Supporting Information

Visible-Light Photoredox Intramolecular Difluoroacetamidation: Facile Synthesis of 3,3-Difluoro-2-Oxindoles from Bromodifluoroacetamides

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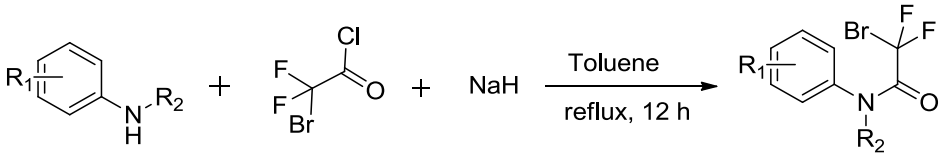
1. General Information

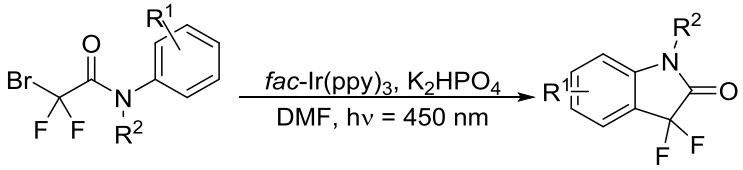
^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM-400 MHz instruments, and the chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz, and are given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ^{1}H), $CDCl_3$ (77.0 ppm for ^{13}C). The peak information was described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra were obtained on Bruker ESQ6K4 and Shimadzu API 2000. High resolution mass spectra and Elemental analyses were performed on Bruker maXis 4G. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Column chromatography was performed with silica gel (200-300 meshes) in petroleum (boiling point is between 60-90 ℃). All reactions were carried out under argon atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. The photocatalysts *fac*-$Ir(ppy)_3$ were purchased from Nichem Co. Ltd.

2. Synthesis of Starting Materials：



To a solution of N-alkyl-N-arylamide (5.0 mmol) in toluene (10 mL) was added NaH (240 mg, 1.5 mmol) and then cooled to 0 ^{o}C in the ice water bath then the mixture was stirred at 0 ^{o}C for 15 min. Bromodifluoroacetyl chloride (1.5 equiv, 2.45 g, 1.5 mmol) was slowly added to the solution at 0 ^{o}C and then the mixture was stirred at reflux for 12 h. The reaction was quenched by water and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes/AcOEt = 6:1) to afford desired starting material.

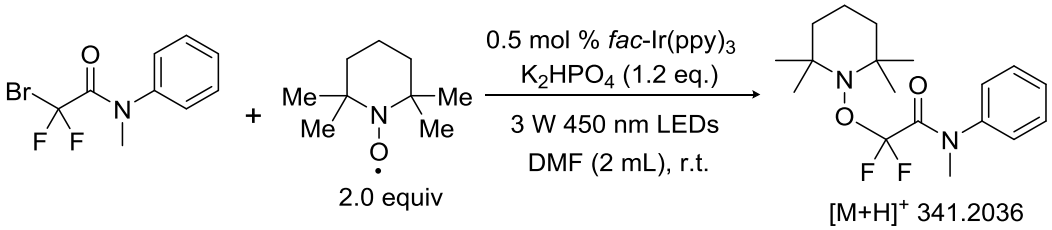
3. General Procedures:



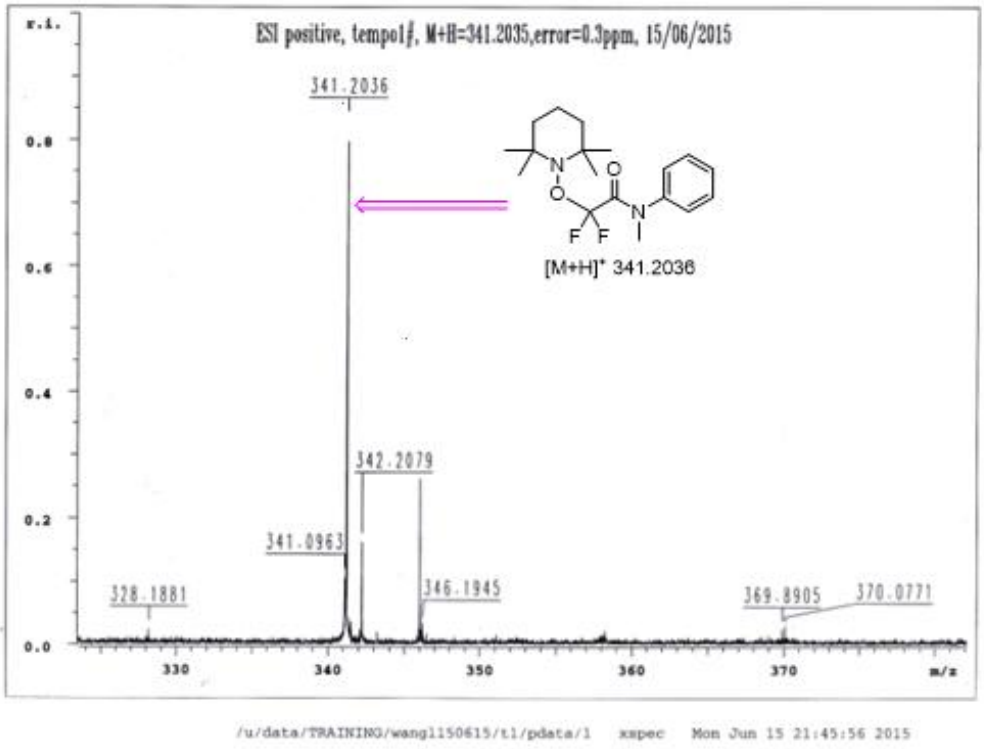
In a 10 mL snap cap vial equipped with a magnetic stirring bar and fitted with a septum, bromodifluoroacetamide (0.2 mmol), K_2HPO_4 (0.24 mmol), *fac*-$Ir(ppy)_3$ (0.005 mmol, 0.5 mol %) were dissolved in DMF (3 ml, 0.15 mL/mmol). The mixture was bubbled with a stream of argon for 20 min via a syringe needle. The vial was then irradiated using a 3 W 450 nm blue LEDs. The process of the reaction was monitored by thin-layer chromatography at regular intervals. After 24

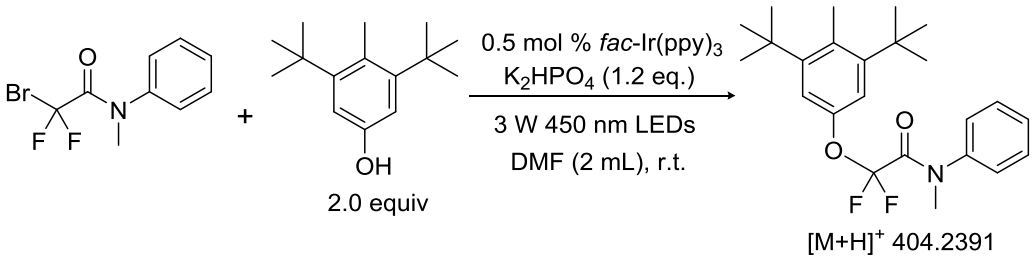
hours, the mixture was poured into a separatory funnel containing 10 mL of H_2O and 10 mL of AcOEt. The layers were separated and the aqueous layer was extracted with AcOEt (2 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product.

4. The Radical Trapping Experiments.

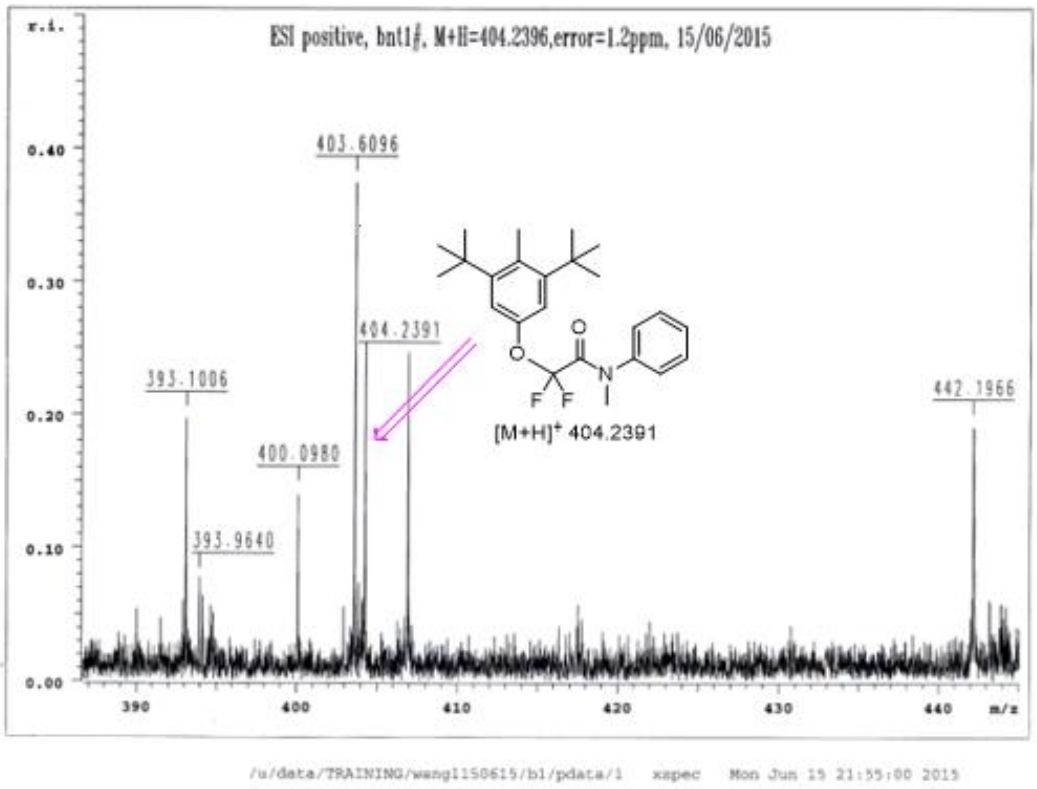


In a 10 mL snap cap vial equipped with a magnetic stirring bar and fitted with a septum, the Bromodifluoroacetyl amide (0.2 mmol), K_2HPO_4 (0.24 mmol), *fac*-Ir(ppy)$_3$ (0.001 mmol), TEMPO (0.40 mmol, 2.0 equiv.) were dissolved in DMF (2 ml, 0.1 mmol/mL). The mixture was bubbled with a stream of argon for 20 min via a syringe needle. The vial was irradiated under a 3 W 450 nm blue LEDs for 24 hours and then be characterized by high resolution mass spectra.

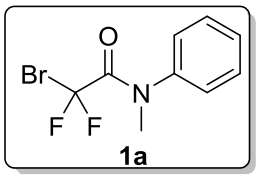




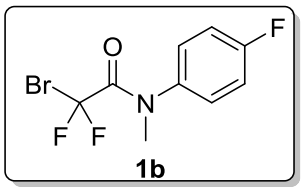
In a 10 mL snap cap vial equipped with a magnetic stirring bar and fitted with a septum, the Bromodifluoroacetyl amide (0.2 mmol), K_2HPO_4 (0.24 mmol), *fac*-Ir(ppy)$_3$ (0.001 mmol), BHT (0.40 mmol, 2.0 equiv.) were dissolved in DMF (2 ml, 0.1 mmol/mL). The mixture was bubbled with a stream of argon for 20 min via a syringe needle. The vial was irradiated under a 3 W 450 nm blue LEDs for 24 hours and then be characterized by high resolution mass spectra.



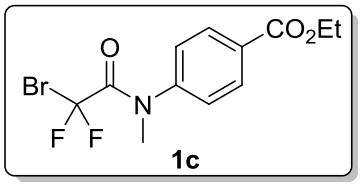
5. Characterization of Substrates



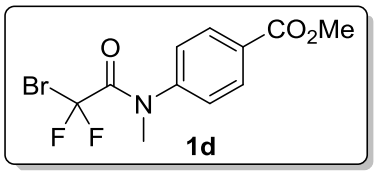
2-bromo-2, 2-difluoro-N-methyl-N-phenylacetamide(1a): Prepared according to the general procedure using N-methylaniline (5.0 mmol, 539 mg), K_2CO_3 (10.0 mmol, 1.38 g, 2 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by flash column chromatography (hexanes/EtOAc: 10/1) to provide **1a** as a pale yellow liquid (1.2 g, 91%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.45-7.43 (m, 3H), 7.30-7.29 (m, 2H), 3.36 (s, 3H). ESI-MS: m/z $[M+H]^+$: 264.0.



2-bromo-2, 2-difluoro-N-(4-fluorophenyl)-N-methylacetamide(1b): Prepared according to the general procedure using 4-fluoro-N-methylaniline (5.0 mmol, 625 mg), NaH (6.0 mmol, 240 mg, 1.2 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 2.45 g, 1.5 mmol) and 10 mL toluene.The crude product was purified by flash column chromatography (hexanes/EtOAc: 10/1) to provide 1b as a pale yellow solid (0.98 g, 71%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.31-7.28 (m, 2H), 7.14-7.10 (m, 2H), 3.35 (s, 3H). ESI-MS: m/z $[M+H]^+$:282.0

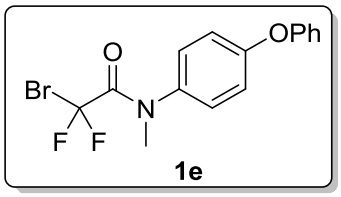


Ethyl 4-(2-bromo-2,2-difluoro-N-methylacetamido)benzoate(1c): Prepared according to the general procedure using ethyl 4-(methylamino)benzoate (5.0 mmol, 895 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 8/1) to provide 1c as a yellowish liquid (1.50 g, 90%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.13 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.41 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H). ESI-MS: m/z $[M+H]^+$: 336.1



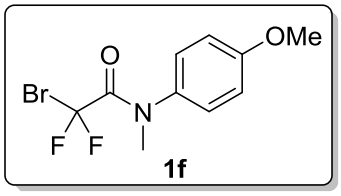
Methyl 4-(2-bromo-2,2-difluoro-N-methylacetamido)benzoate(1d): Prepared according to the general procedure using methyl 4-(methylamino)benzoate (5.0 mmol, 825 mg), NaH (7.5 mmol,

300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 8/1) to provide 1d as a yellowish liquid (1.41 g, 88%). **^{1}HNMR**: (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3H), 3.32 (s, 3H). ESI-MS: m/z $[M+H]^+$: 321.9.



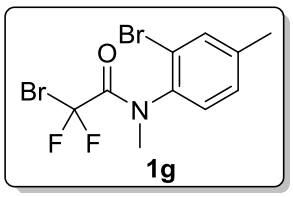
1e

2-bromo-2, 2-difluoro-N-methyl-N-(4-phenoxyphenyl)acetamide(1e)： Prepared according to the general procedure using N-methyl-4-phenoxyaniline (5.0 mmol, 995 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 9/1) to provide **1e** as a white solide (1.2 g, 70%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.42-7.38 (m, 2H), 7.26-7.24 (m, 2H), 7.20-7.17 (m, 1H), 7.08-7.00 (m, 4H), 3.37 (s, 3H). ESI-MS: m/z $[M+H]^+$:356.1



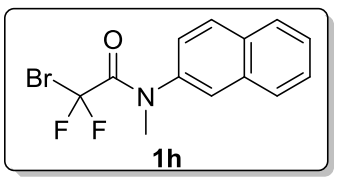
1f

2-bromo-2, 2-difluoro-N-(4-methoxyphenyl)-N-methylacetamide(1f)： Prepared according to the general procedure using 4-methoxy-N-methylaniline (5.0 mmol, 685 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 8/1) to provide **1f** as a white solid (1.4 g, 95%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.21 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.33 (s, 3H). ESI-MS: m/z $[M+H]^+$: 294.0



1g

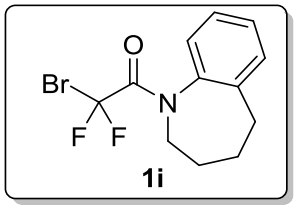
2-bromo-N-(2-bromo-4-methylphenyl)-2,2-difluoro-N-methylacetamide(1g): Prepared according to the general procedure using 2-bromo-N,4-dimethylaniline (5.0 mmol, 995 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 10/1) to provide **1g** as a white solid (0.97 g, 55%). **^{1}H NMR** ($CDCl_3$, 400 MHz)：δ = 7.49 (s, 1H), 7.30-7.27 (m, 1H), 7.19-7.16 (m, 1H), 3.29 (s, 3H), 2.38 (s, 3H). ESI-MS: m/z $[M+H]^+$: 355.9



1h

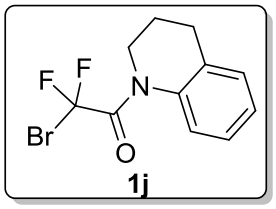
2-bromo-2, 2-difluoro-N-methyl-N-(naphthalen-2-yl) acetamide(1h): Prepared according to the

general procedure using N-methylnaphthalen-2-amine (5.0 mmol, 785 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 10/1) to provide 1h as a white solid (0.86 g, 55%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.96-7.92 (m, 2H), 7.81-7.79 (m, 1H), 7.64-7.60 (m, 2H), 7.58-7.49 (m, 2H), 3.49 (s, 3H). ESI-MS: m/z $[M+H]^+$: 314.0.



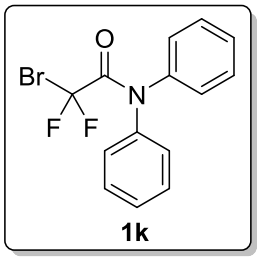
1i

2-bromo-2,2-difluoro-1-(2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)ethanone (1i): Prepared according to the general procedure using 2,3,4,5-tetrahydro-1H-benzo[b]azepine (5.0 mmol, 735 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 15/1) to provide 1i as a white solid (1.2 g, 80%). **^{1}H NMR**: (400 MHz, $CDCl_3$): δ = 7.30-7.22 (m, 4H), 4.57 (q, *J* = 2.8 Hz, 1 H), 2.89-2.69 (m, 1H), 2.69-2.63 (m, 2H), 1.97-1.90 (m, 2H), 1.79-1.75 (m, 1H), 1.48-1.38 (m, 1H). ESI-MS: m/z $[M+H]^+$:304.1



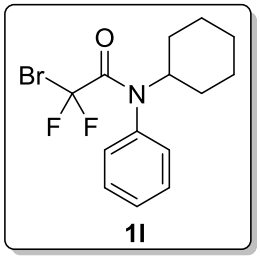
1j

2-bromo-1-(3, 4-dihydroquinolin-1(2H)-yl)-2,2-difluoroethanone (1j): Prepared according to the general procedure using 1,2,3,4-tetrahydroquinoline (5.0 mmol, 666 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 10/1) to provide 1j as a yellowish solid (1.40 g, 95%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.67 (s, 1H), 7.25-7.16 (m, 3H), 3.92 (t, *J* = 6.4 Hz, 2H), 2.88 (s, 2H), 2.16-2.09 (m, 2H). ESI-MS: m/z $[M+H]^+$: 289.9

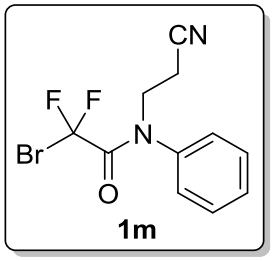


1k

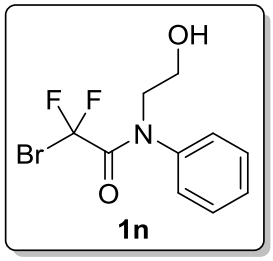
2-bromo-2, 2-difluoro-N, N-diphenylacetamide(1k): Prepared according to the general procedure using diphenylamine (5.0 mmol, 845 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 10/1) to provide 1k as a yellowish liquid (1.40 g, 95%).**^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.43-7.37 (m, 10H). ESI-MS: m/z $[M+H]^+$: 326.0



2-bromo-N-cyclohexyl-2,2-difluoro-N-phenylacetamide(1l): Prepared according to the general procedure using N-cyclohexylaniline (5.0 mmol, 875 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 10/1) to provide 1l as a white solide (0.99 g, 60%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.41-7.37 (m, 3H), 7.22-7.19 (m, 2H), 4.13 (tt, *J* = 3.6 Hz, 12.0 Hz, 1H), 1.89-1.86 (m, 2H), 1.78-1.75 (m, 2H),1.61-1.57 (m, 1H), 1.45-1.34 (m, 2H). **ESI-MS:** m/z $[M+H]^+$: 332.2.

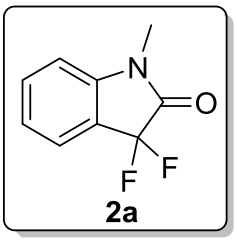


2-bromo-N-(2-cyanoethyl)-2,2-difluoro-N-phenylacetamide(1m): Prepared according to the general procedure using 3-(phenylamino)propanenitrile (5.0 mmol, 730 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 8/1) to provide 1m as a white solid (0.51 g, 34%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.50-7.43 (m, 3H), 7.38-7.36 (m, 2H), 4.01 (t, *J* = 6.8 Hz, 2H), 2.75 (t, *J* = 6.8 Hz, 2H). ESI-MS: m/z $[M+Na]^+$: 324.9.



