Supporting Information for

Rhodium-catalyzed transannulation of *N*-(per)fluoroalkyl-1,2,3-triazoles in microwave conditions – a general route to *N*-(per)fluoroalkyl-substituted five-membered heterocycles†

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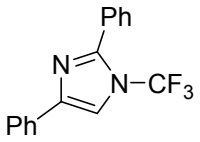
General

Chloroform stabilized with ethanol (~1%) was dried by activated molecular sieves (3 and 4 Å) and stored under argon. All commercially available chemicals were used as received unless stated otherwise. Starting triazoles were prepared according to procedures published in literature.[1, 2] Triazole **1q** was supplied by CF Plus Chemicals (www.cfplus.cz). Flash column chromatography was performed using silica gel 60 (0.040–0.063 mm). Automated flash column chromatography was performed on Teledyne ISCO CombiFlash Rf+ Lumen Automated Flash Chromatography System with UV/Vis detection. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured at ambient temperature using 5 mm diameter NMR tubes. ^{13}C spectra were proton decoupled. The chemical shift values (δ) are reported in ppm relative to internal Me_4Si (0 ppm for ^{1}H and ^{13}C NMR) or residual solvents and internal $CFCl_3$ (0 ppm for ^{19}F NMR). Coupling constants (J) are reported in Hertz. Structural elucidation was aided by additional acquisition of ^{13}C APT and/or various 2D spectra (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{13}C-^{19}F HMBC). GC-MS spectra were recorded on Agilent 7890A GC (column HP-5MS, 30 m × 0.25 mm × 0.25 μm, 5% phenyl methylpolysiloxane) coupled with 5975C quadrupole mass selective electron impact (EI) detector (70 eV). High resolution MS spectra (HRMS) were recorded on a Waters Micromass AutoSpec Ultima or Agilent 7890A GC coupled with Waters GCT Premier orthogonal acceleration time-of-flight detector using electron impact (EI) ionization. Rhodium catalyst $Rh_2(Oct)_4$ was used as a 0.01 M solution in dry chloroform. Biotage Initiator EXP EU (300 W power) was used for reactions carried out in a microwave reactor.

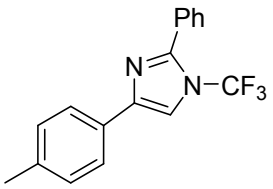
General procedure for synthesis of N-(per)fluoroalkyl-imidazoles 3a-3q. Initial *N*-(per)fluoroalkyl-triazole **1a-1q** (0.20 mmol) was dissolved in dry $CHCl_3$ (2 mL) in a 5 mL microwave tube. Nitrile (2 equiv., 0.40 mmol) and a solution of rhodium (II) octanoate (0.002 mmol; 0.01 M in dry $CHCl_3$) were added. The vial was capped and heated at 140°C for 20 min in a microwave reactor. The resulting mixture was evaporated on silica gel (100 mg) and purified either by filtration through silica gel (washing with CH_2Cl_2) and further evaporation (55°C, 3 Torr) to remove the nitrile or by CombiFlash automatic column chromatography (EtOAc/cyclohexane, 0:100 to 10:90).

1. Z. E. Blastik, S. Voltrova, V. Matousek, B. Jurasek, D. W. Manley, B. Klepetarova and P. Beier, *Angew. Chem., Int. Ed.*, 2017, **56**, 346-349.
2. S. Voltrova, M. Muselli, J. Filgas, V. Matousek, B. Klepetarova and P. Beier, *Org. Biomol. Chem.*, 2017, **15**, 4962–4965.

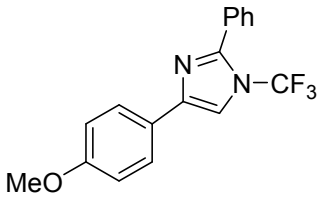
*2,4-Diphenyl-1-(trifluoromethyl)-1H-imidazole (**3a**)*: Yield: 57%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.85 (m, 1H), 7.85–7.83 (m, 1H), 7.71–7.67 (m, 2H), 7.57 (q, $^4J_{H\text{-}F}$ = 0.9 Hz, 1H), 7.52–7.46 (m, 3H), 7.45–7.39 (m, 2H), 7.36–7.30 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 142.2, 132.4, 130.2, 129.7, 129.3 (q, $J_{C\text{-}F}$ = 1.5 Hz), 128.9, 128.6, 128.1, 125.6, 118.4 (q, $^1J_{C\text{-}F}$ = 265.1 Hz, N-CF_3), 112.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.7 (s); HRMS (EI+) *m/z* calcd for $C_{16}H_{11}F_3N_2$ [M]+: 288.0874, found 288.0875.



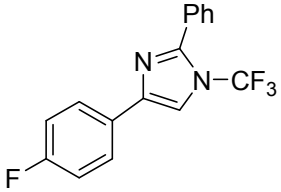
*2-Phenyl-4-(p-tolyl)-1-(trifluoromethyl)-1H-imidazole (**3b**)*: Yield: 84%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.72 (m, 2H), 7.72–7.67 (m, 2H), 7.54–7.52 (m, 1H), 7.51–7.44 (m, 3H), 7.25–7.21 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 142.2, 137.8, 130.0, 129.7, 129.5, 129.4, 129.2 (q, $J_{C\text{-}F}$ = 1.5 Hz), 128.4, 125.3, 118.3 (q, $^1J_{C\text{-}F}$ = 265.1 Hz, N-CF_3), 111.9, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.7 (s); HRMS (EI+) *m/z* calcd for $C_{17}H_{13}F_3N_2$ [M]+: 302.1031 , found 302.1032.



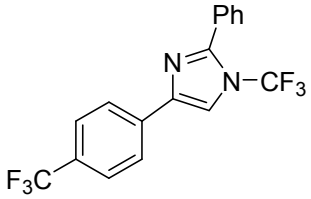
*4-(4-Methoxyphenyl)-2-phenyl-1-(trifluoromethyl)-1H-imidazole (**3c**)*: Yield: 72%; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.70–7.65 (m, 2H), 7.53–7.43 (m, 4H), 6.99–6.91 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 147.0, 142.0, 130.2, 129.7, 129.3 (q, $J_{C\text{-}F}$ = 1.5 Hz), 128.6, 126.9, 125.1, 118.4 (q, $^1J_{C\text{-}F}$ = 265.1 Hz, N-CF_3), 114.3, 111.4, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.7 (s); HRMS (EI+) *m/z* calcd for $C_{17}H_{13}F_3N_2O$ [M]+: 318.0980, found 318.0981.



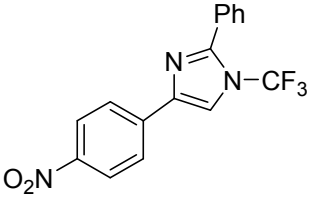
*4-(4-Fluorophenyl)-2-phenyl-1-(trifluoromethyl)-1H-imidazole (**3d**)*: Yield: 64%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.78 (m, 2H), 7.72–7.63 (m, 2H), 7.54–7.44 (m, 4H), 7.15–7.06 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, $^1J_{C\text{-}F}$ = 246.9 Hz), 147.3, 141.4, 130.3, 129.6, 129.3 (q, $J_{C\text{-}F}$ = 1.4 Hz), 128.7 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 128.6, 127.3 (d, $^3J_{C\text{-}F}$ =8.1 Hz), 118.3 (q, $^1J_{C\text{-}F}$ = 265.5 Hz, N-CF_3), 115.8 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 112.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.7 (s, 3F), -114.5 (s, 1F); HRMS (EI+) *m/z* calcd for $C_{16}H_{10}F_4N_2$ [M]+: 306.0780, found 306.0778.

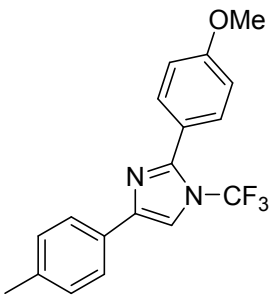


*2-Phenyl-1-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-1H-imidazole (**3e**)*: Yield: 63%; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.93 (m, 2H), 7.74–7.63 (m, 5H), 7.55–7.45 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 140.8, 135.9 (q, $J_{C\text{-}F}$ = 1.4 Hz), 130.4, 130.0 (q, $^3J_{C\text{-}F}$ = 32.48 Hz), 129.4, 129.3 (q, $J_{C\text{-}F}$ = 1.4), 128.7, 125.9, (q, $^4J_{C\text{-}F}$ = 3.8 Hz), 125.7, (q, $^1J_{C\text{-}F}$ = 272.07 Hz), 125.7, 118.3 (q, $^1J_{C\text{-}F}$ = 265.7 Hz, N-CF_3), 113.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.7 (s, 3F), -63.0 (s, 3F); HRMS (EI+) *m/z* calcd for $C_{17}H_{10}F_6N_2$ [M]+: 356.0748, found 356.0746.



*4-(4-Nitrophenyl)-2-phenyl-1-(trifluoromethyl)-1H-imidazole (**3f**)*: Yield: 52%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33–8.25 (m, 2H), 8.05–7.99 (m, 2H), 7.76–7.73 (m, 1H), 7.71–7.67 (m, 2H), 7.57–7.46 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 147.4, 140.0, 138.7, 130.6, 129.3 (q, $J_{C\text{-}F}$ = 1.5 Hz), 129.1, 128.7, 126.0, 124.4, 118.2 (q, $^1J_{C\text{-}F}$ = 266.2 Hz, N-CF_3) 114.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.8 (s); HRMS (EI+) *m/z* calcd for $C_{16}H_{10}F_3N_3O_2$ [M]+: 333.0725, found 333.0726.

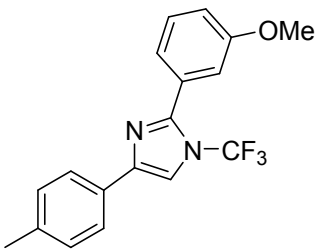




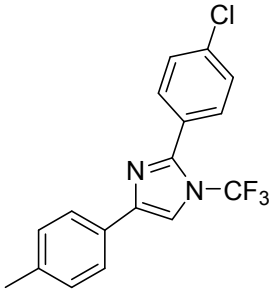
*2-(4-Methoxyphenyl)-4-(p-tolyl)-1-(trifluoromethyl)-1H-imidazole (**3g**)*: Yield: 78%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.69 (m, 2H), 7.67–7.58 (m, 2H), 7.49 (q, $^4J_{H\text{-}F}$ = 0.8 Hz, 1H), 7.24–7.20 (m, 2H), 7.05–6.94 (m, 2H), 3.87 (s, 3H), 2.38 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 147.0, 142.0, 137.8, 130.8 (q, J_{C-F} = 1.5 Hz), 129.7, 129.5, 125.4, 122.2, 118.4 (q, $^1J_{C-F}$ = 264.9 Hz, N-CF_3), 114.0, 111.8, 55.5, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.7 (s); HRMS (EI+) *m/z* calcd for $C_{18}H_{15}F_3N_2O$ [M]+: 332.1136, found 332.1134.

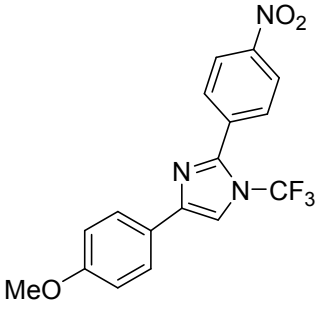
*2-(3-Methoxyphenyl)-4-(p-tolyl)-1-(trifluoromethyl)-1H-imidazole (**3h**)*: Yield: 94%; pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79–7.70 (m, 2H), 7.51 (q, $^4J_{H-F}$ = 0.9 Hz, 1H), 7.41–7.35 (m, 1H), 7.28–7.21 (m, 4H, *signal overlap with solvent*), 7.04 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 3.86 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 146.9, 142.2, 137.9, 130.9, 129.6 (3C), 125.4, 121.7 (q, J_{C-F} = 1.5 Hz), 118.4 (q, $^1J_{C-F}$ = 265.2, N-CF_3), 116.3, 114.6 (q, J_{C-F} = 1.2 Hz), 112.0 (q, J_{C-F} = 1.2 Hz), 55.5, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.6 (s); HRMS (EI+) *m/z* calcd for $C_{18}H_{15}F_3N_2O$ [M]+: 332.1136, found 332.1133.



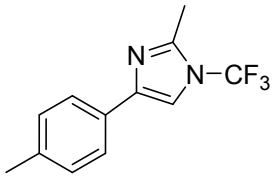
*2-(4-Chlorophenyl)-4-(p-tolyl)-1-(trifluoromethyl)-1H-imidazole (**3i**)*: Yield: 82%; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.68 (m, 2H), 7.67–7.59 (m, 2H), 7.52 (q, $^4J_{H-F}$ = 0.9 Hz, 1H), 7.50–7.42 (m, 2H), 7.25–7.21 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 142.5, 138.1, 136.5, 130.7 (q, J_{C-F} = 1.4 Hz), 129.6, 129.4, 128.9, 128.2, 125.4, 118.3 (q, $^1J_{C-F}$ = 265.1 Hz, N-CF_3), 112.2, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.7 (s); HRMS (EI+) *m/z* calcd for $C_{17}H_{12}ClF_3N_2$ [M]+: 336.0641, found 336.0642.



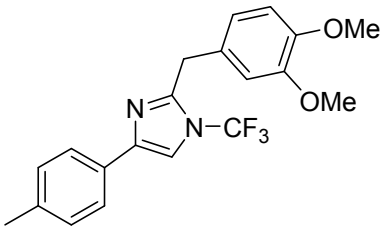
*4-(4-Methoxyphenyl)-2-(4-nitrophenyl)-1-(trifluoromethyl)-1H-imidazole (**3j**)*: Yield: 33%; purification by column chromatographny on C18 reverse-phase silica (H_2O/MeCN, 80:20 to 20:80); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.37–8.32 (m, 2H), 7.95–7.88 (m, 2H), 7.81–7.73 (m, 2H), 7.53 (q, $^4J_{H-F}$ = 0.9 Hz, 1H), 7.03–6.92 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 148.7, 144.4, 142.9, 135.7, 130.3, 126.9, 124.6, 123.8 (m), 118.3 (q, $^1J_{C-F}$ = 265.6 Hz, N-CF_3), 114.4 (m), 112.4, 55.5 (q, J_{C-F} = 10.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.4 (s); HRMS (EI+) *m/z* calcd for $C_{17}H_{12}F_3N_3O_3$ [M]+: 363.0831, found 363.0828.



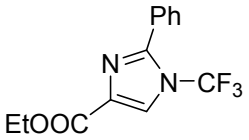
*2-Methyl-4-(p-tolyl)-1-(trifluoromethyl)-1H-imidazole (**3k**)*: Yield: 71%; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67–7.57 (m, 2H), 7.33 (s, 1H), 7.23–7.16 (m, 2H), 2.59 (q, $^5J_{H-F}$ = 1.4 Hz, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 141.4, 137.7, 129.7, 129.5, 125.2, 118.5 (q, $^1J_{C-F}$ = 263.8 Hz, N-CF_3), 110.8, 21.4, 14.4 (q, $^4J_{C-F}$ = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.2 (s); HRMS (EI+) *m/z* calcd for $C_{12}H_{11}F_3N_2$ [M]+: 240.0874, found 240.0876.



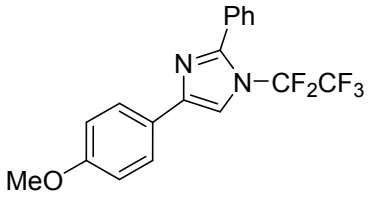
2-(3,4-Dimethoxybenzyl)-4-(p-tolyl)-1-(trifluoromethyl)-1H-imidazole ***(3l)***: Yield: 56%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.65 (m, 2H), 7.35 (d, J_{H-H} = 0.8 Hz, 1H), 7.23–7.19 (m, 2H), 6.86 (s, 1H), 6.79 (d, J_{H-H} = 1.0 Hz, 2H), 4.20 (d, J_{H-H} = 1.1 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.1, 146.6, 141.7, 137.8, 129.8, 129.6, 129.5,128.5, 125.3, 120.9–120.5 (m), 118.4 (q, $^{1}J_{C-F}$ 264.6 Hz, N-CF_3), 111.9 (m), 111.2 (m), 56.0 (q, J_{C-F} = 11.2 Hz), 34.5–33.8 (m), 21.4 (q, J_{C-F} = 7.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.1 (s); HRMS (EI+) *m/z* calcd for $C_{20}H_{19}F_3N_2O_2$ [M]+: 376.1399, found 376.1397.



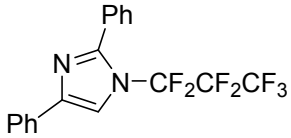
Ethyl 2-phenyl-1-(trifluoromethyl)-1H-imidazole-4-carboxylate ***(3m)***: Yield: 65%, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (q, $^{4}J_{H-F}$ = 0.9 Hz, 1H), 7.67–7.59 (m, 2H), 7.55–7.41 (m, 3H), 4.42 (q, $^{3}J_{H-H}$ = 7.2 Hz, 2H), 1.39 (t, $^{3}J_{H-H}$ = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 161.9, 147.6, 134.2, 130.7, 129.4 (q, J_{C-F} = 1.3 Hz), 128.6, 128.5, 122.9 (q, J_{C-F} = 1.2 Hz), 117.9 (q, $^{1}J_{C-F}$ = 267.1 Hz, N-CF_3), 61.4, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.1 (s); HRMS (EI+) *m/z* calcd for $C_{13}H_{11}F_3N_2O_2$ [M]+: 284.0773, found 284.0770.



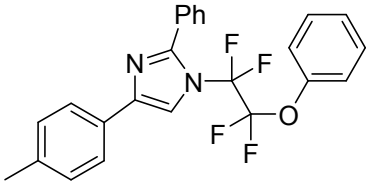
4-(4-Methoxyphenyl)-1-(perfluoroethyl)-2-phenyl-1H-imidazole ***(3n)***: Yield: 92%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.73 (m, 2H), 7.62–7.54 (m, 2H), 7.52–7.41 (m, 3H), 7.39–7.35 (m, 1H), 7.01–6.90 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 148.2, 142.8, 130.5, 130.0 (2C), 128.2, 126.9, 125.0, 117.6 (qt, $^{1}J_{C-F}$ = 288.0 Hz, $^{2}J_{C-F}$ = 44.9 Hz, CF_3), 114.3, 111.6, 110.6 (tq, $^{1}J_{C-F}$ = 269.2 Hz, $^{2}J_{C-F}$ = 44.9 Hz, N-CF_2), 55.5; ^{19}FNMR (376 MHz, $CDCl_3$) δ -84.8 (s, 3F), -93.9 (s, 2F); HRMS (EI+) *m/z* calcd for $C_{18}H_{13}F_5N_2O$ [M]+: 368.0948, found 368.0954.



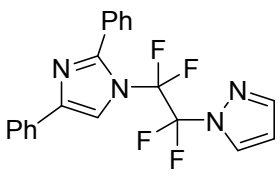
1-(Perfluoropropyl)-2,4-diphenyl-1H-imidazole ***(3o)***: Yield: 71%,white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91–7.84 (m, 2H), 7.61–7.55 (m, 2H), 7.51–7.39 (m, 6H), 7.37–7.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 142.7, 132.2, 130.4, 130.1, 128.9, 122.2 (2C), 125.6, 117.4 (qtt, $^{1}J_{C-F}$ = 287.7 Hz, $^{2}J_{C-F}$ = 33.3 Hz, $^{3}J_{C-F}$ = 2.1 Hz, CF_3), 112.9, 112.4 (tt, $^{1}J_{C-F}$ = 269.8 Hz, $^{2}J_{C-F}$ = 32.1 Hz, N-CF_2), 110.2–105.6 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.6 (t, $^{3}J_{F-F}$ = 9.7 Hz, 3F), -89.8 (q, $^{3}J_{F-F}$ = 9.7 Hz, 2F), -126.1 (s, 2F); HRMS (EI+) *m/z* calcd for $C_{18}H_{11}F_7N_2$ [M]+: 388.0810, found 388.0809.



2-Phenyl-1-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-4-(p-tolyl)-1H-imidazole ***(3p)***: Yield: 57%; brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.73 (m, 2H), 7.68–7.62 (m, 2H), 7.56 (s, 1H), 7.52–7.38 (m, 3H), 7.40–7.30 (m, 2H), 7.30–7.19 (m, 3H, *signal overlap with solvent*), 7.10–7.02 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 148.4, 142.3, 137.7, 131.2, 130.1, 129.9 (2C), 129.7, 129.5, 128.0, 127.0, 125.4, 121.5, 116.3 (tt, $^{1}J_{C-F}$ = 277.3 Hz, $^{2}J_{C-F}$ = 40.8 Hz), 113.2, 111.9 (tt, $^{1}J_{C-F}$ = 268.8 Hz, $^{2}J_{C-F}$ = 40.8 Hz), 21.4; ^{19}F NMR (376 MHz, CDCl3) δ -86.3 (t, $^{3}J_{F-F}$ = 4.2 Hz, 2F), -93.7 (t, $^{3}J_{F-F}$ = 4.2 Hz, 2F); HRMS (EI+) *m/z* calcd for $C_{24}H_{18}F_4N_2O$ [M]+: 426.1355, found 426.1356.

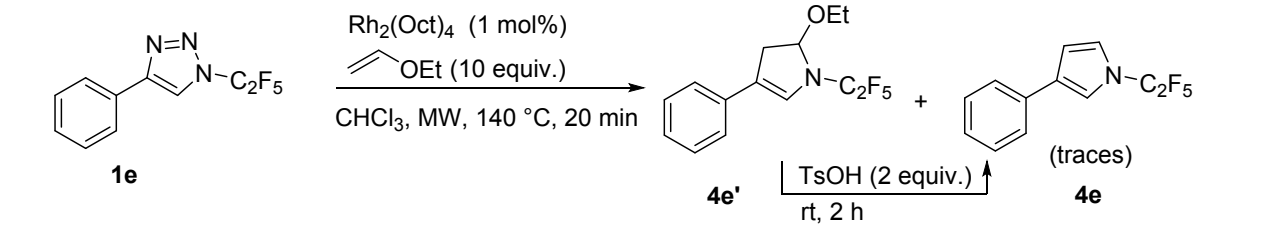


1-(2-(2,4-Diphenyl-1H-imidazol-1-yl)-1,1,2,2-tetrafluoroethyl)-1H-pyrazole ***(3q)***: Yield: 70%; red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.76 (m, 2H), 7.72 (qd, *J* = 1.5, 0.6 Hz, 1H), 7.64–7.58 (m, 1H), 7.54–7.35 (m, 7H), 7.35–7.26 (m, 1H), 7.25 (s, 1H, *signal overlap with solvent*), 6.42 (dd, *J* = 2.7, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 143.9, 142.4, 132.4, 130.5, 130.0, 129.8, 129.1, 128.8, 128.0 (2C), 125.5, 113.1, 112.6 (tt, $^{1}J_{C-F}$ = 271.3 Hz, $^{2}J_{C-F}$ = 42.1 Hz), 112.5 (tt, $^{1}J_{C-F}$ = 269.2 Hz, $^{2}J_{C-F}$ = 42.1 Hz), 108.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.1 (t, $^{3}J_{F-F}$ = 4.7 Hz, 2F), -98.2 (t, $^{3}J_{F-F}$ = 4.7 Hz, 2F); HRMS (EI+) *m/z* calcd for $C_{20}H_{14}F_4N_4$ [M]+: 386.1155, found 386.1156.

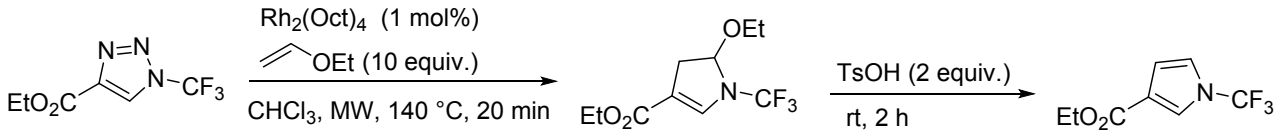


General procedure for synthesis of N-(per)fluoroalkyl-pyrroles 4a-4i. *N*-(per)fluoroalkyl-triazole **1** (0.20 mmol) was dissolved in dry $CHCl_3$ (2 mL) in a 5 mL microwave tube. Vinyl ether (10 equiv., 2.0 mmol) and a solution of rhodium (II) octanoate (0.002 mmol; 0.01 M in dry $CHCl_3$) were added. The vial was capped and heated at 140°C for 20 min in a microwave reactor. The resulting mixture was evaporated on silica gel (100 mg) and purified by CombiFlash automatic column chromatography (cyclohexane).

In case of derivatives **4e** and **4g** the non-eliminated products were observed. For preparation of the desired pyrroles was developed one-pot two-step procedure.



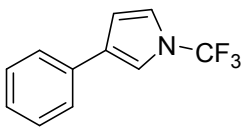
1e **4e'** **4e**



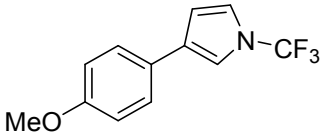
1g **4g'** **4g**

One-pot two-step procedure for preparation of pyrroles 4e and 4g. *N*-perfluoroalkyl-triazole (0.20 mmol) was dissolved in dry $CHCl_3$ (2 mL) in a 5 mL microwave tube. Vinyl ether (10 equiv., 2.0 mmol) and a solution of rhodium (II) octanoate (0.002 mmol; 0.01 M in dry $CHCl_3$) were added. The vial was capped and heated at 140°C for 20 min in microwave reactor. Then $TsOH \cdot H_2O$ (0.40 mmol; 76.1 mg) was added. The resulting suspension was stirred at rt for 2 h filtered, evaporated on silica gel (100 mg) and purified by CombiFlash automatic column chromatography (cyclohexane).

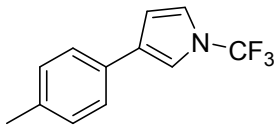
*3-Phenyl-1-(trifluoromethyl)-1H-pyrrole (**4a**)*: Yield: 96%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.48 (m, 2H), 7.41–7.34 (m, 2H), 7.30–7.21 (m, 2H), 7.03 (dd, J = 3.3, 2.3 Hz, 1H), 6.63 (ddq, J = 3.3, 1.6, 0.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 128.9, 128.4, 127.0, 125.8, 119.5 (q, $^1J_{C\text{-}F}$ = 260.1 Hz, N-CF_3), 118.8, 113.9, 110.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.5 (s); HRMS (EI+) *m/z* calcd for $C_{11}H_8F_3N$ [M]+: 211.0609, found 211.0611.



*3-(4-Methoxyphenyl)-1-(trifluoromethyl)-1H-pyrrole (**4b**)*: Yield: 93%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.40 (m, 2H), 7.16 (t, J = 2.0 Hz, 1H), 7.01 (dd, J = 3.3, 2.3 Hz, 1H), 6.96–6.88 (m, 2H), 6.57 (ddq, J = 3.2, 1.7, 0.7 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 128.1, 126.9, 126.7, 119.1 (q, $^1J_{C\text{-}F}$ = 260.2 Hz, N-CF_3), 118.7, 114.4, 113.1, 110.5, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.5 (s); HRMS (EI+) *m/z* calcd for $C_{12}H_{10}F_3NO$ [M]+: 241.0714, found 241.0712.

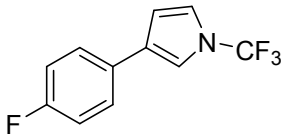


*3-(p-Tolyl)-1-(trifluoromethyl)-1H-pyrrole (**4c**)*: Yield: 82%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.39 (m, 2H), 7.25–7.16 (m, 3H), 7.02 (dd, J = 3.2, 2.3 Hz, 1H), 6.60 (ddq, J = 3.2, 1.5, 0.7

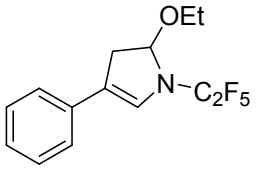


Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 131.1, 129.6, 128.4, 125.6, 119.1 (q, $^1J_{C\text{-}F}$ = 260.2 Hz, N-CF_3), 118.7, 113.5, 110.6, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.5 (s); HRMS (EI+) *m/z* calcd for $C_{12}H_{10}F_3N$ [M]+: 225.0765, found 225.0762.

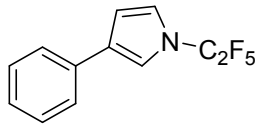
*3-(4-Fluorophenyl)-1-(trifluoromethyl)-1H-pyrrole (**4d**)*: Yield: 80%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.42 (m, 2H), 7.19 (t, *J* = 2.0 Hz, 1H), 7.10–7.04 (m, 2H), 7.03 (dd, *J* = 3.2, 2.3 Hz, 1H), 6.57 (ddq, *J* = 3.3, 1.5, 0.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (d, $^1J_{C\text{-}F}$ = 245.7 Hz), 130.1 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 127.5, 127.3 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 119.2 (q, $^1J_{C\text{-}F}$ = 260.8 Hz, N-CF_3), 118.9, 115.8 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 113.7, 110.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.5 (s, 3F), -116.2 (s, 1F); HRMS (EI+) *m/z* calcd for $C_{11}H_7F_4N$ [M]+: 229.0515, found 229.0514.



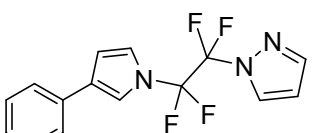
*2-Ethoxy-1-(perfluoroethyl)-4-phenyl-2,3-dihydro-1H-pyrrole (**4e'**): not isolated;* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 4H), 7.24–7.18 (m, 1H) ,6.56 (s, 1H), 5.45 (d, *J* = 7.6 Hz, 1H), 3.62 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.52 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.32–3.20 (m, 1H), 2.85 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.3 (s, 3F), -93.4 (d, $^2J_{F\text{-}F}$ = 212.9 Hz, 1F), -95.8 (d, $^2J_{F\text{-}F}$ = 212.9 Hz, 1F).



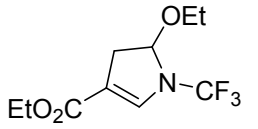
*1-(Perfluoroethyl)-3-phenyl-1H-pyrrole (**4e**)*: Yield: 89%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.48 (m, 2H), 7.42–7.34 (m, 2H), 7.31–7.22 (m, 1H), 7.20 (tt, *J* = 1.7, 0.8 Hz, 1H), 7.02–6.95 (m, 1H), 6.67 (ddt, *J* = 3.4, 1.7, 0.9 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 133.9, 129.0, 128.6, 127.0, 125.8, 119.3, 117.8 (qt, $^1J_{C\text{-}F}$ = 287.6 Hz, $^2J_{C\text{-}F}$ = 47.0 Hz, CF_3), 114.4 110.9, 110.8 (tq, $^1J_{C\text{-}F}$ = 263.8 Hz, $^2J_{C\text{-}F}$ = 41.8 Hz, N-CF_2); ^{19}F NMR (376 MHz, CDCl3) δ -85.9 (s, 3F), -99.1 (s, 2F); HRMS (EI+) *m/z* calcd for $C_{12}H_8F_5N$ [M]+: 261.0577, found 261.0578.



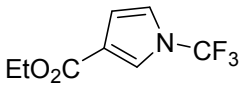
*1-(1,1,2,2-Tetrafluoro-2-(3-phenyl-1H-pyrrol-1-yl)ethyl)-1H-pyrazole (**4f**)*: Yield: 92%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (tq, *J* = 1.5, 0.7 Hz, 1H), 7.58–7.51 (m, 1H), 7.48–7.43 (m, 2H), 7.39–7.32 (m, 2H), 7.28–7.19 (m, 1H), 6.96 (ddt, *J* = 2.3, 1.6, 0.7 Hz, 1H), 6.77 (ddd, *J* = 3.3, 1.9, 0.6 Hz, 1H), 6.57 (ddt, *J* = 3.2, 1.8, 1.0 Hz, 1H), 6.41 (ddt, *J* = 2.8, 1.7, 0.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 134.0, 129.1, 128.9, 128.1, 126.8, 125.6, 119.3, 114.4, 112.8 (tt, $^1J_{C\text{-}F}$ = 268.1 Hz, $^2J_{C\text{-}F}$ = 40.9 Hz), 112.7 (tt, $^1J_{C\text{-}F}$ = 269.2 Hz, $^2J_{C\text{-}F}$ = 43.5 Hz), 110.3, 108.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.8 (t, $^3J_{F\text{-}F}$ = 5.6 Hz, 2F), -100.1 (t, $^3J_{F\text{-}F}$ = 5.6 Hz, 2F); HRMS (EI+) *m/z* calcd for $C_{15}H_{11}F_4N_3$ [M]+: 309.0889, found 309.0888.



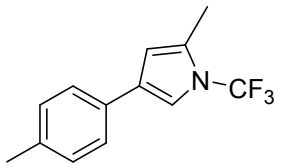
*Ethyl 5-ethoxy-1-(trifluoromethyl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**4g'**): not isolated;* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–7.08 (m, 1H), 5.41 (ddq, *J* = 8.1, 2.3, 0.9 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.68–3.56 (m, 1H), 3.54–3.44 (m, 1H), 3.11–2.99 (m, 1H), 2.83–2.74 (m, 1H), 1.28 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H), 1.20 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9 (s).



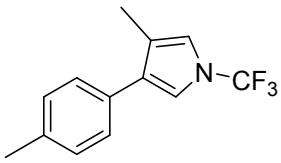
*Ethyl 1-(trifluoromethyl)-1H-pyrrole-3-carboxylate (**4g**)*: Yield: 92%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 2.3, 1.6 Hz, 1H), 6.96 (dd, J = 3.3, 2.3 Hz, 1H), 6.72 (ddq, J = 3.3, 1.7, 0.9 Hz, 1H), 4.30 (q, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 2H), 1.35 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 122.5, 120.2, 118.5, 118.5 (q, $^{1}J_{C\text{-}F}$ = 262.6 Hz, N-CF_3), 112.6, 60.6, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9 (s); HRMS (EI+) *m/z* calcd for $C_8H_8F_3NO_2$ [M]+: 207.0507, found 207.0506.



*2-Methyl-4-(p-tolyl)-1-(trifluoromethyl)-1H-pyrrole (**4h**)*: Yield: 63%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.33 (m, 2H), 7.17 (dddd, J = 7.6, 2.0, 1.2, 0.6 Hz, 2H), 7.13 (dt, J = 1.9, 0.6 Hz, 1H), 6.34–6.28 (m, 1H), 2.38 (dq, J = 2.0, 1.4 Hz, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 136.4, 131.3, 129.7, 129.6, 125.4, 119.5 (q, $^{1}J_{C\text{-}F}$ = 261.0 Hz, N-CF_3), 113.5 (q, J = 2.1 Hz), 110.4 (q, J = 1.6 Hz), 21.3, 12.7 (q, J = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.7 (s); HRMS (EI+) *m/z* calcd for $C_{13}H_{12}F_3N$ [M]+: 239.0922, found 239.0921.



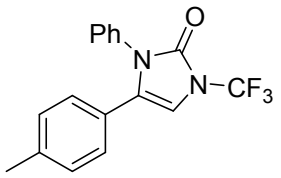
*3-Methyl-4-(p-tolyl)-1-(trifluoromethyl)-1H-pyrrole (**4i**)*: Yield: 19%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.24–7.17 (m, 2H), 6.98 (d, J = 2.5 Hz, 1H), 6.84–6.78 (m, 1H), 2.38 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 131.6, 129.4, 128.6, 128.0, 121.2, 119.1 (q, $^{1}J_{C\text{-}F}$ = 259.5 Hz, N-CF_3), 116.3, 115.2, 21.3, 11.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6 (s); HRMS (EI+) *m/z* calcd for $C_{13}H_{12}F_3N$ [M]+: 239.0922, found 239.0924.



Preparation of imidazolone 6

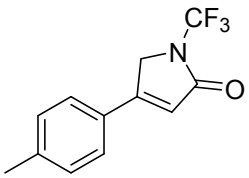
N-perfluoroalkyl-triazole **1b** (0.20 mmol) was dissolved in dry $CHCl_3$ (2 mL) in a 5 mL microwave tube. Phenyl isocyanate (2 equiv., 0.4 mmol) and a solution of rhodium (II) octanoate (0.002 mmol; 0.01 M in dry $CHCl_3$) were added. The vial was capped and heated at 120°C for 20 min in a microwave reactor. The resulting mixture was evaporated on silica gel (100 mg) and purified by CombiFlash automatic column chromatography using the (EtOAc/cyclohexane).

*3-Phenyl-4-(p-tolyl)-1-(trifluoromethyl)-1,3-dihydro-2H-imidazol-2-one (**6**):* Yield: 75%; brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 3H), 7.21–7.15 (m, 2H), 7.08–7.02 (m, 2H), 6.98–6.92 (m, 2H), 6.56 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 138.9, 134.2, 129.5, 129.2, 128.0, 127.7, 127.4, 127.1, 125.0, 118.5 (q, $^{1}J_{C\text{-}F}$ = 263.0 Hz, N-CF_3), 103.3 (q, J = 1.4 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.1 (s); HRMS (EI+) *m/z* calcd for $C_{17}H_{13}F_3N_2O$ [M]+: 318.0980, found 318.0979.



Preparation of pyrrolone 7

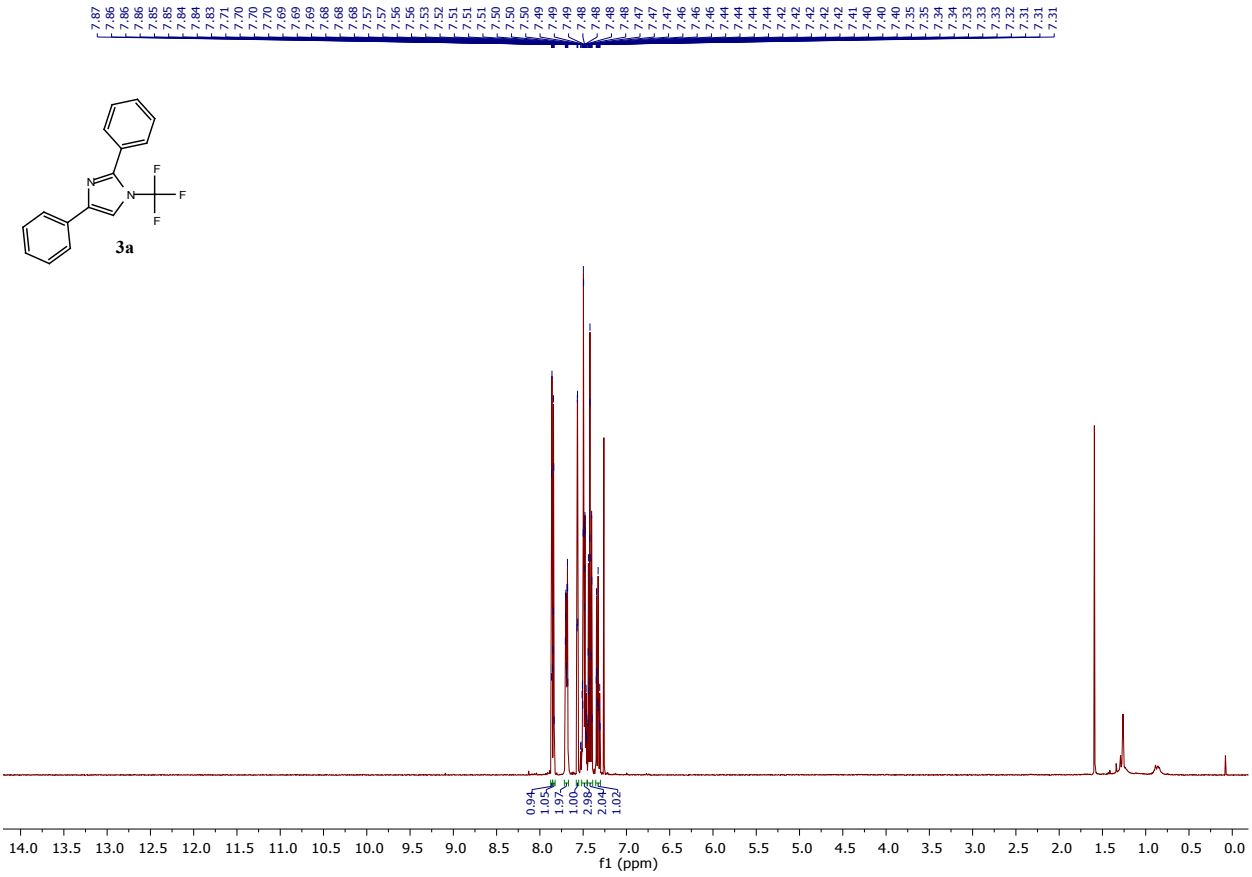
N-perfluoroalkyl-triazole **1b** (0.20 mmol) was dissolved in dry $CHCl_3$ (2 mL) in a 5 mL microwave tube. Ketene t-butyldimethylsilyl methyl acetal (2 equiv., 0.4 mmol) and a solution of rhodium (II) octanoate (0.002 mmol; 0.01 M in dry $CHCl_3$) were added. The vial was capped and heated at 120°C for 15 min in microwave reactor. Then 1M solution of TBAF (5 equiv., 1 mmol) in THF was added and resulting solution was stirred for 1 h, evaporated on silica gel (100 mg) and purified by CombiFlash automatic column chromatography (EtOAc/cyclohexane).



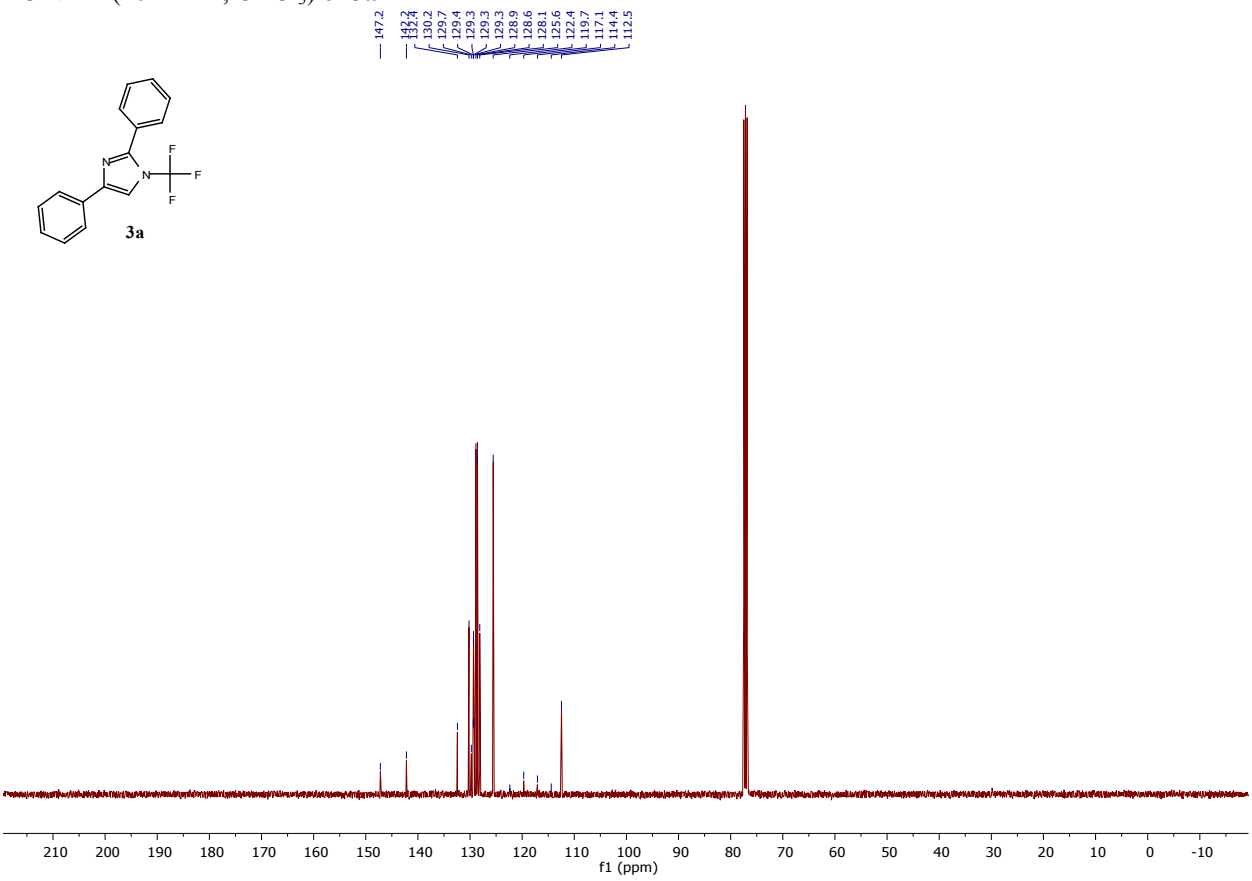
4-(p-Tolyl)-1-(trifluoromethyl)-1,5-dihydro-2H-pyrrol-2-one (7): Yield: 63%; slightly yellow crystals; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 2H), 7.30–7.22 (m, 2H, *signal overlap with solvent*), 6.39–6.33 (m, 1H), 4.64–4.59 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 157.2, 142.2, 130.0, 127.7, 126.1, 119.6 (q, $^{1}J_{C\text{-}F}$ = 261.3 Hz, N-CF_3), 118.0 (q, J = 2.0 Hz), 49.5, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.7 (s); HRMS (EI+) *m/z* calcd for $C_{12}H_{10}F_3NO$ [M]+: 241.0714, found 241.0711.

