Supporting Information

for

Visible light mediated C-H trifluoromethylation of (hetero)arenes

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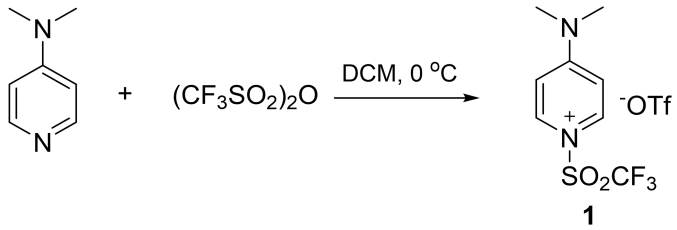
1. General Information

The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on 400MHz NMR spectrometers (400 MHz for ^{1}H, 100MHz for ^{13}C and 375 MHz for ^{19}F respectively). The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of solvents ($CHCl_3$ at 7.26 ppm for ^{1}H NMR) while the chemical shifts (δ) for ^{19}F NMR are given in ppm relative to trichlorofluoromethane (CCl_3F) as standard. Coupling constants (*J*) are reported in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t= triplet, q = quartet, hept=heptet, m = multiplet, brs = broad singlet. All reactions were monitored by TLC or ^{19}F NMR. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure. Mass spectra were obtained on GC-MS or LC-MS (ESI) High resolution mass spectrometry (HRMS) was performed on a Waters Premier GC-TOF MS instrument with electron impact (EI) ionization mode, or on a Thermo Scientific Q Exactive HF Orbitrap-FTMS instrument with electrospray ionization (ESI) mode. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification.

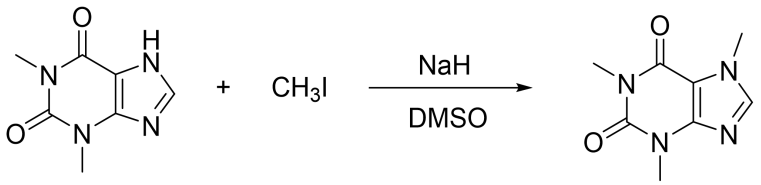
2. General Procedures for preparation of 1



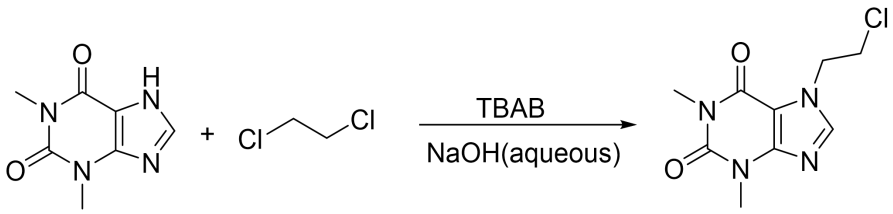
1

1 was synthesized according to the reported literature.[1] To a stirred solution of DMAP (7.3 g, 60 mmol, 1 equiv.) in DCM (180 mL) was added Tf_2O (11.1 mL, 66 mmol, 1.1 equiv.) dropwise at 0 ℃ in 10 min. Upon completion, the reaction mixture was warmed to room temperature and stirred for another 30 min. The mixture was precipitated, washed with DCM (40 mL x 3) to afford the product as white solid (19.6 g, 81%). **^{1}H NMR** (400 MHz, CD_3CN) δ 8.29 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.42 (s, 6H). **^{19}F NMR** (376 MHz, CD_3CN) δ -74.59, -79.32. The spectrums were in accordance with literature.

3. General Procedures for Synthesis of Substrates



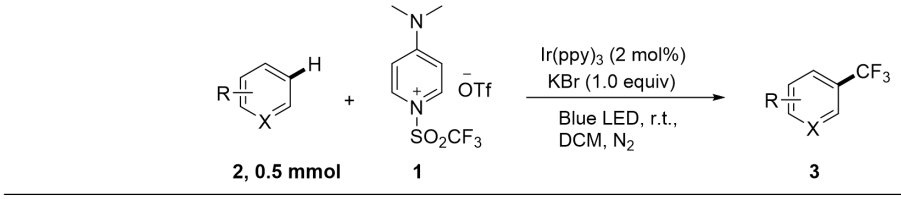
Theophylline (5.0 mmol, 0.9 g) was dissolved in dimethyl sulfoxide (20 mL). The solution was stirred at room temperature for 5 h. Two equivalents of NaH (10 mmol, 0.4 g) were added carefully to the DMSO solution, followed by addition of methyl iodide (7.5 mmol, 0.46 mL). The reaction mixture was stirred for 1 h at room temperature. The mixture was quenched with water, and neutralized with dilute HCl. The crude residue was extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was subjected to flash column chromatography (EtOAc) to give the final product as white solid.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 3.99 (s, 3H), 3.59 (s, 3H), 3.41 (s, 3H).

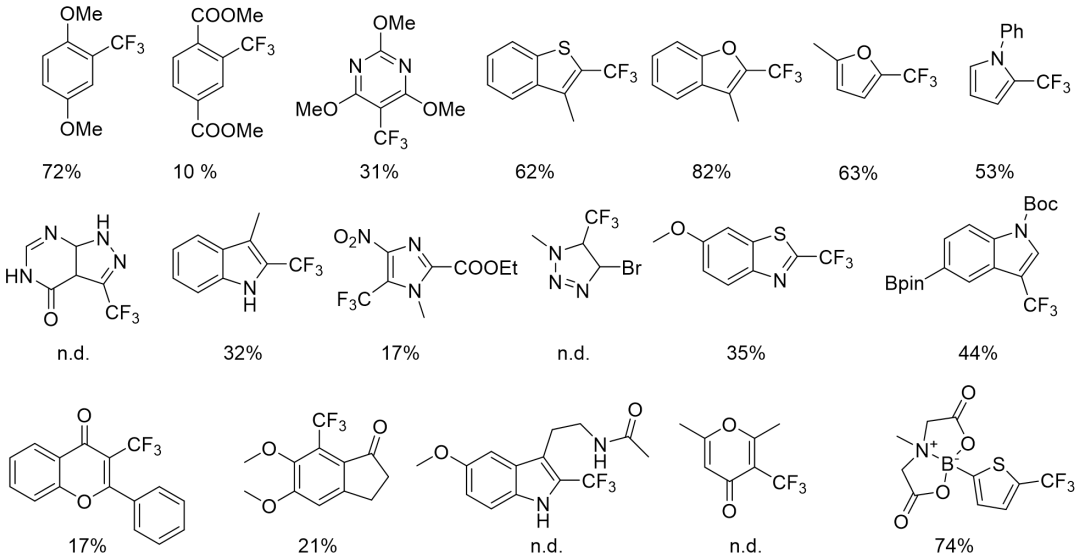


Theophylline (10.0 mmol, 1.8 g) and Tetrabutylammonium bromide (TBAB, 1 mmol, 0.3 g) was dissolved in 1,2-Dichloroethane (20 mL). Then the 50% aqueous sodium hydroxide was added to the solution. The reaction mixture was stirred under reflux for a few hours. The mixture was quenched with water, and neutralized with dilute HCl. The crude residue was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was subjected to flash column chromatography (PE: EtOAc= 2:1-1:1) to give the final product as white solid.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 4.57 (t, J = 5.4 Hz, 2H), 3.92 (t, J = 5.4 Hz, 2H), 3.58 (s, 3H), 3.38 (s, 3H).

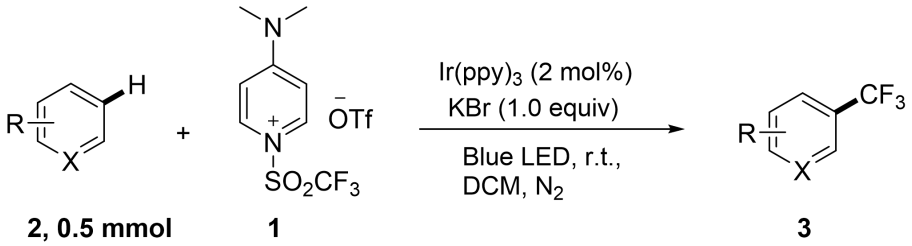
4. Selected example of unpurified and failed products

The products shown in were not isolated due to at least one of four reasons mentioned below:1) The relatively low yields determined by ^{19}F NMR. 2) The lowing boiling point attached to the products.3) The difficulty of separation. 3) The lack of representativeness.





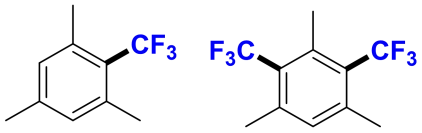
5. General Procedures for C-H Trifluoromethylation of (Hetero)arenes



Into a 15 mL Schlenk tube were added $Ir(ppy)_3$ (6.6 mg, 0.01 mmol, 2 mol%), KBr

(59.5 mg, 0.5 mmol, 1.0 equiv), Substrates **2** (0.5 mmol, 1.0 equiv.) and **1** (505.3 mg, 1.25 mmol, 2.5 equiv.) in DCM (6 mL). The resulting mixture was stirred at RT and irradiated with blue LEDs for 12 h under a N_2 atmosphere. When the reaction was completed, as monitored by ^{19}F NMR spectroscopy, the crude reaction mixture was diluted with DCM (20 mL). The solution was washed with water (3×20 mL) and brine (20 mL), and then dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was subjected to flash column chromatography to give the final product **3a-3x**.

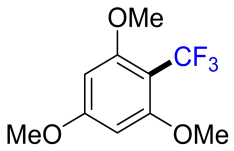
1,3,5-Trimethyl-2-(trifluoromethyl)benzene (3a-mono)[4]; 1,3,5-Trimethyl-2,4-bis(trifluoromethyl)benzene (3a-bis)[5]



3a-mono **3a**-bis

The product mixture was purified by silica gel column chromatography (hexane) to afford **3a** (86.0 mg, 81%) as colorless oil. **3a**-mono: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 2.44 (q, *J* = 3.4 Hz, 6H), 2.29 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -53.77-53.73. (hept, *J* = 3.4 Hz, 3F); **LRMS (EI)** m/z: $[M]^+$ calcd for $C_{10}H_{11}F_3$ 188.1; found 188.1;**3a**-bis: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 2.52 (hept, *J* = 2.9 Hz, 3H), 2.47 (q, *J* = 4.1 Hz, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -52.95-52.94 (hept, *J* = 2.9 Hz, 3F); **LRMS (EI)** m/z: $[M]^+$ calcd for $C_{11}H_{10}F_6$ 256.1; found 256.1.

1,3,5-Trimethoxy-4-(trifluoromethyl)benzene (3b)[6]

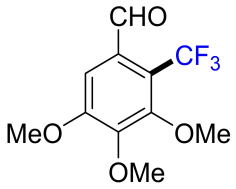


3b

The product mixture was purified by column chromatography on silica gel (hexane/EtOAc = 40:1) to afford **3b** (92.9 mg, 79%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.12 (s, 2H), 3.83 (d, *J* = 1.1 Hz, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -54.09 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 160.4(q, *J* = 1.1 Hz), 124.4 (q, *J*

= 273.3 Hz), 100.3 (q, *J* = 29.8 Hz), 91.2, 56.2, 55.3. **LRMS (EI)** m/z: $[M]^+$ calcd for $C_{10}H_{11}F_3O_3$ 236.1; found 236.1.

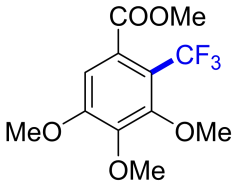
2-(Trifluoromethyl)-3,4,5-trimethoxybenzaldehyde (3c)[7]



3c

The product mixture was purified by column chromatography on silica gel (hexane/EtOAc = 40:1) to afford **3c** (85.2 mg, 65%) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (q, *J* = 2.5 Hz, 1H), 7.32 (s, 1H), 3.94 (s, 6H), 3.92 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -51.20 (d, *J* = 2.6 Hz, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.1 (q, *J* = 6.0 Hz), 155.8, 152.8 (q, *J* = 2.2 Hz), 147.3, 130.8, 124.2 (q, *J* = 275.1 Hz), 117.9 (q, *J* = 31.0 Hz), 107.2, 62.0, 61.0, 56.2. **LRMS (EI)** m/z: $[M]^+$ calcd for $C_{11}H_{11}F_3O_4$ 264.1; found 264.1.

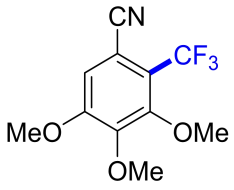
Methyl 3,4,5-trimethoxy-2-(trifluoromethyl)benzoate (3d)[6]



3d

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 8:1) to afford **3d** (91.9mg, 62%) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.74 (s, 1H), 3.93 (s, 3H), 3.89 (s, 3H), 3.87 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.97 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 155.9, 153.0 (q, *J* = 1.9 Hz), 144.2, 128.4 (q, *J* = 2.8 Hz), 123.1 (q, *J* = 273.3 Hz), 114.6 (q, *J* = 30.8 Hz), 106.9, 61.8, 60.9, 56.2, 53.0. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_{12}H_{13}F_3O_5$ 294.1; found 294.1.

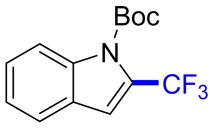
(3,4,5-Trimethoxy-2-(trifluoromethyl)benzonitrile (3e)



3e

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 4:1-2:1) to afford **3e** (62.8mg, 48%) as light yellow solid (m.p. 87~88°C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 3.95 – 3.94 (m, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.70 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 153.5(q, *J* = 1.5 Hz), 147.1, 122.2 (q, *J* = 273.9 Hz), 119.8 (q, *J* = 31.0 Hz), 116.1, 113.2, 105.1 (q, *J* = 2.8 Hz), 62.1, 61.1, 56.5. **HRMS (EI)** calcd for $C_{11}H_{10}F_3NO_3$ $[M]^+$: 261.0613, found: 261.0607. **IR (KBr)**: 2994, 2951, 2849, 2232, 1575, 1503, 1458, 1407, 1340, 1303, 1128, 1005, 865, 827, 736 cm^{-1}.

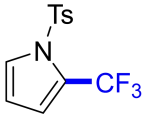
***tert*-Butyl 2-(trifluoromethyl)-1*H*-indole-1-carboxylate (3f)[8]**



3f

The product mixture was purified by column chromatography on silica gel (PE) to afford **3f** (84.1mg, 59%) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.62 (d, *J* = 7.9, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 1.68 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.15 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.6, 137.7, 127.01, 126.95 (q, *J* = 39.0 Hz), 126.5, 123.5, 122.0, 120.8 (q, *J* = 267.5 Hz), 116.1, 113.5 (q, *J* = 5.2 Hz), 85.4, 27.9. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_{14}H_{14}F_3NO_2$ 285.1; found 285.1.

1-Tosyl-2-(trifluoromethyl)-1*H*-pyrrole (3g)[9]

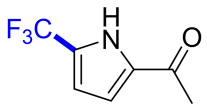


3g

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 50:1) to afford **3g** (93.1mg, 64%) as white solid. **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.49 (dd, *J* = 3.4, 1.9 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.76 (brs, 1H), 6.30 (t, *J* = 3.5 Hz, 1H), 2.41 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.87 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 135.4, 130.0, 127.5, 122.5 (q, *J* = 40.8 Hz), 120.0 (q, *J* = 267.5 Hz), 118.9 (q, *J* = 4.4 Hz), 110.9, 21.6. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_{12}H_{10}F_3NO_2S$ 289.0; found 289.1.

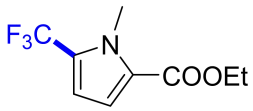
1-(5-(Trifluoromethyl)-1*H*-pyrrol-2-yl)ethan-1-one (3h)[10]



3h

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 20:1) to afford **3h** (57.5mg, 65%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 6.87 (brs, 1H), 6.60 (brs, 1H), 2.49 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.76 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.0, 133.5, 125.9 (q, *J* = 40.7 Hz), 120.4 (q, *J* = 267.8 Hz), 115.8, 110.9 (q, *J* = 2.9 Hz), 25.6. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_7H_6F_3NO$ 177.0; found 177.0.

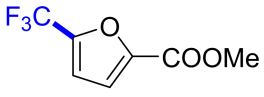
Ethyl 1-methyl-5-(trifluoromethyl)-1*H*-pyrrole-2-carboxylate (3i)



3i

The product mixture was purified by column chromatography on silica gel (PE/DCM = 10:1-8:1) to afford **3i** (90.9mg, 82%) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 4.2 Hz, 1H), 6.52 (d, *J* = 4.2 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.73(s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8, 127.0 (q, *J* = 37.6 Hz), 126.7 (d, *J* = 2.3 Hz), 120.7 (q, *J* = 267.8 Hz), 115.8, 110.3 (q, *J* = 3.6 Hz), 60.5, 33.6 (q, *J* = 2.2 Hz), 14.3. **HRMS (EI)** calcd. for $C_9H_{10}F_3NO_2$ $[M]^+$: 221.0664, found: 221.0658. **IR (KBr)**: 2983, 2932, 1716, 1548, 1497, 1467, 1401, 1257, 1152, 1114, 1076, 927, 913, 797, 756 cm^{-1}.

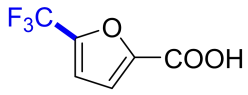
Methyl 5-(trifluoromethyl)furan-2-carboxylate (3j)[9]



3j

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 40:1) to afford **3j** (72.8mg, 75%) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 3.7 Hz, 1H), 6.87 (d, *J* = 3.1 Hz, 1H), 3.91 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.62 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 146.3 (q, *J* = 1.8 Hz), 144.6 (q, *J* = 43.3 Hz), 118.3 (q, *J* = 268.1 Hz), 117.5, 112.8 (q, *J* = 2.8 Hz), 52.4. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_7H_5F_3O_3$ 194.0; found 194.0.

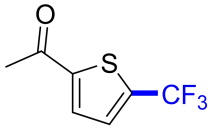
5-(Trifluoromethyl)furan-2-carboxylic acid (3k)[9]



3k

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 4:1) to afford **3k** (47.3mg, 53%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.35 (dd, *J* = 3.6, 1.0 Hz, 1H), 6.94 (dd, *J* = 3.6, 1.1 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.61 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 145.7 (q, *J* = 43.5 Hz), 145.4, 119.7, 118.15 (q, *J* = 268.6 Hz), 113.1 (q, *J* = 2.7 Hz). **LRMS (ESI)** m/z: $[M]^+$ calcd. for $C_6H_3F_3O_3$ 180.0; found 180.0.

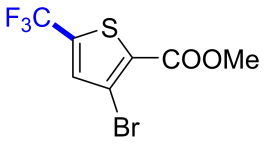
1-(5-(Trifluoromethyl)thiophen-2-yl)ethan-1-one (3l)[11]



3l

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 10:1) to afford **3l** (57.9mg, 48%) as light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 5.2 Hz, 1H), 7.36 (d, *J* = 5.2 Hz, 1H), 2.63 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.89(s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.05, 143.04 (q, *J* = 2.8 Hz), 132.03 (q, *J* = 35.8 Hz), 130.43, 128.42 (q, *J* = 4.5 Hz), 121.48 (q, *J* = 271.7 Hz), 29.28 (q, *J* = 2.2 Hz). **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_7H_8BrF_3O_2S$ 194.0; found 194.1.

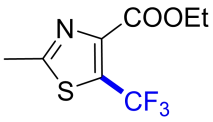
Methyl 3-bromo-5-(trifluoromethyl)thiophene-2-carboxylate (3m)[9]



3m

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 50:1) to afford **3m** (70.6mg, 49%) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 3.93 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.12(s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 135.8 (q, J = 39.7 Hz), 133.5 (q, J = 3.6 Hz), 130.3, 121.1 (q, J = 270.4 Hz), 116.2, 52.8. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_7H_8BrF_3O_2S$ 289.9; found 289.9.

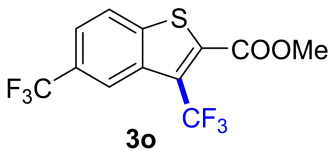
Ethyl 2-methyl-5-(trifluoromethyl)thiazole-4-carboxylate (3n)



3n

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 10:1) to afford **3n** (57.9mg, 48%) as light-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.44 (q, J = 7.1 Hz, 2H), 2.76 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -52.65(s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 160.0, 145.3 (q, J = 2.4 Hz), 131.4 (q, J = 39.4 Hz), 121.0 (q, J = 270.6 Hz), 62.3, 19.3, 14.0. **HRMS (EI)** calcd. for $C_8H_8F_3NO_2S$ $[M]^+$: 239.0228, found: 239.0222. **IR (KBr)**: 2985, 2933, 1735, 1524, 1485, 1446, 1331, 1288, 1220, 1151, 1028, 913, 746 cm^{-1}.

Methyl 3,5-bis(trifluoromethyl)benzo[b]thiophene-2-carboxylate (3o)

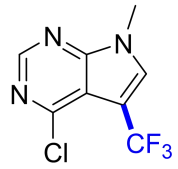


3o

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 20:1) to afford **3o** (73.6mg, 45%) as white solid (m.p. 82~83 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 4.01 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -55.78(s, 3F), -62.12(s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8, 142.2, 137.8 (d, J = 3.4 Hz), 135.1, 128.9 (q, J =

33.5 Hz), 127.3 (q, J = 36.0 Hz), 124.0 (q, *J* = 272.6 Hz), 121.6 (q, *J* = 274.0 Hz), 123.5 (q, J = 3.3 Hz), 123.4, 122.2 (p, *J* = 4.5 Hz), 53.6. **HRMS (EI)** calcd. for $C_{12}H_6F_6O_2S$ $[M]^+$: 327.9993, found: 327.9987. **IR (KBr)**: 3083, 2963, 2922, 2850, 1735, 1537, 1454, 1436, 1331, 1257, 1204, 1152, 1125, 827, 765, 743 cm^{-1}.

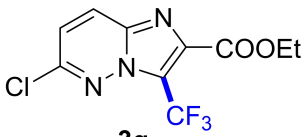
4-Chloro-7-methyl-5-(trifluoromethyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine(3p)



3p

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 50:1-30:1) to afford **3p** (61.8mg, 53%) as white solid (m.p. 53~54 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.03 (s, 1H), 3.96 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.31(s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.5, 153.0, 152.2, 129.0 (q, *J* = 38.7 Hz), 120.4 (q, *J* = 269.1 Hz), 115.5, 101.9 (q, *J* = 4.3 Hz), 29.8 (q, *J* = 2.0 Hz). **HRMS (EI)** calcd. for $C_8H_5ClF_3N_3$ $[M]^+$: 235.0124, found: 235.0119. **IR (KBr)**: 3183, 2960,1596, 1557, 1537, 1481, 1349, 1281, 1250, 1203, 1153, 1132, 1047, 951, 862, 779 cm^{-1}.

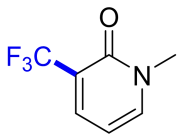
Ethyl 6-chloro-3-(trifluoromethyl) imidazo[1,2-*b*] pyridazine-2-carboxylate (3q)



3q

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 5:1-3:1) to afford **3q** (70.2mg, 48%) as off-white solid (m.p. 193~194 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.6 Hz, 1H), 7.32 (d, *J* = 9.6 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.40 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 149.8, 137.9, 137.2, 128.3, 123.1, 119.4 (q, *J* = 270.3 Hz), 119.4 (q, *J* = 42.4 Hz), 62.5, 14.1. **HRMS (EI)** calcd. for $C_{10}H_7ClF_3N_3O_2$ $[M]^+$: 293.0179, found: 293.0173. **IR (KBr)**: 3075, 3018, 1722, 1529, 1477, 1459, 1376, 1307, 1285, 1241, 1171, 1130, 1107, 863, 792, 758, 748, cm^{-1}.

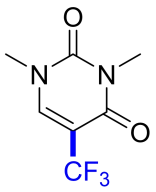
1-Methyl-3-(trifluoromethyl)pyridin-2(1*H*)-one (3r)[12]



3r

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 3:1-1:1) to afford **3r** (44.7mg, 50%) as off-white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.3, 2.4 Hz, 1H), 7.53 (dd, *J* = 6.8, 2.1 Hz, 1H), 6.22 (t, *J* = 6.9 Hz, 1H), 3.57 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.05 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 142.3, 138.9 (q, *J* = 5.1 Hz), 122.8 (q, *J* = 271.4 Hz), 120.3 (q, *J* = 30.9 Hz), 104.0, 37.8. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_7H_6F_3NO$ 177.0; found 177.0.

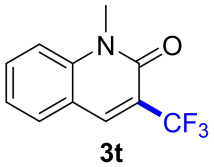
1,3-Dimethyl-5-(trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione (3s)[12]



3s

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 5:1-3:1) to afford **3s** (46.8mg, 45%) as light yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 3.47 (s, 3H), 3.34 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.85 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 150.9, 143.7 (q, *J* = 5.8 Hz), 122.0 (q, *J* = 269.8 Hz), 104.0 (q, *J* = 33.0 Hz), 37.7, 28.0. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_7H_7F_3N_2O_2$ 208.0; found 208.1.

1-Methyl-3-(trifluoromethyl)-2(1*H*)-quinolinone (3t)[13]

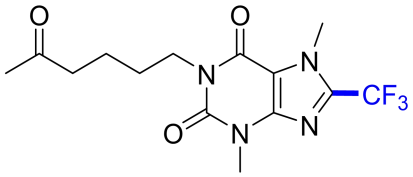


3t

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 5:1-3:1) to afford **3t** (58.1mg, 51%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.75 – 7.61 (m, 2H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 3.74 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.20 (s, 3F). **^{13}C NMR** (101

MHz, $CDCl_3$) δ 158.0, 141.0, 138.9 (q, J = 5.2 Hz), 133.2, 130.4, 122.9, 122.4 (q, J = 272.0 Hz), 121.2 (q, J = 30.5 Hz), 118.1, 114.4, 29.5. **LRMS (EI)** m/z: $[M]^+$ calcd. For $C_{11}H_8F_3NO$ 227.1; found 227.1.

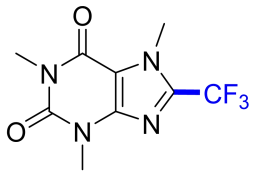
3,7-Dimethyl-1-(5-oxohexyl)-8-(trifluoromethyl)-3,7-dihydro-1H-purine-2,6-dione (3u)[12]



3u

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 3:1) to afford **3u** (71.9mg, 42%) as light yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.09 (s, 3H), 3.95 (t, J = 6.8 Hz, 2H), 3.51 (s, 3H), 2.44 (t, J = 6.7 Hz, 3H), 2.08 (s, 2H), 1.61 – 1.56 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.51 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.5, 155.2, 151.0, 146.5, 138.8 (q, J = 39.7 Hz), 118.2 (q, J = 271.3 Hz), 109.6, 43.0, 41.0, 33.1 (q, J = 2.2 Hz), 29.9, 29.7, 27.2, 20.8. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_{14}H_{17}F_3N_4O_3$ 346.1; found 346.1.

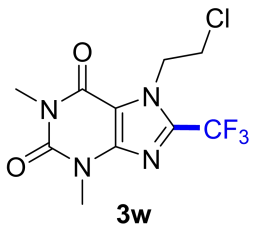
1,3,7-Trimethyl-8-(trifluoromethyl)-3,7-dihydro-1*H*-purine-2,6-dione (3v)[7]



3v

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 4:1) to afford **3v** (64.6mg, 49%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.12 (s, 3H), 3.54 (s, 3H), 3.37 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.50 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.4, 151.3, 146.5, 138.9 (q, J = 40.0 Hz), 118.2 (q, J = 271.2 Hz), 109.6, 33.1 (q, J = 2.3 Hz), 29.8, 28.1. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_9H_9F_3N_4O_2$ 262.1; found 262.1.

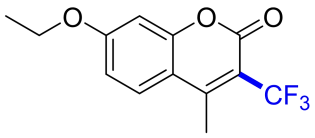
7-(2-Chloroethyl)-1,3-dimethyl-8-(trifluoromethyl)-3,7-dihydro-1*H*-purine-2,6-dione (3w)[12]



3w

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 4:1-2:1) to afford **3w** (50.6mg, 33%) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.75 (t, *J* = 6.4 Hz, 2H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.59 (s, 3H), 3.40 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.59 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.1, 151.2, 147.1, 139.3 (q, *J* = 40.2 Hz), 118.1 (q, *J* = 271.8 Hz), 109.0, 47.9 (q, *J* = 1.9 Hz), 41.7, 30.0, 28.3. **LRMS (EI)** m/z: $[M]^+$ calcd. for $C_{10}H_{10}ClF_3N_4O_2$ 310.0; found 310.1.

7-Ethoxy-4-methyl-3-(trifluoromethyl)-2*H*-chromen-2-one (3x)



3x

The product mixture was purified by column chromatography on silica gel (PE/EtOAc = 20:1) to afford **3x** (111.3mg, 82%) as white solid (m.p. 88~89 ℃). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 9.0 Hz, 1H), 6.86 (d, *J* = 9.1 Hz, 1H), 6.69 – 6.68 (m, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 2.58 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.35 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 156.3, 155.2, 155.1, 127.2, 123.2 (q, *J* = 274.7 Hz), 113.6, 112.2, 111.7 (q, *J* = 30.1 Hz), 100.8, 64.5, 15.6 (q, *J* = 4.1 Hz), 14.4. **HRMS (EI)** calcd for $C_{13}H_{11}F_3O_3$ $[M]^+$: 272.0660, found: 272.0655. **IR (KBr)**: 3063, 2992, 2908, 1719, 1622, 1596, 1556,1385,1186, 1139, 1112, 842, 825, 773 cm^{-1}.

