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

Supporting Information

Trifluoromethylthiolation of Alcohols Using Triphenylphosphine and N-Trifluoromethylthiophthalimide

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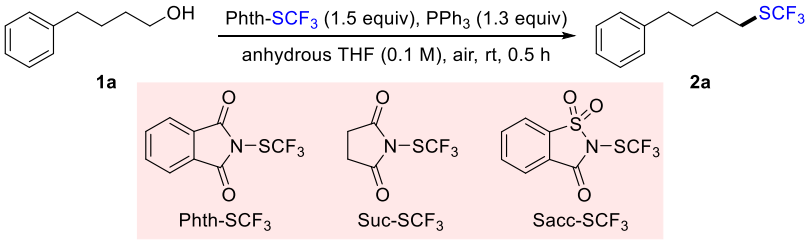
1. General information

All the reactions were conducted under air conditions unless otherwise noted. All solvents were obtained from commercial suppliers and used without further purification. Reagents were purchased from Energy Chemical, Bide pharma, and etc. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh).

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ (δH = 0.0 ppm, δC = 77.02 ppm as standard). Data for ^{1}H NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). High-resolution mass spectra were obtained by EI on a TOF mass analyzer. Mass spectra were obtained by EI on ISQ mass analyzer.

2. Optimizations of the reaction conditions

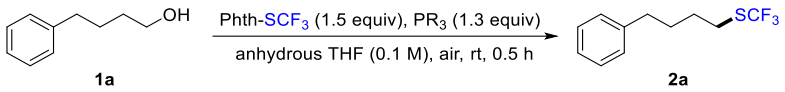
Table S1. Optimization of the Reaction Conditions[a]



Entry	Variations from optimal conditions	Yield (%)[b]
1	none	90 (85)
2	Anhydrous DCE as solvent	22
3	Anhydrous CH_3CN as solvent	14
4	Anhydrous DMF as solvent	44
5	THF as solvent	15
6	Suc-SCF_3 instead of Phth-SCF_3	38
7	Sacc-SCF_3 instead of Phth-SCF_3	24
8	Without Ph_3P	ND
9	Adding $FeCl_3$ (5 mol%)	53

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), Phth-SCF_3 (0.15 mmol, 1.5 equiv), PPh_3 (0.13 mmol, 1.3equiv), anhydrous THF (1.0 mL), rt, 0.5 h. [b]GC yield using the acetophenone as the internal standard. The number in parentheses is the isolated yield. ND = not detected.

Table S2. Optimization of organic phosphines[a]

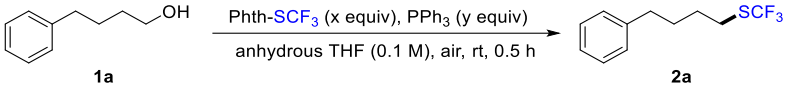


1a 2a

Entry	PR_3	Yield (%)[b]
1	PPh_3	91
2	$P(p\text{-}OMeC_6H_4)_3$	23
3	PPh_2CH_3	trace
4	$P(OCH_2CH_3)_3$	trace
5	$P(^tBu)_3$	37

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), Phth-SCF_3 (0.15 mmol, 1.5 equiv), PR_3 (0.13 mmol, 1.3equiv), anhydrous THF (1.0 mL), rt, 0.5 h. [b]GC yield using the acetophenone as the internal standard.

Table S3. The screen of the amounts of reactants.

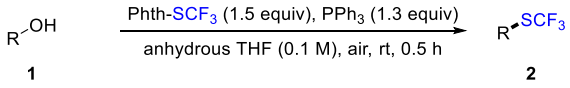


1a 2a

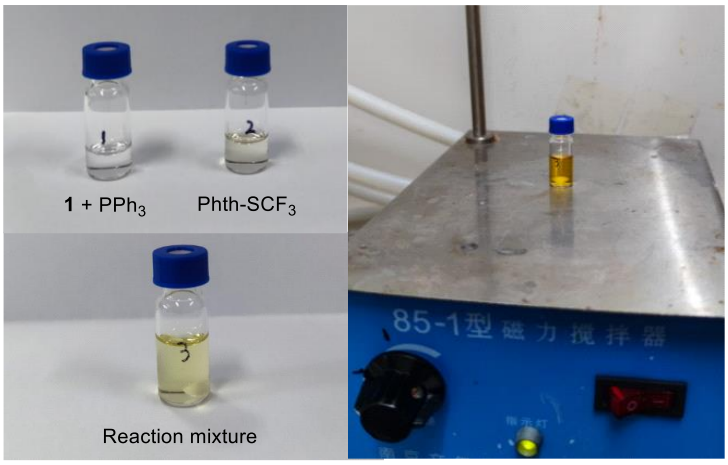
Entry	x	y	Yield (%)[b]
1	1.3	1.3	72%
2	1.5	1.3	89%
3	1.3	1.5	71%

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), Phth-SCF_3 (x equiv), PPh_3 (y equiv), anhydrous THF (1.0 mL), rt, 0.5 h. [b]GC yield using the acetophenone as the internal standard.

3. General procedure for trifluoromethylthiolation of alcohols



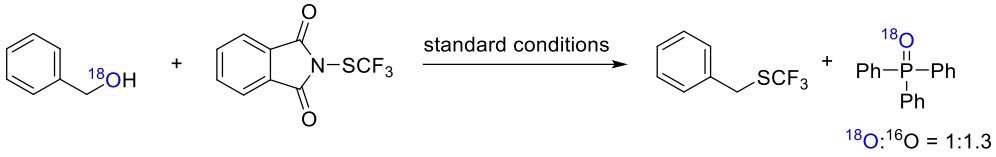
1 2

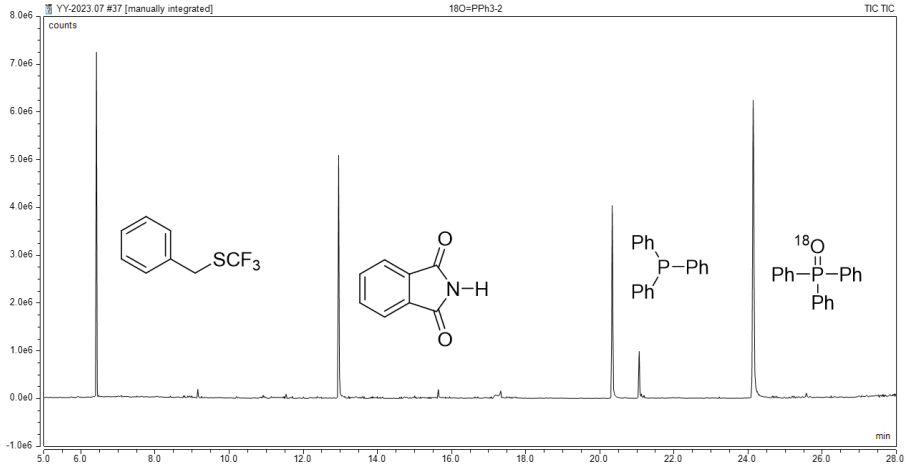


Three dried 2.0 mL resealable screw-capped vials were prepared. Alcohol (1.0 equiv, 0.1 mmol), triphenylphosphine (PPh_3, 1.3 equiv, 0.13 mmol, 34.1 mg) were placed n vial **1**. The solvent anhydrous tetrahydrofuran (THF, 0.5 mL) was added under air conditions. *N*-(trifluoromethylthio)phthalimide (Phth-SCF_3, 1.5 equiv, 0.15 mmol, 37.1 mg) and anhydrous tetrahydrofuran (THF, 0.5 mL) were added to vial **2**. The reaction mixtures in vial **1** and vial **2** were transferred in sequence to vial **3** with a Teflon-coated stir bar under air. The final reaction mixtures were stirred at room temperature for 30 minutes. When the reaction finished, the solvent was evaporated under reduced pressure and purified by flash column chromatography using a solvent mixture (ethyl acetate/petroleum ether) as an eluent to afford the purified product.

4. Investigation of the reaction mechanism

4.1 ^{18}O-labelled experiment





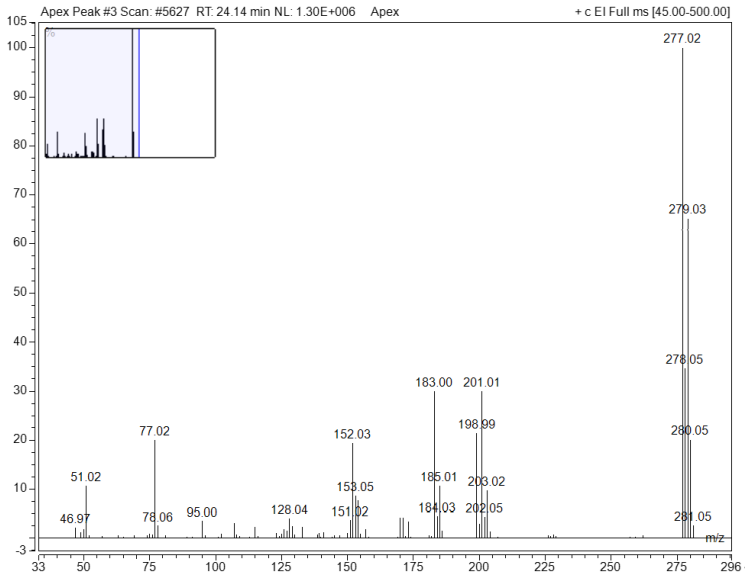
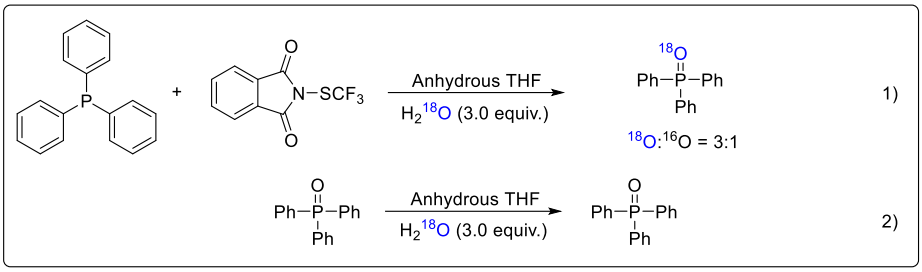
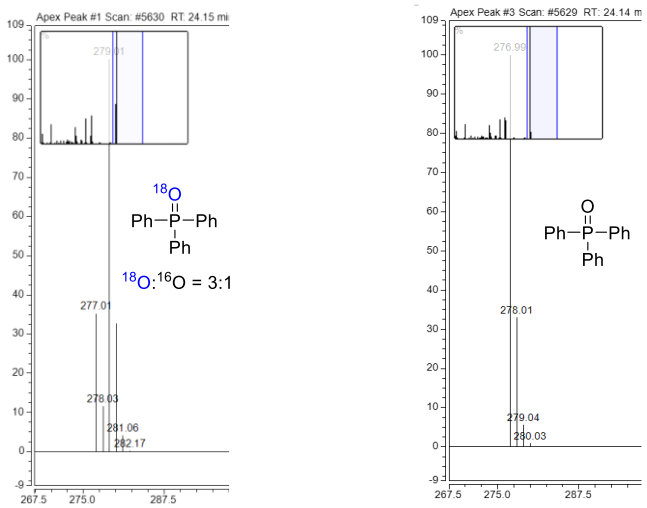


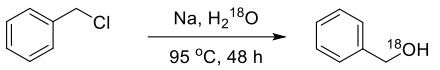
Fig. S1 The TIC spectrogram and MS spectrogram of the reaction mixture.

This ^{18}O-labelled experiment suggested that PPh_3 was responsible for the deoxygenation. However, $^{16}O{=}PPh_3$ was detected. The ^{16}O atoms probably originate from $H_2{}^{16}O$. When 3.0 equiv of $H_2{}^{18}O$ was added in anhydrous THF, trifluoromethylthiophosphonium ion was directly hydrolyzed, giving $^{18}O{=}PPh_3$ (eq 1). In addition, there's no isotope exchange (eq 2). These results further demonstrated that H_2O could quench the reaction, delivering $O{=}PPh_3$.





Preparation of ^{18}O-labelled benzylic alcohol (Ref. A. Yadav, M. D. Ambule, R. Kant and A. K. Srivastava, *Eur. J. Org. Chem.*, 2020, **2020**, 5709-5713.)



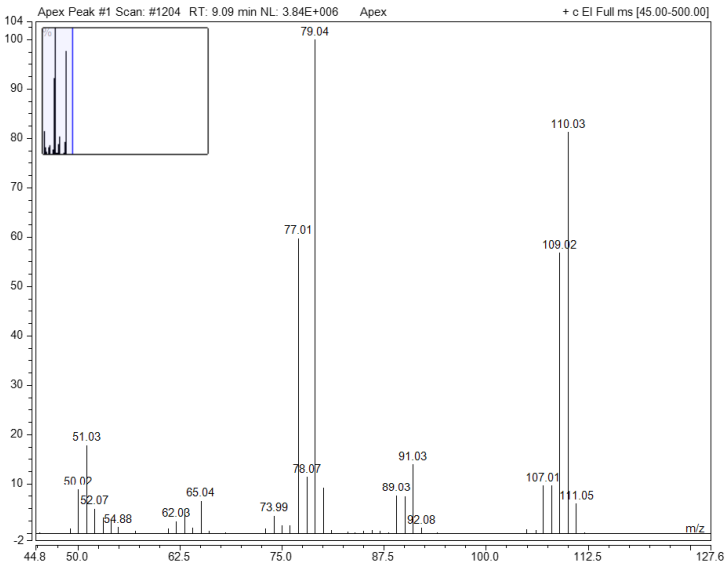
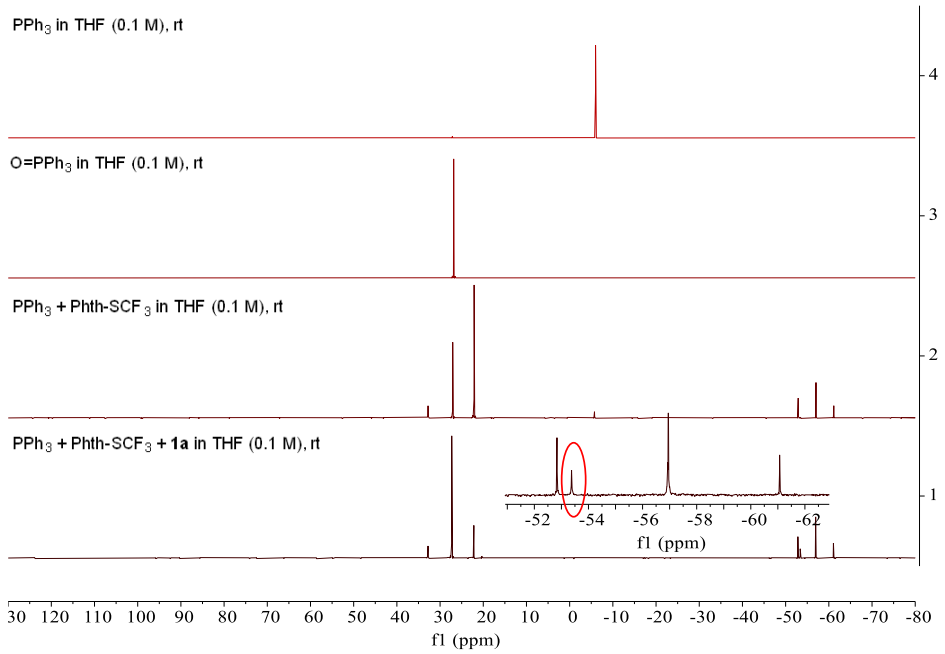


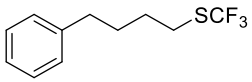
Fig. S2 The MS spectrogram of ^{18}O-labelled benzylic alcohol.

4.2 ^{31}P NMR study of reaction

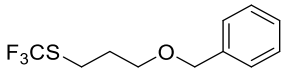


A simple ^{31}P NMR study of reaction mixture was conducted to clarify the different P species. When mixing PPh_3 and Phth-SCF_3 in THF, we are surprised to find that is formed (δ = 27.07 ppm). This result could also explain why the ^{16}O-triphenylphosphorus oxide was produced when using ^{18}O-benzylic alcohol. The peak at 22.12 ppm can be assigned to trifluoromethylthiophodphonium **III**. Under the standard conditions, two new signals were detected at δ = 20.36, and -53.38 ppm. A peak at -53.38 ppm could be assigned to the intermediate **IV** and the other may be assigned to the intermediate **V**.

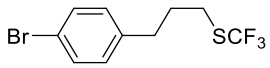
5. Characterization of products



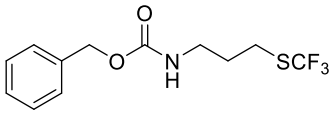
(4-phenylbutyl)(trifluoromethyl)sulfane (**2a**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5 h, 20.3 mg, 85%, purified by flash chromatography, yellow oil; Rf = 0.5 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.3 Hz, 2H), 7.23 – 7.13 (m, 3H), 2.88 (t, *J* = 5.5 Hz, 2H), 2.64 (t, *J* = 4.9 Hz, 2H), 1.78 – 1.67 (m, 4H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.59; GCMS (EI) m/z 233 $(M)^+$.



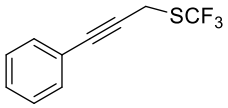
(3-(benzyloxy)propyl)(trifluoromethyl)sulfane (**2b**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5 h, 17.8 mg, 71%, purified by flash chromatography, yellow oil; Rf = 0.6 (petroleum ether/ethylacetate 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 5H), 4.50 (s, 2H), 3.57 (t, *J* = 5.8 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 1.99 (p, *J* = 6.5 Hz, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.81; GCMS (EI) m/z 250 $(M)^+$.



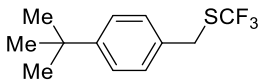
(3-(4-bromophenyl)propyl)(trifluoromethyl)sulfane (**2c**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5 h, 22.8 mg, 78%, purified by flash chromatography, yellow oil; Rf = 0.8 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 6.8 Hz, 2H), 2.86 (t, *J* = 6.7 Hz, 2H), 2.69 (t, *J* = 7.1 Hz, 2H), 2.00 (p, *J* = 7.1, 6.6 Hz, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.0; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.4, 131.6, 131.1 (q, *J* = 308.4 Hz), 130.2, 120.1, 33.7, 30.8, 29.1 (q, *J* = 2.0 Hz); HRMS (EI) cacld for $C_{10}H_{10}BrF_3S$ (M^+): 297.9633, found 297.9639.



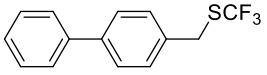
benzyl (3-((trifluoromethyl)thio)propyl)carbamate (**2d**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5 h, 22.9 mg, 78%, purified by flash chromatography, white solid; Rf = 0.5 (petroleum ether/ ethylacetate 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 5H), 5.10 (s, 2H), 4.90 (s, 1H), 3.40 – 3.21 (m, 2H), 3.01 – 2.82 (m, 2H), 2.01 – 1.81 (m, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.19; GCMS (EI) m/z 292 $(M)^+$.



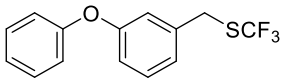
(3-phenylprop-2-yn-1-yl)(trifluoromethyl)sulfane (**2e**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5 h, 15.4 mg, 70%, purified by flash chromatography, yellow oil; Rf = 0.6 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.28 (m, 3H), 3.89 (s, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.9; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.8, 130.4 (q, *J* = 308.7), 128.7, 128.3, 122.3, 84.6, 82.2, 19.5 (q, *J* = 3.4 Hz). HRMS (EI) cacld for $C_{10}H_7F_3S$ (M^+): 216.0215, found 216.0216.



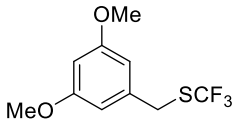
(4-(tert-butyl)benzyl)(trifluoromethyl)sulfane (**2f**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5 h, 18.1 mg, 72%, purified by flash chromatography, colorless solid; Rf = 0.6 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 4.10 (s, 2H), 1.31 (s, 9H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.26; GCMS (EI) m/z 248 $(M)^+$.



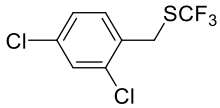
([1,1'-biphenyl]-4-ylmethyl)(trifluoromethyl)sulfane (**2g**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 15.4 mg, 67%, purified by flash chromatography, yellow solid; Rf = 0.5 (petroleum ether); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 (ddt, *J* = 8.2, 5.8, 2.4 Hz, 4H), 7.47 – 7.41 (m, 3H), 7.41 – 7.32 (m, 2H), 4.17 (s, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.04; GCMS (EI) m/z 267 $(M)^+$.



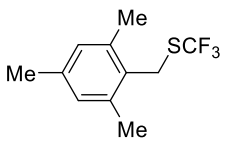
(3-phenoxybenzyl)(trifluoromethyl)sulfane (**2h**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5 h, 19.3 mg, 68%, purified by flash chromatography, yellow oil; Rf = 0.5 (petroleum ether); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 7.00 – 6.98 (m, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 4.06 (s, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.6; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.7, 156.8, 137.0, 130.5 (q, *J* = 308.4 Hz), 130.2, 129.8, 123.6, 123.6, 119.1, 119.1, 118.2, 34.0 (q, *J* = 2.4 Hz). HRMS (EI) cacld for $C_{14}H_{11}F_3OS$ (M^+): 284.0477, found 284.0482.



(3,5-dimethoxybenzyl)(trifluoromethyl)sulfane (**2i**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5 h, 17.1 mg, 68%, purified by flash chromatography, yellow oil; Rf = 0.3 (petroleum ether/ethylacetate 100:1); ^1H NMR (400 MHz, Chloroform-*d*) δ 6.48 (d, *J* = 2.0 Hz, 2H), 6.39 (t, *J* = 2.0 Hz, 1H), 4.05 (s, 2H), 3.79 (s, 6H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.91; GCMS (EI) m/z 251 $(M)^+$.

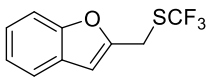


(2,4-dichlorobenzyl)(trifluoromethyl)sulfane (**2j**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 18.5 mg, 71%, purified by flash chromatography, yellow oil; Rf = 0.7 (petroleum ether/ethylacetate 20:1); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.22 (m, 1H), 4.17 (s, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.4; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.9, 134.8, 131.6, 131.3, 130.7 (q, *J* = 308.7 Hz), 129.8, 127.5, 31.5 (q, *J* = 2.5 Hz). HRMS (EI) cacld for $C_8H_5Cl_2F_3S$ (M^+): 259.9436, found 259.9445.

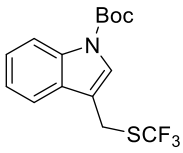


(trifluoromethyl)(2,4,6-trimethylbenzyl)sulfane (**2k**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5

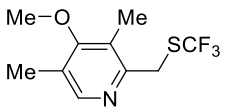
h, 18.9 mg, 80%, purified by flash chromatography, yellow oil; Rf = 0.7 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (s, 2H), 4.19 (s, 2H), 2.38 (s, 6H), 2.26 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.97; GCMS (EI) m/z 233 $(M)^+$.



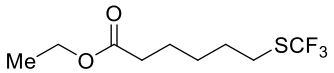
2-(((trifluoromethyl)thio)methyl)benzofuran (**2l**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv PPh_3 reagent with reaction time of 0.5 h, 13.1 mg, 57%, purified by flash chromatography, yellow oil; Rf = 0.5 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.68 (s, 1H), 4.25 (s, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.6; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.2, 151.4, 130.4 (q, *J* = 308.1 Hz) 128.1, 124.7, 123.1, 121.0, 111.2, 105.7, 27.1 (q, *J* = 2.9 Hz). HRMS (EI) cacld for $C_{10}H_7F_3OS$ (M^+): 232.0164, found 232.0173.



tert-butyl 3-(((trifluoromethyl)thio)methyl)-1H-indole-1-carboxylate (**2m**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 26.3 mg, 79%, purified by flash chromatography, yellow solid; Rf = 0.6 (petroleum ether/ethylacetate 50:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 4.27 (s, 2H), 1.67 (s, 9H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.8; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 135.6, 130.7 (q, *J* = 308.4 Hz), 128.9, 125.0, 125.0, 122.8, 118.9, 115.5, 113.8, 84.1, 28.2, 24.9 (q, *J* = 2.8 Hz). HRMS (EI) cacld for $C_{15}H_{16}F_3NO_2S$ (M^+): 331.0848, found 331.0860.

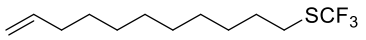


4-methoxy-3,5-dimethyl-2-(((trifluoromethyl)thio)methyl)pyridine (**2n**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 9.55 mg, 48%, purified by flash chromatography, yellow solid; Rf = 0.3 (petroleum ether/ethylacetate 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 4.29 (s, 2H), 3.77 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.32; GCMS (EI) m/z 250 $(M)^+$.

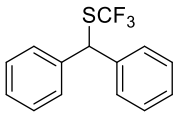


ethyl 6-((trifluoromethyl)thio)hexanoate (**2o**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 17.8 mg, 73%, purified by flash chromatography, colorless oil; Rf = 0.6 (petroleum ether/ethylacetate 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.13 (q, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.31 (t, *J* =

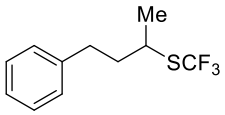
7.4 Hz, 2H), 1.73 (dd, *J* = 15.2, 7.7 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.49 – 1.42 (m, 2H), 1.28 (d, *J* = 3.8 Hz, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.24; GCMS (EI) m/z 243 $(M)^+$.



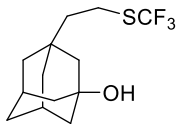
(trifluoromethyl)(undec-10-en-1-yl)sulfane (**2p**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 37.4 mg, 75%, purified by flash chromatography,colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.81 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.03 – 4.89 (m, 2H), 2.87 (t, *J* = 7.4 Hz, 1H), 2.04 (q, *J* = 7.0 Hz, 2H), 1.85 – 1.76 (m, 1H), 1.68 (p, *J* = 7.4 Hz, 2H), 1.43 – 1.27 (m, 12H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.59.



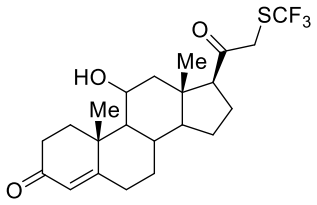
benzhydryl(trifluoromethyl)sulfane (**2q**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 1 h, 16.6 mg, 59%, purified by flash chromatography, colorless oil; Rf = 0.8 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.5 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.27 (t, *J* = 7.2 Hz, 2H), 5.69 (s, 1H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.36; GCMS (EI) m/z 268 $(M)^+$.



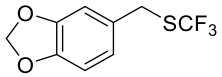
(4-phenylbutan-2-yl)(trifluoromethyl)sulfane (**2r**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 1 h, 25.4 mg, 55%, purified by flash chromatography, colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.20 (dd, *J* = 11.2, 7.2 Hz, 3H), 3.30 (h, *J* = 6.8 Hz, 1H), 2.75 (t, *J* = 7.9 Hz, 2H), 1.95 (dh, *J* = 14.6, 7.3 Hz, 2H), 1.46 (d, *J* = 6.8 Hz, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.28; GCMS (EI) m/z 234 $(M)^+$.



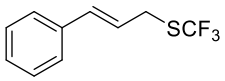
(1s,3r,5R,7S)-3-(2-((trifluoromethyl)thio)ethyl)adamantan-1-ol (**3a**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 12.3 mg, 44%, purified by flash chromatography, yellow oil; Rf = 0.4 (petroleum ether/ethylacetate 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.12 (q, *J* = 7.1 Hz, 2H), 3.48 (s, 1H), 2.89 – 2.79 (m, 1H), 2.05 (s, 3H), 1.67 (q, *J* = 11.7, 11.2 Hz, 3H), 1.60 – 1.51 (m, 2H), 1.48 – 1.40 (m, 3H), 1.26 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.0 (q, *J* = 307.0 Hz) 68.7, 60.4, 49.4, 44.6, 42.8, 40.5, 36.4, 35.3, 30.5, 24.3, 21.0, 14.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.4; HRMS (ESI) cacld for $C_{13}H_{19}F_3NaOS^+$ $(M+Na)^+$: 303.1001, found 303.1003.



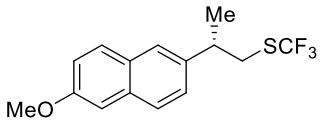
(10R,13S,17S)-11-hydroxy-10,13-dimethyl-17-(2-((trifluoromethyl)thio)acetyl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one. (**3b**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 24.2 mg, 57%, purified by flash chromatography, yellow oil; Rf = 0.6 (petroleum ether/ethylacetate 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.69 (s, 1H), 4.43 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 1H), 3.84 (d, *J* = 3.7 Hz, 2H), 2.61 (t, *J* = 8.9 Hz, 1H), 2.54 – 2.43 (m, 2H), 2.36 (dt, *J* = 16.6, 4.2 Hz, 1H), 2.28 – 2.14 (m, 4H), 2.02 (d, *J* = 8.9 Hz, 2H), 1.83 (dtd, *J* = 22.9, 15.3, 14.5, 7.0 Hz, 4H), 1.45 (s, 3H), 1.30 – 1.24 (m, 2H), 1.17 (dd, *J* = 11.3, 5.2 Hz, 1H), 1.08 (dd, *J* = 13.5, 4.3 Hz, 1H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.8, 199.5, 171.9, 131.6 (q, *J* = 307.0Hz) 122.4, 67.9, 61.9, 57.4, 56.3, 47.9, 43.7, 41.6 (q, *J* = 1.8 Hz), 39.2, 35.0, 33.8, 32.5, 32.0, 31.3, 24.3, 23.1, 20.9, 16.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.4; HRMS (EI) cacld for $C_{22}H_{29}F_3O_3S$ (M^+):412.1678, found 412.1694.



5-(((trifluoromethyl)thio)methyl)benzo[d][1,3]dioxole (**4a**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 14.5 mg, 62%, purified by flash chromatography, yellow oil; Rf = 0.6 (petroleum ether/ethylacetate 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.81 (d, *J* = 6.7 Hz, 1H), 6.78 (s, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.96 (s, 2H), 4.05 (s, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.19; GCMS (EI) m/z 235 $(M)^+$.

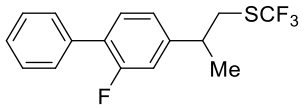


cinnamyl(trifluoromethyl)sulfane (**4b**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 14.2 mg, 65%, purified by flash chromatography, yellow oil; Rf = 0.6 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.24 (m, 3H), 6.59 (d, *J* = 15.7 Hz, 1H), 6.21 (dt, *J* = 15.2, 7.4 Hz, 1H), 3.71 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.1, 134.4, 130.8 (q, *J* = 308.1 Hz), 128.7, 128.1, 126.5, 123.0, 32.7 (q, *J* = 2.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.9; HRMS (EI) cacld for $C_{10}H_9F_3S$ (M^+): 218.0372, found 218.0873.

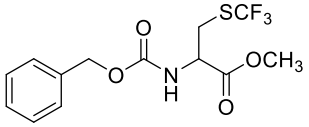


(S)-(2-(6-methoxynaphthalen-2-yl)propyl)(trifluoromethyl)sulfane (**4c**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with

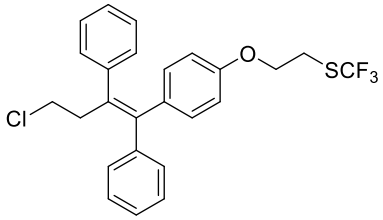
reaction time of 0.5 h, 18.7 mg, 63%, purified by flash chromatography, yellow solid; Rf = 0.5 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (dd, *J* = 8.2, 6.1 Hz, 2H), 7.56 (s, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.18 – 7.08 (m, 2H), 3.90 (s, 3H), 3.26 – 3.19 (m, 1H), 3.13 (ddd, *J* = 24.0, 11.8, 6.2 Hz, 2H), 1.45 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.6, 139.0, 133.7, 131.2 (q, *J* = 307.0 Hz), 129.2, 128.9, 127.3, 125.6, 125.3, 119.1, 105.6, 55.3, 39.6, 37.7 (q, *J* = 1.7 Hz), 20.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.2; HRMS (EI) cacld for $C_{15}H_{15}F_3OS$ (M^+): 300.0790, found 300.0798.



