Electronic Supporting Information

Oxidative Decarboxylative Radical Trifluoromethylthiolation of Alkyl Carboxylic Acids Using Silver(I) Trifluoromethanethiolate and Selectfluor

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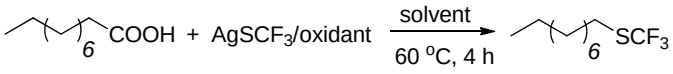
General information

NMR spectra were obtained on a 400 MHz spectrometer using $CDCl_3$ or $(CD_3)_2CO$ as deuterated solvents, with proton, carbon and fluorine resonances at 400 MHz, 100 MHz and 376 MHz, respectively. Chemical shifts were reported in parts per million (ppm) relative to TMS as an internal standard (δ_{TMS} = 0 ppm) for ^1H and ^{13}C NMR spectra and $CFCl_3$ as an external standard (negative for upfield) for ^{19}F NMR spectra. GC-MS (EI) data were determined on an Agilent 5975C. HRMS (EI) data were tested on a Water Micromass GCT Premier. Acetone was distilled from anhydrous $CaCl_2$. $AgSCF_3$ was prepared according to our previous report.[1] All the other solvents or reagents were used as commercial sources without purification if not noted. All reactions were performed in standard sealed tubes and monitored by thin-layer chromatography (TLC), ^{19}F NMR or GC-MS. Flash column chromatography was carried out using 300-400 mesh silica gel.

Table S1. Optimization of Reaction Conditions[a]



1a **2a**

entry	$AgSCF_3$ (equiv)	oxidant (equiv)	Ligand	solvent	Yield (%)[b]
1	1.0	$Na_2S_2O_8$ (2.0)	——	CH_3CN	37[c]
2	1.0	$Na_2S_2O_8$ (2.0)	——	DMSO	0
3	1.0	$Na_2S_2O_8$ (2.0)	——	DMF	0
4	1.0	$Na_2S_2O_8$ (2.0)	——	acetone	0
5	1.0	$Na_2S_2O_8$ (2.0)	——	CH_3CN/acetone (1:1 v/v)	0
6	1.0	$Na_2S_2O_8$ (2.0)	——	CH_3CN/DMSO (1:1 v/v)	0
7	1.0	$Na_2S_2O_8$ (2.0)	——	CH_3CN/H_2O/DCE (6:2:1 v/v/v)	5
8	2.0	selectfluor (4.0)	2,2'-Bipyridine	acetone	0
9	2.0	selectfluor (4.0)	1,10-Phenanthroline	acetone	0
10	2.0	selectfluor (4.0)	4-Dimethylaminopyridine	acetone	0
11	2.0	selectfluor (4.0)	N,N,N,N-Tetramethyl -Ethylenediamine	acetone	0
12	2.0	selectfluor (4.0)	2,6-lutidine	acetone	82
13	2.0	selectfluor (4.0)	Triphenylphosphine	acetone	5
14	2.0	selectfluor (4.0)	Tricyclohexylphosphine	acetone	0
15	2.0	selectfluor (4.0)	1,2-Bis(diphenylphosphino) -ethane	acetone	25

[a] Reaction conditions: Decanoic acid (0.2 mmol,1.0 equiv), $AgSCF_3$ (1.0-2.0 equiv), oxidant (2.0-4.0 equiv), and solvent (2.0 mL) at 60 °C for 4 hours under Ar atmosphere. [b] Yields were determined by ^{19}F NMR spectroscopy with benzotrifluoride as the internal standard. [c] A di-trifluoromethylthiolation isomer mixture was obtained.

Figure S1. Reaction time effect on the oxidative decarboxylative radical trifluoromethylthiolation reaction of 1j

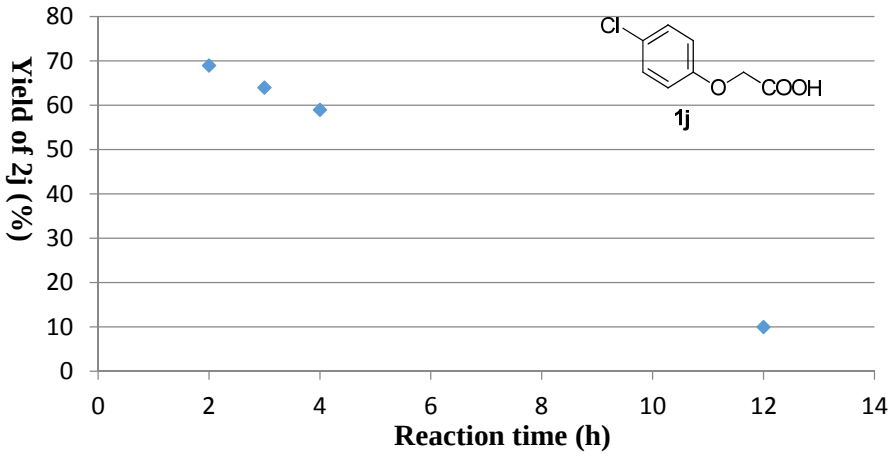
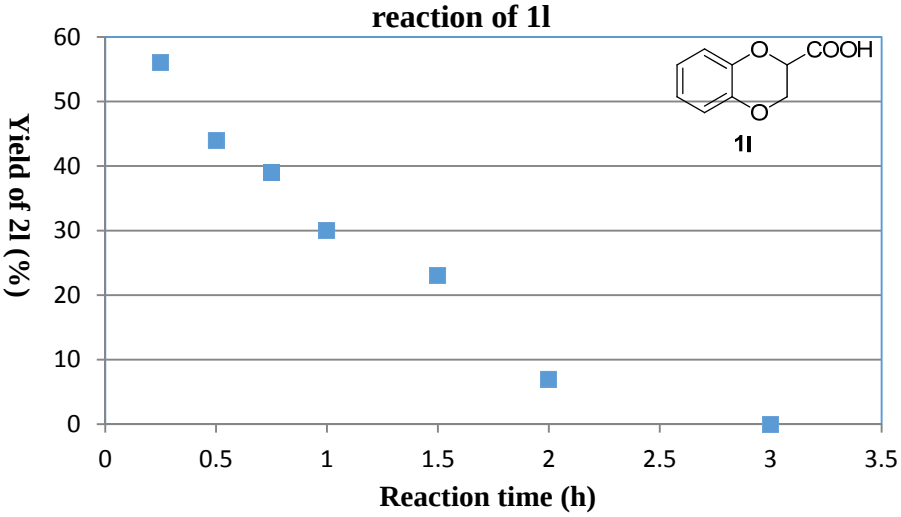
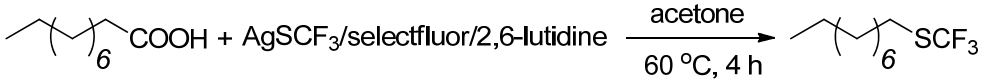


Figure S2. Reaction time effect on the oxidative decarboxylative radical trifluoromethylthiolation reaction of 1l



Scheme S1. Mechanistic Experiments



A : standard conditions	82%
B : +20%mmol Hydroquinone	7%
C : +1eq TEMPO	1%

X-ray crystallographic studies

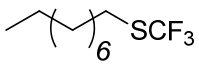
Suitable crystals were mounted on grass fibers or sealed in thin-walled glass capillaries. X-ray intensity data of **2k** was collected on a Bruker SMART CCD-APEX diffractometer employing graphite monochromated Mo-Kα radiation (λ=0.71073 Å) and using the ω-2θ scan technique. The intensity data were corrected for Lorentz and polarization effects. Refinement was by full-matrix least-squares techniques based on *F* to minimize the quantity $\sum w(|Fo|-|Fc|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. Crystal data and data collection parameters are summarized in Table S2.

Table S2. Crystallographic Data for $C_{24}H_{33}F_3O_3S_1$ (2k).

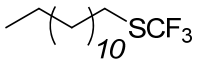
	$C_{24}H_{33}F_3O_3S_1$
CCDC No.	1484006
empirical formula	C24 H33 F3 O3 S1
formula mass	458.56
crystallization	CH_3CN/Et_2O
dimensions [mm^3]	0.220 x 0.140 x 0.100
crystal system	Monoclinic
space group	P 21
a [Å]	11.2125(19)
b [Å]	6.7337(11)
c [Å]	15.886(3)
α[°]	90
β[°]	104.314(4)
γ[°]	90
V [$Å^3$]	1162.2(3)
Z	2
d_{calcd} [Mg m^{-3}]	1.310
absorption coefficient [mm^{-1}]	0.186
T [k]	293(2)
$2\theta_{max}$ [°]	25.242
measured reflections	6458
unique reflections	3830
R_{int}	0.0293
R1 [I>2σ(I)]	0.0744
*w*R2 [I>2σ(I)]	0.1911
R1(all data)	0.0946
*w*R2(all data)	0.2107

General procedures for oxidative decarboxylative radical trifluoromethylthiolation of various aliphatic carboxylic acids.

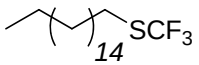
To an oven dried Schleck tube was added aliphatic carboxylic acid substrate (0.2 mmol), $AgSCF_3$ (45 mg, 0.4 mmol), selectfluor (283 mg, 0.8 mmol), 2,6-lutidine (47 ul, 0.4 mmol) and acetone (2 mL) under Ar atmosphere at room temperature. The mixture was stirred at 60 ºC for 4 h. The resulting mixture was cooled down to room temperature and added an internal standard (trifluorotoluene) to calculate the ^{19}F NMR yield. Furthermore, the reaction mixture was filtered through a pad of celite and analyzed by GC−MS or dried and analyzed by ^{1}H NMR. To isolate the pure oxidative decarboxylative trifluoromethylthiolated product, the reaction was carried out with aliphatic carboxytic acid substrate (0.5 mmol), $AgSCF_3$ (223 mg, 1.0 mmol), selectfluor (708 mg, 2.0 mmol), 2,6-lutidine (116 ul, 1.0 mmol) and acetone (5 mL) under Ar atmosphere at 60 ºC for 4 h. The resulting mixture was cooled down to room temperature and filtered through a pad of celite. After removal of the solvent under reduced pressure with a rotary evaporator, the crude product was purified by column chromatography on silica gel to give the desired oxidative decarboxylative radical trifluoromethylthiolated product.



nonyl(trifluoromethyl)sulfane (2a): Obtained as a colorless liquid in 70% yield (80 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (t, *J = 6* Hz, 2H, characteristic CH_2-SCF_3), 1.70-1.63 (m, 2H), 1.40-1.26 (m, 12H), 0.86 (t, *J* = 6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -41.33 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.2 (q, *J* = 304 Hz, SCF_3), 31.8, 29.9, 29.4, 29.4, 29.2, 29.0, 28.5, 22.6, 14.0. GC-MS (EI): *m/z* = 227.1 ($M\text{-}H^+$). HRMS (EI): calcd for $C_{10}H_{18}F_3S$ ($M\text{-}H^+$) 227.1081, found 227.1073. IR (film): ν_{max} (cm^{-1}) = 2927.6, 2856.5, 1463.7, 1379.0, 1261.0, 1116.2, 805.0, 756.2, 723.8.

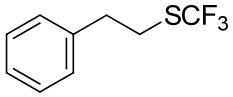


tridecyl(trifluoromethyl)sulfane (2b): Obtained as a colorless liquid in 63% yield (89 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.86 (t, *J = 6 Hz*, 2H, characteristic CH_2-SCF_3), δ 1.70-1.63 (m, 2H), 1.40-1.25 (m, 20H), 0.87 (t, *J* = 6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -41.36 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.2 (q, *J* = 304 Hz, SCF_3), 31.9, 29.9, 29.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.0, 28.5, 22.7, 14.0. GC-MS (EI): *m/z* = 339 ($M\text{-}H^+$). HRMS (EI): calcd for $C_{14}H_{26}F_3S$ ($M\text{-}H^+$) 283.1707, found 283.1712. IR (film): ν_{max} (cm^{-1}) = 2926.1, 2853.3, 1466.6, 1378.9, 1153.9, 1118.5, 756.3, 722.0.

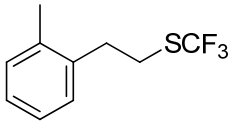


heptadecyl(trifluoromethyl)sulfane (2c): Obtained as a colorless liquid in 84% yield (143 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (t, *J* = 6 Hz, 2H, characteristic CH_2-SCF_3), δ 1.70-1.63 (m, 2H), 1.39-1.24 (m, 28H), 0.86 (t, *J* = 6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -41.31 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.2 (q, *J* = 304 Hz, SCF_3), 31.9, 29.9, 29.9, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.0, 28.5,

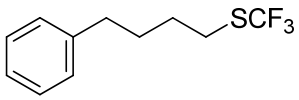
22.7, 14.1. GC-MS (EI): *m/z* = 339 (M-H$^+$). HRMS (EI): calcd for $C_{18}H_{34}F_3S$ (M-H$^+$) 339.2333, found 339.2327. IR (film): ν_{max} (cm^{-1}) = 2925.2, 2854.3, 1466.7, 1378.2, 1154.4, 1118.8, 756.2, 721.5.



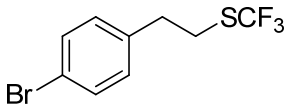
phenethyl(trifluoromethyl)sulfane (2d):[2] Obtained as a colorless liquid in 43% yield (44 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.19 (m, 5H), 3.13 (t, *J* = 8 Hz, 2H, characteristic C*H*$_2$-SCF$_3$), 2.99 (t, *J* = 6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -41.07 (s, 3F). GC-MS (EI): *m/z* = 206.0 (M$^+$). HRMS (EI): calcd for $C_9H_9F_3S$ (M$^+$) 206.0377, found 206.0371. IR (film): ν_{max} (cm^{-1}) = 3395.9, 2960.8, 2923.4, 2850.4, 1739.0, 1674.8, 1462.6, 1413.1, 1377.3, 1261.0, 1100.0, 1019.8, 864.9, 800.2, 698.7.



(2-methylphenethyl)(trifluoromethyl)sulfane (2e): Obtained as a colorless liquid in 60% yield (66 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.14 (m, 4H), 3.09-2.97 (m, 4H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -41.05 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.2 (q, *J* = 304 Hz, SCF_3), 137.2, 135.9, 130.6, 129.1, 127.1, 126.3, 33.7, 29.9, 19.1. GC-MS (EI): *m/z* = 220.0 (M$^+$). HRMS (EI): calcd for $C_{10}H_{11}F_3S$ (M$^+$) 220.0534, found 220.0533. IR (film): ν_{max} (cm^{-1}) = 2954.9, 2918.0, 2849.1, 1558.7, 1463.1, 1377.7, 1239.9, 1116.1, 1027.0, 890.4, 802.0, 743.8, 419.1.

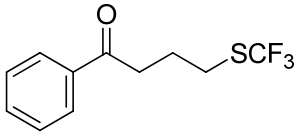


(4-phenylbutyl)(trifluoromethyl)sulfane (2f): Obtained as a colorless liquid in 48% yield (56 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.15 (m, 5H), 2.88 (t, *J* = 8 Hz, 2H, characteristic C*H*$_2$-SCF$_3$), 2.63 (t, *J* = 8 Hz, 2H, characteristic C*H*$_2$-CH$_2$SCF$_3$), 1.75-1.71 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -41.25 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.2 (q, *J* = 304 Hz, SCF_3), 141.6, 128.4, 128.3, 35.2, 30.2, 29.7, 29.0. GC-MS (EI): *m/z* = 234.0 (M$^+$). HRMS (EI): calcd for $C_{11}H_{13}F_3S$ (M$^+$) 234.0690, found 234.0687. IR (film): ν_{max} (cm^{-1}) = 3064.2, 3028.0, 2927.3, 2857.9, 1603.9, 1496.7, 1454.5, 1326.7, 1115.7, 1030.6, 909.1, 842.9, 754.8, 698.9, 660.7.

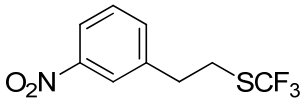


(4-bromophenethyl)(trifluoromethyl)sulfane (2g): Obtained as a colorless liquid in 49% yield (70 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8 Hz, 2H), 7.07 (d, *J* = 8 Hz, 2H), 3.09 (t, *J* = 6 Hz, 2H, characteristic C*H*$_2$-SCF$_3$), 2.94 (t, *J* = 8 Hz , characteristic C*H*$_2$-CH$_2$SCF$_3$). ^{19}F NMR (376 MHz, $CDCl_3$): δ -41.51 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.0 (q, *J* = 306 Hz, SCF_3), 137.8, 131.8, 130.3, 120.8, 35.4, 31.0. GC-MS (EI): *m/z* = 284.0 (M$^+$). HRMS (EI): calcd for $C_9H_8F_3SBr$ (M$^+$) 283.9482, found 283.9480. IR (film): ν_{max} (cm^{-1}) = 3026.4, 2928.6, 2857.1, 1592.4, 1488.9, 1449.5, 1405.0, 1291.3, 1239.8, 1112.0, 1073.3, 1012.1, 893.3, 842.0, 802.4,

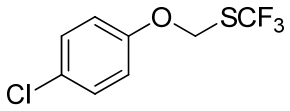
756.1, 660.0, 598.6, 505.1, 483.2, 463.1.



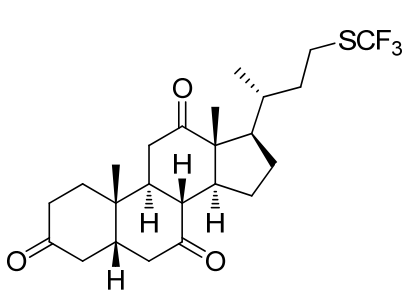
1-phenyl-4-((trifluoromethyl)thio)butan-1-one (2h): Obtained as a light yellow liquid in 63% yield (78 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.93 (d, *J* = 8 Hz, 2H), 7.58-7.54 (t, *J* = 8 Hz, 1H), 7.47-7.43 (t, *J* = 8 Hz, 2H), 3.12 (t, *J* = 8 Hz, 2H, characteristic C*H*$_2$-SCF_3), 3.00 (t, *J* = 6 Hz, 2H), 2.17-2.11 (m, 5H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -40.99 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.0 (q, *J* = 304 Hz, SCF_3), 198.6, 136.7, 133.3, 128.7, 128.0, 36.4, 29.4, 23.8. GC-MS (EI): *m/z* = 248.0 (M^+). HRMS (EI): calcd for $C_{11}H_{11}OF_3S$ (M^+) 248.0483, found 248.0480. IR (film): ν_{max} (cm^{-1}) = 3063.2, 2928.0, 1686.4, 1598.0, 1581.6, 1449.4, 1410.3, 1368.0, 1323.8, 1295.8, 1227.9, 1199.9, 1115.9, 1026.7, 1001.4, 756.1, 745.4, 689.9, 568.1.

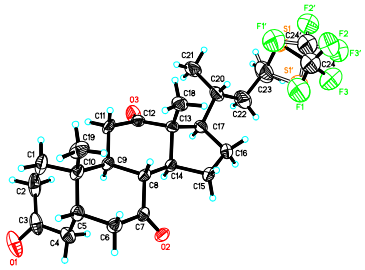


(3-nitrophenethyl)(trifluoromethyl)sulfane (2i): Obtained as a light yellow liquid in 54% yield (68 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.10 (d, *J* = 8 Hz, 1H), 8.07 (s, 1H), 7.55-7.47 (m, 2H), 3.18-3.08 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -40.93 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.9 (q, *J* = 304 Hz, SCF_3), 148.5, 140.7, 134.9, 129.7, 123.5, 122.1, 35.5, 30.7. GC-MS (EI): *m/z* = 251.0 (M^+). HRMS (EI): calcd for $C_9H_8F_3NO_2S$ (M^+) 251.0228, found 251.0222. IR (film): ν_{max} (cm^{-1}) = 3072.7, 2935.6, 2869.2, 1583.3, 1529.6, 1480.7, 1448.5, 1352.7, 1315.1, 1243.6, 1112.1, 913.1, 895.0, 852.1, 819.5, 805.7, 781.0, 756.5, 734.3, 680.4, 463.0.

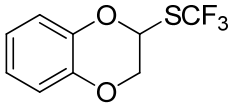


((4-chlorophenoxy)methyl)(trifluoromethyl)sulfane (2j): Obtained as a yellow liquid in 71% yield (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.27 (d, *J* = 8 Hz, 2H), δ 6.87-6.85 (d, *J* = 8 Hz, 2H), δ 5.47 (s, characteristic C*H*$_2$-SCF_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ -40.29 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.0 (q, *J* = 306 Hz, SCF_3), 154.5, 129.7, 128.2, 117.8, 68.5. GC-MS (EI): *m/z* = 242.0 (M^+). HRMS (EI): calcd for $C_8H_6OF_3SCl$ (M^+) 241.9780, found 241.9779. IR (film): ν_{max} (cm^{-1}) = 2928.4, 1595.1, 1490.7, 1442.9, 1328.3, 1288.6, 1256.8, 1208.1, 1115.1, 1031.6, 1009.1, 950.4, 908.7, 825.5, 800.5, 756.9, 735.6, 682.8, 636.1, 624.5.

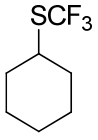




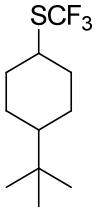
(5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-4-((trifluoromethyl)thio)butan-2-yl)decahydro-1H-cyclopenta[a]phenanthrene-3,7,12(2H,4H,8H)-trione (2k): Obtained as a colorless white crystal in 49% yield (112 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.01-2.94 (m, 1H), 2.90-2.72 (m, 4H), 2.35-1.73 (m, 14H), 1.61-1.44 (m, 2H), 3.39 (s, 3H), 1.30-1.13 (m, 3H), 1.03 (s, 3H), 0.83-0.82 (d, J = 4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -41.18 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.1 (q, J = 304 Hz, SCF_3), 211.8, 208.9, 208.6, 56.9, 51.8, 49.0, 46.8, 45.5, 45.5, 45.0, 42.8, 38.6, 36.4, 36.0, 35.2, 35.2, 35.0, 27.6, 27.5, 25.1, 21.9, 18.4,11.8. GC-MS (EI): m/z = 458.0 (M^+). HRMS (EI): calcd for $C_{24}H_{34}O_3F_3S$ ($M+H^+$) 459.2175, found 459.2170. IR (film): ν_{max} (cm^{-1}) = 2961.3, 2870.4, 1842.3, 1704.4, 1468.7, 1436.8, 1423.7, 1387.0, 1362.6, 1352.5, 1338.0, 1299.0, 1287.8, 1274.6, 1252.5, 1228.5, 1212.9, 1183.3, 1119.8, 1027.9, 1007.8, 952.3, 925.3, 872.9, 754.4, 681.4, 618.8, 524.2.



