Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Bromide-catalyzed Electrochemical Trifluoromethyl/Cyclization of N-arylacrylamides with Low Catalyst Loading

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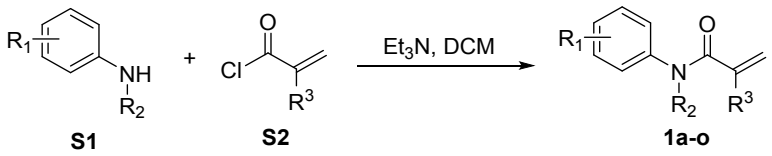
Table of Contents

1 General information

Unless otherwise special indicated, all the reagents were purchased from commercial supplies unless otherwise stated. And all the solvents were used without any purification. Thin-layer chromatography (TLC) was performed on plastic plates coated with silica gel GF254 with 0.2 mm thickness (Yantai Yuanbo Biological Technology Co., Ltd.) and all compounds were visualized with a UV light at 254nm. Flash column chromatography was performed using silica gel (300-400 mesh, Yantai Yuanbo Biological Technology Co., Ltd.). NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400 MHz or 300 MHz (^{1}H NMR) and 100 MHz or 75 MHz (^{13}C NMR). Chemical shifts were reported in ppm downfield and referenced as follows: ^{1}H: residual internal $CHCl_3$ (δ 7.26 ppm); ^{13}C: internal $CDCl_3$ (δ 77.2 ppm). Coupling constants were quoted in Hz(*J*). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

2 General procedure for the synthesis of starting materials 1[1]



S1 **S2** **1a-o**

In a typical procedure, *N*-substituted aminobenzene **S1** (10 mmol, 1.0 equiv.) was dissolved in 20 mL dry DCM and cooled to 0 °C. After addition of Et_3N (1.2134 g, 12 mmol, 1.2 equiv.), acid chloride **S2** (12 mmol, 1.2 equiv.) dissolved in 10 mL dry DCM was added dropwise and the mixture was stirred at r.t. for 6 h. After completion of the reaction, saturated aqueous $NaHCO_3$ (10 mL) was added and the reaction mixture was extracted with DCM (3 x 20 mL). The combined organic phases were washed with 1 M HCl (3 x 10 mL), brine (3 x 10 mL) and water (3 x 10 mL), dried over Na_2SO_4, and contracted *in vacuo*. The residue was purified by column chromatography on silica gel.

3 General procedure for the synthesis of trifluoromethyl-substituted oxoindoles 3

An undivided cell was equipped with a carbon anode (2.50 × 2 cm^2) and a Pt wire cathode (2.5 × 2 cm^2) and connected to a DC regulated power supply (Figure S1). To the cell was

added acrylamide (0.5 mmol), sodium sulfonate (1.5 mmol), *n*-Bu_4NBr (2 mol %) and 12 mL of CH_3CN. The mixture was electrolyzed using constant current conditions (~2 mA cm^{-2}) at 75 ^oC under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the acrylamide), the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous solution of $Na_2S_2O_3$ and the product was then extracted with DCM (3×20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired pure product.

Figure S1. The structure of the undivided cell

4 Optimization of the reaction conditions

Table S1. Optimization of Reaction Condition [a]

Entry	**1a**/**2a**	Catalyst (mol %)	Solvent (V:V)	Yield (%)[b]
1	1/1.2	NH_4Br (50)	1,4-dioxane:H_2O (1:1)	19
2	1/1.5	NH_4Br (50)	1,4-dioxane:H_2O (1:1)	35
3	1/3	NH_4Br (50)	1,4-dioxane:H_2O (1:1)	50
4	1/4	NH_4Br (50)	1,4-dioxane:H_2O (1:1)	42

[a] Reaction conditions: **1a** (1.0 mmol) and **2a** in 12 mL of solvent, undivided cell, 75 ^oC, current density of 2 mA cm^{-2}, graphite plate anode and cathode (working area: 5 cm^2) and electrolyze for 8 hours. [b] Yield determined by ^{1} HNMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

5 General procedure of control experiments

A divided cell was equipped with a carbon anode (2.50 × 2 cm^2) and a Pt wire cathode (2.5 × 2 cm^2) and connected to a DC regulated power supply (Figure S2).

For the anodic reaction, the anodic cell was added **1a** (0.5 mmol), **2a** (1.5 mmol), *n*-Bu_4NBr (2 mol %) and 12 mL of CH_3CN. The cathodic cell was only added 12 mL of 0.1 M $LiClO_4/CH_3CN$.

For the cathodic reaction, the cathodic cell was added 1a (0.5 mmol), 4 (1.5 mmol) and 12 mL of 0.1 M $LiClO_4/CH_3CN$. The anodic cell was only added 12 mL of 0.1 M $LiClO_4/CH_3CN$.

The mixture was electrolyzed using constant current conditions (~2 mA cm^{-2}) at 75 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the **1a**), the solvent (in the anodic cell or cathodic cell) was removed under reduced pressure. The residue was poured into a saturated aqueous solution of $Na_2S_2O_3$ and the product was then extracted with DCM (3×20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired pure product.

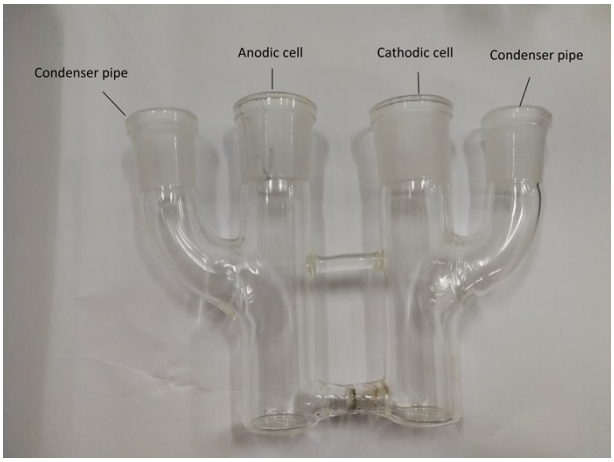
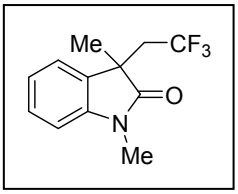


Figure S2. The structure of the divided cell

6 Characterization data of the trifluoromethyl-substituted oxoindoles 3a-o

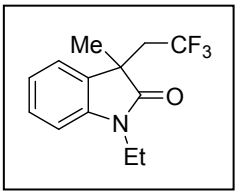
1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3a) [2]



Following the general procedure, the title compound was obtained as colorless oil, 91.1 mg, 75%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.39 (s, 3H), 2.56-2.72 (m, 1H), 2.73-2.89 (m, 1H), 3.21 (s, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.24-7.32 (m, 2H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 24.8, 26.2, 40.5 (q, J_{CF} = 27.8 Hz), 44.2 (q, J_{CF} = 2.6 Hz), 108.3, 122.5, 123.4, 125.2 (q,

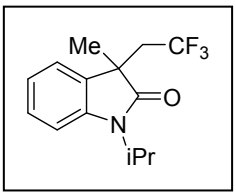
J_{CF} = 276.8 Hz), 128.4, 130.9, 142.8, 178.4.

1-ethyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3b) [2]



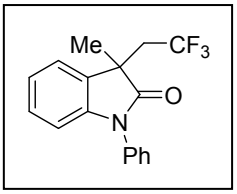
Following the general procedure, the title compound was obtained as yellowish oil, 109.2 mg, 85%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.25 (t, *J* = 7,2 Hz, 3H), 1.39 (s, 3H), 2.56-2.72 (m, 1H), 2.76-2.92 (m, 1H), 3.63-3.75 (m, 1H), 3.81-3.94 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 6.9 Hz, 1H), 7.25-7.33 (m, 2H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 12.2, 25.0, 34.7, 40.6 (q, J_{CF} = 27.8 Hz), 44.2 (q, J_{CF} = 2.3 Hz), 108.5, 122.3, 123.7, 125.2 (q, J_{CF} = 276.5 Hz), 128.4, 131.2, 141.9, 178.0.

