Supporting information *for*

Synthesis of 2-trifluoromethyl benzimidazoles, -benzoxazoles, and -benzothiazoles via condensation of diamines or amino(thio)phenols with CF_3CN

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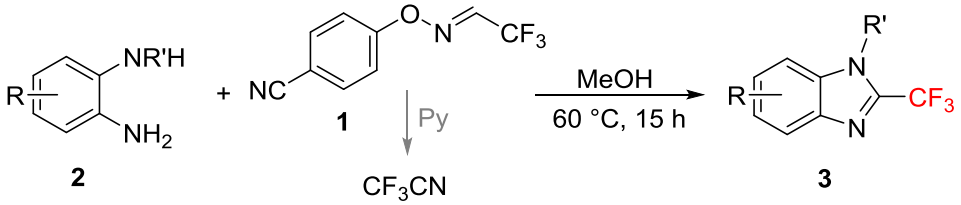
Table of Contents

General information

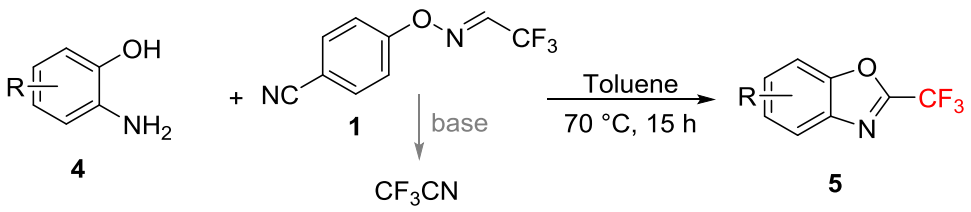
^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR (chloroform-*d* δ 7.26; DMSO-d_6 δ 2.50 ppm; methanol-d_4 δ 3.31 ppm), ^{13}C NMR (chloroform-*d* δ 77.0; DMSO-d_6 δ 39.52 ppm; methanol-d_4 δ 49.0 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Solvents are directly purchased commercially without further purification. The infrared(IR) spectra were recorded using a Nicolet iS 50 at room temperature. HRMS data were recorded on a high-resolution Thermo Scientific Exactive Plus instrument. 2,2,2-Trifluoroacetaldehyde *O*-(4′-cyanophenyl)oxime was prepared according to the published procedures.[1]

General procedure for the synthesis of 2-trifluoromethyl benzimidazoles (3)



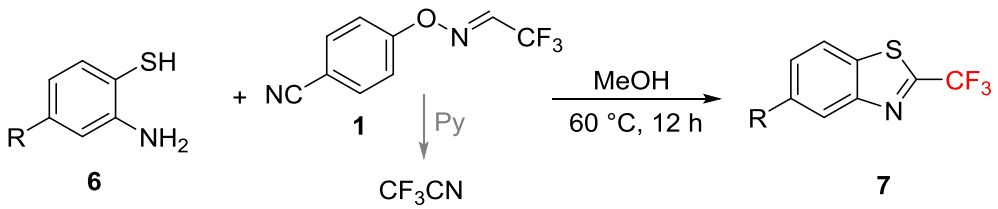
Diamines **2** (0.30 mmol), 2,2,2-trifluoroacetaldehyde *O*-(4′-cyanophenyl)oxime **1** (96.4 mg, 0.45 mmol, 1.5 equiv), MeOH (2 ml), and pyridine (35.6 mg, 1.5 mmol, 1.5 equiv) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 60 ℃ for 15 hours. After the reaction was terminated, the filtrate was vacuumed to remove the solvent. The crude product was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate as eluent to obtain 2-trifluoromethyl benzimidazoles **3**.

General procedure for the synthesis of 2-trifluoromethyl benzoxazoles (5)



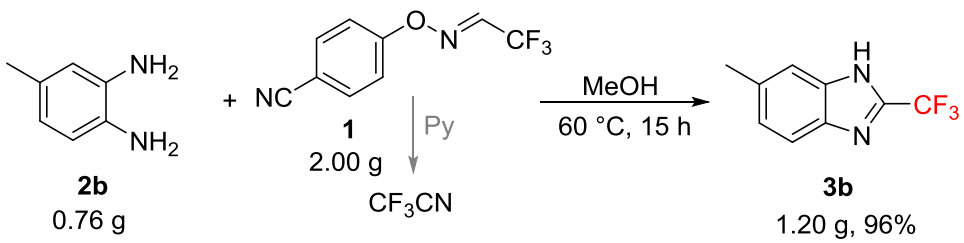
Aminophenols **4** (0.30 mmol), 2,2,2-trifluoroacetaldehyde *O*-(4′-cyanophenyl)oxime **1** (96.4 mg, 0.45 mmol, 1.5 equiv), toluene (2 ml), and pyridine (35.6 mg, 1.5 mmol, 1.5 equiv) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 70 ℃ for 15 hours. After the reaction was terminated, the resulting solution was vacuumed to remove the solvent. The crude product was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate as eluent to obtain 2-trifluoromethyl benzoxazoles **5**.

General procedure for the synthesis of 2-trifluoromethyl benzothiazoles (7)

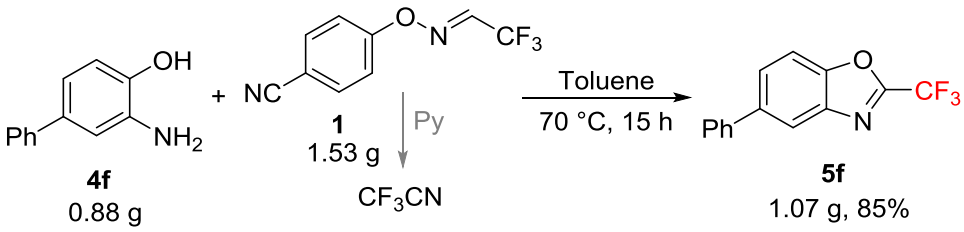


Aminothiophenols **6** (0.30 mmol), 2,2,2-trifluoroacetaldehyde *O*-(4′-cyanophenyl)oxime **1** (96.4 mg, 0.45 mmol, 1.5 equiv), MeOH (2 ml), and pyridine (36.6 mg, 1.5 mmol, 1.5 equiv) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 60 ℃ for 15 hours. After the reaction was terminated, the resulting solution was vacuumed to remove the solvent. The crude product was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate as eluent to obtain 2-trifluoromethyl benzothiazoles **7**.

Procedure for gram scale reaction

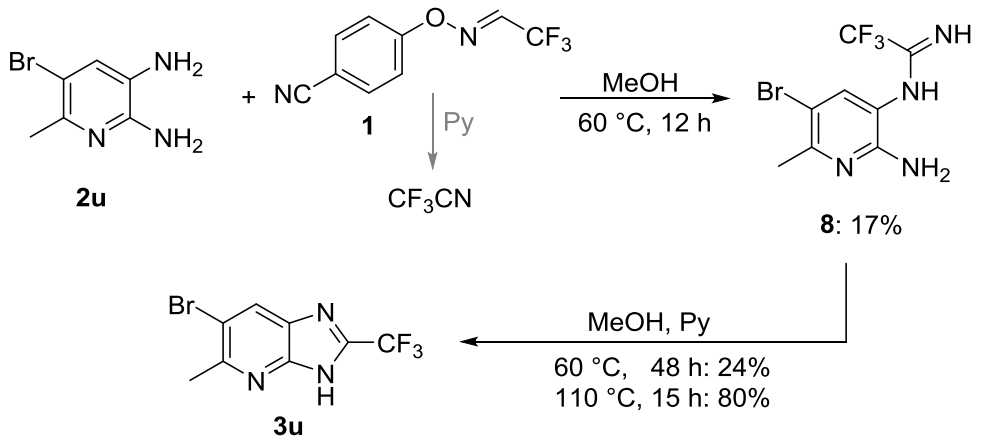


4-Methylbenzene-1,2-diamine **2b** (0.76 g, 6.25 mmol), 2,2,2-trifluoroacetaldehyde *O*-(4′-cyanophenyl)oxime **1** (2.00 g, 9.37 mmol, 1.5 equiv), MeOH (10 ml), and pyridine (1.11 g, 9.37 mmol, 1.5 equiv) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 60 ℃ for 15 hours. After the reaction was terminated, the resulting solution was vacuumed to remove the solvent. The crude product was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate as eluent to obtain 6-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole **3b** (1.20 g, 96%).



3-Amino-[1,1'-biphenyl]-4-ol **4f** (0.88 g, 4.75 mmol), 2,2,2-trifluoroacetaldehyde *O*-(4′-cyanophenyl)oxime **1** (1.53 g, 7.12 mmol, 1.5 equiv), toluene (10 ml), and pyridine (0.84 g, 7.12 mmol, 1.5 equiv) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 70 ℃ for 15 hours. After the reaction was terminated, the filtrate was vacuumed to remove the solvent. The crude product was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate as eluent to obtain 5-phenyl-2-(trifluoromethyl)benzo[*d*]oxazole **5f** (1.07, 85%).

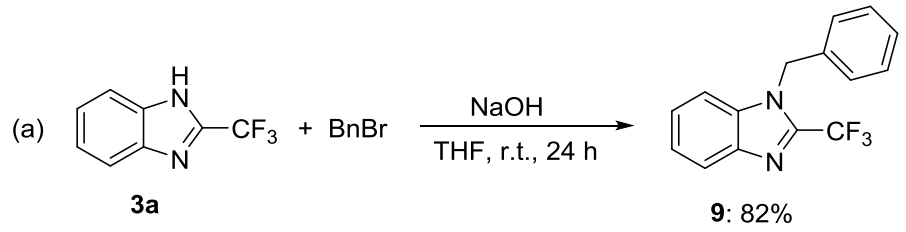
Control experiments



5-Bromo-6-methylpyridine-2,3-diamine **2u** (202.0 mg, 1.0 mmol), 2,2,2-trifluoroacetaldehyde *O*-(4′-cyanophenyl)oxime **1** (214.0 mg, 1.5 mmol, 1.5 equiv), MeOH (5 mL), and pyridine (118.6 mg, 1.5 mmol, 1.5 equiv) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 60 ℃ for 12 hours. After the reaction was terminated, the resulting solution was vacuumed to remove the solvent. The crude product was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate as eluent to obtain *N*-(2-amino-5-bromo-6-methylpyridin-3-yl)-2,2,2-trifluoroacetimidamide **8** (50.3 mg, 17%).

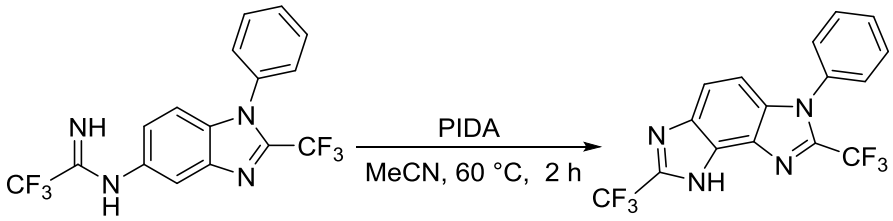
N-(2-amino-5-bromo-6-methylpyridin-3-yl)-2,2,2-trifluoroacetimidamide **8** (29.5 mg, 0.10 mmol), MeOH (1.0 mL), and pyridine (11.9 mg, 1.5 mmol, 1.5 equiv) were added to a reaction tube equipped with a stir bar. The reaction mixture was stirred at 60 ℃ for 48 hours or 110 ℃ for 15 hours. After the reaction was terminated, the resulting solution was vacuumed to remove the solvent. The crude product was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate as eluent to obtain 6-bromo-5-methyl-2-(trifluoromethyl)-3*H*-imidazo[4,5-*b*]pyridine **3u** (6.7 mg, 24% or 22.3 mg, 80%, respectively).

Elaboration of 2-trifluoromethyl benzimidazole products



3a **9**: 82%

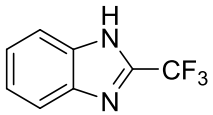
A Schlenk tube was charged with 2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole **3a** (186.1 mg, 1.0 mmol, 1.0 equiv), sodium hydroxide (40 mg, 1.0 mmol, 1.0 equiv), magnetic stir bar and 20 mL tetrahydrofuran (THF) in sequence. Then the reaction mixture is stirred for 10 minutes at room temperature. Bromomethylbenzene (171.0 mg, 118.8 μL, 1.0 mmol, 1.0 equiv) was added to the mixture. The mixture was allowed to stir overnight at room temperature. After the reaction was terminated, organic layer was extracted with ethyl acetate for 3 times and washed with water and brine. The solution was dried over sodium sulfate and concentrated. The residue was purification by flash column chromatography to obtain 1-benzyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**9**)[2] as a white solid in 82% yield (226.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.21 (m, 6H), 7.10 (d, *J* = 6.9 Hz, 2H), 5.51 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.5 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2 (s), 140.9 (q, *J* = 38.5 Hz), 135.6 (s), 134.9 (s), 129.0 (s), 128.3 (s), 126.3 (s), 125.6 (s), 123.8 (s), 121.6 (s), 119.2 (q, *J* = 271.4 Hz), 111.2 (s), 48.4 (q, *J* = 2.0 Hz). GC-MS (EI) m/z 276 (M^+).

(b) 

3z **10**: 90%

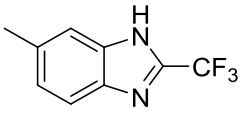
A Schlenk tube was charged with 2,2,2-trifluoro-*N*-(1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-5-yl)acetimida mide **3z** (37.2 mg, 0.10 mmol, 1.0 equiv), phenyliodine diacetate (PIDA) (38.6 mg, 0.12 mmol, 1.2 equiv), magnetic stir bar and 1 mL MeCN in sequence. Then the reaction mixture is stirred for 2 hours at 60 ^{o}C. After the reaction was terminated and the solution was concentrated. The residue was purification by flash column chromatography to obtain 6-phenyl-2,7-bis(trifluoromethyl)-1,6-dihydrobenzo[1,2-*d*:3,4-*d*']diimidazole (**10**) as a white solid in 90% yield (33.3 mg). Mp: 127.1 – 128.9 ℃. R_f (petroleum ether/ethyl acetate = 5:1) = 0.63. ^{1}H NMR (400 MHz, methanol-d_4) δ 7.73 – 7.65 (m, 4H), 7.61 – 7.54 (m, 2H), 7.14 (d, *J* = 9.0 Hz, 1H), N*H* was not observed. ^{19}F NMR (376 MHz, methanol-d_4) δ -61.5 (s, 3F), -65.1 (s, 3F). ^{13}C NMR (101 MHz, methanol-d_4) δ 139.8 (q, *J* = 39.8 Hz), 139.4 (q, *J* = 38.8 Hz), 135.0 (s), 134.3 (s), 130.1 (s), 130.0 (s), 129.7 (s), 127.4 (s), 127.3 (s), 119.0 (q, *J* = 269.5 Hz), 118.9 (q, *J* = 270.8 Hz), 112.6 (s), 111.5 (s), 108.5 (s). IR (ATR): ν 1635, 1514, 1413, 1340, 1134, 971 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_8F_6N_4$ $[M]^+$: 370.0648; found: 370.0649.

Data for compounds



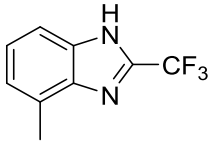
2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3a)[3]

Obtained as a white solid in 92% yield (51.4 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.93 (br s, 1H), 7.78 – 7.66 (m, 2H), 7.44 – 7.36 (m, 2H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.50 (q, J = 39.4 Hz), 138.4 (br), 124.6 (s), 119.5 (q, J = 270.4 Hz), 117.0 (br). GC-MS (EI) m/z 186 (M^+).



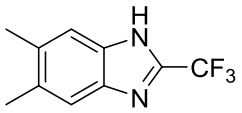
6-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3b)[4]

Obtained as a white solid in 99% yield (59.4 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.72 (br s, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.49 (s, 1H), 7.19 (d, J = 8.4 Hz, 1H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.1 (q, J = 39.1 Hz), 137.6 (br), 134.2 (s), 132.7 (s), 126.1 (s), 124.1 (s), 119.6 (q, J = 270.2 Hz), 116.7 (br), 21.7 (s). GC-MS (EI) m/z 200 (M^+).



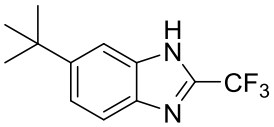
4-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3c)[5]

Obtained as a white solid in 85% yield (51.1 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.83 (br s, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.26 (t, J = 7.7 Hz, 1H), 7.15 (d, J = 7.3 Hz, 1H), 2.56 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.0 (q, J = 39.4 Hz), 138.8 (br), 136.9 (br), 127.5 (br), 126.1(s), 124.6 (d, J = 21.7 Hz), 119.6 (q, J = 270.4 Hz), 113.6 (br), 17.0 (s). GC-MS (EI) m/z 200 (M^+).



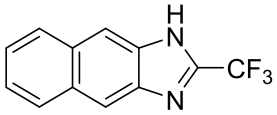
5,6-dimethyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3d)[4]

Obtained as a white solid in 89% yield (57.2 mg). ^{1}H NMR (400 MHz, methanol-d_4) δ 7.39 (s, 2H), 5.02 (br s, 1H), 2.34 (s, 6H). ^{19}F NMR (376 MHz, methanol-d_4) δ -65.5 (s, 3F). ^{13}C NMR (101 MHz, methanol-d_4) δ 139.6 (q, J = 40.2 Hz), 136.0 (br), 133.9 (s), 119.1 (q, J = 269.5 Hz), 115.4 (br), 19.1 (s). GC-MS (EI) m/z 214 (M^+).



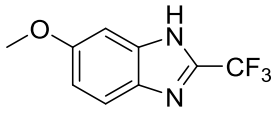
6-(*tert*-butyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3e)

Obtained as a white solid in 99% yield (71.9 mg). Mp: 157.3 – 158.6 ℃. R_f (petroleum ether/ethyl acetate = 5:1) = 0.70. ^{1}H NMR (400 MHz, methanol-d_4) δ 7.66 (s, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 5.04 (br s, 1H), 1.36 (s, 9H). ^{19}F NMR (376 MHz, methanol-d_4) δ -65.6 (s, 3F). ^{13}C NMR (101 MHz, methanol-d_4) δ 148.2 (s), 140.4 (q, J = 40.2 Hz), 137.3 (br), 135.7 (br), 122.8 (s), 119.0 (q, J = 269.8 Hz), 115.6 (br), 111.2 (br), 34.4 (s), 30.6 (s). IR (ATR): ν 2961, 1548, 1324, 1164, 1129, 983, 807, 651 cm^{-1}. HRMS (ESI) m/z: calcd. For $C_{12}H_{14}F_3N_2$ $[M + H]^+$: 243.1104; found: 243.1099.



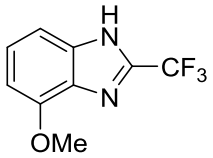
2-(trifluoromethyl)-1*H*-naphtho[2,3-*d*]imidazole (3f)[4]

Obtained as a white solid in 65% yield (46.1 mg). ^{1}H NMR (400 MHz, methanol-d_4) δ 8.13 (s, 2H), 8.01 – 7.84 (m, 2H), 7.45 – 7.26 (m, 2H), 4.99 (br s, 1H). ^{19}F NMR (376 MHz, methanol-d_4) δ -66.4 (s, 3F). ^{13}C NMR (101 MHz, methanol-d_4) δ 144.6 (q, J = 40.0 Hz), 137.5 (br), 131.4 (s), 127.7 (s), 124.4 (s), 118.8 (q, J = 270.7 Hz), 112.6 (br). GC-MS (EI) m/z 236 (M^+).



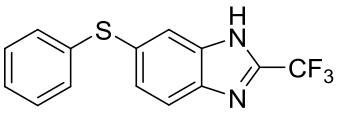
6-methoxy-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3g)[3, 5]

Obtained as a white solid in 92% yield (59.7 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 13.00 (br s, 1H), 7.68 – 7.58 (m, 1H), 7.19 – 6.95 (m, 2H), 3.86 (s, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -63.6 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 161.6 (s), 158.2 (s), 140.4 (q, J = 40.7 Hz), 134.3 (s), 119.8 (s), 118.9 (q, J = 270.6 Hz), 116.8 (s), 115.6 (s), 55.8 (s). GC-MS (EI) m/z 216 (M^+).



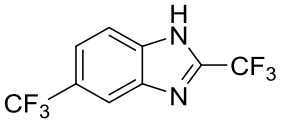
4-methoxy-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3h)[5]

Obtained as a white solid in 70% yield (45.4 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 12.08 (br s, 1H), δ 7.39 – 7.21 (m, 2H), 6.81 (d, J = 7.7 Hz, 1H), 3.94 (s, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -63.9 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 161.2 (s), 139.8 (q, J = 42.2 Hz), 134.1 (s), 119.7 (s), 118.7 (q, J = 270.6 Hz), 116.7 (s), 104.8 (br), 102.6 (s), 55.7 (s). GC-MS (EI) m/z 216 (M^+).



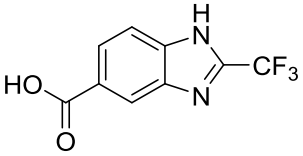
6-(phenylthio)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3i)

Obtained as a white solid in 96% yield (84.8 mg). Mp: 119.9 – 120.8 ℃. R_f (petroleum ether/ethyl acetate = 5:1) = 0.70. ^{1}H NMR (400 MHz, chloroform-*d*) δ 13.45 (br s, 1H), δ 7.76 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.40 – 7.21 (m, 5H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -63.8 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 141.9 (q, *J* = 41.0 Hz), 138.1 (br), 137.2 (br), 136.0 (s), 132.5 (s), 130.7 (s), 129.3 (s), 128.7 (s), 127.2 (s), 124.9 (s), 119.1 (br), 118.8 (q, *J* = 271.1 Hz). IR (ATR): ν 2826, 1544, 1439, 1308, 1142, 982, 807, 735, 688, 622, 592 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{14}H_{10}F_3N_2S$ $[M + H]^+$: 295.0511; found: 295.0508.



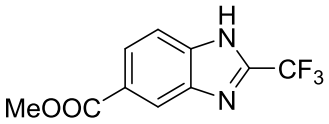
2,5-bis(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3j)[4]

Obtained as a white solid in 70% yield (53.4 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.47 (br s, 1H), 8.14 (s, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -59.4 (s, 3F), -63.2 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.0 (q, *J* = 39.8 Hz), 139.5 (br), 138.5 (br), 125.1 (q, *J* = 31.9 Hz), 125.0 (q, *J* = 271.8 Hz), 121.3 (s), 117.3 (br), 115.9 (br), 119.2 (q, *J* = 270.9 Hz). GC-MS (EI) m/z 254 (M^+).



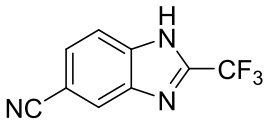
2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole-5-carboxylic acid (3k)[5]

Obtained as a brown solid in 74% yield (51.1 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.29 (br s, 1H), 12.93 (br s, 1H), 8.41 – 8.21 (m, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.79 (s, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.1 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.8 (s), 142.6 (q, J = 39.6 Hz), 136.9 (s), 129.9 (s), 127.1 (br), 125.6 (br), 122.4 (s), 120.2 (s), 119.2 (q, J = 270.8 Hz). GC-MS (EI) m/z 230 (M^+).



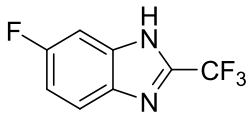
methyl 2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole-5-carboxylate (3l)[6]

Obtained as a white solid in 35% yield (25.6 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (s, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 3.85 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.4 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.6 (s), 140.6 (br), 138.6 (br), 142.8 (q, J = 39.8 Hz), 125.7 (s), 125.2 (s), 119.6 (br), 119.2 (q, J = 270.6 Hz), 116.3 (br), 52.5 (s). GC-MS (EI) m/z 244 (M^+).



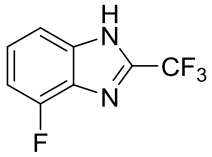
2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole-5-carbonitrile (3m)[7]

Obtained as a brown solid in 68% yield (28.7 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.46 (br s, 1H), 8.35 (s, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.3 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.4 (q, J = 40.0 Hz), 129.4 (s), 127.8 (s), 123.9 (br s), 123.1 (s), 121.7 (s), 119.7 (s), 119.1 (q, J = 271.0 Hz), 106.7 (s). GC-MS (EI) m/z 211 (M^+).



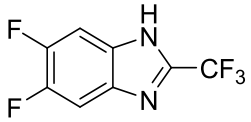
6-fluoro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3n)[4]

Obtained as a white solid in 92% yield (56.3 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.04 (br s, 1H), 7.80 – 7.70 (m, 1H), 7.59 – 7.46 (m, 1H), 7.28 – 7.19 (m, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.1 (s, 3F), δ -117.6 (s, 1F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.0 (d, J = 239.2 Hz), 141.7 (q, J = 40.7, 39.5 Hz), 138.2 (br), 135.2 (br), 119.3 (q, J = 270.5 Hz), 118.6 (br), 113.2 (d, J = 26.1 Hz), 102.5 (br). GC-MS (EI) m/z 204 (M^+).



4-fluoro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3o)[4]

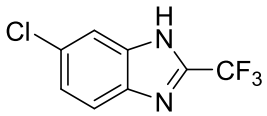
Obtained as a white solid in 83% yield (50.8 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.29 (br s, 1H), 7.50 (s, 1H), 7.39 (s, 1H), 7.18 (s, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.9 (s, 3F), -127.7 (s, 1F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.2 (d, J = 252.5 Hz), 141.1 (q, J = 39.9 Hz), 138.6 (br), 129.5 (br), 125.9 (d, J = 7.1 Hz), 119.2 (q, J = 270.7 Hz), 111.1 (br), 109.0 (d, J = 16.7 Hz). GC-MS (EI) m/z 204 (M^+).



5,6-difluoro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3p)[4]

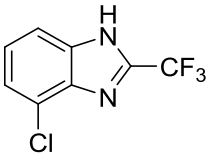
Obtained as a white solid in 82% yield (54.6 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.76 (br s, 1H), 7.92 – 7.72 (m, 2H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.0 (s, 3F), -140.7 (s, 2F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.6 (dd, J = 242.5, 15.9 Hz), 142.2 (q, J = 40.0 Hz), 133.6 (s), 119.1 (q, J = 270.4 Hz), 104.7 (br). GC-MS (EI) m/z

222 (M^+).



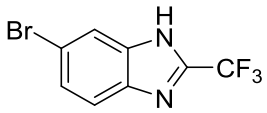
6-chloro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3q)[4]

Obtained as a white solid in 83% yield (54.9 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.97 (br s, 1H), 7.79 (s, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.1 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.7 (q, *J* = 39.6 Hz), 139.1 (br), 136.9 (br), 128.9 (s), 125.0 (s), 119.3 (q, *J* = 270.7 Hz), 118.4 (br), 116.8 (br). GC-MS (EI) m/z 220 (M^+).



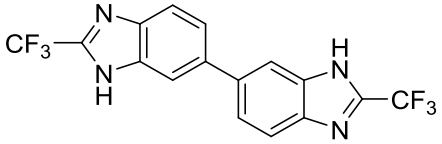
4-chloro-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3r)

Obtained as a white solid in 96% yield (63.5 mg). R_f (petroleum ether/ethyl acetate = 5:1) = 0.53. ^{1}H NMR (400 MHz, chloroform-*d*) δ 14.16 (br s, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -63.8 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 141.9 (q, *J* = 41.3 Hz), 138.2 (br), 135.9 (br), 125.7 (s), 124.9 (s), 124.3 (s), 118.7 (q, *J* = 271.3 Hz), 112.4 (br). IR (ATR): ν 2983, 2905, 2758, 1708, 1456, 1316, 1199, 1139, 1043, 954, 784, 745, 612 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_8H_5ClF_3N_2$ $[M + H]^+$: 221.0088; found: 221.0084.



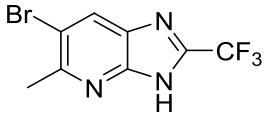
6-bromo-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3s)[4]

Obtained as a White solid in 90% yield (71.56 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.17 (br s, 1H), 7.93 (d, J = 6.1 Hz, 1H), 7.67 (t, J = 7.9 Hz, 1H), 7.60 – 7.39 (m, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.1 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.5 (q, J = 39.6 Hz), 139.7 (br), 136.8 (br), 127.6 (s), 119.7 (br), 119.2 (q, J = 270.7 Hz), 118.9 (br), 116.8 (s). GC-MS (EI) m/z 264 (M^+).



2,2'-bis(trifluoromethyl)-3*H*,3'*H*-5,5'-bibenzo[*d*]imidazole (3t)[4]

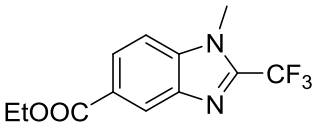
Obtained as a Brown solid in 80% yield (88.86 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.05 (br s, 2H), 8.70 – 7.30 (m, 6H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.8 (s, 6F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.1 (q, J = 39.3 Hz), 137.6 (s), 134.7 (br), 124.7 (br), 124.3 (br), 119.9 (s), 119.5 (q, J = 270.4 Hz), 116.9 (s). GC-MS (EI) m/z 370 (M^+).



6-bromo-5-methyl-2-(trifluoromethyl)-3*H*-imidazo[4,5-*b*]pyridine (3u)

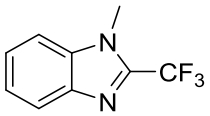
Obtained as a white solid in 36% yield (30.2 mg). Mp: 174.4 – 175.0 ℃. R_f (petroleum ether/ethyl acetate = 5:1) = 0.36. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (s, 1H), 2.66 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.4 (s, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.9 (s), 148.3 (s), 142.4 (q, J = 40.1 Hz), 130.5 (s), 119.1 (q, J = 270.9 Hz), 116.8 (s), 115.9 (s), 25.7 (s). IR (ATR): ν 3066, 2949, 2784, 2691, 1545,

1450, 1356, 1258, 1187, 1137, 988, 956, 780, 727, 670, 552 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_8H_6BrF_3N_3$ $[M + H]^+$: 279.9692; found: 279.9690.



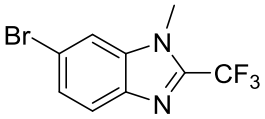
ethyl 1-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole-5-carboxylate (3v)[5]

Obtained as a white solid in 80% yield (65.3 mg). ^{1}H NMR (400 MHz, chloroform-d) δ 8.59 (s, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 3.98 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, chloroform-d) δ -62.9 (s, 3F). ^{13}C NMR (101 MHz, chloroform-d) δ 166.5 (s), 142.5 (q, *J* = 39.0 Hz), 140.6 (s), 138.9 (s), 126.5 (s), 126.4 (s), 124.0 (s), 118.8 (q, *J* = 271.6 Hz), 109.9 (s), 61.2 (s), 31.1 (s), 14.3 (s). GC-MS (EI) m/z 272 (M^+).



1-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3w)[4]

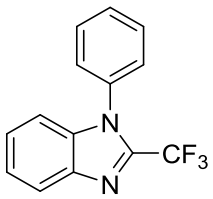
Obtained as a white solid in 79% yield (47.4 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.91 – 7.82 (m, 1H), 7.61 – 7.21 (m, 3H), 4.09 – 3.61 (m, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 140.9 (s), 140.4 (q, *J* = 38.5 Hz), 136.0 (s), 125.3 (s), 123.6 (s), 121.5 (s), 119.1 (q, *J* = 271.2 Hz), 110.1 (s), 30.7 (s). GC-MS (EI) m/z 200 (M^+).



6-bromo-1-methyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3x)

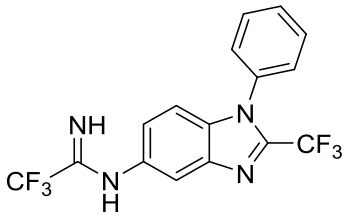
Obtained as a white solid in 40% yield (33.7 mg). Mp: 134.7 – 135.2 ℃. R_f

(petroleum ether/ethyl acetate = 5:1) = 0.76. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.70 (d, *J* = 8.7 Hz, 1H), 7.59 (s, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 141.4 (q, *J* = 38.8 Hz), 139.8 (s), 136.9 (s), 127.2 (s), 122.8 (s), 118.8 (s), 118.7 (q, *J* = 271.5 Hz), 113.3 (s), 30.9 (d, *J* = 2.2 Hz). IR (ATR): ν 2957, 2924, 1614, 1522, 1479, 1405, 1259, 1221, 1117, 1081, 822, 728, 646, 596 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_7BrF_3N_2$ $[M + H]^+$: 278.9739; found: 278.9737.



1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3y)[4]

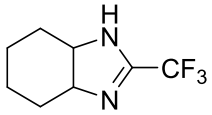
Obtained as a yellow liquid in 73% yield (57.4 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.47 – 7.33 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 1H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -60.5 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 140.8 (q, *J* = 38.5 Hz), 140.7 (s), 137.3 (s), 134.4 (s), 129.9 (s), 129.8 (s), 127.4 (s), 125.9 (s), 124.1 (s), 121.4 (s), 118.9 (q, *J* = 271.9 Hz), 111.2 (s). GC-MS (EI) m/z 262 (M^+).



2,2,2-trifluoro-*N*-(1-phenyl-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-5-yl)acetimidamide (3z)

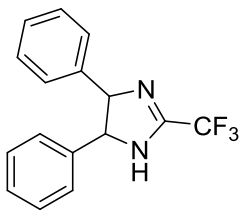
Obtained as a white solid in 41% yield (45.8 mg). Mp: 185.4 – 186.6 ℃. R_f (petroleum ether/ethyl acetate = 5:1) = 0.59. ^{1}H NMR (400 MHz, chloroform-*d*) δ

7.65 – 7.59 (m, 3H), 7.49 – 7.38 (m, 3H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 5.25 (s, 2H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -60.5 (s, 3F), -73.1 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 146.1 (q, *J* = 35.5 Hz), 142.2 (d, *J* = 175.5 Hz), 141.3 (q, *J* = 38.3 Hz), 134.4 (s), 134.2 (s), 130.1 (s), 129.9 (s), 127.3 (s), 120.6 (s), 118.7 (q, *J* = 272.0 Hz), 118.2 (q, *J* = 278.0 Hz), 116.4, 112.5 (s), 111.8 (s). IR (ATR): ν 3276, 3093, 1674, 1499, 1440, 1262, 1195, 1134, 876, 762, 696, 653, 626, 536, 487, 441 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{16}H_{11}F_6N_4$ $[M + H]^+$: 373.0882; found: 373.0879.



2-(trifluoromethyl)-3a,4,5,6,7,7a-hexahydro-1*H*-benzo[*d*]imidazole (3aa)

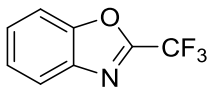
Obtained as a white solid in 60% yield (34.6 mg). Mp: 114.0 – 115.2 ℃. R_f (petroleum ether/ethyl acetate = 5:1) = 0.63. ^{1}H NMR (400 MHz, chloroform-*d*) δ 5.27 (s, 1H), 3.13 (d, *J* = 8.1 Hz, 2H), 2.50 – 2.01 (m, 2H), 1.84 (d, *J* = 9.9 Hz, 2H), 1.60 – 1.15 (m, 4H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -70.1 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 156.7 (q, *J* = 37.3 Hz), 118.0 (q, *J* = 274.3 Hz), 72.6 (s), 67.5 (s), 30.3 (s), 25.2 (s), 24.2 (s). IR (ATR): ν 3121, 2937, 2860, 1716, 1603, 1186, 1138, 1077, 969, 740 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_8H_{12}F_3N_2$ $[M + H]^+$: 193.0947; found: 193.0948.



4,5-diphenyl-2-(trifluoromethyl)-4,5-dihydro-1*H*-imidazole (3ab)

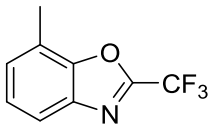
Obtained as a white solid in 88% yield (76.6 mg). Mp: 160.4 – 161.2 ℃. R_f (petroleum ether/ethyl acetate = 8:1) = 0.59. ^{1}H NMR (400 MHz, chloroform-*d*) δ

7.66 – 6.87 (m, 10H), 5.69 (br s, 1H), 5.23 – 4.72 (m, 2H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -69.4 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 154.3 (q, *J* = 37.5 Hz), 141.4 (s), 128.9 (s), 128.1 (s), 126.4 (s), 117.7 (q, *J* = 274.9 Hz), 79.9 (s), 69.8 (s). IR (ATR): ν 3089, 2857, 1629, 1515, 1455, 1385, 1157, 1146, 1078, 1007, 925, 751, 691, 614, 523 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{16}H_{14}F_3N_2$: 291.1104; found: 291.1100.



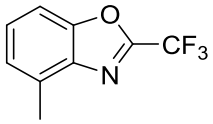
2-(trifluoromethyl)benzo[*d*]oxazole (5a)[3]

Obtained as a yellow oil in 80% yield (44.9 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.47 (m, 2H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.3 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 151.7 (q, *J* = 43.6 Hz), 150.6 (s), 139.4 (s), 127.9 (s), 125.9 (s), 121.9 (s), 116.8 (q, *J* = 271.7 Hz), 111.6 (s). GC-MS (EI) m/z 187 (M^+).



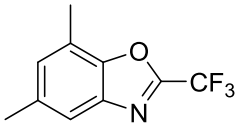
7-methyl-2-(trifluoromethyl)benzo[*d*]oxazole (5b)

Obtained as a yellow oil in 90% yield (54.3 mg). R_f (petroleum ether/ethyl acetate = 10:1) = 0.41. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.73 – 7.65 (m, 1H), 7.42 – 7.31 (m, 2H), 2.60 (s, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.3 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 151.4 (q, *J* = 43.4 Hz), 149.9 (s), 138.9 (s), 134.2 (s), 128.7 (s), 125.9 (s), 118.9 (s), 116.9 (q, *J* = 271.6 Hz), 14.9 (s). IR (ATR): ν 3235, 2959, 2227, 1736, 1609, 1587, 1513, 1374, 1286, 1241, 1168, 1045, 839, 548, 523 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_7F_3NO$ $[M + H]^+$: 202.0474; found: 202.0473.



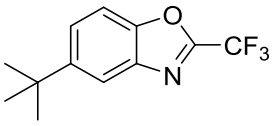
4-methyl-2-(trifluoromethyl)benzo[*d*]oxazole (5c)

Obtained as a yellow oil in 92% yield (56.7 mg). R_f (petroleum ether/ethyl acetate = 10:1) = 0.42. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.51 – 7.39 (m, 2H), 7.28 (d, *J* = 6.8 Hz, 1H), 2.68 (s, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.2 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 150.9 (q, *J* = 43.4 Hz), 150.4 (s), 138.8 (s), 132.7 (s), 127.5 (s), 126.3 (s), 116.9 (q, *J* = 271.5 Hz), 108.8 (s), 16.3 (s). IR (ATR): ν 2928, 1632, 1586, 1370, 1317, 1227, 1203, 1158, 1118, 777, 755 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_7F_3NO$ $[M + H]^+$: 202.0474; found: 202.0475.



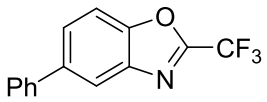
5,7-dimethyl-2-(trifluoromethyl)benzo[*d*]oxazole (5d)

Obtained as a white solid in 92% yield (59.4 mg). Mp: 40.8 – 41.2 ℃. R_f (petroleum ether/ethyl acetate = 10:1) = 0.48. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.46 (s, 1H), 7.14 (s, 1H), 2.54 (s, 3H), 2.47 (s, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.3 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 151.4 (q, *J* = 43.3 Hz), 148.3 (s), 139.2 (s), 135.9 (s), 130.0 (s), 121.6 (s), 118.6 (s), 116.9 (q, *J* = 271.4 Hz), 21.4 (s), 14.9 (s). IR (ATR): ν 2927, 1366, 1315, 1204, 1153, 1141, 1110, 941, 849, 750, 597, 564 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{10}H_9F_3NO$ $[M + H]^+$: 216.0631; found: 216.0629.



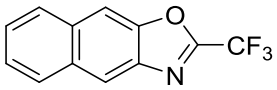
5-(*tert*-butyl)-2-(trifluoromethyl)benzo[*d*]oxazole (5e)

Obtained as a colorless oil in 90% yield (65.7 mg). R_f (petroleum ether/ethyl acetate = 10:1) = 0.48. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.89 (s, 1H), 7.72 – 7.50 (m, 2H), 1.41 (s, 9H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.3 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 151.8 (q, *J* = 43.4 Hz), 149.8 (s), 148.7 (s), 139.4 (s), 125.8 (s), 118.1 (s), 116.9 (q, *J* = 271.5 Hz), 110.8 (s), 35.1 (s), 31.6 (s). IR (ATR): ν 2964, 1482, 1365, 1210, 1158, 1135, 1105, 943, 837, 812, 745, 652 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{12}H_{13}F_3NO$ $[M + H]^+$: 244.0945; found: 244.0944.



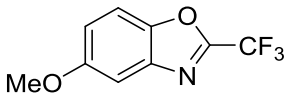
5-phenyl-2-(trifluoromethyl)benzo[*d*]oxazole (5f)[8]

Obtained as a white solid in 88% yield (69.5 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.07 (s, 1H), 7.86 – 7.70 (m, 2H), 7.66 – 7.60 (m, 2H), 7.57 – 7.40 (m, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.2 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 152.2 (q, *J* = 43.7 Hz), 150.1 (s), 140.2 (s), 140.1 (s), 140.0 (s), 129.1 (s), 127.8 (s), 127.5 (s), 120.1 (s), 116.8 (q, *J* = 271.8 Hz), 111.7 (s). GC-MS (EI) m/z 263 (M^+).



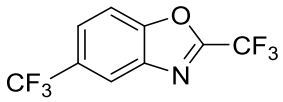
2-(trifluoromethyl)naphtho[2,3-*d*]oxazole (5g)

Obtained as a brown solid in 65% yield (46.3 mg). Mp: 110.8 – 111.1 ℃. R_f (petroleum ether/ethyl acetate = 10:1) = 0.45. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.36 (s, 1H), 8.08 – 7.97 (m, 3H), 7.62 – 7.53 (m, 2H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.7 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 153.6 (q, *J* = 43.6 Hz), 148.9 (s), 138.7 (s), 132.8 (s), 131.7 (s), 128.9 (s), 128.1 (s), 126.8 (s), 125.6 (s), 120.1 (s), 116.8 (q, *J* = 272.2 Hz), 107.8 (s). IR (ATR): ν 2981, 1738, 1626, 1401, 1338, 1240, 1209, 1152, 1123, 1078, 1045, 936, 865, 841, 749, 736, 551 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{12}H_7F_3NO$ $[M + H]^+$: 238.0474; found: 238.0473.



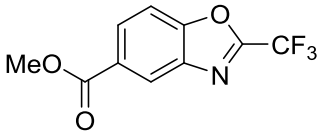
5-methoxy-2-(trifluoromethyl)benzo[*d*]oxazole (5h)

Obtained as a colorless oil in 82% yield (53.4 mg). R_f (petroleum ether/ethyl acetate = 10:1) = 0.43. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.54 (d, *J* = 9.1 Hz, 1H), 7.30 (d, *J* = 2.6 Hz, 1H), 7.16 – 7.10 (m, 1H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.3 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 158.3 (s), 152.2 (q, *J* = 43.4 Hz), 145.2 (s), 140.3 (s), 117.3 (s), 116.8 (q, *J* = 271.5 Hz), 111.9 (s), 103.6 (s), 55.9 (s). IR (ATR): ν 2943, 1737, 1485, 1371, 1269, 1207, 1147, 1119, 1023, 945, 833, 807, 741, 626 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_7F_3NO_2$ $[M + H]^+$: 218.0423; found: 218.0422.



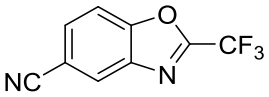
2,5-bis(trifluoromethyl)benzo[*d*]oxazole (5i)

Obtained as a colorless oil in 40% yield (30.6 mg). R_f (petroleum ether/ethyl acetate = 10:1) = 0.84. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.21 (s, 1H), 7.96 – 7.64 (m, 2H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -61.5 (s, 3F), -66.4 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 153.3 (q, *J* = 44.3 Hz), 139.5 (s), 129.0 (q, *J* = 33.4 Hz), 125.2 (q, *J* = 3.6 Hz), 125.2 (s), 123.6 (q, *J* = 272.4 Hz), 119.8 (q, *J* = 4.1 Hz), 116.5 (q, *J* = 272.0 Hz), 112.5 (s). IR (ATR): ν 1586, 1436, 1371, 1324, 1271, 1217, 1162, 1128, 1099, 1047, 893, 821, 669 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_4F_6NO$ $[M + H]^+$: 256.0192; found: 256.0191.



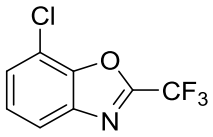
methyl 2-(trifluoromethyl)benzo[*d*]oxazole-5-carboxylate (5j)

Obtained as a white solid in 40% yield (29.4 mg). Mp: 55.8 – 56.7 ℃. R_f (petroleum ether/ethyl acetate = 10:1) = 0.76. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.60 (s, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 7.76 – 7.72 (m, 1H), 4.01 (s, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.3 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 166.0 (s), 153.2 (s), 152.9 (q, *J* = 44.1 Hz), 139.5 (s), 129.5 (s), 128.6 (s), 124.0 (s), 116.6 (q, *J* = 272.3 Hz), 111.6 (s), 52.6 (s). IR (ATR): ν 2957, 1726, 1435, 1307, 1297, 1211, 1159, 1100, 941, 766, 752 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{10}H_7F_3NO_3$ $[M + H]^+$: 246.0373; found: 246.0374.



2-(trifluoromethyl)benzo[*d*]oxazole-5-carbonitrile (5k)

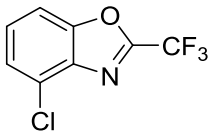
Obtained as a white solid in 40% yield (25.5 mg). Mp: 110.9 – 112.6 ℃. R_f (petroleum ether/ethyl acetate = 5:1) = 0.75. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.27 (s, 1H), 7.97 – 7.74 (m, 2H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.3 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 153.7 (q, *J* = 44.5 Hz), 152.7 (s), 139.8 (s), 131.6 (s), 126.9 (s), 117.7 (s), 116.3 (q, *J* = 272.5 Hz), 113.3 (s), 110.5 (s). IR (ATR): ν 2984, 1736, 1372, 1235, 1166, 1096, 1044, 938, 846, 631 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_4F_3N_2O$ $[M + H]^+$: 213.0275; found: 213.0270.



7-chloro-2-(trifluoromethyl)benzo[*d*]oxazole (5l)

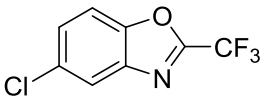
Obtained as a yellow oil in 65% yield (43.0 mg). R_f (petroleum ether/ethyl acetate = 10:1) = 0.47. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.86 – 7.76 (m, 1H), 7.60 – 7.51

(m, 1H), 7.50 – 7.41 (m, 1H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.1 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 152.0 (q, *J* = 44.3 Hz), 147.3 (s), 140.6 (s), 128.2 (s), 126.7 (s), 120.3 (s), 117.1 (s), 116.5 (q, *J* = 272.1 Hz). IR (ATR): ν 2957, 2925, 2855, 1723, 1460, 1266, 1101, 1019, 967, 800, 731 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_8H_4ClF_3NO$ $[M + H]^+$: 221.9928; found: 221.9929.



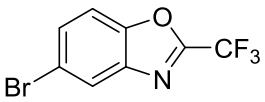
4-chloro-2-(trifluoromethyl)benzo[*d*]oxazole (5m)

Obtained as a colorless oil in 84% yield (55.8 mg). R_f (petroleum ether/ethyl acetate = 5:1) = 0.84. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.63 – 7.58 (m, 1H), 7.54 – 7.47 (m, 2H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.1 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 152.1 (q, *J* = 44.3 Hz), 151.2 (s), 137.5 (s), 128.4 (s), 126.8 (s), 126.3 (s), 116.6 (q, *J* = 272.1 Hz), 110.3 (s). IR (ATR): ν 2927, 1615, 1418, 1372, 1208, 1156, 1110, 952, 781, 747, 648 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_8H_4ClF_3NO$ $[M + H]^+$: 221.9928; found: 221.9929.



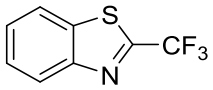
5-chloro-2-(trifluoromethyl)benzo[*d*]oxazole (5n)[8]

Obtained as a yellow oil in 72% yield (47.9 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88 (d, *J* = 2.1 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.55 – 7.51 (m, 1H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.4 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 152.9 (q, *J* = 44.0 Hz), 149.1 (s), 140.4 (s), 131.7 (s), 128.5 (s), 121.9 (s), 117.9 (q, *J* = 272.2 Hz), 112.5 (s). GC-MS (EI) m/z 221 (M^+).



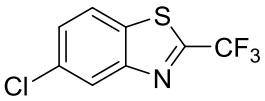
5-bromo-2-(trifluoromethyl)benzo[*d*]oxazole (5o)[8]

Obtained as a white solid in 88% yield (70.2 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.05 (d, *J* = 1.9 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.58 (d, *J* = 8.8 Hz, 1H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -66.3 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 152.7 (q, *J* = 44.1 Hz), 149.6 (s), 140.9 (s), 131.2 (s), 124.9 (s), 118.9 (s), 116.5 (q, *J* = 272.1 Hz), 112.9 (s). GC-MS (EI) m/z 265 (M^+).



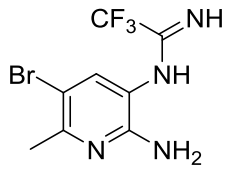
2-(trifluoromethyl)benzo[*d*]thiazole (7a)[9]

Obtained as a colorless oil in 84% yield (50.4 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.23 – 8.14 (m, 1H), 8.00 – 7.93 (m, 1H), 7.63 – 7.50 (m, 2H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -61.7 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 155.9 (q, *J* = 40.5 Hz), 152.1 (s), 135.0 (s), 127.5 (s), 127.3 (s), 125.0 (s), 122.0 (s), 119.9 (q, *J* = 273.2 Hz). GC-MS (EI) m/z 203 (M^+).



5-chloro-2-(trifluoromethyl)benzo[*d*]thiazole (7b)[9]

Obtained as a yellow oil in 90% yield (63.9 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.21 (d, *J* = 2.0 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.55 (m, 1H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -61.9 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 157.8 (q, *J* = 40.8 Hz), 152.9 (s), 133.7 (s), 133.2 (s), 128.3 (s), 124.8 (s), 122.8 (s), 119.5 (q, *J* = 273.6 Hz). GC-MS (EI) m/z 237 (M^+).



_N_-(2-amino-5-bromo-6-methylpyridin-3-yl)-2,2,2-trifluoroacetimidamide (8)

Obtained as a white solid in 17% yield (15.1 mg). Mp: 152.7 – 153.4 ℃. R_f (petroleum ether/ethyl acetate = 5:1) = 0.31. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.21 (s, 1H), 5.55 (s, 2H), 4.61 (s, 2H), 2.43 (s, 3H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -72.9 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 150.8 (s), 150.4 (s), 146.8 (q, *J* = 35.7 Hz), 130.4 (s), 125.5 (s), 117.9 (q, *J* = 278.0 Hz), 107.6 (s), 23.8 (s). IR (ATR): ν 3404, 3072, 1671, 1598, 1453, 1428, 1219, 1200, 1148, 987, 902, 723, 701, 636, 513 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_8H_9BrF_3N_4$ $[M + H]^+$: 296.9957; found: 296.9958.

Crystal structure analyses

The crystal samples of **3z**, **8**, and **10** were prepared by slow volatilization in ethyl acetate. The suitable crystals of **3z** (CCDC 2251314), **8** (CCDC 2251569), and **10** (CCDC 2251569) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 ℃, using MoKα radiation (λ 0.71073 Å) and CuKα radiation (λ 1.54184 Å). The data was corrected for Lorentz and polarisation effect with the **SMART** suite of programs and for absorption effects with SADABS.[10] Structure solution and refinement were carried out with the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

Note: Some Alert level A and Alert B were appeared in the check cif file of compound **8**. We still did not solve the alert when we tried to give additional refinement cycles or use new space group. But we have given sufficient evidence to prove the accuracy of this structure by ^{1}H, ^{13}C and ^{19}F NMR as well as high resolution mass spectra.