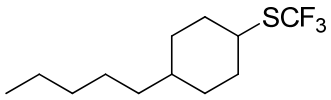
2-((trifluoromethyl)thio)-2,3-dihydrobenzo[b][1,4]dioxine (2l): Obtained as a colorless liquid in 59% yield (69 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97-6.89 (m, 4H), 6.06 (s, 1H, characteristic C*H*-SCF_3), 4.45-4.35 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -39.17 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.2 (q, J = 306 Hz, SCF_3), 142.5, 139.8, 123.1, 122.7, 118.4, 117.4, δ 77.2 (q, J = 2 Hz, *CH*-SCF_3). GC-MS (EI): m/z = 236.0 (M^+). HRMS (EI): calcd for $C_9H_7O_2F_3S$ (M^+) 236.0119, found 236.0116. IR (film): ν_{max} (cm^{-1}) = 3048.1, 2926.5, 2876.9, 1598.0, 1493.4, 1466.1, 1368.6, 1336.5, 1304.1, 1256.2, 1226.4, 1127.3, 1107.6, 1077.1, 991.1, 929.4, 898.4, 862.8, 805.5, 751.0, 735.0, 640.7, 538.4, 469.0



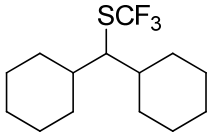
cyclohexyl(trifluoromethyl)sulfane (2m): 69% ^{19}F NMR yield. Characterization of **2m** in reaction solution: GC-MS (EI): m/z = 184.0 (M^+). HRMS (EI) calcd for $C_7H_{11}F_3S$ (M^+):184.0534, found 184.0538. Crude ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 3.23-3.17 (m, characteristic C*H*-SCF_3), the other hydrogen signals are at δ 1.46-1.09 (m, 10H). Crude ^{19}F NMR (376 MHz, $(CD_3)_2CO$): δ −39.56 (s, 3F).



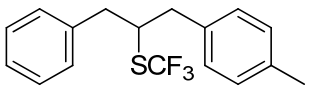
(4-(tert-butyl)cyclohexyl)(trifluoromethyl)sulfane (2n, cis+trans): Obtained as a colorless liquid in 76% yield (91 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.71 (s, 0.68H, characteristic C*H*-SCF_3), 3.11-3.03 (m, 0.32H, characteristic C*H*-SCF_3), 2.17-2.01 (dd, J_1 = 12 Hz, J_2 = 16 Hz, 2H), 1.86-1.63 (m, 3H), 1.43-0.94 (m, 4H), 0.89-0.83 (m, 9H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -38.93 (s, 0.91F), -40.12 (s, 2.09F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.6 (q, *J* = 304 Hz, SCF_3), 47.8, 43.1, 32.5, 27.6, 27.4, 27.3, 22.2, δ 131.2(q, *J* = 304 Hz, SCF_3), 46.9, 44.0, 34.4, 27.6, 27.3, 22.2. GC-MS (EI): *m/z* = 240.0 (M^+). HRMS (EI): calcd for $C_{11}H_{19}F_3S$ (M^+) 240.1160, found 240.1165. IR (film): ν_{max} (cm^{-1}) = 2952.6, 2865.5, 1479.6, 1469.5, 1449.6, 1395.3, 1367.6, 1315.9, 1268.0, 1238.2, 1115.8, 1081.2, 1039.7, 1023.2, 1001.1, 930.8, 901.2, 862.0, 771.0, 756.0, 700.9, 488.3



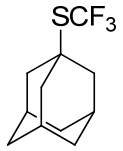
(4-pentylcyclohexyl)(trifluoromethyl)sulfane (2o, cis+trans): Obtained as a colorless liquid in 77% yield (99 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63 (t, *J* = 4 Hz, 0.63H, characteristic C*H*-SCF_3), 3.15-3.07 (m, 0.36H, characteristic C*H*-SCF_3), 1.94-1.76 (m, 3H), 1.63-1.61 (m, 1H), 1.37-1.15 (m, 12H), 1.05-0.98 (m, 1H), 0.88 (t, *J* = 6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -38.94 (s, 1.09F), -39.94 (s, 1.91F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5 (q, *J* = 304 Hz, SCF_3), 43.5, 36.4, 36.2, 33.1, 32.1, 28.4, 26.5, 22.6, 14.0, δ 131.2(q, *J* = 304 Hz, SCF_3), 44.0, 36.8, 36.9, 33.9, 31.4, 28.4, 26.5, 22.6, 14.0. GC-MS (EI): *m/z* = 254.0 (M^+). HRMS (EI): calcd for $C_{12}H_{21}F_3S$ (M^+) 254.1316, found 254.1313. IR (film): ν_{max} (cm^{-1}) = 2926.9, 2855.4, 1449.6, 1378.9, 1355.5, 1112.5, 962.8, 895.5, 756.9, 716.3.



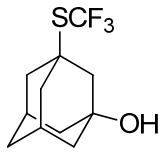
(dicyclohexylmethyl)(trifluoromethyl)sulfane (2p): Obtained as a colorless liquid in 50% yield (70 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (t, *J* = 6 Hz, 1H, characteristic C*H*-SCF_3), 1.90-1.87 (d, *J* = 12 Hz, 2H), 1.76-1.73 (m, 4H), 1.66-1.63 (m, 6H), 1.33-1.15 (m, 8H), 1.02-0.93 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -39.05 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5 (q, *J* = 303 Hz, SCF_3), 59.3, 39.6, 31.5, 29.4, 26.4, 26.3, 26.3. GC-MS (EI): *m/z* = 280.0 (M^+). HRMS (EI): calcd for $C_{14}H_{23}F_3S$ (M^+) 280.1473, found 280.1472. IR (film): ν_{max} (cm^{-1}) = 2927.6, 2854.2, 2666.4, 1449.5, 1350.0, 1307.9, 1252.4, 1225.8, 1200.0, 1145.7, 1108.4, 975.6, 949.2, 916.2, 894.9, 883.0, 849.6, 792.3, 757.1, 708.8, 661.0, 622.2, 469.1.



(1-phenyl-3-(p-tolyl)propan-2-yl)(trifluoromethyl)sulfane (2q): Obtained as a colorless liquid in 49% yield (76 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.07 (m, 9H), 3.67 (m, 1H, characteristic C*H*-SCF_3), 3.05-2.92 (m, 4H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -38.84 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.1 (q, J = 305 Hz, SCF_3), 137.9, 136.5, 134.7, 129.3, 129.2, 129.2, 126.9, 48.8, 40.8, 40.5, 21.1. GC-MS (EI): *m/z* = 310.0 (M^+). HRMS (EI): calcd for $C_{17}H_{17}F_3S$ (M^+) 310.1003, found 310.0998. IR (film): ν_{max} (cm^{-1}) = 2955.1, 2917.6, 2849.0, 1463.2, 1377.1, 1260.3, 1116.6, 1026.3, 891.2, 802.4, 743.7.



(3s,5s,7s)-adamantan-1-yl(trifluoromethyl)sulfane (2r):[1] Obtained as a colorless liquid in 51% yield (60 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3H), 2.05(s, 6H), 1.71 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -33.91 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.1 (q, J = 306 Hz, SCF_3), 50.9, 43.7, 35.8, 29.8. GC-MS (EI): *m/z* = 236.0 (M^+). HRMS (EI): calcd for $C_{11}H_{15}F_3S$ (M^+) 236.0847, found 236.0846. IR (film): ν_{max} (cm^{-1}) = 2911.5, 2854.3, 1452.2, 1303.4, 1184.4, 1114.2, 1034.0, 976.4, 755.5.

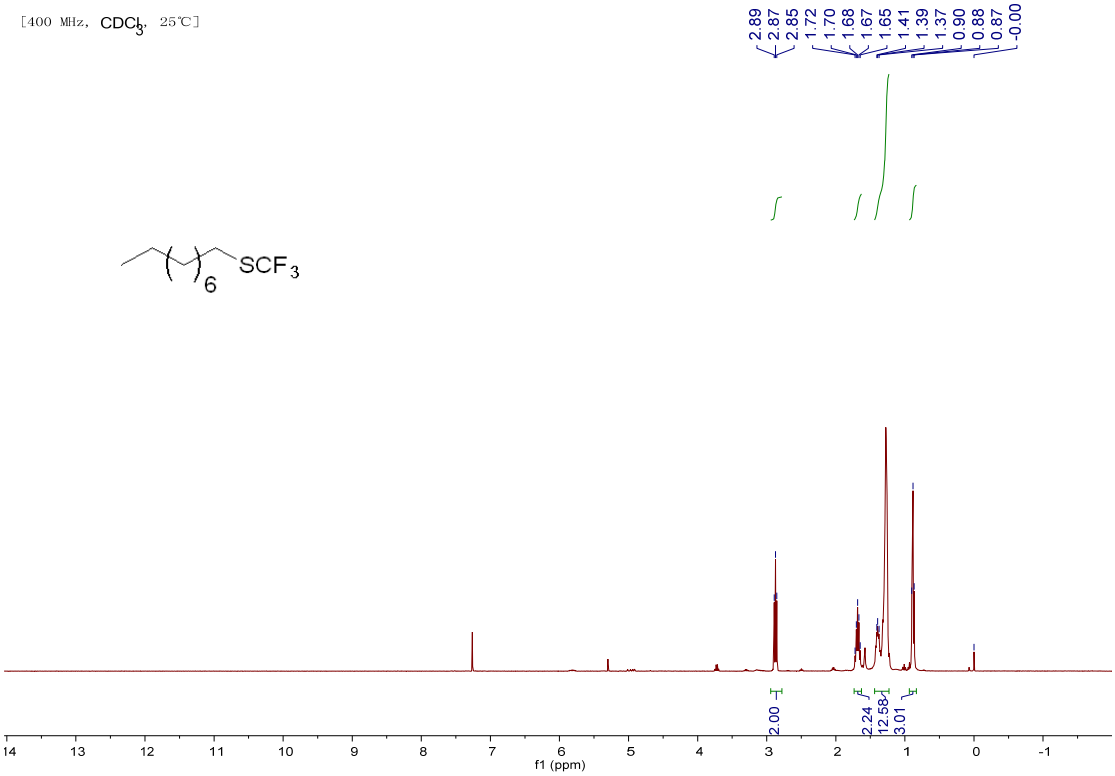


(1r,3s,5R,7S)-3-((trifluoromethyl)thio)adamantan-1-ol (2s):[3] Obtained as a colorless liquid in 62% yield (78 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 2H), 1.99 (s, 2H), 1.93 (s, 4H), 1.70-1.69 (d, J =4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -34.10 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.9 (q, J = 306 Hz, SCF_3), 69.0, 51.1, 43.7, 42.3, 34.4, 31.3. GC-MS (EI): *m/z* = 252.0 (M^+). HRMS (EI): calcd for $C_{11}H_{15}OF_3S$ (M^+) 252.0796, found 252.0792. IR (film): ν_{max} (cm^{-1}) = 3379.0, 2923.7, 2857.9, 1724.6, 1456.0, 1375.4, 1351.8, 1306.2, 1256.0, 1114.3, 1091.8, 1046.3, 977.2, 932.0, 849.3, 756.6, 735.0, 552.8.

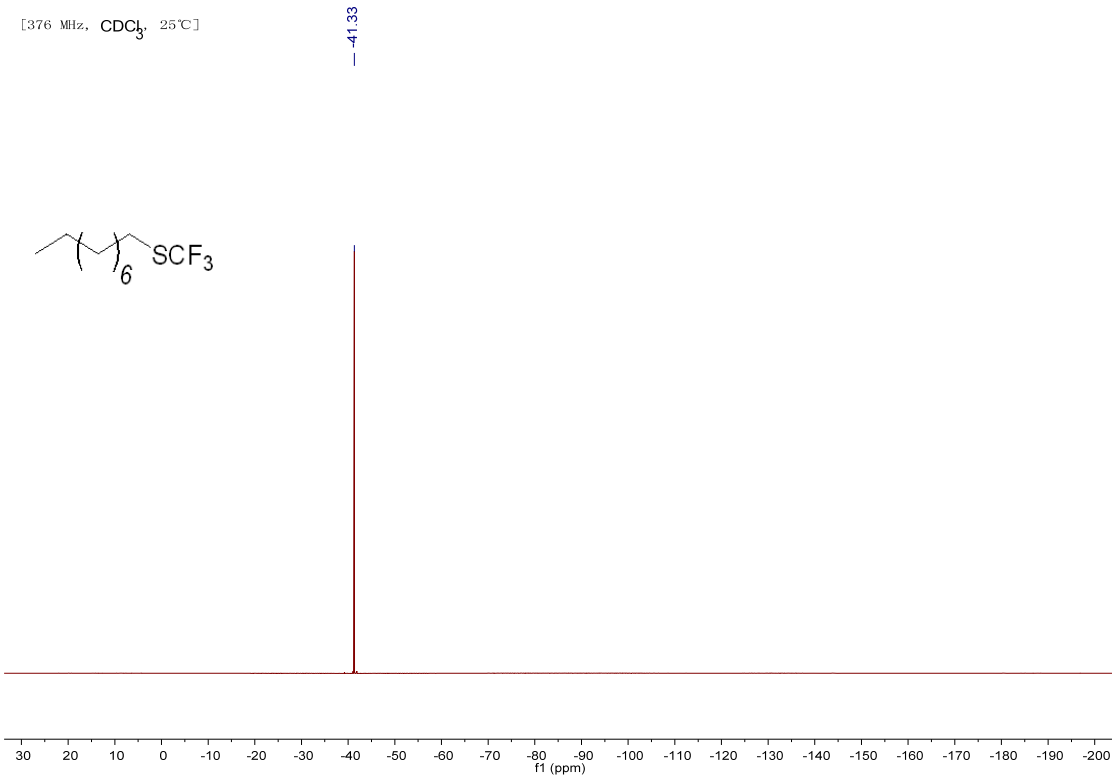
Reference:

(1) Wu, H.; Xiao, Z.; Wu, J.; Guo, Y.; Xiao, J.-C.; Liu, C.; Chen, Q.-Y. *Angew. Chem. Int. Ed*. **2015**, *54*, 4070 –4074.
(2) Timoshenko, V. M.; Charles Portella. *Journal of Fluorine Chemistry.* **2009**, *130*, 586–590.
(3) Hu, F.; Shao, X.; Zhu, D.; Lu, L.; Shen, Q. *Angew. Chem. Int. Ed*. **2014**, *53*, 6105 –6109.

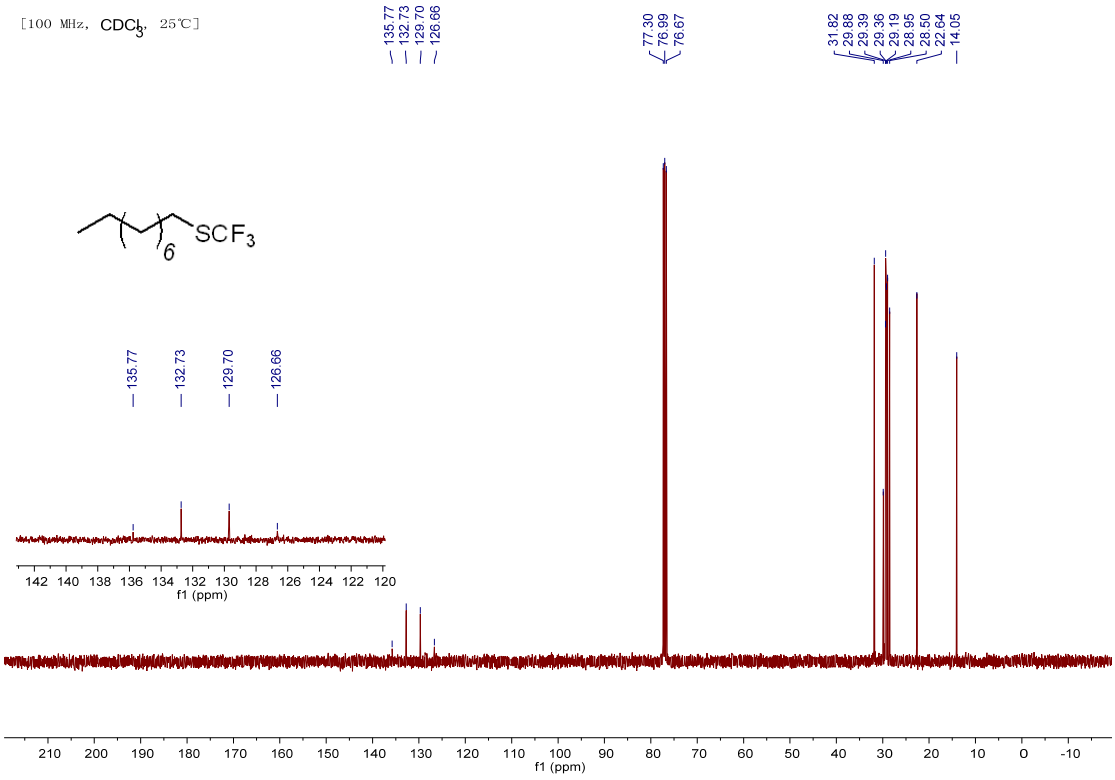
^{1}H NMR spectrum of nonyl(trifluoromethyl)sulfane 2a



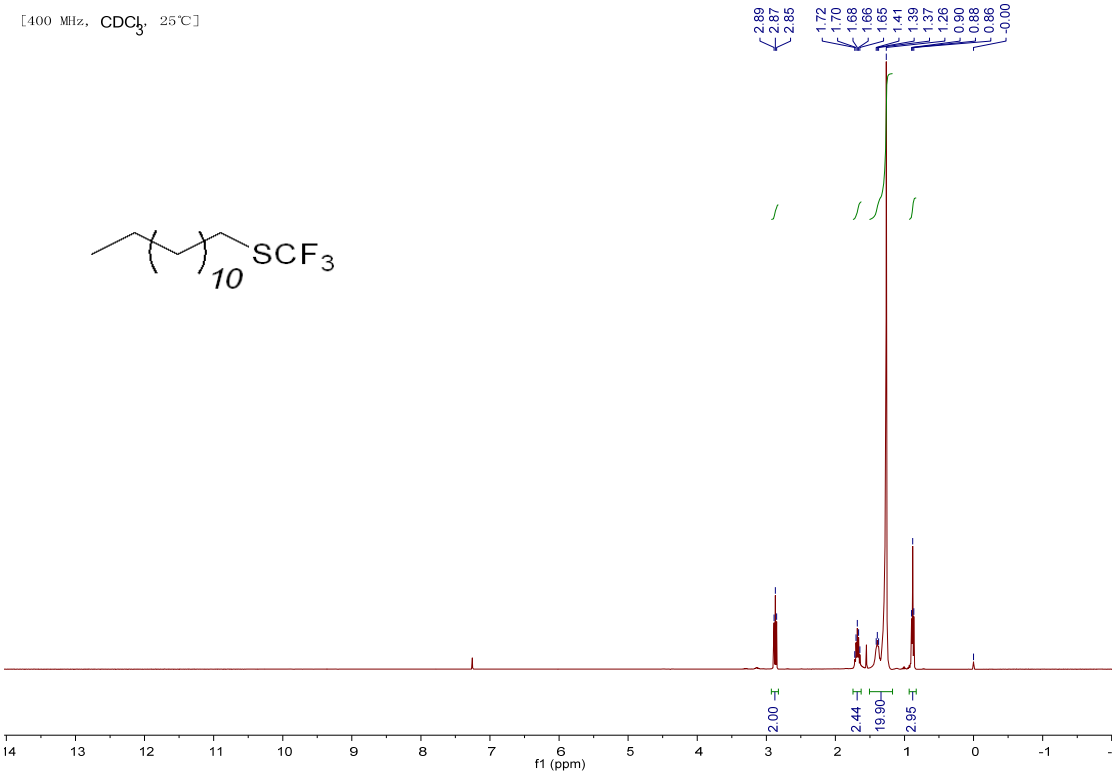
^{19}F NMR spectrum of nonyl(trifluoromethyl)sulfane 2a



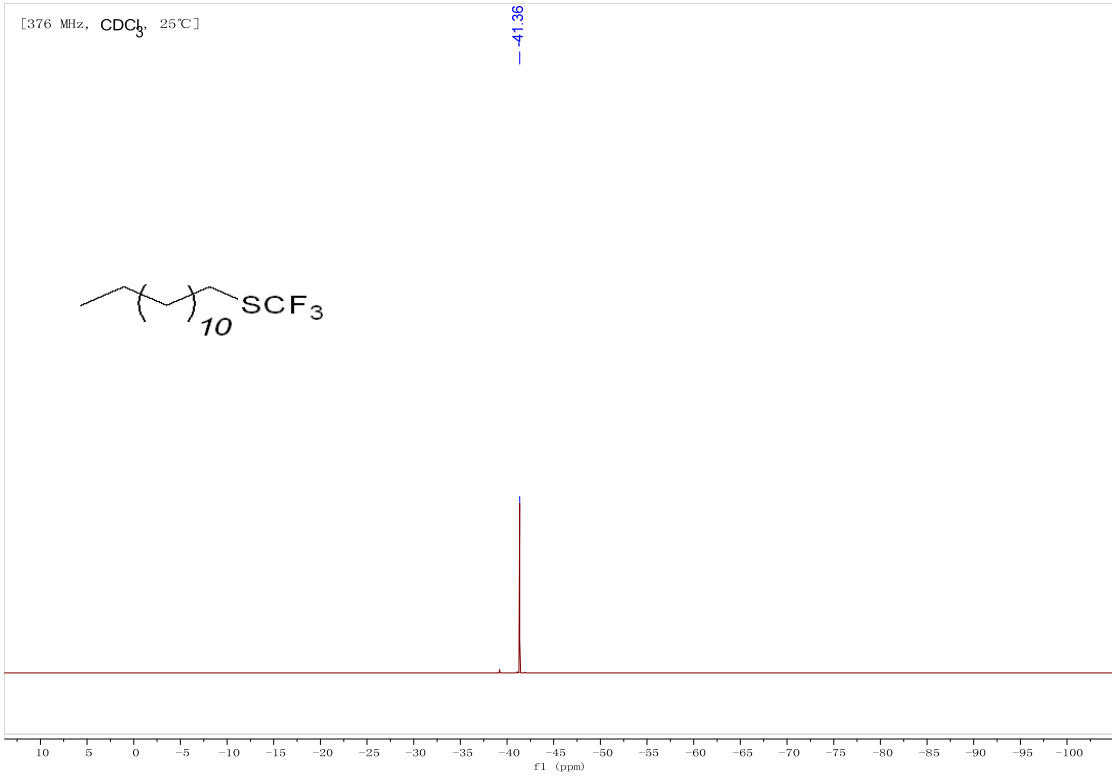
^{13}C NMR spectrum of nonyl(trifluoromethyl)sulfane 2a



