Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Practical and Regioselective Halo-Trifluoromethylthiolation of Sulfur Ylides

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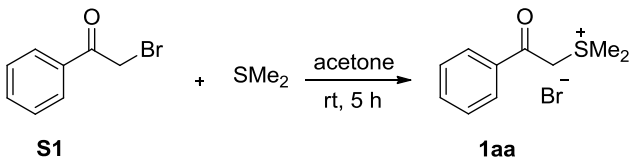
I. General

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz. ^{1}H NMR spectra were referenced to tetramethylsilane (s, 0.00 ppm) using $CDCl_3$, $(CD_3)_2SO$ and CD_3OD as solvent. ^{13}C NMR spectra were referenced to solvent carbons (77.16 ppm for $CDCl_3$, 39.52 ppm for $(CD_3)_2SO$ and 49.00 ppm for CD_3OD). ^{19}F NMR spectra were referenced to 2% perfluorobenzene (s, -164.90 ppm) in $CDCl_3$. Glassware was dried at 120 ^{o}C for at least 3 hours and cooled under an argon atmosphere before used. Unless otherwise indicated, all reagents were obtained from commercial suppliers and used without prior purification. THF, $CHCl_3$, PhMe, EtOAc, DMF, and MeCN were dried and freshly distilled prior to use. $SOCl_2$ and $(COCl)_2$ was distilled prior to use. Flash chromatography was performed on silica gel (200 - 300 mesh) with either EtOAc/petroleum ether (PE, 60-90 ^{o}C). High-resolution mass spectrometry (HRMS) were recorded on a Waters Micromass GCT Premier or Thermo Fisher Scientific LTQ FT Ultra, or a Asilent LCMS-1100 spectrometer. HPLC purification were performed on SHIMADZU SIL-20A.

Trifluoromethylthiolation reagents **2a**[1-2] were prepared according to reported procedures.

II. Synthesis of substrates



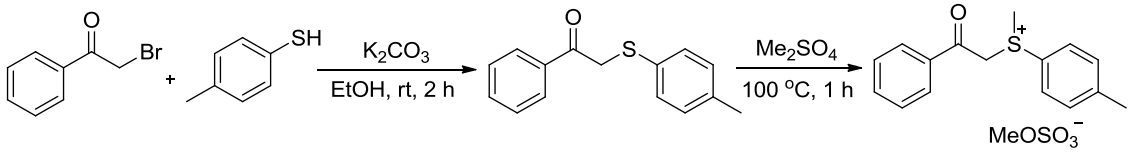
S1 **1aa**

Dimethyl(2-oxo-2-phenylethyl)sulfonium bromide (1aa)[3]

Dimethyl sulfide (0.31 g, 5.0 mmol) was added to a solution of 2-bromoacetophenone (1.0 g, 5.0 mmol) in acetone (1.0 mL). After the mixture had been stirred for 5 h, the residue was filtered and washed with Et_2O. The desired product **1aa** was obtained as a white solid in 90% yield (1.17 g, 4.5 mmol).

Melting point: 150-152 ^oC

^1H NMR (400 MHz, CD_3OD) δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 4.90 (s, 2H), 3.01 (d, *J* = 22.8 Hz, 6H).



S1 **S2** **S3** **1ab**

Methyl(2-oxo-2-phenylethyl)(*p*-tolyl)sulfonium (1ab)[4]

4-Methylbenzenethiol **S2** (1.0 equiv, 20.0 mmol, 2.48 g) was charged into a dry 100 mL flask along with EtOH (20.0 mL), magnetic stir bar and K_2CO_3 (1.0 equiv, 20.0 mmol, 2.76 g). The α-bromo ketone **S1** (1.0 equiv, 20.0 mmol) was added in one portion. The resulting suspension was stirred for 2 h at room temperature. The crude reaction mixture was filtered through a pad of celite and washed with EtOH. The solvent was removed in vacuo. The residue was purified by flash silica gel chromatography. The resulting sulfide was transferred into 25 mL vial. In an argon-filled glovebox, Me_2SO_4 (1.0 equiv) was added and the vial was sealed. The vial was then stirred for 1 h at 100 ^oC and allowed to cool to room temperature. The resulting gel was purified by flash silica gel column chromatography (CH_2Cl_2 / MeOH= 20:1) to afford the title compound (recrystallization from MeOH / Et_2O if necessary).

Melting point: 98-102 ^{o}C

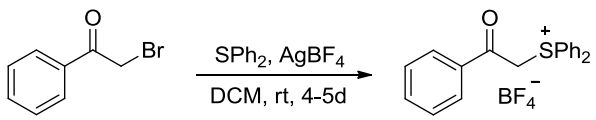
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 11.3, 8.2 Hz, 4H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 4H), 6.03 (dd, *J* = 49.4, 17.6 Hz, 2H), 3.63 (s, 3H), 3.51 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 145.5, 134.9, 133.6, 131.7, 130.9, 129.1 (d, *J* = 18.2 Hz), 121.2, 56.4, 54.5, 26.4, 21.6.

IR (neat): *v* = 3414, 3011, 2961, 2919, 1675, 1596, 1581, 1497, 1453, 1426, 1406, 1392, 1332, 1303, 1205, 1183, 1085, 1053, 992, 895, 867, 810, 753, 700, 680 cm^{-1}

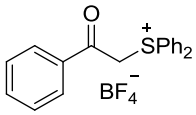
HRMS-ESI m/z : $[M\text{-}MeSO_4]^+$ calcd for $C_{16}H_{17}OS^+$ 257.0995, found 257.0994.

General Procedure A: (**1ac** as an example)[5-6]



S1 **1ac**

A solution of diphenyl sulfide (0.93 g, 5.0 mmol) and 2-bromo-1-phenylethanone (1.19 g, 6.0 mmol) in dry DCM (10.0 mL) was added to $AgBF_4$ (0.97 g, 5 mmol) under inert atmosphere (argon). The reaction mixture was stirred at room temperature for 4-5 days. The reaction mixture was filtered, the precipitate washed with DCM. The solvent was removed in vacuo. The residue was washed with diethyl ether (3 x 4 mL). Crystallization twice from DCM and Et_2O afforded the pure compound.



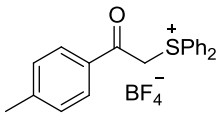
(2-Oxo-2-phenylethyl)diphenylsulfonium tetrafluoroborate (1ac)[6]

The titled compound was obtainted as white solid in 72% yield (1.41 g, 3.6 mmol).

Melting point: 160-162 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.07 (m, 6H), 7.76 – 7.63 (m, 7H), 7.52 (t, *J* = 7.7 Hz, 2H), 6.12 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.0.



(2-Oxo-2-(*p*-tolyl)ethyl)diphenylsulfonium tetrafluoroborate (1b)

The titled compound was obtained as white solid in 66% yield (1.34 g, 3.3 mmol).

Melting point: 165-167 ^{o}C

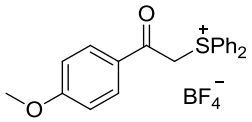
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (d, *J* = 7.2 Hz, 4H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.82 – 7.70 (m, 6H), 7.44 (d, *J* = 7.9 Hz, 2H), 6.57 (s, 2H), 2.40 (s, 3H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.0.

^{13}C NMR (101 MHz, DMSO-d_6) δ 189.9, 146.6, 134.2, 131.2, 131.0, 130.6, 129.8, 129.3, 126.1, 54.6, 21.5.

IR (neat): *v* = 2927, 1679, 1603, 1581, 1482, 1446, 1411, 1383, 1327, 1305, 1221, 1206, 1184, 1164, 1052, 1015, 1002, 980, 931, 902, 853, 812, 748, 684 cm^{-1}

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{21}H_{19}OS^+$ 319.1151, found 319.1153.



(2-(4-Methoxyphenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1c)

The titled compound was obtained as white solid in 66% yield (1.39 g, 3.3 mmol).

Melting point: 129-130 ^{o}C

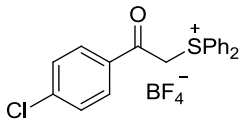
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (d, *J* = 7.3 Hz, 4H), 8.07 (d, *J* = 8.9 Hz, 2H), 7.81 – 7.69 (m, 6H), 7.13 (d, *J* = 8.9 Hz, 2H), 6.50 (s, 2H), 3.88 (s, 3H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.2.

^{13}C NMR (101 MHz, DMSO-d_6) δ 188.5, 165.1, 134.2, 131.9, 131.2, 130.7, 126.4, 126.2, 114.6, 56.1, 54.5.

IR (neat): *v* = 2927, 1679, 1603, 1581, 1482, 1446, 1411, 1383, 1327, 1305, 1221, 1206, 1184, 1164, 1052, 1015, 1002, 980, 931, 902, 853, 812, 748, 685 cm^{-1}

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{21}H_{19}O_2S^+$ 335.1100, found 335.1099.



(2-(4-Chlorophenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1d)

The titled compound was obtained as white solid in 57% yield (1.22 g, 2.9 mmol).

Melting point: 115-116 ^{o}C

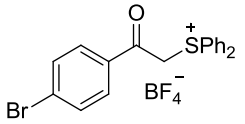
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (dd, *J* = 14.4, 8.0 Hz, 6H), 7.83 – 7.69 (m, 8H), 6.55 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.1.

^{13}C NMR (101 MHz, DMSO-d_6) δ 189.6, 140.6, 134.2, 132.2, 131.2, 131.1, 130.7, 129.4, 125.9, 54.6.

IR (neat): *v* = 1686, 1592, 1575, 1448, 1404, 1317, 1300, 1207, 1182, 1032, 997, 985, 903, 817, 756, 749, 704, 685 cm^{-1}

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{20}H_{16}ClOS^+$ 339.0605, found 339.0609.



(2-(4-Bromophenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1e)

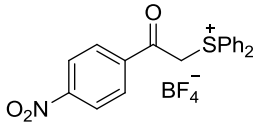
The titled compound was obtained as white solid in 58% yield (1.37 g, 2.9 mmol).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (d, *J* = 7.2 Hz, 4H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.80 – 7.69 (m, 6H), 6.56 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.0.

^{13}C NMR (101 MHz, DMSO-d_6) δ 189.9, 134.2, 132.5, 132.4, 131.2, 131.1, 130.7, 129.9, 125.9, 54.5.

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{20}H_{16}BrOS^+$ 383.0100, found 383.0102.



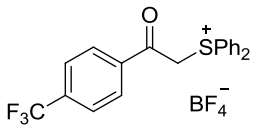
(2-(4-Nitrophenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1f)[5]

The titled compound was obtained as light yellow solid in 62% yield (1.36 g, 3.1 mmol).

Melting point: 107-109 ^{o}C

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40 (dd, *J* = 20.8, 7.7 Hz, 4H), 8.20 (d, *J* = 6.4 Hz, 4H), 7.77 (d, *J* = 7.6 Hz, 6H), 6.62 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.1.



(2-Oxo-2-(4-(trifluoromethyl)phenyl)ethyl)diphenylsulfonium tetrafluoroborate (1g)

The titled compound was obtained as white solid in 80% yield (1.84 g, 4.0 mmol).

Melting point: 196-198 ^{o}C

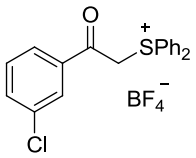
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (d, *J* = 8.2 Hz, 2H), 8.18 (d, *J* = 7.4 Hz, 4H), 8.03 (d, *J* = 8.3 Hz, 2H), 7.83 – 7.71 (m, 6H), 6.59 (s, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.0, -143.4.

^{13}C NMR (101 MHz, DMSO-d_6) δ 190.2, 136.6, 134.2, 131.1, 130.7, 130.0, 126.1, 126.1, 125.8, 123.6 (q, *J* = 272.8 Hz), 54.6.

IR (neat): *v* = 2999, 2929, 1688, 1584, 1481, 1449, 1413, 1313, 1301, 1210, 1171, 1129, 1063, 1029, 1014, 987, 934, 857, 834, 753, 745, 682 cm^{-1}

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{21}H_{16}F_3OS^+$ 373.0868, found 373.0864.



(2-(3-Chlorophenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1h)

The titled compound was obtained as white solid in 62% yield (1.32 g, 3.1 mmol).

Melting point: 186-190 ^{o}C

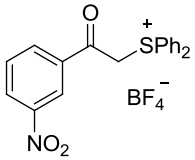
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (s, 1H), 8.16 (d, *J* = 7.2 Hz, 4H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 9.1 Hz, 1H), 7.84 – 7.71 (m, 6H), 7.66 (t, *J* = 7.9 Hz, 1H), 6.55 (s, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -143.4.

^{13}C NMR (101 MHz, DMSO-d_6) δ 189.7, 135.2, 135.0, 134.1, 134.1, 131.1, 130.6, 129.1, 127.5, 125.9, 54.5.

IR (neat): *v* = 1689, 1575, 1477, 1448, 1427, 1375, 1304, 1206, 1033, 997, 928, 882, 822, 781, 768, 752, 685, 674 cm^{-1}

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{20}H_{16}ClOS^+$ 339.0605, found 339.0603.



(2-(3-Nitrophenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1i)

The titled compound was obtained as white solid in 65% yield (1.42 g, 3.3 mmol).

Melting point: 184-188 ^{o}C

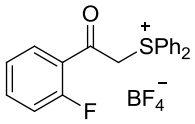
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 1H), 8.61 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 7.8 Hz, 1H), 8.19 (d, *J* = 7.5 Hz, 4H), 7.93 (t, *J* = 8.0 Hz, 1H), 7.84 – 7.71 (m, 6H), 6.65 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.2.

^{13}C NMR (101 MHz, DMSO-d_6) δ 189.4, 148.2, 135.0, 134.7, 134.2, 131.1, 131.0, 130.7, 129.4, 125.8, 123.7, 54.6.

IR (neat): *v* = 3103, 3015, 2947, 1693, 1612, 1581, 1535, 1475, 1443, 1350, 1304, 1289, 1212, 1194, 1099, 1029, 1012, 923, 879, 797, 747, 729, 668 cm^{-1}

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{20}H_{16}NO_3S^+$ 350.0845, found 350.0842.



(2-(2-Fluorophenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1j)

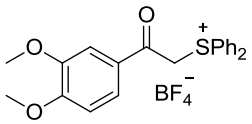
The titled compound was obtained as white solid in 67% yield (1.37 g, 3.4 mmol).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (d, *J* = 7.5 Hz, 4H), 8.01 (t, *J* = 7.2 Hz, 1H), 7.89 – 7.72 (m, 7H), 7.53 – 7.40 (m, 2H), 6.43 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -107.4, -148.1.

^{13}C NMR (101 MHz, DMSO-d_6) δ 187.7, 161.9 (d, *J* = 257.8 Hz), 138.0, 134.3, 131.3, 131.0, 130.7, 125.7, 125.5, 121.9, 117.4 (d, *J* = 22.3 Hz), 57.1.

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{20}H_{16}FOS^+$ 323.0900, found 323.0900.



(2-(3,4-Dimethoxyphenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1k)

The titled compound was obtained as white solid in 68% yield (1.54 g, 3.4 mmol).

Melting point: 161-164 ^oC

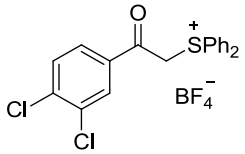
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (d, *J* = 7.5 Hz, 4H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.71 (m, 6H), 7.52 (s, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 6.57 (s, 2H), 3.89 (s, 3H), 3.83 (s, 3H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.0.

^{13}C NMR (101 MHz, DMSO-d_6) δ 188.5, 155.1, 149.0, 134.1, 131.2, 130.6, 126.1, 125.0, 111.3, 110.7, 56.2, 55.8, 54.5.

IR (neat): *v* = 1670, 1584, 1516, 1467, 1449, 1442, 1422, 1304, 1288, 1262, 1246, 1198, 1185, 1160, 1036, 1016, 997, 924, 872, 865, 809, 798, 769, 746, 681 cm^{-1}

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{22}H_{21}O_3S^+$ 365.1206, found 365.1208.



(2-(3,4-Dichlorophenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1l)

The titled compound was obtained as white solid in 76% yield (1.75 g, 3.8 mmol).

Melting point: 174-177 ^oC

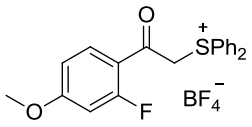
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.47 (d, *J* = 1.7 Hz, 1H), 8.16 (d, *J* = 7.5 Hz, 4H), 8.03 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.70 (m, 6H), 6.53 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -143.4.

^{13}C NMR (101 MHz, DMSO-d_6) δ 188.9, 138.2, 134.1, 133.6, 132.2, 131.5, 131.3, 131.1, 130.7, 128.7, 125.8, 54.4.

IR (neat): *v* = 2987, 1694, 1587, 1477, 1447, 1396, 1371, 1304, 1285, 1200, 1127, 1051, 1032, 1020, 995, 974, 884, 832, 816, 759, 750, 685 cm^{-1}

HRMS-ESI m/z : $[M-BF_4]^+$ calcd for $C_{20}H_{15}Cl_2OS^+$ 373.0215, found 373.0213.



(2-(2-Fluoro-4-methoxyphenyl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1m)

The titled compound was obtained as white solid in 70% yield (1.54 g, 3.5 mmol).

Melting point: 134-138 ^oC

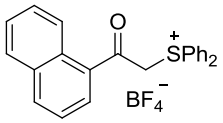
^1H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, *J* = 7.3 Hz, 4H), 7.95 (t, *J* = 8.8 Hz, 1H), 7.82 – 7.70 (m, 6H), 7.10 (dd, *J* = 13.7, 2.1 Hz, 1H), 6.99 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.37 (d, *J* = 1.8 Hz, 2H), 3.90 (s, 3H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -103.4, -148.1.

^{13}C NMR (101 MHz, DMSO-d_6) δ 185.9, 166.8 (d, *J* = 12.5 Hz), 163.9 (d, *J* = 257.9 Hz), 134.2, 132.6, 131.2, 130.6, 125.9, 114.7 (d, *J* = 10.6 Hz), 112.1, 102.4 (d, *J* = 26.3 Hz), 57.0, 56.7.

IR (neat): *v* = 1664, 1608, 1570, 1497, 1480, 1465, 1444, 1378, 1350, 1322, 1278, 1236, 1211, 1160, 1051, 1012, 991, 950, 899, 860, 825, 756, 743, 684 cm^{-1}

HRMS-ESI m/z : $[M-BF_4]^+$ calcd for $C_{21}H_{18}FO_2S^+$ 353.1006, found 353.1007.



(2-(Naphthalen-1-yl)-2-oxoethyl)diphenylsulfonium (2-oxo-2-phenylethyl) diphenylsulfonium tetrafluoroborate (1n)

The titled compound was obtained as white solid in 58% yield (1.37 g, 2.9 mmol).

Melting point: 141-143 ^oC

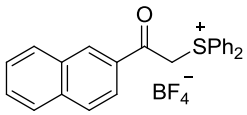
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.61 (d, *J* = 7.2 Hz, 1H), 8.35 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 7.1 Hz, 4H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.82 – 7.72 (m, 7H), 7.65 (dt, *J* = 14.5, 6.9 Hz, 2H), 6.75 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.0.

^{13}C NMR (101 MHz, DMSO-d_6) δ 192.6, 136.1, 134.2, 133.6, 133.0, 131.2, 130.7, 129.6, 129.5, 129.4, 129.2, 127.1, 126.0, 124.9, 124.8, 56.6.

IR (neat): *v* = 3006, 1669, 1595, 1572, 1507, 1481, 1445, 1390, 1297, 1262, 1236, 1217, 1173, 1145, 1037, 998, 942, 902, 798, 777, 755, 744, 683 cm^{-1}

HRMS-ESI m/z : $[M-BF_4]^+$ calcd for $C_{24}H_{19}OS^+$ 355.1151, found 355.1150.



(2-(Naphthalen-2-yl)-2-oxoethyl)diphenylsulfonium (2-oxo-2-phenylethyl) diphenylsulfonium tetrafluoroborate (1o)

The titled compound was obtained as white solid in 65% yield (1.44 g, 3.3 mmol).

Melting point: 196-199 ^{o}C

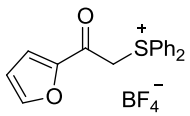
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.96 (s, 1H), 8.21 (dd, *J* = 17.3, 7.5 Hz, 5H), 8.05 (ddd, *J* = 13.9, 9.9, 5.0 Hz, 3H), 7.76 (ddd, *J* = 15.6, 11.3, 7.5 Hz, 8H), 6.72 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.0.

^{13}C NMR (101 MHz, DMSO-d_6) δ 190.4, 136.0, 134.2, 132.6, 132.0, 131.2, 130.8, 130.7, 130.0, 129.9, 129.0, 128.1, 127.8, 126.1, 123.2, 54.8.

IR (neat): *v* = 2978, 2926, 1672, 1625, 1596, 1483, 1473, 1446, 1374, 1360, 1309, 1284, 1211, 1190, 1158, 1128, 1044, 1032, 992, 976, 941, 892, 796, 824, 751, 743, 680 cm^{-1}

HRMS-ESI m/z : $[M-BF_4]^+$ calcd for $C_{24}H_{19}OS^+$ 355.1151, found 355.1154.



(2-(Furan-2-yl)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1p)

The titled compound was obtained as white solid in 82% yield (1.57 g, 4.1 mmol).

Melting point: 113-115 ^{o}C

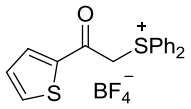
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (s, 1H), 8.14 (d, *J* = 7.7 Hz, 4H), 7.87 (d, *J* = 3.5 Hz, 1H), 7.82 – 7.71 (m, 6H), 6.88 (d, *J* = 3.5 Hz, 1H), 6.28 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.2.

^{13}C NMR (101 MHz, DMSO-d_6) δ 177.2, 150.4, 148.9, 134.2, 131.1, 130.6, 129.6, 125.8, 113.5, 52.7.

IR (neat): *v* = 3632, 1668, 1588, 1571, 1478, 1448, 1402, 1317, 1299, 1207, 1183, 1069, 1031, 997, 984, 902, 841, 814, 760, 749, 684 cm^{-1}

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{18}H_{15}O_2S^+$ 295.0787, found 295.0788.



(2-oxo-2-(Thiophen-2-yl)ethyl)diphenylsulfonium tetrafluoroborate (1q)

The titled compound was obtained as white solid in 60% yield (1.19 g, 3.0 mmol).

Melting point: 114-116 ^{o}C

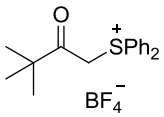
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (s, 1H), 8.28 – 8.10 (m, 5H), 7.75 (d, *J* = 6.3 Hz, 6H), 7.40 (s, 1H), 6.49 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.0.

^{13}C NMR (101 MHz, DMSO-d_6) δ 182.8, 139.5, 138.5, 137.6, 134.3, 131.2, 130.7, 129.7, 125.9, 53.6.

IR (neat): *v* = 1655, 1582, 1517, 1478, 1448, 1411, 1357, 1306, 1288, 1247, 1170, 1063, 1019, 932, 974, 895, 864, 848, 760, 748, 733, 708, 682 cm^{-1}

HRMS-ESI m/z : $[M\text{-}BF_4]^+$ calcd for $C_{18}H_{15}OS_2^+$ 311.0559, found 311.0558.



(3,3-Dimethyl-2-oxobutyl)diphenylsulfonium tetrafluoroborate (1r)

The titled compound was obtained as white solid in 66% yield (1.23 g, 3.3 mmol).

Melting point: 156-159 ^{o}C

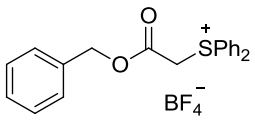
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (d, *J* = 7.3 Hz, 4H), 7.81 – 7.69 (m, 6H), 6.09 (s, 2H), 1.15 (s, 9H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.1.

^{13}C NMR (101 MHz, DMSO-d_6) δ 206.9, 134.3, 131.2, 130.6, 125.7, 53.7, 44.2, 25.6.

IR (neat): *v* = 3102, 2951, 1706, 1581, 1480, 1464, 1453, 1385, 1372, 1322, 1291, 1247, 1225, 1188, 1055, 996, 939, 887, 840, 796, 761, 744, 690, 683 cm^{-1}

HRMS-ESI m/z : [M-BF_4]$^{+}$ calcd for $C_{18}H_{21}OS^{+}$ 285.1308, found 285.1308.



(2-(Benzyloxy)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1s)

The titled compound was obtained as white solid in 55% yield (1.16 g, 2.8 mmol).

Melting point: 119-121 ^{o}C

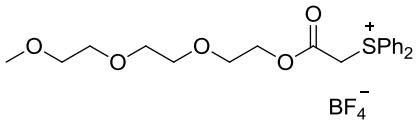
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (d, *J* = 8.0 Hz, 4H), 7.79 (t, *J* = 7.3 Hz, 2H), 7.72 (t, *J* = 7.7 Hz, 4H), 7.37 – 7.33 (m, 3H), 7.24 (d, *J* = 3.4 Hz, 2H), 5.77 (s, 2H), 5.21 (s, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -148.2.

^{13}C NMR (101 MHz, DMSO-d_6) δ 163.9, 134.6, 134.6, 131.3, 130.6, 128.8, 128.7, 128.5, 125.6, 68.5, 46.3.

IR (neat): *v* = 3003, 1733, 1479, 1450, 1387, 1306, 1217, 1177, 1030, 997, 943, 904, 826, 780, 742, 699, 680 cm^{-1}

HRMS-ESI m/z : [M-BF_4]$^{+}$ calcd for $C_{21}H_{19}O_2S^{+}$ 335.1100, found 335.1097.

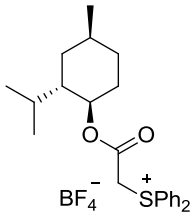


(12-Oxo-2,5,8,11-tetraoxatridecan-13-yl)diphenylsulfonium tetrafluoroborate (1t)

The titled compound was obtained as white solid in 53% yield (1.24 g, 2.6 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 4H), 7.67 – 7.53 (m, 6H), 5.21 (s, 2H), 4.23 – 4.17 (m, 2H), 3.71 – 3.42 (m, 10H), 3.23 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -153.8.



(2-(((*1R,2S,4S*)-2-Isopropyl-4-methylcyclohexyl)oxy)-2-oxoethyl)diphenylsulfonium tetrafluoroborate (1u)

The titled compound was obtained as white solid in 75% yield (1.76 g, 3.8 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.92 (m, 4H), 7.76 – 7.57 (m, 6H), 5.17 (dd, *J* = 59.4, 16.3 Hz, 2H), 4.69 (td, *J* = 11.0, 4.4 Hz, 1H), 1.84 (d, *J* = 12.1 Hz, 1H), 1.62 (d, *J* = 10.6 Hz, 2H), 1.48 (dq, *J* = 6.6, 4.3 Hz, 1H), 1.40 – 1.25 (m, 2H), 0.93 (ddd, *J* = 15.7, 9.7, 7.3 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.76 (d, *J* = 6.9 Hz, 3H), 0.56 (d, *J* = 6.9 Hz, 3H).

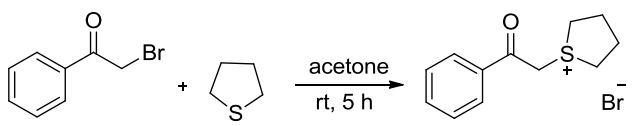
^{19}F NMR (376 MHz, $CDCl_3$) δ -153.9 (d, *J* = 2.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 134.8, 134.8, 131.7, 131.6, 130.7, 130.6, 124.1, 124.0, 79.0, 47.2, 46.6, 40.0, 33.8, 31.5, 25.8, 22.9, 21.9, 20.8, 15.8.

IR (neat): *v* = 2955, 2870, 1729, 1580, 1477, 1447, 1389, 1369, 1311, 1267, 1201, 1051, 997, 939, 907, 845, 741, 685 cm^{-1}

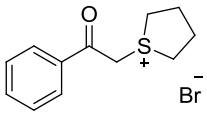
HRMS-ESI m/z : $[M-BF_4]^+$ calcd for $C_{24}H_{31}O_2S^+$ 383.2039, found 383.2040.

General Procedure B: (**3a** as an example)[5]



S1 **3a**

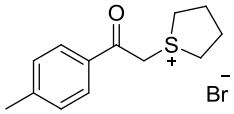
Tetrahydrothiophene (0.44 g, 5.0 mmol) was added to a solution of 2-bromoacetophenone (1.00 g, 5.0 mmol) in acetone (1.0 mL). After the mixture had been stirred for 5 h, the residue was filtered and washed with acetone or Et_2O.



1-(2-Oxo-2-phenylethyl)tetrahydro-1H-thiophen-1-ium bromide (3a)[5]

The titled compound was obtained as white solid in 80% yield (1.15 g, 4.0 mmol).

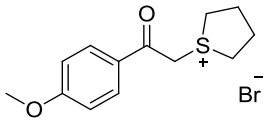
^{1}H NMR (400 MHz, CD_3OD) δ 8.08 (d, *J* = 7.3 Hz, 2H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 4.89 (s, 2H), 3.71 (dt, *J* = 13.4, 6.6 Hz, 2H), 3.65 – 3.57 (m, 2H), 2.50 – 2.39 (m, 2H), 2.34 (dd, *J* = 12.3, 5.7 Hz, 2H).



1-(2-Oxo-2-(*p*-tolyl)ethyl)tetrahydro-1H-thiophen-1-ium bromide (3b)[5]

The titled compound was obtained as white solid in 78% yield (1.17 g, 3.9 mmol).

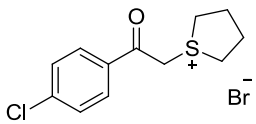
^{1}H NMR (400 MHz, CD_3OD) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 4.91 (s, 2H), 3.63 (ddt, *J* = 25.3, 12.8, 6.5 Hz, 4H), 2.45 (s, 3H), 2.44 – 2.25 (m, 4H).



1-(2-(4-Methoxyphenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3c)[7]

The titled compound was obtained as white solid in 78% yield (1.24 g, 3.9 mmol).

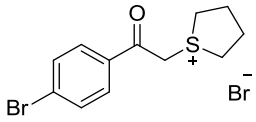
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 8.9 Hz, 2H), 4.92 (s, 2H), 3.91 (s, 3H), 3.63 (dtd, *J* = 25.4, 12.9, 6.6 Hz, 4H), 2.39 (ddd, *J* = 31.5, 10.7, 5.0 Hz, 4H).



1-(2-(4-Chlorophenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3d)[7]

The titled compound was obtained as white solid in 73% yield (1.17 g, 3.7 mmol).

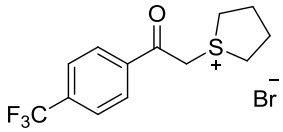
^{1}H NMR (400 MHz, CD_3OD) δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 4.85 (s, 2H), 3.80 – 3.61 (m, 4H), 2.54 – 2.29 (m, 4H).



1-(2-(4-Bromophenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3e)[7]

The titled compound was obtained as white solid in 90% yield (1.65 g, 4.5 mmol).

^{1}H NMR (400 MHz, CD_3OD) δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 4.87 (s, 2H), 3.68 (ddt, *J* = 36.1, 12.3, 6.3 Hz, 4H), 2.53 – 2.26 (m, 4H).



1-(2-Oxo-2-(4-(trifluoromethyl)phenyl)ethyl)tetrahydro-1H-thiophen-1-ium bromide (3f)

The titled compound was obtained as white solid in 83% yield (1.47 g, 4.2 mmol).

Melting point: 129-131 ^{o}C

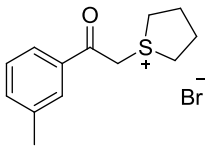
^{1}H NMR (400 MHz, CD_3OD) δ 8.27 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 4.84 (s, 2H), 3.74 (dtd, *J* = 19.0, 12.9, 6.4 Hz, 4H), 2.44 (ddt, *J* = 15.7, 9.0, 4.0 Hz, 4H).

^{19}F NMR (376 MHz, CD_3OD) δ -64.4.

^{13}C NMR (101 MHz, CD_3OD) δ 192.2, 138.3, 136.5 (q, *J* = 33.1 Hz), 130.7, 127.1 (q, *J* = 3.7 Hz), 125.0 (q, *J* = 272.1 Hz), 44.3, 29.8.

IR (neat): *v* = 3007, 2976, 2947, 2920, 2896, 2162, 1685, 1581, 1516, 1414, 1360, 1314, 1205, 1173, 1133, 1112, 1063, 1017, 992, 953, 921, 882, 861, 829, 793, 774, 742, 732, 672 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{13}H_{14}F_3OS^+$ 275.0712, found 275.0713.



1-(2-Oxo-2-(*m*-tolyl)ethyl)tetrahydro-1H-thiophen-1-ium bromide (3g)

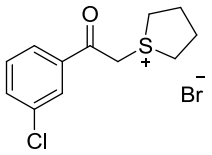
The titled compound was obtained as white solid in 90% yield (1.36 g, 4.5 mmol).

Melting point: 124-126 ^{o}C

^{1}H NMR (400 MHz, CD_3OD) δ 7.98 – 7.78 (m, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 4.91 (s, 2H), 3.64 (ddt, *J* = 25.5, 12.9, 6.6 Hz, 4H), 2.45 (s, 3H), 2.44 – 2.25 (m, 4H).

^{13}C NMR (101 MHz, CD_3OD) δ 192.7, 140.4, 136.9, 135.4, 130.3, 130.1, 127.2, 44.1, 29.7, 21.3.

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{13}H_{17}OS^+$ 221.0995, found 221.0995.



1-(2-(3-Chlorophenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3h)

The titled compound was obtained as white solid in 87% yield (1.40 g, 4.4 mmol).

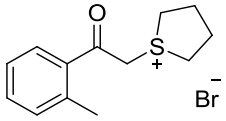
Melting point: 147-150 ^{o}C

^{1}H NMR (400 MHz, CD_3OD) δ 8.06 (t, *J* = 1.7 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.80 – 7.69 (m, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 4.91 (s, 2H), 3.77 – 3.56 (m, 4H), 2.50 – 2.27 (m, 4H).

^{13}C NMR (101 MHz, CD_3OD) δ 191.7, 137.0, 136.3, 135.8, 131.9, 129.6, 128.3, 44.2, 29.7.

IR (neat): *v* = 2987, 2967, 2930, 2872, 1979, 1672, 1590, 1567, 1477, 1459, 1444, 1413, 1350, 1320, 1264, 1204, 1160, 1100, 1074, 1005, 995, 954, 896, 872, 835, 792, 700, 676, 663 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{12}H_{14}ClOS^+$ 241.0448, found 241.0449.



1-(2-Oxo-2-(*o*-tolyl)ethyl)tetrahydro-1H-thiophen-1-ium bromide (3i)

The titled compound was obtained as white solid in 93% yield (1.40 g, 4.7 mmol).

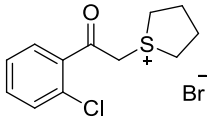
Melting point: 148-150 ^{o}C

^{1}H NMR (400 MHz, CD_3OD) δ 7.99 (d, *J* = 7.5 Hz, 1H), 7.66 – 7.52 (m, 1H), 7.41 (dd, *J* = 15.4, 7.7 Hz, 2H), 4.91 (s, 2H), 3.76 – 3.53 (m, 4H), 2.59 (s, 3H), 2.49 – 2.25 (m, 4H).

^{13}C NMR (101 MHz, CD_3OD) δ 194.6, 141.8, 135.0, 134.1, 133.6, 132.4, 127.4, 44.0, 29.7, 22.2.

IR (neat): ν = 2972, 2907, 2859, 2162, 1671, 1601, 1567, 1493, 1456, 1433, 1386, 1312, 1199, 1169, 1140, 1040, 982, 957, 920, 886, 873, 819, 760, 725, 714 $cm^{-1,}$

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{13}H_{17}OS^+$ 221.0995, found 221.0995.



1-(2-(2-Chlorophenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3j)

The titled compound was obtained as white solid in 78% yield (1.25 g, 3.9 mmol).

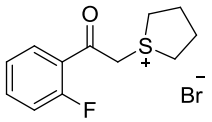
Melting point: 128-129 ^oC

^1H NMR (400 MHz, CD_3OD) δ 8.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.56 – 7.48 (m, 1H), 4.84 (s, 2H), 3.79 – 3.61 (m, 4H), 2.52 – 2.41 (m, 2H), 2.39 – 2.28 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 135.8, 134.6, 134.1, 132.8, 132.7, 128.6, 44.3, 29.8.

IR (neat): ν = 3062, 3008, 2980, 2932, 2869, 2162, 1965, 1686, 1588, 1565, 1471, 1428, 1362, 1303, 1272, 1259, 1197, 1159, 1066, 1043, 984, 913, 880, 860, 814, 748, 712, 685, 666 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{12}H_{14}ClOS^+$ 241.0448, found 241.0447.



1-(2-(2-Fluorophenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3k)

The titled compound was obtained as white solid in 88% yield (1.34 g, 4.4 mmol).

Melting point: 120-122 ^oC

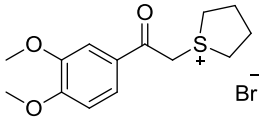
^1H NMR (400 MHz, CD_3OD) δ 8.05 (td, *J* = 7.7, 1.8 Hz, 1H), 7.78 (tdd, *J* = 7.2, 5.2, 1.8 Hz, 1H), 7.44 – 7.32 (m, 2H), 4.90 (s, 2H), 3.65 (ddt, *J* = 39.2, 12.8, 6.4 Hz, 4H), 2.46 – 2.28 (m, 4H).

^{19}F NMR (376 MHz, CD_3OD) δ -108.5.

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 164.0 (d, *J* = 256.7 Hz), 138.5 (d, *J* = 9.6 Hz), 131.8, 126.2 (d, *J* = 3.3 Hz), 123.5 (d, *J* = 11.4 Hz), 118.1 (d, *J* = 23.1 Hz), 44.1, 29.7.

IR (neat): *v* = 3000, 2945, 1675, 1608, 1576, 1480, 1456, 1448, 1382, 1321, 1287, 1269, 1211, 1158, 1050, 1038, 997, 909, 841, 780, 771, 747, 683 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{12}H_{14}FOS^+$ 225.0744, found 225.0745.



1-(2-(3,4-Dimethoxyphenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3l)

The titled compound was obtained as white solid in 89% yield (1.55 g, 4.5 mmol).

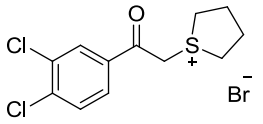
Melting point: 139-141 ^oC

^1H NMR (400 MHz, CD_3OD) δ 7.74 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.52 (s, 1H), 7.08 (t, *J* = 8.6 Hz, 1H), 4.85 (s, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 3.67 (ddt, *J* = 40.1, 12.7, 6.4 Hz, 4H), 2.54 – 2.25 (m, 4H).

^{13}C NMR (101 MHz, CD_3OD) δ 190.9, 156.4, 150.5, 128.1, 125.7, 112.0, 111.6, 56.8, 56.7, 44.1, 29.7.

IR (neat): *v* = 3486, 2943, 2030, 1660, 1585, 1516, 1452, 1420, 1353, 1311, 1291, 1261, 1244, 1189, 1152, 1043, 1013, 876, 853, 831, 770, 722 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{14}H_{19}O_3S^+$ 267.1049, found 267.1048.



1-(2-(3,4-Dichlorophenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3m)

The titled compound was obtained as white solid in 76% yield (1.35 g, 3.8 mmol).

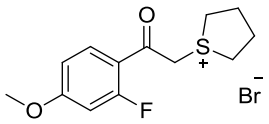
Melting point: 127-129 ^oC

^1H NMR (400 MHz, CD_3OD) δ 8.21 (d, *J* = 2.0 Hz, 1H), 7.98 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 4.91 (s, 2H), 3.64 (ddd, *J* = 19.0, 13.0, 6.5 Hz, 4H), 2.47 – 2.29 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 190.7, 140.3, 135.1, 134.5, 132.4, 131.6, 129.2, 44.1, 29.6.

IR (neat): *v* = 3335, 3093, 3011, 2866, 2161, 1678, 1583, 1557, 1466, 1392, 1363, 1310, 1286, 1255, 1205, 1167, 1132, 1030, 951, 923, 886, 839, 818, 779, 699, 674 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{12}H_{13}Cl_2OS^+$ 275.0059, found 275.0059.



1-(2-(2-Fluoro-4-methoxyphenyl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3n)

The titled compound was obtained as white solid in 87% yield (1.46 g, 4.4 mmol).

Melting point: 139-143 ^oC

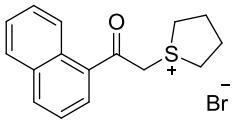
^1H NMR (400 MHz, CD_3OD) δ 7.99 (t, *J* = 8.8 Hz, 1H), 6.91 (ddd, *J* = 15.9, 11.3, 2.3 Hz, 2H), 4.84 (s, 2H), 3.93 (s, 3H), 3.73 (dt, *J* = 13.3, 6.7 Hz, 2H), 3.61 (dt, *J* = 12.8, 6.2 Hz, 2H), 2.49 – 2.29 (m, 4H).

^{19}F NMR (376 MHz, CD_3OD) δ -105.0.

^{13}C NMR (101 MHz, CD_3OD) δ 188.3 (d, *J* = 3.4 Hz), 168.5 (d, *J* = 12.5 Hz), 165.9 (d, *J* = 256.8 Hz), 133.3 (d, *J* = 3.6 Hz), 116.3 (d, *J* = 12.0 Hz), 112.9 (d, *J* = 2.1 Hz), 102.9 (d, *J* = 26.9 Hz), 57.1, 44.0, 29.7.

IR (neat): *v* = 3365, 3029, 2925, 2867, 2162, 1673, 1651, 1614, 1573, 1505, 1471, 1460, 1425, 1382, 1342, 1277, 1261, 1237, 1210, 1177, 1124, 1113, 1022, 994, 950, 908, 874, 855, 811, 751, 660 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{13}H_{16}FO_2S^+$ 255.0850, found 255.0849.



1-(2-(Naphthalen-1-yl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3o)

The titled compound was obtained as white solid in 87% yield (1.47 g, 4.4 mmol).

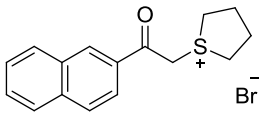
Melting point: 125-127 ^oC

^1H NMR (400 MHz, CD_3OD) δ 9.00 (d, *J* = 8.6 Hz, 1H), 8.29 (dd, *J* = 22.8, 7.8 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.60 (m, 3H), 4.92 (s, 2H), 3.77 – 3.61 (m, 4H), 2.51 – 2.30 (m, 4H).

^{13}C NMR (101 MHz, CD_3OD) δ 194.8, 137.0, 135.4, 133.6, 131.6, 131.1, 130.1, 130.0, 128.0, 126.6, 125.7, 44.1, 29.7.

IR (neat): *v* = 3481, 2926, 2870, 2162, 2036, 1673, 1616, 1592, 1574, 1508, 1463, 1437, 1417, 1387, 1338, 1307, 1239, 1216, 1172, 1093, 1075, 1021, 982, 948, 912, 861, 802, 790, 771, 732, 710 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{16}H_{17}OS^+$ 257.0995, found 257.0994.



1-(2-(Naphthalen-2-yl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3p)

The titled compound was obtained as white solid in 80% yield (1.35 g, 3.9 mmol).

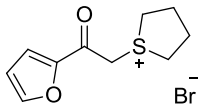
Melting point: 123-126 ^oC

^{1}H NMR (400 MHz, CD_3OD) δ 8.72 (s, 1H), 8.27 – 7.93 (m, 4H), 7.68 (dt, *J* = 25.4, 7.0 Hz, 2H), 4.91 (s, 2H), 3.81 – 3.59 (m, 4H), 2.55 – 2.26 (m, 4H).

^{13}C NMR (101 MHz, CD_3OD) δ 192.5, 137.7, 133.7, 133.1, 132.6, 131.0, 130.7, 130.0, 129.0, 128.4, 124.2, 54.0, 44.3, 29.7.

IR (neat): *v* = 3492, 2934, 2877, 2161, 1980, 1665, 1626, 1596, 1578, 1505, 1470, 1440, 1405, 1353, 1307, 1291, 1243, 1205, 1183, 1139, 1124, 1103, 997, 955, 942, 901, 873, 817, 789, 752, 727, 685 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{16}H_{17}OS^+$ 257.0995, found 257.0993.



1-(2-(Furan-2-yl)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3q)

The titled compound was obtained as white solid in 88% yield (1.22 g, 4.4 mmol).

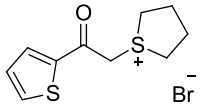
Melting point: 133-135 ^oC

^{1}H NMR (400 MHz, CD_3OD) δ 7.95 (d, *J* = 1.0 Hz, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 6.77 (dd, *J* = 3.7, 1.6 Hz, 1H), 4.88 (s, 2H), 3.74 – 3.58 (m, 4H), 2.48 – 2.29 (m, 4H).

^{13}C NMR (101 MHz, CD_3OD) δ 180.1, 151.5, 150.5, 122.0, 114.3, 44.4, 29.7.

IR (neat): *v* = 3141, 3102, 3074, 2999, 2911, 2822, 1662, 1562, 1468, 1400, 1374, 1338, 1311, 1254, 1207, 1171, 1082, 1048, 1008, 950, 917, 880,852, 773, 718 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{10}H_{13}O_2S^+$ 197.0631, found 197.0632.



1-(2-Oxo-2-(thiophen-2-yl)ethyl)tetrahydro-1H-thiophen-1-ium bromide (3r)

The titled compound was obtained as white solid in 91% yield (1.33 g, 4.6 mmol).

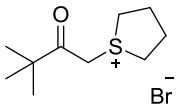
Melting point: 141-143 ^oC

^{1}H NMR (400 MHz, CD_3OD) δ 8.05 (t, *J* = 3.6 Hz, 2H), 7.33 – 7.27 (m, 1H), 4.91 (s, 2H), 3.64 (ddt, *J* = 25.3, 12.9, 6.6 Hz, 4H), 2.50 – 2.25 (m, 4H).

^{13}C NMR (101 MHz, CD_3OD) δ 185.0, 141.3, 138.2, 137.2, 130.1, 44.4, 29.7.

IR (neat): *v* = 3096, 3047, 3004, 2893, 2837, 2162, 1642, 1518, 1463, 1408, 1356, 1327, 1313, 1226, 1178, 1108, 1080, 1062, 956, 908, 863, 851, 779, 755, 734, 708 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{10}H_{13}OS_2^+$ 213.0402, found 213.0403.



1-(3,3-Dimethyl-2-oxobutyl)tetrahydro-1H-thiophen-1-ium bromide (3s)

The titled compound was obtained as white solid in 90% yield (1.20 g, 4.5 mmol).

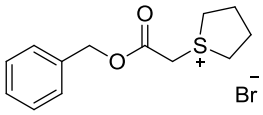
Melting point: 186-188 ^oC

^{1}H NMR (400 MHz, CD_3OD) δ 4.91 (s, 2H), 3.63 (dt, *J* = 13.6, 6.8 Hz, 2H), 3.45 (dd, *J* = 12.7, 6.3 Hz, 2H), 2.44 – 2.21 (m, 4H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, CD_3OD) δ 209.5, 45.2, 44.1, 29.7, 26.5.

IR (neat): *v* = 2970, 2952, 2906, 2162, 1980, 1705, 1482, 1459, 1446, 1433, 1396, 1363, 1338, 1306, 1271, 1226, 1203, 1167, 1136, 1103, 1065, 1027, 1010, 955, 937, 903, 891, 866, 811, 733 cm^{-1}

HRMS-ESI m/z : $[M-Br]^+$ calcd for $C_{10}H_{19}OS_2^+$ 187.1151, found 187.1150.



1-(2-(Benzyloxy)-2-oxoethyl)tetrahydro-1H-thiophen-1-ium bromide (3t)

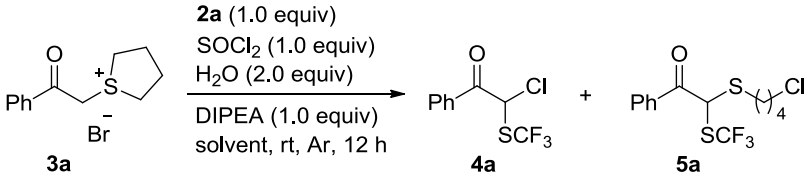
The titled compound was obtained as white solid in 92% yield (1.46 g, 4.6 mmol). **3t** is a known compound. [CAS: 1787295-44-6]

^{1}H NMR (400 MHz, CD_3OD) δ 7.42 (ddd, *J* = 15.7, 10.1, 4.4 Hz, 5H), 5.29 (s, 2H), 4.50 (s, 2H), 3.62 (dtd, *J* = 19.0, 12.8, 6.2 Hz, 4H), 2.45 – 2.24 (m, 4H).

III. Typical Procedure for condition optimization:

In a dry reaction tube, trifluoromethylthiolation reagent **2a** (0.1 mmol, 1.0 equiv) and 1-(2-oxo-2-phenylethyl)tetrahydro-1H-thiophen-1-ium bromide **3a** (0.1 mmol, 1.0 equiv) were dissolved in 1.0 mL anhydrous DMF under the argon atmosphere at the room temperature. Then, DIPEA (0.1 mmol, 1.0 equiv) and H_2O (0.2 mmol, 2.0 equiv) was added to the tube. $SOCl_2$ (0.1 mmol, 1.0 equiv) was added to the reaction mixture in the end. The mixture kept stirring at the same temperature for 12 hours. The reaction solution was analyzed by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

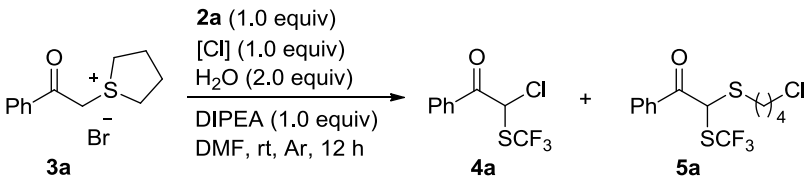
Table S1. Effect of solvent



Entry	Solvent	Yield of **4a** (%)	Yield of **5a** (%)
1	DMF	60	40
2	$CHCl_3$	28	20
3	MeOH	11	11
4	DMSO	36	7
5	THF	44	43
6	PhMe	15	24
7	NMP	51	47

Reaction condition: **2a** (0.1 mmol, 1.0 equiv), **3a** (0.1 mmol, 1.0 equiv), H_2O (0.2 mmol, 2.0 equiv), $SOCl_2$ (0.1 mmol, 1.0 equiv), DIPEA (0.1 mmol, 1.0 equiv) in solvent (1.0 mL) at rt for 12 h. Yields determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

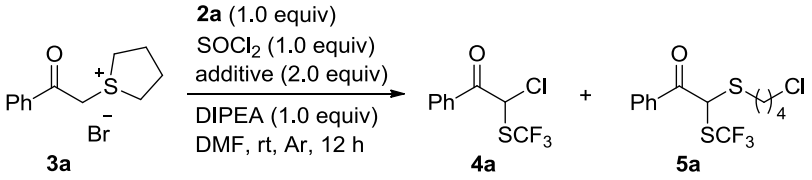
Table S2. Effect of chlorine source



Entry	[Cl] source	Yield of **4a** (%)	Yield of **5a** (%)
1	$SOCl_2$	59	39
2	TMSCl	28	20
3	$(COCl)_2$	56	37
4	NCS	20	13
5	AcCl	27	19
6	Bu_4NCl	-	-
7	HCl (37% solution in water)	37	26

Reaction condition: **2a** (0.1 mmol, 1.0 equiv), **3a** (0.1 mmol, 1.0 equiv), H_2O (0.2 mmol, 2.0 equiv), Cl source (0.1 mmol, 1.0 equiv), DIPEA (0.1 mmol, 1.0 equiv) in DMF (1.0 mL) at rt for 12 h. Yields determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

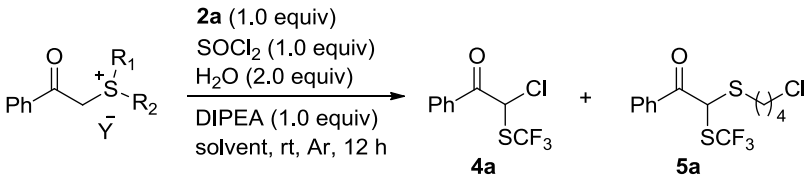
Table S3. Effect of additive



Entry	Additive	Yield of **4a** (%)	Yield of **5a** (%)
1	H_2O	60	39
2	MeOH	23	37
3	EtOH	58	39
4	tBuOH	51	32
5	AcOH	52	27
6	none	-	-

Reaction condition: **2a** (0.1 mmol, 1.0 equiv), **3a** (0.1 mmol, 1.0 equiv), additive (0.2 mmol, 2.0 equiv), $SOCl_2$ (0.1 mmol, 1.0 equiv), DIPEA (0.1 mmol, 1.0 equiv) in DMF (1.0 mL) at rt for 12 h. Yields determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

Table S4. Effect of sulfonium salt



Entry	Sulfonium salt	Yield of **4a** (%)	Yield of **5a** (%)
1	**3a**	60	40
2	**1aa**	54	-
3	**1ab**	95	-
4	**1ac**	>99	-

Reaction condition: **2a** (0.1 mmol, 1.0 equiv), sulfonium salt (0.1 mmol, 1.0 equiv), H_2O (0.2 mmol, 2.0 equiv), $SOCl_2$ (0.1 mmol, 1.0 equiv), DIPEA (0.1 mmol, 1.0 equiv) in DMF (1.0 mL) at rt for 12 h. Yields determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

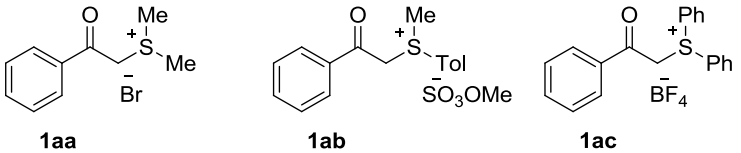
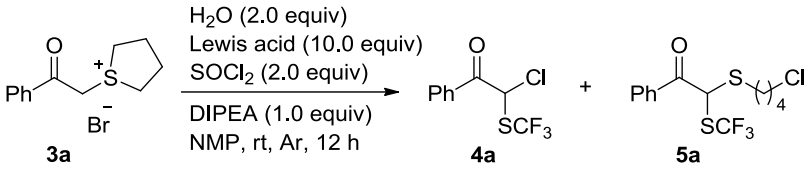


Table S5. Effect of Lewis acid

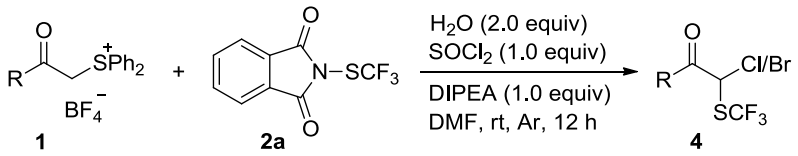


Entry	Lewis acid	Yield of **4a** (%)	Yield of **5a** (%)
1	LiCl	15	85
2	NaCl	50	49
3	KCl	47	51
4	$CaCl_2$	18	82
5	$MgCl_2$	24	73
6	$BaCl_2$	47	52
7	$AlCl_3$	-	-
8	$ZnCl_2$	3	4
9	none	50	49

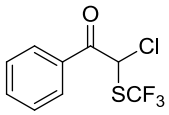
Reaction condition: Lewis acid (1.0 mmol, 10.0 equiv), NMP (1.0 mL) DIPEA (0.1 mmol, 1.0 equiv), **2a** (0.1 mmol, 1.0 equiv) and **3a** (0.1 mmol, 1.0 equiv), H_2O (0.2 mmol, 2.0 equiv), $SOCl_2$ (0.2 mmol, 2.0 equiv) added in order at rt for 12 h. Yields determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

IV. Isolation of products

General Procedure C: (for disubstituted halo-trifluoromethylthiolation of sulfur ylides)



In an argon-filled glovebox, a dry reaction tube was charged with **1** (0.5 mmol, 1.0 equiv), **2a** (0.5 mmol, 1.0 equiv), DMF (5.0 mL), DIPEA (0.5 mmol, 1.0 equiv), and H_2O (1.0 mmol, 2.0 equiv), $SOCl_2$ (0.5 mmol, 1.0 equiv) was added to the reaction mixture at the room temperature in the end. The mixture kept stirring at room temperature for 12 hours. Then, water (5.0 mL) was added to quench the reaction. The resulting mixture was extracted with petroleum ether or ethyl acetate for three times (3 x 8.0 mL) and the combined organic solution was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 100:1) to afford the desired product.



2-Chloro-1-phenyl-2-((trifluoromethyl)thio)ethanone (4a)

The product (127.3 mg, 97% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

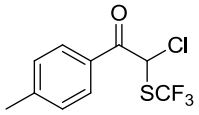
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.97 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 6.68 (s, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -43.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 135.2, 131.7, 129.7 (q, *J* = 309.2 Hz), 129.7, 129.3, 62.1.

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_9H_6ClF_3OS$ 253.9780, found 253.9784.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_9H_6ClF_3OS$ 256.0, found 256.0.



2-Chloro-1-(*p*-tolyl)-2-((trifluoromethyl)thio)ethanone (4b)

The product (129.0 mg, 96% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 1H), 2.44 (s, 3H).

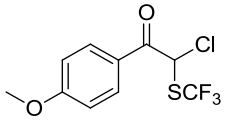
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3, 146.6, 130.0, 129.8, 129.8 (q, *J* = 309.1 Hz), 129.1, 62.2, 21.9.

IR (neat): *v* = IR (neat): v = 2926, 1683, 1607, 1573, 1410, 1318, 1285, 1203, 1103, 999, 841, 829, 757, 729, 701 cm^{-1}.

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_{10}H_8ClF_3OS$ 267.9936, found 267.9943.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_{10}H_8ClF_3OS$ 270.0, found 270.0.



2-Chloro-1-(4-methoxyphenyl)-2-((trifluoromethyl)thio)ethanone (4c)

The product (135.2 mg, 95% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 80/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.67 (s, 1H), 3.89 (s, 3H).

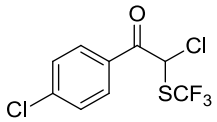
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.2, 165.2, 132.2, 129.8 (q, *J* = 309.1 Hz), 124.2, 114.5, 62.2, 55.7.

IR (neat): *v* = 2940, 2844, 1674, 1596, 1572, 1513, 1462, 1424, 1313, 1265, 1210, 1162，1102, 1027, 989, 845, 801, 777, 757, 734 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_{10}H_8ClF_3O_2S$ 283.9886, found 283.9892.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_{10}H_8ClF_3O_2S$ 286.0, found 286.0.



2-Chloro-1-(4-chlorophenyl)-2-((trifluoromethyl)thio)ethanone (4d)

The product (131.5 mg, 91% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 6.64 (s, 1H).

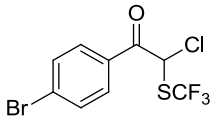
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.6.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.6, 141.9, 131.1, 130.0, 129.7, 129.6 (q, *J* = 309.3 Hz), 62.0.

IR (neat): *v* = 1687, 1590, 1570, 1490, 1402, 1311, 1282, 1208, 1105, 1091, 1014, 993, 846，826, 782, 756, 695 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_9H_5Cl_2F_3OS$ 287.9390, found 287.9393.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_9H_5Cl_2F_3OS$ 289.9, found 289.9.



1-(4-Bromophenyl)-2-chloro-2-((trifluoromethyl)thio)ethanone (4e)

The product (160.1 mg, 96% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 6.63 (s, 1H).

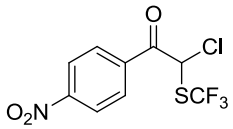
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.6.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.8, 132.7, 131.1, 130.8, 130.4, 129.6 (q, *J* = 309.4 Hz), 61.9.

IR (neat): v = 2927, 1688, 1585, 1566, 1487, 1398, 1309, 1286, 1209, 1103, 1070, 1011, 991, 844, 825, 777, 753, 698, 677 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_9H_5BrClF_3OS$ 331.8885, found 331.8882.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_9H_5BrClF_3OS$ 333.9, found 333.9.



2-Chloro-1-(4-nitrophenyl)-2-((trifluoromethyl)thio)ethanone (4f)

The product (139.3 mg, 93% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 50/1) as a light yellow solid.

Melting point: 51-53 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.6 Hz, 2H), 8.27 (d, *J* = 8.6 Hz, 2H), 6.77 (s, 1H).

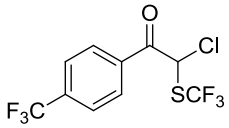
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.3.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.3, 151.2, 136.3, 130.9, 129.2 (q, *J* = 309.3 Hz), 124.3, 62.00.

IR (neat): *v* = 3113, 2998, 1696, 1600, 1519, 1493, 1409, 1348, 1323, 1309, 1286, 1218, 1185, 1170, 1133, 1104, 1012, 999, 980, 870, 857, 828, 791, 762, 756, 726, 688, 680 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_9H_5ClF_3NO_3S$ 298.9631, found 298.9620.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_9H_5ClF_3NO_3S$ 301.0, found 301.0.



2-Chloro-1-(4-(trifluoromethyl)phenyl)-2-((trifluoromethyl)thio)ethanone (4g)

The product (153.3 mg, 95% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 2H), 6.70 (s, 1H).

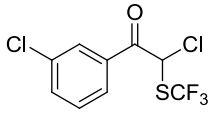
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.4, -66.5.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9, 136.2 (q, *J* = 33.1 Hz), 134.6, 130.1, 129.6 (q, *J* = 309.3 Hz), 126.3 (q, *J* = 3.0 Hz), 123.4 (q, *J* = 272.9 Hz), 62.0.

IR (neat): *v* = 1698, 1583, 1513, 1412, 1327, 1315, 1283, 1103, 1066, 1017, 996, 858, 829, 792, 775, 758, 743, 669 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_{10}H_5ClF_6OS$ 321.9654, found 321.9654.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_{10}H_5ClF_6OS$ 324.0, found 324.0.



2-Chloro-1-(3-chlorophenyl)-2-((trifluoromethyl)thio)ethanone (4h)

The product (134.4 mg, 93% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 6.63 (s, 1H).

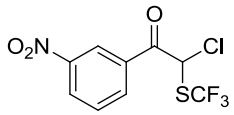
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.6.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.5, 135.7, 135.1, 133.2, 130.5, 129.6, 129.6 (q, *J* = 309.4 Hz), 127.7, 61.9.

IR (neat): *v* = 1692, 1573, 1474, 1422, 1286, 1266, 1208, 1102, 1021, 999, 901, 880, 812, 757, 693, 674 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_9H_5Cl_2F_3OS$ 287.9390, found 287.9381.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_9H_5Cl_2F_3OS$ 289.9, found 289.9.



2-Chloro-1-(3-nitrophenyl)-2-((trifluoromethyl)thio)ethanone (4i)

The product (140.8 mg, 94% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 50/1) as a light yellow oil.

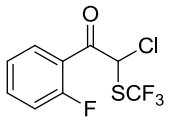
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.56 (d, *J* = 7.2 Hz, 1H), 8.40 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 6.73 (s, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -43.4.

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.8, 148.6, 135.1, 133.0, 130.7, 129.4 (q, *J* = 309.6 Hz), 129.2, 124.5, 61.9.

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_9H_5ClF_3NO_3S$ 298.9631, found 298.9633.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_9H_5ClF_3NO_3S$ 301.0, found 301.0.



2-Chloro-1-(2-fluorophenyl)-2-((trifluoromethyl)thio)ethanone (4j)

The product (126.8 mg, 93% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (td, *J* = 7.7, 1.7 Hz, 1H), 7.67 (tdd, *J* = 7.2, 5.2, 1.8 Hz, 1H), 7.34 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.22 (dd, *J* = 11.4, 8.5 Hz, 1H), 6.68 (d, *J* = 2.7 Hz, 1H).

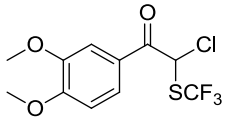
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.6, -111.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.9 (d, *J* = 3.6 Hz), 161.5 (d, *J* = 255.8 Hz), 137.0 (d, *J* = 9.5 Hz), 132.3, 129.6 (q, *J* = 309.2 Hz), 125.4 (d, *J* = 3.2 Hz), 120.9 (d, *J* = 11.6 Hz), 117.1 (d, *J* = 23.7 Hz), 65.4 (d, *J* = 11.1 Hz).

IR (neat): *v* = 2929, 1687, 1610, 1578, 1482, 1454, 1302, 1213, 1104, 996, 845, 815, 794, 756, 704 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_9H_5ClF_4OS$ 271.9686, found 271.9688.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_9H_5ClF_4OS$ 274.0, found 274.0.



2-Chloro-1-(3,4-dimethoxyphenyl)-2-((trifluoromethyl)thio)ethanone (4k)

The product (147.9 mg, 94% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 80/1) as a white solid.

Melting point: 59-61 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.49 (d, *J* = 1.8 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.65 (s, 1H), 3.94 (s, 3H), 3.90 (s, 3H).

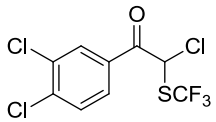
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.7

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.3, 155.1, 149.6, 129.7 (q, *J* = 309.1 Hz), 124.7, 124.4, 111.3, 110.3, 62.0, 56.3, 56.1.

IR (neat): *v* = 3025, 2965, 2936, 2842, 1667, 1594, 1584, 1516, 1464, 1449, 1439, 1423, 1355, 1300, 1281, 1260, 1204, 1178, 1157, 1133, 1103, 1021, 891, 874, 815, 807, 775, 764, 757, 732, 718 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_{11}H_{10}ClF_3O_3S$ 313.9991, found 313.9989.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_{11}H_{10}ClF_3O_3S$ 316.0, found 316.0.



2-Chloro-1-(3,4-dichlorophenyl)-2-((trifluoromethyl)thio)ethanone (4l)

The product (153.7 mg, 95% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a white solid.

Melting point: 41-42 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.8 Hz, 1H), 7.85 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 6.59 (s, 1H).

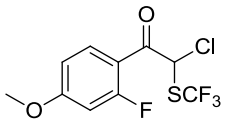
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.6.

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.7, 140.1, 134.2, 131.5, 131.4, 131.2, 129.5 (q, *J* = 309.4 Hz), 128.5, 61.8.

IR (neat): ν = 1691, 1583, 1557, 1467, 1391, 1282, 1254, 1208, 1131, 1103, 1031, 1004, 907, 884, 827, 810, 757, 703, 677 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_9H_4Cl_3F_3OS$ 321.9001, found 321.8996.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_9H_4Cl_3F_3OS$ 323.9, found 323.9.



2-Chloro-1-(2-fluoro-4-methoxyphenyl)-2-((trifluoromethyl)thio)ethanone (4m)

The product (146.8 mg, 97% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, J = 8.7 Hz, 1H), 6.84 (dd, J = 8.9, 1.8 Hz, 1H), 6.73 – 6.56 (m, 2H), 3.91 (s, 3H).

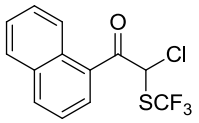
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.6, -107.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4, 166.9 (d, J = 12.4 Hz), 163.4 (d, J = 256.2 Hz), 133.9 (d, J = 3.5 Hz), 129.7 (q, J = 309.1 Hz), 113.2 (d, J = 10.9 Hz), 112.1, 102.0 (d, J = 27.6 Hz), 65.3 (d, J = 11.6 Hz), 56.3.

IR (neat): ν = 2985, 2848, 2621, 1675, 1614, 1571, 1505, 1445, 1344, 1295, 1276, 1234, 1196, 1160, 1116, 1030, 999, 972, 952, 846, 831, 781, 754, 701 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_{10}H_7ClF_4O_2S^+$ 301.9791, found 301.9787.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_{10}H_7ClF_4O_2S^+$ 304.0, found 304.0.



2-Chloro-1-(naphthalen-1-yl)-2-((trifluoromethyl)thio)ethanone (4n)

The product (124.9 mg, 82% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a white solid.

Melting point: 63-66 ^oC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.5 Hz, 1H), 8.04 – 7.78 (m, 3H), 7.65 – 7.40 (m, 3H), 6.78 (s, 1H).

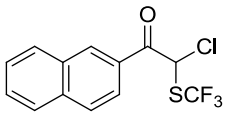
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.5.

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 135.4, 134.1, 131.1, 129.8 (q, *J* = 309.2 Hz), 129.5, 129.5, 129.2, 128.9, 127.2, 125.5, 124.2, 64.1.