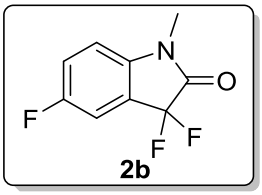
2-bromo-2,2-difluoro-N-(2-hydroxyethyl)-N-phenylacetamide(1n): Prepared according to the general procedure using 2-(phenylamino)ethan-1-ol (5.0 mmol, 685 mg), NaH (7.5 mmol, 300 mg, 1.5 equiv), Bromodifluoroacetyl chloride (1.5 equiv, 1.45 g, 7.5 mmol) and 10 mL toluene. The crude product was purified by silica gel chromatography (hexanes/EtOAc: 4/1) to provide 1n as a white solid (0.58 g, 40%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.46-7.43 (m, 3H), 7.37-7.35 (m, 2H), 4.15-4.06 (m, 2H), 3.68-3.47 (m, 2H). ESI-MS: m/z $[M+H]^+$: 293.9.

6. Characterization of Products



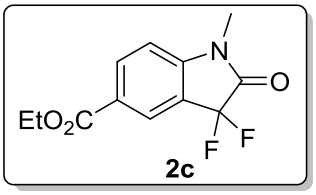
2a

3, 3-difluoro-1-methylindolin-2-one(2a): Prepared according to the general procedure using a mixture solution of 2-bromo-2,2-difluoro-N-methyl-N-phenylacetamide **1a** (0.2 mmol, 52.6 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by gradient flash column chromatography (hexanes/EtOAc: 5/1 to 3/1) to provide **2a** as a white solid (34.0 mg, 93%). This compound is known and results were in accordance with the data reported in the literature.[a, b] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.54-7.48 (m, 2H), 7.19-7.16 (m, 1H), 6.92-6.90 (m, 1H), 3.21 (s, 3H). **^{13}C NMR** ($CDCl_3$, 400 MHz): δ = 165.22 (t, *J* = 30 Hz), 143.89(t, *J* = 7 Hz), 124.52, 123.87, 120.00 (t, *J* = 23 Hz), 110.83 (t, *J* = 247 Hz), 109.44, 67.90, 26.21, 25.54. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −112.4 (s, 2F). ESI-MS: m/z $[M+H]^+$:184.1



2b

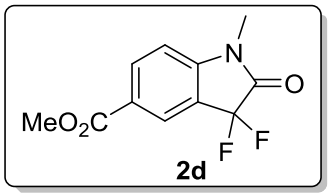
3, 3, 5-trifluoro-1-methylindolin-2-one(2b): Prepared according to the general procedure using a mixture solution of 2-bromo-2, 2-difluoro-N-(4-fluorophenyl)-N-methylacetamide **1b** (0.2 mmol, 56.2 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by gradient flash column chromatography (hexanes/EtOAc: 5/1 to 3/1) to provide **2b** as a yellow solid (39.0 mg, 97%). This compound is known and results were in accordance with the data reported in the literature.[c, d] **^{1}H NMR** ($CDCl_3$, 400MHz): δ = 7.30-7.28 (m, 1H), 7.25-7.21 (m, 1H), 6.89-6.86 (m, 1H), 3.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 400 MHz): δ = 164.94, 160.63, 158.19, 139.87, 121.25, 121.17, 120.12, 119.89, 112.84 (t, *J* = 12 Hz), 110.47, 110.35 (t, *J* = 250 Hz), 29.66, 26.41. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −112.7 (s, 2F), −118.2 (s, 1F). ESI-MS: m/z $[M+H]^+$: 202.1



2c

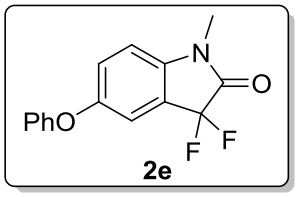
Ethyl 3,3-difluoro-1-methyl-2-oxoindoline-5-carboxylate(2c): Prepared according to the general procedure using a mixture solution of Ethyl 4-(2-bromo-2,2-difluoro-N-methyl-acetamido)benzoate **1c** (0.2 mmol, 67.0 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room

temperature for 24 h. The crude product was purified by gradient flash column chromatography (hexanes/EtOAc: 4/1 to 3/1) to provide **2c** as a white solid (47.4 mg, 93%). This compound is new. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.26-8.23 (m, 2H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.27 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H)); **^{13}C NMR** ($CDCl_3$, 400 MHz): δ = 165.12, 147.60, 135.77, 126.51, 126.03, 120.08 (t, *J* = 23 Hz), 112.61, 110.12 (t, *J* = 249 Hz), 109.13, 107.63, 61.42, 26.56, 14.30. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −112.5 (s, 2F). **IR** ($CDCl_3$): 2923.4, 2371.9, 1749.7, 1713.1, 1619.5, 1370.6, 1243.3, 1085.6, 1021.7, 849.8, 758.0 cm^{-1}. **HRMS** (ESI, m/z) Calculated for $[C_{12}H_{12}F_2NO_3]$ $(M+Na)^+$: 278.0599, found 278.0597.



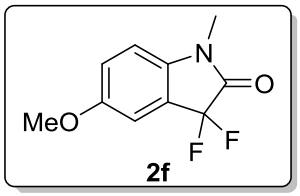
2d

Methyl 3,3-difluoro-1-methyl-2-oxoindoline-5-carboxylate(2d): Prepared according to the general procedure using a mixture solution of Methyl 4-(2-bromo-2,2-difluoro-N-methyl acetamido)benzoate **1d** (0.2 mmol, 64.2 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by gradient flash column chromatography (hexanes/EtOAc: 4/1 to 3/1) to provide **2d** as a white solid (43.5 mg, 90%). This compound is known and results were in accordance with the data reported in the literature.[a] **^{1}H NMR**: (400 MHz, $CDCl_3$): δ 8.17-8.05 (m, 2H), 7.28-6.88 (m, 1H), 3.86 (s, 3H), 3.19 (s, 3H). **^{13}C NMR** (100 Hz, $CDCl_3$): δ 165.57 (t, *J* = 25 Hz), 147.69, 135.78, 131.53, 131.35, 126.03, 127.11 (t, *J* = 24 Hz), 111.07 (t, *J* = 249 Hz), 109.19, 52.35, 26.52. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −112.8 (s, 2F). ESI-MS: m/z $[M+H]^+$: 242.1.



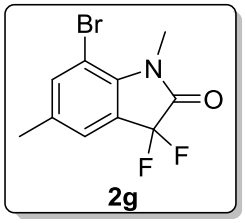
2e

3,3-difluoro-1-methyl-5-phenoxyindolin-2-one(2e): Prepared according to the general procedure using a mixture solution of 2-bromo-2,2-difluoro-N-methyl-N-(4-phenoxy phenyl)acetamide **1e** (0.2 mmol, 71.0 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by gradient flash column chromatography (hexanes/EtOAc: 6/1 to 4/1) to provide **2e** as a white solid (41.5 mg, 76%). This compound is new. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.39-7.35 (m, 2H), 7.25-7.24 (m, 1H), 7.19-7.01 (m, 2H), 7.01-6.99 (m, 2H), 6.88-6.86 (m, 1H), 3.23 (s, 3H); **^{13}C NMR** ($CDCl_3$, 400 MHz): δ = 130.01, 123.80, 123.74, 118.61, 116.18, 110.43, 26.43. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −112.2 (s, 2F). **IR** ($CDCl_3$): 3390.3, 2923.9, 2376.2, 1751.8, 1590.9, 1468.1, 1292.5, 1224.3, 1114.7, 1021.1, 753.7 cm^{-1}. **HRMS** (ESI, m/z) Calculated for $[C_{15}H_{11}F_2NO_2]$ $(M+H)^+$: 276.0831, found 256.0828.



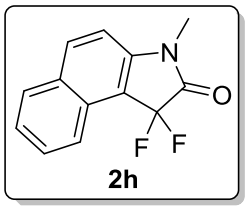
2f

3,3-difluoro-5-methoxy-1-methylindolin-2-one(2f): Prepared according to the general procedure using a mixture solution of 2-bromo-2,2-difluoro-N-methyl-N-(4-methoxy phenyl)acetamide **1f** (0.2 mmol, 58.5 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by gradient flash column chromatography (hexanes/EtOAc: 5/1 to 4/1) to provide **2f** as a colourless liquid (29.4 mg, 69%). This compound is known and results were in accordance with the data reported in the literature.[d] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.15-7.14 (m, 1H), 7.03-7.01 (m, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 3H), 3.20 (s, 3H); **^{13}C NMR** ($CDCl_3$, 400 MHz): δ = 165.11, 156.72, 137.06, 136.99, 120.96(t, *J* = 23 Hz), 118.34, 113.50, 111.10 (t, *J* = 240 Hz), 111.02, 55.92, 29.67, 26.32. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −112.4 (s, 2F). ESI-MS: m/z $[M+H]^+$:214.1



2g

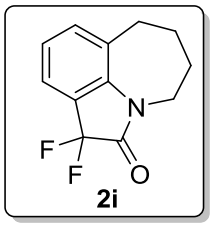
7-bromo-3, 3-difluoro-1,5-dimethylindolin-2-one(2g): Prepared according to the general procedure using a mixture solution of 2-bromo-N-(2-bromo-4-methylphenyl)-2,2-difluoro -N-methylacetamide **1g** (0.2 mmol, 71.0 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by gradient flash column chromatography (hexanes/EtOAc: 6/1 to 4/1) to provide **2g** as a white solid (22.0 mg, 40%). This compound is known and results were in accordance with the data reported in the literature.[e] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.42 (s, 1H), 7.31 (s, 1H), 3.58 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 400 MHz): δ = 165.67, 138.88 (t, *J* = 10 Hz), 135.51, 124.57, 123.18, 122.95, 109.90 (t, *J* = 247 Hz), 103.23, 29.82, 29.69, 20.36. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −111.9 (s, 2F). **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −111.9 (s, 2F). ESI-MS: m/z $[M+H]^+$: 276.0.



2h

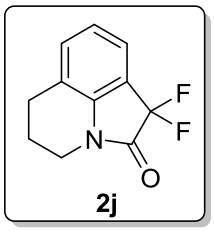
3,3-difluoro-1-methyl-1H-benzo[f]indol-2(3H)-one(2h): Prepared according to the general procedure using a mixture solution of 2-bromo-2, 2-difluoro-N-methyl-N-(naphthalen-2-yl) acetamide **1h** (0.2 mmol, 62.5 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by gradient flash column chromatography

(hexanes/EtOAc: 7/1 to 6/1) to provide **2h** as a white solid (28.5 mg, 57%). This compound is new. **^{1}H NMR**: (400 MHz, $CDCl_3$): δ 8.13-8.09 (m, 2H), 7.77-7.70 (m, 2H), 7.70-7.55 (m, 1H), 7.24-7.22 (m, 1H), 3.68 (s, 3H). **^{13}C NMR** (100 Hz, $CDCl_3$): δ. 132.61, 131.77, 131.76, 131.71, 127.15, 127.12, 127.10, 126.86, 126.19, 126.16, 126.12, 124.09, 111.56, 29.07. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −81.1 (s, 2F). **IR** ($CDCl_3$): 3368.0, 2921.1, 2373.3, 1687.8, 1596.0, 1465.7, 1399.1, 1285.4, 1202.4, 1034.4, 825.0 cm^{-1}. **HRMS** (ESI, m/z) Calculated for $[C_{13}H_9F_2NONa]$ $(M+H)^+$: 234.0725, found 234.0729.



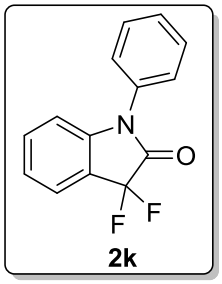
2i

1,1-difluoro-4,5,6,7-tetrahydroazepino[3,2,1-hi]indol-2(1H)-one(2i): Prepared according to the general procedure using a mixture solution of 2-bromo-2,2-difluoro-1-(2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)ethanone **1i** (0.2 mmol, 60.6 mg), photocatalyst *fac*-$Ir(ppy)_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by flash column chromatography (hexanes/EtOAc: 7/1) to provide **2i** as a white solid (35.2 mg, 79%). This compound is known and results were in accordance with the data reported in the literature.[a] **^{1}H NMR**: (400 MHz, $CDCl_3$): δ 7.28-7.26 (m, 1H), 7.21-7.18 (m, 1 H), 7.13-7.11 (m, 1H), 6.97-6.93 (m, 1H), 3.85-3.83 (m, 2H), 2.89-2.86 (m, 2H), 1.97-1.91 (m, 4H). **^{13}C NMR** (100 Hz, $CDCl_3$): δ 165.59 (t, *J* = 29 Hz), 134.87, 127.11 (t, *J* = 34 Hz), 123.74, 122.20, 111.01 (t, *J* = 247 Hz), 48.12, 41.16, 30.39, 25.77, 25.54. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −112.2 (s, 2F). ESI-MS: m/z $[M+H]^+$: 224.1



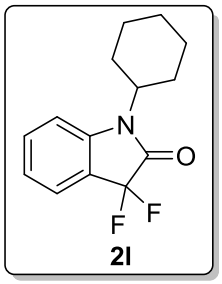
2j

1,1-difluoro-5, 6-dihydro-1H-pyrrolo[3, 2, 1-ij]quinolin-2(4H)-one(2j): Prepared according to the general procedure using a mixture solution of 2-bromo-1-(3, 4-dihydroquinolin-1(2H)-yl)-2,2-difluoroethanone **1j** (0.2 mmol, 57.8 mg), photocatalyst *fac*-$Ir(ppy)_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by flash column chromatography (hexanes/EtOAc: 7/1) to provide **2i** as a white solid (38.4 mg, 92%). This compound is known and results were in accordance with the data reported in the literature.[a] **^{1}H NMR** ($CDCl_3$, 400MHz): δ = 7.35-7.33 (m, 1H), 7.24-7.22 (m, 1H), 7.06-7.02 (m, 1H), 3.70 (t, *J* = 5.6 Hz, 2H), 2.78 (t, *J* = 6.0 Hz, 2H), 2.06-2.00 (m, 2H); **^{13}C NMR** ($CDCl_3$, 400 MHz): δ = 163.98 (t, *J* = 30 Hz), 139.61 (t, *J* = 7 Hz), 132.32, 123.24 (t, *J* = 2 Hz), 122.21, 121.59, 118.51 (t, *J* = 23 Hz), 114.52, 112.01 (t, *J* = 251 Hz), 109.50, 38.62, 23.99, 20.38. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −112.9 (s, 2F). ESI-MS: m/z $[M+H]^+$:210.1



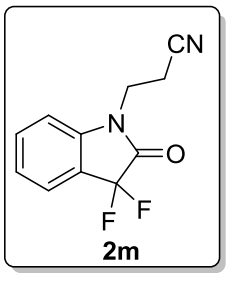
2k

3,3-difluoro-1-phenylindolin-2-one(2k): Prepared according to the general procedure using a mixture solution of 2-bromo-2, 2-difluoro-N, N-diphenylacetamide **1k** (0.2 mmol, 65.0 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by flash column chromatography (hexanes/EtOAc: 7/1) to provide **2k** as a white solid (43.0 mg, 88%). This compound is known and results were in accordance with the data reported in the literature.[b,d] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.65 (m, 1H), 7.64-7.59 (m, 2H), 7.58-7.42 (m, 4H), 7.25-7.21 (m, 1H), 6.90-6.88 (m, 1H); **^{13}C NMR** ($CDCl_3$, 400 MHz): δ = 164.52, 144.17 (t, *J* = 7 Hz), 133.48, 132.62, 129.91, 129.36, 128.92, 126.18, 124.96, 124.35, 119.90 (t, *J* = 23 Hz), 113.21, 110.74. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −110.8 (s, 2F). ESI-MS: m/z $[M+H]^+$:246.0



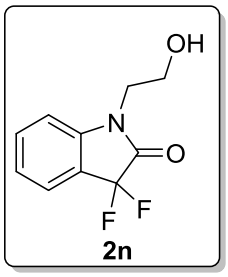
2l

3-cyclohexyl-1,1-difluoro-1H-inden-2(3H)-one(2l): Prepared according to the general procedure using a mixture solution of 2-bromo-N-cyclohexyl-2,2-difluoro-N-phenylacetamide **1l** (0.2 mmol, 66.0 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by flash column chromatography (hexanes/EtOAc: 6/1) to provide **2l** as a white solid (40.3 mg, 80%). This compound is new. **^{1}H NMR:** (400 MHz, $CDCl_3$): δ 7.54-7.52 (m, 1H), 7.48-7.44 (m, 1 H), 7.15-7.12 (m, 1H), 7.09-7.07 (m, 1H), 4.07-3.99 (m, 1H), 2.17-2.07 (m, 2H), 1.93-1.83 (m, 2H), 1.80-1.79 (m, 2H), 1.76-1.73 (m, 1H), 1.45-1.34 (m, 2H), 1.31-1.23 (m, 1H). **^{13}C NMR** (100 Hz, $CDCl_3$): δ 165.04 (t, *J* = 30 Hz), 143.23 (t, *J* = 7 Hz), 133.27, 124.77, 123.25, 120.40 (t, *J* = 30 Hz), 111.03, 110.41 (t, *J* = 247 Hz), 52.99, 28.84, 25.72, 25.07. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −112.2 (s, 2F). **IR** ($CDCl_3$): 3390.7, 2931.3, 2371.0, 1745.6, 1619.9, 1473.1, 1284.1, 1201.7, 1086.9, 769.5, 750.1 cm^{-1}. **HRMS** (ESI, m/z) Calculated for $[C_{14}H_{15}F_2NO]$ $(M+H)^+$: 252.1194, found 252.1197.



2m

3-(3,3-difluoro-2-oxo-2,3-dihydro-1H-inden-1-yl)propanenitrile(2m): Prepared according to the general procedure using a mixture solution of 2-bromo-N-(2-cyanoethyl)-2,2-difluoro-N-phenylacetamide **1m** (0.2 mmol, 65.0 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by flash column chromatography (hexanes/EtOAc: 5/1) to provide **2m** as a white solid (37.8 mg, 85%). This compound is new. **^{1}H NMR:** (400 MHz, $CDCl_3$): δ 7.60-7.52 (m, 2H), 7.27-7.21 (m, 1H), 7.05-7.03 (m, 1H), 4.02 (t, *J* = 6.8 Hz, 2H), 2.80 (t, *J* = 6.8 Hz, 2H). **^{13}C NMR** (100 Hz, $CDCl_3$): δ 165.30 (t, *J* = 30 Hz), 142.00 (t, *J* = 7 Hz), 133.84, 130.39, 128.12, 125.18, 124.51, 119.84 (t, *J* = 23 Hz), 116.70, 110.38 (t, *J* = 248 Hz), 109.46, 46.14, 36.17, 16.27. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −111.5 (s, 2F). **IR** ($CDCl_3$): 2925.0, 2253.0, 1755.1, 1622.5, 1473.8, 1372.0, 1287.9, 1188.0, 1152.0, 1082.8, 768.6, cm^{-1}. **HRMS** (ESI, m/z) Calculated for [$C_{11}H_8F_2N_2ONa$] $(M + NH_4)^+$: 240.0943, found 240.0941.



2n

1,1-difluoro-3-(2-hydroxyethyl)-1H-inden-2(3H)-one(2n): Prepared according to the general procedure using a mixture solution of 2-bromo-2,2-difluoro-N-(2-hydroxyethyl)-N-phenyl acetamide **1n** (0.2 mmol, 58.5 mg), photocatalyst *fac*-Ir(ppy)$_3$ (0.5 mol %, 0.005 mmol, 3.3 mg) and K_2HPO_4 (0.24 mmol, 1.2 equiv, 41.8 mg) in anhydrous DMF (3.0 mL) at room temperature for 24 h. The crude product was purified by flash column chromatography (hexanes/EtOAc: 3/1) to provide **2m** as a white solid (38.3 mg, 90%). This compound is new. **^{1}H NMR**: (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 1H), 7.54-7.50 (m, 1 H), 7.22-7.18 (m, 1H), 7.02-6.99 (m, 1H), {4.12 (t, *J* = 6.8 Hz), 4.05 (t, *J* = 6.4 Hz), 2H}, {3.78 (t, *J* = 6.0 Hz), 3.60 (t, *J* = 6.8 Hz), 2H}. **^{13}C NMR** (100 Hz, $CDCl_3$): δ 165.50 (t, *J* = 30 Hz), 143.13, 143.07, 142.99, 142.83, 133.59, 120.00 (t, *J* = 27 Hz), 111.52 (t, *J* = 247 Hz), 42.07, 41.87, 40.04. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −111.7 (s, 2F). **IR** ($CDCl_3$): 3367.8, 2923.8, 2370.4, 1753.9, 1621.7, 1473.2, 1375.2, 1286.1, 1143.5, 1085.0, 768.0 cm^{-1}. ESI-MS: m/z $[M+H]^+$:214.1. **HRMS** (ESI, m/z) Calculated for [$C_{10}H_9F_2NO_2$] $(M+H)^+$ 214.0674, found 214.0678.