Table S1. Crystal data and structure refinement for compounds

Compound	**3z** (CCDC 2251314)	**8** (CCDC 2251569)	**10** (CCDC 2260578)
Empirical formula	$C_{16}H_{10}F_6N_4$	$C_8H_8BrF_3N_4$	$C_{16}H_8F_6N_4{\cdot}H_2O$
Formula weight	372.28	297.09	388.28
Temperature/K	293(2)	293(2)	293(2)
Wavelength/Å	1.54184	1.15184	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic
a/Å	10.1807(3)	29.3359(4)	14.5247(5)
b/Å	21.2316(5)	9.24130(10)	7.3697(3)
c/Å	16.3707(4)	38.2126(6)	15.8219(6)
α/°	90	90	90
β/°	104.958 (3)	90.0520(10)	102.633(4)
γ/°	90	90	90
Volume/$Å^3$	3418.66(16)	10359.5(2)	1652.62(11)
Z	8	32	4
Density (calc.)/cm^3	1.447	1.524	1.561
Absorption coefficient /mm^{-1}	1.199	4.544	1.314
F(000)	1504.0	4672.0	784.0
Crystal size/mm	0.10 × 0.10× 0.10	0.10 × 0.10× 0.05	0.10 × 0.05× 0.05
Theta range for data collection / °	6.97~136.458	4.624~136.55	3.127~67.5070
Reflections collected	8658	38924	7782
Independent reflections	3105 [R(int) = 0.0434]	17263 [R(int) = 0.0752]	2986 [R(int) = 0.1052]
Data/restraints/parameters	3105 / 48 /239	17263 / 0 /1184	2986/0/252
Goodness-of-fit on F^2	1.070	1.414	1.060
Final R indexes [I>=2σ (I)]	0.0998	0.1209	0.0958
Final R indexes [all data]	0.1253	0.1346	0.1317
Largest diff. peak and hole / e $Å^{-3}$	0.57/-0.46	2.08/-2.01	0.30/-0.40

ORTEP diagrams

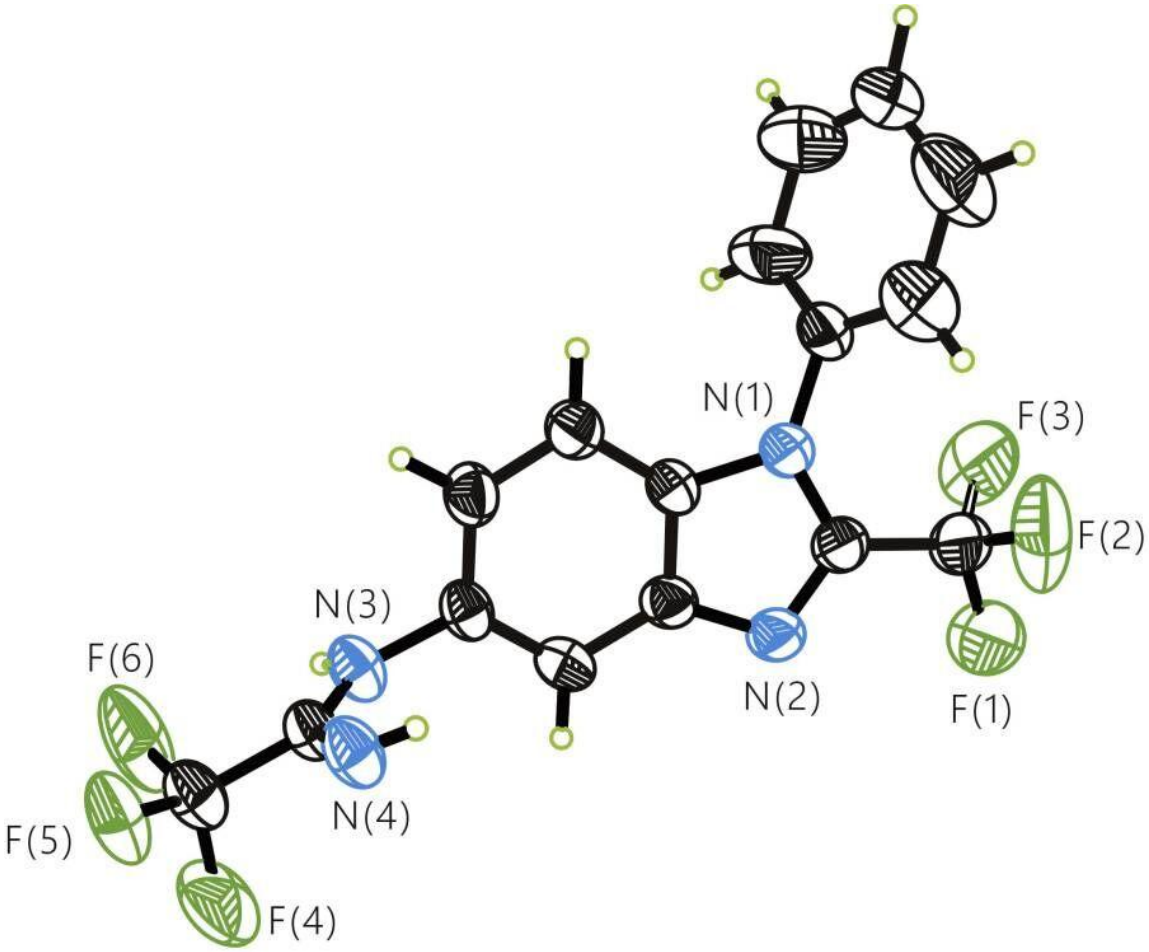


Figure S1. ORTEP diagram of 3z with thermal ellipsoids at the 40% probability level

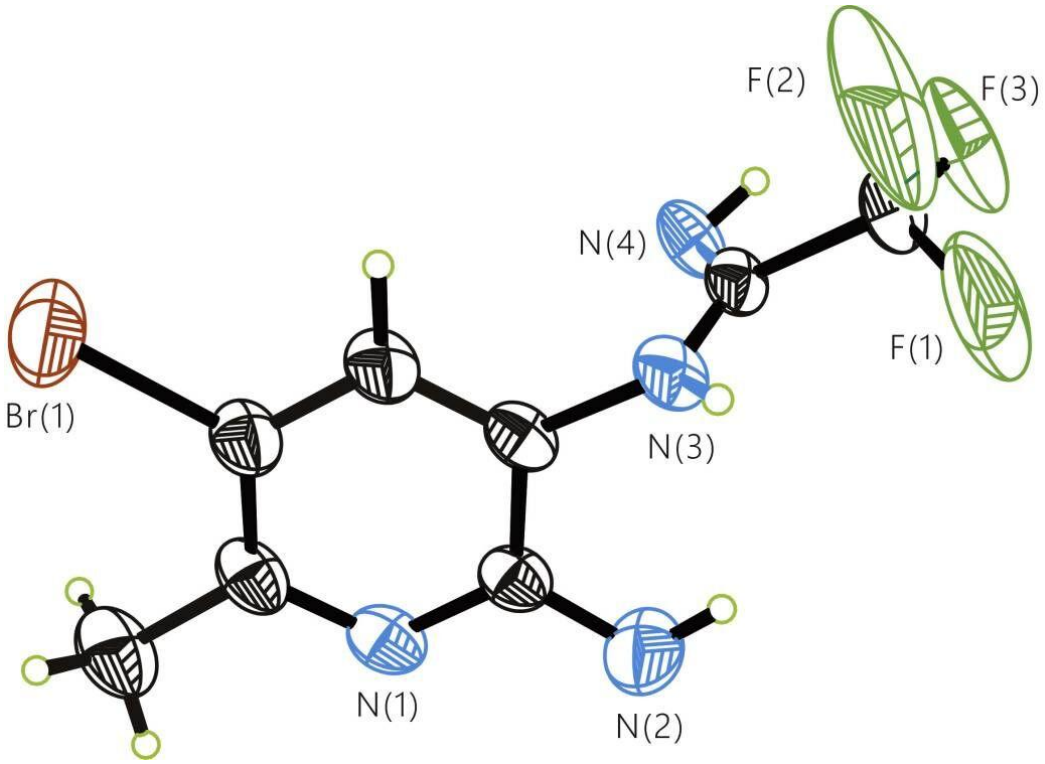


Figure S2. ORTEP diagram of 8 with thermal ellipsoids at the 40% probability level

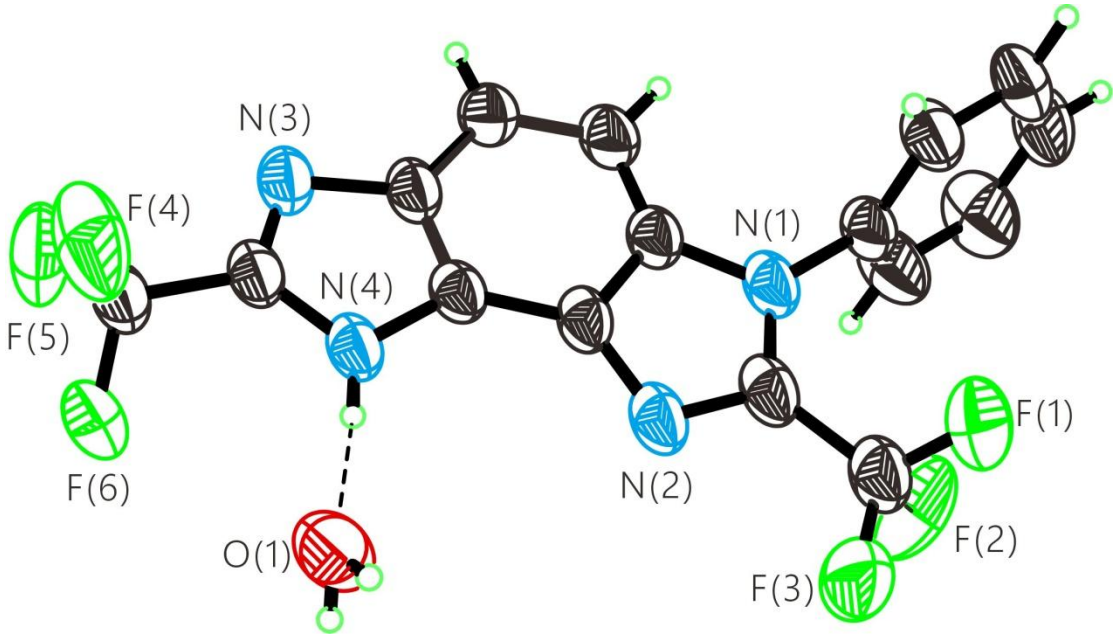


Figure S3. ORTEP diagram of 10·H_2O with thermal ellipsoids at the 40% probability level

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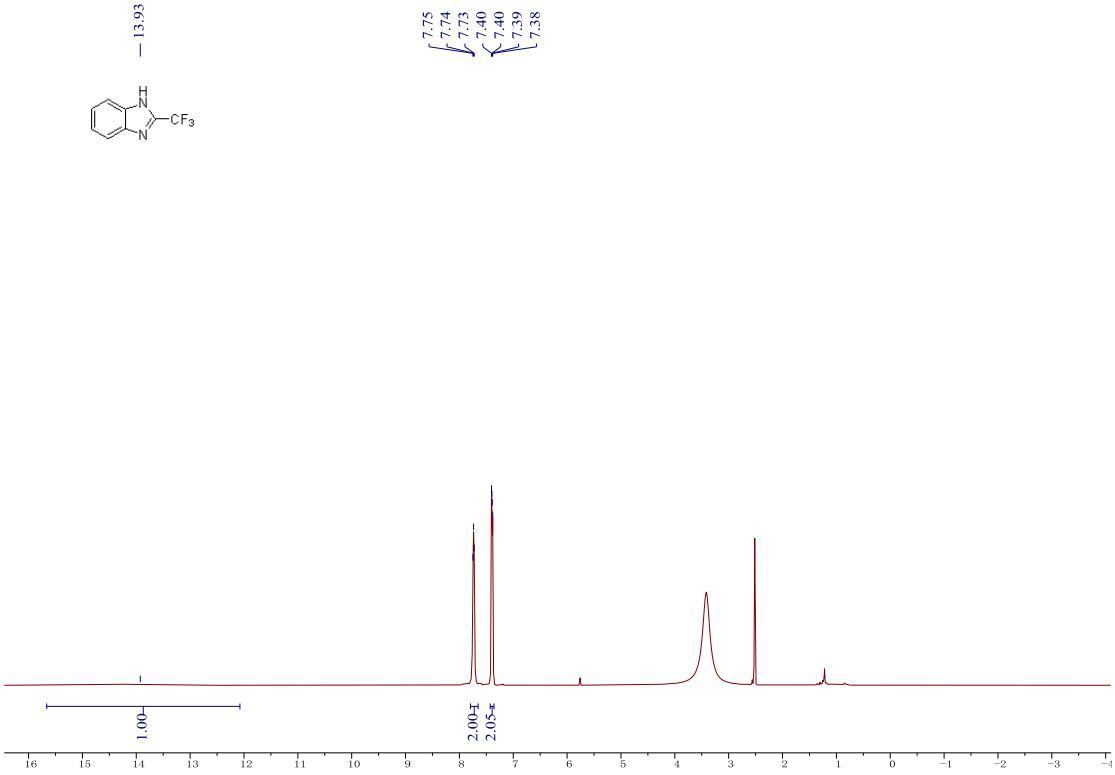
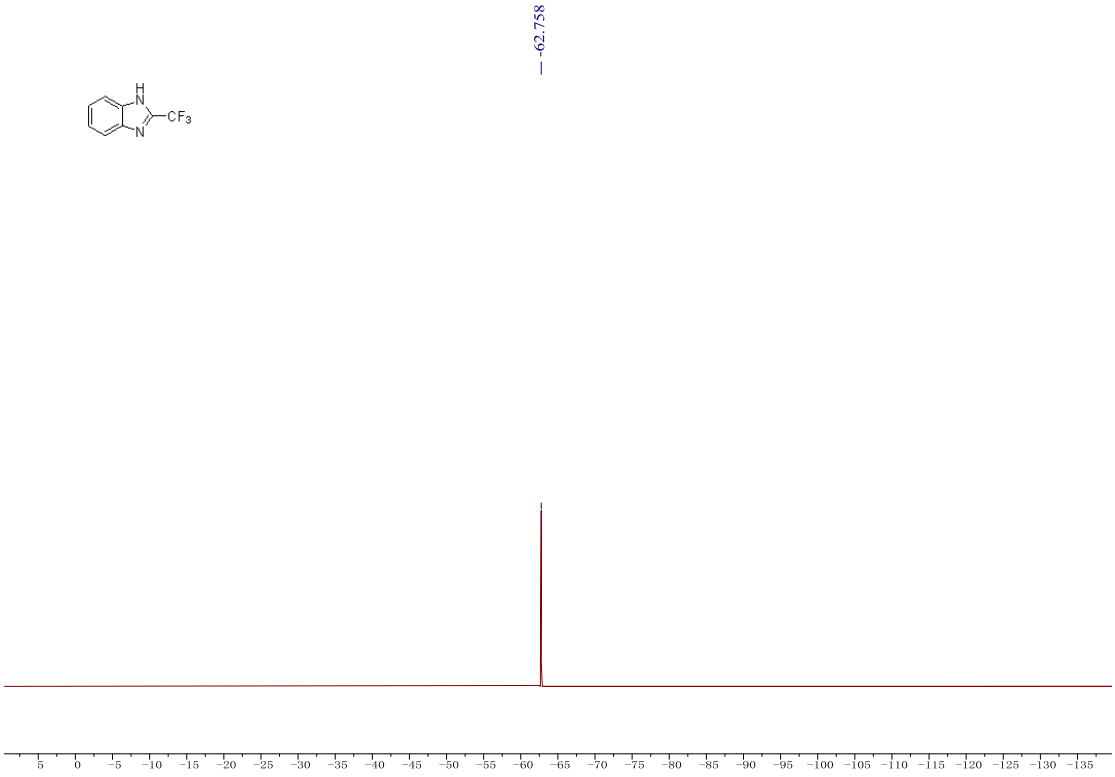
Copies of ^{1}H NMR, ^{19}FNMR and ^{13}C NMR spectra

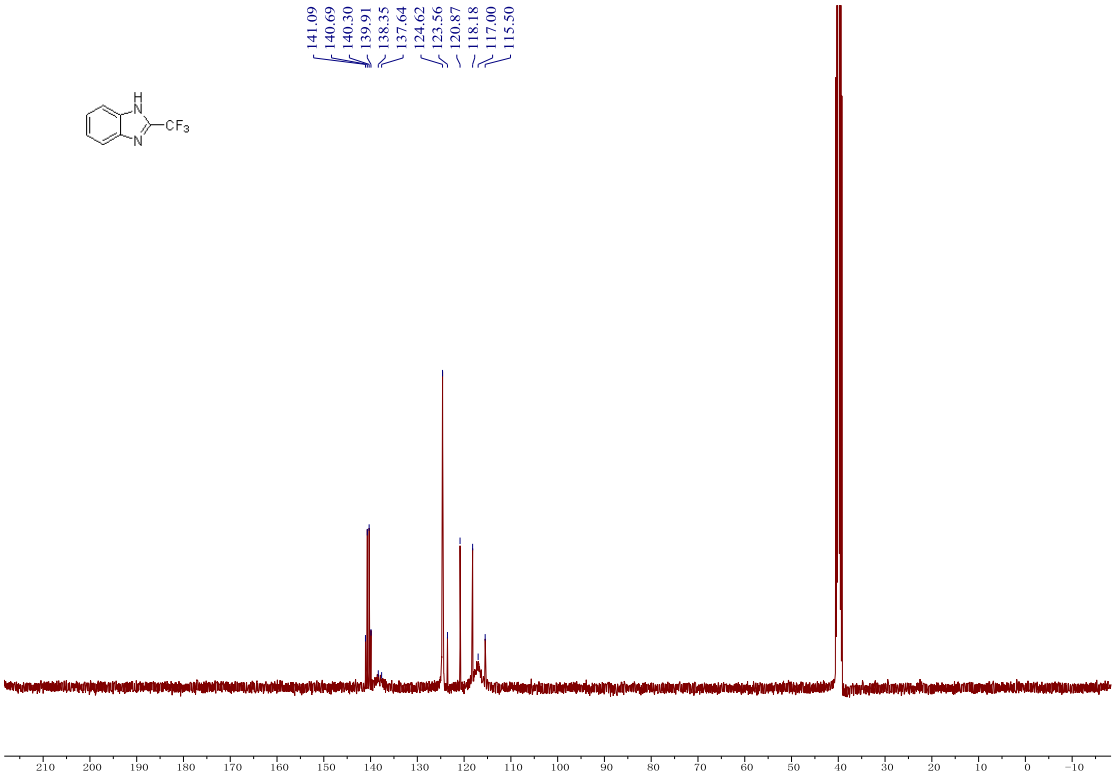
^{1}H NMR spectra of **3a** in DMSO-d_6



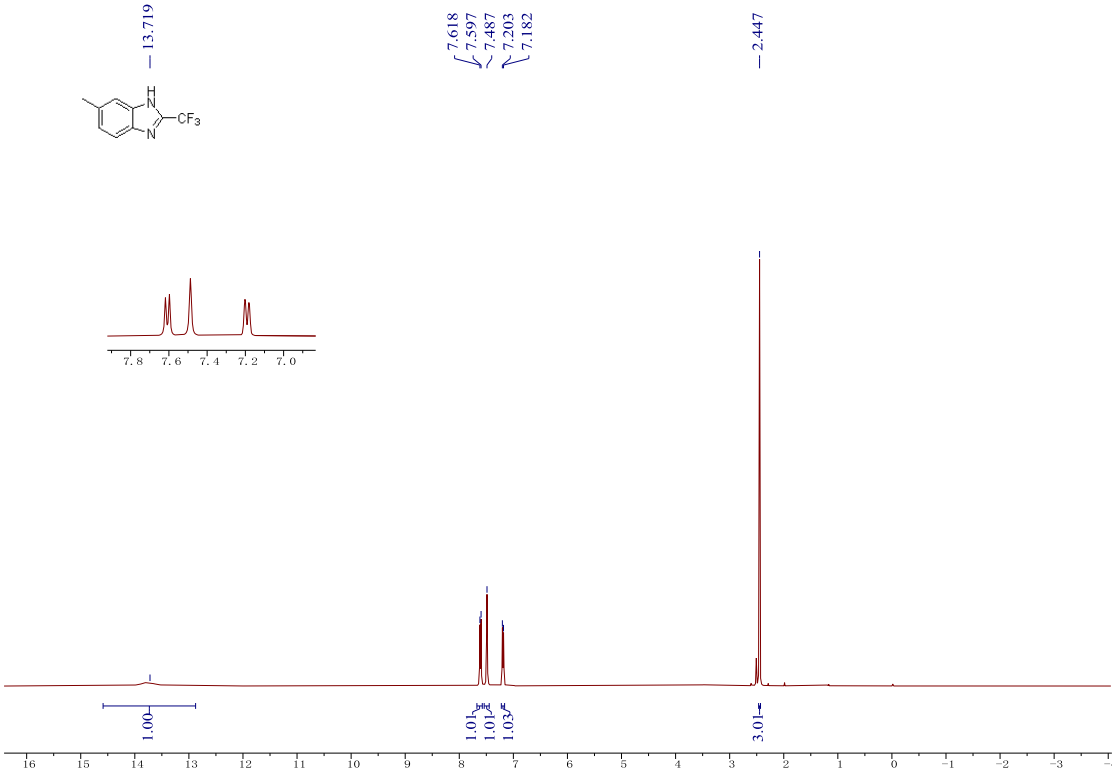
^{19}F NMR spectra of **3a** in DMSO-d_6



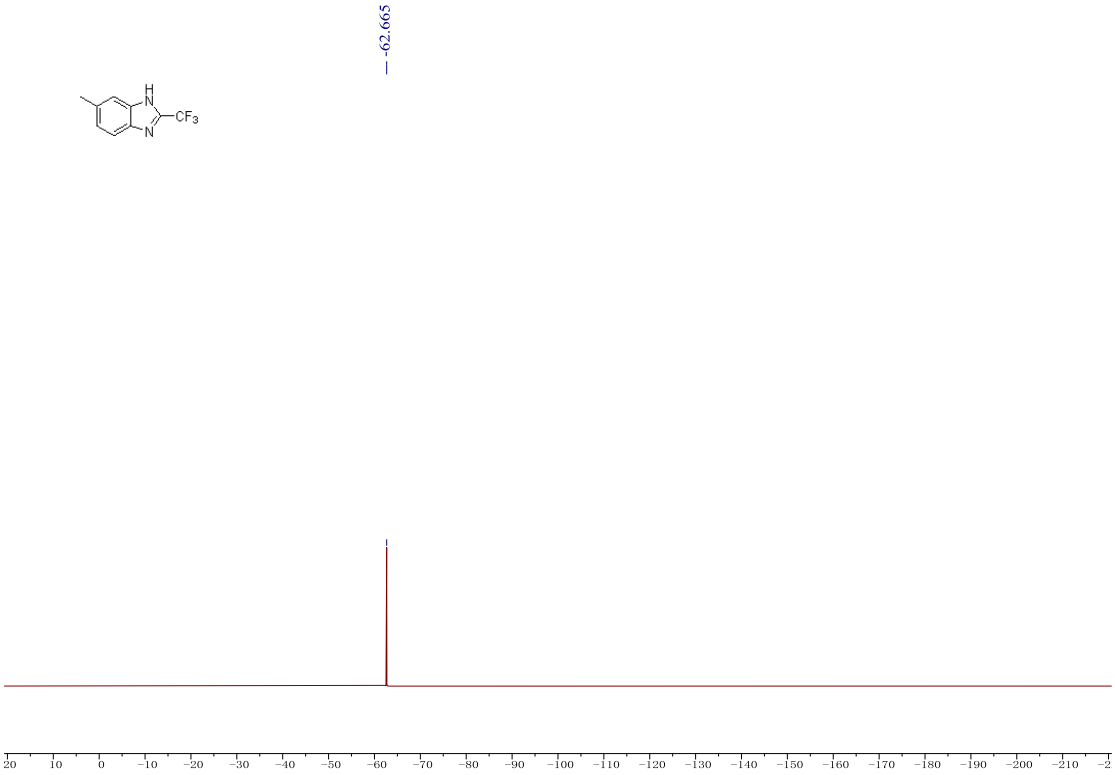
$^{13}C\{^{1}H\}$ NMR spectra of **3a** in DMSO-d_6



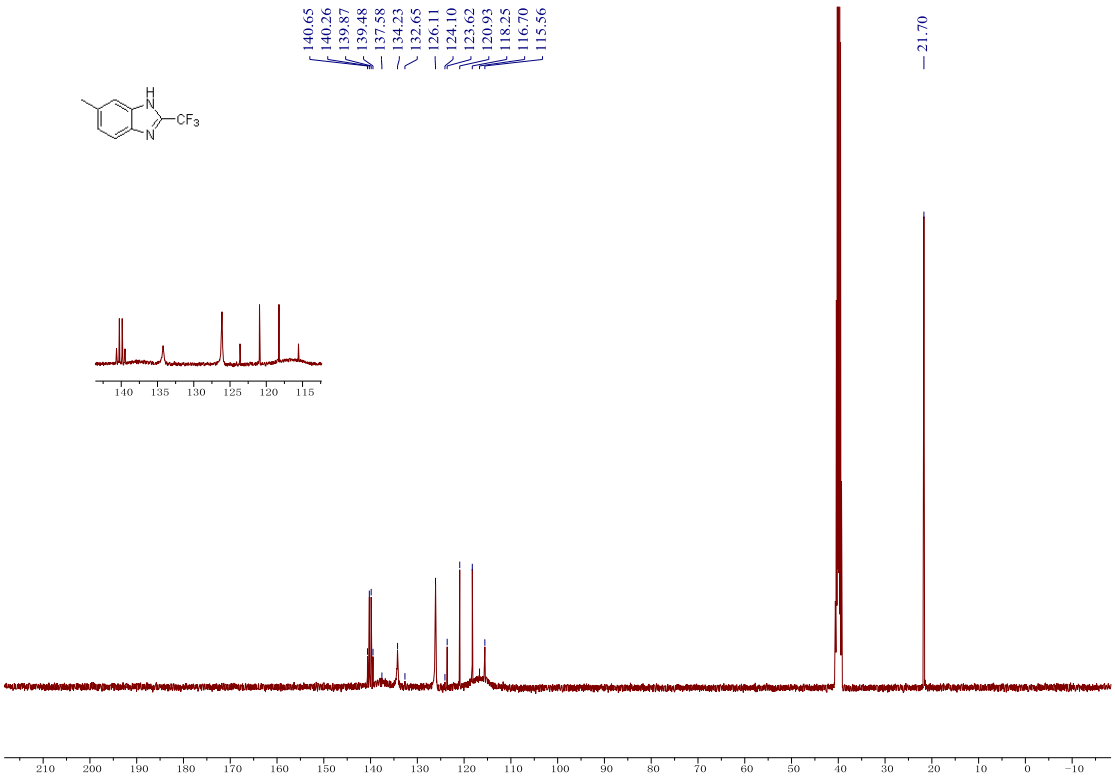
^{1}H NMR spectra of **3b** in DMSO-d_6



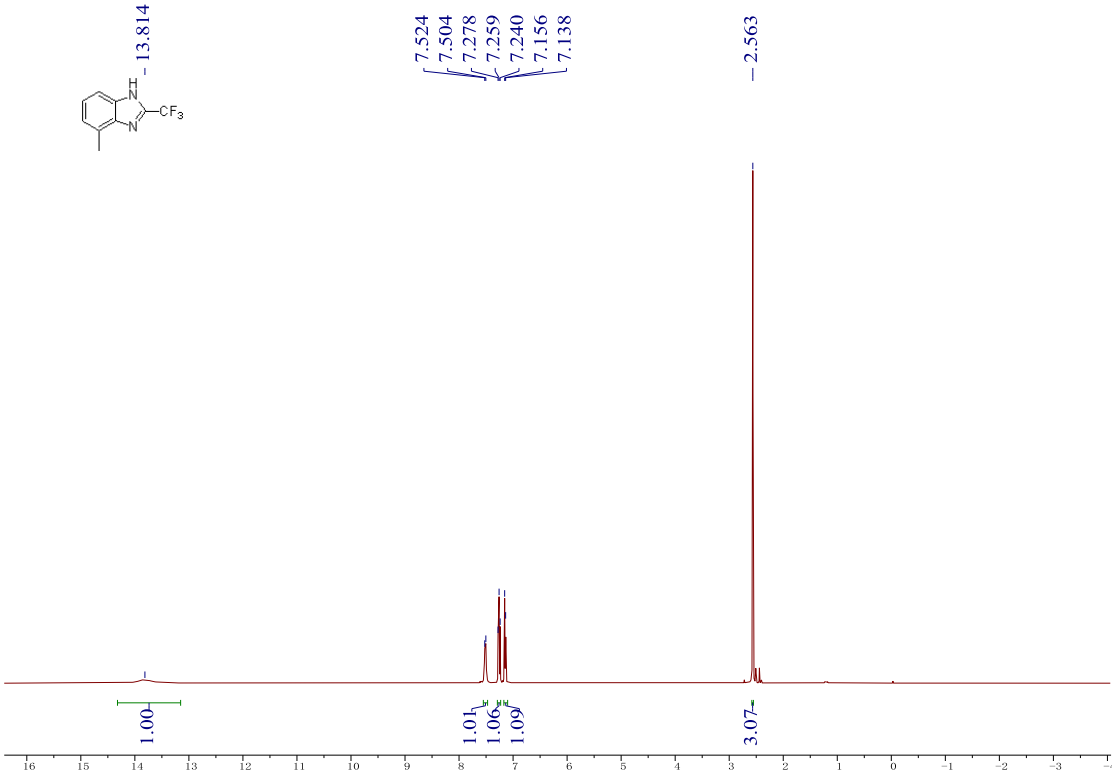
^{19}F NMR spectra of **3b** in DMSO-d_6



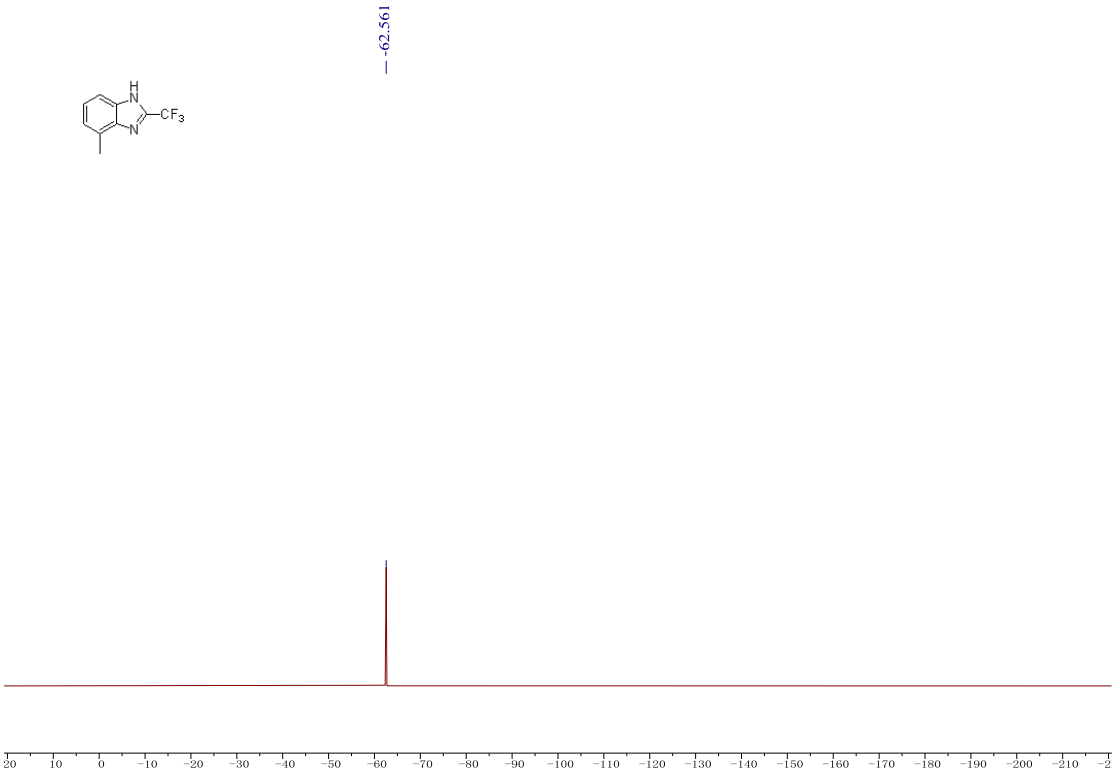
^{13}C{^{1}H} NMR spectra of **3b** in DMSO-d_6



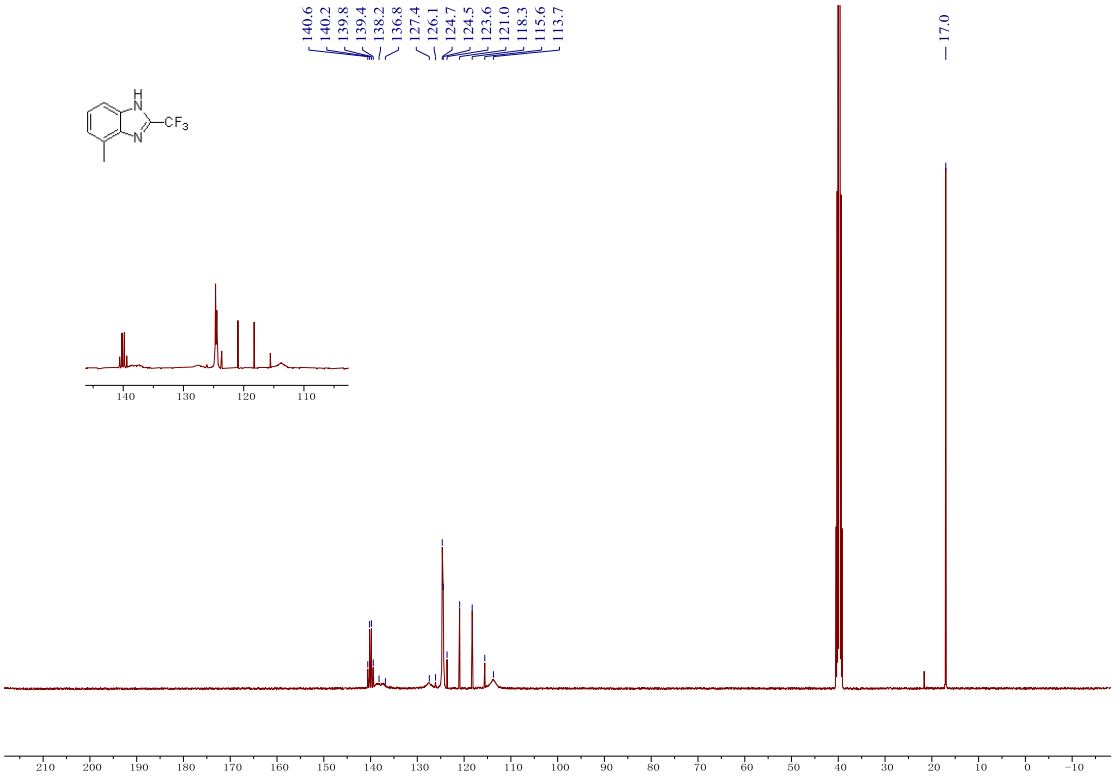
^{1}H NMR spectra of **3c** in DMSO-d_6



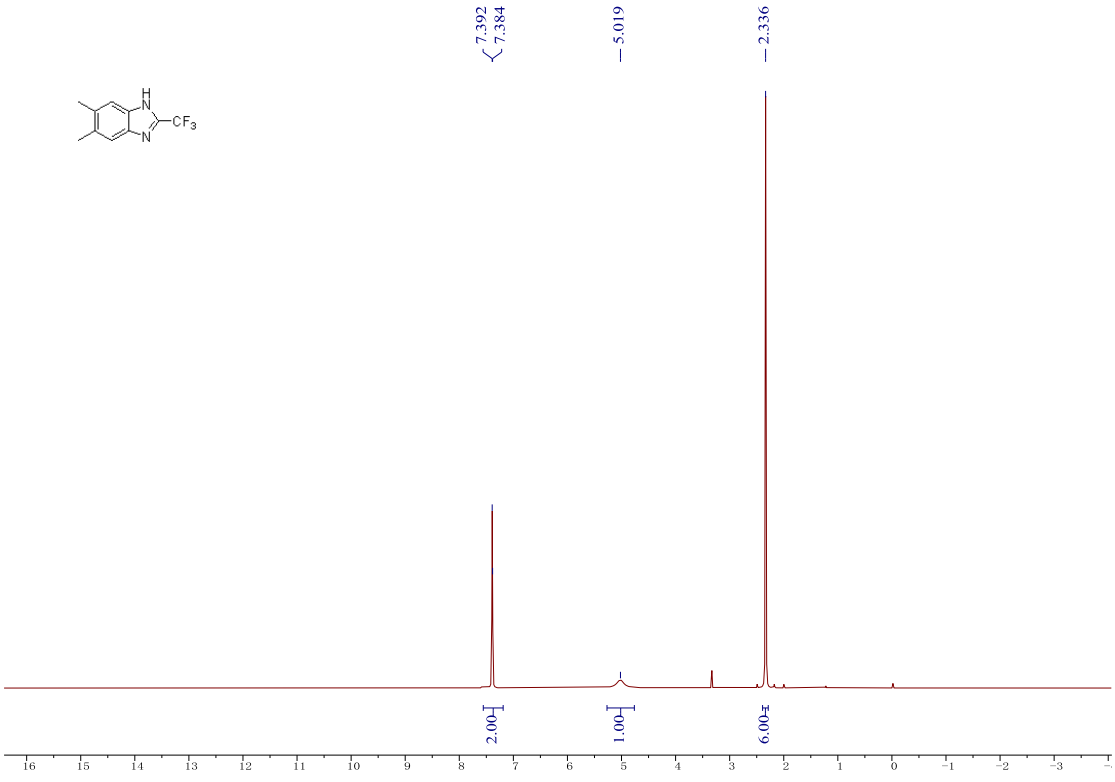
^{19}F NMR spectra of **3c** in DMSO-d_6



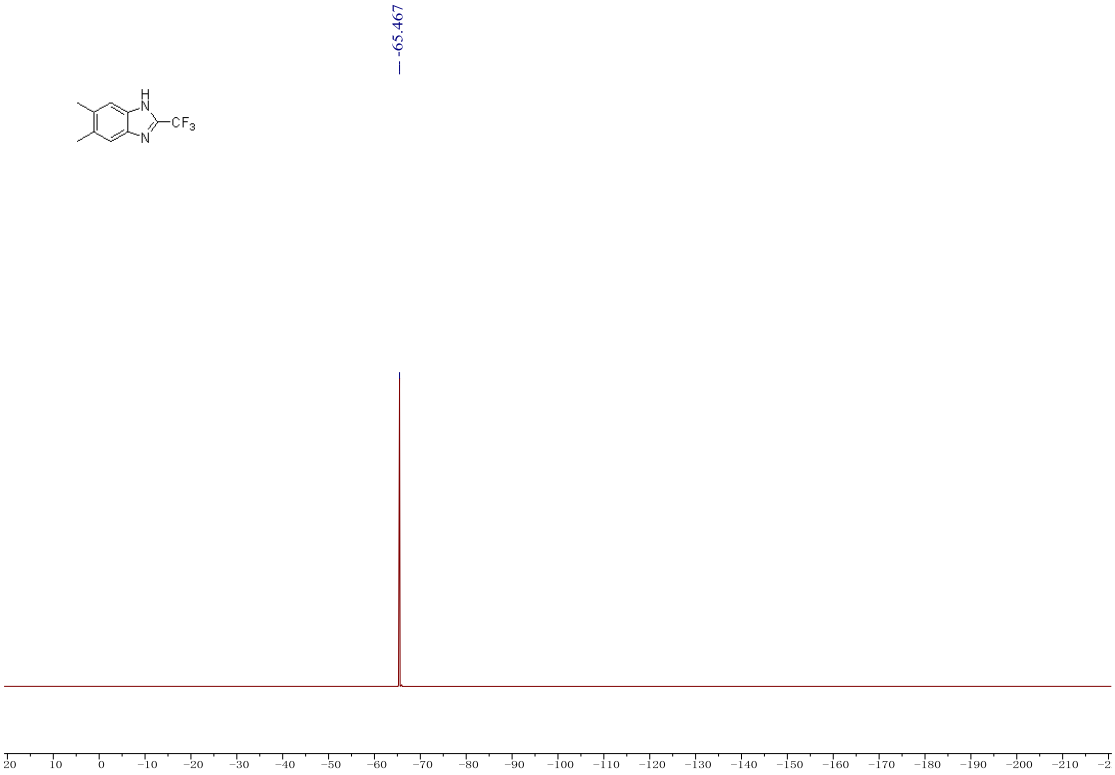
$^{13}C\{^{1}H\}$ NMR spectra of **3c** in DMSO-d_6



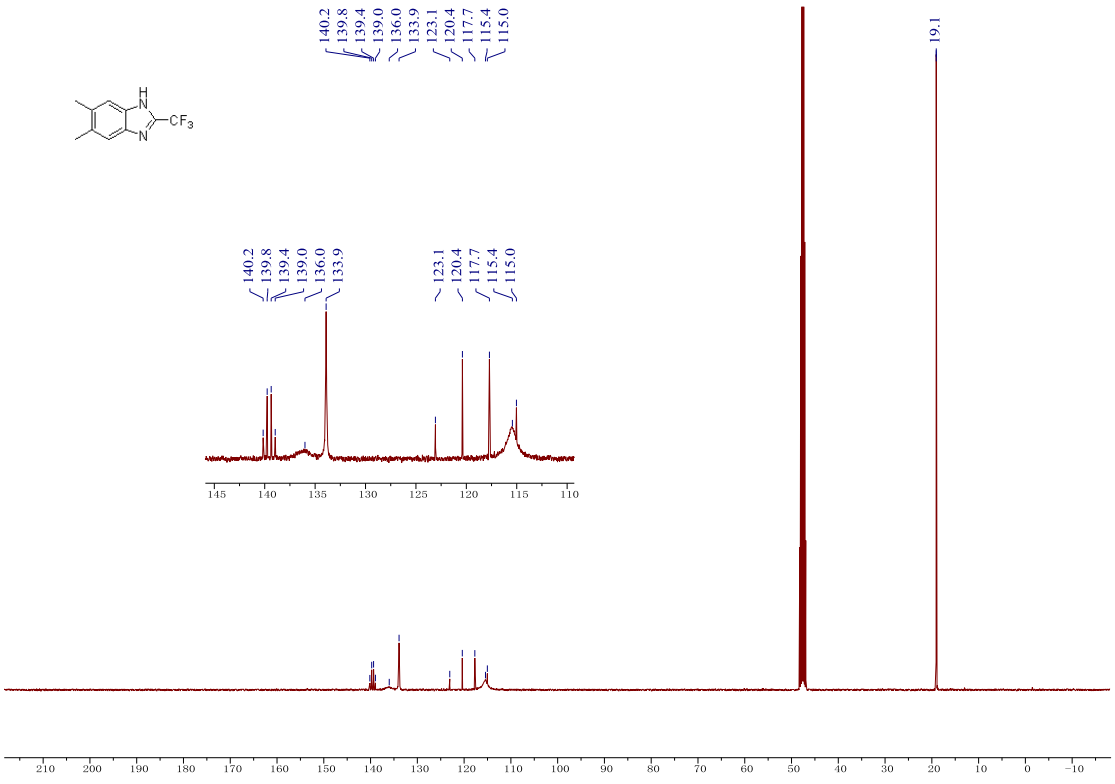
^{1}H NMR spectra of **3d** in methanol-d_4



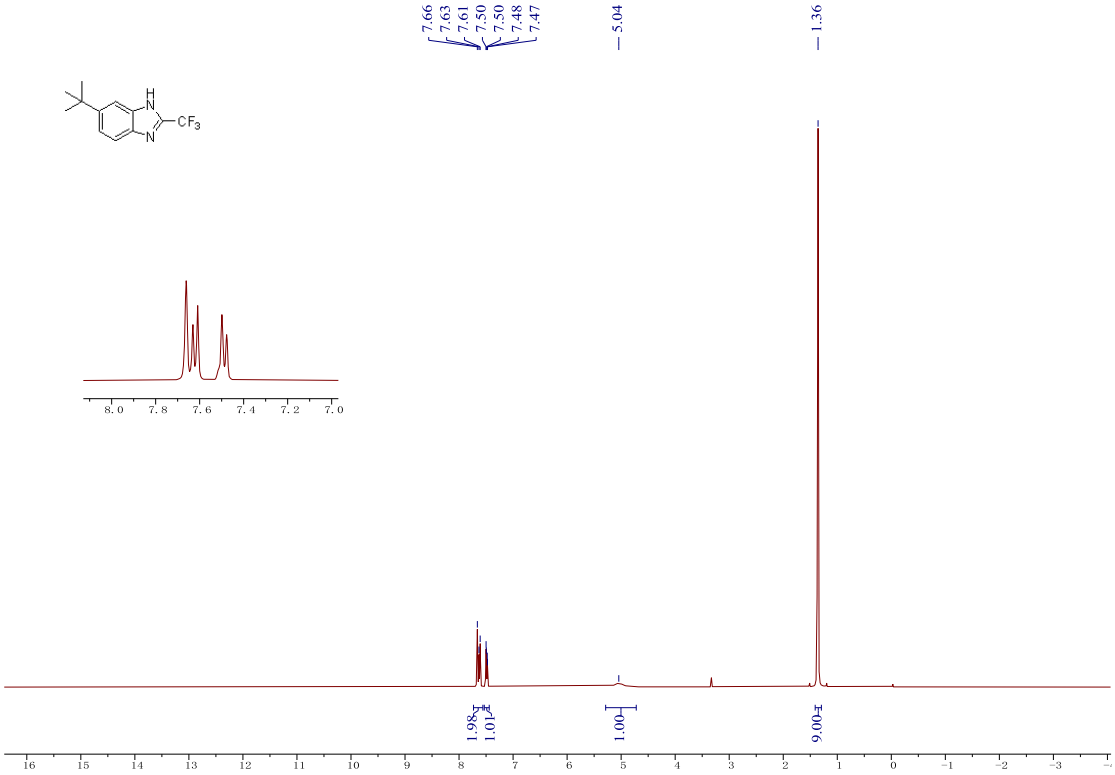
^{19}F NMR spectra of **3d** in methanol-d_4



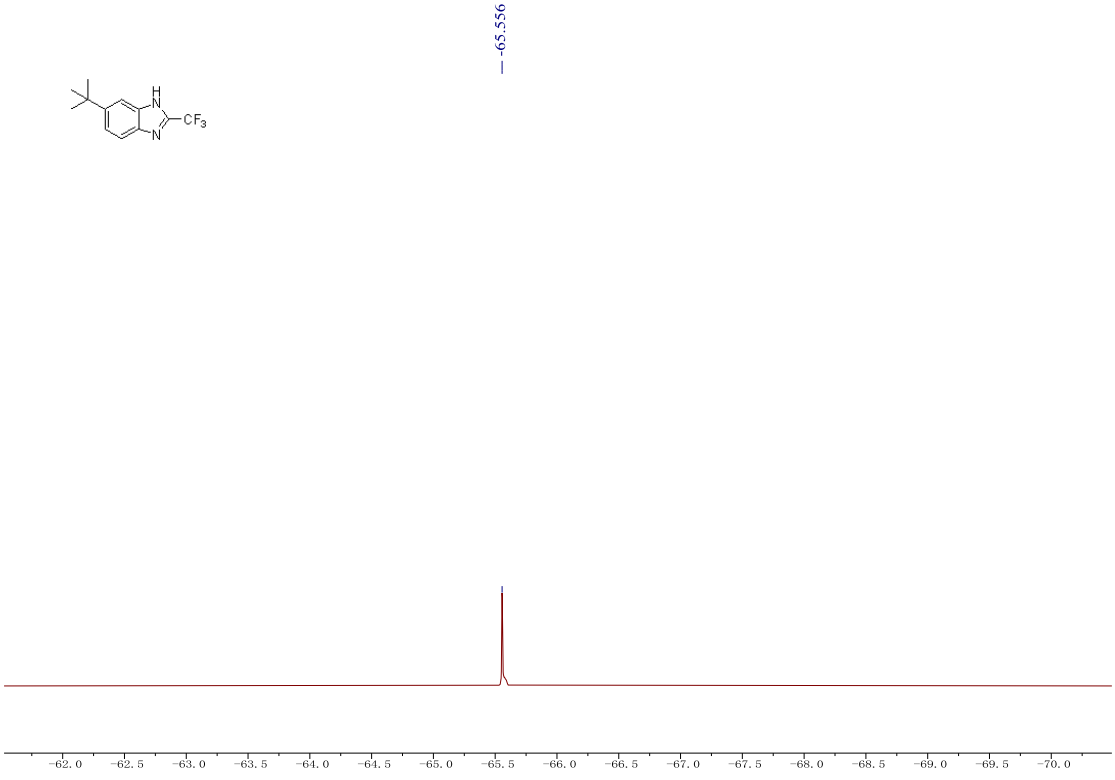
^{13}C{^{1}H} NMR spectra of **3d** in methanol-d_4



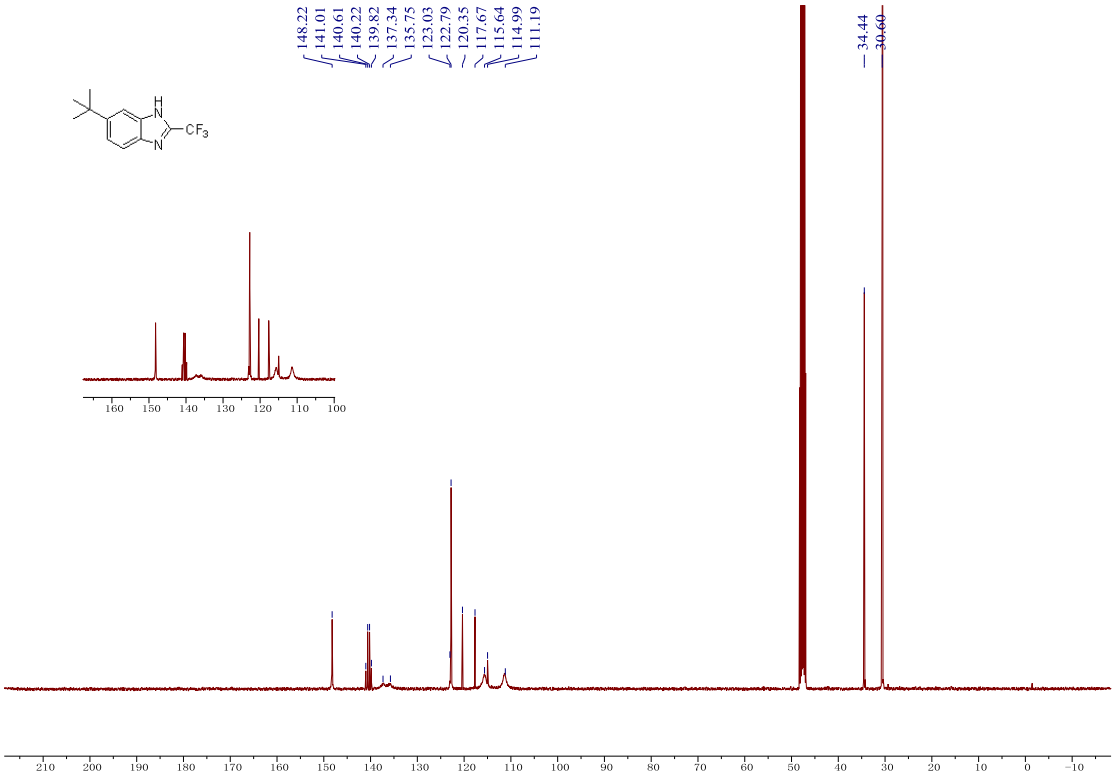
^{1}H NMR spectra of **3e** in methanol-d_4



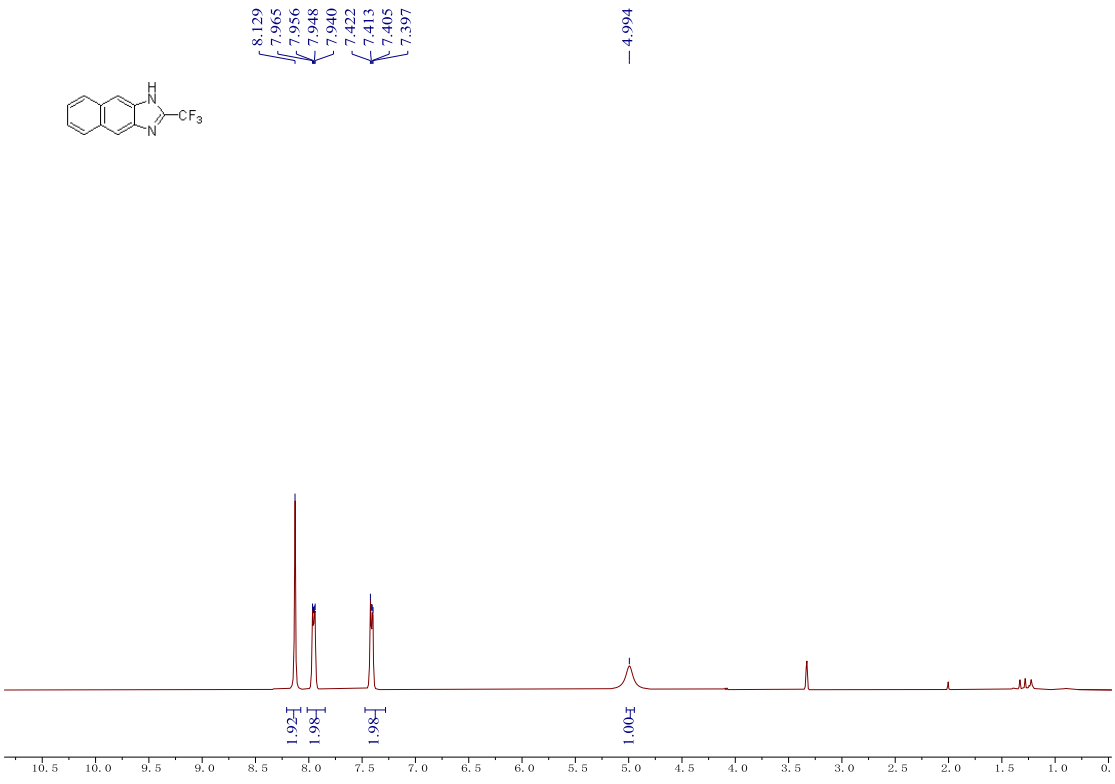
^{19}F NMR spectra of **3e** in methanol-d_4



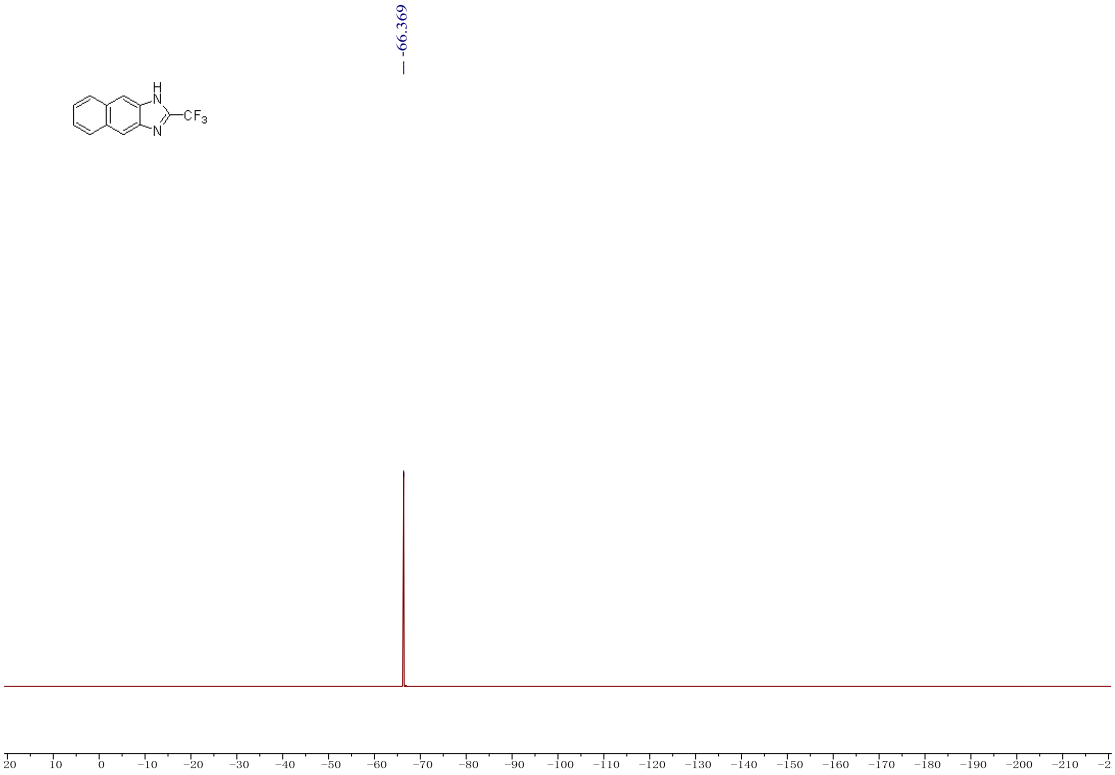
$^{13}C\{^{1}H\}$ NMR spectra of **3e** in methanol-d_4



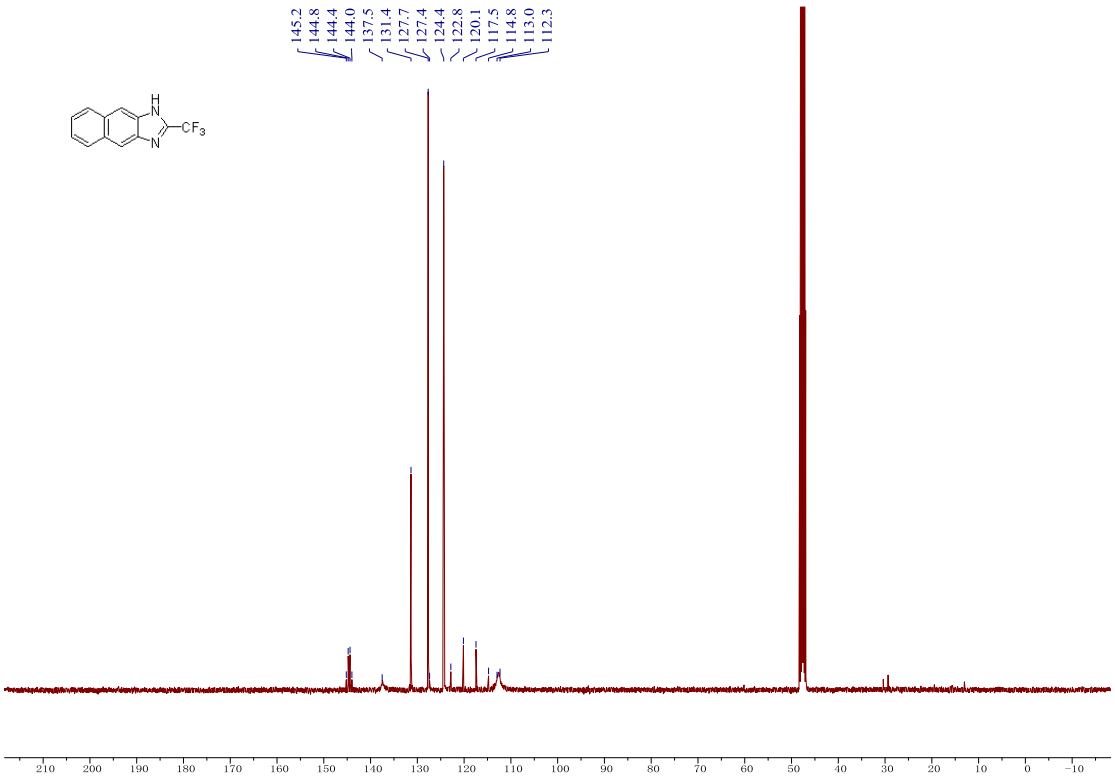
^{1}H NMR spectra of **3f** in Methanol-d_4



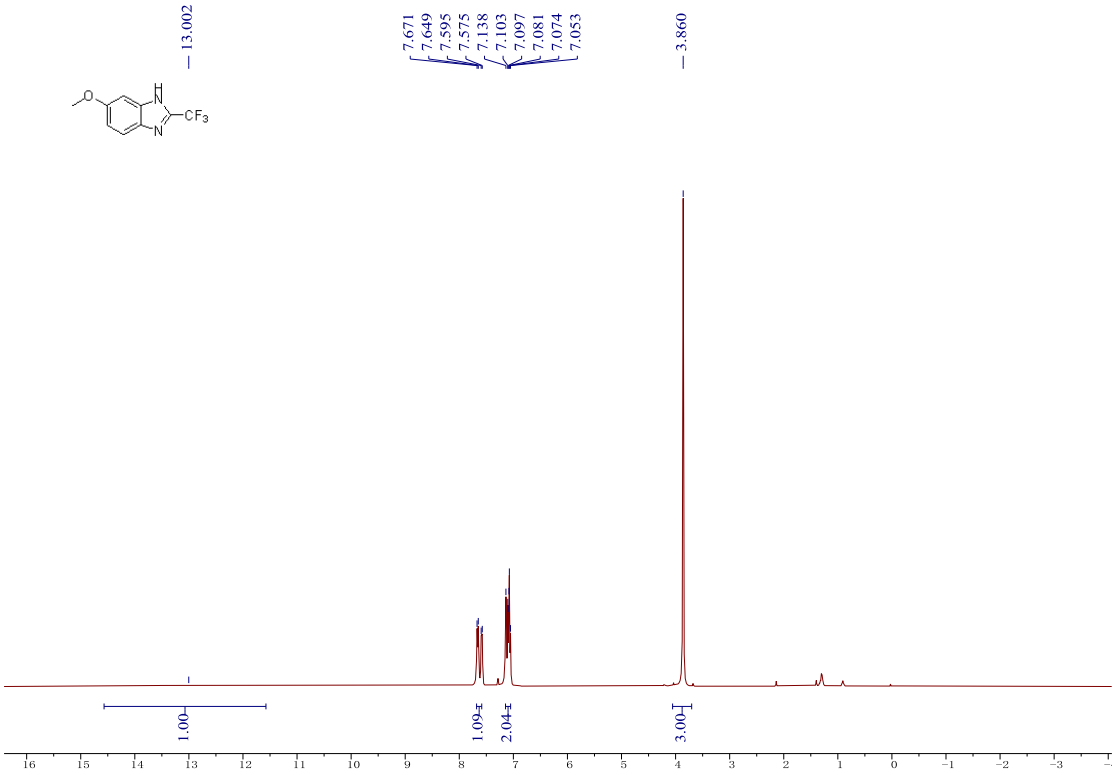
^{19}F NMR spectra of **3f** in methanol-d_4



