

*Supporting Information*

**Copper-catalyzed cyclization reaction: synthesis of  
trifluoromethylated indolinyl ketones**

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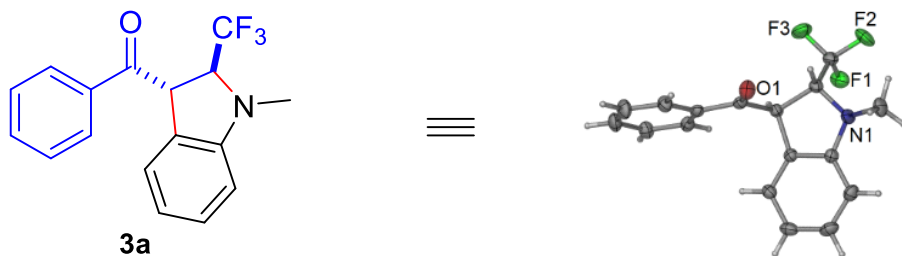
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**1. General Information**

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{19}\text{F}$  NMR spectra were measured at 300 MHz, 400 MHz (or 500 MHz) and 100 MHz (or 125 MHz) in  $\text{CDCl}_3$  using TMS signal ( $\delta$  0.00 ppm) and the residual signals from  $\text{CHCl}_3$  ( $\delta$  77.0 ppm) as internal references for  $^1\text{H}$  and  $^{13}\text{C}$  NMR respectively. Data for  $^1\text{H}$  NMR spectra are reported as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Aniline were commercially available. According to the literatures <sup>[1]</sup>, the starting material  $\beta$ - $\text{CF}_3$ -enones were prepared.

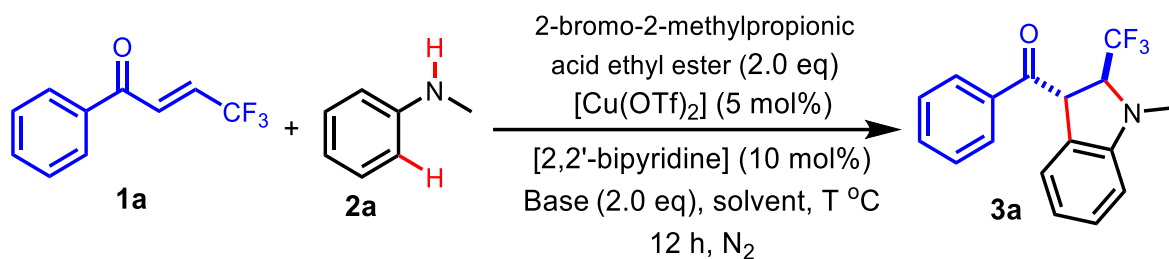
## 2. Figure S1. The X-ray crystallographic data of 3a

Recrystallization in hexane and dichloromethane afforded single crystals suitable for X-ray analysis. The **3a** was dissolved in DCM and hexane was added slowly and there is an upper layer formed. The small bottle was covered by a parafilm on the top with few small holes and the solvents was slowly evaporated until the crystal was formed.



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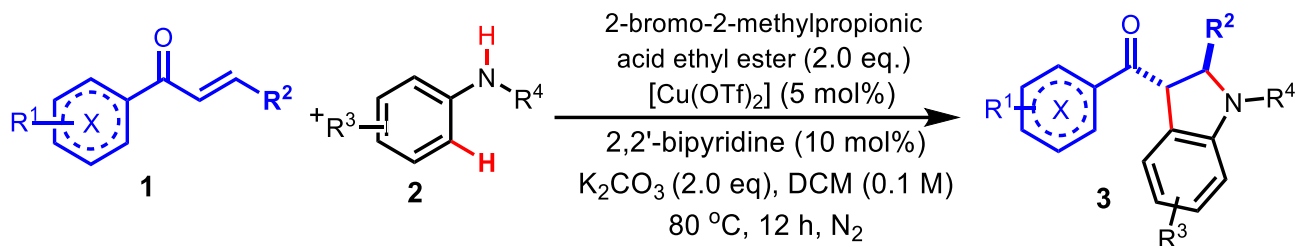
### 3. Optimization of Reaction Conditions<sup>a</sup>

**Table S1.**

Entry	[Base]	[T]/ °C	Solvent	Yield [%] <sup>b,c</sup>
1	$\text{K}_3\text{PO}_4$	80	DCM	69
2	$\text{Na}_2\text{CO}_3$	80	DCM	40
3	$\text{NaHCO}_3$	80	DCM	Trace
4	$\text{KHCO}_3$	80	DCM	70
5	KOH	80	DCM	ND
6	NaOH	80	DCM	Trace
7	$\text{Cs}_2\text{CO}_3$	80	DCM	ND
8	$\text{K}_2\text{CO}_3$	80	DCM	78
9	$\text{K}_2\text{CO}_3$	100	DCM	76
10	$\text{K}_2\text{CO}_3$	60	DCM	68
11	$\text{K}_2\text{CO}_3$	40	DCM	30
12	$\text{K}_2\text{CO}_3$	25	DCM	Trace
15	$\text{K}_2\text{CO}_3$	80	Acetone	ND
16	$\text{K}_2\text{CO}_3$	80	dioxane	ND

<sup>[a]</sup>Unless otherwise noted, all reactions were carried out with 0.2 mmol of **1a**, 0.2 mmol of **2a**, 2.0 equiv of base, 2.0 equiv of 2-bromo-2-methylpropionic acid ethyl ester, 5 mol% of catalyst ( $[\text{Cu}]$  to L = 1:2) in 2.0 mL solvent for 12 h. <sup>[b]</sup>Isolated yield. <sup>[c]</sup> Unless otherwise noted, the dr > 20:1, the diastereomeric ratio was determined by  $^1\text{H}$  NMR analysis of the crude products. ND = no detected.

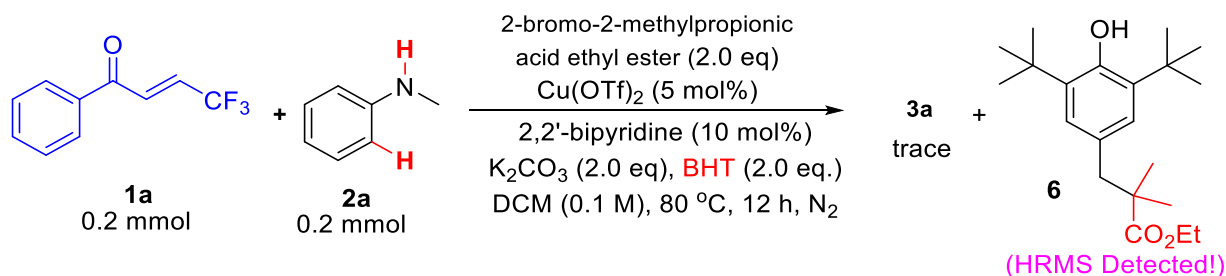
#### 4. General procedure for tandem annulation Reaction