(2-(2-fluoro-[1,1'-biphenyl]-4-yl)propyl)(trifluoromethyl)sulfane (**4d**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 26.3 mg, 82%, purified by flash chromatography, colorless oil; Rf = 0.4 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 11.6 Hz, 1H), 3.20 – 3.13 (m, 1H), 3.08 (td, *J* = 11.7, 9.8, 5.3 Hz, 2H), 1.42 (d, *J* = 6.2 Hz, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.1, -117.5; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8 (d, *J* = 248.6 Hz), 145.5 (d, *J* = 7.1 Hz), 135.5 (d, *J* = 1.2 Hz), 131.1 (q, *J* = 307.4), 130.9 (d, *J* = 4.0 Hz), 129.0, 128.9, 128.5, 127.7, 123.0 (d, *J* = 3.3 Hz), 114.5 (d, *J* = 23.2 Hz), 39.4, 37.4 (q, *J* = 1.9 Hz), 20.7; HRMS (EI) cacld for $C_{16}H_{14}F_4S$ (M^+): 314.0747, found 314.0758.

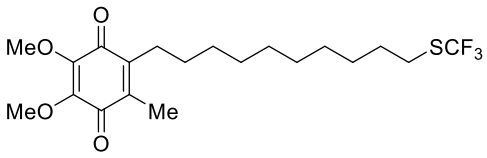


methyl N-((benzyloxy)carbonyl)-S-(trifluoromethyl)cysteinate (**4e**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 18.3 mg, 54%, purified by flash chromatography, orange oil; Rf = 0.7 (petroleum ether/ ethylacetate 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 5H), 5.63 (s, 1H), 5.13 (s, 2H), 4.72 – 4.65 (m, 1H), 3.79 (s, 3H), 3.49 (dd, *J* = 14.1, 4.0 Hz, 1H), 3.34 (dd, *J* = 14.1, 4.8 Hz, 1H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.0; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 155.5, 135.9, 130.4 (q, *J* = 308.1 Hz), 128.6, 128.3, 128.1, 67.4, 53.3, 53.0 (q, *J* = 2.4 Hz). GCMS (EI) m/z 337 (M^+).

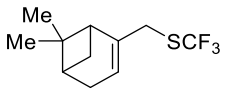


(Z)-(2-(4-(4-chloro-1,2-diphenylbut-1-en-1-yl)phenoxy)ethyl)(trifluoromethyl)sulfane (**4f**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 31.8 mg, 69%, purified by flash chromatography,

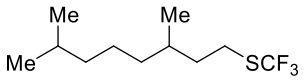
colorless oil; Rf = 0.6 (petroleum ether/ethylacetate 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.26 (m, 5H), 7.23 – 7.10 (m, 5H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 8.6 Hz, 2H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.41 (t, *J* = 7.4 Hz, 2H), 3.16 (t, *J* = 6.5 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.3; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.2, 142.7, 141.6, 140.9, 135.6, 131.8, 130.9 (q, *J* = 309.1 Hz), 129.5, 128.4, 128.2, 127.0, 126.7, 113.6, 66.2, 42.8, 38.6, 28.9 (q, *J* = 2.1 Hz); HRMS (EI) cacld for $C_{25}H_{22}ClF_3OS$ (M^+): 462.1026, found 462.1042.



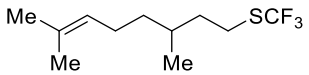
2,3-dimethoxy-5-methyl-6-(10-((trifluoromethyl)thio)decyl)cyclohexa-2,5-diene-1,4-dione (**4g**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 34.9 mg, 83%, purified by flash chromatography, brown oil; Rf = 0.5 (petroleum ether/ethylacetate 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.02 – 3.96 (m, 6H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.01 (s, 3H), 1.68 (p, *J* = 7.4 Hz, 2H), 1.36 (dd, *J* = 14.8, 7.4 Hz, 14H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.28; GCMS (EI) m/z 422 $(M)^+$.



((6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methyl)(trifluoromethyl)sulfane (**4h**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 18.5 mg, 78%, purified by flash chromatography, yellow oil; Rf = 0.7 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.56 (s, 1H), 3.58 – 3.43 (m, 2H), 2.42 (dt, *J* = 8.8, 5.7 Hz, 1H), 2.35 – 2.22 (m, 2H), 2.19 (t, *J* = 5.5 Hz, 1H), 2.13 – 2.06 (m, 1H), 1.49 – 1.36 (m, 1H), 1.30 (s, 3H), 0.82 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.3; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.2, 131.9 (q, *J* = 308.1 Hz), 122.4, 45.0, 40.4, 36.2 (q, *J* = 2.2 Hz), 34.4, 31.6, 31.3, 26.1, 21.1; HRMS (EI) cacld for $C_{11}H_{15}F_3S$ (M^+): 236.0841, found 236.0844.

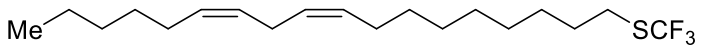


(3,7-dimethyloctyl)(trifluoromethyl)sulfane (**4i**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 17.1 mg, 72%, purified by flash chromatography, yellow oil; Rf = 0.5 (petroleum ether); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.97 – 2.80 (m, 2H), 1.53 (dd, *J* = 13.0, 6.4 Hz, 4H), 1.30 (dd, *J* = 13.7, 7.5 Hz, 3H), 1.17 – 1.11 (m, 3H), 0.90 (d, *J* = 6.1 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 6H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.24.



(3,7-dimethyloct-6-en-1-yl)(trifluoromethyl)sulfane (**4j**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5

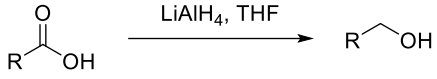
h, 19.1 mg, 79%, purified by flash chromatography, yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.08 (t, *J* = 7.1 Hz, 1H), 2.97 – 2.80 (m, 2H), 1.98 (dt, *J* = 15.7, 7.3 Hz, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.53 (ddd, *J* = 17.4, 11.7, 6.0 Hz, 2H), 1.39 – 1.29 (m, 2H), 0.91 (d, *J* = 6.4 Hz, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.24; GCMS (EI) m/z 240 $(M)^{+}$.



((9Z,12Z)-octadeca-9,12-dien-1-yl)(trifluoromethyl)sulfane (**4k**) According to the general procedure in 0.1 mmol scale using 1.5 equiv Phth-SCF_3 reagent and 1.3 equiv Ph_3P reagent with reaction time of 0.5 h, 25.4 mg, 73%, purified by flash chromatography, yellow oil; Rf = 0.6 (petroleum ether/ethylacetate 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.40 (dd, *J* = 10.7, 7.0 Hz, 2H), 5.32 (dd, *J* = 10.7, 7.1 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.77 (t, *J* = 6.3 Hz, 2H), 2.05 (q, *J* = 6.4 Hz, 4H), 1.68 (p, *J* = 7.3 Hz, 2H), 1.38 (dd, *J* = 14.8, 6.3 Hz, 6H), 1.33 – 1.28 (m, 10H), 0.89 (t, *J* = 6.7 Hz, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.6; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 130.2, 131.2 (q, *J* = 307.0 Hz), 130.0, 128.1, 127.9, 31.6, 31.4, 29.9 (q, *J* = 2.0 Hz), 29.4, 29.4, 29.3, 29.2, 28.9, 28.5, 27.2, 27.2, 25.6, 22.6, 14.1.

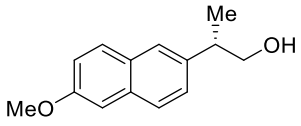
6. Preparation of substrates.

General procedure:



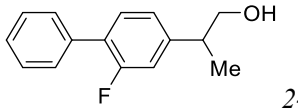
R = alkyl, aryl

The following reactants were prepared from the carboxylic acid according to general procedure (Ref. (a) X. Jiang, Z. Deng and P. Tang, *Angew Chem. Int. Ed.*, 2018, **57**, 292; (b) L. Wang, T. Li, S. Perveen, S. Zhang, X. Wang, Y. Ouyang and P. Li, *Angew Chem. Int. Ed.*, 2022, **61**, e202213943; (c) G. P. Choudhary, K. Soni and P. Soni, *Journal of Drug Delivery and Therapeutics*, 2019, **9**, 316.).



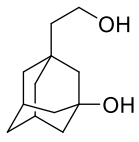
(S)-2-(6-methoxynaphthalen-2-yl)propan-1-ol

4.5 mmol scale, white solid, 426.6 mg, 66%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.66 (m, 2H), 7.59 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.16 – 7.08 (m, 2H), 3.90 (s, 3H), 3.75 (d, *J* = 6.7 Hz, 2H), 3.06 (h, *J* = 6.9 Hz, 1H), 1.45 (s, 1H), 1.34 (d, *J* = 7.0 Hz, 3H); GCMS (EI) m/z 216 $(M)^+$.



2-(2-fluoro-[1,1'-biphenyl]-4-yl)propan-1-ol

2.0 mmol scale, white solid, 302.0 mg, 66%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 14.6, 7.6 Hz, 2H), 7.07 (dd, *J* = 17.6, 9.9 Hz, 2H), 3.73 (d, *J* = 6.7 Hz, 2H), 2.98 (h, *J* = 6.9 Hz, 1H), 1.50 (s, 1H), 1.30 (d, *J* = 7.0 Hz, 3H); GCMS (EI) m/z 230 $(M)^+$.

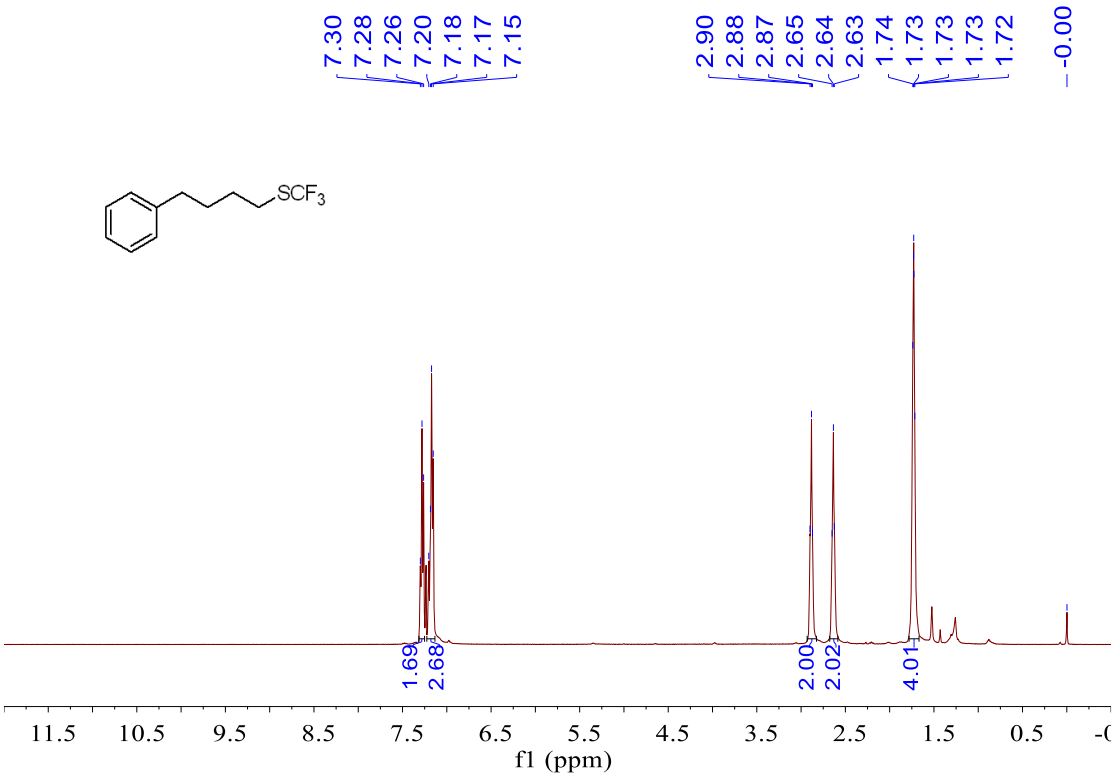


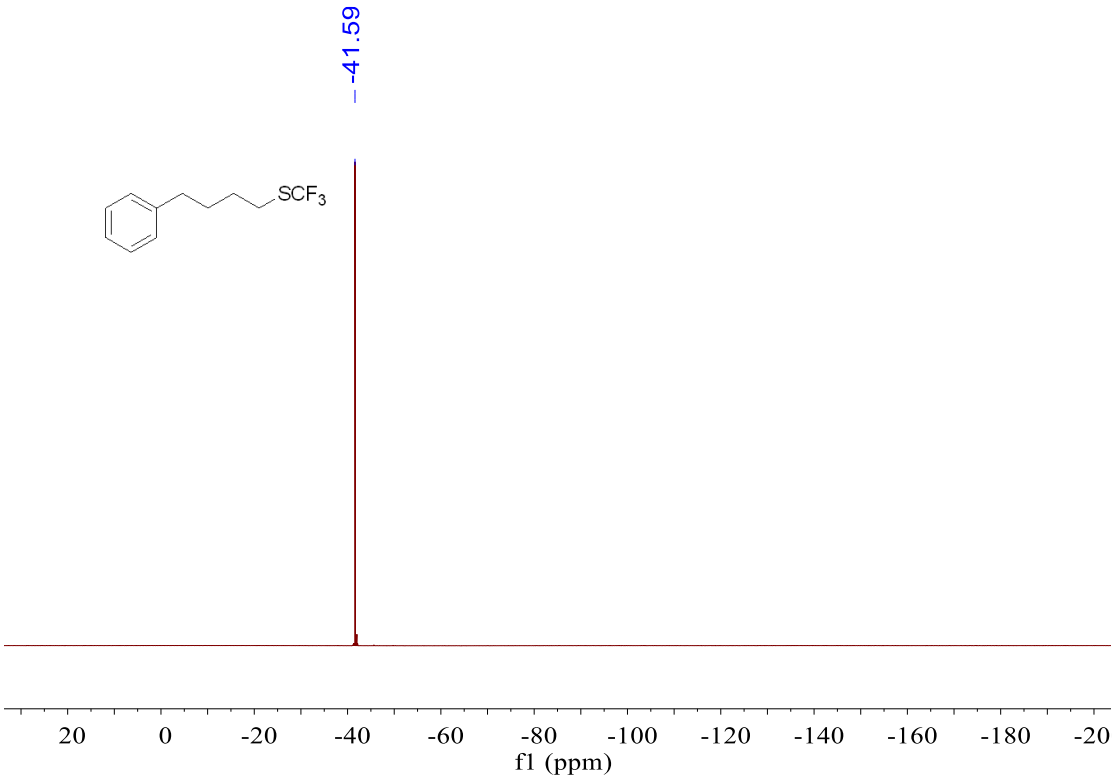
(1s,3s,5R,7S)-3-(2-hydroxyethyl)adamantan-1-ol

4.0 mmol scale, white solid, 385.6 mg, 98%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.71 (t, *J* = 7.4 Hz, 2H), 2.19 (s, 2H), 1.68 (d, *J* = 11.5 Hz, 2H), 1.63 (d, *J* = 11.7 Hz, 3H), 1.54 (s, 2H), 1.46 (d, *J* = 12.8 Hz, 8H); GCMS (EI) m/z 196 $(M)^+$.

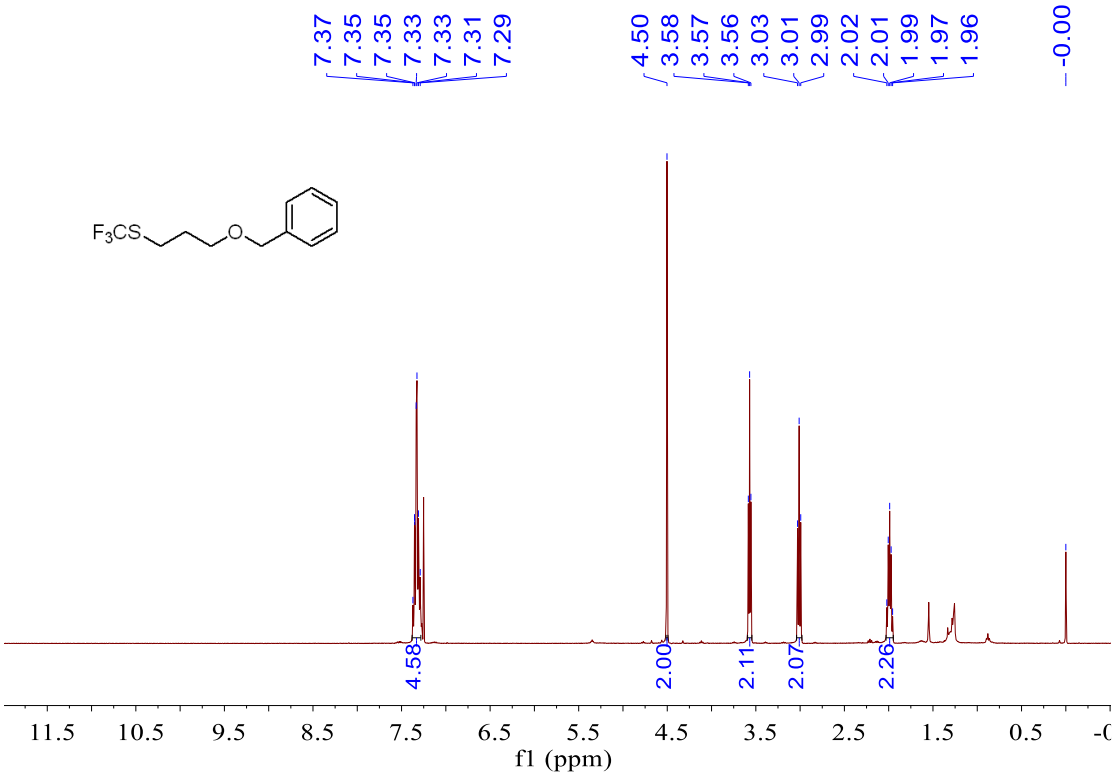
7. NMR spectras of products.

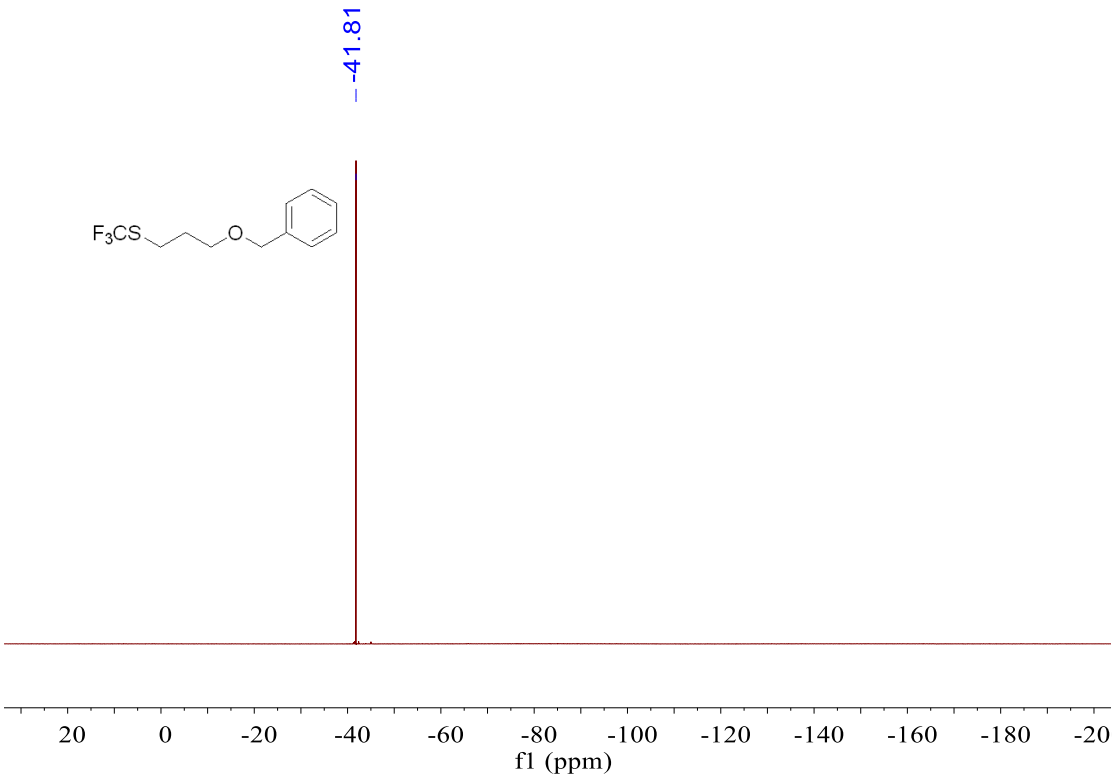
(4-phenylbutyl)(trifluoromethyl)sulfane (**2a**)



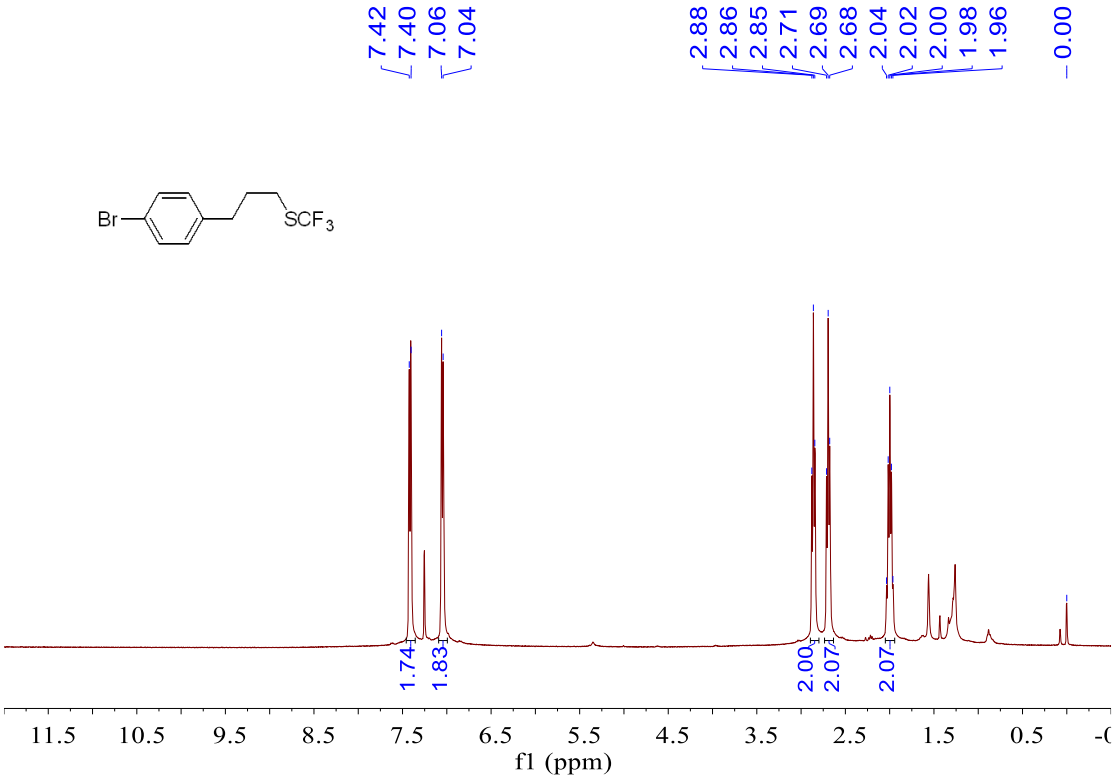


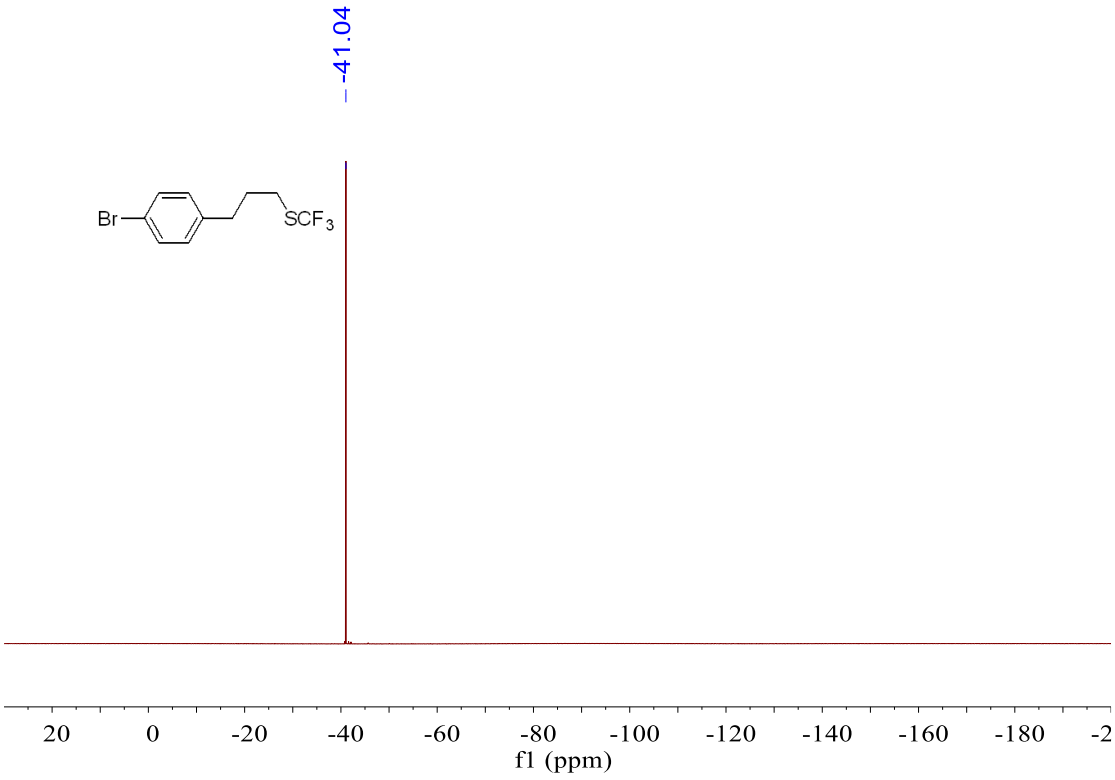
(3-(benzyloxy)propyl)(trifluoromethyl)sulfane (**2b**)

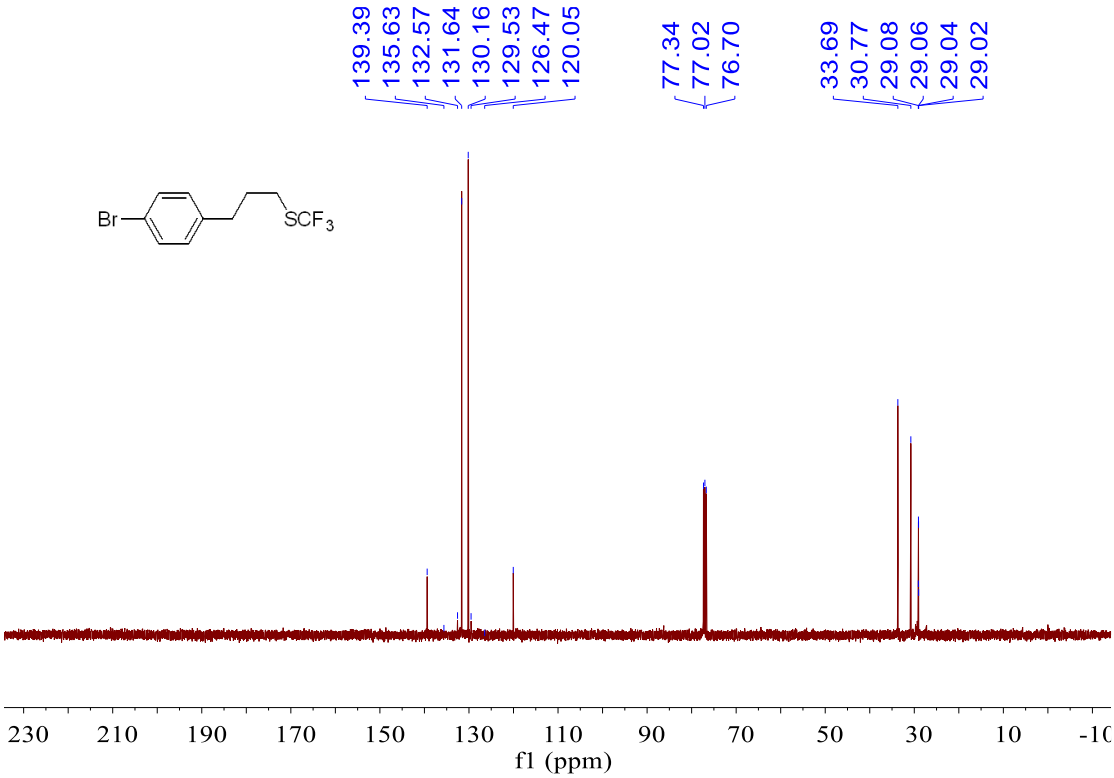




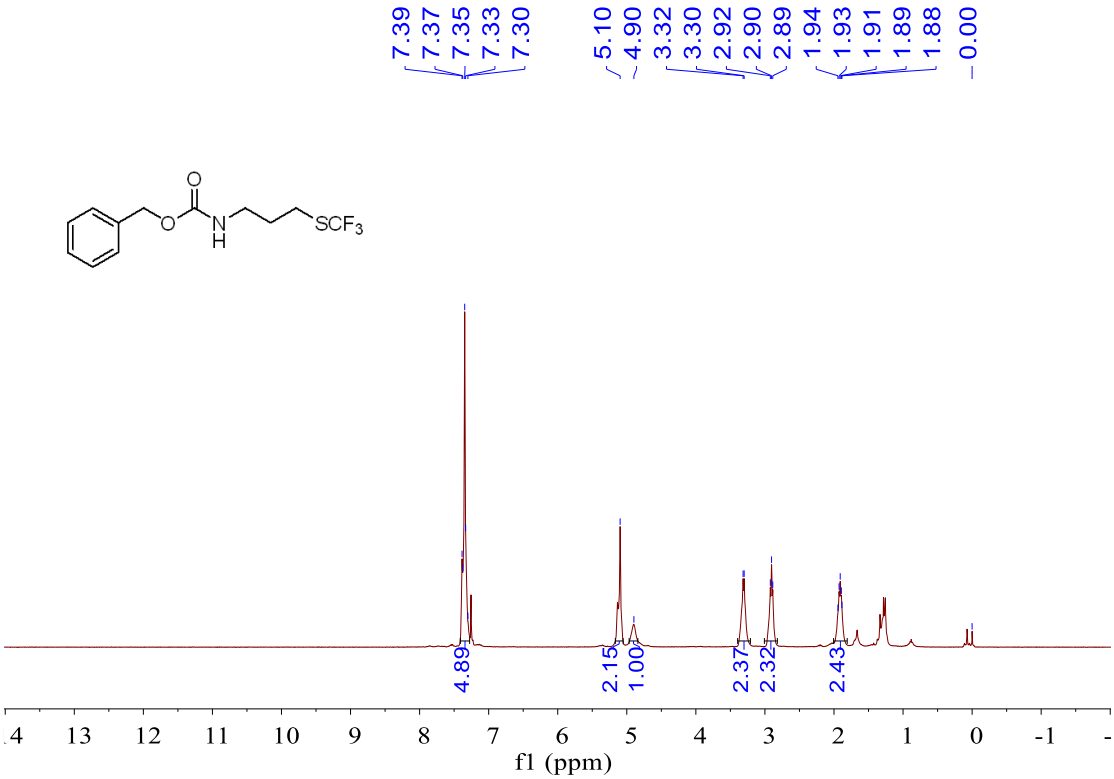
(3-(4-bromophenyl)propyl)(trifluoromethyl)sulfane (**2c**)