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

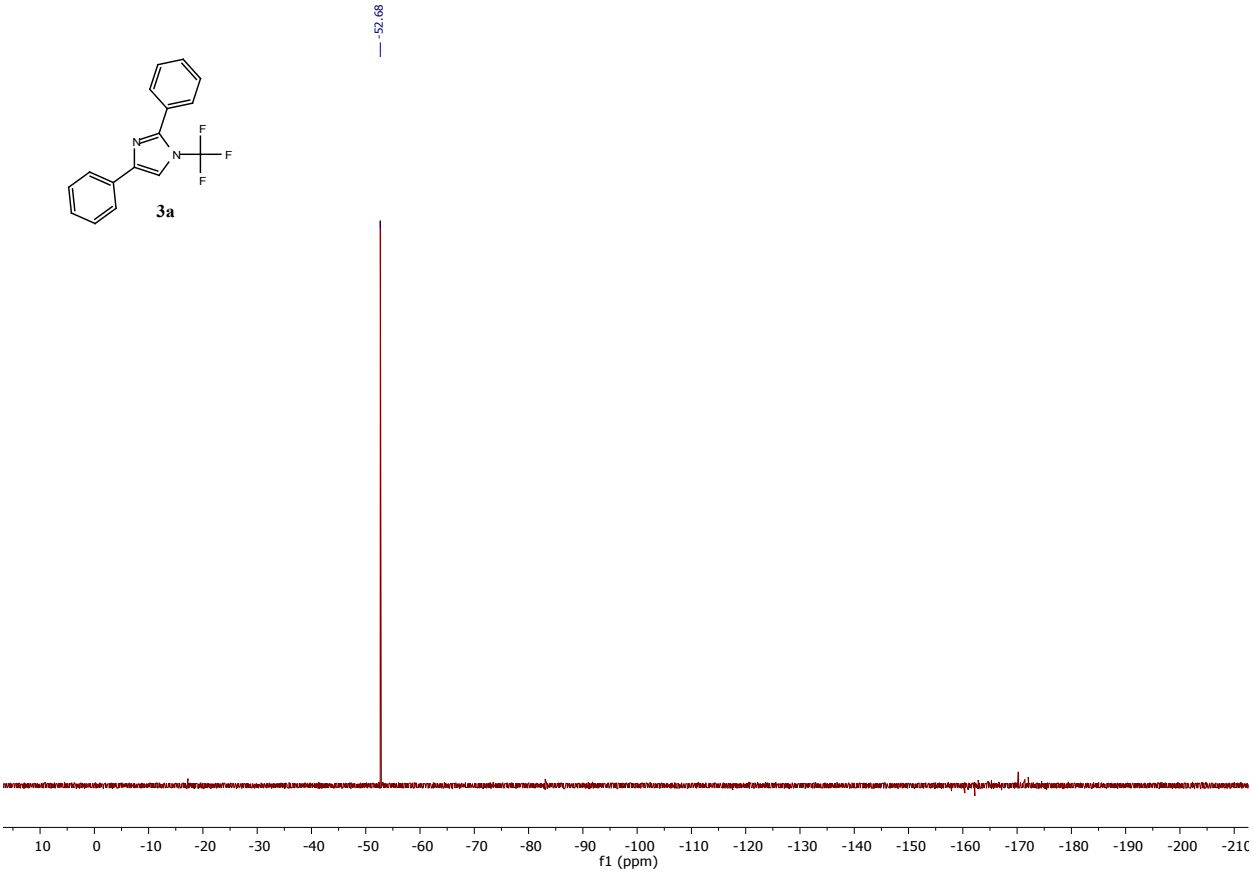
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



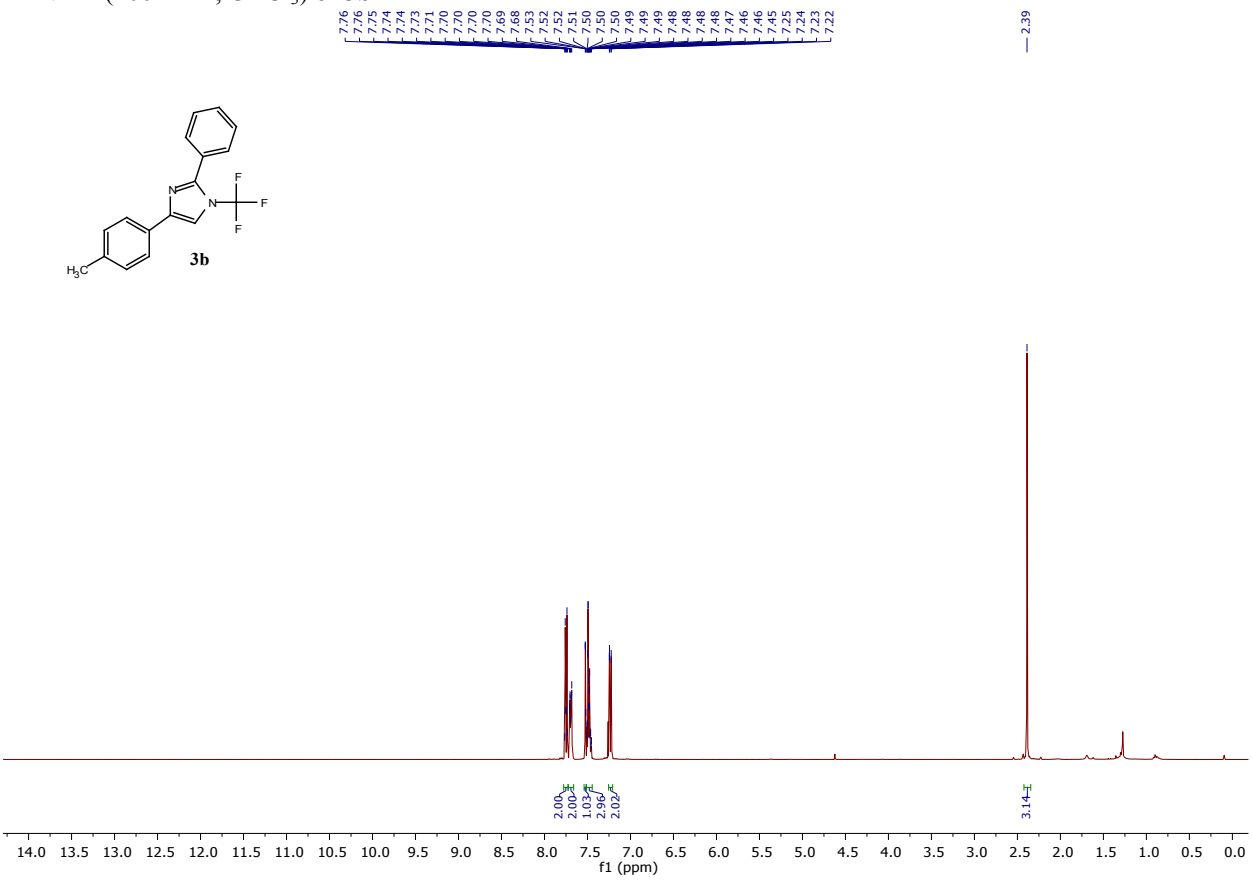
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



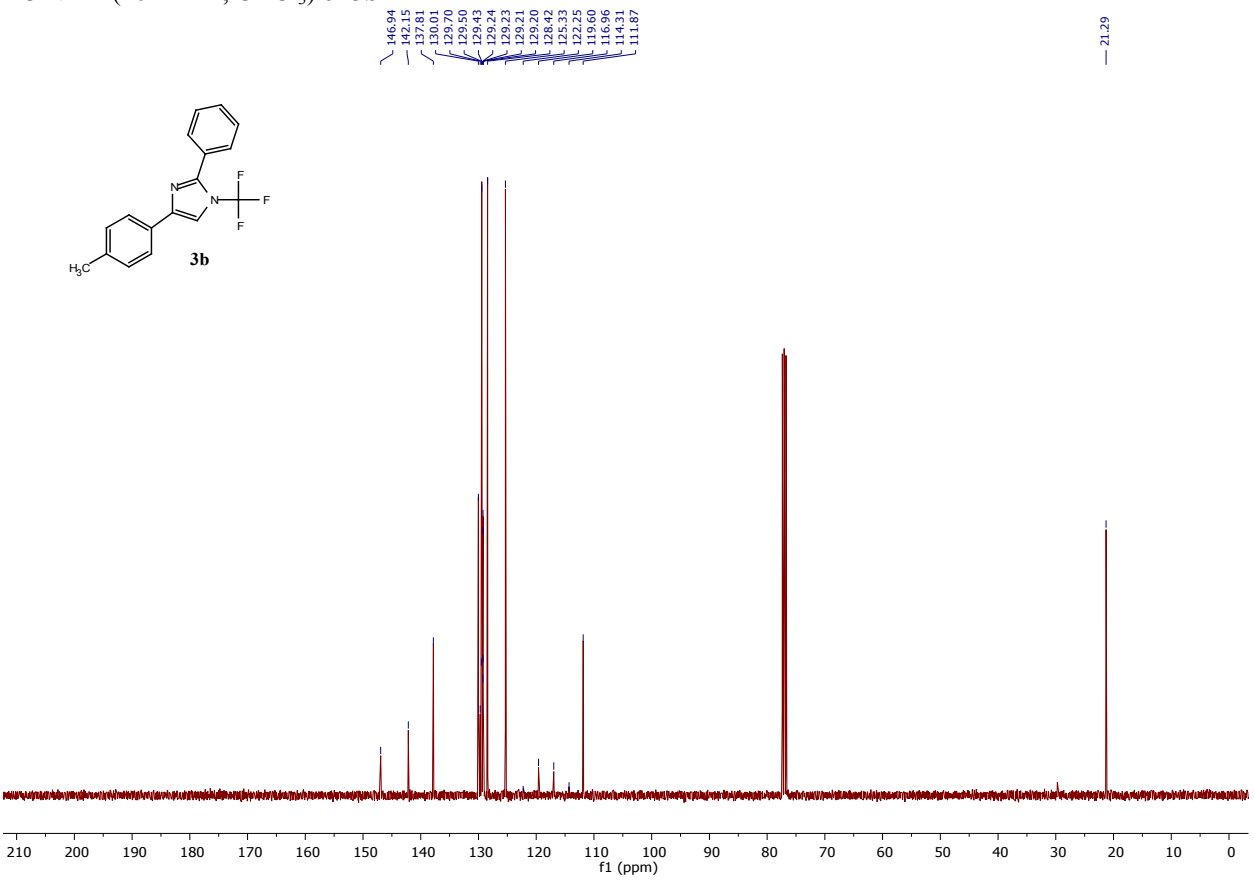
^{19}F NMR (376 MHz, $CDCl_3$) of **3a**



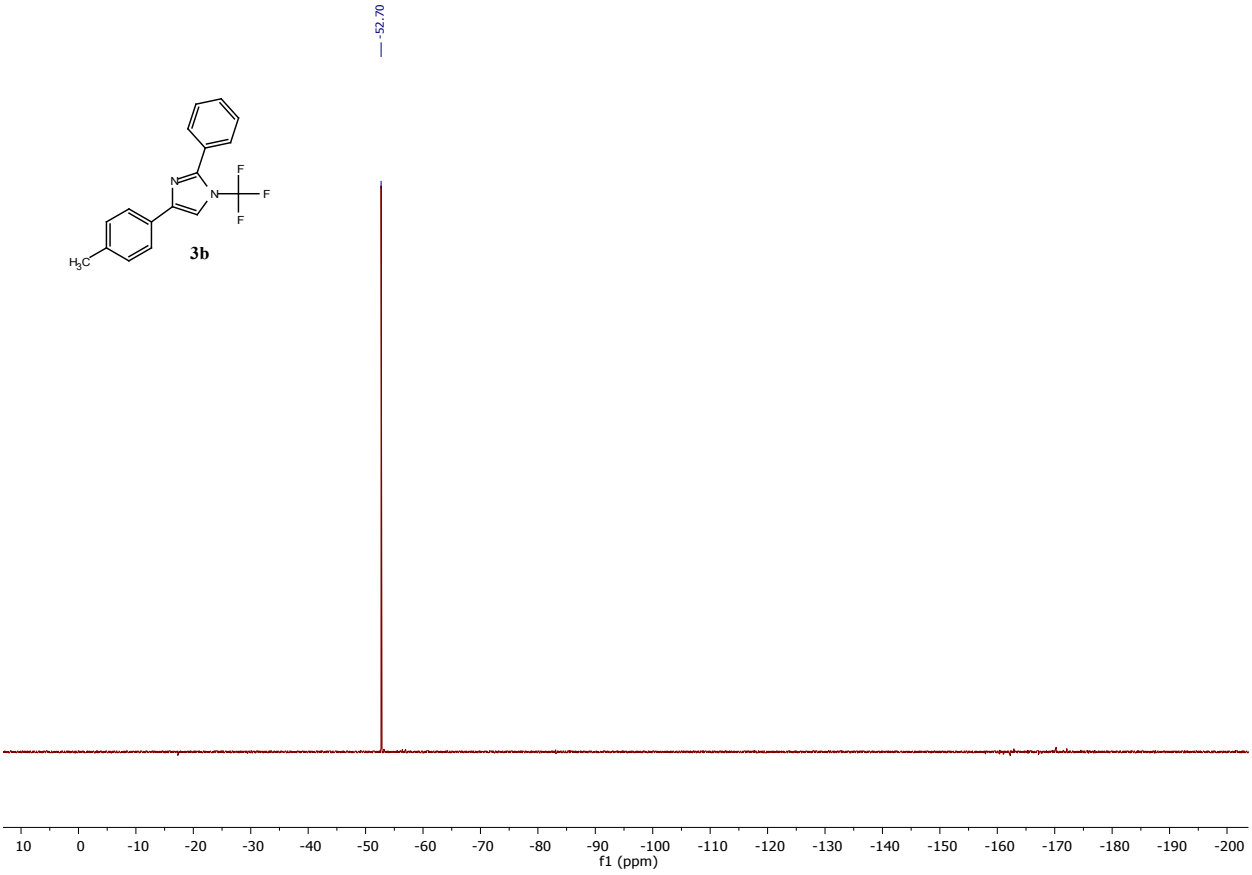
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



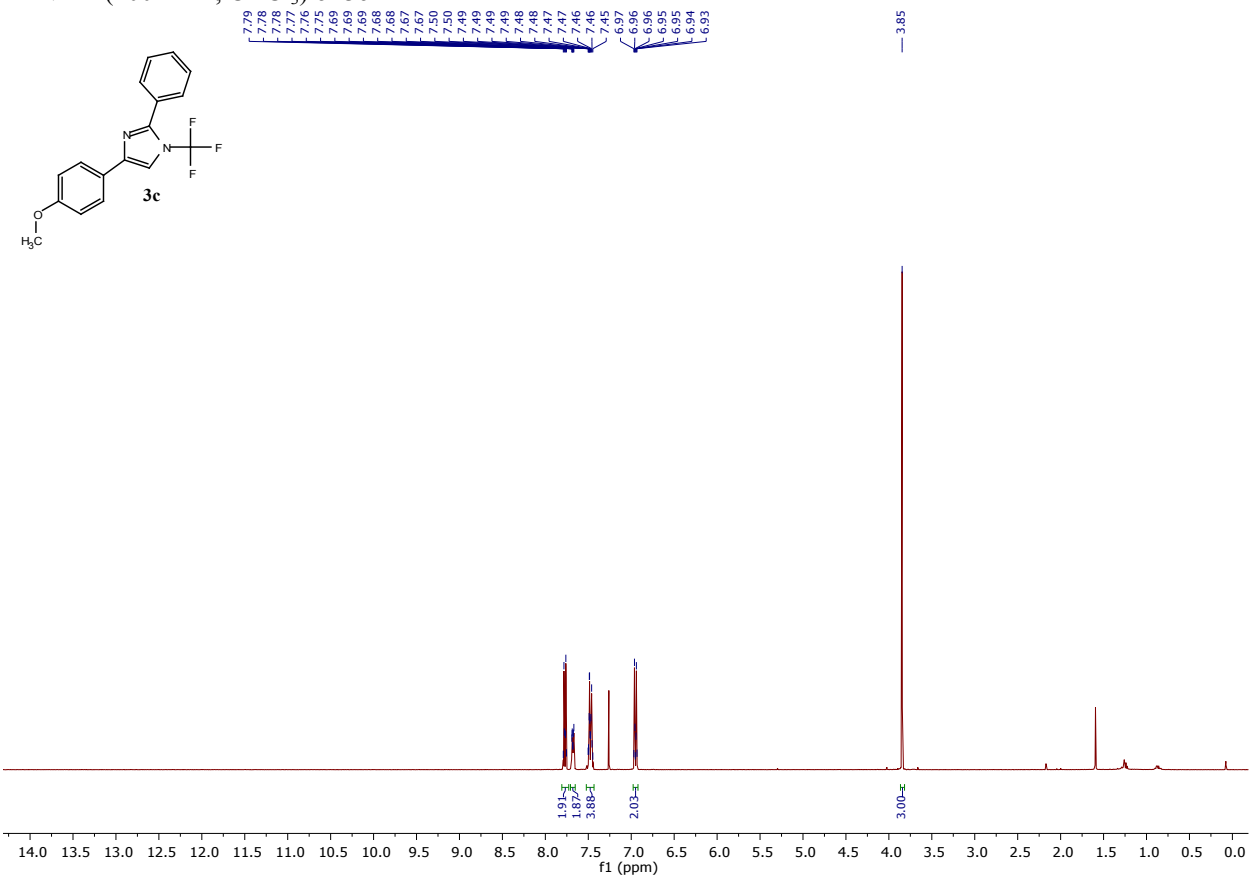
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



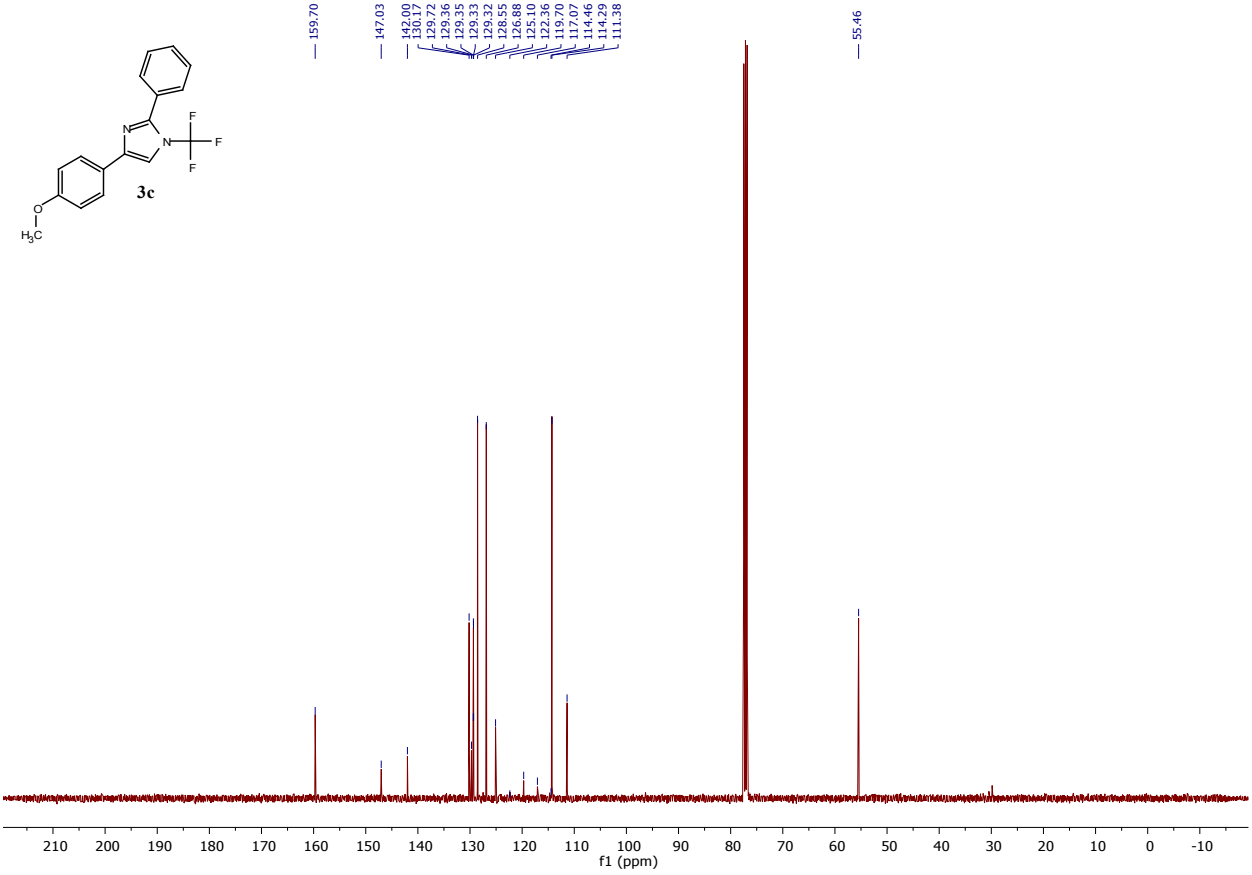
^{19}F NMR (376 MHz, $CDCl_3$) of **3b**



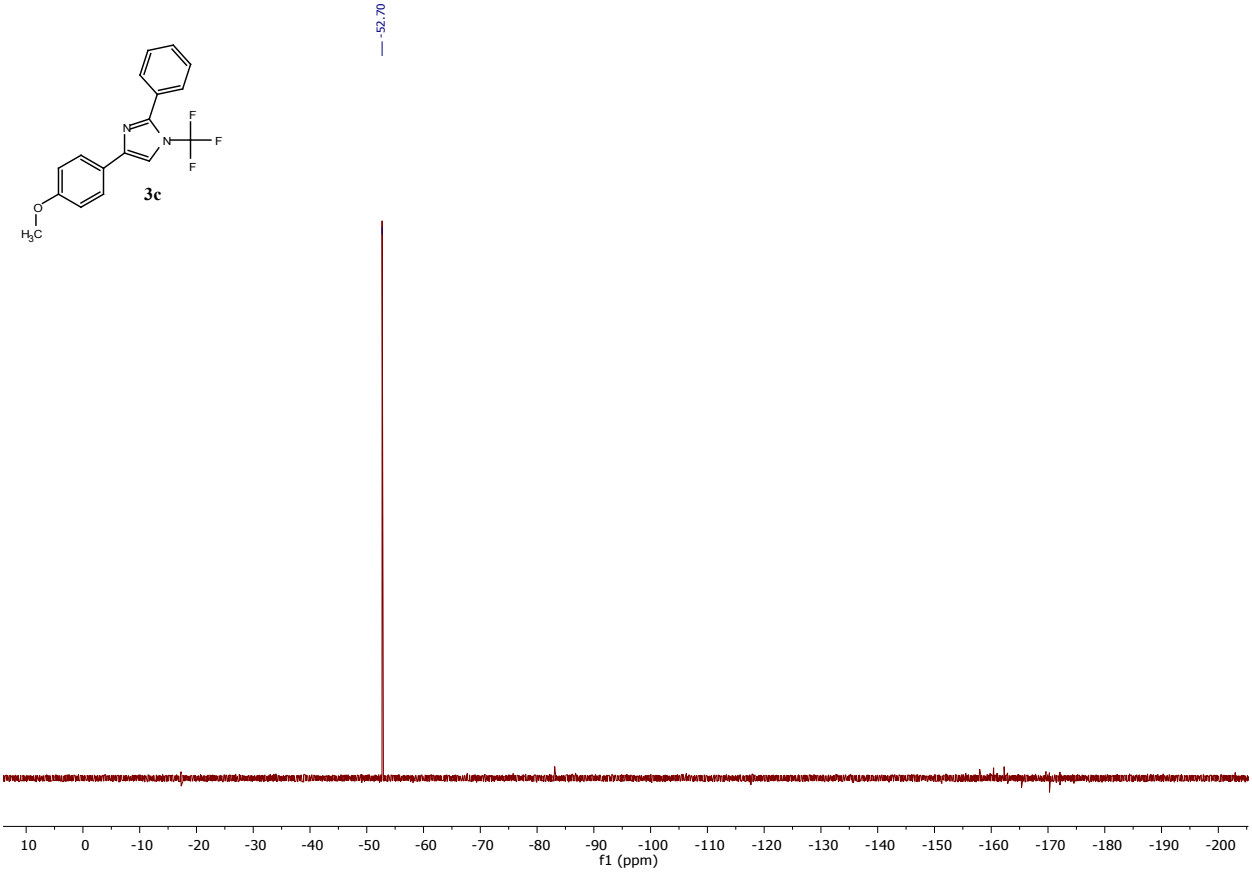
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



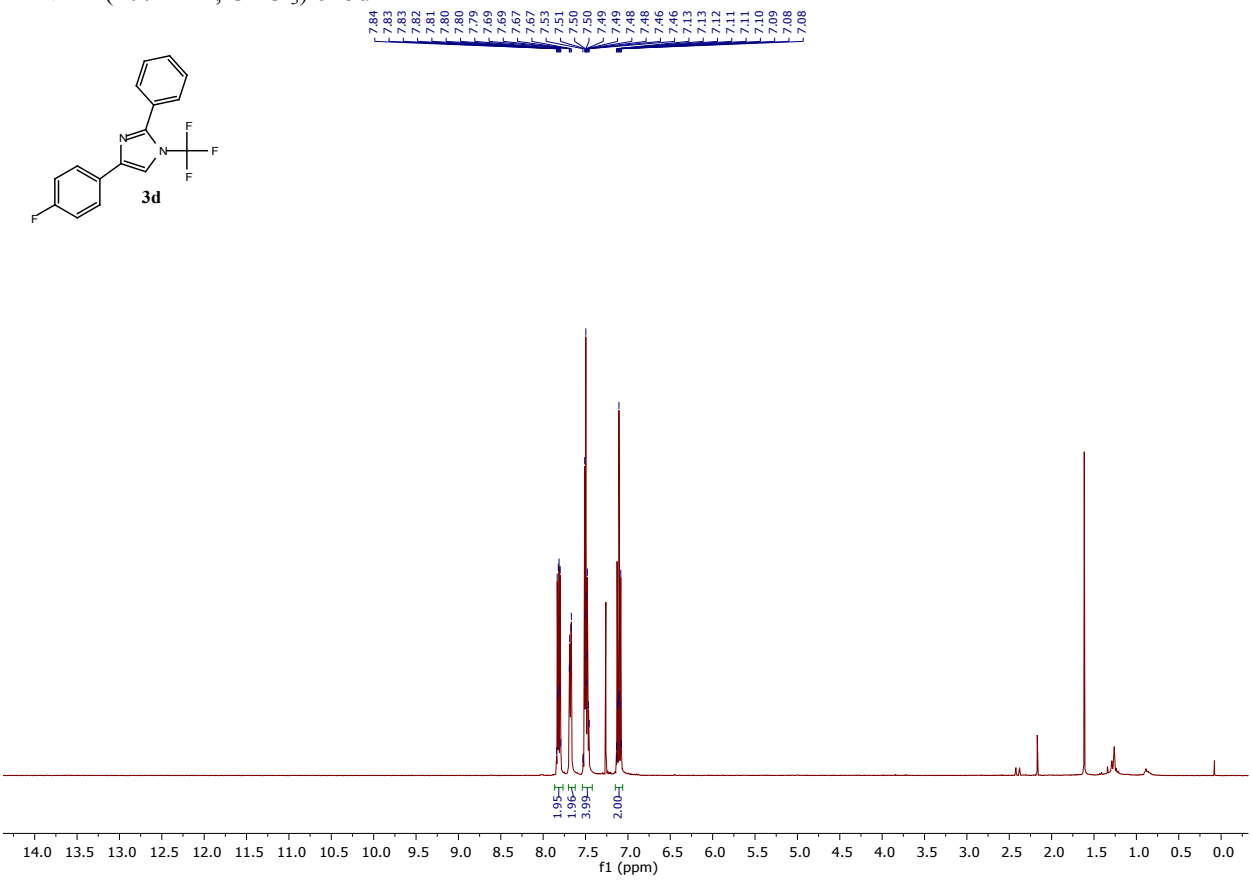
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



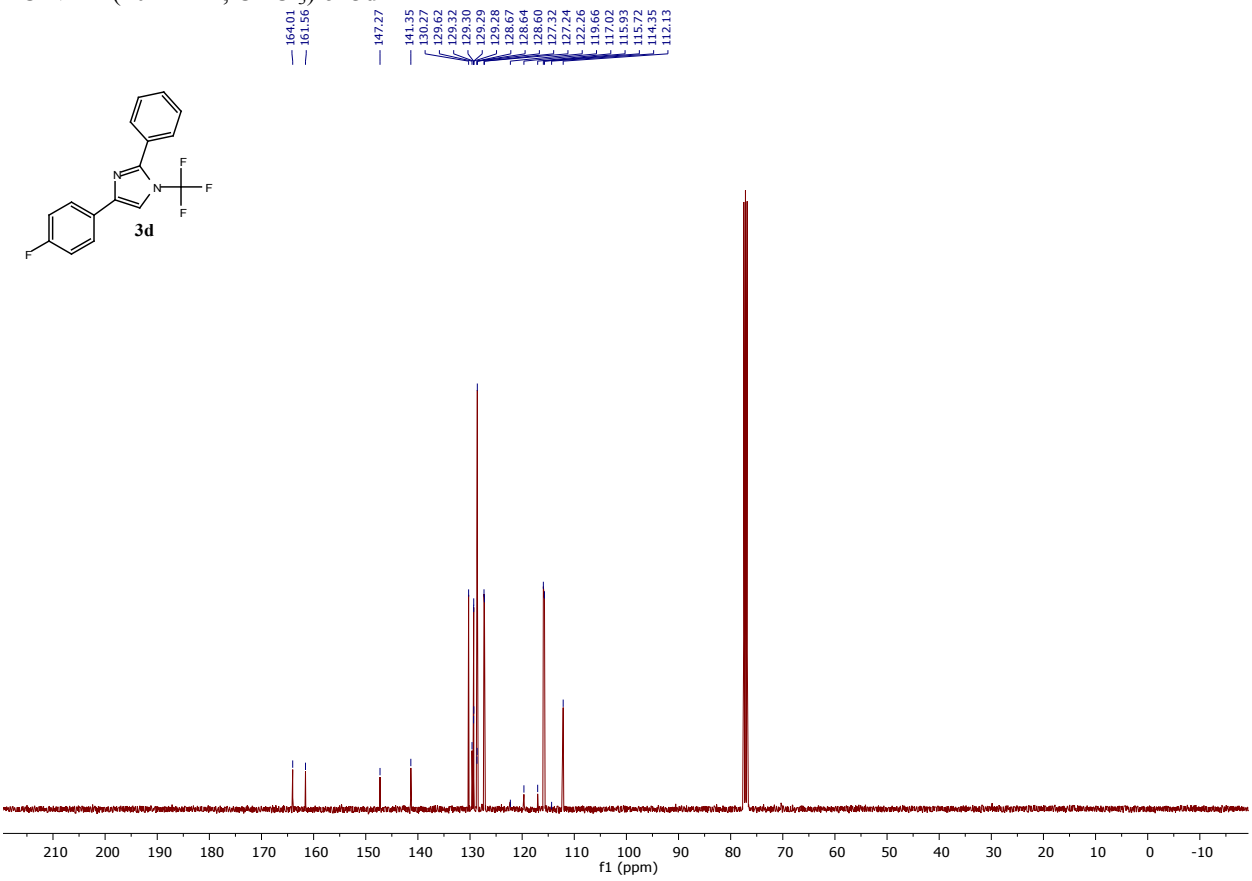
^{19}F NMR (376 MHz, $CDCl_3$) of **3c**



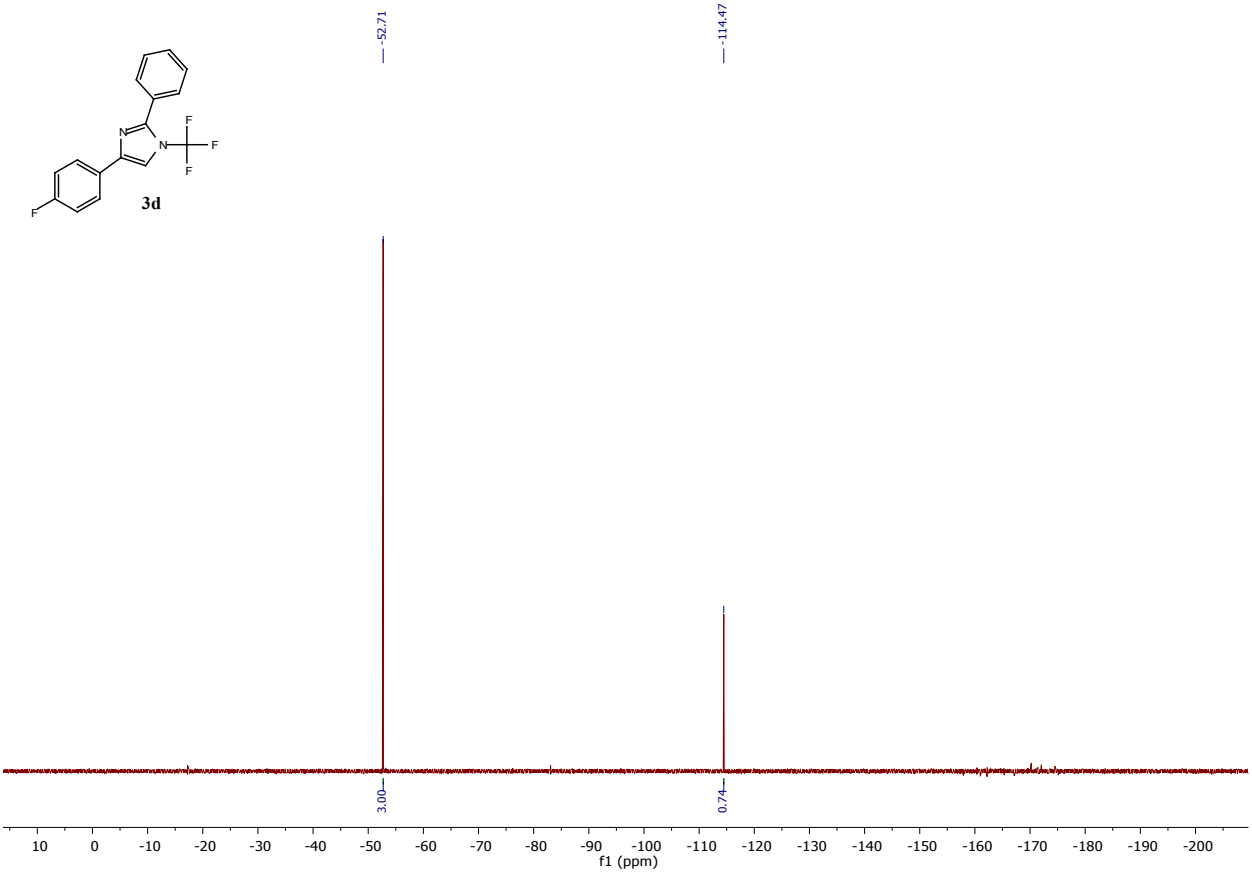
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



^{13}C NMR (101 MHz, $CDCl_3$) of **3d**

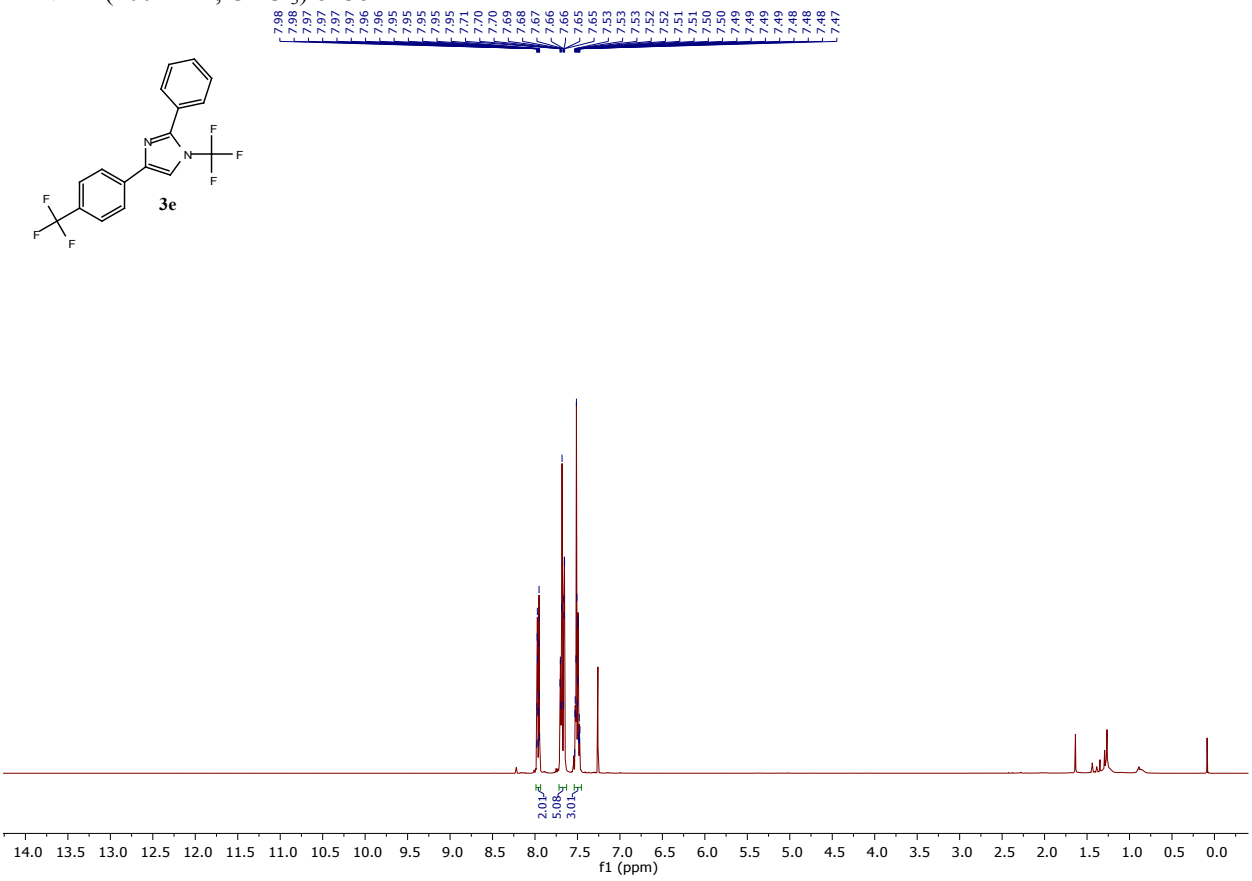


^{19}F NMR (376 MHz, $CDCl_3$) of **3d**

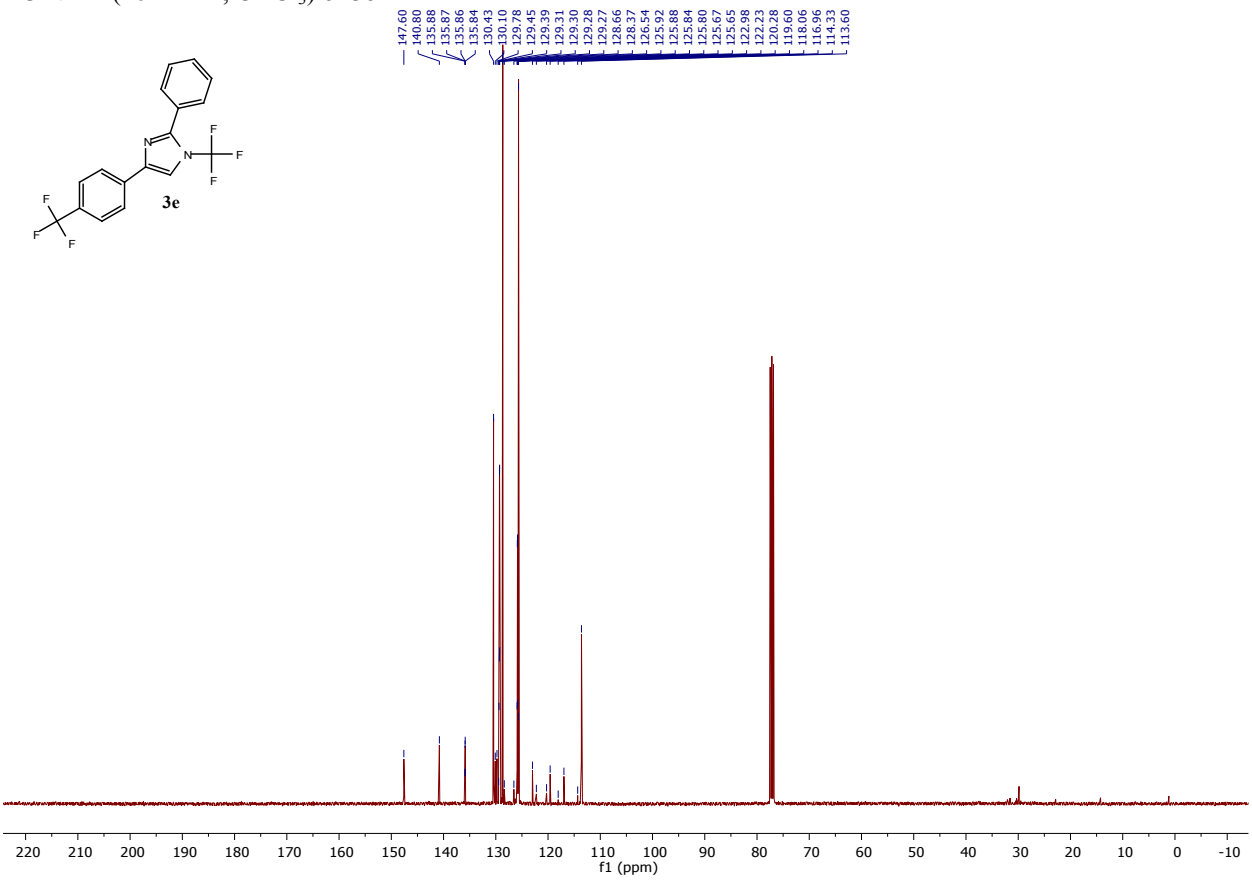


3d

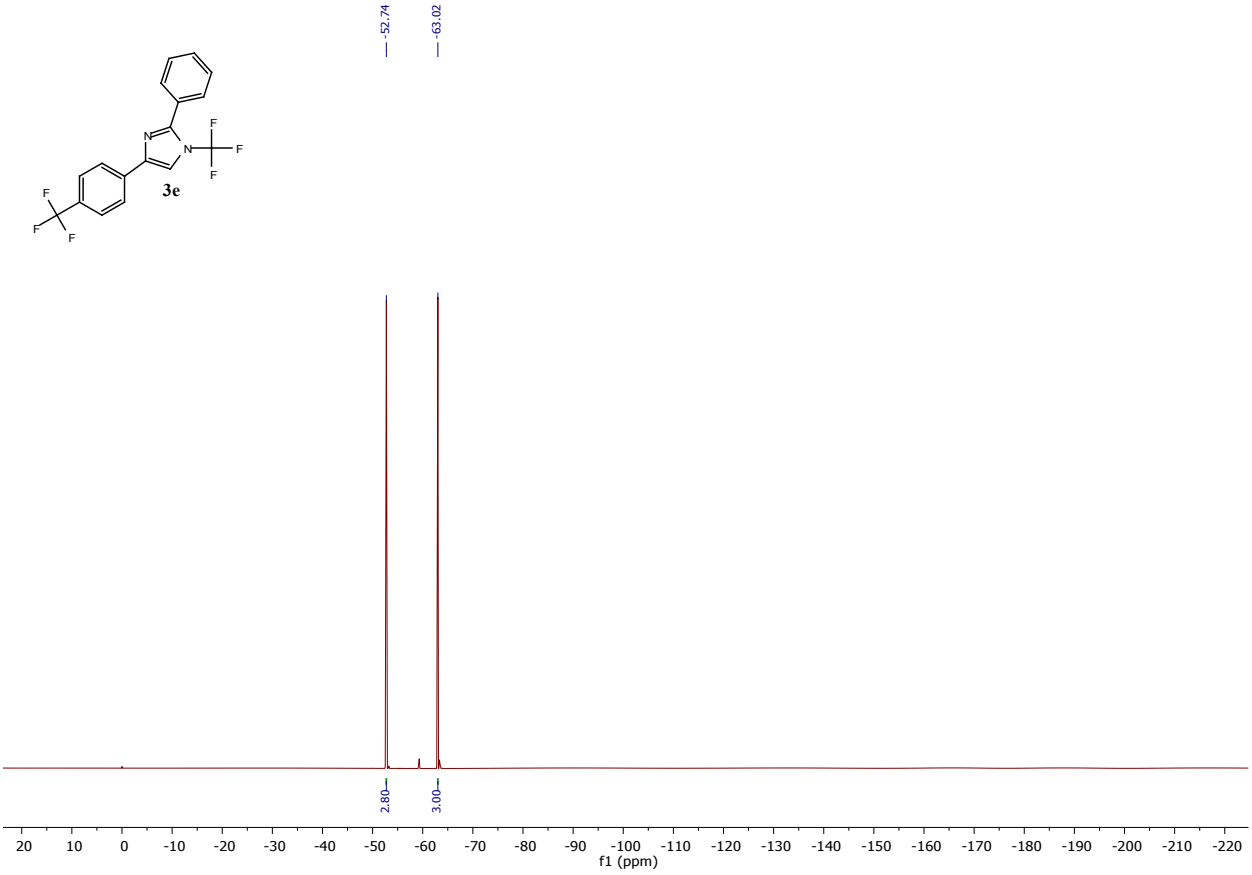
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