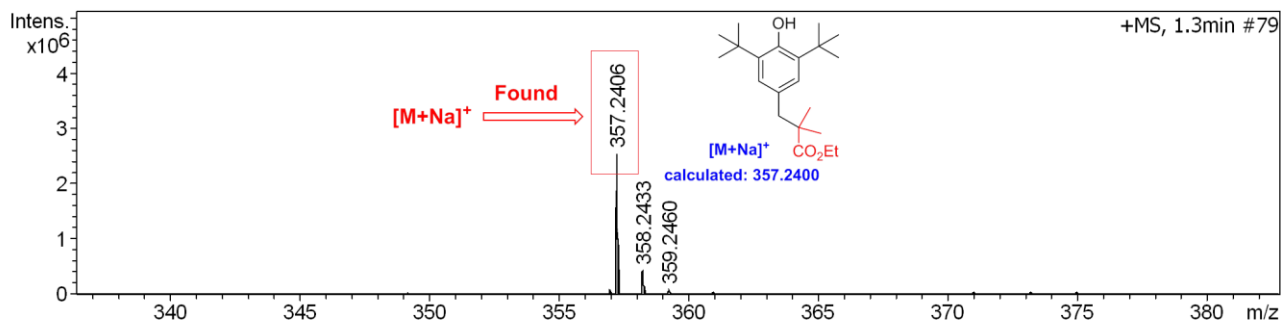
A mixture of  $\text{Cu}(\text{OTf})_2$  (3.6 mg, 5 mol%), 2,2'-bipyridine (3.1 mg, 10 mol%),  $\text{K}_2\text{CO}_3$  (0.4 mmol) in DCM (2.0 mL) under nitrogen atmosphere, then **1** (0.2 mmol), **2** (0.2 mmol), 2-bromo-2-methylpropionic acid ethyl ester (0.4 mmol) were added to this mixture. The resulting mixture was then stirred at 80 °C for about 12 h. After cooling to room temperature, the solution was removed by reducing pressure distillation to yield a residue, which was purified by chromatography on a short silica gel column (hexane/EtOAc = 100/1) to afford the desired product **3**.

## 5. Preliminary mechanistic study

### 5.1 Free radical-trapping with BHT

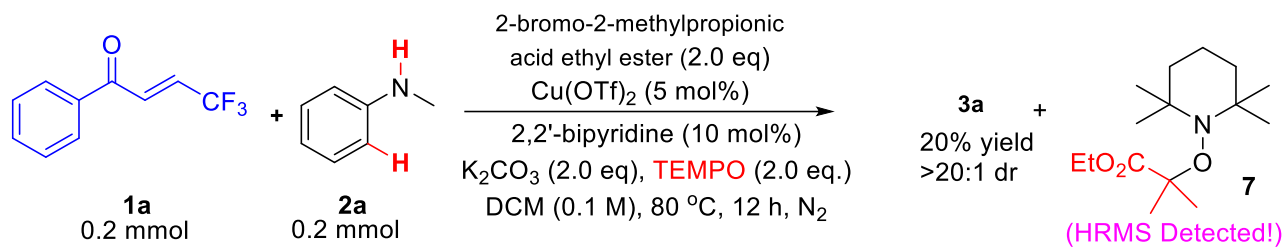


A mixture of  $\text{Cu}(\text{OTf})_2$  (3.6 mg, 5 mol%), 2,2'-bipyridine (3.1 mg, 10 mol%),  $\text{K}_2\text{CO}_3$  (0.4 mmol) in DCM (2.0 mL) under nitrogen atmosphere, then **1a** (0.2 mmol), **2a** (0.2 mmol), 2-bromo-2-methylpropionic acid ethyl ester (0.4 mmol) and BHT (88.1 mg, 0.40 mmol) were added to this mixture. The resulting mixture was then stirred at 80 °C for about 12 h. The reaction was completely inhibited, along with the formation of its adduct **6** with BHT. The following figure is the HRMS analysis of reaction mixture (Figure S2).

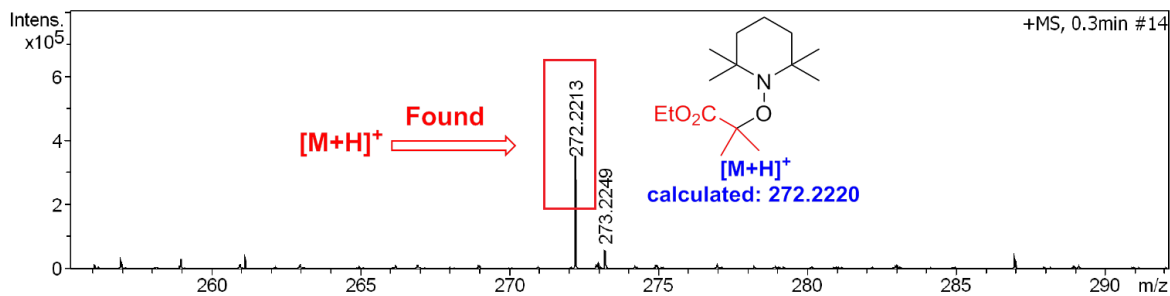


**Figure S2.** Analysis of reaction mixture by HRMS

## 5.2 Free radical-trapping with TEMPO



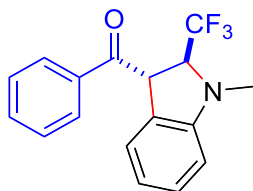
A mixture of Cu(OTf)<sub>2</sub> (3.6 mg, 5 mol%), 2,2'-bipyridine (3.1 mg, 10 mol%), K<sub>2</sub>CO<sub>3</sub> (0.4 mmol) in DCM (2.0 mL) under nitrogen atmosphere, then **1a** (0.2 mmol), **2a** (0.2 mmol), 2-bromo-2-methylpropionic acid ethyl ester (0.4 mmol) and TEMPO (62.5 mg, 0.40 mmol) were added to this mixture. The resulting mixture was then stirred at 80 °C for about 12 h. The compound **7** via an addition of 2-methylpropionic acid ethyl ester and TEMPO was detected. The following figure is the HRMS analysis of reaction mixture (Figure S3).



**Figure S3.** Analysis of reaction mixture by HRMS

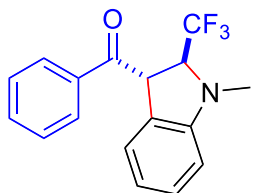


## 6. Characterization data for the products



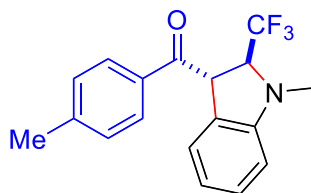
**(1-methyl-2-(trifluoromethyl)indolin-3-yl)(phenyl)methanone: 3a**

White solid. 48.0 mg, 78% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.10 – 8.07 (m, 2H), 7.70 – 7.65 (m, 1H), 7.59 – 7.54 (m, 2H), 7.14 (t,  $J = 7.8$  Hz, 1H), 6.74 (d,  $J = 7.6$  Hz, 1H), 6.61 – 6.55 (m, 2H), 5.19 (d,  $J = 6.6$  Hz, 1H), 4.77 – 4.69 (m, 1H), 3.04 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.61, 152.02, 136.06, 134.04, 129.45, 129.36, 129.08, 126.02 (q,  $J = 278.6$  Hz), 124.73, 124.25, 118.88, 109.03, 67.62 (q,  $J = 29.9$  Hz), 49.99, 36.89;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.03; HRMS (ESI)  $[(\text{M}+\text{Na}^+)]$  Calcd. For  $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NNaO}$ : 328.0920, Found: 328.0911.