1-isopropyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3c) [2]



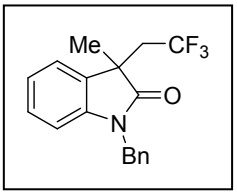
Following the general procedure, the title compound was obtained as colorless oil, 98.9 mg, 85%. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.40 (s, 3H), 1.49 (d, *J* = 4.8 Hz, 3H), 1.50 (d, *J* = 5.2 Hz, 3H), 2.57-2.69 (m, 1H), 2.80-2.92 (m, 1H), 4.64 (dq, *J* = 5.2 Hz, 7.2 Hz, 1H), 7.04-7.09 (m, 2H), 7.26-7.31 (m, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 19.0, 19.2, 25.3, 40.8 (q, J_{CF} = 28.0 Hz), 44.0, 44.1 (q, J_{CF} = 2.0 Hz), 110.1, 122.0, 123.7, 122.0, 123.7, 125.3 (q, J_{CF} = 276.0 Hz), 128.2, 131.4, 141.2, 178.2.

3-methyl-1-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3d) [2]



Following the general procedure, the title compound was obtained as colorless solid, mp 99.3 - 102.9 °C, 93.0 mg, 61%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.53 (s, 3H), 2.64-2.80 (m, 1H), 2.88-3.04 (m, 1H), 6.83 (d, *J* = 7.8 Hz), 7.11 (dt, *J* = 0.9 Hz, 7.5 Hz, 1H), 7.23 (dt, *J* = 1.2 Hz, 7.7 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.40 (dt, *J* = 1.1 Hz, 9.2 Hz), 7.52 (t, *J* = 7.4 Hz). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 25.4, 41.1 (q, J_{CF} = 28.5 Hz), 44.5 (q, J_{CF} = 2.3 Hz), 109.7, 123.0. 123.7, 125.3 (q, J_{CF} = 276.5 Hz), 126.6, 128.2, 128.4, 129.6, 130.7, 134.3, 142.9, 177.9.

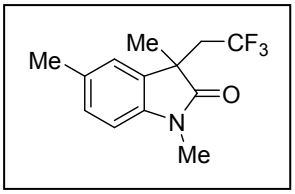
1-benzyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3e) [2]



Following the general procedure, the title compound was obtained as colorless oil, 143.6 mg, 90%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.47 (s, 3H), 2.63-2.78 (m, 1H), 2.84-2.99 (m, 1H), 4.94 (q, *J* = 15.9 Hz, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 7.05 (dt, *J* = 0.8 Hz, 6.9 Hz, 1H), 7.19 (dt, *J* = 1.1 Hz, 7.7 Hz, 1H), 7.28-7.35 (m, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 25.6, 40.5 (q, J_{CF} = 27.8 Hz), 44.0, 44.4

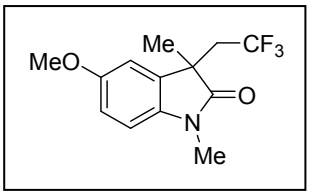
(q, J_{CF} = 1.5 Hz), 109.6, 122.6, 123.6, 125.3 (q, J_{CF} = 276.8 Hz), 127.2, 127.6, 128.4, 128.8, 131.0, 135.7, 142.0, 178.6.

1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3h) [2]



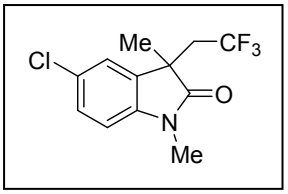
Following the general procedure, the title compound was obtained as colorless solid, mp 50.9 – 52.1 °C, 82.2 mg, 64%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.38 (s, 3H), 2.34 (s, 3H), 2.57-2.69 (m, 1H), 2.71-2.83 (m, 1H), 3.20 (s, 3H), 6.75 (d, *J* = 7.8 Hz), 7.07-7.26 (m, 2H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 21.0, 24.9, 26.3, 40.6 (q, J_{CF} = 27.8 Hz), 44.3 (q, J_{CF} = 2.3 Hz), 108.1, 124.3, 125.2 (q, J_{CF} = 276.5 Hz), 128.7, 131.0, 132.1, 140.4, 178.4.

5-methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3i) [2]



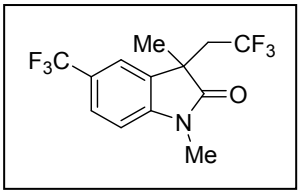
Following the general procedure, the title compound was obtained as colorless oil, 81.9 mg, 60%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.41 (s, 3H), 2.58-2.70 (m, 1H), 2.77-2.89 (m, 1H), 3.23 (s, 3H), 3.82 (s, 3H), 6.79-6.89 (m, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 25.0, 26.5, 40.6 (q, J_{CF} = 21.0 Hz), 44.78 (q, J_{CF} = 1.5 Hz), 55.8, 108.7, 111.3, 122.6, 125.3 (q, J_{CF} = 207.8 Hz), 132.4, 136.4, 156.1, 178.1.

5-chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3j) [2]



Following the general procedure, the title compound was obtained as yellowish solid, mp 76.3 – 77.7 °C, 81.9 mg, 60%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.39 (s, 3H), 2.55-2.70 (m ,1H), 2.74-2.90 (m, 1H), 3.21 (s, 3H), 6.80 (d, *J* = 8.1 Hz, 1H), 7.24-7.29 (m, 2H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 24.8, 26.5, 40.5 (q, J_{CF} = 28.5 Hz), 44.5 (q, J_{CF} = 2.3 Hz), 109.4, 124.1, 125.0 (q, J_{CF} = 176.4 Hz), 128.0, 128.5, 132.7, 141.4, 177.9.

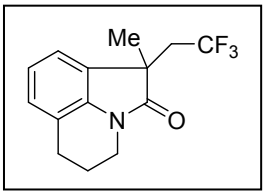
1,3-dimethyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (3l) [2]



Following the general procedure, the title compound was obtained as light yellow solid, mp xx, 91.7 mg, 59%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.46 (s, 3H), 2.64-2.76 (m, 1H), 2.82-2.94 (m, 1H), 3.29 (s, 3H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 24.8, 26.5, 40.5 (q, J_{CF} = 21.0 Hz), 44.29 (q, J_{CF} = 1.5 Hz), 108.3, 120.6, 124.3 (q, J_{CF} = 202.5 Hz), 125.0 (q, J_{CF} = 207.0 Hz), 125.0 (q, J_{CF} = 24.0 Hz),

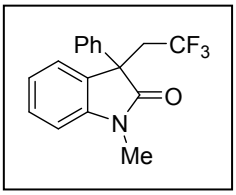
126.3 (q, J_{CF} = 3.0 Hz), 131.6, 145.9, 178.3.

1-methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3m) [2]



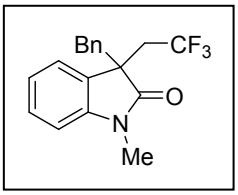
Following the general procedure, the title compound was obtained as colorless solid, mp 66.4 – 70.2 °C, 81.4 mg, 61%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.42 (s, 3H), 1.98-2.06 (m, 2H), 2.57-2.70 (m, 2H), 2.72-2.86 (m, 3H), 3.73 (t, *J* = 6.3 Hz, 2H), 6.95-7.00 (m, 1H), 7.05-7.27 (m, 2H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 21.1, 24.5, 24.6, 39.0, 40.4 (q, J_{CF} = 27.8 Hz), 45.6 (q, J_{CF} = 2.3 Hz), 120.5, 121.4, 122,0, 125.2 (q. J_{CF} = 244.6 Hz), 127.2, 129.7, 138.6, 177.3.

1-methyl-3-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3n) [2]



Following the general procedure, the title compound was obtained as colorless oil, 114.3 mg, 75%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 3.01-3.13 (m, 1H), 3.25 (s, 3H), 3.40-3.51 (m, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.96 (d, 1H, *J* = 8.0 Hz), 7.16-7.20 (m, 3H), 7.20-7.37 (m, 4H).