IR (neat): *v* = 2985, 1980, 1844, 1676, 1619, 1595, 1571, 1508, 1455, 1436, 1399, 1351, 1284, 1238, 1218, 1184, 1155, 1105, 1082, 1026, 982, 967, 941, 924, 877, 839, 822, 780, 761, 753, 735, 705 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_{13}H_8ClF_3OS$ 303.9936, found 303.9931.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_{13}H_8ClF_3OS$ 306.0, found 306.0.



2-Chloro-1-(naphthalen-2-yl)-2-((trifluoromethyl)thio)ethanone (4o)

The product (146.3 mg, 96% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a white solid.

Melting point: 48-51 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.96 – 7.77 (m, 4H), 7.56 (dt, *J* = 14.5, 7.0 Hz, 2H), 6.82 (s, 1H).

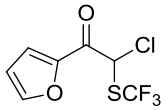
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.5.

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6, 136.3, 132.2, 132.0, 129.9, 129.8 (q, *J* = 309.2 Hz), 129.8, 129.2, 128.7, 127.9, 127.4, 124.1, 62.2.

IR (neat): *v* = 3064, 3006, 1666, 1626, 1598, 1506, 1468, 1439, 1393, 1376, 1358, 1300, 1219, 1204, 1169, 1156, 1110, 1023, 993, 943, 914, 867, 823, 807, 781, 767, 757, 741, 721 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_{13}H_8ClF_3OS$ 303.9936, found 303.9944.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_{13}H_8ClF_3OS$ 306.0, found 306.0.



2-Chloro-1-(furan-2-yl)-2-((trifluoromethyl)thio)ethanone (4p)

The product (110.1 mg, 90% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.50 (d, *J* = 3.6 Hz, 1H), 6.70 (d, *J* = 2.1 Hz, 1H), 6.53 (s, 1H).

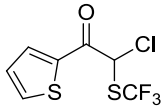
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 148.7, 148.0, 129.5 (q, *J* = 309.3 Hz), 121.8, 113.7, 61.0.

IR (neat): *v* = 3189, 1675, 1567, 1460, 1395, 1303, 1229, 1103, 1041, 1021, 1001, 908, 883, 846, 815, 765, 757, 718 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_7H_4ClF_3O_2S$ 243.9573, found 243.9570.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_7H_4ClF_3O_2S$ 246.0, found 246.0.



2-Chloro-1-(thiophen-2-yl)-2-((trifluoromethyl)thio)ethanone (4q)

The product (121.2 mg, 93% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 3.9 Hz, 1H), 7.85 (d, *J* = 4.9 Hz, 1H), 7.31 – 7.20 (m, 1H), 6.52 (s, 1H).

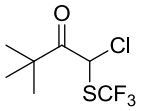
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.7

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.6, 137.9, 137.4, 135.2, 129.5 (q, *J* = 309.5 Hz), 129.0, 62.3.

IR (neat): *v* = 3098, 1662, 1515, 1409, 1356, 1294, 1242, 1102, 1065, 978, 947, 862, 820, 770, 757, 724, 700, 661 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_7H_4ClF_3OS_2$ 259.9344, found 259.9338.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_7H_4ClF_3OS_2$ 261.9, found 261.9.



1-Chloro-3,3-dimethyl-1-((trifluoromethyl)thio)butan-2-one (4r)

The product (95.1 mg, 81% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

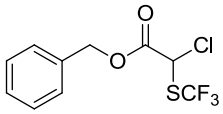
^1H NMR (400 MHz, $CDCl_3$) δ 6.16 (s, 1H), 1.30 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -44.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 129.7 (q, *J* = 309.1 Hz), 59.3, 44.8, 26.6.

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_7H_{10}ClF_3OS$ 234.0093, found 234.0092.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_7H_{10}ClF_3OS$ 236.0, found 236.0.



Benzyl 2-chloro-2-((trifluoromethyl)thio)acetate (4s)

The product (129.5 mg, 91% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 5H), 5.73 (s, 1H), 5.30 – 5.20 (m, 2H).

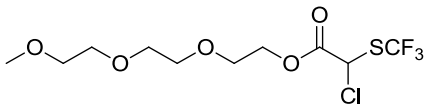
^{19}F NMR (376 MHz, $CDCl_3$) δ -44.0.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 134.1, 129.1, 129.1 (q, *J* = 309.6 Hz), 128.9, 128.6, 69.4, 57.9.

IR (neat): *v* = 1744, 1499, 1457, 1378, 1295, 1269, 1138, 1101, 960, 906, 882, 814, 757, 741, 695 cm^{-1}

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_{10}H_8ClF_3O_2S$ 283.9886, found 283.9884.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_{10}H_8ClF_3O_2S$ 286.0, found 286.0.



2-(2-(2-Methoxyethoxy)ethoxy)ethyl 2-chloro-2-((trifluoromethyl)thio)acetate (4t)

The product (115.9 mg, 68% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 3/1) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 1H), 4.42 (dd, *J* = 5.4, 3.9 Hz, 2H), 3.79 – 3.75 (m, 2H), 3.68 – 3.64 (m, 6H), 3.56 (dd, *J* = 5.7, 3.5 Hz, 2H), 3.39 (s, 3H).

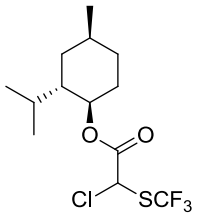
^{19}F NMR (376 MHz, $CDCl_3$) δ -44.1.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 129.1 (q, *J* = 309.6 Hz), 72.0, 70.9, 70.7, 68.5, 66.8, 59.2, 57.9 (d, *J* = 3.0 Hz).

IR (neat): *v* = 2878, 2360, 1746, 1453, 1353, 1300, 1101, 1026, 966, 852, 808, 758 cm^{-1}

HRMS-ESI m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{10}H_{17}ClF_3O_5S^+$ 341.0432, found 341.0431.

MS-ESI m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{10}H_{17}ClF_3O_5S^+$ 343.0, found 343.0.



(*1R,2S,4S*)-2-Isopropyl-4-methylcyclohexyl 2-chloro-2-((trifluoromethyl)thio) acetate (4u)

The product (126.5 mg, 76% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil and as an inseparable mixture of diastereoisomers (*d. r.* = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (s, 0.5H), 5.67 (s, 0.5H), 4.77 (td, *J* = 11.0, 3.7 Hz, 1H), 2.06 – 2.00 (m, 1H), 1.97 – 1.86 (m, 1H), 1.75 – 1.68 (m, 2H), 1.54 – 1.45 (m, 2H), 1.06 (ddd, *J* = 16.4, 9.5, 6.8 Hz, 2H), 0.92 (t, *J* = 6.5 Hz, 7H), 0.78 (s, 1.5H), 0.76 (s, 1.5H).

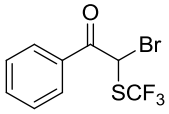
^{19}F NMR (376 MHz, $CDCl_3$) δ -44.2, -44.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 164.2, 129.2 (q, *J* = 309.7 Hz), 78.7, 78.6, 58.5, 58.4, 47.0, 47.0, 40.2, 34.1, 31.5, 23.4, 23.3, 22.0, 20.8, 20.8, 16.2, 16.1.

IR (neat): ν = 2958, 2873, 1741, 1457, 1371, 1296, 1267, 1165, 1138, 1106, 1038, 1008, 979, 964, 942, 911, 847, 815, 757, 721 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+NH_4]^+$ calcd for $C_{13}H_{24}ClF_3NO_2S^+$ 350.1163, found 350.1160.

MS-DART m/z : for ^{37}Cl $[M+NH_4]^+$ calcd for $C_{13}H_{24}ClF_3NO_2S^+$ 352.1, found 352.1.



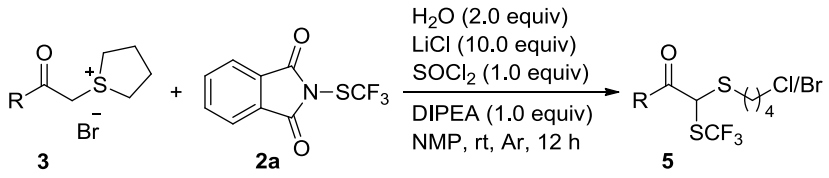
2-Bromo-1-phenyl-2-((trifluoromethyl)thio)ethanone (4v)[8]

The product (136.1 mg, 91% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 6.68 (s, 1H).

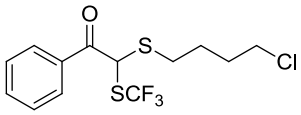
^{19}F NMR (376 MHz, $CDCl_3$) δ -44.3.

General Procedure D: (for halo-trifluoromethylthiolation of sulfur ylides involving ring opening of cyclic thioether)



In an argon-filled glovebox, LiCl (5.0 mmol, 10.0 equiv) and DIPEA (0.5 mmol, 1.0 equiv) were dissolved in 5.0 mL anhydrous NMP at room temperature. Then, **3** (0.5 mmol) and **2a** (0.5 mmol, 1.0 equiv) were added to the tube at the same time, and then H_2O (1.0 mmol, 2.0 equiv) was added. $SOCl_2$ (1.0 mmol, 2.0 equiv) was added to the reaction mixture at the room temperature in the end. The mixture kept stirring at room temperature for 12 hours. Water (5.0 mL) was added to quench the reaction. The resulting mixture was extracted with petroleum ether or ethyl acetate for three times (3 x 8.0 mL) and the combined organic solution was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was

purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 100:1) to afford the desired product.



2-((4-Chlorobutyl)thio)-1-phenyl-2-((trifluoromethyl)thio)ethanone (5a)

The product (140.6 mg, 82% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 5.93 (s, 1H), 3.50 (t, *J* = 6.3 Hz, 2H), 2.80 (dt, *J* = 14.1, 7.1 Hz, 1H), 2.57 (dt, *J* = 12.4, 7.0 Hz, 1H), 1.86 – 1.70 (m, 4H).

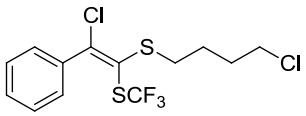
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.3.

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 134.5, 133.1, 130.1 (d, *J* = 308.6 Hz), 129.2, 129.1, 53.8, 44.3, 31.5, 29.5, 25.8.

IR (neat): *v* = 2959, 1679, 1601, 1569, 1486, 1456, 1383, 1289, 1259, 1102, 978, 810, 740, 715 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+NH_4]^+$ calcd for $C_{13}H_{18}ClF_3NOS_2^+$ 360.0465, found 360.0461.

MS-DART m/z : for ^{37}Cl $[M+NH_4]^+$ calcd for $C_{13}H_{18}ClF_3NOS_2^+$ 362.0, found 362.0.



(2-Chloro-1-((4-chlorobutyl)thio)-2-phenylvinyl)(trifluoromethyl)sulfane (5a')

The product (101.0 mg, 56% yield, E/Z = 2:1) was purified with a reverse phase preparative HPLC (SPD-20A, UV detector, 254 nm), RP C18 column (5 μm, 4.6 × 100 mm), a gradient elution of 80% acetonitrile in water 120 min (flow rate 10.0 mL/min) get product as a colorless oil. The NMR of the *E*-configured product are shown below.

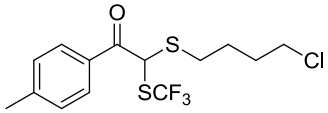
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.27 (m, 5H), 3.58 (t, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 7.1 Hz, 2H), 2.08 – 1.90 (m, 2H), 1.81 (dt, *J* = 9.8, 7.1 Hz, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -44.9.

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 138.2, 129.4, 129.2, 128.4 (q, *J* = 312.4 Hz), 128.3, 121.3, 44.5, 33.2, 31.3, 26.8.

HRMS-DART m/z : for ^{35}Cl $[M]^+$ calcd for $C_{13}H_{13}Cl_2F_3S_2^+$ 359.9782, found 359.9785.

MS-DART m/z : for ^{37}Cl $[M]^+$ calcd for $C_{13}H_{13}Cl_2F_3S_2^+$ 362.0, found 362.0.



2-((4-Chlorobutyl)thio)-1-(*p*-tolyl)-2-((trifluoromethyl)thio)ethanone (5b)

The product (141.0 mg, 79% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

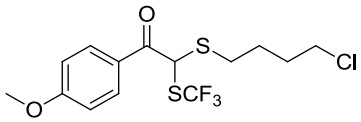
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.92 (s, 1H), 3.48 (t, *J* = 6.3 Hz, 2H), 2.79 (dt, *J* = 14.1, 7.1 Hz, 1H), 2.56 (dt, *J* = 12.5, 7.0 Hz, 1H), 2.43 (s, 3H), 1.84 – 1.68 (m, 4H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 145.6, 130.4, 130.1 (q, *J* = 308.7 Hz), 129.7, 129.2, 53.9, 44.2, 31.4, 29.1, 25.7, 21.8.

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3OS_2^+$ 357.0356, found 357.0350.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3OS_2^+$ 359.0, found 359.0.



2-((4-Chlorobutyl)thio)-1-(4-methoxyphenyl)-2-((trifluoromethyl)thio)ethanone (5c)

The product (145.1 mg, 78% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 80/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.92 (s, 1H), 3.88 (s, 3H), 3.48 (t, *J* = 6.3 Hz, 2H), 2.80 (dt, *J* = 12.5, 7.1 Hz, 1H), 2.58 (dt, *J* = 12.5, 7.0 Hz, 1H), 1.85 – 1.67 (m, 4H).

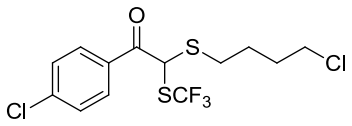
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.1.

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 164.5, 131.6, 130.1 (q, *J* = 310.1 Hz), 125.6, 114.2, 55.6, 53.9, 44.2, 31.4, 29.1, 25.7.

IR (neat): *v* = 2959, 1663, 1597, 1573, 1511, 1460, 1421, 1312, 1262, 1101, 1028, 992, 910, 844, 798, 777, 755, 731 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3O_2S_2^+$ 373.0305, found 373.0301.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3O_2S_2^+$ 375.0, found 375.0.



2-((4-Chlorobutyl)thio)-1-(4-chlorophenyl)-2-((trifluoromethyl)thio)ethanone (5d)

The product (128.8 mg, 68% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

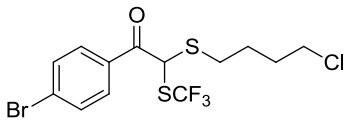
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 5.87 (s, 1H), 3.50 (t, *J* = 6.3 Hz, 2H), 2.79 (dt, *J* = 12.3, 7.1 Hz, 1H), 2.56 (dt, *J* = 12.3, 7.0 Hz, 1H), 1.86 – 1.69 (m, 4H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 140.9, 131.4, 130.6, 130.0 (q, *J* = 308.8 Hz), 129.4, 53.8, 44.2, 31.4, 29.3, 25.7.

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{13}H_{14}Cl_2F_3OS_2^+$ 376.9810, found 376.9805.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{13}H_{14}Cl_2F_3OS_2^+$ 379.0, found 379.0.



1-(4-Bromophenyl)-2-((4-chlorobutyl)thio)-2-((trifluoromethyl)thio)ethanone (5e)

The product (157.4 mg, 75% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 5.87 (s, 1H), 3.50 (t, *J* = 6.3 Hz, 2H), 2.79 (dt, *J* = 12.4, 7.1 Hz, 1H), 2.55 (dt, *J* = 12.3, 7.0 Hz, 1H), 1.85 – 1.68 (m, 4H).

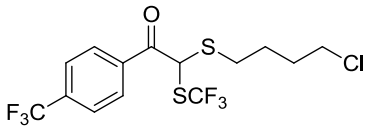
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 132.3, 131.8, 130.6, 129.9 (q, *J* = 308.7 Hz), 129.7, 53.7, 44.2, 31.4, 29.2, 25.7.

IR (neat): *v* = 2957, 1675, 1585, 1567, 1485, 1446, 1397, 1308, 1272, 1103, 1070, 996, 844, 771, 756 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{13}H_{14}BrClF_3OS_2^+$ 420.9305, found 420.9298.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{13}H_{14}BrClF_3OS_2^+$ 422.9, found 422.9.



2-((4-Chlorobutyl)thio)-1-(4-(trifluoromethyl)phenyl)-2-((trifluoromethyl)thio)ethanone (5f)

The product (125.7 mg, 61% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 5.88 (s, 1H), 3.51 (t, *J* = 6.2 Hz, 2H), 2.87 – 2.76 (m, 1H), 2.62 – 2.51 (m, 1H), 1.79 (ddt, *J* = 15.6, 8.3, 4.1 Hz, 4H).

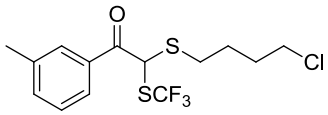
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2, -66.5.

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 136.1, 135.5 (q, *J* = 33.0 Hz), 129.9 (q, *J* = 308.8 Hz), 129.6, 126.2 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.9 Hz), 53.7, 44.2, 31.5, 29.4, 25.8.

IR (neat): *v* = 2960, 1683, 1582, 1512, 1410, 1326, 1315, 1272, 1102, 1065, 1017, 1001, 857, 788, 756, 732 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+NH_4]^+$ calcd for $C_{14}H_{17}ClF_6NOS_2^+$ 428.0339, found 428.0335.

MS-DART m/z : for ^{37}Cl $[M+NH_4]^+$ calcd for $C_{14}H_{17}ClF_6NOS_2^+$ 430.0, found 430.0.



2-((4-Chlorobutyl)thio)-1-(*m*-tolyl)-2-((trifluoromethyl)thio)ethanone (5g)

The product (157.7 mg, 86% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

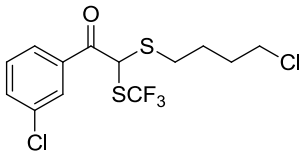
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.9 Hz, 2H), 7.50 – 7.36 (m, 2H), 5.93 (s, 1H), 3.49 (t, *J* = 6.2 Hz, 2H), 2.80 (dt, *J* = 13.8, 7.1 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.43 (s, 3H), 1.77 (ddd, *J* = 29.5, 13.9, 7.1 Hz, 4H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 139.0, 135.2, 133.1, 130.1 (q, *J* = 308.6 Hz), 129.6, 128.9, 126.3, 53.8, 44.2, 31.5, 29.2, 25.8, 21.4.

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3OS_2^+$ 357.0356, found 357.0350

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3OS_2^+$ 359.0, found 359.0.



2-((4-Chlorobutyl)thio)-1-(3-chlorophenyl)-2-((trifluoromethyl)thio)ethanone (5h)

The product (109.8 mg, 58% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.61 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 5.85 (s, 1H), 3.51 (t, *J* = 6.2 Hz, 2H), 2.79 (dt, *J* = 14.1, 7.1 Hz, 1H), 2.56 (dt, *J* = 12.5, 7.0 Hz, 1H), 1.87 – 1.69 (m, 4H).

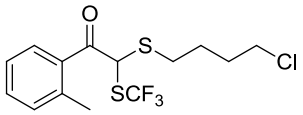
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3, 135.4, 134.7, 134.3, 130.3, 129.9 (q, *J* = 308.8 Hz), 129.2, 127.2, 53.7, 44.2, 31.4, 29.3, 25.7.

IR (neat): *ν* = 2958, 1678, 1571, 1421, 1257, 1196, 1102, 999, 901, 848, 810, 755, 677 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{13}H_{14}Cl_2F_3OS_2^+$ 376.9810, found 376.9804.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{13}H_{14}Cl_2F_3OS_2^+$ 379.0, found 379.0.



2-((4-Chlorobutyl)thio)-1-(*o*-tolyl)-2-((trifluoromethyl)thio)ethanone (5i)

The product (162.3 mg, 91% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 10.8, 4.2 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 2H), 5.74 (s, 1H), 3.50 (t, *J* = 6.2 Hz, 2H), 2.82 (dt, *J* = 12.4, 7.0 Hz, 1H), 2.62 (dt, *J* = 12.3, 7.1 Hz, 1H), 2.50 (s, 3H), 1.87 – 1.72 (m, 4H).

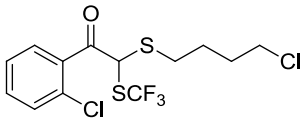
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.3.

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 140.1, 134.2, 132.7, 132.4, 130.1 (q, *J* = 309.4 Hz), 128.4, 126.0, 55.4, 44.3, 31.4, 29.6, 25.8, 21.2.

IR (neat): *v* = 2960, 1679, 1601, 1569, 1486, 1456, 1383, 1289, 1259, 1102, 978, 841, 810, 740, 715 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3OS_2^+$ 357.0356, found 357.0349.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3OS_2^+$ 359.0, found 359.0.



2-((4-Chlorobutyl)thio)-1-(2-chlorophenyl)-2-((trifluoromethyl)thio)ethanone (5j)

The product (134.3 mg, 71% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

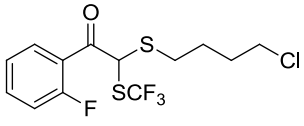
^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 3.2 Hz, 2H), 7.41 – 7.35 (m, 1H), 5.93 (s, 1H), 3.52 (t, *J* = 6.3 Hz, 2H), 2.79 (dt, *J* = 12.2, 7.0 Hz, 1H), 2.57 (dt, *J* = 12.1, 7.1 Hz, 1H), 1.80 (ddt, *J* = 16.5, 9.6, 4.7 Hz, 4H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -43.1.

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 135.5, 133.0, 131.7, 130.9, 130.5, 130.0 (q, *J* = 308.8 Hz), 127.2, 56.5, 44.3, 31.5, 29.2, 25.7.

HRMS-EI m/z : for ^{35}Cl [M+] calcd for $C_{13}H_{13}Cl_2F_3OS_2$ 375.9737, found 375.9731.

MS-EI m/z : for ^{37}Cl [M+] calcd for $C_{13}H_{13}Cl_2F_3OS_2$ 378.0, found 378.0.



2-((4-Chlorobutyl)thio)-1-(2-fluorophenyl)-2-((trifluoromethyl)thio)ethanone (5k)

The product (116.0 mg, 64% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (td, *J* = 7.7, 1.7 Hz, 1H), 7.67 – 7.58 (m, 1H), 7.30 (dt, *J* = 11.0, 2.0 Hz, 1H), 7.23 – 7.15 (m, 1H), 5.94 (d, *J* = 2.7 Hz, 1H), 3.49 (t, *J* = 6.3 Hz, 2H), 2.76 (dt, *J* = 12.5, 7.1 Hz, 1H), 2.51 (dt, *J* = 12.3, 7.0 Hz, 1H), 1.85 – 1.68 (m, 4H).

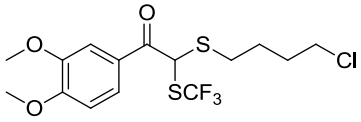
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.3, -110.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2 (d, *J* = 4.6 Hz), 161.4 (d, *J* = 254.7 Hz), 136.0 (d, *J* = 9.5 Hz), 131.9 (d, *J* = 1.5 Hz), 130.0 (q, *J* = 309.7 Hz), 125.2 (d, *J* = 3.2 Hz), 122.1 (d, *J* = 11.6 Hz), 117.0 (d, *J* = 24.0 Hz), 57.4 (d, *J* = 9.9 Hz), 44.2, 31.4, 28.7, 25.6.

IR (neat): *ν* = 2959, 1673, 1609, 1577, 1482, 1453, 1290, 1211, 1102, 1000, 841, 818, 794, 756, 729 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{13}H_{14}ClF_4OS_2^+$ 361.0105, found 361.0089.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{13}H_{14}ClF_4OS_2^+$ 363.0, found 363.0.



2-((4-Chlorobutyl)thio)-1-(3,4-dimethoxyphenyl)-2-((trifluoromethyl)thio)ethanone (5l)

The product (176.4 mg, 88% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 50/1) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 5.92 (s, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.50 (t, *J* = 6.3 Hz, 2H), 2.82 (dt, *J* = 14.1, 7.1 Hz, 1H), 2.60 (dt, *J* = 12.5, 7.0 Hz, 1H), 1.87 – 1.70 (m, 4H).

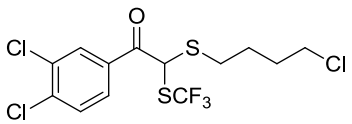
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 154.4, 149.4, 130.1 (q, *J* = 308.6 Hz), 125.8, 123.9, 111.2, 110.2, 56.2, 56.1, 53.6, 44.2, 31.4, 29.3, 25.8.

IR (neat): *v* = 2938, 1662, 1583, 1515, 1463, 1418, 1342, 1272, 1102, 1020, 909, 878, 820, 768, 755, 730, 704 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{15}H_{19}ClF_3O_3S_2^+$ 403.0411, found 403.0404.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{15}H_{19}ClF_3O_3S_2^+$ 405.0, found 405.0.



2-((4-Chlorobutyl)thio)-1-(3,4-dichlorophenyl)-2-((trifluoromethyl)thio)ethanone (5m)

The product (124.8 mg, 61% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a white solid.

Melting point: 42-43 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.0 Hz, 1H), 7.84 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 5.81 (s, 1H), 3.51 (t, *J* = 6.2 Hz, 2H), 2.79 (dt, *J* = 12.4, 7.1 Hz, 1H), 2.55 (dt, *J* = 12.3, 7.1 Hz, 1H), 1.93 – 1.60 (m, 4H).

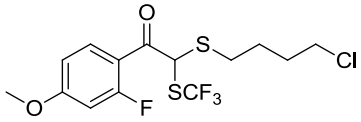
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 139.1, 133.9, 132.7, 131.1, 131.1, 129.8 (q, *J* = 308.9 Hz), 128.1, 53.6, 44.2, 31.4, 29.4, 25.8.

IR (neat): *v* = 2958, 1678, 1582, 1557, 1466, 1378, 1275, 1249, 1197, 1101, 1030, 1007, 907, 882, 828, 756, 729, 696 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{13}H_{13}Cl_3F_3OS_2^+$ 410.9420, found 410.9414.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{13}H_{13}Cl_3F_3OS_2^+$ 412.9, found 412.9.



2-((4-Chlorobutyl)thio)-1-(2-fluoro-4-methoxyphenyl)-2-((trifluoromethyl)thio)ethanone (5n)

The product (155.7 mg, 80% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 8.8 Hz, 1H), 6.82 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.66 (dd, *J* = 13.6, 2.2 Hz, 1H), 5.90 (d, *J* = 2.6 Hz, 1H), 3.89 (s, 3H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.84 – 2.71 (m, 1H), 2.57 – 2.47 (m, 1H), 1.85 – 1.66 (m, 4H).

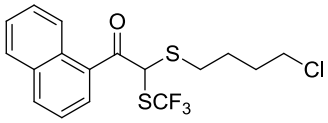
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.3, -106.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.2 (d, *J* = 5.3 Hz), 166.1 (d, *J* = 12.4 Hz), 163.1 (d, *J* = 255.0 Hz), 133.5 (d, *J* = 3.8 Hz), 130.1 (q, *J* = 308.5 Hz), 114.4 (d, *J* = 11.6 Hz), 111.8 (d, *J* = 2.1 Hz), 102.0 (d, *J* = 28.0 Hz), 57.5 (d, *J* = 10.4 Hz), 56.1, 44.3, 31.5, 28.6, 25.7.

IR (neat): v = 2955, 1664, 1611, 1571, 1504, 1443, 1343, 1273, 1232, 1198, 1153, 1097, 1032, 997, 953, 840, 778, 755, 735 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{14}H_{16}ClF_4O_2S_2^+$ 391.0211, found 391.0208.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{14}H_{16}ClF_4O_2S_2^+$ 393.0, found 393.0.



2-((4-Chlorobutyl)thio)-1-(naphthalen-1-yl)-2-((trifluoromethyl)thio)ethanone (5o)

The product (187.6 mg, 96% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a white solid.

Melting point: 37-38 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.93 (dd, *J* = 19.2, 7.3 Hz, 2H), 7.66 – 7.50 (m, 3H), 5.89 (s, 1H), 3.46 (t, *J* = 6.2 Hz, 2H), 2.87 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.76 – 2.63 (m, 1H), 1.78 (tdd, *J* = 16.3, 5.5, 4.1 Hz, 4H).

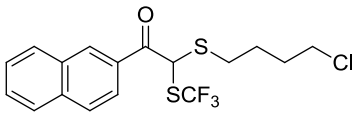
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.3.

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 134.2, 134.1, 132.3, 131.2, 130.1 (q, *J* = 308.8 Hz), 128.9, 128.7, 127.9, 127.1, 125.3, 124.3, 55.9, 44.3, 31.4, 29.7, 25.9.

IR (neat): v = 2927, 1674, 1593, 1573, 1508, 1446, 1367, 1279, 1240, 1105, 990, 946, 865, 815, 781, 756, 723 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{17}H_{17}ClF_3OS_2^+$ 393.0356, found 393.0352.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{17}H_{17}ClF_3OS_2^+$ 395.0, found 395.0.



2-((4-Chlorobutyl)thio)-1-(naphthalen-2-yl)-2-((trifluoromethyl)thio)ethanone (5p)

The product (155.2 mg, 79% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a white solid.

Melting point: 41-43 ^oC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.01 – 7.85 (m, 4H), 7.70 – 7.49 (m, 2H), 6.07 (d, *J* = 11.7 Hz, 1H), 3.46 (t, *J* = 6.2 Hz, 2H), 2.83 (dt, *J* = 12.4, 7.1 Hz, 1H), 2.59 (dt, *J* = 12.4, 7.0 Hz, 1H), 1.81 – 1.69 (m, 4H).

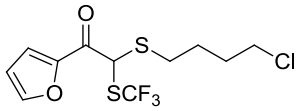
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.1.

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 136.1, 132.4, 131.2, 130.3, 130.2 (q, *J* = 308.7 Hz), 129.9, 129.4, 129.0, 127.9, 127.3, 124.3, 54.1, 44.3, 31.5, 29.3, 25.8.

IR (neat): v = 2957, 1968, 1664, 1623, 1592, 1571, 1507, 1463, 1438, 1387, 1359, 1321, 1281, 1245, 1154, 1099, 1032, 1015, 967, 944, 922, 874, 826, 780, 756, 740, 711, 699 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{17}H_{17}ClF_3OS_2^+$ 393.0356, found 393.0353.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{17}H_{17}ClF_3OS_2^+$ 395.0, found 395.0.



2-((4-Chlorobutyl)thio)-1-(furan-2-yl)-2-((trifluoromethyl)thio)ethanone (5q)

The product (132.7 mg, 80% yield) was purified with silica gel chromatography (petroleum

ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 0.9 Hz, 1H), 7.41 (d, *J* = 3.6 Hz, 1H), 6.64 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.73 (s, 1H), 3.53 (t, *J* = 6.3 Hz, 2H), 2.85 (dt, *J* = 12.5, 7.0 Hz, 1H), 2.67 (dt, *J* = 12.4, 7.1 Hz, 1H), 1.95 – 1.59 (m, 4H).

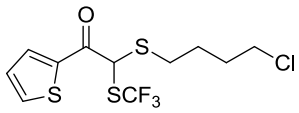
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.4.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 149.2, 147.6, 129.8 (q, *J* = 308.9 Hz), 120.1, 113.3, 52.4 (d, *J* = 1.7 Hz), 44.2, 31.4, 29.6, 25.8.

IR (neat): v = 3126, 3097, 2964, 1652, 1560, 1463, 1396, 1312, 1246, 1212, 1136, 1101, 1051, 999, 919, 881, 849, 821, 769, 758, 718, 707, 696, 654 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{11}H_{13}ClF_3O_2S_2^+$ 332.9992, found 332.9989.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{11}H_{13}ClF_3O_2S_2^+$ 335.0, found 335.0.



2-((4-Chlorobutyl)thio)-1-(thiophen-2-yl)-2-((trifluoromethyl)thio)ethanone (5r)

The product (158.6 mg, 91% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 3.9 Hz, 1H), 7.76 (d, *J* = 4.9 Hz, 1H), 7.21 (dd, *J* = 23.1, 19.1 Hz, 1H), 5.72 (s, 1H), 3.51 (t, *J* = 6.2 Hz, 2H), 2.84 (dt, *J* = 12.5, 7.0 Hz, 1H), 2.67 (dt, *J* = 12.4, 7.0 Hz, 1H), 1.89 – 1.72 (m, 4H).

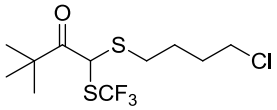
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.3.

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.1, 139.1, 135.8, 133.9, 129.8 (q, *J* = 308.9 Hz), 128.6, 54.2, 44.2, 31.3, 29.7, 25.7.

IR (neat): v = 2957, 1652, 1516, 1409, 1355, 1285, 1239, 1101, 1063, 977, 949, 861, 755, 723, 686, 656 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{11}H_{13}ClF_3OS_3^+$ 348.9764, found 348.9758.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{11}H_{13}ClF_3OS_3^+$ 351.0, found 351.0.



1-((4-Chlorobutyl)thio)-3,3-dimethyl-1-((trifluoromethyl)thio)butan-2-one (5s)

The product (150.1 mg, 93% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 3.55 (t, *J* = 6.3 Hz, 2H), 2.80 (dt, *J* = 12.3, 7.2 Hz, 1H), 2.58 (dt, *J* = 12.3, 7.2 Hz, 1H), 1.92 – 1.73 (m, 4H), 1.29 (s, 9H).

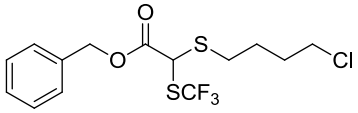
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.6.

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 130.0 (q, *J* = 308.5 Hz), 51.2, 44.5, 44.2, 31.5, 29.0, 27.3, 25.8.

IR (neat): v = 2966, 1694, 1478, 1397, 1368, 1285, 1104, 1054, 996, 855, 756 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{11}H_{19}ClF_3OS_2^+$ 323.0512, found 323.0510.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{11}H_{19}ClF_3OS_2^+$ 325.1, found 325.1.



Benzyl 2-((4-chlorobutyl)thio)-2-((trifluoromethyl)thio)acetate (5t)

The product (170.7 mg, 92% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 5H), 5.25 – 5.16 (m, 2H), 4.82 (s, 1H), 3.48 (t, *J* = 6.2 Hz, 2H), 2.77 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.71 – 2.61 (m, 1H), 1.83 – 1.67 (m, 4H).

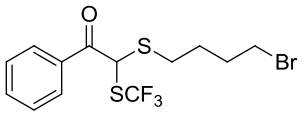
^{19}F NMR (376 MHz, $CDCl_3$) δ -44.2.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 134.7, 129.3 (q, *J* = 309.6 Hz), 128.8, 128.7, 128.5, 68.4, 49.0, 44.1, 31.3, 30.8, 25.9.

IR (neat): v = 2959, 1739, 1499, 1456, 1376, 1283, 1213, 1100, 966, 907, 810, 738, 696 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3O_2S_2^+$ 373.0305, found 373.0298.

MS-DART m/z : for ^{37}Cl $[M+H]^+$ calcd for $C_{14}H_{17}ClF_3O_2S_2^+$ 375.0, found 375.0.



2-((4-Bromobutyl)thio)-1-phenyl-2-((trifluoromethyl)thio)ethanone (5u)

The product (133.6 mg, 69% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

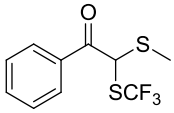
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.65 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 5.92 (s, 1H), 3.36 (t, *J* = 6.5 Hz, 2H), 2.80 (dt, *J* = 12.3, 7.3 Hz, 1H), 2.57 (dt, *J* = 12.3, 7.2 Hz, 1H), 1.95 – 1.86 (m, 2H), 1.78 – 1.69 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -43.3.

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 134.4, 133.1, 130.1 (q, J = 308.6 Hz), 129.2, 129.1, 53.8, 32.8, 31.6, 29.1, 27.0.

HRMS-DART m/z : for ^{79}Br $[M+H]^+$ calcd for $C_{13}H_{15}BrF_3OS_2^+$ 386.9694, found 386.9692.

MS-DART m/z : for ^{81}Br $[M+H]^+$ calcd for $C_{13}H_{15}BrF_3OS_2^+$ 389.0, found 389.0.



2-(Methylthio)-1-phenyl-2-((trifluoromethyl)thio)ethanone (5v)

The product (107.9 mg, 81% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 100/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.67 – 7.60 (m, 1H), 7.50 (dd, *J* = 10.7, 4.8 Hz, 2H), 5.97 (s, 1H), 2.13 (s, 3H).

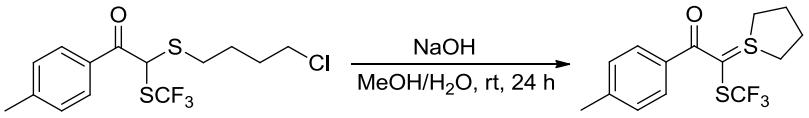
^{19}F NMR (376 MHz, $CDCl_3$) δ -43.1.

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 134.4, 133.2, 130.2 (q, *J* = 308.3 Hz), 129.2, 129.1, 54.3 (d, *J* = 1.6 Hz), 12.1.

IR (neat): v = 2923, 1675, 1596, 1580, 1449, 1433, 1320, 1271, 1101, 994, 806, 756, 728, 745, 700, 684 cm^{-1}

HRMS-DART m/z : $[M+H]^+$ calcd for $C_{10}H_{10}F_3OS_2^+$ 267.0120, found 267.1022.

V. Transformation of the product



5b **6**

2-Trifluoromethylthio-2-(tetrahydrothien-1-ylidene)-1-(*p*-tolyl)ethanone (6)

To a solution of **5b** (0.1 mmol, 35.7 mg) and NaOH (0.25 mmol, 10.0 mg) in 1.0 mL of $MeOH/H_2O$ = 1.0/0.1, and the mixture stirred at room temperature for 24 hours. The mixture was concentrated in vacuo. The product (32.0 mg, 99% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow solid.

Melting point: 118-122 ^{o}C

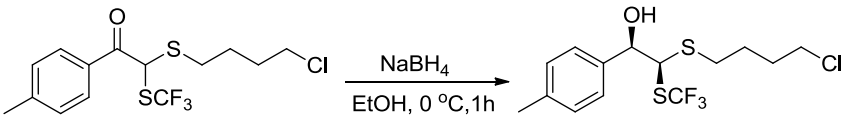
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.66 (d, *J* = 5.0 Hz, 2H), 3.29 (dt, *J* = 11.6, 6.0 Hz, 2H), 2.72 (dd, *J* = 9.3, 5.8 Hz, 2H), 2.36 (s, 3H), 2.03 (dd, *J* = 10.4, 5.4 Hz, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -53.6.

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 139.3, 137.9, 129.6 (q, *J* = 315.6 Hz), 128.4, 128.2, 54.8, 42.5, 28.6, 21.6.

IR (neat): v = 2951, 1682, 1609, 1575, 1532, 1435, 1409, 1315, 1300, 1282, 1257, 1212, 1181, 1110, 1020, 963, 897, 878, 840, 823, 798, 771, 745, 704 cm^{-1}

HRMS-ESI m/z : $[M+H]^+$ calcd for $C_{14}H_{16}F_3OS_2^+$ 321.0589, found 321.0588.



5b **7**

(cis)-2-((4-Chlorobutyl)thio)-1-(*p*-tolyl)-2-((trifluoromethyl)thio)ethanol (7)

To a solution of **5b** (0.1 mmol, 35.7 mg) in 1 mL of EtOH at 0 ^{o}C was added $NaBH_4$ (0.2 mmol, 7.6 mg) slowly. The mixture stirred for 1 hour until **5b** was completely transformed. The mixture was concentrated in vacuo. The product (27.5 mg, 82% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 50/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 5.15 (t, *J* = 3.3 Hz, 1H), 4.37 (d, *J* = 3.3 Hz, 1H), 3.41 (t, *J* = 5.8 Hz, 2H), 2.76 (d, *J* = 4.1 Hz, 1H), 2.66 – 2.49 (m, 2H), 2.36 (s, 3H), 1.74 – 1.63 (m, 3H), 1.59 – 1.46 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -43.4.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 136.4, 130.4 (q, *J* = 309.5 Hz), 129.1, 126.4, 75.9, 59.3, 44.3, 31.3, 31.2, 25.9, 21.3.

IR (neat): *v* = 3446, 2924, 1514, 1447, 1286, 1146, 1100, 1020, 862, 816, 785, 755, 725 cm^{-1}

HRMS-DART m/z : for ^{35}Cl $[M+NH_4]^+$ calcd for $C_{14}H_{22}ClF_3NOS_2^+$ 376.0778, found 376.0781.

MS-DART m/z : for ^{37}Cl $[M+NH_4]^+$ calcd for $C_{14}H_{22}ClF_3NOS_2^+$ 378.1, found 378.1.

VI. References

[1] C. Xu, B. Ma, Q. Shen, *Angew. Chem., Int. Ed*. **2014**, *53*, 9316-9320.

[2] K. Kang, C. Xu, Q. Shen, *Org. Chem. Front*. **2014**, *1*, 294-297.

[3] L. Liu, Z. Yuan, R. Pan, Y. Zeng, A. Lin, H. Yao, Y. Huang, *Org. Chem. Front.* **2018**, *5*, 623-628.

[4] Q. Wang, T.-R. Li, L.-Q. Lu, M.-M. Li, K. Zhang, W.-J. Xiao, *J. Am. Chem. Soc.* **2016**, *138*, 8360-8363.

[5] T. A. Podrugina, V. A. Alferova, A. V. Mironov, E. D. Matveeva, R. Gleiter, N. S. Zefirov, *Tetrahedron* **2016**, *72*, 6955-6962.

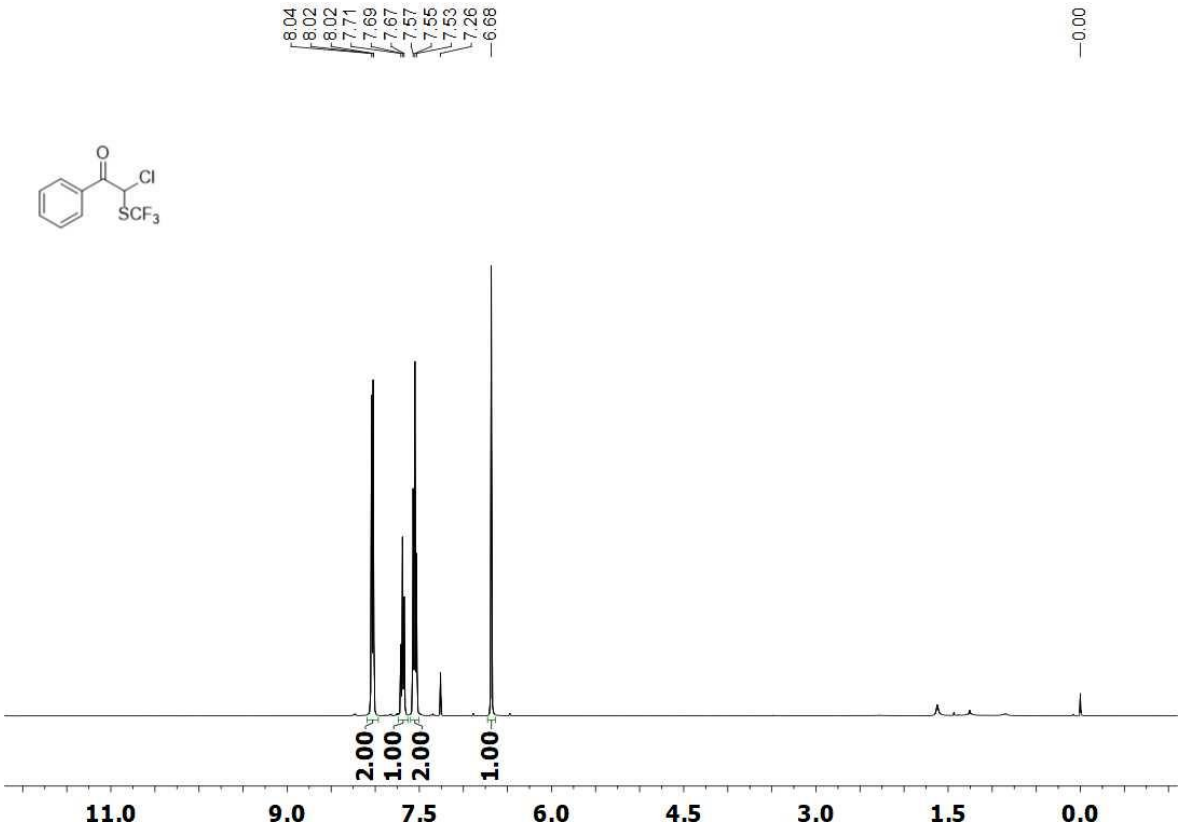
[6] K. Kaya, J. Kreutzer, Y. Yagci, *J. Polym. Sci. Pol. Chem.* **2018**, *56*, 451-457.

[7] A. Biswas, S. De Sarkar, L. Tebben, A. Studer, *Chem. Commun*. **2012**, *48*, 5190-5192.

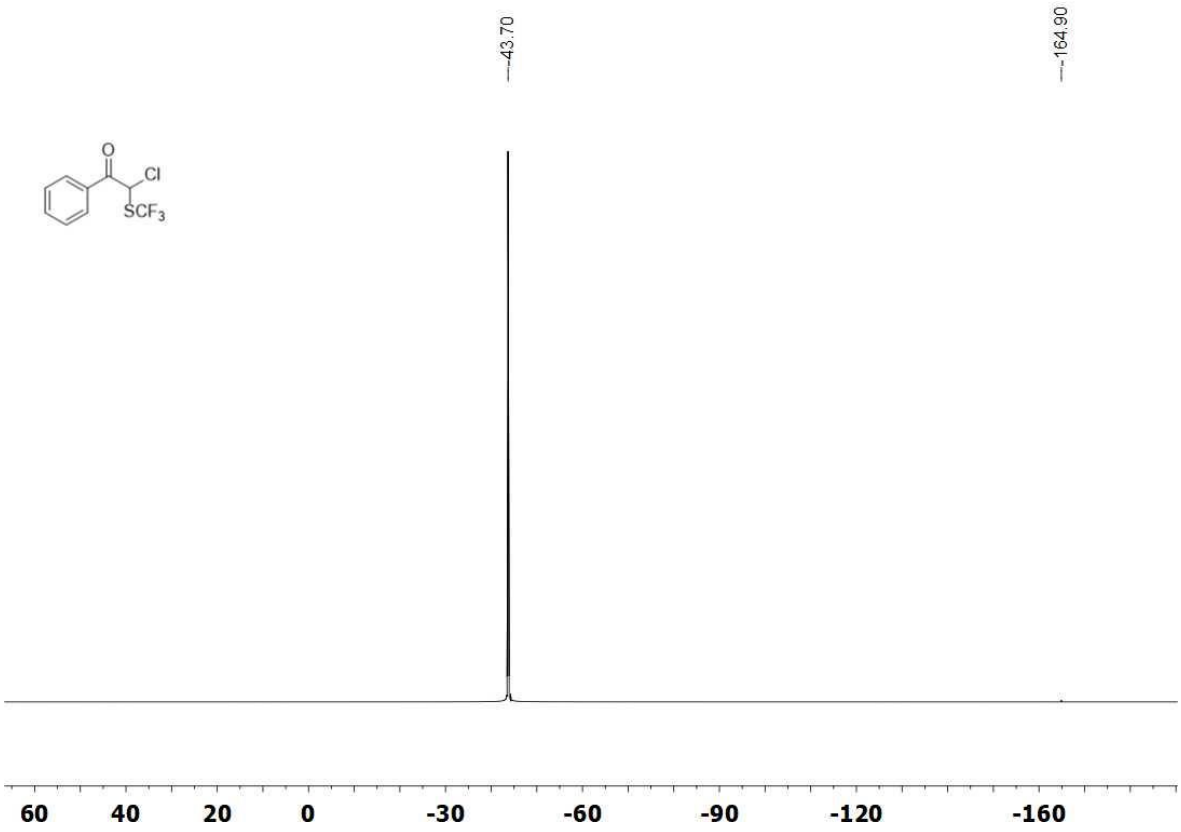
[8] S. Alazet, L. Zimmer, T. Billard, *Chem. Eur. J.* **2014**, *20*, 8589-8593.