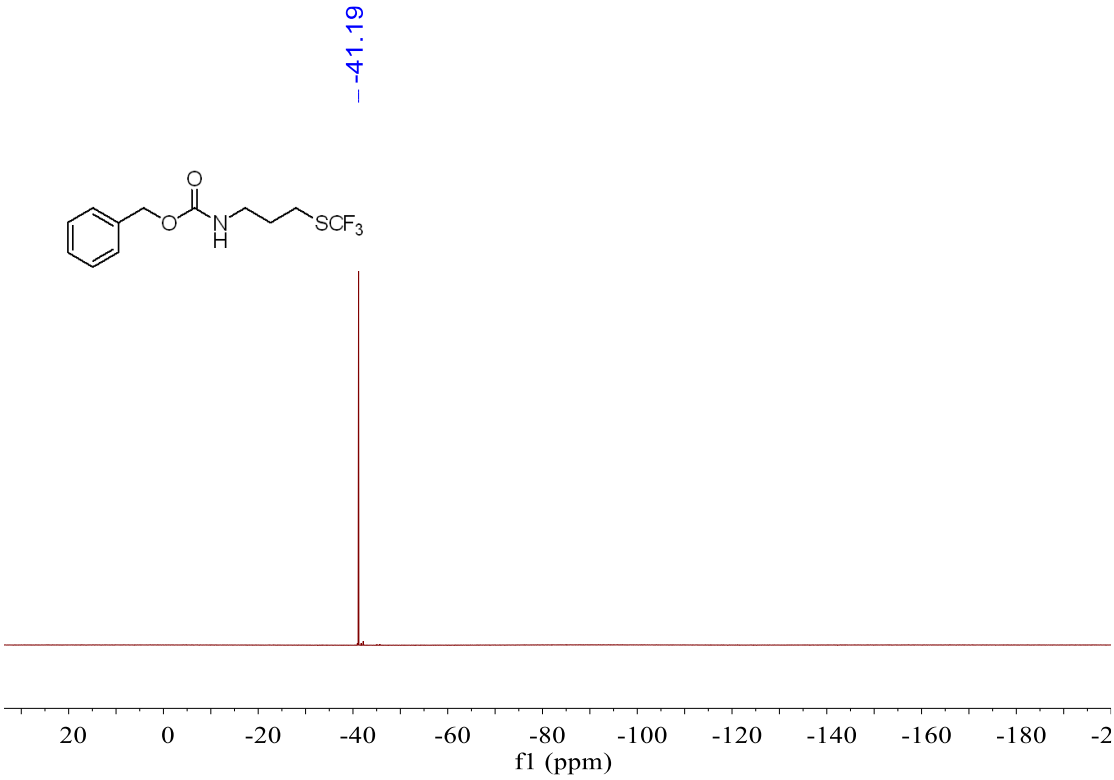




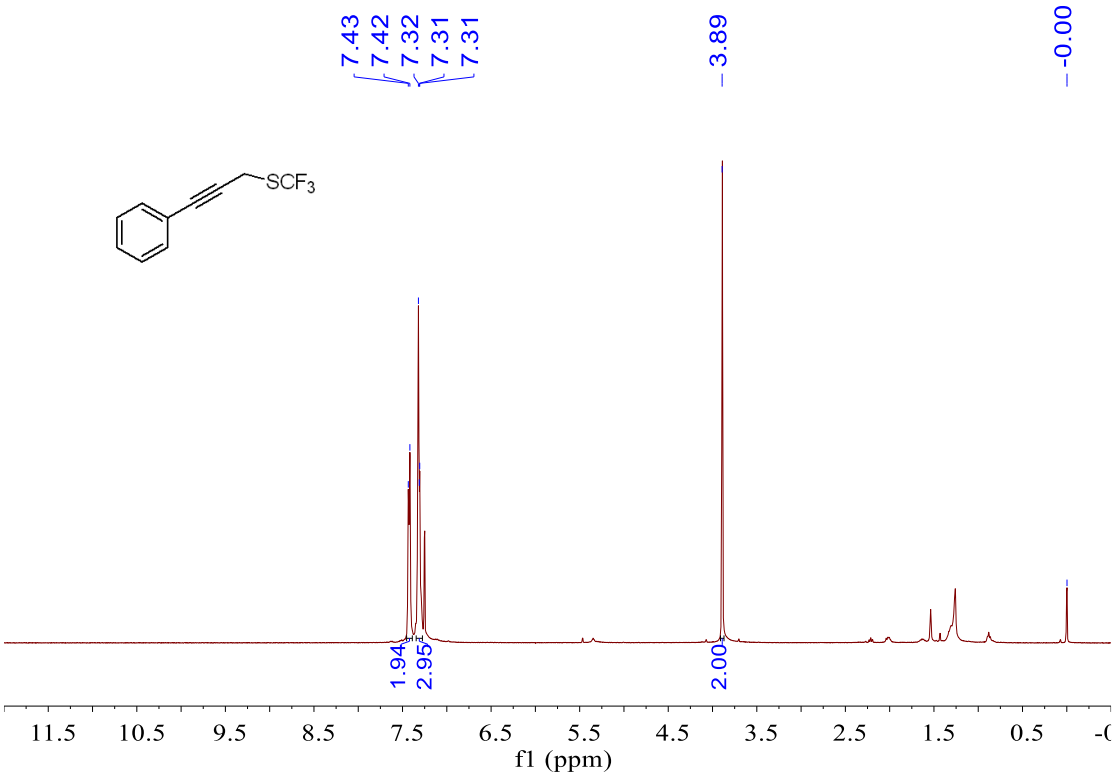


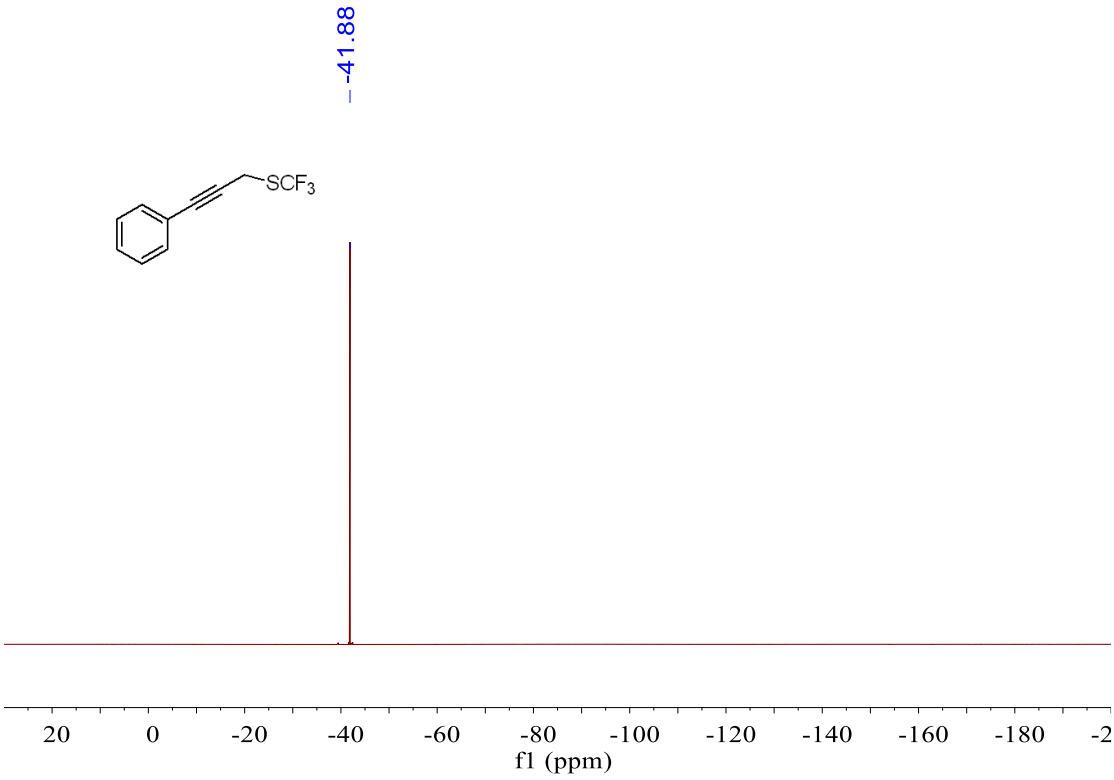
benzyl (3-((trifluoromethyl)thio)propyl)carbamate (**2d**)

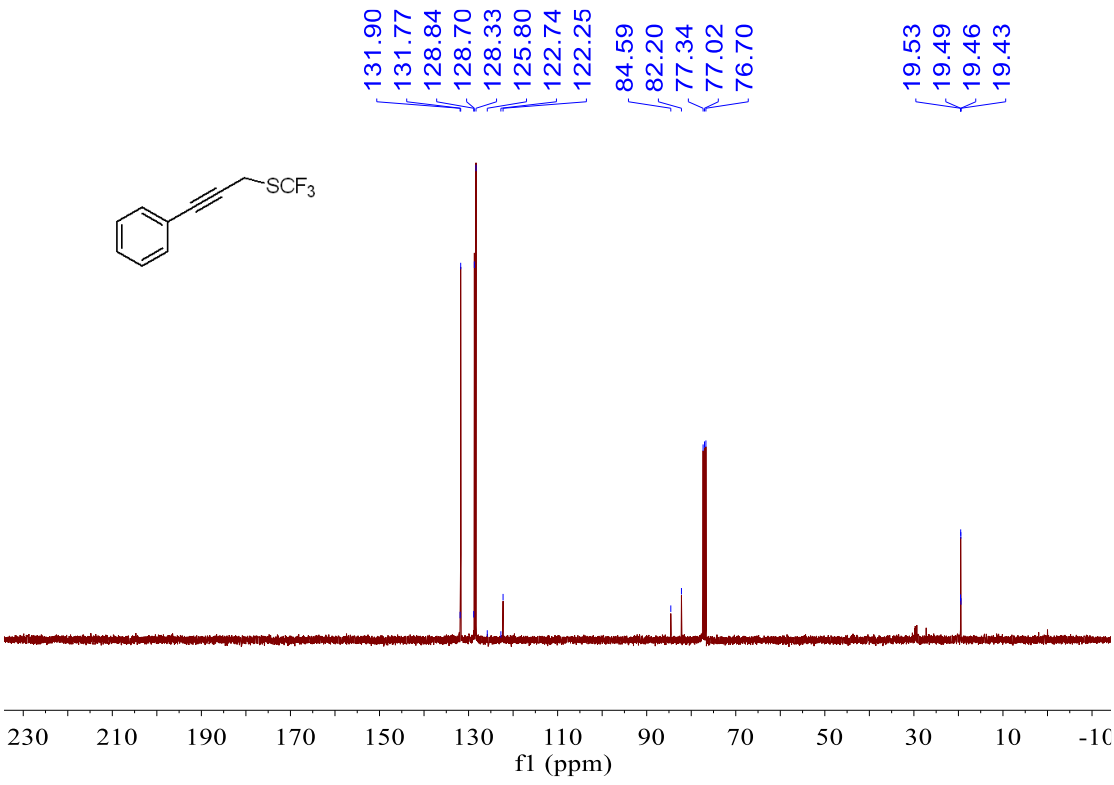




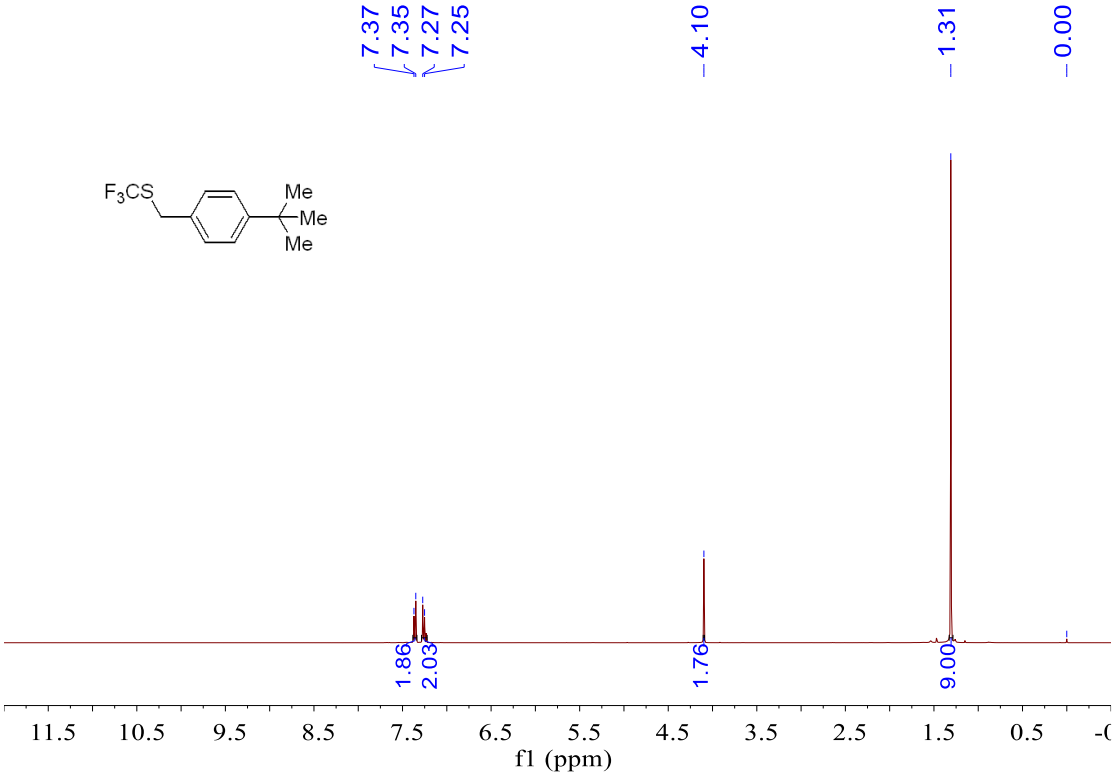
(3-phenylprop-2-yn-1-yl)(trifluoromethyl)sulfane (**2e**)

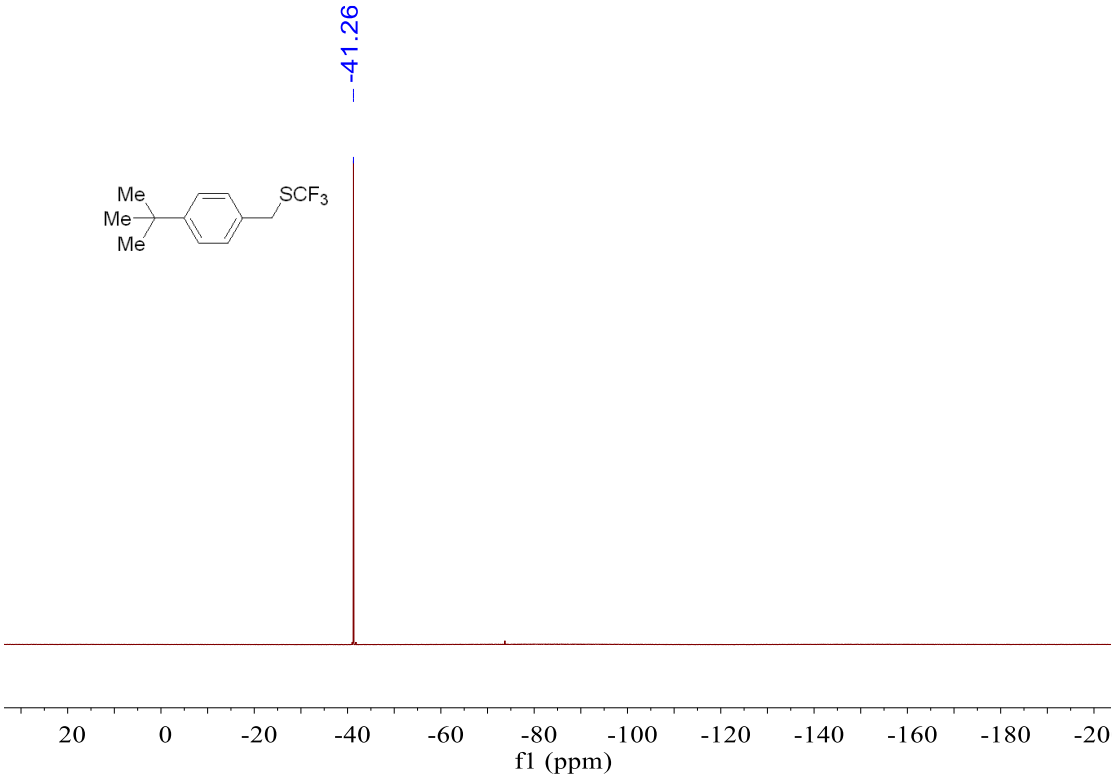



-41.88
SCF3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-2
f1 (ppm)

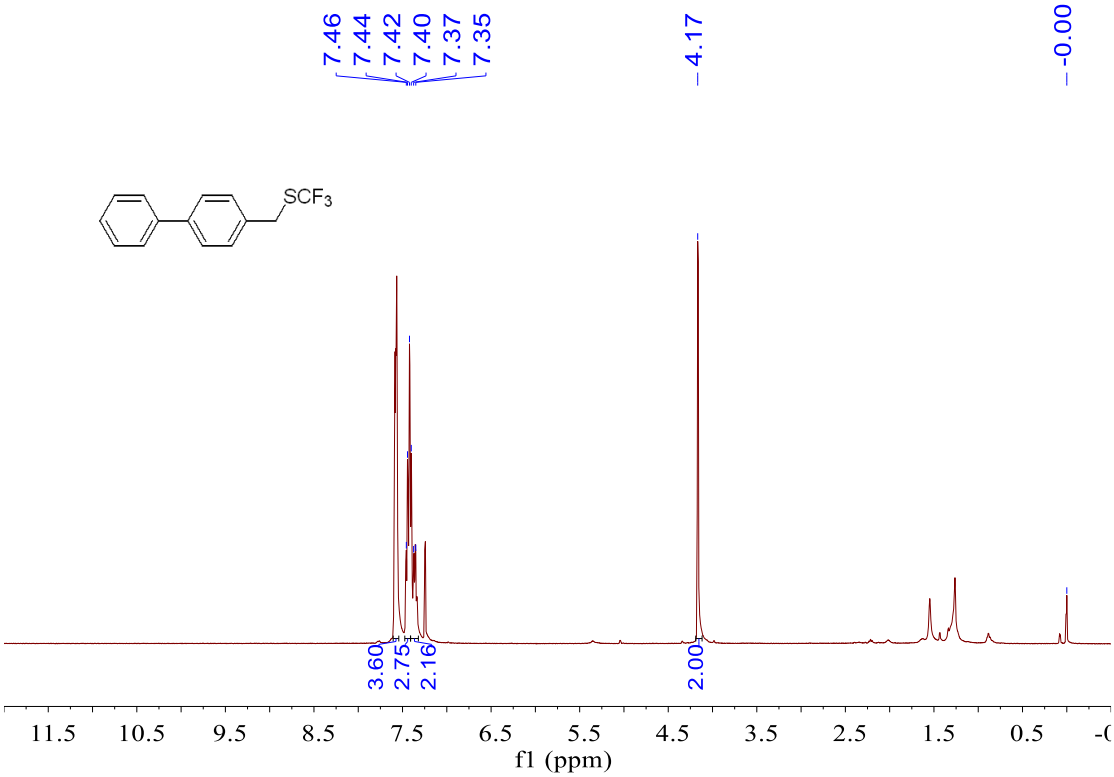

131.90
131.77
128.84
128.70
128.33
125.80
122.74
122.25
84.59
82.20
77.34
77.02
76.70
19.53
19.49
19.46
19.43
SCF3
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)

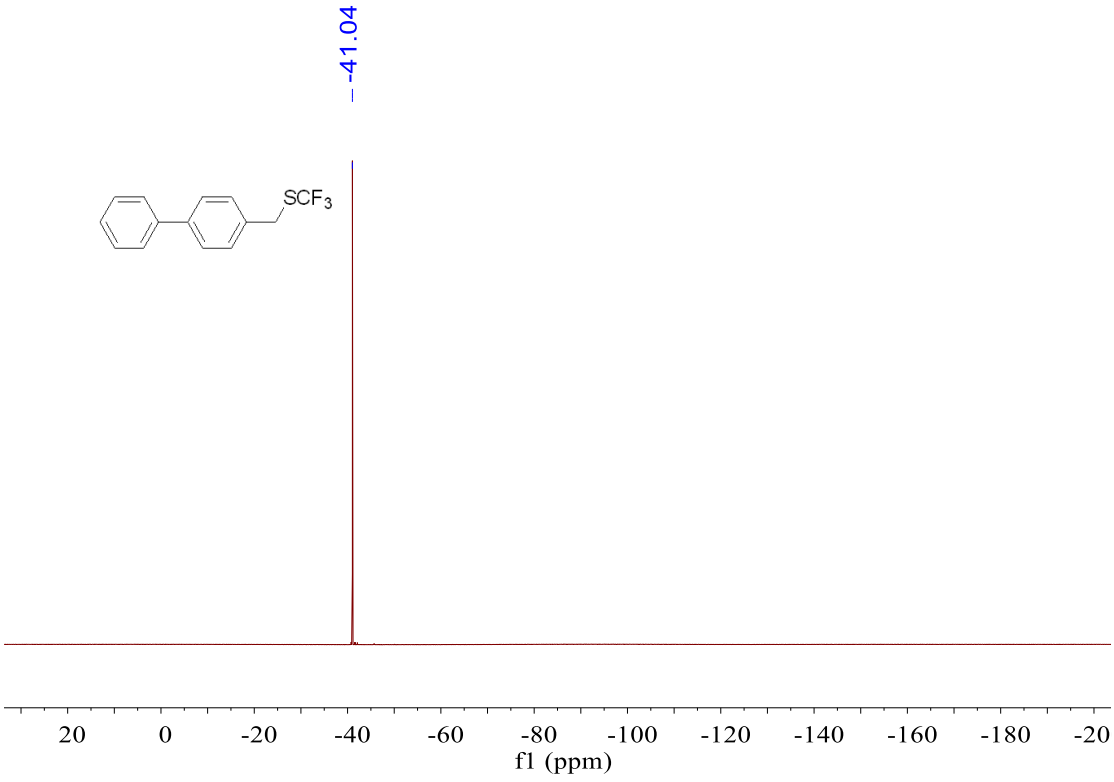
(4-(tert-butyl)benzyl)(trifluoromethyl)sulfane (**2f**)



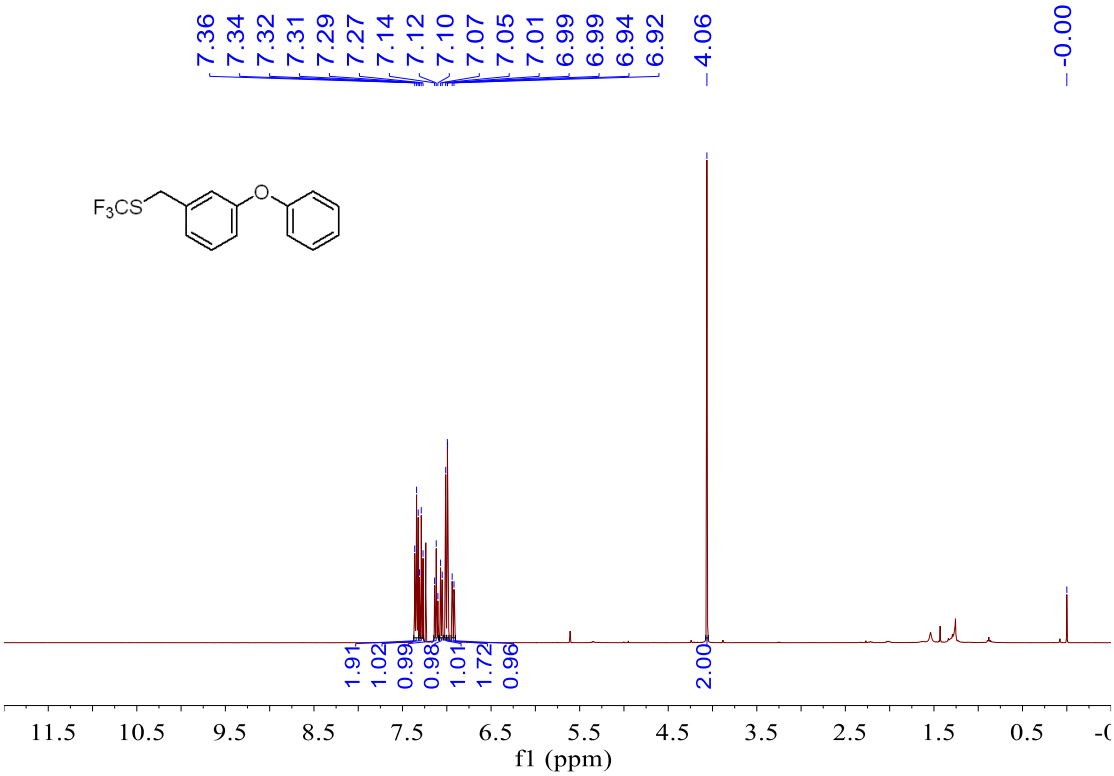


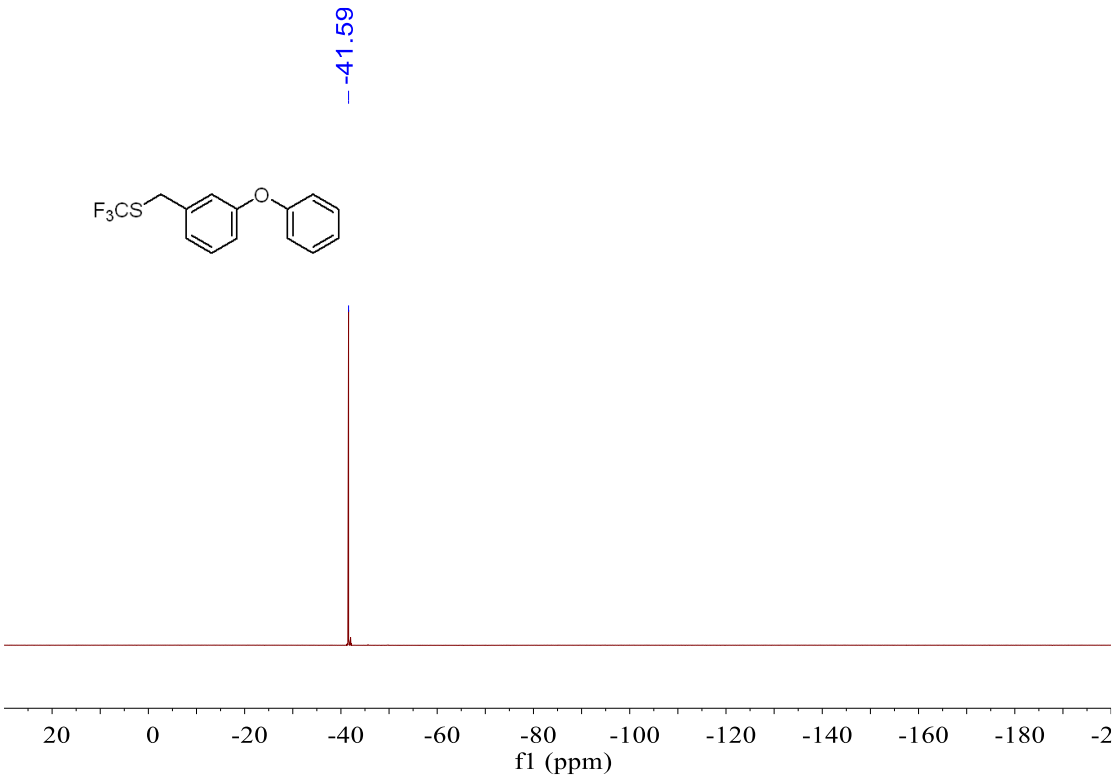
([1,1'-biphenyl]-4-ylmethyl)(trifluoromethyl)sulfane (**2g**)

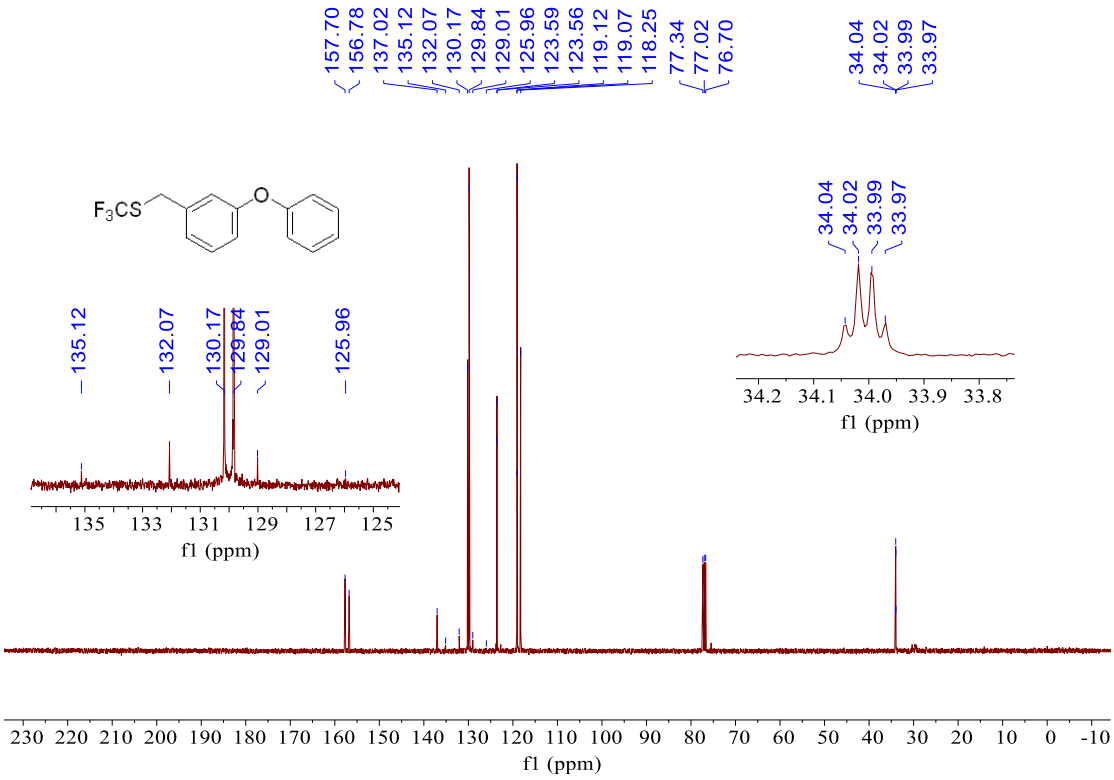




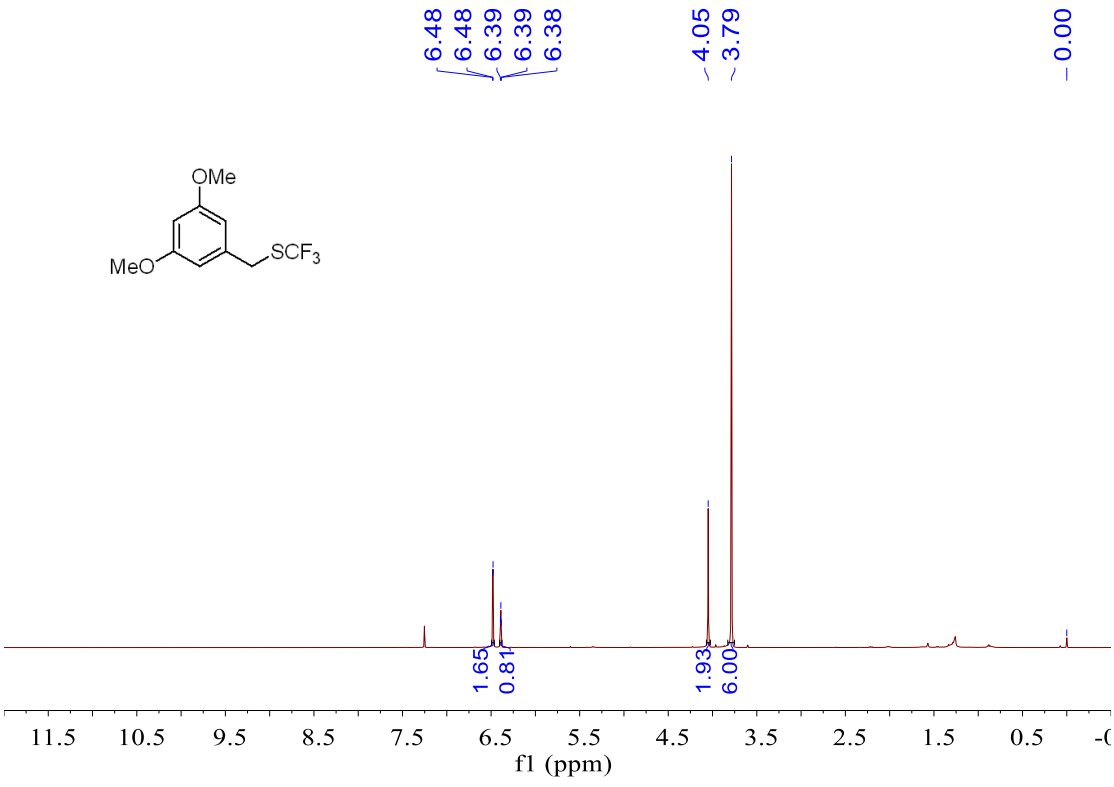
(3-phenoxybenzyl)(trifluoromethyl)sulfane (**2h**)