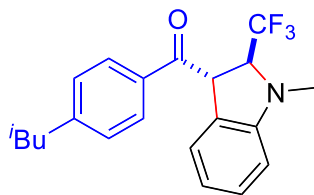
**(1-methyl-2-(trifluoromethyl)indolin-3-yl)(phenyl)methanone: from Z-enone, 3a**

White solid. 41.5 mg, 68% yield:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.09 (t,  $J = 7.4$  Hz, 2H), 7.69 (t,  $J = 7.0$  Hz, 1H), 7.58 (t,  $J = 8.0$  Hz, 2H), 7.14 (t,  $J = 7.5$  Hz, 1H), 6.74 (d,  $J = 7.5$  Hz, 1H), 6.61 – 6.57 (m, 2H), 5.19 (d,  $J = 6.5$  Hz, 1H), 4.76 – 4.70 (m, 1H), 3.04 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.62, 152.03, 136.04, 134.09, 129.49, 129.38, 129.11, 126.01 (q,  $J = 278.5$  Hz), 124.72, 124.27, 118.90, 109.06, 67.59 (q,  $J = 29.8$  Hz), 49.98, 36.95;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.05; HRMS (ESI)  $[(\text{M}+\text{Na}^+)]$  Calcd. For  $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NNaO}$ : 328.0920, Found: 328.0912.



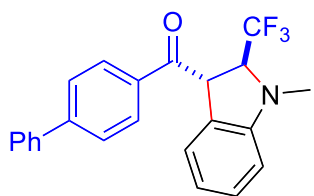
**(1-methyl-2-(trifluoromethyl)indolin-3-yl)(p-tolyl)methanone: 3b**

White solid. 49.2 mg, 77% yield.:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.99 (d,  $J = 8.0$  Hz, 2H), 7.36 (d,  $J = 8.0$  Hz, 2H), 7.13 (t,  $J = 7.5$  Hz, 1H), 6.76 (d,  $J = 7.5$  Hz, 1H), 6.60 – 6.56 (m, 2H), 5.16 (d,  $J = 7.0$  Hz, 1H), 4.75 – 4.70 (m, 1H), 3.03 (s, 3H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.18, 152.05, 145.17, 133.49, 129.81, 129.63, 129.30, 126.06 (q,  $J = 278.5$  Hz), 124.98, 124.27, 118.88, 109.04, 67.64 (q,  $J = 29.8$  Hz), 49.87, 36.97, 21.76;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -74.98; HRMS (ESI)  $[(\text{M}+\text{Na}^+)]$  Calcd. For  $\text{C}_{18}\text{H}_{16}\text{F}_3\text{NNaO}$ : 342.1076, Found: 342.1082.



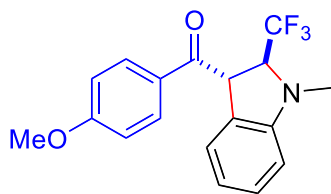
**(4-isobutylphenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3c**

White solid. 47.0 mg, 65% yield.:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.01 (d,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 8.0$  Hz, 2H), 7.14 (t,  $J = 7.6$  Hz, 1H), 6.77 (d,  $J = 7.6$  Hz, 1H), 6.61 – 6.57 (m, 2H), 5.17 (d,  $J = 6.4$  Hz, 1H), 4.75 – 4.69 (m, 1H), 3.04 (s, 3H), 2.59 (d,  $J = 7.2$  Hz, 2H), 2.02 – 1.90 (m, 1H), 0.95 (d,  $J = 6.4$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.27, 152.06, 148.83, 133.74, 129.80, 129.47, 129.27, 126.04 (q,  $J = 278.6$  Hz), 125.04, 124.24, 118.86, 109.00, 67.71 (q,  $J = 29.8$  Hz), 49.87, 45.47, 36.95, 30.12, 22.38;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -74.96; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{21}\text{H}_{22}\text{F}_3\text{NNaO}$ : 384.1546, Found: 384.1539.



**[1,1'-biphenyl]-4-yl(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3d**

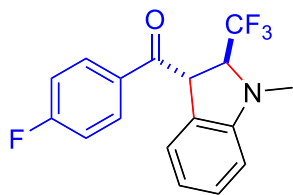
White solid. 61.0 mg, 80% yield.:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.17 (d,  $J = 8.4$  Hz, 2H), 7.80 (d,  $J = 8.4$  Hz, 2H), 7.69 – 7.67 (m, 2H), 7.50 (t,  $J = 7.2$  Hz, 2H), 7.45 – 7.41 (m, 1H), 7.15 (t,  $J = 7.6$  Hz, 1H), 6.82 (d,  $J = 7.6$  Hz, 1H), 6.62 – 6.59 (m, 2H), 5.22 (d,  $J = 6.4$  Hz, 1H), 4.78 – 4.72 (m, 1H), 3.05 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.17, 152.08, 146.82, 139.56, 134.65, 130.12, 129.41, 129.11, 128.60, 127.71, 127.39, 126.05 (q,  $J = 278.3$  Hz), 124.86, 124.31, 118.95, 109.10, 67.67 (q,  $J = 29.8$  Hz), 50.01, 36.99;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -74.96; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{23}\text{H}_{18}\text{F}_3\text{NNaO}$ : 404.1233, Found: 404.1233.



**(4-methoxyphenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone:**

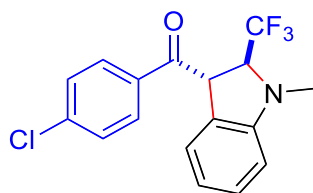
**3e**

White solid. 55.7 mg, 83% yield:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.08 (d,  $J = 9.2$  Hz, 2H), 7.14 (t,  $J = 7.6$  Hz, 1H), 7.05 (d,  $J = 8.8$  Hz, 2H), 6.78 (d,  $J = 7.6$  Hz, 1H), 6.61 – 6.58 (m, 2H), 5.13 (d,  $J = 6.8$  Hz, 1H), 4.75 – 4.68 (m, 1H), 3.92 (s, 3H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.08, 164.36, 152.10, 131.86, 129.29, 128.87, 126.08 (q,  $J = 278.1$  Hz), 125.24, 124.19, 118.89, 114.32, 109.05, 67.76 (q,  $J = 29.8$  Hz), 55.65, 49.66, 37.04;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -74.95; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{18}\text{H}_{16}\text{F}_3\text{NNaO}_2$ : 358.1025, Found: 358.1029.



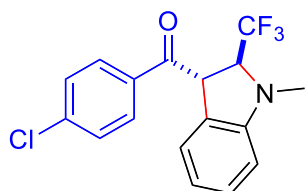
**(4-fluorophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3f**

White solid. 45.3 mg, 70% yield.:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.14 – 8.09 (m, 2H), 7.27 – 7.22 (m, 2H), 7.15 (t,  $J = 7.6$  Hz, 1H), 6.73 (d,  $J = 7.6$  Hz, 1H), 6.61 – 6.58 (m, 2H), 5.13 (d,  $J = 6.8$  Hz, 1H), 4.74 – 4.67 (m, 1H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.10, 166.37 (d,  $J = 255.2$  Hz), 152.03, 132.45 (d,  $J = 2.9$  Hz), 132.13 (d,  $J = 37.6$  Hz), 129.48, 127.34 (q,  $J = 278.7$  Hz), 124.54, 124.09, 118.91, 116.32 (q,  $J = 21.8$  Hz), 109.11, 67.67 (q,  $J = 29.9$  Hz), 49.93, 36.84;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.01, -103.23; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{17}\text{H}_{13}\text{F}_4\text{NNaO}$ : 346.0825, Found: 346.0826.