VII. Copies of the NMR spectra

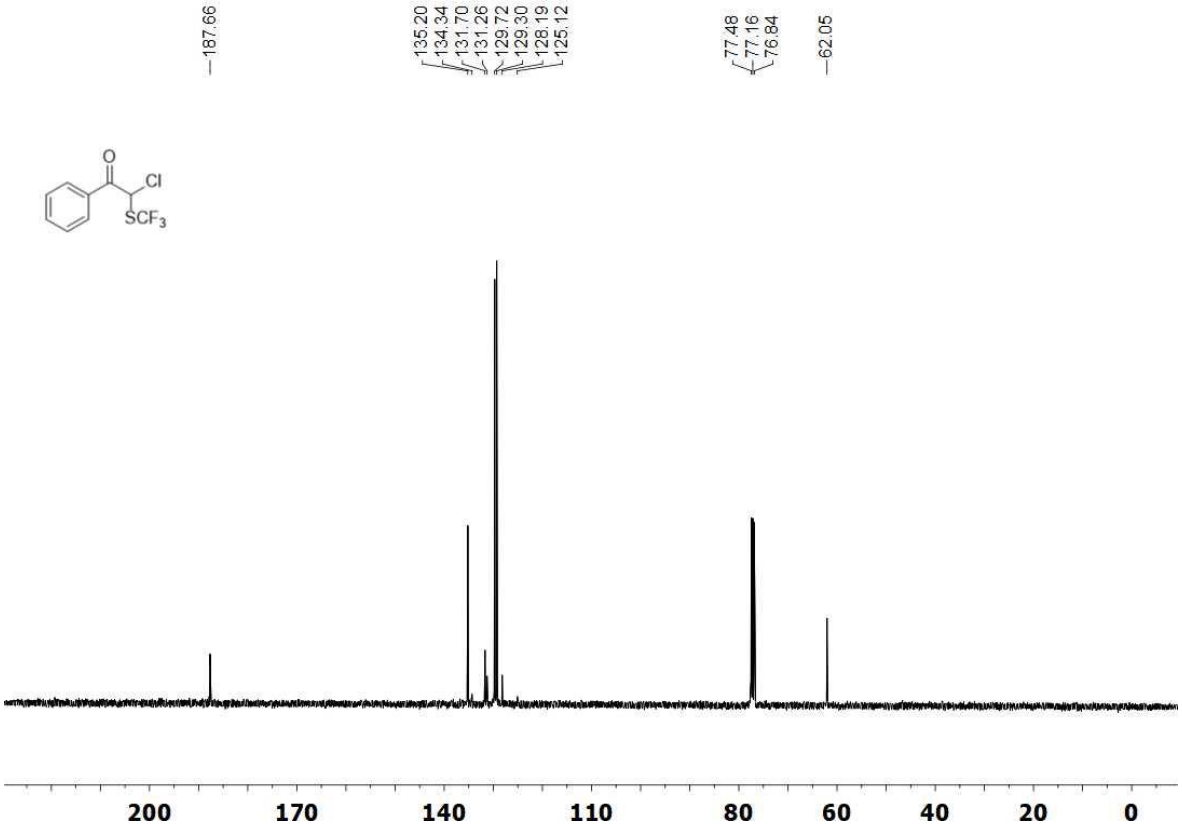
^{1}H NMR of compound **4a**



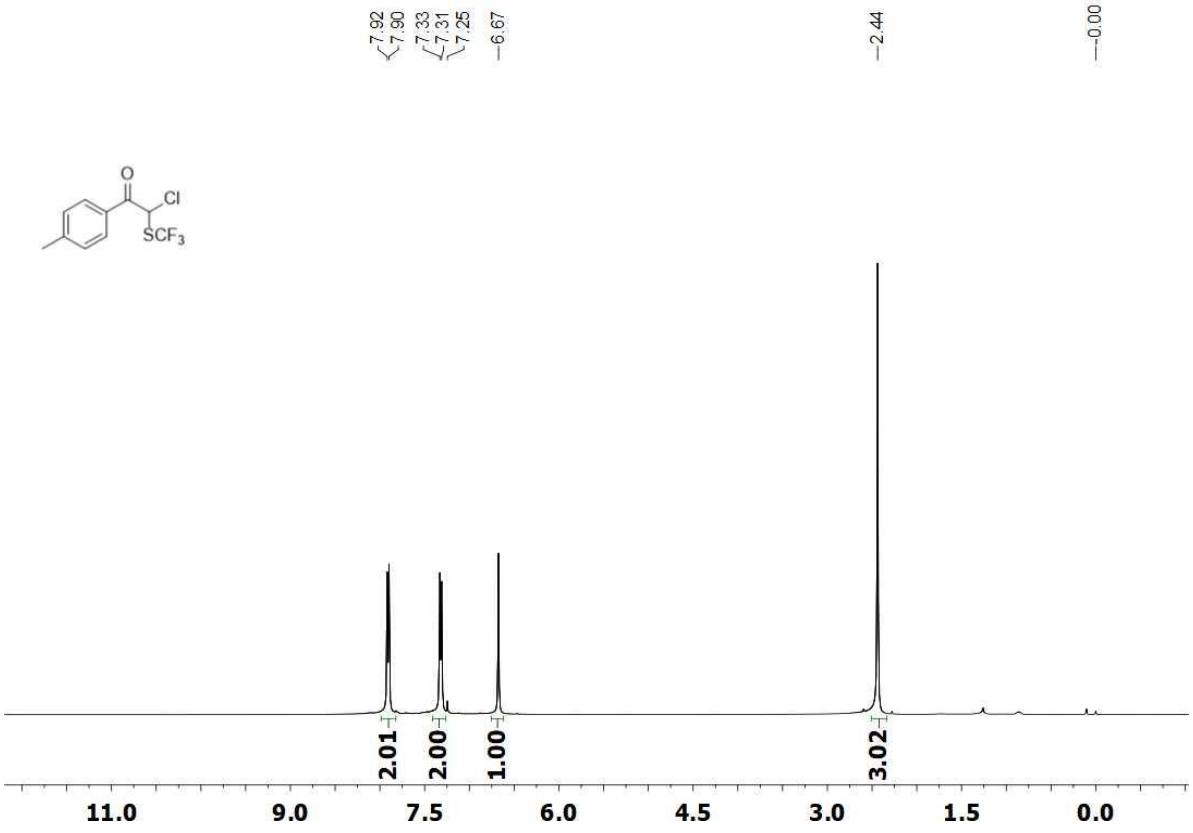
^{19}F NMR of compound **4a**



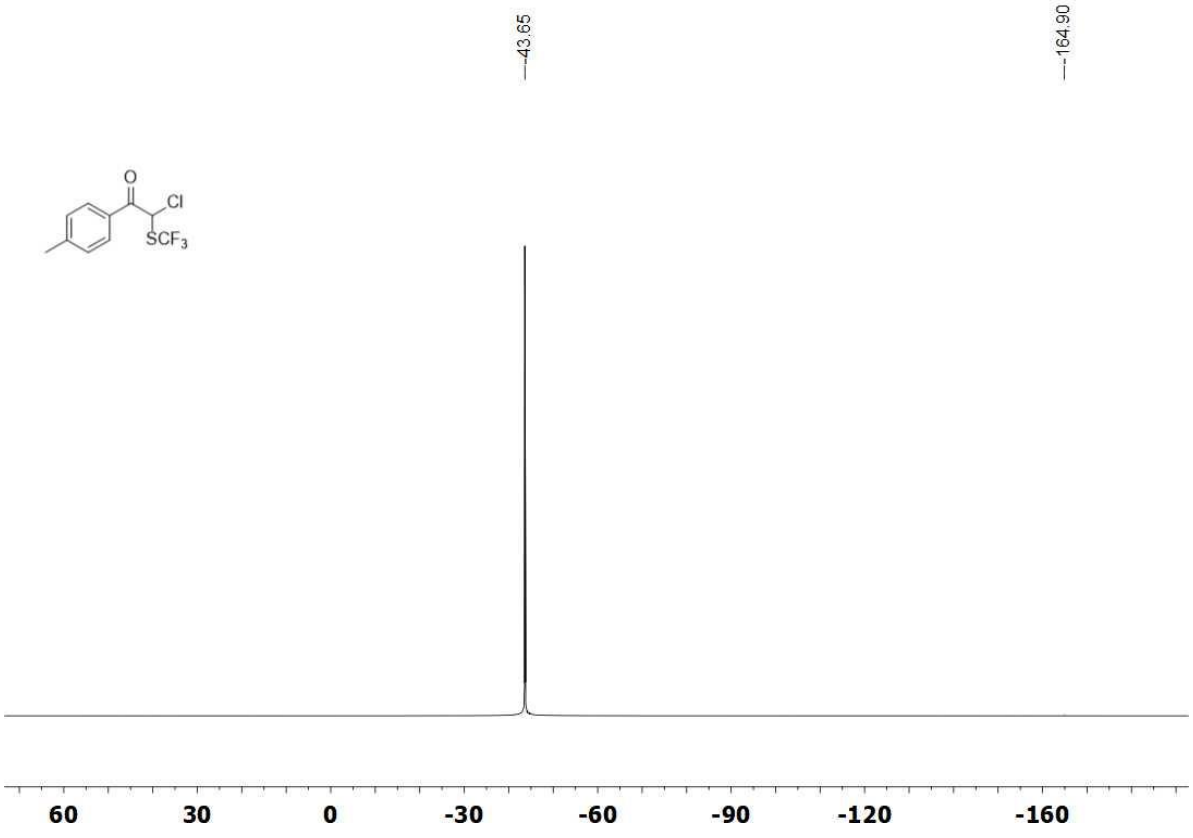
^{13}C NMR of compound **4a**



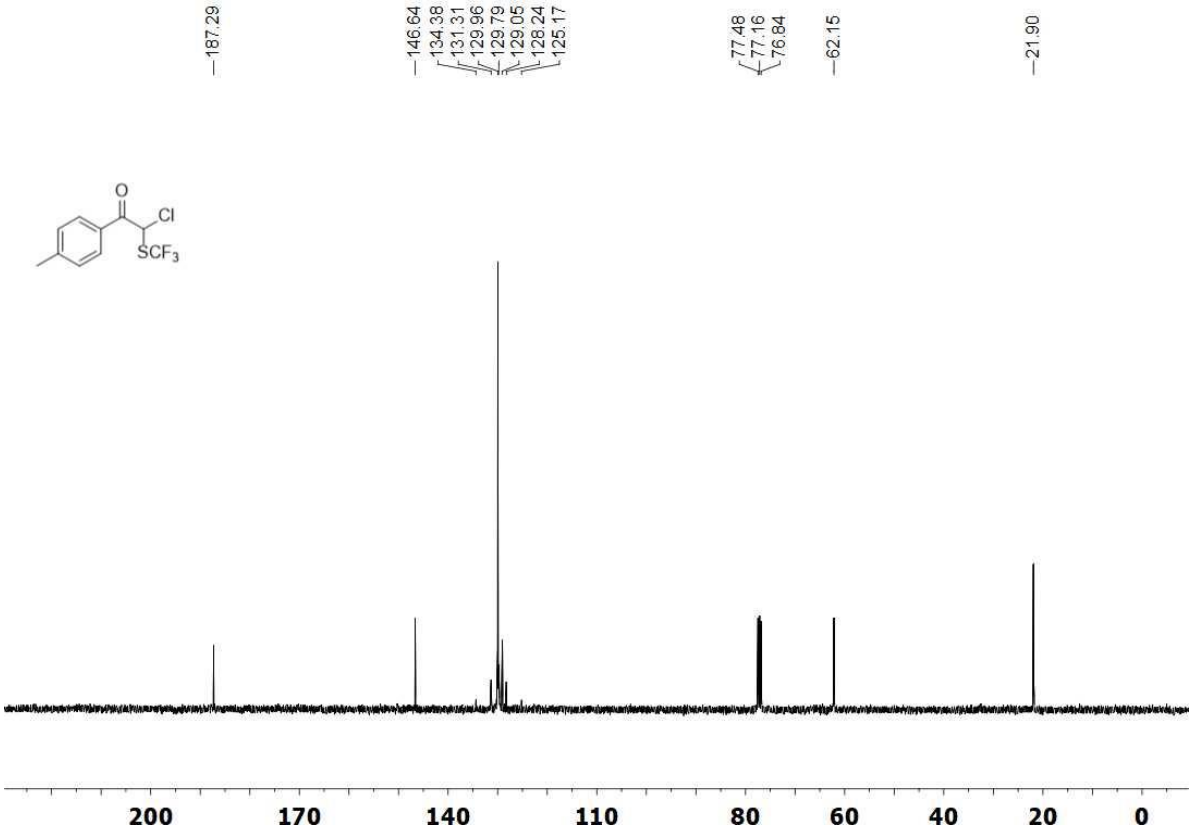
^{1}H NMR of compound **4b**



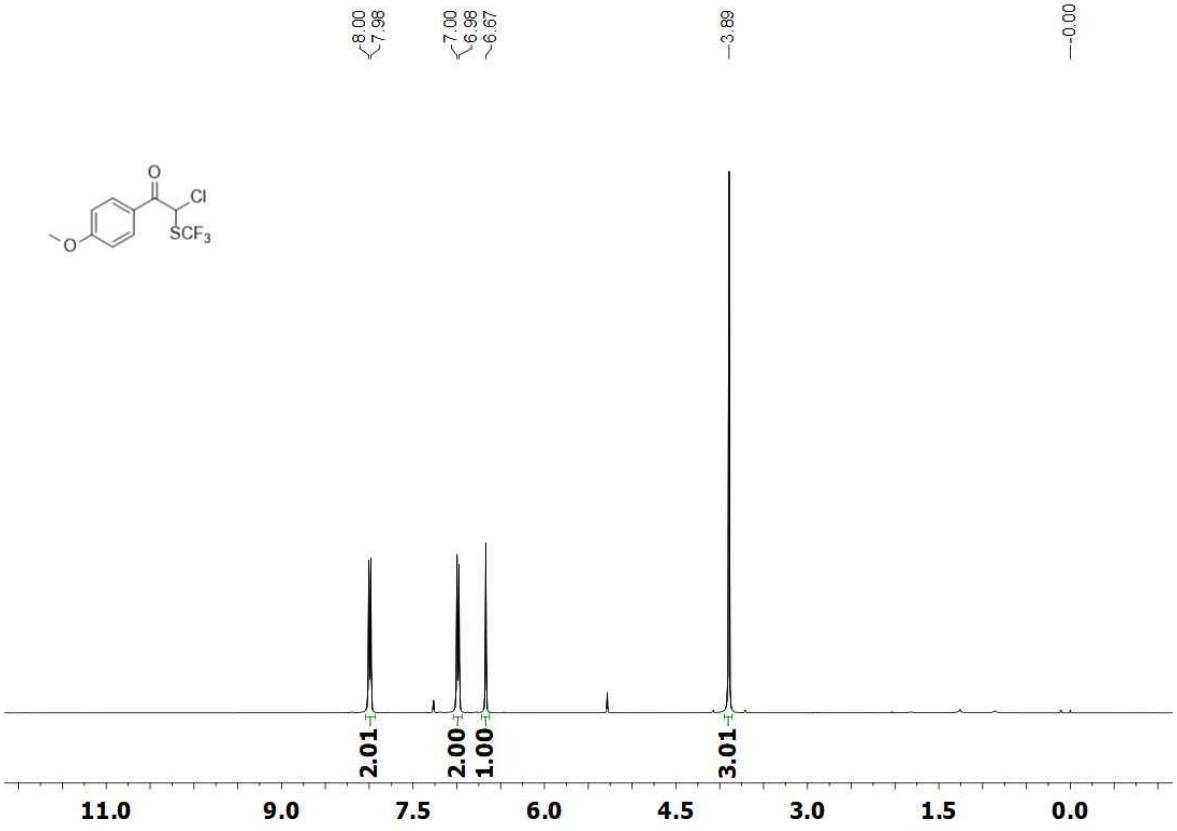
^{19}F NMR of compound **4b**



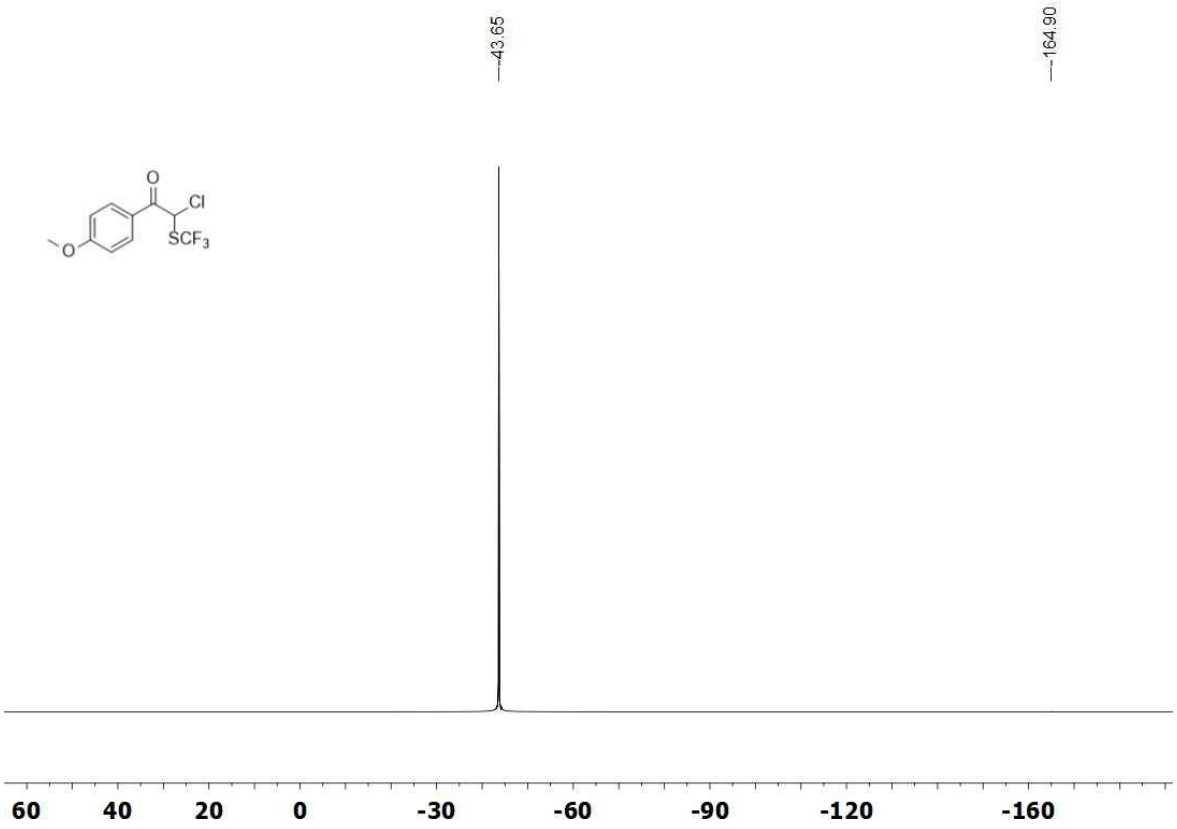
^{13}C NMR of compound **4b**



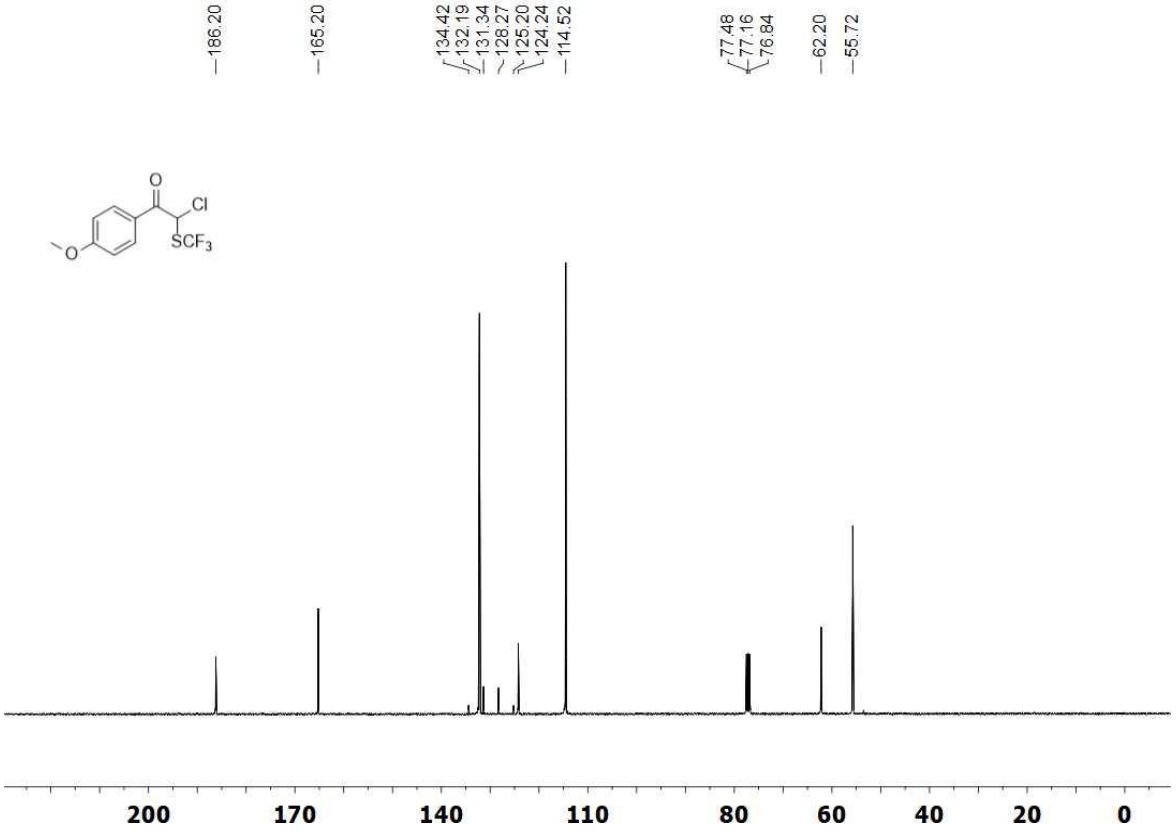
^{1}H NMR of compound **4c**



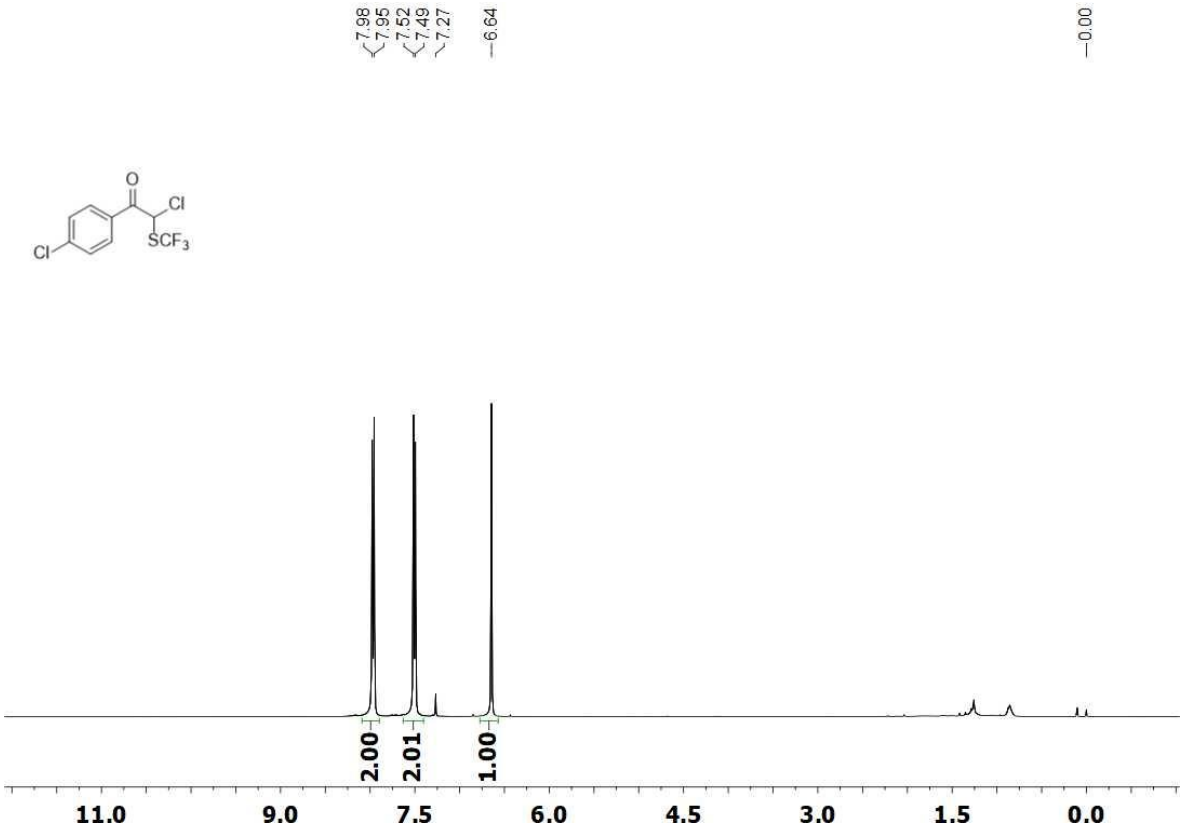
^{19}F NMR of compound **4c**



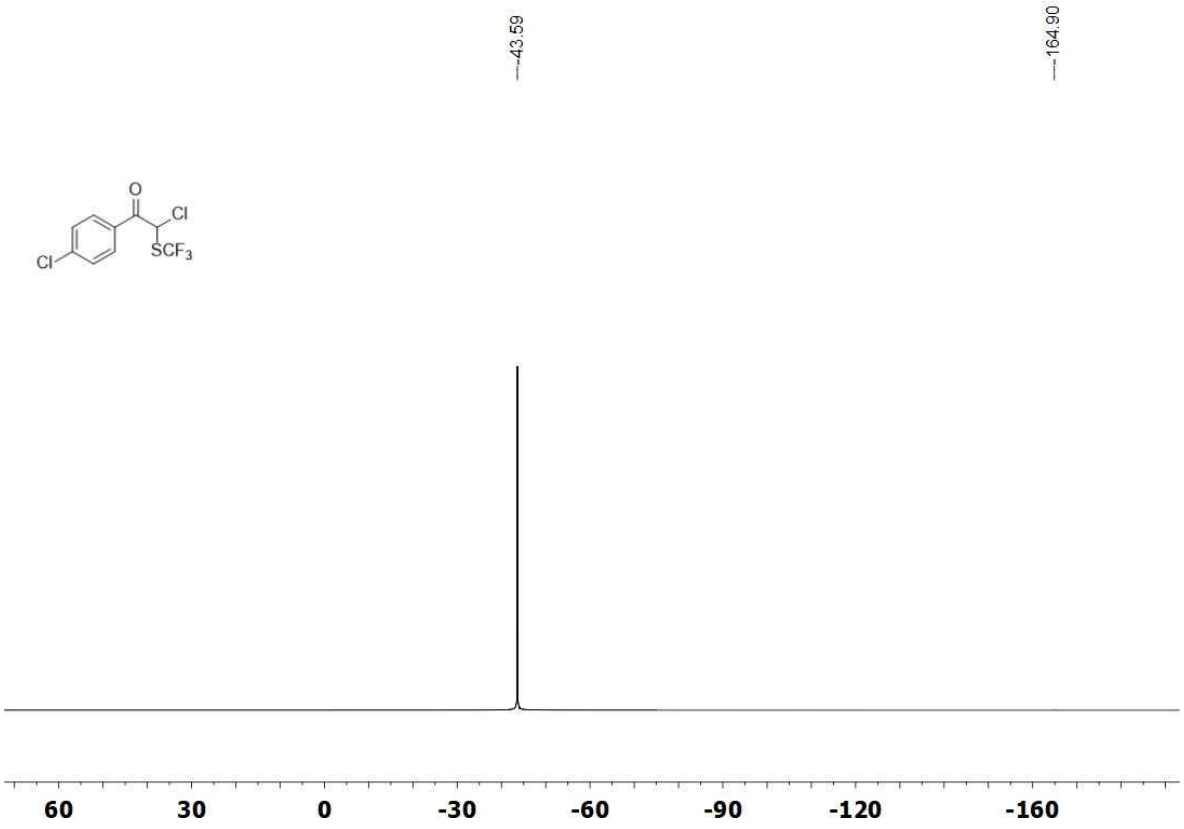
^{13}C NMR of compound **4c**



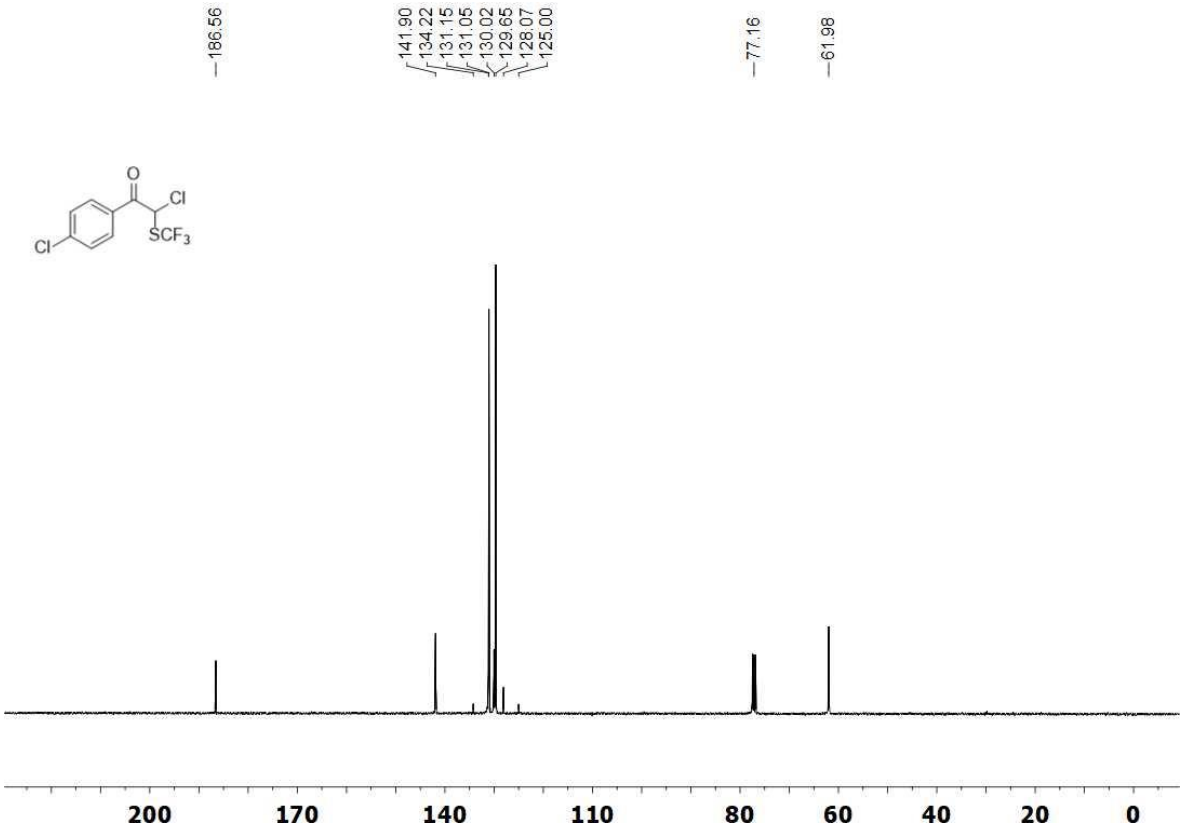
^{1}H NMR of compound **4d**



^{19}F NMR of compound **4d**



^{13}C NMR of compound **4d**



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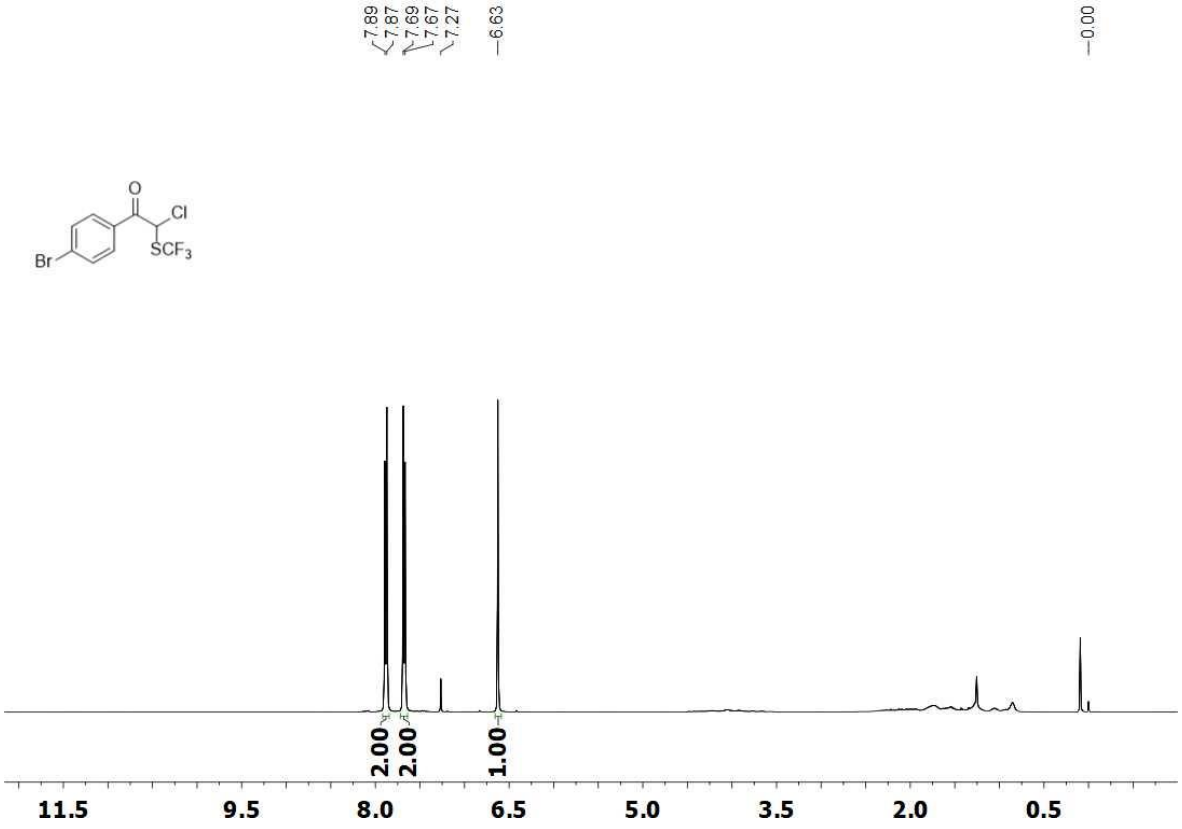
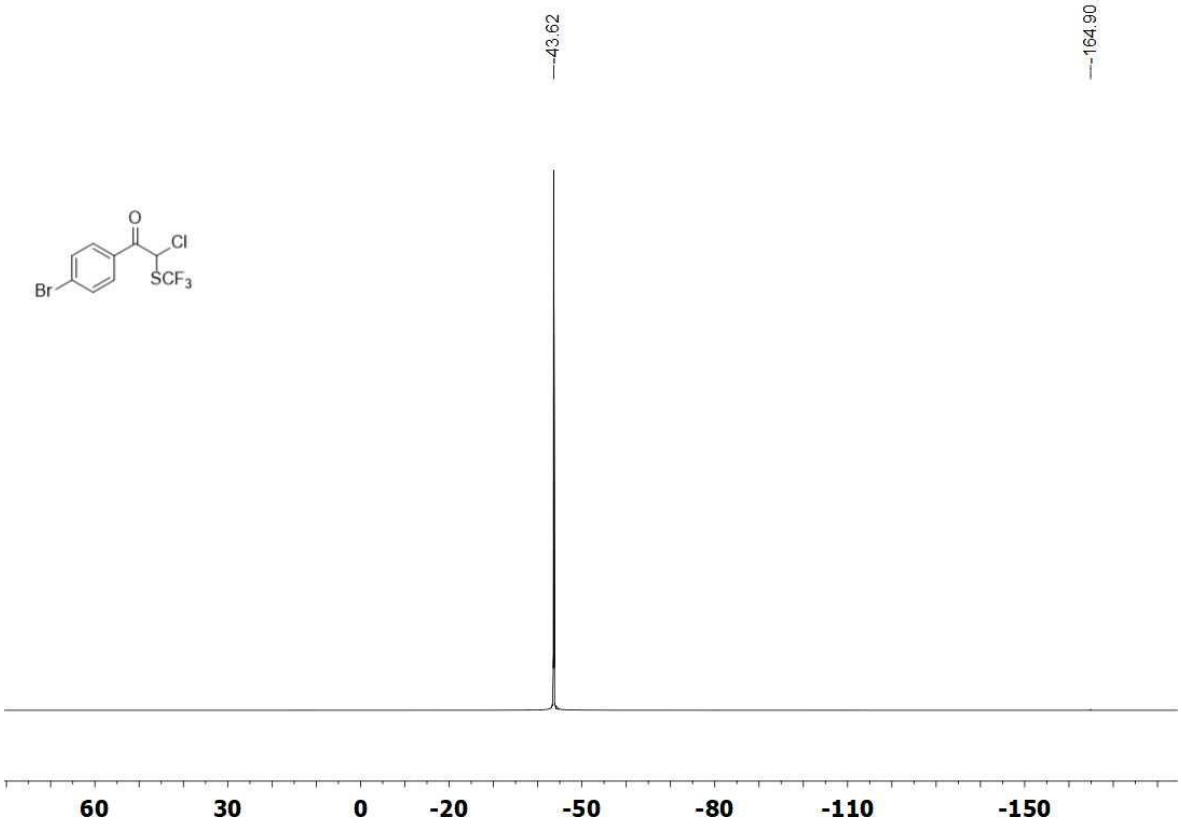
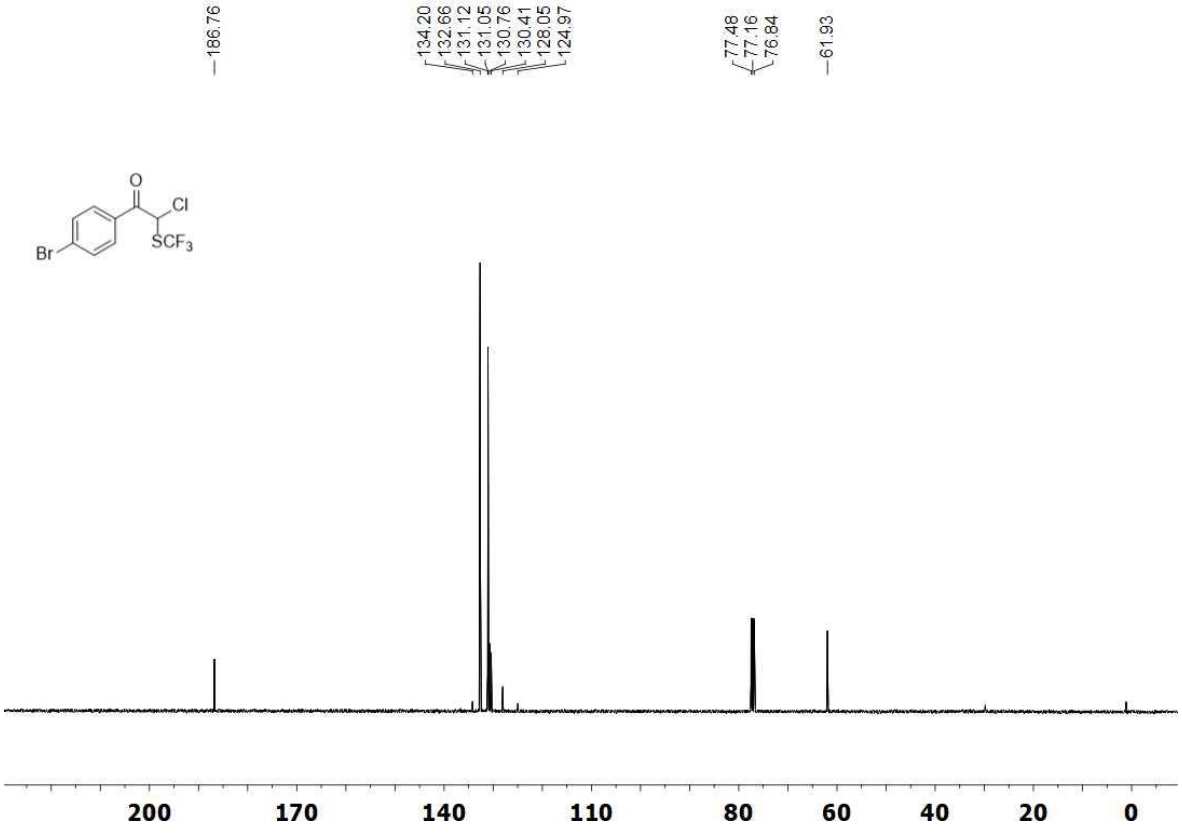


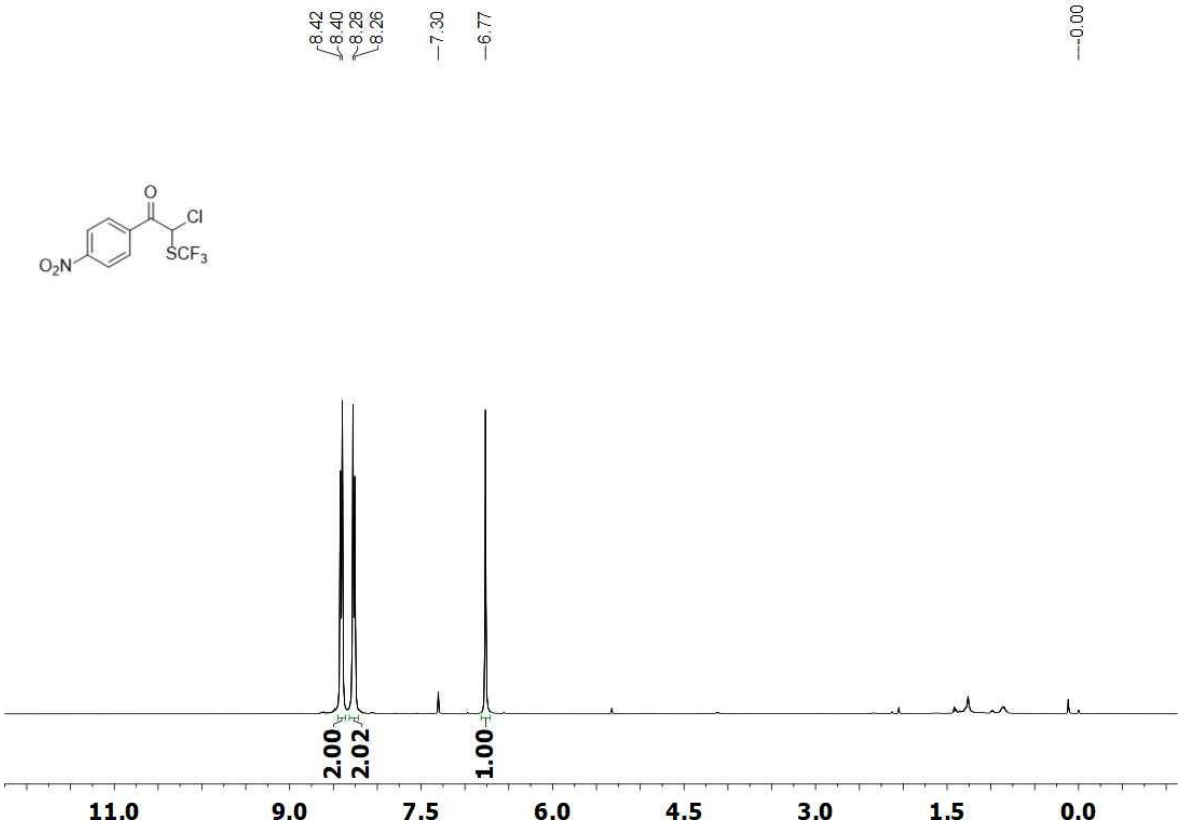
^{19}F NMR of compound **4e**



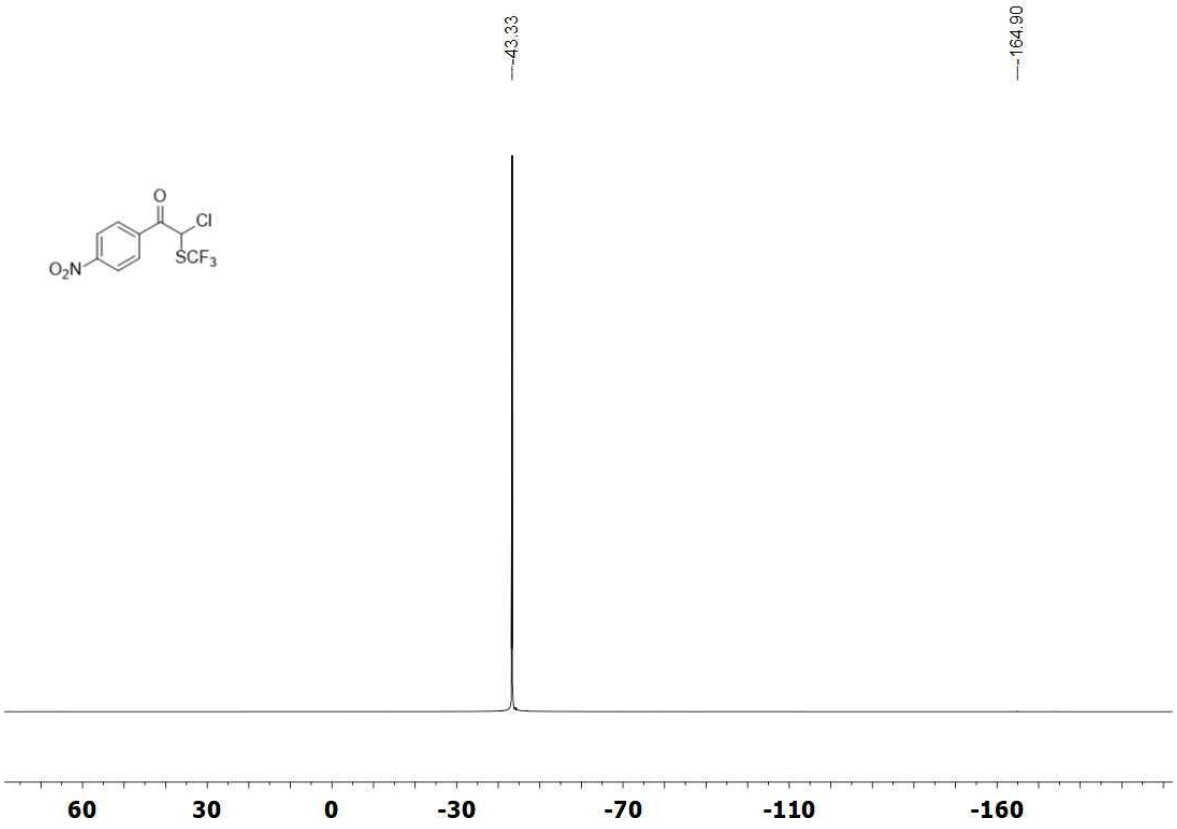
^{13}C NMR of compound **4e**



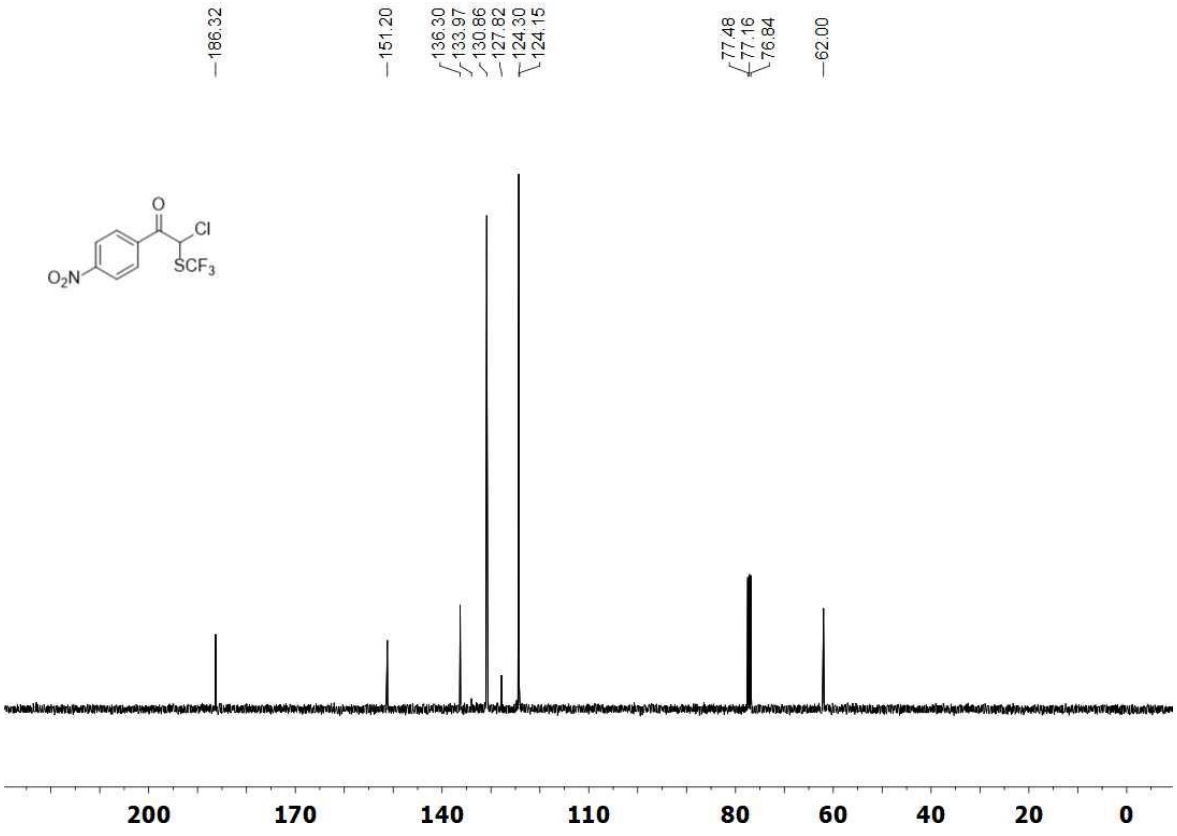
^{1}H NMR of compound **4f**



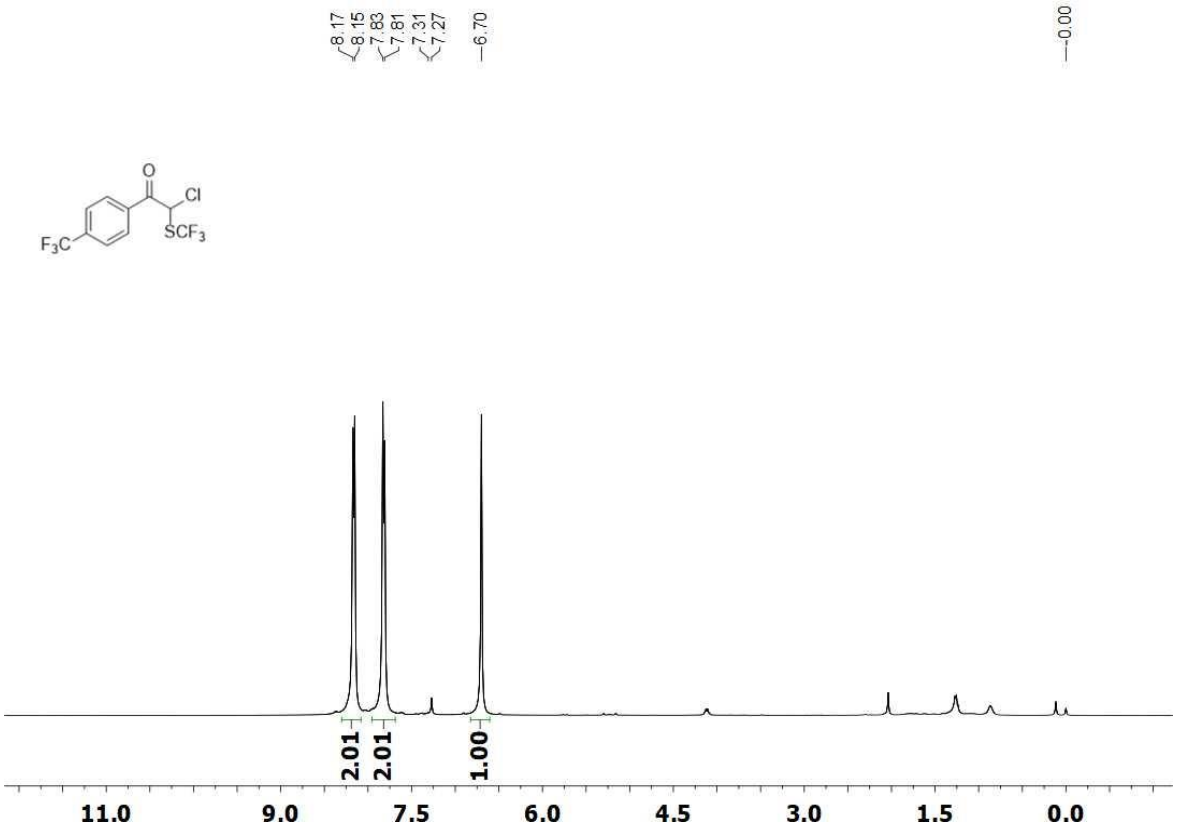
^{19}F NMR of compound **4f**



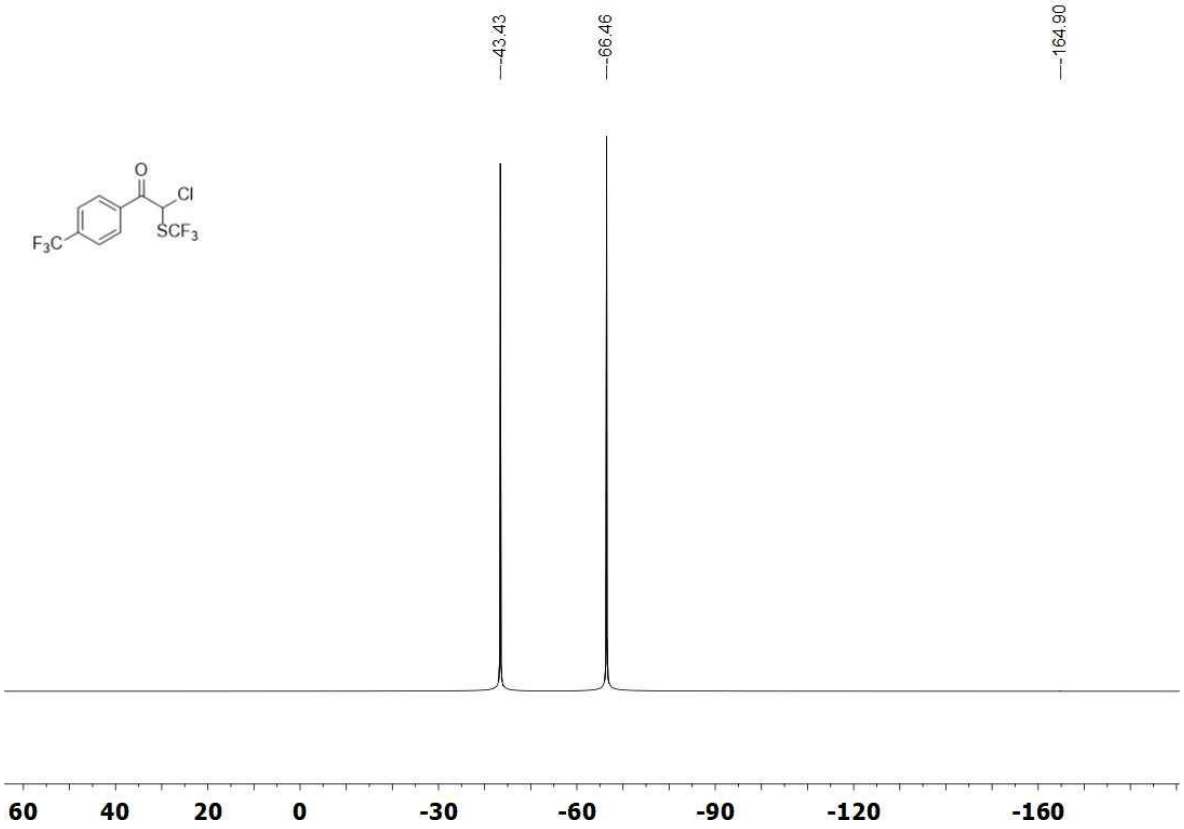
^{13}C NMR of compound **4f**



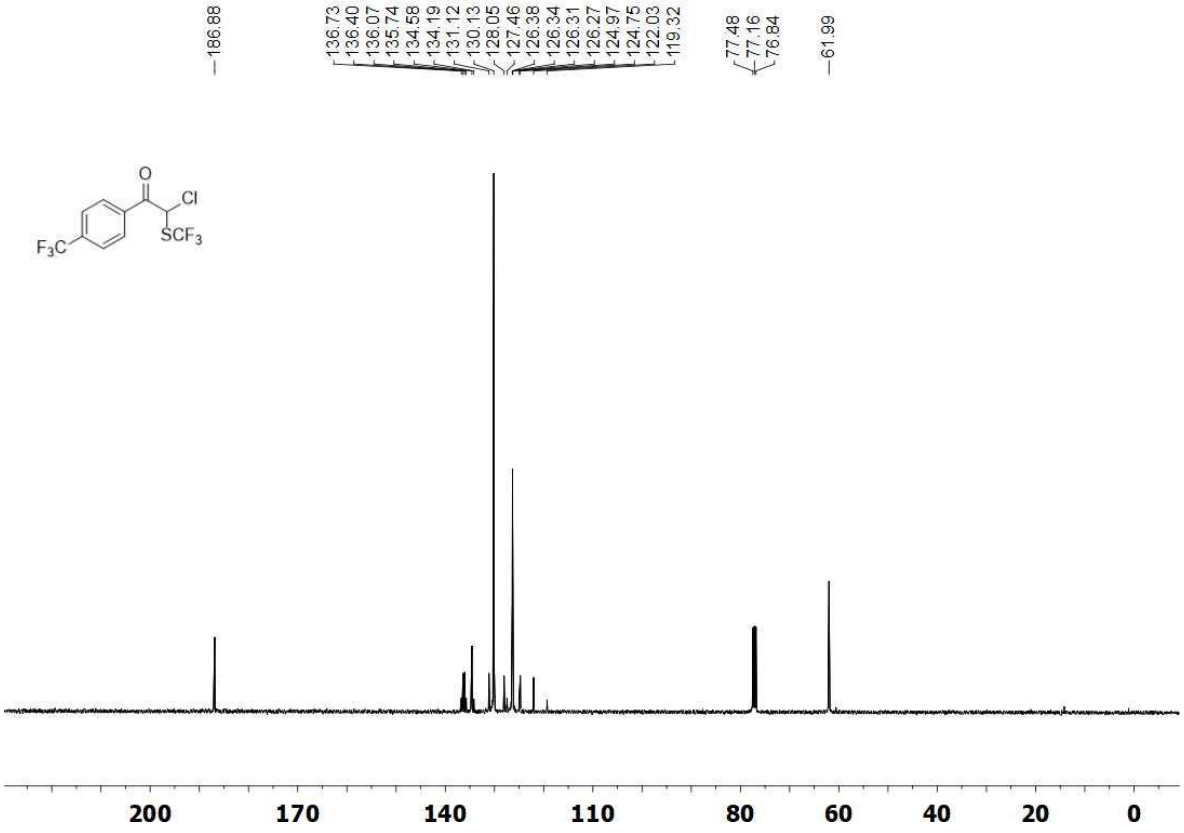
^{1}H NMR of compound **4g**



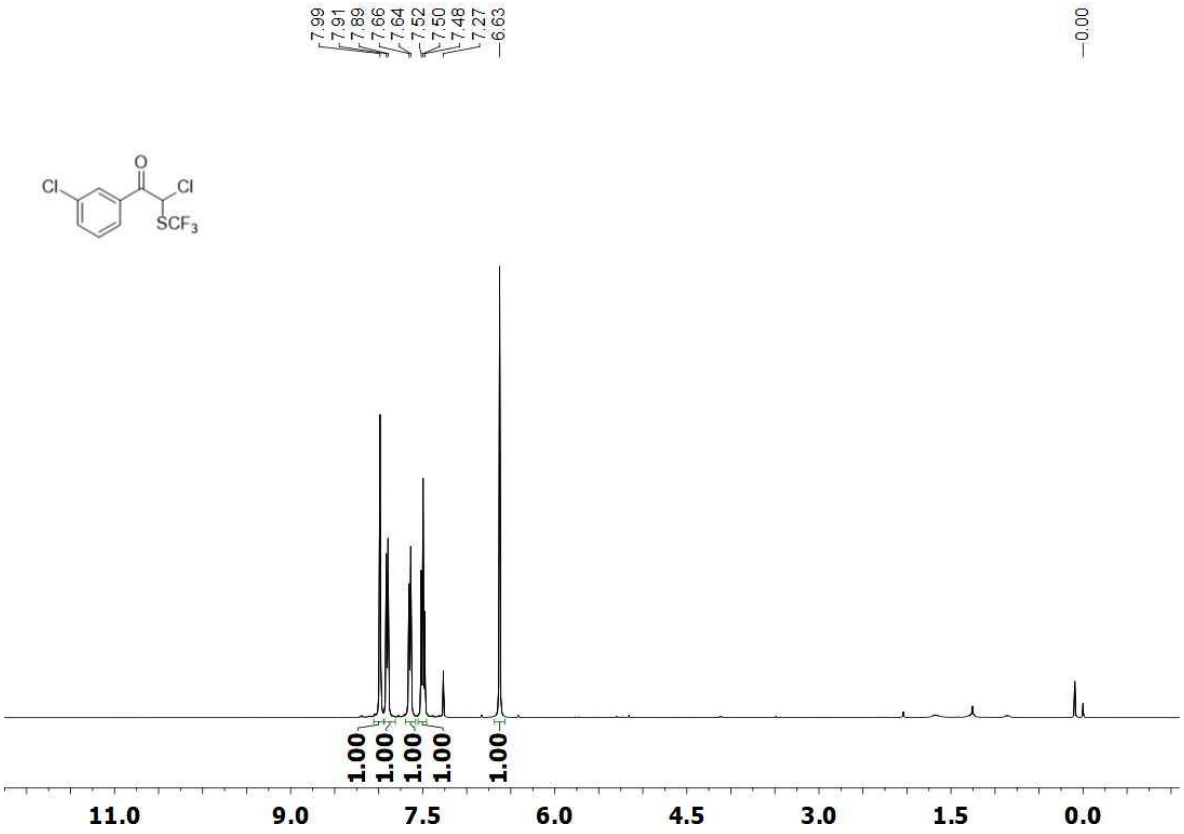
^{19}F NMR of compound **4g**



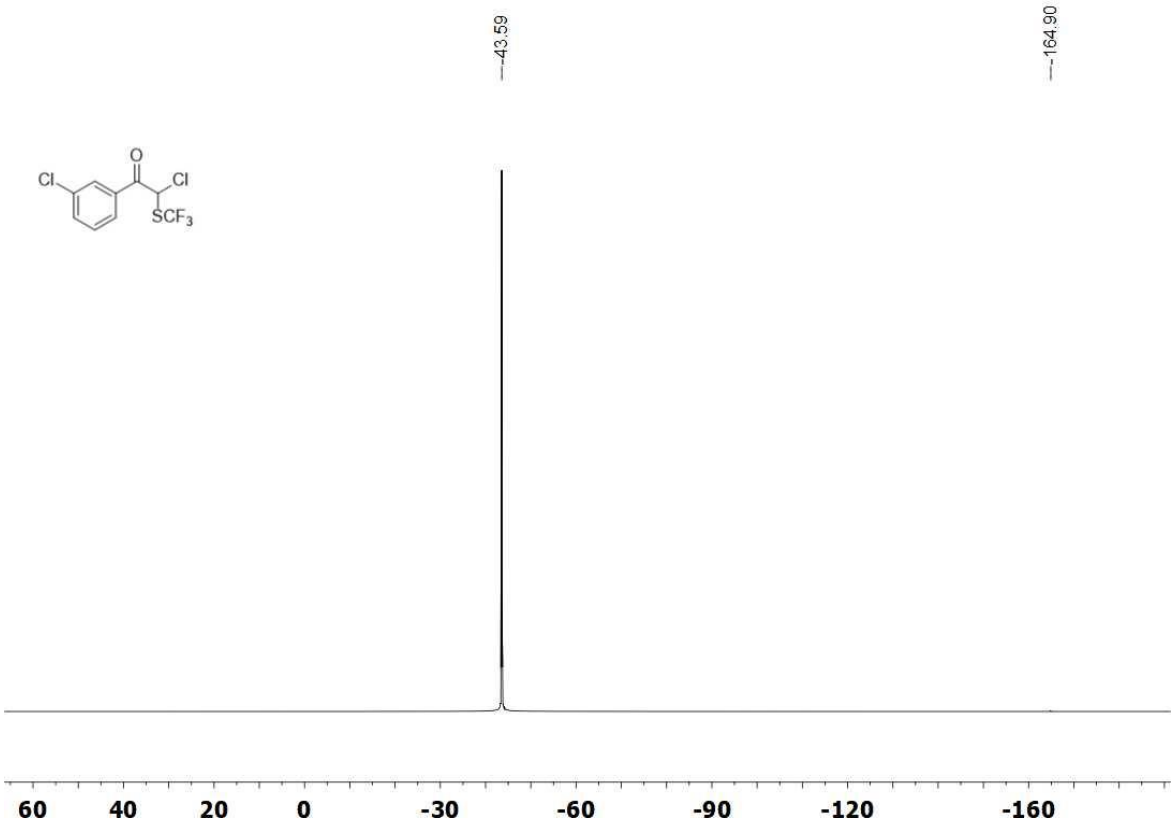
^{13}C NMR of compound **4g**



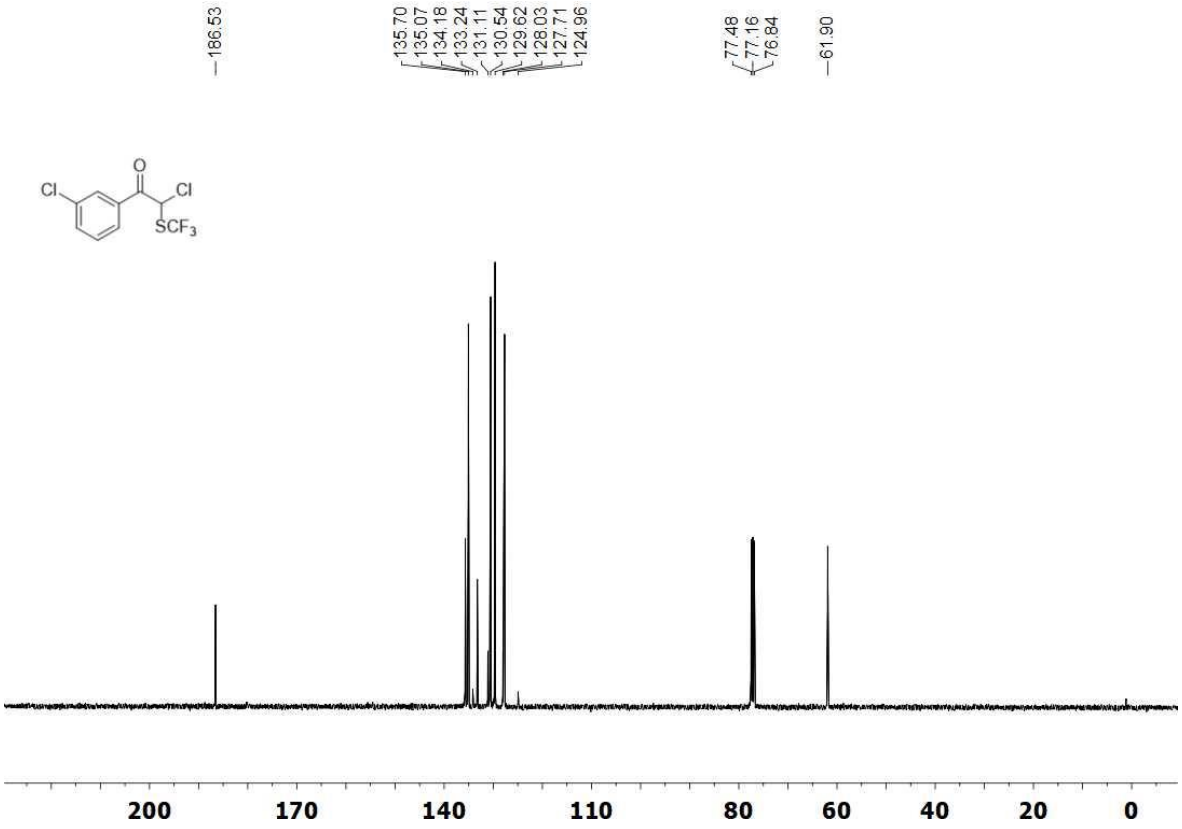
^{1}H NMR of compound **4h**



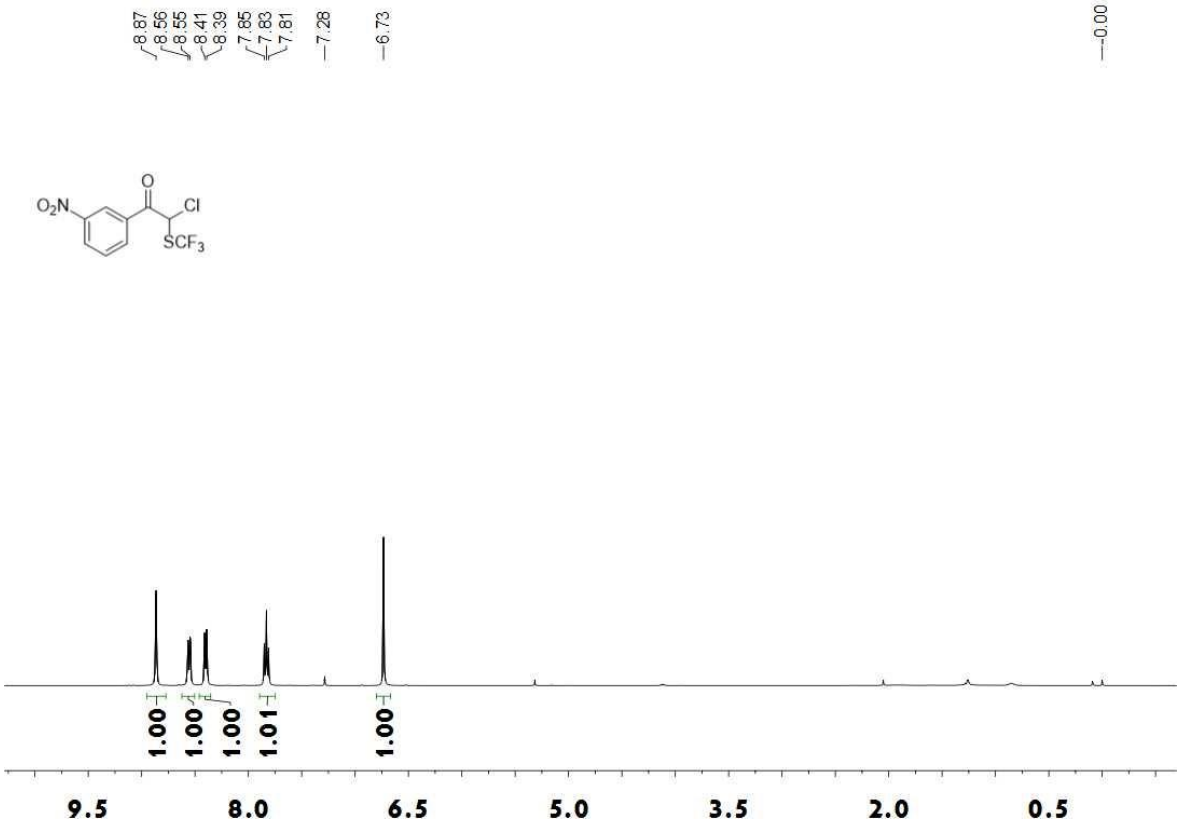
^{19}F NMR of compound **4h**



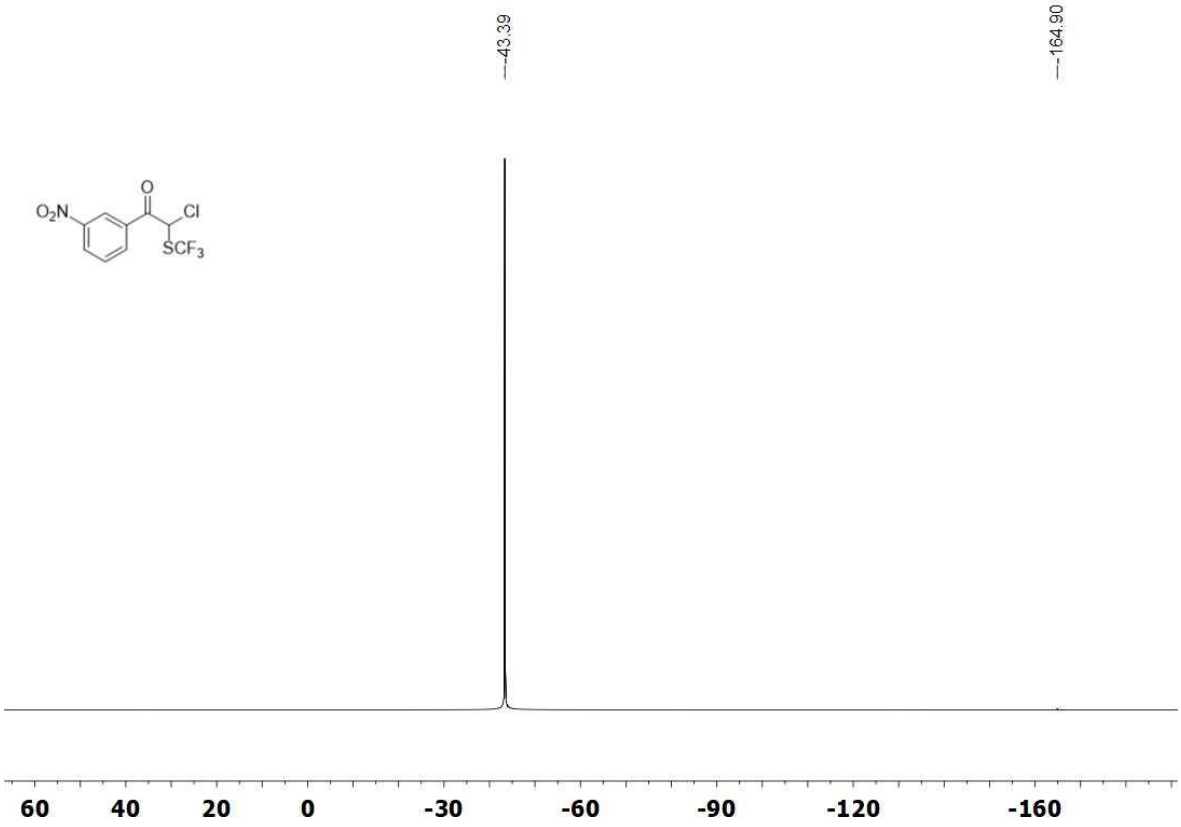
^{13}C NMR of compound **4h**



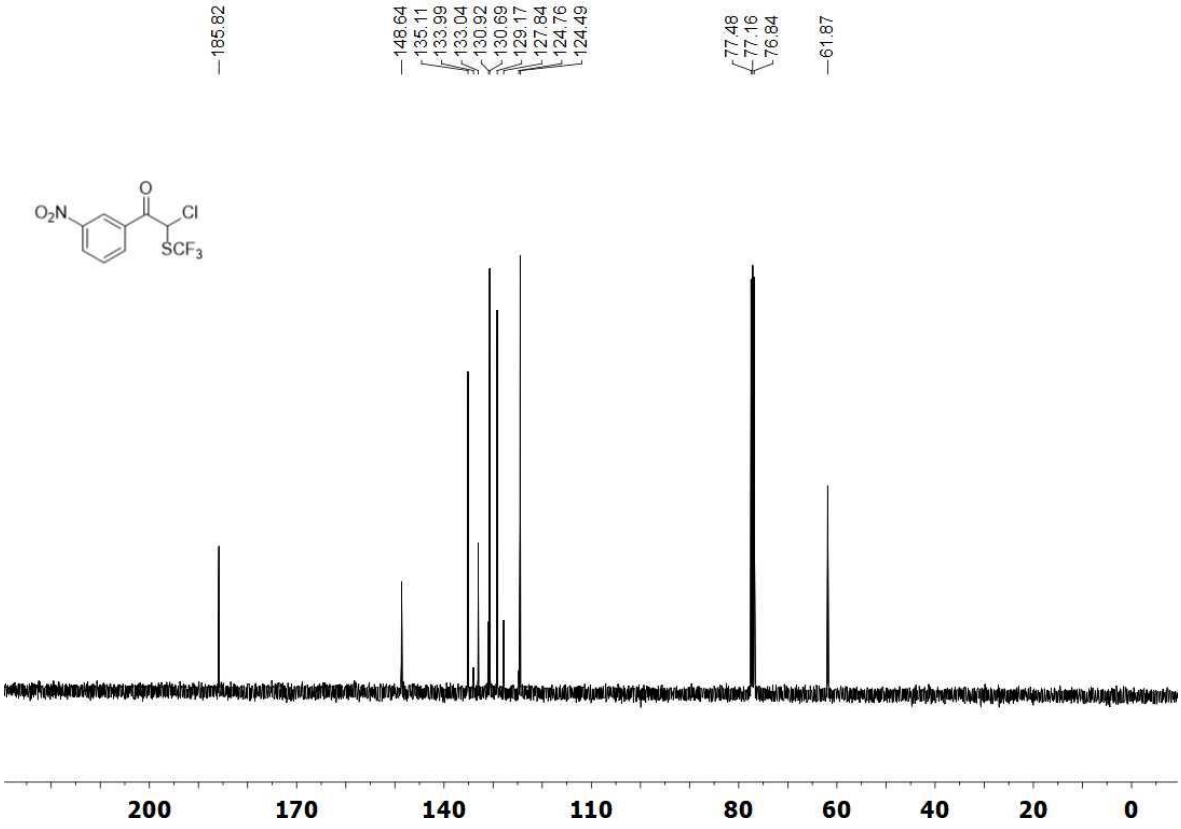
^{1}H NMR of compound **4i**



^{19}F NMR of compound **4i**



^{13}C NMR of compound **4i**



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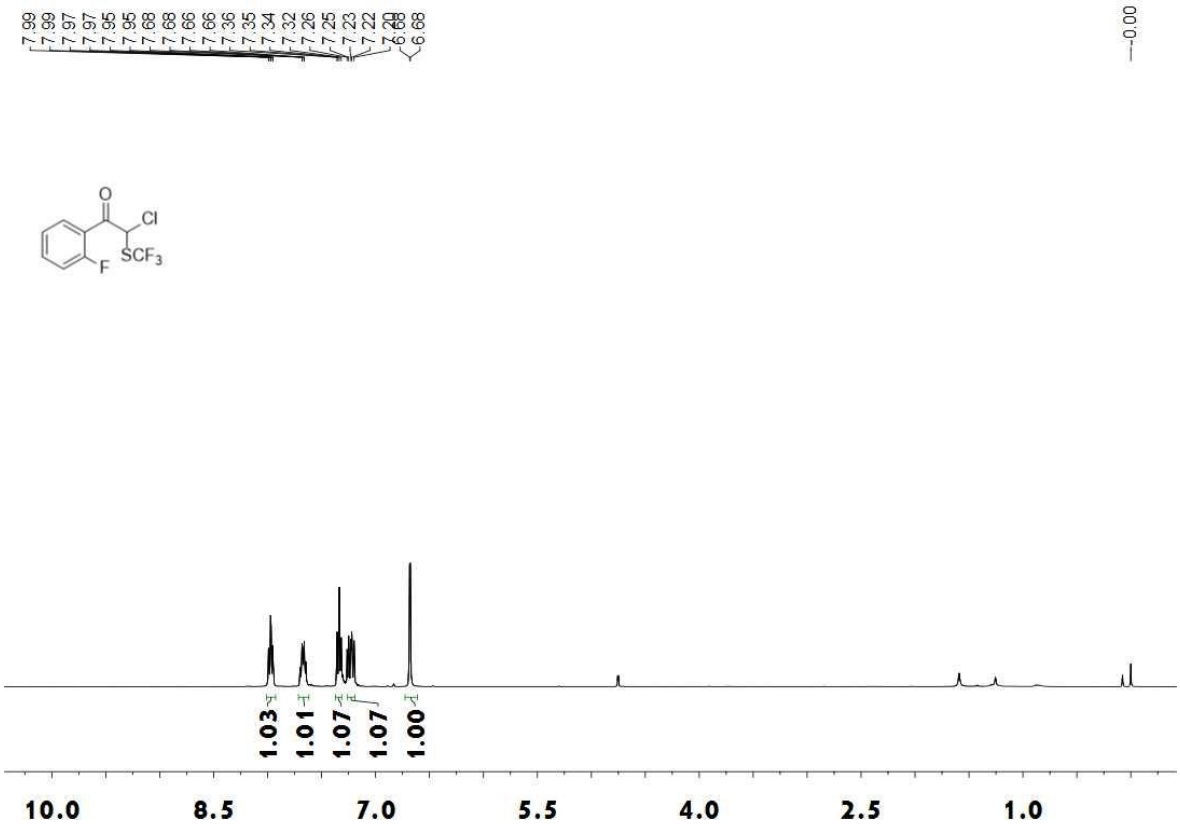

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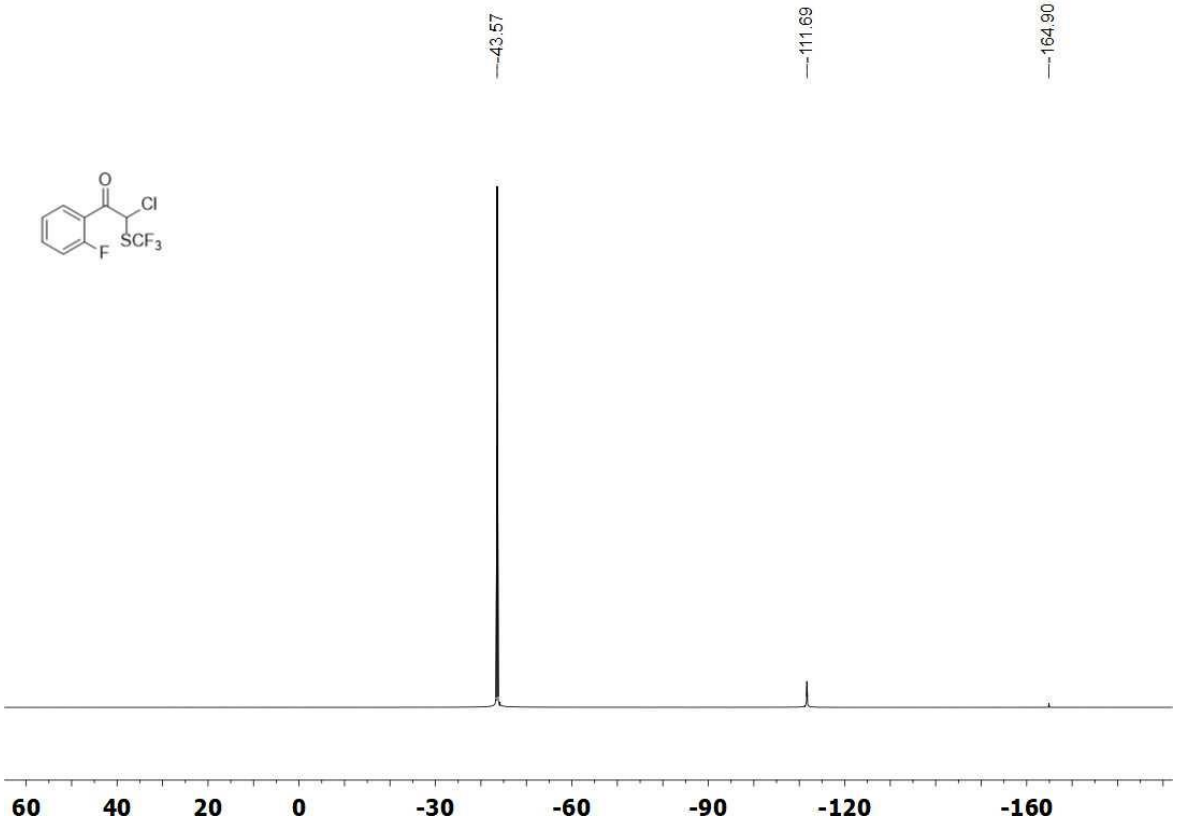

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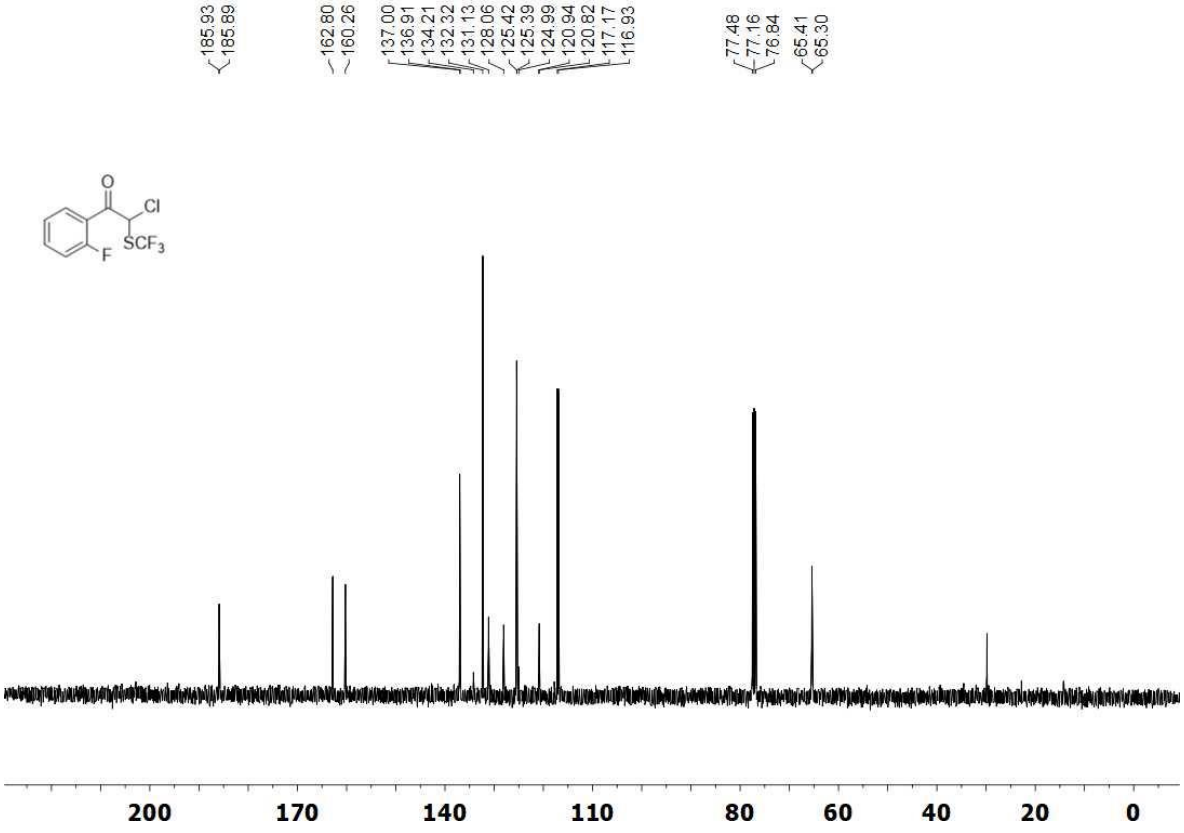