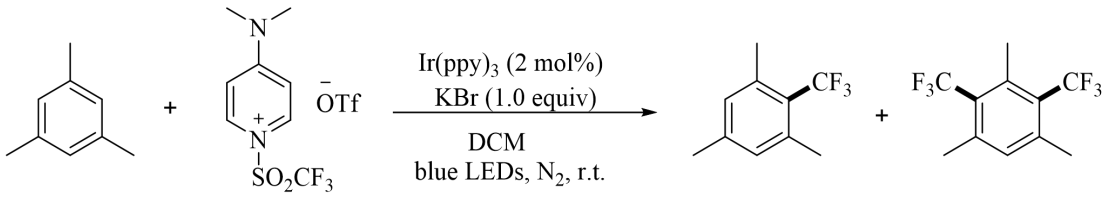
6. Preliminary Mechanistic Studies

6.1 Radical Trapping Experiments

Into a 15 mL Schlenk tube were added $Ir(ppy)_3$ (2.6 mg, 0.001 mmol, 2 mol%), KBr (1.3 mg, 1.0 equiv), **1** (161.7 mg, 0.4 mmol, 2.0 equiv.) and a radical scavenger (0.4

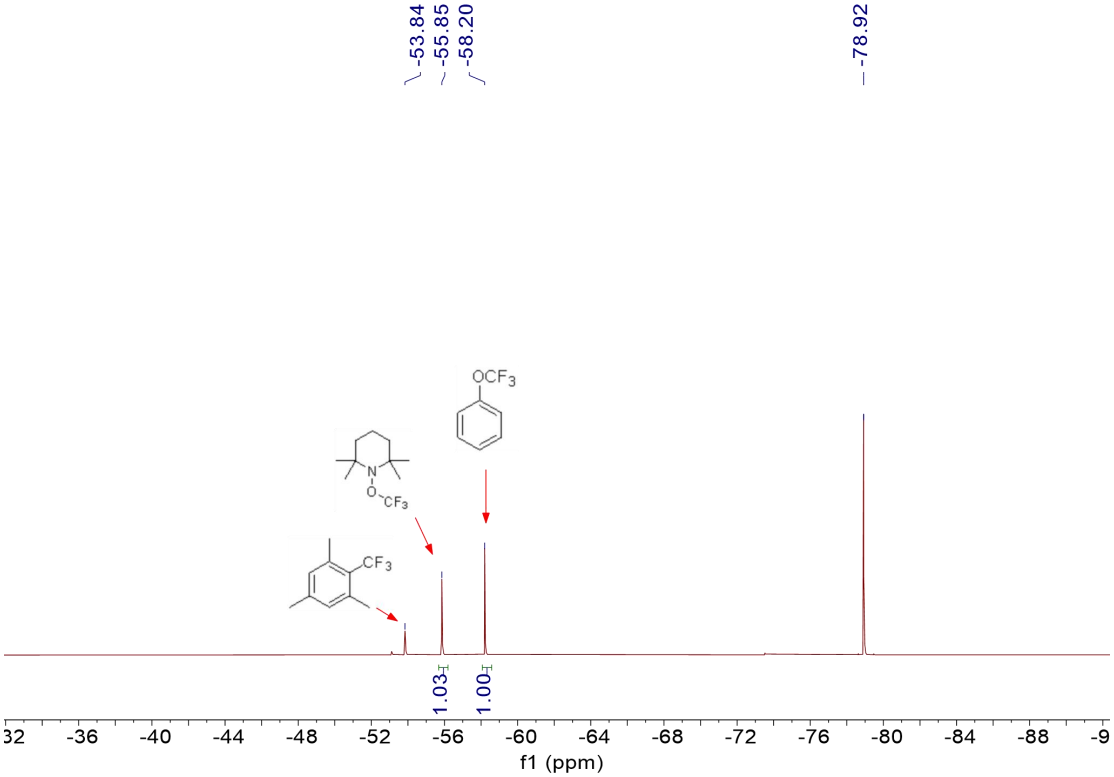
mmol, 2.0 equiv.) under a N_2 atmosphere. Then **2a** (20.8 mg, 0.2 mmol, 1.0 equiv.), and DCM (3 mL) were added. The resulting mixture was stirred at room temperature under the irradiation of 11.5 W blue LEDs for 12 h under a N_2 atmosphere. (Trifluoromethoxy)benzene (0.2 mmol), an internal standard, was added into the reaction mixture for the calculation of the yield of product **3a**.

Table S2. Radical Trapping Experiments.



2, 0.2 mmol **1** **3a-mono** **3a-bis**

In the case of TEMPO, ^{19}F NMR and GC-MS analysis of the reaction mixture revealed that TEMPO-CF_3 was produced (52% yield determined by ^{19}F NMR spectroscopy), which suggested the existence of trifluoromethylation radical. The ^{19}F NMR spectrum is shown as follows. Characterization data of TEMPO-CF_3: **^{19}F NMR** (376 MHz, $CDCl_3$) δ -55.8 (s, 3F). **LRMS (EI)** m/z: $[M]^+$ calcd for $C_{11}H_8F_3N$ 225.1; found 225.1.



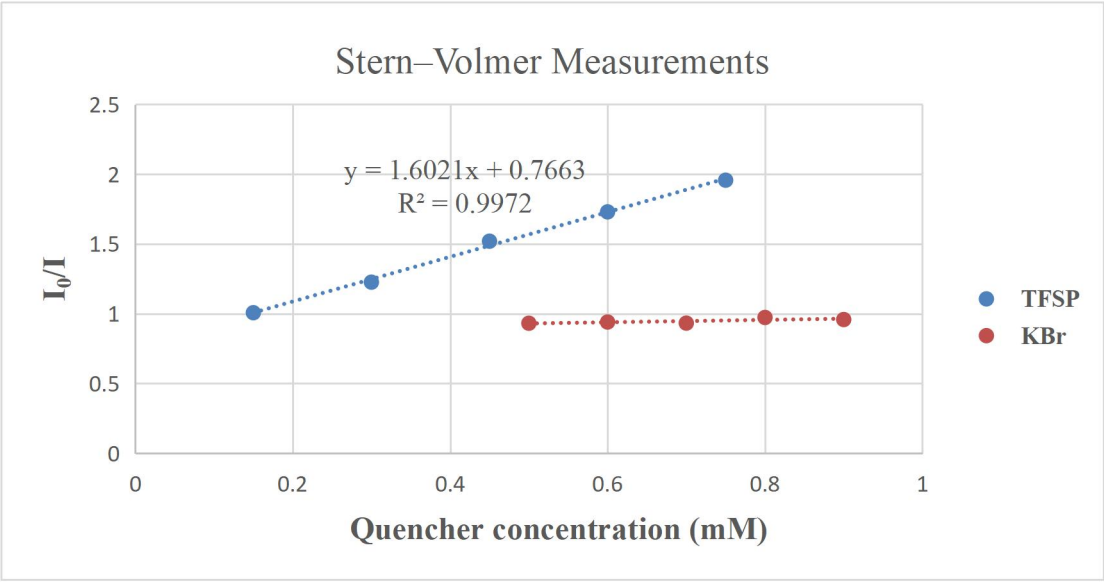
Scheme S1. The ^{19}F NMR of TEMPO-CF_3.

6.2 Stern–Volmer Measurements

Emission intensities were recorded using HITACHI F-2700 fluorescence spectrometer for all experiments. All $Ir(ppy)_3$ solutions were excited at 428 nm and emission intensity at 517 nm was collected.

Typical procedure for the preparation of a sample: Into a solution of $Ir(ppy)_3$ in MeCN (5×10^{-4} M, 5 mL) was added **1** (303 mg, 0.75 mmol) or KBr (29.7 mg, 0.25 mmol) under a N_2 atmosphere. 3 mL of the resulting solution (the concentration of **1** was 0.15 mM) was added into a screw top 1.0 cm quartz cuvette under a N_2 atmosphere. The emission spectra of five samples containing varied concentration of **1** (0, 0.15, 0.30, 0.45, 0.60 and 0.75 mM) and KBr (0.5, 0.6, 0.7, 0.8 and 0.9 mM) were collected.

I_0 is the luminescence intensity without the quencher and I is the intensity with the quencher. The emission quenching of $Ir(ppy)_3$ indicated that the photoexcited complex $Ir(ppy)_3$ could be easily quenched by **1** rather than KBr.



Scheme S2. $Ir(ppy)_3$ emission quenching with 1 and KBr

7. References

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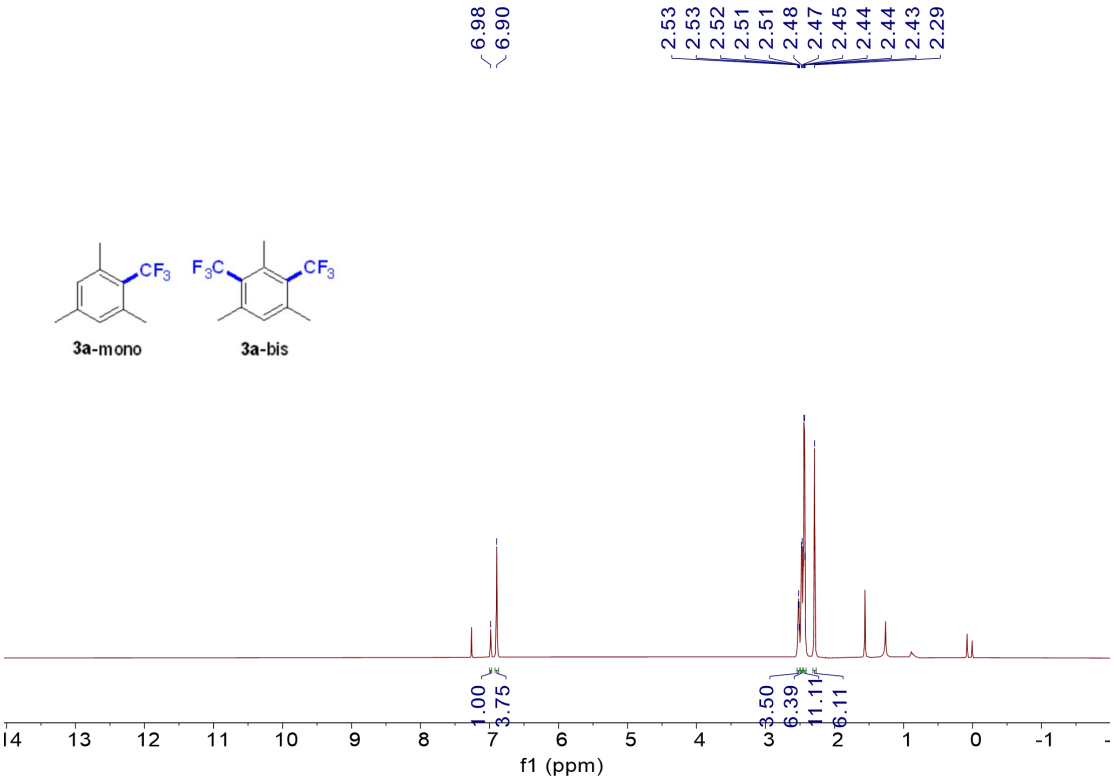
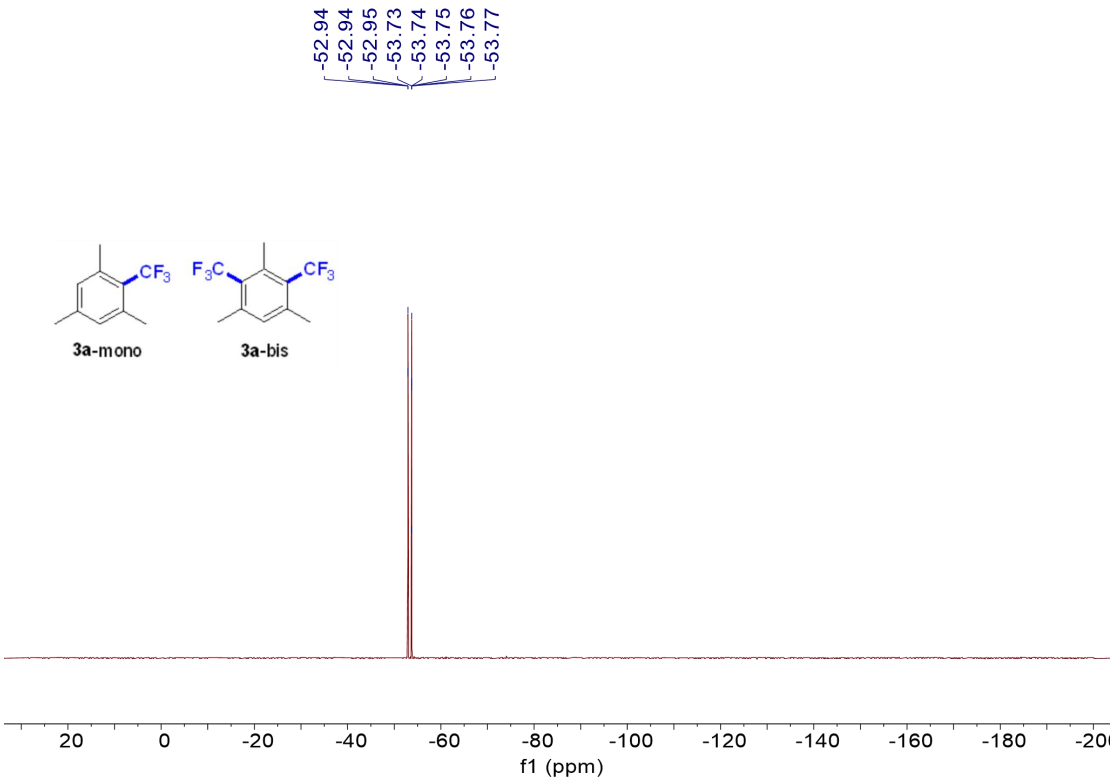
8. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra of Products

