

Supporting Information

Synthesis of oxindoles through trifluoromethylation of *N*-aryl acrylamides by photoredox catalysis

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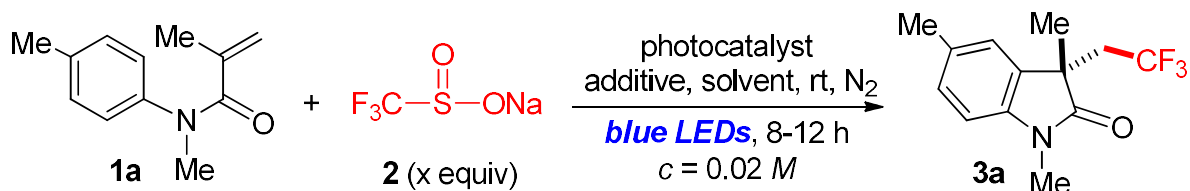
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Materials and methods

All the chemicals were purchased commercially, and used without further purification. Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. ^1H NMR spectra were recorded on JEOL spectrometers (400 MHz) and were reported relative to deuterated solvent signals. Data for ^1H NMR spectra were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on JEOL Spectrometers (100 MHz). ^{19}F NMR spectra were recorded on JEOL Spectrometers (376 MHz). Data for ^{13}C NMR and ^{19}F NMR spectra were reported in terms of chemical shift. Mass spectrometric data were obtained using Bruker Apex IV RTMS. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

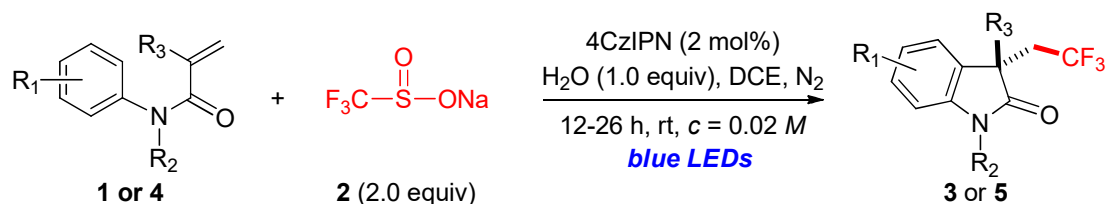
Screenings of reaction conditions



entry	2a (equiv)	PC (x mol%) ^h	additive (equiv)	solvent	yield (%) ^g
1 ^a	1.5	eosin Y (2)	/	DCE	trace
2 ^a	1.5	4CzIPN (2)	/	DCE	18
3 ^b	1.5	4CzIPN (2)	/	DCE	47
4 ^b	1.5	4CzIPN (2)	NaOAc (1.0)	DCE	decomp
5 ^b	1.5	4CzIPN (2)	HOAc (1.0)	DCE	21
6 ^b	1.5	4CzIPN (2)	H ₂ O (1.0)	DCE	62
7 ^b	1.5	4CzIPN (2)	MeOH (1.0)	DCE	33
8 ^{b,c}	1.5	4CzIPN (2)	H ₂ O (1.0)	DCE	72
9 ^{b,c}	1.5	4CzIPN (2)	H ₂ O (1.0)	DCM	34
10 ^{b,c}	1.5	4CzIPN (2)	H ₂ O (1.0)	ACN	26
11 ^{b,c}	1.5	4CzIPN (2)	H ₂ O (1.0)	DMSO	decomp
12 ^{b,c}	1.5	4CzIPN (2)	H ₂ O (1.0)	C ₆ H ₅ Cl	47
13^{b,c}	2.0	4CzIPN (2)	H₂O (1.0)	DCE	83
14 ^{b,c,d}	2.0	[Ir-cat. 1] (2)	H ₂ O (1.0)	DCE	64
15 ^{b,c,e}	2.0	[Ir-cat. 2] (2)	H ₂ O (1.0)	DCE	71
16 ^{b,c}	2.0	[Ru(bpy) ₃ Cl ₂] (2)	H ₂ O (1.0)	DCE	trace

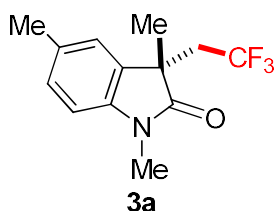
^aIrradiation with white LEDs. ^bIrradiation with blue LEDs. ^cReaction mixture was purged thoroughly with nitrogen for 10 mins. ^d[Ir-cat. 1] = Ir(ppy)₂(dtbpy)PF₆. ^e[Ir-cat. 2] = Ir[dF(CF₃)ppy]₂(dtbpy)PF₆. ^fNo light. ^gYield of isolated product. ^h4CzIPN = 1,2,3,5-tetra-kis(carbazol-9-yl)-4,6-dicyanobenzene.

General procedure for CF₃-containing oxindoles synthesis



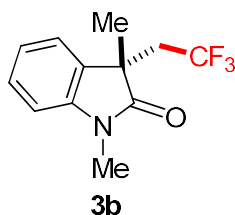
A flame-dried flask (15 mL) was equipped with magnetic stir bar and charged with *N*-aryl-acrylamides **1** (0.145 mmol, 1.0 equiv), CF₃SO₂Na **2** (0.29 mmol, 2.0 equiv), 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) (0.00290 mmol, 0.02 equiv), H₂O (0.145 mmol, 1.0 equiv) and DCE (8.0 mL). The reaction mixture was degassed by purging thoroughly with nitrogen (with 0.5 mol % of oxygen) for 10 minutes, then irradiated by blue LED (18 W) under a balloon nitrogen atmosphere (with 0.5 mol % of oxygen) at room temperature until the starting material disappeared from the TLC. After that the reaction mixture was directly concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using hexane/EtOAc (10/1 to 4/1) to afford the desired pure product **3** or **5** in 41-91% yield.

¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra data of compounds 3a-3p, 5a-5l

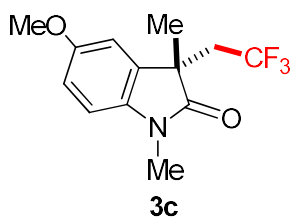


1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3a): ¹H NMR (400 MHz,

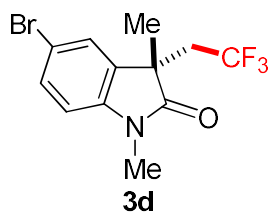
CDCl₃) δ 7.12-7.08 (m, 2H), 6.78-6.76 (d, $J = 7.6$ Hz, 1H), 3.22 (s, 3H), 2.84-2.77 (m, 2H), 2.66-2.60 (m, 2H), 2.35 (s, 3H), 1.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.5, 140.5, 132.3, 131.1, 128.8, 125.6 (q, $J = 276.6$ Hz), 124.4, 108.2, 44.5, 40.7 (q, $J = 27.8$ Hz), 26.5, 25.1, 21.2; These data are consistent with literature values, see: Zhang, L.; Li, Z.; Liu, Z.-Q. *Org. Lett.* **2014**, *16*, 3688.