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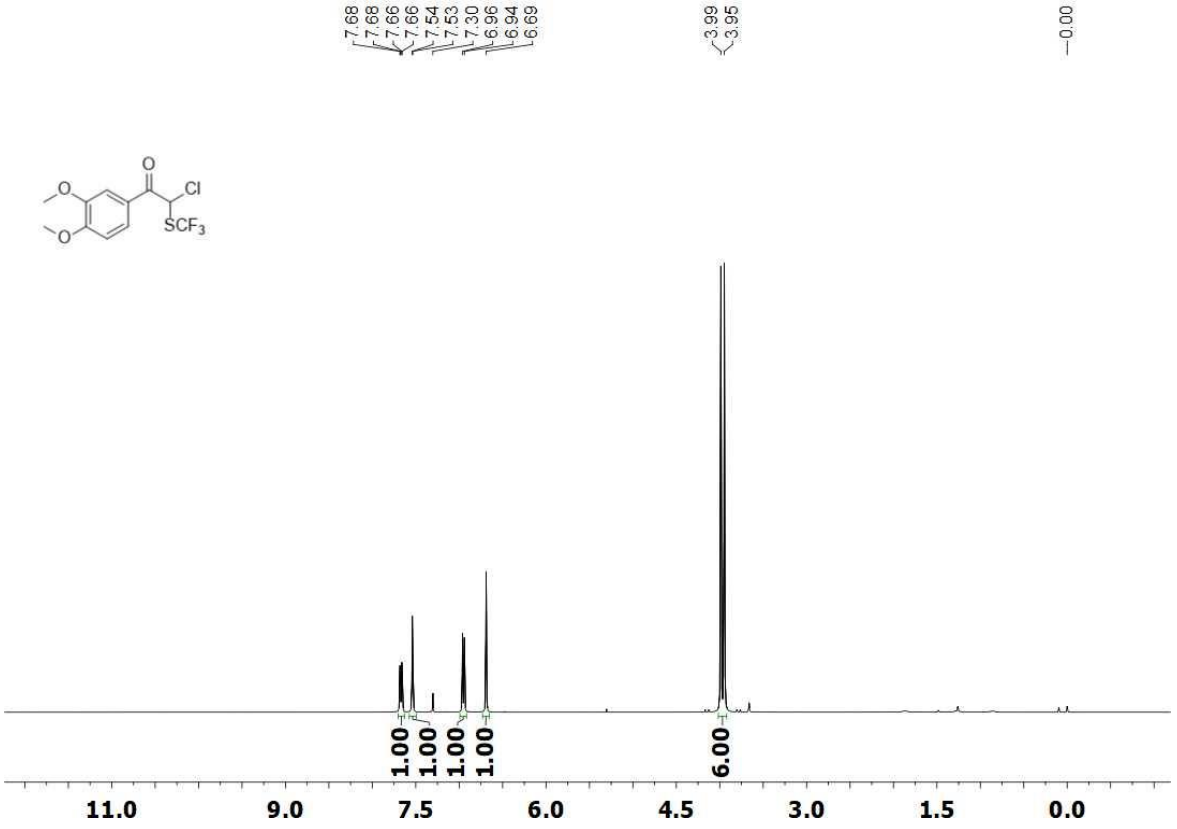

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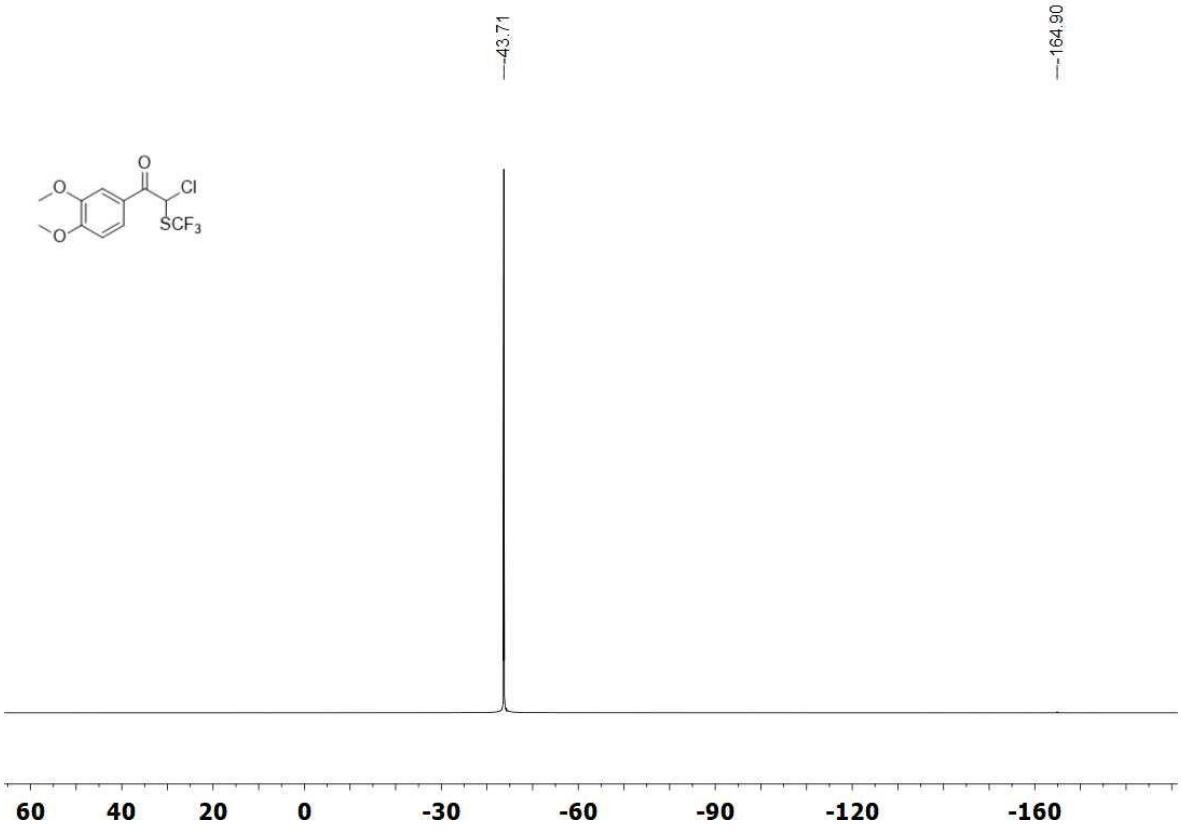

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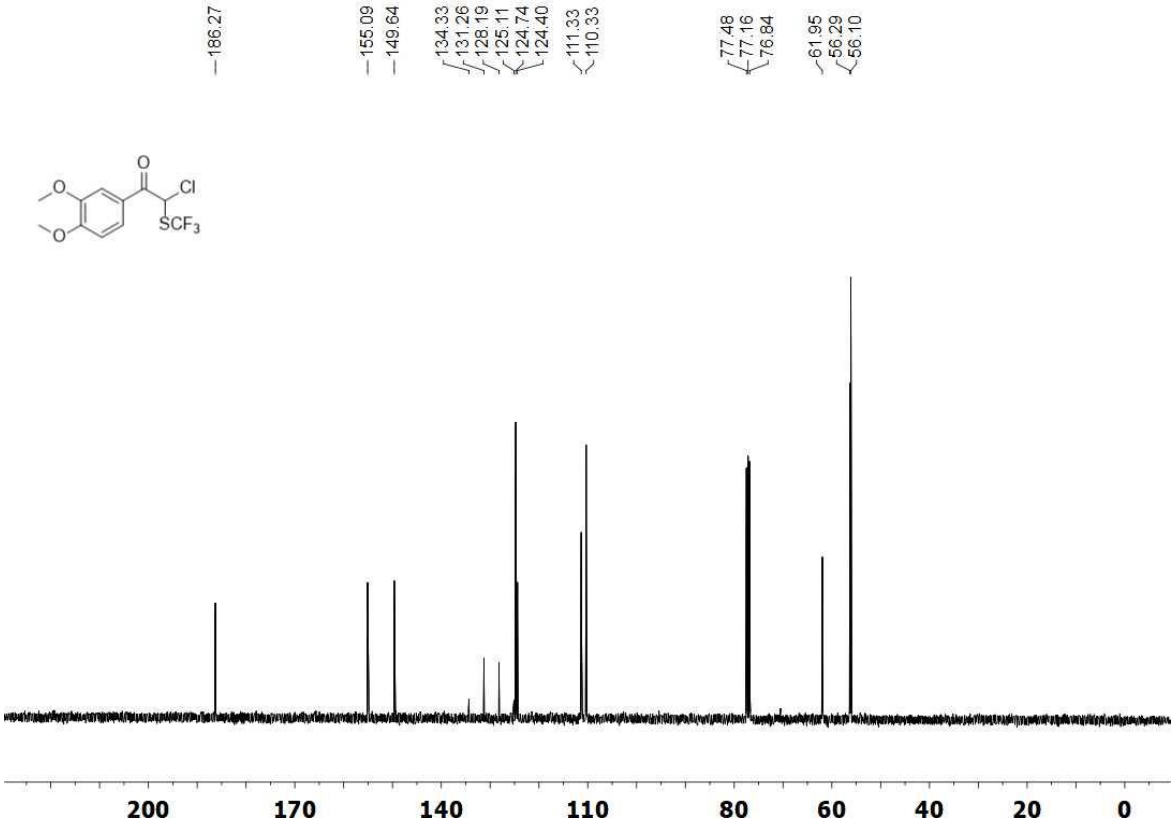
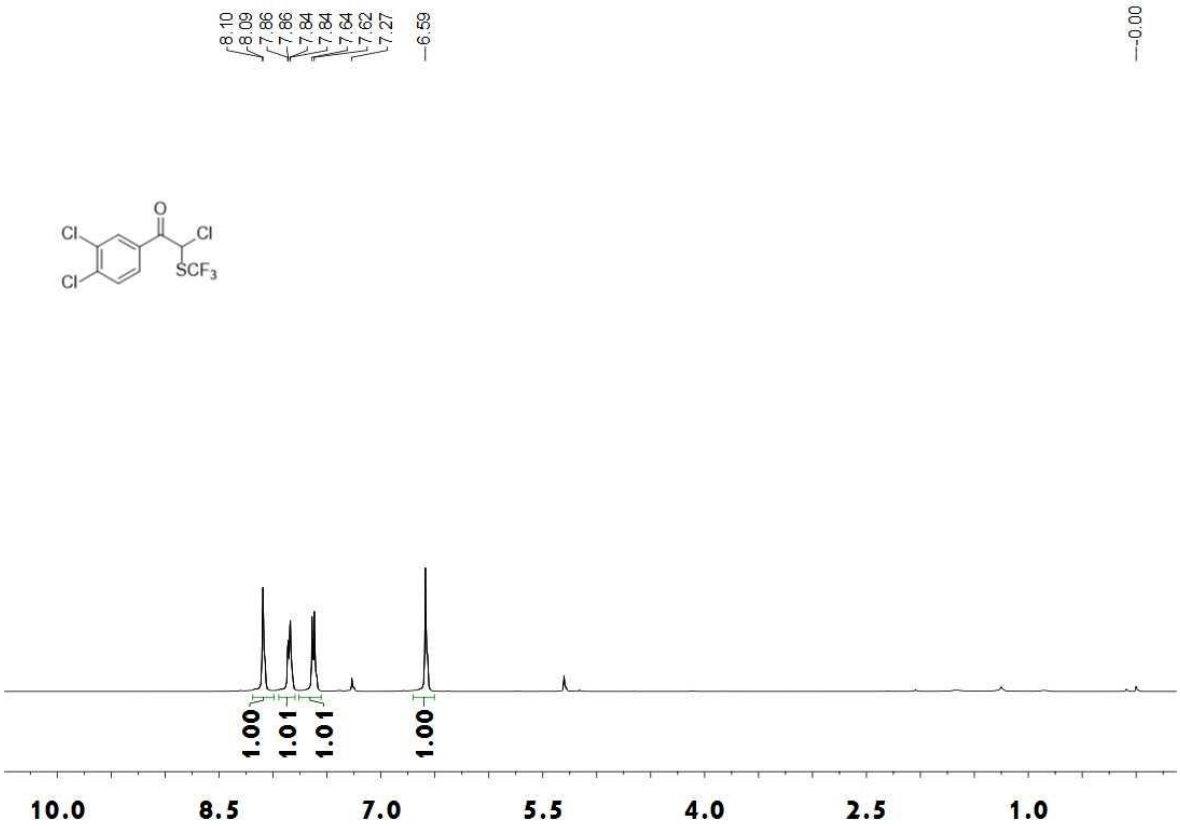


^{1}H NMR of compound **4l**



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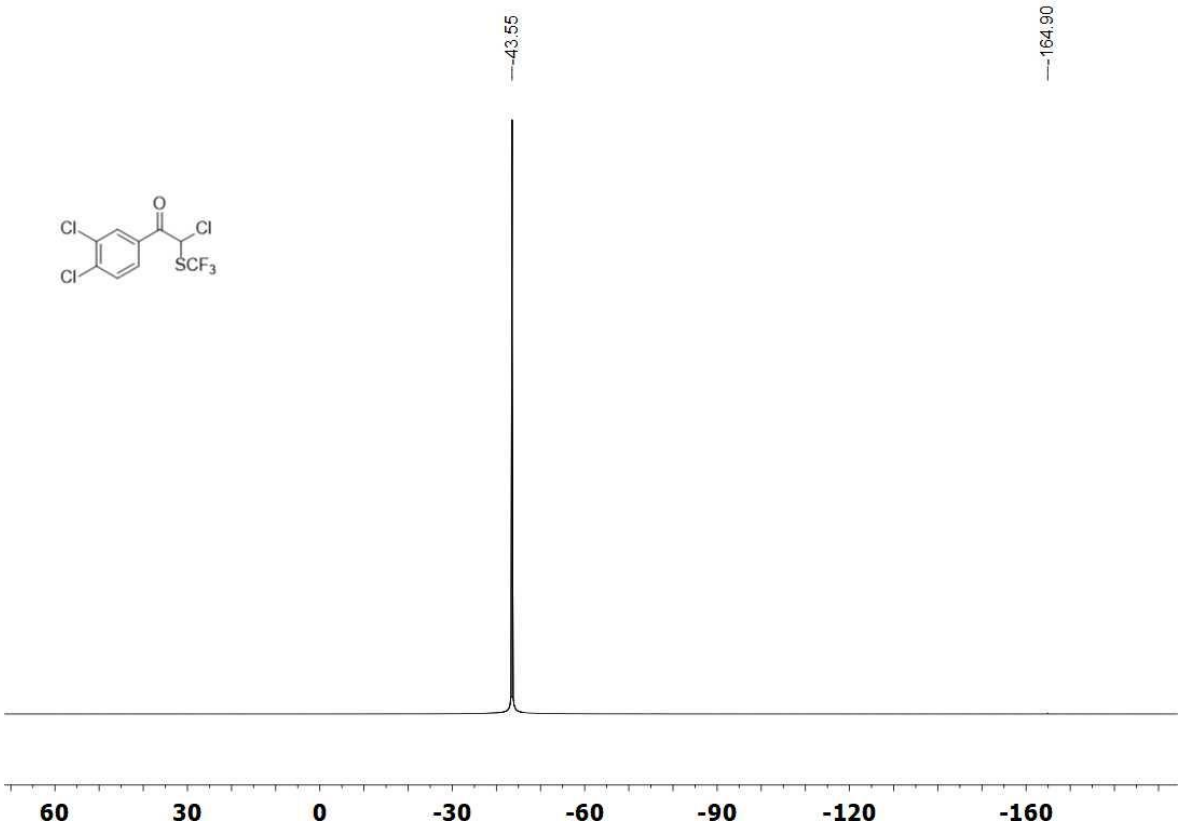

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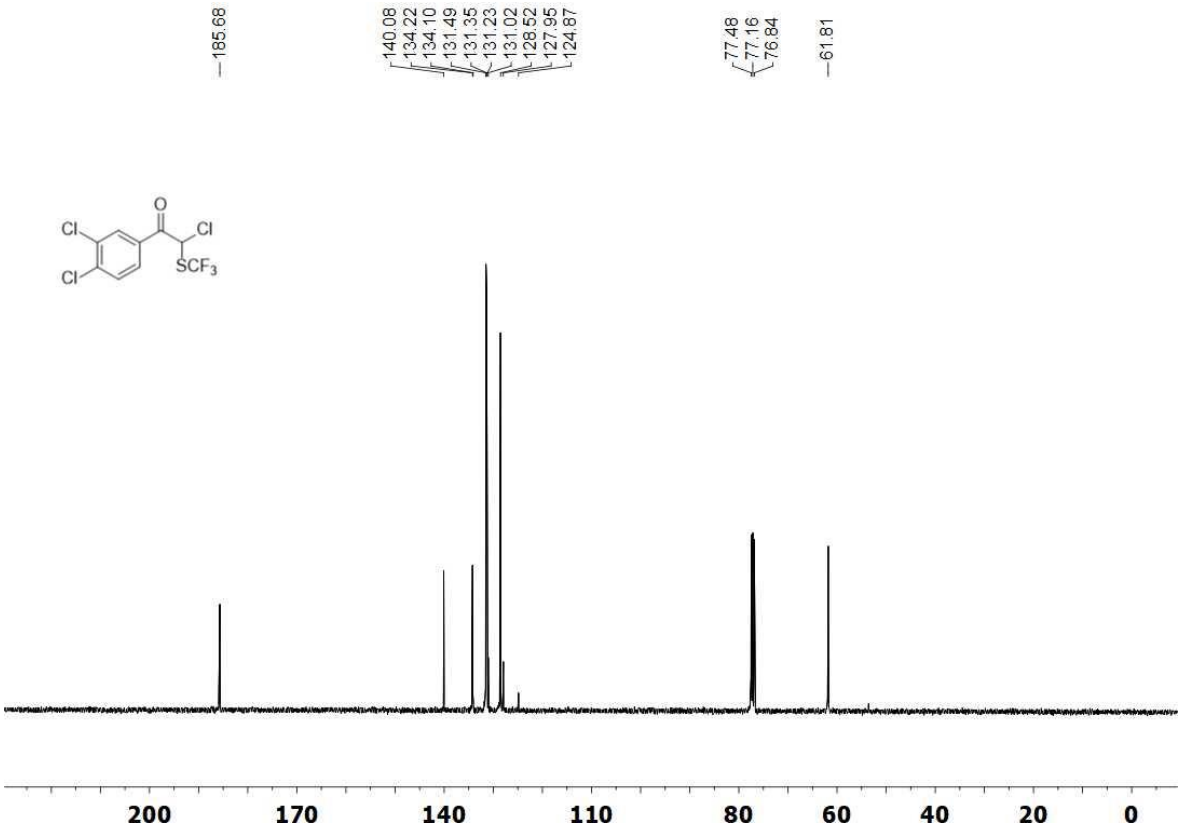

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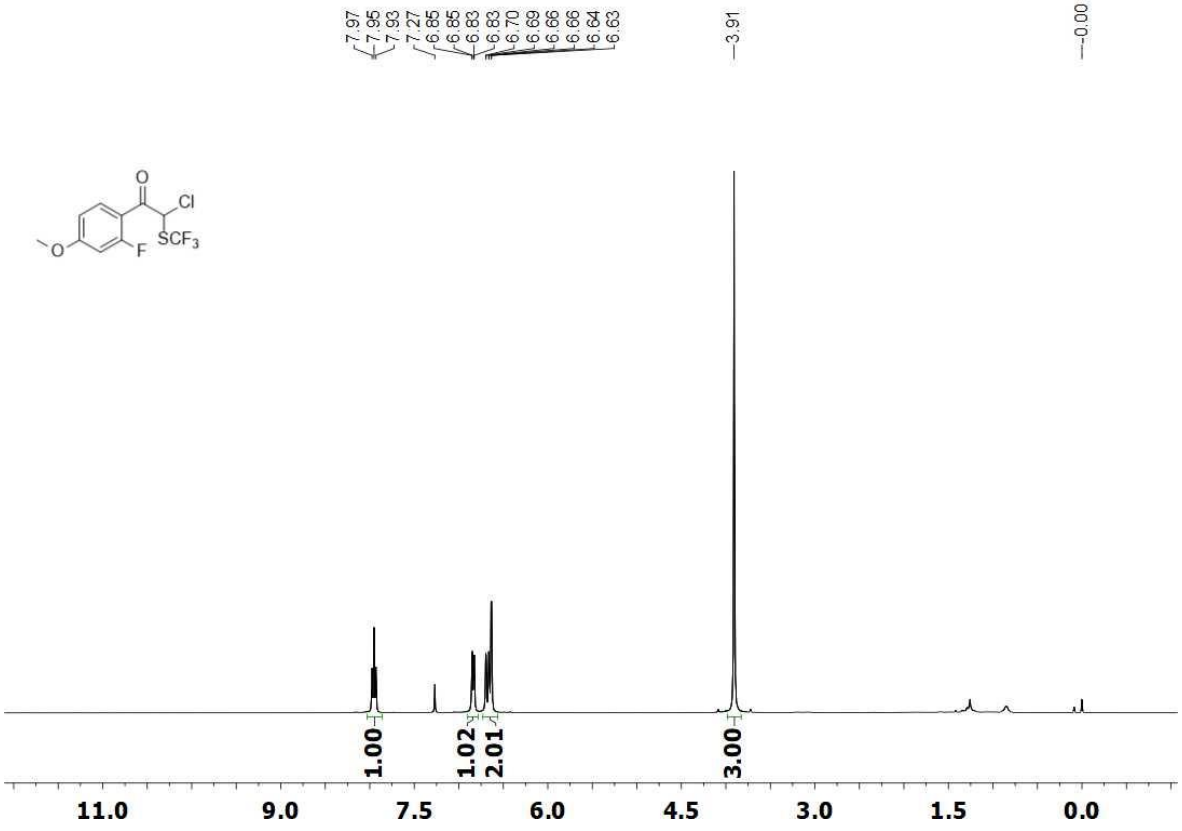
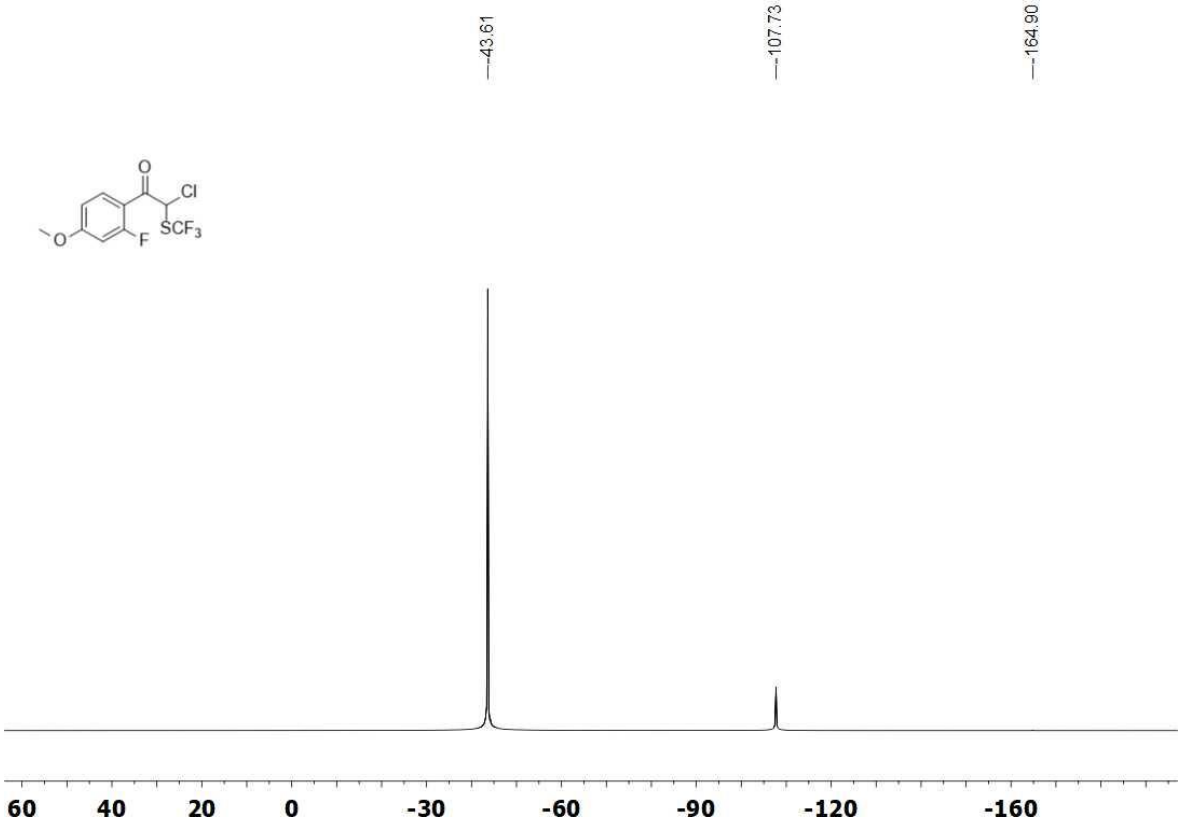
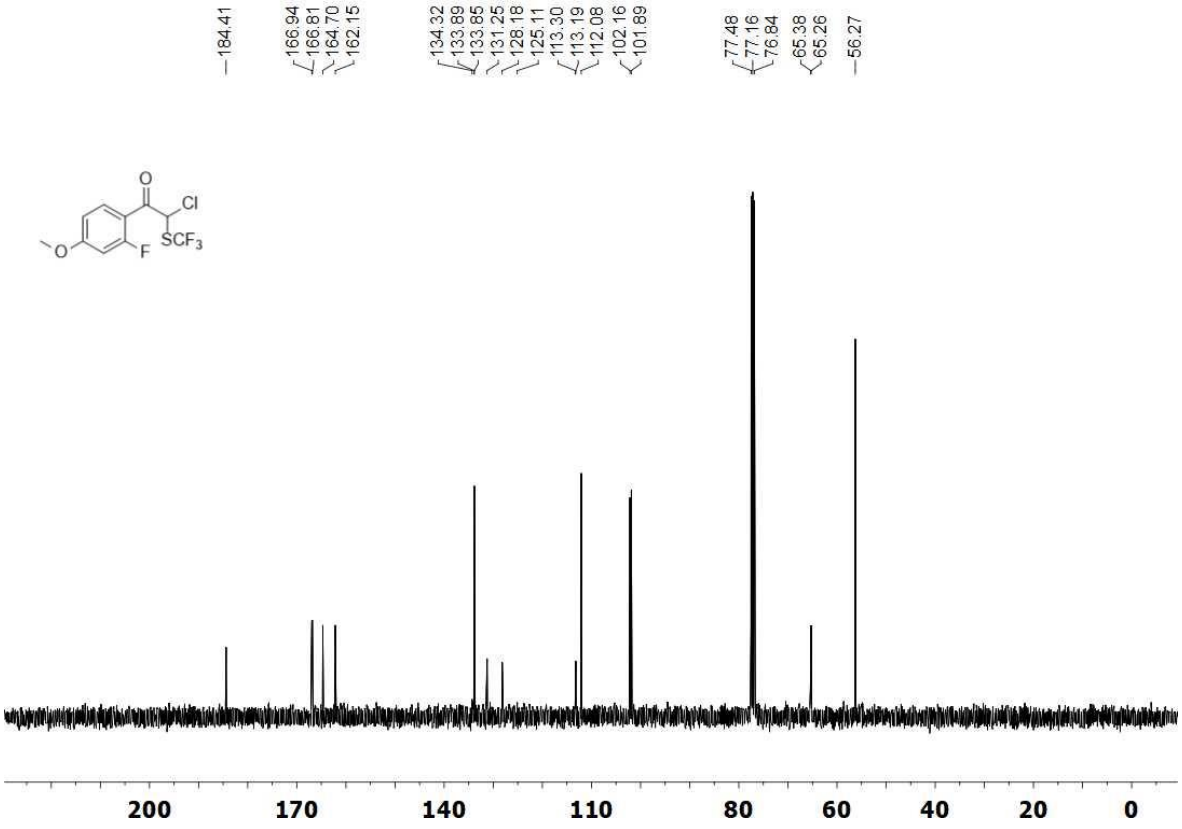


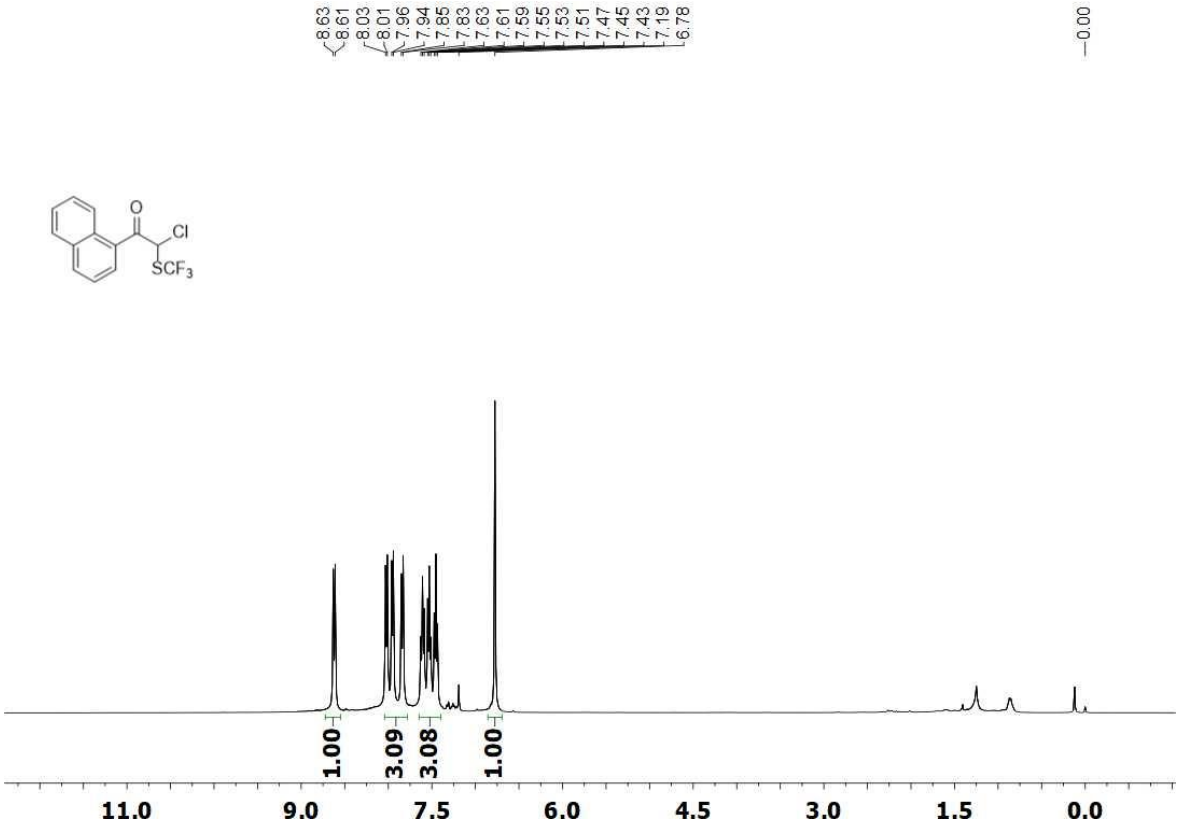
^{19}F NMR of compound **4m**



^{13}C NMR of compound **4m**



^{1}H NMR of compound **4n**



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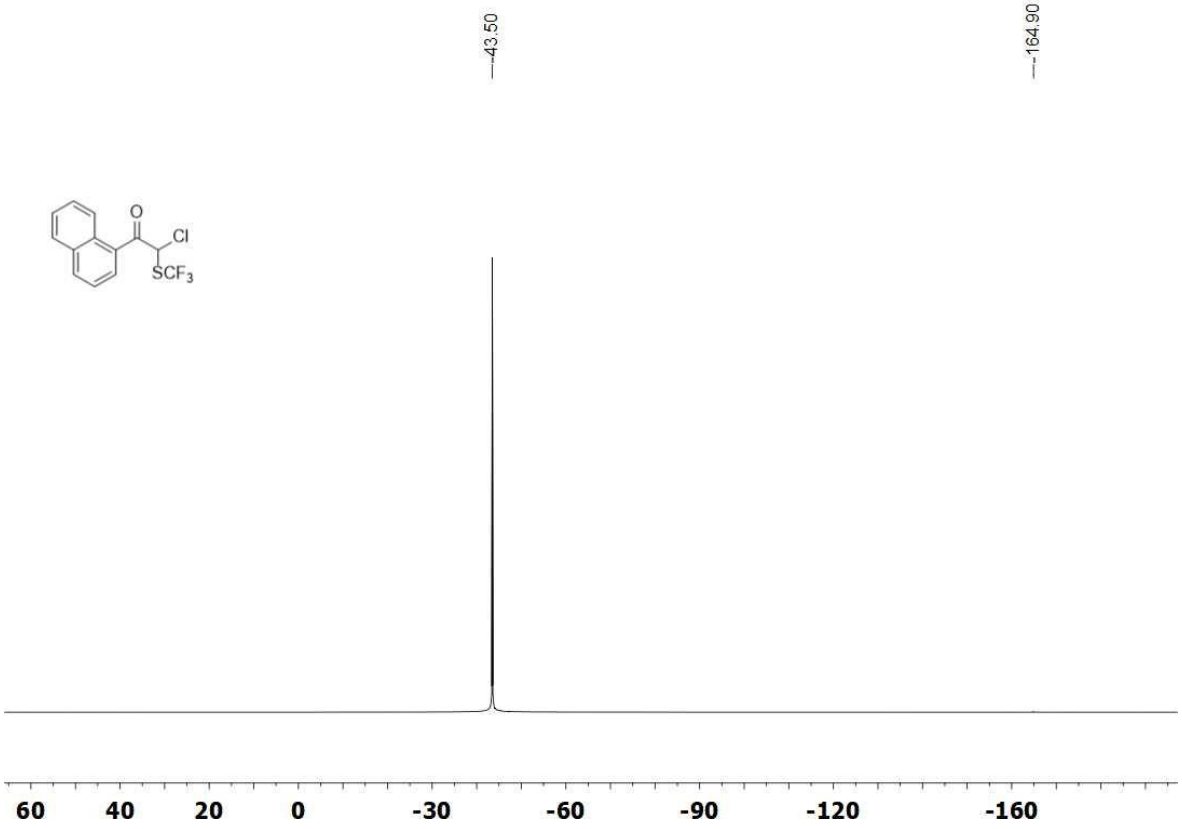
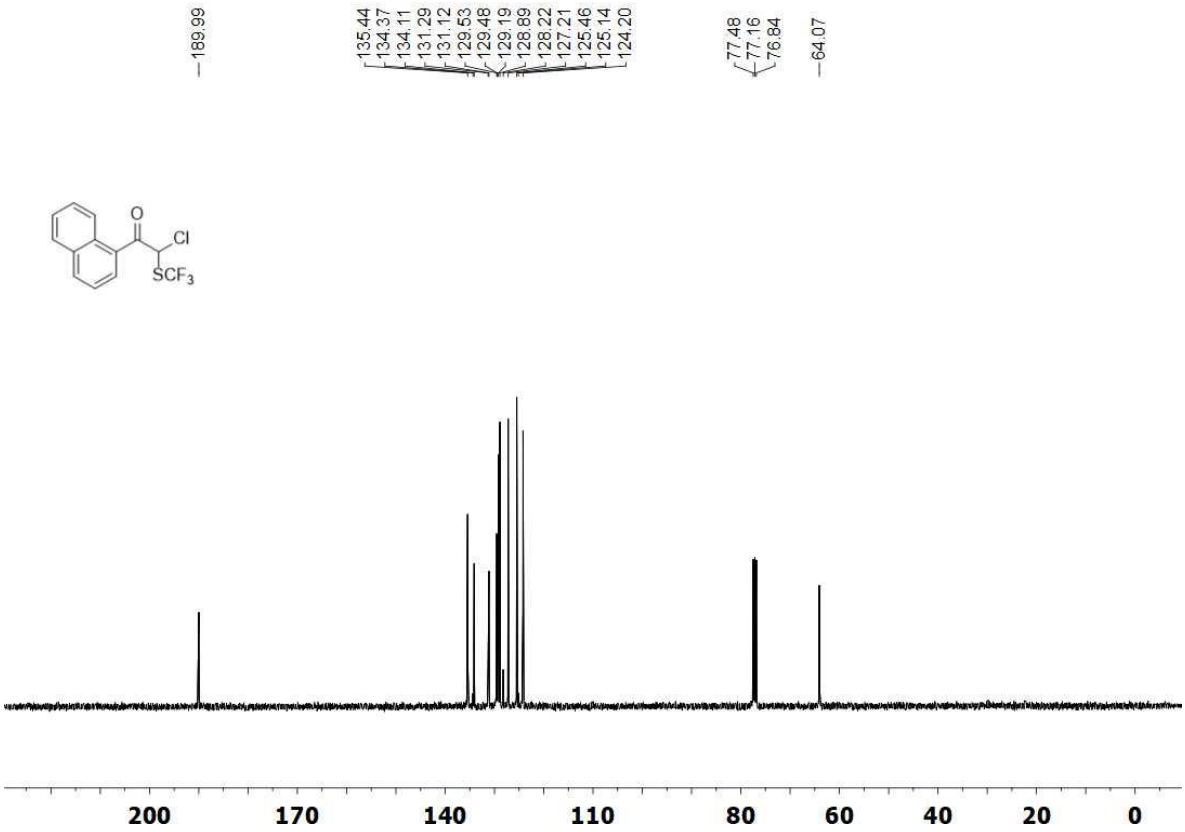


^{13}C NMR of compound **4n**



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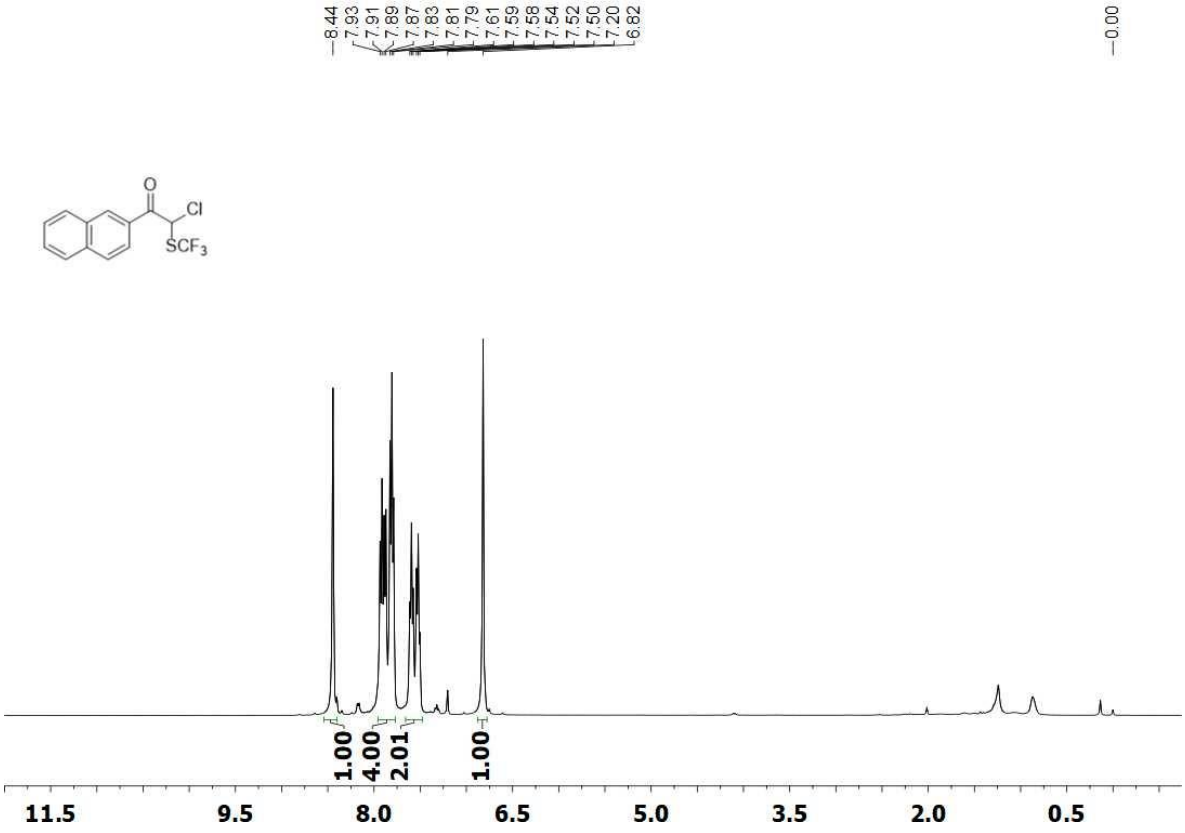

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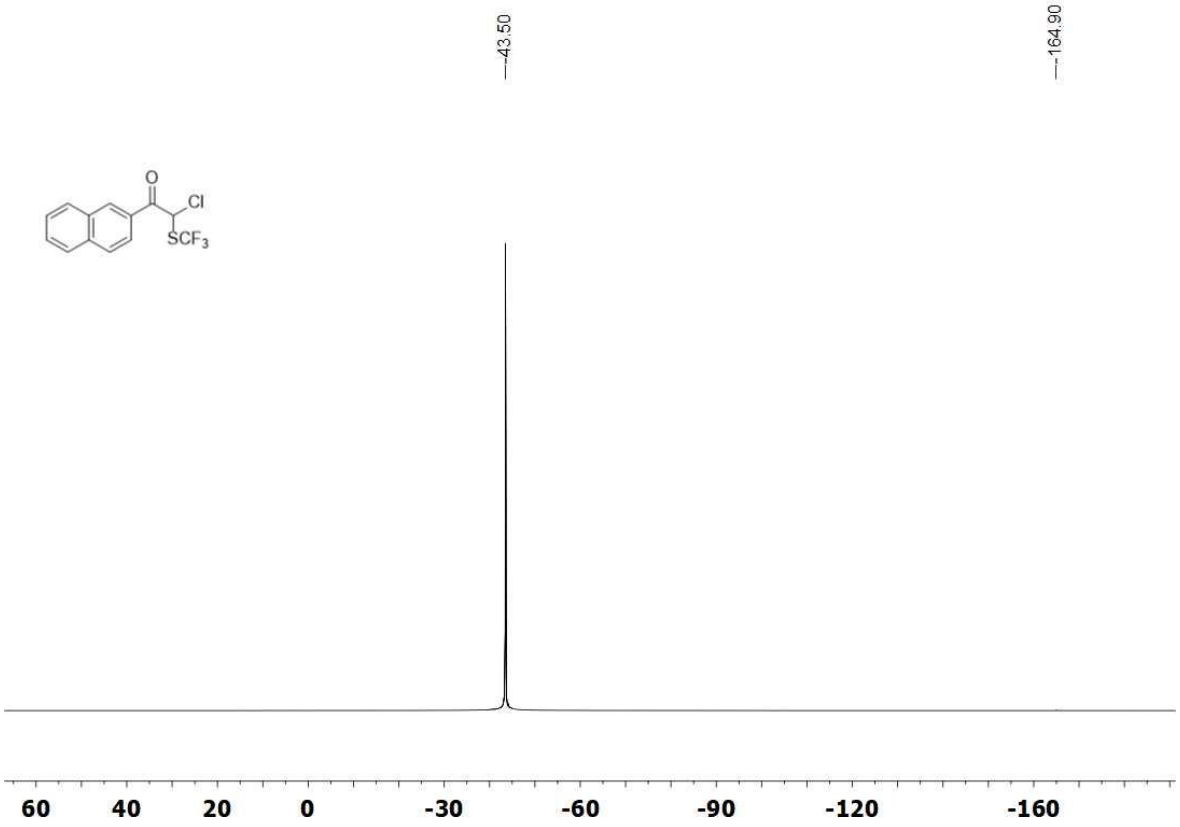
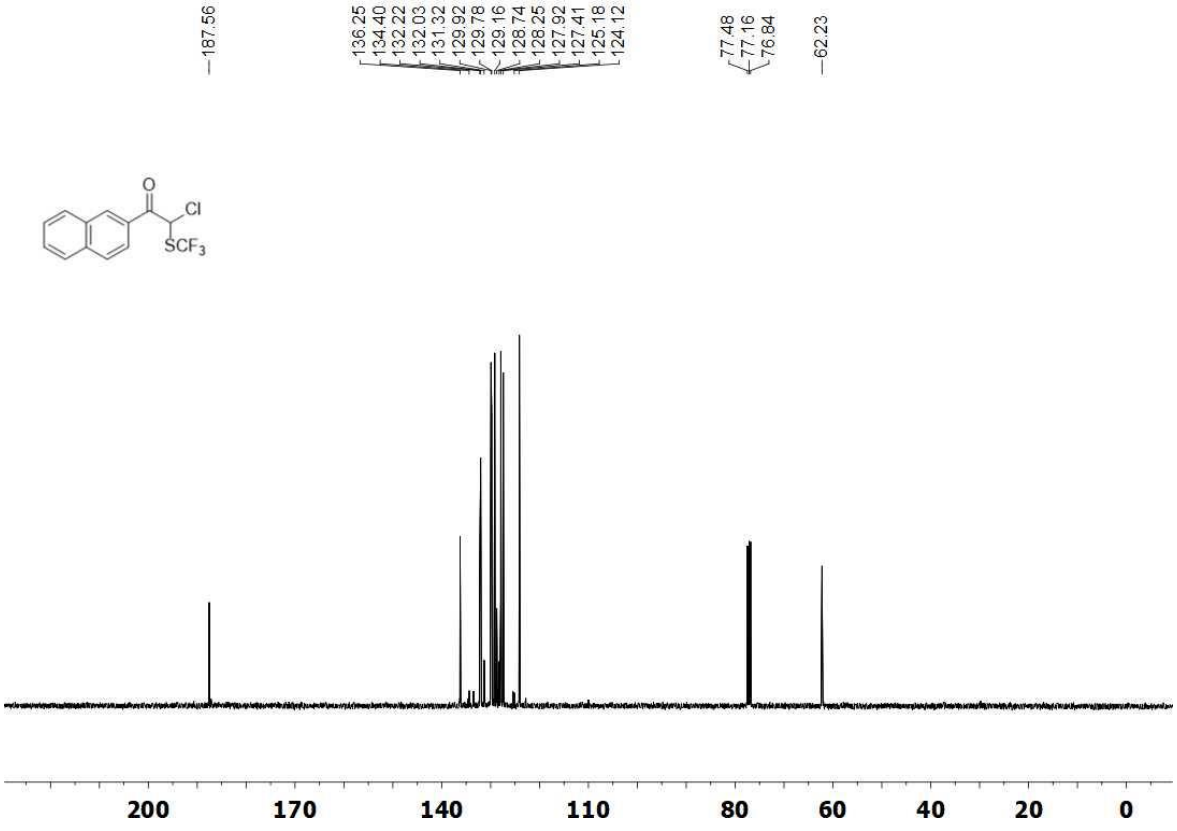
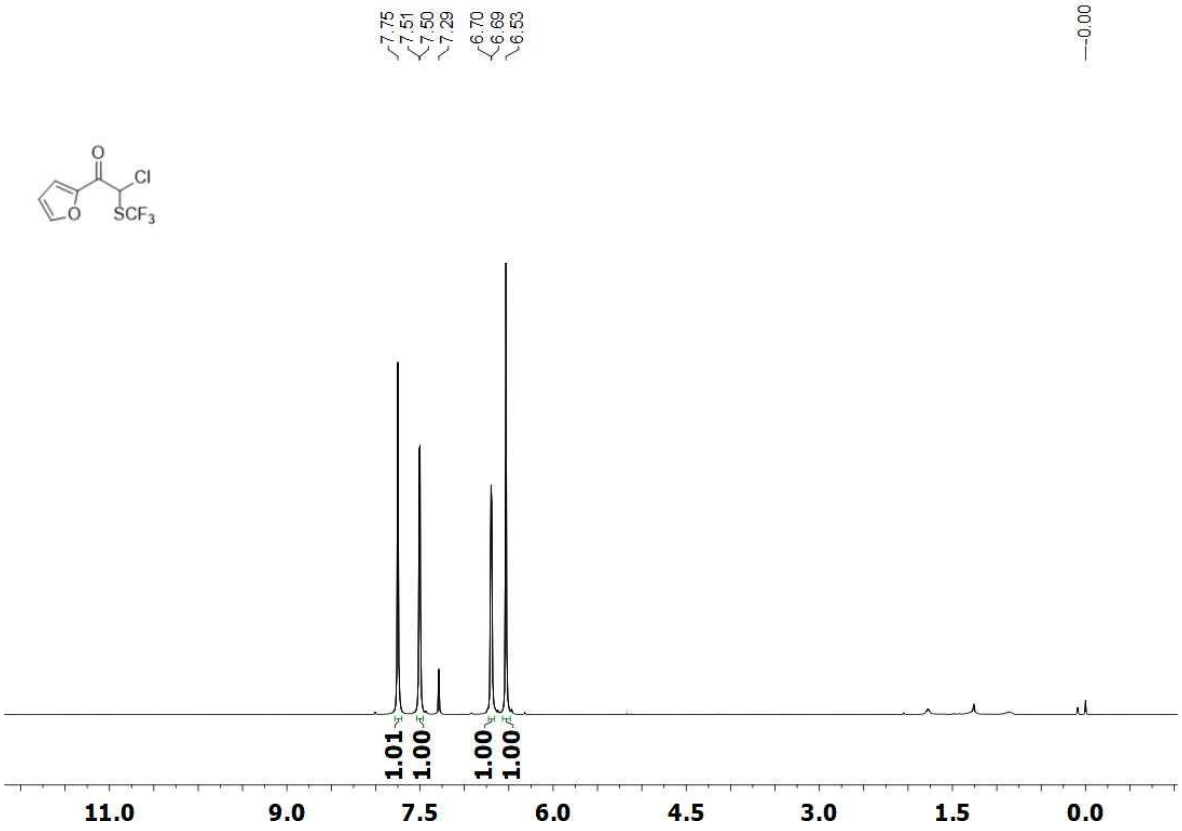


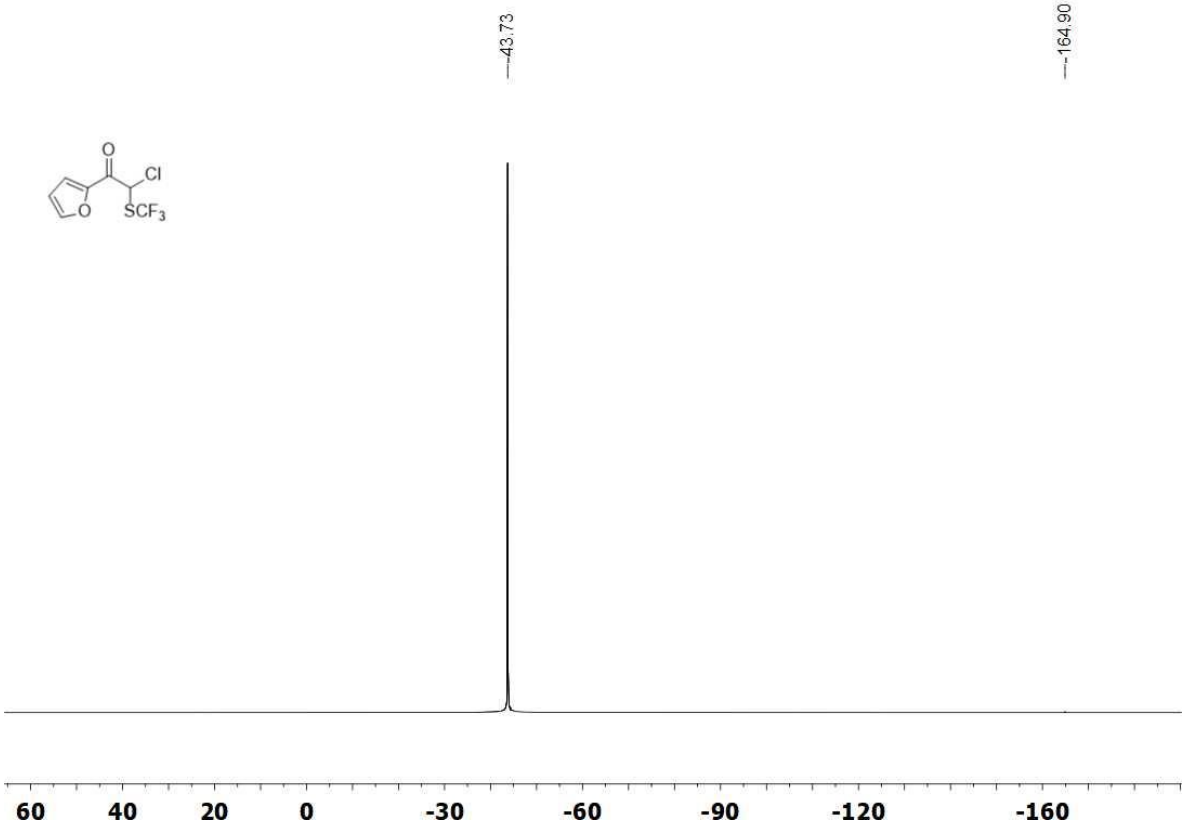
^{13}C NMR of compound **4o**



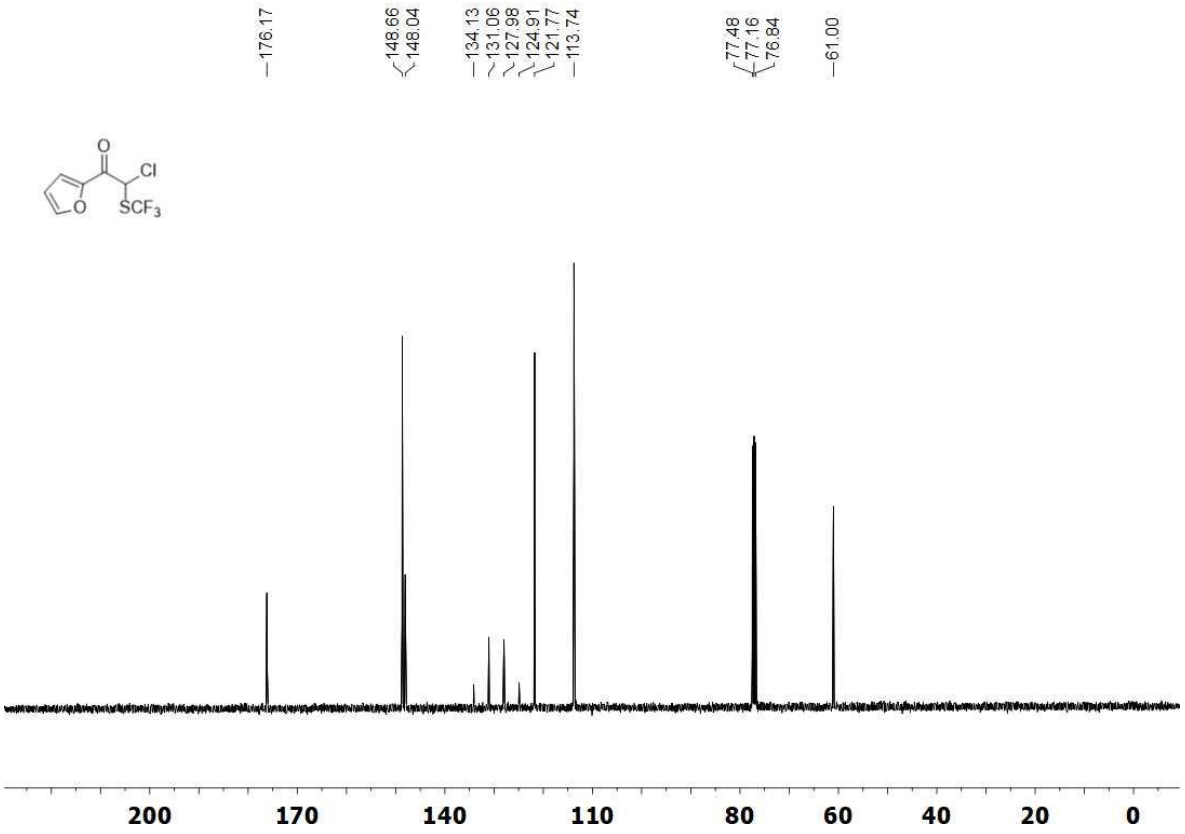
^{1}H NMR of compound **4p**



^{19}F NMR of compound **4p**



^{13}C NMR of compound **4p**



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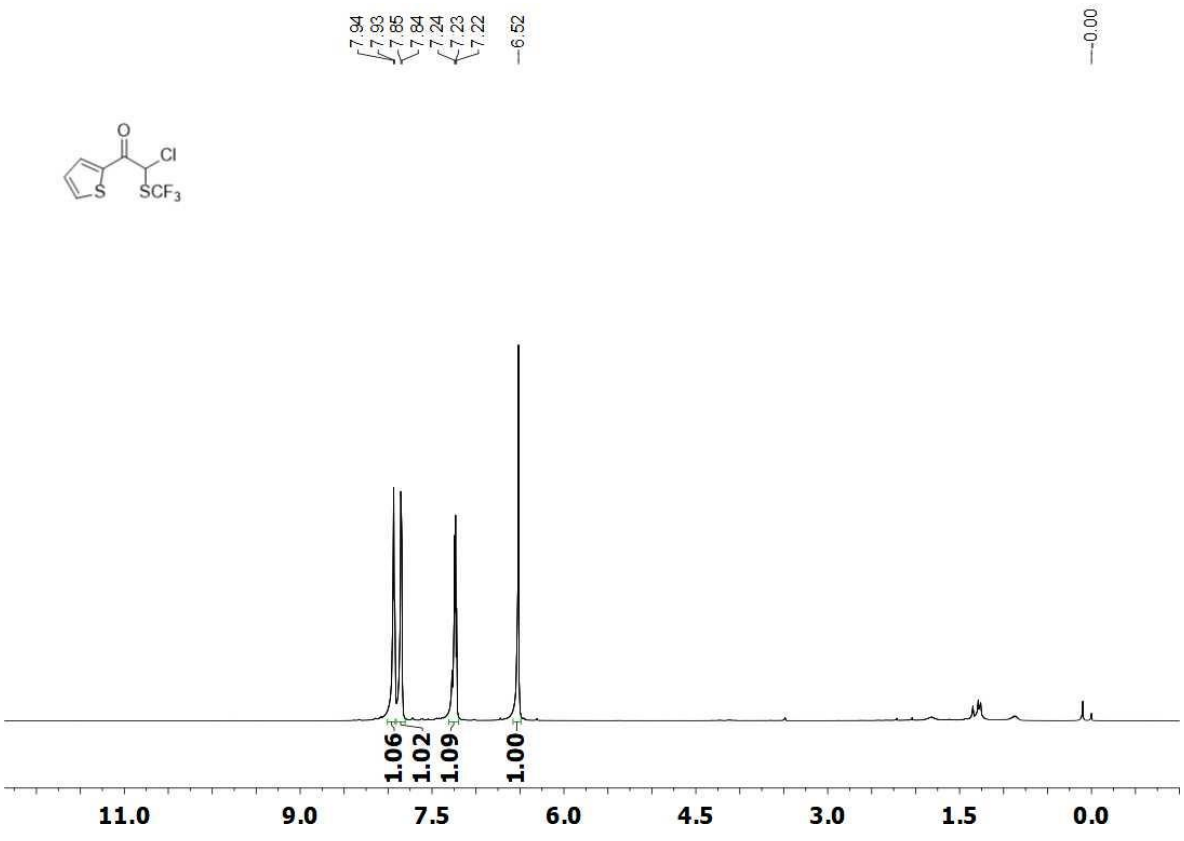

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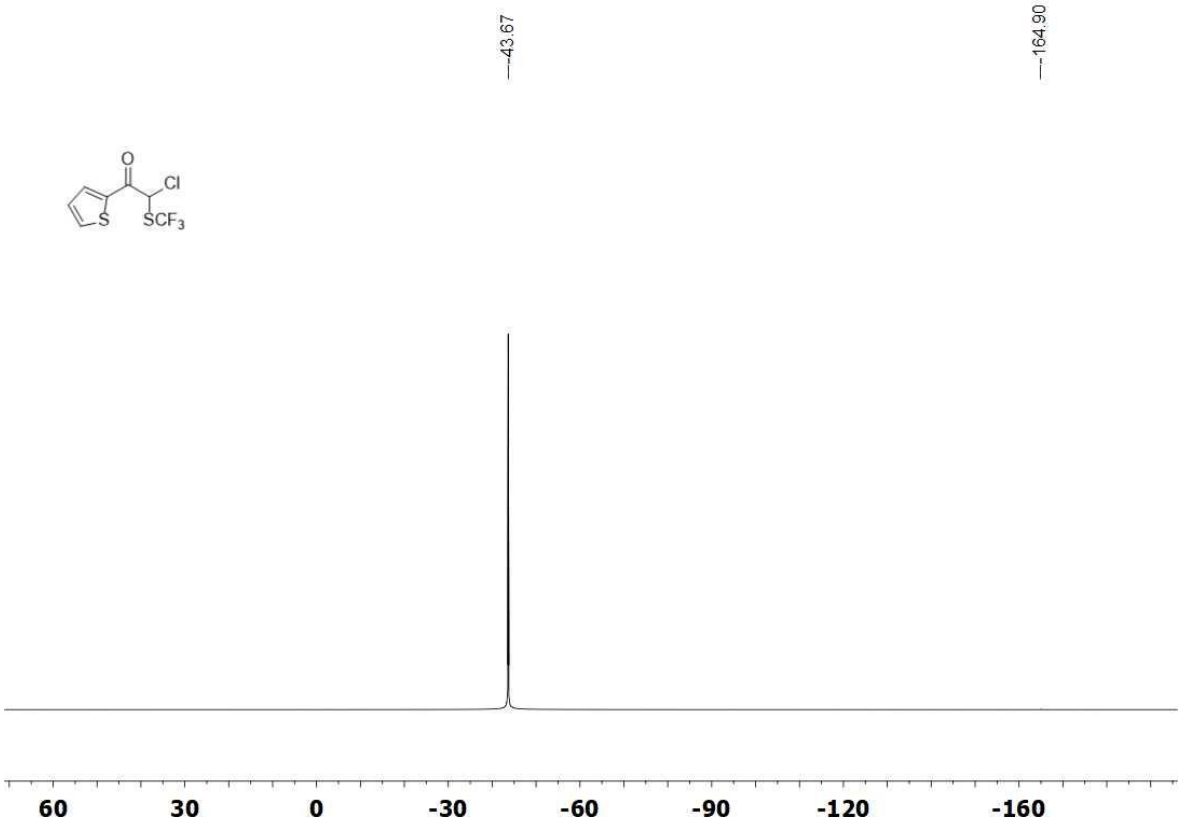
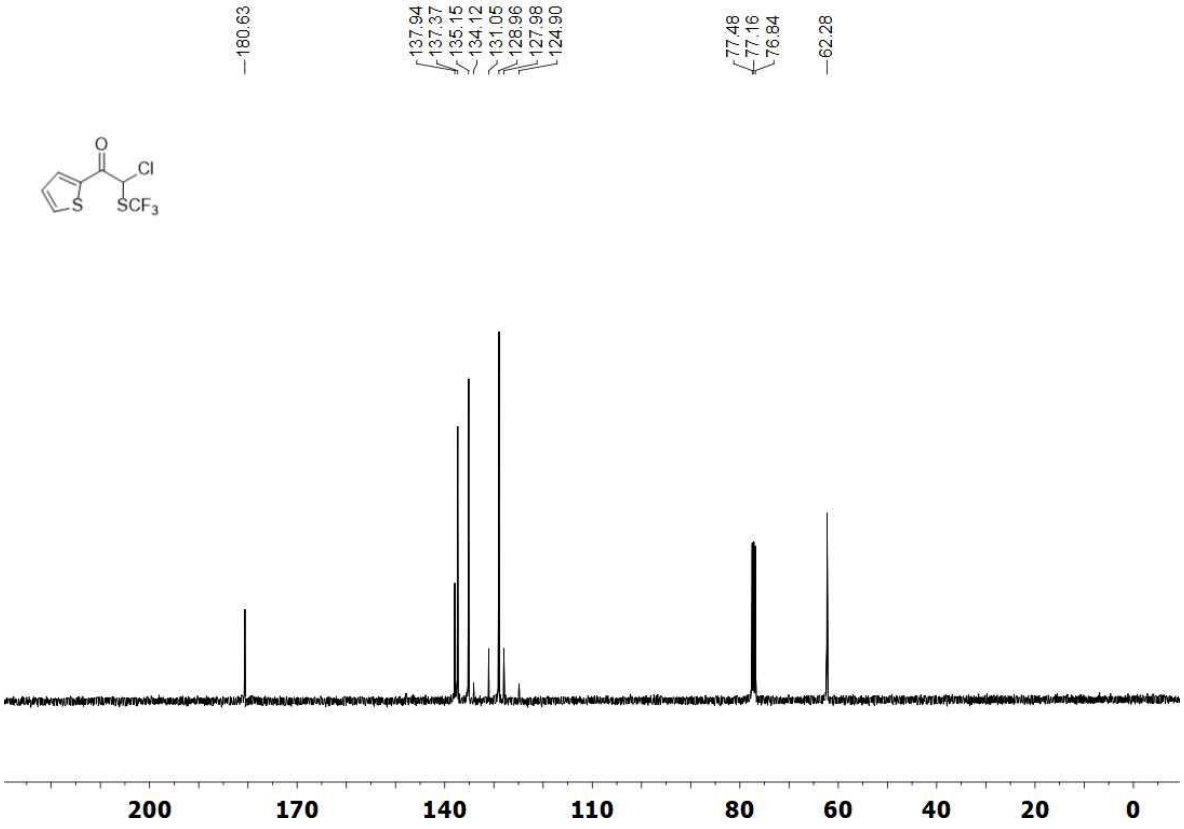


^{13}C NMR of compound **4q**



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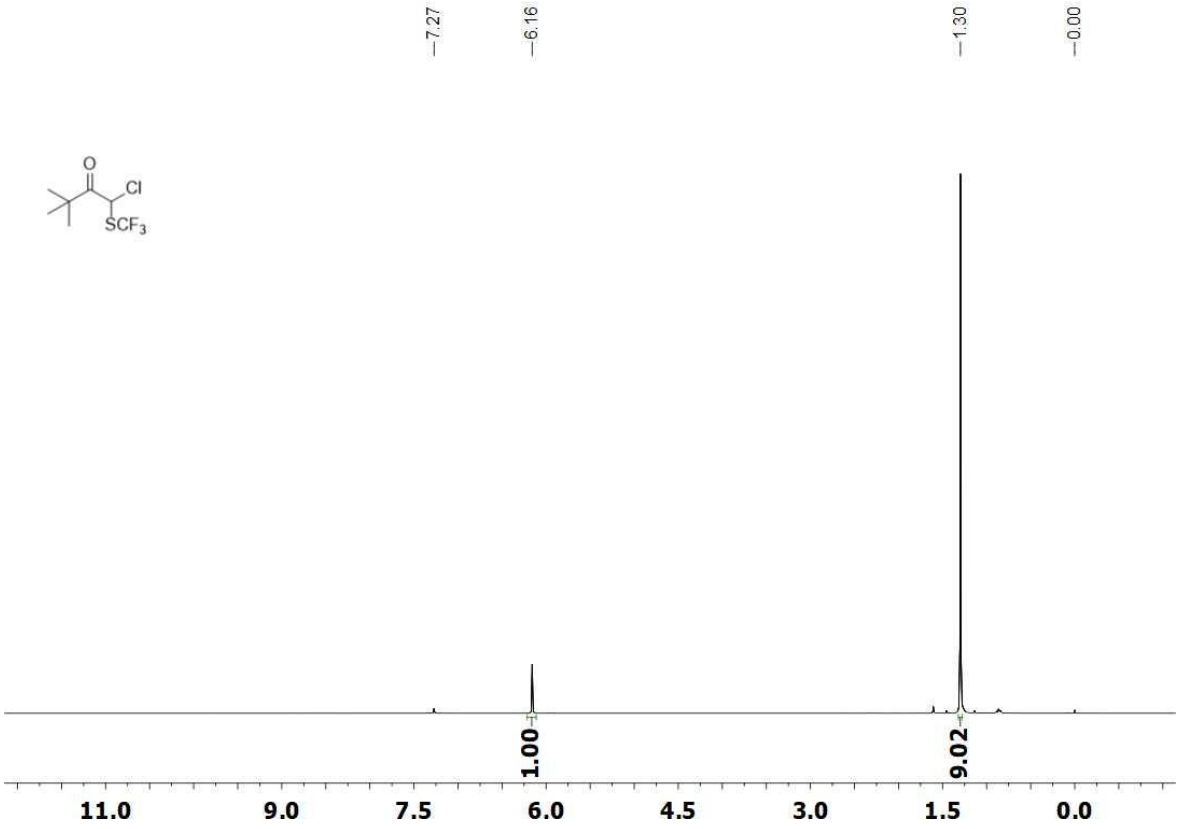
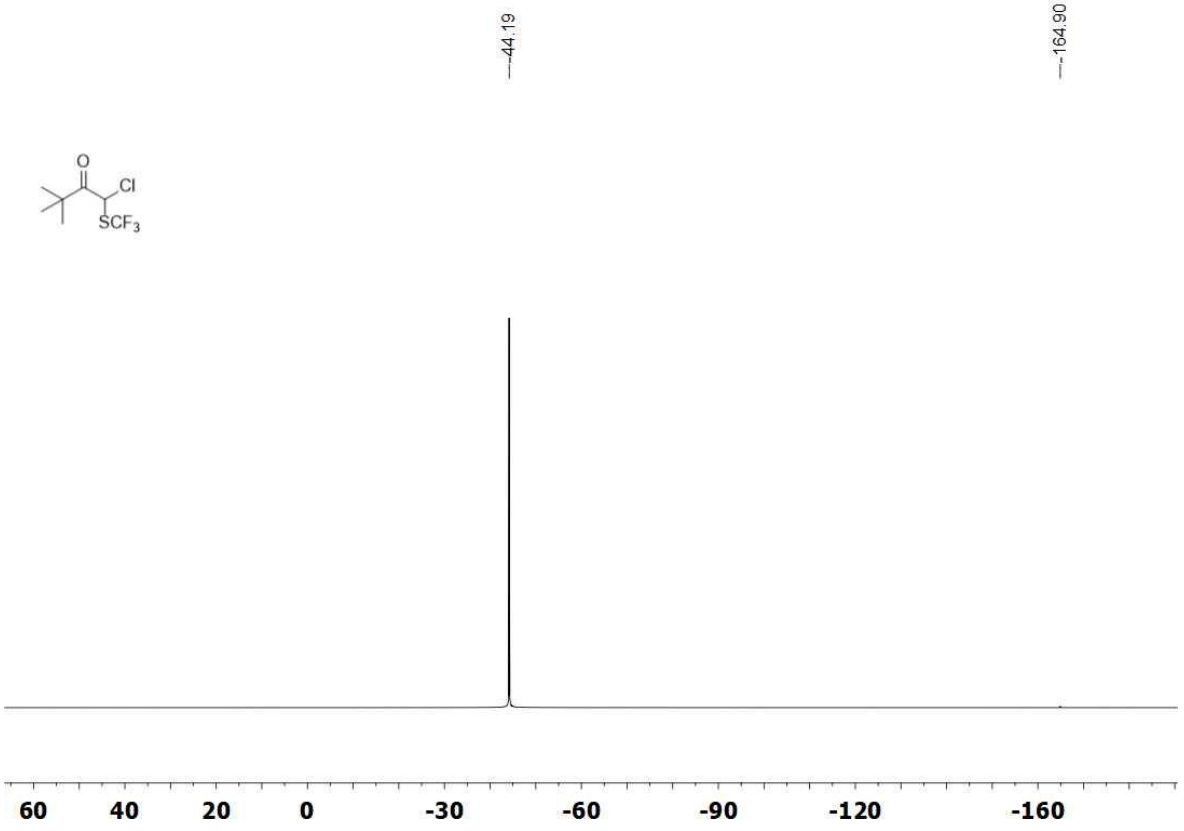