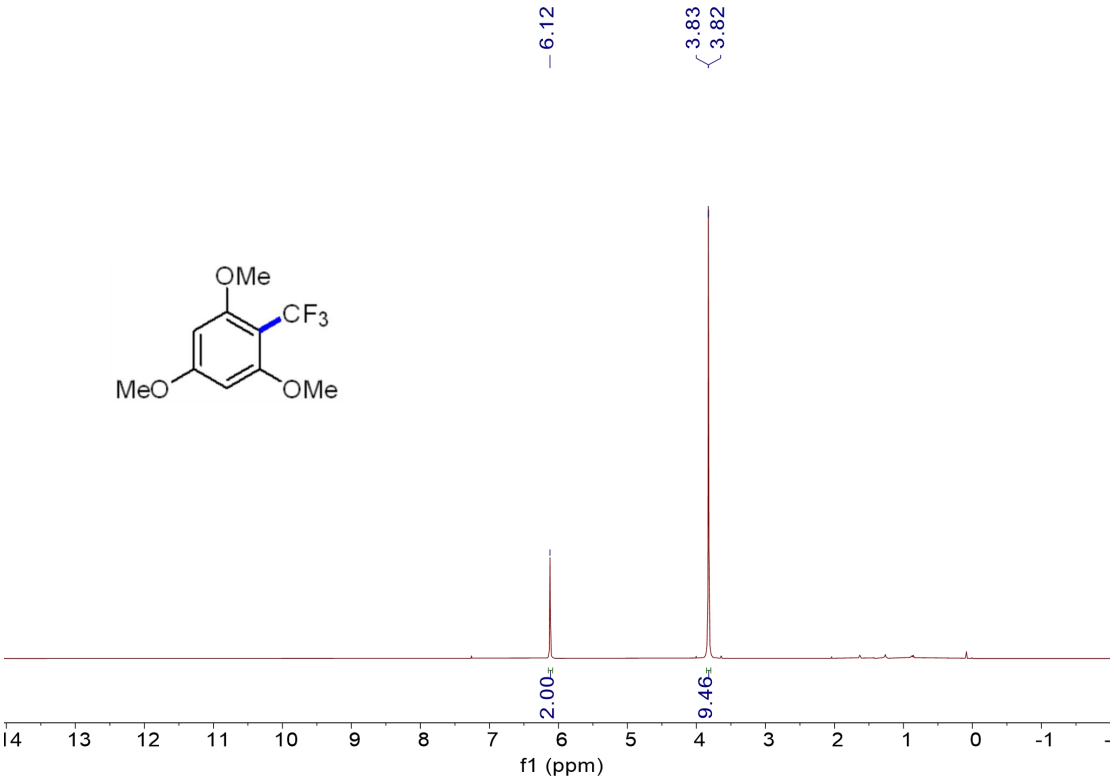
^{1}H NMR Spectrum of **3a**



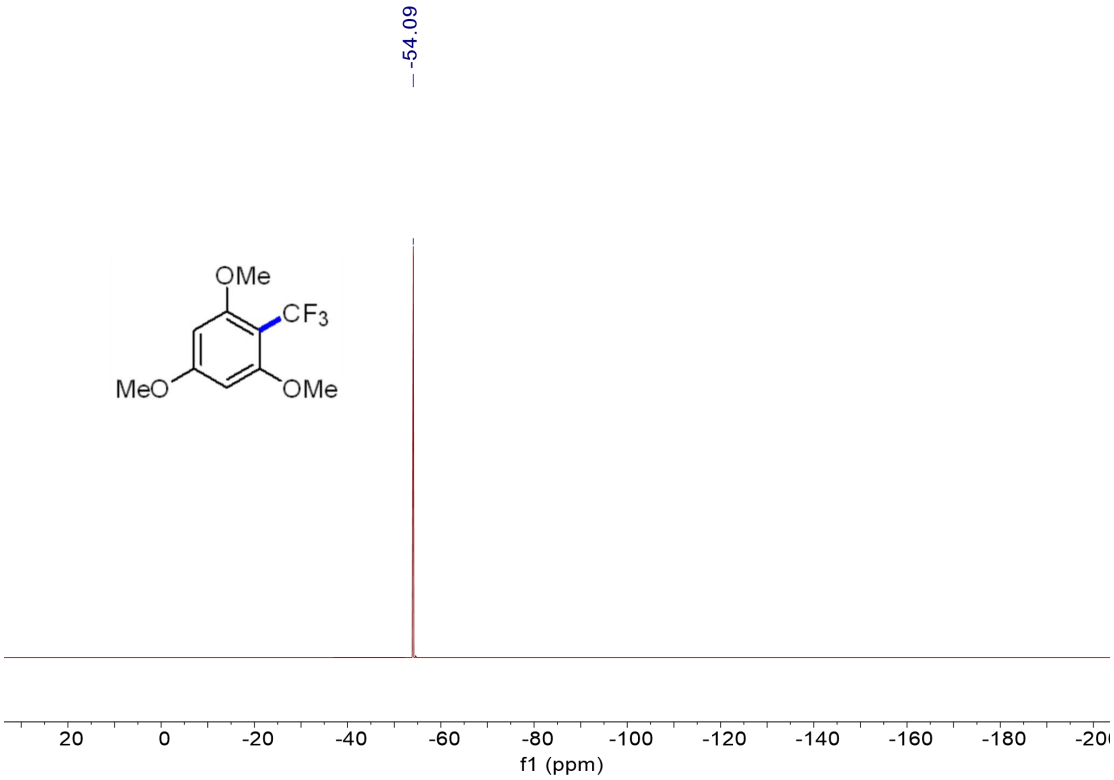
^{19}F NMR Spectrum of **3a**



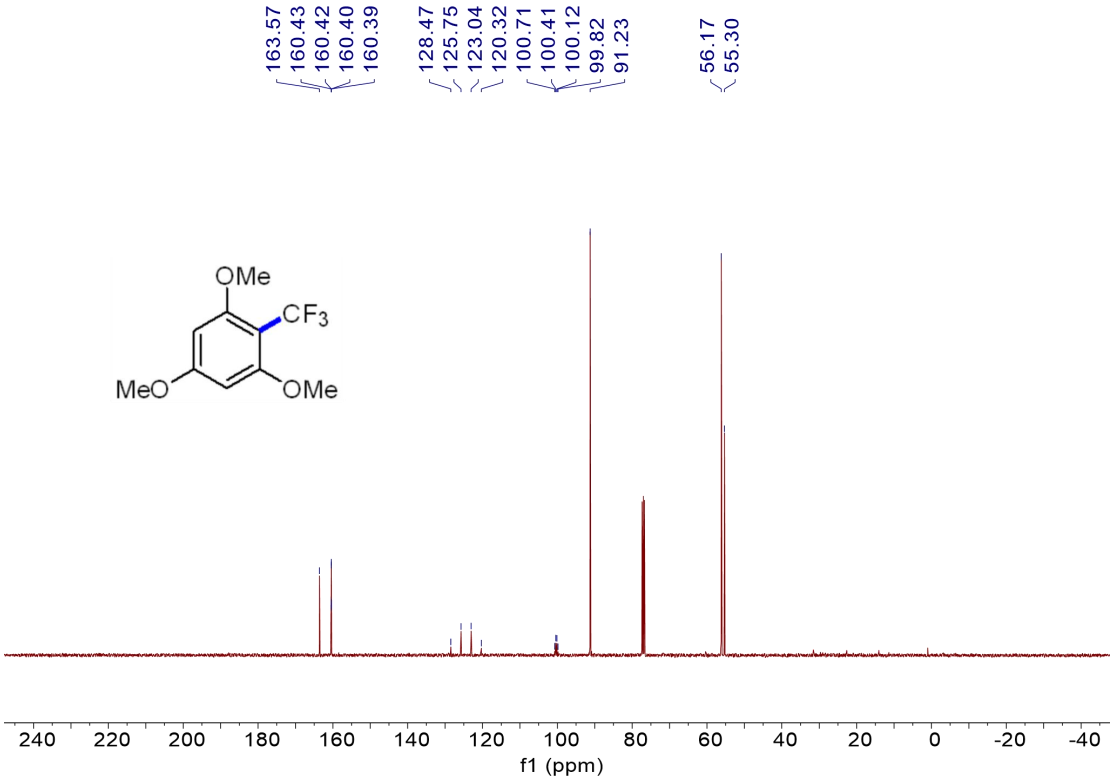
^{1}H NMR Spectrum of **3b**



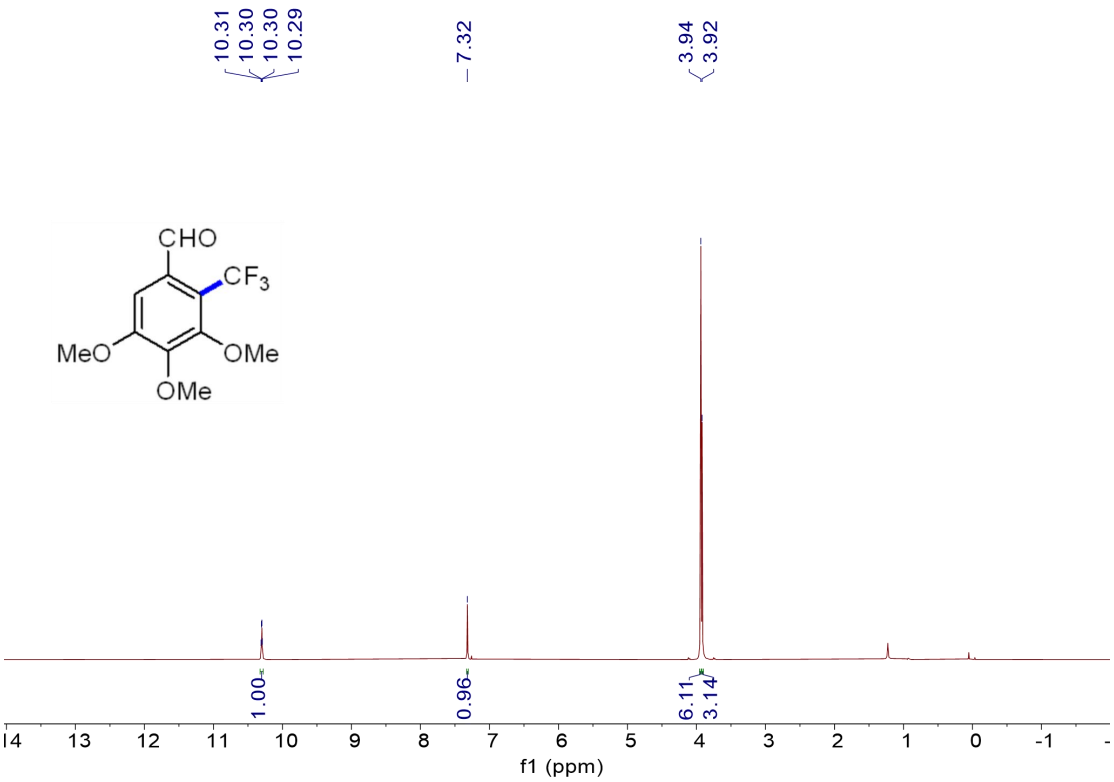
^{19}F NMR Spectrum of **3b**



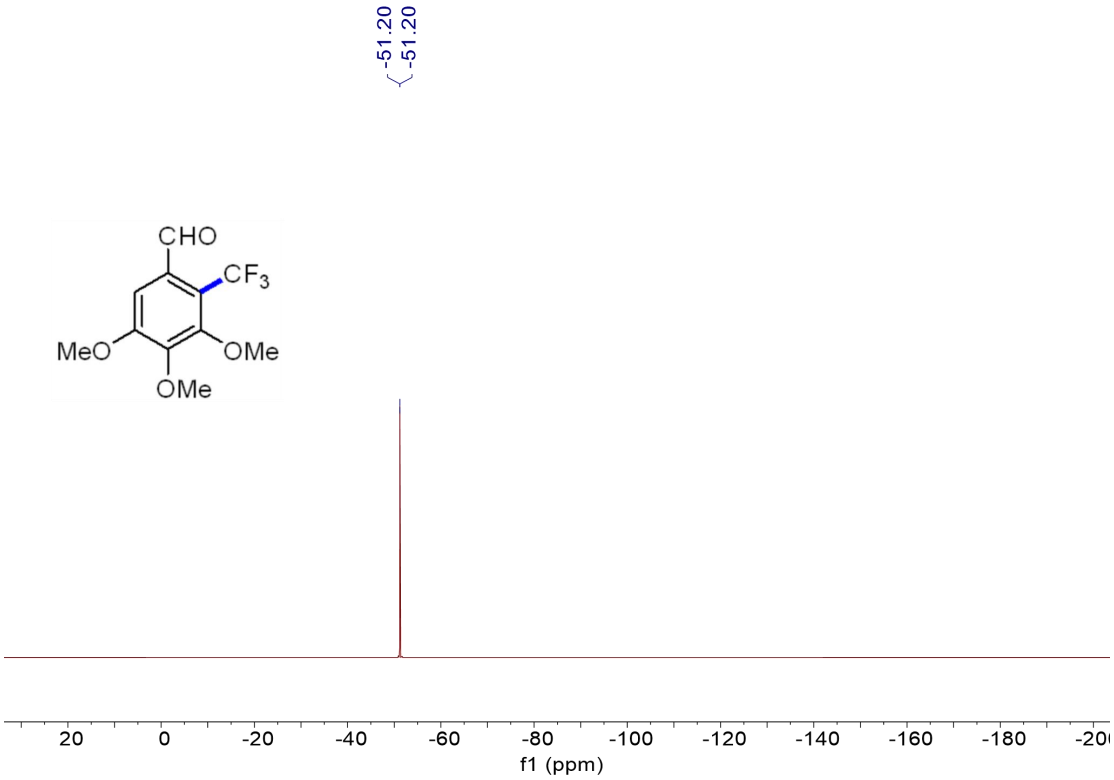
^{13}C NMR Spectrum of **3b**



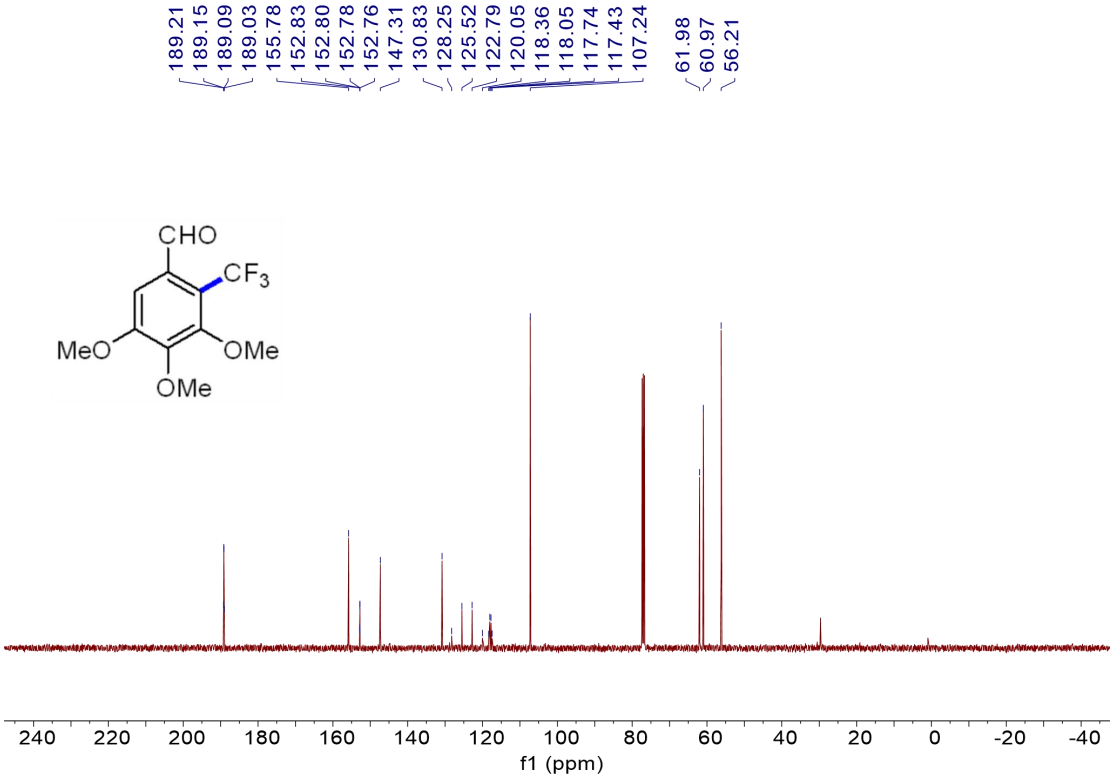
^{1}H NMR Spectrum of **3c**



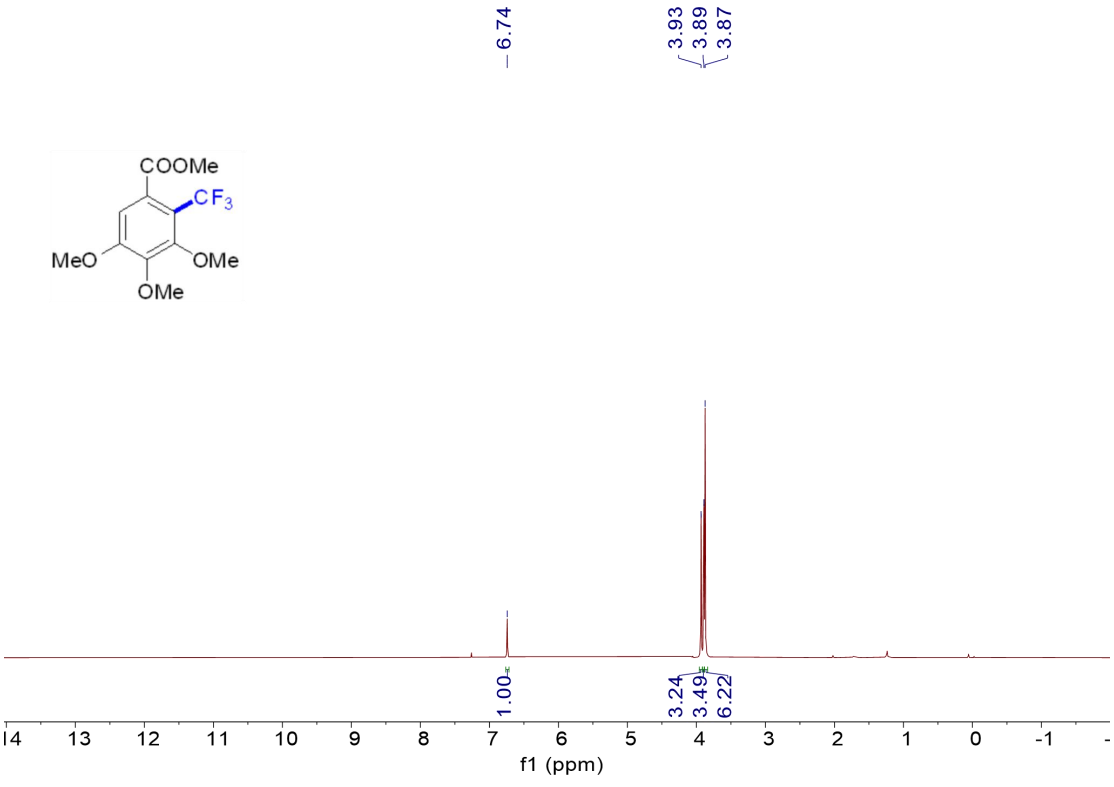
^{19}F NMR Spectrum of **3c**



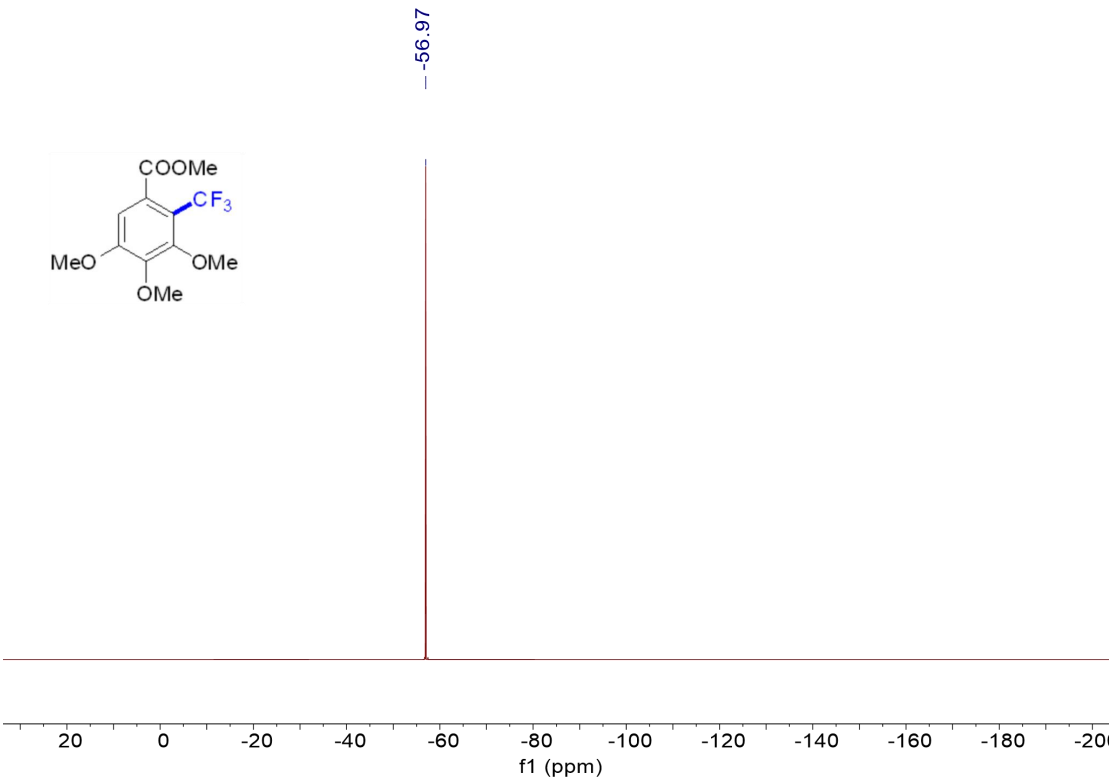
^{13}C NMR Spectrum of **3c**



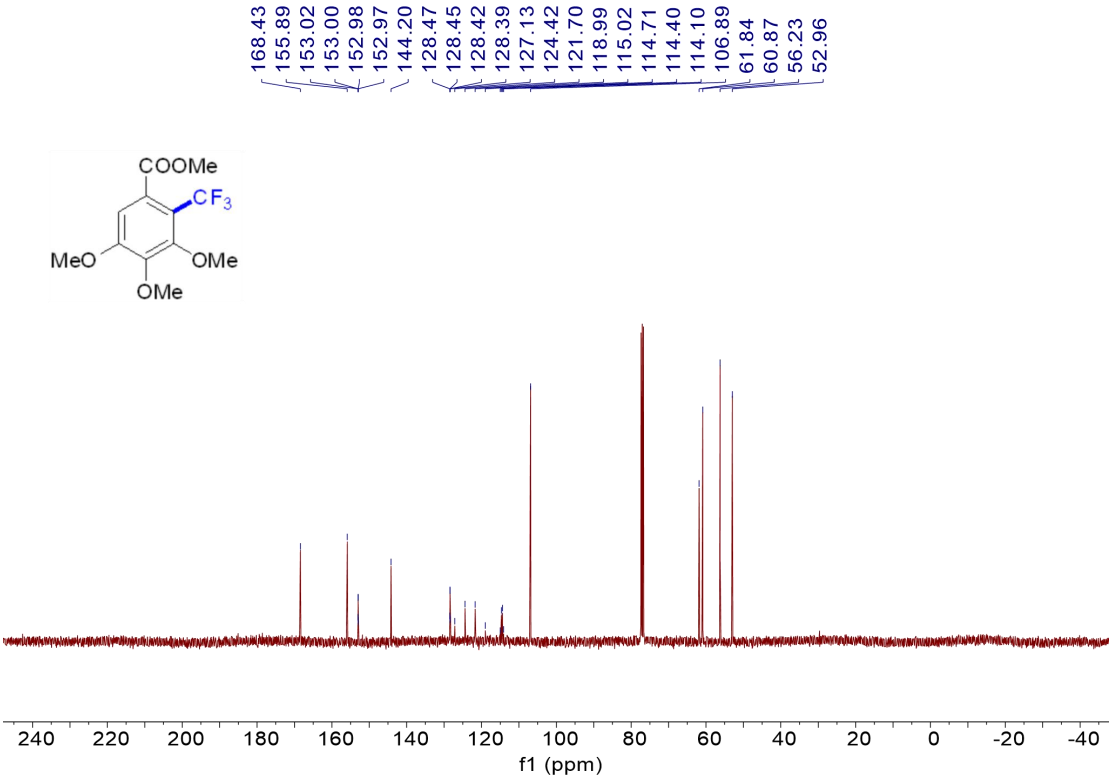
^{1}H NMR Spectrum of **3d**



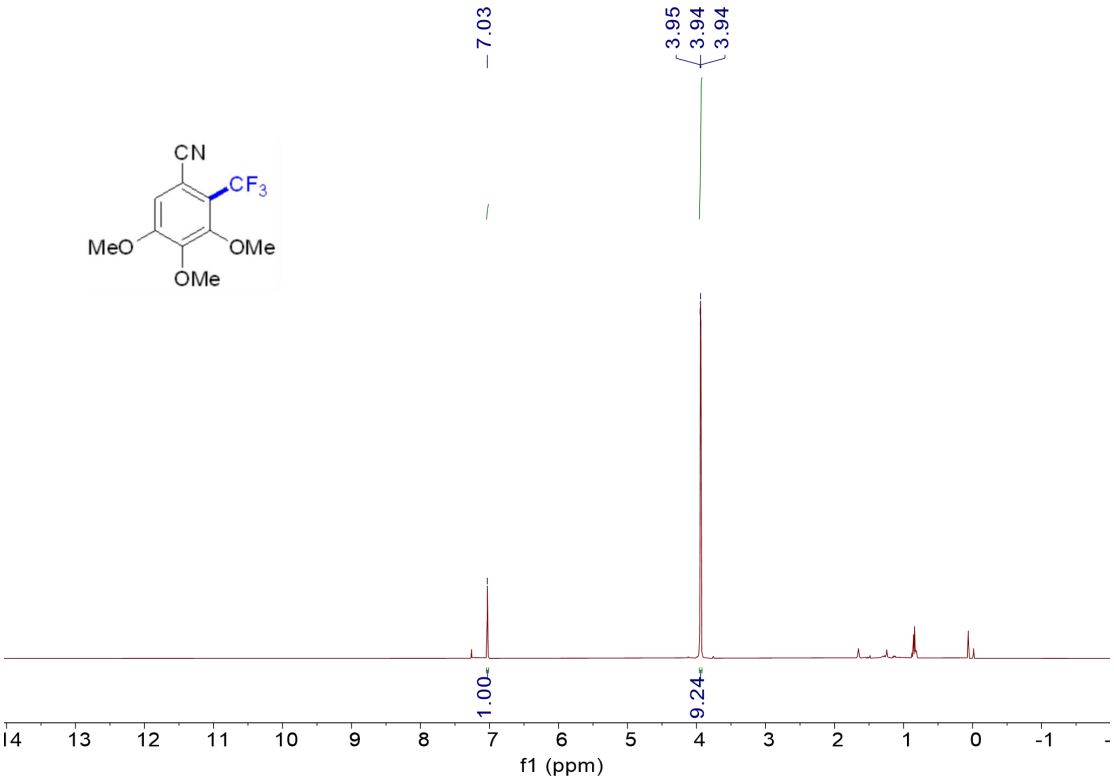
^{19}F NMR Spectrum of **3d**



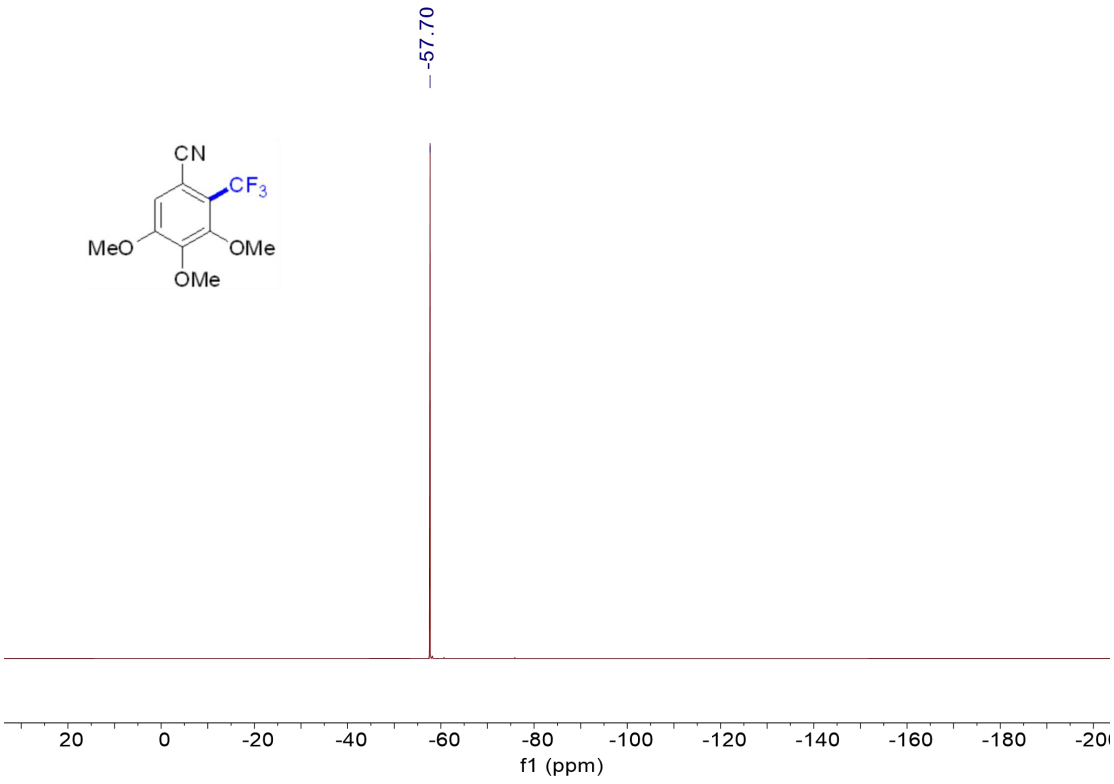
^{13}C NMR Spectrum of **3d**



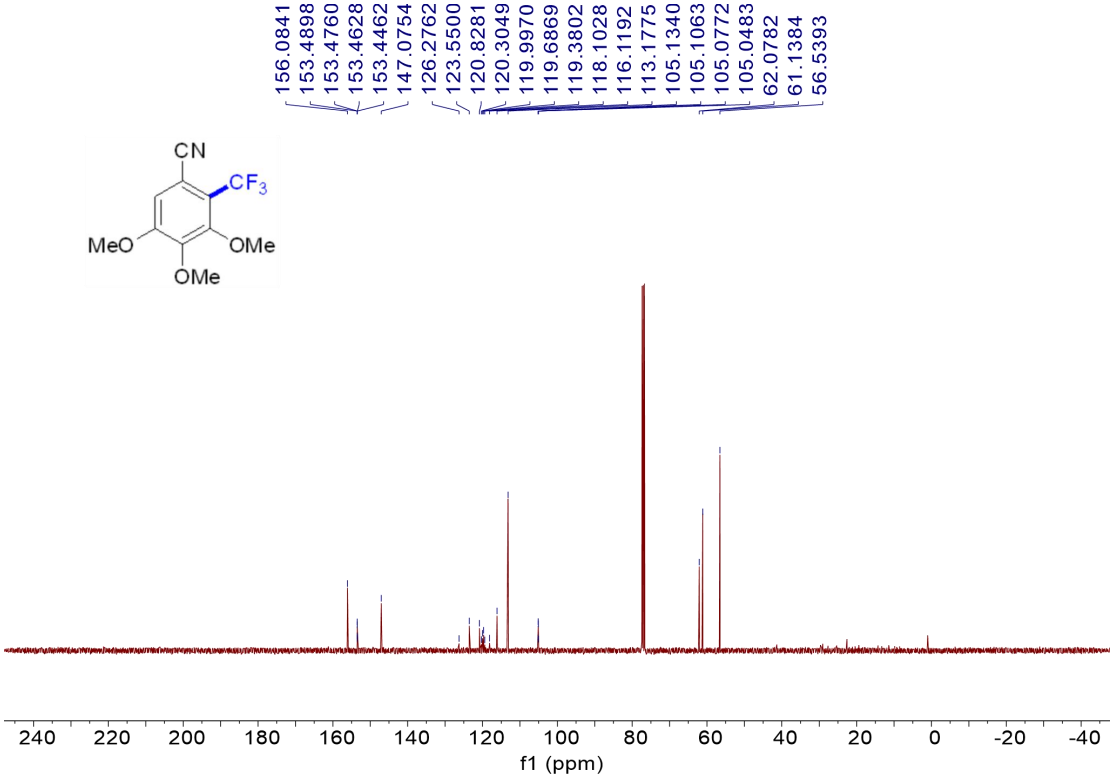
^{1}H NMR Spectrum of **3e**



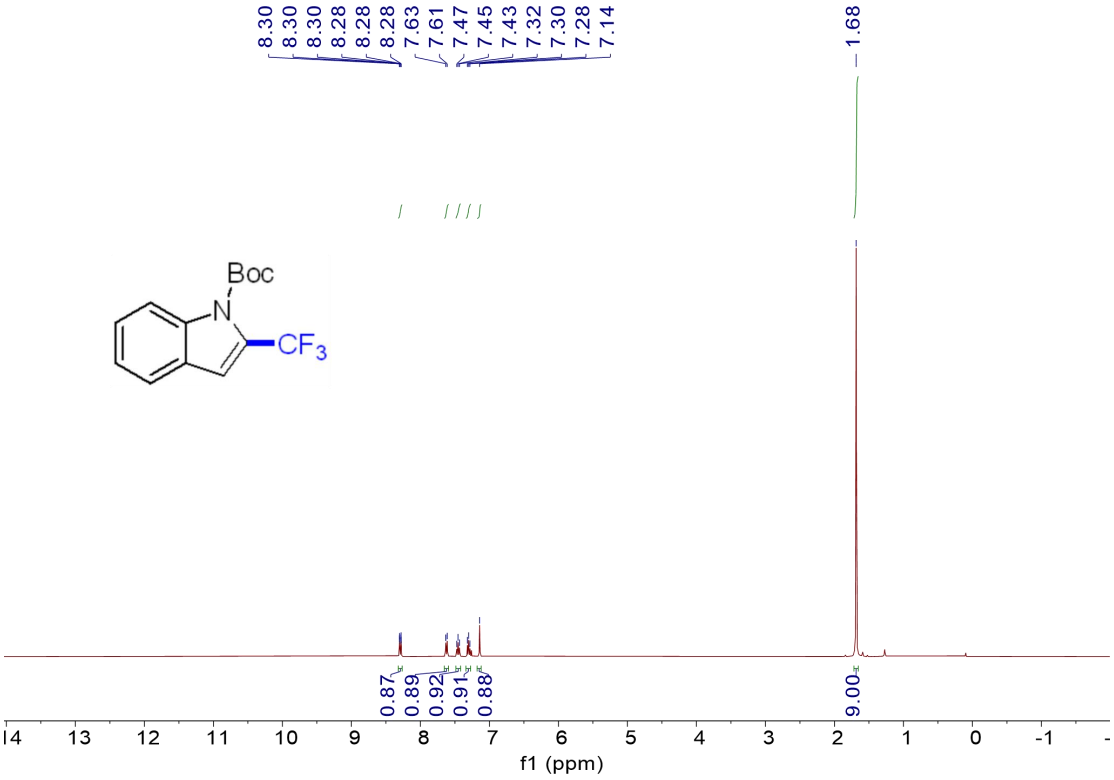