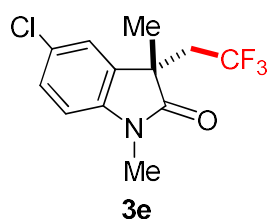
1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3b): ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.26 (m, 2H), 7.12-7.10 (m, 1H), 6.90-6.88 (d, $J = 7.6$ Hz, 1H), 3.24 (s, 3H), 2.83-2.80 (m, 1H), 2.69-2.62 (m, 1H), 1.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.6, 142.9, 131.1, 128.6, 125.2 (q, $J = 277.0$ Hz), 123.6, 122.7, 108.5, 44.5, 40.6 (q, $J = 27.8$ Hz), 26.5, 25.1. These data are consistent with literature values, see: Zhang, L.; Li, Z.; Liu, Z.-Q. *Org. Lett.* **2014**, *16*, 3688.



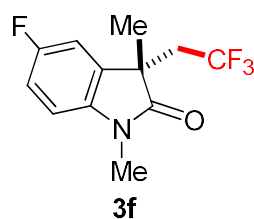
5-methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3c): ¹H NMR (400 MHz, CDCl₃) δ 6.88-6.78 (m, 3H), 3.80 (s, 3H), 3.22 (s, 3H), 2.82-2.78 (m, 1H), 2.66-2.62 (m, 1H), 1.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.2, 156.1, 136.4, 132.5, 125.2 (q, $J = 279.9$ Hz), 112.6, 111.3, 108.8, 55.9, 44.9, 40.6 (q, $J = 28.2$ Hz), 26.6, 25.1. These data are consistent with literature values, see: Tang, X.-J.; Thomason, C. S.; Dolbier, Jr., W. R. *Org. Lett.* **2014**, *16*, 4594.



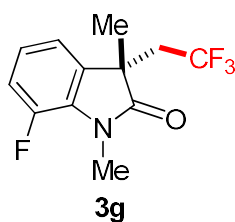
5-bromo-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3d): ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.37 (m, 2H), 6.77-6.75 (d, $J = 8.4$ Hz, 1H), 3.22 (s, 3H), 2.86-2.80 (m, 1H), 2.66-2.59 (m, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.9, 141.9, 133.2 (d, $J = 2.0$ Hz), 131.5, 126.9, 125.1 (q, $J = 277.0$ Hz), 115.5, 110.0, 44.6, 40.6 (q, $J = 28.7$ Hz), 26.6, 25.0. These data are consistent with literature values, see: Zhang, L.; Li, Z.; Liu, Z.-Q. *Org. Lett.* **2014**, *16*, 3688.



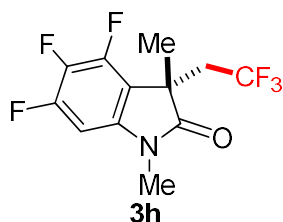
5-chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3e): ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.25 (m, 2H), 6.83-6.80 (m, 1H), 3.22 (s, 3H), 2.84-2.80 (m, 1H), 2.67-2.63 (m, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.1, 141.5, 132.7, 128.7, 128.6, 128.2, 125.1 (q, $J = 275.9$ Hz), 124.2, 109.5, 44.7, 40.6 (q, $J = 27.7$ Hz), 26.6, 25.0. These data are consistent with literature values, see: Zhang, L.; Li, Z.; Liu, Z.-Q. *Org. Lett.* **2014**, *16*, 3688.



5-fluoro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3f): ^1H NMR (400 MHz, CDCl_3) δ 7.03-7.00 (m, 2H), 6.83-6.80 (m, 1H), 3.23 (s, 3H), 2.84-2.80 (m, 1H), 2.67-2.63 (m, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.2, 160.6 (d, $J = 239.6$ Hz), 138.9, 129 (d, $J = 8.6$ Hz), 125.1 (d, $J = 275.9$ Hz), 123.8, 115.0 (d, $J = 23.0$ Hz), 111.8 (d, $J = 24.5$ Hz), 109.1 (d, $J = 7.7$ Hz), 44.9, 40.6 (q, $J = 27.8$ Hz), 26.7, 25.0. These data are consistent with literature values, see: L. Zhang, Z. Li and Z.-Q. Liu, *Org. Lett.*, 2014, **16**, 3688.

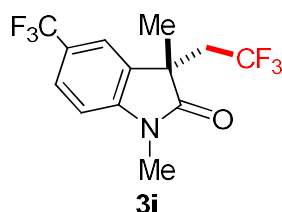


7-fluoro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3g): ^1H NMR (400 MHz, CDCl_3) δ 7.04-7.02 (m, 3H), 3.45 (s, 3H), 2.91-2.78 (m, 1H), 2.67-2.60 (m, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.2, 148.0 (d, $J = 242.5$ Hz), 133.9, 130.0, 125.1 (q, $J = 276.9$ Hz), 123.3 (d, $J = 6.7$ Hz), 119.4, 116.5 (d, $J = 19.2$ Hz), 44.7, 40.9 (d, $J = 27.8$ Hz), 29.0 (d, $J = 5.7$ Hz), 25.4; ^{19}F NMR (376 MHz, CDCl_3) δ -61.9, -65.1; HRMS calculated for $\text{C}_{12}\text{H}_{12}\text{F}_4\text{NO}$ ($\text{M} + \text{H}^+$): 262.0855, found: 262.0853.

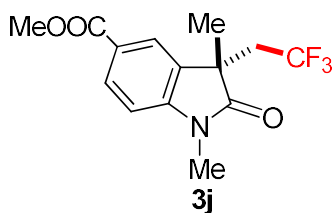


4,5,6-trifluoro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3h): ^1H NMR (400 MHz, CDCl_3) δ 6.57-6.53 (m, 1H), 3.20 (s, 3H), 2.96-2.87 (m, 1H), 2.84-2.78 (m, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.5, 151.9 (d, $J = 248.2$ Hz),

148.6 (d, $J = 246.3$ Hz), 138.2 (d, $J = 95.9$ Hz), 124.8 (q, $J = 277.0$ Hz), 135.4 (t, $J = 15.3$ Hz), 112.9 (d, $J = 17.3$ Hz), 44.2, 39.8 (d, $J = 27.8$ Hz), 26.9, 23.8; ^{19}F NMR (376 MHz, CDCl_3) δ -64.2, -132.9, -140.5, -168.8; HRMS calculated for $\text{C}_{12}\text{H}_{10}\text{F}_6\text{NO}$ ($\text{M} + \text{H}^+$): 298.0667, found: 298.0660.

