Supporting Information

Bistrifluoromethylated Organocuprate $[Ph_4P]^+[Cu(CF_3)_2]^-$: Synthesis, Characterization and Its Application for Trifluoromethylation of Activated Heteroaryl Bromides, Chlorides and iodides

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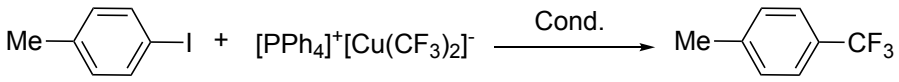
General information. All reactions were maintained under an argon atmosphere unless otherwise stated. All solvents were purified by standard methods. ^{1}H, ^{13}C , ^{31}P, ^{19}F NMR spectra were acquired on spectrometer (400 MHz for ^{1}H ; 101 or 126 MHz for ^{13}C; 121 MHz for ^{31}P; 375 MHz for ^{19}F). ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to fluorobenzene as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. 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.

Materials. All reagents were received from commercial sources. Solvents were freshly dried and degassed according to the purification handbook Purification of Laboratory Chemicals before using.

Table S1. Optimization of the reaction conditions for the trifluoromethylation of aryl iodide[a,b]

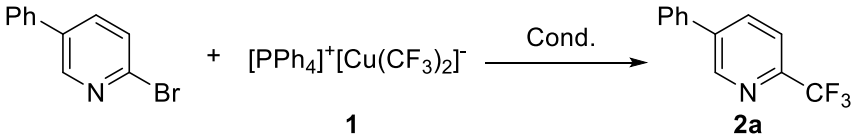


1

entry	**1** (eq.)	[Cu] (1.0 eq.)	solvent	temp. (^{o}C)	yield (%)
1	1.2	-	DMF	80	18
2	1.2	-	DMF	100	62
3	1.2	CuI	DMF	100	93
4	1.2	CuI	PhCN	100	91
5	1.2	CuI	DMAc	100	90
6	1.2	CuI	DMSO	100	14
7	1.2	CuI	NMP	100	86
8	1.2	CuI	THF	100	55
9	1.2	CuCl	DMF	100	77
10	1.2	CuBr	DMF	100	88
11	1.2	$CuBr_2$	DMF	100	79
12	1.2	Cu	DMF	100	56
13	1.2	CuI	DMF	120	93
14	1.2	CuI	DMF	110	92
15	1.2	CuI	DMF	90	88
16	1.5	CuI	DMF	80	81
17	2.0	CuI	DMF	100	93
18	1.0	CuI	DMF	100	93
19	1.2	CuI	DMF	100	86
20	1.2	CuI (0.8 eq.)	DMF	100	89
21	1.2	CuI (1.2 eq.)	DMF	100	85

[a]Reaction conditions: 4-methyl-iodobenzene (0.050 mmol), complex **1**, [Cu] in 1.0 mL of solvent for 3 h; [b]Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with fluorobenzene as an internal standard.

Table S2. Optimization of the reaction conditions for the trifluoromethylation of heteroaryl bromide[a,b]

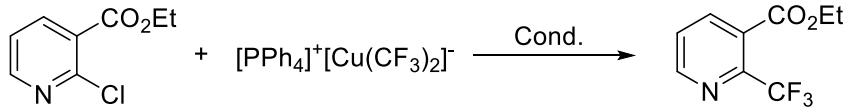


1 **2a**

entry	**1** (eq.)	[Cu] (1.0 eq.)	solvent	temp. (^{o}C)	yield (%)
1	1.2	-	DMF	100	33
2	1.2	CuI	DMF	100	96
3	1.0	CuI	DMF	100	96
4	0.8	CuI	DMF	100	67
5	1.0	CuI	DMF	90	78
6	1.0	CuI	DMF	80	64
7	1.0	CuI	PhCN	100	70
8	1.0	CuI	DMAc	100	86
9	1.0	CuI	DMSO	100	17
10	1.0	CuCl	NMP	100	85
11	1.0	CuBr	DMF	100	66
12	1.0	Cu	DMF	100	75
13	1.0	CuI	DMF	100	38
14	1.0	CuI (0.8 eq.)	DMF	100	87
15	1.0	CuI (0.5 eq.)	DMF	100	84

[a]Reaction conditions: 5-phenyl-2-bromopyridine (0.050 mmol), complex **1**, [Cu] (0.050 mmol) in 1.0 mL of solvent for 3 h; [b]Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with fluorobenzene as an internal standard.

Table S3. Optimization of the reaction conditions for the trifluoromethylation of heteroaryl chloride[a,b]

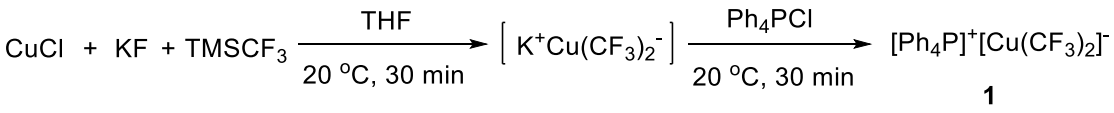


1 **3b**

entry	[Cu] (1.0 eq.)	1 (eq.)	solvent	temp. (°C)	yield (%)
1	-	-	DMF	100	n.d.
2	CuI	1.0	DMF	100	71
3	CuI	1.0	CH_3CN	100	22
4	CuI	1.0	DMAc	100	63
5	CuI	1.0	DMSO	100	n.d.
6	CuI	1.0	NMP	100	58
7	CuI	1.0	DMF	120	59
8	CuI	1.0	DMF	110	71
9	CuI	1.0	DMF	90	43
10	CuCl	1.0	DMF	100	58
11	CuBr	1.0	DMF	100	68
12	CuTc	1.0	DMF	100	40
13	Cu	1.0	DMF	100	8
14	CuI	1.2	DMF	100	80
15	CuI (0.8 eq.)	1.2	DMF	100	50
16	CuI (1.2 eq.)	1.2	DMF	100	74

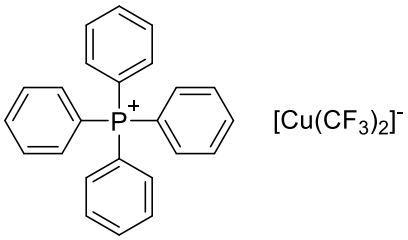
[a]Reaction conditions: ethyl 2-chloronicotinate (0.050 mmol), complex **1** , [Cu] (0.050 mmol) in 1.0 mL of solvent for 3 h; [b]Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with fluorobenzene as an internal standard.

General procedure for preparation of bis(trifluoromethyl)copper(I) complex 1



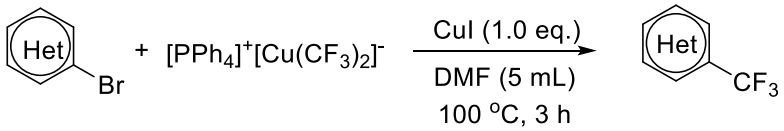
In an argon-filled glove box, CuCl (1.00 g, 10.0 mmol), KF (3.80 g, 65.0 mmol) and 30.0 mL THF were placed into an oven-dried 100 mL Schlenk tube equipped with a stirring bar. Then $TMSCF_3$ (5.00 g, 5.20 mL, 35.0 mmol) was slowly added into the solution, and the reaction system was stirred at 20 °C for 30 min. Then tetraphenylphosphonium chloride (3.74 g, 10.0 mmol) was added and the suspension was maintained for another 30 min. The suspension was filtered through a short plug of Celite to give a colorless solution, and then the solvent was evaporated. The residue was washed by methyl *tert*-butyl ether (50 mL×3) and dried under vaccum to give $[Ph_4P]^+[Cu(CF_3)_2]^-$ as a white solid (3.98 g, 74%).

Tetraphenylphosphonium bis(trifluoromethyl)copper(I) (1)



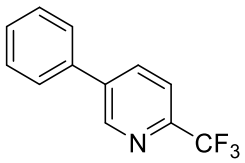
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, J = 7.6 Hz, 4 H), 7.76 (td, ^2J = 8.0 Hz, ^3J = 3.2 Hz, 8 H), 7.64 (d, J = 8.0 Hz, 4 H), 7.60 (d, J = 8.0 Hz, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -31.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.39 ppm. Anal. Calcd for $C_{25}H_{20}PF_6Cu$: C, 57.73; H, 3.73; Found: C, 57.35; H, 3.43.

General procedure for trifluoromethylation of heteroaryl bromides 2a-x



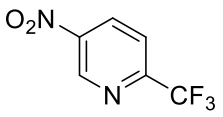
In an argon-filled glovebox, heteroaryl halide (0.50 mmol), complex **1** (0.50 mmol), CuI (0.50 mmol) and 5.0 mL DMF were added into a 25 mL oven-dried sealed tube with a stirring bar. Then the sealed tube was set into the pre-heated oil bath at 100 °C for 3 h. Fluorobenzene (72 mg, 0.75 mmol) was added as an internal standard to determine the yield by ^{19}F NMR spectroscopy. 10 mL of water was added and the mixture was extracted with dichloromethane (50 mL × 3). The combined organic phase was dryed over anhydrous $MgSO_4$, filtered and concentrated under vaccum. The residue was further purified by flash chromatography to give the corresponding trifluoromethylated heteroarene.

5-Phenyl-2-trifluoremethylpyridine[1] (2a)



White solid (56 mg, 51%); ^{19}F NMR yield: 96%. Eluent: petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1 H), 8.03 (d, J = 8.4 Hz, 1 H), 7.75 (d, J = 8.0 Hz, 1 H), 7.59 (d, J = 8.0 Hz, 2 H), 7.52 (d, J = 7.6 Hz, 1 H), 7.49 – 7.46 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 146.8 (q, J = 35.4 Hz), 139.5, 136.3, 135.3, 129.3, 129.0, 127.3, 121.7 (q, J = 275.7 Hz), 121.4 (q, J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.7 ppm. LRMS (EI, m/z): 223 [M^+]; HRMS (EI, m/z) [M^+] calcd. for $C_{12}H_8NF_3$, 223.0609; Found: 223.0602. IR (thin film): ν_{max} = 3038, 1338, 1174, 1132, 1088 cm^{-1}.

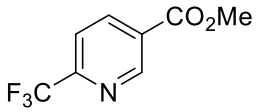
5-Nitro-2-(trifluoromethyl)pyridine[2] (2b)



Light-yellow solid (37 mg, 38%); ^{19}F NMR yield: 99%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1 H), 8.68 (d, J = 8.0 Hz, 1 H), 7.93 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7 (q, J = 36.4

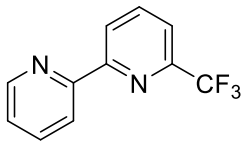
Hz), 145.5, 141.2 (br), 132.9, 121.2 (q, J = 3.3 Hz), 120.5 (q, J = 275.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.1 ppm. LRMS (EI, m/z): 192 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_6H_3N_2O_2F_3$, 192.0147; Found: 192.0146. IR (thin film): ν_{max} = 3062, 1610, 1534, 1329, 1174 cm^{-1}.

Methyl 6-(trifluoromethyl)pyridine-3-carboxylate[3] (2c)



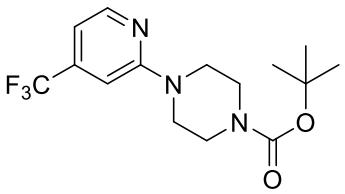
White solid (39 mg, 39%); ^{19}F NMR yield: 96%. Eluent: dichloromethane : petroleum ether = 1:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1 H), 8.46 (d, J = 8.0 Hz, 1 H), 7.76 (d, J = 8.0 Hz, 1 H), 3.97 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 151.2 (q, J = 35.3 Hz), 151.0, 138.7, 128.5, 121.1 (q, J = 276.7 Hz), 120.2, 52.8 ppm (q, J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.4 ppm. LRMS (EI, m/z): 205 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_8H_6O_2F_3$, 205.0351. Found: 205.0350. IR (thin film): ν_{max} = 3070, 1724, 1438, 1288, 1118 cm^{-1}.

6-Trifluoromethyl-2,2′-bipyridine[4] (2d)



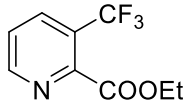
White solid (45 mg, 40%); ^{19}F NMR yield: 93%. Eluent: dichloromethane : petroleum ether = 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (ddd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, ^5J = 0.4 Hz, 1 H), 8.63 (d, J = 8.0 Hz, 1 H), 8.52 (dt, ^2J = 7.6 Hz, ^3J = 1.2 Hz, 1 H), 7.99 (t, J = 7.6 Hz, 1 H), 7.85 (td, ^2J = 7.8 Hz, ^3J = 1.6 Hz, 1 H), 7.68 (dd, ^2J = 8.0 Hz, ^3J = 0.4 Hz, 1 H), 7.35 (ddd, ^2J = 8.4 Hz, ^3J = 4.8 Hz, ^4J = 0.8 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 154.7, 147.7 (q, J = 35.4 Hz), 138.2, 137.1, 125.7, 124.4, 123.5, 123.0 (q, J = 275.7 Hz), 121.6, 120.1 (q, J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.1 ppm. LRMS (EI, m/z): 224 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{11}H_7N_2F_3$, 224.0561; Found: 224.0560. IR (thin film): ν_{max} = 1998, 1587, 1349, 1193, 1117 cm^{-1}.

***tert*-Butyl 4-[4-(trifluoromethyl)-2-pyridyl]piperazine-1-carboxylate (2e)**



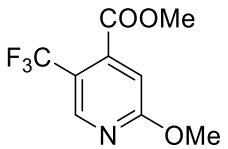
White solid (70 mg, 42%); ^{19}F NMR yield: 81%. Eluent: ethyl acetate : petroleum ether = 1:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 5.2 Hz, 1 H), 6.78 (d, J = 6.0 Hz, 2 H), 3.58-3.60 (m, 4 H), 3.54-3.55 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 154.7, 149.2, 139.8 (q, J = 33.3 Hz), 123.1 (q, J = 274.7 Hz), 108.5 (q, J = 3.0 Hz), 102.5 (q, J = 4.0 Hz), 80.1, 44.8, 43.2, 28.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.6 ppm. LRMS (EI, m/z): 331 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{15}H_{20}N_3O_2F_3$, 331.1508; Found: 331.1507. IR (thin film): ν_{max} = 2984, 1686, 1325, 1164, 980 cm^{-1}. m.p. 94.4 ~ 95.2 °C.

Ethyl 3-(trifluoromethyl)pyridine-2-carboxylate (2f)



Yellow liquid (55 mg, 50%); ^{19}F NMR yield: 74%. Eluent: ethyl acetate : petroleum ether = 1:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 4.0 Hz, 1 H), 8.07 (d, J = 8.0 Hz, 1 H), 7.55 (dd, ^{2}J = 8.0 Hz, ^{3}J = 4.0 Hz, 1 H), 4.47 (q, J = 7.2 Hz, 2 H), 1.41 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 151.1, 148.2, 133.9 (q, J = 5.1 Hz), 123.9 (q, J = 34.4 Hz), 123.8, 121.7 (q, J = 274.7 Hz), 61.7, 12.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.3 ppm. LRMS (EI, m/z): 219 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_9H_8NO_2F_3$, 219.0507; Found: 219.0502. IR (thin film): ν_{max} = 2988, 1744, 1322, 1303, 1145 cm^{-1}.

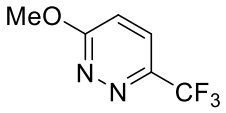
Methyl 2-methoxy-5-(trifluoromethyl)pyridine-4-carboxylate (2g)



White solid (89 mg, 76%); ^{19}F NMR yield: 98%. Eluent: ethyl acetate : petroleum ether = 1:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1 H), 7.04 (s, 1 H), 3.99 (s, 3 H), 3.93 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 164.2, 145.6 (q, J = 6.1 Hz), 139.8, 122.3 (q, J = 273.7 Hz), 115.9 (q, J = 31.3 Hz), 110.8, 53.4, 52.2; ^{19}F NMR

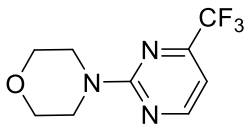
(376 MHz, $CDCl_3$) δ -58.9 ppm. LRMS (EI, m/z): 235 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_9H_8NO_3F_3$, 235.0456; Found: 235.0458. IR (thin film): ν_{max} = 2963, 1261, 1101, 1019, 801 cm^{-1}. m.p. 46.7 ~ 49.9 °C.

3-Methoxy-6-(trifluoromethyl)pyridazine (2h)



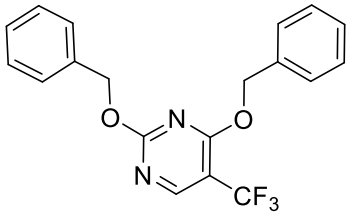
White solid (46 mg, 52%); ^{19}F NMR yield: 94%. Eluent: ethyl acetate : petroleum ether = 1:10. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.8 Hz, 1 H), 7.10 (d, J = 8.8 Hz, 1 H), 4.20 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 147.5 (q, J = 35.3 Hz), 126.4 (q, J = 2.52 Hz), 121.5 (q, J = 274.7 Hz), 117.9, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 ppm. LRMS (EI, m/z): 178 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_6H_5N_2OF_3$, 178.0354; Found: 178.0355; IR (thin film): ν_{max} = 3073, 1599, 1484, 1368, 1127 cm^{-1}. m.p. 77.9 ~ 79.9 °C.

4-[4-Trifluoromethyl)pyrimidin-2-yl]morpholine (2i)



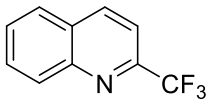
White solid (76 mg, 65%); ^{19}F NMR yield: 96%. Eluent: ethyl acetate : petroleum ether = 1:3. ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 4.8 Hz, 1 H), 6.77 (d, J = 4.8 Hz, 1 H), 3.84 (t, J = 4.8 Hz, 4 H), 3.75 (t, J = 4.8 Hz, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 159.7, 155.8 (q, J = 35.3 Hz), 120.1 (q, J = 275.9 Hz), 104.5 (q, J = 2.52 Hz), 66.3, 43.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.9 ppm. LRMS (EI, m/z): 233 [M+]; HRMS (EI, m/z) [M+] Calcd. for $C_9H_{10}ON_3F_3$, 233.0776; Found: 233.0781; IR (thin film): ν_{max} = 2995, 1590, 1570, 1493, 1333, 1131 cm^{-1}. m.p. 38.3 ~ 39.4 °C.

2,4-Bis(benzyloxy)-5-trifluoromethylpyrimidine (2j)



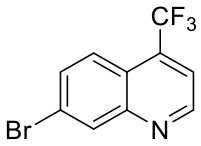
White solid (70 mg, 39%); ^{19}F NMR yield: 79%. Eluent: dichloromethane : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1 H), 7.45 (d, J = 8.0 Hz, 2 H), 7.33-7.39 (m, 8 H), 5.52 (s, 2 H), 5.45 (s, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.5, 157.6 (q, J = 4.0 Hz), 135.9, 135.4, 128.7, 128.7, 128.5, 128.4, 128.3, 127.6, 123.0 (q, J = 271.7 Hz), 106.4 (q, J = 34.3 Hz), 70.1, 69.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5 ppm. LRMS (EI, m/z): 361.1 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{19}H_{16}O_2N_2F_3$, 361.1158; Found: 361.1157. IR (thin film): ν_{max} = 3064, 1608, 1436, 1288, 1131 cm^{-1}. m.p. 75.2 ~ 77.1 °C.

2-Trifluoromethylquinoline[1] (2k)



White solid (55 mg, 56%); ^{19}F NMR yield: 100%. Eluent: dichloromethane : petroleum ether = 1:7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.4 Hz, 1 H), 8.22 (d, J = 8.4 Hz, 1 H), 7.90 (d, J = 8.4 Hz, 1 H), 7.82 (t, J = 7.6 Hz, 1 H), 7.73 (d, J = 8.4 Hz, 1 H), 7.67 (t, J = 7.6 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0 (q, J = 35.4 Hz), 147.2, 138.1, 130.8, 130.2, 128.9, 128.6, 127.7, 121.6 (q, J = 275.7 Hz), 116.8 (q, J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.5 ppm. LRMS (EI, m/z): 197 [M^+]; HRMS (EI, m/z) [M^+] calcd. for $C_{10}H_6NF_3$, 197.0452; Found: 197.0450. IR (thin film): ν_{max} = 3436, 1344, 1172, 1147, 1086 cm^{-1}.

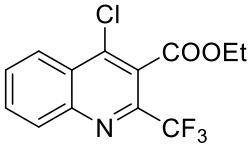
7-Bromo-4-(trifluoromethyl)quinolone (2l)



White solid (72 mg, 52%); ^{19}F NMR yield: 94%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1 H), 8.40 (s, 1 H), 8.00 (d, J = 6.0 Hz, 1 H), 7.77 (d, J = 9.2 Hz, 1 H), 7.70 (d, J = 3.6 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 149.6, 134.6 (q, J = 32.3 Hz), 132.8, 131.9, 125.4 (q, J = 2.0 Hz), 124.6, 123.1 (q, J = 275.7 Hz), 121.8, 118.2 (q, J = 5.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 ppm. LRMS (EI, m/z): 275 [M^+]; HRMS (EI, m/z) [M+] Calcd. for

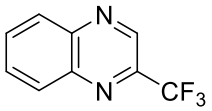
$C_{10}H_5NBrF_3$, 274.9557; Found: 274.9560. IR (thin film): ν_{max} = 3055, 1606, 1500, 1325, 1120 cm^{-1}. m.p. 61.4 ~ 62.7 °C.

Ethyl 4-chloro-2-(trifluoromethyl)quinoline-3-carboxylate (2m)



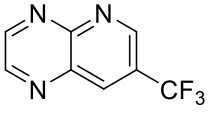
White solid (47 mg, 31%); ^{19}F NMR yield: 49%. Eluent: ethyl acetate : petroleum ether = 1:20. ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1 H), 8.23 (d, J = 8.4 Hz, 1 H), 7.91 (t, J = 7.6 Hz, 1 H), 7.81 (t, J = 8.0 Hz, 1 H), 4.51 (q, J = 6.4 Hz, 2 H), 1.43 (d, J = 8.4 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 146.7, 143.7 (q, J = 35.5 Hz), 142.1, 132.3, 130.6, 130.5, 126.3, 124.8, 124.5, 120.7 (q, J = 276.7 Hz), 63.0, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 ppm. LRMS (EI, m/z): 303 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{13}H_9NO_2F_3Cl$, 303.0274; Found: 303.0269. IR (thin film): ν_{max} = 2989, 1736, 1194, 1140 cm^{-1} m.p. 56.3 ~ 58.1 °C.

2-(Trifluoromethyl)quinoxaline[5] (2n)



White solid (58 mg, 59%); ^{19}F NMR yield: 93%. Eluent: dichloromethane : petroleum ether = 1:10. ^1H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1 H), 8.20 (td, ^2J = 6.4 Hz, ^3J = 1.2 Hz, 2 H), 7.94 – 7.88 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 142.8 (q, J = 35.3 Hz), 140.9, 140.8, 132.4, 131.6, 130.0, 129.5, 121.1 (q, J = 276.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0 ppm. LRMS (EI, m/z): 198.0 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_9H_5N_2F_3$, 198.0405; Found: 198.0399. IR (thin film): ν_{max} = 3014, 2 1174, 1150, 1130, 1084 cm^{-1}.

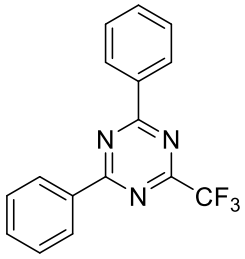
7-(Trifluoromethyl)pyrido[2,3-b]pyrazine (2o)



White solid (39 mg, 40%); ^{19}F NMR yield: 64%. Eluent: ethyl acetate : petroleum ether = 1:5. ^1H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1 H), 9.18 (s, 1 H), 9.05 (s, 1 H), 8.76 (s, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 150.0 (q, J = 2.2 Hz), 149.7,

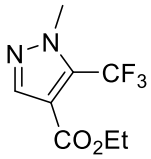
136.9 (q, J = 3.0 Hz), 128.5, 128.2, 128.0 (q, J = 34.3 Hz), 123.4 (q, J = 274.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.1 ppm. LRMS (EI, m/z): 199 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_8H_4N_3F_3$, 199.0357; Found: 199.0363. IR (thin film): ν_{max} = 3016, 1339, 1192, 1180, 1137 cm^{-1}. m.p. 142.8 ~ 143.5 ^{o}C.

2,4-Diphenyl-6-(trifluoromethyl)-1,3,5-triazine[6] (2p)



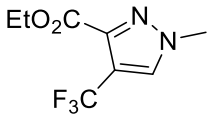
White solid (94 mg, 62%); ^{19}F NMR yield: 99%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 7.6 Hz, 4 H), 7.64 (t, J = 4.8 Hz, 2 H), 3.84 (t, J = 7.2 Hz, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 165.4 (q, J = 37.4 Hz), 134.6, 133.9, 129.6, 129.0, 119.2 (q, J = 277.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.5 ppm. LRMS (EI, m/z): 301 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{16}H_{10}N_3F_3$, 301.0827; Found: 301.0834. IR (thin film): ν_{max} = 3067, 1556, 1526, 1421, 1378 cm^{-1}.

Ethyl 1-methyl-5-(trifluoromethyl)pyrazole-4-carboxylate[7] (2q)



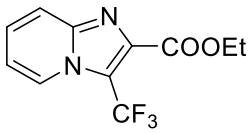
Light-yellow liquid (73 mg, 65%); ^{19}F NMR yield: 100%. Eluent: ethyl acetate : petroleum ether = 1:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1 H), 4.28 (q, J = 7.2 Hz, 2 H), 4.03 (s, 3 H), 1.31 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 141.2, 131.8 (q, J = 40.4 Hz), 119.5 (q, J = 272.7 Hz), 115.9 (q, J = 1.1 Hz), 60.9, 40.2 (q, ^4J = 40.4 Hz), 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.2 ppm. LRMS (EI, m/z): 222 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_8H_9N_2O_2F_3$, 222.0616; Found: 222.0612. IR (thin film): ν_{max} = 2986, 1736, 1299, 1223, 1040 cm^{-1}.

Ethyl 1-methyl-4-(trifluoromethyl)pyrazole-3-carboxylate (2r)



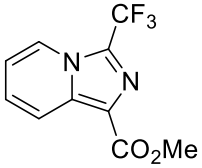
White solid (53 mg, 48%); ^{19}F NMR yield: 63%. Eluent: ethyl acetate : petroleum ether = 1:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1 H), 4.40 (q, J = 7.2 Hz, 2 H), 3.97 (s, 3 H), 1.37 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 139.9, 131.7 (q, J = 4.0 Hz), 121.0 (q, J = 267.6 Hz), 114.7 (q, J = 39.4 Hz), 61.1, 39.5, 13.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.4 ppm. LRMS (EI, m/z): 207 [[M-CH_3]$^+$]; HRMS (EI, m/z) [M^+] Calcd. for $C_8H_9N_2O_2F_3$, 222.0616; Found: 222.0622 . IR (thin film): ν_{max} = 3102, 1729, 1304, 1116, 1044 cm^{-1}.m.p. 71.8 ~ 72.8 ^{o}C.

Ethyl 3-(trifluoromethyl)imidazo[1,2-a]pyridine-2-carboxylate (2s)



Light-yellow liquid (66 mg, 51%); ^{19}F NMR yield: 89%. Eluent: ethyl acetate : petroleum ether = 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 5.6 Hz, 1 H), 7.81 (d, J = 7.2 Hz, 1 H), 7.44 (t, J = 6.4 Hz, 1 H), 7.08 (t, J = 5.6 Hz, 1 H), 4.50 (q, J = 5.6 Hz, 2 H), 1.45 (t, J = 5.6 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 144.4, 136.7, 126.7, 124.8 (q, J = 5.1 Hz), 119.9 (q, J = 269.7 Hz), 118.4, 114.5, 113.9 (q, J = 42.4 Hz), 61.1, 13.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.1 ppm. LRMS (EI, m/z): 258 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{11}H_9N_2O_2F_3$, 258.0616; Found: 258.0621. IR (thin film): ν_{max} = 2963, 1738, 1261, 1096, 1023 cm^{-1}.

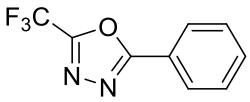
Methyl 3-(trifluoromethyl)imidazo[1,5-a]pyridine-1-carboxylate (2t)



White solid (82 mg, 68%); ^{19}F NMR yield: 96%. Eluent: dichloromethane : petroleum ether = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 9.2 Hz, 1 H), 8.23 (d, J = 7.2 Hz, 1 H), 7.30 (dd, ^{2}J = 9.2 Hz, ^{3}J = 6.8 Hz, 1 H), 7.01 (t, J = 6.8 Hz, 1 H), 3.99 (s, 3

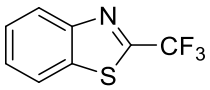
H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 136.3, 126.7 (q, J = 42.4 Hz), 126.0, 123.0, 121.7, 120.2, 119.2 (q, J = 270.7 Hz), 116.4, 52.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1 ppm. LRMS (EI, m/z): 244 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{10}H_7N_2O_2F_3$, 244.0453; Found: 244.0460. IR (thin film): ν_{max} = 3077, 1703, 1519, 1235, 1167, 1056 cm^{-1}. m.p. 106.1 ~ 107.8 °C.

2-Phenyl-5-(trifluoromethyl)-1,3,4-oxadiazole (2u)



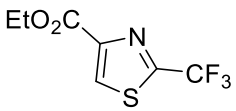
White solid (41 mg, 38%); ^{19}F NMR yield: 60%. Eluent: ethyl acetate : petroleum ether = 1:8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 6.8 Hz, 2 H), 7.60-7.61 (m, 1 H), 7.55-7.57 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 154.8 (q, J = 45.5 Hz), 133.1, 129.3, 127.5, 122.2, 116.3 (q, J = 272.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 ppm. LRMS (EI, m/z): 214 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_9H_5N_2OF_3$, 214.0354; Found: 214.0356; IR (thin film): ν_{max} = 3052, 1610, 1453, 1206, 1171 cm^{-1}. m.p. 45.7 ~ 47.2 °C.

2-(Trifluoromethyl)-1,3-benzothiazole[8] (2v)



Stick oil (47 mg, 46%); ^{19}F NMR yield: 85%. Eluent: dichloromethane : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.60 (td, ^2J = 8.0 Hz, ^3J = 1.2 Hz, 1 H), 7.55 (td, ^2J = 8.0 Hz, ^3J = 1.2 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1 (q, J = 35.4 Hz), 152.2, 135.1, 127.6, 127.5, 125.1, 122.2, 120.0 (q, J = 274.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.7 ppm. LRMS (EI, m/z): 203 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_8H_4NF_3S$, 203.0017; Found: 203.0014. IR (thin film): ν_{max} = 2962, 2917, 1261, 1097, 800 cm^{-1}.

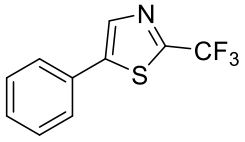
Ethyl 2-(trifluoromethyl)thiazole-4-carboxylate[9] (2w)



White solid (51 mg, 45%); ^{19}F NMR yield: 99%. Eluent: ethyl acetate : petroleum ether = 1:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1 H), 4.44 (q, J = 8.0 Hz, 2 H),

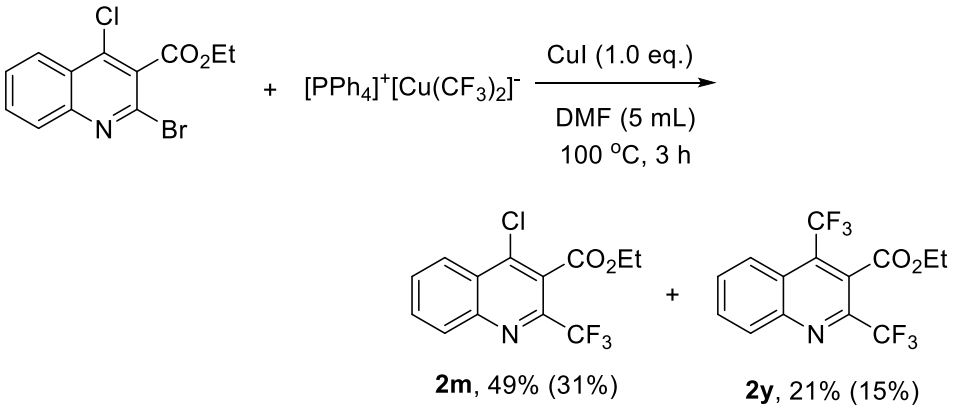
1.40 (q, J = 8.0 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 156.4 (q, J = 42.4 Hz), 148.5, 129.8, 119.2 (q, J = 274.7 Hz), 62.1, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.1 ppm. LRMS (EI, m/z): 225 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_7H_6NSO_2F_3$, 225.0071; Found: 225.0077. IR (thin film): ν_{max} = 3096, 1725, 1501, 1242, 1040 cm^{-1}.

5-Phenyl-2-(trifluoromethyl)thiazole[9] (2x)



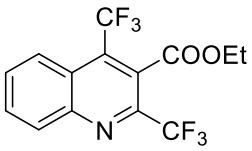
White solid (58 mg, 50%); ^{19}F NMR yield: 99%. Eluent: ethyl acetate : petroleum ether = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1 H), 7.57 (d, J = 4.8 Hz, 2 H), 7.44 (m, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1 (q, J = 41.4 Hz), 143.7, 139.1, 129.7, 129.6, 129.4, 127.2, 119.7 (q, J = 273.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.1 ppm. LRMS (EI, m/z): 229 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{10}H_6NSF_3$, 229.0173; Found: 229.0168. IR (thin film): ν_{max} = 2926, 1455, 1326, 1151, 1032 cm^{-1}.

Bistrifluoromethylation of of ethyl 2-bromo-4-chloroquinoline-3-carboxylate



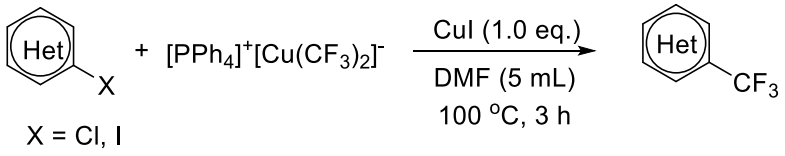
During the study for the trifluoromethylation of ethyl 2-bromo-4-chloroquinoline-3-carboxylate, trifluoromethylated product **2m** and *di*-trifluormethylated product **2y** were detected and isolated. This interesting result showed that the ethyl acetated group in the *ortho*-position of the chloride could facilitate the trifluoromethylation of heteroaryl chloride substrates. The compound **2y** was analyzed by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, LRMS, HRMS and IR.

Ethyl 2,4-di-(trifluoromethyl)quinoline-3-carboxylate (2y)



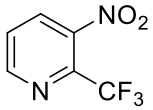
White solid (25 mg, 15%); ^{19}F NMR yield: 21%. Eluent: dichloromethane : petroleum ether = 1:20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.4 Hz, 1 H), 8.20 (d, J = 8.4 Hz, 1 H), 7.90 (t, J = 7.2 Hz, 1 H), 7.80 (t, J = 7.6 Hz, 1 H), 4.43 (q, J = 7.2 Hz, 2 H), 1.36 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 142.2, 138.8 (q, J = 35.4 Hz), 128.5 (q, J = 32.3 Hz), 127.3, 126.4, 126.4, 120.0 (q, J = 3.0 Hz), 119.6, 118.6, 118.3 (q, J = 278.8 Hz), 116.0 (q, J = 277.8 Hz), 58.5, 8.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.0, -64.2 ppm. LRMS (EI, m/z): 337 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{14}H_9NO_2F_6$, 337.0537; Found: 337.0531; IR (thin film): ν_{max} = 2988, 1748, 1269, 1183, 1142 cm^{-1}. m.p. 41.0 ~ 42.6 °C.

General procedure for trifluoromethylation of heteroaryl chlorides and iodides 3a-x



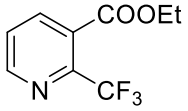
In an argon-filled glovebox, heteroaryl halide (0.50 mmol), complex **1** (0.60 mmol), CuI (0.50 mmol) and 5.0 mL DMF were added into a 25 mL oven-dried sealed tube with a stirring bar. Then the sealed tube was set into the pre-heated oil bath at 100 °C for 3 h. Fluorobenzene (72 mg, 0.75 mmol) was added as an internal standard to determine the yield by ^{19}F NMR spectroscopy. 10 mL of water was added and the mixture was extracted with dichloromethane (50 mL × 3). The combined organic phase was dryed over anhydrous $MgSO_4$, filtered and concentrated under vaccum. The residue was further purified by flash chromatography to give the corresponding trifluoromethylated heteroarene.

2-Trifluoromethyl-3-nitro-pyridine[10] (3a)



White solid (49 mg, 66%); ^{19}F NMR yield: 100%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 4.0 Hz, 1 H), 8.23 (d, J = 8.0 Hz, 1 H), 7.75 (dd, ^{2}J = 8.2 Hz, ^{3}J = 4.8 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 150.3, 145.1 (q, J = 36.4 Hz), 137.7, 132.0, 124.6 (q, J = 275.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 ppm. LRMS (EI, m/z): 192 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_6H_3N_2O_2F_3$, 192.0147; Found: 192.0150. IR (thin film): ν_{max} = 3088, 1534, 1363, 1313, 1054 cm^{-1}.

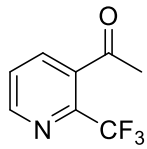
Ethyl 2-(trifluoromethyl)pyridine-3-carboxylate[11] (3b)



Light-yellow liquid (54 mg, 50%); ^{19}F NMR yield: 80%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 4.0 Hz, 1 H), 8.07 (d, J = 8.0 Hz, 1 H), 7.54 (dd, ^{2}J = 8.0 Hz, ^{3}J = 4.0 Hz, 1 H), 4.39 (q, J = 6.8 Hz , 2 H), 1.36 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 150.6, 145.5 (q, J =

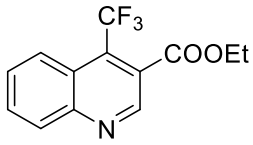
35.4 Hz), 138.2, 128.2, 126.0, 121.1 (q, J = 275.7 Hz), 62.55, 13.77; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.4 ppm. LRMS (EI, m/z): 219 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_9H_8NO_2F_3$, 219.0507; Found: 219.0500. IR (thin film): ν_{max} = 2988, 1736, 1322, 1148, 1061 cm^{-1}.

1-[2-(Trifluoromethyl)-3-pyridyl]ethanone (3c)



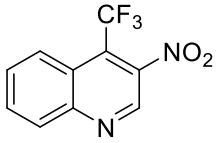
Light-yellow liquid (55 mg, 58%); ^{19}F NMR yield: 85%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 4.0 Hz, 1 H), 7.78 (d, J = 7.6 Hz, 1 H), 7.85 (dd, ^2J = 7.2 Hz, ^3J = 4.8 Hz, 1 H), 2.57 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.89, 150.25, 143.6 (q, J = 35.4 Hz), 136.5, 135.5, 126.2, 121.3 (q, J = 275.7 Hz), 30.76; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4 ppm. LRMS (EI, m/z): 189 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_8H_6NOF_3$, 189.0401; Found: 189.0399. IR (thin film): ν_{max} = 3405, 1712, 1324, 1184, 1110 cm^{-1}.

Ethyl 4-trifluoromethylquinoline-3-carboxylate (3d)



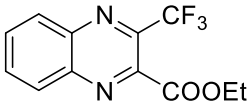
Stick yellow oil (61 mg, 50%); ^{19}F NMR yield: 65%. Eluent: ethyl acetate : petroleum ether = 1:8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1 H), 8.22 (d, J = 8.4 Hz, 2 H), 7.85 (t, J = 7.6 Hz, 1 H), 7.72 (t, J = 7.2 Hz, 1 H), 4.48 (q, J = 7.2 Hz , 2 H), 1.42 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 149.1, 147.7, 131.1, 131.0 (q, J = 32.3 Hz), 130.5, 129.1, 125.5 (q, J = 3.0 Hz), 124.8 (q, J = 4.0 Hz), 123.1 (q, J = 277.8 Hz), 122.3, 62.8, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.4 ppm. LRMS (EI, m/z): 269 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{13}H_{10}NO_2F_3$, 269.0664; Found: 269.0662. IR (thin film): ν_{max} = 2985, 1736, 1505, 1277, 1234 cm^{-1}.

3-Nitro-4-(trifluoromethyl)quinoline (3e)



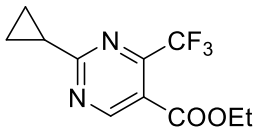
White solid (68 mg, 56%); ^{19}F NMR yield: 73%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1 H), 8.25-8.28 (m, 2 H), 7.96 (t, J = 7.2 Hz, 1 H), 7.84 (t, J = 7.6 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 142.8, 141.6 (br), 132.3, 130.8, 130.5, 125.5 (q, $^{5}J_{FC}$ = 3.78 Hz), 125.3 (q, J = 34.0 Hz), 121.8, 121.6 (q, J = 277.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.4 ppm. LRMS (EI, m/z): 242 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{10}H_5N_2O_2F_3$, 242.0303; Found: 242.0302. IR (thin film): ν_{max} = 2893, 1538, 1366, 1213, 1123 cm^{-1}. m.p. 82.4 ~ 84.3 ^{o}C.

Ethyl 3-trifluoromethyquinoxaline-2-carboxylate (3f)



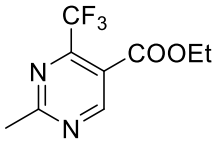
Light-yellow liquid (73 mg, 53%); ^{19}F NMR yield: 100%. Eluent: ethyl acetate : petroleum ether = 1:20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (m, 2 H), 7.95 (m, 2 H), 4.56 (q, J = 7.2 Hz , 2 H), 1.46 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 143.6, 141.7, 140.5, 140.2 (q, J = 36.5 Hz), 133.2, 132.7, 129.8, 129.6, 120.6 (q, J = 275.9 Hz), 63.2, 13.9 ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.7 ppm. LRMS (EI, m/z): 270 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{12}H_9N_2O_2F_3$, 270.0616; Found: 270.0620. IR (thin film): ν_{max} = 2921, 1745, 1538, 1150, 1123 cm^{-1}.

Ethyl 2-cyclopropyl-4-(trifluoromethyl)pyrimidine-5-carboxylate (3g)



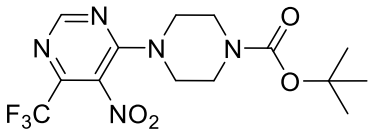
Suspension (93 mg, 72%); ^{19}F NMR yield: 90%. Eluent: ethyl acetate : petroleum ether = 1:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1 H), 4.38 (q, J = 7.2 Hz, 2 H), 2.34-2.37 (m, 1 H), 1.35 (t, J = 7.2 Hz, 3 H), 1.22-1.24 (m, 2 H), 1.17-1.20 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 162.6, 158.7, 152.1 (q, J = 37.4 Hz), 119.6, 119.1 (q, J = 277.8 Hz), 61.6, 17.8, 12.8, 11.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.5 ppm. LRMS (EI, m/z): 260 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{11}H_{11}N_2O_2F_3$, 260.0773; Found: 260.0768. IR (thin film): ν_{max} = 2987, 1741, 1582, 1457, 1311, 1158 cm^{-1}.

Ethyl 2-methyl-4-trifluoromethylpyrimidine-5-carboxylate (3h)



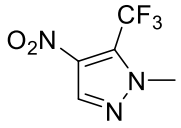
Light-yellow liquid (48 mg, 41%); ^{19}F NMR yield: 88%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1 H), 4.41 (q, J = 7.2 Hz , 2 H), 2.84 (s, 3 H), 1.37 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 163.5, 159.7, 153.1 (q, J = 36.5 Hz), 121.4, 120.1 (q, J = 275.9 Hz), 62.8, 26.0, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 ppm. LRMS (EI, m/z): 234 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_9H_9N_2O_2F_3$, 234.0616; Found: 234.0618. IR (thin film): ν_{max} = 2988, 1743, 1583, 1316, 1158 cm^{-1}.

***tert*-Butyl 4-[5-nitro-6-(trifluoromethyl)pyrimidin-4-yl]piperazine-1-carboxylate (3i)**



Yellow solid (115 mg, 61%); ^{19}F NMR yield: 82%. Eluent: ethyl acetate : petroleum ether = 1:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1 H), 3.63 (s, 4 H), 3.55 (s, 4 H), 1.45 (s, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 154.3, 154.1, 147.5 (q, J = 36.4 Hz), 130.0, 119.6 (q, J = 278.8 Hz), 80.7, 46.0, 42.7 (br), 28.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 ppm. LRMS (EI, m/z): 377 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{14}H_{18}N_5O_4F_3$, 377.1311; Found: 377.1313. IR (thin film): ν_{max} = 2999, 1686, 1587, 1538, 1177 cm^{-1}. m.p. 107.7 ~ 109.1 ^{o}C.

1-Methyl-4-nitro-5-(trifluoromethyl)pyrazole (3j)



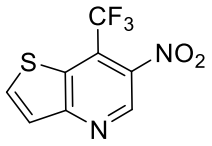
Light-yellow liquid (42 mg, 43%); ^{19}F NMR yield: 65%. Eluent: ethyl acetate : petroleum ether = 1:8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1 H), 4.12 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 136.6, 129.6 (q, J = 41.4 Hz), 120.1 (q, J = 271.7 Hz), 43.3 (q, ^{4}J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.6 ppm. LRMS (EI, m/z):

195 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_5H_4N_3O_2F_3$, 195.0256; Found: 195.0259. IR (thin film): ν_{max} = 3136, 1530, 1329, 1279, 1162 cm^{-1}.

4-(Trifluoromethyl)thieno[3,2-d]pyrimidine (3k)

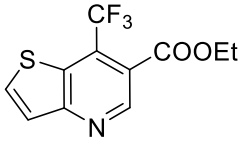
White solid (42 mg, 41%); ^{19}F NMR yield: 76%. Eluent: ethyl acetate : petroleum ether = 1:5. ^1H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1 H), 8.18 (q, J = 5.6 Hz, 1 H), 7.68 (d, J = 5.6 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 154.2, 149.9 (q, J = 37.4 Hz), 138.7 (q, J = 1.0 Hz), 126.2, 124.5, 120.8 (q, J = 276.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.0 ppm. LRMS (EI, m/z): 204 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_7H_3N_2SF_3$, 203.9969; Found: 203.9972. IR (thin film): ν_{max} = 3084, 1560, 1530, 1330, 1158 cm^{-1}. m.p. 72.7 ~ 74.2 °C.

6-Nitro-7-(trifluoromethyl)thieno[3,2-b]pyridine (3l)



Light-yellow solid (78 mg, 63%); ^{19}F NMR yield: 94%. Eluent: ethyl acetate : petroleum ether = 1:6. ^1H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1 H), 8.18 (d, J = 5.6 Hz, 1 H), 7.74 (d, J = 5.6 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 143.1, 139.8, 138.1 (q, J = 3.03 Hz), 129.0, 125.9 (q, J = 36.4 Hz), 125.1, 121.5 (q, J = 277.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 ppm. LRMS (EI, m/z): 248 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_8H_3N_2O_2F_3S$, 247.9867; Found: 247.9868. IR (thin film): ν_{max} = 3114, 1526, 1504, 1264, 1151 cm^{-1}. m.p. 81.4 ~ 82.8 °C.

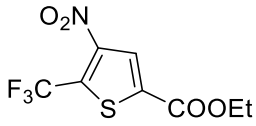
Ethyl 7-(trifluoromethyl)thieno[3,2-b]pyridine-6-carboxylate (3m)



Light-yellow liquid (88 mg, 64%); ^{19}F NMR yield: 96%. Eluent: ethyl acetate : petroleum ether = 1:5. ^1H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1 H), 8.00 (d, J = 5.6 Hz, 1 H), 7.66 (d, J = 5.6 Hz, 1 H), 4.46 (q, J = 7.2 Hz, 2 H), 1.41 (t, J = 7.2 Hz, 3 H);

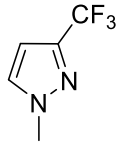
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 159.5, 148.1, 135.2 (q, J = 3.0 Hz), 131.0 (q, J = 35.4 Hz), 128.7, 125.0, 122.7 (q, J = 276.7 Hz), 121.6, 62.6, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.8 ppm. LRMS (EI, m/z): 275 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{11}H_8NO_2F_3S$, 275.0228; Found: 275.0227. IR (thin film): ν_{max} = 2985, 1735, 1301, 1270, 1176 cm^{-1}.

Ethyl 4-nitro-5-trifluoromethylthiophene-2-carboxylate (3n)



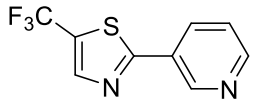
Light-yellow liquid (59 mg, 38%); ^{19}F NMR yield: 67%. Eluent: ethyl acetate : petroleum ether = 1:20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1 H), 4.41 (q, J = 7.2 Hz , 2 H), 1.39 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 145.4 (q, J = 2.5 Hz), 134.8, 134.0 (q, J = 40.3 Hz), 129.4, 119.8 (q, J = 272.2 Hz), 63.0, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.0 ppm. LRMS (EI, m/z): 269 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_8H_6NO_4F_3S$, 268.9970; Found: 268.9965. IR (thin film): ν_{max} = 3119, 1732, 1540, 1337, 1274 cm^{-1}.

1-Methyl-3-(trifluoromethyl)-1H-pyrazole[12] (3o)



Colorless liquid (44 mg, 59%); ^{19}F NMR yield: 90%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 1 H), 6.44 (s, 1 H), 3.89 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2 (q, J = 38.4 Hz), 131.3, 121.3 (q, J = 269.7 Hz), 104.4 (q, J = 3.0 Hz), 39.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.0 ppm. LRMS (EI, m/z): 150[M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_5H_5N_2F_3$, 150.0405; Found: 150.0402. IR (thin film): ν_{max} = 3130, 1498, 1381, 1248, 1139 cm^{-1}.

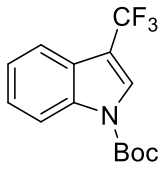
2-Phenyl-5-(trifluoromethyl)thiazole (3p)



Yellow solid (65 mg, 57%); ^{19}F NMR yield: 100%. Eluent: petroleum ether. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.18 (s, 1 H), 8.73 (s, 1 H), 8.22 (d, J = 7.6 Hz, 1 H), 8.15 (s, 1

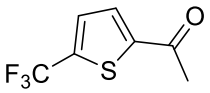
H), 7.42 (s, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 151.9, 147.8, 144.7 (q, J = 4.0 Hz), 133.9, 128.6, 127.1 (q, J = 38.4 Hz), 124.0, 121.8 (q, J = 270.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.4 ppm. LRMS (EI, m/z): 230 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_9H_5N_2F_3S$, 230.0126; Found: 230.0118. IR (thin film): ν_{max} = 3087, 1586, 1318, 1142, 1046 cm^{-1}. m.p. 47.6 ~ 49.3 °C.

***tert*-Butyl 3-(trifluoromethyl)indole-1-carboxylate[12] (3q)**



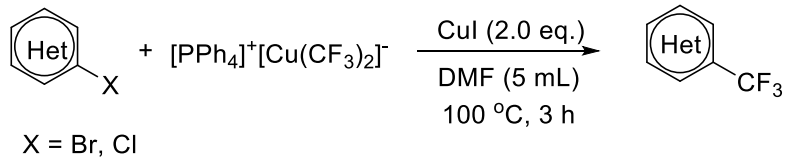
Yellow solid (47 mg, 33%); ^{19}F NMR yield: 44%. Eluent: ethyl acetate : petroleum ether = 1:10. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1 H), 7.92 (s, 1 H), 7.68 (d, J = 7.6 Hz, 1 H), 7.40 (t, J = 7.6 Hz, 1 H), 7.32 (t, J = 7.6 Hz, 1 H), 1.68 (s, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 134.8, 125.5 (q, J = 5.1 Hz), 125.1, 125.0, 123.2, 122.8 (q, J = 267.6 Hz), 119.2, 115.0, 111.2 (q, J = 37.4 Hz), 84.6, 27.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.3 ppm. LRMS (EI, m/z): 285 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{14}H_{14}NO_2F_3$, 285.0977; Found: 285.0967. IR (thin film): ν_{max} = 2983, 1750, 1454, 1289, 1151 cm^{-1}.

1-[5-(Trifluoromethyl)-2-thienyl]ethanone (3r)



Brown liquid (80 mg, 82%); ^{19}F NMR yield: 99%. Eluent: dichloromethane : petroleum ether = 1:10. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 1 H), 7.42 (s, 1 H), 2.57 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 147.2, 138.0 (q, J = 39.4 Hz), 131.0, 128.9 (q, J = 4.0 Hz), 121.8 (q, J = 271.7 Hz), 26.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.5 ppm. LRMS (EI, m/z): 194 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_7H_5F_3OS$, 194.0013; Found: 194.0015. IR (thin film): ν_{max} = 3107, 1677, 1543, 1296, 1267 cm^{-1}.

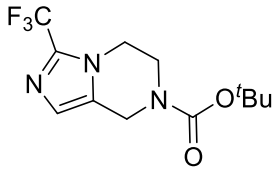
General procedure for trifluoromethylation of drug intermediates and derivatives 4-7



X = Br, Cl

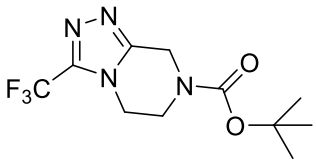
In an argon-filled glovebox, heteroaryl halides (0.50 mmol), complex **1** (1.0 mmol), CuI (1.0 mmol) and 5.0 mL DMF were added into a 25 mL oven-dried sealed tube with a stirring bar. Then the sealed tube was set into the pre-heated oil bath at 100 °C for 3 h. Fluorobenzene (72 mg, 0.75 mmol) was added as an internal standard to determine the yield by ^{19}F NMR spectroscopy. 10 mL of water was added and the mixture was extracted with dichloromethane (50 mL × 3). The combined organic phase was dryed over anhydrous $MgSO_4$, filtered and concentrated under vaccum. The residue was further purified by flash chromatography to give the corresponding trifluoromethylated heteroarene.

***tert*-Butyl 3-(trifluoromethyl)-6,8-dihydro-5H-imidazo[1,5-a]pyrazine-7-carboxylate (4)**



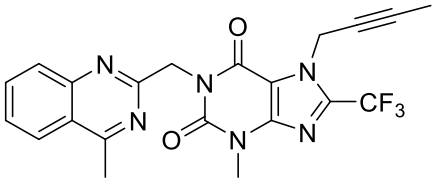
White solid (98 mg, 68%); ^{19}F NMR yield: 94%. Eluent: ethyl acetate: petroleum ether = 1:8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 1 H), 4.67 (s, 2 H), 4.13 (t, J = 4.4 Hz, 2 H), 3.83 (t, J = 4.4 Hz, 2 H), 1.48 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 134.4 (q, J = 40.3 Hz), 127.8, 123.8, 118.9 (q, J = 269.6 Hz), 81.4, 43.3, 41.0 (br), 40.2 (br), 28.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.1 ppm. LRMS (EI, m/z): 291 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{12}H_{16}N_3O_2F_3$, 291.1195; Found: 291.1200. IR (thin film): ν_{max} = 3127, 2980, 1714, 1491, 1232, 1112 cm^{-1}. m.p. 124.2 ~ 125.7 °C.

***tert*-Butyl 3-(trifluoromethyl)-6,8-dihydro-5H-[1,2,4]triazolo[4,3-a] pyrazine-7-carboxylate (5)**



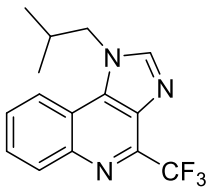
White solid (48 mg, 33%); ^{19}F NMR yield: 52%. Eluent: ethyl acetate: petroleum ether = 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (s, 2 H), 4.14 (t, J = 4.8 Hz, 2 H), 3.89 (t, J = 4.8 Hz, 2 H), 1.47 (s, 9 H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 150.4, 143.6 (q, J = 37.8 Hz), 118.3 (q, J = 270.9 Hz), 82.0, 43.5, 41.2, 39.3, 28.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.9 ppm. LRMS (EI, m/z): 277 [[M-CH_3]$^+$]; HRMS (EI, m/z) [M^+] Calcd. for $C_{11}H_{15}N_4O_2F_3$, 292.1147; Found: 292.1154. IR (thin film): ν_{max} = 3005, 1683, 1511, 1187, 1134 cm^{-1}. m.p. 101.9 ~ 103.4 °C.

7-But-2-ynyl-3-methyl-1-[(4-methylquinazolin-2-yl)methyl]-8-(trifluoromethyl)purine-2,6-dione (6)



Light-yellow solid (99 mg, 45%); ^{19}F NMR yield: 91%. Eluent: ethyl acetate: petroleum ether = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 1 H), 7.84 (d, J = 7.6 Hz, 1 H), 7.76 (m, 1 H), 7.52 (m, 1 H), 5.56 (s, 2 H), 5.28 (s, 2 H), 3.61 (s, 3 H), 2.88 (s, 3 H), 1.76 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 159.8, 154.7, 151.0, 149.5, 146.6, 138.1 (q, J = 40.3 Hz), 133.0, 128.4, 126.5, 124.5, 122.8, 117.8 (q, J = 272.1 Hz), 108.4, 82.4, 70.9, 46.2, 36.4, 29.5, 21.4, 3.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.8 ppm. LRMS (EI, m/z): 442 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{21}H_{17}O_2N_6F_3$, 442.1365; Found: 442.1367. IR (thin film): ν_{max} = 2993, 1712, 1664, 1147, 769 cm^{-1}. m.p. 238.1 ~ 240.0 °C.

1-Isobutyl-4-(trifluoromethyl)imidazo[4,5-c]quinolone (7)



White solid (84 mg, 57%); ^{19}F NMR yield: 71%. Eluent: ethyl acetate: petroleum ether = 1:20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.38 (m, 1 H), 8.12-8.15 (m, 1 H), 7.77 (s, 1 H), 7.72-7.77 (m, 2 H), 4.39 (q, J = 7.6 Hz, 2 H), 2.30-2.41 (m, 1 H), 1.06 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 142.4, 140.7 (q, J = 35.4 Hz), 134.3, 133.8, 131.3, 128.0, 127.5, 121.0 (q, J = 276.7 Hz), 119.4, 118.3, 54.7, 28.4, 19.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.6 ppm. LRMS (EI, m/z): 293 [M^+]; HRMS (EI, m/z) [M^+] Calcd. for $C_{15}H_{14}N_3F_3$, 293.1140; Found: 293.1143. IR (thin film): ν_{max} = 3100, 2962, 1340, 1137, 1079 cm^{-1}. m.p. 112.3 ~ 114.2 ^oC.