7. References and notes:

(a). S.-L. Shi and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2015, **54**, 1646-1650.

(b). R. P. Singh , U. Majumder and J. M. Shreeve, *J. Org. Chem.*, **2001**, *66*, 6263–6267.

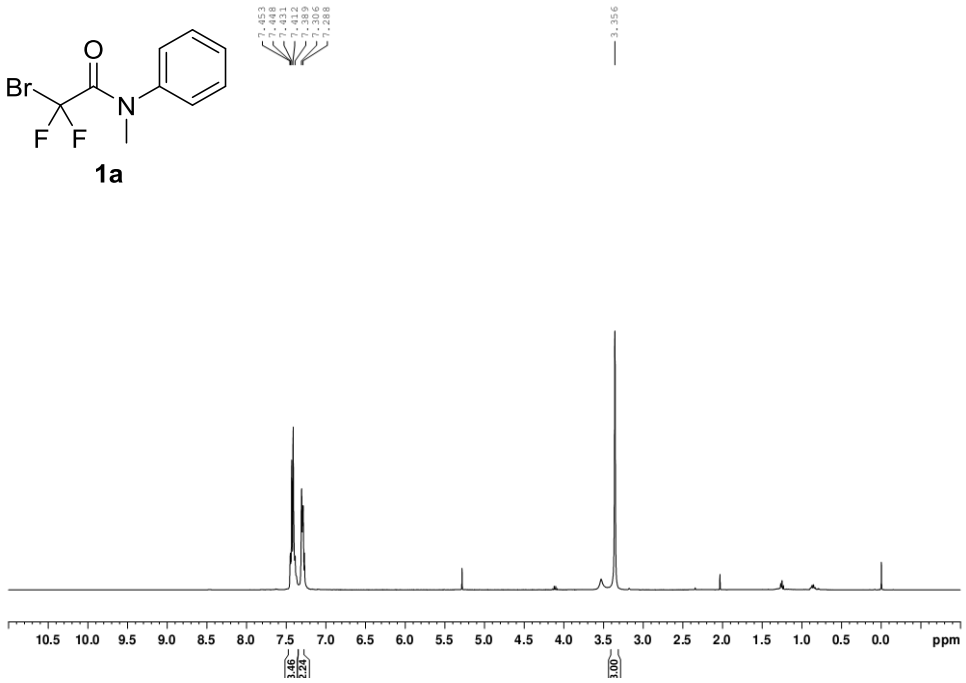
(c). L. A. McAllister, R. A. McCormick, K. M. James, S. Brand, N. Willetts and D. J. Procter, *Chem. Eur. J.*, 2007, **13**, 1032

(d). J. Zhu, W. Zhang, L. Zhang, J. Liu, J. Zheng and J. Hu, *J. Org. Chem.*, 2010, **75**, 5505-5512.

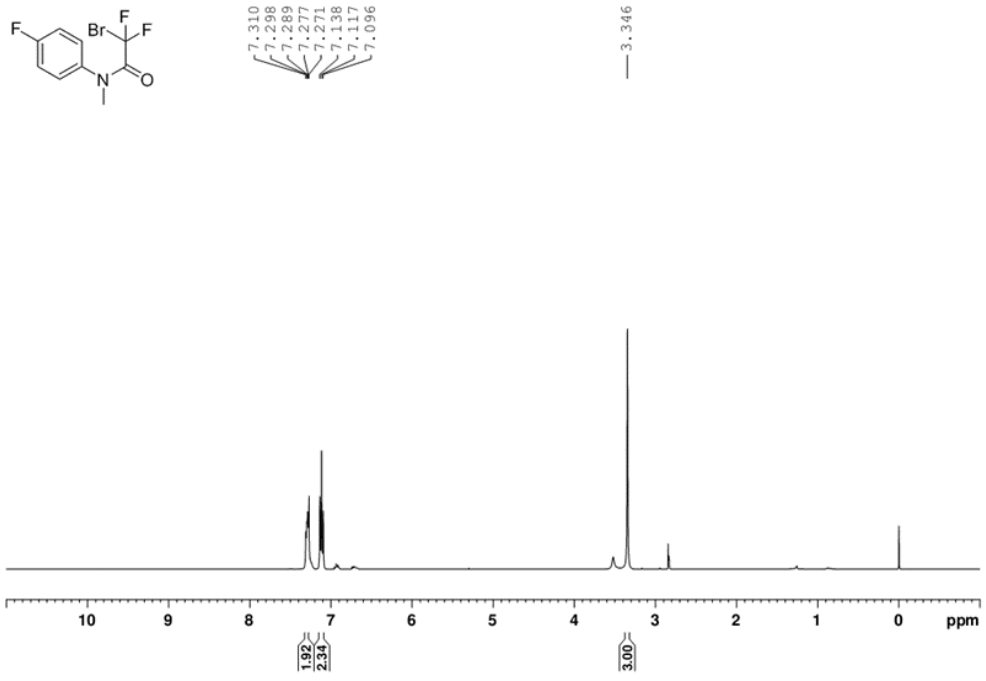
(e). Y. H. Lim, Q. Ong, H. A. Duong, T. M. Nguyen and C. W. Johannes, *Org. Lett.*, 2012, **14**, 5676-5679.