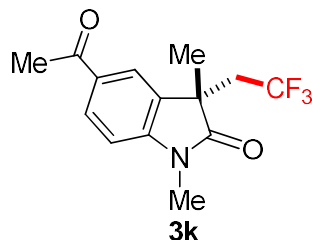


1,3-dimethyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (3i): ^1H NMR (400 MHz, CDCl_3) δ 7.62-7.60 (m, 1H), 7.50 (s, 1H), 6.98-6.96 (d, $J = 8.4$ Hz, 1H), 3.28 (s, 3H), 2.90-2.84 (m, 1H), 2.72-2.66 (m, 1H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.5, 146.0, 131.6, 126.5, 126.4, 125.0 (q, $J = 277.0$ Hz), 120.7, 108.4, 44.4, 40.6 (q, $J = 27.8$ Hz), 26.7, 25.0. These data are consistent with literature values, see: Tang, X.-J.; Thomason, C. S.; Dolbier, Jr., W. R. *Org.Lett.* **2014**, *16*, 4594.

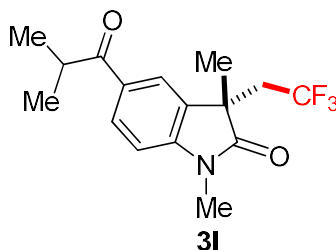


methyl 1,3-dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carboxylate (3j): ^1H NMR (400 MHz, CDCl_3) δ 8.08-8.06 (d, $J = 8.4$ Hz, 1H), 7.95-7.94 (d, $J = 1.2$ Hz, 1H), 6.94-6.92 (d, $J = 8.0$ Hz, 1H), 3.92 (s, 3H), 3.28 (s, 3H), 2.90-2.84 (m, 1H), 2.73-2.69 (m, 1H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.8, 166.8, 147.0, 131.3, 131.0, 125.1 (q, $J = 276.9$ Hz), 124.9, 124.8, 108.1, 52.2, 44.3, 40.7 (d, $J = 27.8$ Hz), 26.7, 25.1. These data are consistent with literature values, see: Tang, X.-J.;

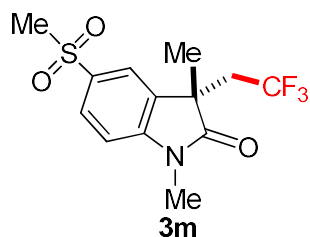
Thomson, C. S.; Dolbier, Jr., W. R. *Org.Lett.* **2014**, *16*, 4594.



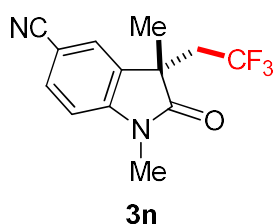
5-acetyl-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3k): ^1H NMR (400 MHz, CDCl_3) δ 7.99-7.97 (dd, $J = 8.4, 1.2$ Hz 1H), 7.92 (d, $J = 1.2$ Hz, 1H), 6.95-6.93 (d, $J = 8.4$ Hz, 1H), 3.29 (s, 3H), 2.88-2.85 (m, 1H), 2.74-2.65 (m, 1H), 2.60 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 178.8, 147.2, 132.3, 131.4, 130.7, 125.1 (q, $J = 276.9$ Hz), 123.5, 108.0, 44.2, 40.7 (q, $J = 27.8$ Hz), 26.8, 26.5, 25.1. These data are consistent with literature values, see: Liu, C.; Zhao, W.; Huang, Y.; Wang, H.; Zhang, B. *Tetrahedron* **2015**, *71*, 4344.



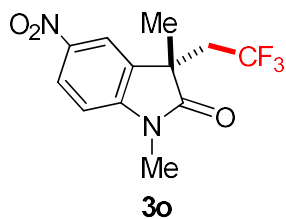
5-isobutyryl-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3l): ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.96 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.88 (d, $J = 1.2$ Hz, 1H), 6.93-6.91 (d, $J = 8.0$ Hz, 1H), 3.53-3.50 (m, 1H), 3.26 (s, 3H), 2.86-2.82 (m, 1H), 2.72-2.69 (m, 1H), 1.41 (s, 3H), 1.21-1.19 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 203.1, 178.9, 147.0, 131.3, 130.3, 125.1 (q, $J = 276.0$ Hz), 123.8, 108.1, 44.3, 40.6 (q, $J = 28.8$ Hz), 35.2, 26.8, 25.1, 19.5, 19.2; ^{19}F NMR (376 MHz, CDCl_3) δ -61.9; HRMS calculated for $\text{C}_{16}\text{H}_{19}\text{F}_3\text{NO}_2$ ($\text{M} + \text{H}^+$): 314.1368, found: 314.1372.



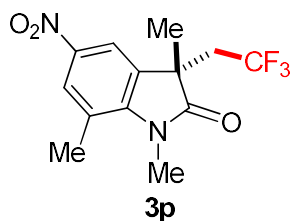
1,3-dimethyl-5-(methylsulfonyl)-3-(2,2,2-trifluoroethyl)indolin-2-one (3m): ^1H NMR (400 MHz, CDCl_3) δ 7.97-7.94 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.84-7.83 (d, $J = 1.6$ Hz, 1H), 7.06-7.04 (d, $J = 8.4$ Hz, 1H), 3.30 (s, 3H), 3.06 (s, 3H), 2.95-2.89 (m, 1H), 2.75-2.69 (m, 1H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.4, 147.8, 134.6, 132.1, 129.4, 125.0 (q, $J = 277.0$ Hz), 123.0, 108.8, 45.1, 40.6 (q, $J = 27.8$ Hz), 26.9, 25.0; ^{19}F NMR (376 MHz, CDCl_3) δ -62.0; HRMS calculated for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{NO}_3\text{S}$ ($\text{M} + \text{H}^+$): 322.0725, found: 322.0716.



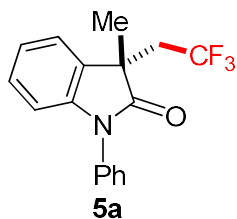
1,3-dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carbonitrile (3n): ^1H NMR (400 MHz, CDCl_3) δ 7.67 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.65 (d, $J = 1.6$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 3.74 (s, 3H), 2.95-2.82 (m, 1H), 2.75-2.61 (m, 1H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.2, 146.8, 134.0, 132.0, 131.0, 127.1, 125.1 (q, $J = 276.9$ Hz), 119.1, 109.1, 106.0, 44.2, 43.5, 40.6 (q, $J = 27.8$ Hz), 26.8, 24.9. These data are consistent with literature values, see: Liu, C.; Zhao, W.; Huang, Y.; Wang, H.; Zhang, B. *Tetrahedron* **2015**, *71*, 4344.