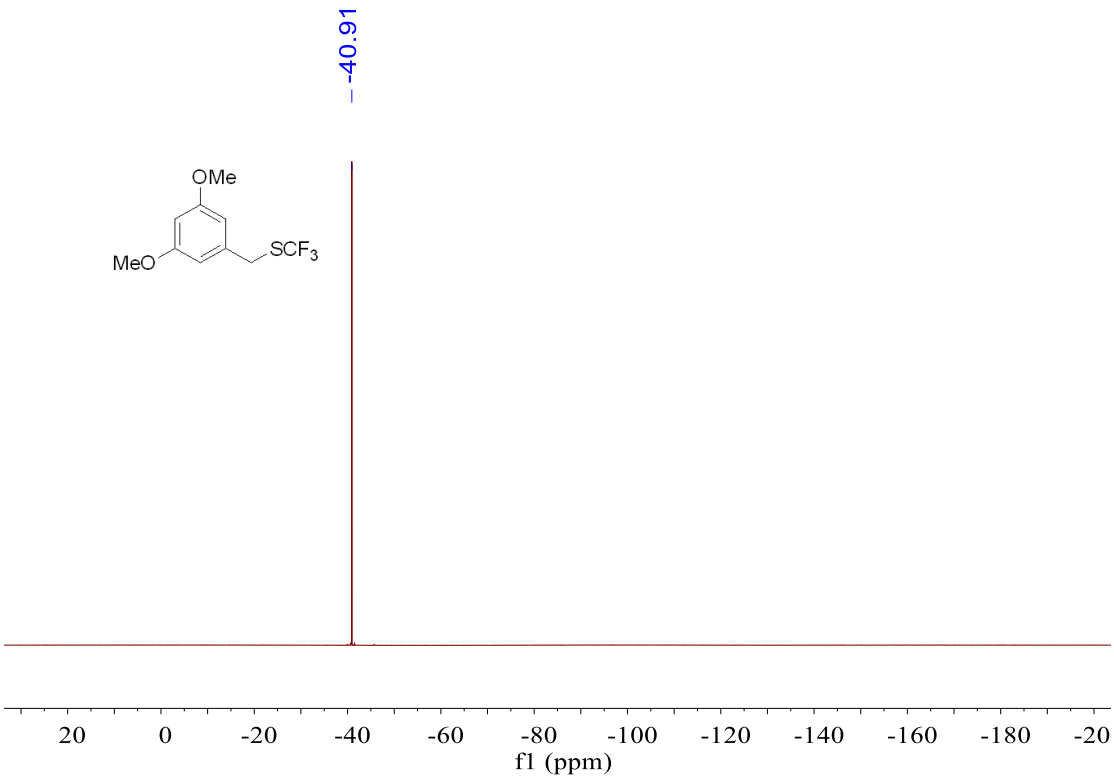




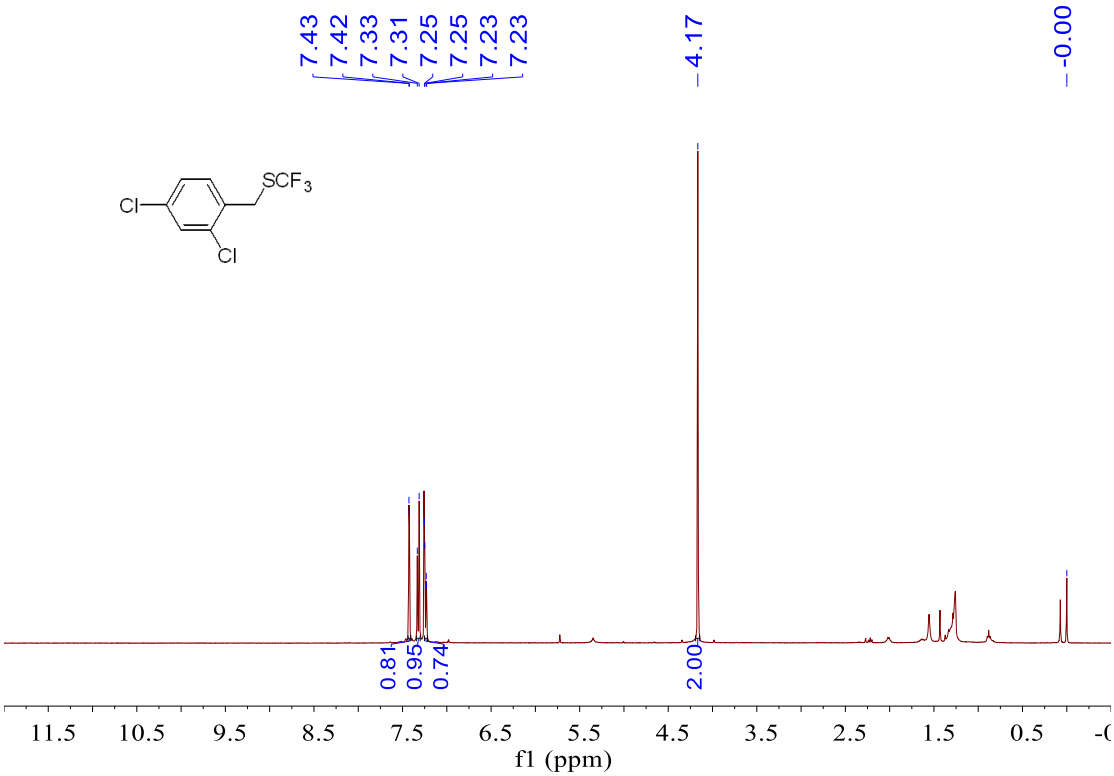


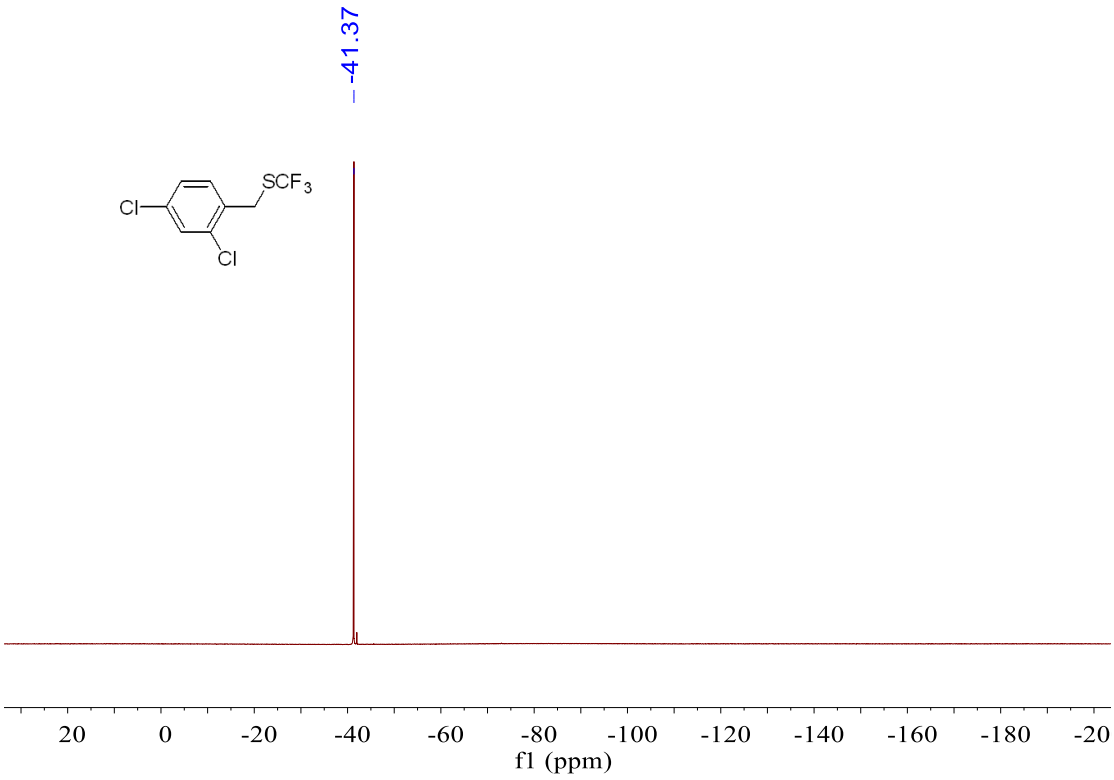
(3,5-dimethoxybenzyl)(trifluoromethyl)sulfane (**2i**)





(2,4-dichlorobenzyl)(trifluoromethyl)sulfane (**2j**)




-41.37
SCF3
Cl
Cl
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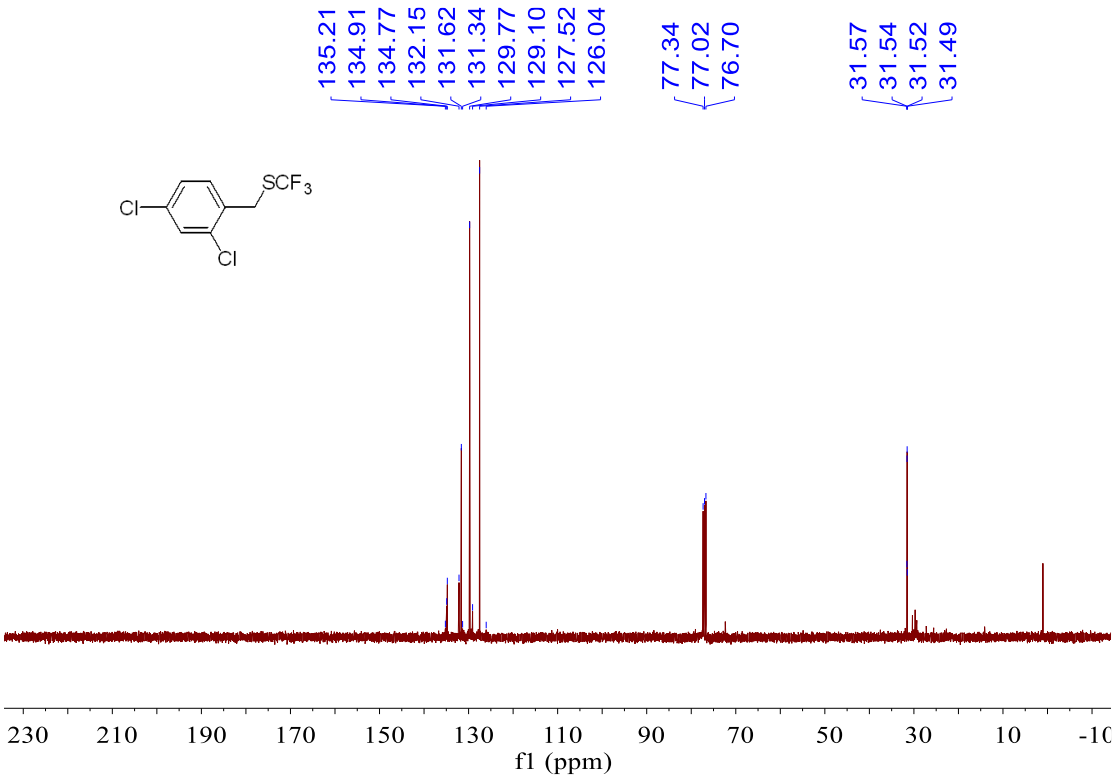
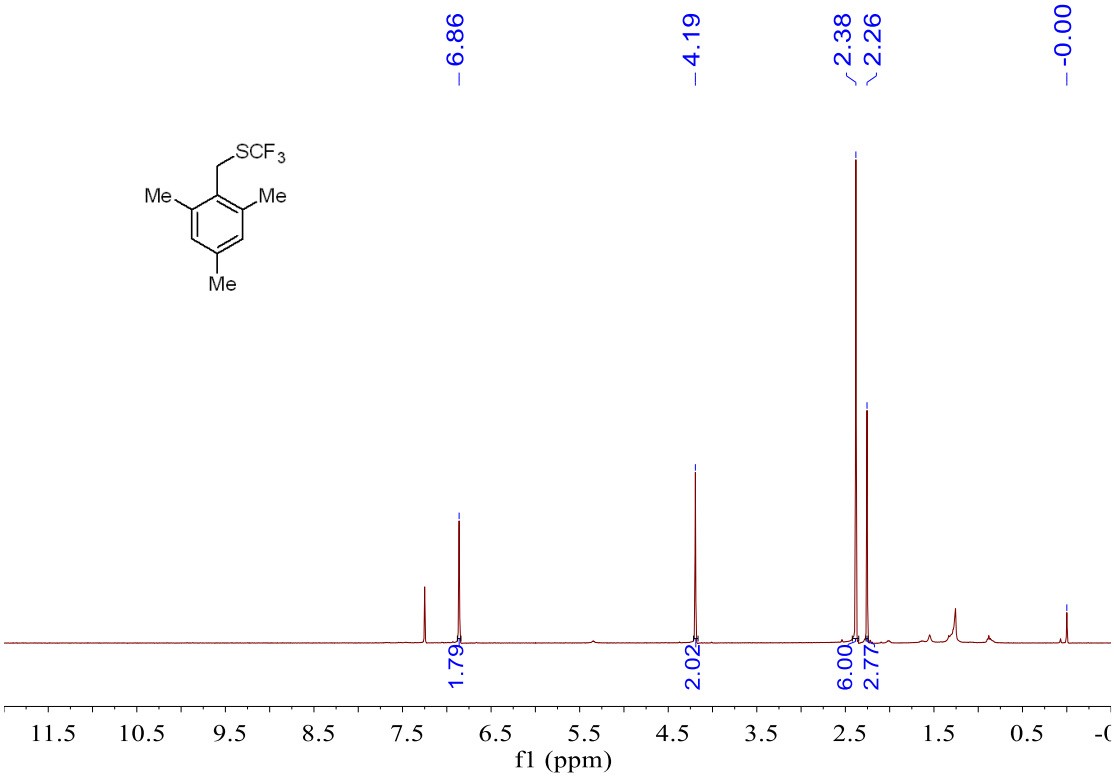
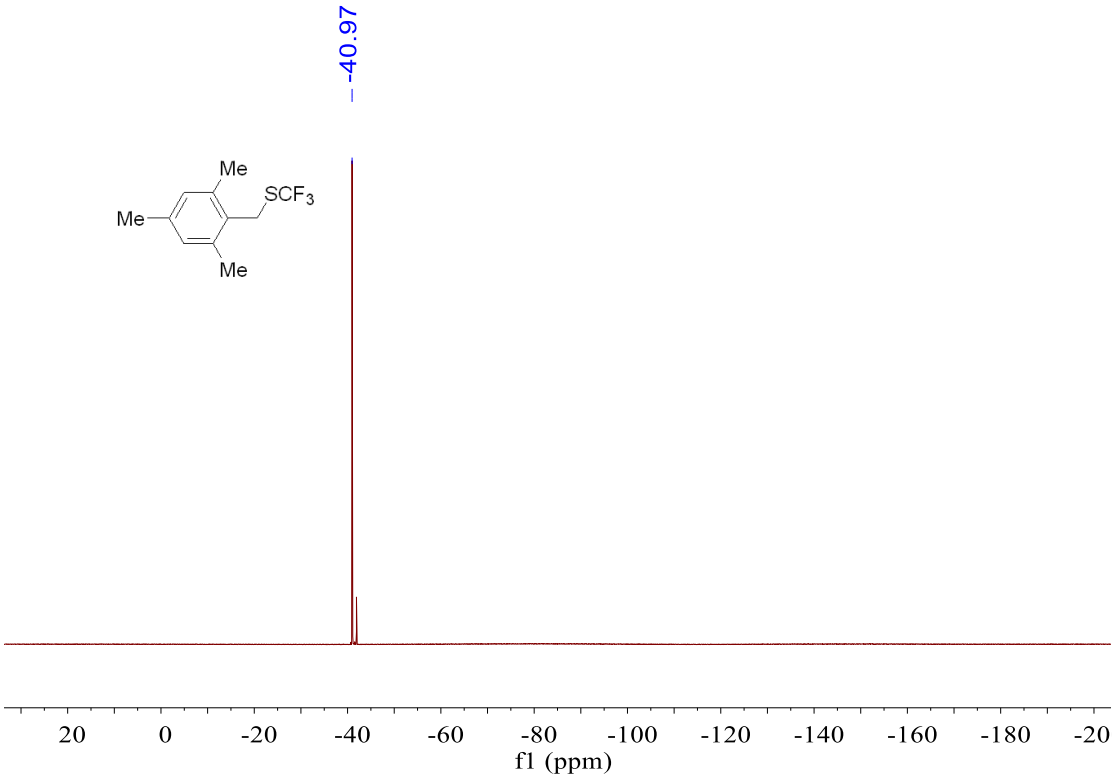
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-20
f1 (ppm)

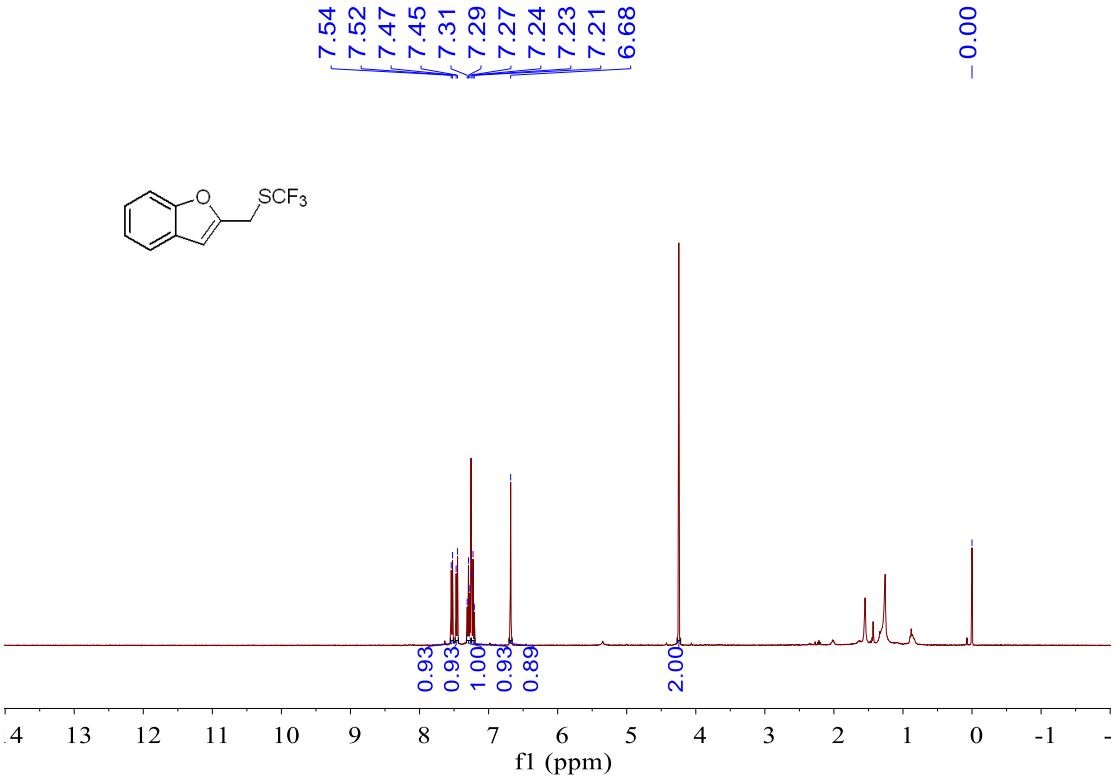

135.21
134.91
134.77
132.15
131.62
131.34
129.77
129.10
127.52
126.04
77.34
77.02
76.70
31.57
31.54
31.52
31.49
SCF3
Cl
Cl
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)

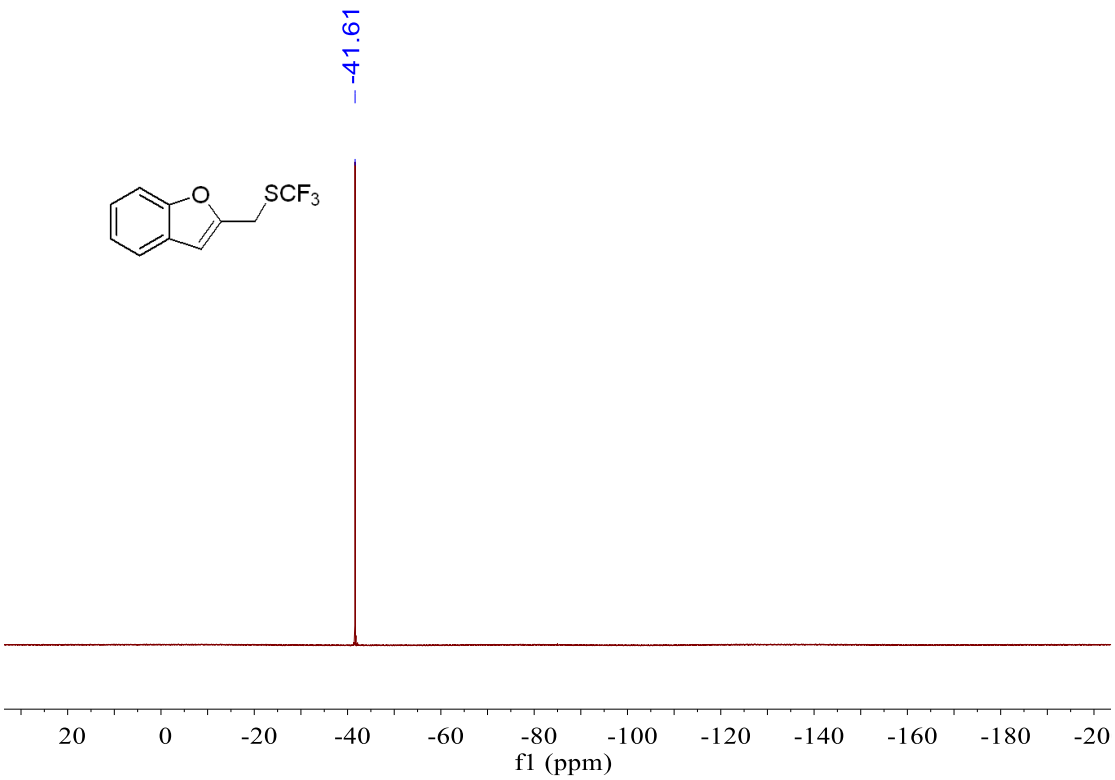
(trifluoromethyl)(2,4,6-trimethylbenzyl)sulfane (**2k**)

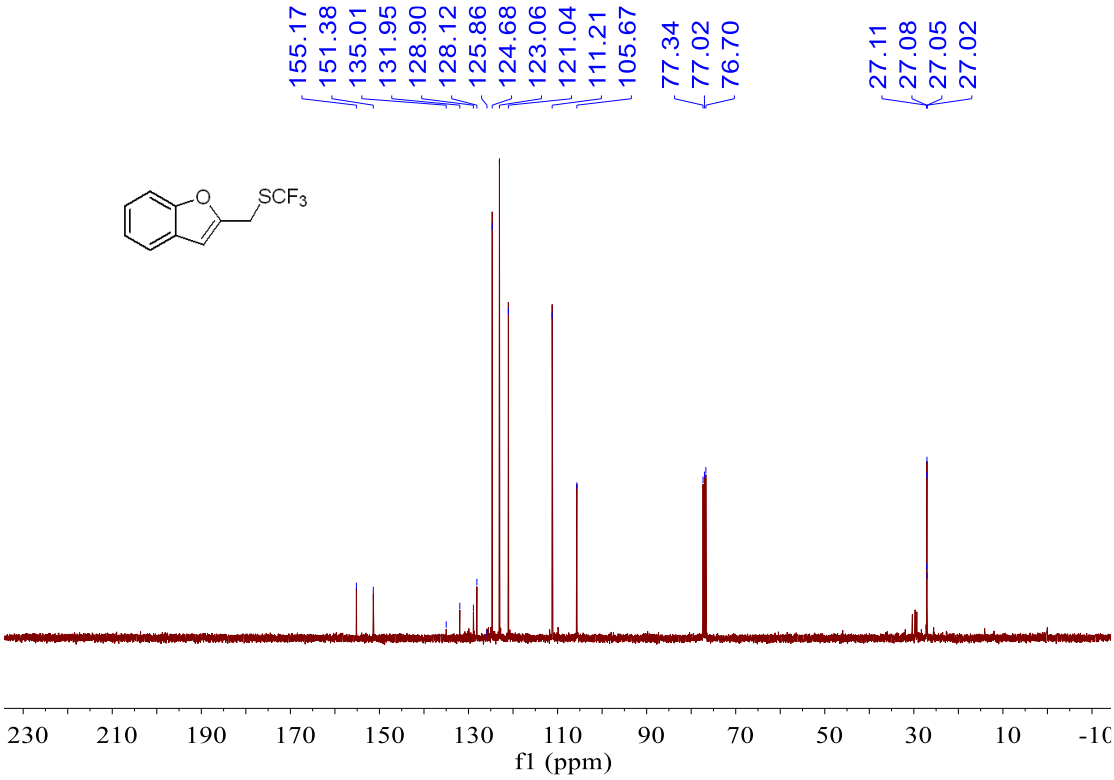




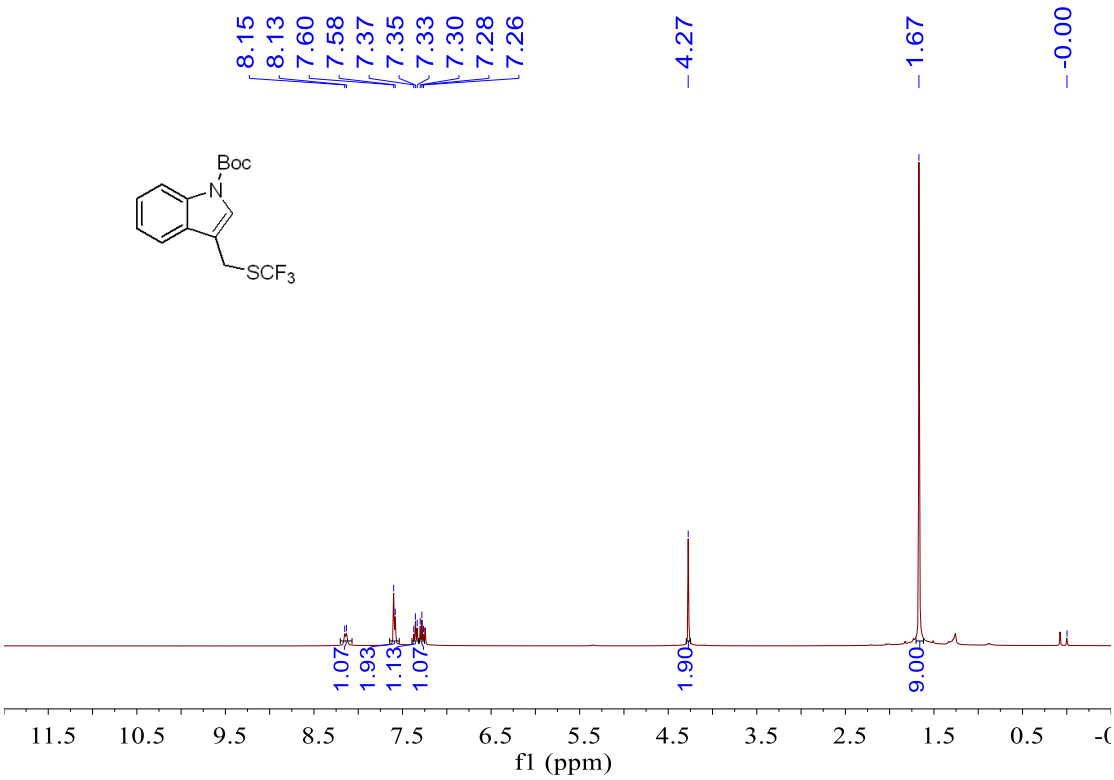
2-(((trifluoromethyl)thio)methyl)benzofuran (**2l**)