3-benzyl-1-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3o)[2]



Following the general procedure, the title compound was obtained as colorless solid, mp 106.3 – 108.3 °C, 108.5 mg, 68%. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 2.72-2.83 (m, 1H), 2.94 (s, 3H), 2.98-3.08 (m, 3H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.77 (dd, *J* = 1.2 Hz, 8.0 Hz, 2H), 7.02-7.10 (m, 4H), 7.20-7.26 (m, 2H).

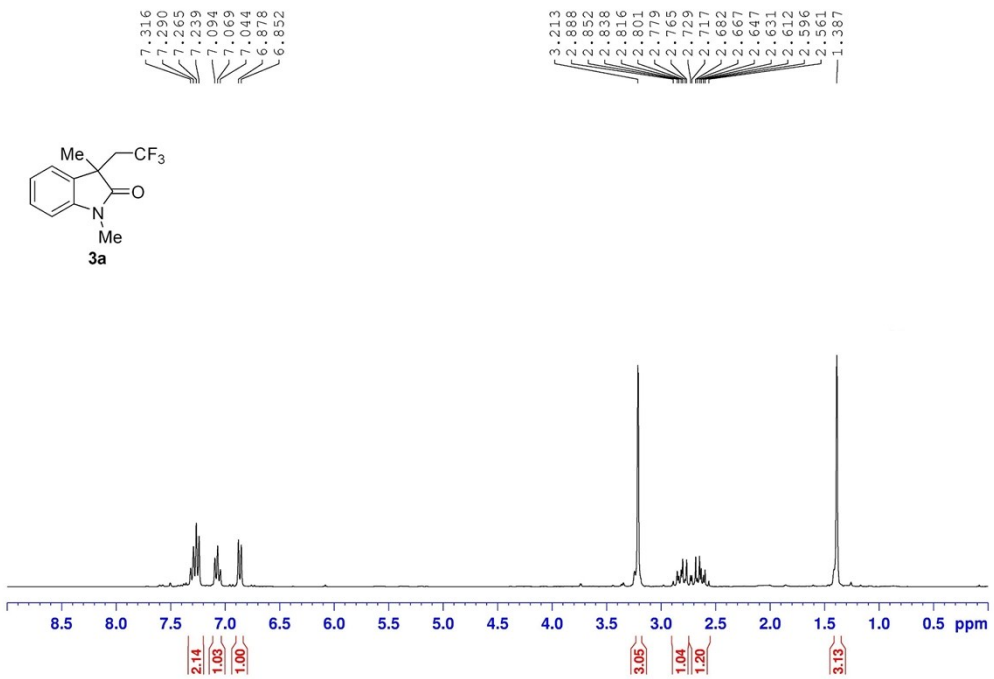
6 Reference

1 D. C. Fabry, M. Stodulski, S. Hoerner and T. Gulder, *Chem. Eur. J.* **2012**, 10834.

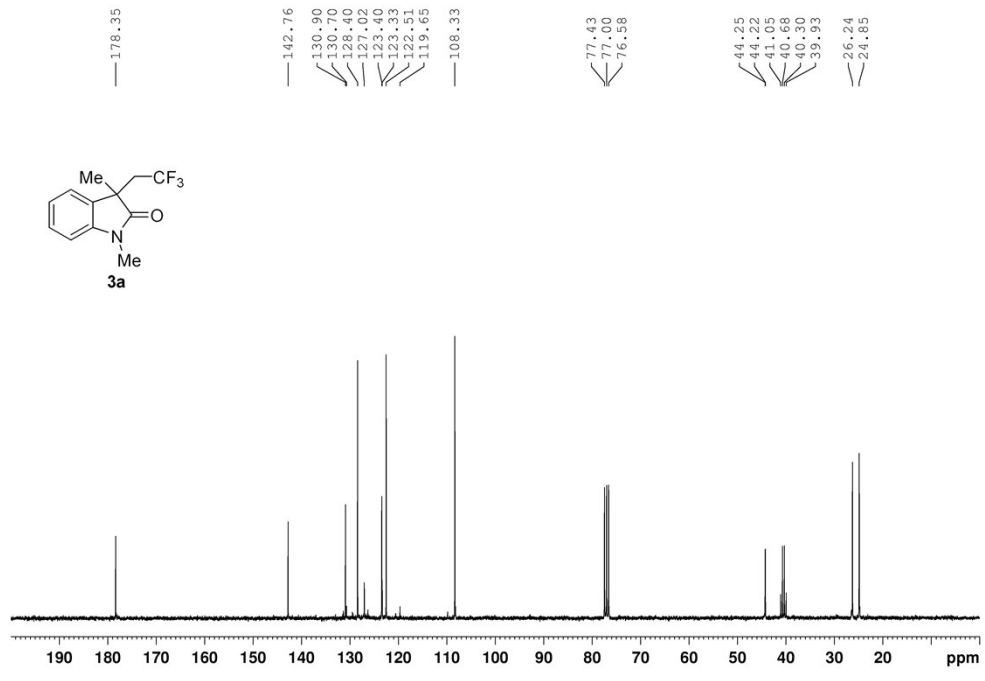
2 L. L Shi, X. B. yang, Y. Y. Wang, H. J. Yang and H. Fu, *Adv. Synth. Catal.* **2014**, 356, 1021.

7 Copies of NMR spectra for the oxindoles

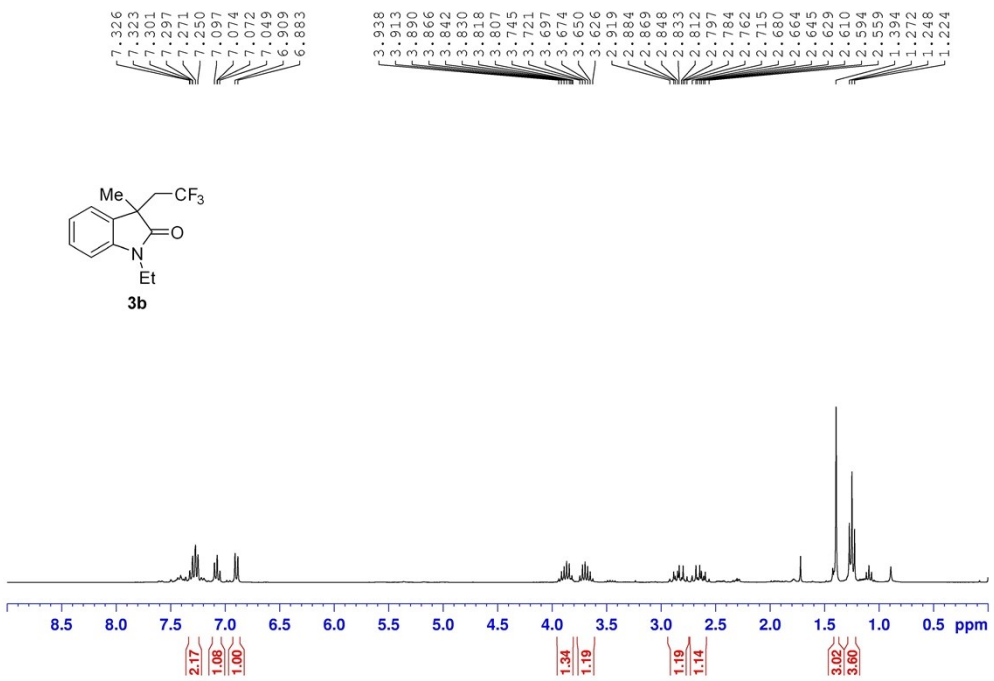
[1] H NMR of 1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3a)