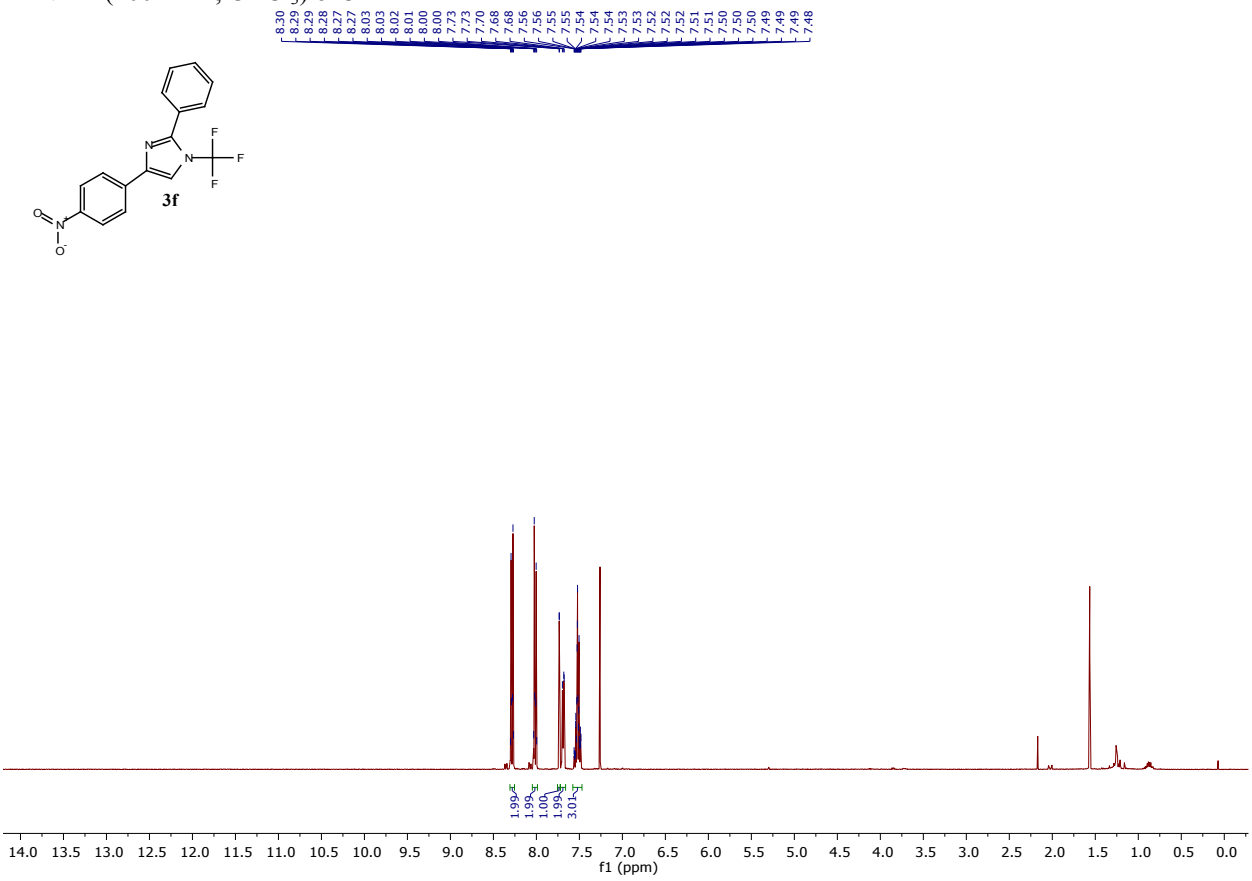
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



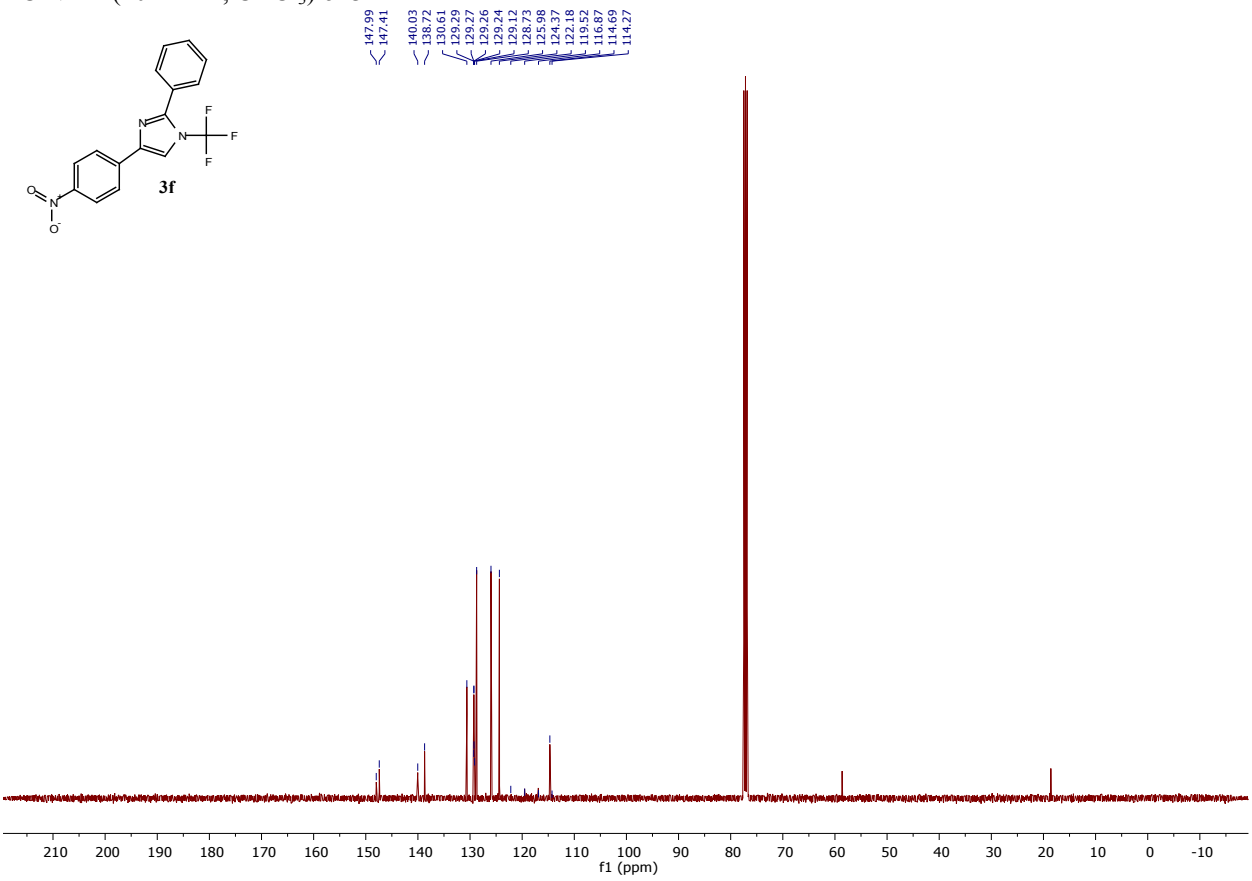
^{19}F NMR (376 MHz, $CDCl_3$) of **3e**



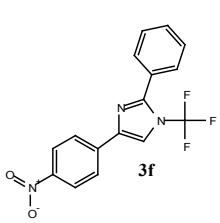
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



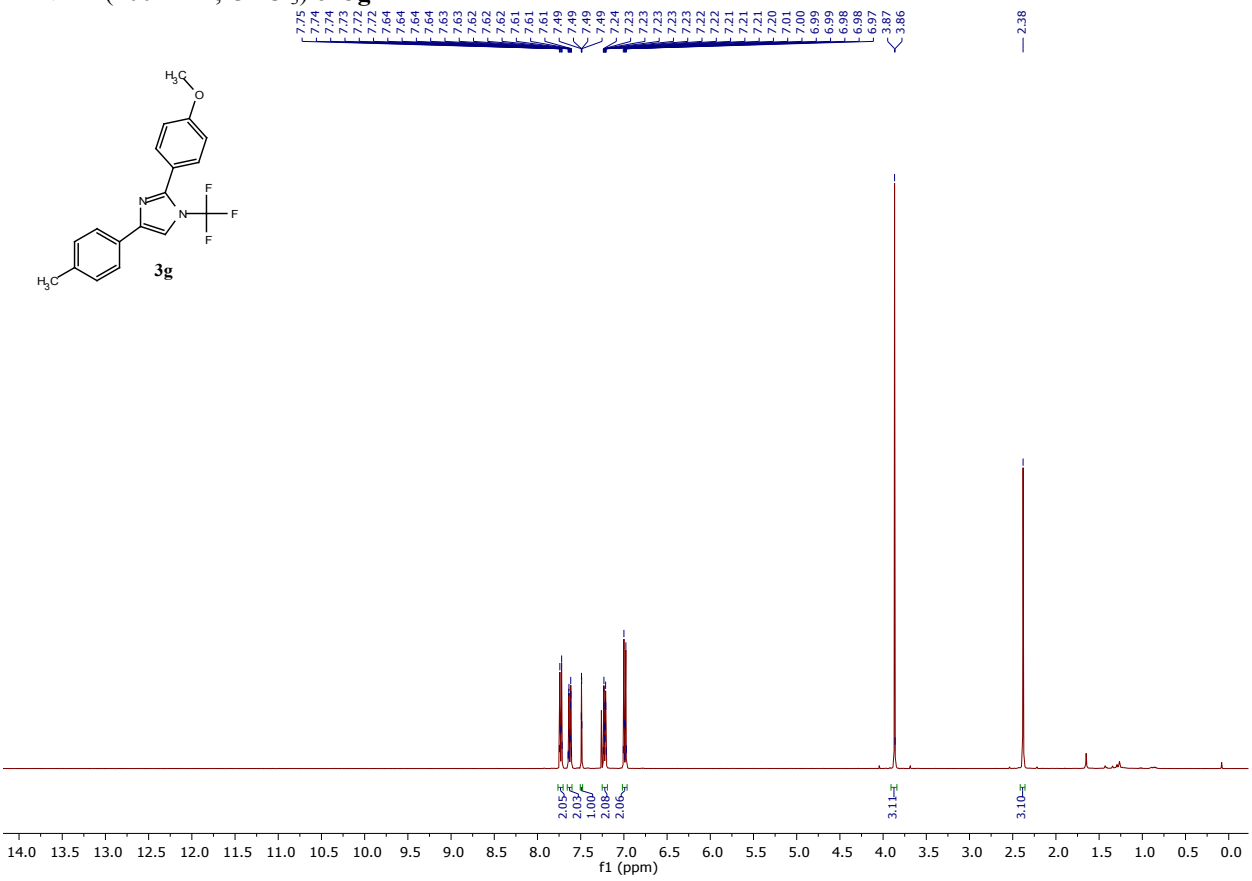
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



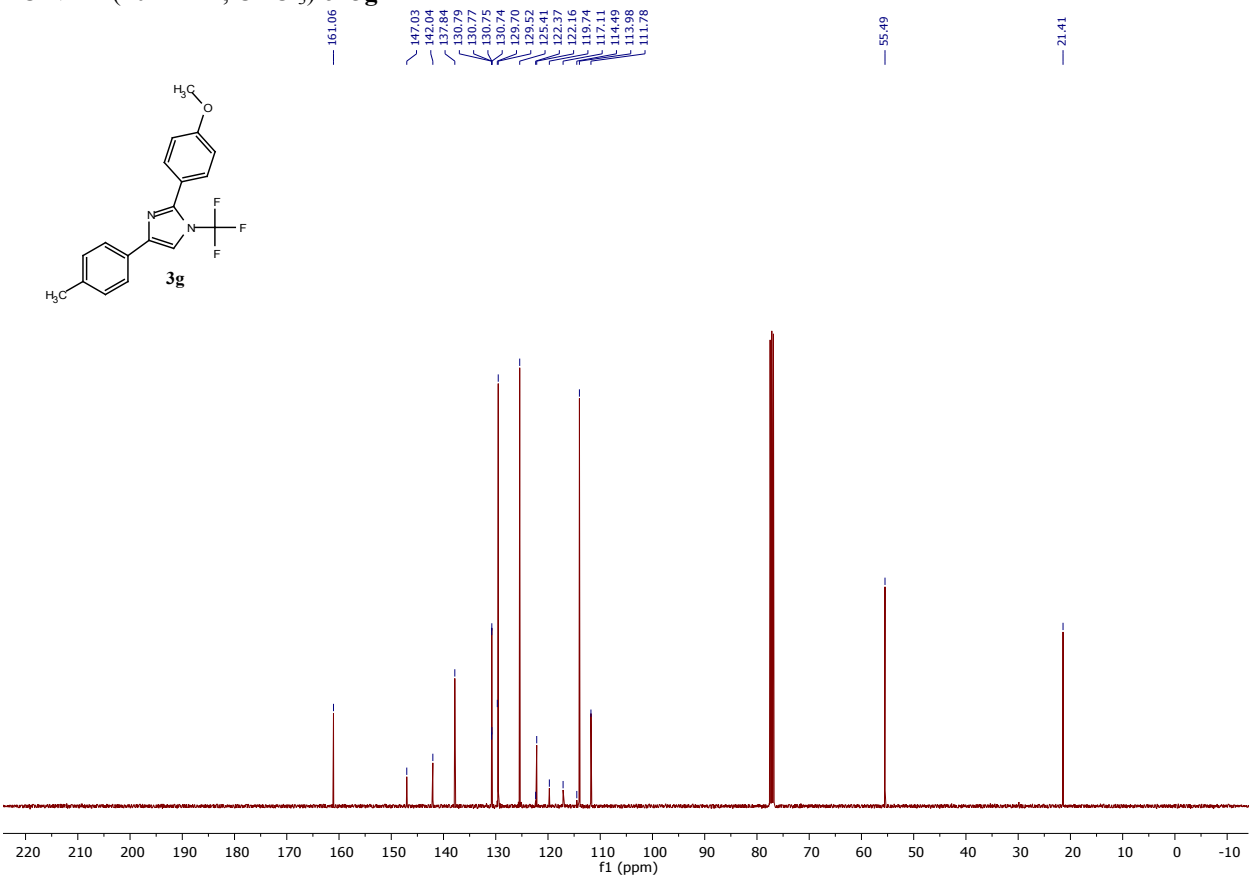
^{19}F NMR (376 MHz, $CDCl_3$) of **3f**



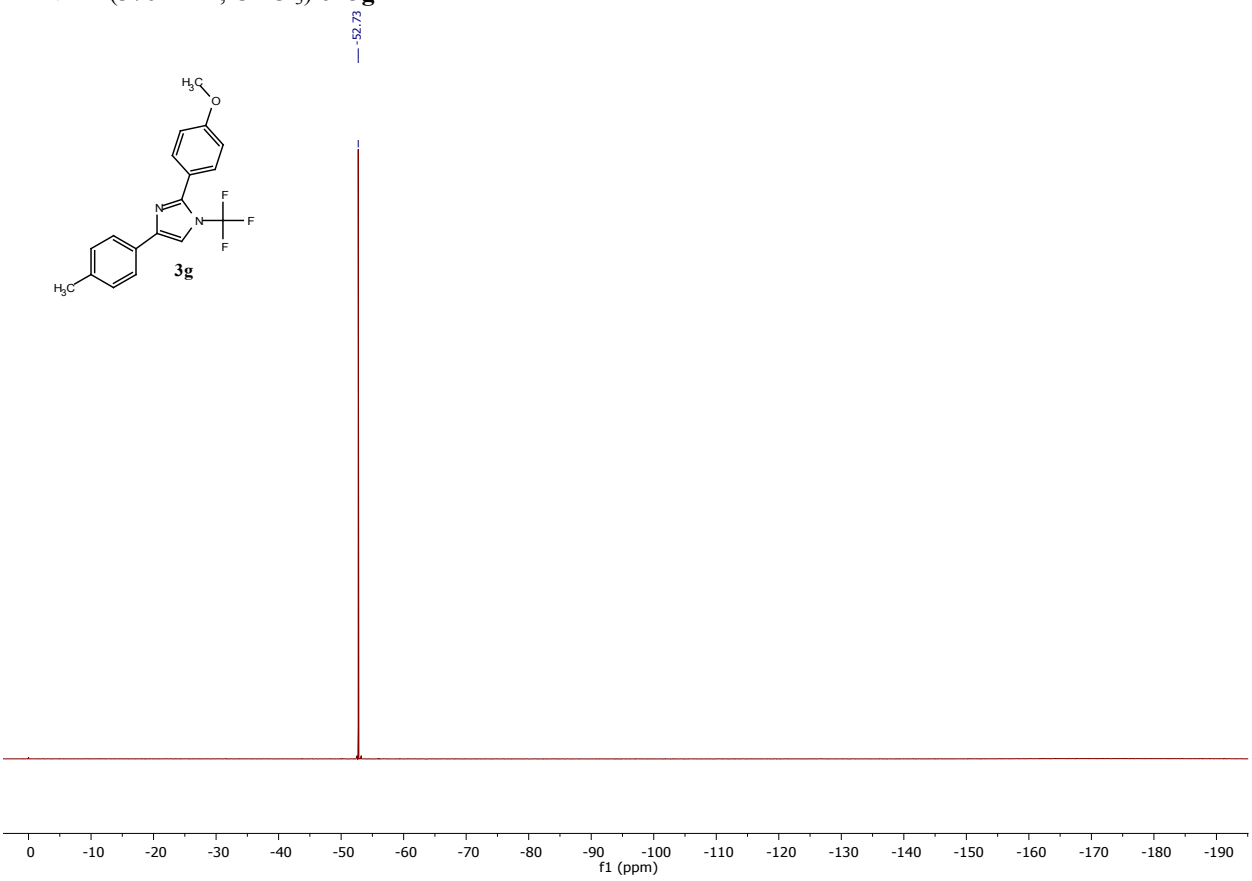
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



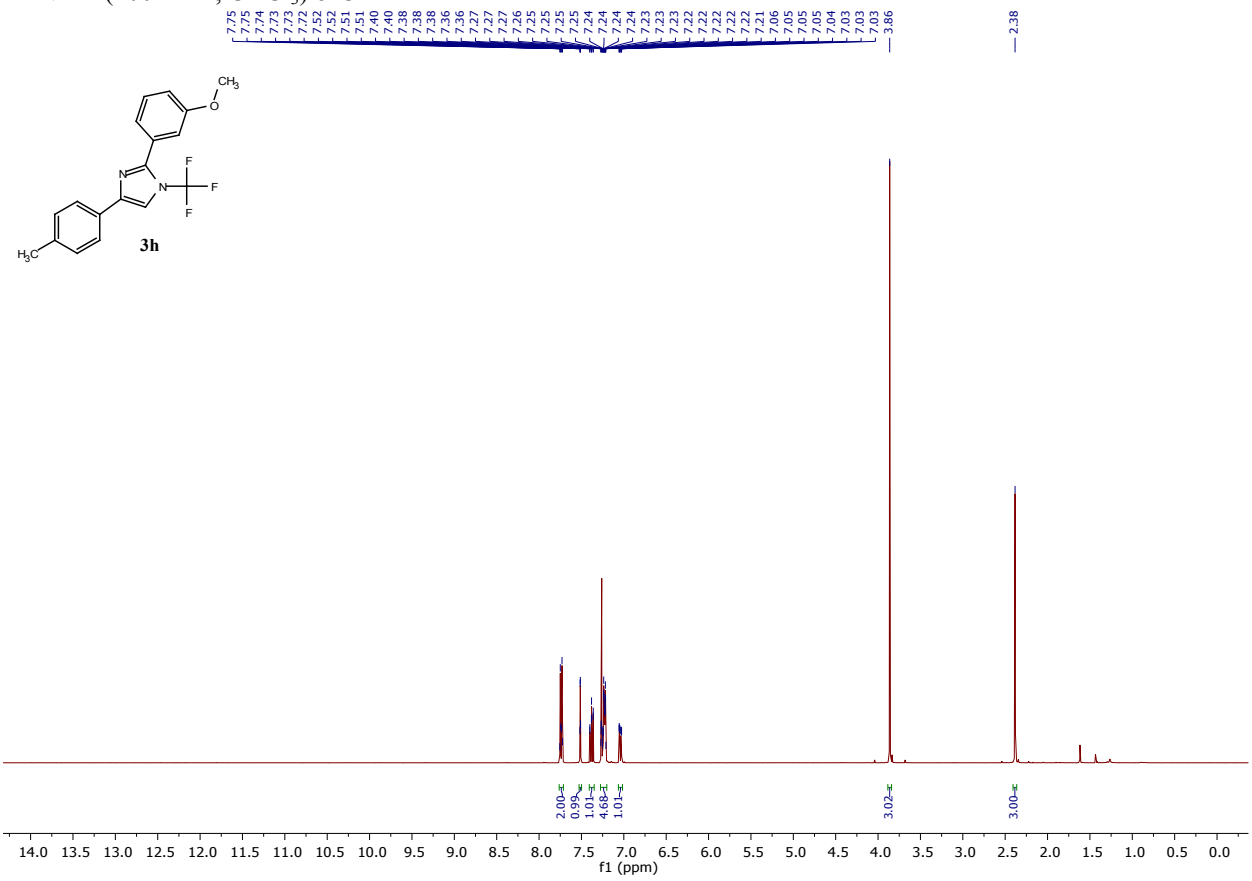
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



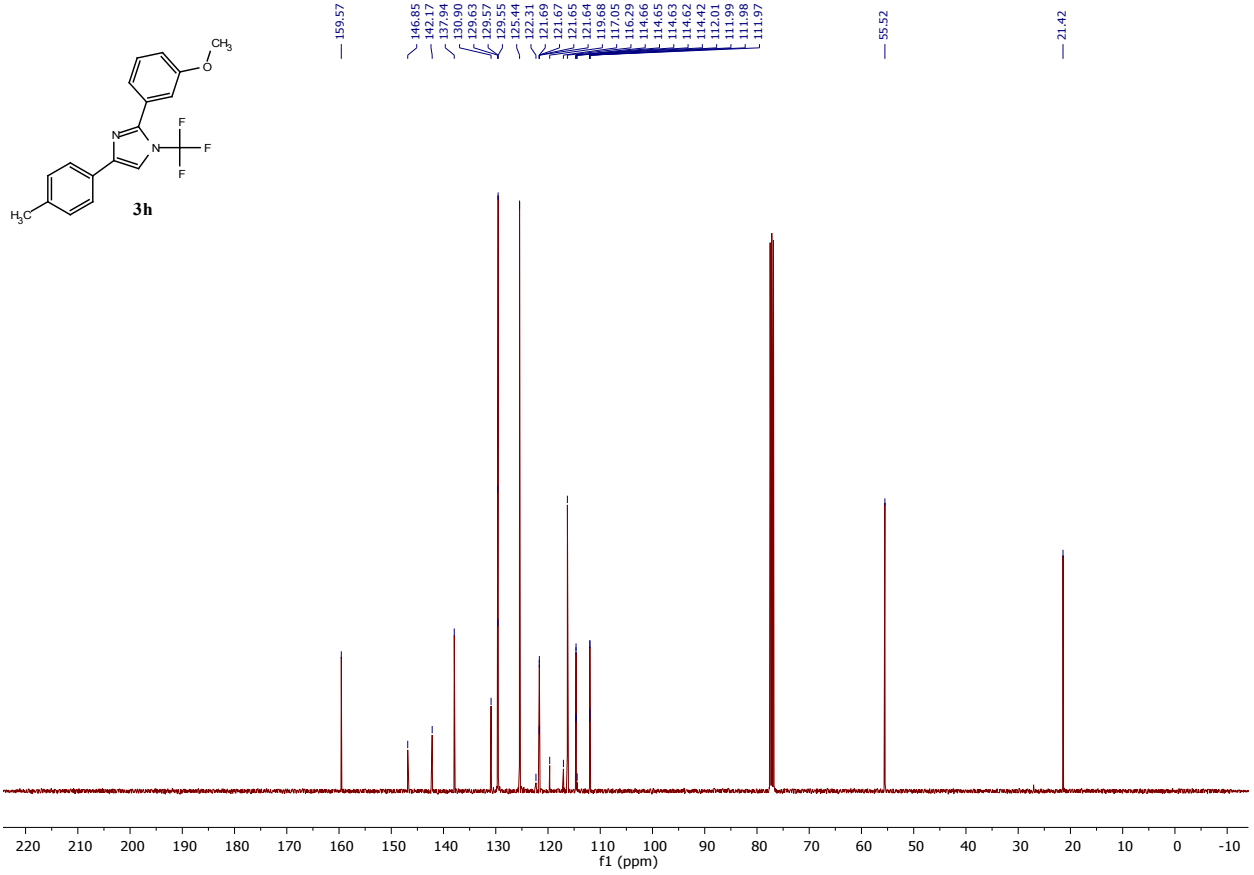
^{19}F NMR (376 MHz, $CDCl_3$) of **3g**



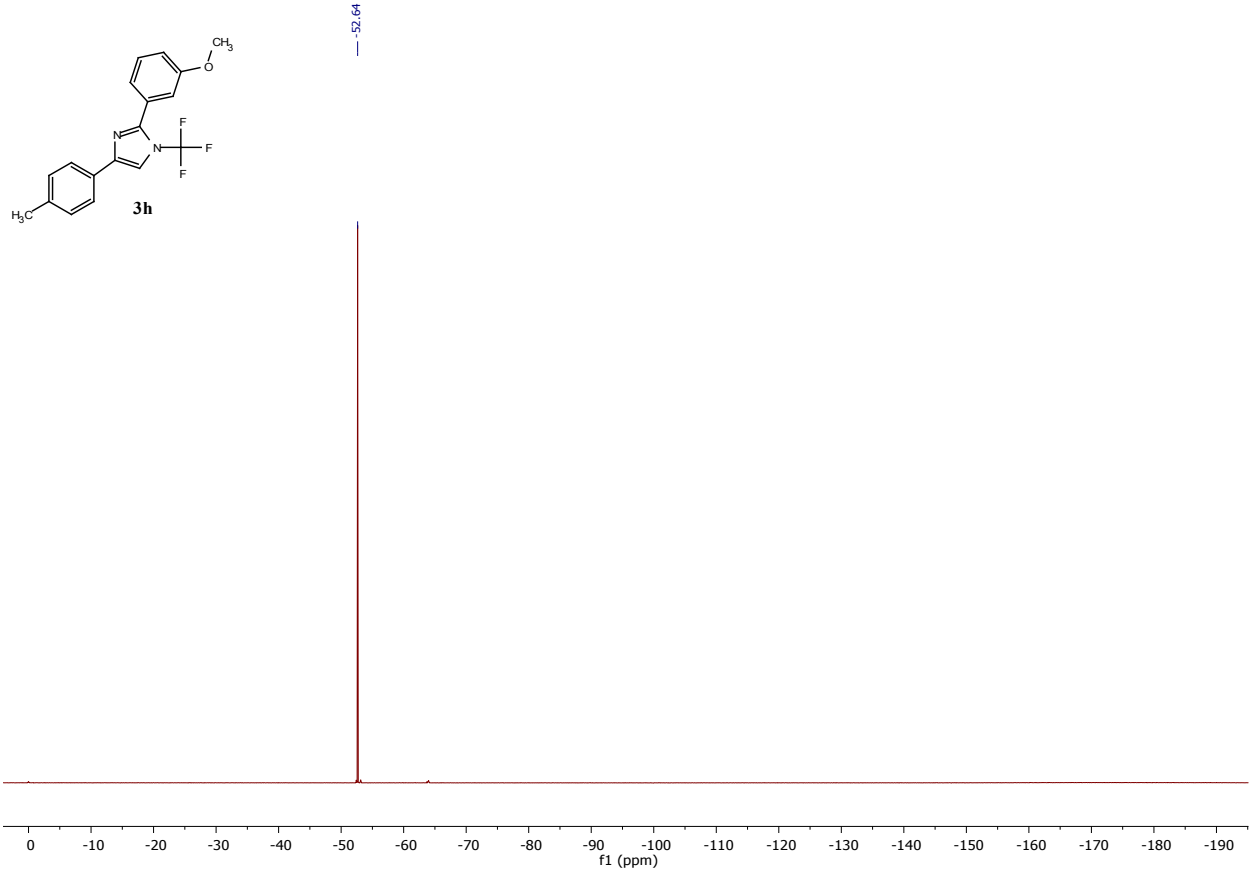
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



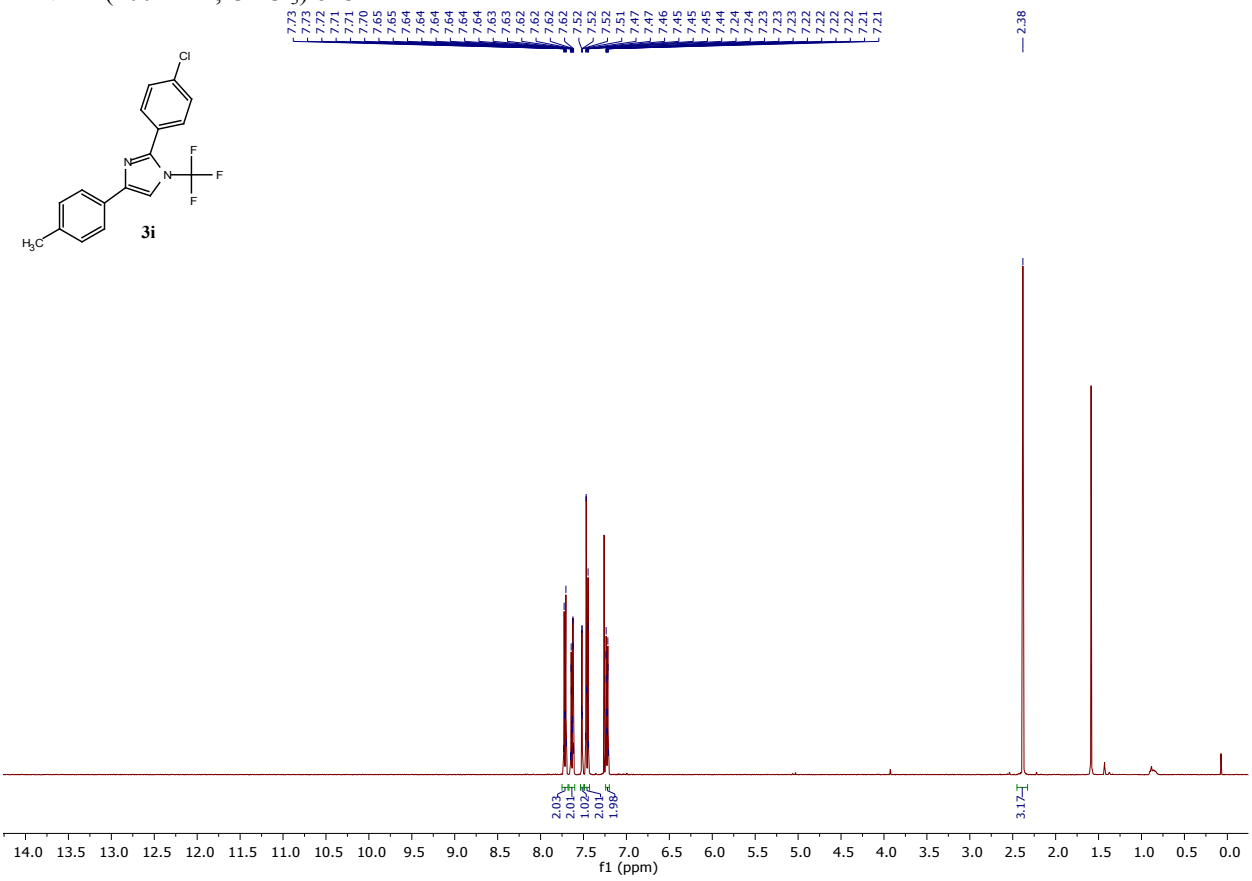
^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



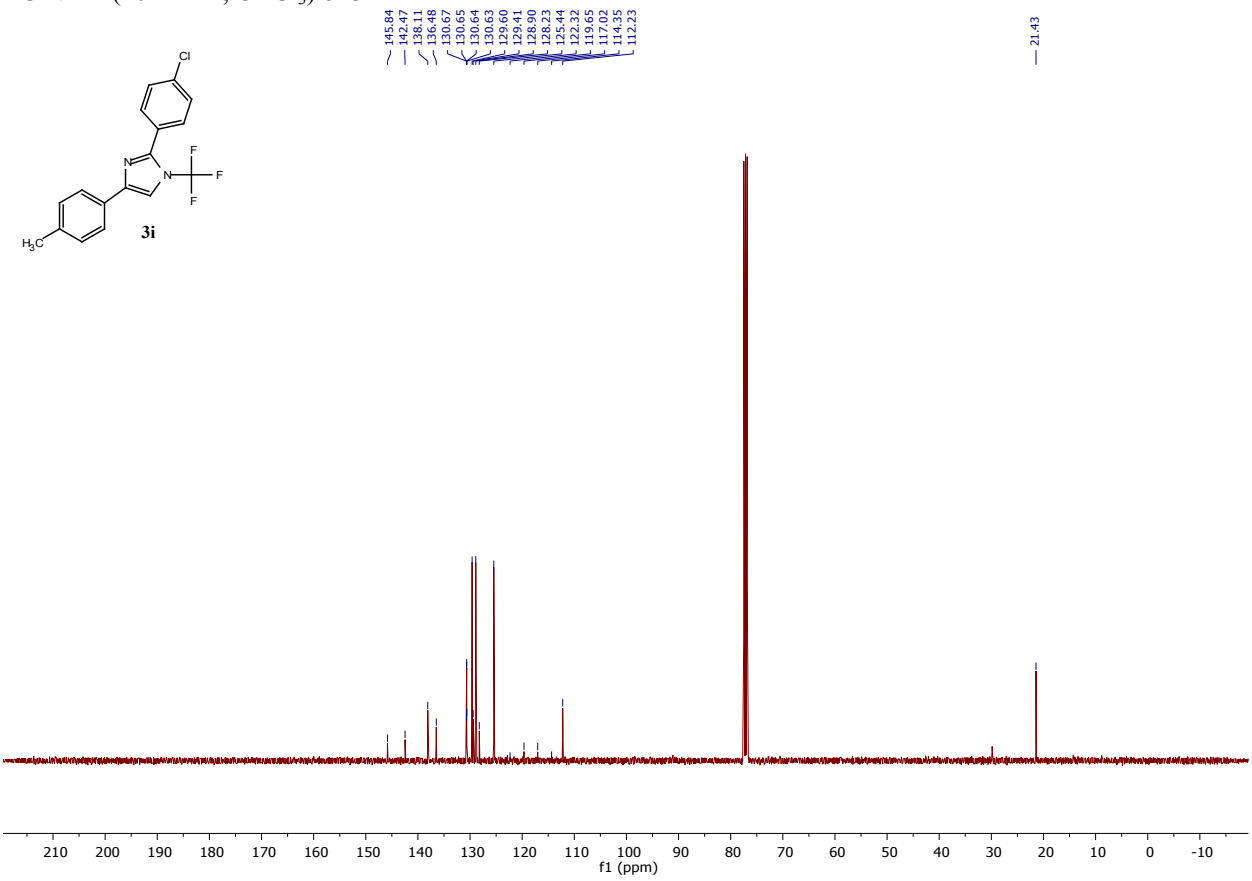
^{19}F NMR (376 MHz, $CDCl_3$) of **3h**



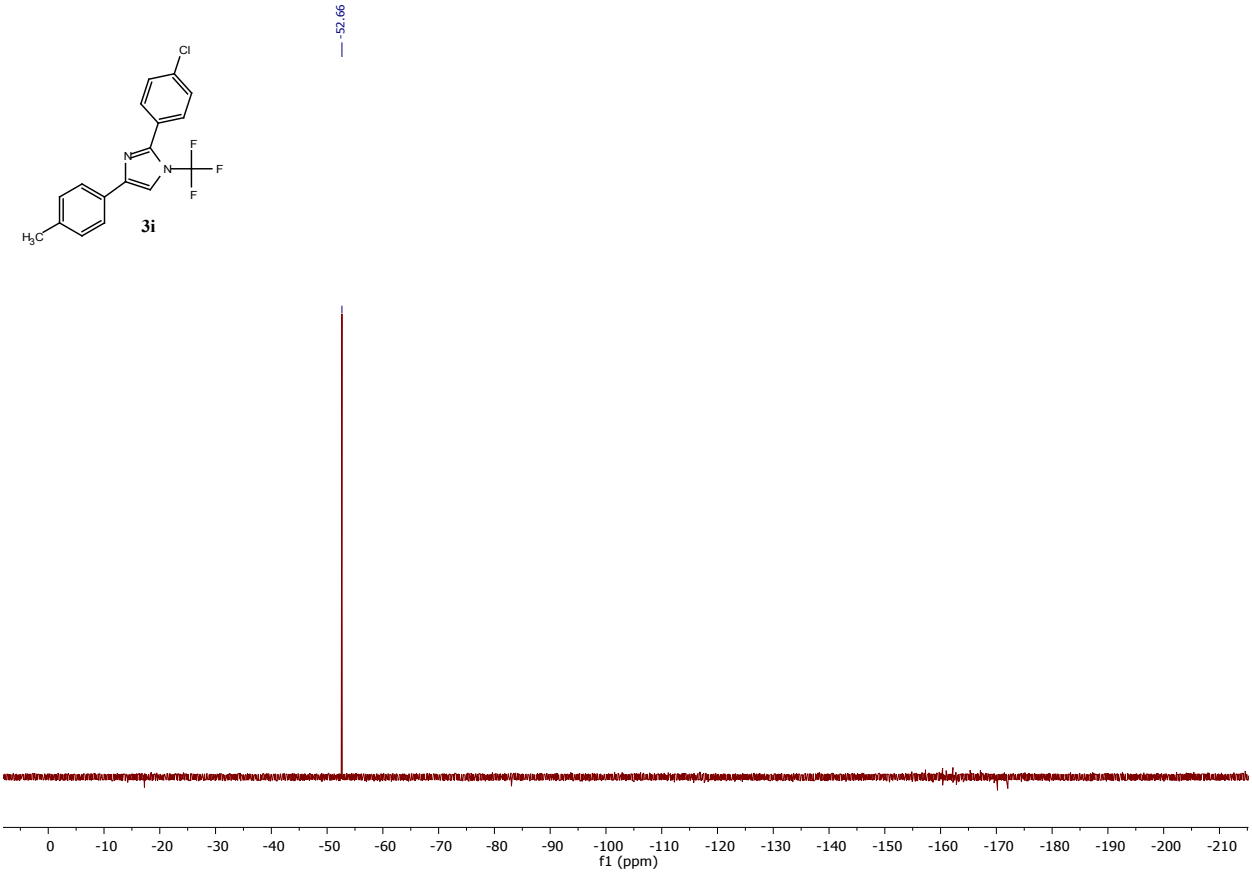
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



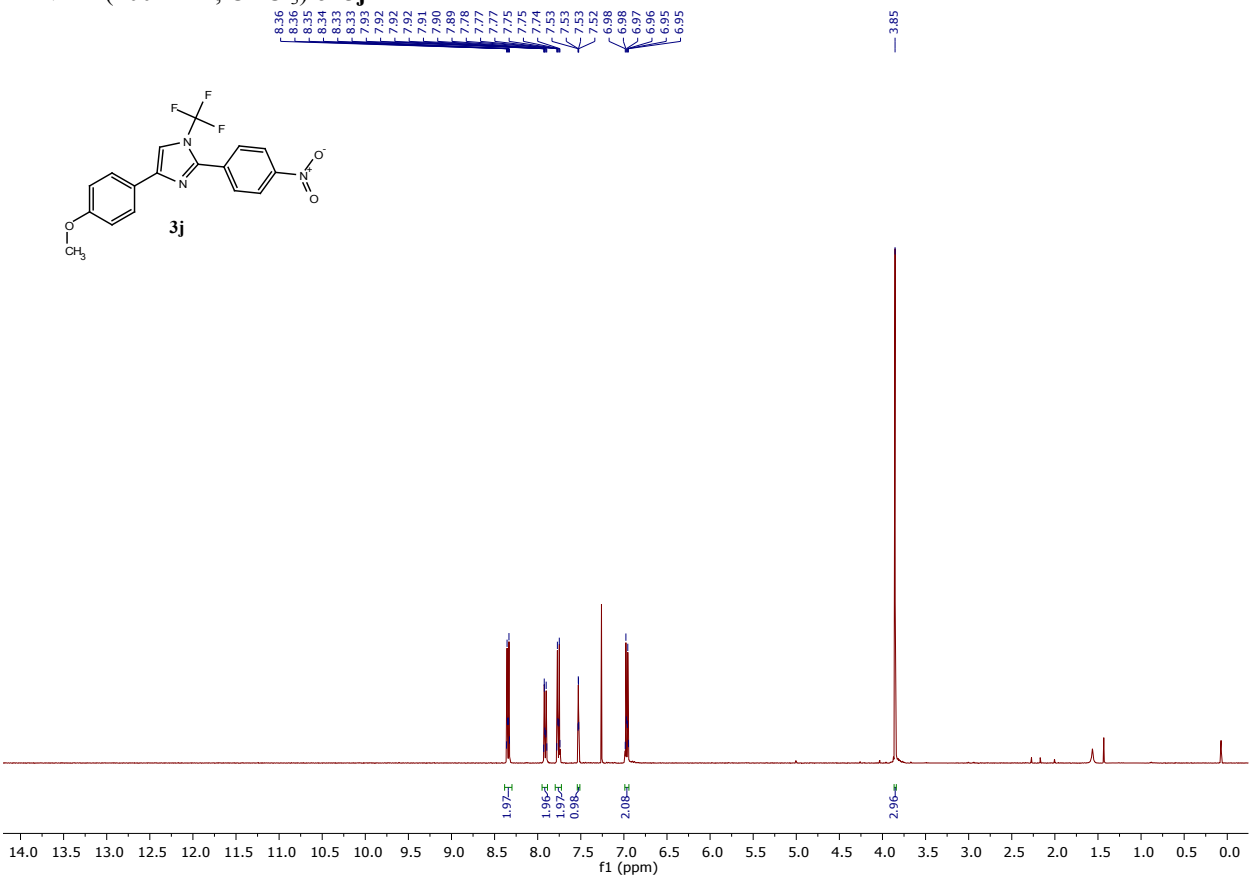
^{13}C NMR (101 MHz, $CDCl_3$) of **3i**



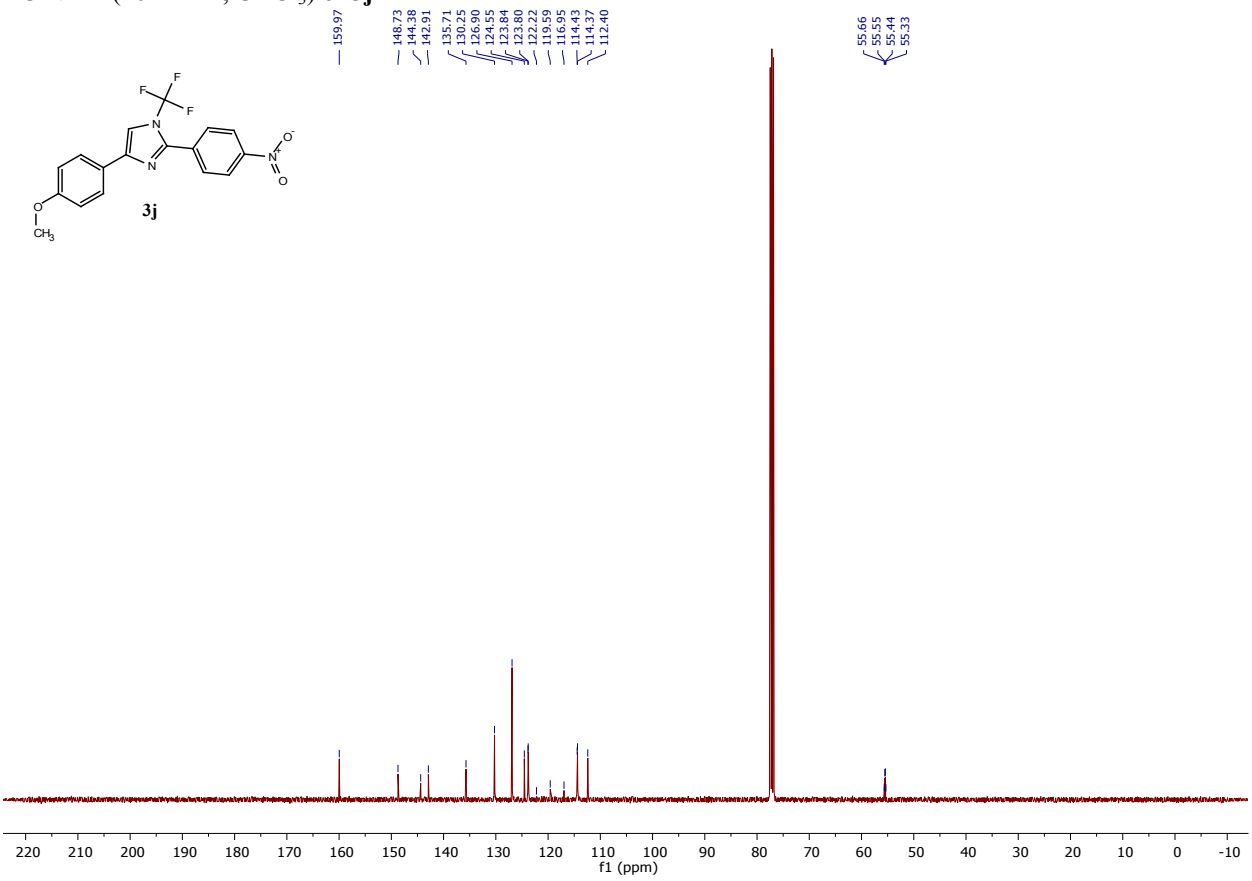
^{19}F NMR (376 MHz, $CDCl_3$) of **3i**