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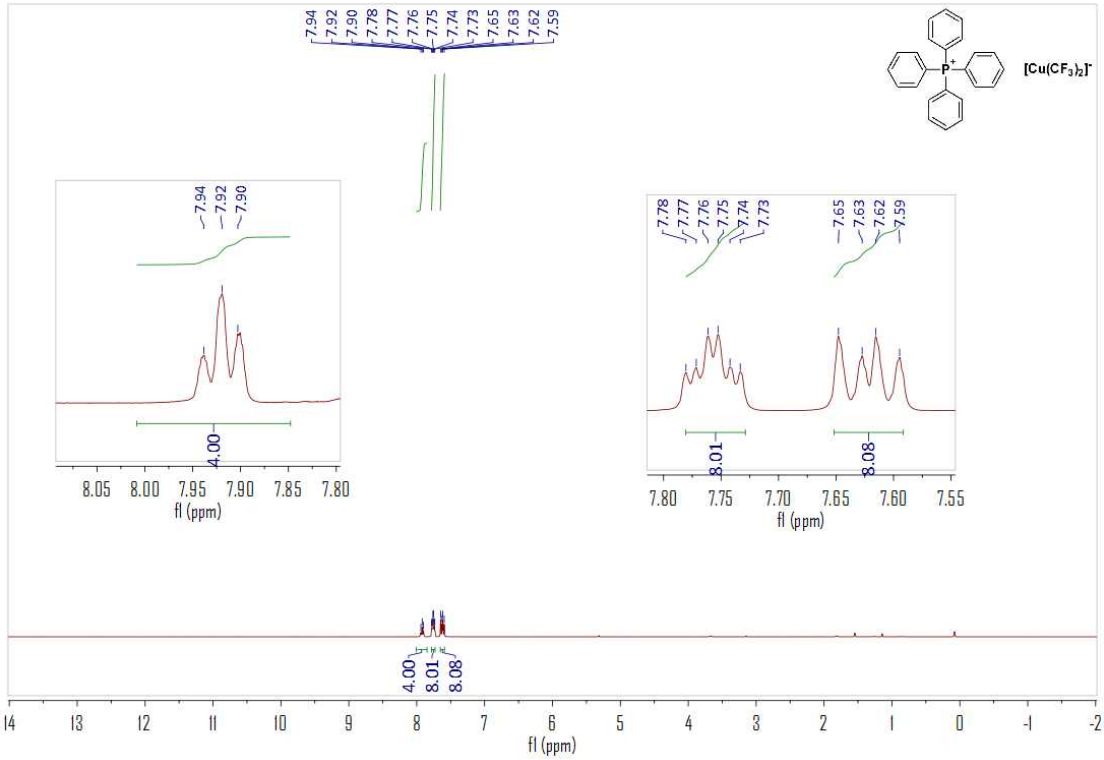
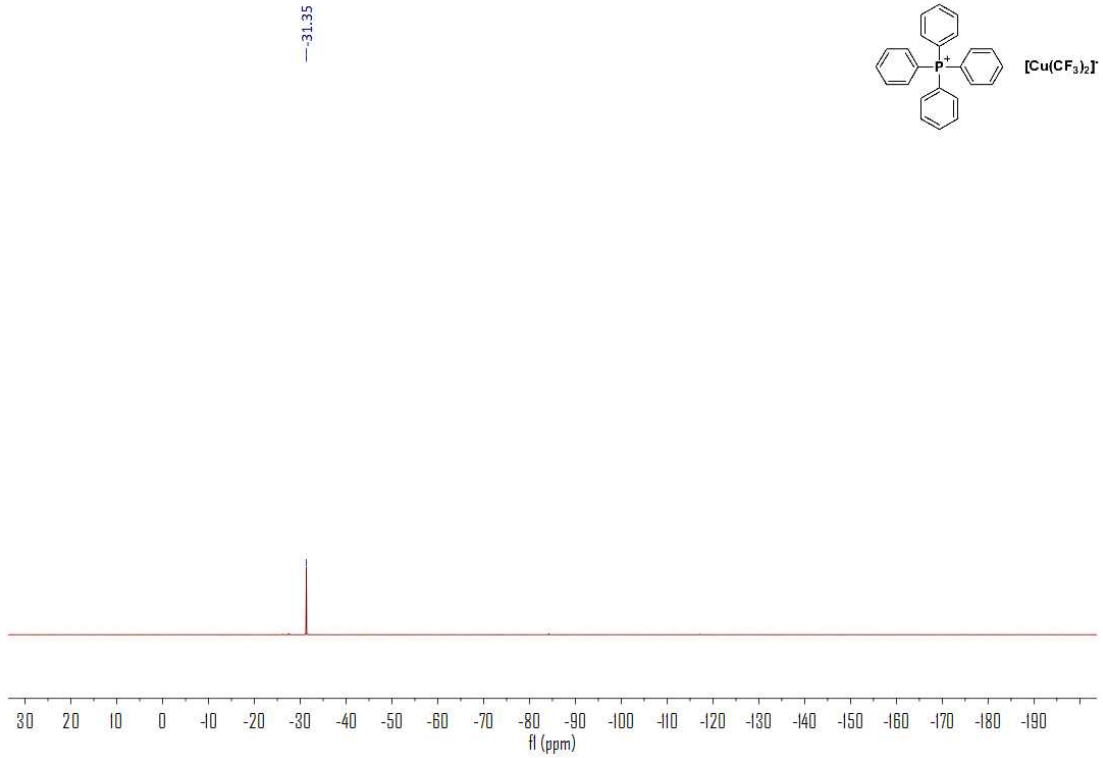
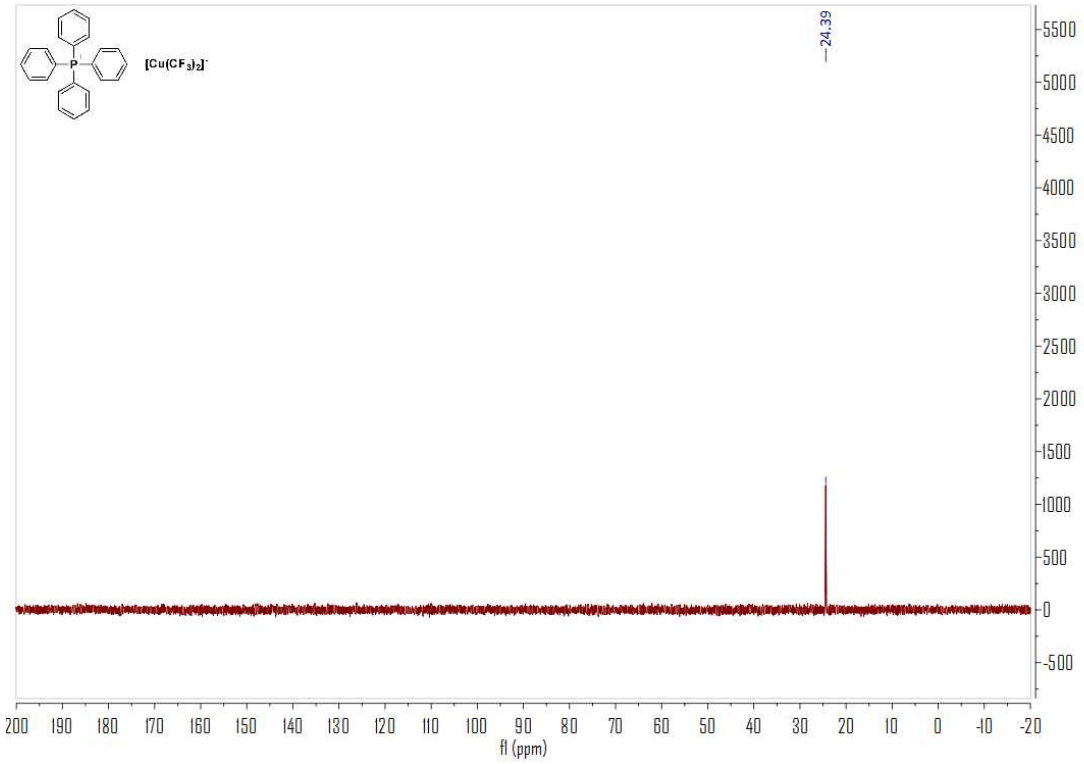
^{1}H NMR spectrum of tetraphenylphosphonium bis(trifluoromethyl)copper(I) (1)



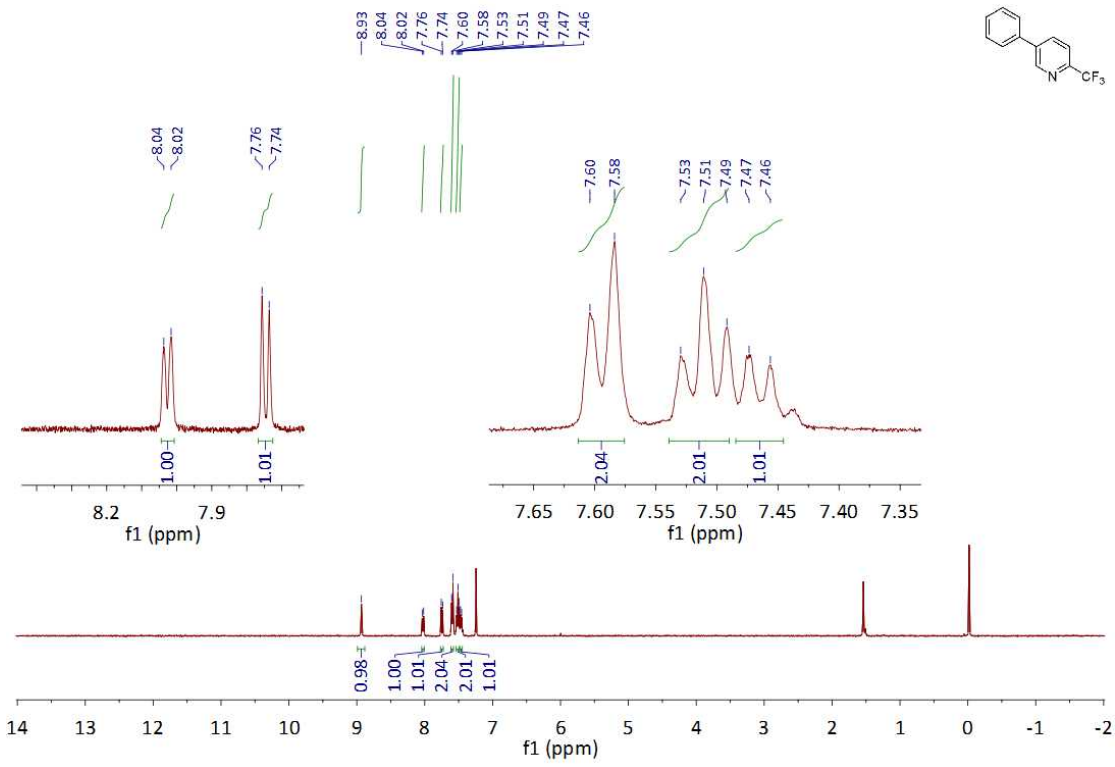
^{19}F NMR spectrum of tetraphenylphosphonium bis(trifluoromethyl)copper(I) (1)



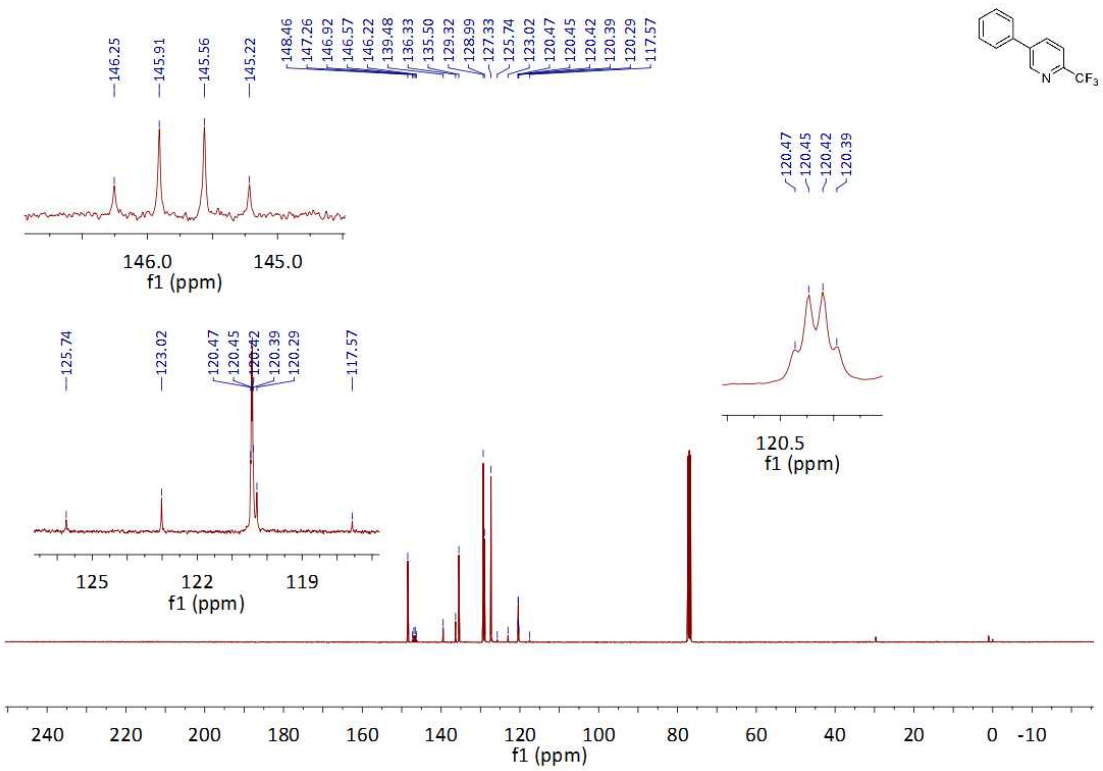
^{31}P NMR spectrum of tetraphenylphosphonium bis(trifluoromethyl)copper(I) (1)



^{1}H NMR spectrum of 5-phenyl-2-trifluoremethylpyridine (2a)



^{13}C NMR spectrum of 5-phenyl-2-trifluoremethylpyridine (2a)



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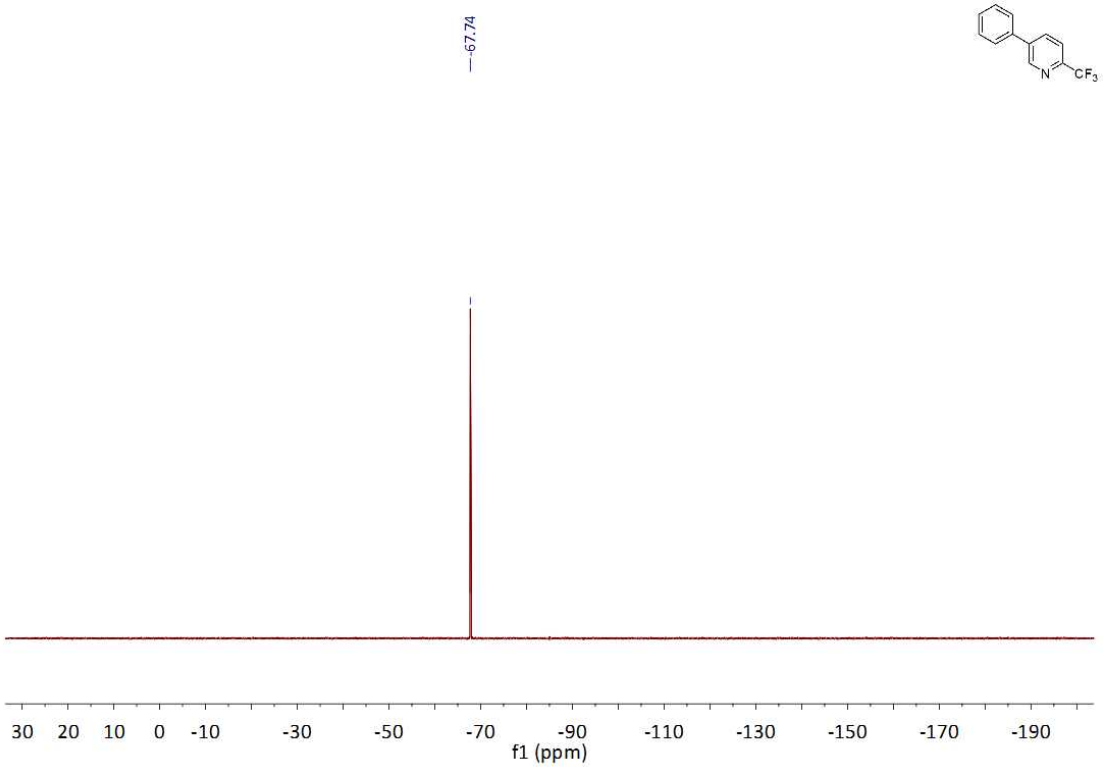
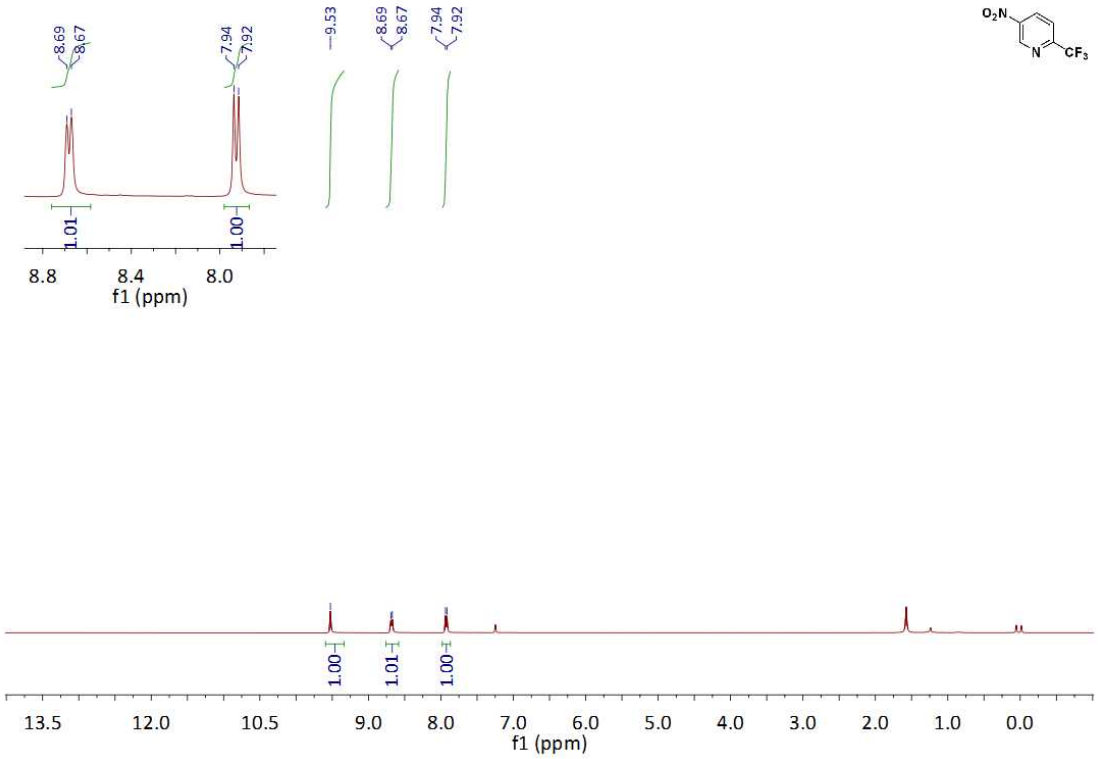
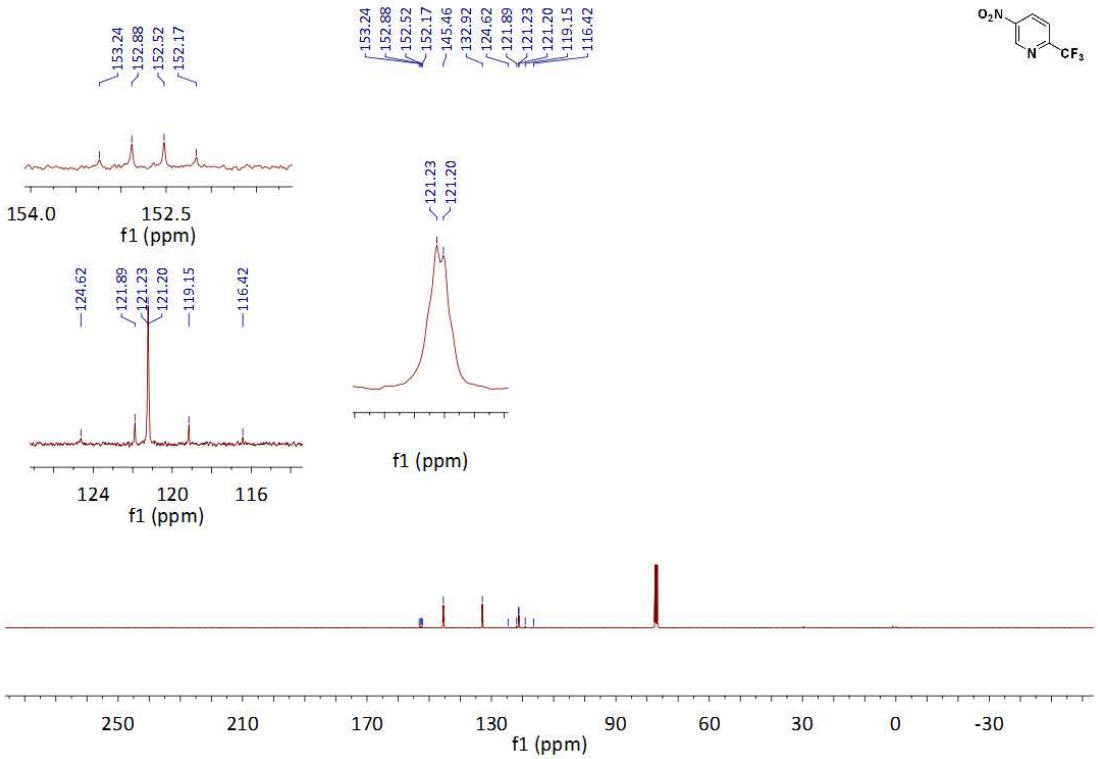


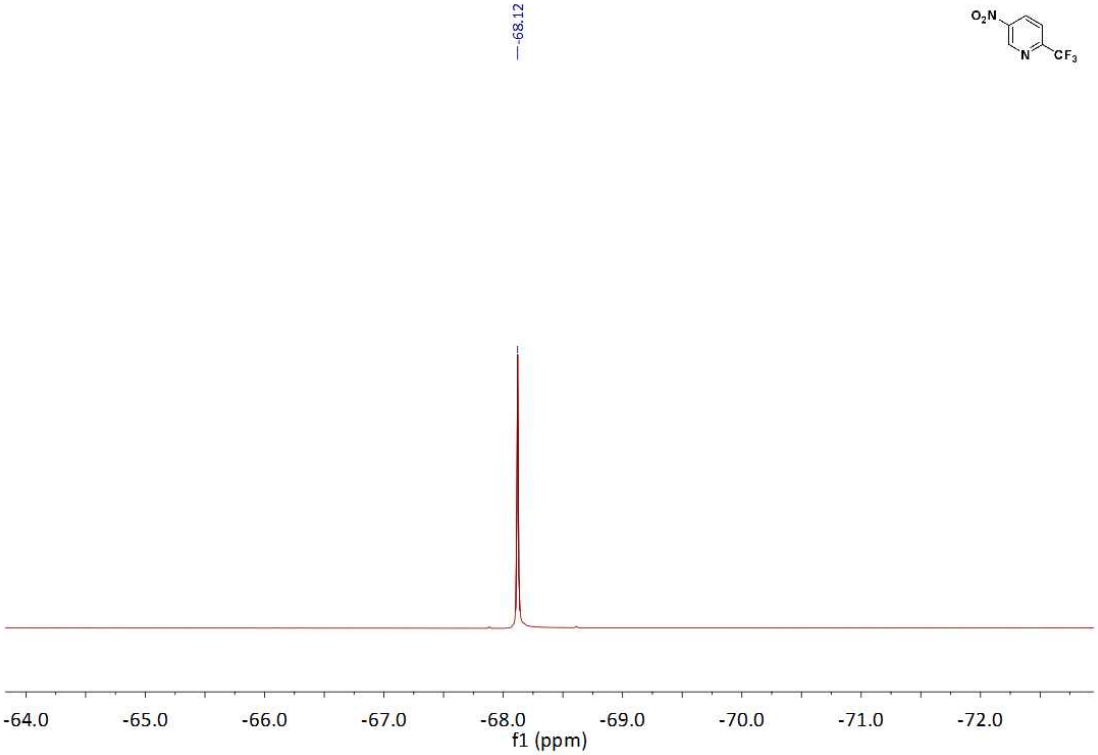
^{1}H NMR spectrum of 5-nitro-2-(trifluoromethyl)pyridine (2b)



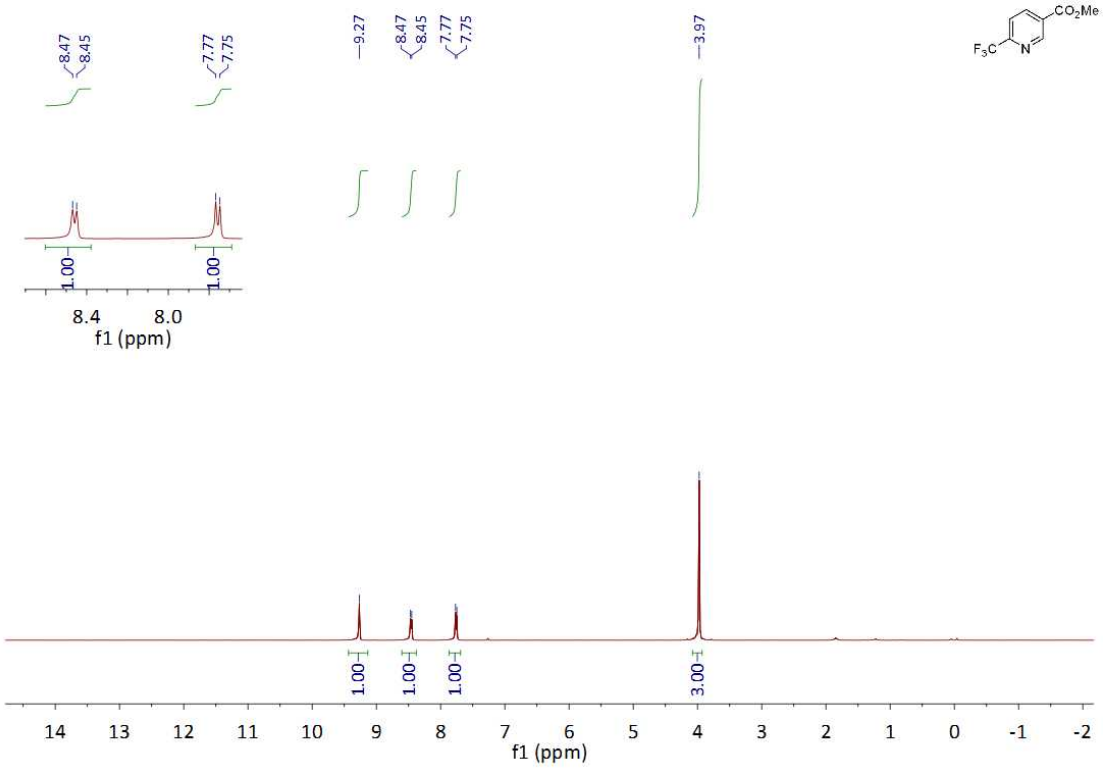
^{13}C NMR spectrum of 5-nitro-2-(trifluoromethyl)pyridine (2b)



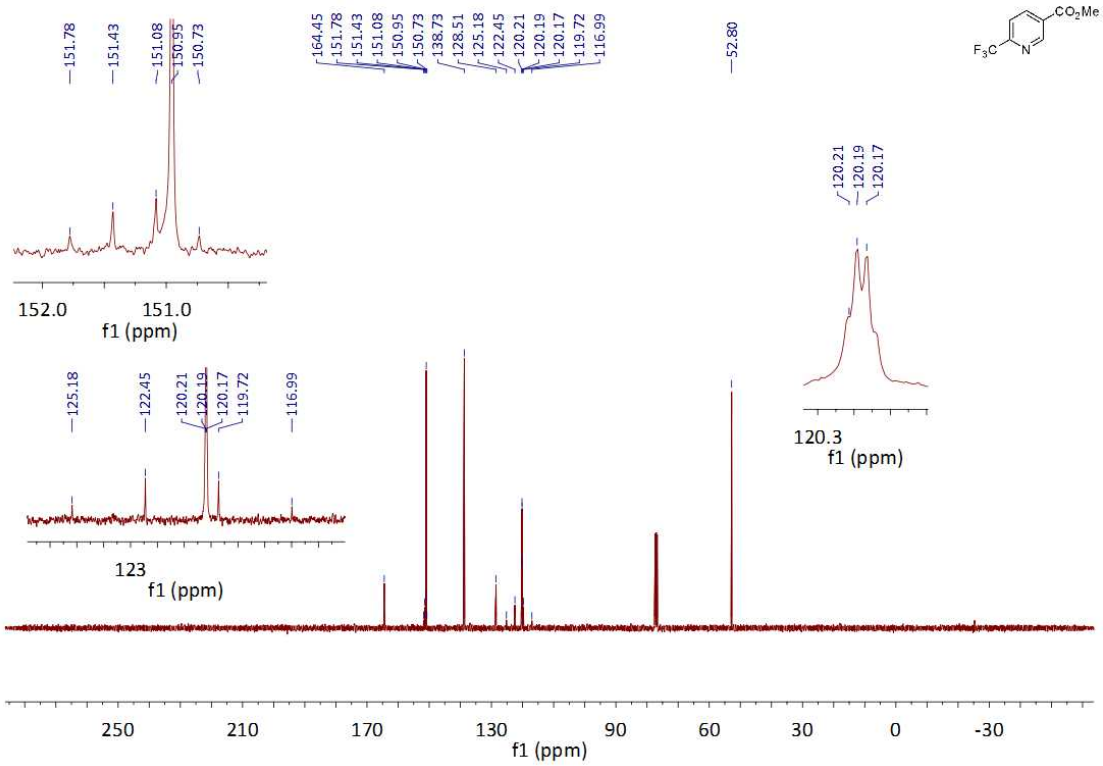
^{19}F NMR spectrum of 5-nitro-2-(trifluoromethyl)pyridine (2b)



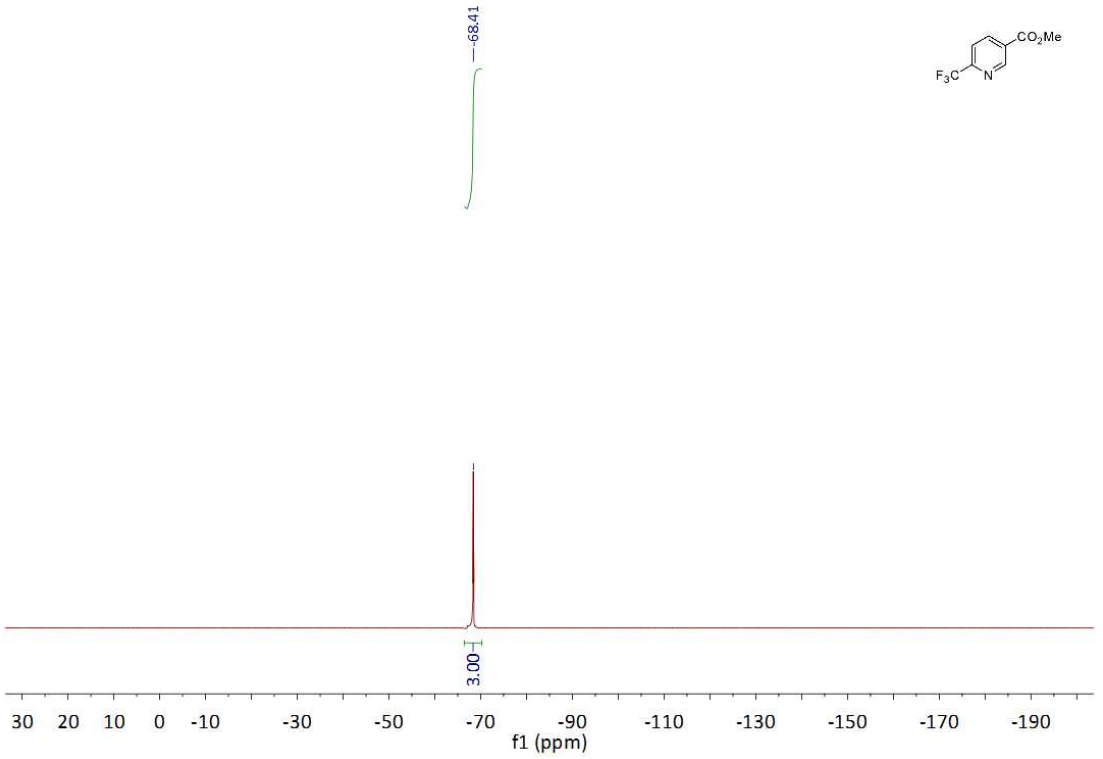
^{1}H NMR spectrum of methyl 6-(trifluoromethyl)pyridine-3-carboxylate (2c)



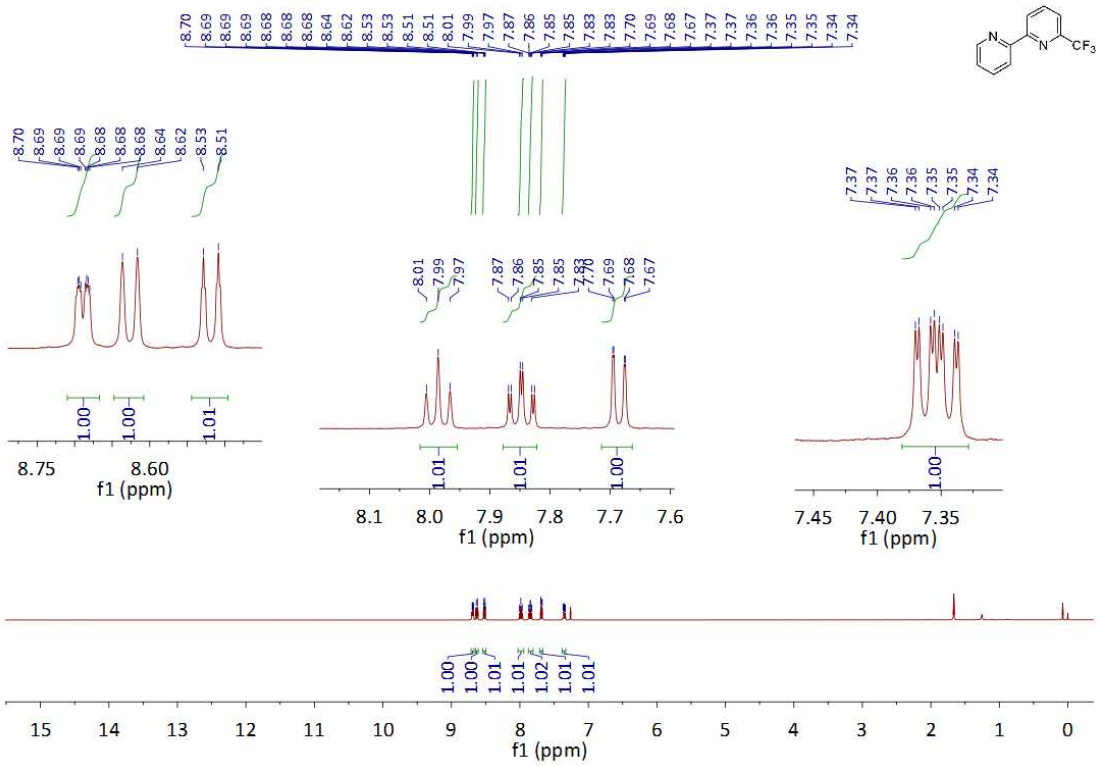
^{13}C NMR spectrum of methyl 6-(trifluoromethyl)pyridine-3-carboxylate (2c)



^{19}F NMR spectrum of methyl 6-(trifluoromethyl)pyridine-3-carboxylate (2c)



^{1}H NMR spectrum of 6-trifluoromethyl-2,2′-bipyridine (2d)



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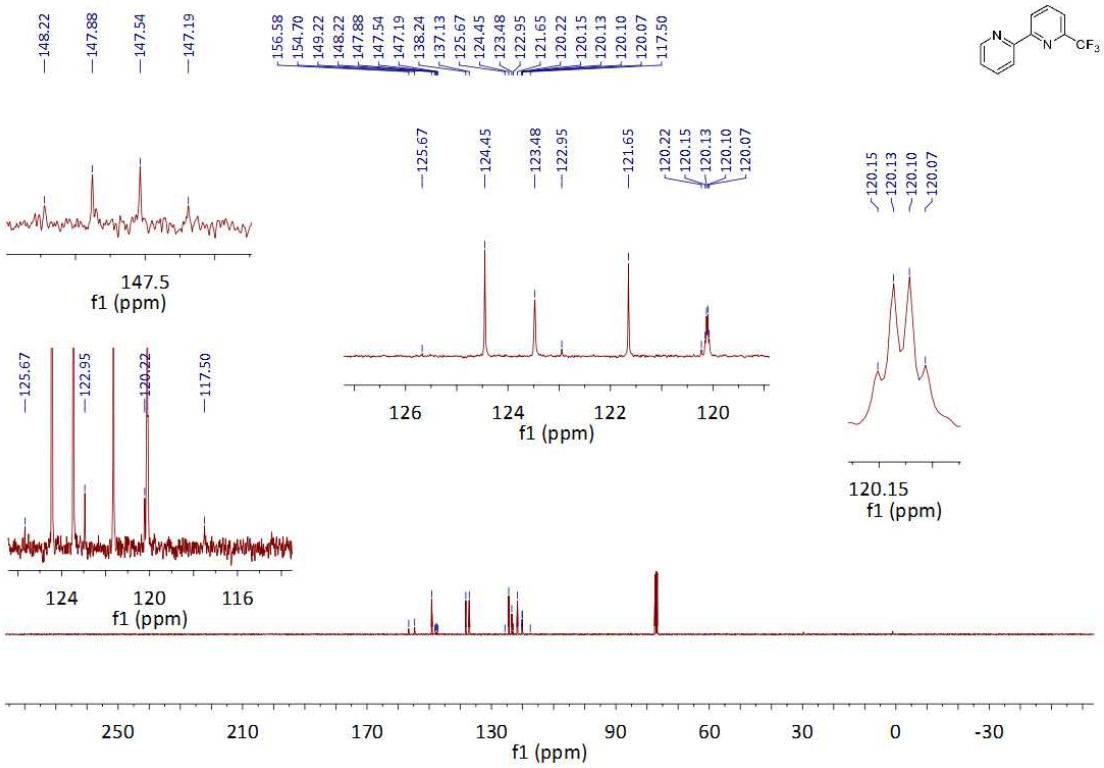
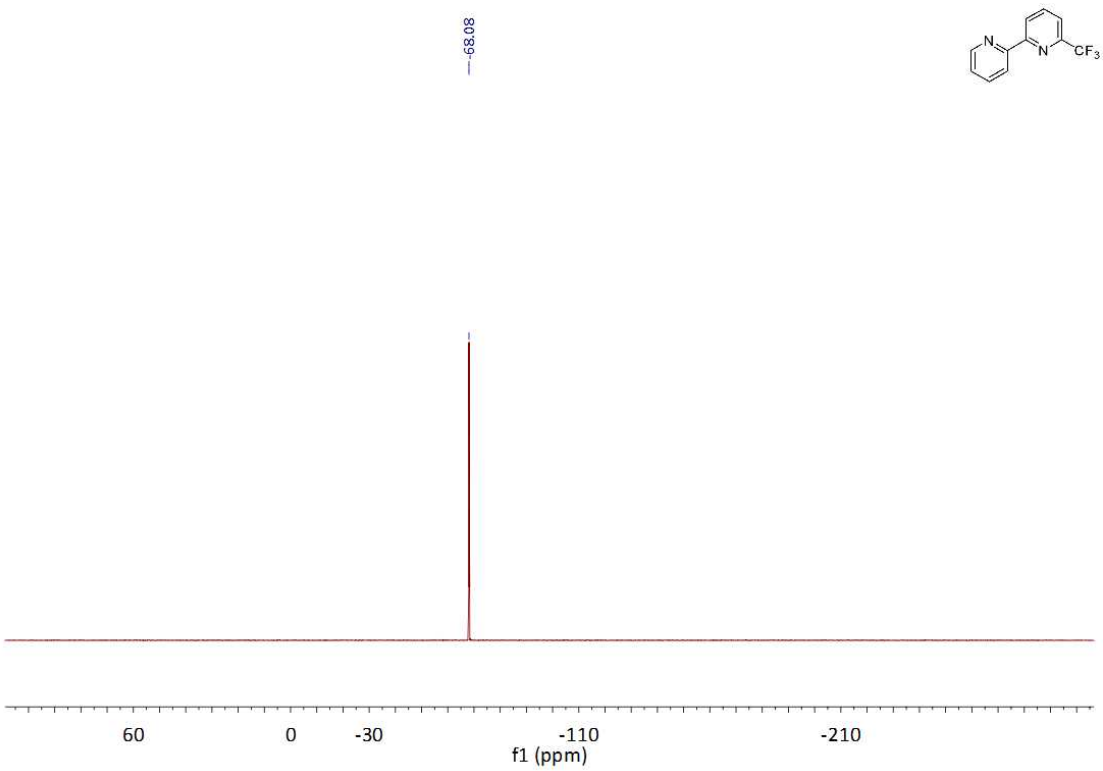
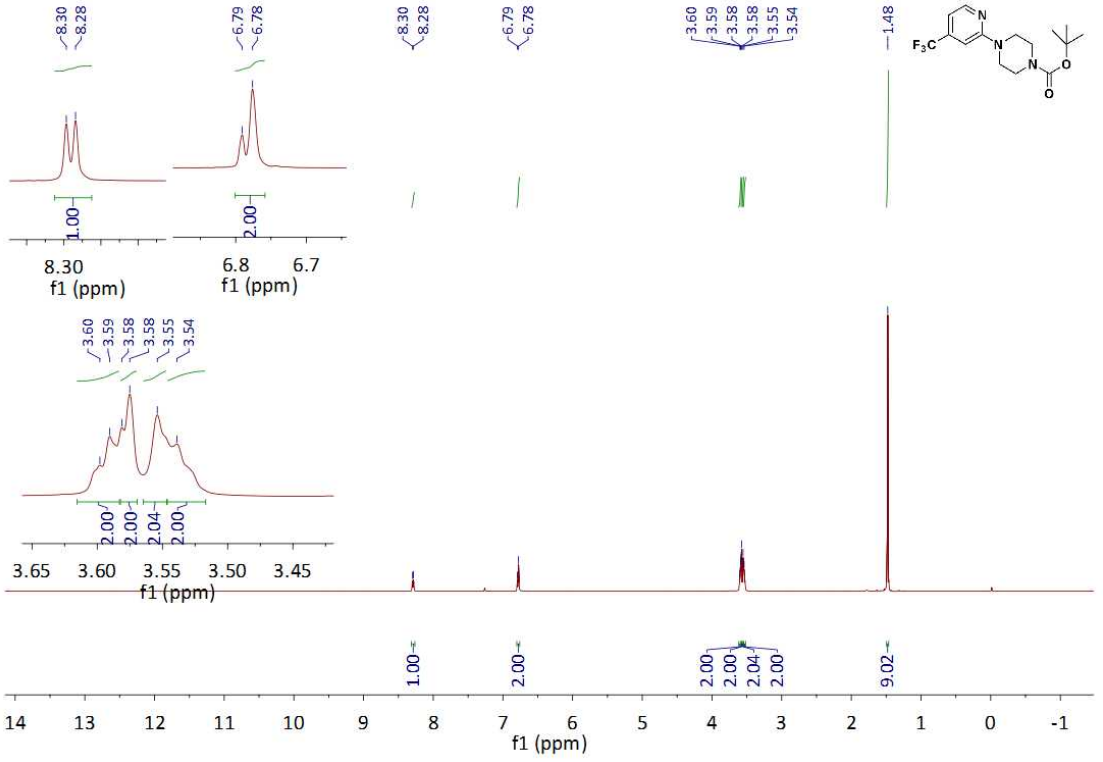


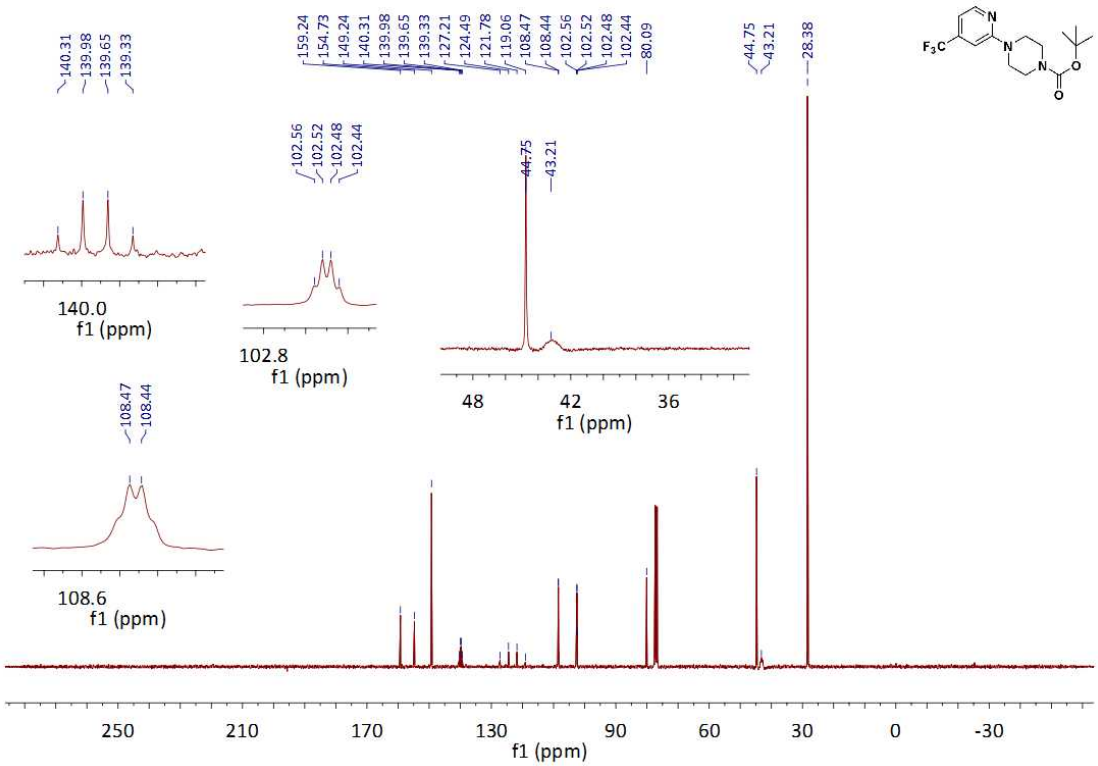
^{19}F NMR spectrum of 6-trifluoromethyl-2,2′-bipyridine (2d)



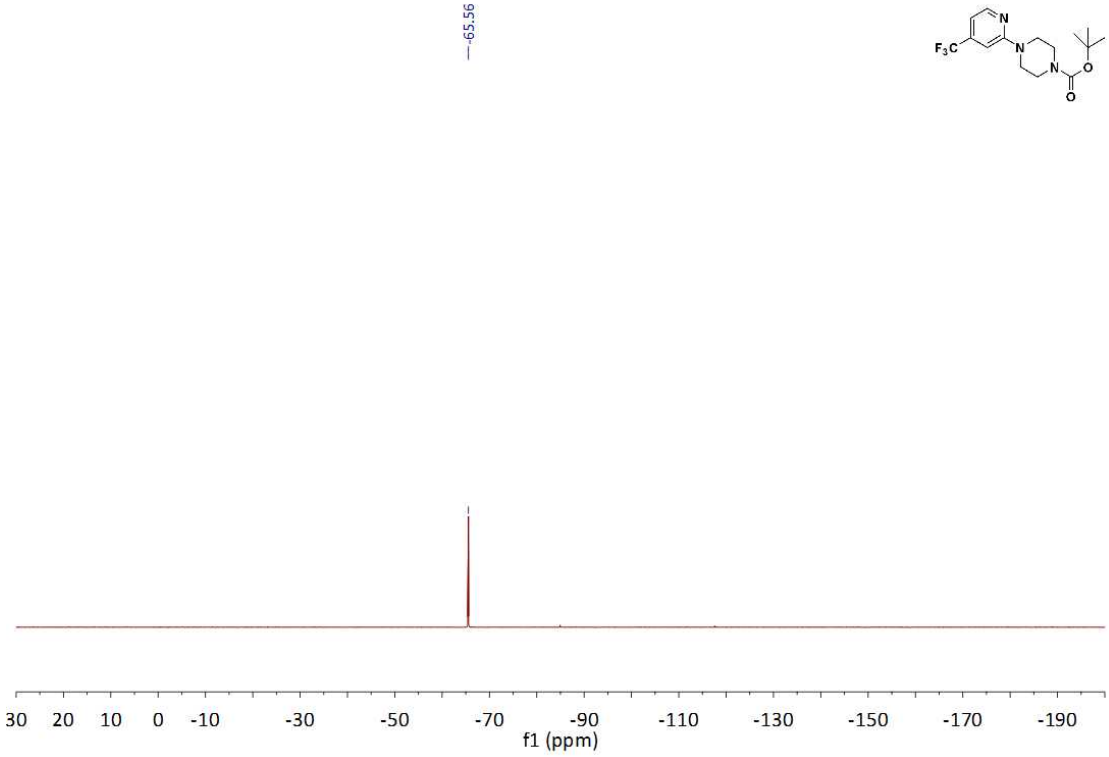
^{1}H NMR spectrum of *tert*-butyl 4-[4-(trifluoromethyl)-2-pyridyl]piperazine-1-carboxylate (2e)



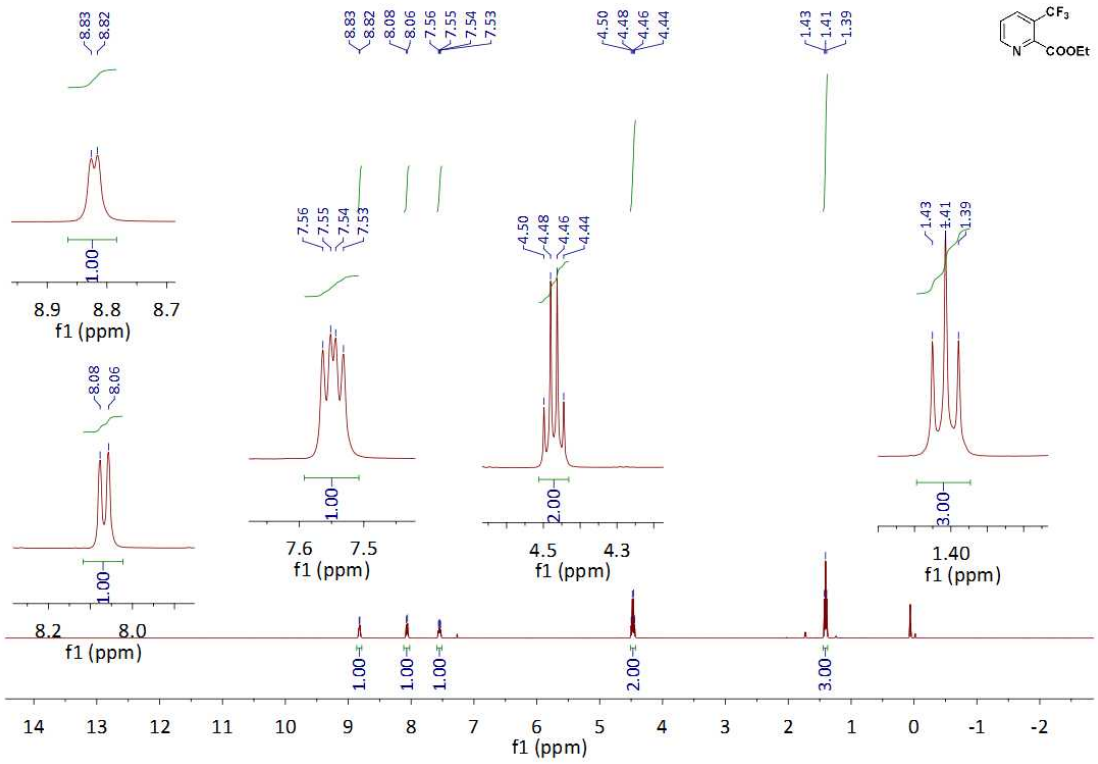
^{13}C NMR spectrum of *tert*-butyl 4-[4-(trifluoromethyl)-2-pyridyl]piperazine-1-carboxylate (2e)



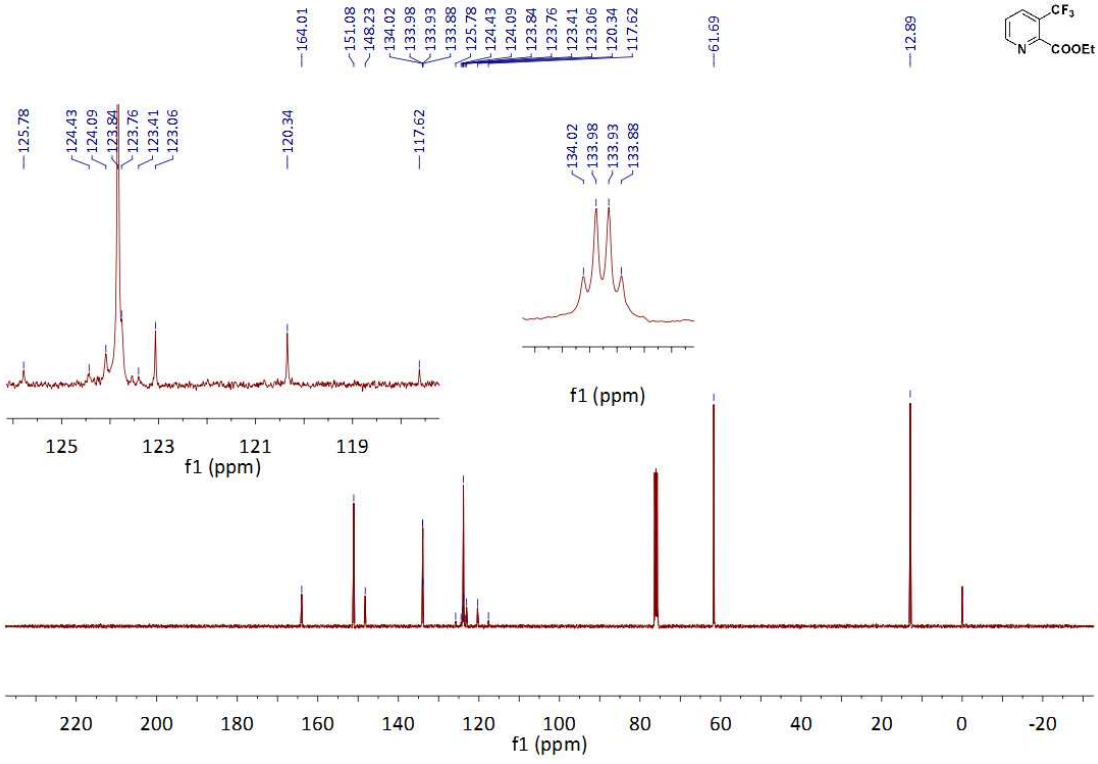
^{19}F NMR spectrum of *tert*-butyl 4-[4-(trifluoromethyl)-2-pyridyl]piperazine-1-carboxylate (2e)



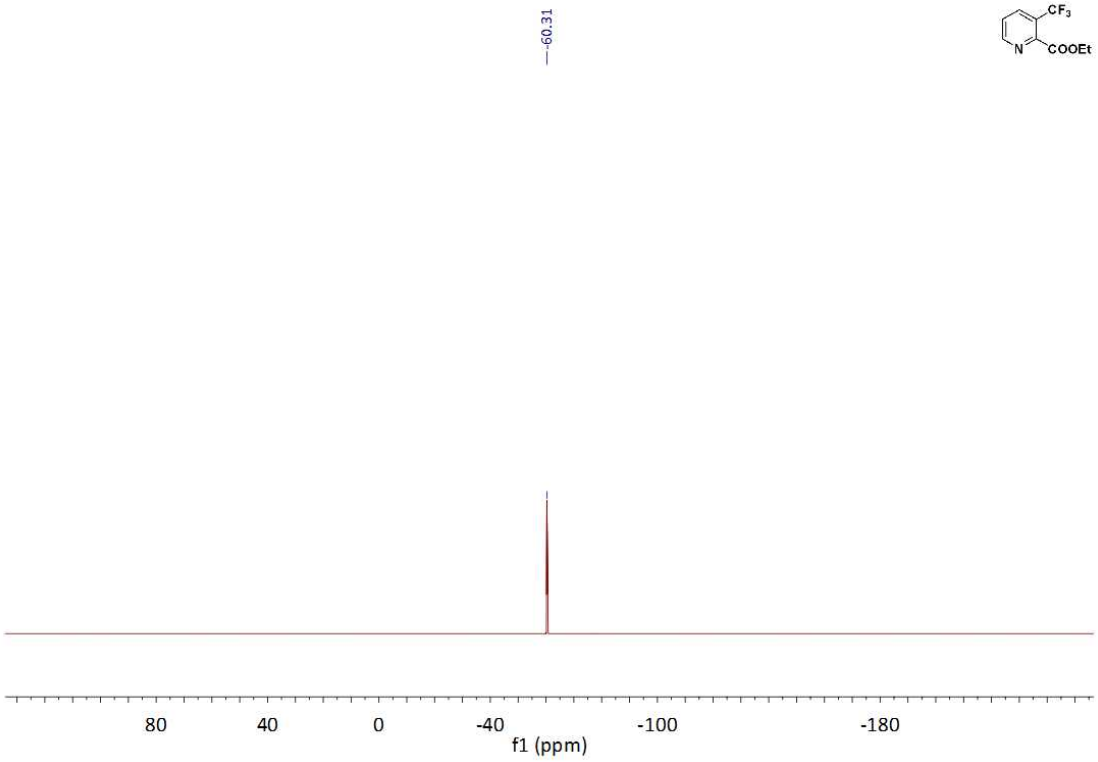
^{1}H NMR spectrum of ethyl 3-(trifluoromethyl)pyridine-2-carboxylate (2f)