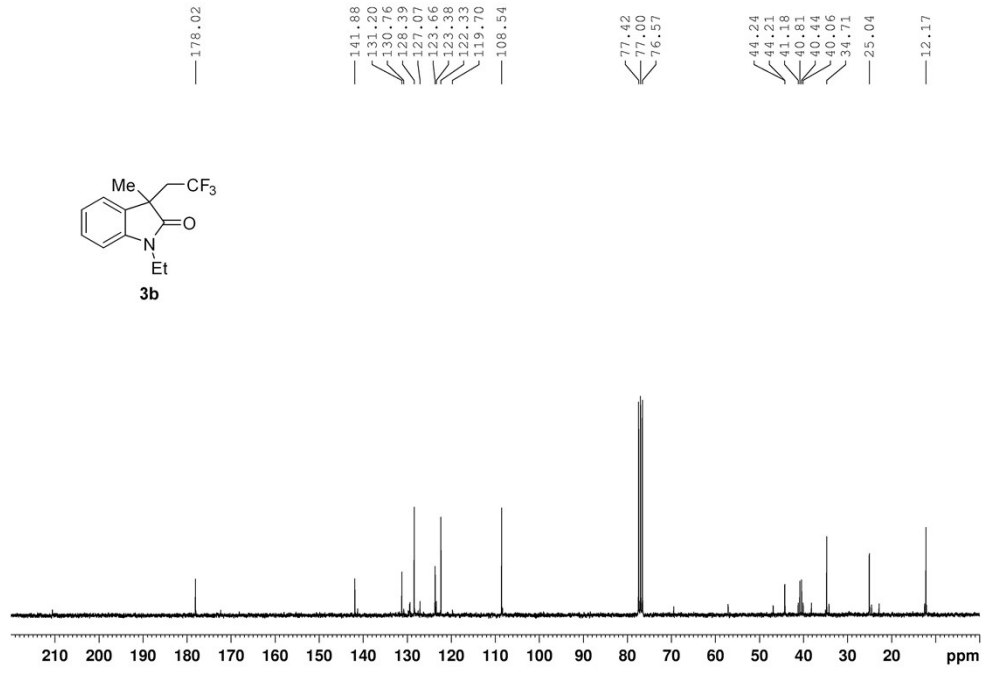
[13] C NMR of 1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3a)



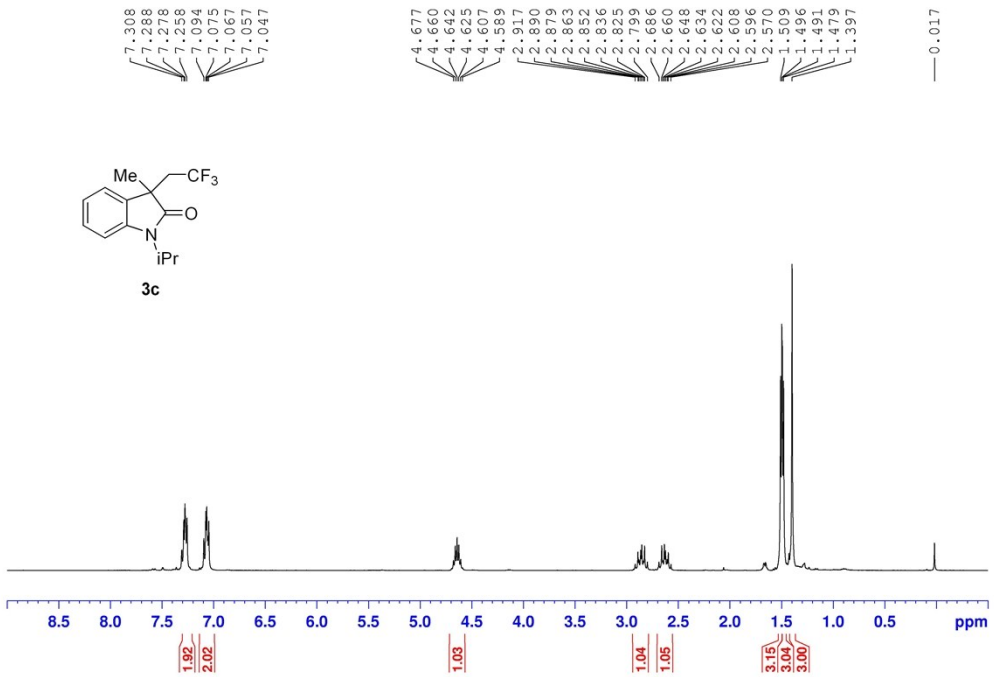
[1] H NMR of 1-ethyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3b)



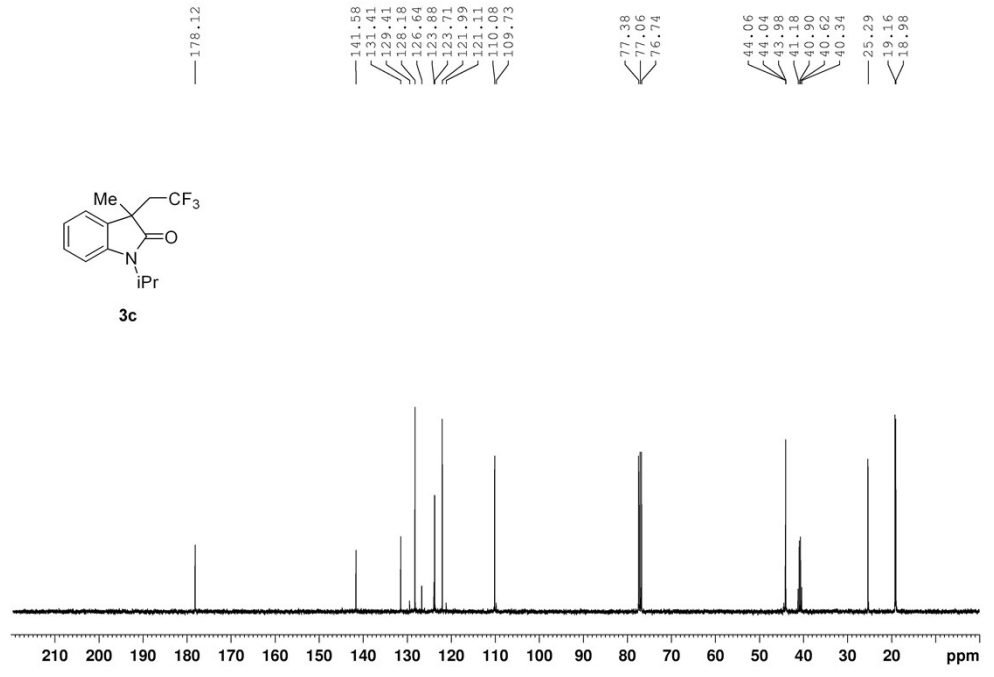
[13] C NMR of 1-ethyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3b)



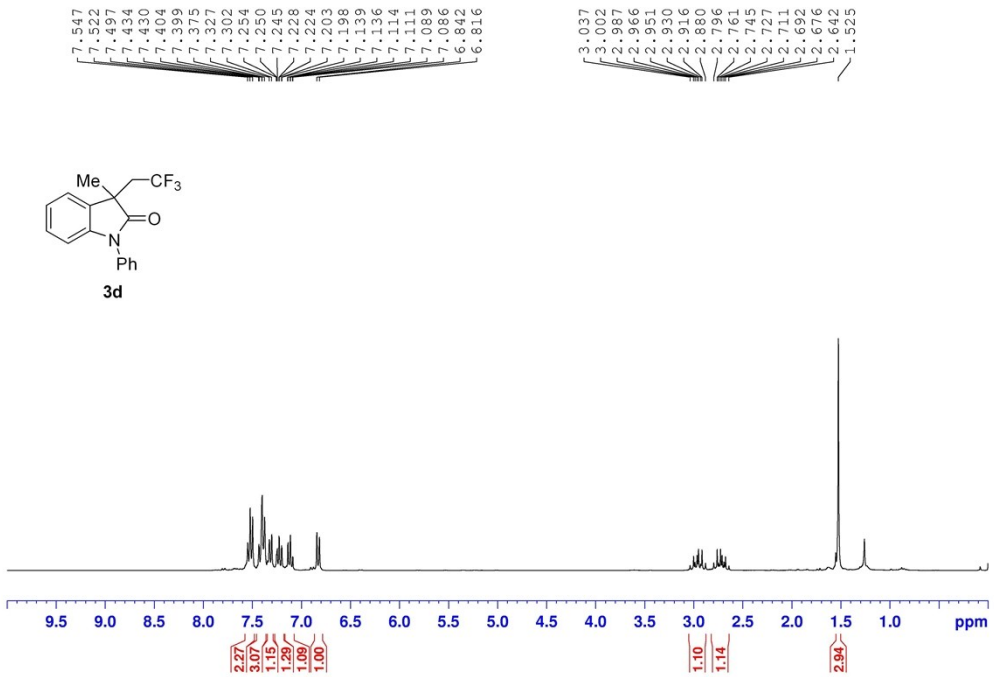
[1] H NMR of 1-isopropyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3c)