8. Copy of NMR Spectra for Desired Products

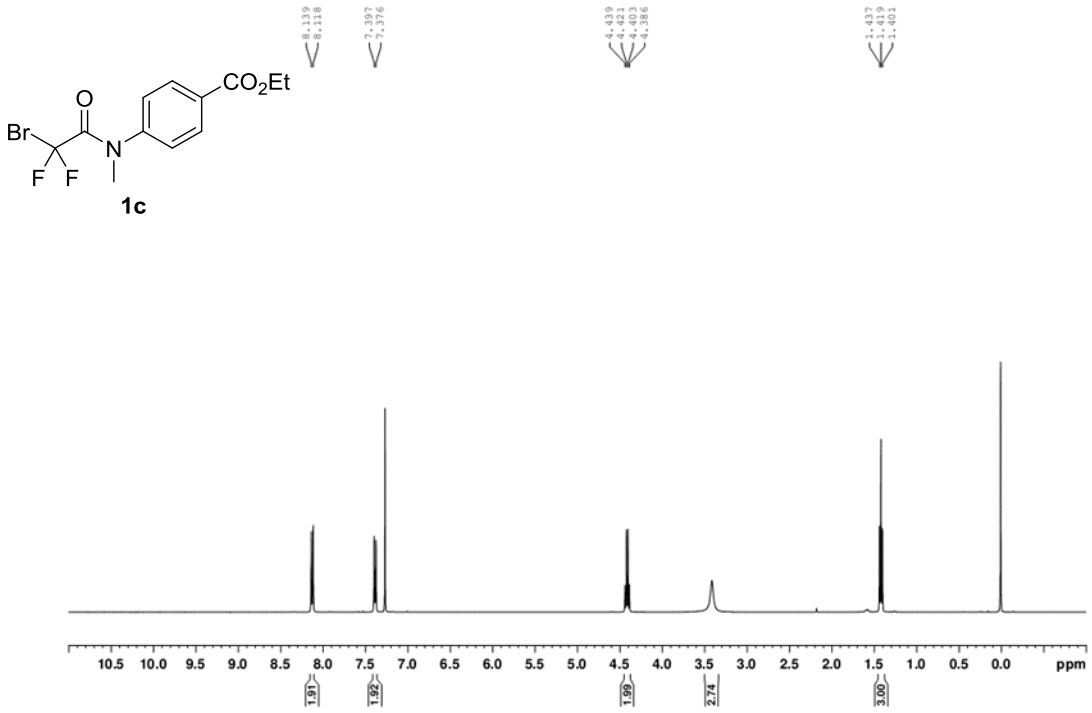
^{1}H NMR spectra of compound **1a.**



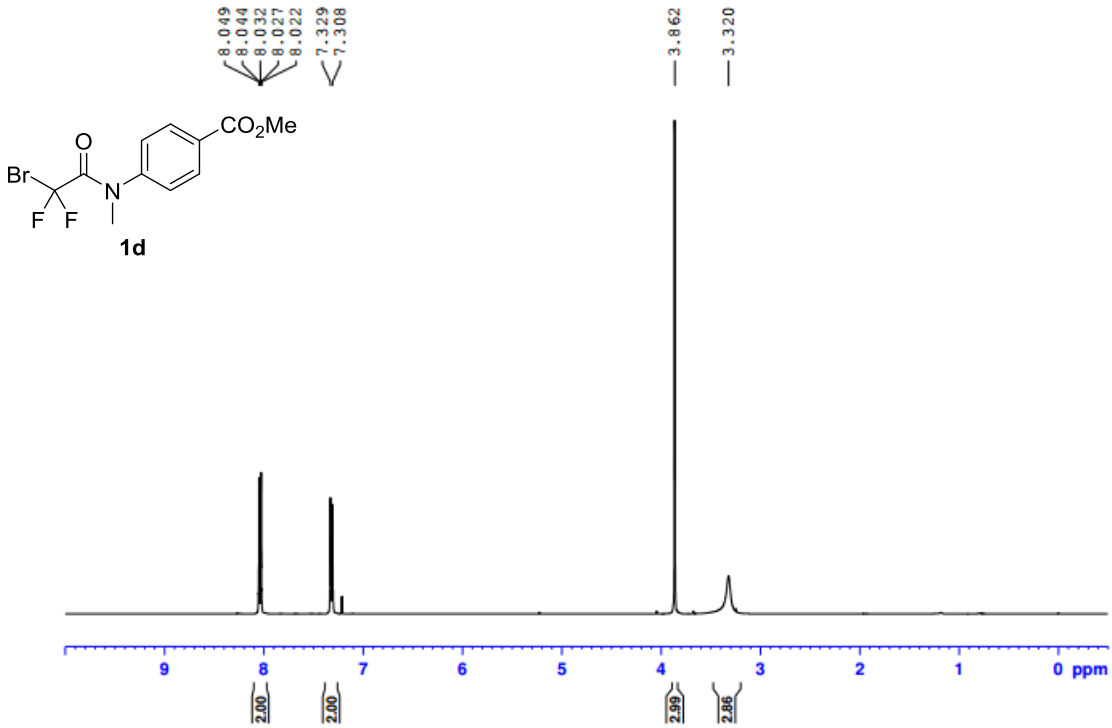
^{1}H NMR spectra of compound **1b.**



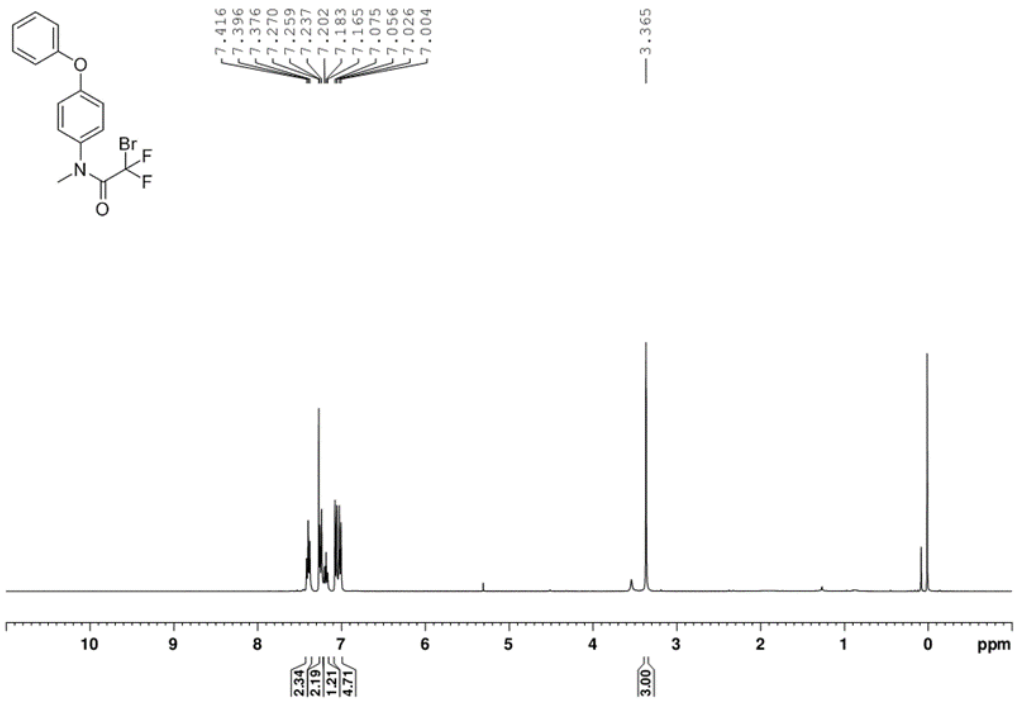
^{1}H NMR spectra of compound **1c.**



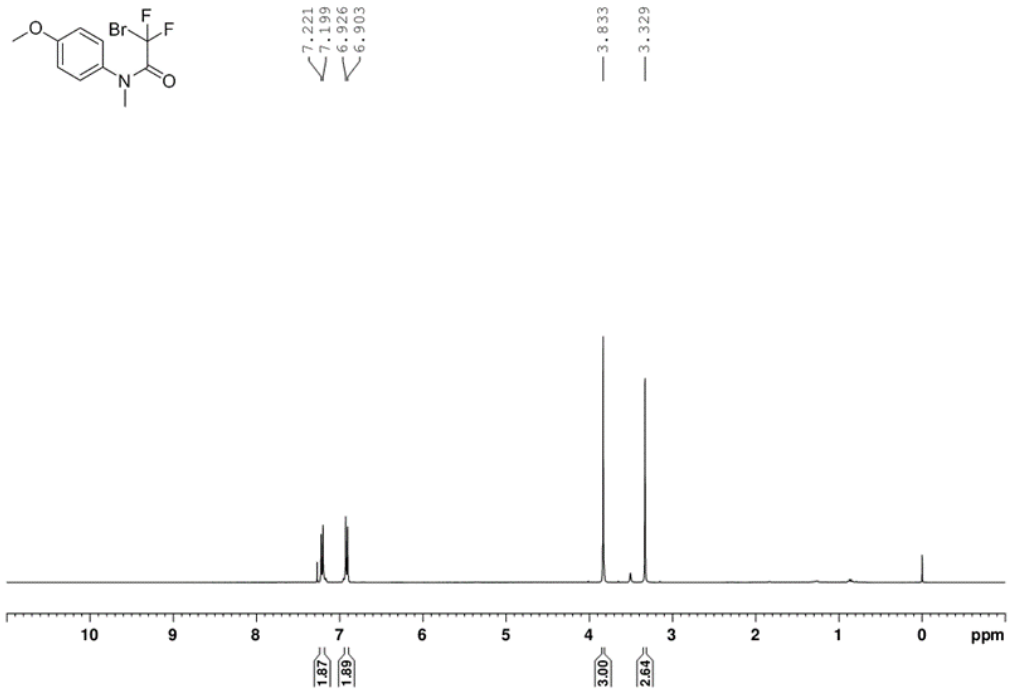
^{1}H NMR spectra of compound **1d.**



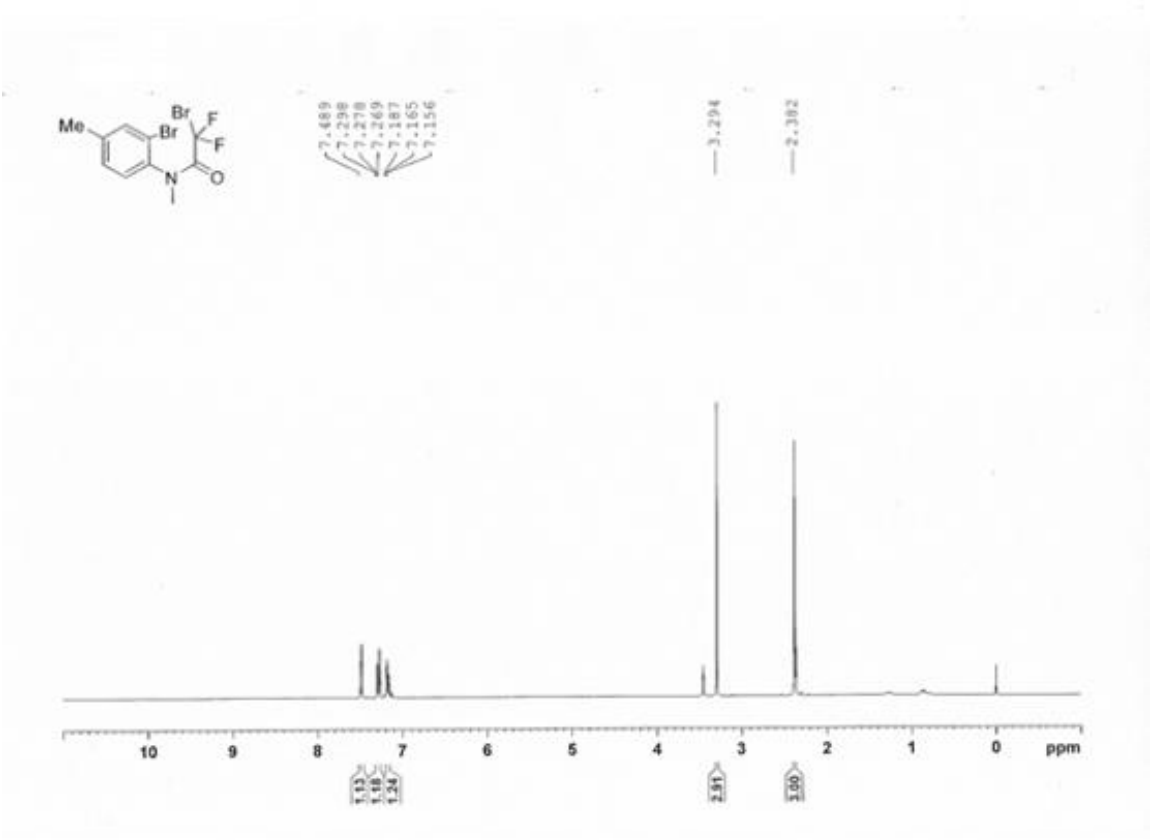
^{1}H NMR spectra of compound **1e.**



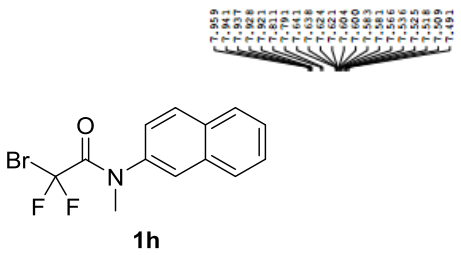
^{1}H NMR spectra of compound **1f.**



^{1}H NMR spectra of compound **1g.**

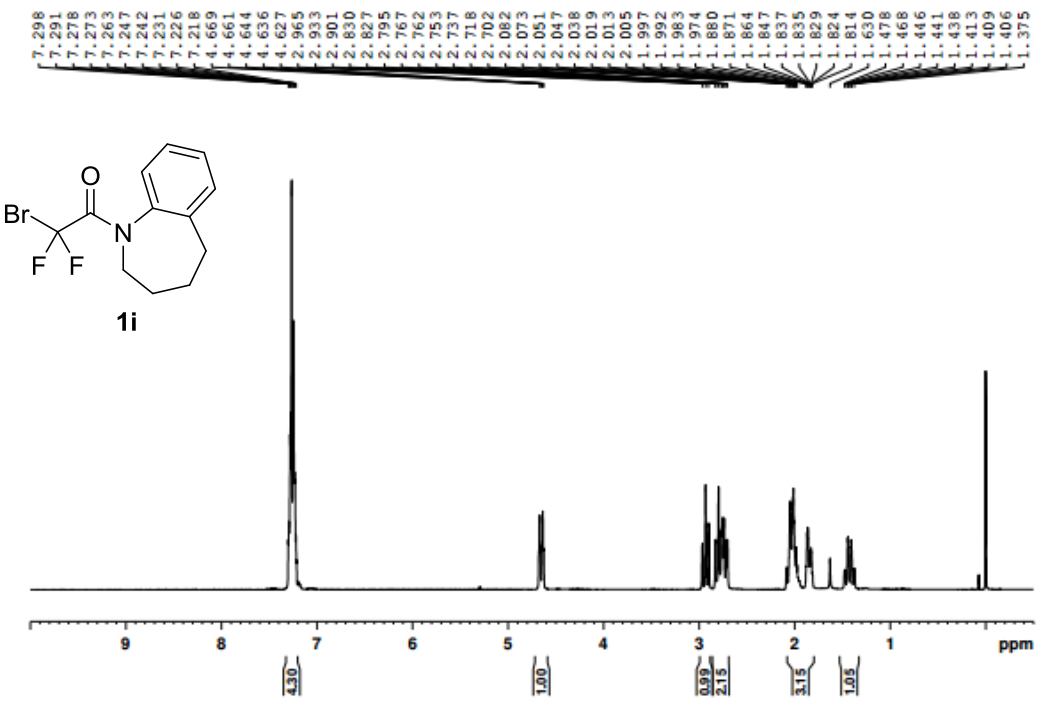


^{1}H NMR spectra of compound **1h.**

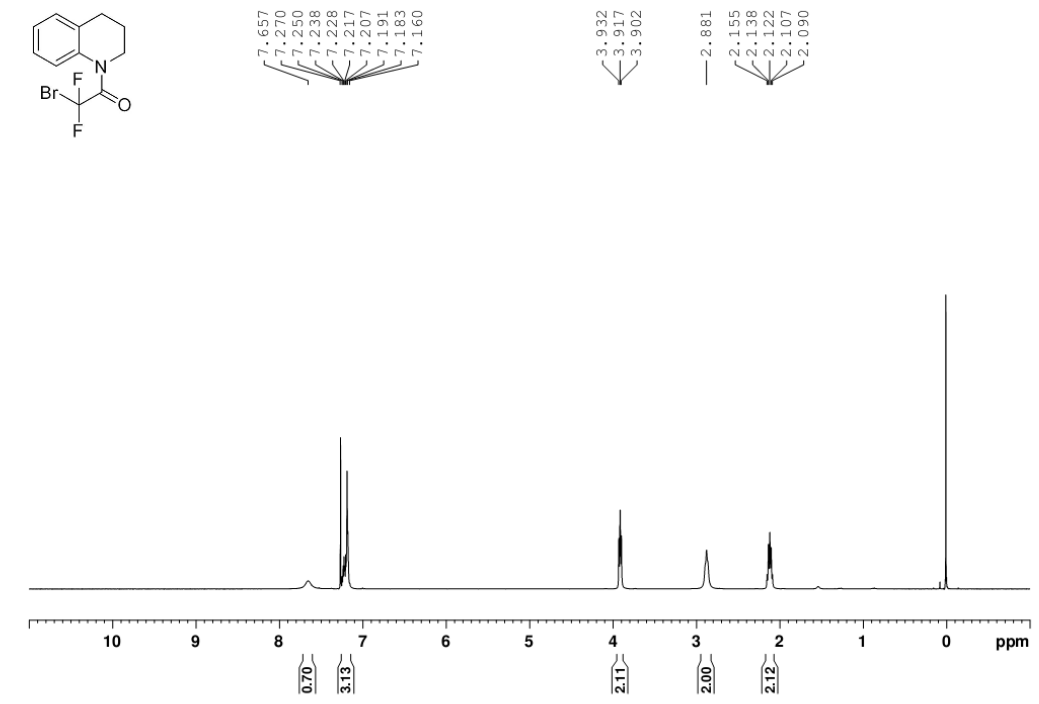


1h

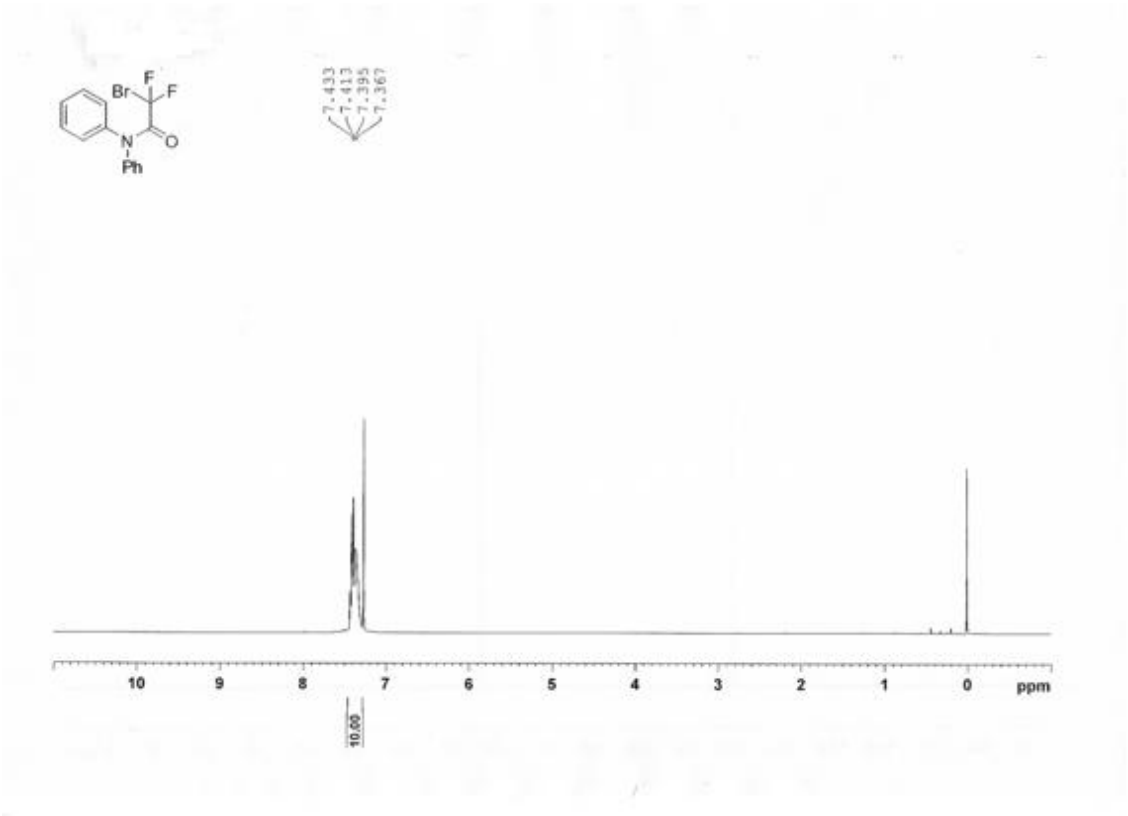
^{1}H NMR spectra of compound **1i.**



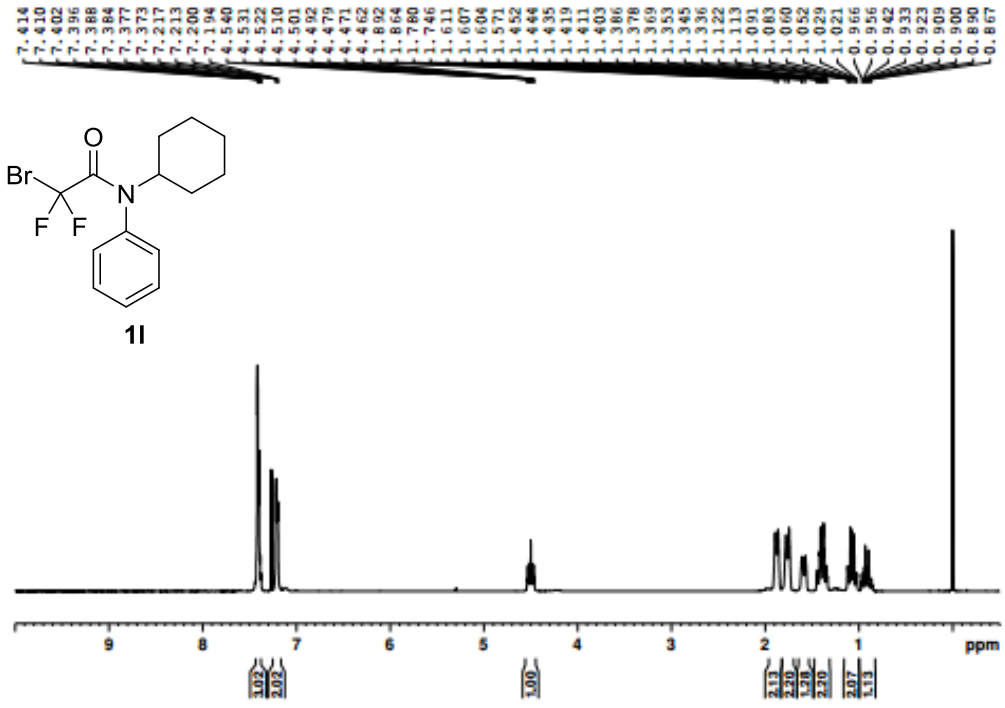
^{1}H NMR spectra of compound **1j.**



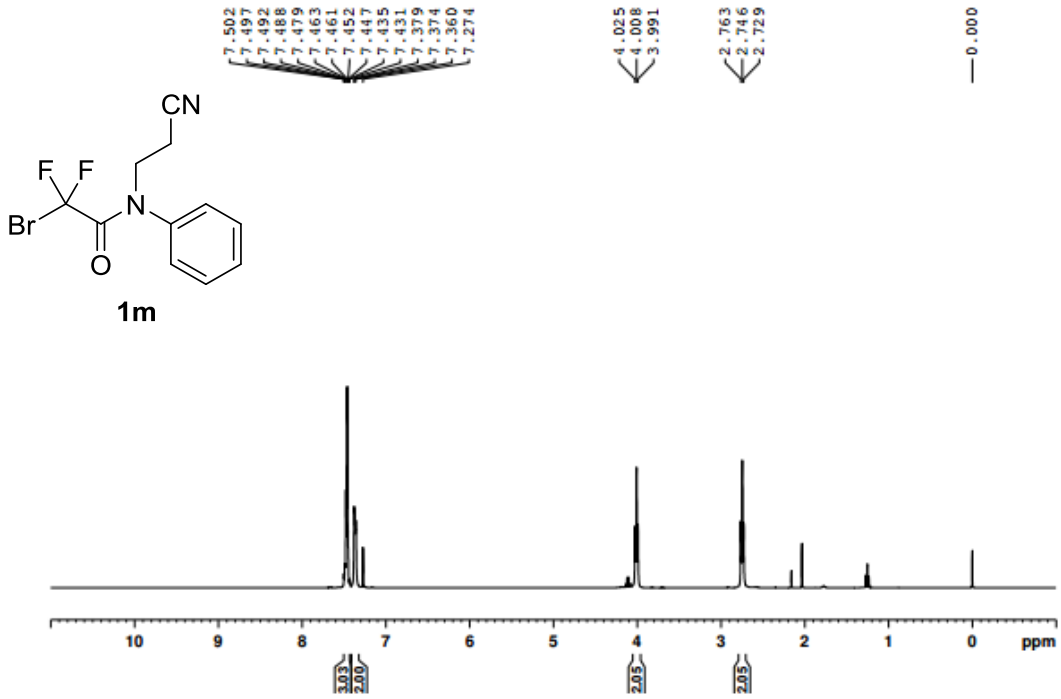
