Electronic Supplementary Information

Photocatalyst and additive-free visible light induced trifluoromethylation - arylation of *N*-arylacrylamides with Umemoto′s reagent

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1. General Procedures

Glassware and stir bars were dried in an oven at 140 °C for at least 12 h and then cooled in a desiccator cabinet prior to use. Optimization and substrate screens were performed in 10-mL Schlenk Storage Tubes (with High Vacuum Valves**,** SYNTHWARE, Mfr. No. F580010). Reactions were carried out under an nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All other reactions were performed in round-bottom flasks sealed with rubber septa. Plastic syringes or glass pipets were used to transfer liquid reagents and solvents. Reactions were stirred magnetically using Teflon-coated, magnetic stir bars. Analytical thin-layer chromatography (TLC) was performed using plates pre-coated with 0.25 mm of 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm) supplied. TLC plates were visualized by exposure to ultraviolet light and/or exposure to $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Flash-column chromatography was performed on silica gel (Qingdao Haiyang Chemical Co., Ltd., 200–300 meshes) under pressure.

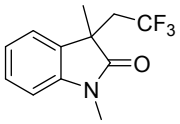
2. Materials and Instrumentation

Nuclear magnetic resonance spectra were recorded at ambient temperature (unless otherwise stated) on a Bruker Avance III 500 MHz NMR spectrometer. All values for proton chemical shifts are reported in parts per million (δ) and are calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: δ = 7.26 ppm). All values for carbon chemical shifts are reported in parts per million (δ) and are calibrated against the deuterated solvent peak ($CDCl_3$: δ = 77.16 ppm). All values for fluorine chemical shifts are reported in parts per million (δ) from $CFCl_3$ (δ 0 ppm) as the external standard. NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sext = sextet, sep = septet, dd = doublet of doublets, td = triplet of doublets, dq = doublet of quartets, qq = quartet of quartets, m = multiplet, br = broad), coupling constant (Hz), and integration. High-resolution mass spectra were obtained using a liquid chromatography-electrospray ionization and Time-of-flight mass spectrometer. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Adamas-beta®. The *N*-Arylmethacrylamides were prepared according to the reported procedures.[S1,2] Umemoto's reagent was purchased from Bide Pharmatech Ltd. (98% HPLC).

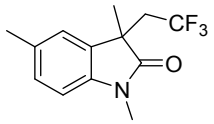
3. Experimental Procedures and Characterization Data for Compounds

A flame-dried 10-mL Schlenk tube was equipped with a rubber septum and magnetic stir bar and was charged with *N*-arylacrylamide **1** (0.20 mmol, 1.0 equiv) and Umemoto's reagent **2** (0.30 mmol, 1.5 equiv). The tube was evacuated and backfilled with nitrogen for three times, and then DMF (2.0 mL) were added with a syringe under nitrogen. The mixture was then irradiated by 3 W blue LEDs with stirring. After the reaction mixture was stirred for 24 h, the mixture was poured into a separatory funnel and diluted with 20 mL of H_2O and 20 mL of ethyl acetate. The layers were separated and the aqueous layer was extracted with ethyl acetate(2 × 20 mL). The combined organic layers were successively washed with $NaHCO_3$ aqueous and brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residue was purified by silica column chromatography (eluent: petroleum ether/EtOAc = 10/1 to 5/1, v/v) to give the desired product **3**.

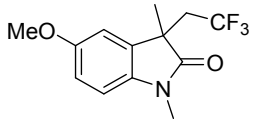
Analytical data for compounds 3a-3v:



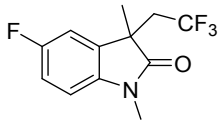
1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3a**). White solid, 39.4 mg, 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (td, J = 7.7, 0.50 Hz, 1H), 7.26 (d, J = 7.0 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.5Hz, 1H), 3.23 (s, 3H), 2.82 (dq, J = 15.0, 10.7, 1H), 2.65 (dq, J = 15.5, 10.5 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.6, 143.0, 131.1, 128.6, 125.4 (q, J = 278.7 Hz), 123.6, 122.7, 108.6, 44.5 (q, J = 2.1 Hz), 40.7 (q, J = 28.3 Hz), 26.5, 25.1; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.95 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3a-b and S3d-i])



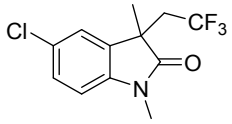
1,3,5-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3b**). White solid, 39.7 mg, 77%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11–7.07 (m, 2H), 6.76 (d, J = 8.0 Hz, 1H), 3.21 (s, 3H), 2.80 (dq, J = 15.0, 10.8 Hz, 1H), 2.62 (dq, J = 15.0, 10.5 Hz, 1H), 2.35 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.5, 140.6, 132.3, 131.2, 128.9, 125.4 (q, J = 278.7 Hz), 124.4, 108.3, 44.5 (q, J = 1.9 Hz), 40.7 (q, J = 28.3 Hz), 26.6, 25.1, 21.2; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.90 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3a-b, S3d and S3f-i])



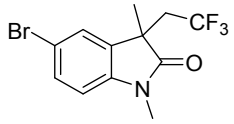
5-Methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3c**). White solid, 41.4 mg, 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (d, J = 2.5 Hz), 6.82 (dd, J = 8.5, 2.5 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 3.79 (s, 3H), 3.20 (s, 3H), 2.80 (dq, J = 15.3, 10.8 Hz, 1H), 2.61 (dq, J = 15.0, 10.5 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.2, 156.2, 136.5, 132.5, 125.4 (q, J = 278.7 Hz), 112.7, 111.3, 108.8, 55.9, 44.9 (q, J = 2.0 Hz), 40.7 (q, J = 28.3 Hz), 26.6, 25.1; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.88 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3a-b, S3d-g and S3i])



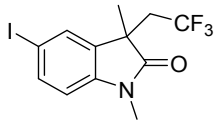
5-Fluoro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3d**). White solid, 28.8 mg, 55%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03–6.99 (m, 2H), 6.80 (dd, J = 9.5, 4.5 Hz, 1H), 3.22 (s, 3H), 2.82 (dq, J = 15.3, 10.8 Hz, 1H), 2.62 (dq, J = 15.0, 10.5 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.2, 159.4 (d, J = 241.3 Hz), 138.9 (d, J = 1.9 Hz), 132.7 (d, J = 8.1 Hz), 125.2 (q, J = 278.6 Hz), 115.0 (d, J = 23.6 Hz), 111.9 (dd, J = 25.1, 1.4 Hz), 109.1 (d, J = 8.2 Hz), 44.9 (quin, J = 1.9 Hz), 40.7 (q, J = 28.5 Hz), 26.7, 25.0; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.98 (t, J = 10.3 Hz), -120.39 (sext, J = 4.2 Hz). (Known compound; spectra data were identical to the literature.[3a-b, S3d and S3f-i])



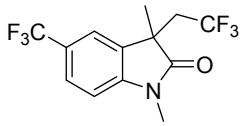
5-Chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3e**). White solid, 34.0 mg, 61%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (dd, J = 8.0, 2.0 Hz, 1H), 7.24 (d, J = 1.5 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 3.22 (s, 3H), 2.82 (dq, J = 15.3, 10.5 Hz, 1H), 2.62 (dq, J = 15.3, 10.5 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.0, 141.6, 132.8, 128.6, 128.2, 125.2 (q, J = 278.6 Hz), 124.2, 109.5, 44.7 (q, J = 2.0 Hz), 40.7 (q, J = 28.5 Hz), 26.7, 25.0; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.97 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3a-b, S3d and S3f-i])



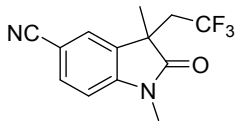
5-Bromo-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3f**). White solid, 44.6 mg, 69%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (dd, J = 8.0, 2.0 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 3.20 (s, 3H), 2.81 (dq, J = 15.5, 10.7 Hz, 1H), 2.62 (dq, J = 15.3, 10.5 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.9, 142.1, 133.2, 131.5, 126.9, 125.2 (q, J = 278.7 Hz), 115.4, 110.0, 44.6 (q, J = 2.0 Hz), 40.7 (q, J = 28.5 Hz), 26.6, 25.0; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.95 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3a-b and S3d-i])



5-Iodo-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3g**). White solid, 56.2 mg, 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (dd, J = 8.0, 1.5 Hz, 1H), 7.53 (d, J = 1.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.19 (s, 3H), 2.80 (dq, J = 15.0, 10.7 Hz, 1H), 2.61 (dq, J = 15.0, 10.5 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.7, 142.7, 137.5, 133.5, 132.5, 125.1 (q, J = 278.8 Hz), 110.6, 85.2, 44.4, 40.7 (q, J = 28.5 Hz), 26.6, 25.0; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.94 (t, J = 10.3 Hz). (Known compound; spectra data were identical to the literature.[S3a-b, S3d, S3g and S3i])

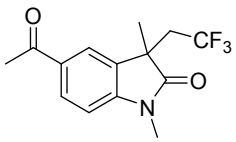


1,3-Dimethyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (**3h**). White solid, 41.1 mg, 66%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7..60 (dd, J = 8.0, 1.0 Hz, 1H), 7.49 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 3.27 (s, 3H), 2.86 (dq, J = 15.8, 10.8 Hz, 1H), 2.68 (dq, J = 15.5, 10.3 Hz, 1H), 1.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.5, 146.0, 131.7, 126.5 (q, J = 4.0 Hz), 125.15 (q, J = 32.9 Hz), 125.13 (q, J = 278.6 Hz), 124.4 (q, J = 271.9 Hz), 120.8 (q, J = 2.0 Hz), 108.4, 44.5 (q, J = 2.1 Hz), 40.7 (q, J = 28.6 Hz), 26.8, 25.0; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.54 (s), -62.08 (t, J = 10.3 Hz). (Known compound; spectra data were identical to the literature.[S3e-f and S3h-i])

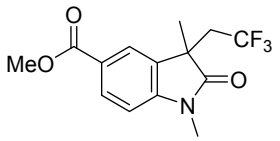


1,3-Dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carbonitrile (**3i**). White solid, 34.2 mg, 64%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (dd, J = 8.0, 1.5 Hz, 1H), 7.51 (d, J = 1.0 Hz, 1H), 6.96

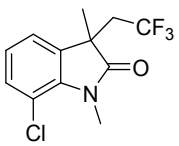
(d, J = 8.5 Hz, 1H), 3.26 (s, 3H), 2.86 (dq, J = 15.5, 10.5 Hz, 1H), 2.67 (dq, J = 15.3, 10.3 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.2, 146.8, 134.0, 132.1, 127.1, 125.0 (q, J = 278.6 Hz), 119.1, 109.1, 106.1, 44.3 (q, J = 2.1 Hz), 40.6 (q, J = 28.6 Hz), 26.8, 24.9; ^{19}F NMR (470 MHz, $CDCl_3$): δ -62.03 (t, J = 10.3 Hz). (Known compound; spectra data were identical to the literature.[S3b and S3d-i])



5-Acetyl-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3j**). White solid, 41.3 mg, 72%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (dd, J = 8.3, 1.8 Hz, 1H), 7.89 (d, J = 1.0 Hz, 1H), 6.92 (d, J = 8.0, 1H), 3.26 (s, 3H), 2.85 (dq, J = 15.0, 10.5 Hz, 1H), 2.69 (dq, J = 15.0, 10.3 Hz, 1H), 2.58 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 196.8, 178.8, 147.3, 132.4, 131.4, 130.7, 125.1 (q, J = 278.7 Hz), 123.5, 108.0, 44.3 (q, J = 2.0 Hz), 40.7 (q, J = 28.4 Hz), 26.8, 26.5, 25.1; ^{19}F NMR (470 MHz, $CDCl_3$): δ -62.08 (t, J = 10.3 Hz). (Known compound; spectra data were identical to the literature.[S3f-g])

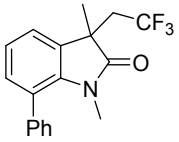


Methyl 1,3-dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carboxylate (**3k**). White solid, 40.8 mg, 68%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (dd, J = 8.3, 1.8 Hz, 1H), 7.92 (d, J =1.0 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 3.89 (s, 3H), 3.25 (s, 3H), 2.85 (dq, J = 15.3, 10.8 Hz, 1H), 2.68 (dq, J = 15.5, 10.5 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.8, 166.8, 147.1, 131.3, 131.1, 125.1 (q, J = 278.7 Hz), 124.9, 124.8, 108.2, 52.2, 44.3 (q, J = 2.1 Hz), 40.7 (q, J = 28.4 Hz), 26.7, 25.1; ^{19}F NMR (470 MHz, $CDCl_3$): δ -62.11 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3e and S3h])

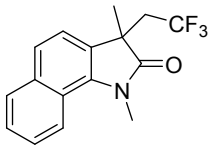


7-Chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3l**). White solid, 28.9 mg, 52%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (dd, J = 8.0, 1.0 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 6.99 (t, J = 8.0 Hz, 1H), 3.60 (s, 3H), 2.85 (dq, J = 15.0, 10.7 Hz, 1H), 2.62 (dq, J = 15.5, 10.3 Hz, 1H), 1.39

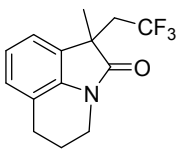
(s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.8, 139.0, 133.8, 131.0, 125.1 (q, J = 278.6 Hz), 123.5, 122.1, 116.0, 44.3 (q, J = 2.1 Hz), 41.0 (q, J = 28.4 Hz), 30.0, 25.6; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.97 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3d and S3i])



1,3-Dimethyl-7-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3m**). White solid, 37.1 mg, 58%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.40 (m, 3H), 7.38–7.34 (m, 2H), 7.26 (dd, J = 7.5, 0.50 Hz, 1H), 7.14 (dd, J = 8.0, 1.5 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 2.87 (dq, J = 15.0, 10.7 Hz, 1H), 2.75 (s, 3H), 2.68 (dq, J = 15.3, 10.5 Hz, 1H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.6, 139.9, 138.9, 132.1, 131.6, 130.1, 129.9, 128.0, 127.8, 126.0, 125.4 (q, J = 278.8 Hz), 122.6, 122.0, 43.8 (q, J = 2.0 Hz), 41.1 (q, J = 28.2 Hz), 30.6, 25.5; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.84 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3a and S3d])

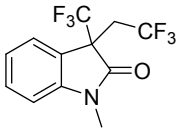


1,3-Dimethyl-3-(2,2,2-trifluoroethyl)-1,3-dihydro-2H-benzo[g]indol-2-one (**3n**). White solid, 27.6 mg, 47%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (dd, J = 8.0, 0.5 Hz, 1H), 7.56–7.53 (m, 2H), 7.46–7.42 (m, 2H), 6.98 (d, J = 7.5 Hz, 1H), 3.56 (s, 3H), 3.48 (dq, J = 15.0, 10.5 Hz, 1H), 2.77 (dq, J = 15.0, 10.0 Hz, 1H), 1.73 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.5, 136.3, 135.0, 133.6, 126.9, 126.8, 126.6, 125.7 (q, J = 279.4 Hz), 123.5, 123.0, 119.1, 108.9, 45.5 (q, J = 26.9 Hz), 43.9 (q, J = 2.2 Hz), 33.3, 30.0; ^{19}F NMR (470 MHz, $CDCl_3$): δ -60.92 (t, J = 10.1 Hz). (Known compound; spectra data were identical to the literature.[S3c and S3i])

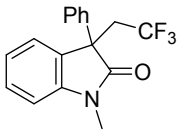


1-Methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1*H*)-one (**3o**). White solid, 40.8 mg, 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (d, J = 7.5 Hz, 1H), 7.05 (dd, J = 7.8, 0.80 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 3.72 (t, J = 7.0 Hz, 2H), 2.84–2.72 (m, 3H), 2.64 (dq, J = 15.3, 10.7 Hz, 1H), 2.04–1.98 (m, 2H), 1.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.5, 138.7, 129.8, 127.4, 125.5 (q, J = 278.7 Hz), 122.2, 121.6, 120.6, 45.8 (q, J = 2.1 Hz), 40.6 (q, J = 28.3

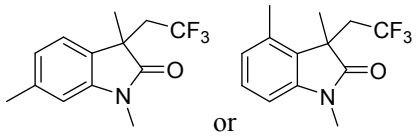
Hz), 39.2, 24.72, 24.66, 21.2; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.82 (t, J = 10.8 Hz). (Known compound; spectra data were identical to the literature.[S3a-b, S3d and S3f-i])



1-Methyl-3-(2,2,2-trifluoroethyl)-3-(trifluoromethyl)indolin-2-one (**3p**). White solid, 31.5 mg, 53%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (td, J = 7.8, 0.83 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 3.27 (s, 3H), 3.26 (dq, J = 15.0, 10.2 Hz, 1H), 3.00 (dq, J = 15.0, 9.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.8 (q, J = 1.7 Hz), 144.5, 131.0, 126.1, 124.5 (q, J = 278.0 Hz), 124.0 (q, J = 283.5 Hz), 123.3, 121.1, 52.7 (qq, J = 27.7, 2.3 Hz), 35.0 (qq, J = 30.1, 2.3 Hz), 27.0; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.44 (t, J = 9.9 Hz), -73.80 (s); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{10}F_6NO$ 298.0661, found 298.0658.

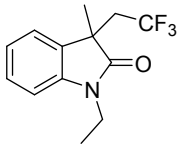


1-Methyl-3-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3q**). White solid, 44.6 mg, 73%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (td, J = 7.8, 1.0 Hz, 1H), 7.35–7.26 (m, 6H), 7.17 (td, J = 7.8, 0.5 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 3.43 (dq, J = 15.0, 10.5 Hz, 1H), 3.23 (s, 3H), 3.05 (dq, J = 15.0, 10.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 176.8, 143.9, 138.8, 129.2, 129.0, 128.9, 128.1, 126.6, 126.2, 125.2 (q, J = 278.7 Hz), 122.7, 108.9, 52.1 (q, J = 1.8 Hz), 41.0 (q, J = 28.1 Hz), 26.8; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.15 (t, J = 10.3 Hz). (Known compound; spectra data were identical to the literature.[S3a-b, S3e-f and S3h])

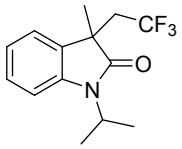


1,3,6(or 4)-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3r**+**3r′**). White solid, 36.6 mg, 71%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (t, J = 7.8 Hz, 1H), 7.13 (d, J = 7.5 Hz, 0.57H), 6.90 (d, J = 7.5 Hz, 0.57H), 6.85 (d, J = 8.0 Hz, 1H), 6.73–6.71 (m, 1.57H), 3.22 (s, 3H), 3.21 (s, 1.71H), 2.96 (dq, J = 15.0, 10.8 Hz, 1H), 2.88–2.74 (m, 1.57H), 2.62 (dq, J = 15.0, 10.5 Hz, 0.57H), 2.39 (s, 1.71H), 2.38 (s, 3H), 1.45 (s, 3H), 1.38 (s, 1.71H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.0, 178.7, 143.3, 143.0, 138.8, 134.9, 128.5, 128.2, 128.0, 125.43 (q, J = 278.6 Hz), 125.29, 125.19 (q, J =

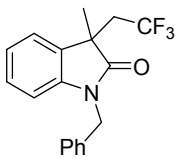
278.3 Hz), 123.4, 123.3, 109.5, 106.3, 45.0 (q, J = 2.1 Hz), 44.3 (q, J = 2.1 Hz), 40.8 (q, J = 28.0 Hz), 39.8 (q, J = 28.1 Hz), 26.6, 26.5, 25.2, 23.2, 21.9, 18.4; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.91 (t, J = 10.6 Hz), -63.95 (t, J = 10.3 Hz). (Known compound; spectra data were identical to the literature.[S3i])



1-Ethyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3s**). White solid, 40.1 mg, 78%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (td, J = 7.8, 1.0 Hz, 1H), 7.26 (d, J = 7.5 Hz, 1H),7.07 (td, J = 7.5, 0.50 Hz, 1H), 6.89 (d, J = 7.5 Hz, 1H), 3.87 (dq, J = 14.5, 7.0 Hz, 1H), 3.68 (dq, J = 14.0, 7.0 Hz, 1H), 2.84 (dq, J = 15.0, 10.7 Hz, 1H), 2.63 (dq, J = 15.0, 10.5 Hz, 1H), 1.39 (s, 3H), 1.24 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.2, 142.0, 131.3, 128.6, 125.4 (q, J = 278.7 Hz), 123.8, 122.5, 108.7, 44.4 (q, J = 2.1 Hz), 40.8 (q, J = 28.3 Hz), 34.9, 25.2, 12.4; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.92 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3c-d and S3g-i])

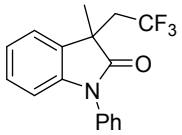


1-Isopropyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3t**). White solid, 40.8 mg, 75%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.24 (m, 2H), 7.07–7.03 (m, 2H), 4.62 (sep, J = 7.0 Hz, 1H), 2.84 (dq, J = 15.3, 10.8 Hz, 1H), 2.61 (dq, J = 15.0, 10.3 Hz, 1H), 1.47 (t, J = 6.5 Hz, 6H), 1.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.3, 141.7, 131.5, 128.3, 125.4 (q, J = 278.8 Hz), 123.9, 122.1, 110.3, 44.2 (q, J = 2.0 Hz), 44.1, 40.9 (q, J = 28.2 Hz), 25.5, 19.3, 19.2; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.97 (t, J = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3c-d])



1-Benzyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3u**). White solid, 48.1 mg, 75%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.25 (m, 6H), 7.19 (td, J = 7.8, 1.0 Hz, 1H), 7.06 (td, J = 7.5, 0.50 Hz, 1H), 6.77 (d, J = 7.5 Hz, 1H), 4.99 (d, J = 16.0 Hz, 1H), 4.90 (d, J = 15.5 Hz, 1H), 2.92 (dq, J

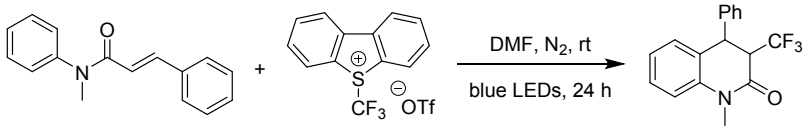
= 15.0, 10.7 Hz, 1H), 2.71 (dq, *J* = 15.0, 10.5 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.7, 142.1, 135.8, 131.1, 128.9, 128.5, 127.8, 127.3, 125.4 (q, *J* = 278.6 Hz), 123.7, 122.8, 109.7, 44.6 (q, *J* = 2.0 Hz), 44.1, 40.6 (q, *J* = 28.4 Hz), 25.8; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.68 (t, *J* = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3c-e, S3g and S3i])



3-Methyl-1-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3v**). White solid, 38.6 mg, 63%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55–7.51 (m, 2H), 7.44–7.38 (m, 3H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.24 (td, *J* = 7.8, 1.5 Hz, 1H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 2.97 (dq, *J* = 15.0, 10.7 Hz, 1H), 2.73 (dq, *J* = 15.0, 10.3 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.1, 143.1, 134.4, 130.8, 129.8, 128.6, 128.4, 126.7, 125.4 (q, *J* = 278.7 Hz), 123.9, 123.2, 109.9, 44.6 (q, *J* = 2.0 Hz), 41.2 (q, *J* = 28.2 Hz), 25.6; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.85 (t, *J* = 10.6 Hz). (Known compound; spectra data were identical to the literature.[S3a-b and S3d-i])

4. Additional Examples and Unsuccessful Substrates

(1) Reaction of *N*-arylcinnamamide with Umemoto's reagent

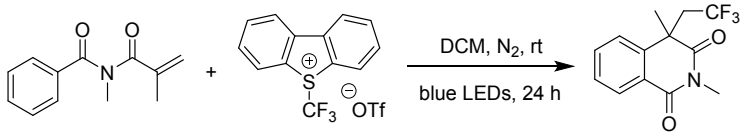


1w (1.0 equiv) **2** (1.5 equiv) **3w**, 22% yield

1-Methyl-4-phenyl-3-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (**3w**). Colorless oil, 13.4 mg, 22%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.35 (m, 1H), 7.29–7.27 (m, 2H), 7.24–7.21 (m, 2H), 7.13–7.10 (m, 2H), 7.01–7.00 (m, 2H), 4.50 (s, 1H), 3.66 (qd, *J* = 9.3, 1.3 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.6, 140.2, 139.3, 129.33, 129.29, 128.8, 127.8, 127.1, 124.7, 124.6 (q, *J* = 283.4 Hz), 124.3, 115.4, 53.6 (q, *J* = 26.5 Hz), 42.1, 30.4; ^{19}F NMR (470 MHz,

$CDCl_3$): δ −67.27 (d, J = 8.9 Hz). (Known compound; spectra data were identical to the literature.[4])

(2) Reaction of *N*-methacryloyl-*N*-methylarylamide with Umemoto's reagent

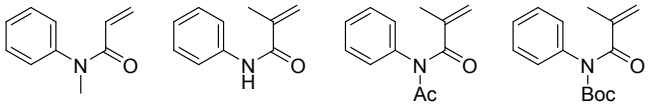


1x (1.0 equiv) **2** (1.5 equiv) **3x**, 26% yield

2,4-Dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2*H*,4*H*)-dione (**3x**). Colorless oil, 14.0 mg, 26%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (dd, J = 8.0, 1.0 Hz, 1H), 7.65 (td, J = 7.8, 1.3 Hz, 1H), 7.47 (td, J = 7.8, 0.83 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 3.39 (s, 3H), 3.34 (dq, J = 15.3, 10.5 Hz, 1H), 2.80 (dq, J = 15.3, 9.8 Hz, 1H), 1.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.7, 163.8, 140.5, 133.9, 129.4, 128.2, 125.8, 125.1 (q, J = 279.2 Hz), 124.3, 44.5 (q, J = 27.6 Hz), 43.7 (q, J = 2.1 Hz), 31.3, 27.5; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.66 (t, J = 9.9 Hz). (Known compound; spectra data were identical to the literature.[5])

(3) Unsuccessful substrates

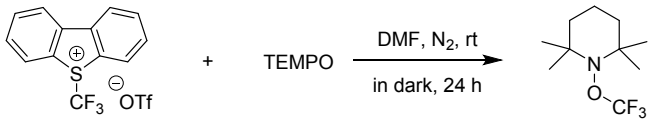
For the following acrylamides, lack of a substituent at the α-position of the acrylamide or lack of substitution on the amide, or replacement of the methyl by either an acetyl or *N*-*tert*-butyloxycarbonyl substituent, shut down the cyclization process completely and gave a complex mixture.



4. Experimental Details for Mechanistic Studies

4-1 The TEMPO trapping experiments

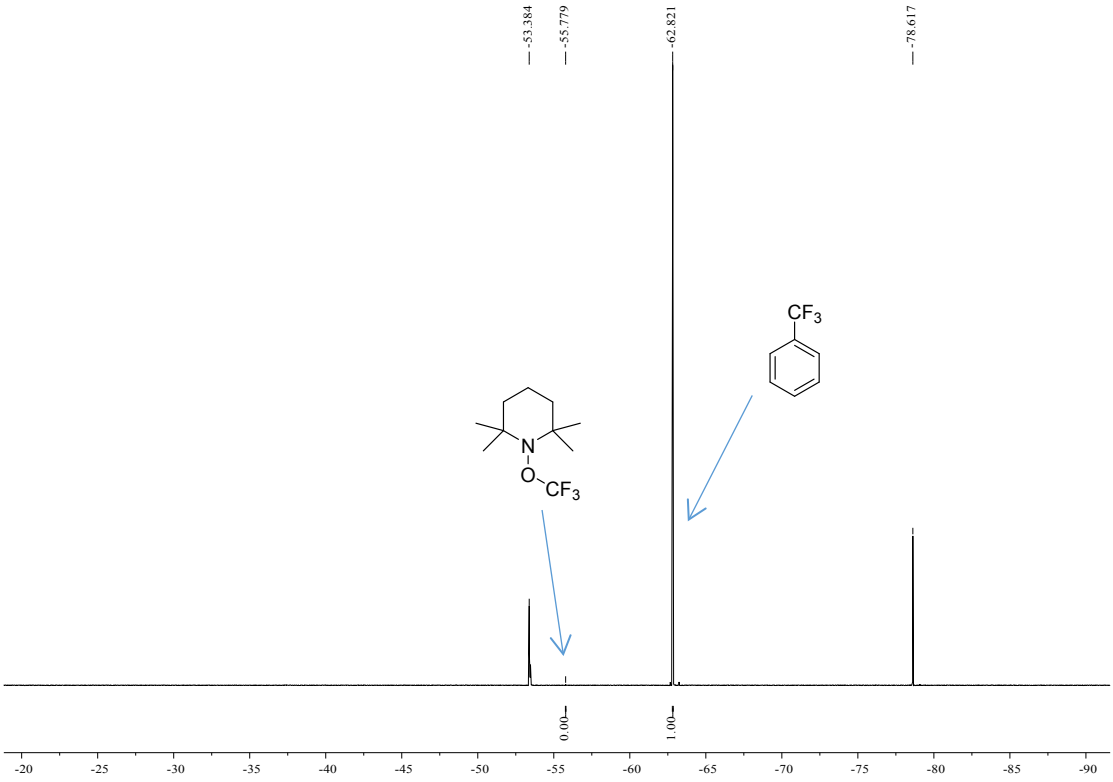
(1)



2 **4** trace

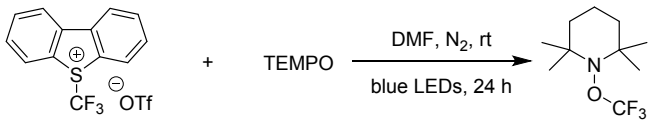
A 10.0 mL Schlenk tube was equipped with a rubber septum and magnetic stir bar and was charged with Umemoto's reagent **2** (40.2 mg, 0.10 mmol, 1.0 equiv) and TEMPO (15.6 mg, 0.10 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen for three times, and then DMF (1.0 mL) were added with a syringe under nitrogen. The mixture was stirred under dark for

24 hours and then determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene (3.4 mg, 0.023 mmol) as an internal standard.



