Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Transition-Metal Free Selective C(α)-C(β) Bond Cleavage of Trifluoromethyl Ketones with Amidines under Air: Facile Access to 5-Trifluoromethylated Imidazol-4-ones

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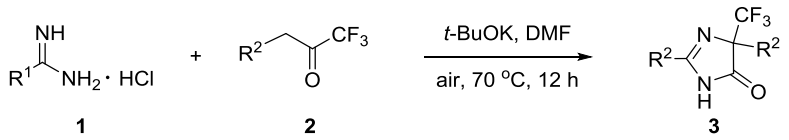
A. General Information

Melting points were measured using a melting point instrument and are uncorrected. Chemical shifts were reported in ppm from the solvent resonance as the internal standard (d_6-DMSO δ_H = 2.50 ppm, δ_C = 39.50 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants were reported in Hertz (Hz). IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC-MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100−400 mesh silica gel plates (GF_{254}). X-ray structural analyses were conducted on an x-ray analysis instrument.

Materials. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone; 1,2-dichloroethane (DCE) was distilled from calcium hydride; acetonitrile (CH_3CN) was distilled from phosphorus pentoxide. Other commercially available reagents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF_{254}) using UV light as a visualizing agent. Flash column chromatography was carried out using silica gel (200–300 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes. All the reaction temperatures reported are oil bath temperatures.

B. General Procedure for the Synthesis of 5-Trifluoromethylated Imidazol-4-ones

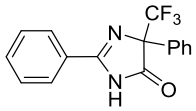


1 2 3

A 25 mL oven-dried test tube equipped with a magnetic stirring bar, amidine **1** (0.2 mmol), trifluoromethyl ketone **2** (0.2 mmol), *t*-BuOK (0.5 mmol), and DMF (2 mL) was vigorously stirred at 70 °C for 12 h under air. Then the mixture was cooled to room temperature, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine (15 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the product **3**.

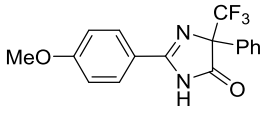
C. Analysis Data for the Products

2,5-Diphenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3a)



58.4 mg, 96% yield; white soild, mp: 186−187 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.47 (s, 1H), 8.17 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 6.8 Hz, 2H), 7.71 (t, J = 7.2 Hz, 1H), 7.63 (t, J = 7.6 Hz, 2H), 7.47−7.52 (m, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.4, 164.7, 133.5, 132.0, 130.0, 129.5, 129.1, 128.0, 127.9, 127.8, 123.3 (q, $^1J_{C\text{-}F}$ = 281.3 Hz), 75.4 (q, $^2J_{C\text{-}F}$ = 27.4 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr): 3187, 1735, 1629, 1443, 1257, 1172 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{11}F_3N_2O$+H, 305.0896; found, 305.0898

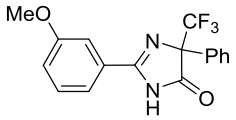
2-(4-Methoxyphenyl)-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3b)



64.8 mg, 97% yield; light yellow soild, mp: 192−193 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.29 (s, 1H), 8.12 (d, J = 5.2 Hz, 2H), 7.93 (s, 2H), 7.47 (s, 3H), 7.15 (d, J = 6.8 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.6, 164.1, 163.6, 132.2, 130.0, 129.9, 129.0, 127.8, 123.3 (q, $^1J_{C\text{-}F}$ = 281.4 Hz), 119.9, 114.9, 75.0, 56.0; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR

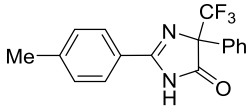
(KBr): 3062, 2851, 2743, 1757, 1609, 1441, 1262, 1175 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{13}F_3N_2O_2$+H, 335.1002; found, 335.1005

2-(3-Methoxyphenyl)-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3c)



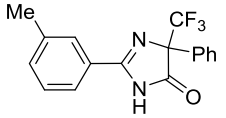
53.4 mg, 80% yield; light yellow soild, mp: 140−141 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.45 (s, 1H), 7.96 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 7.6 Hz, 1H), 7.70 (s, 1H), 7.49−7.56 (m, 4H), 7.28 (d, J = 8.4 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.4, 164.6, 160.0, 131.9, 130.7, 130.0, 129.1, 129.0, 127.9, 123.3 (q, $^1J_{C\text{-}F}$ = 281.4 Hz), 120.3, 119.6, 112.9, 75.4 (q, $^2J_{C\text{-}F}$ = 27.8 Hz), 55.9; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr): 3197, 3095, 2930, 1734, 1606, 1468, 1262, 1168 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{13}F_3N_2O_2$+H, 335.1002; found, 335.1006

5-Phenyl-2-(*p*-Tolyl)-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3d)



57.9 mg, 91% yield; white soild, mp: 214−215 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.38 (s, 1H), 8.06 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 6.8 Hz, 2H), 7.49−7.51 (m, 3H), 7.42 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.5, 164.5, 143.9, 132.1, 130.0, 130.0, 129.1, 128.0, 127.9, 125.0, 123.3 (q, $^1J_{C\text{-}F}$ = 281.2 Hz), 75.2 (q, $^2J_{C\text{-}F}$ = 27.2 Hz), 21.6; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr): 3188, 1735, 1628, 1446, 1251, 1179 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{13}F_3N_2O$+H, 319.1053; found, 319.1057

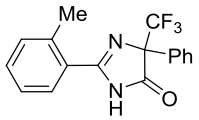
5-Phenyl-2-(*m*-Tolyl)-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3e)



54.1 mg, 85% yield; light yellow oil; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.38 (s, 1H), 7.80 (s, 1H), 7.90−7.94 (m, 3H), 7.45−7.48 (m, 5H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.4, 164.7, 139.0, 134.1, 132.0, 130.0, 129.4, 129.1, 128.3, 127.9, 127.7, 125.2, 123.3 (q, $^1J_{C\text{-}F}$ = 281.5 Hz), 75.4 (q, $^2J_{C\text{-}F}$ = 27.5 Hz), 21.3; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr):

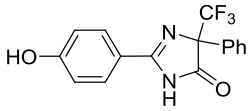
3061, 2926, 2859, 2739, 1749, 1621, 1458, 1260, 1177 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{13}F_3N_2O$+H, 319.1053; found, 319.1058

5-Phenyl-2-(*o*-Tolyl)-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3f)



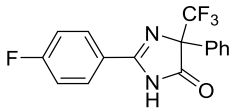
60.4 mg, 95% yield; light yellow solid, mp: 127−128 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.16 (s, 1H), 7.95 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 7.6 Hz, 1H), 7.48−7.54 (m, 4H), 7.37−7.44 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.0, 166.0, 138.2, 132.0, 131.8, 130.0, 129.5, 129.1, 127.9, 126.5, 123.2 (q, $^1J_{C\text{-}F}$ = 281.5 Hz), 75.7 (q, $^2J_{C\text{-}F}$ = 27.4 Hz), 21.0; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.8 (s, 3F); IR (KBr): 3070, 2839, 1750, 1624, 1444, 1259, 1175 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{13}F_3N_2O$+H, 319.1053; found, 319.1057

2-(4-Hydroxyphenyl)-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3g)



38.4 mg, 60% yield; colorless oil; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.23 (s, 1H), 10.43 (s, 1H), 7.91−8.01 (m, 4H), 7.47−7.47 (m, 3H), 6.97 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.5, 164.0, 162.3, 132.4, 130.1, 129.9, 129.0, 127.9, 123.4 (q, $^1J_{C\text{-}F}$ = 281.5 Hz), 118.4, 116.2, 75.2 (q, $^2J_{C\text{-}F}$ = 27.1 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr): 3459, 3131, 2843, 1745, 1608, 1458, 1263, 1177 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{11}F_3N_2O_2$+H, 321.0845; found, 321.0850

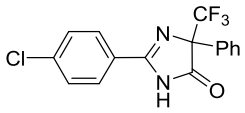
2-(4-Fluorophenyl)-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3h)



52.2 mg, 81% yield; white soild, mp: 226−227 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.47 (s, 1H), 8.22−8.31 (m, 2H), 7.93−7.94 (m, 2H), 7.44−7.46 (m, 5H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.4, 165.3 (d, $^1J_{C\text{-}F}$ = 250.0 Hz), 163.7, 132.0, 130.8 (d, $^3J_{C\text{-}F}$ = 9.3 Hz), 130.0, 129.1, 127.9, 124.4, 123.2 (q, $^1J_{C\text{-}F}$ = 281.5 Hz), 116.7 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 75.5 (q, $^2J_{C\text{-}F}$ = 27.1 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F), −106.0 (s, 1F); IR (KBr): 3183, 2919, 1734, 1631, 1447,

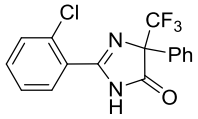
1250, 1174 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}F_4N_2O$+H, 323.0802; found, 323.0804

2-(4-Chlorophenyl)-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3i)



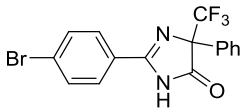
62.9 mg, 93% yield; white soild, mp: 193−194 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.49 (s, 1H), 8.18 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 6.4 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.50−7.51 (m, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.4, 164.0, 138.5, 131.8, 130.0, 129.9, 129.7, 129.1, 127.8, 126.6, 123.2 (q, $^1J_{C\text{-}F}$ = 281.2 Hz), 75.4 (q, $^2J_{C\text{-}F}$ = 28.1 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr): 3177, 1732, 1625, 1437, 1251, 1173 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}ClF_3N_2O$+H, 339.0507; found, 339.0512

2-(2-Chlorophenyl)-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3j)



58.1 mg, 86% yield; light yellow solid, mp: 145−146 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.27 (s, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 7.6 Hz, 1H), 7.63−7.70 (m, 2H), 7.49−7.57 (m, 4H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 177.7, 164.7, 133.6, 132.2, 131.5, 131.3, 130.9, 130.1, 129.2, 128.5, 128.1, 127.9, 123.0 (q, $^1J_{C\text{-}F}$ = 281.3 Hz), 75.6 (q, $^2J_{C\text{-}F}$ = 27.1 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr): 3265, 3070, 1756, 1624, 1437, 1257, 1179 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}ClF_3N_2O$+H, 339.0507; found, 339.0510

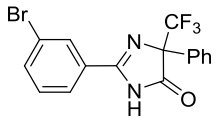
2-(4-Bromophenyl)-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3k)



71.8 mg, 94% yield; white soild, mp: 243−244 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.53 (s, 1H), 8.11 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 6.0 Hz, 2H), 7.85 (d, J = 7.6 Hz, 2H), 7.51−7.52 (m, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.4, 164.2, 132.6, 131.8, 130.0, 130.0, 129.1, 127.9, 127.5, 126.9, 123.1 (q, $^1J_{C\text{-}F}$ = 281.5 Hz), 75.4 (q, $^2J_{C\text{-}F}$ = 27.9 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr): 3178, 1733, 1626, 1436, 1251, 1176 cm^{-1}; HRMS (ESI,

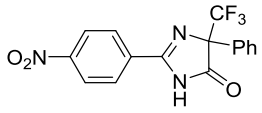
m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}BrF_3N_2O$+H, 383.0001; found, 383.0002

2-(3-Bromophenyl)-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3l)



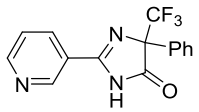
64.9 mg, 85% yield; white soild, mp: 168−169 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.50 (s, 1H), 8.32 (s, 1H), 8.15 (d, J = 7.6 Hz, 1H), 7.90−7.93 (m, 3H), 7.59 (t, J = 8.0 Hz, 1H), 7.49−7.52 (m, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.2, 163.7, 136.3, 132.7, 131.7, 131.7, 130.5, 130.1, 129.9, 129.2, 127.9, 127.1, 123.1 (q, $^1J_{C\text{-}F}$ = 281.4 Hz), 122.7, 75.5 (q, $^2J_{C\text{-}F}$ = 24.1 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr): 3442, 3201, 1738, 1627, 1448, 1257, 1174 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}BrF_3N_2O$+H, 383.0001; found, 383.0005

2-(4-Nitrophenyl)-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3m)



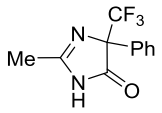
59.3 mg, 85% yield; yellow soild, mp: 202−203 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.73 (s, 1H), 8.39−8.47 (m, 4H), 7.94 (d, J = 6.8 Hz, 2H), 7.51−7.52 (m, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.2, 163.8, 150.5, 133.3, 131.5, 130.2, 129.6, 129.2, 127.8, 124.6, 123.1 (q, $^1J_{C\text{-}F}$ = 281.5 Hz), 75.7 (q, $^2J_{C\text{-}F}$ = 26.7 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.5 (s, 3F); IR (KBr): 3173, 3106, 2883, 1737, 1610, 1531, 1442, 1349, 1255, 1175 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}F_3N_3O_3$+H, 350.0747; found, 350.0750

5-Phenyl-2-(Pyridin-3-yl)-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3n)



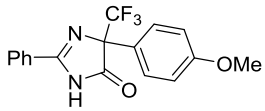
52.5 mg, 86% yield; white soild, mp: 187−188 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.60 (s, 1H), 9.29 (s, 1H), 8.87 (d, J = 2.8 Hz, 1H), 8.51 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 5.2 Hz, 2H), 7.67 (s, 1H), 7.50 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.3, 163.7, 154.0, 148.9, 135.6, 131.7, 130.1, 129.1, 127.9, 124.5, 124.0, 123.1 (q, $^1J_{C\text{-}F}$ = 278.1 Hz), 75.3 (q, $^2J_{C\text{-}F}$ = 27.9 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.4 (s, 3F); IR (KBr): 3443, 3064, 1756, 1615, 1476, 1267, 1173 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{10}F_3N_3O$+H, 306.0849; found, 306.0853

2-Methyl-5-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3o)



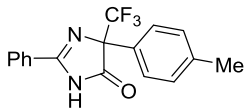
18.9 mg, 39% yield; light yellow oil; ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.63 (s, 1H), 7.81 (d, J = 4.4 Hz, 1H), 7.44−7.48 (m, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 177.8, 166.5, 131.8, 129.9, 129.0, 127.9, 123.2 (q, $^{1}J_{C\text{-}F}$ = 280.9 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 27.7 Hz), 16.6; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.8 (s, 3F); IR (KBr): 3274, 3058, 2924, 2848, 1752, 1643, 1441, 1260, 1178 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{11}H_9F_3N_2O$+H, 243.0740; found, 243.0745

5-(4-Methoxyphenyl)-2-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3p)



60.8 mg, 91% yield; orange soild, mp: 107−108 ^{o}C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.41 (s, 1H), 8.14 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.8 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.62 (t, J = 7.2 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.7, 164.4, 160.6, 133.5, 129.5, 129.2, 128.0, 127.8, 123.7, 123.3 (q, $^{1}J_{C\text{-}F}$ = 281.2 Hz), 114.5, 75.1 (q, $^{2}J_{C\text{-}F}$ = 27.4 Hz), 55.7; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.8 (s, 3F); IR (KBr): 3175, 2933, 1738, 1622, 1509, 1453, 1252, 1171 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{13}F_3N_2O_2$+H, 335.1002; found, 335.1006

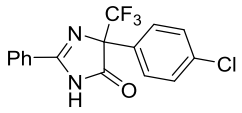
2-Phenyl-5-(*p*-Tolyl)-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3q)



54.1 mg, 85% yield; white soild, mp: 209−210 ^{o}C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.42 (s, 1H), 8.15 (d, J = 7.2 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.70 (t, J = 7.2 Hz, 1H), 7.62 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.6, 164.5, 139.6, 133.5, 129.6, 129.5, 129.0, 128.0, 127.8, 127.7, 122.8 (q, $^{1}J_{C\text{-}F}$ = 281.3 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 26.5 Hz), 21.1; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.6 (s, 3F); IR (KBr): 3194, 3126, 1736, 1629, 1506, 1458, 1423, 1256, 1183 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{13}F_3N_2O$+H,

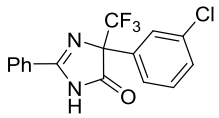
319.1053; found, 319.1052

5-(4-Chlorophenyl)-2-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3r)



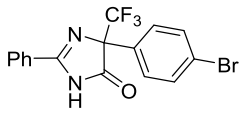
54.8 mg, 81% yield; light yellow solid, mp: 149–150 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.51 (s, 1H), 8.12 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.53−7.68 (m, 5H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.1, 165.1, 135.1, 133.6, 129.8, 129.5, 129.2, 128.1, 127.6, 123.0 (q, $^{1}J_{C\text{-}F}$ = 281.2 Hz), 74.9 (q, $^{2}J_{C\text{-}F}$ = 27.6 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.8 (s, 3F); IR (KBr): 3184, 2942, 2858, 1748, 1622, 1469, 1257, 1177 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}ClF_3N_2O$+H, 339.0507; found, 339.0503

5-(3-Chlorophenyl)-2-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3s)



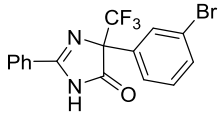
54.1 mg, 80% yield; white solid, mp: 223–224 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.58 (s, 1H), 8.18 (d, J = 7.2 Hz, 2H), 7.94 (s, 2H), 7.58−7.72 (m, 5H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 177.9, 165.3, 134.0, 133.8, 133.7, 131.1, 130.2, 129.5, 128.1, 127.6, 126.7, 123.0 (q, $^{1}J_{C\text{-}F}$ = 281.5 Hz), 74.8 (q, $^{2}J_{C\text{-}F}$ = 27.6 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.7 (s, 3F); IR (KBr): 3187, 2924, 1736, 1631, 1457, 1255, 1177 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}ClF_3N_2O$+H, 339.0507; found, 339.0508

5-(4-Bromophenyl)-2-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3t)



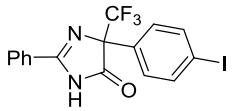
62.6 mg, 82% yield; yellow soild, mp: 141−142 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.52 (s, 1H), 8.13 (d, J = 7.6 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.67−7.72 (m, 3H), 7.60 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.1, 165.1, 133.7, 132.2, 131.2, 130.0, 129.5, 128.1, 127.6, 123.8, 123.0 (q, $^{1}J_{C\text{-}F}$ = 281.4 Hz), 75.0 (q, $^{2}J_{C\text{-}F}$ = 27.3 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.7 (s, 3F); IR (KBr): 3185, 2923, 1737, 1631, 1461, 1255, 1177 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}BrF_3N_2O$+H, 383.0001; found, 382.9998

5-(3-Bromophenyl)-2-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3u)



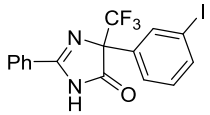
61.1 mg, 80% yield; white soild, mp: 202−203 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.56 (s, 1H), 8.14 (d, J = 7.6 Hz, 2H), 8.05 (s, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.69−7.70 (m, 2H), 7.61 (t, J = 7.2 Hz, 2H), 7.48 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 177.9, 165.3, 134.2, 133.7, 133.1, 131.4, 130.4, 129.5, 128.1, 127.6, 127.1, 122.9 (q, $^{1}J_{C\text{-}F}$ = 281.5 Hz), 122.3, 74.7 (q, $^{2}J_{C\text{-}F}$ = 27.4 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.7 (s, 3F); IR (KBr): 3177, 3123, 1734, 1631, 1456, 1255, 1182 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}BrF_3N_2O$+H, 383.0001; found, 382.9999

5-(4-Iodophenyl)-2-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3v)



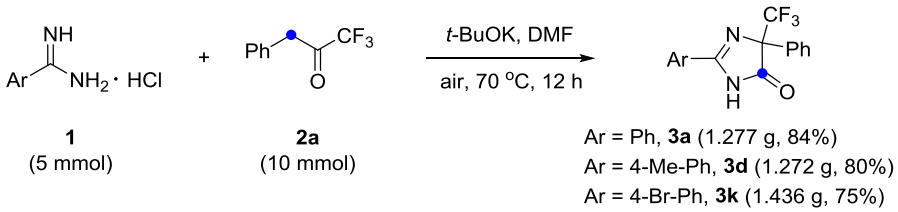
57.6 mg, 67% yield; pale green soild, mp: 187−188 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.50 (s, 1H), 8.13 (d, J = 7.2 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.67−7.71 (m, 3H), 7.60 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.1, 165.1, 138.0, 133.6, 131.7, 130.0, 129.5, 128.1, 127.6, 122.9 (q, $^{1}J_{C\text{-}F}$ = 281.5 Hz), 97.2, 75.1 (q, $^{2}J_{C\text{-}F}$ = 27.8 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.6 (s, 3F); IR (KBr): 3194, 2921, 1737, 1628, 1458, 1251, 1175 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}F_3IN_2O$+H, 430.9863; found, 430.9864

5-(3-Iodophenyl)-2-Phenyl-5-(Trifluoromethyl)-3,5-Dihydro-4*H*-Imidazol-4-one (3w)



55.9 mg, 65% yield; white soild, mp: 170−171 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.54 (s, 1H), 8.22 (s, 1H), 8.14 (d, J = 7.2 Hz, 2H), 7.96 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.61−7.71 (m, 3H), 7.33 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 178.0, 165.3, 138.9, 136.2, 134.0, 133.7, 131.3, 129.6, 128.1, 127.6, 127.4, 123.0 (q, $^{1}J_{C\text{-}F}$ = 281.5 Hz), 95.3, 74.6 (q, $^{2}J_{C\text{-}F}$ = 27.8 Hz); ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.6 (s, 3F); IR (KBr): 3180, 2920, 1733, 1633, 1456, 1253, 1178 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{10}F_3IN_2O$+H, 430.9863; found, 430.9865

D. Procedure for the Gram-Scale Synthesis of 3

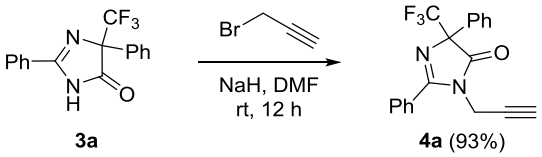


1 (5 mmol) **2a** (10 mmol)

Ar = Ph, **3a** (1.277 g, 84%)
Ar = 4-Me-Ph, **3d** (1.272 g, 80%)
Ar = 4-Br-Ph, **3k** (1.436 g, 75%)

A 250 mL oven-dried round-bottom flask equipped with a reflux condenser and a magnetic stirring bar, amidine **1** (5 mmol), trifluoromethyl ketone **2a** (10 mmol), *t*-BuOK (12.5 mmol), and DMF (50 mL) was vigorously stirred at 70 ^{o}C for 12 h under air. Then the mixture was cooled to room temperature, added water (150 mL), extracted with EtOAc (150 mL × 3). The combined organic phases were washed with brine (150 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the products **3**.

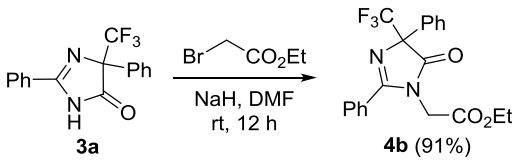
E. Procedure for the Transformations of 3a



3a **4a** (93%)

A 25 mL oven-dried round-bottom flask equipped with a magnetic stirring bar, **3a** (60.8 mg, 0.2 mmol), NaH (8 mg, 60% in oil, 0.4 mmol), and DMF (2 mL) was vigorously stirred at room temperature for 30 min under N_2. Then propargyl bromide (47.6 mg, 0.4 mmol) was added. The resulting mixture was then stirred at room temperature for another 12 h, quenched with water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine (15 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the products **4a**.

63.6 mg, 93% yield; colorless oil; ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.91−7.93 (m, 4H), 7.63−7.73 (m, 3H), 7.51 (s, 3H), 4.40−4.52 (m, 2H), 3.34 (s, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 175.8, 166.2, 132.8, 131.1, 130.3, 129.6, 129.3, 128.7, 128.4, 127.9, 123.0 (q, $^{1}J_{C\text{-}F}$ = 281.5 Hz), 77.9, 76.1, 74.6 (q, $^{2}J_{C\text{-}F}$ = 27.6 Hz), 32.3; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.6 (s, 3F); IR (KBr): 3297, 3066, 2928, 1748, 1623, 1494, 1448, 1381, 1324, 1254, 1165 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{13}F_3N_2O$+H, 343.1053; found, 343.1056

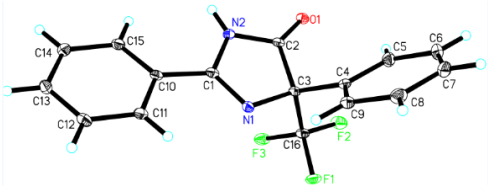


A 25 mL oven-dried round-bottom flask equipped with a magnetic stirring bar, **3a** (60.8 mg, 0.2 mmol), NaH (8 mg, 60% in oil, 0.4 mmol), and DMF (2 mL) was vigorously stirred at room temperature for 30 min under N_2. Then ethyl bromoacetate (66.8 mg, 0.4 mmol) was added. The resulting mixture was then stirred at room temperature for another 12 h, quenched with water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine (15 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the products **4b**.

71.0 mg, 91% yield; colorless oil; ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.91−7.93 (m, 2H), 7.77 (d, J = 7.2 Hz, 2H), 7.59−7.70 (m, 3H), 7.51−7.52 (m, 3H), 4.48−4.58 (m, 2H), 3.97 (q, J = 7.2 Hz, 2H), 1.00 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 176.3, 167.3, 166.5, 132.5, 131.2, 130.3, 129.5, 129.2, 128.6, 128.5, 127.9, 123.0 (q, $^1J_{C\text{-}F}$ = 281.4 Hz), 74.8 (q, $^2J_{C\text{-}F}$ = 27.8 Hz), 61.9, 43.7, 14.0; ^{19}F NMR (376 MHz, d_6-DMSO) δ = −73.3 (s, 3F); IR (KBr): 3067, 2987, 2934, 1750, 1629, 1450, 1380, 1327, 1260, 1211 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{17}F_3N_2O_3$+H, 391.1264; found, 391.1268

F. X-ray Crystallographic Data

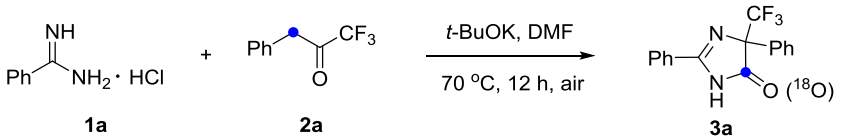
The X-ray crystallographic structures for **3a**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 1847590.



Empirical formula	$C_{16}H_{11}F_3N_2O$
Formula weight	304.27
Temperature	100.00(10)K
Wavelength	1.54184

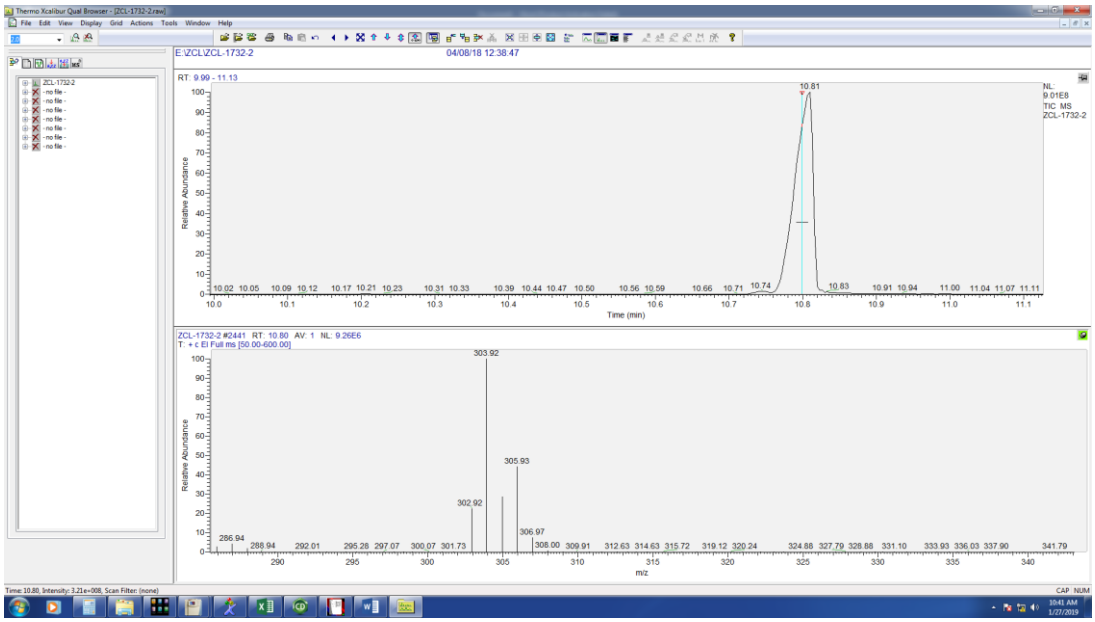
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 6.59270(10) Å alpha = 90 deg. b = 24.4163(4) Å beta = 108.268(2) deg. c = 9.1339(2) Å gamma = 90 deg.
Volume	1396.18(5) $Å^3$
Z, Calculated density	4, 1.448 Mg/m^3
Absorption coefficient	1.028 mm^{-1}
F(000)	624.0
Crystal size	0.13 × 0.12 × 0.11 mm
Theta range for data collection	3.621 to 73.527 deg.
Limiting indices	$-4 \leq h \leq 7$, $-28 \leq k \leq 29$, $-11 \leq l \leq 11$
Reflections collected / unique	5053 / 2717 [R(int) = 0.0312]
Completeness to theta = 66.97	99.88%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2717/0/203
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	$R_1 = 0.0470$, $wR_2 = 0.1251$
R indices (all data)	$R_1 = 0.0517$, $wR_2 = 0.1316$
Largest diff. peak and hole	0.25 and -0.29 e. $Å^{-3}$

G. GC-MS Analysis for ^{18}O-labled Experiments



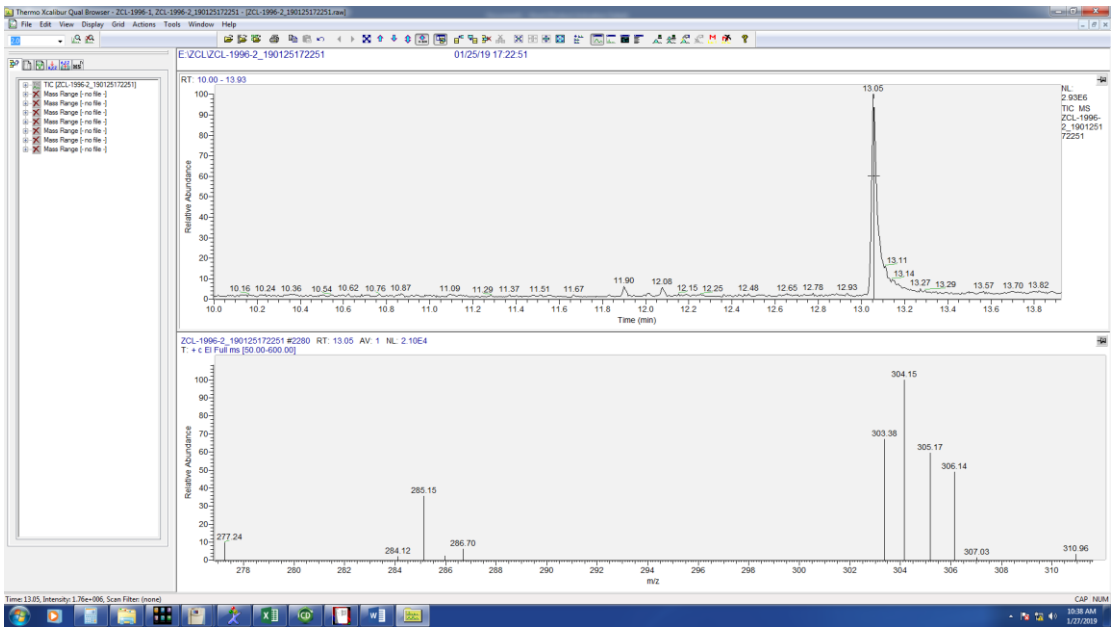
1) Variation the standard reaction conditions: under $^{18}O_2$ atmosphere instead of air.

