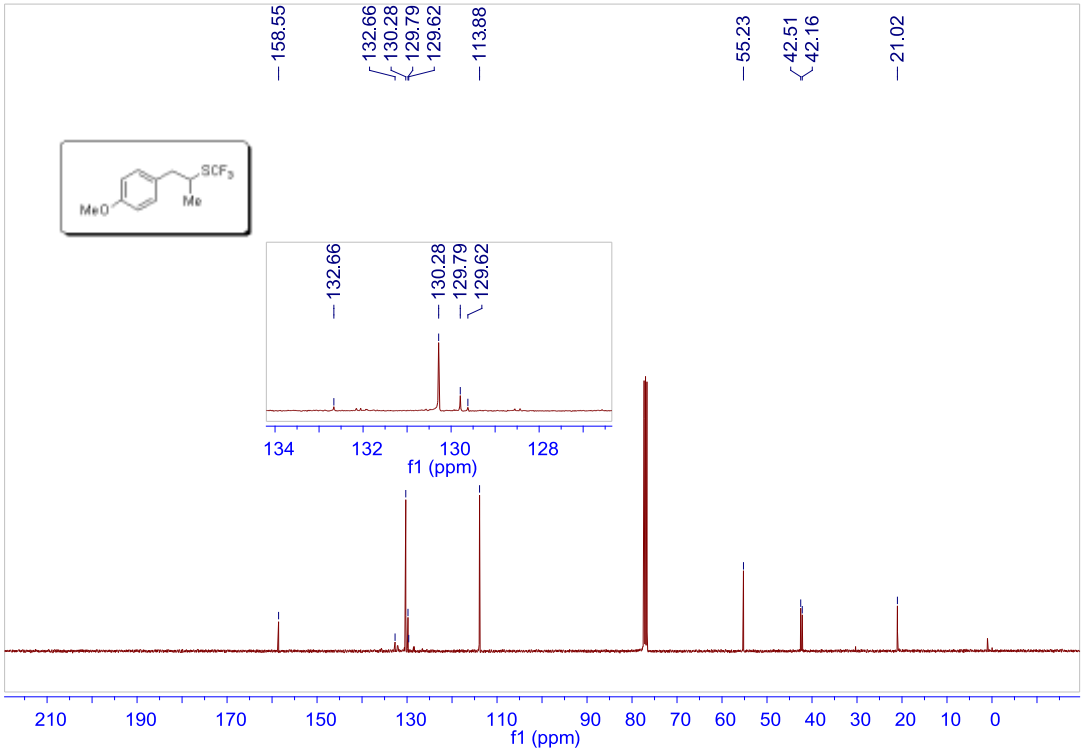
[1] HNMR spectrum for (1-(4-methoxyphenyl)propan-2-yl)(trifluoromethyl)sulfane (3a)



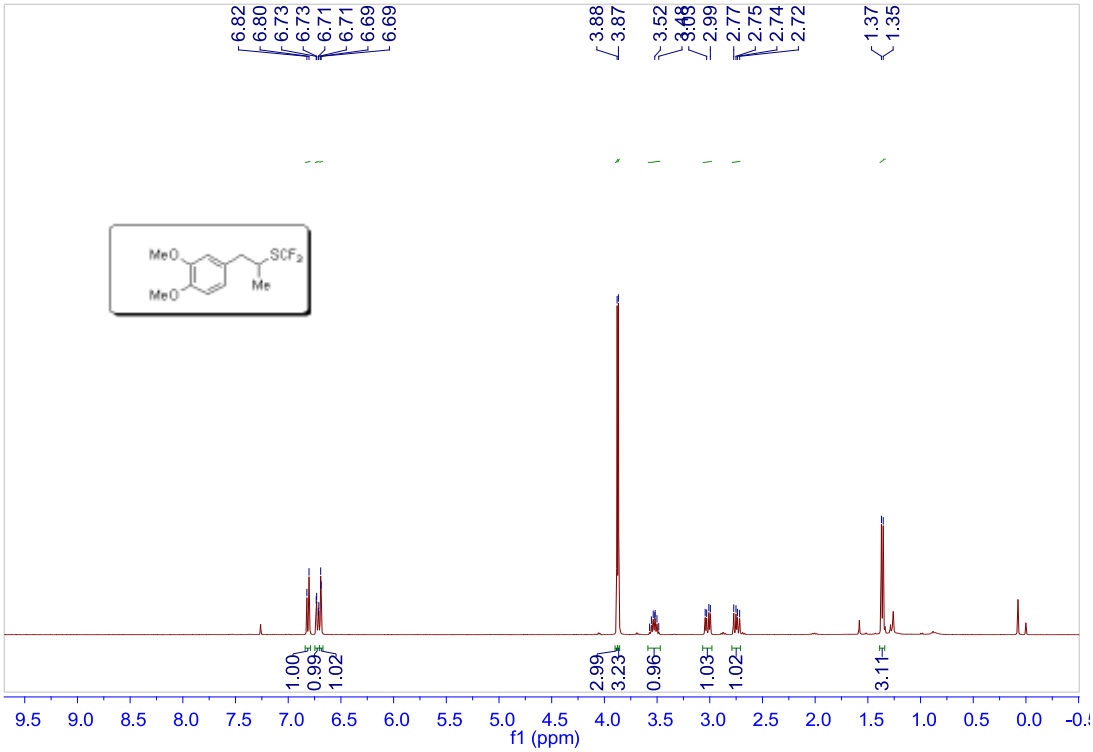
[19] FNMR spectrum for (1-(4-methoxyphenyl)propan-2-yl)(trifluoromethyl)sulfane (3a)



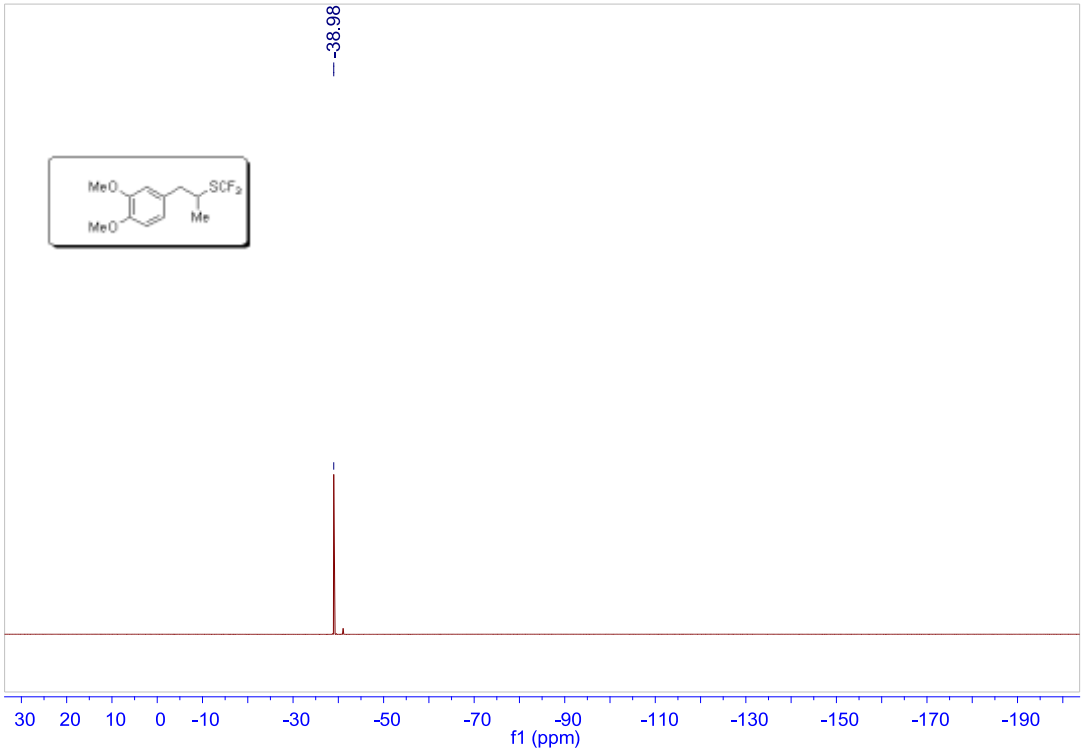
^{13} CNMR spectrum for (1-(4-methoxyphenyl)propan-2-yl)(trifluoromethyl)sulfane (3a)



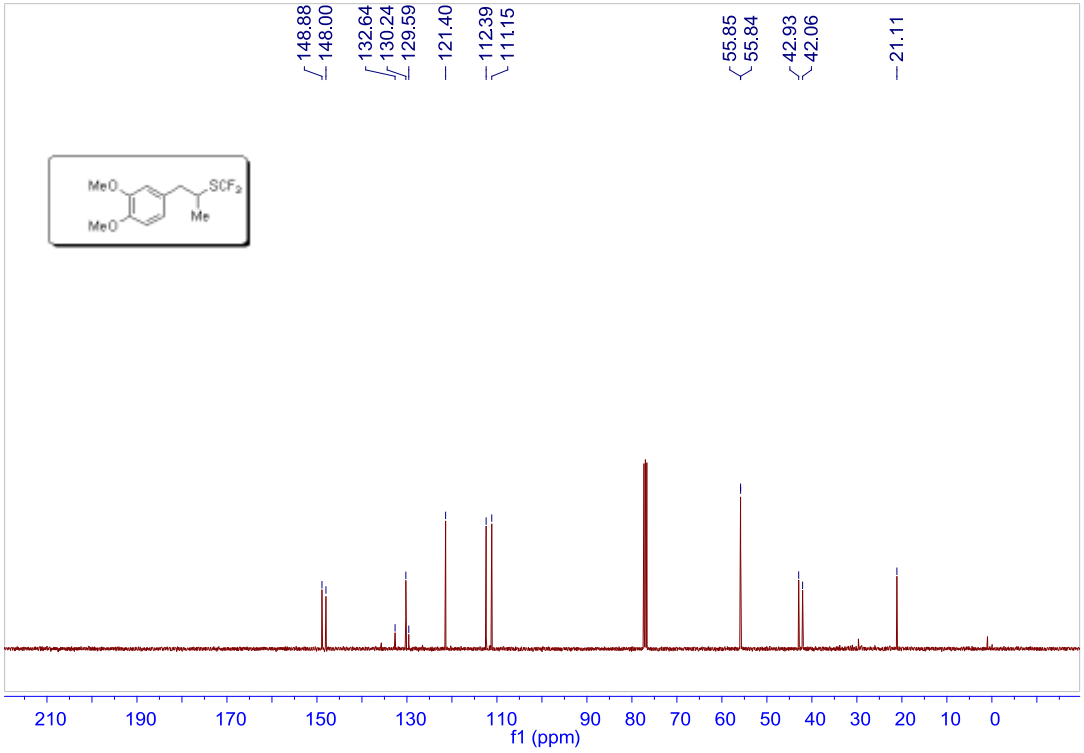
^{1} H NMR spectrum for (1-(3,4-dimethoxyphenyl)propan-2-yl)(trifluoromethyl)sulfane (3b)



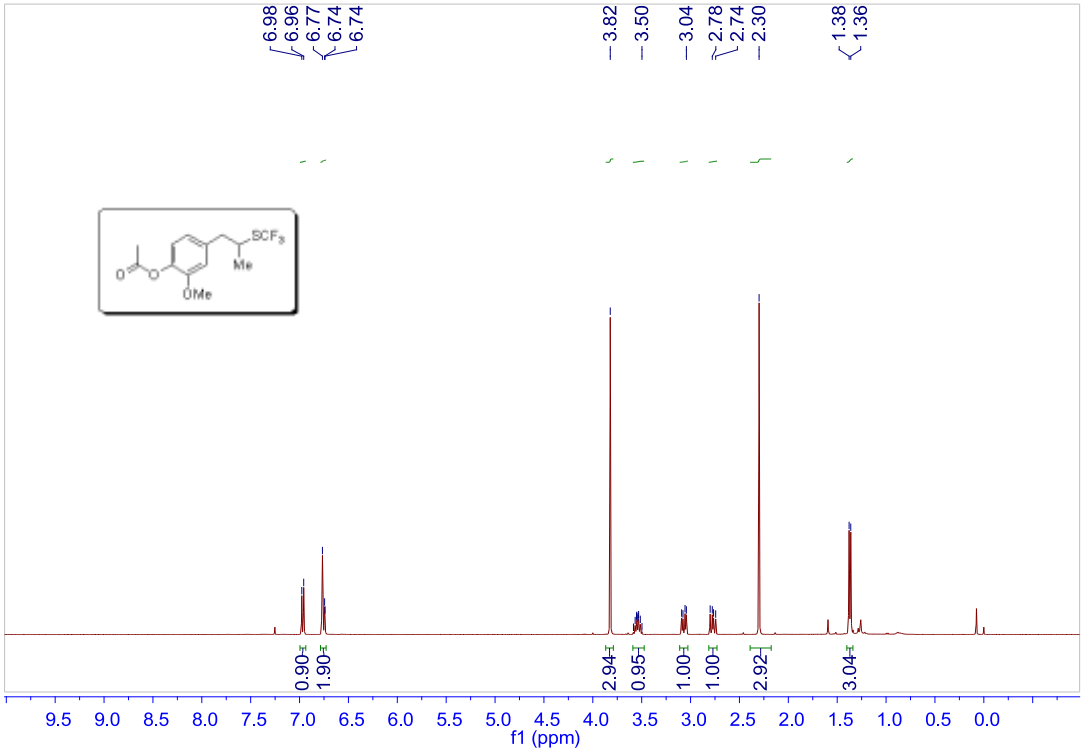
^{19}F NMR spectrum for (1-(3,4-dimethoxyphenyl)propan-2-yl)(trifluoromethyl)sulfane (3b)



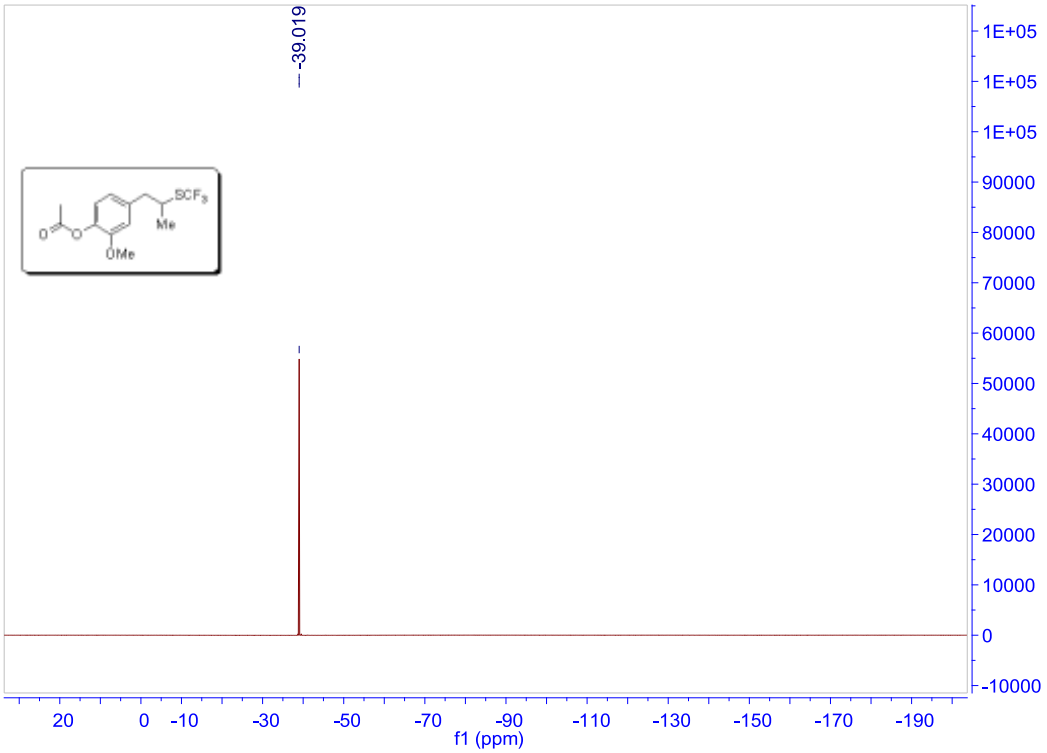
^{13}C NMR spectrum for (1-(3,4-dimethoxyphenyl)propan-2-yl)(trifluoromethyl)sulfane (3b)



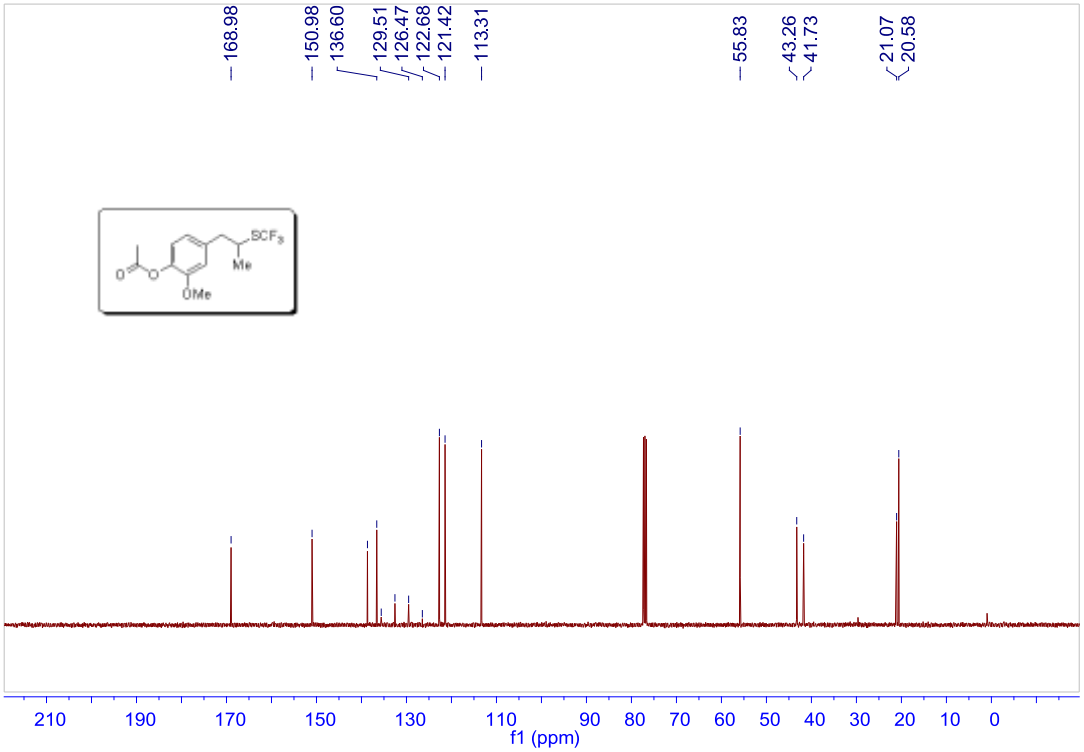
^{1}H NMR spectrum for 2-methoxy-4-(2-(trifluoromethylthio)propyl)phenyl acetate (3c)



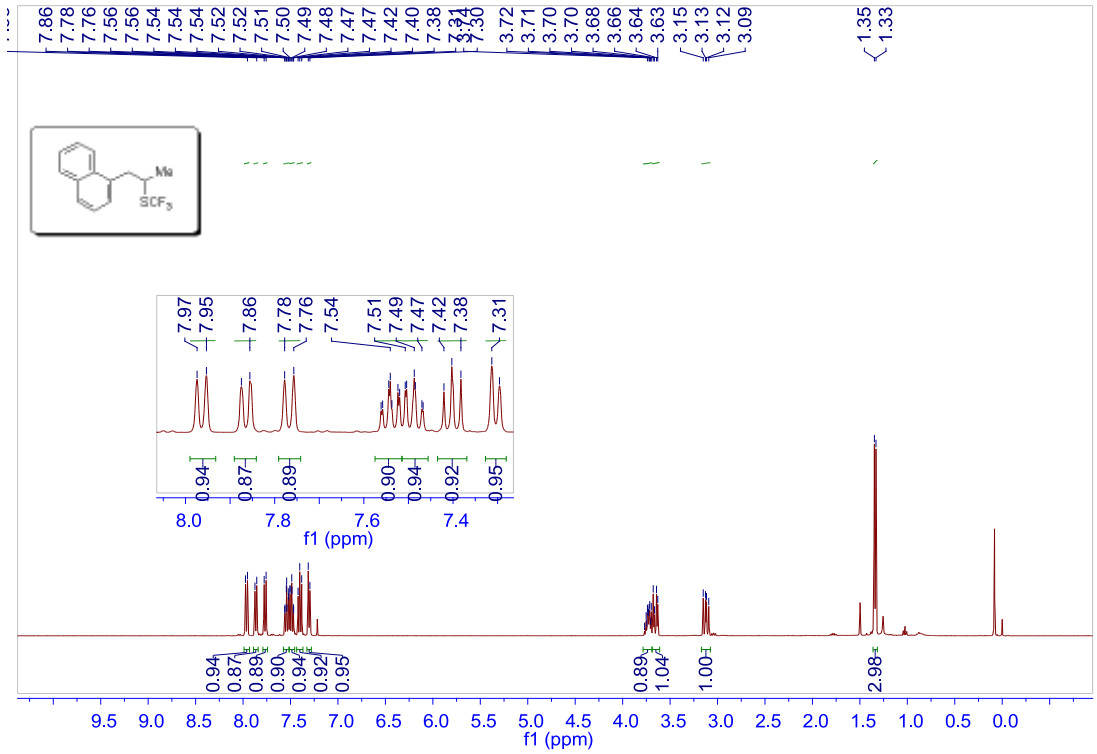
^{19}F NMR spectrum for 2-methoxy-4-(2-(trifluoromethylthio)propyl)phenyl acetate (3c)