^{19}F NMR Spectrum of **3e**



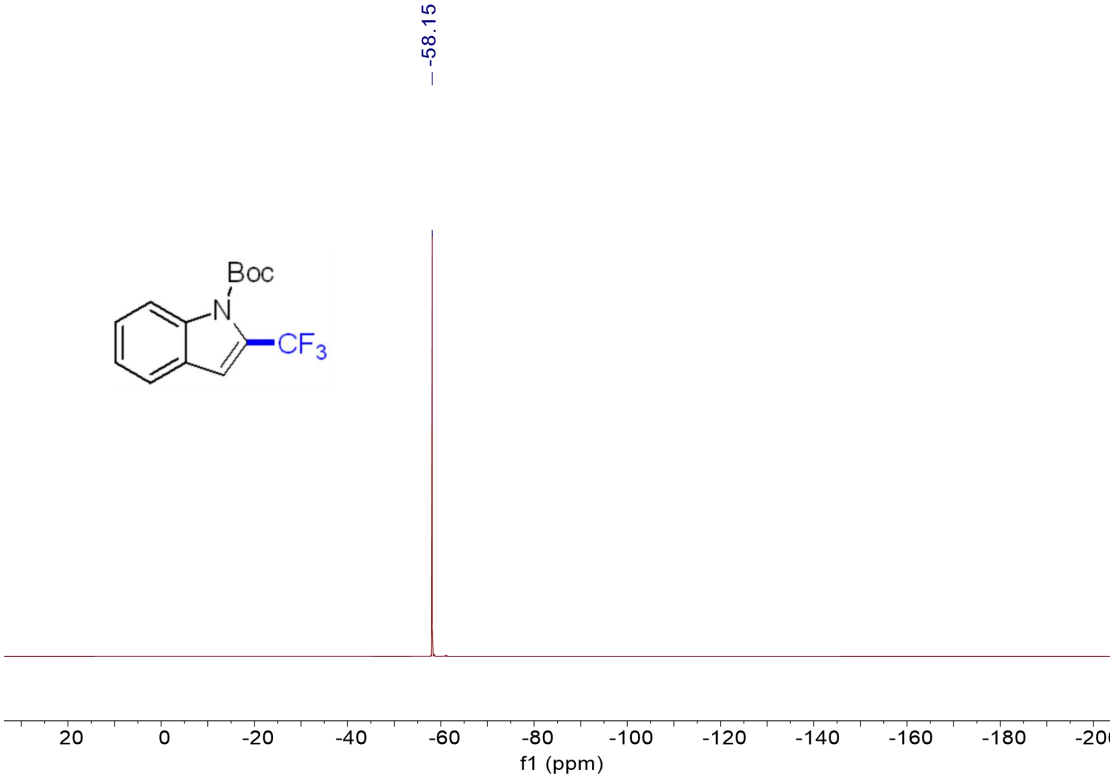
^{13}C NMR Spectrum of **3e**



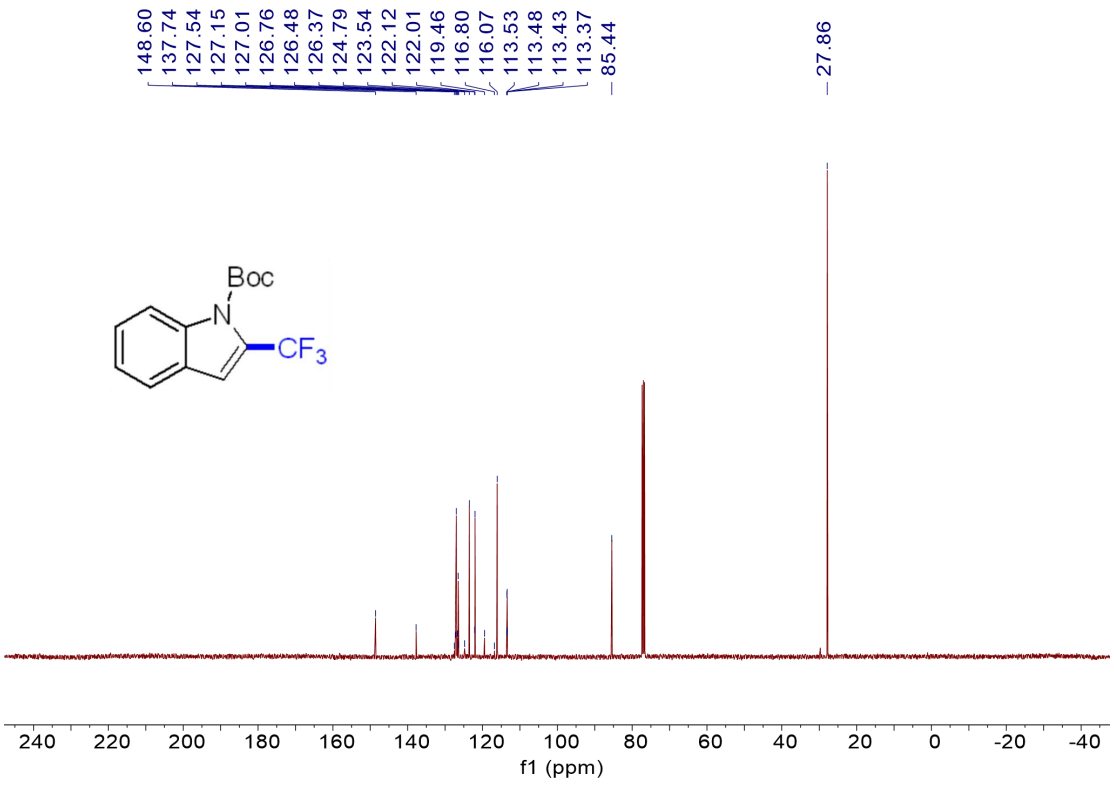
^{1}H NMR Spectrum of **3f**



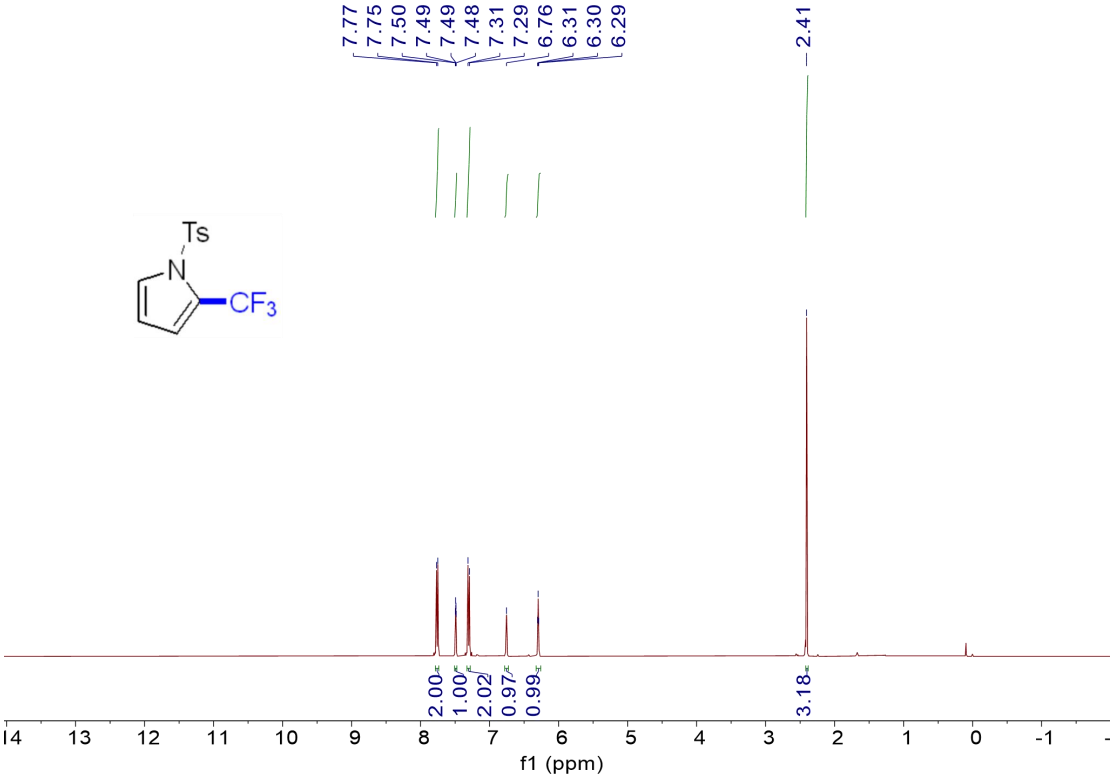
^{19}F NMR Spectrum of **3f**



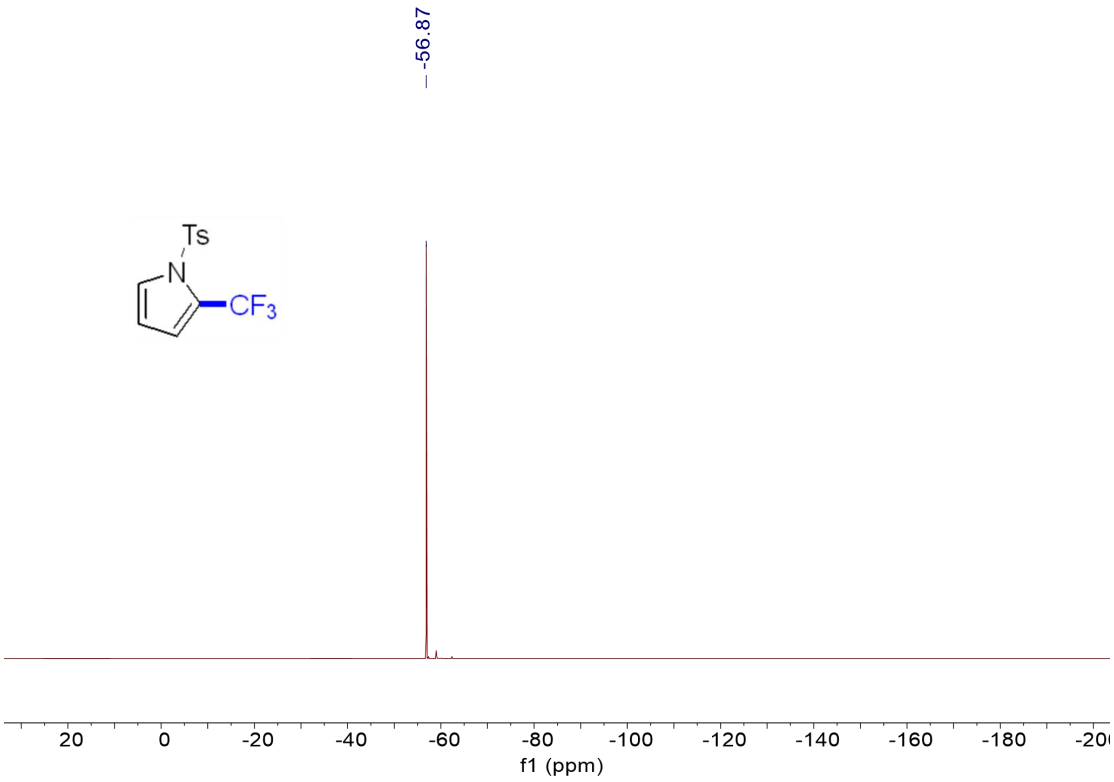
^{13}C NMR Spectrum of **3f**



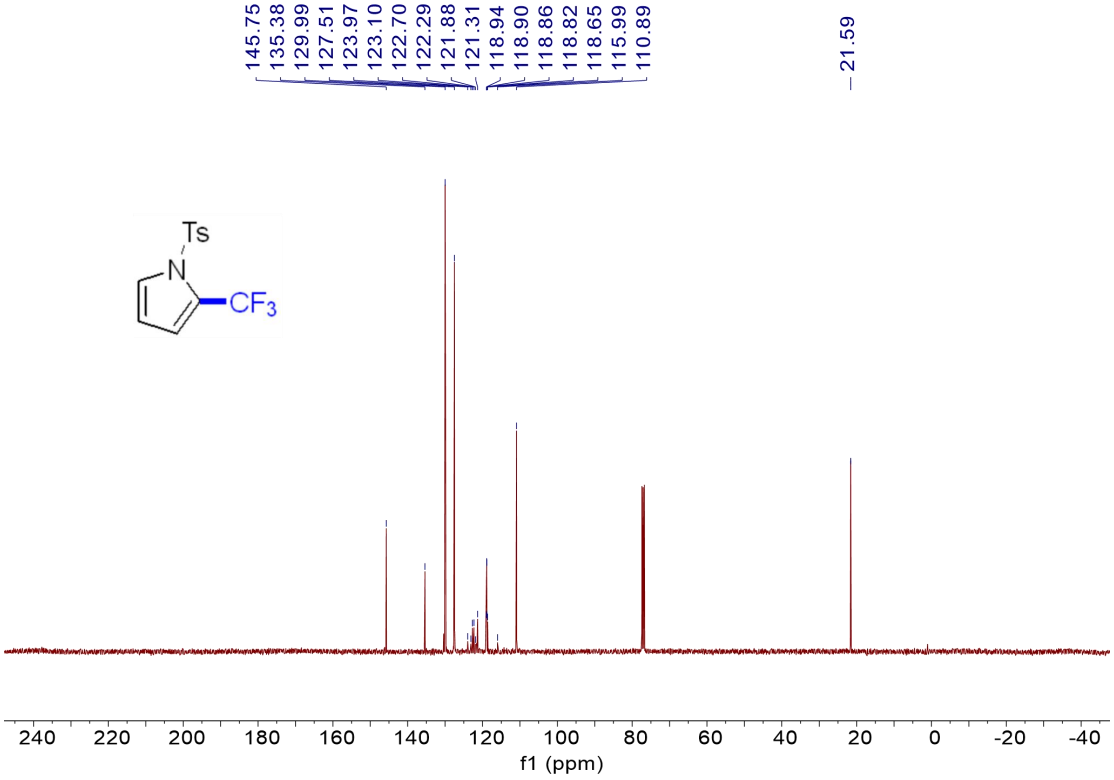
^{1}H NMR Spectrum of **3g**



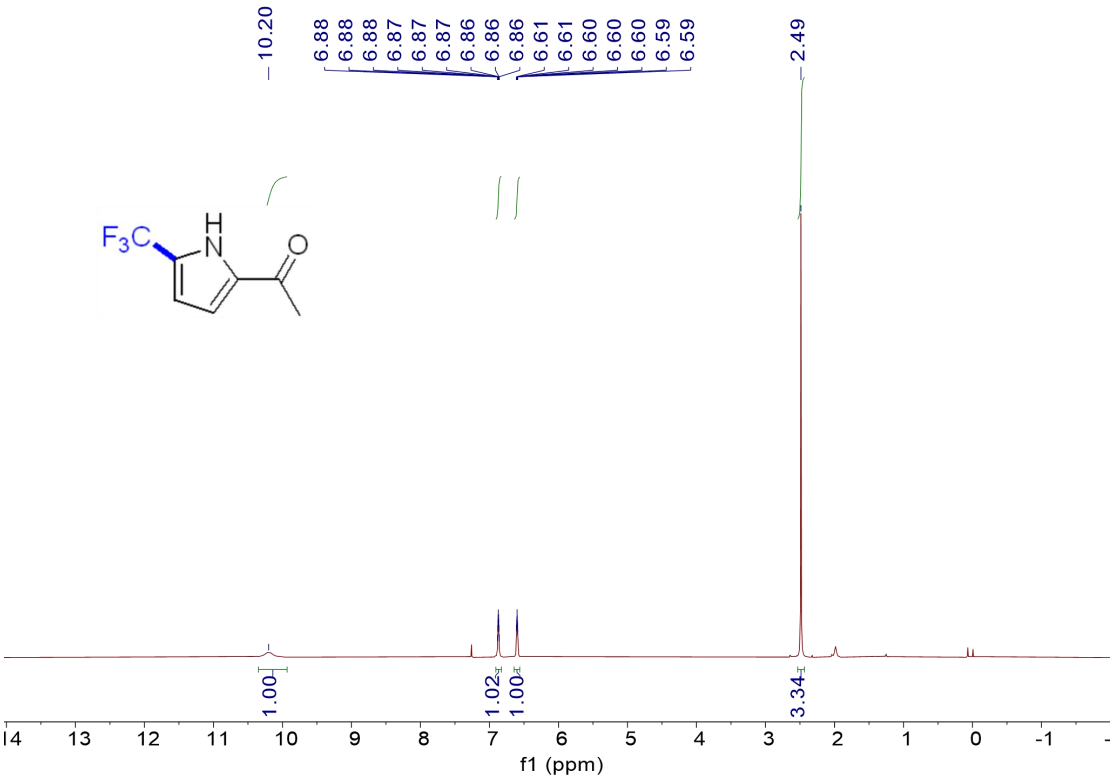
^{19}F NMR Spectrum of **3g**



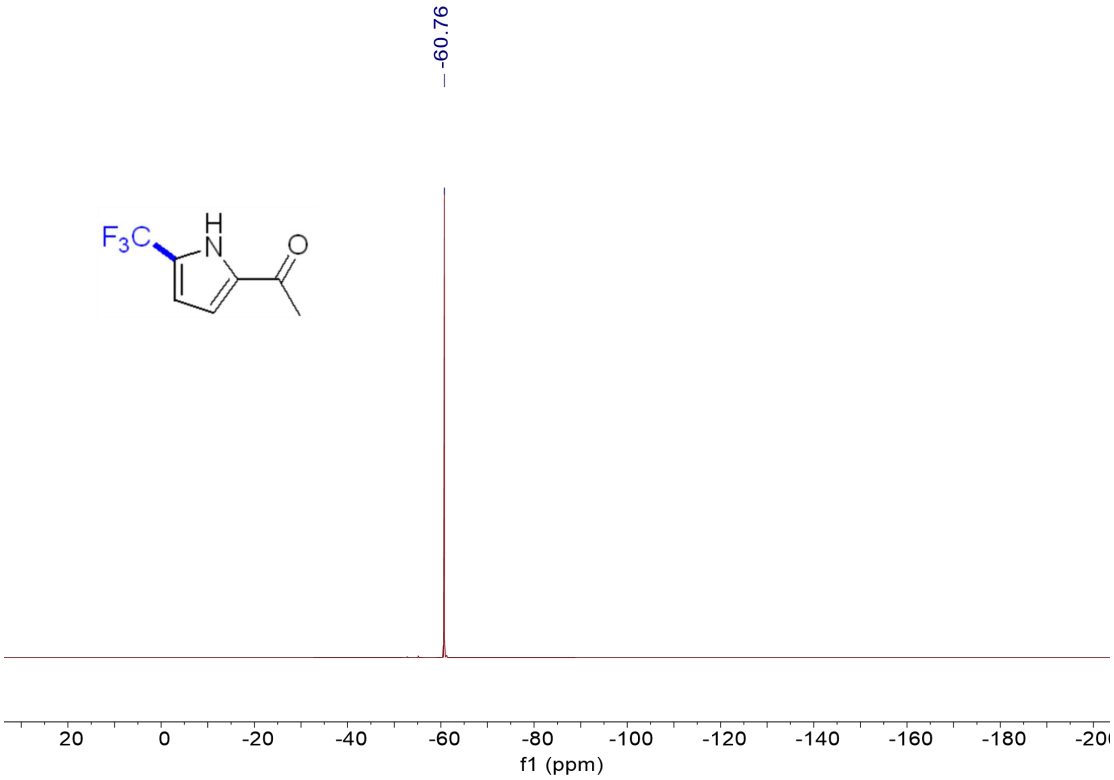
^{13}C NMR Spectrum of **3g**



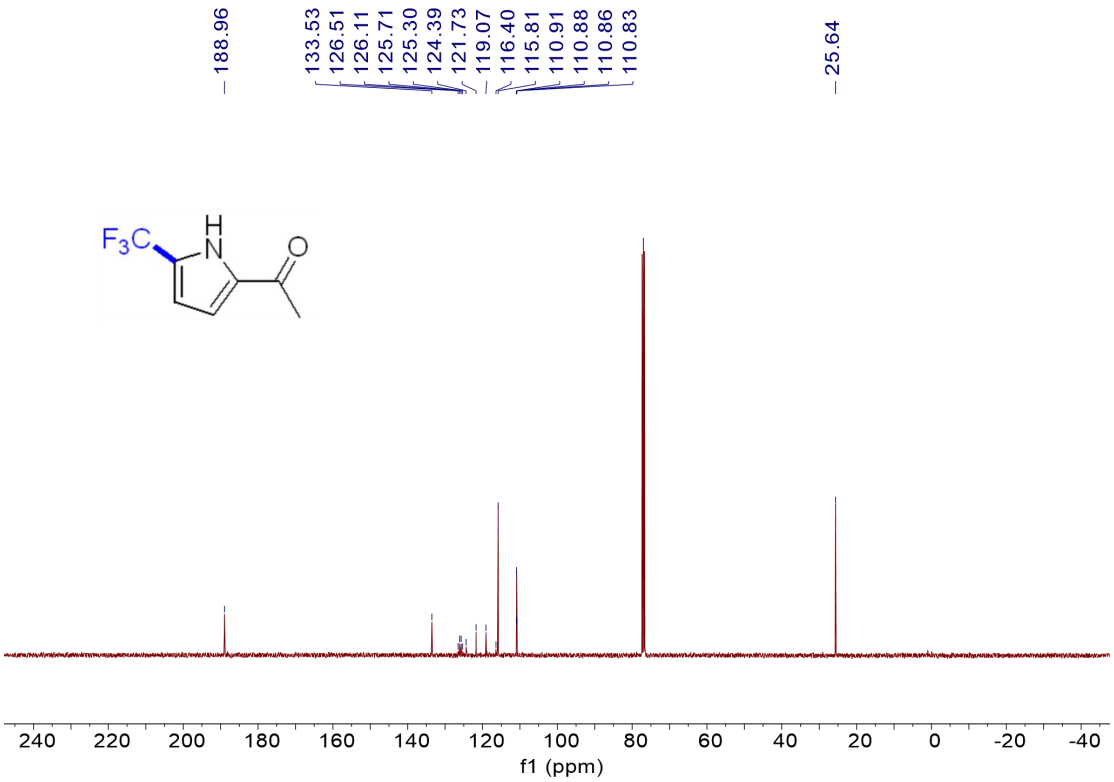
^{1}H NMR Spectrum of **3h**



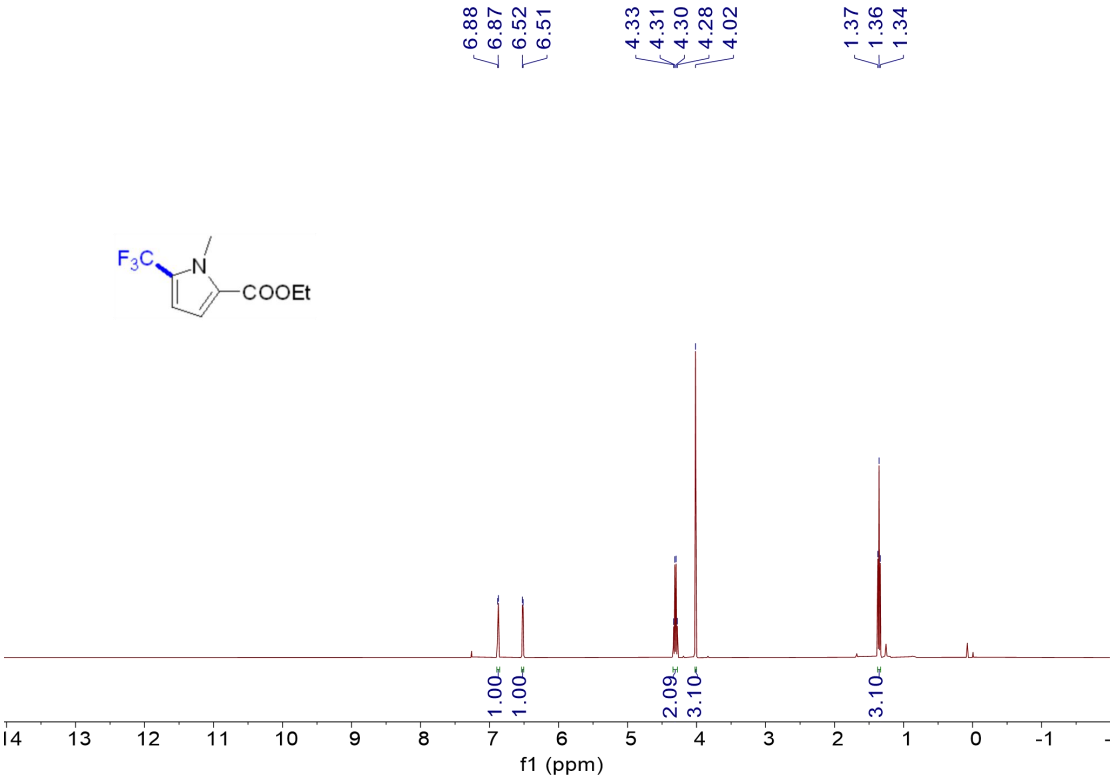
^{19}F NMR Spectrum of **3h**



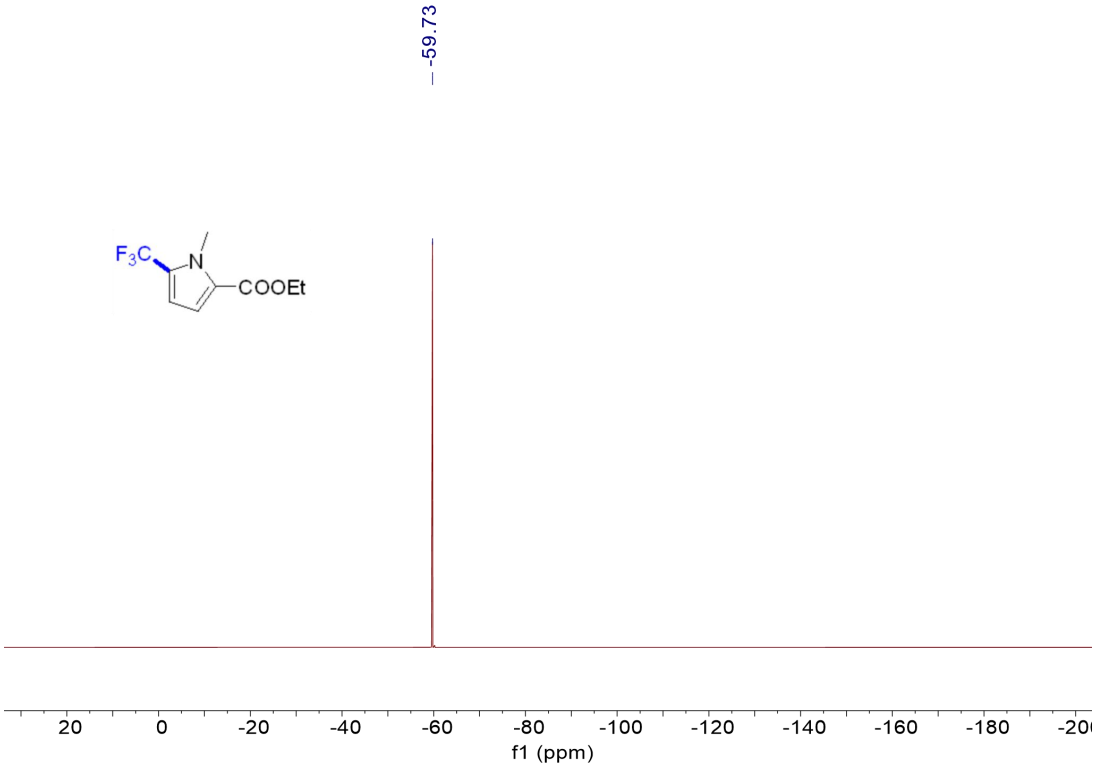
^{13}C NMR Spectrum of **3h**



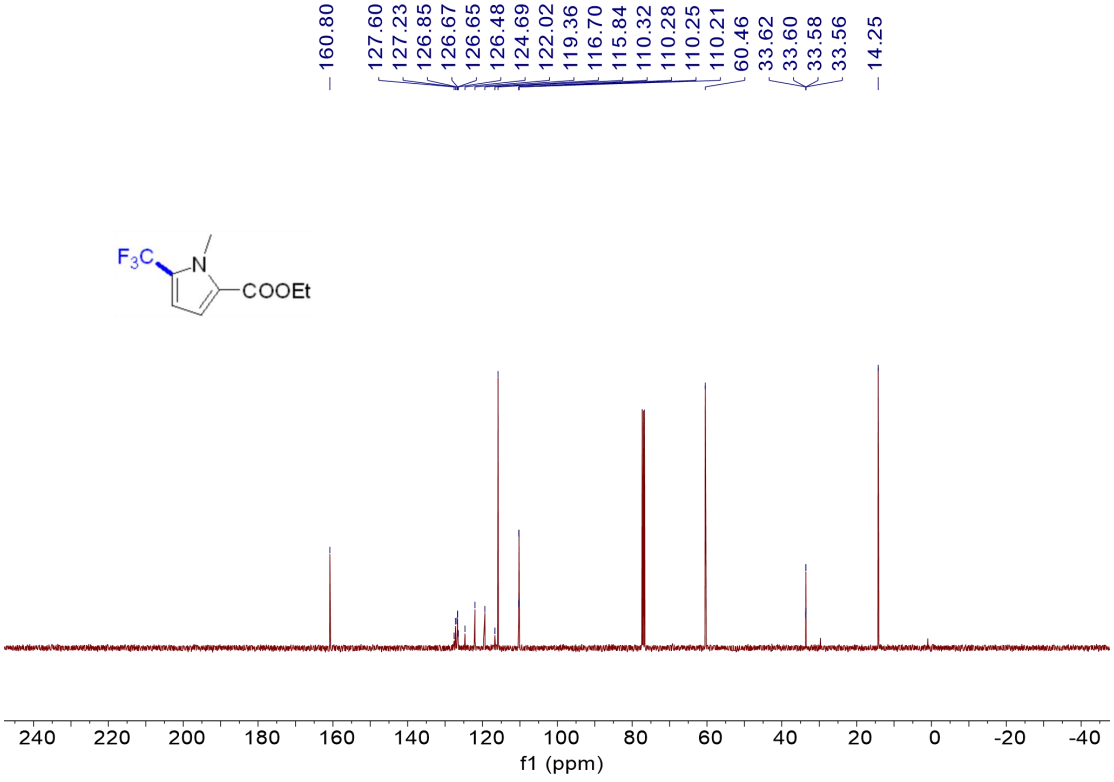
^{1}H NMR Spectrum of **3i**



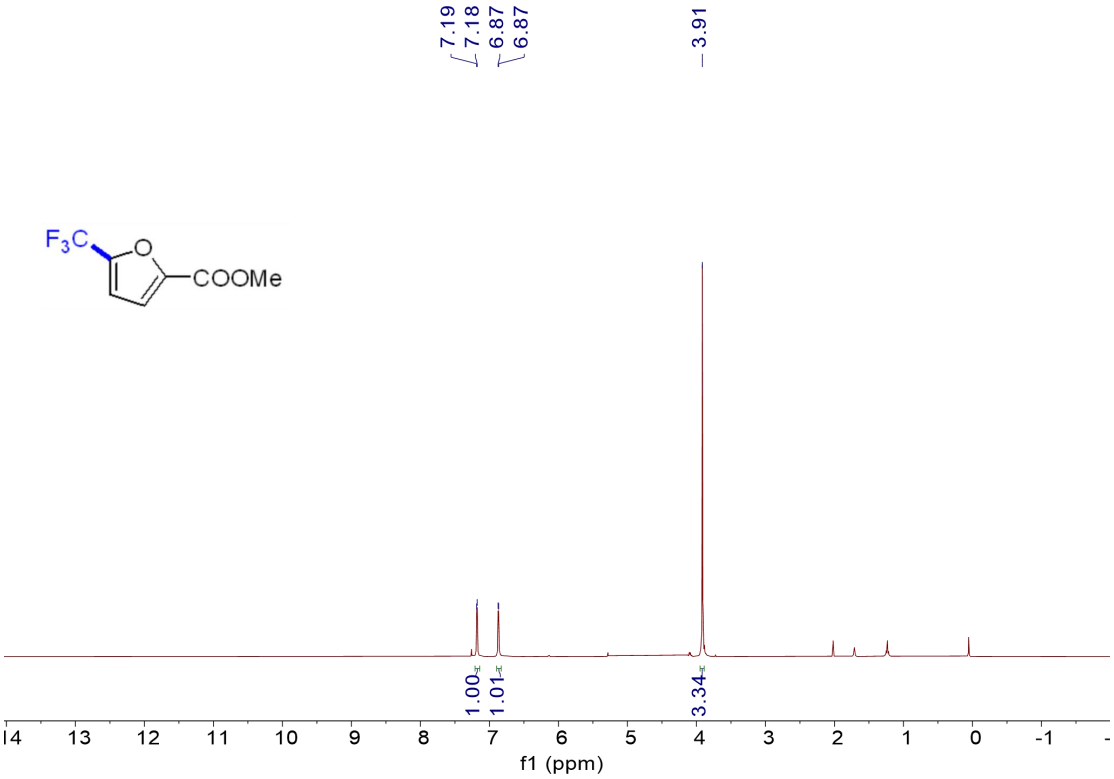