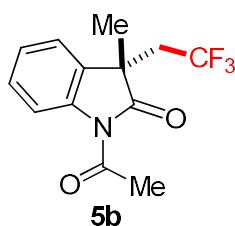
1,3-dimethyl-5-nitro-3-(2,2,2-trifluoroethyl)indolin-2-one (3o): ^1H NMR (400 MHz, CDCl_3) δ 8.33-8.30 (dd, $J = 8.4, 1.2$ Hz, 1H), 8.17 (d, $J = 2.4$ Hz, 1H), 7.00-6.98 (d, $J = 8.4$ Hz, 1H), 3.32 (s, 3H), 2.95-2.89 (m, 1H), 2.77-2.70 (m, 3H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.5, 148.6, 143.6, 131.8, 125.9, 125.1 (q, $J = 276.9$ Hz), 119.6, 108.2, 44.4, 40.6 (q, $J = 27.8$ Hz), 27.0, 25.0. These data are consistent with literature values, see: Tang, X.-J.; Thomason, C. S.; Dolbier, Jr., W. R. *Org.Lett.* **2014**, *16*, 4594.



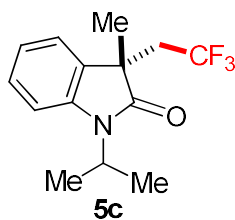
1,3,7-trimethyl-5-nitro-3-(2,2,2-trifluoroethyl)indolin-2-one (3p): ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 2.0$ Hz, 1H), 7.97 (d, $J = 2.0$ Hz, 1H), 3.58 (s, 3H), 2.98-2.88 (m, 1H), 2.78-2.62 (m, 4H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 179.4, 146.6, 143.0, 132.5, 128.7, 125.0 (q, $J = 276.9$ Hz), 120.8, 117.2, 43.8, 40.6 (q, $J = 28.7$ Hz), 30.0, 25.5, 19.3. ^{19}F NMR (376 MHz, CDCl_3) δ -62.0.



3-methyl-1-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5a): ^1H NMR (400 MHz, CDCl_3) δ 7.55-7.51 (m, 2H), 7.45-7.32 (m, 5H), 7.26-7.10 (m, 2H), 6.85-6.83 (d, $J = 7.6$ Hz, 1H), 3.00-2.94 (m, 1H), 2.76-2.70 (m, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.1, 143.0, 134.4, 129.8, 128.5, 128.4, 126.7, 125.1 (q, $J = 276.9$ Hz), 123.9, 123.2, 109.8, 44.6, 41.1 (q, $J = 27.8$ Hz), 25.5. These data are consistent with literature values, see: Tang, X.-J.; Thomason, C. S.; Dolbier, Jr., W. R. *Org.Lett.* **2014**, *16*, 4594.

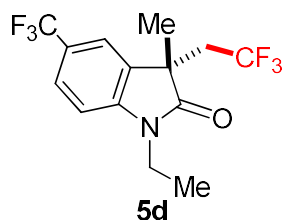


acetyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5b): ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 8.4$ Hz, 1H), 7.36-7.34 (m, 1H), 7.27-7.24 (m, 2H), 2.96-2.89 (m, 1H), 2.72-2.66 (m, 4H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 179.5, 171.0, 139.2, 129.9, 129.1, 125.4, 125.0 (q, $J = 276.9$ Hz), 123.1, 116.9, 45.1, 41.5 (q, $J = 28.8$ Hz), 26.7, 26.4; ^{19}F NMR (376 MHz, CDCl_3) δ -61.9; HRMS calculated for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{NNaO}_2$ ($\text{M} + \text{Na}^+$): 294.0718, found: 294.0697.



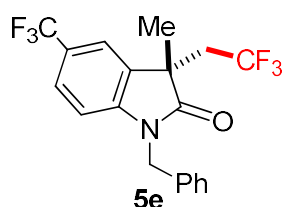
1-isopropyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5c): ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.24 (m, 2H), 7.06-7.03 (m, 2H), 4.65-4.60 (m, 1H), 2.88-2.80 (m, 1H), 1.49-1.46 (m, 6H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.2, 141.6, 131.5, 128.3, 125.0 (q, $J = 277.0$ Hz), 123.9, 122.1, 110.2, 44.1, 40.8 (q, $J =$

27.8 Hz), 25.4, 19.3, 19.1. These data are consistent with literature values, see: Xu, P.; Xie, J.; Xue, Q.; Pan, C.; Cheng, Y.; Zhu, C. *Chem. – Eur. J.* **2013**, *19*, 14039.



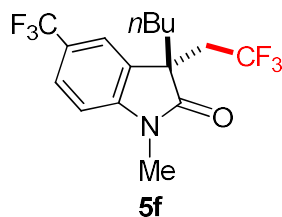
1-ethyl-3-methyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (5d):

^1H NMR (400 MHz, CDCl_3) δ 7.65-7.60 (d, $J = 8.4$ Hz, 1H), 7.50 (s, 1H), 6.98 (d, $J = 8.4$ Hz, 1H), 3.94-3.89 (m, 1H), 3.74-3.68 (m, 1H), 2.92-2.86 (m, 1H), 2.71-2.64 (m, 1H), 1.43 (s, 3H), 1.28-1.24 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.1, 145.0, 131.8, 126.5, 126.4, 120.9, 108.5, 44.3, 40.8 (q, $J = 27.8$ Hz), 35.1, 25.1, 12.2; ^{19}F NMR (376 MHz, CDCl_3) δ -61.4, -61.9; HRMS calculated for $\text{C}_{14}\text{H}_{14}\text{F}_6\text{NO}$ ($\text{M} + \text{H}^+$): 326.0980, found: 326.0982.