^{19}F NMR spectrum of crude reaction mixture (50.0 μL) (470 MHz, $CDCl_3$)

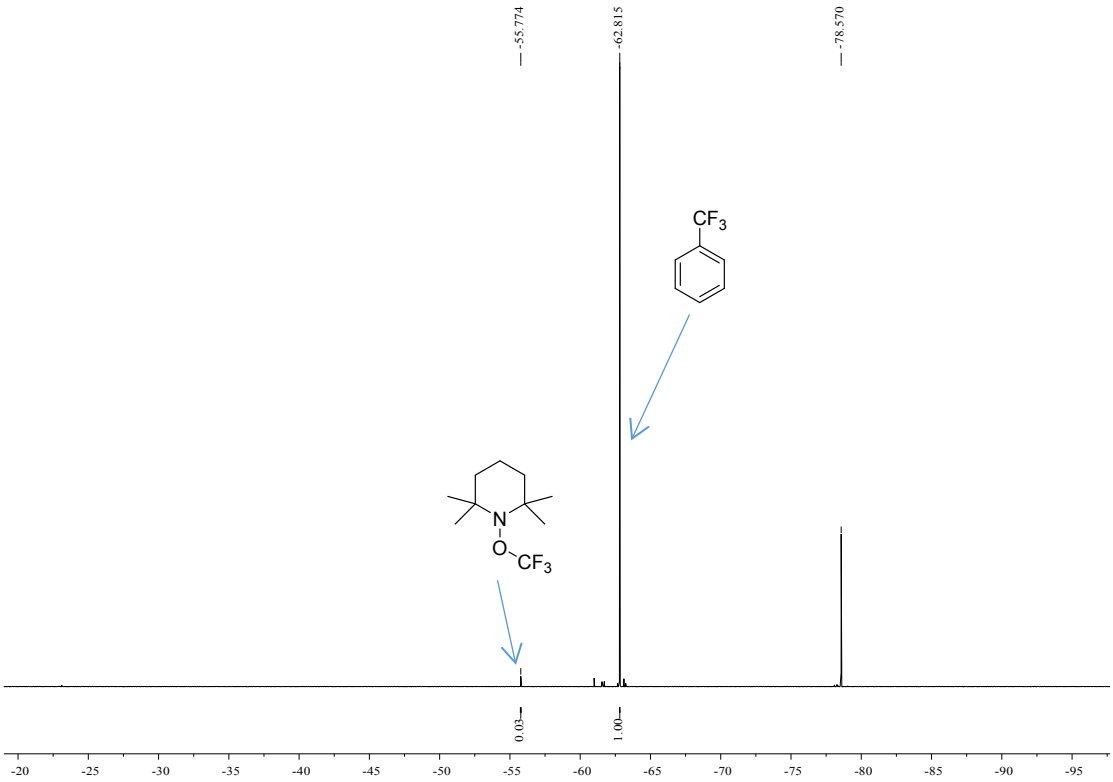
(2)



2 **4**

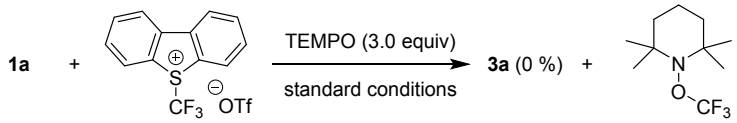
15 %

A 10.0 mL Schlenk tube was equipped with a rubber septum and magnetic stir bar and was charged with Umemoto's reagent **2** (40.2 mg, 0.10 mmol, 1.0 equiv) and TEMPO (15.6 mg, 0.10 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen for three times, and then DMF (1.0 mL) were added with a syringe under nitrogen. The mixture was irradiated by 3 W blue LEDs with stirring for 24 hours and then determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene (3.6 mg, 0.025 mmol) as an internal standard.



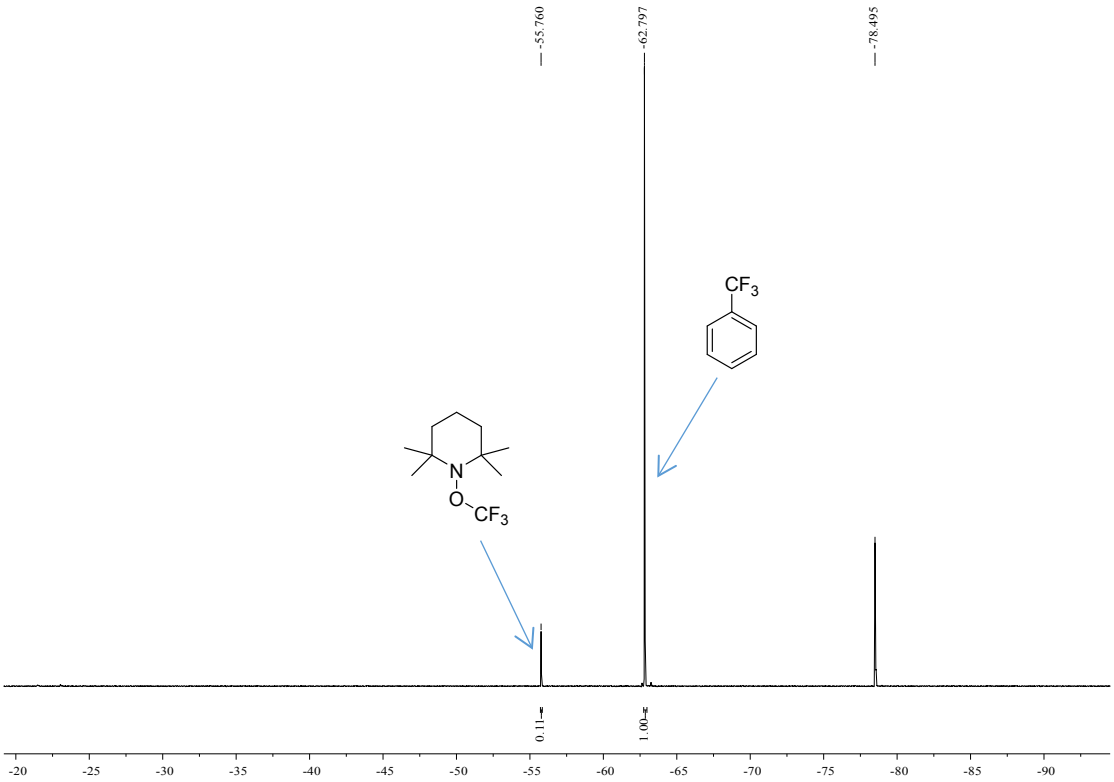
^{19}F NMR spectrum of crude reaction mixture (50.0 μL) (470 MHz, $CDCl_3$)

(3)



2 **4** (51 %)

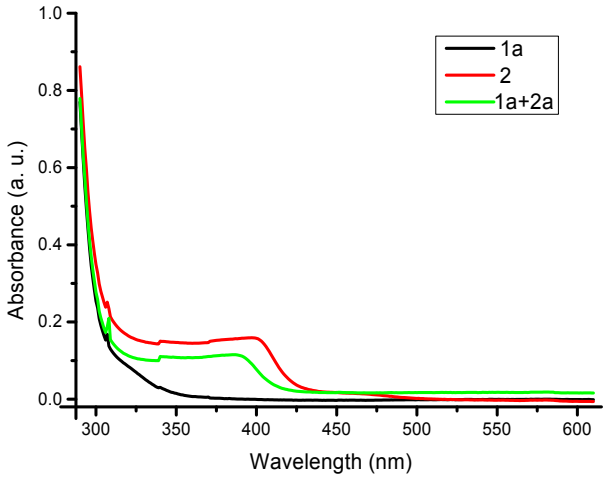
A 10.0 mL Schlenk tube was equipped with a rubber septum and magnetic stir bar and was charged with *N*-phenyl-*N*-methylacrylamide **1a** (17.5 mg, 0.10 mmol, 1.0 equiv), Umemoto's reagent **2** (60.3 mg, 0.15 mmol, 1.5 equiv), and TEMPO (46.9 mg, 0.30 mmol, 3.0 equiv). The tube was evacuated and backfilled with nitrogen for three times, and then DMF (1.0 mL) were added with a syringe under nitrogen. The mixture was irradiated by 3 W blue LEDs with stirring for 24 hours and then determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene (3.4 mg, 0.023 mmol) as an internal standard.



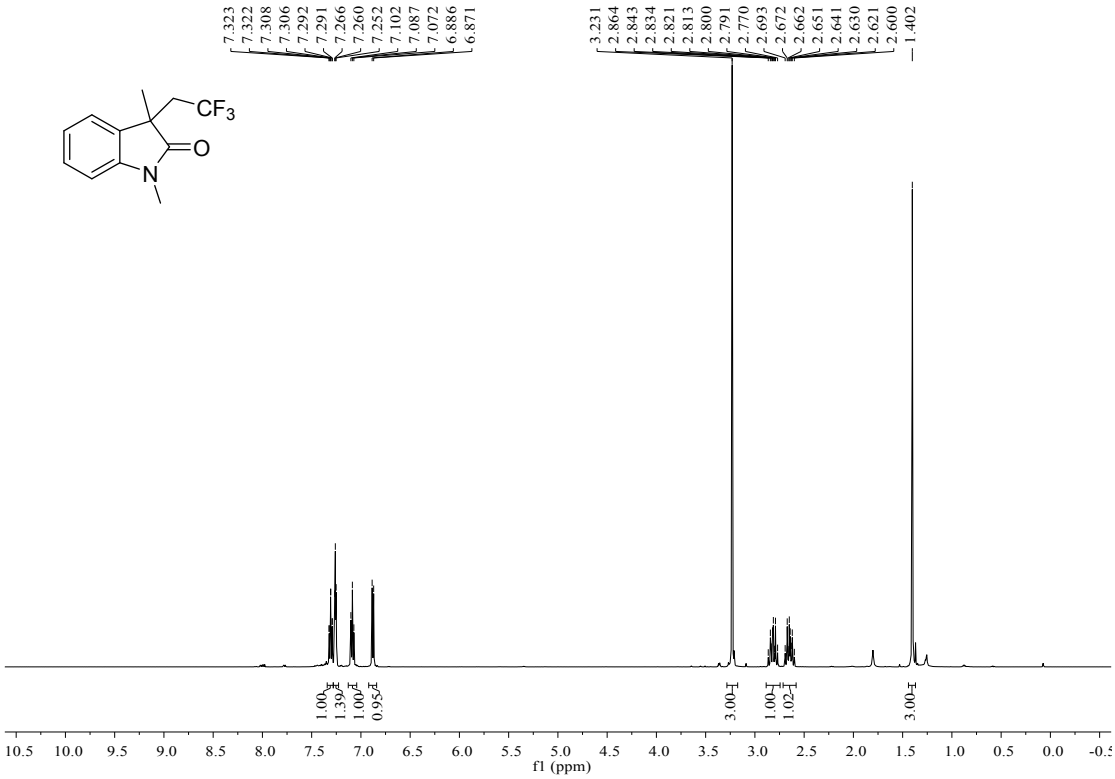
^{19}F NMR spectrum of crude reaction mixture (50.0 μL) (470 MHz, $CDCl_3$)

4-2 UV/Vis absorbance studies

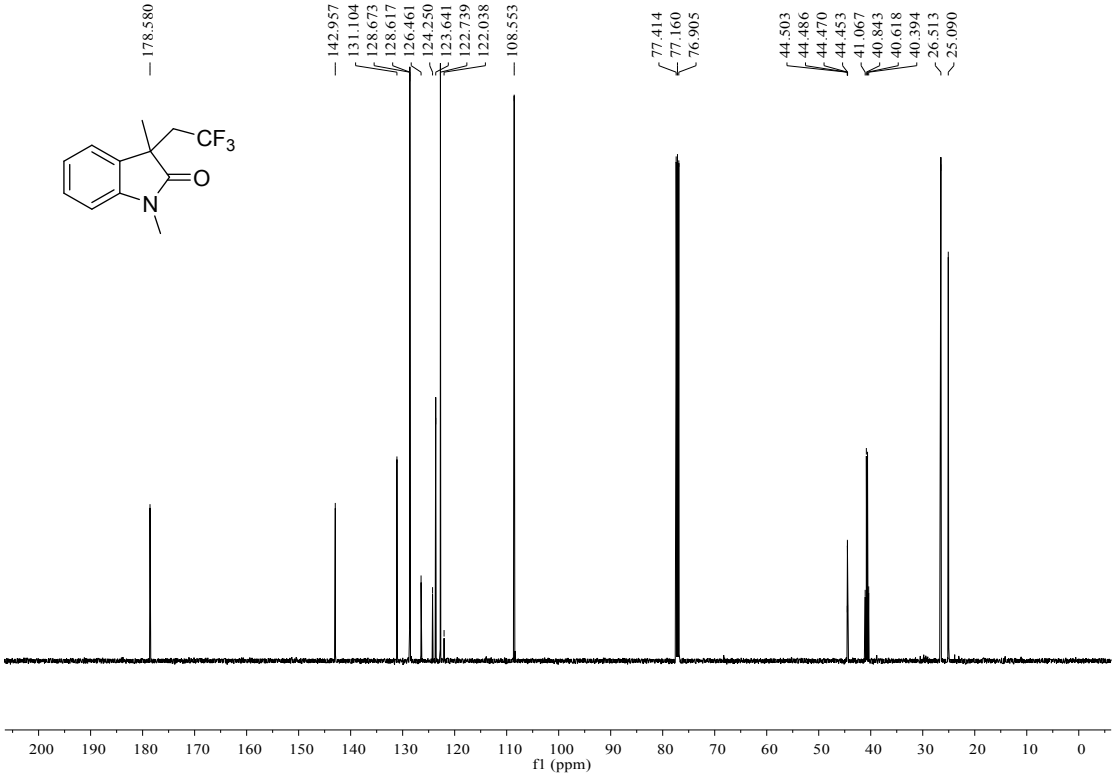
UV absorption spectra of *N*-phenyl-*N*-methylacrylamide **1a** (0.10 M), Umemoto's reagent **2** (0.10 M) and mixture of **1a** and **2** in DMF were recorded. There was no increase in UV absorbance upon mixing **1a** and Umemoto's reagent **2**. This clearly excludes the presence of EDA complex between **1a** and Umemoto's ragent **2**.



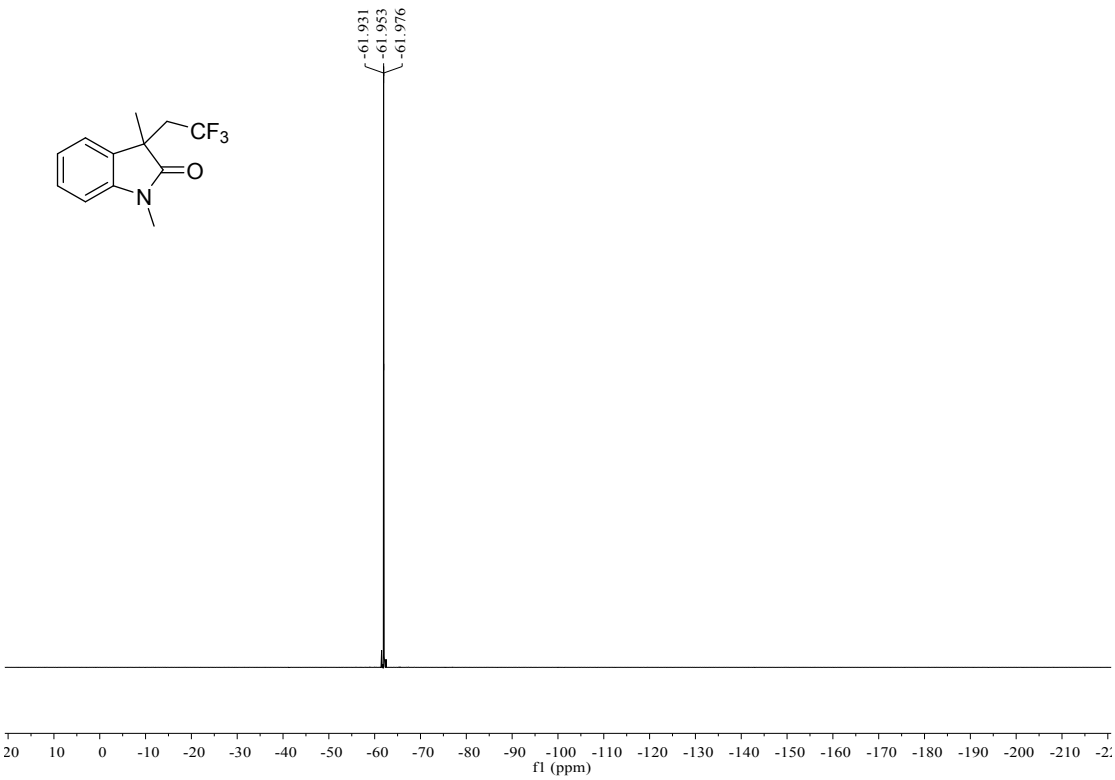
5. Copies of NMR Spectra



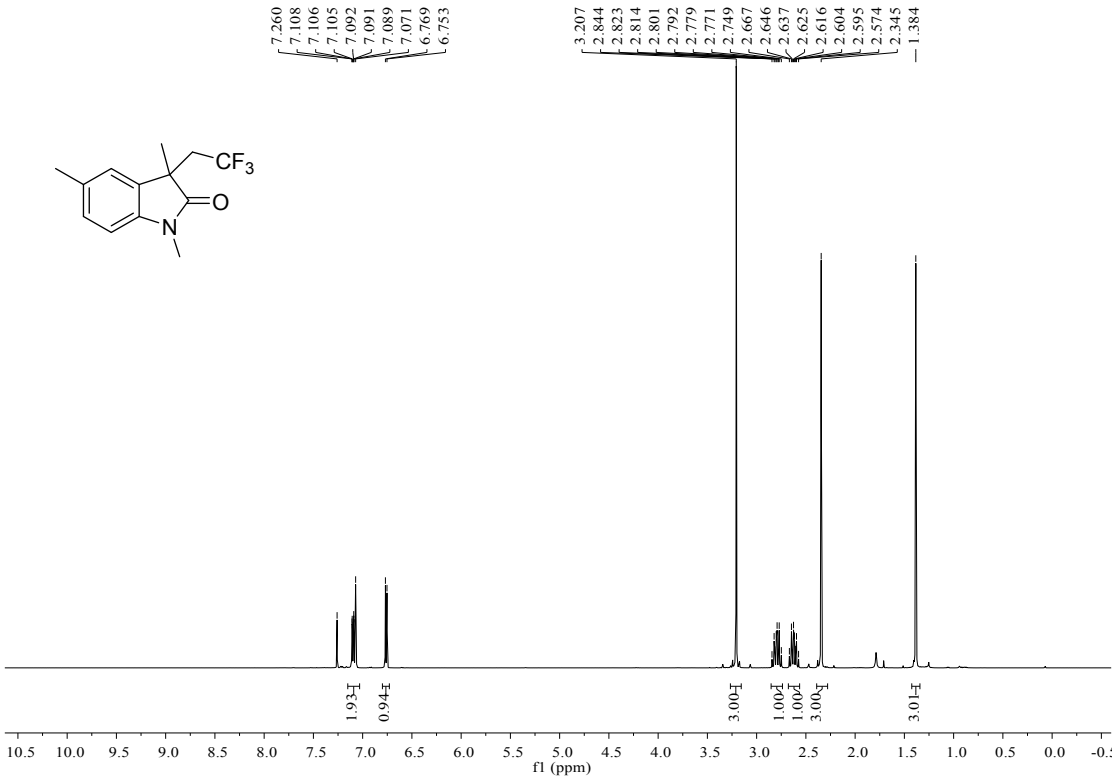
^{1}H NMR Spectrum of **3a** (500 MHz, $CDCl_3$)



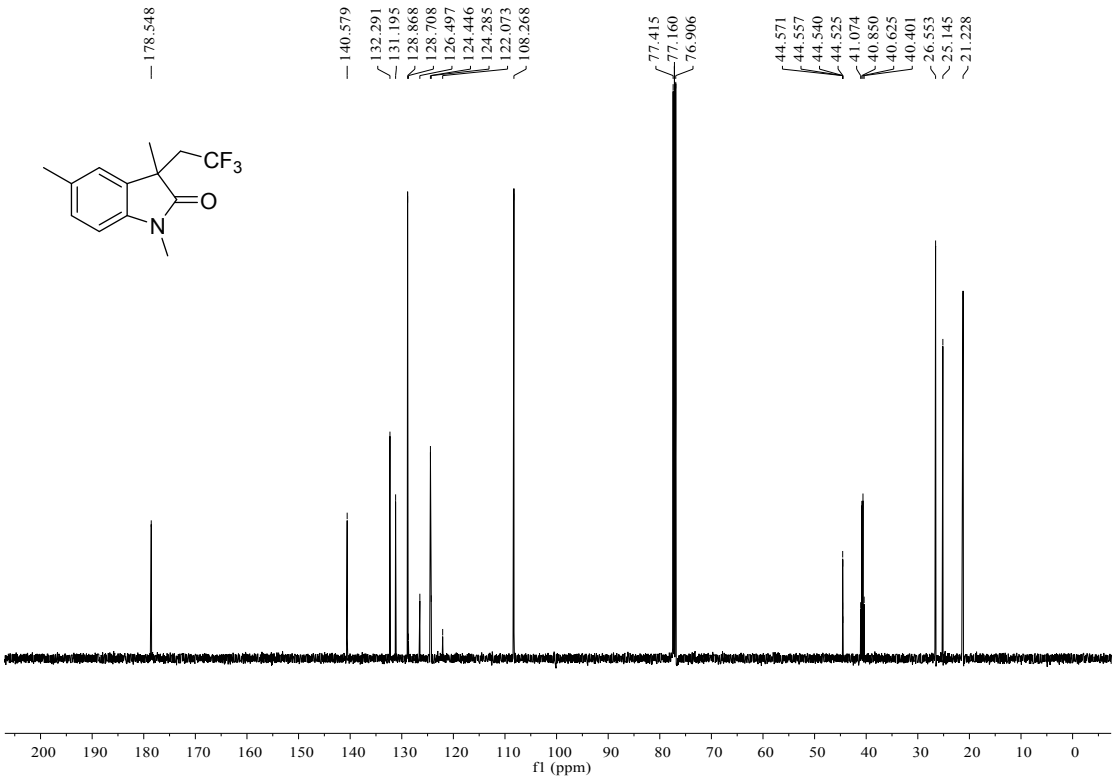
^{13}C NMR Spectrum of **3a** (126 MHz, $CDCl_3$)



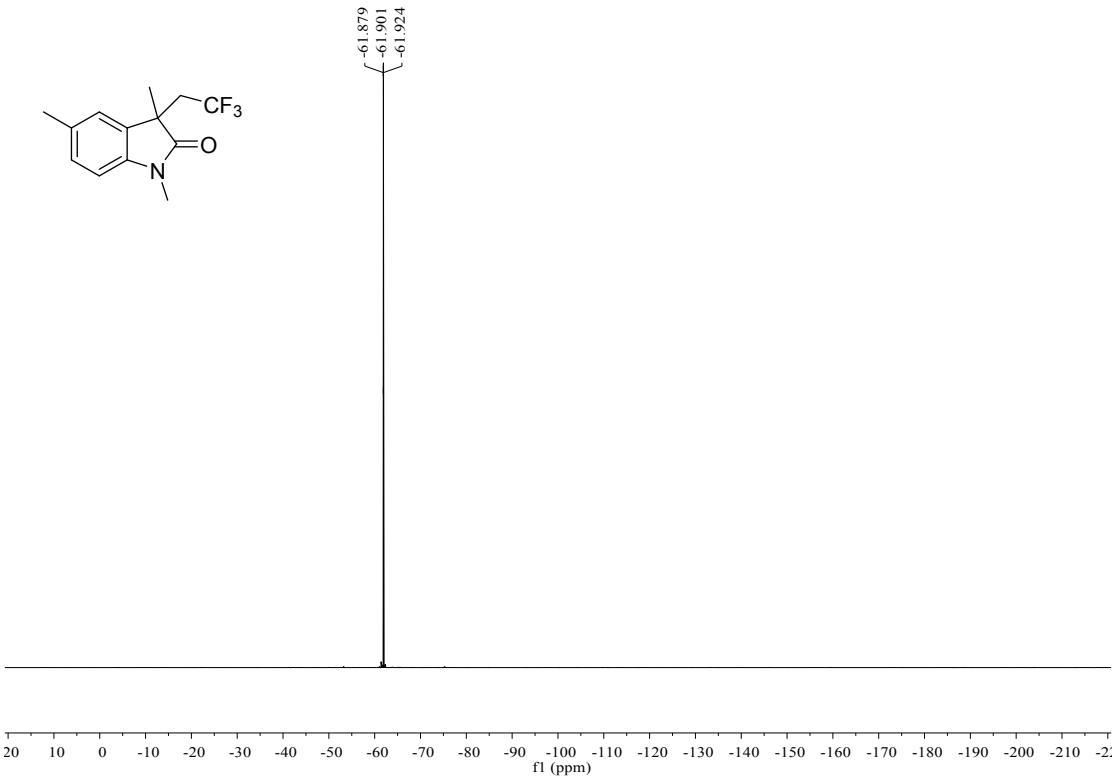
^{19}F NMR Spectrum of **3a** (470 MHz, $CDCl_3$)



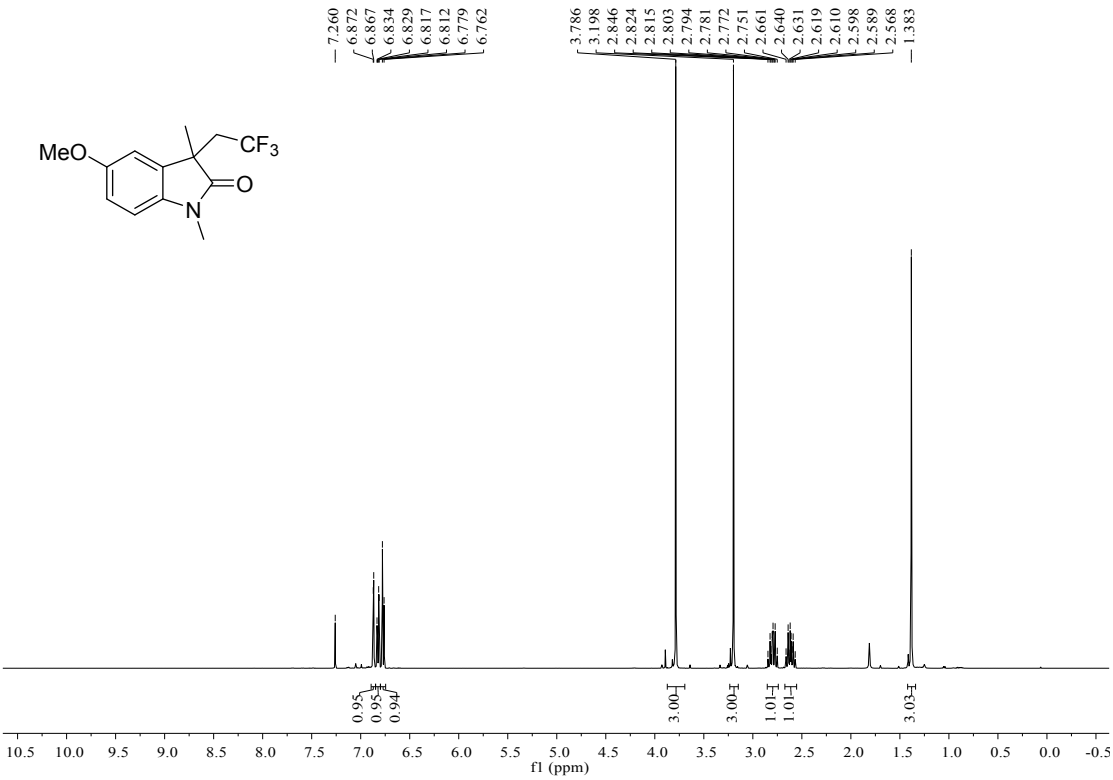
^{1}H NMR Spectrum of **3b** (500 MHz, $CDCl_3$)



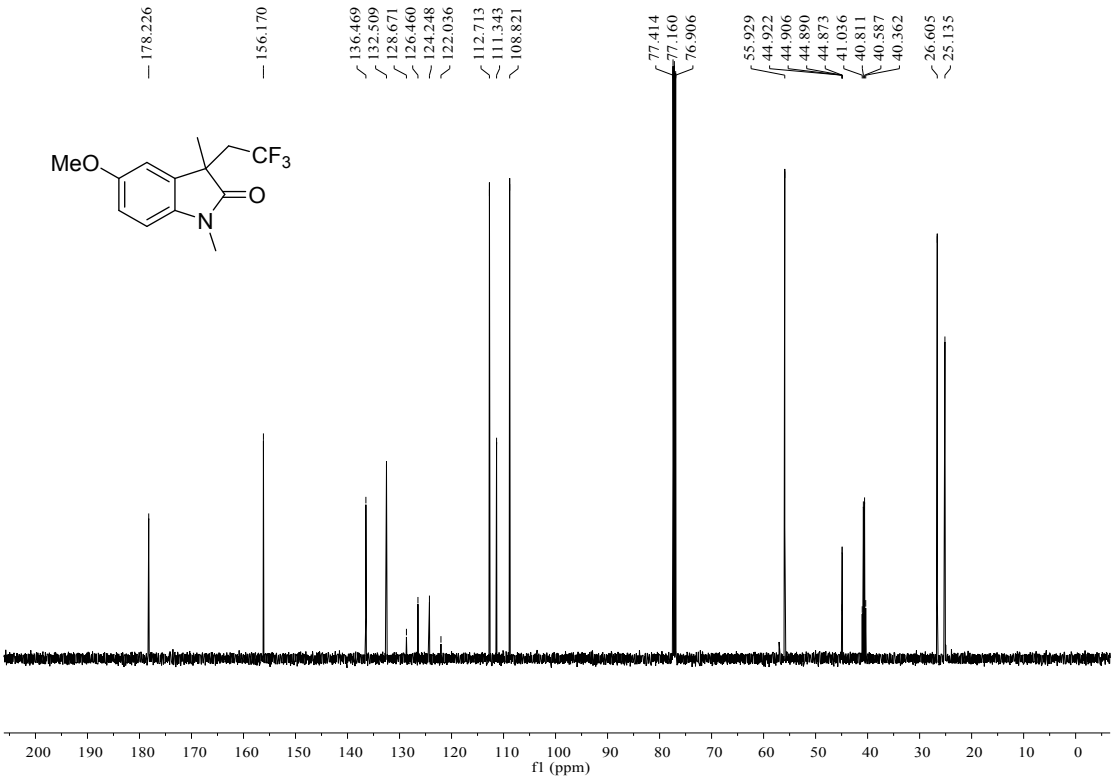
^{13}C NMR Spectrum of **3b** (126 MHz, $CDCl_3$)