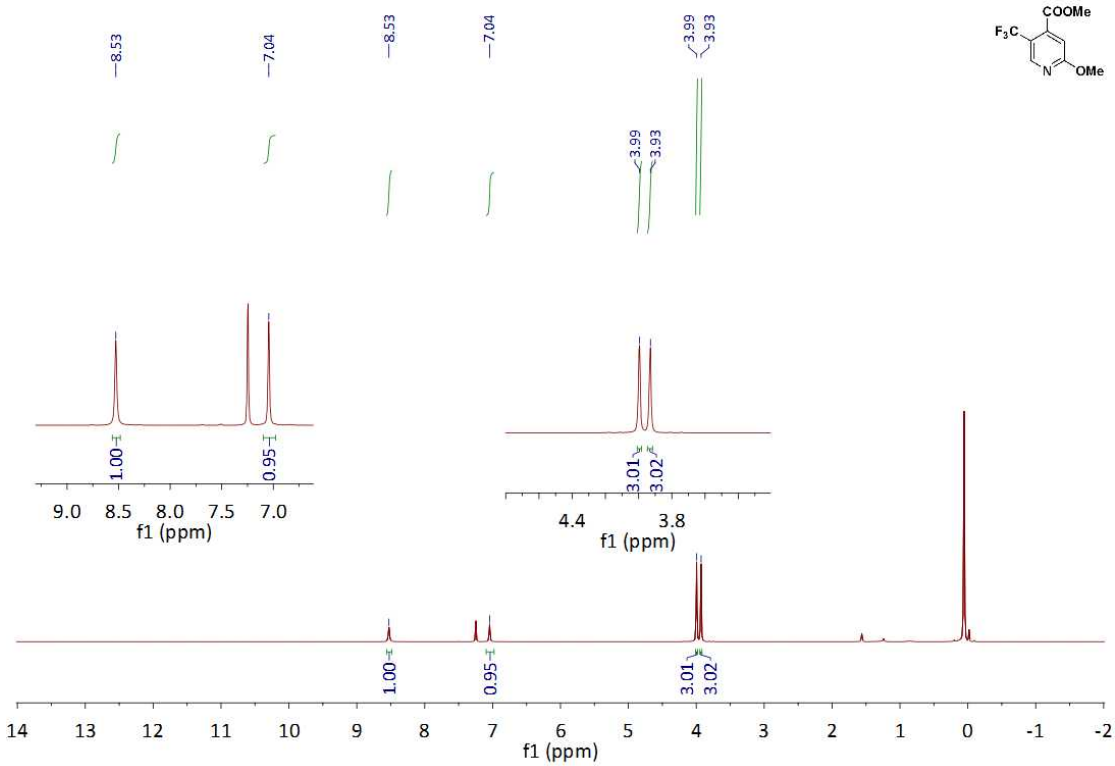
^{13}C NMR spectrum of ethyl 3-(trifluoromethyl)pyridine-2-carboxylate (2f)



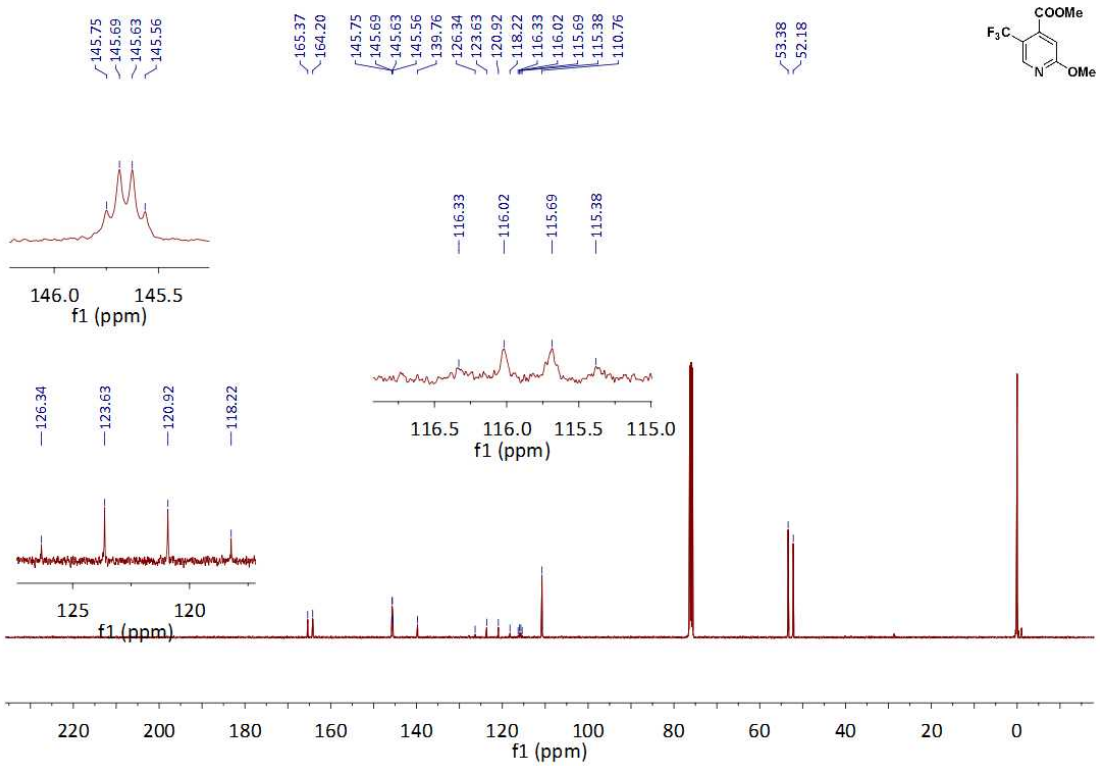
^{19}F NMR spectrum of ethyl 3-(trifluoromethyl)pyridine-2-carboxylate (2f)



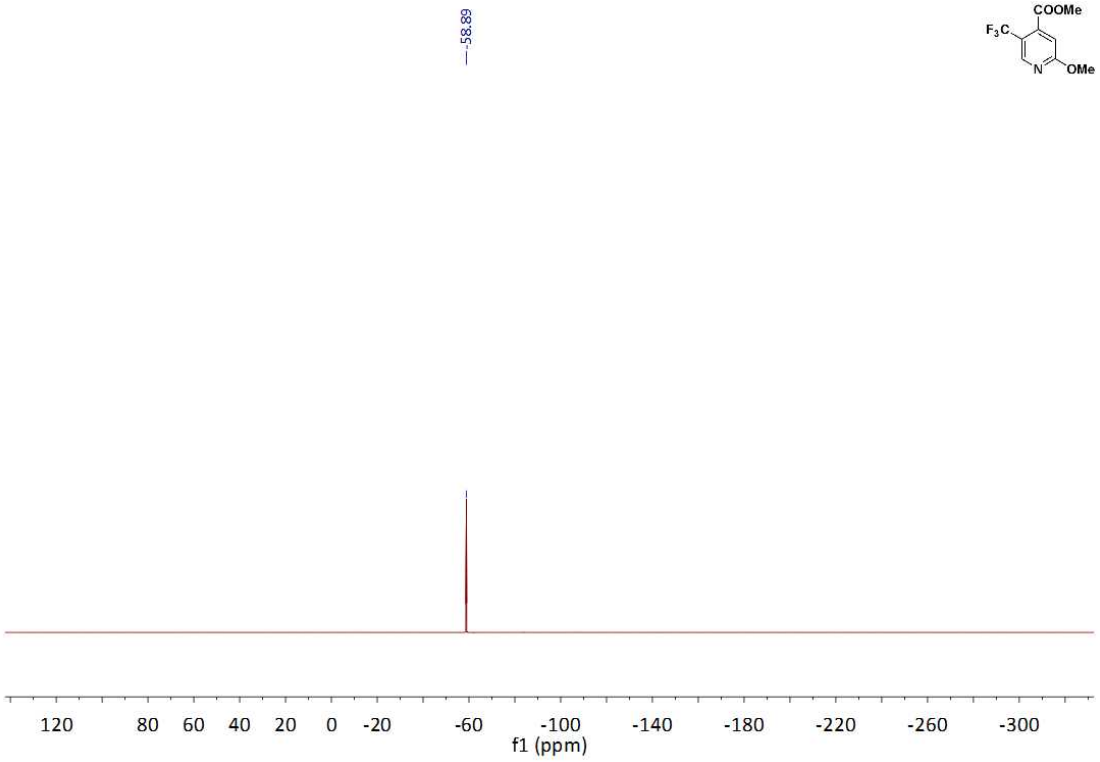
^{1}H NMR spectrum of methyl 2-methoxy-5-(trifluoromethyl)pyridine-4-carboxylate (2g)



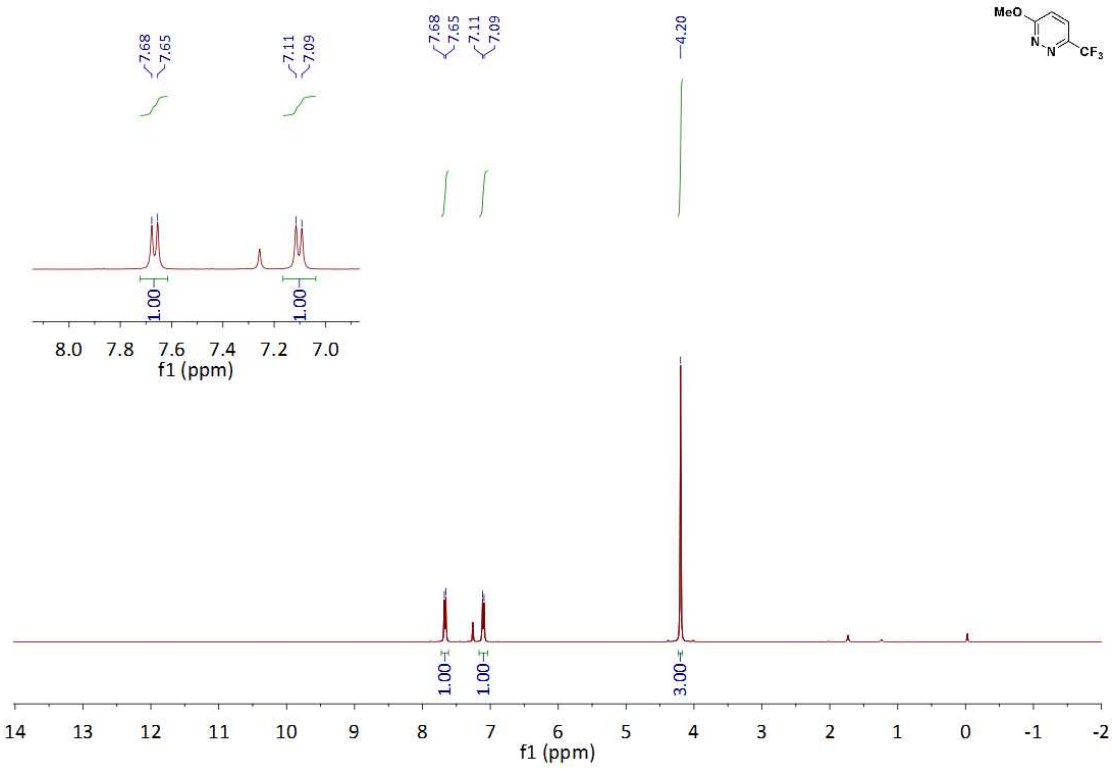
^{13}C NMR spectrum of methyl 2-methoxy-5-(trifluoromethyl)pyridine-4-carboxylate (2g)



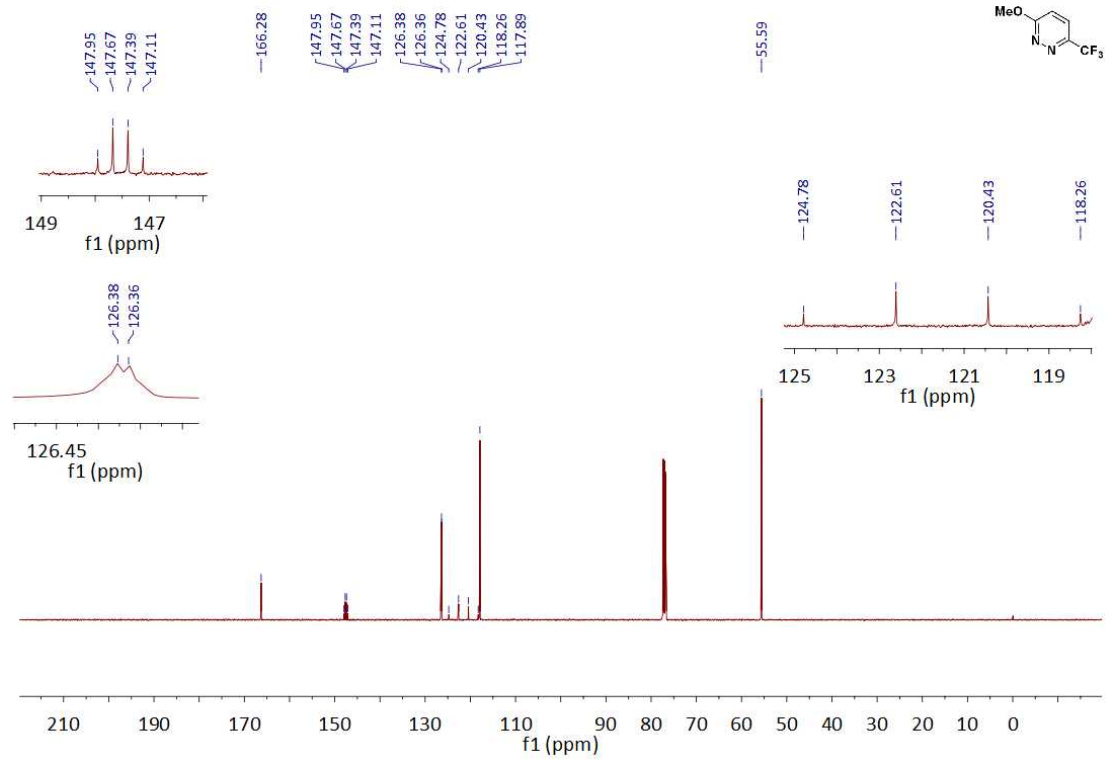
^{19}F NMR spectrum of methyl 2-methoxy-5-(trifluoromethyl)pyridine-4-carboxylate (2g)



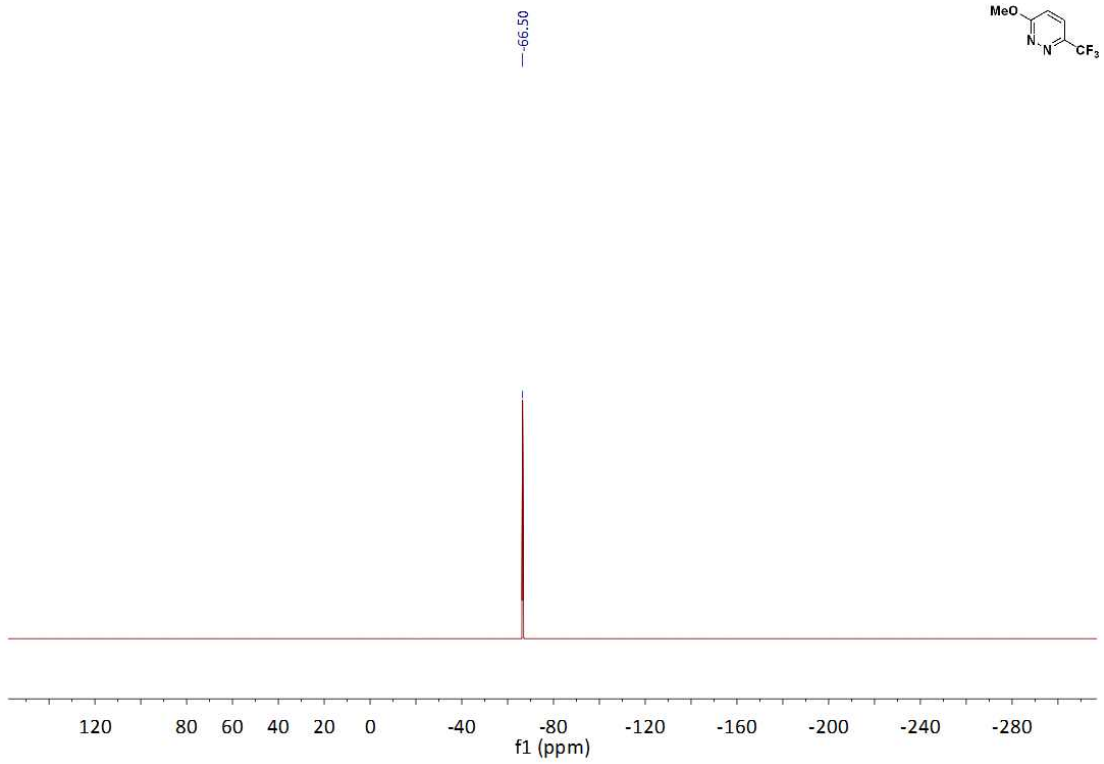
^{1}H NMR spectrum of 3-methoxy-6-(trifluoromethyl)pyridazine (2h)



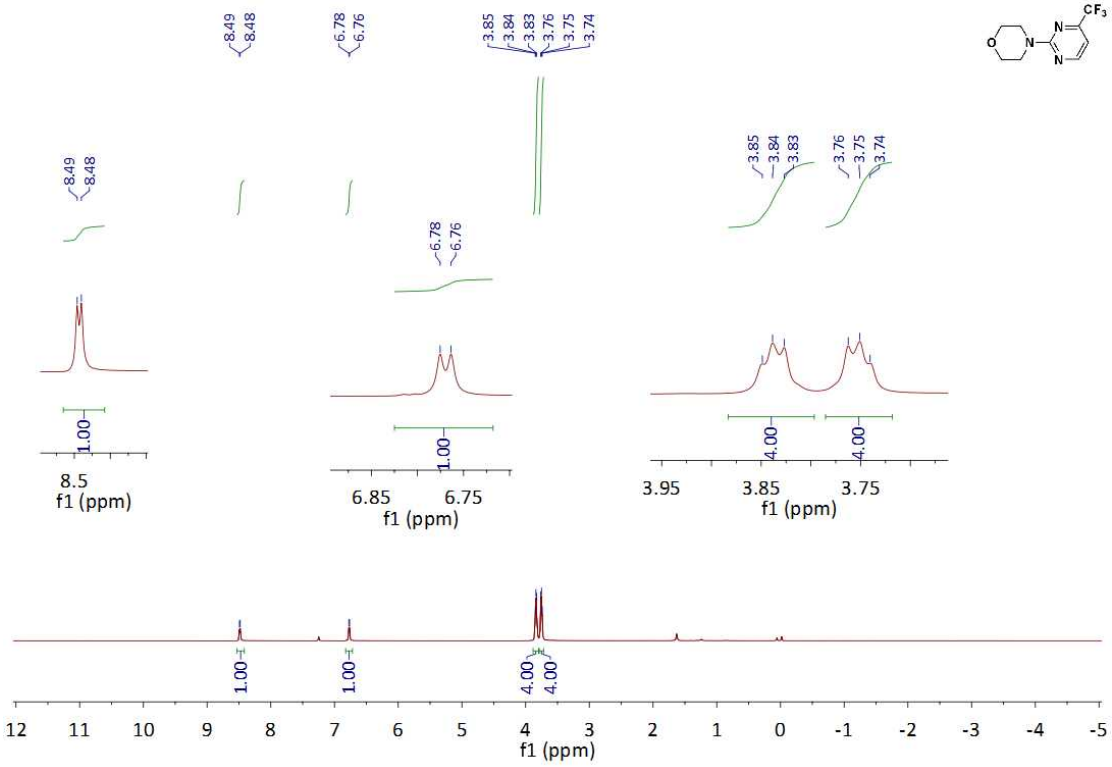
^{13}C NMR spectrum of 3-methoxy-6-(trifluoromethyl)pyridazine (2h)



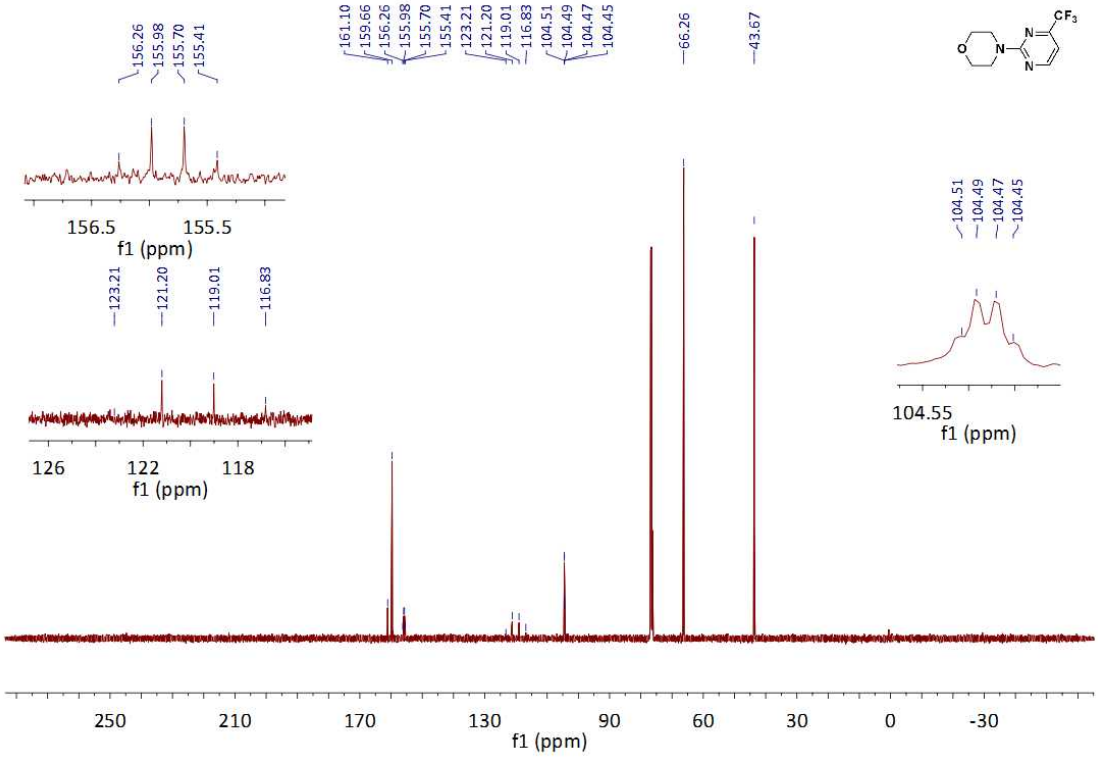
^{19}F NMR spectrum of 3-methoxy-6-(trifluoromethyl)pyridazine (2h)



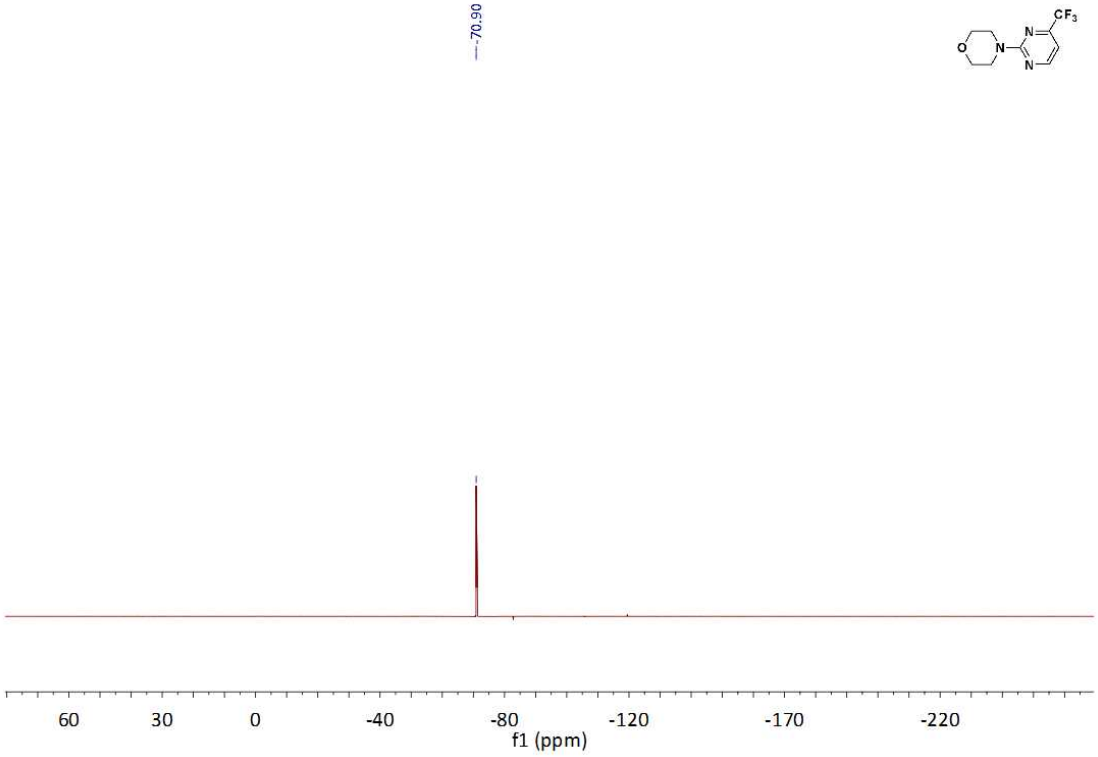
^{1}H NMR spectrum of 4-[4-trifluoromethyl)pyrimidin-2-yl]morpholine (2i)



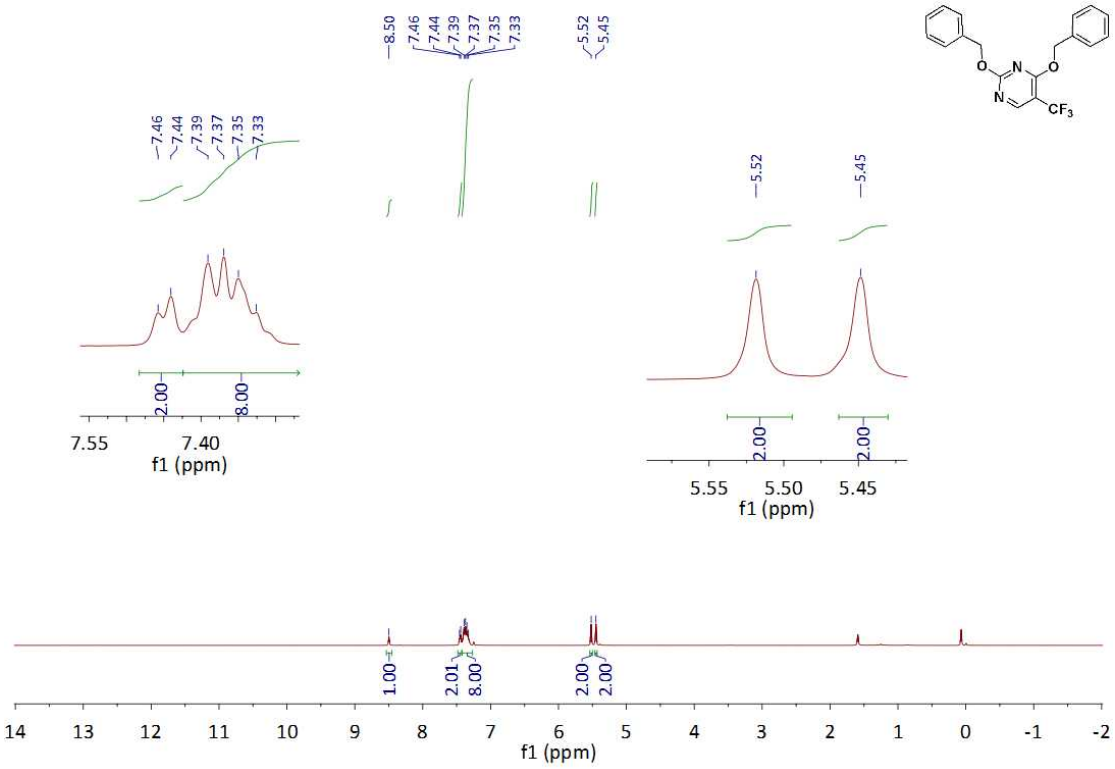
^{13}C NMR spectrum of 4-[4-trifluoromethyl)pyrimidin-2-yl]morpholine (2i)



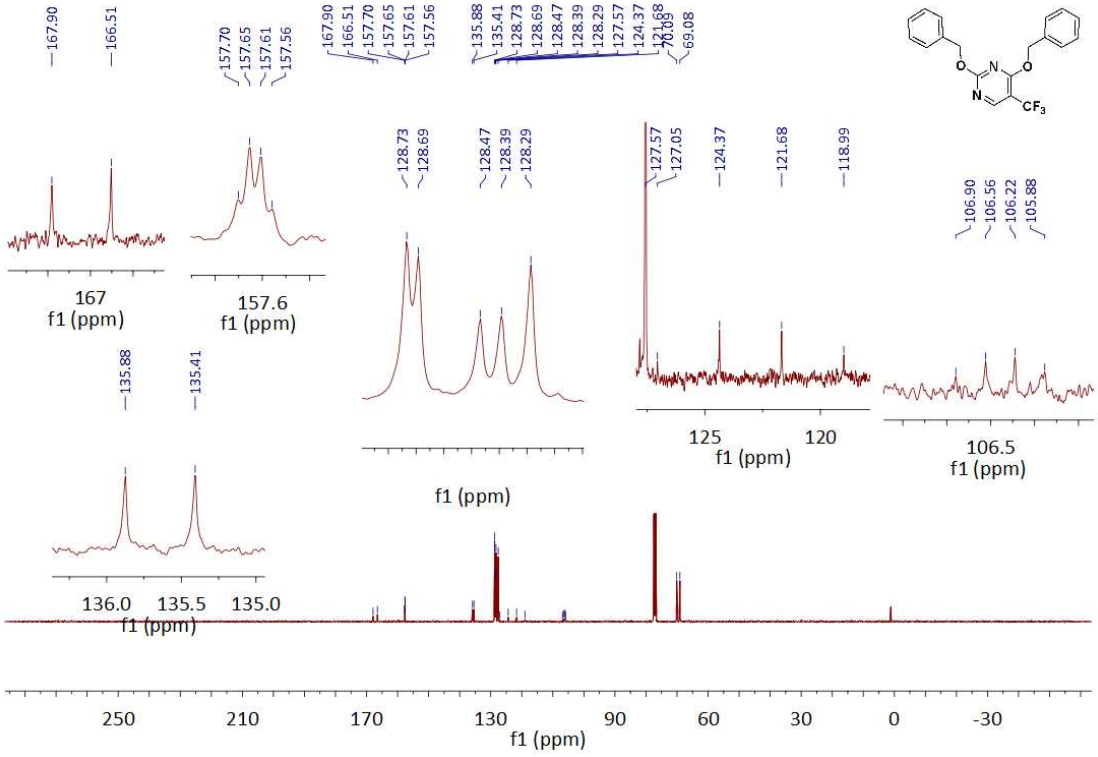
^{19}F NMR spectrum of 4-[4-trifluoromethyl)pyrimidin-2-yl]morpholine (2i)



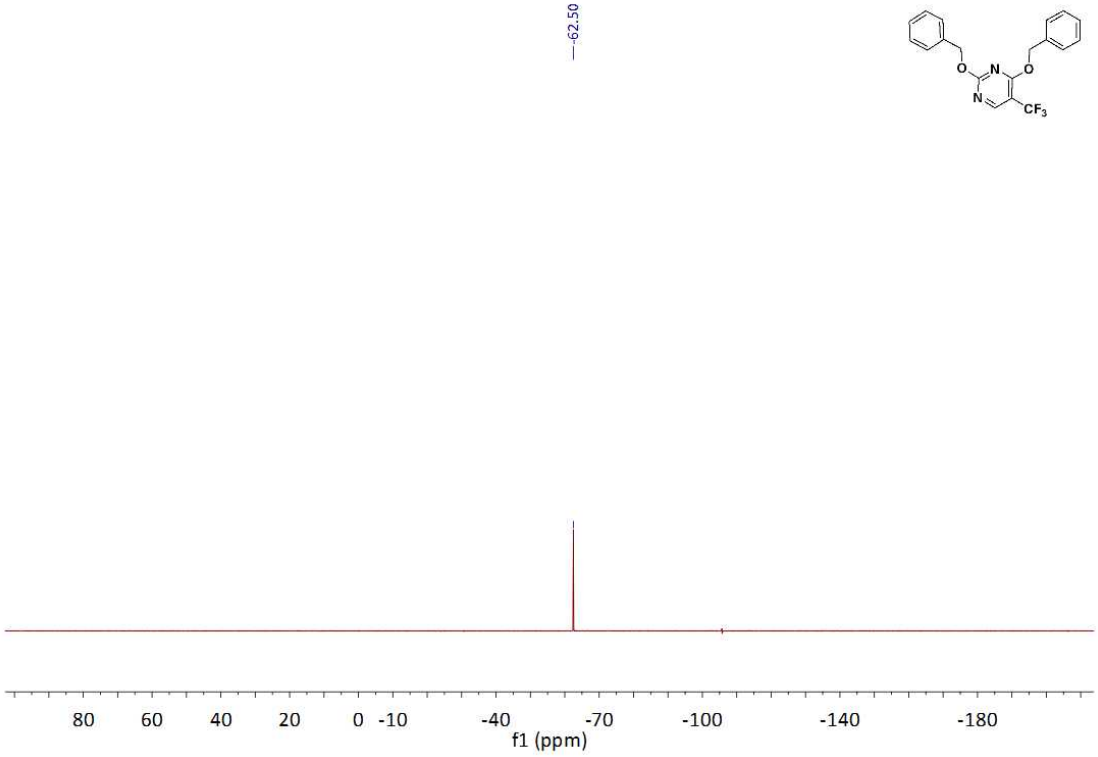
^{1}H NMR spectrum of 2,4-bis(benzyloxy)-5-trifluoromethylpyrimidine (2j)



^{13}C NMR spectrum of 2,4-bis(benzyloxy)-5-trifluoromethylpyrimidine (2j)



^{19}F NMR spectrum of 2,4-bis(benzyloxy)-5-trifluoromethylpyrimidine (2j)



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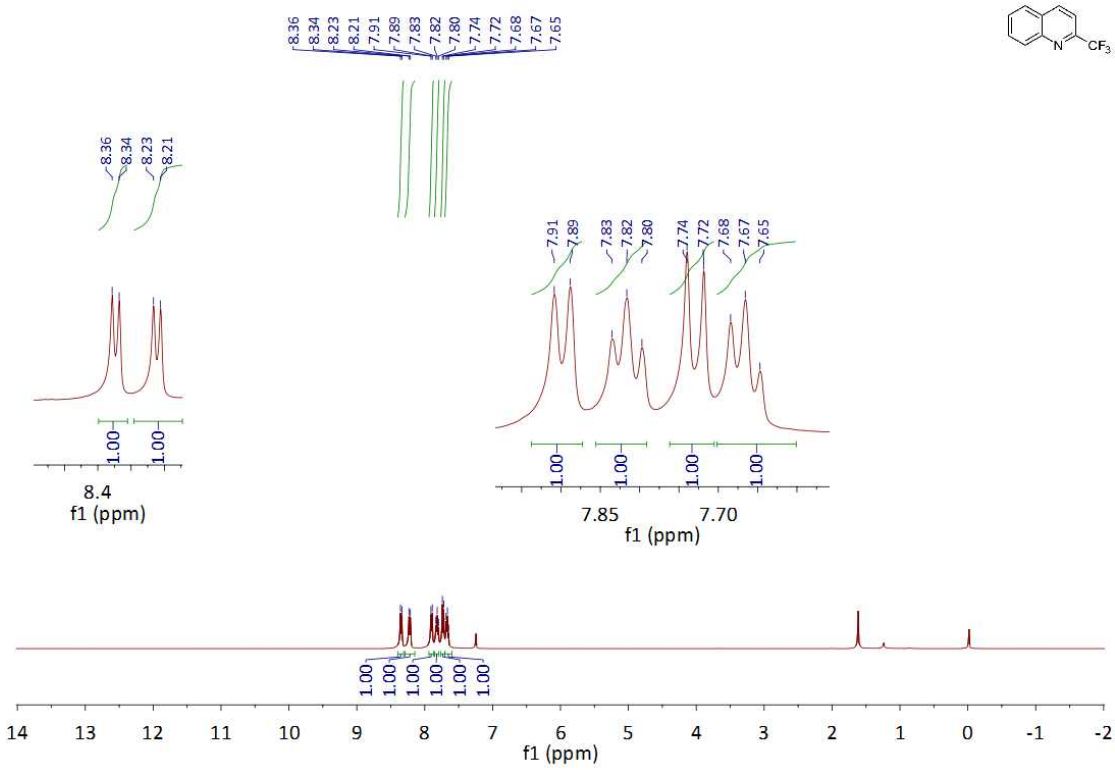
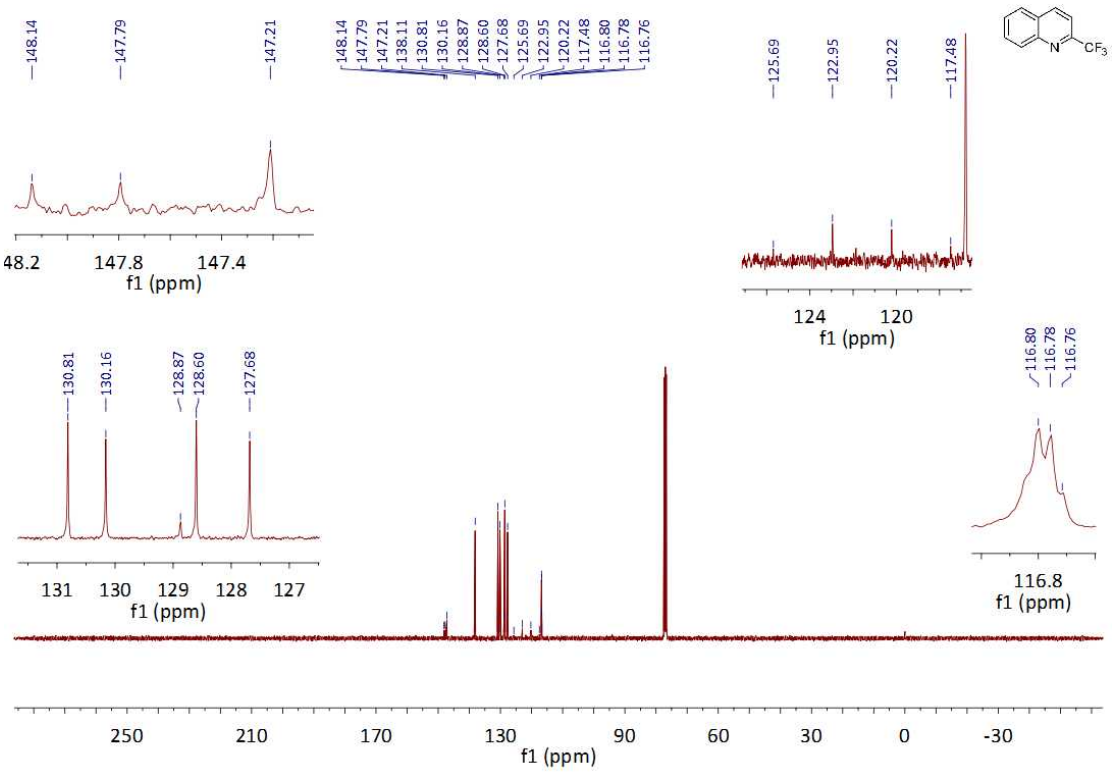
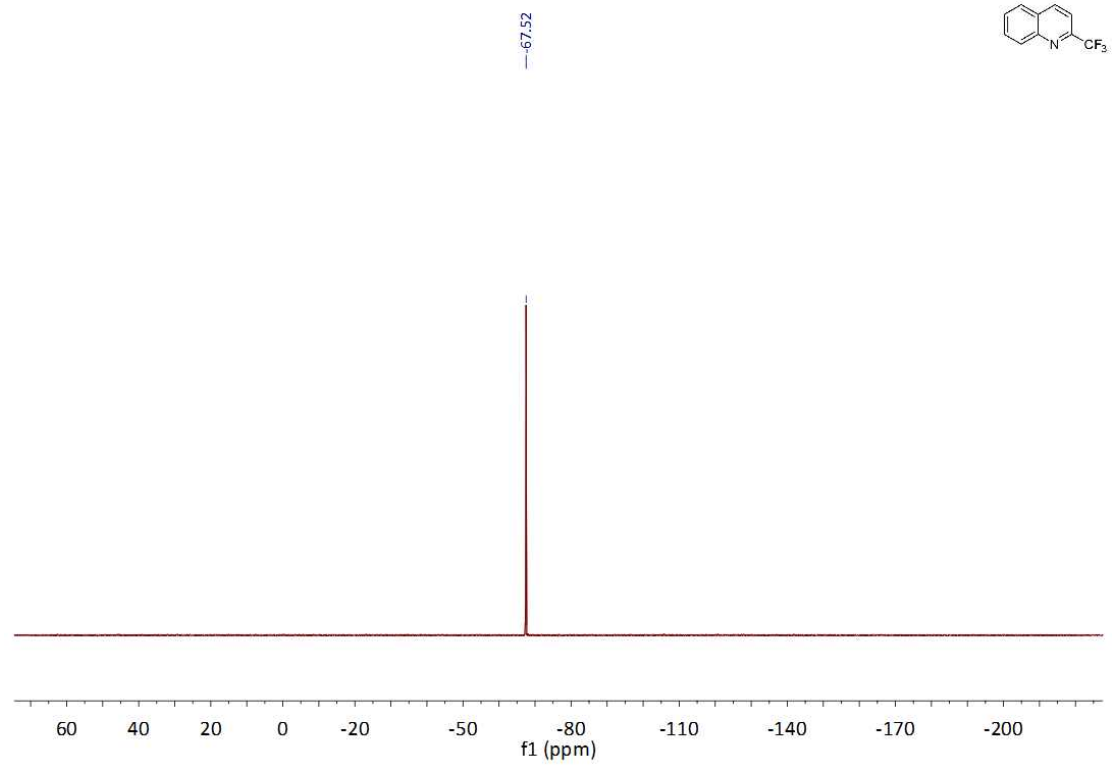


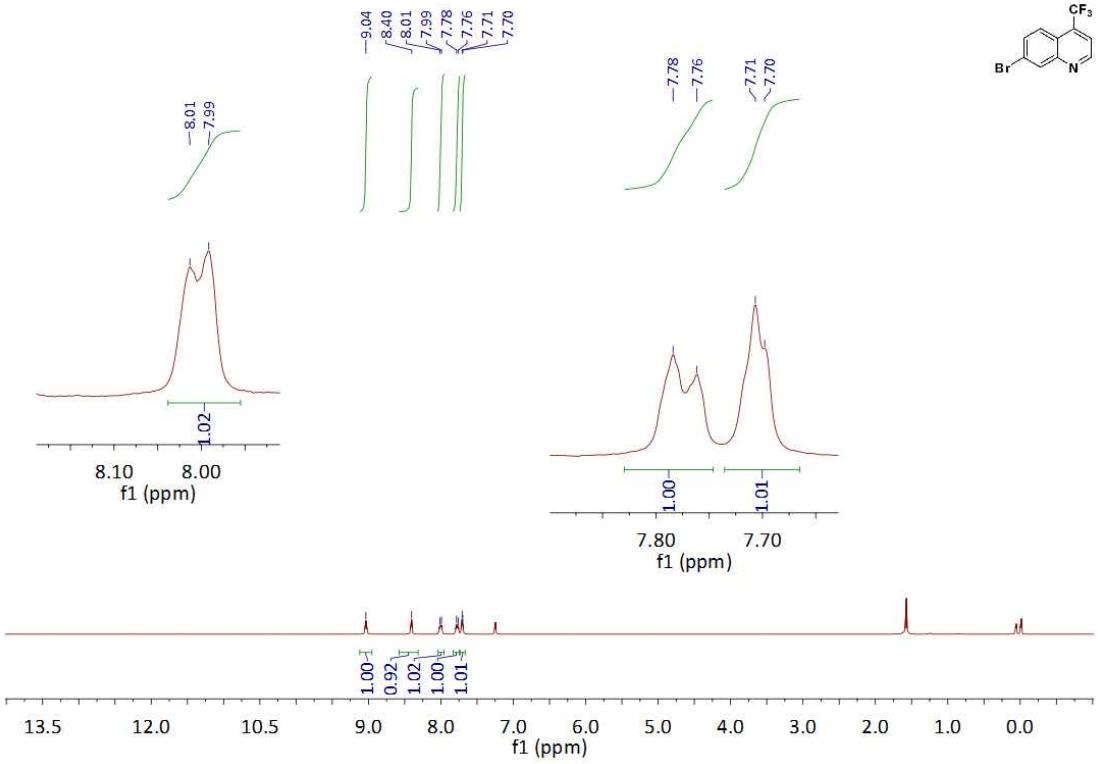
^{13}C NMR spectrum of 2-trifluoromethylquinoline (2k)



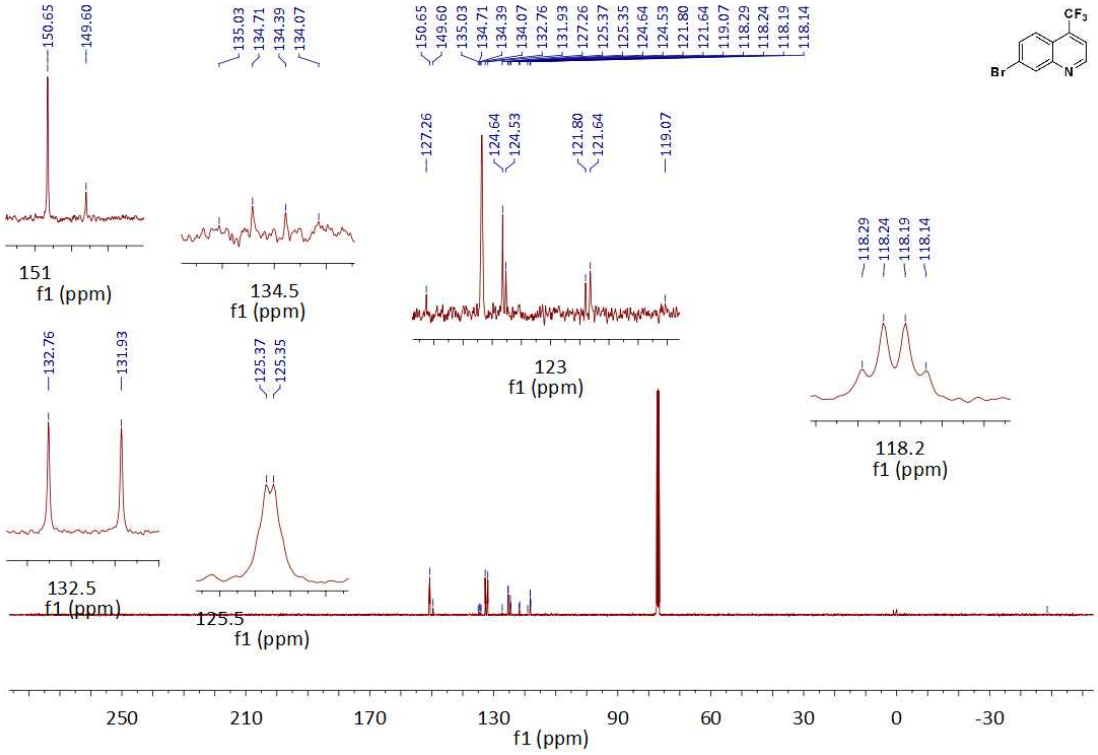
^{19}F NMR spectrum of 2-trifluoromethylquinoline (2k)



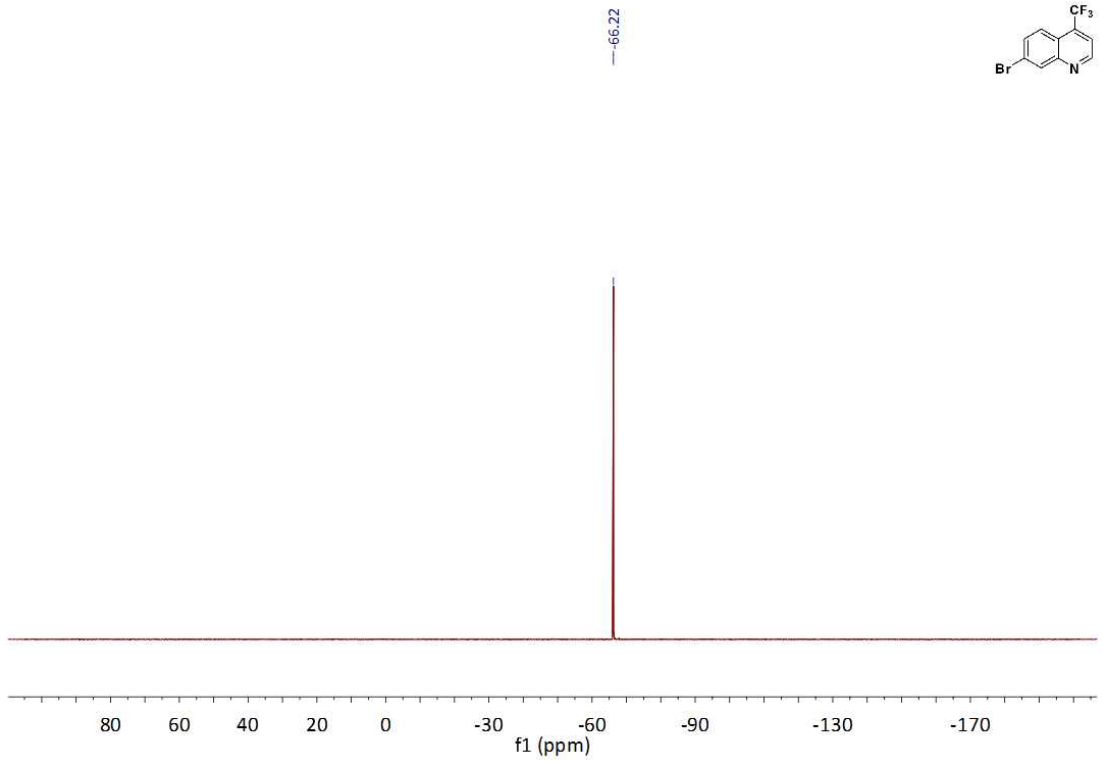
^{1}H NMR spectrum of 7-bromo-4-(trifluoromethyl)quinolone (2l)



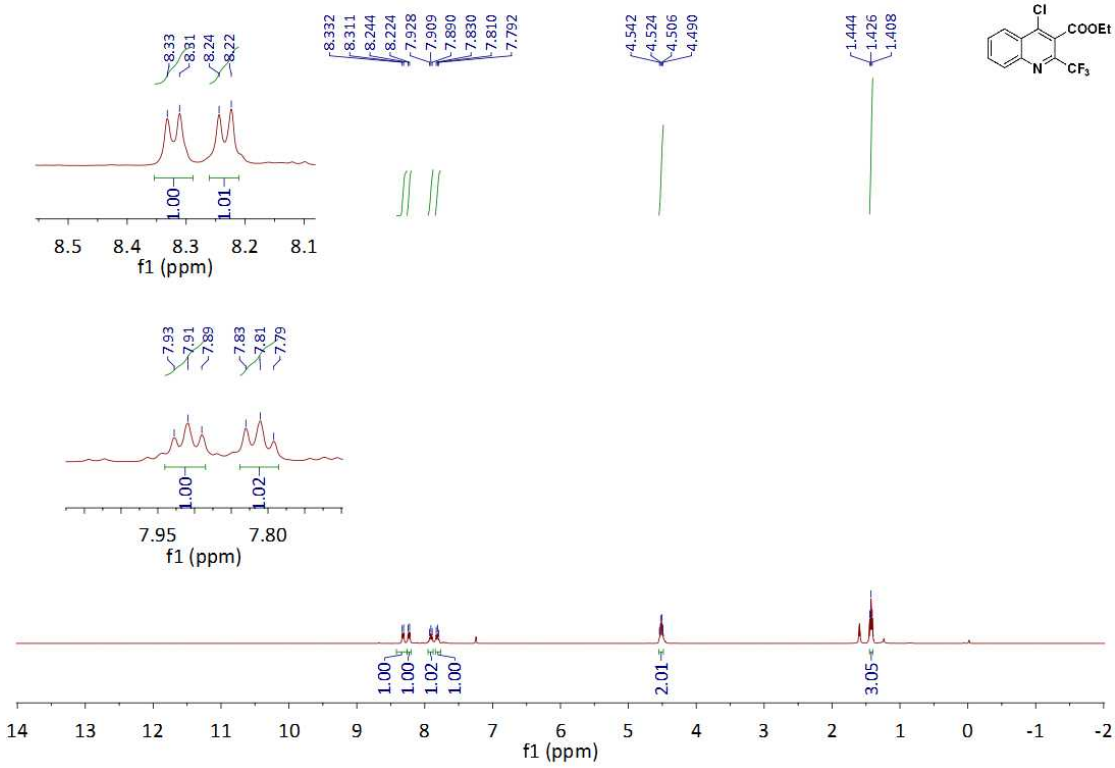
^{13}C NMR spectrum of 7-bromo-4-(trifluoromethyl)quinolone (2l)



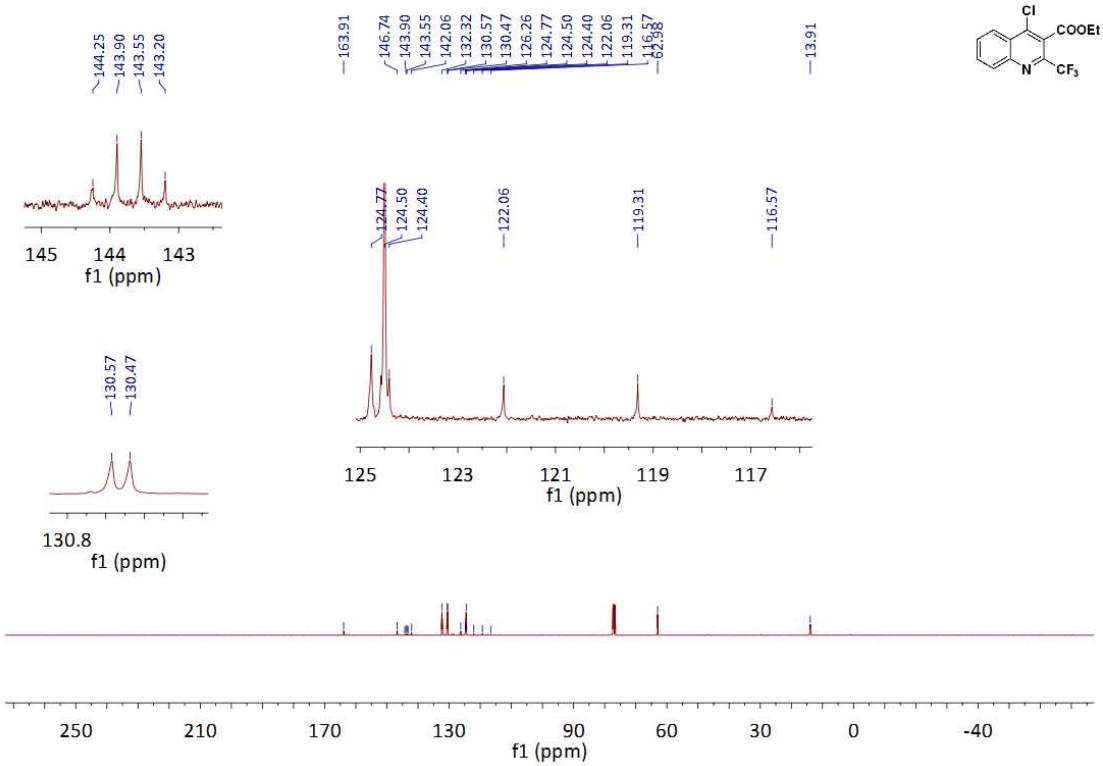
^{19}F NMR spectrum of 7-bromo-4-(trifluoromethyl)quinolone (2l)



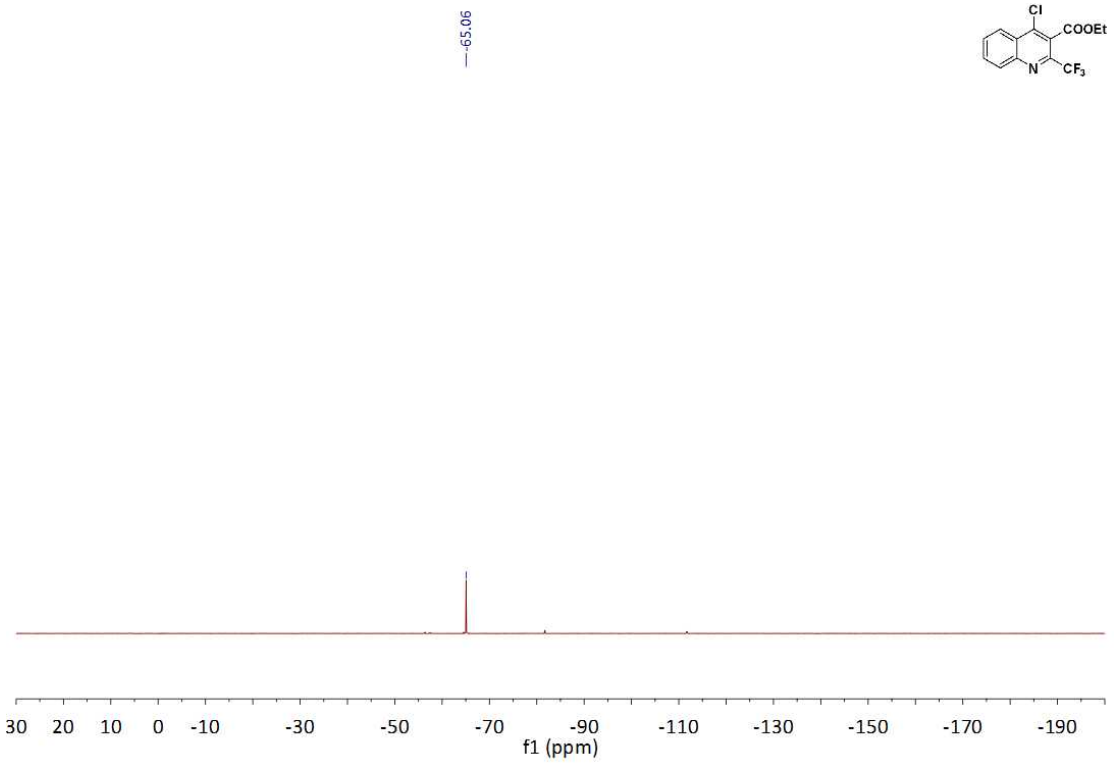
^{1}H NMR spectrum of ethyl 4-chloro-2-(trifluoromethyl)quinoline-3-carboxylate (2m)



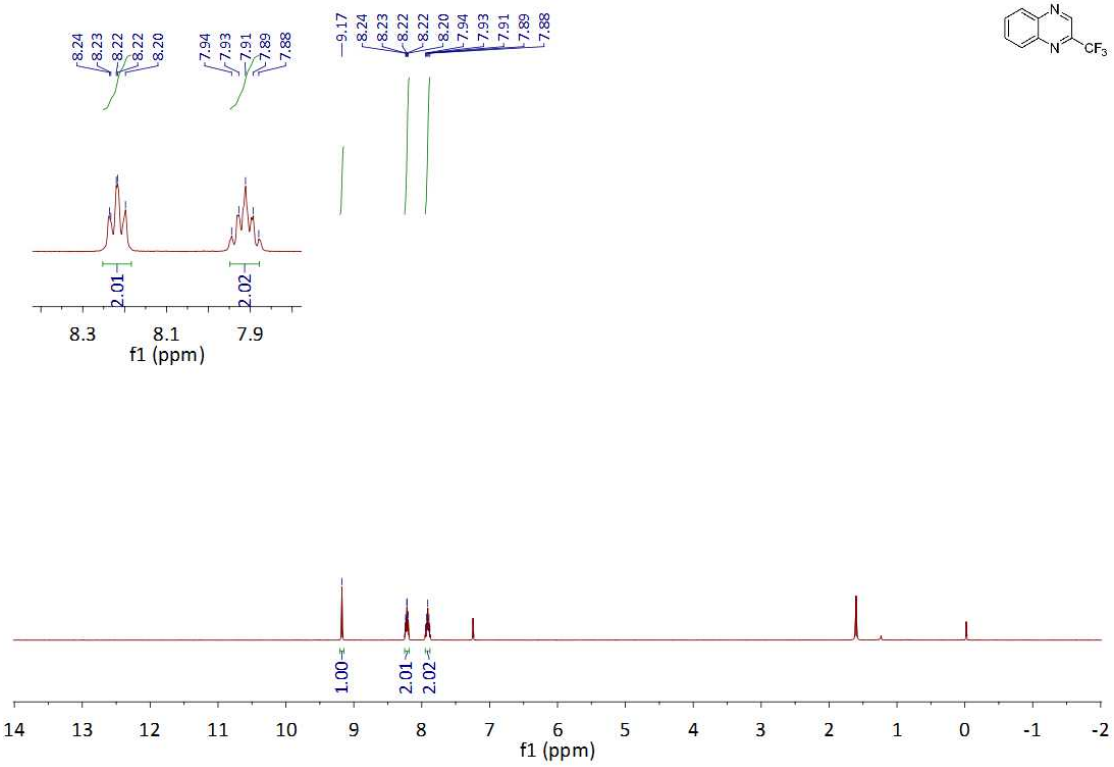
^{13}C NMR spectrum of ethyl 4-chloro-2-(trifluoromethyl)quinoline-3-carboxylate (2m)