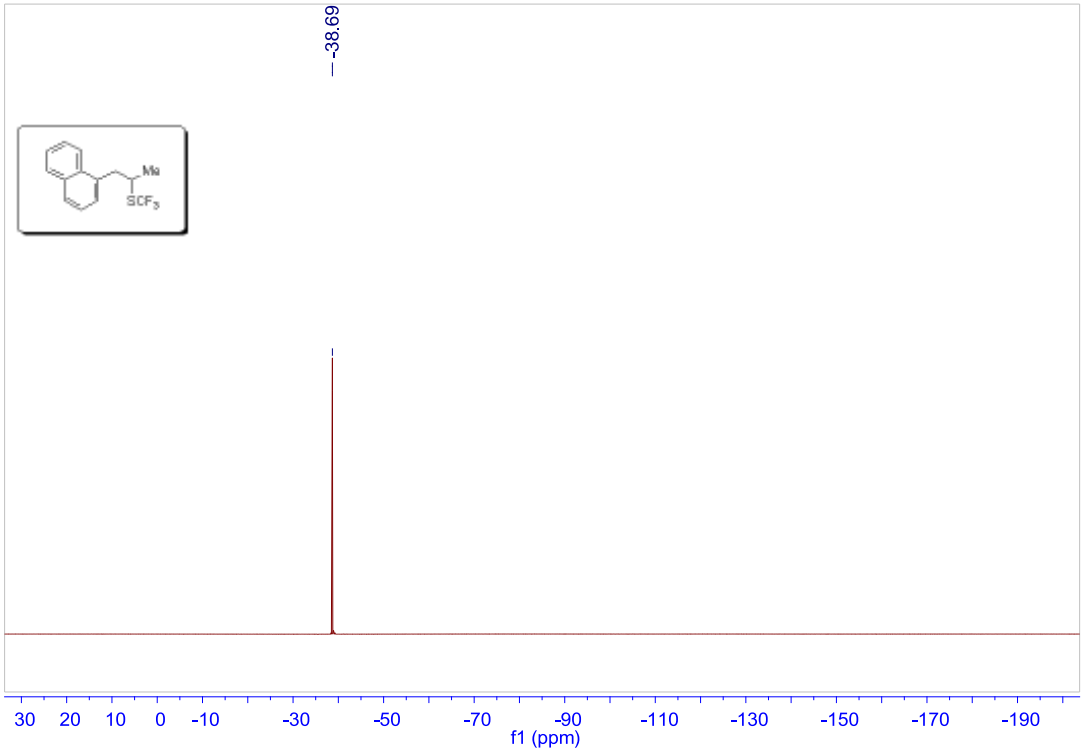
^{13}C NMR spectrum for 2-methoxy-4-(2-(trifluoromethylthio)propyl)phenyl acetate (3c)



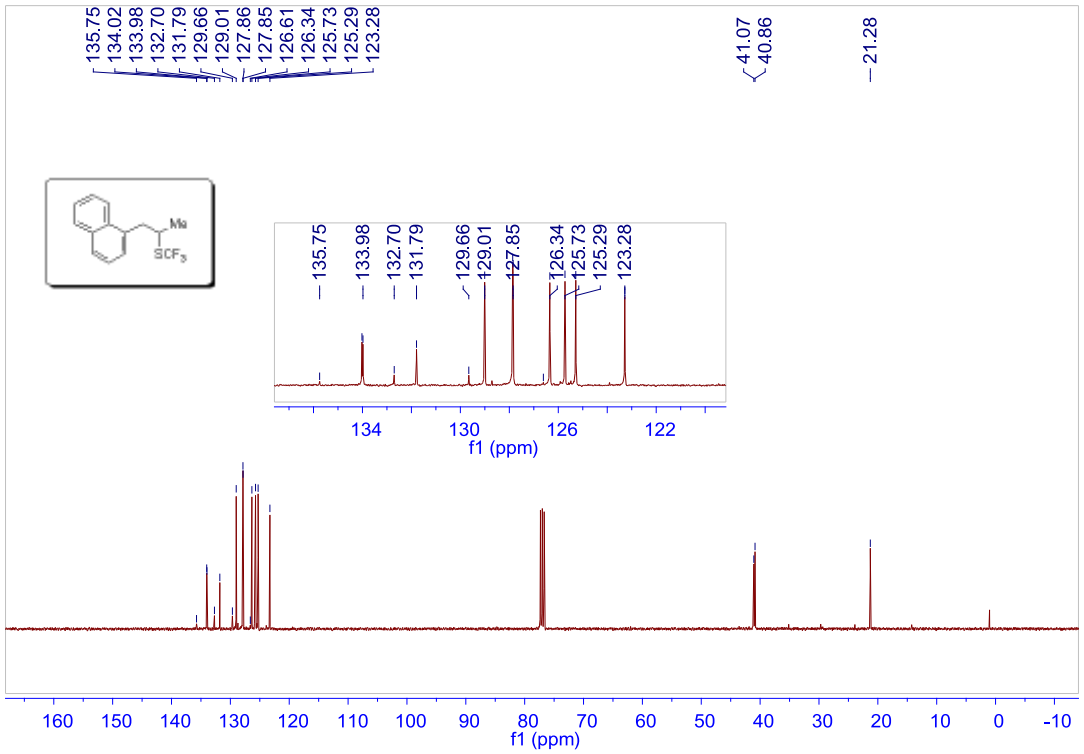
^{1}HNMR spectrum for (1-(naphthalen-1-yl)propan-2-yl)(trifluoromethyl)sulfane (3d)



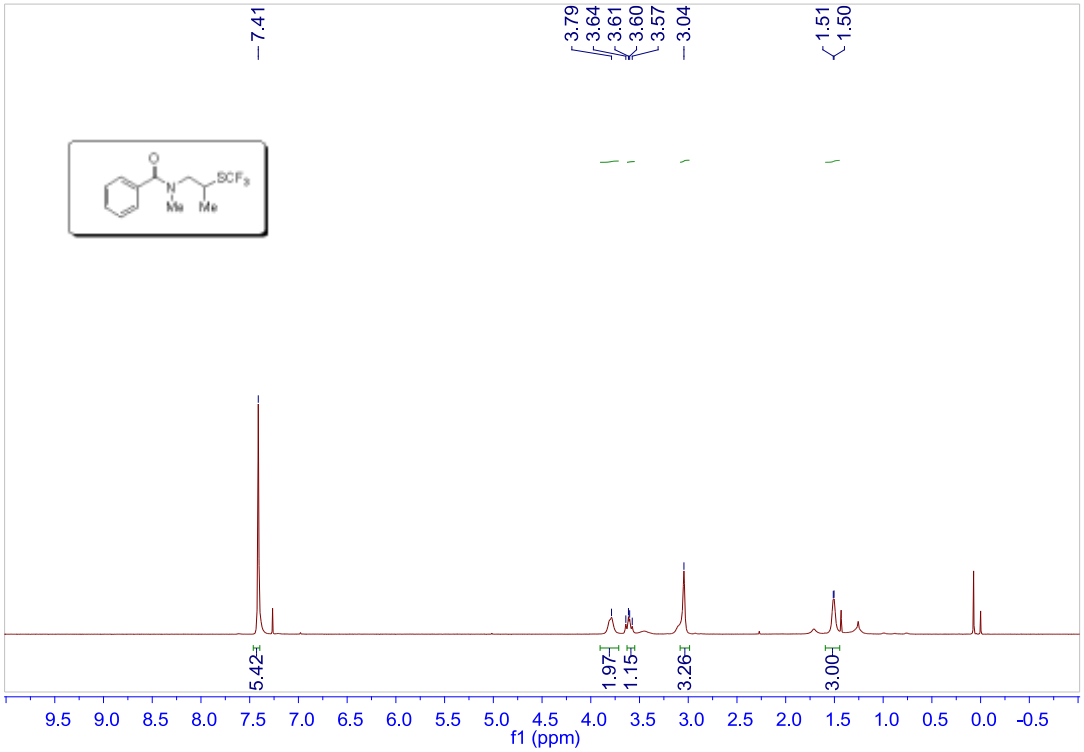
^{19}F NMR spectrum for (1-(naphthalen-1-yl)propan-2-yl)(trifluoromethyl)sulfane (3d)



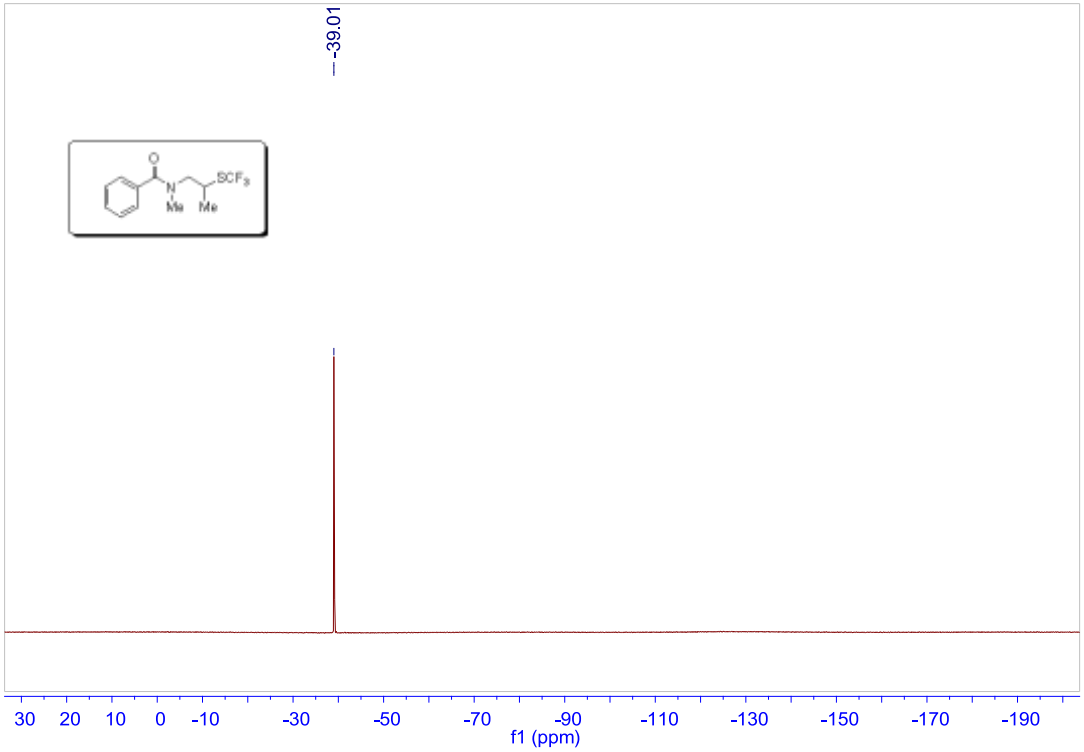
^{13}C NMR spectrum for (1-(naphthalen-1-yl)propan-2-yl)(trifluoromethyl)sulfane (3d)



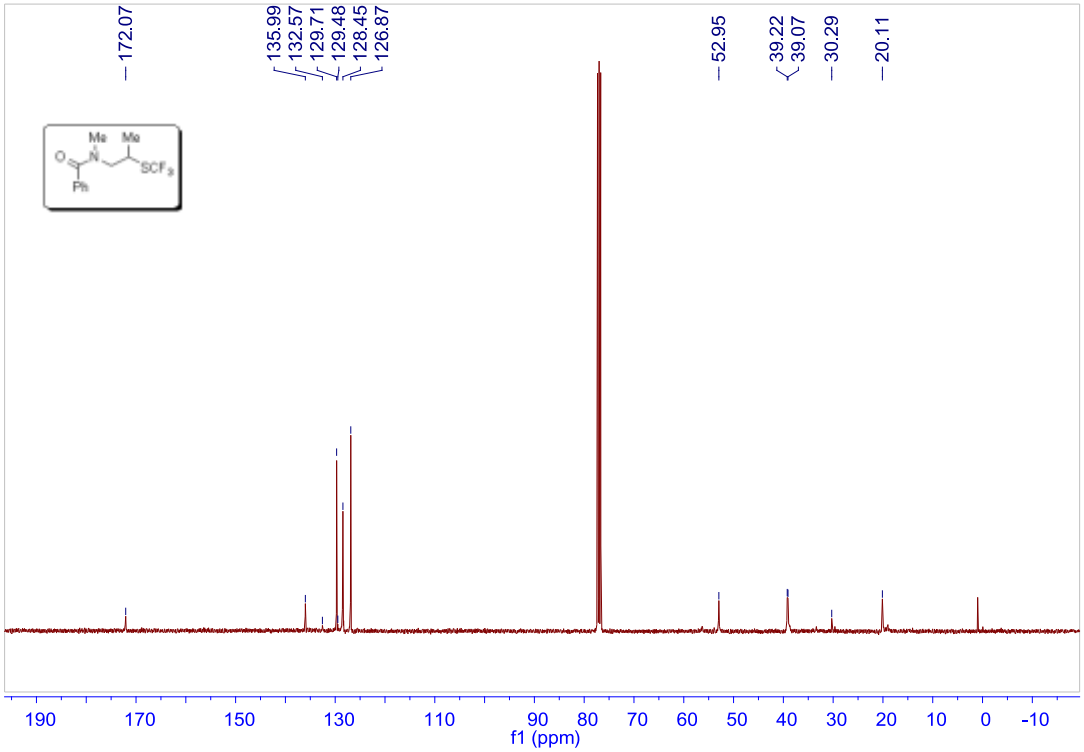
^{1}H NMR spectrum for *N*-methyl-N-(2-(trifluoromethylthio)propyl)benzamide (3e)



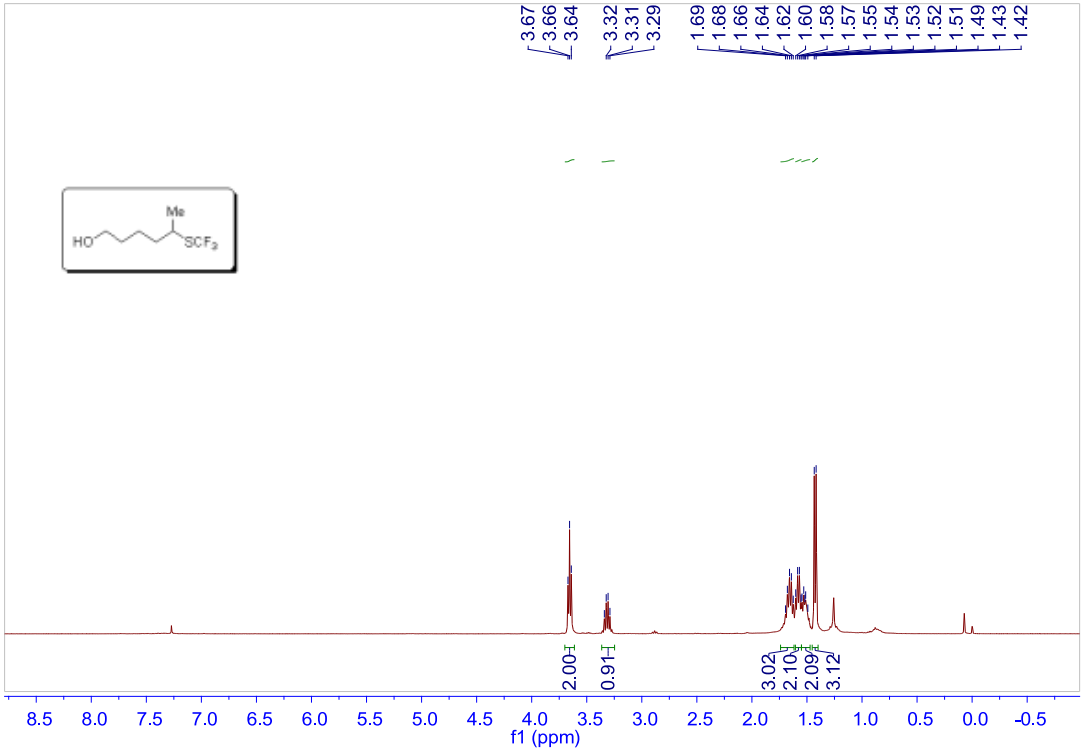
^{19}F NMR spectrum for *N*-methyl-N-(2-(trifluoromethylthio)propyl)benzamide (3e)



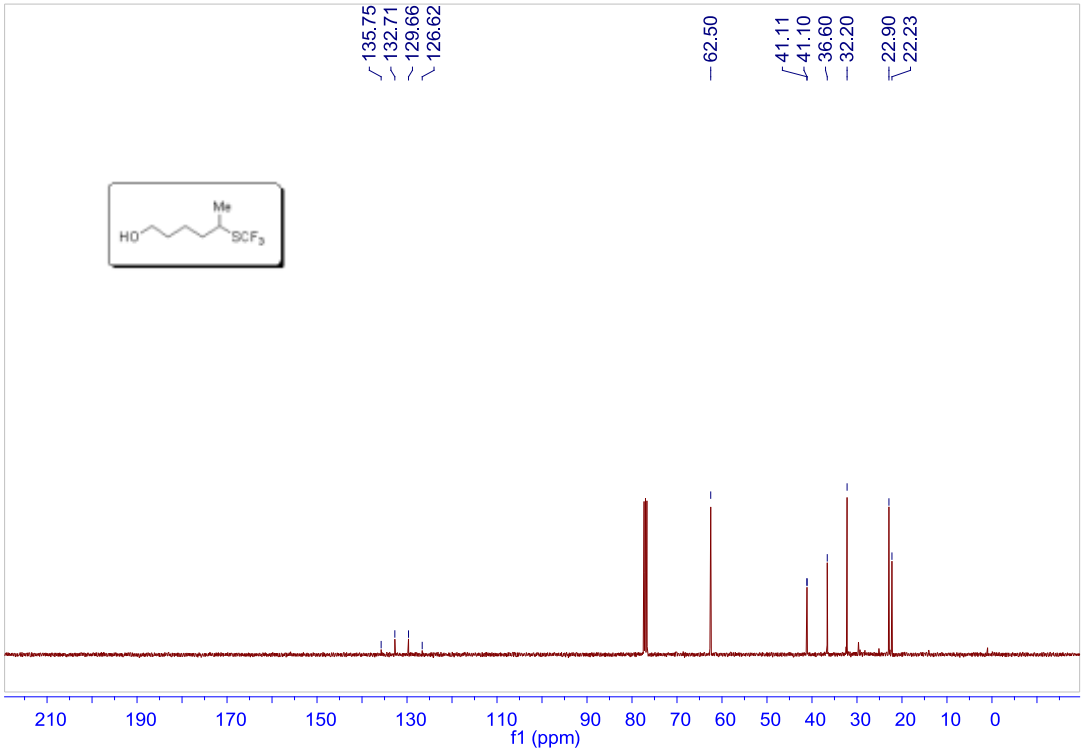
^{13}C NMR spectrum for *N*-methyl-N-(2-(trifluoromethylthio)propyl)benzamide (3e)



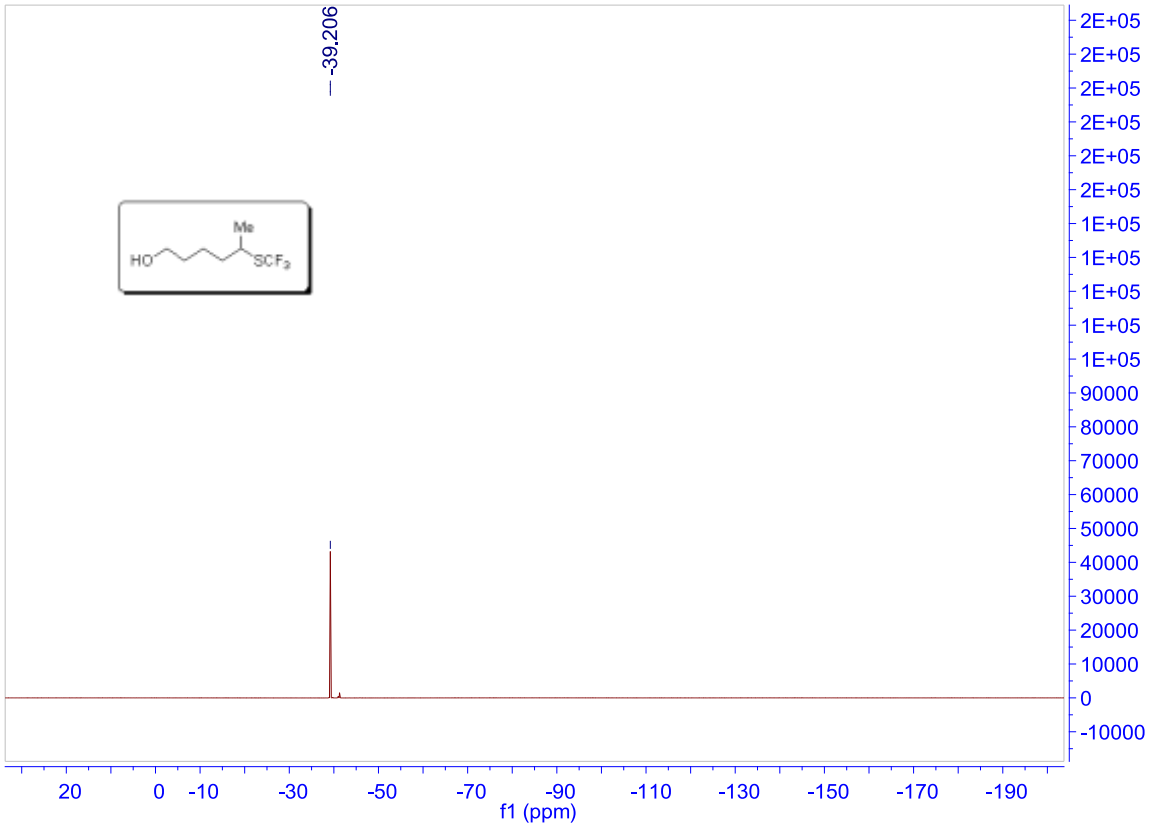
^{1}H NMR spectrum for 5-(trifluoromethylthio)hexan-1-ol (3f)



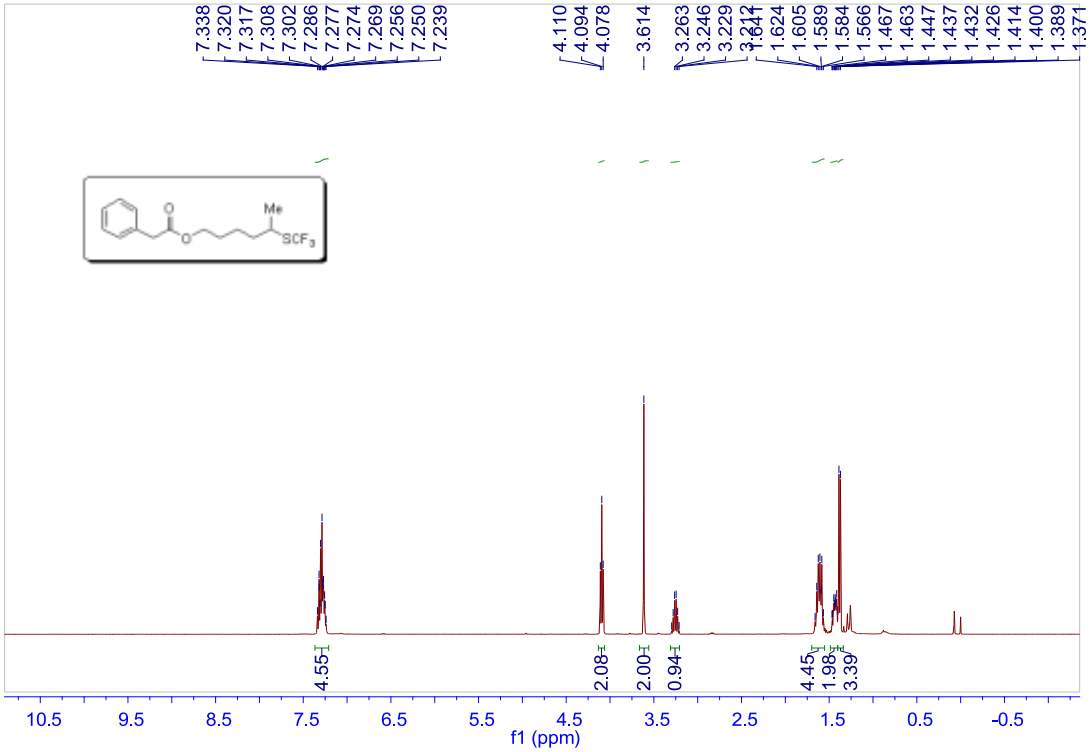
^{13}C NMR spectrum for 5-(trifluoromethylthio)hexan-1-ol (3f)