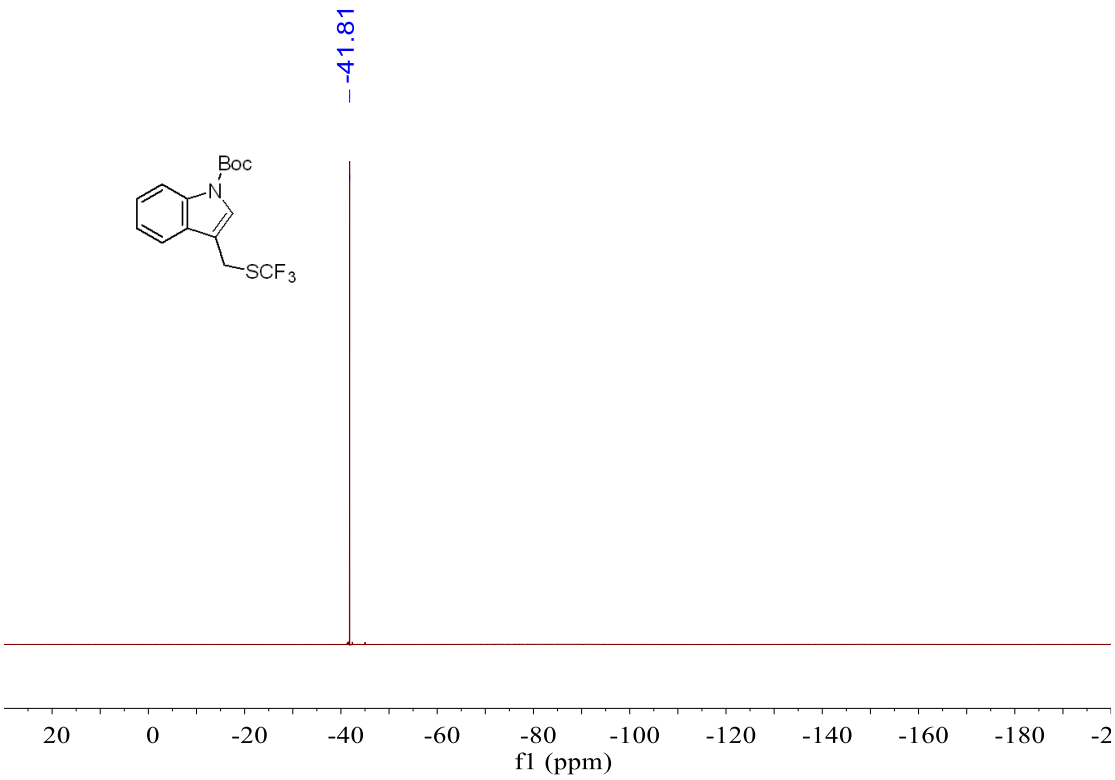


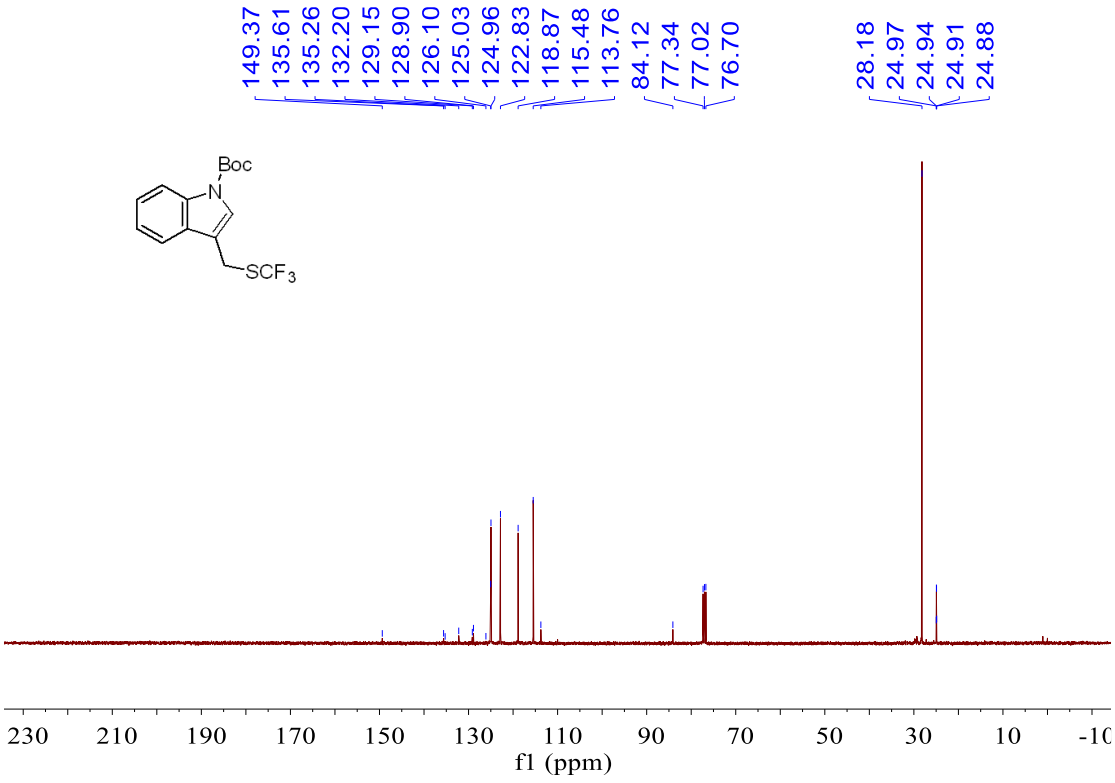




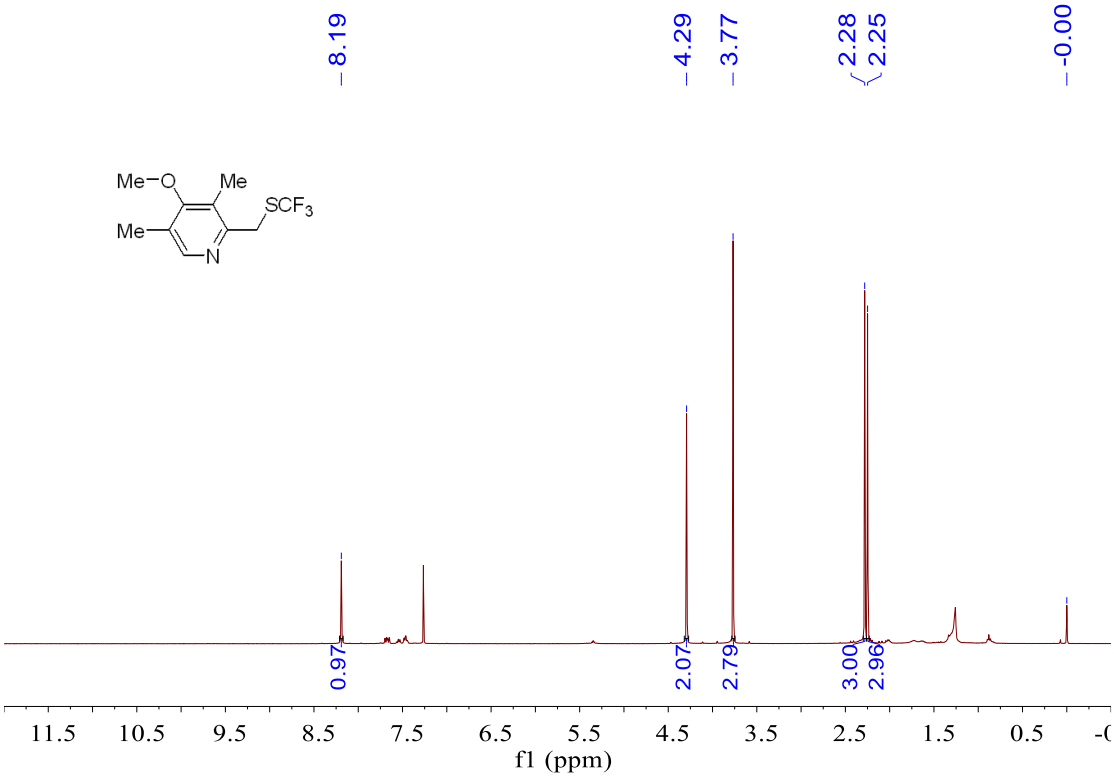
tert-butyl 3-(((trifluoromethyl)thio)methyl)-1H-indole-1-carboxylate (**2m**)

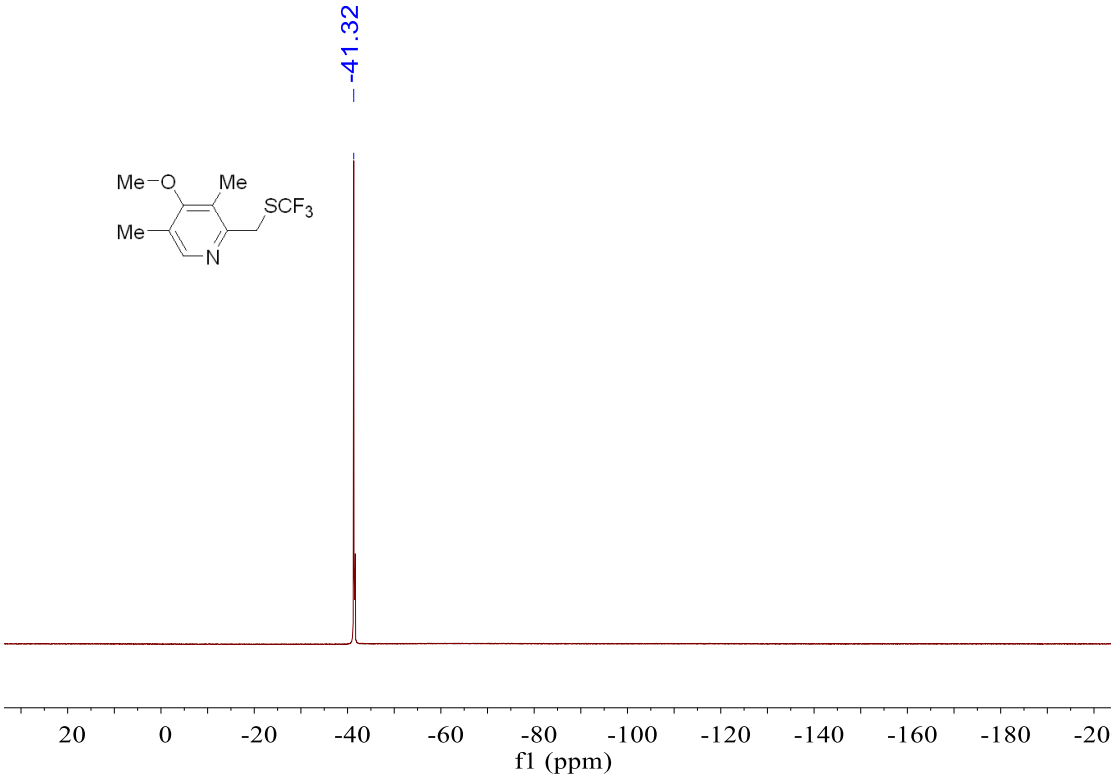



-41.81
Boc
N
SCF3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-2
f1 (ppm)

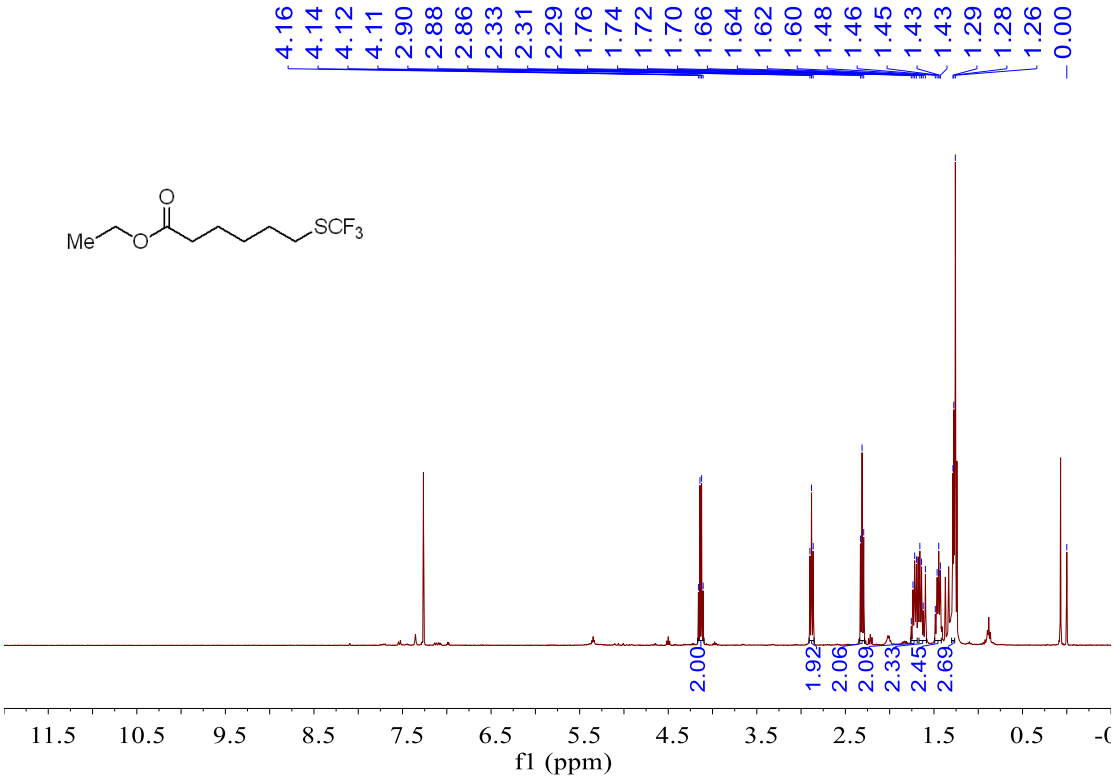

149.37
135.61
135.26
132.20
129.15
128.90
126.10
125.03
124.96
122.83
118.87
115.48
113.76
84.12
77.34
77.02
76.70
28.18
24.97
24.94
24.91
24.88
Boc
N
SCF3
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)

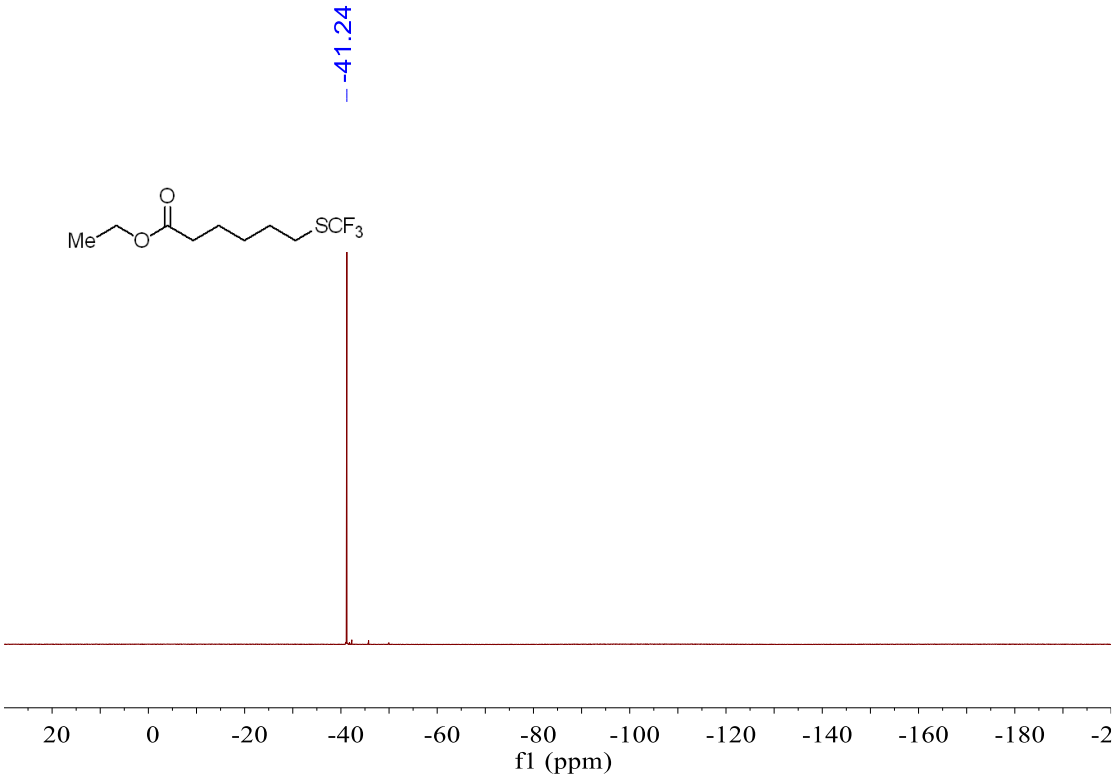
4-methoxy-3,5-dimethyl-2-(((trifluoromethyl)thio)methyl)pyridine (**2n**)



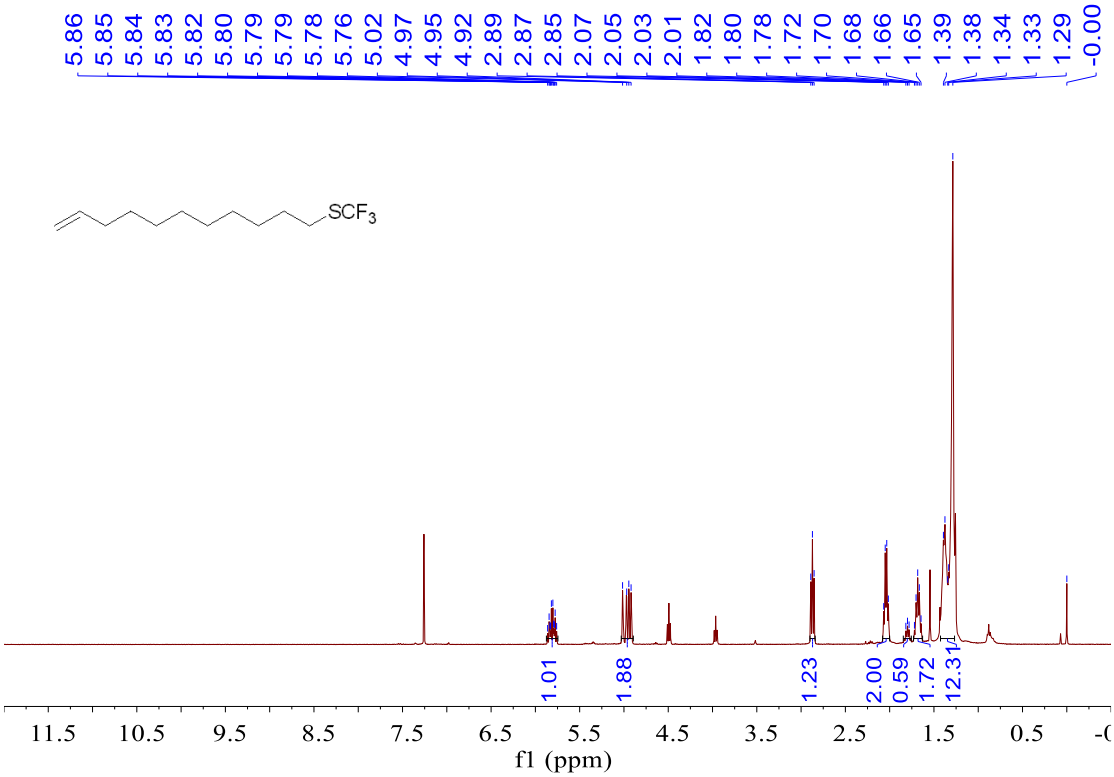


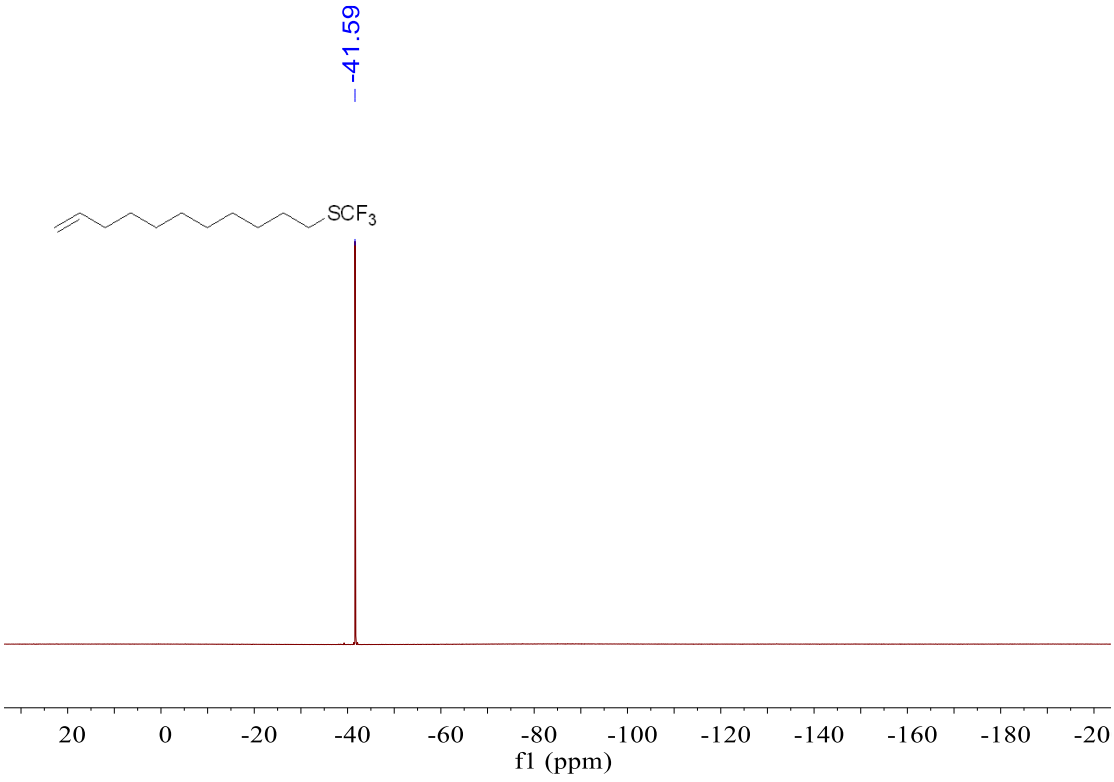
ethyl 6-((trifluoromethyl)thio)hexanoate (**2o**)



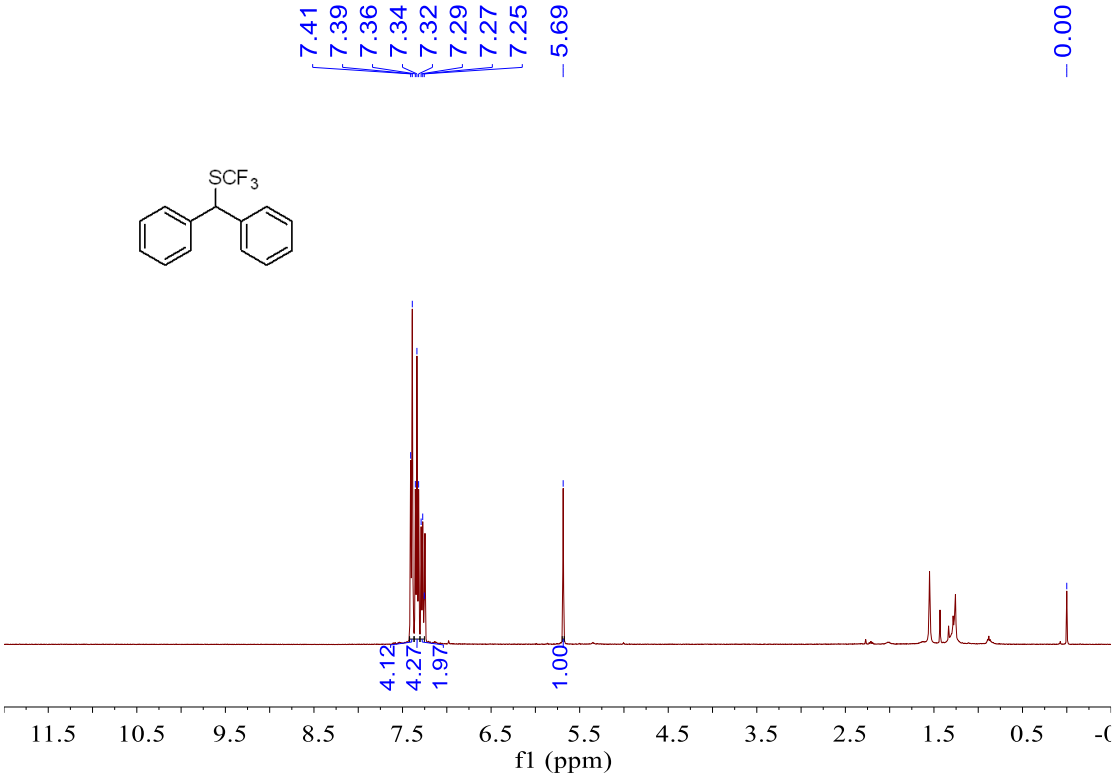


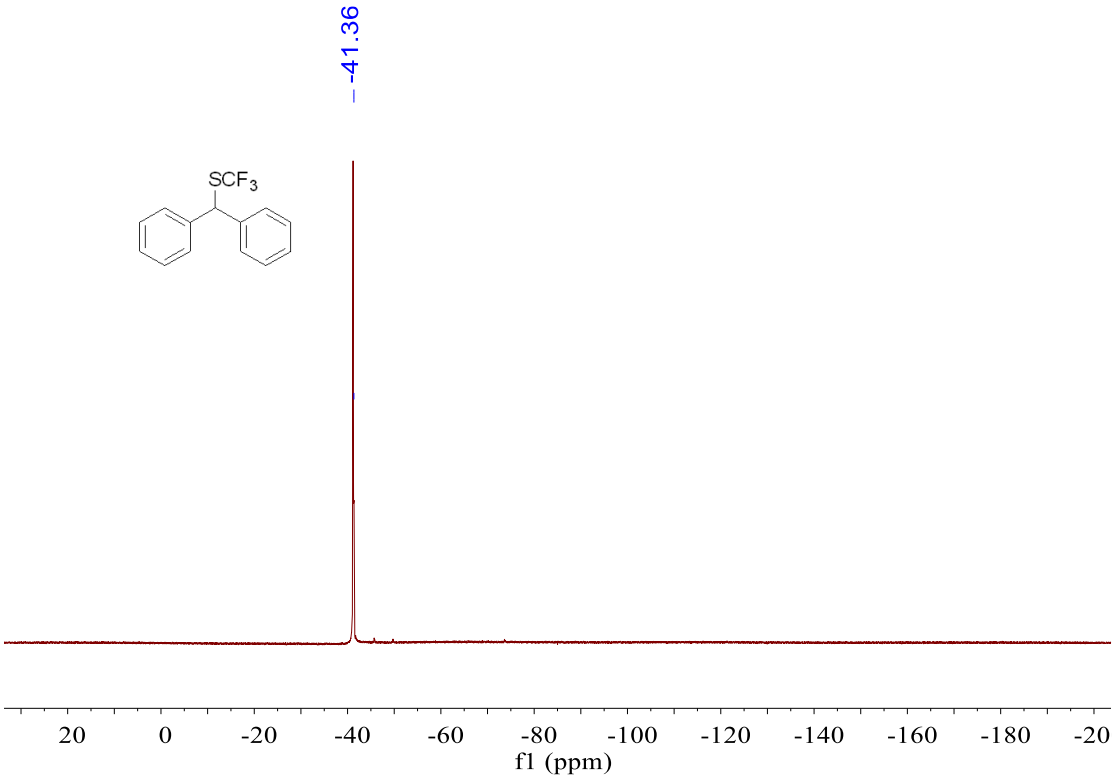
(trifluoromethyl)(undec-10-en-1-yl)sulfane (**2p**)



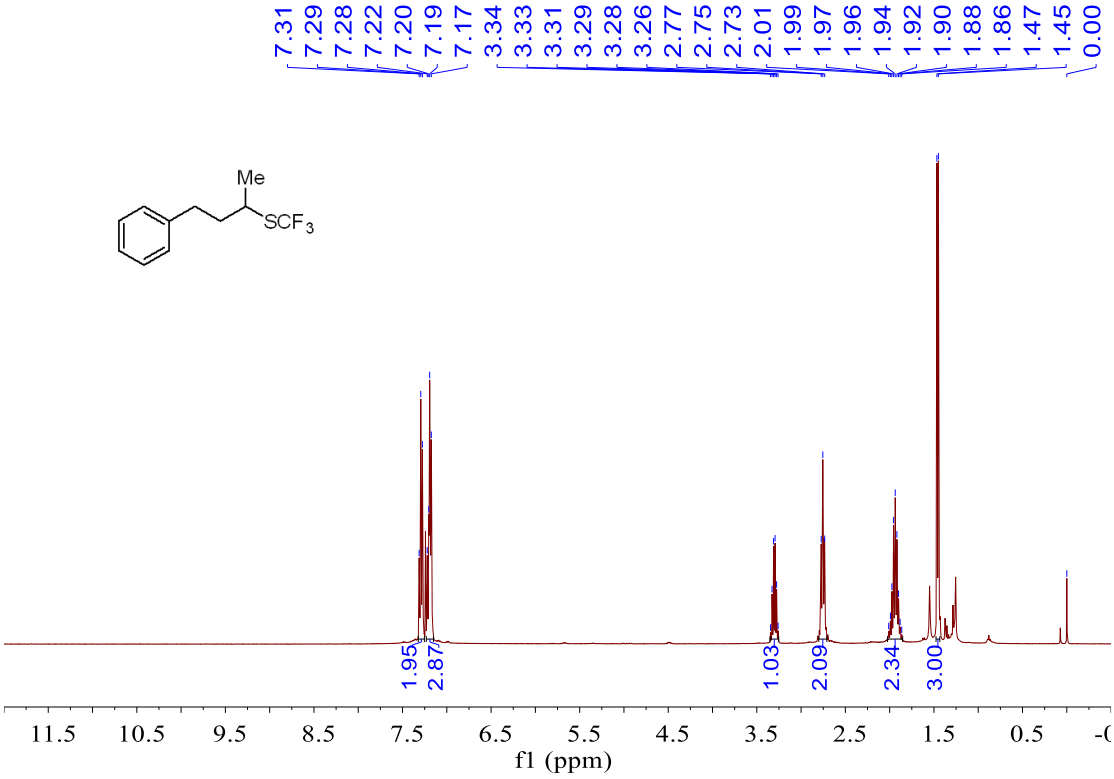


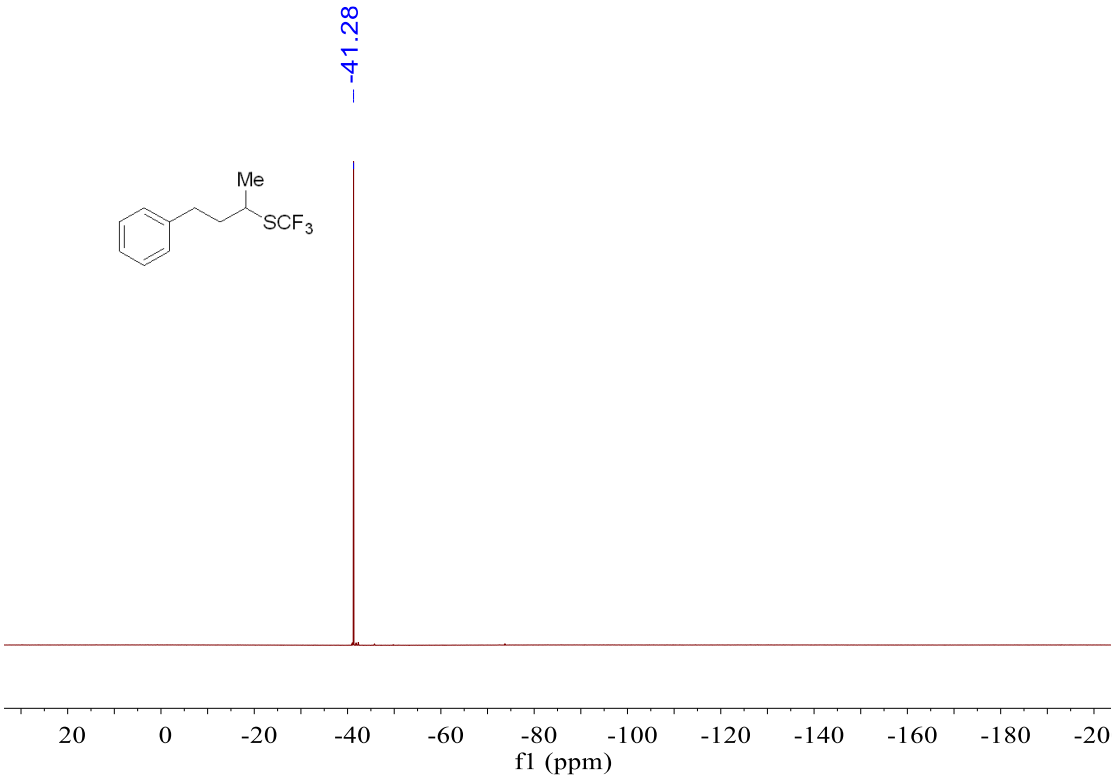
benzhydryl(trifluoromethyl)sulfane (**2q**)