^{1}H NMR spectra of compound **1k.**



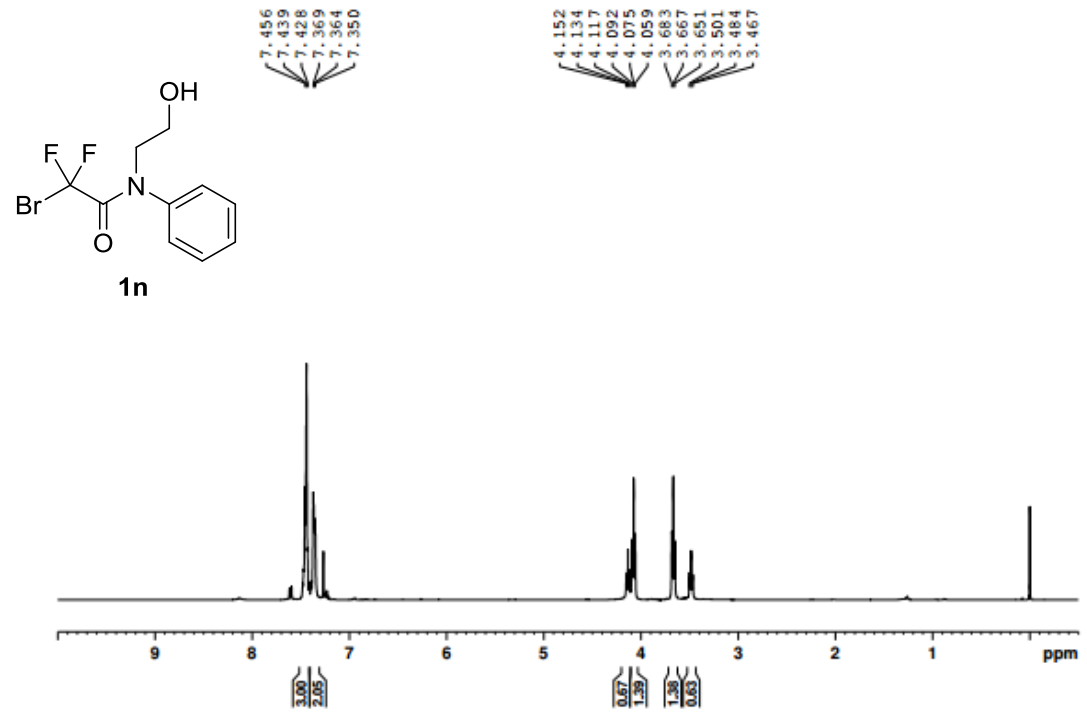
^{1}H NMR spectra of compound **1l.**



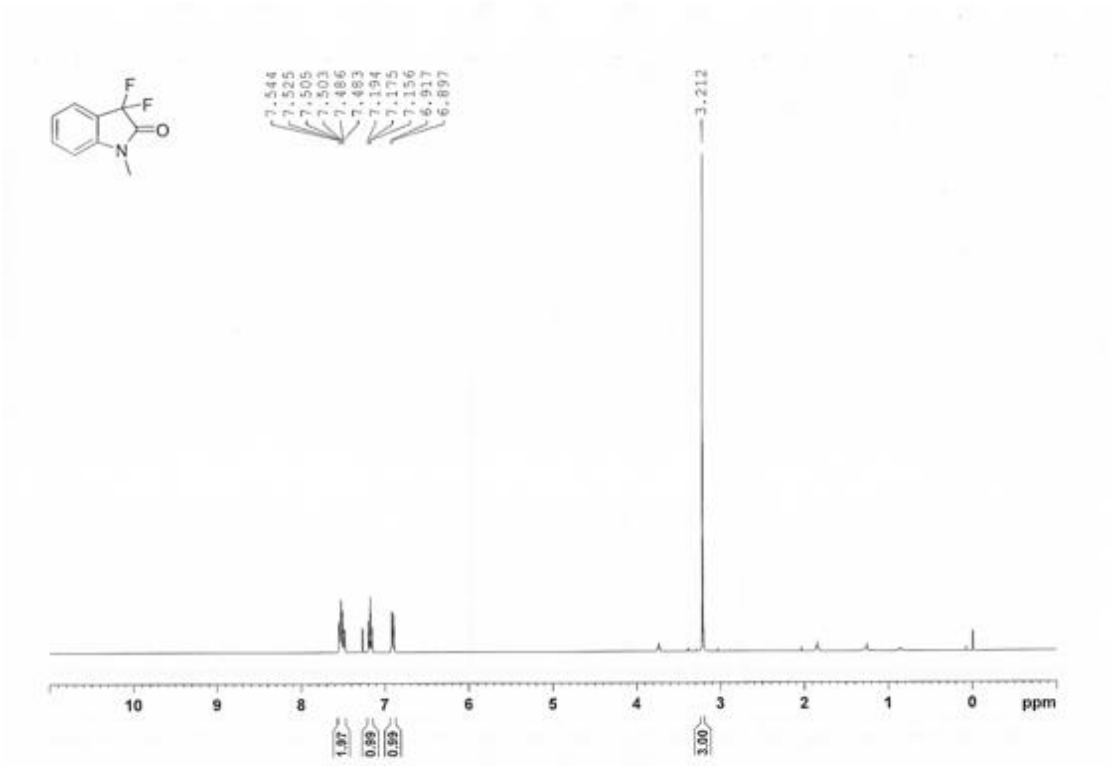
^{1}H NMR spectra of compound **1m.**

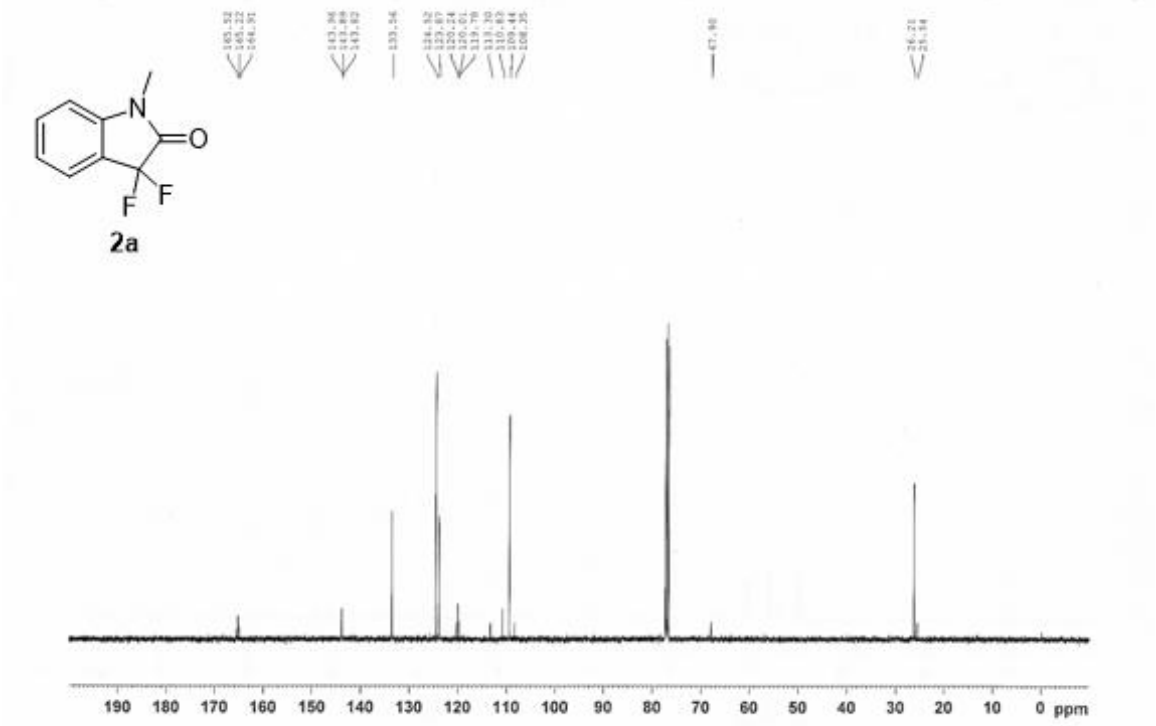


^{1}H NMR spectra of compound **1n.**

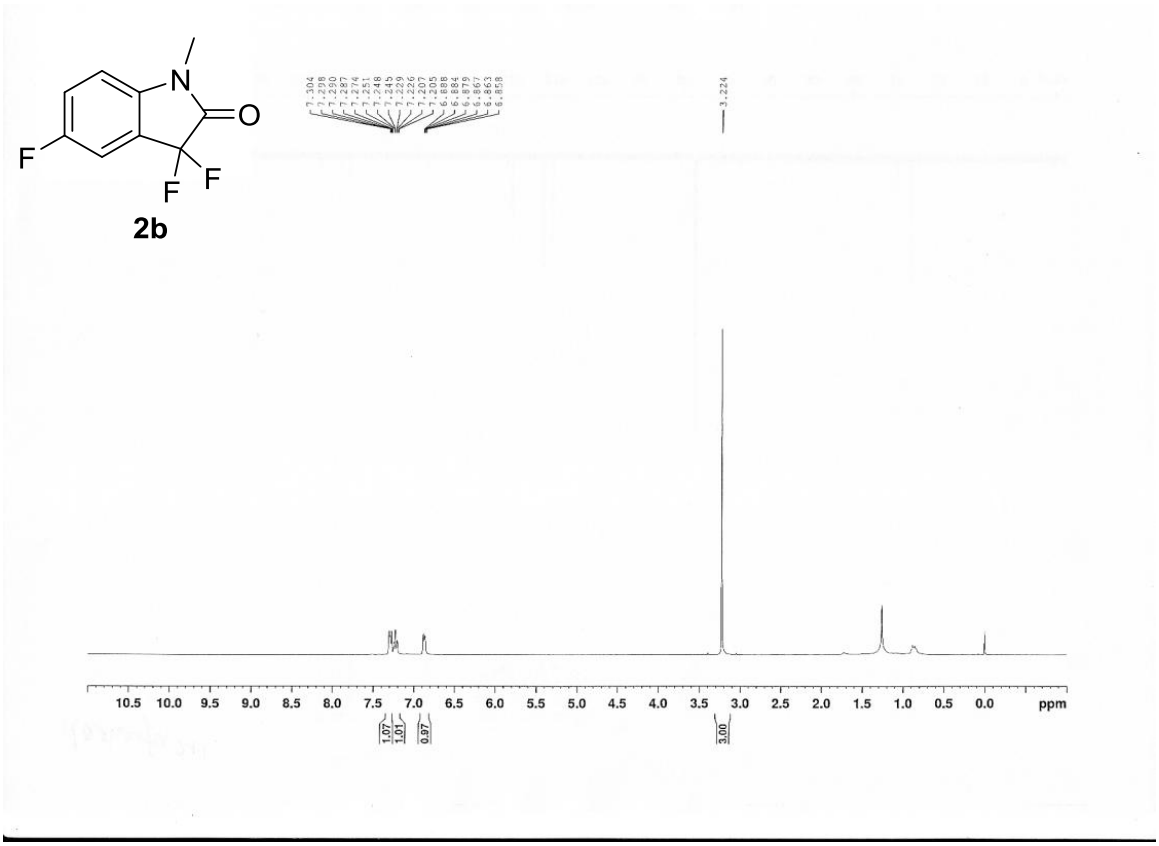


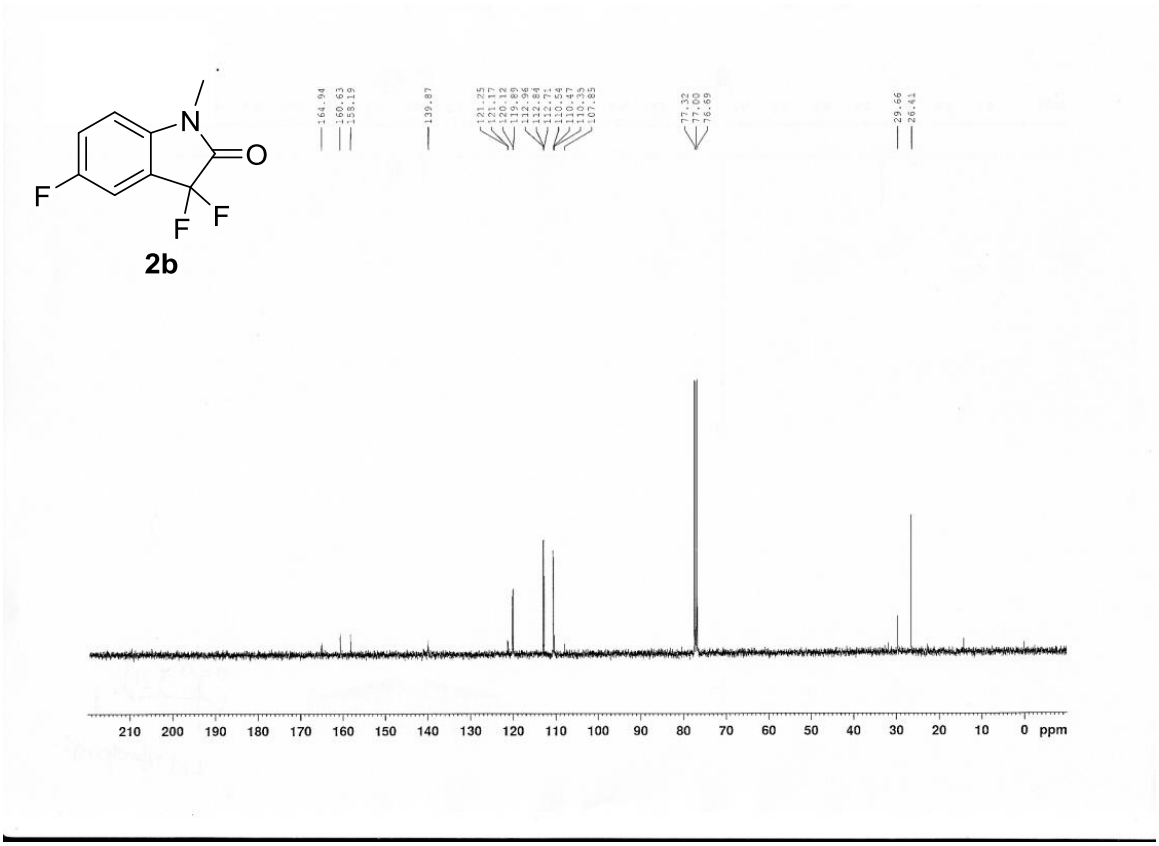
^{1}H NMR and ^{13}C NMR spectra of compound **2a.**



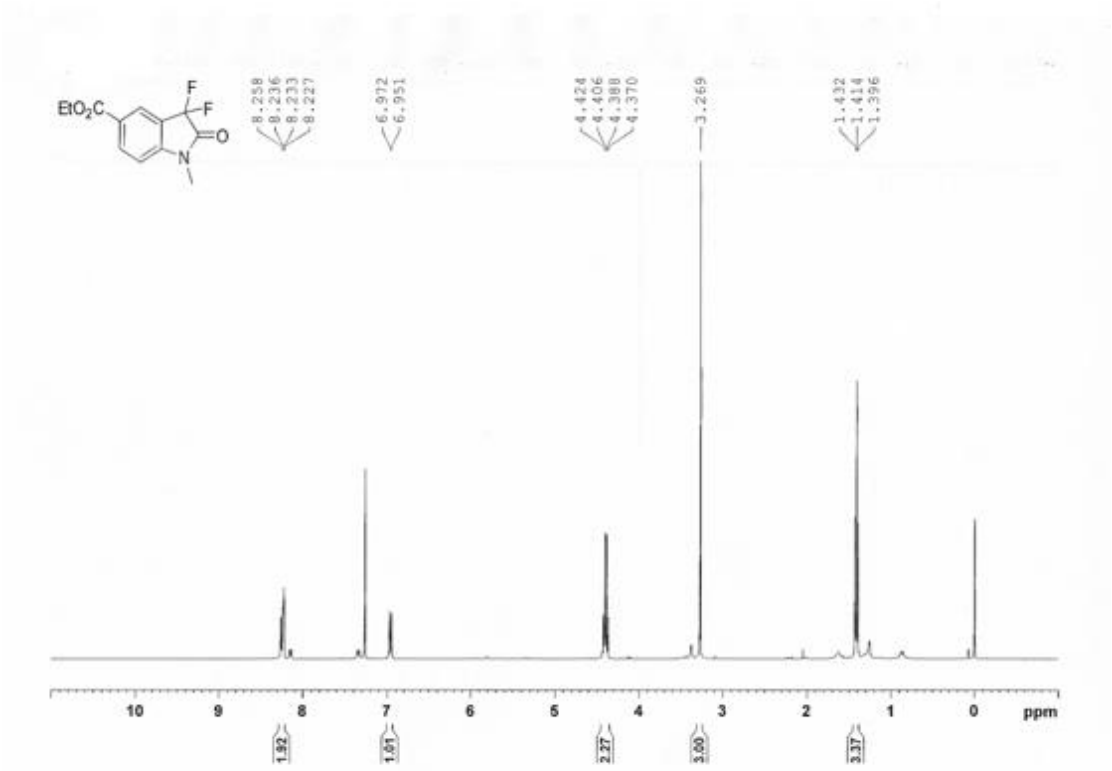


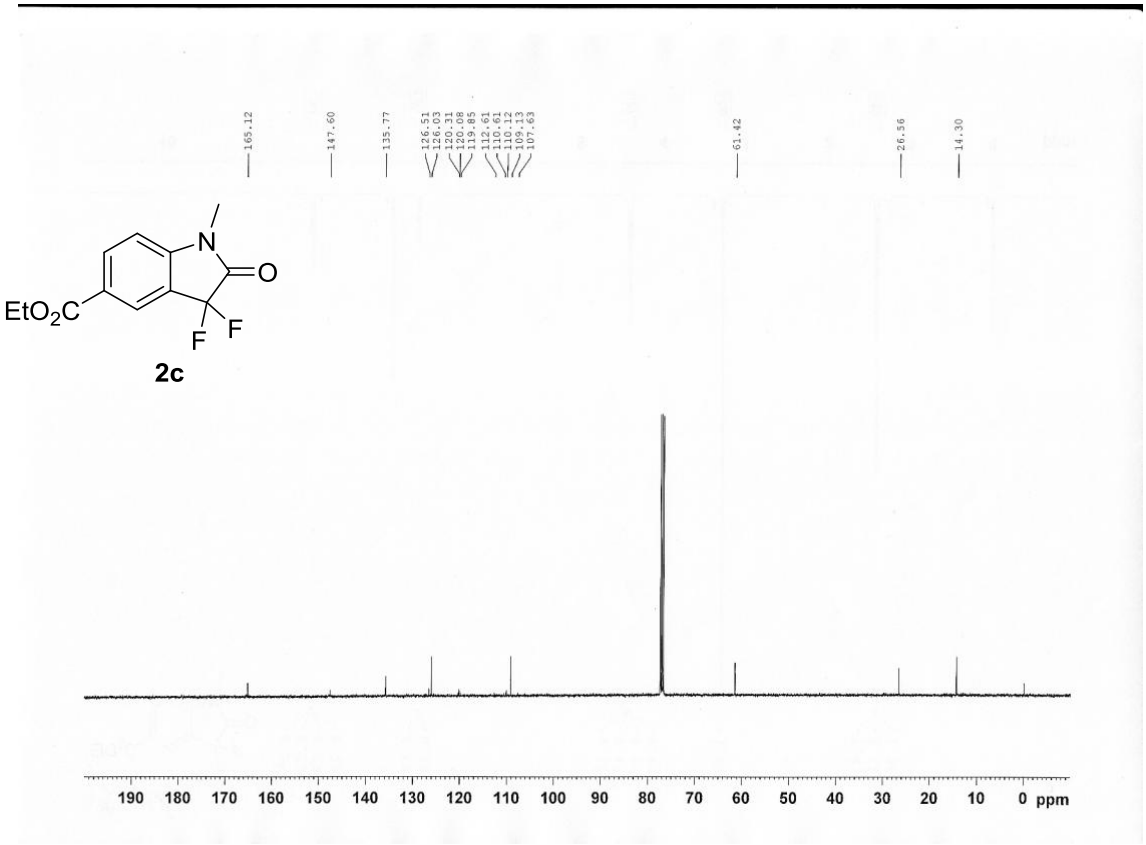
^{1}H NMR and ^{13}C NMR spectra of compound **2b.**

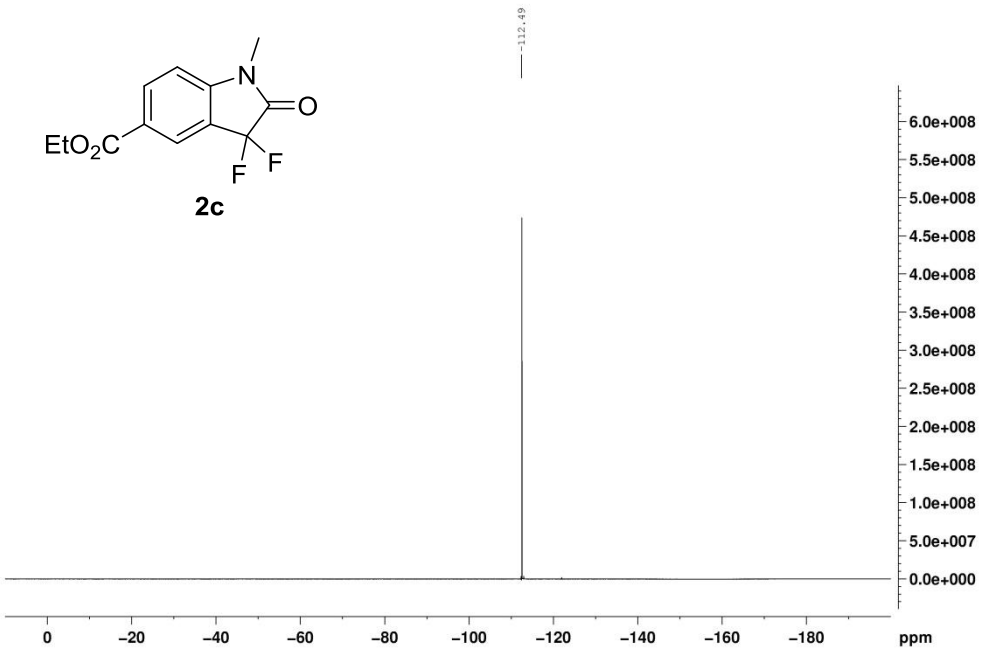




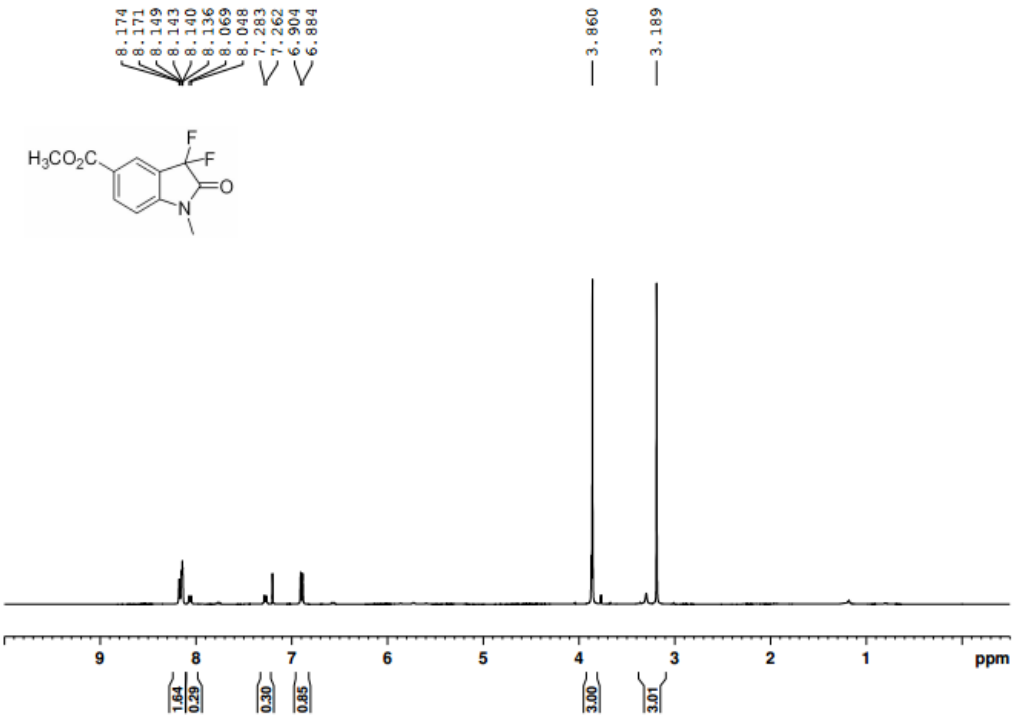
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **2c.**

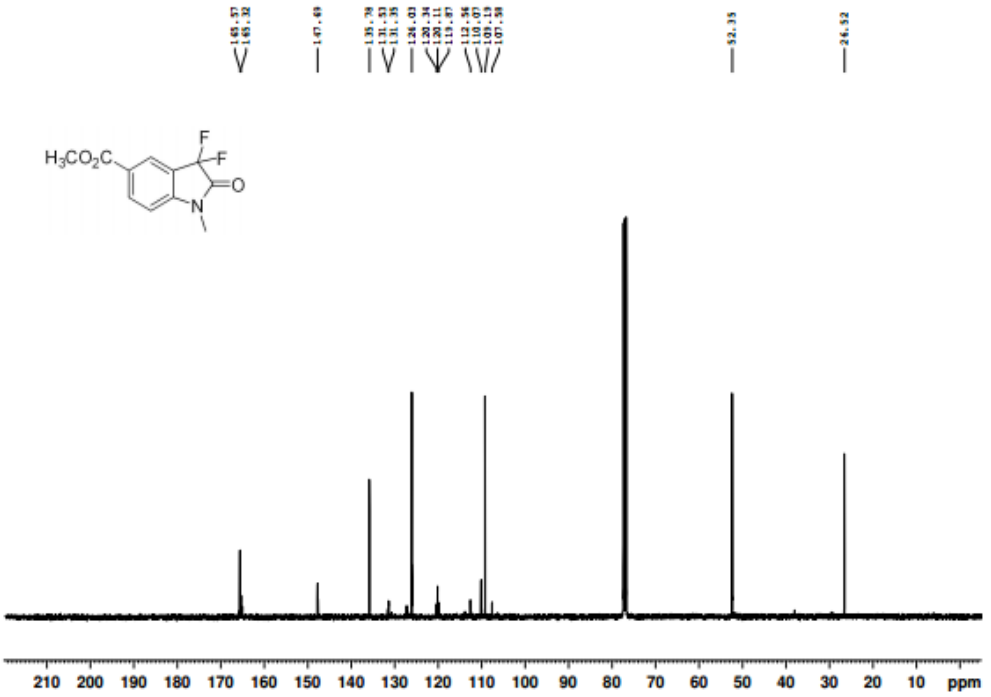




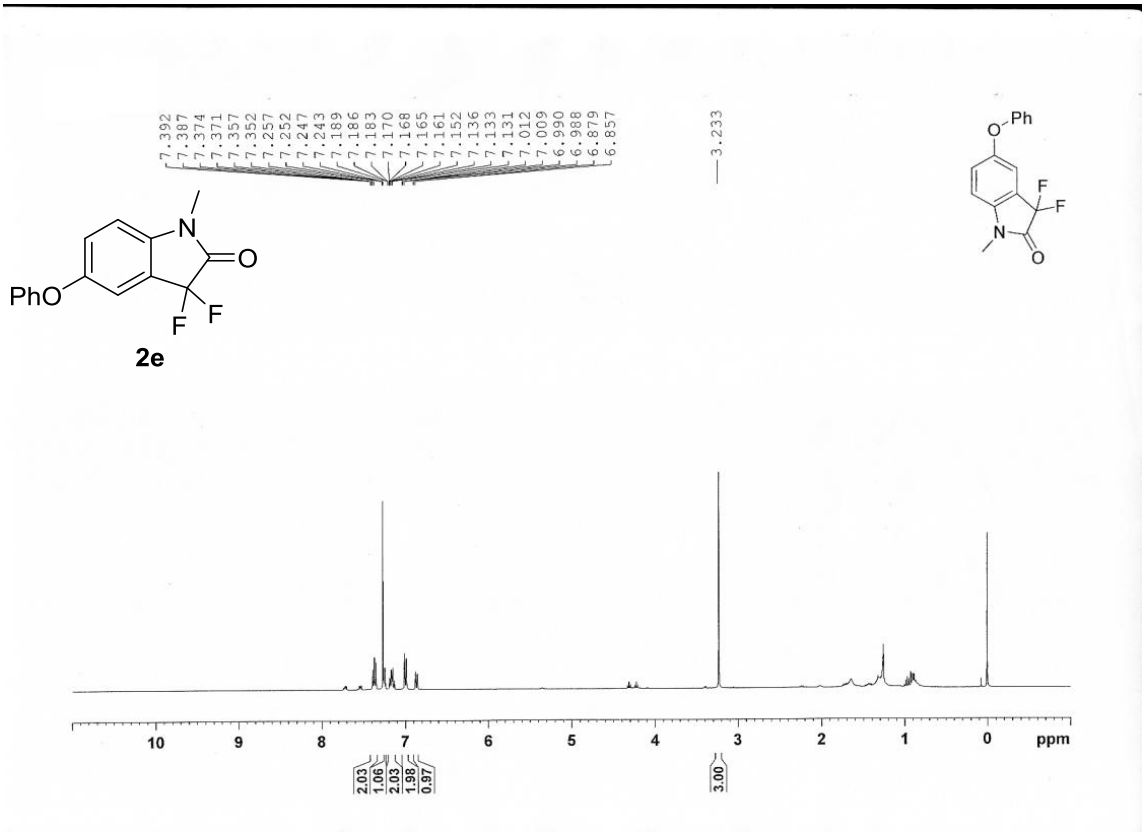


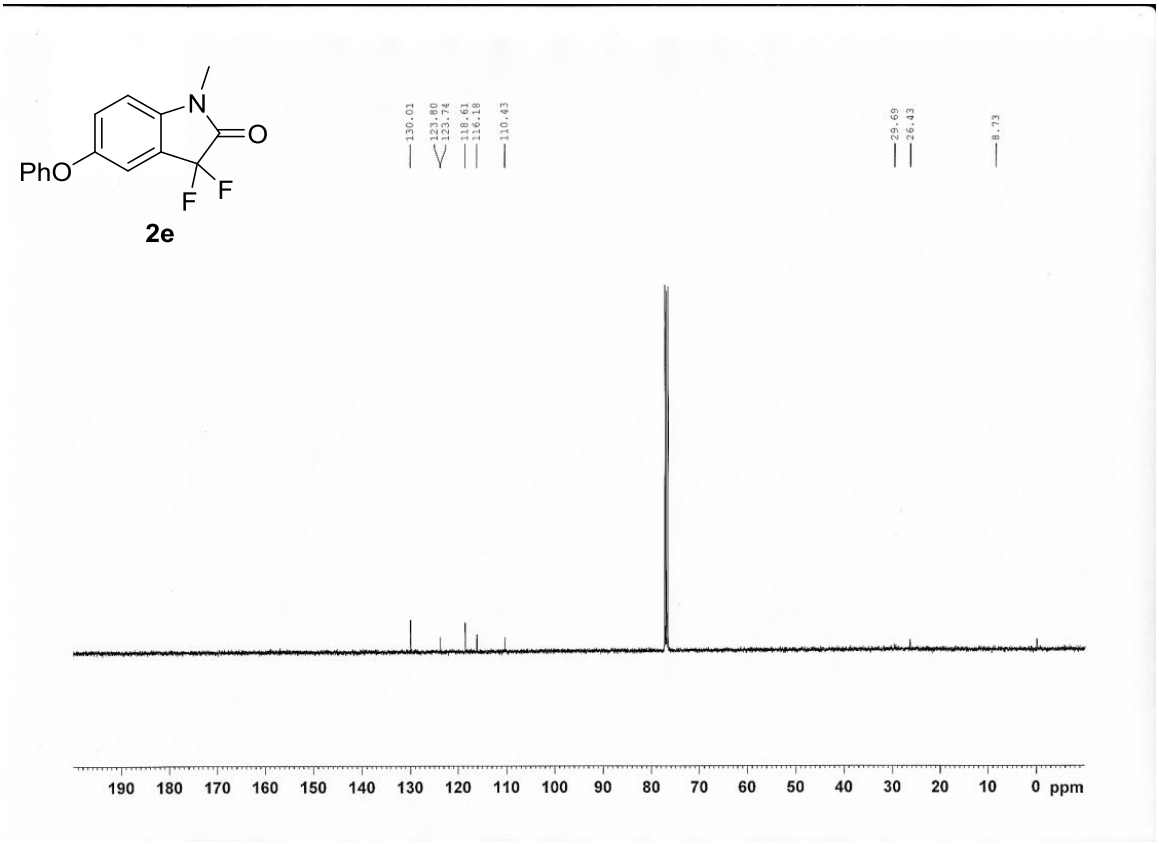
^{1}H NMR and ^{13}C NMR spectra of compound **2d.**