^{19}F NMR Spectrum of **3i**



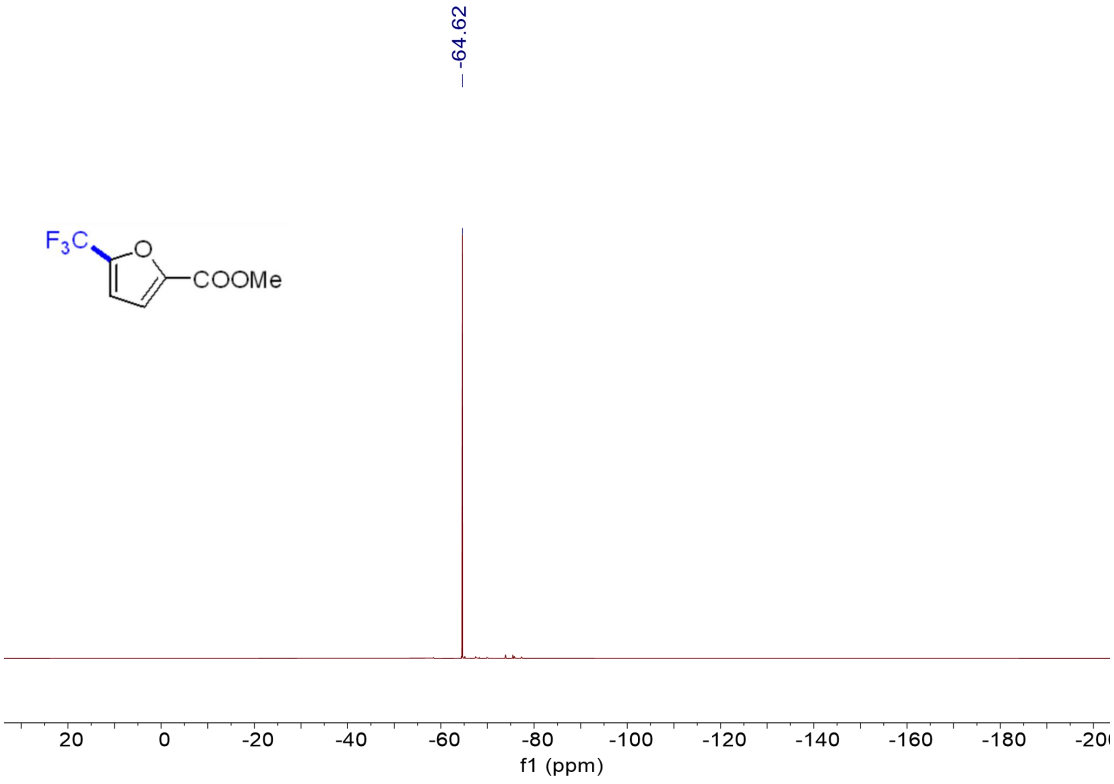
^{13}C NMR Spectrum of **3i**



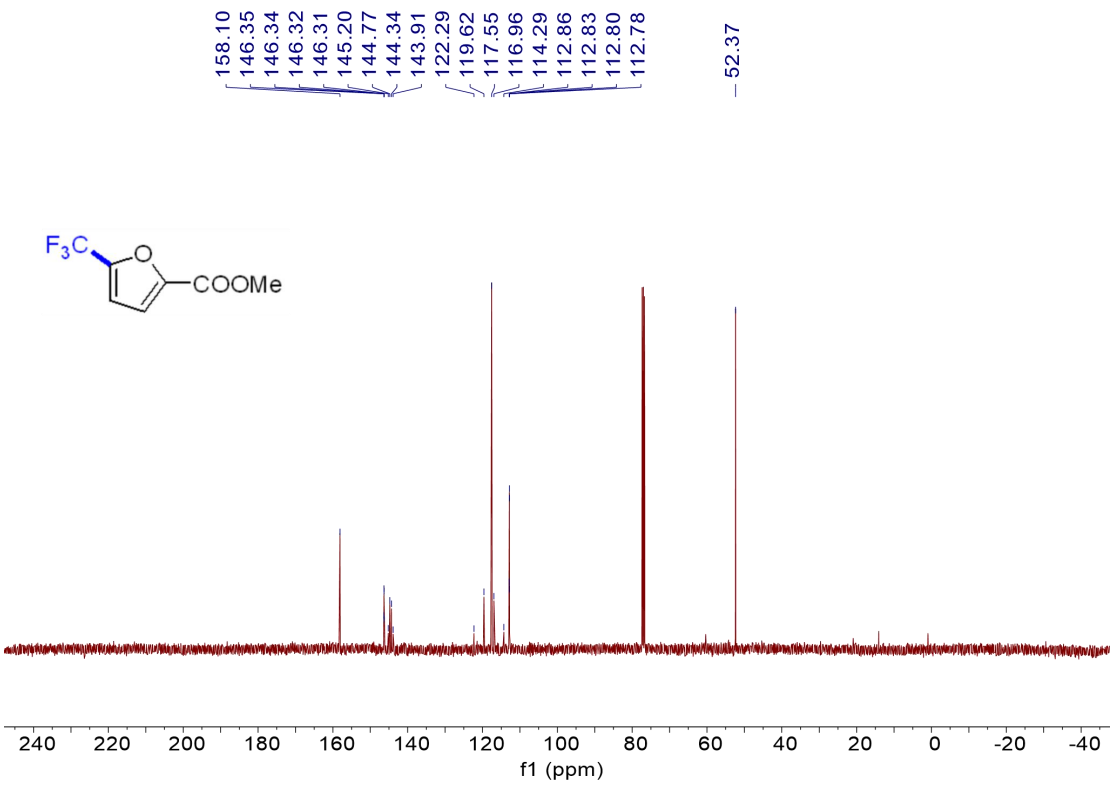
^{1}H NMR Spectrum of **3j**



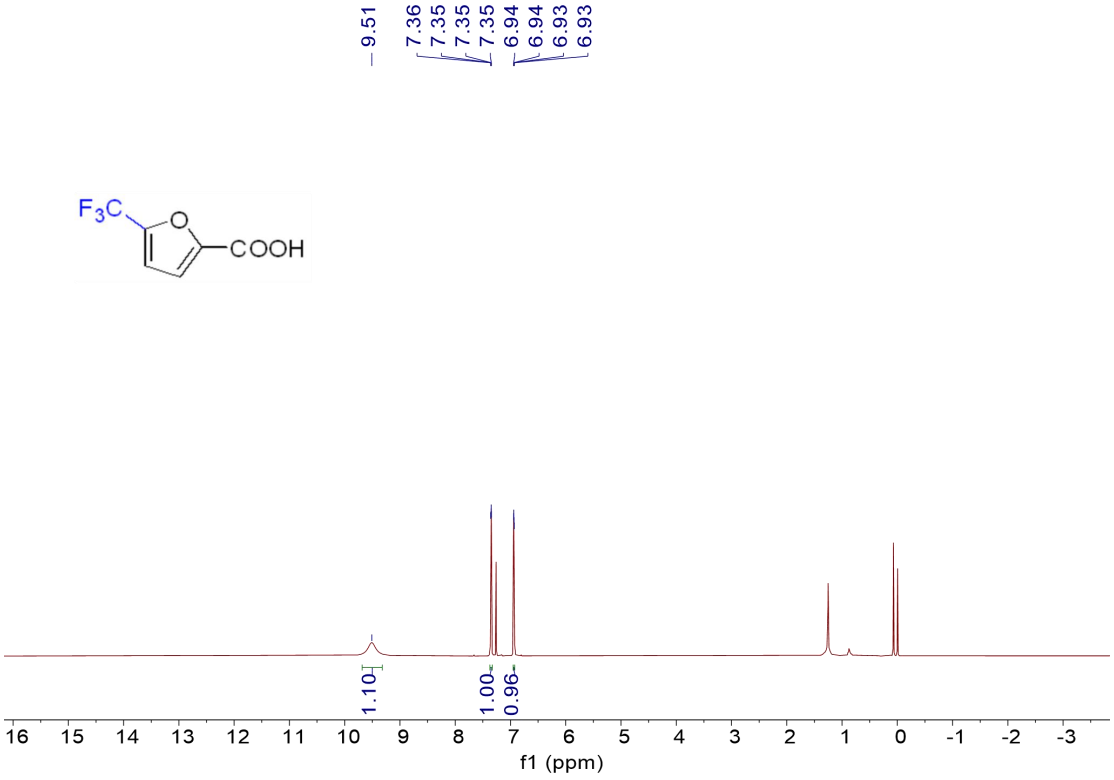
^{19}F NMR Spectrum of **3j**



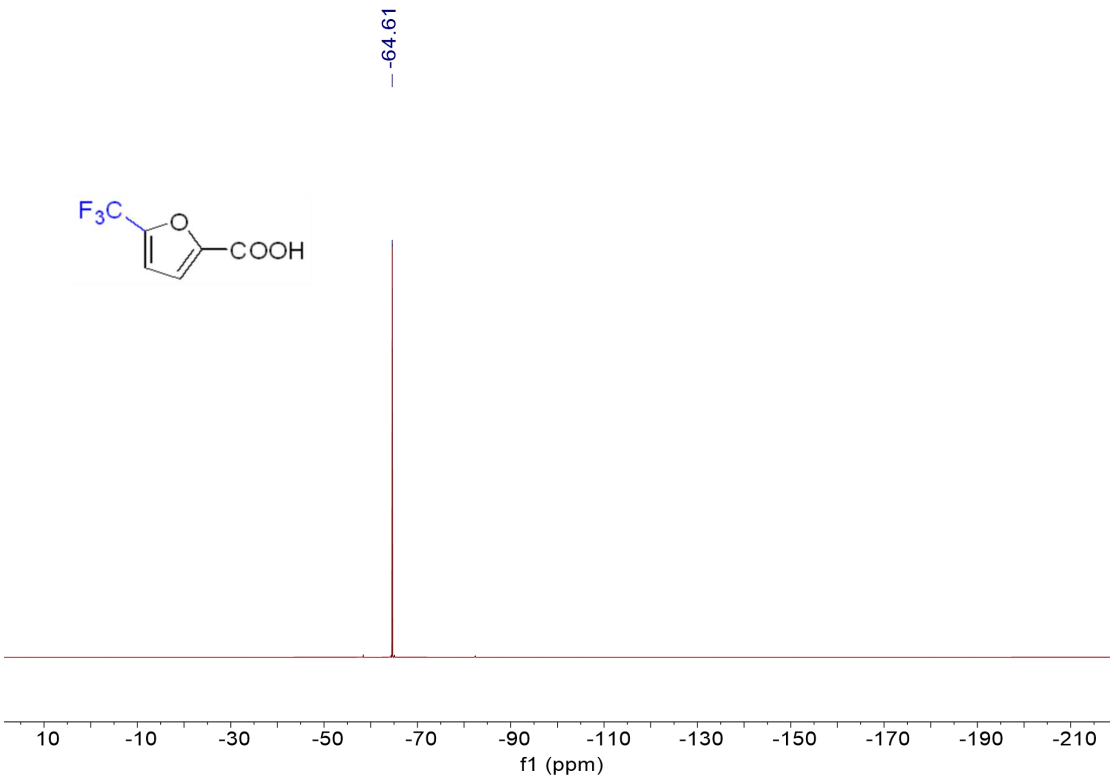
^{13}C NMR Spectrum of **3j**



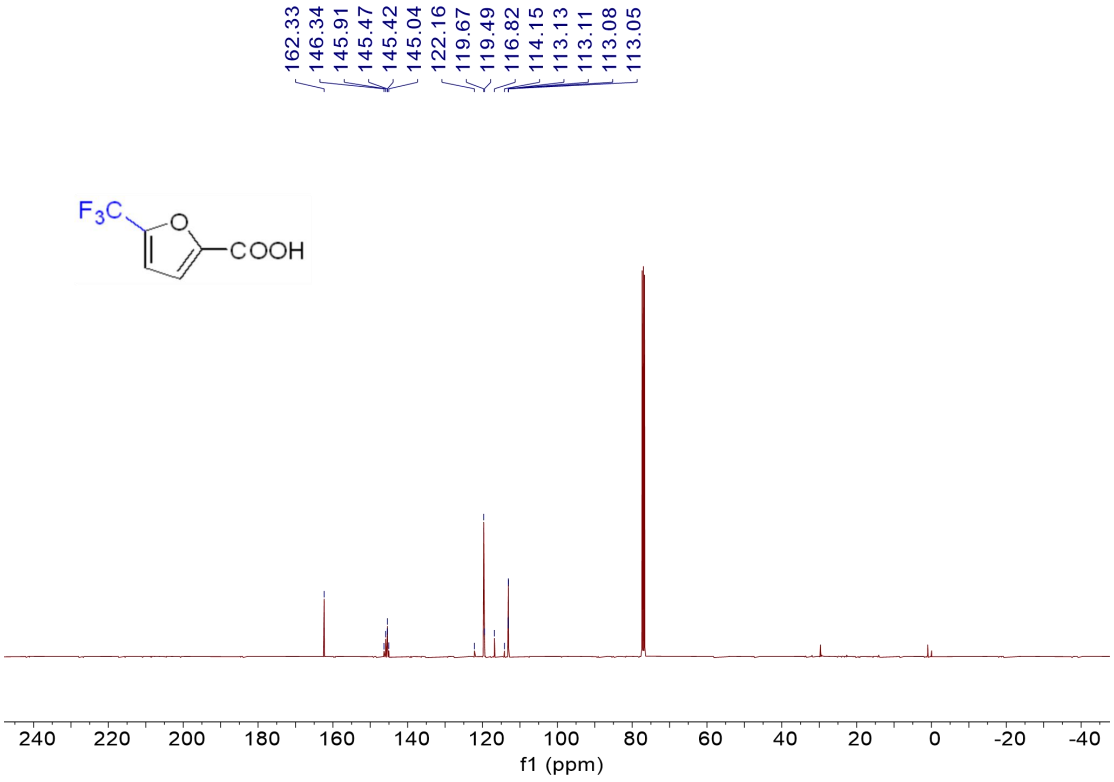
^{1}H NMR Spectrum of **3k**



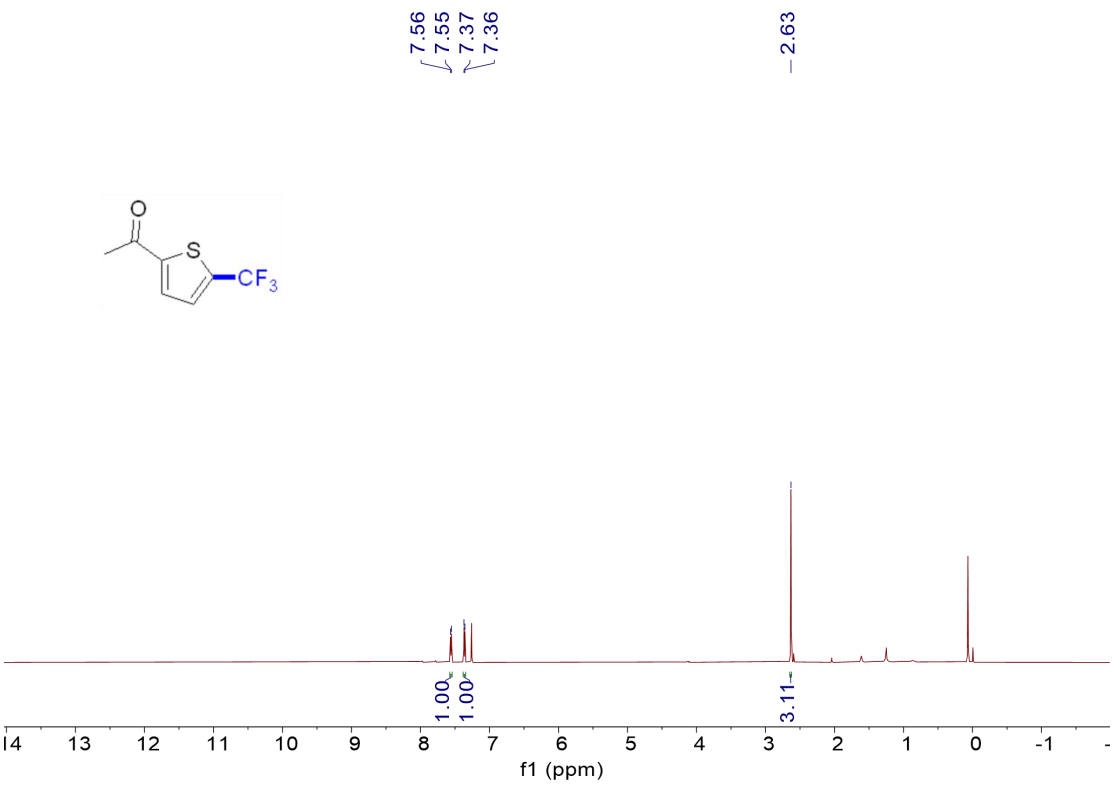
^{19}F NMR Spectrum of **3k**



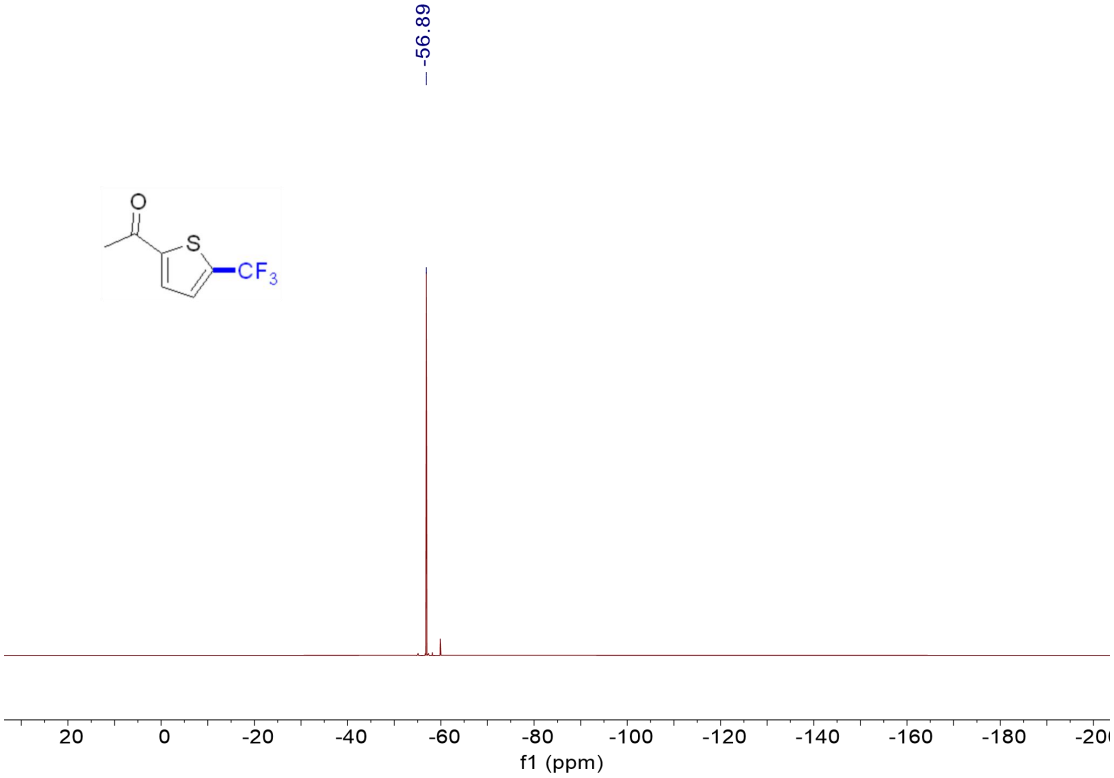
^{13}C NMR Spectrum of **3k**



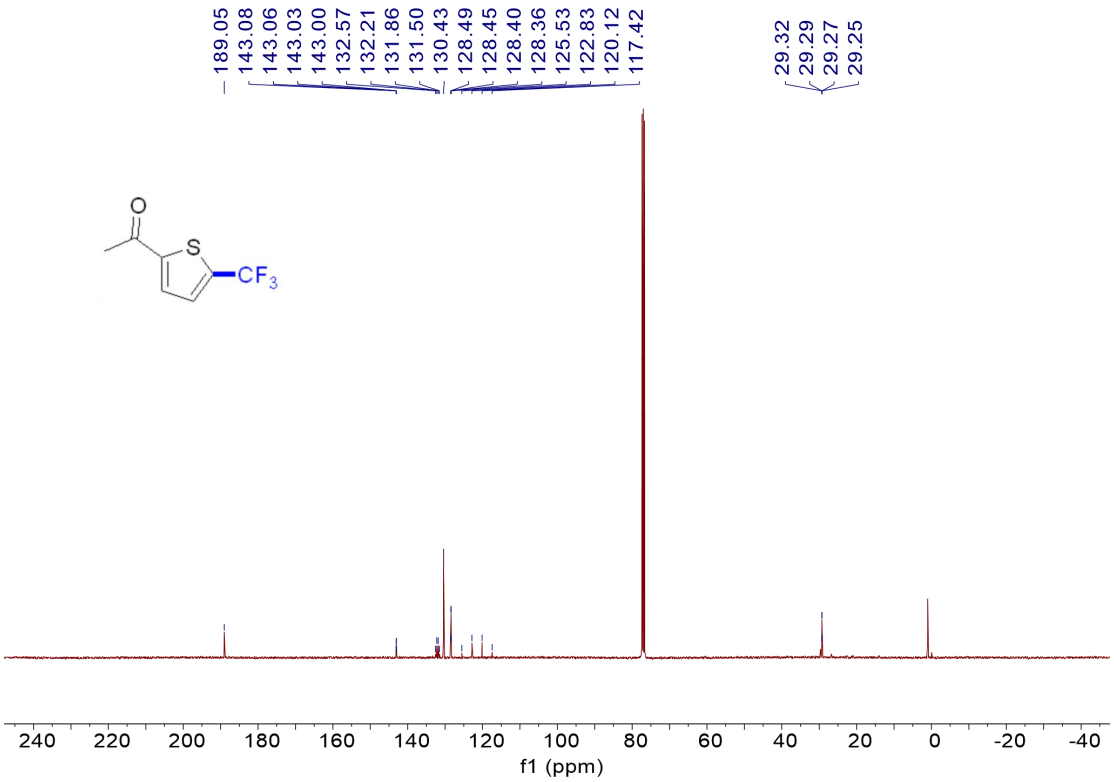
^{1}H NMR Spectrum of **3l**



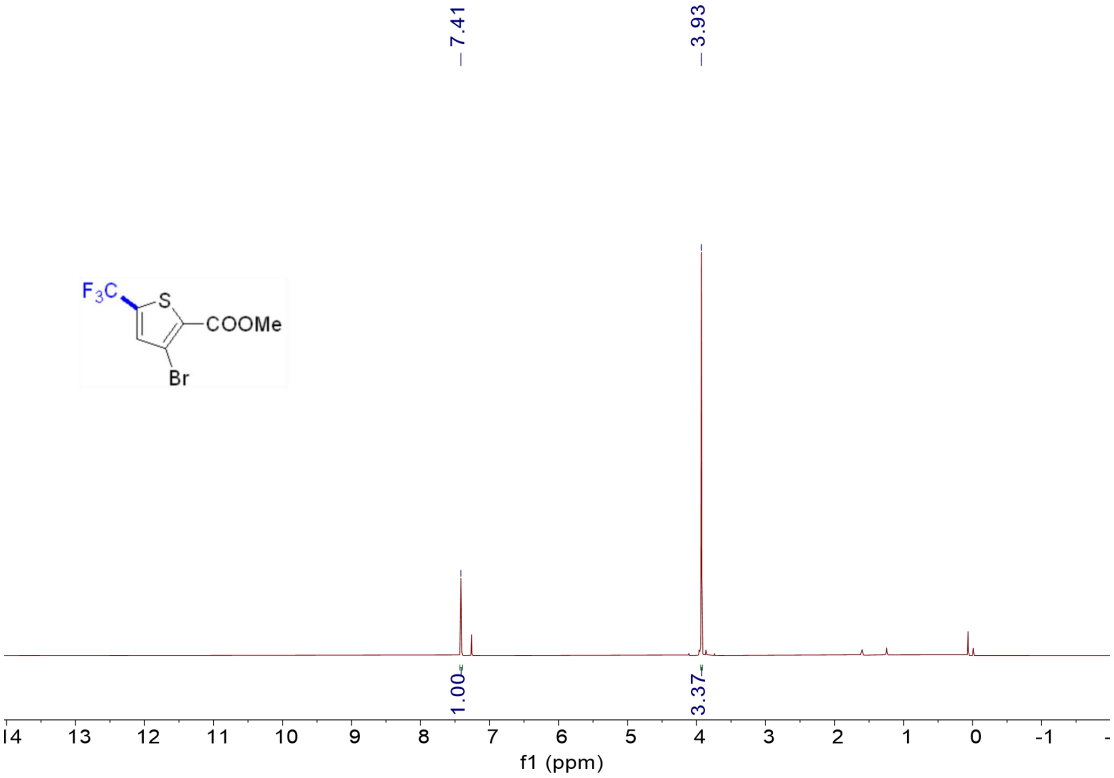
^{19}F NMR Spectrum of **3l**



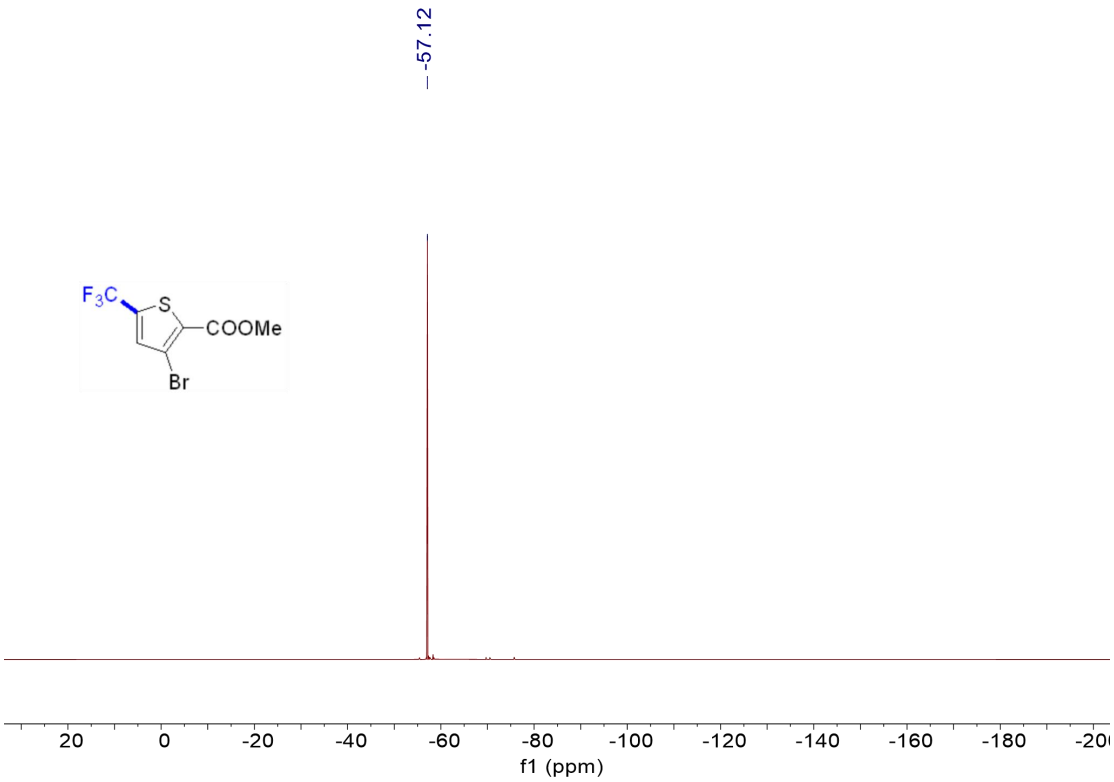
^{13}C NMR Spectrum of **3l**



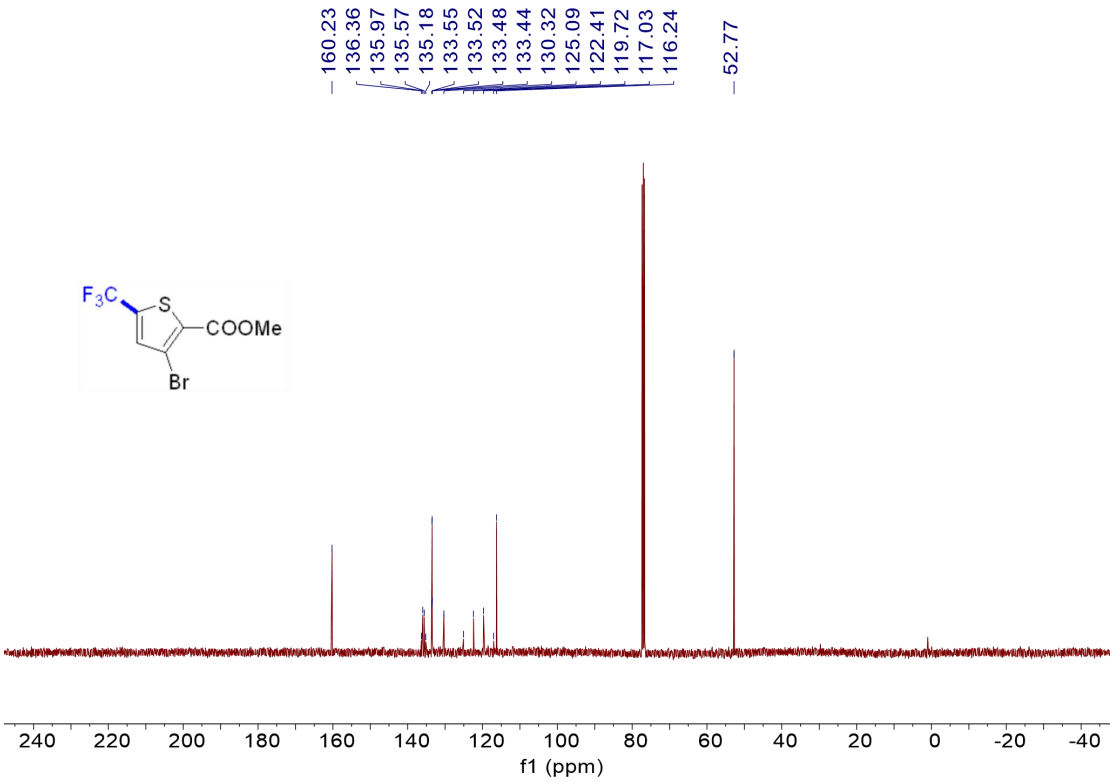
^{1}H NMR Spectrum of **3m**



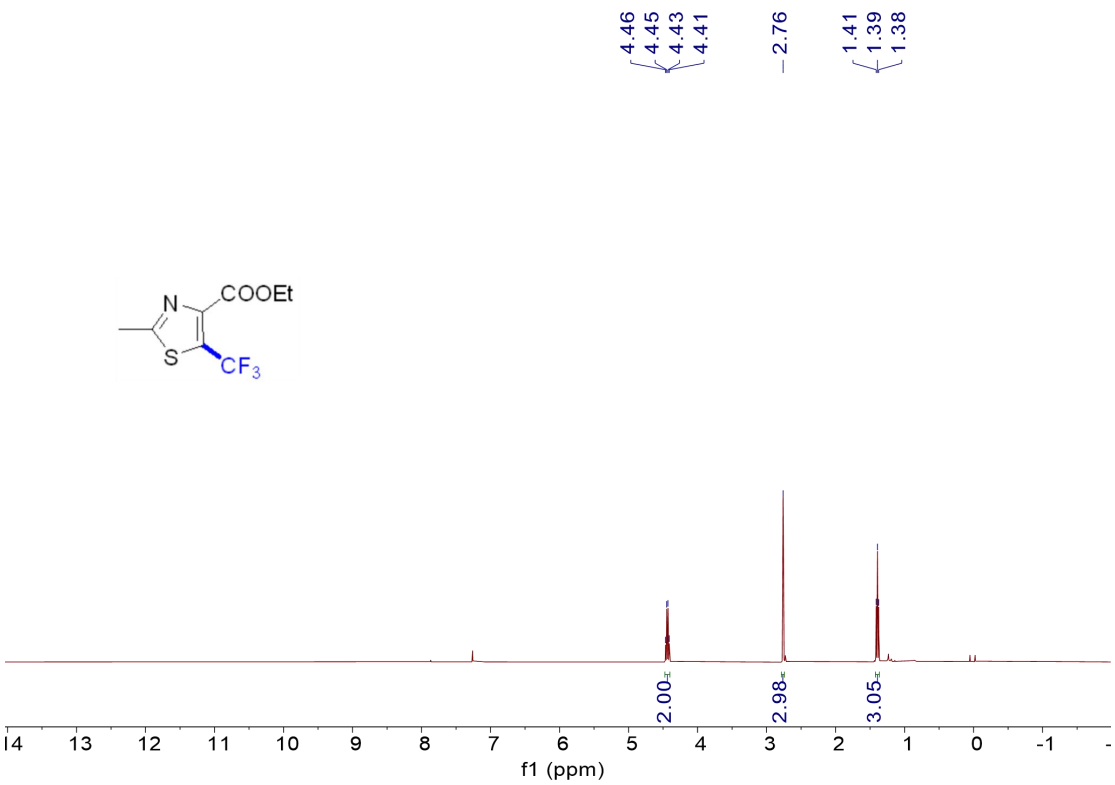
^{19}F NMR Spectrum of **3m**