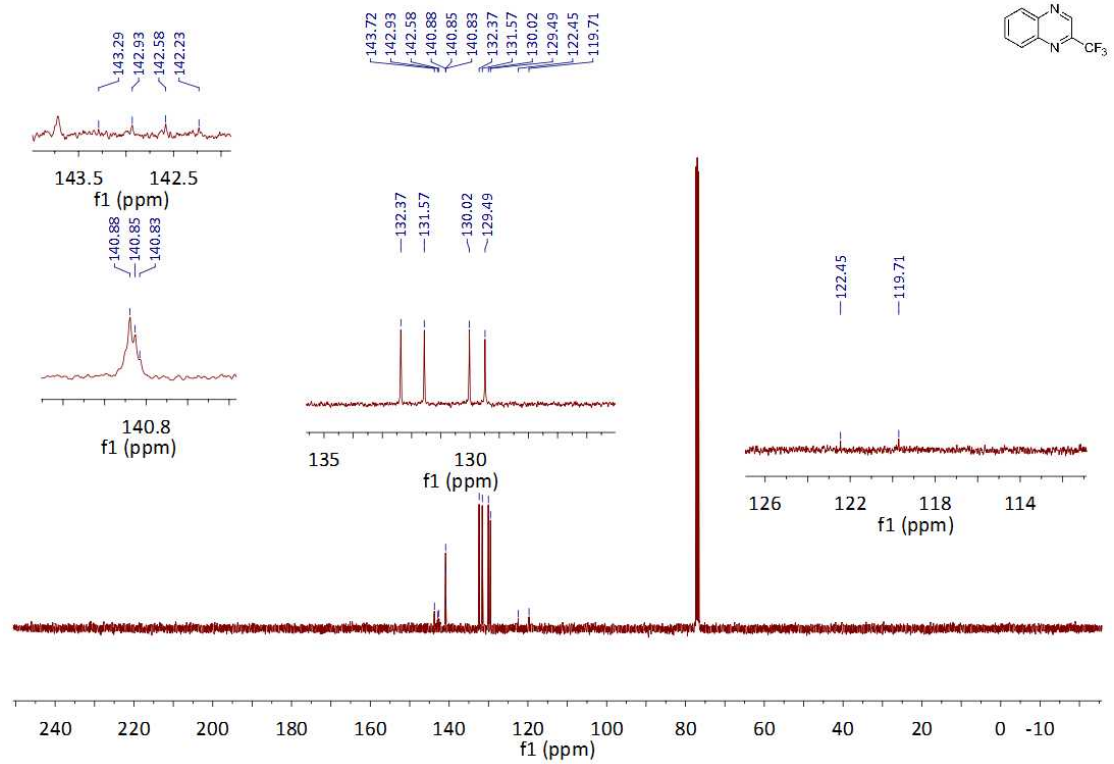
^{19}F NMR spectrum of ethyl 4-chloro-2-(trifluoromethyl)quinoline-3-carboxylate (2m)



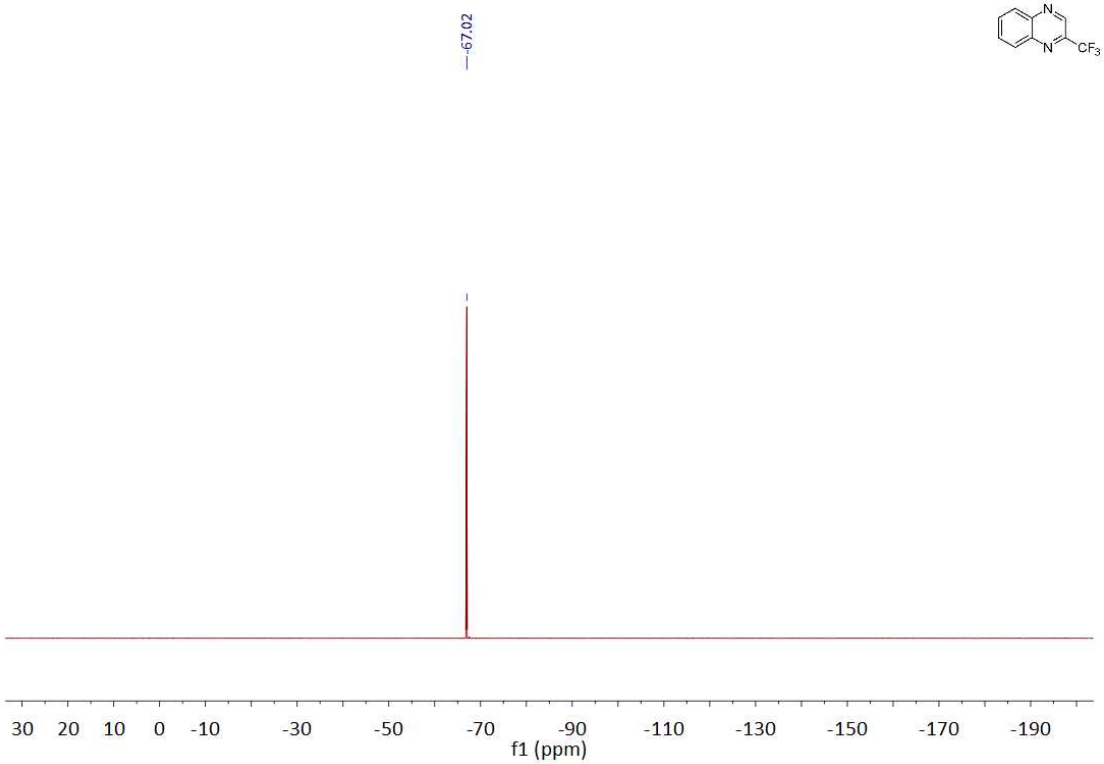
^{1}H NMR spectrum of 2-(trifluoromethyl)quinoxaline (2n)



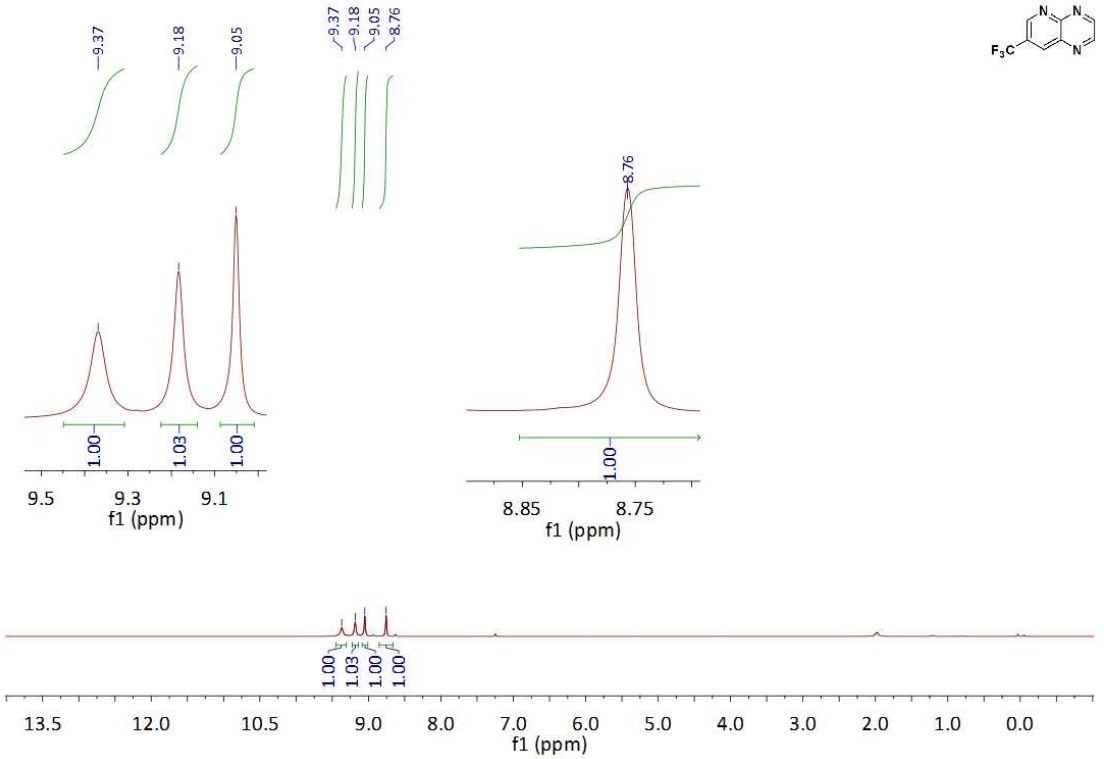
^{13}C NMR spectrum of 2-(trifluoromethyl)quinoxaline (2n)



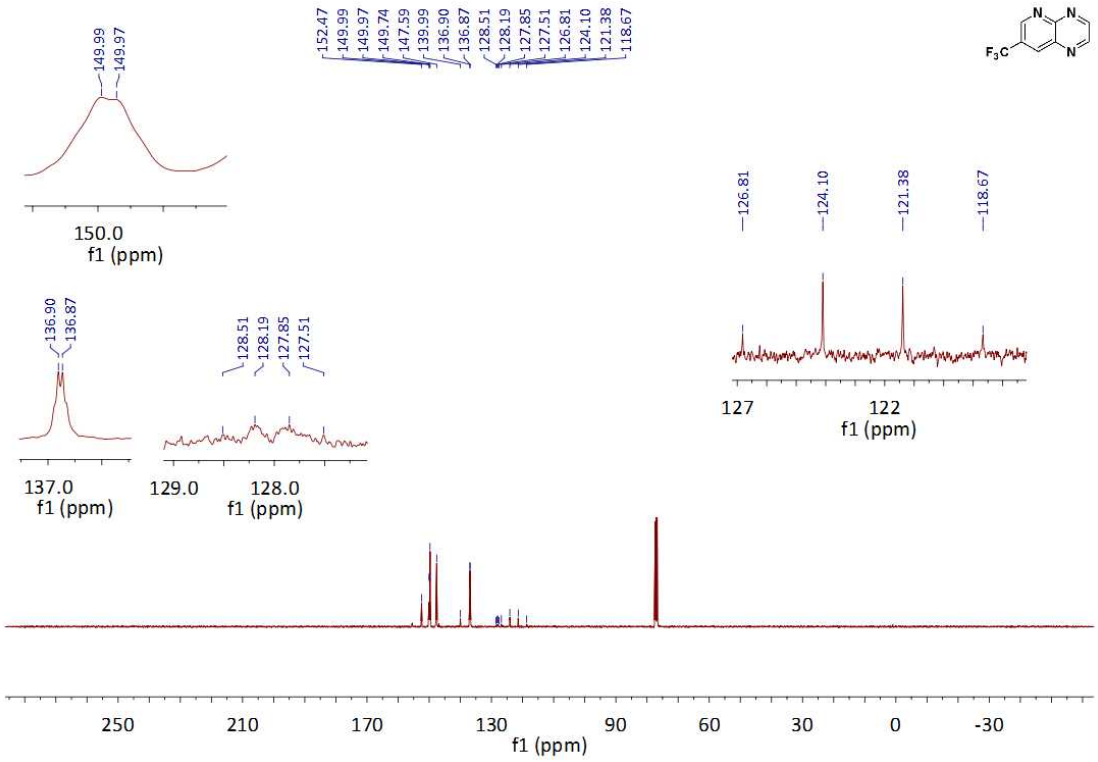
^{19}F NMR spectrum of 2-(trifluoromethyl)quinoxaline (2n)



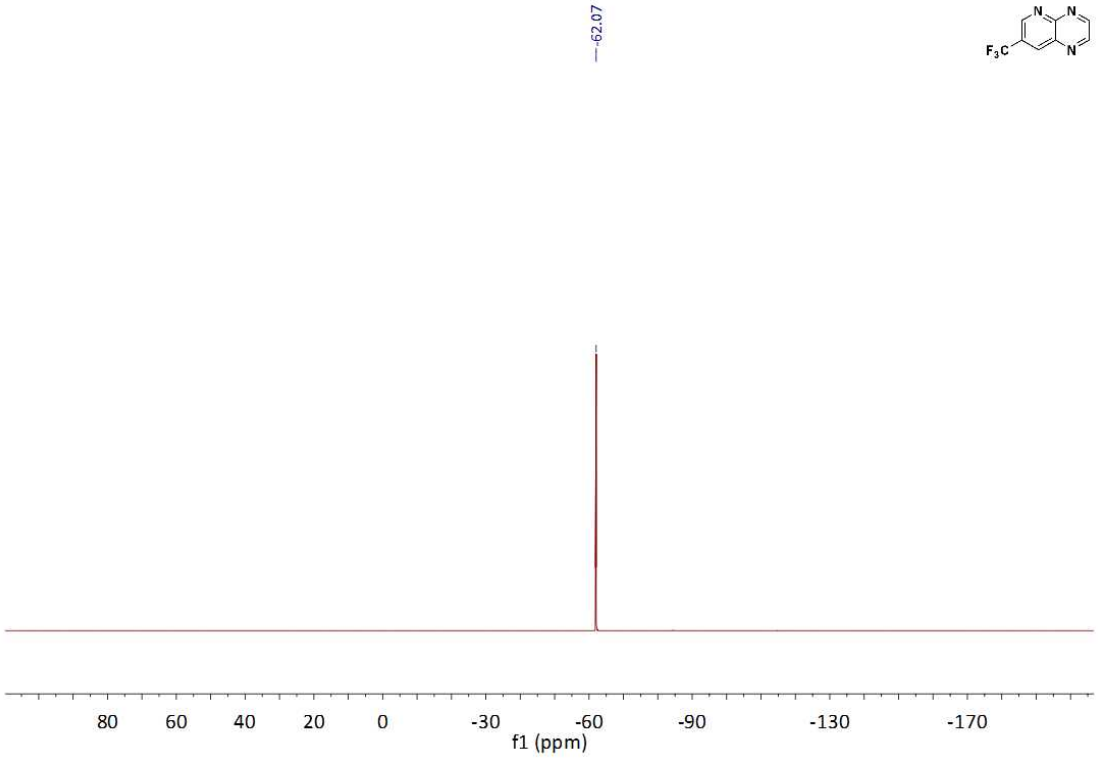
^{1}H NMR spectrum of 7-(trifluoromethyl)pyrido[2,3-b]pyrazine (2o)



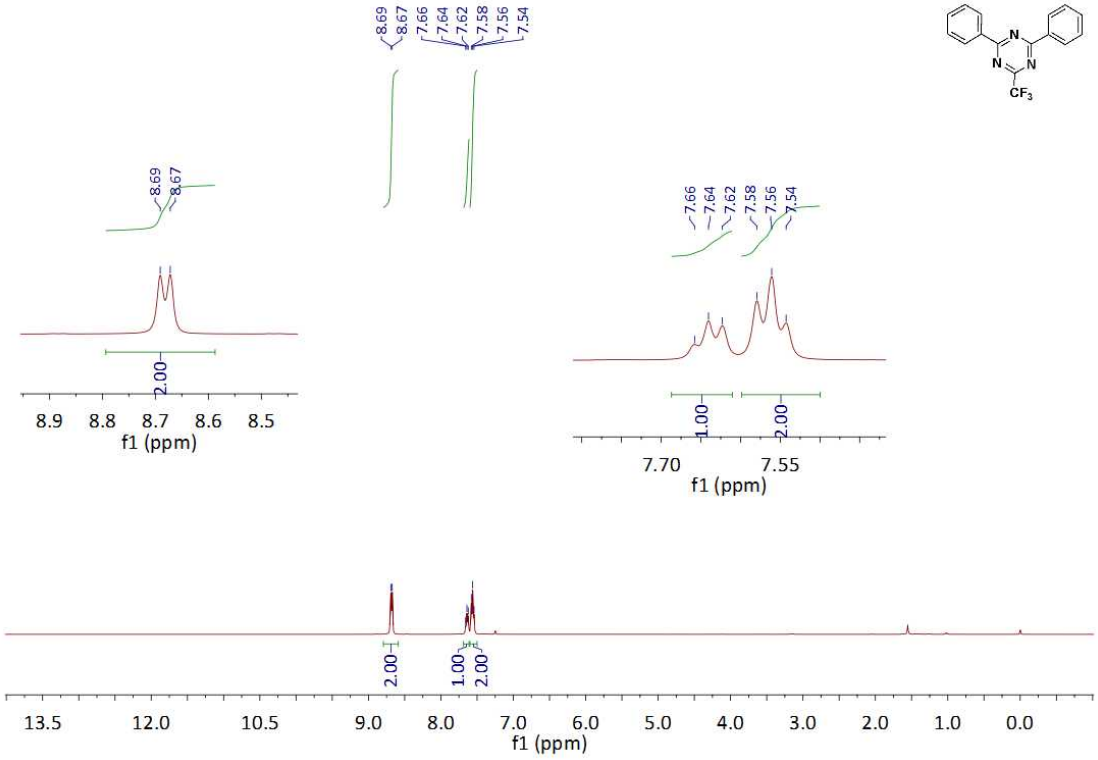
^{13}C NMR spectrum of 7-(trifluoromethyl)pyrido[2,3-b]pyrazine (2o)



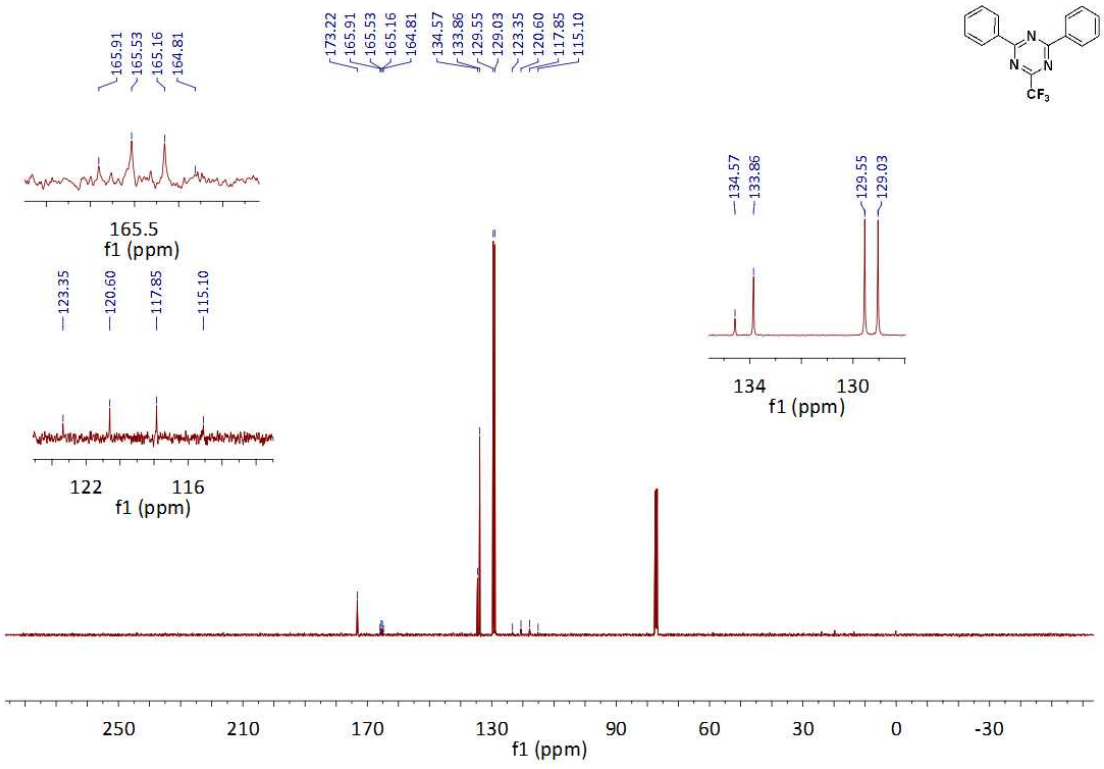
^{19}F NMR spectrum of 7-(trifluoromethyl)pyrido[2,3-b]pyrazine (2o)



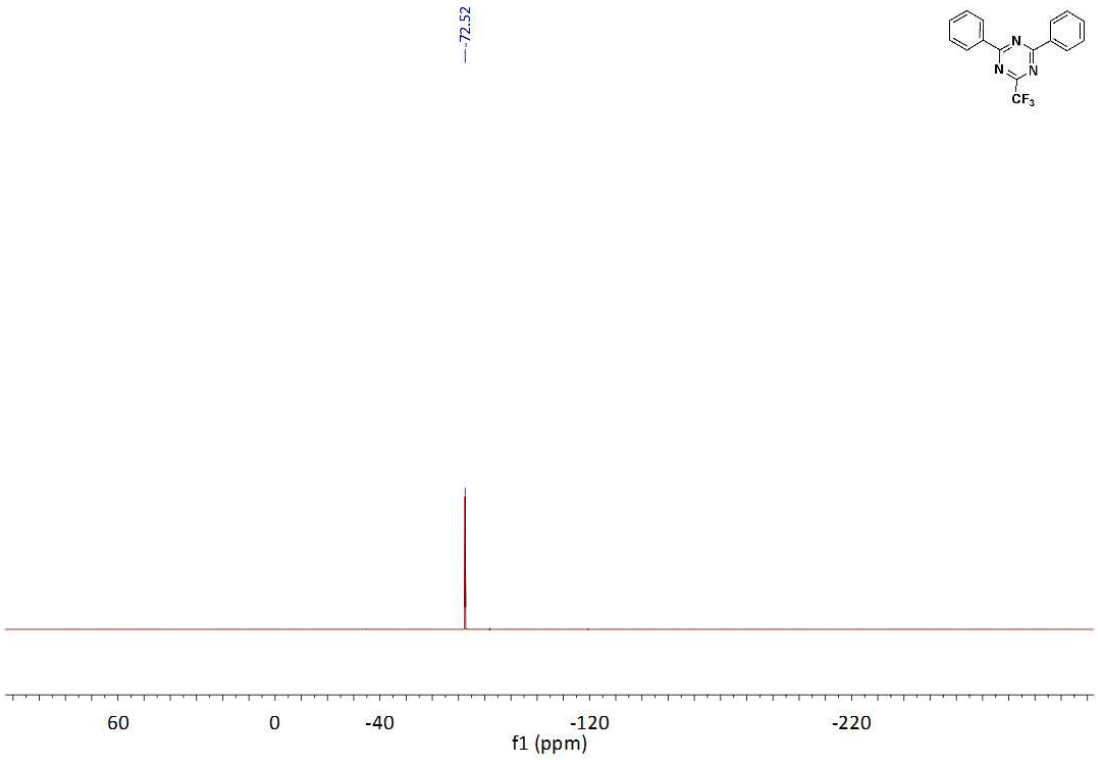
^{1}H NMR spectrum of 2,4-diphenyl-6-(trifluoromethyl)-1,3,5-triazine (2p)



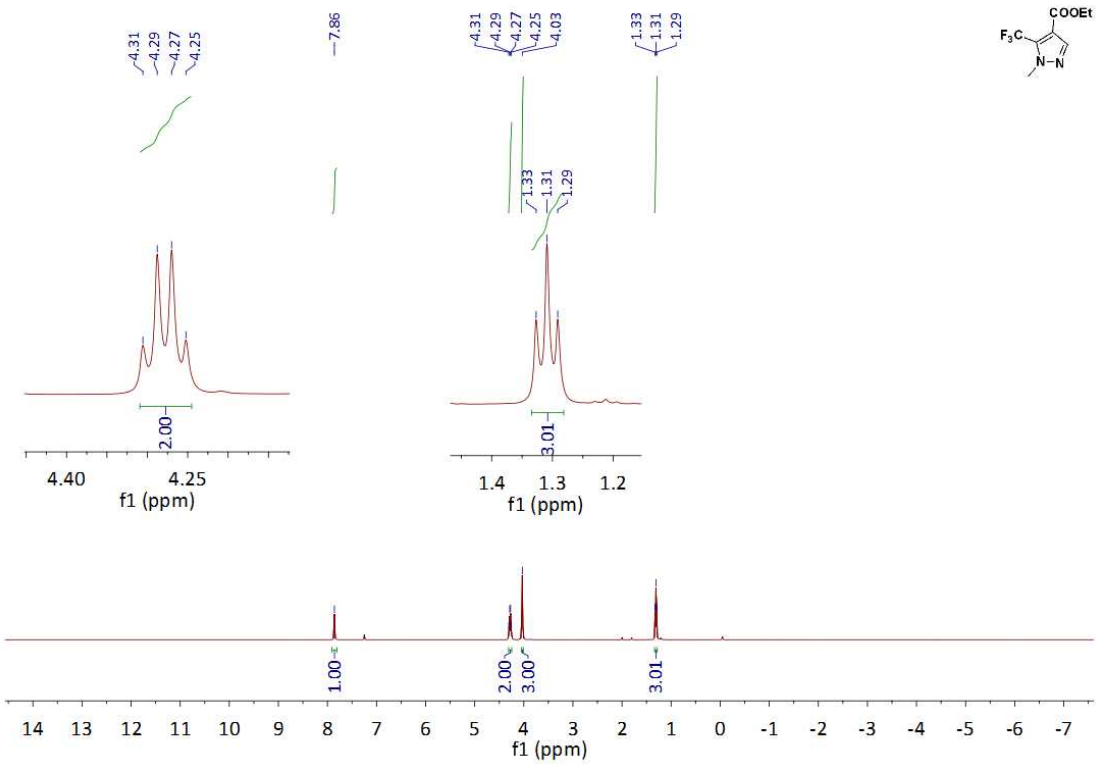
^{13}C NMR spectrum of 2,4-diphenyl-6-(trifluoromethyl)-1,3,5-triazine (2p)



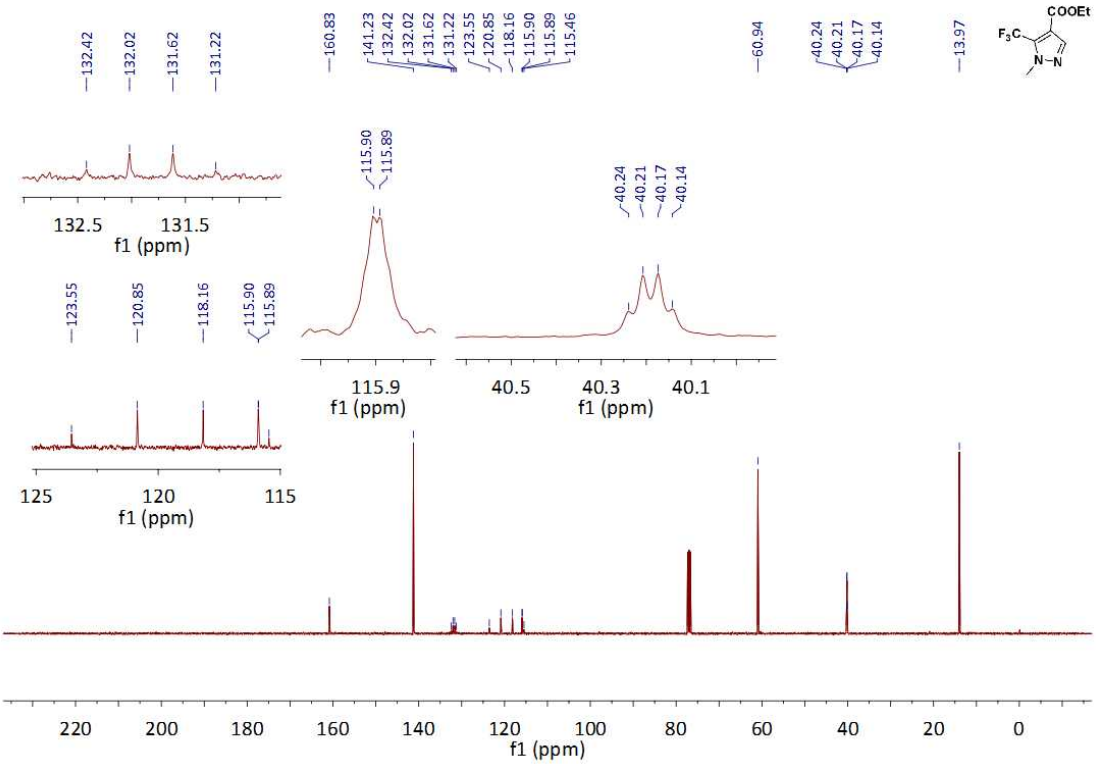
^{19}F NMR spectrum of 2,4-diphenyl-6-(trifluoromethyl)-1,3,5-triazine (2p)



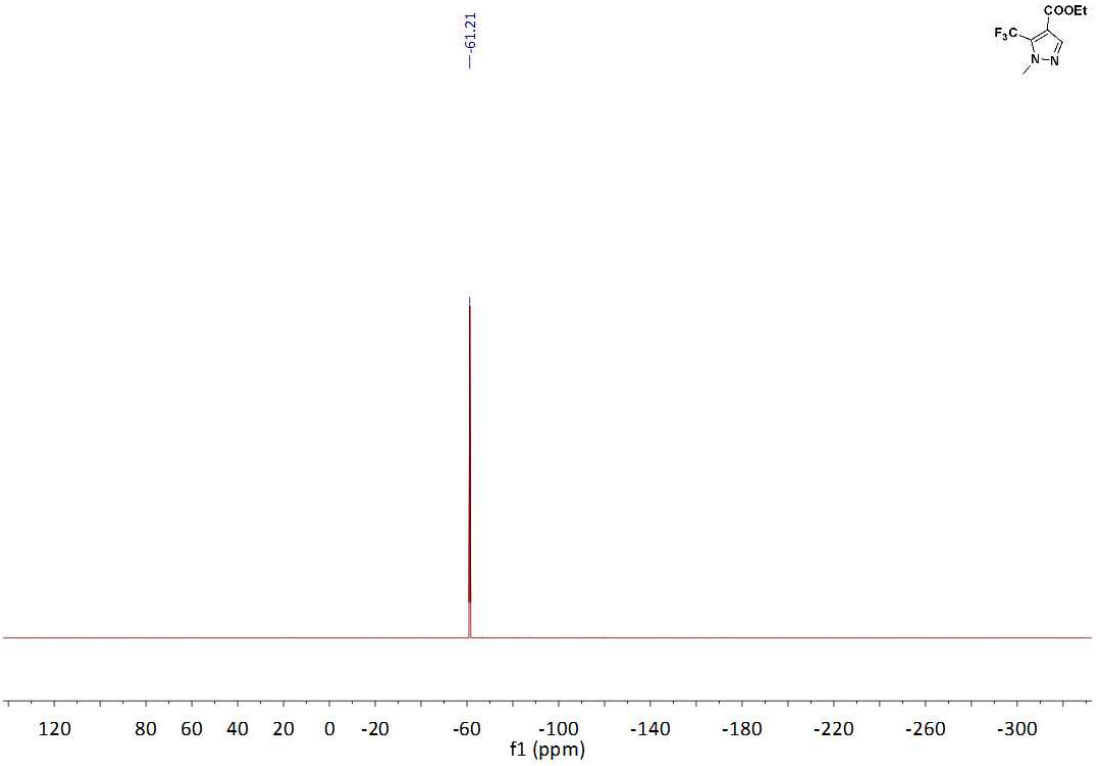
^{1}H NMR spectrum of ethyl 1-methyl-5-(trifluoromethyl)pyrazole-4-carboxylate (2q)



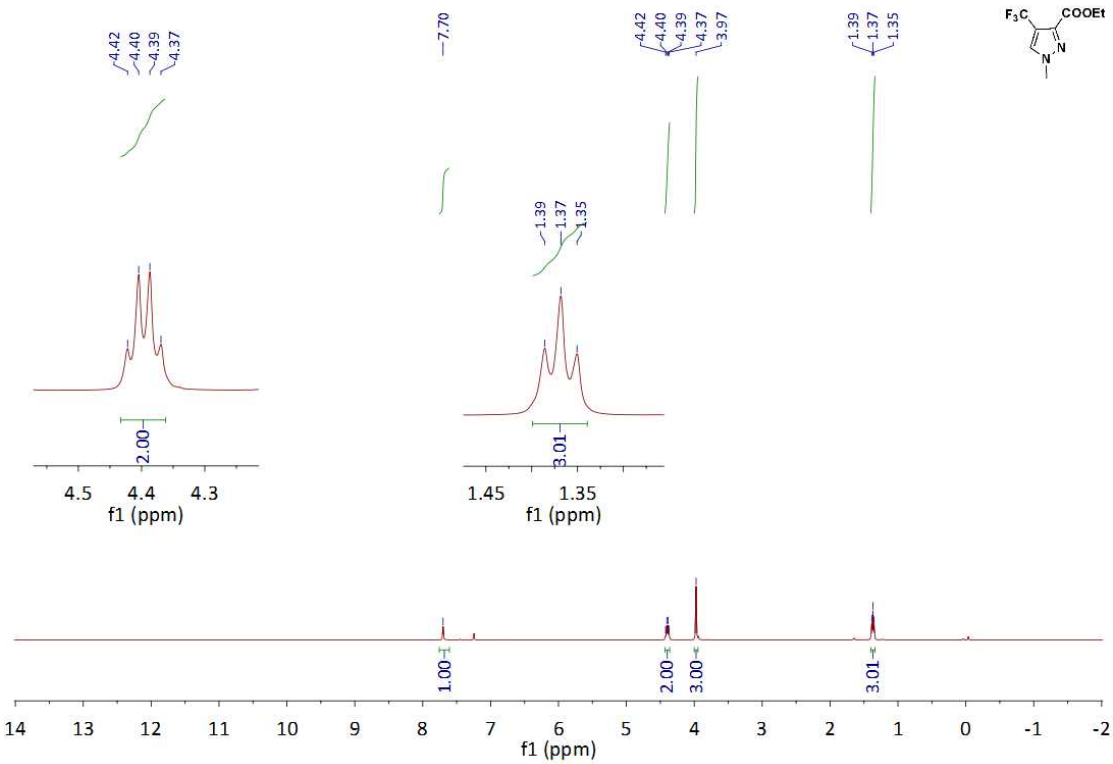
^{13}C NMR spectrum of ethyl 1-methyl-5-(trifluoromethyl)pyrazole-4-carboxylate (2q)



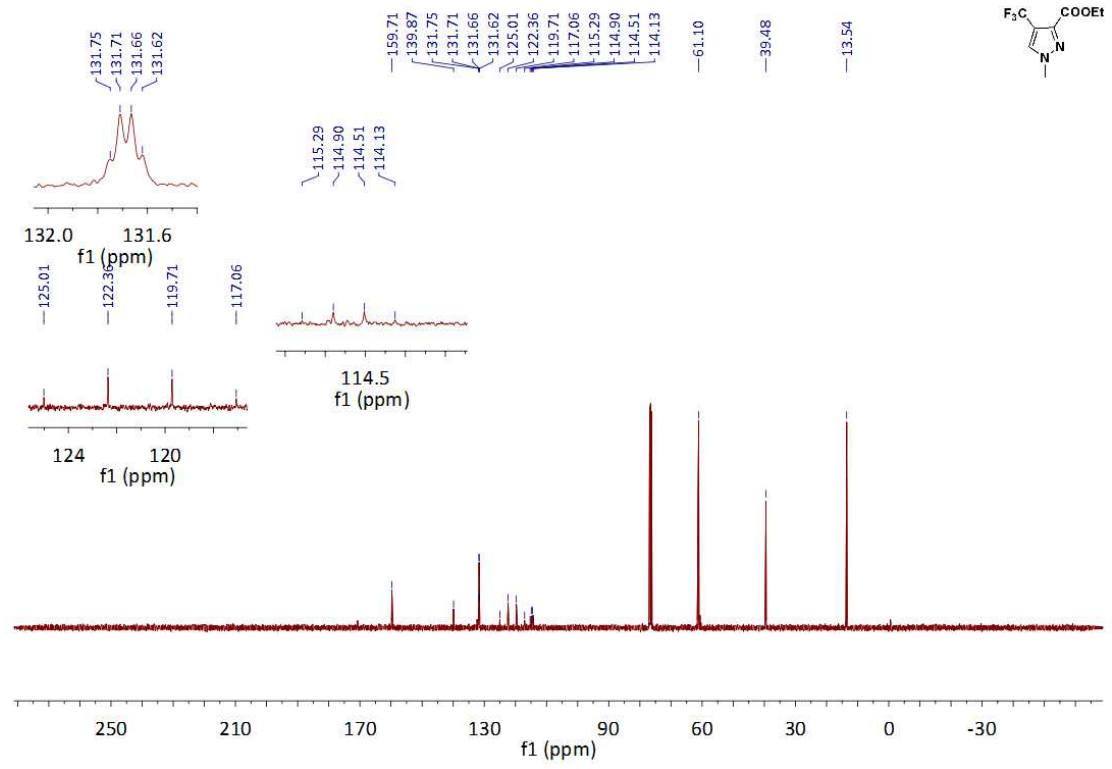
^{19}F NMR spectrum of ethyl 1-methyl-5-(trifluoromethyl)pyrazole-4-carboxylate (2q)



^{1}H NMR spectrum of
ethyl 1-methyl-4-(trifluoromethyl)pyrazole-3-carboxylate (2r)



^{13}C NMR spectrum of
ethyl 1-methyl-4-(trifluoromethyl)pyrazole-3-carboxylate (2r)



^{19}F NMR spectrum of
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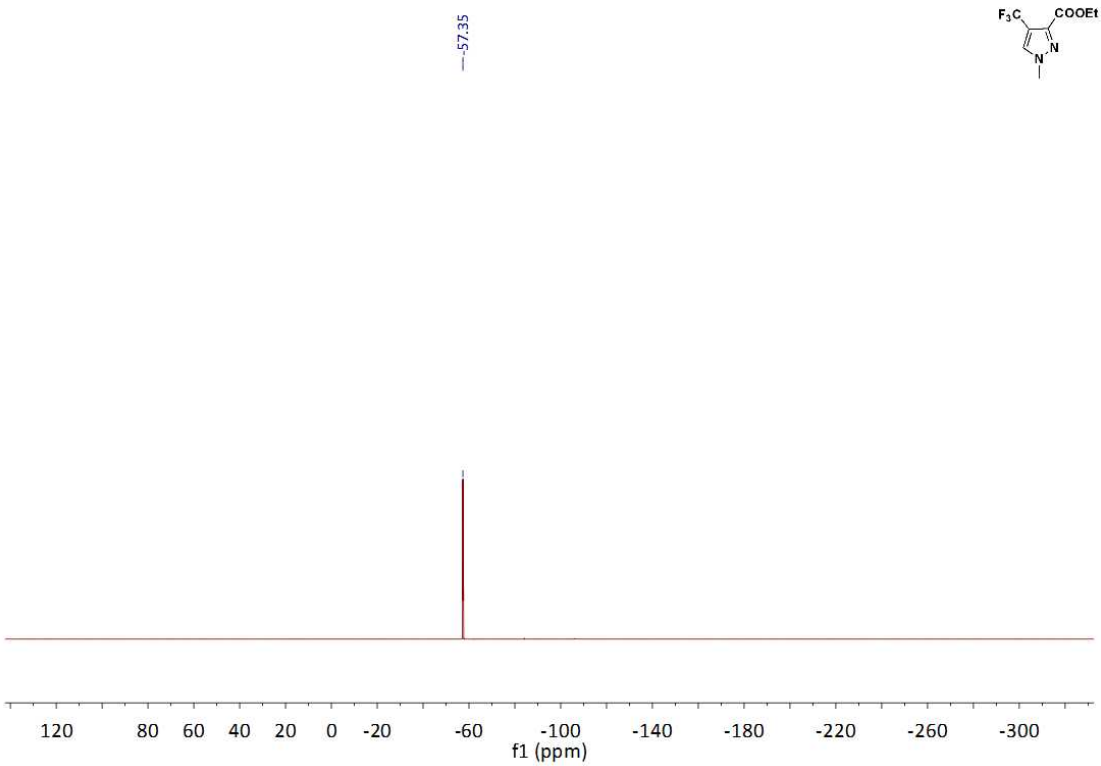
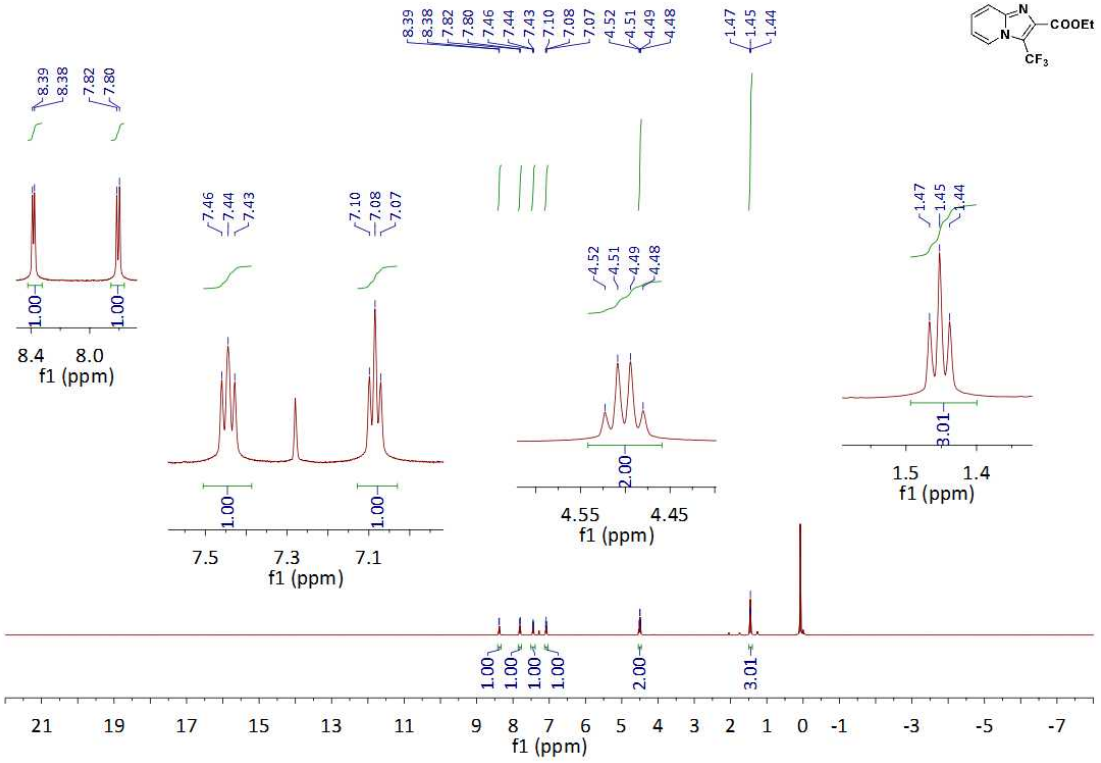
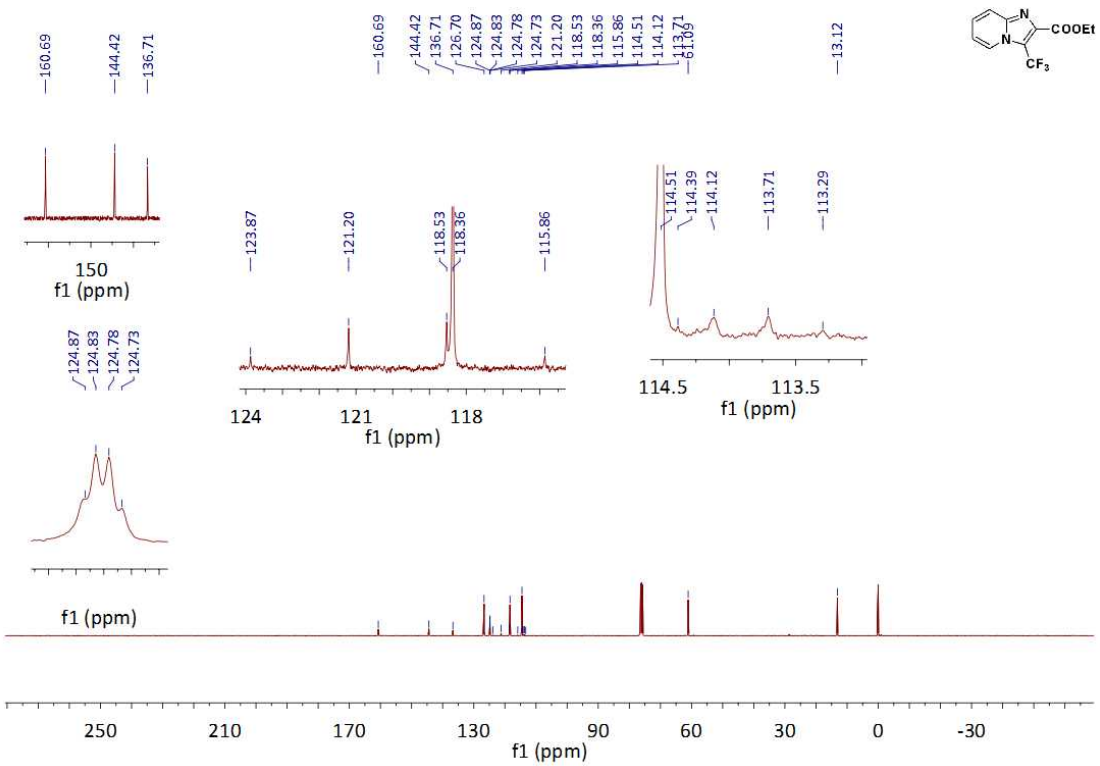


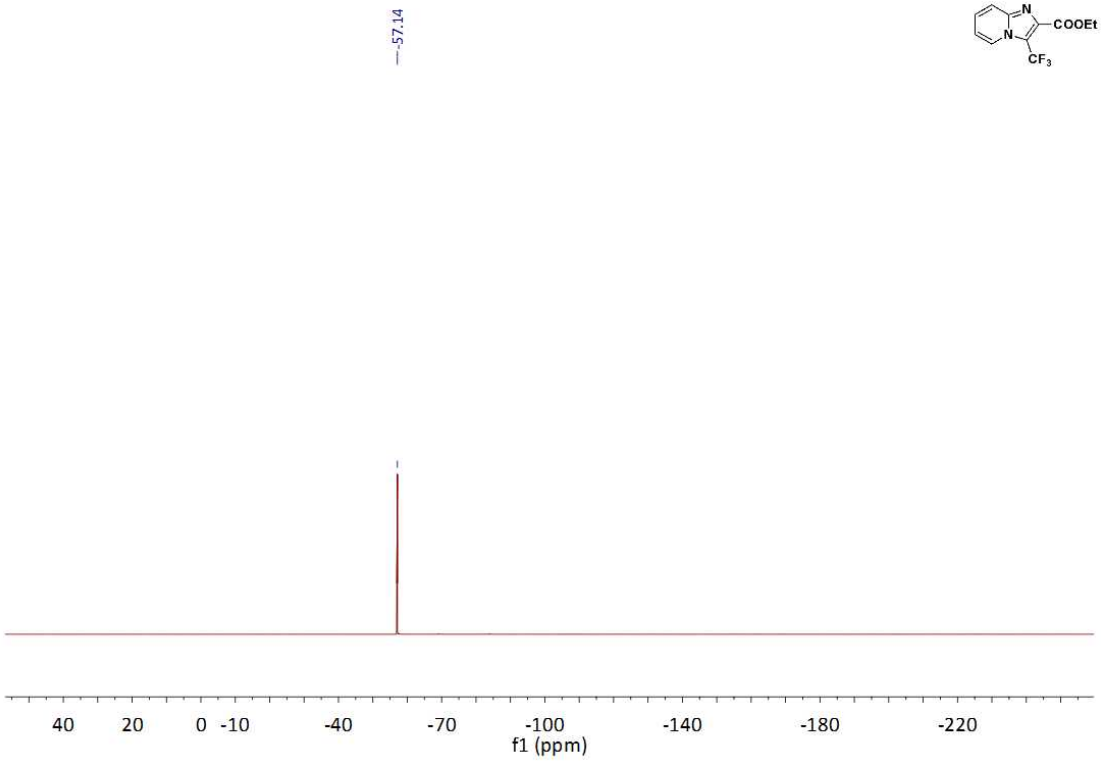
^{1}H NMR spectrum of
ethyl 3-(trifluoromethyl)imidazo[1,2-a]pyridine-2-carboxylate (2s)



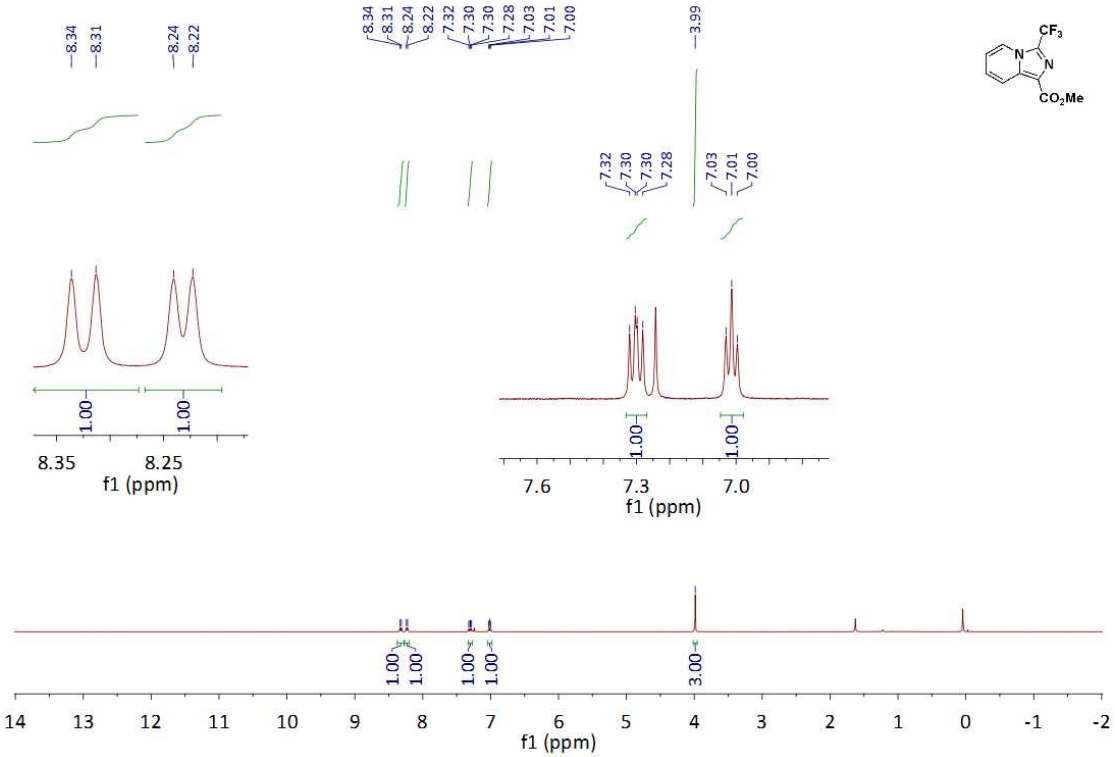
^{13}C NMR spectrum of ethyl 3-(trifluoromethyl)imidazo[1,2-a]pyridine-2-carboxylate (2s)



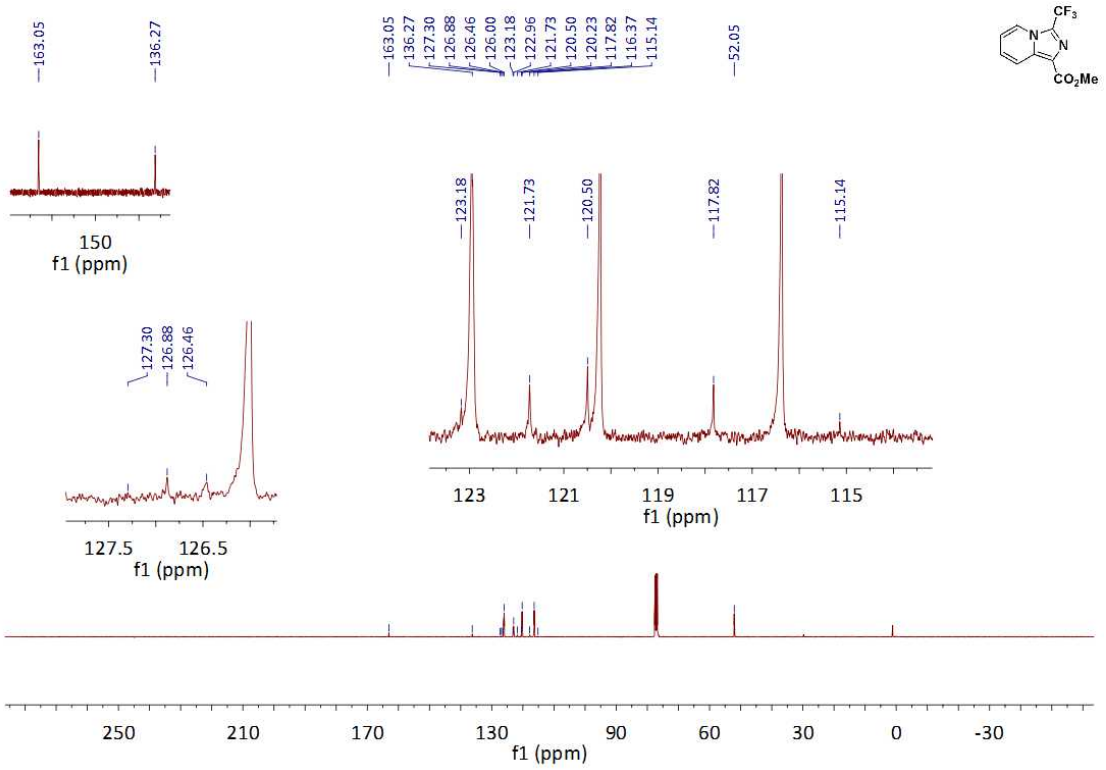
^{19}F NMR spectrum of ethyl 3-(trifluoromethyl)imidazo[1,2-a]pyridine-2-carboxylate (2s)



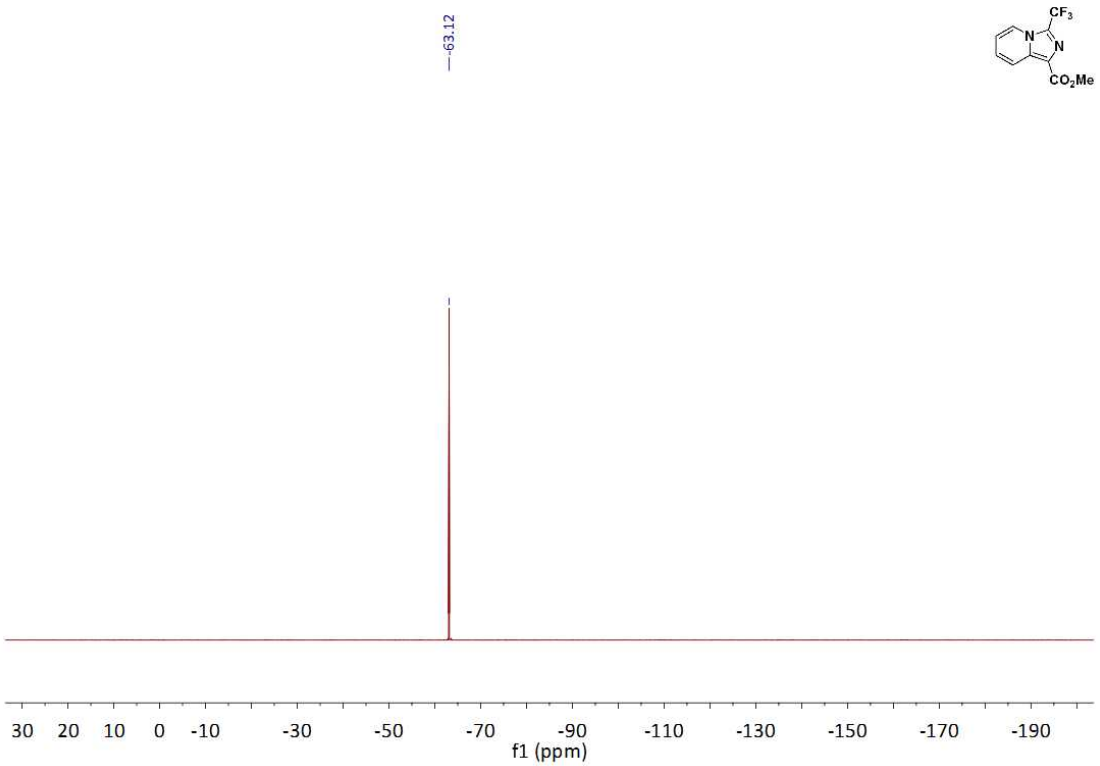
^{1}H NMR spectrum of methyl 3-(trifluoromethyl)imidazo[1,5-a]pyridine-1-carboxylate (2t)



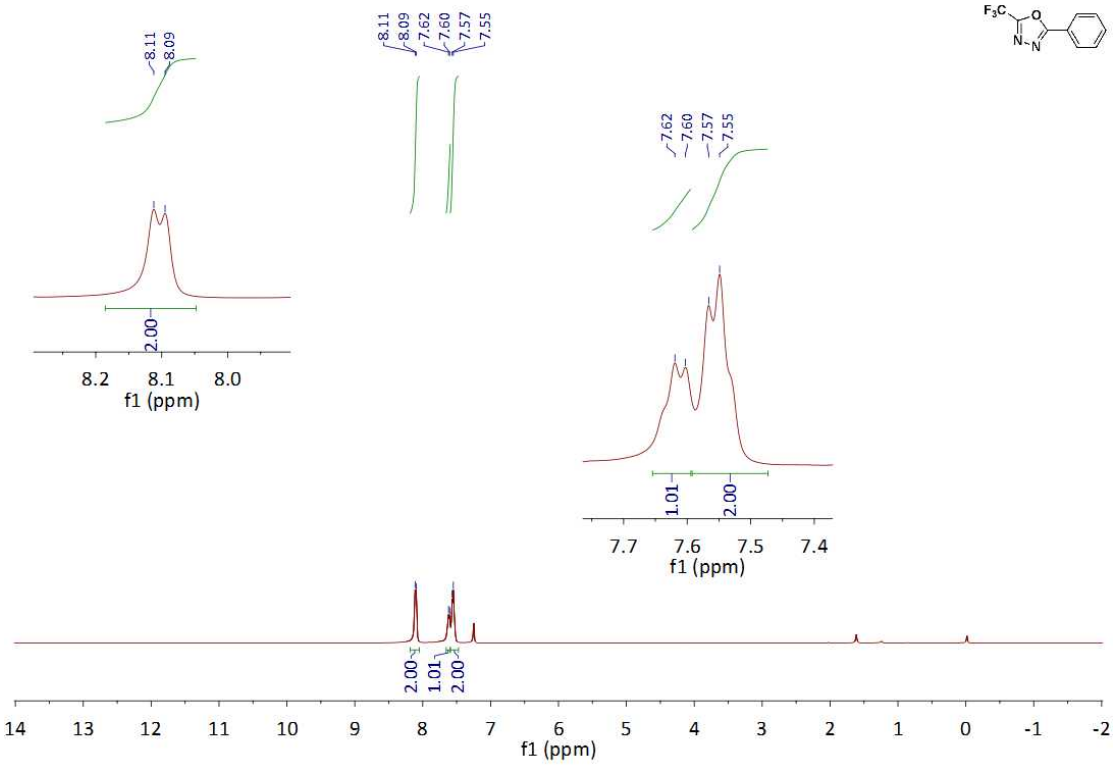
^{13}C NMR spectrum of methyl 3-(trifluoromethyl)imidazo[1,5-a]pyridine-1-carboxylate (2t)