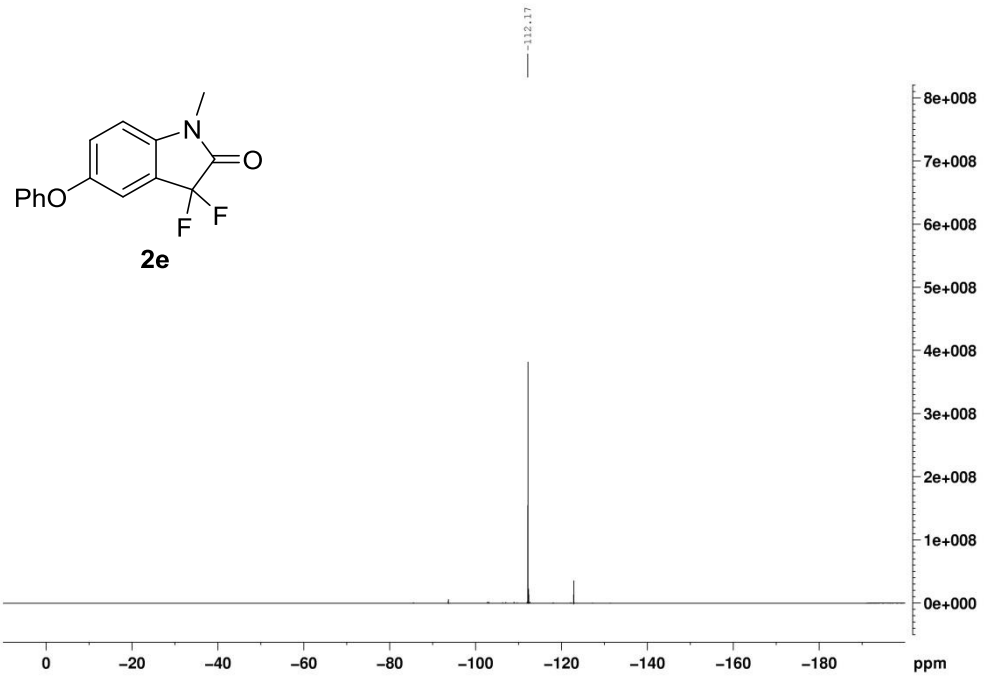




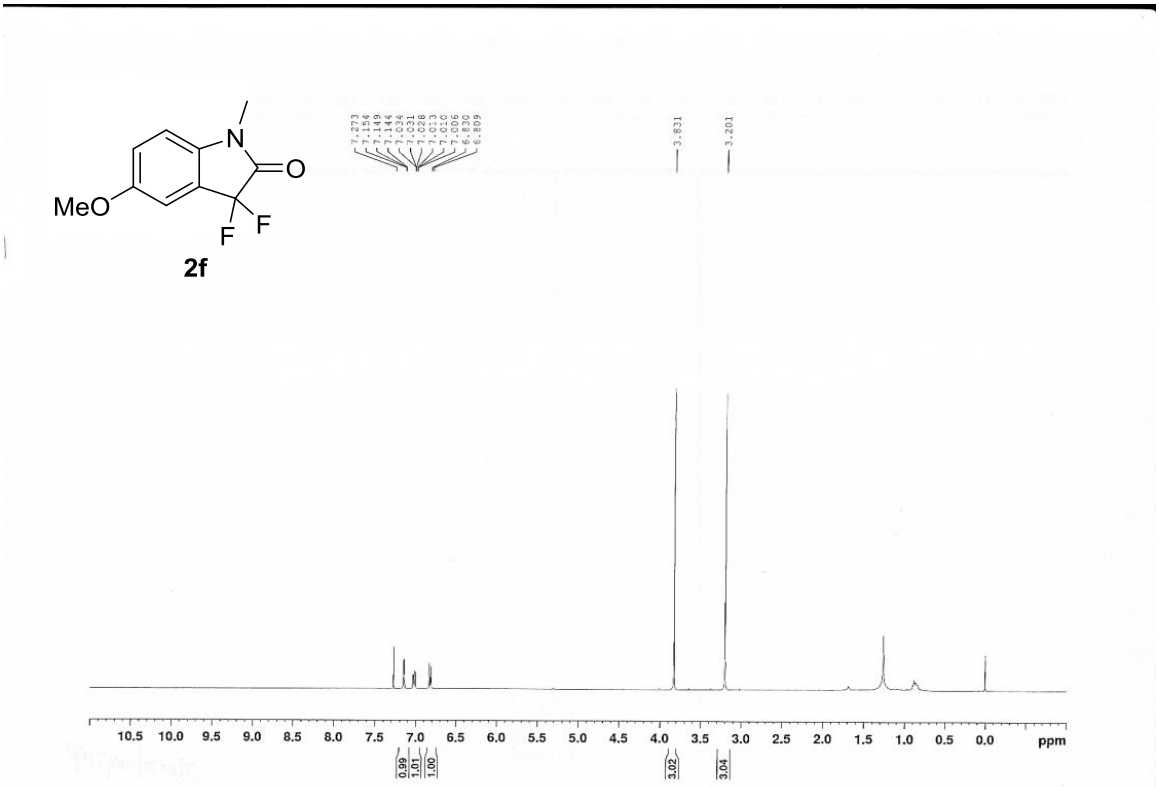
^{1}H NMR , ^{13}C NMR and ^{19}F NMR spectra of compound **2e.**

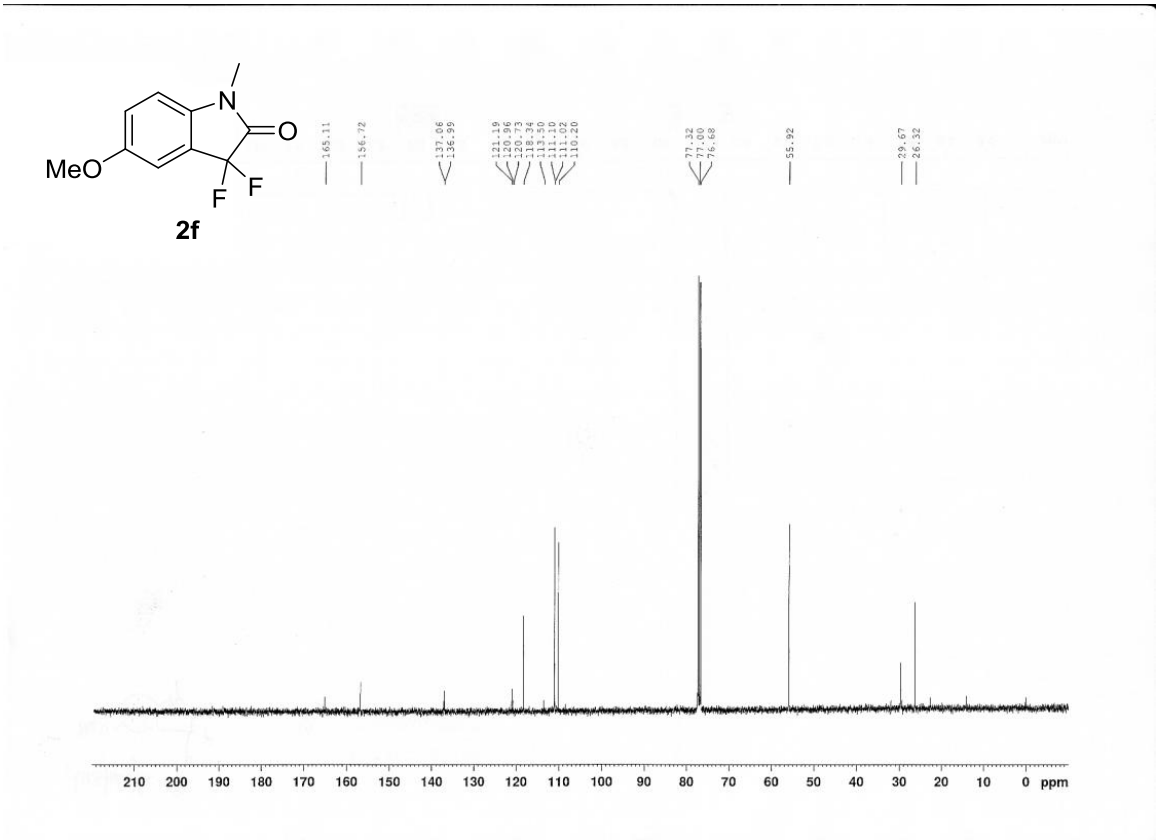



PhO
N
O
F
F
2e
130.01
123.80
123.74
118.61
116.18
110.43
29.69
26.43
8.73
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

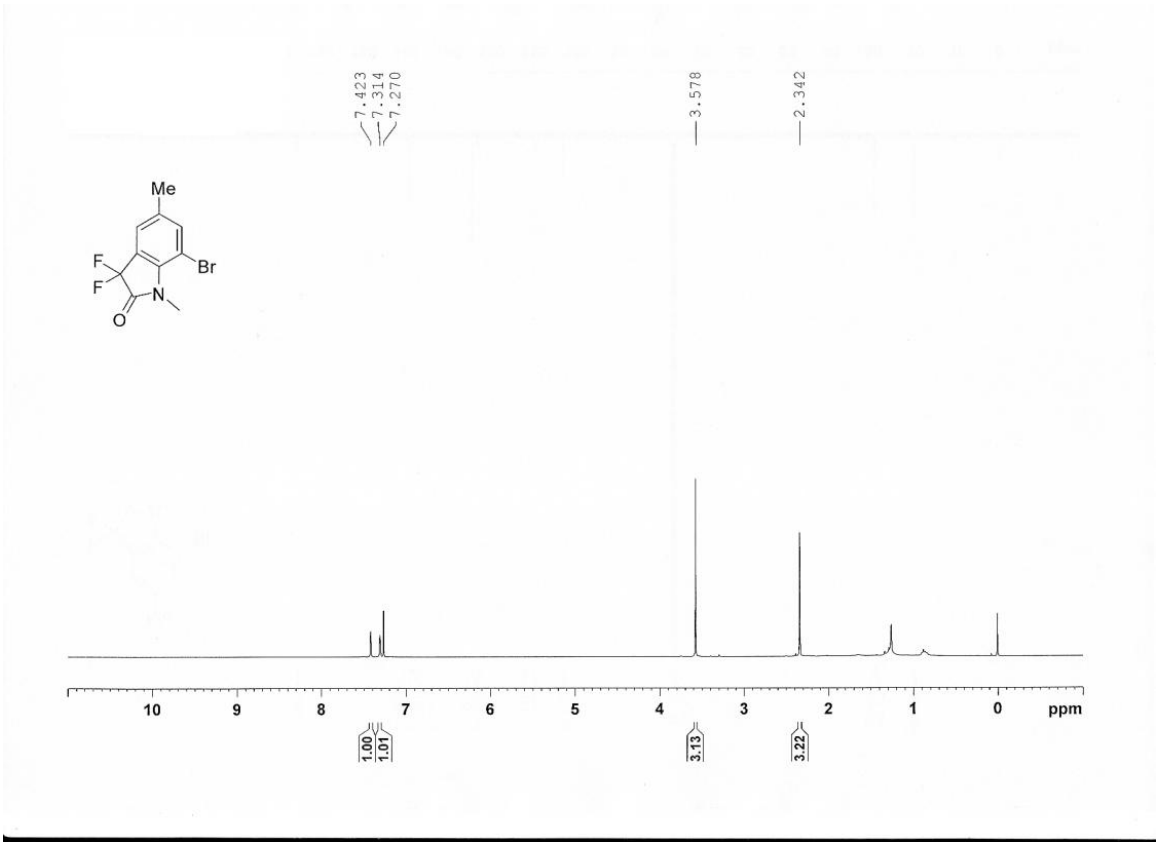

PhO
N
O
F
F
2e
-112.17
8e+008
7e+008
6e+008
5e+008
4e+008
3e+008
2e+008
1e+008
0e+000
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 ppm

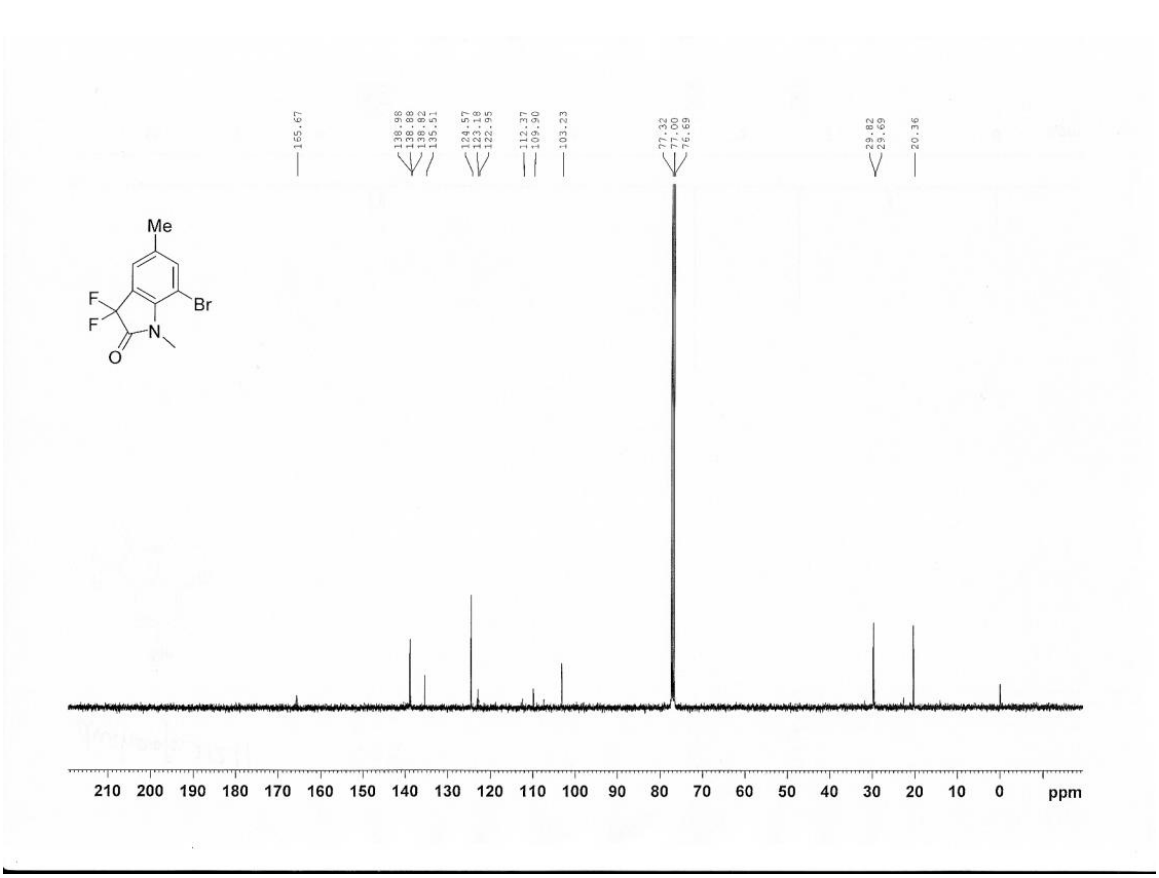
^{1}H NMR and ^{13}C NMR spectra of compound **2f.**



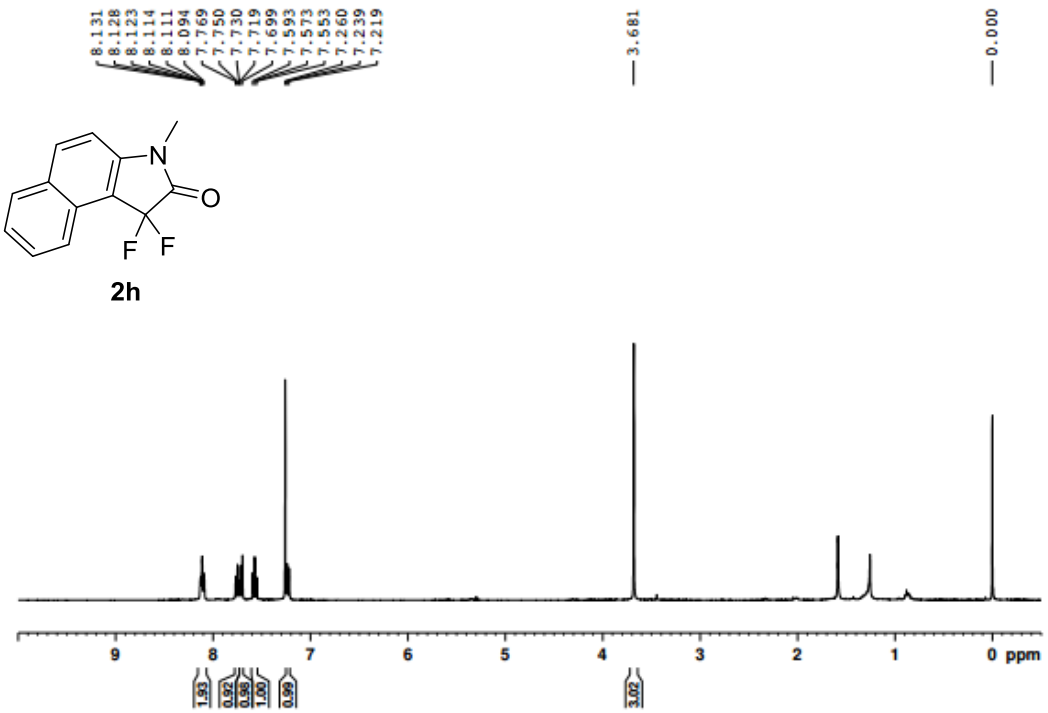


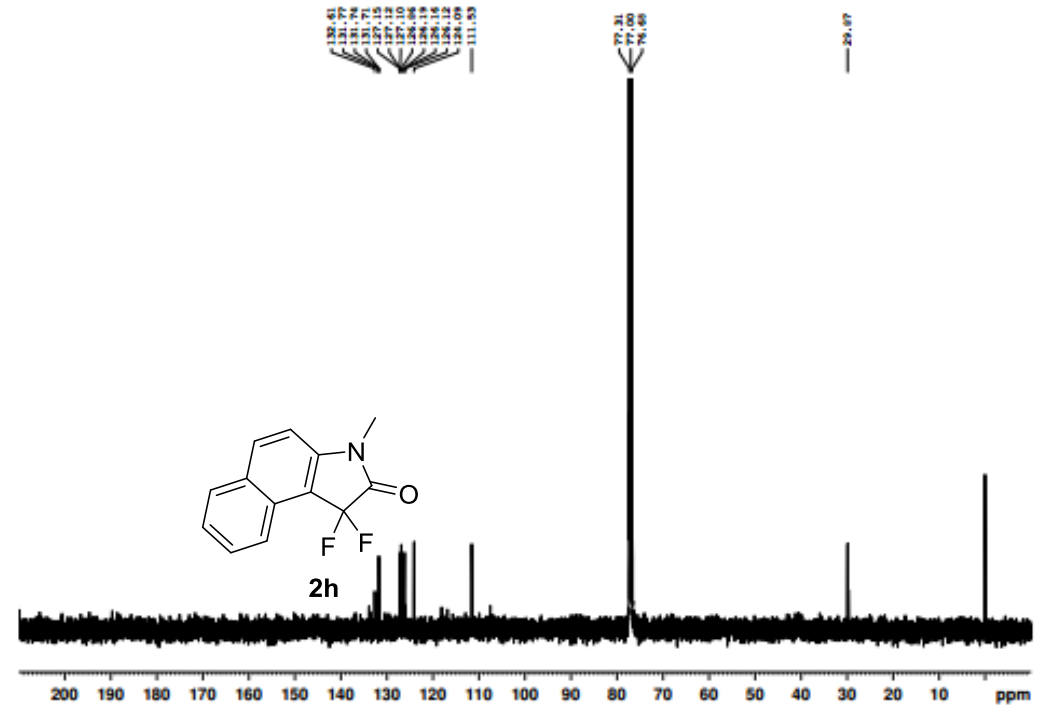
^{1}H NMR and ^{13}C NMR spectra of compound **2g.**