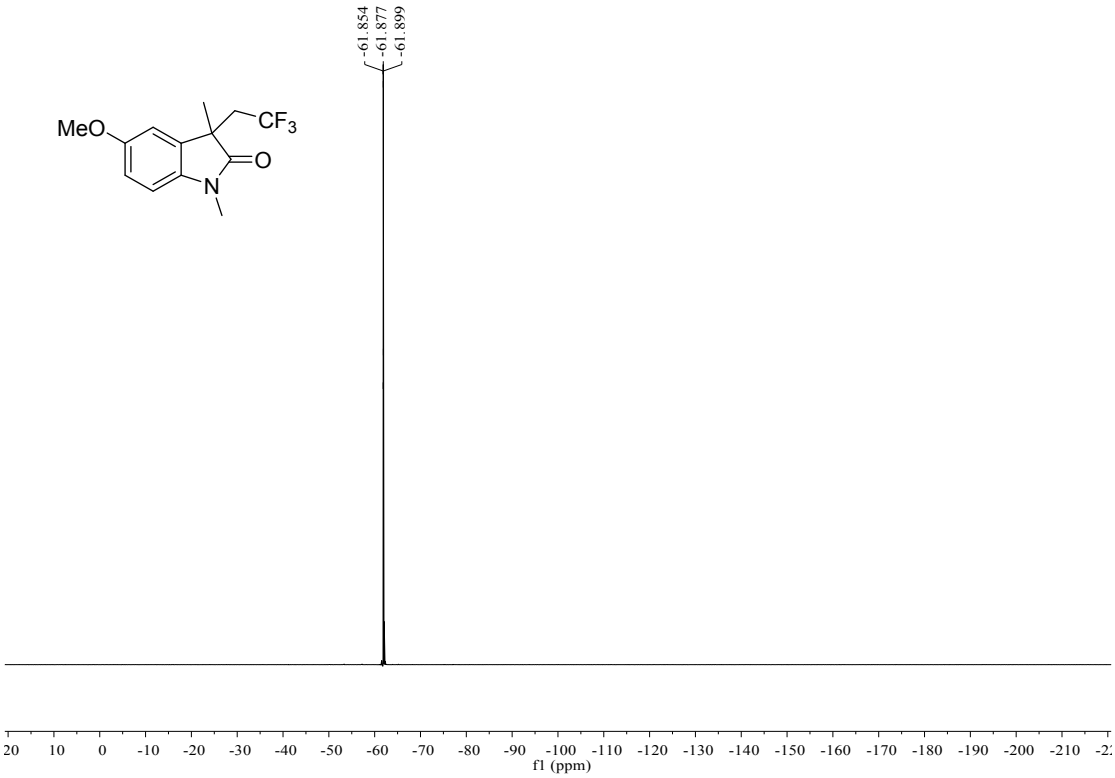
^{19}F NMR Spectrum of **3b** (470 MHz, $CDCl_3$)



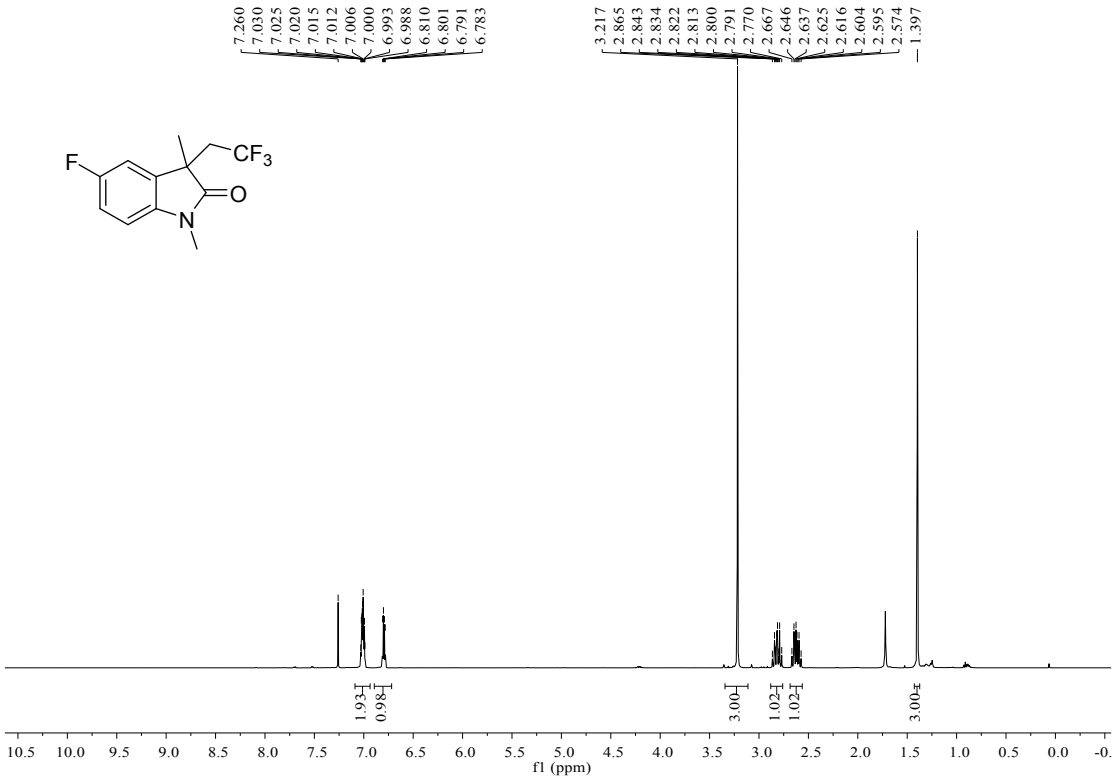
^{1}H NMR Spectrum of **3c** (500 MHz, $CDCl_3$)



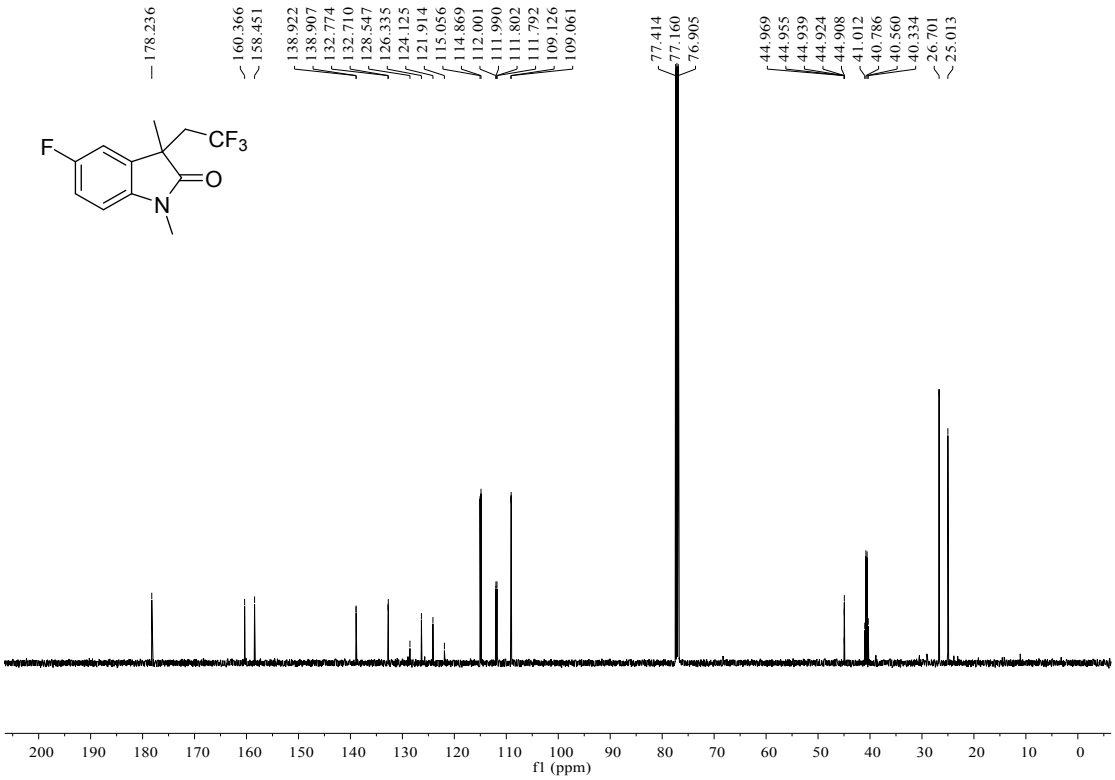
^{13}C NMR Spectrum of **3c** (126 MHz, $CDCl_3$)



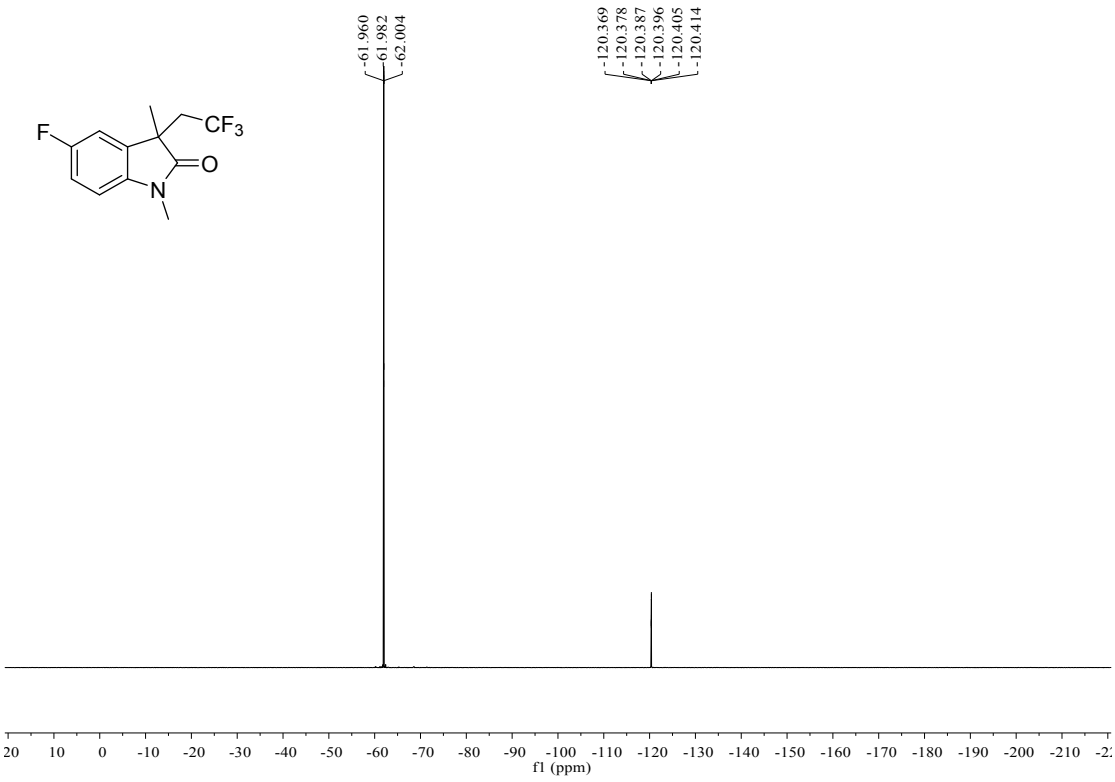
^{19}F NMR Spectrum of **3c** (470 MHz, $CDCl_3$)



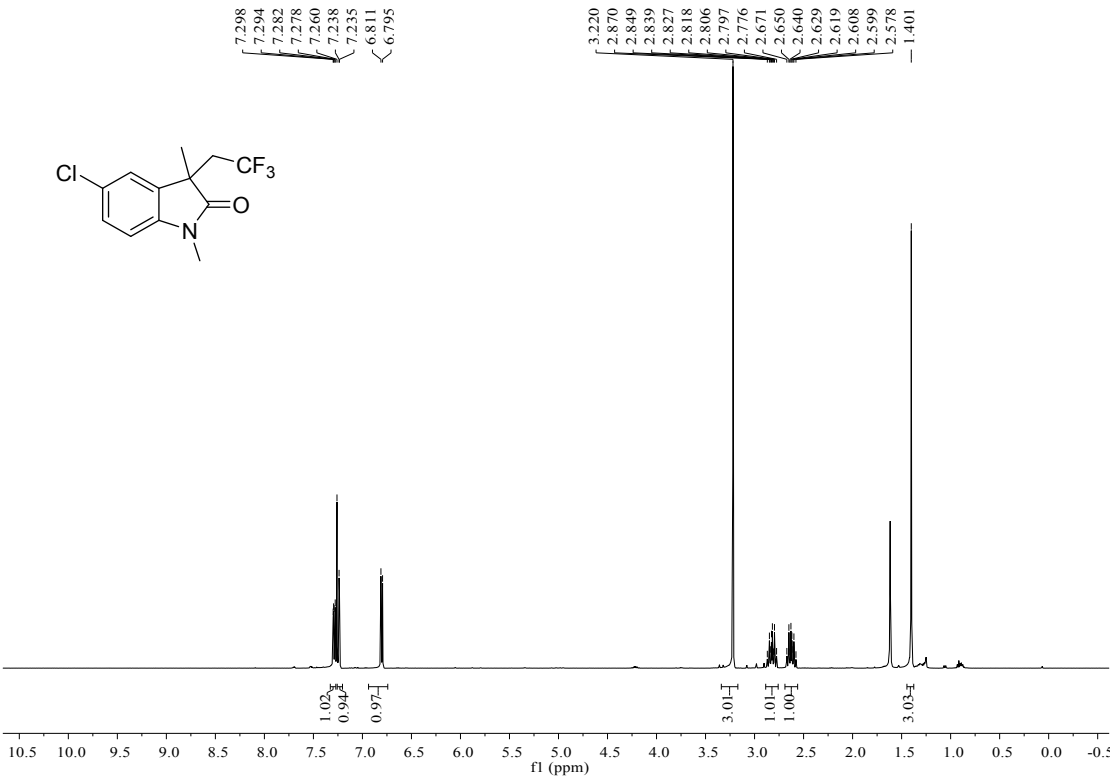
^{1}H NMR Spectrum of **3d** (500 MHz, $CDCl_3$)



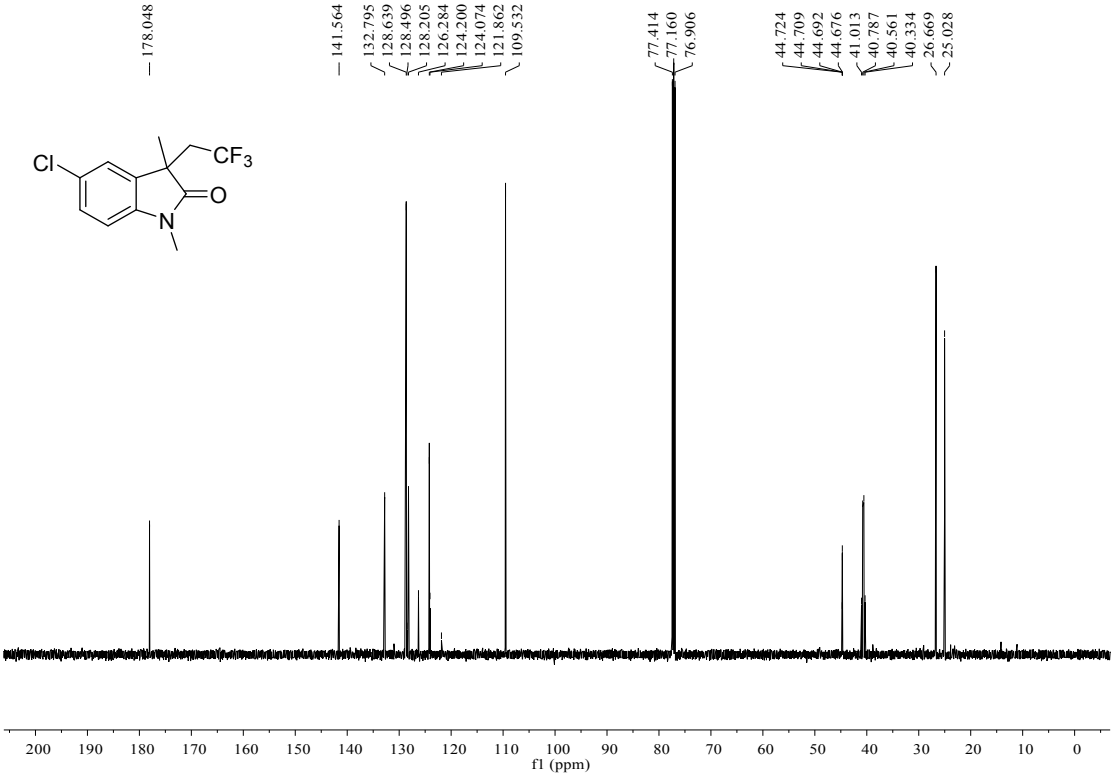
^{13}C NMR Spectrum of **3d** (126 MHz, $CDCl_3$)



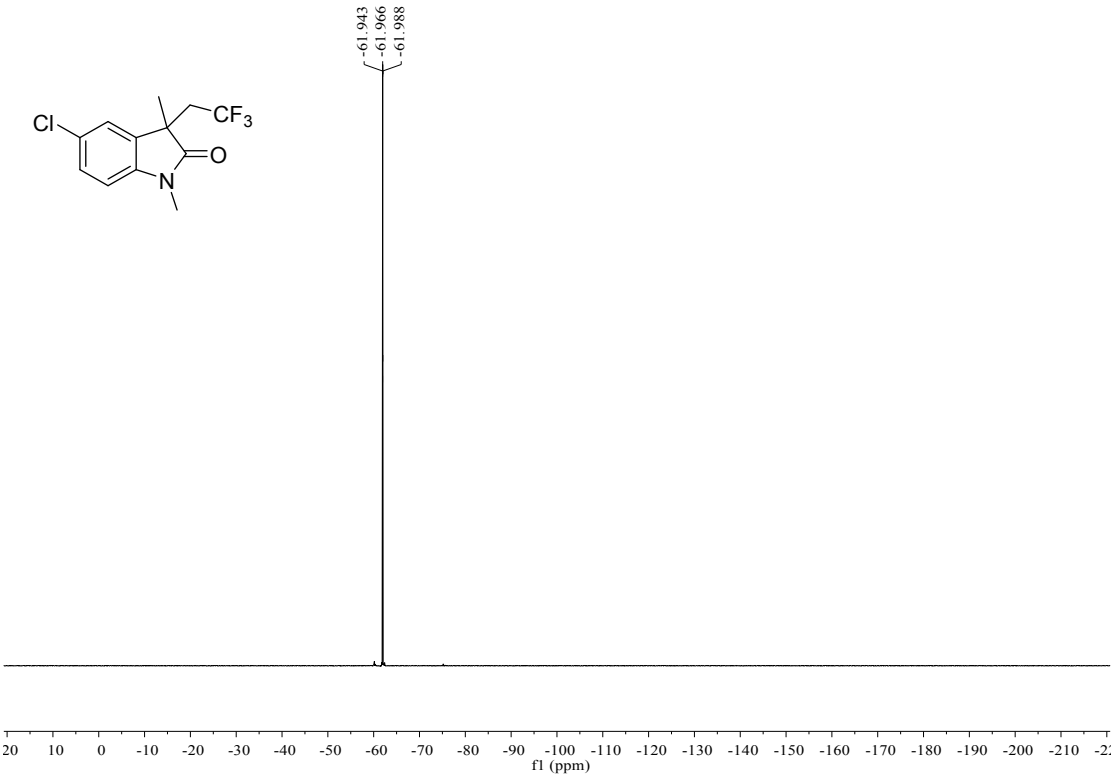
^{19}F NMR Spectrum of **3d** (470 MHz, $CDCl_3$)



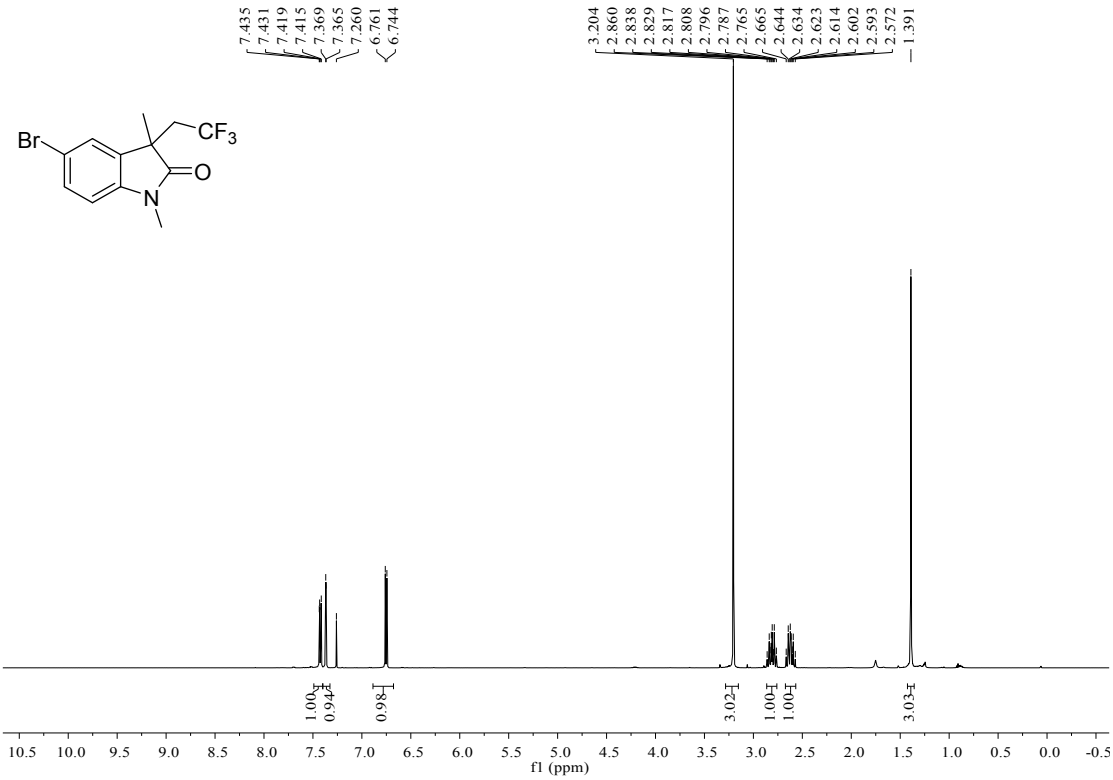
^{1}H NMR Spectrum of **3e** (500 MHz, $CDCl_3$)



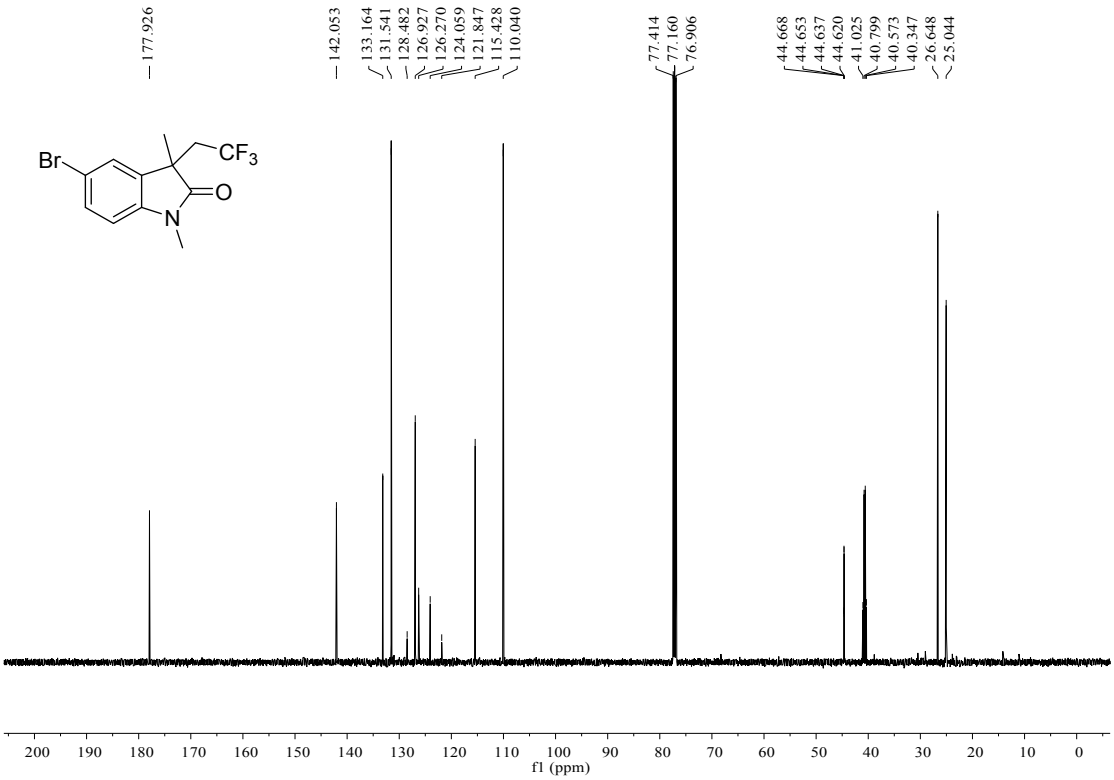
^{13}C NMR Spectrum of **3e** (126 MHz, $CDCl_3$)



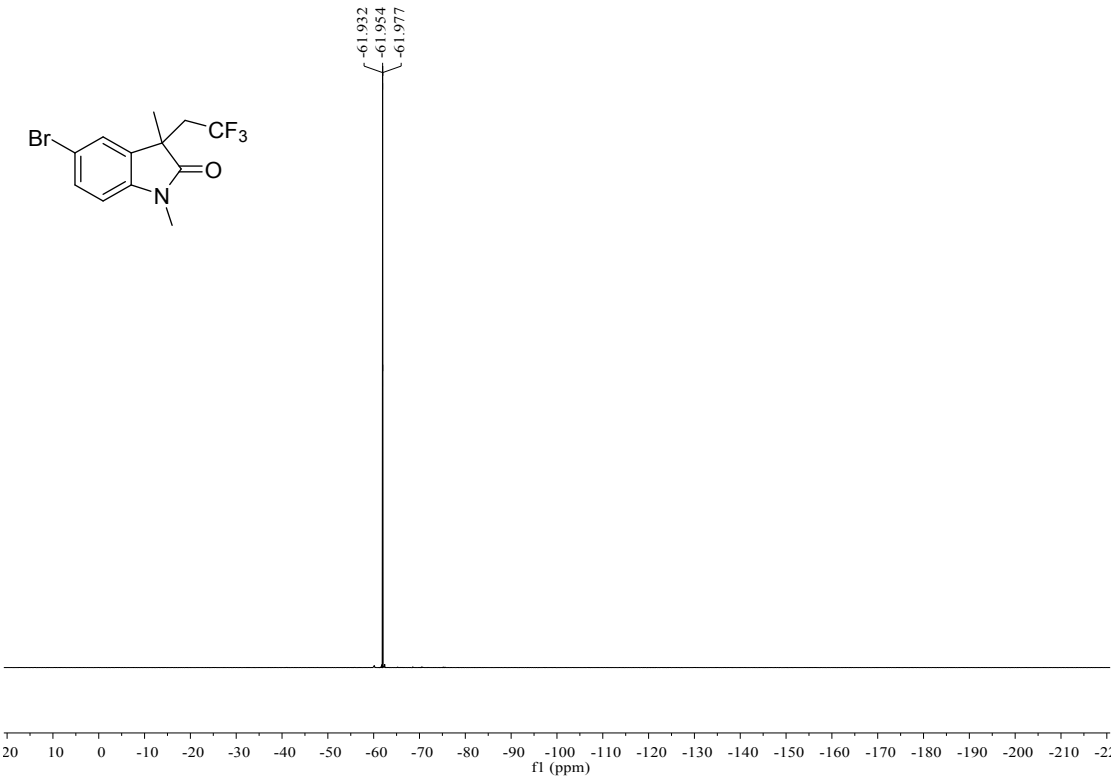
^{19}F NMR Spectrum of **3e** (470 MHz, $CDCl_3$)



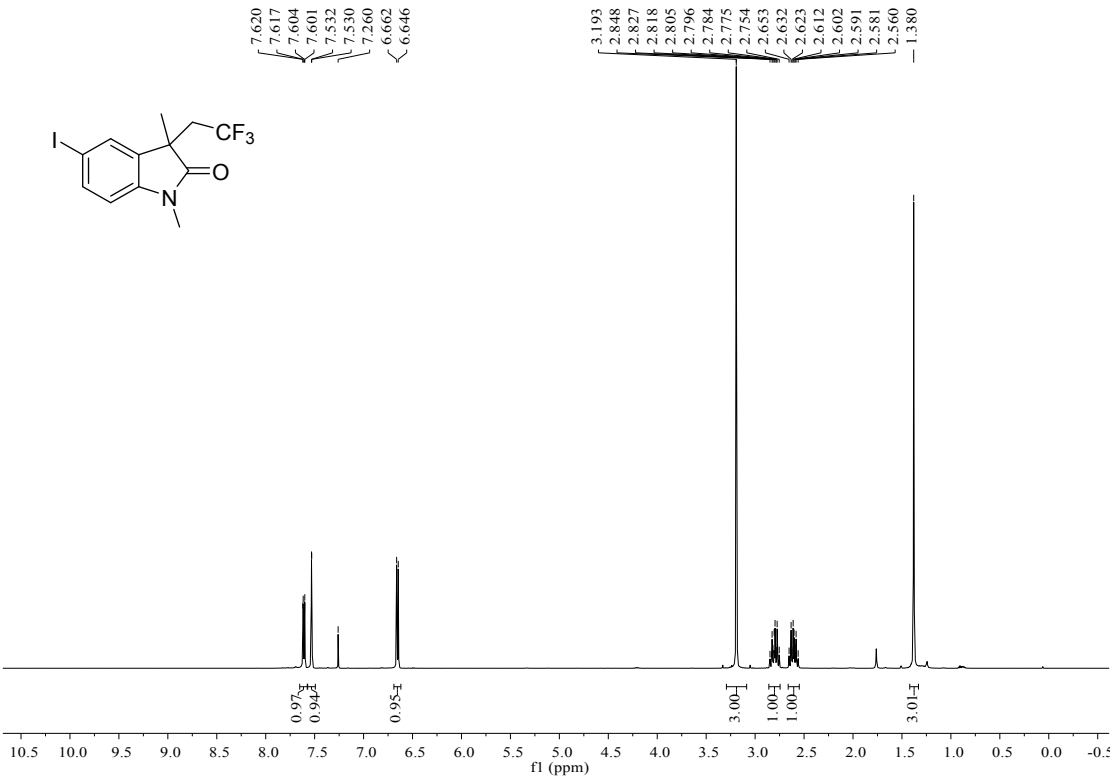
^{1}H NMR Spectrum of **3f** (500 MHz, $CDCl_3$)