The ^{18}O-labled ratio of **3a** under $^{18}O_2$ is 23%



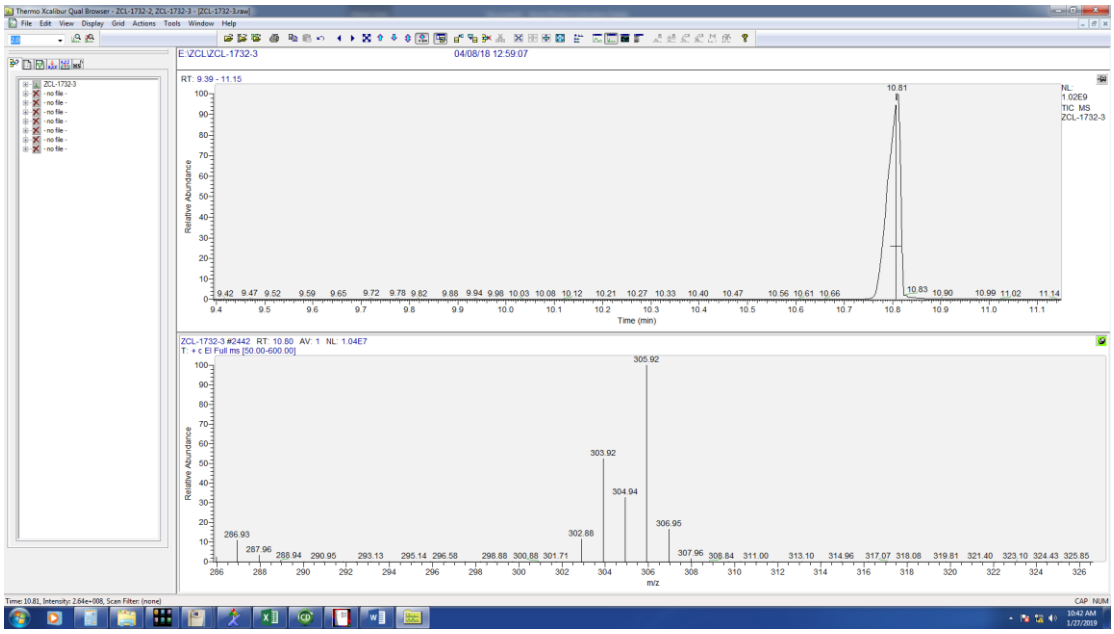
2) Variation the standard reaction conditions: under $^{18}O_2$ atmosphere instead of air, and using molecular sives dried DMF as the solvent.

The ^{18}O-labled ratio of **3a** under $^{18}O_2$ is 33%



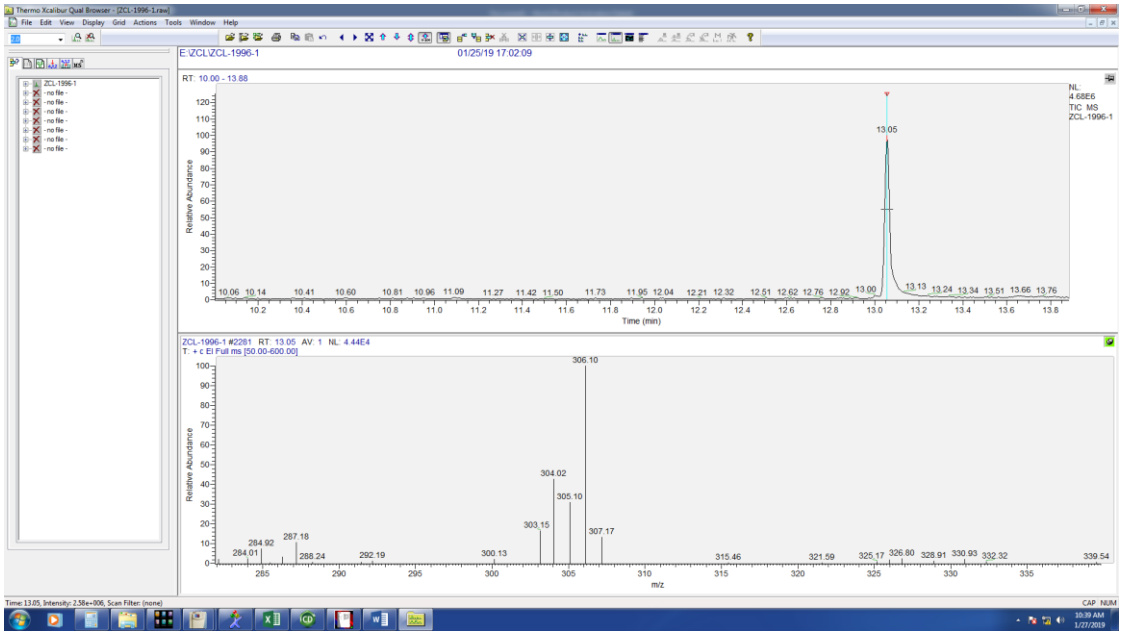
3) Variation the standard reaction conditions: with $H_2{}^{18}O$ (10 equiv) as additive.

The ^{18}O-labled ratio of **3a** under $^{18}O_2$ is 67%

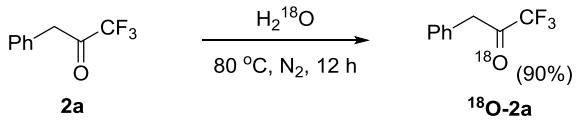


4) Variation the standard reaction conditions: with $H_2{}^{18}O$ (10 equiv) as additive, and using molecular sives dried DMF as the solvent.

The ^{18}O-labled ratio of **3a** under $^{18}O_2$ is 69%



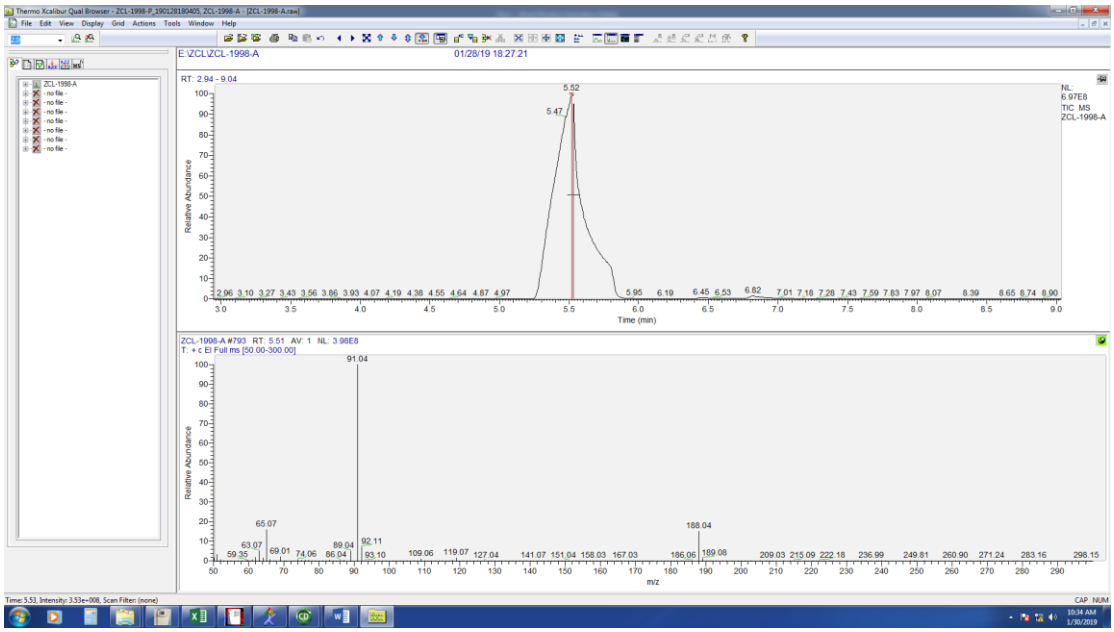
For the synthesis of ^{18}O-labled **2a**



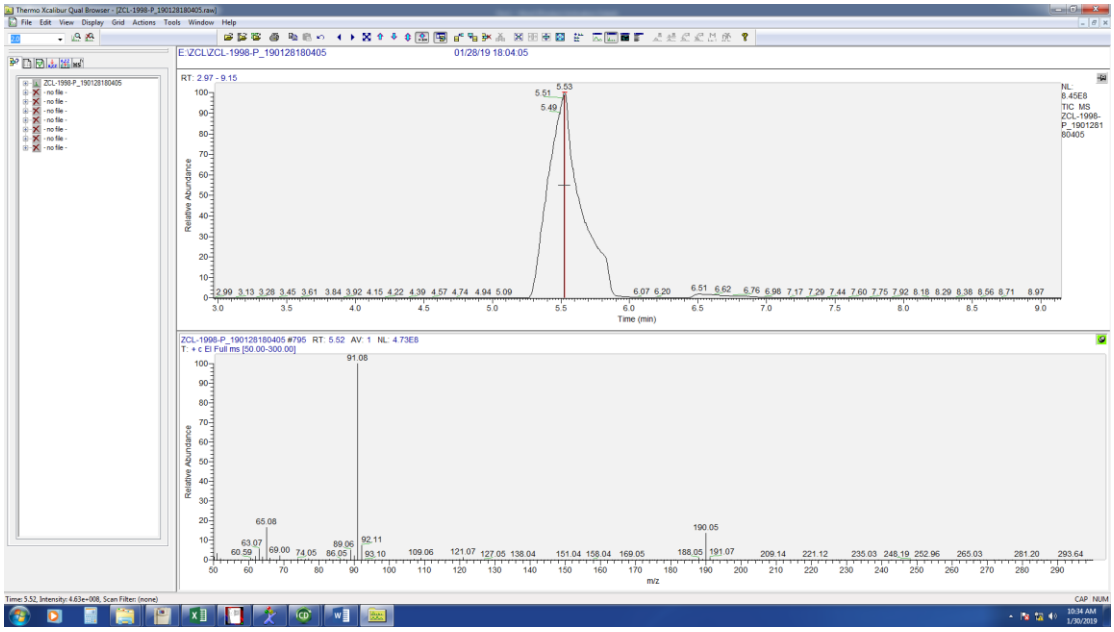
A 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, **2a** (188 mg, 1 mmol), and $H_2{}^{18}O$ (0.6 mL, 30 mmol) was stirred at 80 °C for 12 h under N_2. Then the mixture was cooled to room temperature, extracted with CH_2Cl_2 (10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* at 0 °C to give the desired the **^{18}O-2a** in 76% yield.

144.4 mg, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.36 (m, 3H), 7.18 (d, J = 7.2 Hz, 2H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9 (q, $^2J_{C\text{-}F}$ = 34.8 Hz), 130.4, 129.7, 128.9, 127.9, 115.8 (q, $^1J_{C\text{-}F}$ = 290.7 Hz), 43.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = −78.3 (s, 3F).

The GC-MS spectrum of **2a**

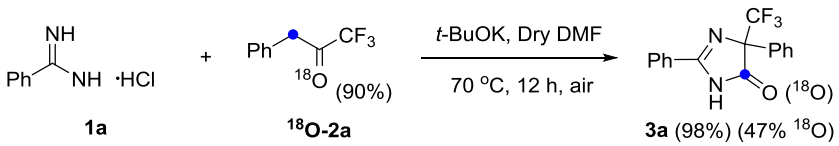


The GC-MS spectrum of **^{18}O-2a**

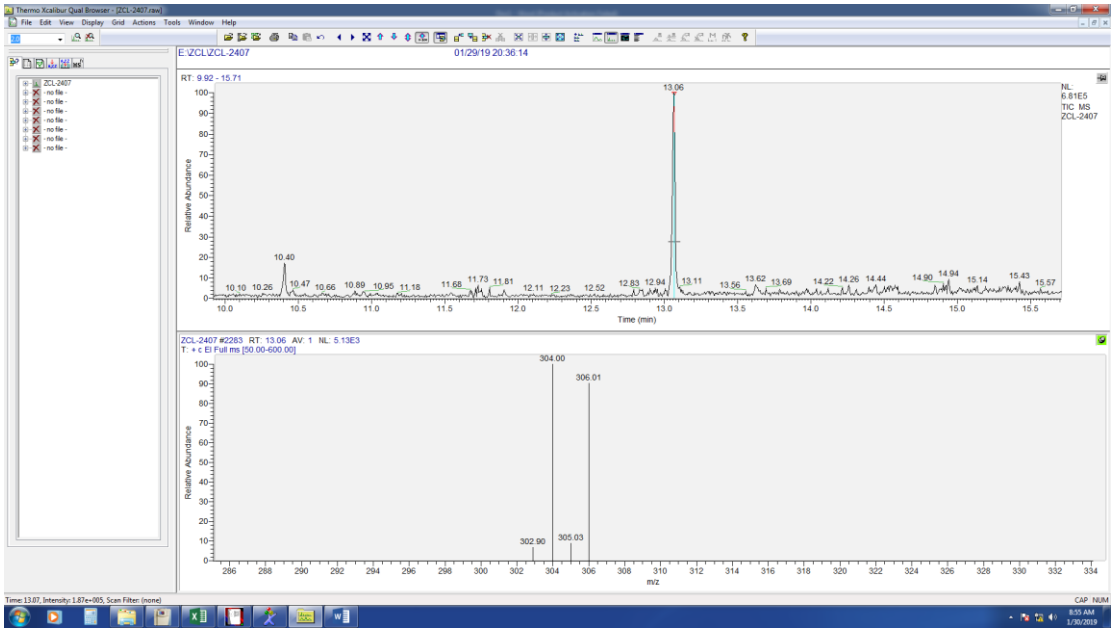


The ^{18}O-labled ratio of **2a** is 90%

Using ^{18}O-labled **2a** as the starting material.

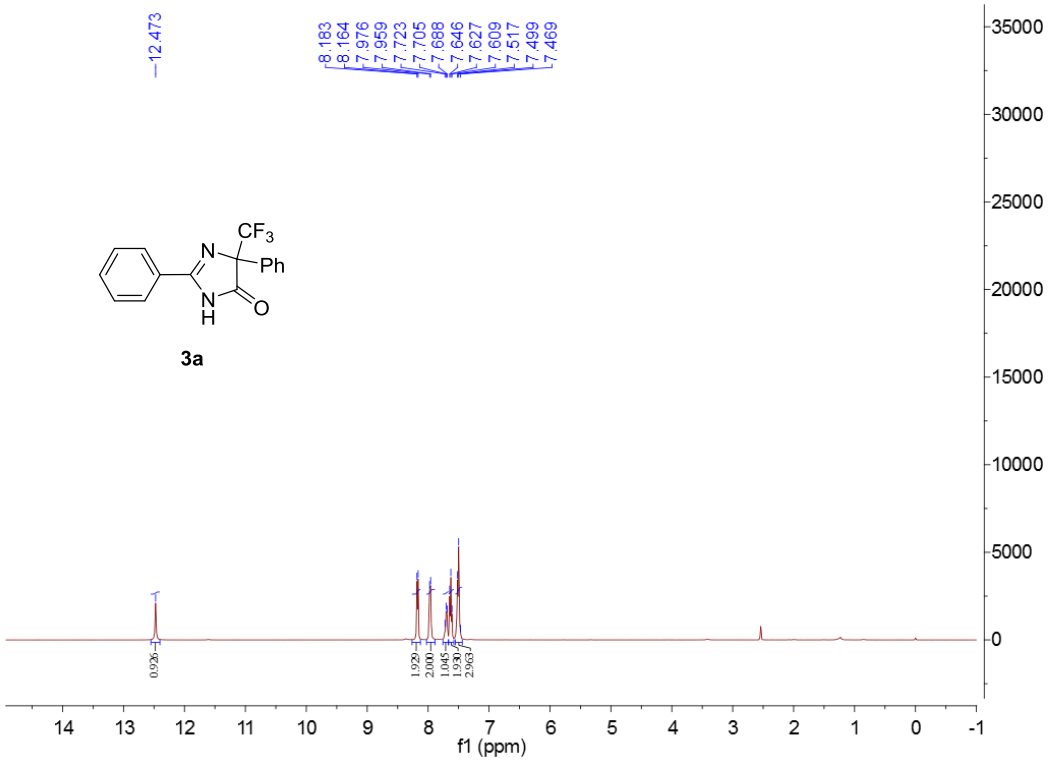


The ^{18}O-labled ratio of **3a** is 47%

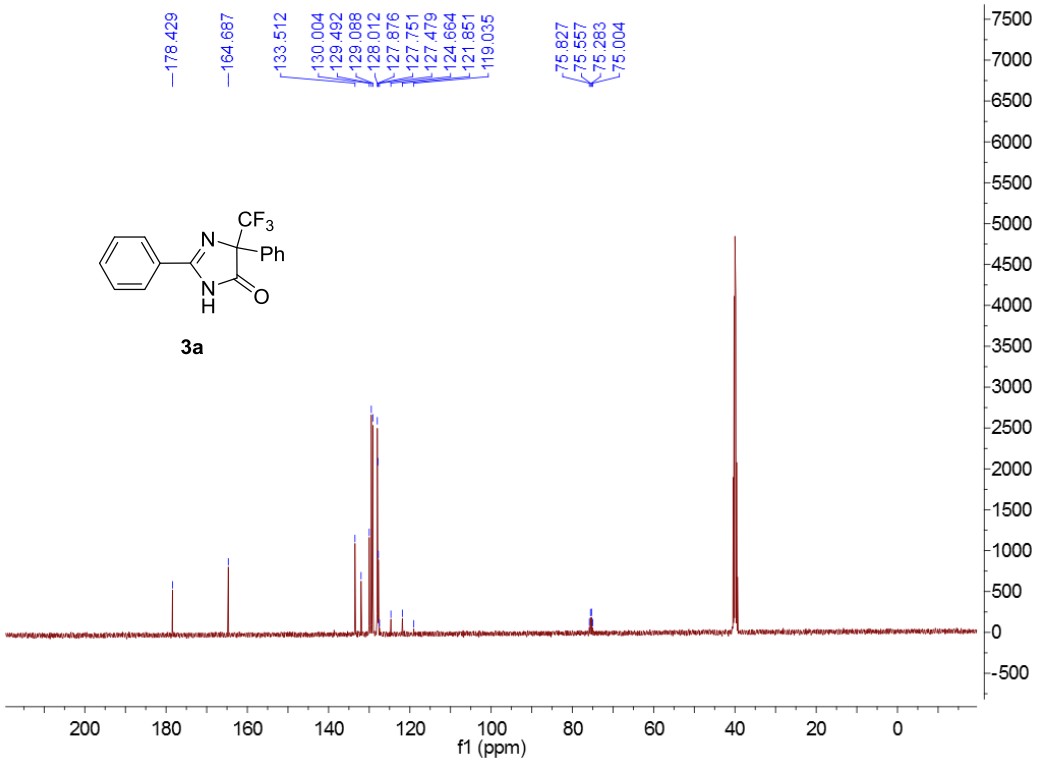


H. NMR Spectra of New Compounds

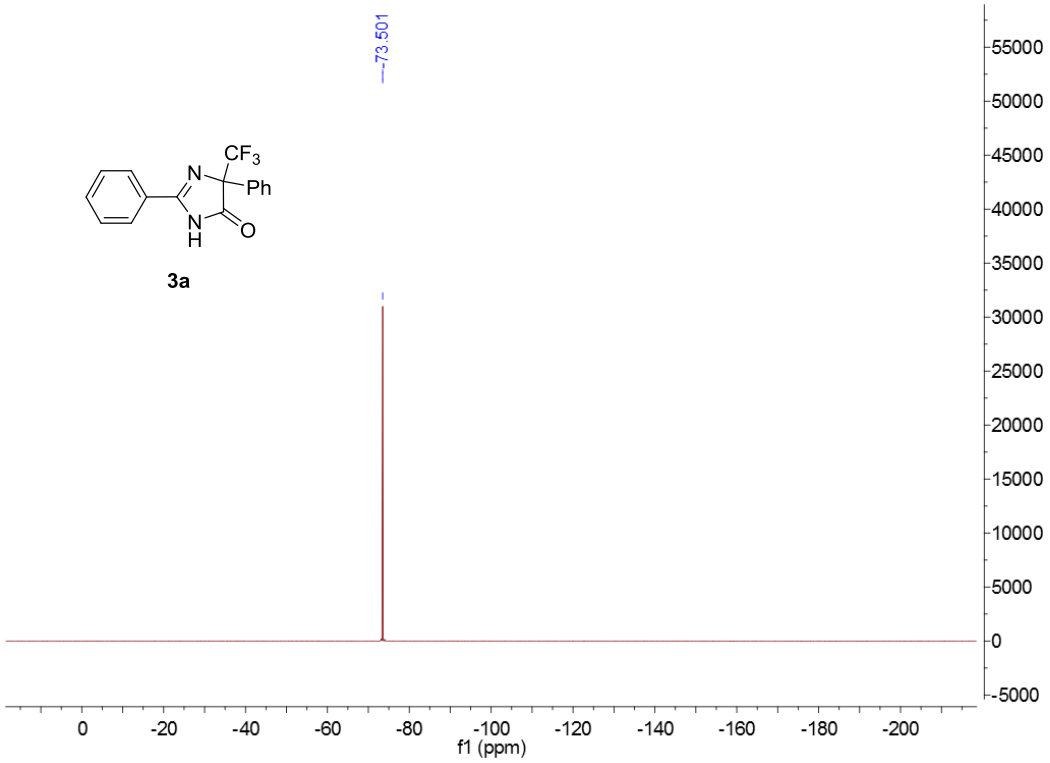
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3a



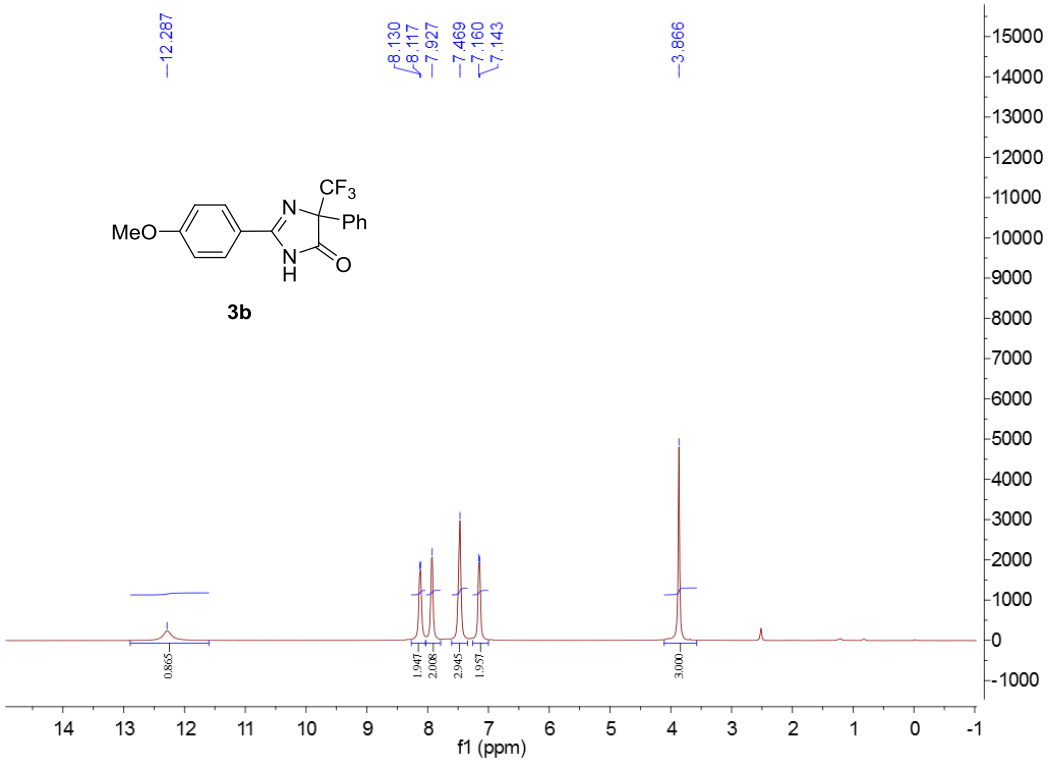
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3a



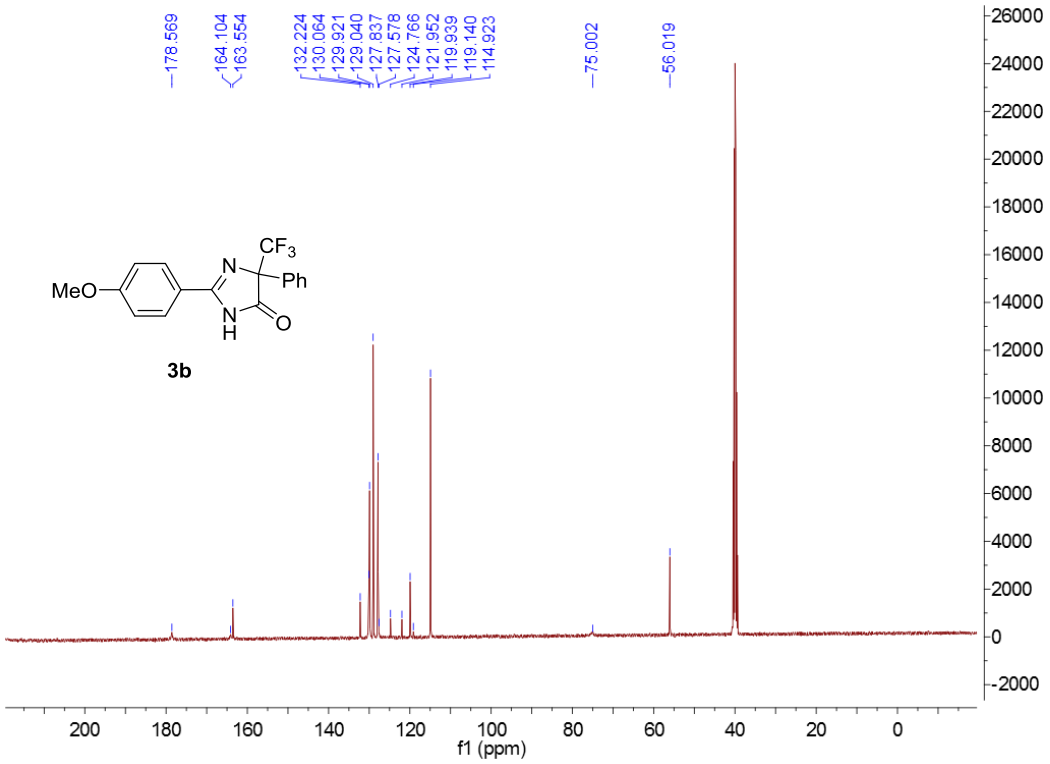
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3a



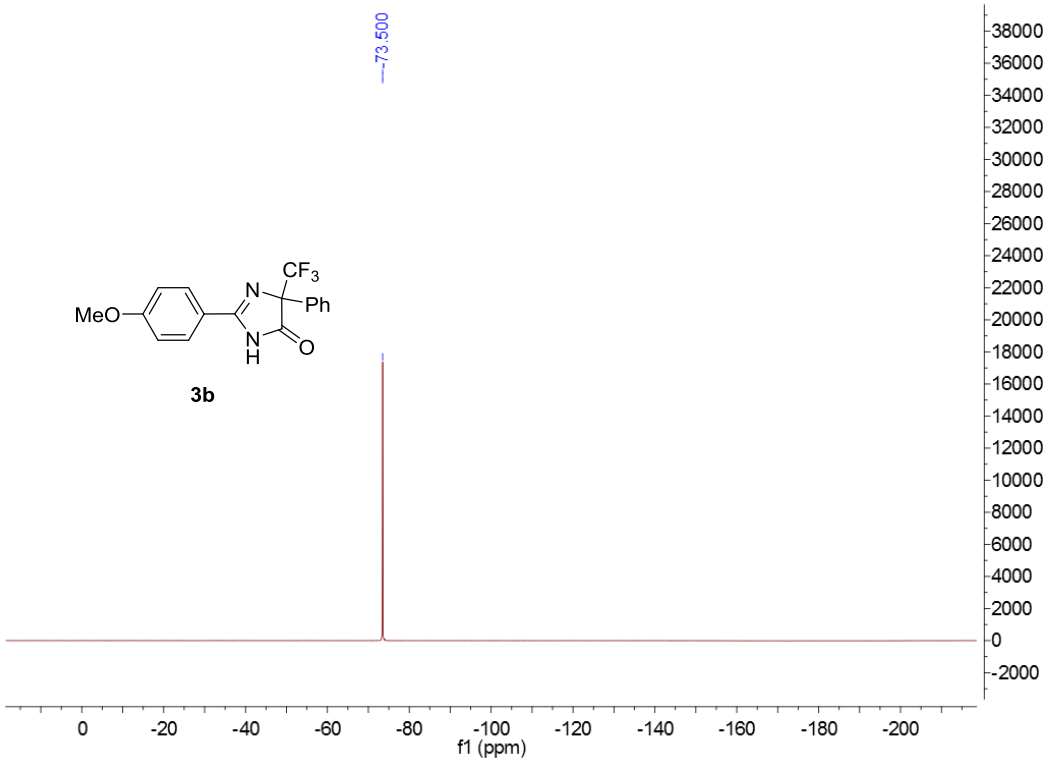
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3b