**(4-chlorophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3g**

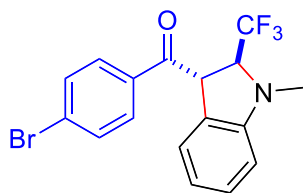
White solid. 49.6 mg, 73% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.02 (d,  $J = 8.8$  Hz, 2H), 7.55 (d,  $J = 8.8$  Hz, 2H), 7.15 (t,  $J = 7.6$  Hz, 1H), 6.71 (d,  $J = 7.6$  Hz, 1H), 6.61 – 6.58 (m, 2H), 5.11 (d,  $J = 6.4$  Hz, 1H), 4.72 – 4.68 (m, 1H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.46, 151.99, 140.74, 134.38, 130.78, 129.51, 129.45, 125.91 (q,  $J = 278.8$  Hz), 124.36, 124.11, 118.92, 109.09, 67.58 (q,  $J = 29.9$  Hz), 49.98, 36.81;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.02; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{17}\text{H}_{13}\text{ClF}_3\text{NNaO}$ : 362.0530, Found: 362.0527.



**(4-chlorophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: from**

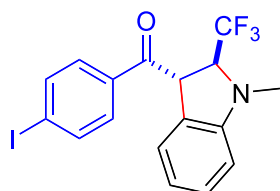
**Z-enone, 3g**

White solid. 39.4 mg, 58% yield:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.02 (d,  $J = 8.5$  Hz, 2H), 7.55 (d,  $J = 8.5$  Hz, 2H), 7.15 (t,  $J = 7.5$  Hz, 1H), 6.72 (d,  $J = 8.0$  Hz, 1H), 6.61 – 6.58 (m, 2H), 5.12 (d,  $J = 6.5$  Hz, 1H), 4.73 – 4.68 (m, 1H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.46, 152.01, 140.78, 134.36, 130.83, 129.55, 129.49, 125.93 (q,  $J = 278.3$  Hz), 124.35, 124.15, 118.95, 109.15, 67.56 (q,  $J = 29.9$  Hz), 49.99, 36.87;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.06; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{17}\text{H}_{13}\text{ClF}_3\text{NNaO}$ : 362.0530, Found: 362.0525.



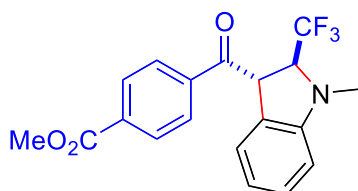
**(4-bromophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3h**

White solid. 57.6 mg, 75% yield.:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.94 (d,  $J = 8.4$  Hz, 2H), 7.72 (d,  $J = 8.8$  Hz, 2H), 7.15 (t,  $J = 7.6$  Hz, 1H), 6.72 (d,  $J = 8.0$  Hz, 1H), 6.61 – 6.58 (m, 2H), 5.11 (d,  $J = 6.4$  Hz, 1H), 4.73 – 4.66 (m, 1H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.66, 151.98, 134.79, 132.45, 130.85, 129.52, 129.50, 125.91 (q,  $J = 278.6$  Hz), 124.32, 124.12, 118.93, 109.10, 67.56 (q,  $J = 29.9$  Hz), 49.98, 36.81;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.01; HRMS (ESI) [(M+Na $^+$ )] Calcd. For  $\text{C}_{17}\text{H}_{13}\text{BrF}_3\text{NNaO}$ : 406.0025, Found: 406.0028.



**(4-iodophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3i**

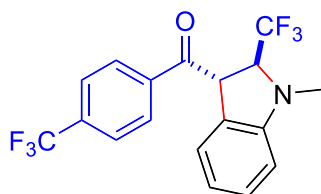
White solid. 65.5 mg, 76% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.94 (d,  $J = 8.8$  Hz, 2H), 7.78 (d,  $J = 8.4$  Hz, 2H), 7.15 (t,  $J = 7.6$  Hz, 1H), 6.72 (d,  $J = 7.6$  Hz, 1H), 6.61 – 6.58 (m, 2H), 5.10 (d,  $J = 6.4$  Hz, 1H), 4.73 – 4.66 (m, 1H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.97, 151.97, 138.45, 135.32, 130.68, 129.51, 125.90 (q,  $J = 278.7$  Hz), 124.31, 124.14, 118.93, 109.09, 102.37, 67.54 (q,  $J = 29.9$  Hz), 49.91, 36.81;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.01; HRMS (ESI) [(M+Na $^+$ )] Calcd. For  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{INNaO}$ : 453.9886, Found: 453.9884.



**Methyl-4-(1-methyl-2-(trifluoromethyl)indoline-3-carbonyl)benzoate:**

**3j**

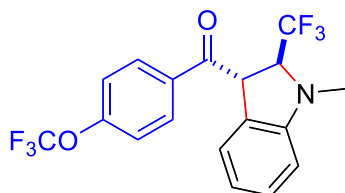
White solid. 50.1 mg, 69% yield.:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.26 (d,  $J = 8.1$  Hz, 2H), 8.16 (d,  $J = 8.4$  Hz, 2H), 7.18 (t,  $J = 7.5$  Hz, 1H), 6.71 (d,  $J = 7.5$  Hz, 1H), 6.65 – 6.57 (m, 2H), 5.21 (d,  $J = 6.3$  Hz, 1H), 4.80 – 4.71 (m, 1H), 4.01 (s, 3H), 3.07 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.15, 166.01, 151.92, 139.30, 134.76, 130.21, 129.55, 129.34, 125.89 (q,  $J = 278.9$  Hz), 124.19, 124.05, 118.90, 109.10, 67.35 (q,  $J = 30.0$  Hz), 52.63, 50.34, 36.78;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.08; HRMS (ESI) [(M+Na $^+$ )] Calcd. For  $\text{C}_{19}\text{H}_{16}\text{F}_3\text{NNaO}_3$ : 386.0974, Found: 386.0966.



**(1-methyl-2-(trifluoromethyl)indolin-3-yl)(4-(trifluoromethyl)phenyl)metha**

**none: 3k**

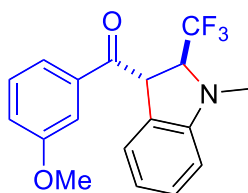
White solid. 49.3 mg, 66% yield:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.18 (d,  $J = 8.0$  Hz, 2H), 7.84 (d,  $J = 8.0$  Hz, 2H), 7.16 (t,  $J = 8.0$  Hz, 1H), 6.68 (d,  $J = 7.6$  Hz, 1H), 6.62 – 6.58 (m, 2H), 5.17 (d,  $J = 6.4$  Hz, 1H), 4.75 – 4.68 (m, 1H), 3.04 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.78, 151.97, 138.81, 135.33 (q,  $J = 32.5$  Hz), 129.77, 129.68, 126.18 (q,  $J = 3.6$  Hz), 125.87 (q,  $J = 278.6$  Hz), 124.13, 123.95, 123.49 (q,  $J = 271.1$  Hz), 119.00, 109.20, 67.48 (q,  $J = 30.0$  Hz), 50.28, 36.77;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -63.21, -75.10; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{18}\text{H}_{13}\text{F}_6\text{NNaO}$ : 396.0794, Found: 396.0793.