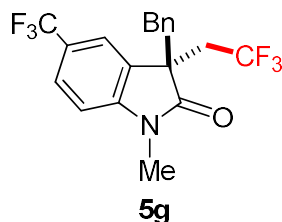
1-benzyl-3-methyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (5e):

^1H NMR (400 MHz, CDCl_3) δ 7.52-7.41 (m, 2H), 7.29-7.20 (m, 5H), 6.84 (d, $J = 7.6$ Hz, 1H), 5.03 (d, $J = 15.6$ Hz, 1H), 4.93 (d, $J = 15.6$ Hz, 1H), 2.99-2.93 (m, 1H), 2.77-2.71 (m, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.5, 145.0, 135.0, 131.6, 129.0, 128.1, 127.3, 126.3, 125.4 (q, $J = 32.5$ Hz), 125.1 (q, $J = 276.9$ Hz), 120.8, 109.5, 44.5, 44.3, 40.4 (q, $J = 27.8$ Hz), 25.7; ^{19}F NMR (376 MHz, CDCl_3) δ -61.5, -61.7; HRMS calculated for $\text{C}_{19}\text{H}_{16}\text{F}_6\text{NO}$ ($\text{M} + \text{H}^+$): 388.1136, found: 388.1132.



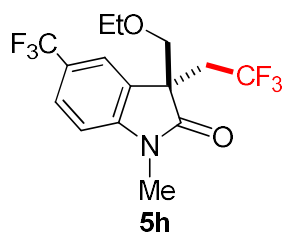
3-butyl-1-methyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (5f):

^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.4$ Hz, 1H), 7.45 (s, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 3.27 (s, 3H), 2.95-2.82 (m, 1H), 2.75-2.62 (m, 1H), 1.95-1.85 (m, 1H), 1.81-1.72 (m, 1H), 1.30-1.12 (m, 2H), 1.00-0.86 (m, 1H), 0.79-0.77 (m, 3H), 0.77-0.76 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.0, 146.7, 129.9, 126.5, 124.8 (q, $J = 32.6$ Hz), 124.4 (q, $J = 270.3$ Hz), 120.7, 108.2, 48.5, 40.4 (q, $J = 28.7$ Hz), 38.5, 26.6, 25.2, 22.5, 13.8; ^{19}F NMR (376 MHz, CDCl_3) δ -61.3, -61.6; HRMS calculated for $\text{C}_{16}\text{H}_{18}\text{F}_6\text{NO}$ ($\text{M} + \text{H}^+$): 354.1293, found: 354.1288.

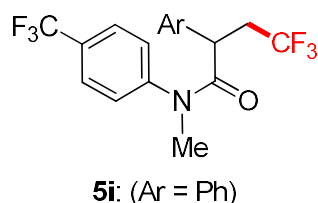


3-benzyl-1-methyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (5g):

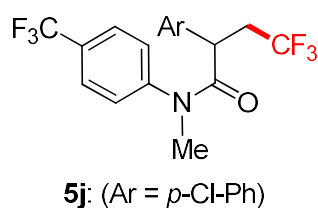
^1H NMR (400 MHz, CDCl_3) δ 7.52-7.50 (m, 1H), 7.40 (s, 1H), 7.14-7.05 (m, 3H), 6.75-6.73 (m, 2H), 3.10-2.99 (m, 5H), 2.85-2.78 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.1, 146.4, 133.4, 130.0, 128.7, 127.9, 127.4, 126.4, 125.1 (q, $J = 270.0$ Hz), 108.0, 50.1, 44.7, 39.3 (q, $J = 28.8$ Hz), 26.3; ^{19}F NMR (376 MHz, CDCl_3) δ -61.2, -61.5; HRMS calculated for $\text{C}_{19}\text{H}_{15}\text{F}_6\text{NNaO}$ ($\text{M} + \text{H}^+$): 410.0956, found: 410.0951.



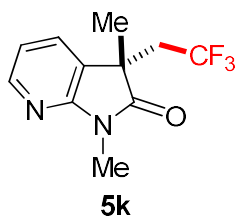
3-(ethoxymethyl)-1-methyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (5h): ^1H NMR (400 MHz, CDCl_3) δ 7.64-7.63 (m, 2H), 6.96-6.94 (d, $J = 8.8$ Hz, 1H), 3.68-3.66 (d, $J = 9.2$ Hz, 1H), 3.46-3.32 (m, 3H), 3.26 (s, 3H), 3.10-3.01 (m, 1H), 2.90-2.82 (m, 1H), 1.17-1.11 (t, $J = 8.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.0, 146.4, 129.1, 126.5, 125.5 (q, $J = 276.9$ Hz), 124.8 (q, $J = 33.6$ Hz), 122.5, 108.1, 74.0, 67.4, 49.5, 36.7 (q, $J = 28.8$ Hz), 26.7, 14.8; ^{19}F NMR (376 MHz, CDCl_3) δ -61.5; -61.6; HRMS calculated for $\text{C}_{15}\text{H}_{16}\text{F}_6\text{NO}_2$ ($\text{M} + \text{H}^+$): 356.1085, found: 356.1083.



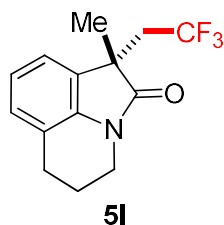
4,4,4-trifluoro-N-methyl-2-phenyl-N-(4-(trifluoromethyl)phenyl)butanamide (5i): ^1H NMR (400 MHz, CDCl_3) δ 7.66-7.64 (d, $J = 8.0$ Hz, 2H), 7.26-7.24 (m, 2H), 7.10-6.98 (m, 2H), 6.98-6.97 (m, 2H), 3.76-3.73 (m, 1H), 3.26 (s, 4H), 2.29-2.22 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 146.3, 137.7, 129.0, 128.5, 127.9, 127.7, 126.3, 126.2 (q, $J = 276.0$ Hz), 43.1, 38.4 (q, $J = 27.8$ Hz), 37.9; ^{19}F NMR (376 MHz, CDCl_3) δ -62.5, -65.1; HRMS calculated for $\text{C}_{18}\text{H}_{16}\text{F}_6\text{NO}$ ($\text{M} + \text{H}^+$): 376.1136, found: 376.1131.



2-(4-chlorophenyl)-4,4,4-trifluoro-N-methyl-N-(4-(trifluoromethyl)phenyl)butanamide (5j): ^1H NMR (400 MHz, CDCl_3) δ 7.70-7.68 (d, $J = 8.8$ Hz, 2H), 7.25-7.23 (d, $J = 8.8$ Hz, 2H), 7.14-7.13 (m, 2H), 6.95-6.93 (d, $J = 8.8$ Hz, 2H), 3.76-3.73 (m, 1H), 3.27 (s, 3H), 3.26-3.19 (m, 1H), 2.29-2.21 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 146.1, 136.1, 133.9, 130.9, 129.2, 129.1, 128.4, 127.2, 126.4 (q, $J = 279.9$ Hz), 123.5 (q, $J = 236.7$ Hz), 42.4, 38.3 (q, $J = 27.8$ Hz), 38.0; ^{19}F NMR (376 MHz, CDCl_3) δ -62.5, -65.1; HRMS calculated for $\text{C}_{18}\text{H}_{15}\text{ClF}_6\text{NO}$ ($\text{M} + \text{H}^+$): 410.0746, found: 410.0740.