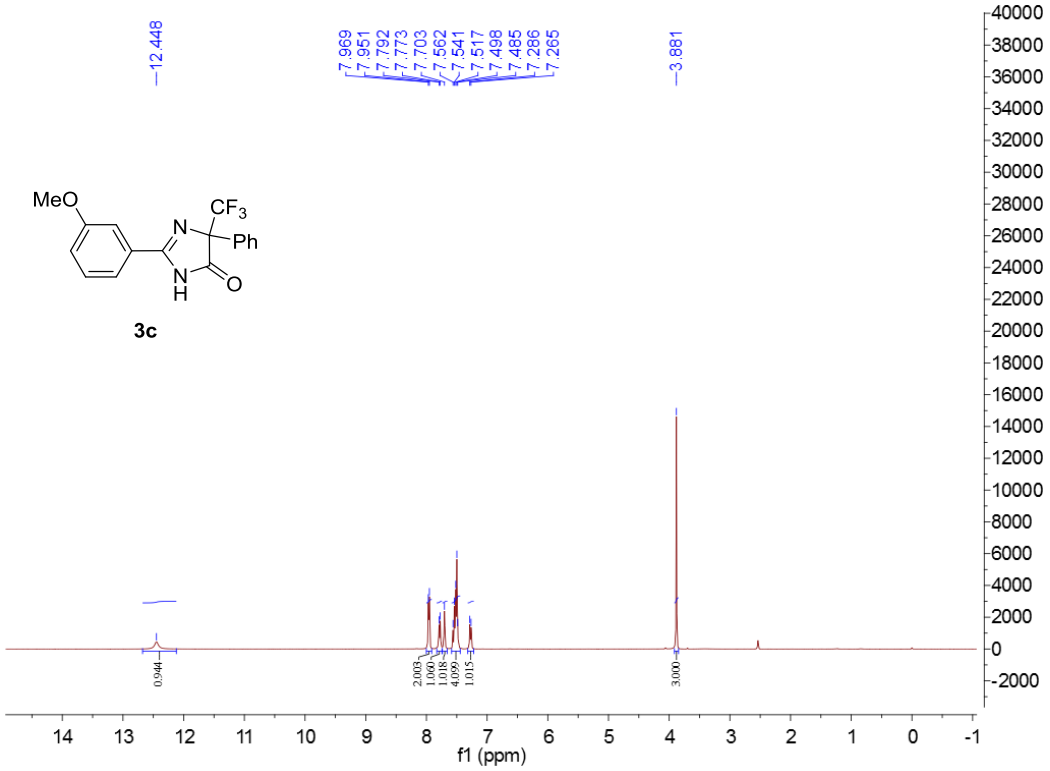
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3b



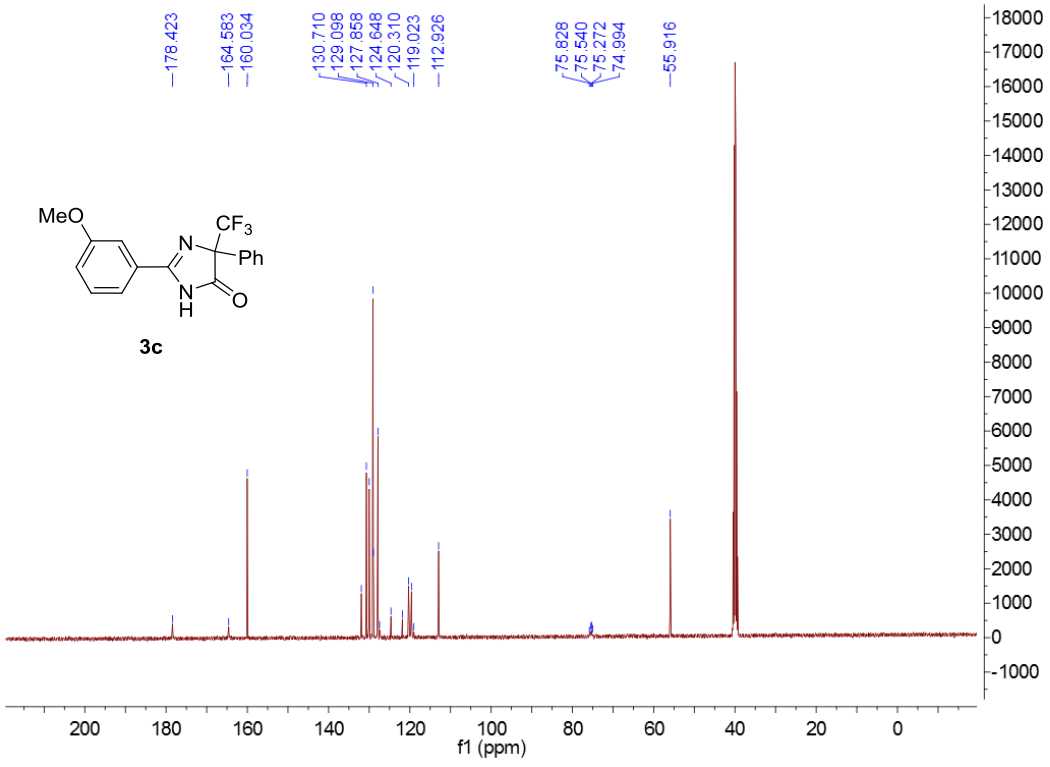
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3b



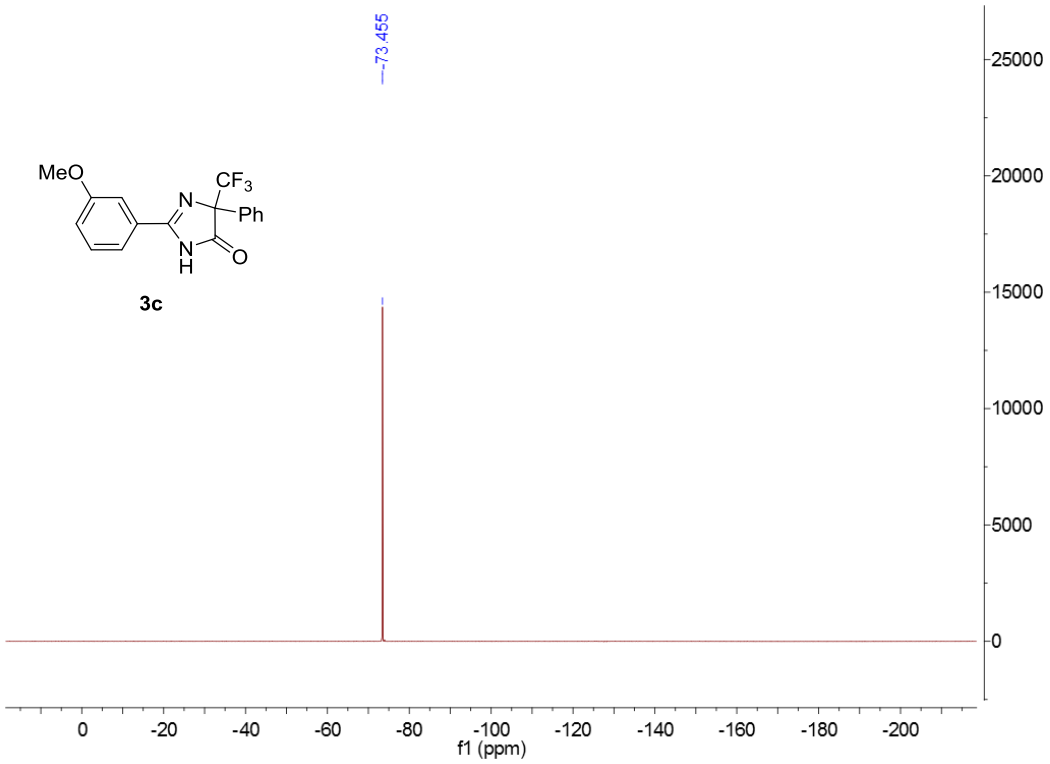
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3c



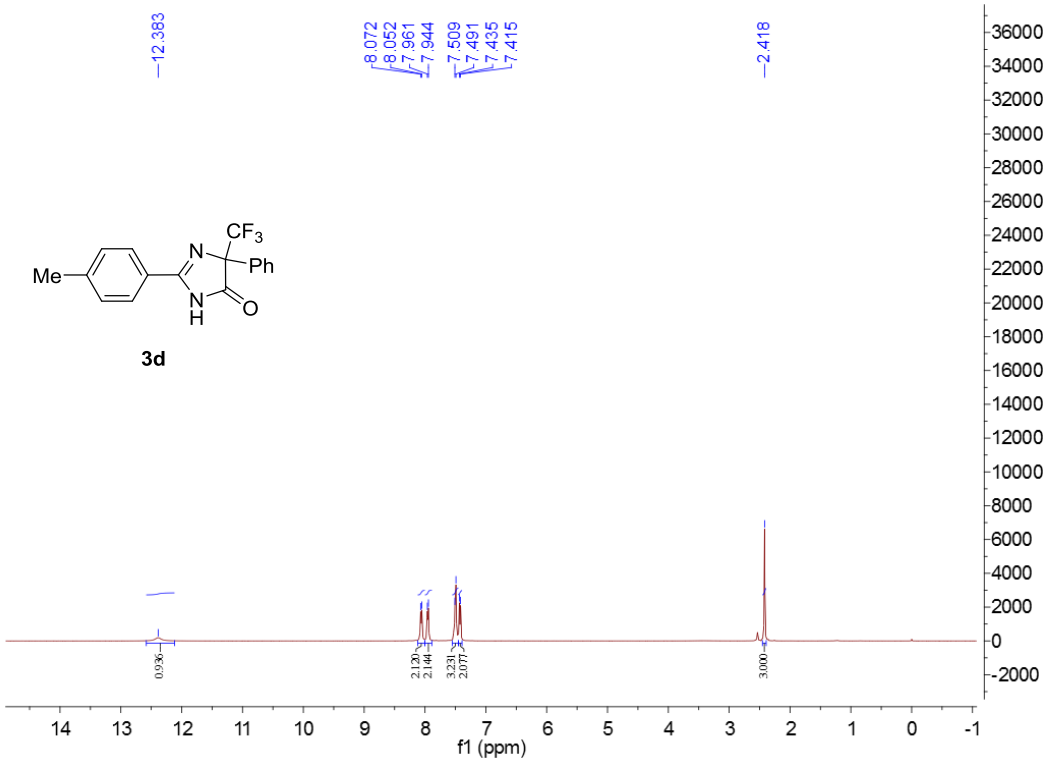
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3c



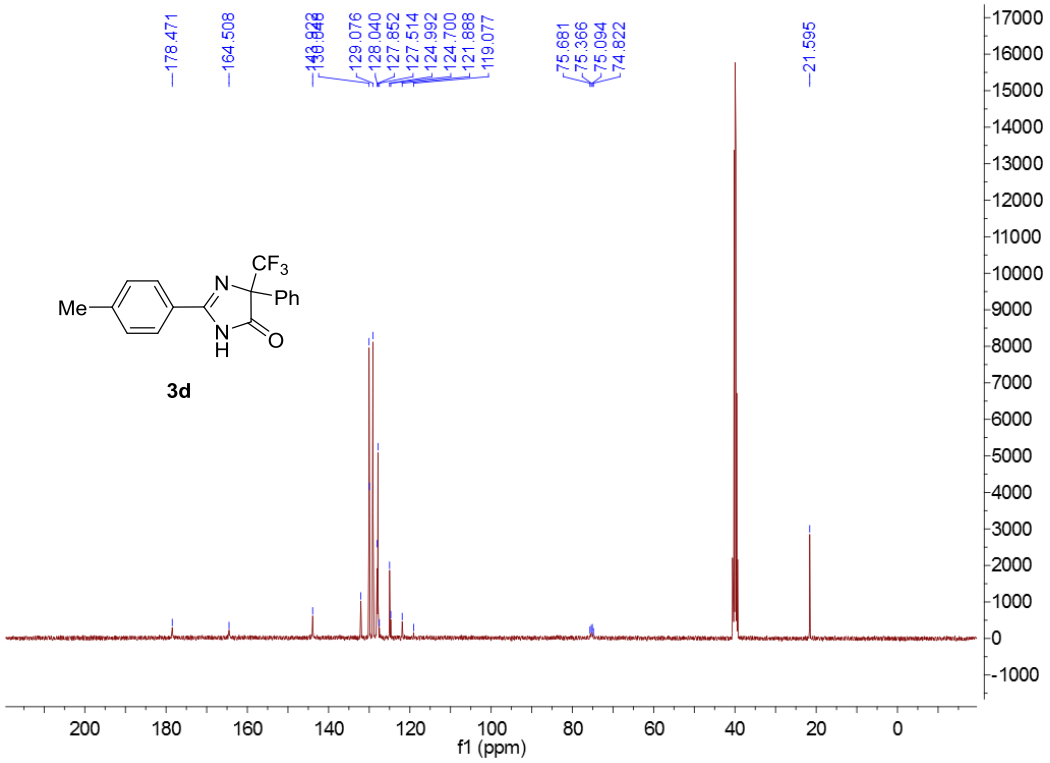
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3c



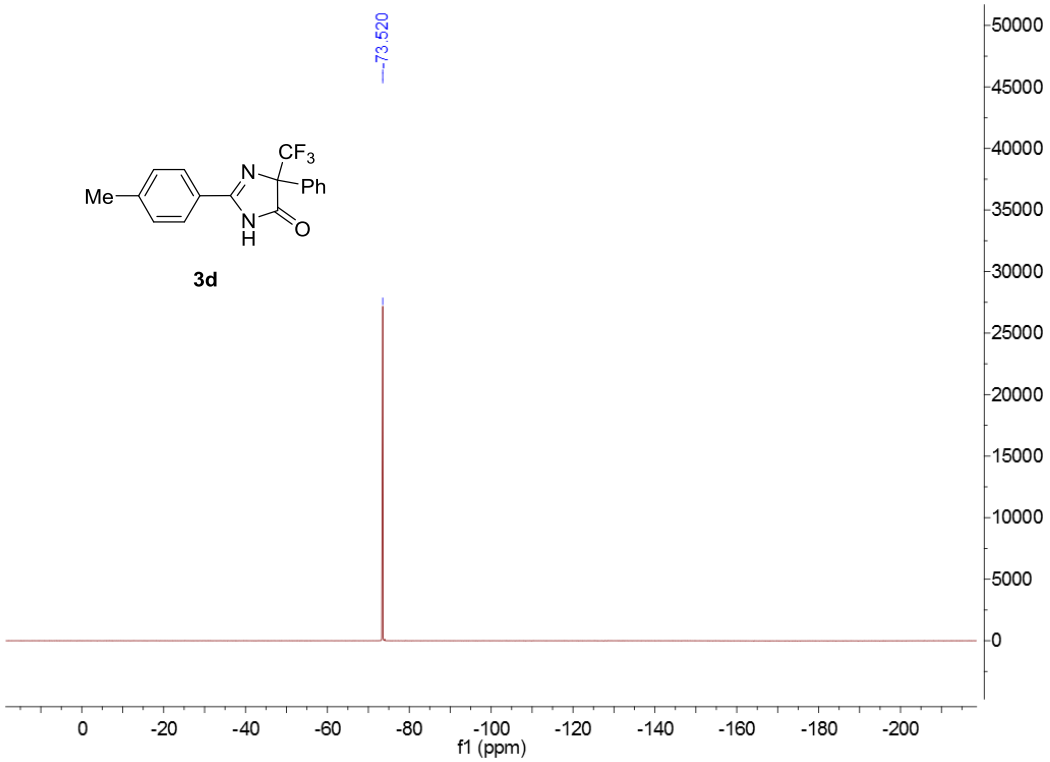
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3d



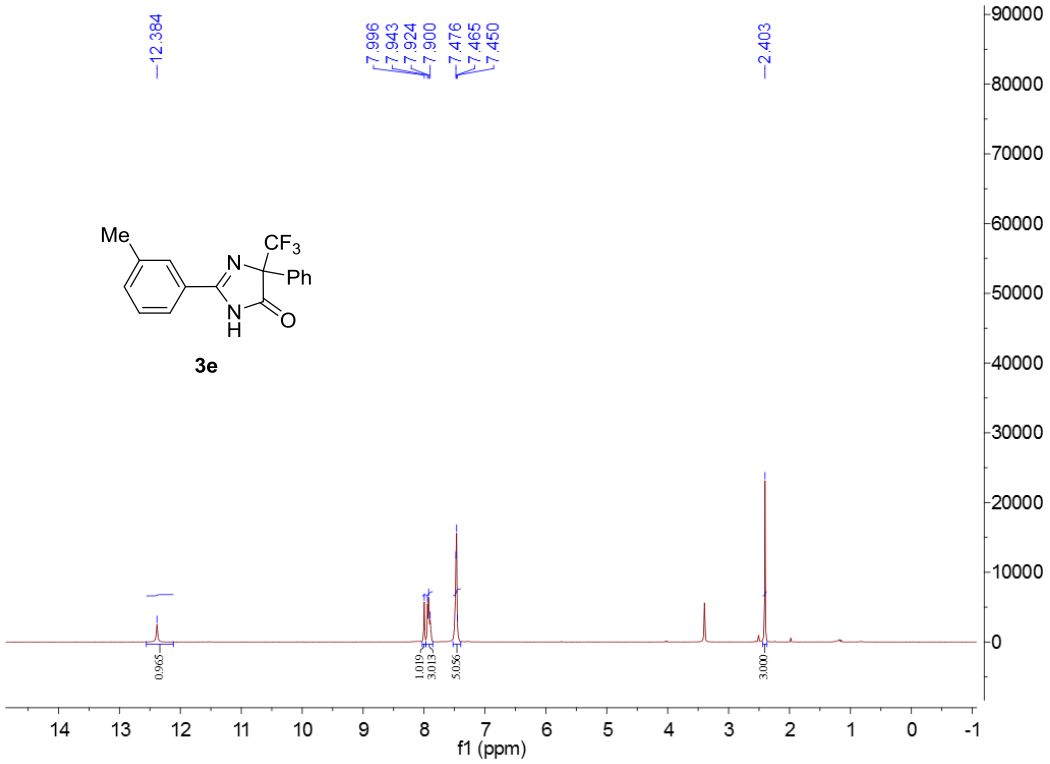
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3d



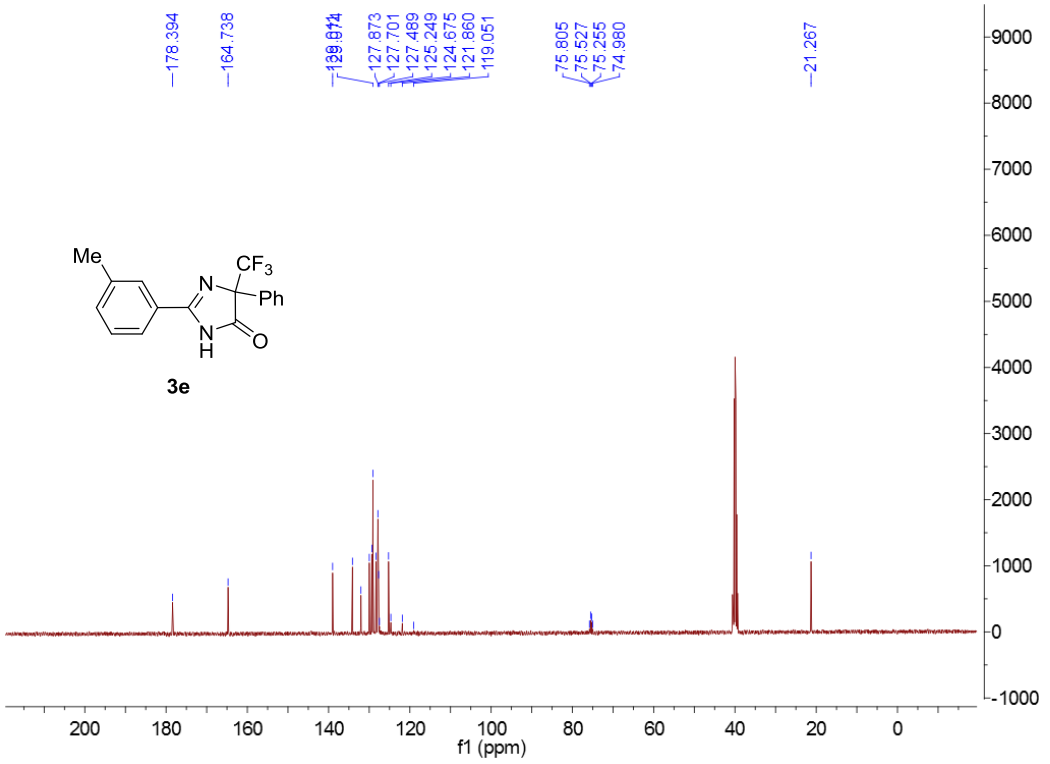
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3d



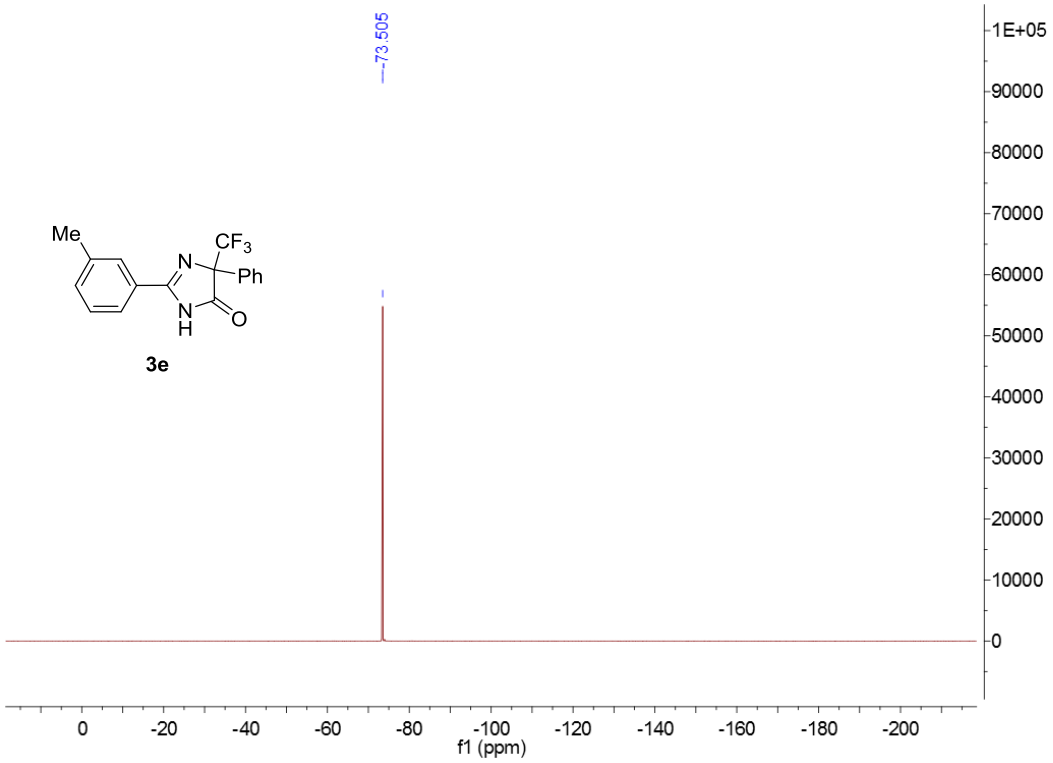
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3e



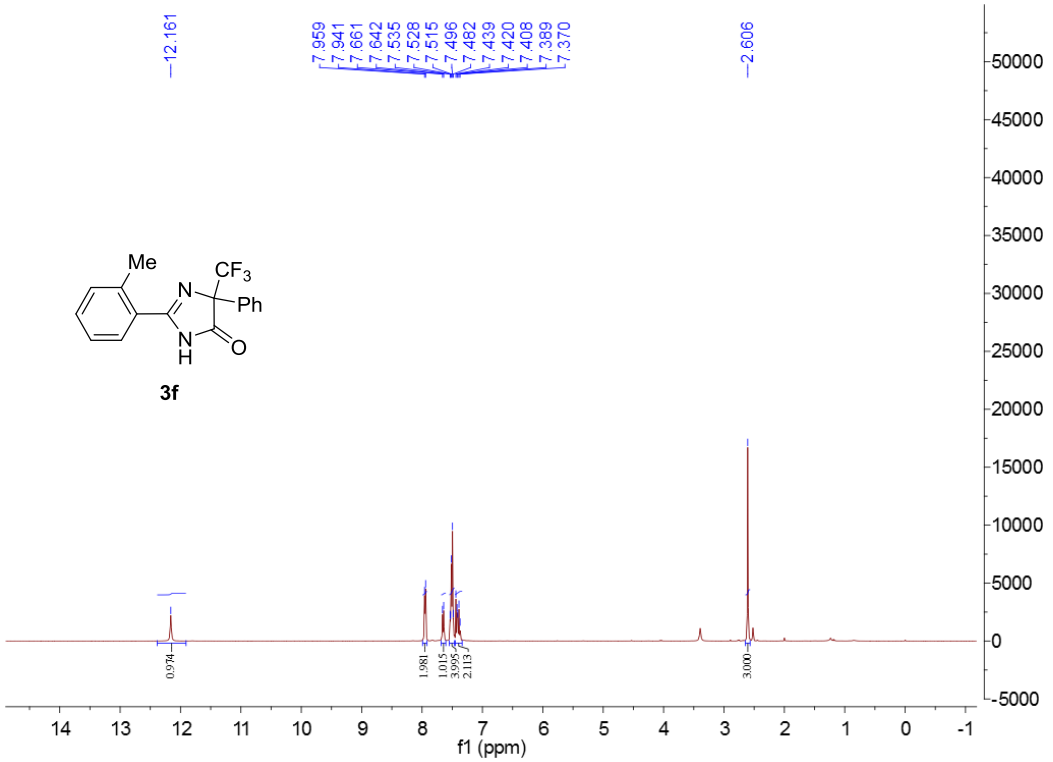
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3e



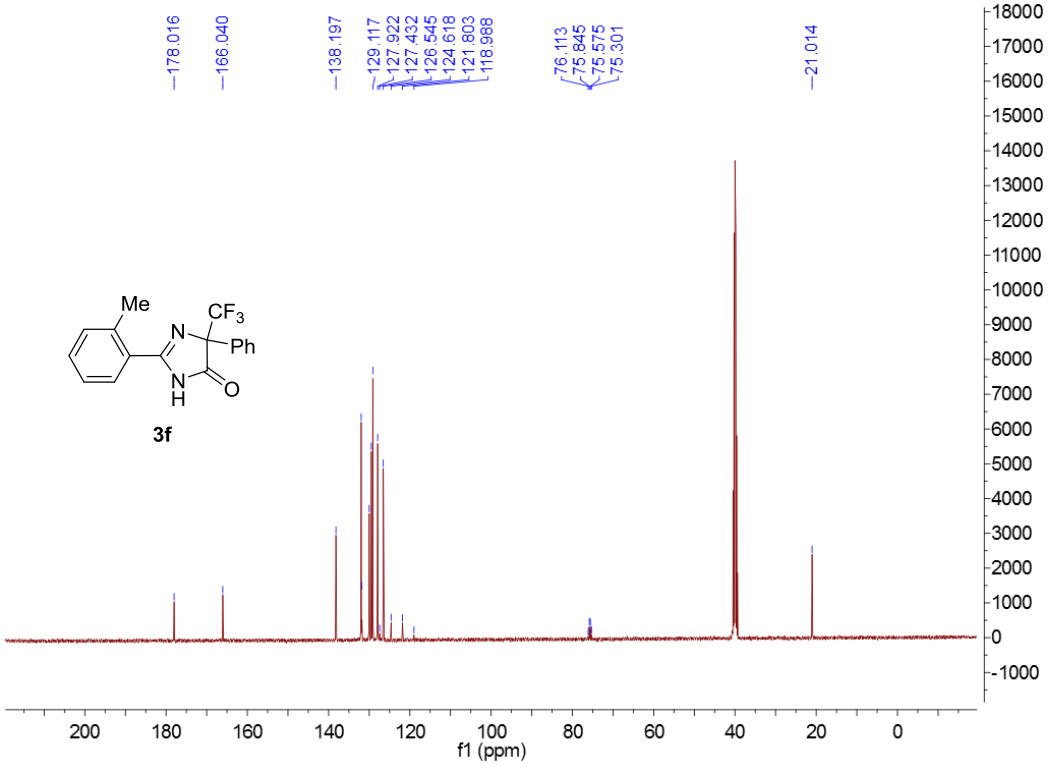
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3e



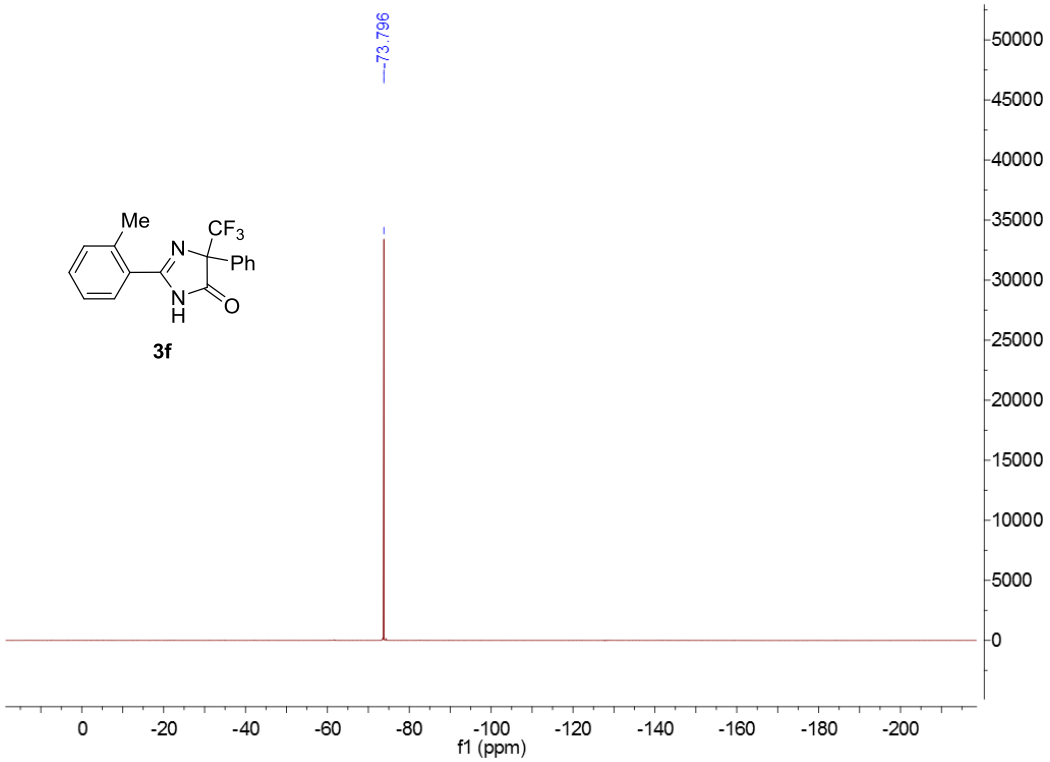
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3f