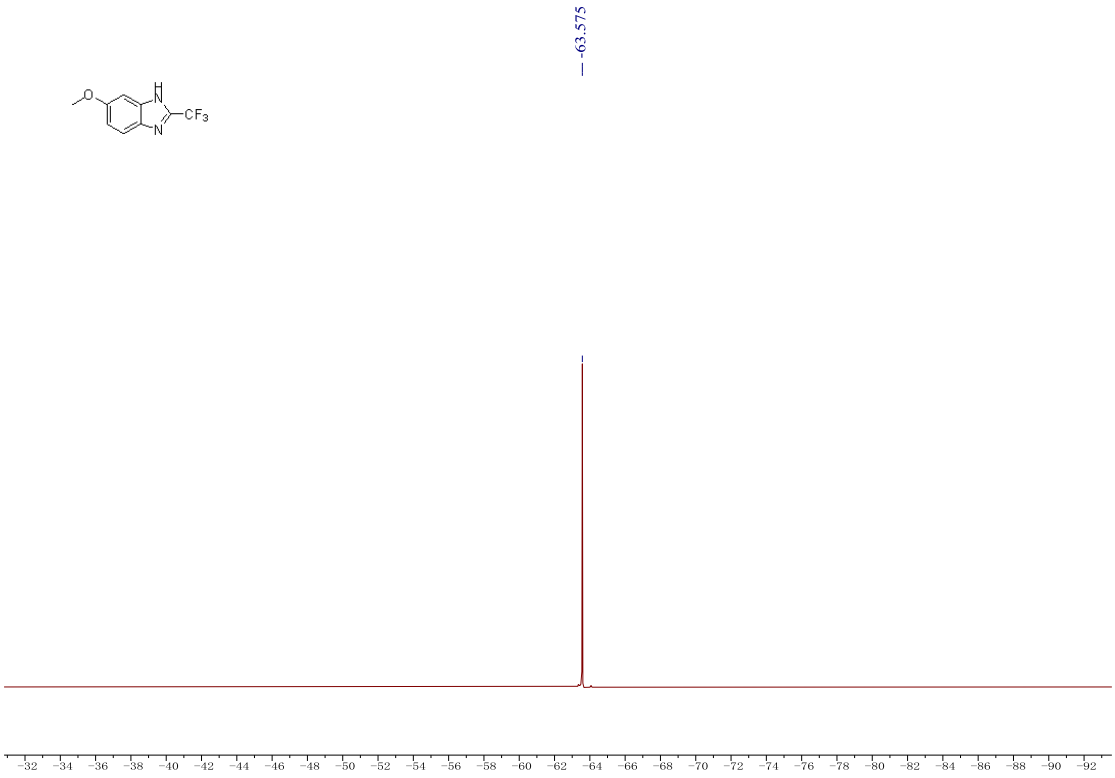
^{13}C{^{1}H} NMR spectra of **3f** in methanol-d_4



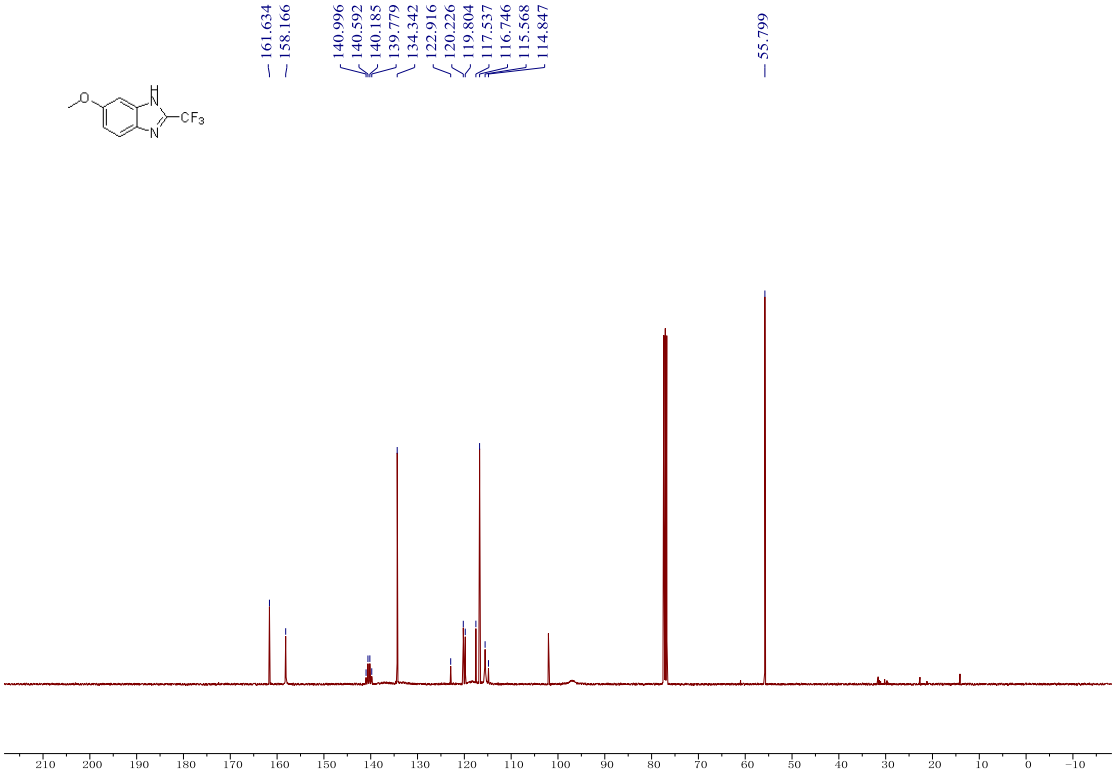
^{1}H NMR spectra of **3g** in $CDCl_3$



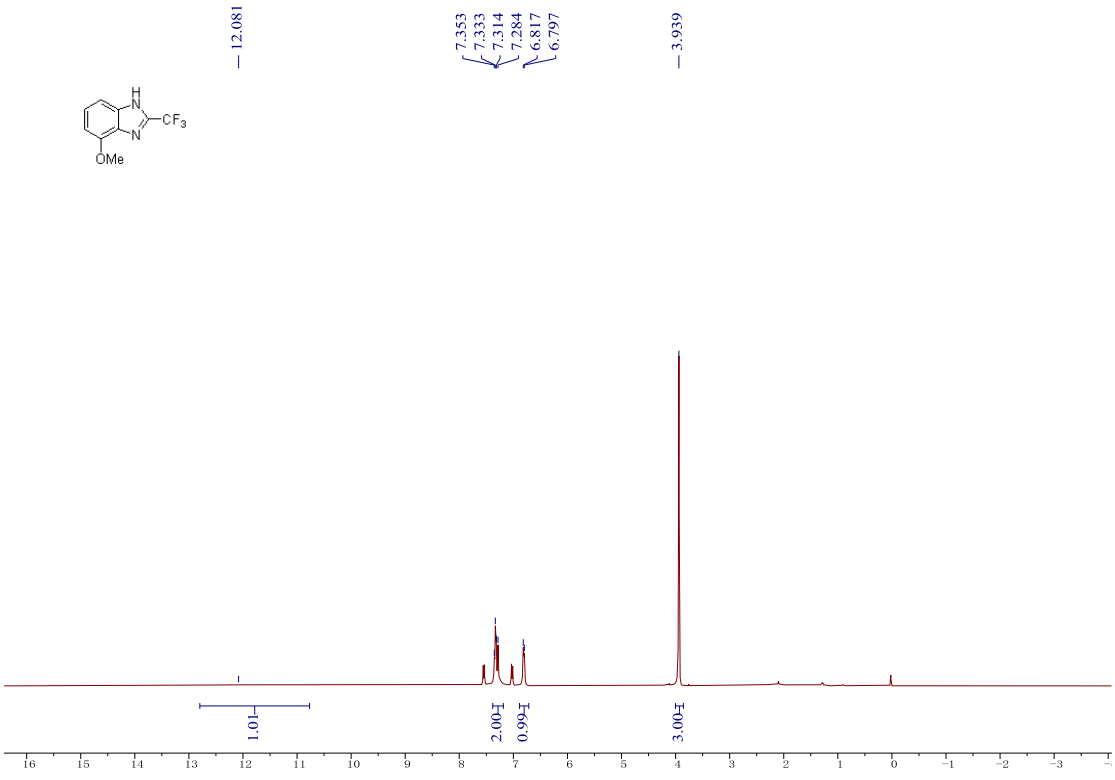
^{19}F NMR spectra of **3g** in $CDCl_3$



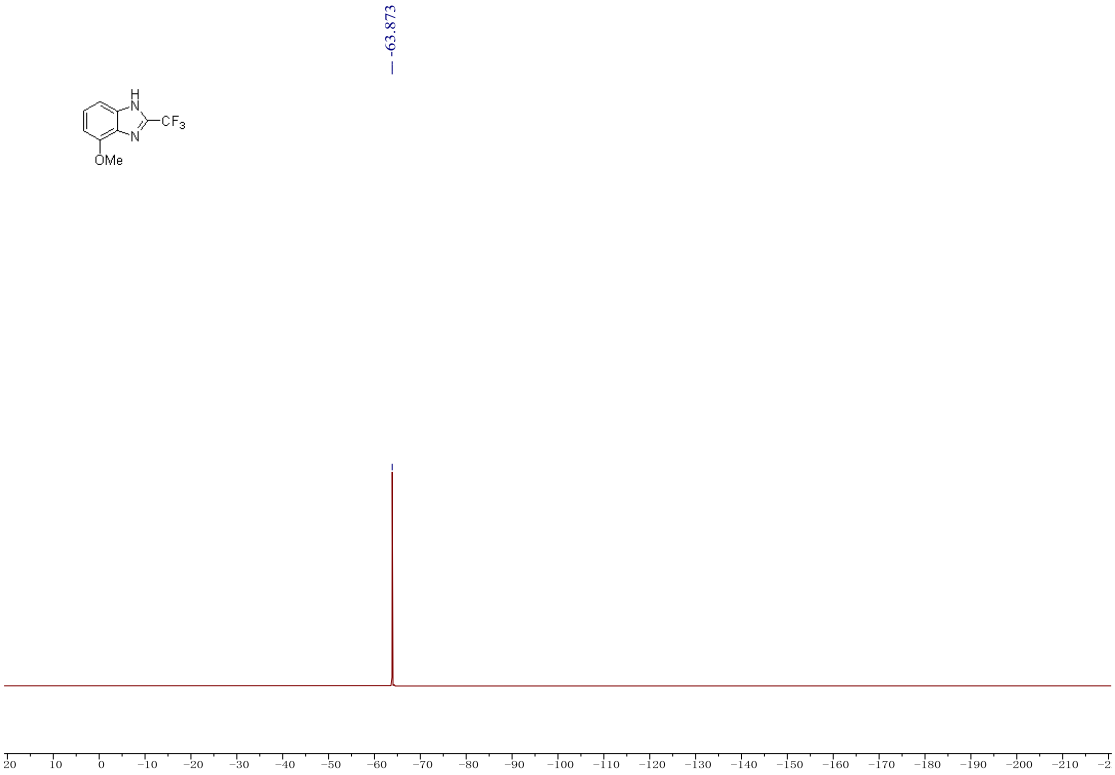
$^{13}C\{^{1}H\}$ NMR spectra of **3g** in $CDCl_3$



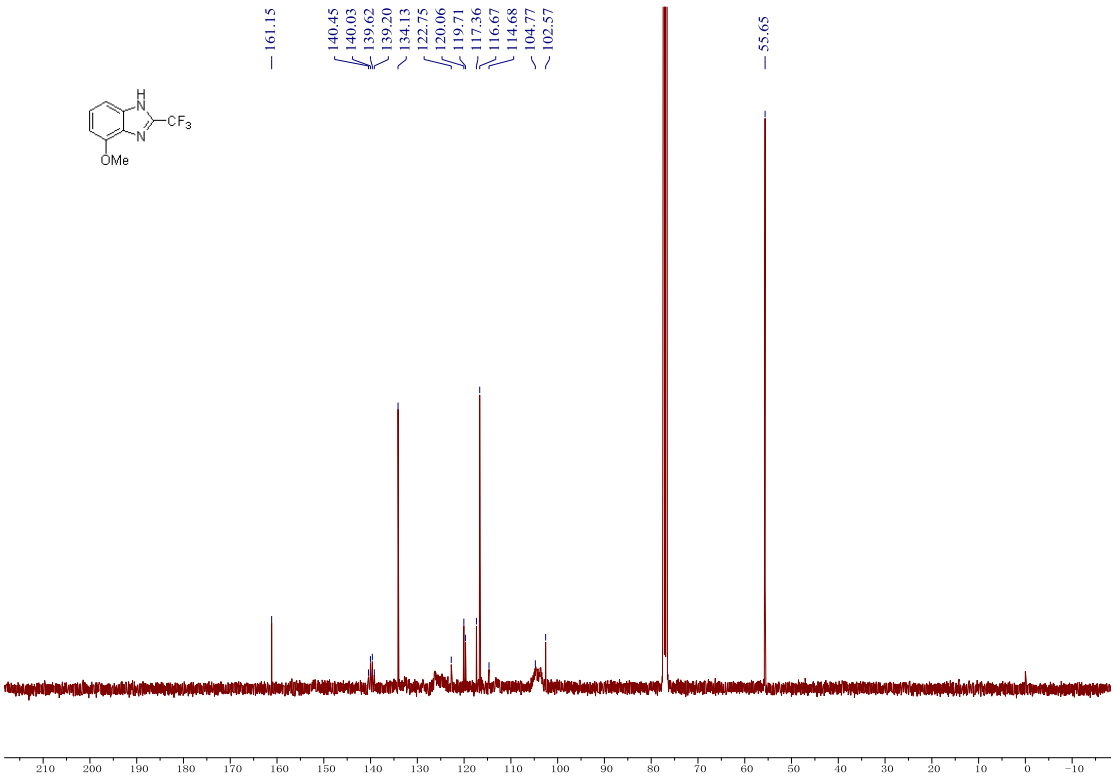
^{1}H NMR spectra of **3h** in $CDCl_3$



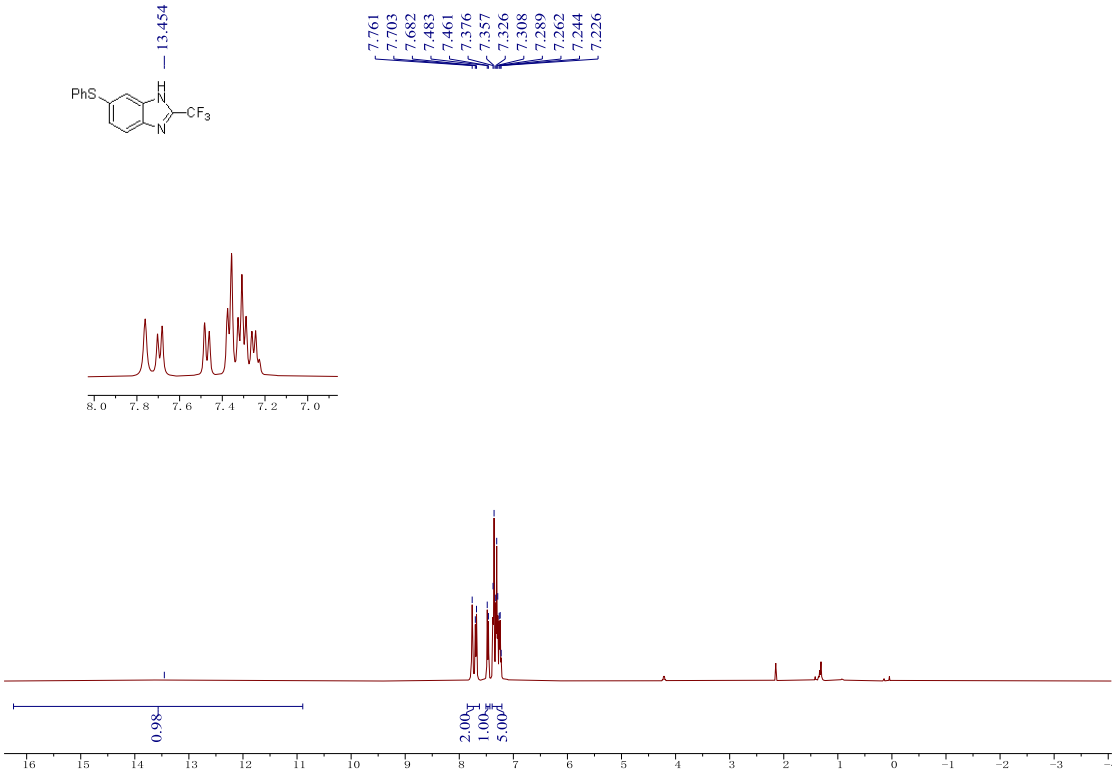
^{19}F NMR spectra of **3h** in $CDCl_3$



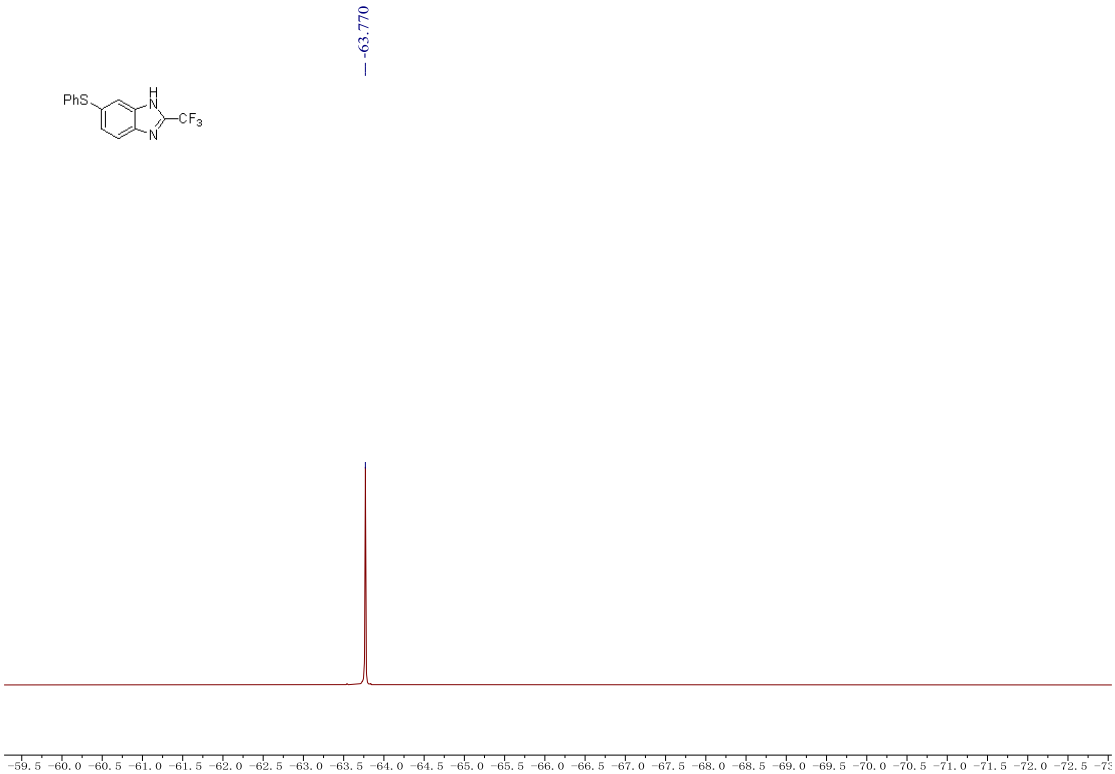
$^{13}C\{^1H\}$ NMR spectra of **3h** in $CDCl_3$



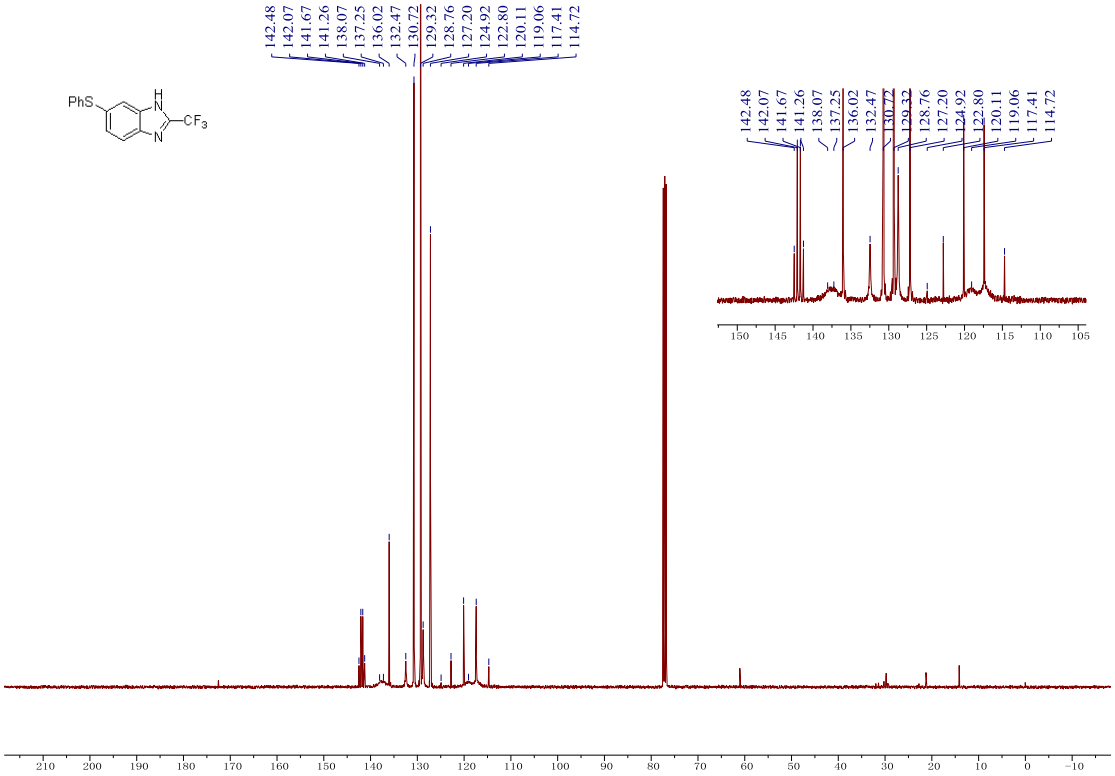
^{1}H NMR spectra of **3i** in $CDCl_3$



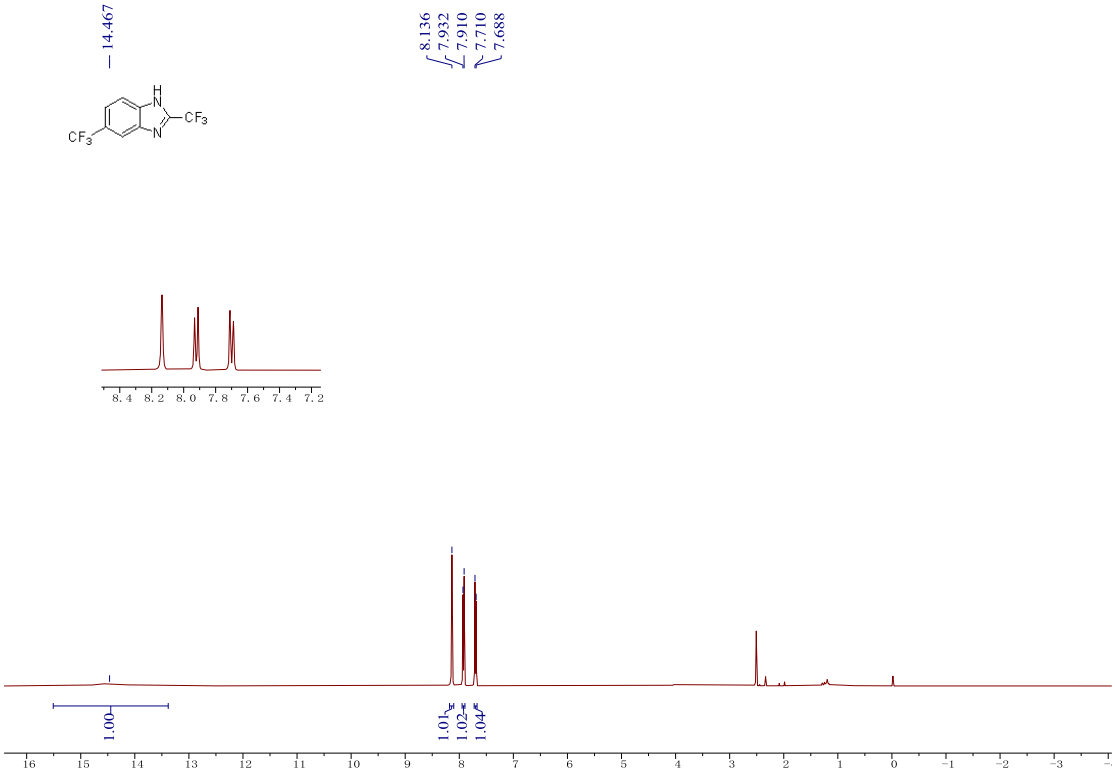
^{19}F NMR spectra of **3i** in $CDCl_3$



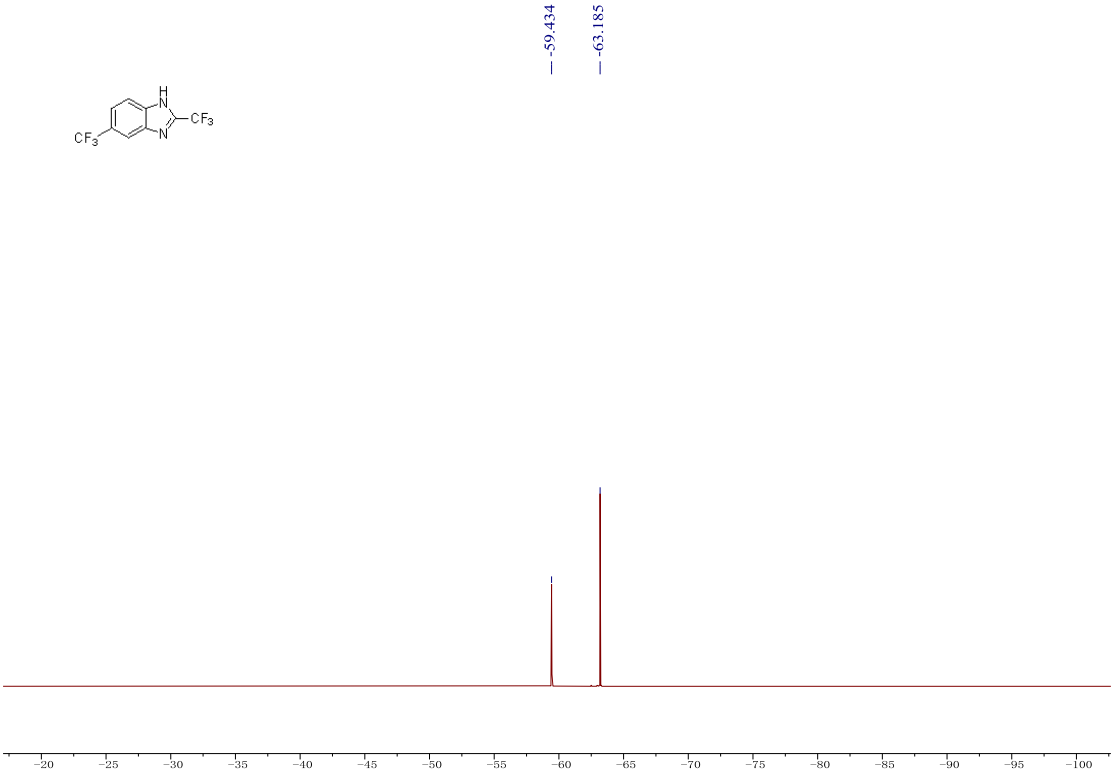
$^{13}C\{^{1}H\}$ NMR spectra of **3i** in $CDCl_3$



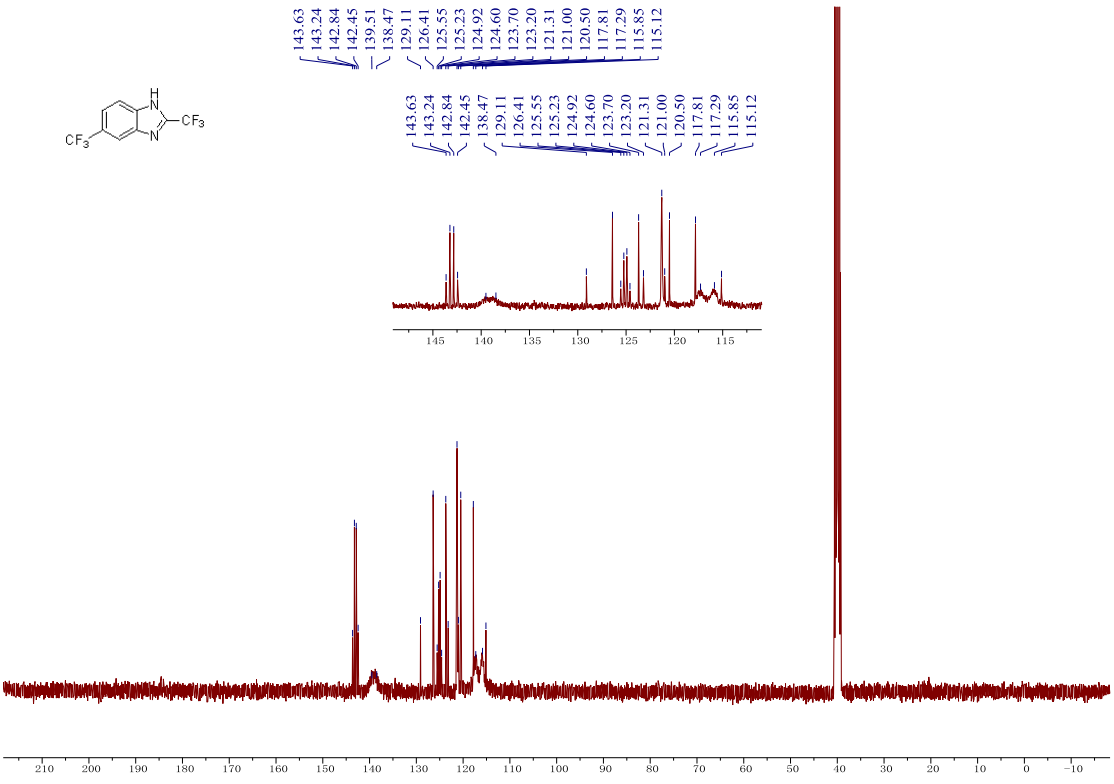
^{1}H NMR spectra of **3j** in DMSO-d_6



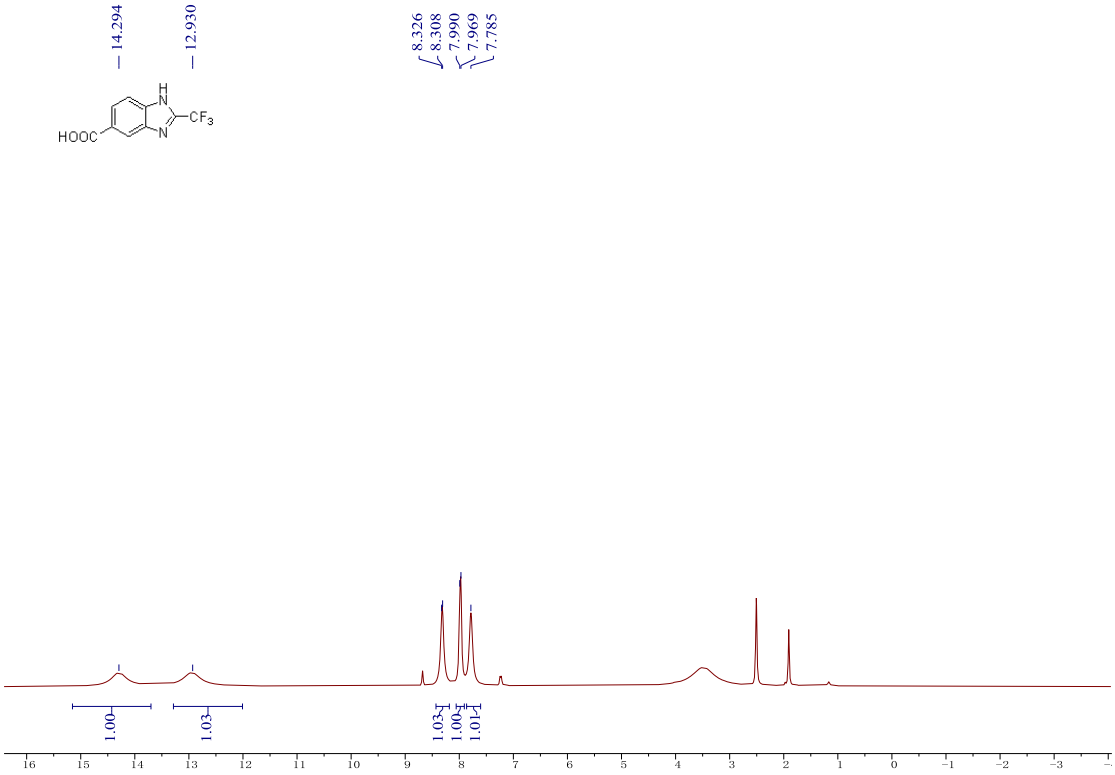
^{19}F NMR spectra of **3j** in DMSO-d_6



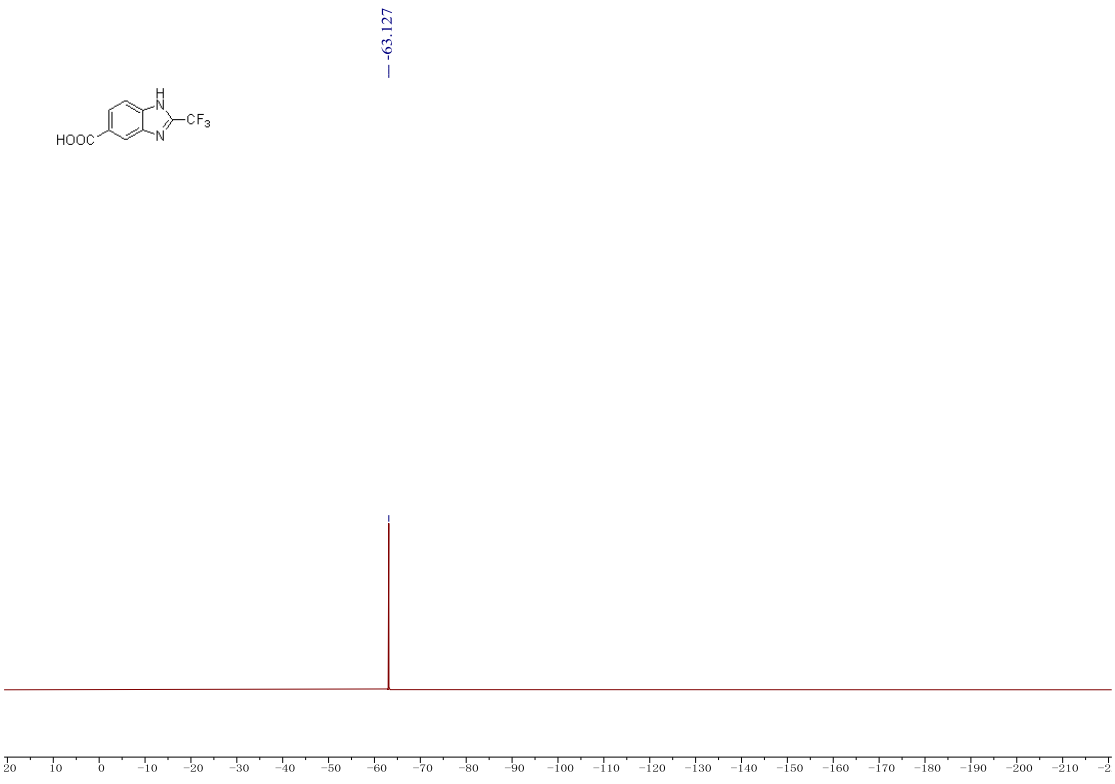
^{13}C{^{1}H} NMR spectra of **3j** in DMSO-d_6



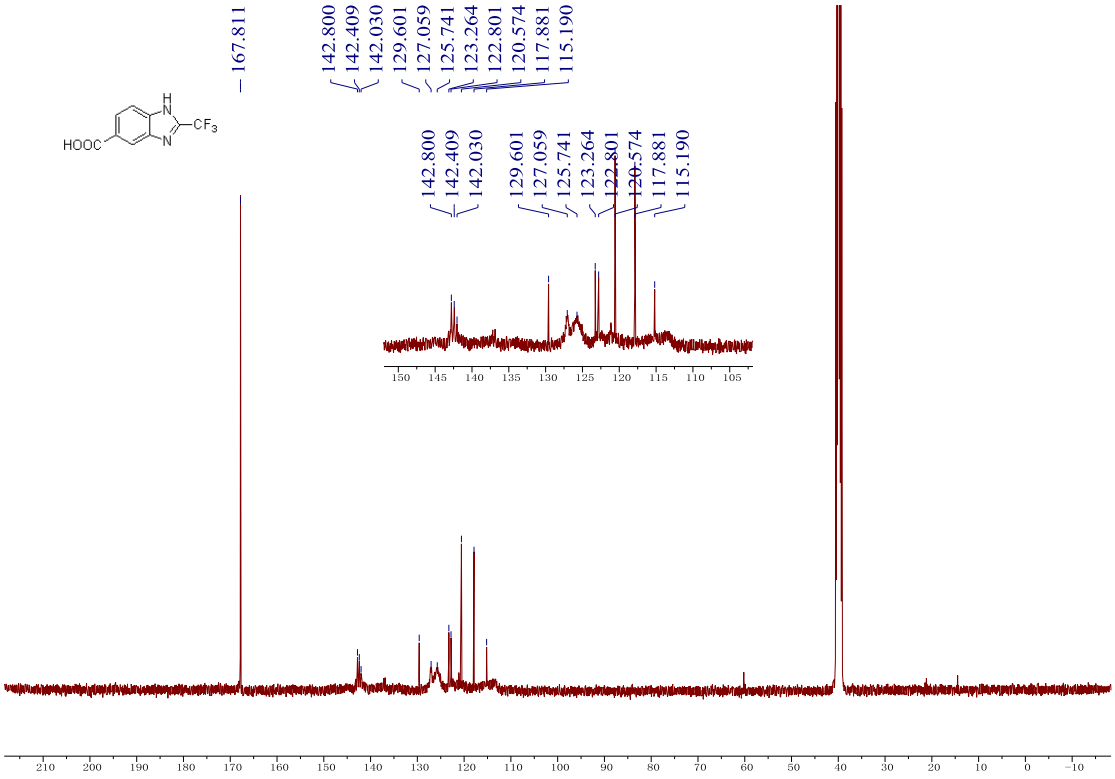
^{1}H NMR spectra of **3k** in DMSO-d_6



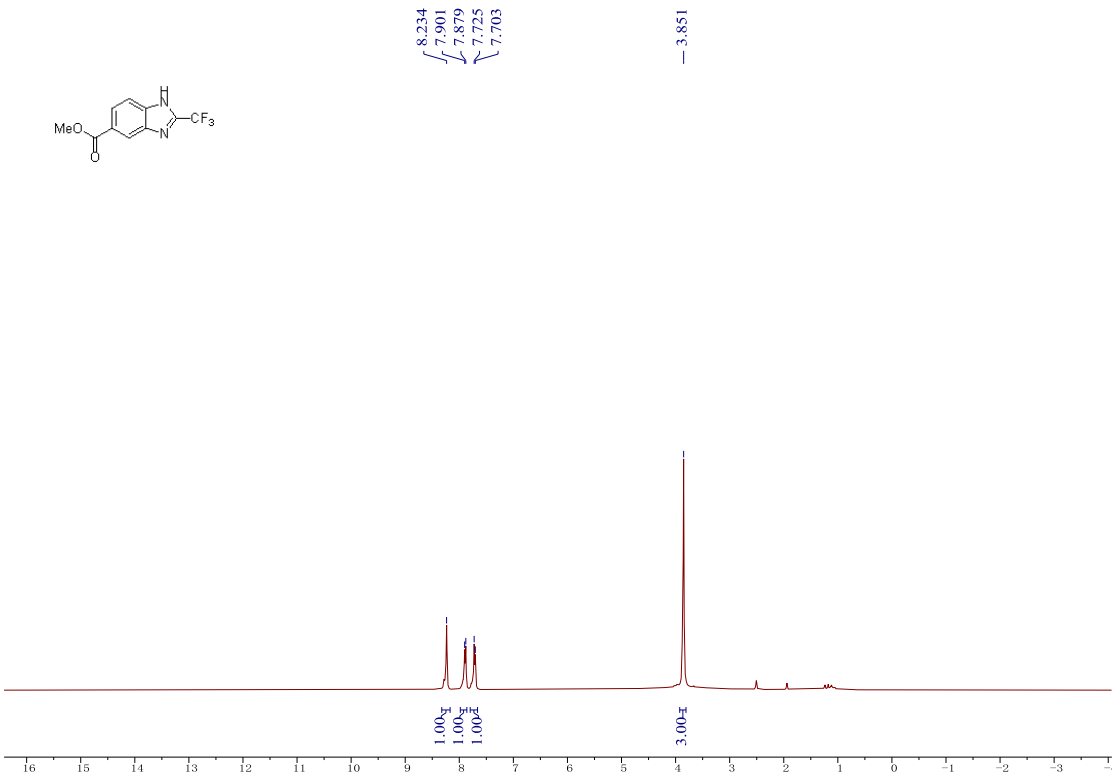
^{19}F NMR spectra of **3k** in DMSO-d_6



$^{13}C\{^{1}H\}$ NMR spectra of **3k** in DMSO-d_6



^{1}H NMR spectra of **3l** in DMSO-d_6



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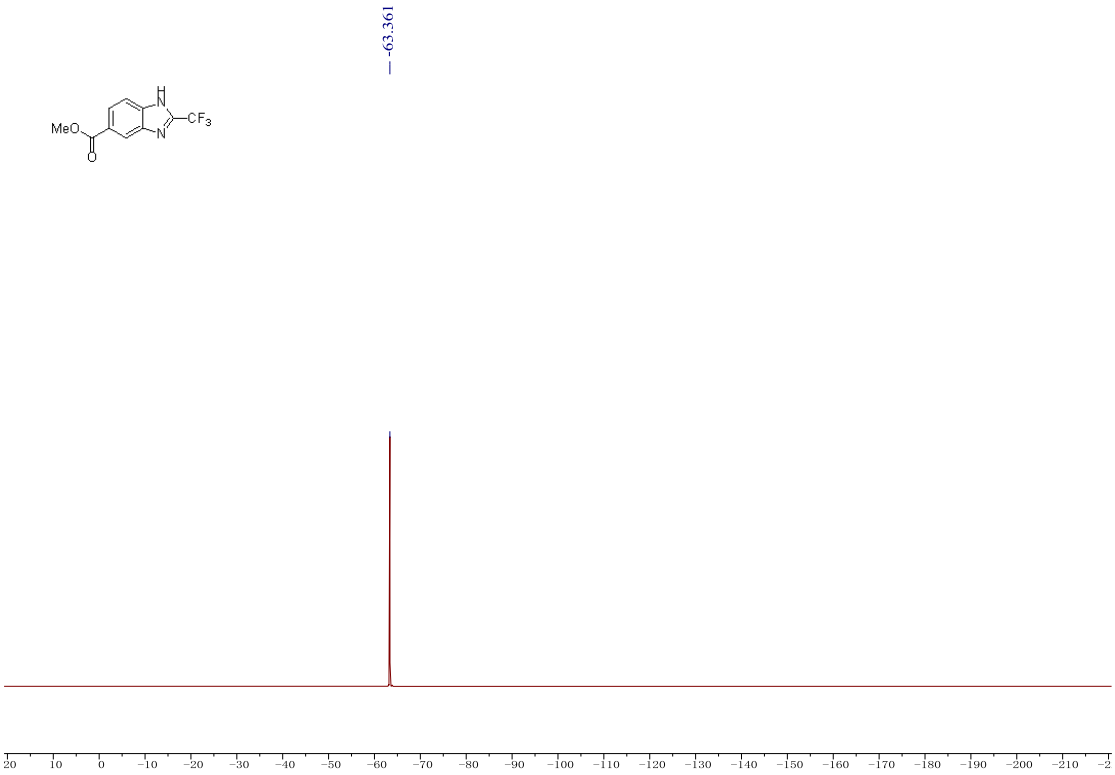
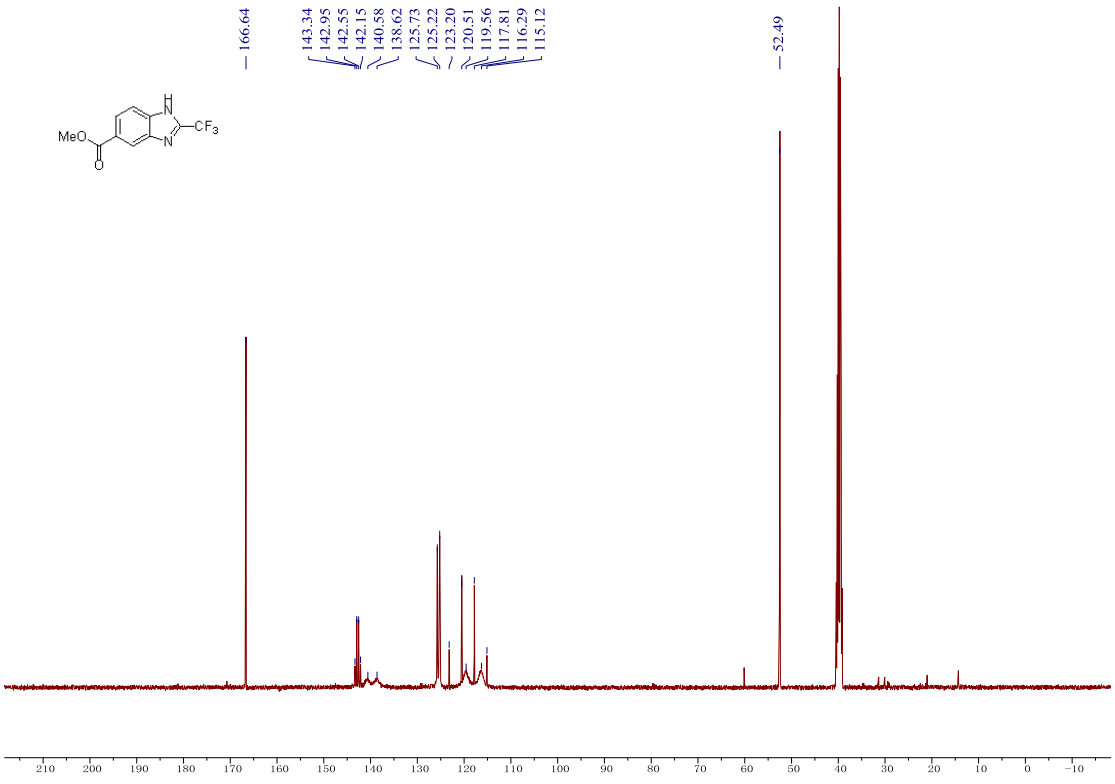
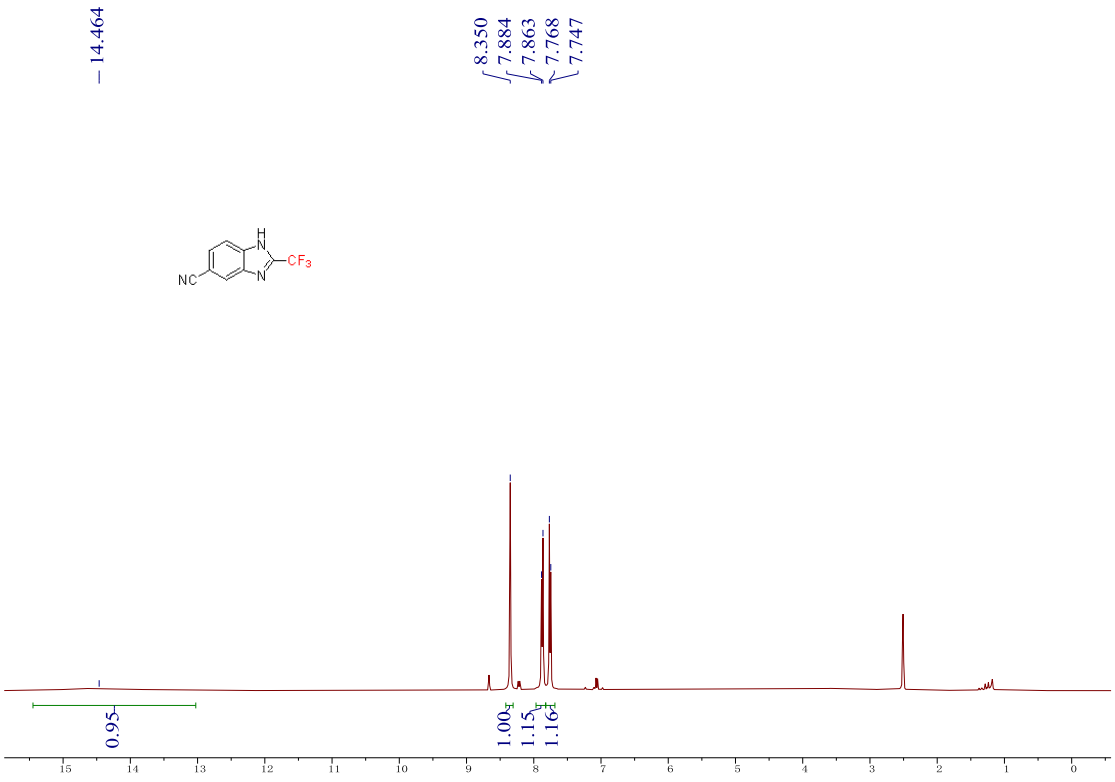


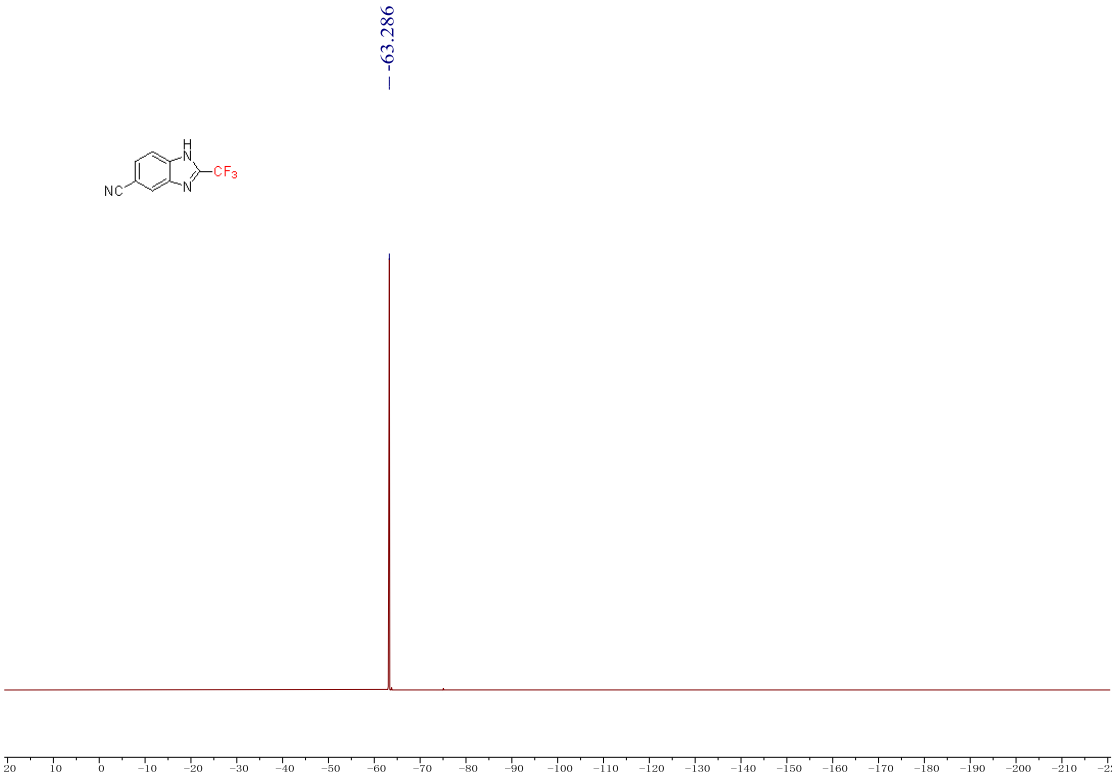
^{13}C{^{1}H} NMR spectra of **3l** in DMSO-d_6



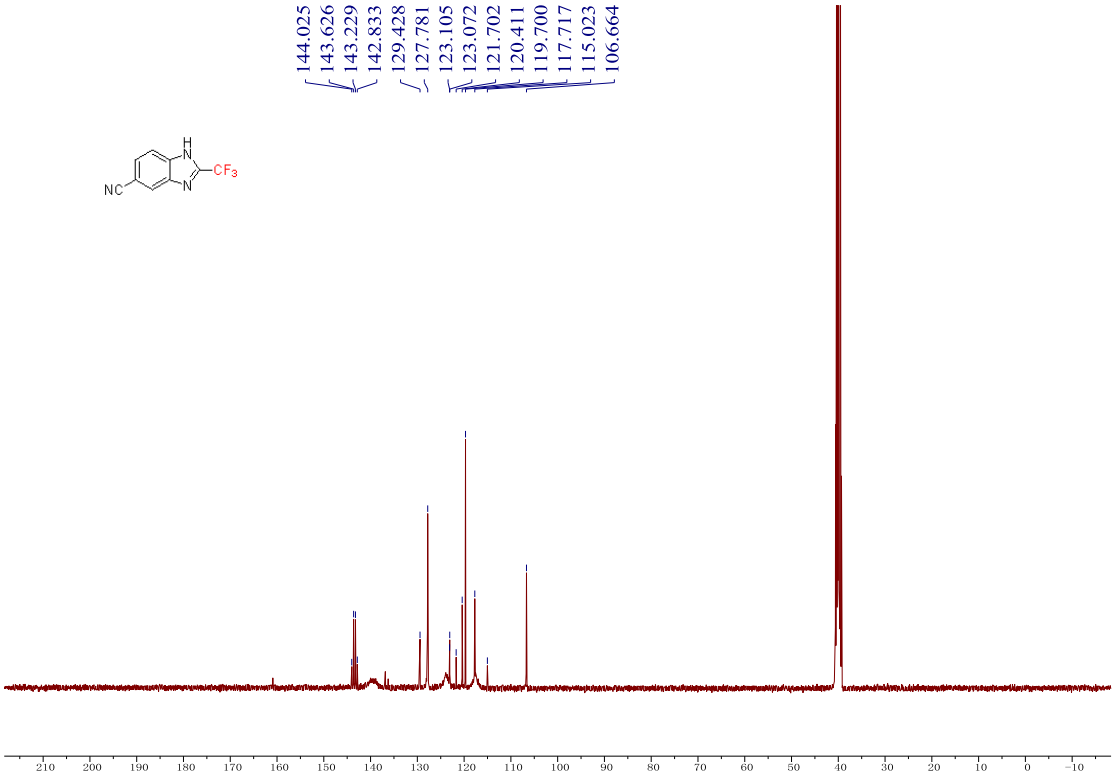
^{1}H NMR spectra of **3m** in DMSO-d_6



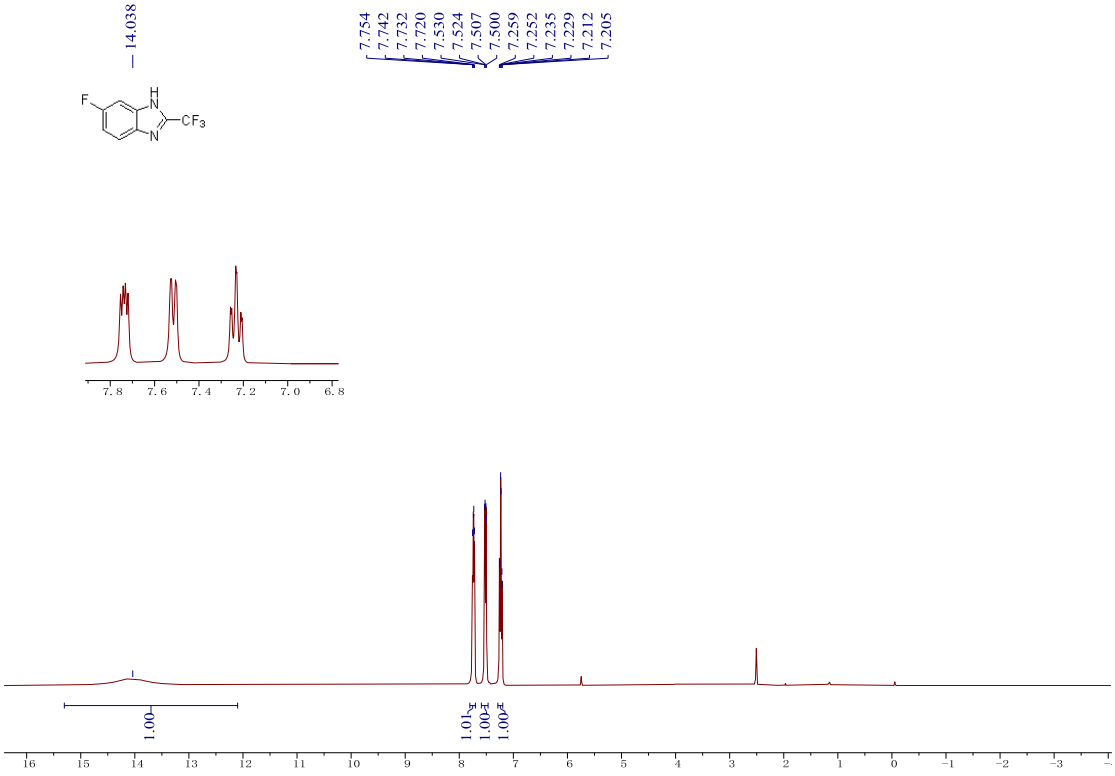
^{19}F NMR spectra of **3m** in DMSO-d_6