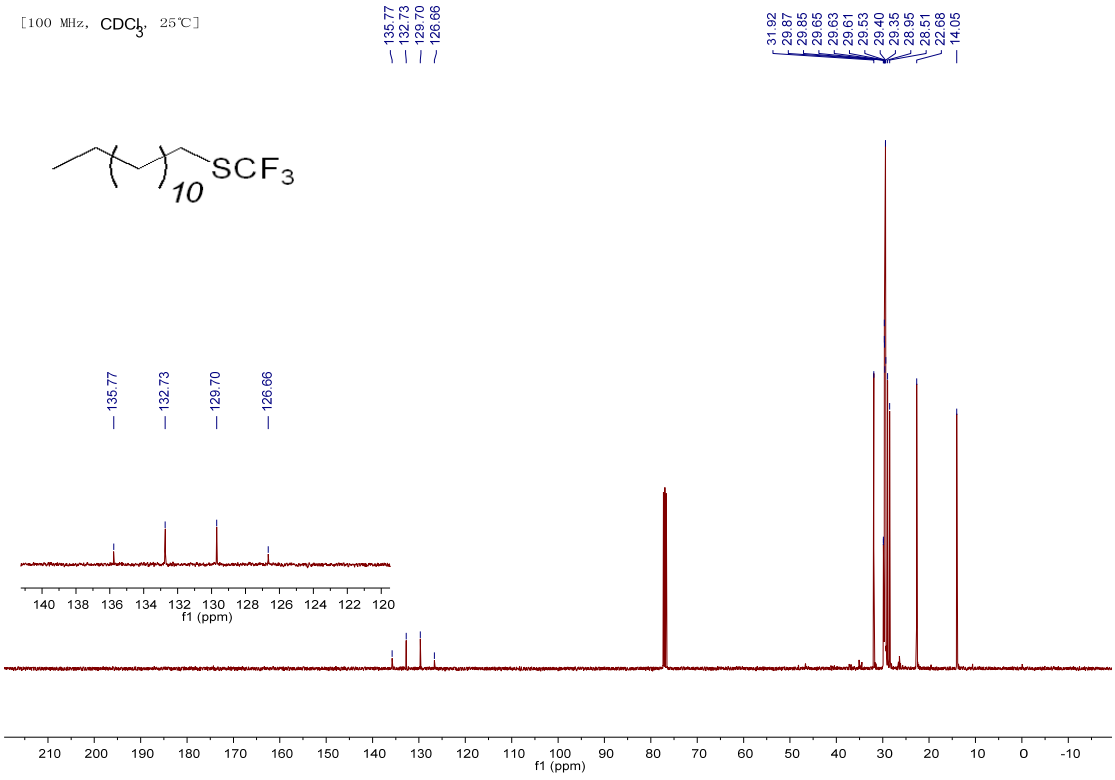
^{1}H NMR spectrum of tridecyl(trifluoromethyl)sulfane 2b



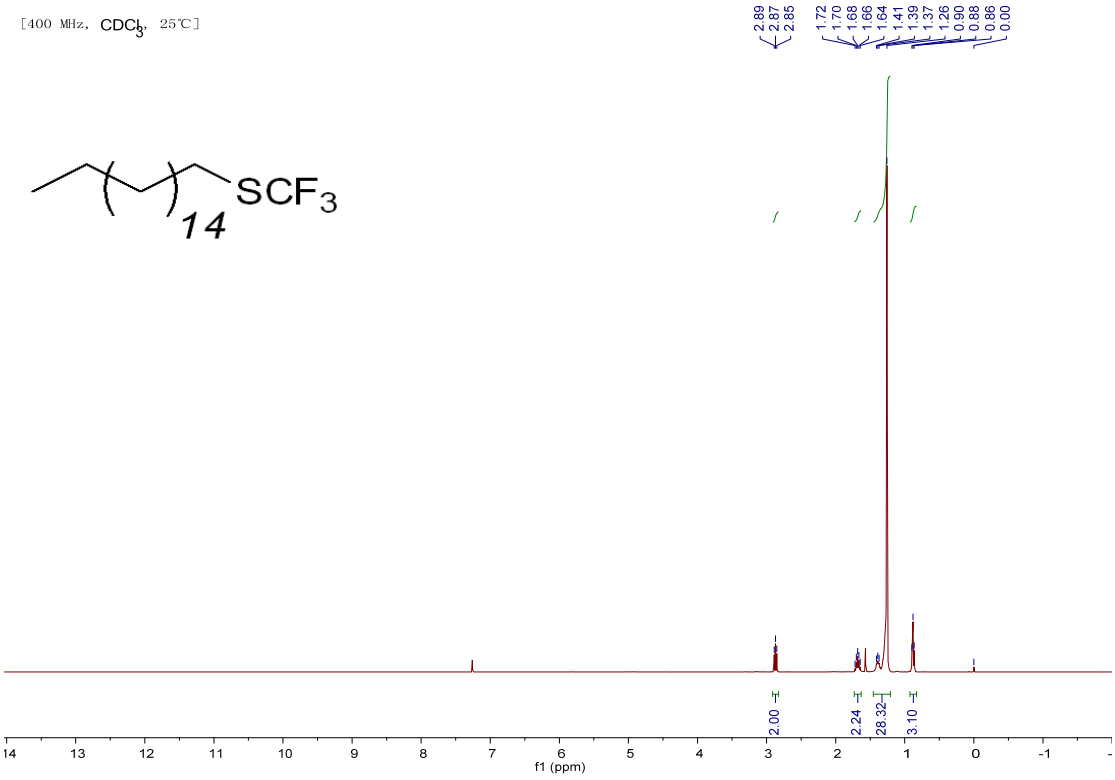
^{19}F NMR spectrum of tridecyl(trifluoromethyl)sulfane 2b



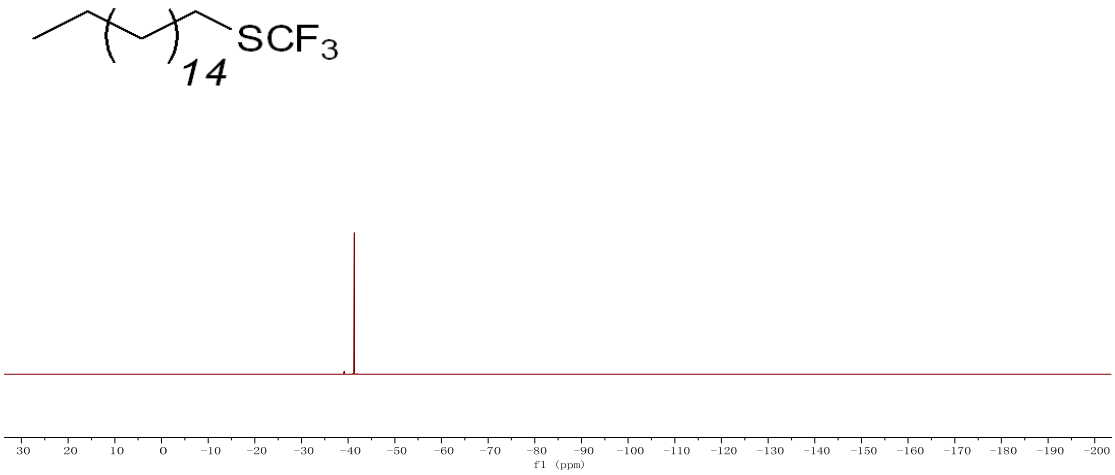
^{13}C NMR spectrum of tridecyl(trifluoromethyl)sulfane 2b



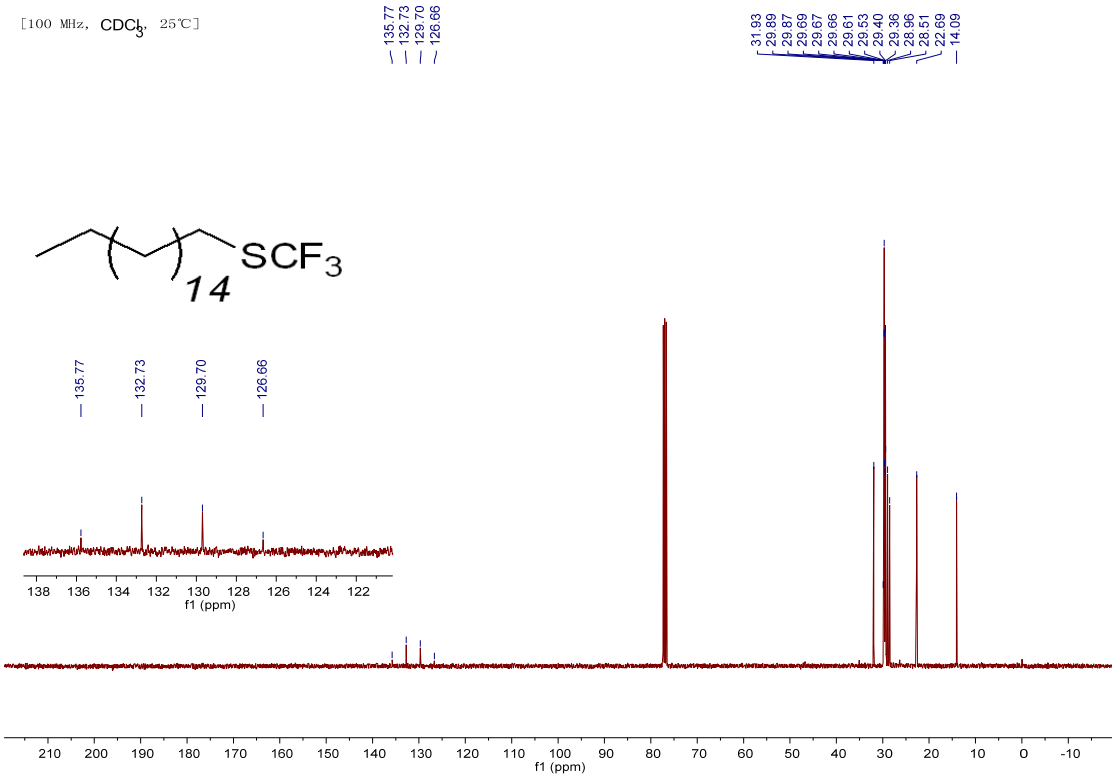
^{1}H NMR spectrum of heptadecyl(trifluoromethyl)sulfane 2c



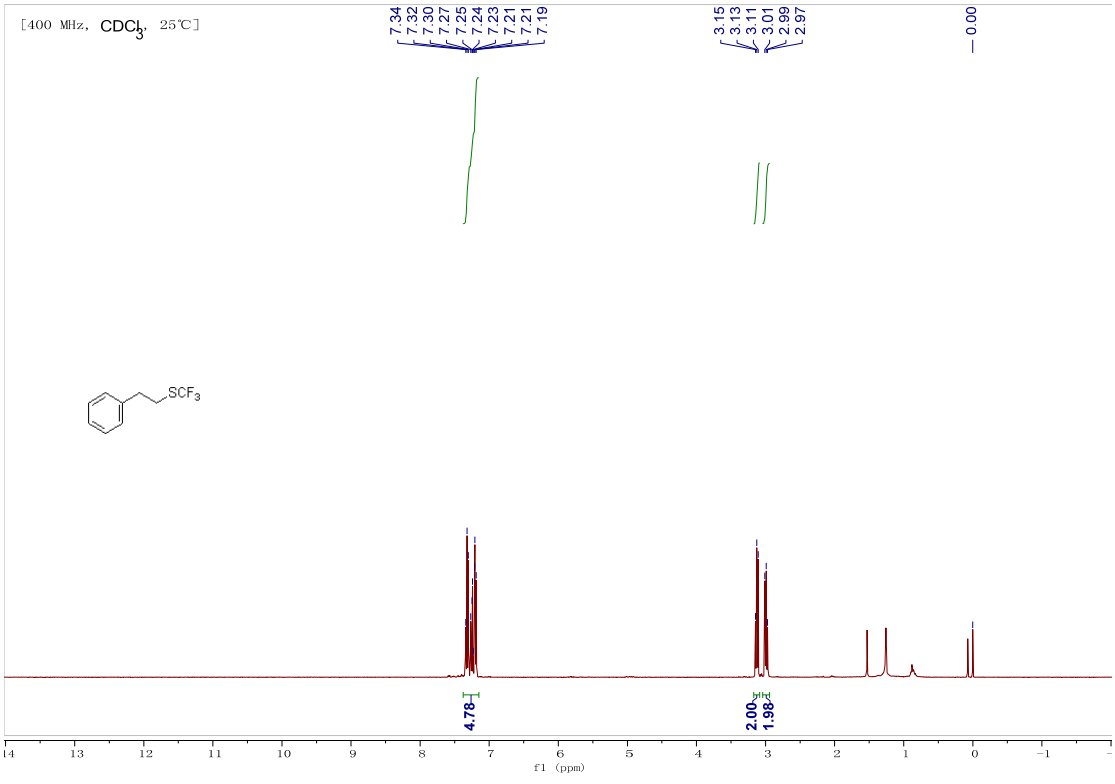
^{19}F NMR spectrum of nonyl(trifluoromethyl)sulfane 2c



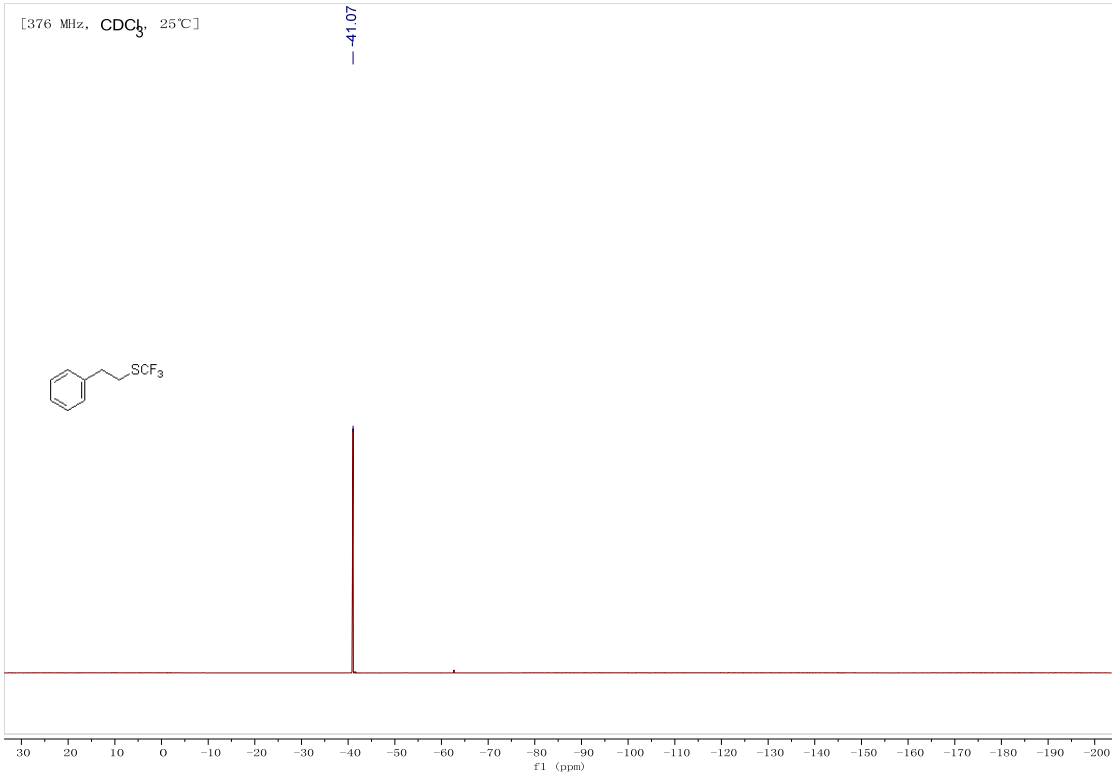
^{13}C NMR spectrum of nonyl(trifluoromethyl)sulfane 2c



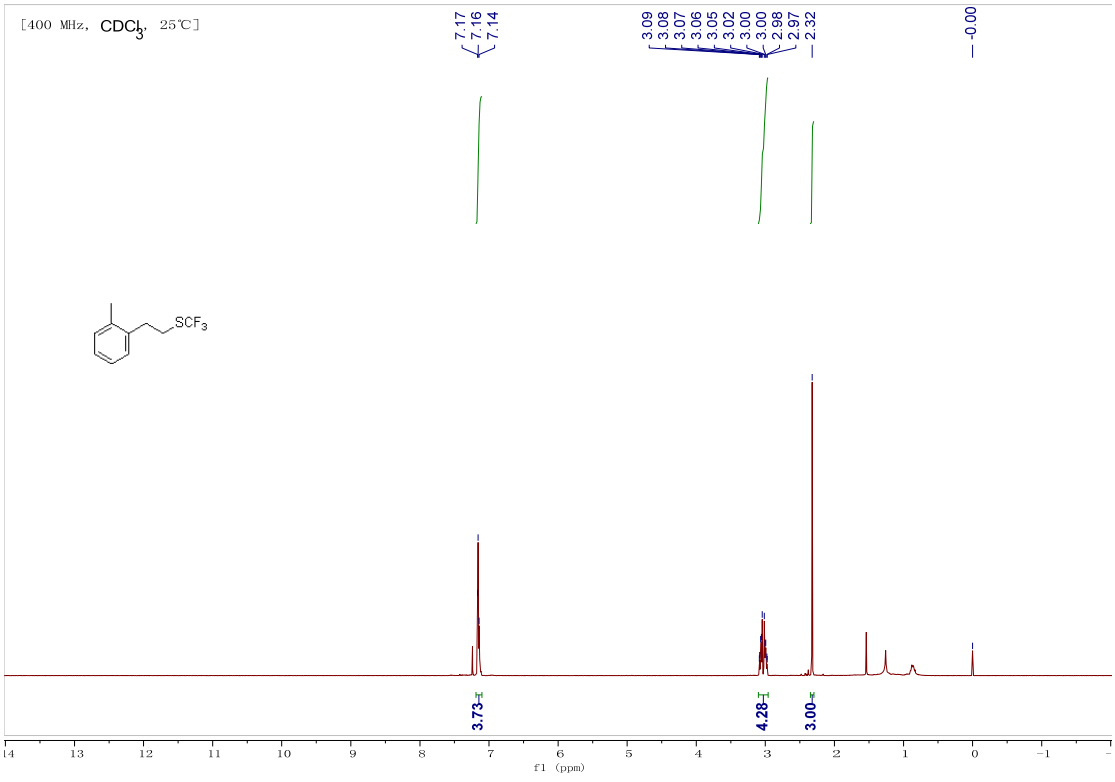
^{1}H NMR spectrum of phenethyl(trifluoromethyl)sulfane 2d



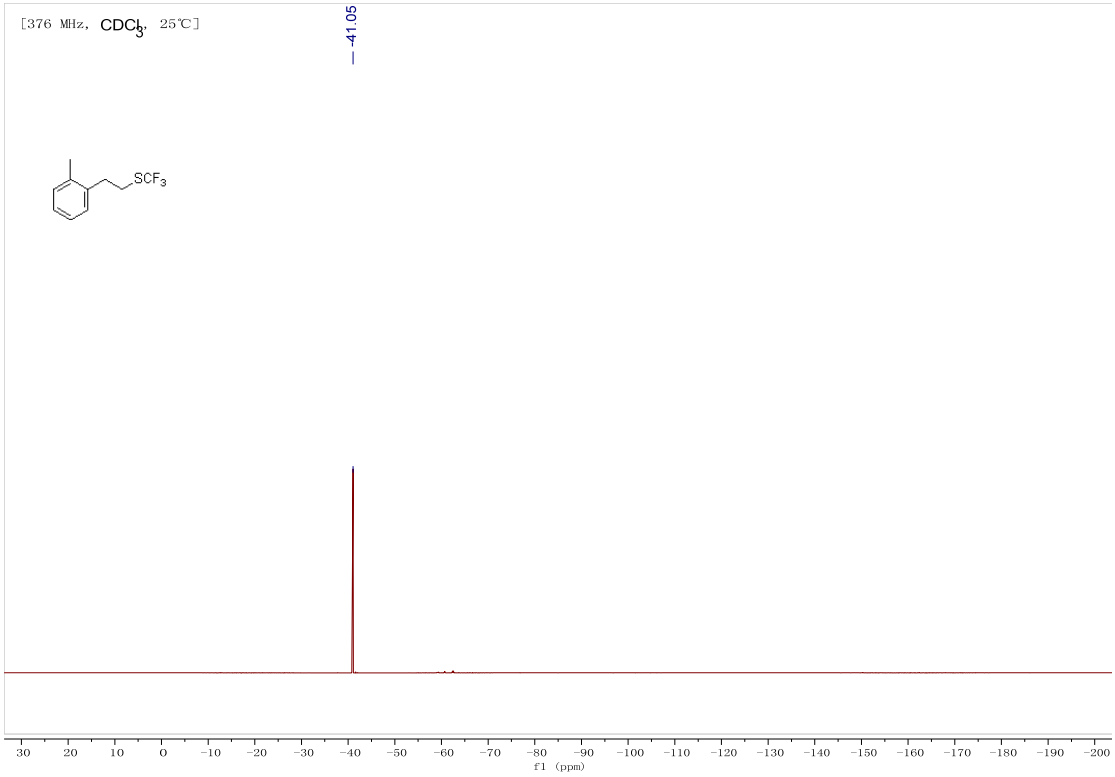
^{19}F NMR spectrum of phenethyl(trifluoromethyl)sulfane 2d



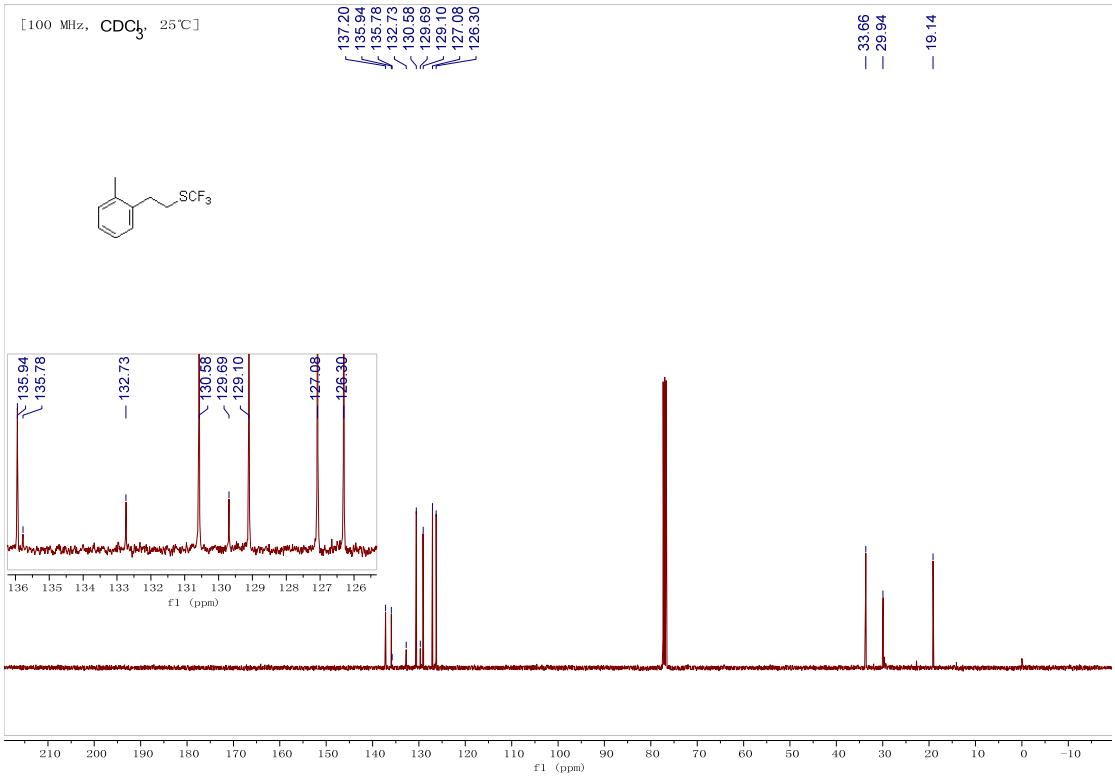
^{1}H NMR spectrum of (2-methylphenethyl)(trifluoromethyl)sulfane 2e