^{19}F NMR of compound **4r**



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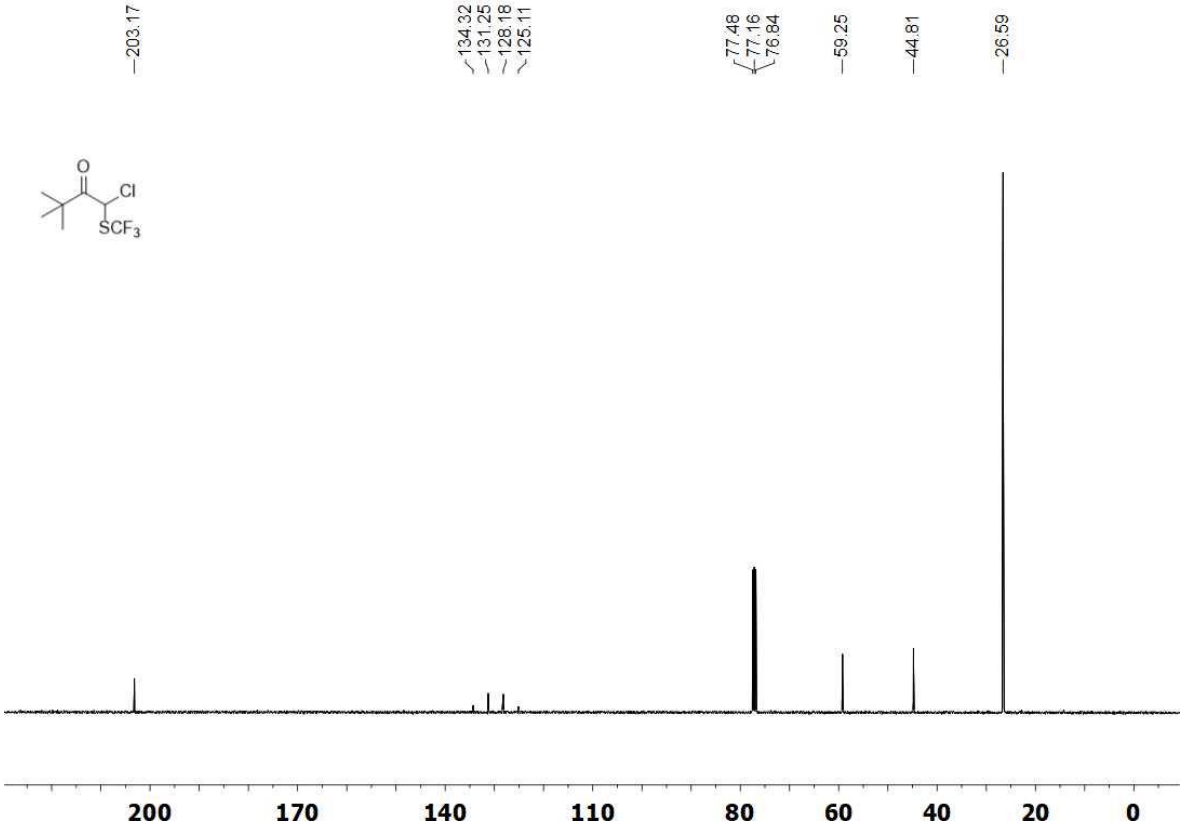

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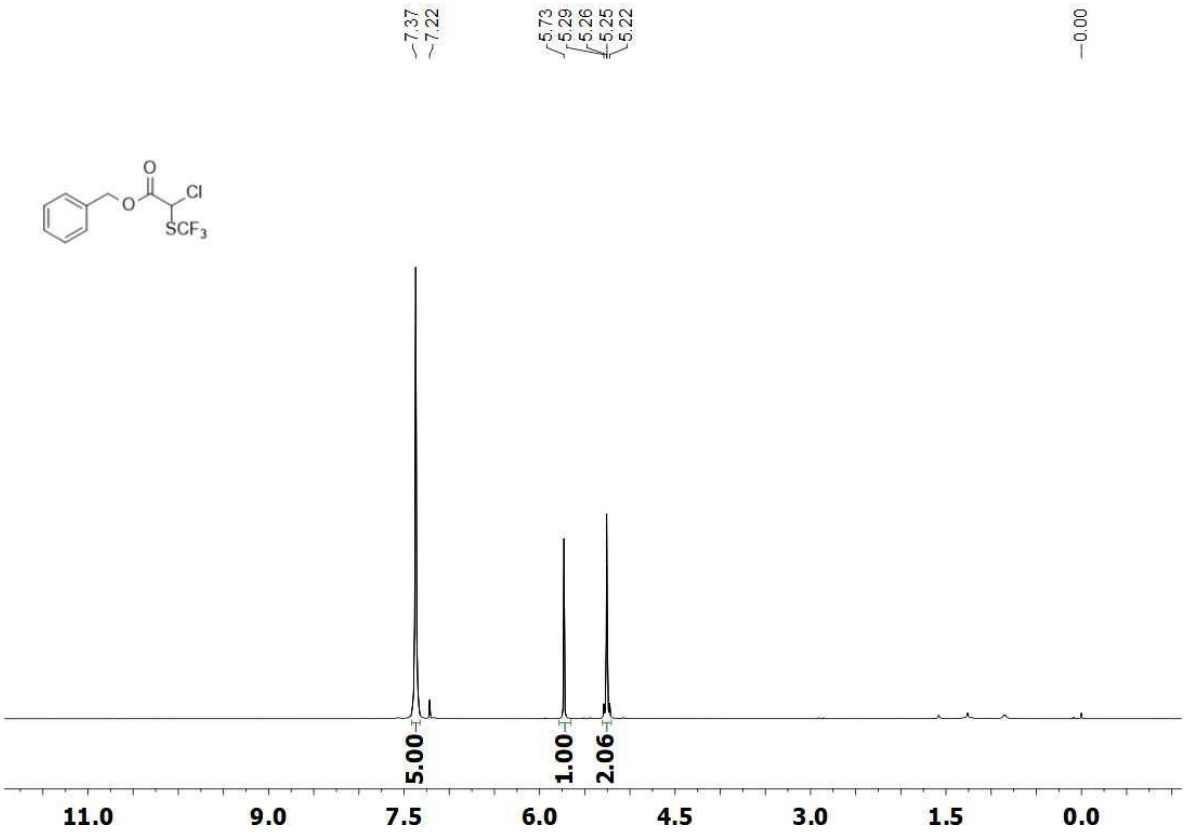

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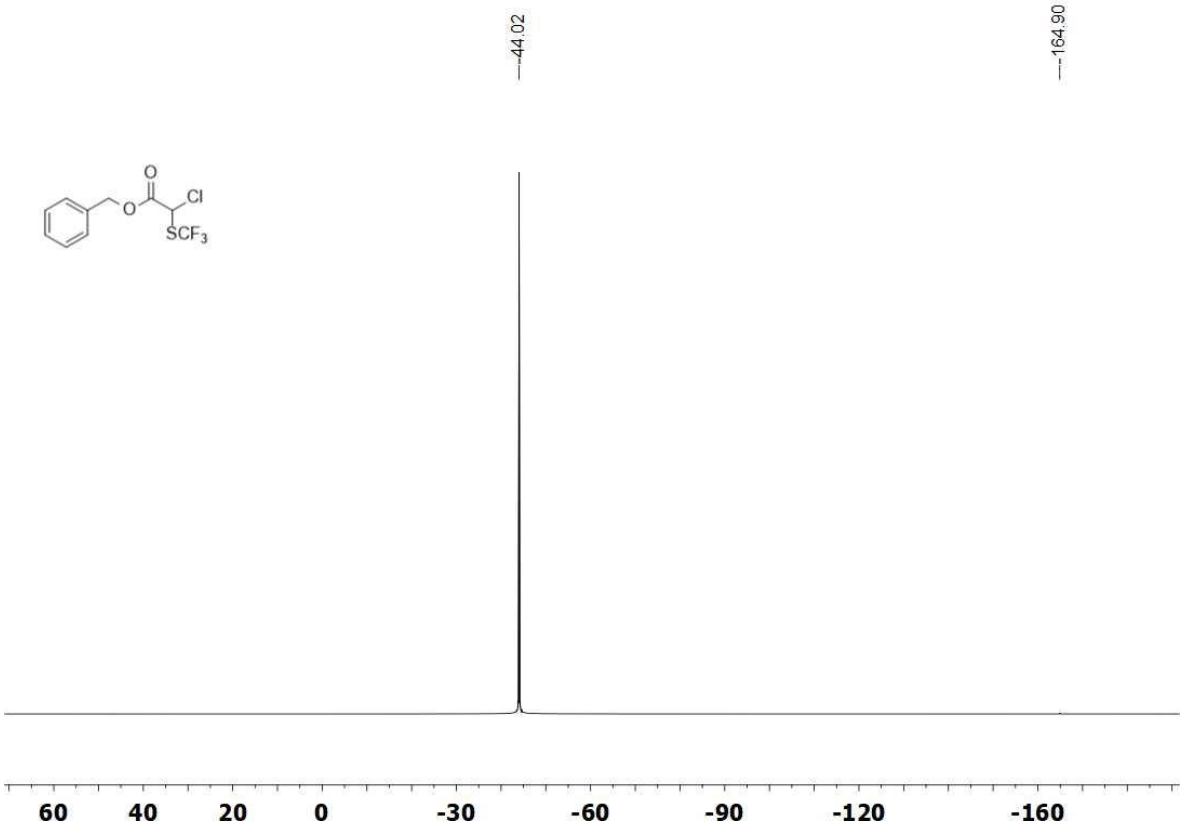

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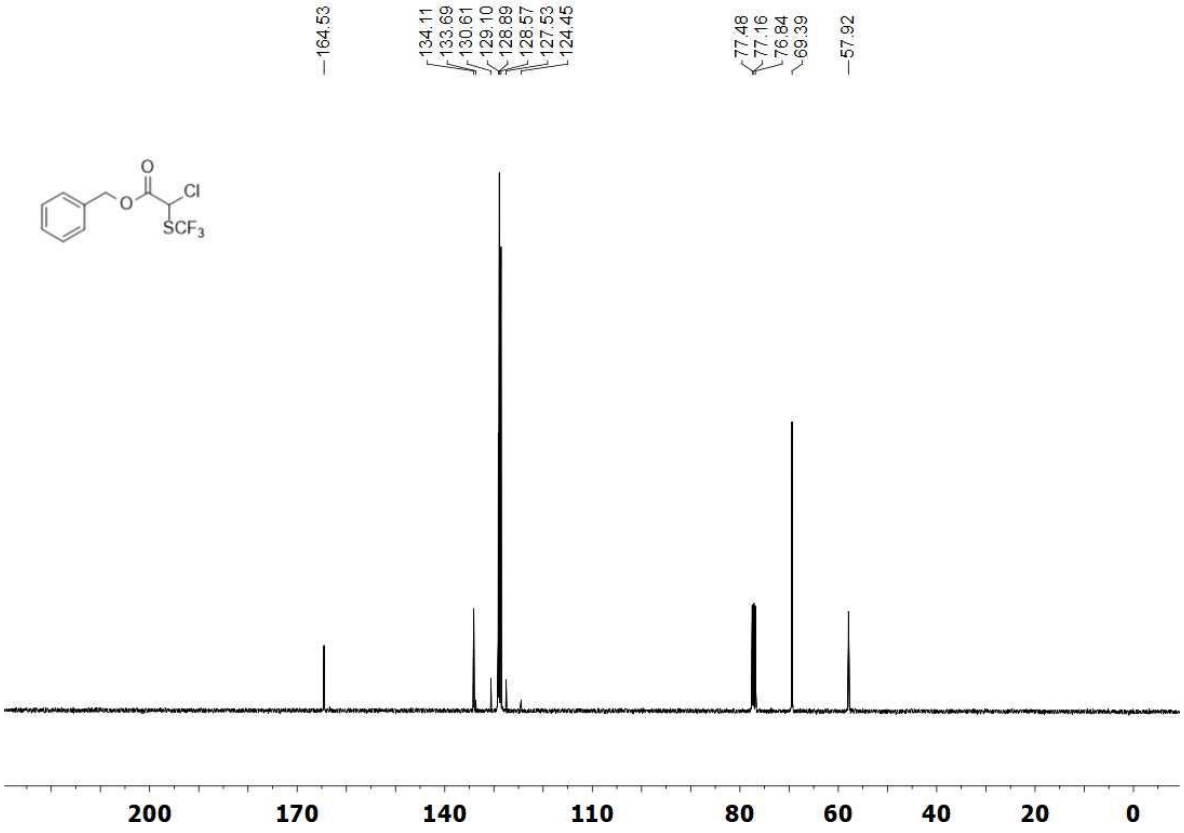

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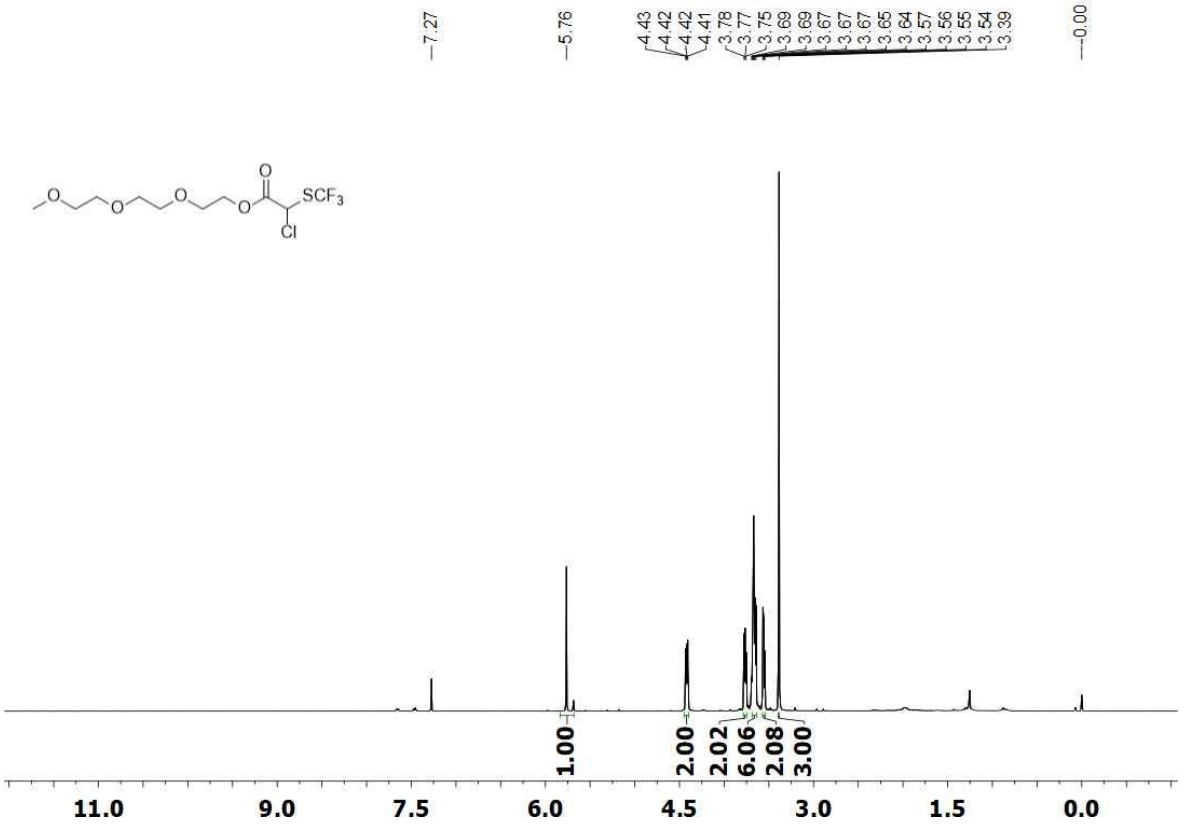

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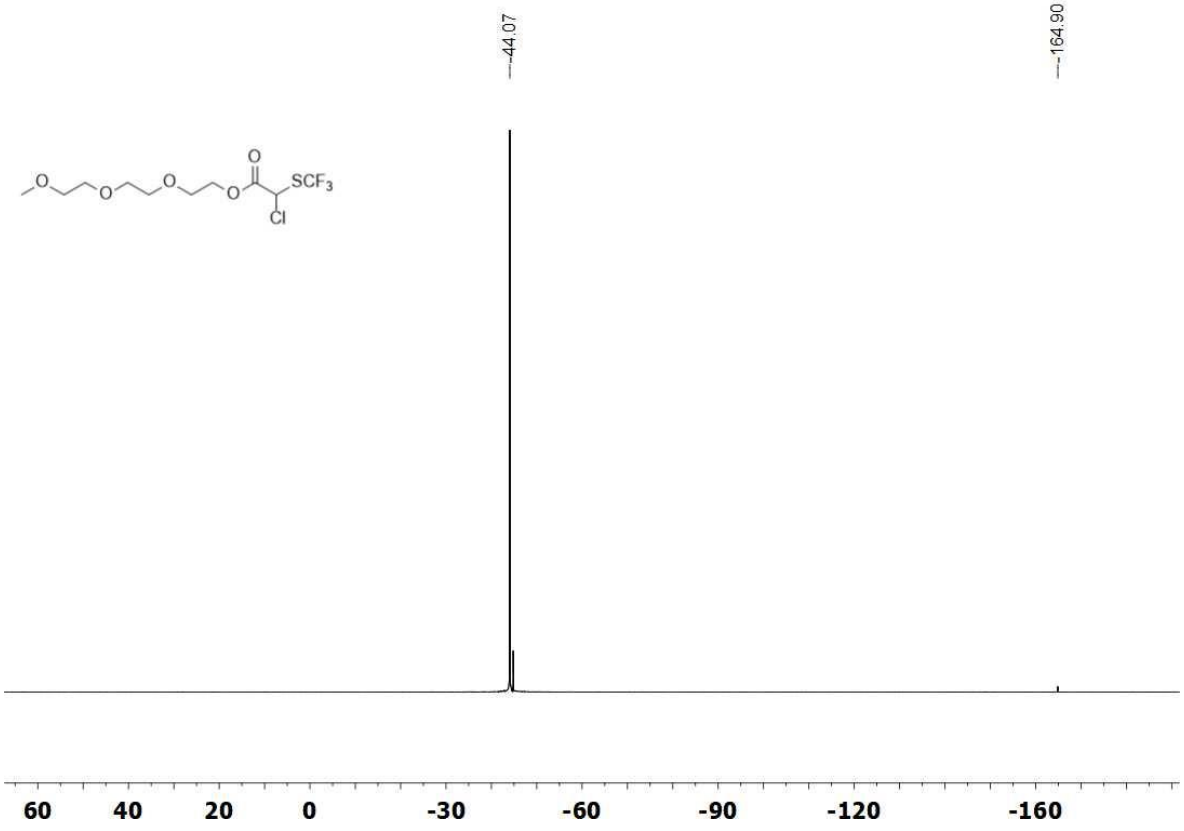

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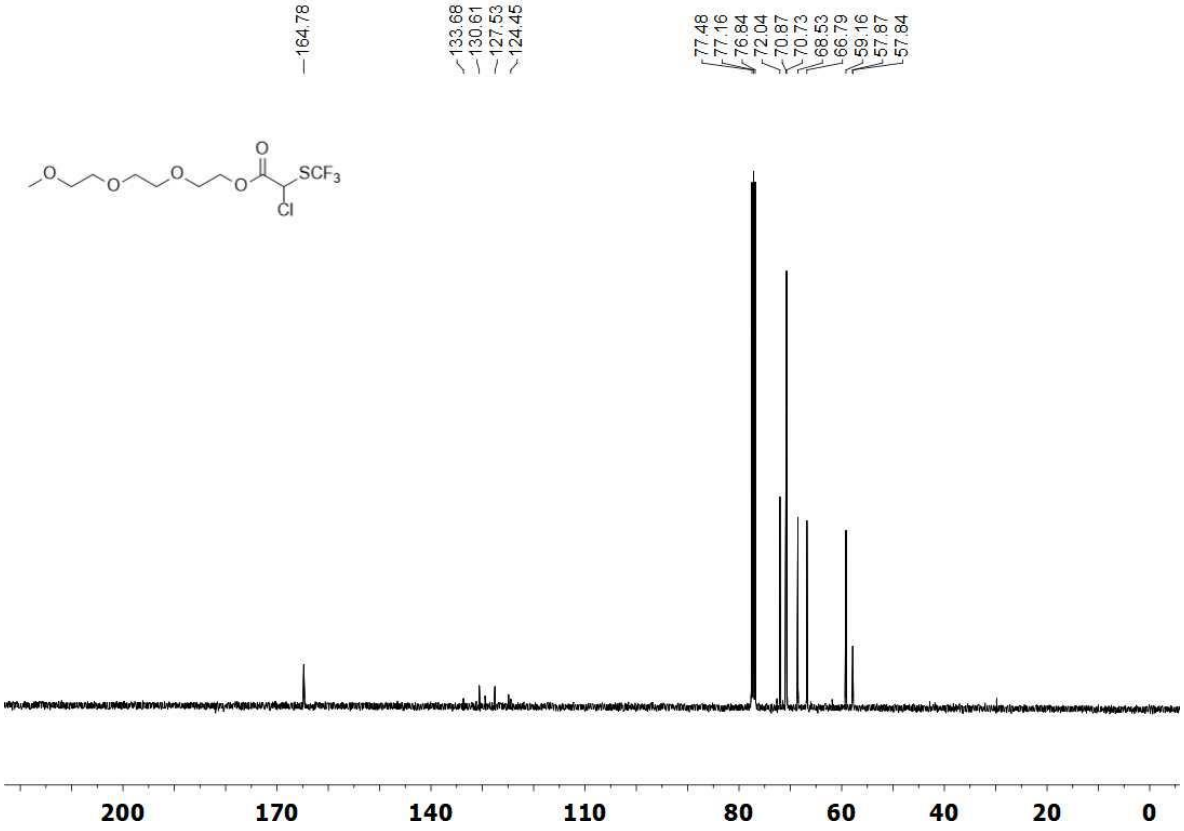
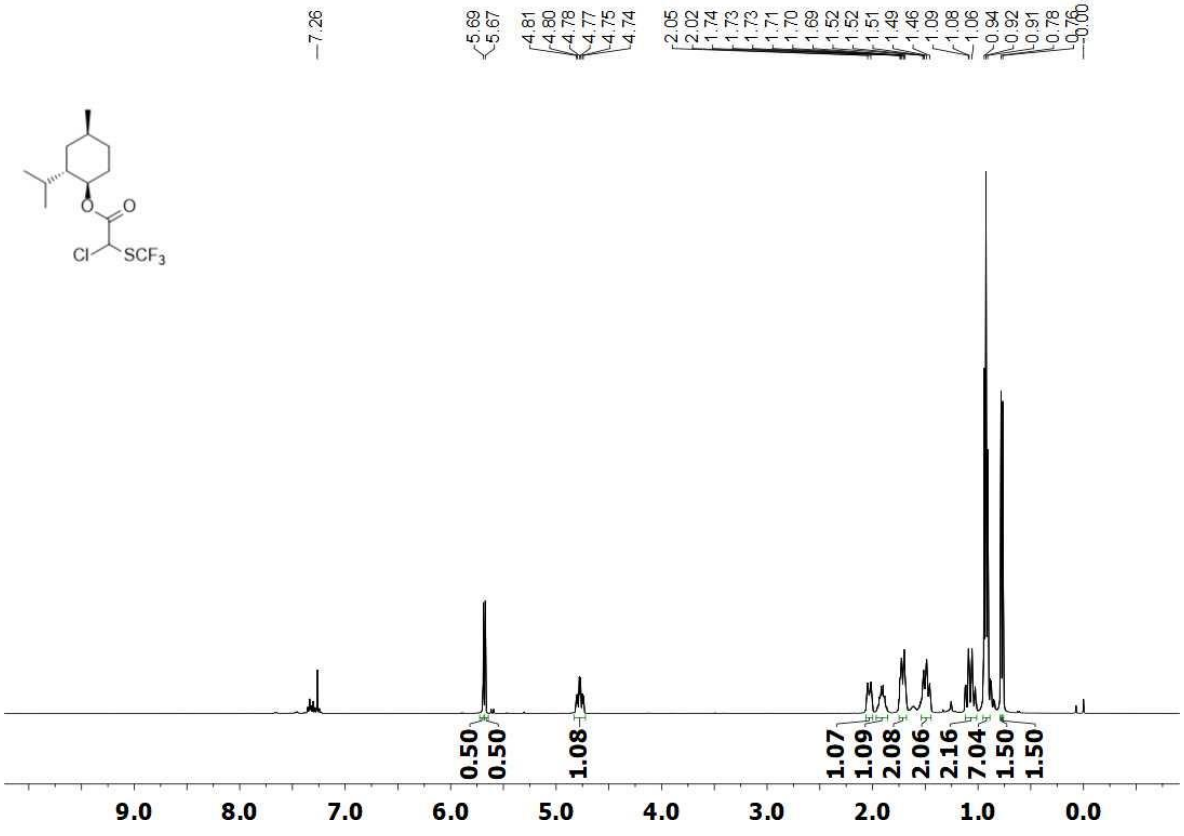
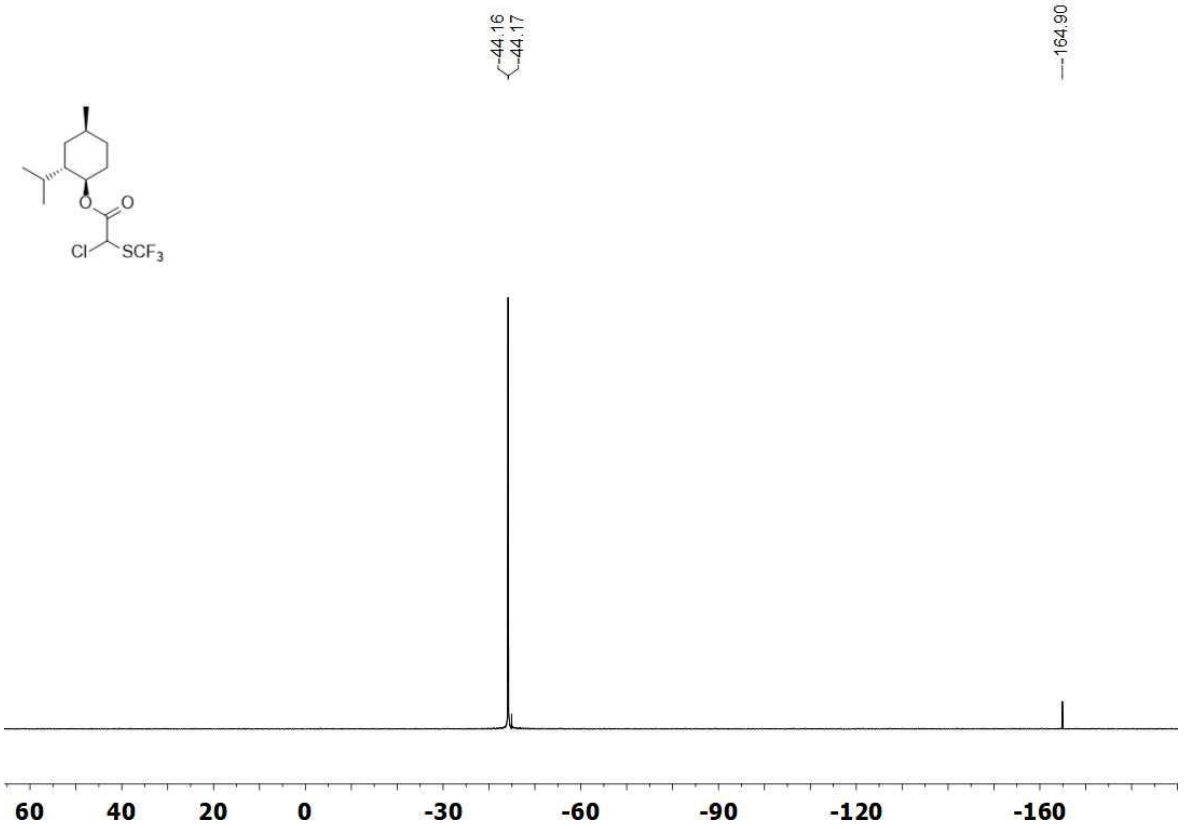