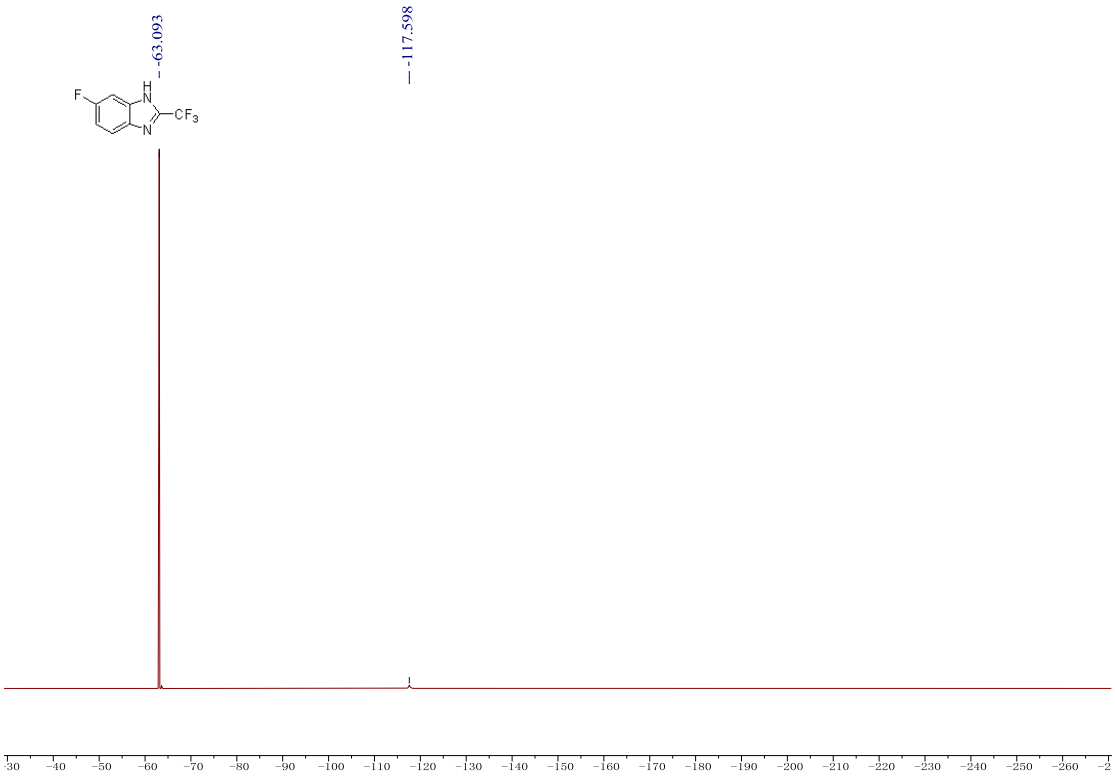
$^{13}C\{^{1}H\}$ NMR spectra of **3m** in DMSO-d_6



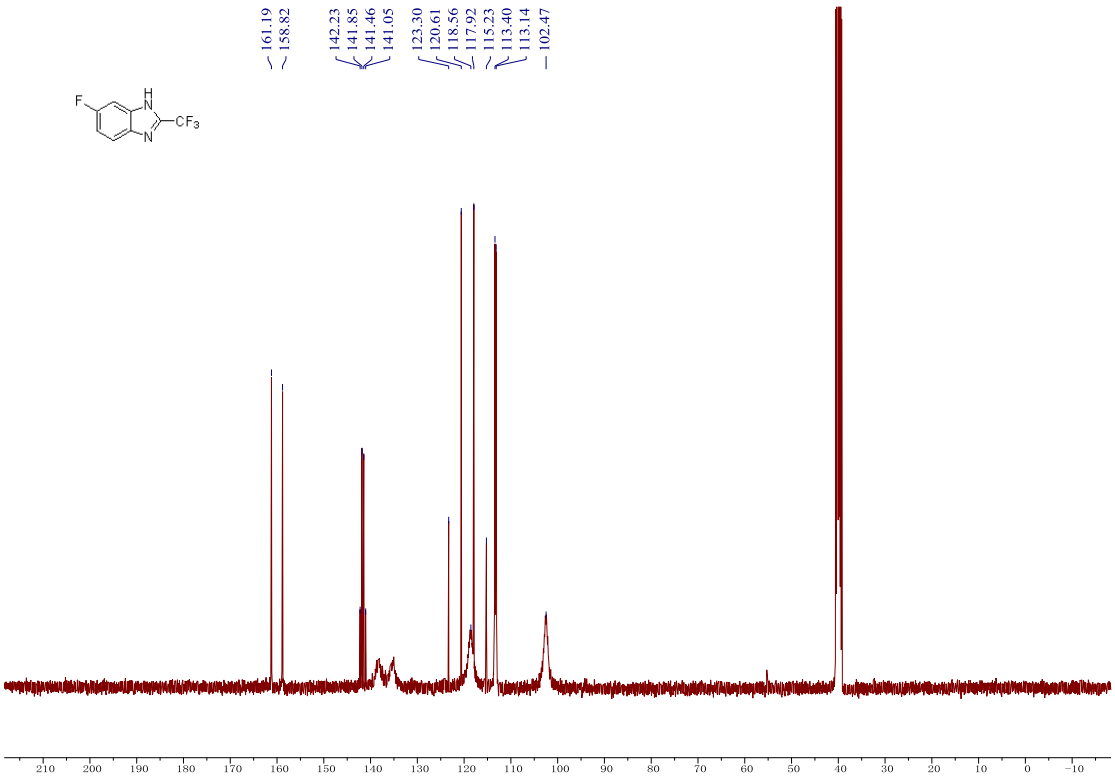
^{1}H NMR spectra of **3n** in DMSO-d_6



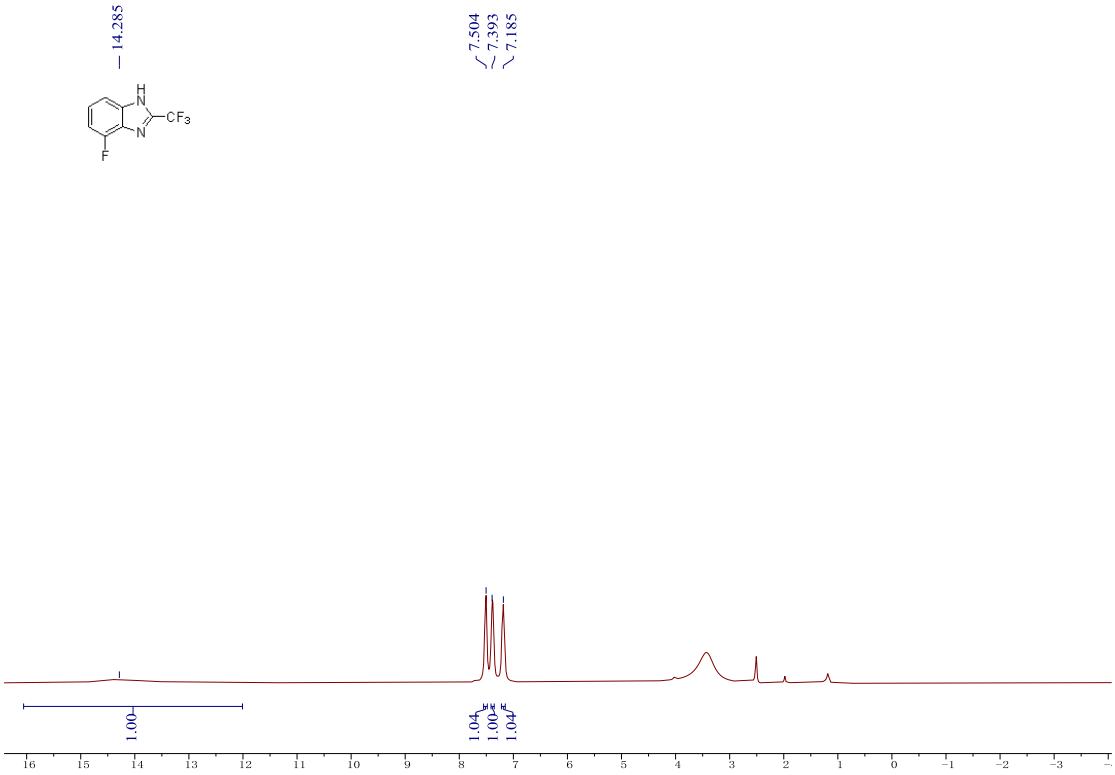
^{19}F NMR spectra of **3n** in DMSO-d_6



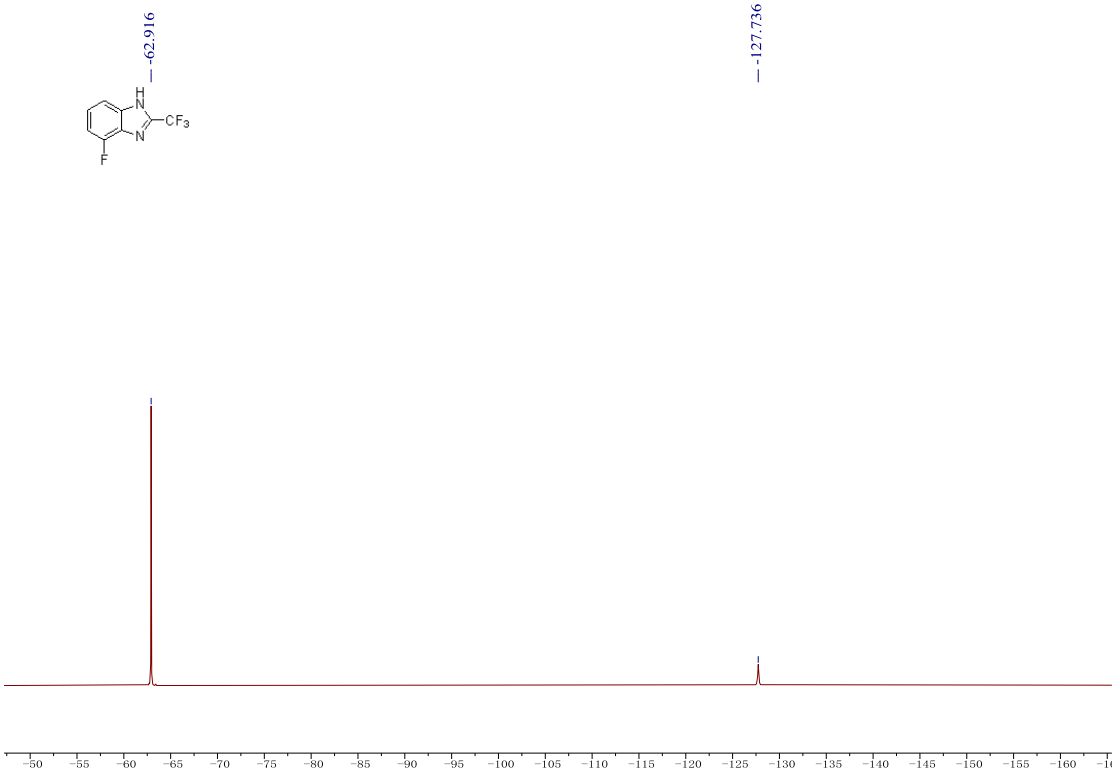
^{13}C{^{1}H} NMR spectra of **3n** in DMSO-d_6



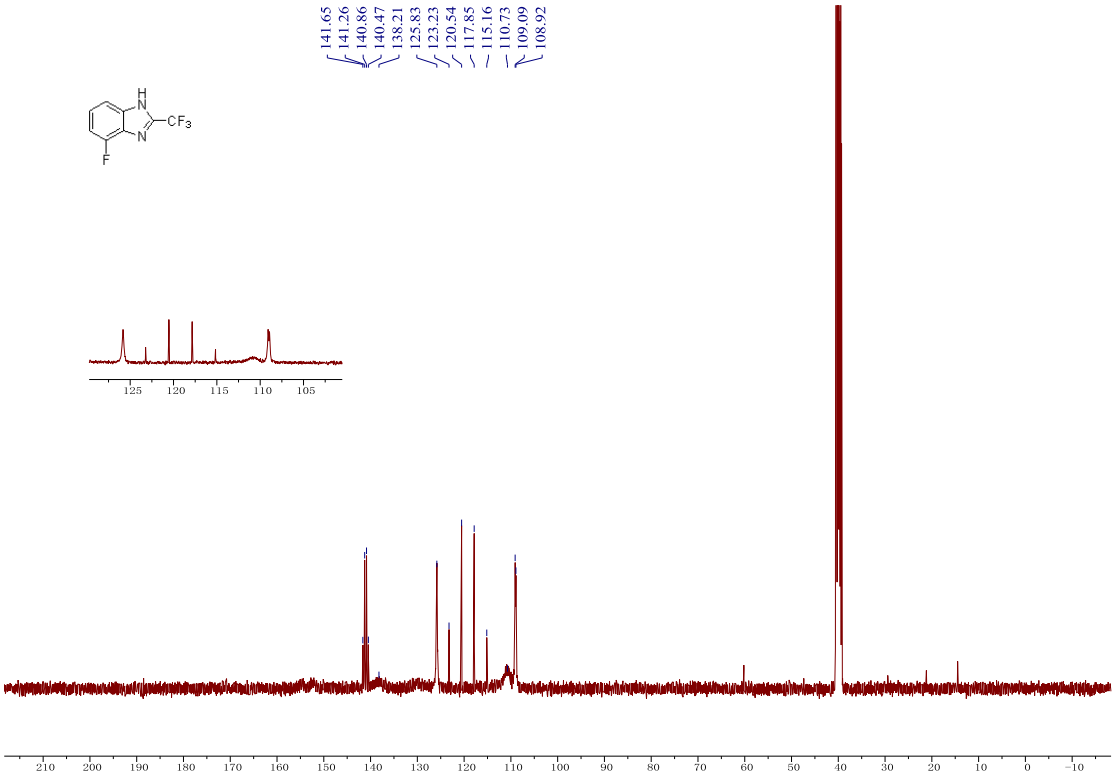
^{1}H NMR spectra of **3o** in DMSO-d_6



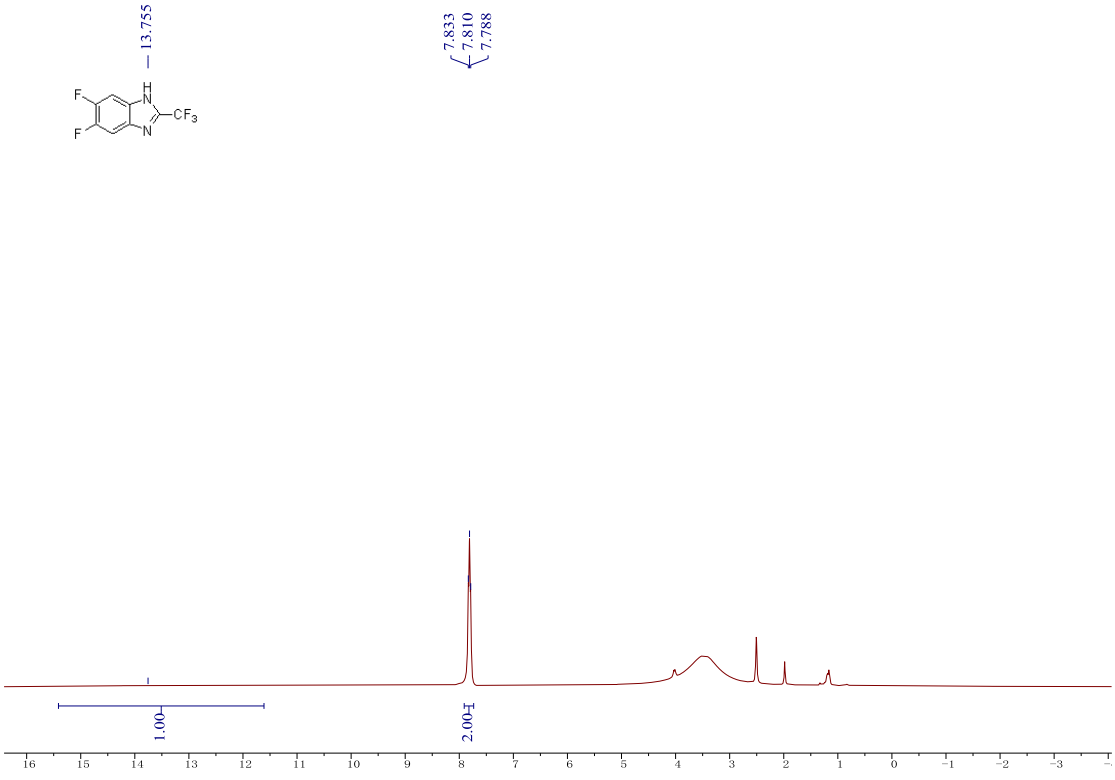
^{19}F NMR spectra of **3o** in DMSO-d_6



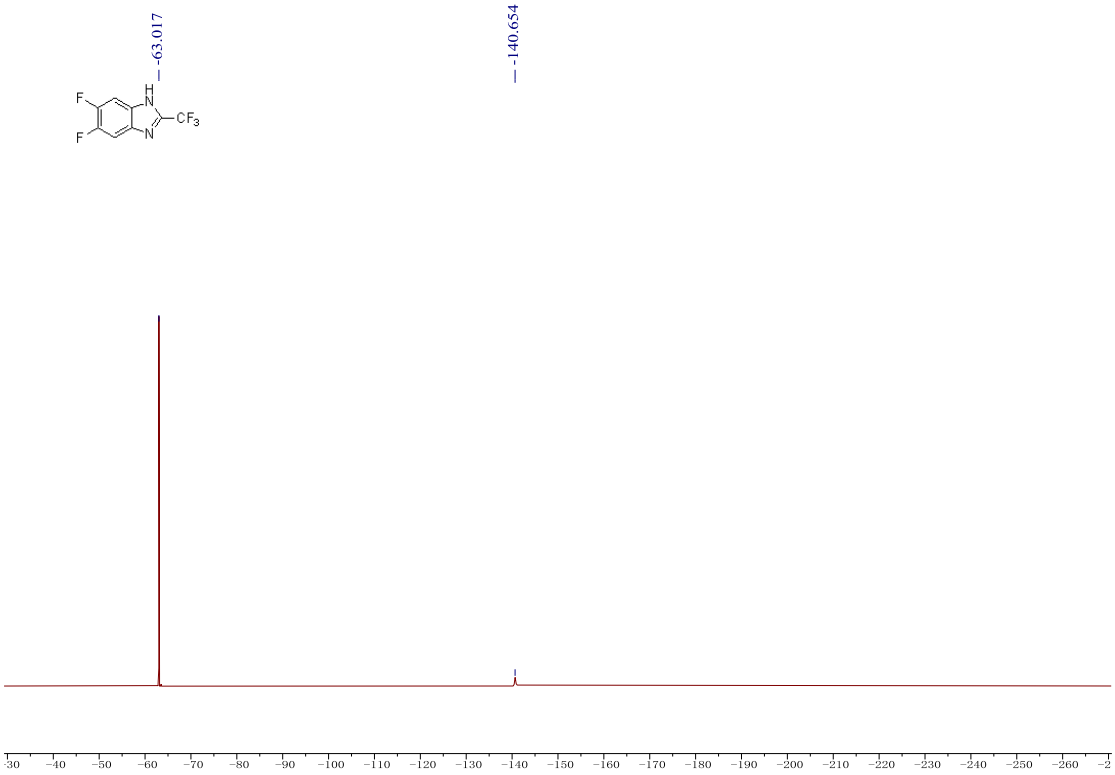
$^{13}C\{^{1}H\}$ NMR spectra of **3o** in DMSO-d_6



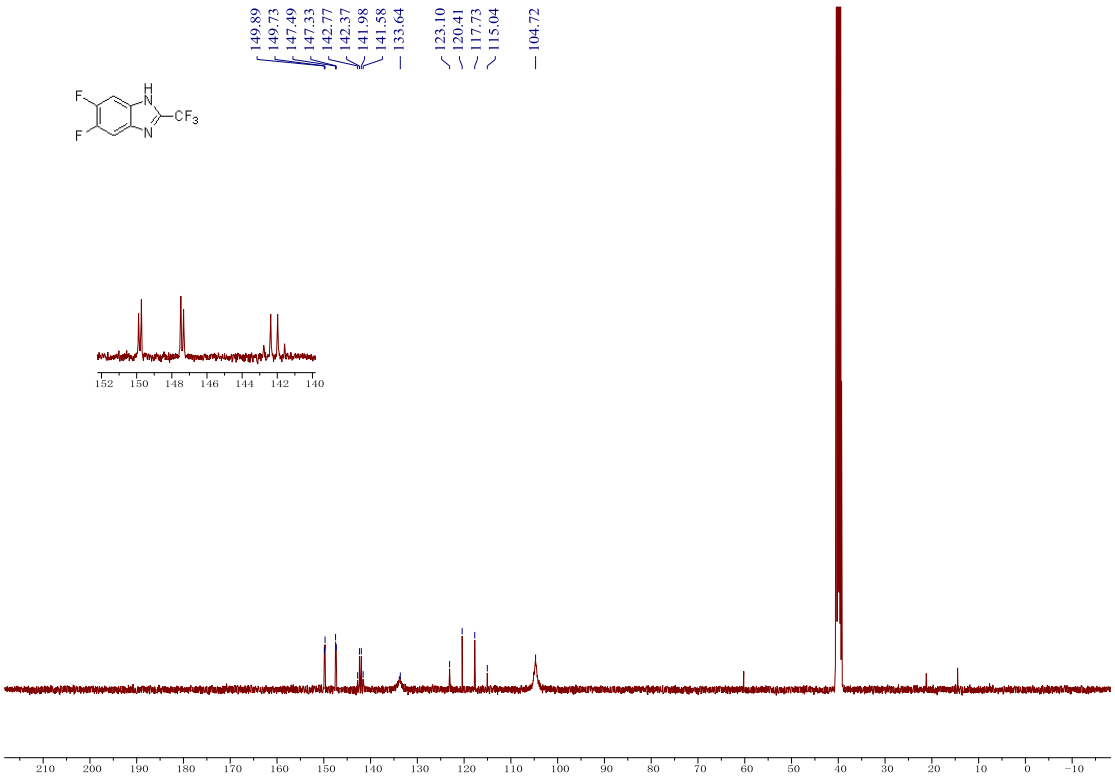
^{1}H NMR spectra of **3p** in DMSO-d_6



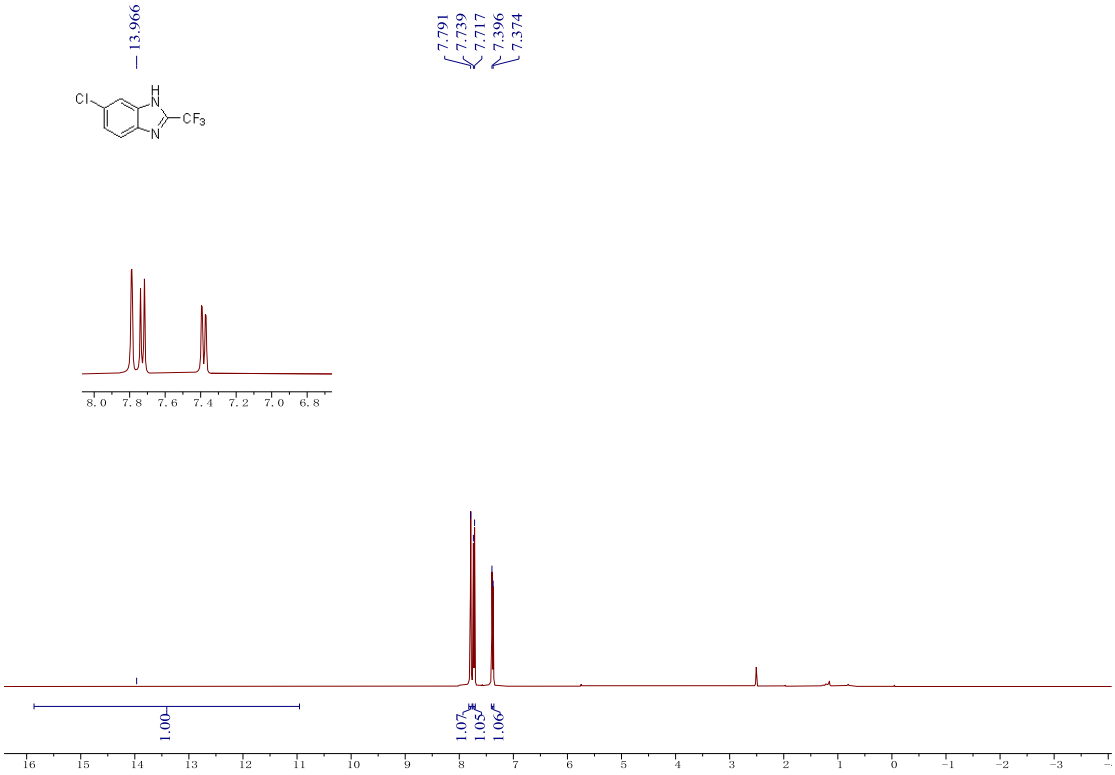
^{19}F NMR spectra of **3p** in DMSO-d_6



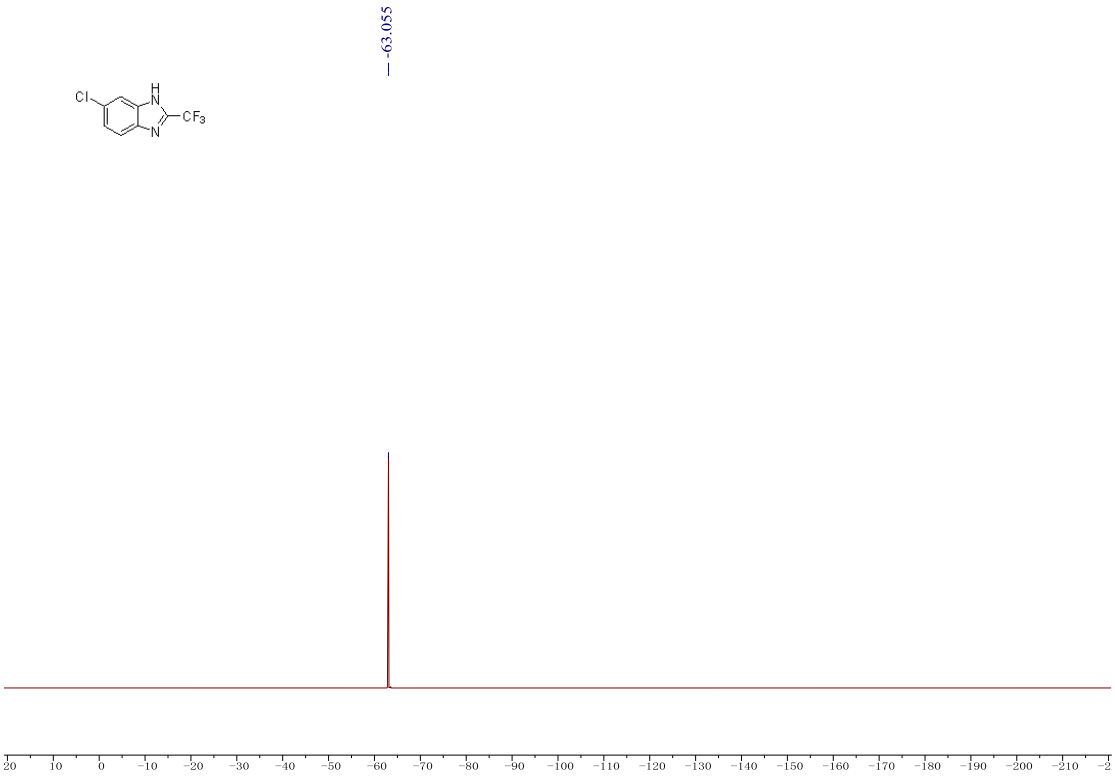
^{13}C{^{1}H} NMR spectra of **3p** in DMSO-d_6



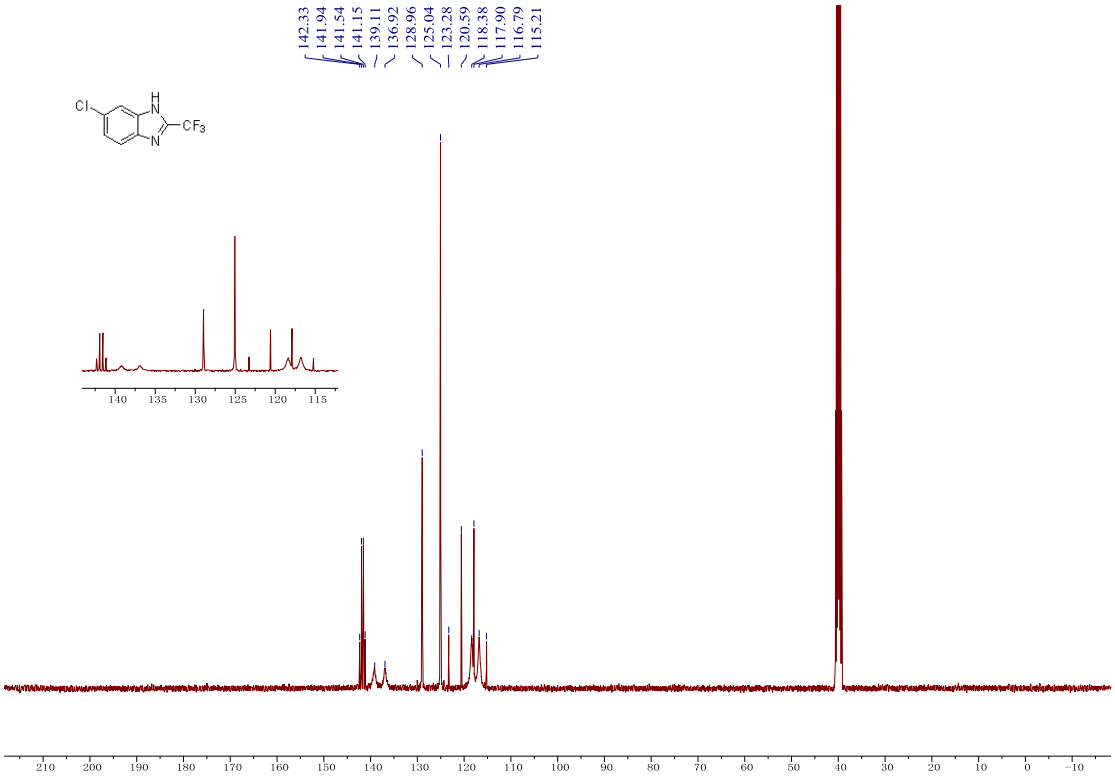
^{1}H NMR spectra of **3q** in DMSO-d_6



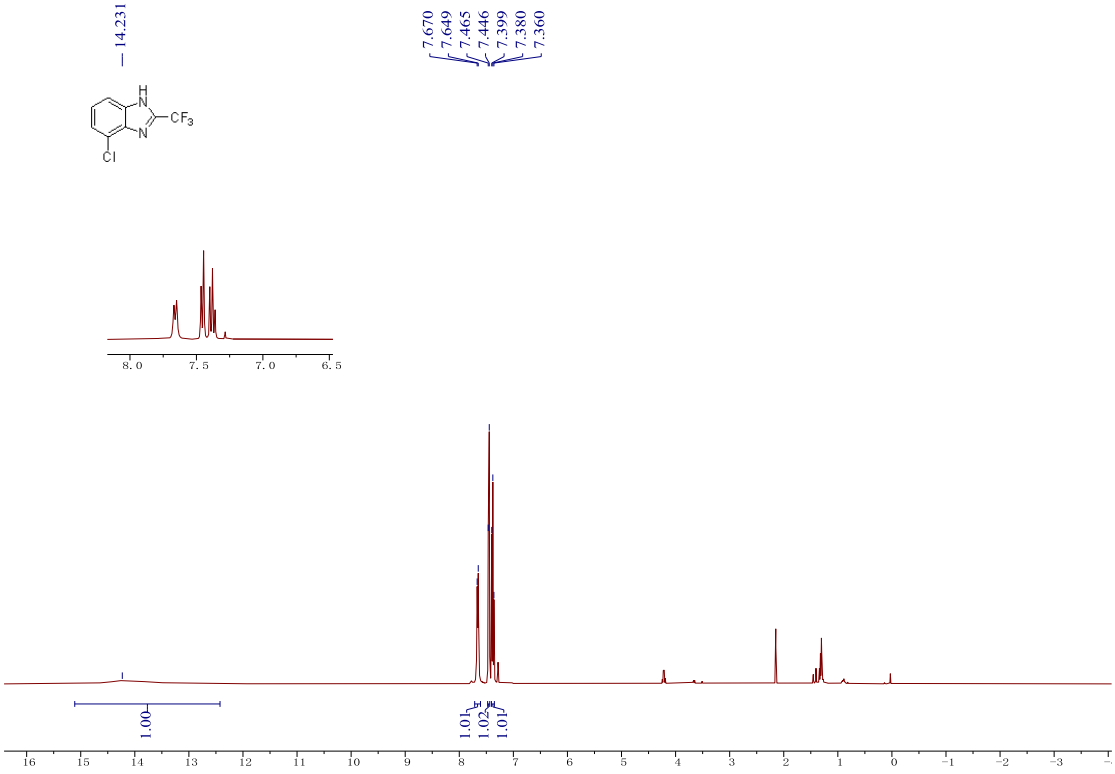
^{19}F NMR spectra of **3q** in DMSO-d_6



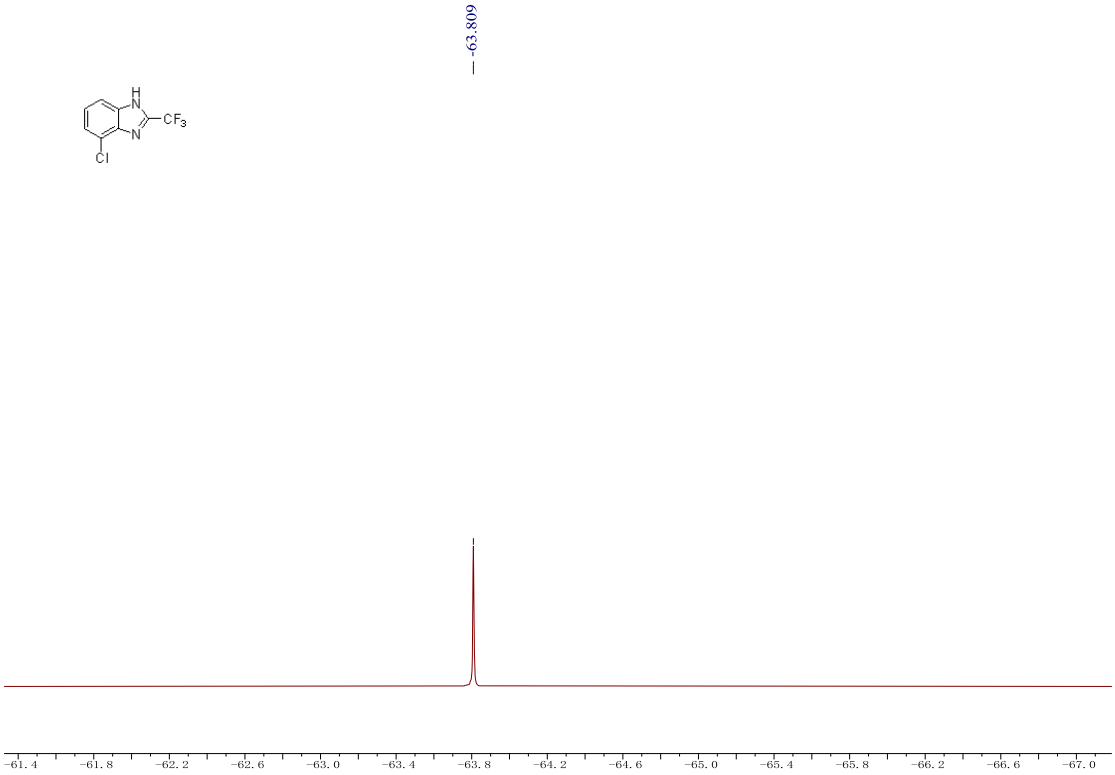
$^{13}C\{^{1}H\}$ NMR spectra of **3q** in DMSO-d_6



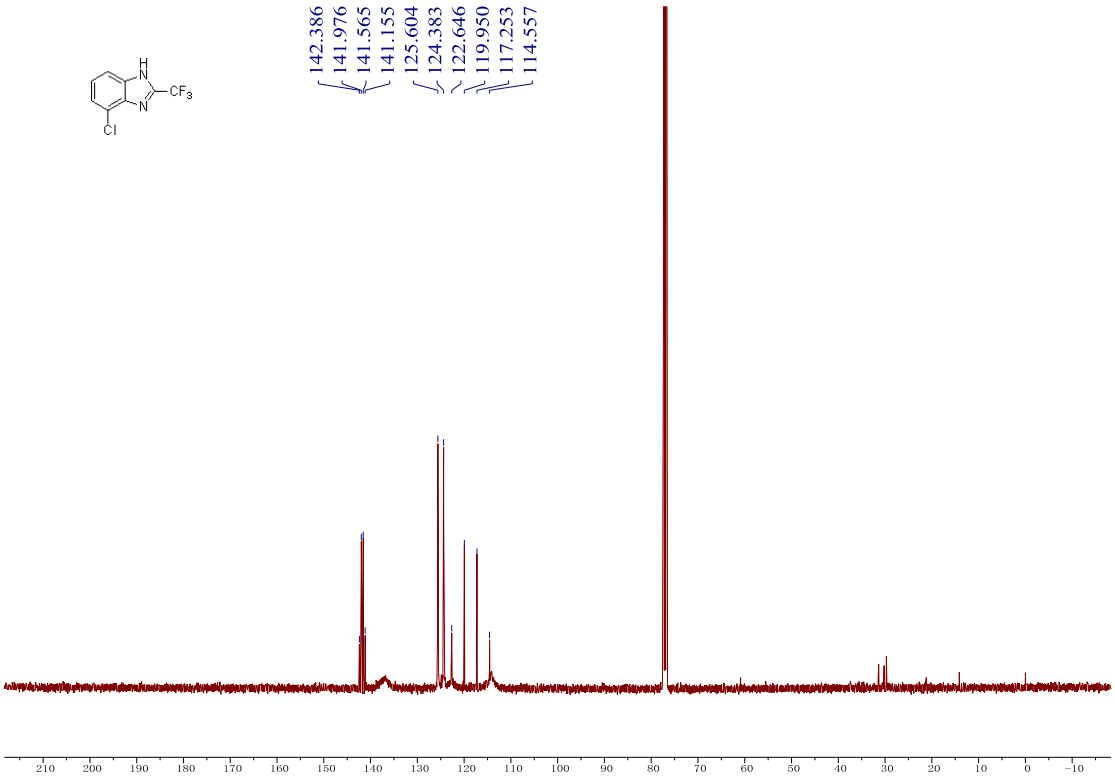
^{1}H NMR spectra of **3r** in $CDCl_3$



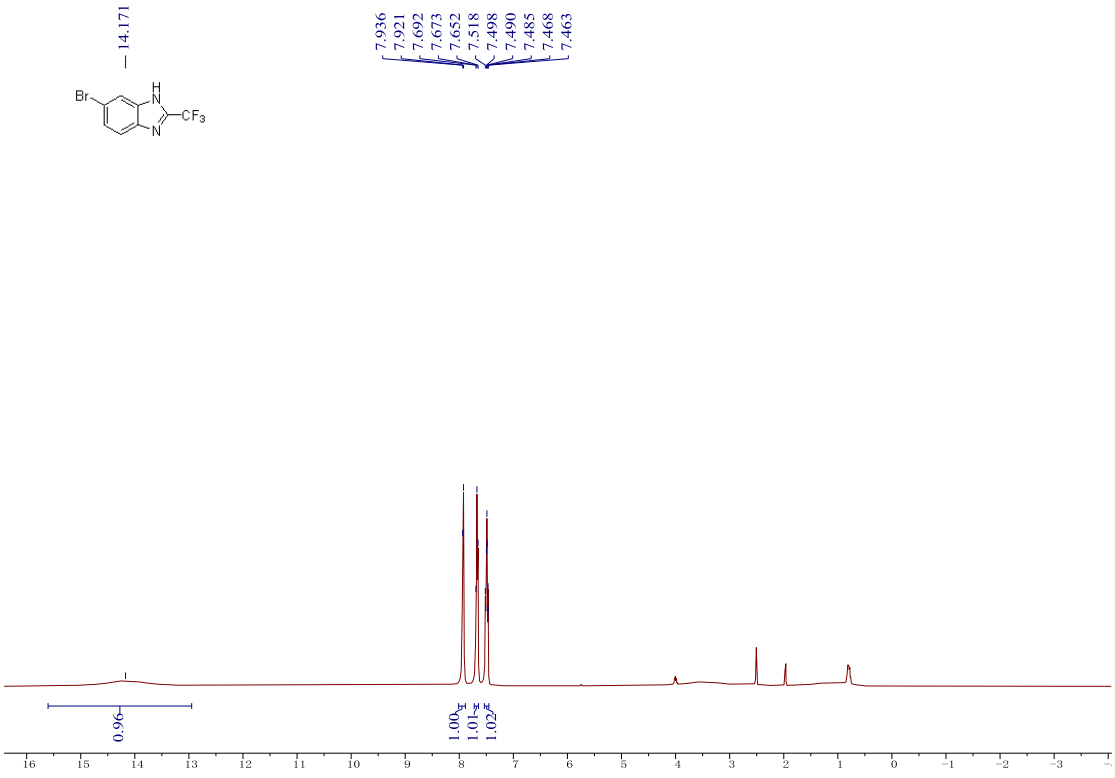
^{19}F NMR spectra of **3r** in $CDCl_3$



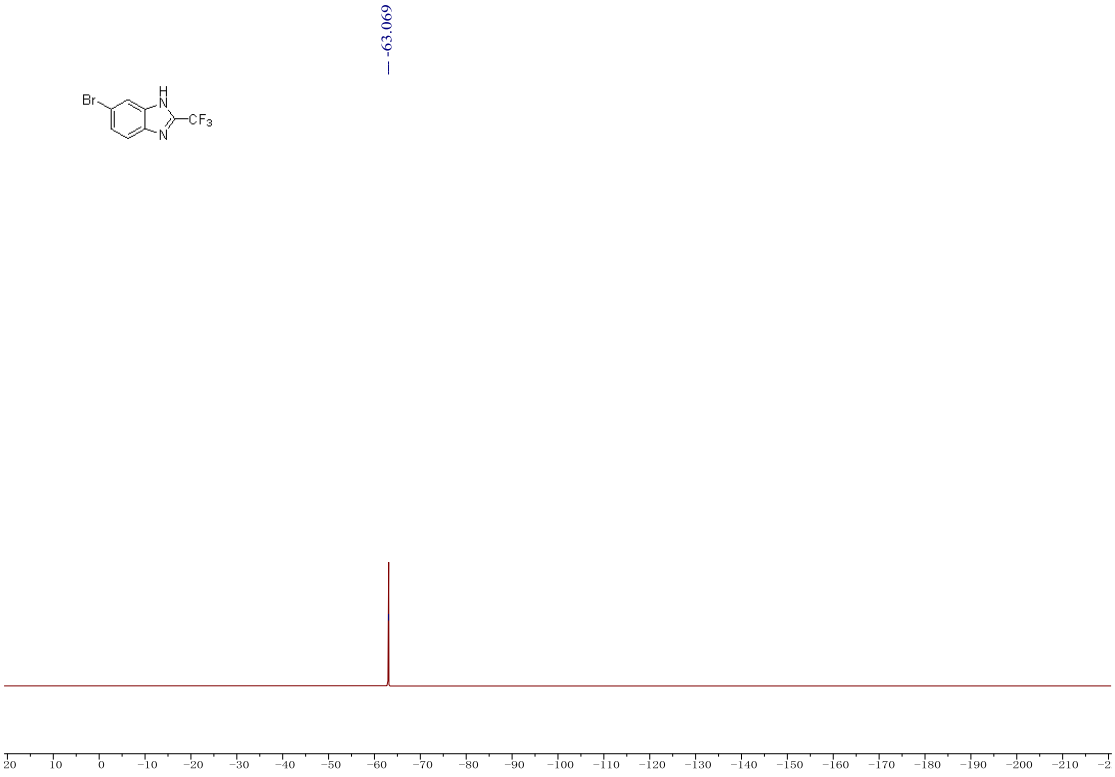
$^{13}C\{^{1}H\}$ NMR spectra of 3**r** in $CDCl_3$



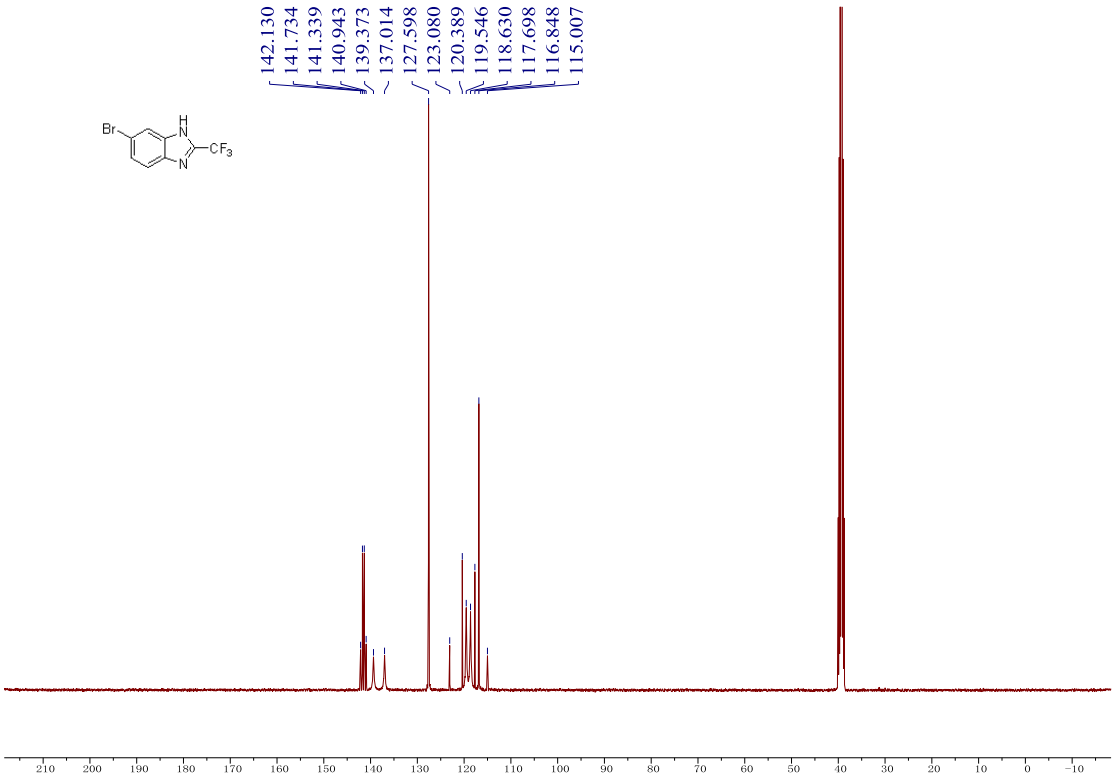
^{1}H NMR spectra of **3s** in DMSO-d_6



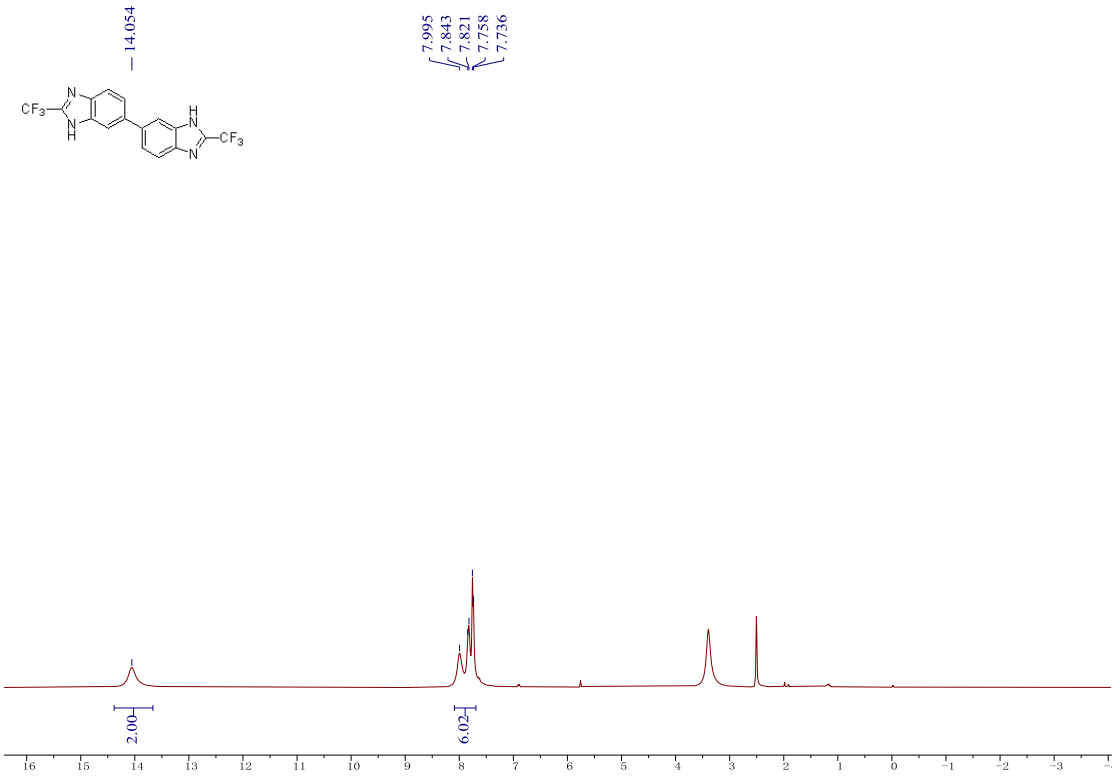
^{19}F NMR spectra of **3s** in DMSO-d_6



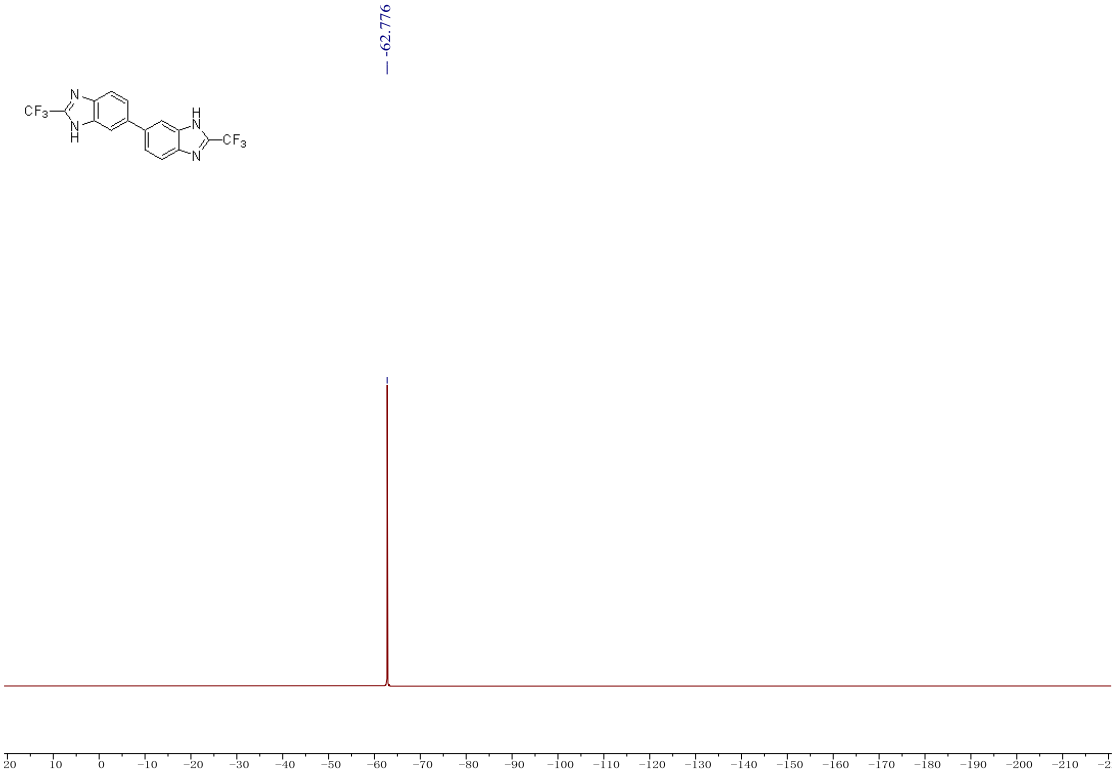
$^{13}C\{^{1}H\}$ NMR spectra of **3s** in DMSO-d_6



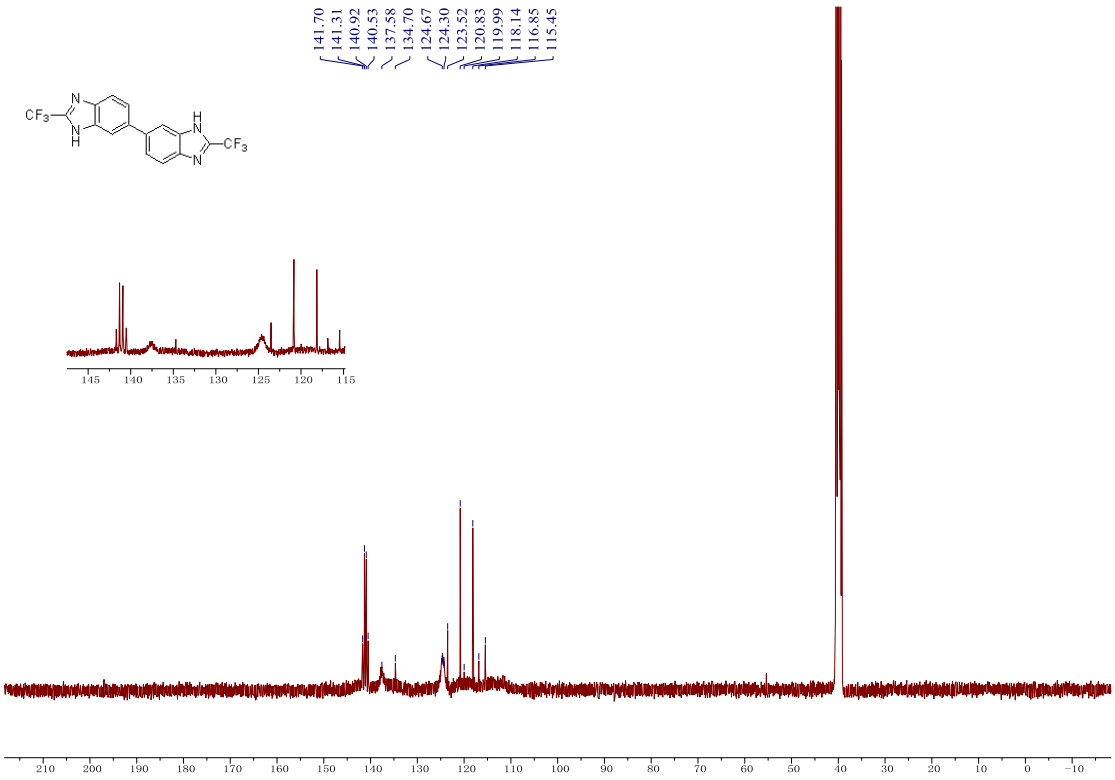
^{1}H NMR spectra of **3t** in DMSO-d_6



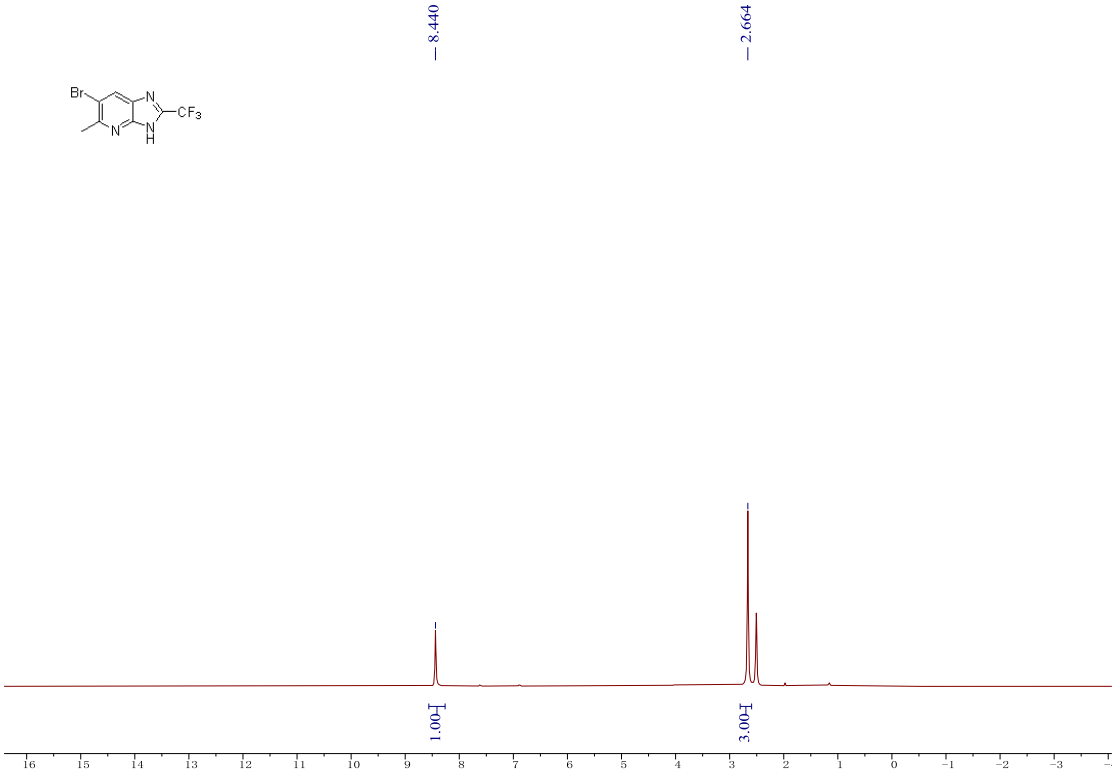
^{19}F NMR spectra of **3t** in DMSO-d_6