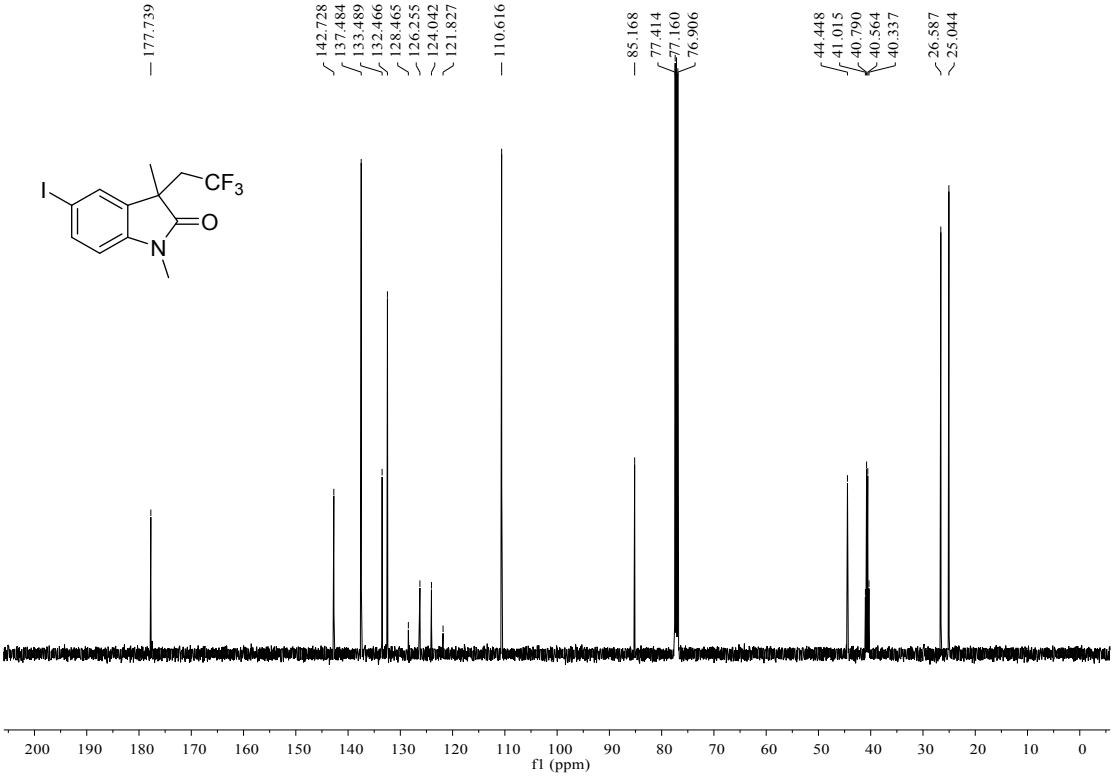
^{13}C NMR Spectrum of **3f** (126 MHz, $CDCl_3$)



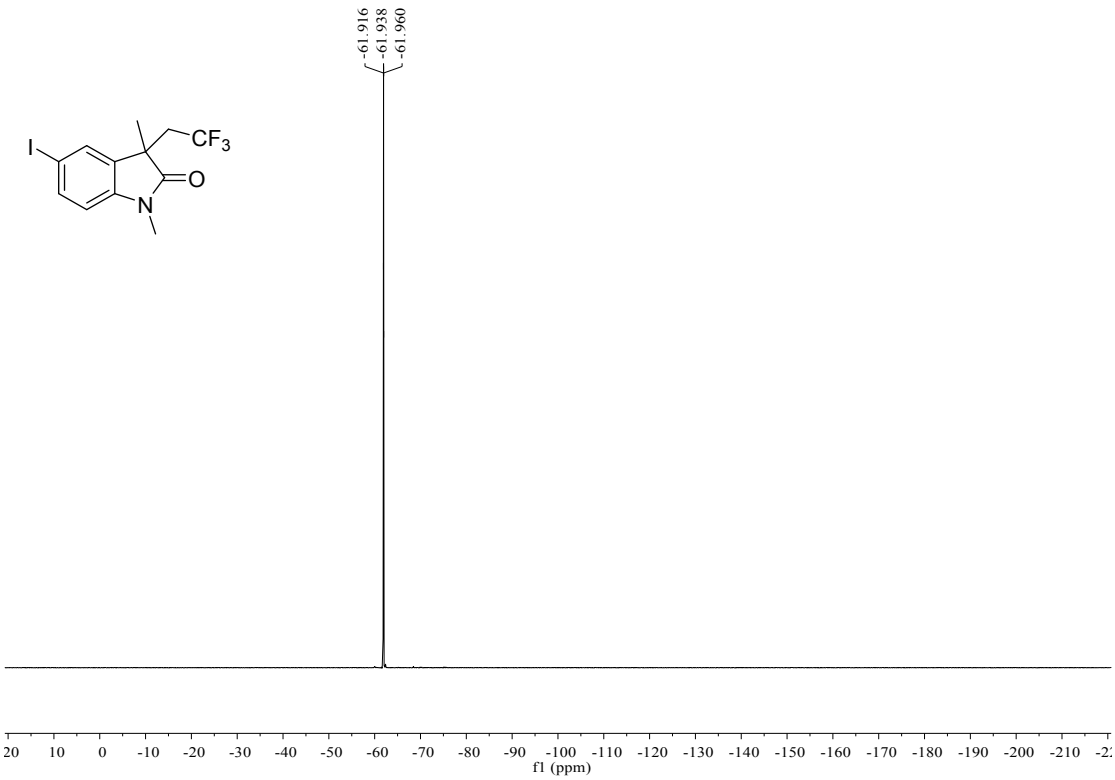
^{19}F NMR Spectrum of **3f** (470 MHz, $CDCl_3$)



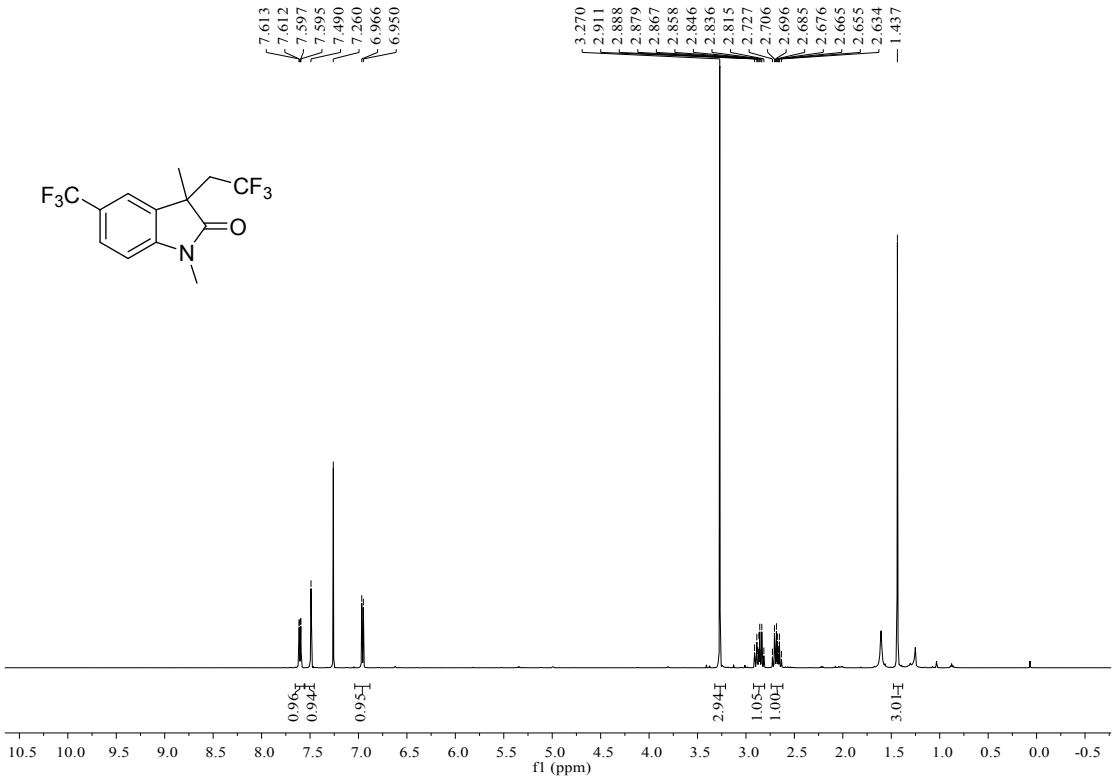
^{1}H NMR Spectrum of **3g** (500 MHz, $CDCl_3$)



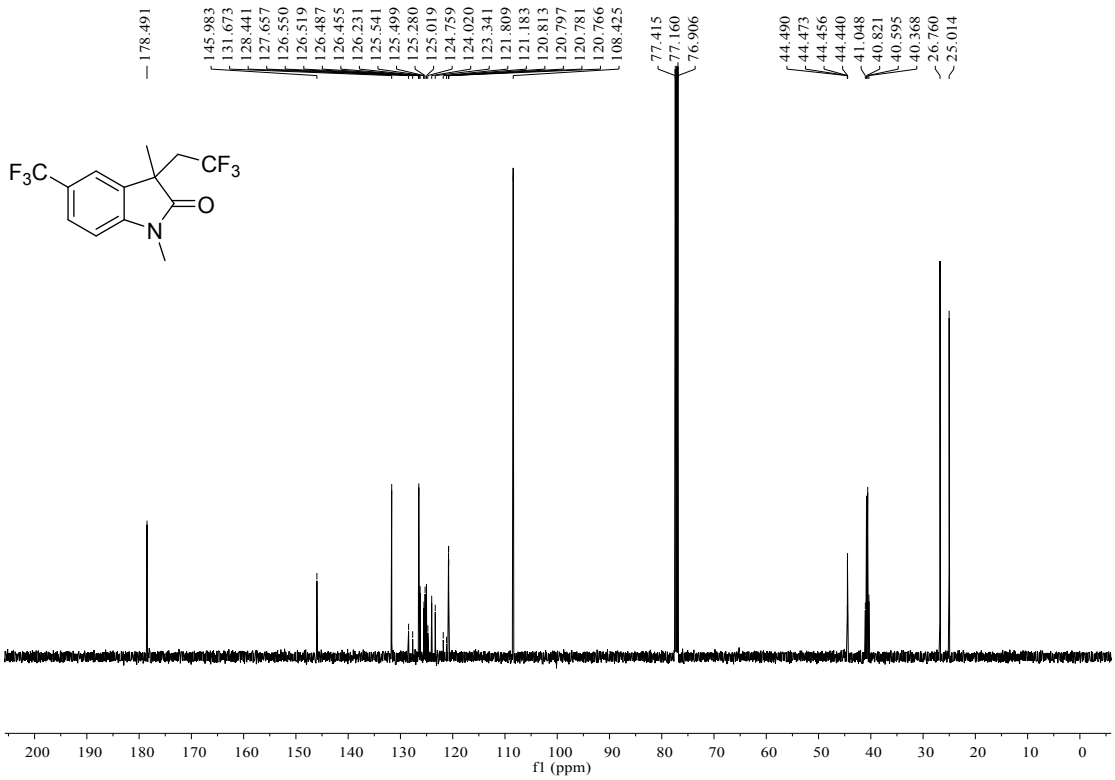
^{13}C NMR Spectrum of **3g** (126 MHz, $CDCl_3$)



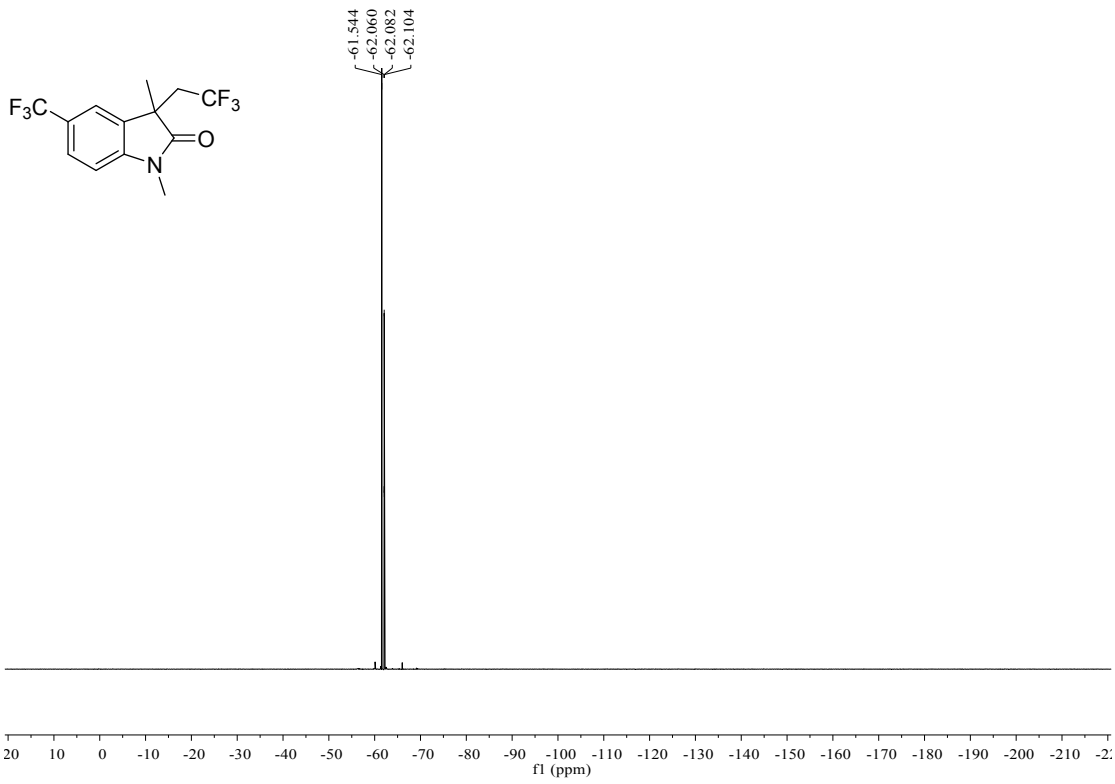
^{19}F NMR Spectrum of **3g** (470 MHz, $CDCl_3$)



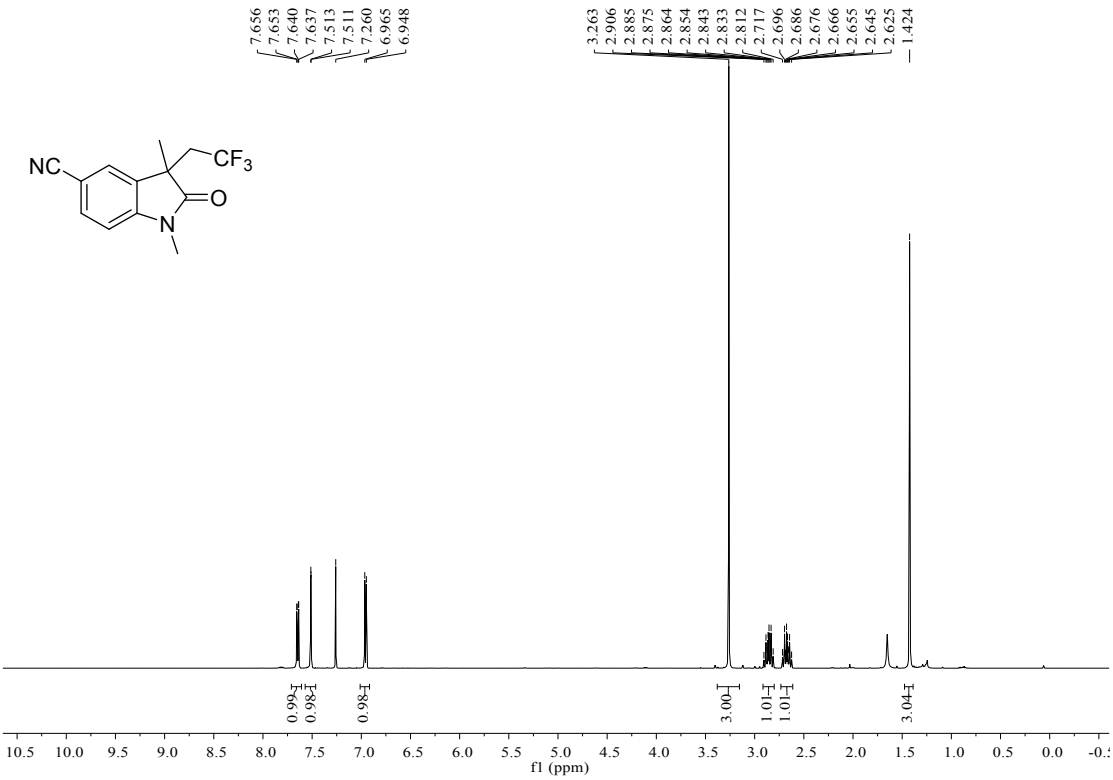
^{1}H NMR Spectrum of **3h** (500 MHz, $CDCl_3$)



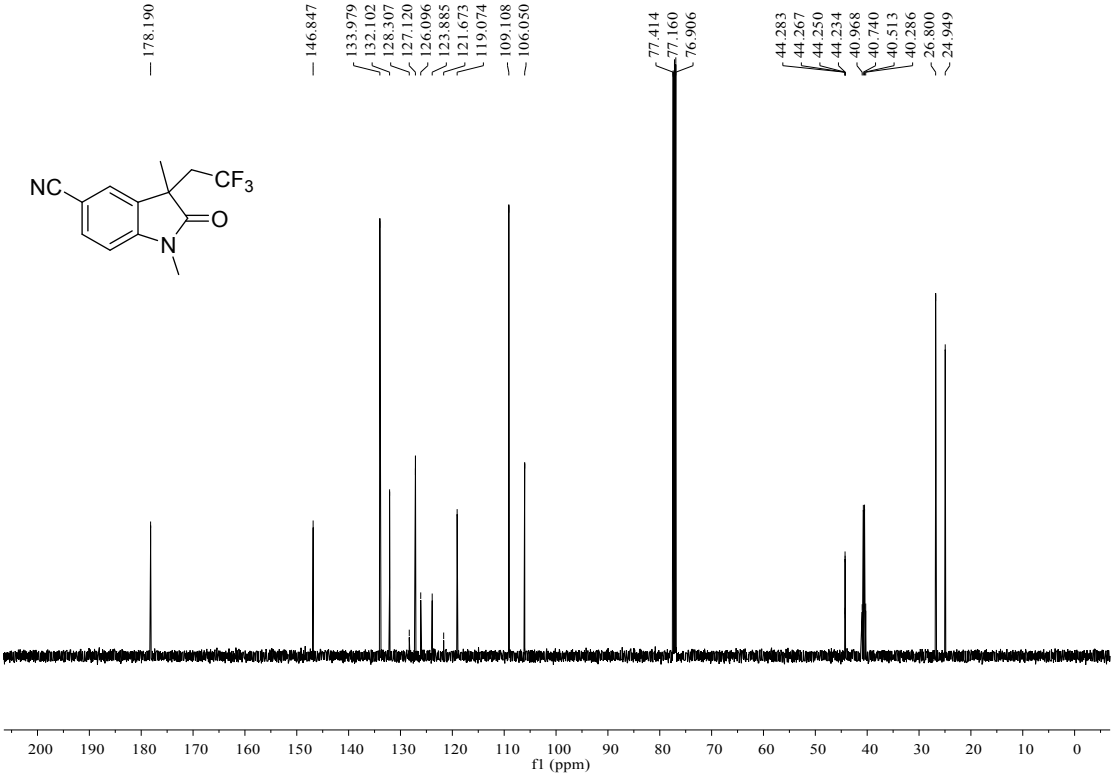
^{13}C NMR Spectrum of **3h** (126 MHz, $CDCl_3$)



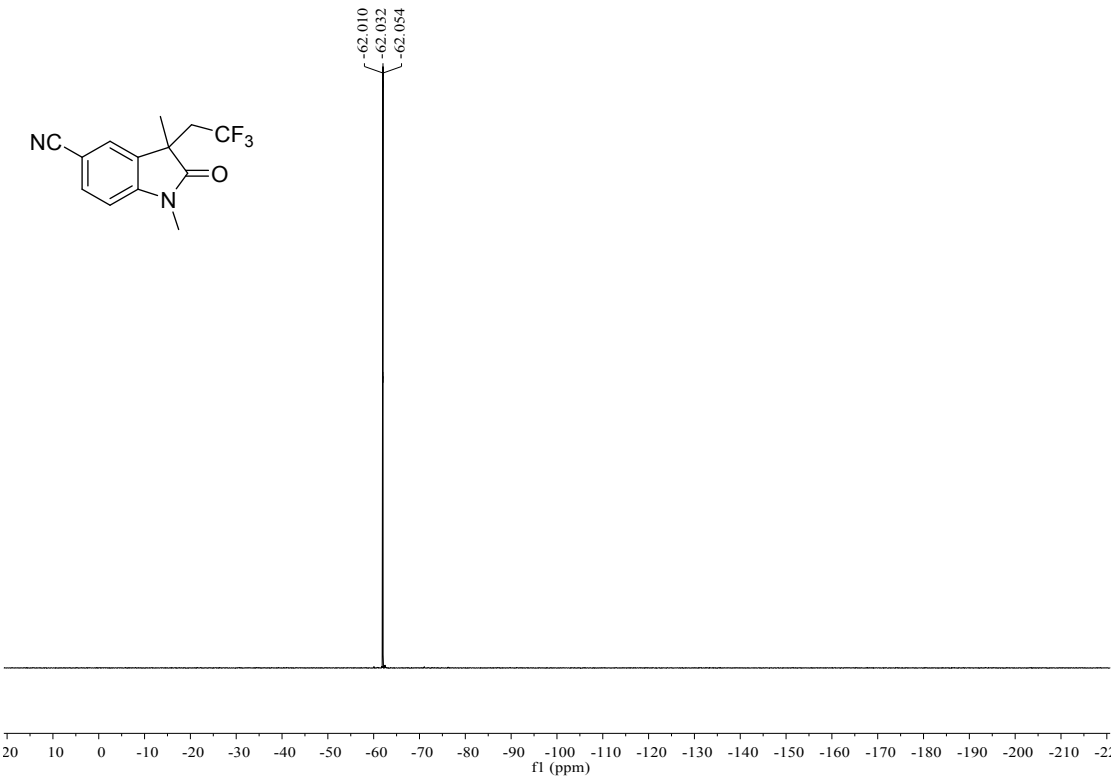
^{19}F NMR Spectrum of **3h** (470 MHz, $CDCl_3$)



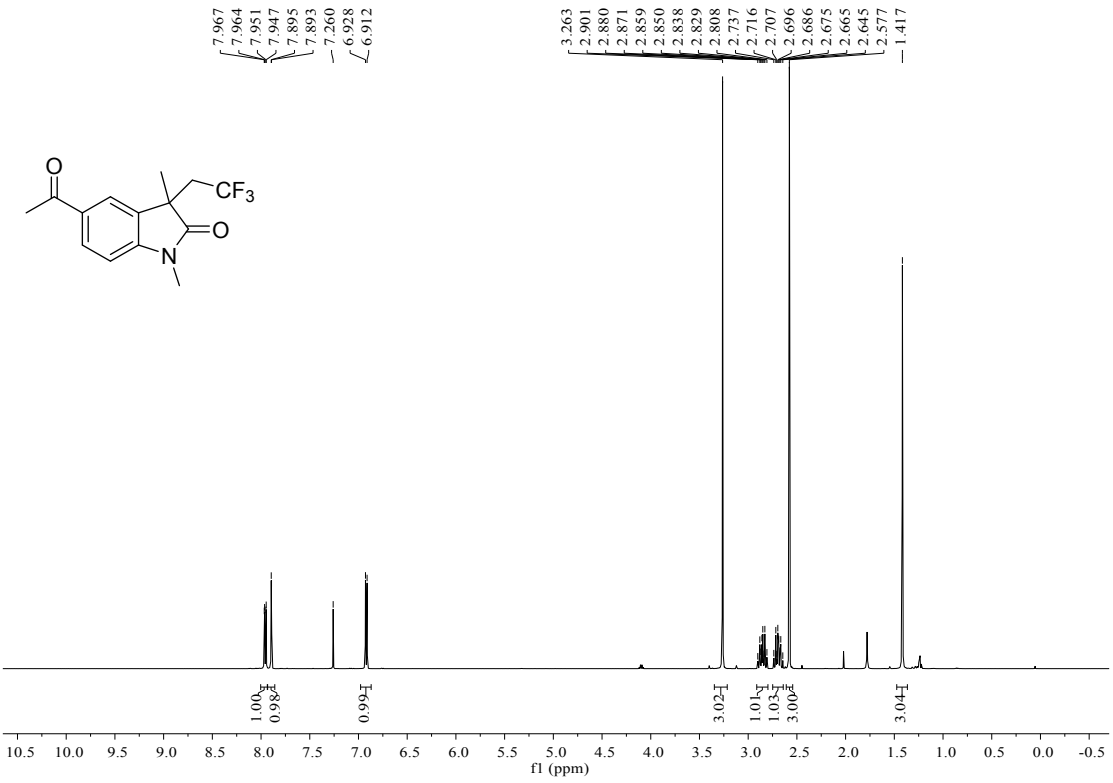
^{1}H NMR Spectrum of **3i** (500 MHz, $CDCl_3$)



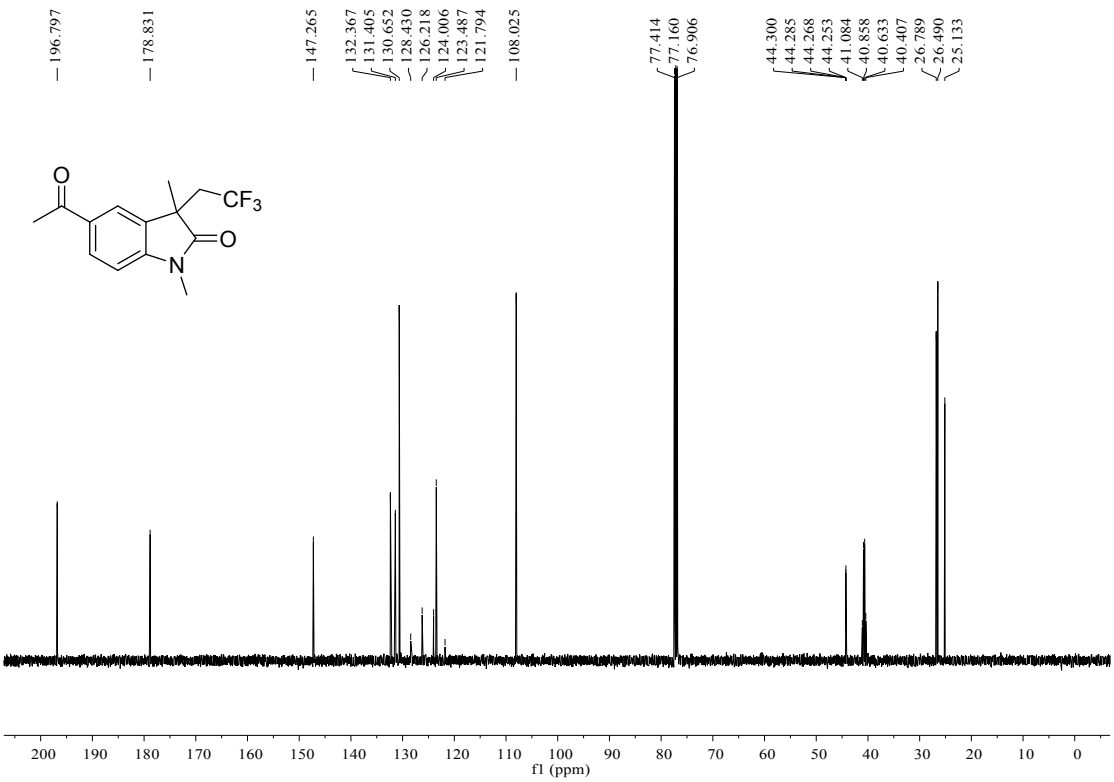
^{13}C NMR Spectrum of **3i** (126 MHz, $CDCl_3$)