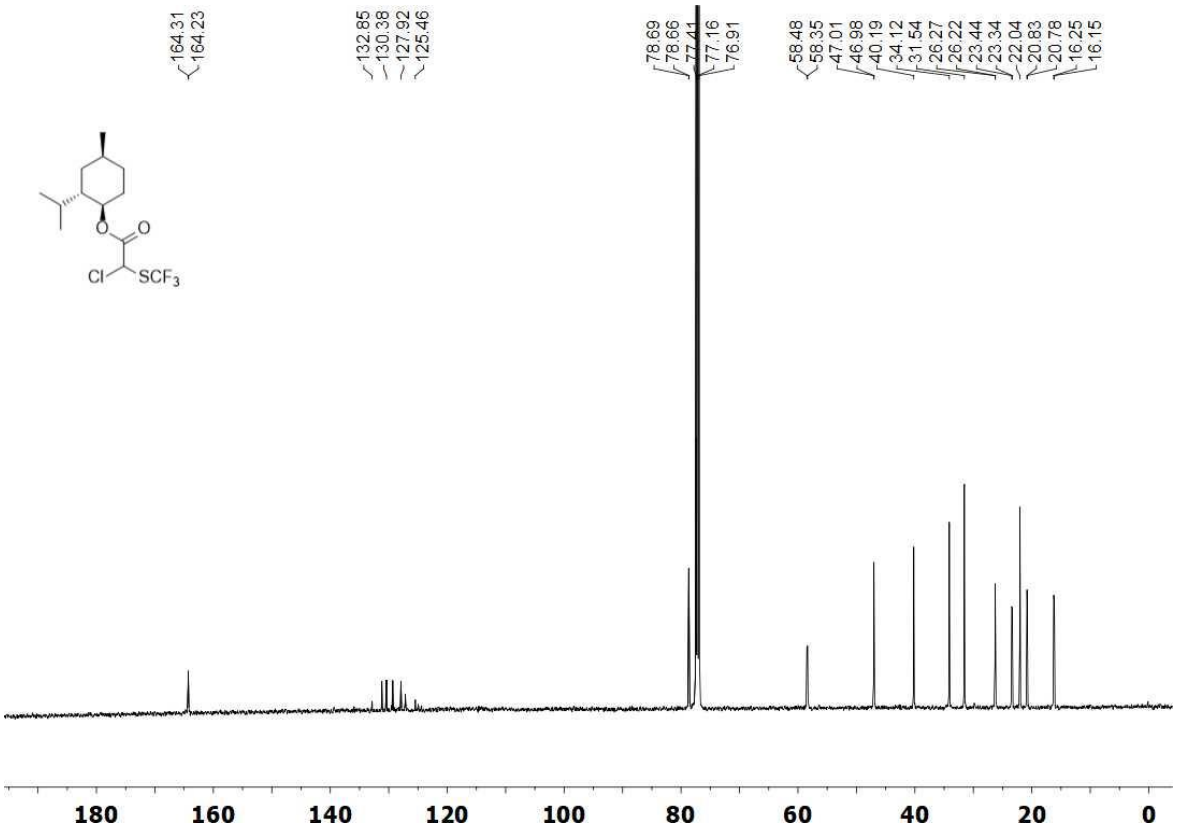
^{1}H NMR of compound **4u**



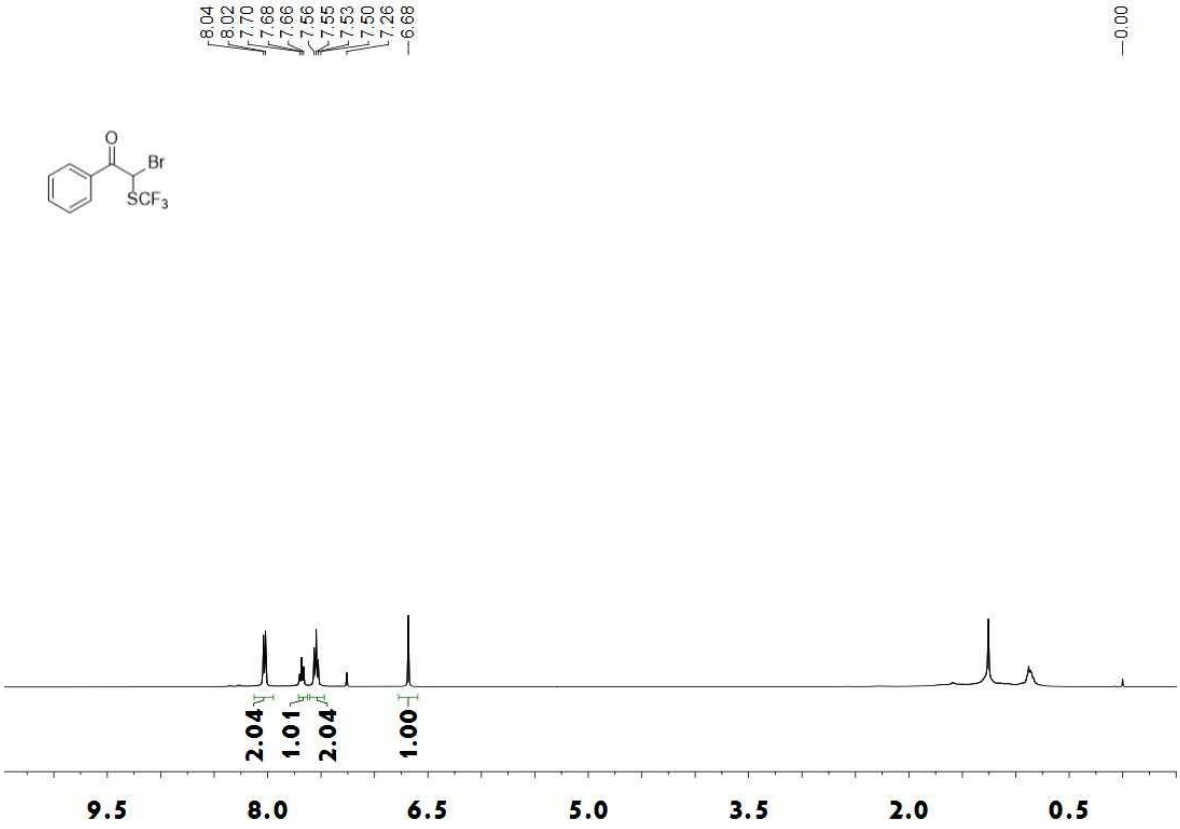
^{19}F NMR of compound **4u**



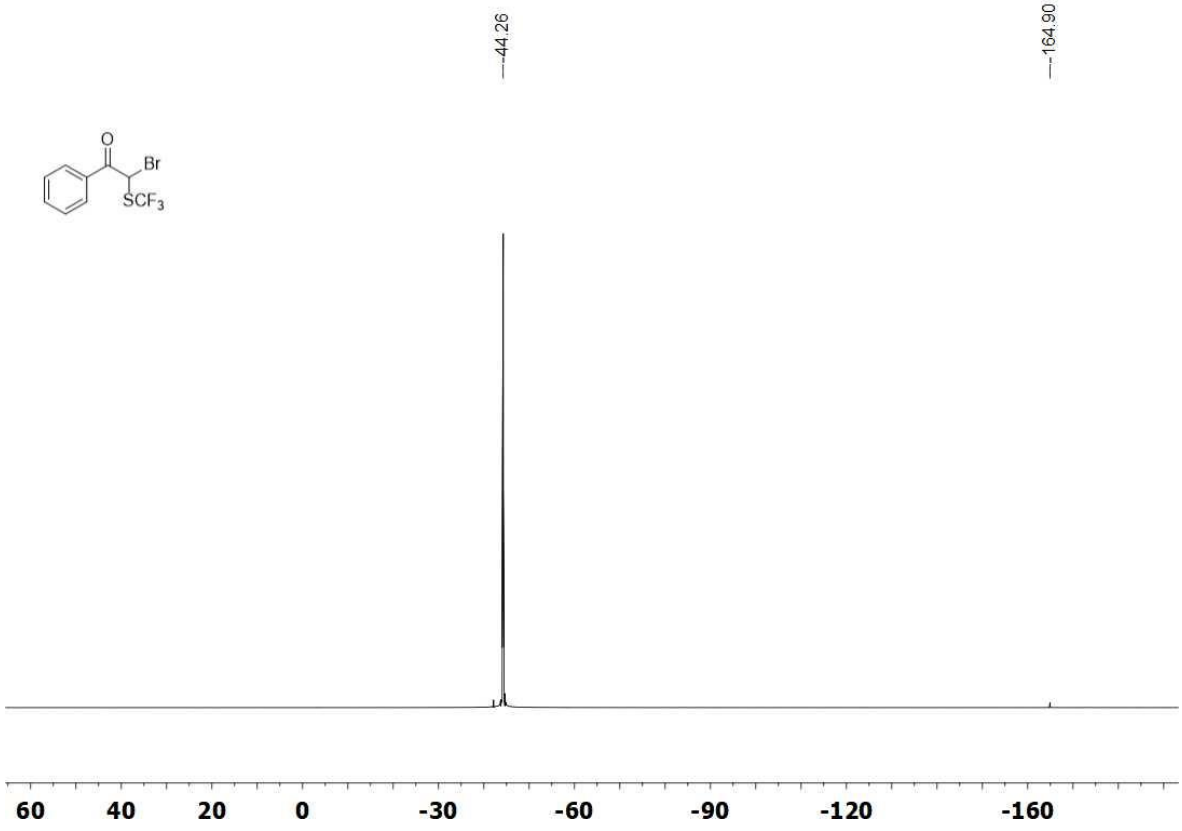
^{13}C NMR of compound **4u**



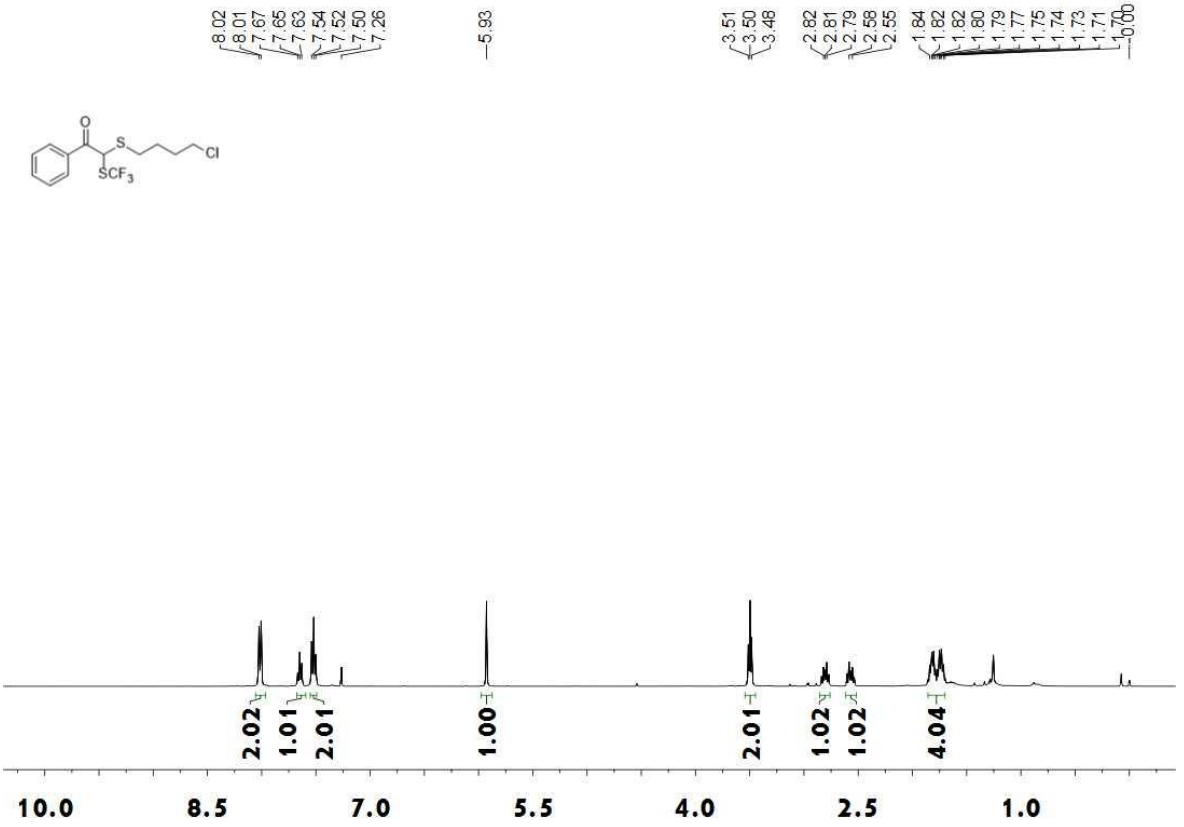
^{1}H NMR of compound **4v**



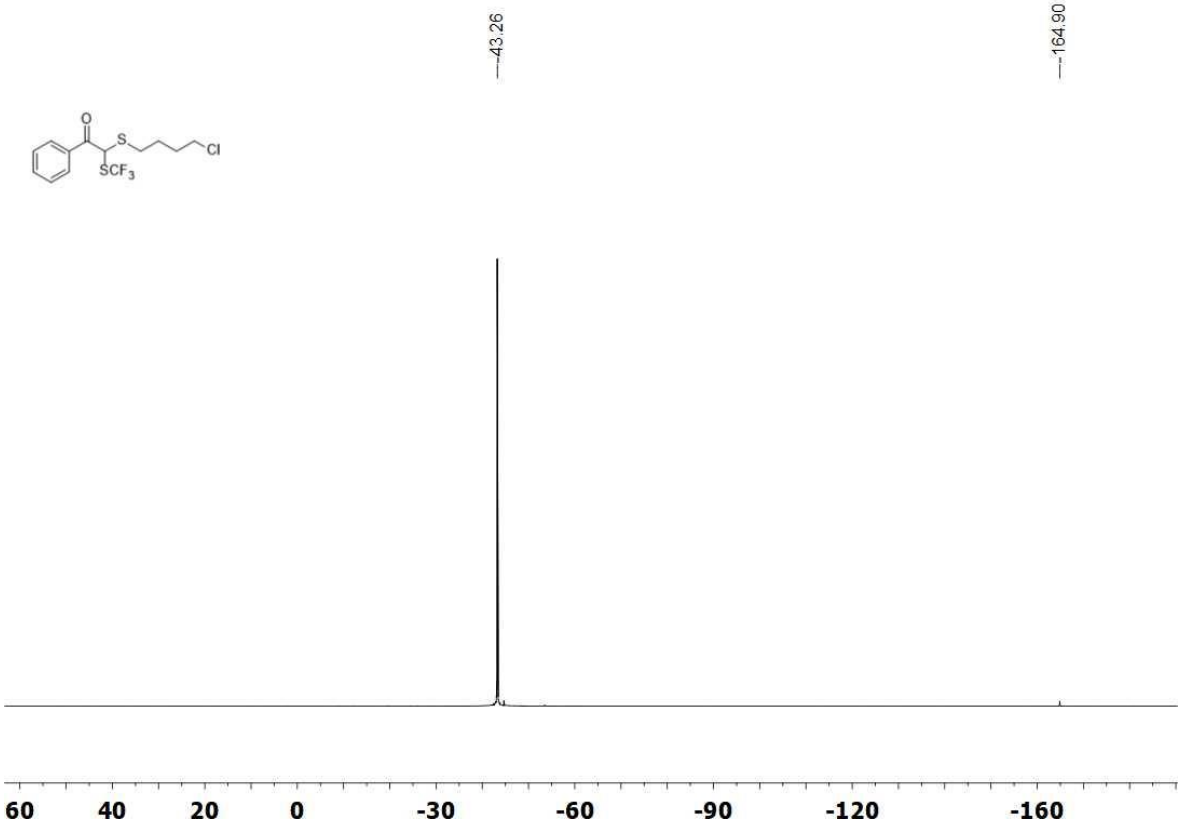
^{19}F NMR of compound **4v**



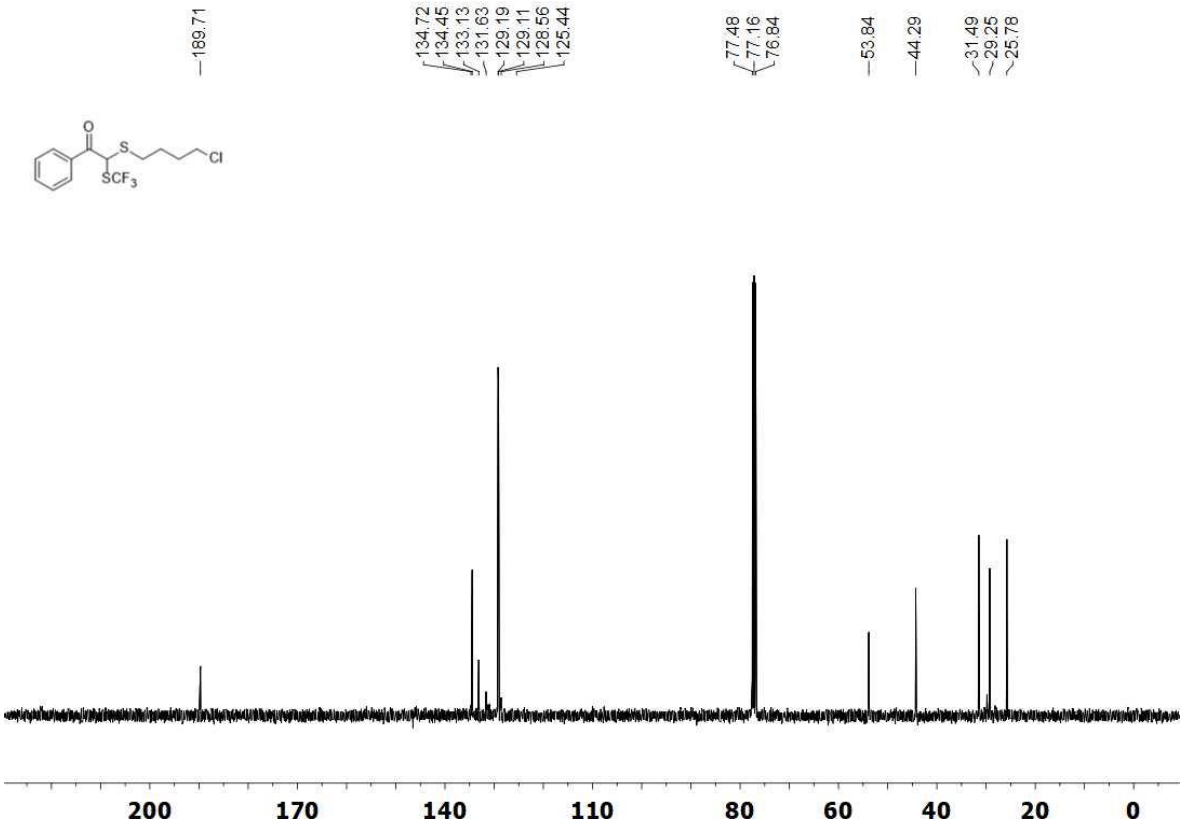
^{1}H NMR of compound **5a**



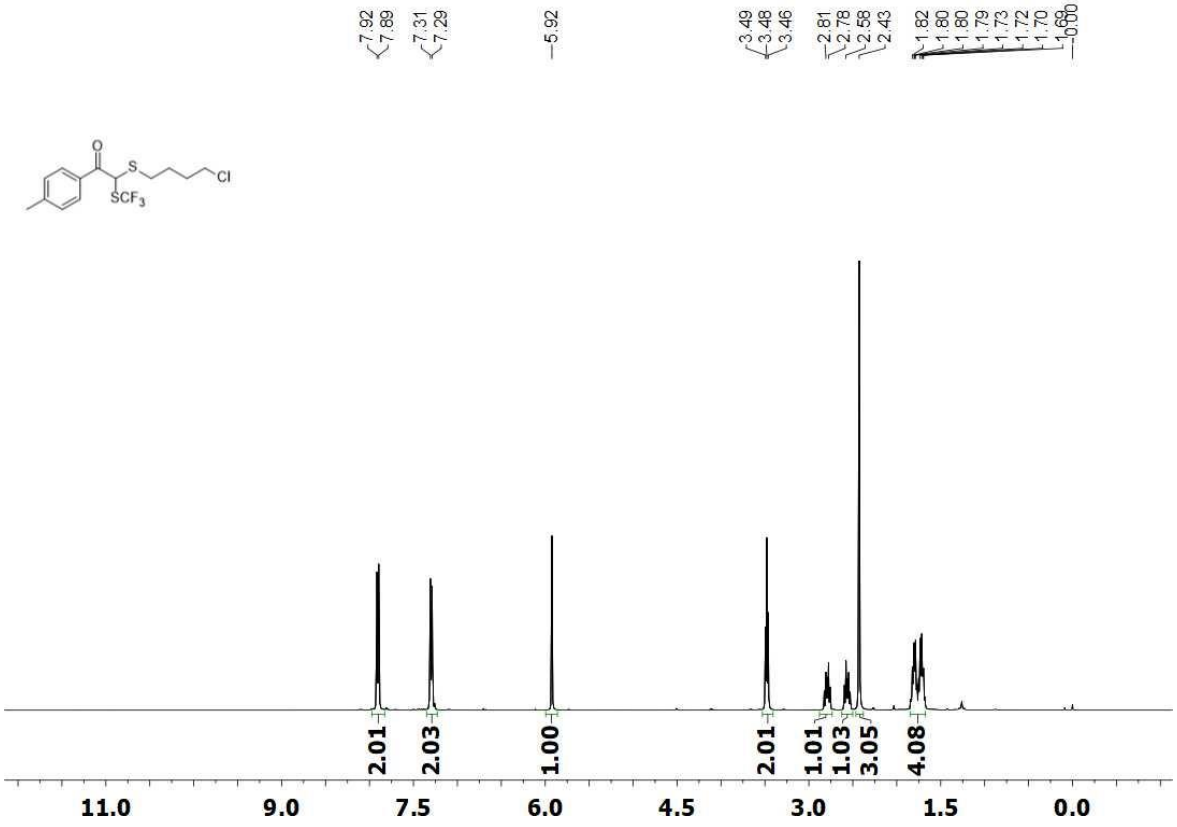
^{19}F NMR of compound **5a**



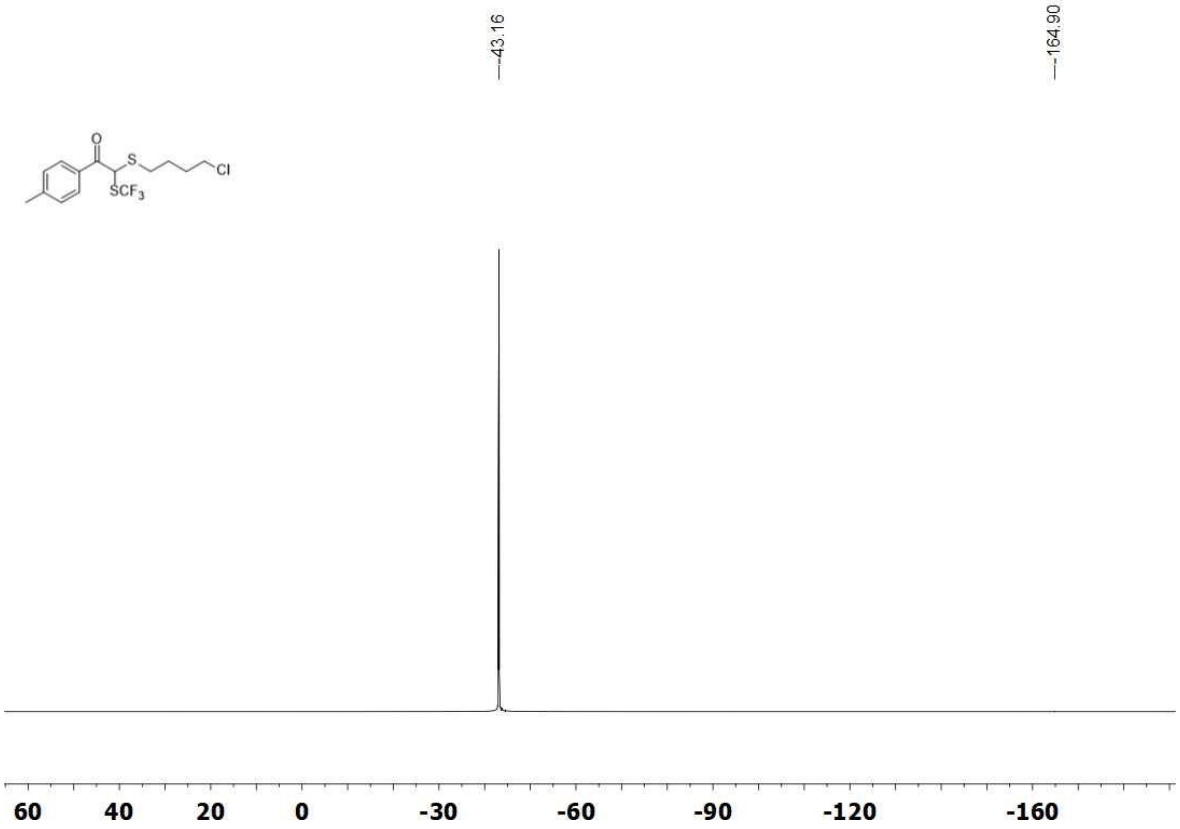
^{13}C NMR of compound **5a**



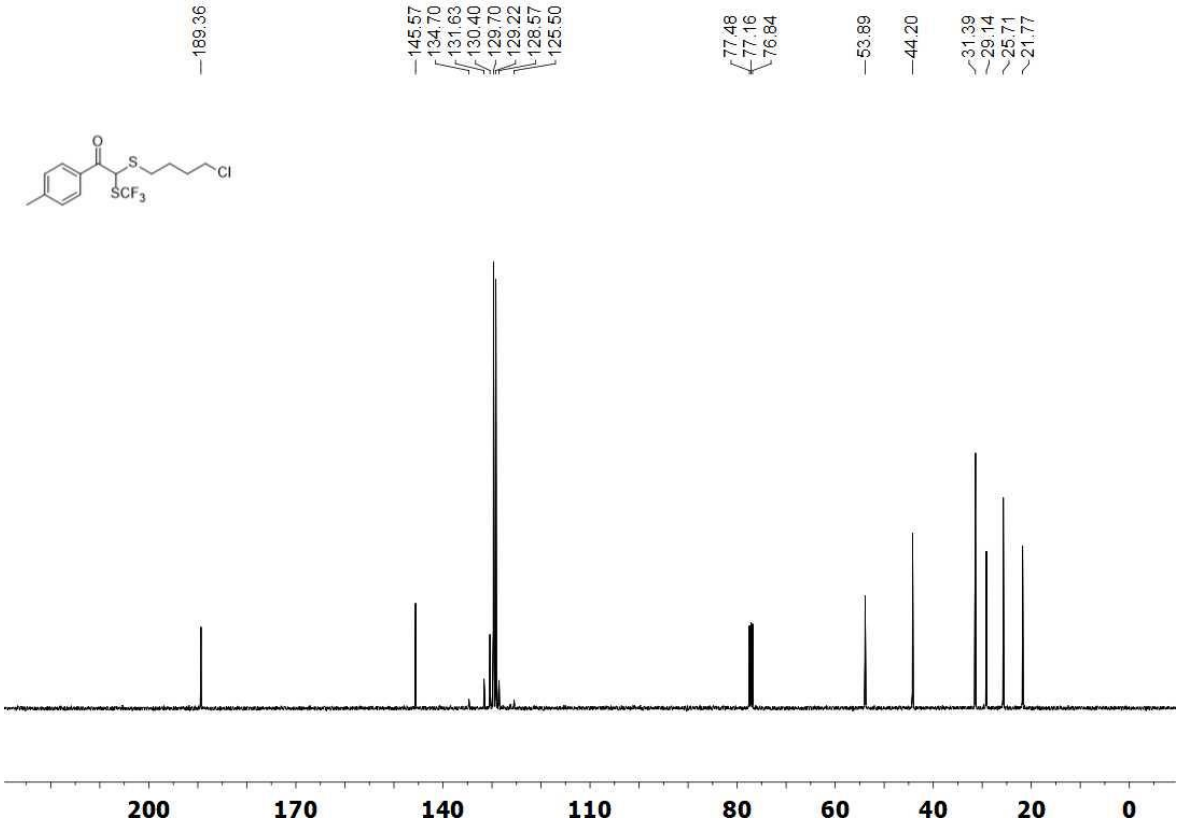
^{1}H NMR of compound **5b**



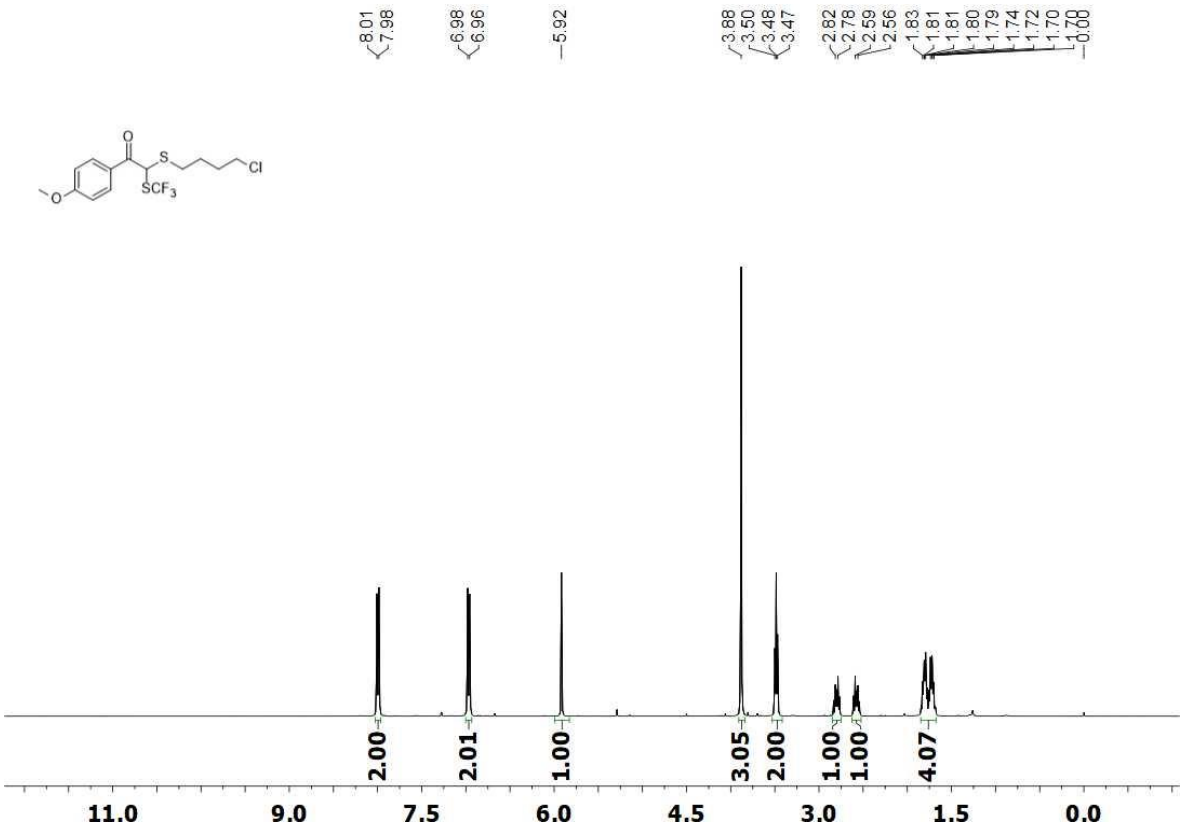
^{19}F NMR of compound **5b**



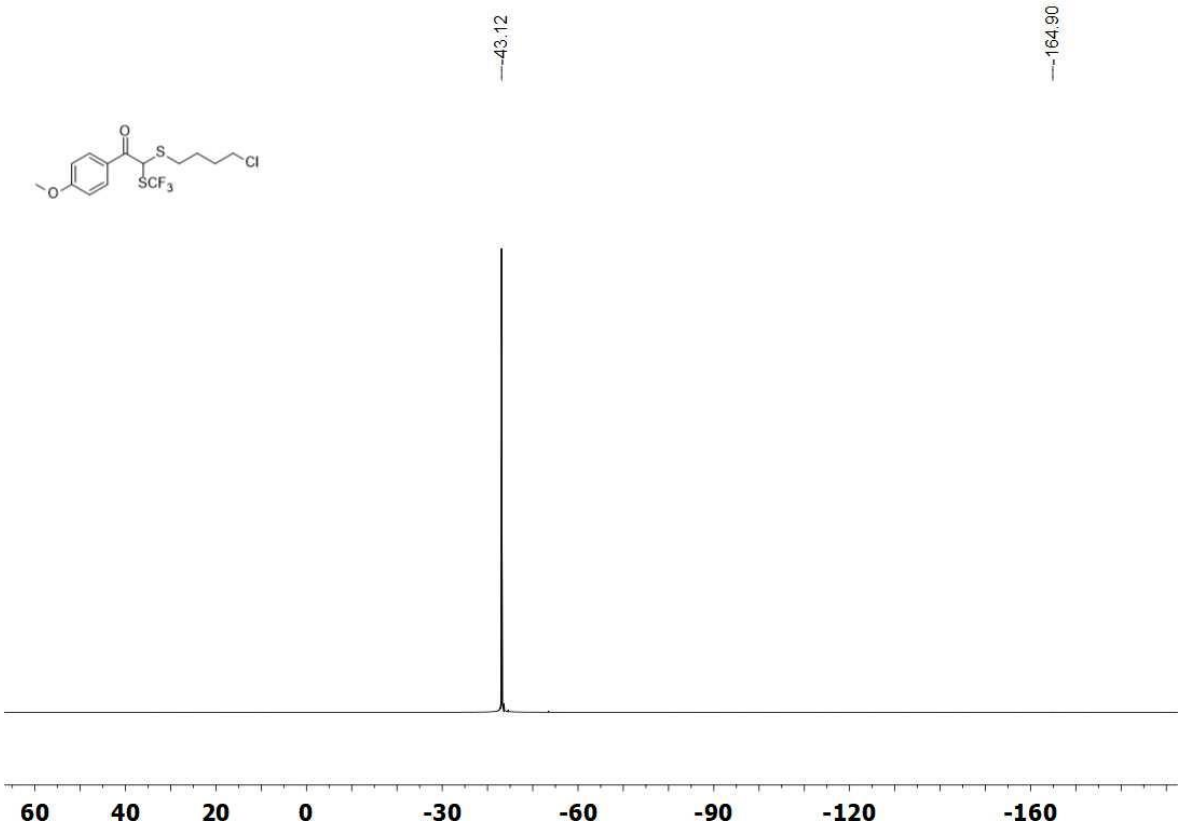
^{13}C NMR of compound **5b**



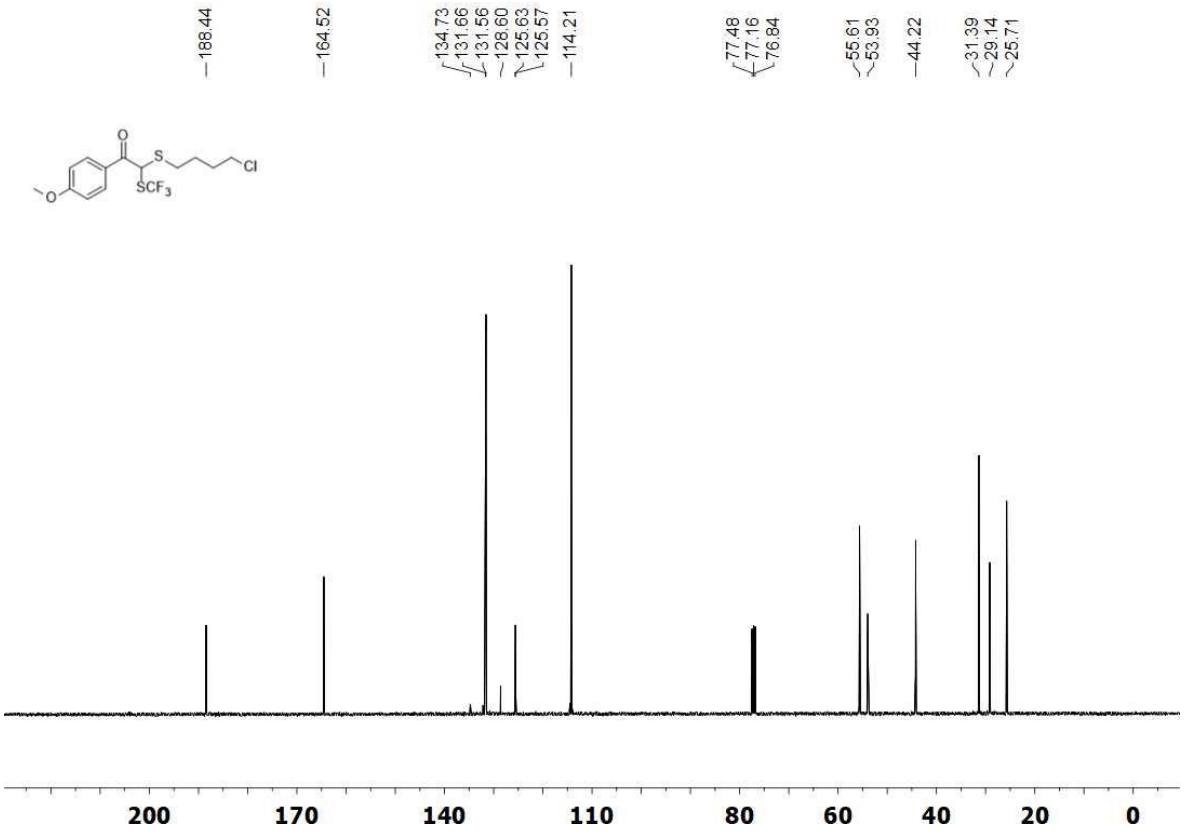
^{1}H NMR of compound **5c**



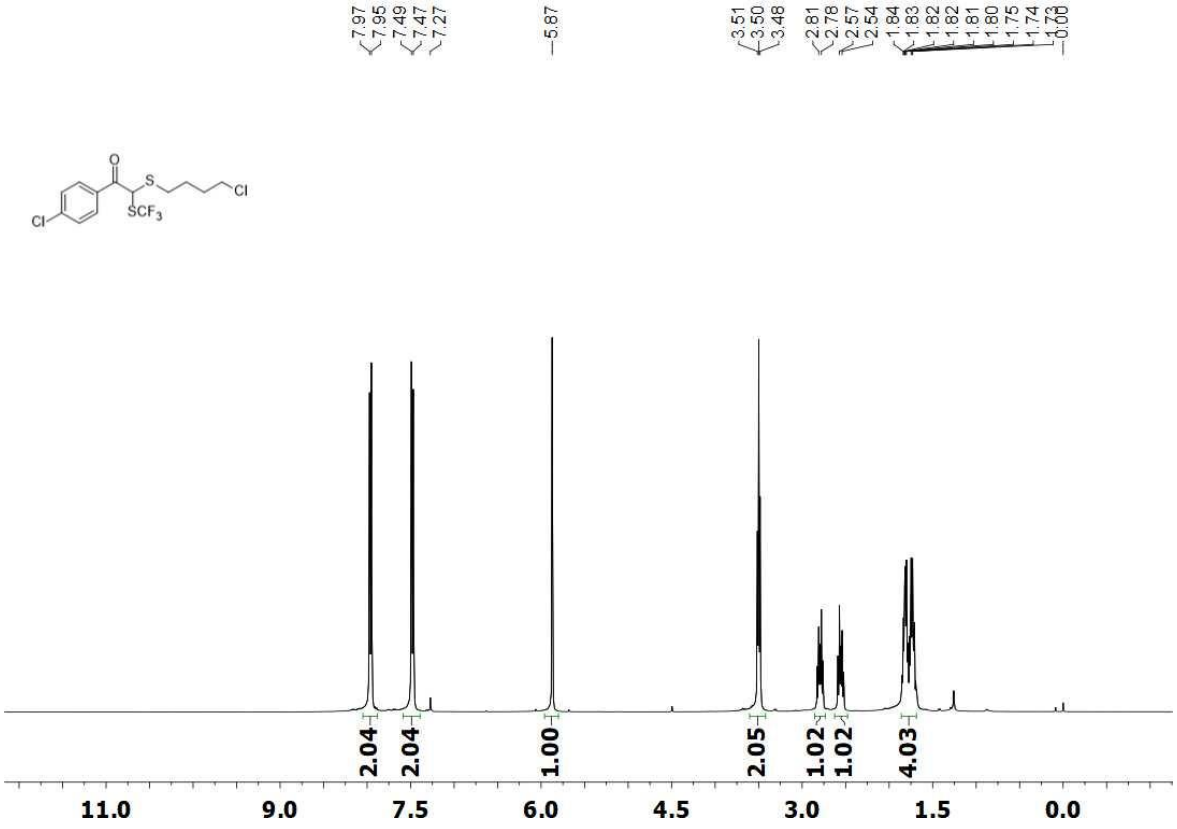
^{19}F NMR of compound **5c**



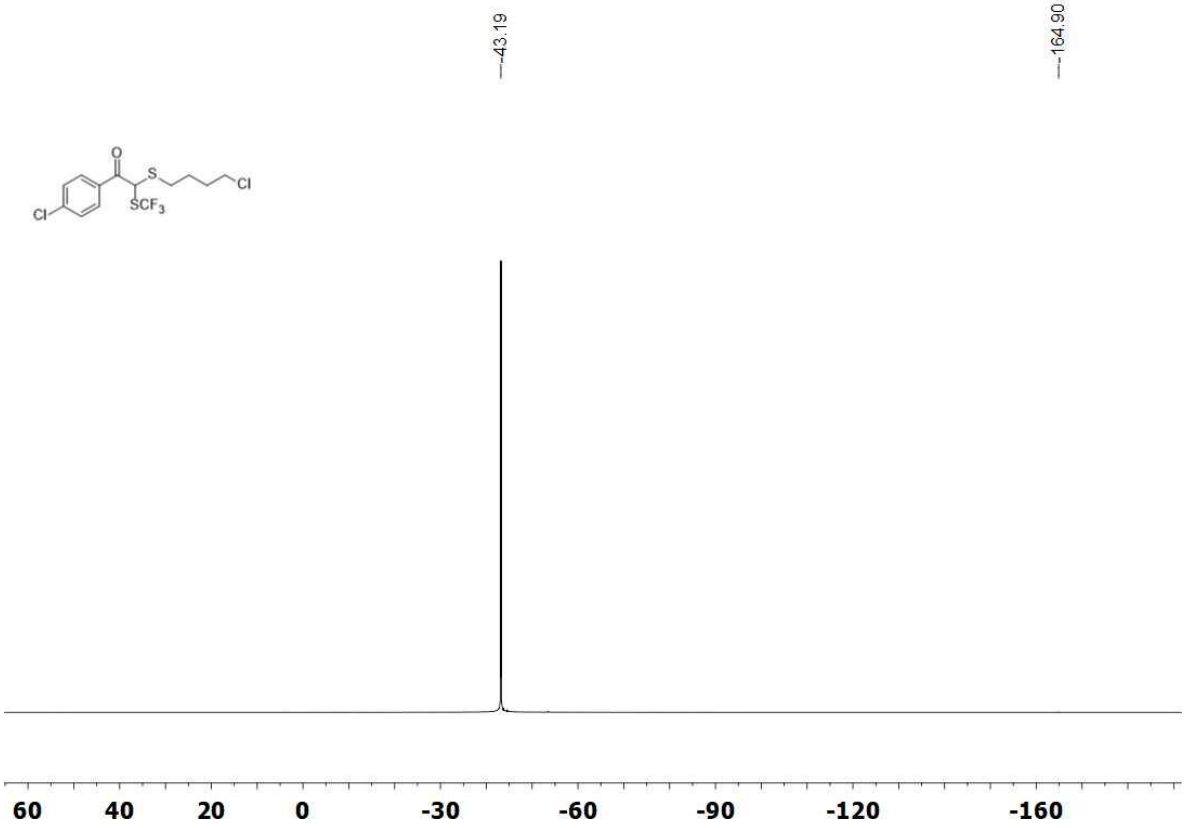
^{13}C NMR of compound **5c**



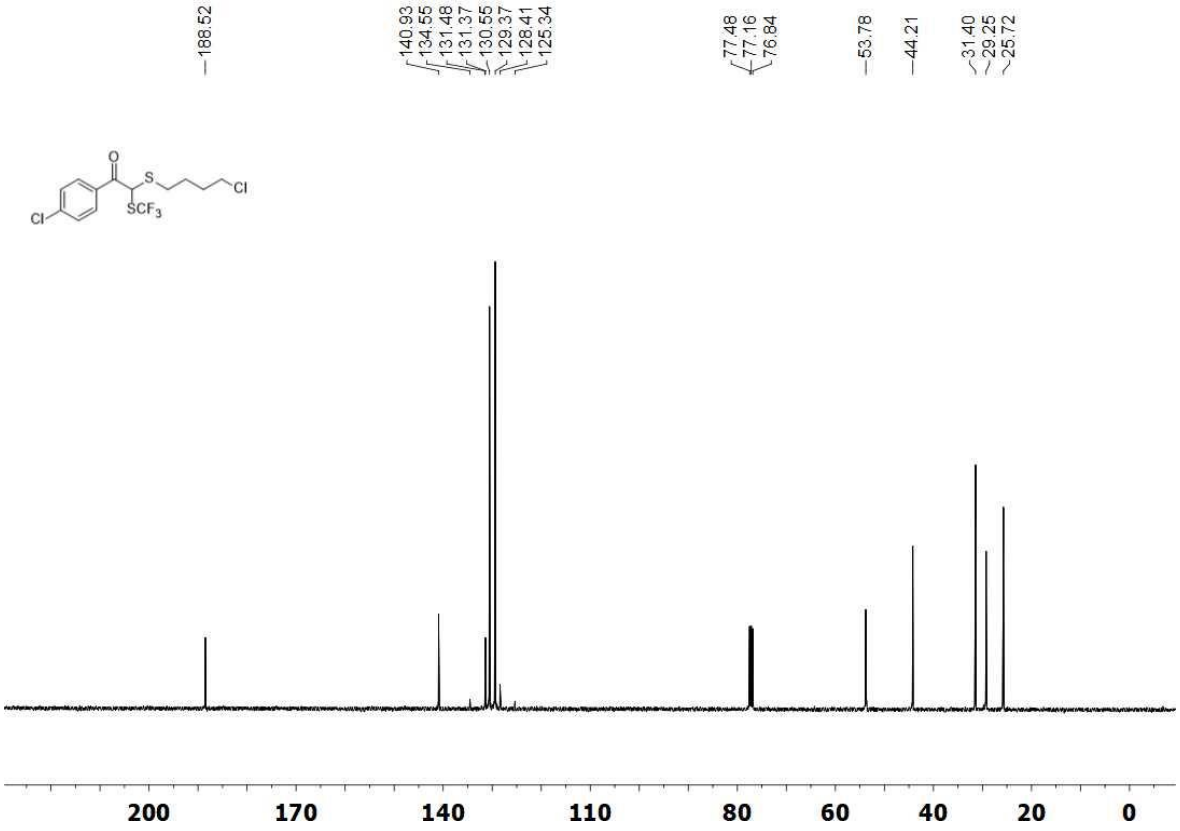
^{1}H NMR of compound **5d**



^{19}F NMR of compound **5d**



^{13}C NMR of compound **5d**



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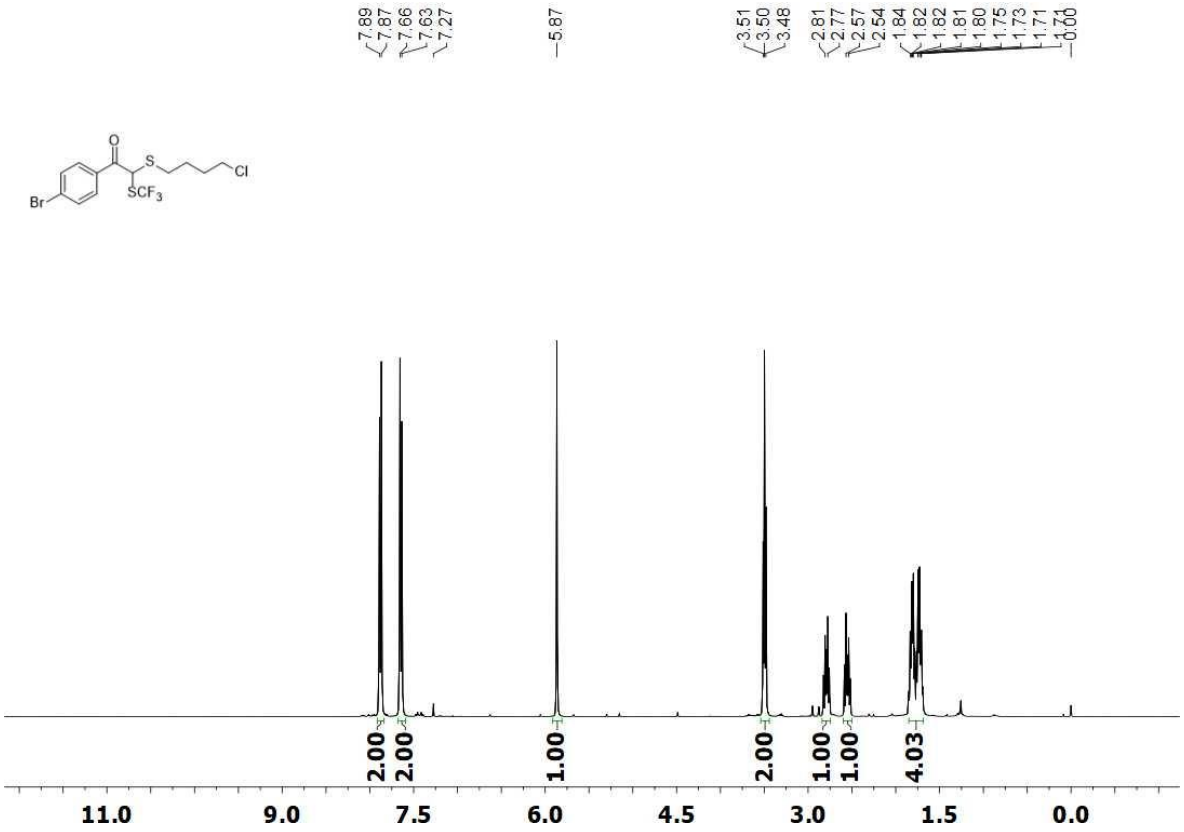
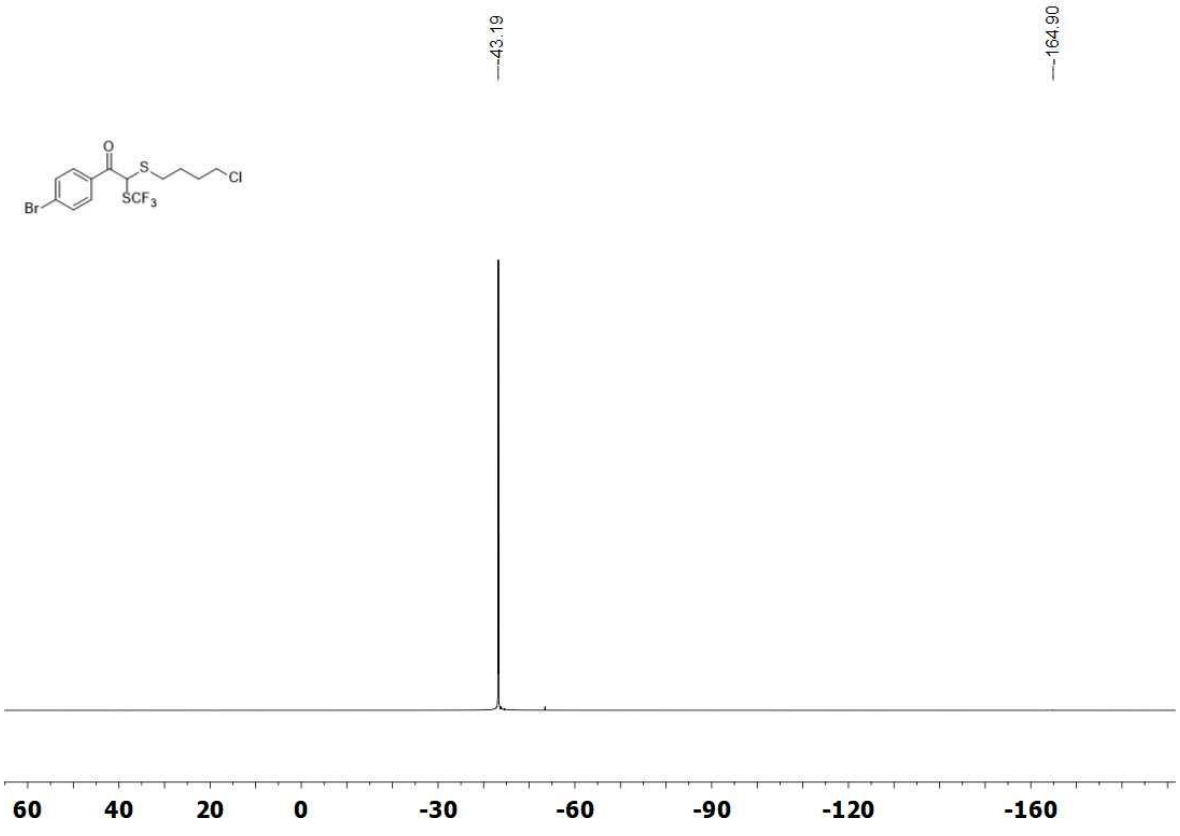
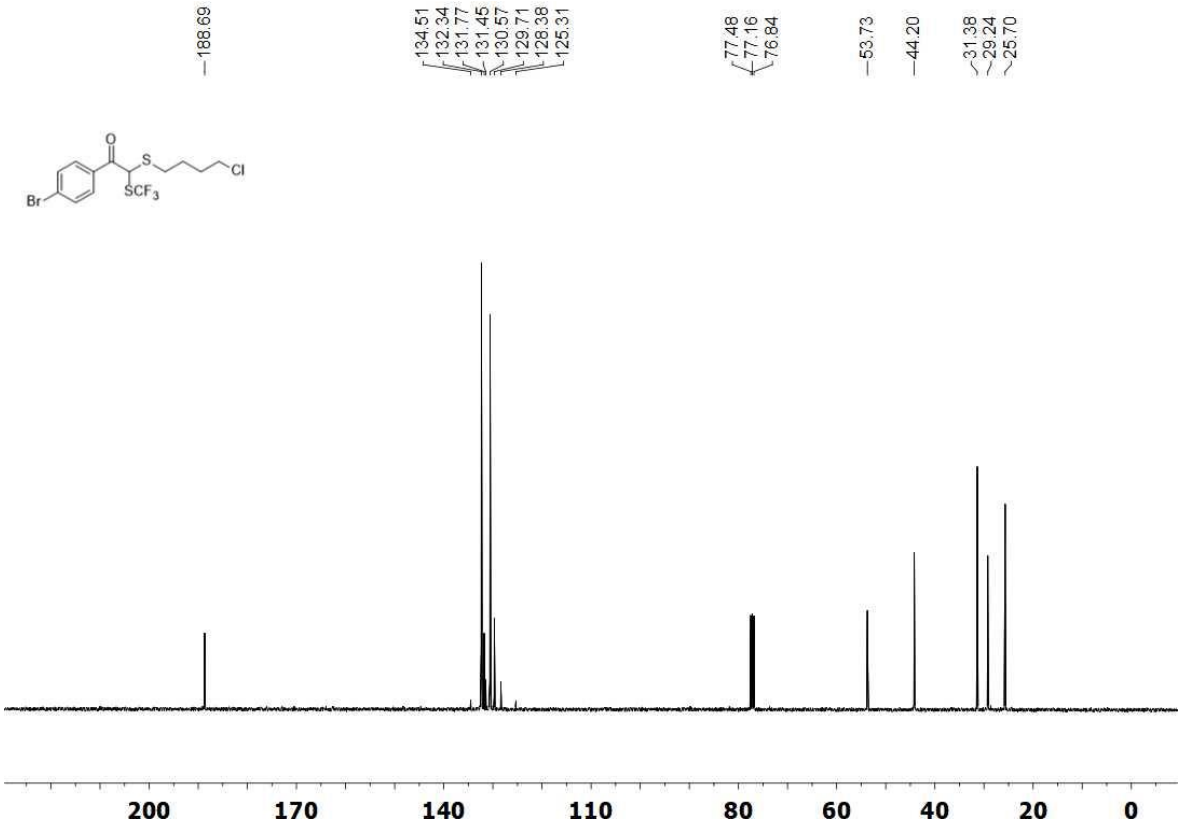


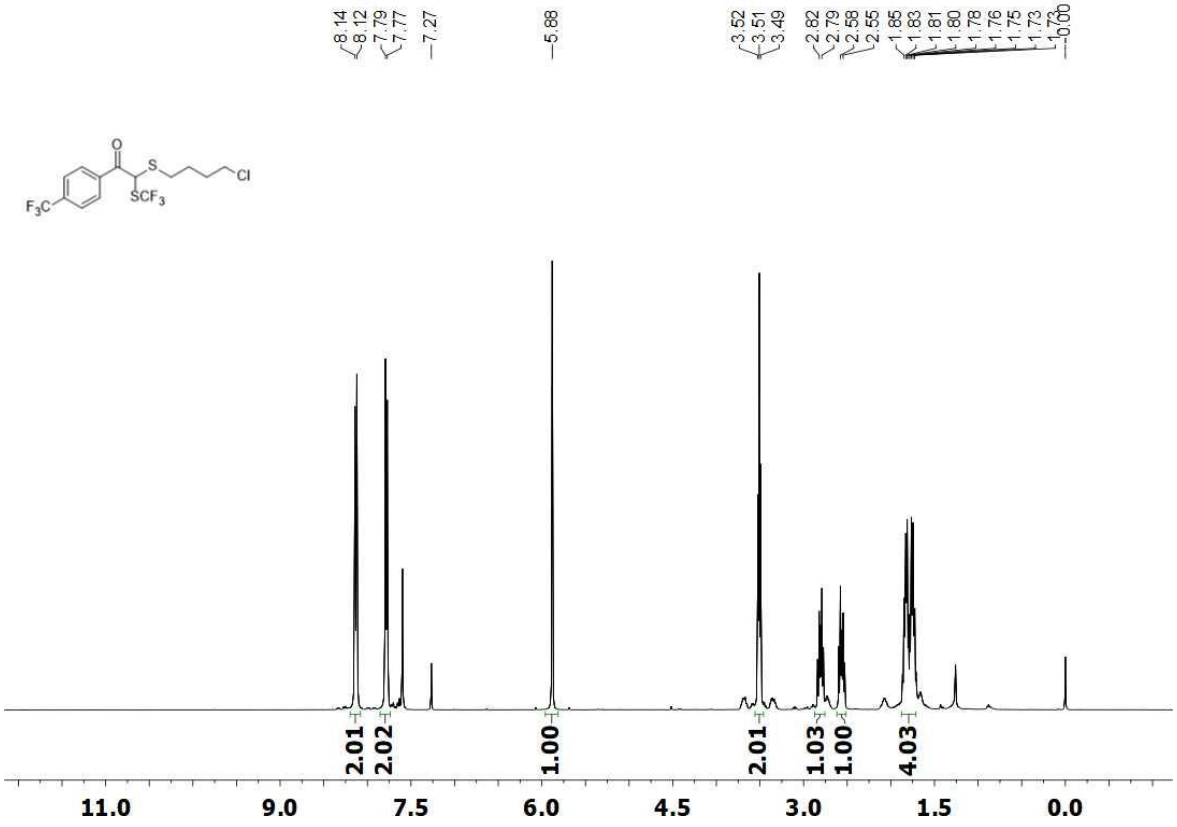
^{19}F NMR of compound **5e**



^{13}C NMR of compound **5e**



^{1}H NMR of compound **5f**



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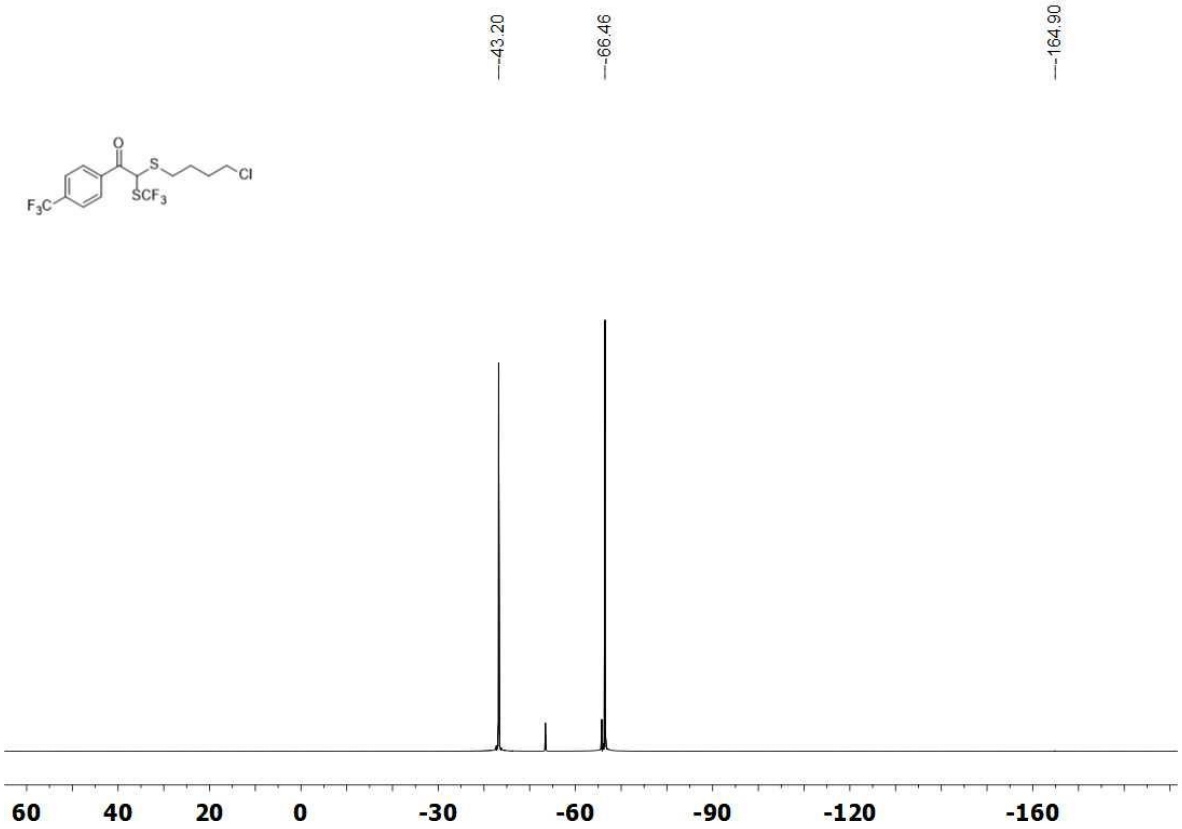
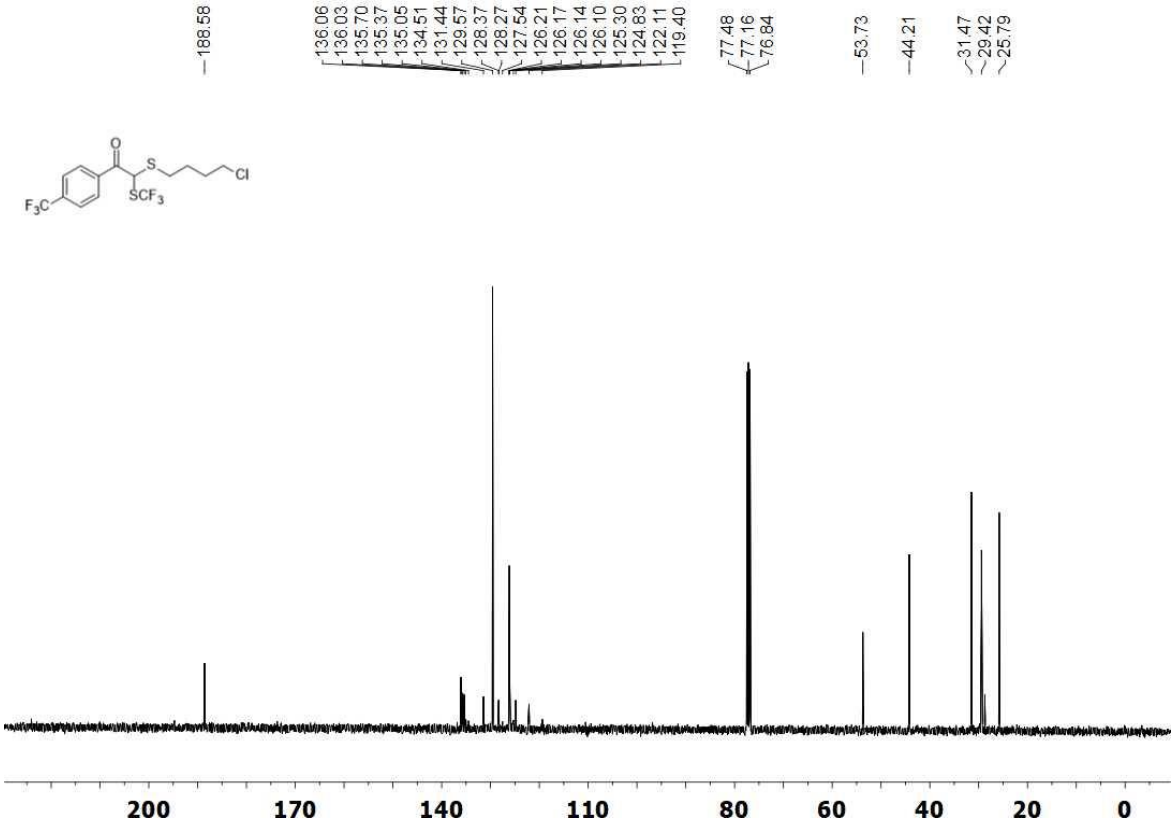
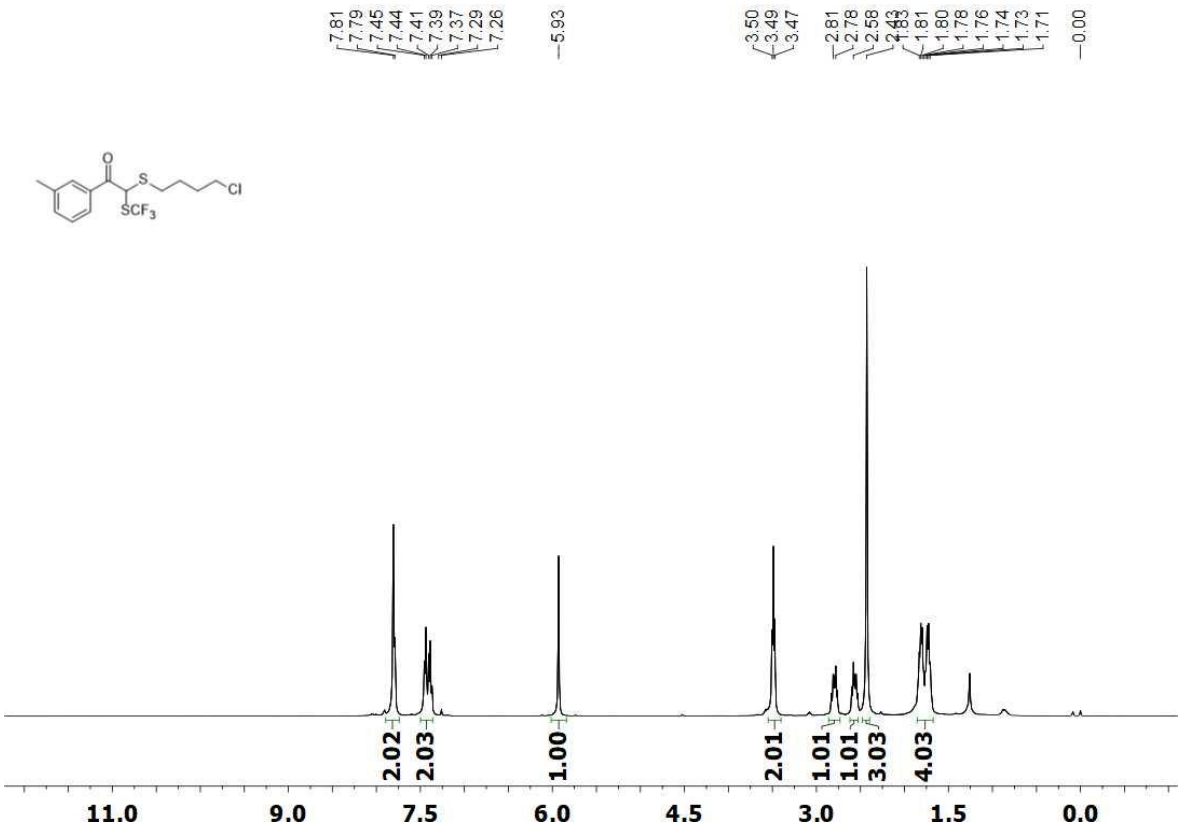


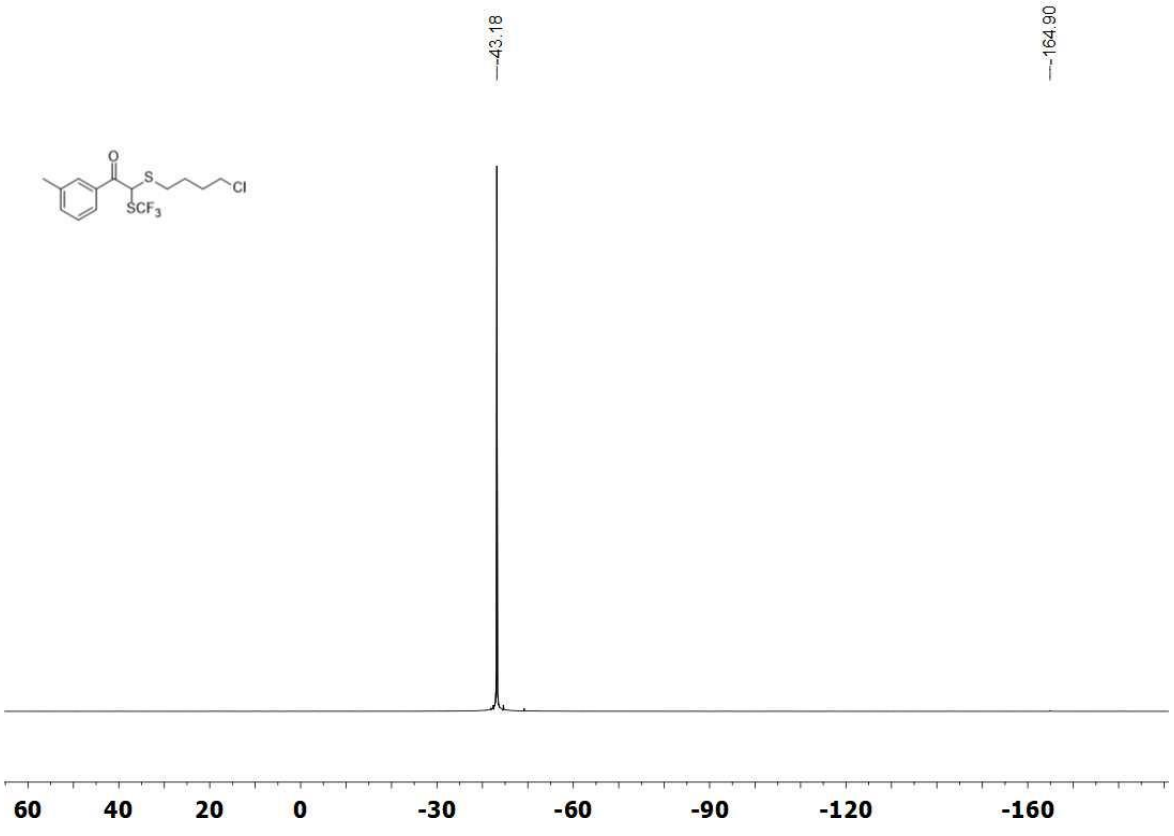
^{13}C NMR of compound **5f**



^{1}H NMR of compound **5g**



^{19}F NMR of compound **5g**



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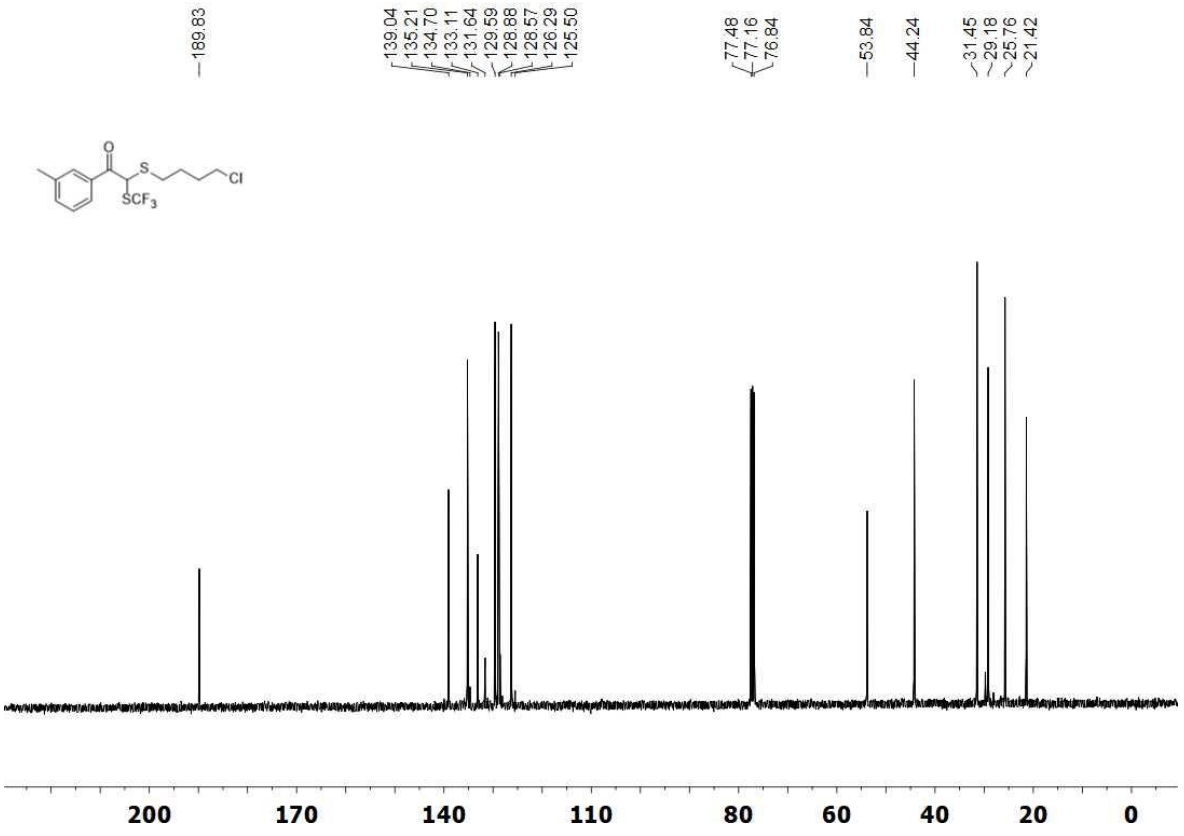
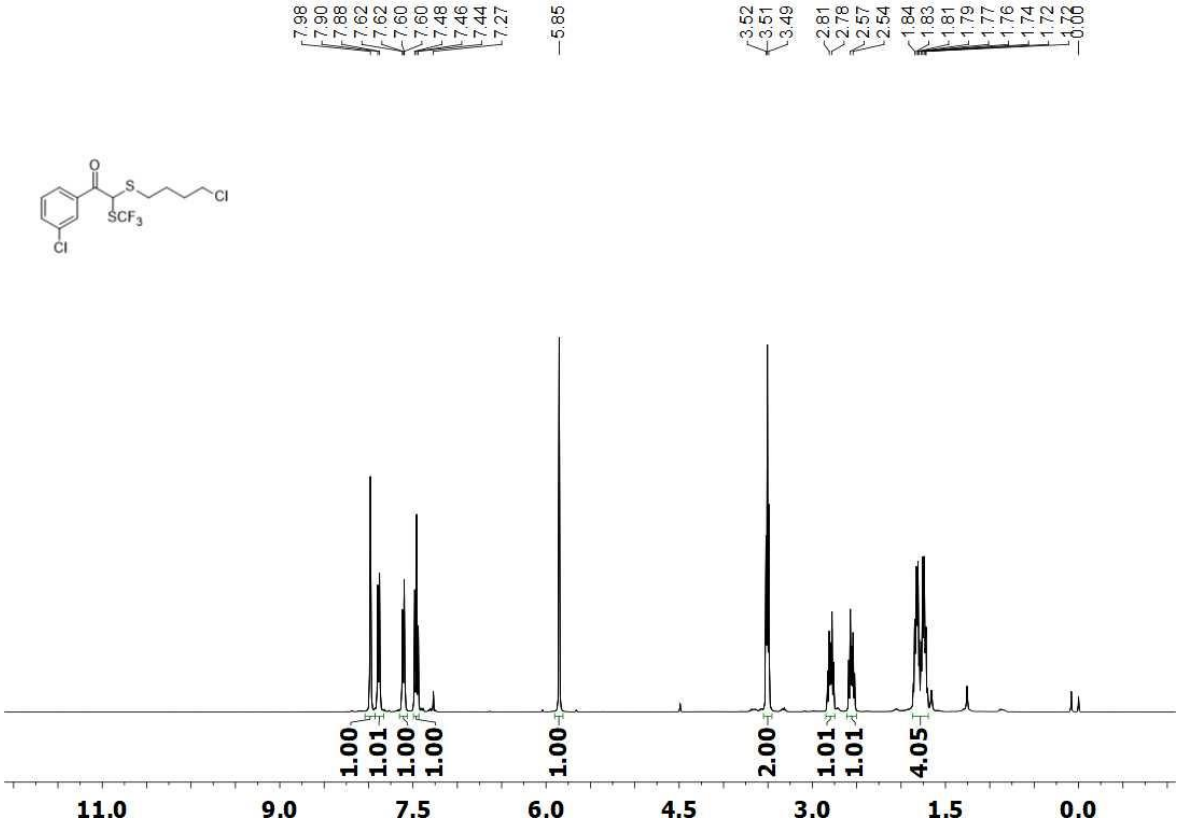


^{1}H NMR of compound **5h**



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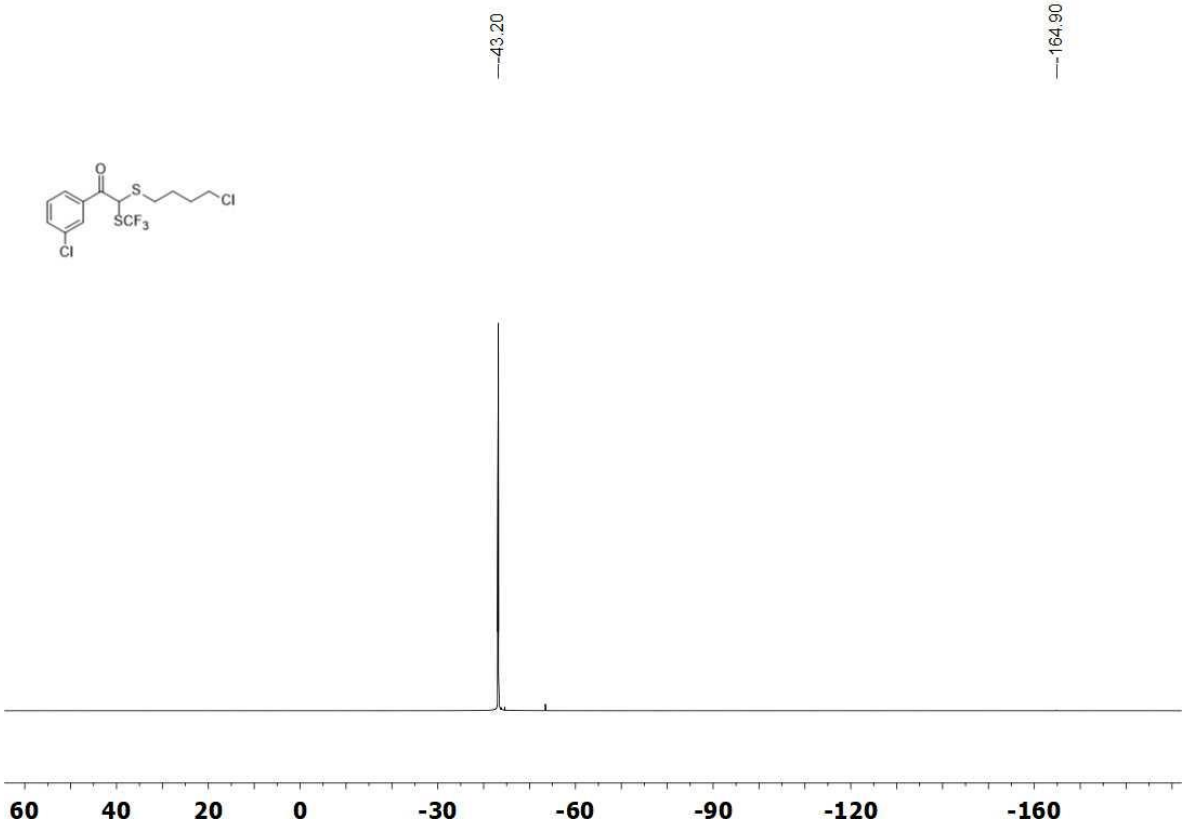

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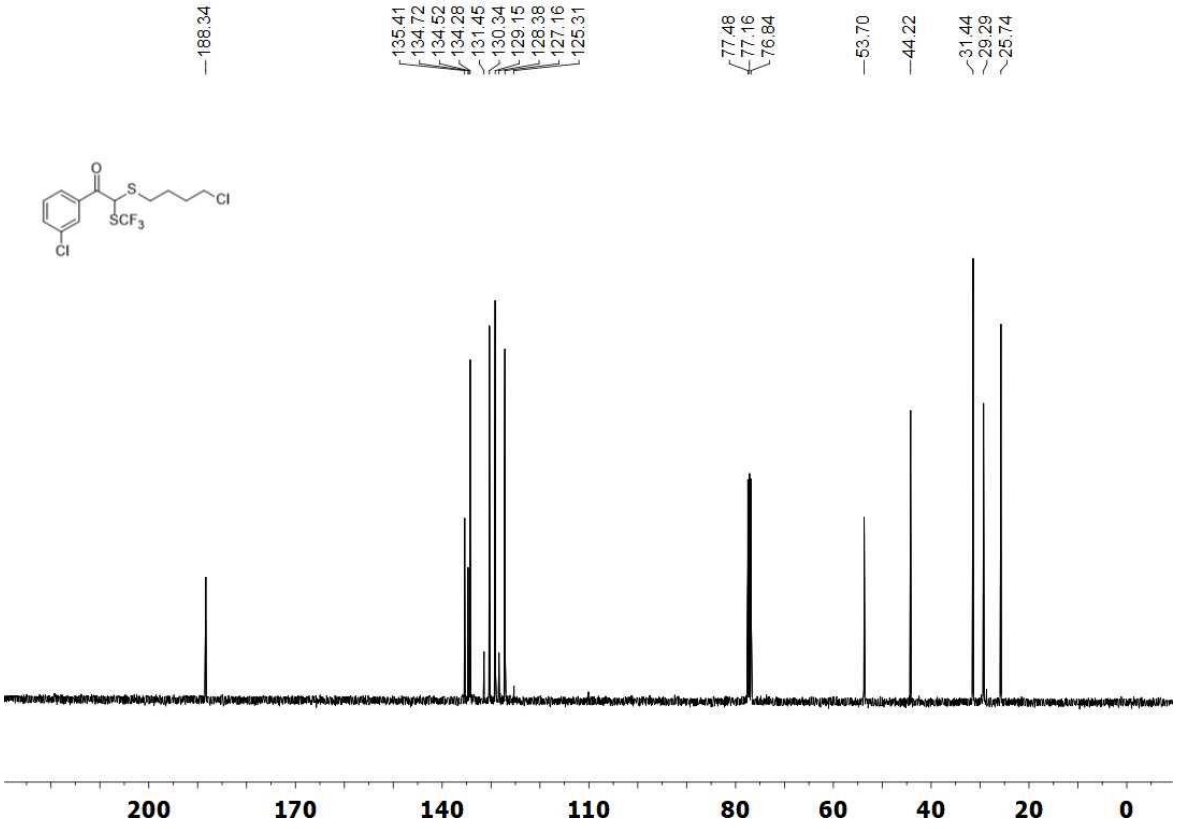
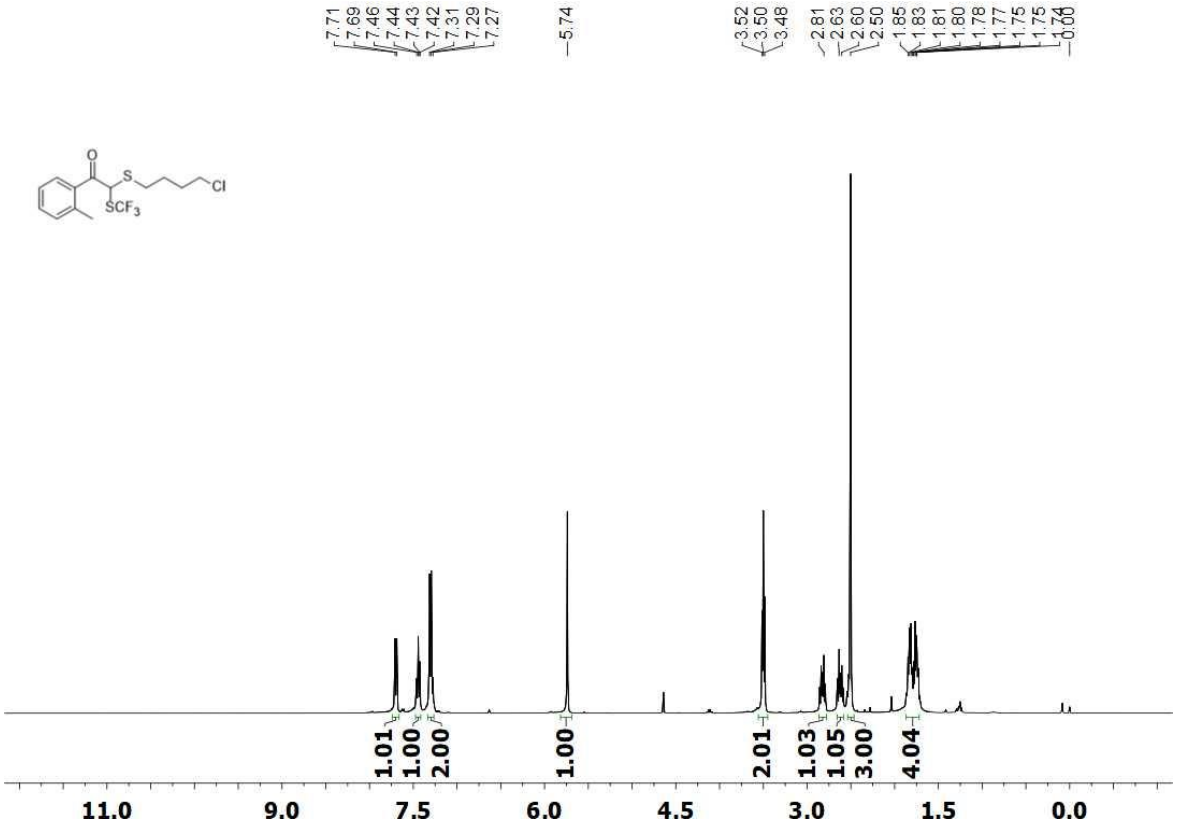


^{1}H NMR of compound **5i**



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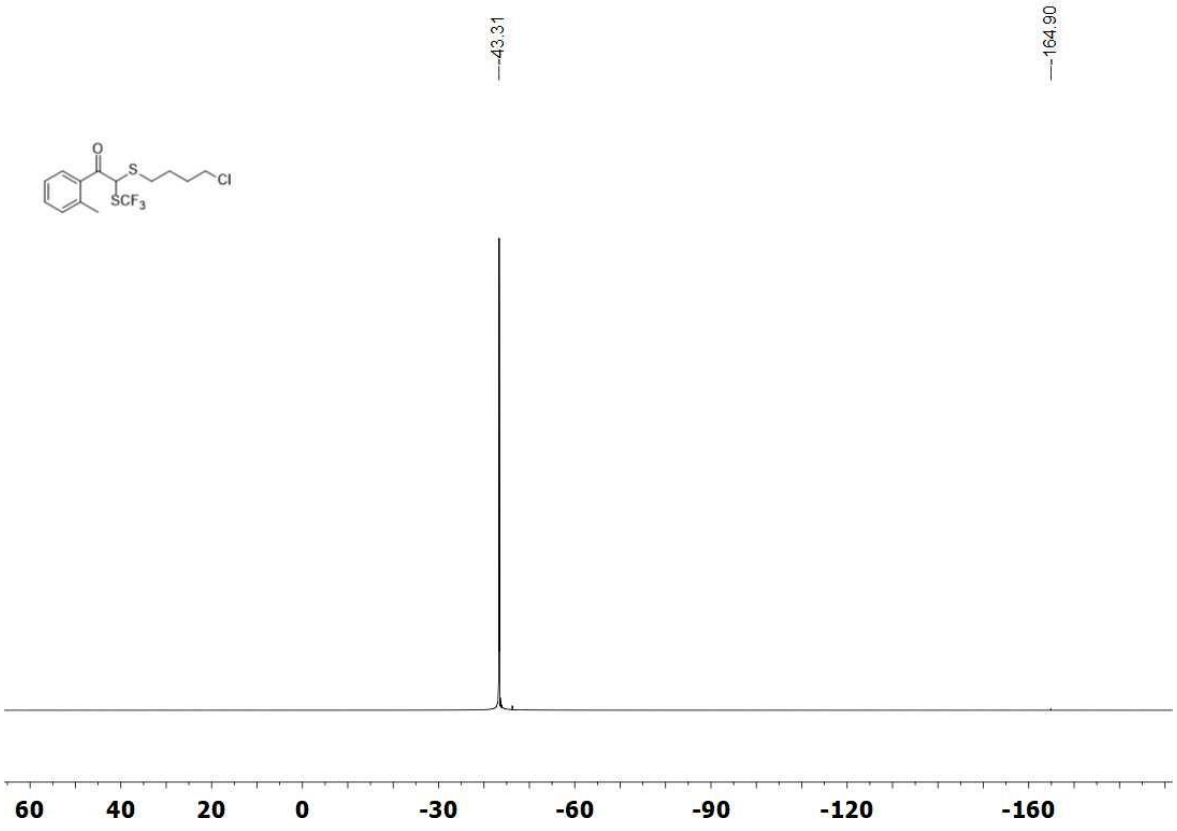
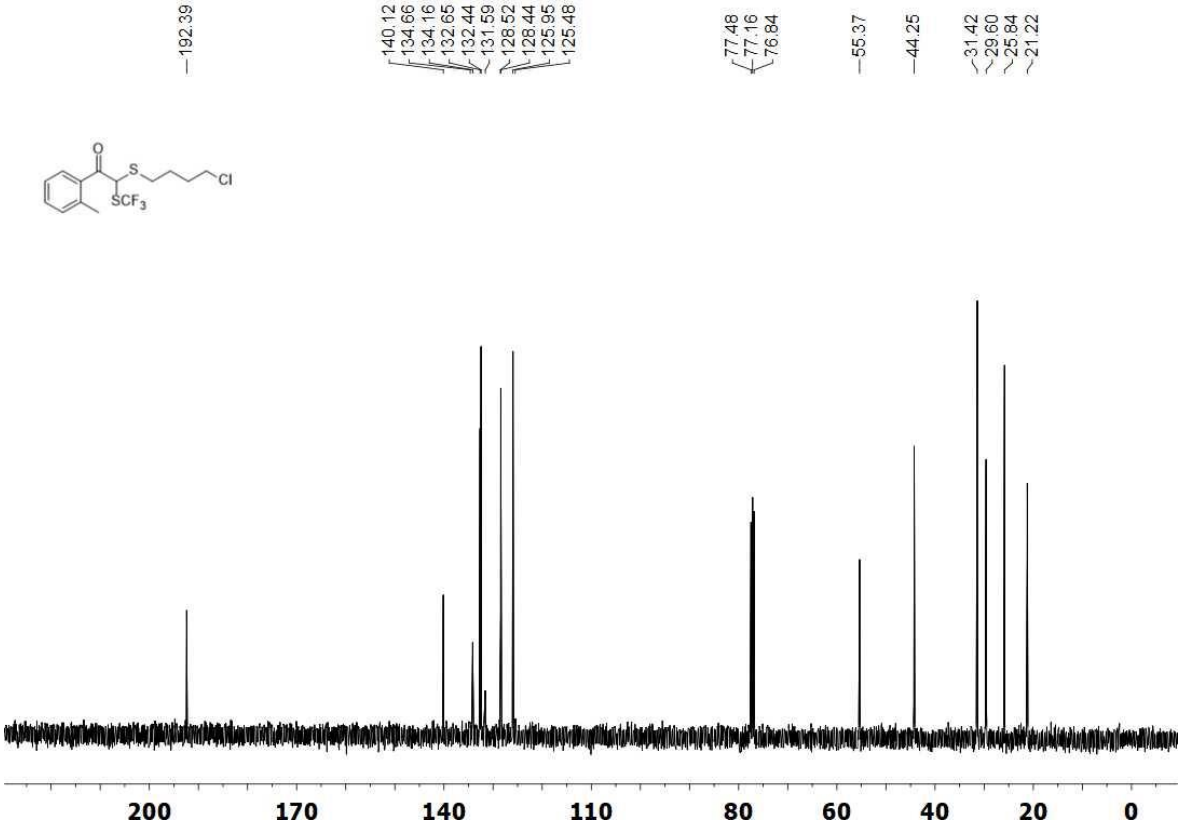


^{13}C NMR of compound **5i**



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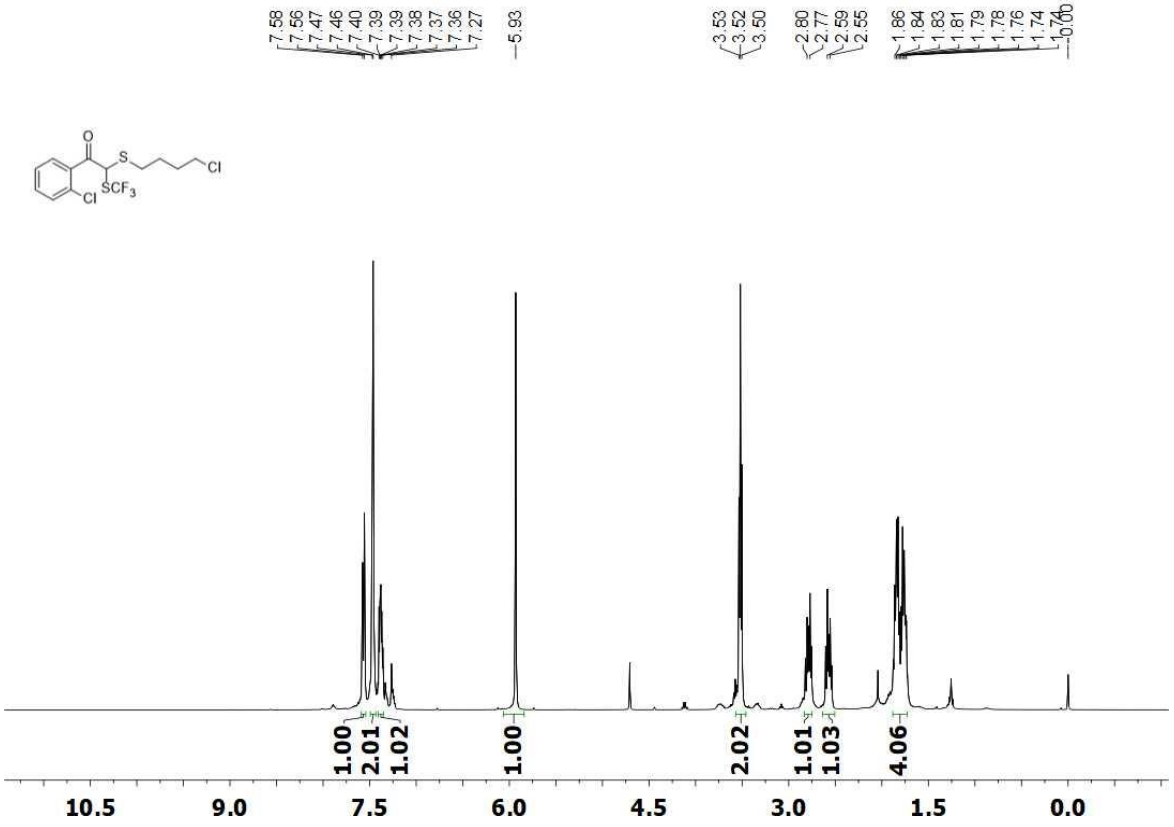

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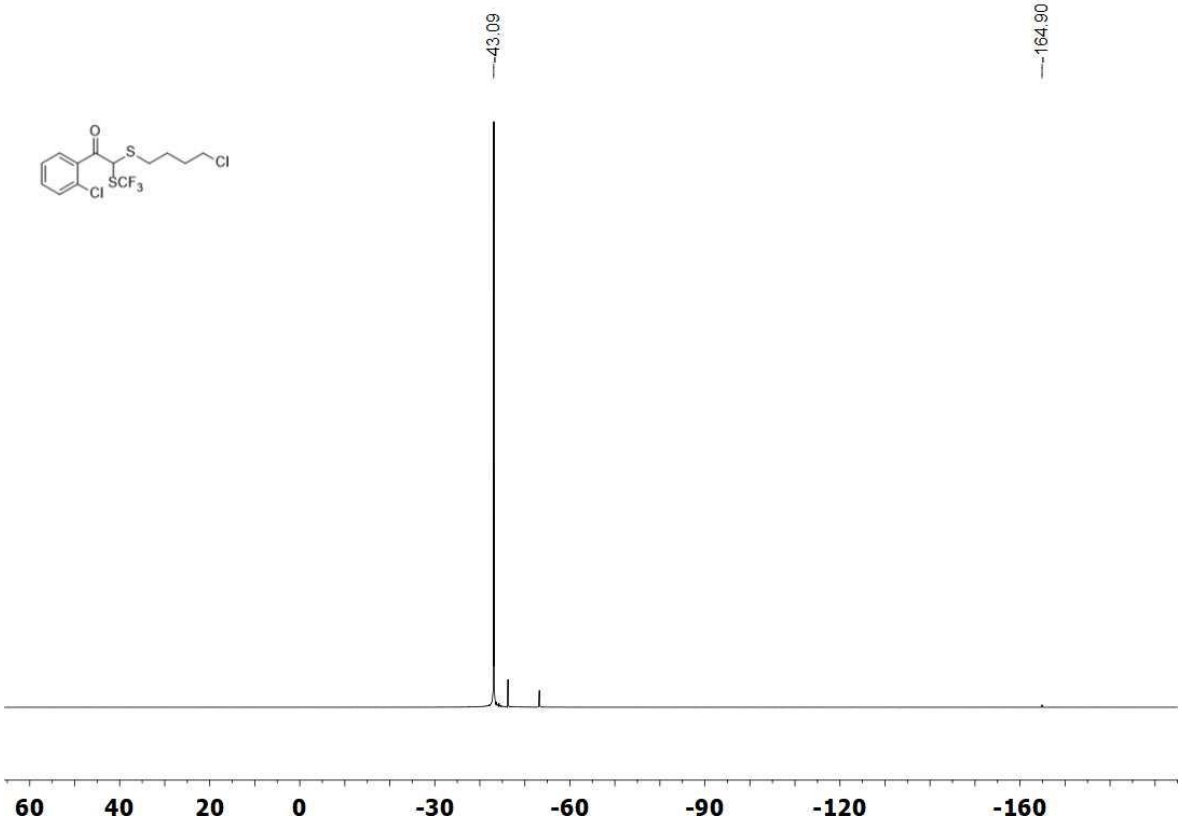

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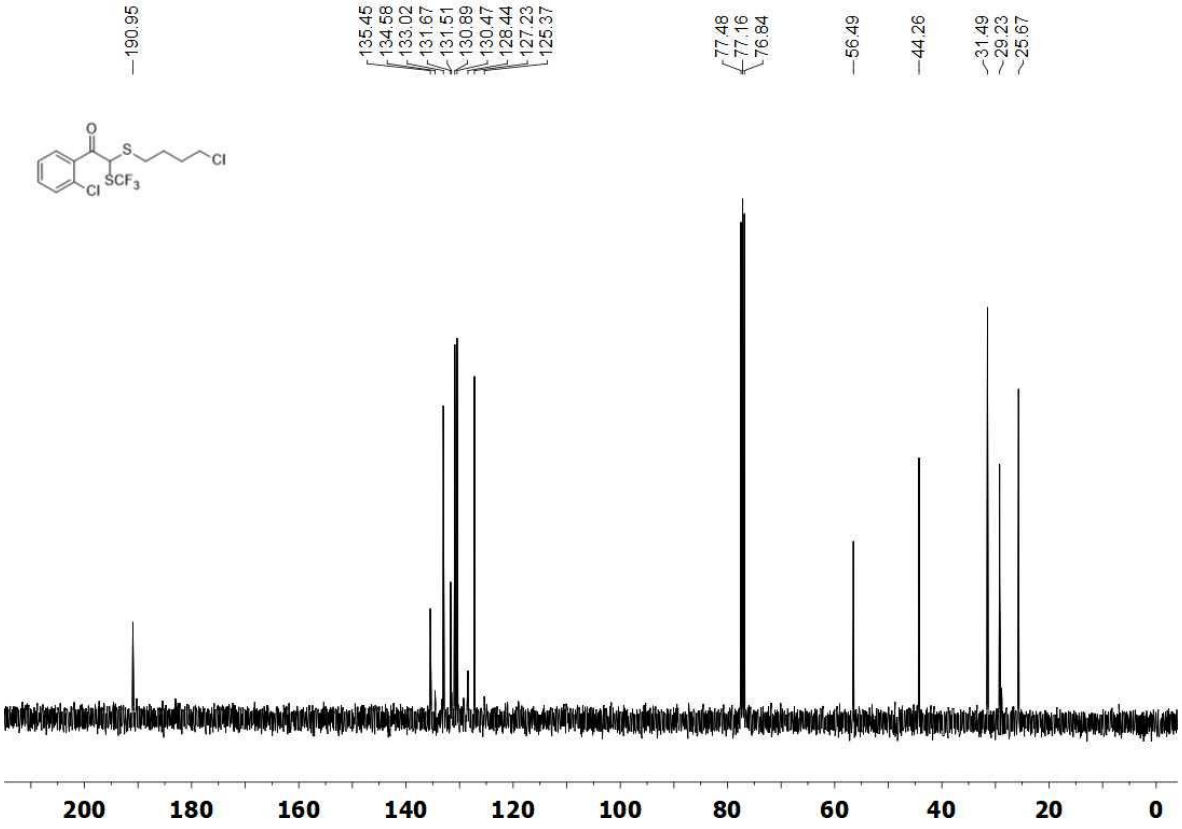

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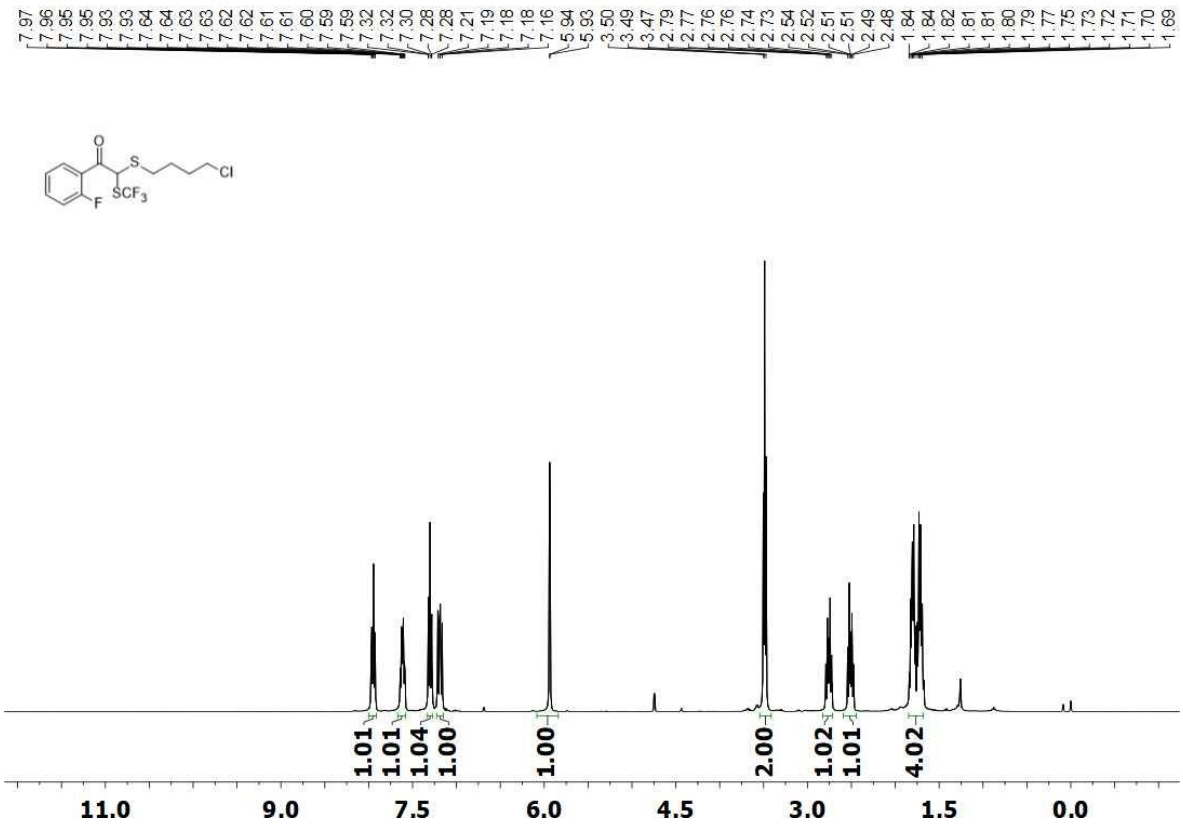