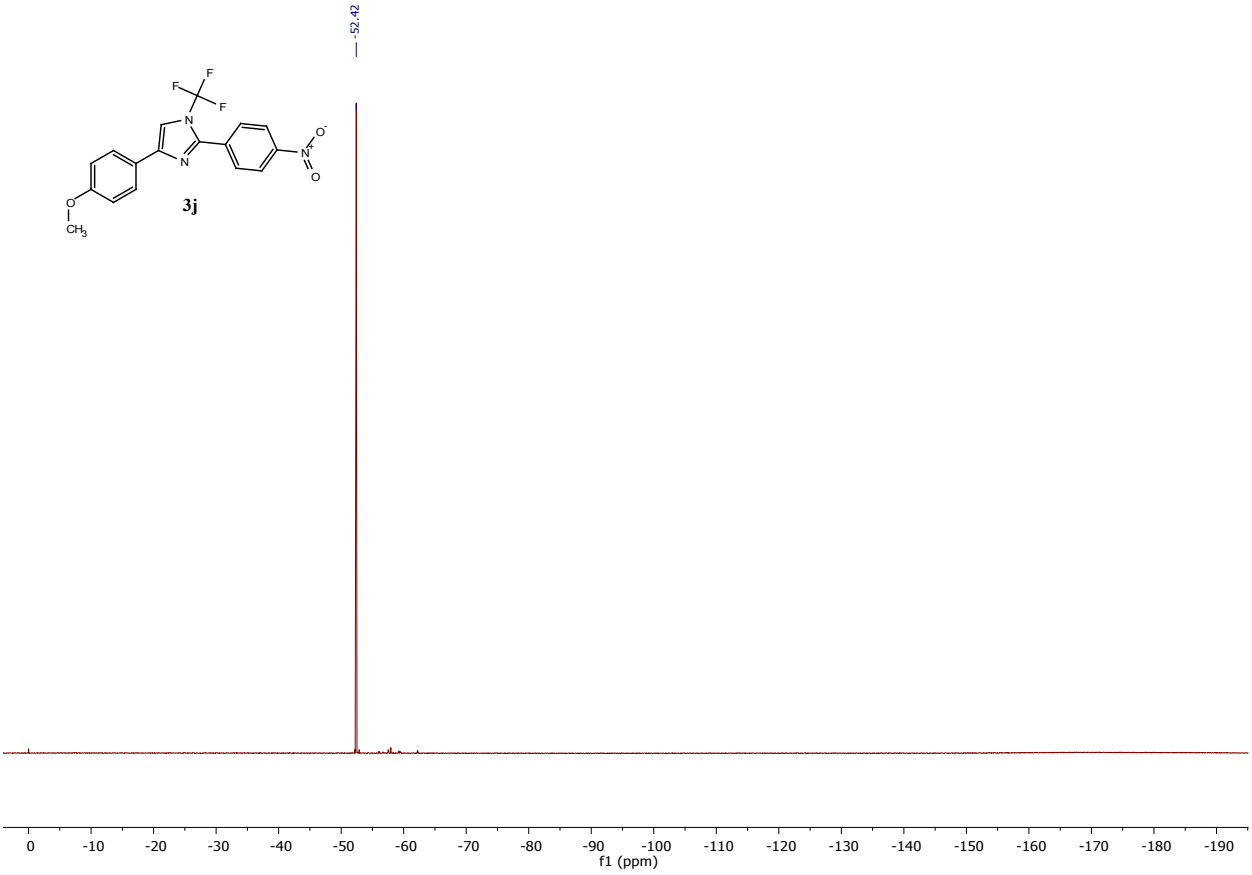
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



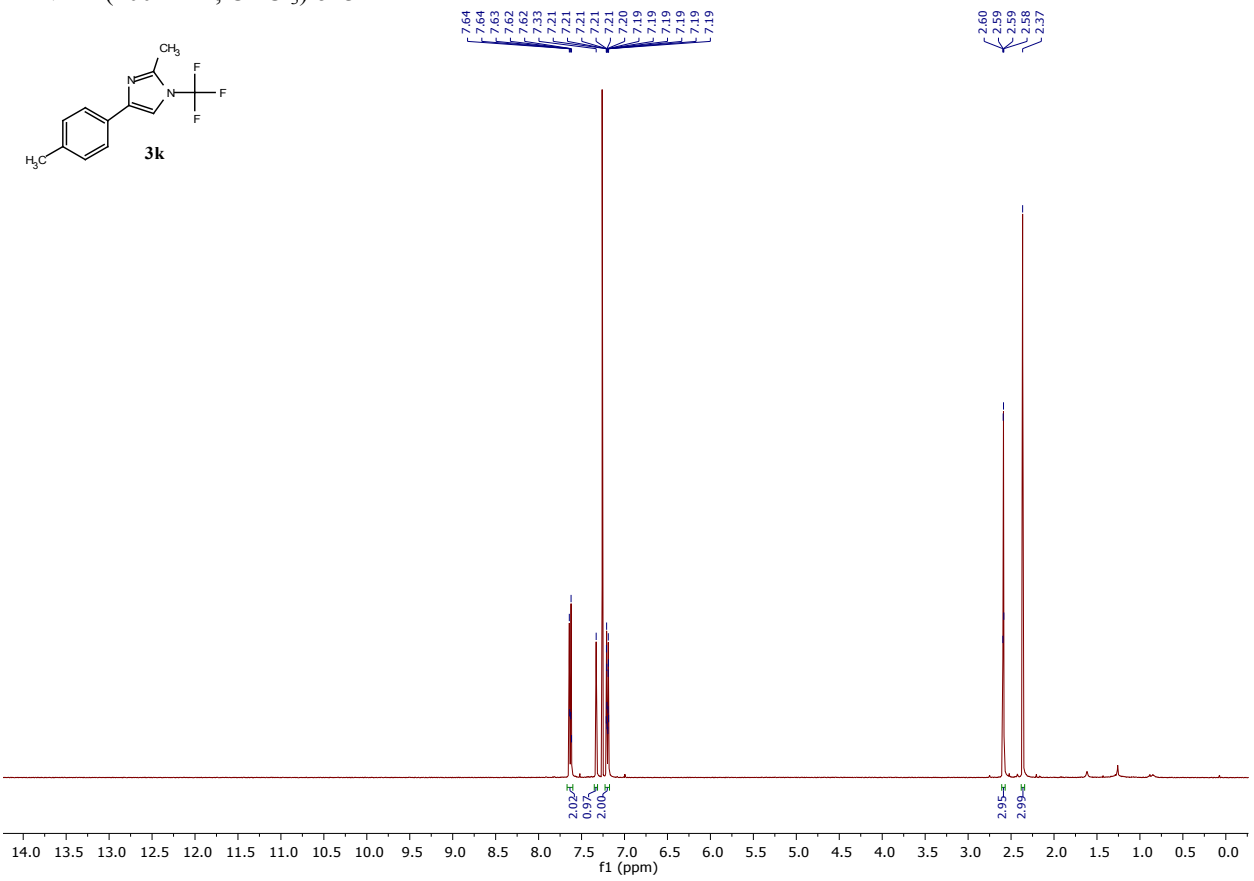
^{13}C NMR (101 MHz, $CDCl_3$) of **3j**



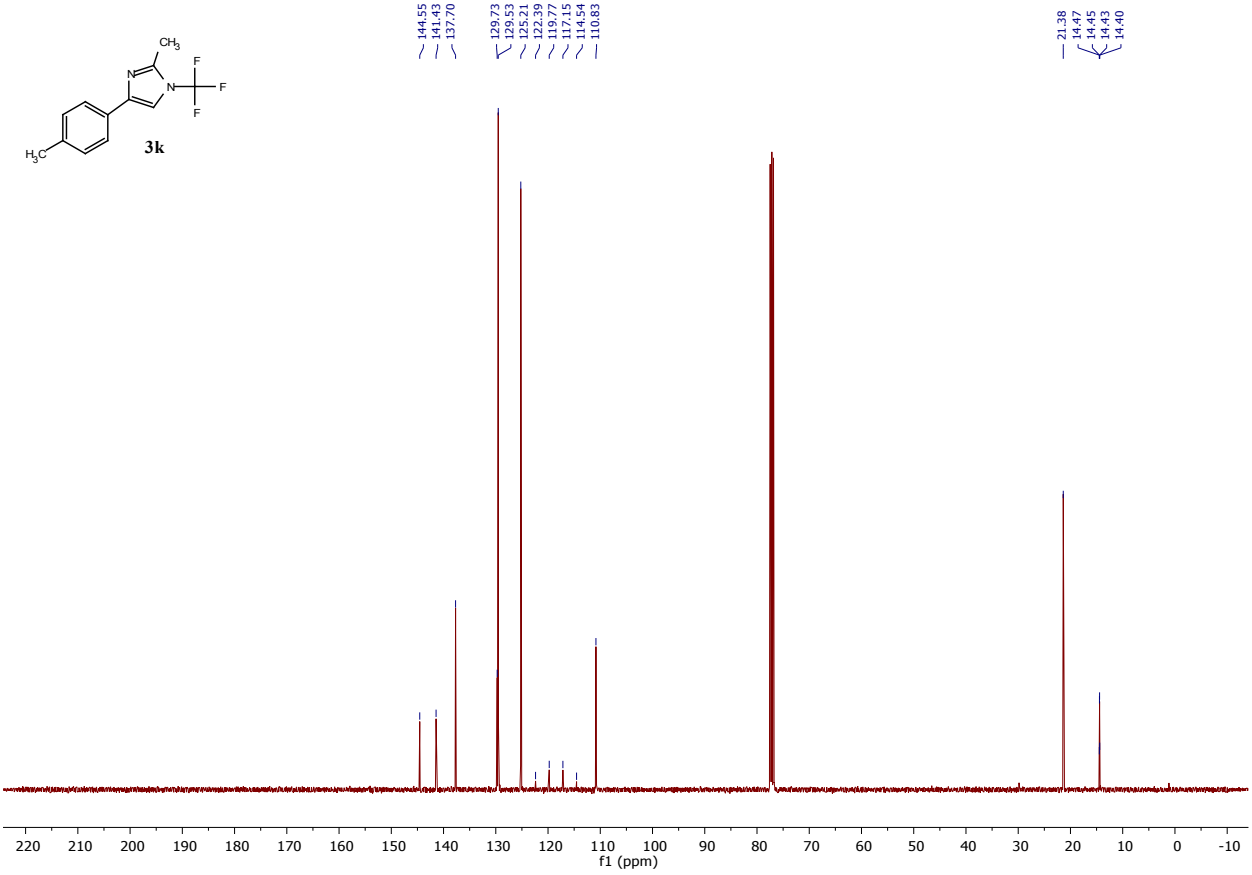
^{19}F NMR (376 MHz, $CDCl_3$) of **3j**



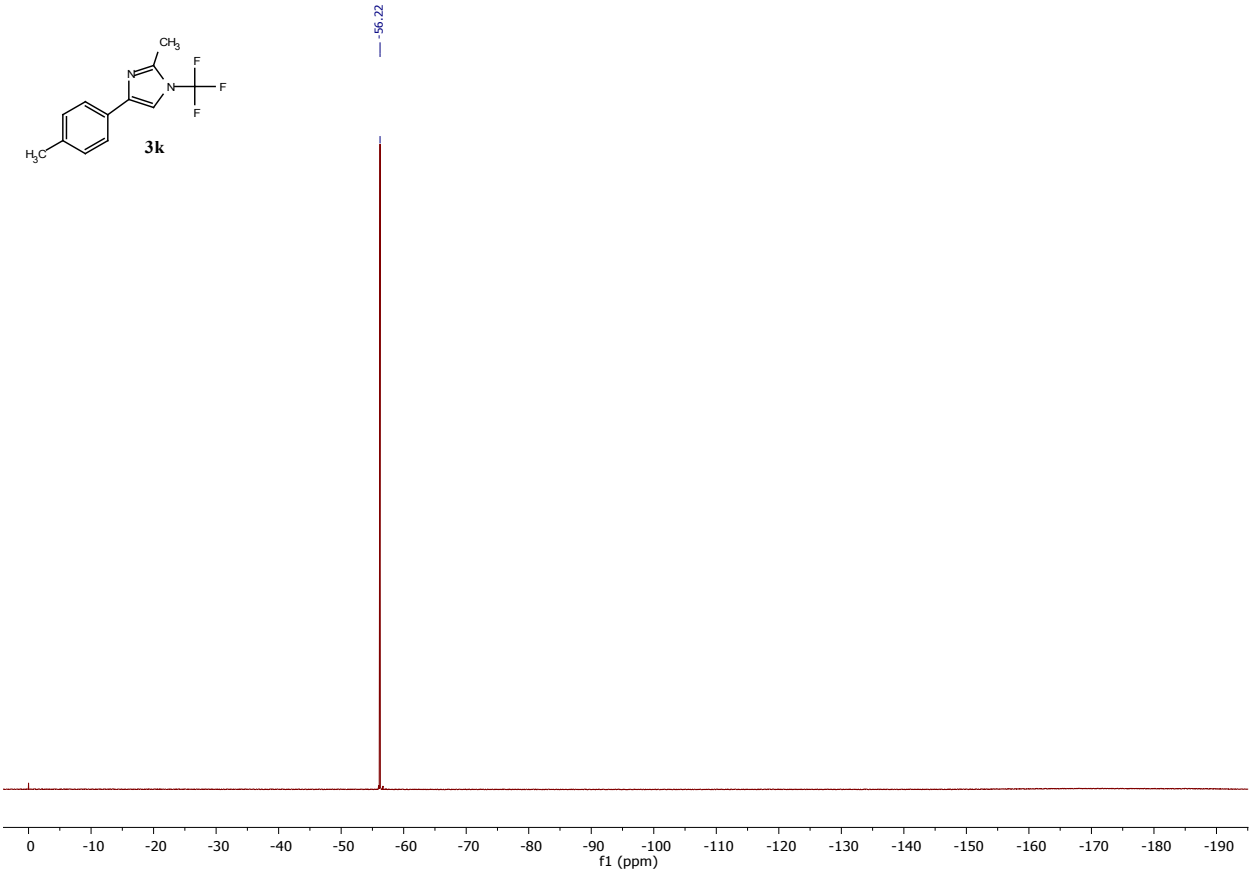
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



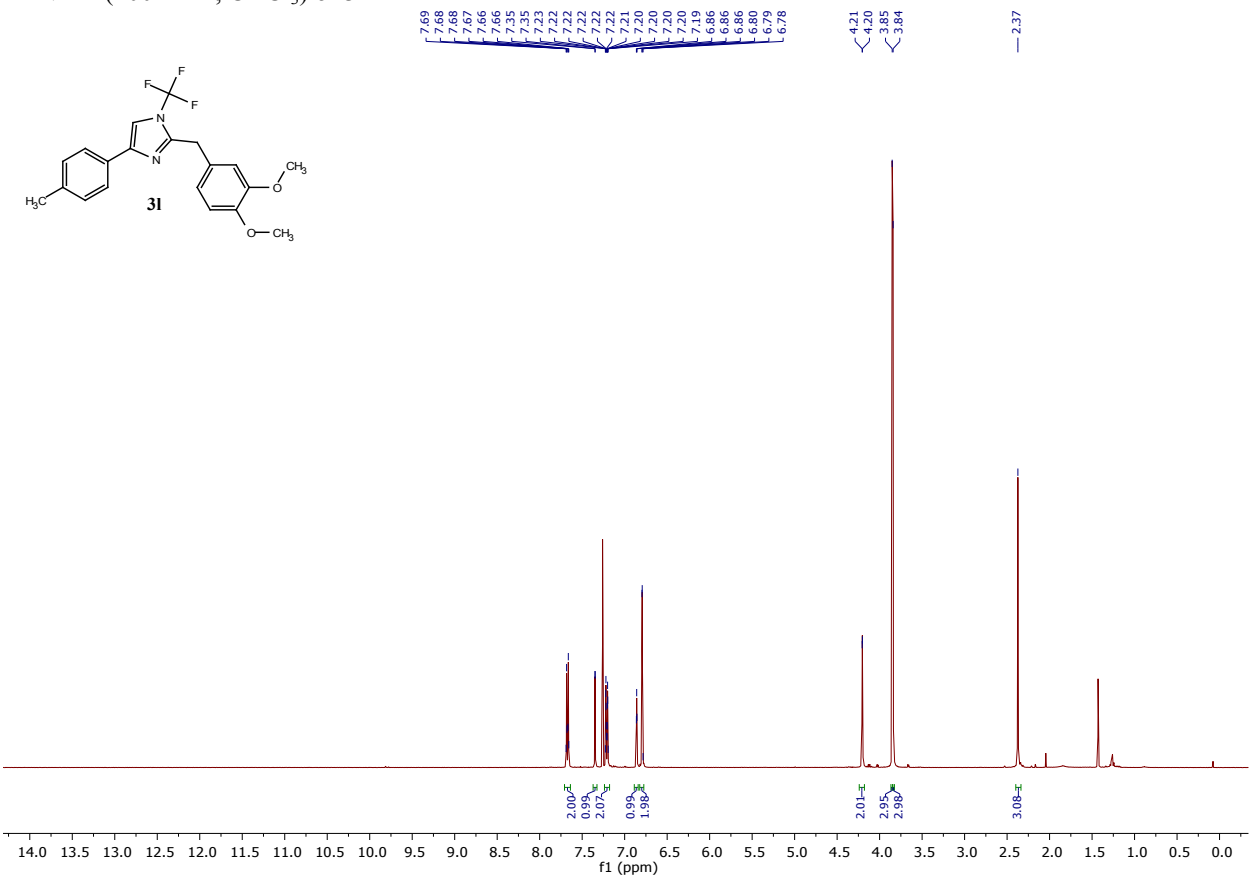
^{13}C NMR (101 MHz, $CDCl_3$) of **3k**



^{19}F NMR (376 MHz, $CDCl_3$) of **3k**

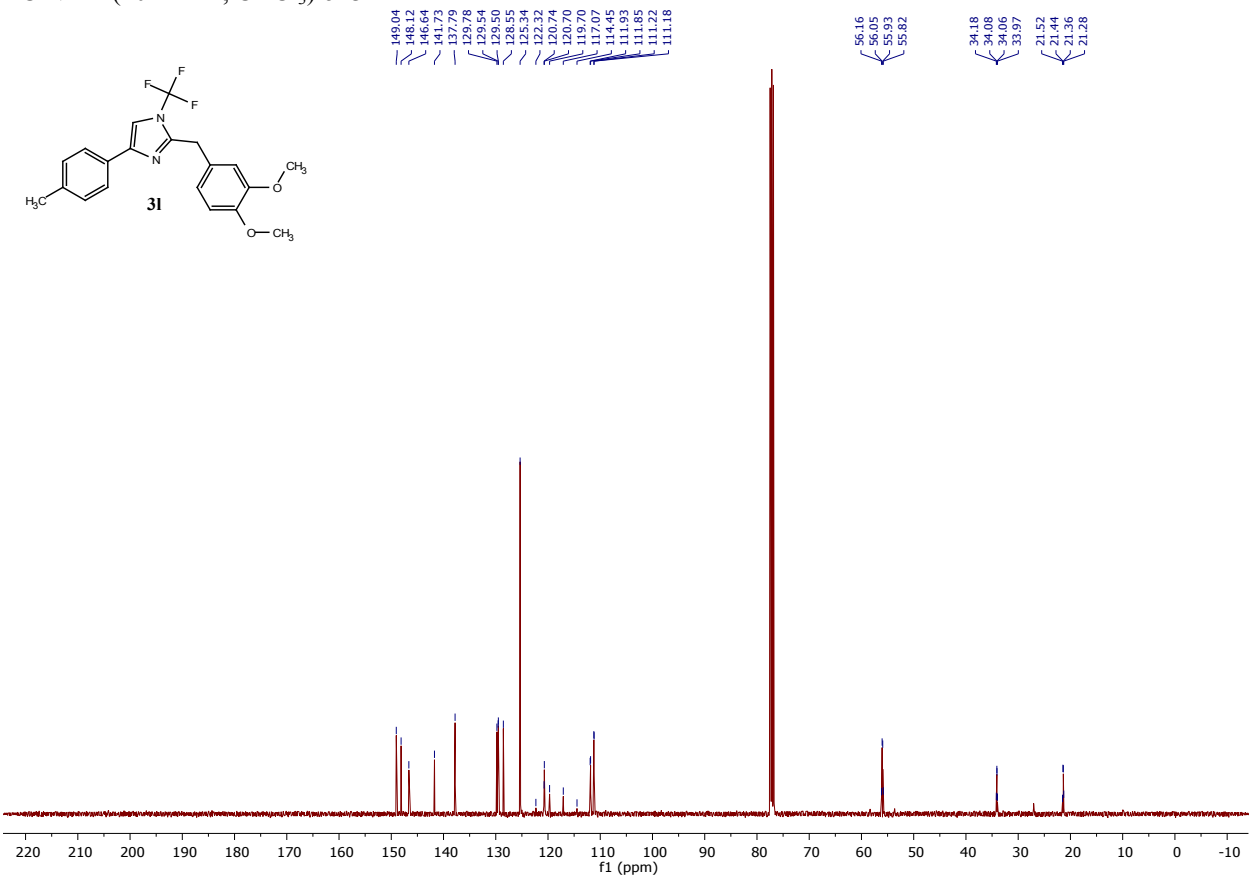


^{1}H NMR (400 MHz, $CDCl_3$) of **3l**

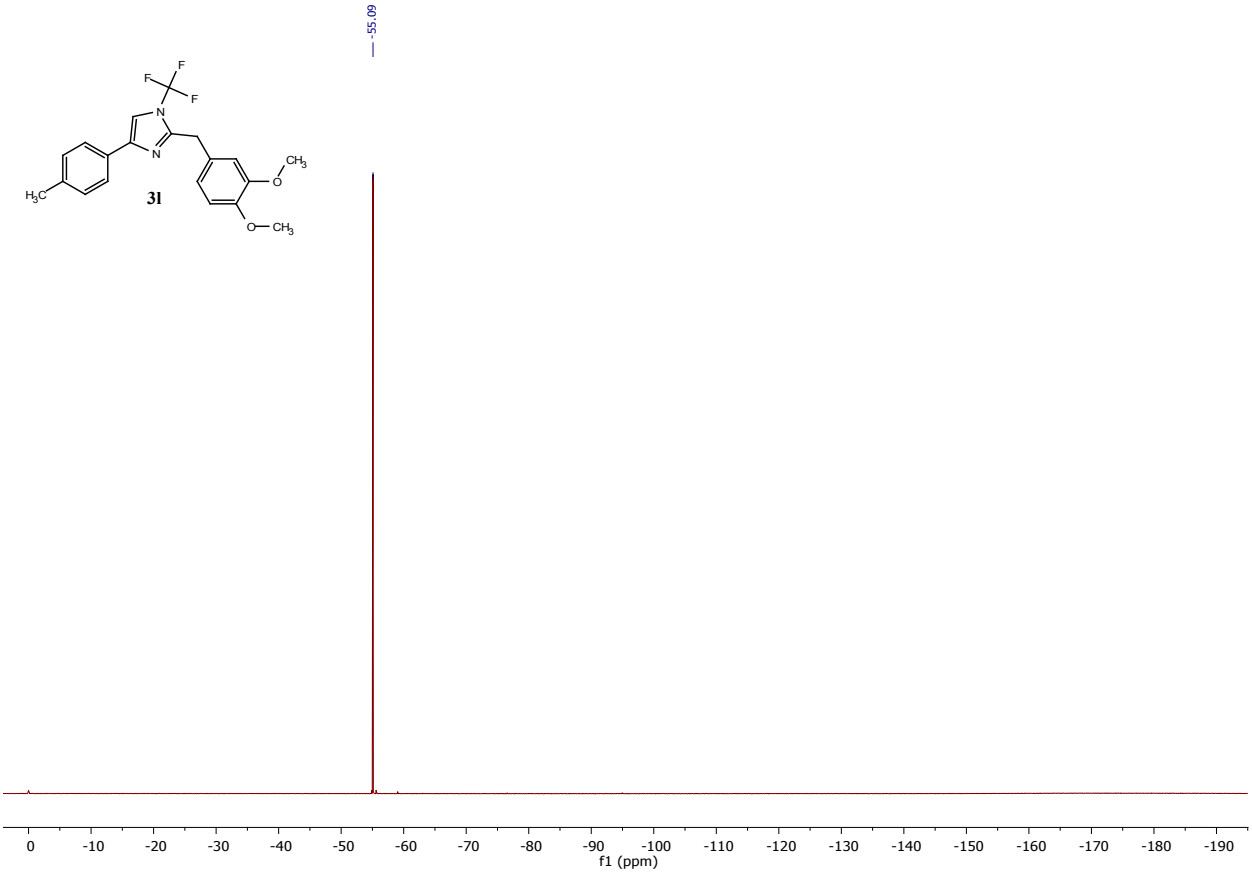


3l

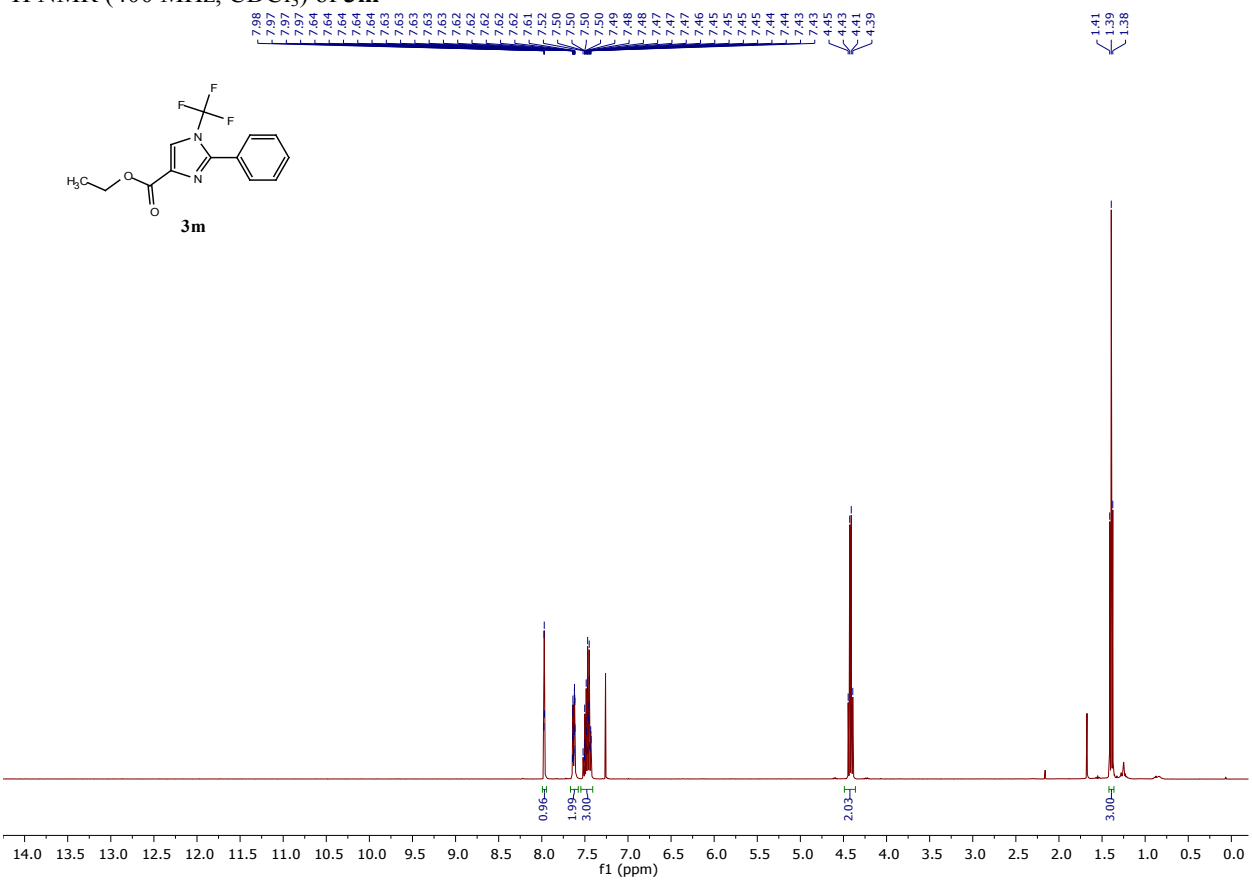
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



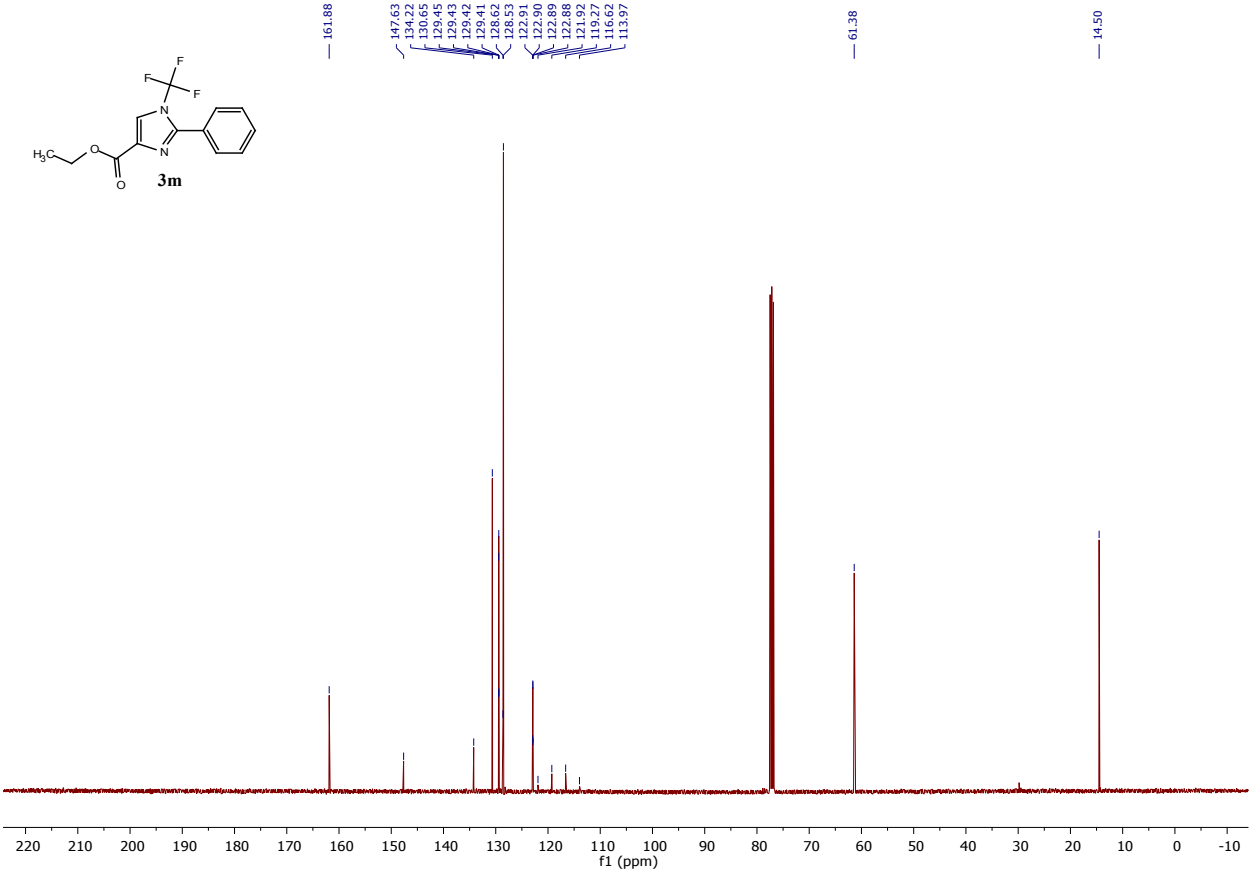
NMR (376 MHz, $CDCl_3$) of **3l**



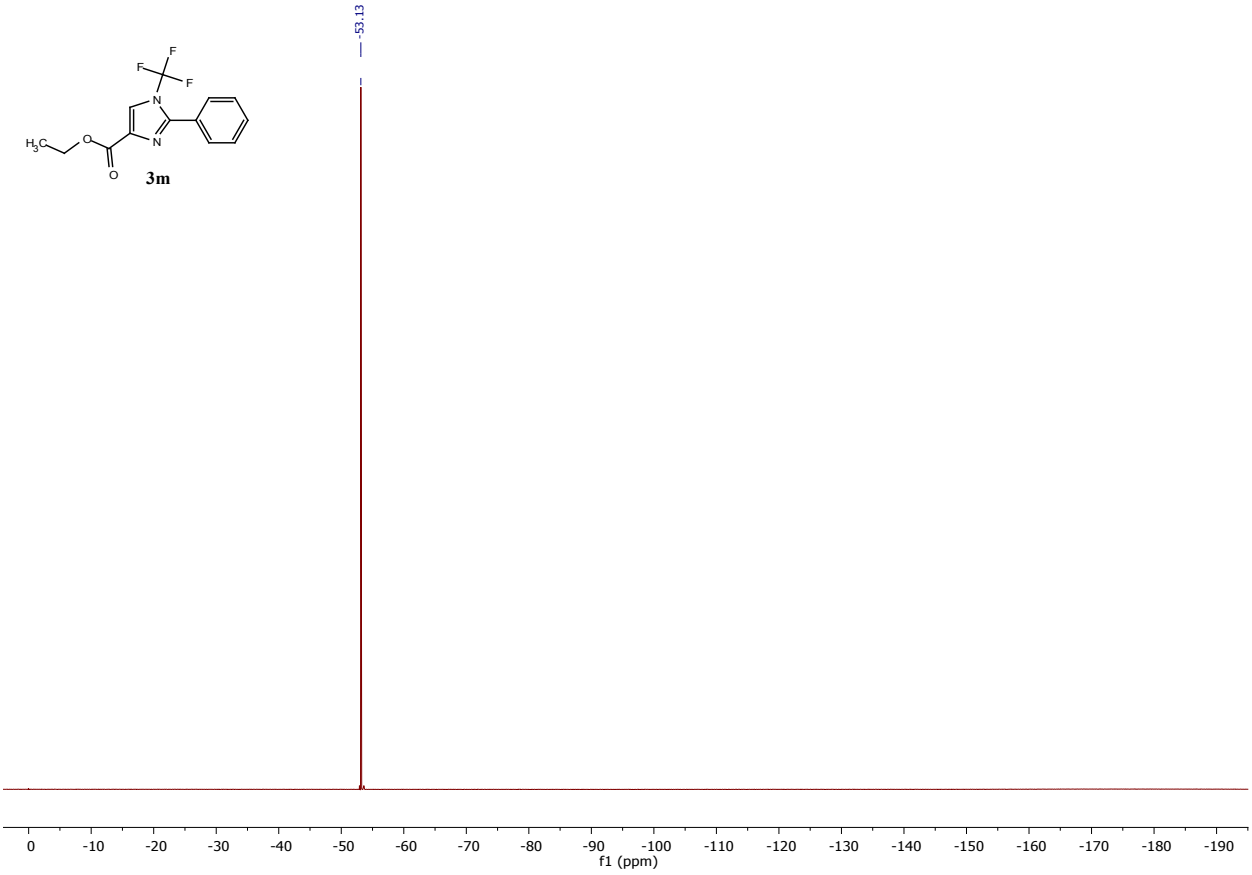
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



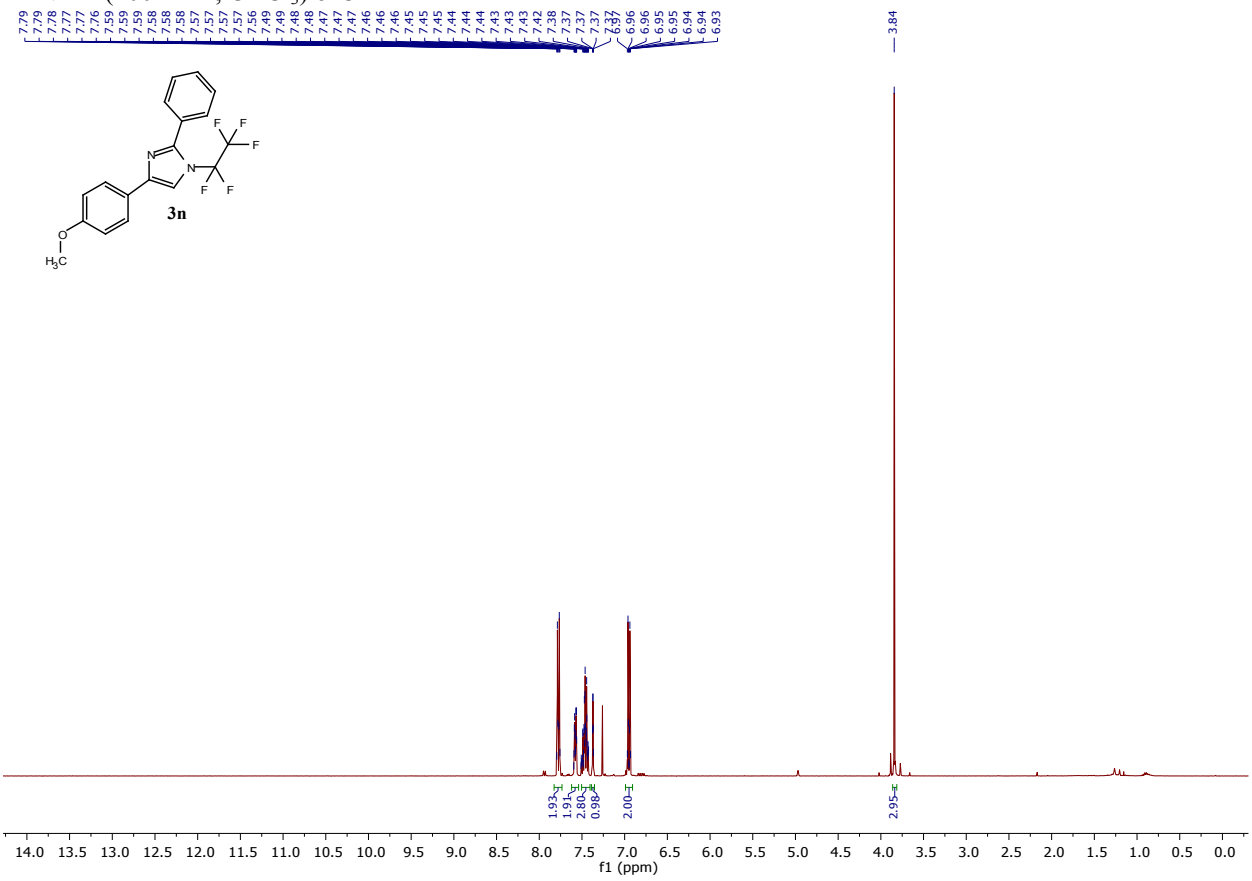
^{13}C NMR (101 MHz, $CDCl_3$) of **3m**



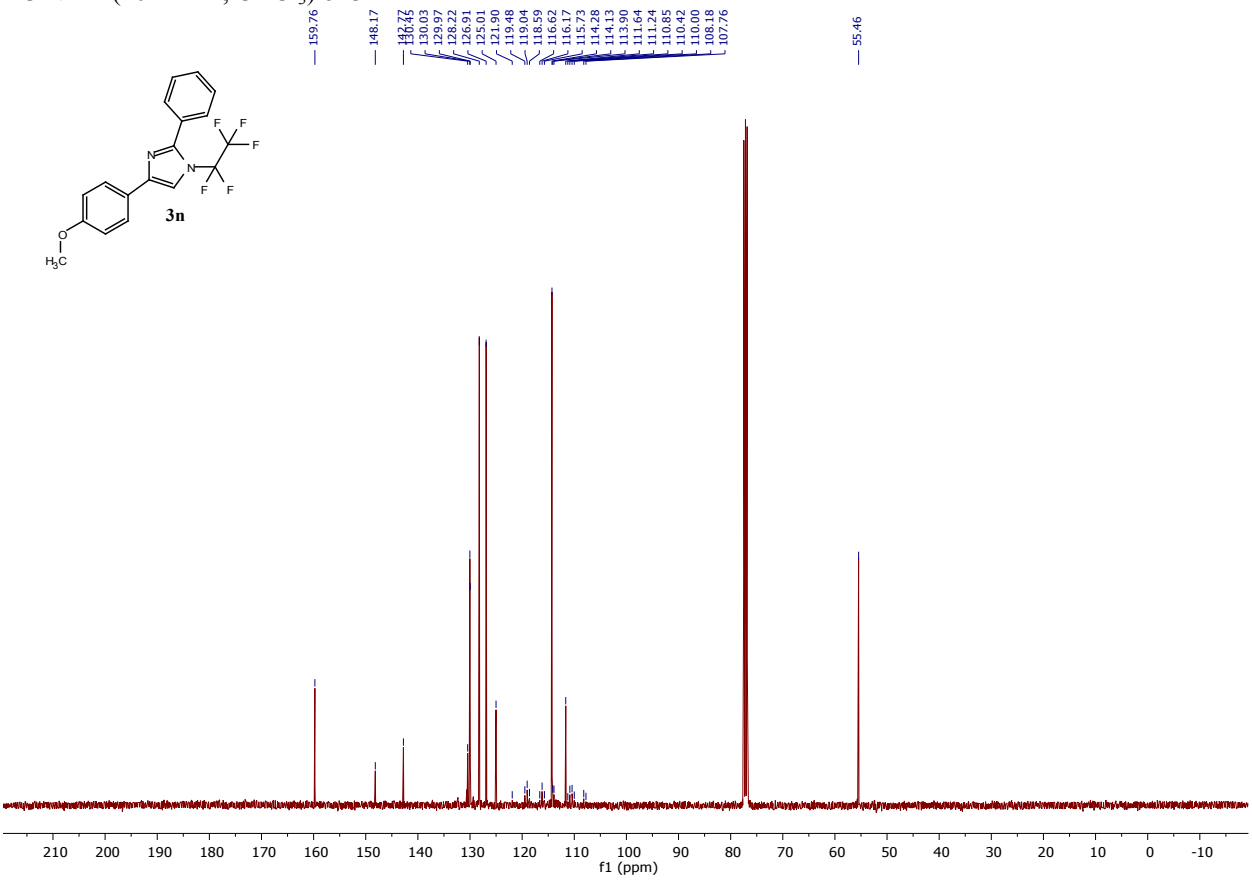
^{19}F NMR (376 MHz, $CDCl_3$) of **3m**



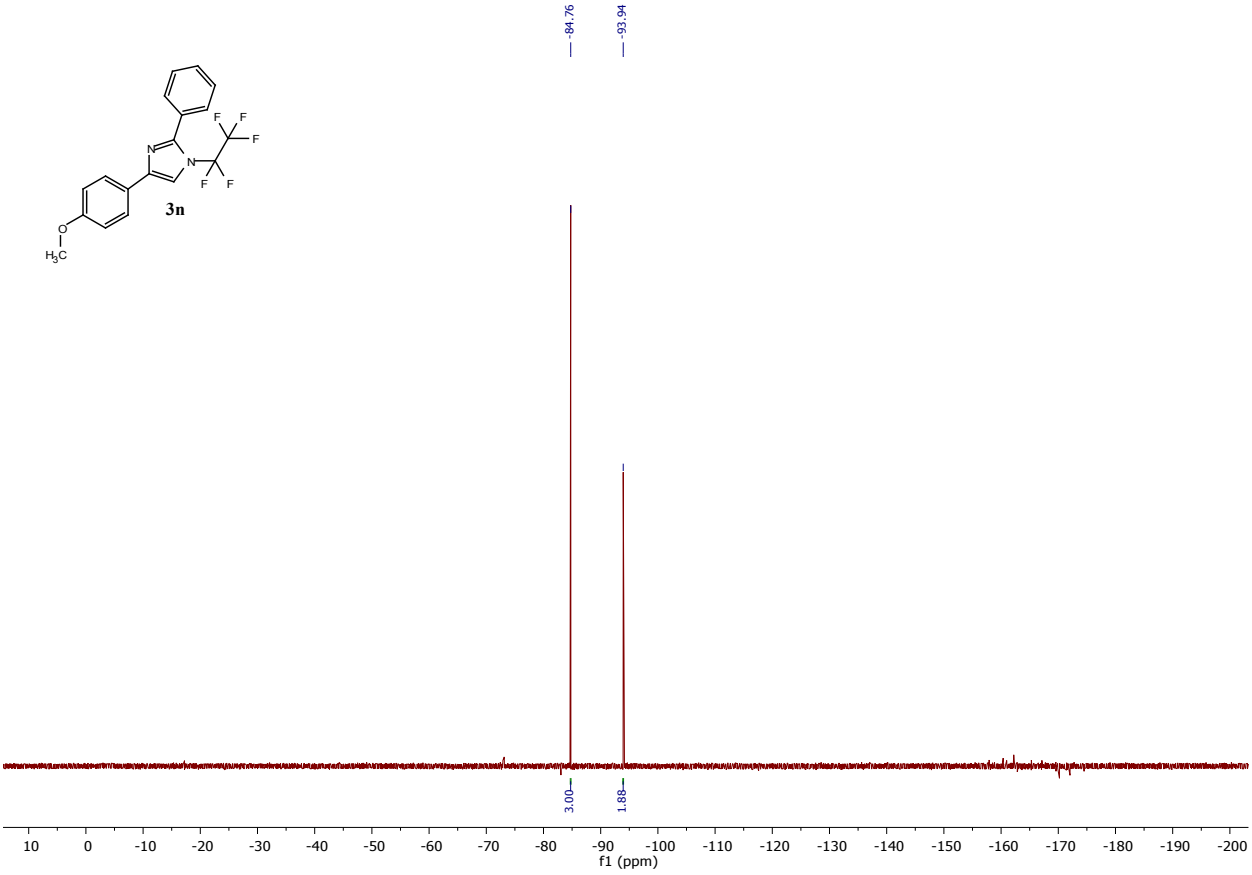
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