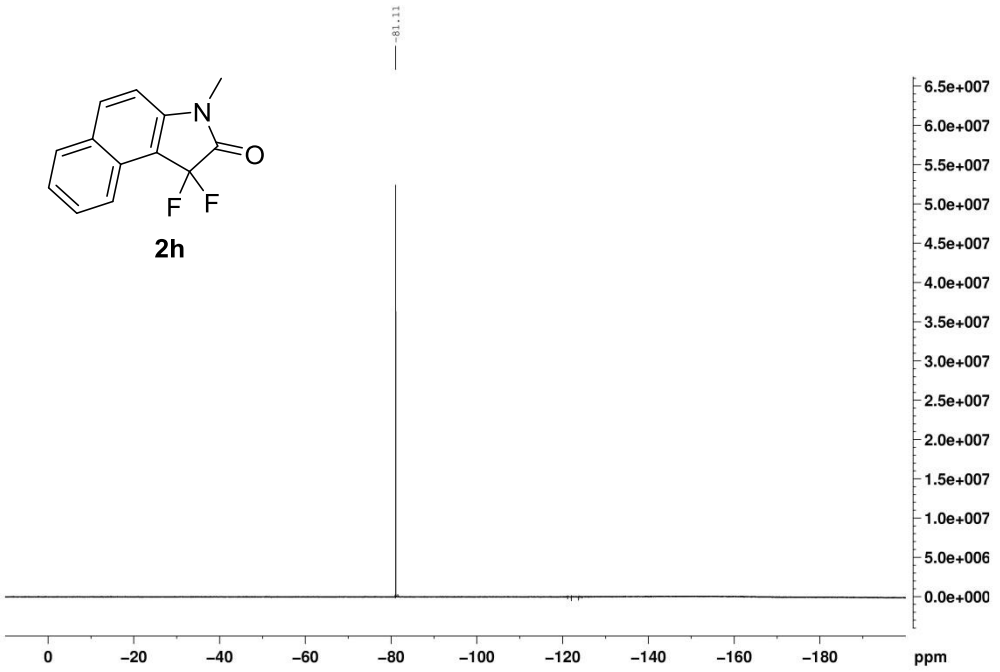




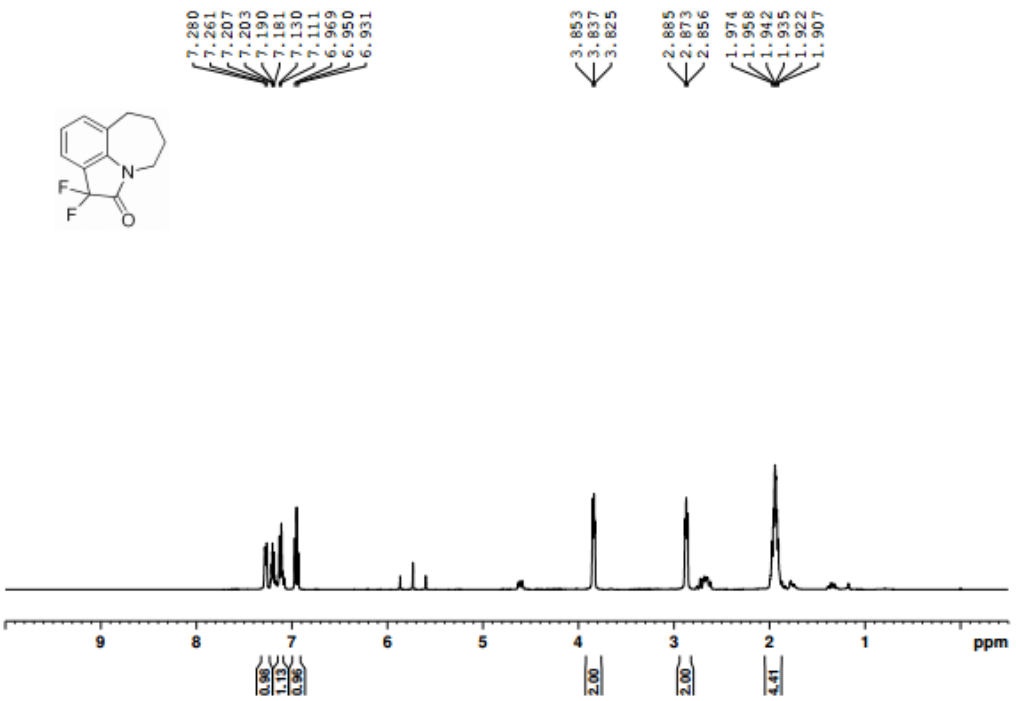
^{1}H NMR , ^{13}C NMR and ^{19}F NMR spectra of compound **2h.**

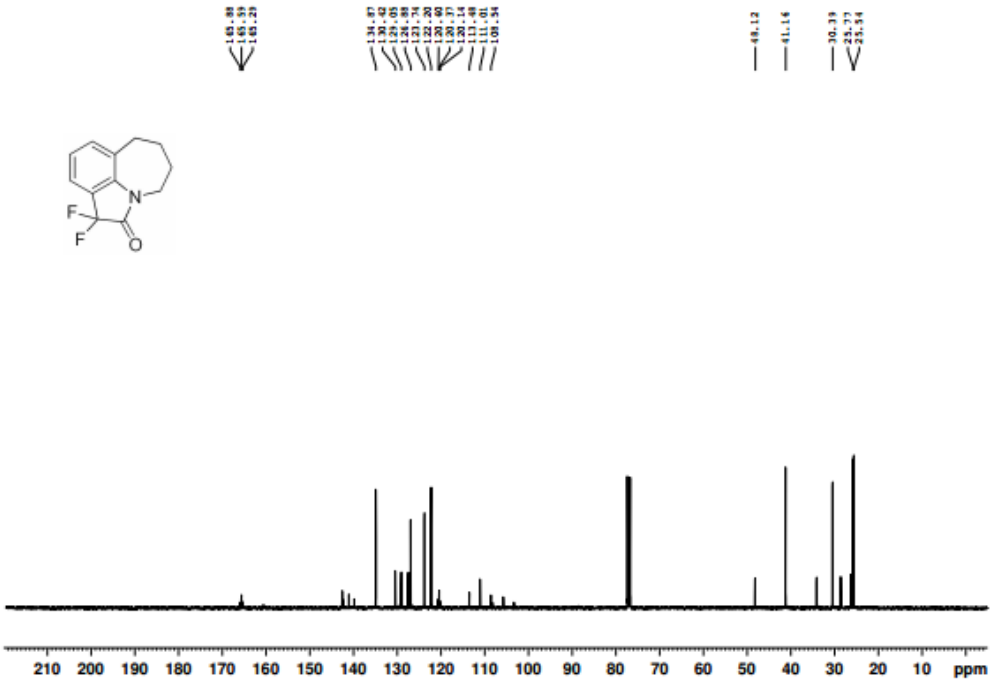




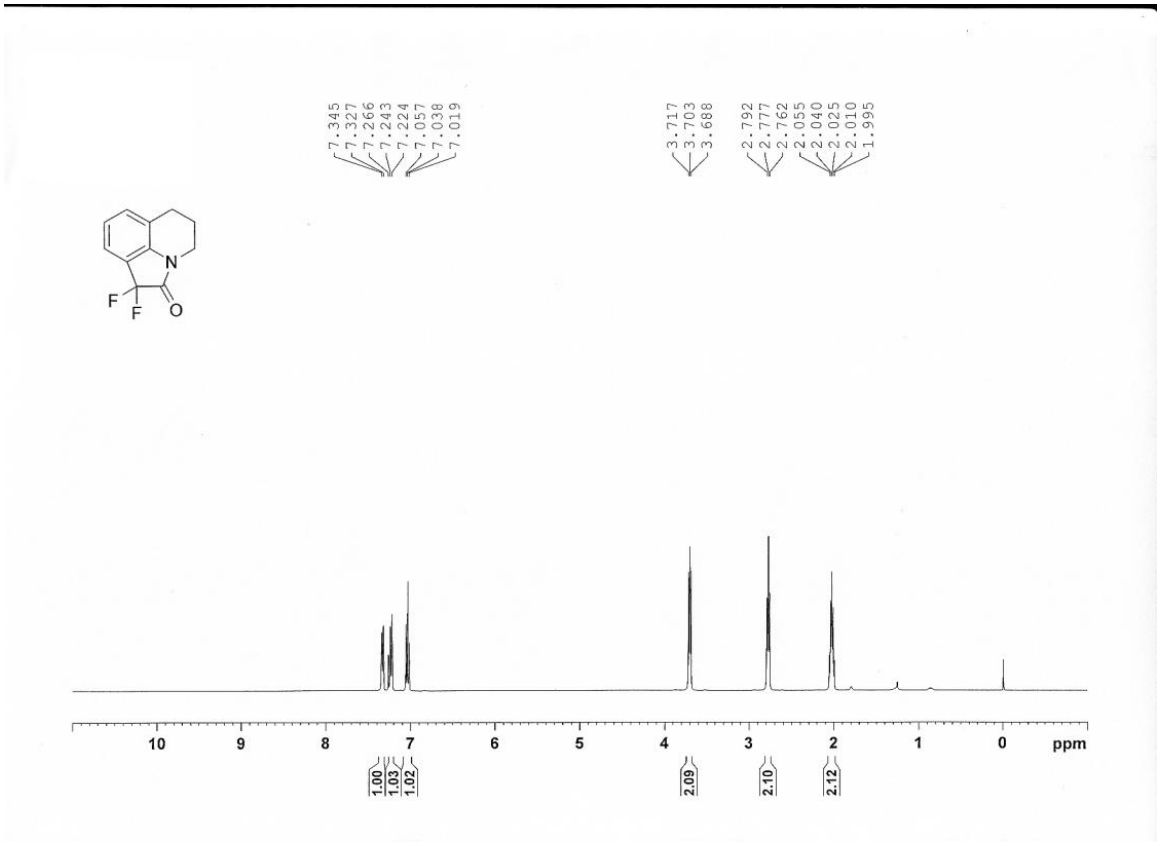


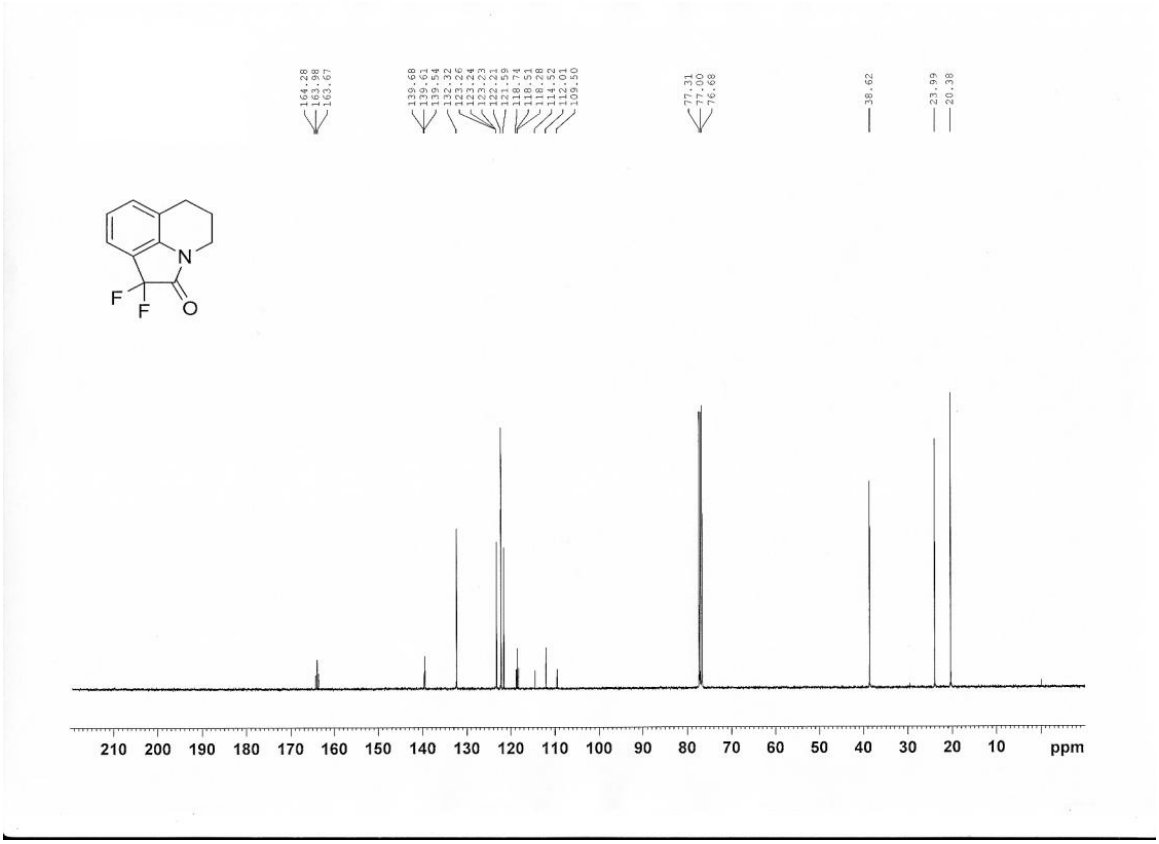
^{1}H NMR and ^{13}C NMR spectra of compound **2i.**



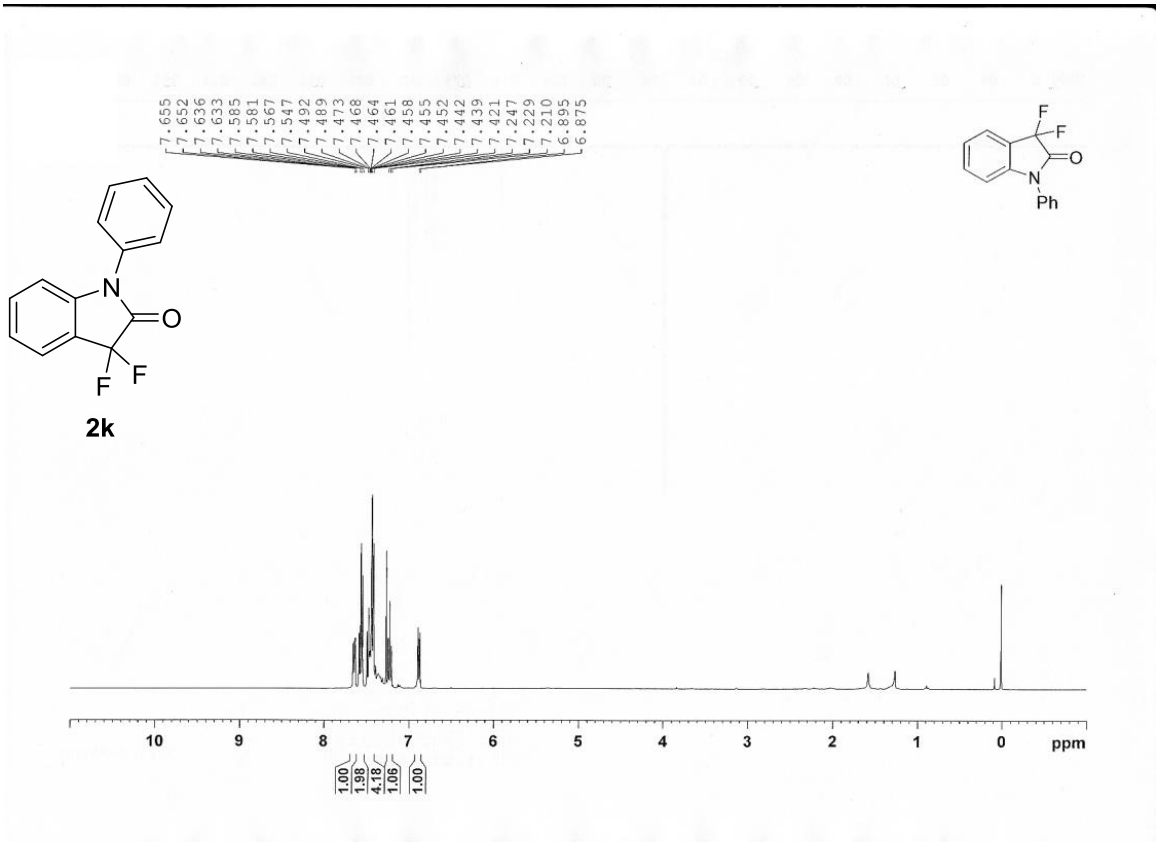


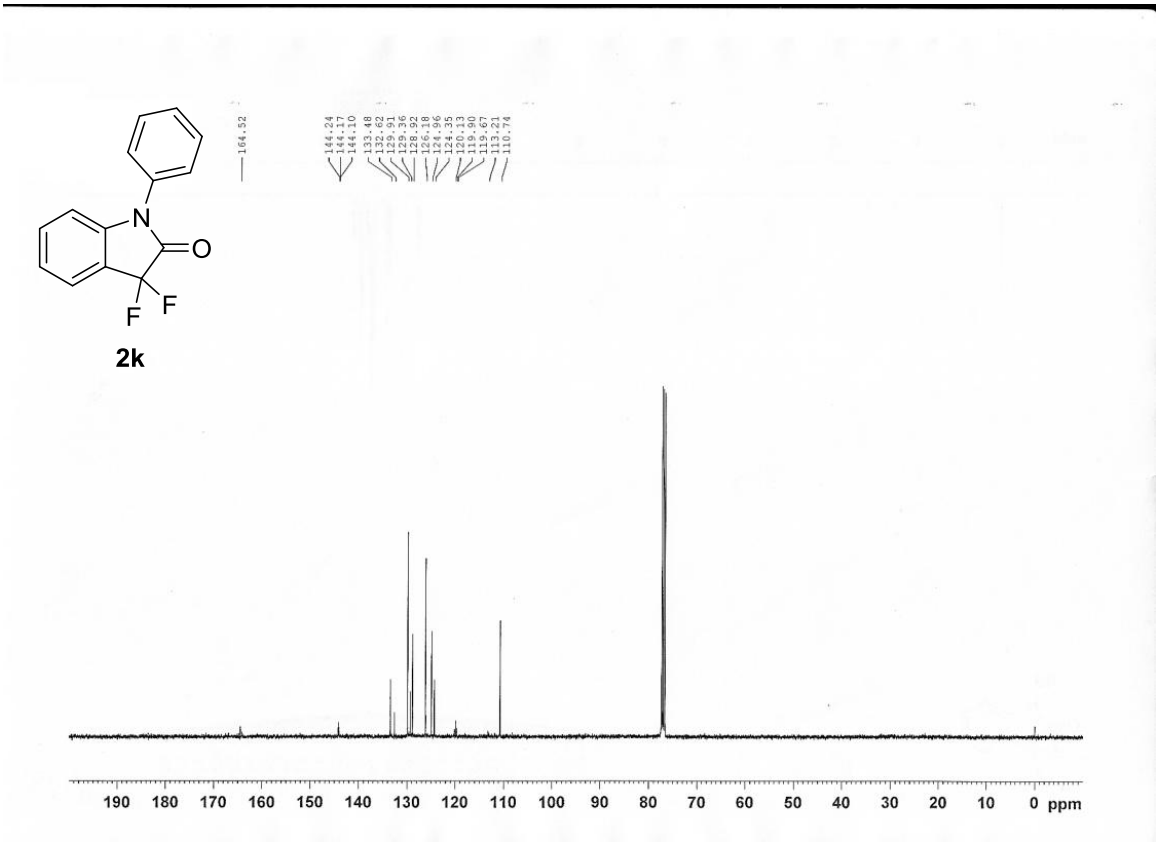
^{1}H NMR and ^{13}C NMR spectra of compound **2j.**