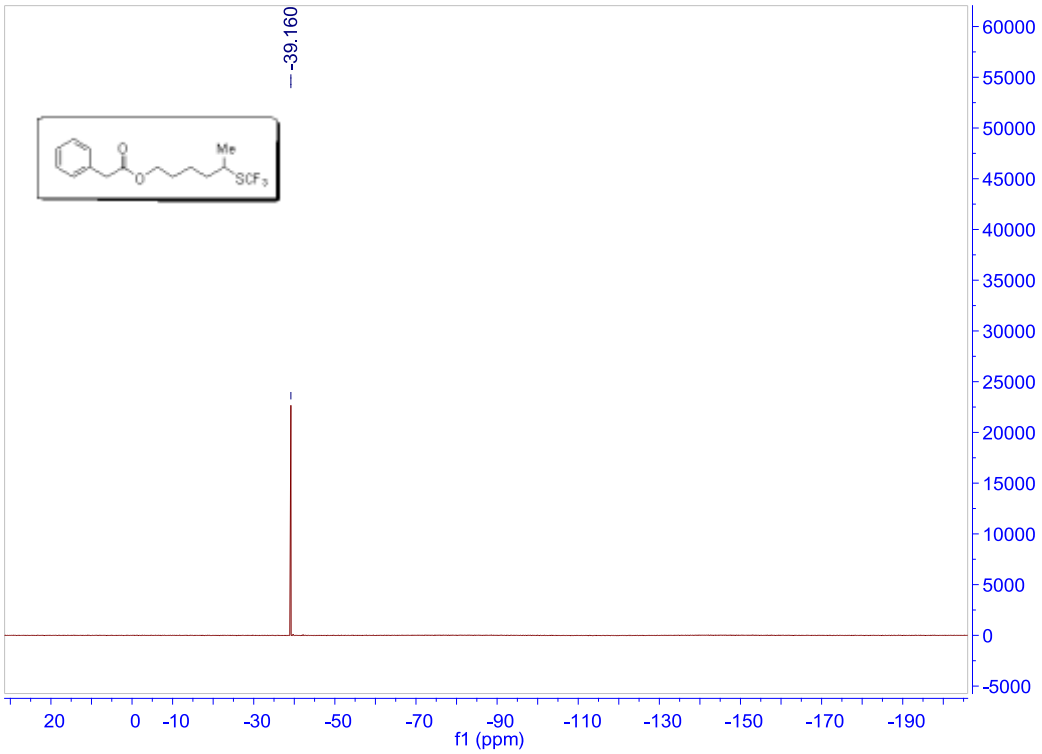
^{19}F NMR spectrum for 5-(trifluoromethylthio)hexan-1-ol (3f)



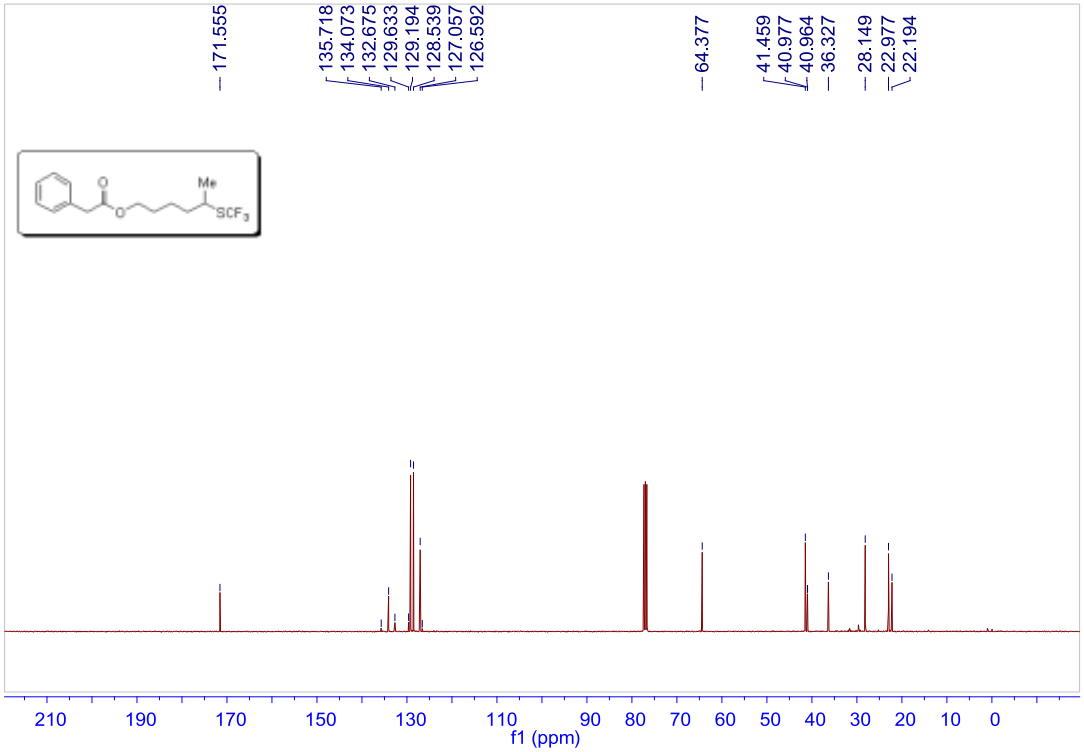
^{1}H NMR spectrum for 5-(trifluoromethylthio)hexyl 2-phenylacetate (3g)



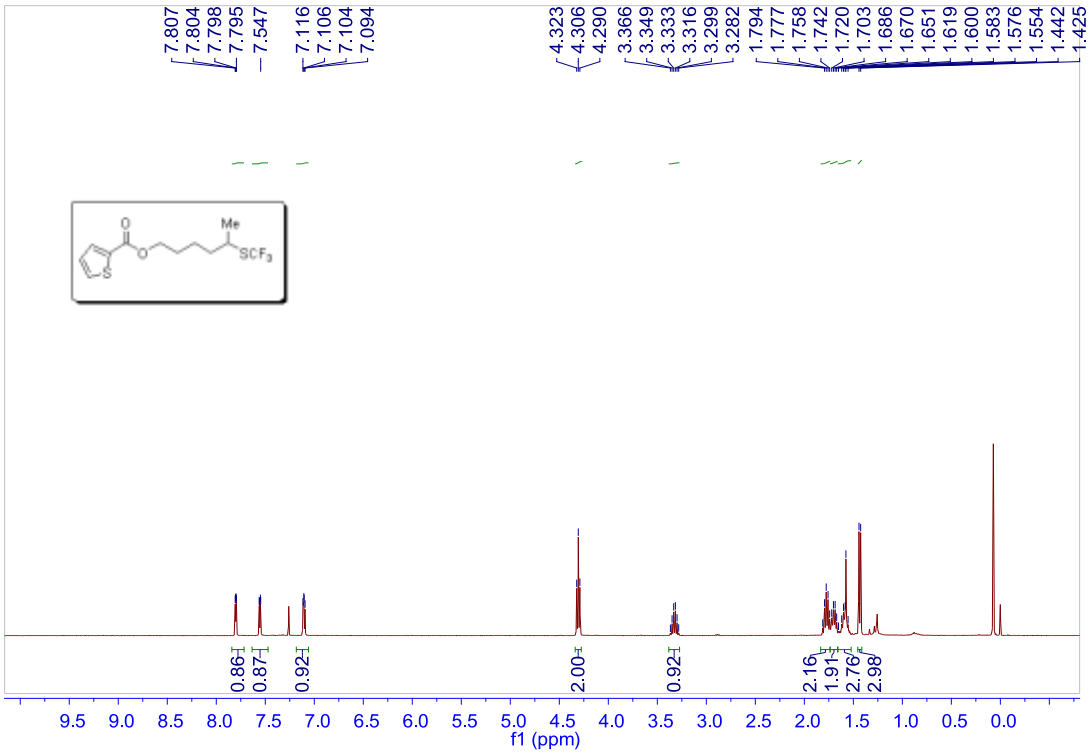
^{19}F NMR spectrum for 5-(trifluoromethylthio)hexyl 2-phenylacetate (3g)



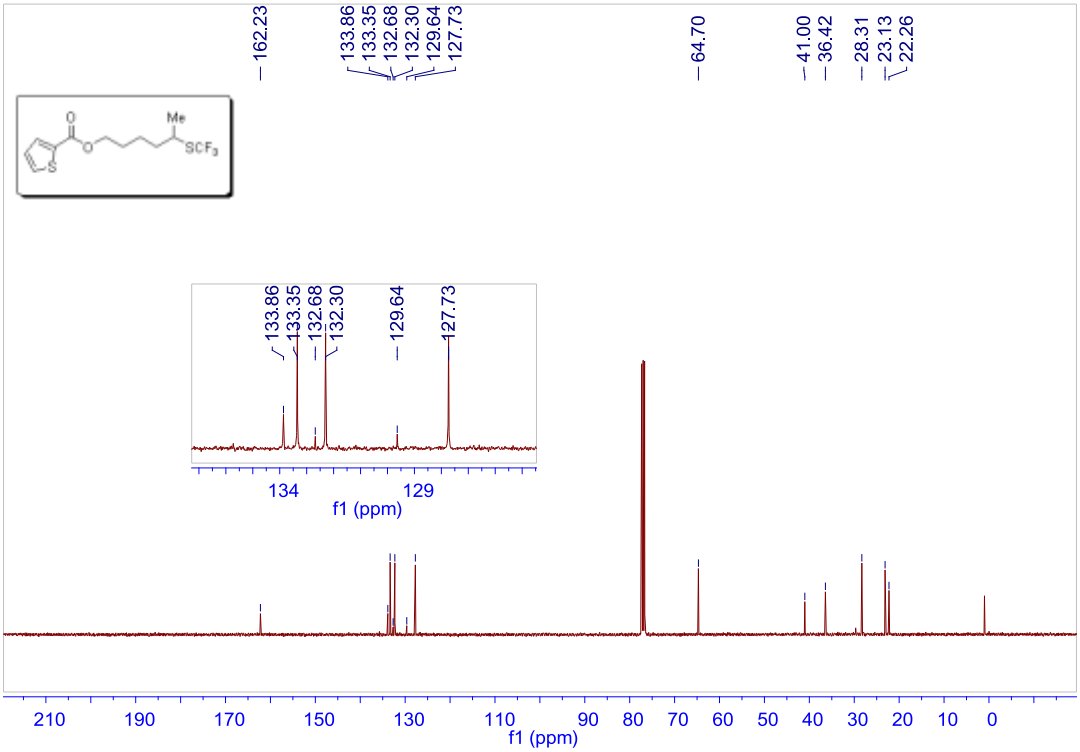
^{13}C NMR spectrum for 5-(trifluoromethylthio)hexyl 2-phenylacetate (3g)



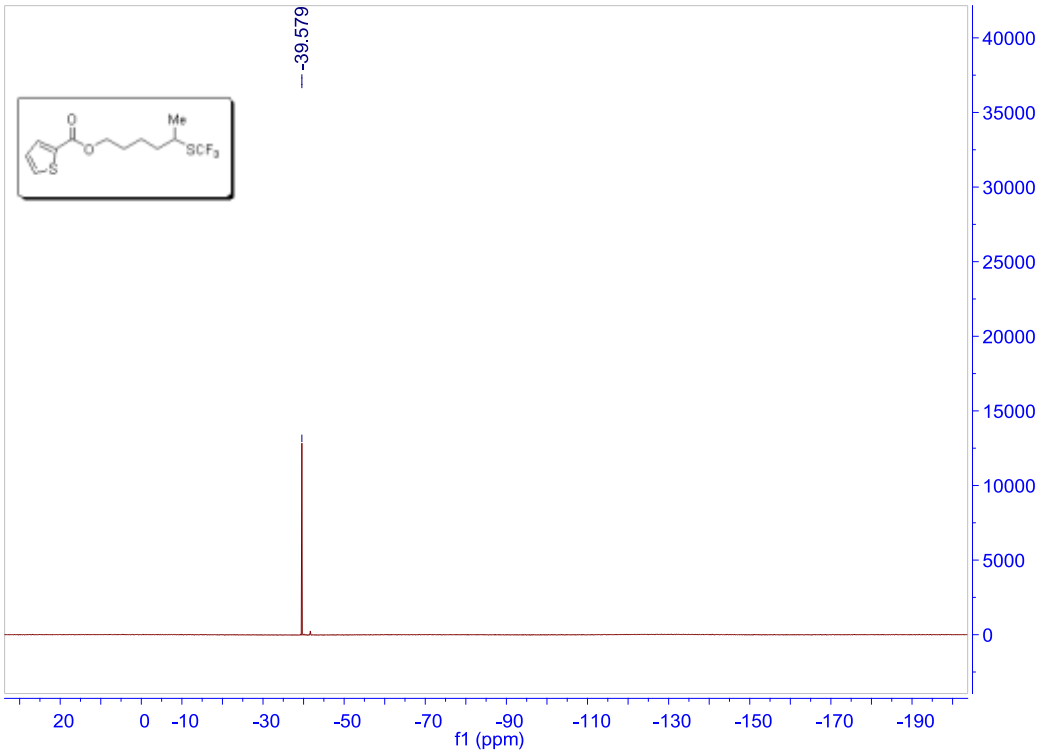
^{1}H NMR spectrum for 5-(trifluoromethylthio)hexyl thiophene-2-carboxylate (3h)



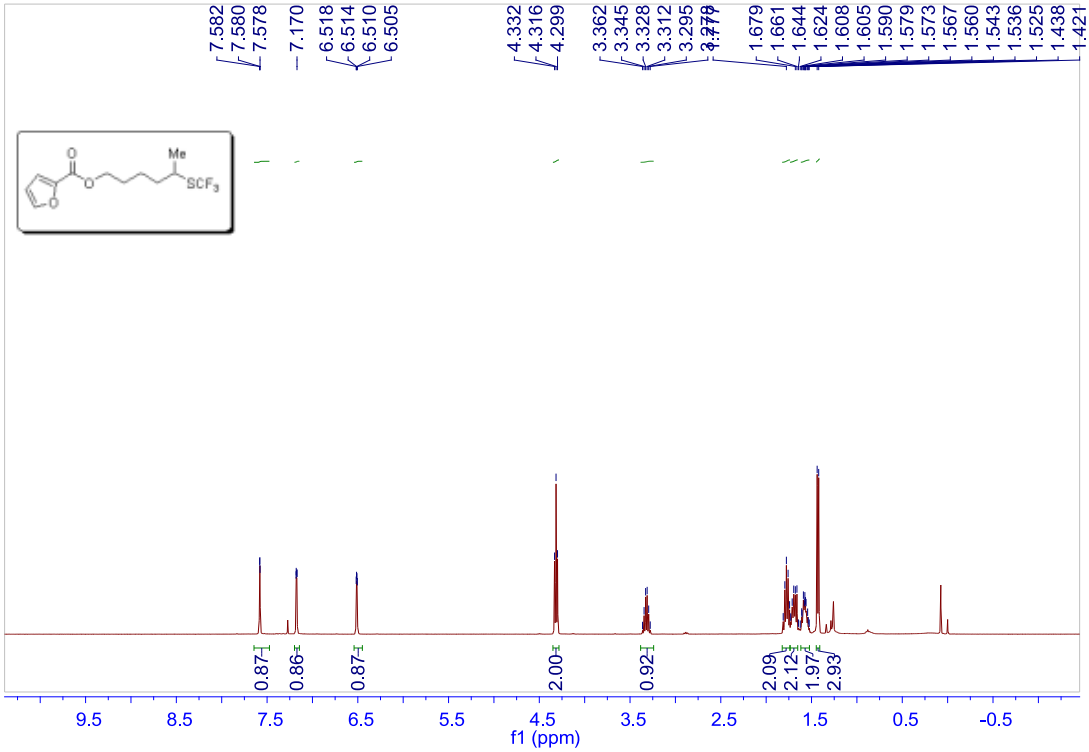
^{13}C NMR spectrum for 5-(trifluoromethylthio)hexyl thiophene-2-carboxylate (3h)



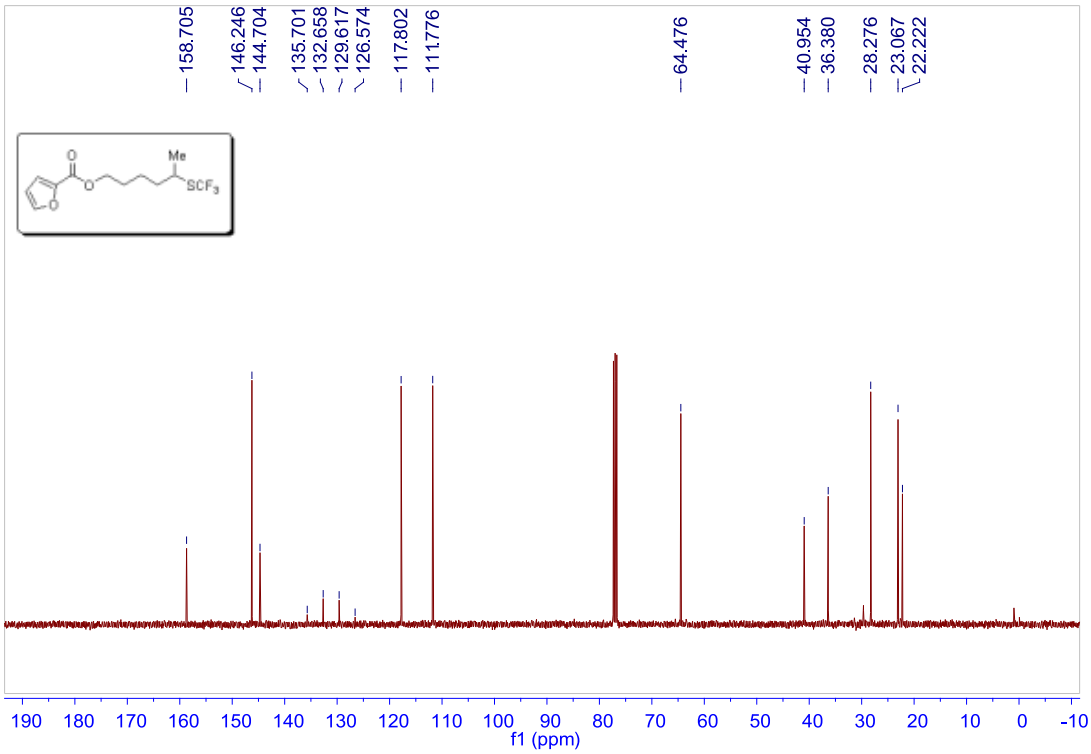
^{19}F NMR spectrum for 5-(trifluoromethylthio)hexyl thiophene-2-carboxylate (3h)



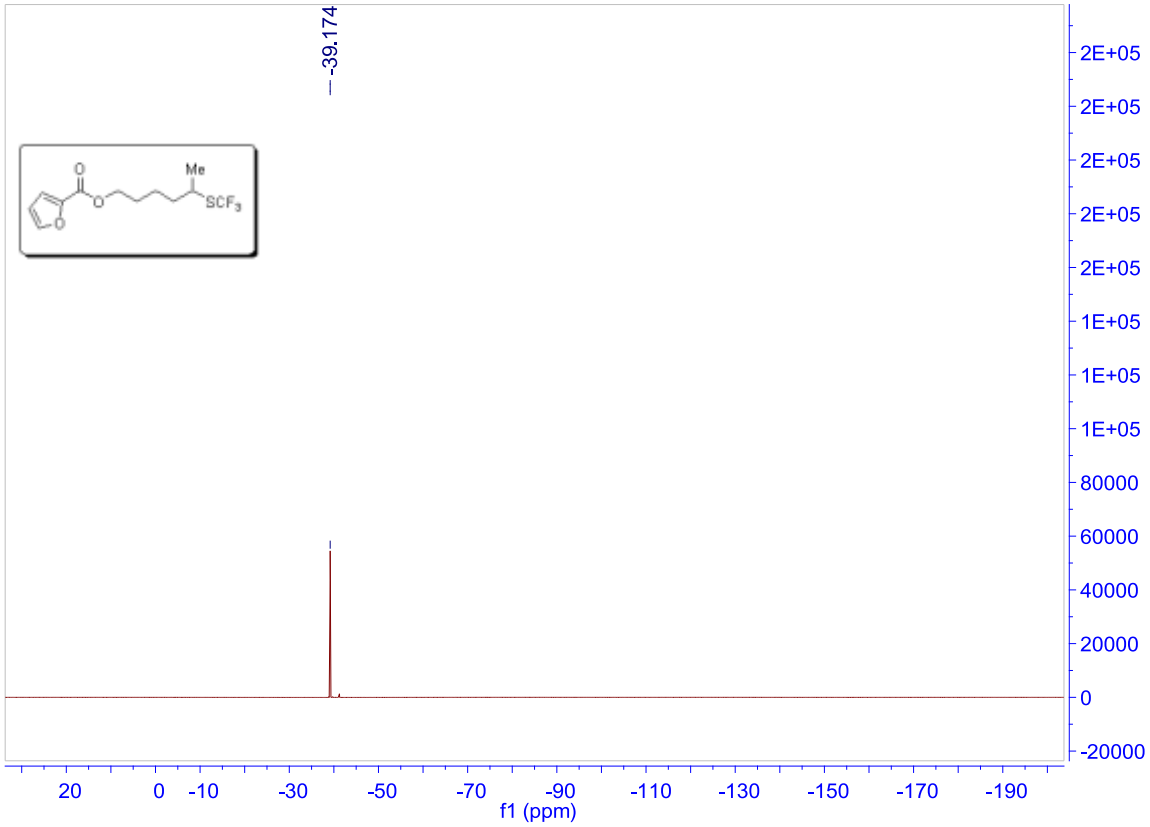
^{1}H NMR spectrum for 5-(trifluoromethylthio)hexyl furan-2-carboxylate (3i)