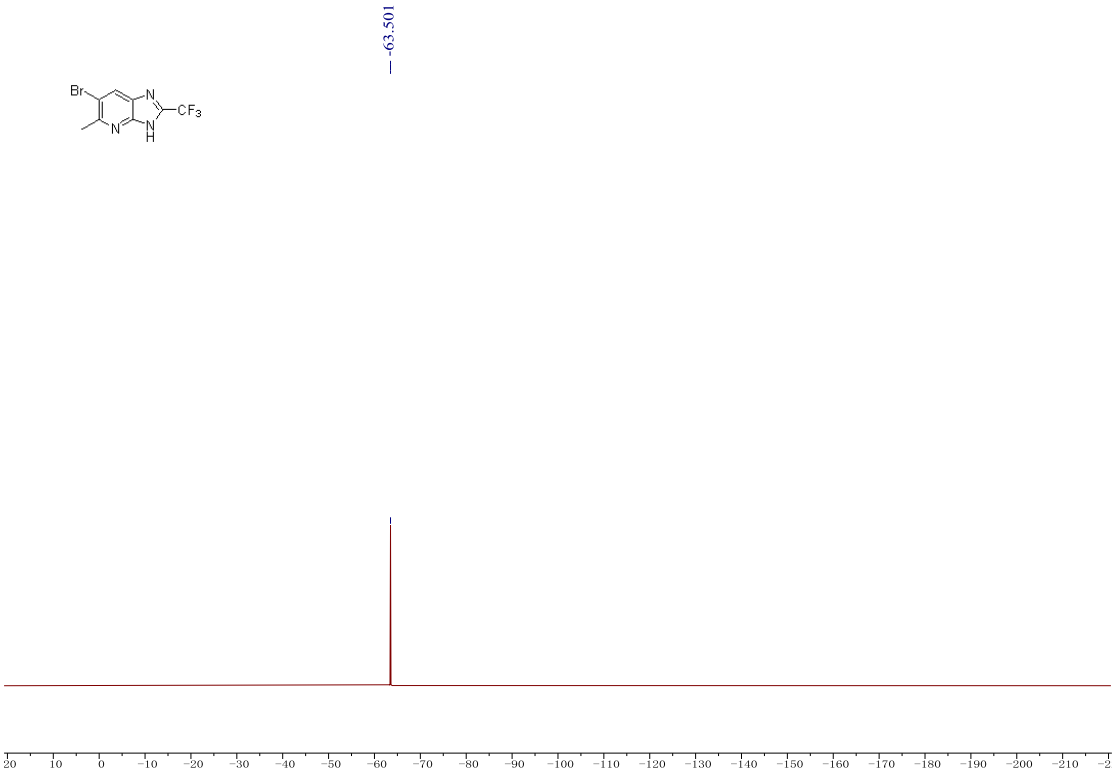
^{13}C{^{1}H} NMR spectra of **3t** in DMSO-d_6



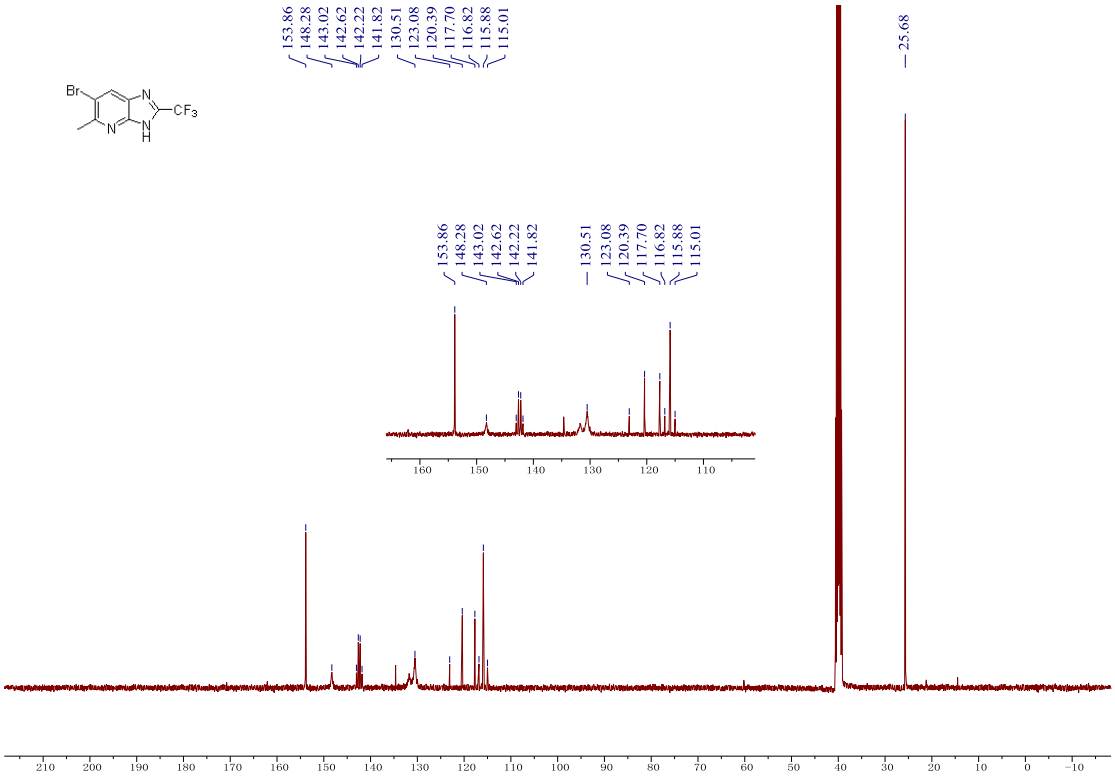
^{1}H NMR spectra of **3u** in DMSO-d_6



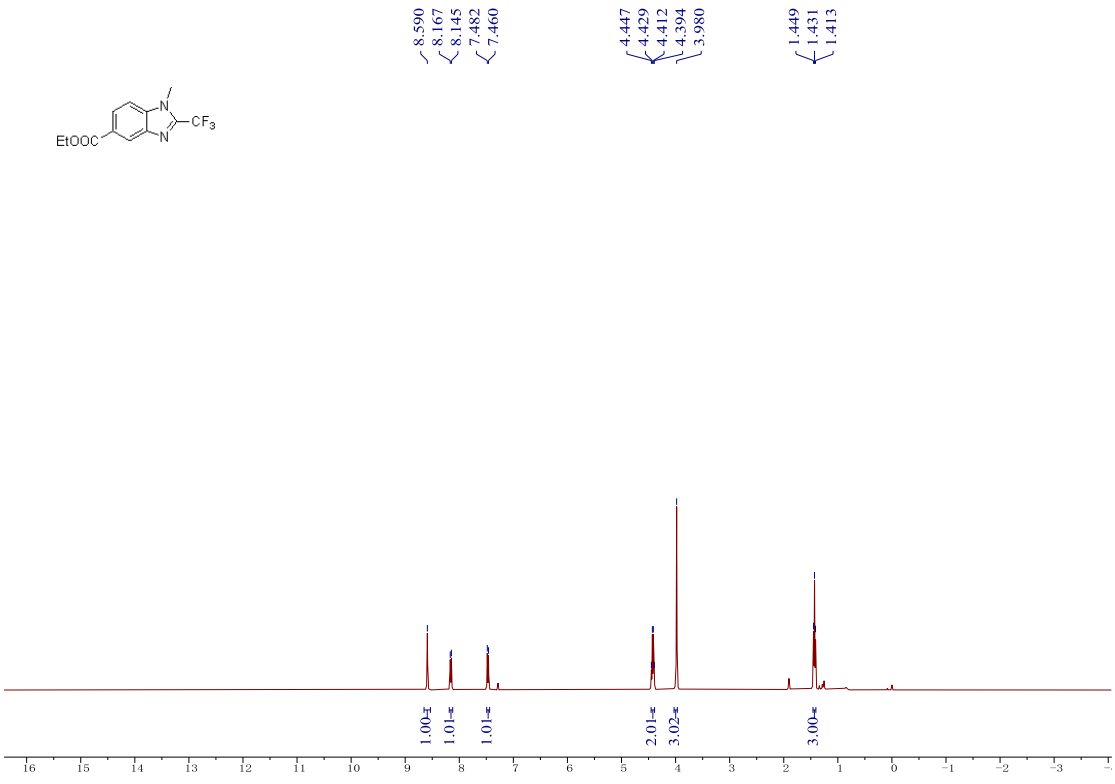
^{19}F NMR spectra of **3u** in DMSO-d_6



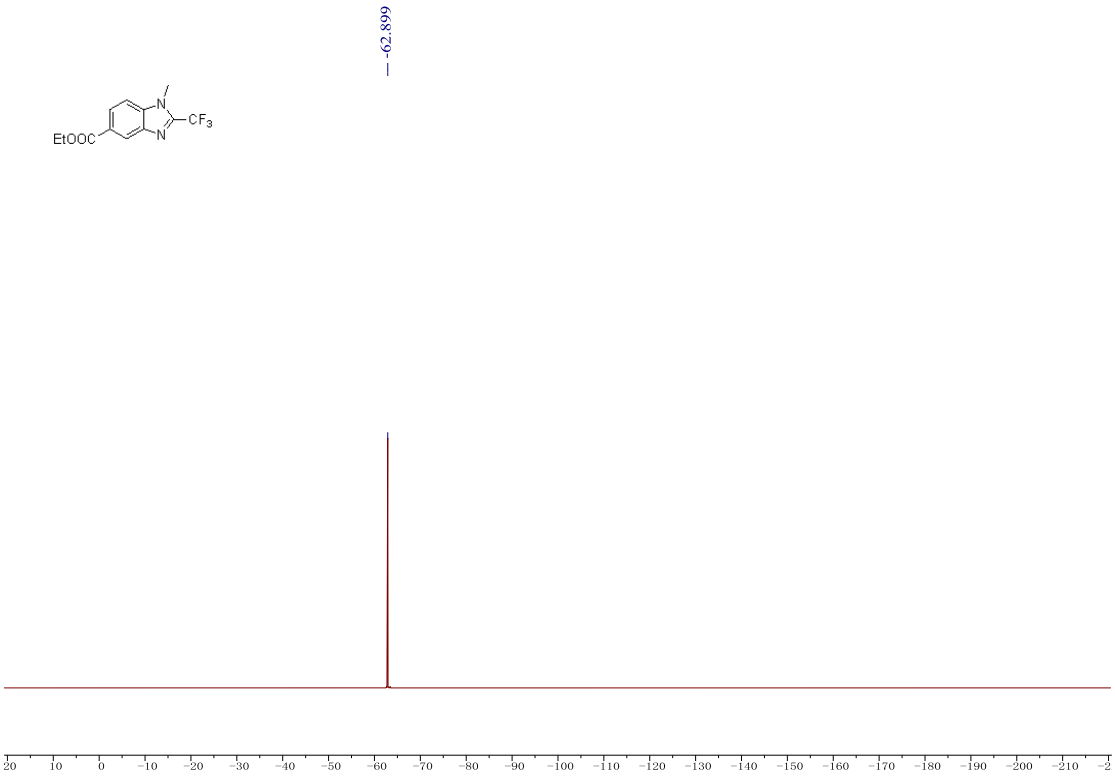
$^{13}C\{^{1}H\}$ NMR spectra of **3u** in DMSO-d_6



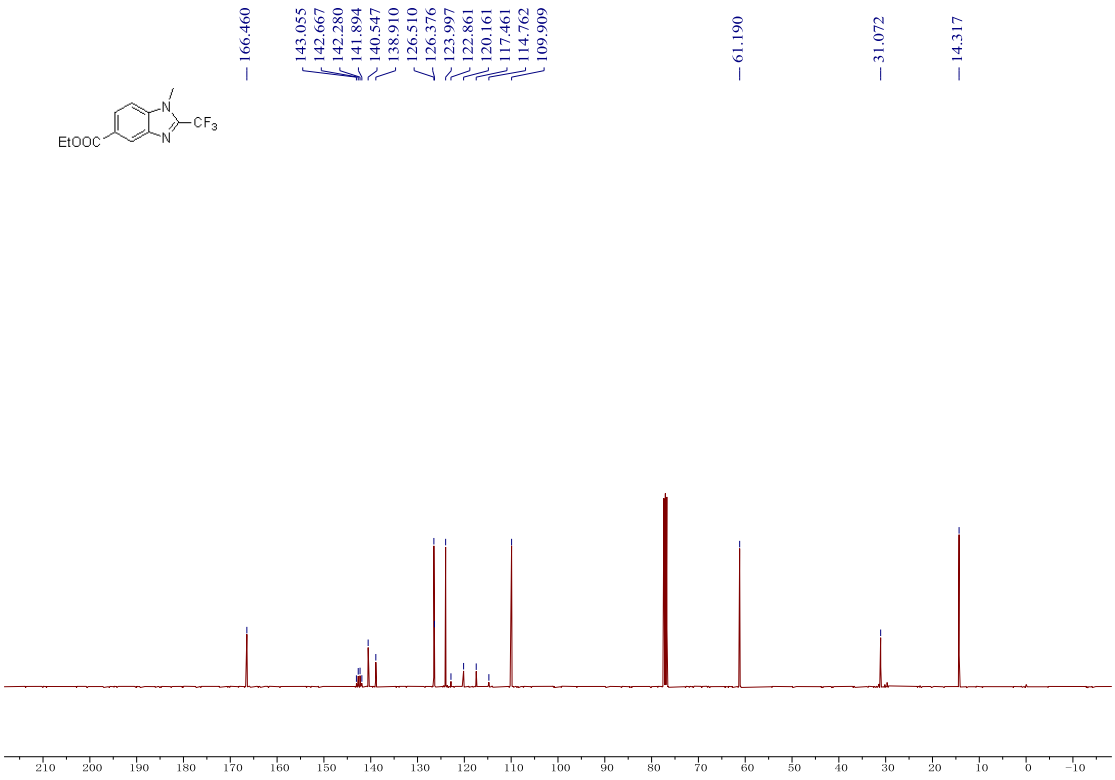
^{1}H NMR spectra of **3v** in $CDCl_3$



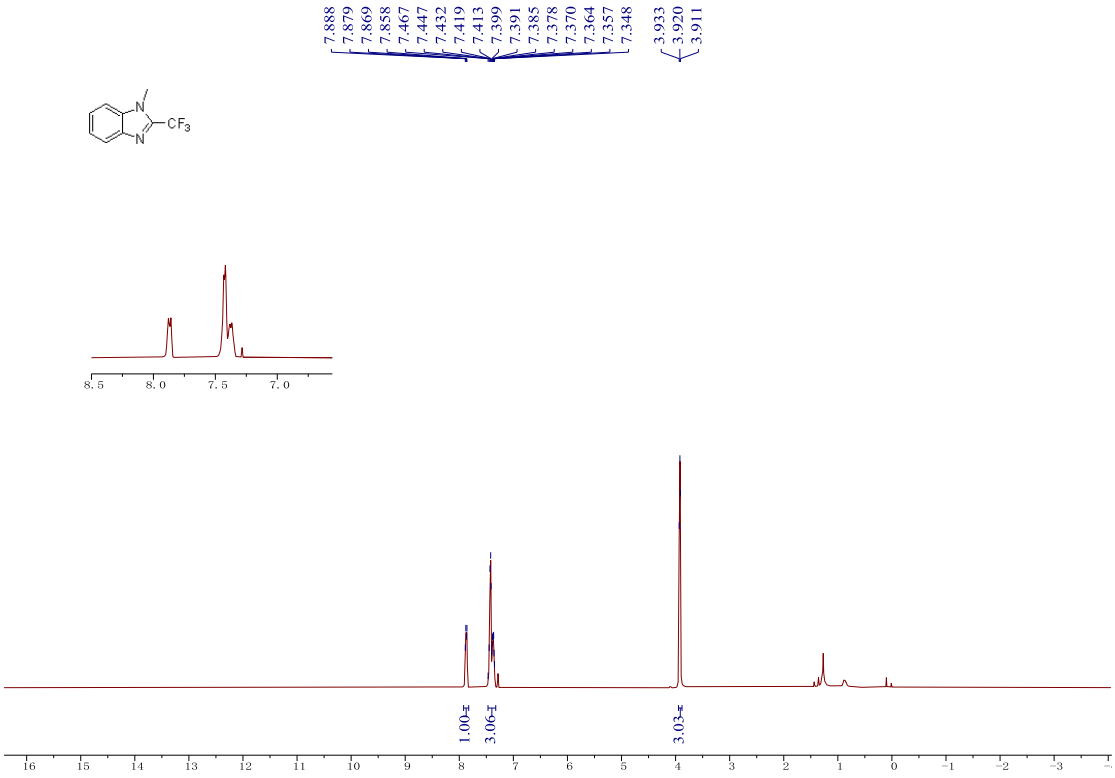
^{19}F NMR spectra of **3v** in $CDCl_3$



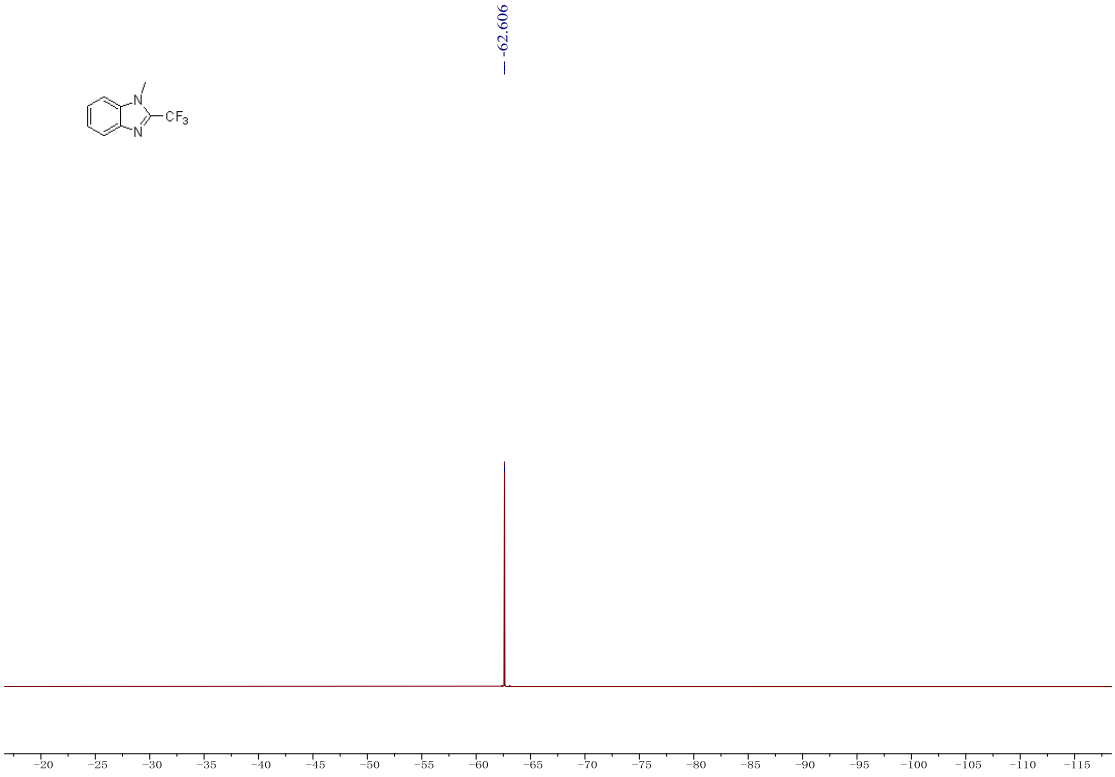
$^{13}C\{^{1}H\}$ NMR spectra of **3v** in $CDCl_3$



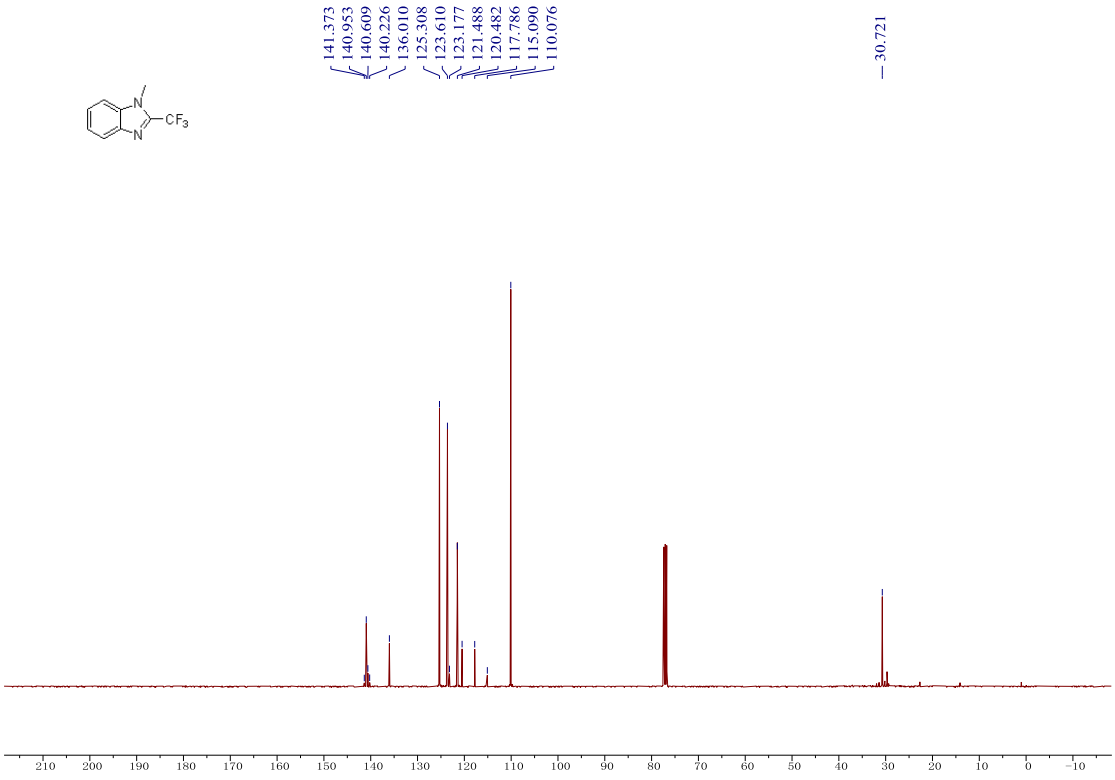
^{1}H NMR spectra of **3w** in $CDCl_3$



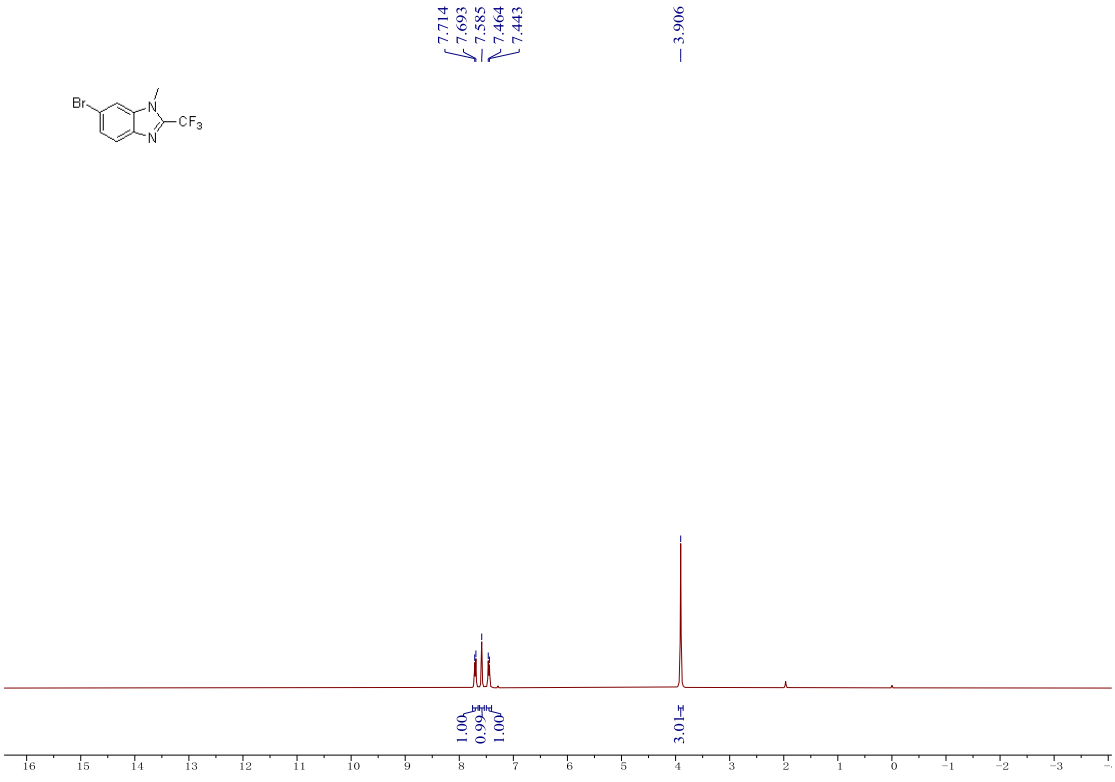
^{19}F NMR spectra of **3w** in $CDCl_3$



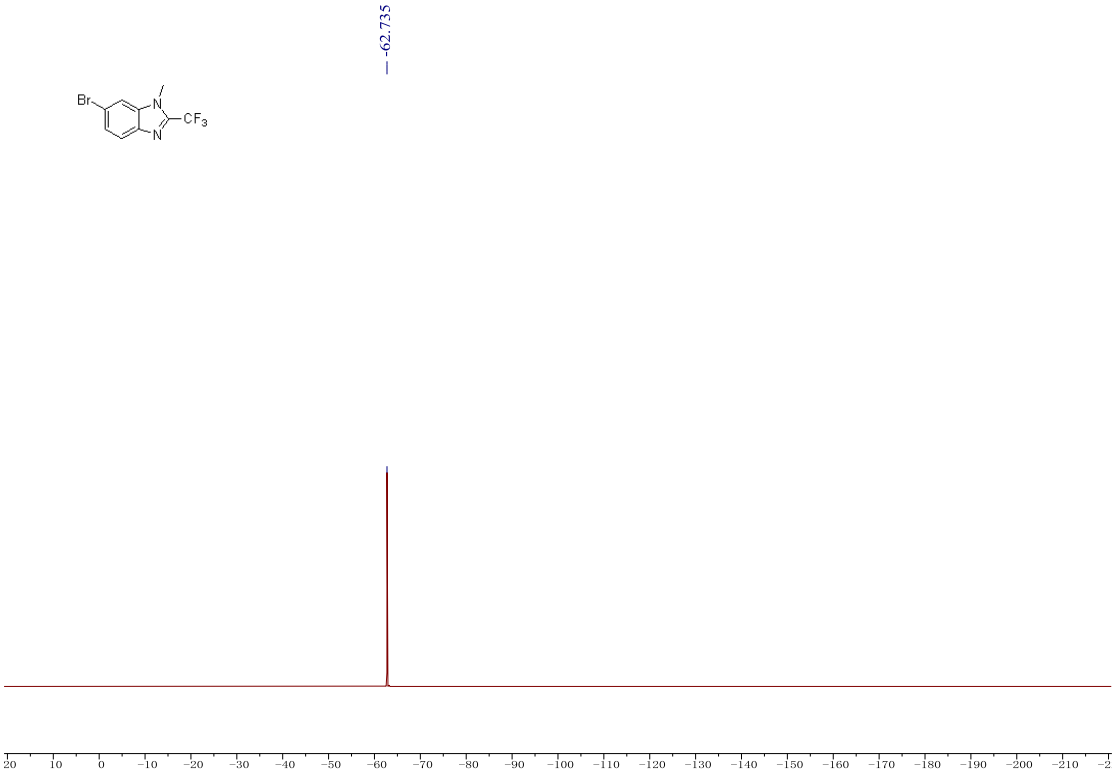
$^{13}C\{^{1}H\}$ NMR spectra of **3w** in $CDCl_3$



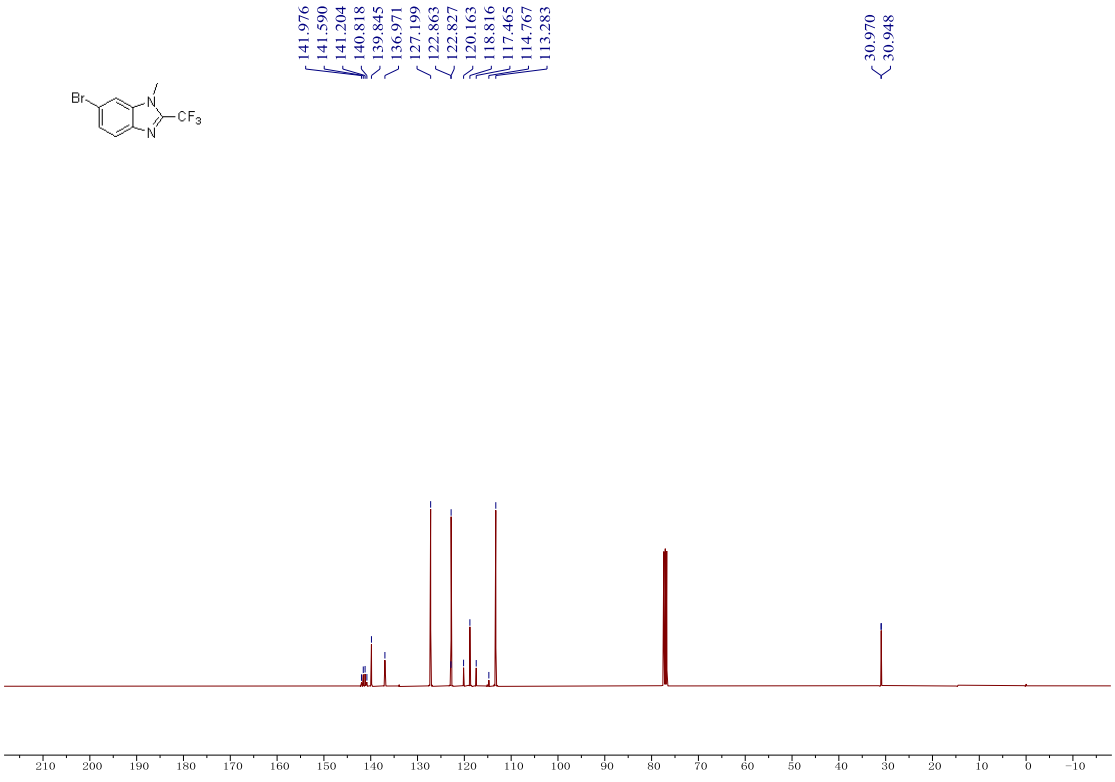
^{1}H NMR spectra of **3x** in $CDCl_3$



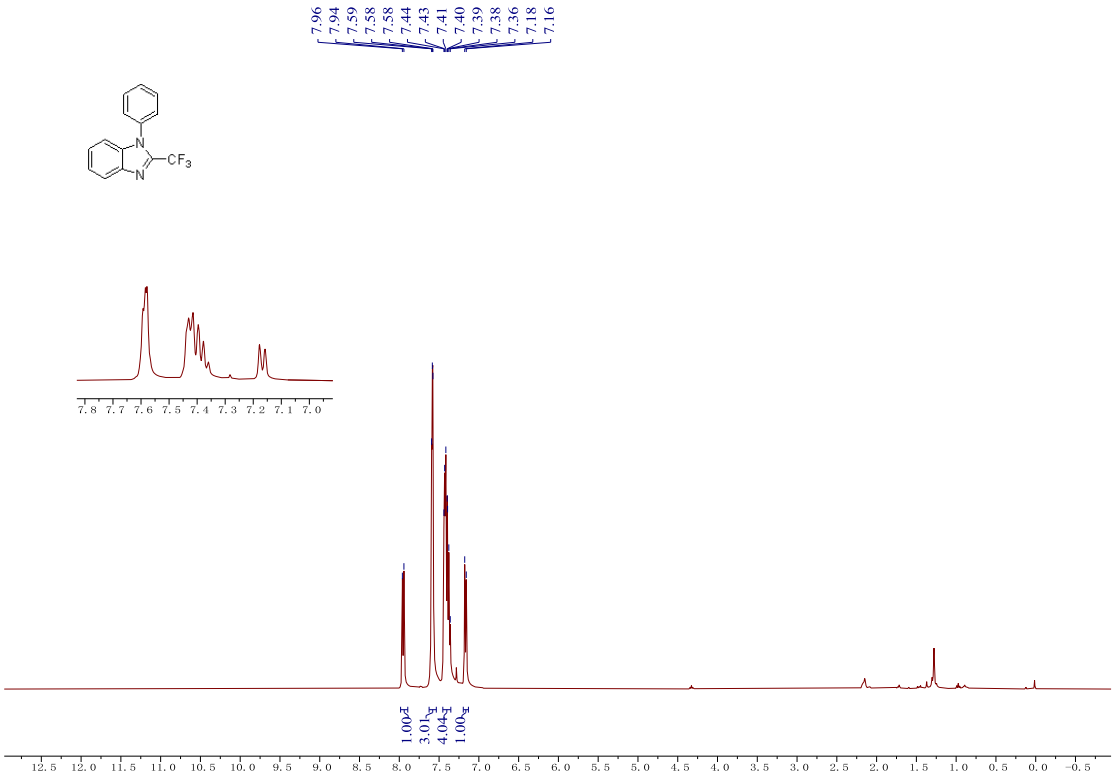
^{19}F NMR spectra of **3x** in $CDCl_3$



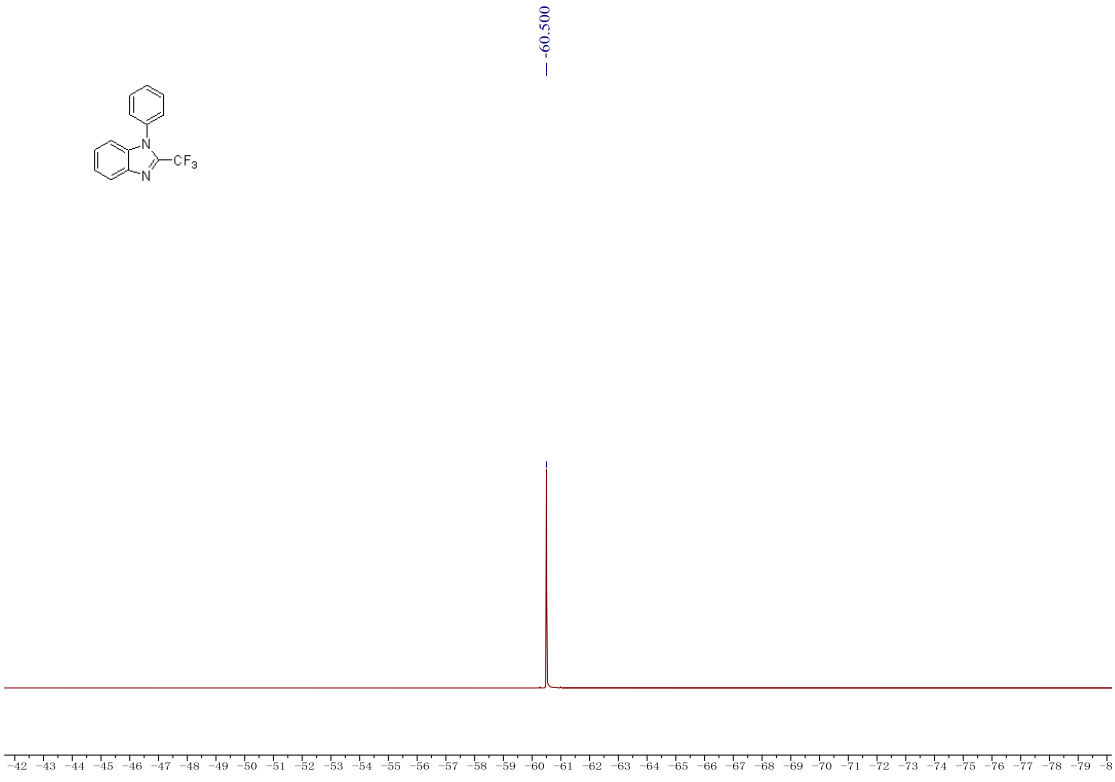
$^{13}C\{^{1}H\}$ NMR spectra of **3x** in $CDCl_3$



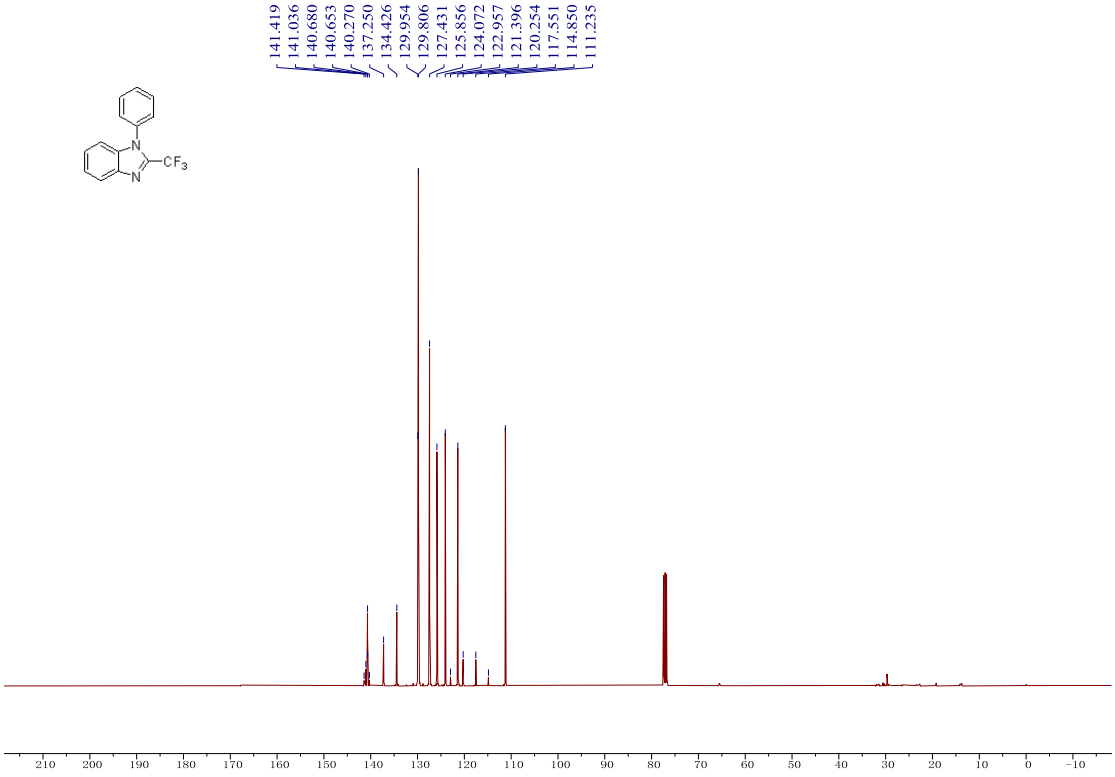
^{1}H NMR spectra of **3y** in $CDCl_3$



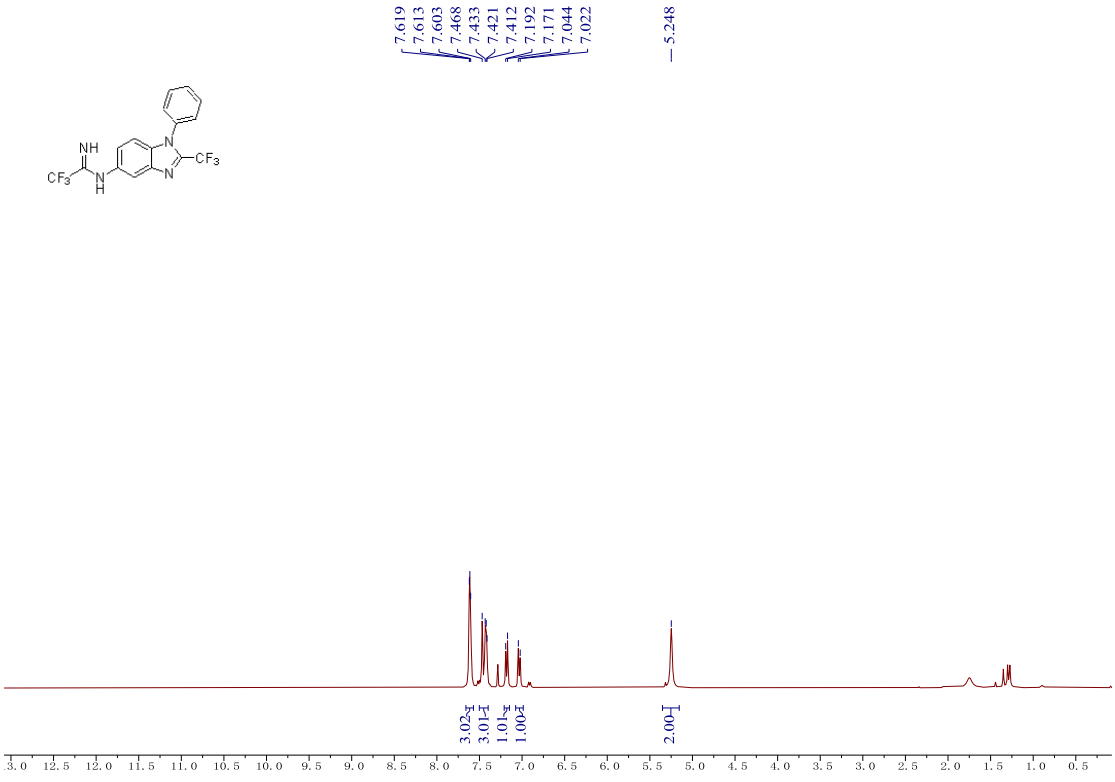
^{19}F NMR spectra of **3y** in $CDCl_3$



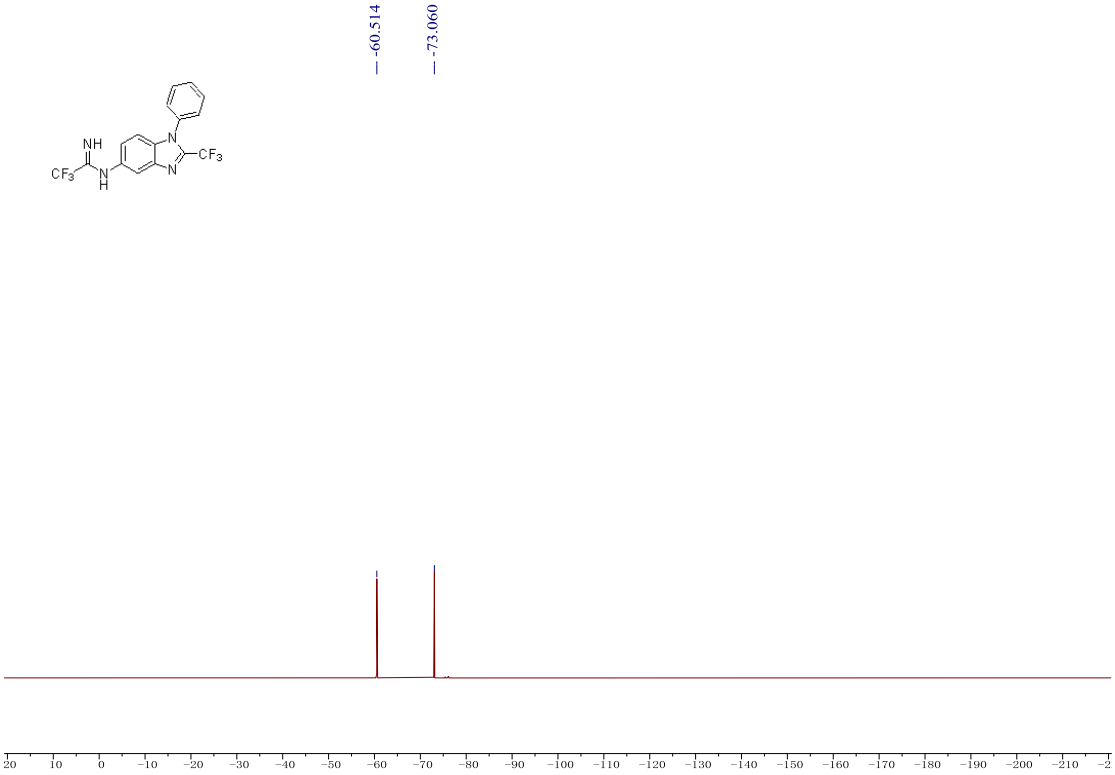
$^{13}C\{^{1}H\}$ NMR spectra of **3y** in $CDCl_3$



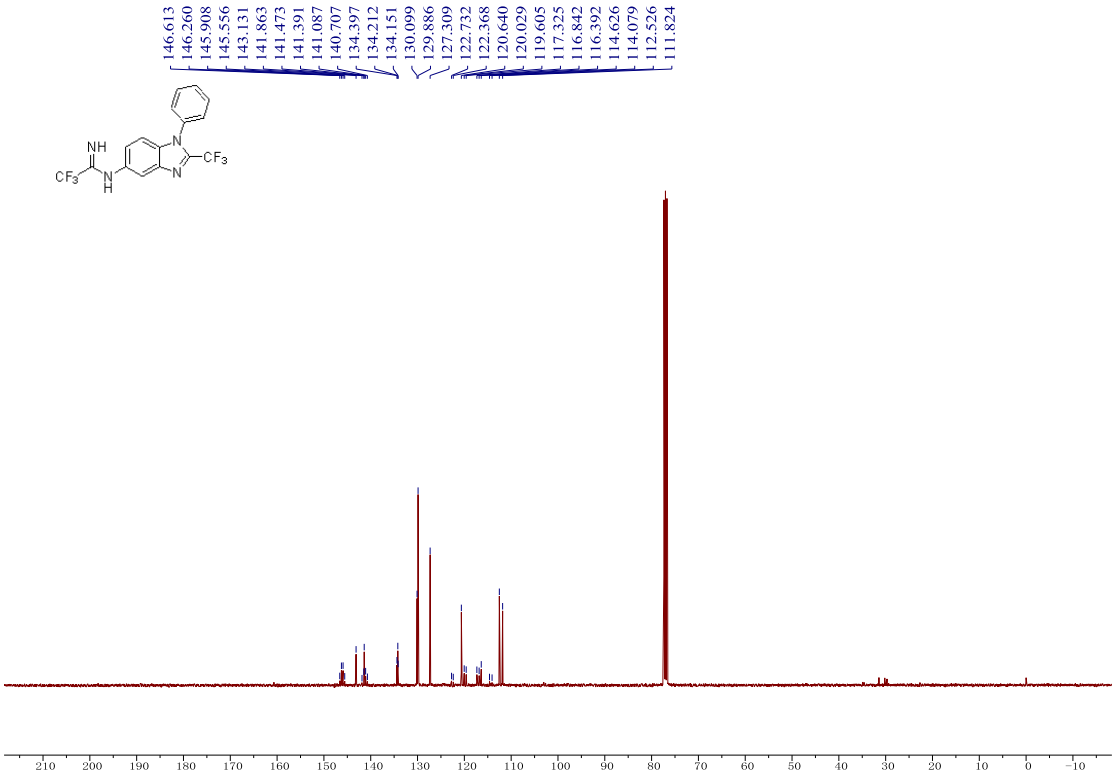
^{1}H NMR spectra of **3z** in $CDCl_3$



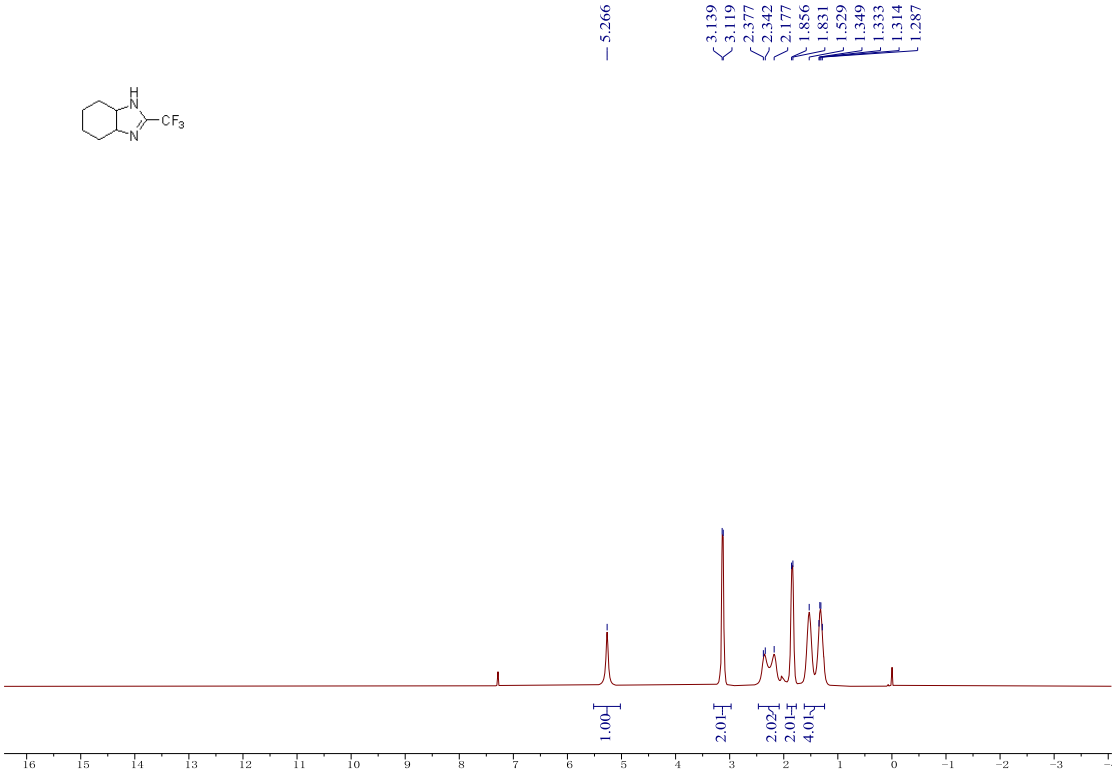
^{19}F NMR spectra of **3z** in $CDCl_3$



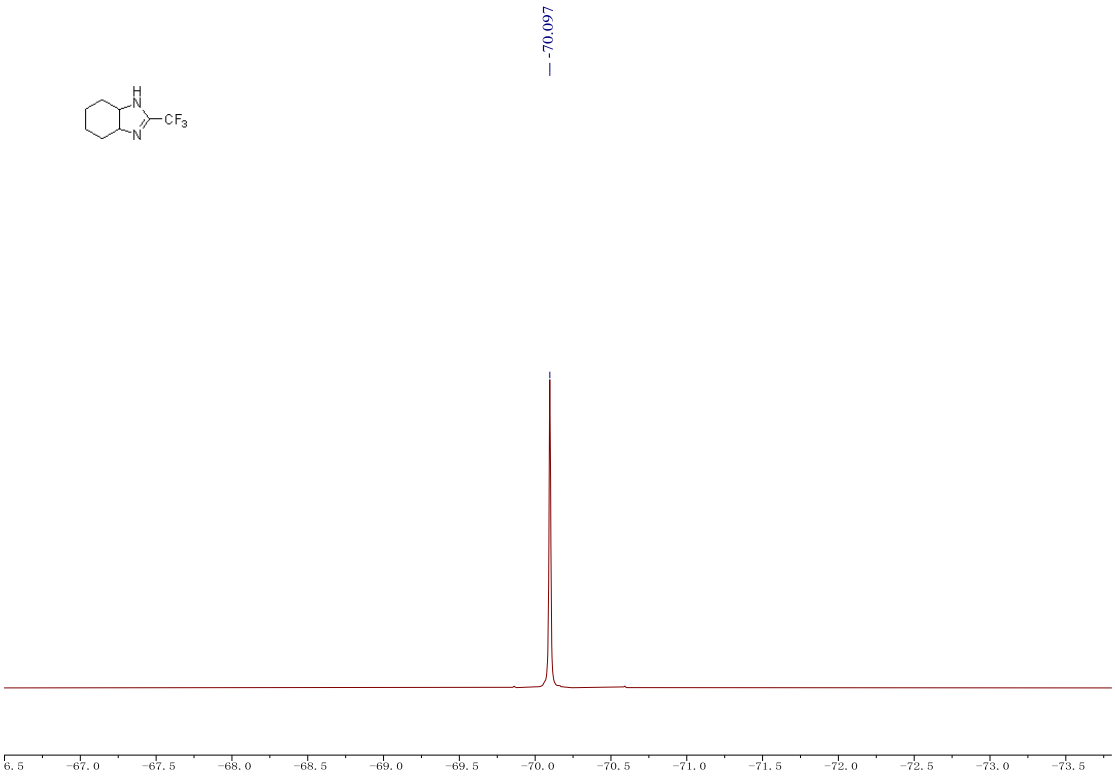
$^{13}C\{^{1}H\}$ NMR spectra of **3z** in $CDCl_3$



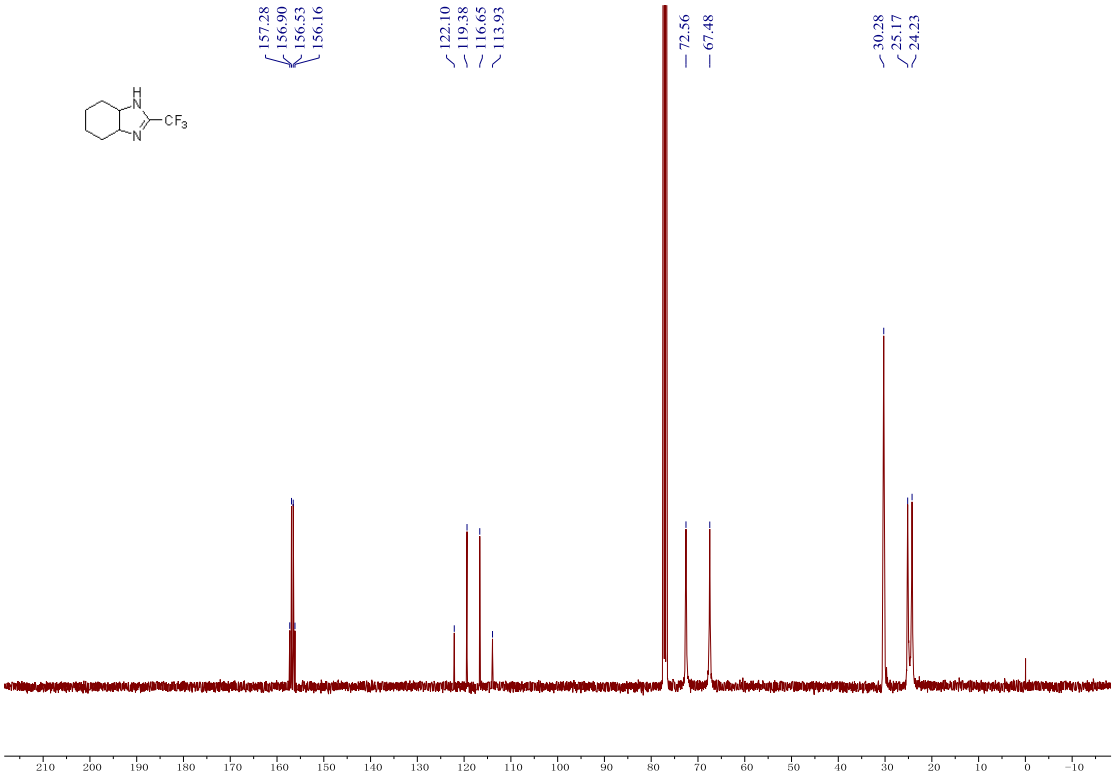
^{1}H NMR spectra of **3aa** in $CDCl_3$