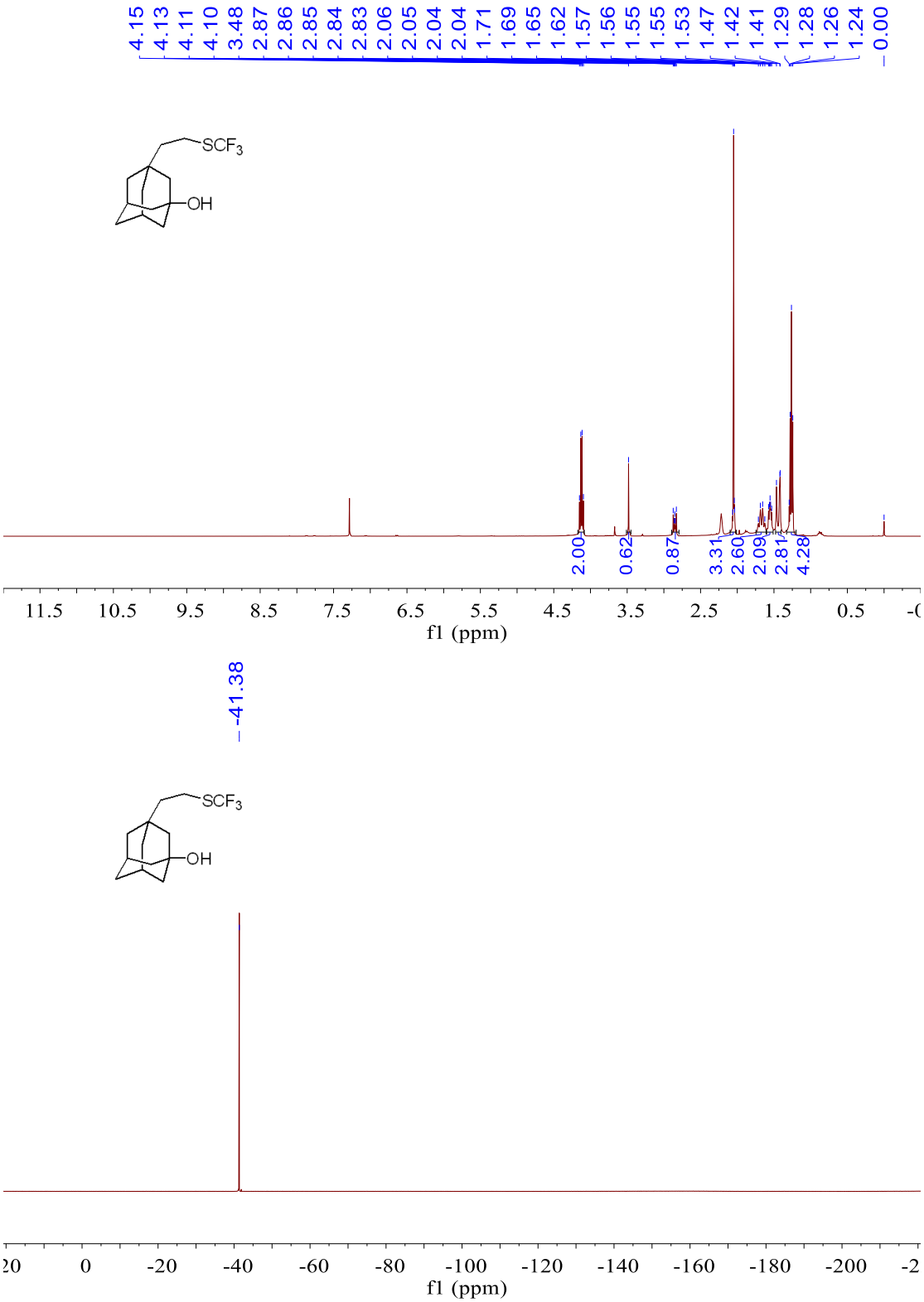


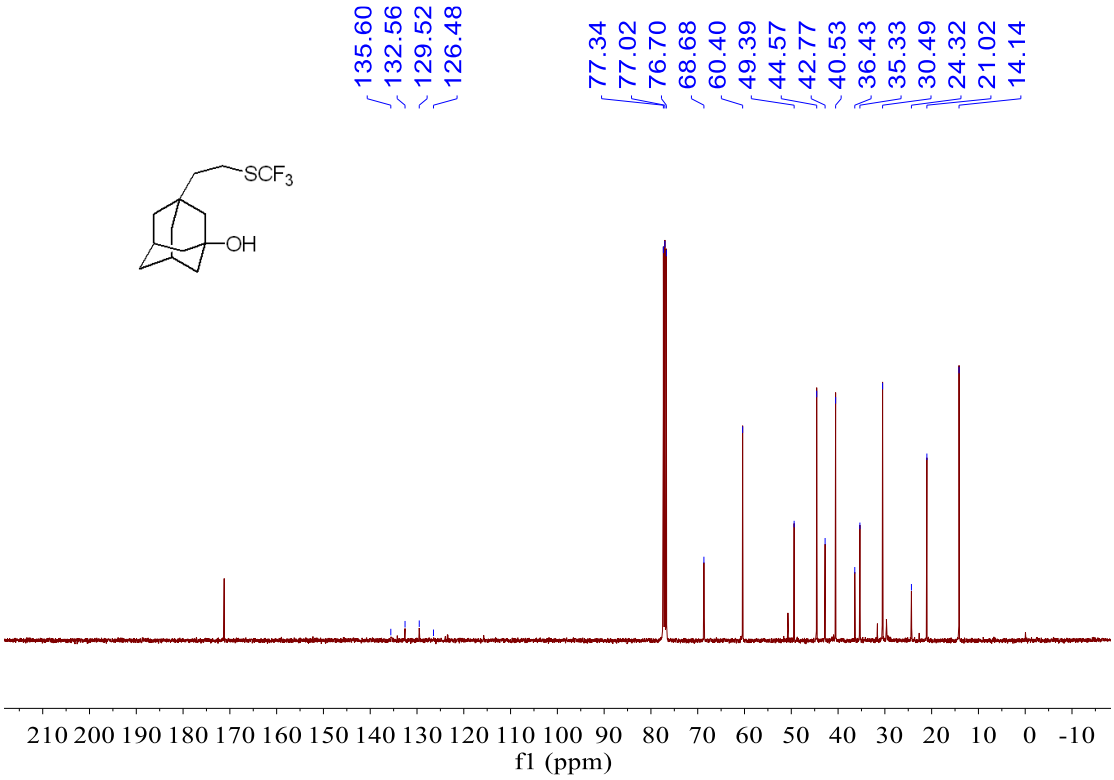
(4-phenylbutan-2-yl)(trifluoromethyl)sulfane (**2r**)



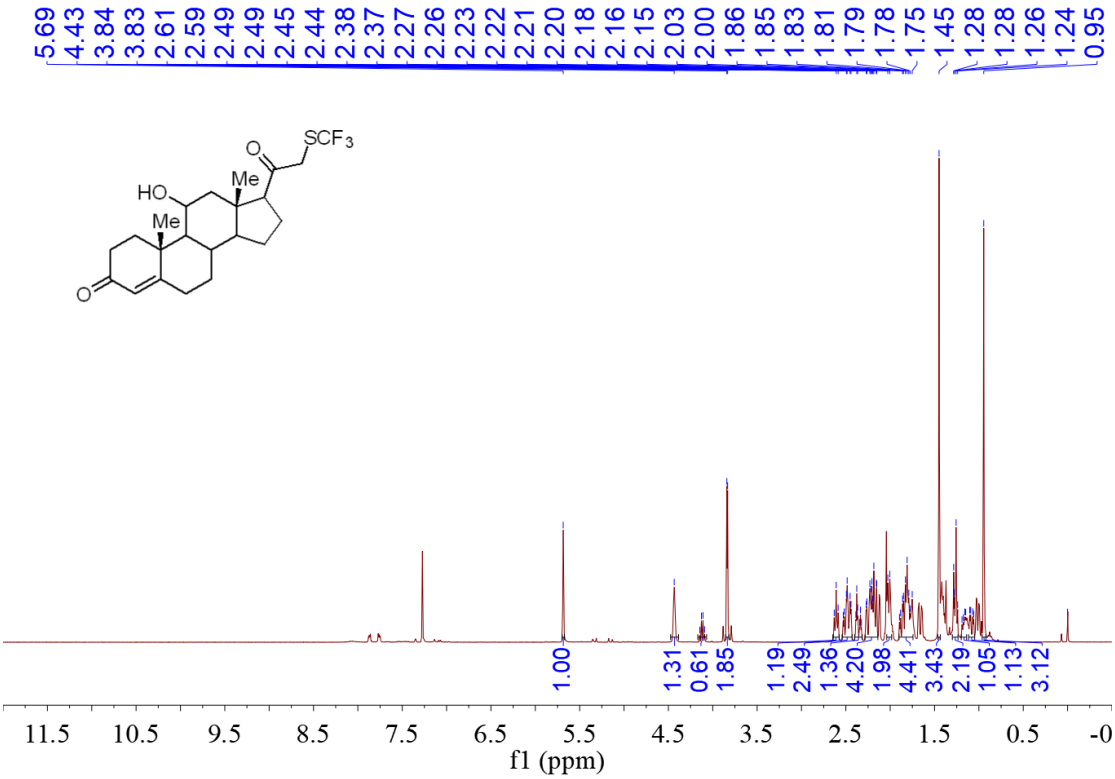


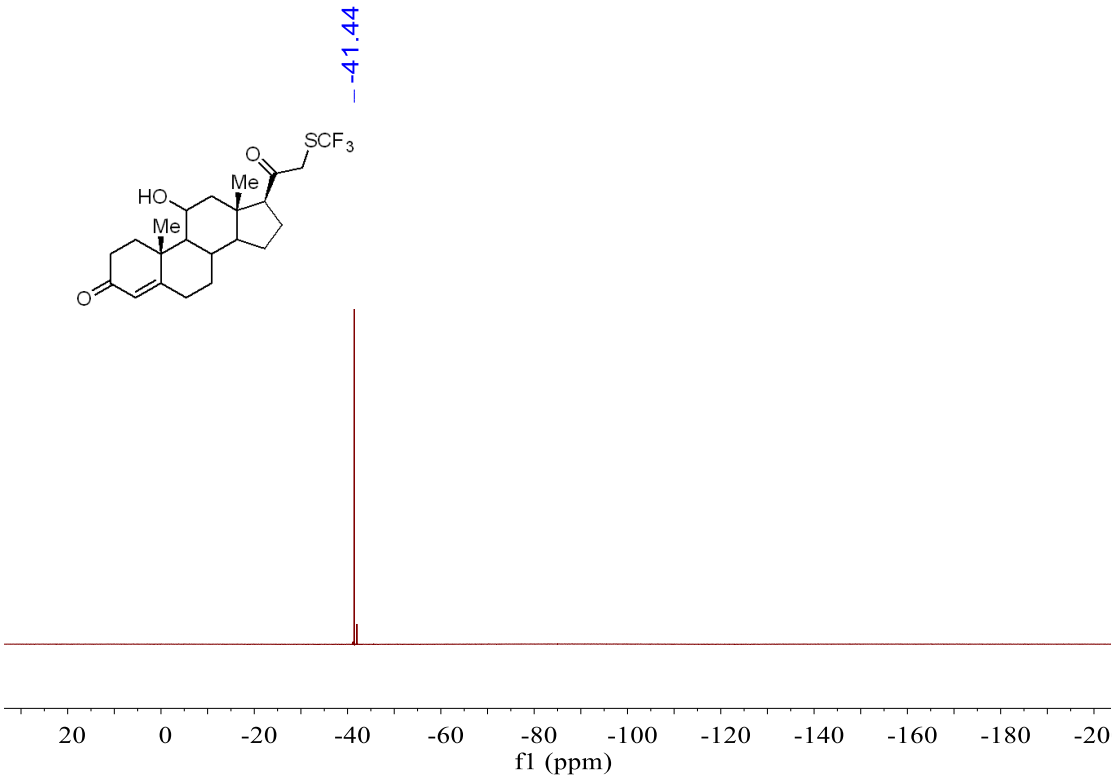
(1s,3r,5R,7S)-3-(2-((trifluoromethyl)thio)ethyl)adamantan-1-ol (**3a**)

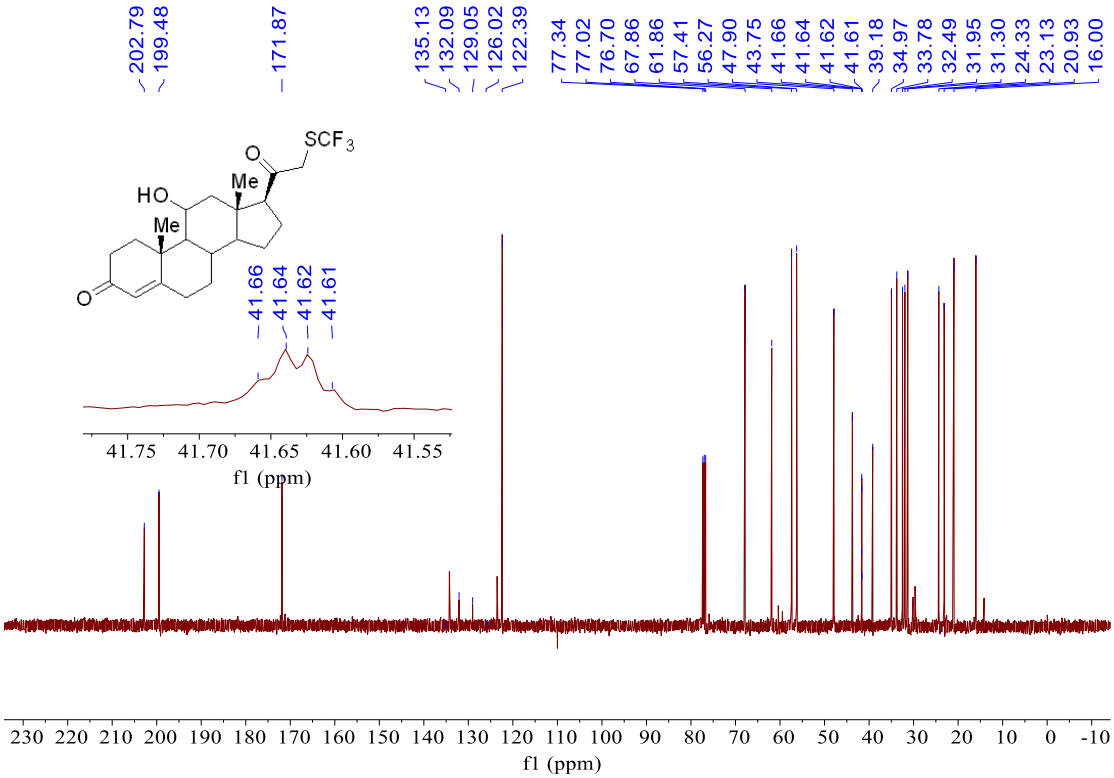




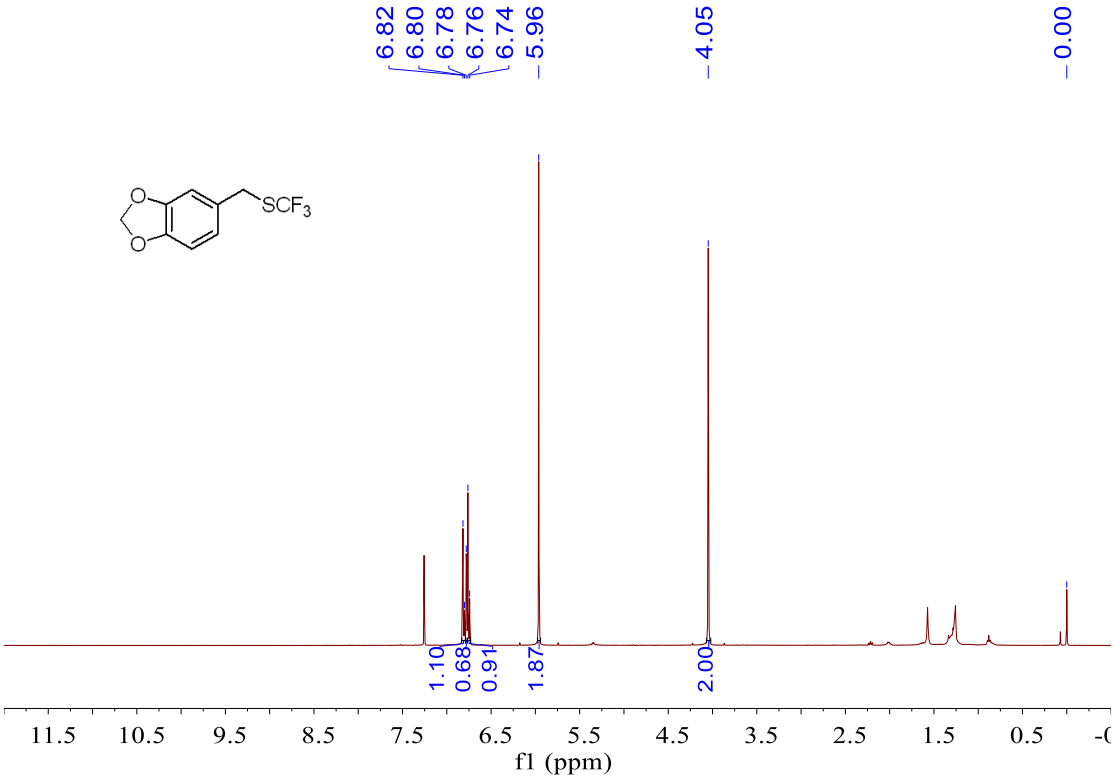
(10R,13S,17S)-11-hydroxy-10,13-dimethyl-17-(2-((trifluoromethyl)thio)acetyl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one. (**3b**)

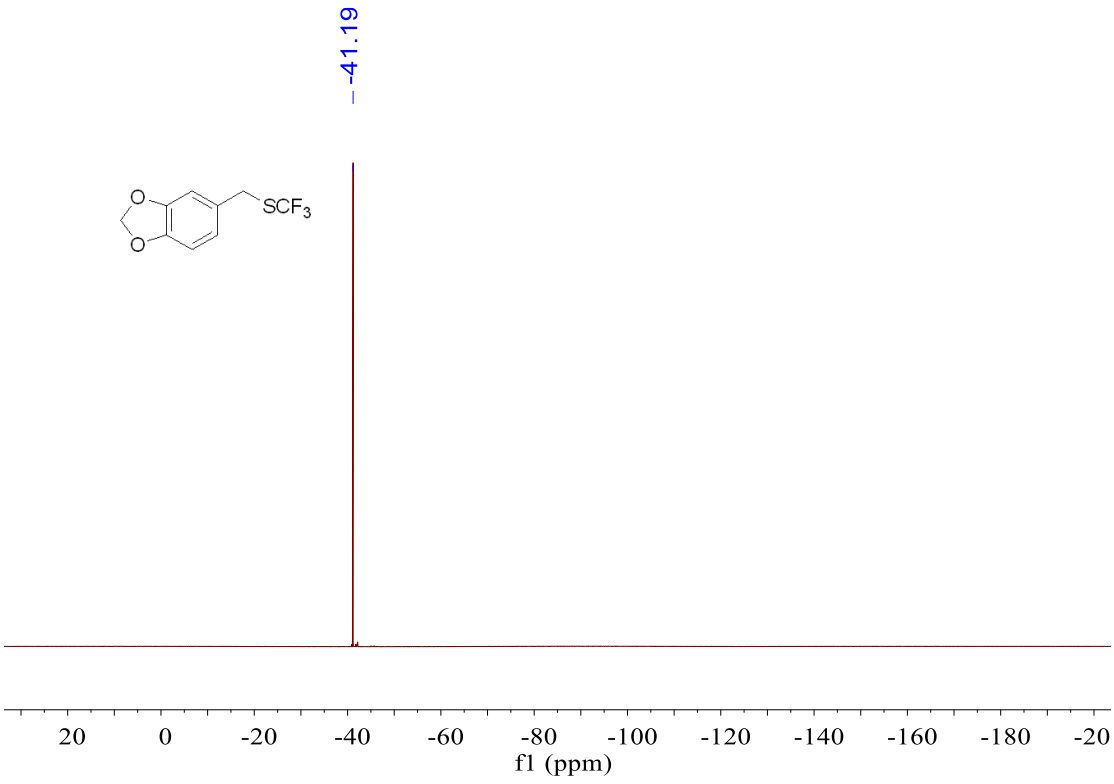



-41.44
SCF3
O
Me
HO
Me
O
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -20
f1 (ppm)

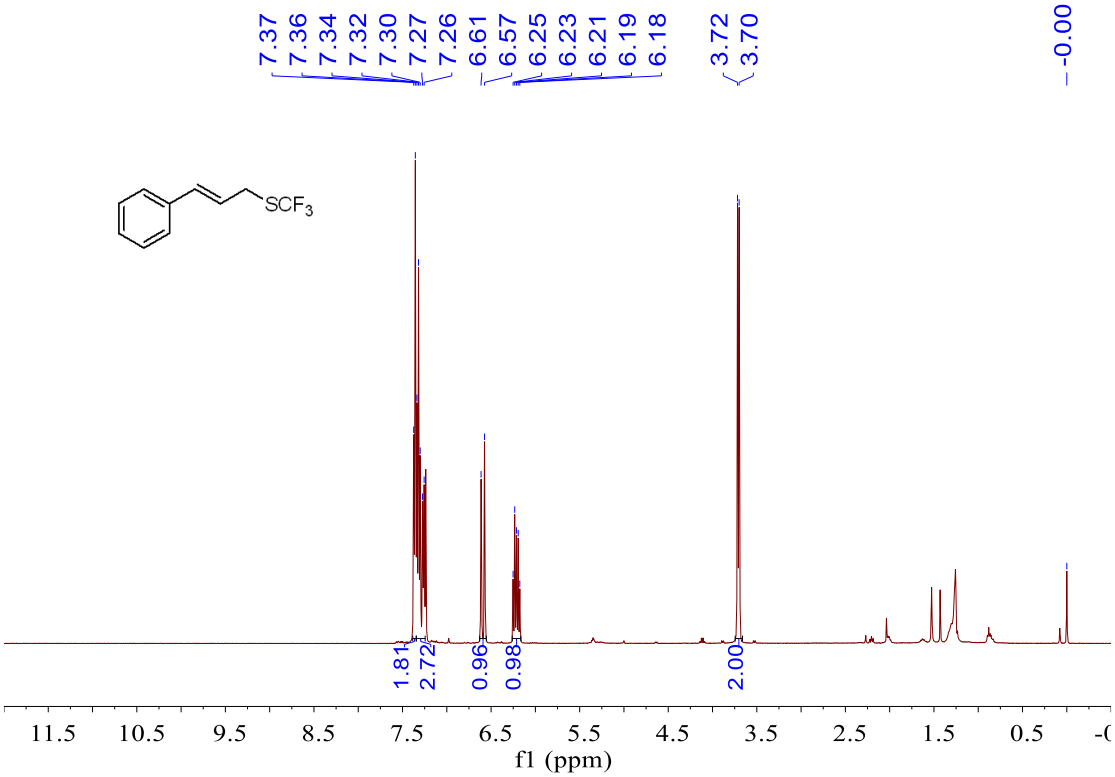

202.79
199.48
171.87
135.13
132.09
129.05
126.02
122.39
77.34
77.02
76.70
67.86
61.86
57.41
56.27
47.90
43.75
41.66
41.64
41.62
41.61
39.18
34.97
33.78
32.49
31.95
31.30
24.33
23.13
20.93
16.00
SCF3
O
Me
HO
Me
O
41.66
41.64
41.62
41.61
41.75 41.70 41.65 41.60 41.55
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

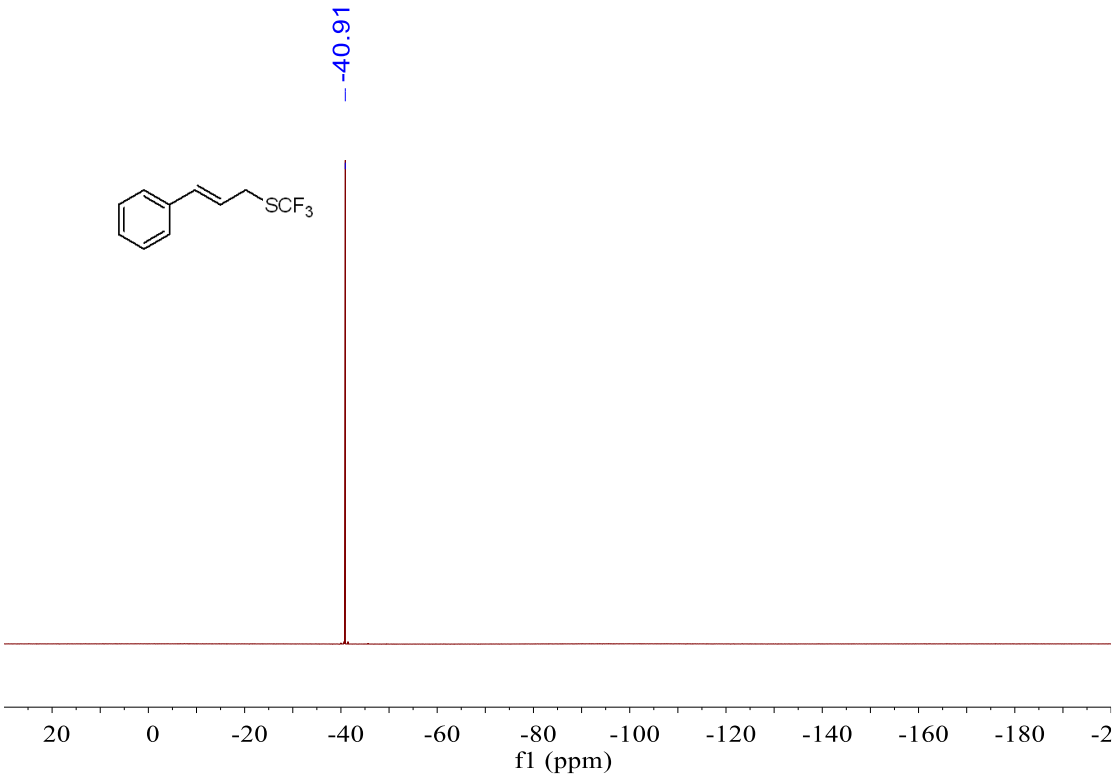
5-(((trifluoromethyl)thio)methyl)benzo[d][1,3]dioxole (**4a**)

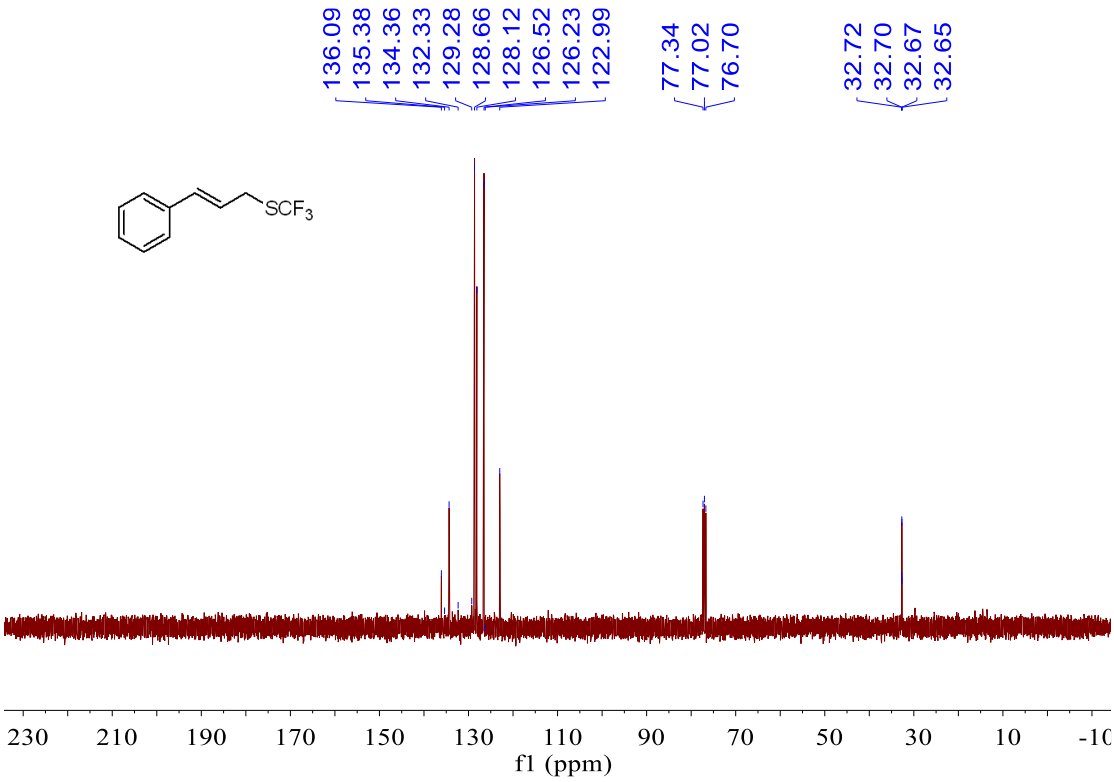




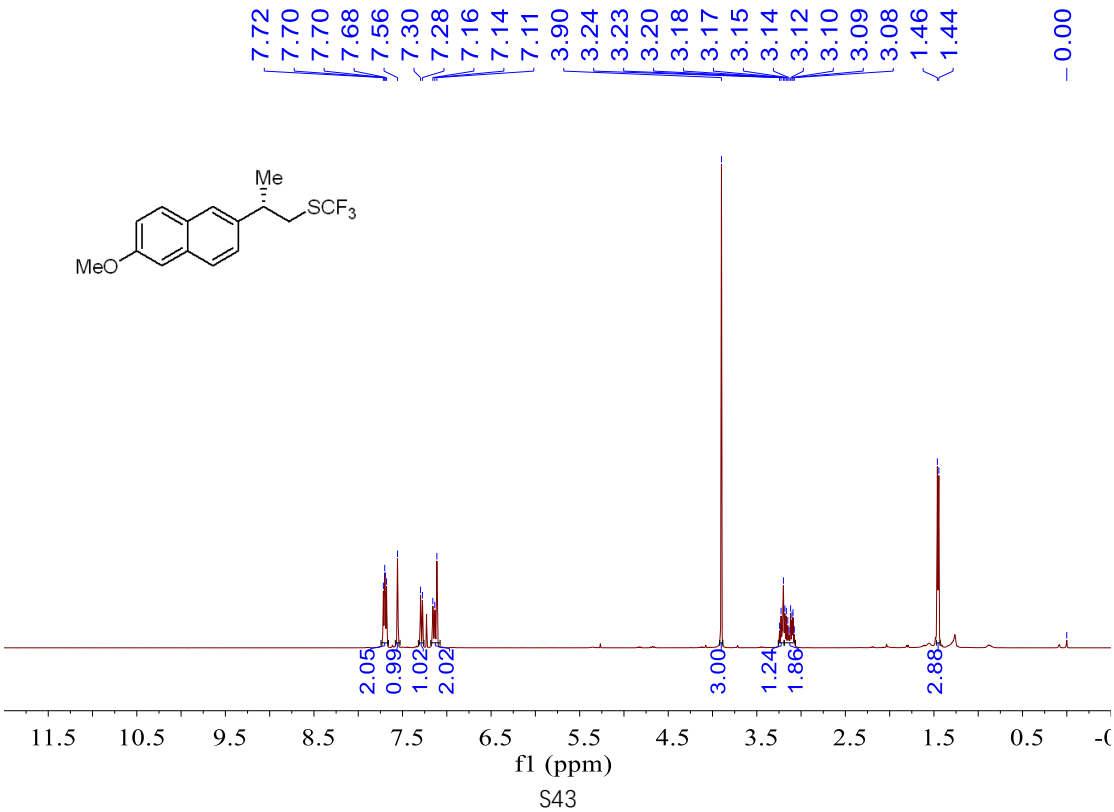
cinnamyl(trifluoromethyl)sulfane (**4b**)