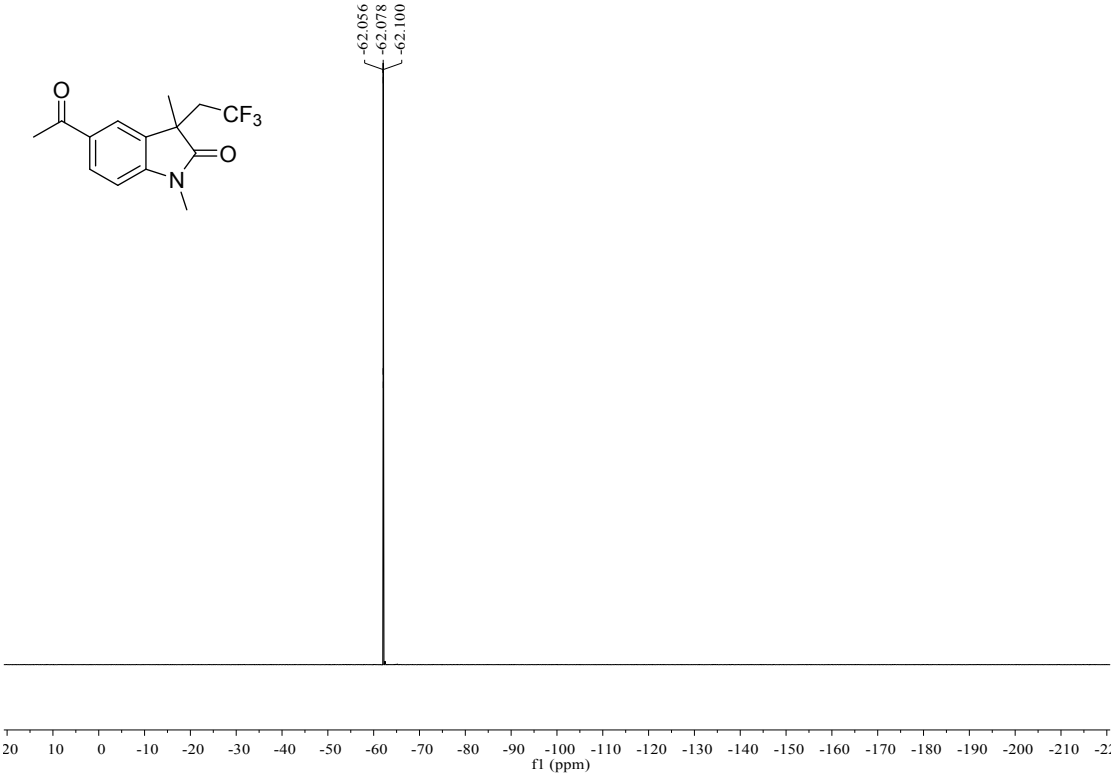
^{19}F NMR Spectrum of **3i** (470 MHz, $CDCl_3$)



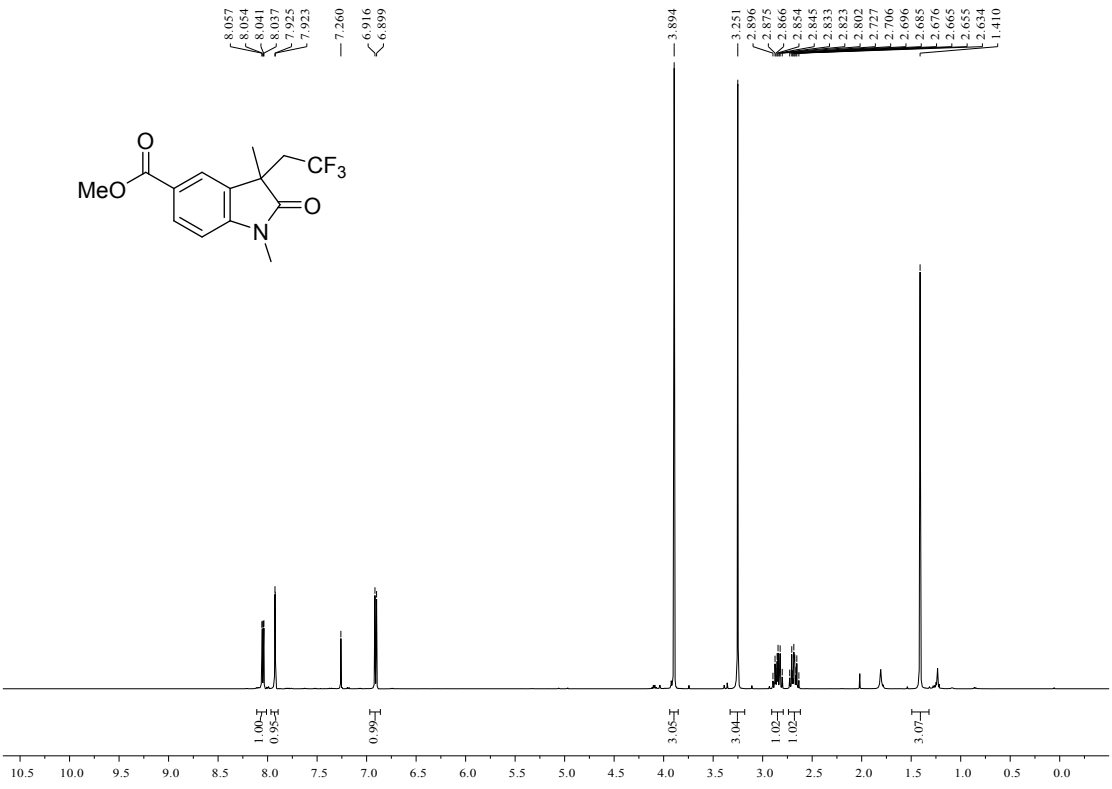
^{1}H NMR Spectrum of **3j** (500 MHz, $CDCl_3$)



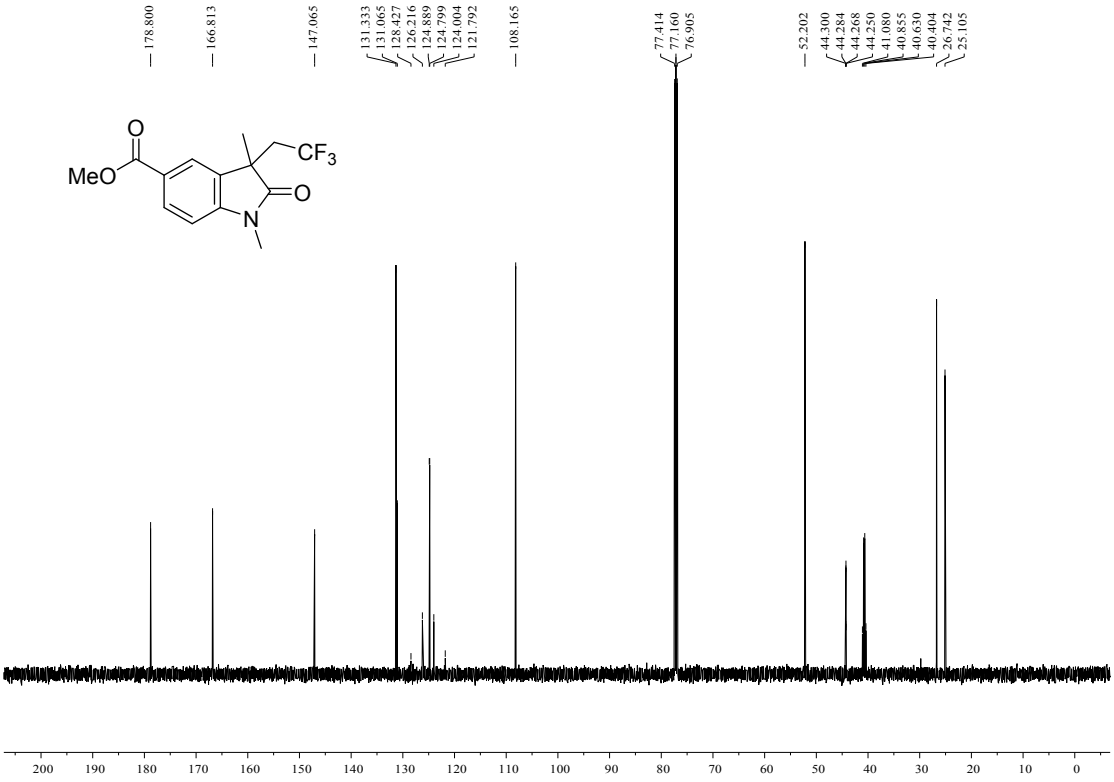
^{13}C NMR Spectrum of **3j** (126 MHz, $CDCl_3$)



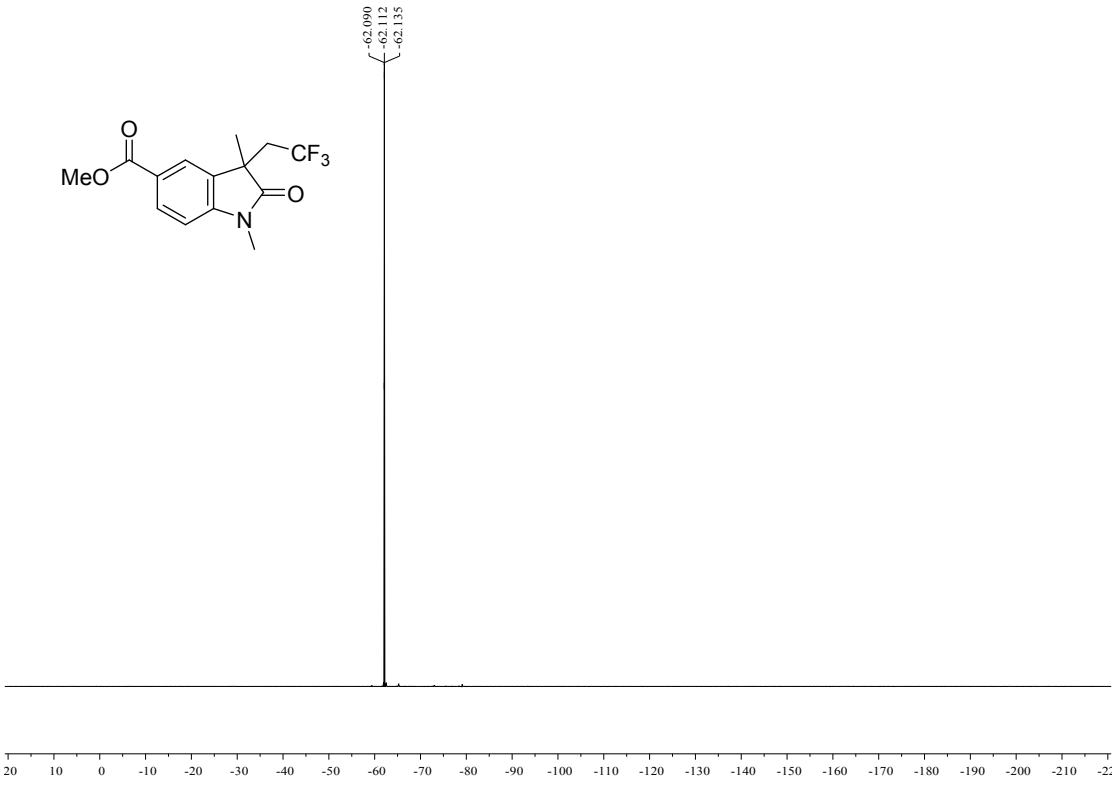
^{19}F NMR Spectrum of **3j** (470 MHz, $CDCl_3$)



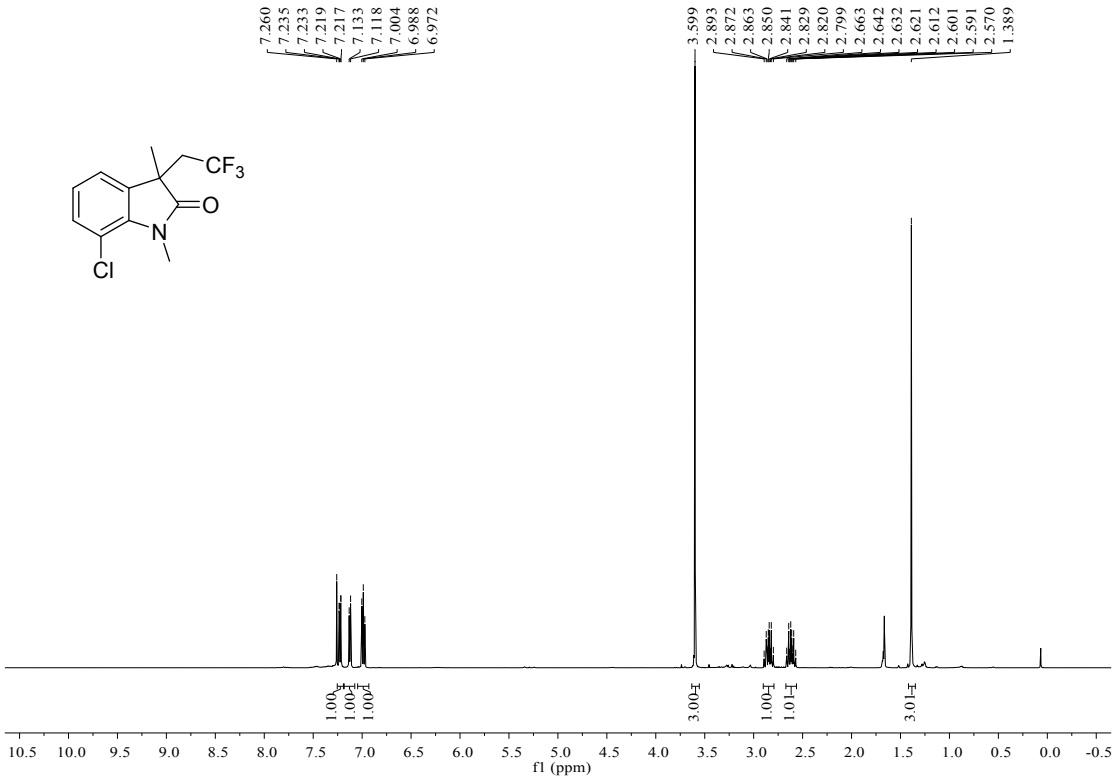
^{1}H NMR Spectrum of **3k** (500 MHz, $CDCl_3$)



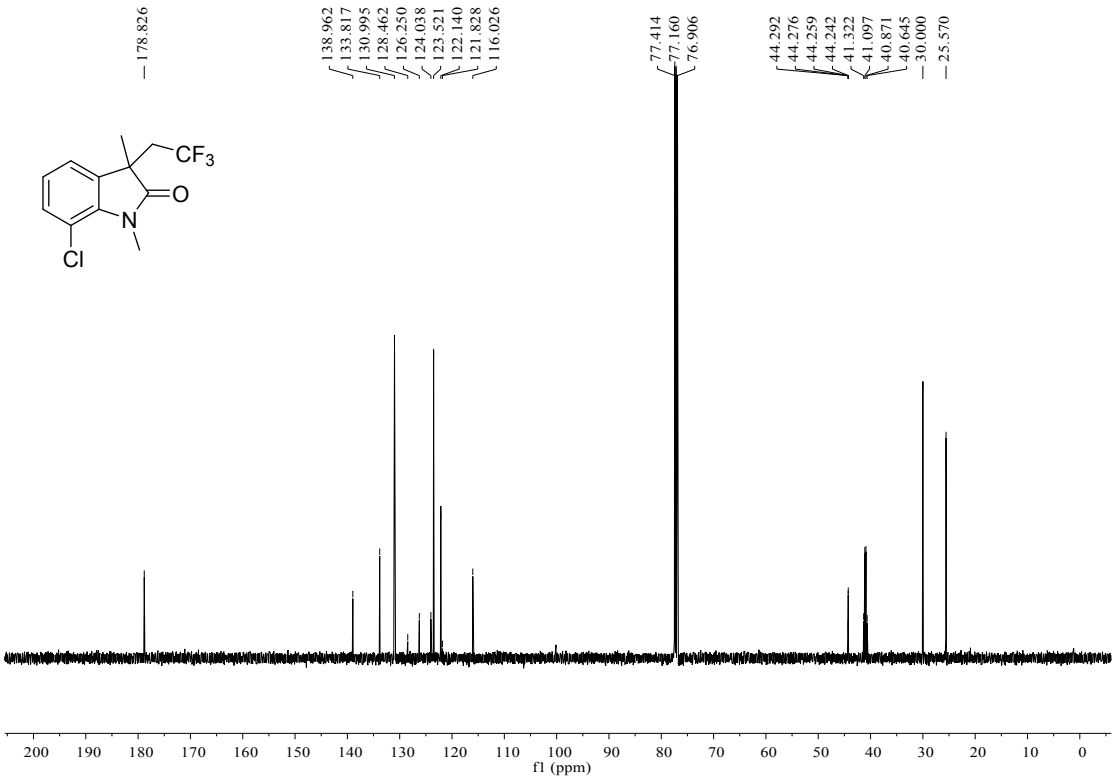
^{13}C NMR Spectrum of **3k** (126 MHz, $CDCl_3$)



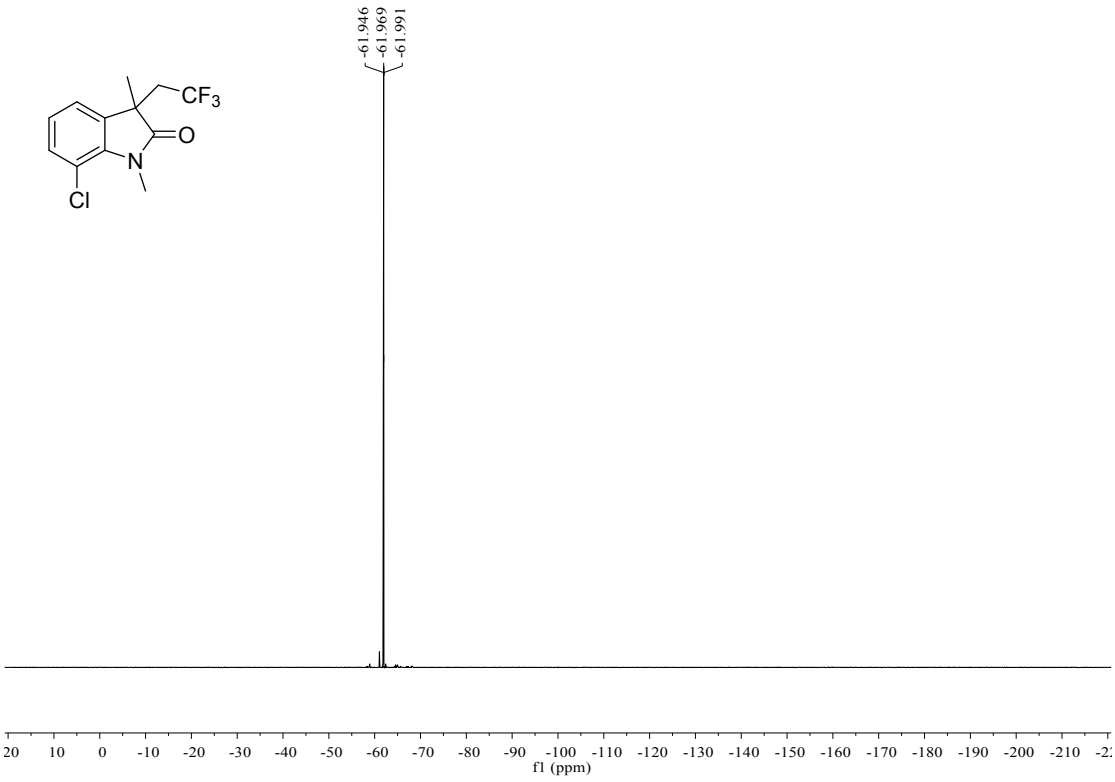
^{19}F NMR Spectrum of **3k** (470 MHz, $CDCl_3$)



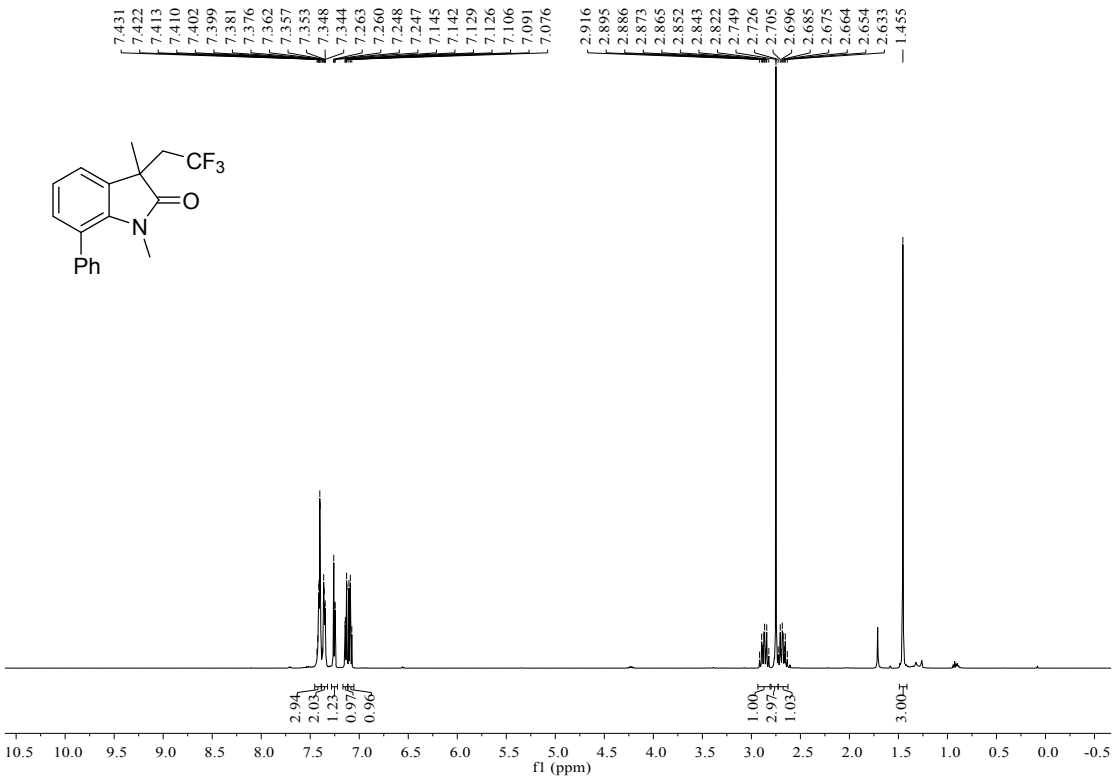
^{1}H NMR Spectrum of **3l** (500 MHz, $CDCl_3$)



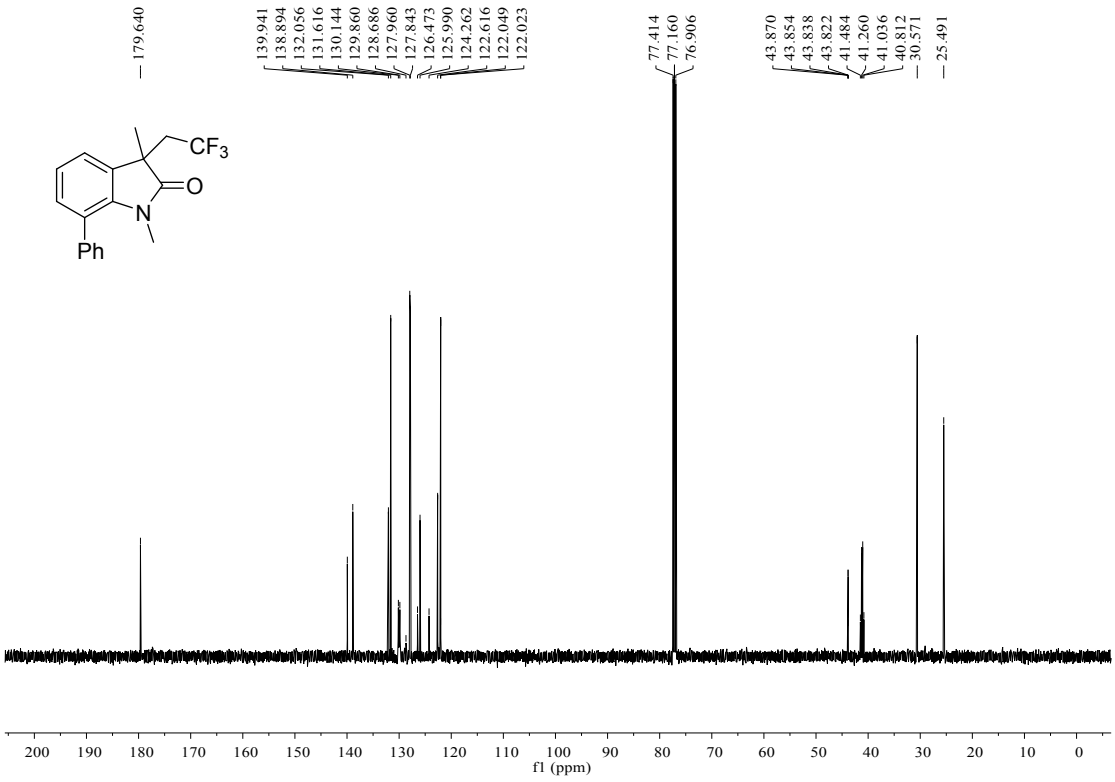
^{13}C NMR Spectrum of **3l** (126 MHz, $CDCl_3$)



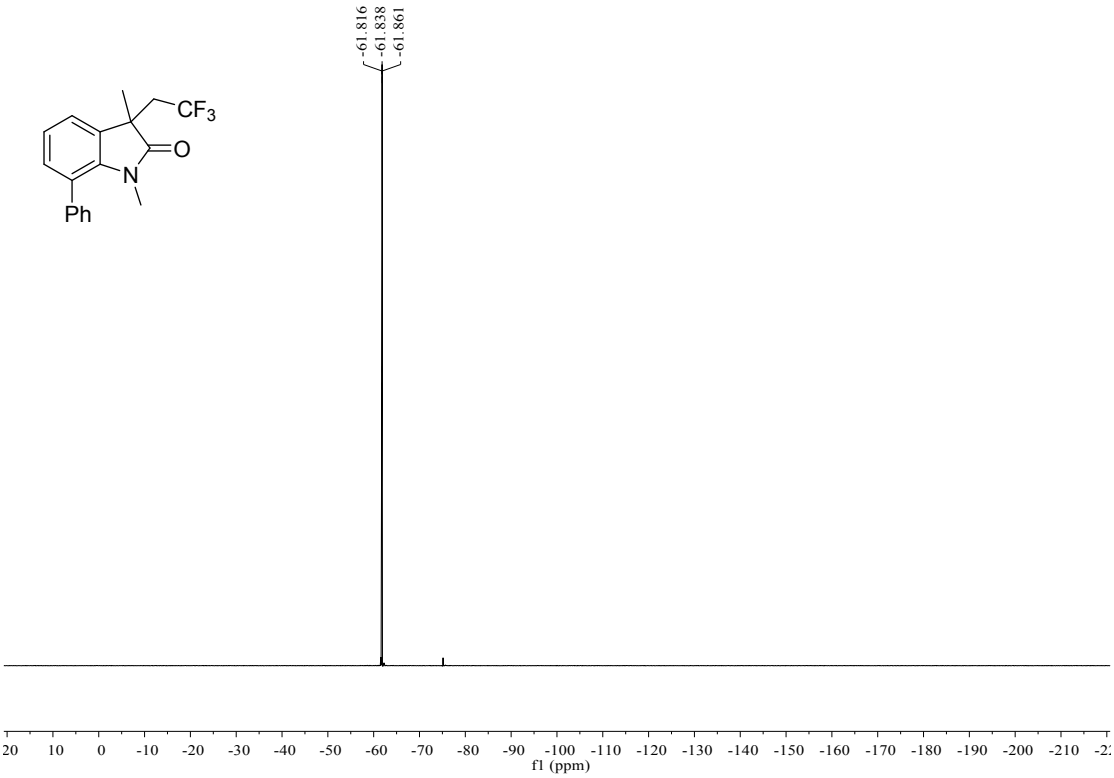
^{19}F NMR Spectrum of **3l** (470 MHz, $CDCl_3$)



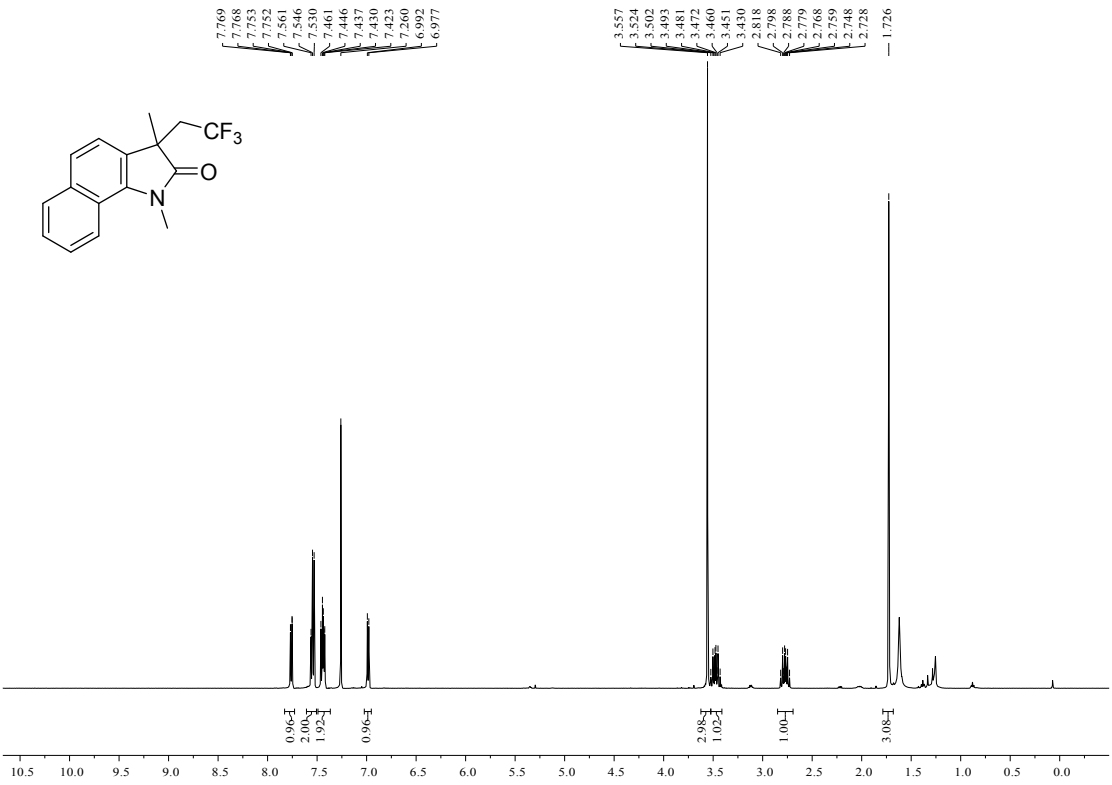
^{1}H NMR Spectrum of **3m** (500 MHz, $CDCl_3$)