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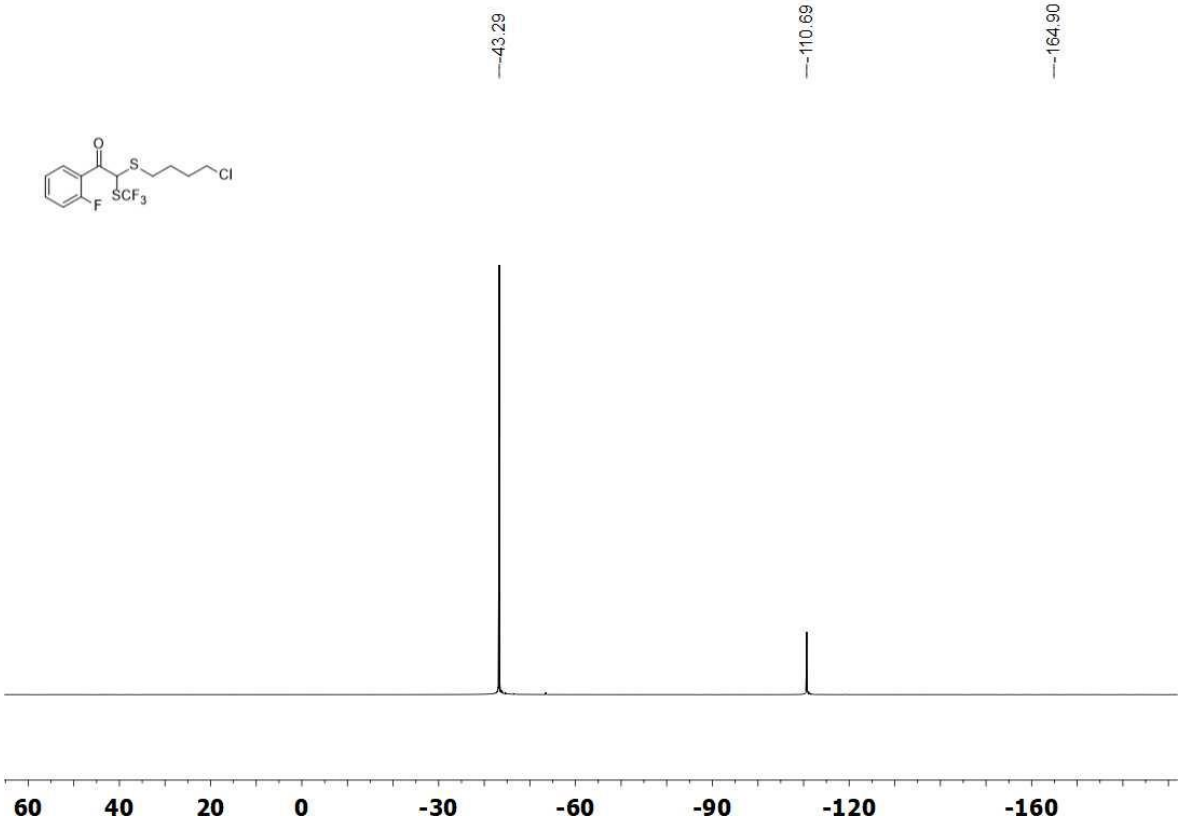

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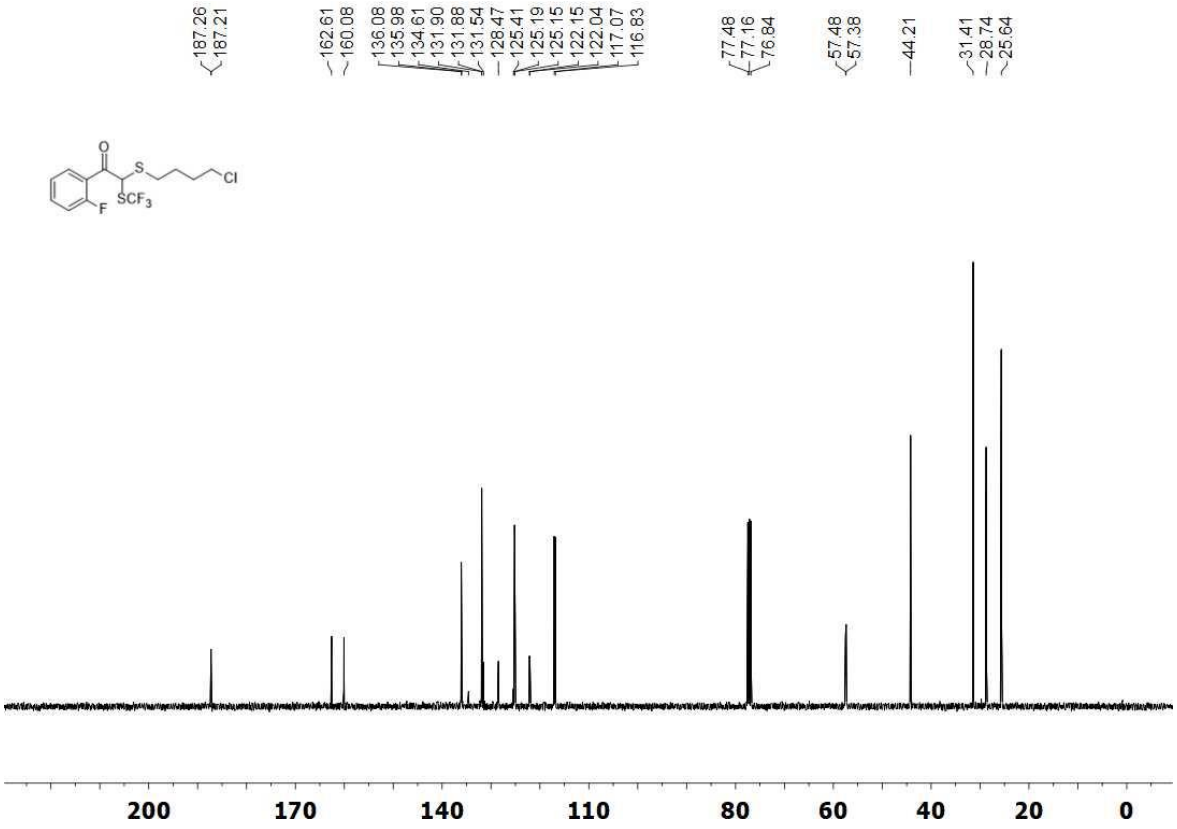
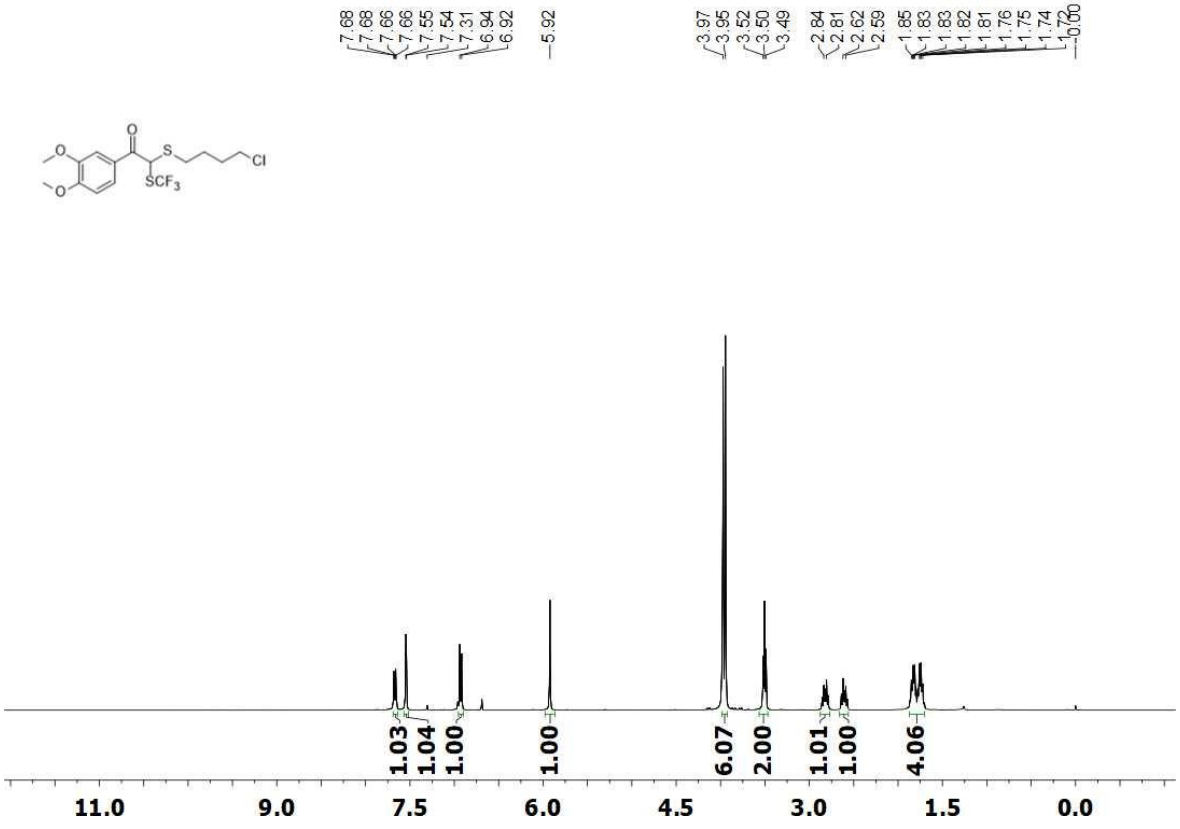


^{1}H NMR of compound **5l**



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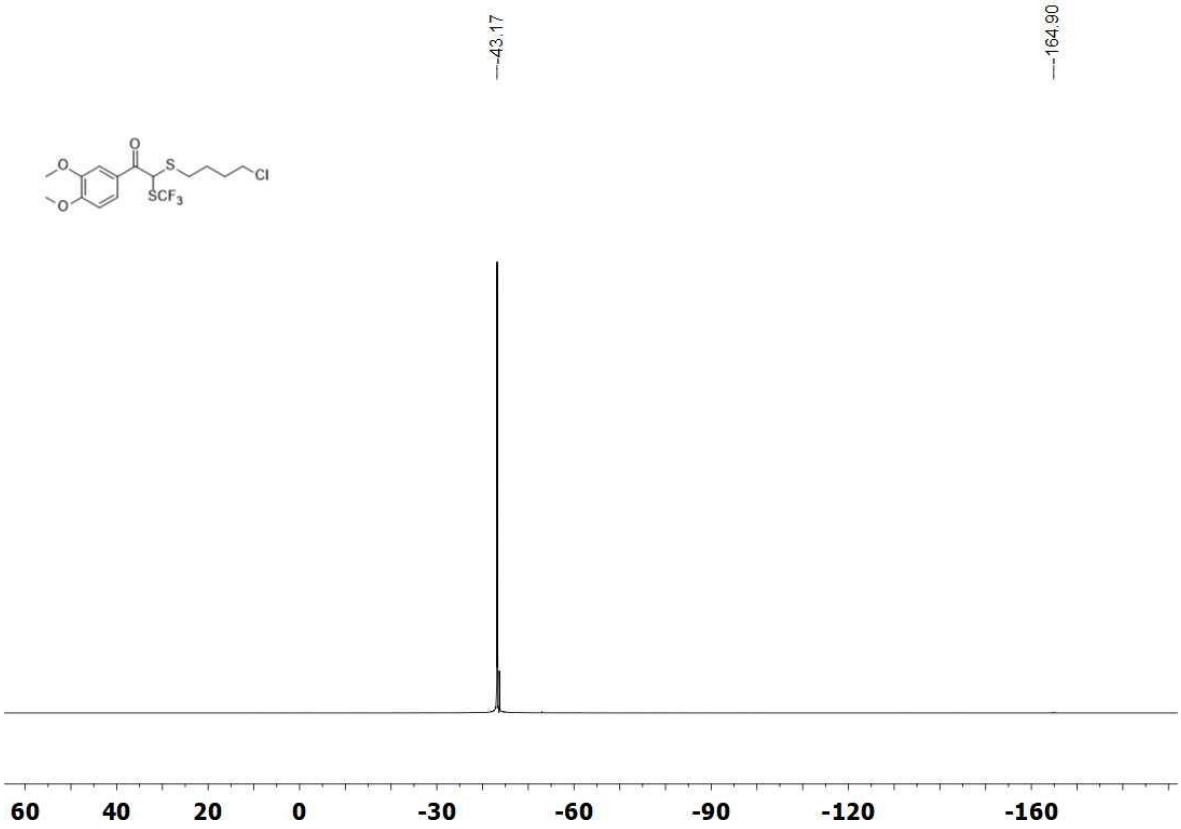

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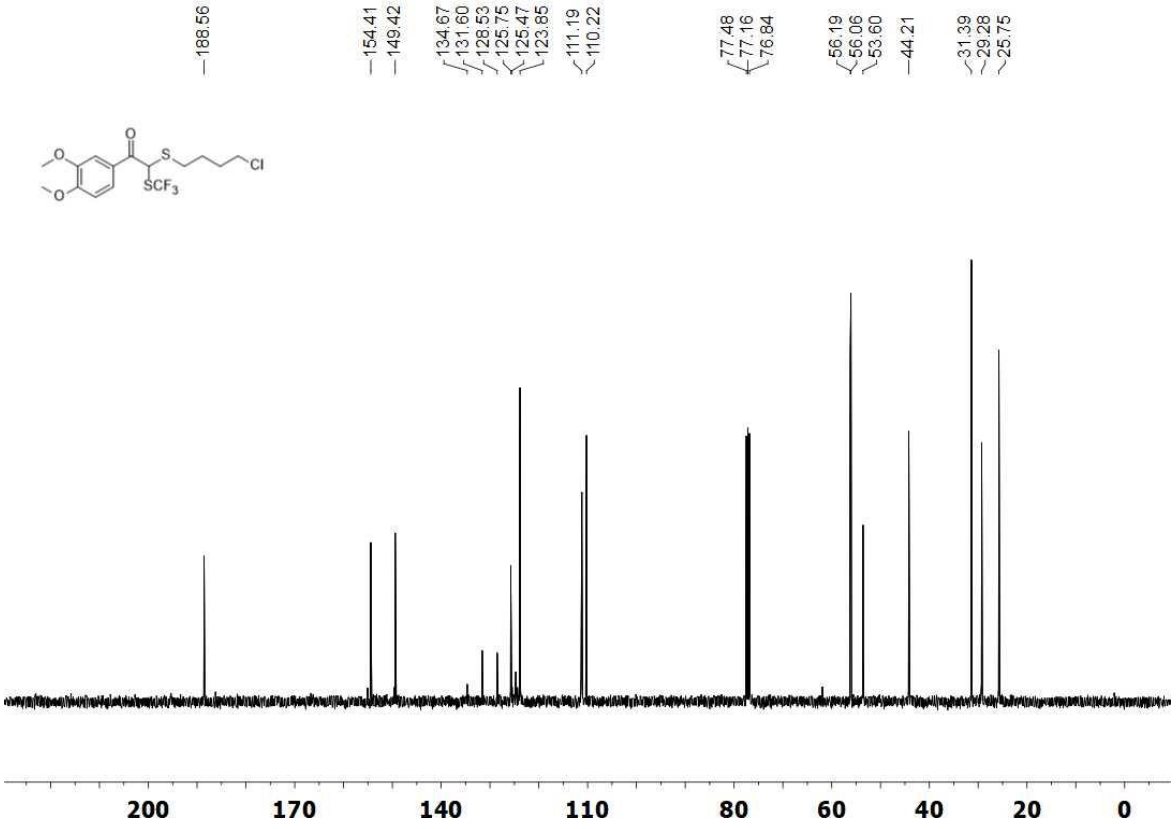

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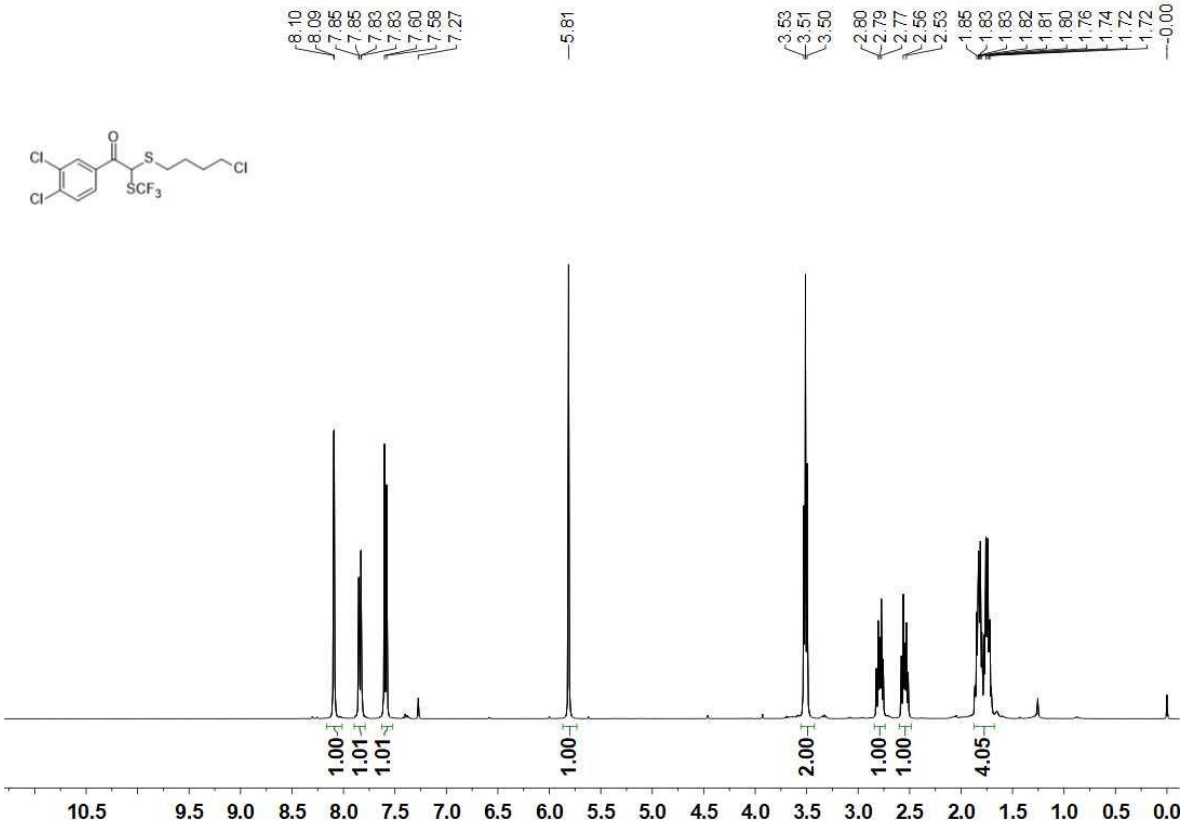

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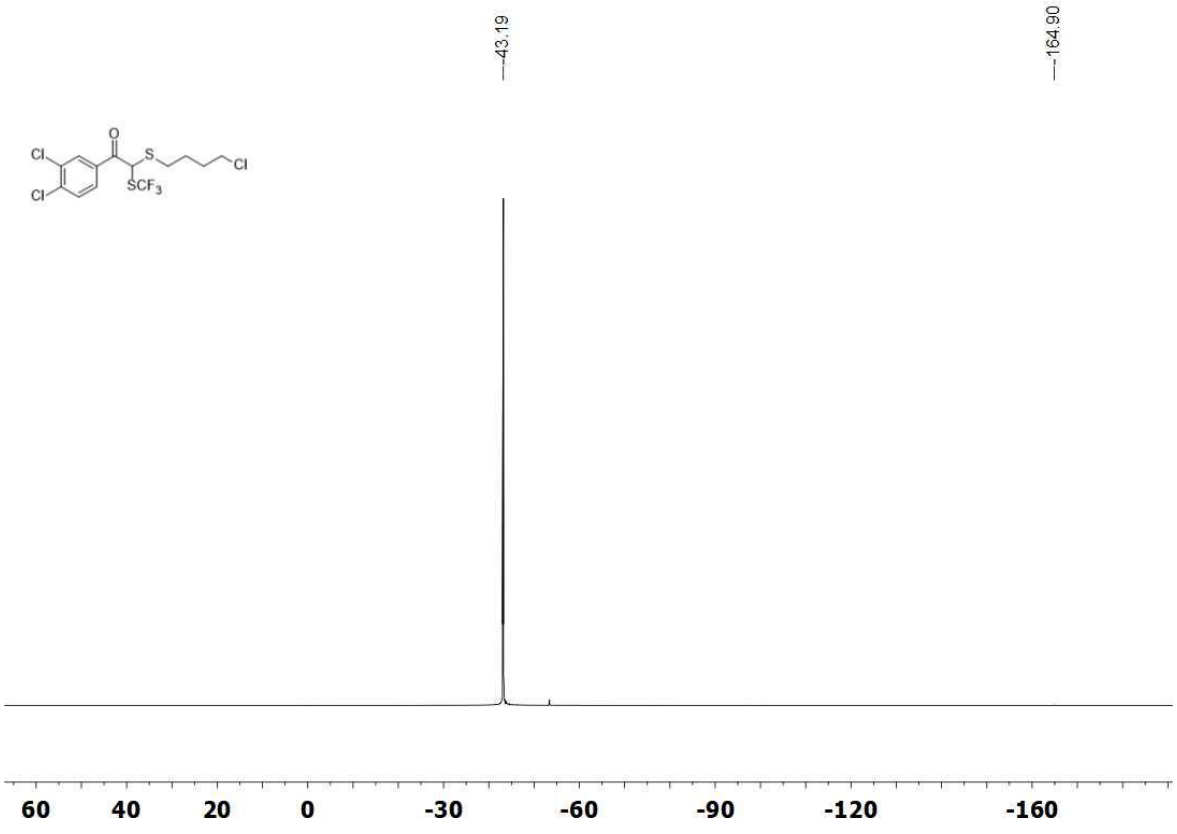

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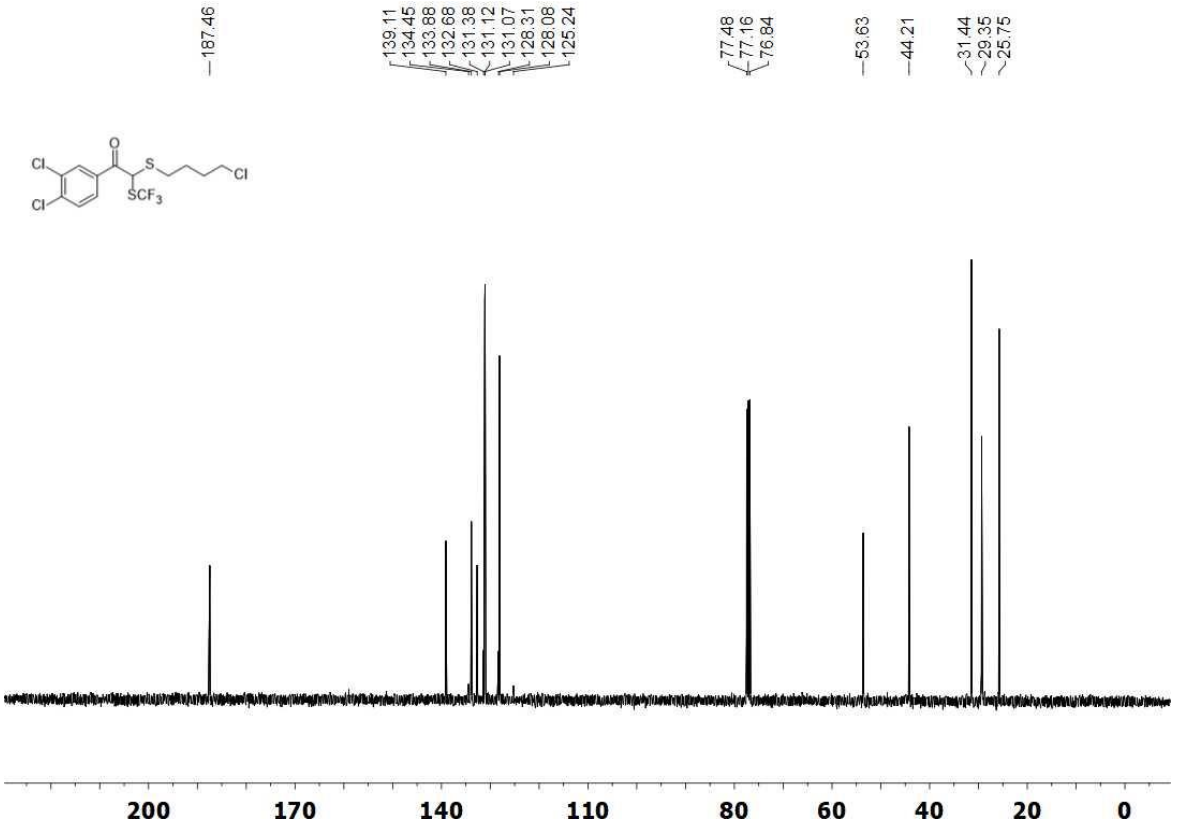

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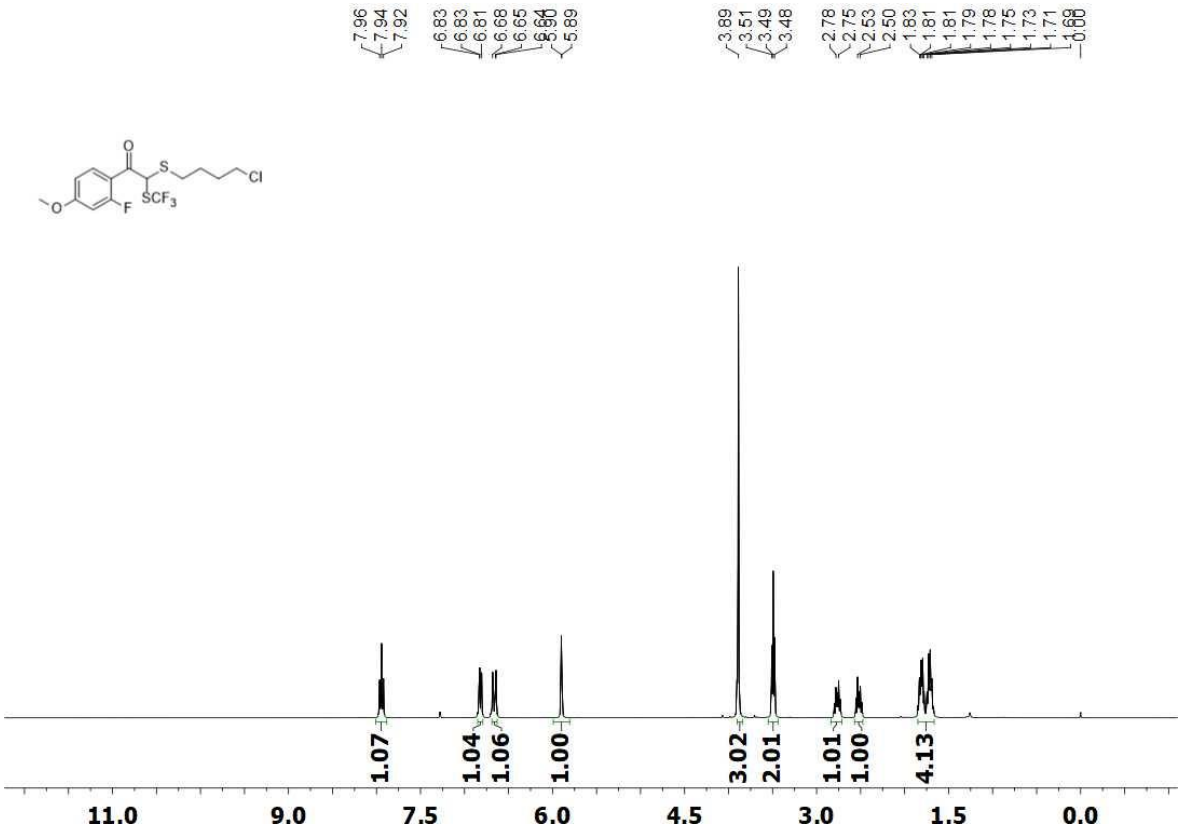

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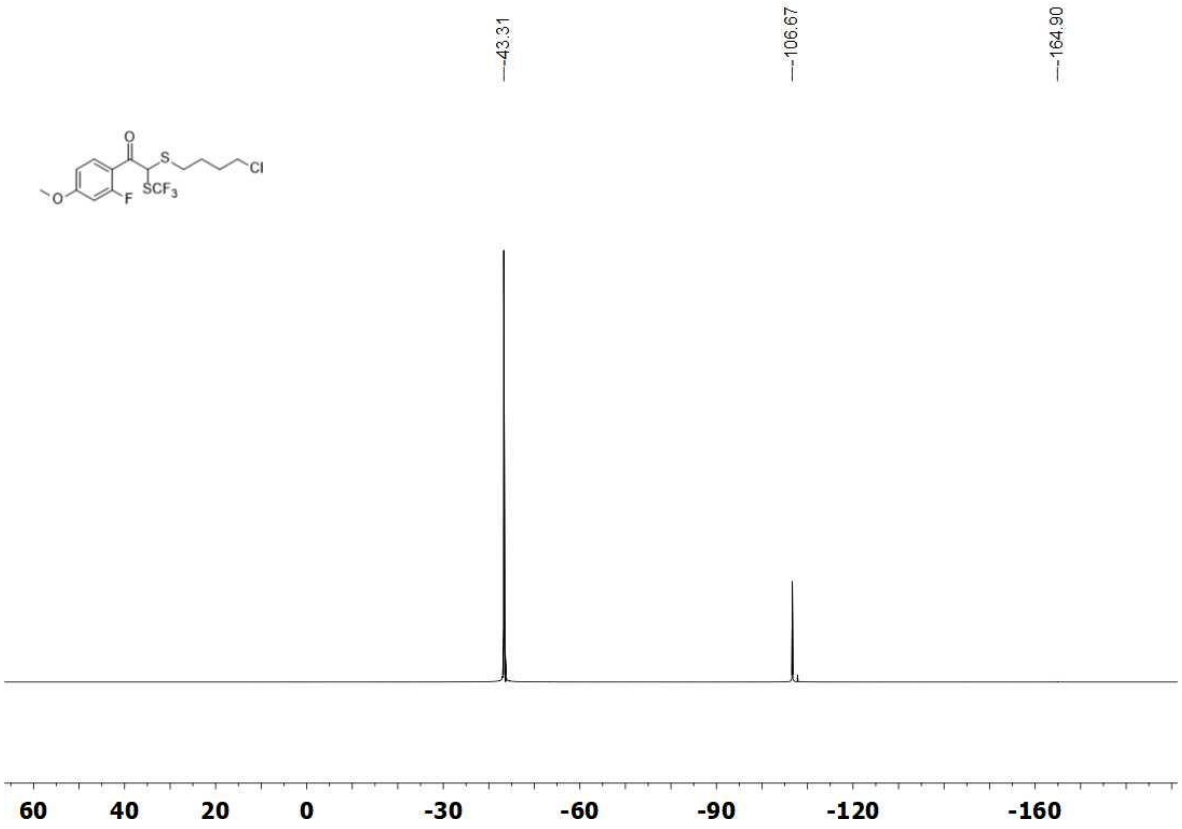

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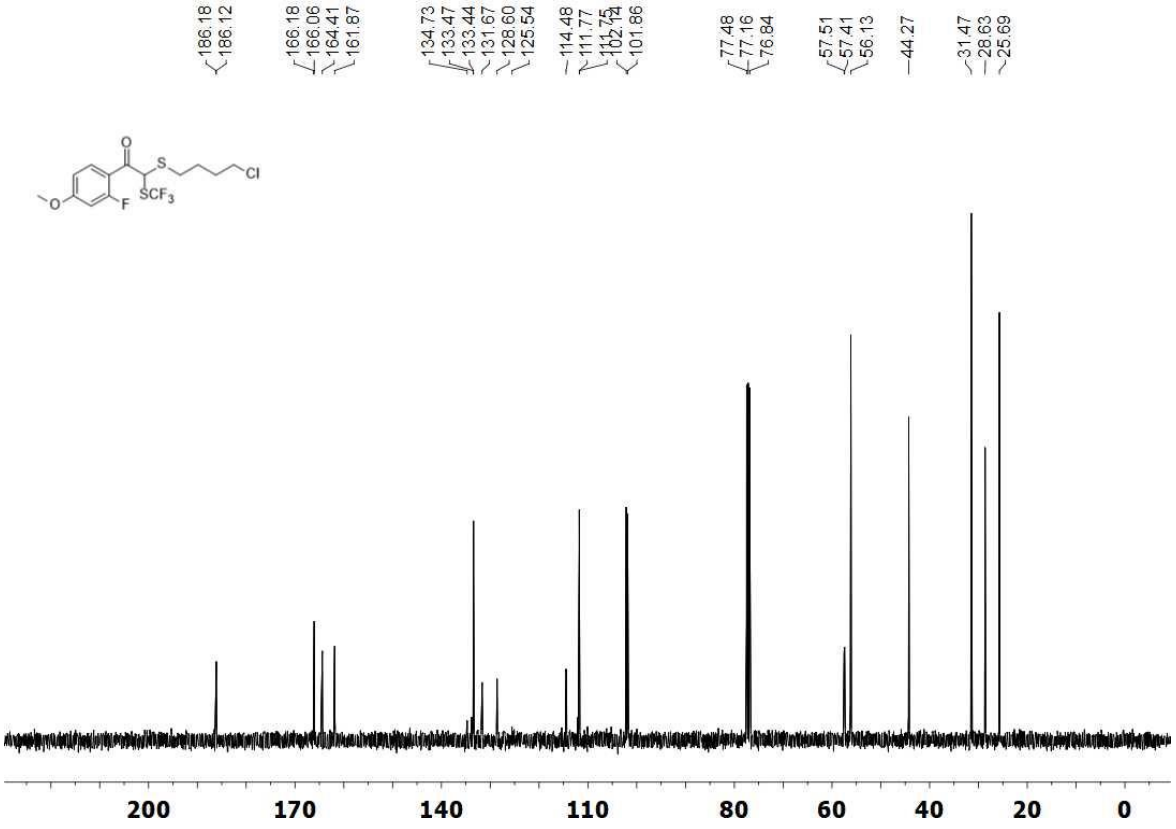

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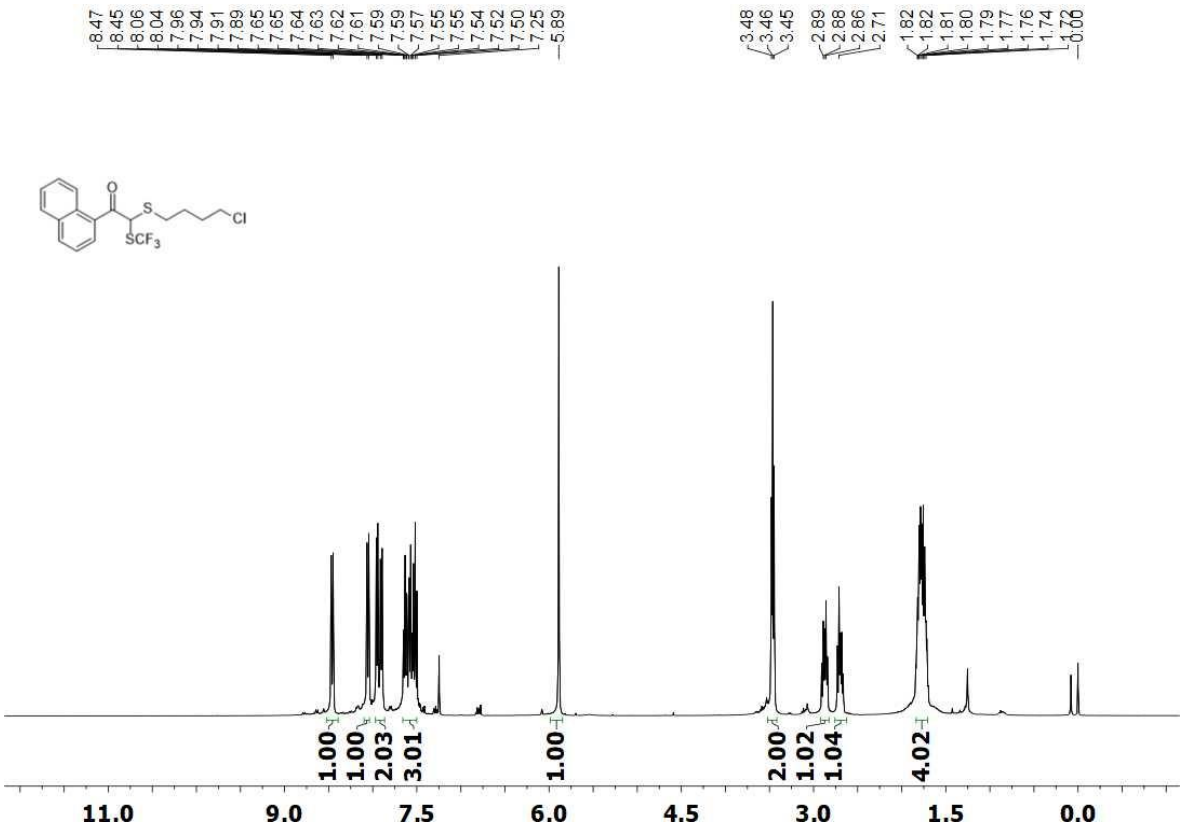

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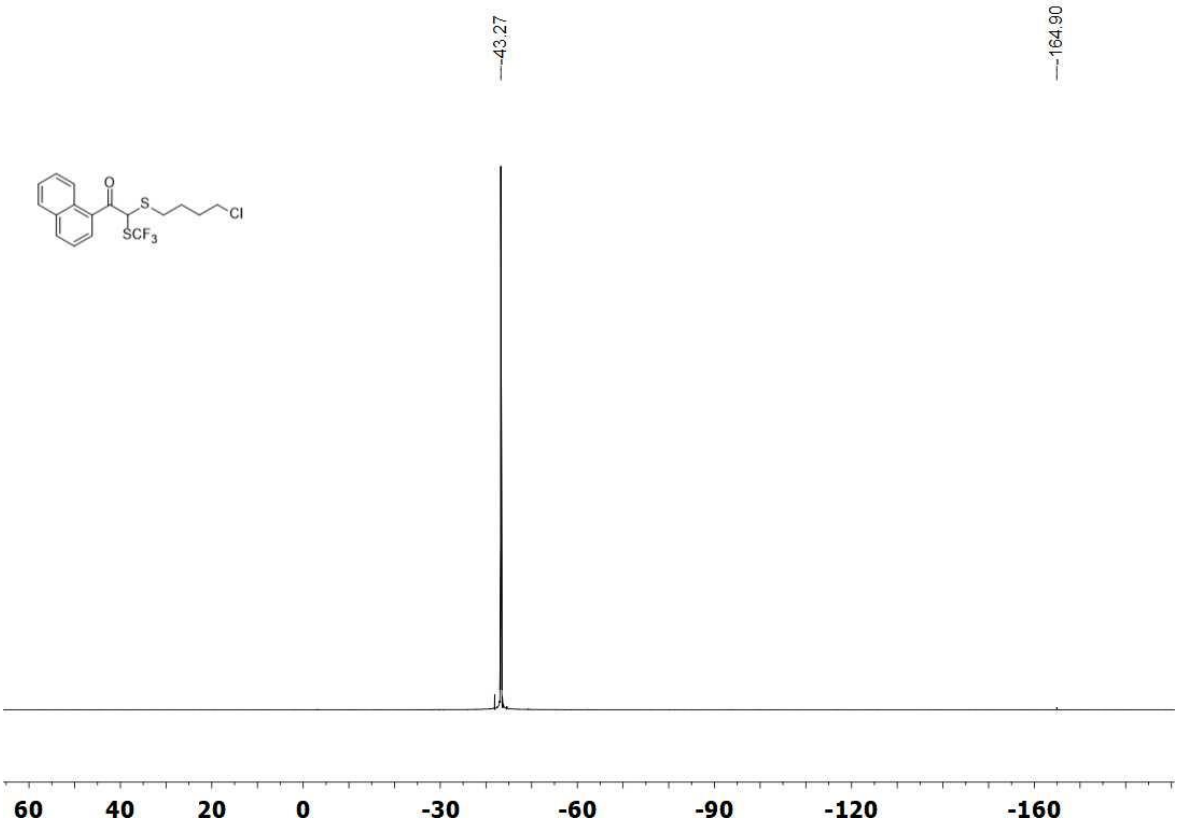
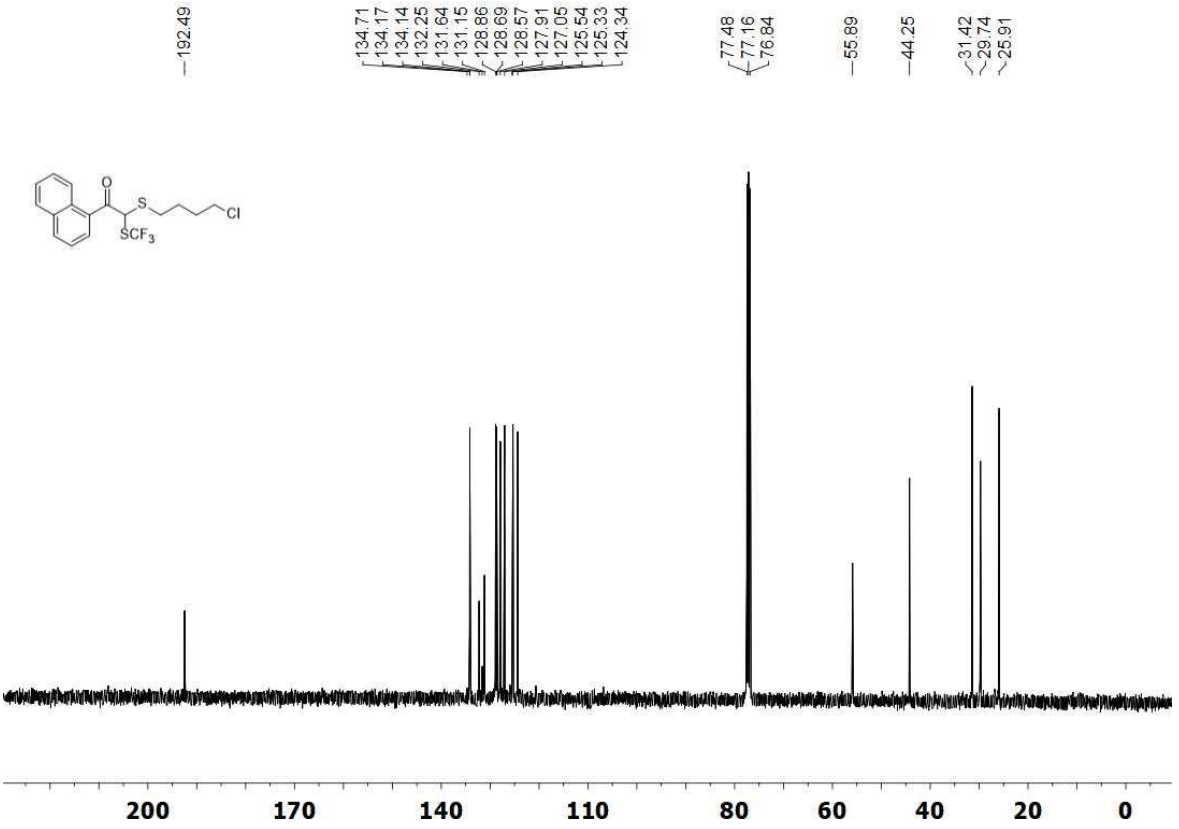


^{13}C NMR of compound **5o**



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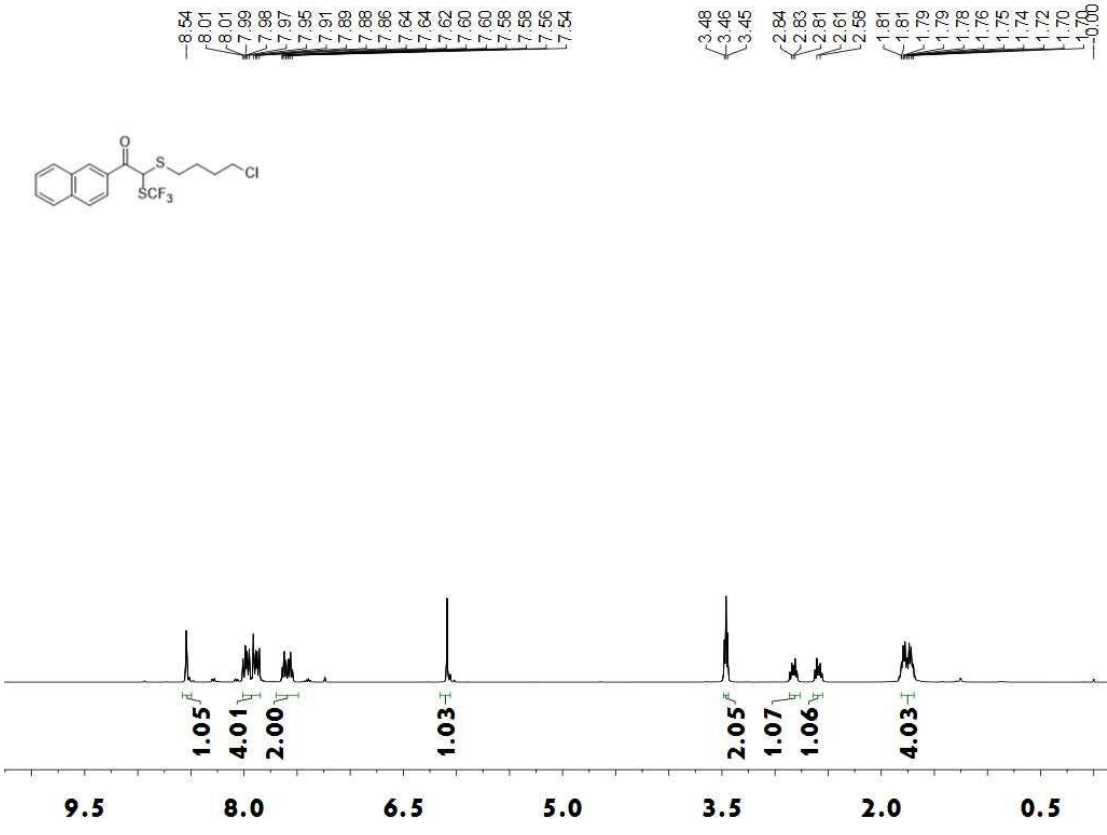

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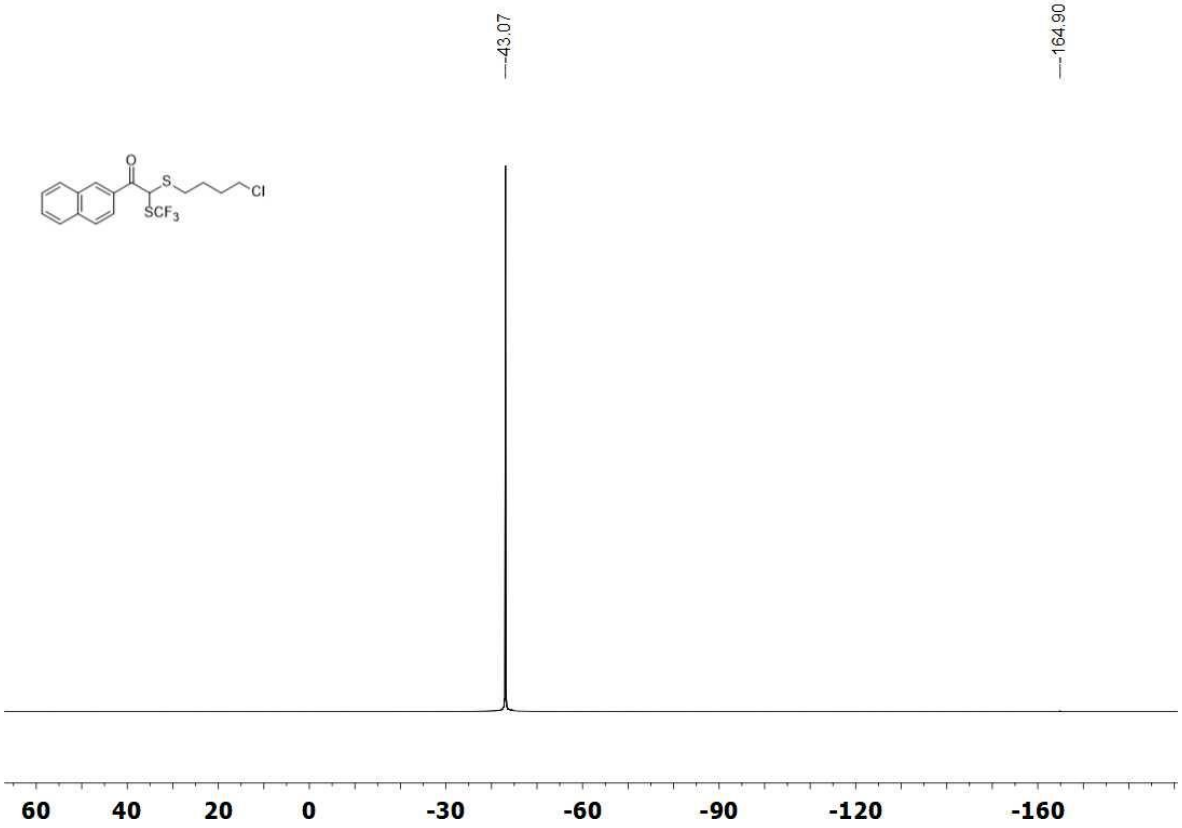

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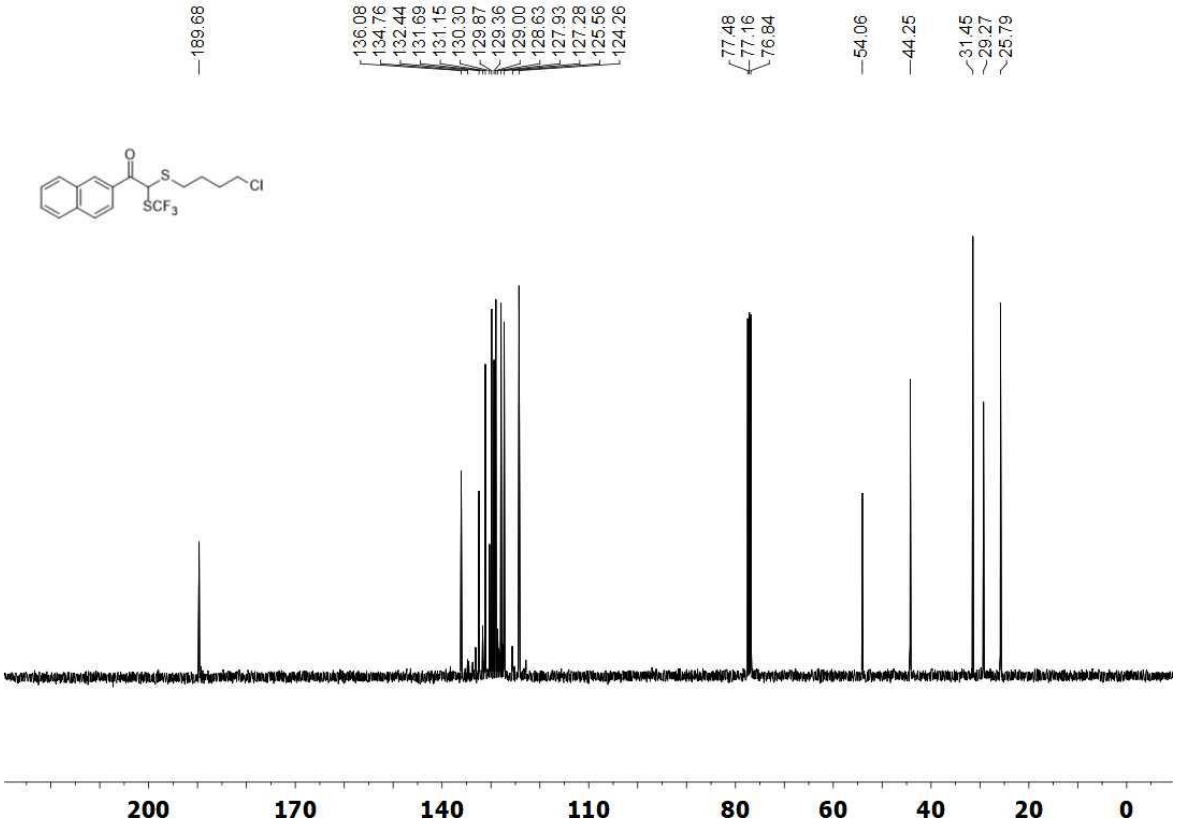
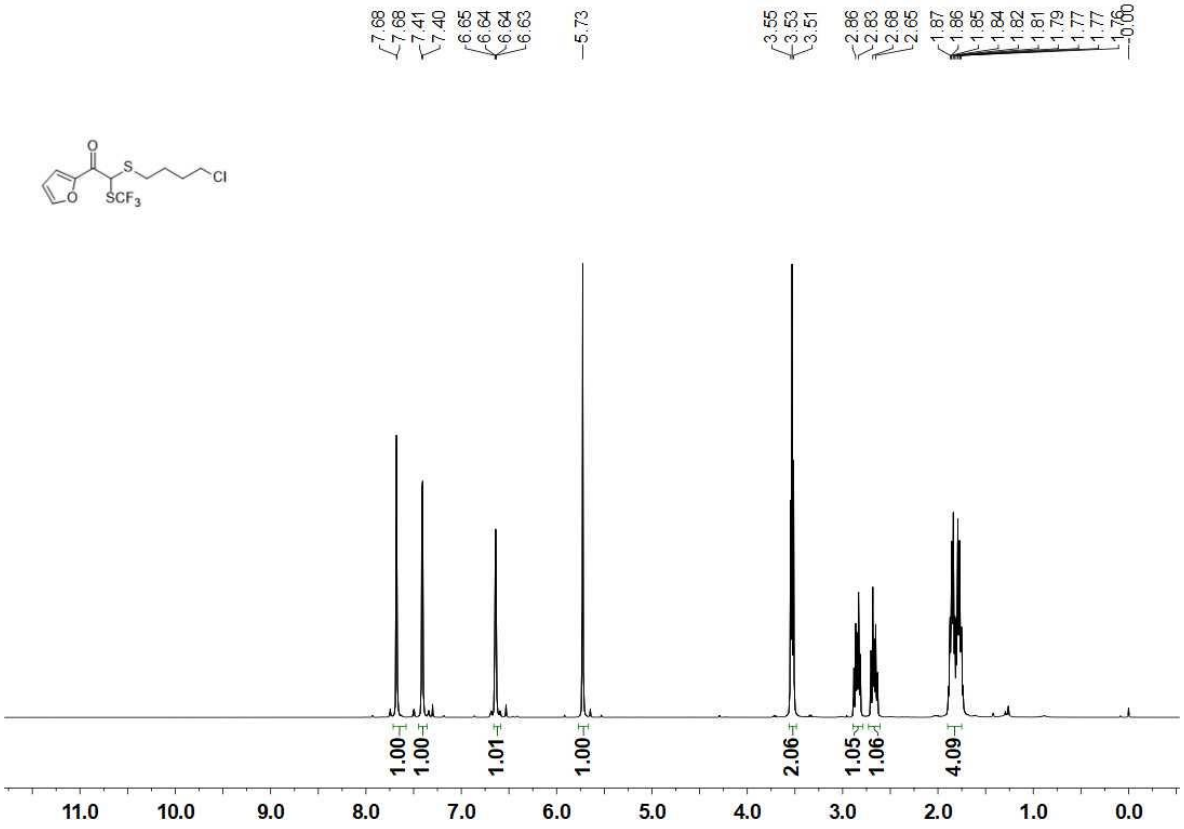


^{1}H NMR of compound **5q**



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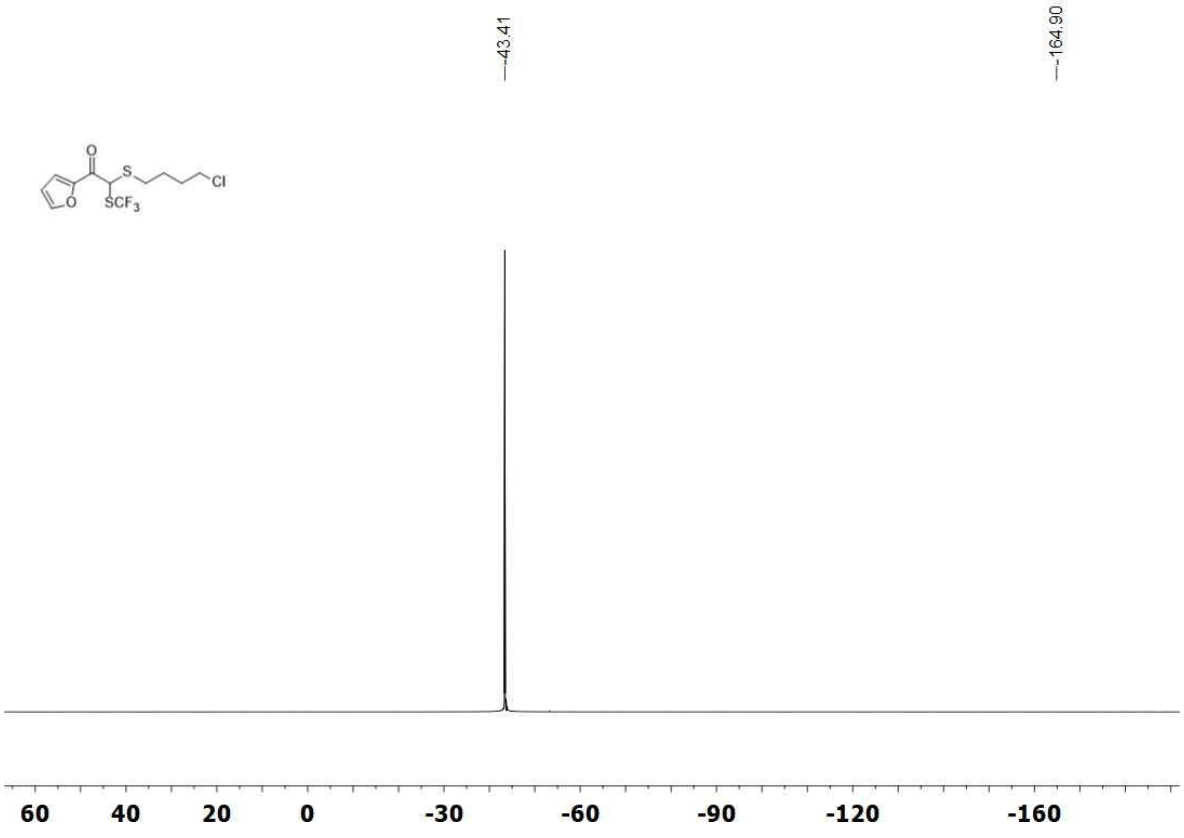
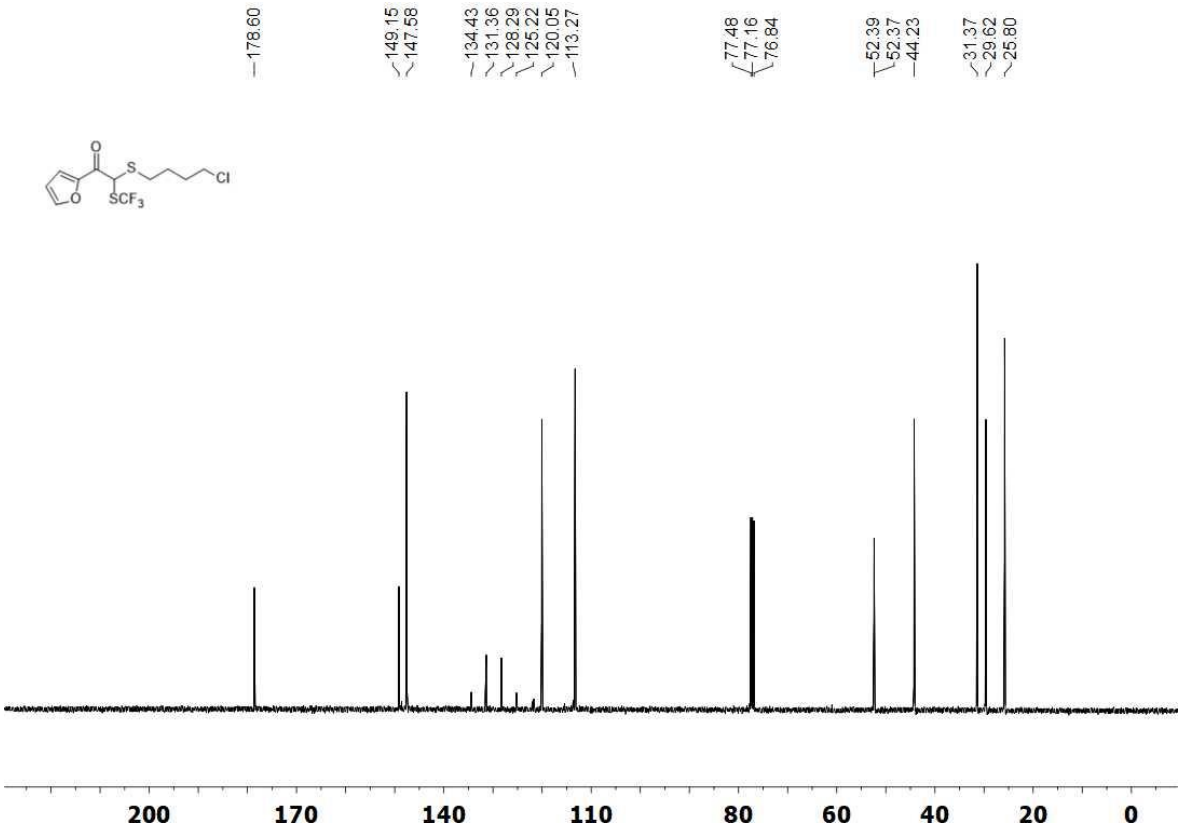
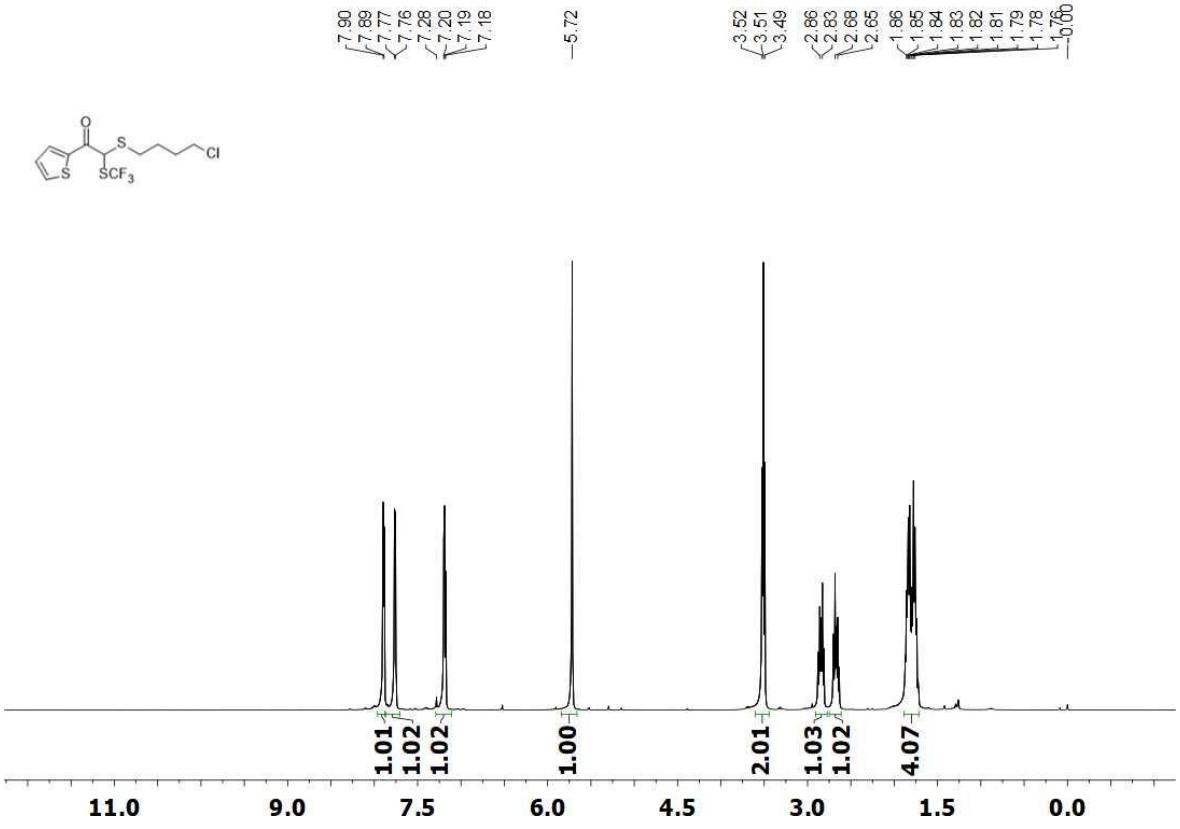