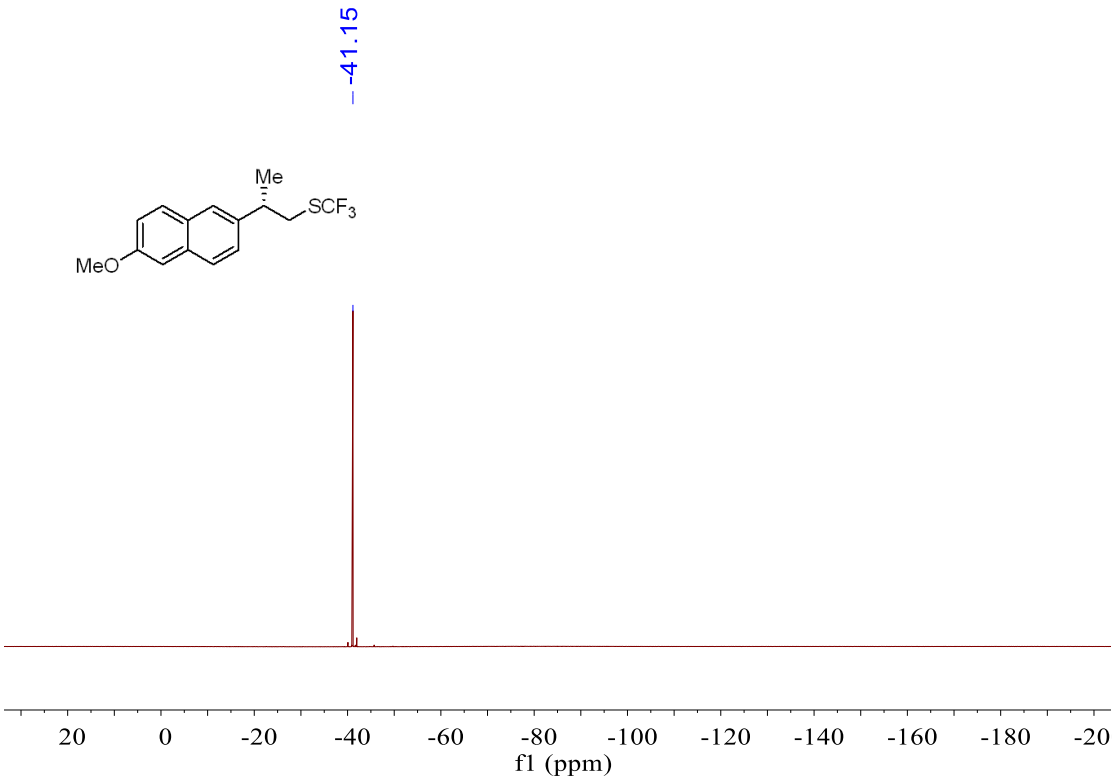


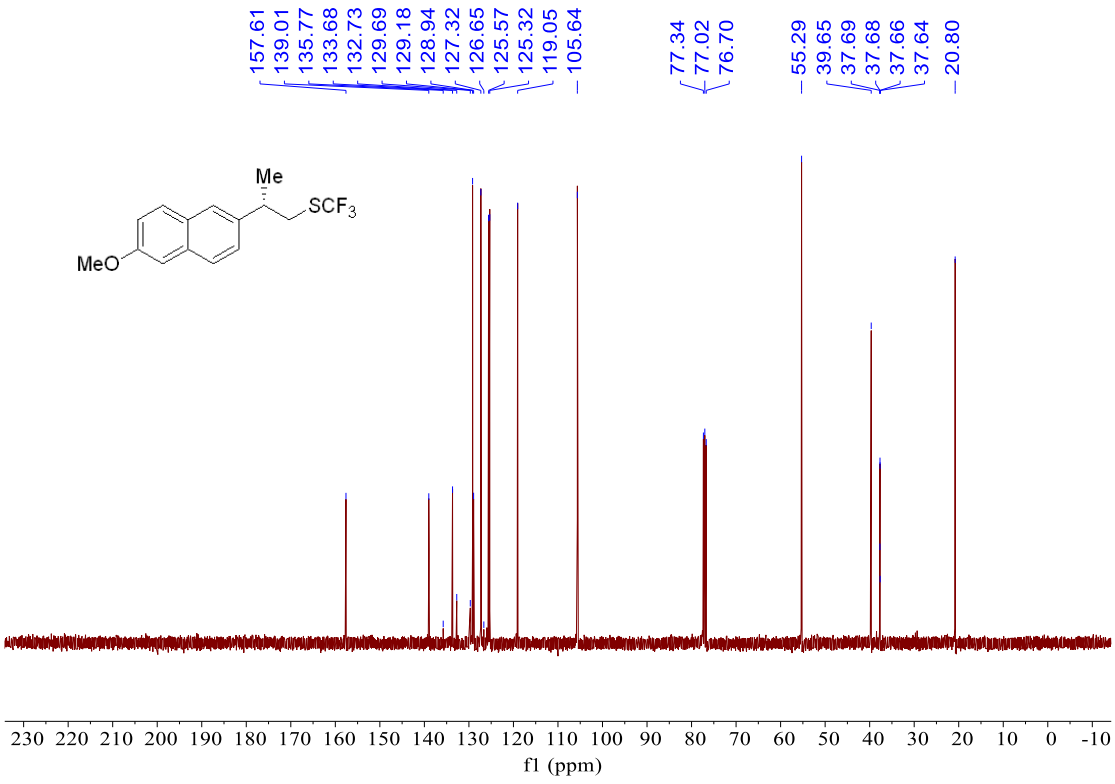




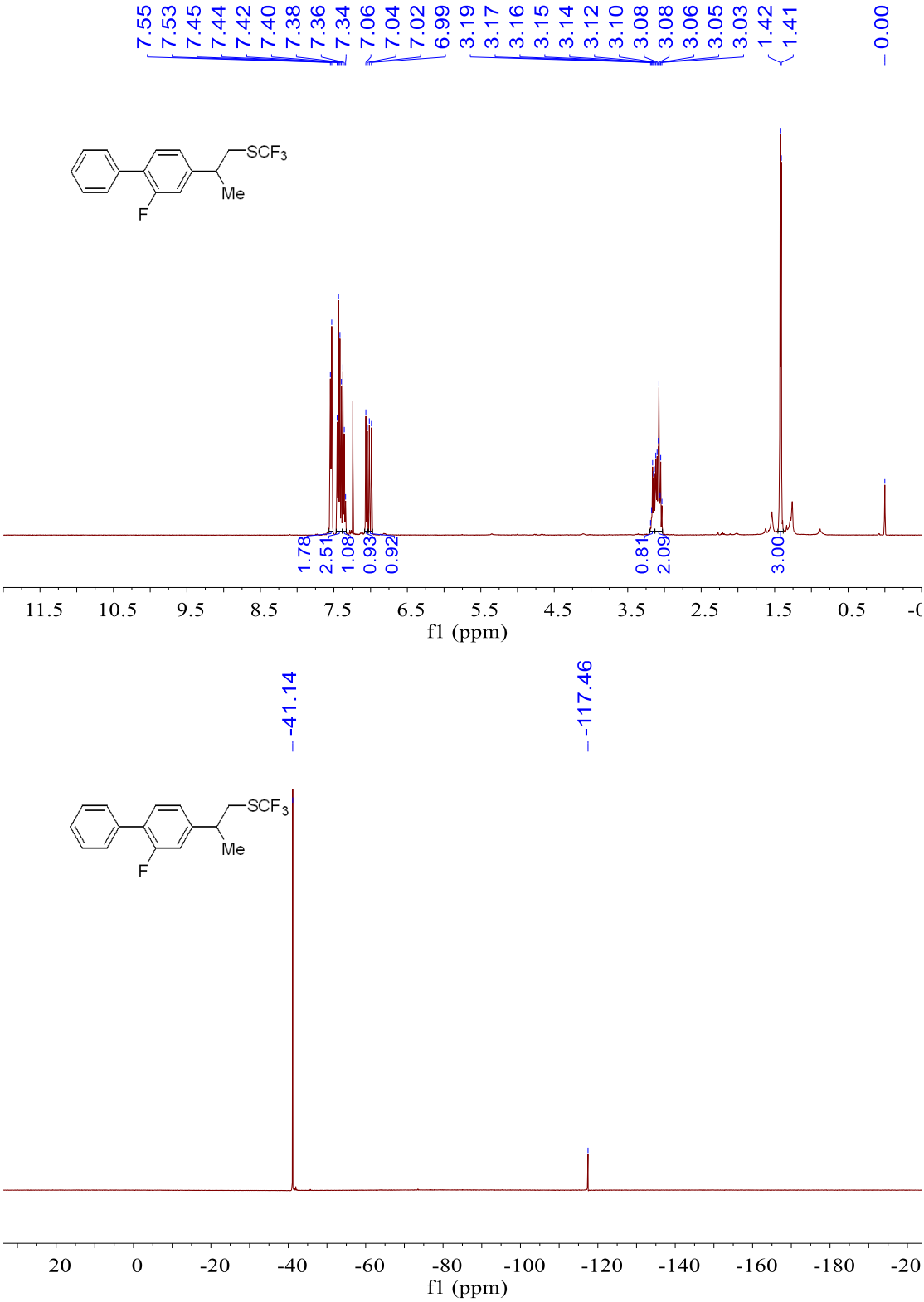
(S)-(2-(6-methoxynaphthalen-2-yl)propyl)(trifluoromethyl)sulfane (**4c**)

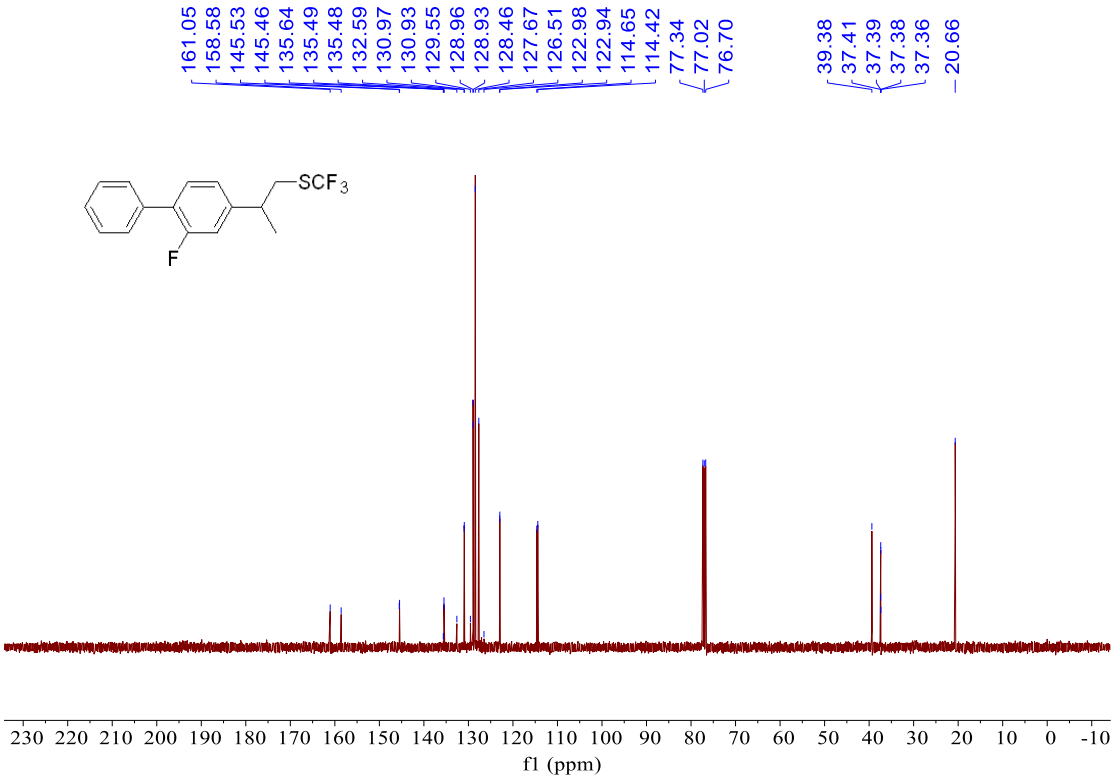



-41.15
Me
SCF3
MeO
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-20
f1 (ppm)

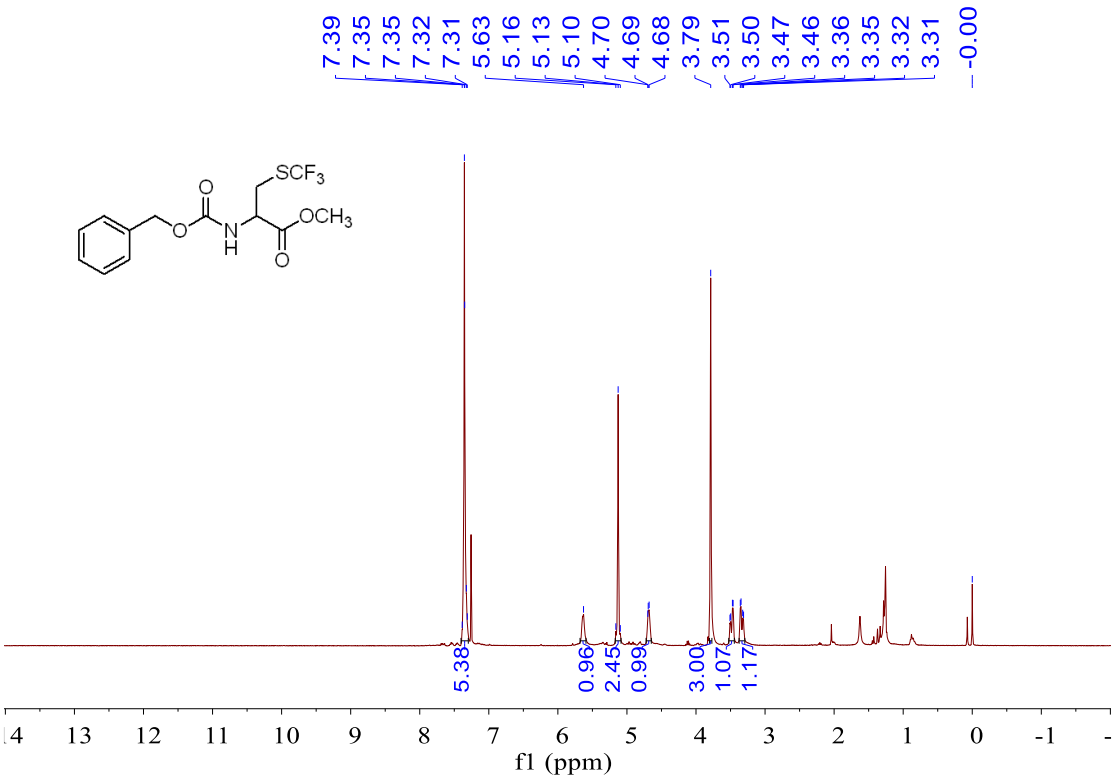

157.61
139.01
135.77
133.68
132.73
129.69
129.18
128.94
127.32
126.65
125.57
125.32
119.05
105.64
77.34
77.02
76.70
55.29
39.65
37.69
37.68
37.66
37.64
20.80
Me
SCF3
MeO
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

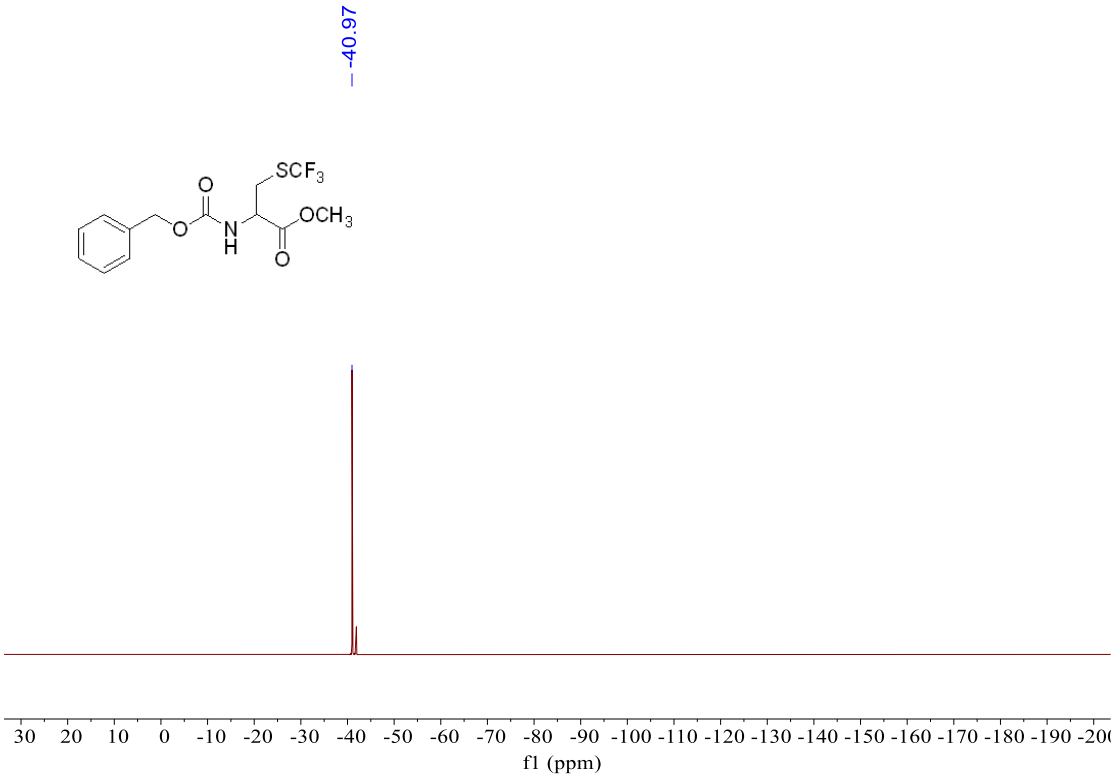
(2-(2-fluoro-[1,1'-biphenyl]-4-yl)propyl)(trifluoromethyl)sulfane (**4d**)

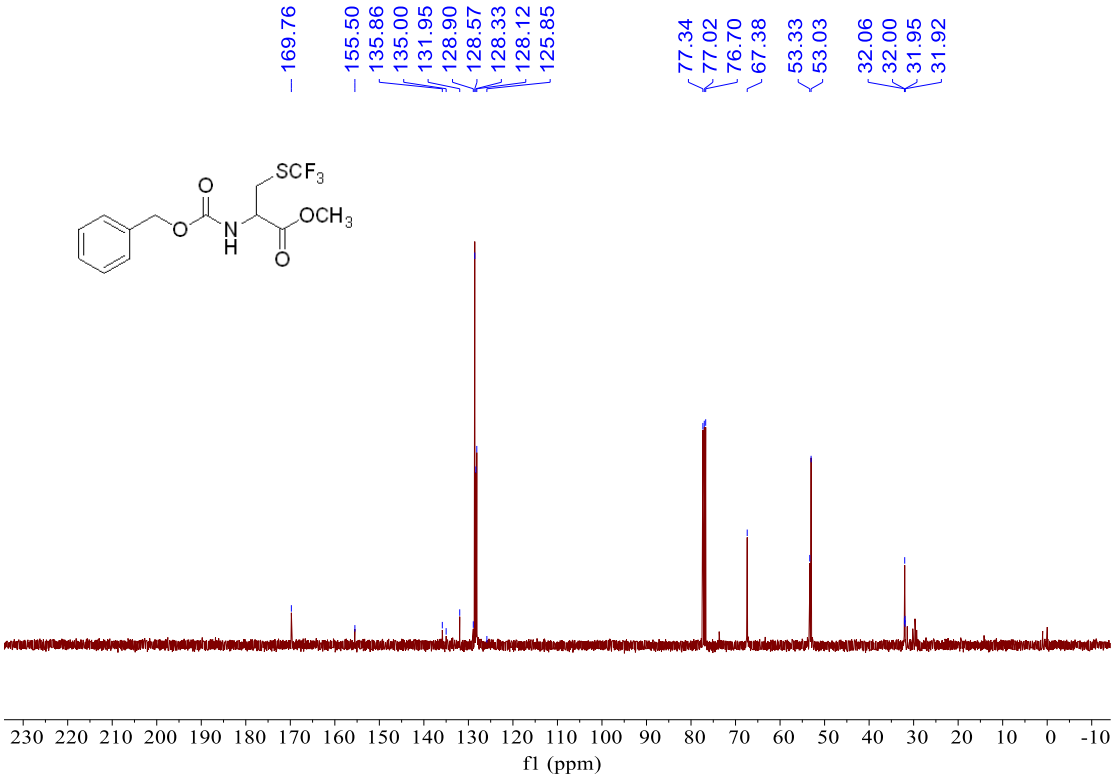




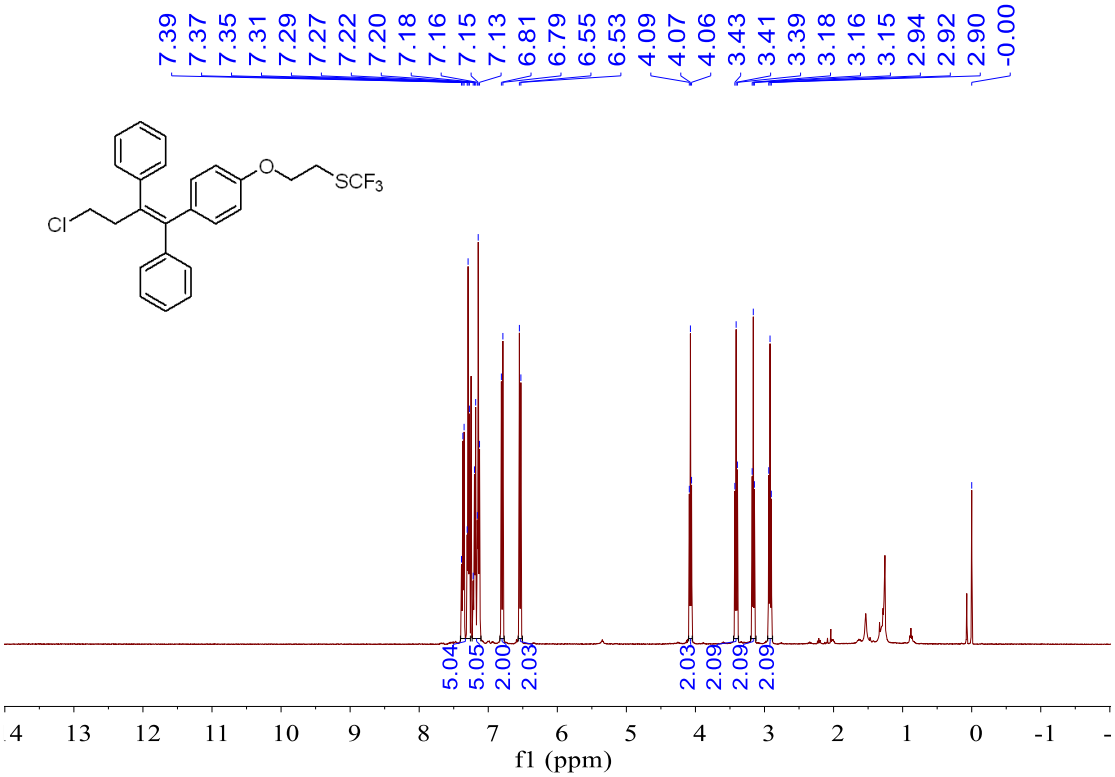
methyl N-((benzyloxy)carbonyl)-S-(trifluoromethyl)cysteinate (**4e**)

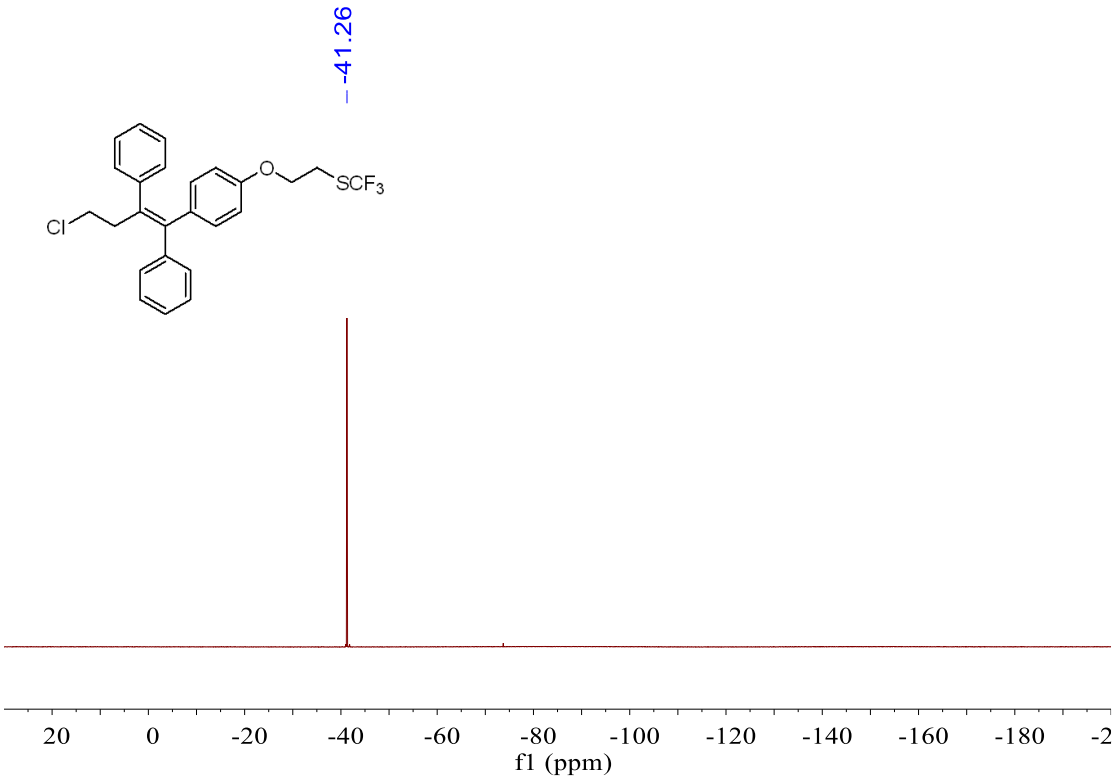


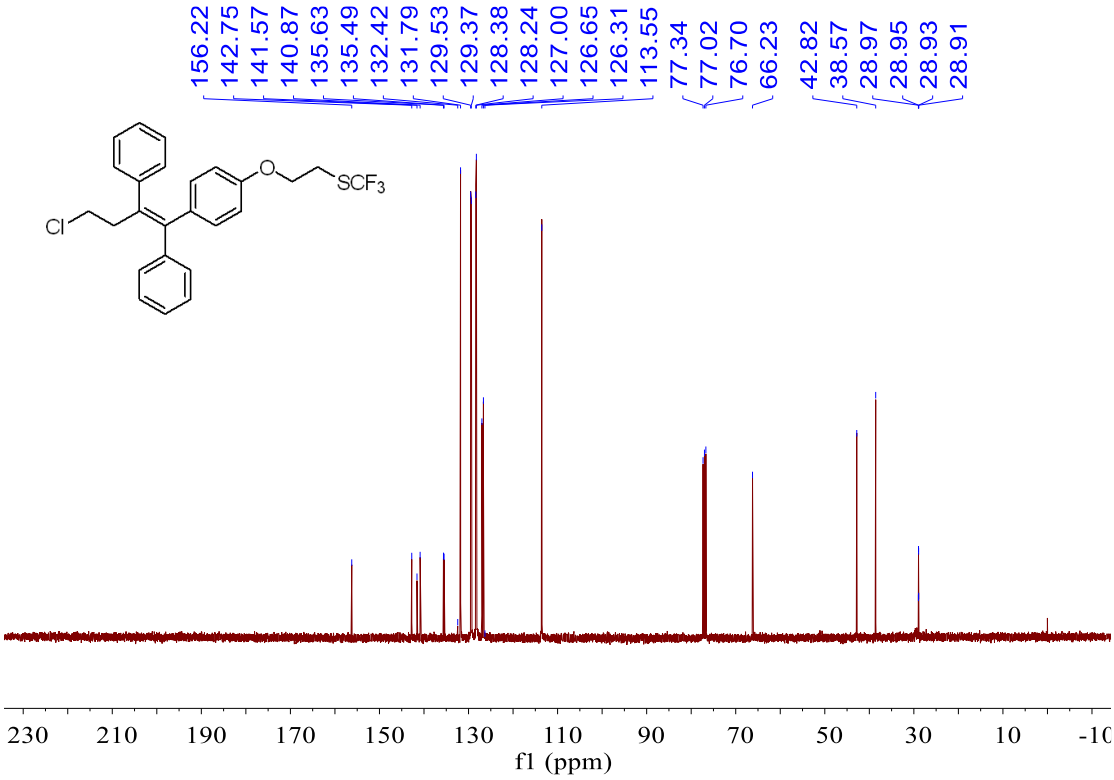

-40.97
SCF3
OCH3
O
N
H
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


169.76
155.50
135.86
135.00
131.95
128.90
128.57
128.33
128.12
125.85
77.34
77.02
76.70
67.38
53.33
53.03
32.06
32.00
31.95
31.92
SCF3
OCH3
O
N
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

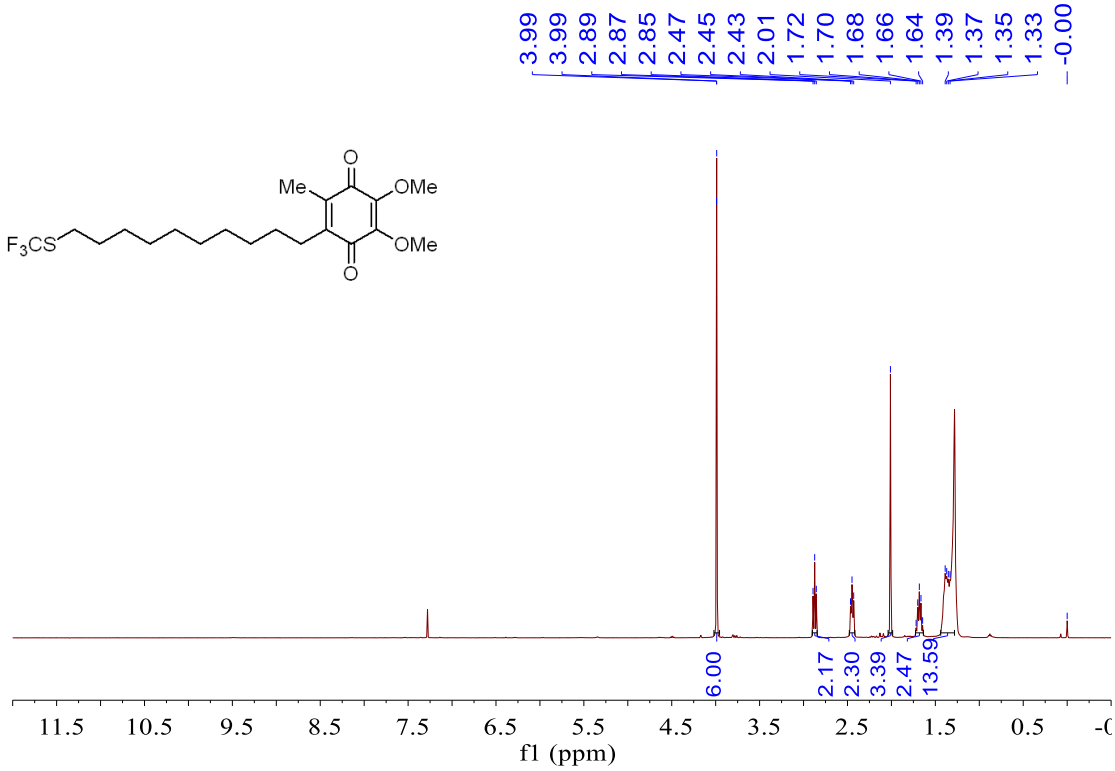
(Z)-(2-(4-(4-chloro-1,2-diphenylbut-1-en-1-yl)phenoxy)ethyl)(trifluoromethyl)sulfane (**4f**)