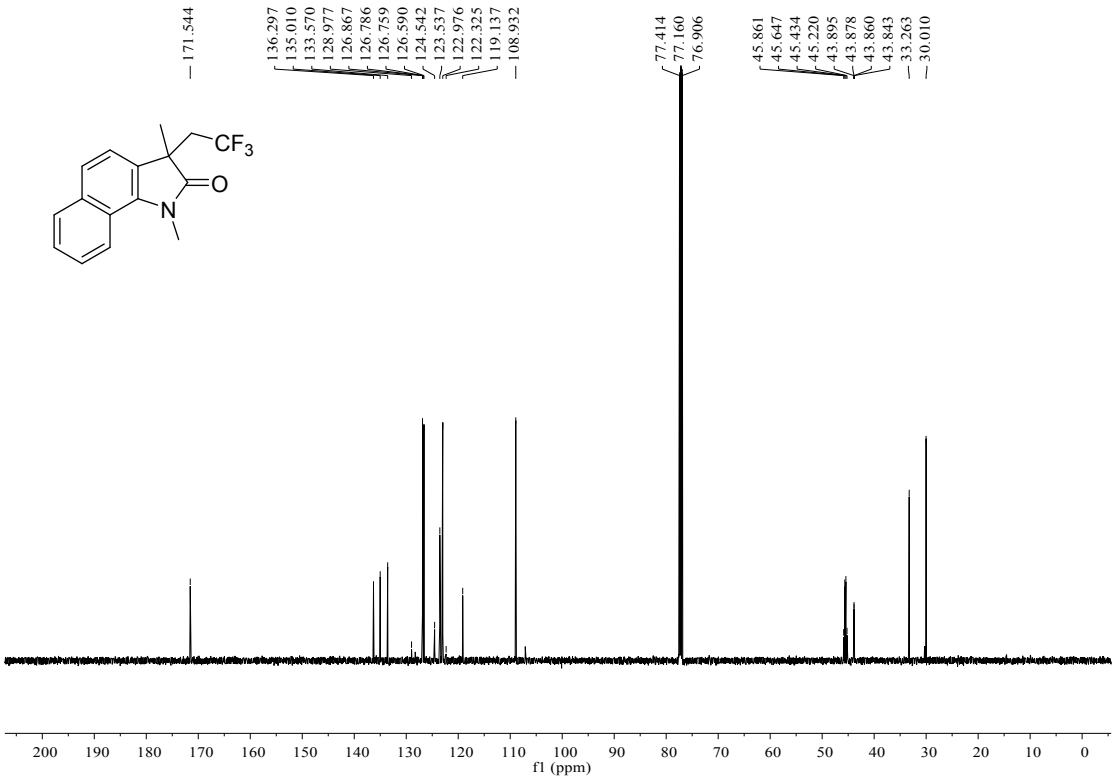
^{13}C NMR Spectrum of **3m** (126 MHz, $CDCl_3$)



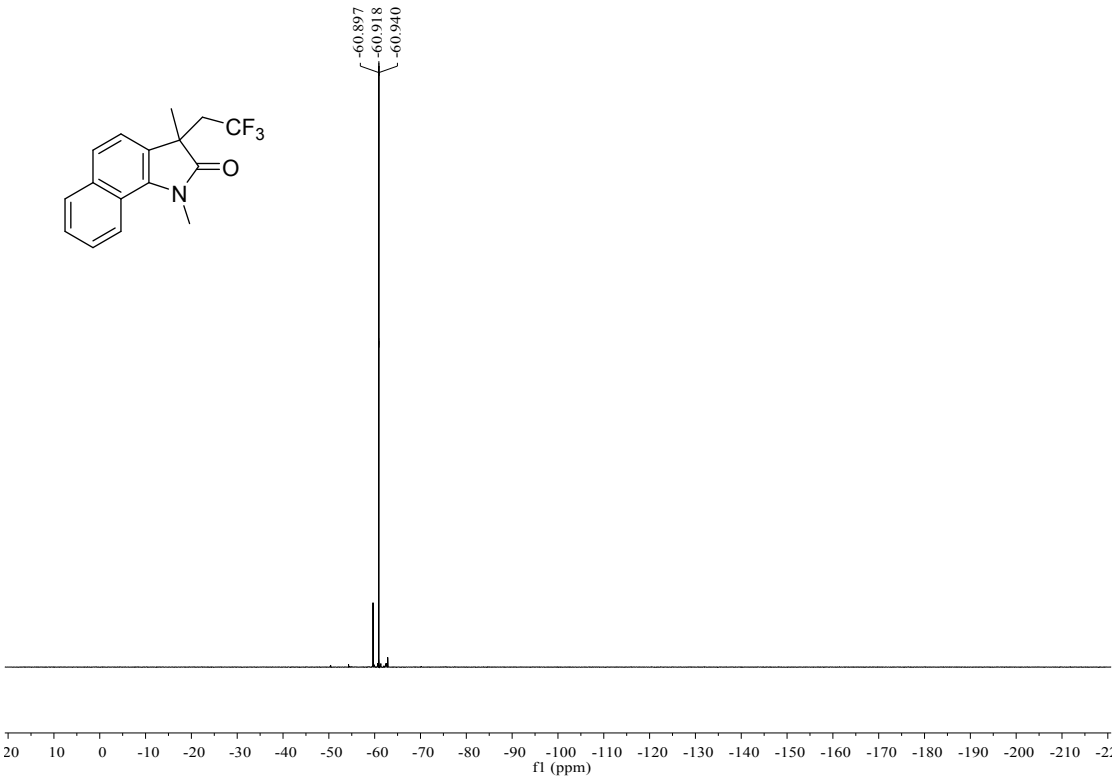
^{19}F NMR Spectrum of **3m** (470 MHz, $CDCl_3$)



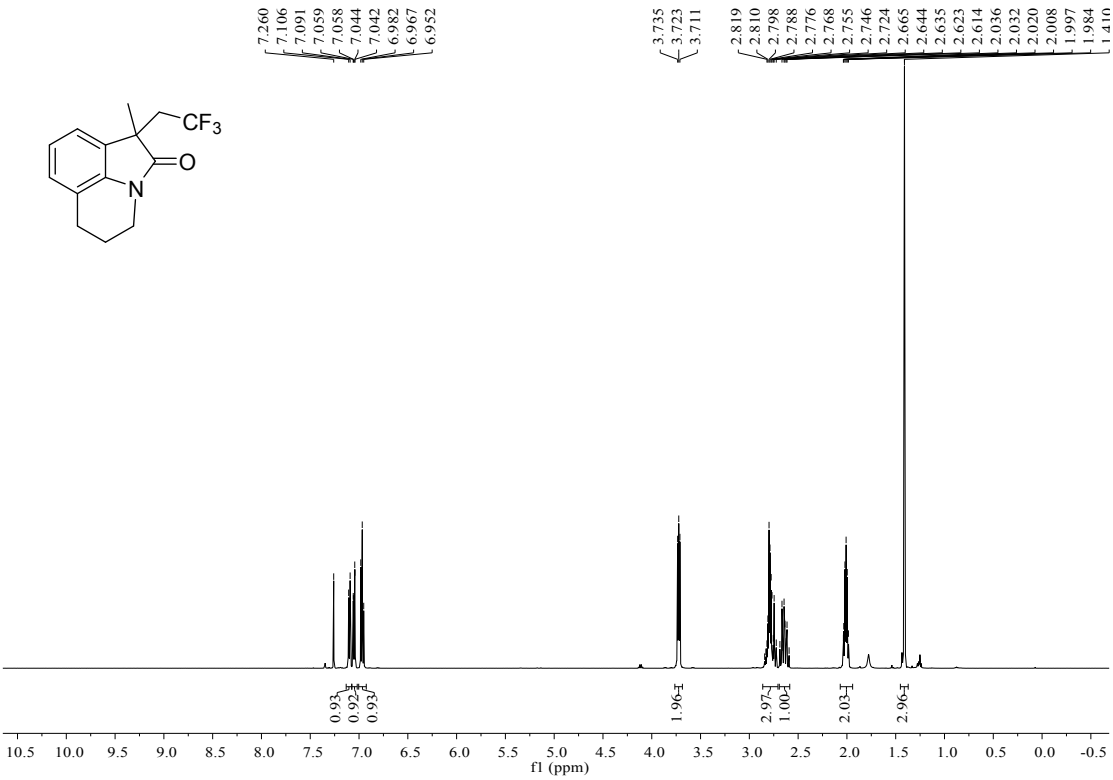
^{1}H NMR Spectrum of **3n** (500 MHz, $CDCl_3$)



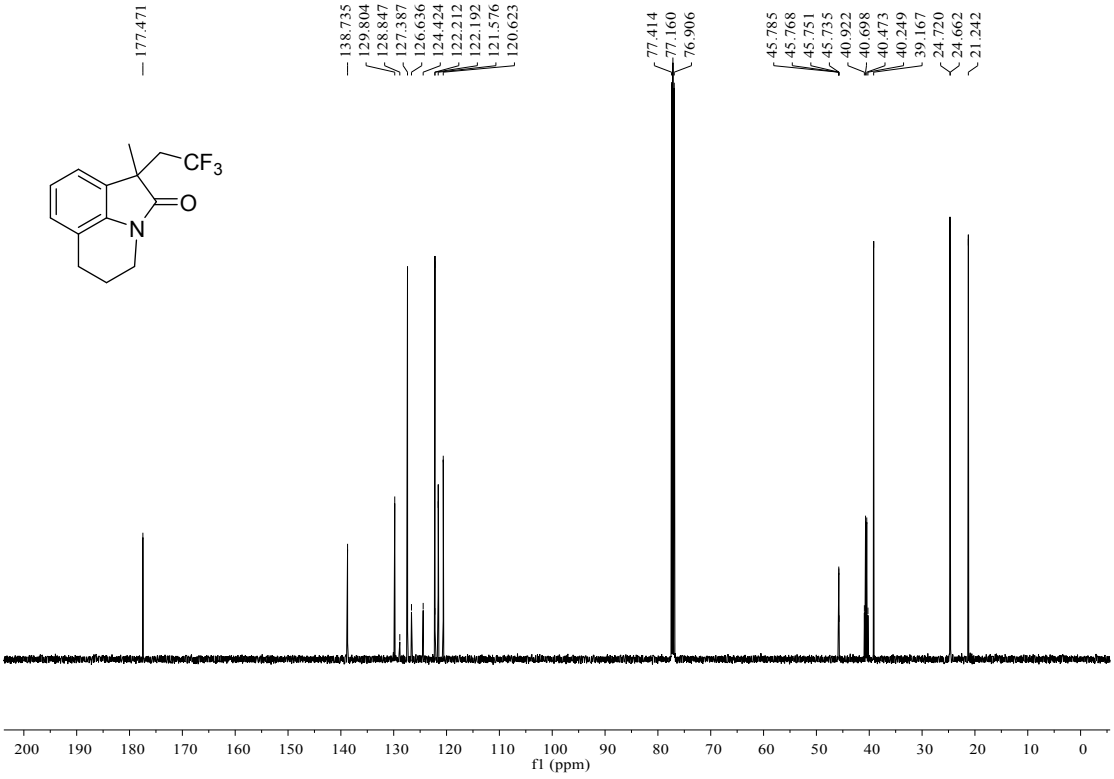
^{13}C NMR Spectrum of **3n** (126 MHz, $CDCl_3$)



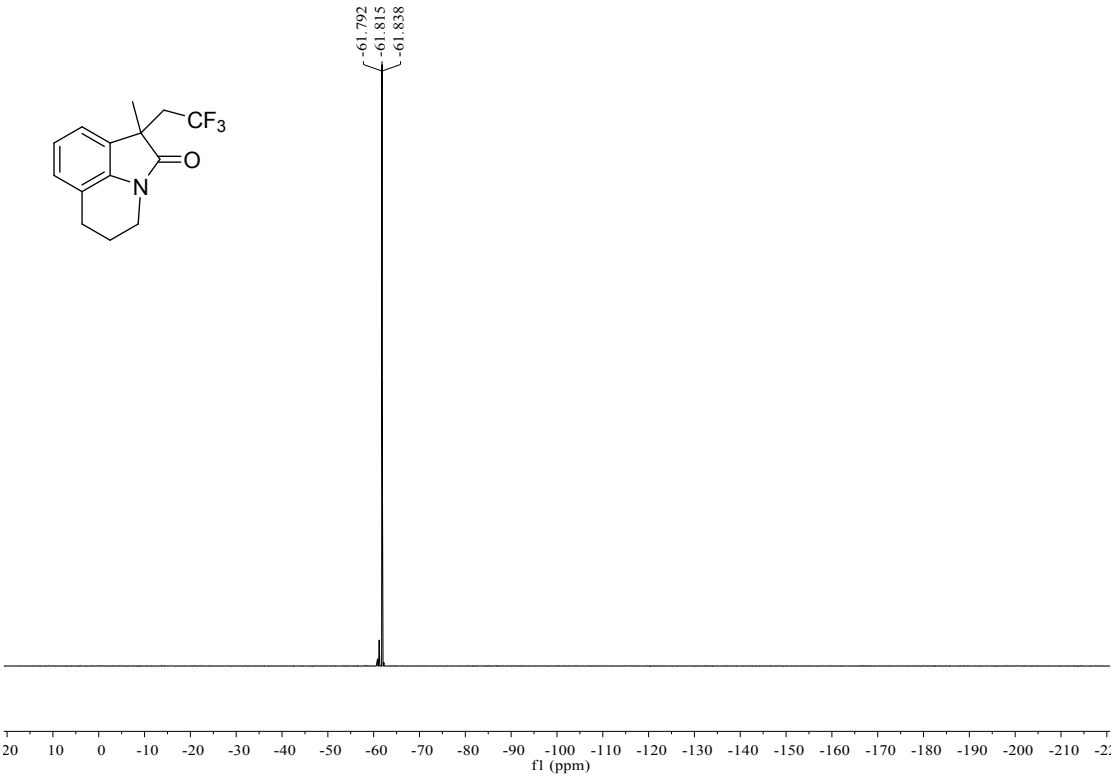
^{19}F NMR Spectrum of **3n** (470 MHz, $CDCl_3$)



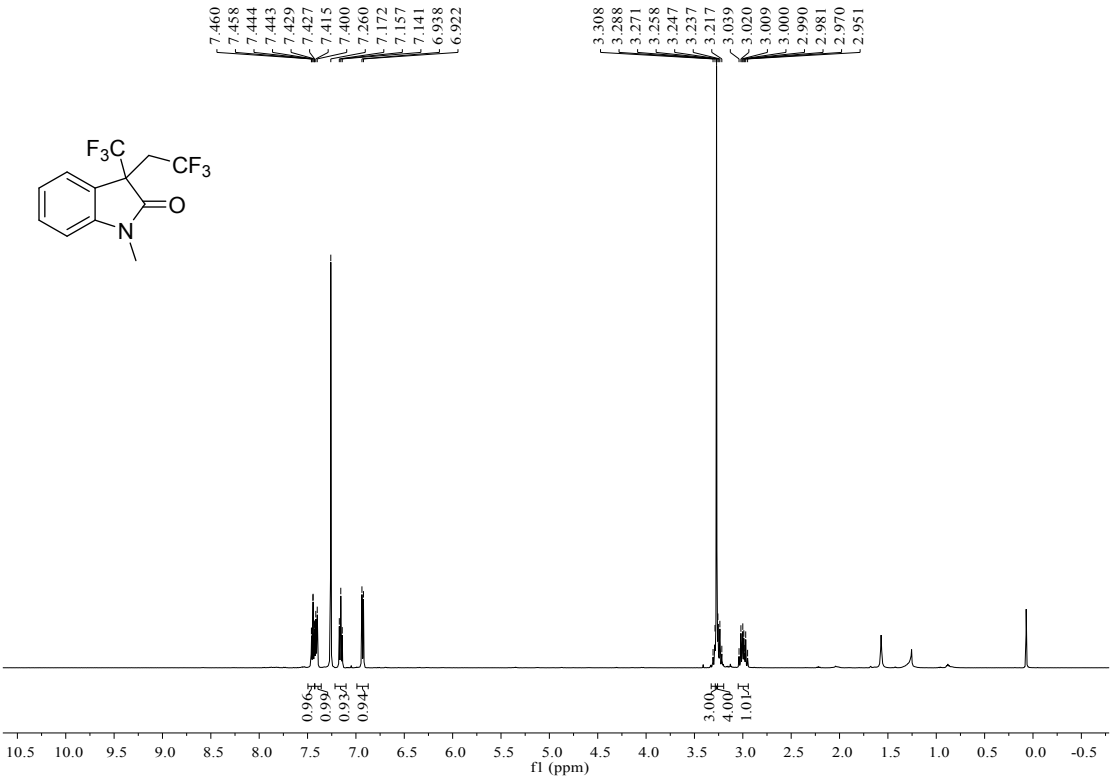
^{1}H NMR Spectrum of **3o** (500 MHz, $CDCl_3$)



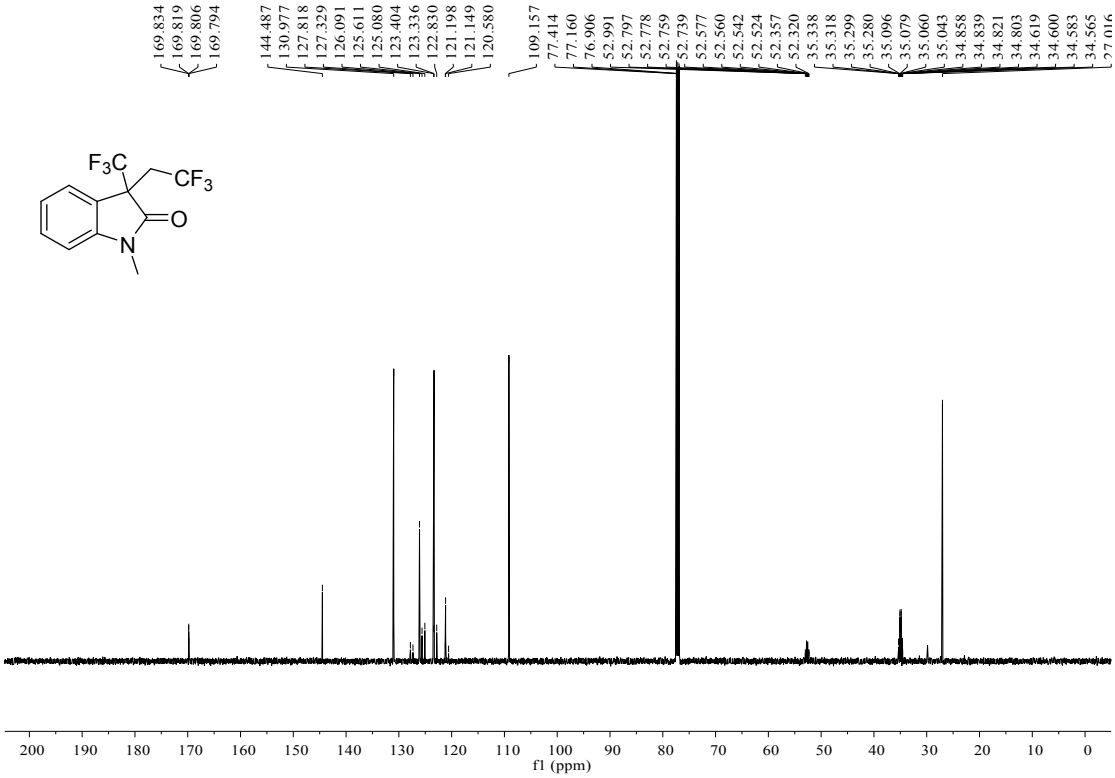
^{13}C NMR Spectrum of **3o** (126 MHz, $CDCl_3$)



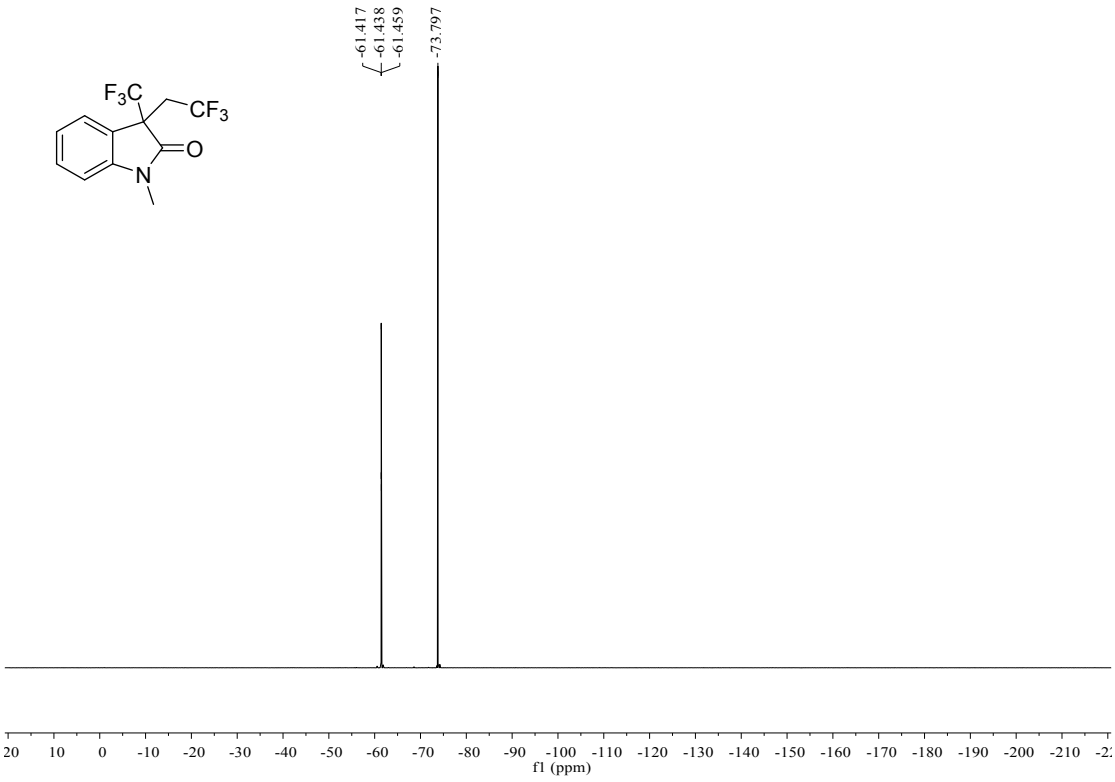
^{19}F NMR Spectrum of **3o** (470 MHz, $CDCl_3$)



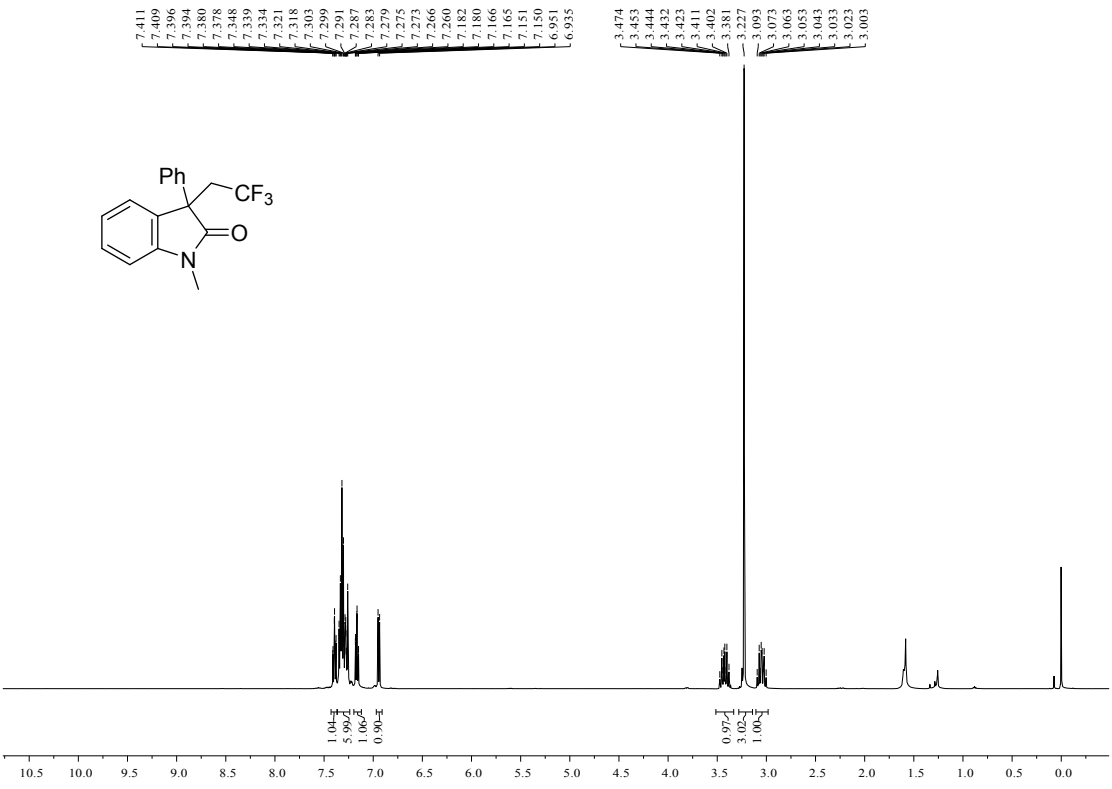
^{1}H NMR Spectrum of **3p** (500 MHz, $CDCl_3$)



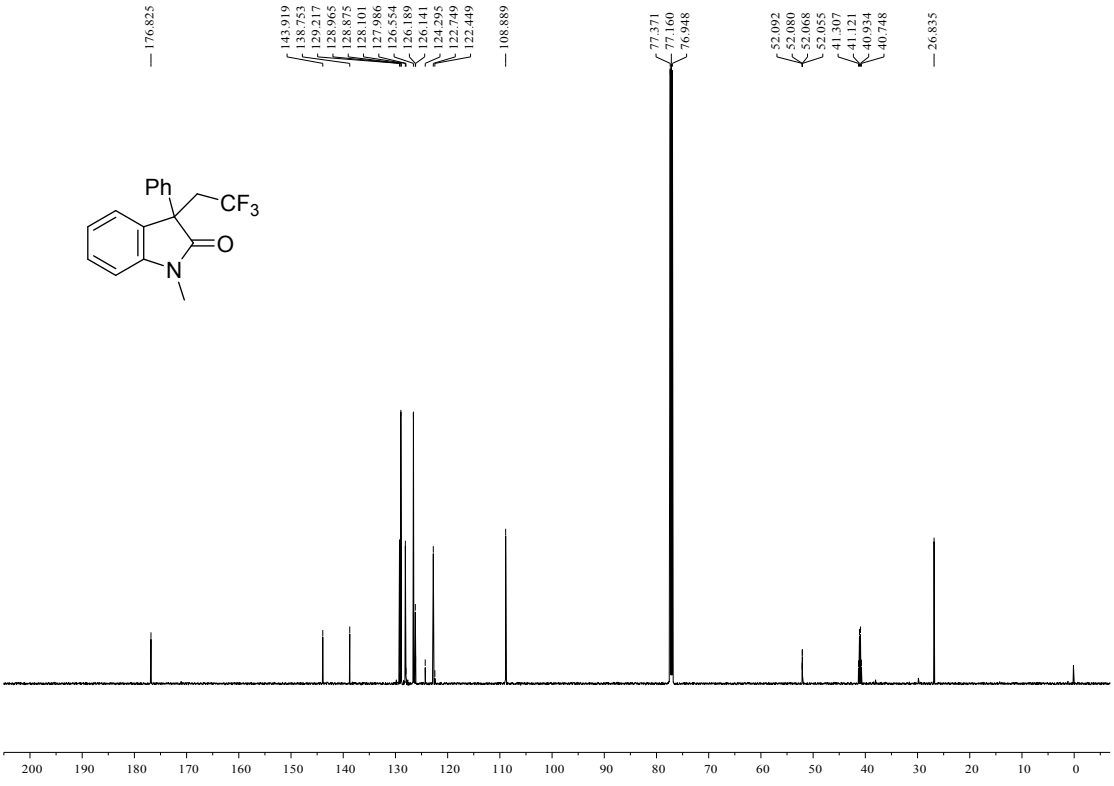
^{13}C NMR Spectrum of **3p** (126 MHz, $CDCl_3$)



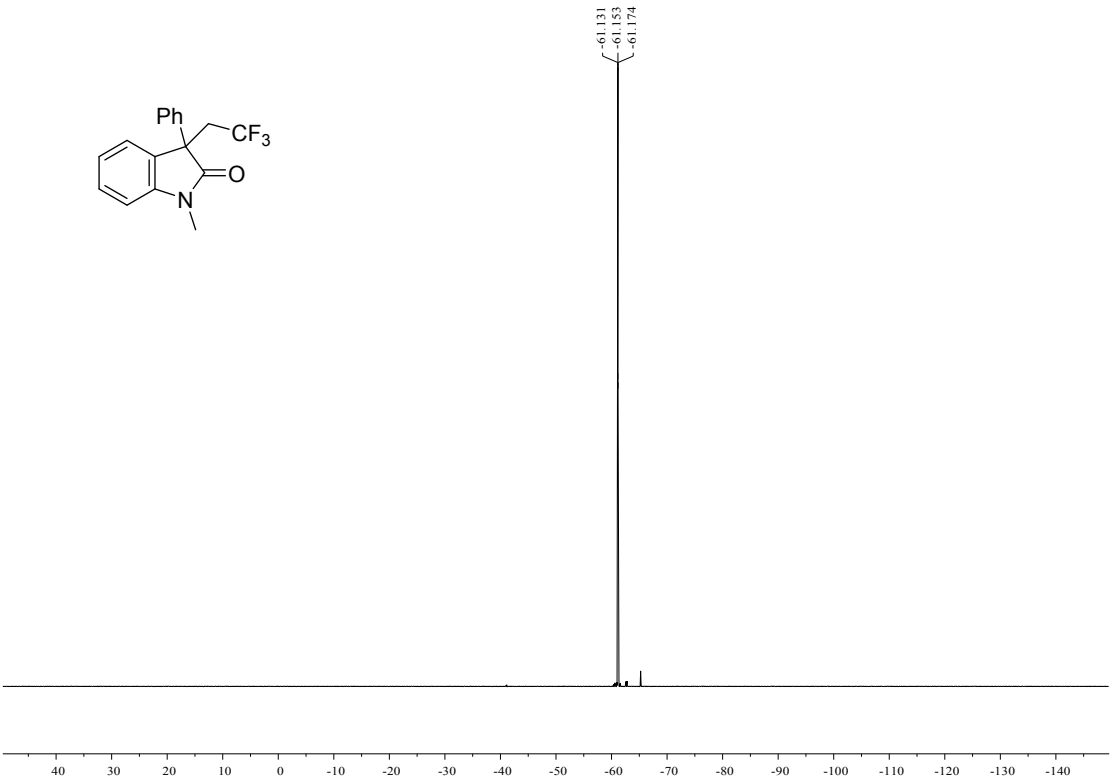
^{19}F NMR Spectrum of **3p** (470 MHz, $CDCl_3$)