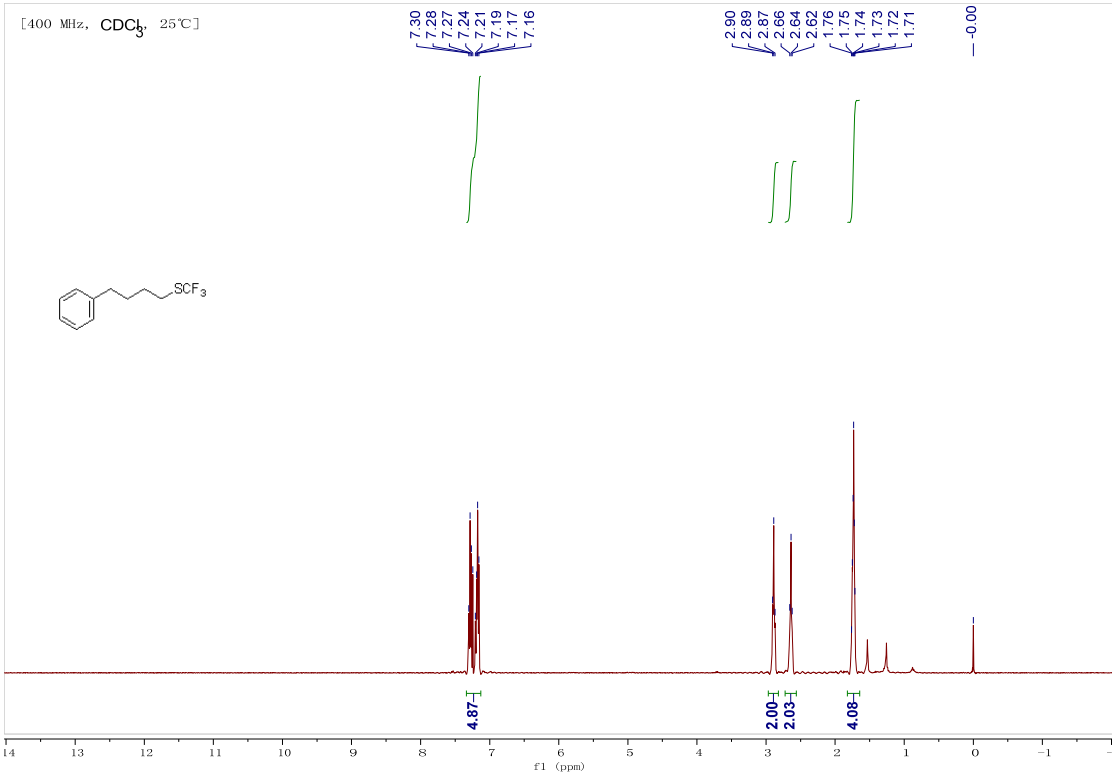
^{19}F NMR spectrum of (2-methylphenethyl)(trifluoromethyl)sulfane 2e



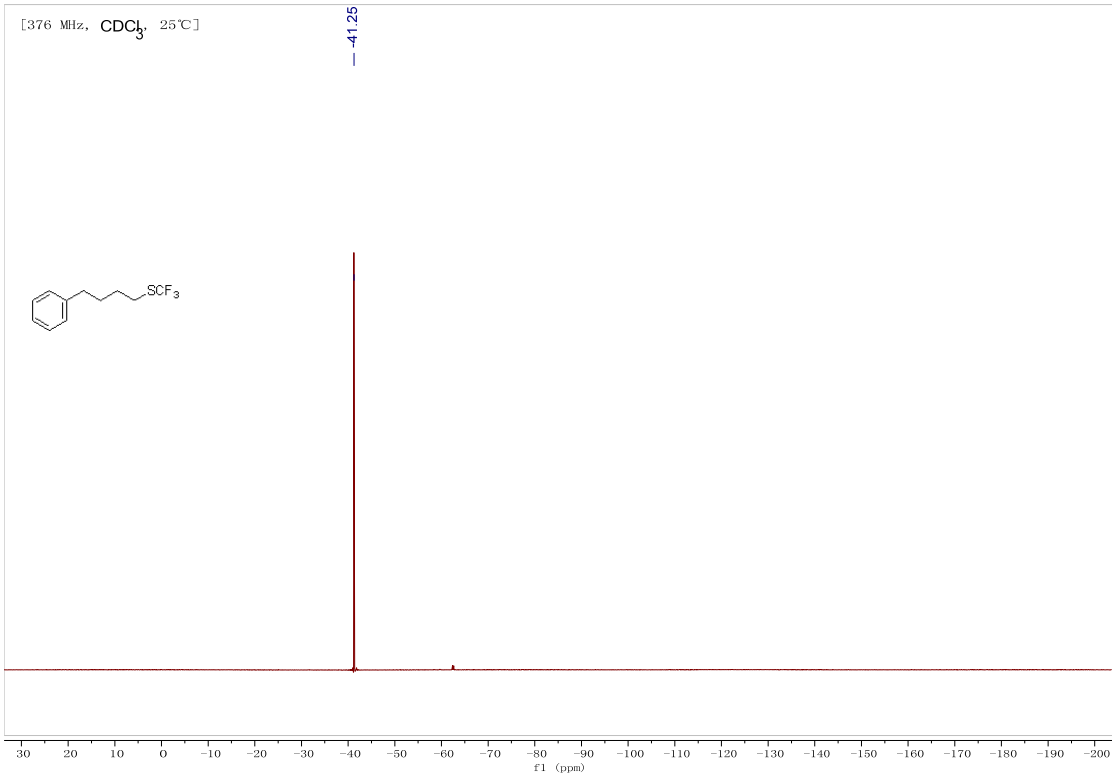
^{13}C NMR spectrum of (2-methylphenethyl)(trifluoromethyl)sulfane 2e



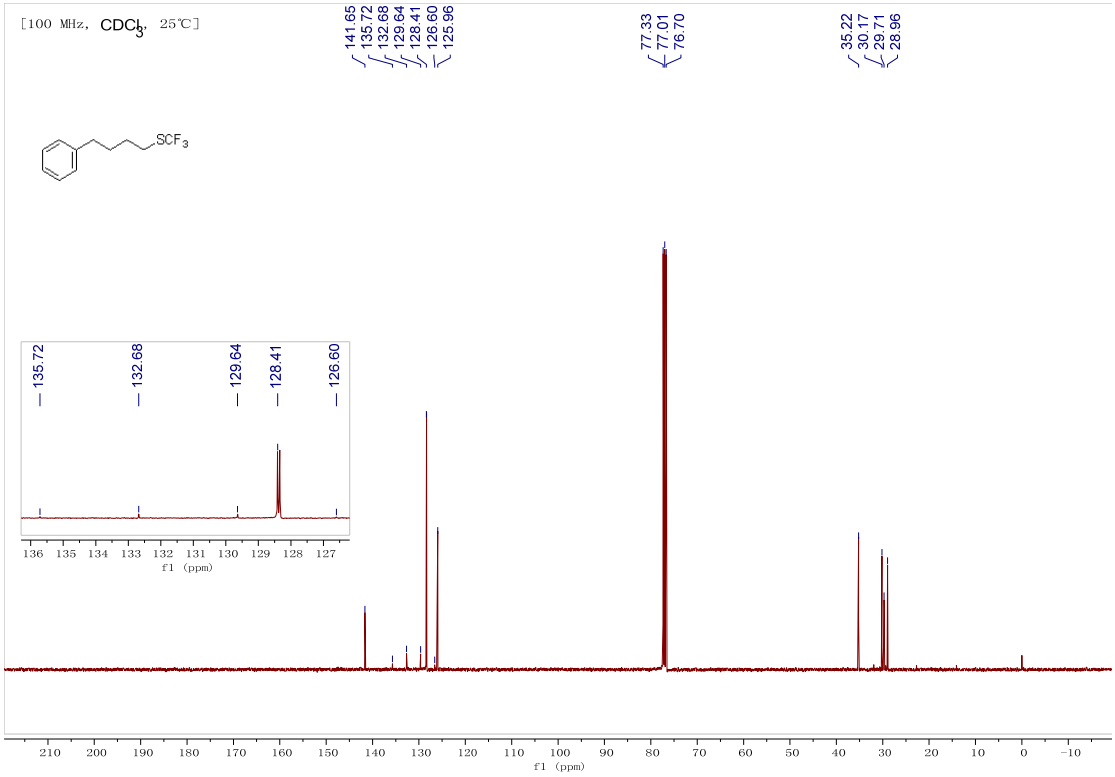
^{1}H NMR spectrum of (4-phenylbutyl)(trifluoromethyl)sulfane 2f



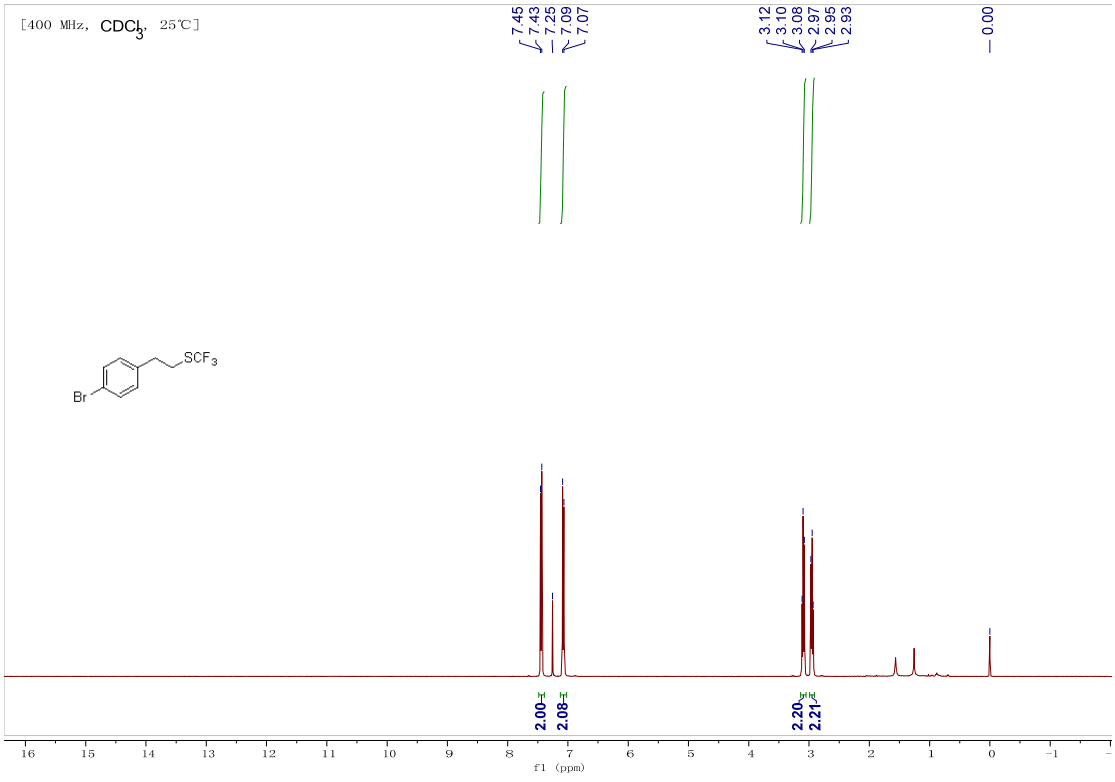
^{19}F NMR spectrum of (4-phenylbutyl)(trifluoromethyl)sulfane 2f



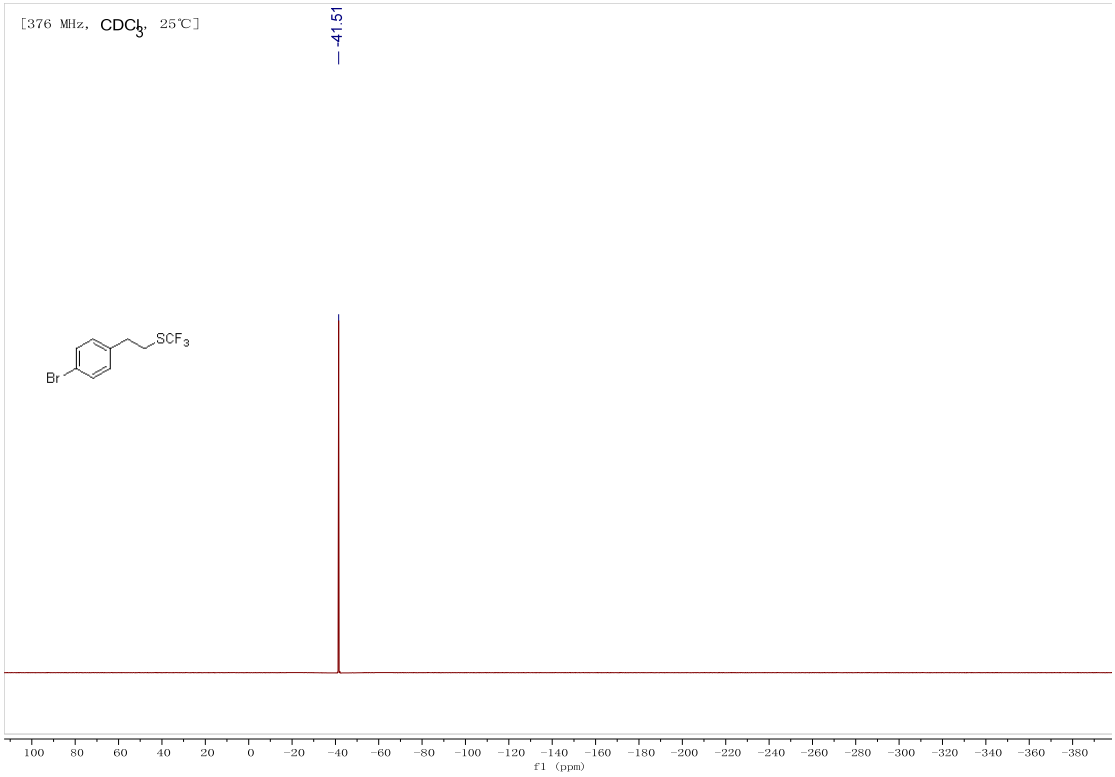
^{13}C NMR spectrum of (4-phenylbutyl)(trifluoromethyl)sulfane 2f



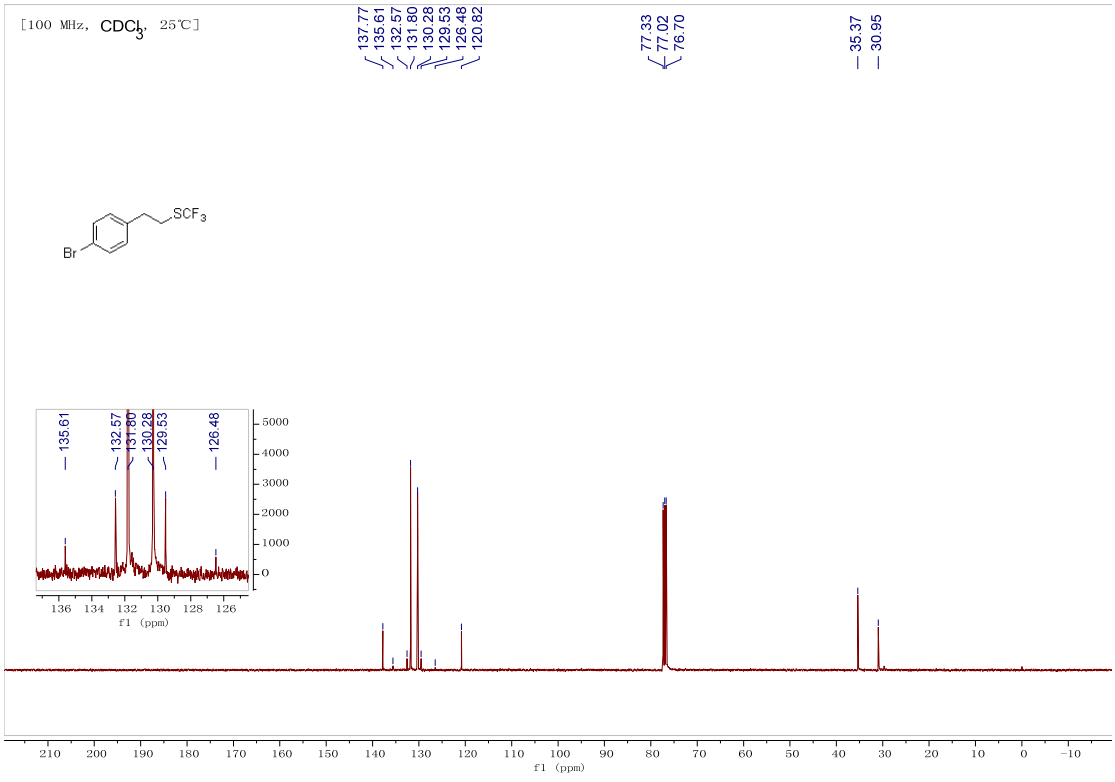
^{1}H NMR spectrum of (4-bromophenethyl)(trifluoromethyl)sulfane 2g



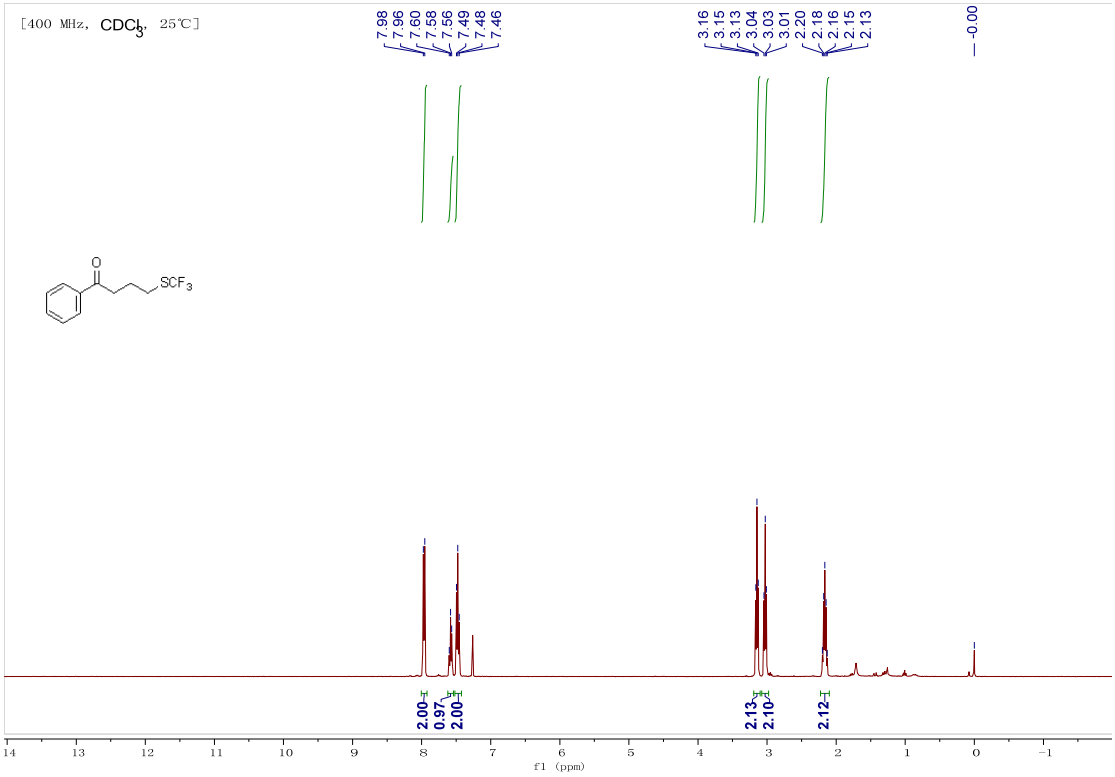
^{19}F NMR spectrum of (4-bromophenethyl)(trifluoromethyl)sulfane 2g



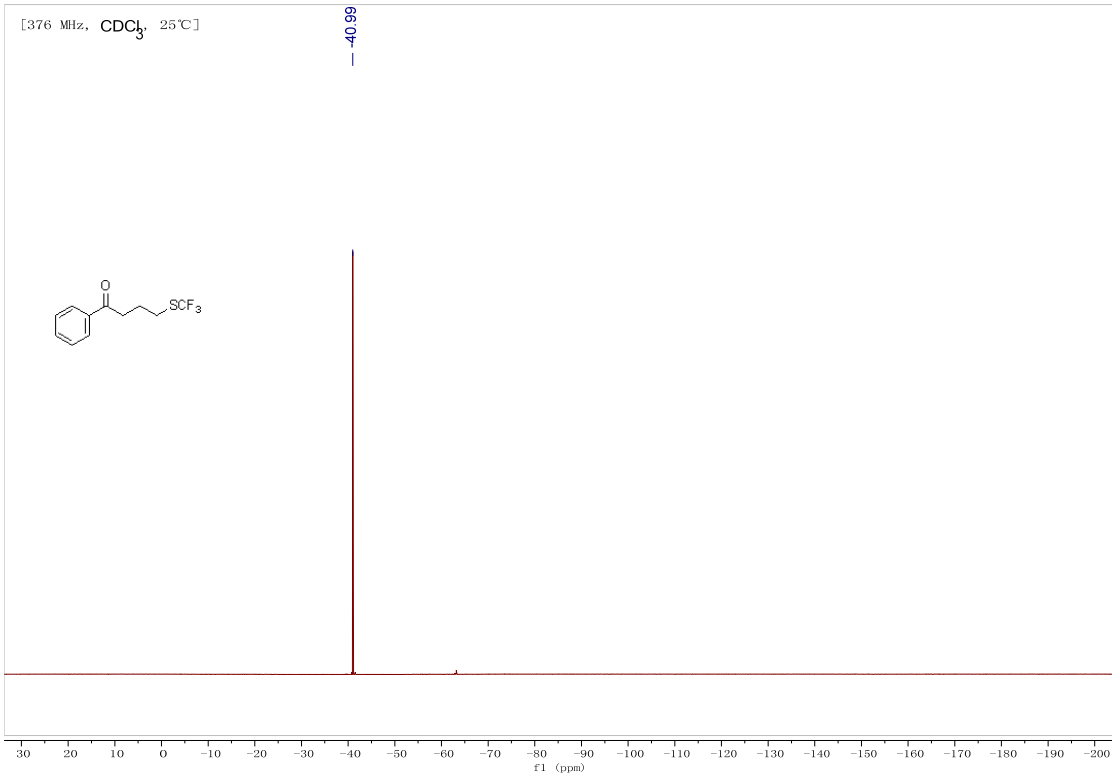
^{13}C NMR spectrum of (4-bromophenethyl)(trifluoromethyl)sulfan 2g