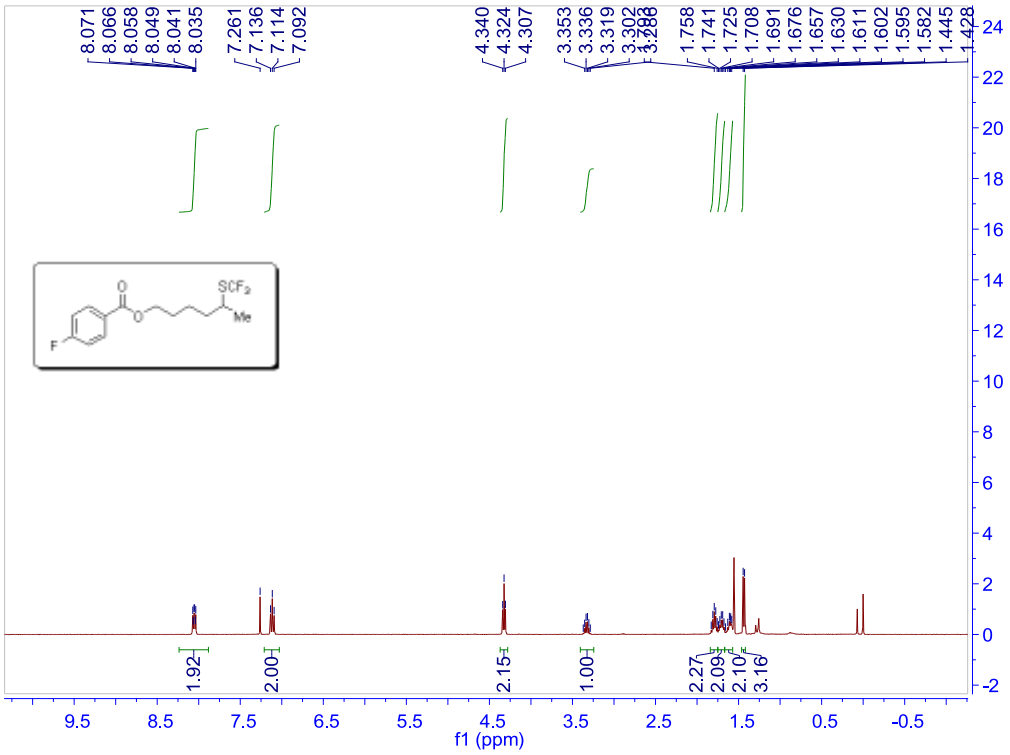
^{13}C NMR spectrum for 5-(trifluoromethylthio)hexyl furan-2-carboxylate (3i)



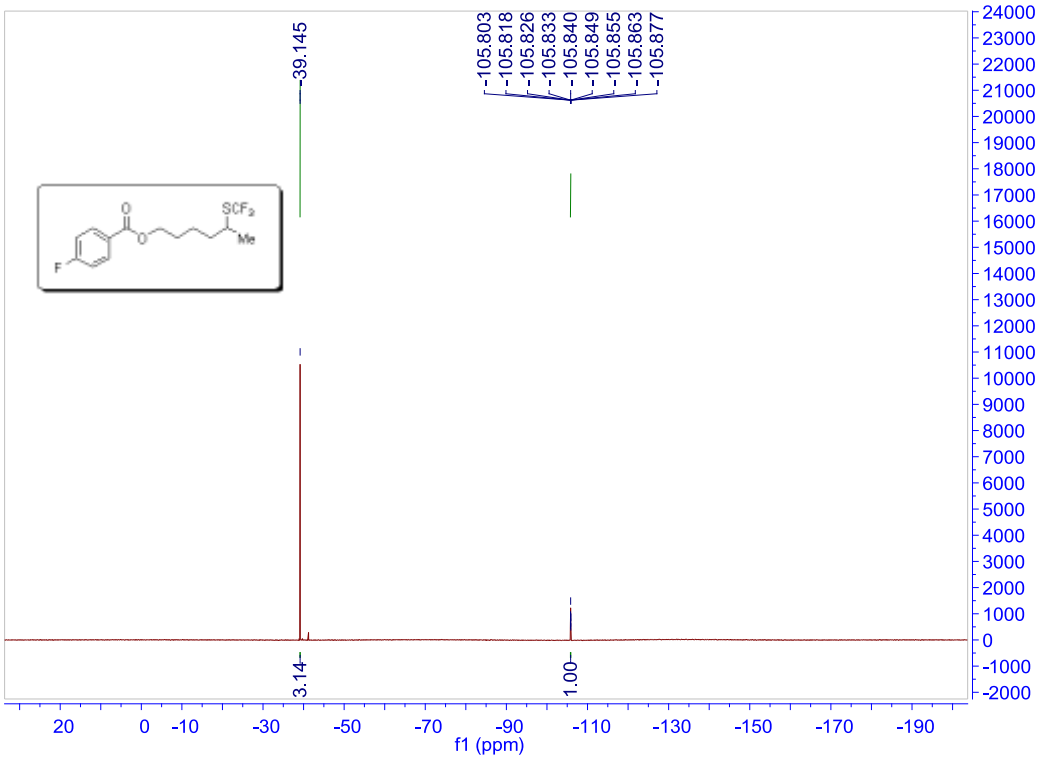
^{19}F NMR spectrum for 5-(trifluoromethylthio)hexyl furan-2-carboxylate (3i)



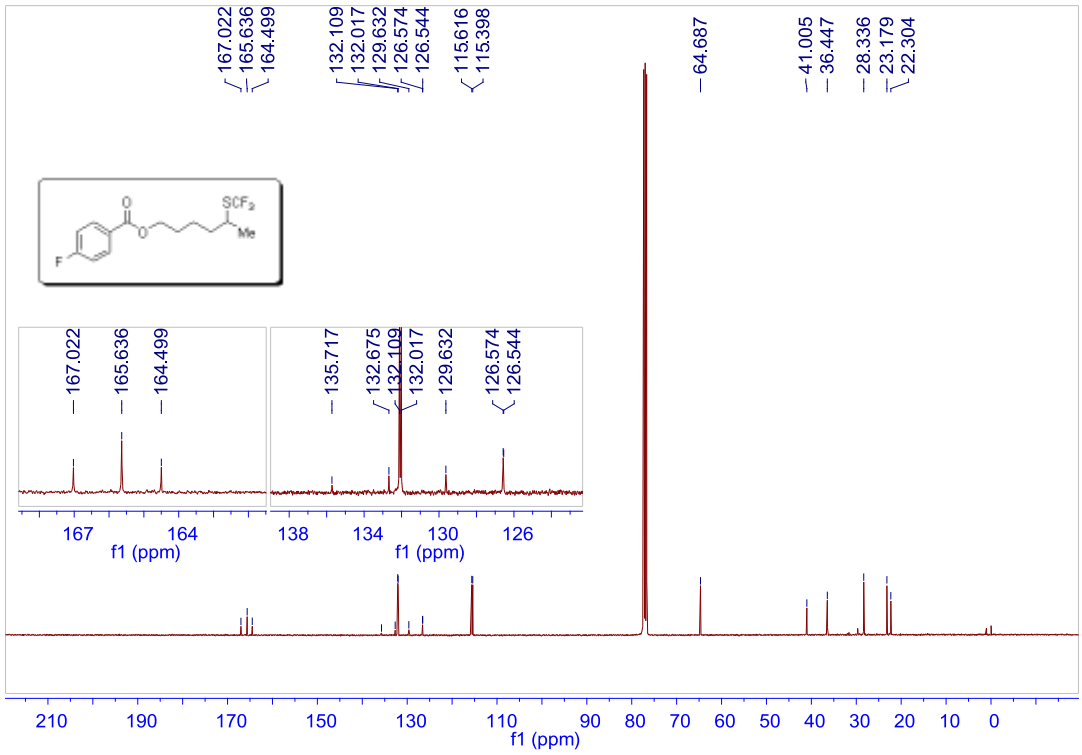
^{1}H NMR spectrum for 5-(trifluoromethylthio)hexyl 4-fluorobenzoate (3j)



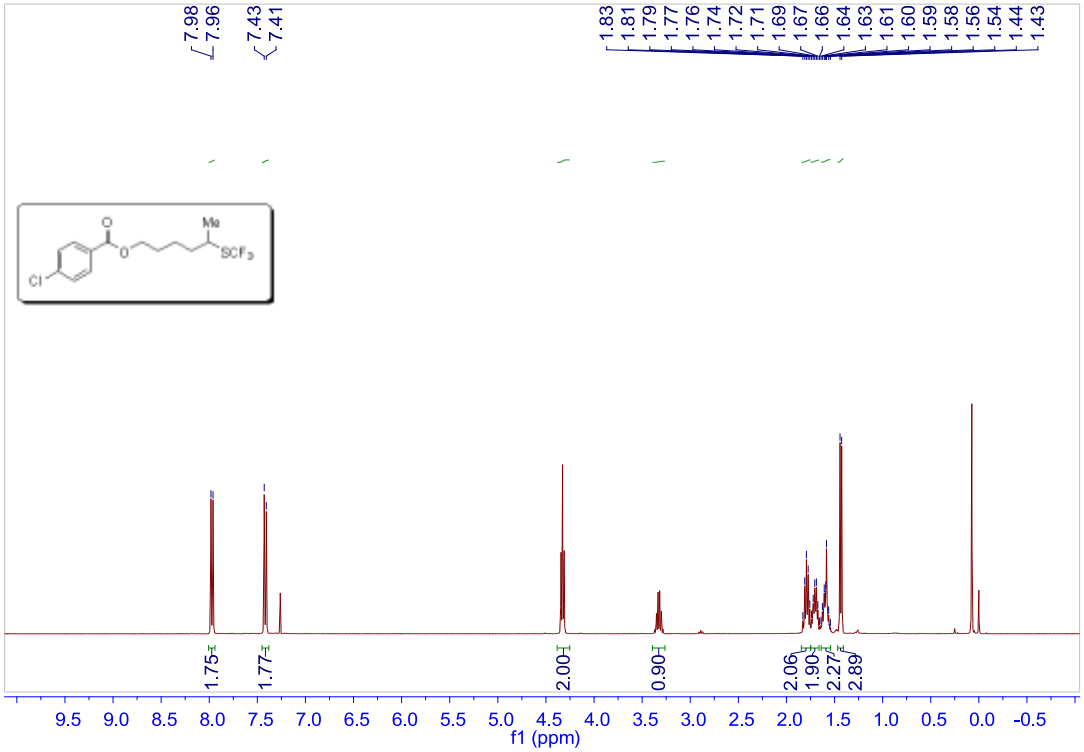
^{19}F NMR spectrum for 5-(trifluoromethylthio)hexyl 4-fluorobenzoate (3j)



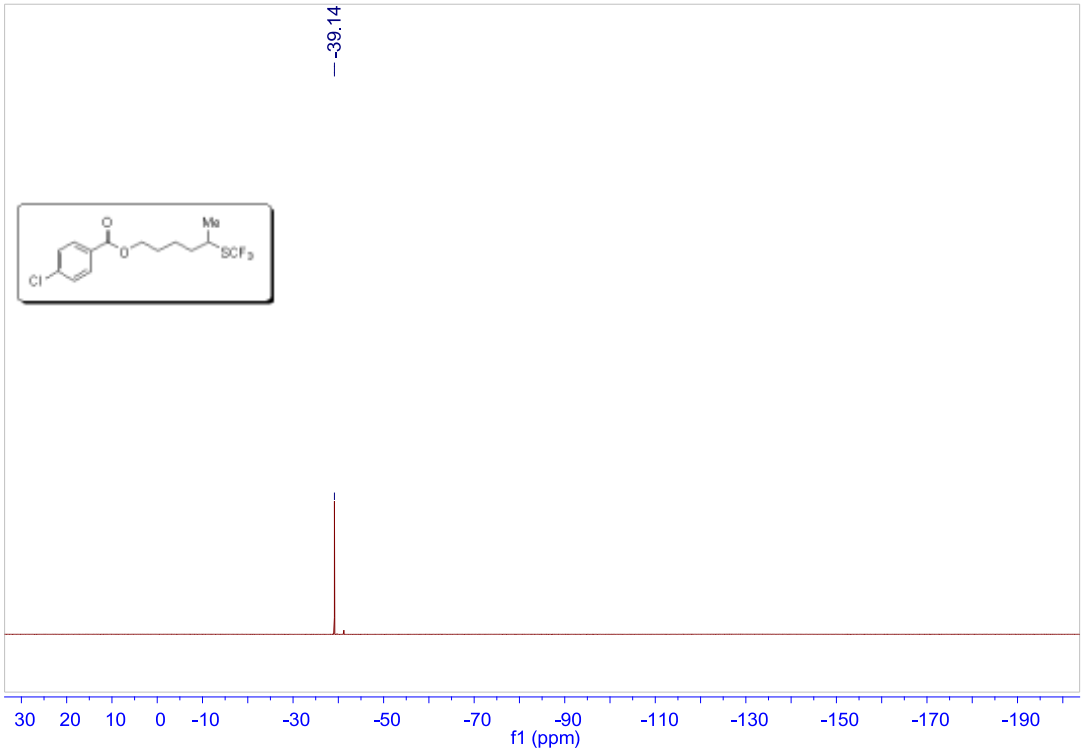
^{13}C NMR spectrum for 5-(trifluoromethylthio)hexyl 4-fluorobenzoate (3j)



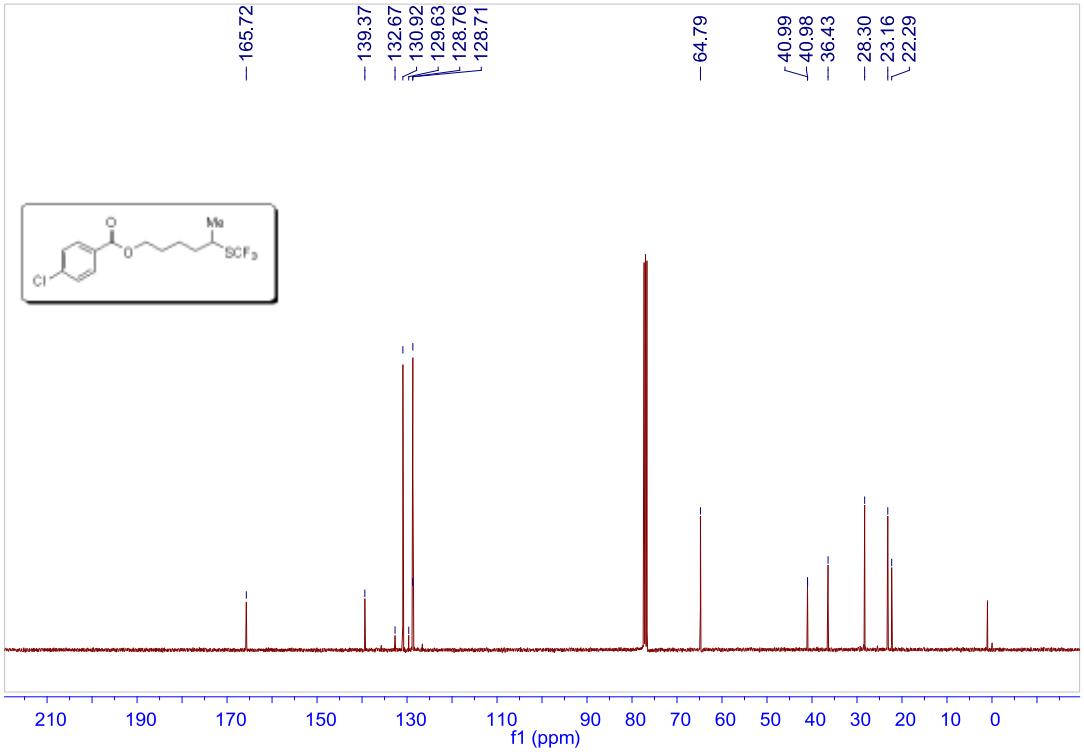
^{1}H NMR spectrum for 5-(trifluoromethylthio)hexyl 4-chlorobenzoate (3k)



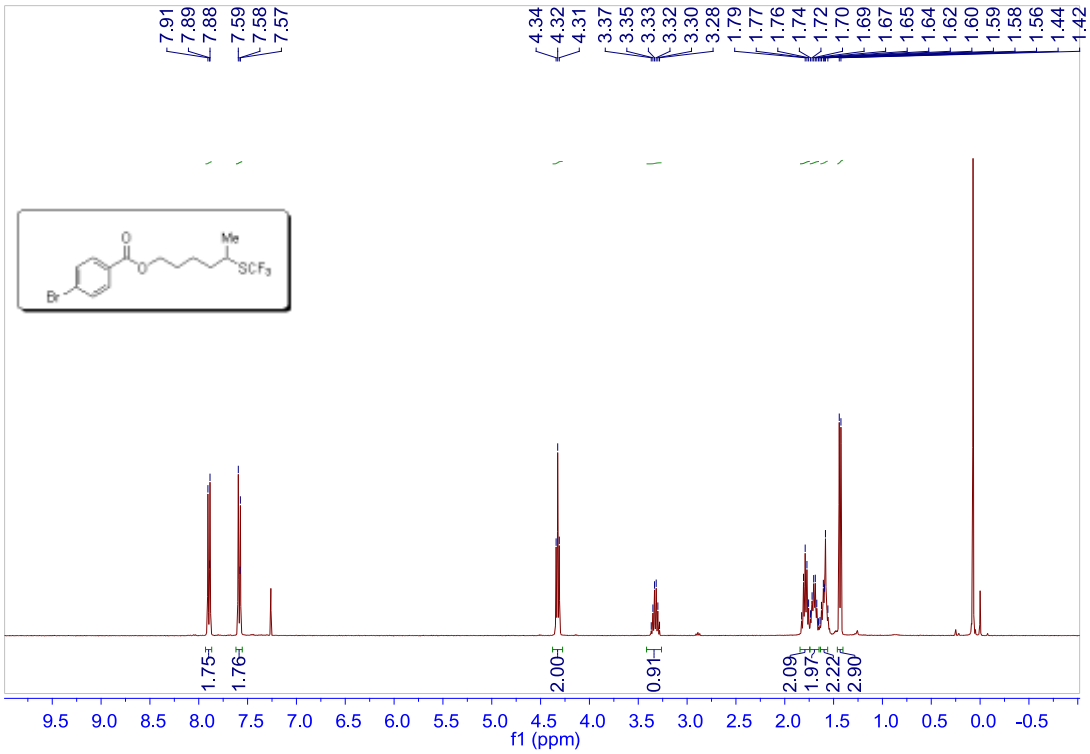
^{19}F NMR spectrum for 5-(trifluoromethylthio)hexyl 4-chlorobenzoate (3k)



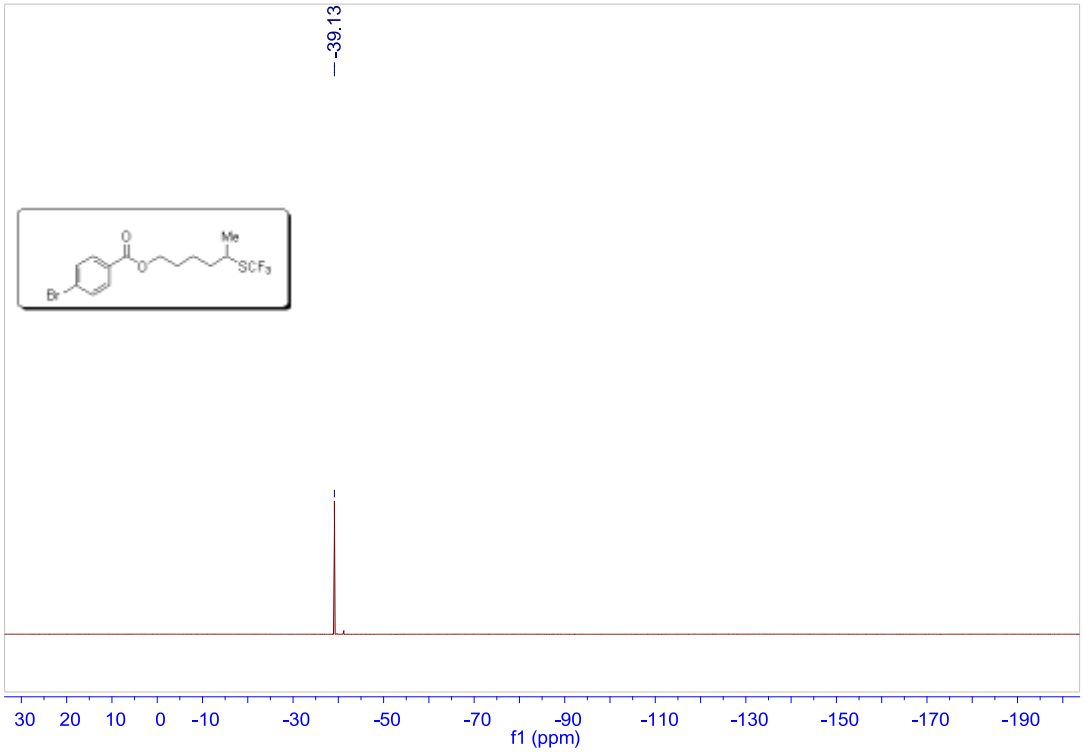
^{13}C NMR spectrum for 5-(trifluoromethylthio)hexyl 4-chlorobenzoate (3k)