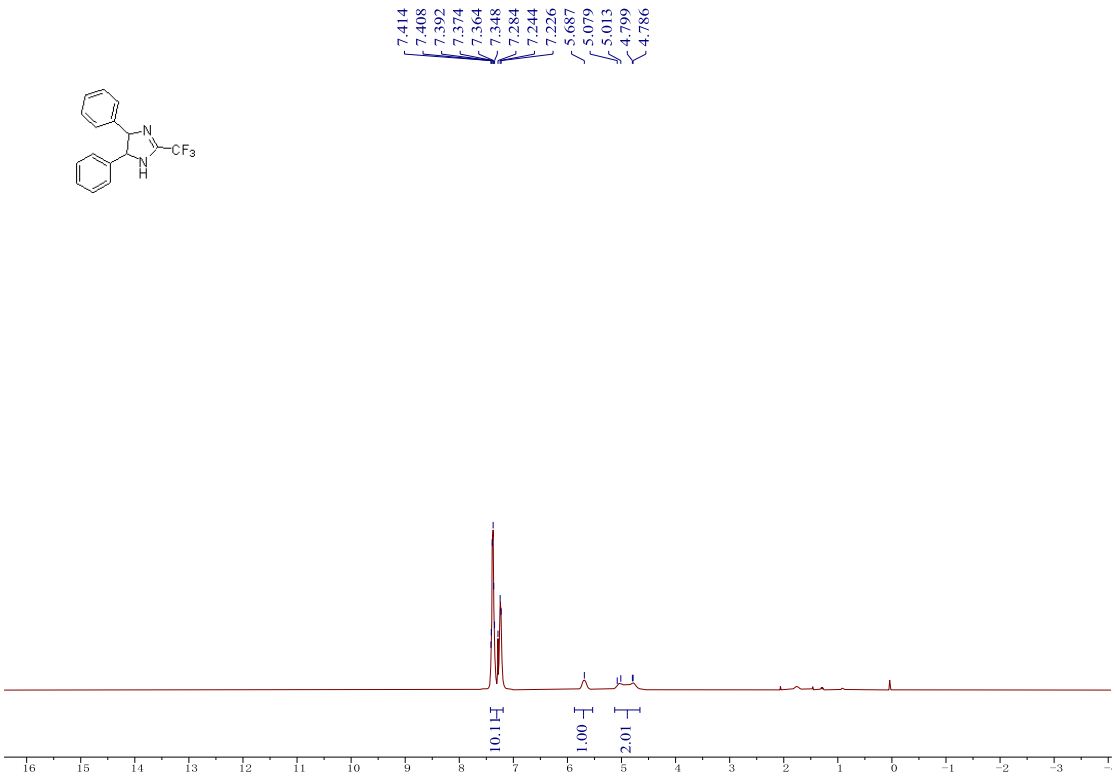
^{19}F NMR spectra of **3aa** in $CDCl_3$



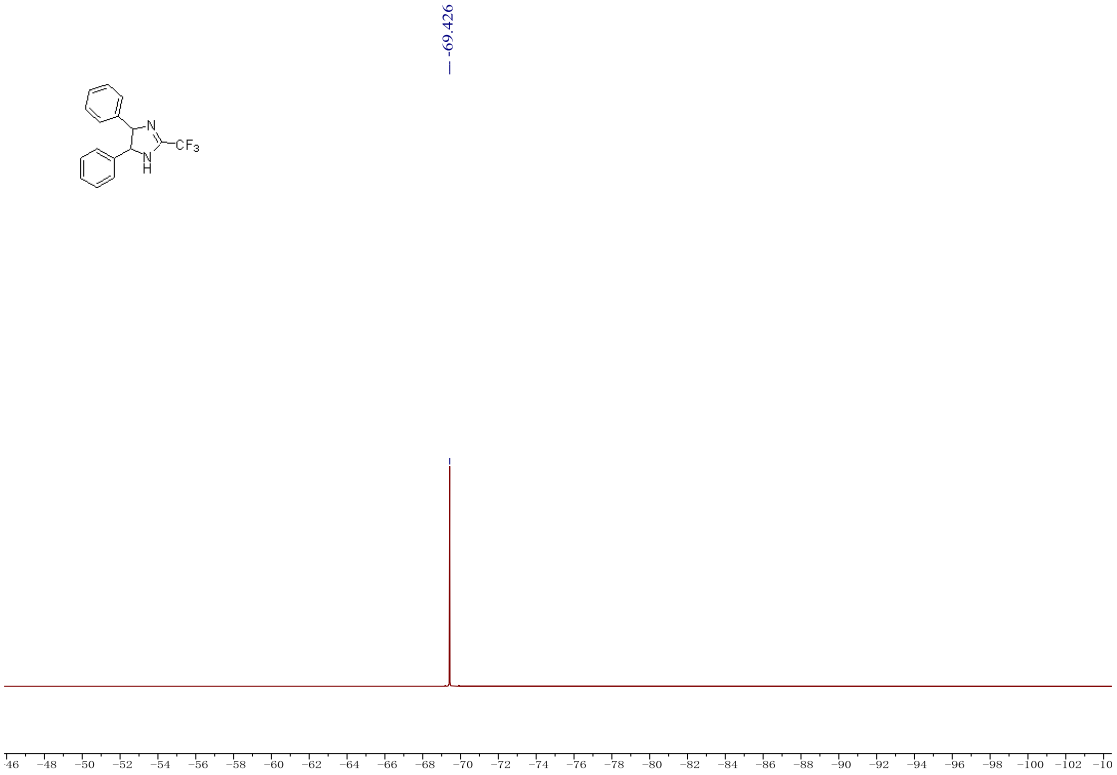
$^{13}C\{^{1}H\}$ NMR spectra of **3aa** in $CDCl_3$



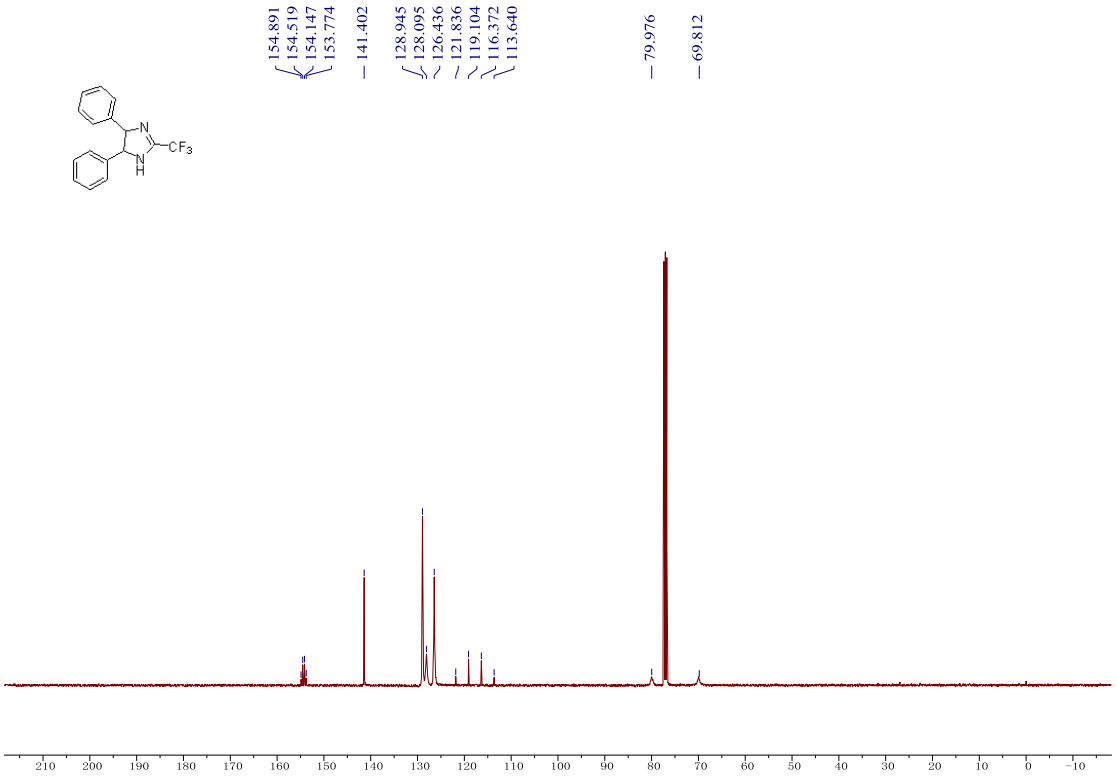
^{1}H NMR spectra of **3ab** in $CDCl_3$



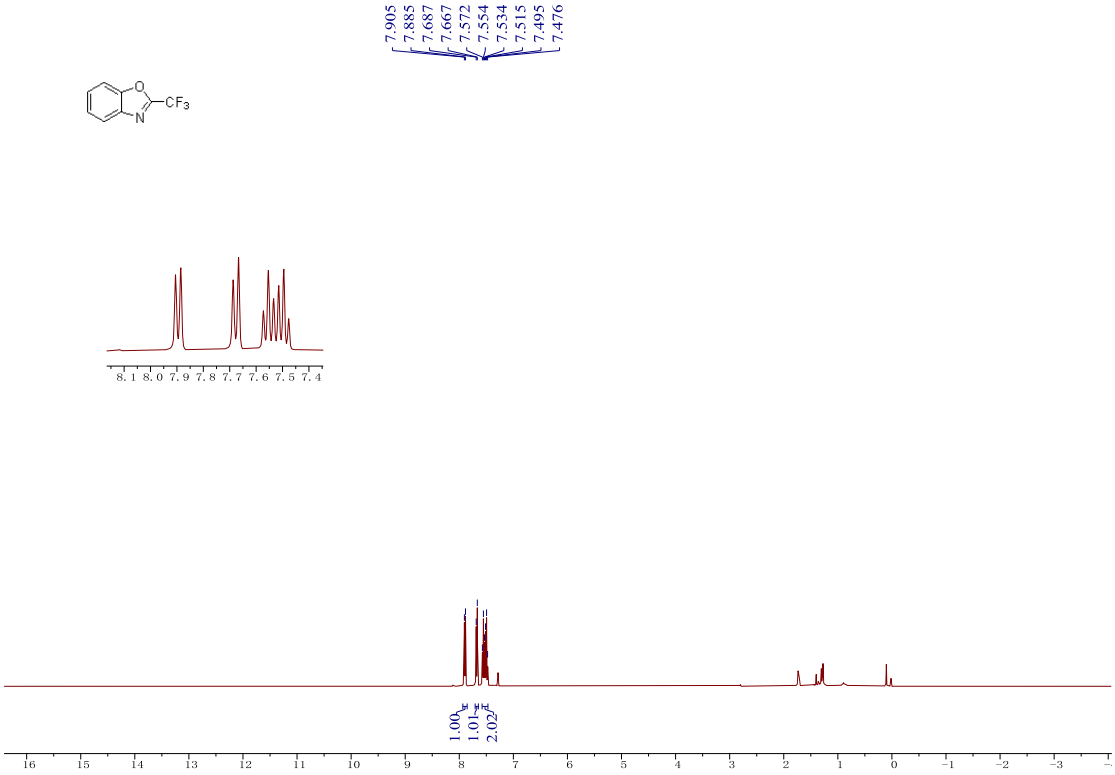
^{19}F NMR spectra of **3ab** in $CDCl_3$



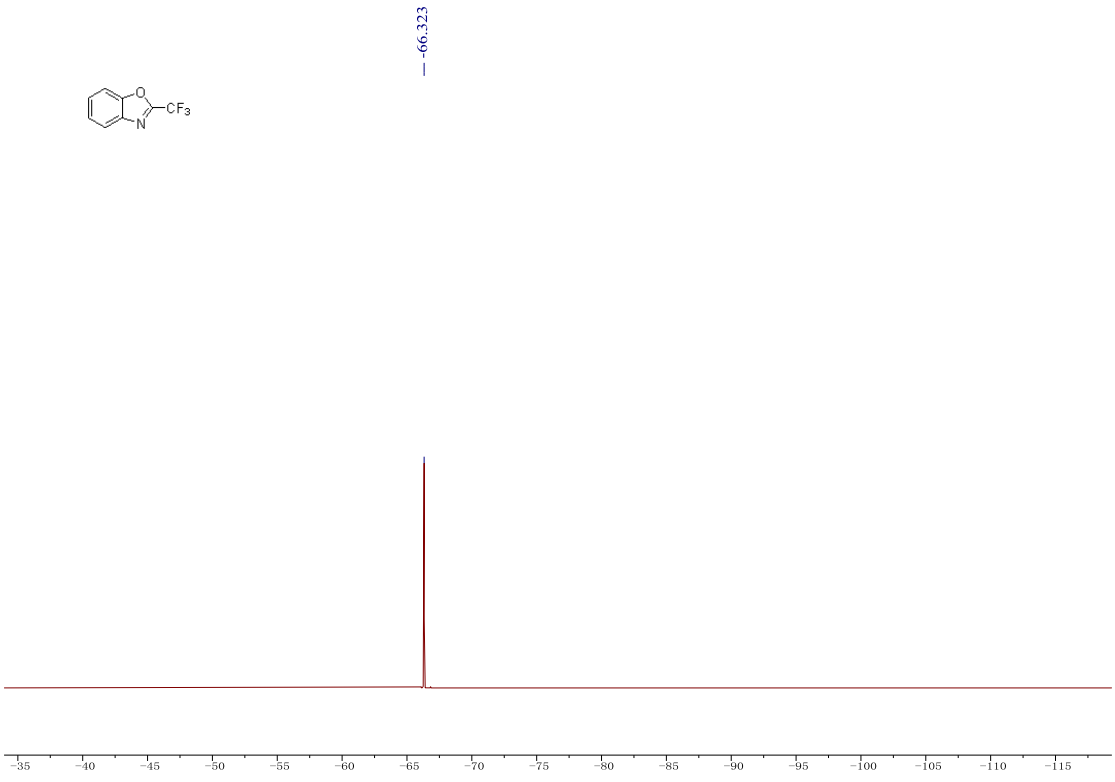
$^{13}C\{^{1}H\}$ NMR spectra of **3ab** in $CDCl_3$



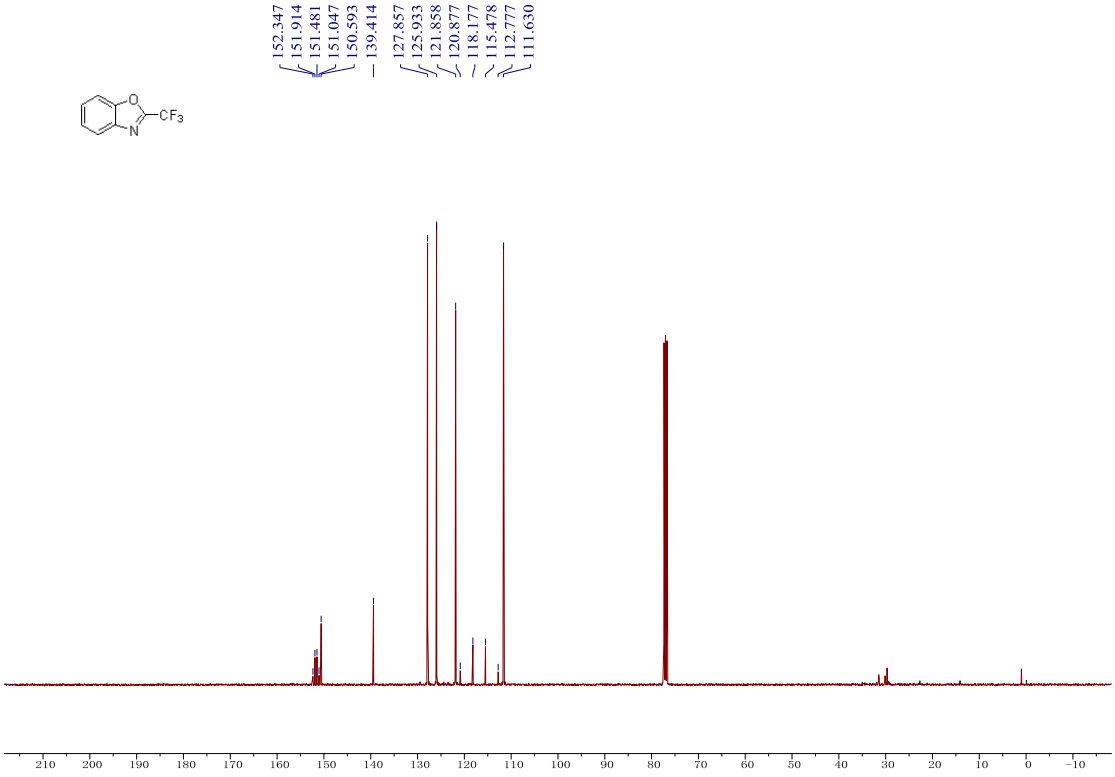
^{1}H NMR spectra of **5a** in $CDCl_3$



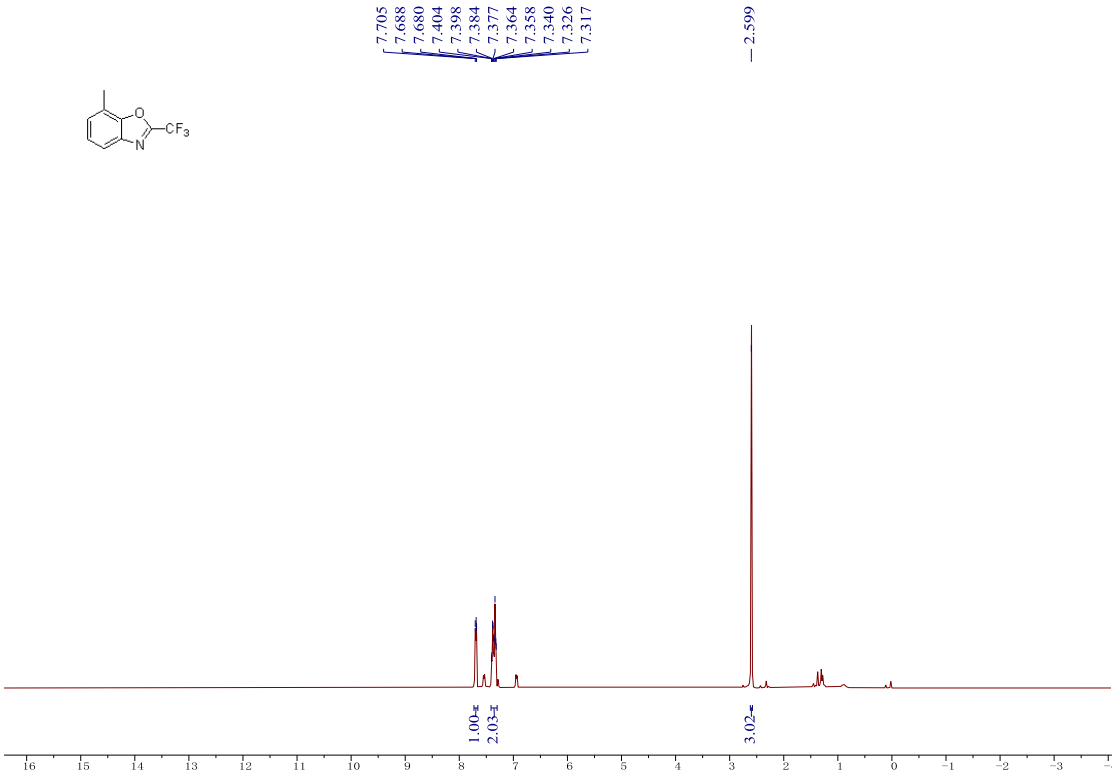
^{19}F NMR spectra of **5a** in $CDCl_3$



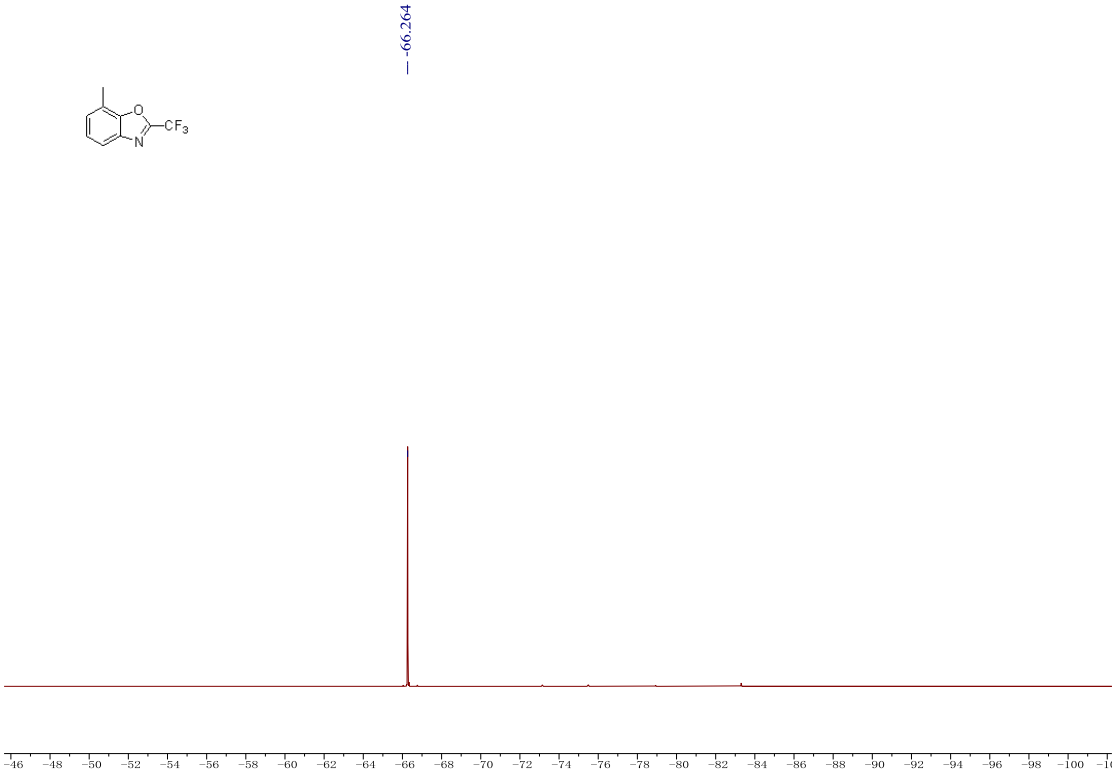
$^{13}C\{^{1}H\}$ NMR spectra of **5a** in $CDCl_3$



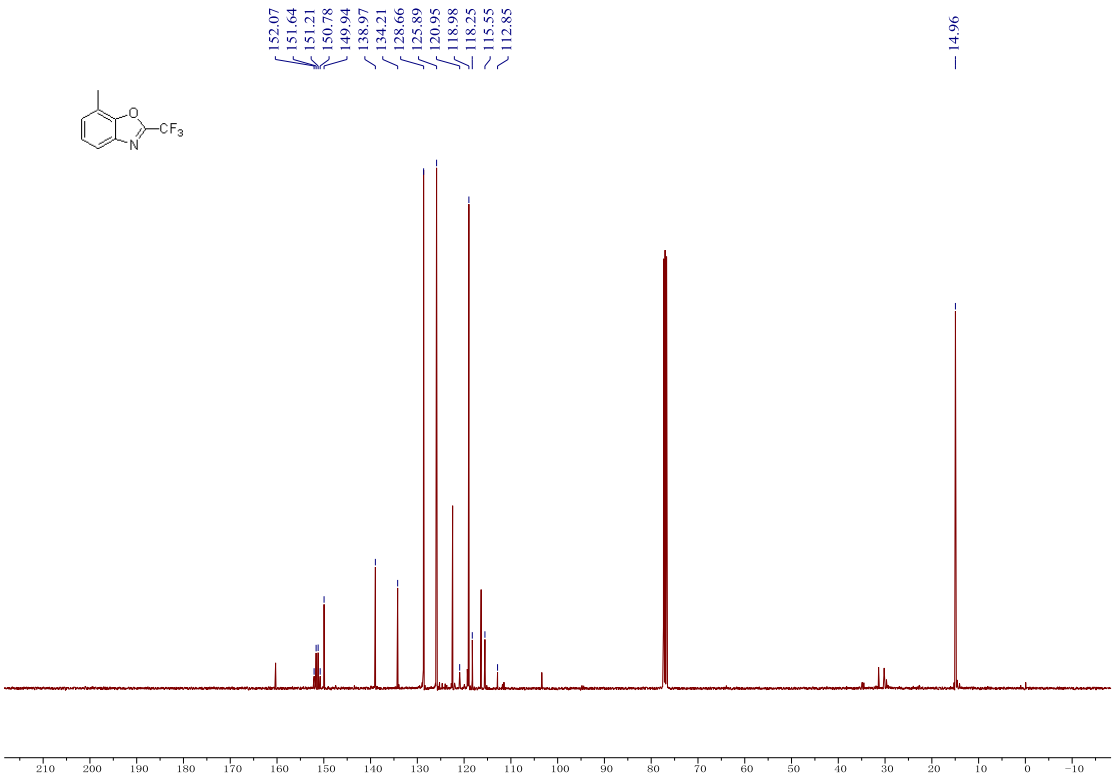
^{1}H NMR spectra of **5b** in $CDCl_3$



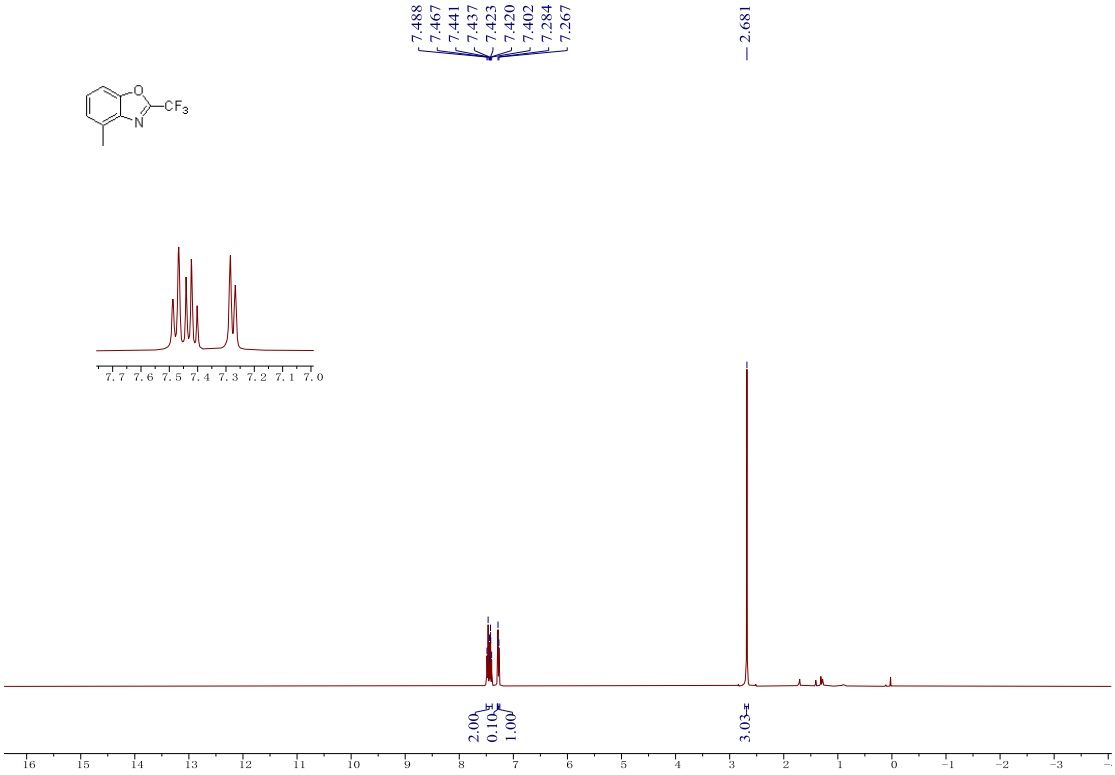
^{19}F NMR spectra of **5b** in $CDCl_3$



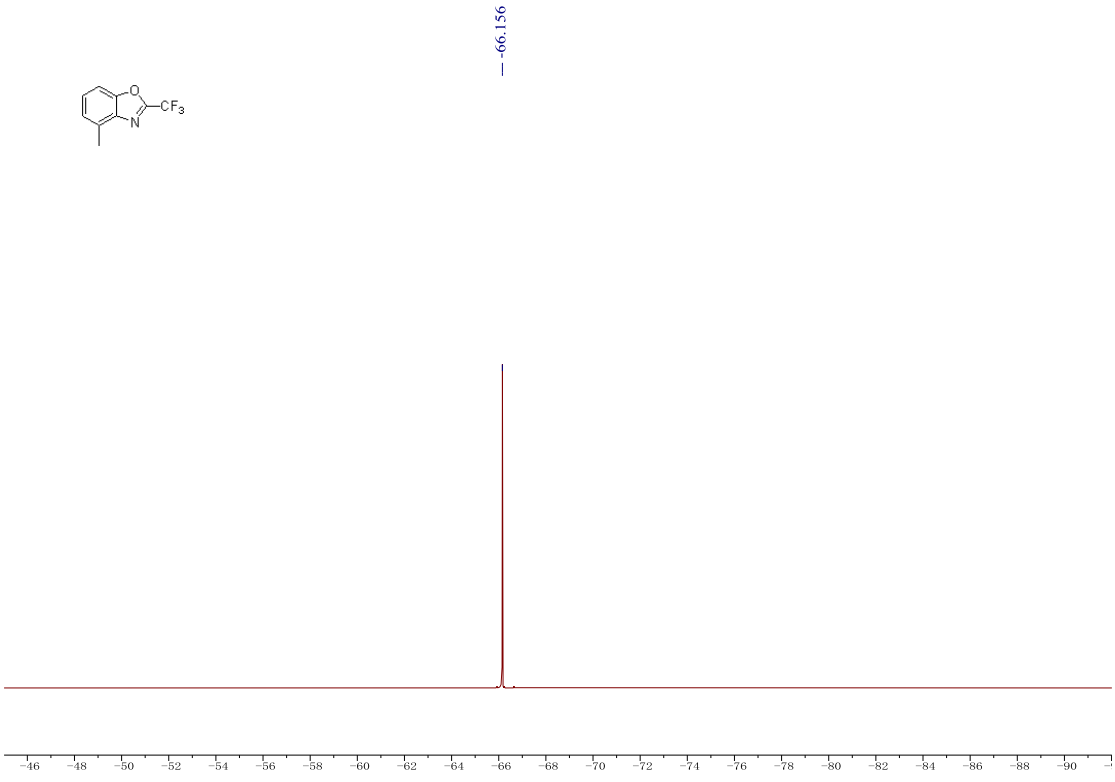
$^{13}C\{^{1}H\}$ NMR spectra of **5b** in $CDCl_3$



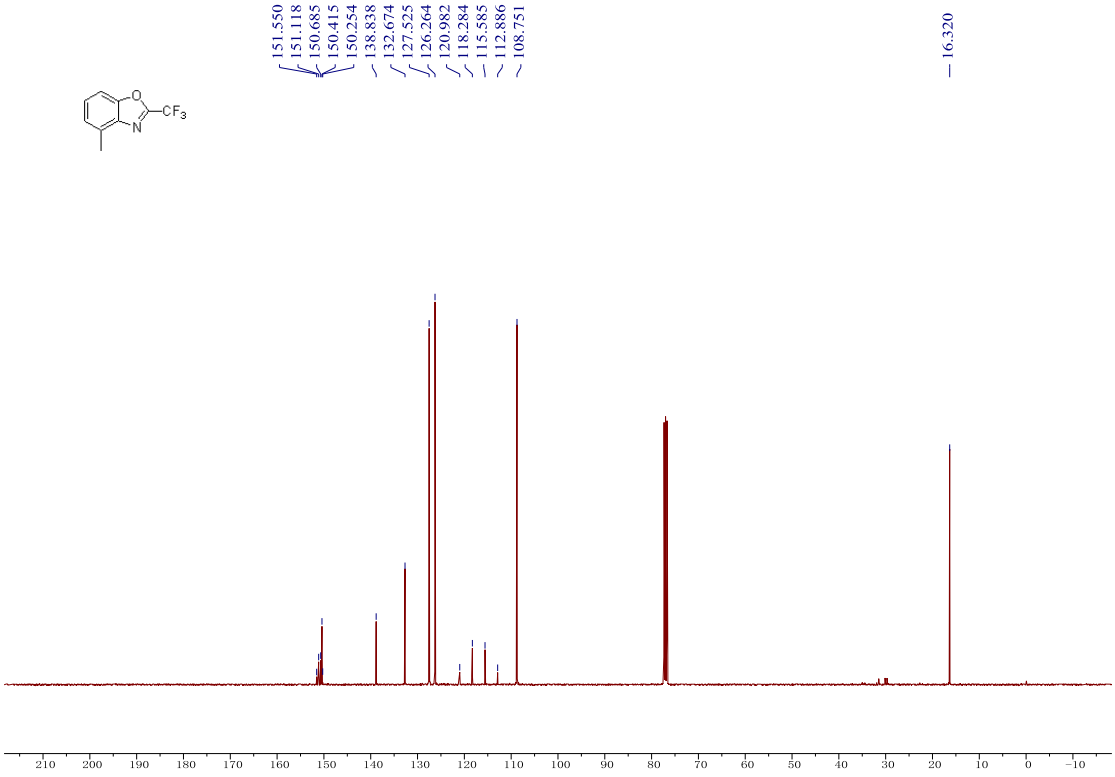
^{1}H NMR spectra of **5c** in $CDCl_3$



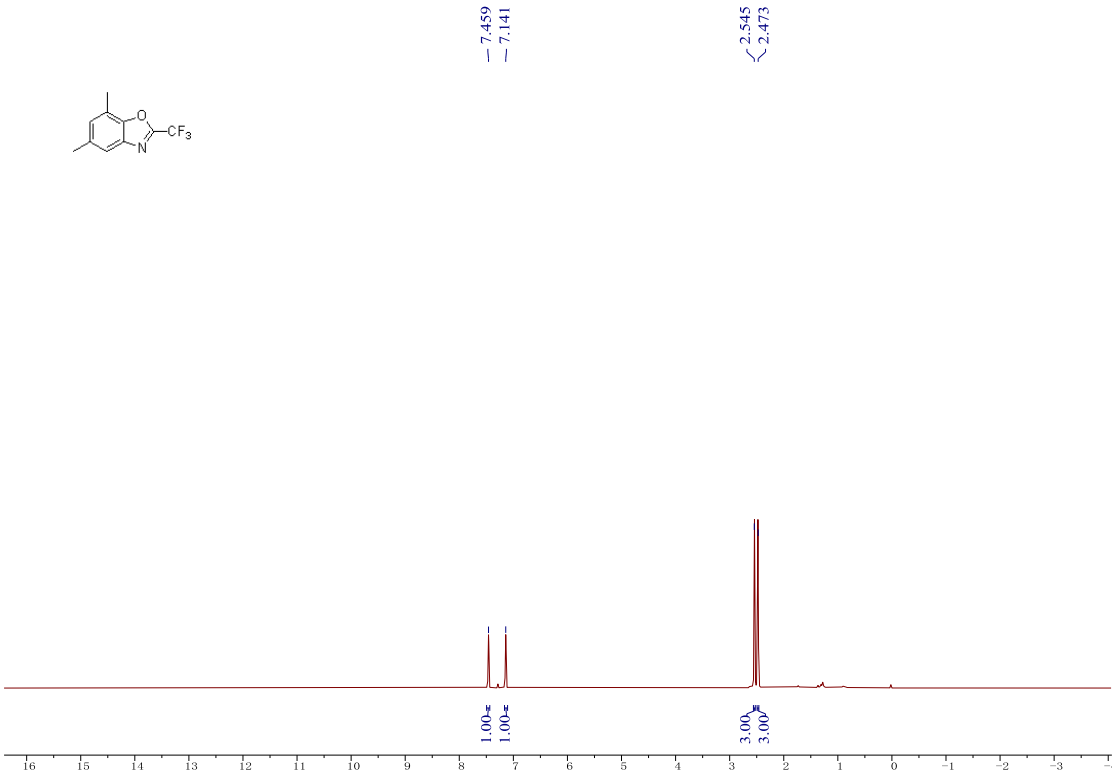
^{19}F NMR spectra of **5c** in $CDCl_3$



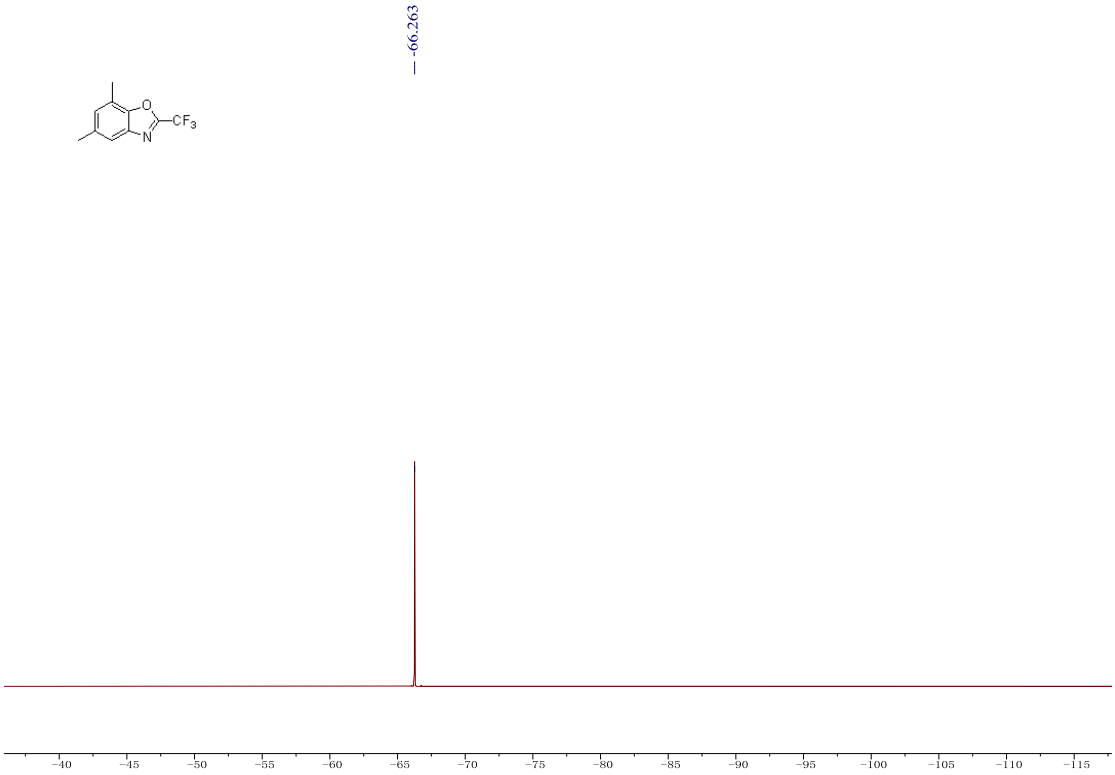
$^{13}C\{^{1}H\}$ NMR spectra of **5c** in $CDCl_3$



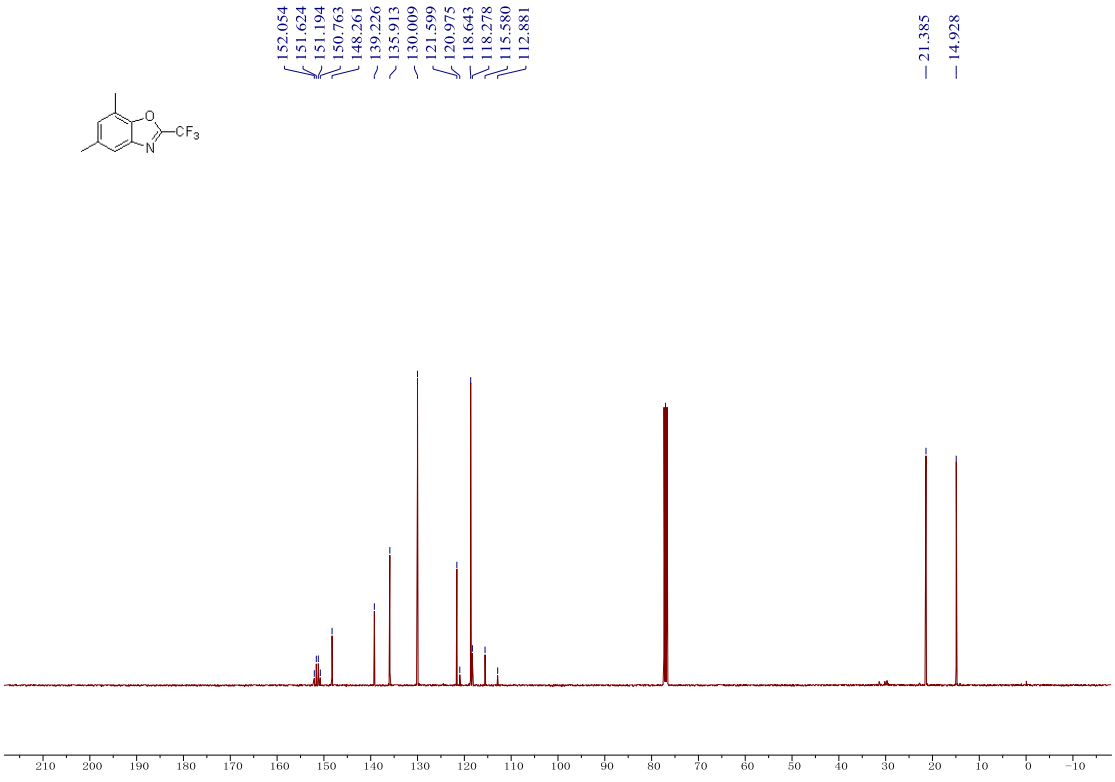
^{1}H NMR spectra of **5d** in $CDCl_3$



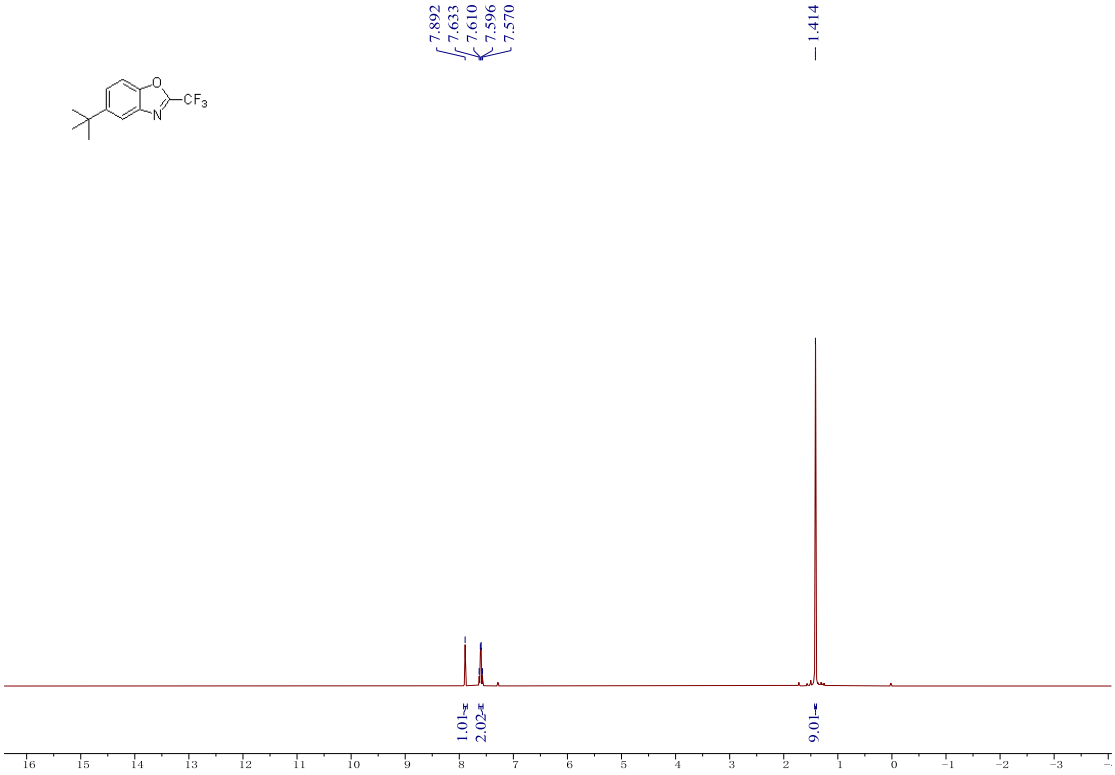
^{19}F NMR spectra of **5d** in $CDCl_3$



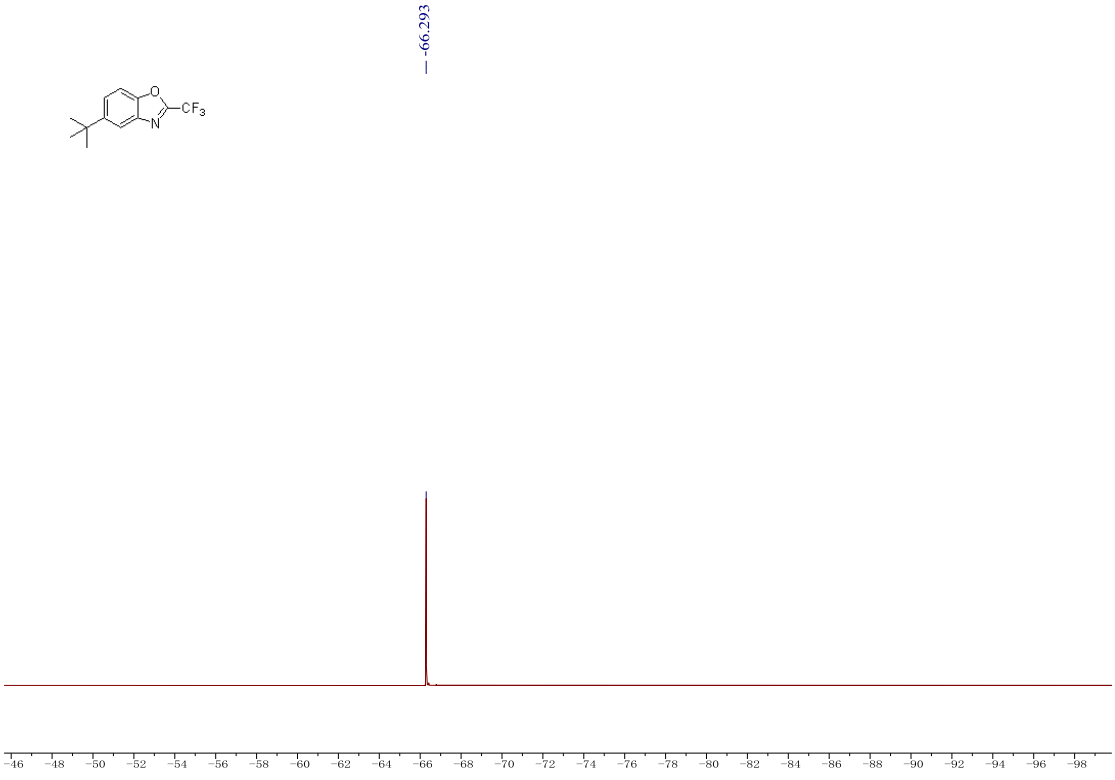
$^{13}C\{^1H\}$ NMR spectra of **5d** in $CDCl_3$



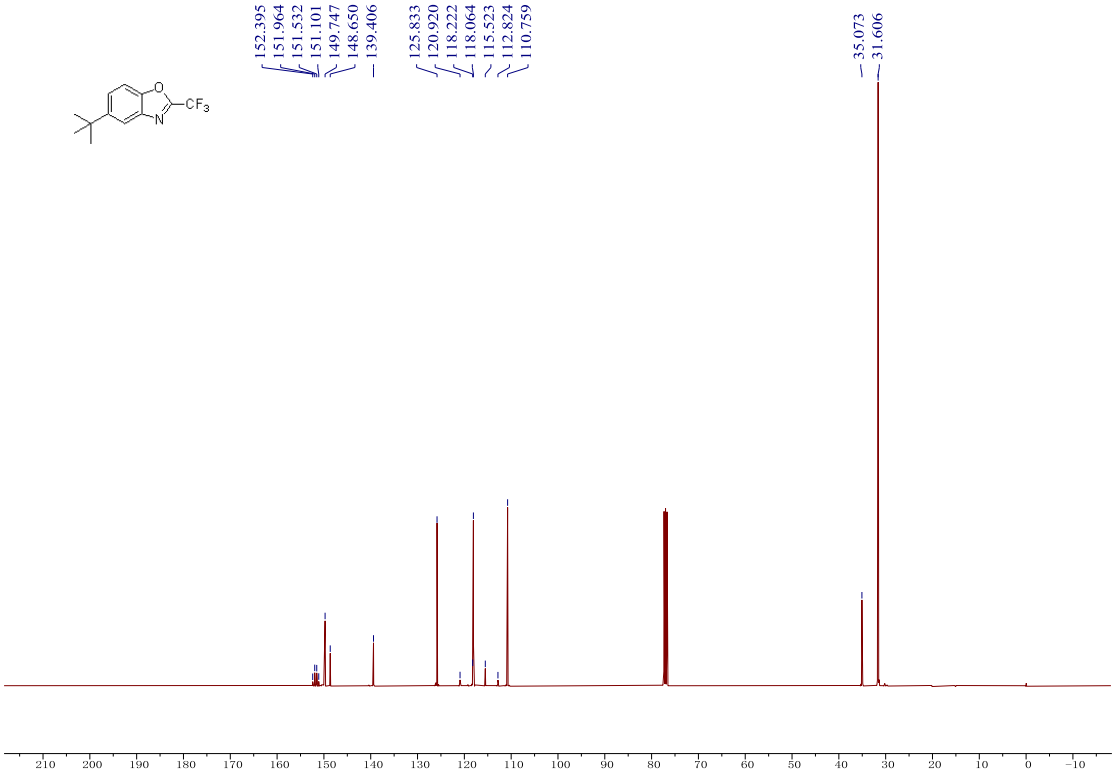
^{1}H NMR spectra of **5e** in $CDCl_3$



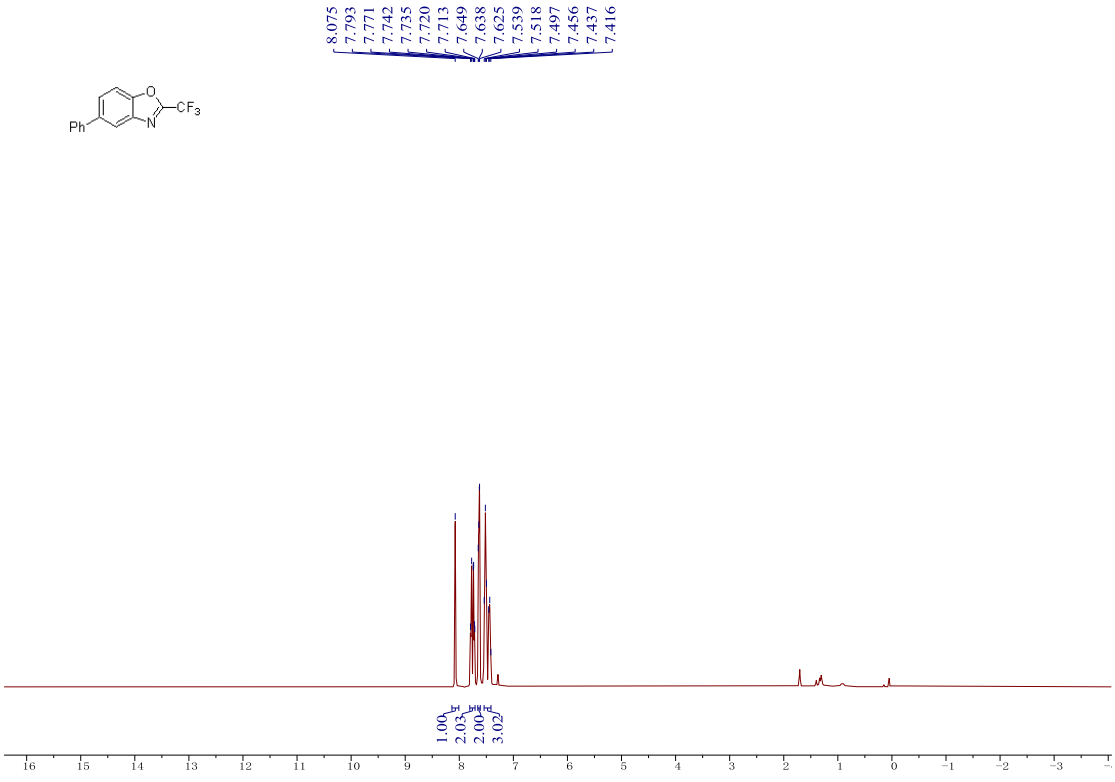
^{19}F NMR spectra of **5e** in $CDCl_3$



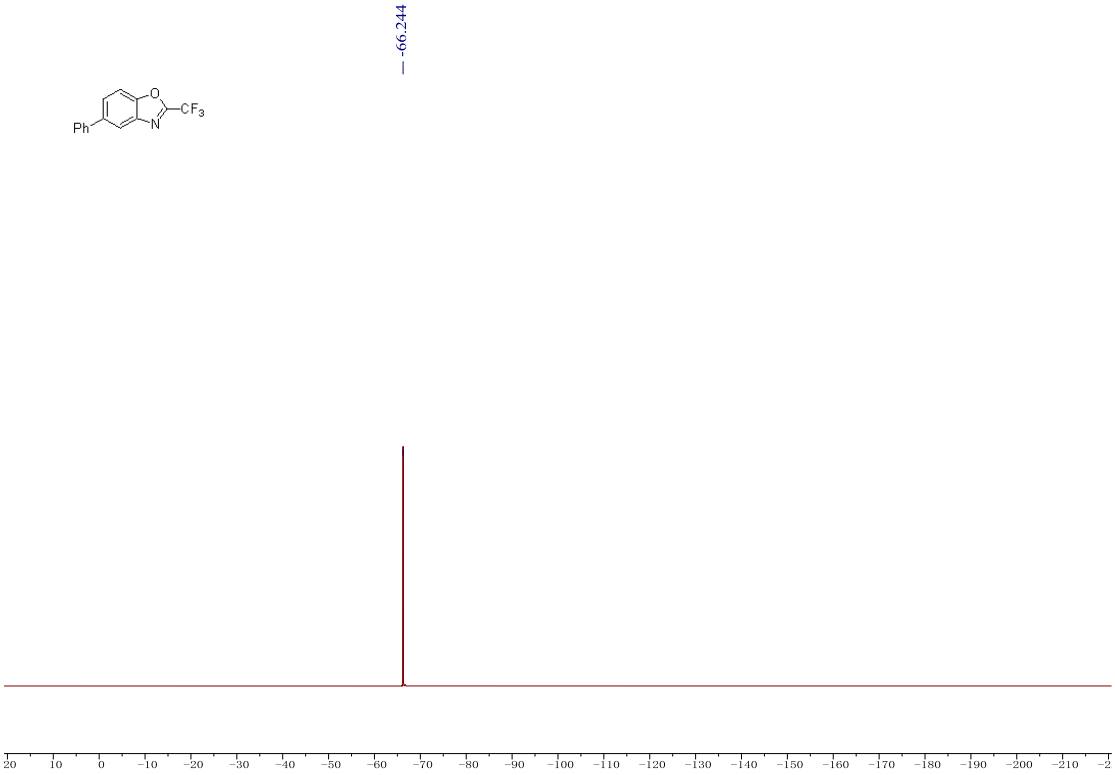
$^{13}C\{^{1}H\}$ NMR spectra of **5e** in $CDCl_3$