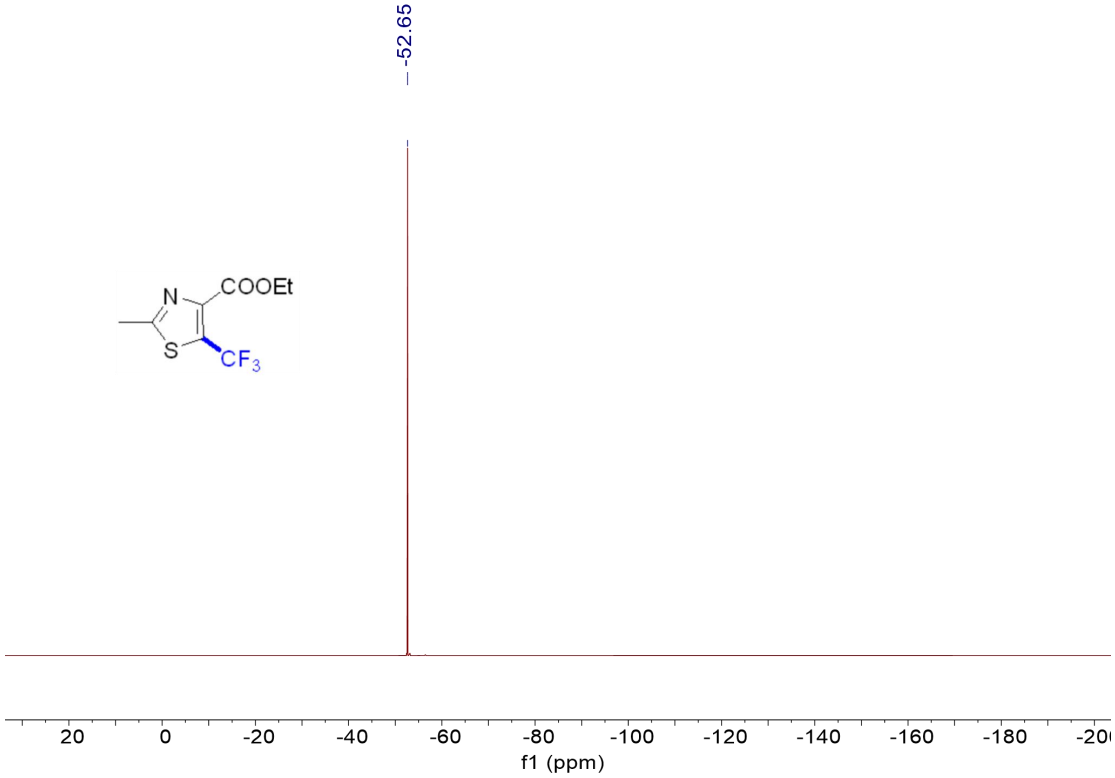
^{13}C NMR Spectrum of **3m**



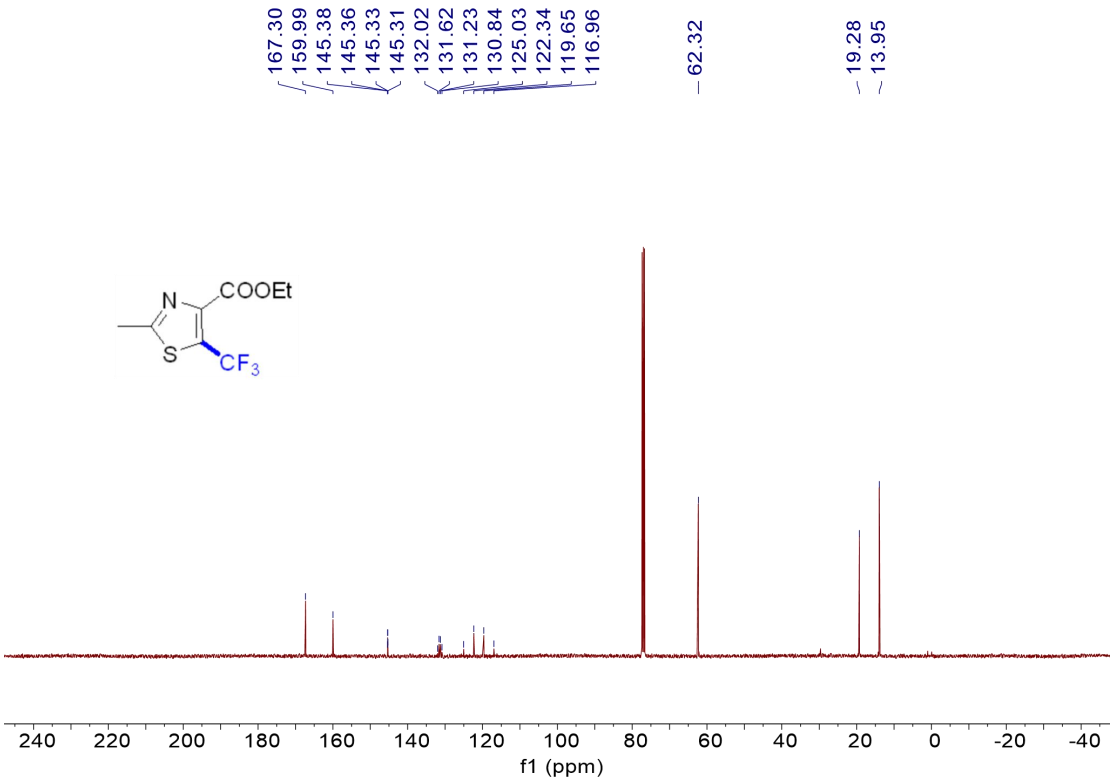
^{1}H NMR Spectrum of **3n**



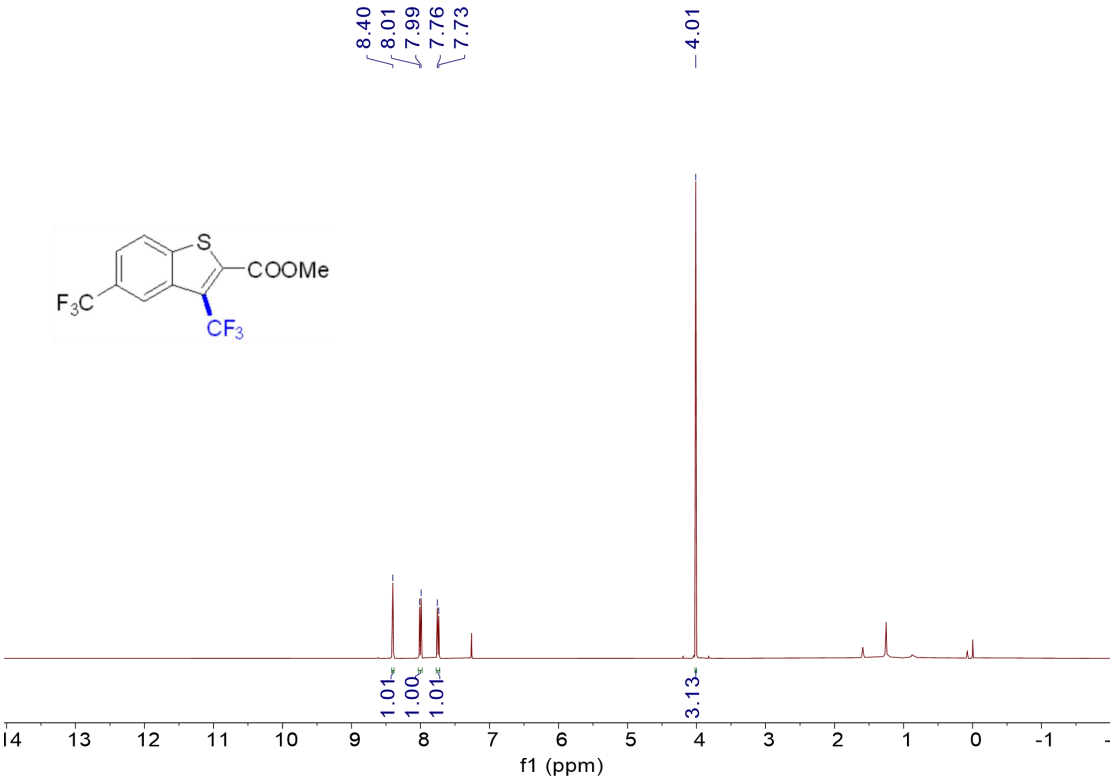
^{19}F NMR Spectrum of **3n**



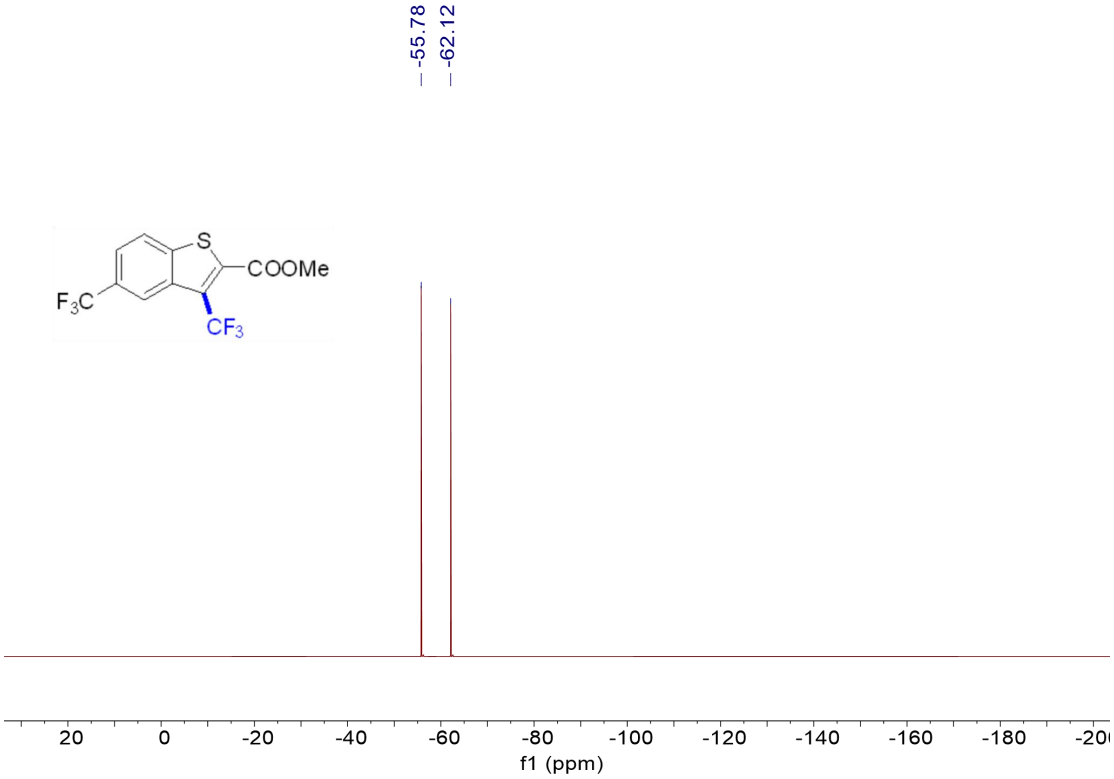
^{13}C NMR Spectrum of **3n**



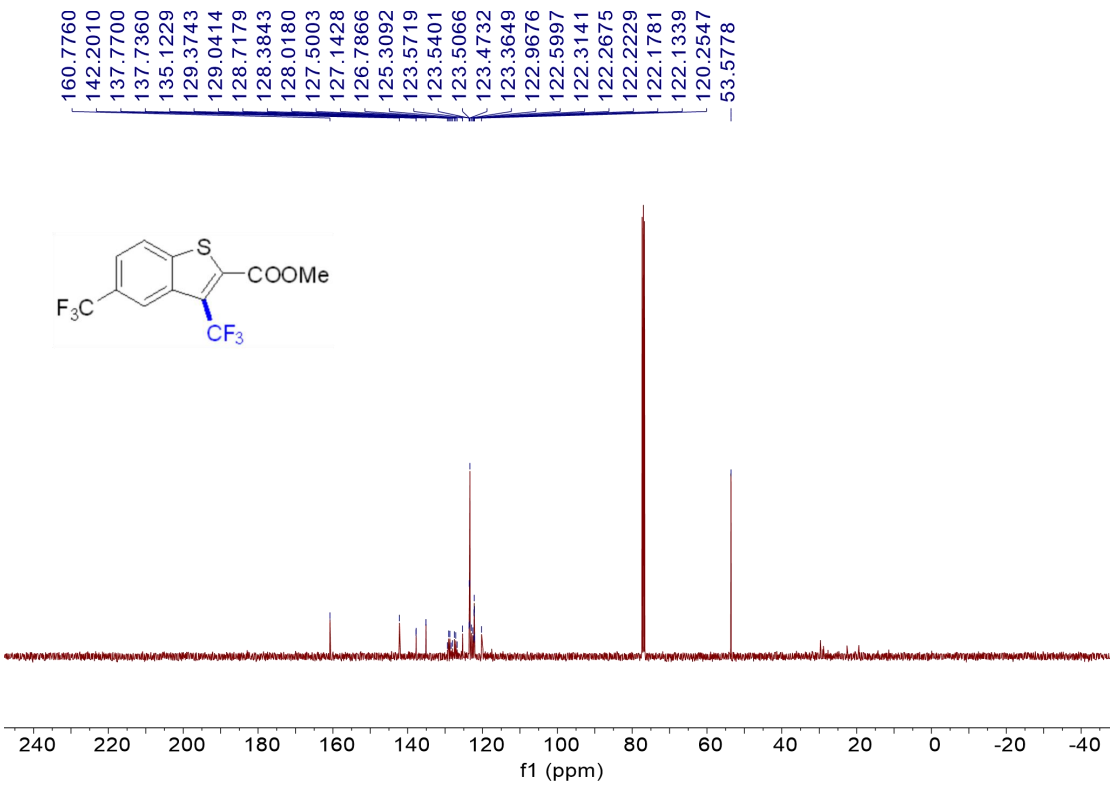
^{1}H NMR Spectrum of **3o**



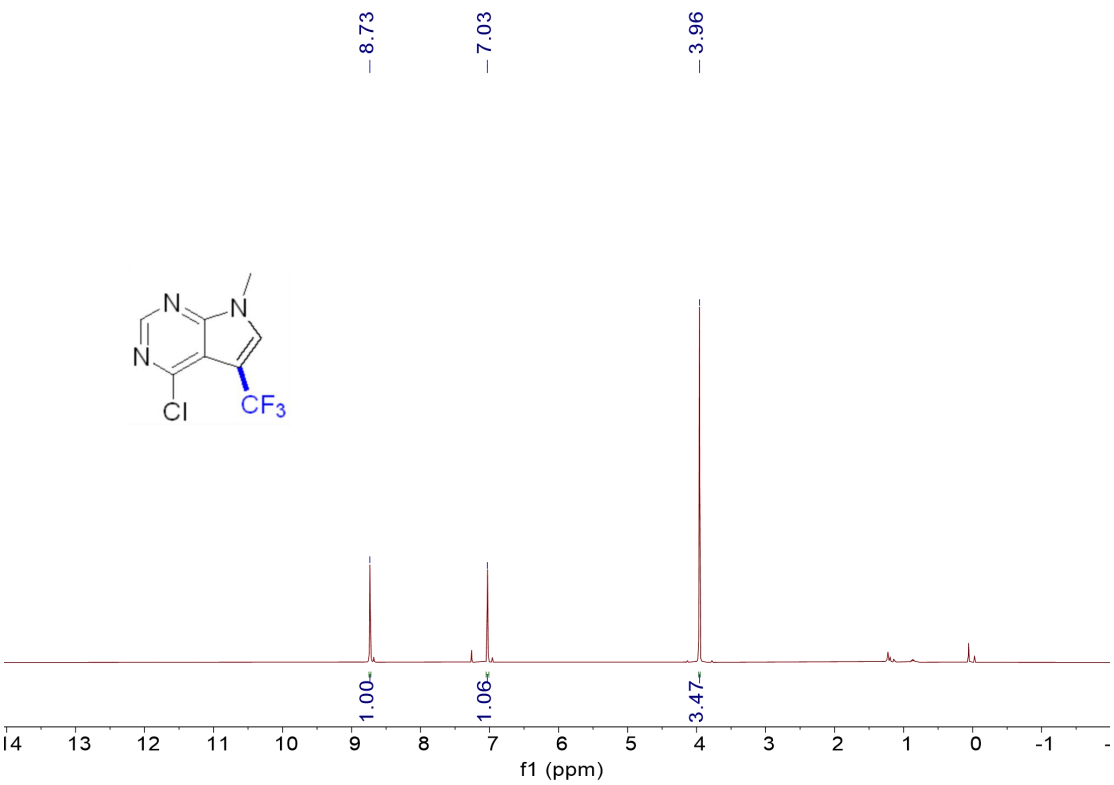
^{19}F NMR Spectrum of **3o**



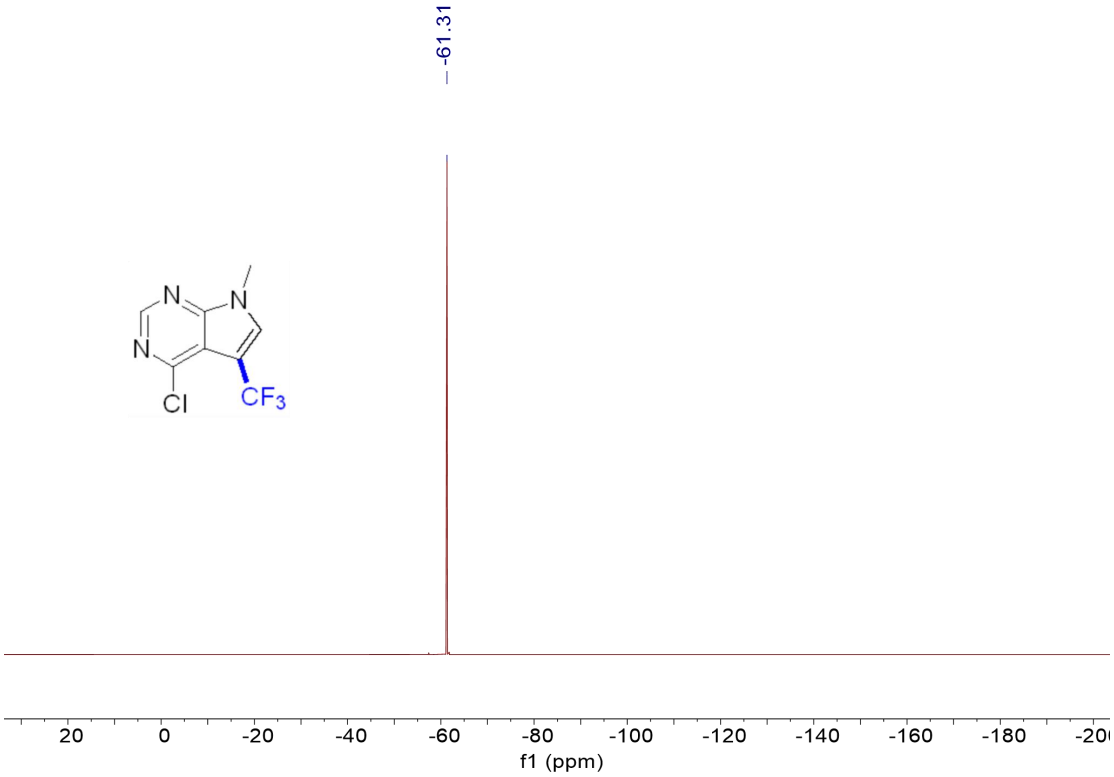
^{13}C NMR Spectrum of **3o**



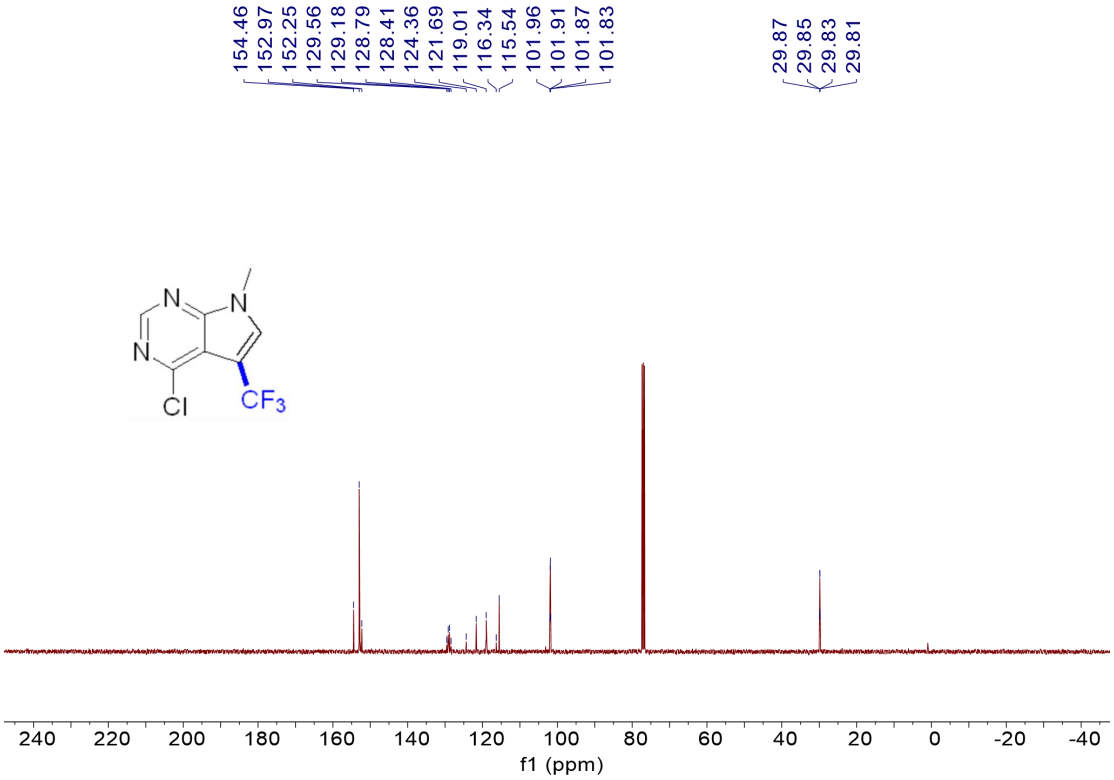
^{1}H NMR Spectrum of **3p**



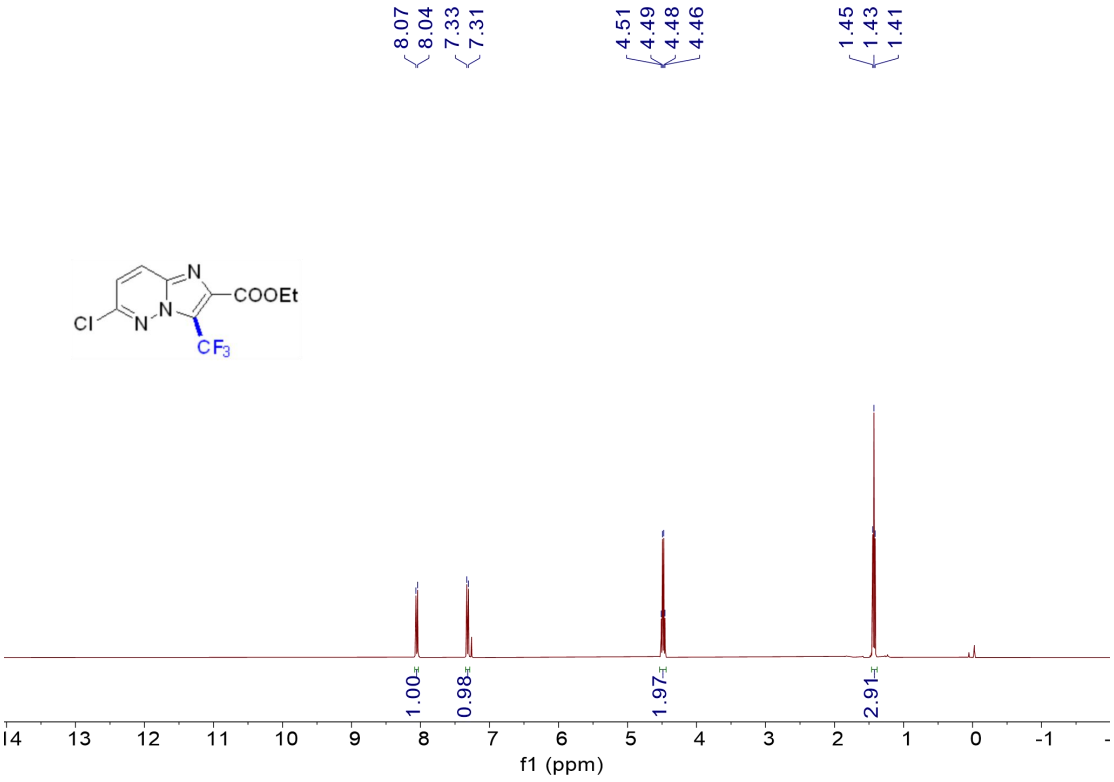
^{19}F NMR Spectrum of **3p**



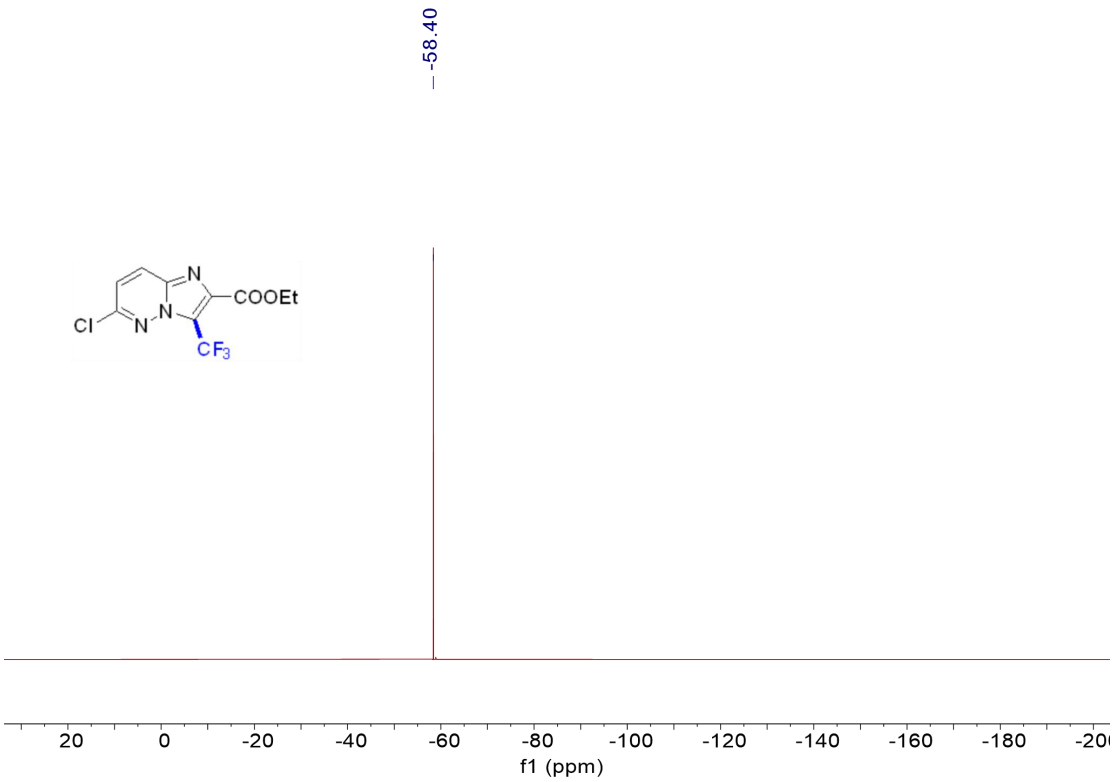
^{13}C NMR Spectrum of **3p**



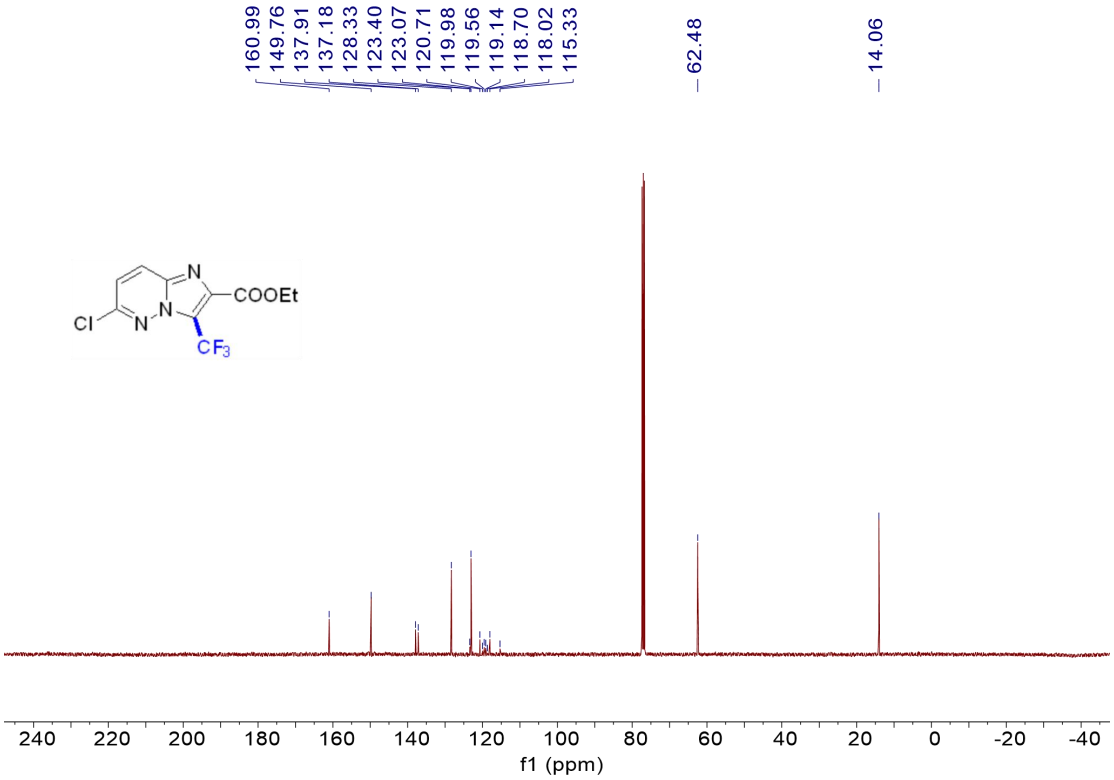
^{1}H NMR Spectrum of **3q**



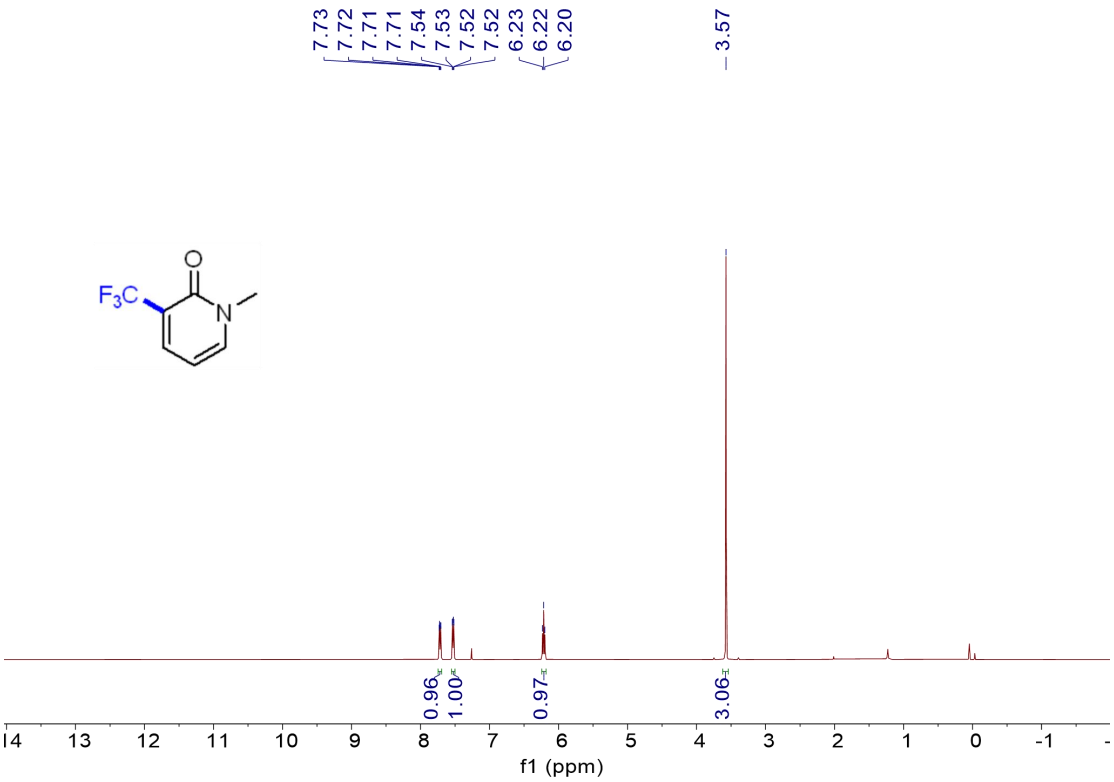
^{19}F NMR Spectrum of **3q**