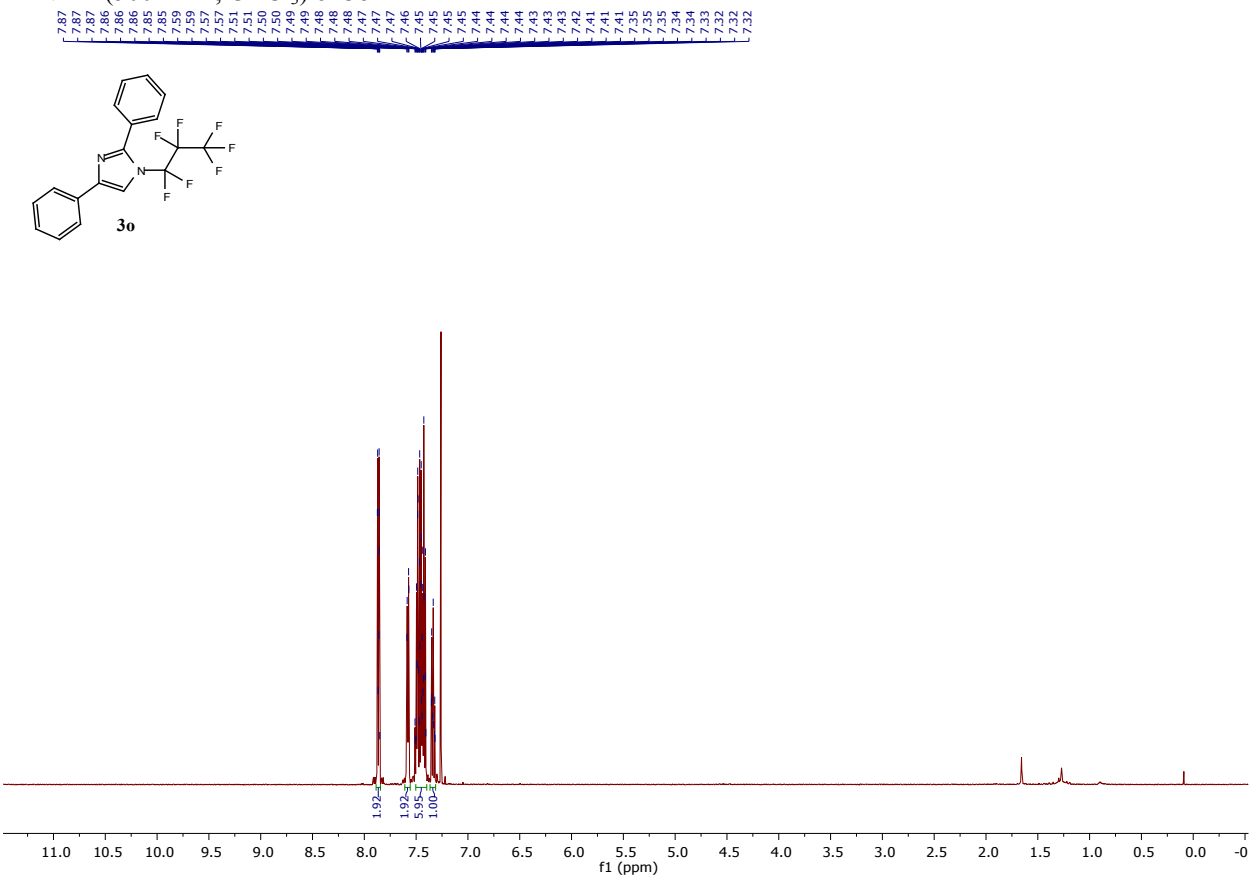
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



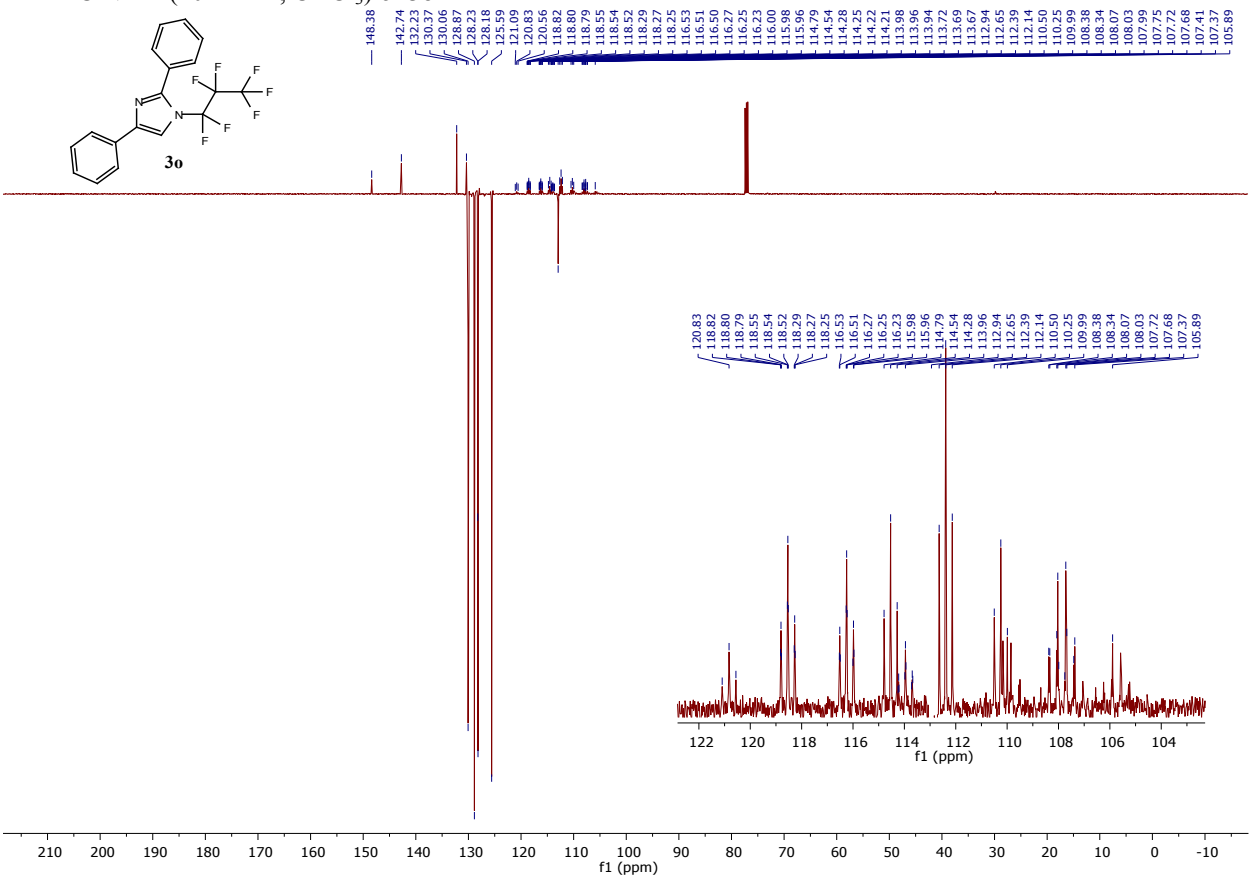
^{19}F NMR (376 MHz, $CDCl_3$) of **3n**



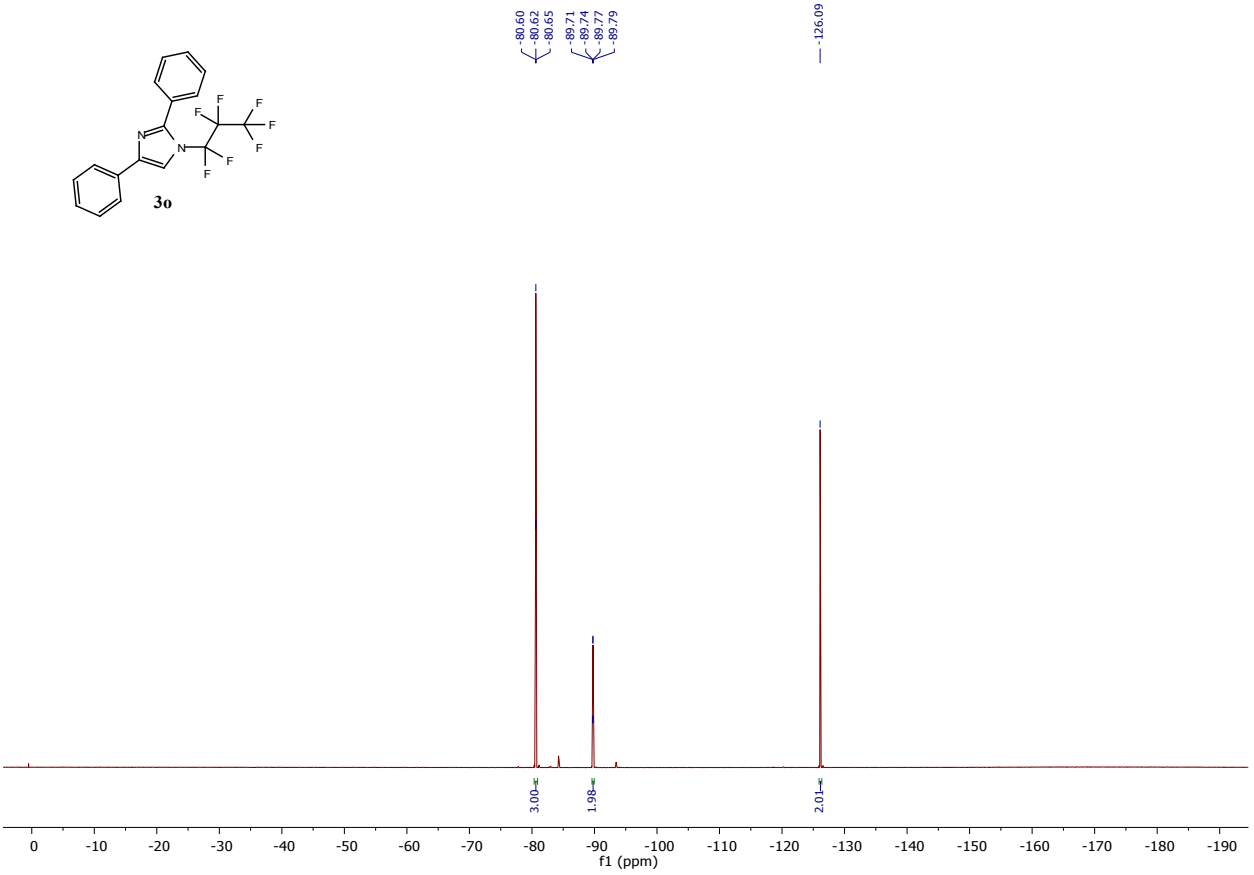
^{1}H NMR (500 MHz, $CDCl_3$) of **3o**



APT ^{13}C NMR (101 MHz, $CDCl_3$) of **3o**

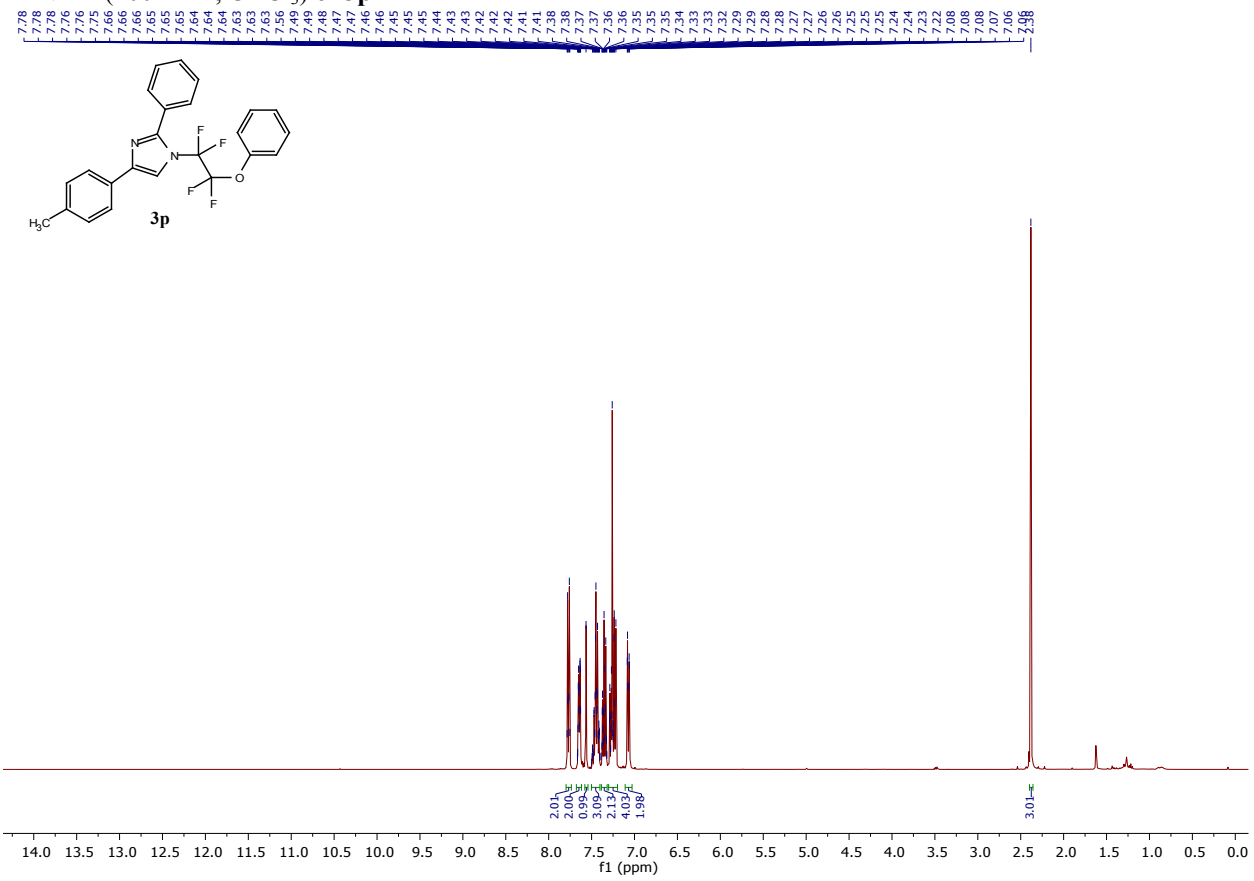


^{19}F NMR (376 MHz, $CDCl_3$) of **3o**

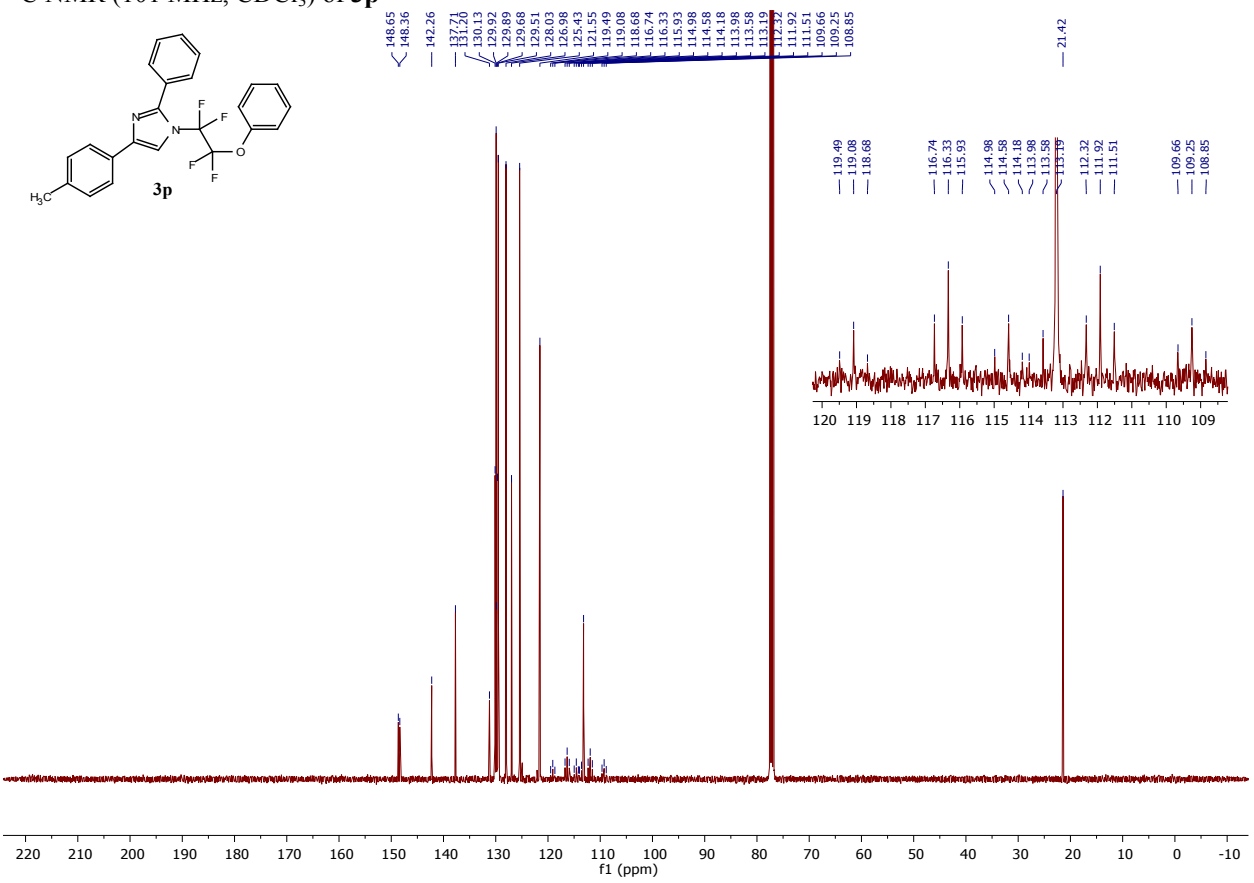


3o

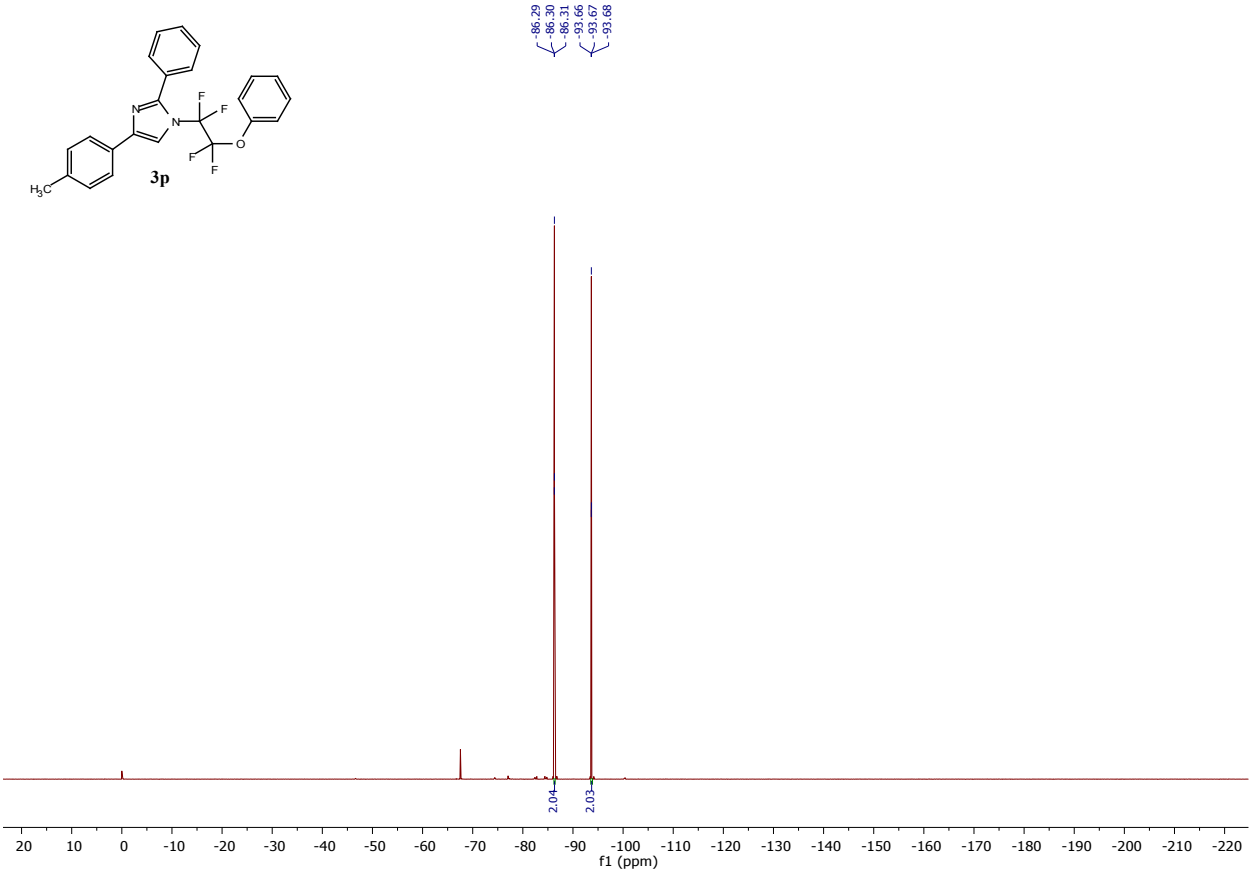
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



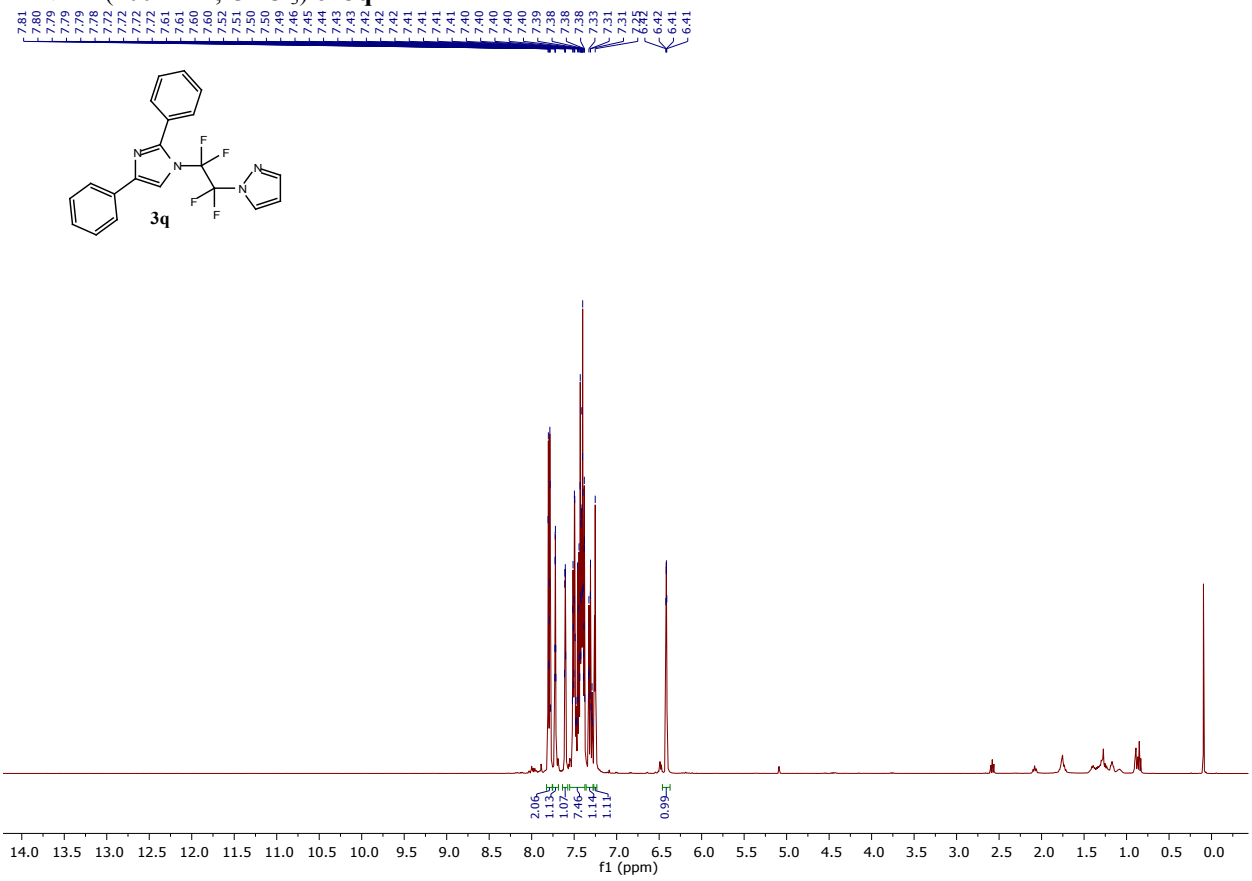
^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



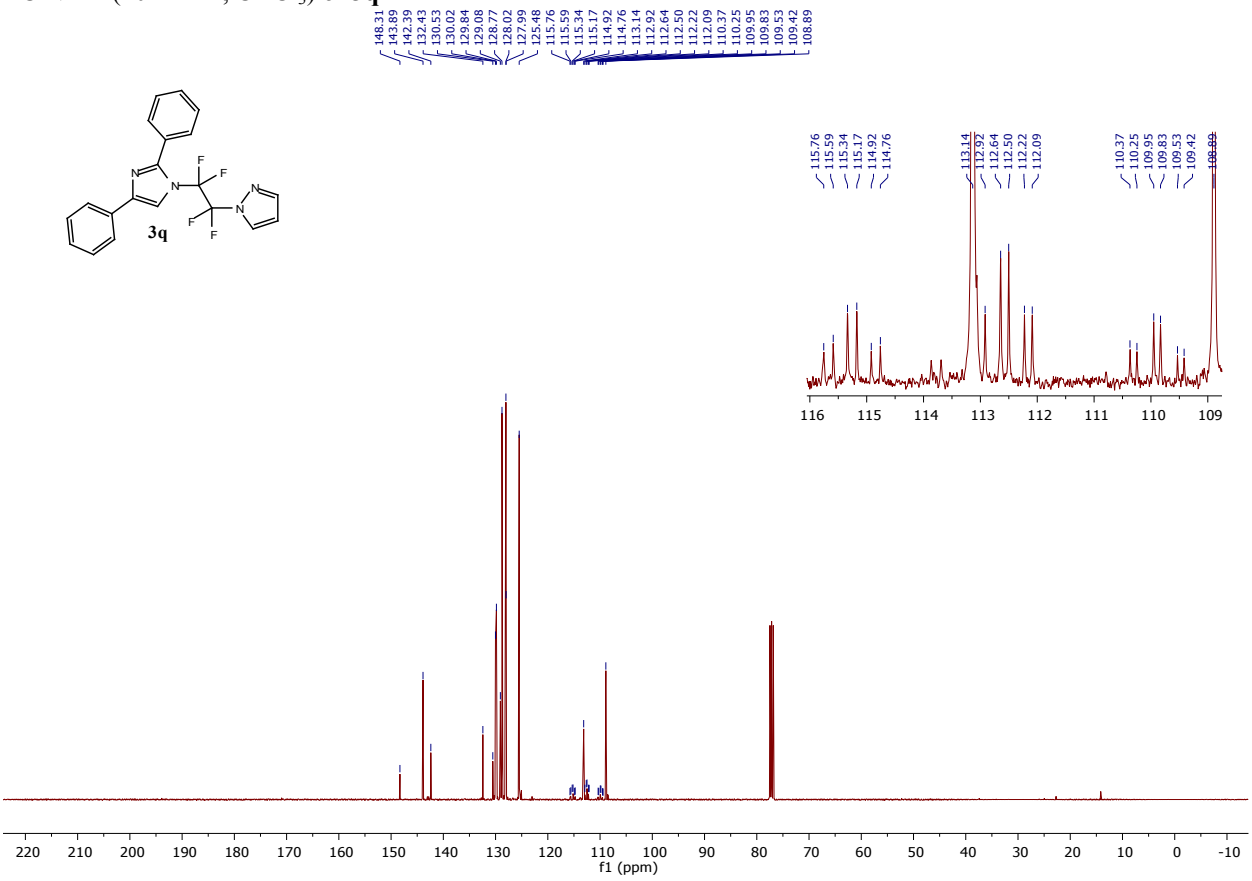
^{19}F NMR (376 MHz, $CDCl_3$) of **3p**



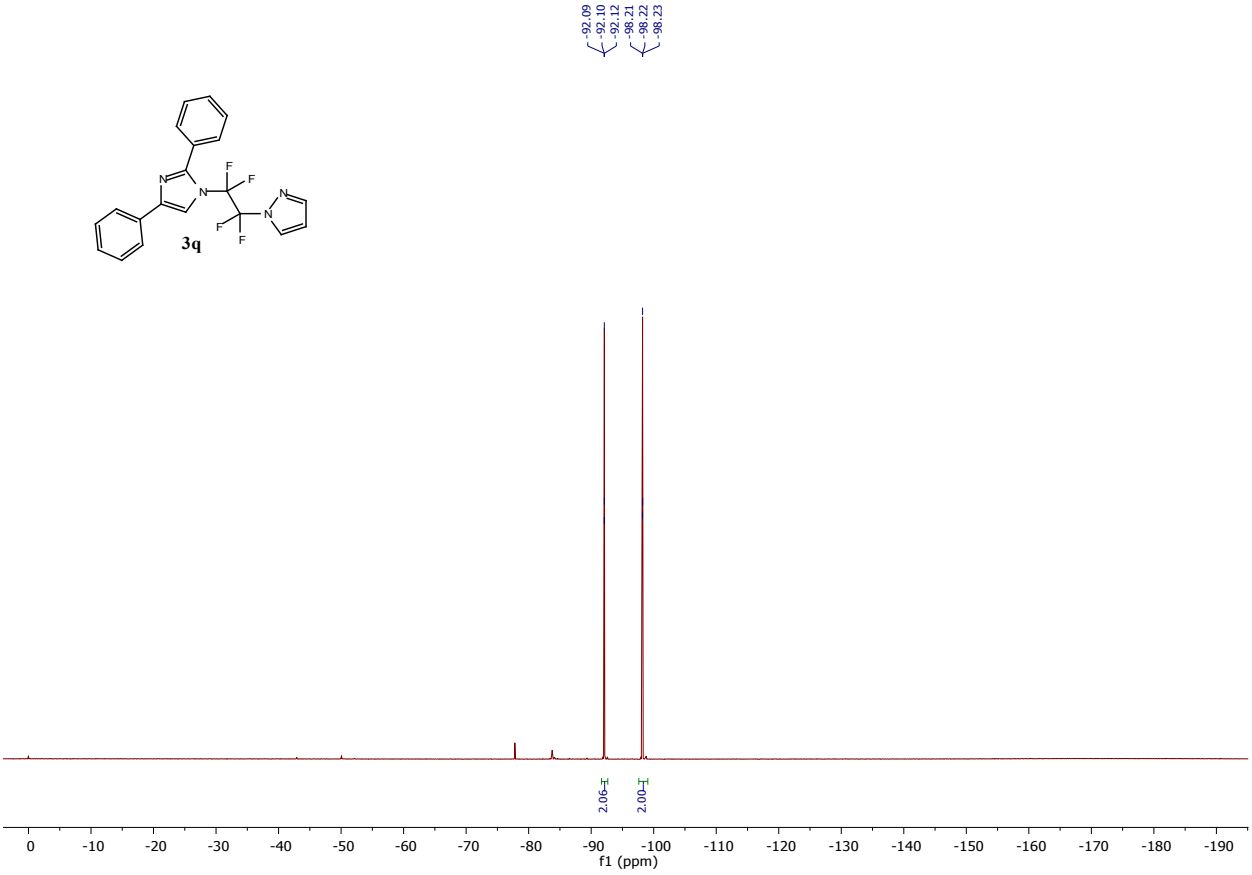
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



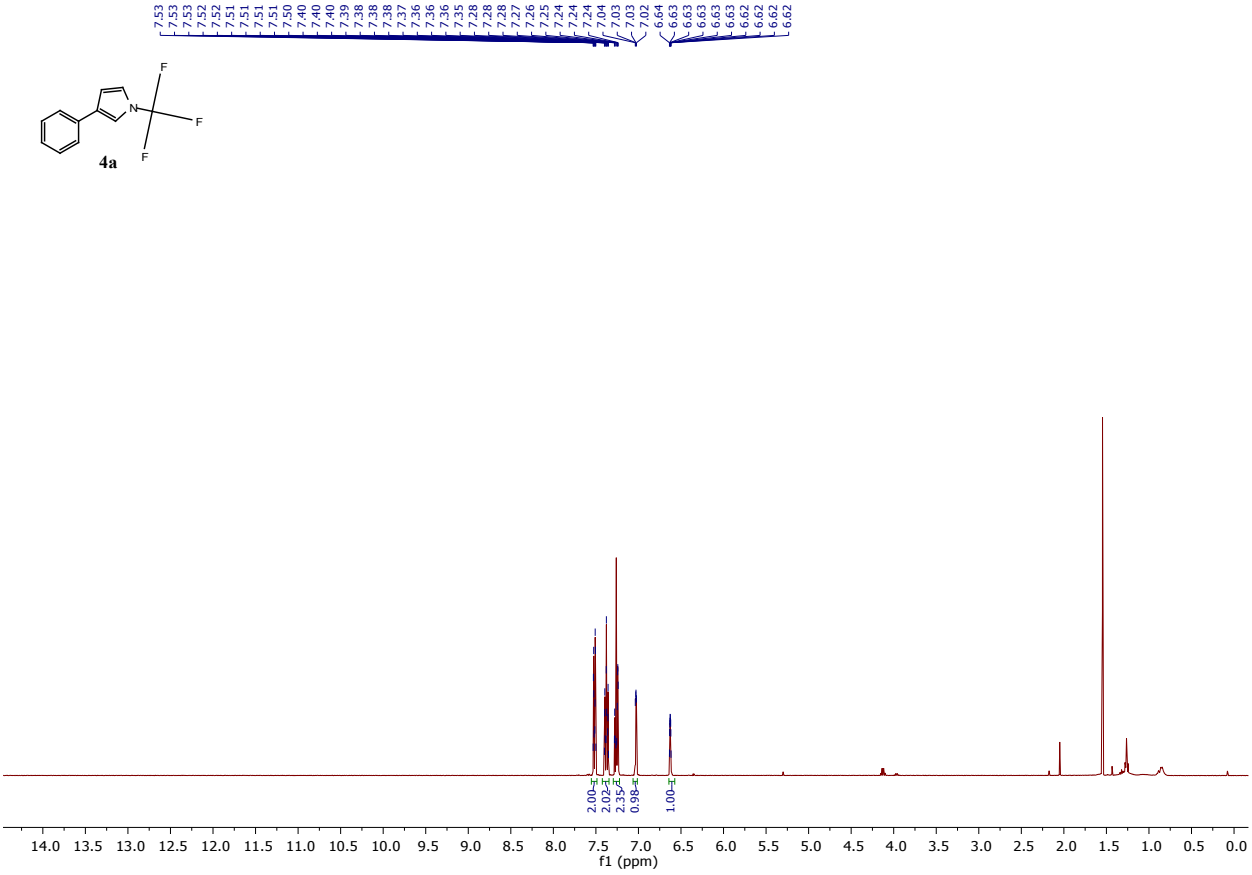
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



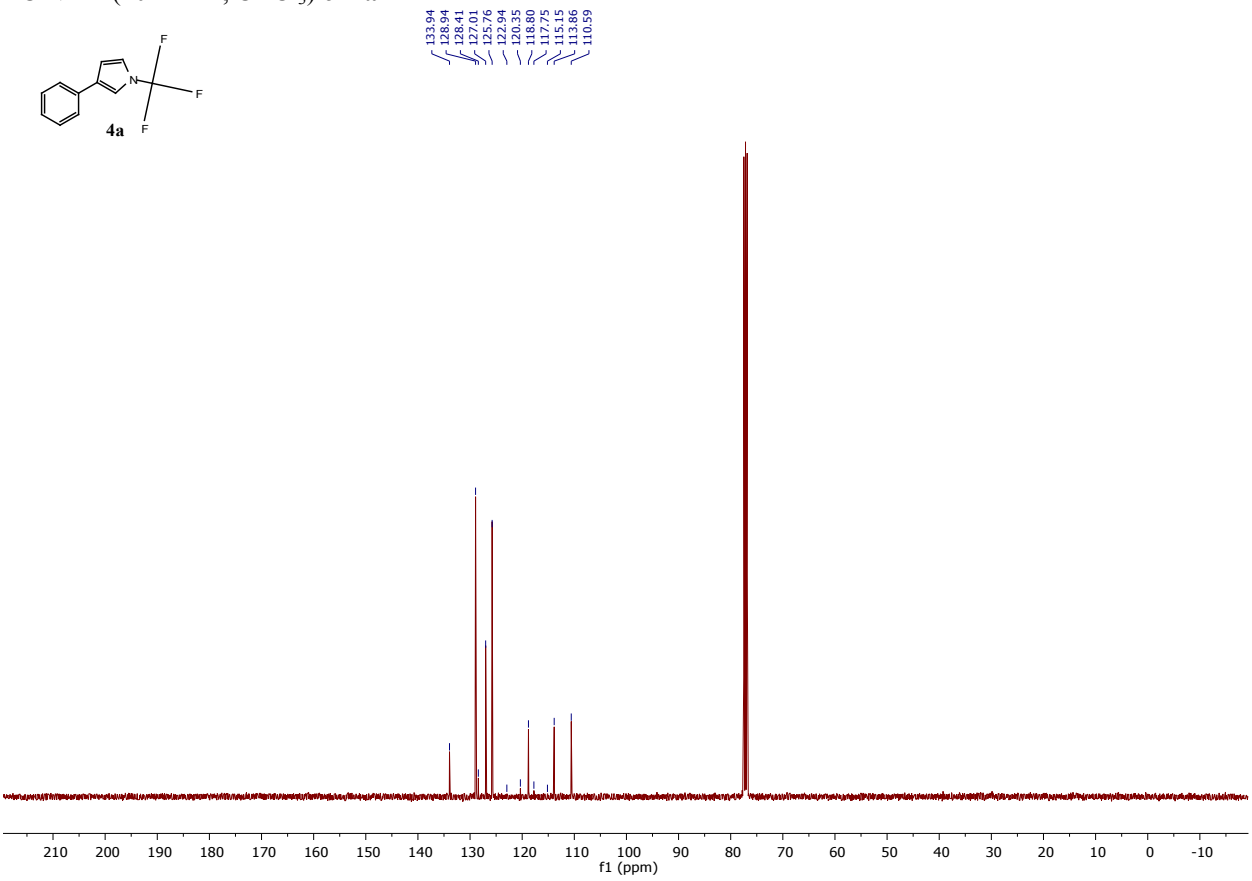
^{19}F NMR (376 MHz, $CDCl_3$) of **3q**



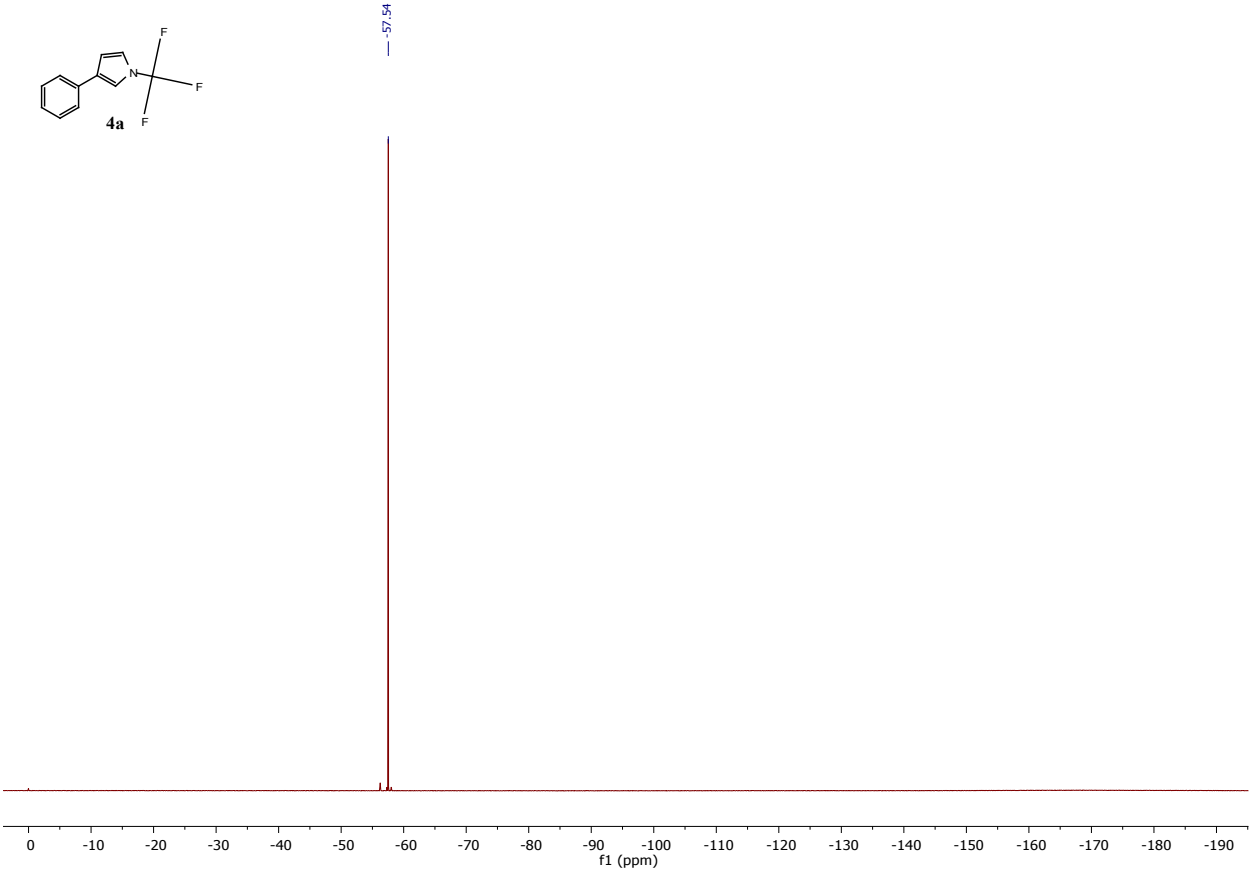
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



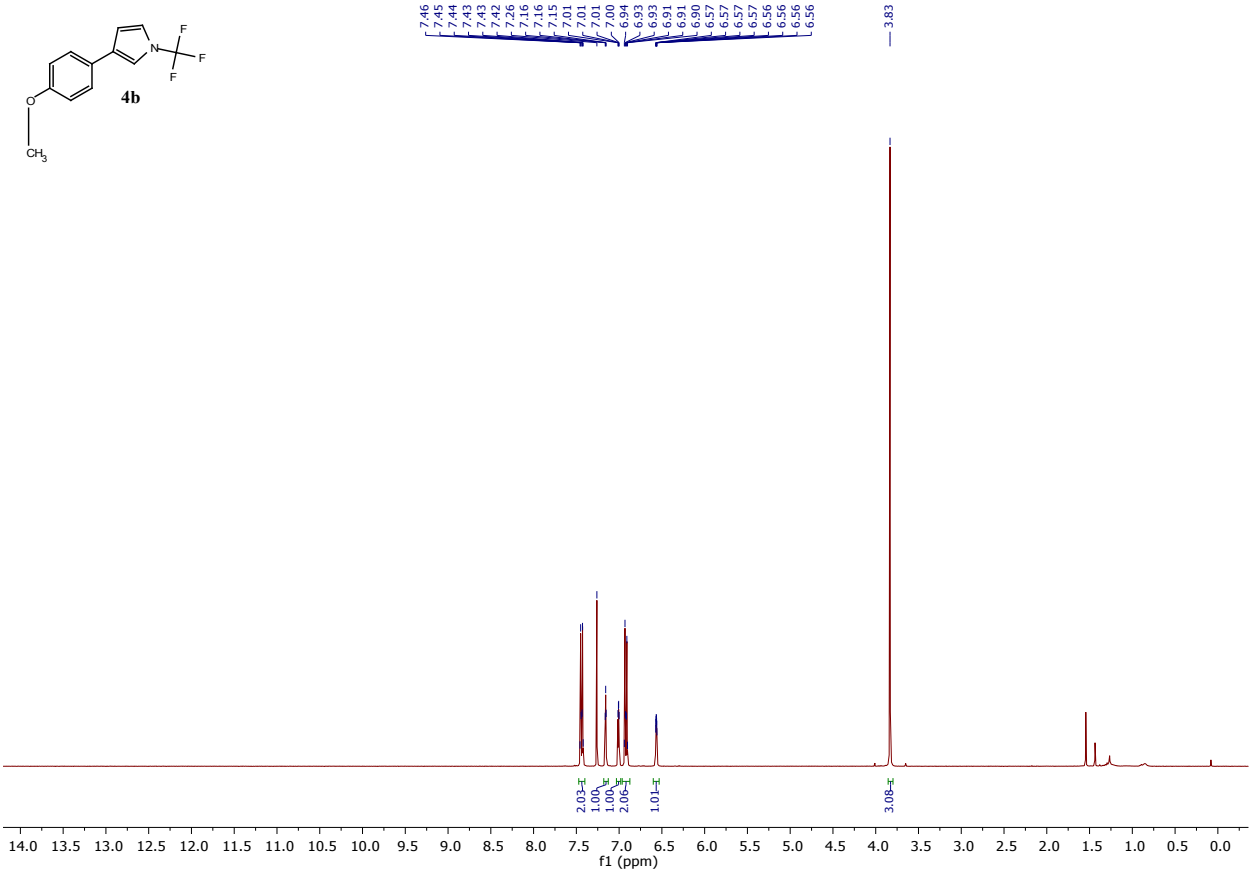
^{13}C NMR (101 MHz, $CDCl_3$) of **4a**