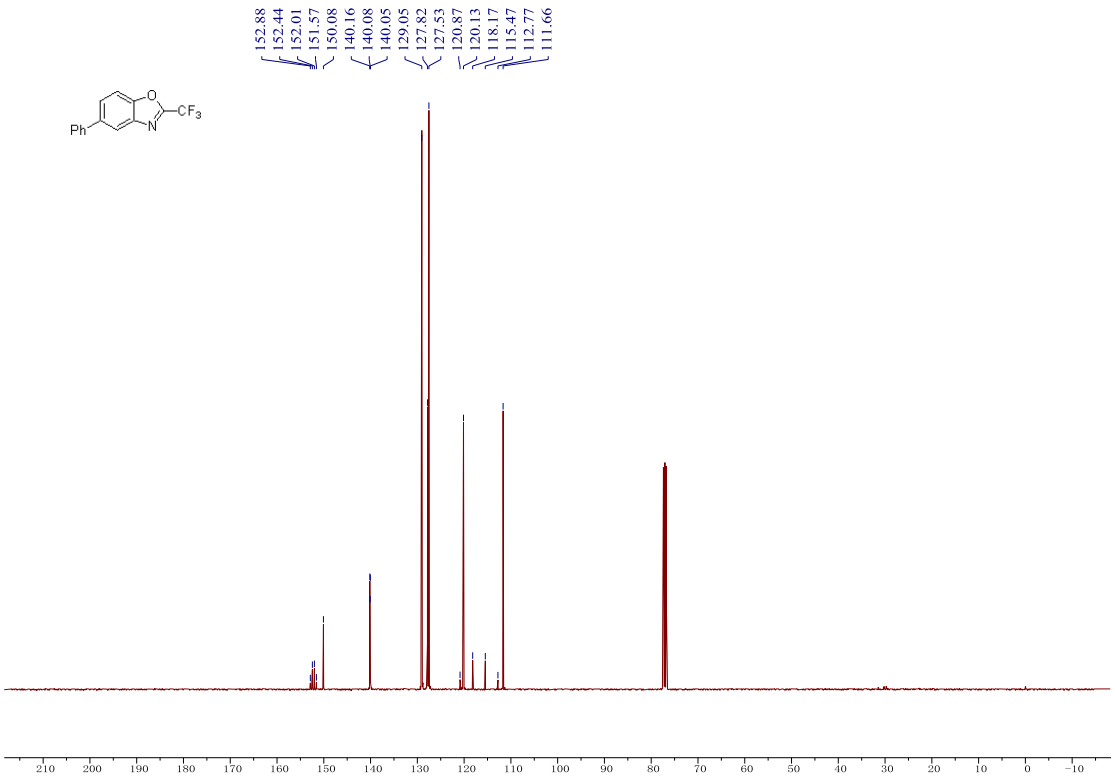
^{1}H NMR spectra of **5f** in $CDCl_3$



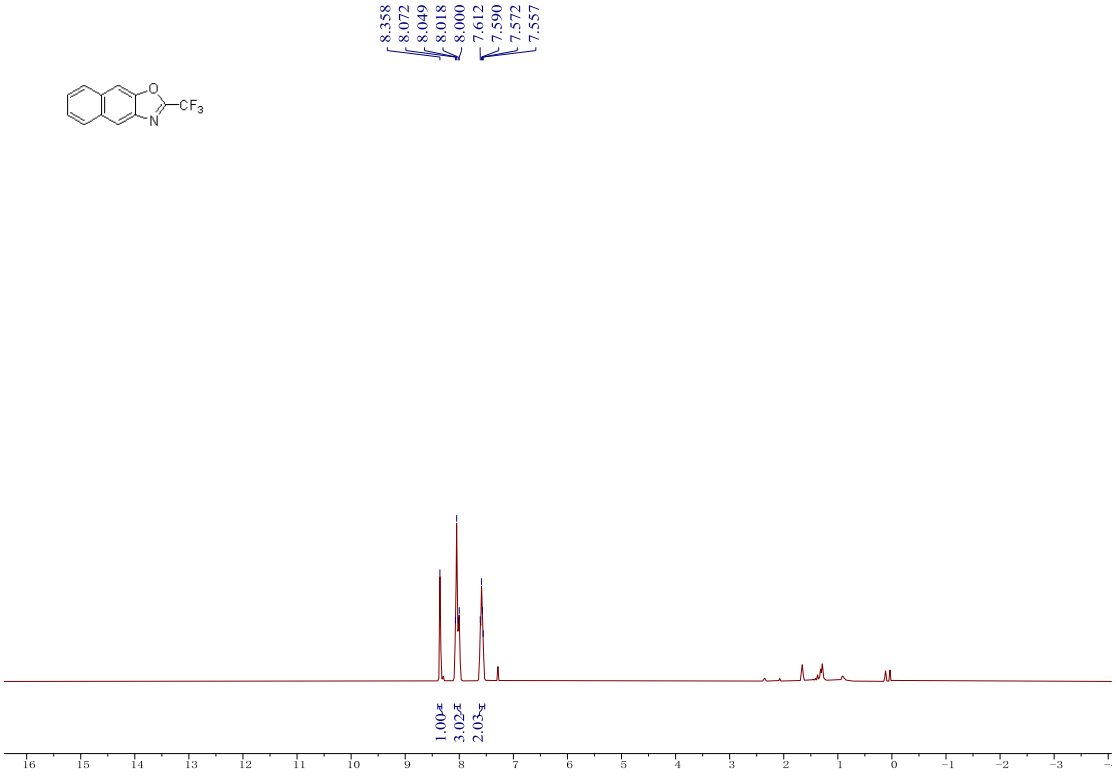
^{19}F NMR spectra of **5f** in $CDCl_3$



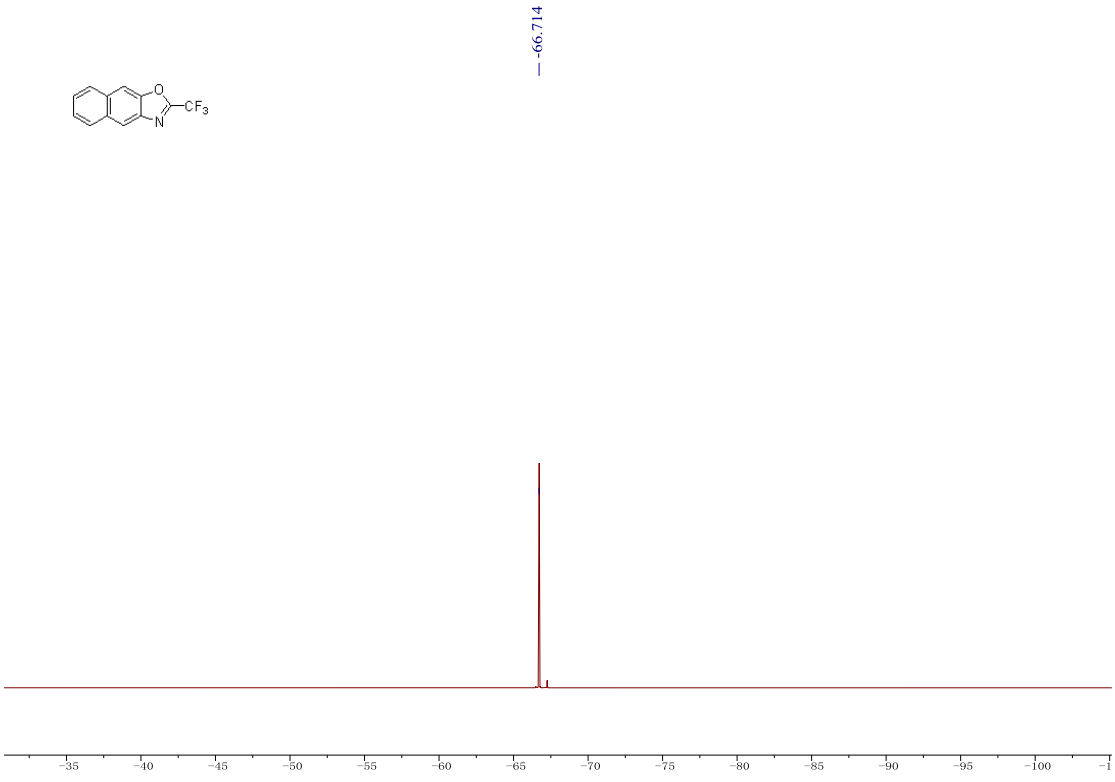
$^{13}C\{^{1}H\}$ NMR spectra of **5f** in $CDCl_3$



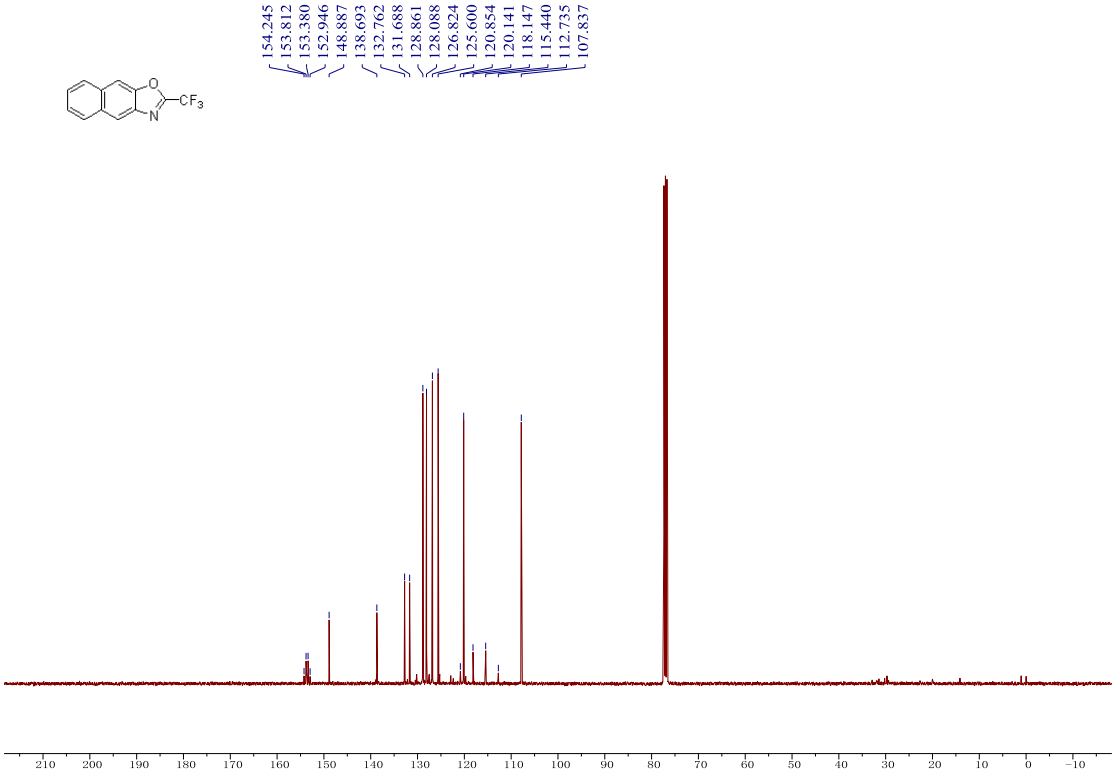
^{1}H NMR spectra of **5g** in $CDCl_3$



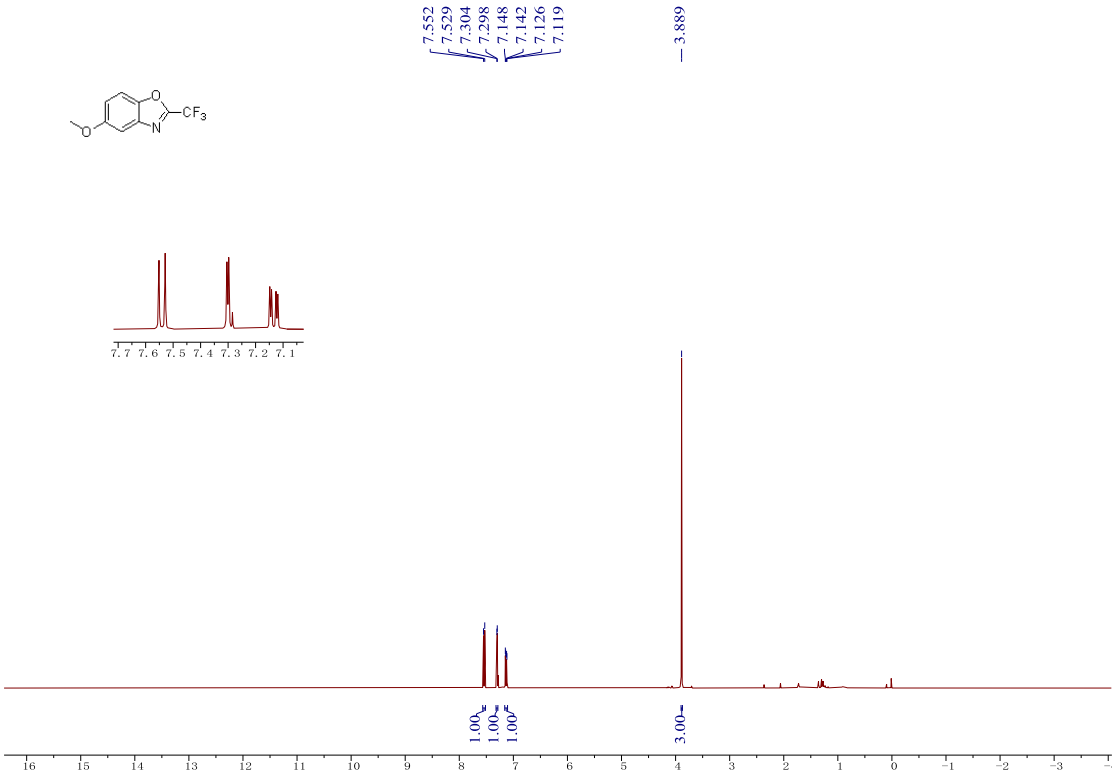
^{19}F NMR spectra of **5g** in $CDCl_3$



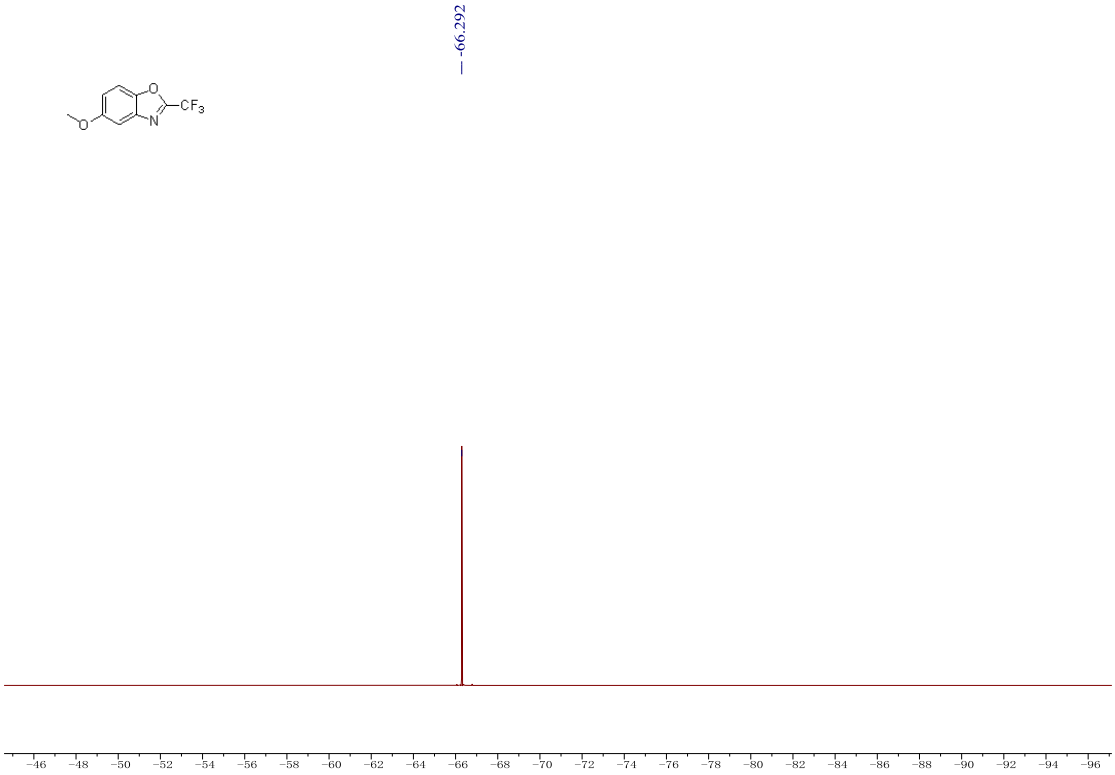
$^{13}C\{^{1}H\}$ NMR spectra of **5g** in $CDCl_3$



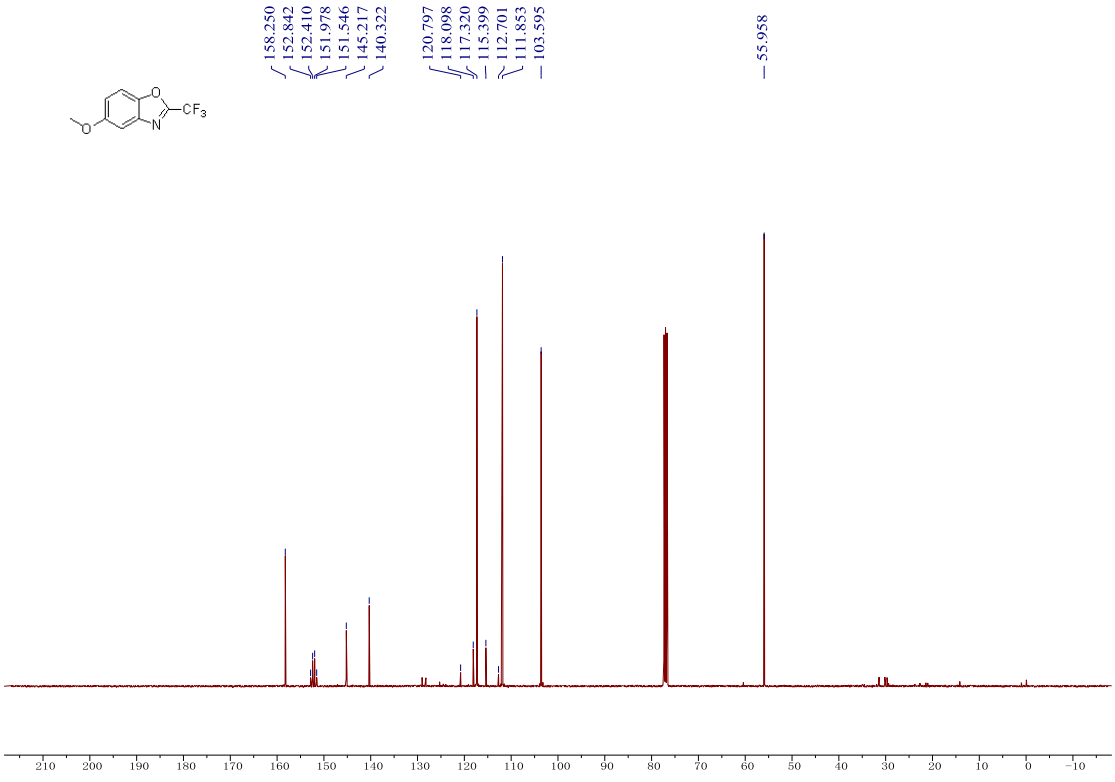
^{1}H NMR spectra of **5h** in $CDCl_3$



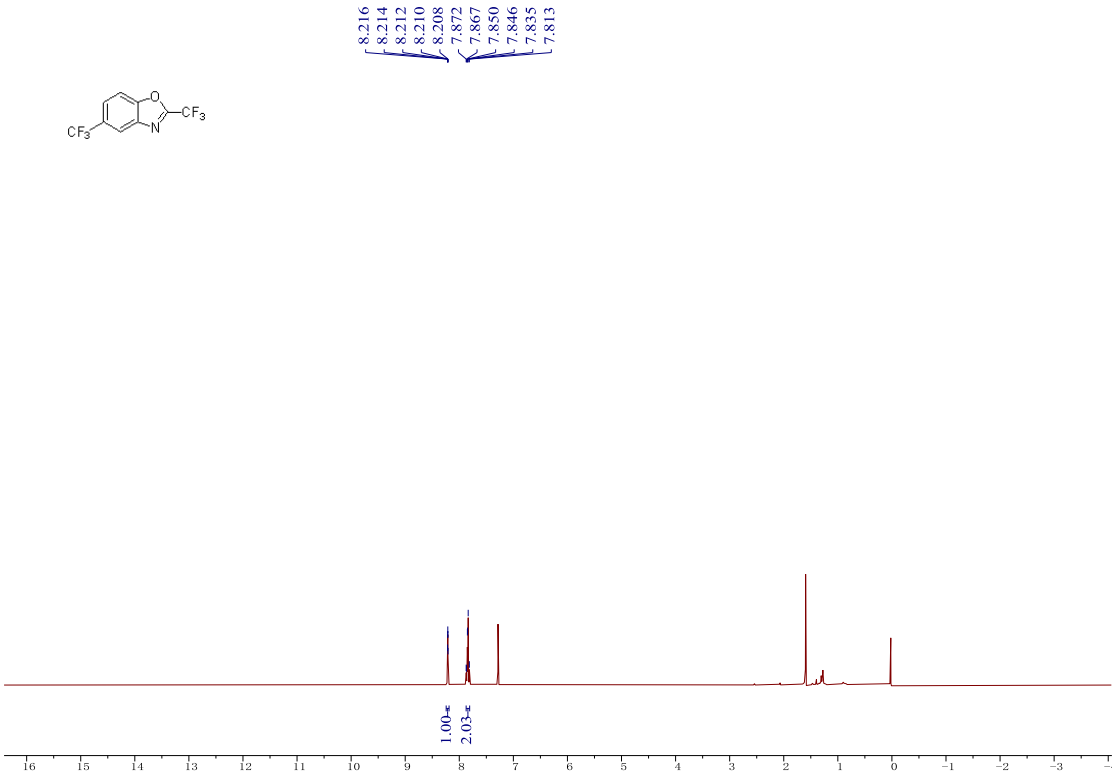
^{19}F NMR spectra of **5h** in $CDCl_3$



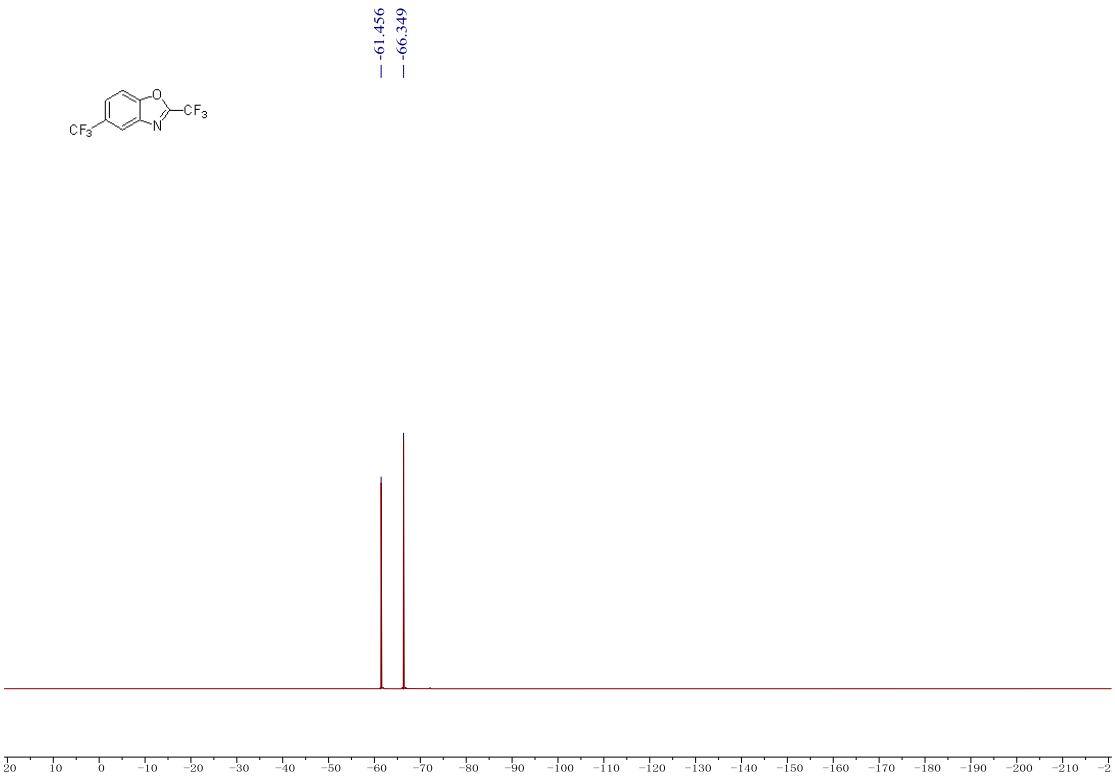
$^{13}C\{^{1}H\}$ NMR spectra of **5h** in $CDCl_3$



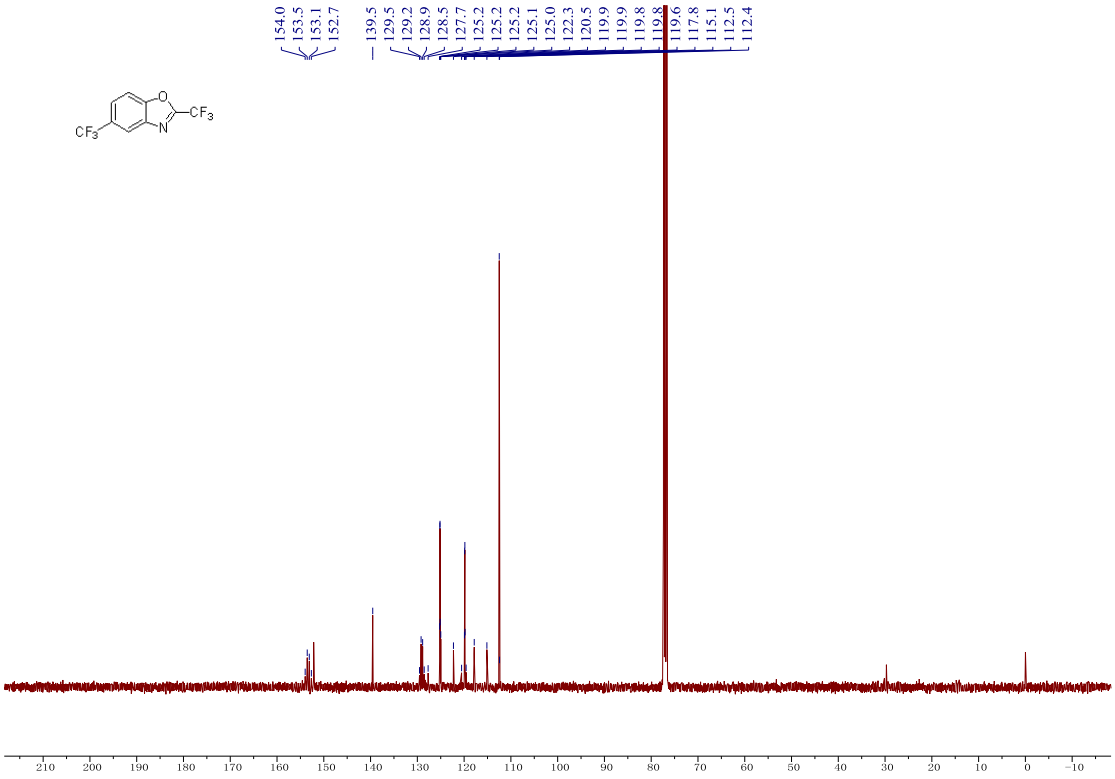
^{1}H NMR spectra of **5i** in $CDCl_3$



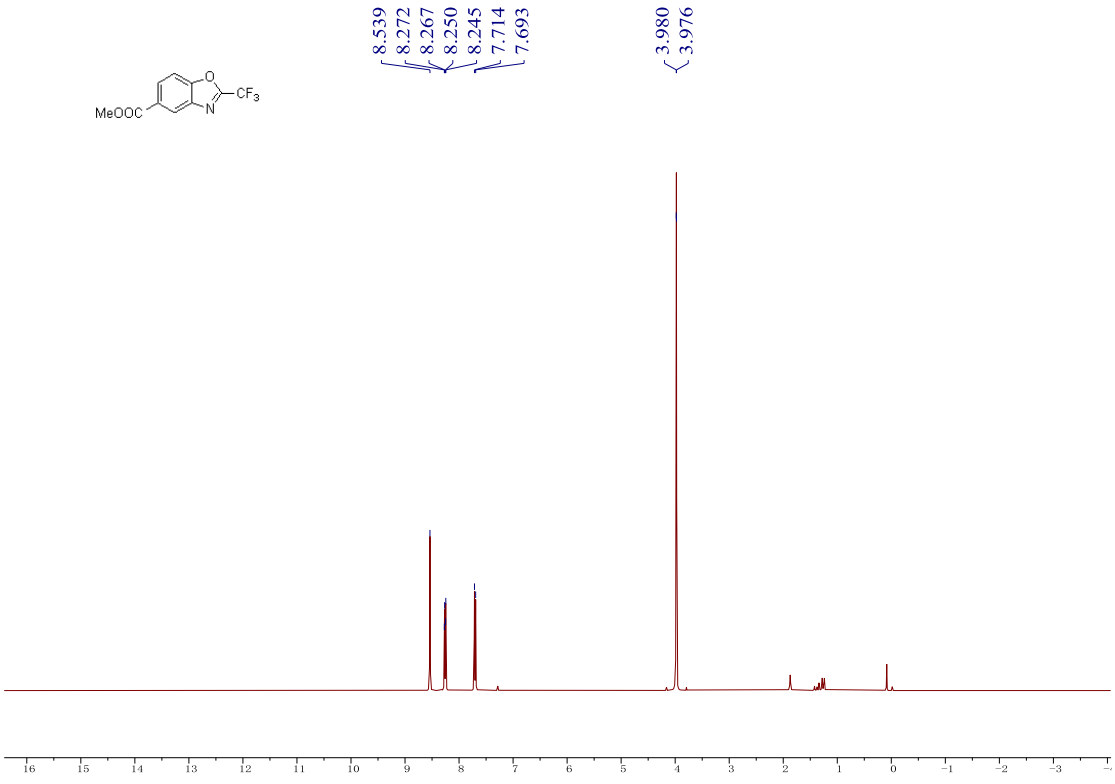
^{19}F NMR spectra of **5i** in $CDCl_3$



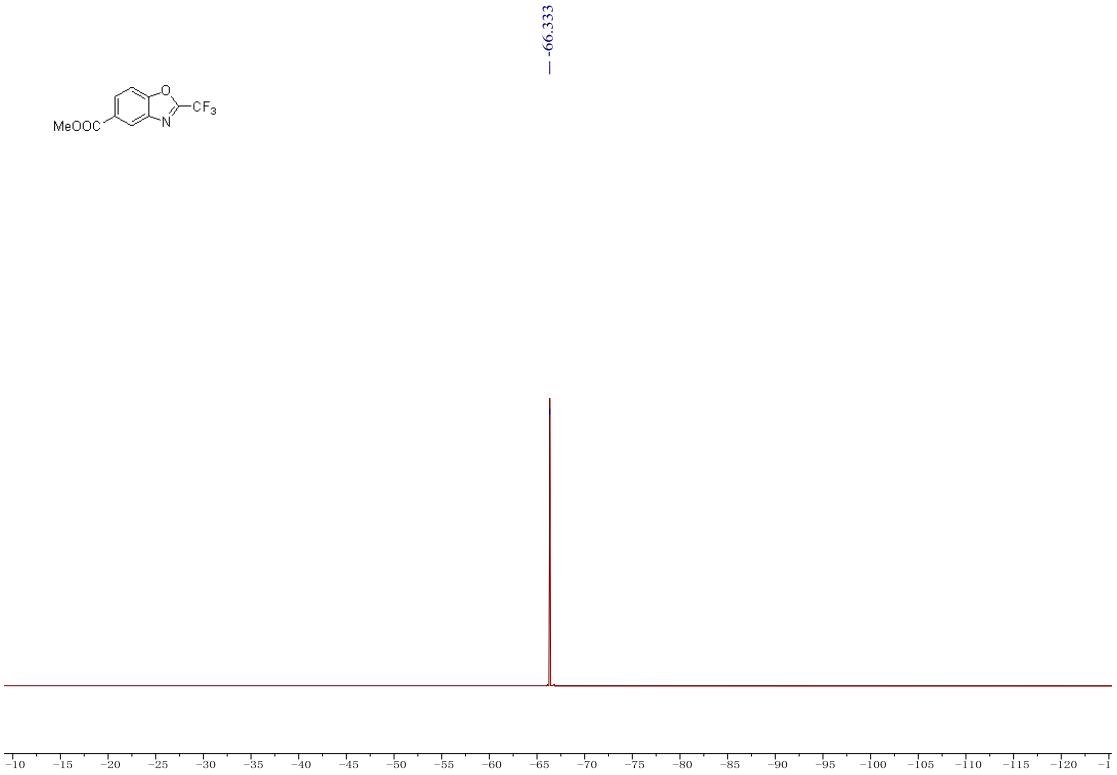
$^{13}C\{^{1}H\}$ NMR spectra of **5i** in $CDCl_3$



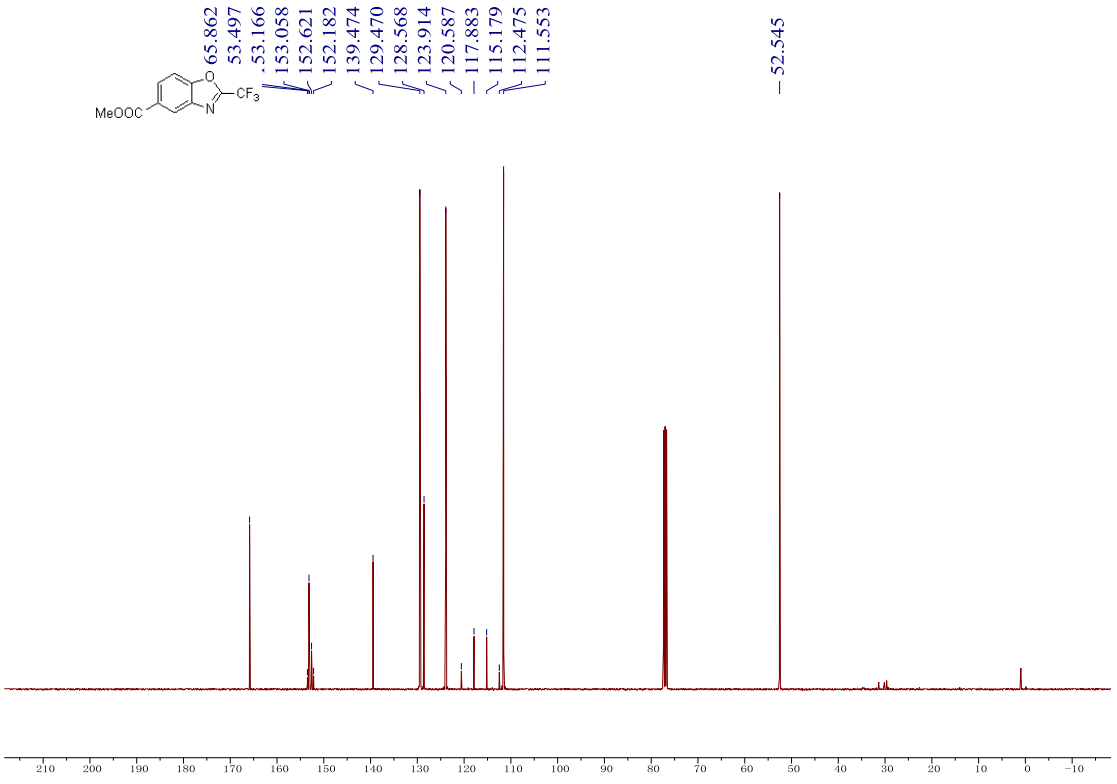
^{1}H NMR spectra of **5j** in $CDCl_3$



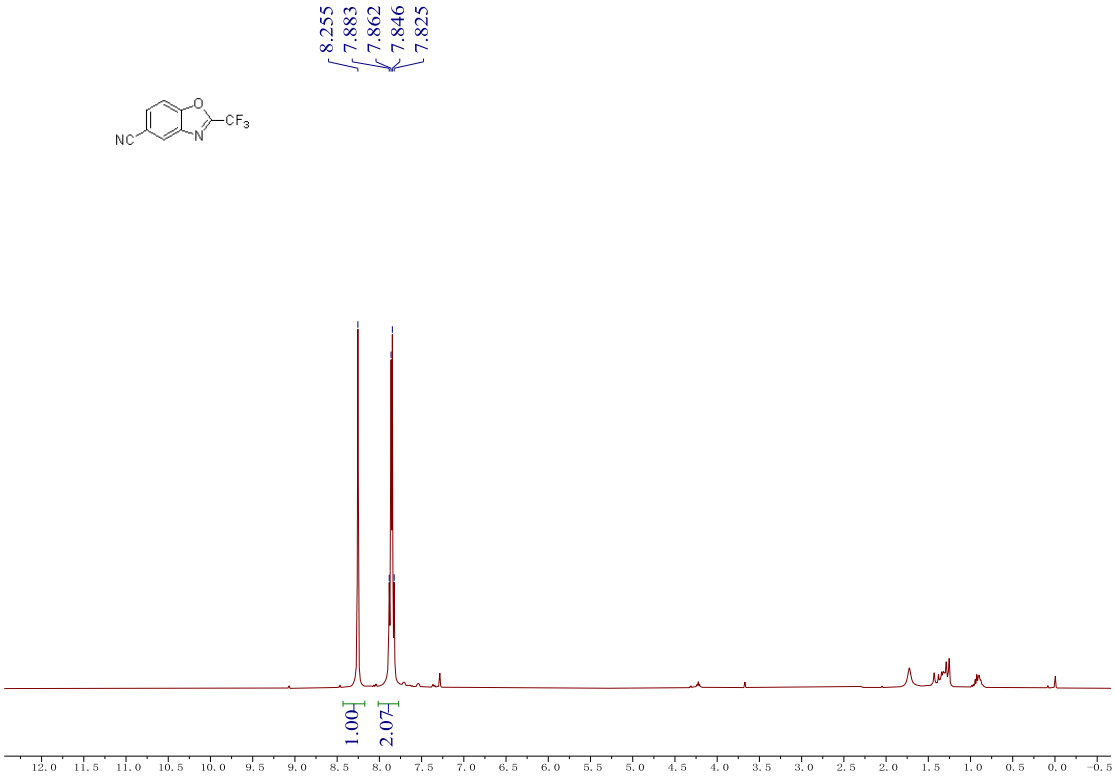
^{19}F NMR spectra of **5j** in $CDCl_3$



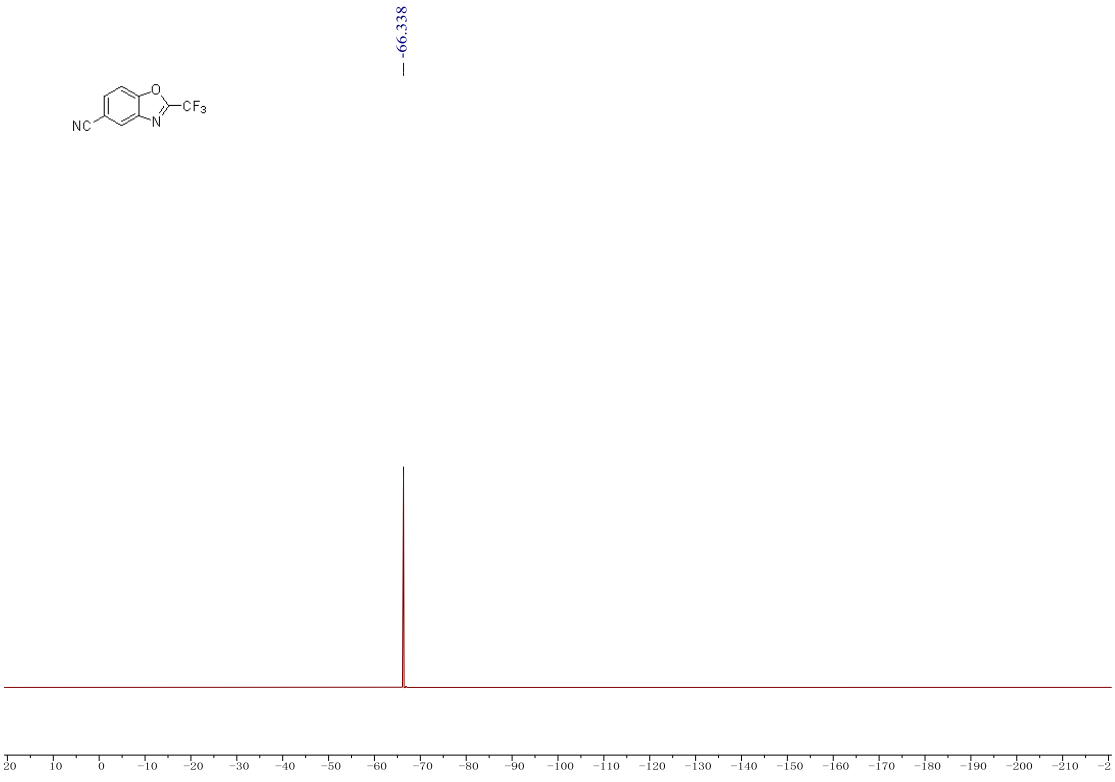
$^{13}C\{^{1}H\}$ NMR spectra of **5j** in $CDCl_3$



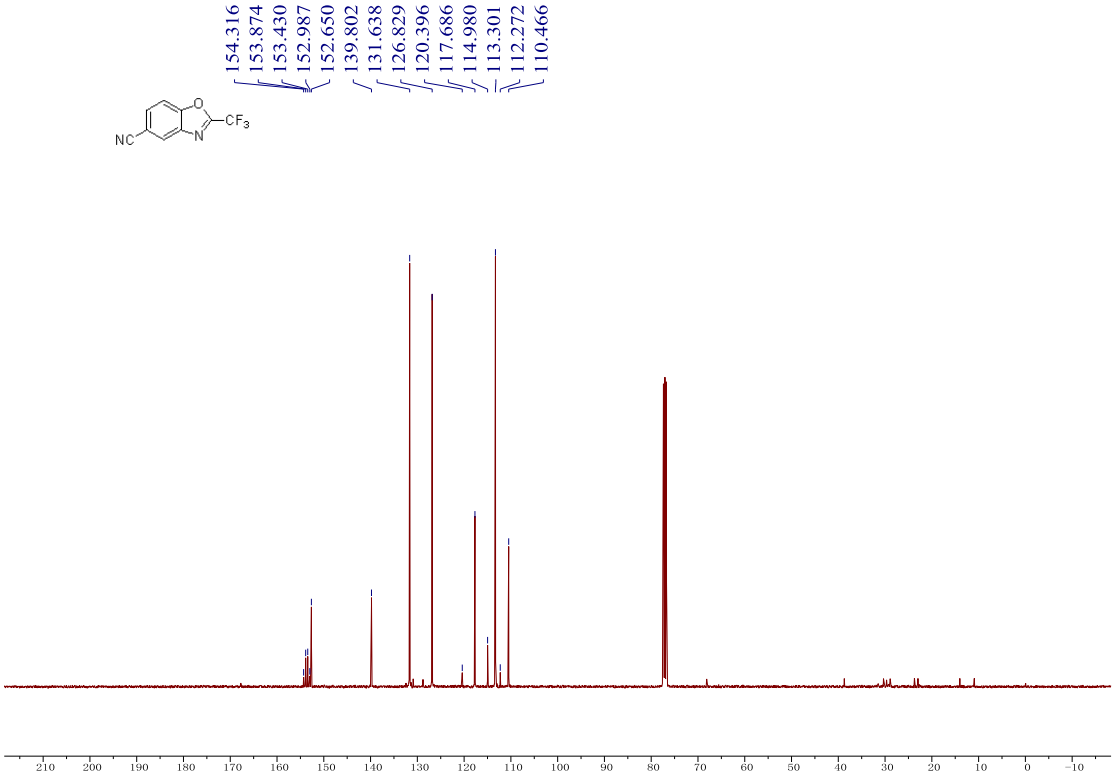
^{1}H NMR spectra of **5k** in $CDCl_3$



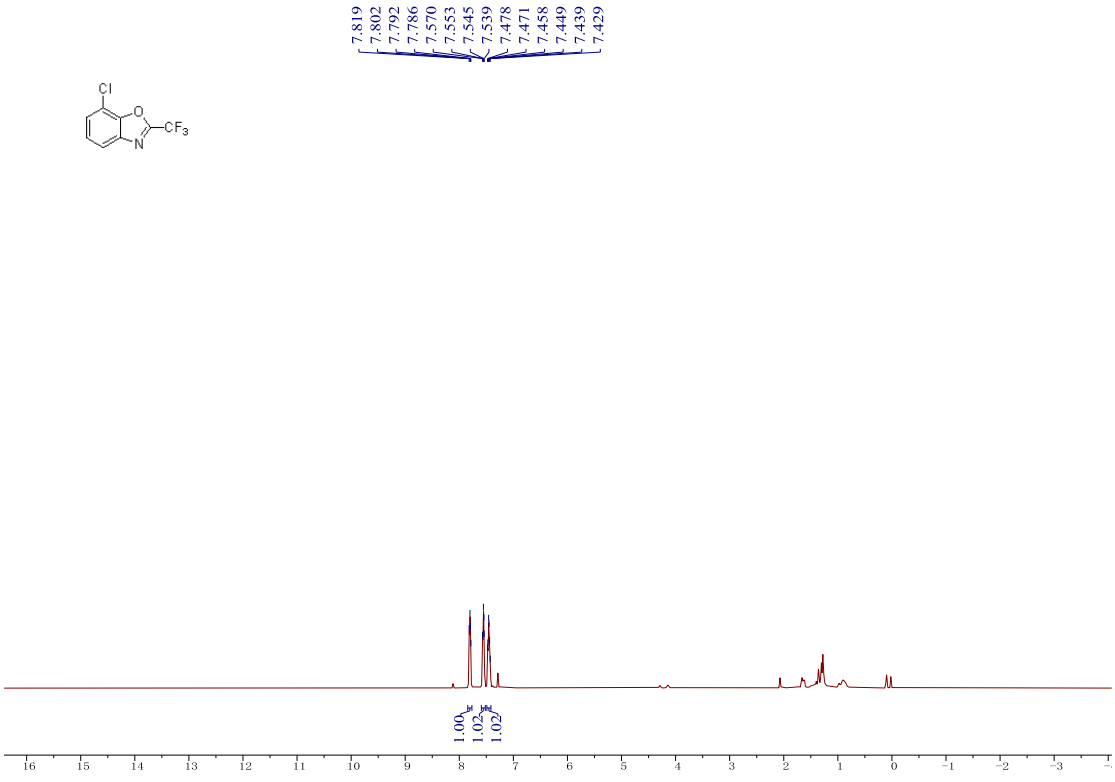
^{19}F NMR spectra of **5k** in $CDCl_3$



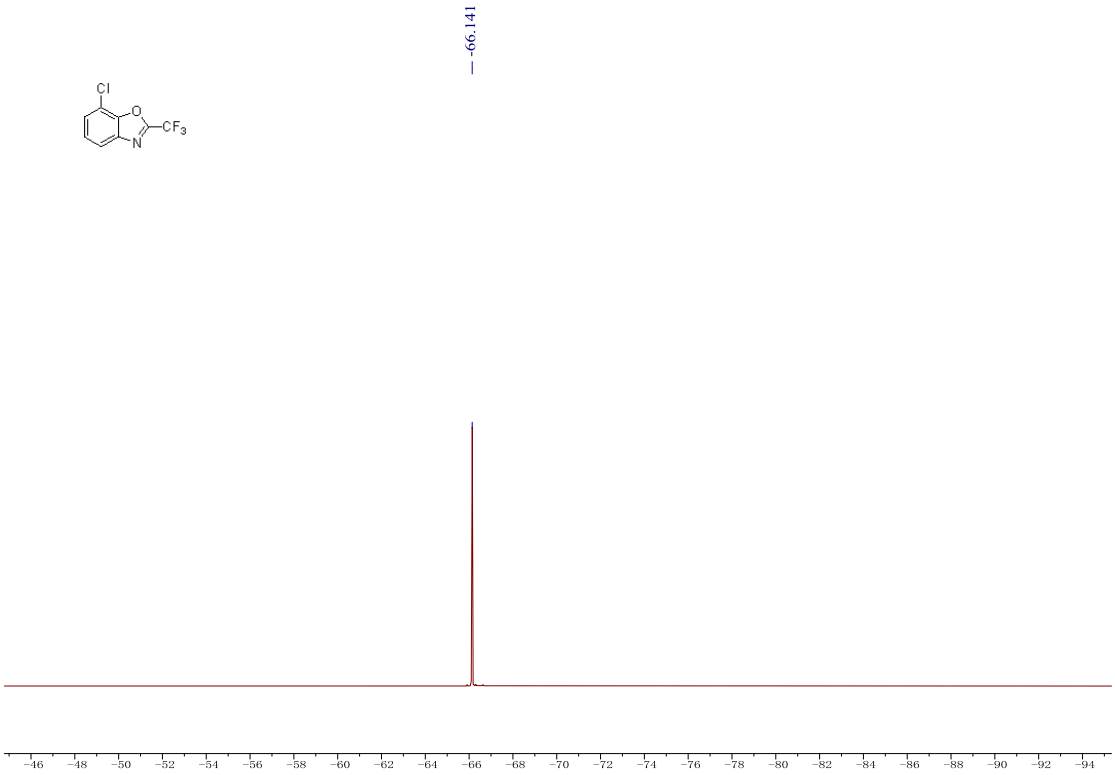
$^{13}C\{^{1}H\}$ NMR spectra of **5k** in $CDCl_3$



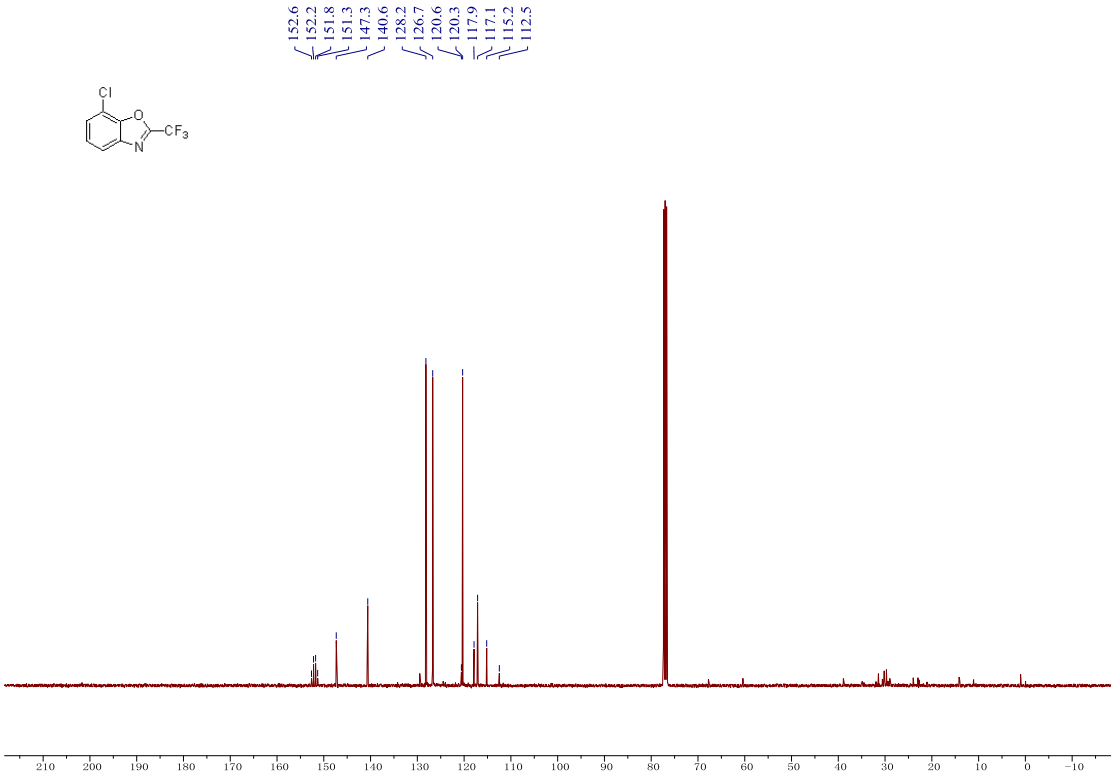
^{1}H NMR spectra of **5l** in $CDCl_3$



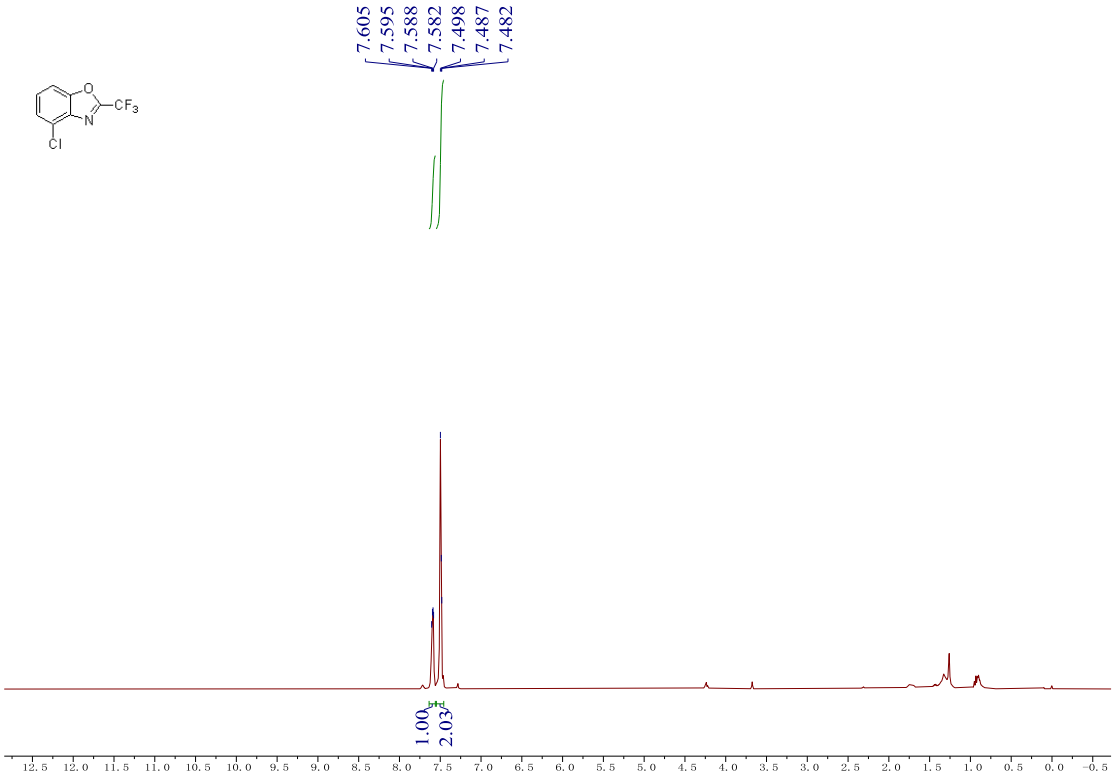
^{19}F NMR spectra of **5l** in $CDCl_3$



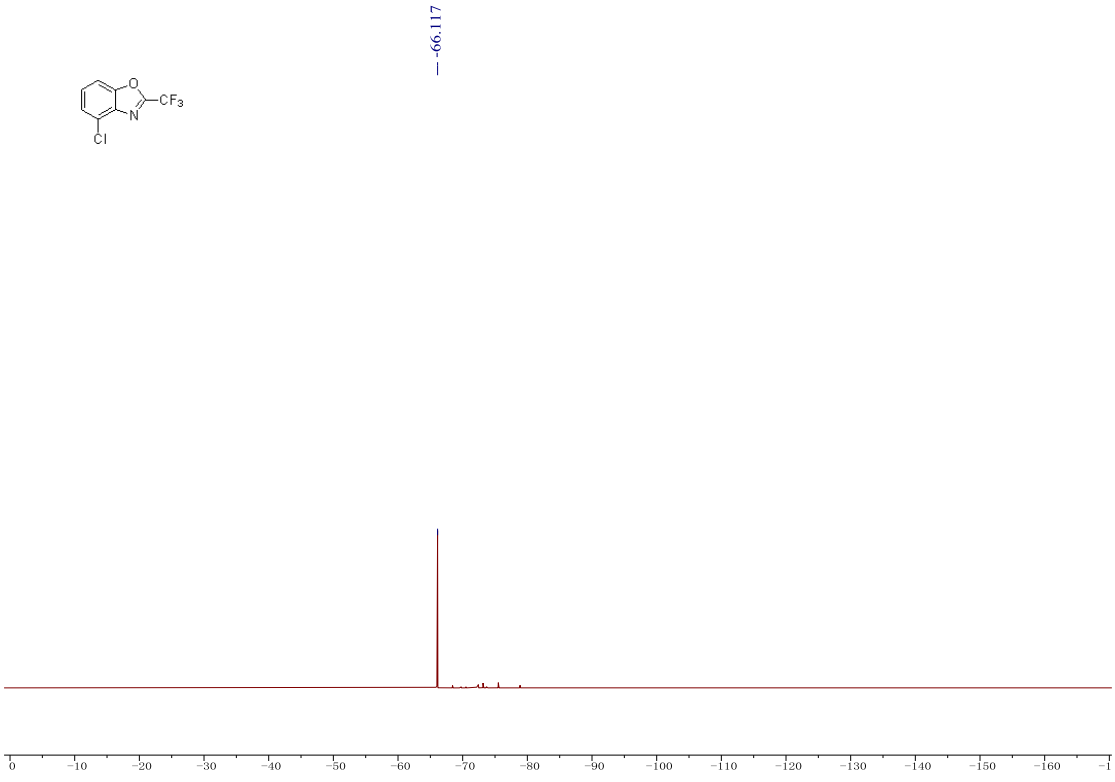
$^{13}C\{^{1}H\}$ NMR spectra of **5l** in $CDCl_3$