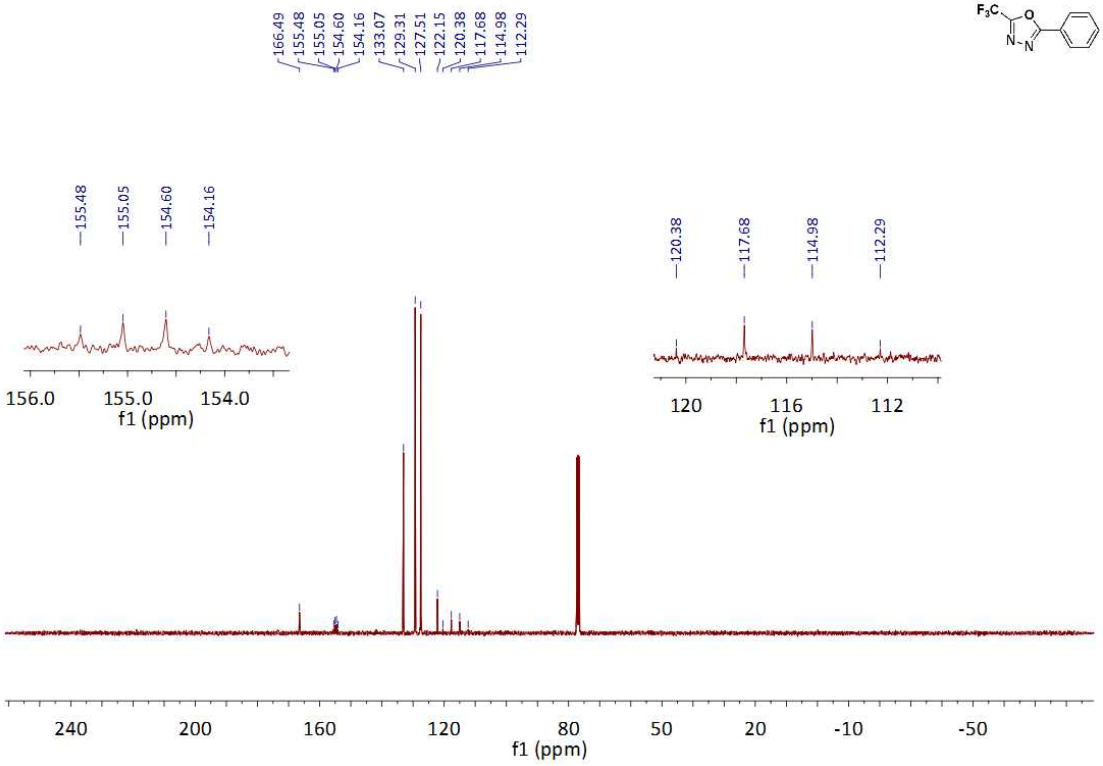
^{19}F NMR spectrum of
methyl 3-(trifluoromethyl)imidazo[1,5-a]pyridine-1-carboxylate (2t)



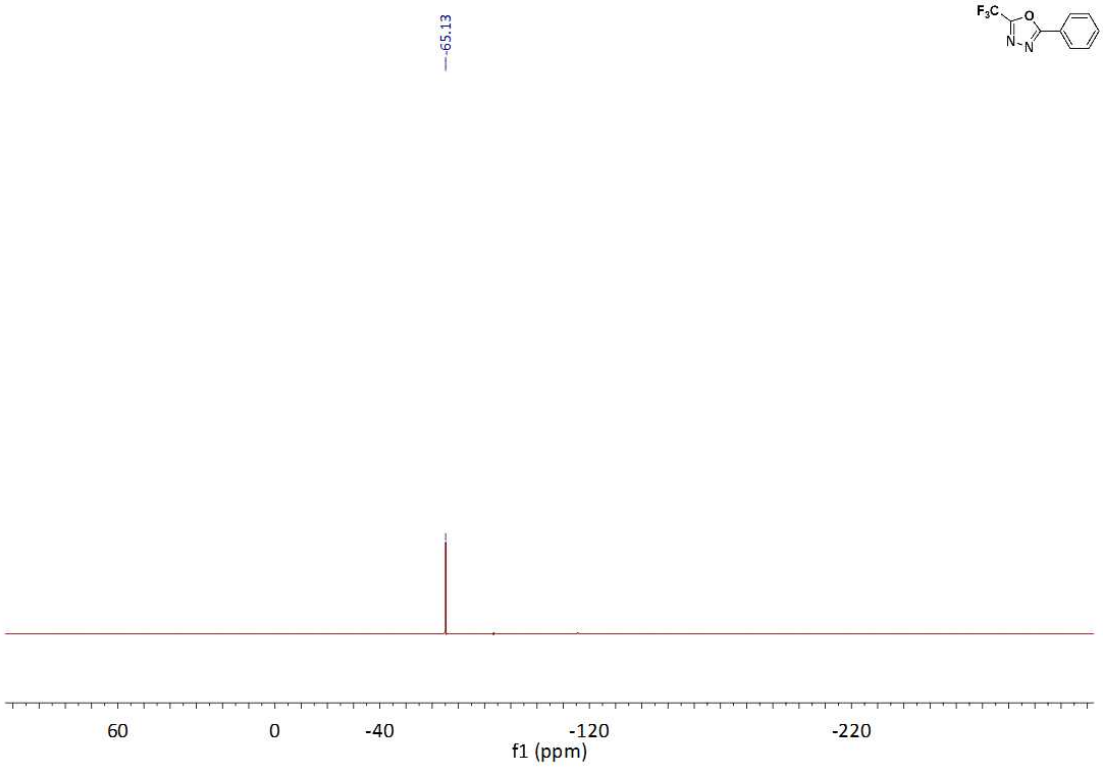
^{1}H NMR spectrum of 2-phenyl-5-(trifluoromethyl)-1,3,4-oxadiazole (2u)



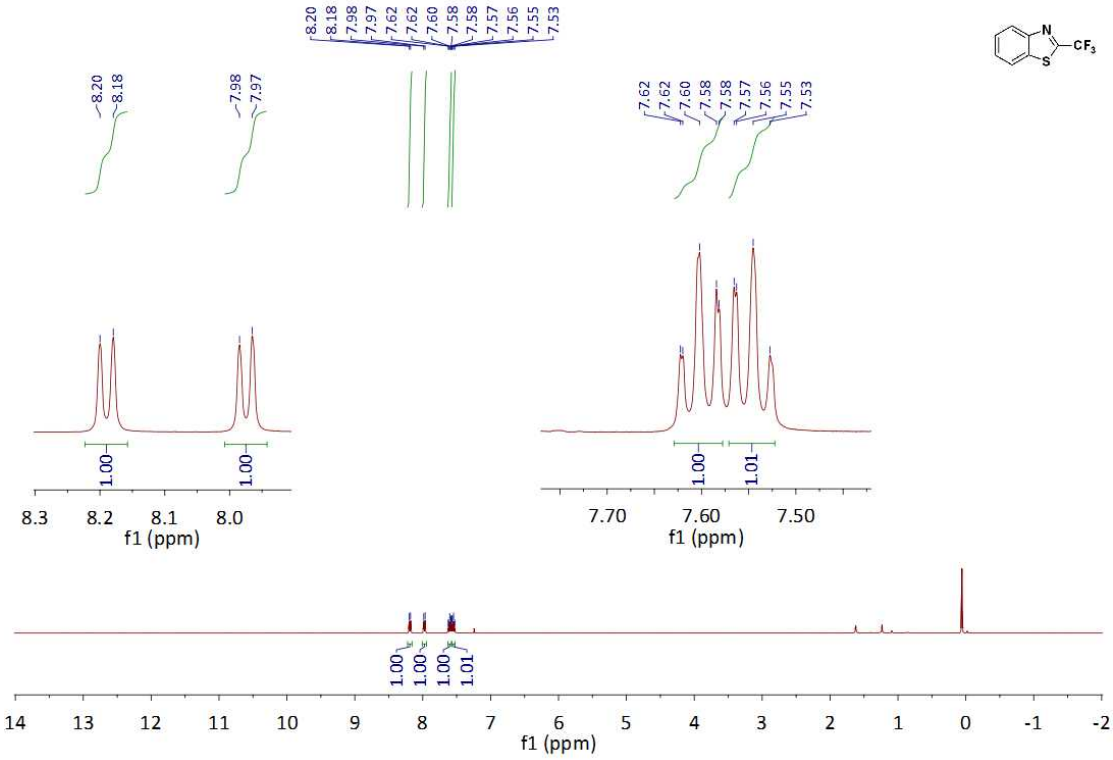
^{13}C NMR spectrum of 2-phenyl-5-(trifluoromethyl)-1,3,4-oxadiazole (2u)



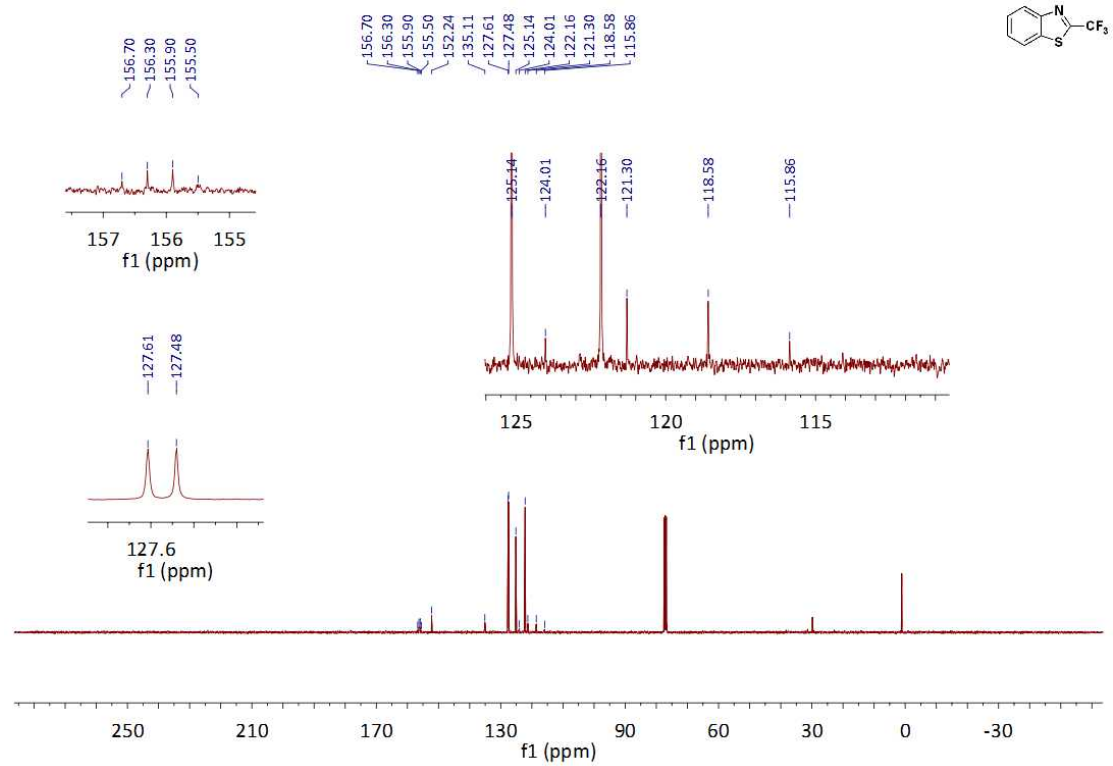
^{19}F NMR spectrum of 2-phenyl-5-(trifluoromethyl)-1,3,4-oxadiazole (2u)



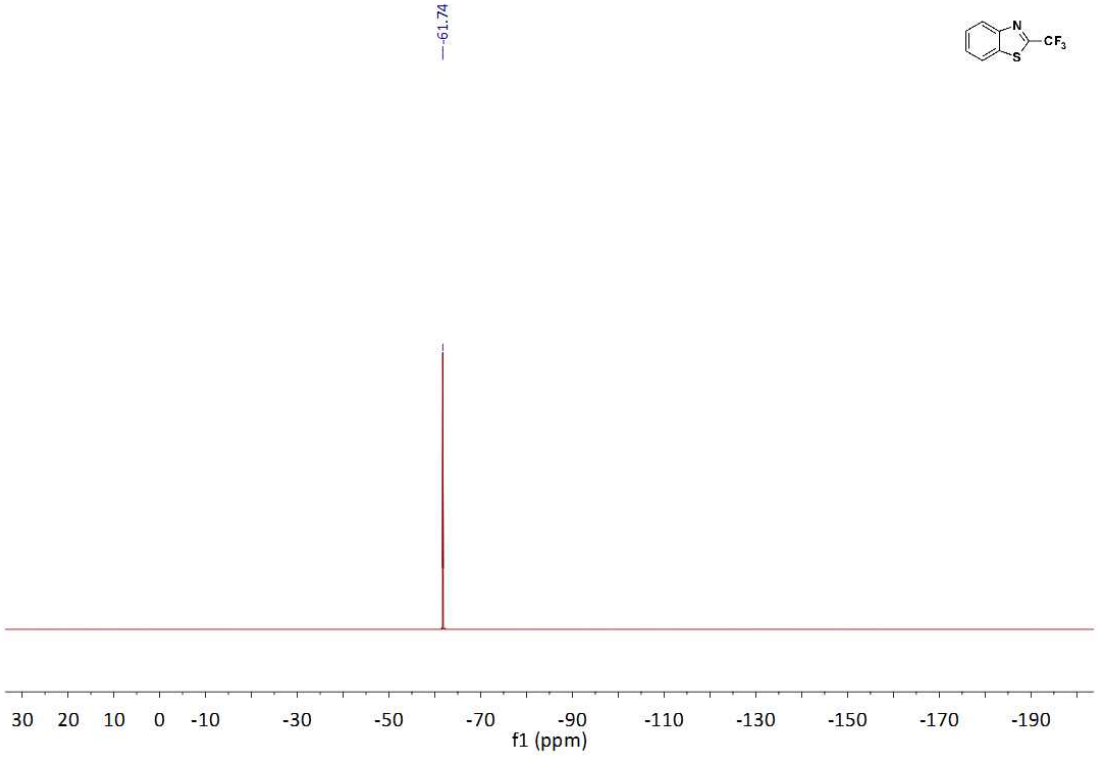
^{1}H NMR spectrum of 2-(trifluoromethyl)-1,3-benzothiazole (2v)



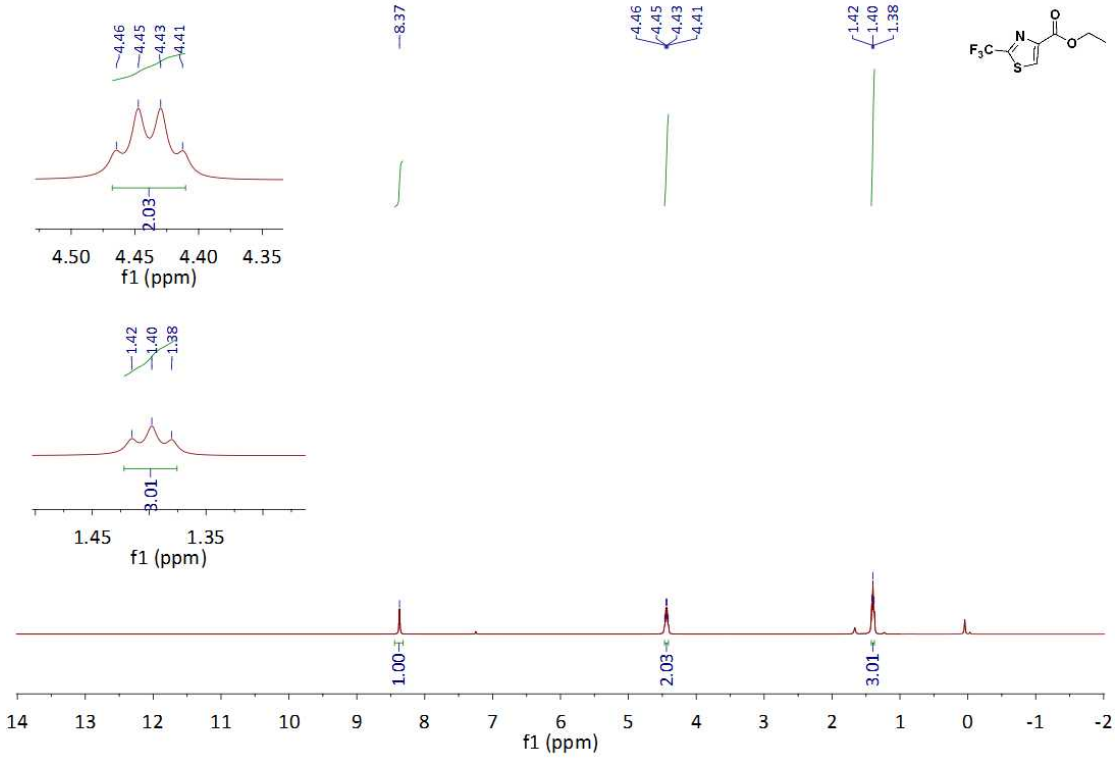
^{13}C NMR spectrum of 2-(trifluoromethyl)-1,3-benzothiazole (2v)



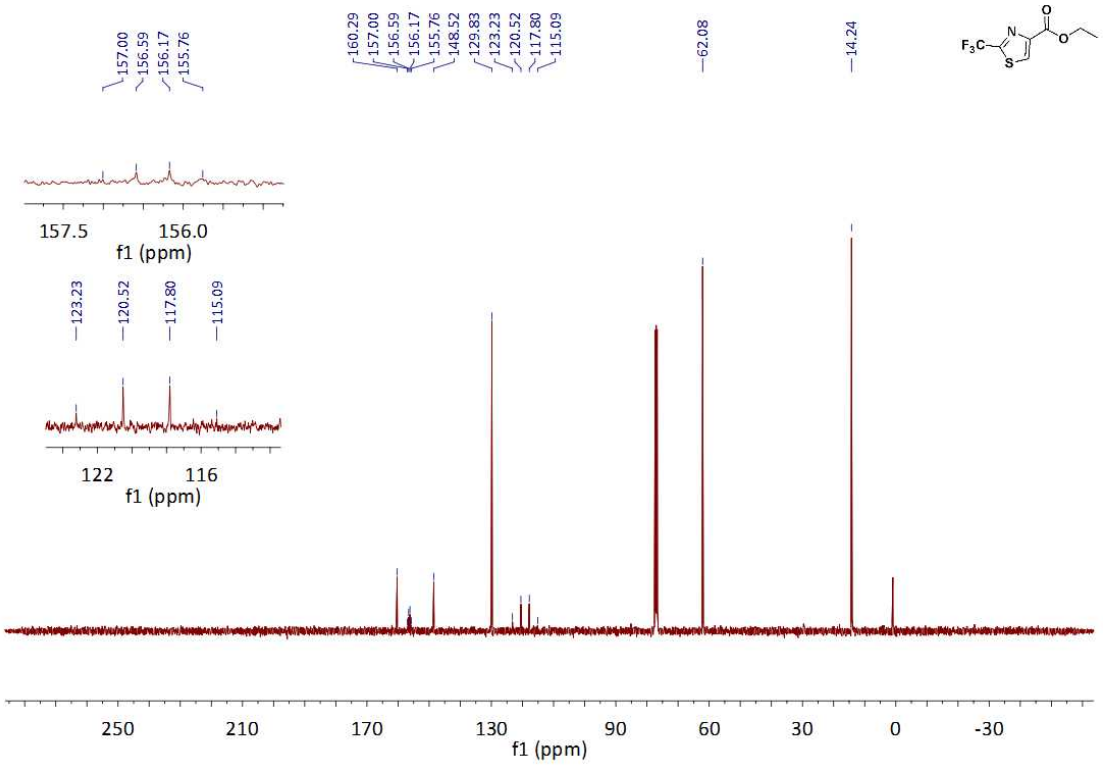
^{19}F NMR spectrum of 2-(trifluoromethyl)-1,3-benzothiazole (2v)



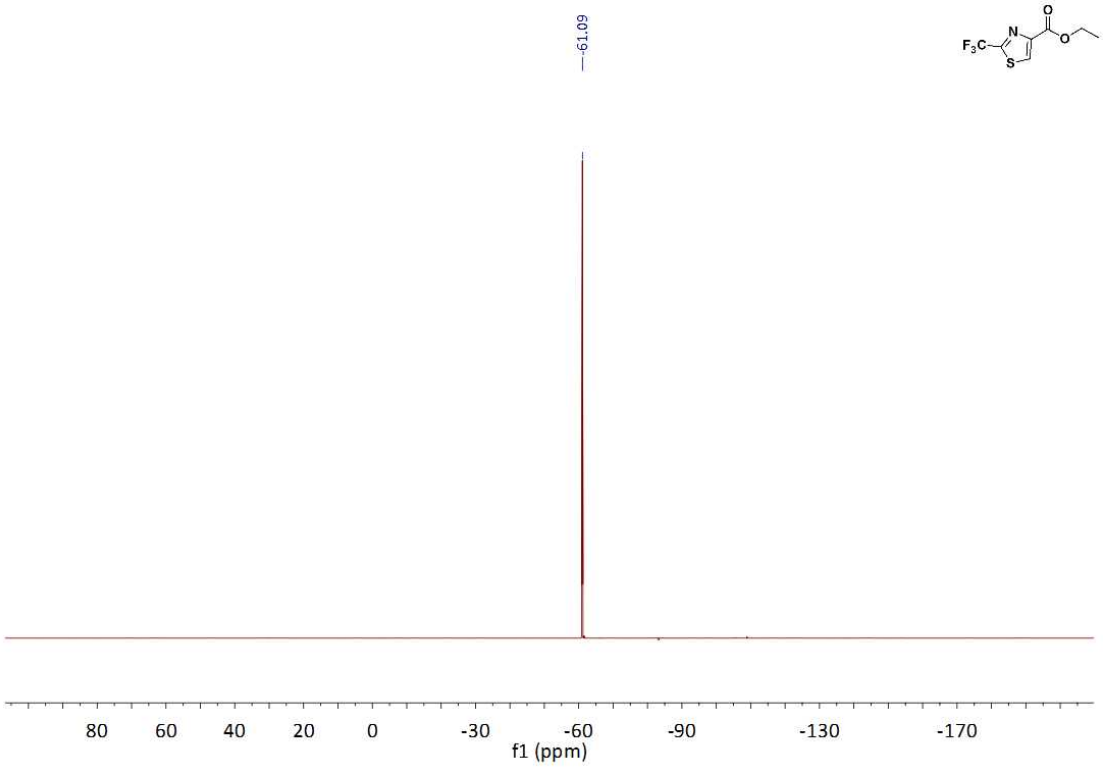
^{1}H NMR spectrum of ethyl 2-(trifluoromethyl)thiazole-4-carboxylate (2w)



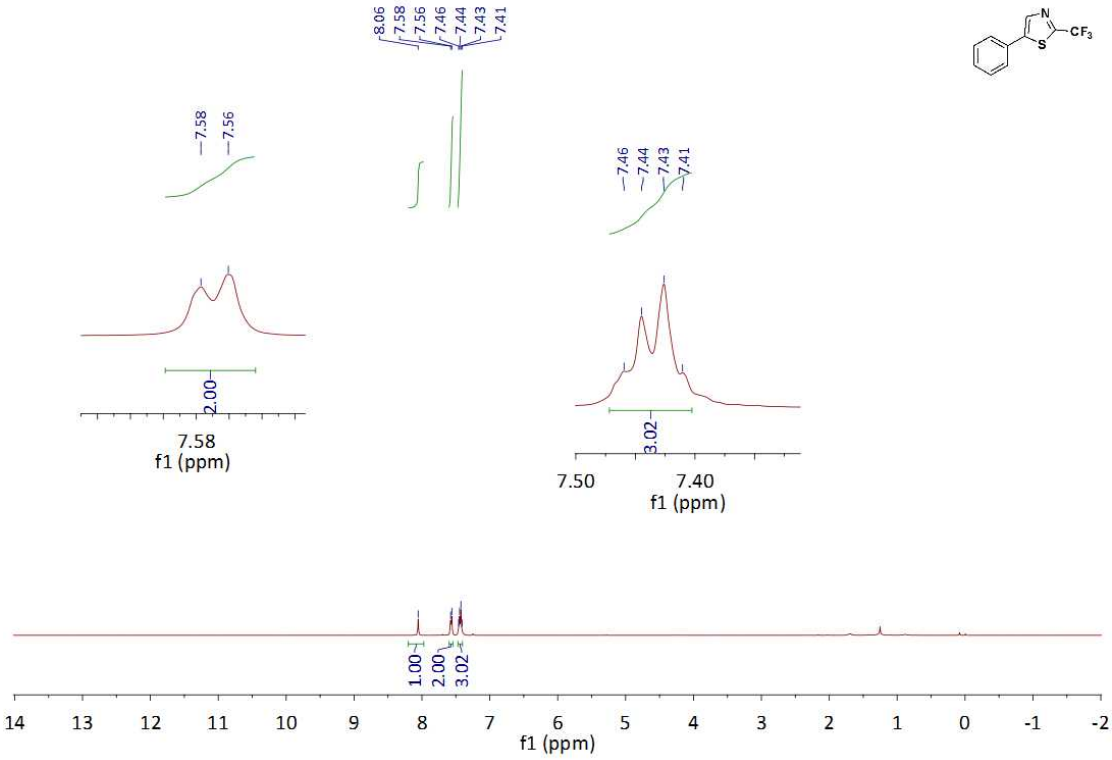
^{13}C NMR spectrum of ethyl 2-(trifluoromethyl)thiazole-4-carboxylate (2w)



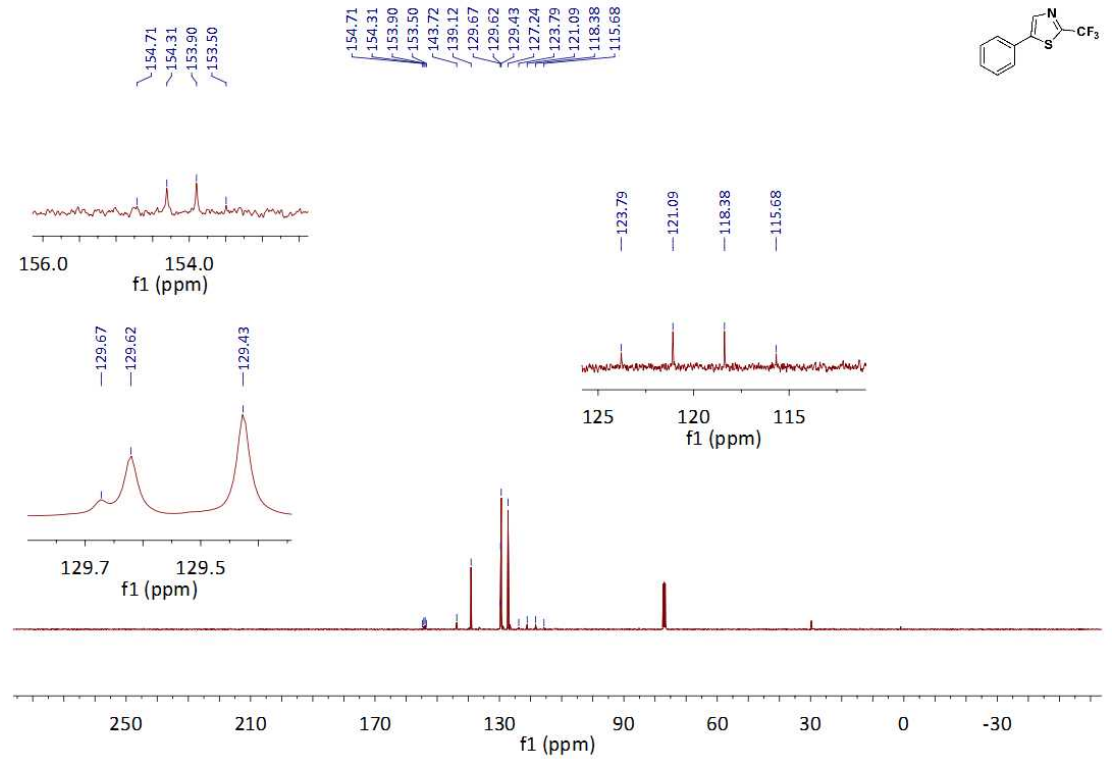
^{19}F NMR spectrum of ethyl 2-(trifluoromethyl)thiazole-4-carboxylate (2w)



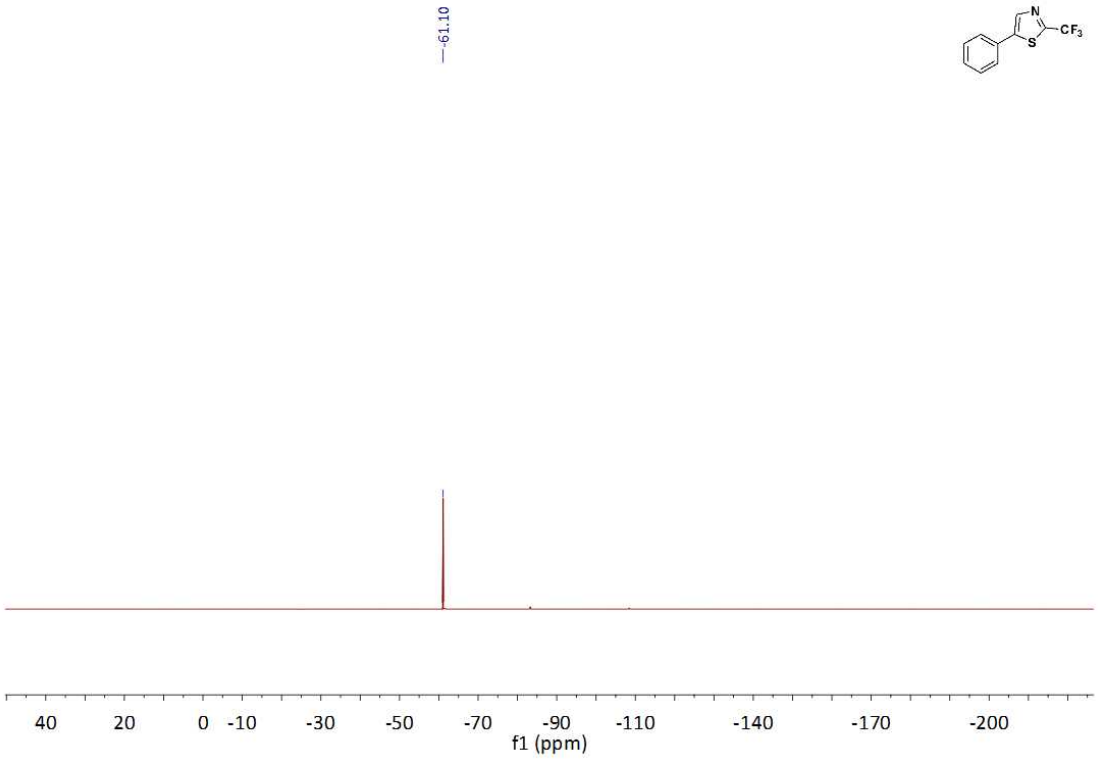
^{1}H NMR spectrum of 5-phenyl-2-(trifluoromethyl)thiazole (2x)



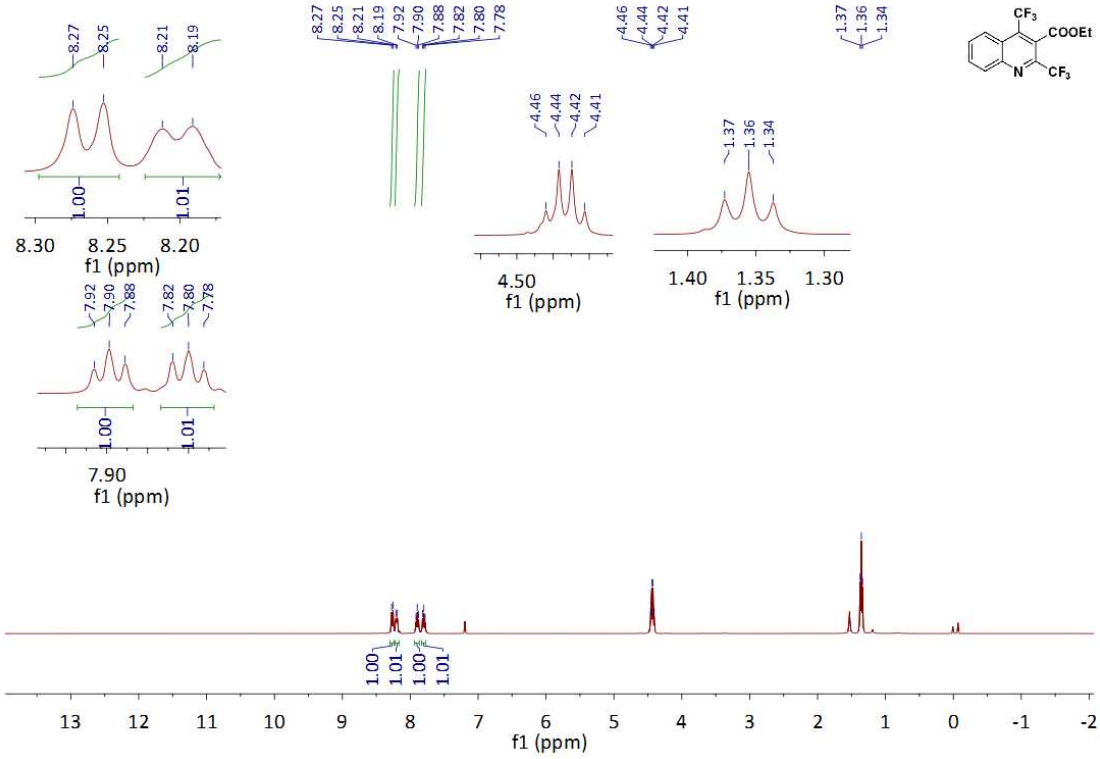
^{13}C NMR spectrum of 5-phenyl-2-(trifluoromethyl)thiazole (2x)



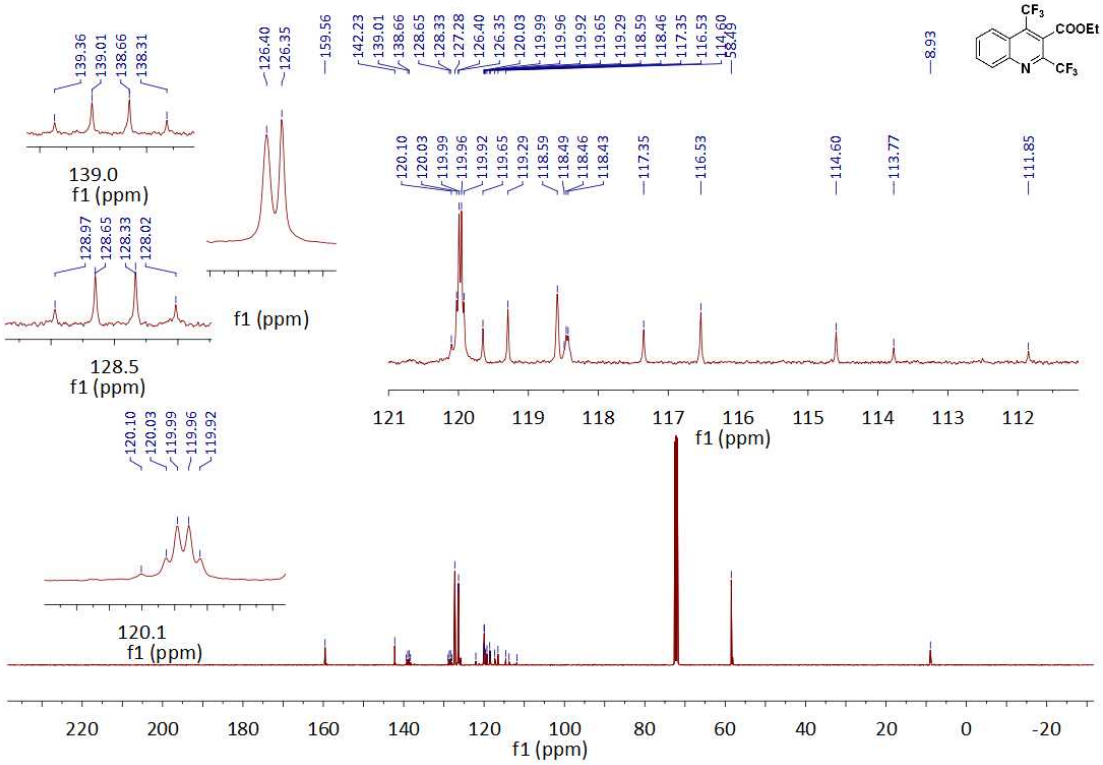
^{19}F NMR spectrum of 5-phenyl-2-(trifluoromethyl)thiazole (2x)



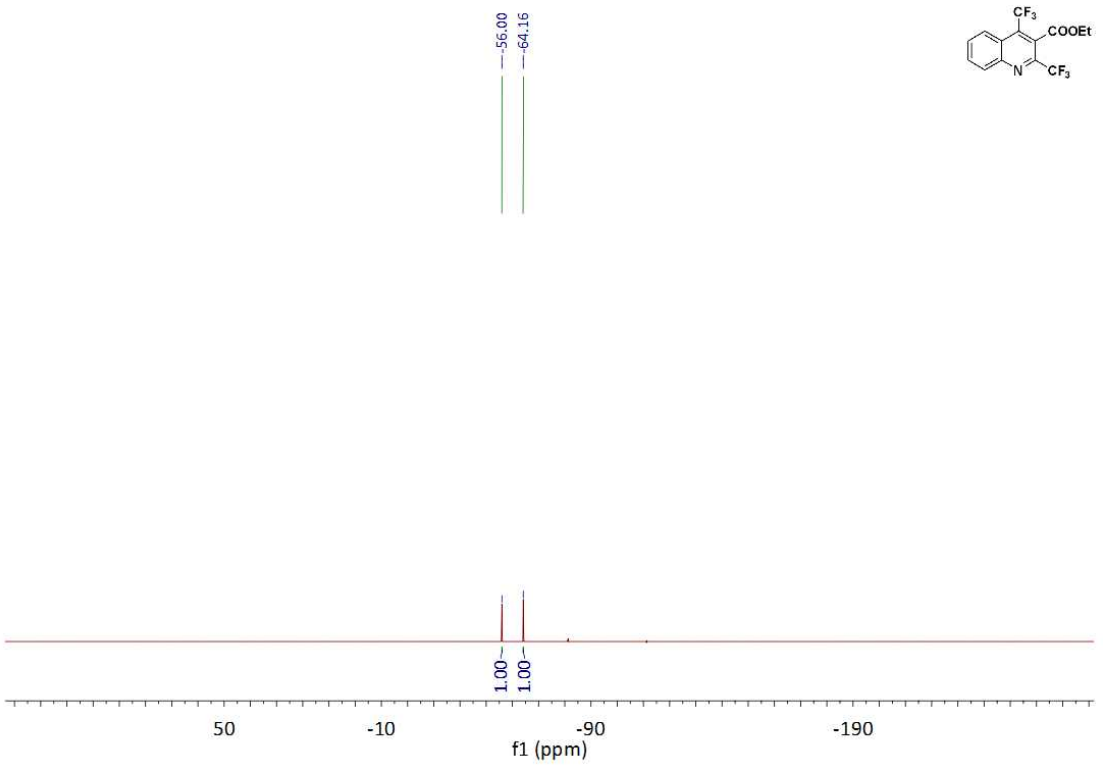
^{1}H NMR spectrum of ethyl 2,4-di-(trifluoromethyl)quinoline-3-carboxylate (2y)



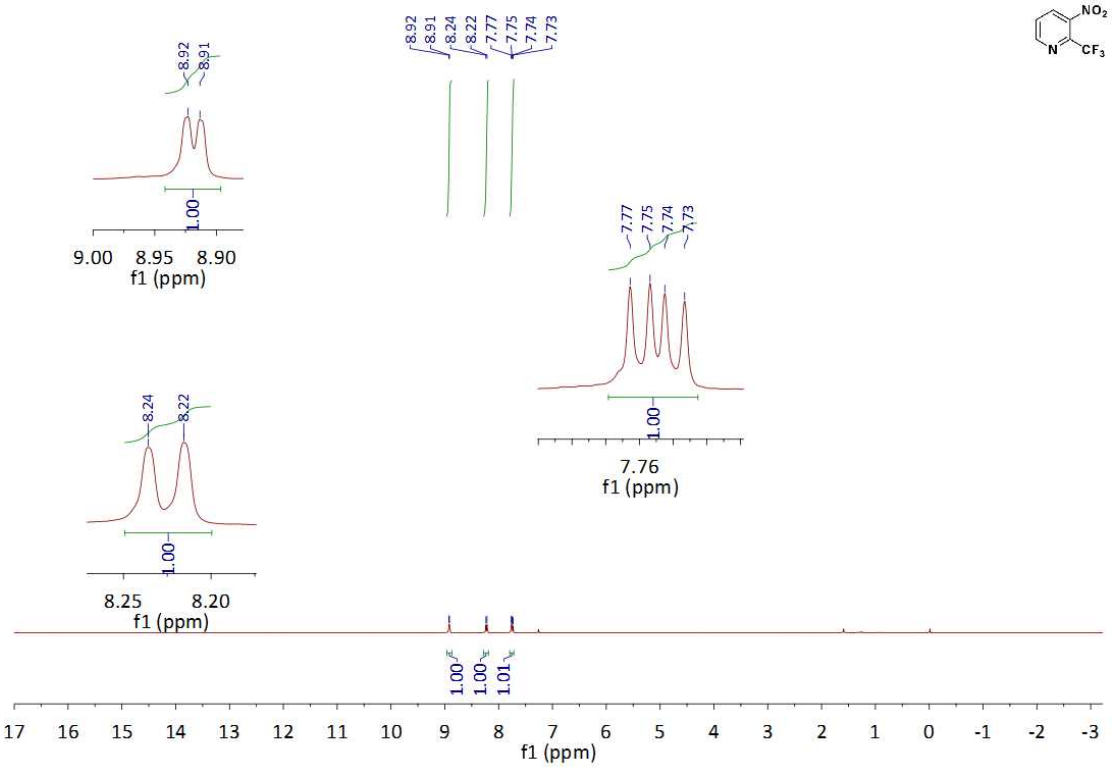
^{13}C NMR spectrum of ethyl 2,4-di-(trifluoromethyl)quinoline-3-carboxylate (2y)



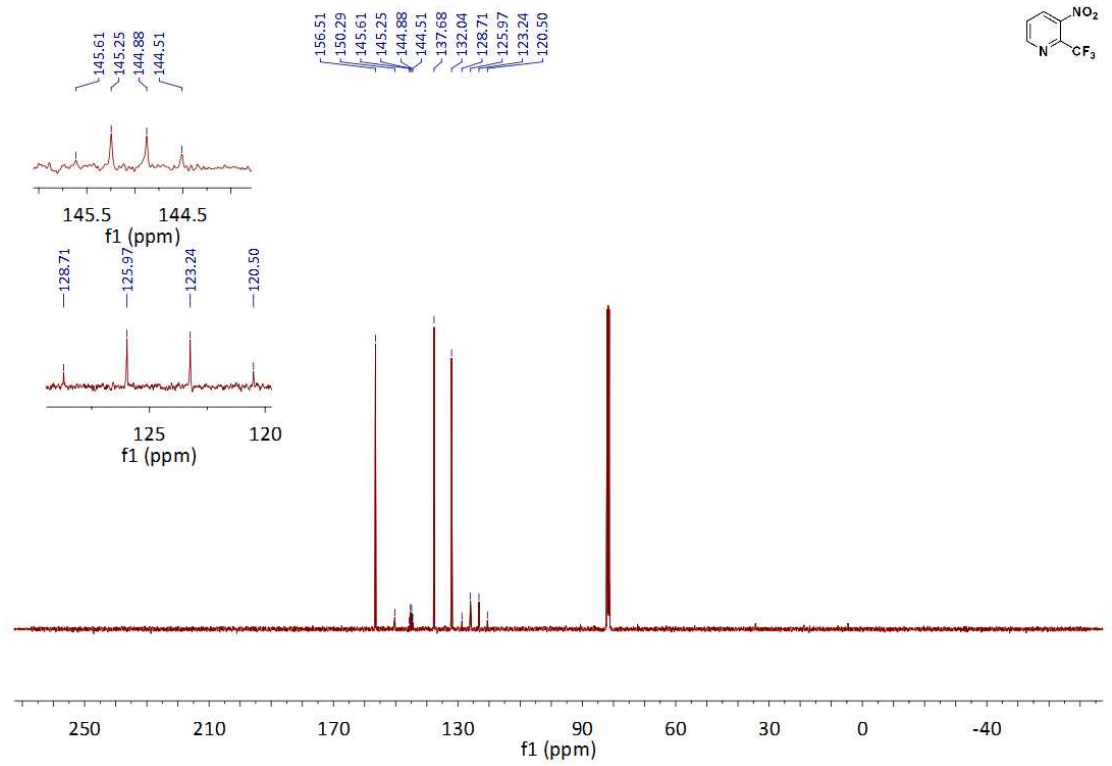
^{19}F NMR spectrum of ethyl 2,4-di-(trifluoromethyl)quinoline-3-carboxylate (2y)



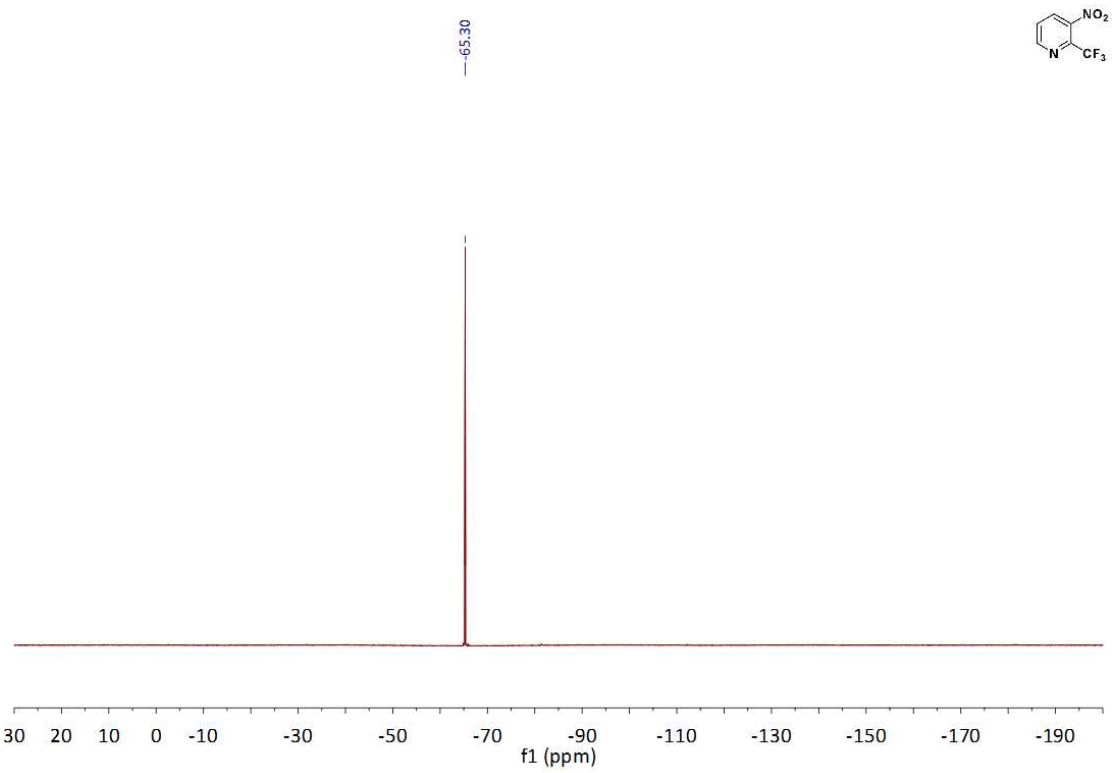
^{1}H NMR spectrum of 2-trifluoromethyl-3-nitro-pyridine (3a)



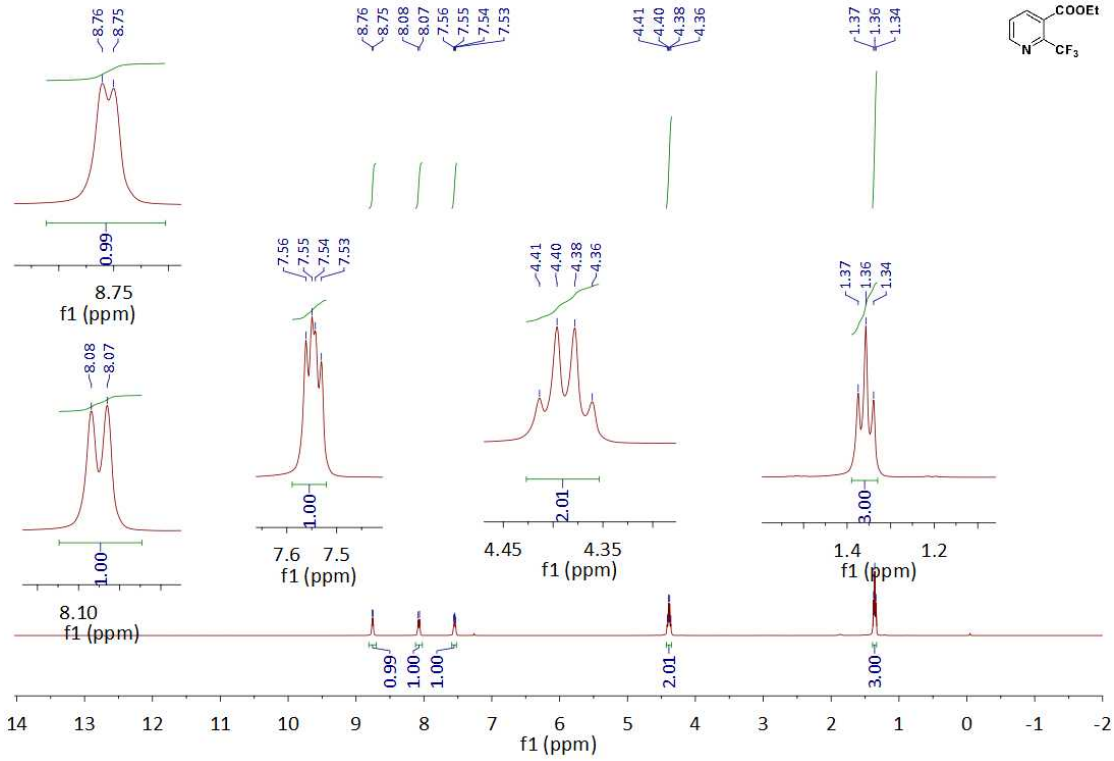
^{13}C NMR spectrum of 2-trifluoromethyl-3-nitro-pyridine (3a)



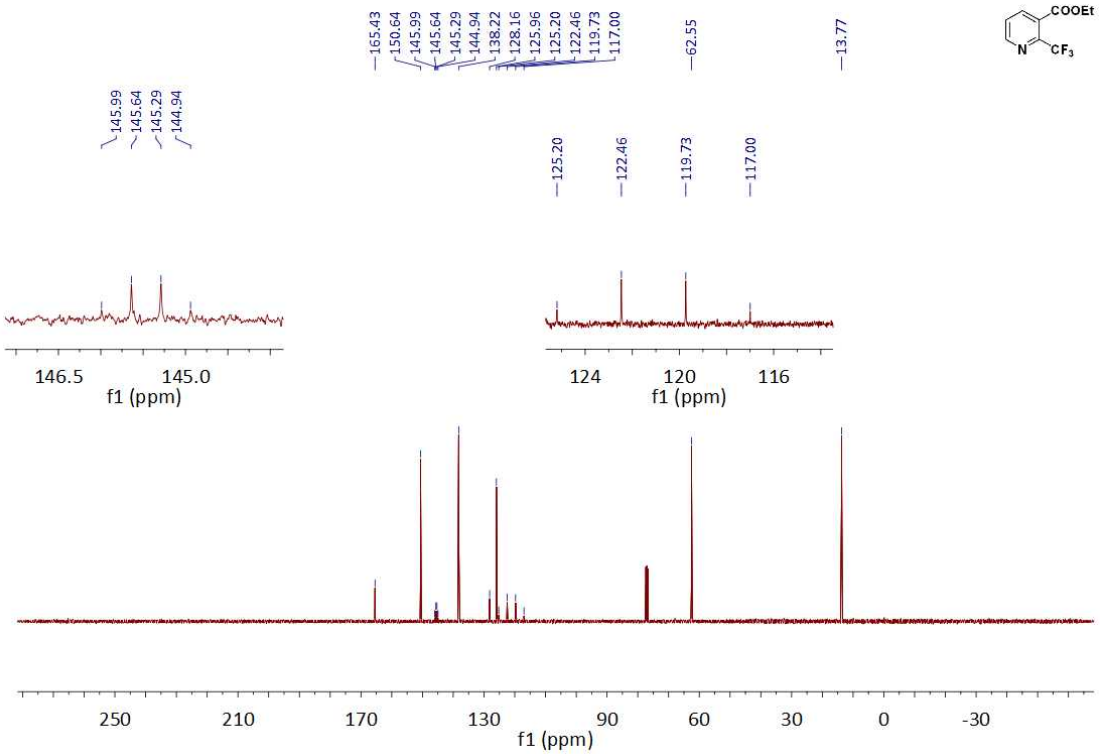
^{19}F NMR spectrum of 2-trifluoromethyl-3-nitro-pyridine (3a)



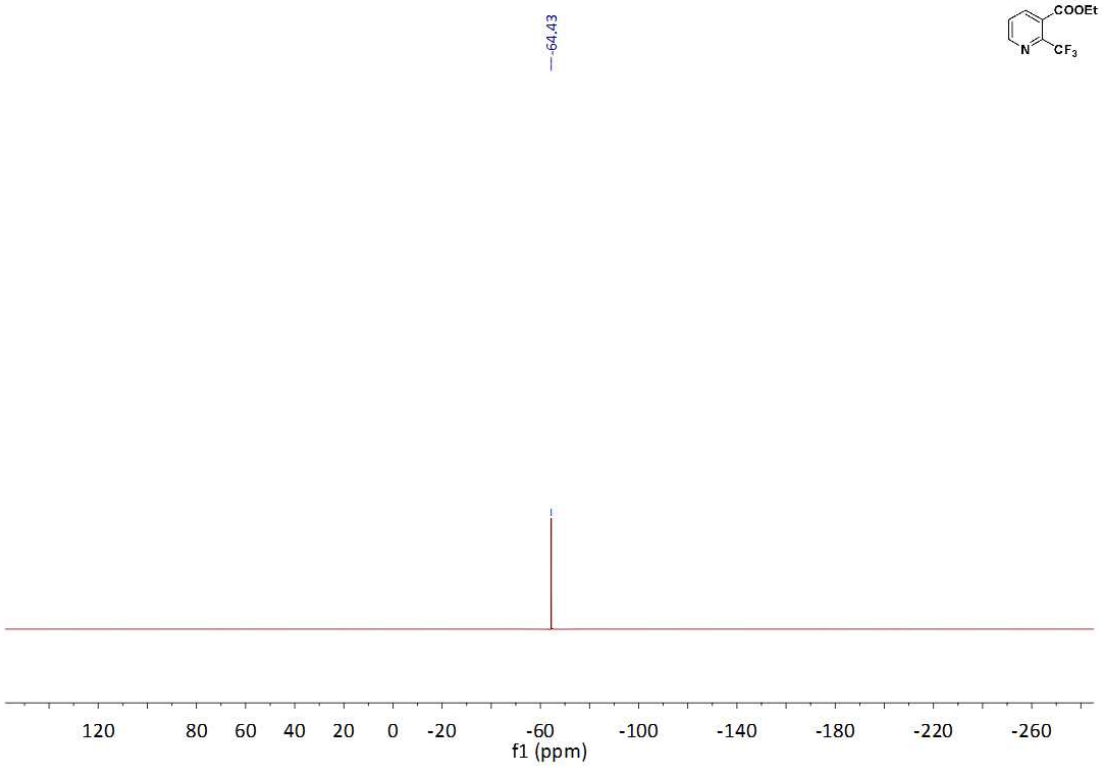
^{1}H NMR spectrum of ethyl 2-(trifluoromethyl)pyridine-3-carboxylate (3b)



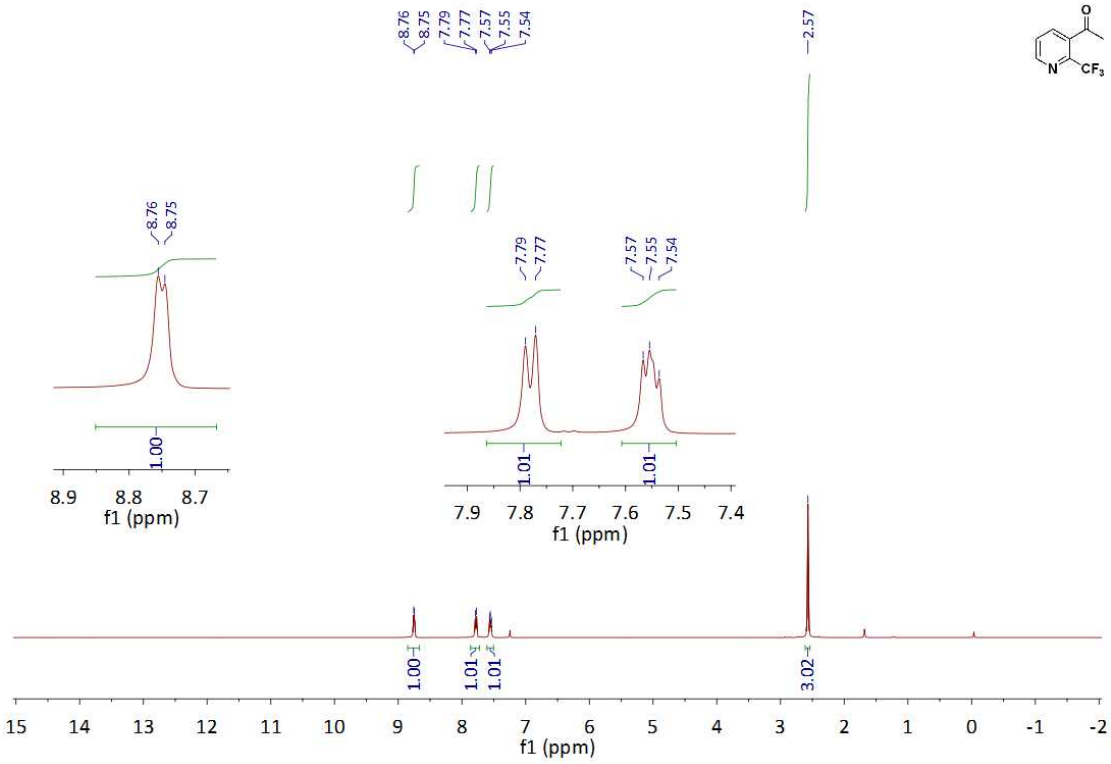
^{13}C NMR spectrum of ethyl 2-(trifluoromethyl)pyridine-3-carboxylate (3b)