^{19}F NMR (376 MHz, $CDCl_3$) of **4a**

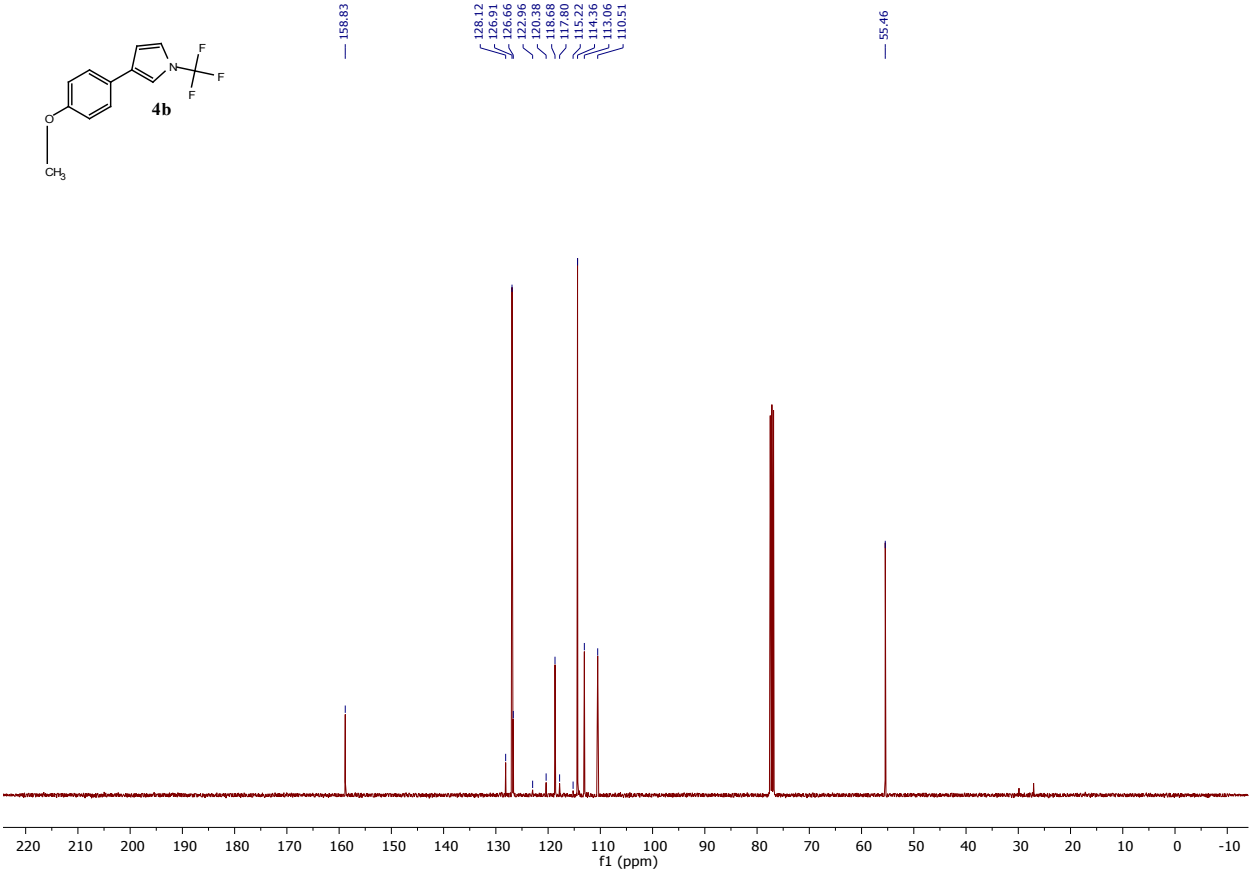


^{1}H NMR (400 MHz, $CDCl_3$) of **4b**

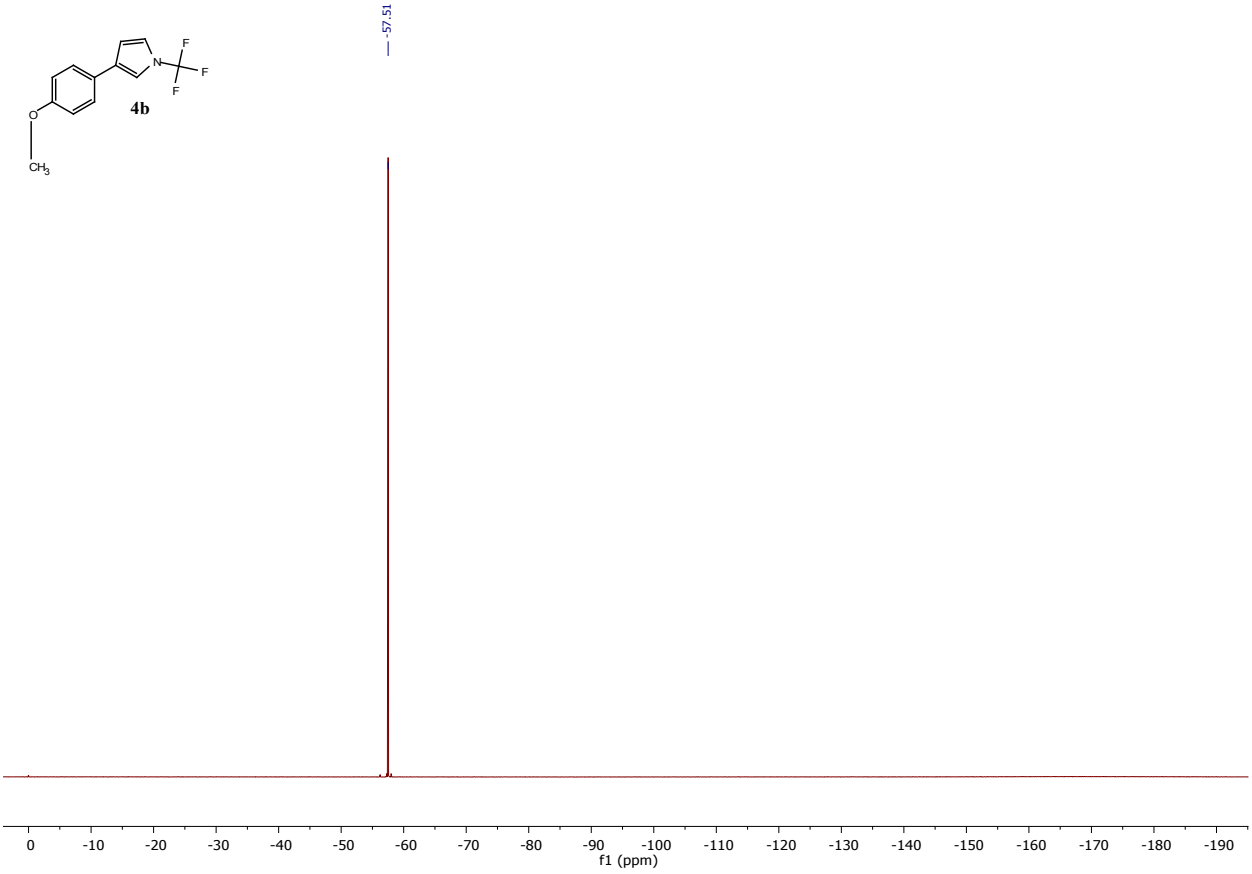


4b

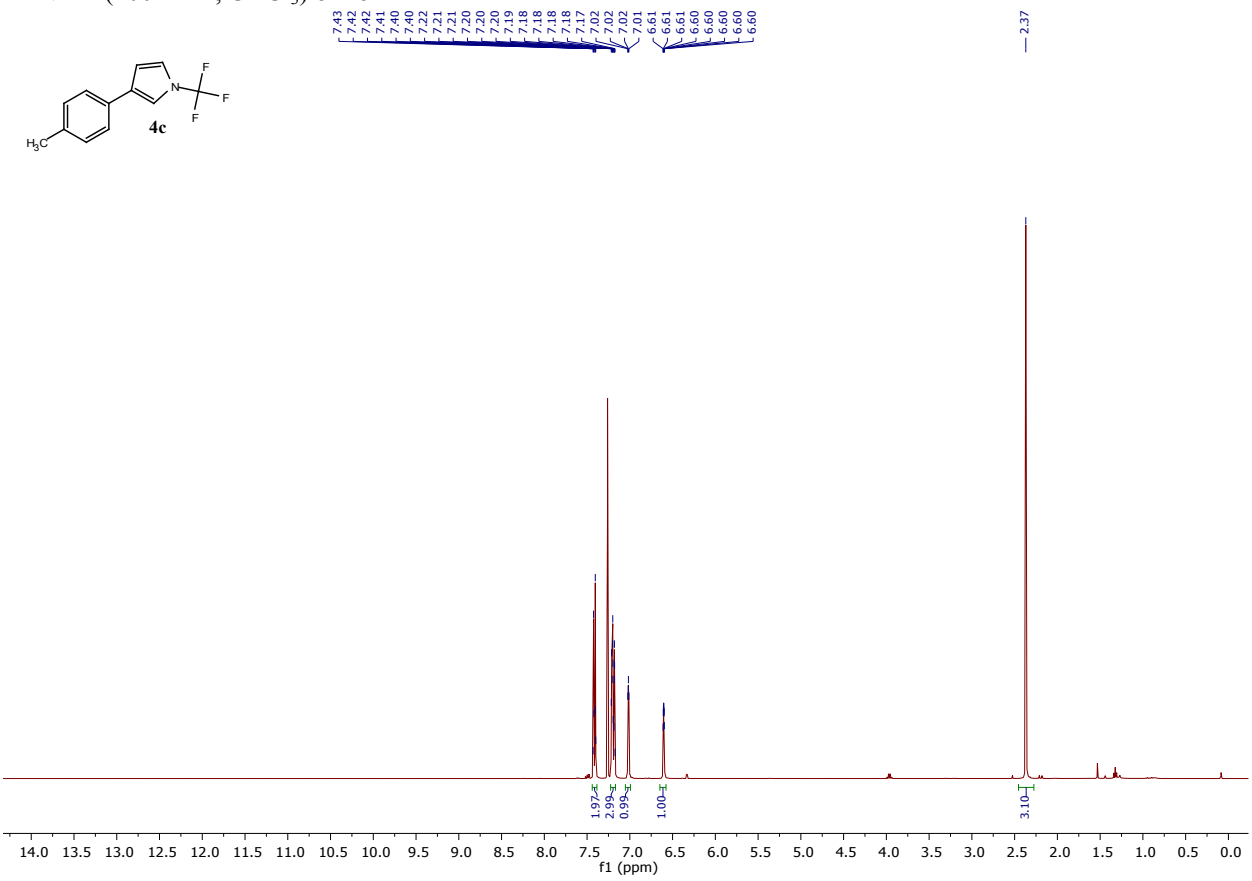
^{13}C NMR (101 MHz, $CDCl_3$) of **4b**



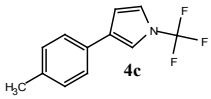
^{19}F NMR (376 MHz, $CDCl_3$) of **4b**



^{1}H NMR (400 MHz, $CDCl_3$) of **4c**

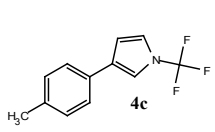


^{13}C NMR (101 MHz, $CDCl_3$) of **4c**



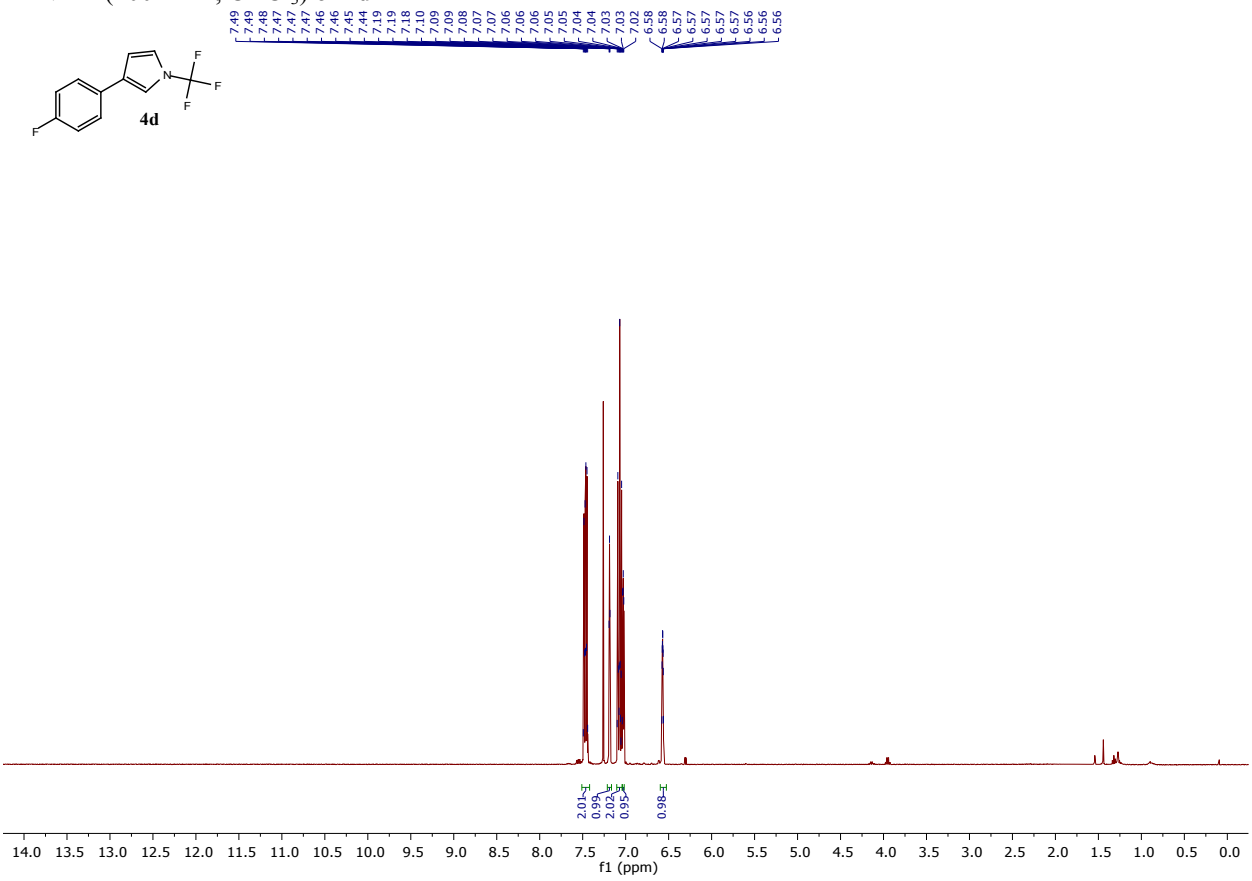
4c

^{19}F NMR (376 MHz, $CDCl_3$) of **4c**

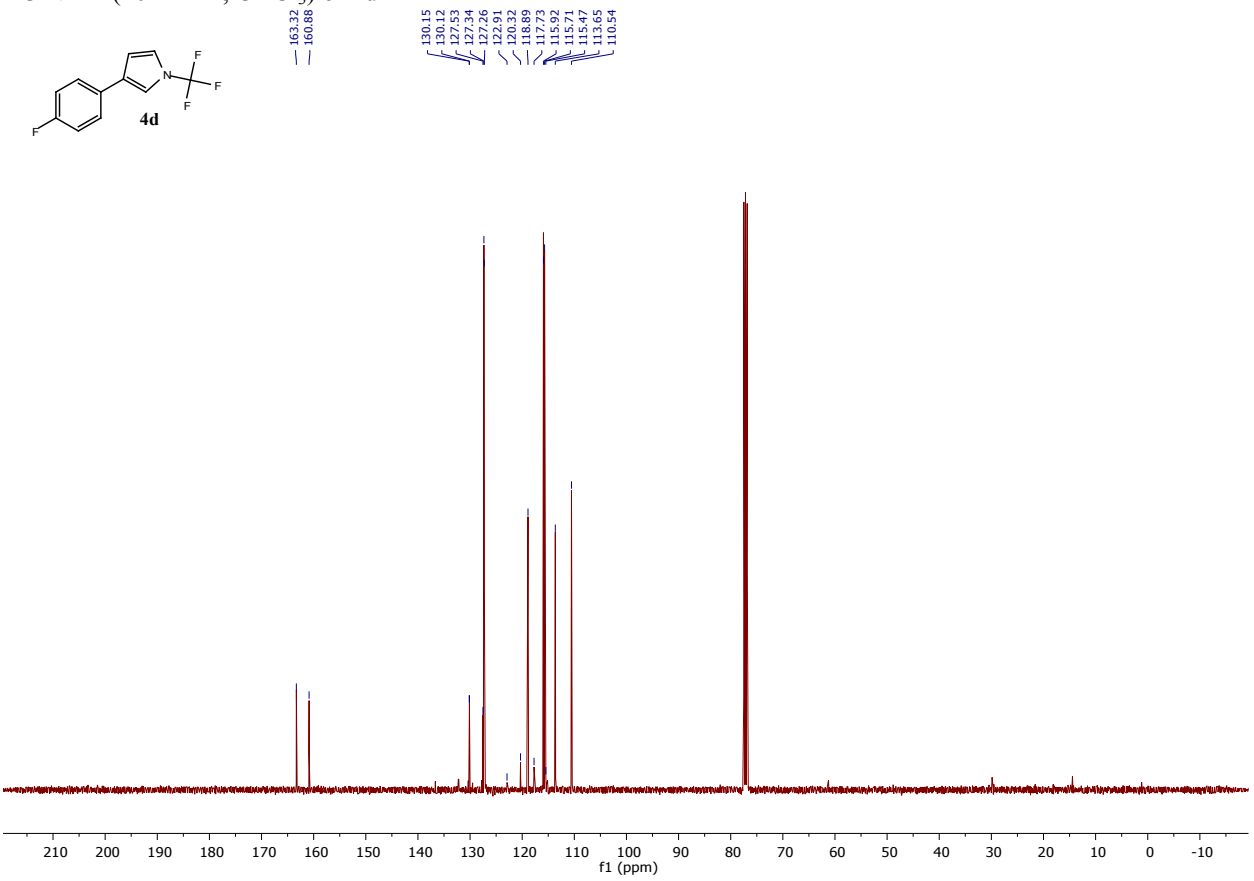


4c

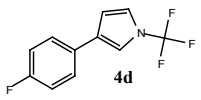
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



^{13}C NMR (101 MHz, $CDCl_3$) of **4d**

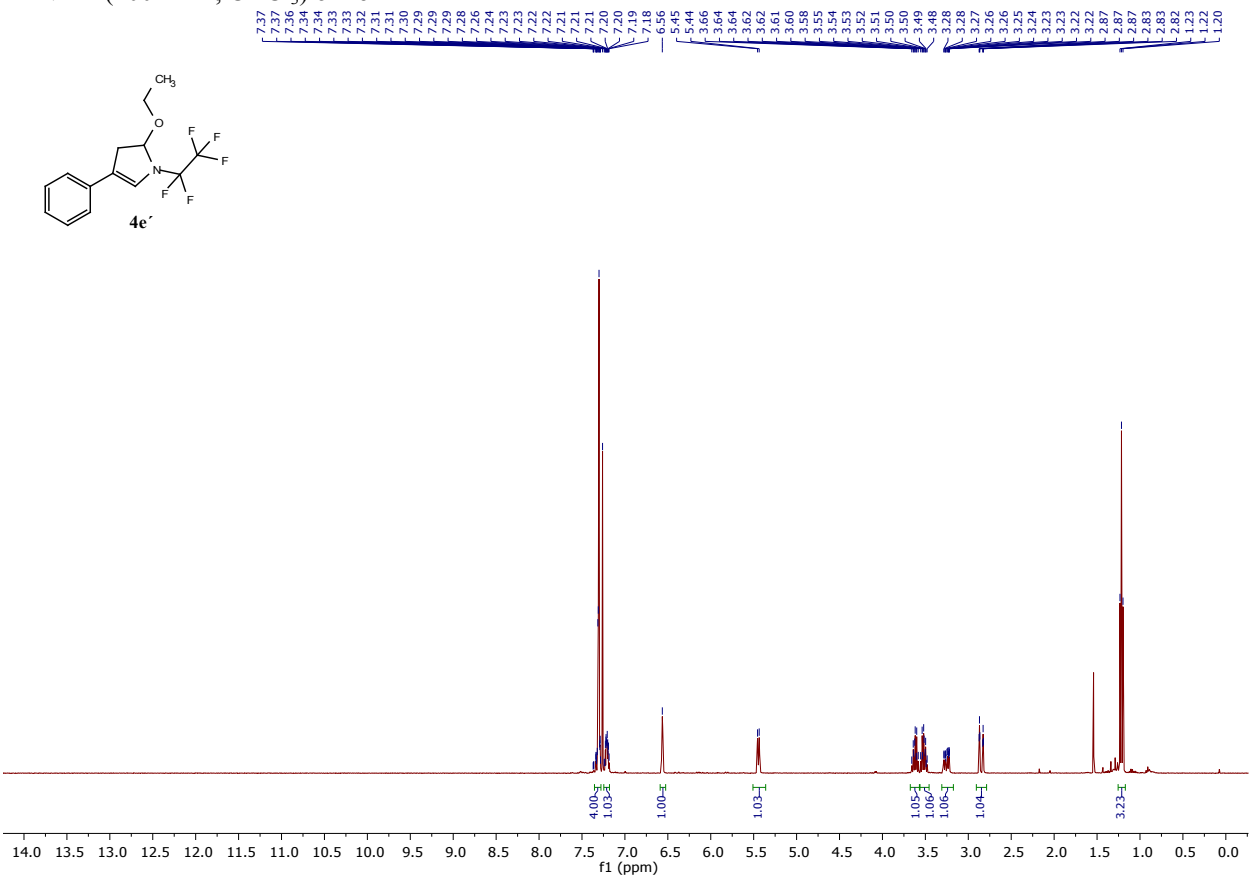


^{19}F NMR (376 MHz, $CDCl_3$) of **4d**

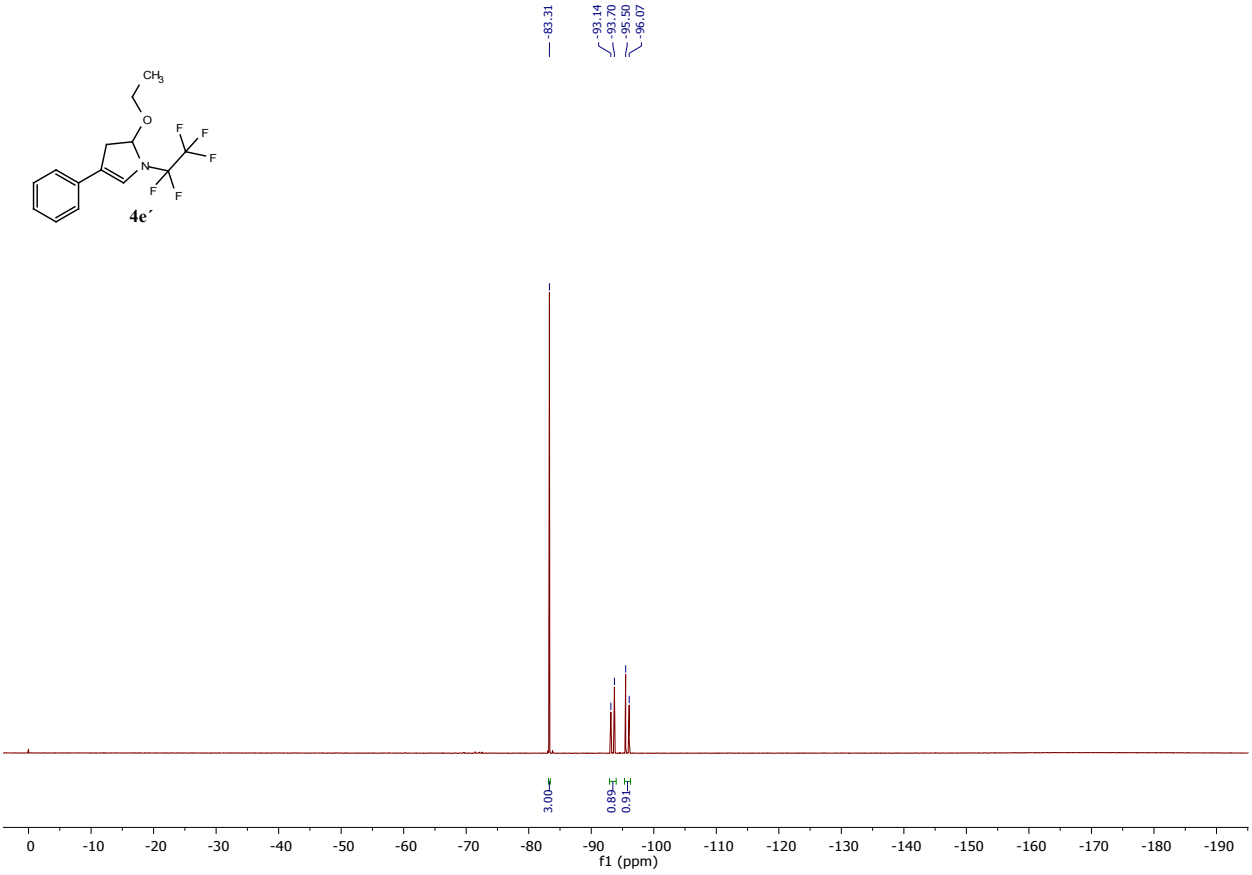


4d

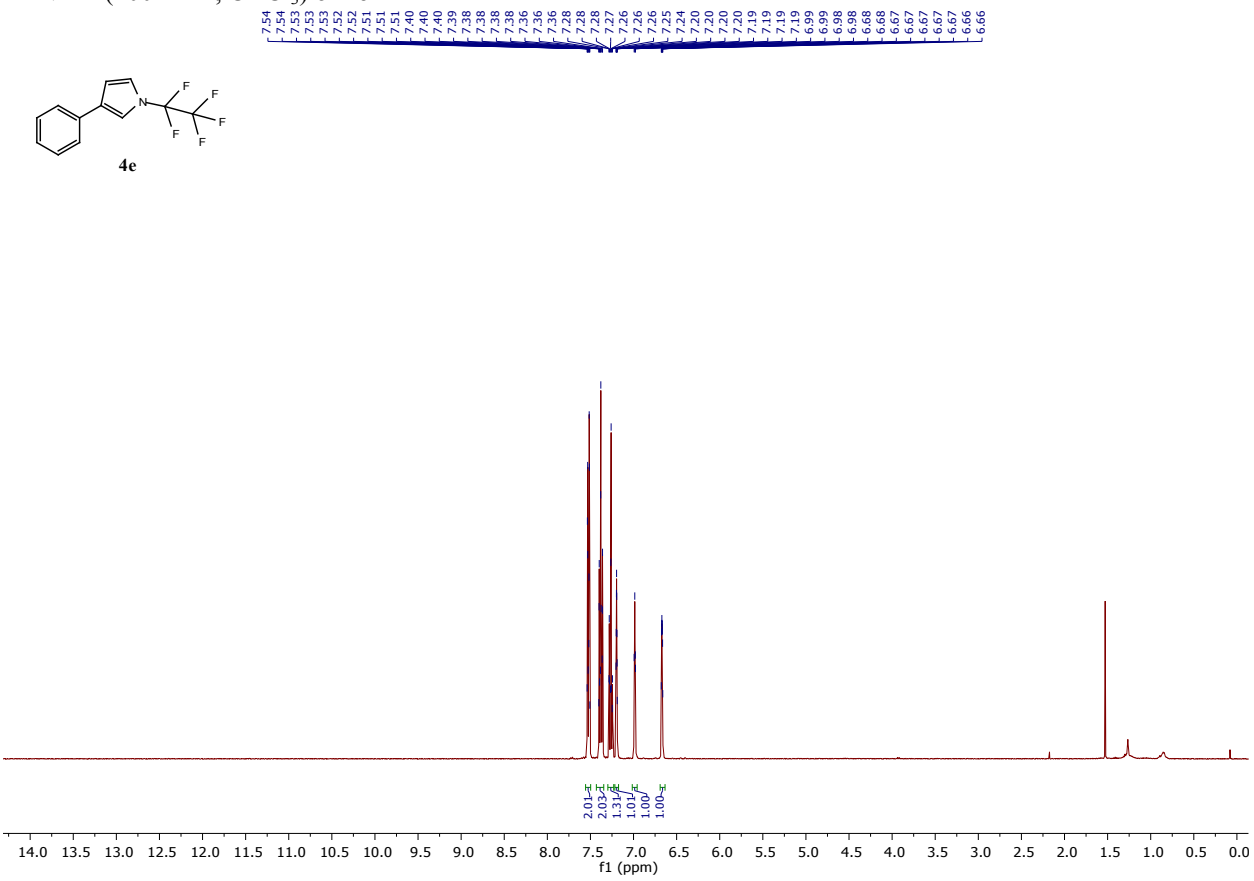
^{1}H NMR (400 MHz, $CDCl_3$) of **4e´**



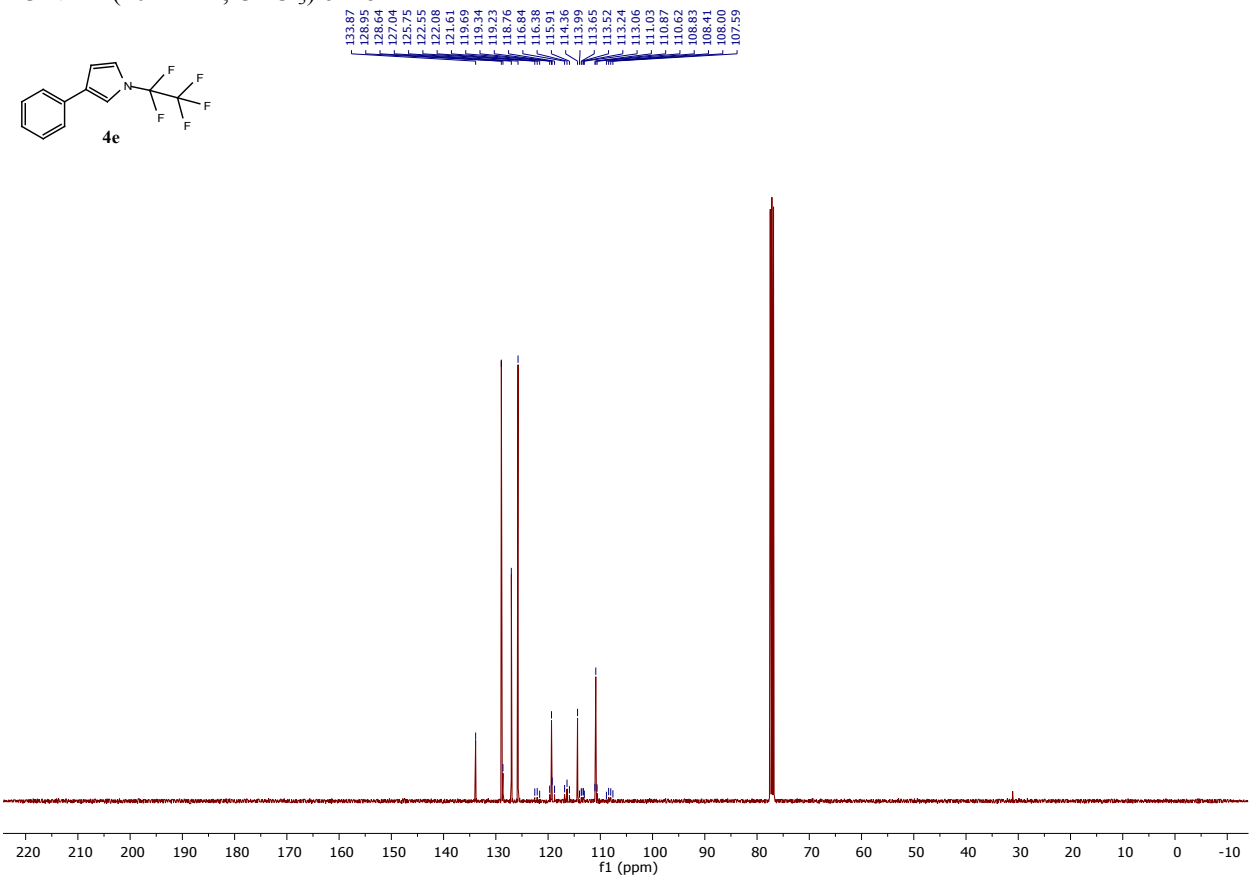
^{19}F NMR (376 MHz, $CDCl_3$) of **4e´**



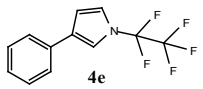
^{1}H NMR (400 MHz, $CDCl_3$) of **4e**



^{13}C NMR (101 MHz, $CDCl_3$) of **4e**

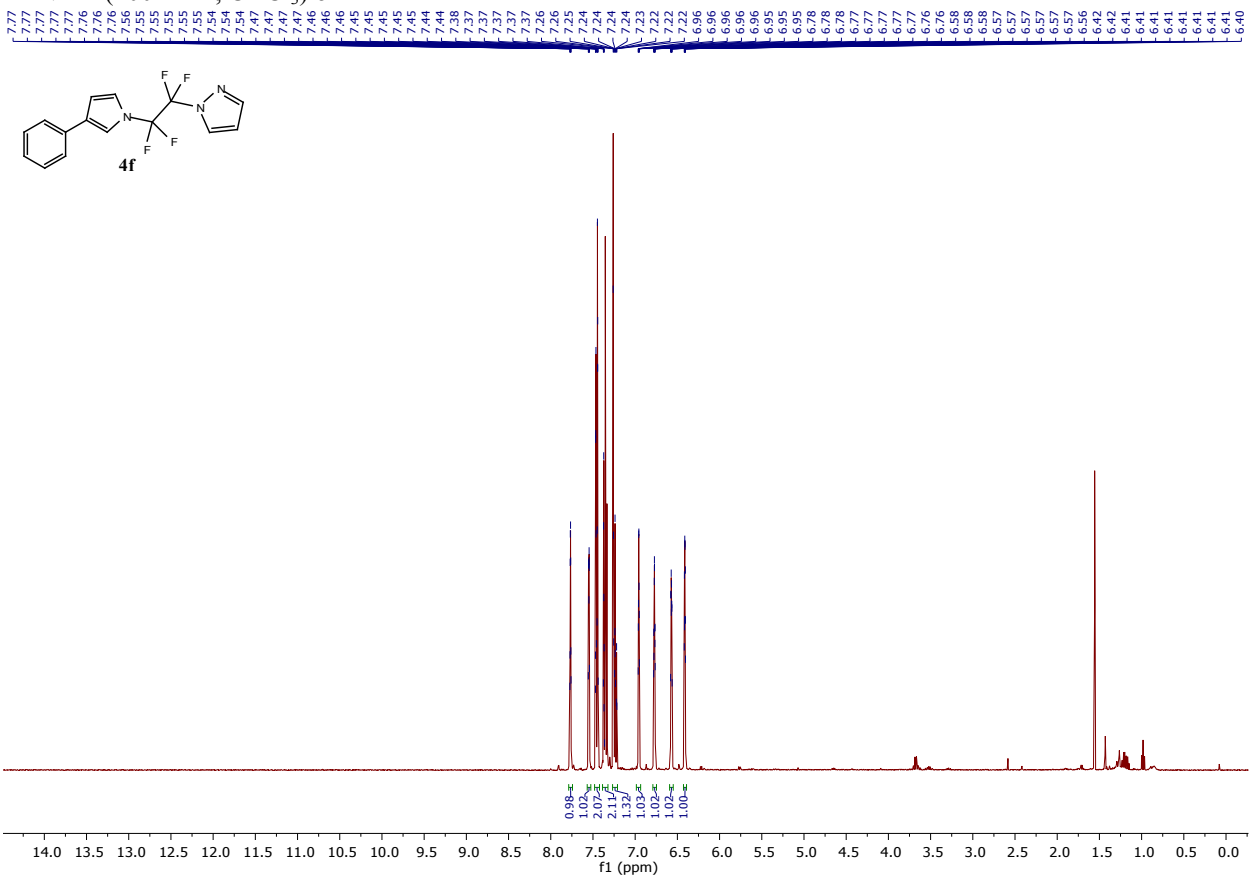


^{19}F NMR (376 MHz, $CDCl_3$) of **4e**

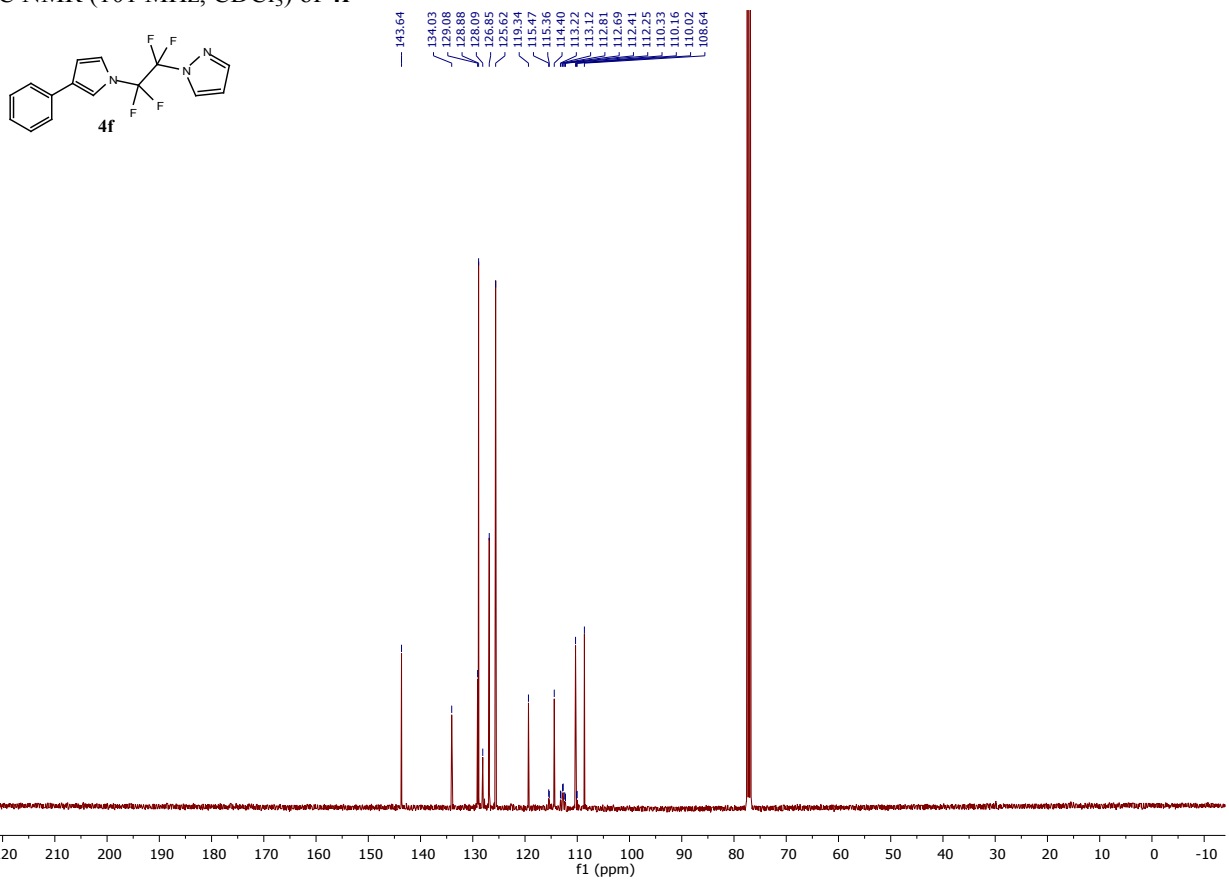


4e

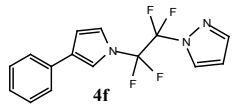
^{1}H NMR (400 MHz, $CDCl_3$) of **4f**



^{13}C NMR (101 MHz, $CDCl_3$) of **4f**

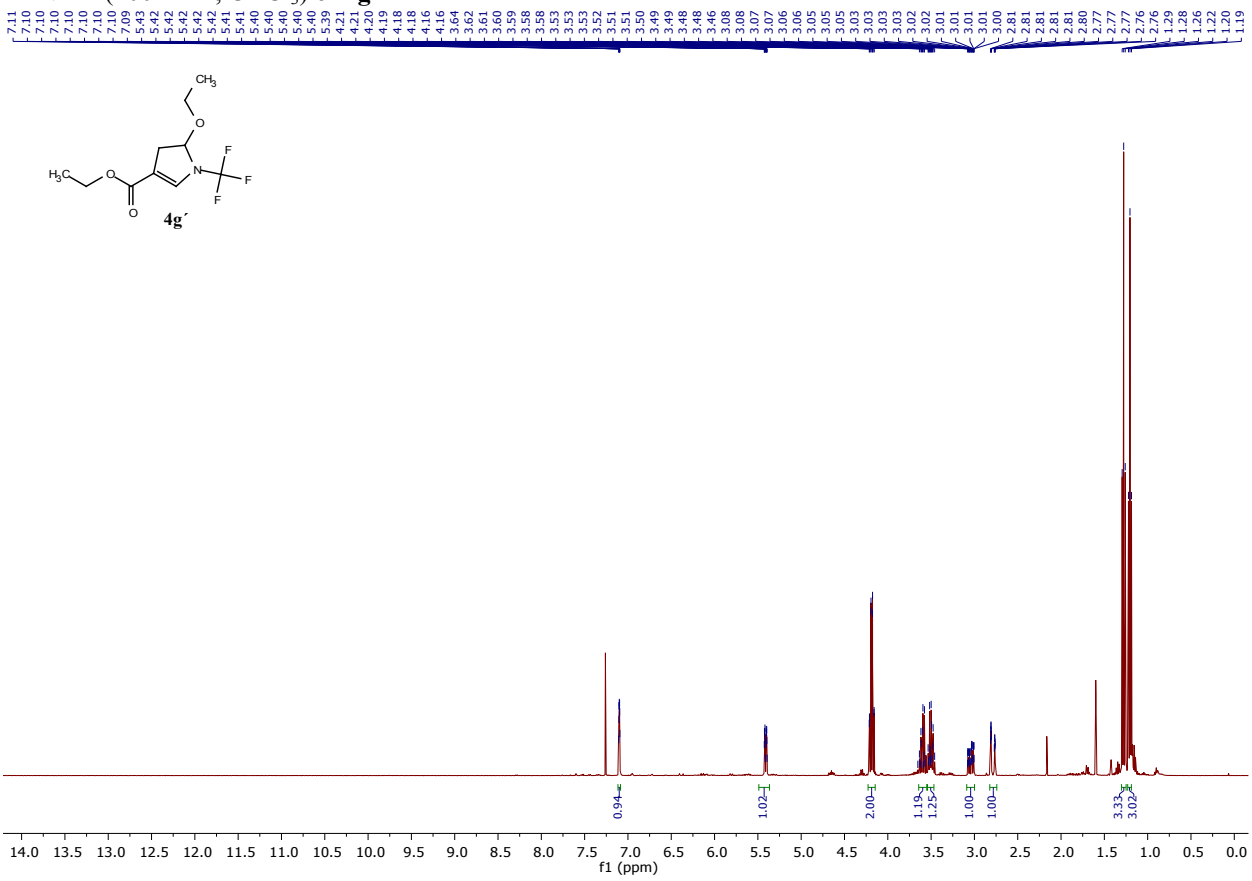


^{19}F NMR (376 MHz, $CDCl_3$) of **4f**

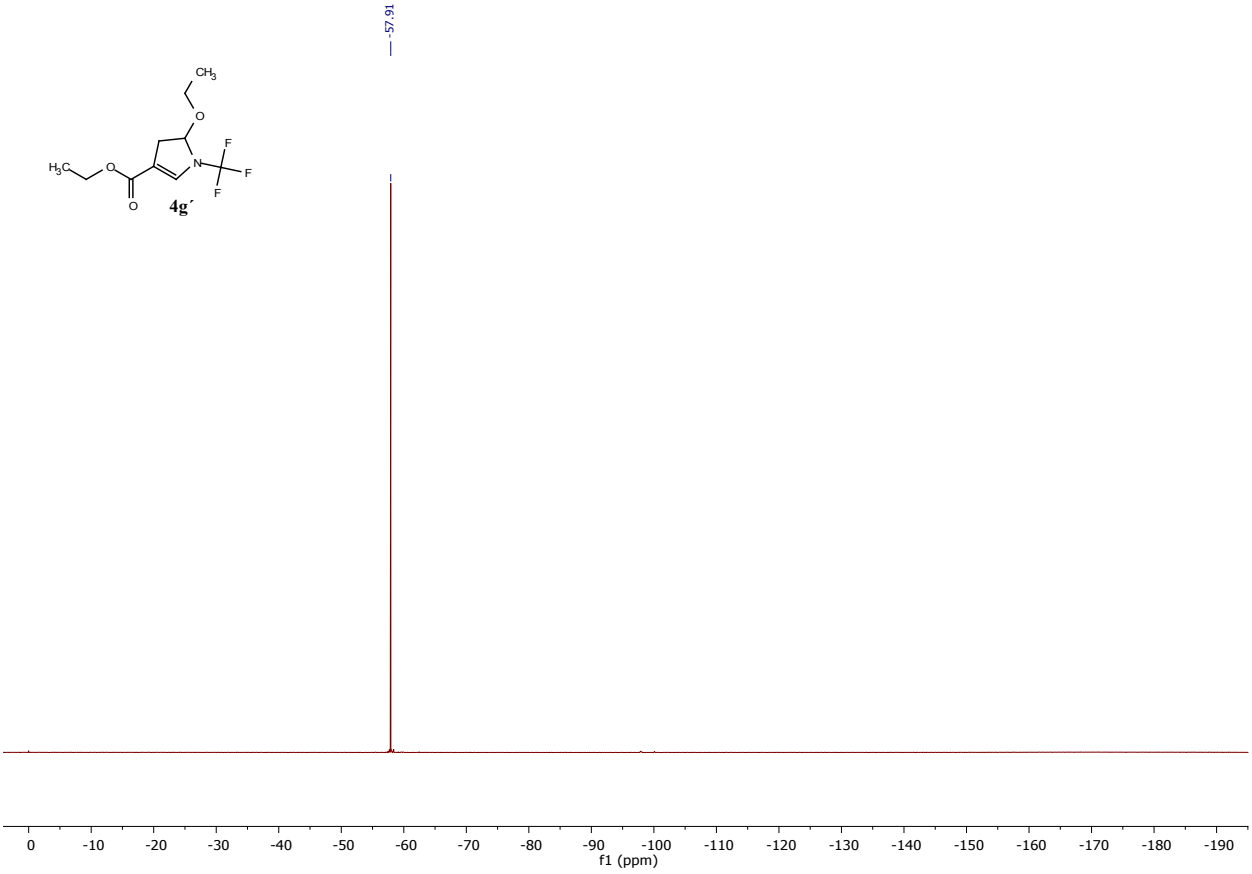


4f

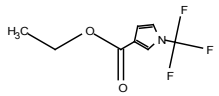
^{1}H NMR (400 MHz, $CDCl_3$) of **4g´**