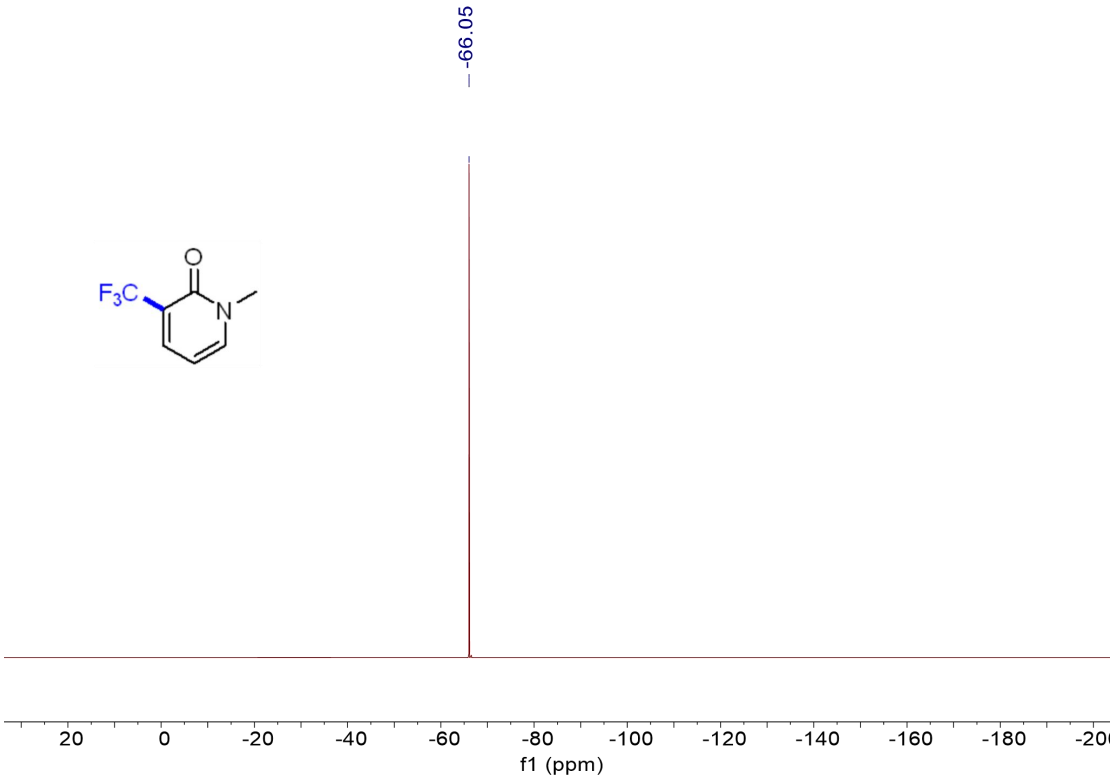
^{13}C NMR Spectrum of **3q**



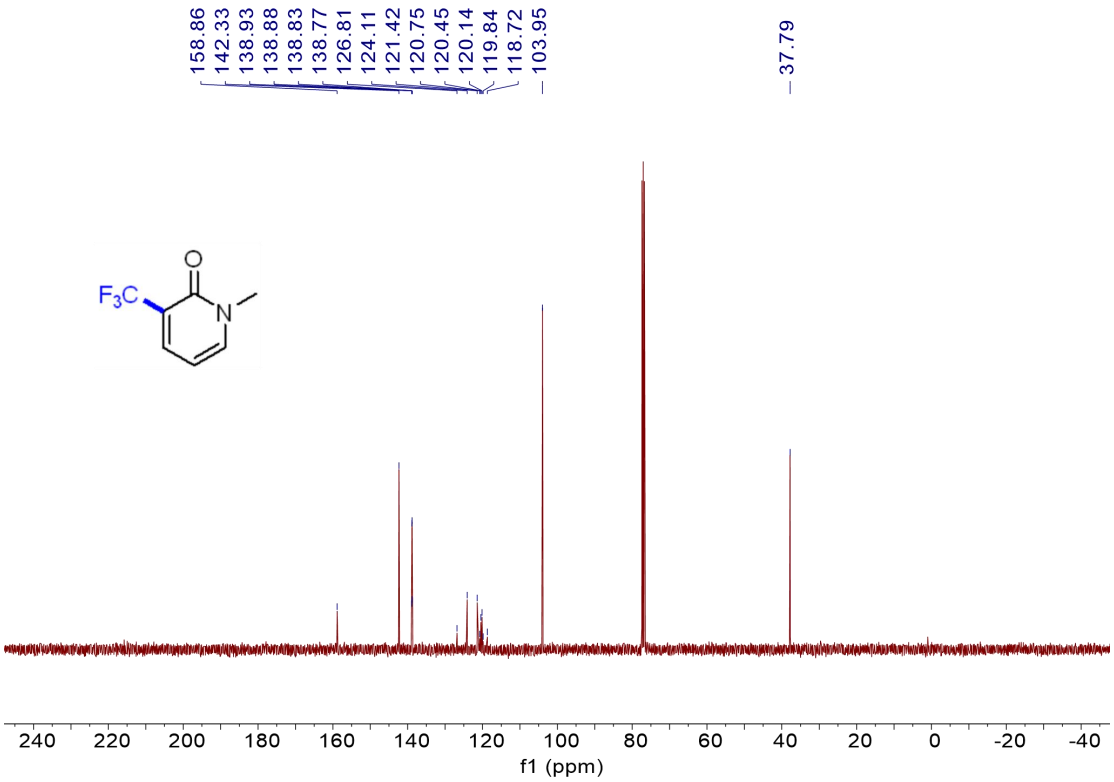
^{1}H NMR Spectrum of **3r**



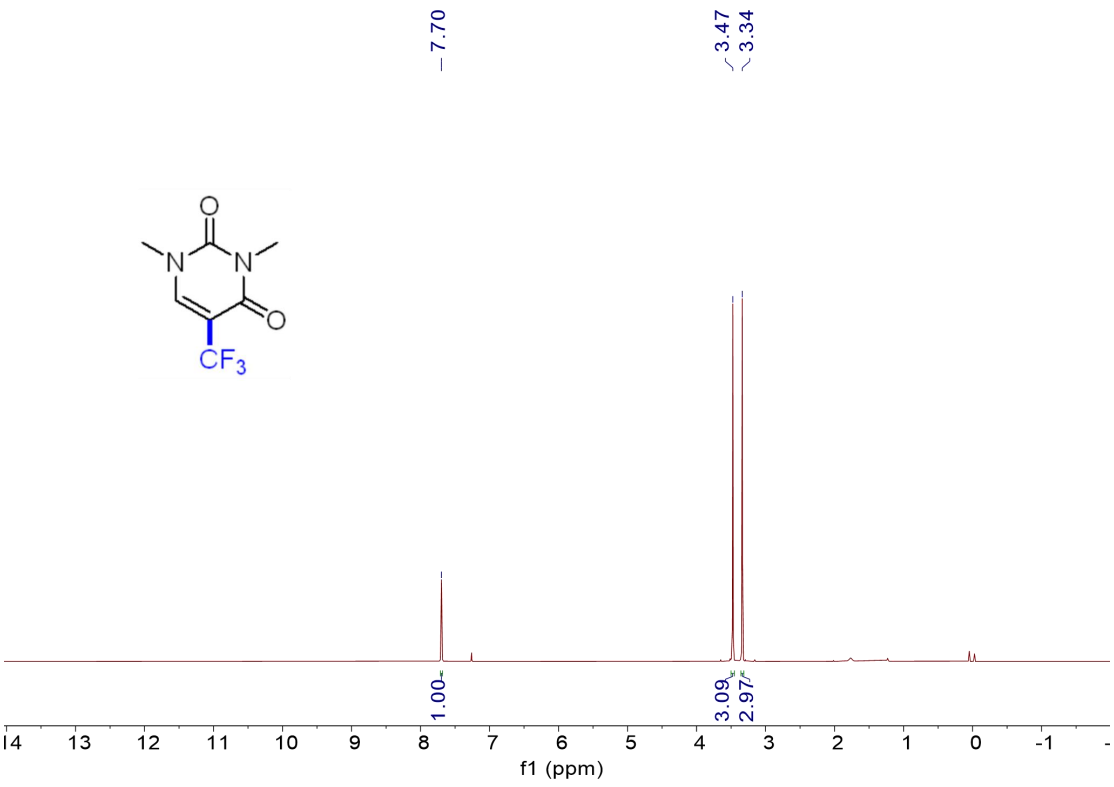
^{19}F NMR Spectrum of **3r**



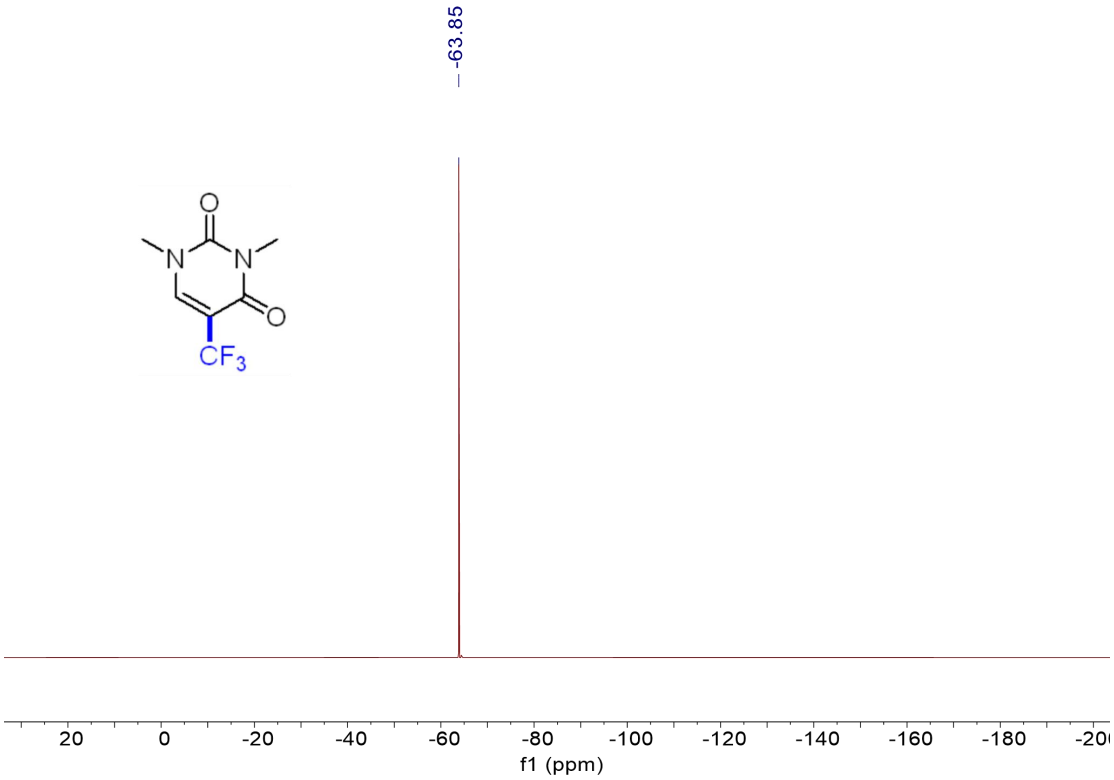
^{13}C NMR Spectrum of **3r**



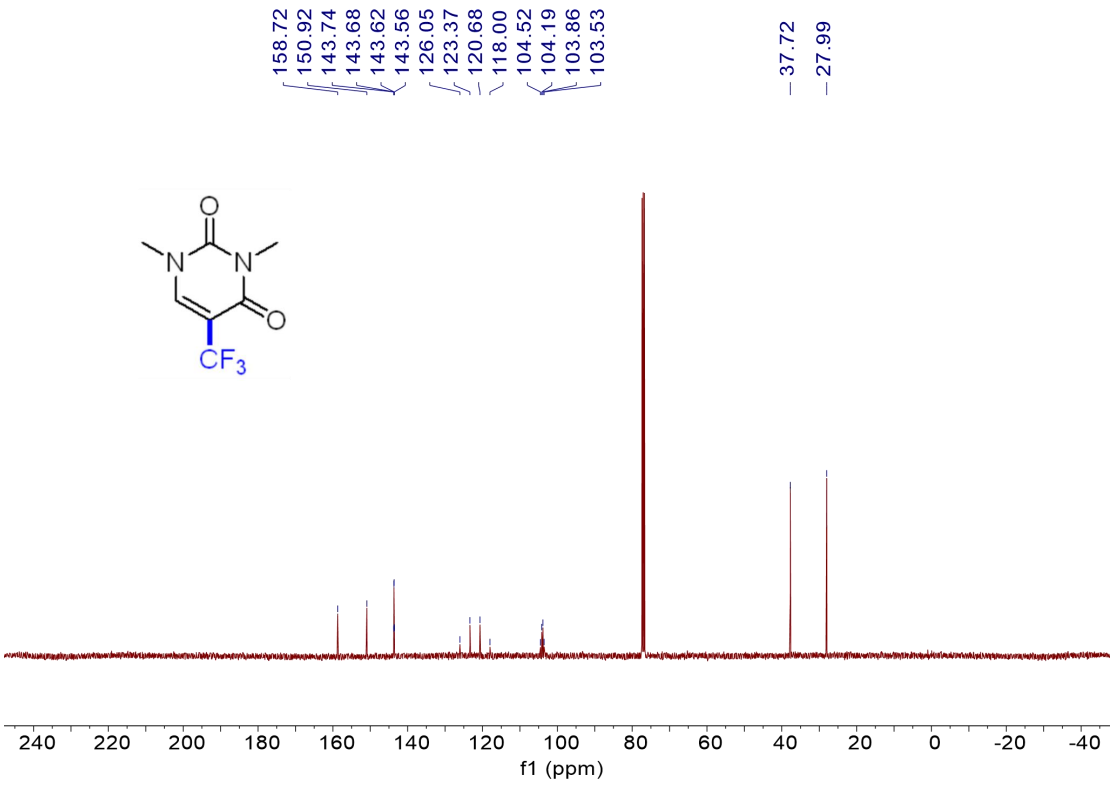
^{1}H NMR Spectrum of **3s**



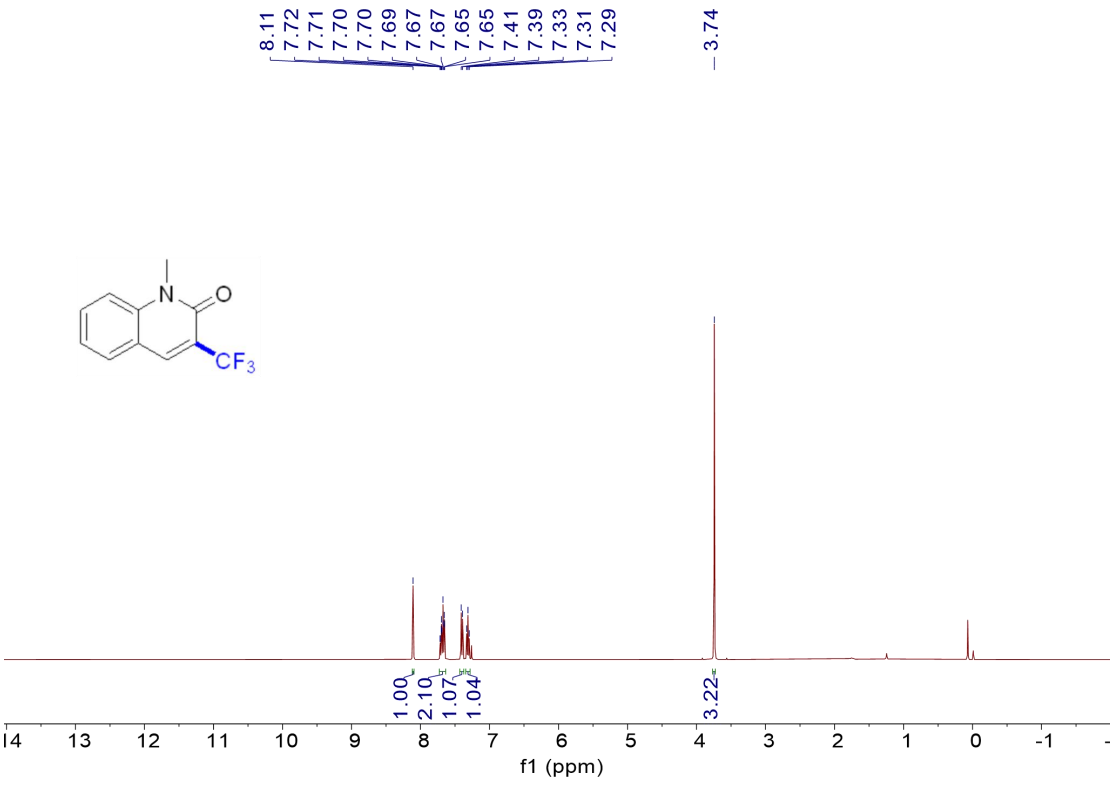
^{19}F NMR Spectrum of **3s**



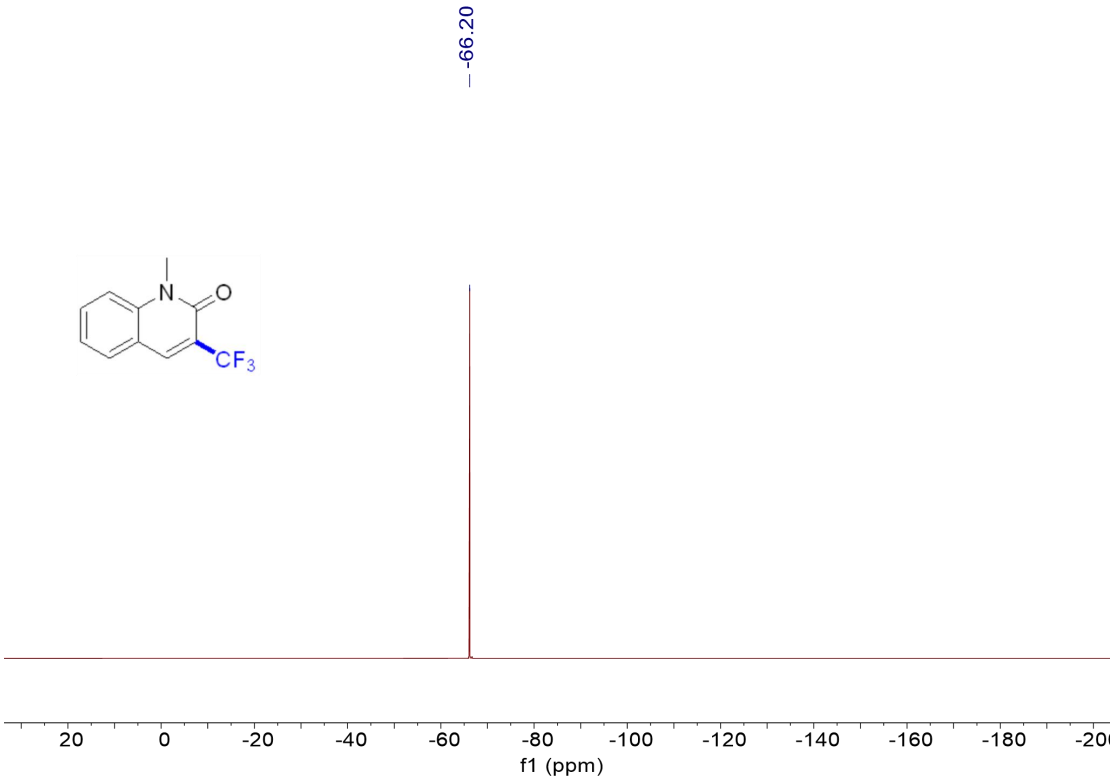
^{13}C NMR Spectrum of **3s**



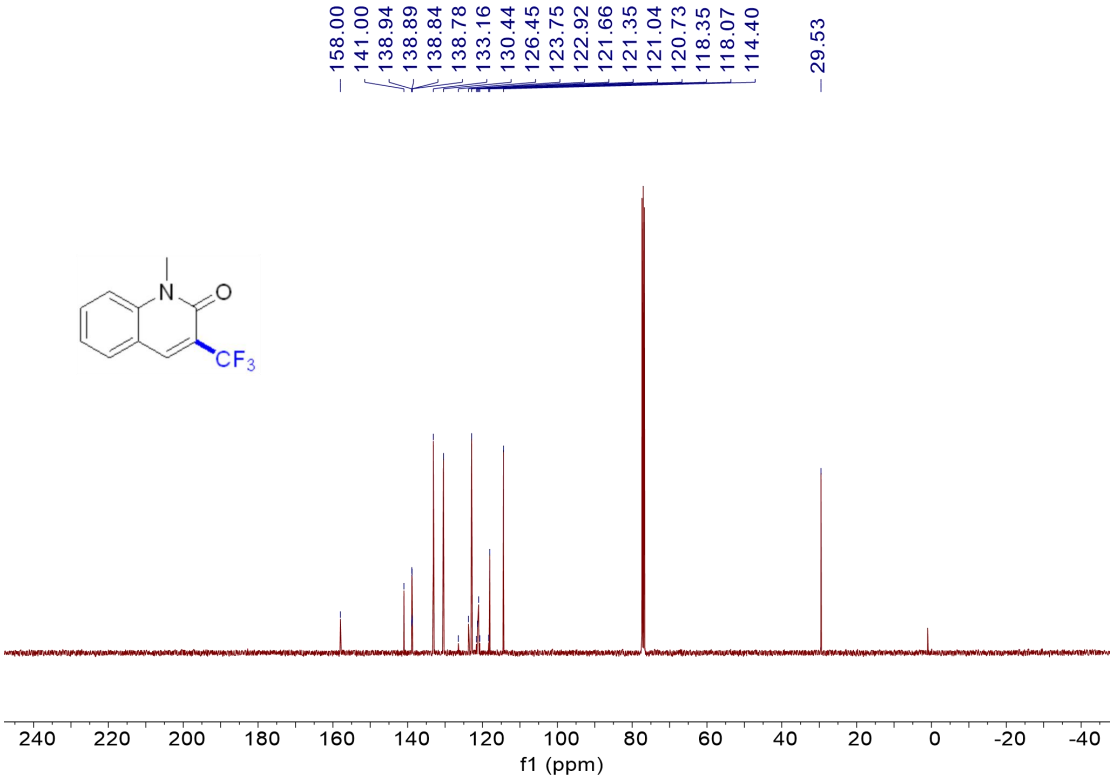
^{1}H NMR Spectrum of **3t**



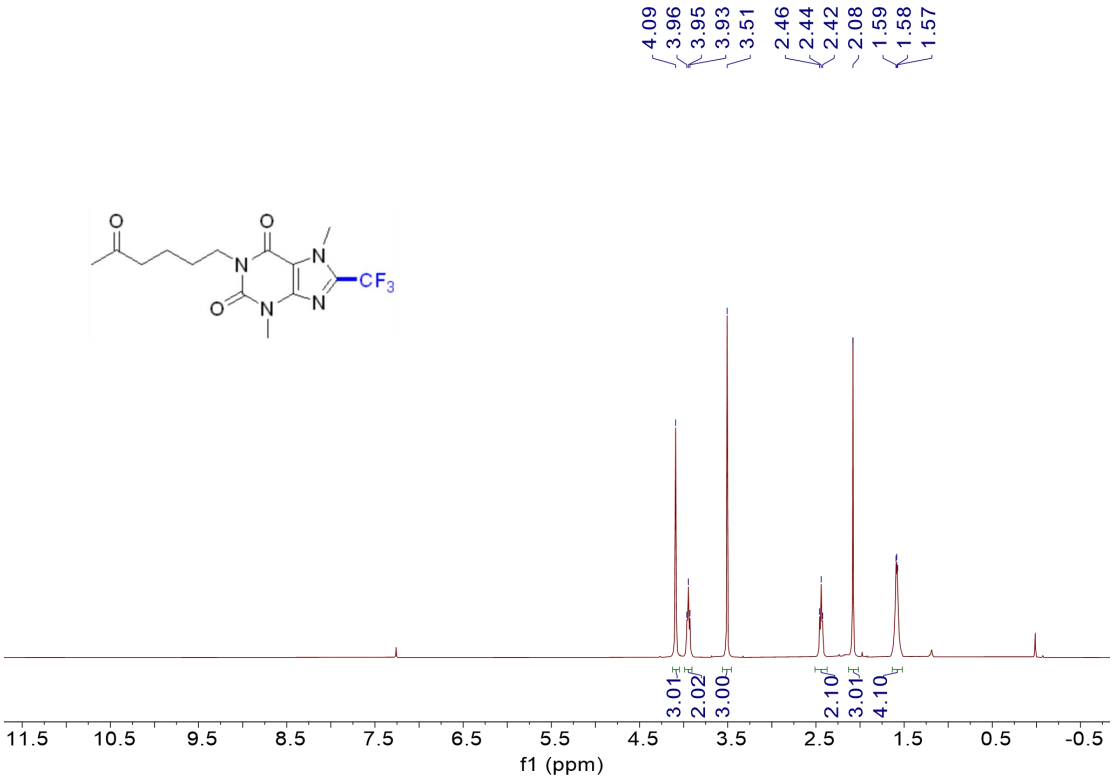
^{19}F NMR Spectrum of **3t**



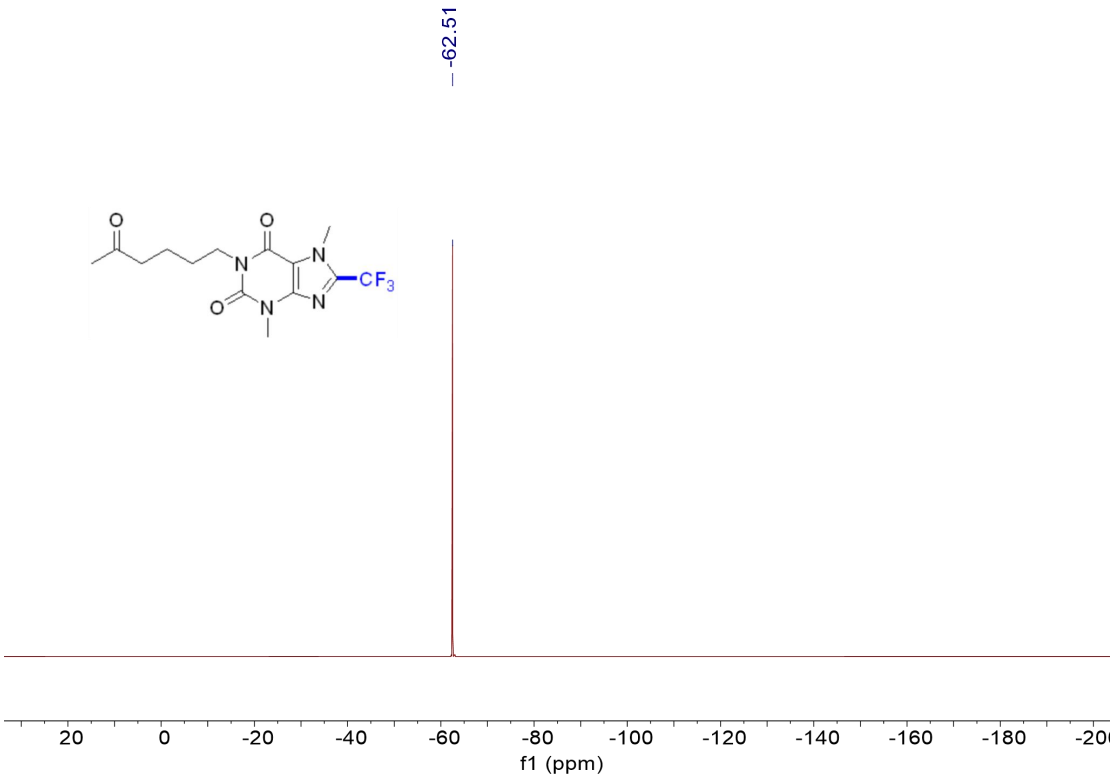
^{13}C NMR Spectrum of **3t**



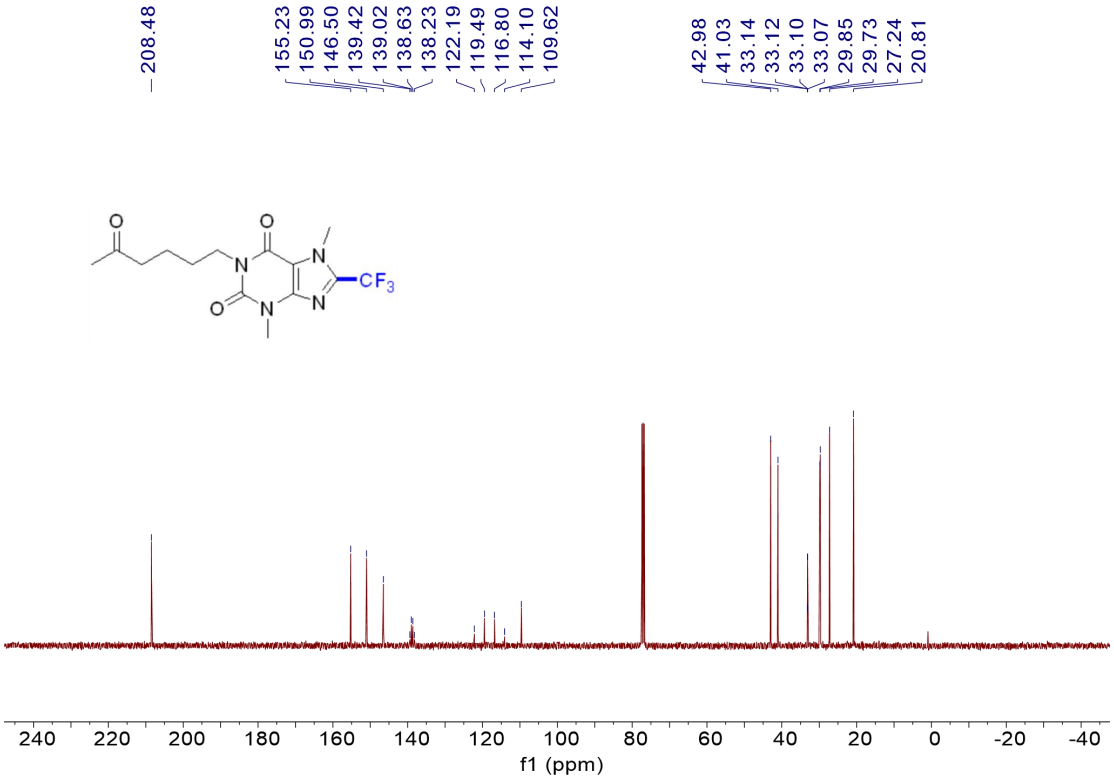
^{1}H NMR Spectrum of **3u**



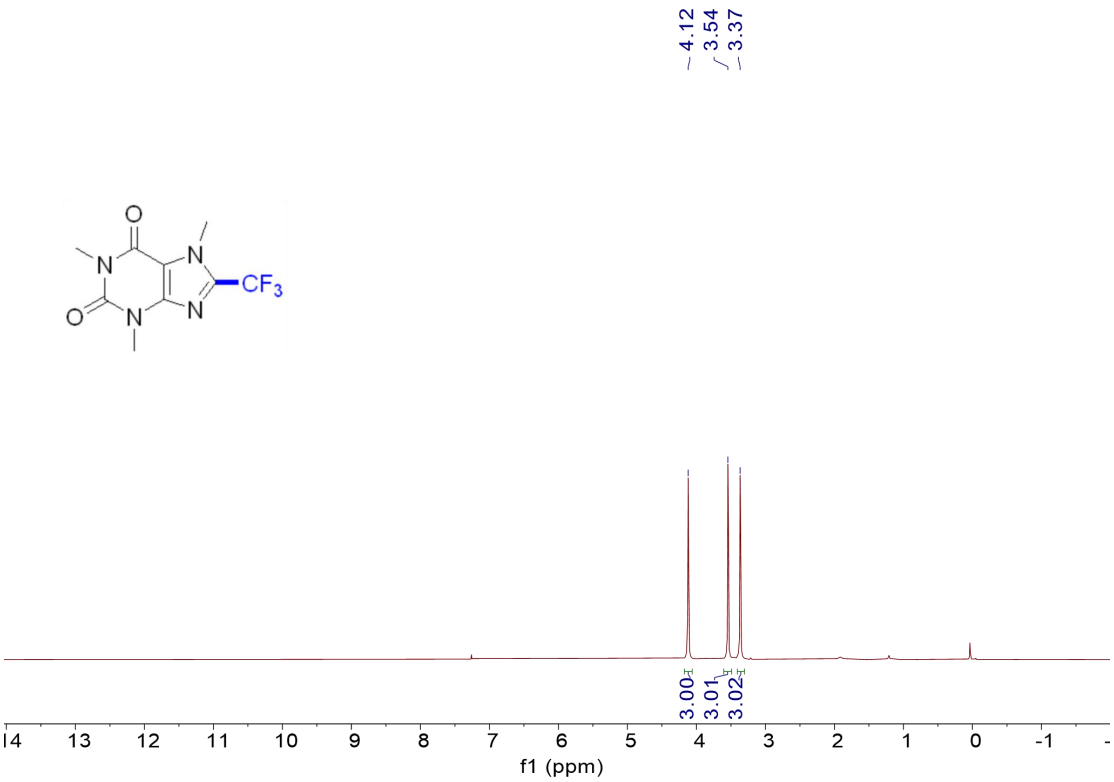
^{19}F NMR Spectrum of **3u**



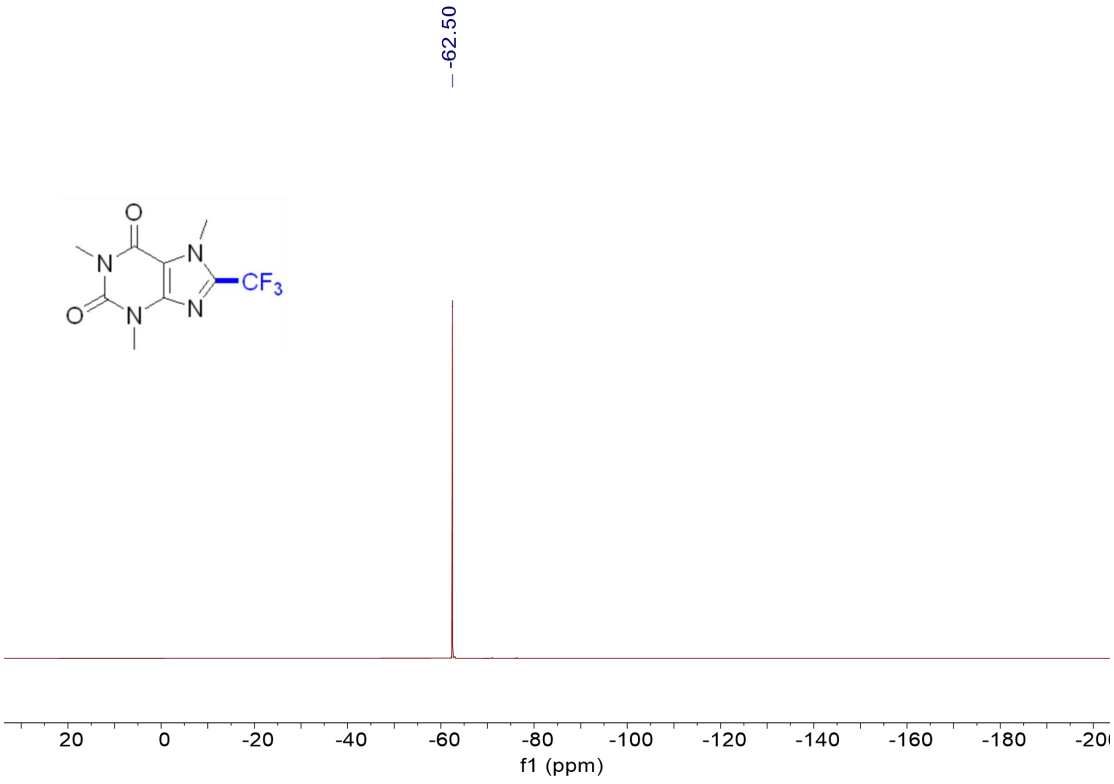