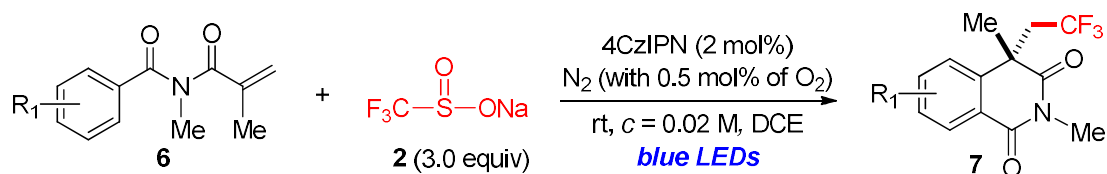
1,3-dimethyl-3-(2,2,2-trifluoroethyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (5k): ^1H NMR (400 MHz, CDCl_3) δ 8.24-8.23 (d, $J = 5.6$ Hz, 1H), 7.53-7.51 (d, $J = 7.2$ Hz, 1H), 7.02-6.99 (m, 1H), 3.33 (s, 3H), 2.83-2.79 (m, 1H), 2.70-2.68 (m, 1H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.2, 156.3, 147.6, 131.3, 125.5, 125.2 (q, $J = 276.9$ Hz), 118.3, 44.2, 40.2 (q, $J = 27.8$ Hz), 25.7, 24.3; ^{19}F NMR (376 MHz, CDCl_3) δ -61.6; HRMS calculated for $\text{C}_{11}\text{H}_{12}\text{F}_3\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$): 245.0902, found: 245.0820.



1-methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one (5l): ^1H NMR (400 MHz, CDCl_3) δ 7.11-7.10 (d, $J = 4.0$ Hz, 1H), 7.07-7.05 (d, J

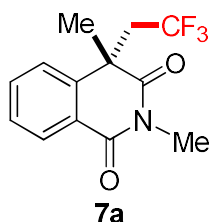
= 8.0 Hz, 1H), 6.99-6.96 (m, 1H), 3.74-3.71 (m, 2H), 2.81-2.78 (m, 3H), 2.75-2.50 (m, 1H), 2.04-2.00 (m, 2H), 1.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 177.4, 138.7, 129.8, 127.4, 125.5 (q, *J* = 276.9 Hz), 122.2, 121.6, 120.6, 45.7, 40.5 (q, *J* = 27.8 Hz), 39.1, 24.7, 24.6, 21.2. These data are consistent with literature values, see: Yang, F.; Klumphu, P.; Liang, Y.-M.; Lipshutz, B. H. *Chem. Commun.* **2014**, *50*, 936.

General procedure for CF₃-containing isoquinolinediones synthesis



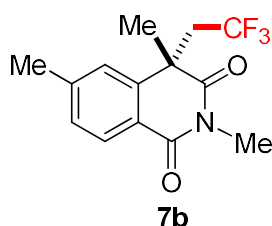
A flame-dried flask (15 mL) was equipped with magnetic stir bar and charged with *N*-acryl-acrylamides **6** (0.145 mmol, 1.0 equiv), CF₃SO₂Na **2** (0.435 mmol, 3.0 equiv), 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) (0.00290 mmol, 0.02 equiv), and DCE (8.0 mL). The reaction mixture was degassed by purging thoroughly with nitrogen (with 0.5 mol % of oxygen) for 10 minutes, then irradiated by blue LED (18 W) under a balloon nitrogen atmosphere (with 0.5 mol % of oxygen) at room temperature until the starting material disappeared from the TLC. After that the reaction mixture was directly concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using hexane/EtOAc (10/1 to 4/1) to afford the desired pure product **7** in 71-85% yield.

¹H NMR and ¹³C NMR spectra data of compounds 7a-7d

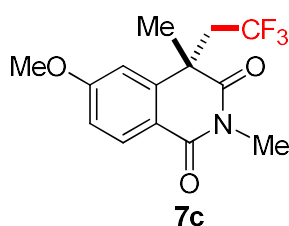


2,4-dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2*H*,4*H*)-dione (7a): ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.67-7.65 (m, 1H), 7.51-7.47 (m, 1H),

7.44-7.42 (d, $J = 8.0$ Hz, 1H), 3.41 (s, 3H), 3.40-3.33 (m, 1H), 2.84-2.77 (m, 1H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 163.9, 140.4, 137.6, 133.9, 130.3, 129.4, 128.2, 125.7, 125.2 (q, $J = 276.9$ Hz), 44.3 (q, $J = 27.7$ Hz), 43.6, 31.3, 27.5. These data are consistent with literature values, see: Liu, C.; Zhao, W.; Huang, Y.; Wang, H.; Zhang, B. *Tetrahedron* **2015**, *71*, 4344.

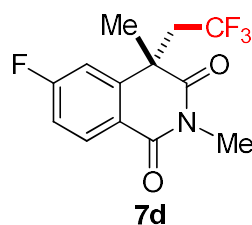


2,4,6-trimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2H,4H)-dione (7b): ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.0$ Hz, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.19 (s, 1H), 3.40 (s, 3H), 3.39-3.26 (m, 1H), 2.85-2.74 (m, 1H), 2.46 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.8, 163.9, 144.8, 140.4, 129.4, 126.1, 125.0 (q, $J = 277.9$ Hz), 121.8, 44.3 (q, $J = 27.8$ Hz), 43.6, 31.3, 27.4, 22.0. These data are consistent with literature values, see: Zheng, L.; Yang, C.; Xu, Z.; Gao, F.; Xia, W. *J. Org. Chem.* **2015**, *80*, 5730.