^{19}F NMR (376 MHz, $CDCl_3$) of **4g´**

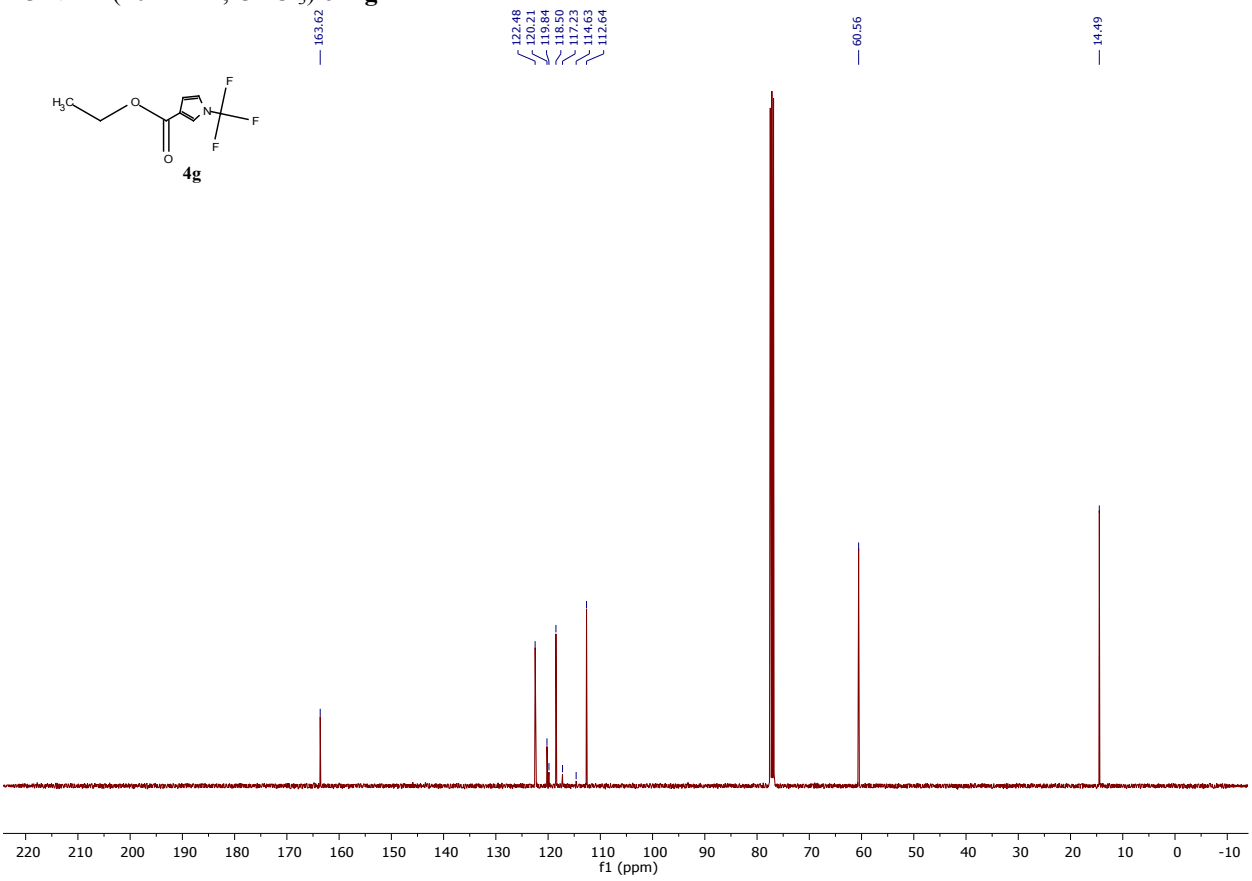


^{1}H NMR (400 MHz, $CDCl_3$) of **4g**

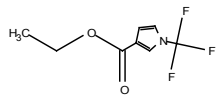


4g

^{13}C NMR (101 MHz, $CDCl_3$) of **4g**

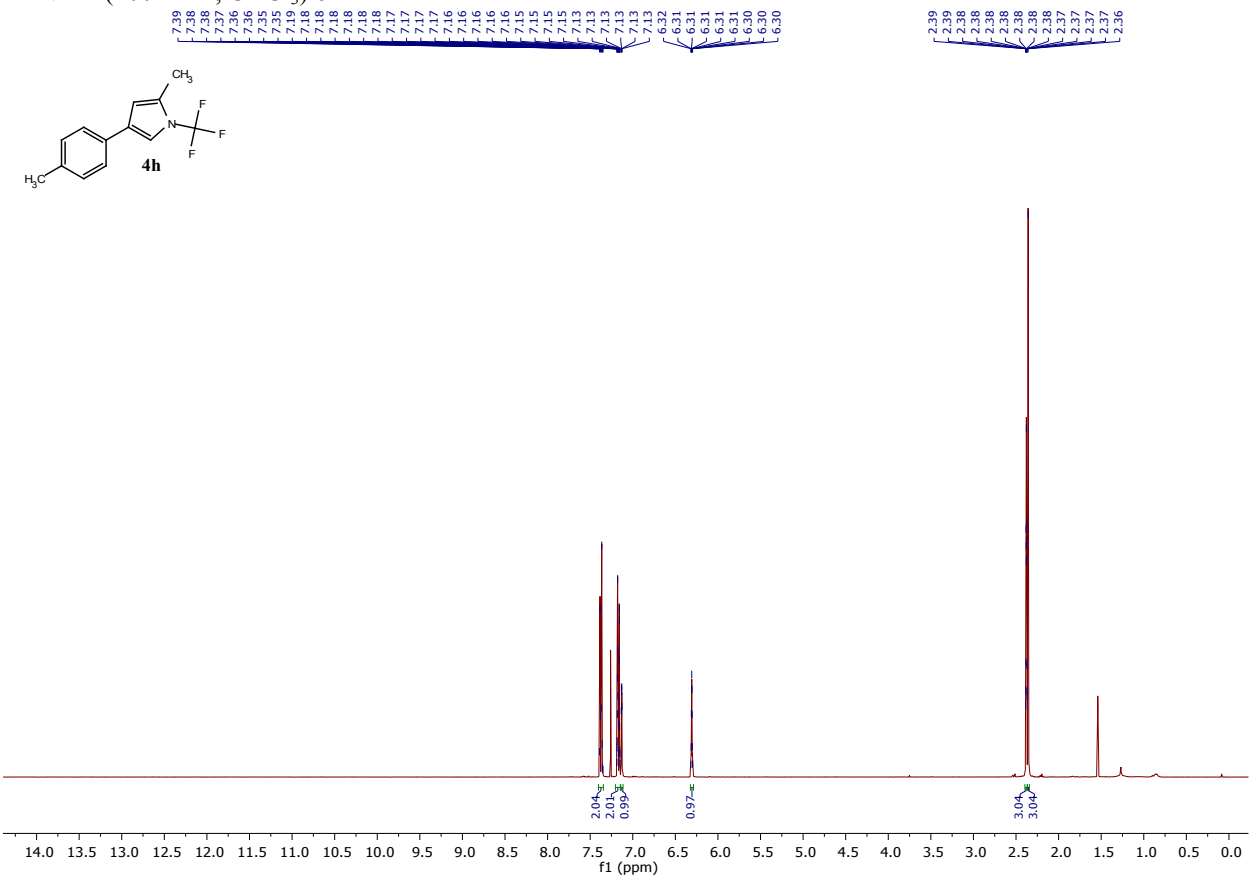


^{19}F NMR (376 MHz, $CDCl_3$) of **4g**

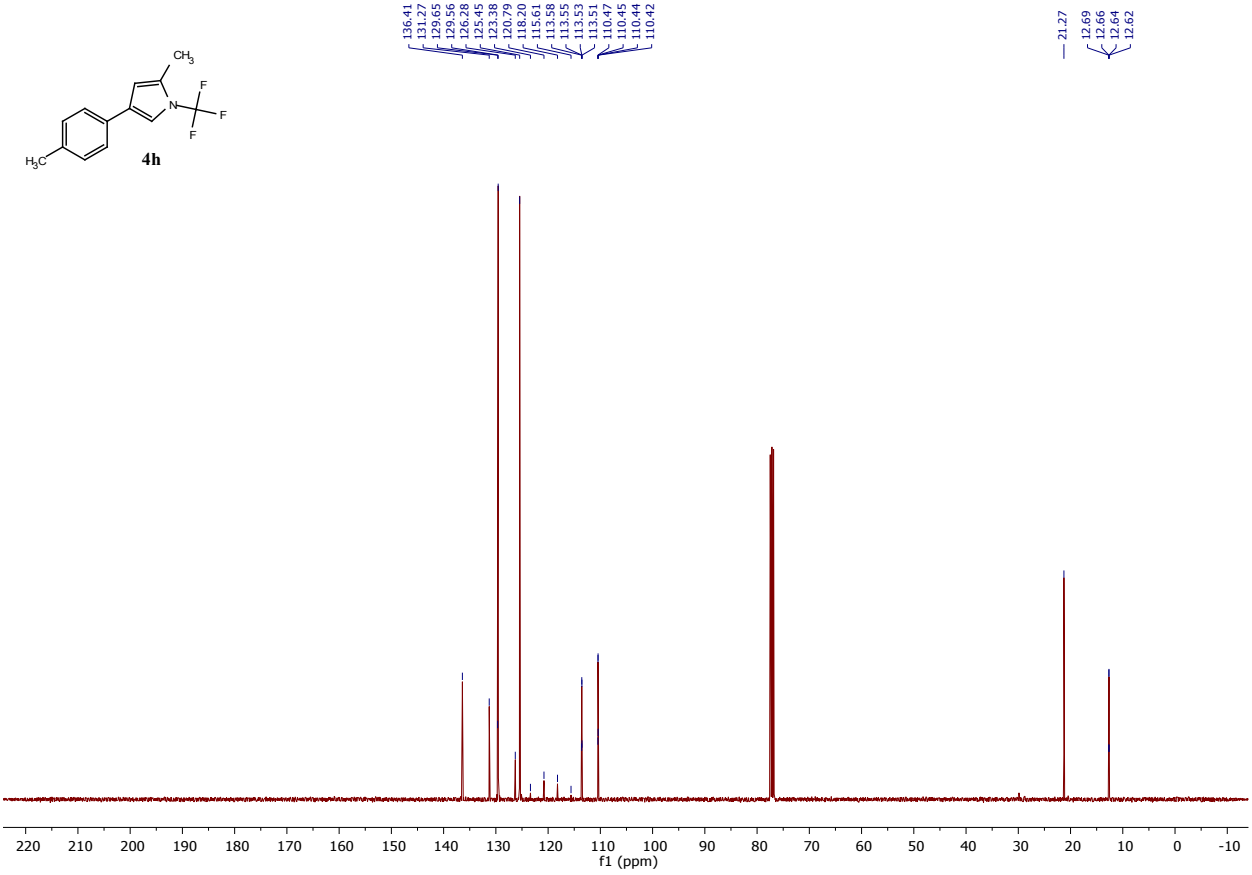


4g

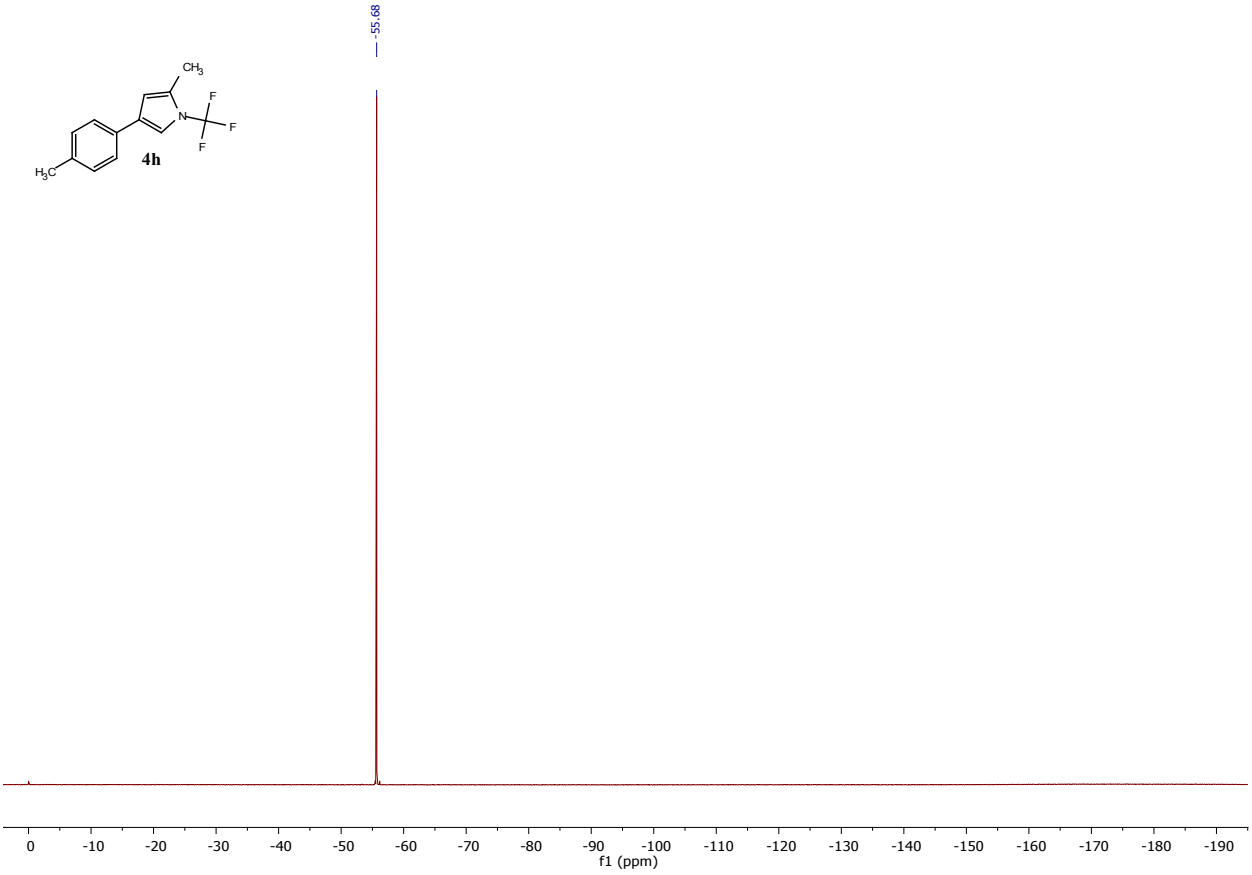
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



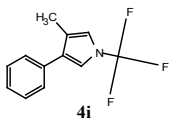
^{13}C NMR (101 MHz, $CDCl_3$) of **4h**



^{19}F NMR (376 MHz, $CDCl_3$) of **4h**

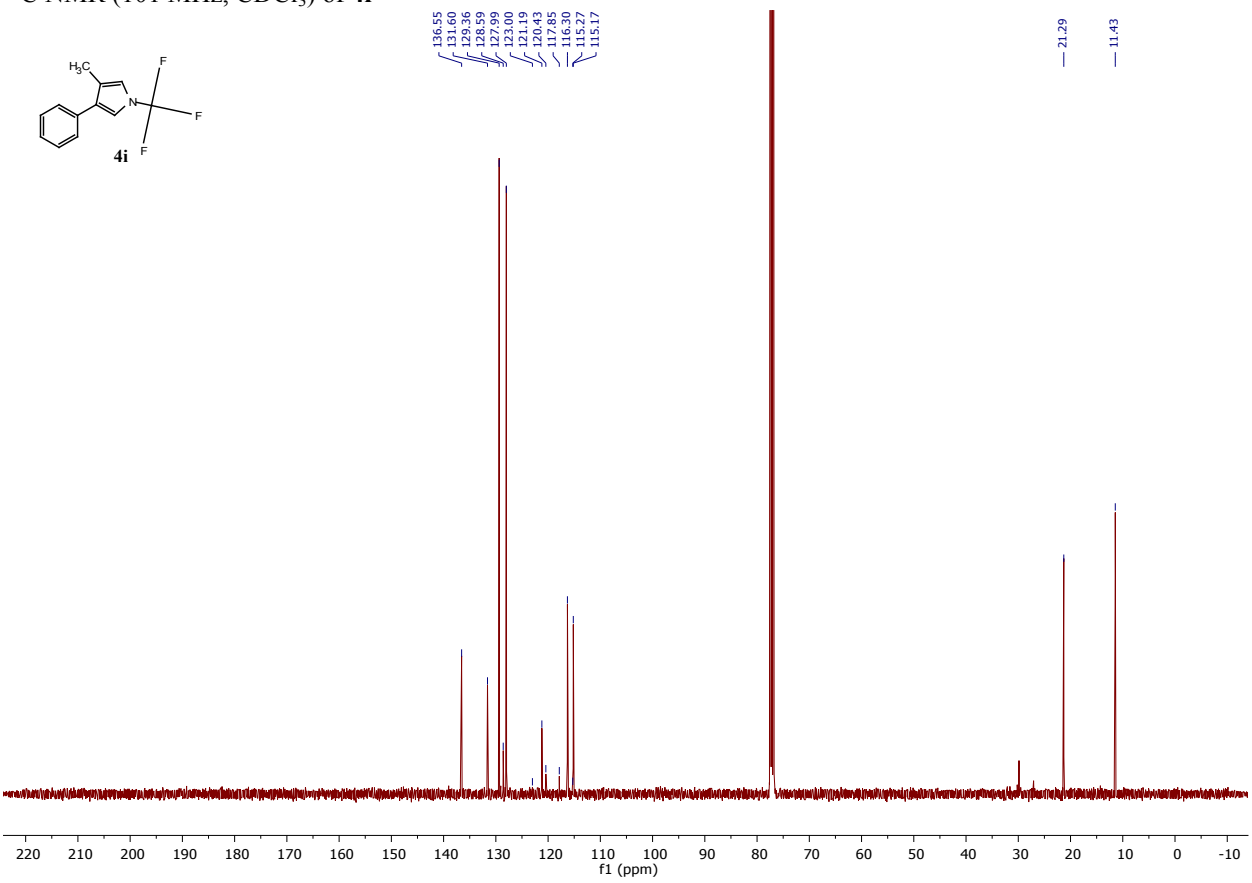


^{1}H NMR (400 MHz, $CDCl_3$) of **4i**

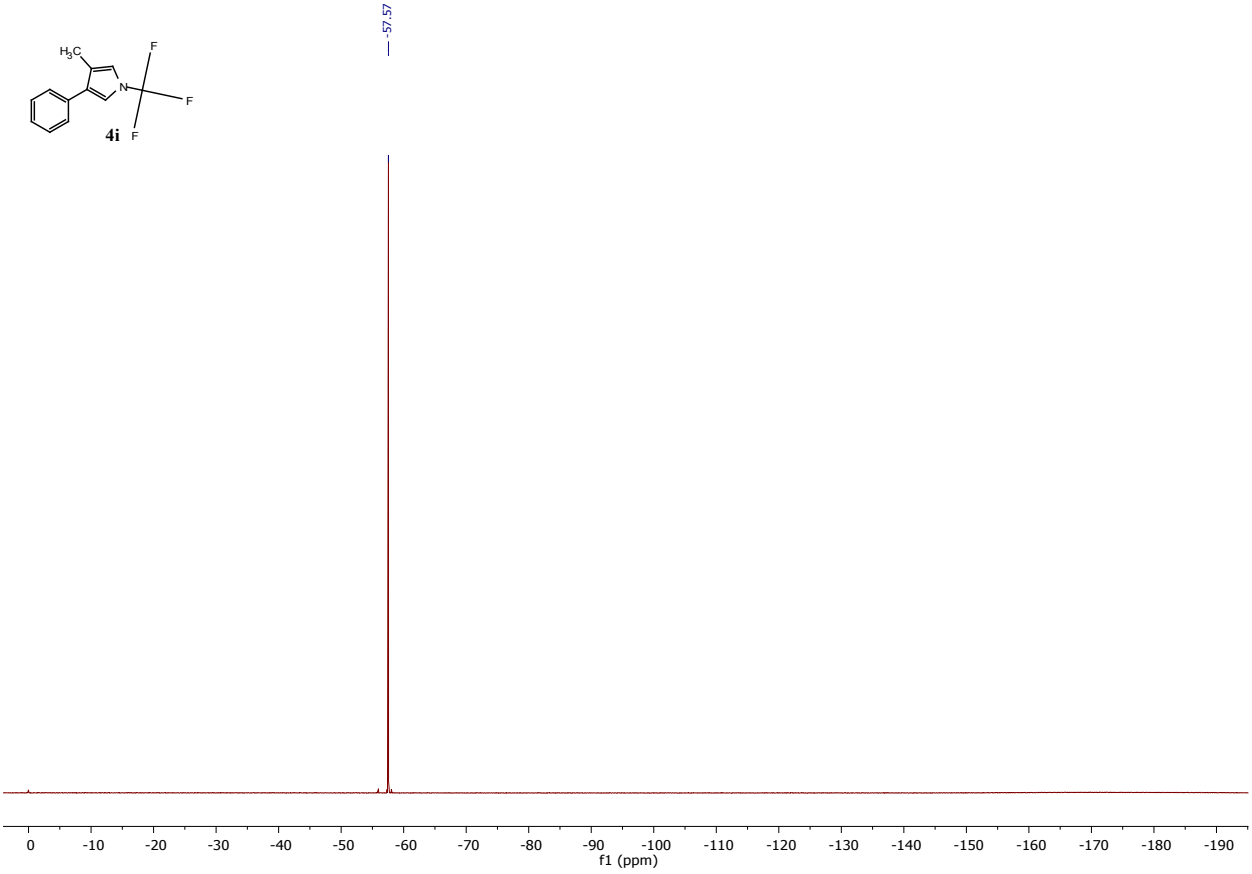


4i

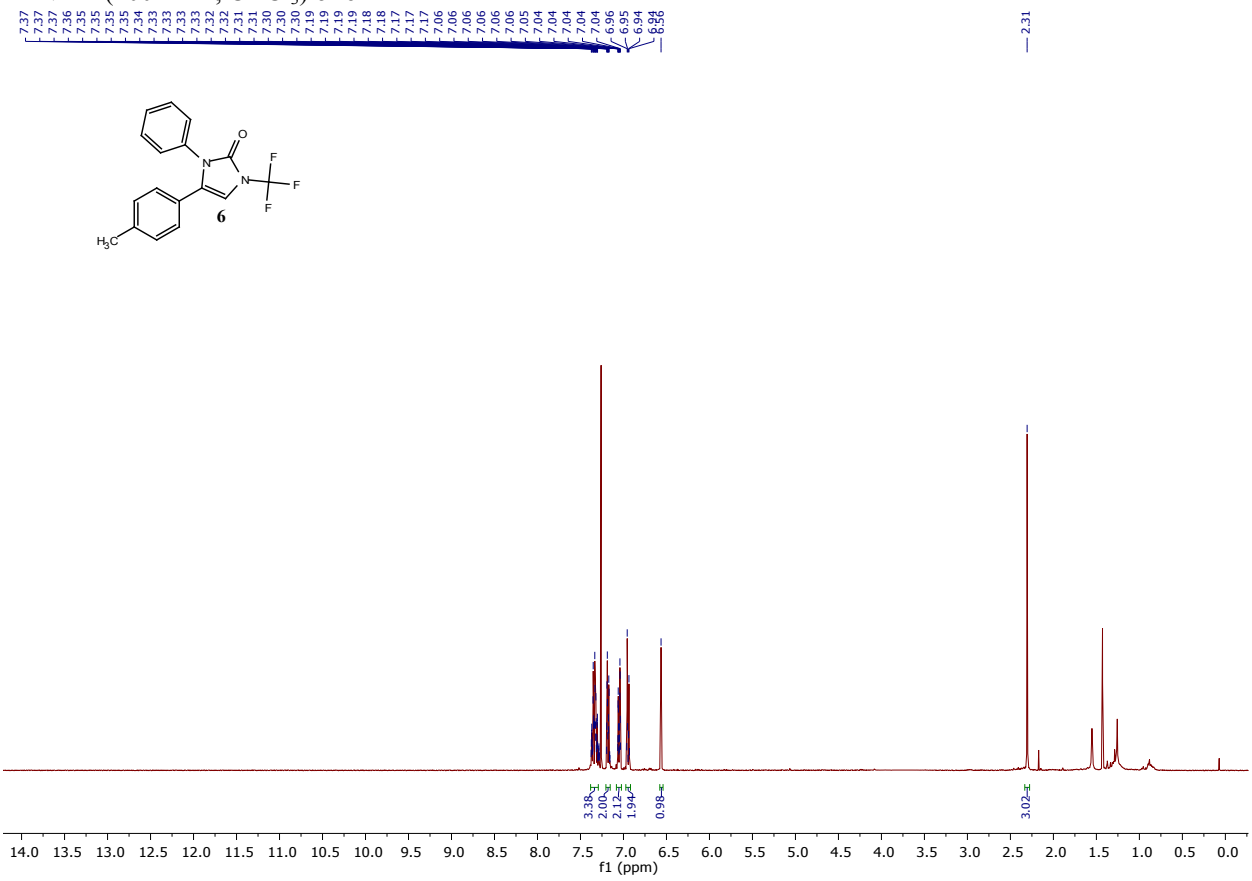
^{13}C NMR (101 MHz, $CDCl_3$) of **4i**



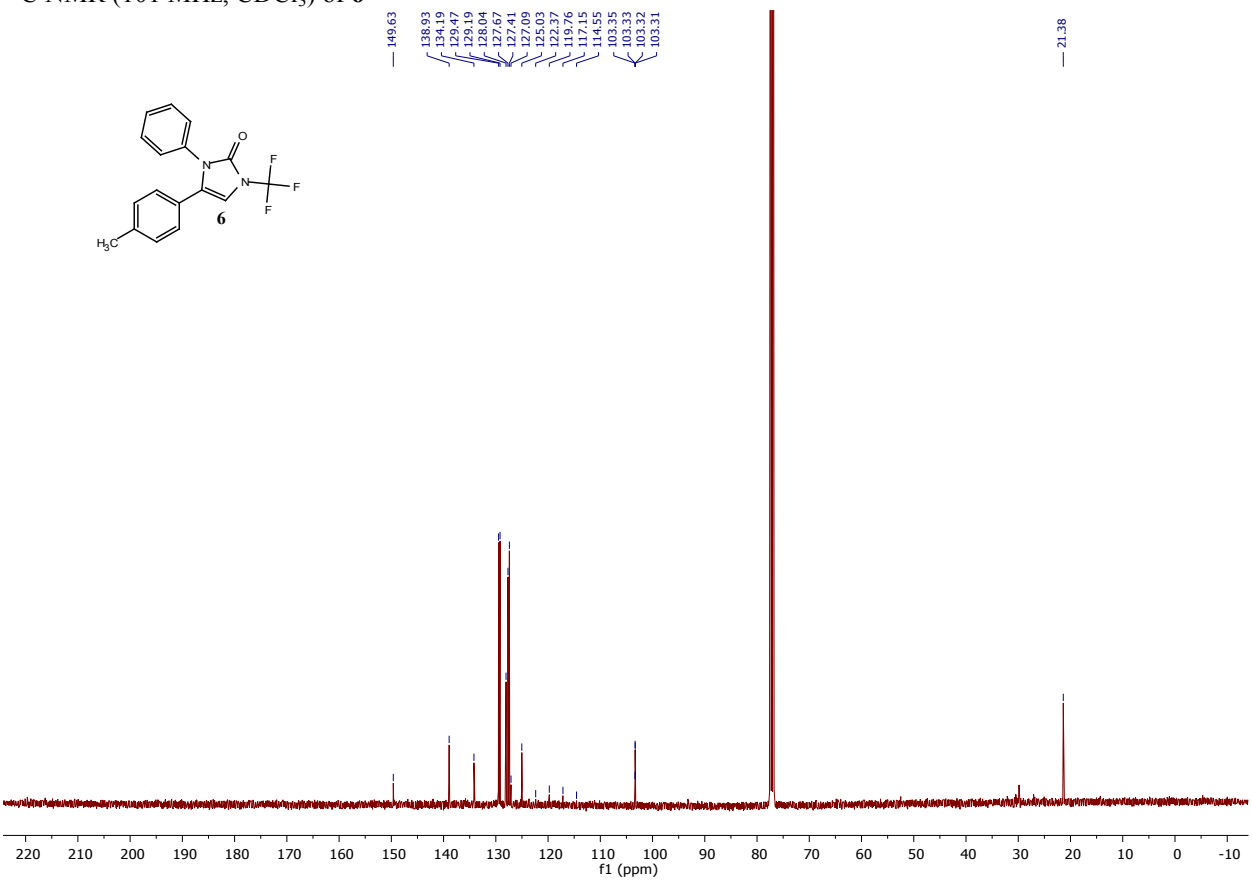
^{19}F NMR (376 MHz, $CDCl_3$) of **4i**



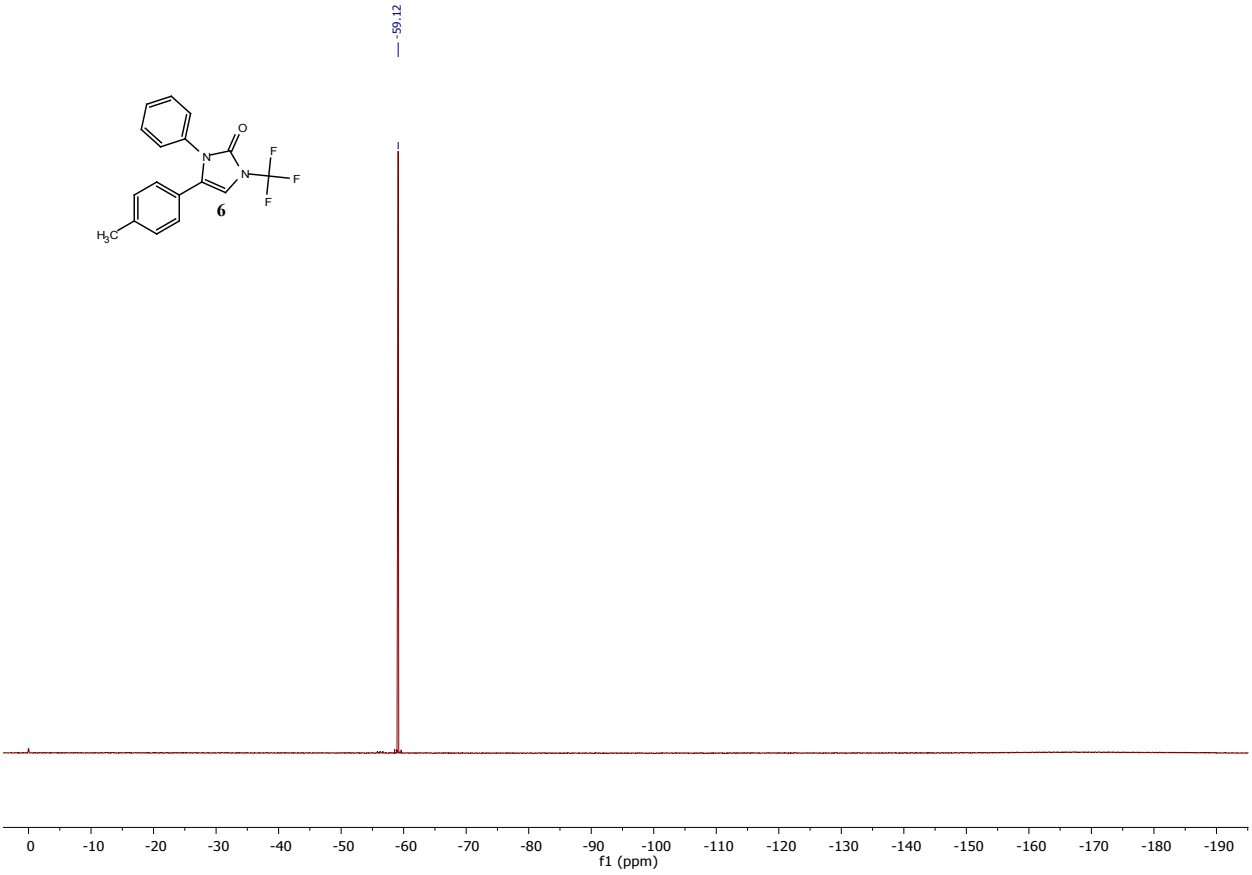
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



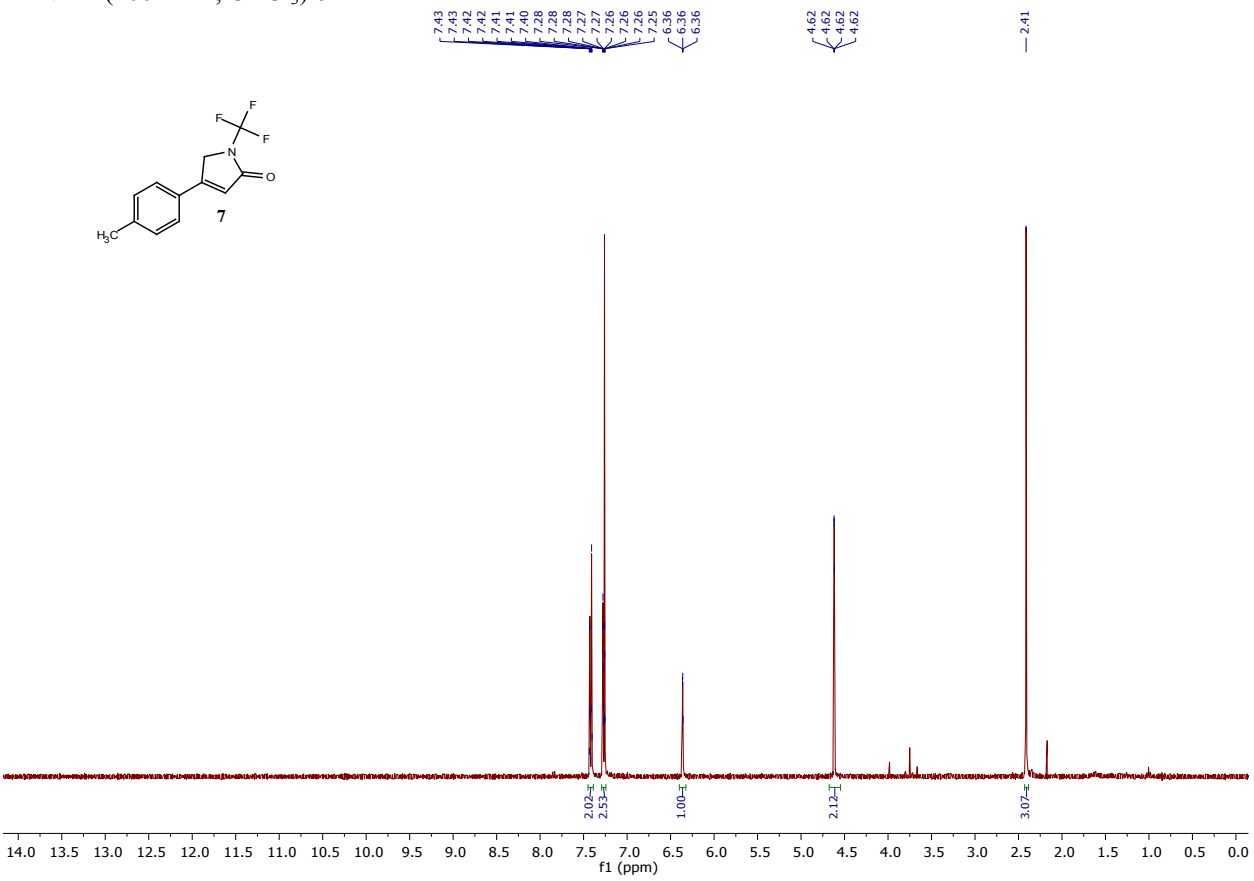
^{13}C NMR (101 MHz, $CDCl_3$) of **6**



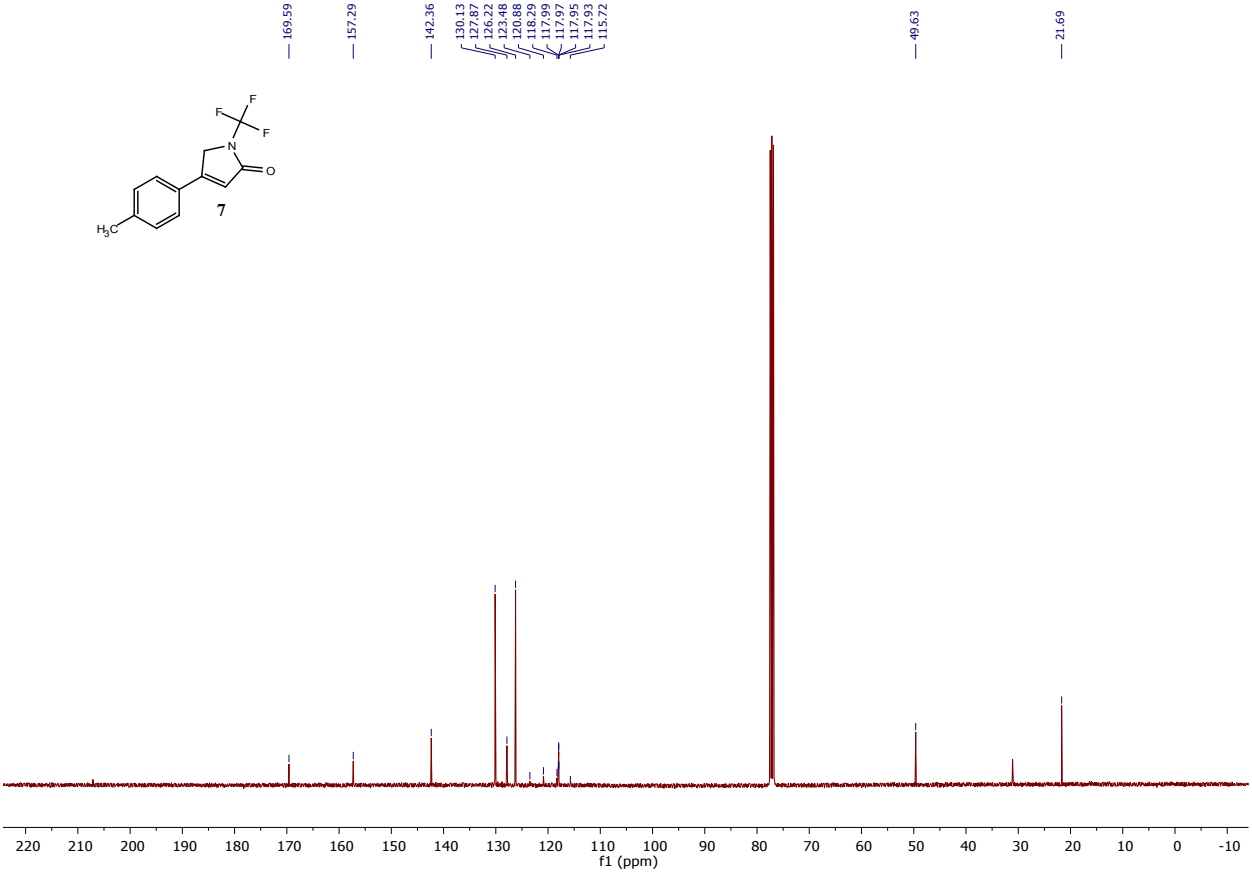
^{19}F NMR (376 MHz, $CDCl_3$) of **6**



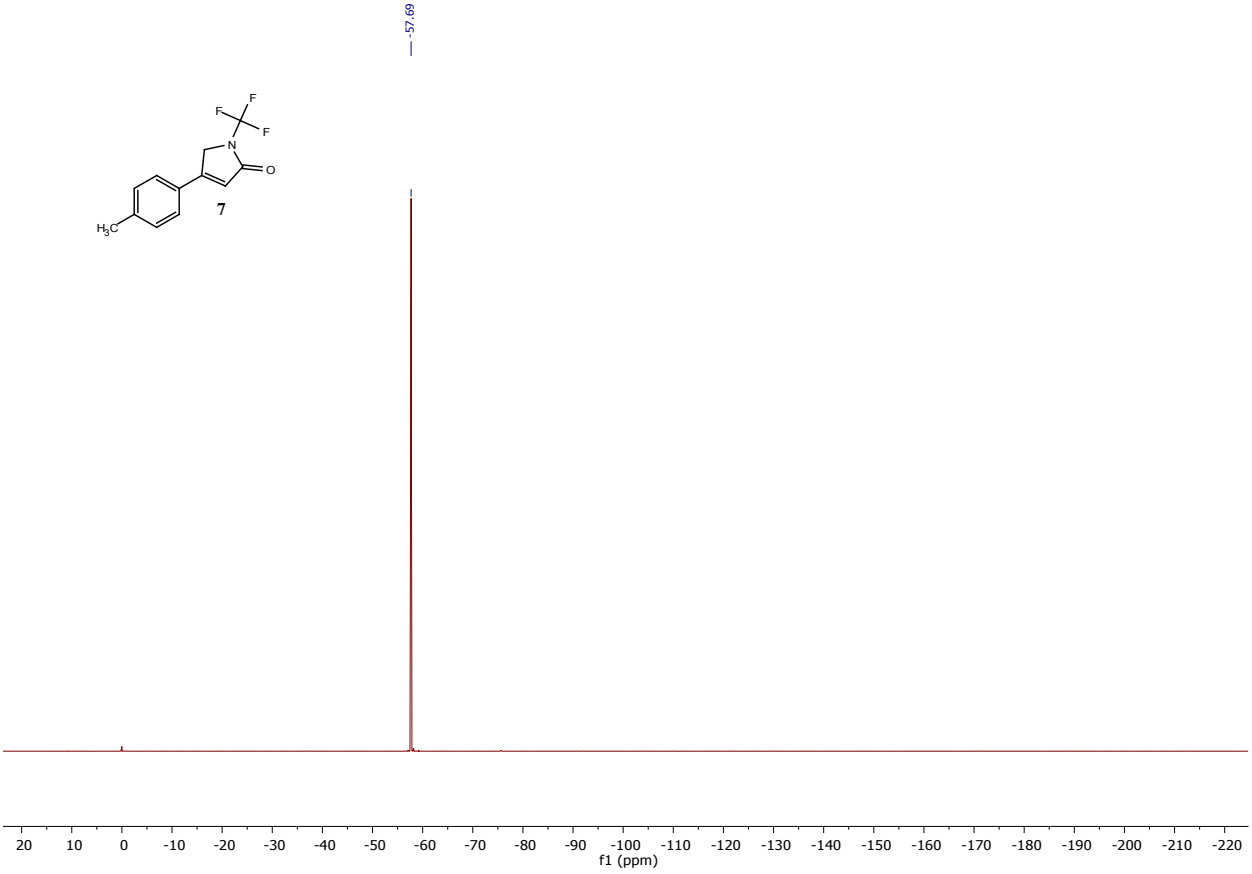
^{1}H NMR (400 MHz, $CDCl_3$) of **7**



^{13}C NMR (101 MHz, $CDCl_3$) of **7**



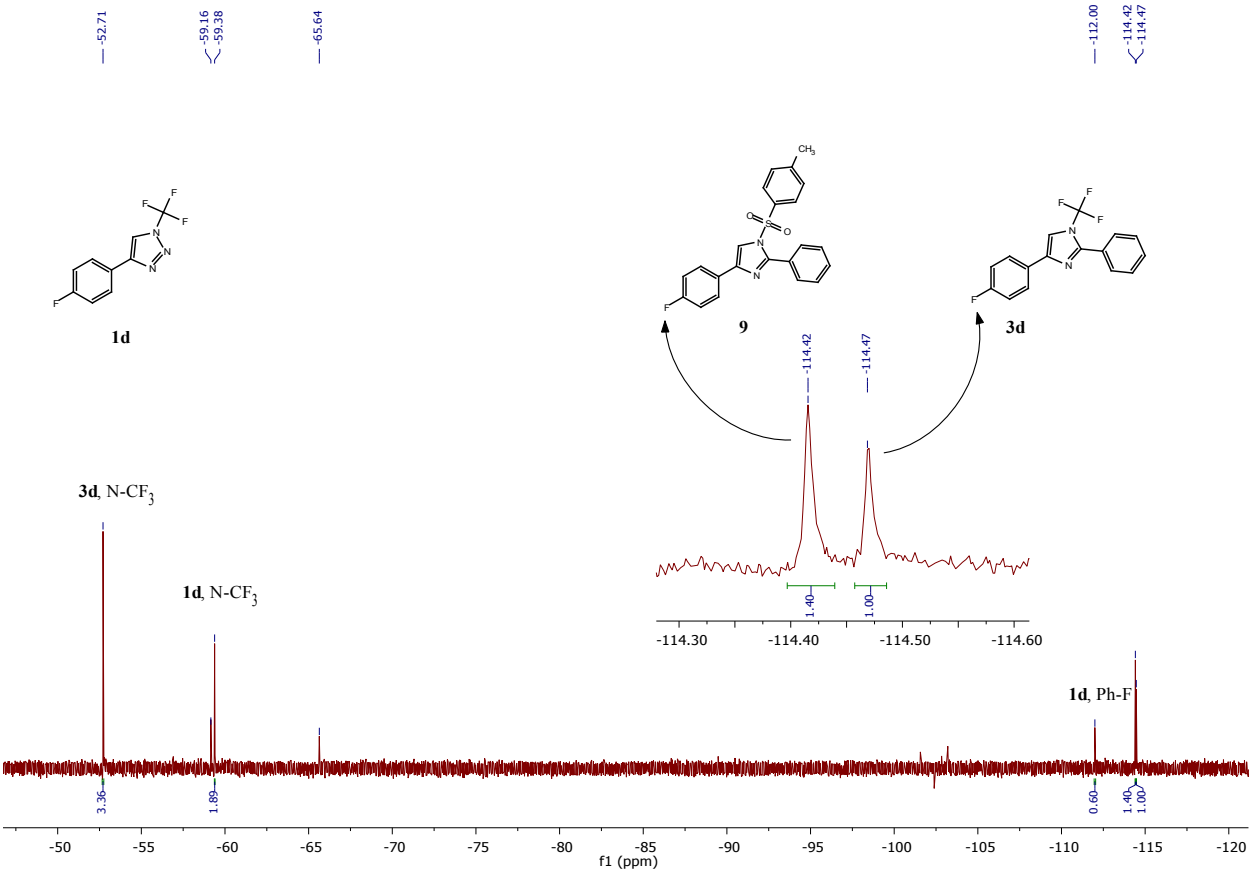
^{19}F NMR (376 MHz, $CDCl_3$) of **7**



Competition experiment

N-perfluoroalkyl triazole **1d** (0.1 mmol; 1 equiv.), N-tosyl triazole **8** (0.1 mmol; 1 equiv.) and benzonitrile (0.1 mmol; 1 equiv.) were dissolved in dry $CHCl_3$ (2 mL) and a solution of rhodium (II) octanoate (0.001 mmol; 0.01 M in dry $CHCl_3$) was added. The vial was capped and mixture was heated at 140°C for 20 min in microwave reactor followed by measurement of ^{19}F $\{^1H\}$ NMR spectra.