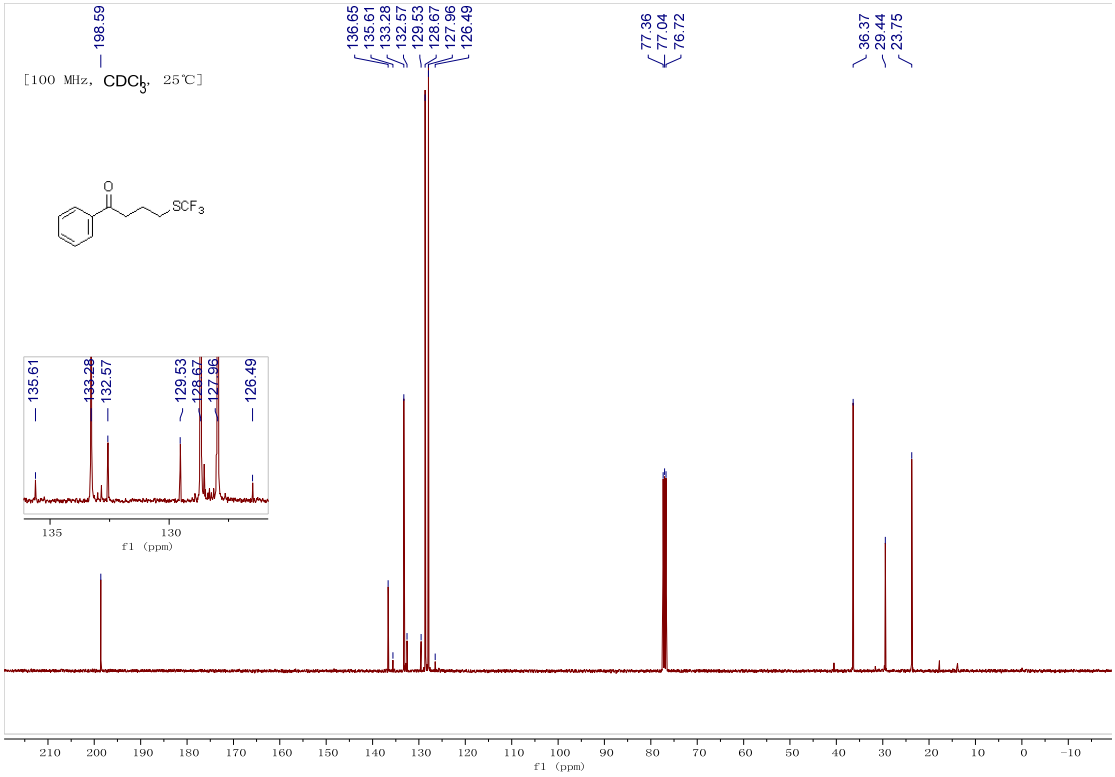
^{1}H NMR spectrum of 1-phenyl-4-((trifluoromethyl)thio)butan-1-one 2h



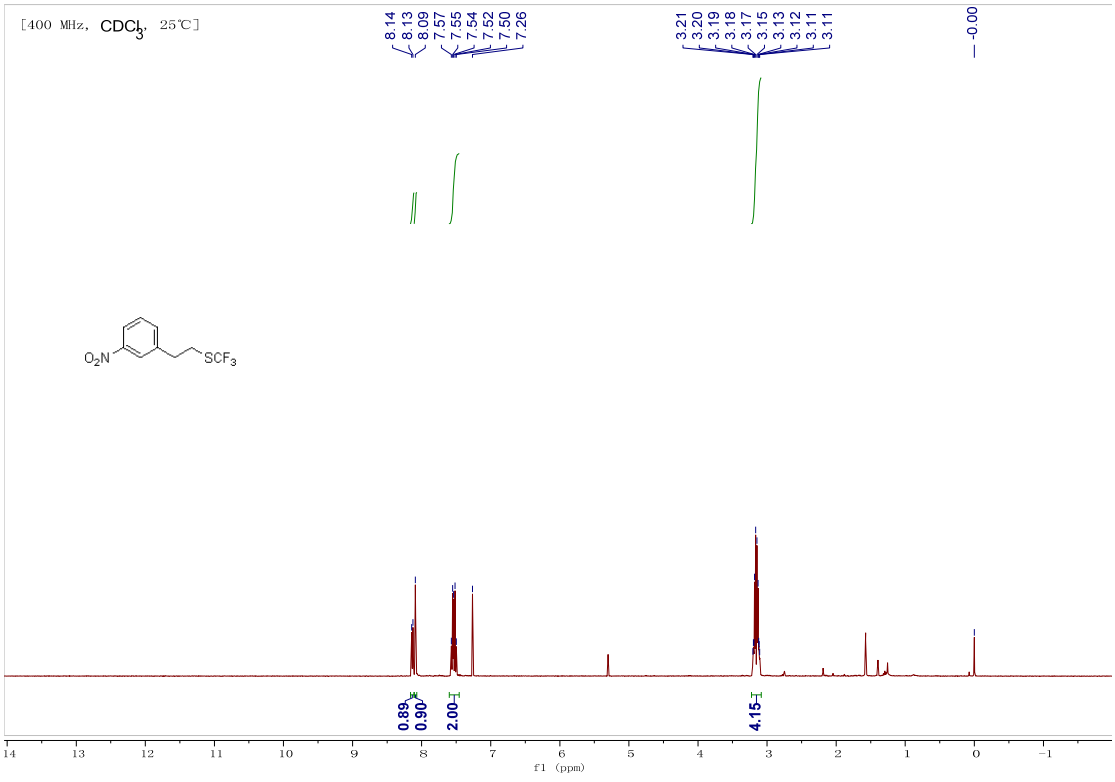
^{19}F NMR spectrum of 1-phenyl-4-((trifluoromethyl)thio)butan-1-one 2h



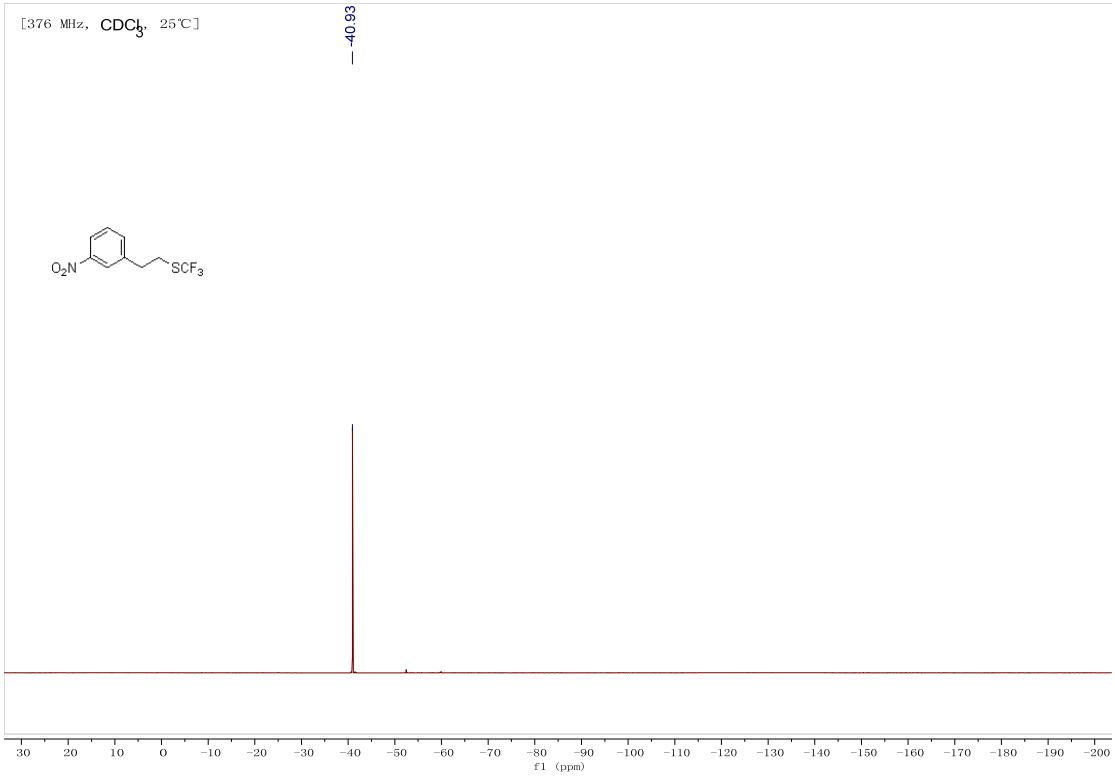
^{13}C NMR spectrum of 1-phenyl-4-((trifluoromethyl)thio)butan-1-one 2h



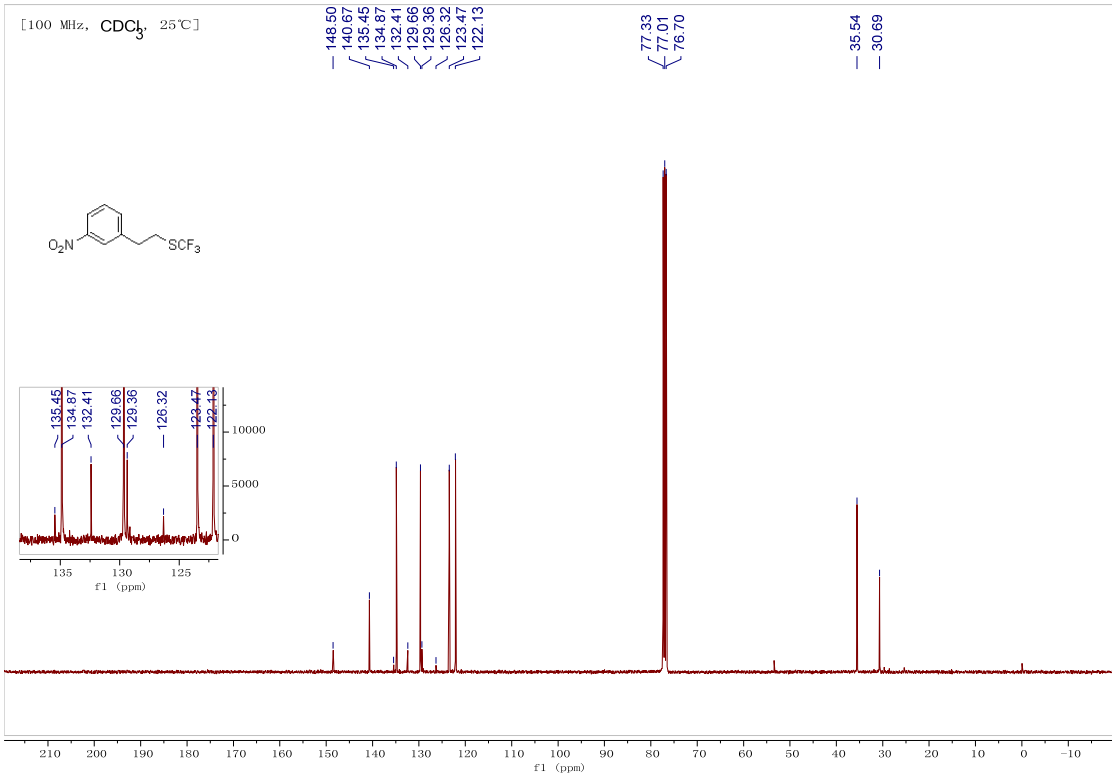
^{1}H NMR spectrum of (3-nitrophenethyl)(trifluoromethyl)sulfane 2i



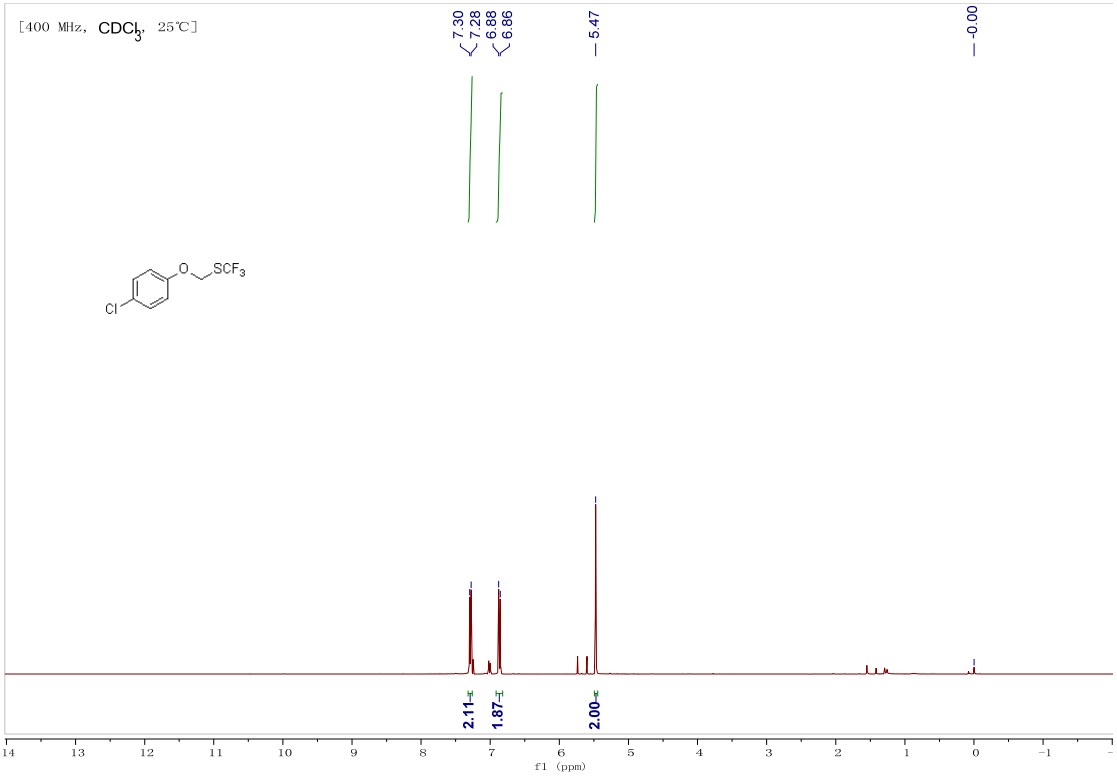
^{19}F NMR spectrum of (3-nitrophenethyl)(trifluoromethyl)sulfane 2i



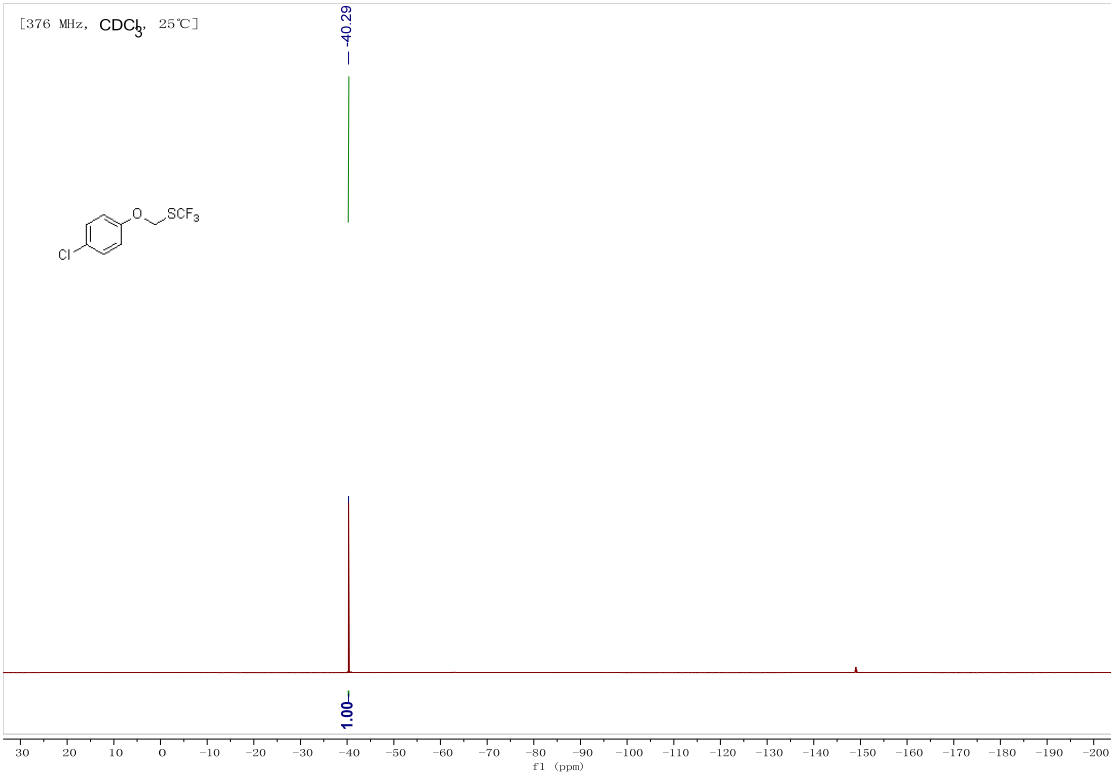
^{13}C NMR spectrum of (3-nitrophenethyl)(trifluoromethyl)sulfane 2i



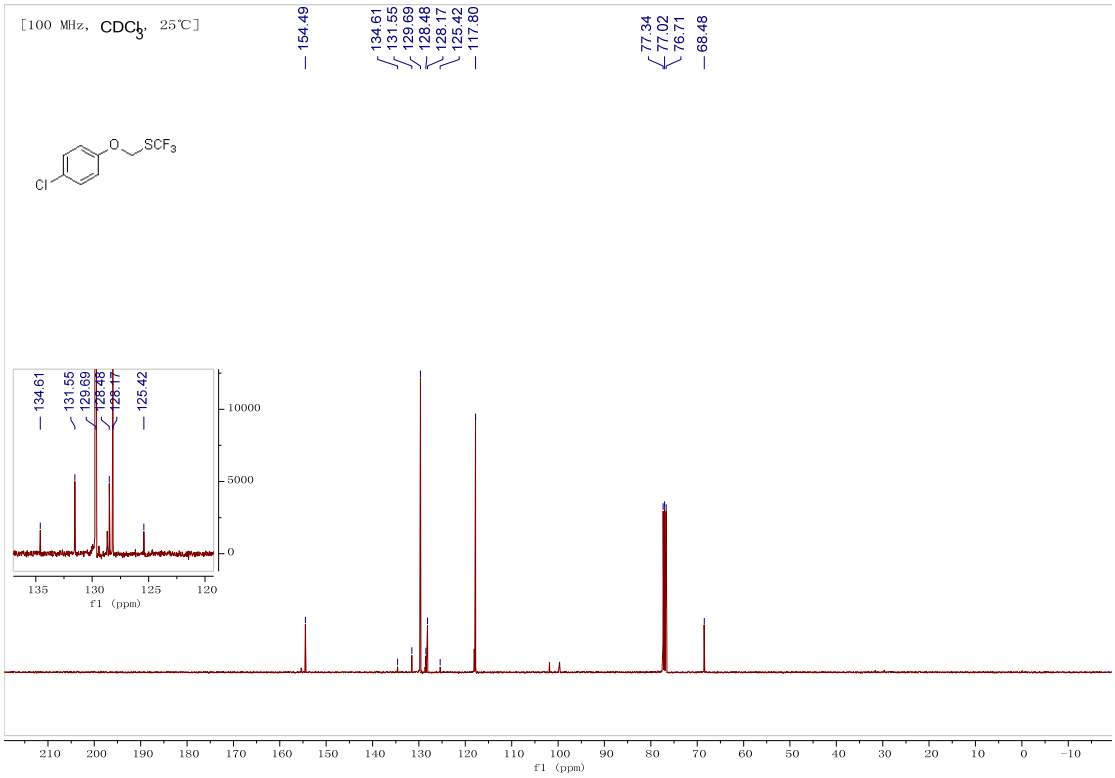
^{1}H NMR spectrum of ((4-chlorophenoxy)methyl)(trifluoromethyl)sulfane 2j



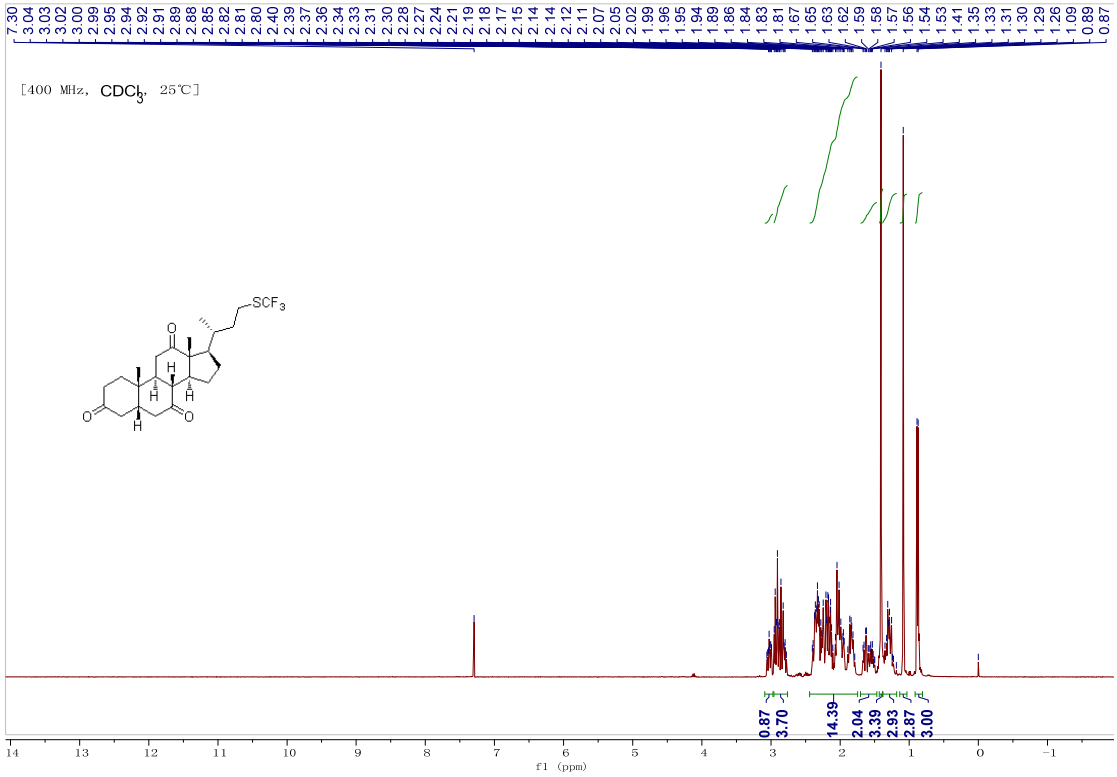
^{19}F NMR spectrum of ((4-chlorophenoxy)methyl)(trifluoromethyl)sulfane 2j