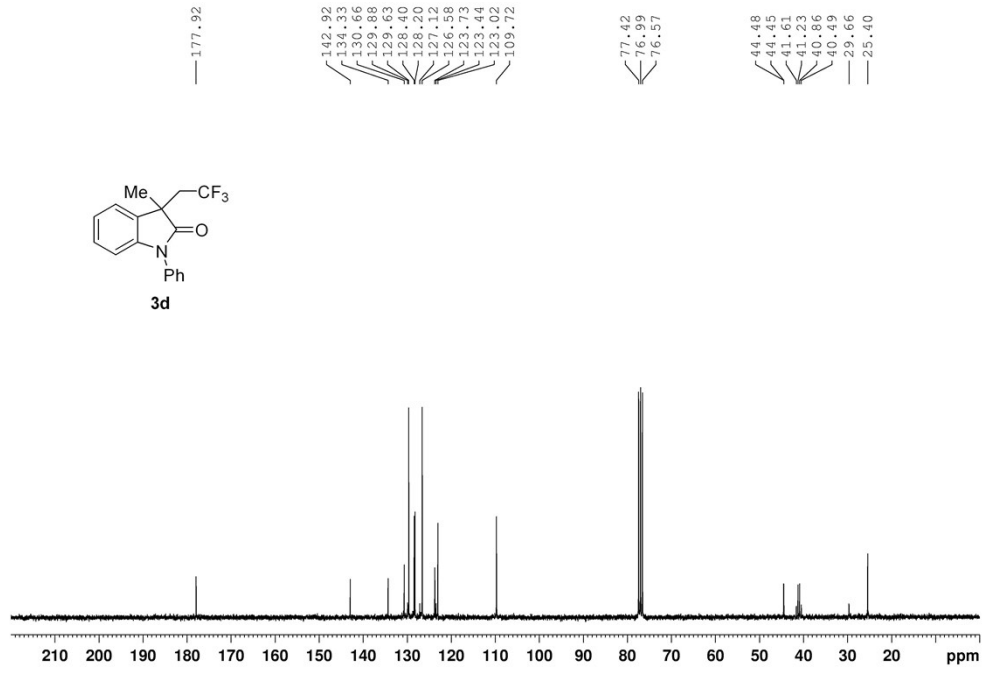
[13] C NMR of 1-isopropyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3c)



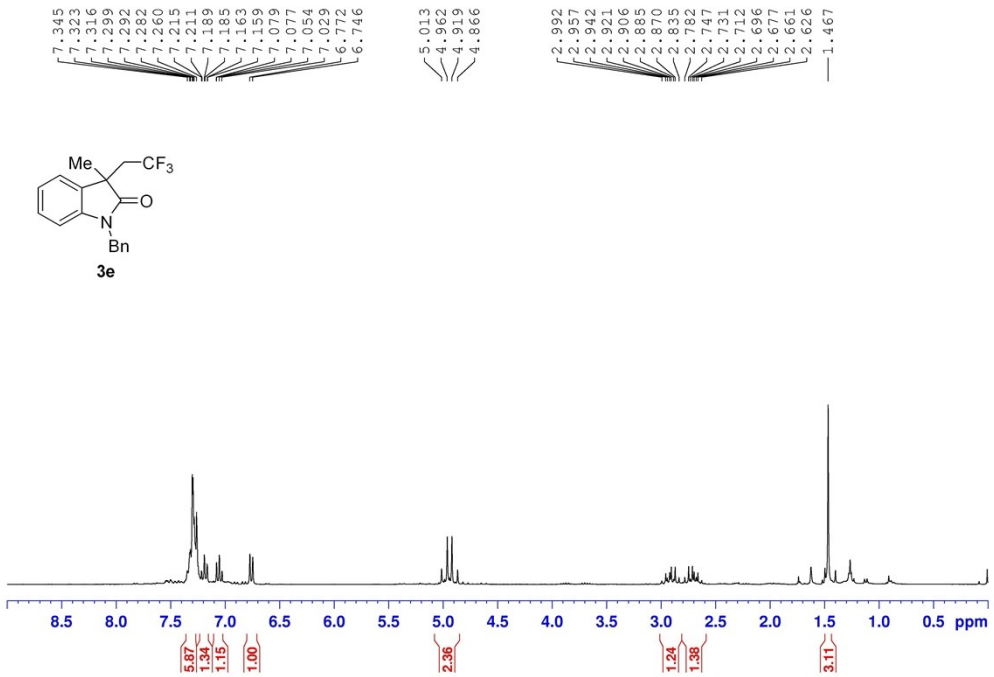
[1] H NMR of 3-methyl-1-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3d)



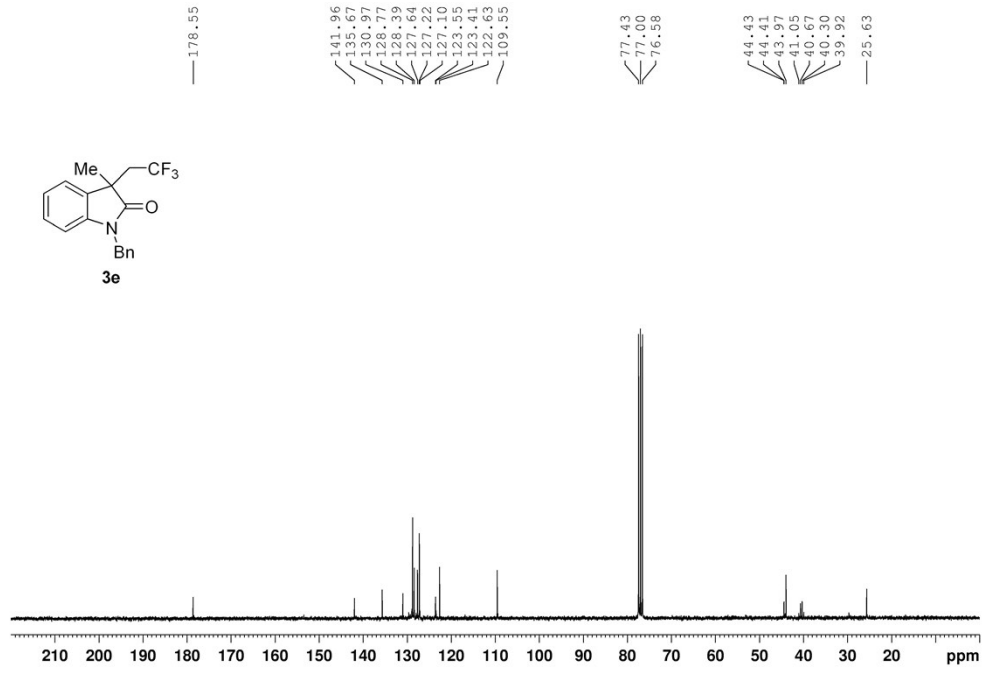
[13] C NMR of 3-methyl-1-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3d)