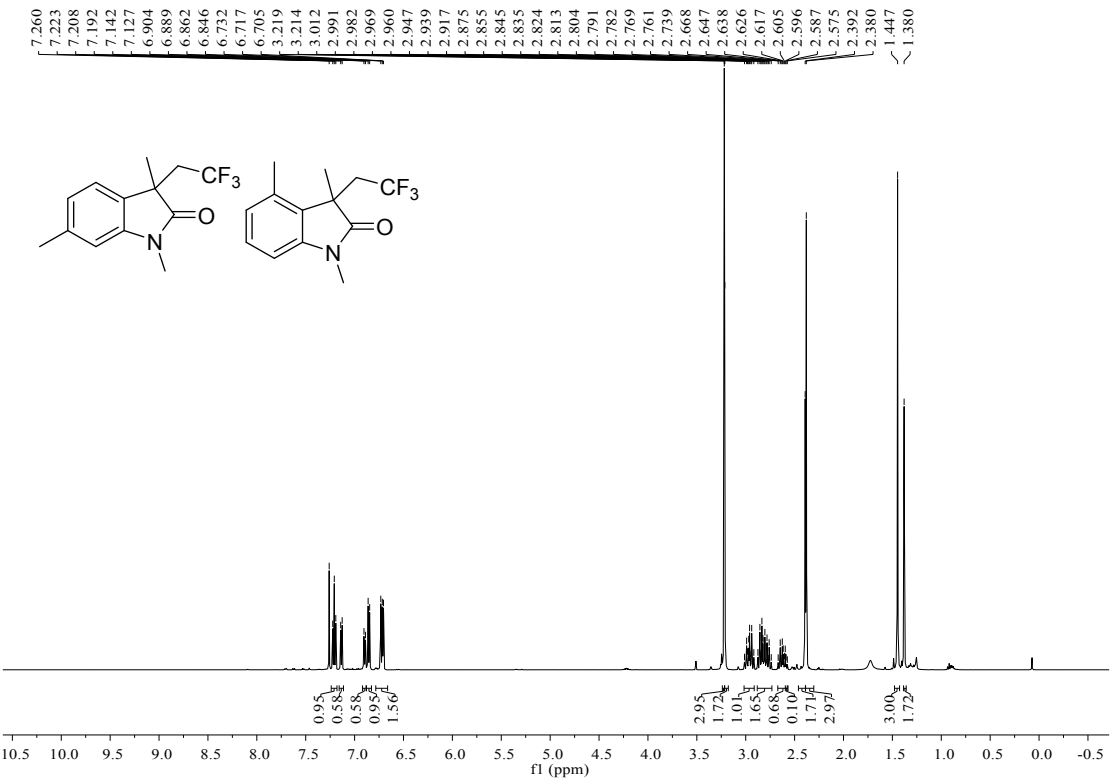
^{1}H NMR Spectrum of **3q** (500 MHz, $CDCl_3$)



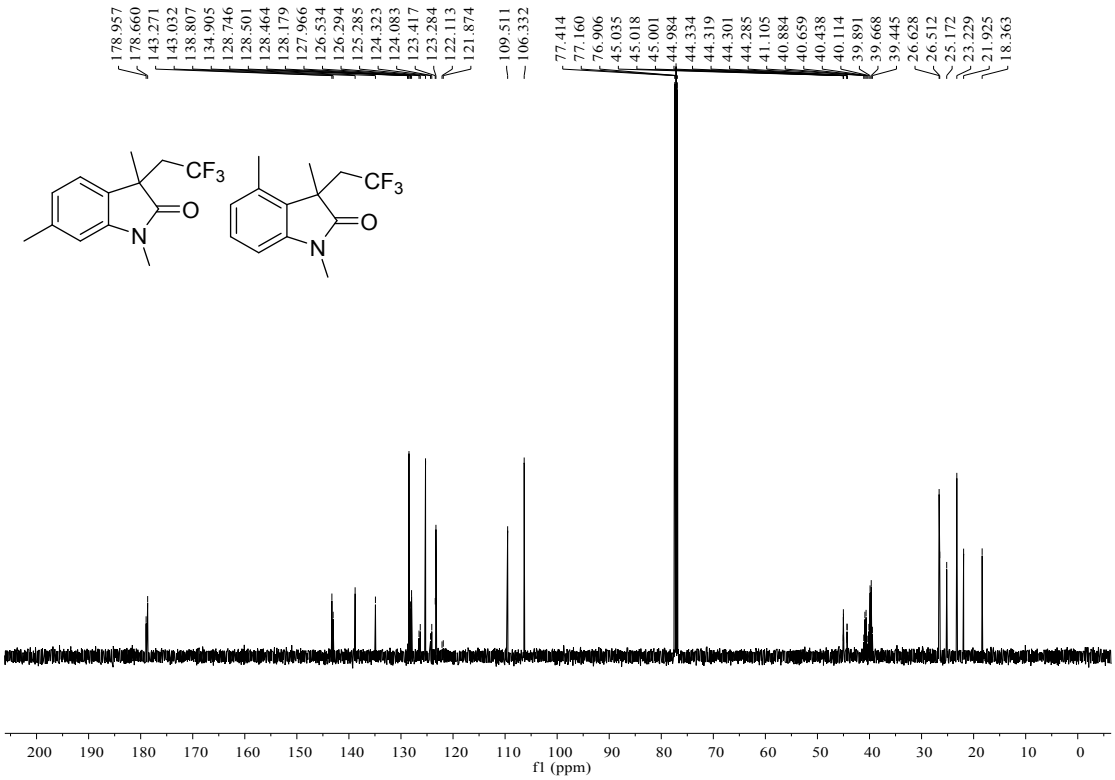
^{13}C NMR Spectrum of **3q** (151 MHz, $CDCl_3$)



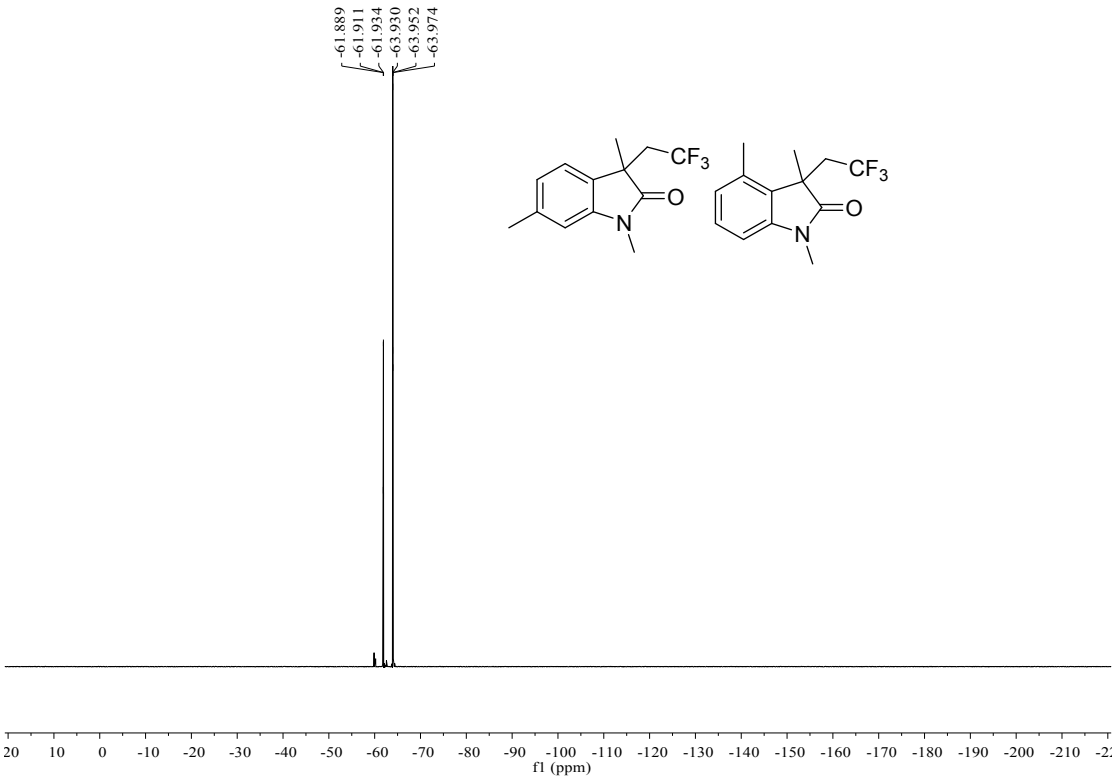
^{19}F NMR Spectrum of **3q** (470 MHz, $CDCl_3$)



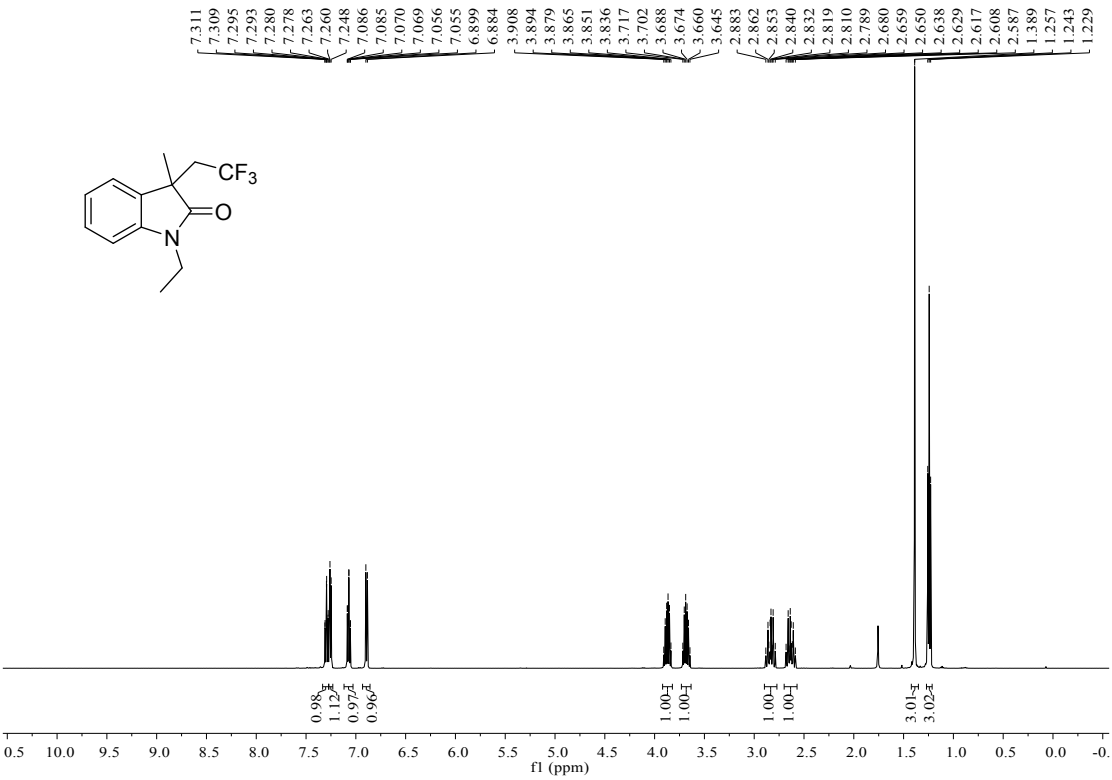
^{1}H NMR Spectrum of **3r**+**3r′** (500 MHz, $CDCl_3$)



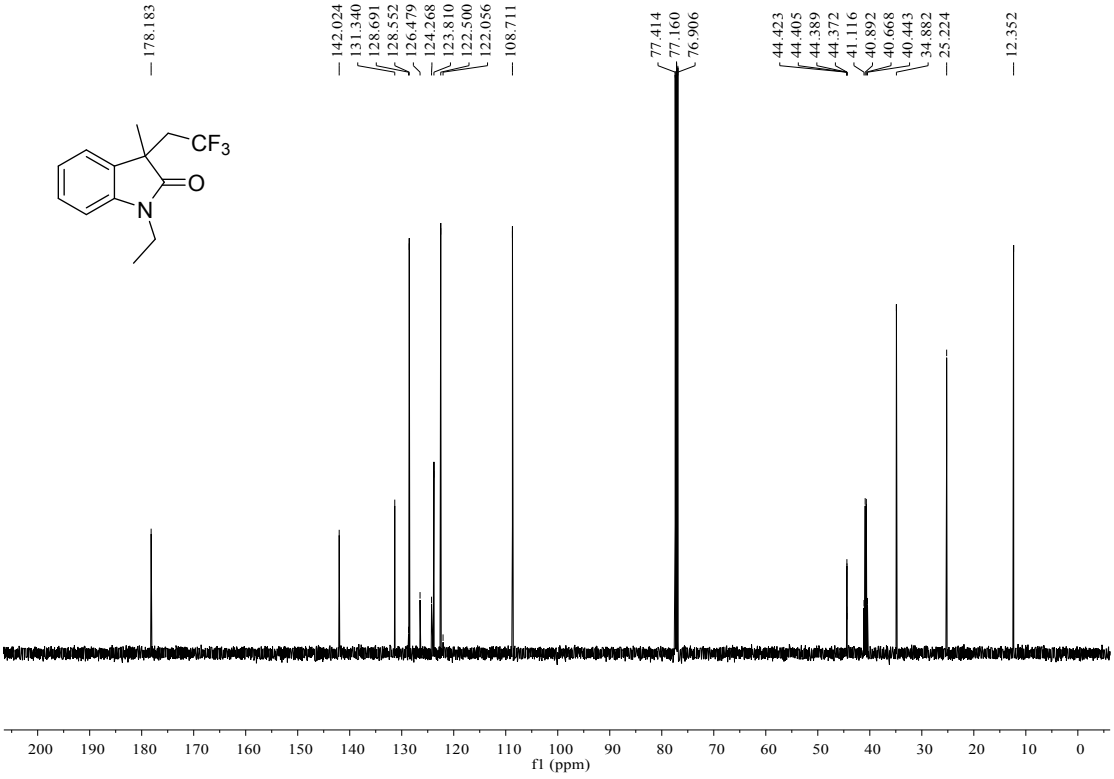
^{13}C NMR Spectrum of **3r**+**3r′** (126 MHz, $CDCl_3$)



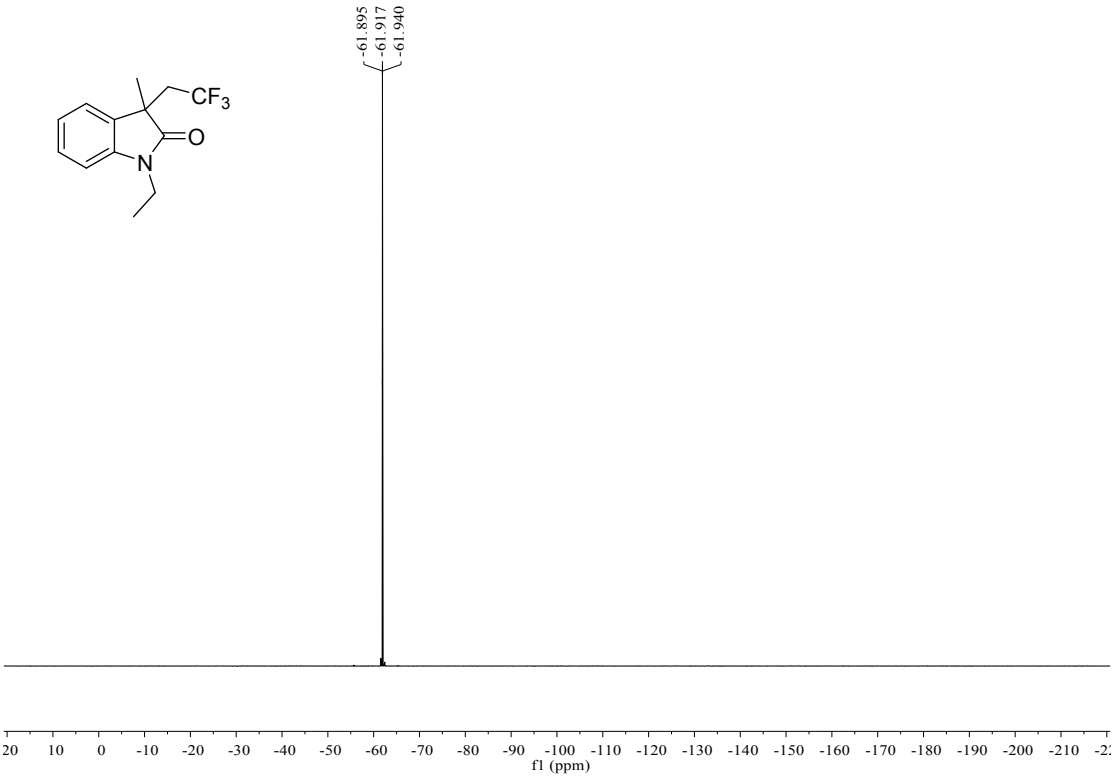
^{19}F NMR Spectrum of **3r**+**3r′** (470 MHz, $CDCl_3$)



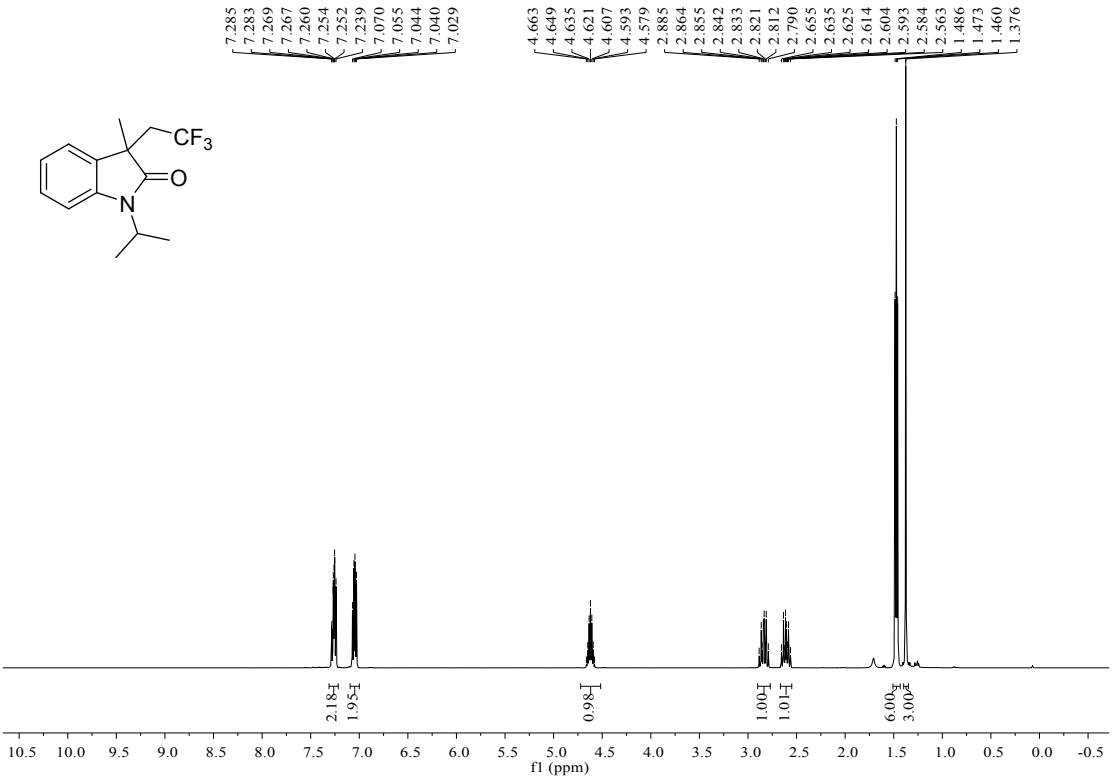
^{1}H NMR Spectrum of **3s** (500 MHz, $CDCl_3$)



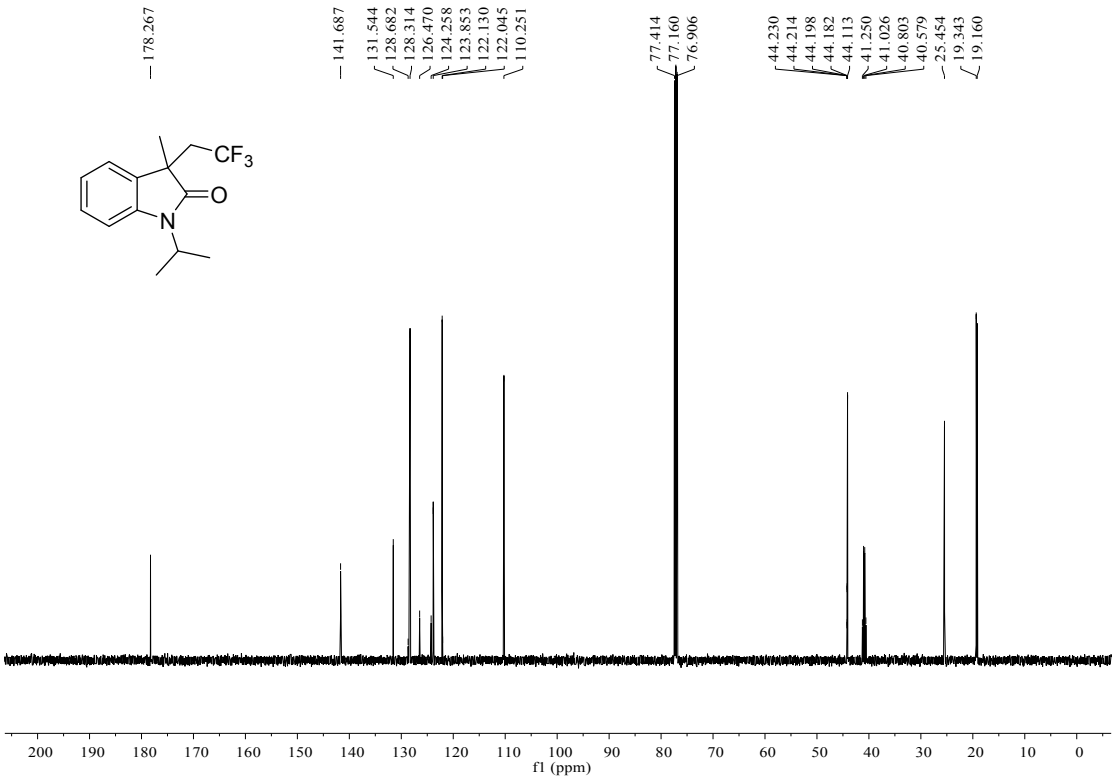
^{13}C NMR Spectrum of **3s** (126 MHz, $CDCl_3$)



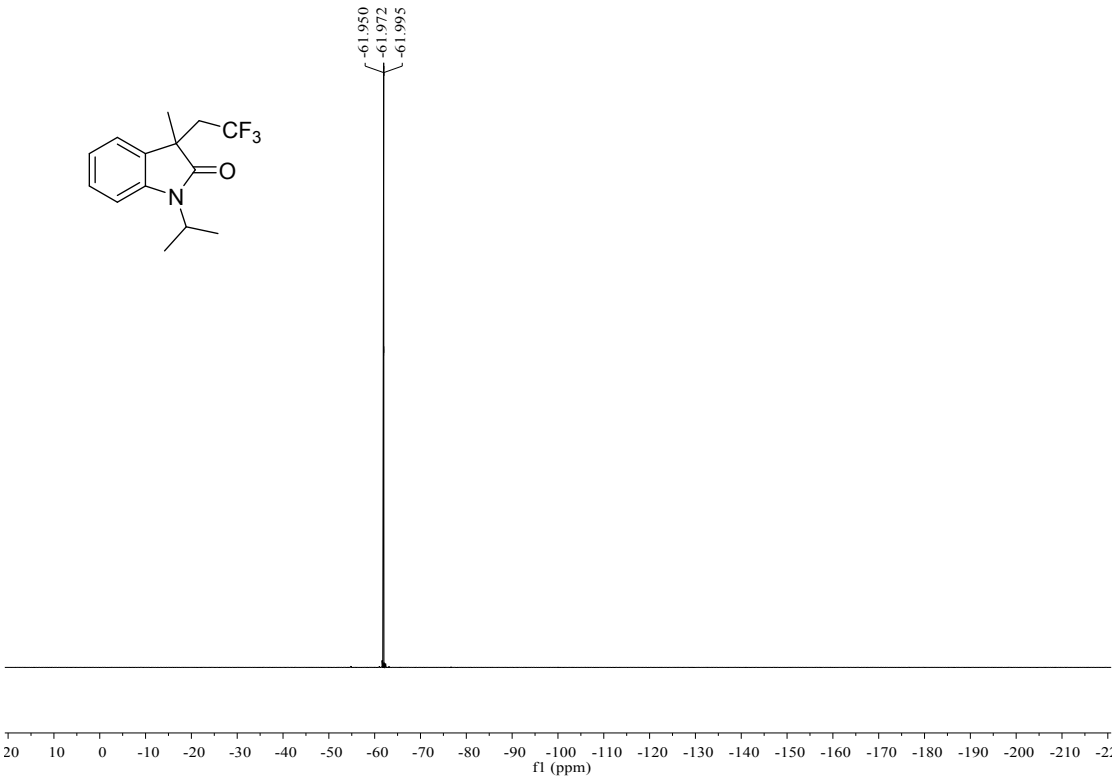
^{19}F NMR Spectrum of **3s** (470 MHz, $CDCl_3$)



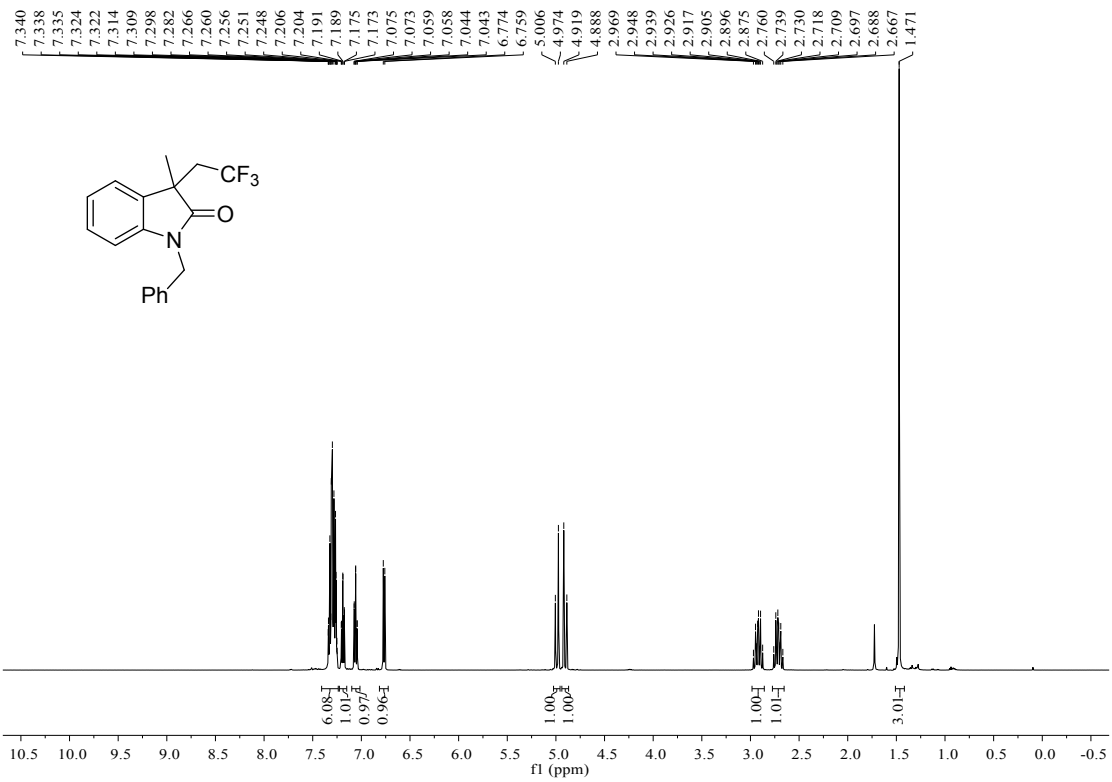
^{1}H NMR Spectrum of **3t** (500 MHz, $CDCl_3$)