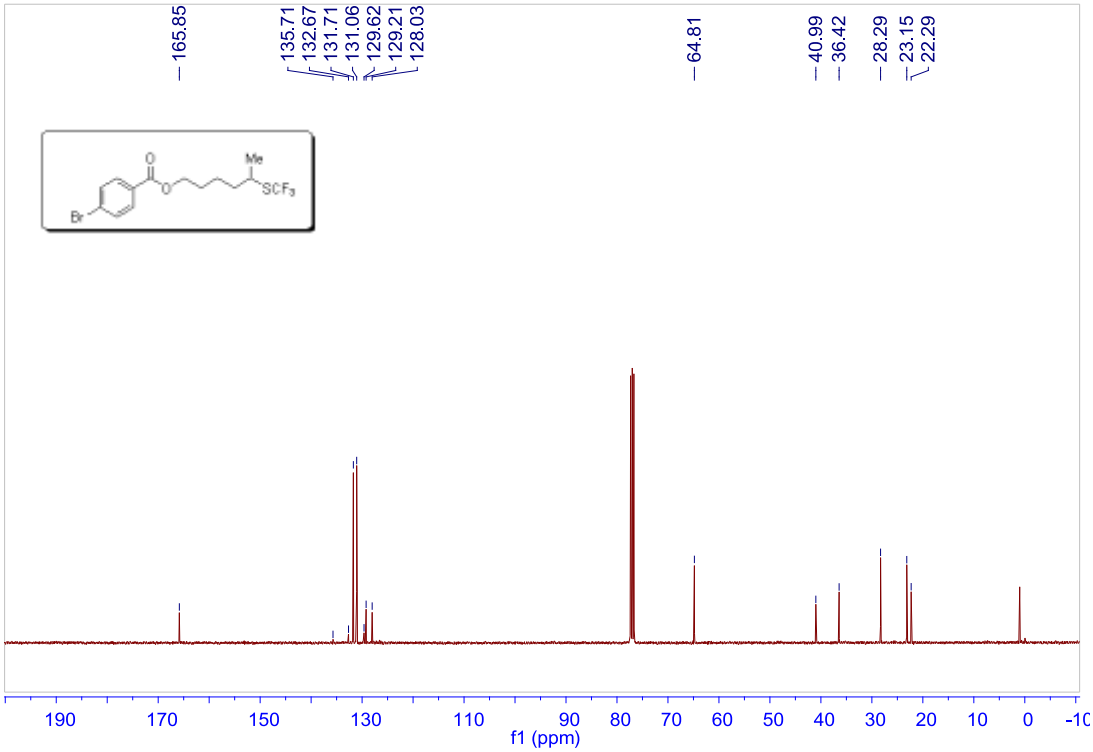
^{1}H NMR spectrum for 5-(trifluoromethylthio)hexyl 4-bromobenzoate (3l)



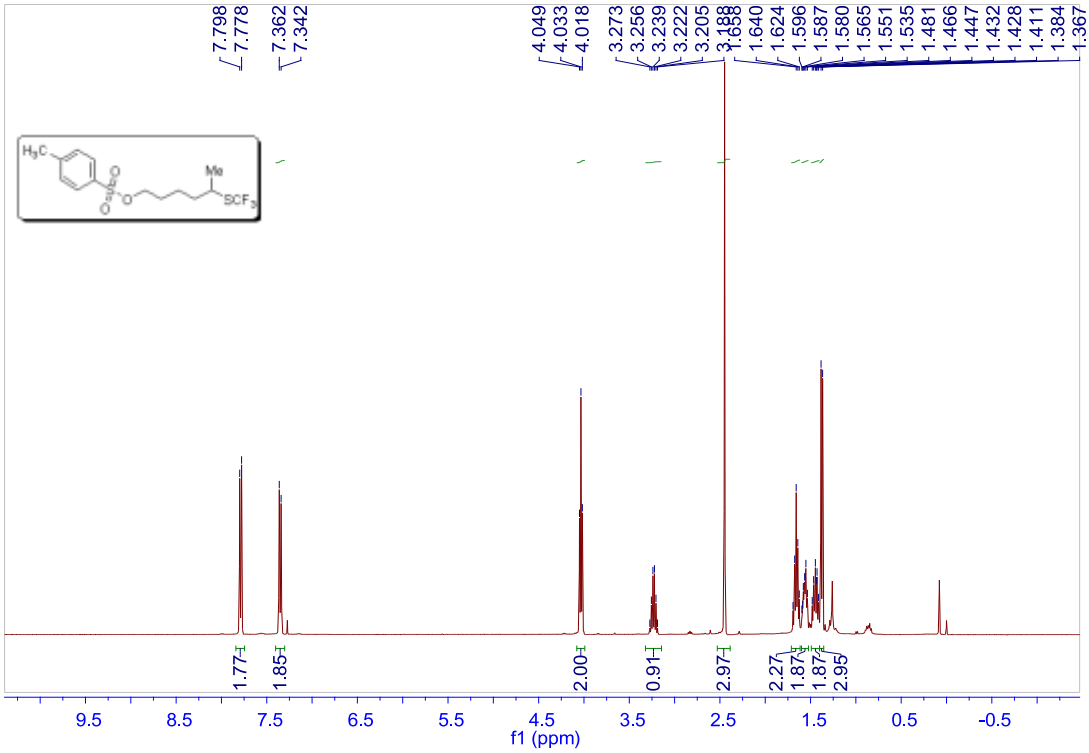
^{19}F NMR spectrum for 5-(trifluoromethylthio)hexyl 4-bromobenzoate (3l)



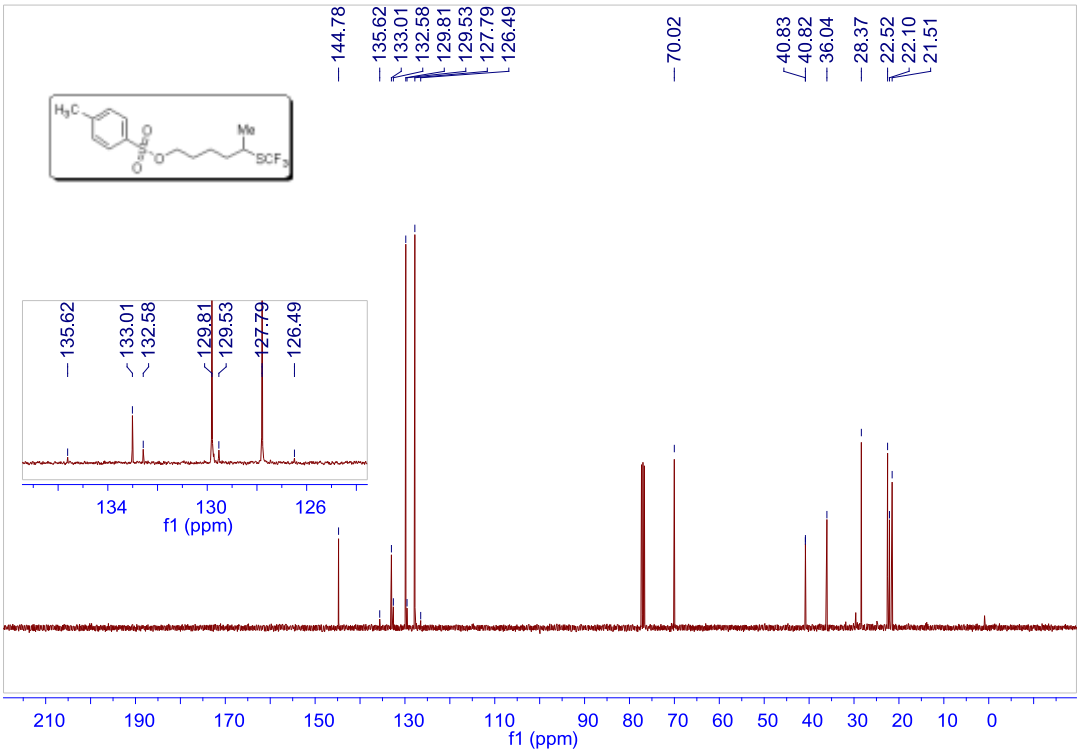
^{13}C NMR spectrum for 5-(trifluoromethylthio)hexyl 4-bromobenzoate (3l)



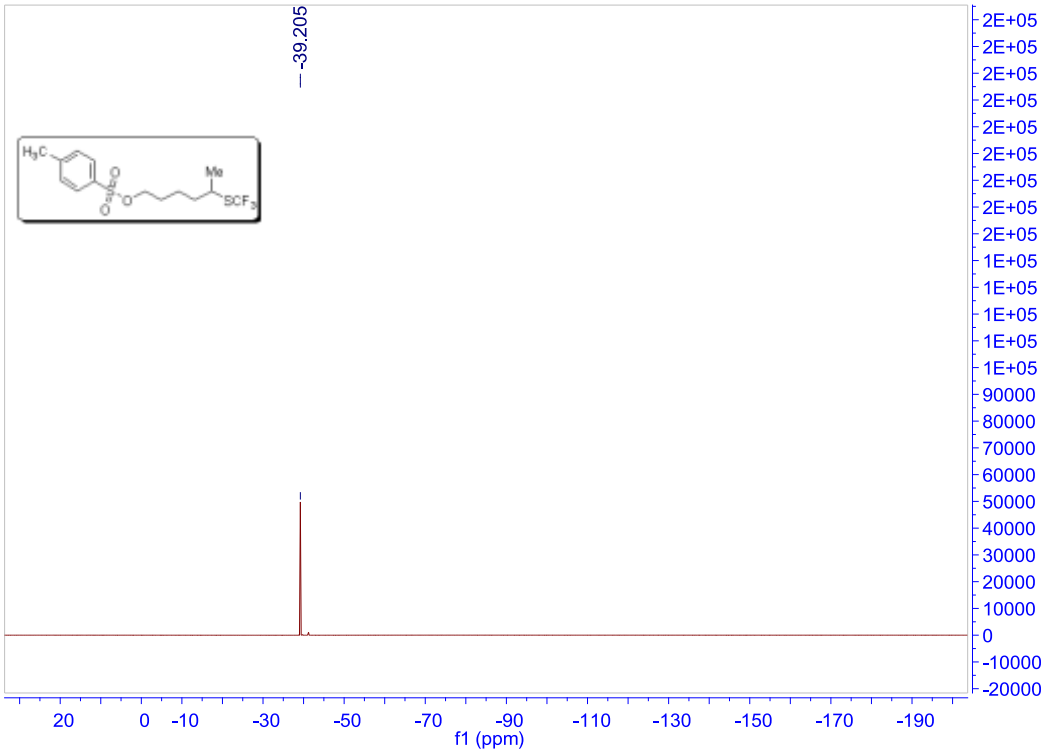
^{1}H NMR spectrum 5-(trifluoromethylthio)hexyl 4-methylbenzenesulfonate (3m)



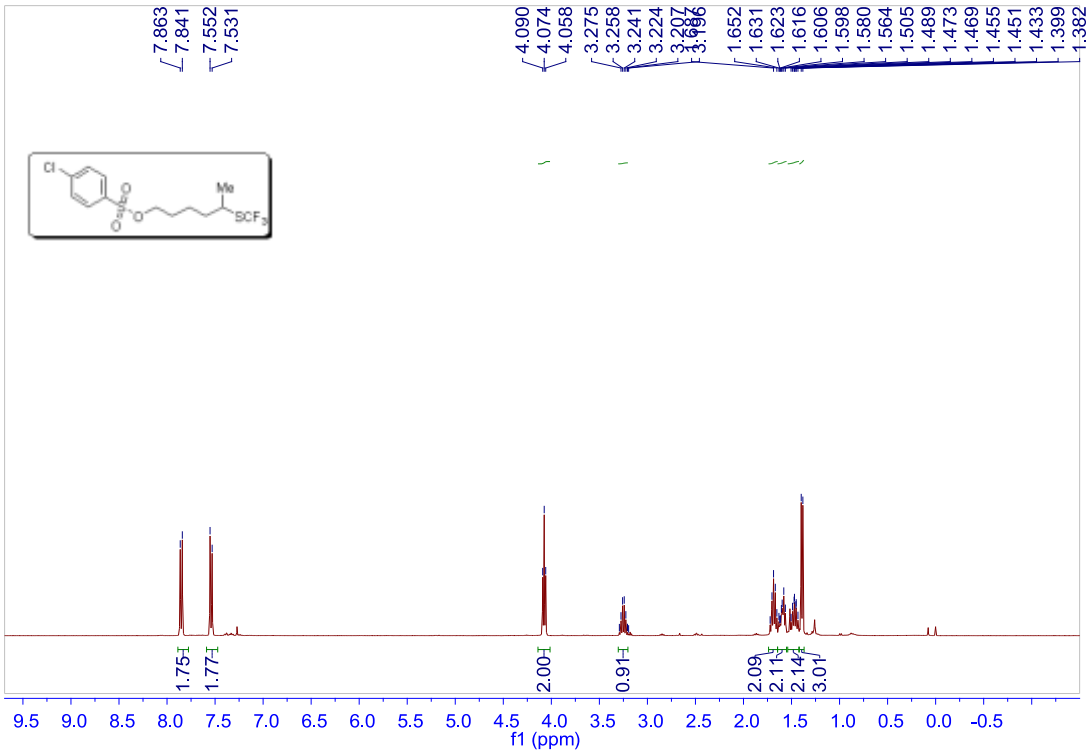
^{13}C NMR spectrum 5-(trifluoromethylthio)hexyl 4-methylbenzenesulfonate (3m)



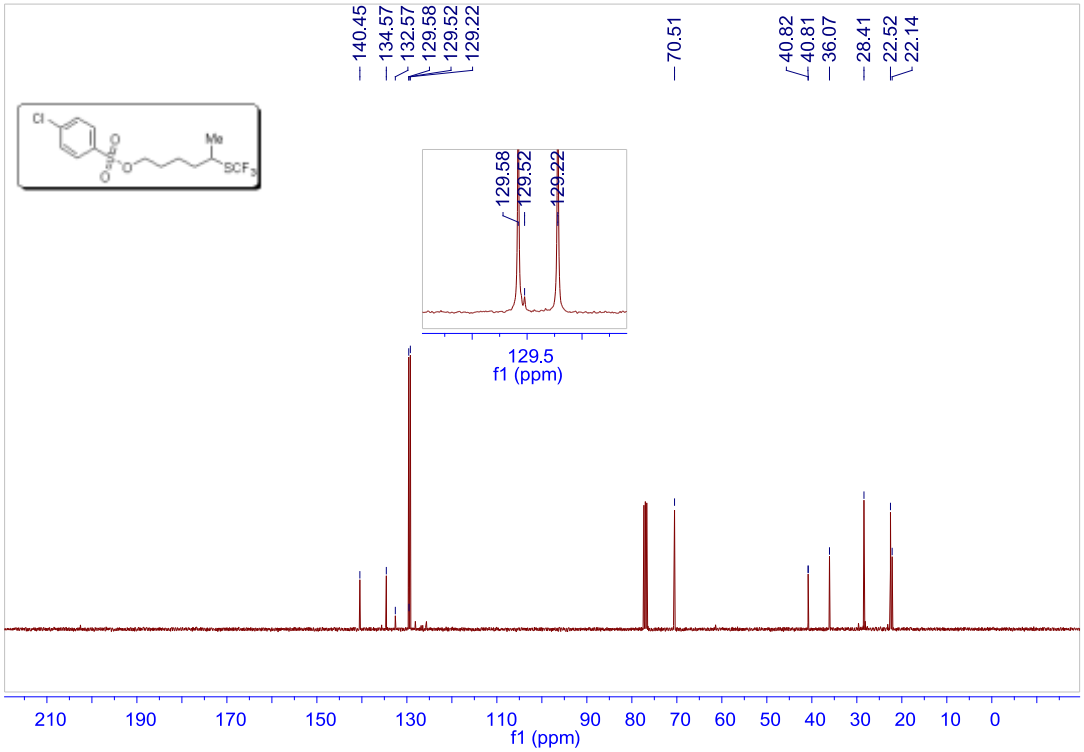
^{19}F NMR spectrum 5-(trifluoromethylthio)hexyl 4-methylbenzenesulfonate (3m)



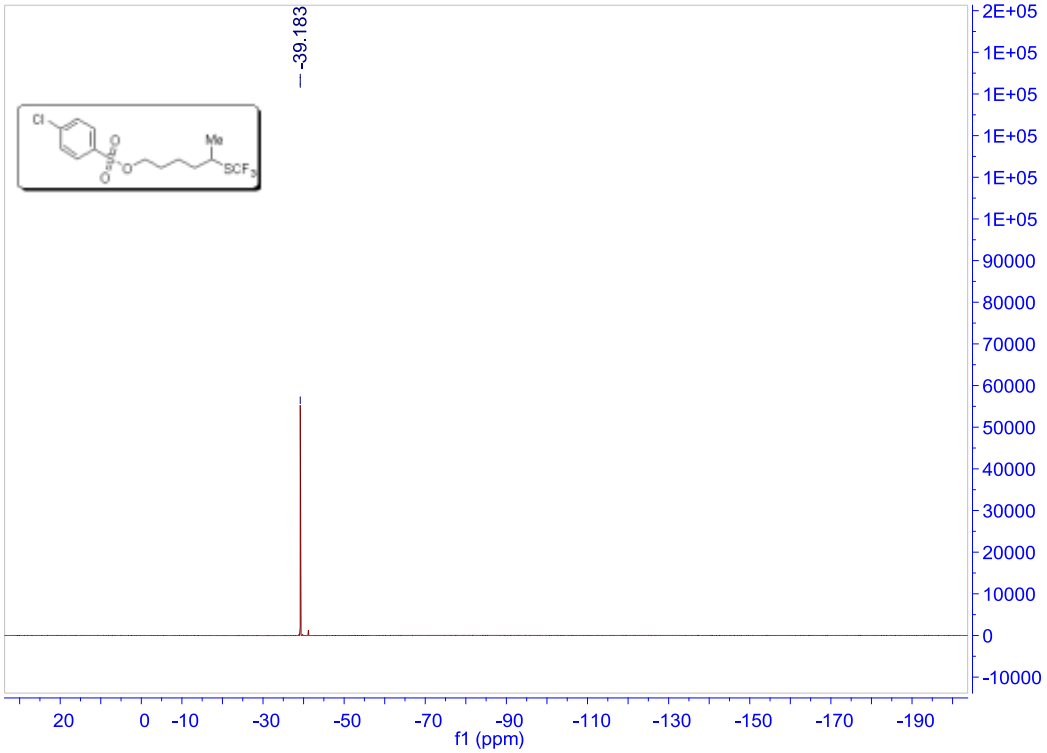
^{1}H NMR spectrum for 5-(trifluoromethylthio)hexyl 4-chlorobenzenesulfonate (3n)



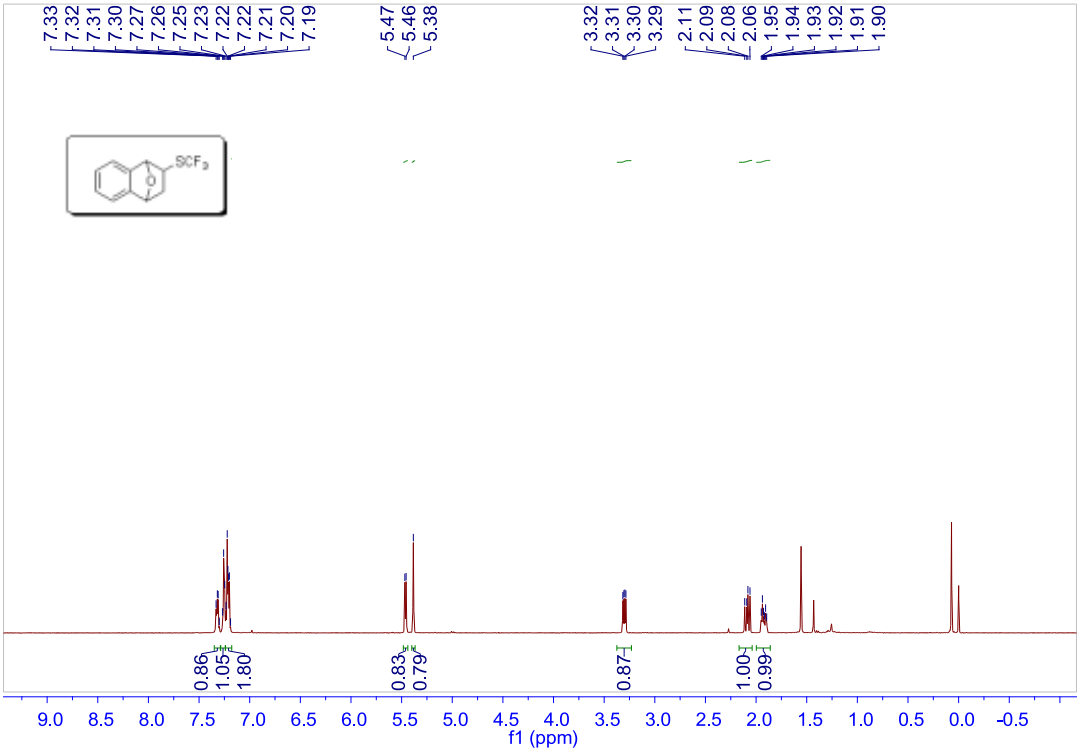
^{13}C NMR spectrum for 5-(trifluoromethylthio)hexyl 4-chlorobenzenesulfonate (3n)



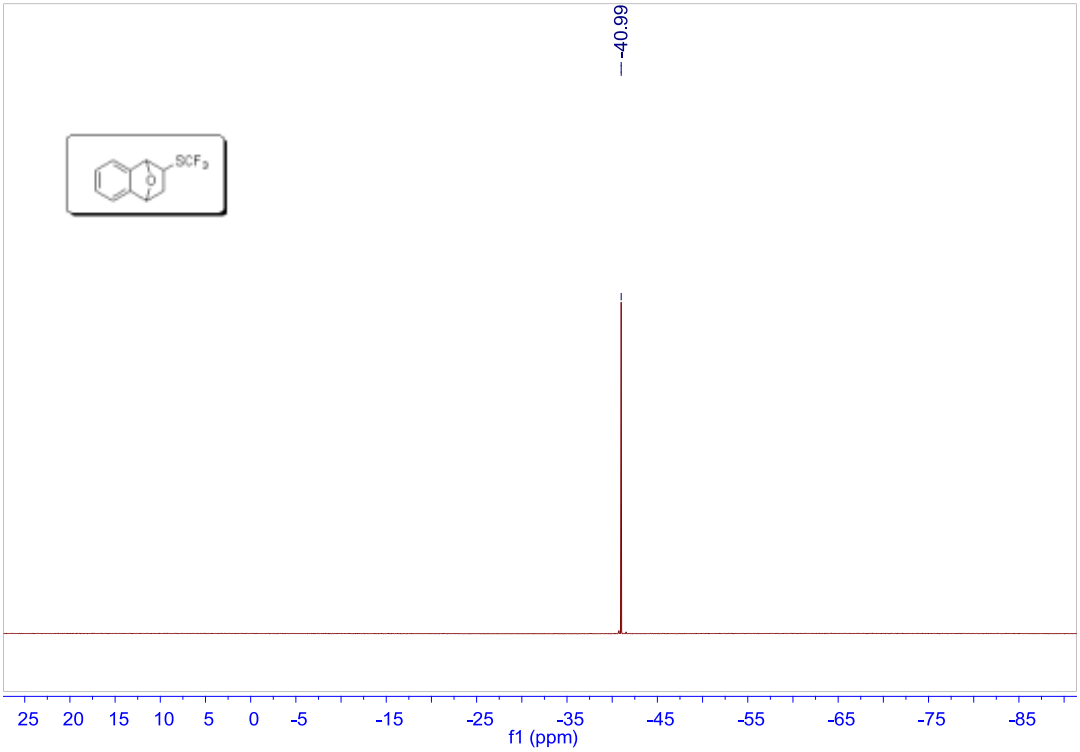
^{19}F NMR spectrum for 5-(trifluoromethylthio)hexyl 4-chlorobenzenesulfonate (3n)