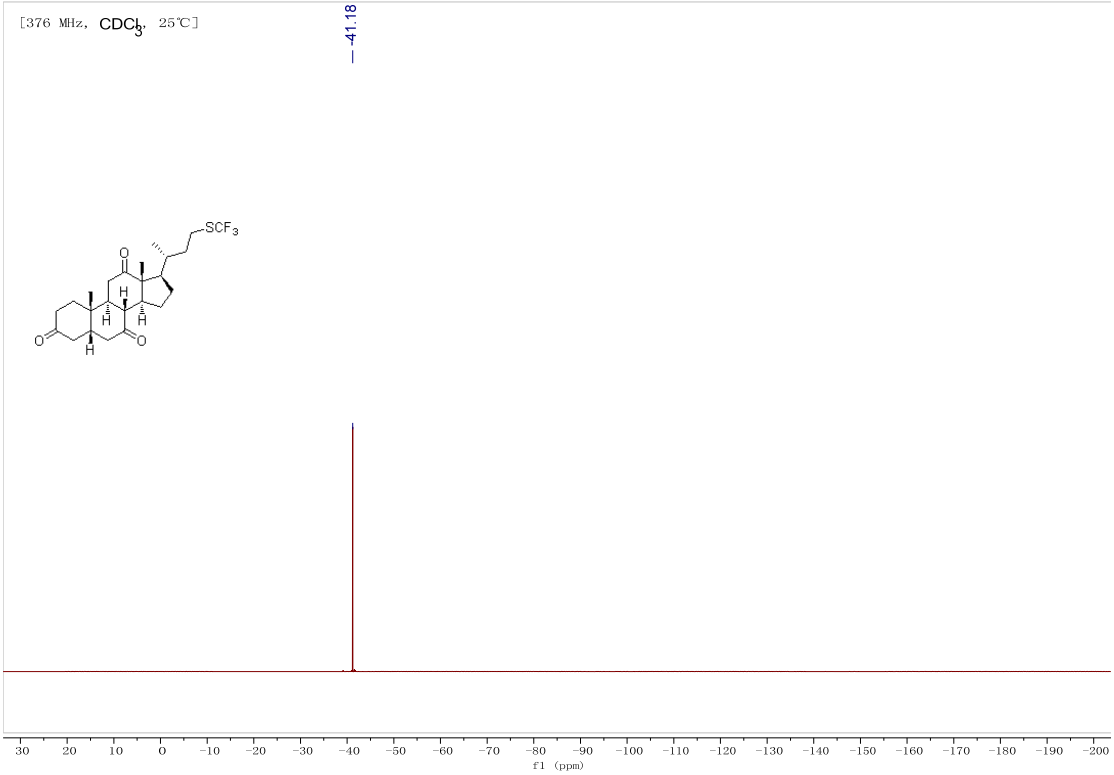
^{13}C NMR spectrum of ((4-chlorophenoxy)methyl)(trifluoromethyl)sulfane 2j



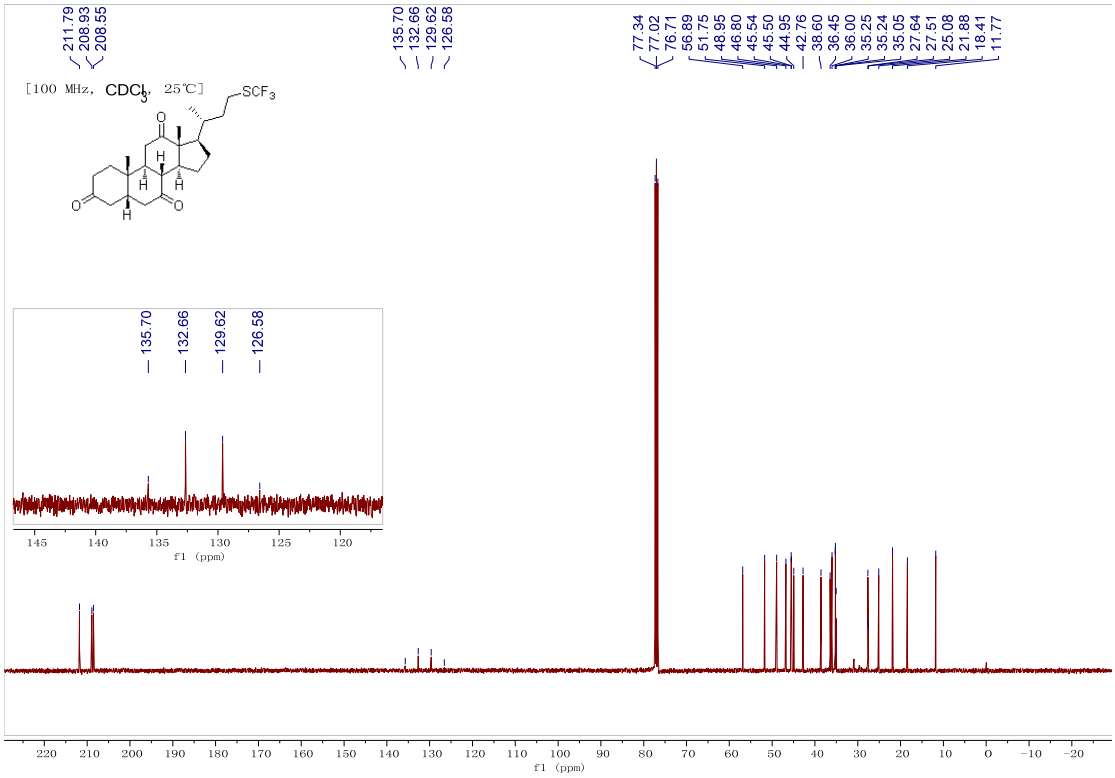
^{1}H NMR spectrum of (5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-4-((trifluoromethyl)thio)butan-2-yl)decahydro-1H-cyclopenta[a]phenanthrene-3,7,12(2H,4H,8H)-trione 2k



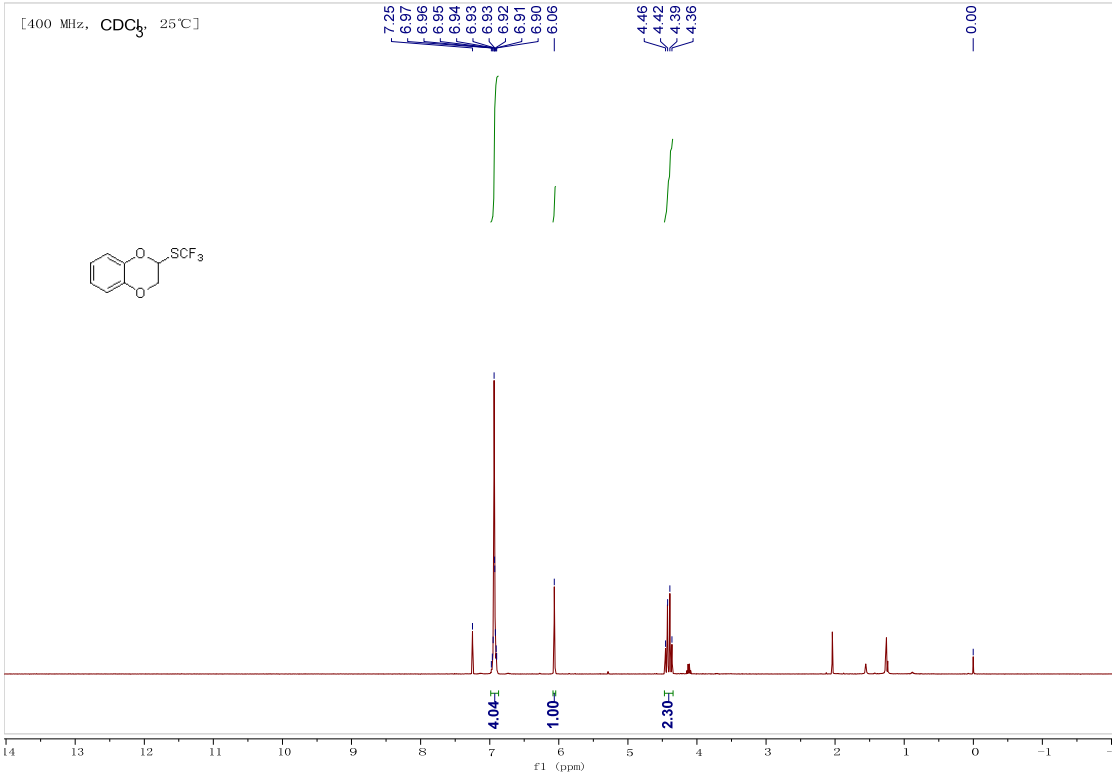
^{19}F NMR spectrum of (5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-4-((trifluoromethyl)thio)butan-2-yl)decahydro-1H-cyclopenta[a]phenanthrene-3,7,12(2H,4H,8H)-trione 2k



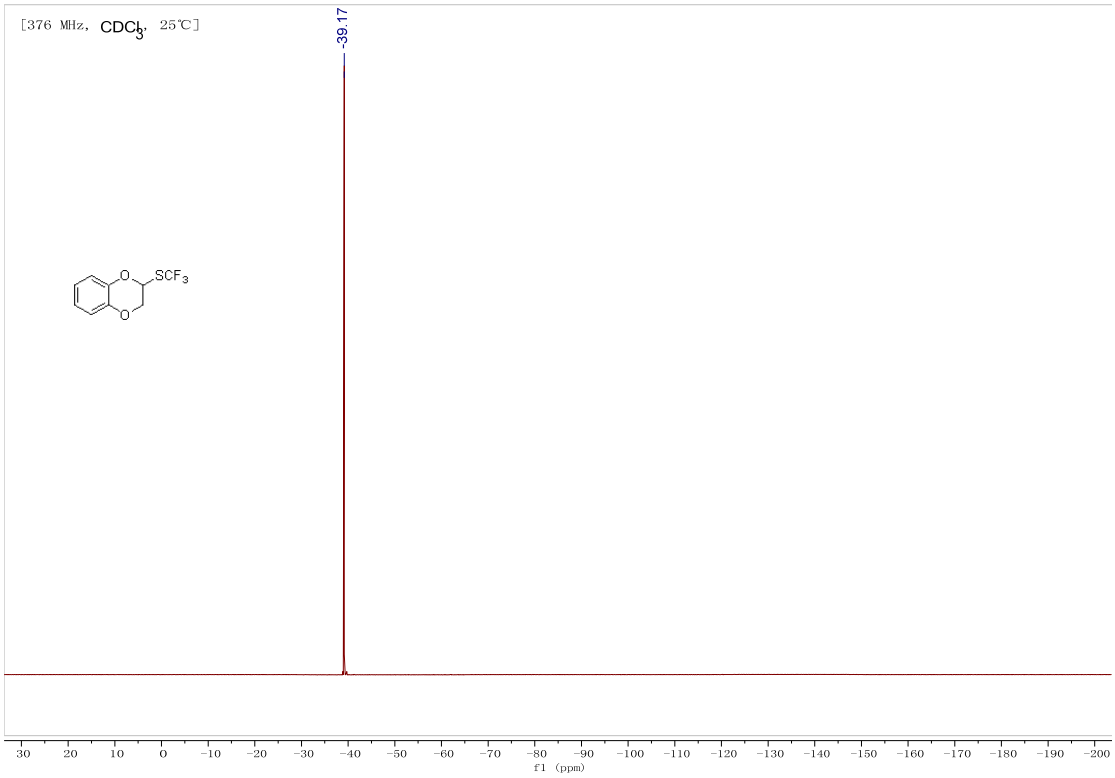
^{13}C NMR spectrum of (5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-4-((trifluoromethyl)thio)butan-2-yl)decahydro-1H-cyclopenta[a]phenanthrene-3,7,12(2H,4H,8H)-trione 2k



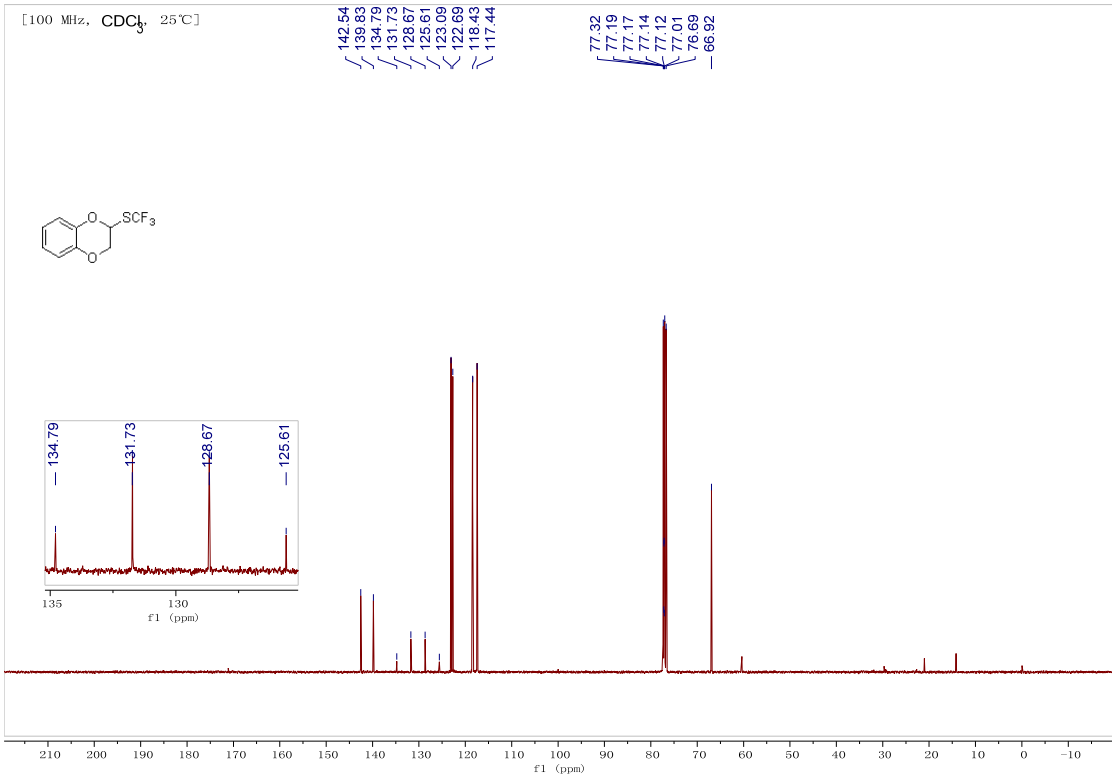
^{1}H NMR spectrum of 2-((trifluoromethyl)thio)-2,3-dihydrobenzo[b][1,4]dioxine 2l



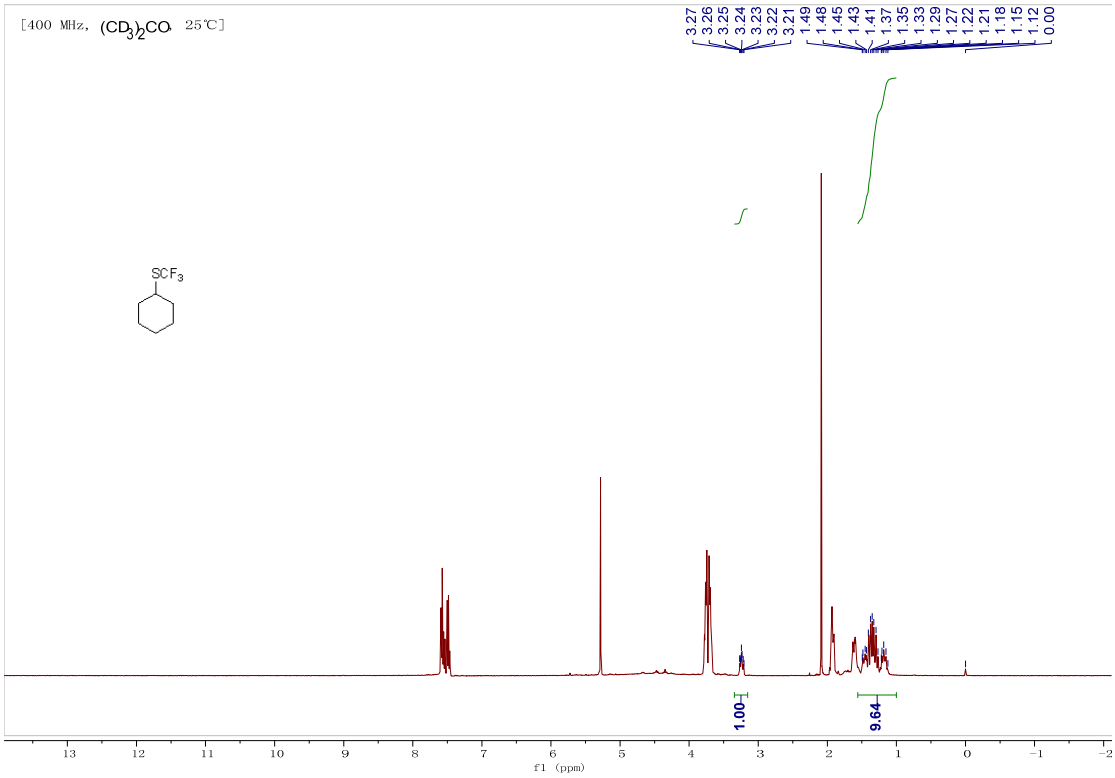
^{19}F NMR spectrum of 2-((trifluoromethyl)thio)-2,3-dihydrobenzo[b][1,4]dioxine 2l



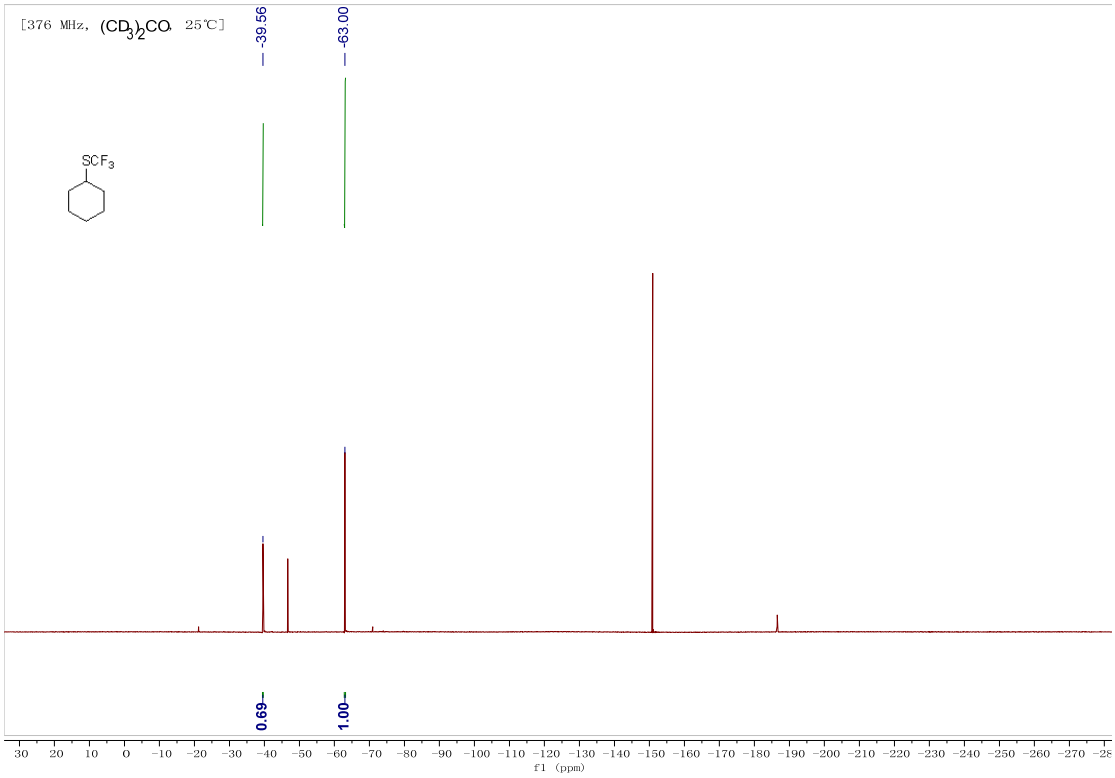
^{13}C NMR spectrum of 2-((trifluoromethyl)thio)-2,3-dihydrobenzo[b][1,4]dioxine 2l



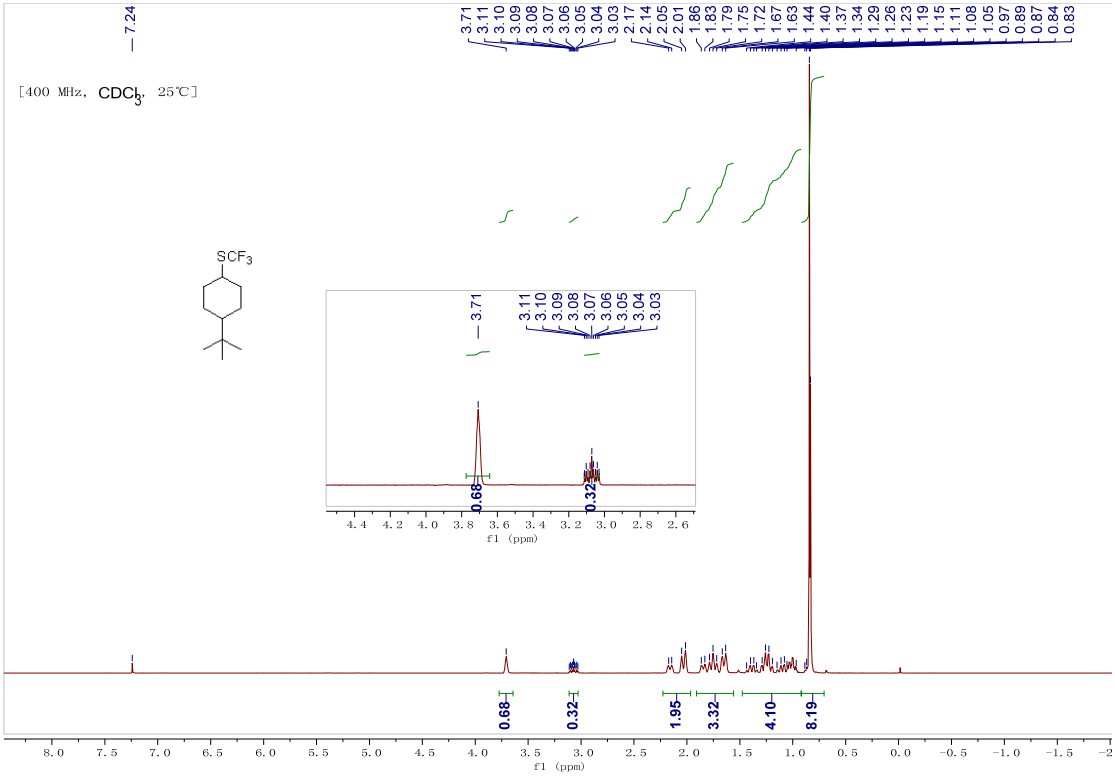
Crude ^{1}H NMR spectrum of cyclohexyl(trifluoromethyl)sulfane 2m