**(1-methyl-2-(trifluoromethyl)indolin-3-yl)(4-(trifluoromethoxy)phenyl)methanone: 3l**

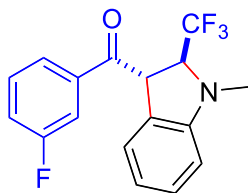
**ethanone: 3l**

White solid. 56.8 mg, 73% yield.:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.15 (d,  $J = 9.0$  Hz, 2H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.16 (t,  $J = 7.5$  Hz, 1H), 6.73 (d,  $J = 8.0$  Hz, 1H), 6.63 – 6.60 (m, 2H), 5.13 (d,  $J = 6.5$  Hz, 1H), 4.73 – 4.67 (m, 1H), 3.04 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.16, 153.38, 152.00, 134.10, 131.50, 129.56, 125.88 (q,  $J = 278.8$  Hz), 124.29, 124.07, 120.68, 120.30 (q,  $J = 258.0$  Hz), 118.96, 109.16, 67.63 (q,  $J = 29.9$  Hz), 49.98, 36.84;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -57.51, -75.03; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{18}\text{H}_{13}\text{F}_6\text{NNaO}_2$ : 412.0743, Found: 412.0733.



**(3-methoxyphenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3m**

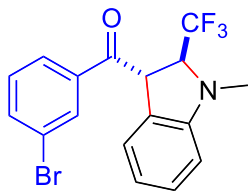
White solid. 46.9 mg, 70% yield:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.68 (d,  $J = 7.5$  Hz, 1H), 7.58 (s, 1H), 7.49 (t,  $J = 8.0$  Hz, 1H), 7.24 – 7.21 (m, 1H), 7.14 (t,  $J = 7.5$  Hz, 1H), 6.78 (d,  $J = 7.5$  Hz, 1H), 6.60 – 6.58 (m, 2H), 5.15 (d,  $J = 6.5$  Hz, 1H), 4.75 – 4.69 (m, 1H), 3.86 (s, 3H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.46, 160.23, 152.02, 137.43, 130.07, 129.41, 126.03 (q,  $J = 278.4$  Hz), 124.74, 124.36, 122.06, 120.66, 118.95, 113.60, 109.07, 67.65 (q,  $J = 29.9$  Hz), 55.54, 50.16, 36.95;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -74.99; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{18}\text{H}_{16}\text{F}_3\text{NNaO}_2$ : 358.1025, Found: 358.1029.



**(3-fluorophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3n**

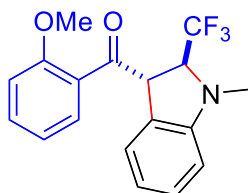
White solid. 47.8 mg, 74% yield.:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.89 (d,  $J = 7.8$  Hz, 1H), 7.77 (dt,  $J = 9.0, 2.7$  Hz, 1H), 7.62 – 7.55 (m, 1H), 7.43 – 7.36 (m, 1H), 7.17 (t,  $J = 7.5$  Hz, 1H), 6.74 (d,  $J = 7.8$  Hz, 1H), 6.63 – 6.59 (m, 2H), 5.13 (d,  $J = 6.6$  Hz, 1H), 4.76 – 4.67 (m, 1H), 3.05 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.48 (d,  $J = 1.8$  Hz), 164.09, 162.11,

151.97, 138.16 (d,  $J = 6.1$  Hz), 130.79 (d,  $J = 7.8$  Hz), 129.55, 125.89 (q,  $J = 278.8$  Hz), 125.17 (d,  $J = 2.9$  Hz), 124.20 (d,  $J = 6.8$  Hz), 121.18 (d,  $J = 21.5$  Hz), 118.94, 116.14 (d,  $J = 22.5$  Hz), 109.13, 67.55 (q,  $J = 29.9$  Hz), 50.15, 36.83;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.05, -110.73; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{17}\text{H}_{13}\text{F}_4\text{NNaO}$ : 346.0825, Found: 346.0816.



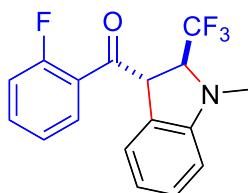
**(3-bromophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3o**

White solid. 60.7 mg, 79% yield.:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.22 (s, 1H), 8.02 (d,  $J = 7.6$  Hz, 1H), 7.82 (d,  $J = 8.0$  Hz, 1H), 7.47 (t,  $J = 8.0$  Hz, 1H), 7.17 (t,  $J = 7.6$  Hz, 1H), 6.74 (d,  $J = 7.6$  Hz, 1H), 6.64 – 6.61 (m, 2H), 5.12 (d,  $J = 6.4$  Hz, 1H), 4.75 – 4.68 (m, 1H), 3.05 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.34, 151.97, 137.81, 136.92, 132.37, 130.61, 129.58, 127.92, 125.89 (q,  $J = 278.9$  Hz), 124.18, 124.14, 123.56, 118.96, 109.13, 67.50 (q,  $J = 29.9$  Hz), 50.12, 36.81;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.01; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{17}\text{H}_{13}\text{BrF}_3\text{NNaO}$ : 406.0025, Found: 406.0010.



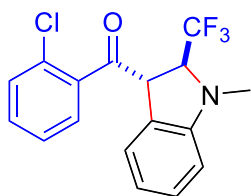
**(2-methoxyphenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3p**

White solid. 45.6 mg, 68% yield:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.59 – 7.52 (m, 2H), 7.10 (t,  $J = 7.6$  Hz, 1H), 7.06 – 7.02 (m, 2H), 6.62 – 6.53 (m, 3H), 5.48 (d,  $J = 6.0$  Hz, 1H), 4.74 – 4.67 (m, 1H), 3.93 (s, 3H), 3.02 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 197.61, 158.38, 151.76, 134.32, 131.45, 128.96, 126.96, 126.15 (q,  $J = 278.6$  Hz), 125.42, 124.20, 121.13, 118.69, 111.75, 108.73, 67.00 (q,  $J = 29.8$  Hz), 55.74, 54.26, 36.83;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.44; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{18}\text{H}_{16}\text{F}_3\text{NNaO}_2$ : 358.1025, Found: 358.1030.