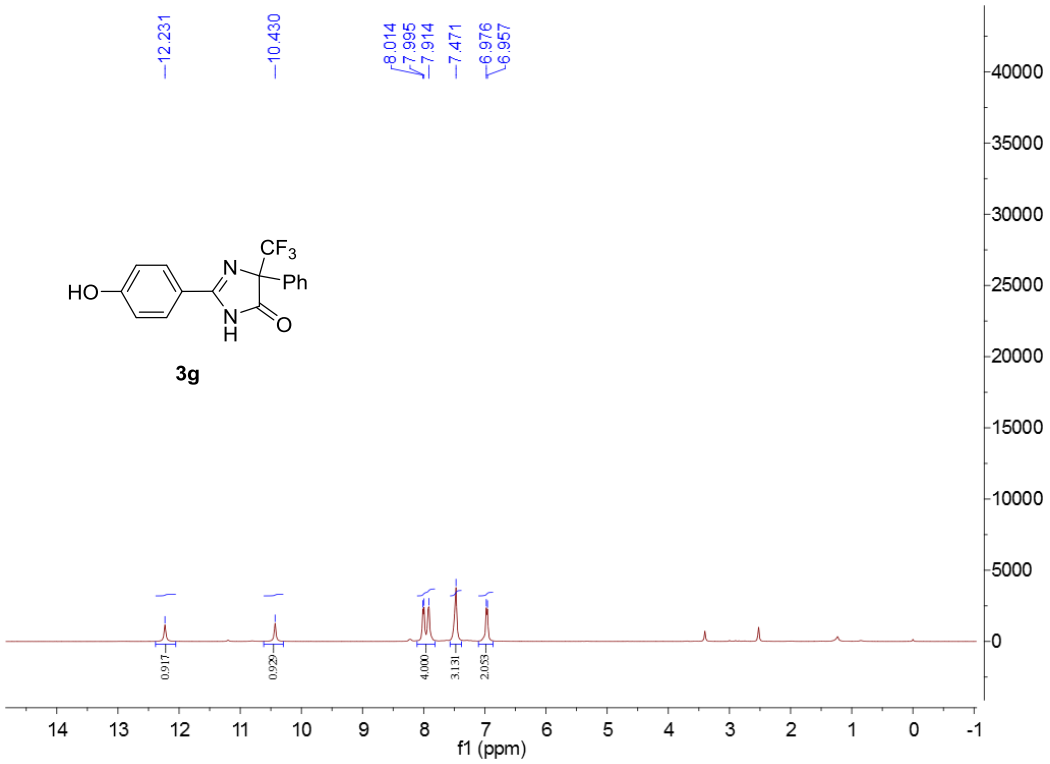
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3f



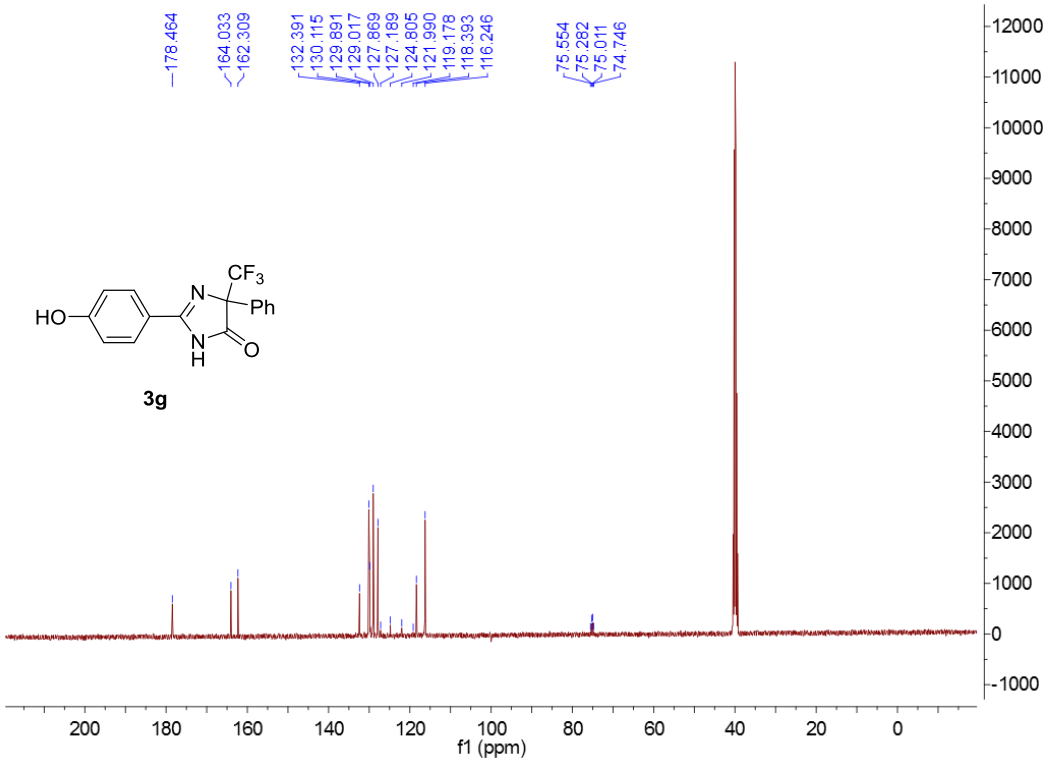
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3f



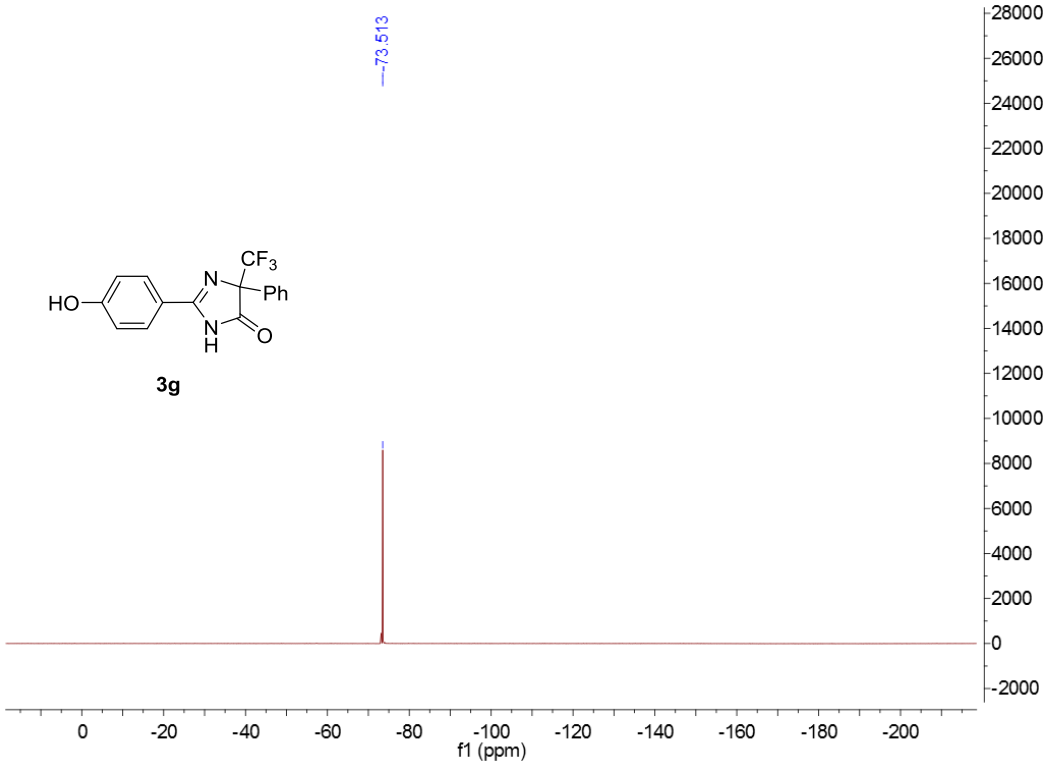
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3g



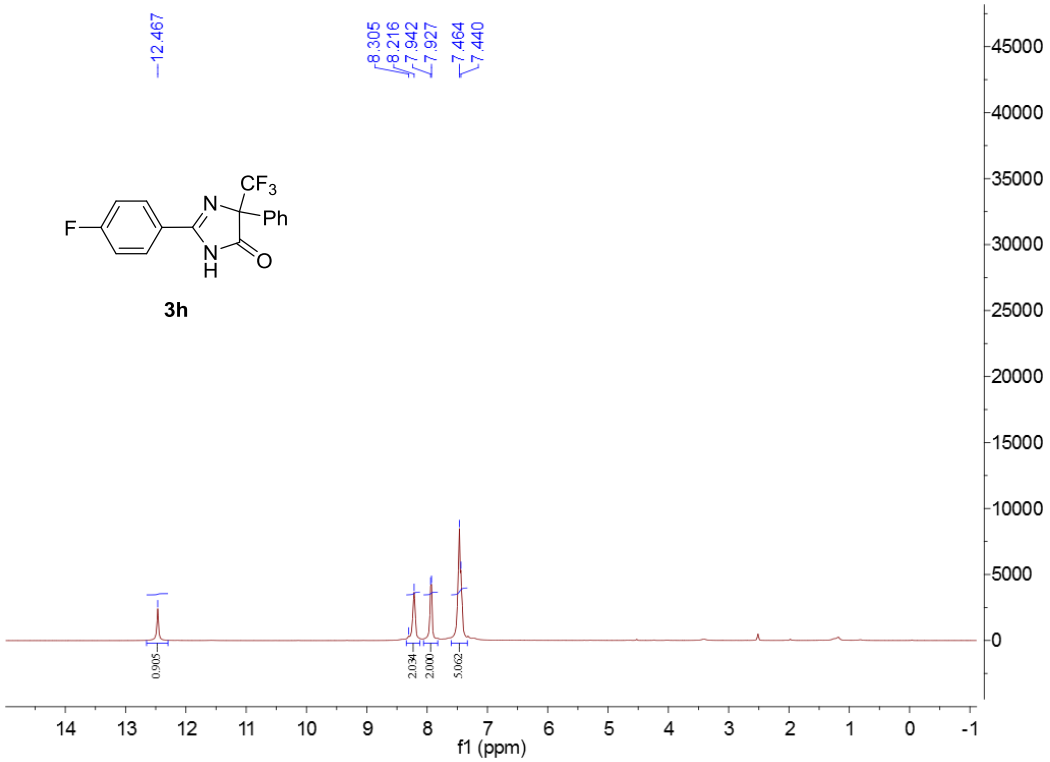
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3g



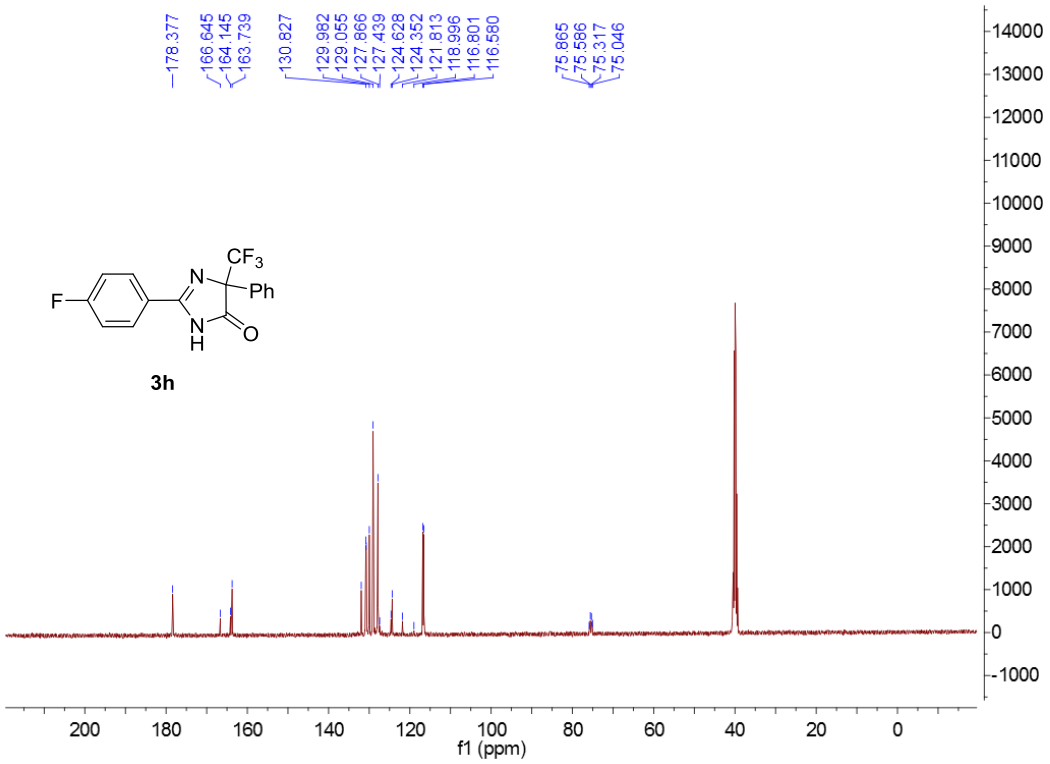
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3g



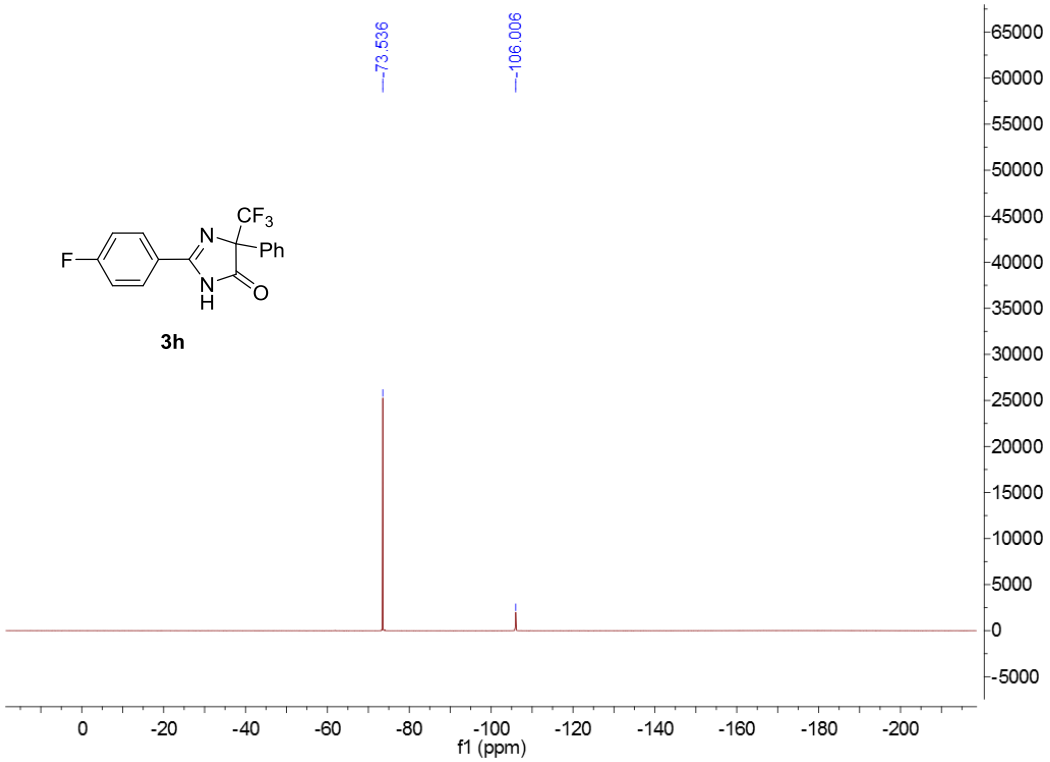
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3h



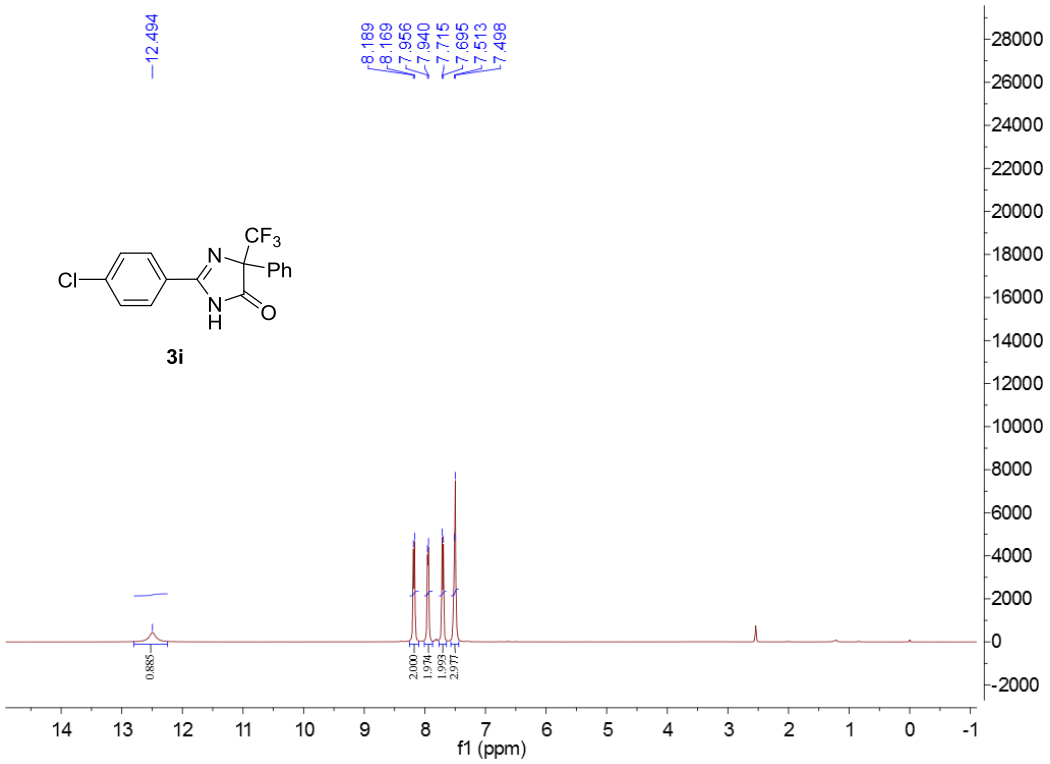
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3h



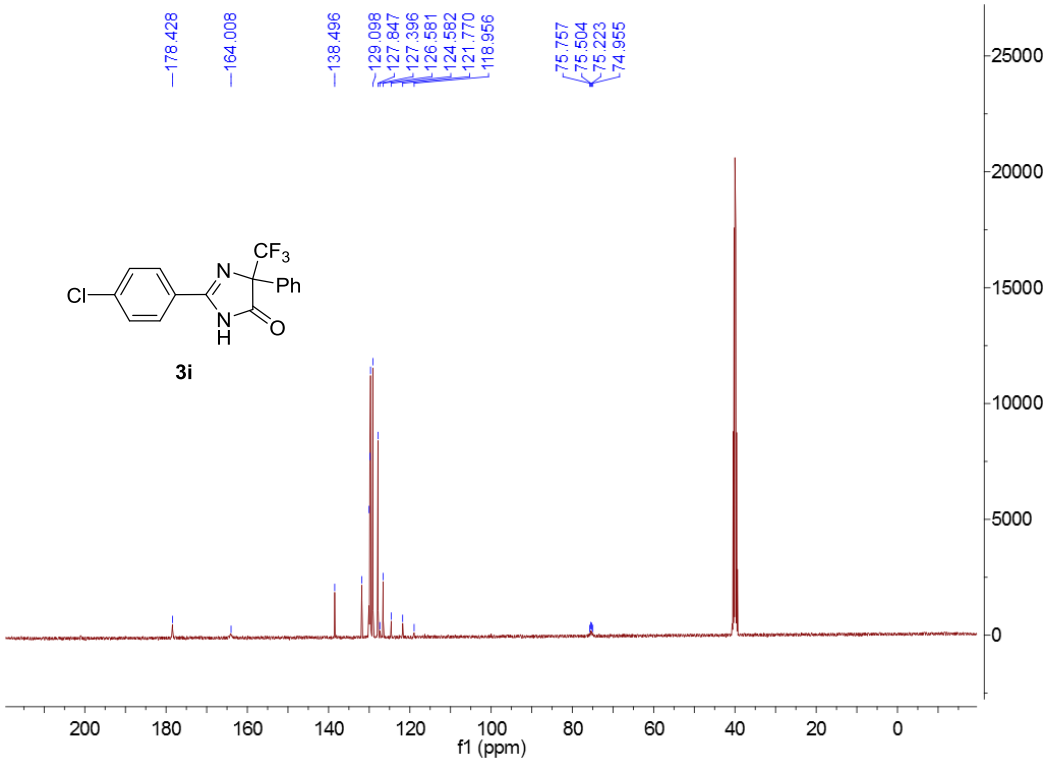
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3h



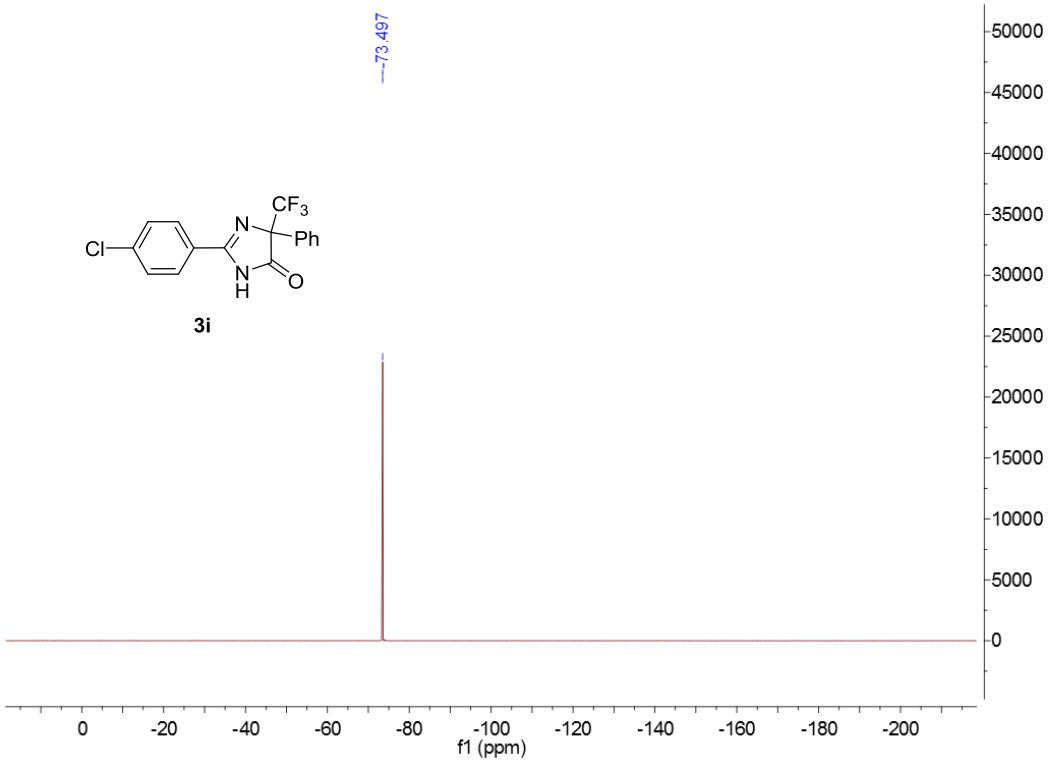
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3i



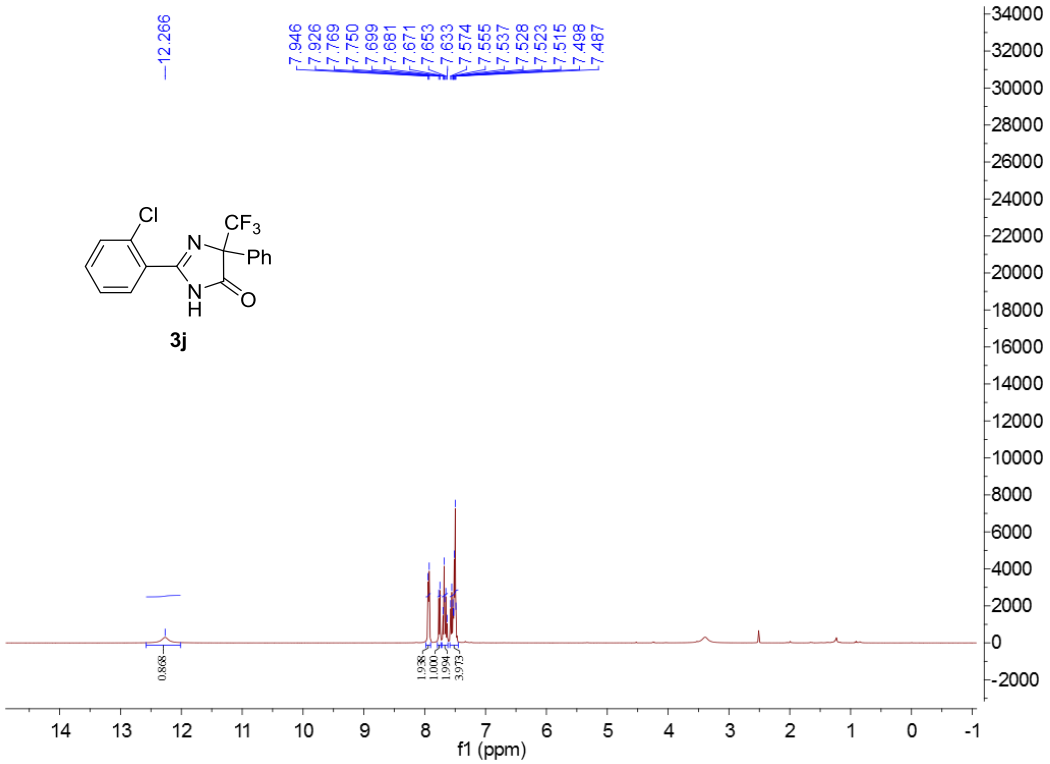
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3i



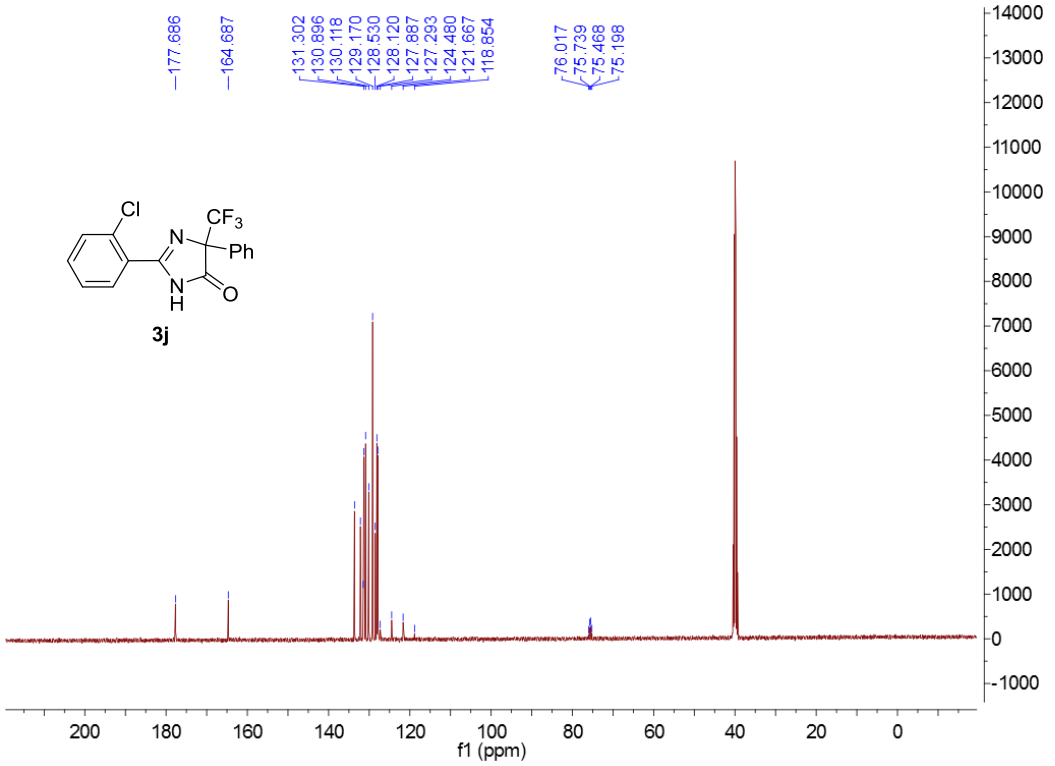
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3i



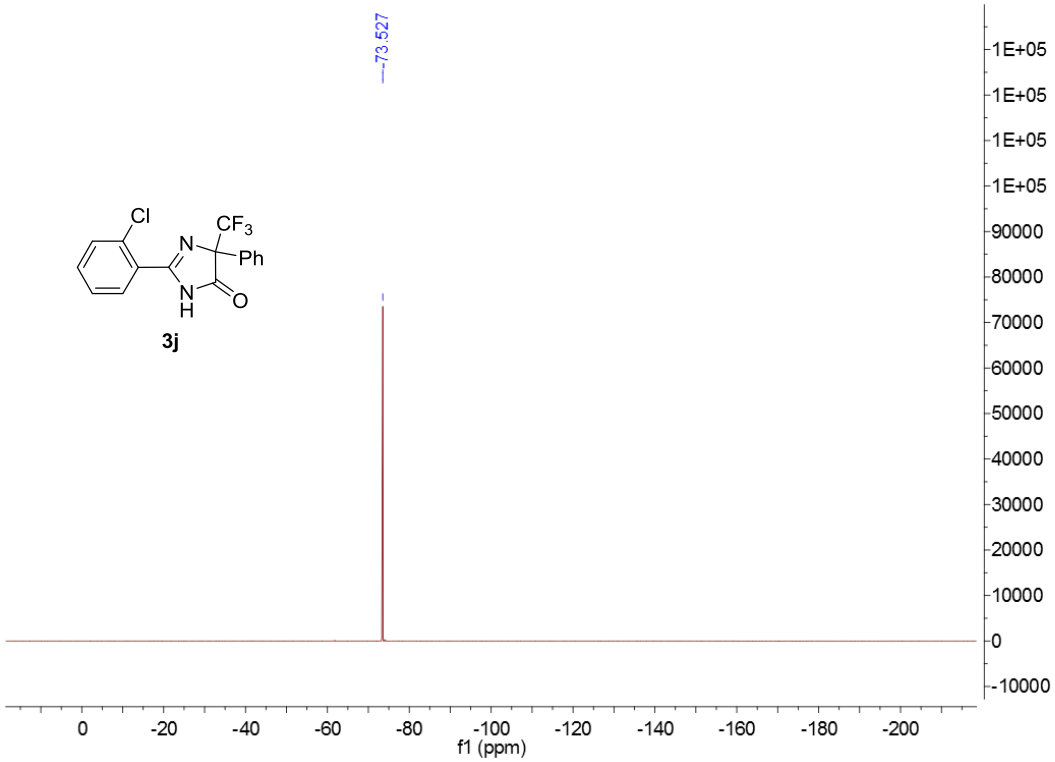
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3j