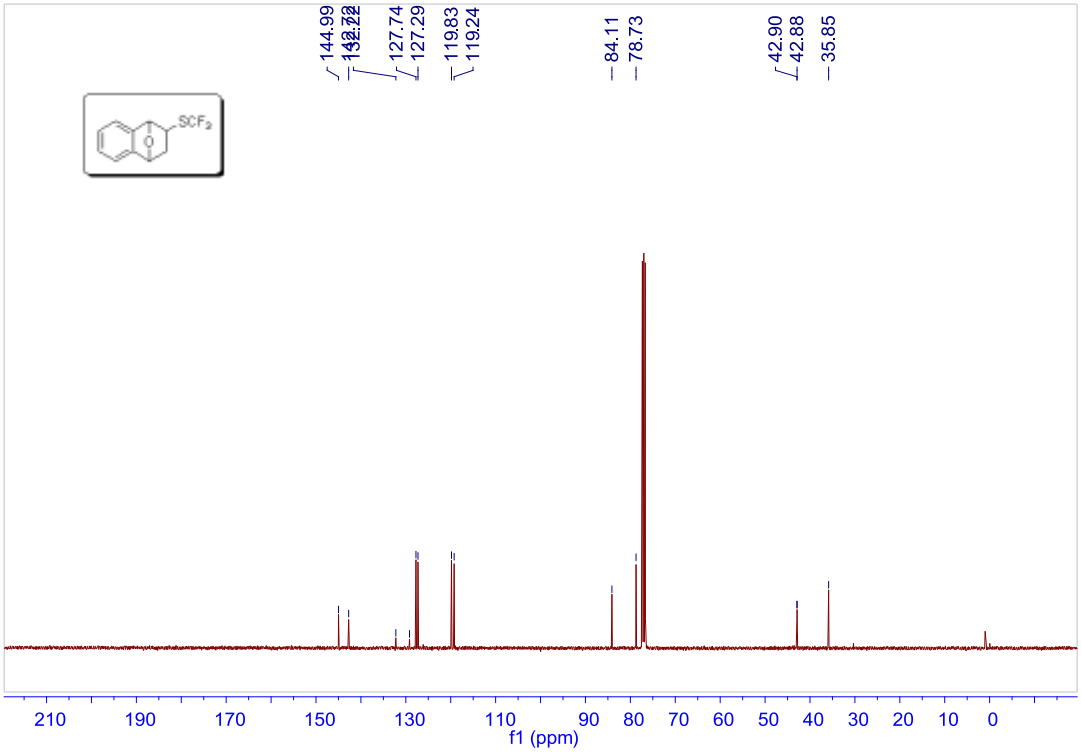
^{1}H NMR spectrum for 1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-(2-trifluoromethyl) sulfane (3o)



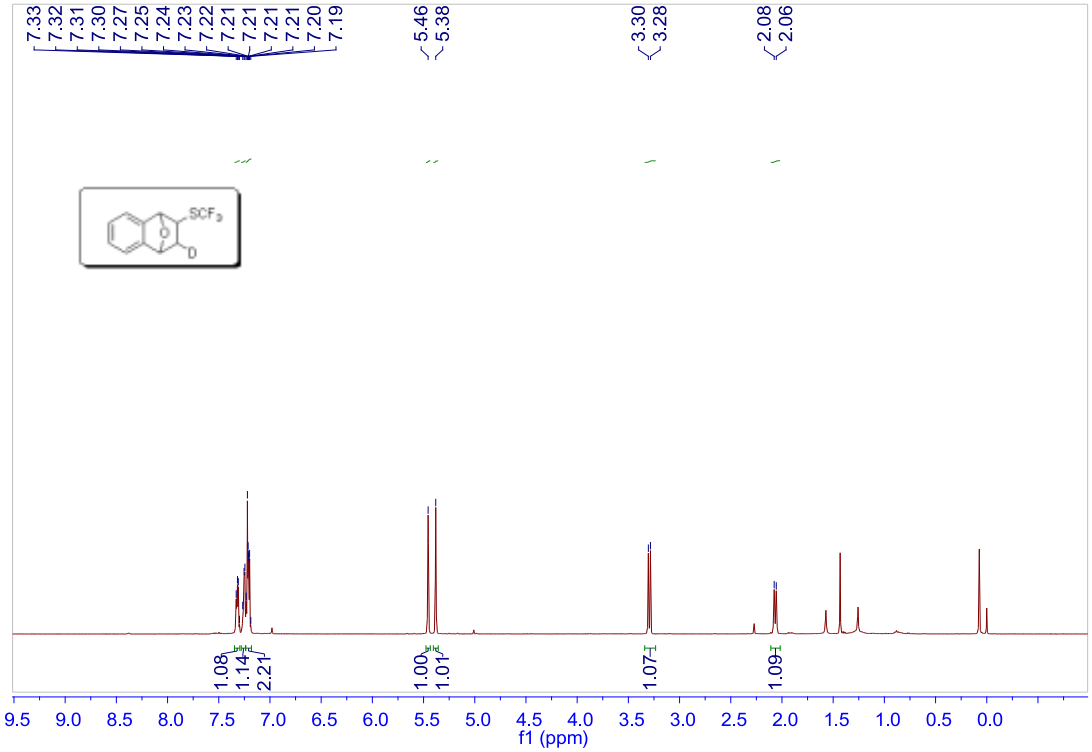
^{19}F NMR spectrum for 1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-(2-trifluoromethyl) sulfane (3o)



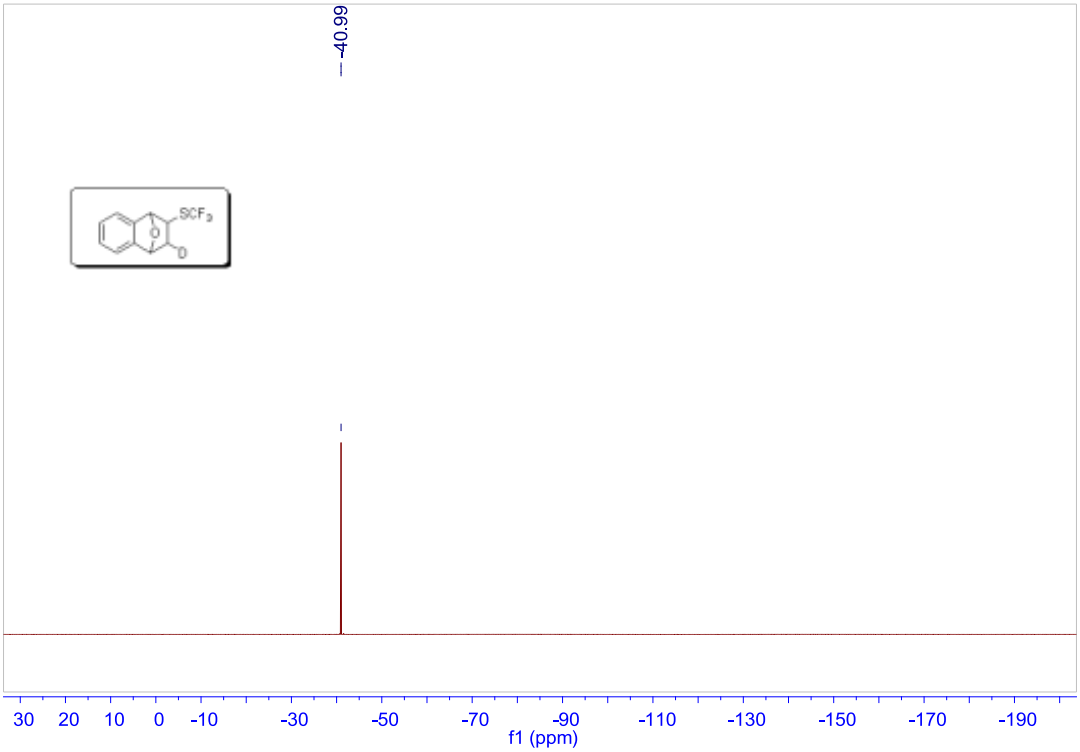
^{13}C NMR spectrum for 1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-(2-trifluoromethyl) sulfane (3o)



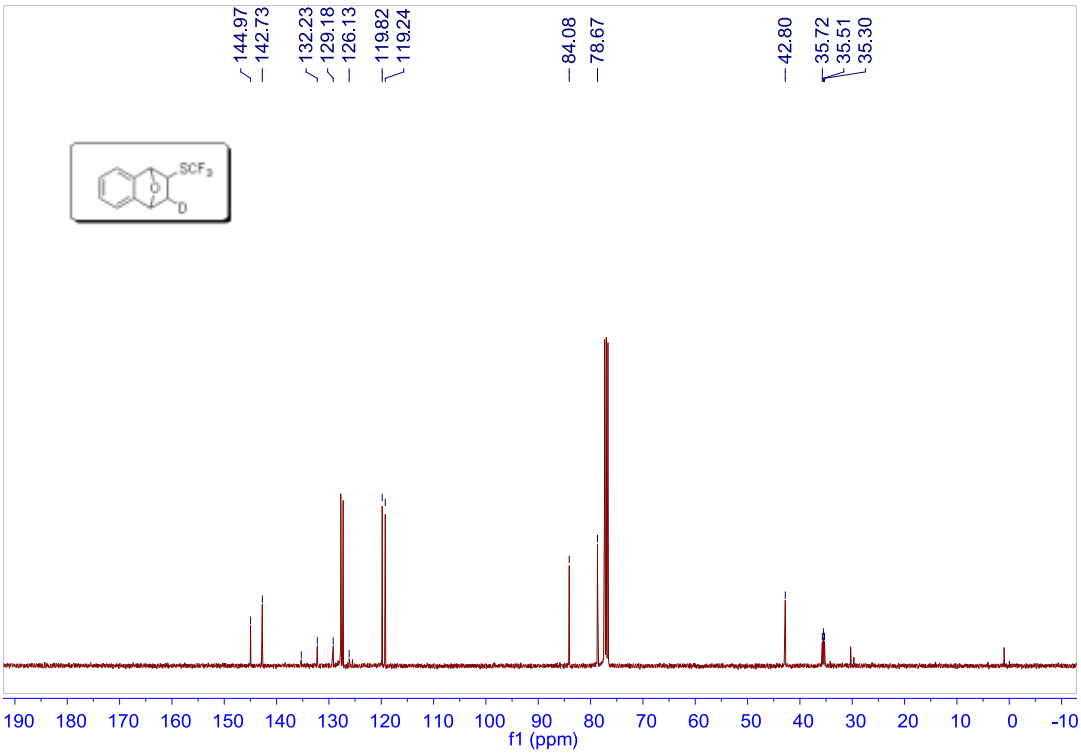
^{1}H NMR spectrum for 1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-(3-deuterium)-(2-trifluoromethyl) sulfane (3p)



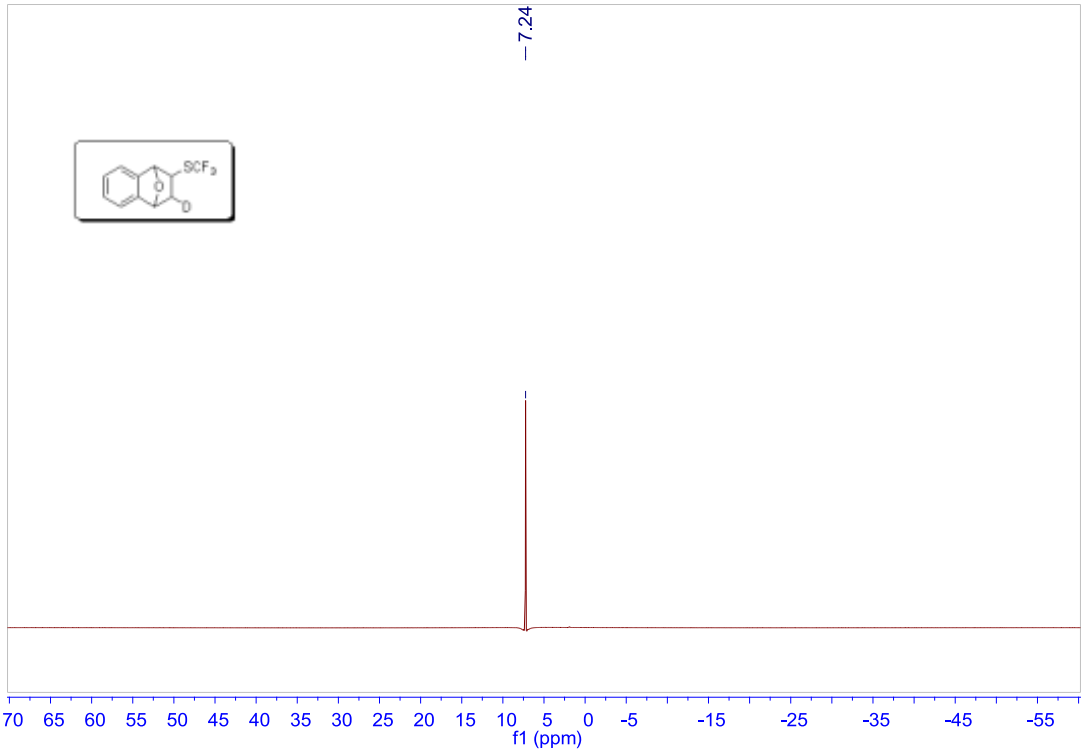
^{19}F NMR spectrum for 1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-(3-deuterium)-(2-trifluoromethyl) sulfane (3p)



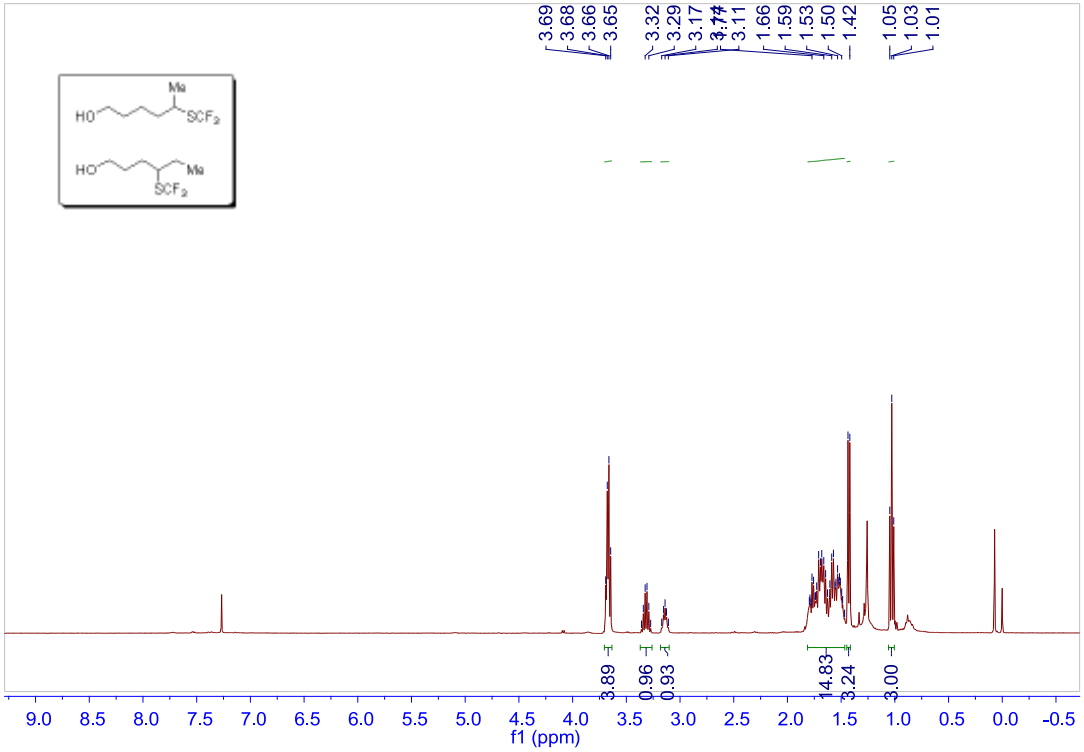
^{13}C NMR spectrum for 1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-(3-deuterium)-(2-trifluoromethyl) sulfane (3p)



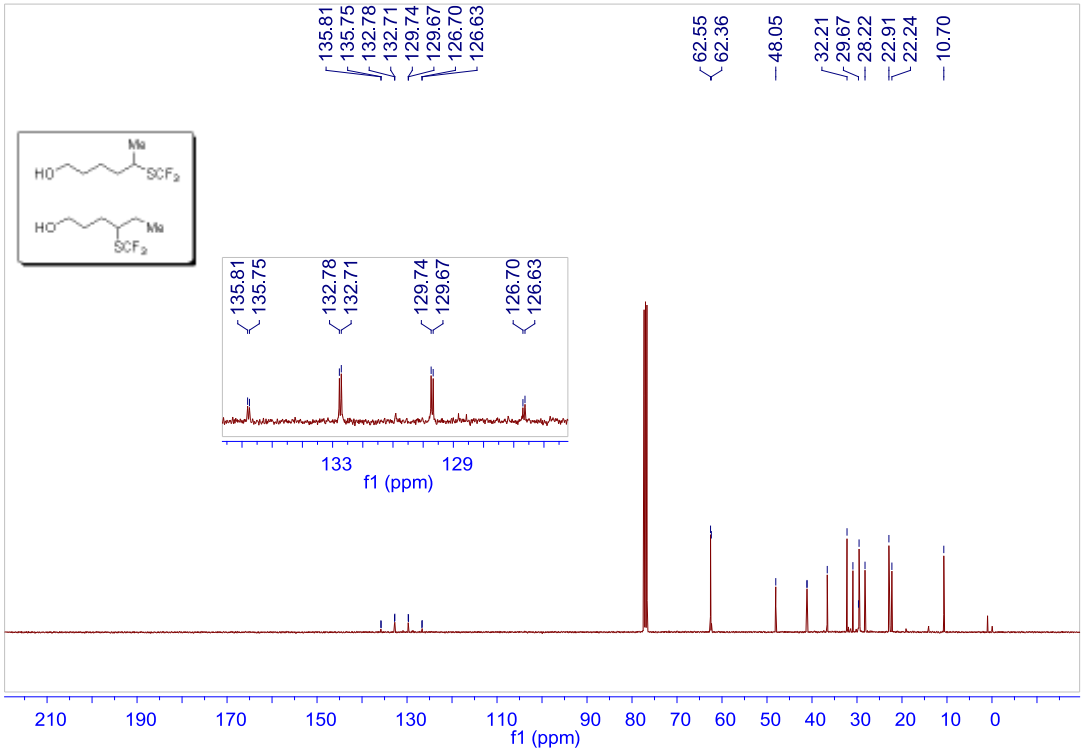
^{2}H NMR spectrum for 1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-(3-deuterium)-(2-trifluoromethyl) sulfane (3p)



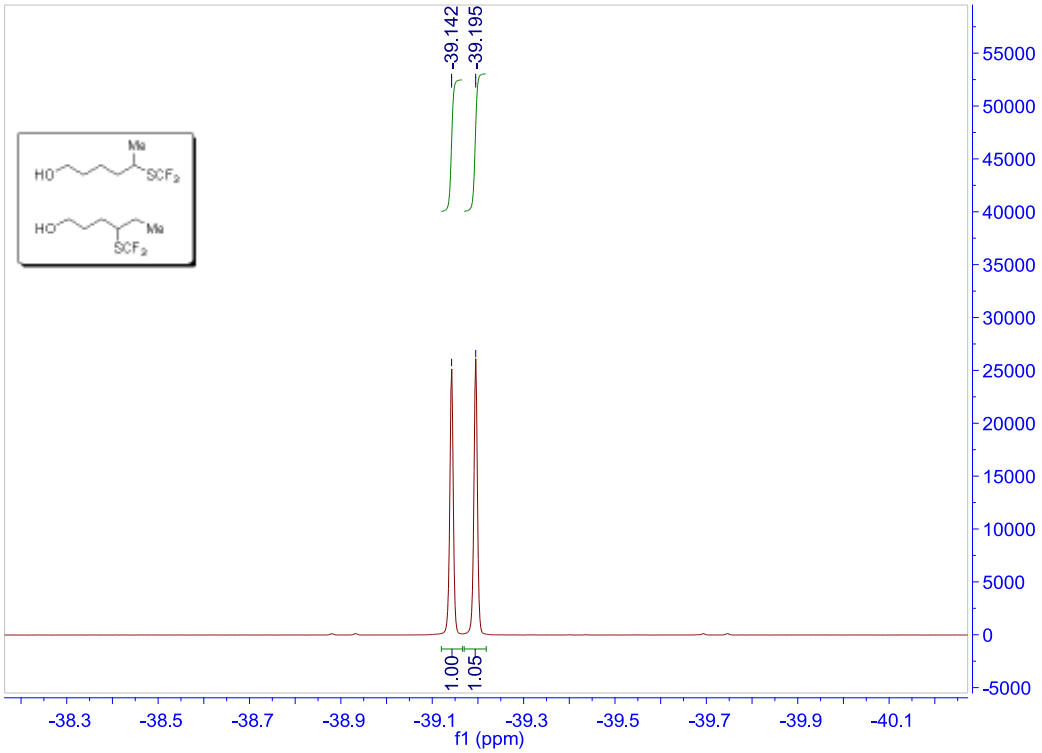
^{1}H NMR spectrum for 4-(trifluoromethylthio)hexan-1-ol and 5-(trifluoromethylthio)hexan-1-ol (3q)