^{13}C NMR Spectrum of **3u**



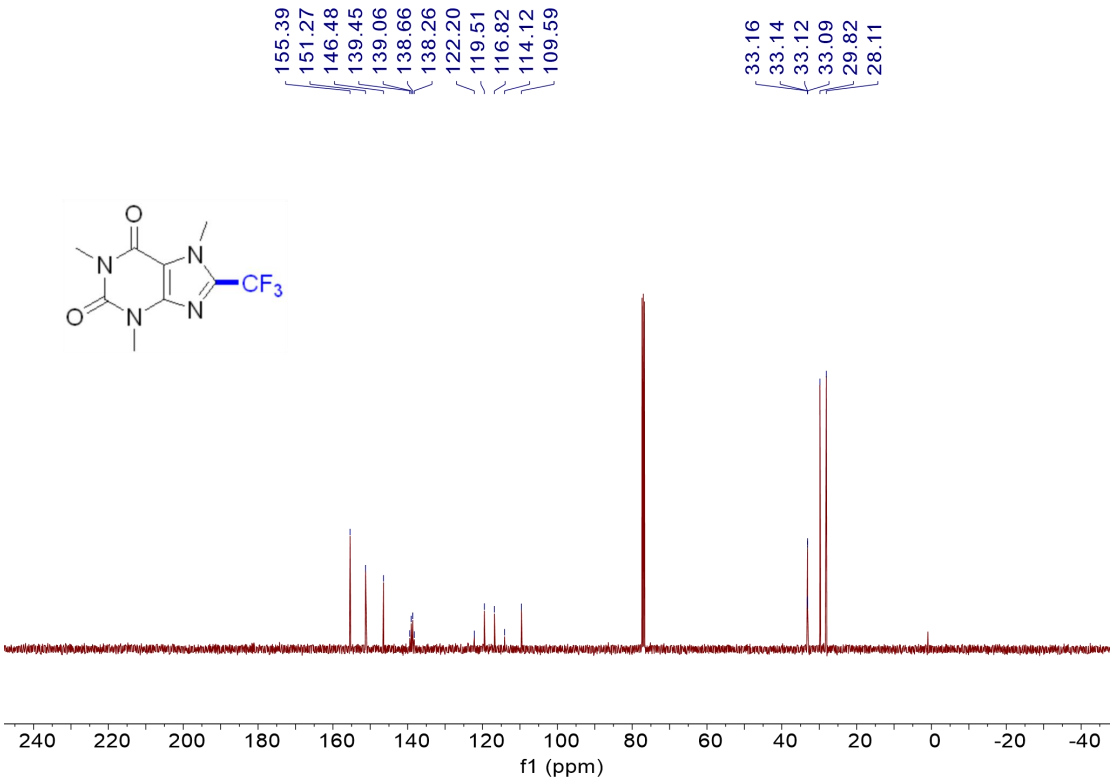
^{1}H NMR Spectrum of **3v**



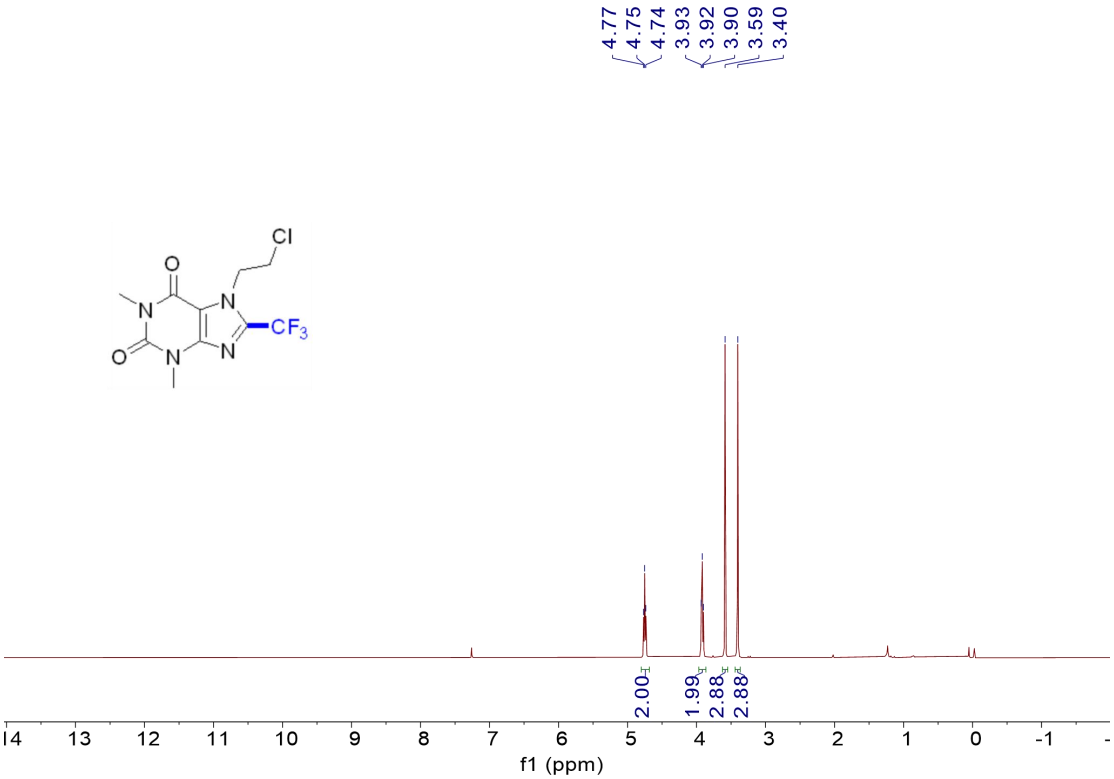
^{19}F NMR Spectrum of **3v**



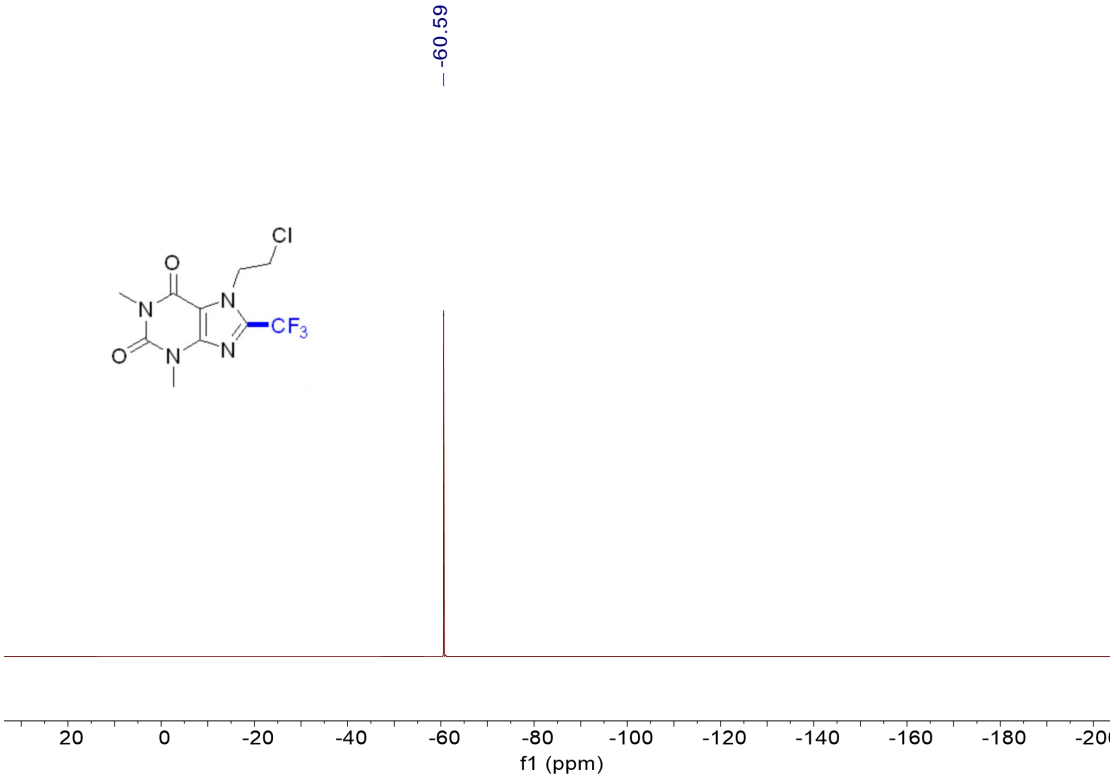
^{13}C NMR Spectrum of **3v**



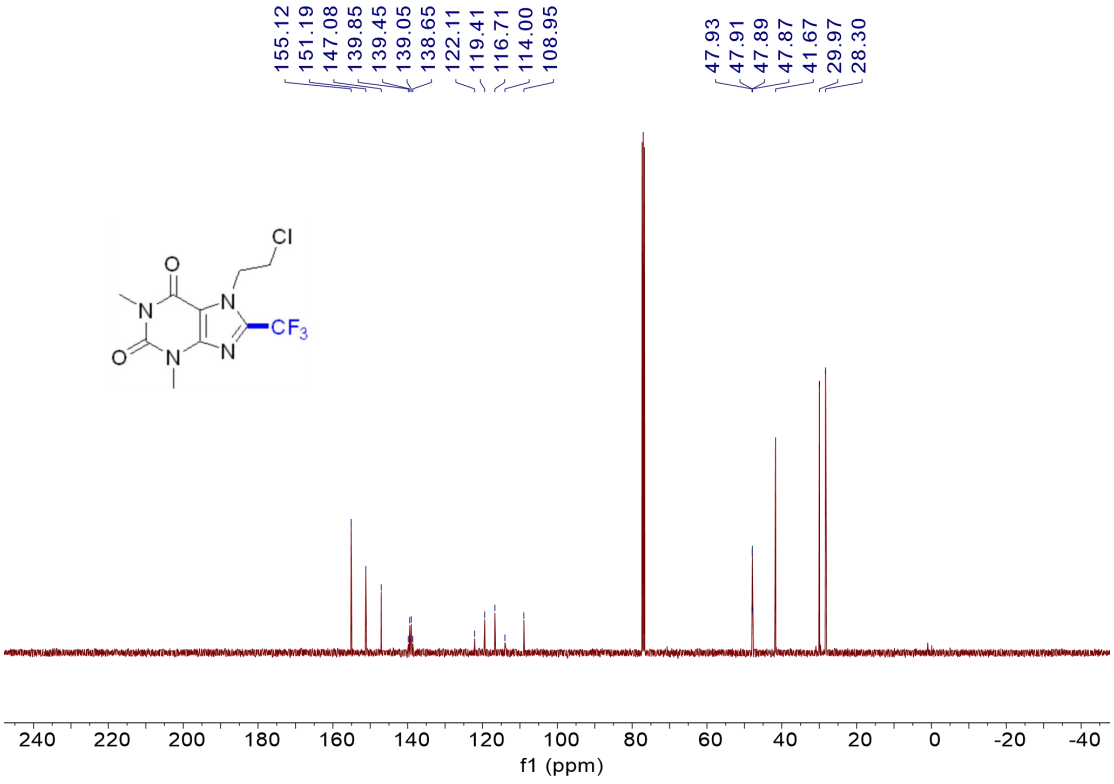
^{1}H NMR Spectrum of **3w**



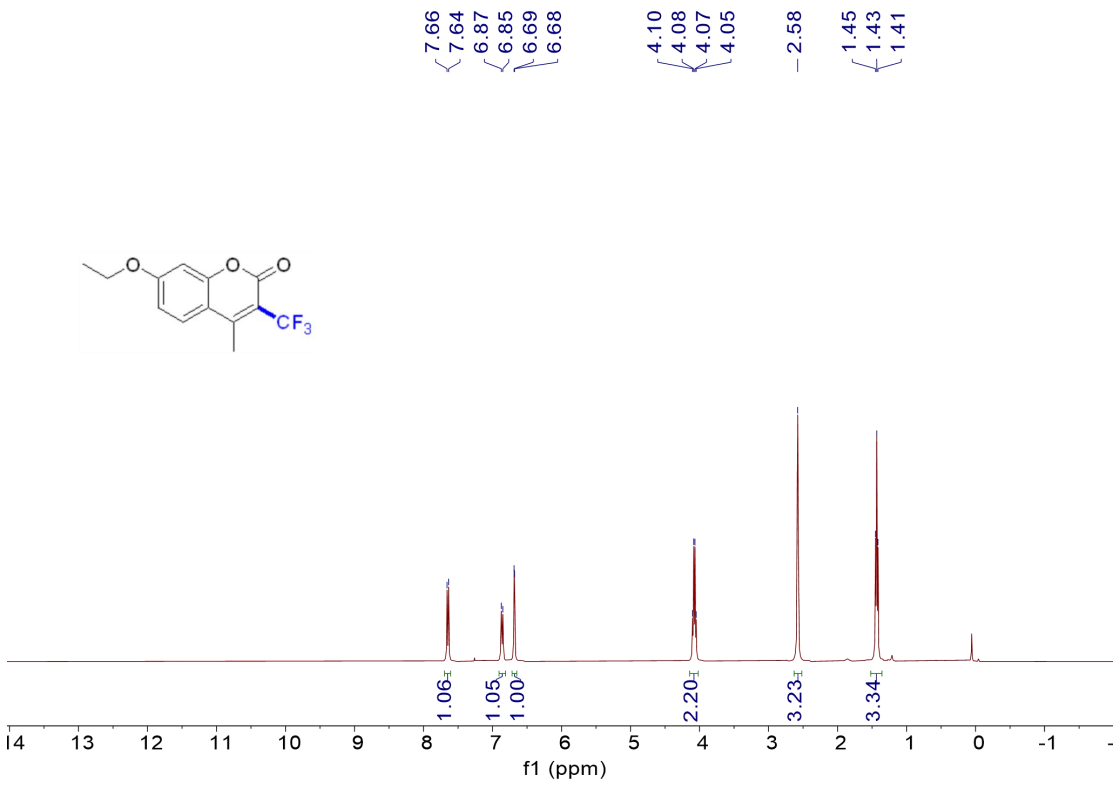
^{19}F NMR Spectrum of **3w**



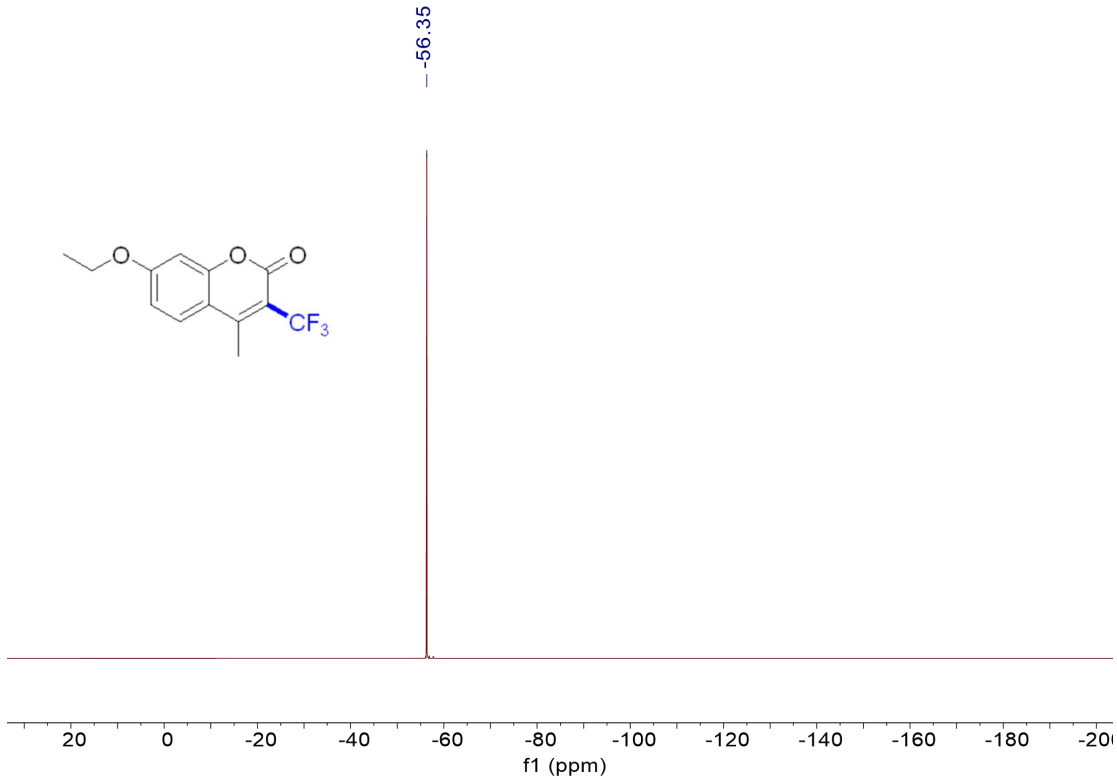
^{13}C NMR Spectrum of **3w**



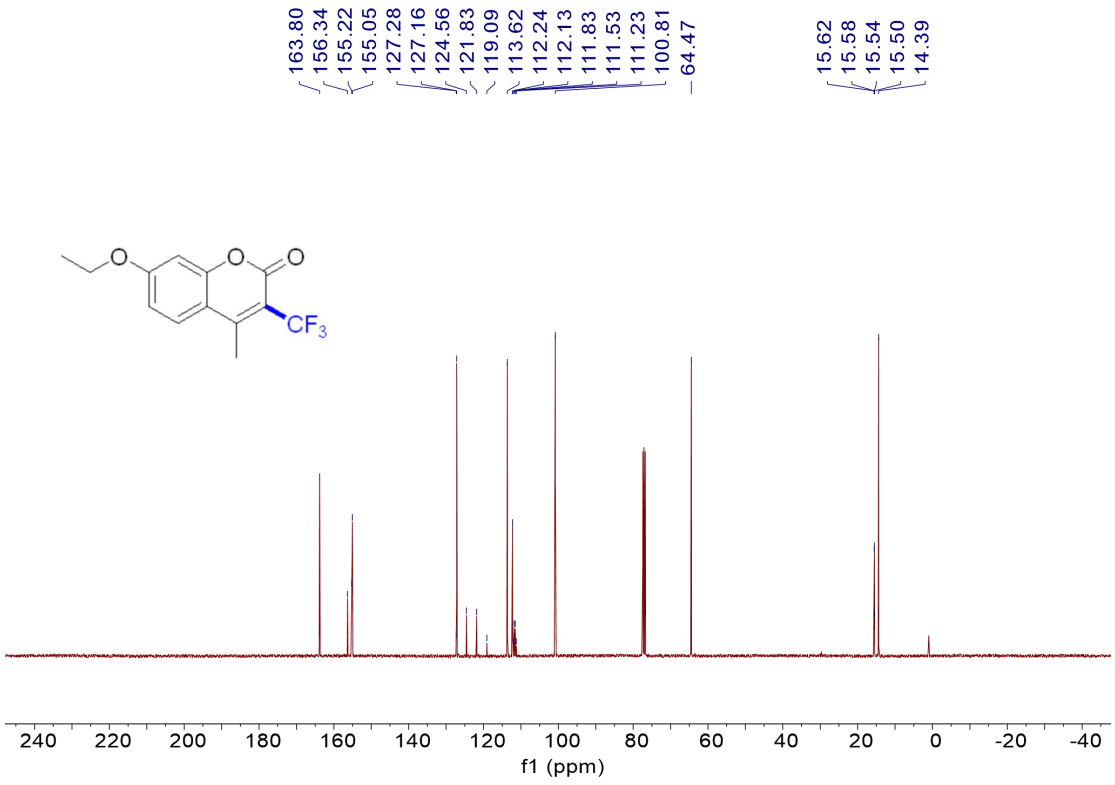
^{1}H NMR Spectrum of **3x**



^{19}F NMR Spectrum of **3x**



^{13}C NMR Spectrum of **3x**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155.22
155.05
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127.16
124.56
121.83
119.09
113.62
112.24
112.13
111.83
111.53
111.23
100.81
64.47
15.62
15.58
15.54
15.50
14.39
O
O
O
CF3
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)