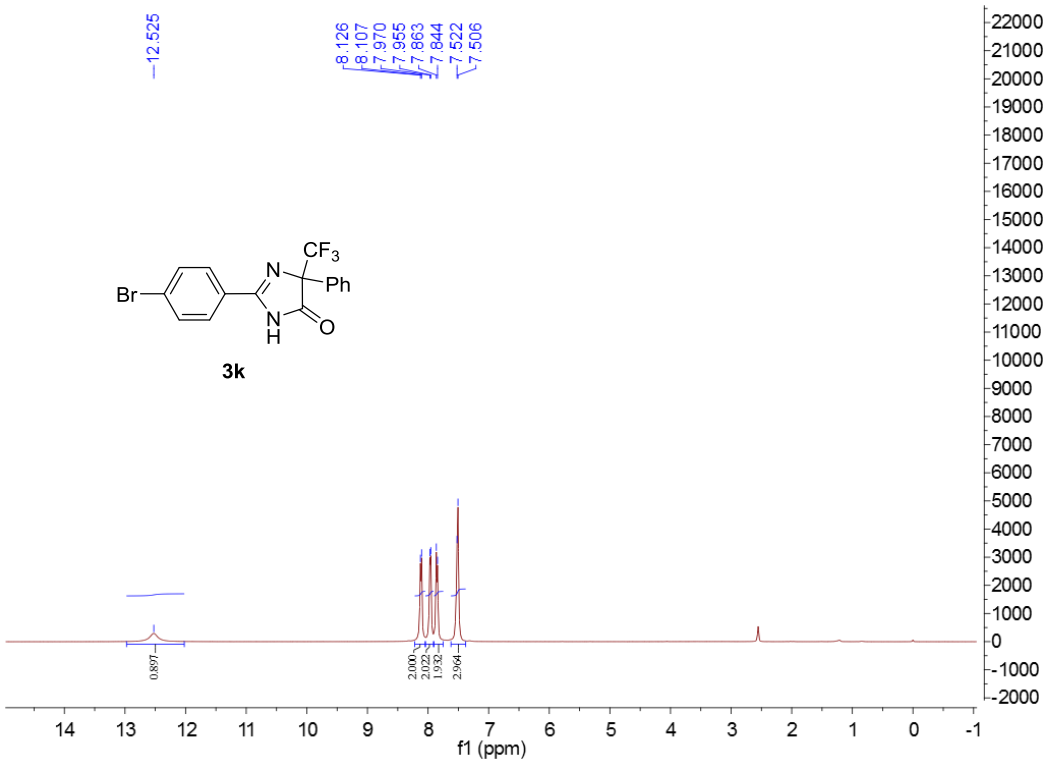
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3j



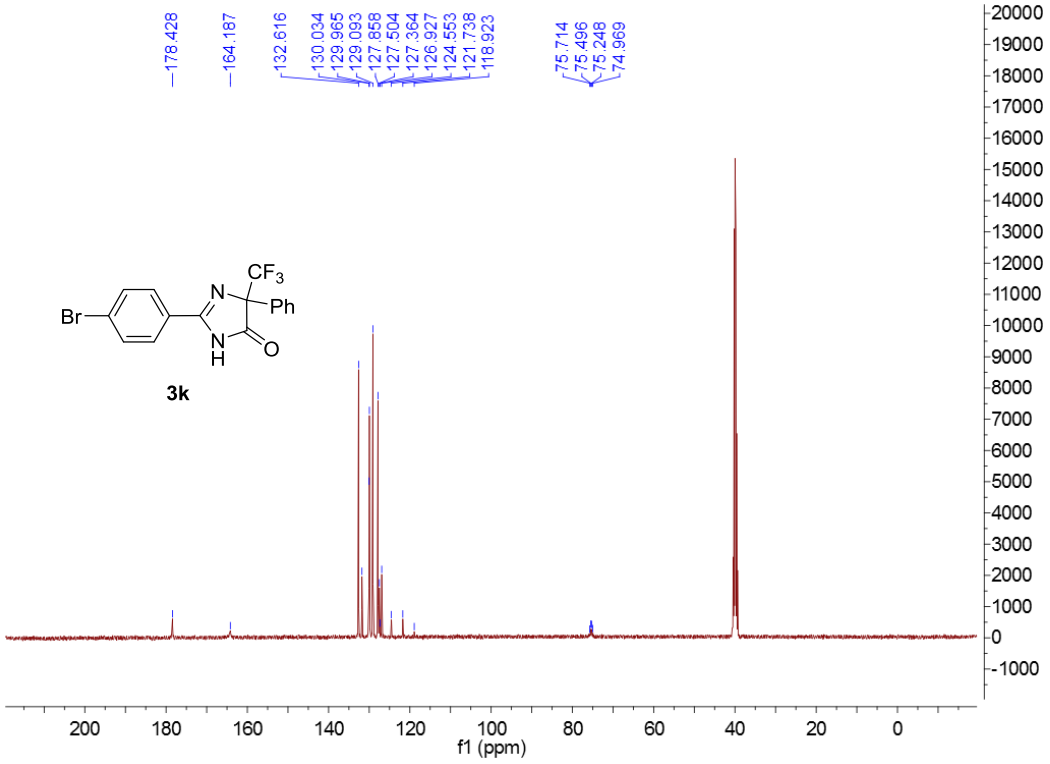
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3j



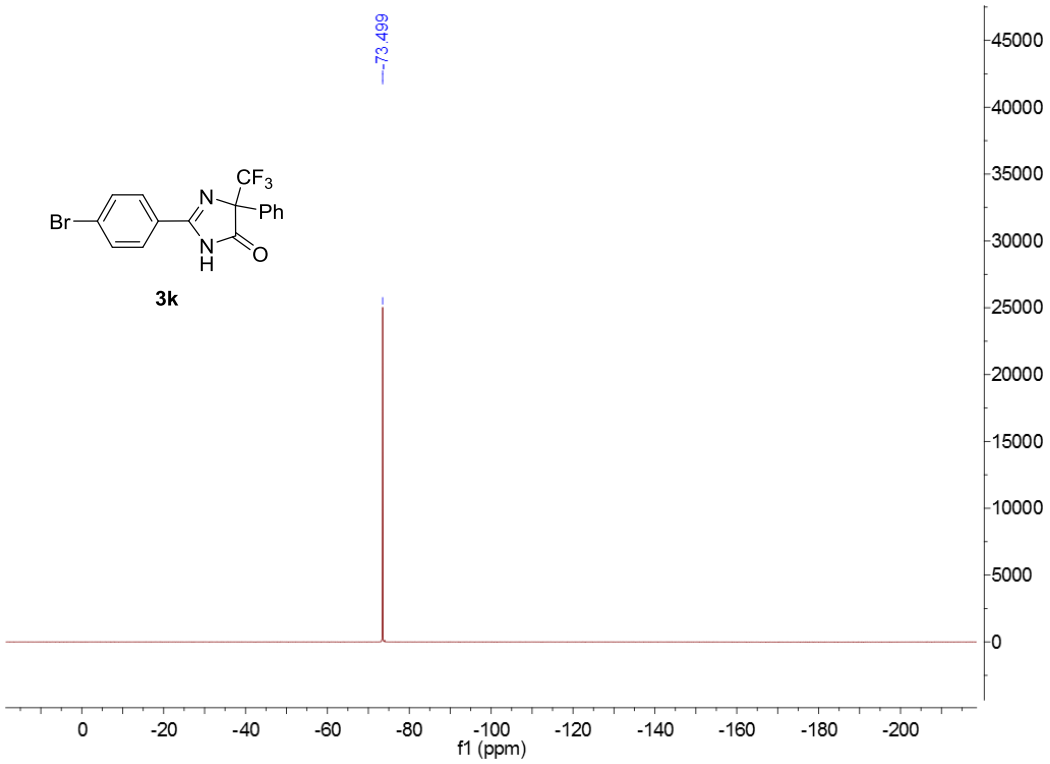
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3k



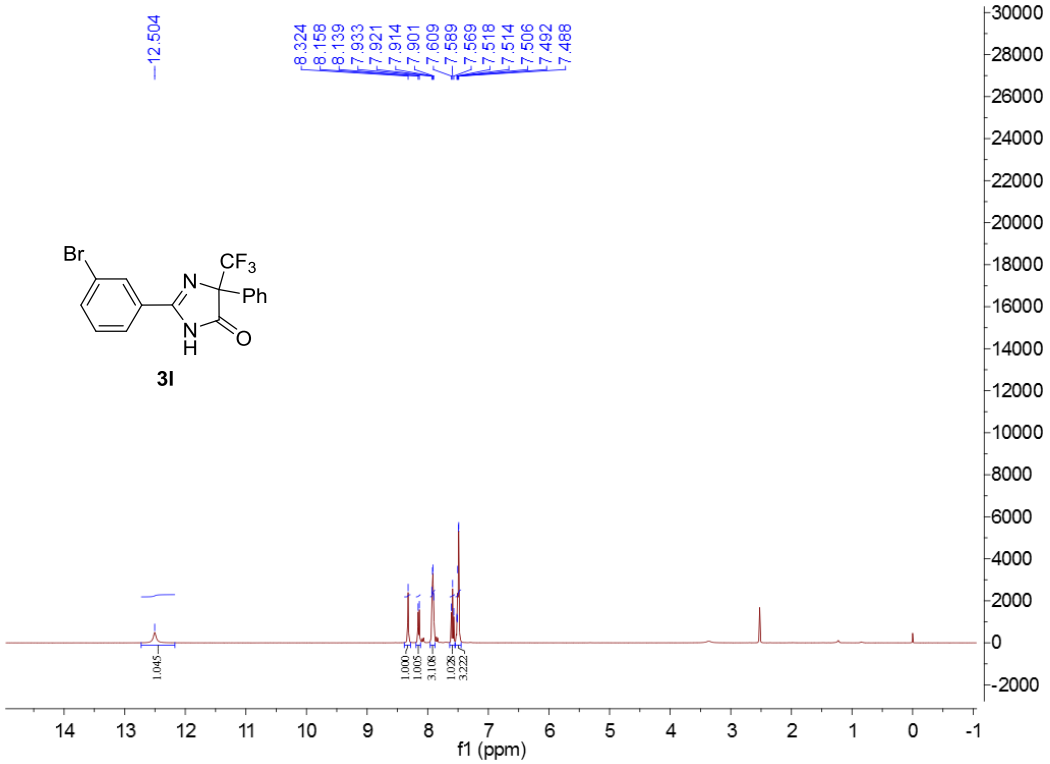
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3k



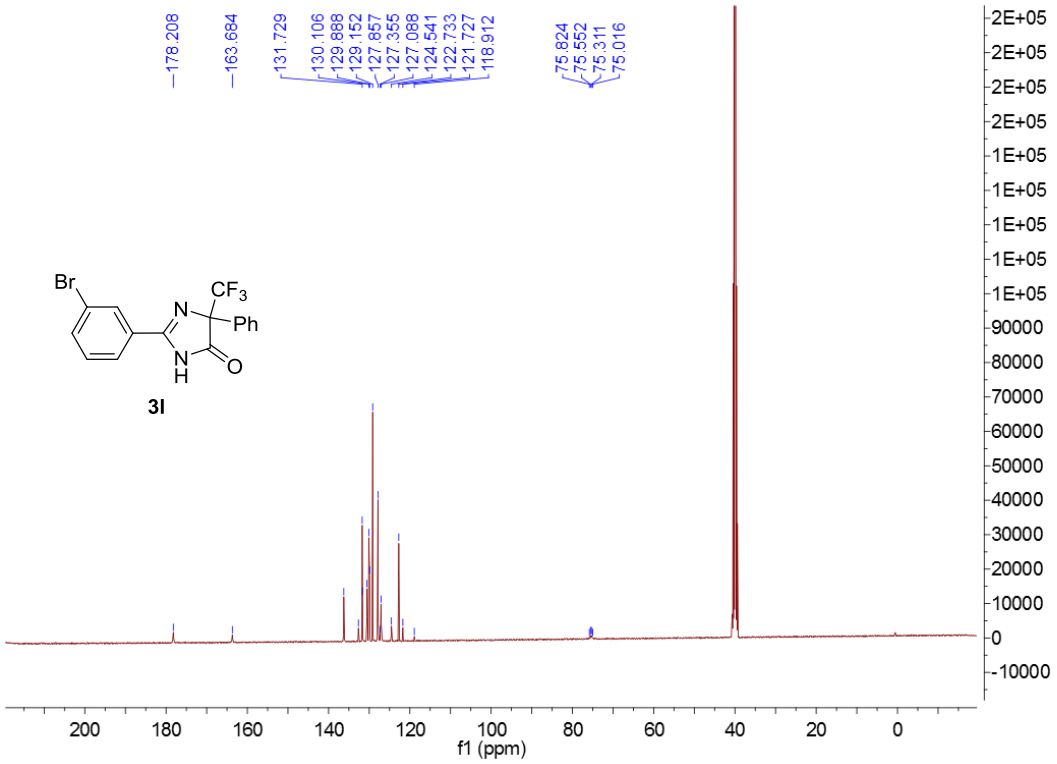
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3k



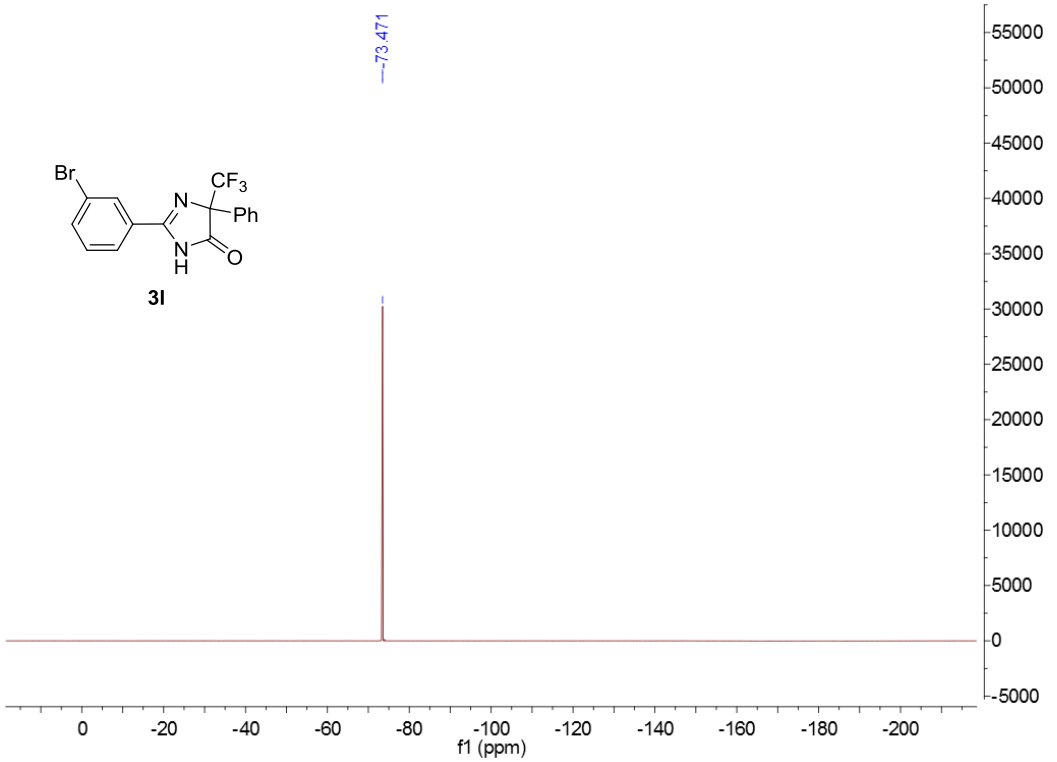
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3l



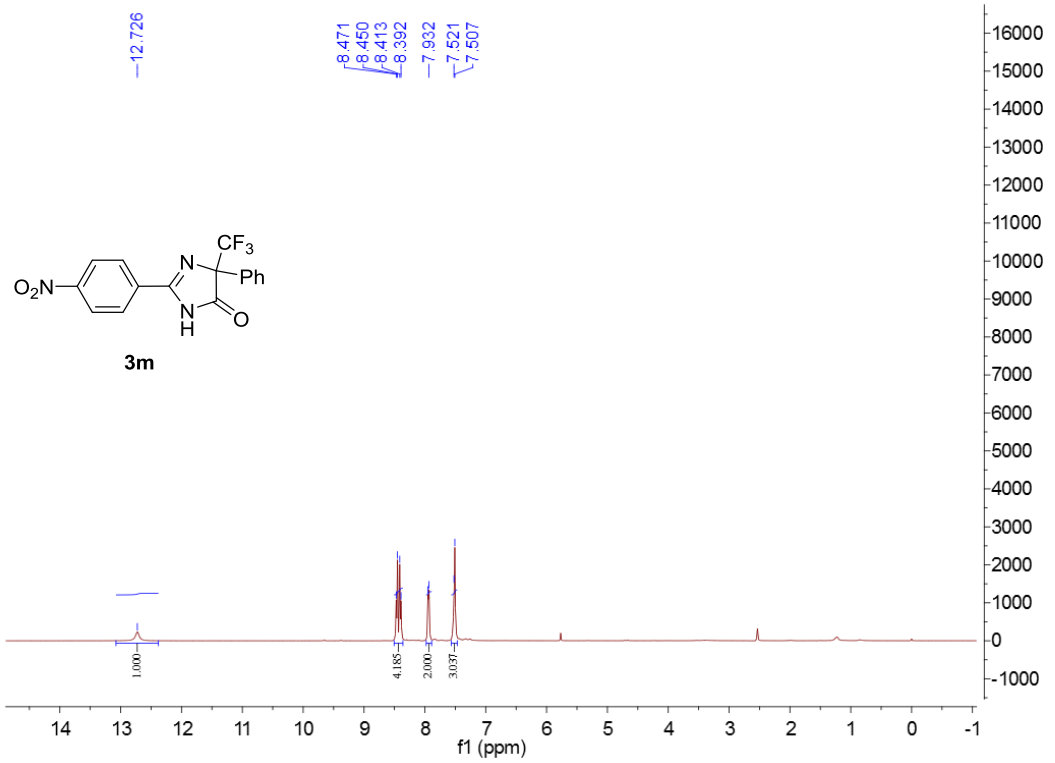
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3l



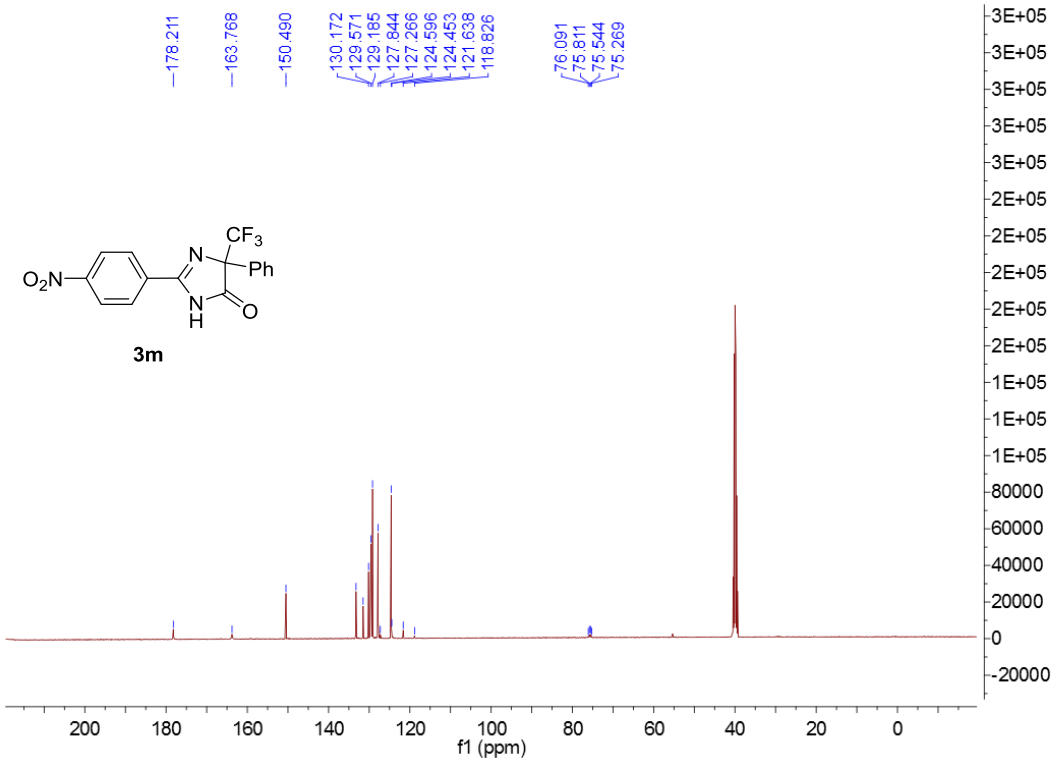
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3l



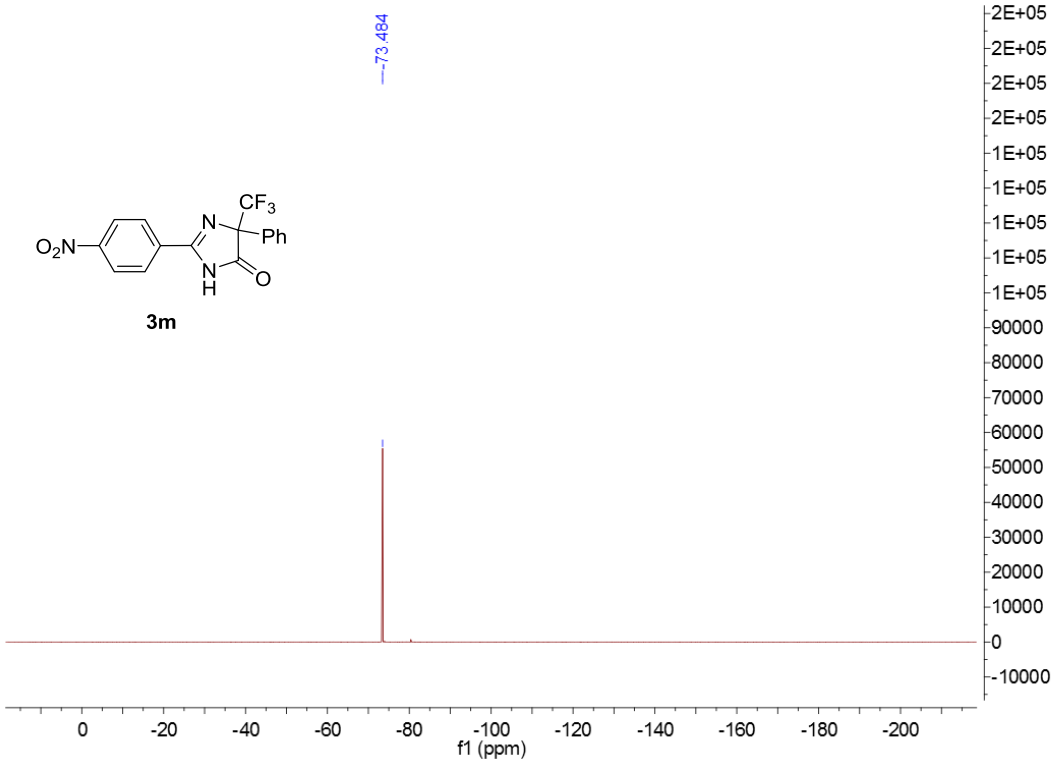
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3m



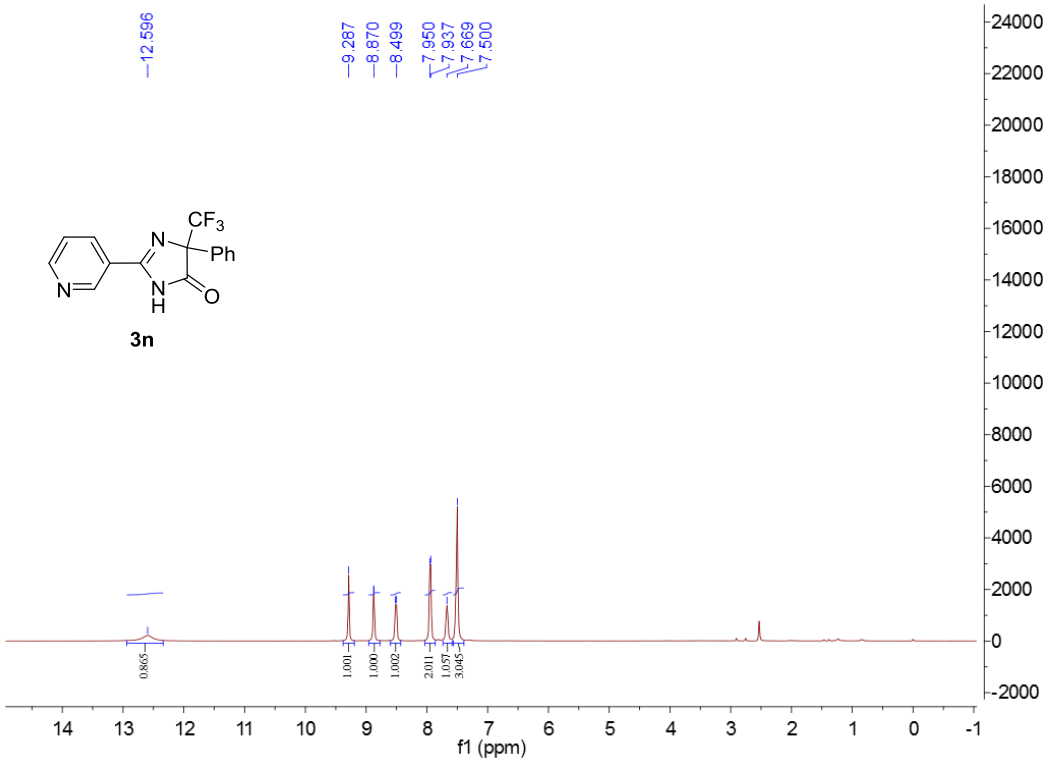
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3m



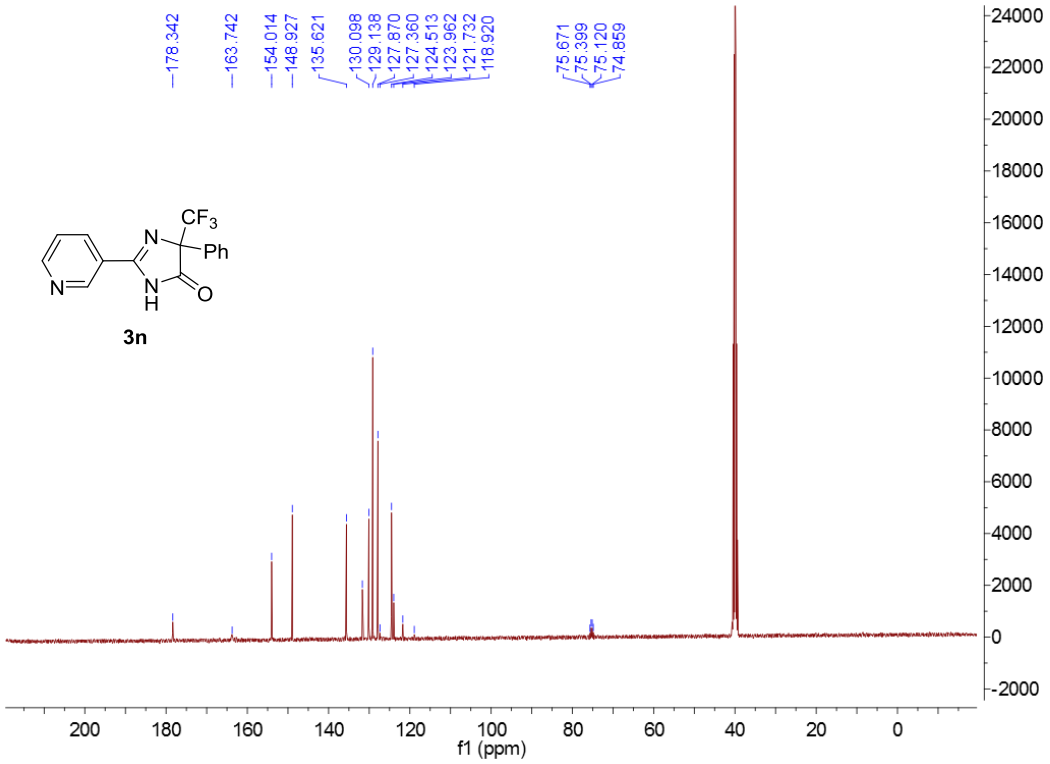
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3m



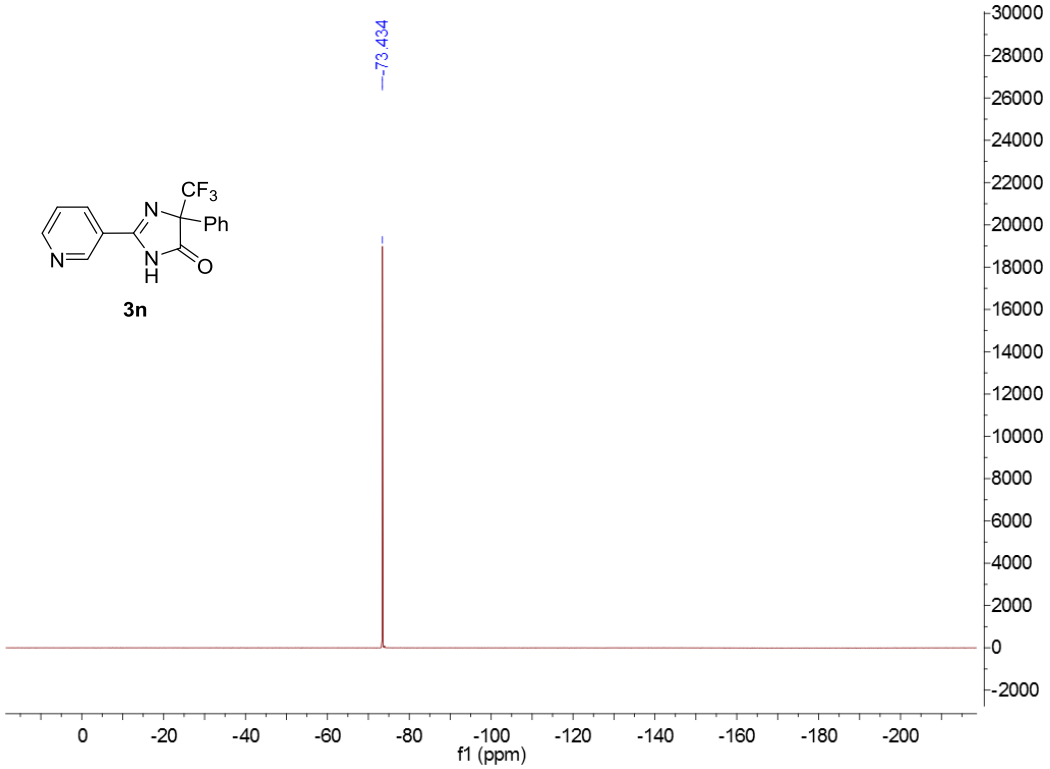
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3n