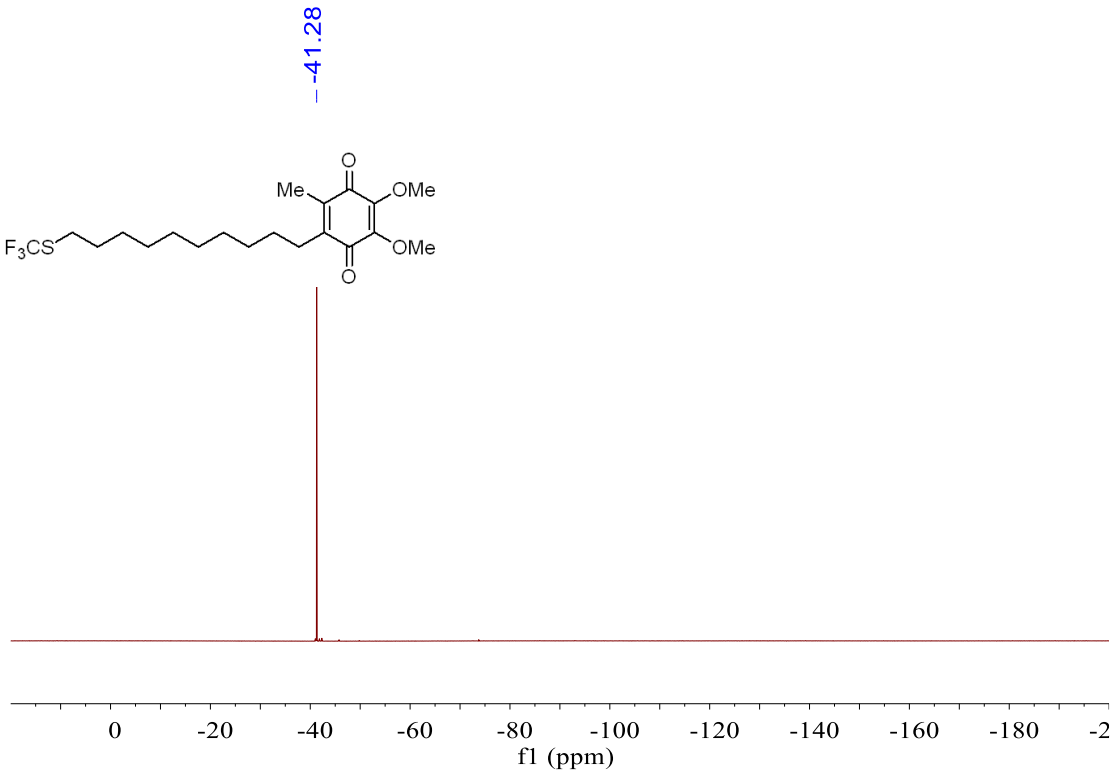




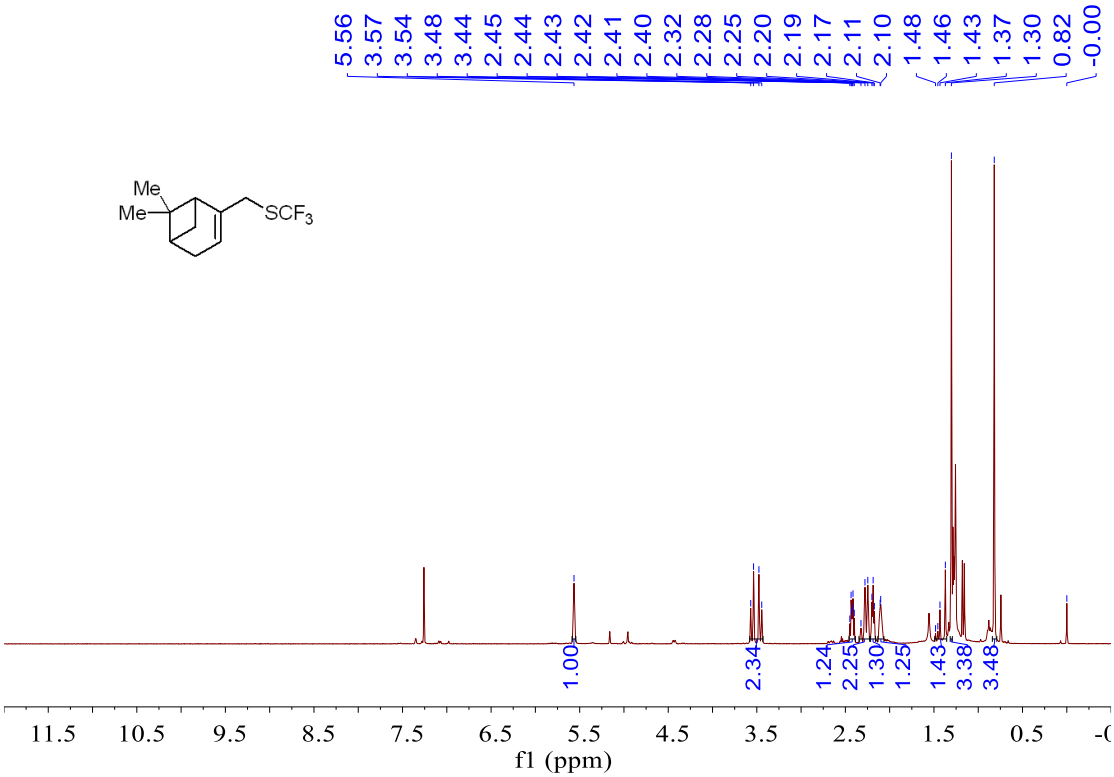


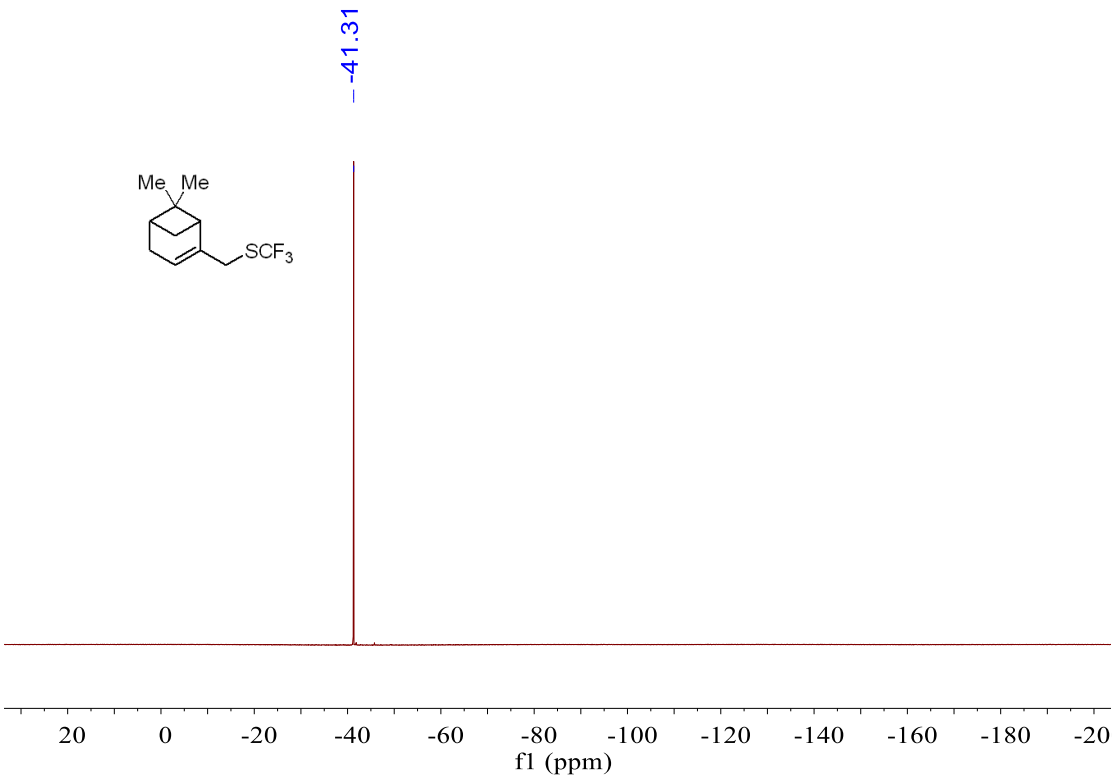
2,3-dimethoxy-5-methyl-6-(10-((trifluoromethyl)thio)decyl)cyclohexa-2,5-diene-1,4-dione (**4g**)

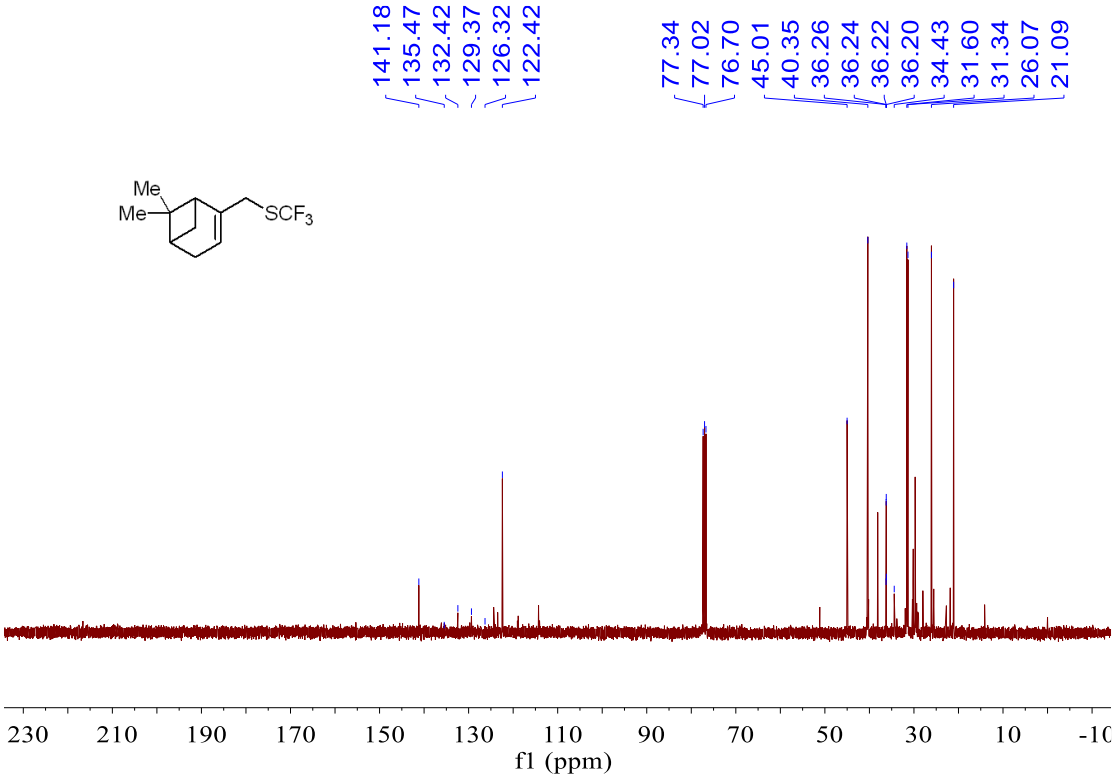




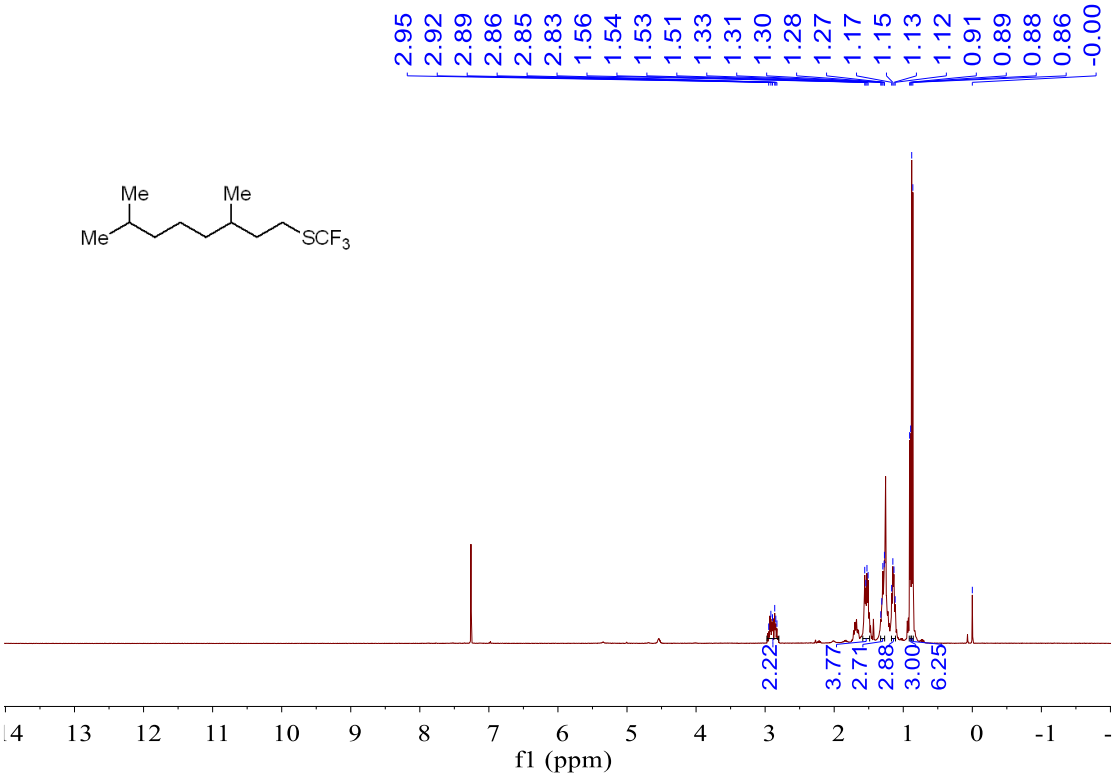
((6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methyl)(trifluoromethyl)sulfane (**4h**)

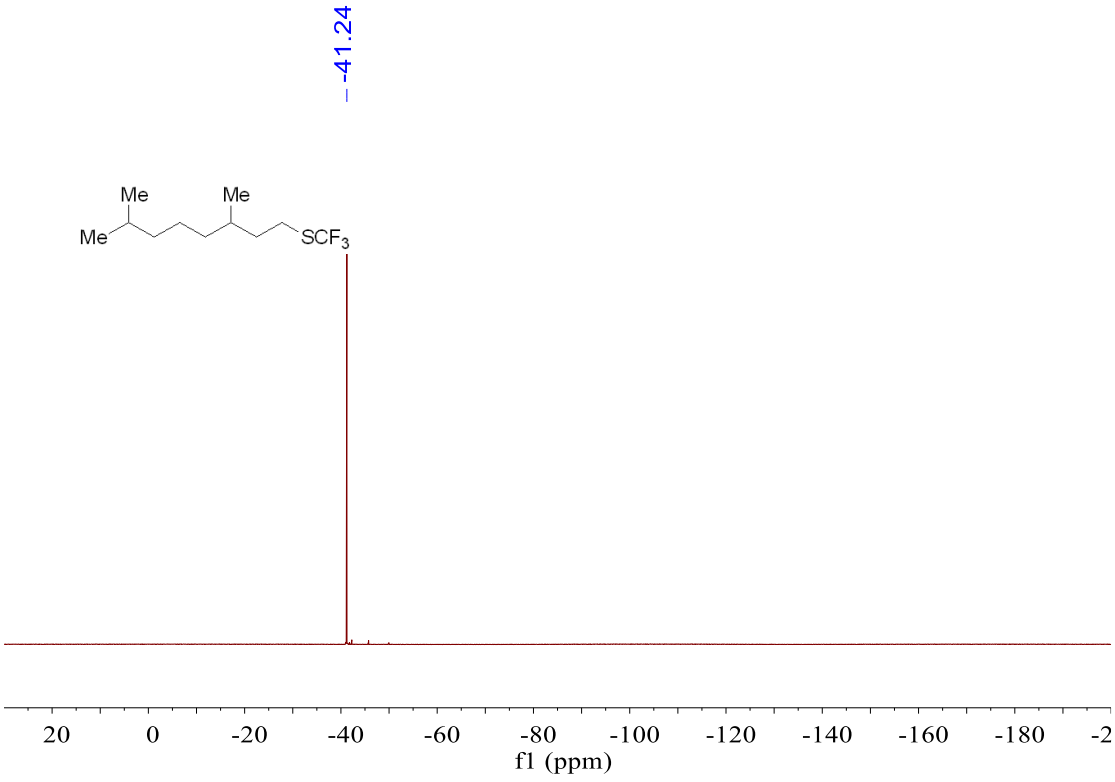



-41.31
Me
Me
SCF3
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-20
f1 (ppm)

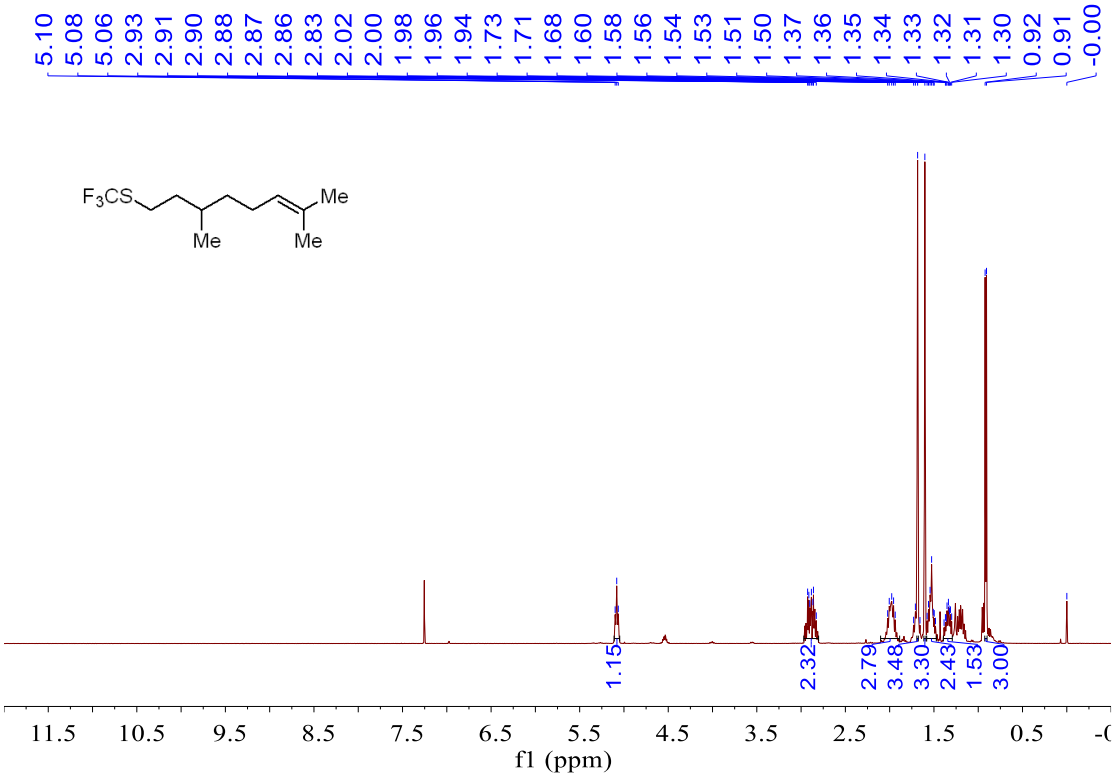

141.18
135.47
132.42
129.37
126.32
122.42
77.34
77.02
76.70
45.01
40.35
36.26
36.24
36.22
36.20
34.43
31.60
31.34
26.07
21.09
Me
Me
SCF3
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)

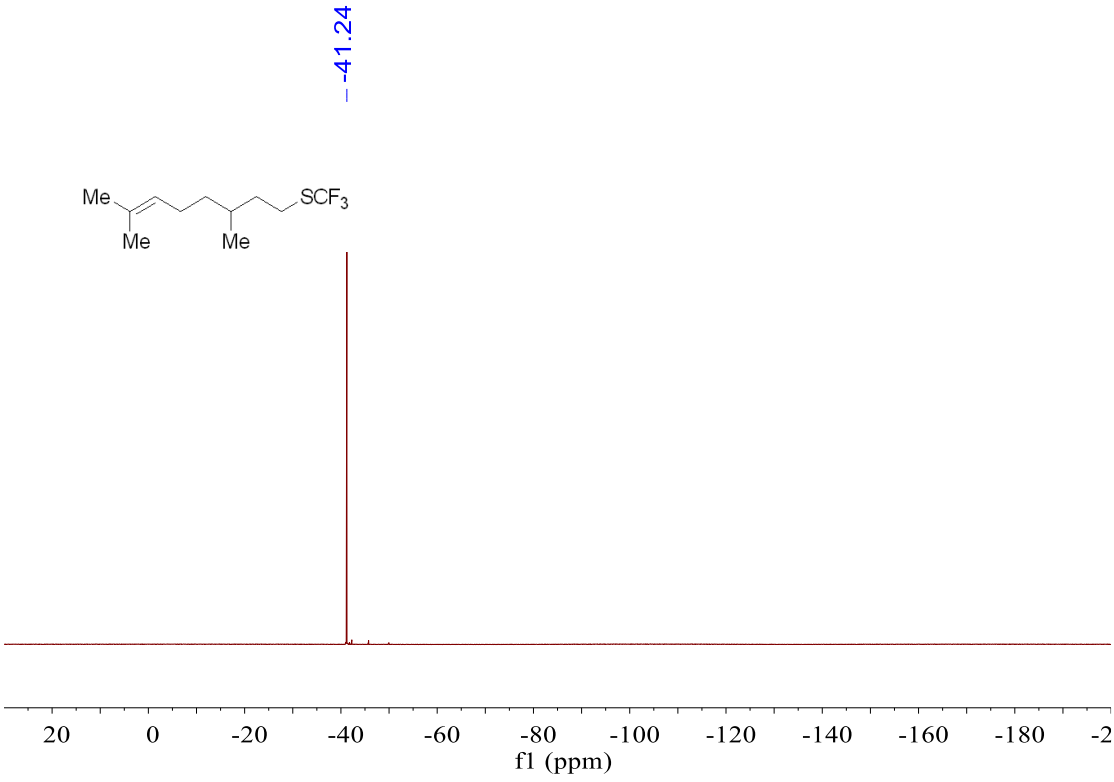
(3,7-dimethyloctyl)(trifluoromethyl)sulfane (**4i**)



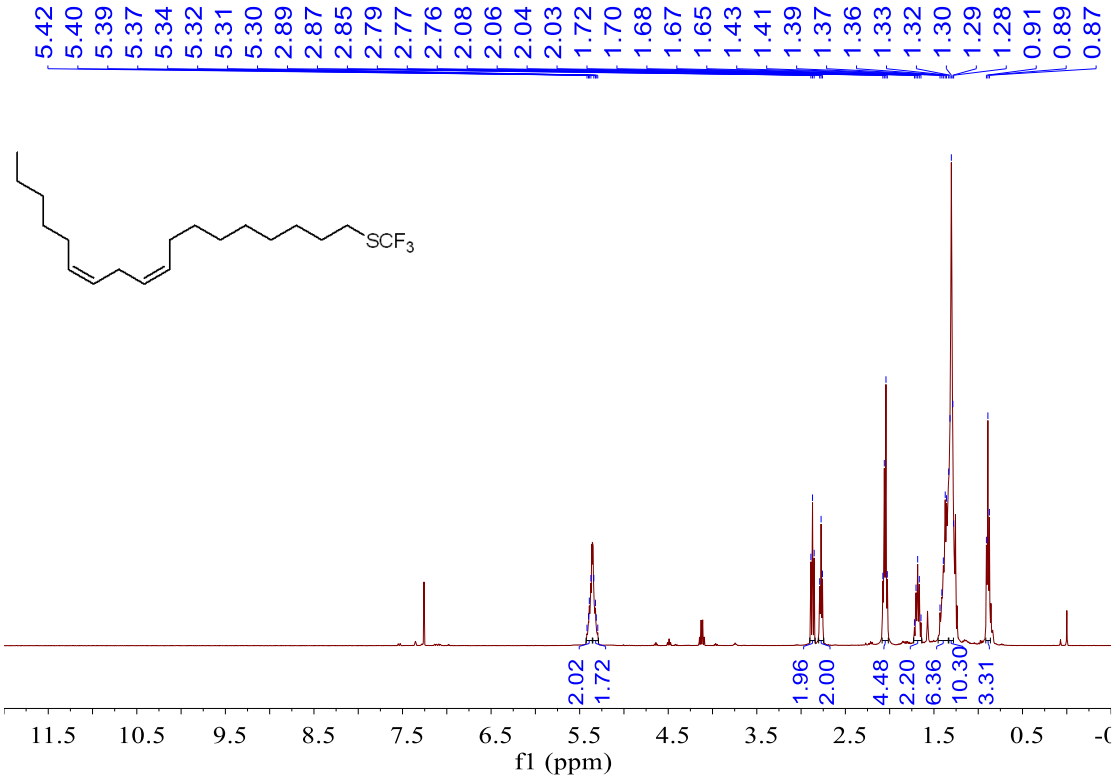


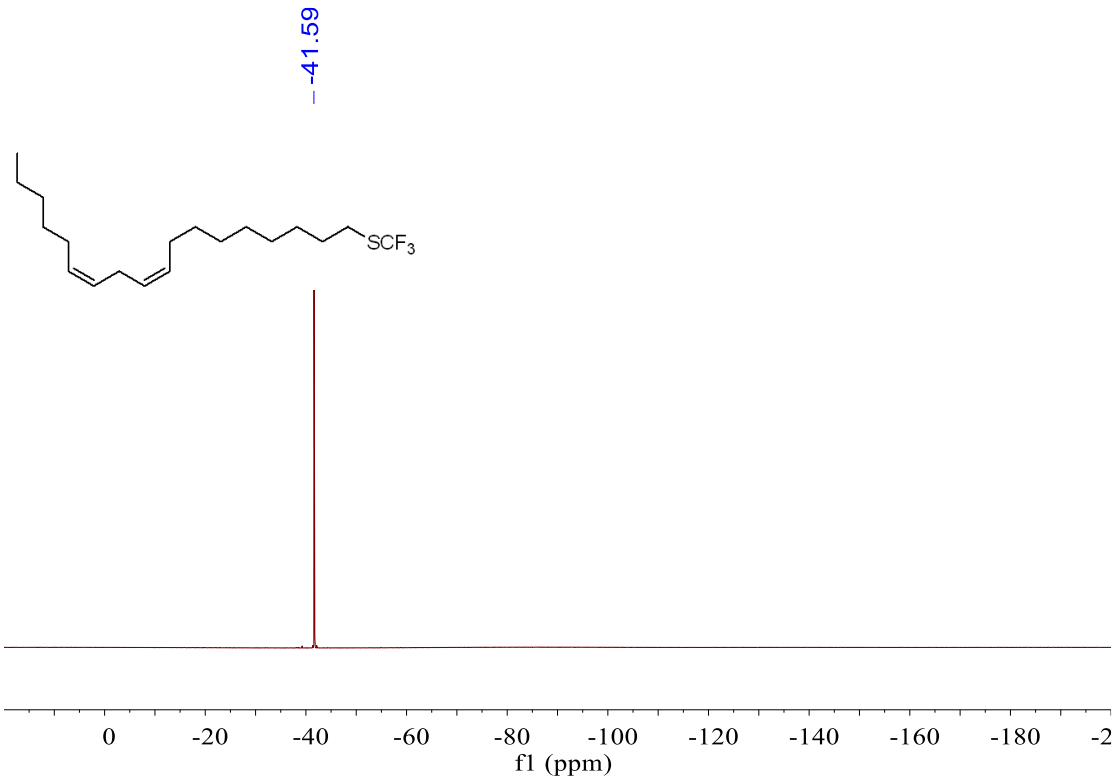
(3,7-dimethyloct-6-en-1-yl)(trifluoromethyl)sulfane (**4j**)

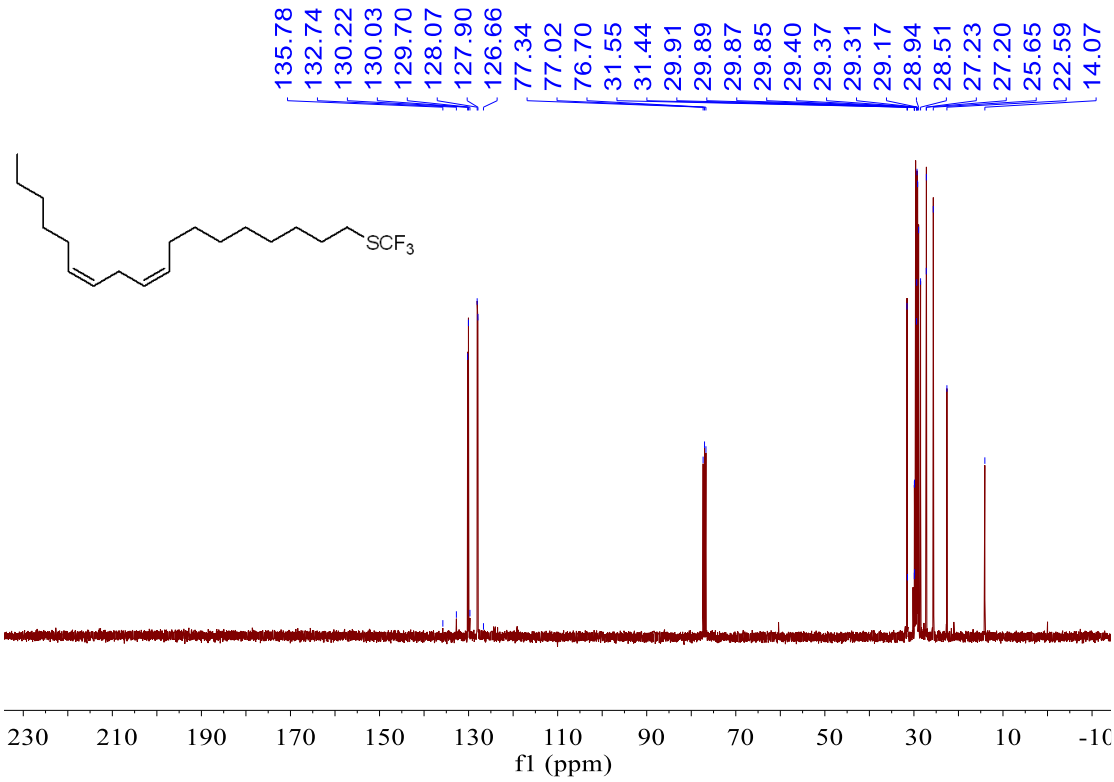




((9Z,12Z)-octadeca-9,12-dien-1-yl)(trifluoromethyl)sulfane (**4k**)






135.78
132.74
130.22
130.03
129.70
128.07
127.90
126.66
77.34
77.02
76.70
31.55
31.44
29.91
29.89
29.87
29.85
29.40
29.37
29.31
29.17
28.94
28.51
27.23
27.20
25.65
22.59
14.07
SCF3
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)