6-methoxy-2,4-dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2H,4H)-dione (7c): ^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.8$ Hz, 1H), 7.02-6.99 (dd, $J = 8.8, 2.0$ Hz, 1H), 6.85 (d, $J = 2.0$ Hz, 1H), 3.90 (s, 3H), 3.38 (s, 3H), 3.38-3.31 (m, 1H), 2.79-2.73 (m, 1H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 164.0, 163.5, 142.6, 131.8, 125.0 (q, $J = 277.0$ Hz), 117.3, 113.7, 111.2, 55.7, 44.3 (q, $J = 26.8$ Hz),

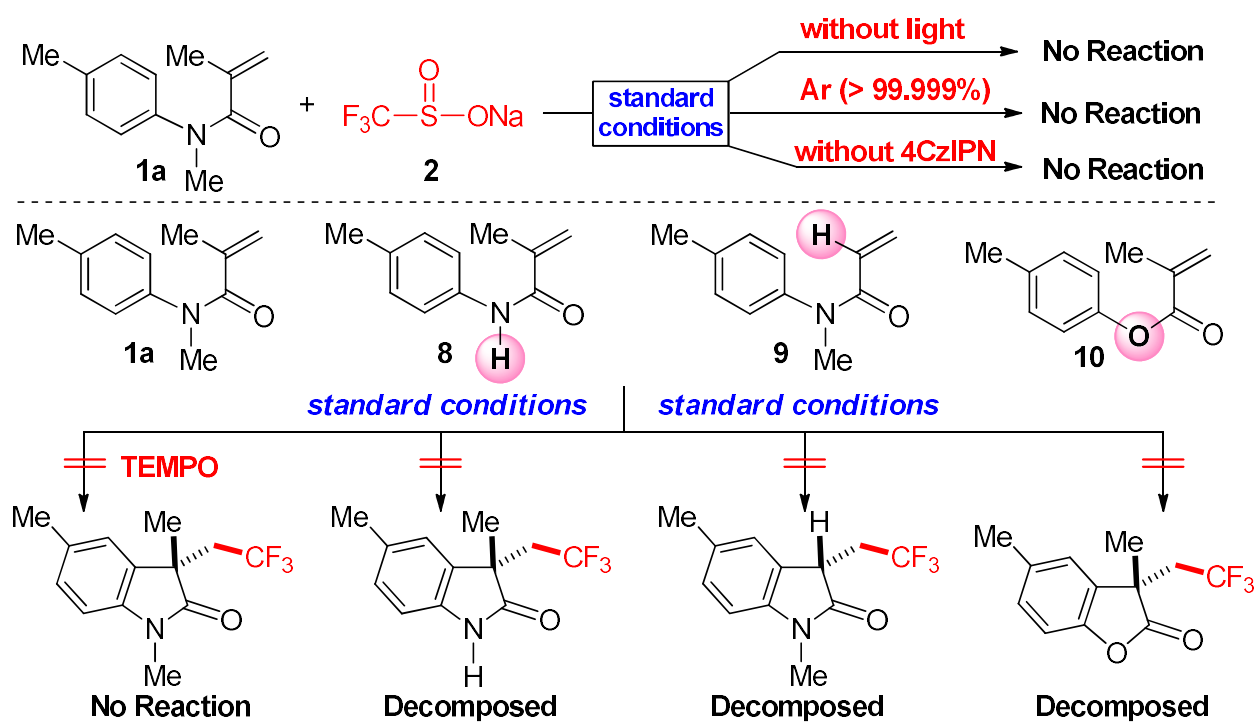
43.8, 31.4, 27.4. These data are consistent with literature values, see: Liu, C.; Zhao, W.; Huang, Y.; Wang, H.; Zhang, B. *Tetrahedron* **2015**, *71*, 4344.



6-fluoro-2,4-dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2H,4H)-dione (7d):

^1H NMR (400 MHz, CDCl_3) δ 8.34-8.30 (m, 1H), 7.21-7.19 (m, 1H), 7.12-7.09 (m, 1H), 3.41 (s, 3H), 3.40-3.34 (m, 1H), 2.78-2.71 (m, 1H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.1, 167.5, 163.8 (d, $J = 207.0$ Hz), 143.5, 132.5 (d, $J = 9.6$ Hz), 124.9 (q, $J = 276.9$ Hz), 120.8, 116.3 (d, $J = 22.1$ Hz), 112.8 (d, $J = 26.0$ Hz), 44.4 (q, $J = 27.8$ Hz), 43.8, 31.1, 27.5. These data are consistent with literature values, see: Zheng, L.; Yang, C.; Xu, Z.; Gao, F.; Xia, W. *J. Org. Chem.* **2015**, *80*, 5730.

Control experiments on reaction parameters



It should be noted that when the reaction mixture was carefully degassed by purging thoroughly with high purity argon (> 99.999%) for 45 mins, complete inhibition of the reactivity was observed under otherwise standard reaction conditions.

On-off switching of the visible light irradiation

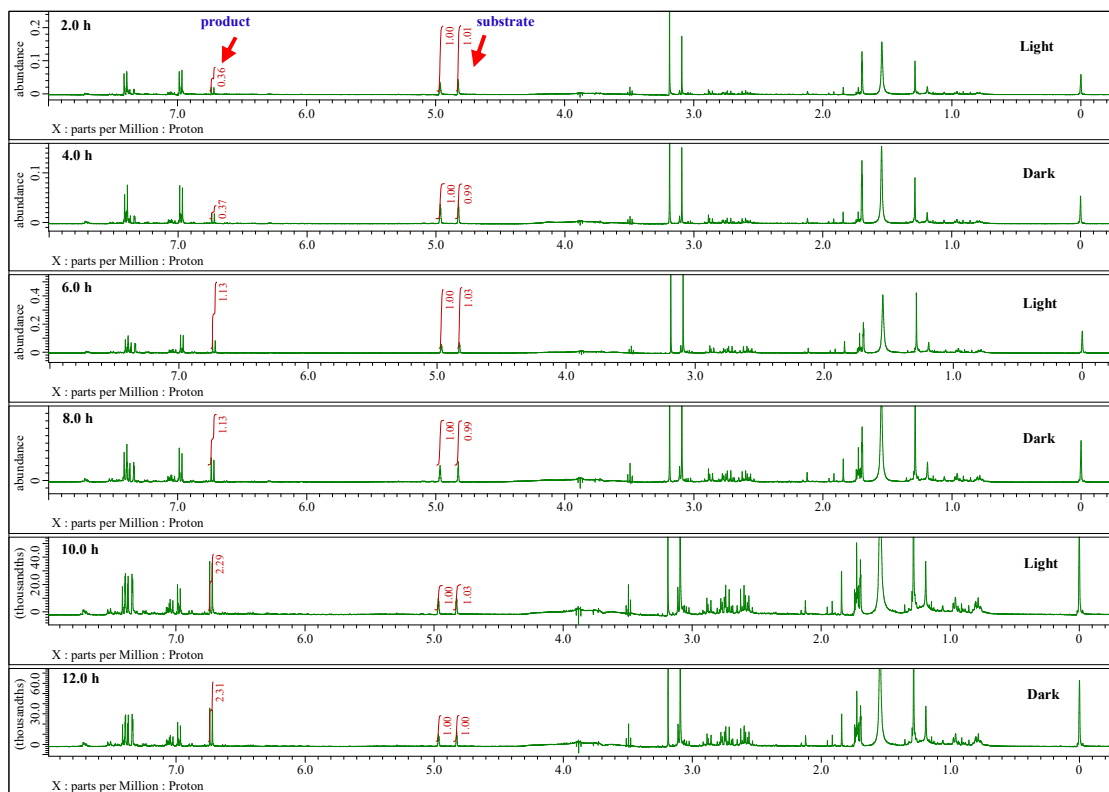


Figure (a). ^1H NMR spectra copies of reaction of **1d** and $\text{CF}_3\text{SO}_2\text{Na}$ with different reaction time