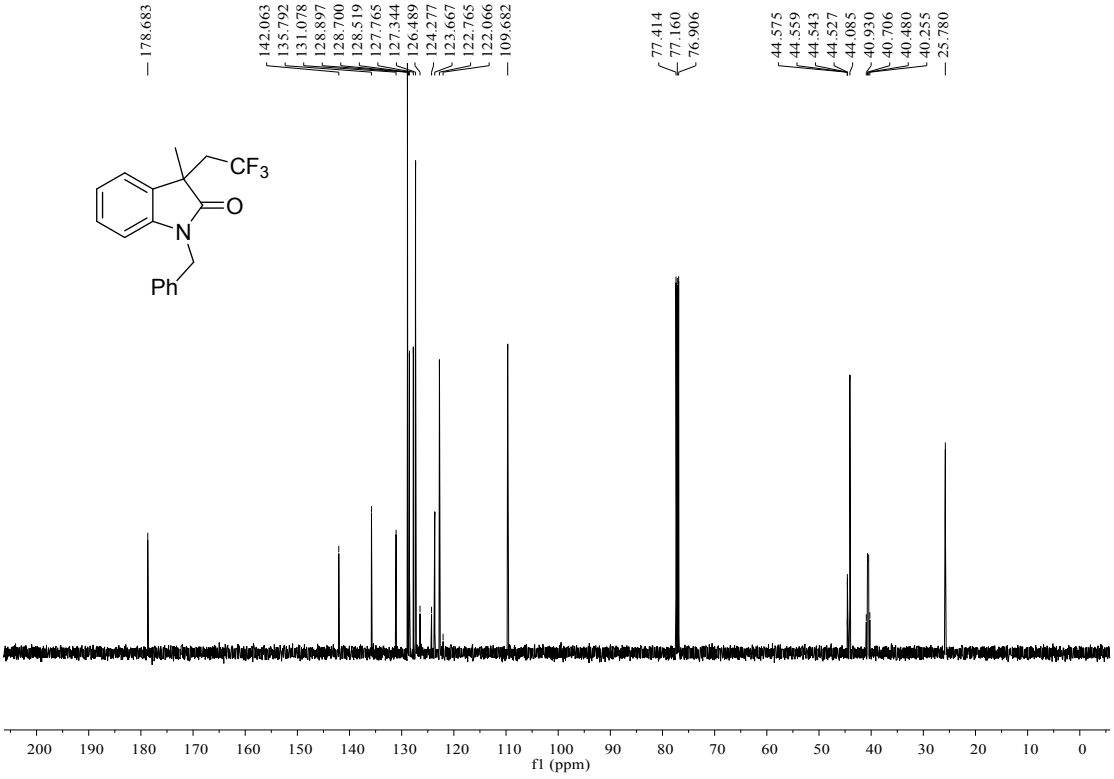
^{13}C NMR Spectrum of **3t** (126 MHz, $CDCl_3$)



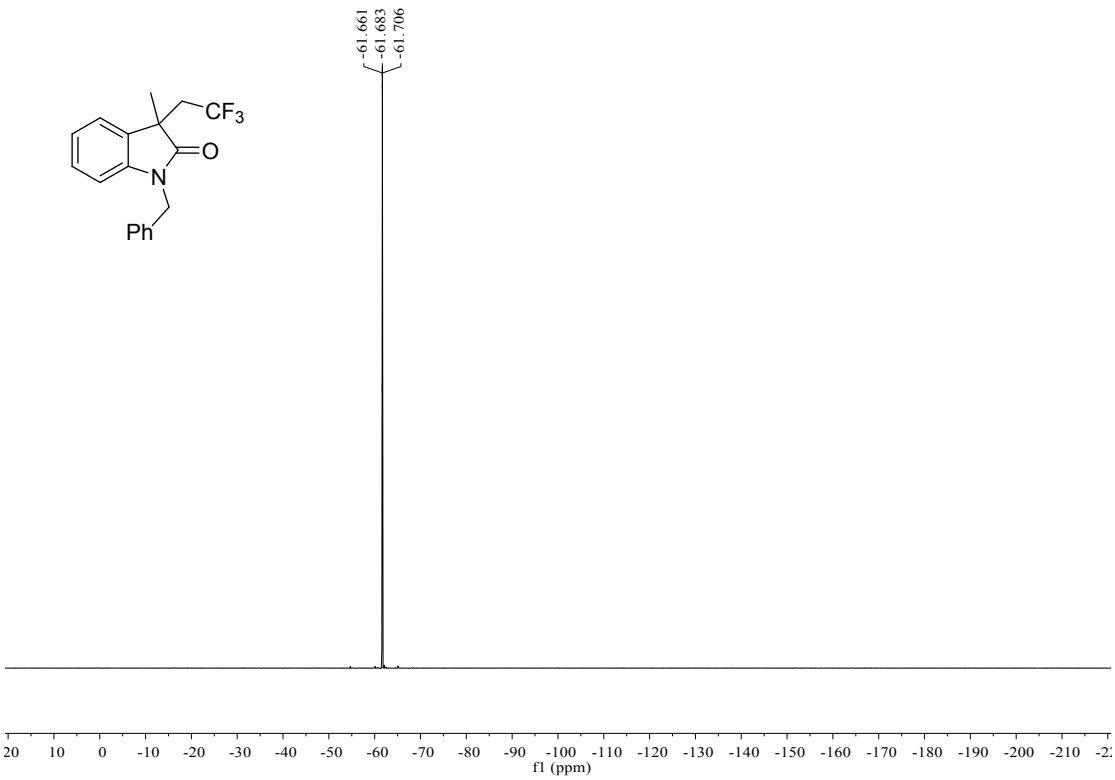
^{19}F NMR Spectrum of **3t** (470 MHz, $CDCl_3$)



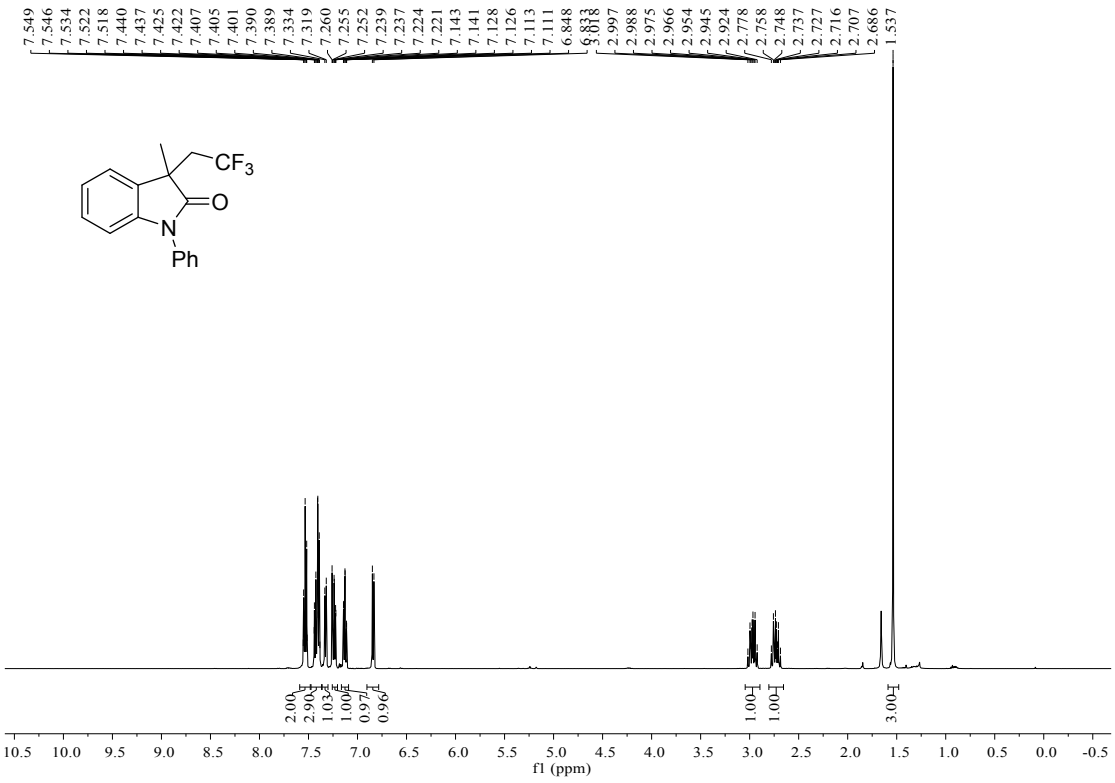
^{1}H NMR Spectrum of **3u** (500 MHz, $CDCl_3$)



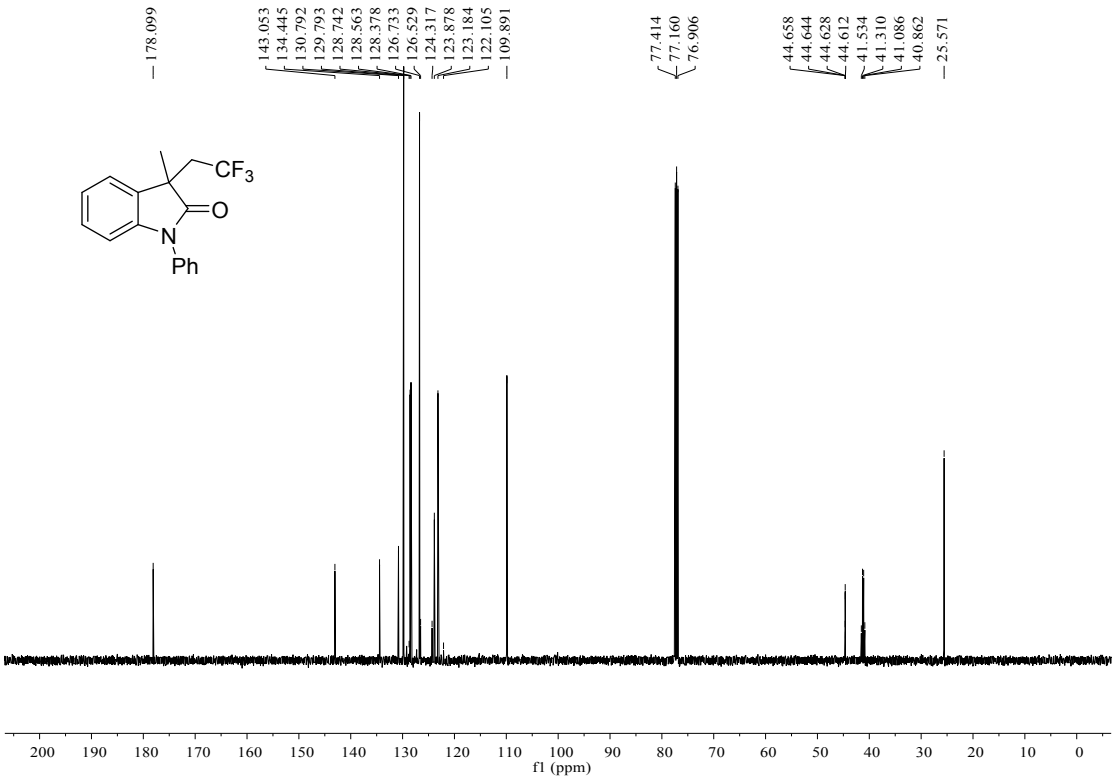
^{13}C NMR Spectrum of **3u** (126 MHz, $CDCl_3$)



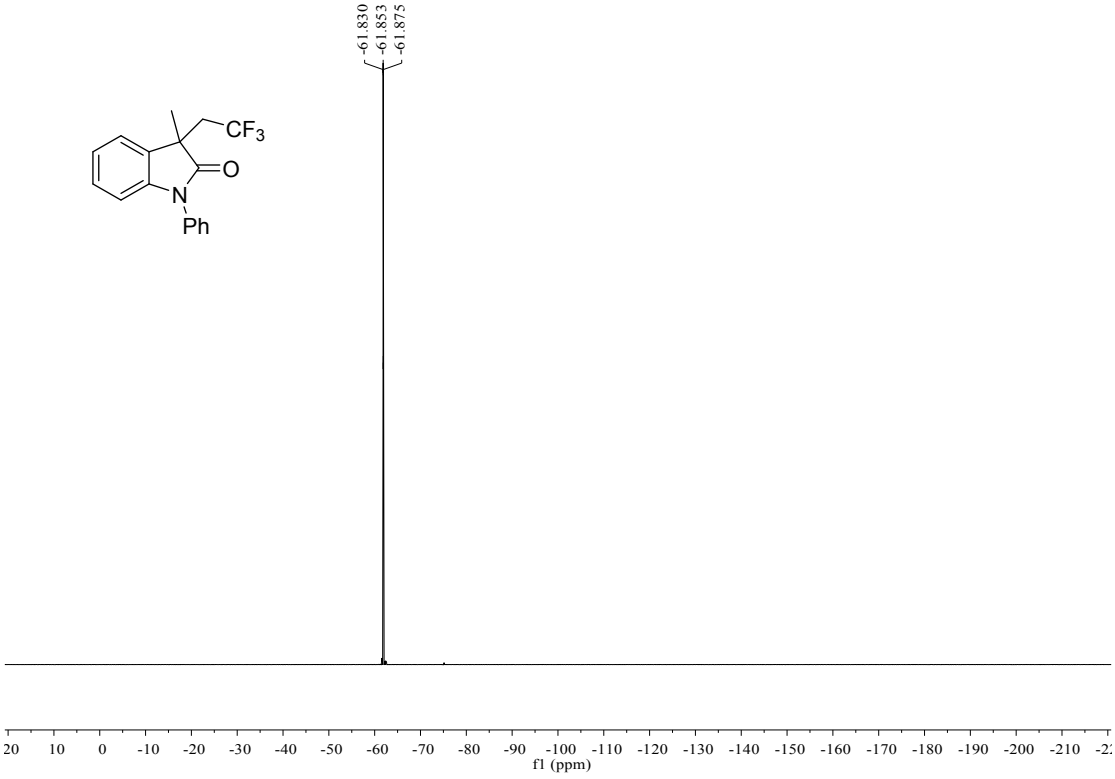
^{19}F NMR Spectrum of **3u** (470 MHz, $CDCl_3$)



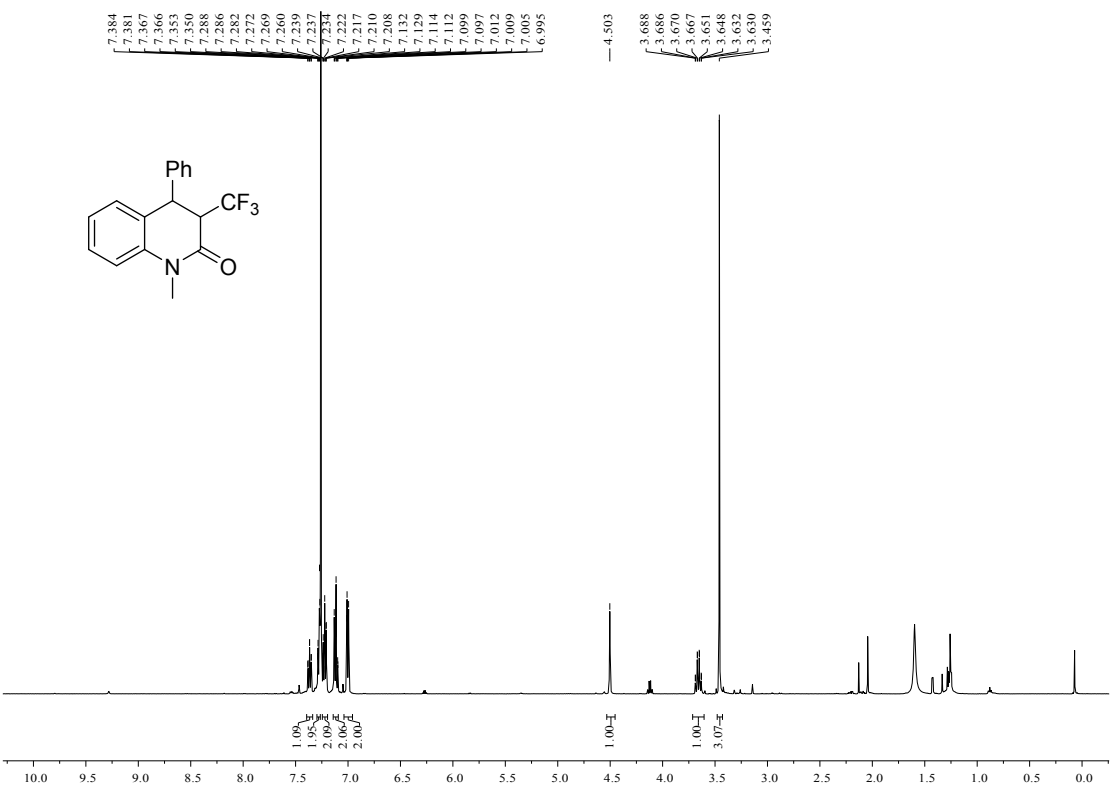
^{1}H NMR Spectrum of **3v** (500 MHz, $CDCl_3$)



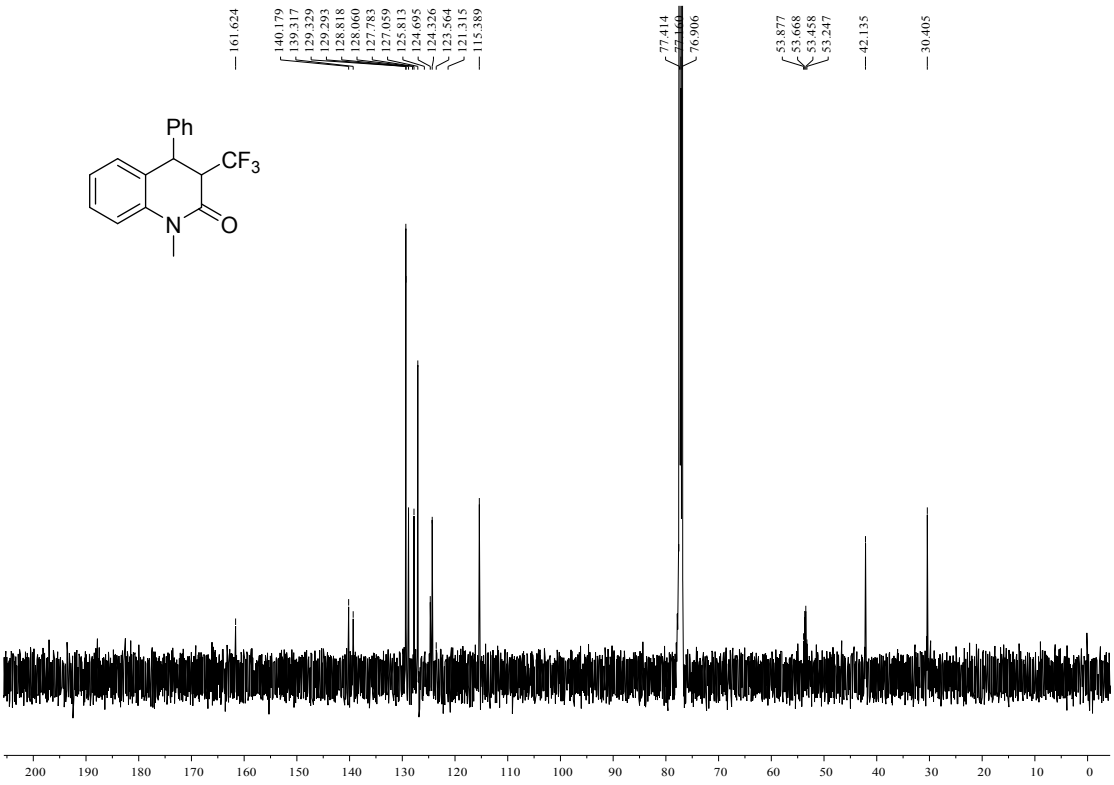
^{13}C NMR Spectrum of **3v** (126 MHz, $CDCl_3$)



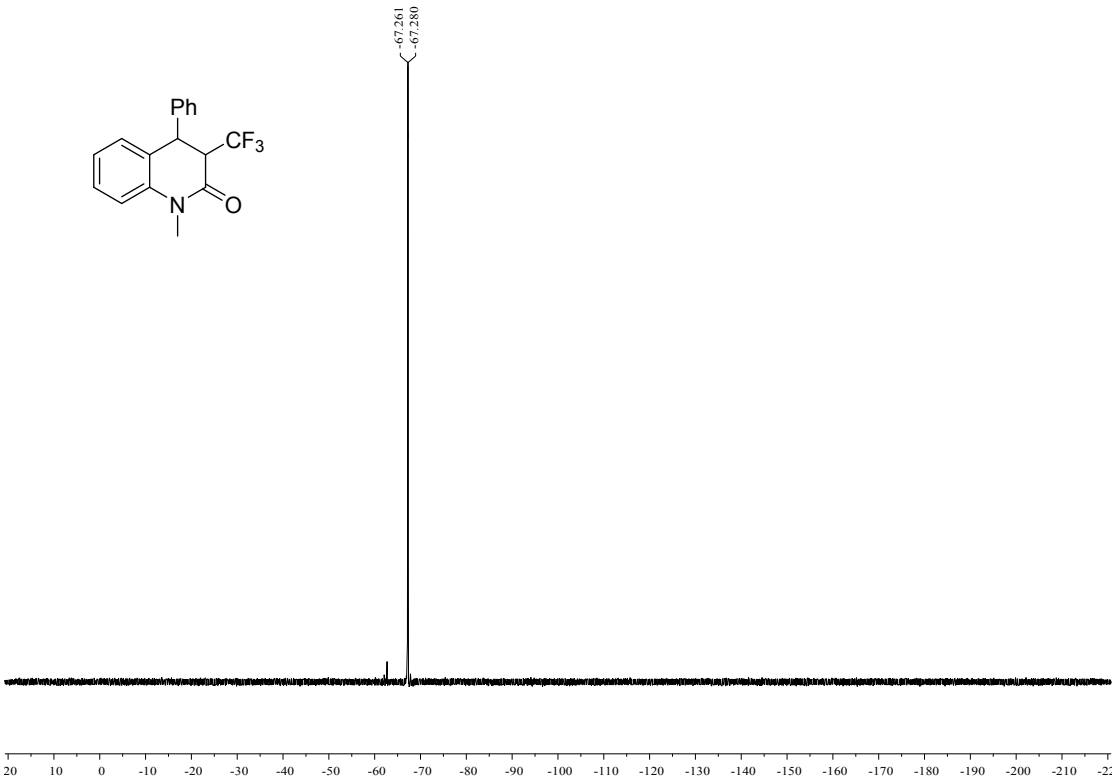
^{19}F NMR Spectrum of **3v** (470 MHz, $CDCl_3$)



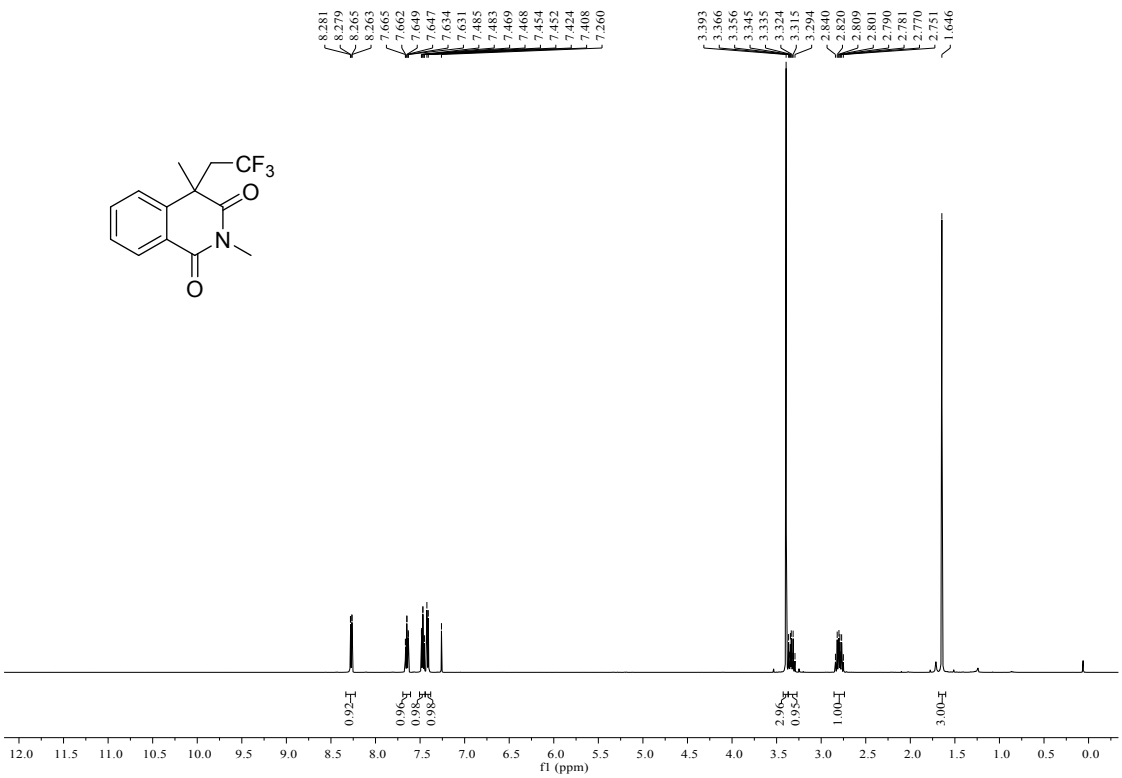
^{1}H NMR Spectrum of **3w** (500 MHz, $CDCl_3$)



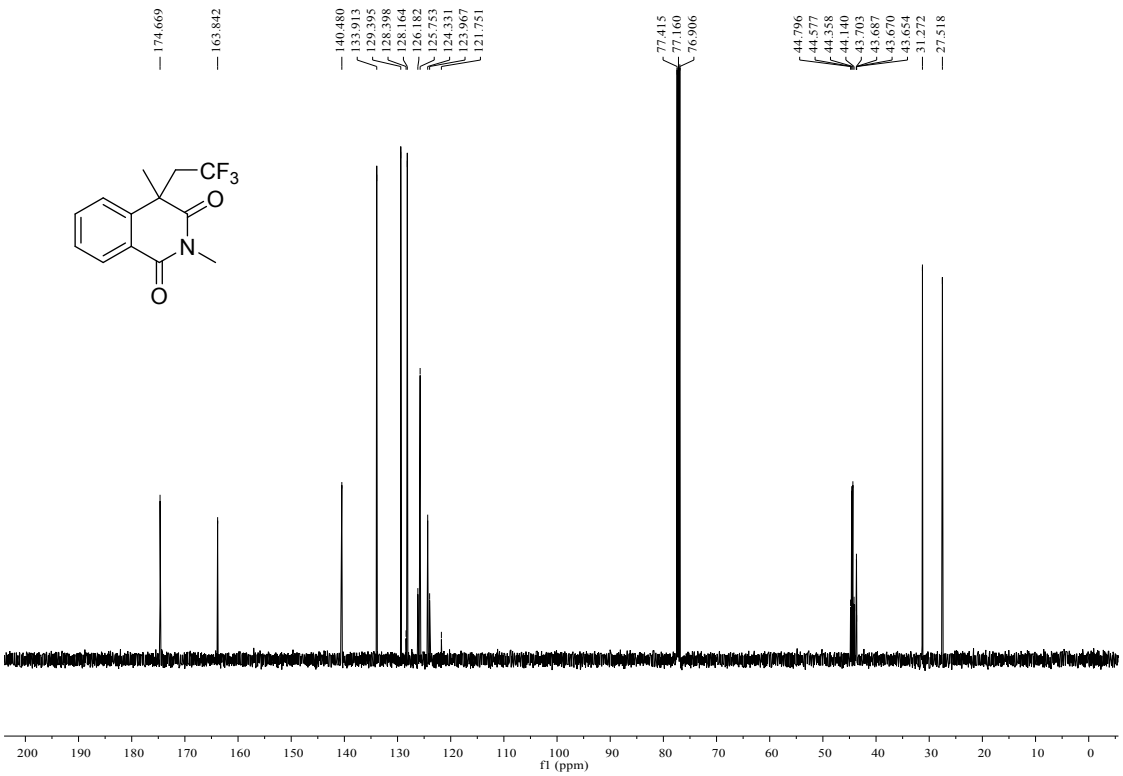
^{13}C NMR Spectrum of **3w** (126 MHz, $CDCl_3$)



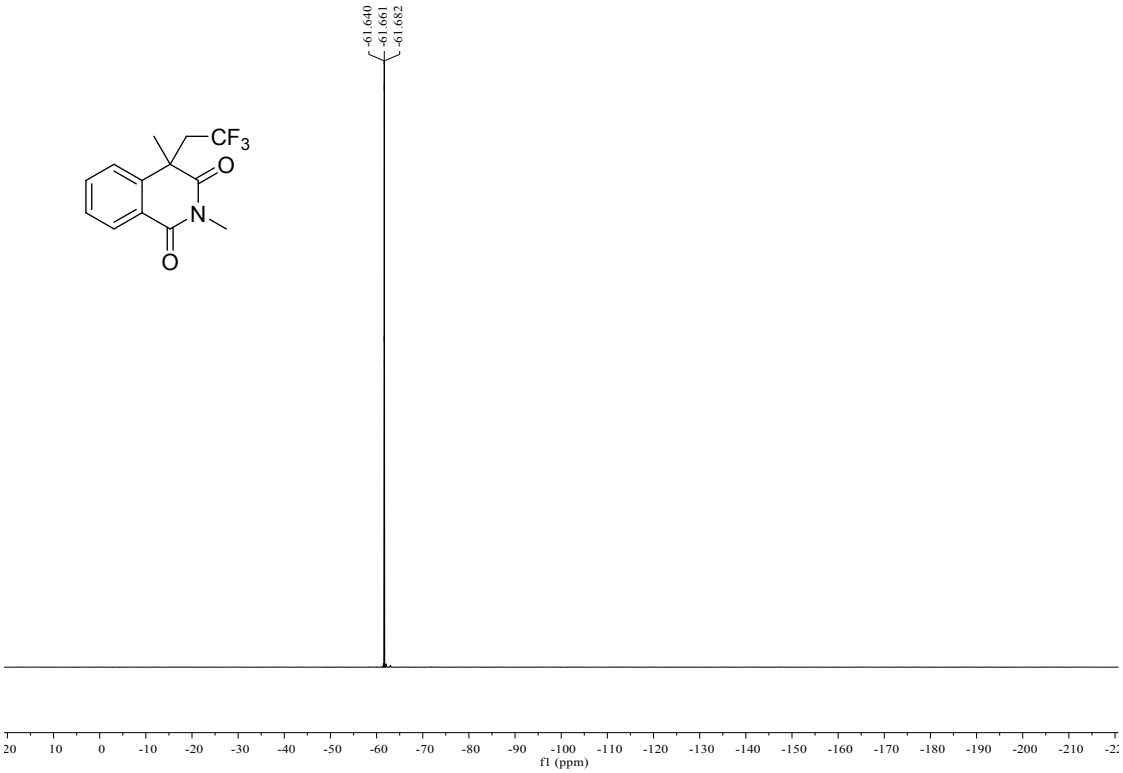
^{19}F NMR Spectrum of **3w** (470 MHz, $CDCl_3$)



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



^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of **3x**



^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of **3x**

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