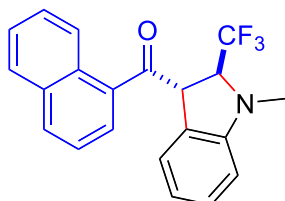
**(2-fluorophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3q**

White solid. 45.9 mg, 71% yield:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.80 (td,  $J = 7.6, 1.6$  Hz, 1H), 7.64 – 7.58 (m, 1H), 7.30 – 7.22 (m, 2H), 7.13 (t,  $J = 8.0$  Hz, 1H), 6.72 (d,  $J = 7.6$  Hz, 1H), 6.59 – 6.55 (m, 2H), 5.19 (d,  $J = 5.6$  Hz, 1H), 4.78 – 4.71 (m, 1H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.48 (d,  $J = 3.8$  Hz), 162.53, 160.51, 151.75, 135.50 (d,  $J = 9.1$  Hz), 131.71 (d,  $J = 1.8$  Hz), 129.41, 125.97 (q,  $J = 278.9$  Hz), 125.02 (d,  $J = 3.4$  Hz), 124.76 (d,  $J = 11.6$  Hz), 124.15 (d,  $J = 1.6$  Hz), 118.84, 117.02 (d,  $J = 23.4$  Hz), 108.90, 66.75 (q,  $J = 30.0$  Hz), 54.29 (d,  $J = 9.0$  Hz), 36.61;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.48, -110.80; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{17}\text{H}_{13}\text{F}_4\text{NNaO}$ : 346.0825, Found: 346.0828.



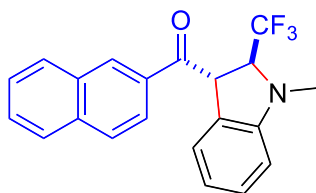
**(2-chlorophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3r**

White solid. 47.6 mg, 70% yield:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.52 – 7.46 (m, 2H), 7.40 – 7.37 (m, 2H), 7.13 (t,  $J = 7.6$  Hz, 1H), 6.57 – 6.53 (m, 2H), 6.47 – 6.45 (m, 1H), 5.18 (d,  $J = 5.6$  Hz, 1H), 4.74 – 4.68 (m, 1H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 197.29, 151.51, 137.66, 132.46, 131.51, 130.82, 130.14, 129.49, 127.07, 125.89 (q,  $J = 279.5$  Hz), 124.40, 123.44, 118.64, 108.77, 66.18 (q,  $J = 30.1$  Hz), 54.11, 36.46;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.54; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{17}\text{H}_{13}\text{ClF}_3\text{NNaO}$ : 362.0530, Found: 362.0523.



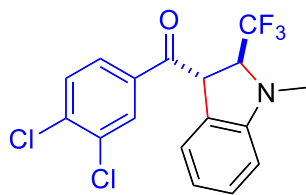
**(1-methyl-2-(trifluoromethyl)indolin-3-yl)(naphthalen-1-yl)methanone: 3s**

White solid. 56.9 mg, 80% yield.:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.28 (d,  $J = 7.5$  Hz, 1H), 8.08 (d,  $J = 8.5$  Hz, 1H), 7.97 (d,  $J = 7.0$  Hz, 1H), 7.92 – 7.90 (m, 1H), 7.60 (t,  $J = 7.5$  Hz, 1H), 7.56 – 7.51 (m, 2H), 7.11 (t,  $J = 7.5$  Hz, 1H), 6.60 (d,  $J = 8.0$  Hz, 1H), 6.46 – 6.42 (m, 2H), 5.27 (d,  $J = 6.0$  Hz, 1H), 4.84 – 4.79 (m, 1H), 3.07 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 197.47, 151.87, 135.24, 134.02, 133.54, 130.83, 129.51, 129.36, 128.50, 128.36, 126.96, 126.16 (q,  $J = 278.5$  Hz), 125.67, 124.50, 124.29, 124.13, 118.87, 109.01, 67.10 (q,  $J = 29.9$  Hz), 53.43, 36.90;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -74.92; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{21}\text{H}_{16}\text{F}_3\text{NNaO}$ : 378.1076, Found: 378.1074.



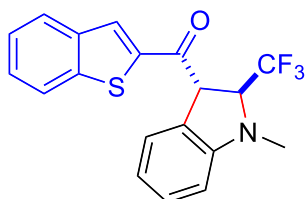
**(1-methyl-2-(trifluoromethyl)indolin-3-yl)(naphthalen-2-yl)methanone: 3t**

White solid. 59.0 mg, 83% yield.:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.63 (s, 1H), 8.12 (dd,  $J = 8.7, 1.8$  Hz, 1H), 8.04 (d,  $J = 8.1$  Hz, 1H), 7.99 – 7.96 (m, 1H), 7.94 – 7.91 (m, 1H), 7.69 – 7.58 (m, 2H), 7.14 (t,  $J = 7.8$  Hz, 1H), 6.78 (d,  $J = 7.5$  Hz, 1H), 6.61 (d,  $J = 7.8$  Hz, 1H), 6.54 (t,  $J = 7.5$  Hz, 1H), 5.36 (d,  $J = 6.6$  Hz, 1H), 4.85 – 4.76 (m, 1H), 3.06 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.46, 152.09, 136.04, 133.43, 132.61, 131.53, 129.84, 129.41, 129.19, 129.08, 127.93, 127.24, 125.72 (q,  $J = 353.6$  Hz), 124.87, 124.70, 124.35, 118.93, 109.10, 67.71 (q,  $J = 29.8$  Hz), 50.08, 36.98;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -74.86; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{21}\text{H}_{16}\text{F}_3\text{NNaO}$ : 378.1076, Found: 378.1071.



**(3,4-dichlorophenyl)(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3u**

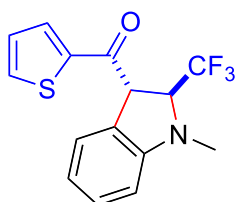
White solid. 47.1 mg, 63% yield:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.15 (d,  $J = 2.0$  Hz, 1H), 7.91 (dd,  $J = 8.5, 2.0$  Hz, 1H), 7.68 (d,  $J = 8.5$  Hz, 1H), 7.17 (t,  $J = 7.5$  Hz, 1H), 6.72 (d,  $J = 7.5$  Hz, 1H), 6.62 (t,  $J = 7.5$  Hz, 2H), 5.06 (d,  $J = 6.5$  Hz, 1H), 4.71 – 4.66 (m, 1H), 3.04 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 192.55, 151.97, 138.94, 135.59, 134.07, 131.30, 131.22, 129.71, 128.31, 125.83 (q,  $J = 278.5$  Hz), 124.10, 123.90, 119.01, 109.21, 67.50 (q,  $J = 30.0$  Hz), 50.07, 36.80;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.03; HRMS (ESI)  $[(\text{M}+\text{Na}^+)]$  Calcd. For  $\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{F}_3\text{NNaO}$ : 396.0140, Found: 396.0135.



**benzo[b]thiophen-2-yl(1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 3v**

3v

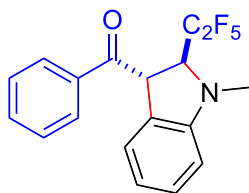
White solid. 57.1 mg, 79% yield:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.19 (s, 1H), 7.99 (d,  $J = 8.0$  Hz, 1H), 7.91 (d,  $J = 8.0$  Hz, 1H), 7.54 – 7.44 (m, 2H), 7.17 (t,  $J = 7.6$  Hz, 1H), 6.97 (d,  $J = 7.6$  Hz, 1H), 6.66 – 6.62 (m, 2H), 5.11 (d,  $J = 6.4$  Hz, 1H), 4.70 – 4.63 (m, 1H), 3.04 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 189.12, 152.16, 143.39, 142.87, 139.09, 131.15, 129.67, 128.17, 126.44, 125.89 (q,  $J = 278.4$  Hz), 125.43, 124.71, 124.29, 123.14, 119.15, 109.29, 67.78 (q,  $J = 30.0$  Hz), 51.29, 37.03;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.02; HRMS (ESI)  $[(\text{M}+\text{Na}^+)]$  Calcd. For  $\text{C}_{19}\text{H}_{14}\text{F}_3\text{NNaOS}$ : 384.0640, Found: 384.0638.