^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) - competition experiment

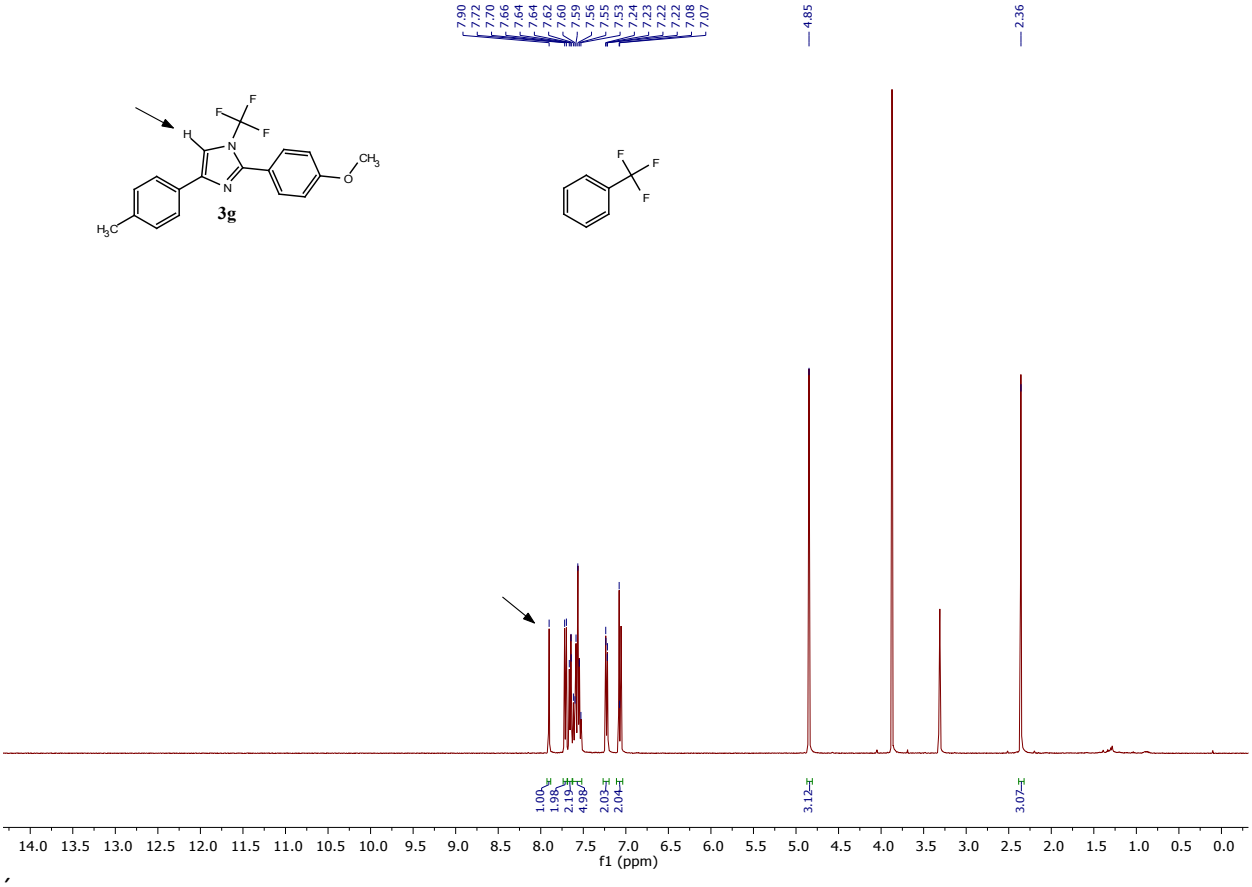


Stability of N-CF_3 imidazole 3g and pyrrole 4b in acidic and basic conditions

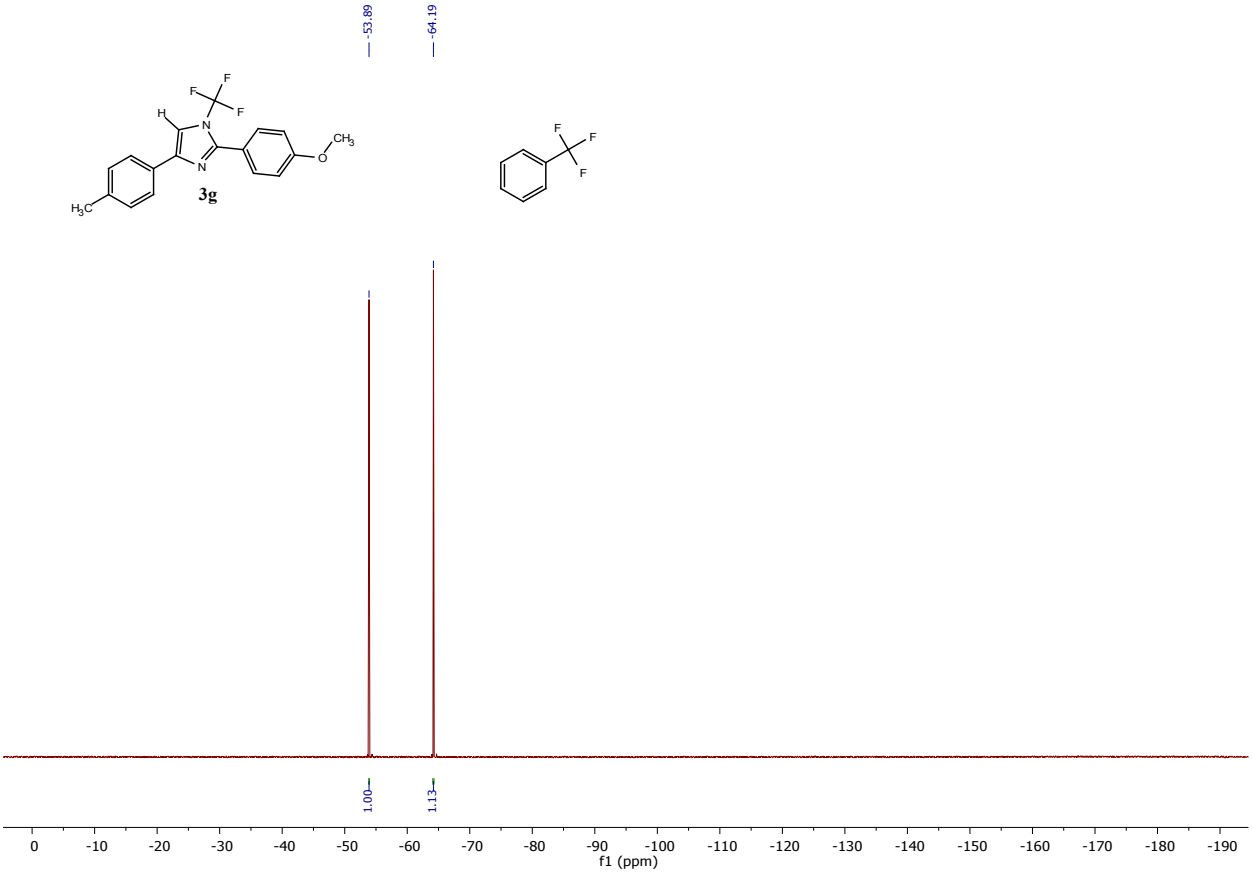
Stability of imidazole 3g

Imidazole **3g** (18 mg; 0.05 mmol) was dissolved in CD_3OD (1.06 mL) and $PhCF_3$ was added as an internal standard. Then ^{19}F and ^{1}H NMR spectra were measured. For stability experiment in basic condition, NaOH (10 mg; 0,25 mmol) was added to the prepared solution (500 µL) and after 18 h at 25 °C ^{19}F and ^{1}H NMR spectra were measured. In case of experiment in acidic conditions, 98% H_2SO_4 in D_2O (40 µL) was added to the prepared solution (560 µL) and after 18 h at room temperature ^{19}F and ^{1}H NMR spectra were measured.

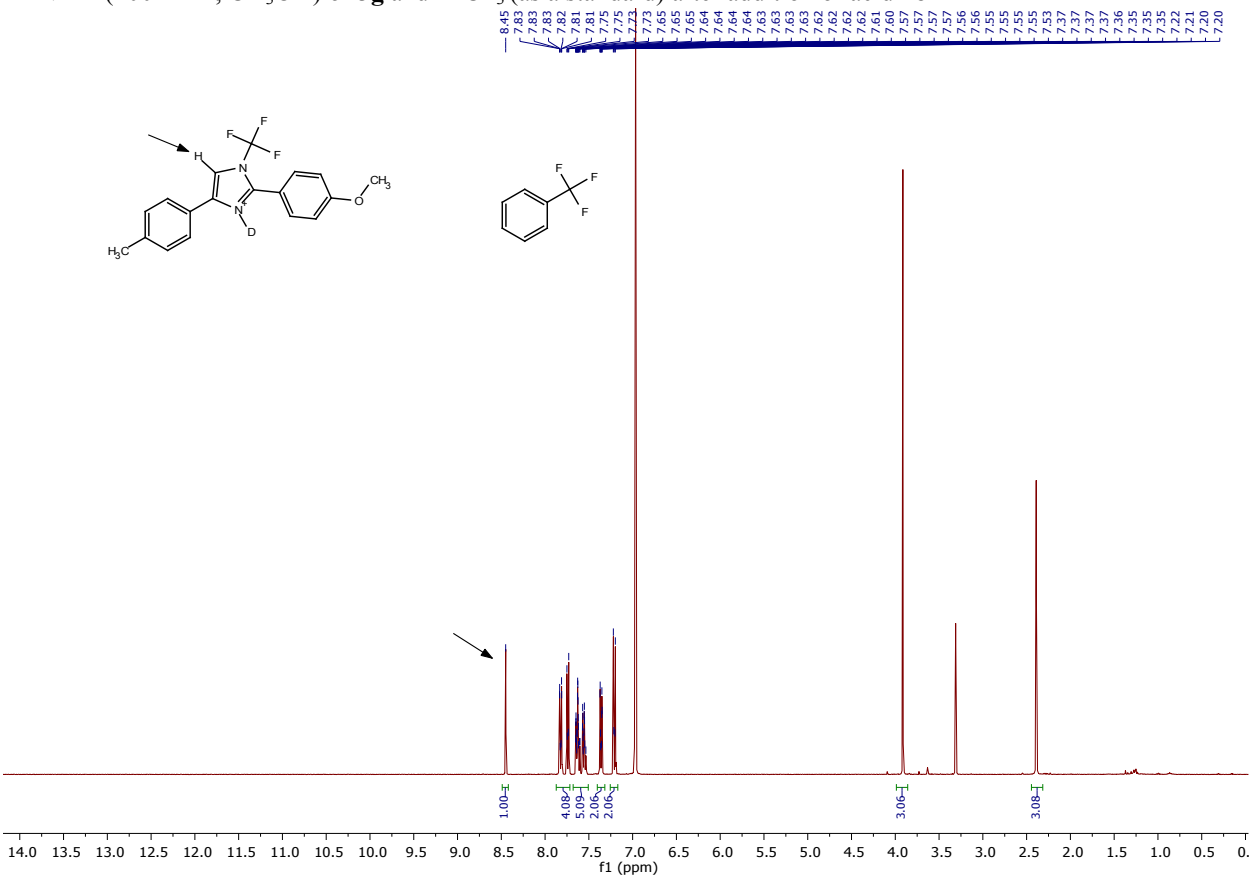
^{1}H NMR (400 MHz, CD_3OD) of **3g** and $PhCF_3$ (as a standard) before experiment



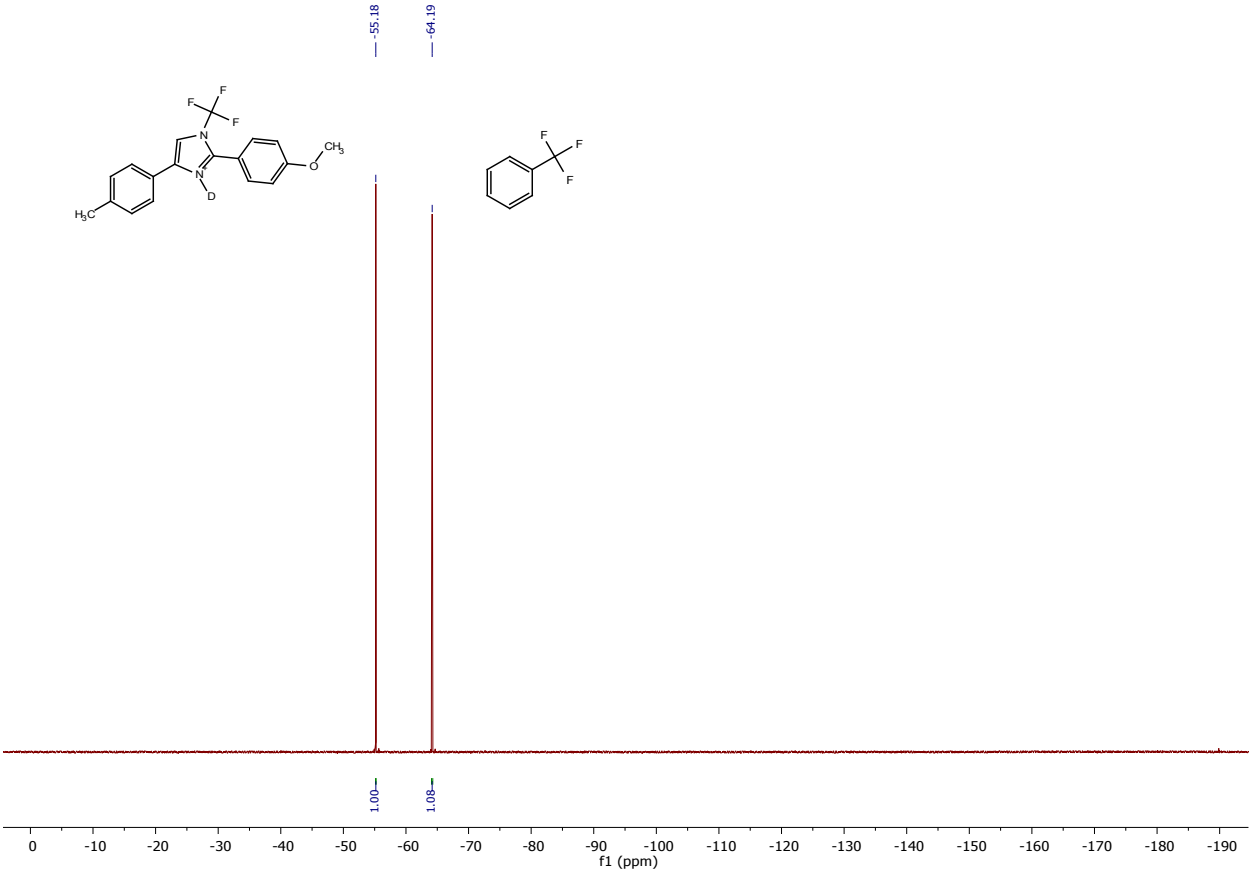
^{19}F NMR (376 MHz, CD_3OD) of **3g** and $PhCF_3$ (as a standard) before experiment



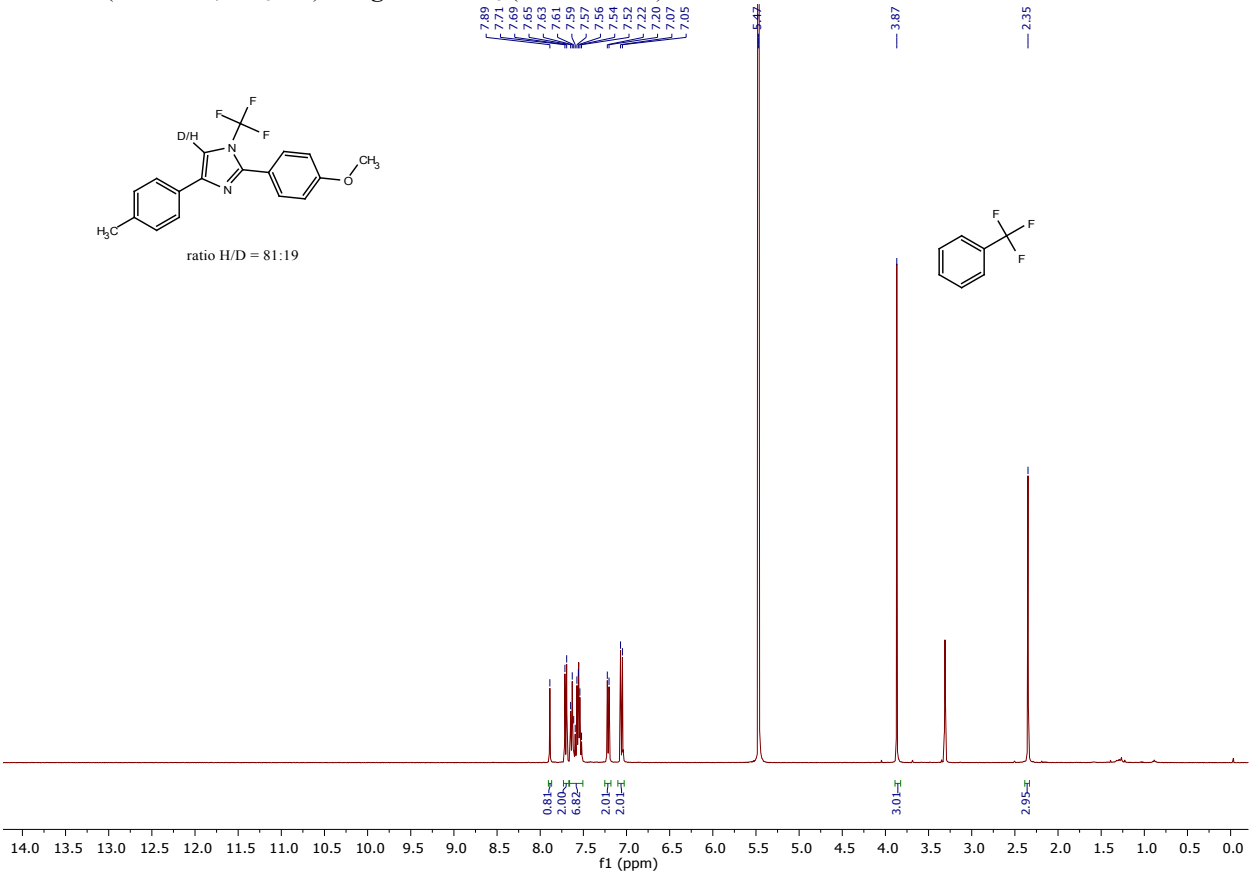
^{1}H NMR (400 MHz, CD_3OD) of **3g** and $PhCF_3$ (as a standard) after addition of acid 18 h



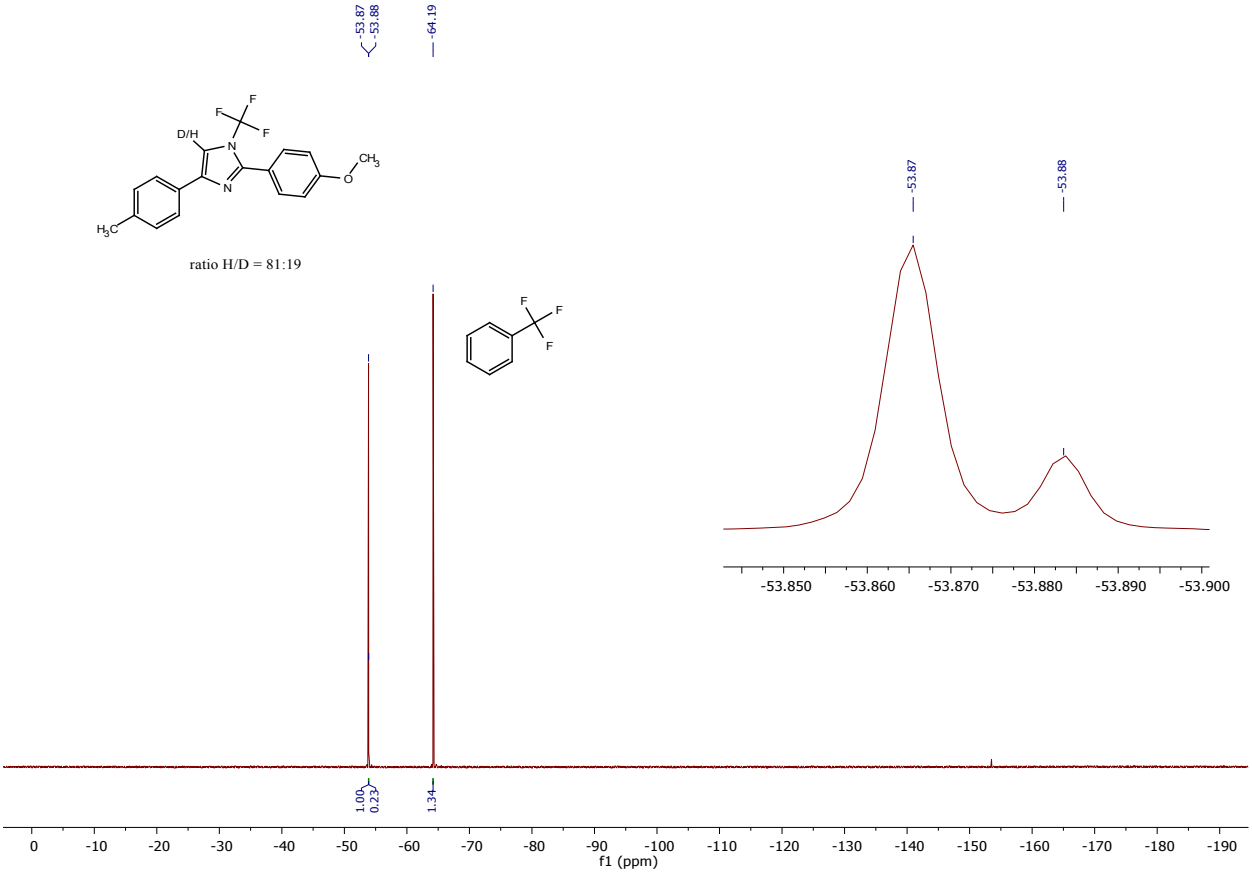
^{19}F NMR (376 MHz, CD_3OD) of **3g** and $PhCF_3$ (as a standard) after addition of acid 18 h



^{1}H NMR (400 MHz, CD_3OD) of **3g** and $PhCF_3$ (as a standard) after addition of base 18 h



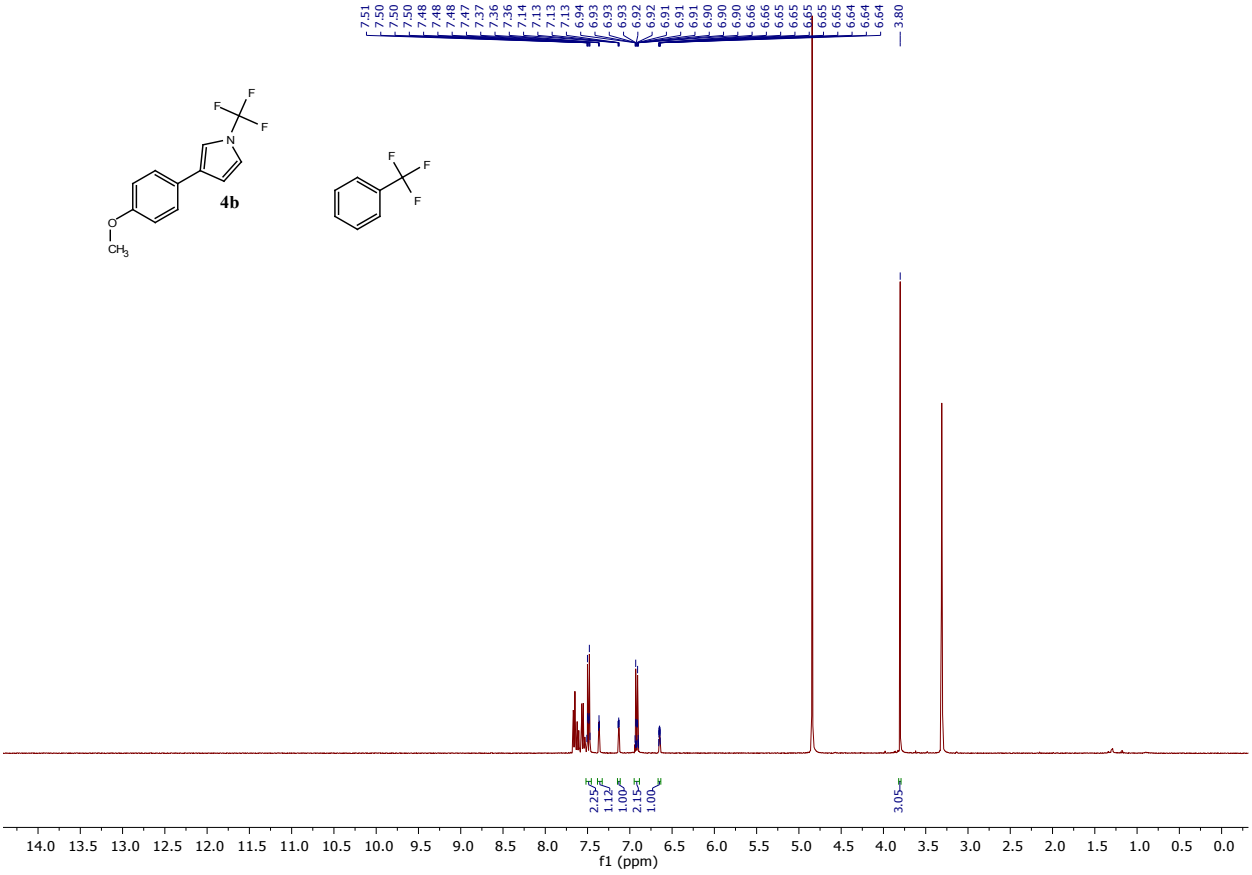
^{19}F NMR (376 MHz, CD_3OD) of **3g** and $PhCF_3$ (as a standard) after addition of base 18 h



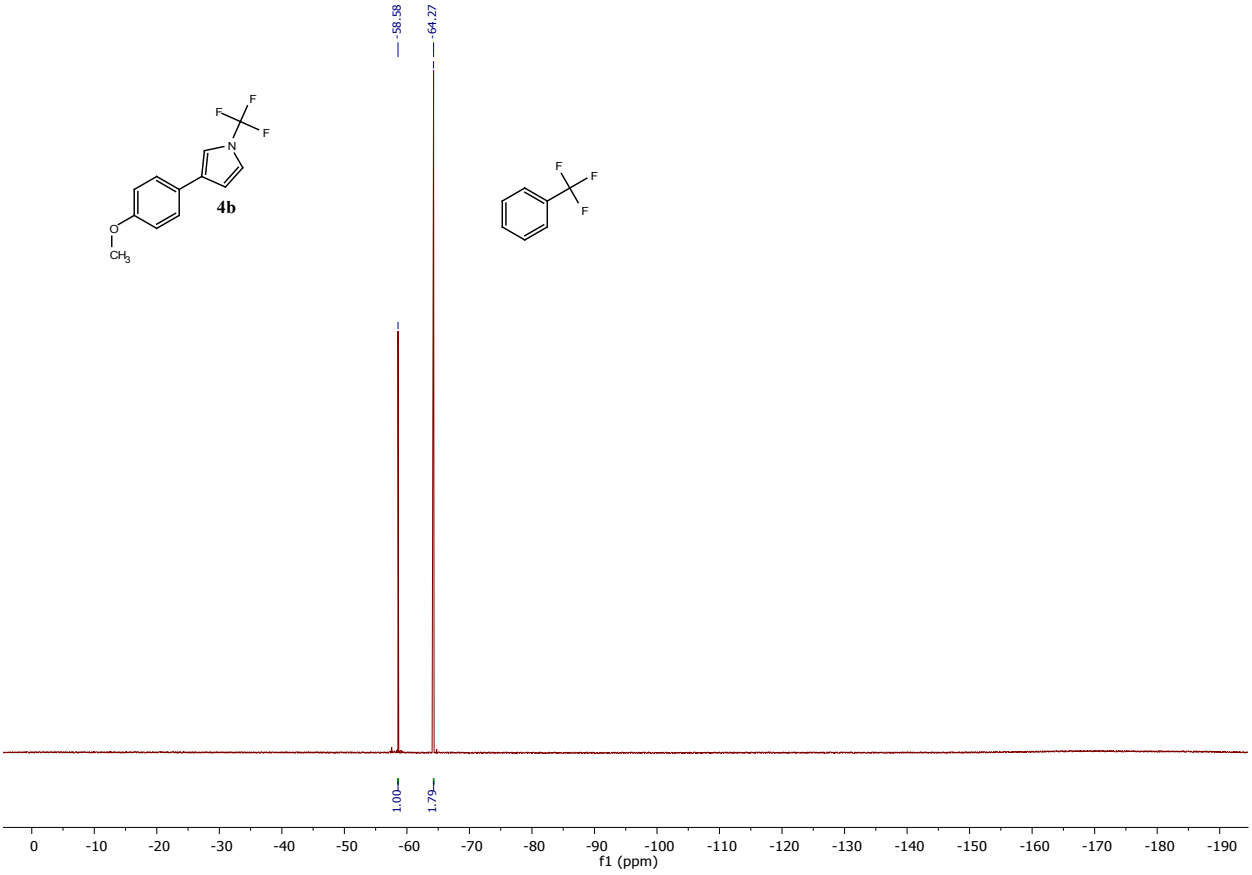
Stability of pyrrole 4b

Pyrrole **4b** (2.4 mg; 0.01 mmol) was dissolved in CD_3OD (1.06 mL) and $PhCF_3$ was added as an internal standard. Then ^{19}F and ^{1}H NMR spectra were measured. For stability experiment in basic condition, NaOH (10 mg; 0,25 mmol) was added to the prepared solution (500 µL) and after 18 h at 25 °C ^{19}F and ^{1}H NMR spectra were measured. In case of experiment in acidic conditions, 98% H_2SO_4 in D_2O (40 µL) was added to the prepared solution (560 µL) and after 18 h at room temperature ^{19}F and ^{1}H NMR spectra were measured.

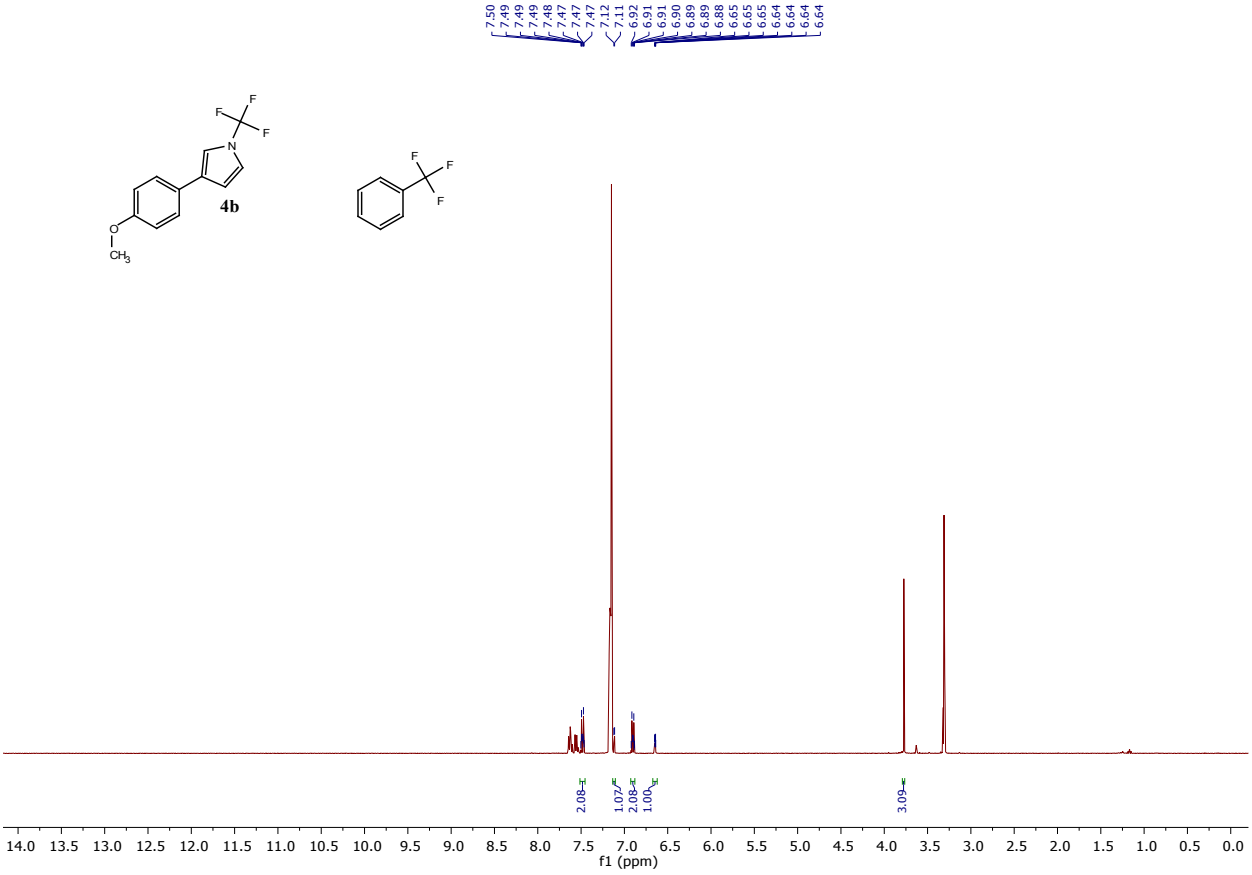
^{1}H NMR (400 MHz, CD_3OD) of **4b** and $PhCF_3$ (as a standard) before experiment



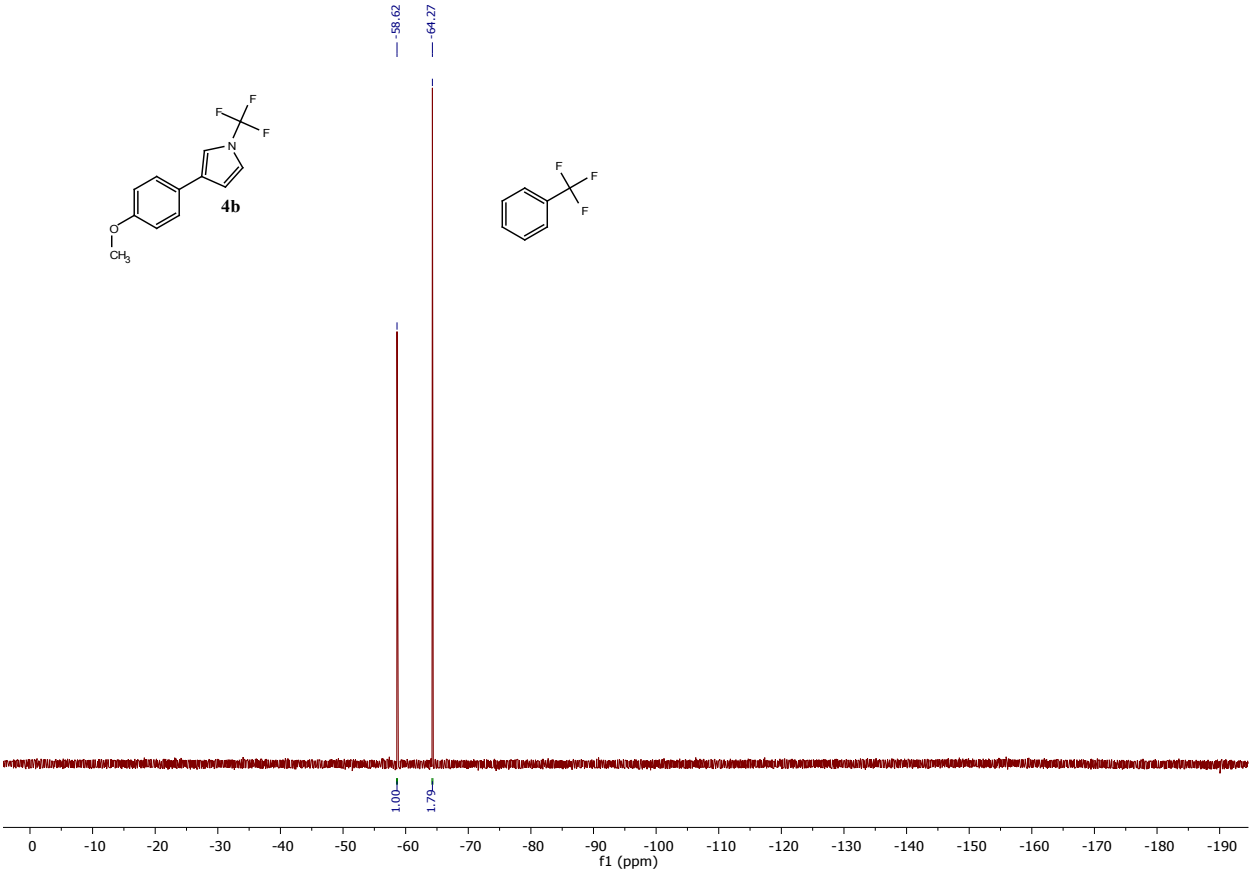
^{19}F NMR (376 MHz, CD_3OD) of **4b** and $PhCF_3$ (as a standard) before experiment



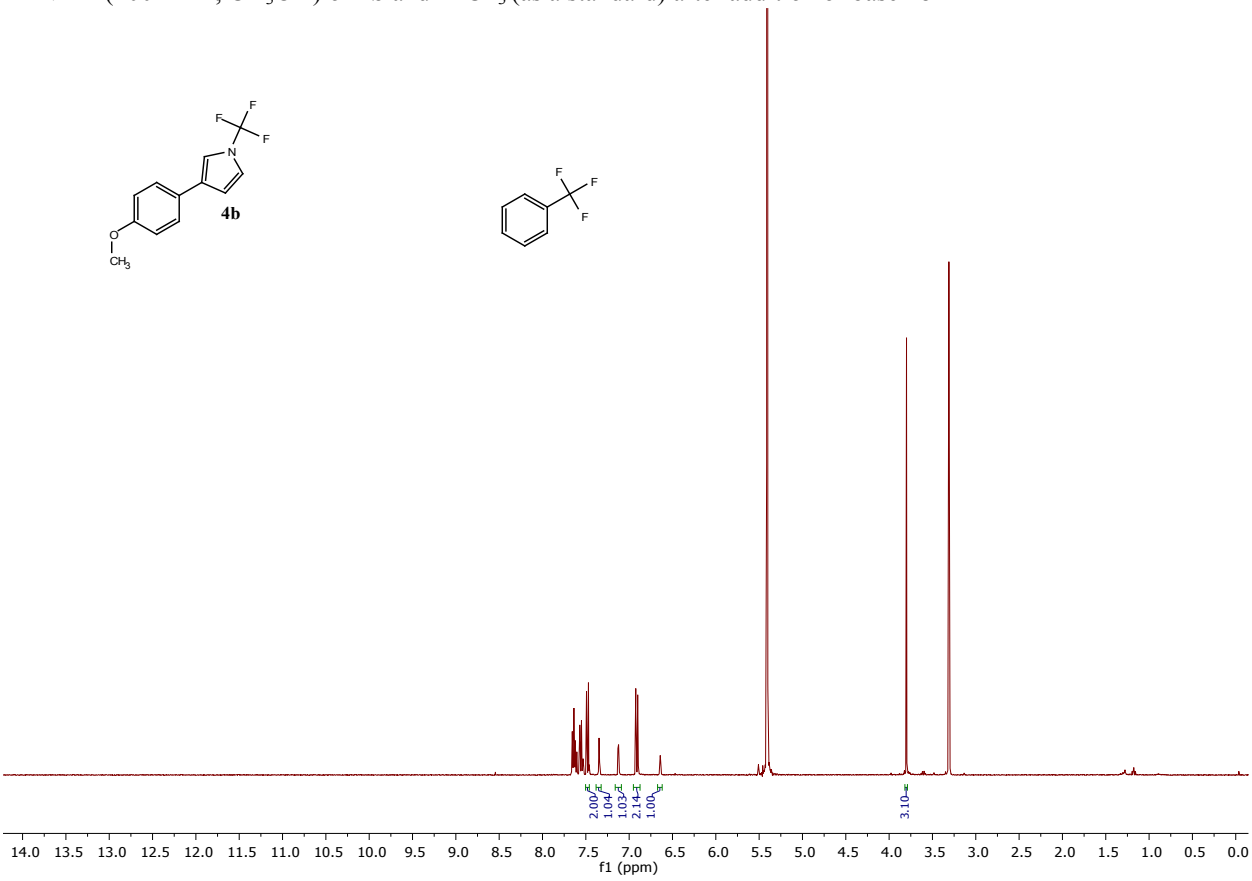
^{1}H NMR (400 MHz, CD_3OD) of **4b** and $PhCF_3$ (as a standard) after addition of acid 18 h



^{19}F NMR (376 MHz, CD_3OD) of **4b** and $PhCF_3$ (as a standard) after addition of acid 18 h



^{1}H NMR (400 MHz, CD_3OD) of **4b** and $PhCF_3$ (as a standard) after addition of base 18 h



^{19}F NMR (376 MHz, CD_3OD) of **4b** and $PhCF_3$ (as a standard) after addition of base 18 h