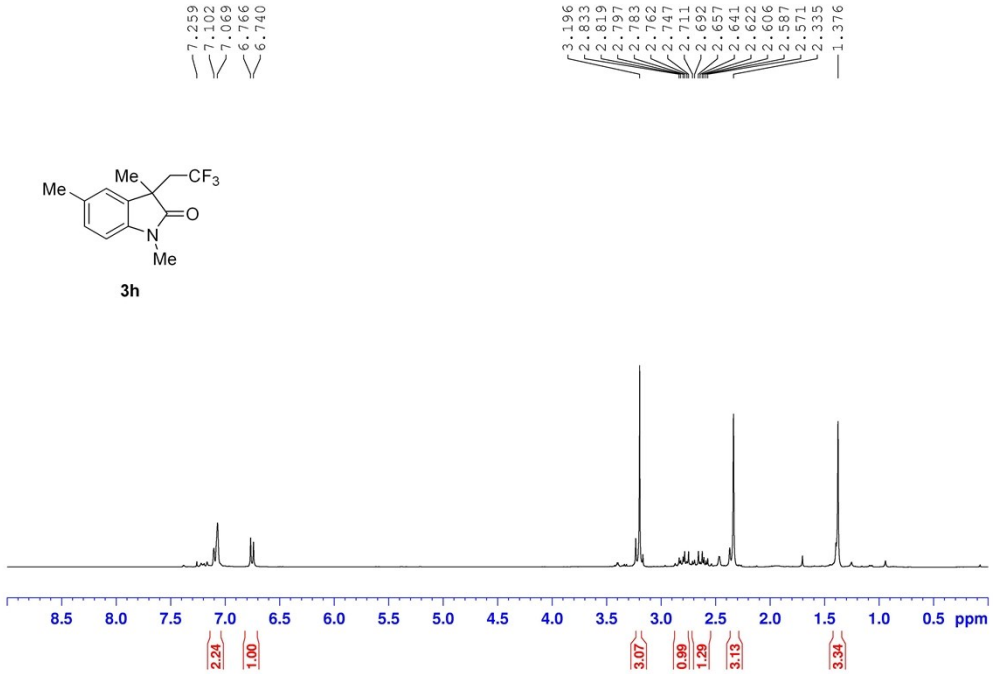
[1] H NMR of 1-benzyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3e)



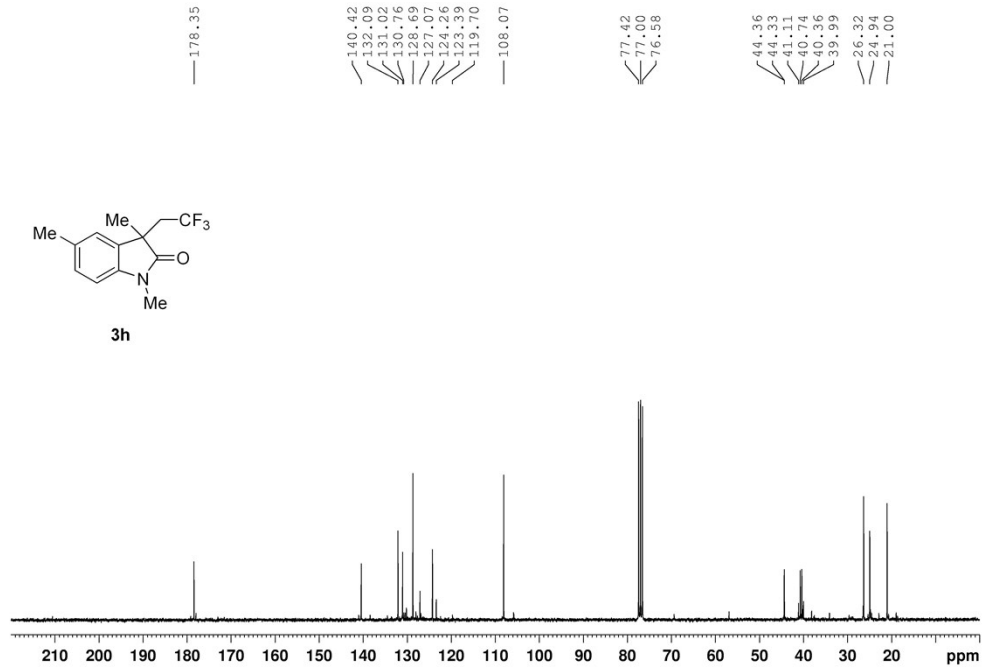
[13] C NMR of 1-benzyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3e)



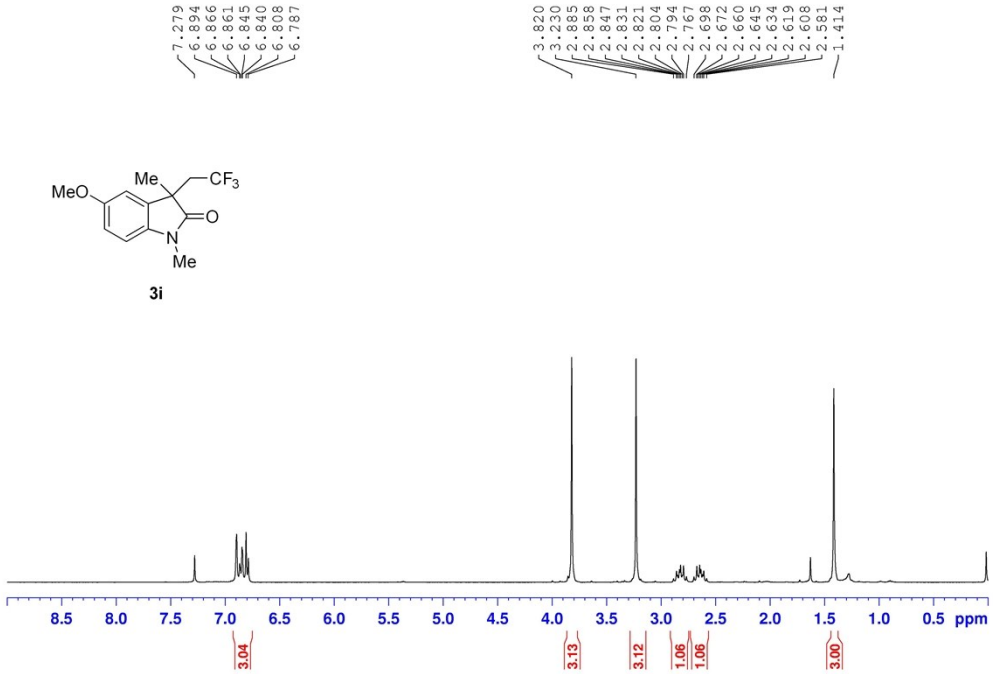
[1] H NMR of 1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3h)



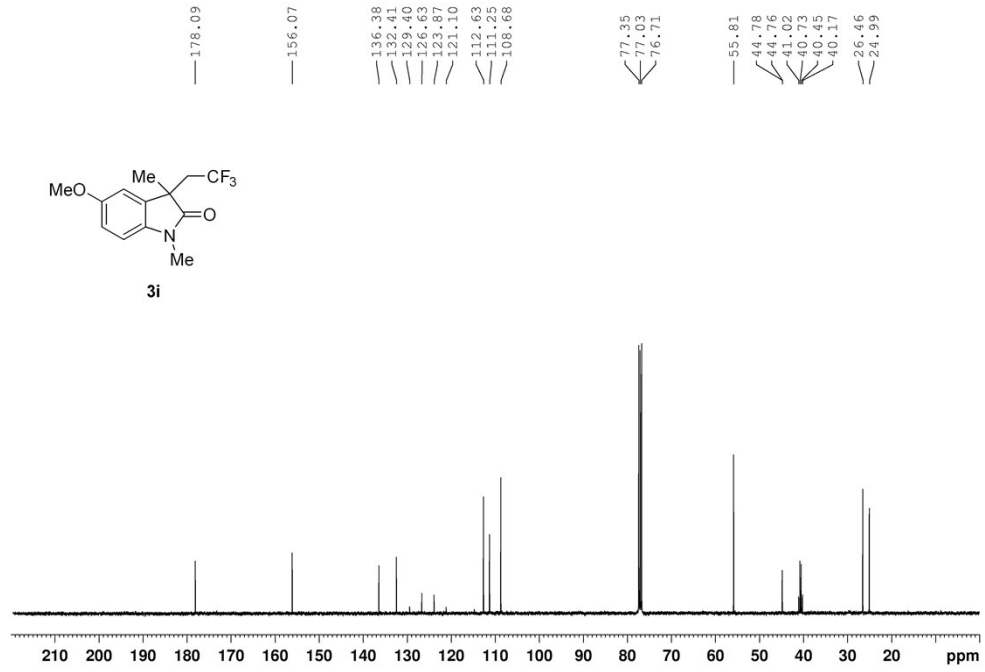
[13] C NMR of 1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3h)