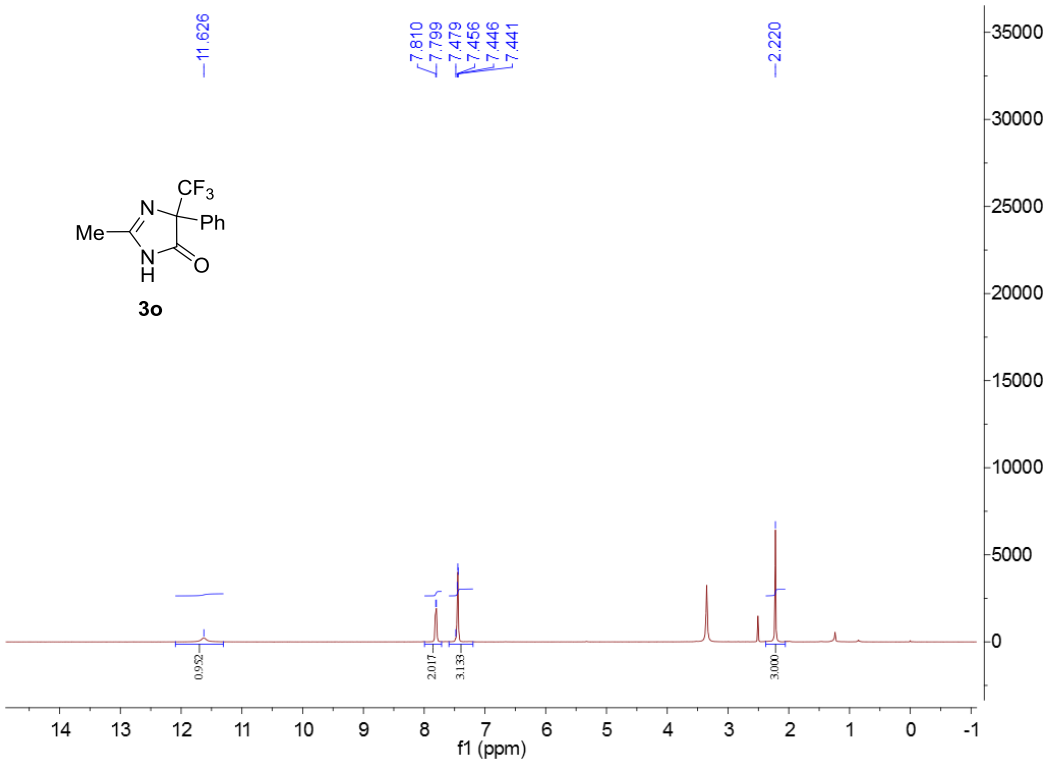
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3n



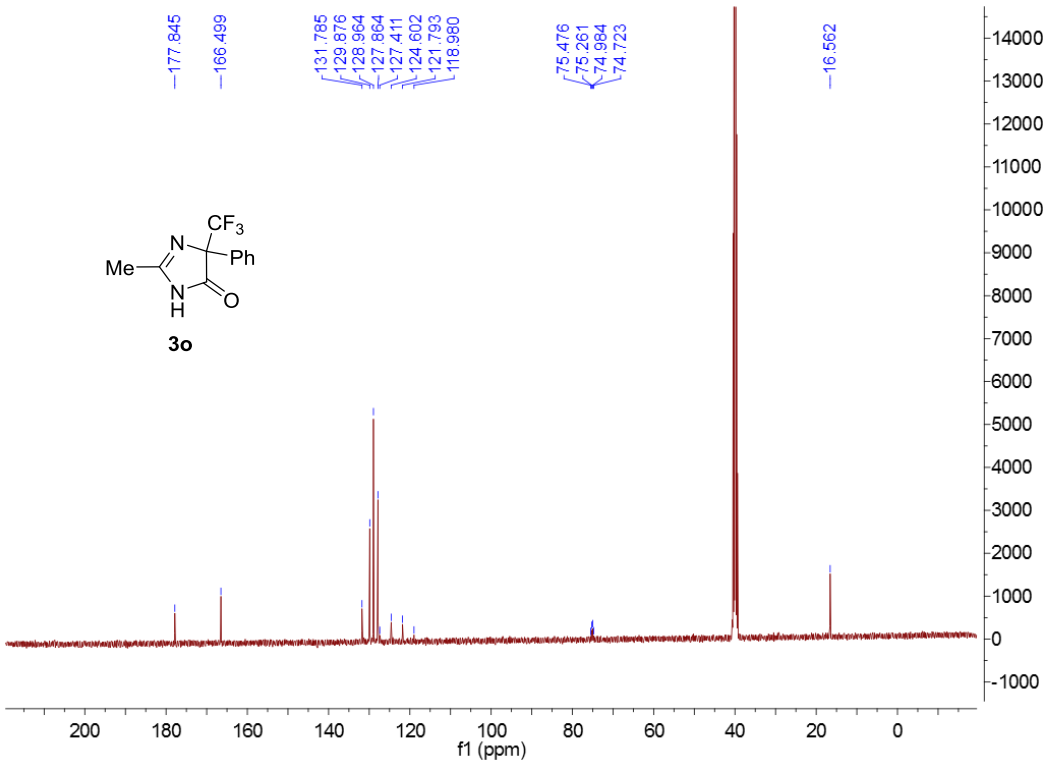
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3n



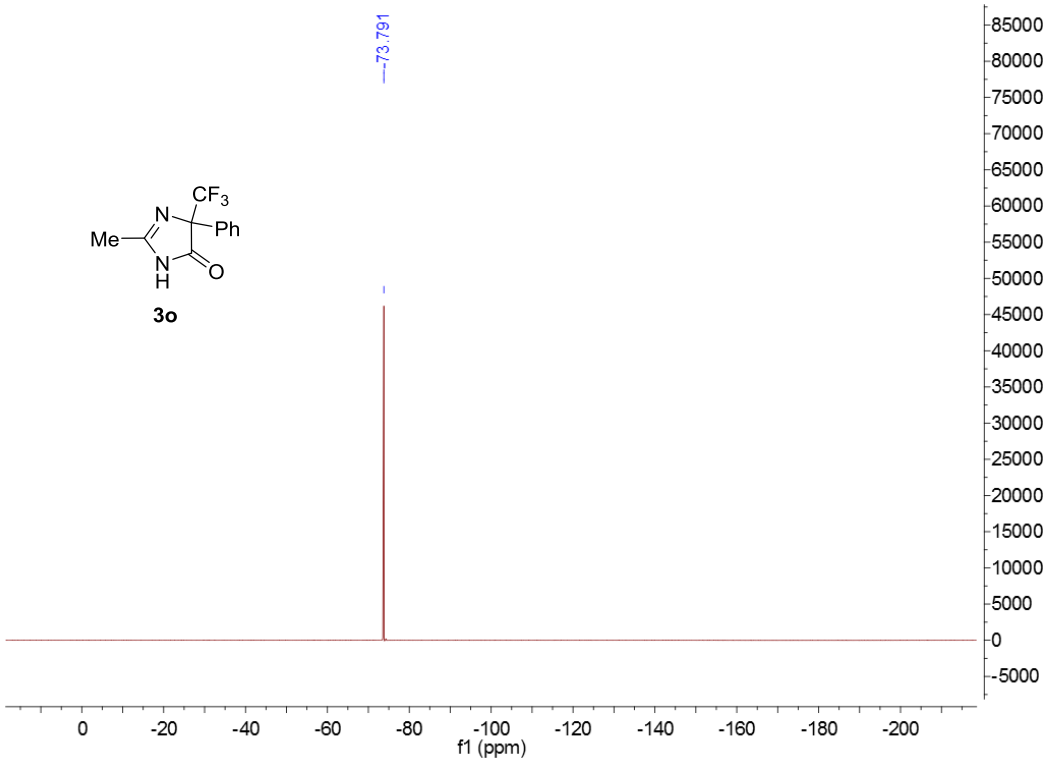
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3o



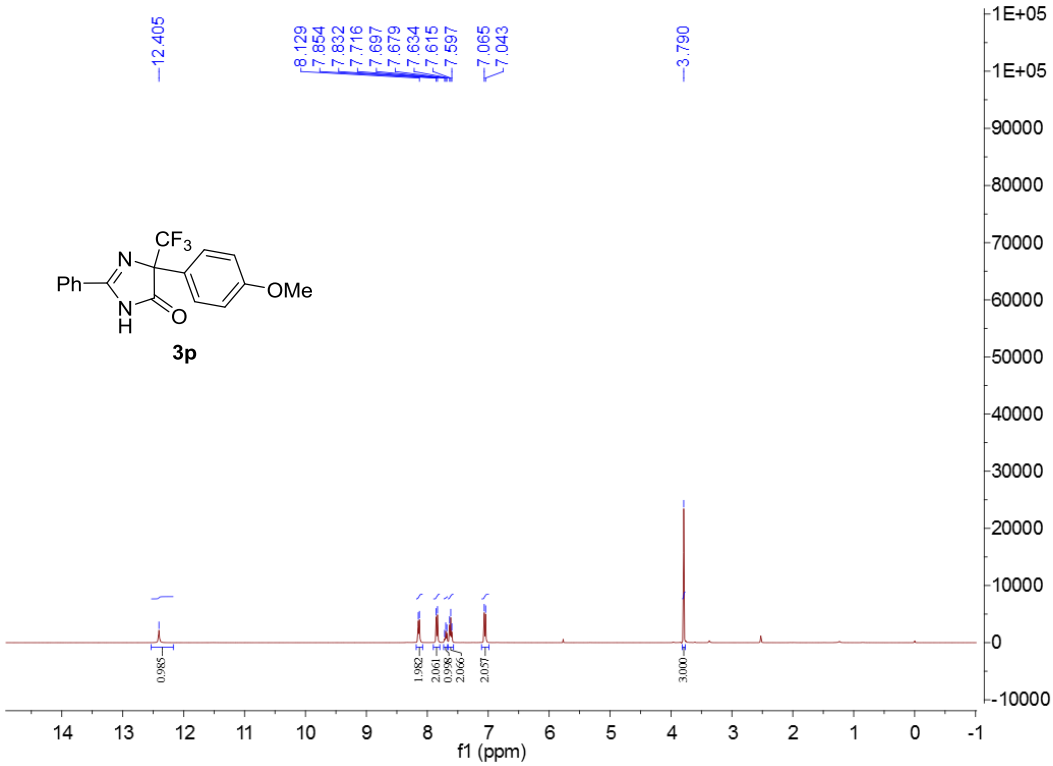
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3o



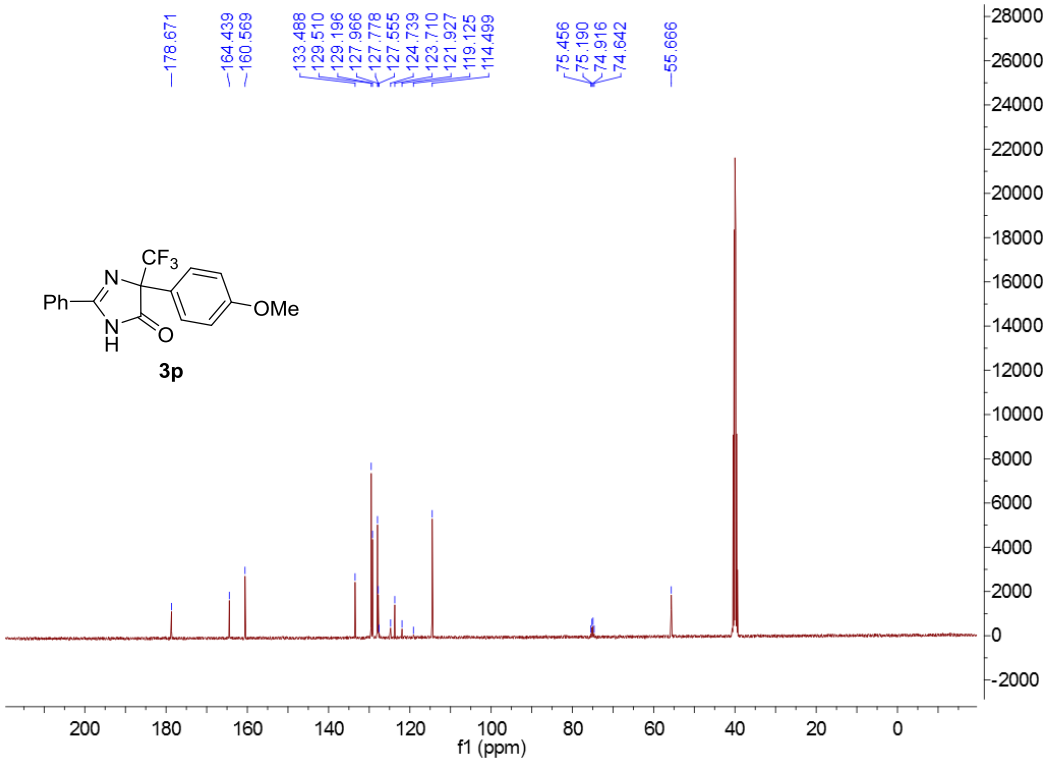
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3o



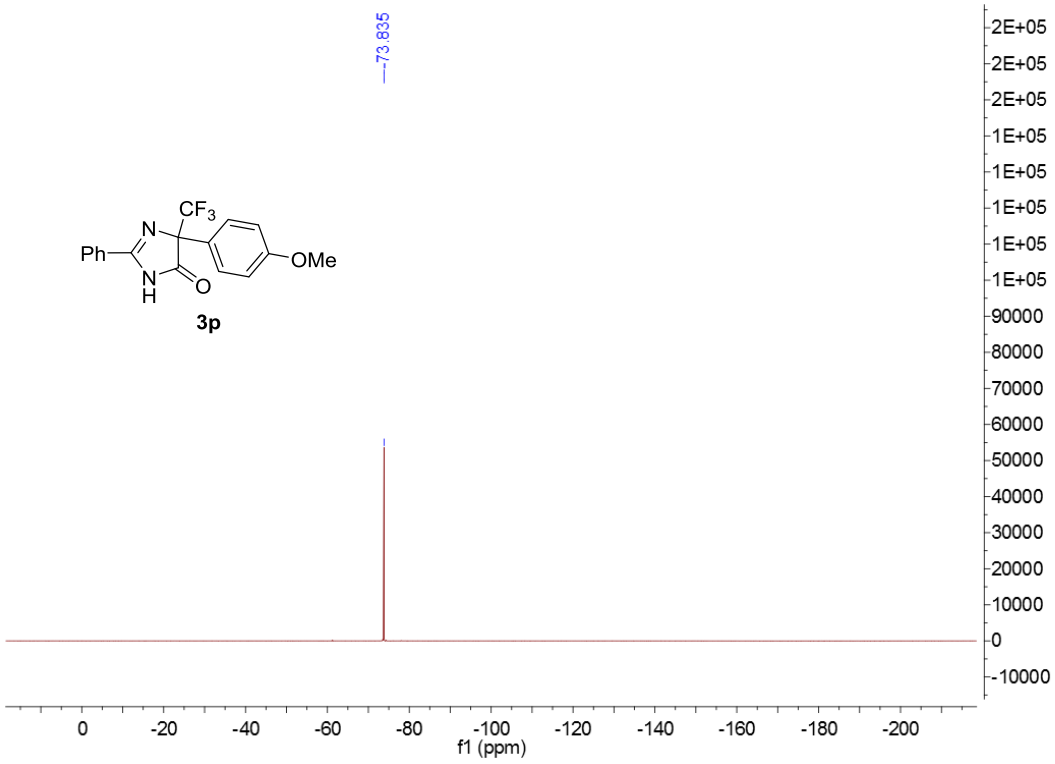
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3p



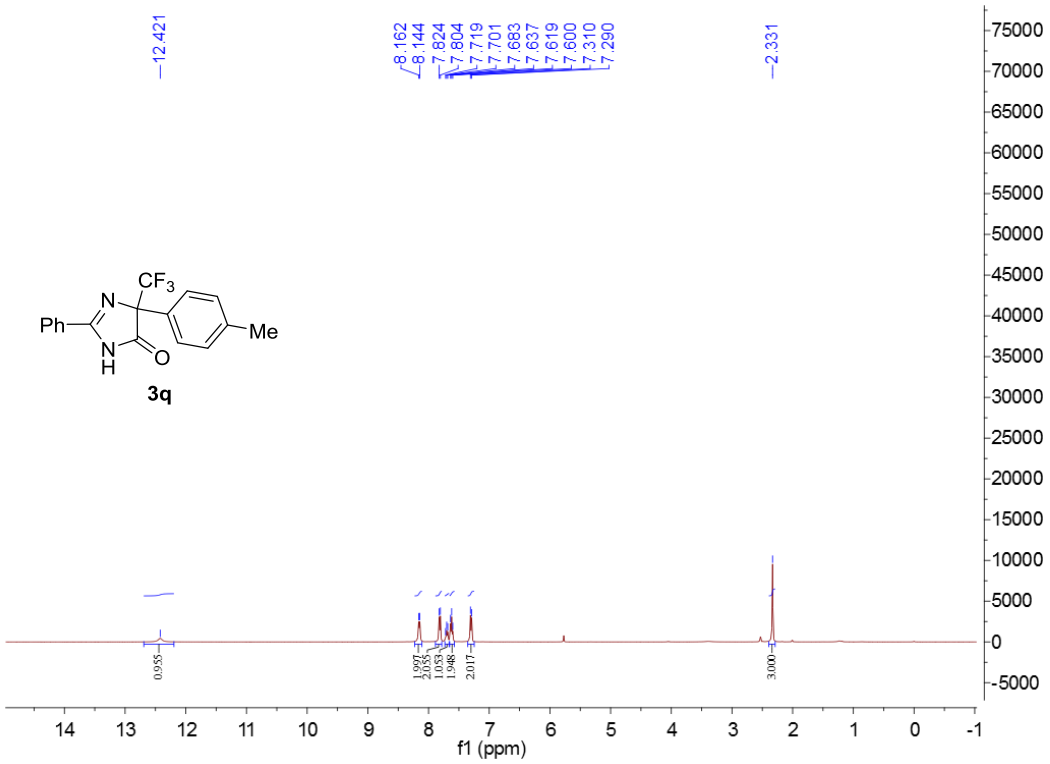
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3p



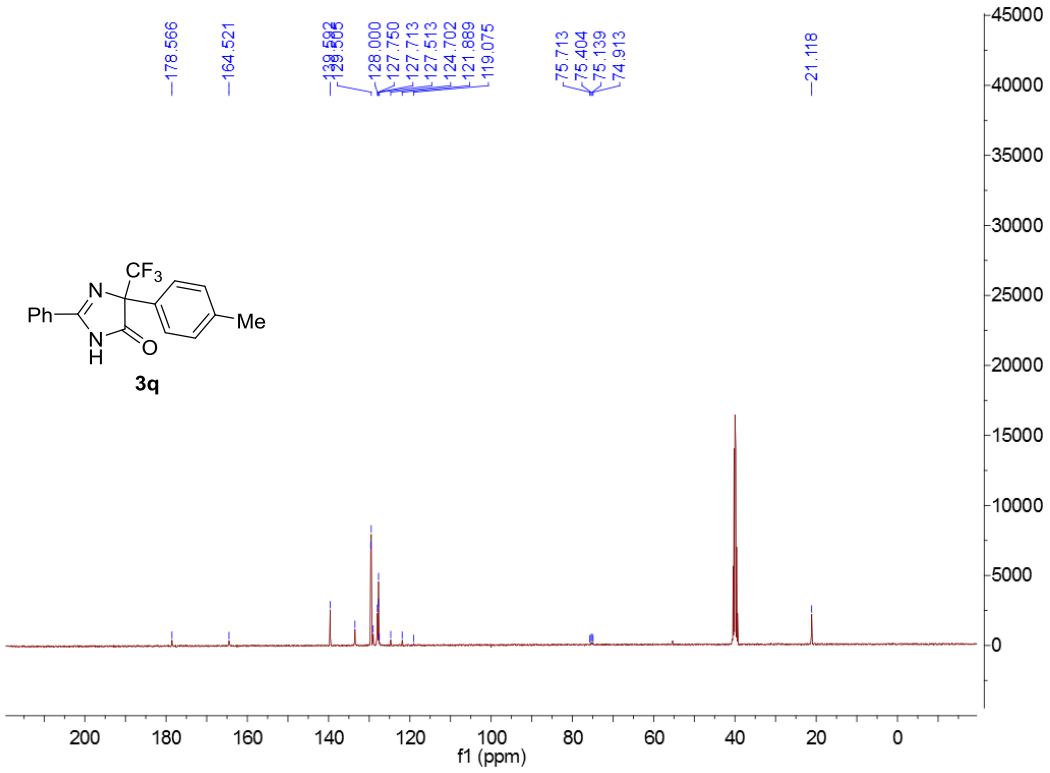
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3p



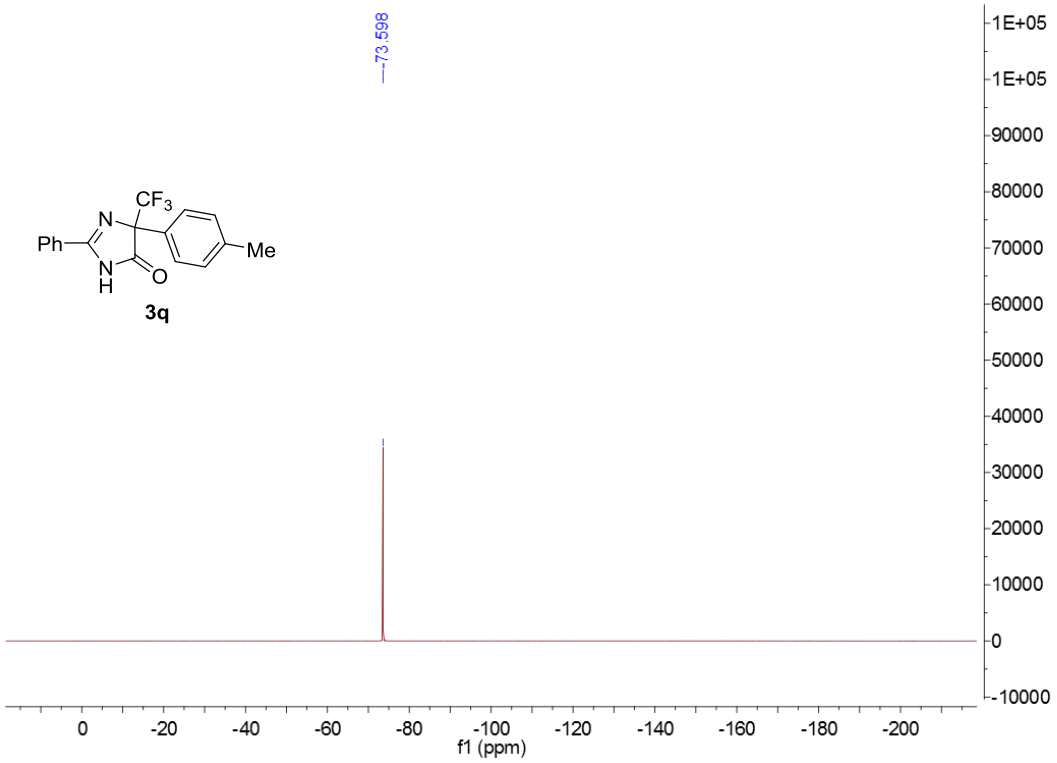
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3q



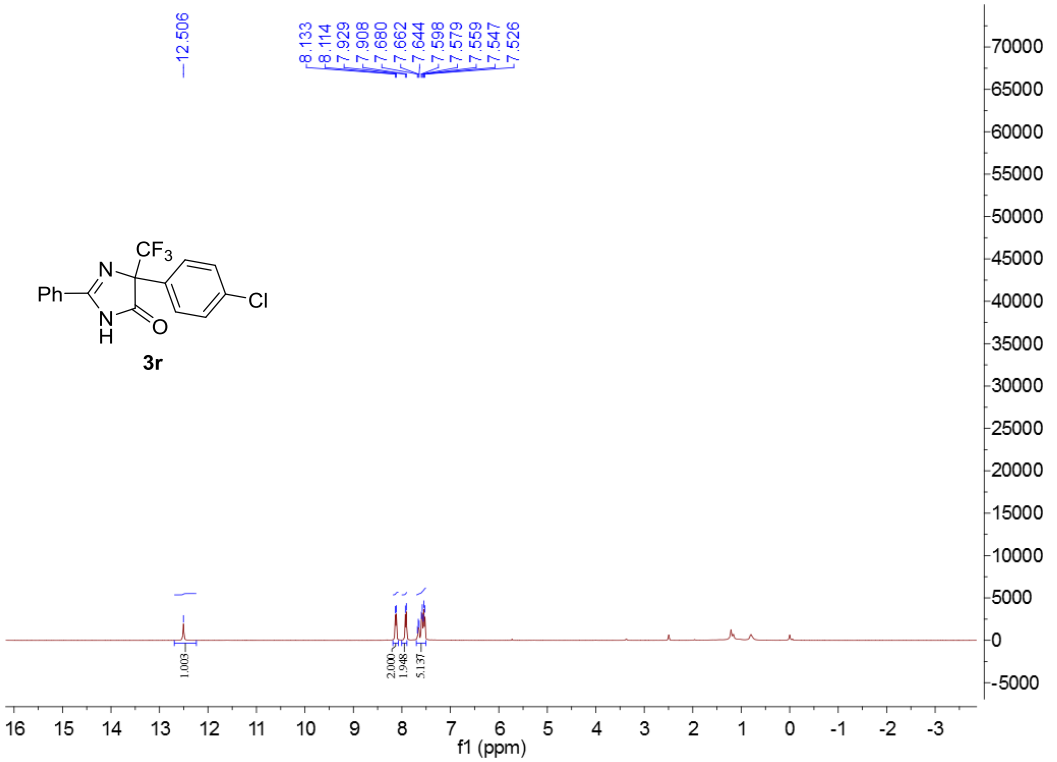
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3q



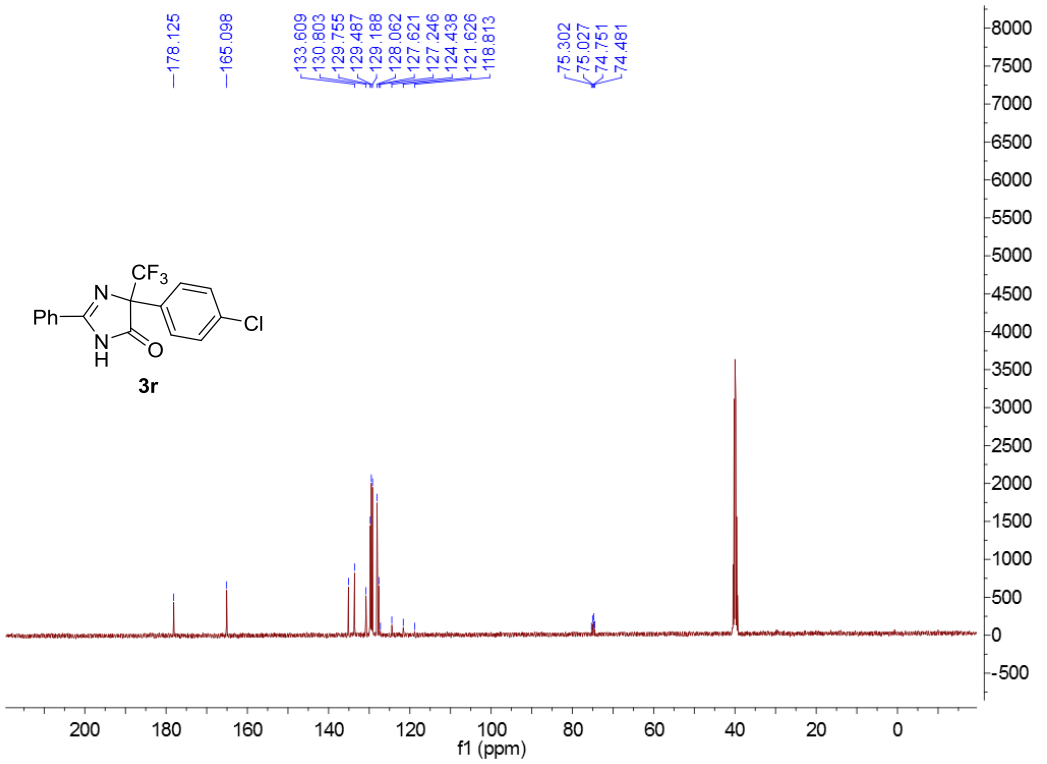
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3q