**(1-methyl-2-(trifluoromethyl)indolin-3-yl)(thiophen-2-yl)methanone: 3w**

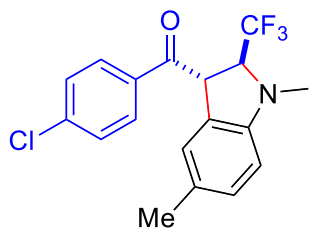
White solid. 49.8 mg, 80% yield:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.92 (dd,  $J = 4.0, 1.2$  Hz, 1H), 7.80 (dd,  $J = 5.2, 1.2$  Hz, 1H), 7.28 – 7.25 (m, 1H), 7.17 (t,  $J = 7.6$  Hz, 1H), 6.91 (d,  $J = 7.6$  Hz, 1H), 6.67 – 6.60 (m, 2H), 4.96 (d,  $J = 6.4$  Hz, 1H), 4.66 – 4.59 (m, 1H), 3.03 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 187.63, 152.16, 143.38, 135.87, 133.80, 129.55, 128.68, 125.87 (q,  $J = 278.4$  Hz), 124.93, 124.18, 119.08, 109.20, 67.77 (q,  $J = 30.0$  Hz), 51.46, 37.02;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.06; HRMS (ESI)  $[(\text{M}+\text{Na}^+)]$  Calcd. For  $\text{C}_{15}\text{H}_{12}\text{F}_3\text{NNaOS}$ : 334.0484, Found: 334.0477.





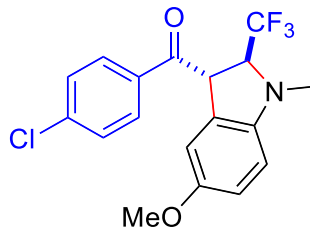
**(1-methyl-2-(perfluoroethyl)indolin-3-yl)(phenyl)methanone: 3x**

White solid. 42.6 mg, 60% yield.:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.08 (d,  $J = 7.5$  Hz, 2H), 7.69 (t,  $J = 7.5$  Hz, 1H), 7.58 (t,  $J = 8.0$  Hz, 2H), 7.14 (t,  $J = 7.5$  Hz, 1H), 6.72 (d,  $J = 7.5$  Hz, 1H), 6.63 (d,  $J = 8.0$  Hz, 1H), 6.59 (t,  $J = 7.5$  Hz, 1H), 5.30 (d,  $J = 6.0$  Hz, 1H), 4.88 – 4.82 (m, 1H), 3.05 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.63, 152.27, 135.87, 134.09, 129.45, 129.37, 129.14, 125.15, 124.16, 119.17, 119.14 (qt,  $J = 285.0, 35.9$  Hz), 114.76 (tq,  $J = 254.2, 35.1$  Hz), 109.92, 66.93 (t,  $J = 21.4$  Hz), 49.88, 38.58;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -81.49 (s, 3F), -121.79 – -123.39 (m, 2F); HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{18}\text{H}_{14}\text{F}_5\text{NO}$ : 378.0888, Found: 378.0886.



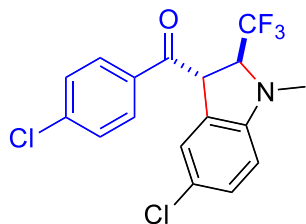
**(4-chlorophenyl)(1,5-dimethyl-2-(trifluoromethyl)indolin-3-yl)methanone: 4a**

White solid. 53.1 mg, 75% yield.:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.03 (d,  $J = 8.5$  Hz, 2H), 7.56 (d,  $J = 8.0$  Hz, 2H), 6.96 (d,  $J = 8.0$  Hz, 1H), 6.53 (s, 2H), 5.10 (d,  $J = 6.0$  Hz, 1H), 4.64 – 4.61 (m, 1H), 3.00 (s, 3H), 2.11 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.80, 150.06, 140.78, 134.42, 130.82, 129.96, 129.50, 128.65, 125.99 (q,  $J = 278.1$  Hz), 124.85, 124.66, 109.39, 68.20 (q,  $J = 29.8$  Hz), 49.91, 37.62, 20.69;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -74.98; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{18}\text{H}_{15}\text{ClF}_3\text{NNaO}$ : 376.0686, Found: 376.0687.



**(4-chlorophenyl)(5-methoxy-1-methyl-2-(trifluoromethyl)indolin-3-yl)methanone: 4b**

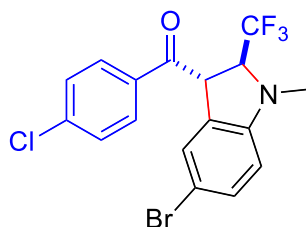
White solid. 51.8 mg, 70% yield.:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.04 – 8.00 (m, 2H), 7.57 – 7.54 (m, 2H), 6.73 (dd,  $J = 8.0, 2.4$  Hz, 1H), 6.56 (d,  $J = 8.8$  Hz, 1H), 6.34 – 6.33 (m, 1H), 5.09 (d,  $J = 6.8$  Hz, 1H), 4.65 – 4.58 (m, 1H), 3.60 (s, 3H), 2.98 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.51, 153.55, 146.45, 140.88, 134.34, 130.75, 129.55, 125.98 (q,  $J = 277.8$  Hz), 125.96, 113.74, 111.75, 110.10, 68.37 (q,  $J = 29.8$  Hz), 55.93, 50.03, 38.41;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.08; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{18}\text{H}_{15}\text{ClF}_3\text{NNaO}_2$ : 392.0636, Found: 392.0631.



**(5-chloro-1-methyl-2-(trifluoromethyl)indolin-3-yl)(4-chlorophenyl)methanone: 4c**

**ne: 4c**

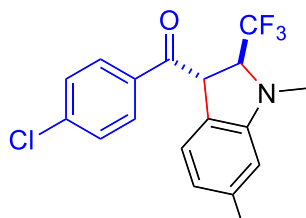
White solid. 50.9 mg, 68% yield.:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.03 – 8.01 (m, 2H), 7.60 – 7.57 (m, 2H), 7.11 (dd,  $J$  = 8.5, 1.5 Hz, 1H), 6.67 (s, 1H), 6.50 (d,  $J$  = 8.5 Hz, 1H), 5.08 (d,  $J$  = 6.5 Hz, 1H), 4.72 – 4.67 (m, 1H), 3.02 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 192.95, 150.65, 141.20, 133.86, 130.75, 129.70, 129.44, 126.01, 125.67 (q,  $J$  = 278.6 Hz), 124.27, 123.57, 109.71, 67.87 (q,  $J$  = 30.3 Hz), 49.45, 36.75;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.21; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{F}_3\text{NO}$ : 373.0248, Found: 373.0245.