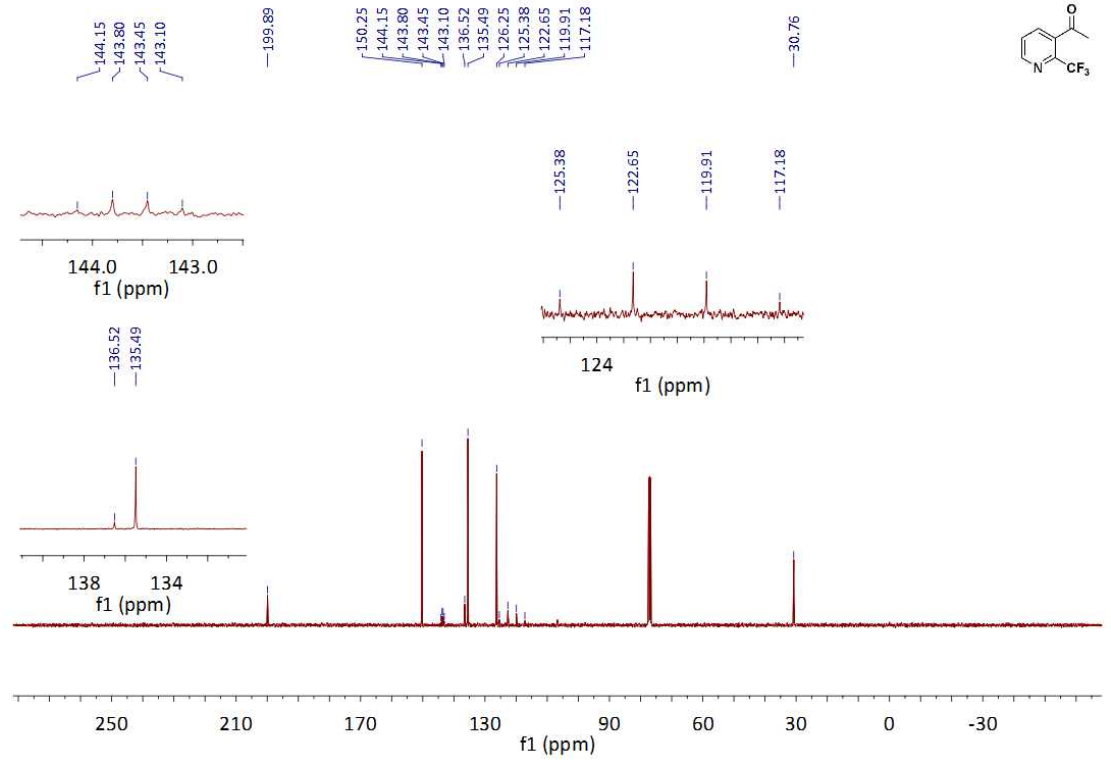
^{19}F NMR spectrum of ethyl 2-(trifluoromethyl)pyridine-3-carboxylate (3b)



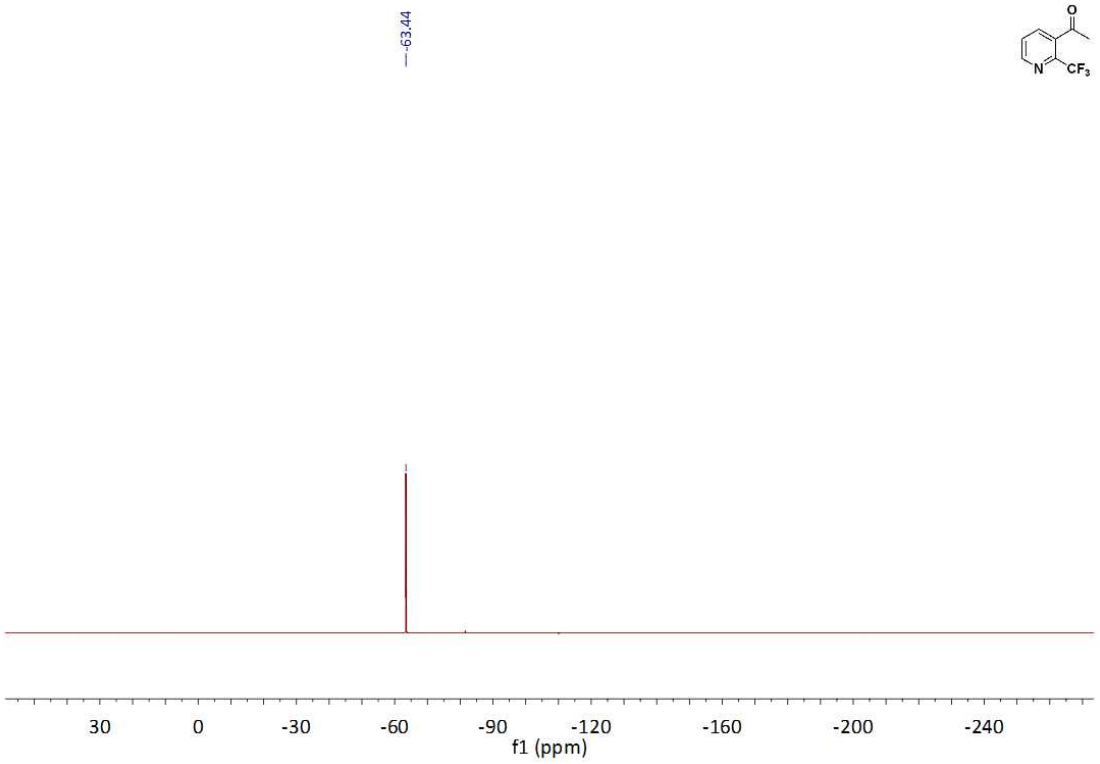
^{1}H NMR spectrum of 1-[2-(trifluoromethyl)-3-pyridyl]ethanone (3c)



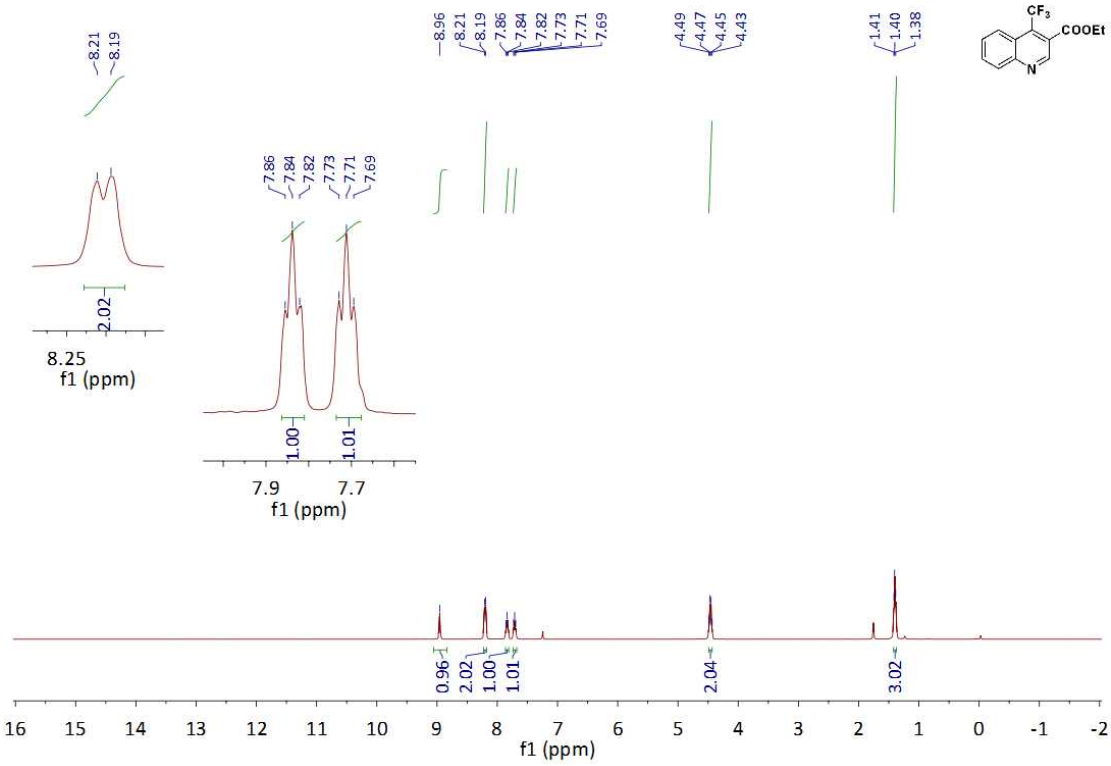
^{13}C NMR spectrum of 1-[2-(trifluoromethyl)-3-pyridyl]ethanone (3c)



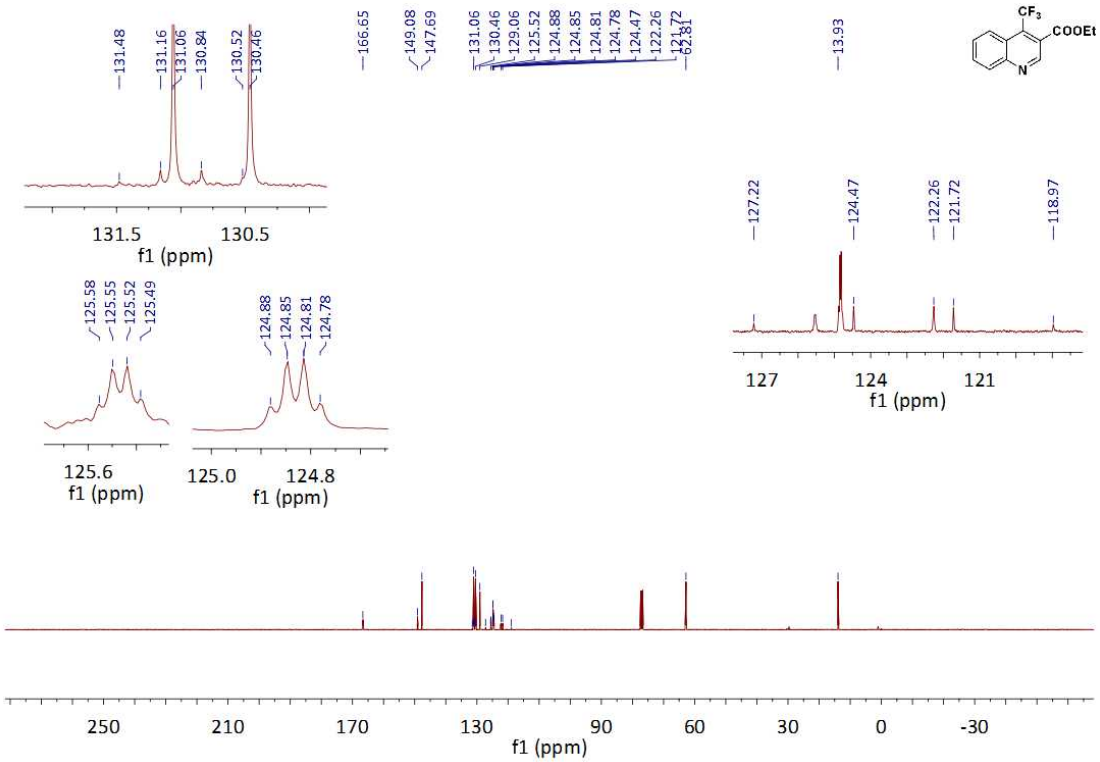
^{19}F NMR spectrum of 1-[2-(trifluoromethyl)-3-pyridyl]ethanone (3c)



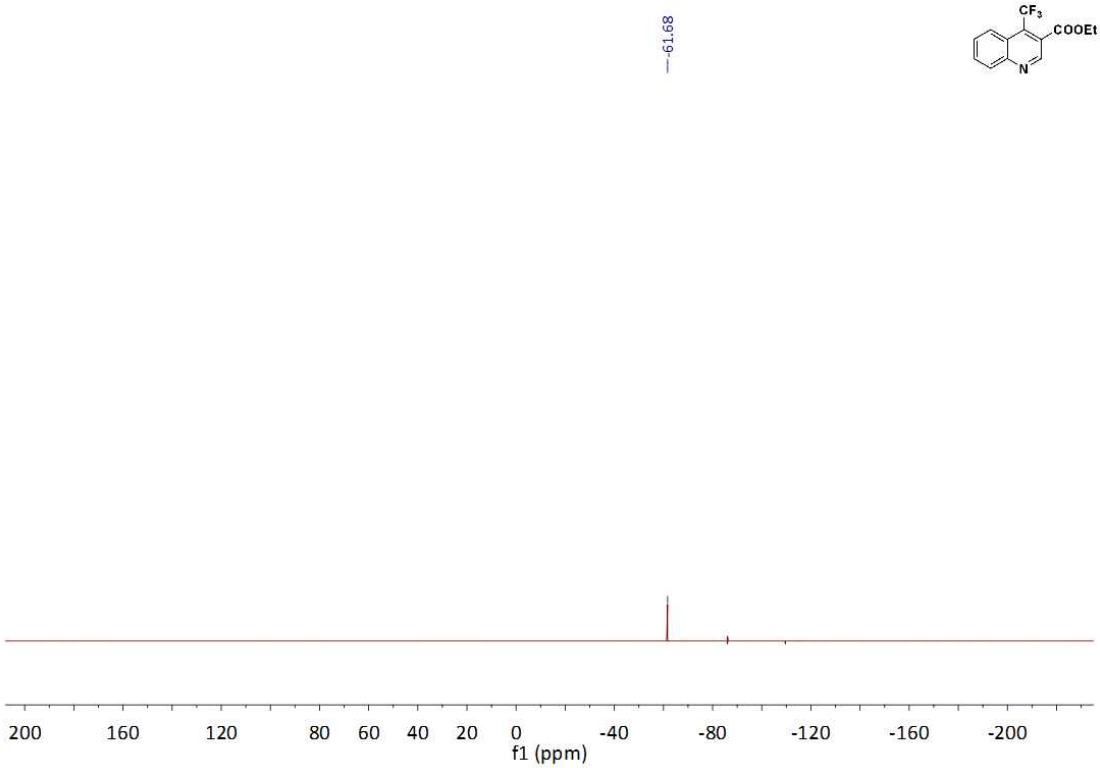
^{1}H NMR spectrum of ethyl 4-trifluoromethylquinoline-3-carboxylate (3d)



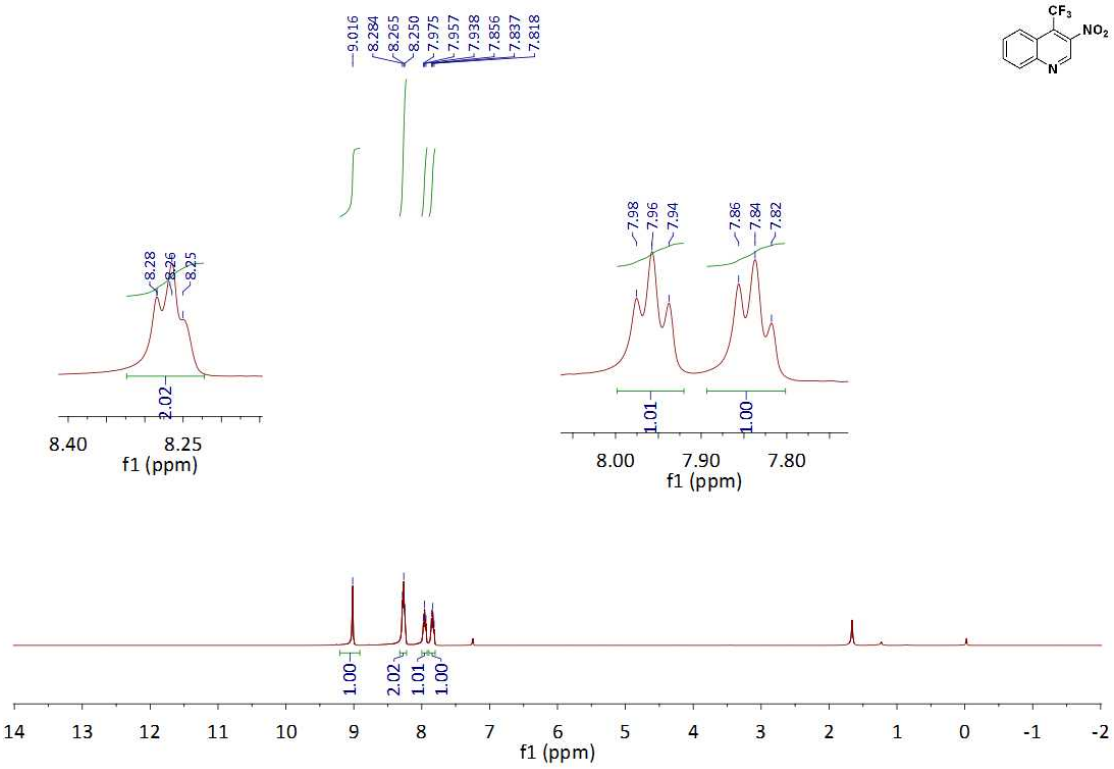
^{13}C NMR spectrum of ethyl 4-trifluoromethylquinoline-3-carboxylate (3d)



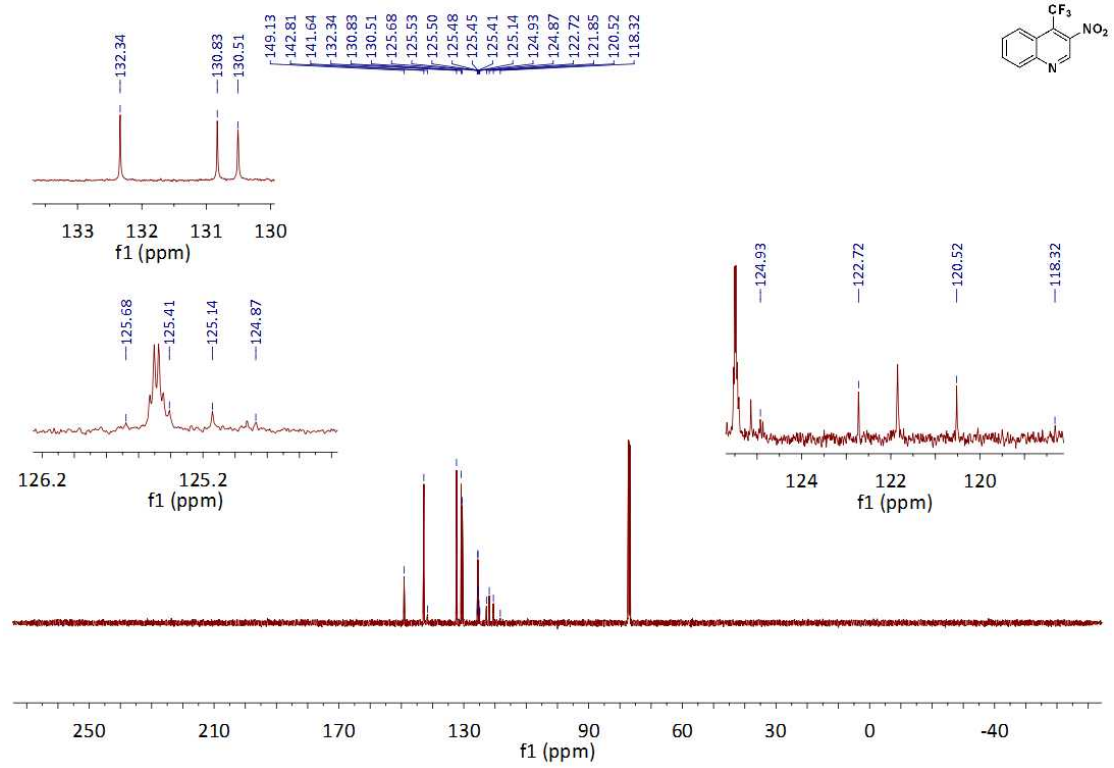
^{19}F NMR spectrum of ethyl 4-trifluoromethylquinoline-3-carboxylate (3d)



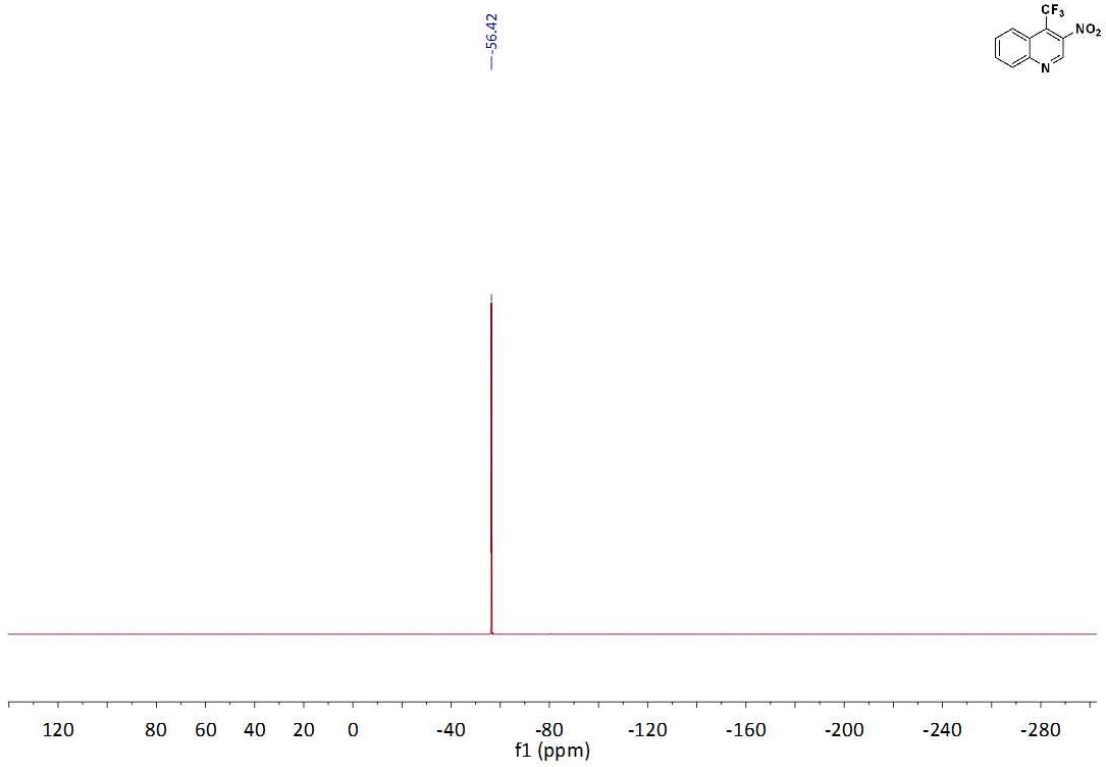
^{1}H NMR spectrum of 3-nitro-4-(trifluoromethyl)quinoline (3e)



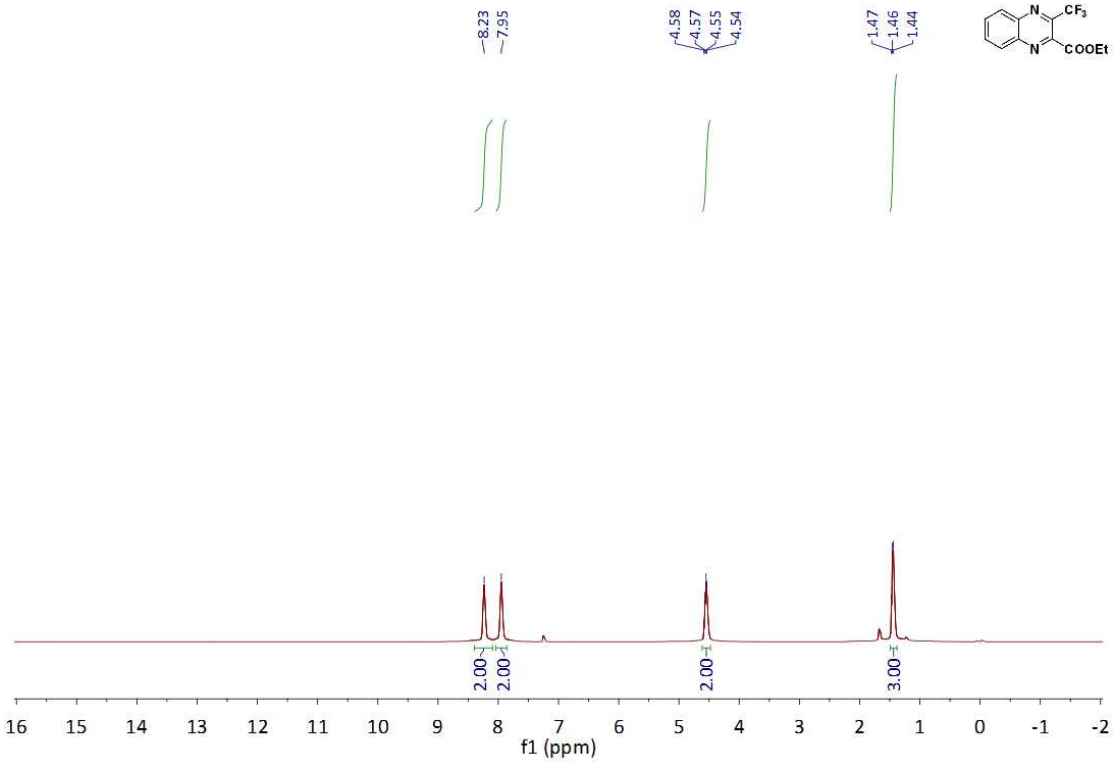
^{13}C NMR spectrum of 3-nitro-4-(trifluoromethyl)quinoline (3e)



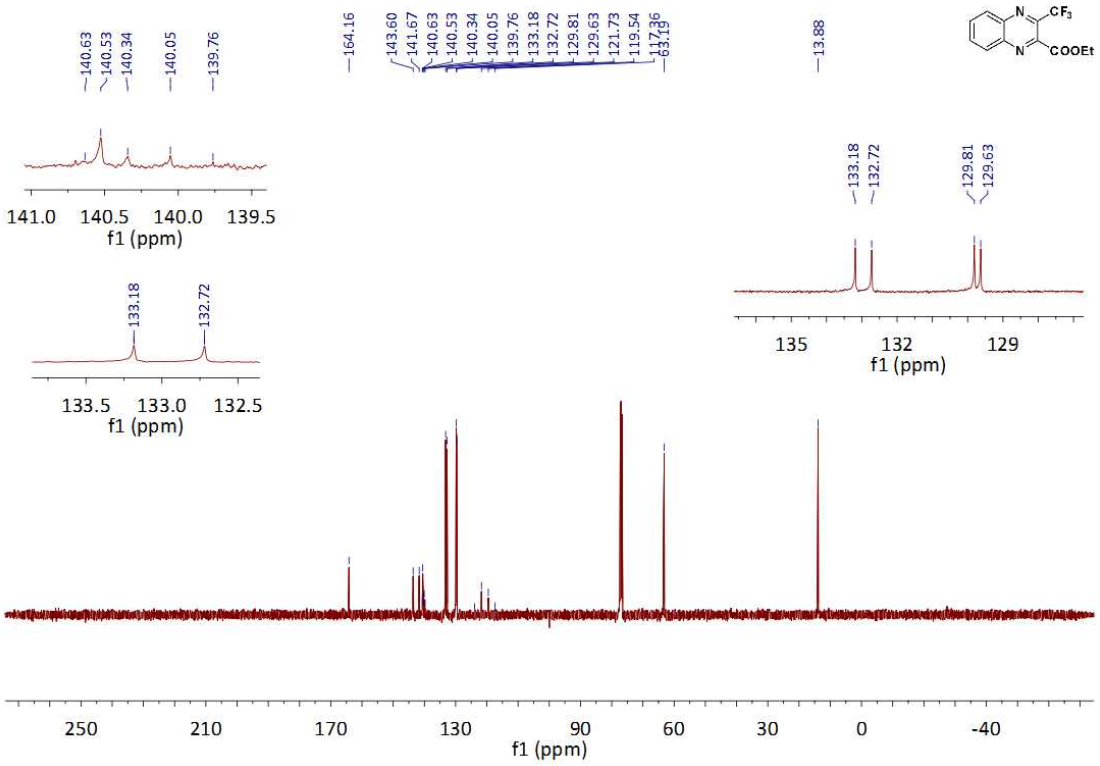
^{19}F NMR spectrum of 3-nitro-4-(trifluoromethyl)quinoline (3e)



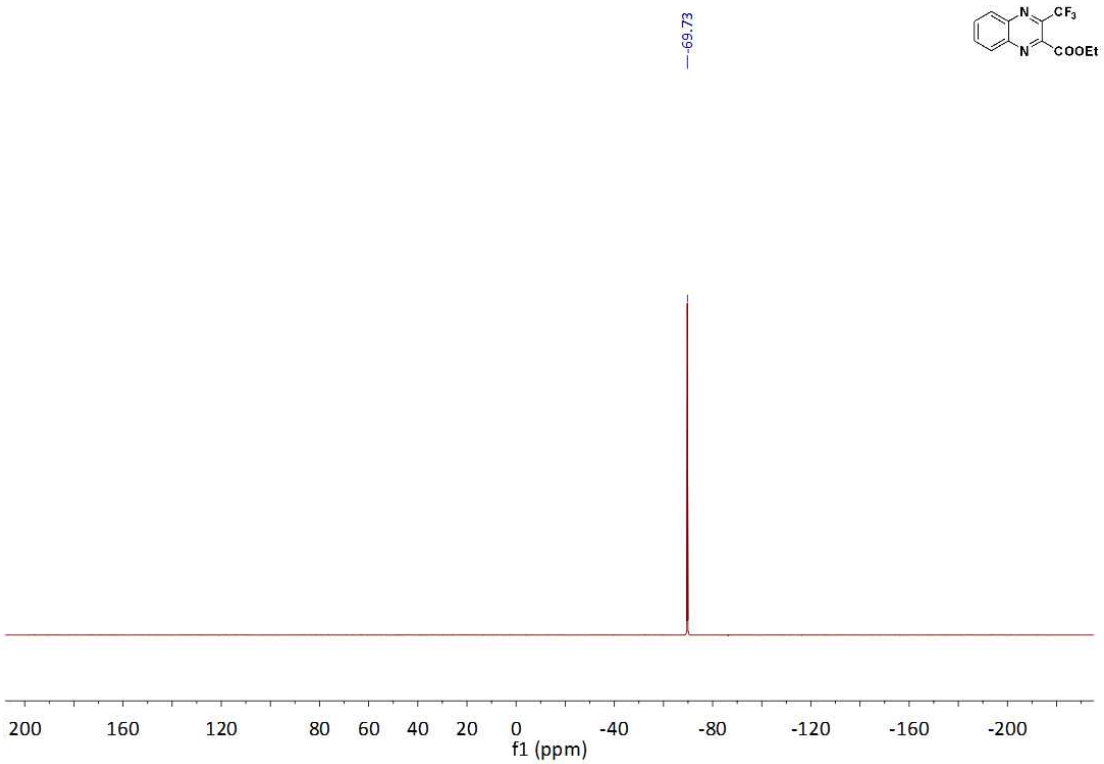
^{1}H NMR spectrum of ethyl 3-trifluoromethyquinoxaline-2-carboxylate (3f)



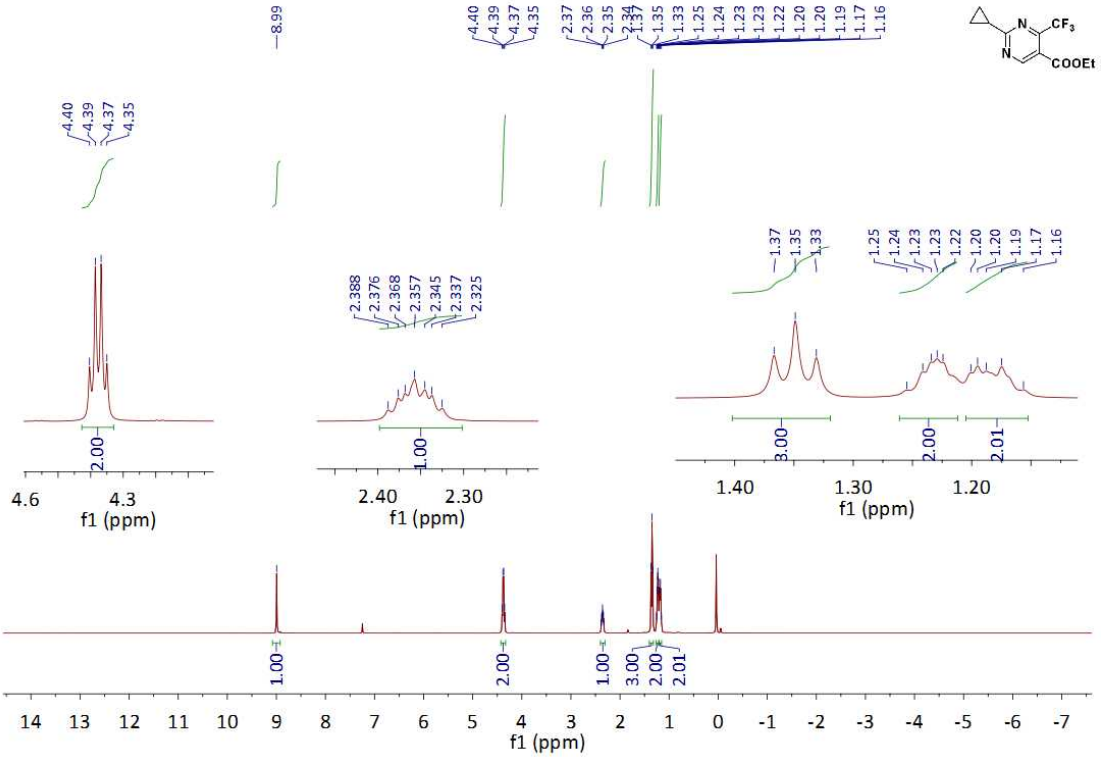
^{13}C NMR spectrum of ethyl 3-trifluoromethyquinoxaline-2-carboxylate (3f)



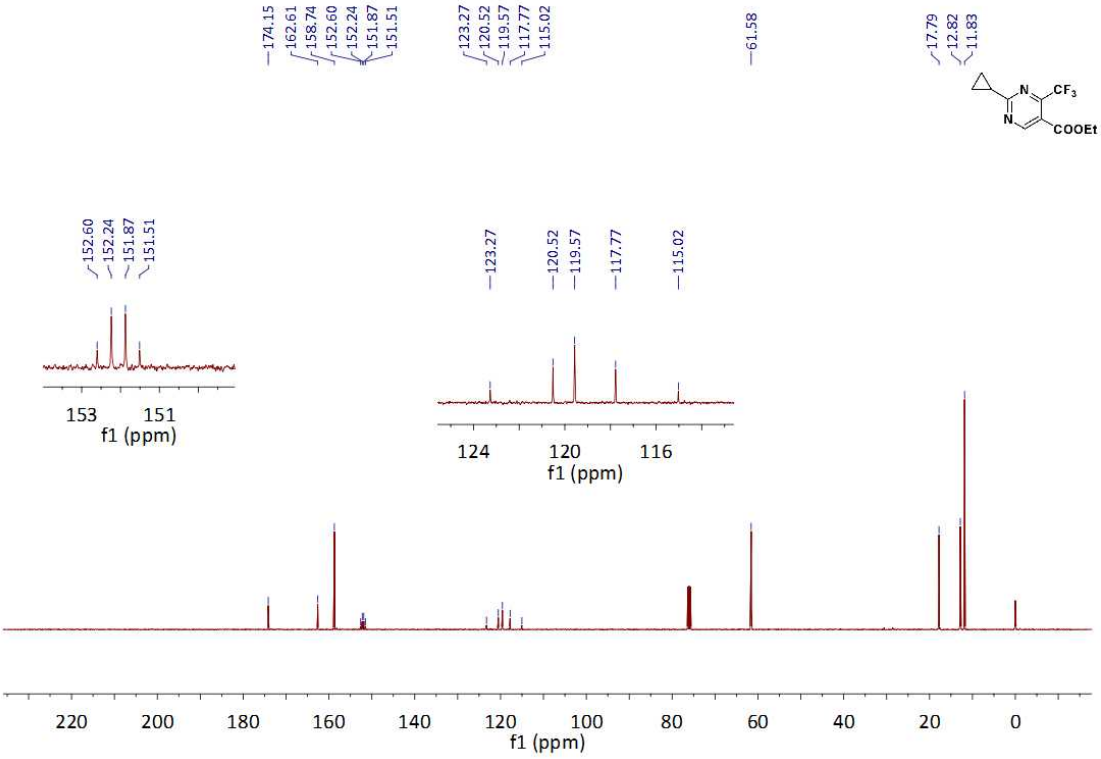
^{19}F NMR spectrum of ethyl 3-trifluoromethyquinoxaline-2-carboxylate (3f)



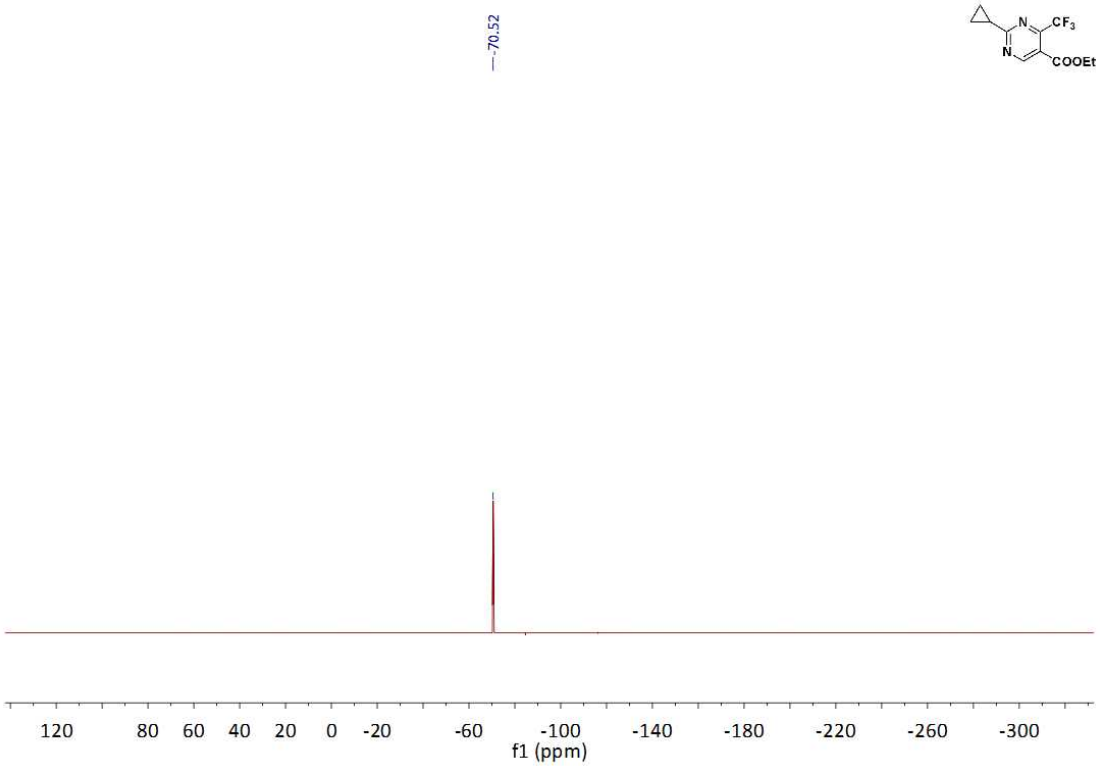
^{1}H NMR spectrum of
ethyl 2-cyclopropyl-4-(trifluoromethyl)pyrimidine-5-carboxylate (3g)



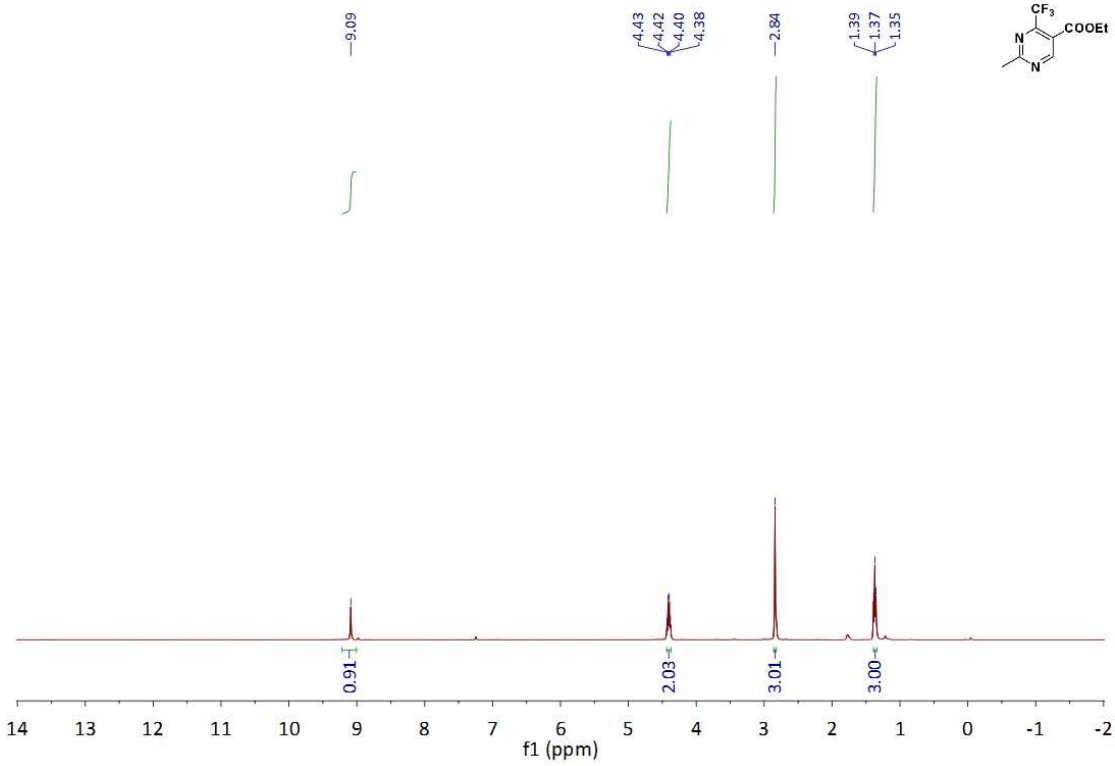
^{13}C NMR spectrum of
ethyl 2-cyclopropyl-4-(trifluoromethyl)pyrimidine-5-carboxylate (3g)



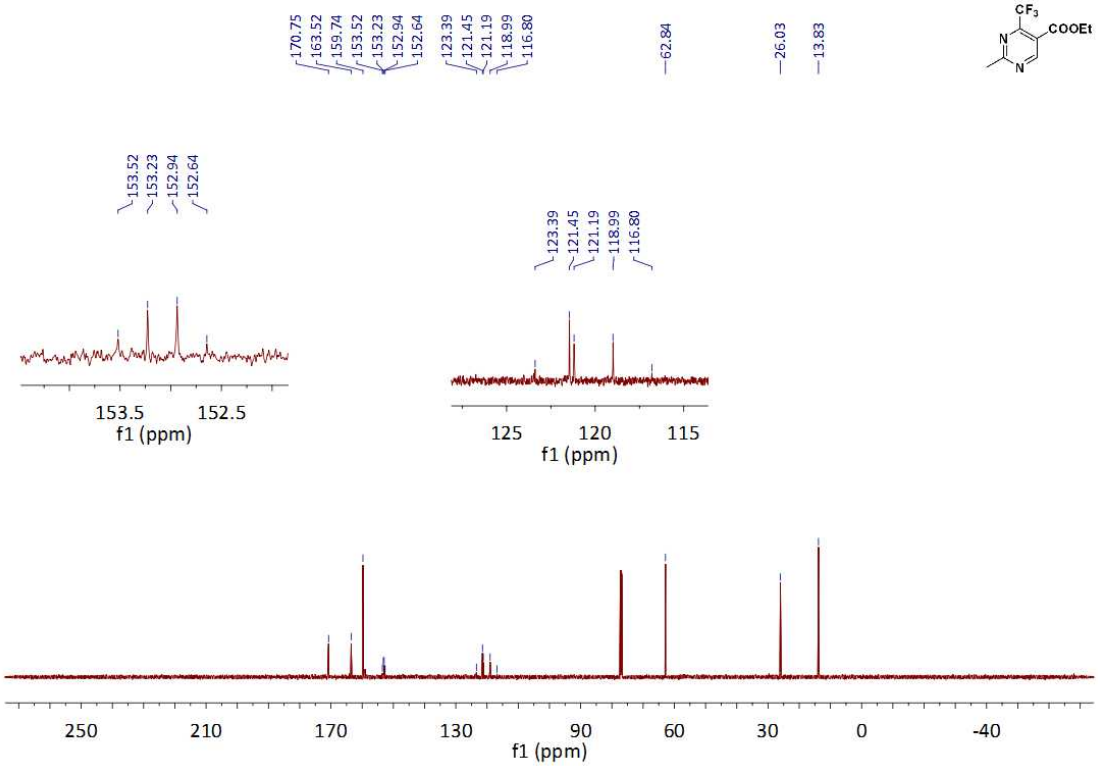
^{19}F NMR spectrum of
ethyl 2-cyclopropyl-4-(trifluoromethyl)pyrimidine-5-carboxylate (3g)



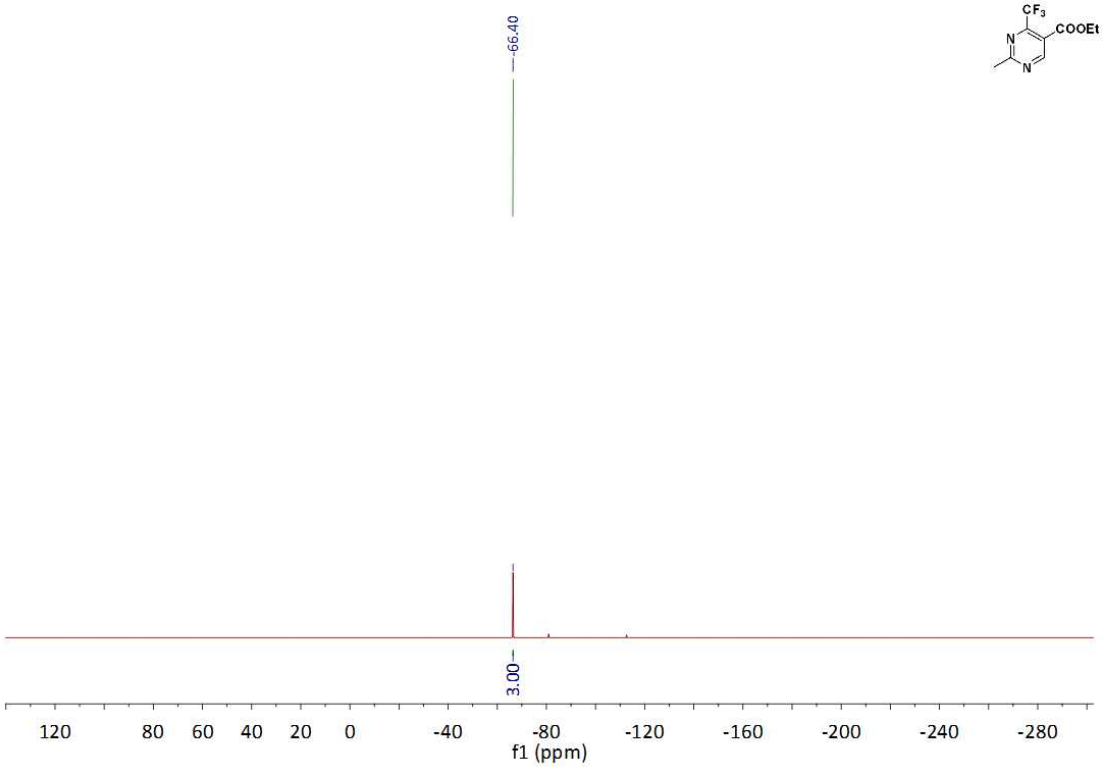
^{1}H NMR spectrum of
ethyl 2-methyl-4-trifluoromethylpyrimidine-5-carboxylate (3h)



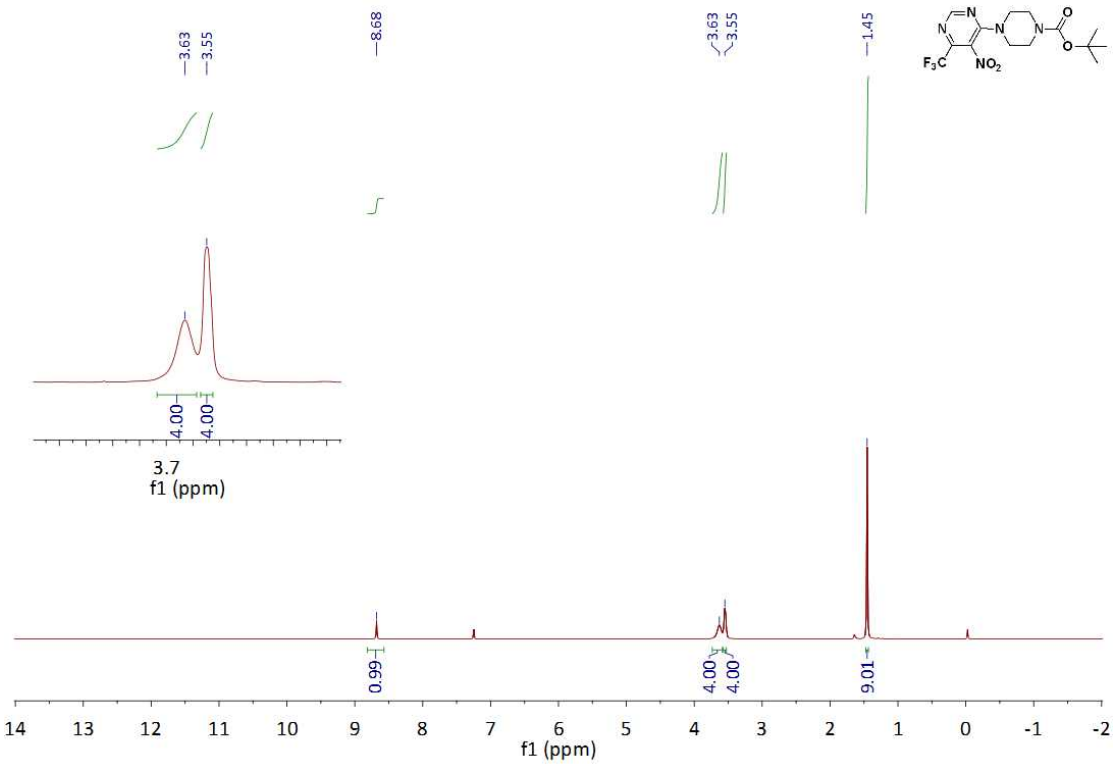
^{13}C NMR spectrum of ethyl 2-methyl-4-trifluoromethylpyrimidine-5-carboxylate (3h)



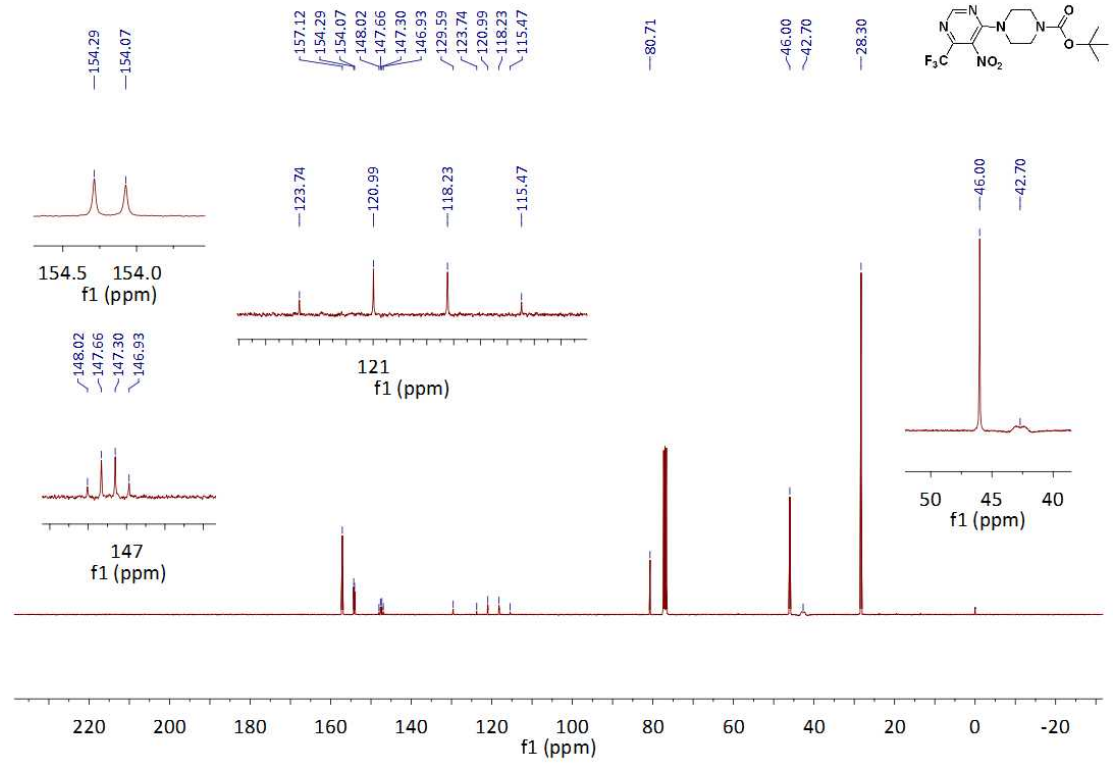
^{19}F NMR spectrum of ethyl 2-methyl-4-trifluoromethylpyrimidine-5-carboxylate (3h)



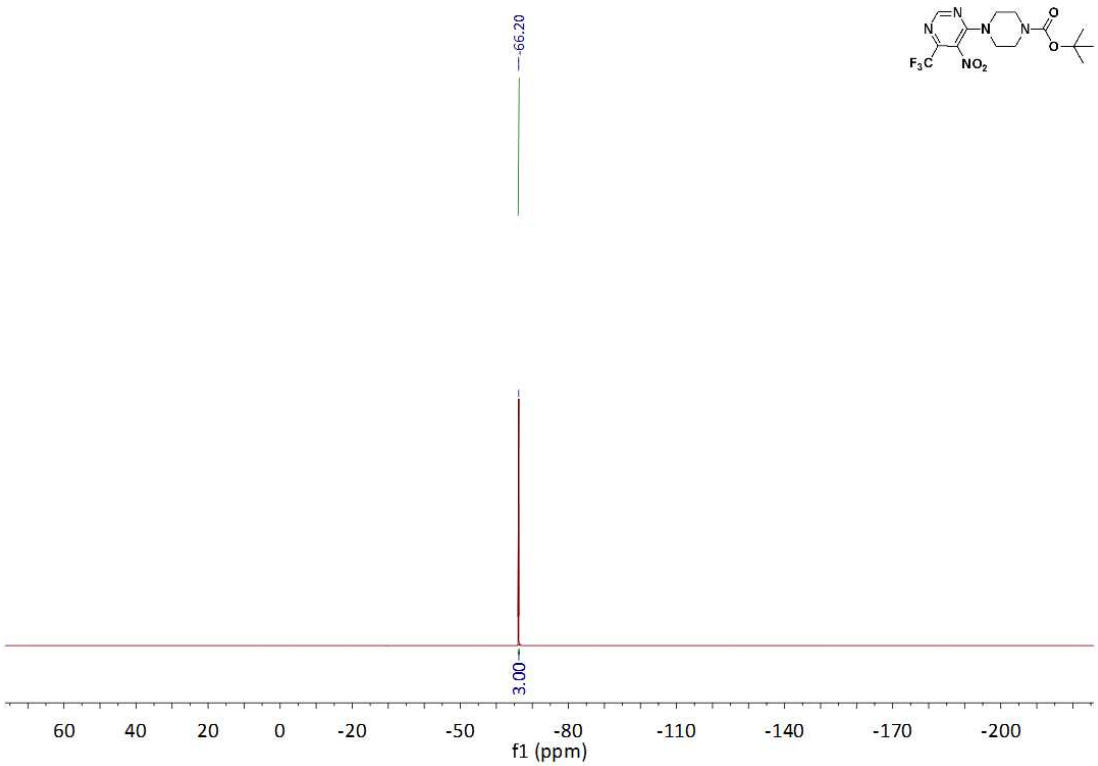
^{1}H NMR spectrum of *tert*-butyl 4-[5-nitro-6-(trifluoromethyl)pyrimidin-4-yl]piperazine-1-carboxylate (3i)



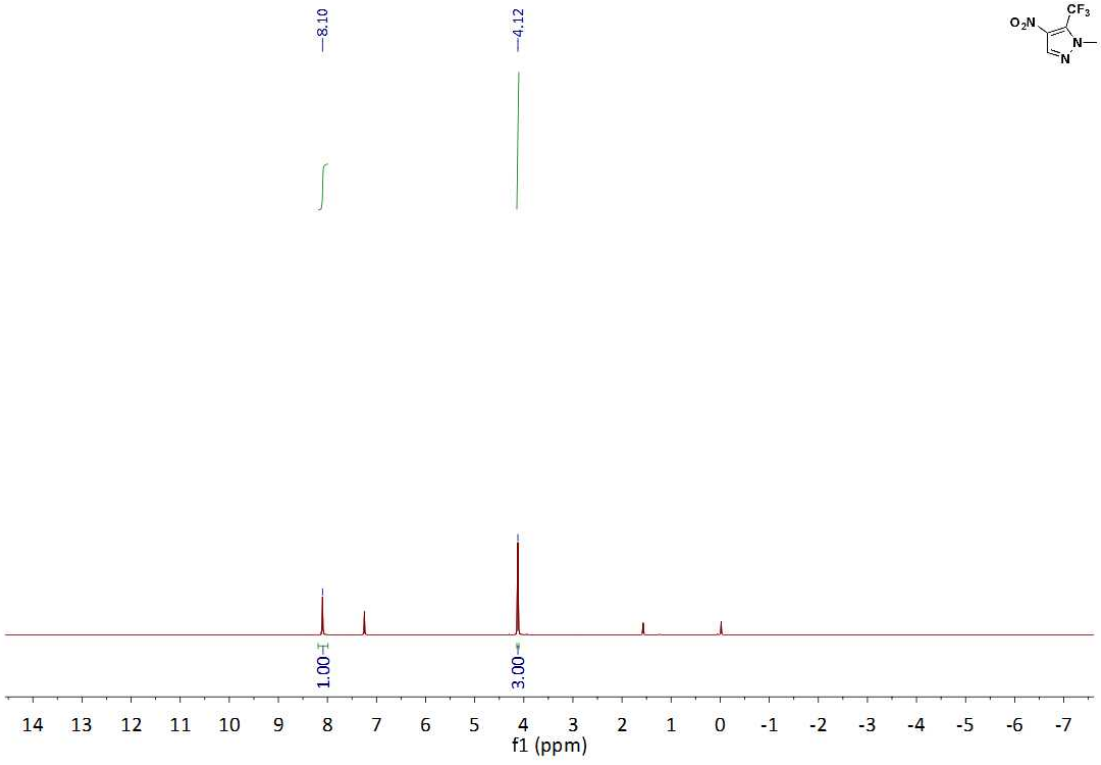
^{13}C NMR spectrum of *tert*-butyl 4-[5-nitro-6-(trifluoromethyl)pyrimidin-4-yl]piperazine-1-carboxylate (3i)