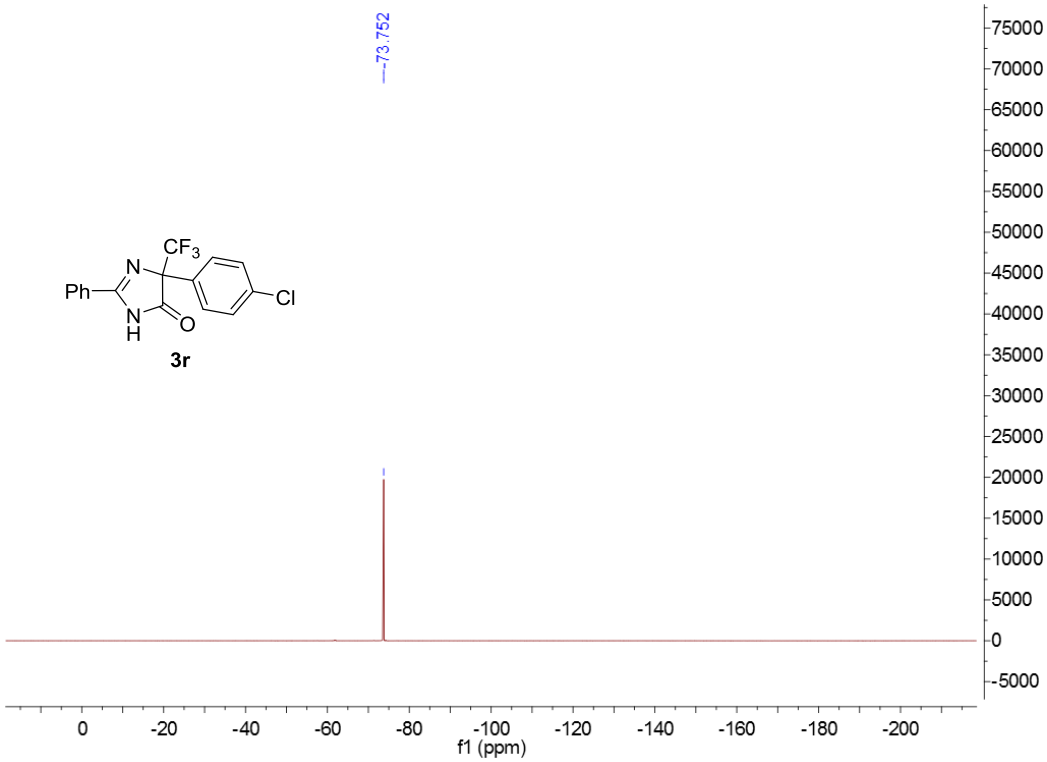
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3r



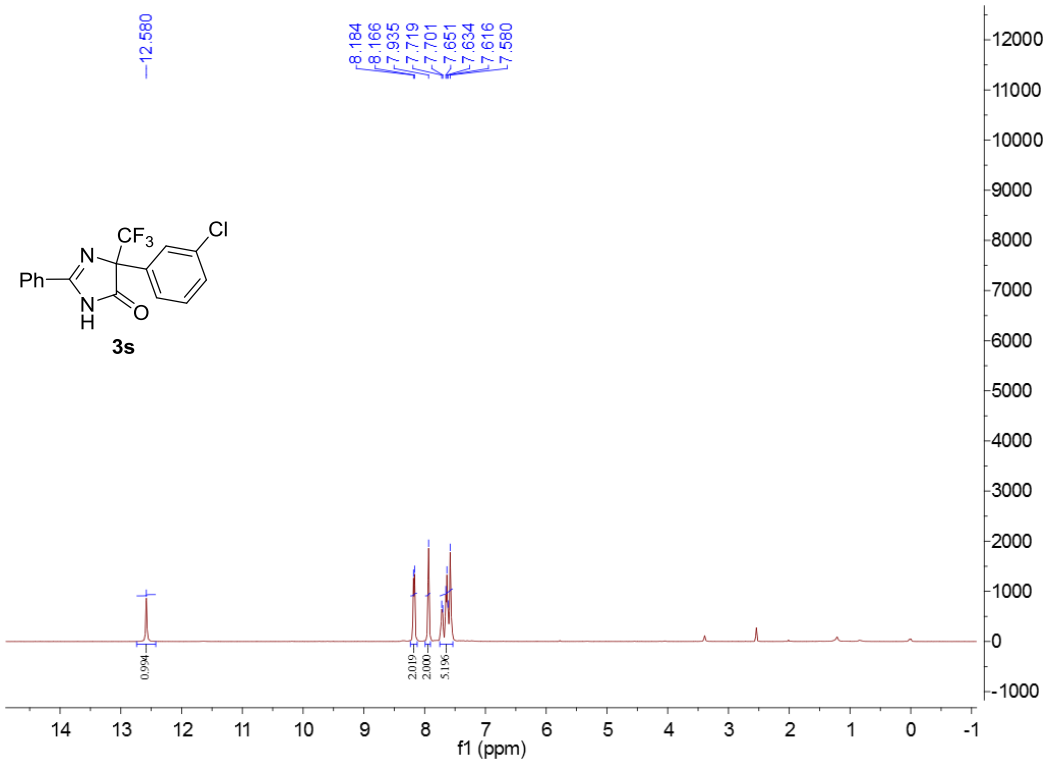
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3r



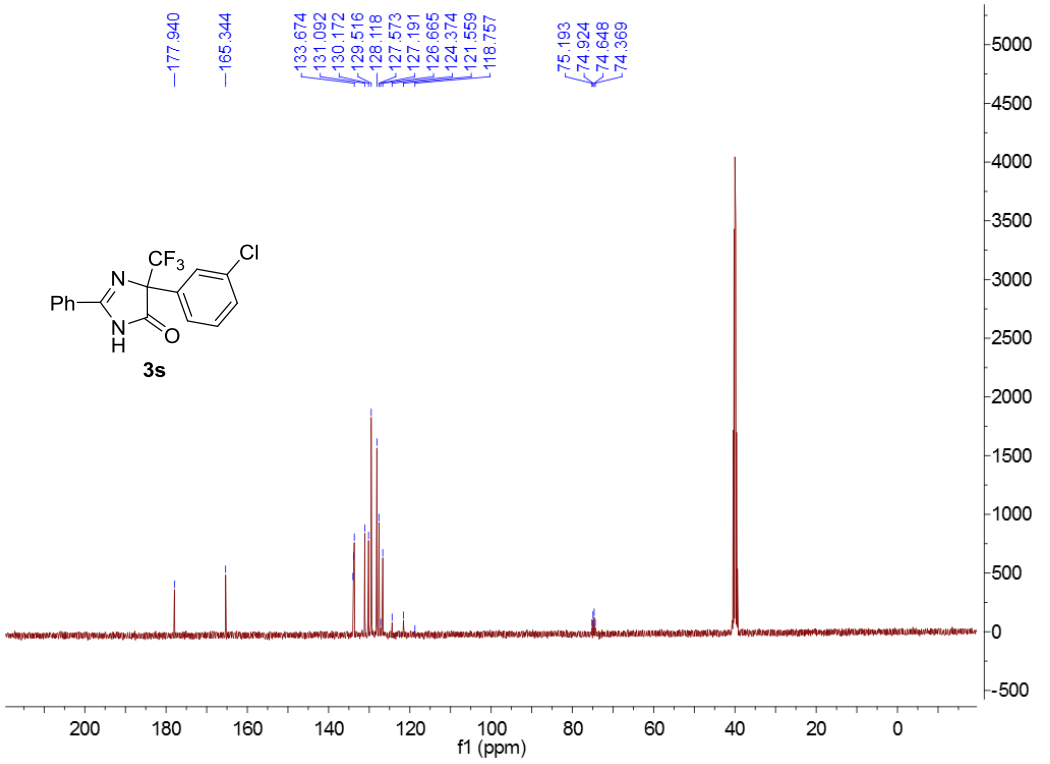
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3r



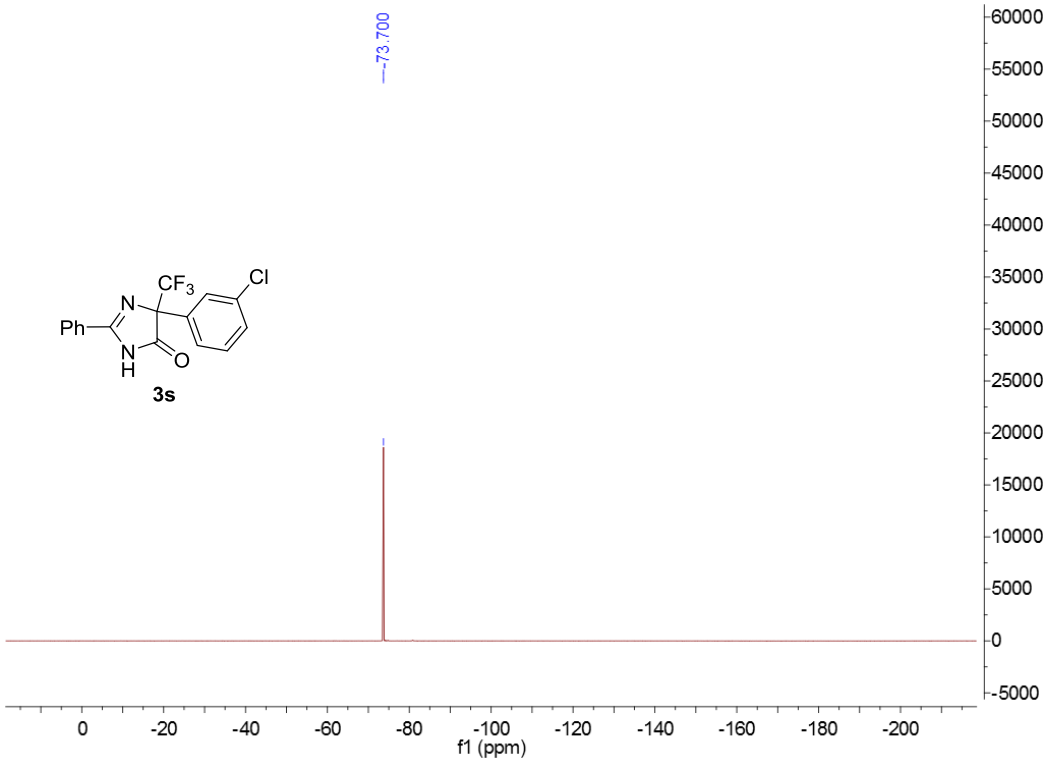
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3s



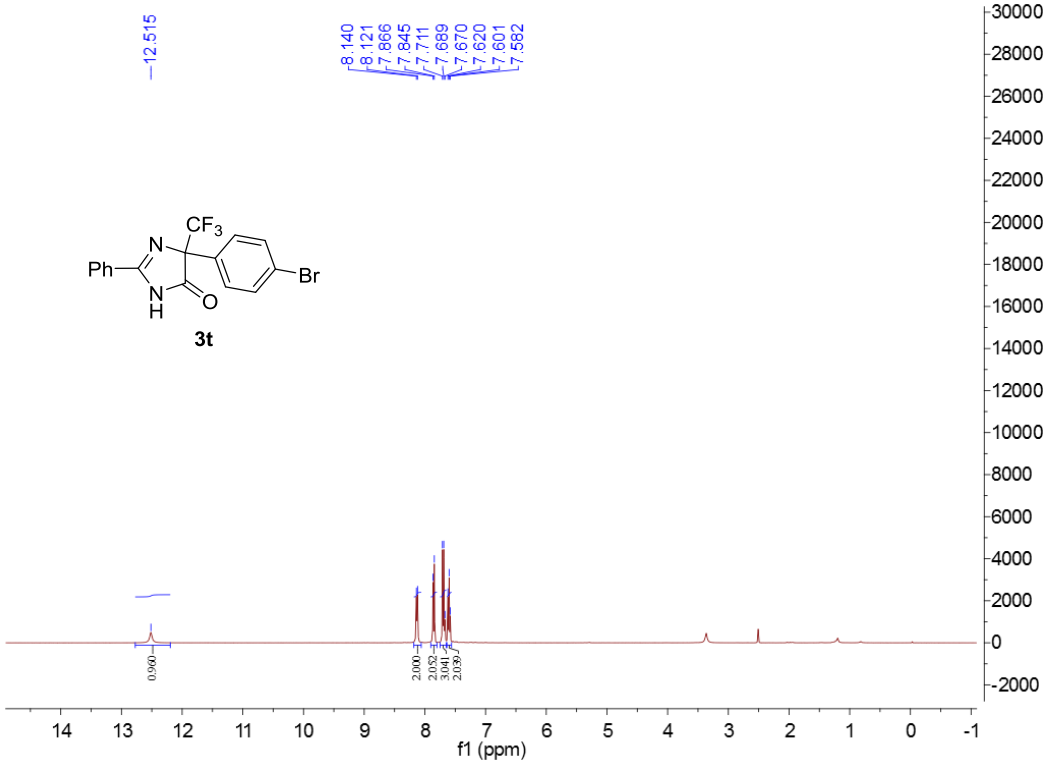
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3s



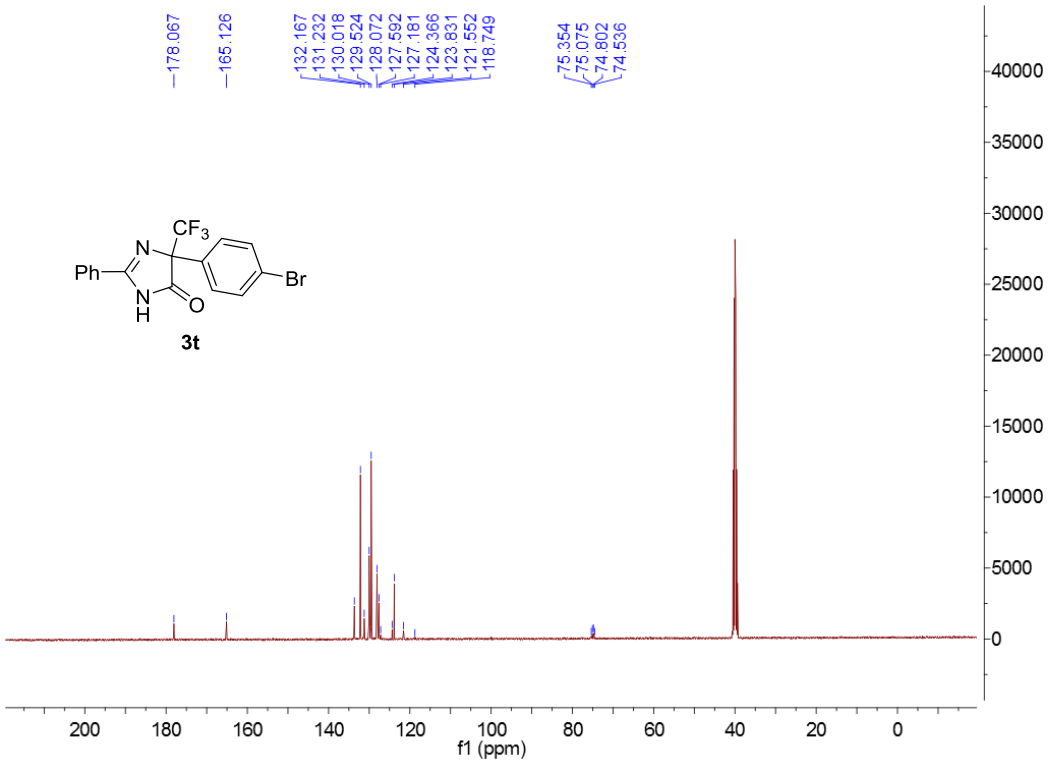
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3s



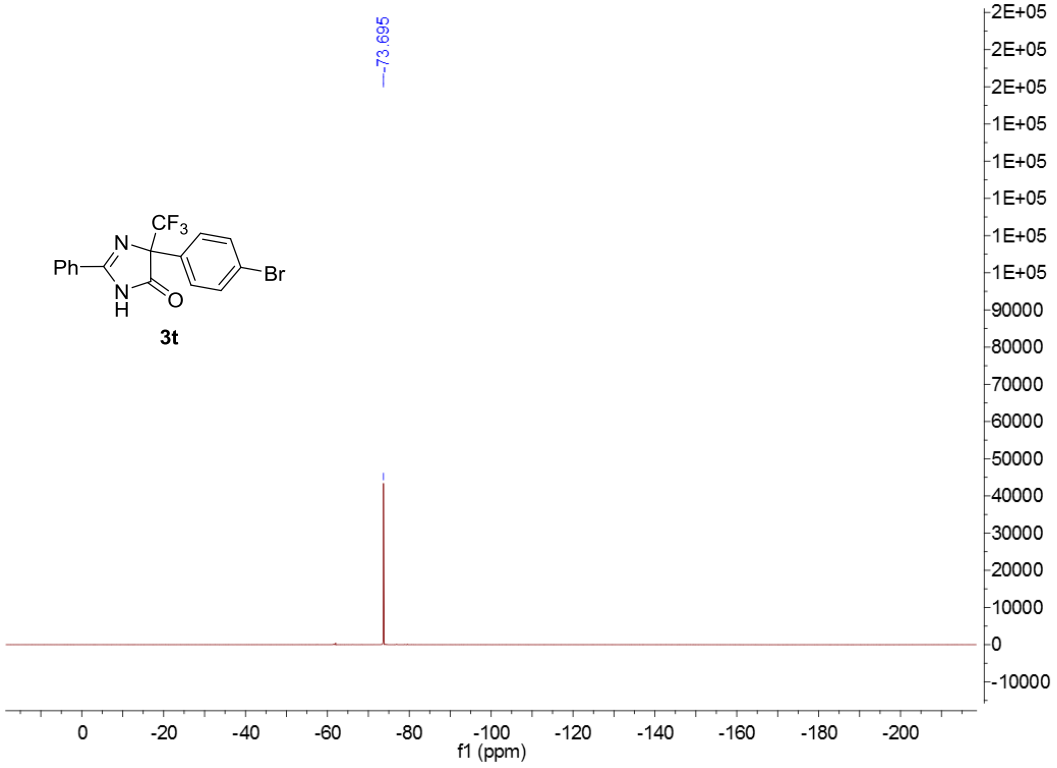
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3t



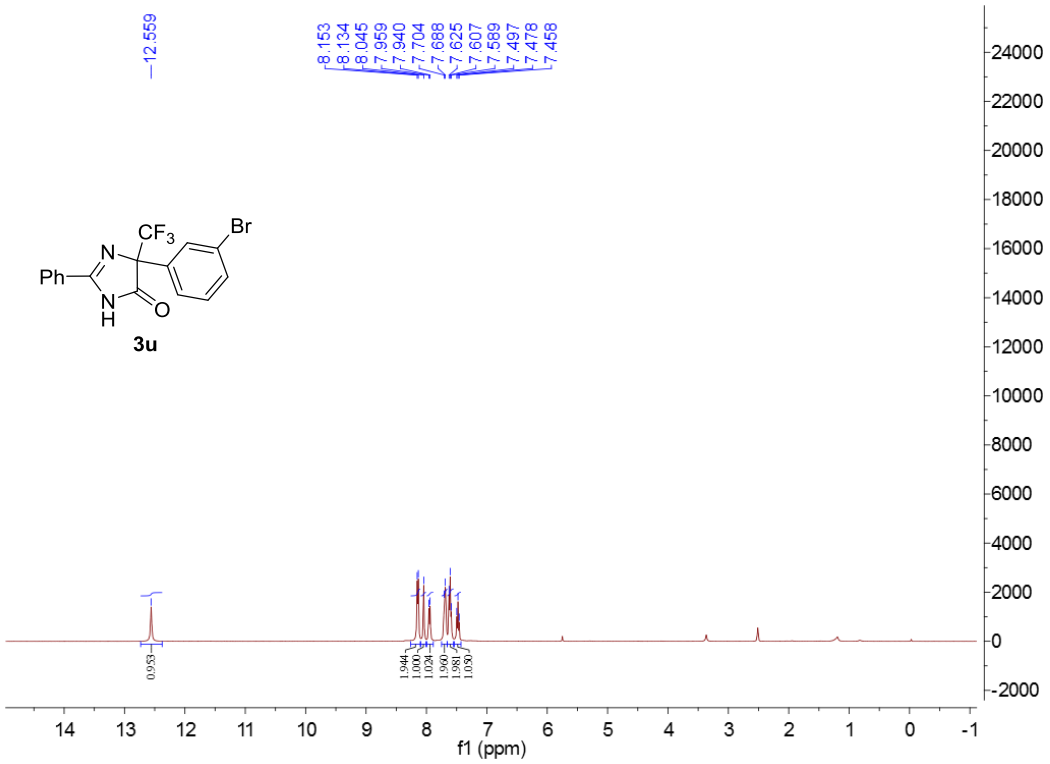
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3t



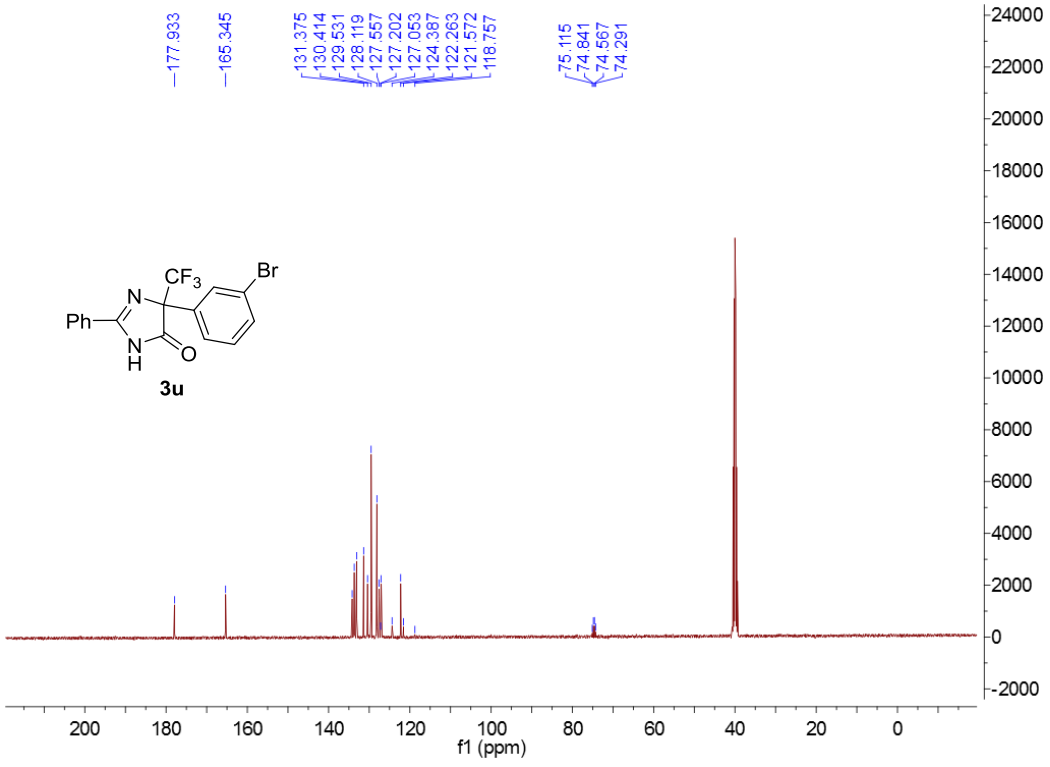
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3t



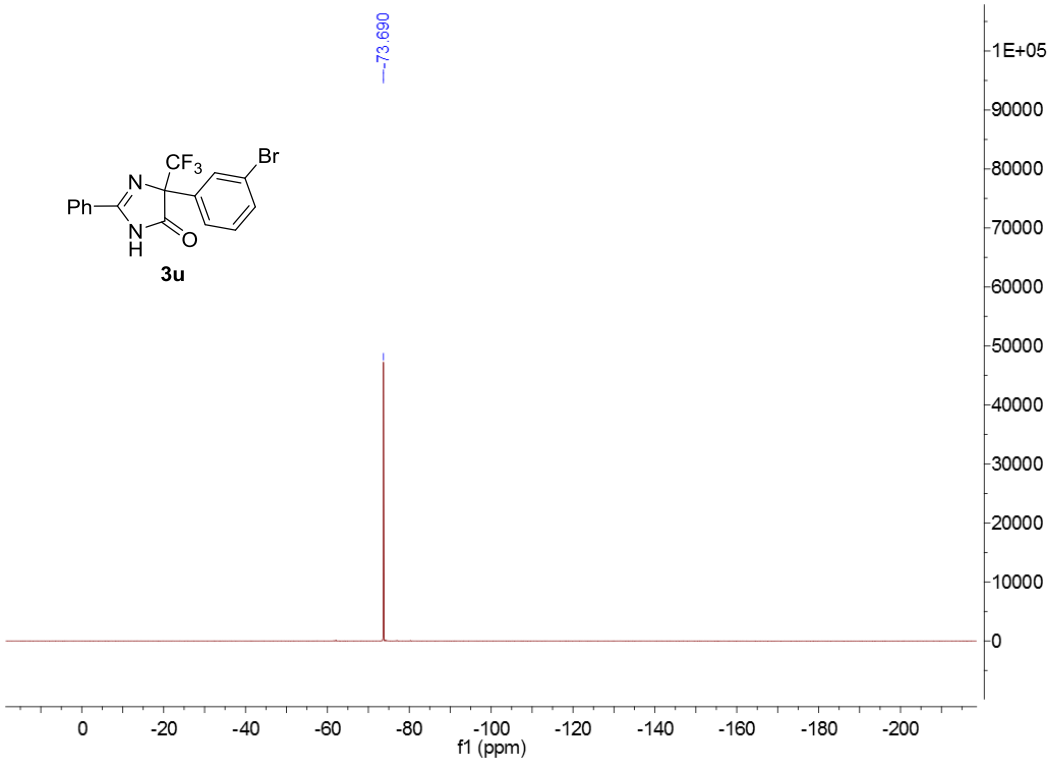
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3u



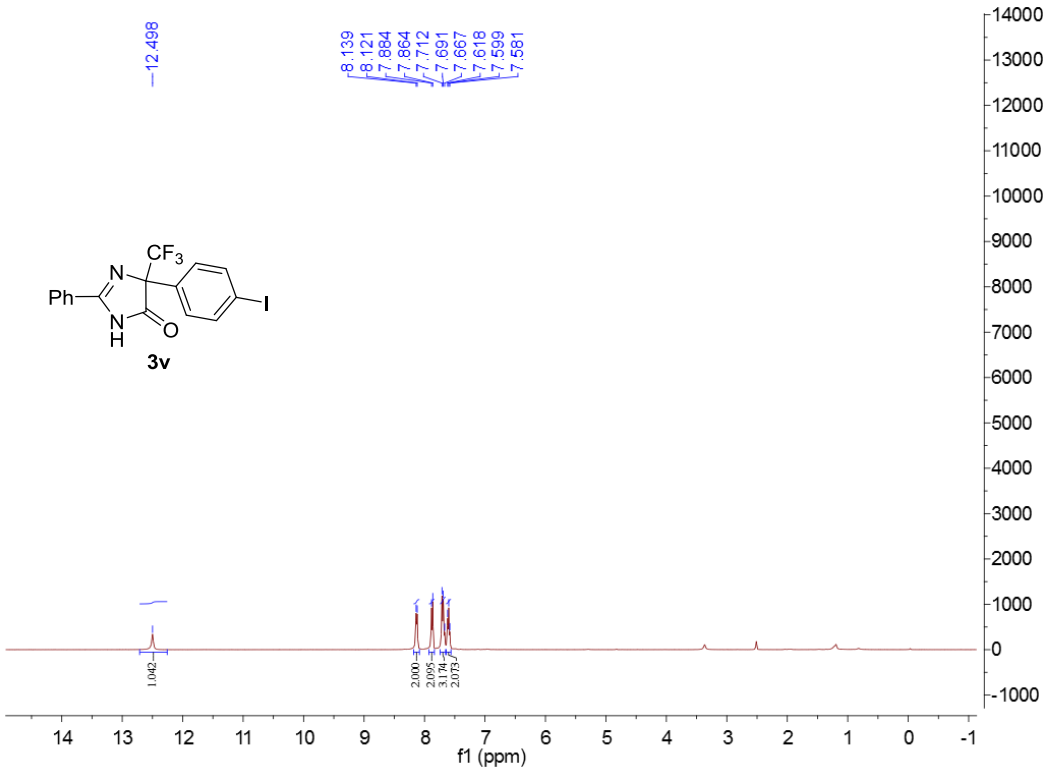
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3u



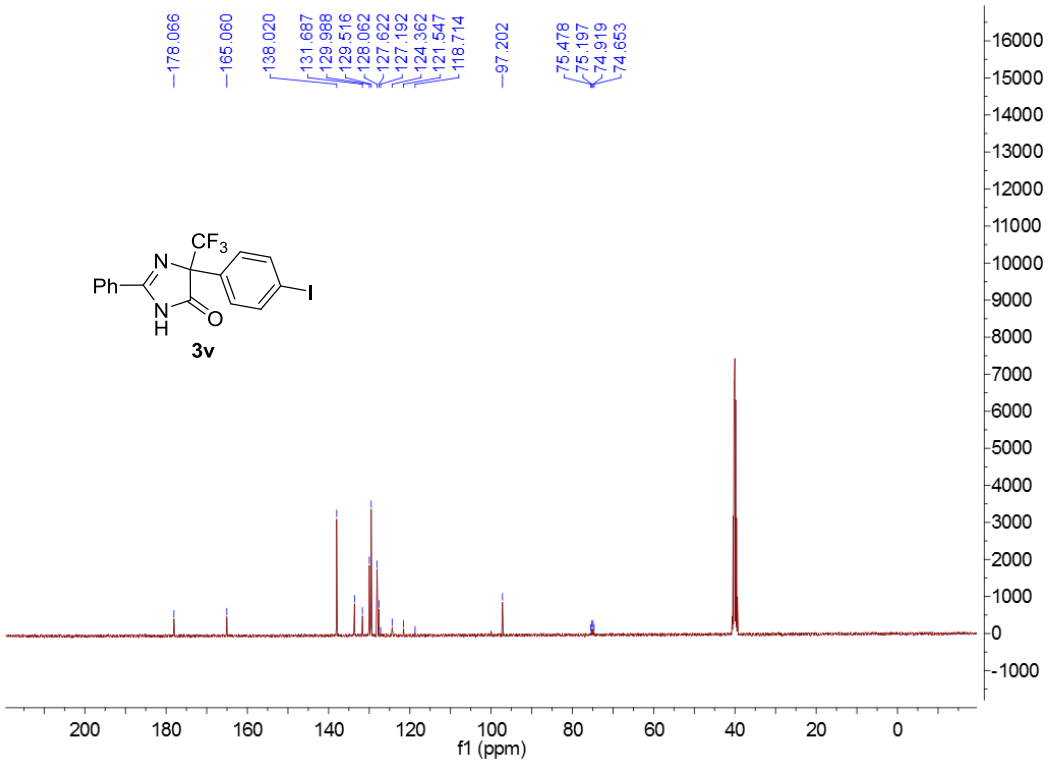
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3u