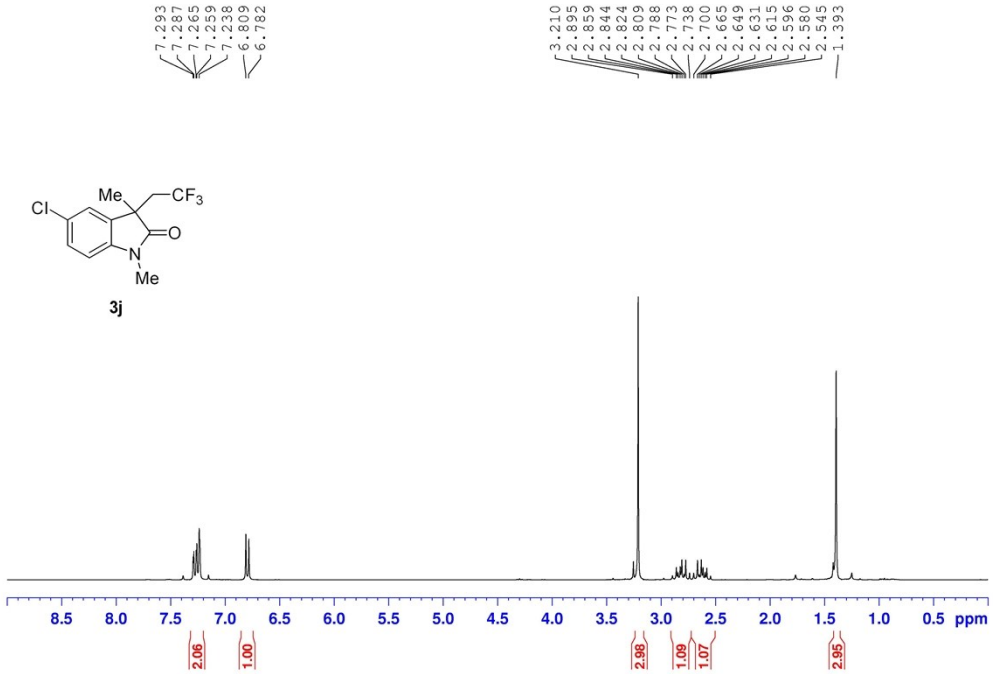
[1] H NMR of 5-methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3i)



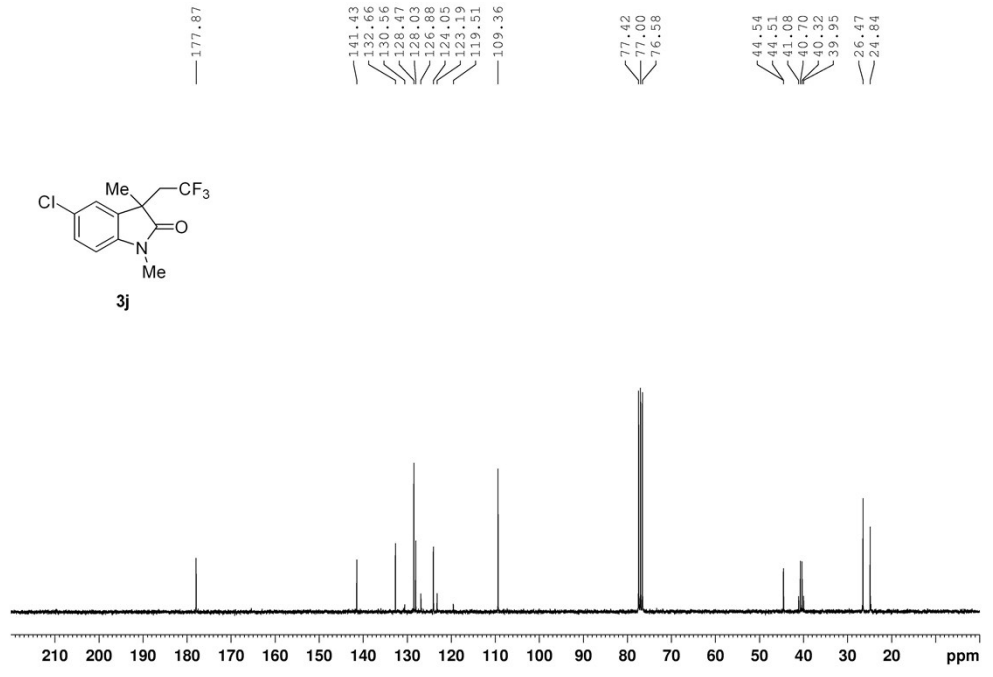
[13] C NMR of 5-methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3i)



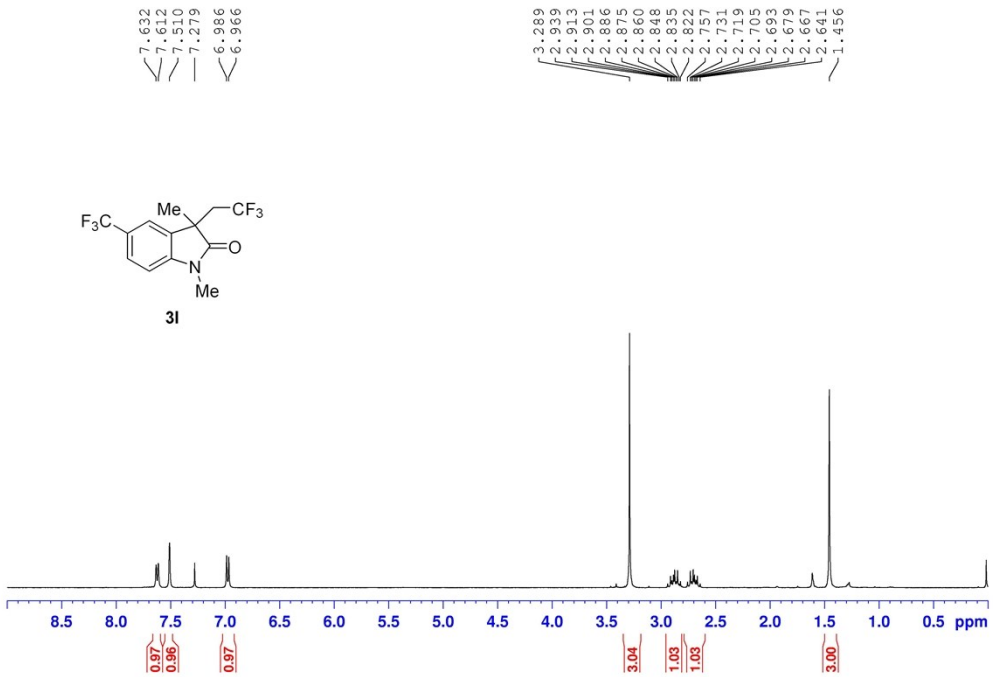
[1] H NMR of 5-chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3j)



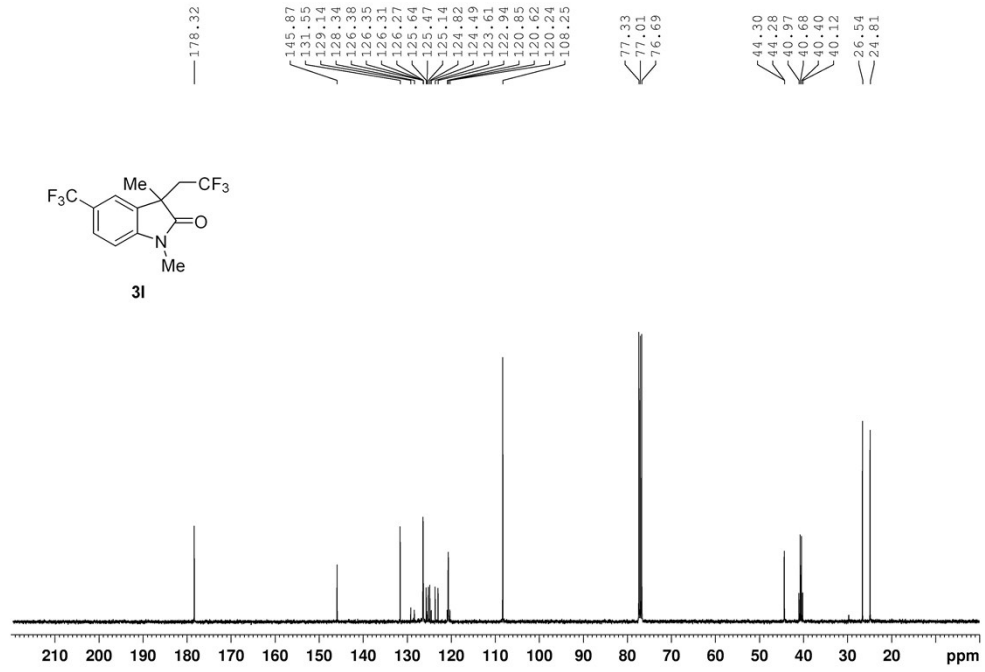
[13] C NMR of 5-chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3j)