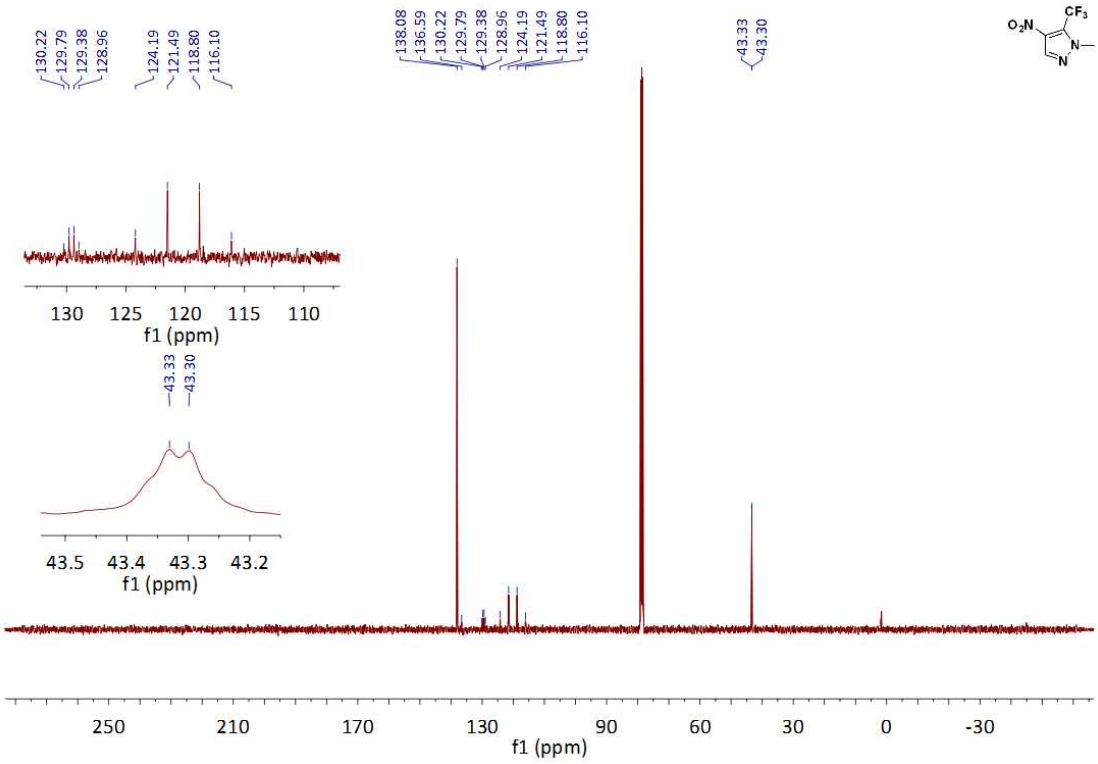
^{19}F NMR spectrum of *tert*-butyl 4-[5-nitro-6-(trifluoromethyl)pyrimidin-4-yl]piperazine-1-carboxylate (3i)



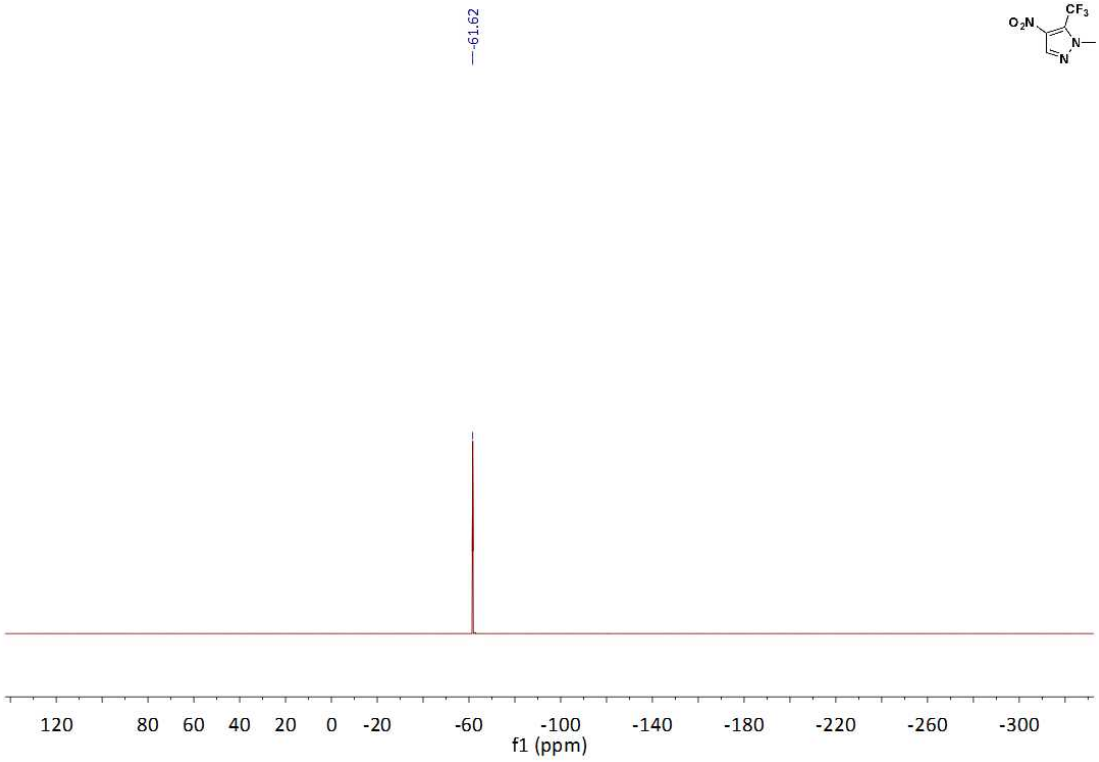
^{1}H NMR spectrum of 1-methyl-4-nitro-5-(trifluoromethyl)pyrazole (3j)



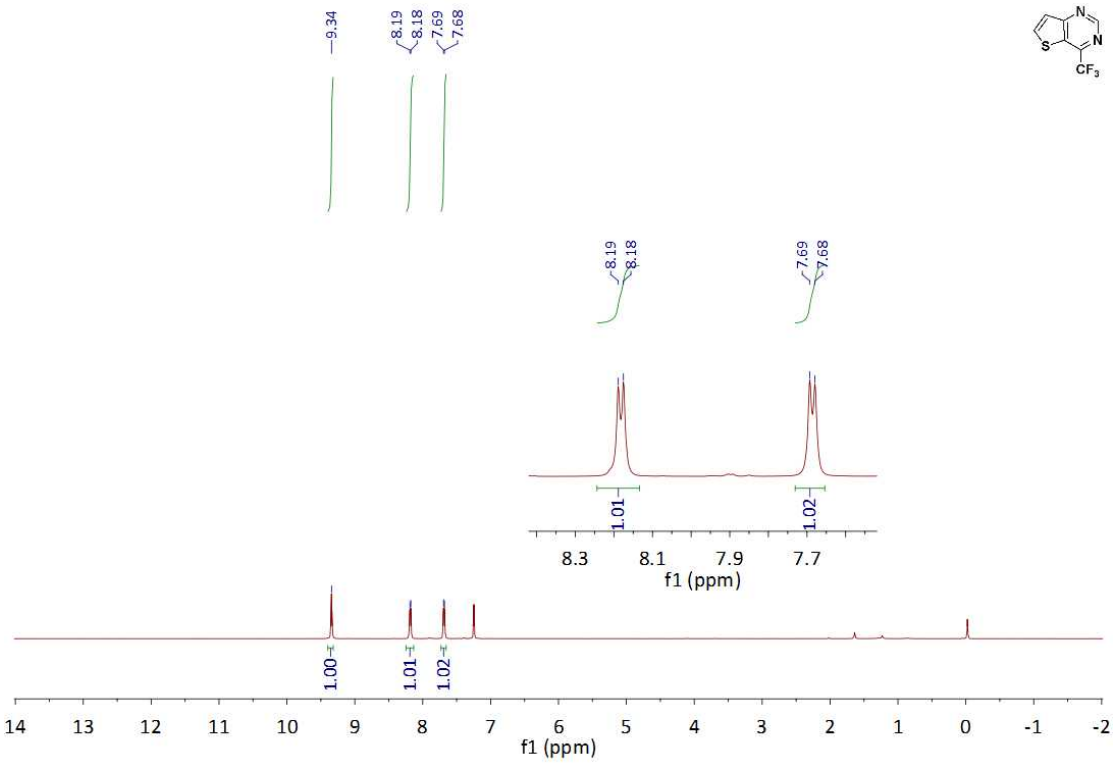
^{13}C NMR spectrum of 1-methyl-4-nitro-5-(trifluoromethyl)pyrazole (3j)



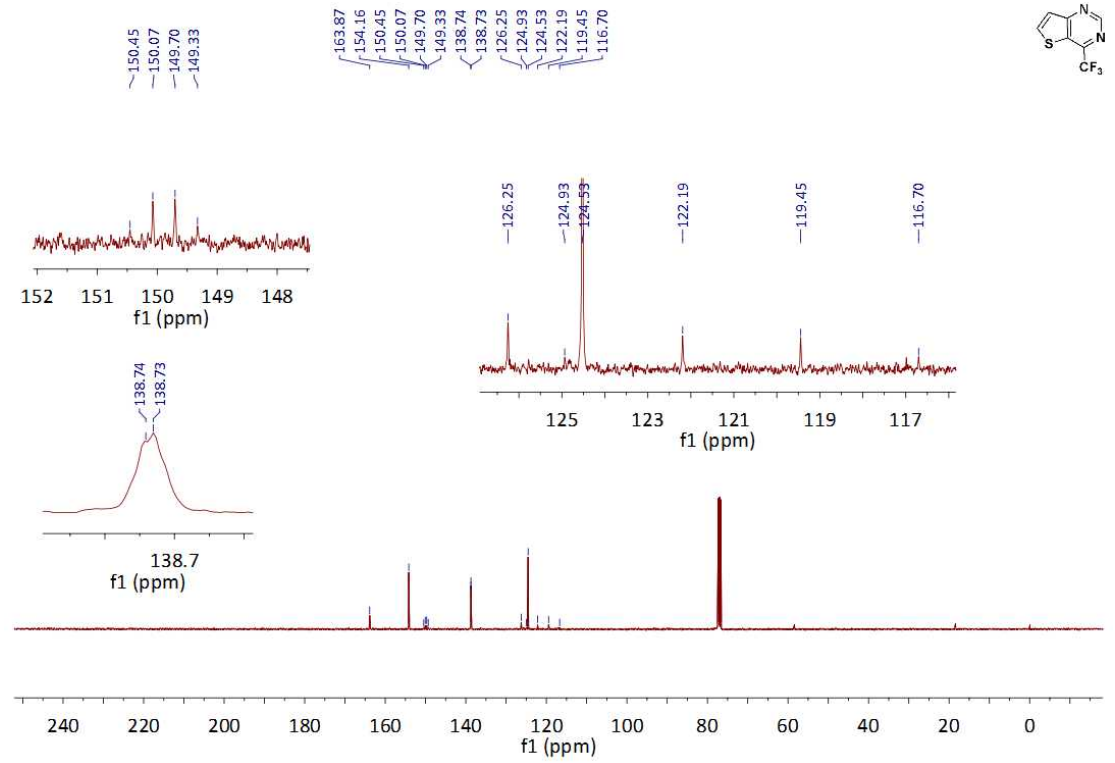
^{19}F NMR spectrum of 1-methyl-4-nitro-5-(trifluoromethyl)pyrazole (3j)



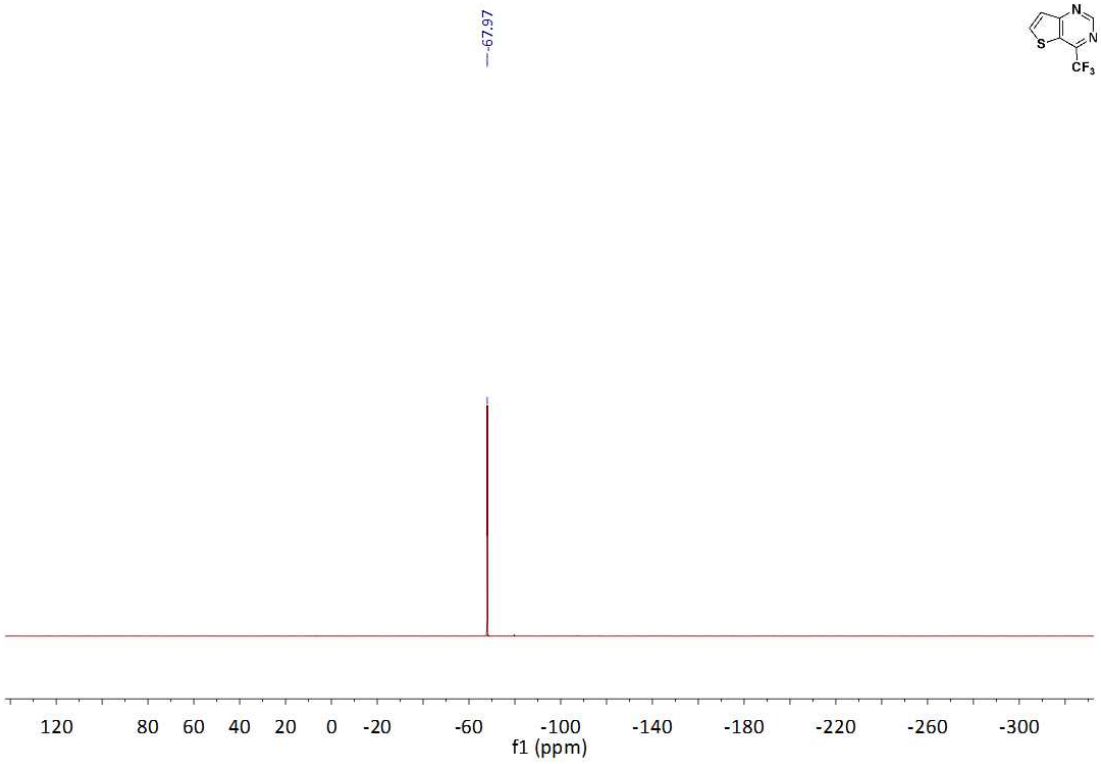
^{1}H NMR spectrum of 4-(trifluoromethyl)thieno[3,2-d]pyrimidine (3k)



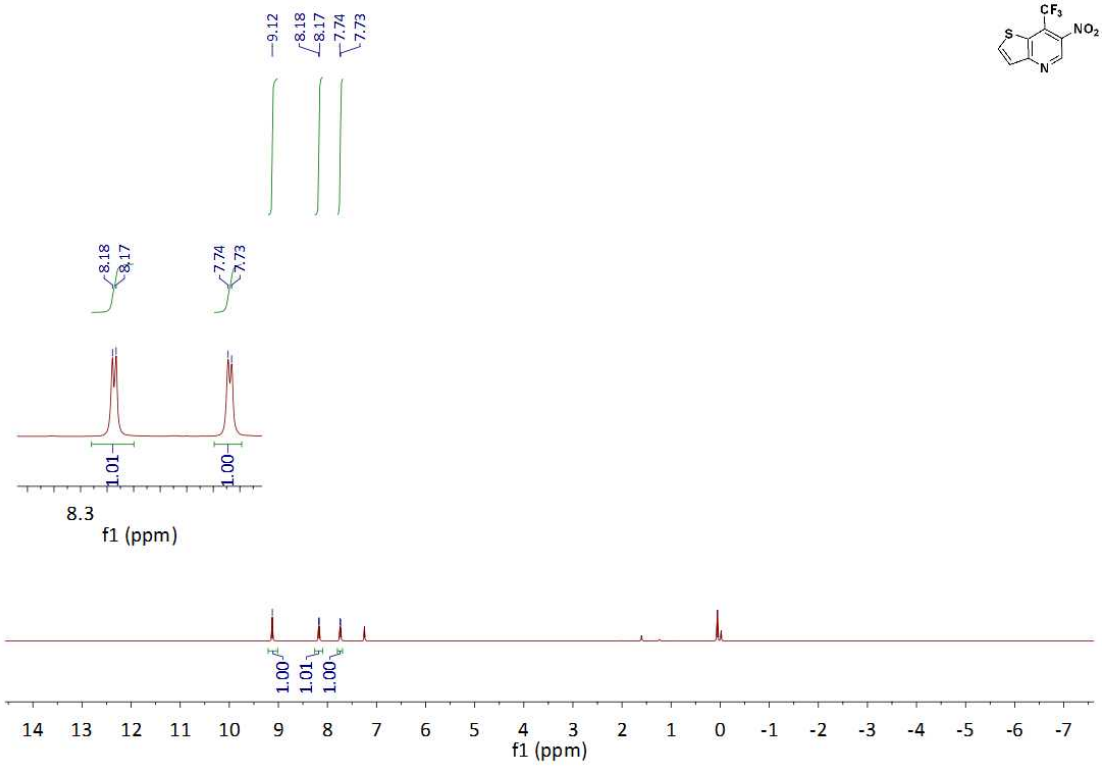
^{13}C NMR spectrum of 4-(trifluoromethyl)thieno[3,2-d]pyrimidine (3k)



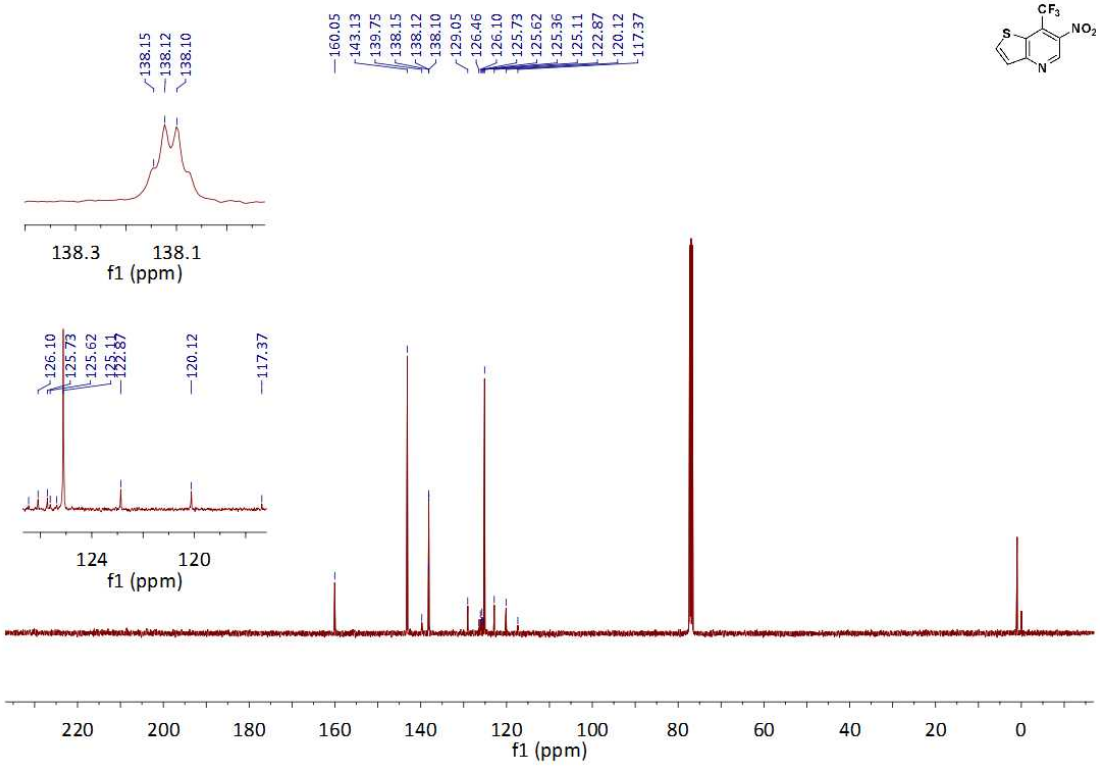
^{19}F NMR spectrum of 4-(trifluoromethyl)thieno[3,2-d]pyrimidine (3k)



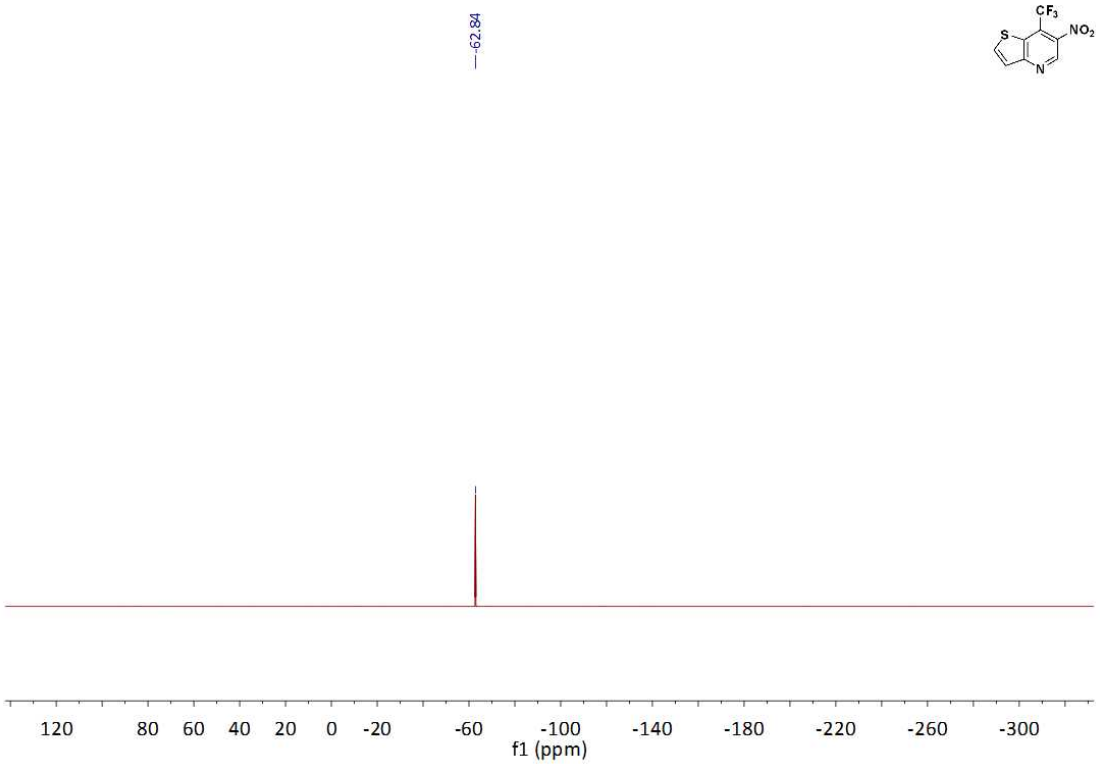
^{1}H NMR spectrum of 6-nitro-7-(trifluoromethyl)thieno[3,2-b]pyridine (3l)



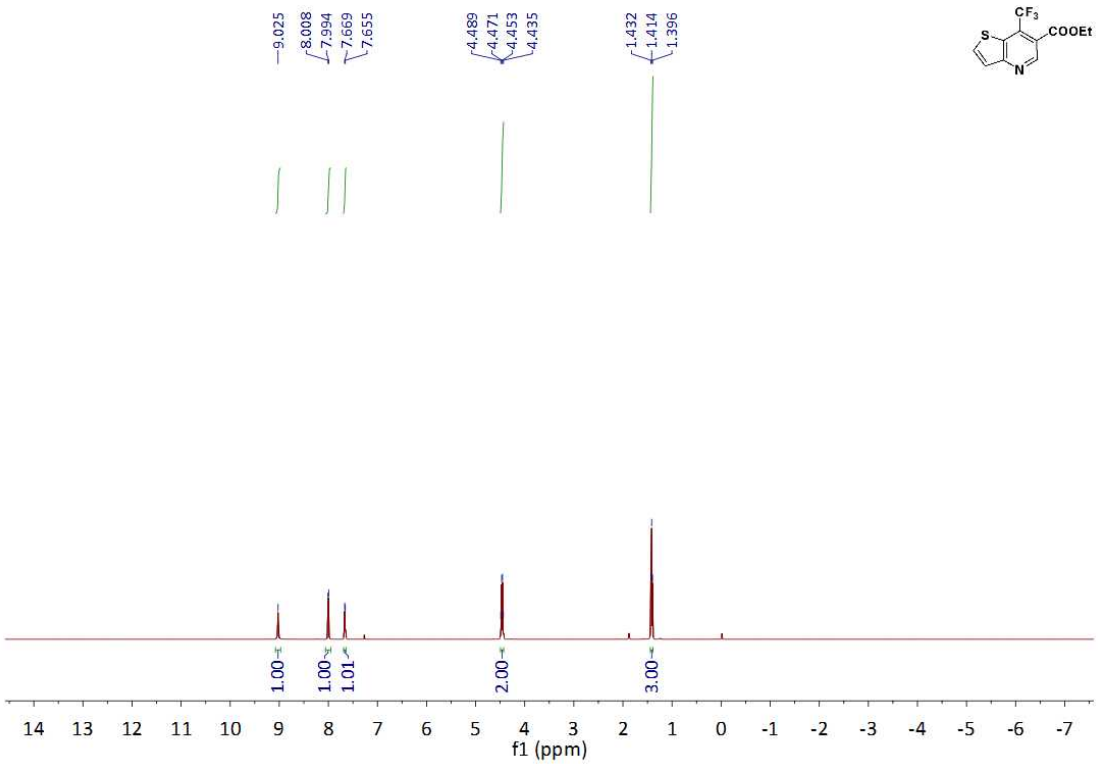
^{13}C NMR spectrum of 6-nitro-7-(trifluoromethyl)thieno[3,2-b]pyridine (3l)



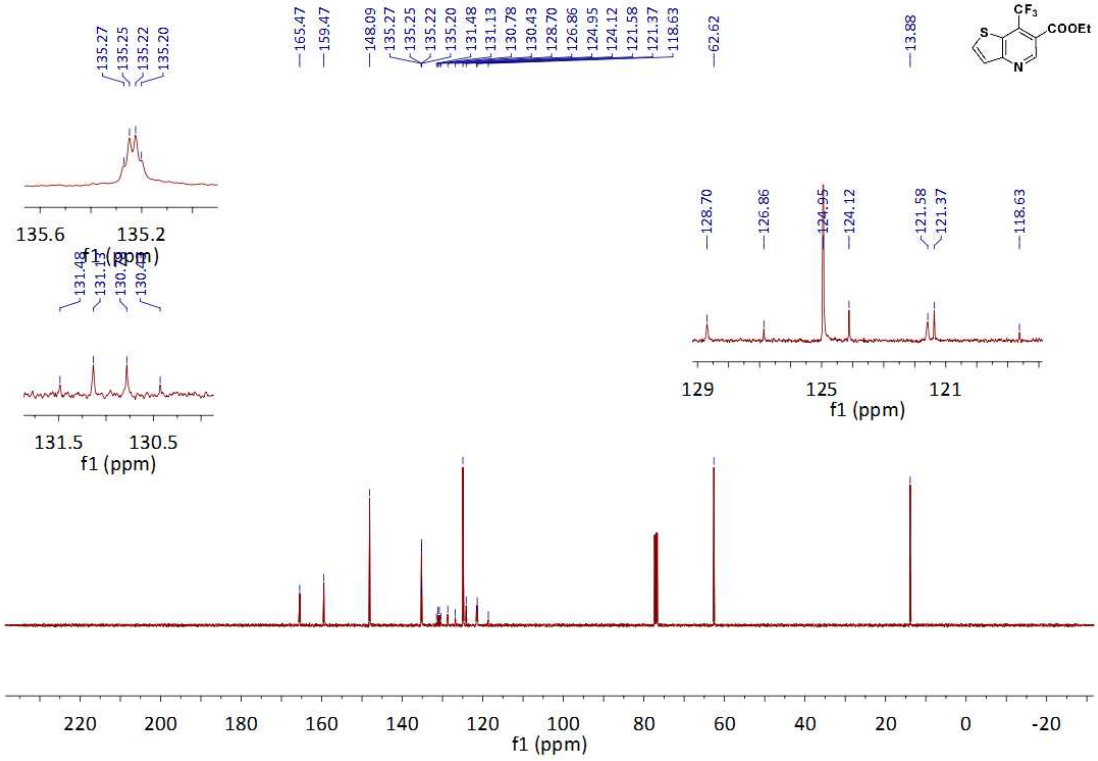
^{19}F NMR spectrum of 6-nitro-7-(trifluoromethyl)thieno[3,2-b]pyridine (3l)



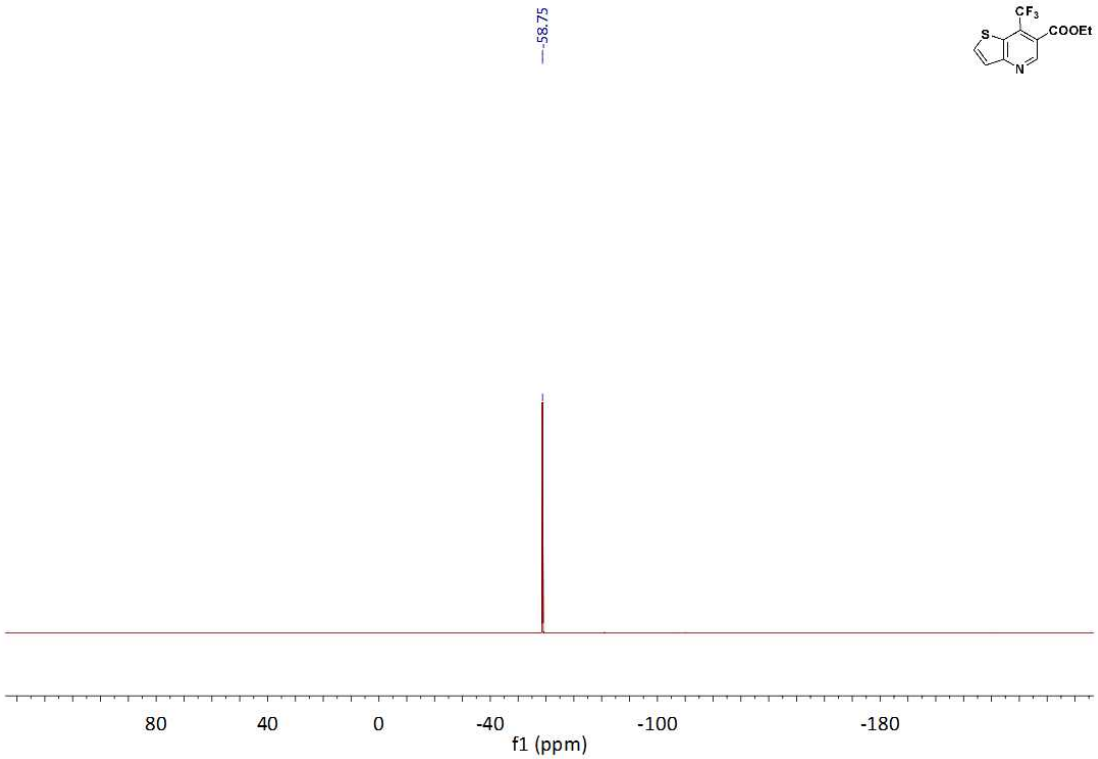
^{1}H NMR spectrum of
ethyl 7-(trifluoromethyl)thieno[3,2-b]pyridine-6-carboxylate (3m)



^{13}C NMR spectrum of
ethyl 7-(trifluoromethyl)thieno[3,2-b]pyridine-6-carboxylate (3m)



^{19}F NMR spectrum of
ethyl 7-(trifluoromethyl)thieno[3,2-b]pyridine-6-carboxylate (3m)



^{1}H NMR spectrum of
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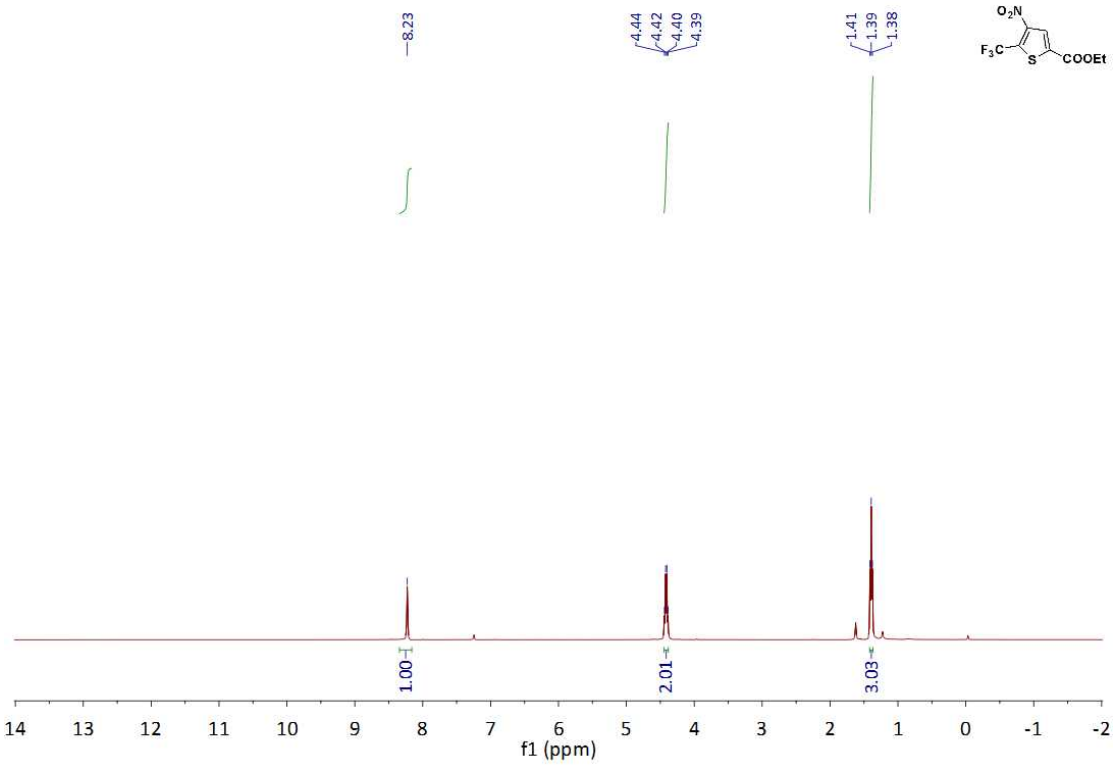
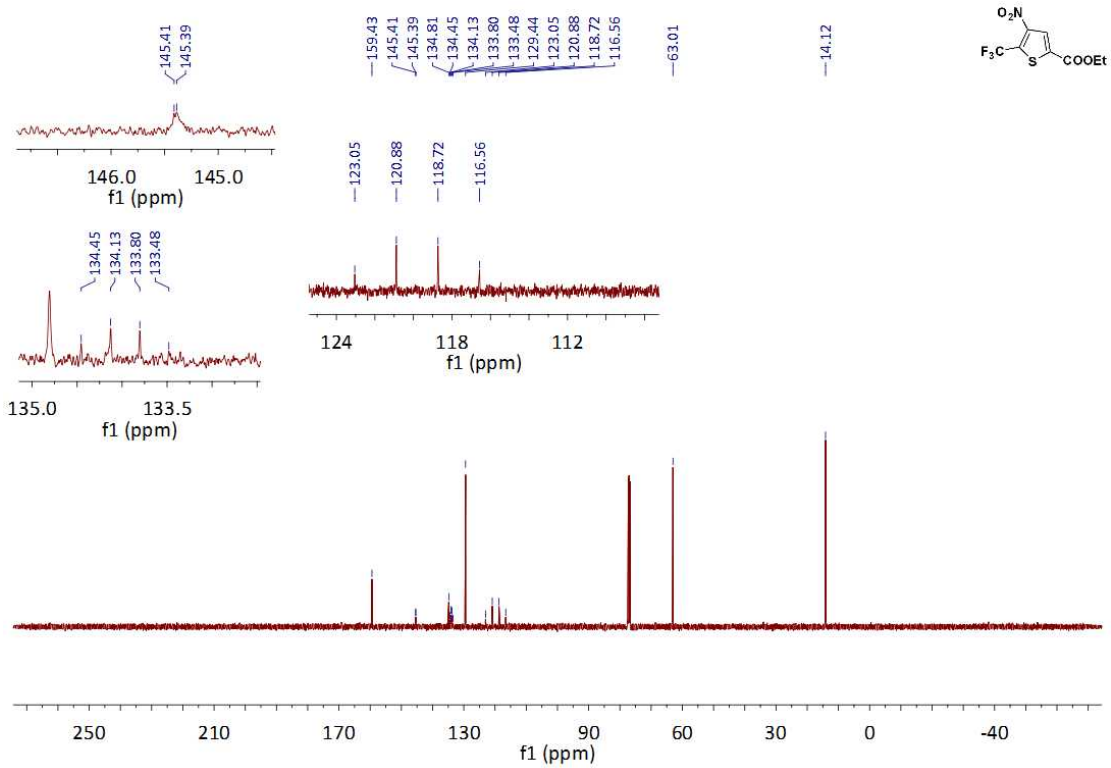
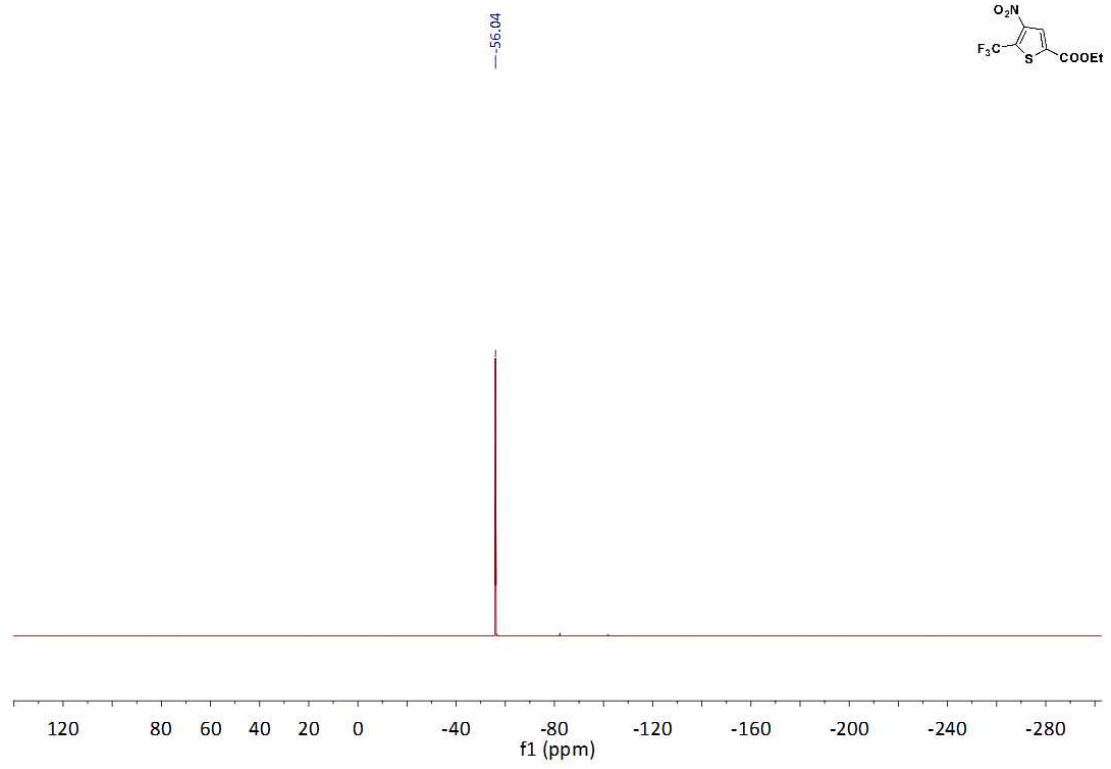


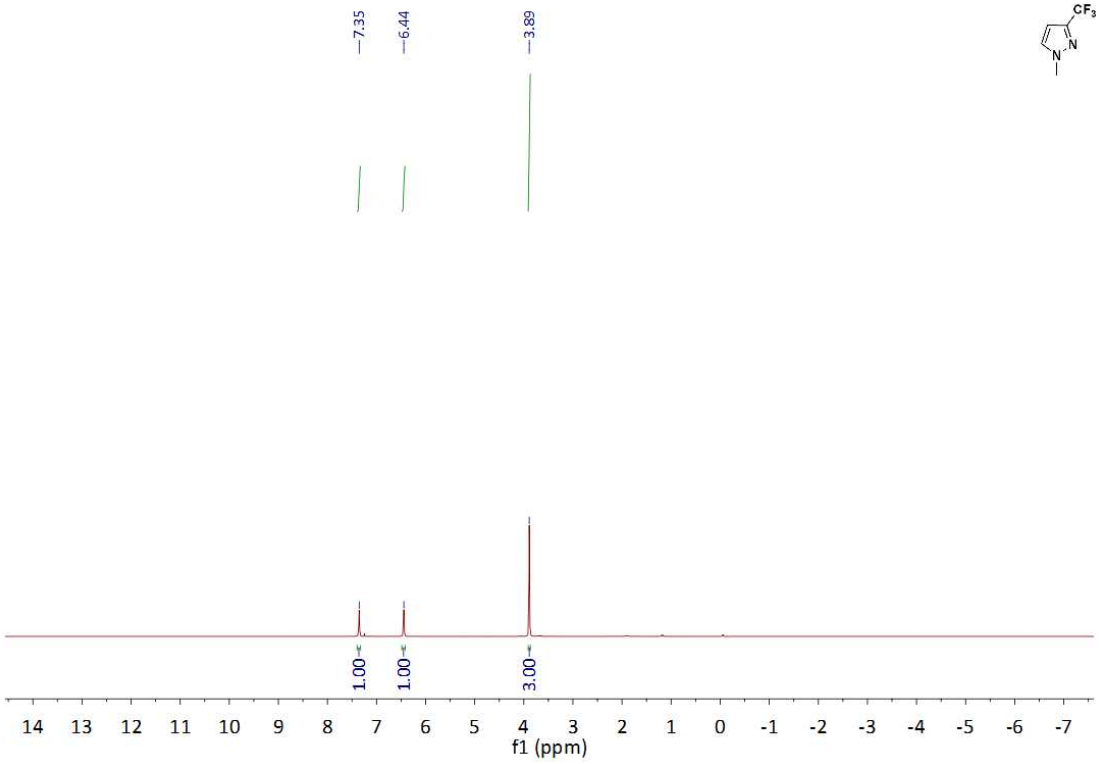
^{13}C NMR spectrum of ethyl 4-nitro-5-trifluoromethylthiophene-2-carboxylate (3n)



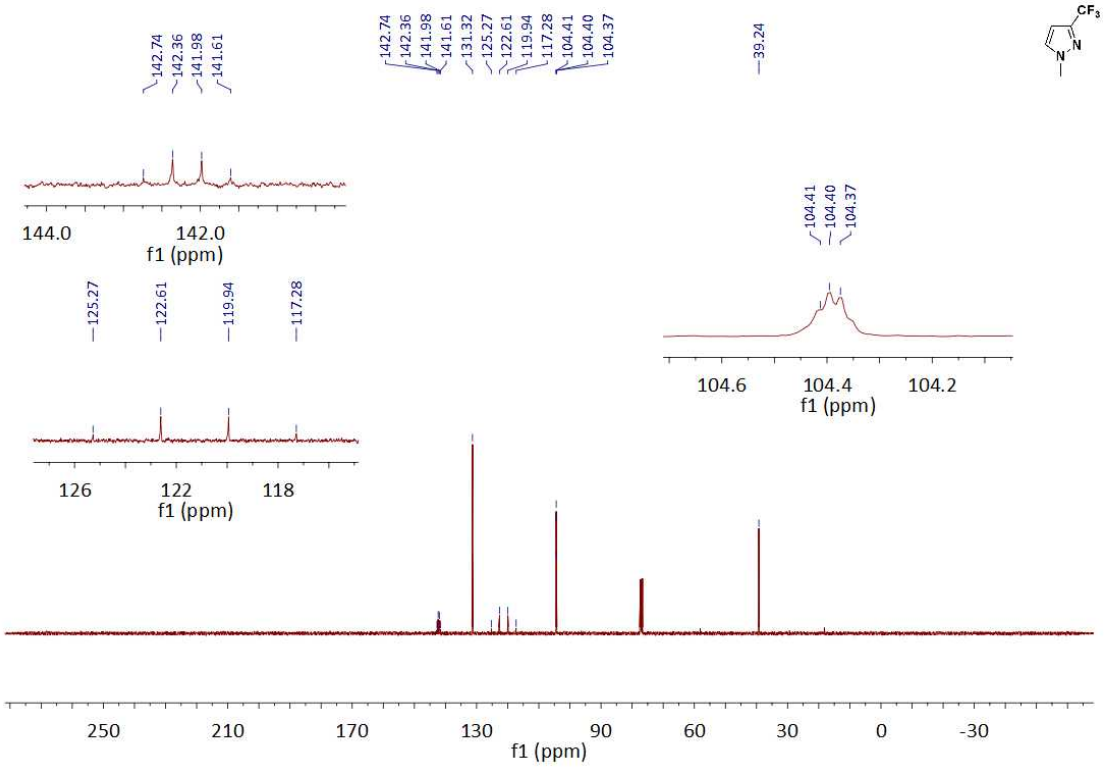
^{19}F NMR spectrum of ethyl 4-nitro-5-trifluoromethylthiophene-2-carboxylate (3n)



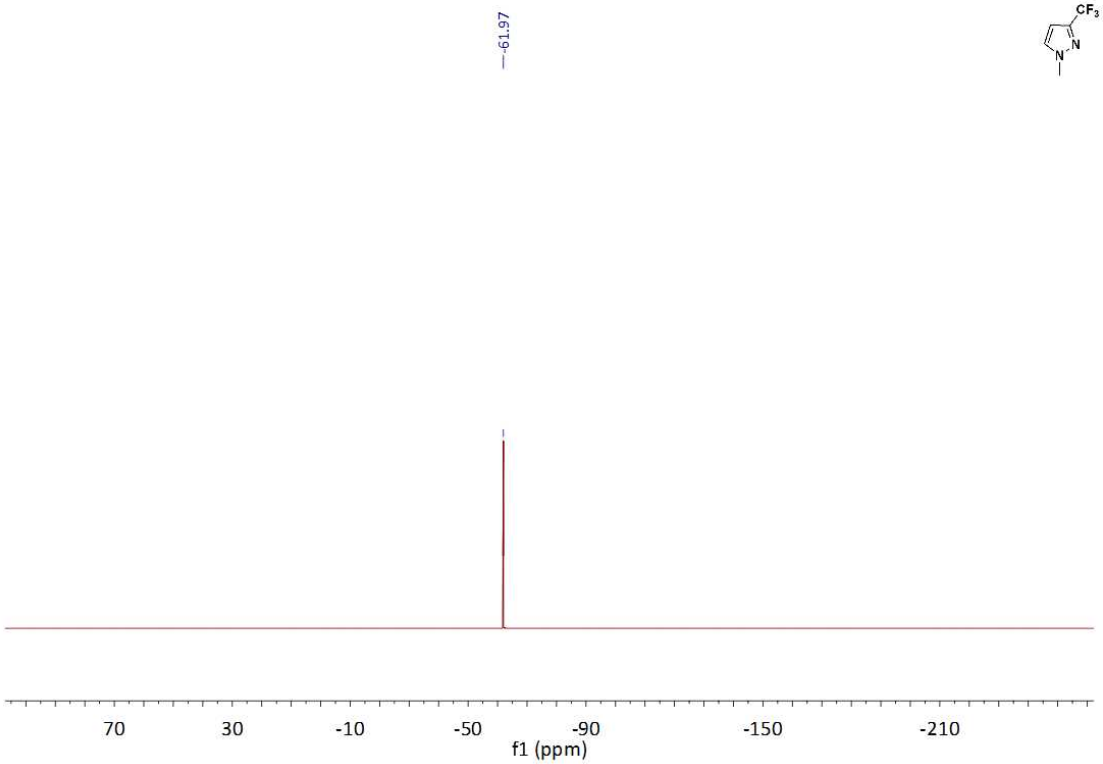
^{1}H NMR spectrum of 1-methyl-3-(trifluoromethyl)-1H-pyrazole (3o)



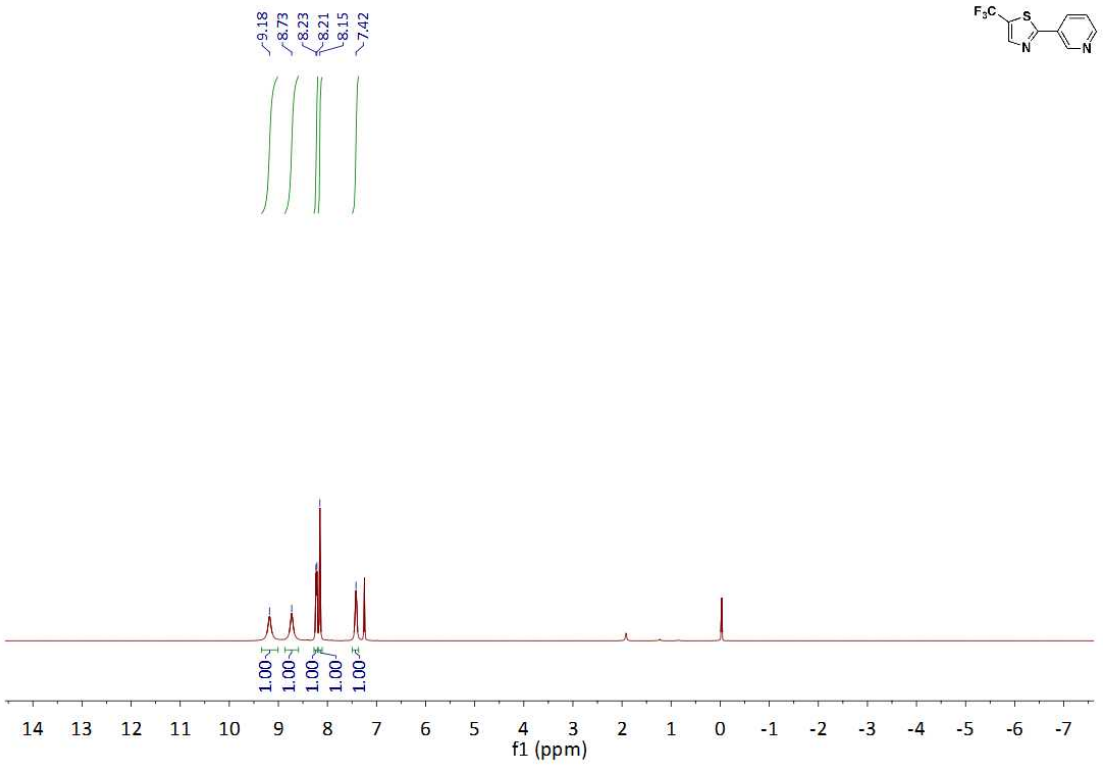
^{13}C NMR spectrum of 1-methyl-3-(trifluoromethyl)-1H-pyrazole (3o)



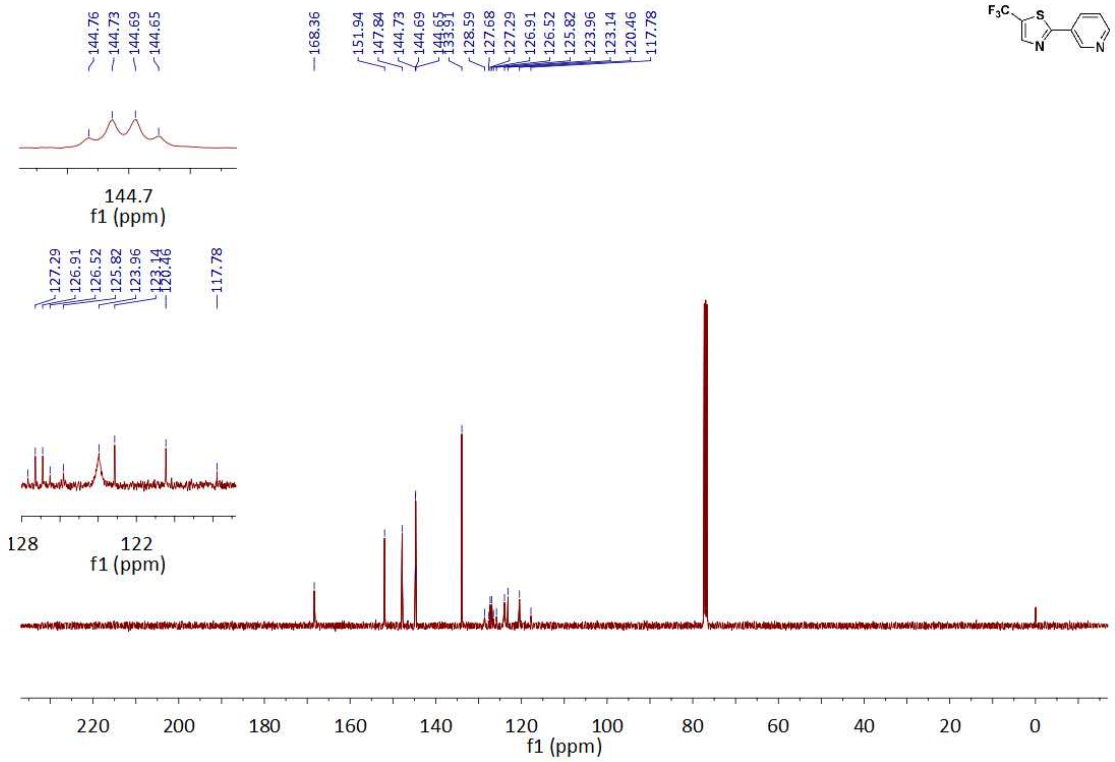
^{19}F NMR spectrum of 1-methyl-3-(trifluoromethyl)-1H-pyrazole (3o)



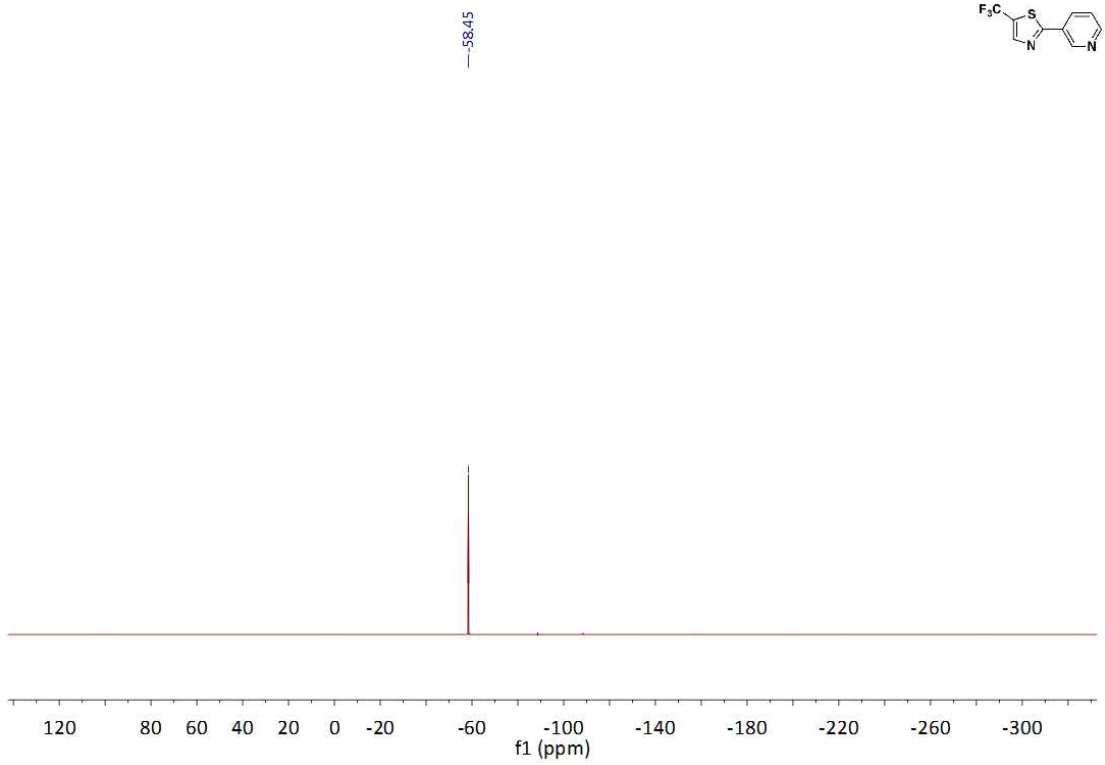
^{1}H NMR spectrum of 2-phenyl-5-(trifluoromethyl)thiazole (3p)



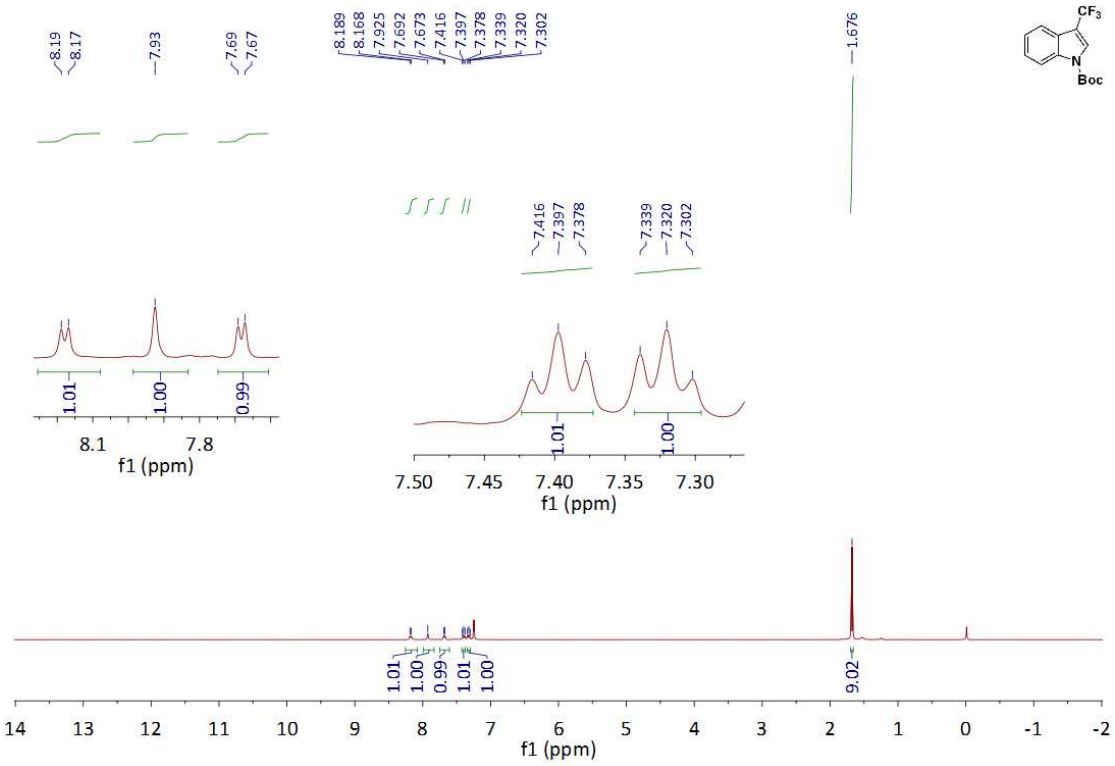
^{13}C NMR spectrum of 2-phenyl-5-(trifluoromethyl)thiazole (3p)