**(5-bromo-1-methyl-2-(trifluoromethyl)indolin-3-yl)(4-chlorophenyl)methanone: 4d**

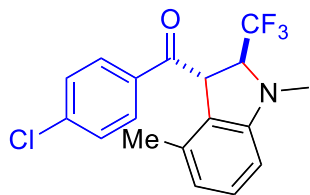
**ne: 4d**

White solid. 60.3 mg, 72% yield:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.02 (d,  $J$  = 8.5 Hz, 2H), 7.58 (d,  $J$  = 8.0 Hz, 2H), 7.26 – 7.24 (m, 1H), 6.80 (s, 1H), 6.46 (d,  $J$  = 8.5 Hz, 1H), 5.09 (d,  $J$  = 6.0 Hz, 1H), 4.71 – 4.66 (m, 1H), 3.02 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 192.97, 151.06, 141.21, 133.83, 132.33, 130.75, 129.71, 127.01, 126.50, 125.62 (q,  $J$  = 278.6 Hz), 110.39, 110.23, 67.82 (q,  $J$  = 30.0 Hz), 49.38, 36.58;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.21; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{17}\text{H}_{12}\text{BrClF}_3\text{NO}$ : 416.9743, Found: 416.9740.



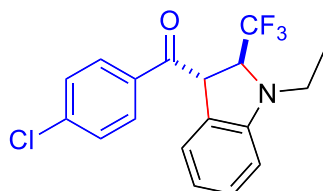
**(4-chlorophenyl)(1,6-dimethyl-2-(trifluoromethyl)indolin-3-yl)methanone: 4e**

White solid. 32.5 mg, 46% yield.:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.03 – 8.00 (m, 2H), 7.56 – 7.53 (m, 2H), 6.59 (d,  $J$  = 7.6 Hz, 1H), 6.42 – 6.40 (m, 2H), 6.06 (d,  $J$  = 6.4 Hz, 1H), 4.72 – 4.65 (m, 1H), 3.02 (s, 3H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.51, 152.12, 140.64, 139.74, 134.37, 130.77, 129.41, 125.95 (q,  $J$  = 278.9 Hz), 123.82, 121.57, 119.66, 109.97, 67.72 (q,  $J$  = 29.8 Hz), 49.75, 36.79, 21.61;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -75.16; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For  $\text{C}_{18}\text{H}_{15}\text{ClF}_3\text{NNaO}$ : 376.0686, Found: 376.0677.



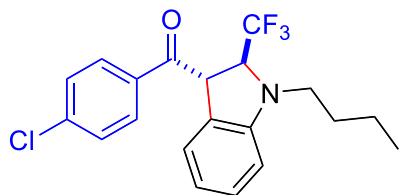
**(4-chlorophenyl)(1,4-dimethyl-2-(trifluoromethyl)indolin-3-yl)methanone 4e'**

White solid. 21.2 mg, 30% yield.: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.97 – 7.94 (m, 2H), 7.50 – 7.46 (m, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.51 (dd, *J* = 13.6, 7.6 Hz, 2H), 5.09 (d, *J* = 6.0 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.00 (s, 3H), 1.90 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.40, 152.54, 140.56, 134.60, 134.06, 130.11, 129.58, 129.38, 125.63 (q, *J* = 279.8 Hz), 125.29, 121.24, 106.62, 70.55 (q, *J* = 29.9 Hz), 49.44, 36.95, 19.50; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -75.02; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For C<sub>18</sub>H<sub>15</sub>ClF<sub>3</sub>NNaO: 376.0686, Found: 376.0686.



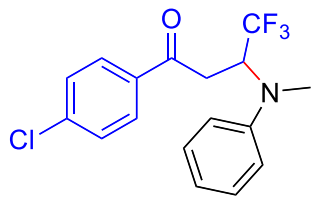
**(4-chlorophenyl)(1-ethyl-2-(trifluoromethyl)indolin-3-yl)methanone: 4f**

White solid. 46.7 mg, 66% yield.: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.03 – 8.00 (m, 2H), 7.56 – 7.53 (m, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 7.1 Hz, 1H), 6.61 – 6.55 (m, 2H), 5.08 (d, *J* = 5.6 Hz, 1H), 4.91 – 4.84 (m, 1H), 3.59 – 3.50 (m, 1H), 3.44 – 3.35 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 193.58, 150.68, 140.68, 134.30, 130.79, 129.46, 129.42, 125.95 (q, *J* = 278.5 Hz), 124.64, 124.32, 118.52, 109.21, 64.45 (q, *J* = 30.0 Hz), 49.94, 43.55, 11.09; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -75.80; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For C<sub>18</sub>H<sub>15</sub>ClF<sub>3</sub>NNaO: 376.0686, Found: 376.0684.



**(1-butyl-2-(trifluoromethyl)indolin-3-yl)(4-chlorophenyl)methanone: 4g**

White solid. 49.6 mg, 65% yield.: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.03 – 8.00 (m, 2H), 7.56 – 7.53 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.58 – 6.53 (m, 2H), 5.08 (d, *J* = 6.0 Hz, 1H), 4.91 – 4.84 (m, 1H), 3.48 – 3.40 (m, 1H), 3.34 – 3.26 (m, 1H), 1.78 – 1.67 (m, 1H), 1.63 – 1.54 (m, 1H), 1.43 – 1.34 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 193.55, 151.15, 140.66, 134.30, 130.79, 129.43, 129.41, 129.06, 125.93 (q, *J* = 279.0 Hz), 124.29, 118.29, 108.94, 65.02 (q, *J* = 30.0 Hz), 49.98, 49.14, 28.46, 20.23, 13.90; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -75.64; HRMS (ESI) [(M+Na<sup>+</sup>)] Calcd. For C<sub>20</sub>H<sub>19</sub>ClF<sub>3</sub>NNaO: 404.0999, Found: 404.0989.



**1-(4-chlorophenyl)-4,4,4-trifluoro-3-(methyl(phenyl)amino)butan-1-one: 5**

White solid. 52.0 mg, 76% yield.:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.89 – 7.84 (m, 2H), 7.46 – 7.41 (m, 2H), 7.28 – 7.23 (m, 2H), 6.97 (d,  $J = 8.1$  Hz, 2H), 6.84 (t,  $J = 7.2$  Hz, 1H), 5.21 – 5.08 (m, 1H), 3.61 (dd,  $J = 17.4, 9.0$  Hz, 1H), 3.24 (dd,  $J = 17.4, 3.9$  Hz, 1H), 2.87 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.01, 149.93, 140.34, 134.66, 129.63, 129.26, 129.25, 126.45 (q,  $J = 285.4$  Hz), 119.53, 115.11, 57.55 (q,  $J = 28.8$  Hz), 35.43, 32.84;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -71.64; HRMS (ESI)  $[(\text{M}+\text{Na}^+)]$  Calcd. For  $\text{C}_{17}\text{H}_{15}\text{ClF}_3\text{NNaO}$ : 364.0686, Found: 364.0689.

## 7. References:

- [1] (a) H. Wang, W. Lu and J. Zhang, *Chem. Eur. J.*, 2017, **23**, 13587–13590. (b) P. Kwiatkowski, A. Cholewiak and A. Kasztelan, *Org. Lett.*, 2014, **16**, 5930–5933.

## 8. $^1\text{H}$ , $^{19}\text{F}$ NMR and $^{13}\text{C}$ NMR spectra of the products