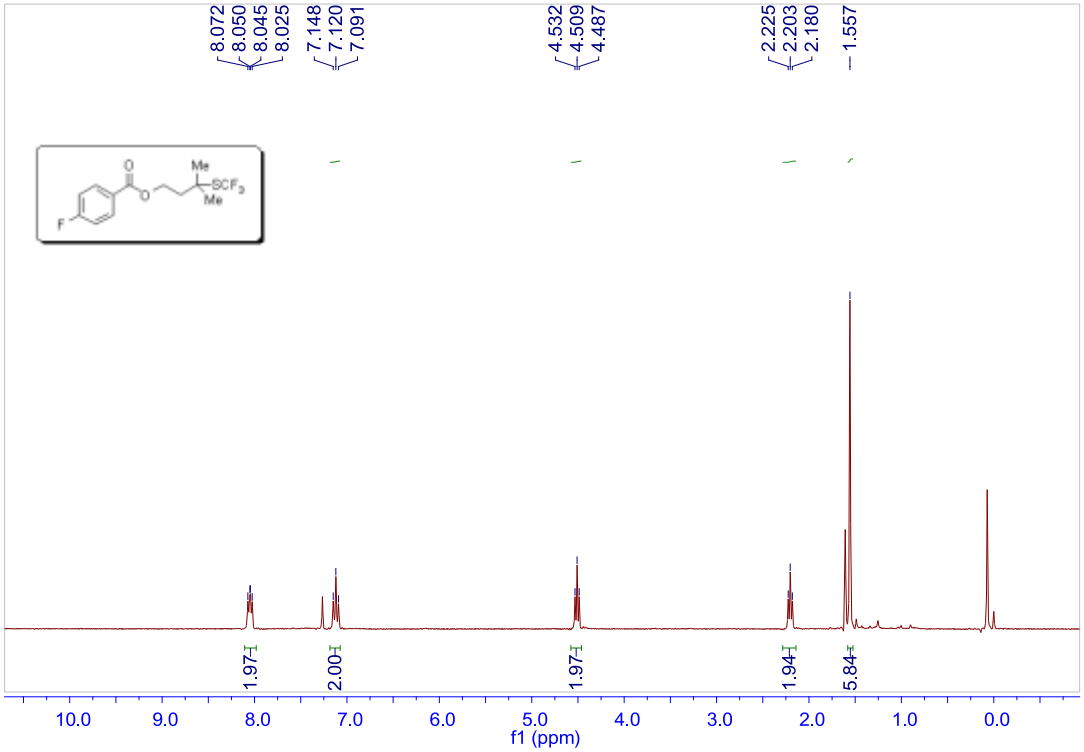
^{13}C NMR spectrum for 4-(trifluoromethylthio)hexan-1-ol and 5-(trifluoromethylthio)hexan-1-ol (3q)



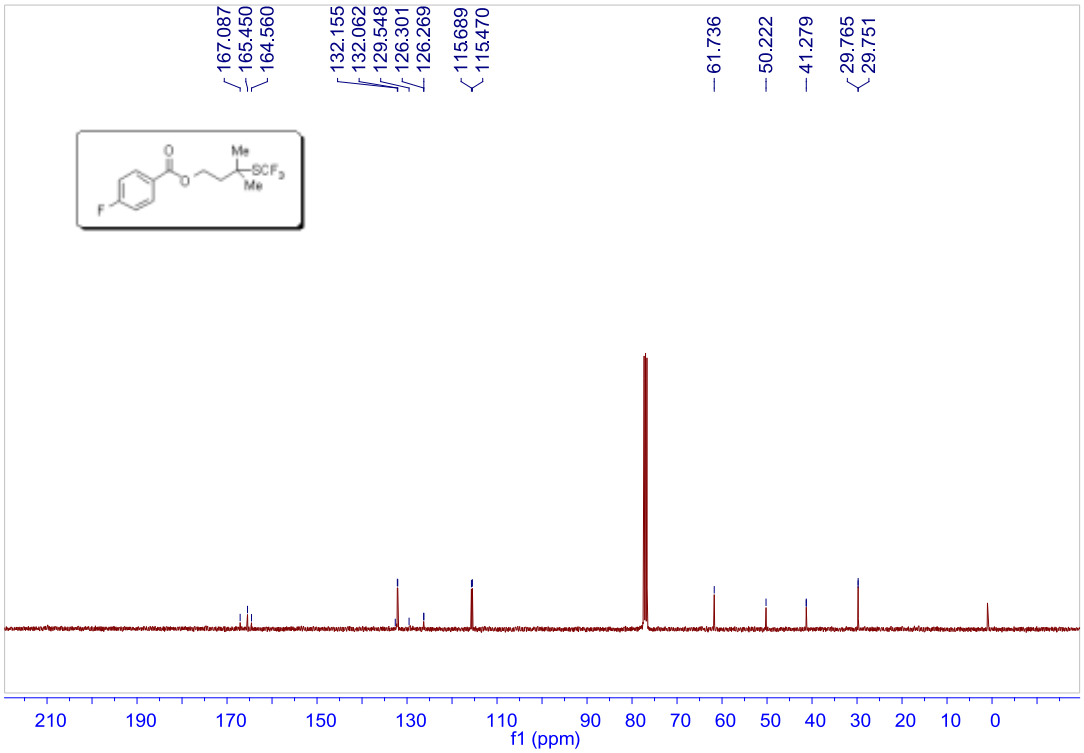
^{19}F NMR spectrum for 4-(trifluoromethylthio)hexan-1-ol and 5-(trifluoromethylthio)hexan-1-ol (3q)



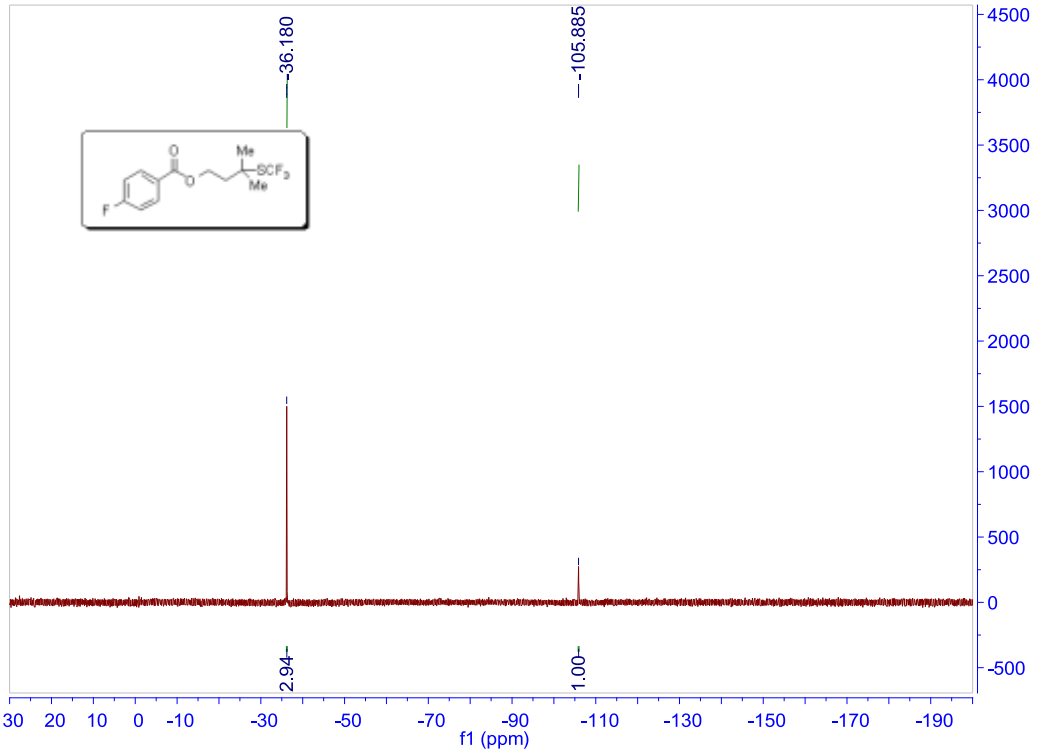
^{1}H NMR spectrum for 3-methyl-3-(trifluoromethylthio)butyl 4-fluorobenzoate (3r)



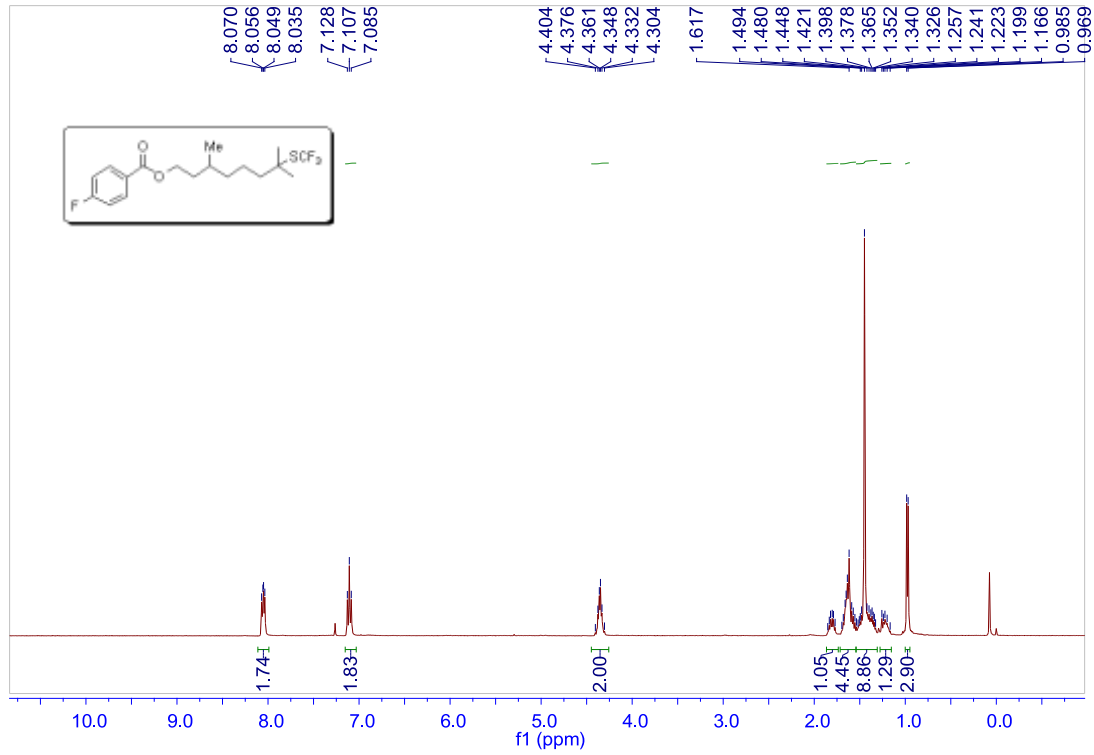
^{13}C NMR spectrum for 3-methyl-3-(trifluoromethylthio)butyl 4-fluorobenzoate (3r)



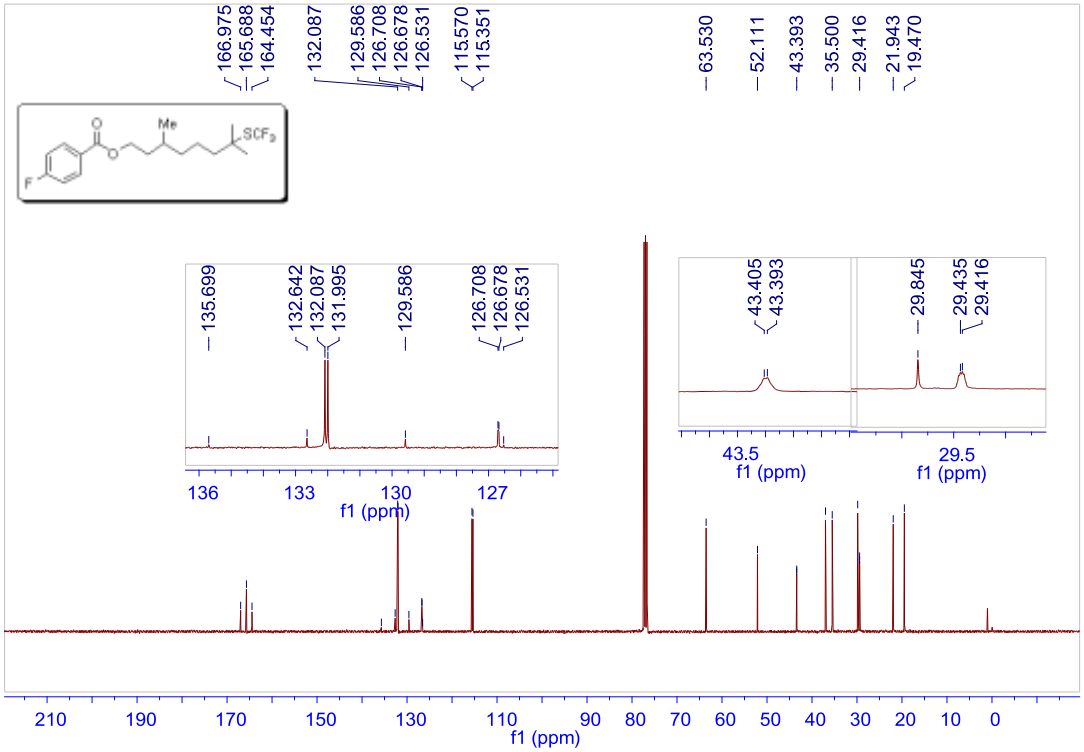
^{19}F NMR spectrum for 3-methyl-3-(trifluoromethylthio)butyl 4-fluorobenzoate (3r)



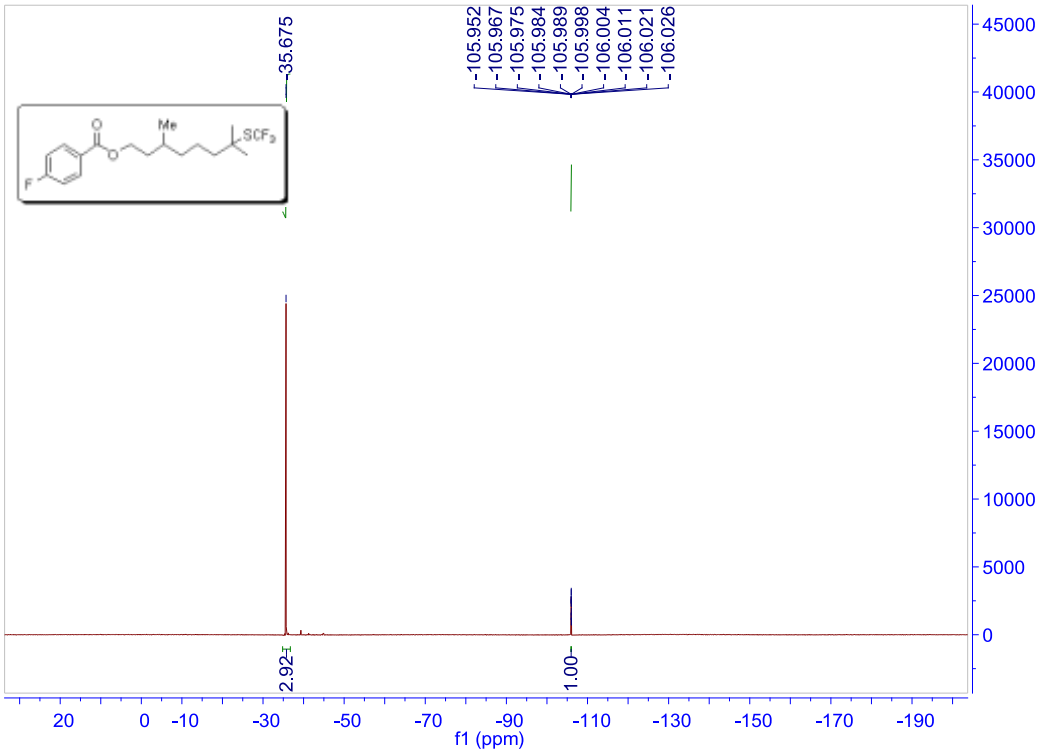
^{1}H NMR spectrum for 3,7-dimethyl-7-(trifluoromethylthio)octyl 4-fluorobenzoate (3s)



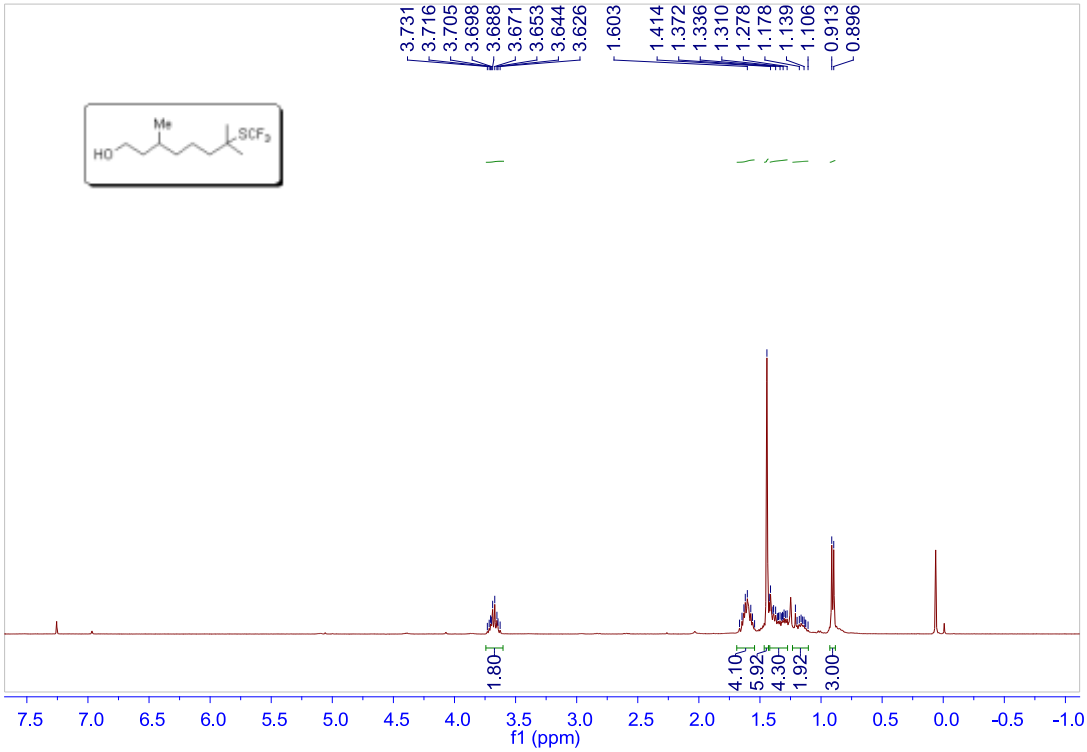
^{13}C NMR spectrum for 3,7-dimethyl-7-(trifluoromethylthio)octyl 4-fluorobenzoate (3s)



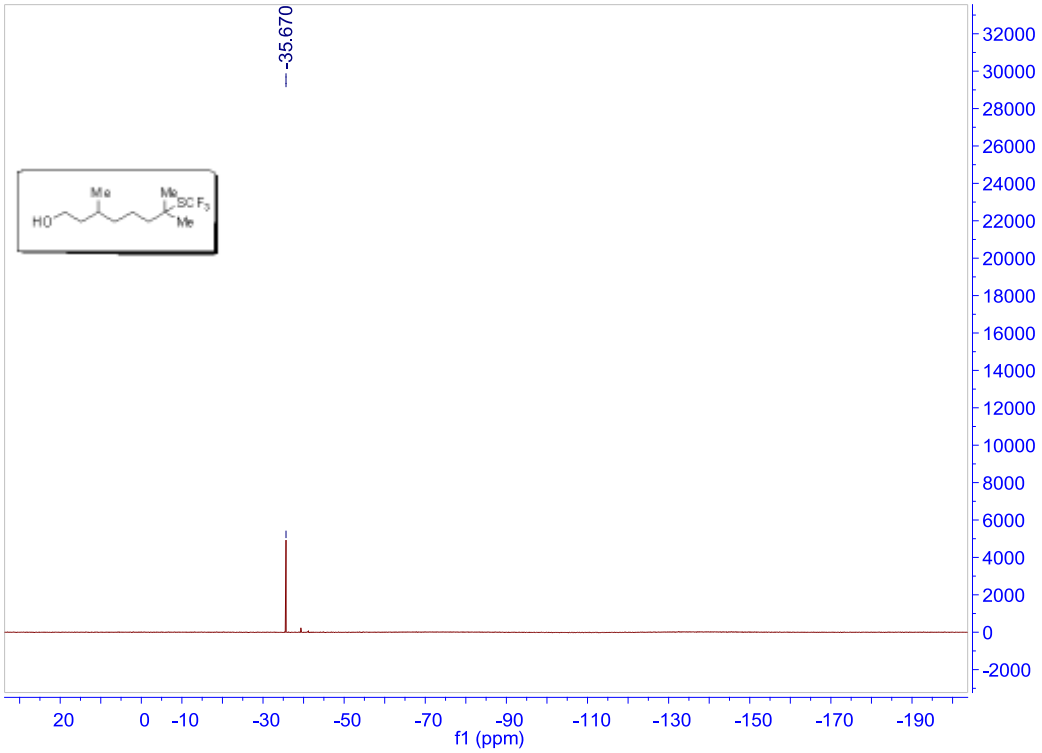
^{19}F NMR spectrum for 3,7-dimethyl-7-(trifluoromethylthio)octyl 4-fluorobenzoate (3s)



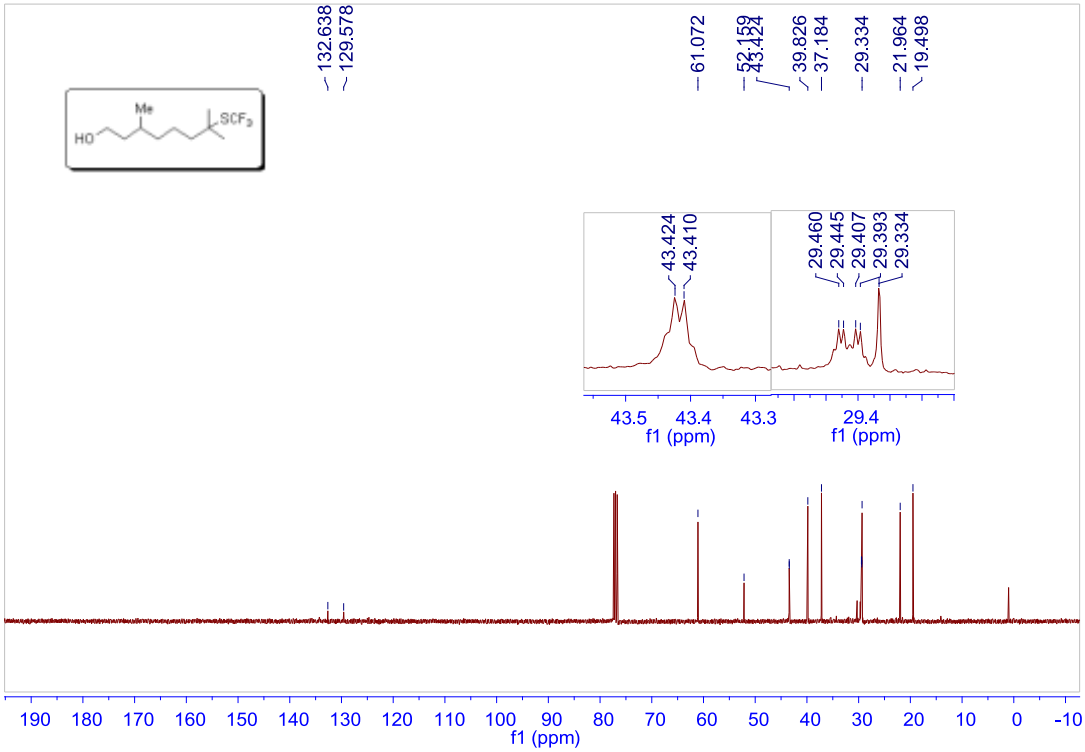
^{1}H NMR spectrum for 3,7-dimethyl-7-(trifluoromethylthio)octan-1-ol (3t)