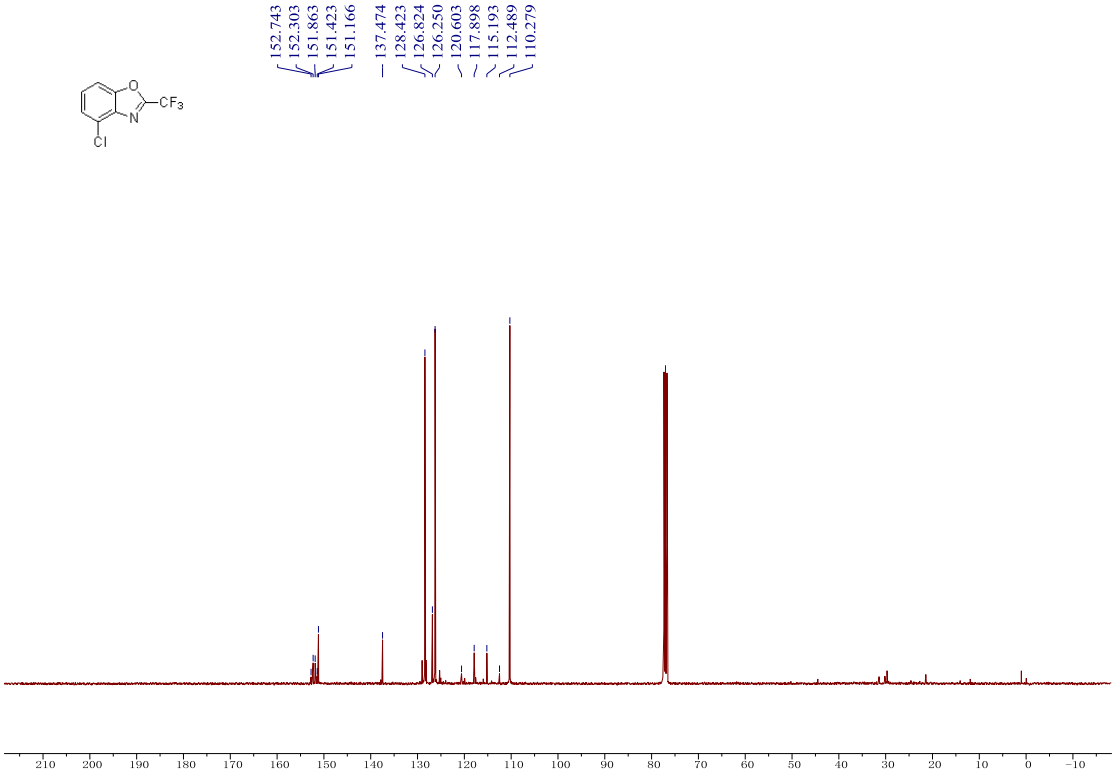
^{1}H NMR spectra of **5m** in $CDCl_3$



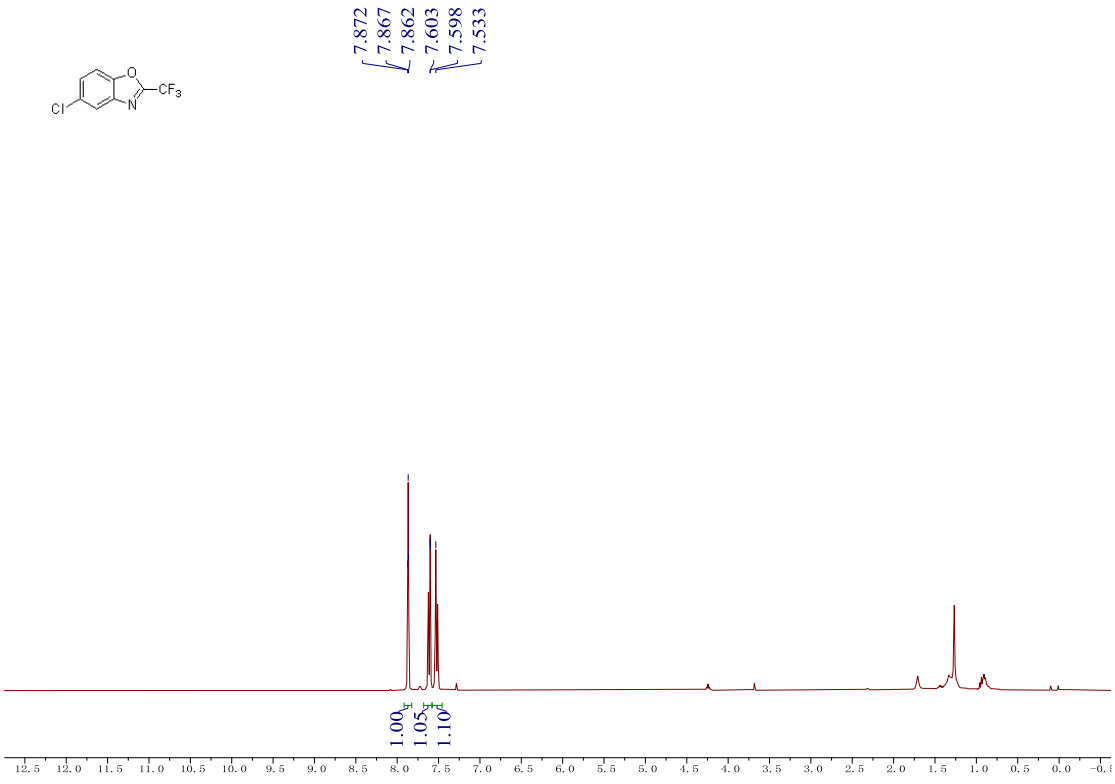
^{19}F NMR spectra of **5m** in $CDCl_3$



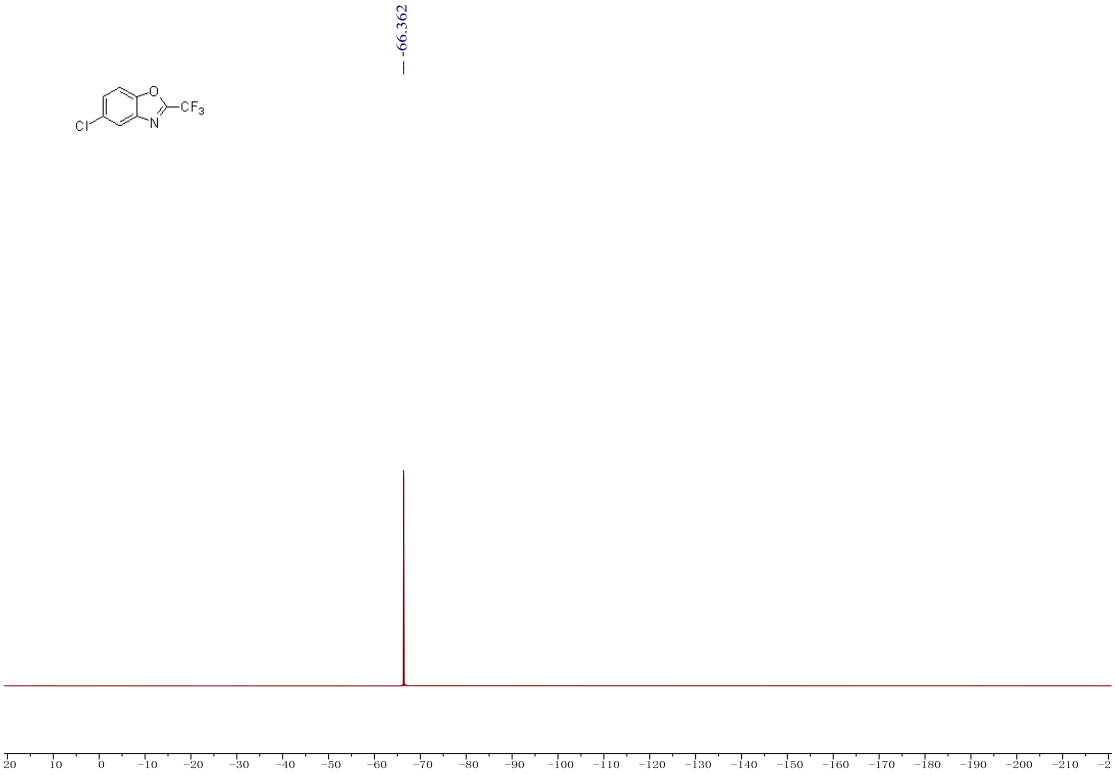
$^{13}C\{^{1}H\}$ NMR spectra of **5m** in $CDCl_3$



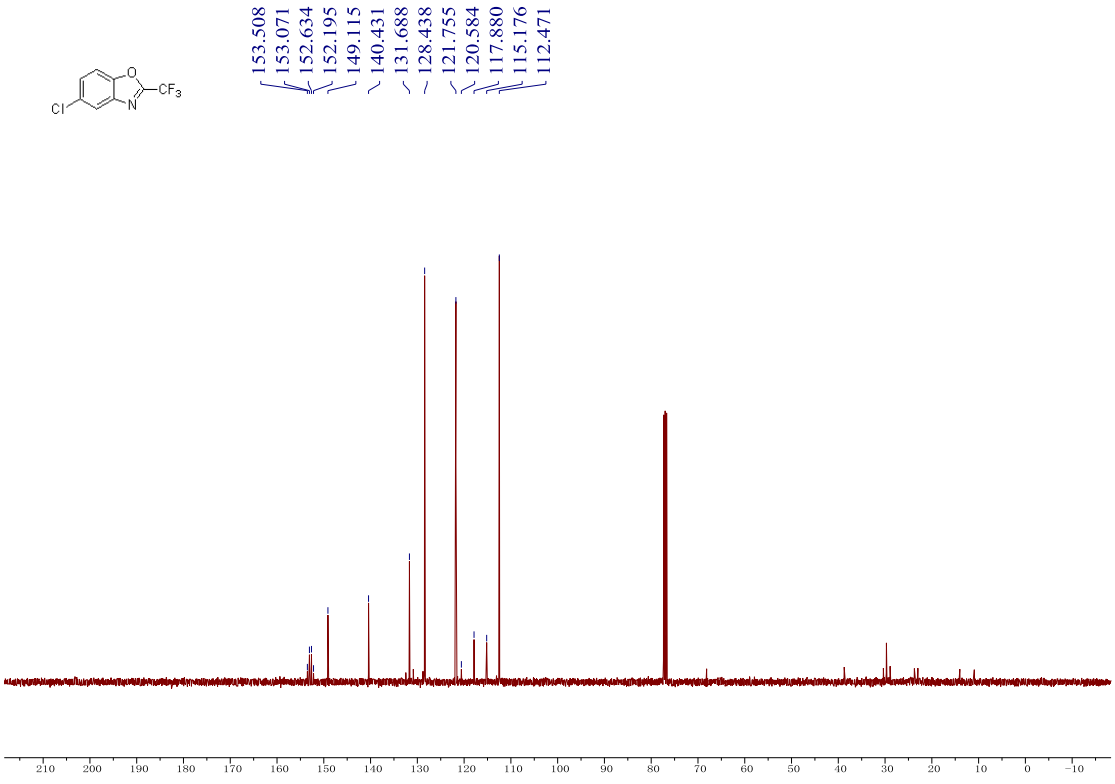
^{1}H NMR spectra of **5n** in $CDCl_3$



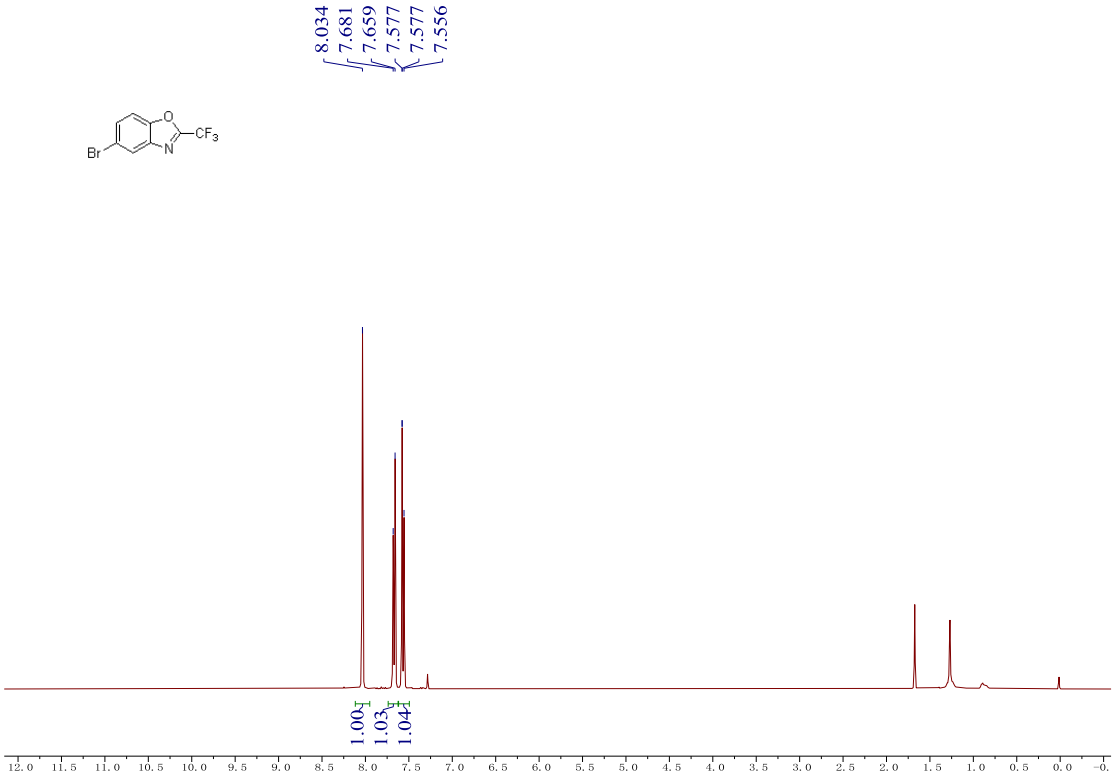
^{19}F NMR spectra of **5n** in $CDCl_3$



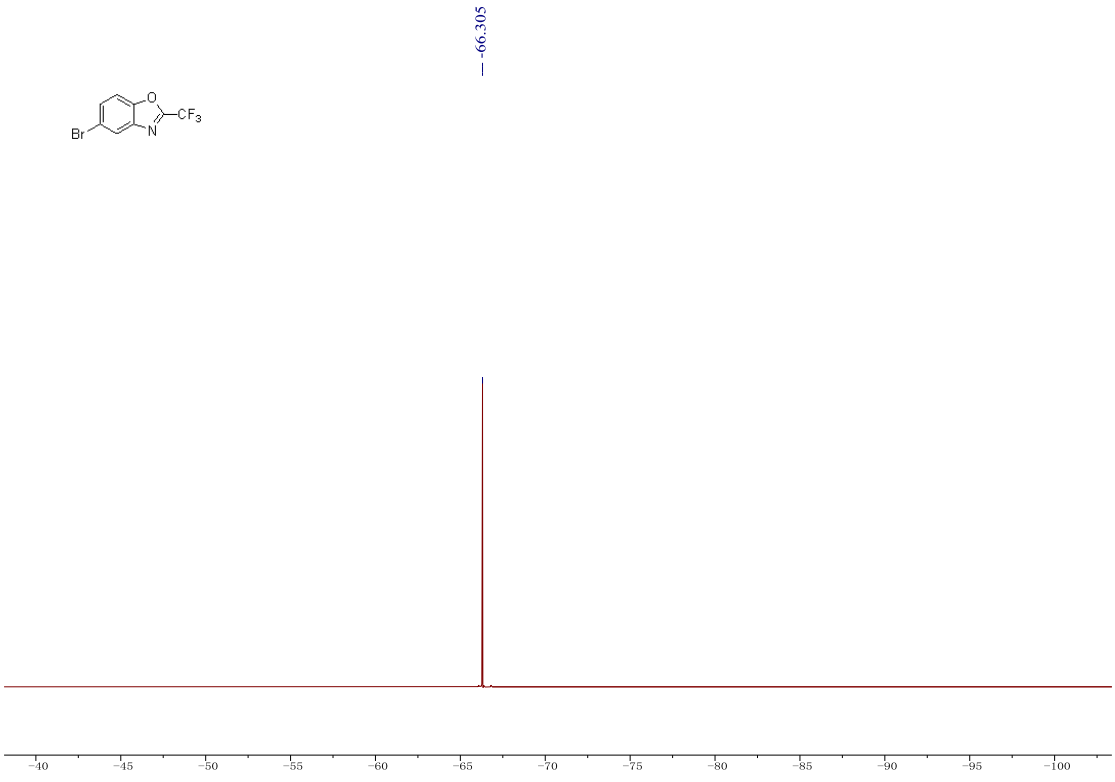
$^{13}C\{^{1}H\}$ NMR spectra of **5n** in $CDCl_3$



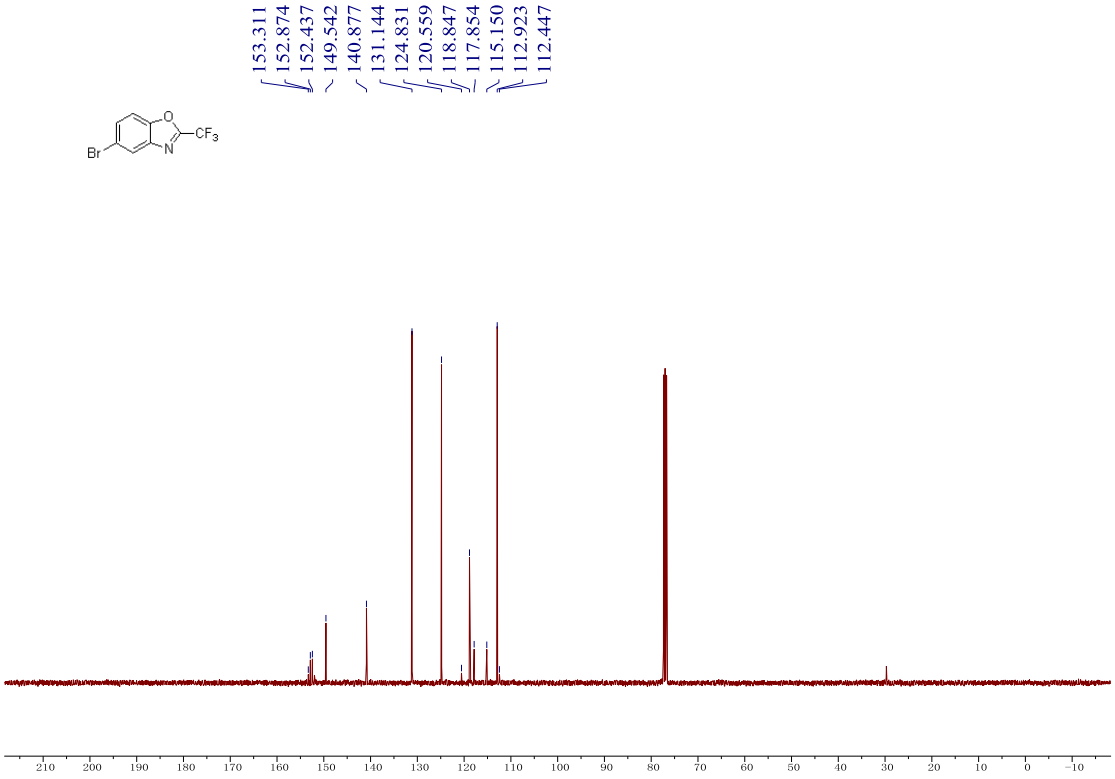
^{1}H NMR spectra of **5o** in $CDCl_3$



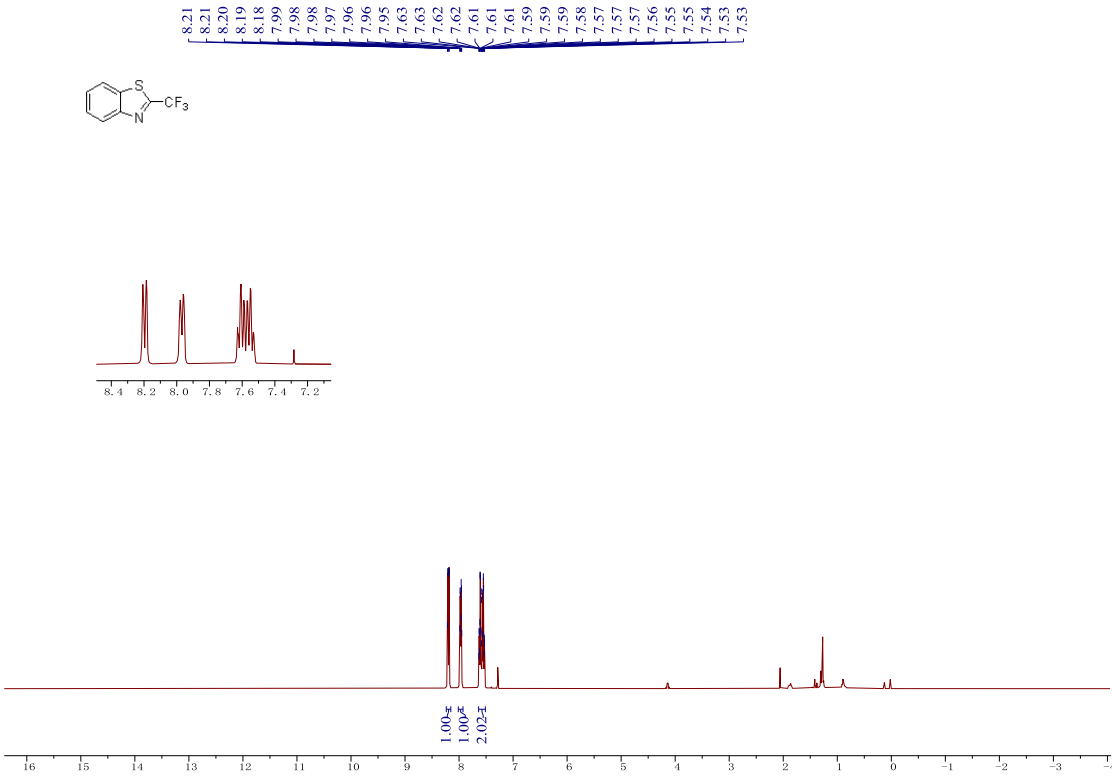
^{19}F NMR spectra of **5o** in $CDCl_3$



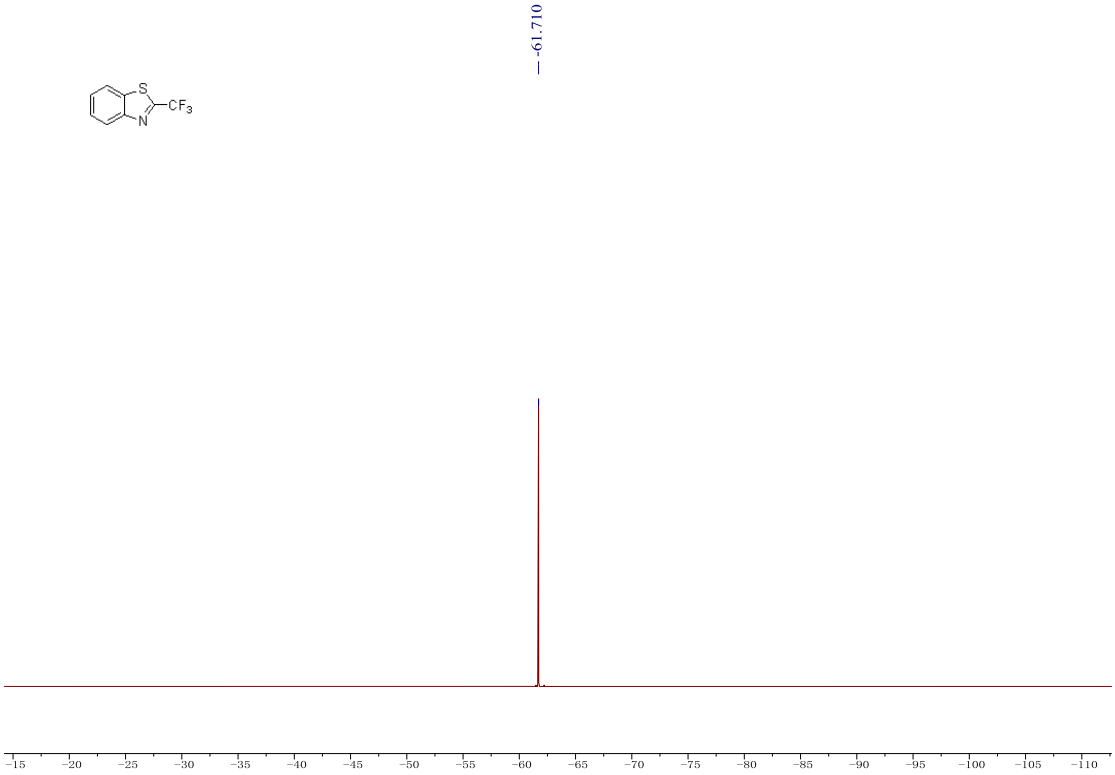
$^{13}C\{^{1}H\}$ NMR spectra of **5o** in $CDCl_3$



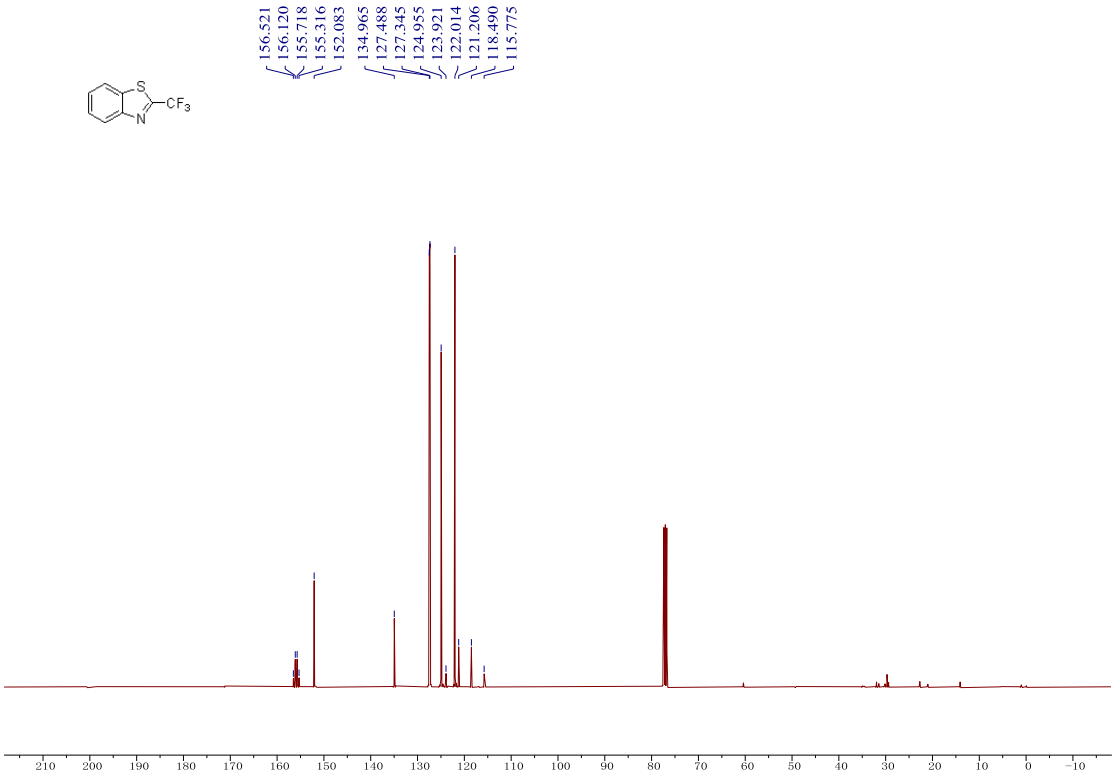
^{1}H NMR spectra of **7a** in $CDCl_3$



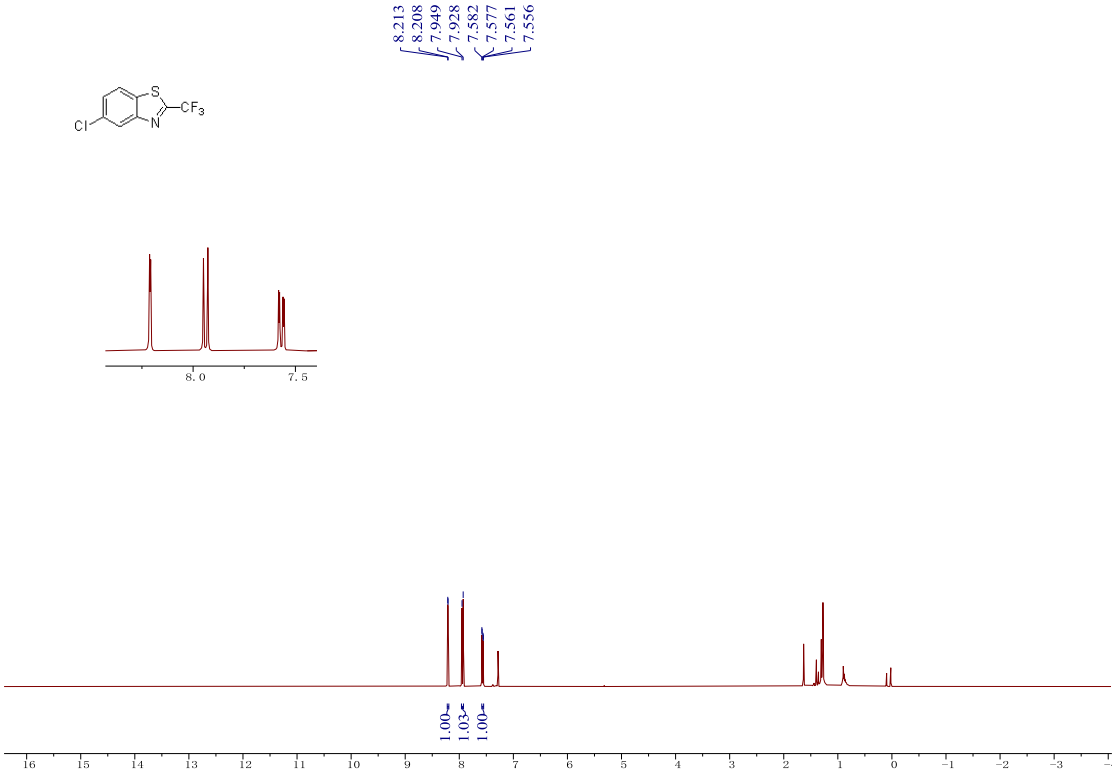
^{19}F NMR spectra of **7a** in $CDCl_3$



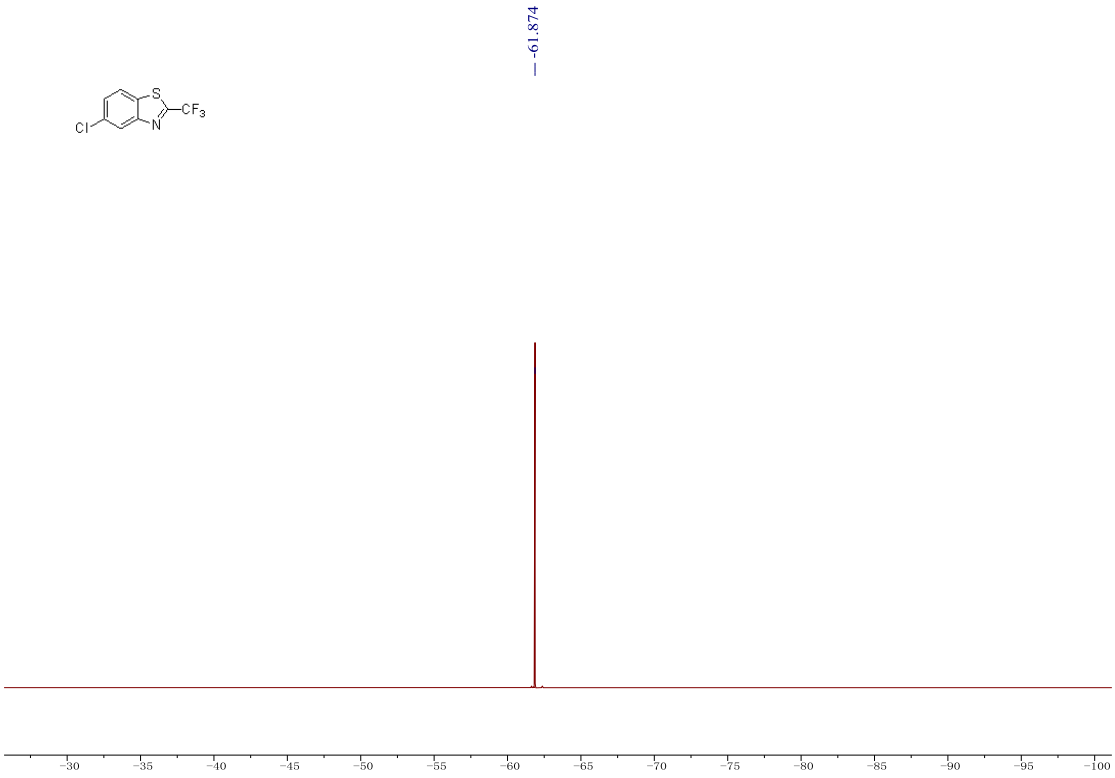
$^{13}C\{^{1}H\}$ NMR spectra of **7a** in $CDCl_3$



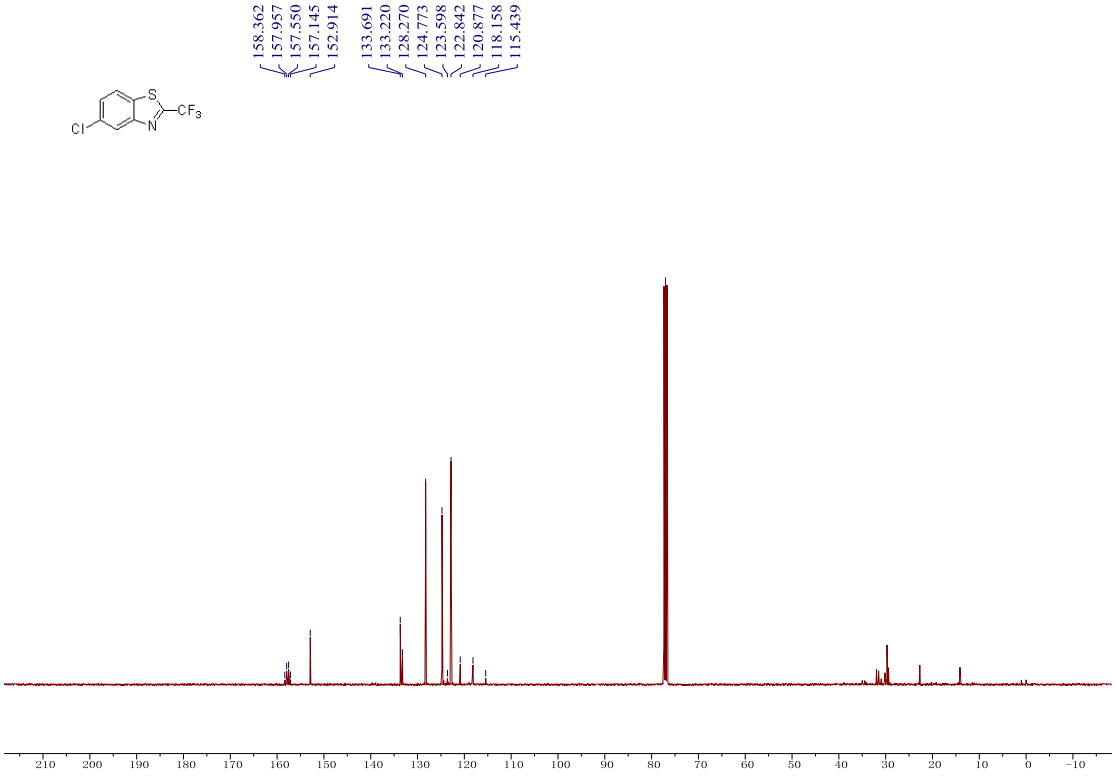
^{1}H NMR spectra of **7b** in $CDCl_3$



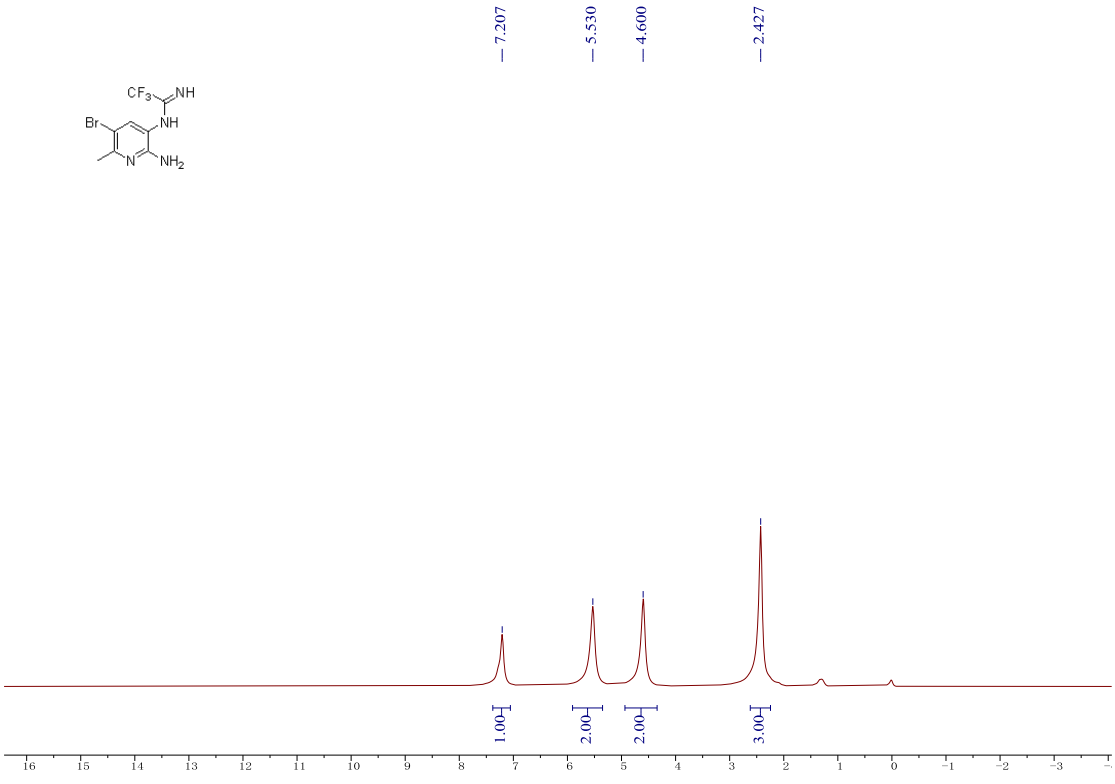
^{19}F NMR spectra of **7b** in $CDCl_3$



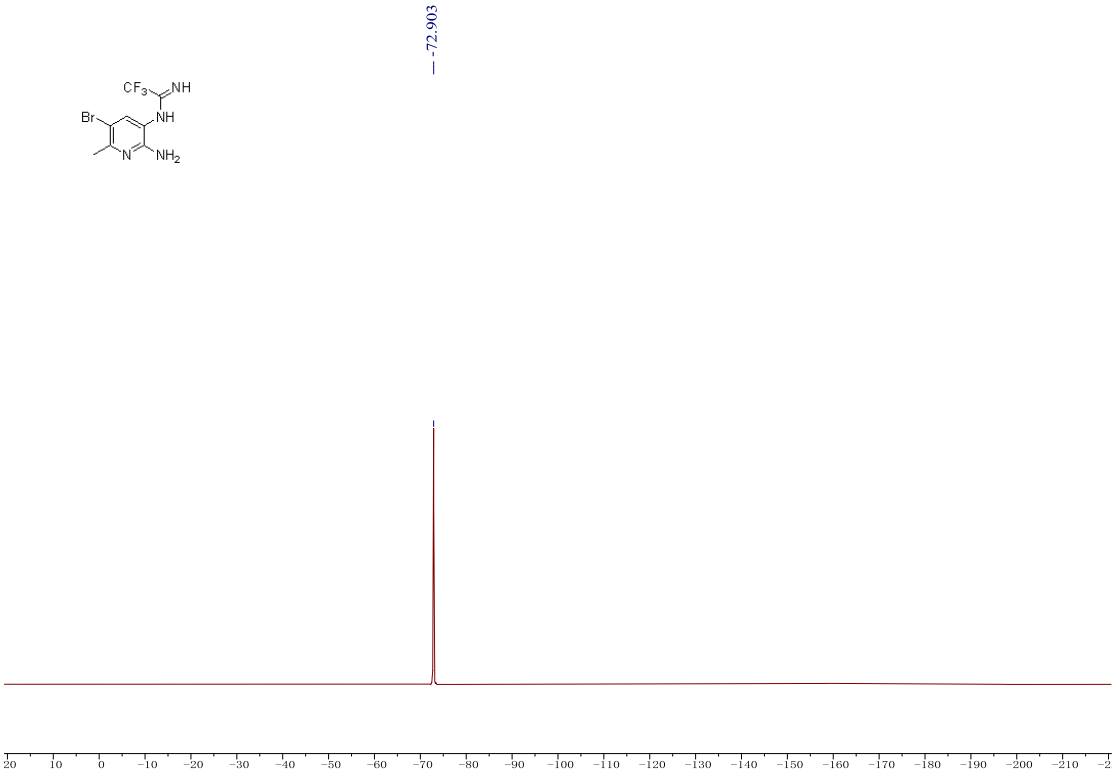
$^{13}C\{^{1}H\}$ NMR spectra of **7b** in $CDCl_3$



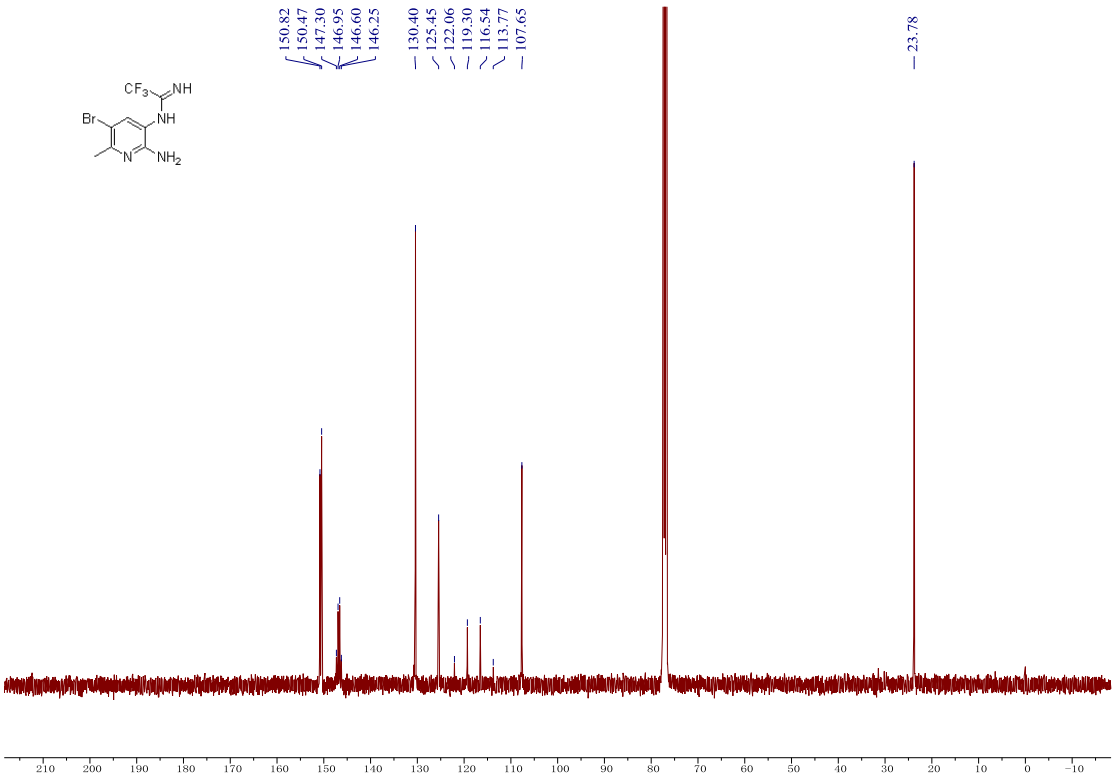
^{1}H NMR spectra of **8** in $CDCl_3$



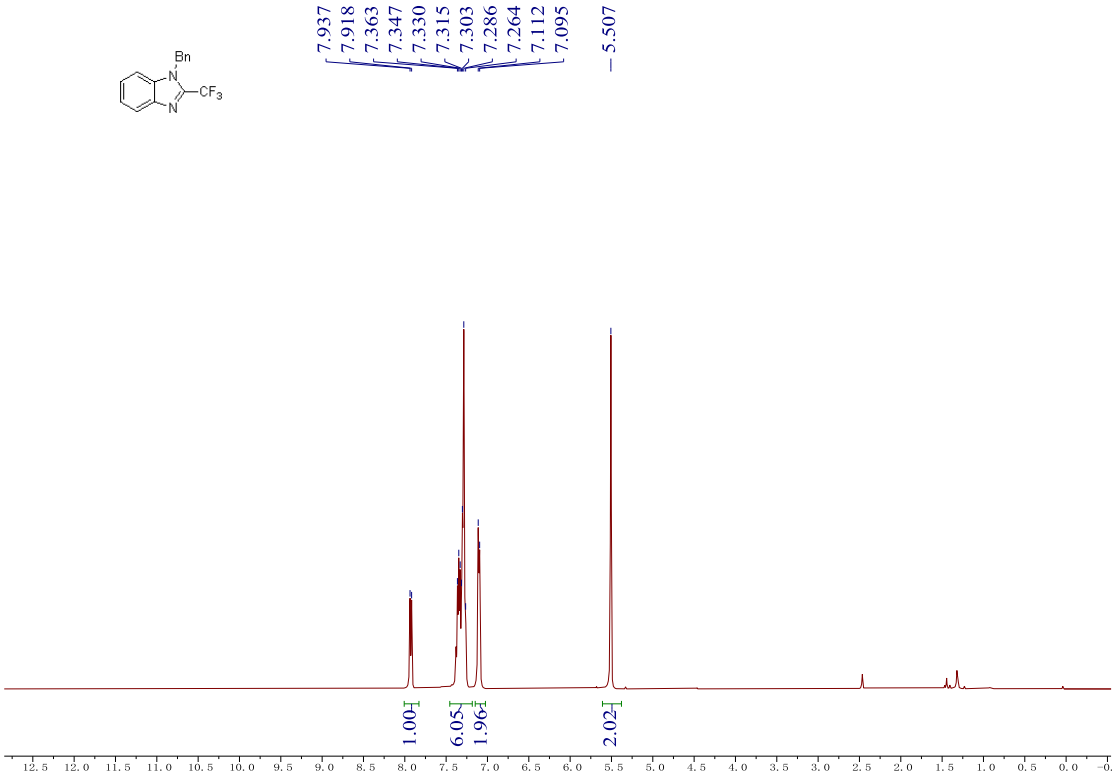
^{19}F NMR spectra of **8** in $CDCl_3$



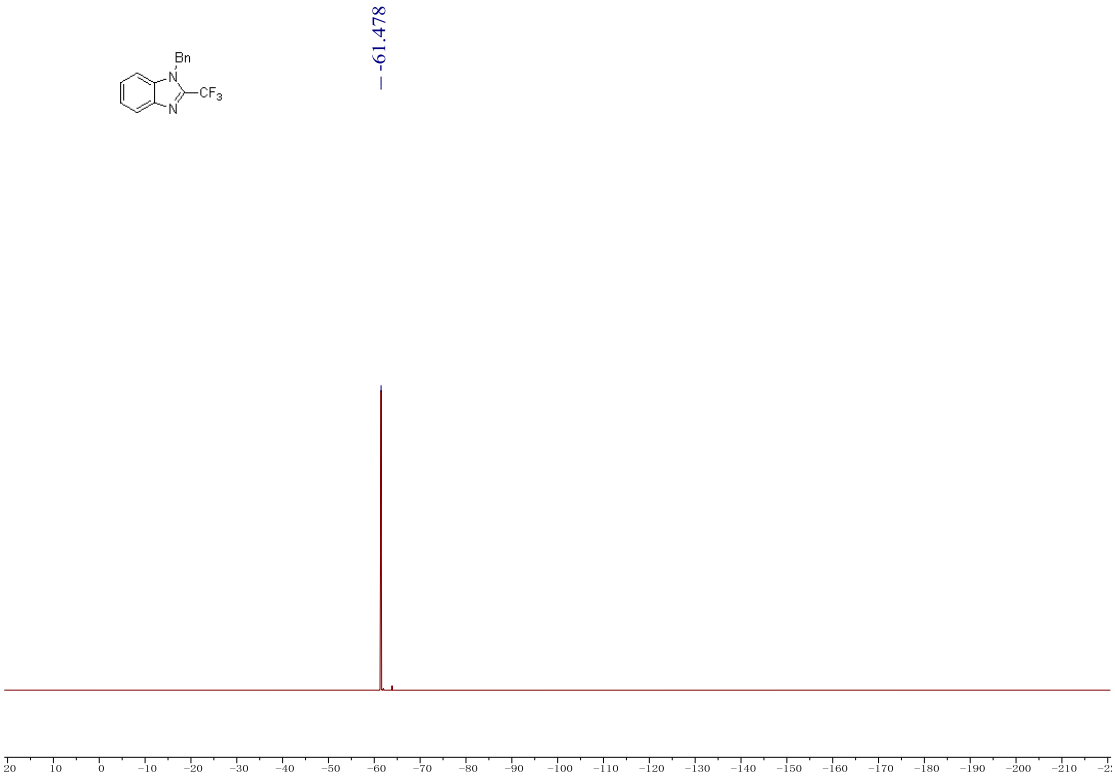
$^{13}C\{^{1}H\}$ NMR spectra of **8** in $CDCl_3$



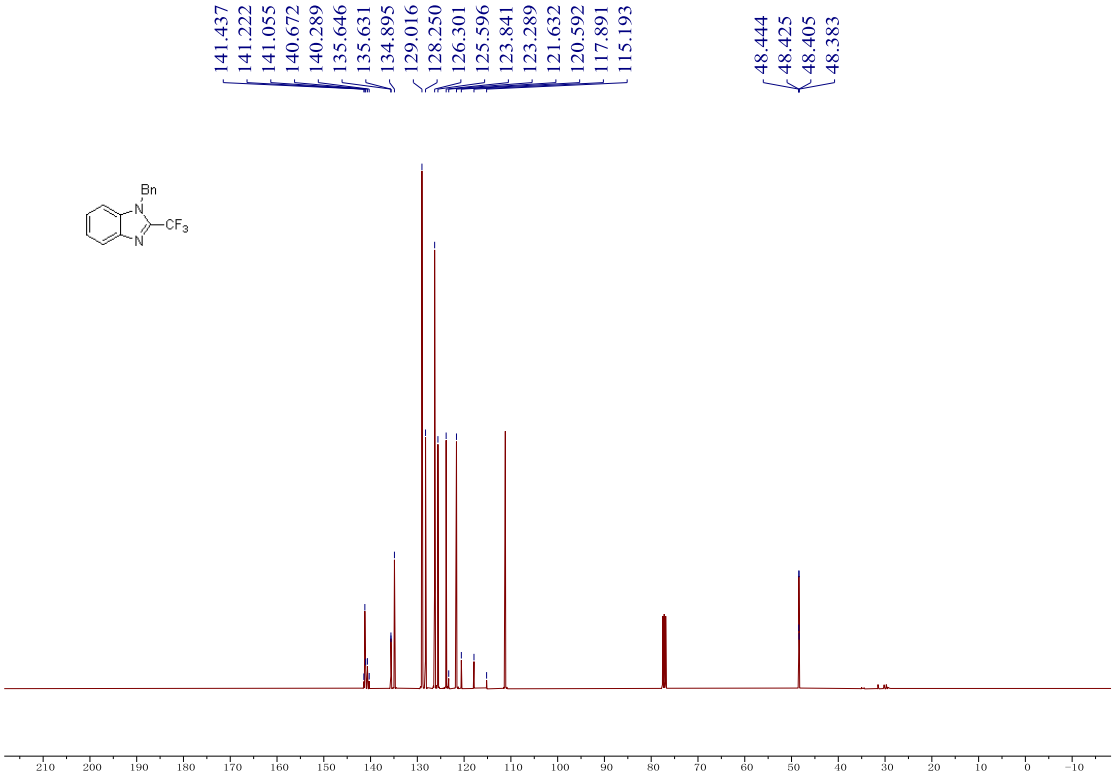
^{1}H NMR spectra of **9** in $CDCl_3$



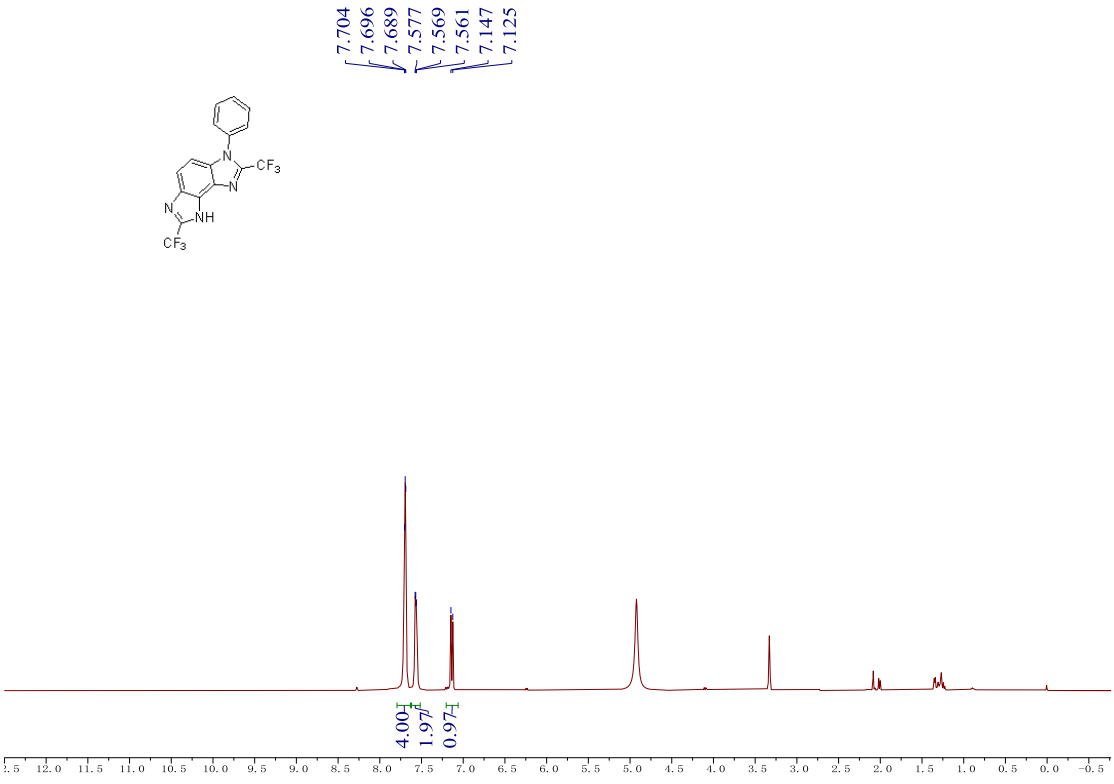
^{19}F NMR spectra of **9** in $CDCl_3$



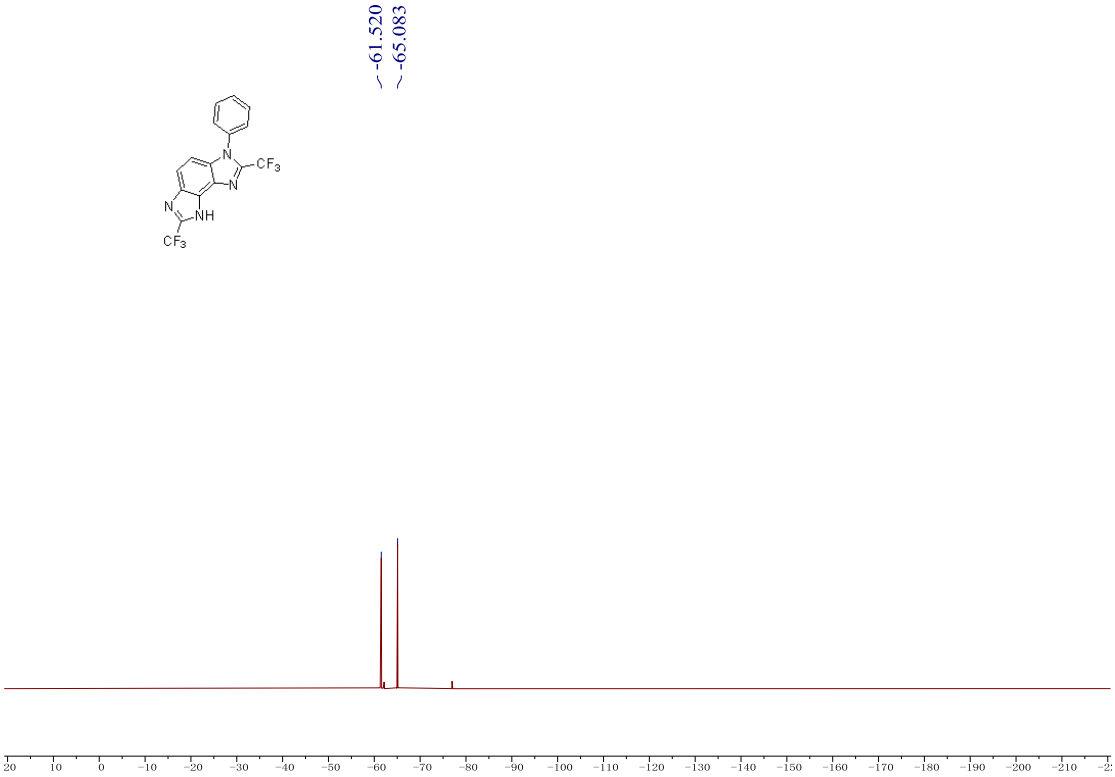
$^{13}C\{^{1}H\}$ NMR spectra of **9** in $CDCl_3$



^{1}H NMR spectra of **10** in methanol-d_4



^{19}F NMR spectra of **10** in methanol-d_4



^{13}C{^{1}H} NMR spectra of **10** in methanol-d_4