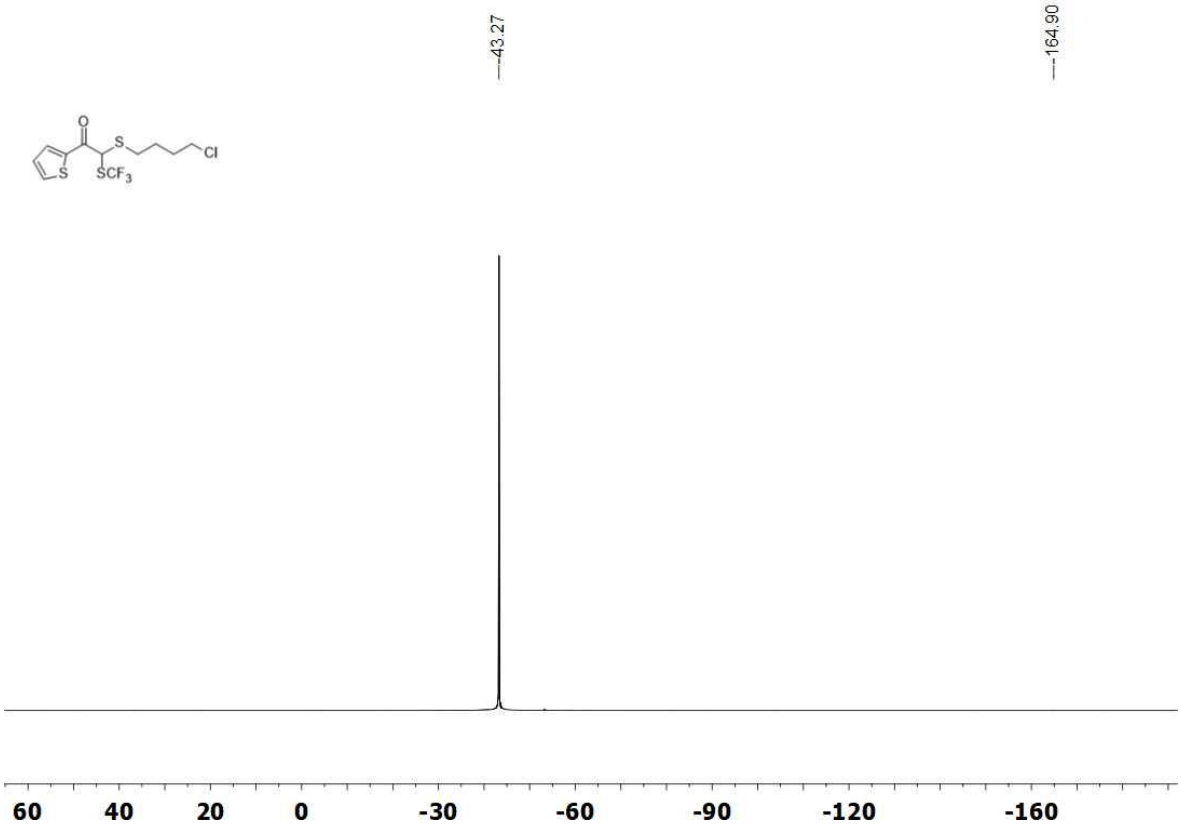
^{13}C NMR of compound **5q**



^{1}H NMR of compound **5r**



^{19}F NMR of compound **5r**



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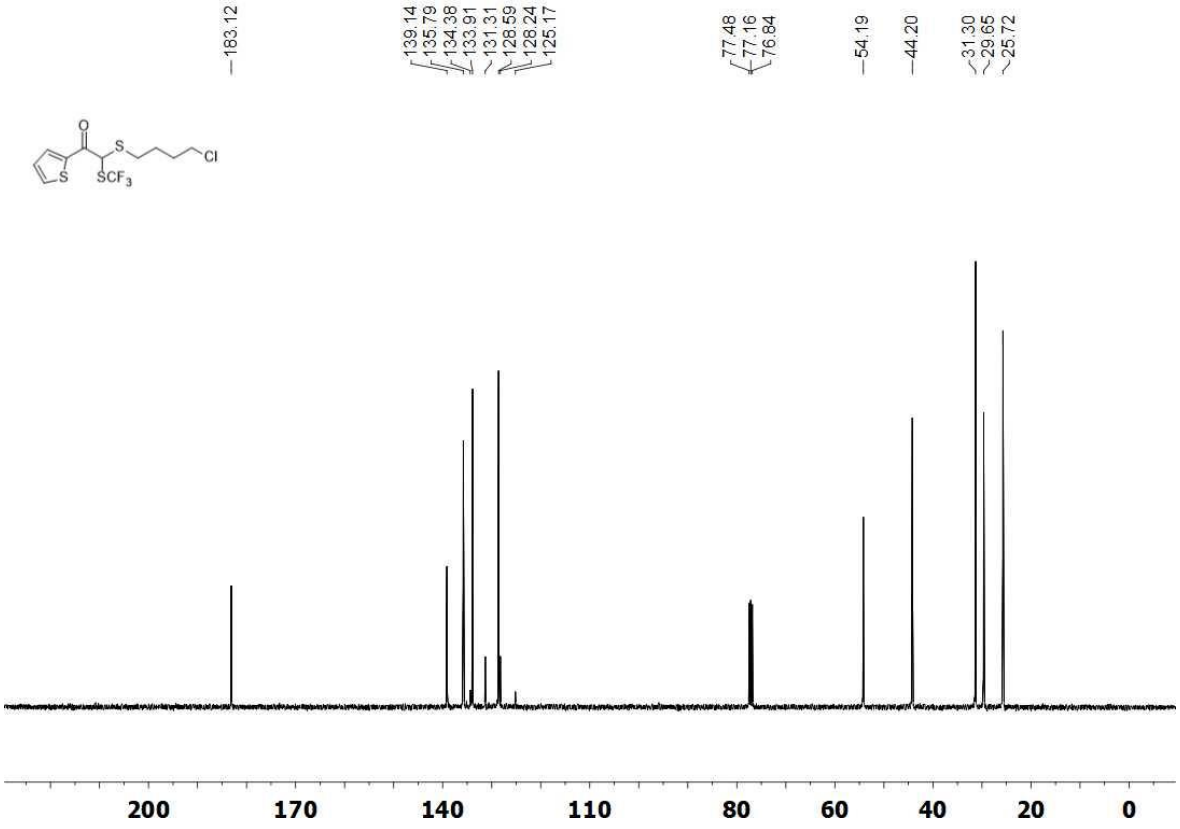

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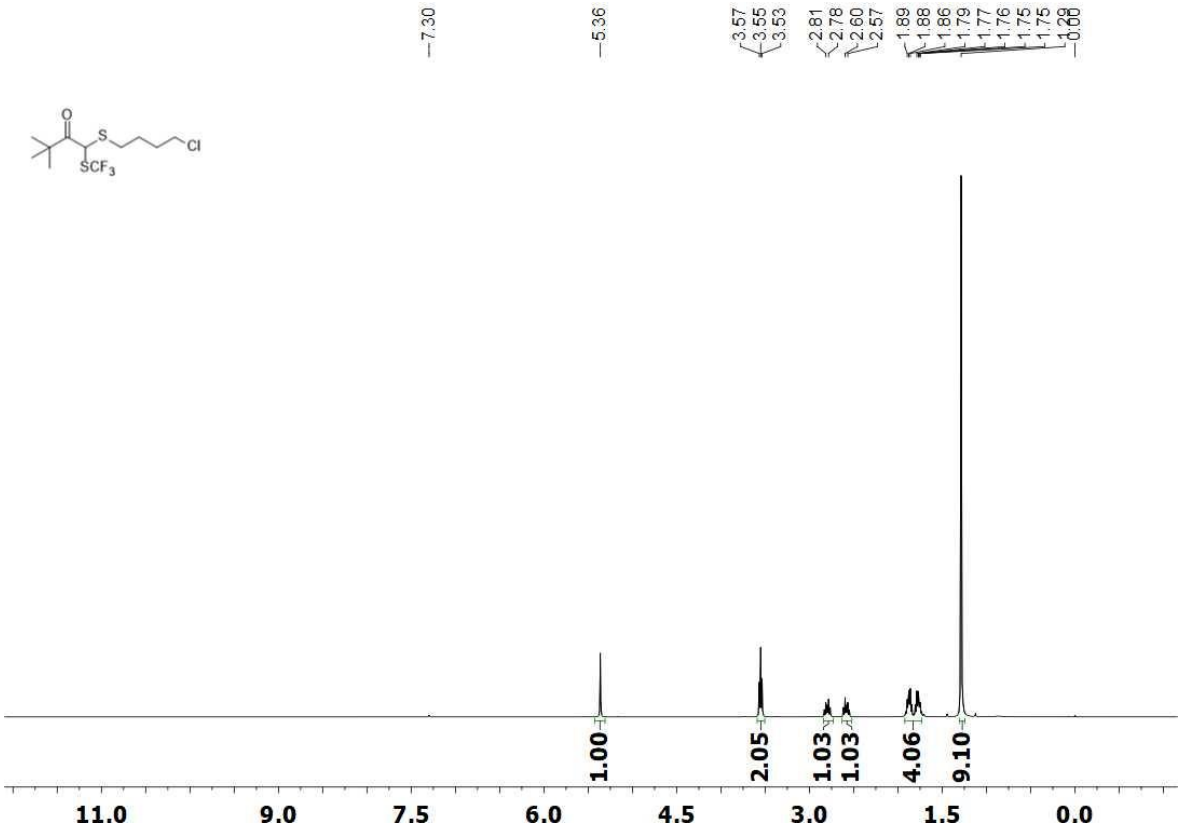

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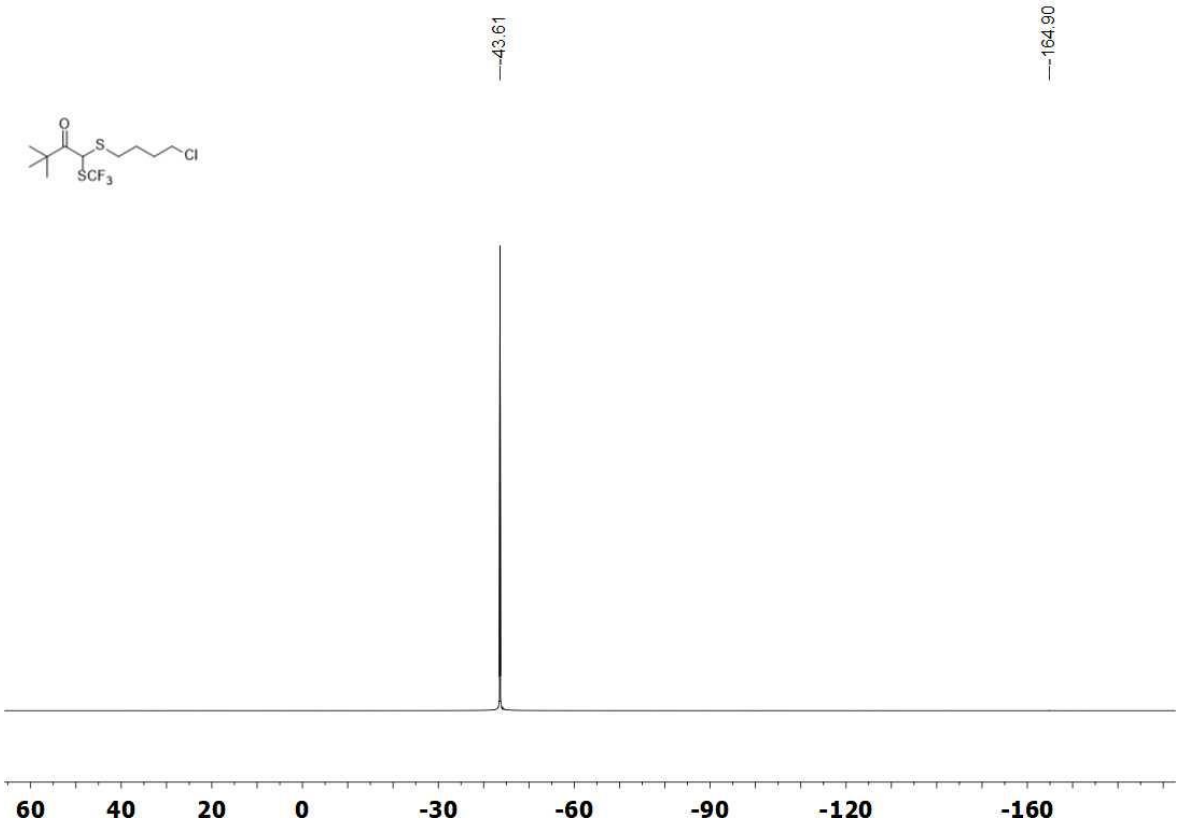

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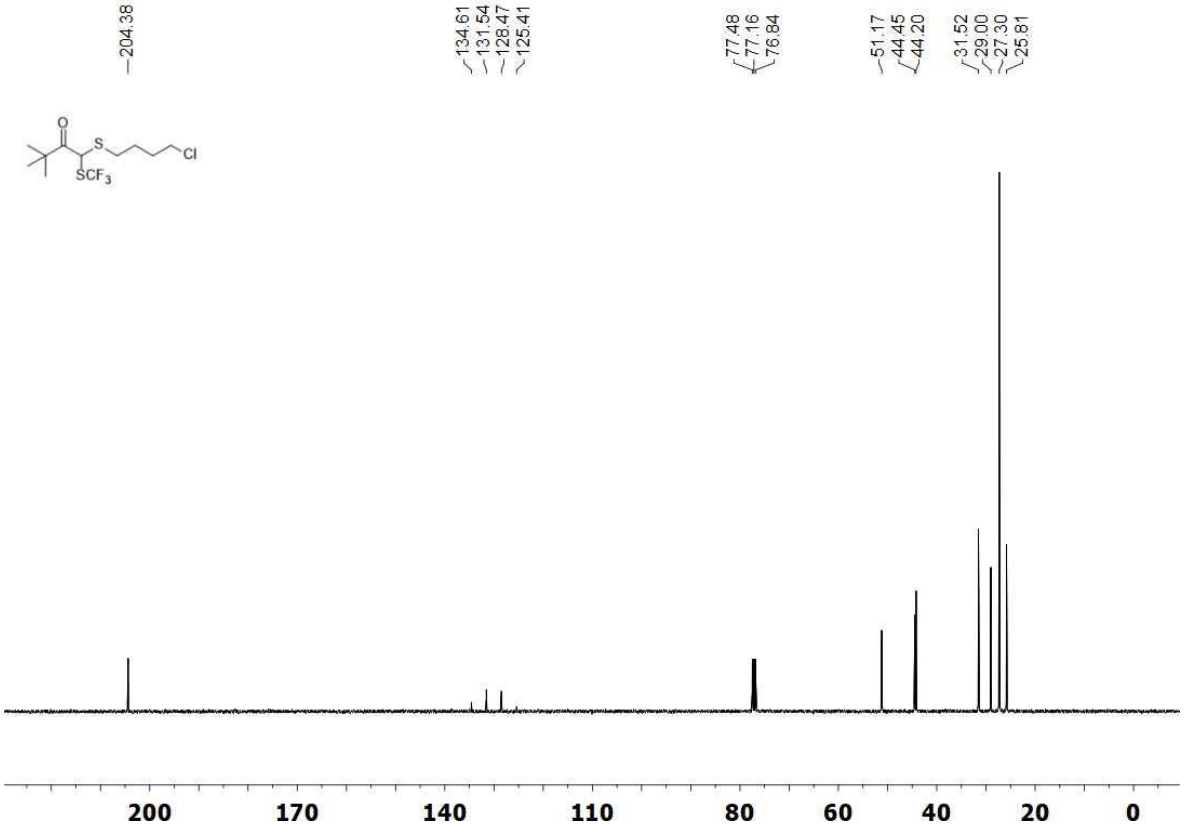

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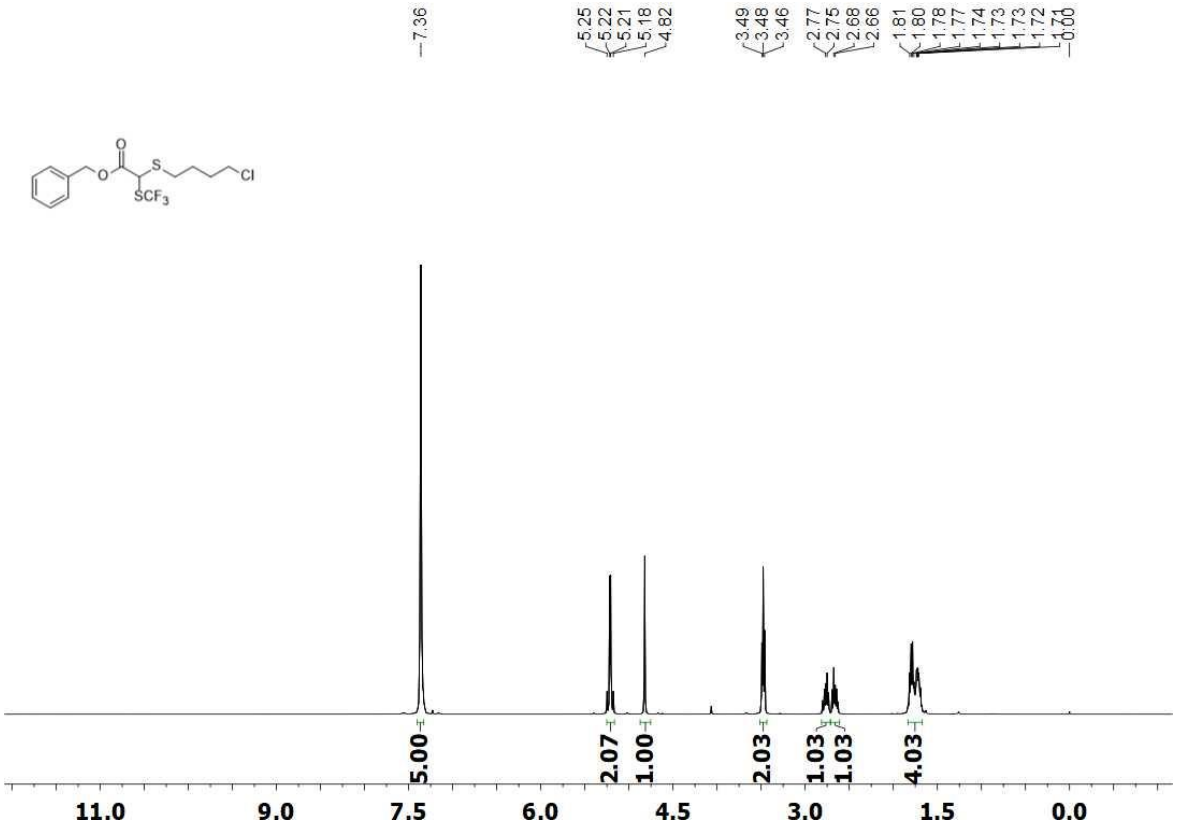

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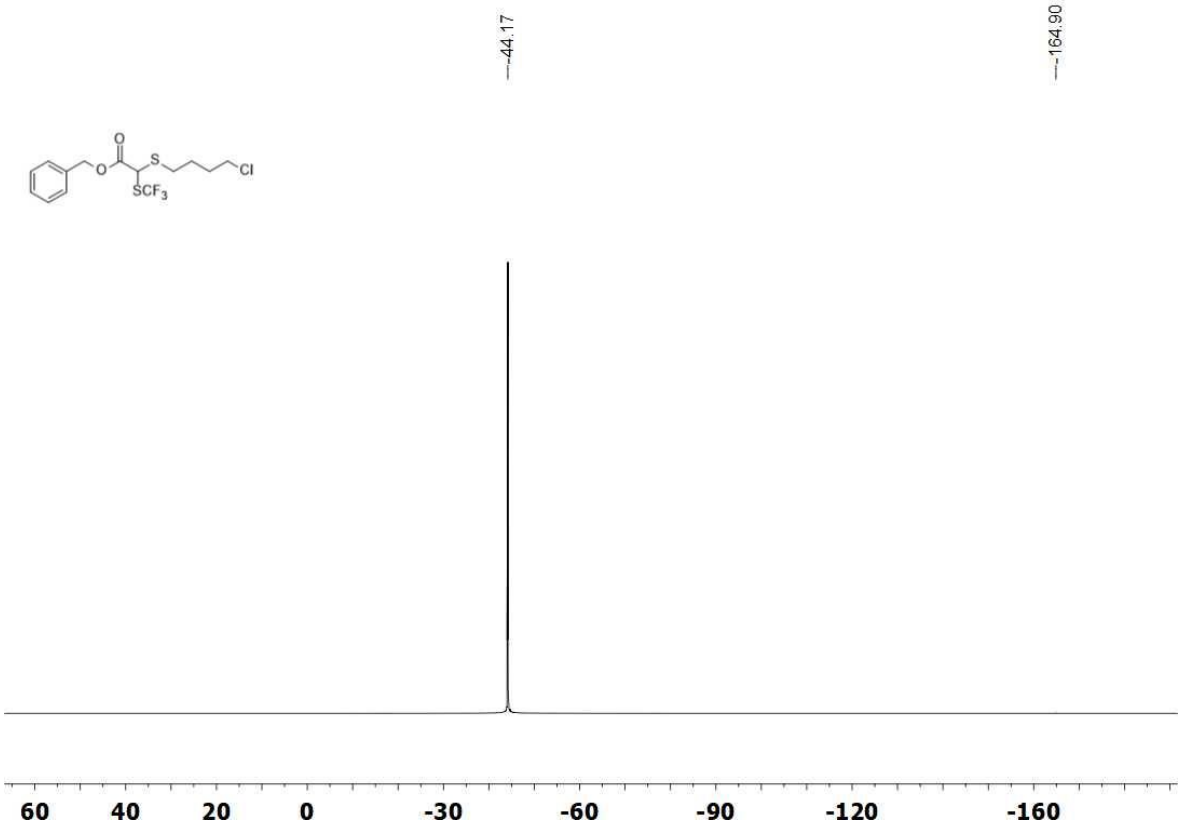

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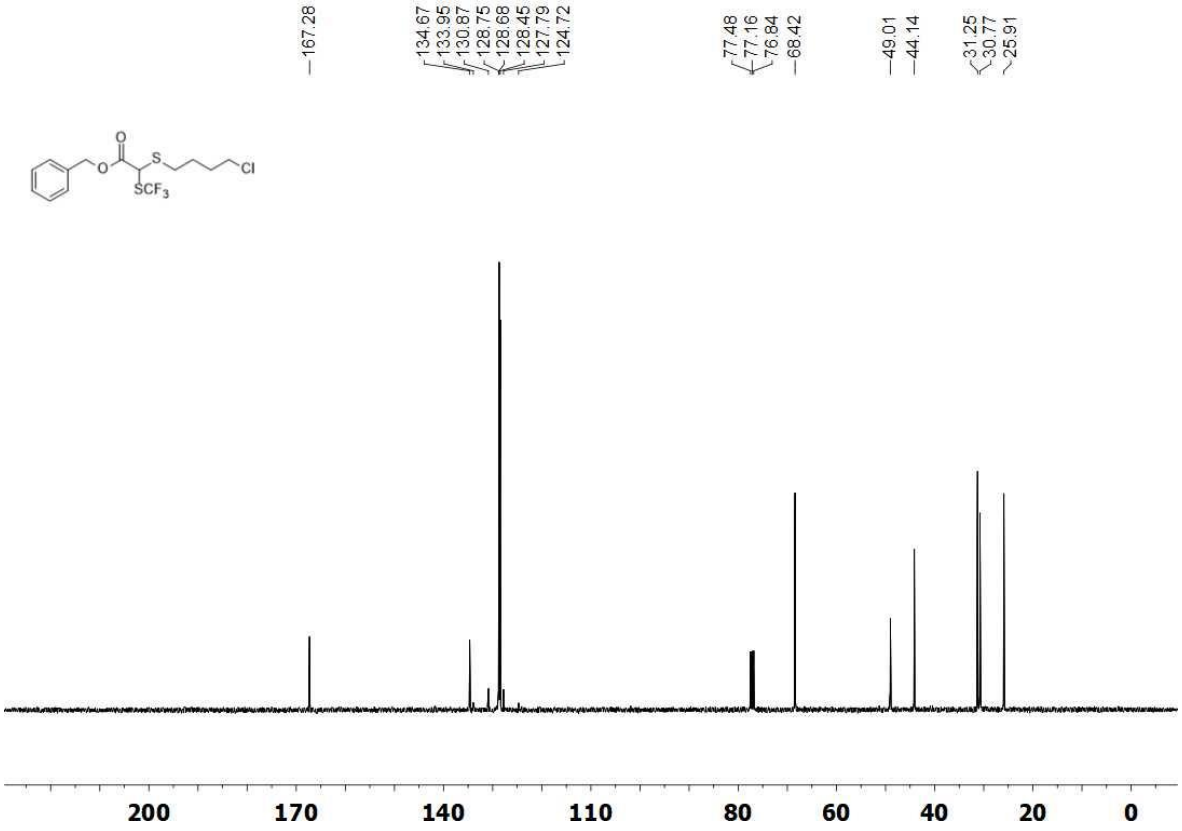

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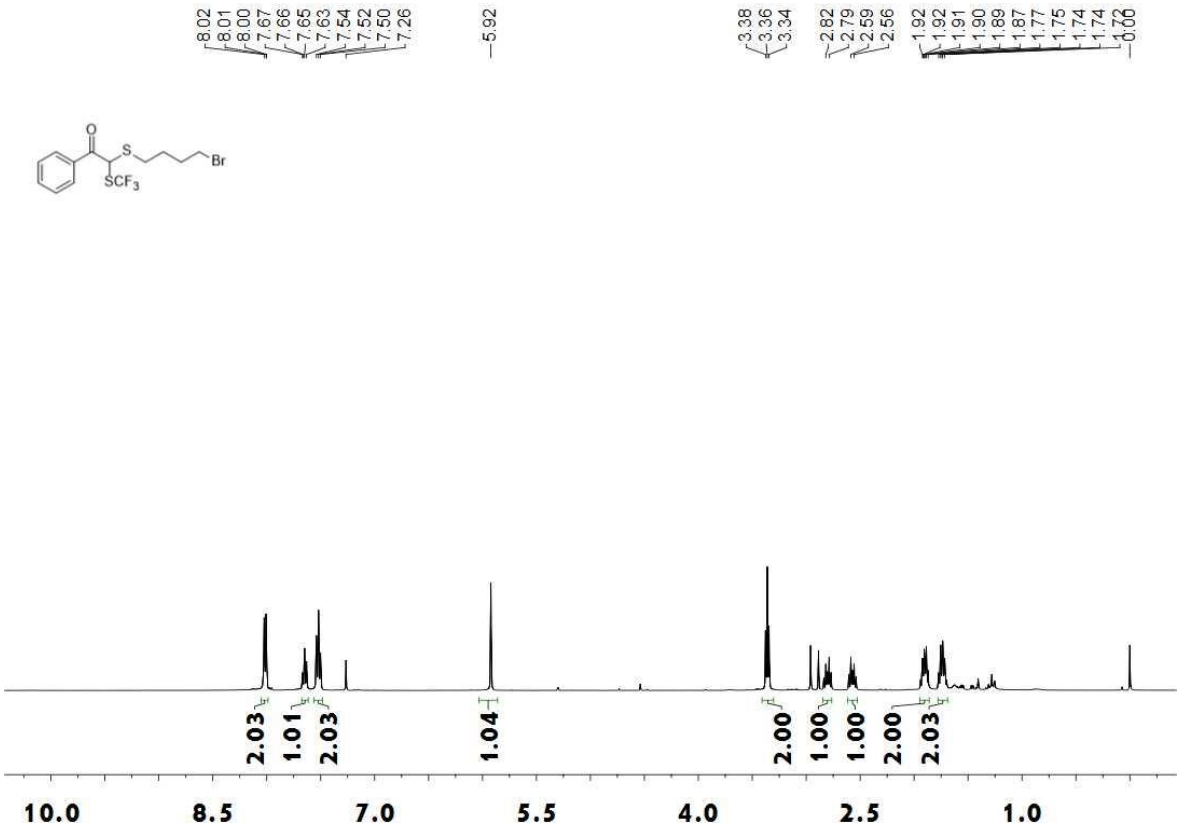

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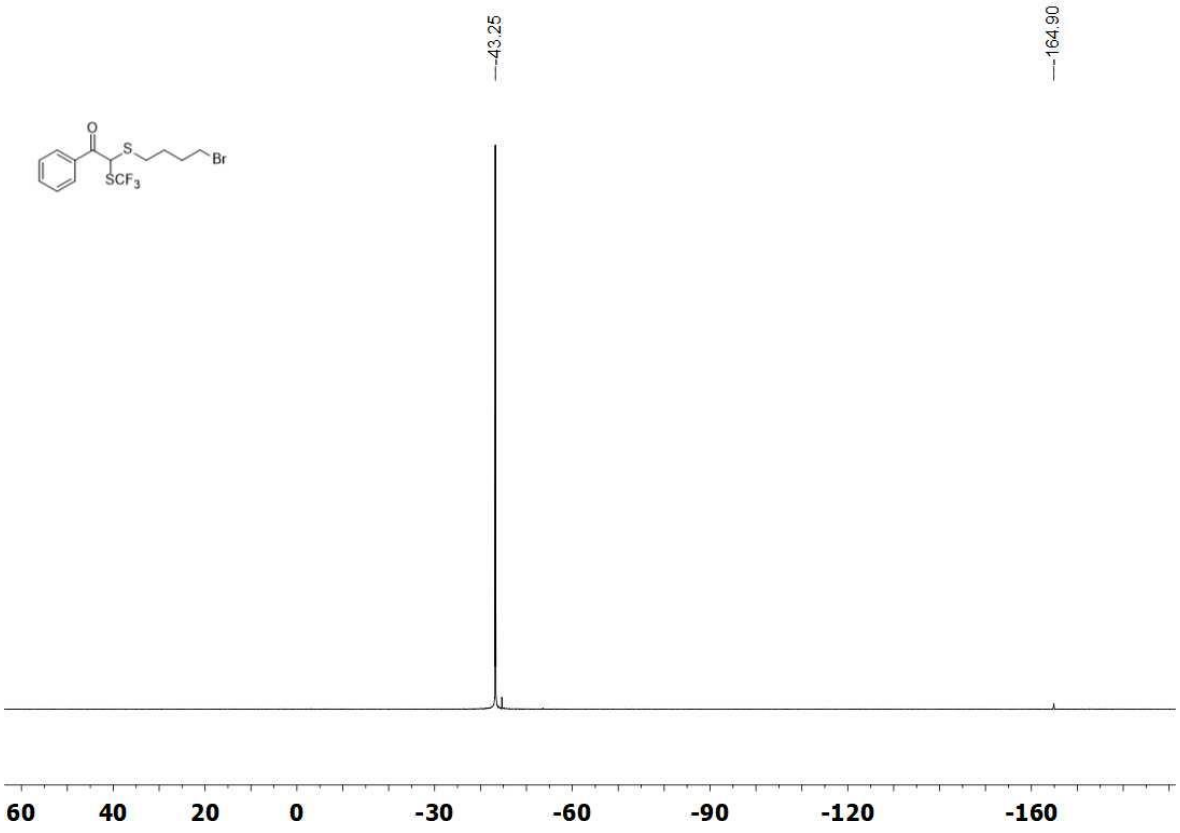

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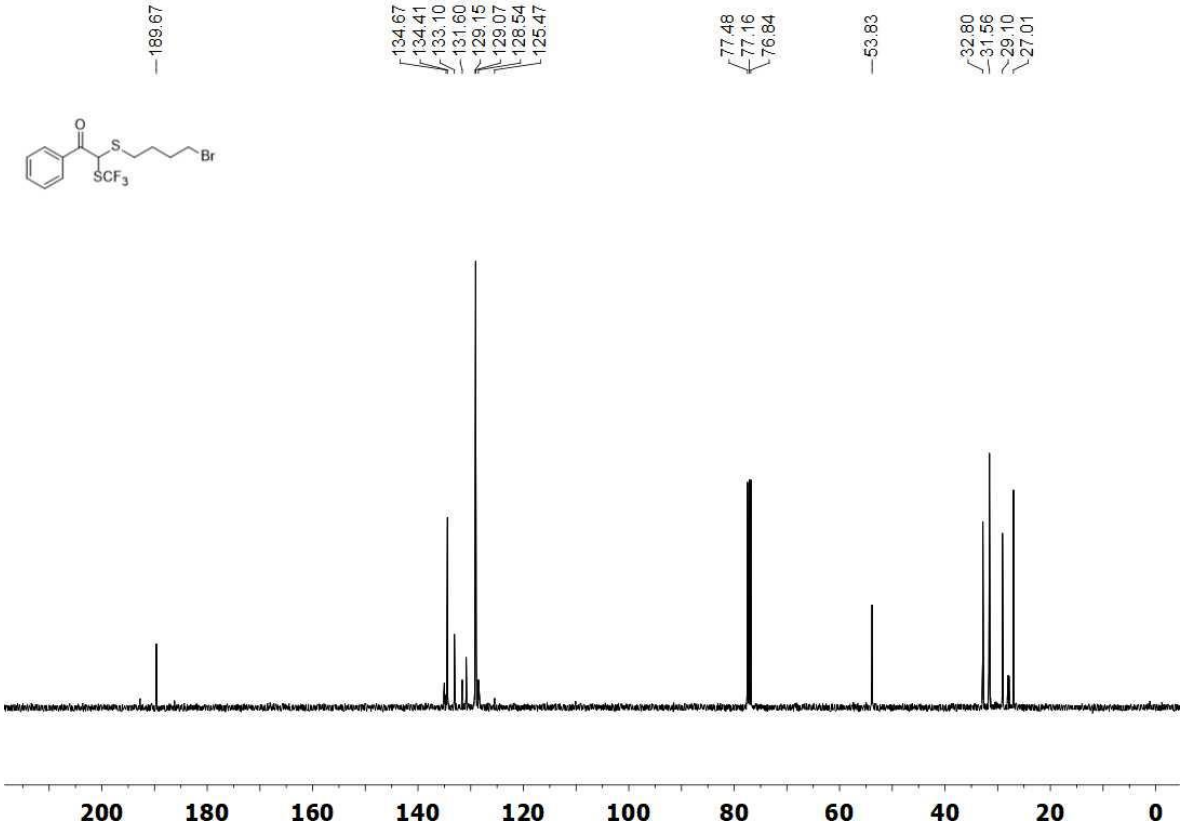
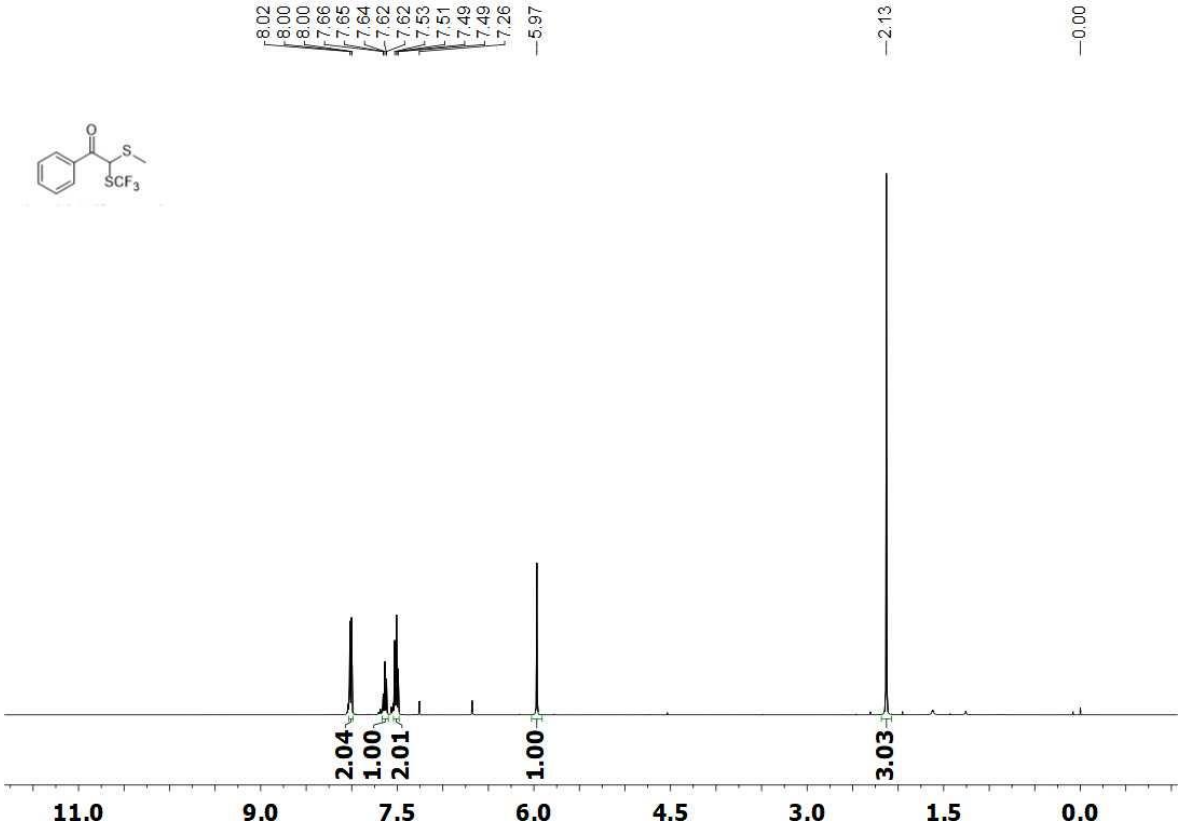
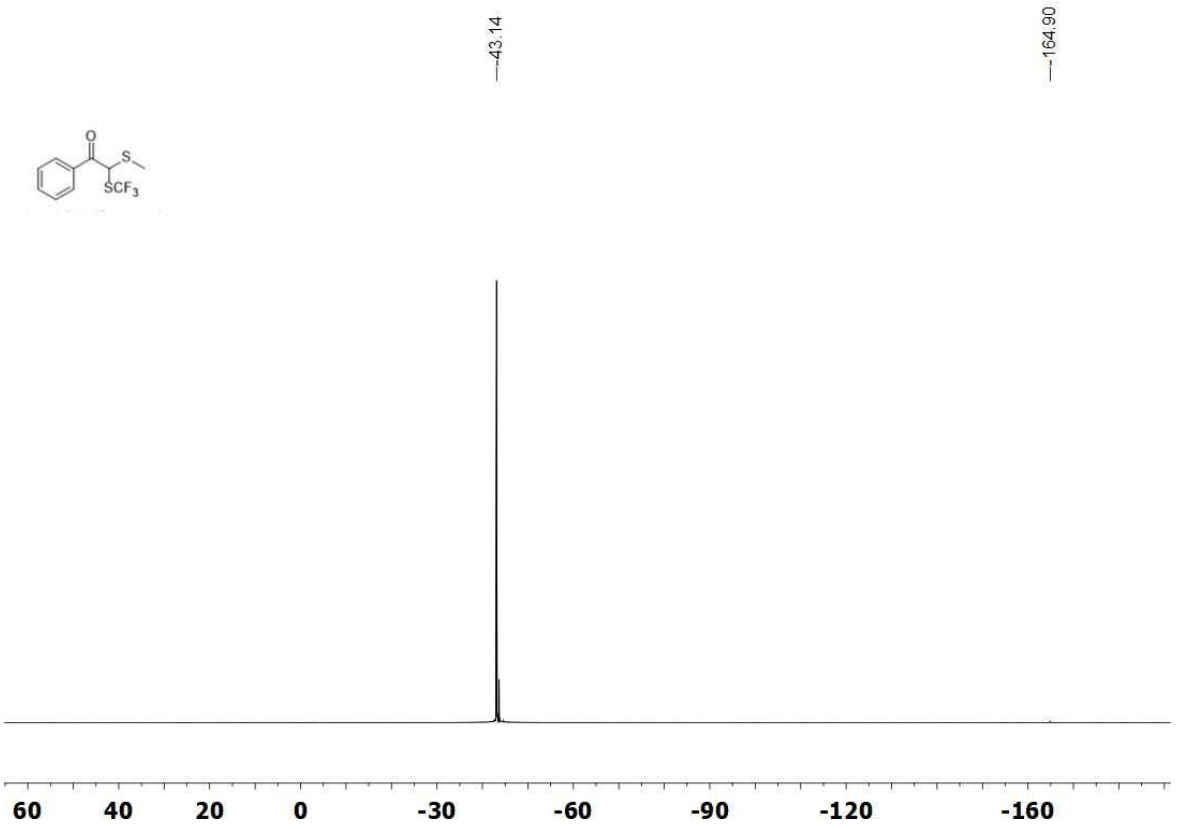


^{1}H NMR of compound **5v**



^{19}F NMR of compound **5v**



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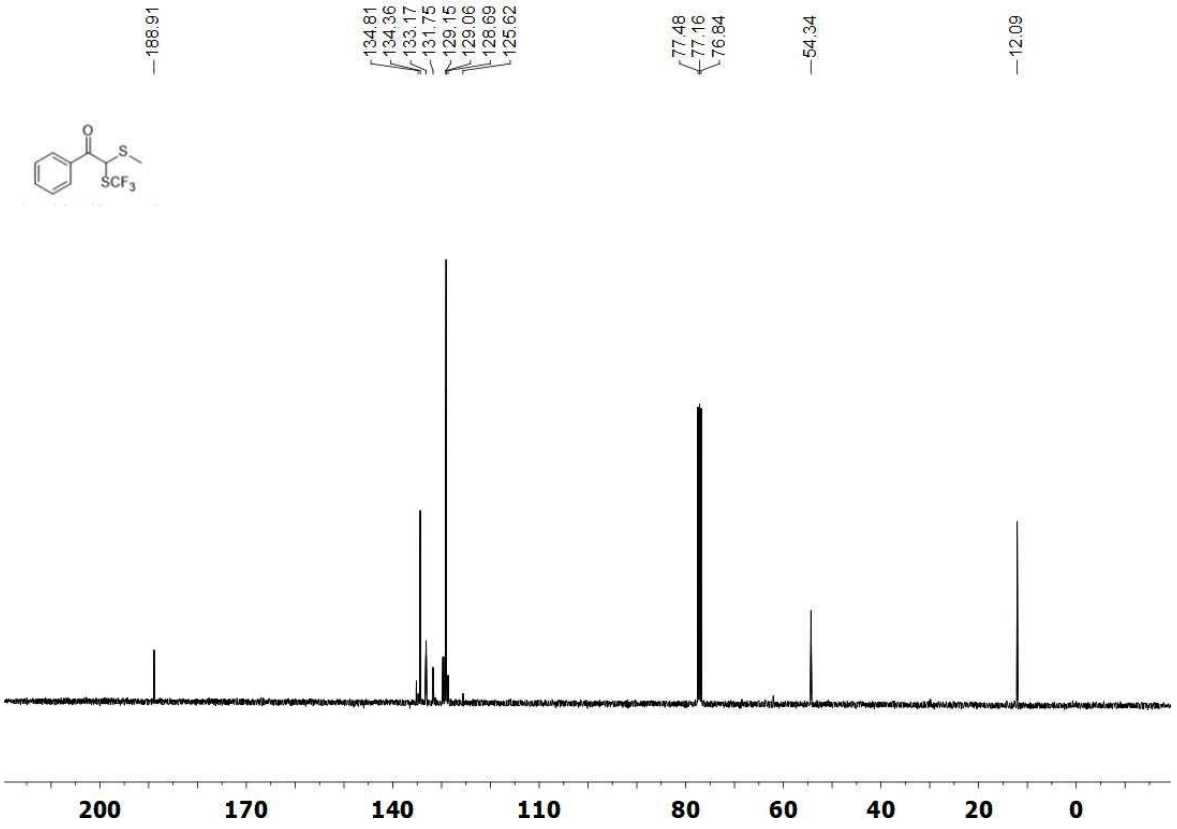
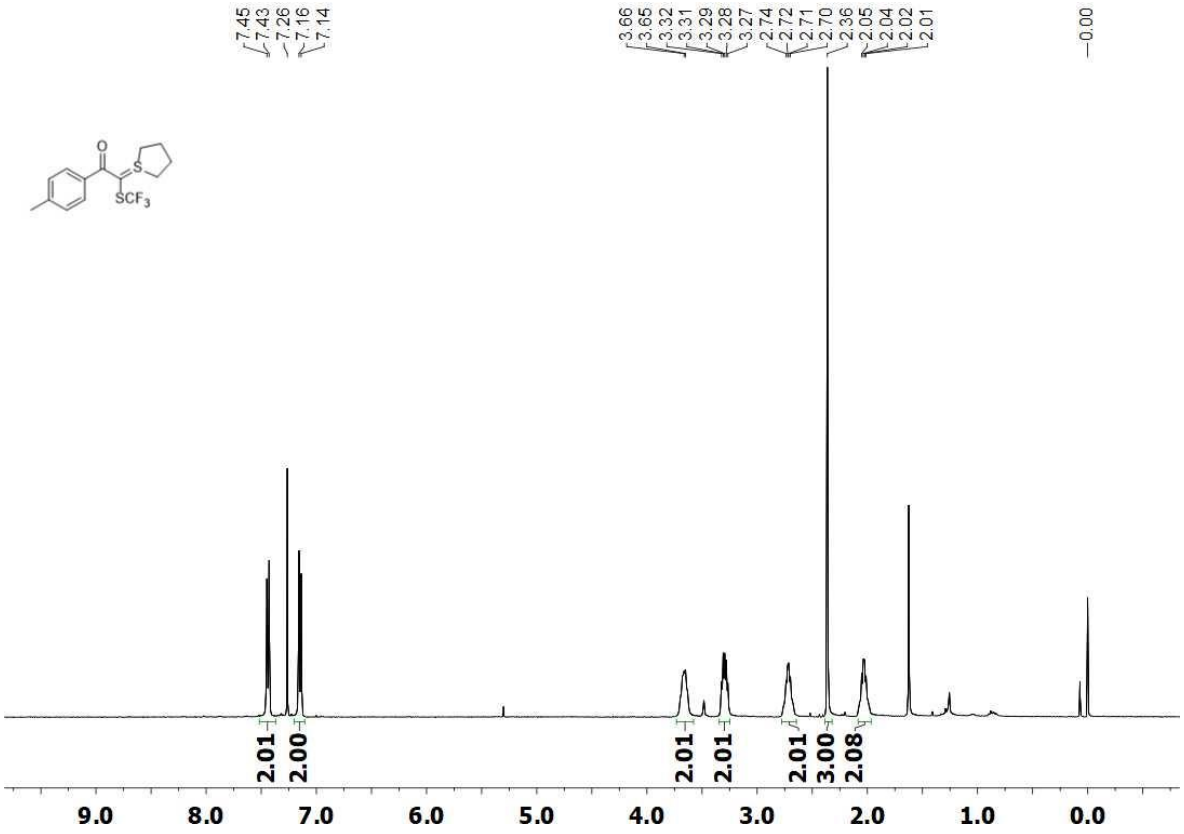
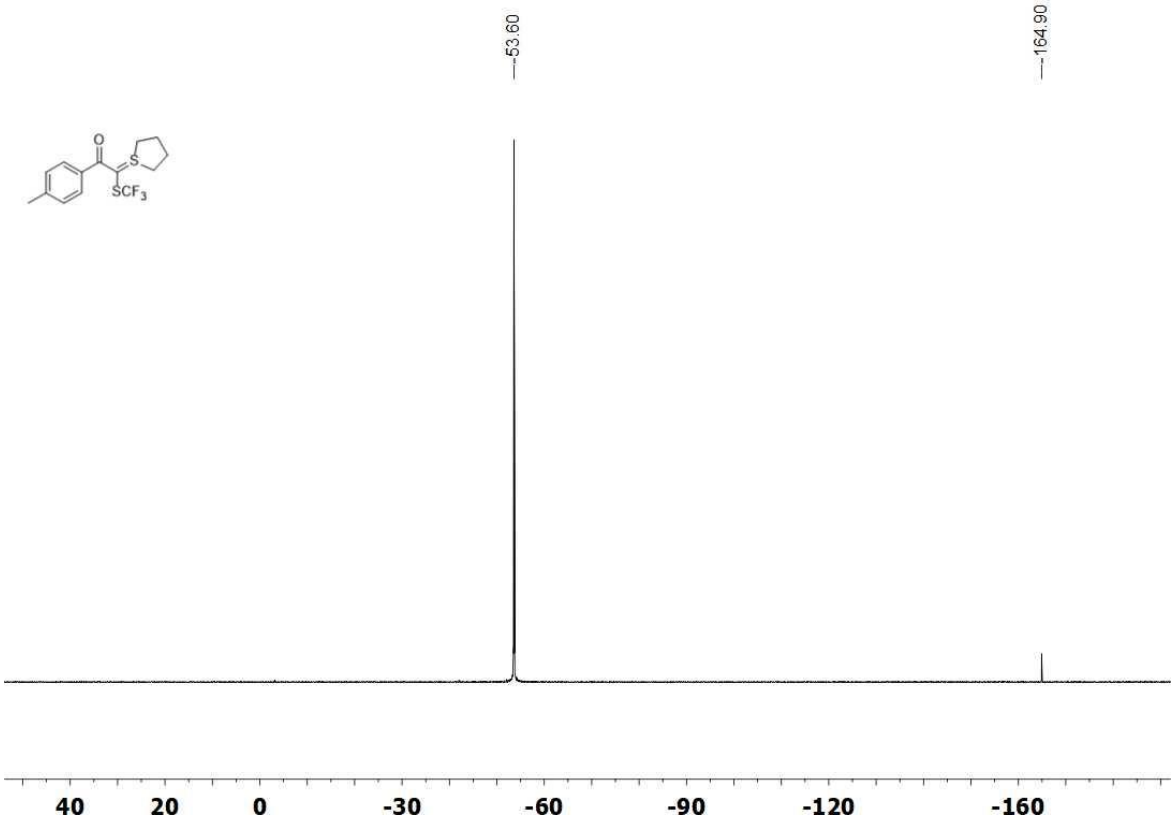


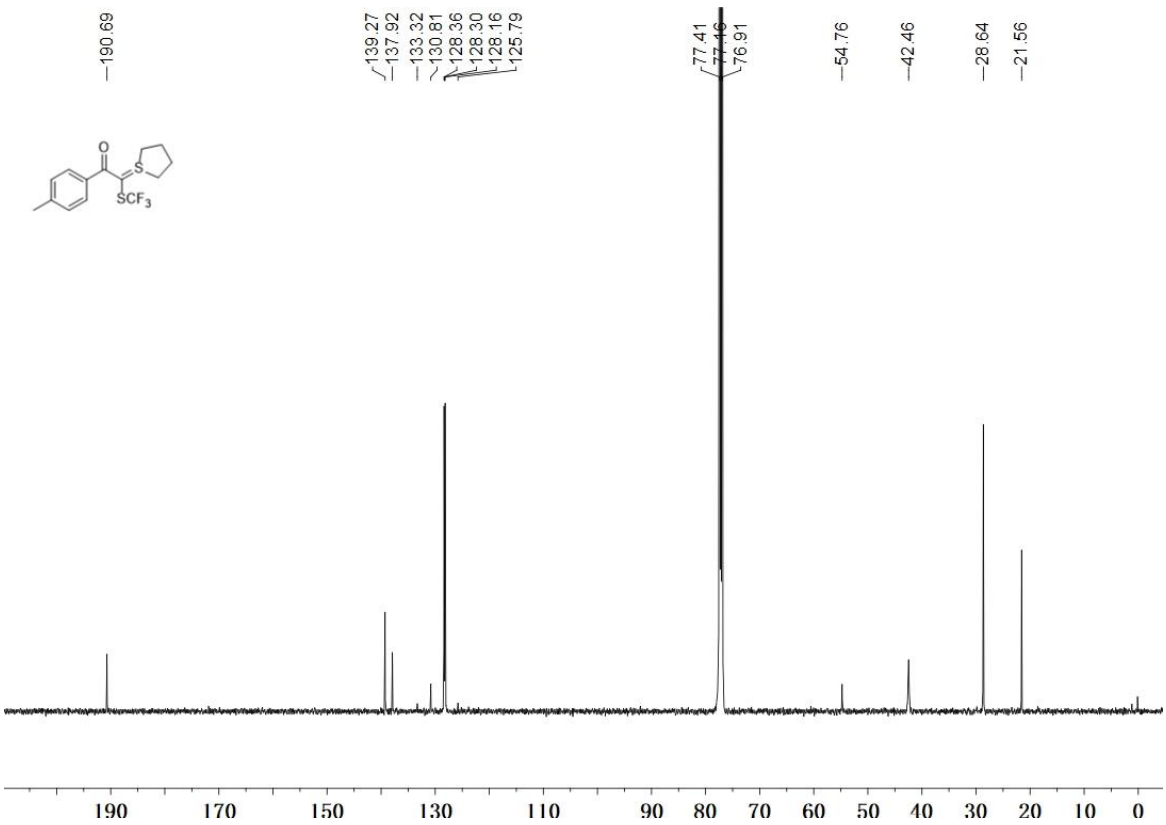
^{1}H NMR of compound **6**



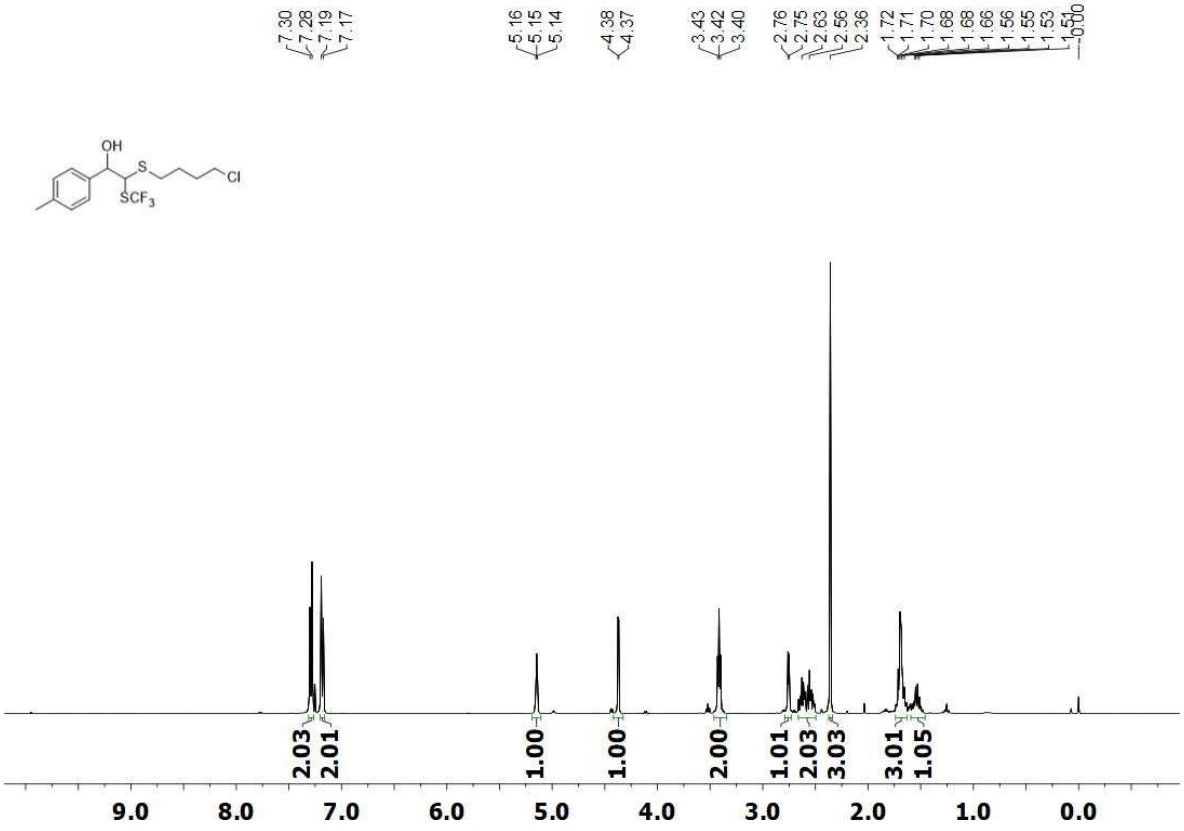
^{19}F NMR of compound **6**



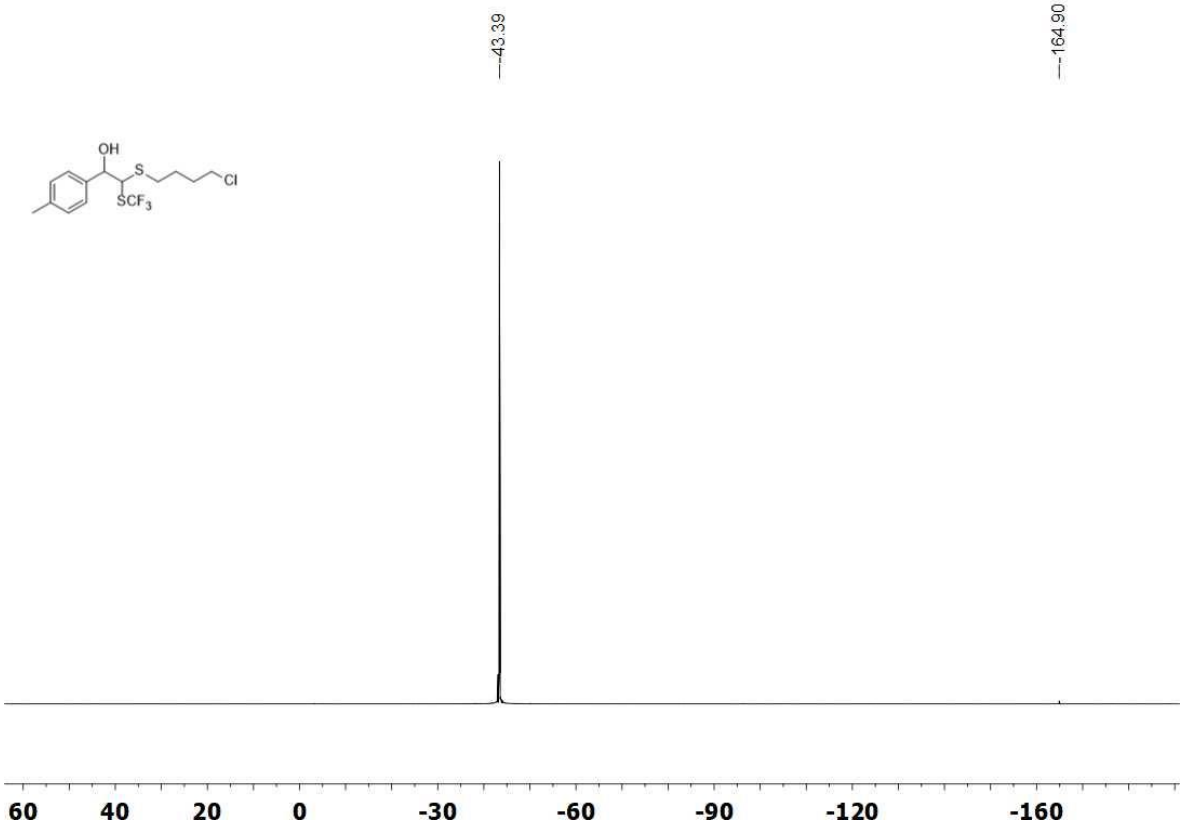
^{13}C NMR of compound **6**



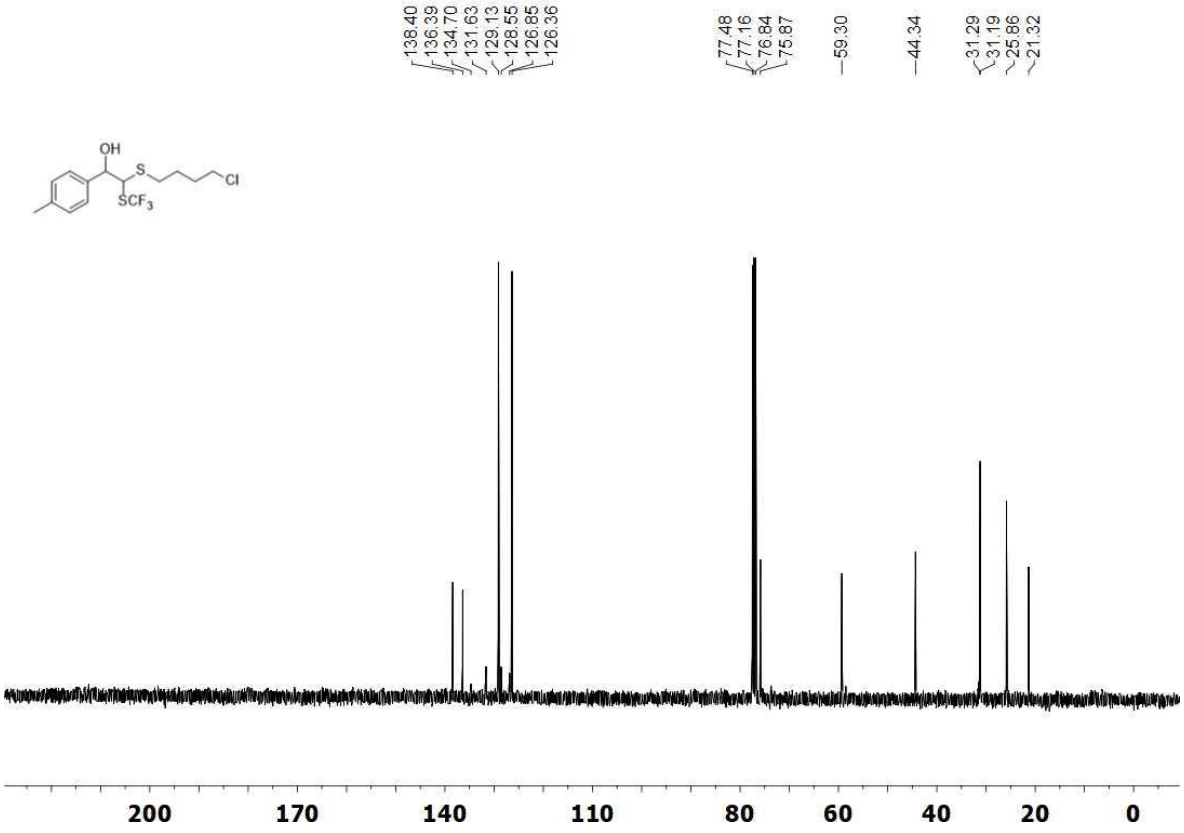
^{1}H NMR of compound **7**



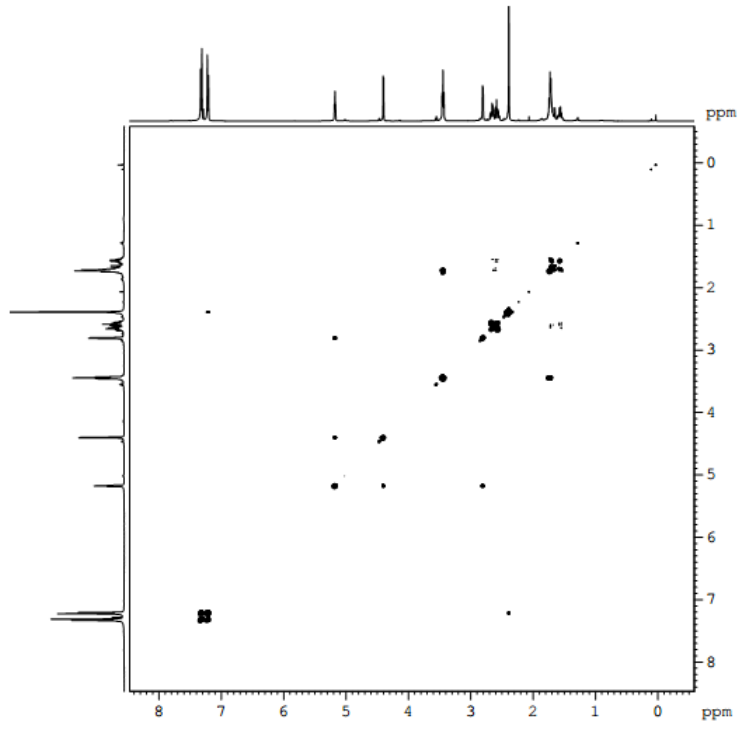
^{19}F NMR of compound **7**



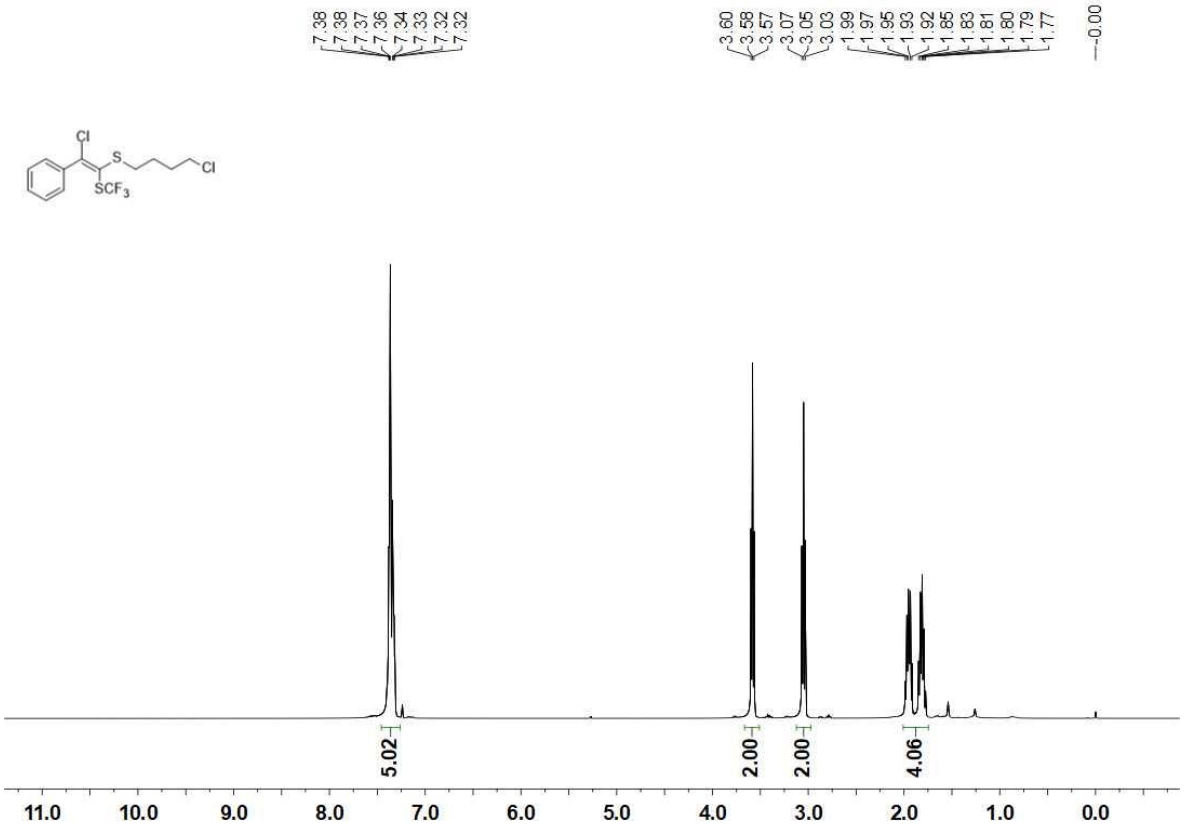
^{13}C NMR of compound **7**



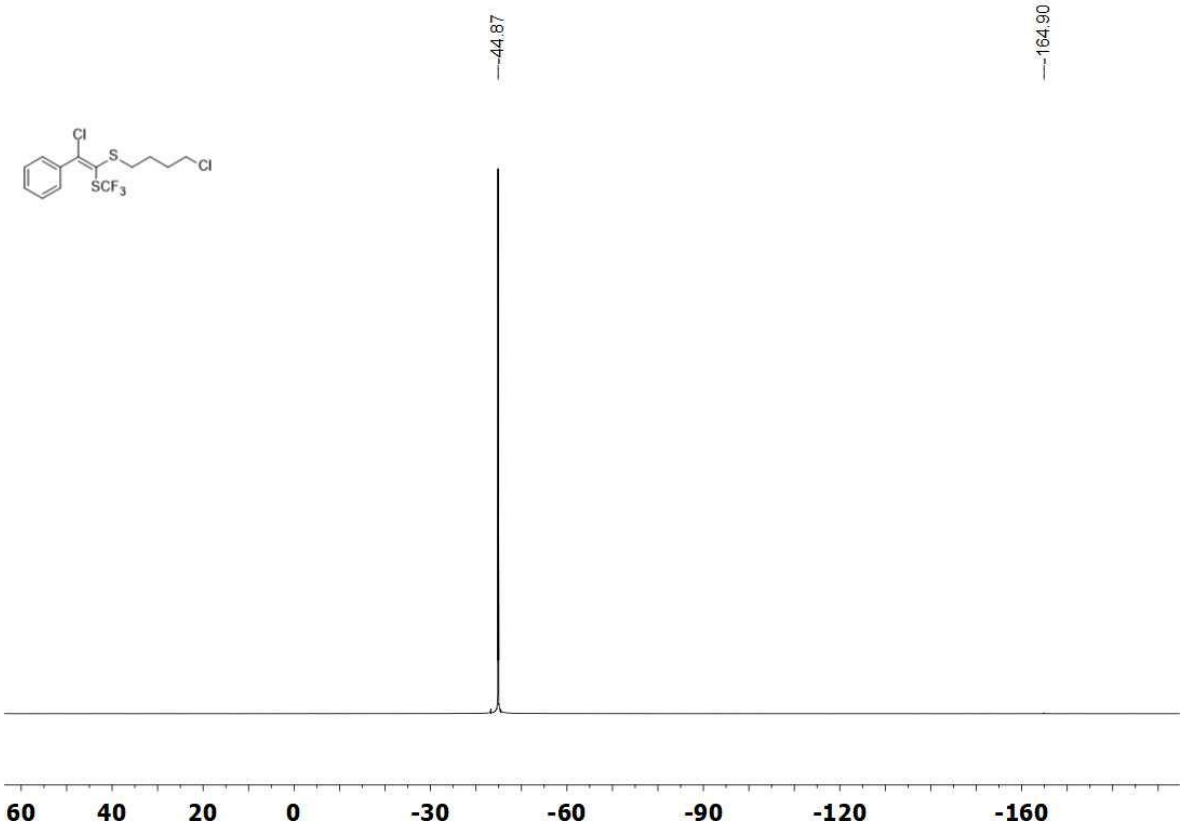
H-H cosy of compound **7**



^{1}H NMR of compound **5a'**



^{19}F NMR of compound **5a'**



^{13}C NMR of compound **5a'**