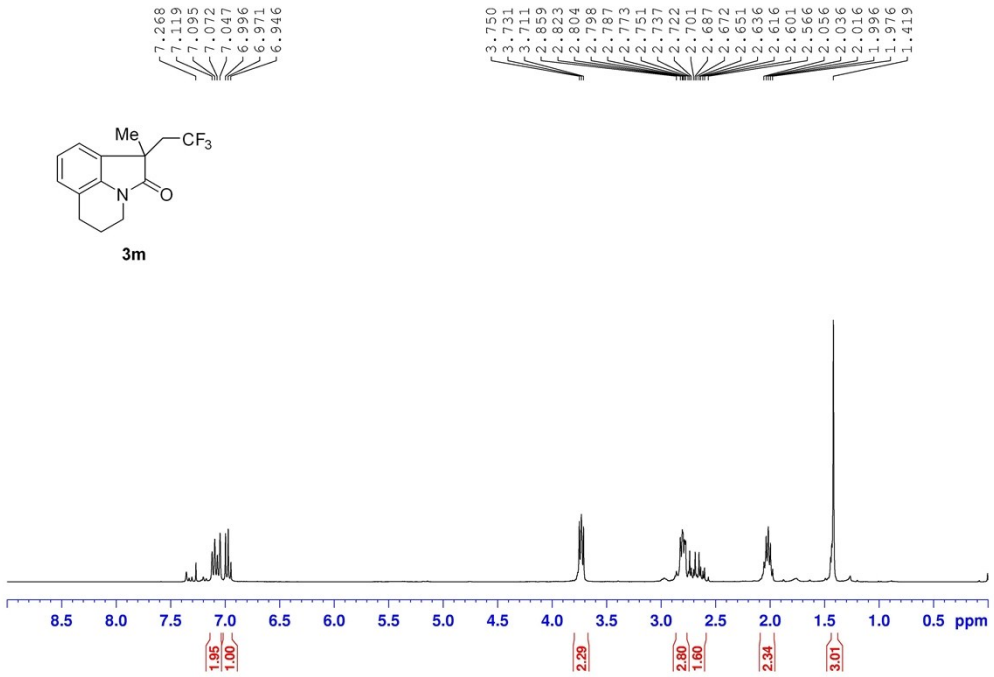
[1] H NMR of 1,3-dimethyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (3l)



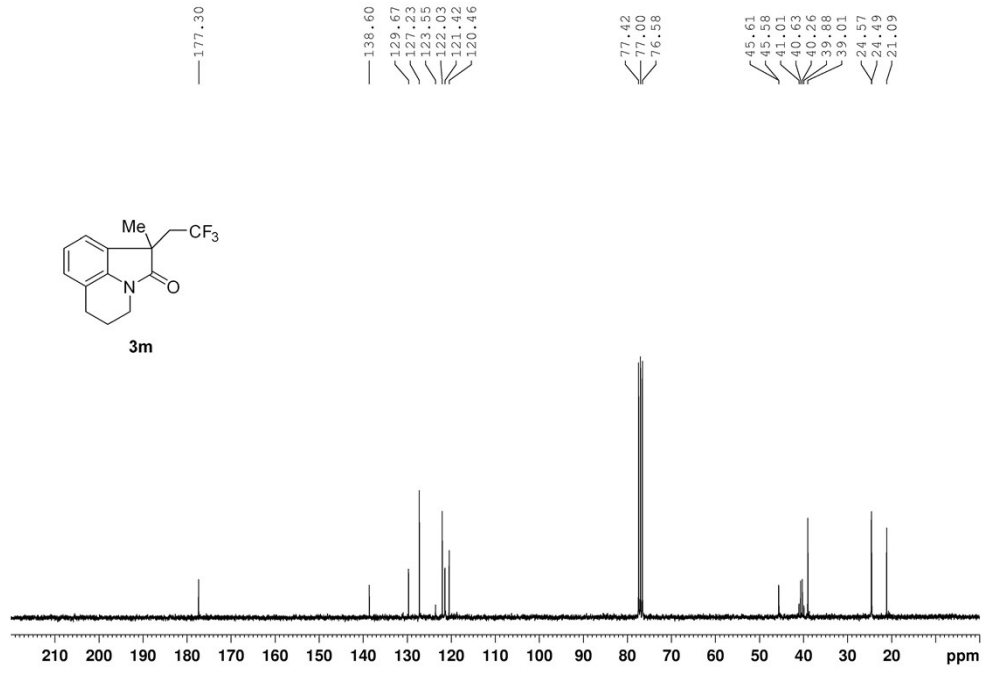
[13] C NMR of 1,3-dimethyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (3l)



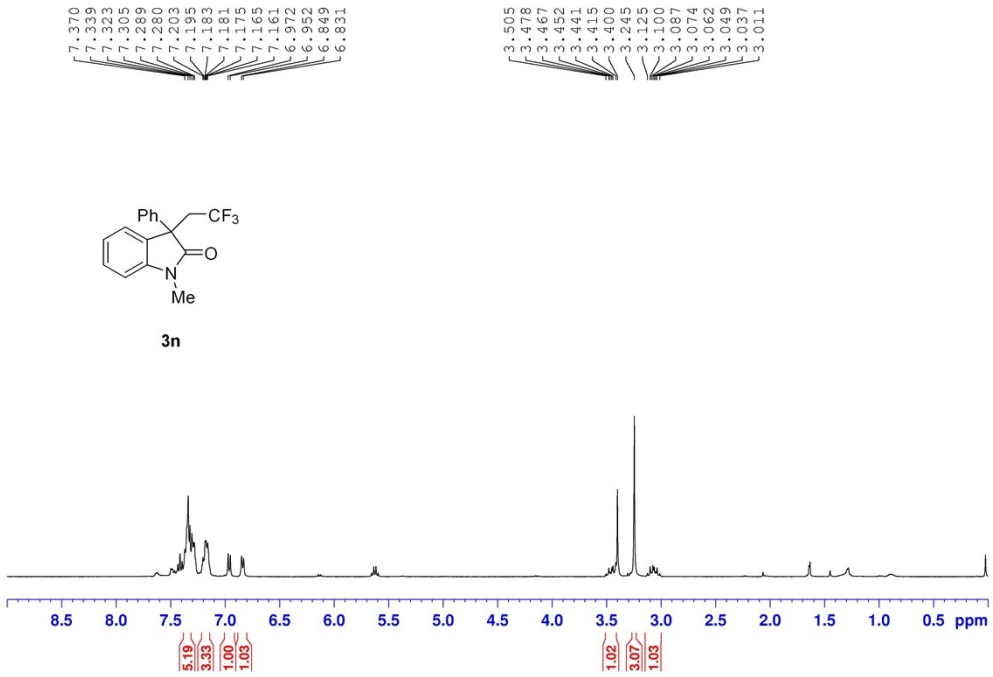
[1] H NMR of 1-methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3m)



[13] C NMR of 1-methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (3m)



[1] H NMR of 1-methyl-3-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3n)



[1] H NMR of 3-benzyl-1-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3o)