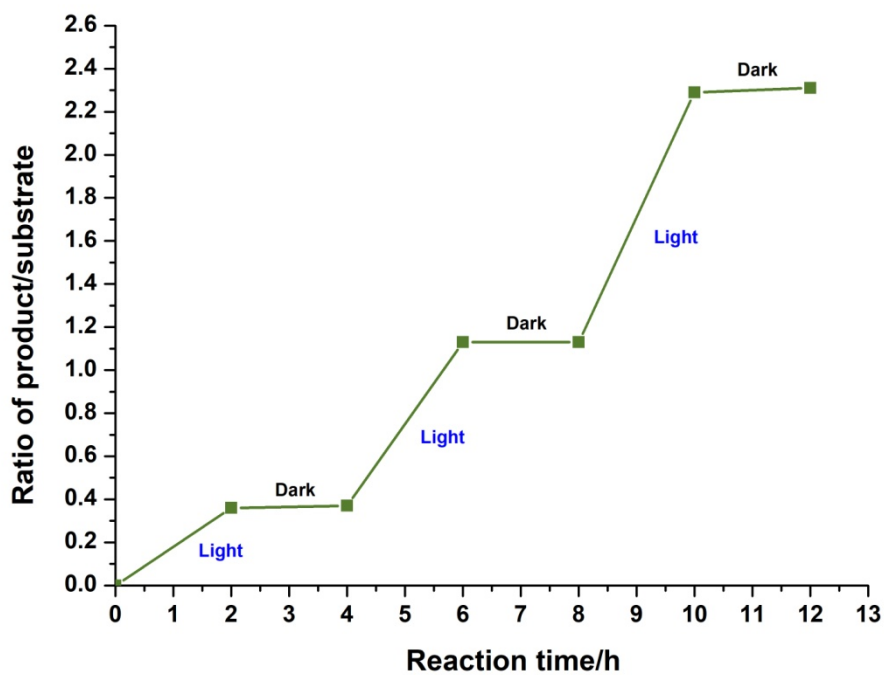


Figure (b). Time profile of visible-light-promoted trifluoromethylation/arylation of **1d** with $\text{CF}_3\text{SO}_2\text{Na}$

Determination of the light intensity at 450 nm:

The quantum yield was measured according to published procedures.¹ The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry.¹⁻² A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H₂SO₄. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H₂SO₄. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at $\lambda = 450$ nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

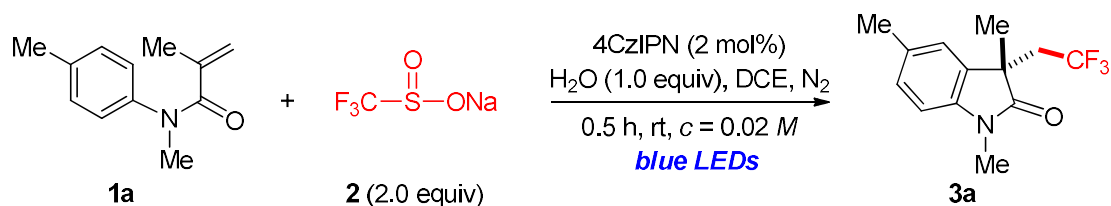
$$\begin{aligned}\text{mol Fe}^{2+} &= (V \cdot \Delta A) / (l \cdot \epsilon) & (1) \\ &= (0.00235 \text{ L} \cdot 0.381) / (1.000 \text{ cm} \cdot 11100 \text{ L mol}^{-1} \text{ cm}^{-1}) \\ &= 8.07 \times 10^{-8} \text{ mol}\end{aligned}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ϵ is the molar absorptivity at 510 nm (11,100 L mol⁻¹ cm⁻¹).¹ The photon flux can be calculated using eq 2.

$$\begin{aligned}\text{photo flux} &= (\text{mol Fe}^{2+}) / (\Phi \cdot t \cdot f) & (2) \\ &= (8.07 \times 10^{-8} \text{ mol}) / (1.01 \cdot 90 \text{ s} \cdot 0.9553) \\ &= 9.29 \times 10^{-10} \text{ einstein/s}\end{aligned}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at $\lambda = 450$ nm),¹ t is the time (90.0 s), and f is the fraction of light absorbed at $\lambda = 450$ nm (0.9553, *vide infra*). The photon flux was calculated to be 9.29×10^{-10} einstein s⁻¹.

Determination of quantum yield:



A cuvette was charged with *N*-aryl-acrylamides **1a** (0.068 mmol, 1.0 equiv), CF₃SO₂Na **2** (0.136 mmol, 2.0 equiv), 4CzIPN (0.00014 mmol, 0.02 equiv), H₂O (0.068 mmol, 1.0 equiv) and 3.0 mL DCE (0.022 M). The sample was stirred and irradiated ($\lambda = 450$ nm) for 1800 s (30 min). After irradiation, the solution was passed through a silica plug. The yield of product generated was determined by crude ¹H NMR to be 8.2% using 1,3,5-trimethoxybenzene as an internal standard. The quantum yield was determined using eq 3. Essentially all incident light ($f > 0.999$, *vide infra*) is absorbed by the 4CzIPN at the reaction conditions described above.

$$\begin{aligned}\Phi &= (\text{mol product})/(\text{photo flux} * t * f) & (3) \\ &= (5.57 \times 10^{-6} \text{ mol})/(9.29 \times 10^{-10} \text{ einstein/s} * 1800 \text{ s} * 1) = 3.33\end{aligned}$$

1. a) Hatchard, C. G.; Parker, C. A. *Proc. Roy. Soc. (London)* **1956**, *A235*, 518. b) Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426.
2. a) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* **2004**, *76*, 2105. b) Monalti, M. *et. al.* *Chemical Actinometry. Handbook of Photochemistry*, 3rd Ed; Taylor & Francis Group, LLC. Boca Raton, FL, **2006**, 601.

Copies of ^1H NMR and ^{13}C NMR spectra