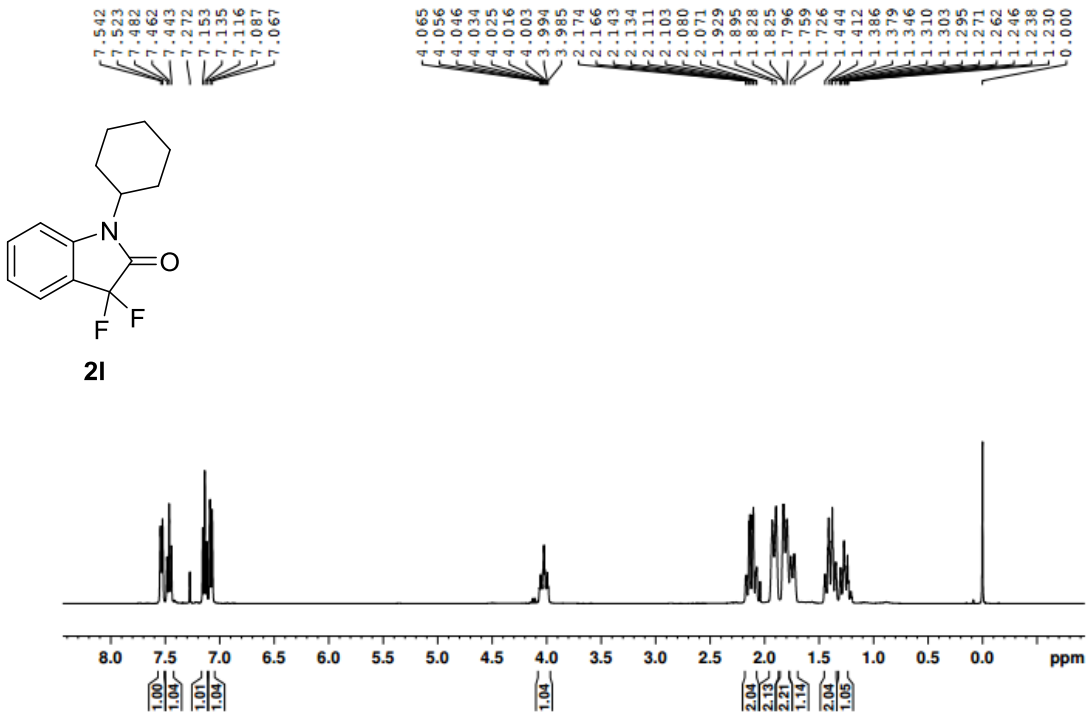


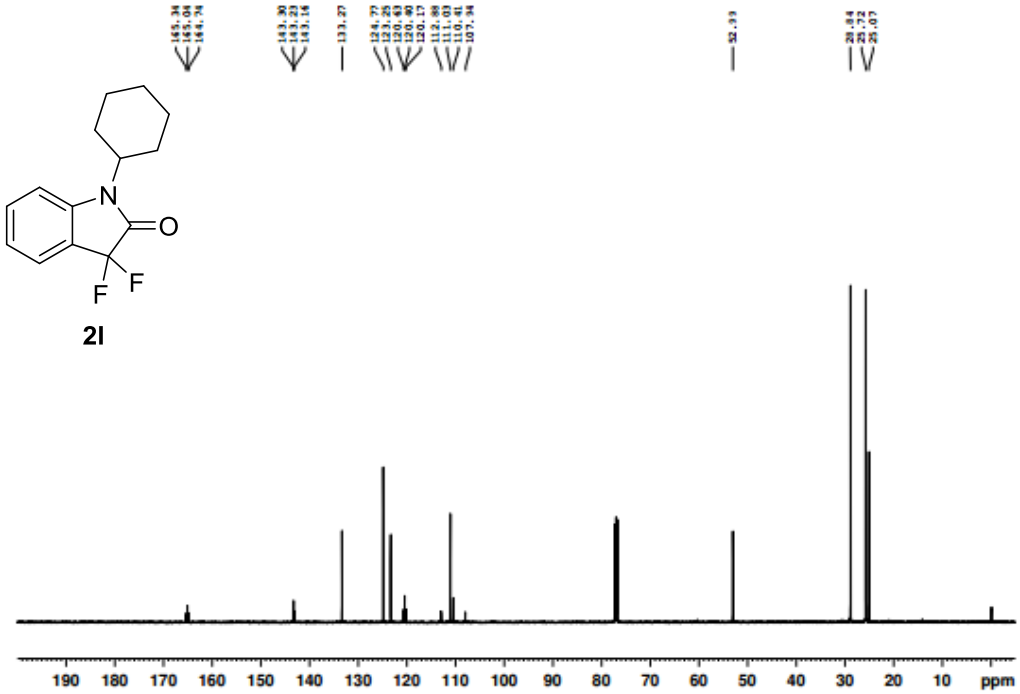
^{1}H NMR and ^{13}C NMR spectra of compound **2k.**

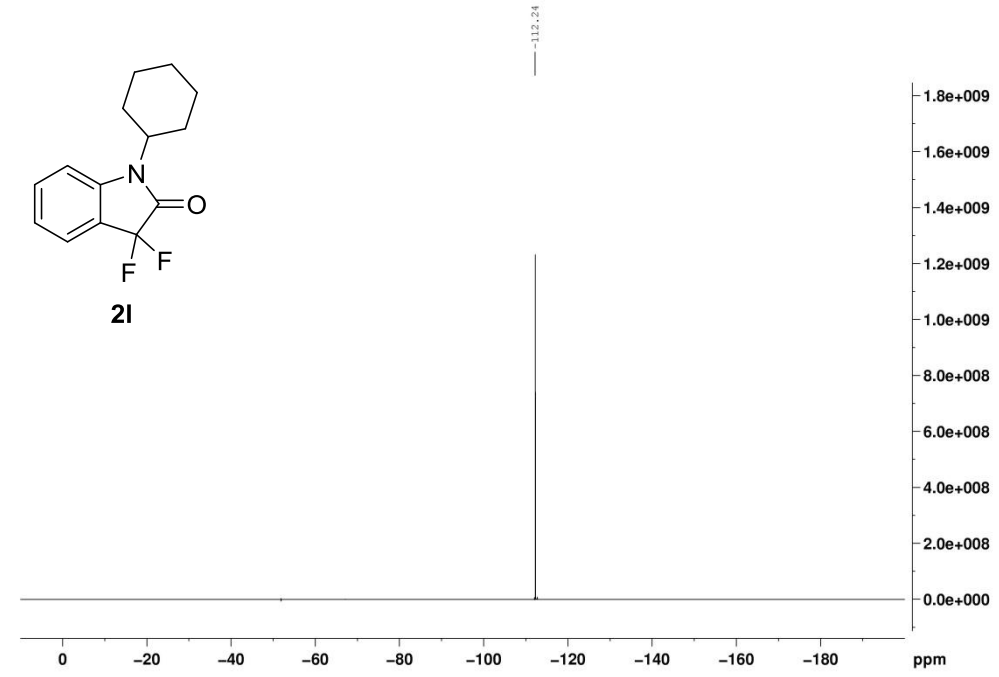




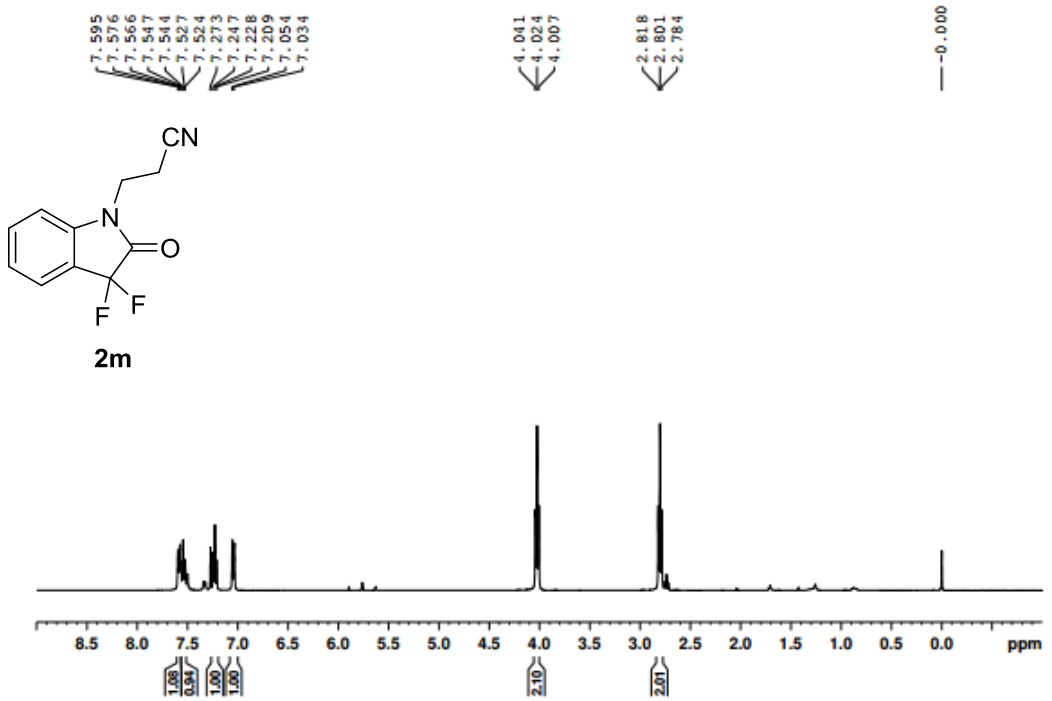
^{1}H NMR , ^{13}C NMR and ^{19}F NMR spectra of compound **2l.**



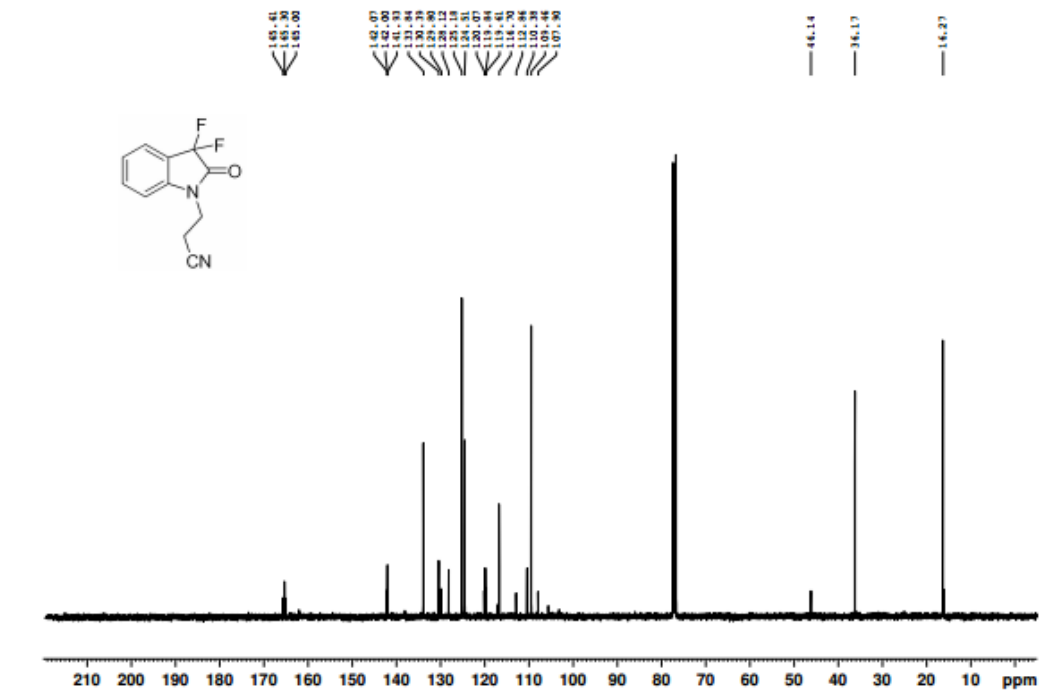

N
O
F
F
2l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

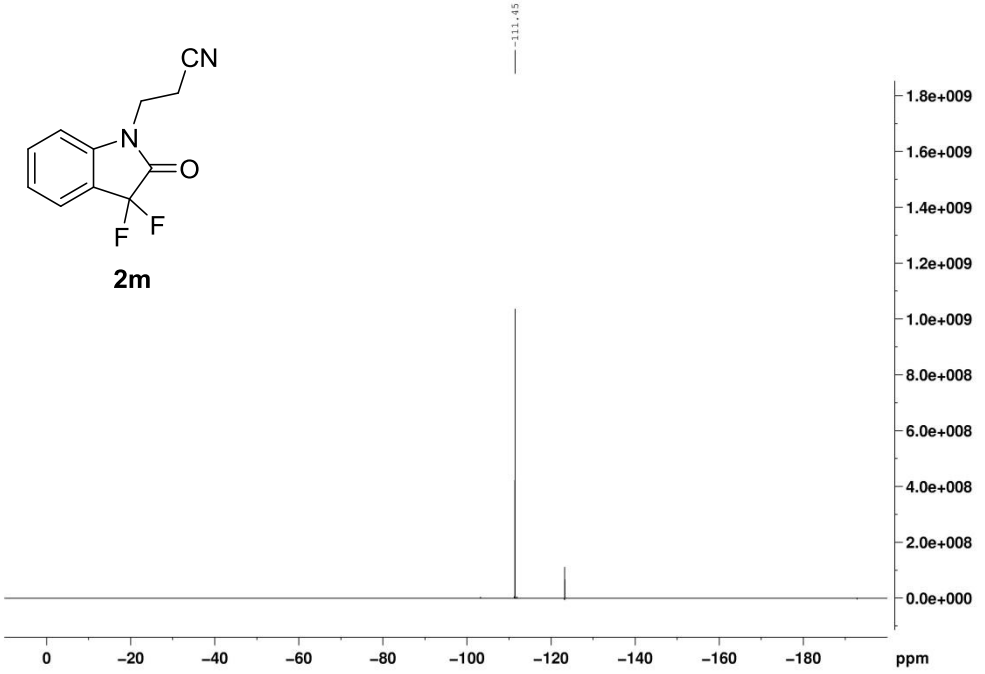

-112.24
N
O
F
F
2l
1.8e+009
1.6e+009
1.4e+009
1.2e+009
1.0e+009
8.0e+008
6.0e+008
4.0e+008
2.0e+008
0.0e+000
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 ppm

^{1}H NMR , ^{13}C NMR and ^{19}F NMR spectra of compound **2m.**

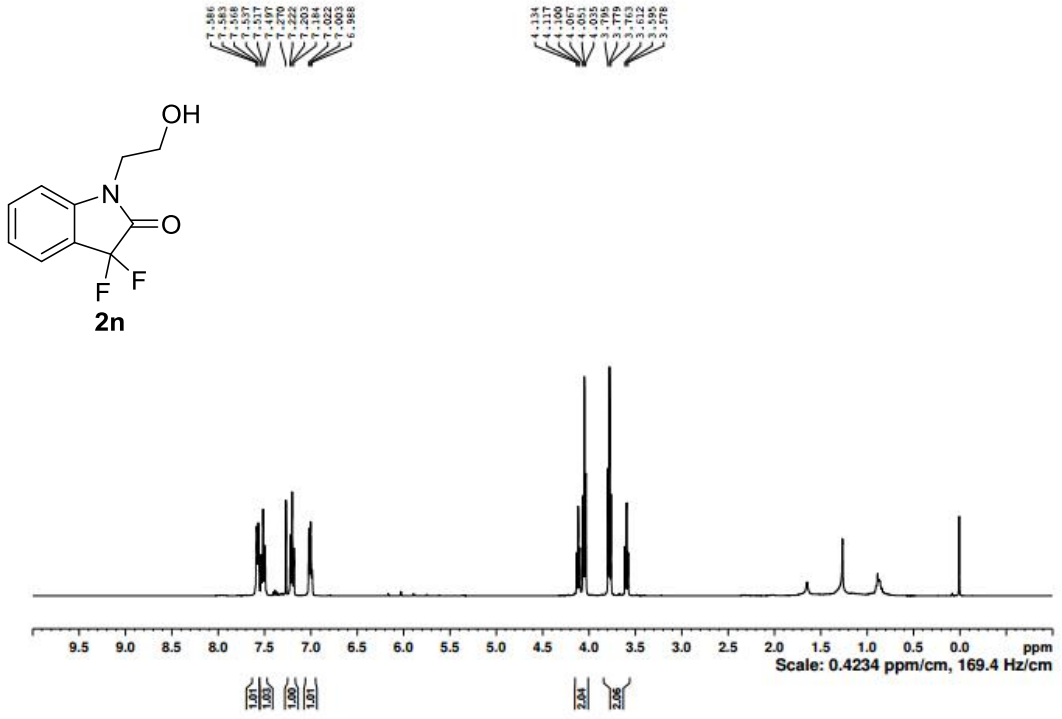


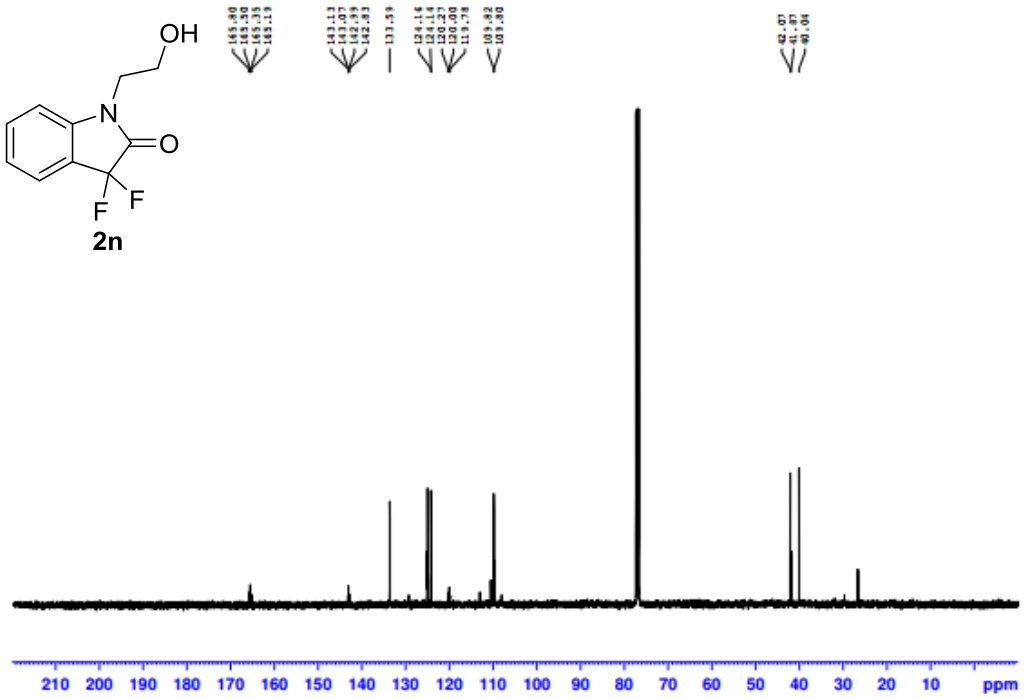
2m

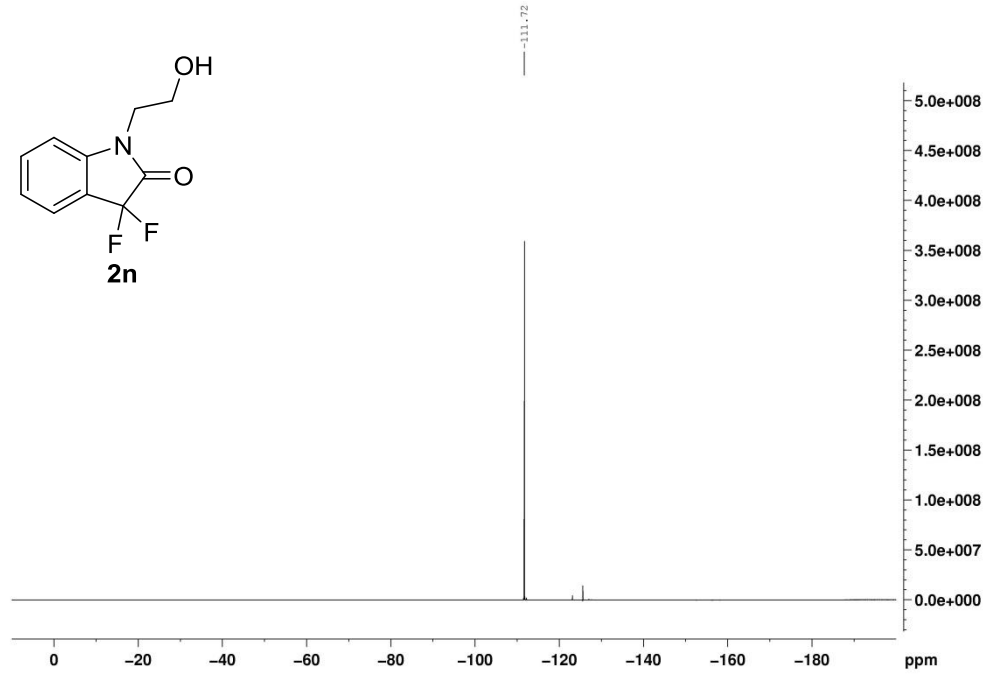




^{1}H NMR , ^{13}C NMR and ^{19}F NMR spectra of compound **2n.**




OH
N
O
F
F
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OH
N
O
F
F
2n
-111.72
5.0e+008
4.5e+008
4.0e+008
3.5e+008
3.0e+008
2.5e+008
2.0e+008
1.5e+008
1.0e+008
5.0e+007
0.0e+000
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 ppm