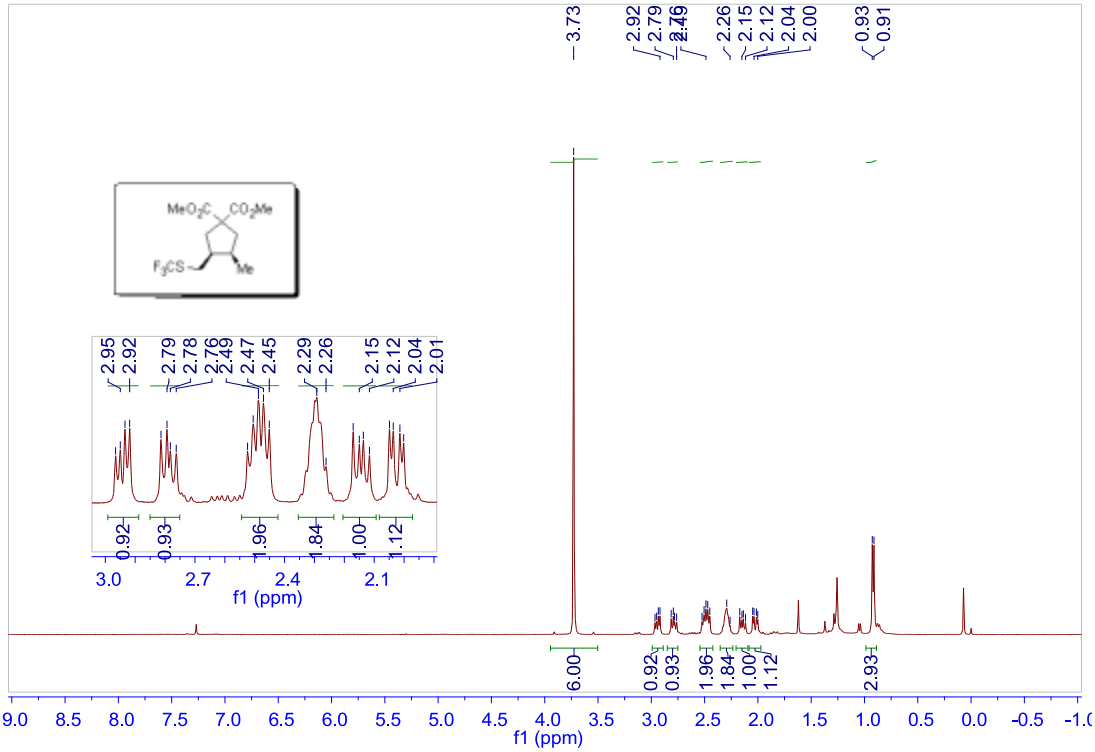
^{19}F NMR spectrum for 3,7-dimethyl-7-(trifluoromethylthio)octan-1-ol (3t)



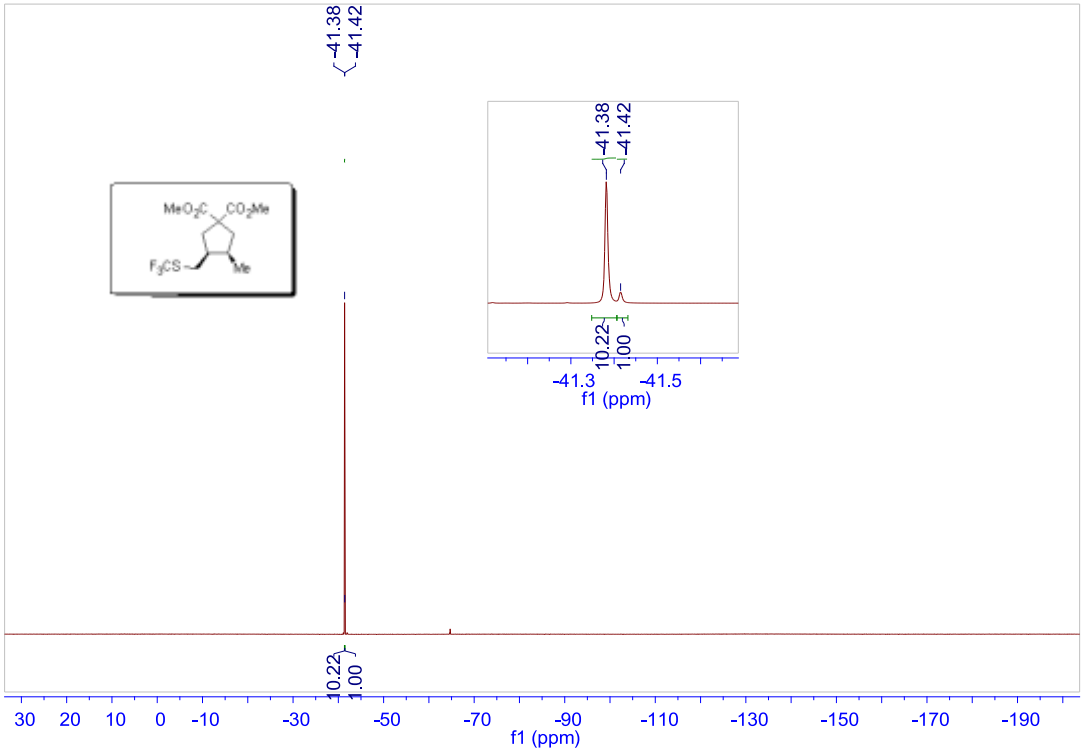
^{13}C NMR spectrum for 3,7-dimethyl-7-(trifluoromethylthio)octan-1-ol (3t)



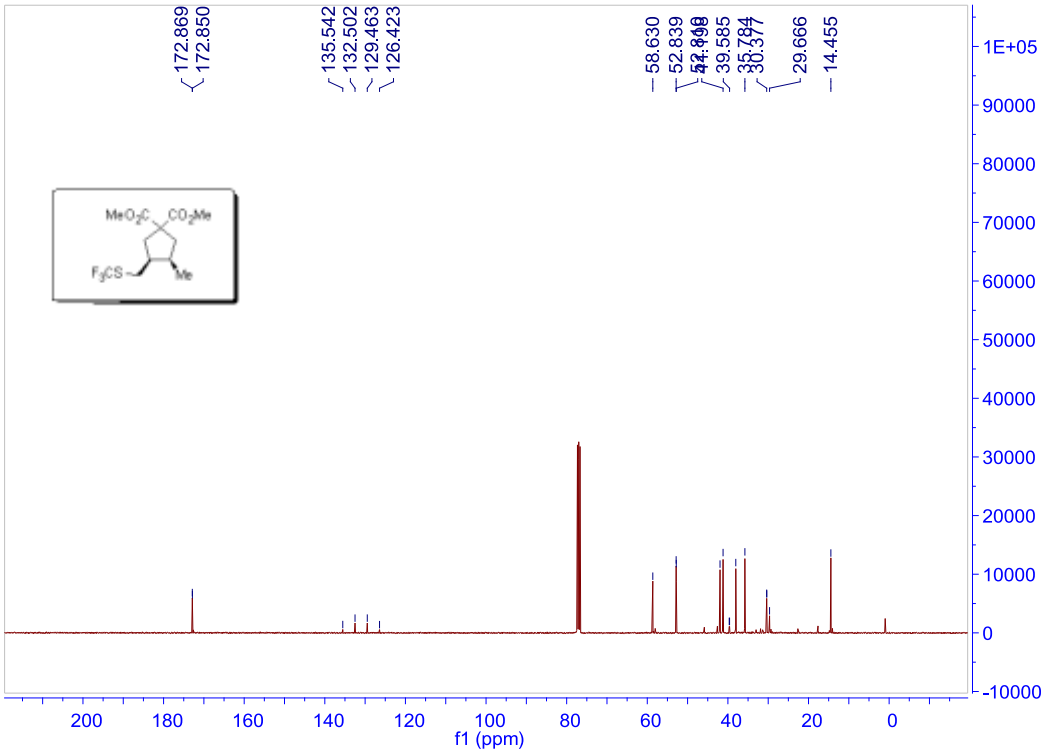
^{1}H NMR spectrum for dimethyl 3-methyl-4-((trifluoromethylthio)methyl)cyclopentane-1,1-dicarboxylate (6)



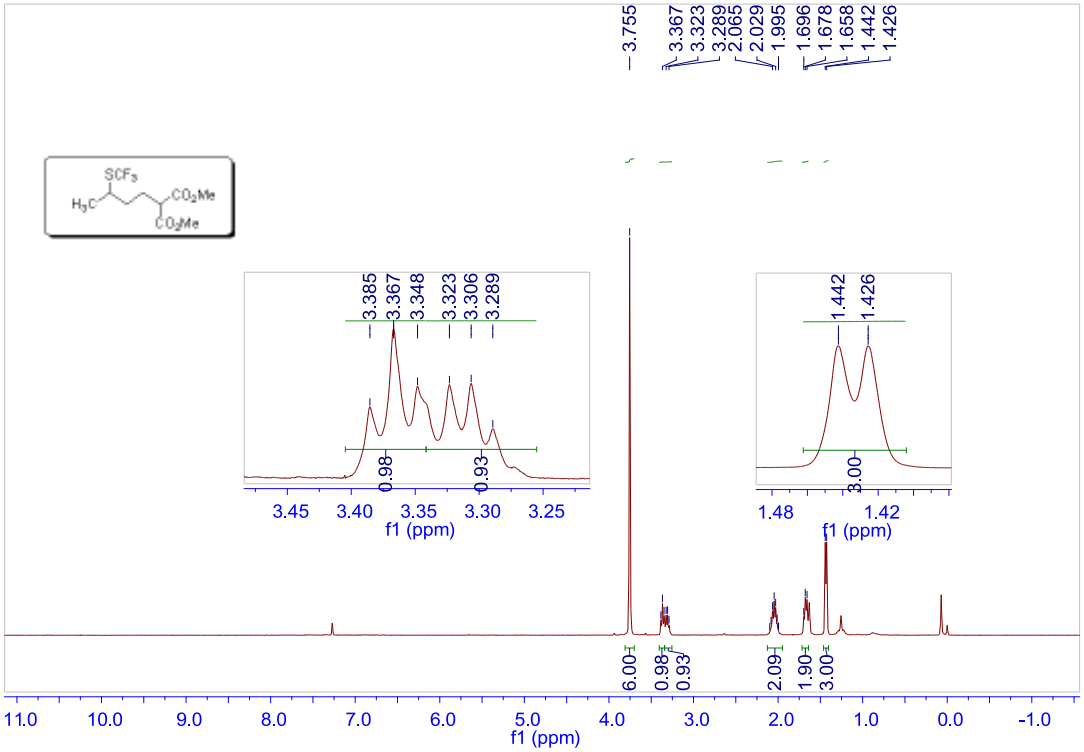
^{19}F NMR spectrum for dimethyl 3-methyl-4-((trifluoromethylthio)methyl)cyclopentane-1,1-dicarboxylate (6)



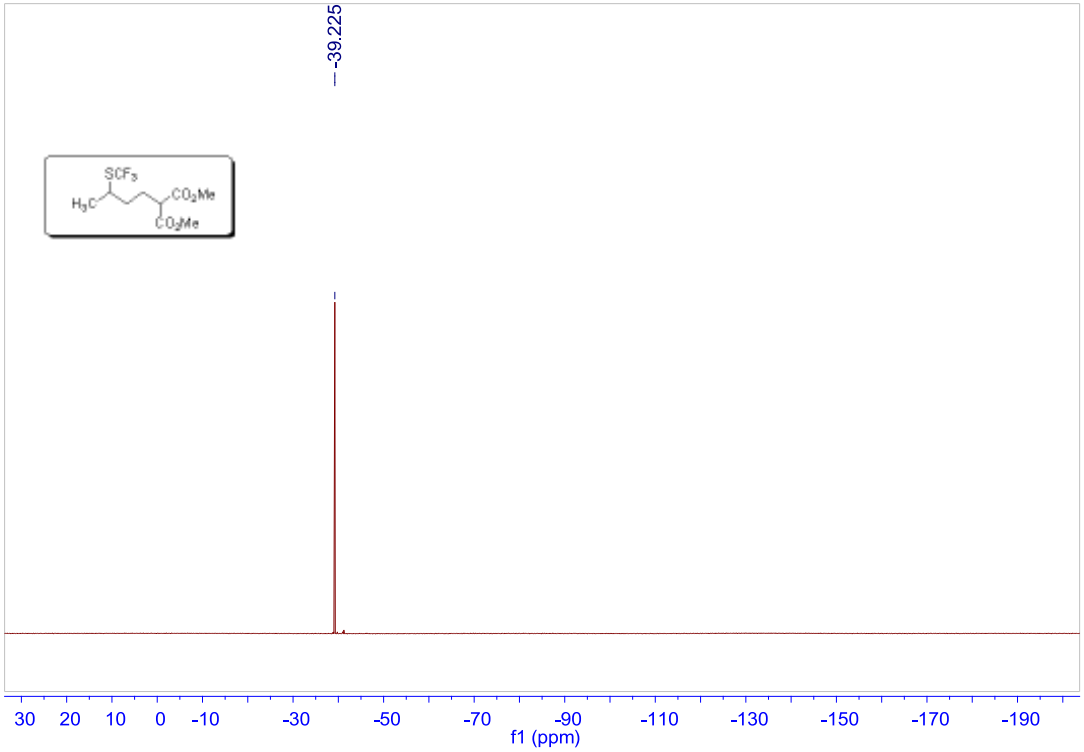
^{13}C NMR spectrum for dimethyl 3-methyl-4-((trifluoromethylthio)methyl)cyclopentane-1,1-dicarboxylate (6)



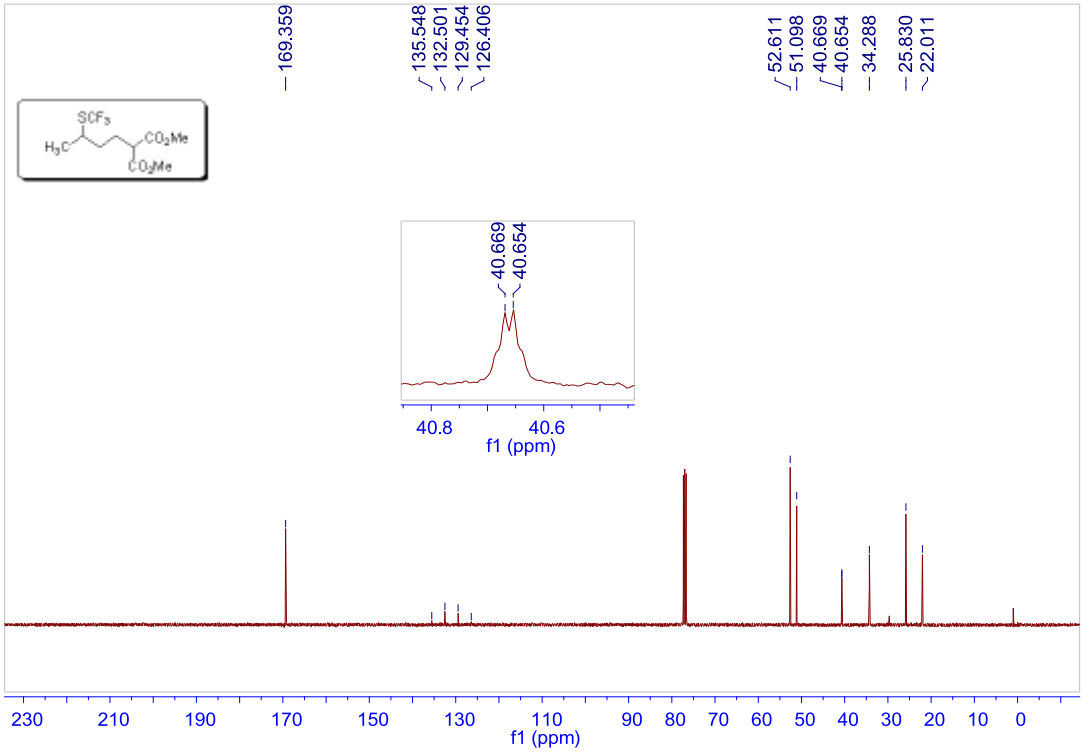
^{1}H NMR spectrum for dimethyl 2-(3-(trifluoromethylthio)butyl)malonate (8a)



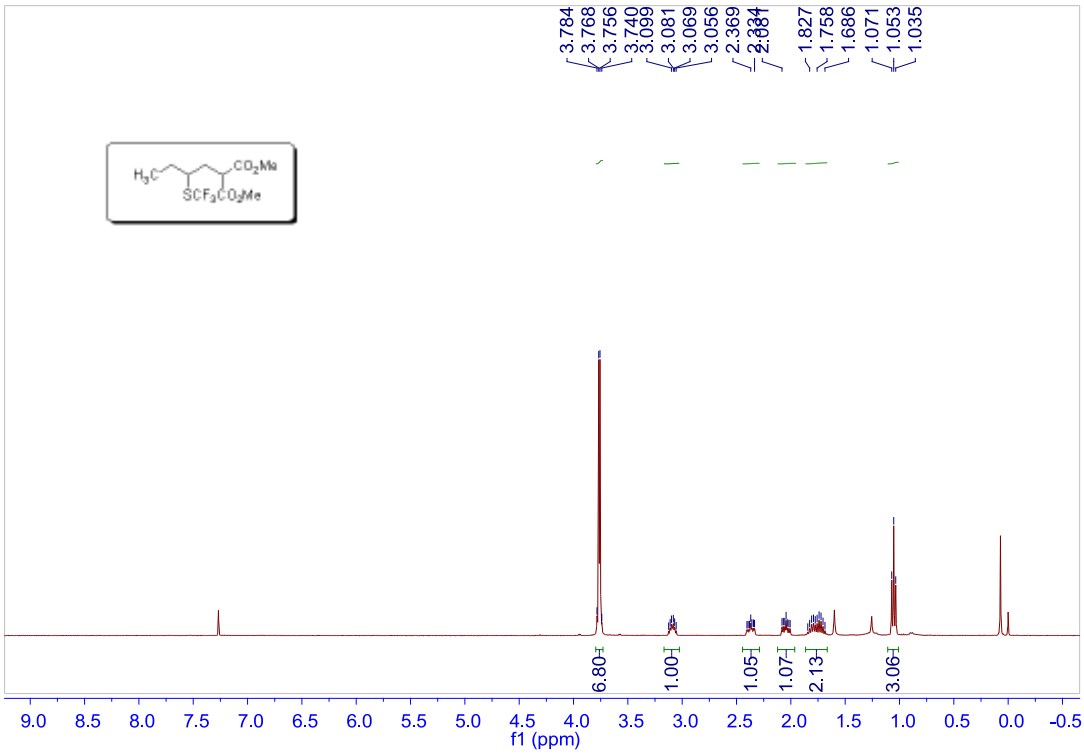
^{19}F NMR spectrum for dimethyl 2-(3-(trifluoromethylthio)butyl)malonate (8a)



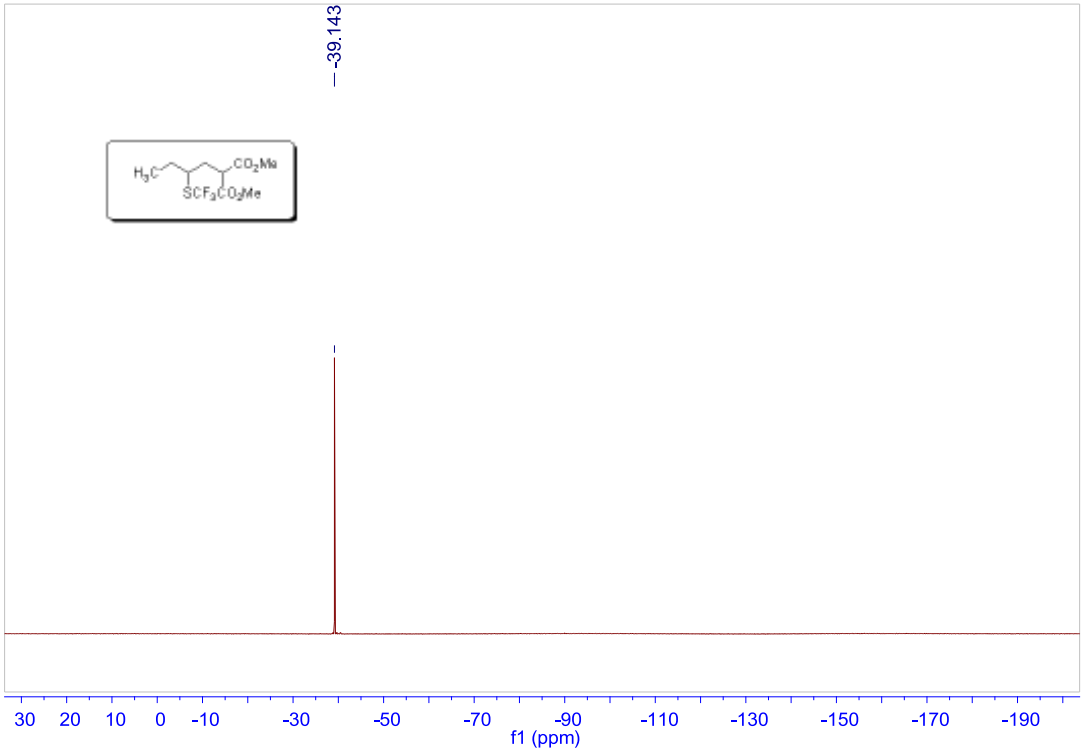
^{13}C NMR spectrum for dimethyl 2-(3-(trifluoromethylthio)butyl)malonate (8a)



^{1}H NMR spectrum for dimethyl 2-(2-(trifluoromethylthio)butyl)malonate (8b)



^{19}F NMR spectrum for dimethyl 2-(2-(trifluoromethylthio)butyl)malonate (8b)



^{13}C NMR spectrum for dimethyl 2-(2-(trifluoromethylthio)butyl)malonate (8b)