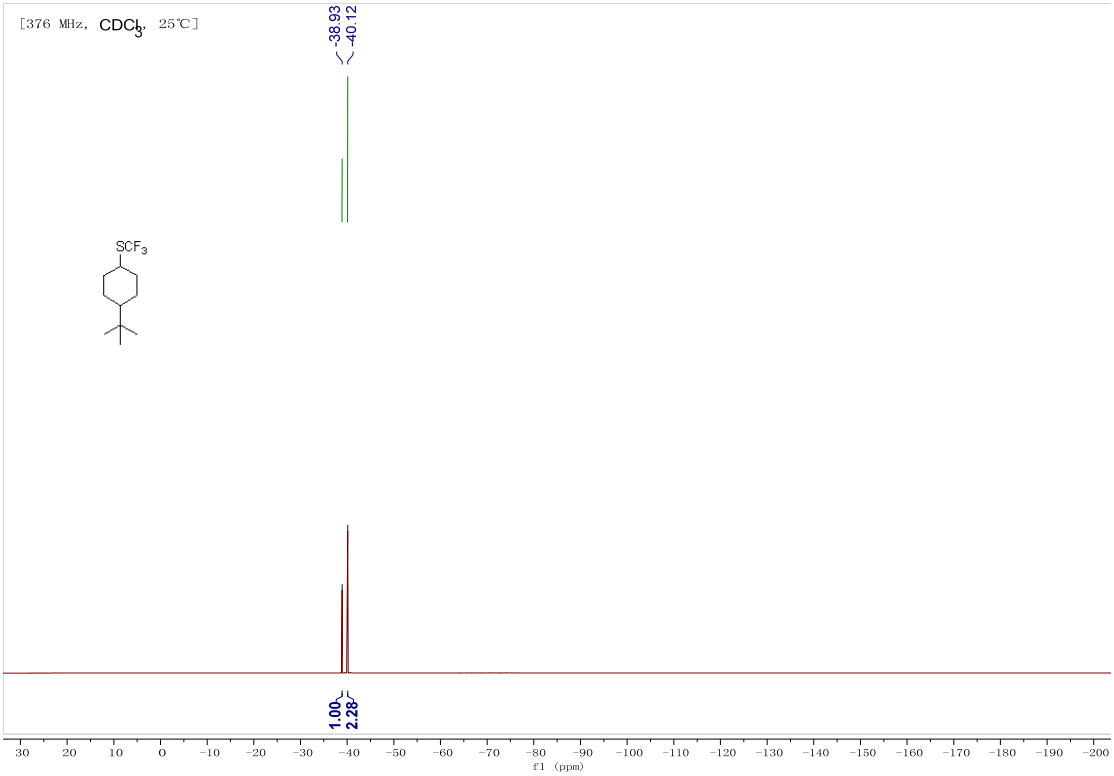
Crude ^{19}F NMR spectrum of cyclohexyl(trifluoromethyl)sulfane 2m



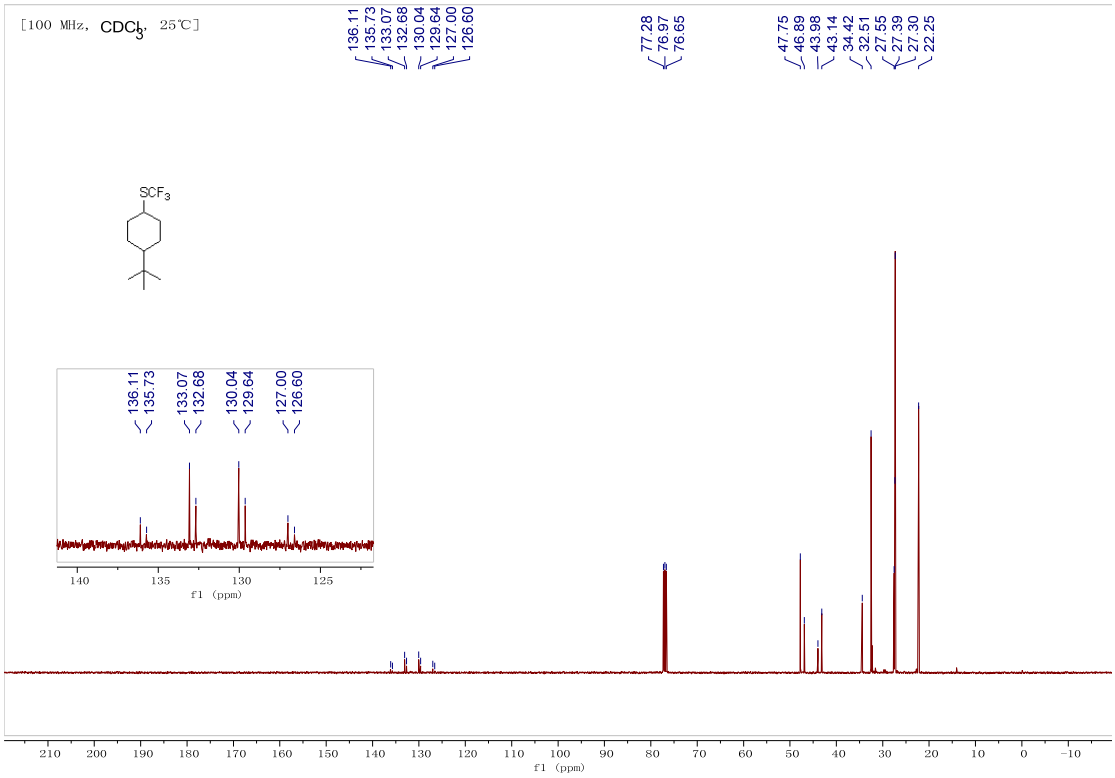
^{1}H NMR spectrum of (4-(tert-butyl)cyclohexyl)(trifluoromethyl)sulfane 2n



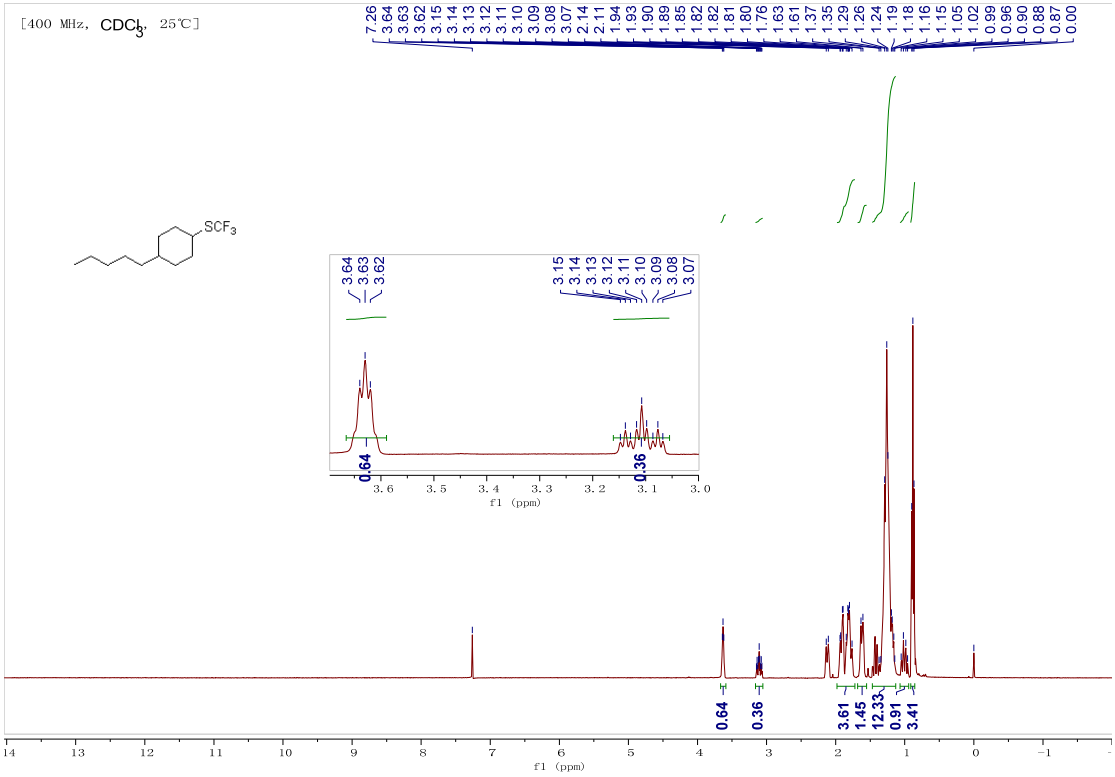
^{19}F NMR spectrum of (4-(tert-butyl)cyclohexyl)(trifluoromethyl)sulfane 2n



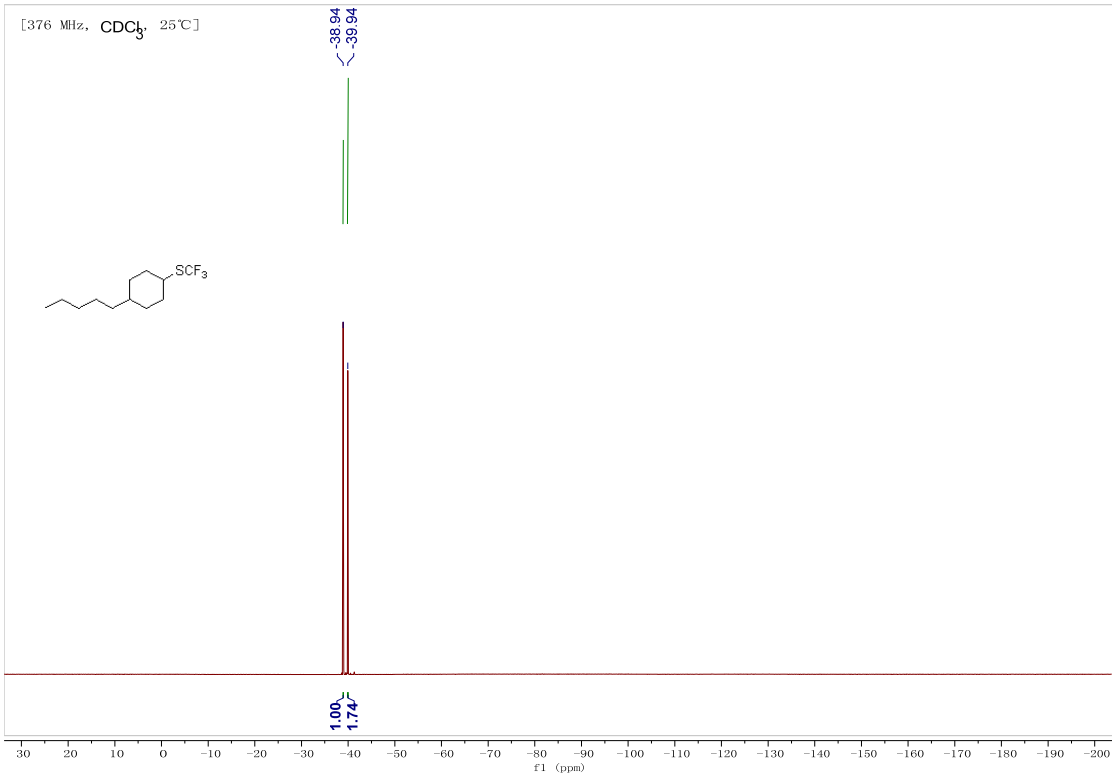
^{13}C NMR spectrum of (4-(tert-butyl)cyclohexyl)(trifluoromethyl)sulfane 2n



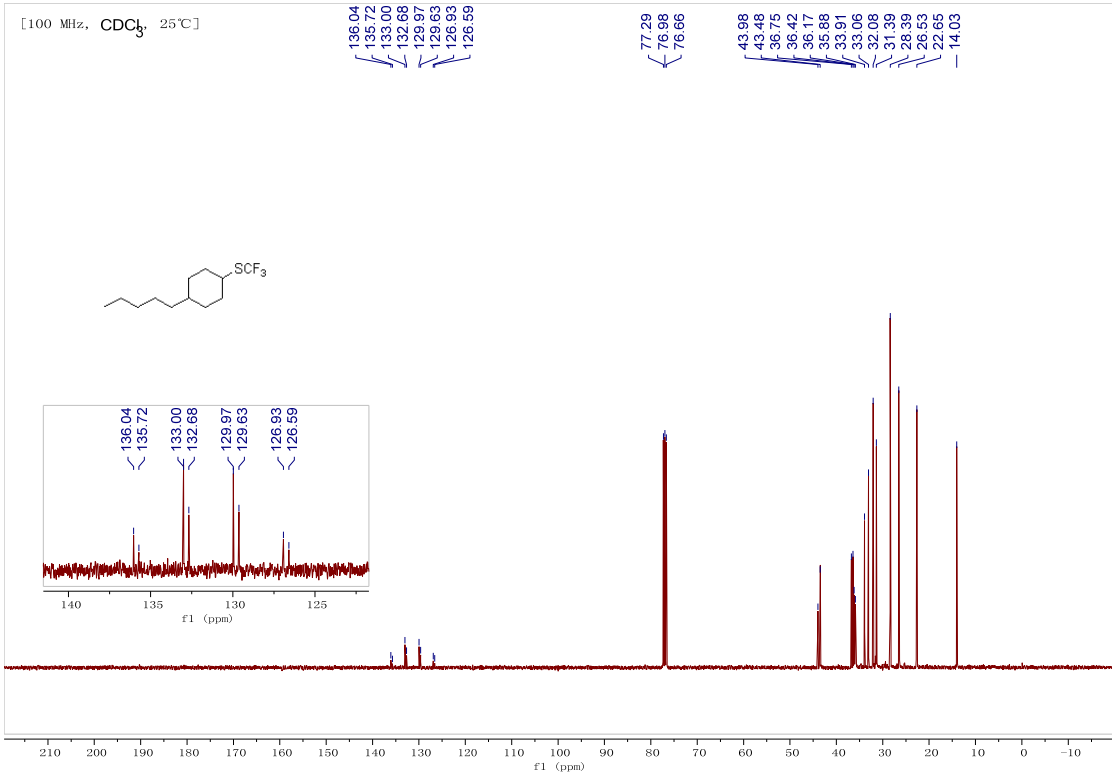
^{1}H NMR spectrum of (4-pentylcyclohexyl)(trifluoromethyl)sulfane 2o



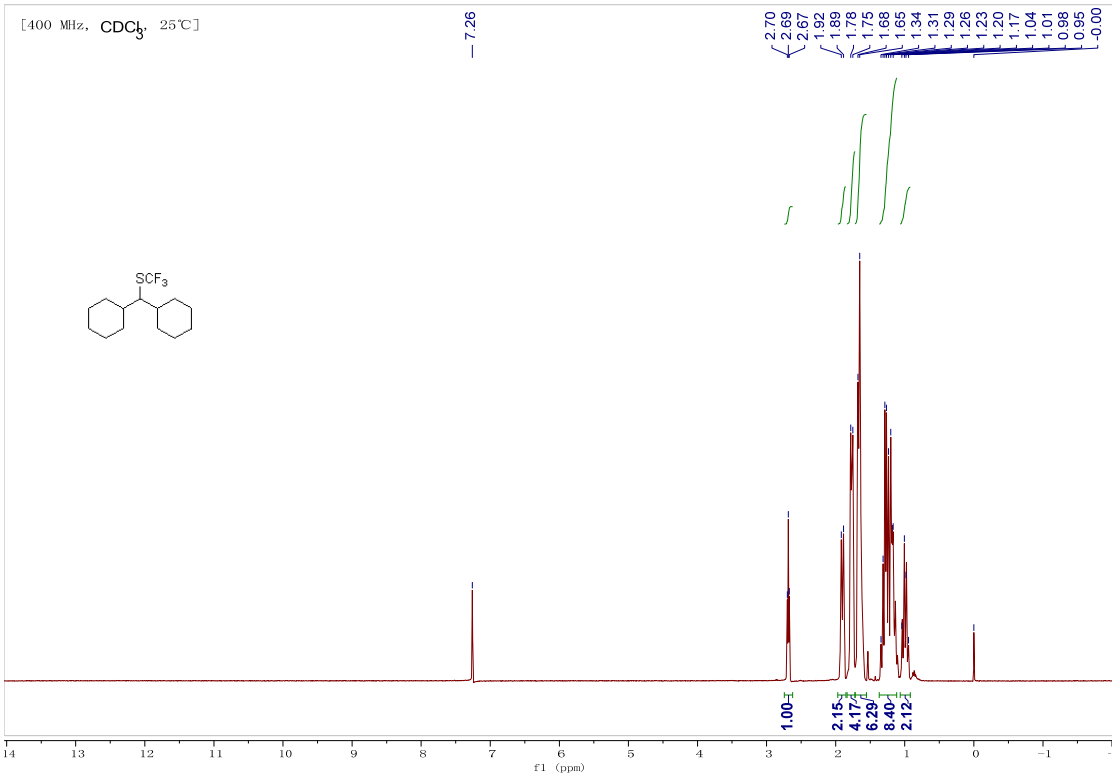
^{19}F NMR spectrum of (4-pentylcyclohexyl)(trifluoromethyl)sulfane 2o



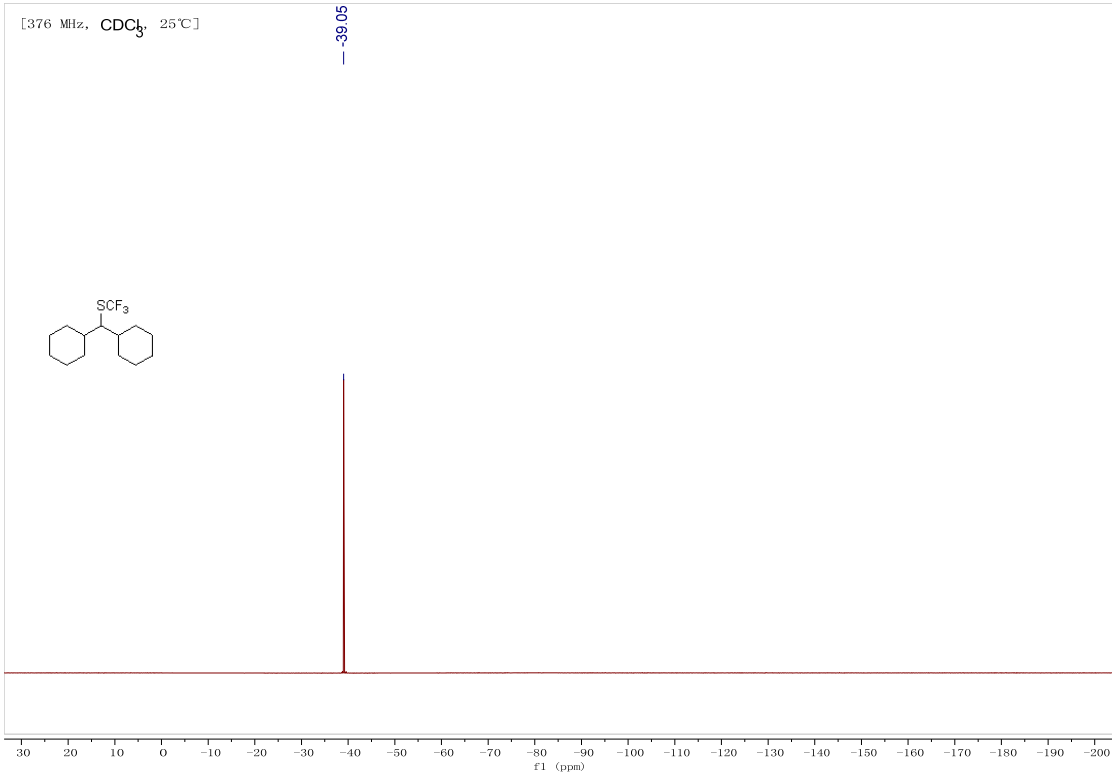
^{13}C NMR spectrum of (4-pentylcyclohexyl)(trifluoromethyl)sulfane 2o



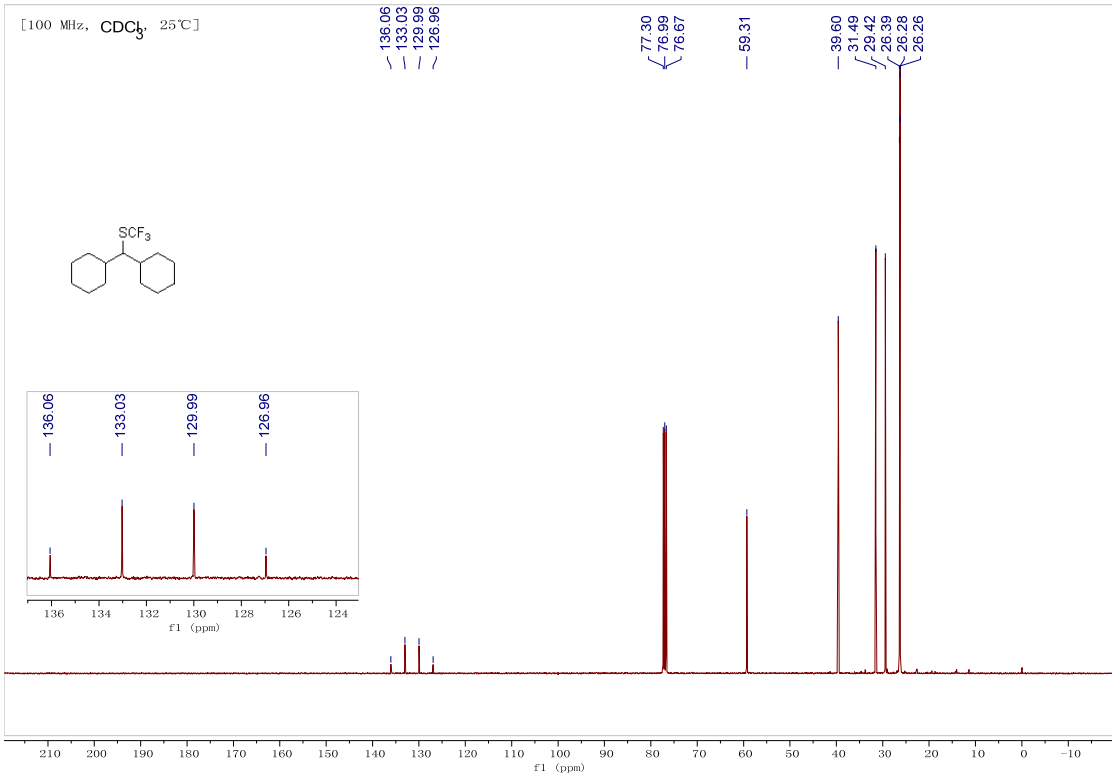
^{1}H NMR spectrum of (dicyclohexylmethyl)(trifluoromethyl)sulfane 2p