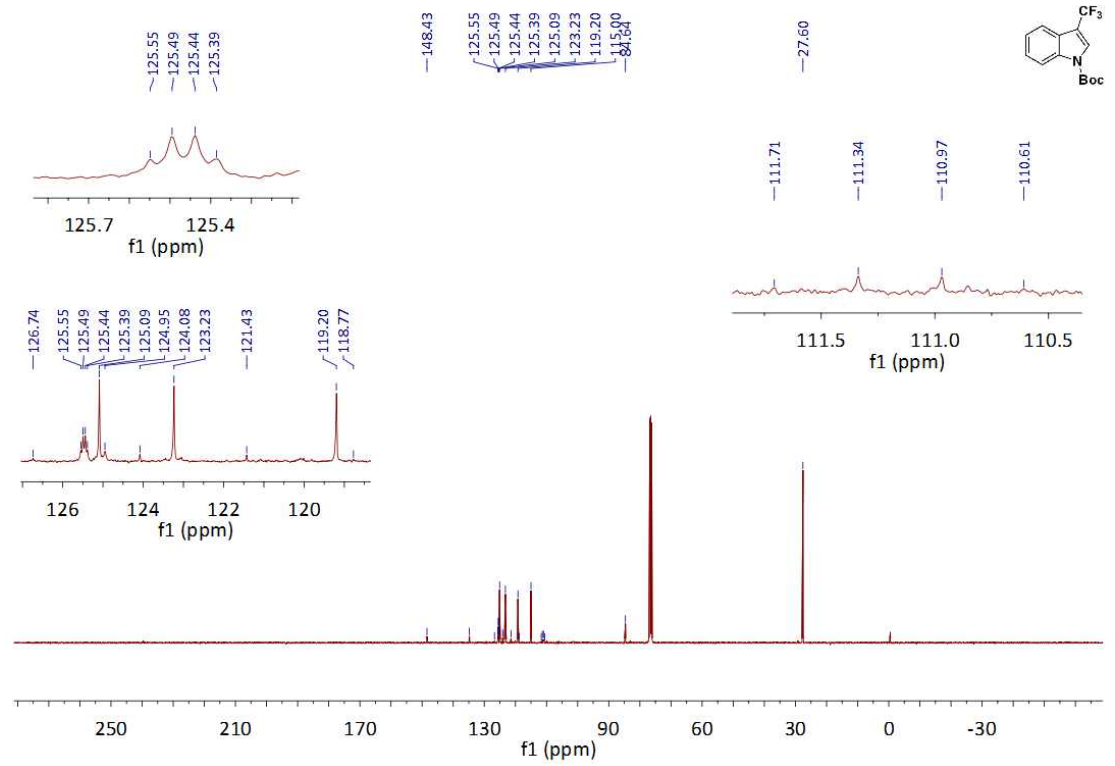
^{19}F NMR spectrum of 2-phenyl-5-(trifluoromethyl)thiazole (3p)



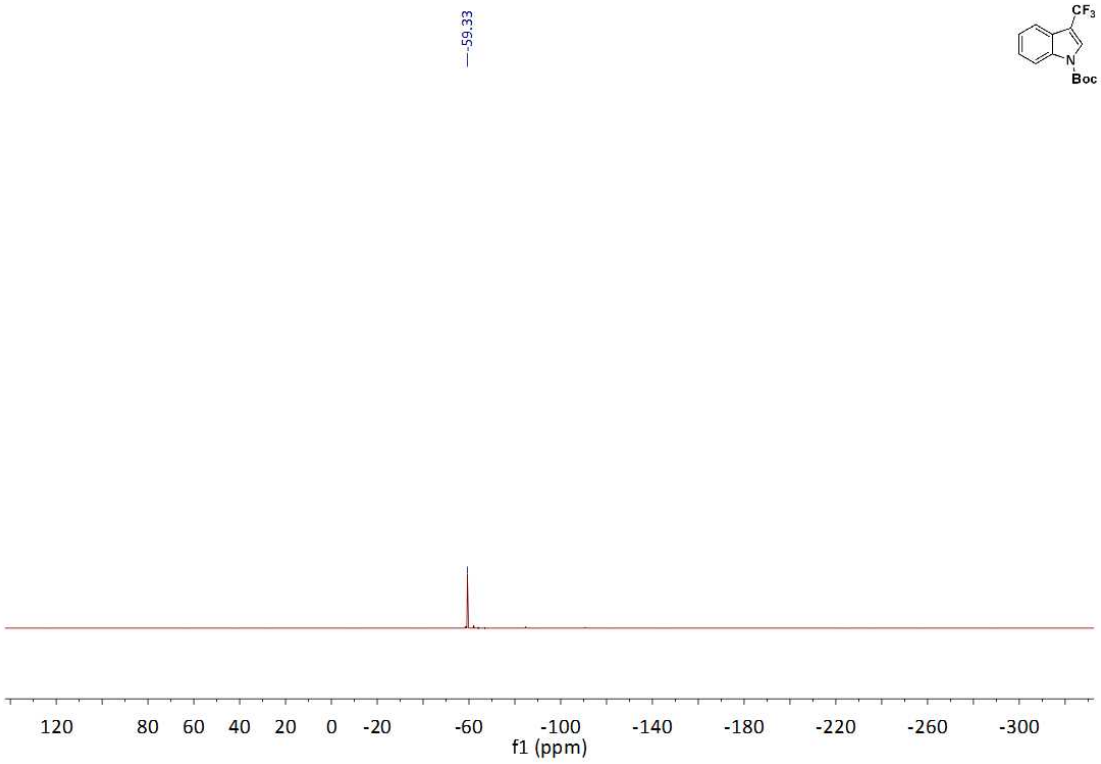
^{1}H NMR spectrum of *tert*-butyl 3-(trifluoromethyl)indole-1-carboxylate (3q)



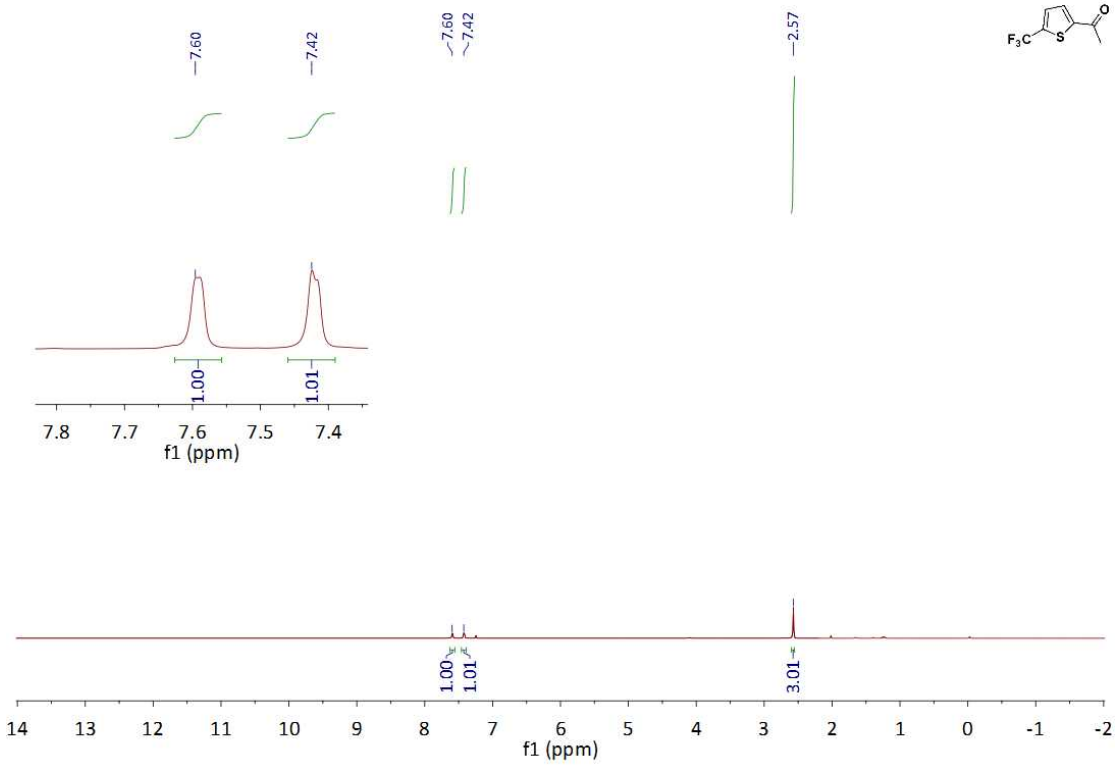
^{13}C NMR spectrum of *tert*-butyl 3-(trifluoromethyl)indole-1-carboxylate (3q)



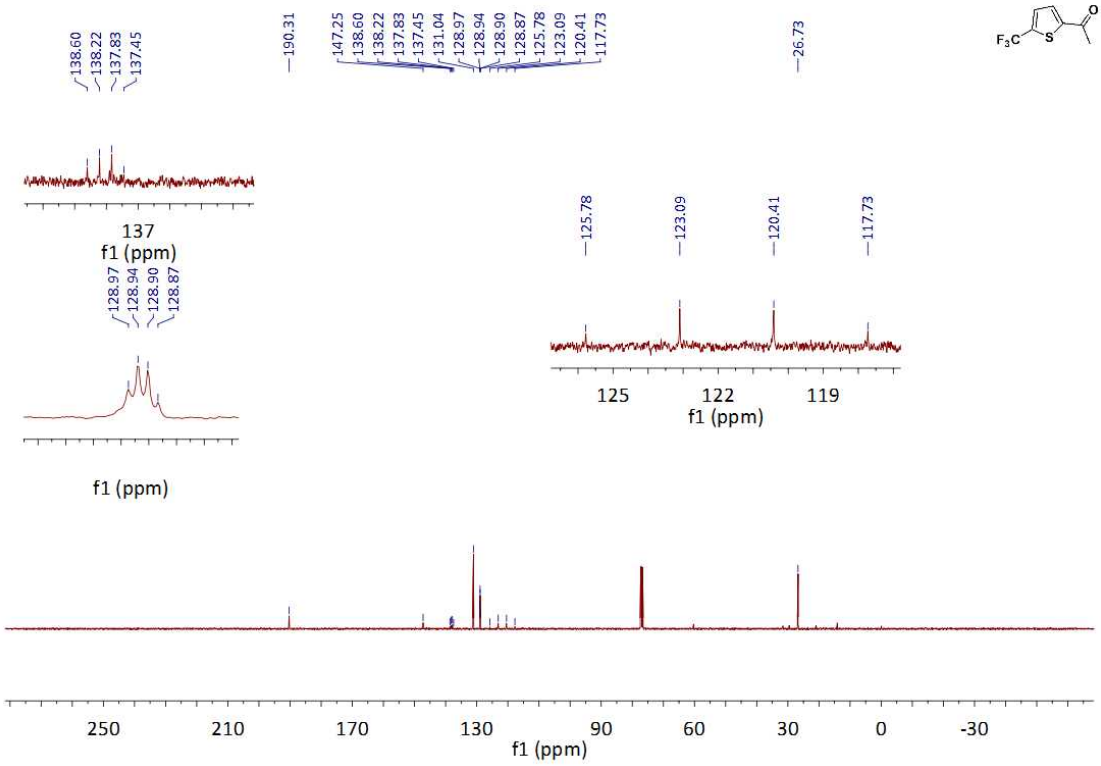
^{19}F NMR spectrum of *tert*-butyl 3-(trifluoromethyl)indole-1-carboxylate (3q)



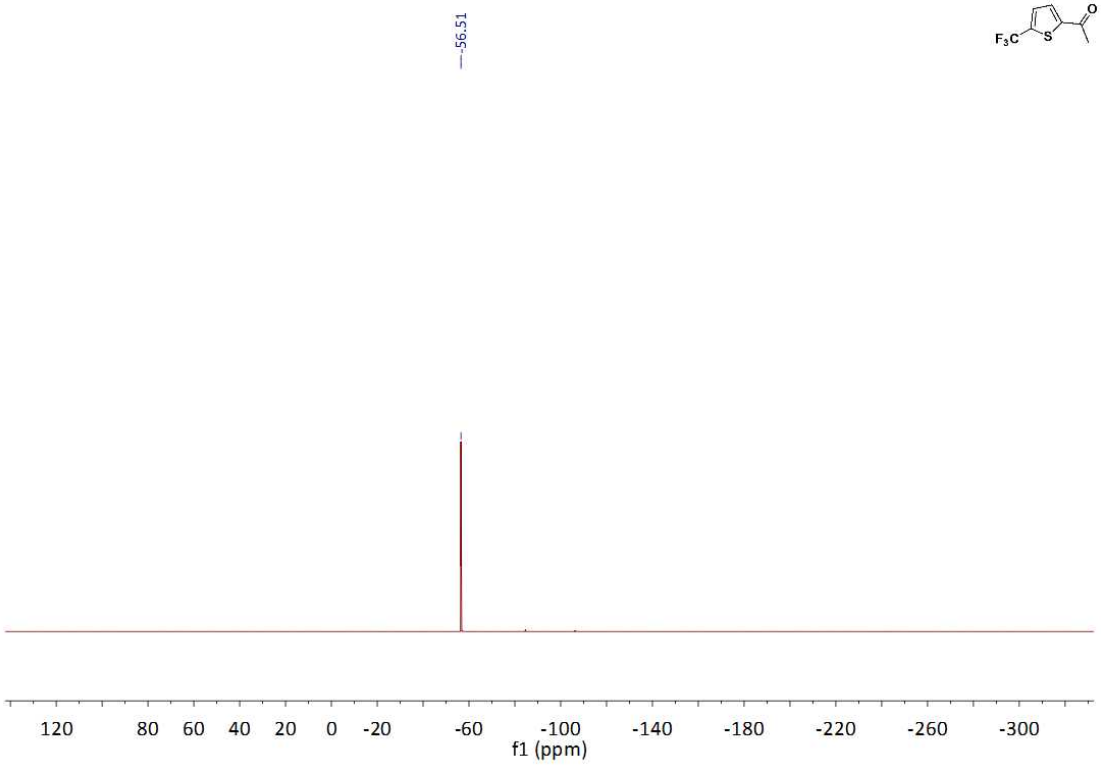
^{1}H NMR spectrum of 1-[5-(trifluoromethyl)-2-thienyl]ethanone (3r)



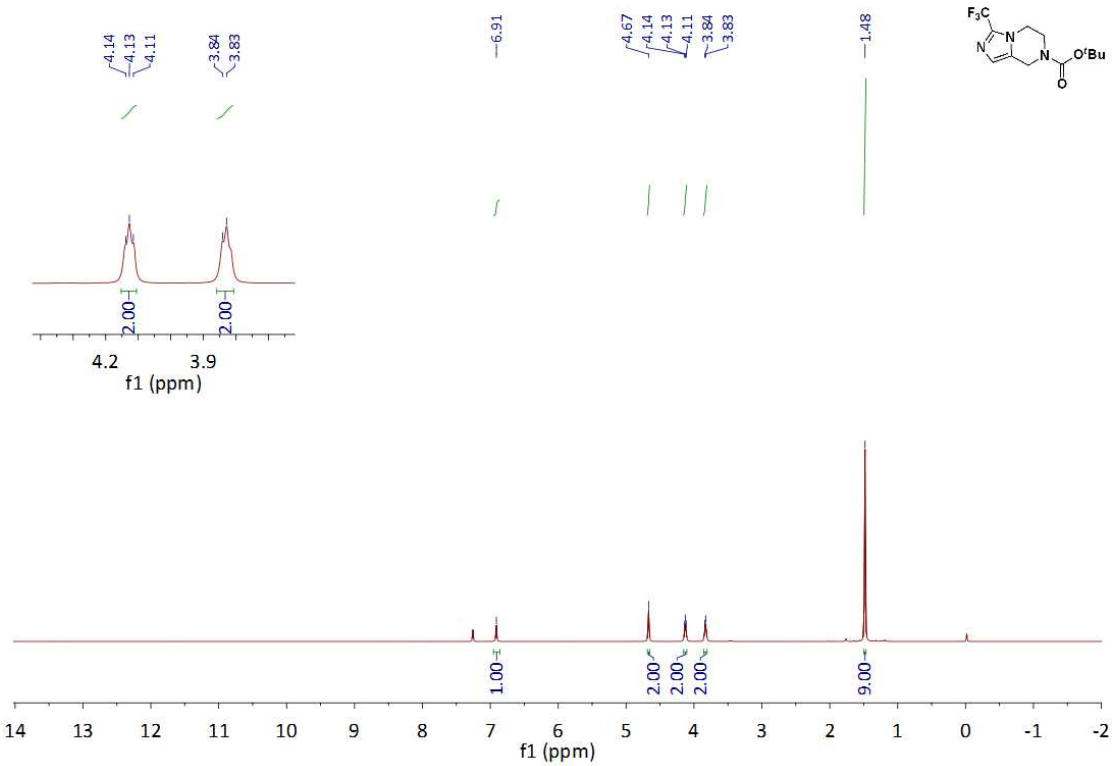
^{13}C NMR spectrum of 1-[5-(trifluoromethyl)-2-thienyl]ethanone (3r)



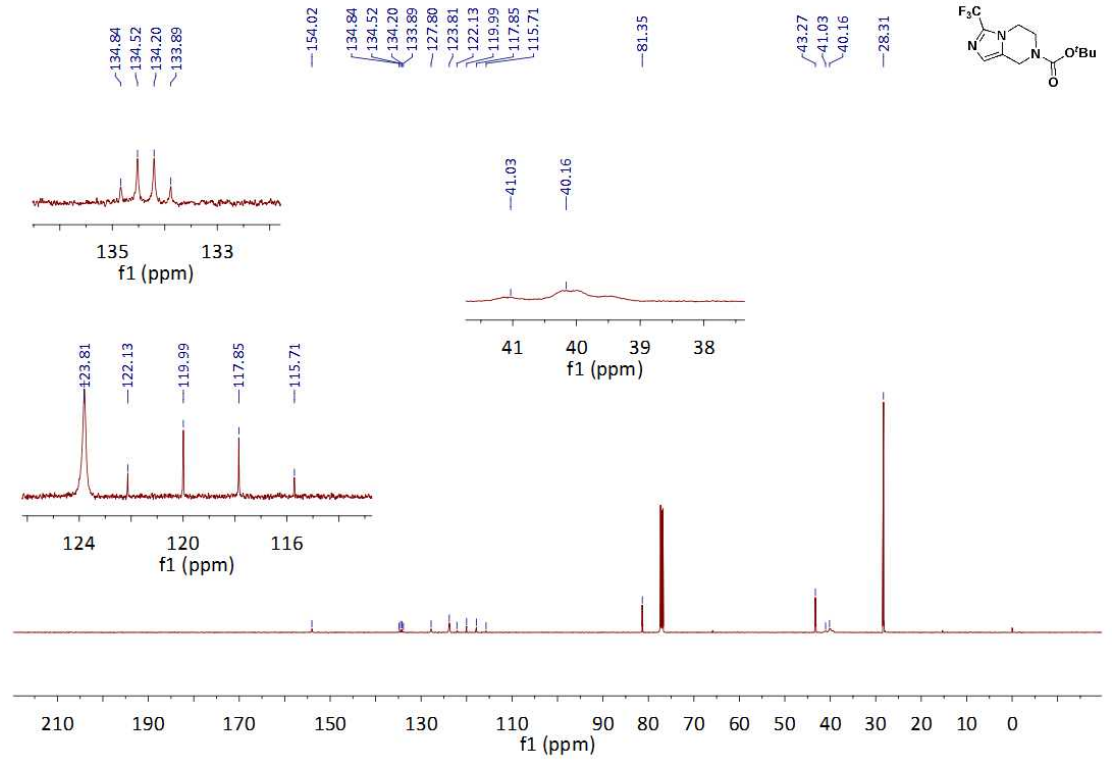
^{19}F NMR spectrum of 1-[5-(trifluoromethyl)-2-thienyl]ethanone (3r)



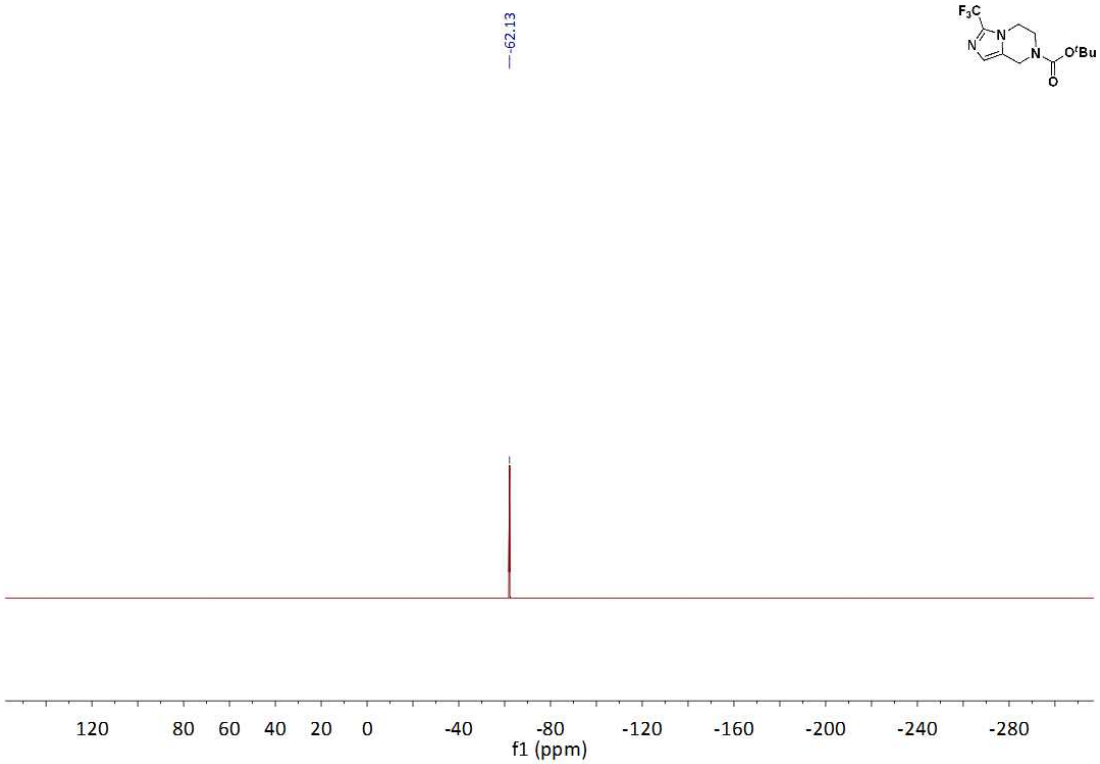
^{1}H NMR spectrum of *tert*-butyl 3-(trifluoromethyl)-6,8-dihydro-5H-imidazo[1,5-a]pyrazine-7-carboxylate (4)



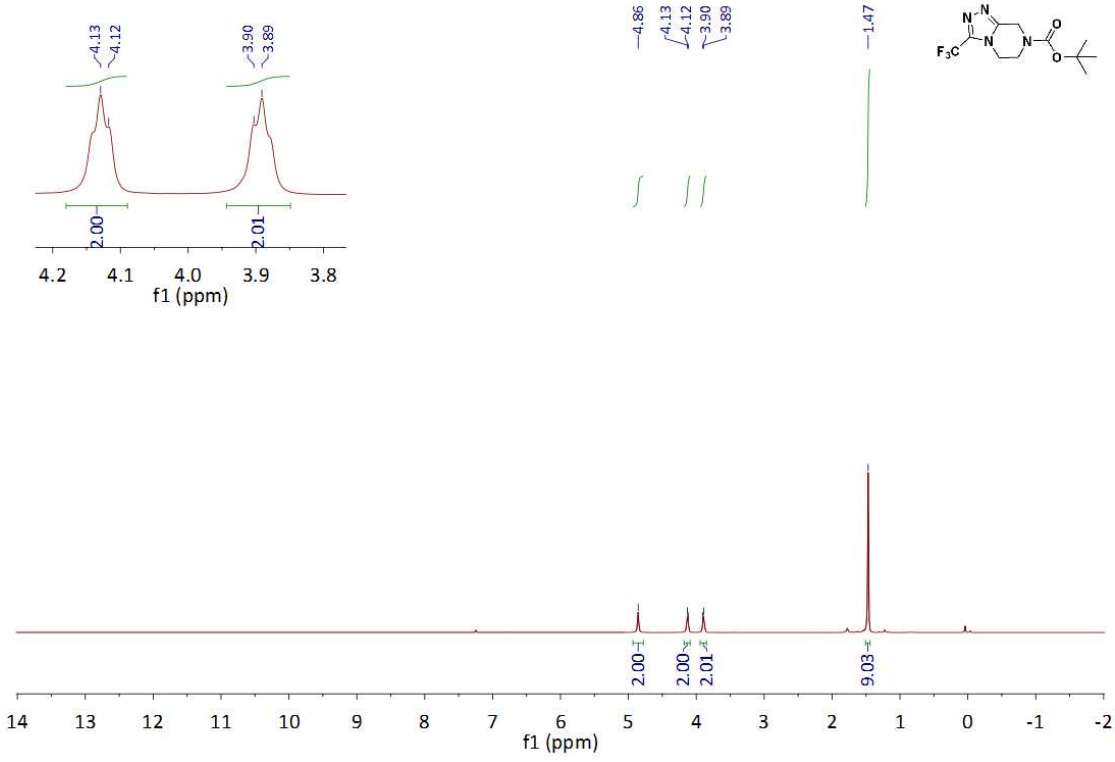
^{13}C NMR spectrum of *tert*-butyl 3-(trifluoromethyl)-6,8-dihydro-5H-imidazo[1,5-a]pyrazine-7-carboxylate (4)



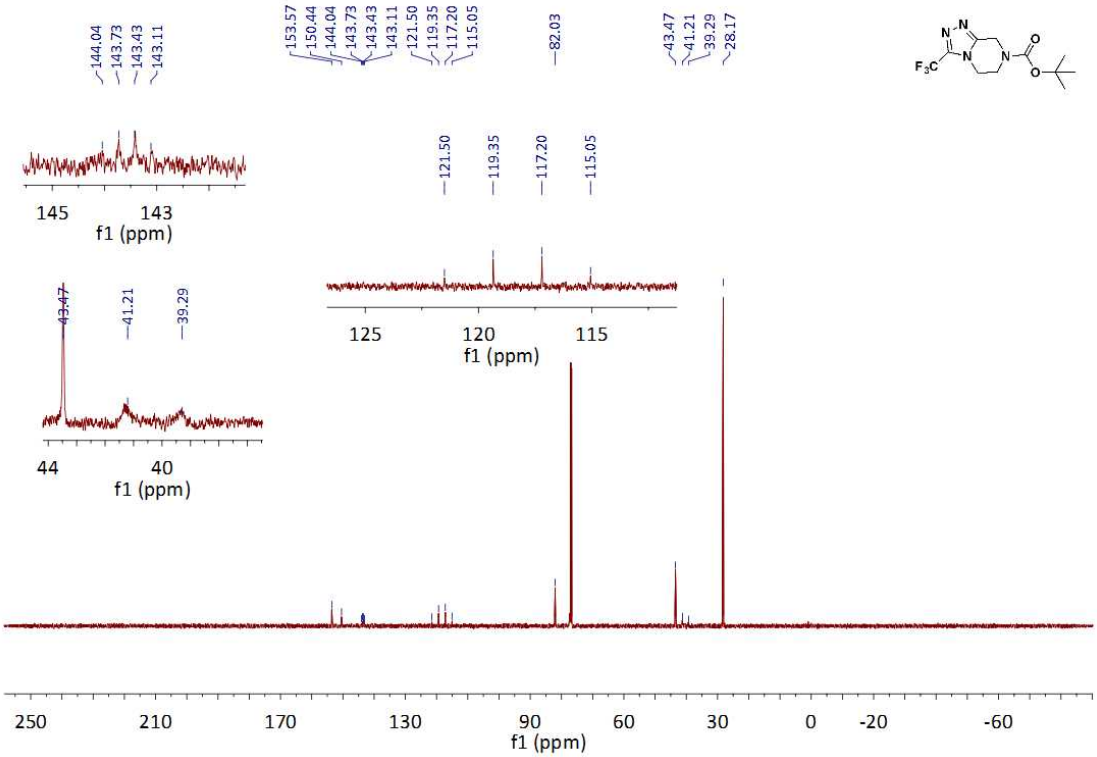
^{19}F NMR spectrum of *tert*-butyl 3-(trifluoromethyl)-6,8-dihydro-5H-imidazo[1,5-a]pyrazine-7-carboxylate (4)



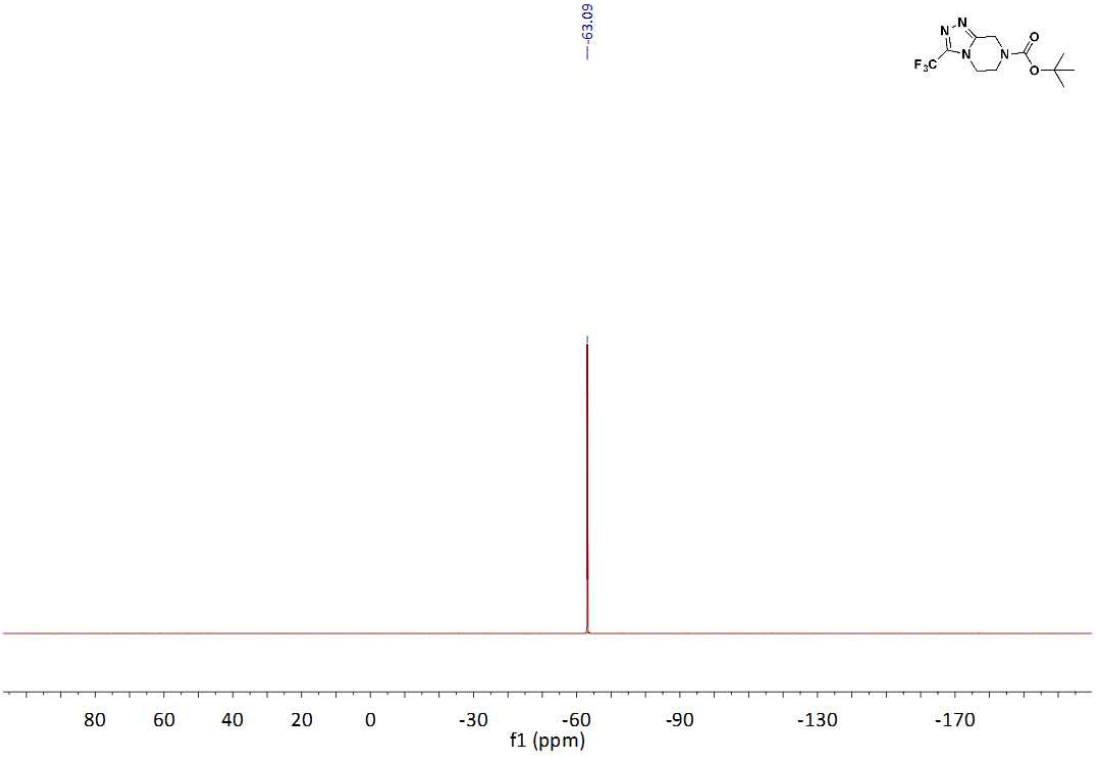
^{1}H NMR spectrum of *tert*-butyl 3-(trifluoromethyl)-6,8-dihydro-5H-[1,2,4]triazolo[4,3-a]pyrazine-7-carboxylate (5)



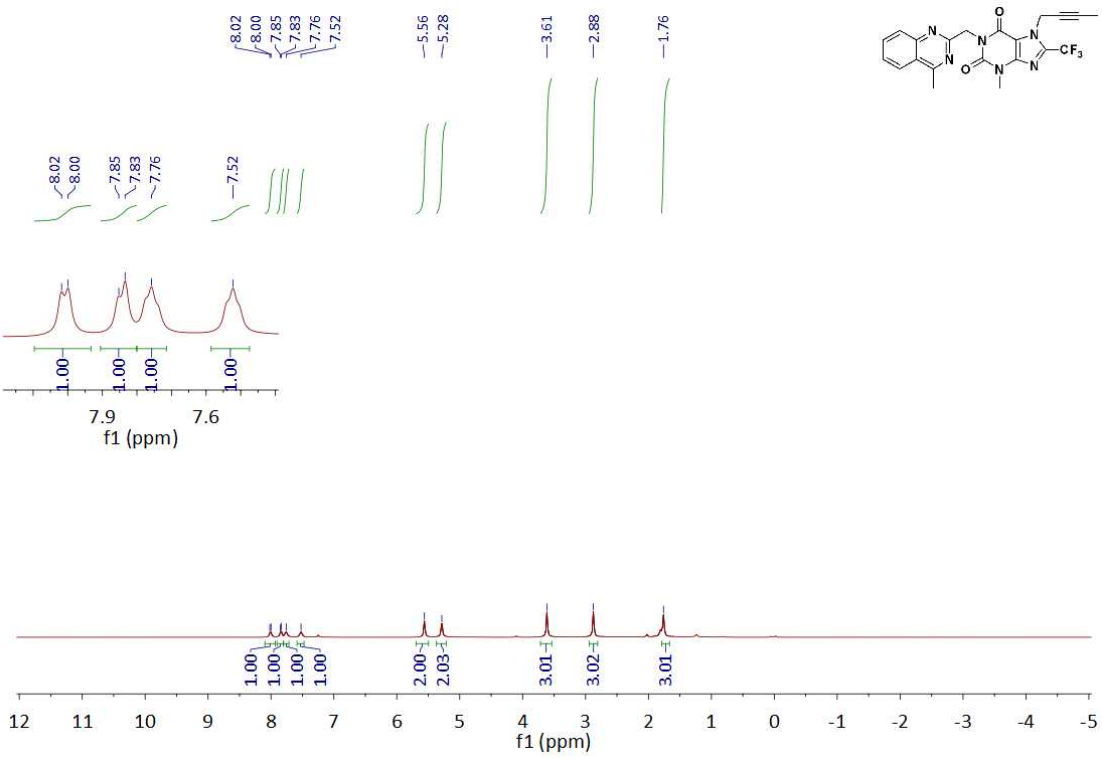
^{13}C NMR spectrum of *tert*-butyl 3-(trifluoromethyl)-6,8-dihydro-5H-[1,2,4]triazolo[4,3-a]pyrazine-7-carboxylate (5)



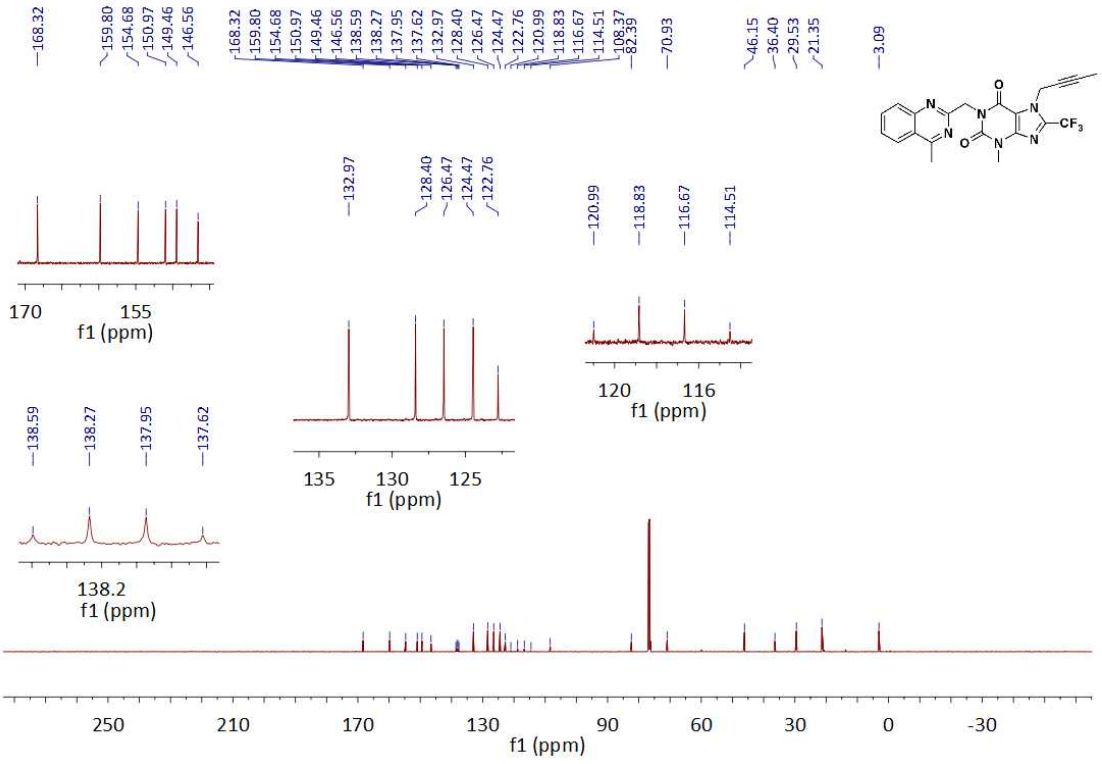
^{19}F NMR spectrum of *tert*-butyl 3-(trifluoromethyl)-6,8-dihydro-5H-[1,2,4]triazolo[4,3-a]pyrazine-7-carboxylate (5)



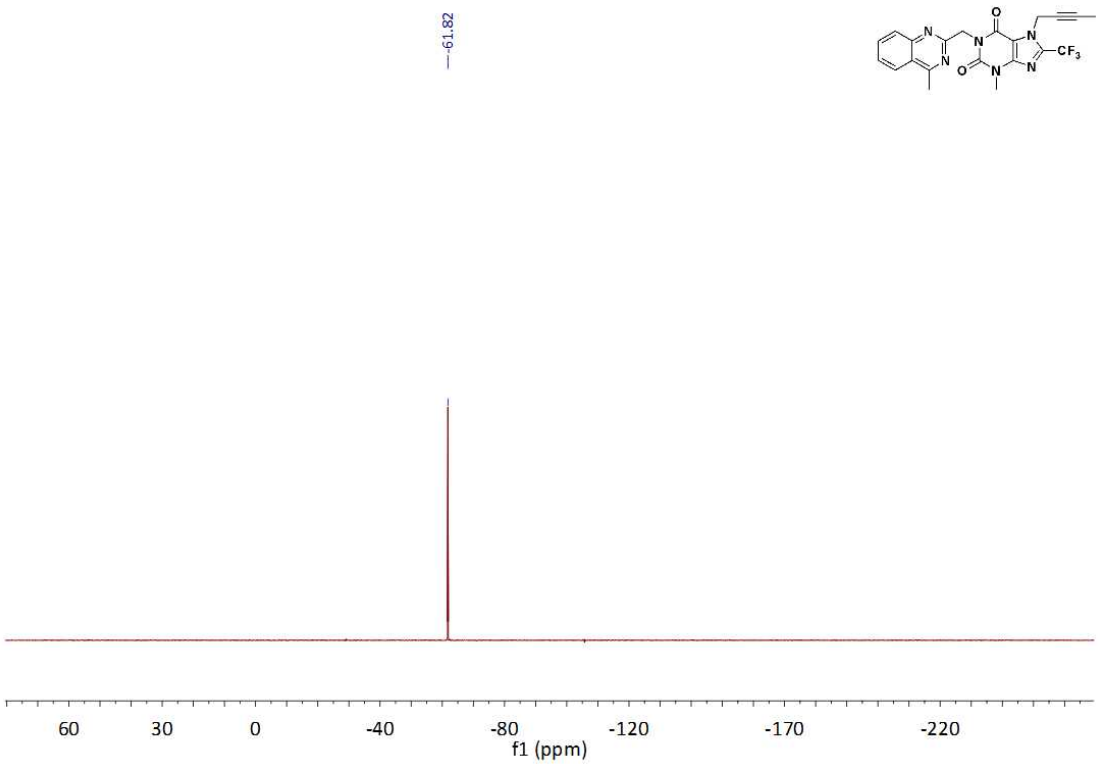
^{1}H NMR spectrum of 7-but-2-ynyl-3-methyl-1-[(4-methylquinazolin-2-yl)methyl]-8-(trifluoromethyl)purine-2,6-dione (6)



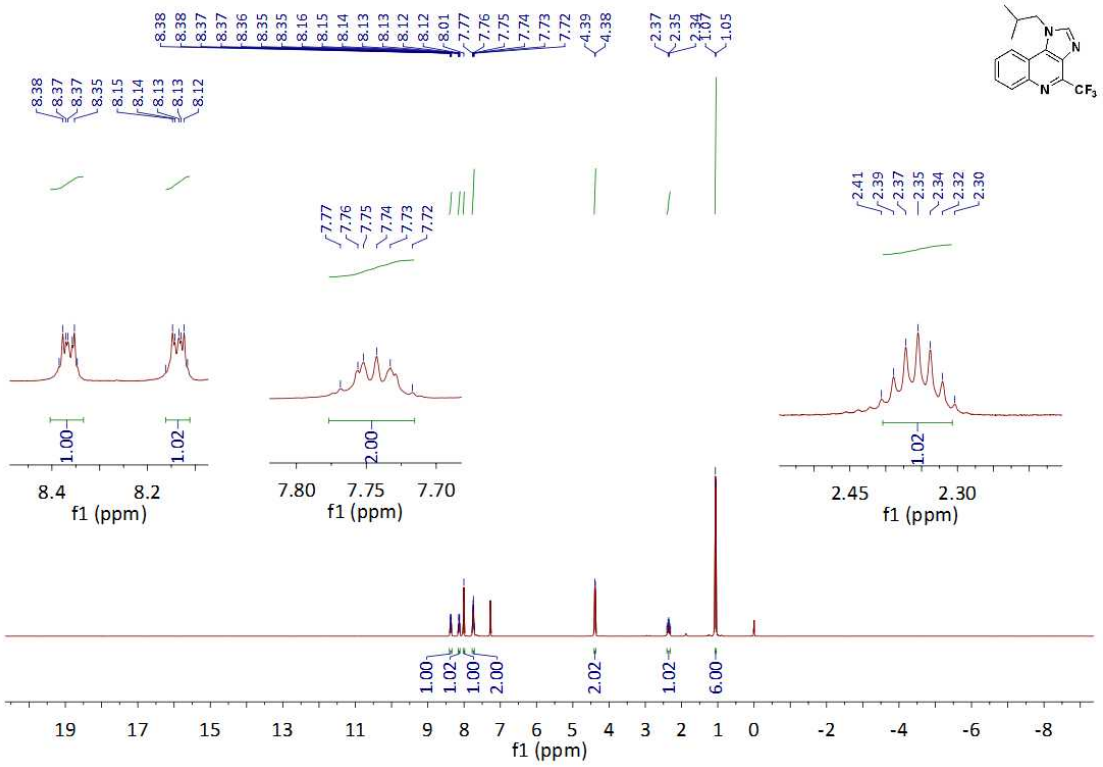
^{13}C NMR spectrum of 7-but-2-ynyl-3-methyl-1-[(4-methylquinazolin-2-yl)methyl]-8-(trifluoromethyl)purine-2,6-dione (6)



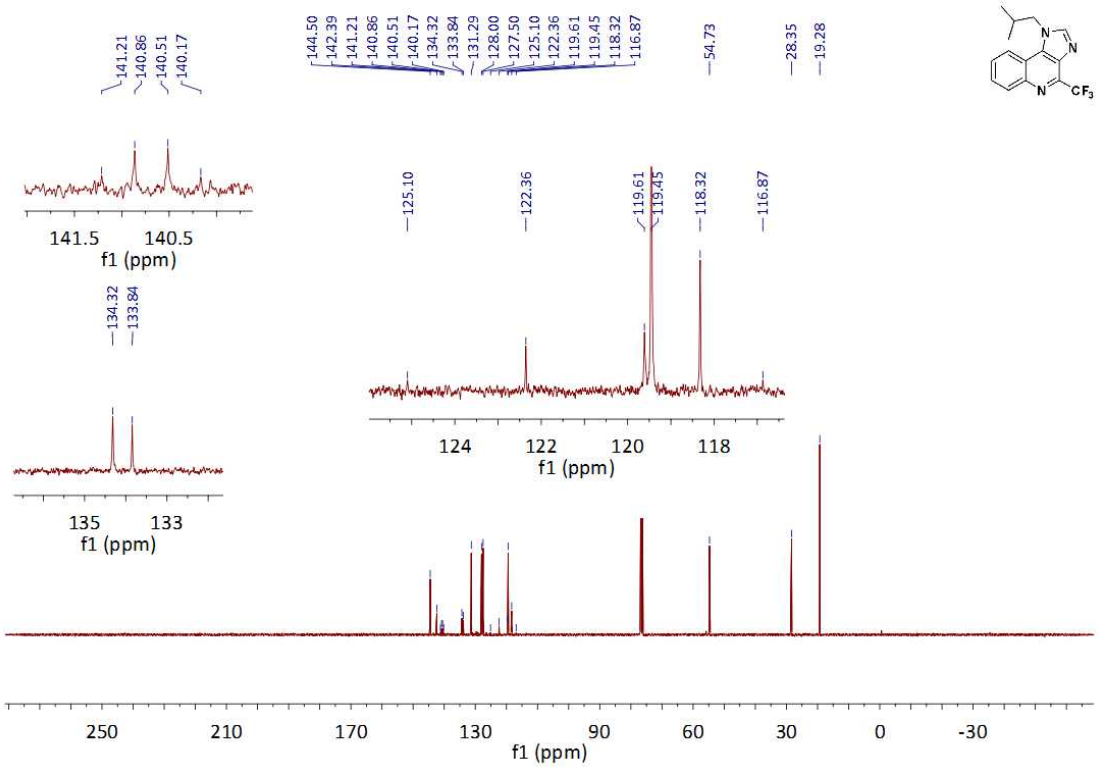
^{19}F NMR spectrum of 7-but-2-ynyl-3-methyl-1-[(4-methylquinazolin-2-yl)methyl]-8-(trifluoromethyl)purine-2,6-dione (6)



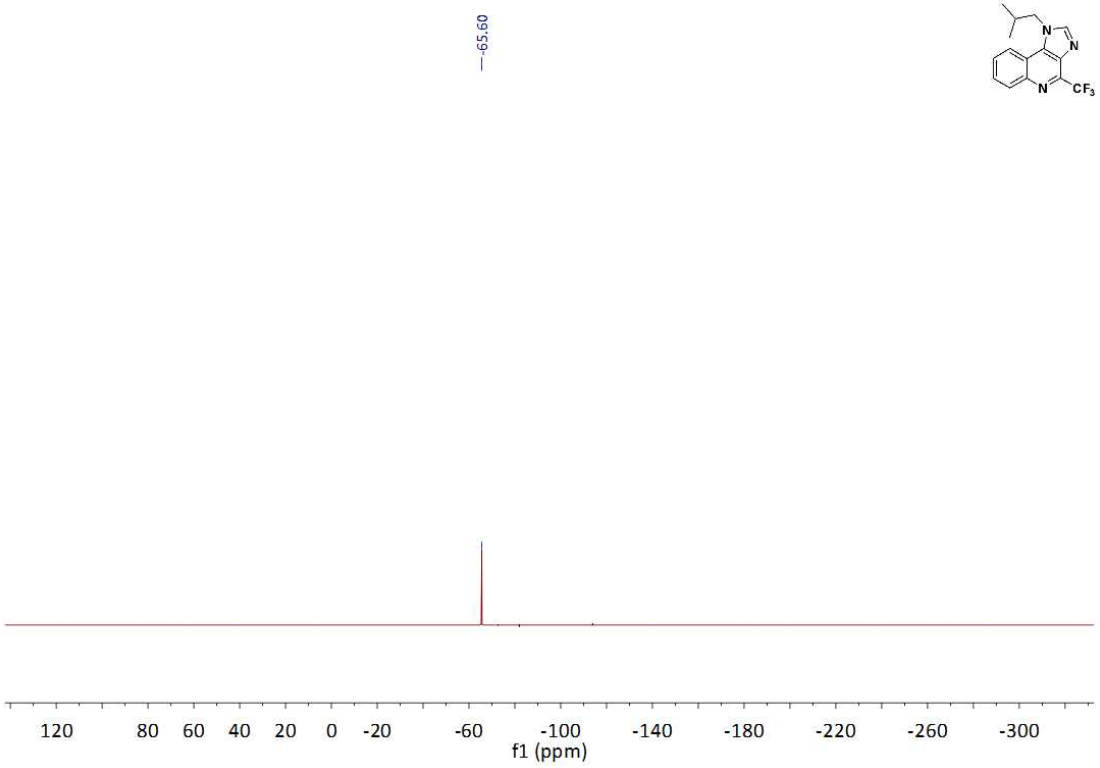
^{1}H NMR spectrum of 1-isobutyl-4-(trifluoromethyl)imidazo[4,5-c]quinolone (7)



^{13}C NMR spectrum of 1-isobutyl-4-(trifluoromethyl)imidazo[4,5-c]quinolone (7)



^{19}F NMR spectrum of 1-isobutyl-4-(trifluoromethyl)imidazo[4,5-c]quinolone (7)



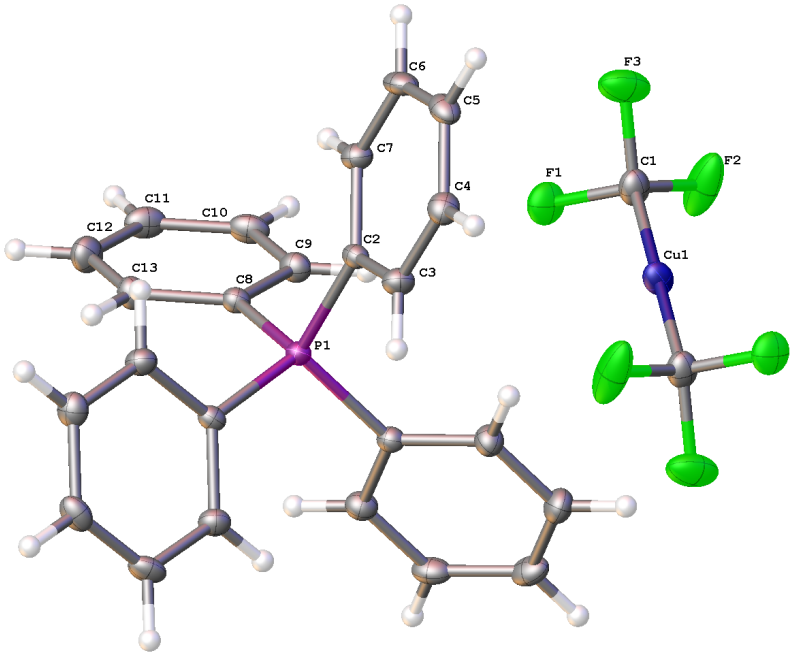


Figure S1. X-ray structure of tetraphenylphosphonium bis(trifluoromethyl)copper(I) 1.

Table S4. Crystal data and structure refinement for 1 (d8v18488)

Identification code	d8v18488	
Empirical formula	C26 H20 Cu F6 P	
Formula weight	540.93	
Temperature	170.01 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 15.5529(6) Å	a= 90°.
	b = 7.3629(3) Å	b= 90°.
	c = 19.8862(6) Å	g = 90°.
Volume	2277.26(15) $Å^3$	
Z	4	
Density (calculated)	1.578 Mg/m^3	
Absorption coefficient	1.091 mm^{-1}	
F(000)	1096	
Crystal size	0.15 x 0.1 x 0.08 mm^3	
Theta range for data collection	2.431 to 27.501°.	
Index ranges	-20<=h<=17, -9<=k<=9, -25<=l<=25	
Reflections collected	12640	
Independent reflections	2612 [R(int) = 0.0320]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6394	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2612 / 0 / 156	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1394	
R indices (all data)	R1 = 0.0570, wR2 = 0.1500	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.959 and -0.799 $e.Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x10^3) for 1 (d8v18488). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	5000	5000	33(1)
F(1)	3914(1)	2817(3)	5791(1)	47(1)
F(2)	3921(2)	1978(4)	4765(1)	85(1)
F(3)	3209(1)	4333(4)	5059(1)	63(1)
C(1)	4001(2)	3496(4)	5146(1)	37(1)
P(1)	5000	4662(1)	7500	21(1)
C(2)	4424(2)	6109(3)	6933(1)	22(1)
C(3)	4872(2)	7473(4)	6598(1)	29(1)
C(4)	4445(2)	8608(4)	6155(1)	33(1)
C(5)	3567(2)	8398(4)	6053(1)	34(1)
C(6)	3119(2)	7060(4)	6393(1)	33(1)
C(7)	3542(2)	5907(4)	6829(1)	29(1)
C(8)	4268(2)	3196(3)	7942(1)	23(1)
C(9)	3915(2)	1719(4)	7593(1)	30(1)
C(10)	3370(2)	540(4)	7927(2)	36(1)
C(11)	3171(2)	815(4)	8598(2)	38(1)
C(12)	3515(2)	2283(4)	8940(2)	38(1)
C(13)	4061(2)	3471(4)	8613(1)	31(1)

Table S6. Bond lengths [Å] and angles [°] for 1 (d8v18488).

Cu(1)-C(1)#1	1.930(3)
Cu(1)-C(1)	1.930(3)
F(1)-C(1)	1.382(3)
F(2)-C(1)	1.356(4)
F(3)-C(1)	1.388(4)
P(1)-C(2)#2	1.792(2)
P(1)-C(2)	1.792(2)
P(1)-C(8)#2	1.798(2)
P(1)-C(8)	1.798(2)
C(2)-C(3)	1.392(4)
C(2)-C(7)	1.394(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.385(4)
C(4)-H(4)	0.9500
C(4)-C(5)	1.390(4)
C(5)-H(5)	0.9500
C(5)-C(6)	1.382(4)
C(6)-H(6)	0.9500
C(6)-C(7)	1.381(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.403(3)
C(8)-C(13)	1.387(4)
C(9)-H(9)	0.9500
C(9)-C(10)	1.384(4)
C(10)-H(10)	0.9500
C(10)-C(11)	1.384(4)
C(11)-H(11)	0.9500
C(11)-C(12)	1.385(4)
C(12)-H(12)	0.9500
C(12)-C(13)	1.381(4)
C(13)-H(13)	0.9500
C(1)#1-Cu(1)-C(1)	180.0
F(1)-C(1)-Cu(1)	115.2(2)
F(1)-C(1)-F(3)	100.9(2)
F(2)-C(1)-Cu(1)	117.6(2)

F(2)-C(1)-F(1)	102.2(3)
F(2)-C(1)-F(3)	102.3(3)
F(3)-C(1)-Cu(1)	116.1(2)
C(2)#2-P(1)-C(2)	107.03(15)
C(2)#2-P(1)-C(8)#2	110.36(11)
C(2)-P(1)-C(8)	110.36(11)
C(2)-P(1)-C(8)#2	111.47(10)
C(2)#2-P(1)-C(8)	111.47(10)
C(8)#2-P(1)-C(8)	106.22(16)
C(3)-C(2)-P(1)	118.63(18)
C(3)-C(2)-C(7)	119.9(2)
C(7)-C(2)-P(1)	121.44(19)
C(2)-C(3)-H(3)	120.0
C(4)-C(3)-C(2)	120.0(2)
C(4)-C(3)-H(3)	120.0
C(3)-C(4)-H(4)	120.1
C(3)-C(4)-C(5)	119.8(3)
C(5)-C(4)-H(4)	120.1
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-C(4)	120.2(2)
C(6)-C(5)-H(5)	119.9
C(5)-C(6)-H(6)	119.8
C(7)-C(6)-C(5)	120.3(2)
C(7)-C(6)-H(6)	119.8
C(2)-C(7)-H(7)	120.1
C(6)-C(7)-C(2)	119.7(2)
C(6)-C(7)-H(7)	120.1
C(9)-C(8)-P(1)	118.14(19)
C(13)-C(8)-P(1)	121.98(19)
C(13)-C(8)-C(9)	119.9(2)
C(8)-C(9)-H(9)	120.4
C(10)-C(9)-C(8)	119.2(3)
C(10)-C(9)-H(9)	120.4
C(9)-C(10)-H(10)	119.7
C(9)-C(10)-C(11)	120.6(3)
C(11)-C(10)-H(10)	119.7
C(10)-C(11)-H(11)	120.0
C(10)-C(11)-C(12)	120.0(3)

C(12)-C(11)-H(11)	120.0
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-C(11)	120.1(3)
C(13)-C(12)-H(12)	120.0
C(8)-C(13)-H(13)	119.9
C(12)-C(13)-C(8)	120.2(3)
C(12)-C(13)-H(13)	119.9

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,y,-z+3/2

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1 (d8v18488).

The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	32(1)	41(1)	28(1)	5(1)	1(1)	-11(1)
F(1)	52(1)	46(1)	43(1)	12(1)	11(1)	-11(1)
F(2)	86(2)	88(2)	81(2)	-54(2)	45(1)	-52(2)
F(3)	33(1)	81(2)	76(2)	26(1)	-6(1)	-9(1)
C(1)	39(2)	41(2)	31(1)	0(1)	5(1)	-10(1)
P(1)	19(1)	22(1)	21(1)	0	-1(1)	0
C(2)	22(1)	22(1)	24(1)	-3(1)	-4(1)	2(1)
C(3)	24(1)	30(1)	34(1)	2(1)	-1(1)	0(1)
C(4)	39(2)	28(1)	33(1)	4(1)	1(1)	4(1)
C(5)	40(2)	30(1)	31(1)	-2(1)	-9(1)	12(1)
C(6)	24(1)	34(1)	42(1)	-7(1)	-10(1)	8(1)
C(7)	24(1)	29(1)	34(1)	-2(1)	-1(1)	2(1)
C(8)	22(1)	22(1)	26(1)	1(1)	-2(1)	-1(1)
C(9)	30(1)	27(1)	33(1)	-3(1)	-3(1)	-2(1)
C(10)	28(1)	27(1)	52(2)	1(1)	-9(1)	-5(1)
C(11)	30(1)	33(1)	52(2)	14(1)	1(1)	-5(1)
C(12)	40(2)	43(2)	32(1)	7(1)	5(1)	-5(1)
C(13)	36(1)	30(1)	28(1)	0(1)	-1(1)	-4(1)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1 (d8v18488).

	x	y	z	U(eq)
H(3)	5471	7626	6675	35
H(4)	4752	9528	5921	40
H(5)	3273	9177	5750	40
H(6)	2517	6933	6326	40
H(7)	3234	4979	7057	35
H(9)	4049	1529	7132	36
H(10)	3130	-467	7694	43
H(11)	2797	-5	8824	46
H(12)	3376	2473	9399	46
H(13)	4295	4479	8848	37