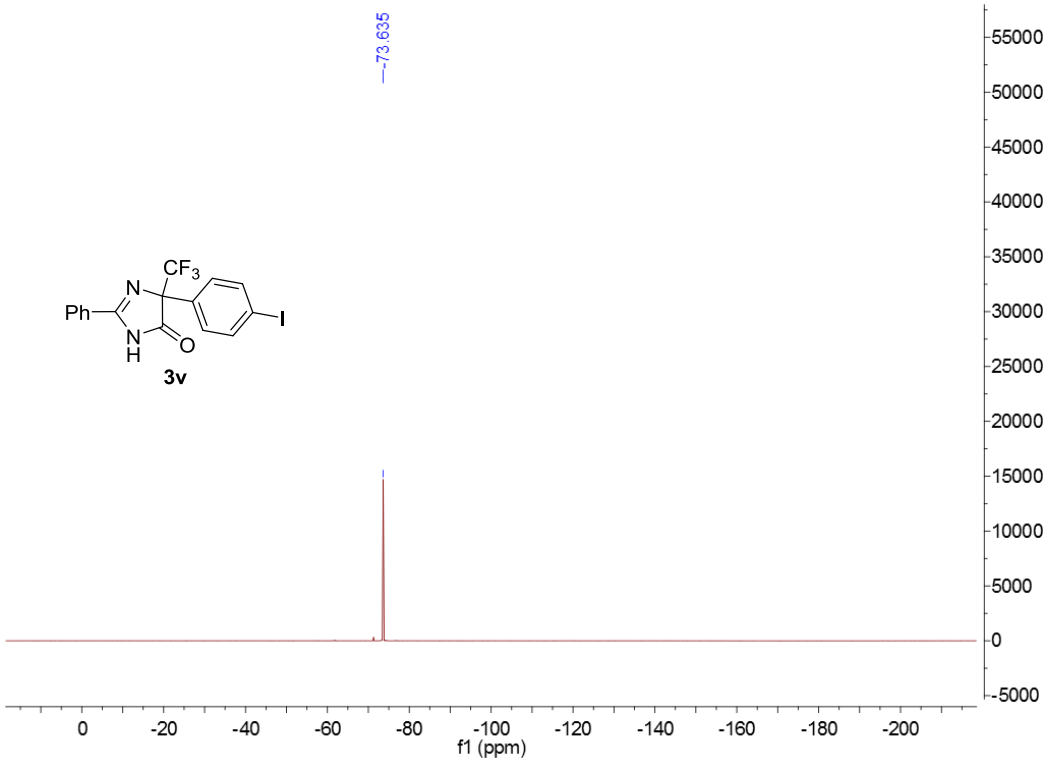
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3v



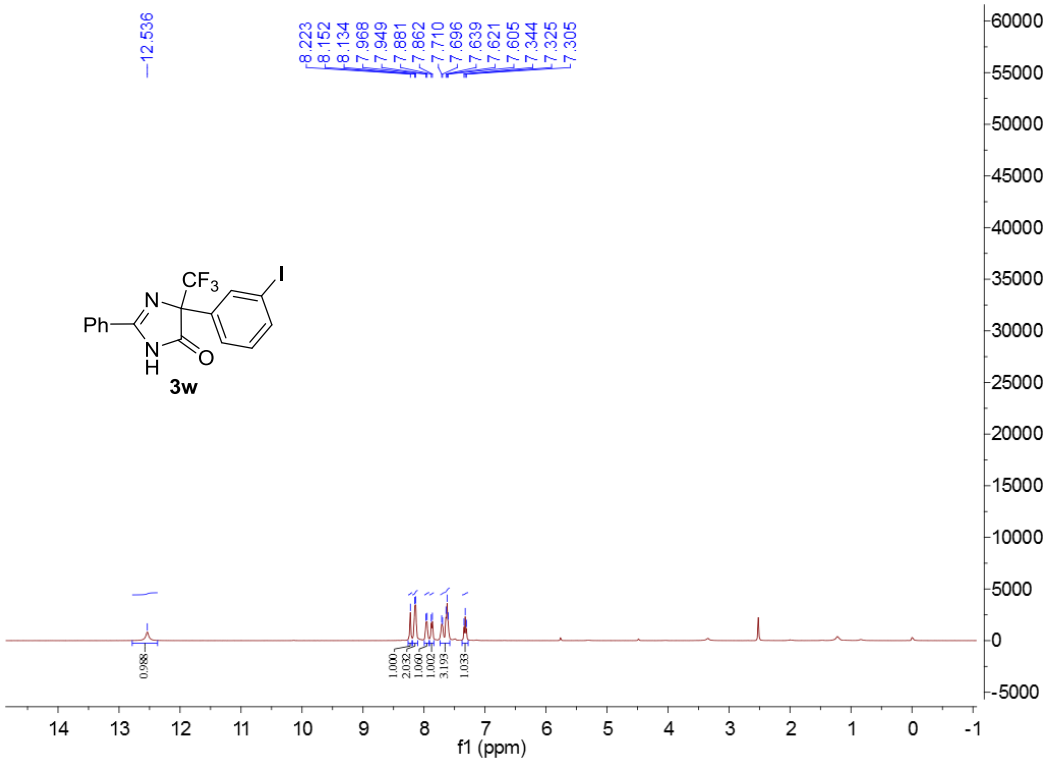
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3v



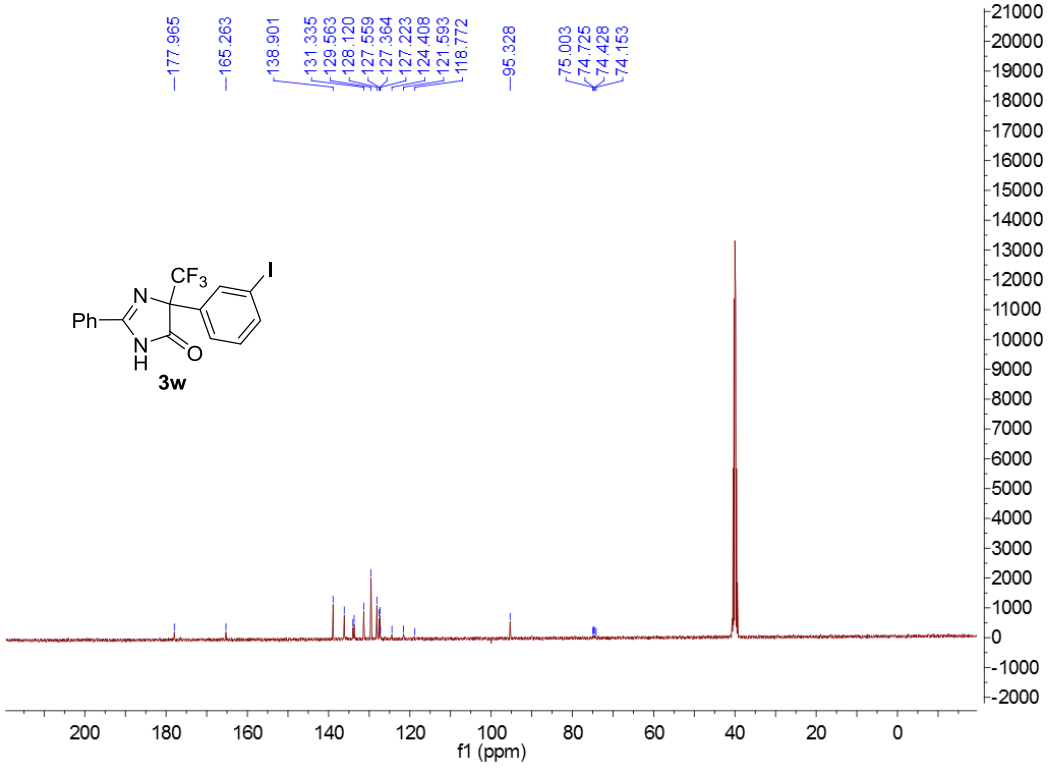
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3v



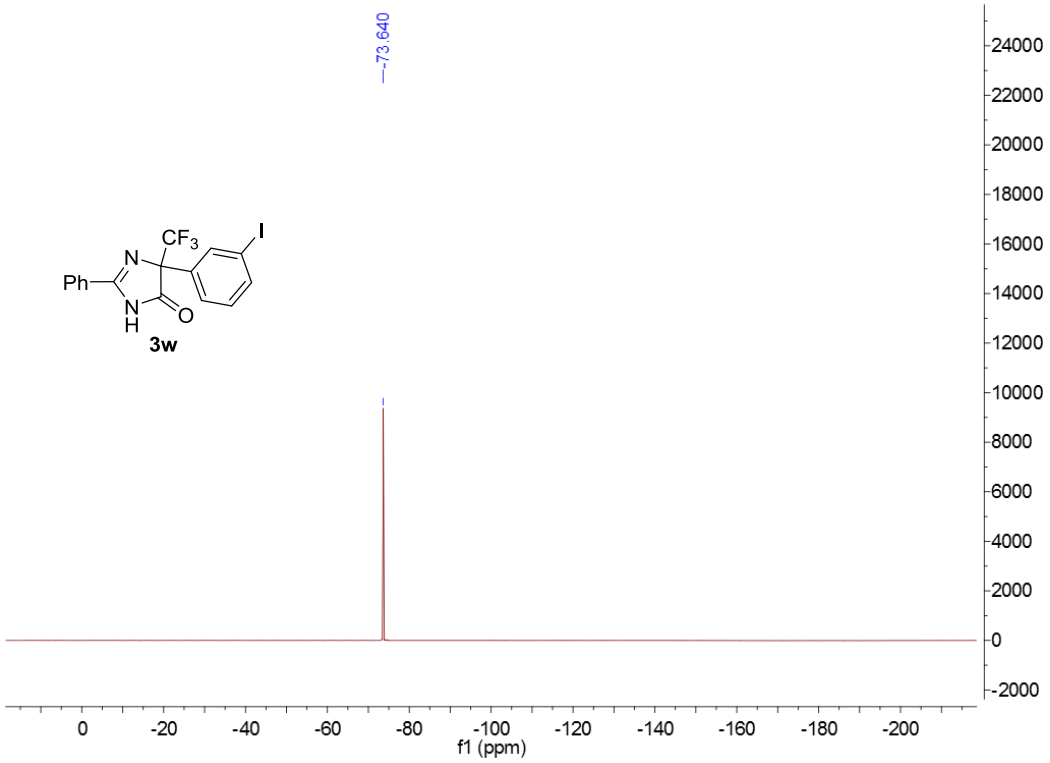
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 3w



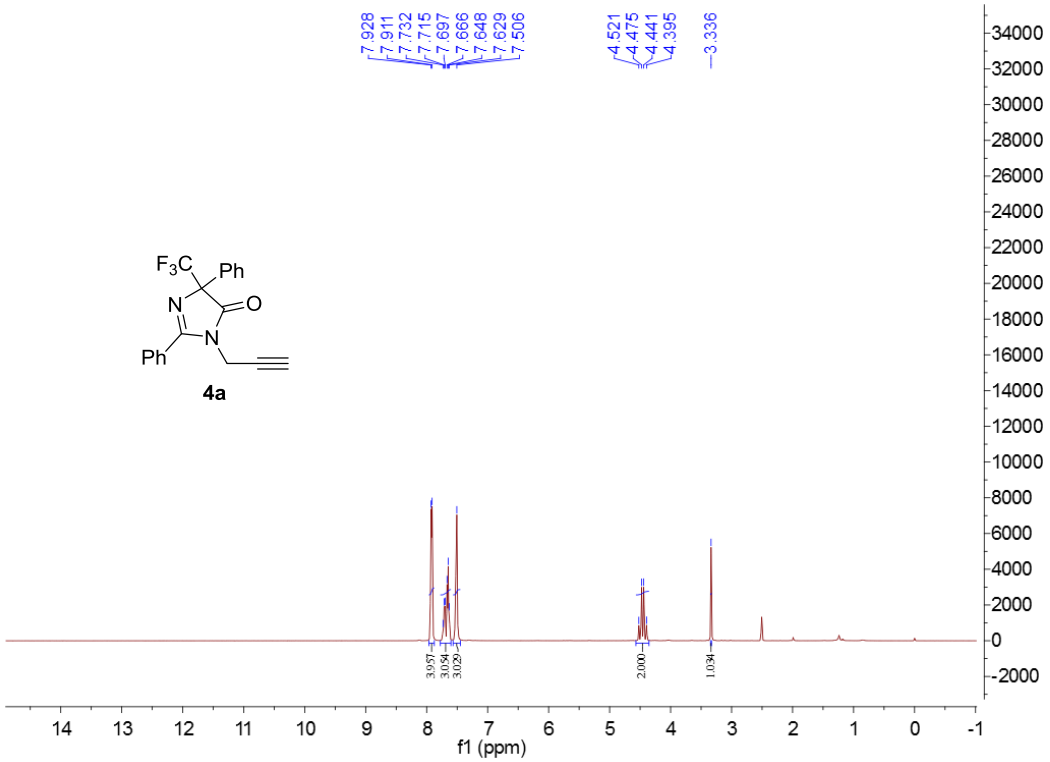
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 3w



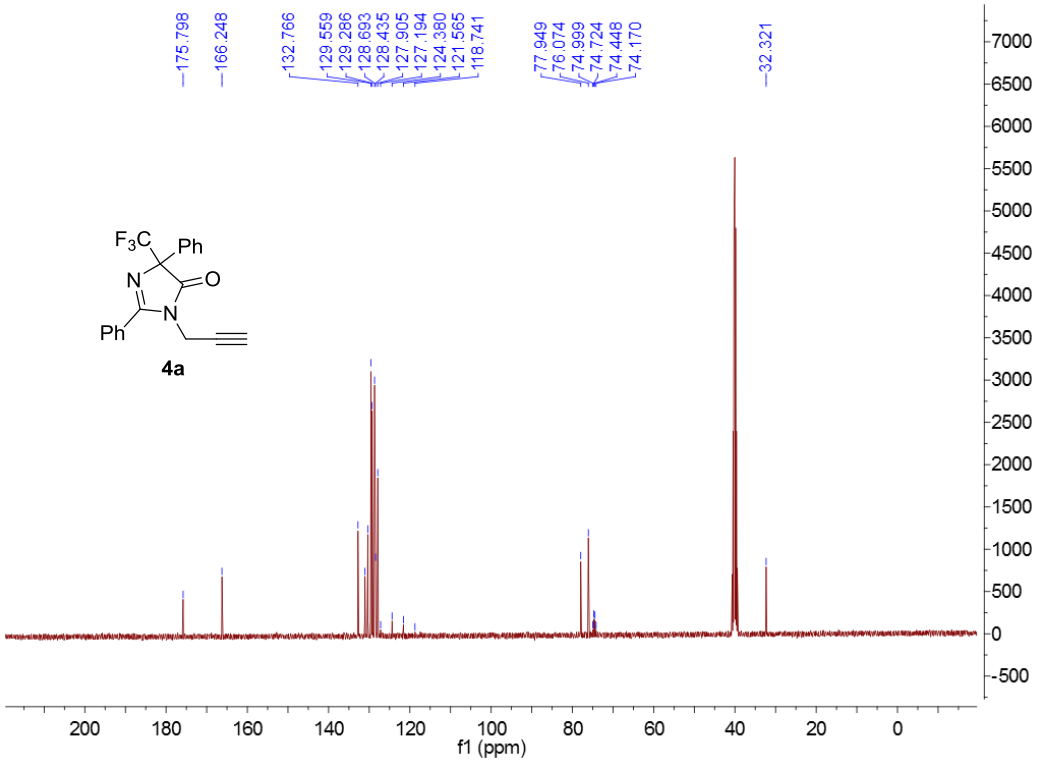
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 3w



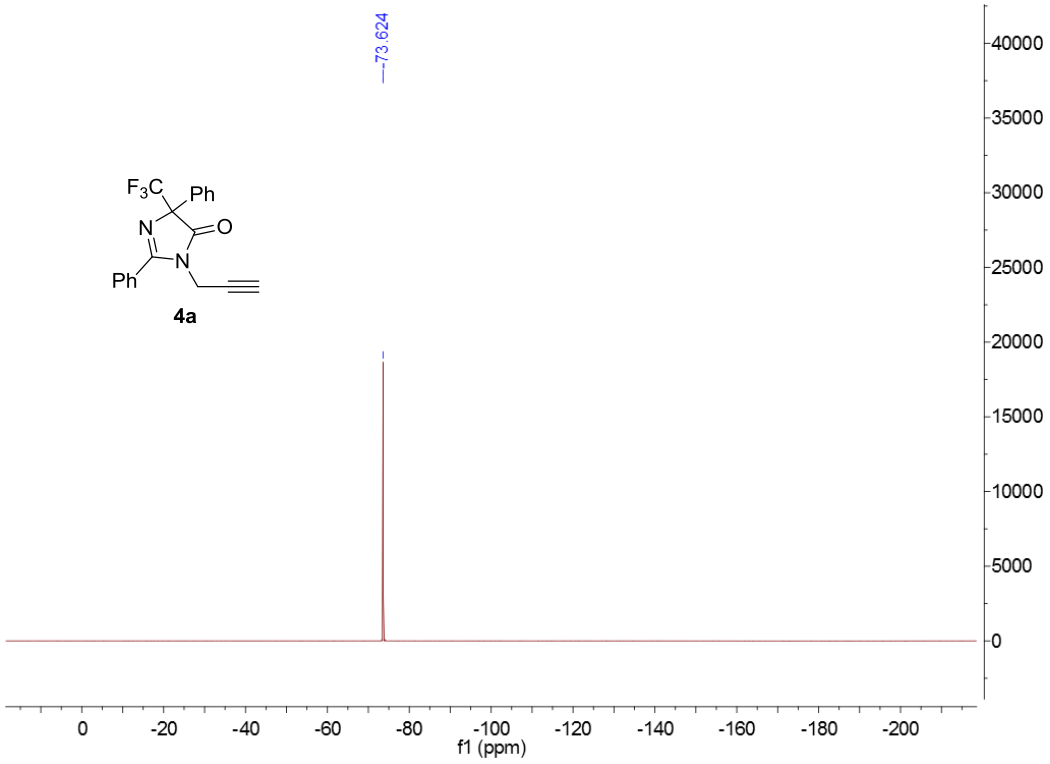
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 4a



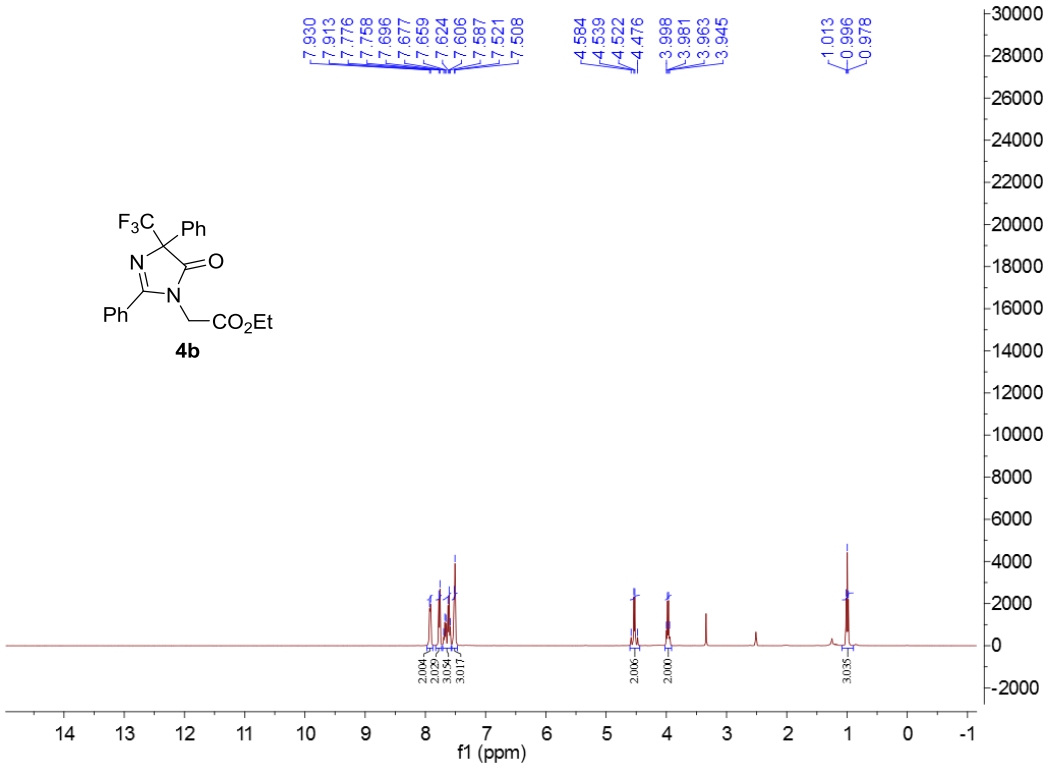
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 4a



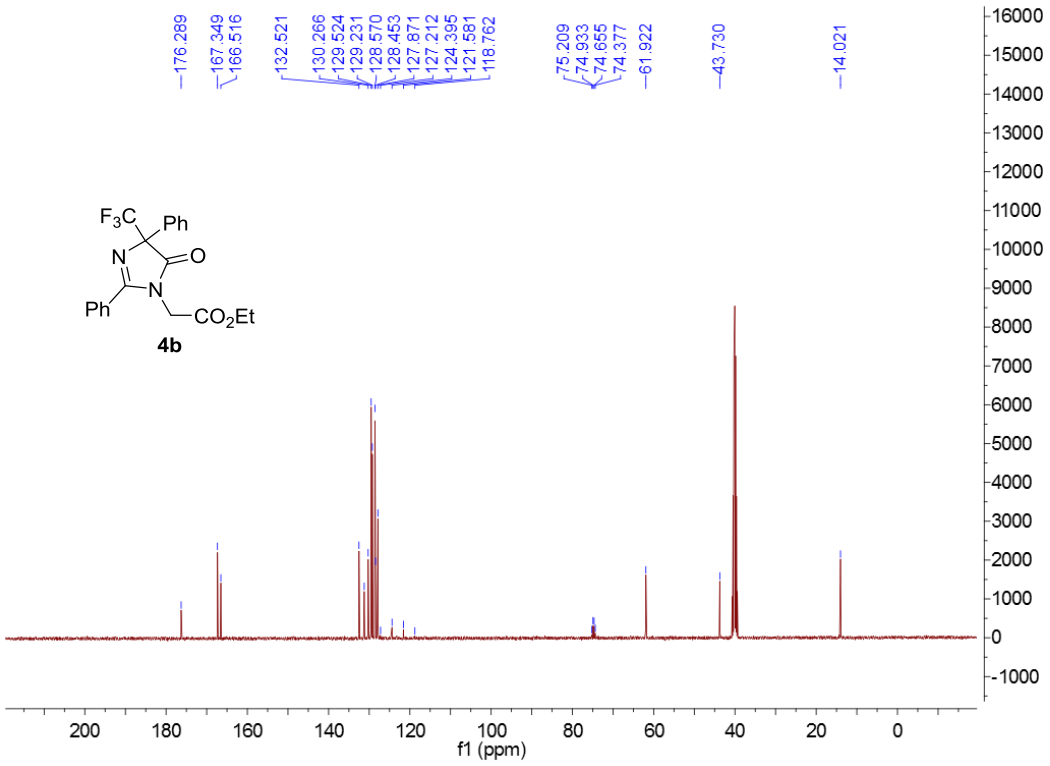
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 4a



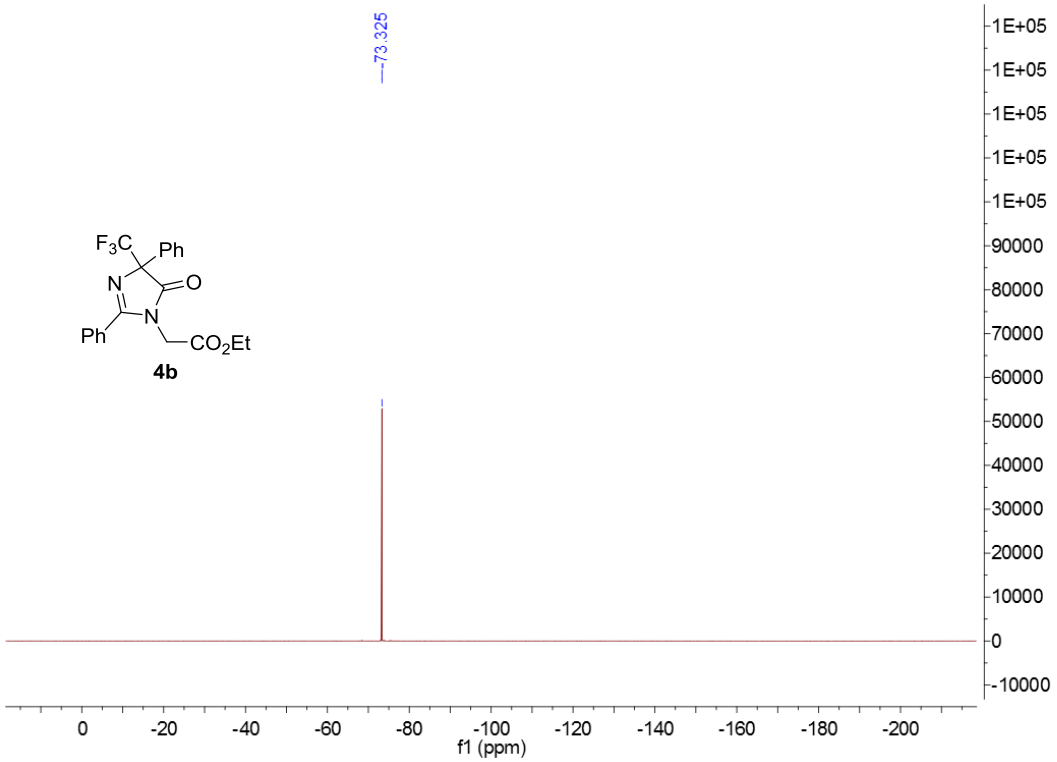
^{1}H NMR (400 MHz, d_6-DMSO) spectrum for 4b



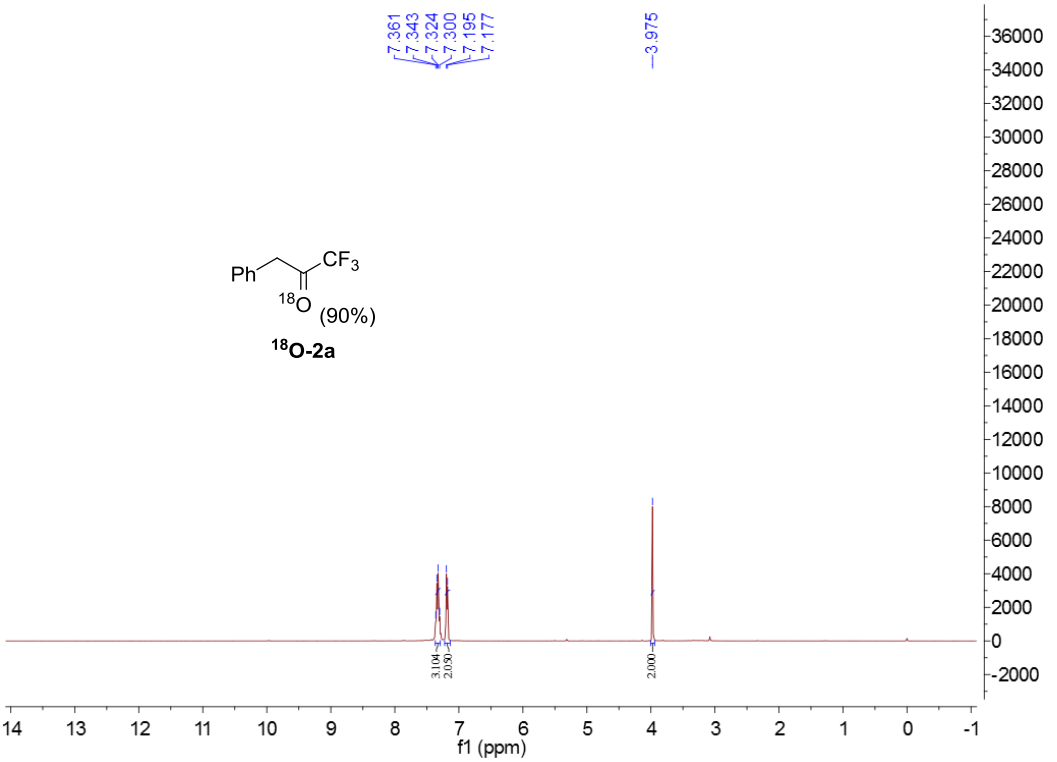
^{13}C NMR (100 MHz, d_6-DMSO) spectrum for 4b



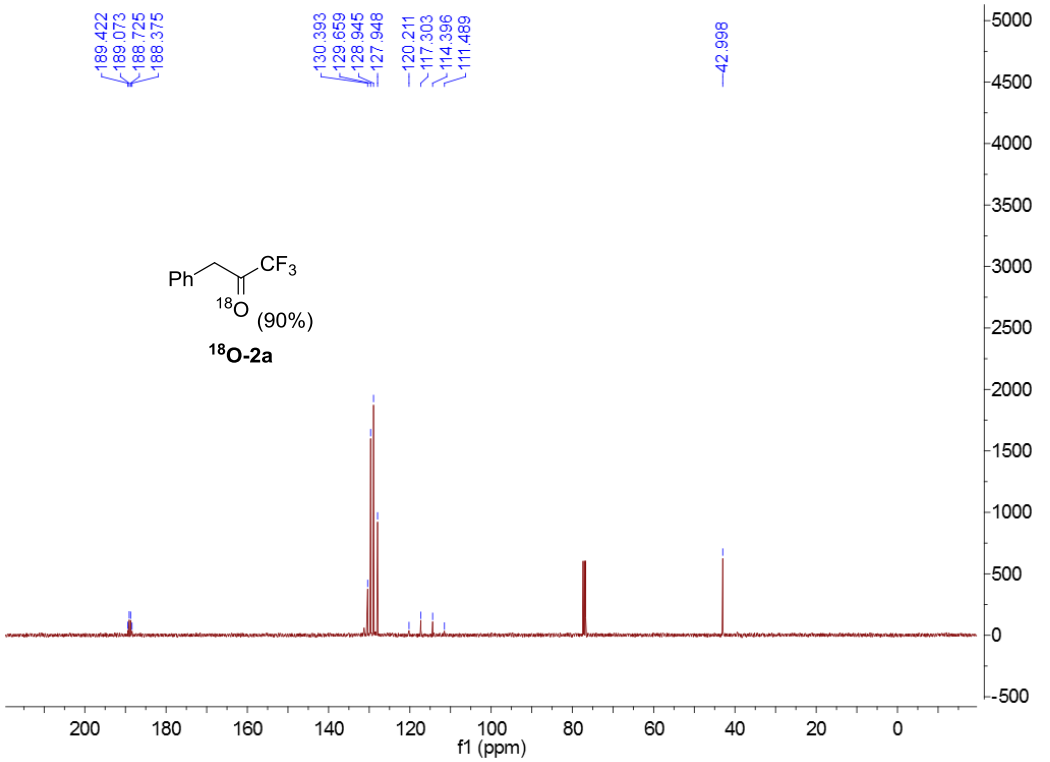
^{19}F NMR (376 MHz, d_6-DMSO) spectrum for 4b



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for ^{18}O-2a



^{13}C NMR (100 MHz, $CDCl_3$) spectrum for ^{18}O-2a



^{19}F NMR (376 MHz, $CDCl_3$) spectrum for ^{18}O-2a