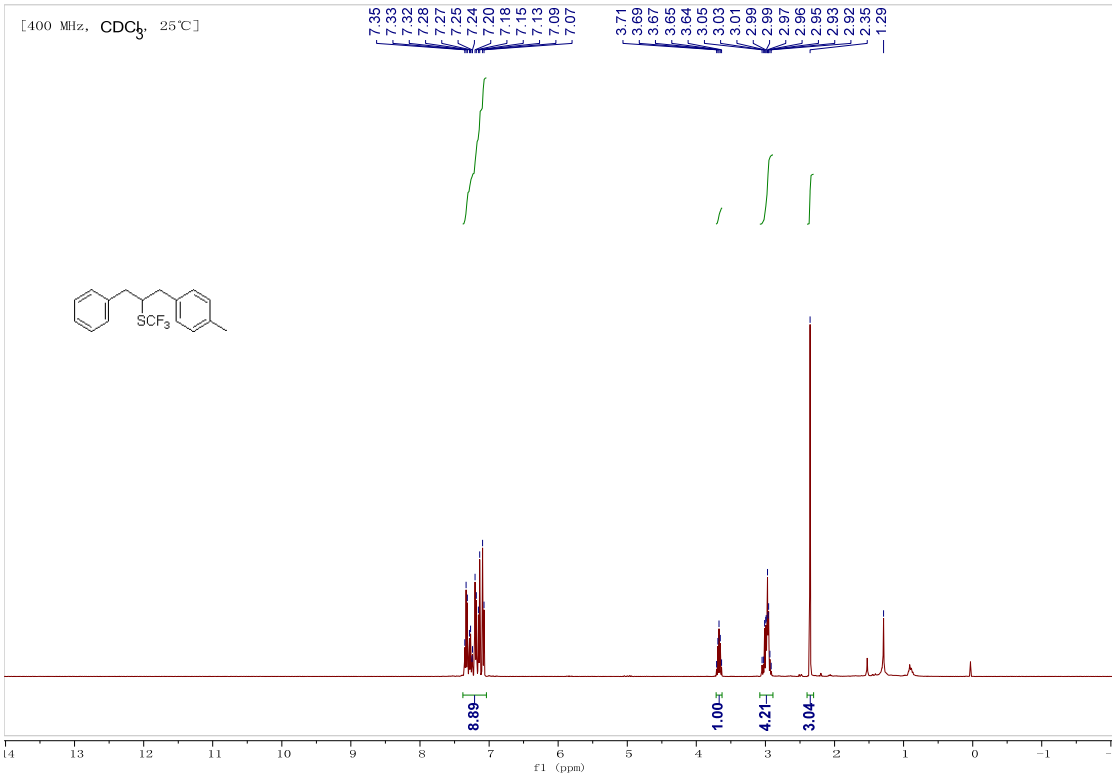
^{19}F NMR spectrum of (dicyclohexylmethyl)(trifluoromethyl)sulfane 2p



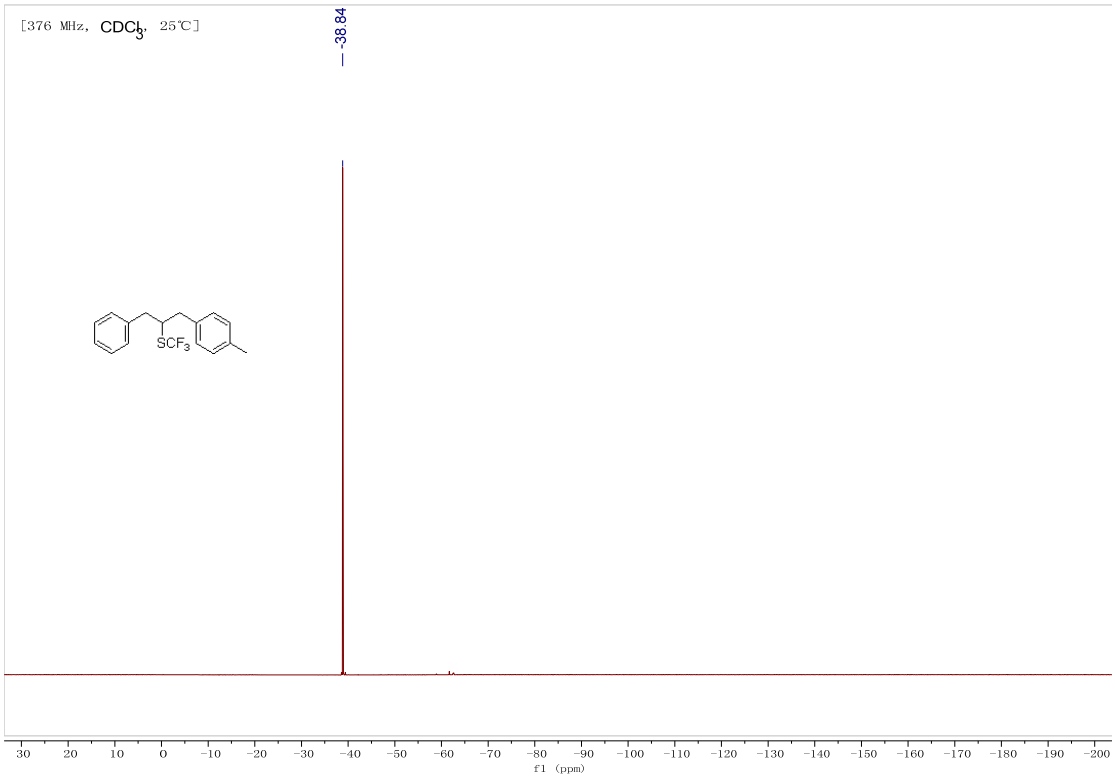
^{13}C NMR spectrum of (dicyclohexylmethyl)(trifluoromethyl)sulfane 2p



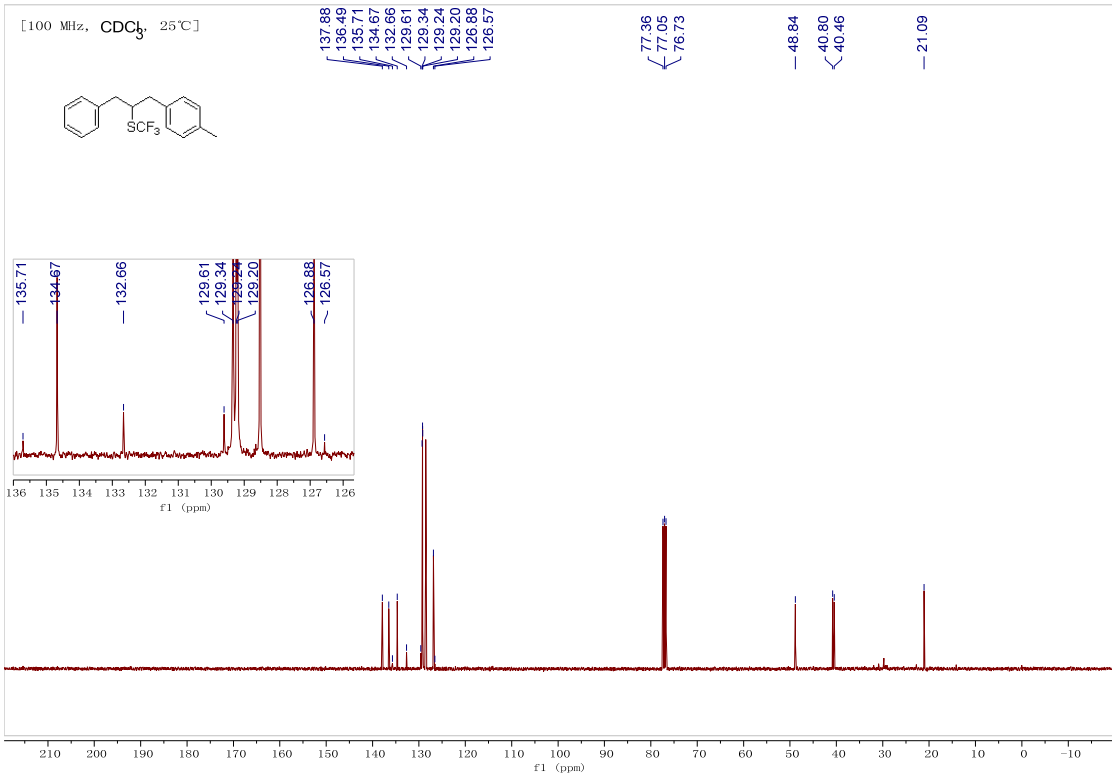
^{1}H NMR spectrum of (1-phenyl-3-(p-tolyl)propan-2-yl)(trifluoromethyl)sulfane 2q



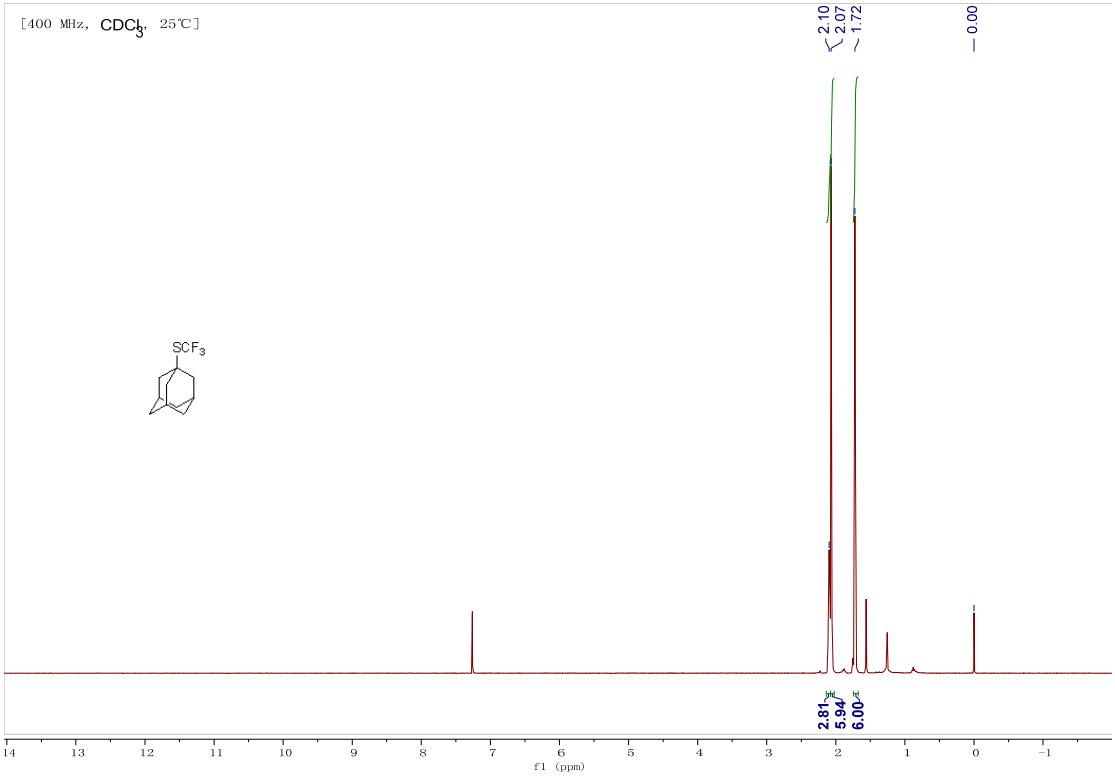
^{19}F NMR spectrum of (1-phenyl-3-(p-tolyl)propan-2-yl)(trifluoromethyl)sulfane 2q



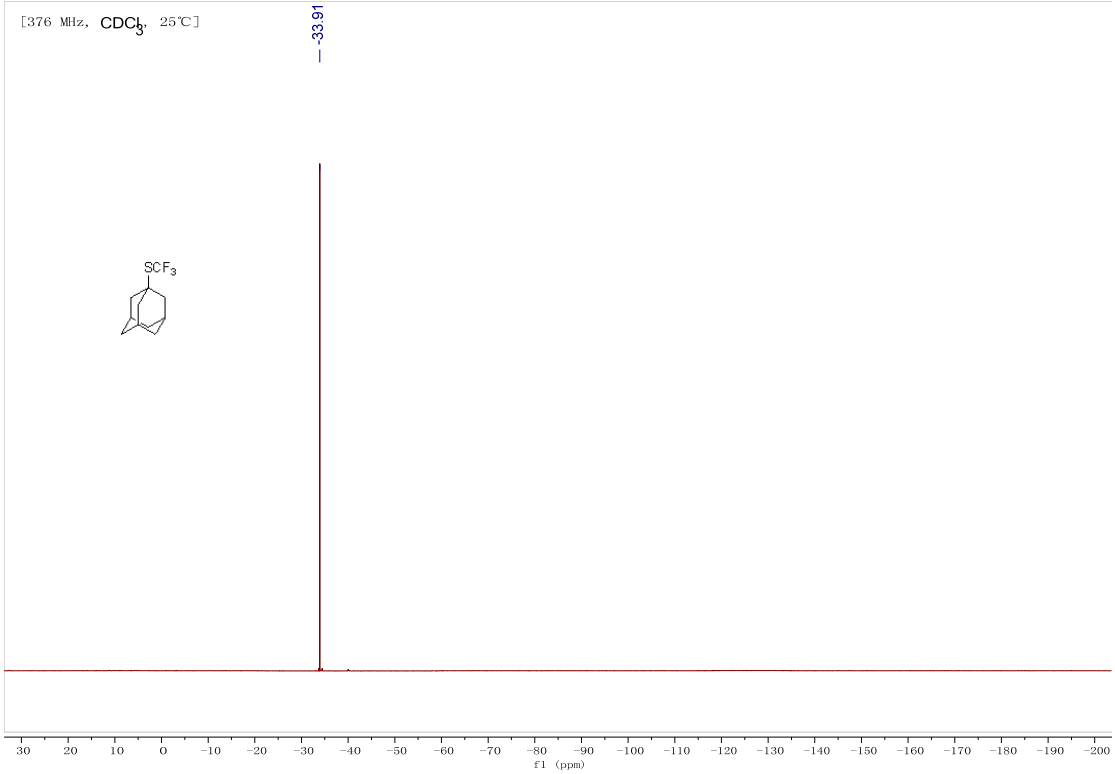
^{13}C NMR spectrum of (1-phenyl-3-(p-tolyl)propan-2-yl)(trifluoromethyl)sulfane 2q



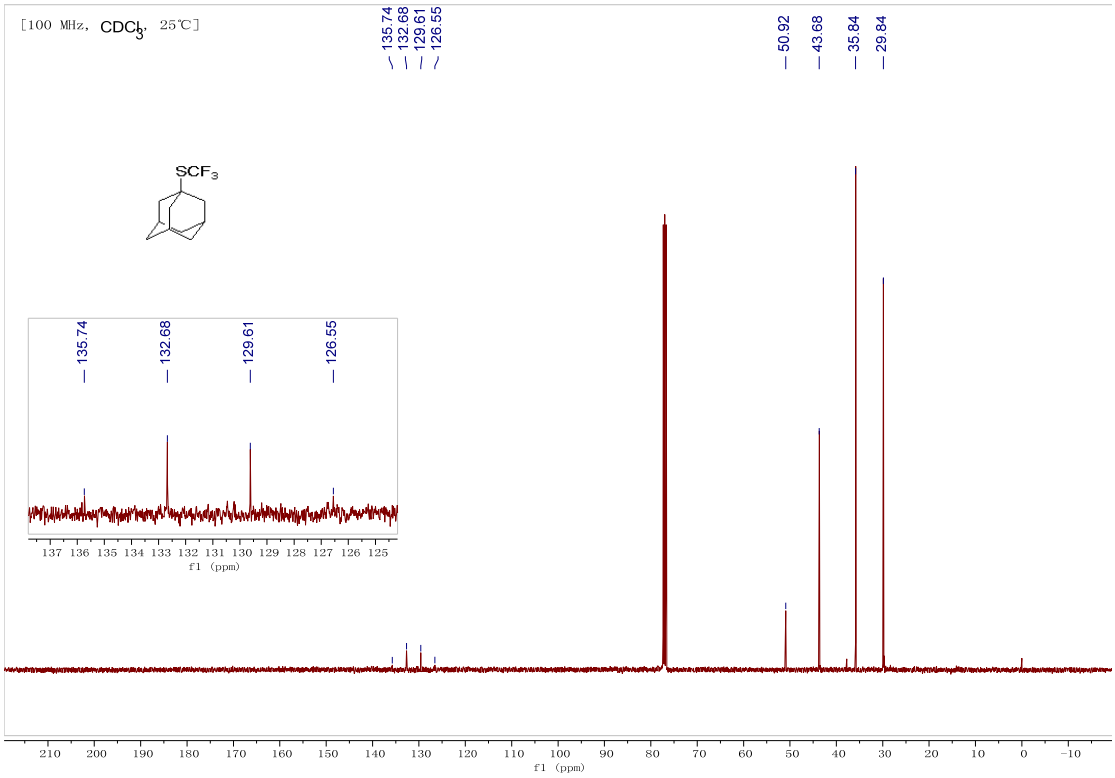
^{1}H NMR spectrum of (3s,5s,7s)-adamantan-1-yl(trifluoromethyl)sulfane 2r



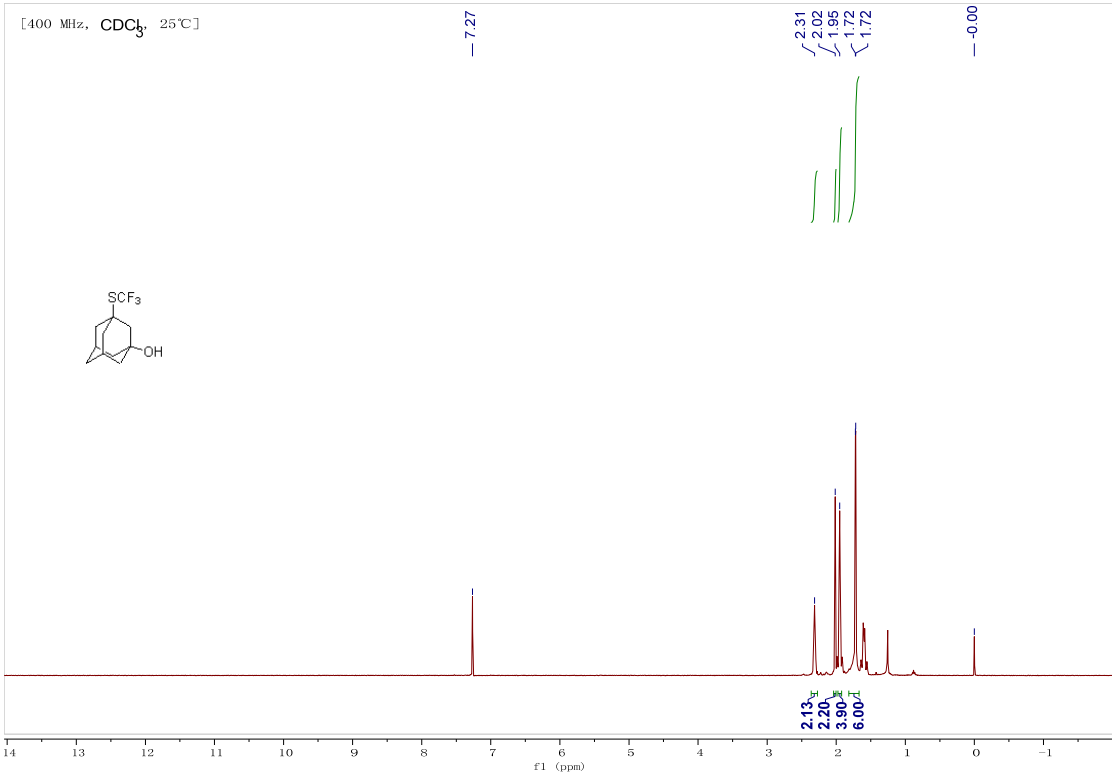
^{19}F NMR spectrum of (3s,5s,7s)-adamantan-1-yl(trifluoromethyl)sulfane 2r



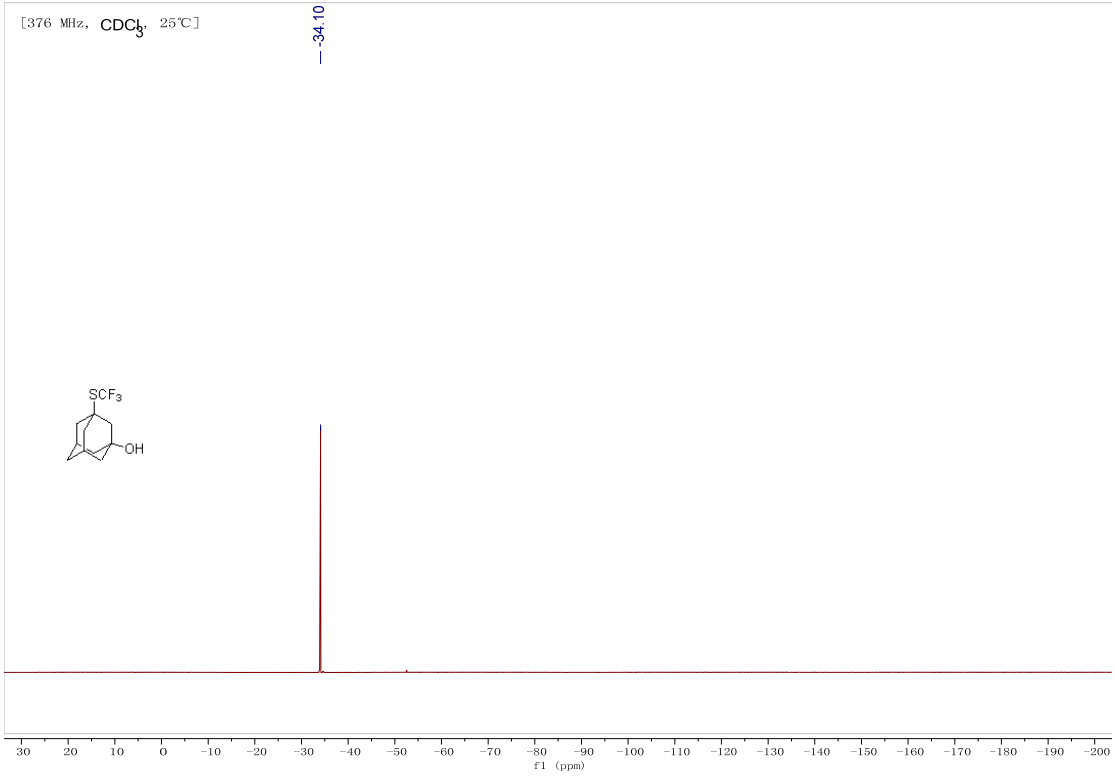
^{13}C NMR spectrum of (3s,5s,7s)-adamantan-1-yl(trifluoromethyl)sulfane 2r



^{1}H NMR spectrum of (1r,3s,5R,7S)-3-((trifluoromethyl)thio)adamantan-1-ol 2s



^{19}F NMR spectrum of (1r,3s,5R,7S)-3-((trifluoromethyl)thio)adamantan-1-ol 2s



^{13}C NMR spectrum of (1r,3s,5R,7S)-3-((trifluoromethyl)thio)adamantan-1-ol 2s