Supporting Information

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

Maojian Lu, Zhiji Liu, Jinwang Zhang, Yu Tian, Honggui Qin, Mingqiang Huang, Shirong Hu, Shunyou Cai,*

a Key Laboratory of Modern Analytical Science and Separation Technology of Fujian Province, School of Chemistry, Chemical Engineering and Environment, Minnan Normal University, Zhangzhou, 363000, China.
b Key Laboratory of Chemical Genomics, School of Chemical Biology and Biotechnology, Shenzhen Graduate School, Peking University, Shenzhen, 518055, China.

E-mail: caishy05@mnnu.edu.cn

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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. $^1$H NMR spectra were recorded on JEOL spectrometers (400 MHz) and were reported relative to deuterated solvent signals. Data for $^1$H 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

![Chemical diagram]

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$^a$Irradiation with white LEDs. $^b$Irradiation with blue LEDs. $^c$Reaction mixture was purged thoroughly with nitrogen for 10 mins. $^d$[Ir-cat. 1] = Ir(ppy)$_2$(tctpy)PF$_6$. $^e$[Ir-cat. 2] = Ir[6F(CF$_3$)ppy]$_2$(dtbpy)]PF$_6$. $^f$No light. $^g$Yield of isolated product. $^h$4CzIPN = 1,2,3,5-tetra-kis(carbazol-9-yl)-4,8-dicyanobenzene.
General procedure for CF$_3$-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), CF$_3$SO$_2$Na 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), H$_2$O (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.

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

1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3a): $^1$H NMR (400 MHz,
CDCl$_3$) 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); $^{13}$C NMR (100 MHz, CDCl$_3$) 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): $^1$H NMR (400 MHz, CDCl$_3$) 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); $^{13}$C NMR (100 MHz, CDCl$_3$) 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): $^1$H NMR (400 MHz, CDCl$_3$) 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); $^{13}$C NMR (100 MHz, CDCl$_3$) 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.; Thomoson, 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): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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): $^1$H 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): $^1$H 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 C$_{12}$H$_{12}$F$_4$NO (M + H$^+$): 262.0855, found: 262.0853.

4,5,6-trifluoro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3h): $^1$H 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 C$_{12}$H$_{10}$F$_6$NO (M + H$^+$): 298.0667, found: 298.0660.

1,3-dimethyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (3i): $^1$H 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.; Thomoson, 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): $^1$H 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.;
5-acetyl-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3k): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ -61.9; HRMS calculated for C$_{16}$H$_{19}$F$_3$NO$_2$ (M + H$^+$): 314.1368, found: 314.1372.
1,3-dimethyl-5-(methylsulfonyl)-3-(2,2,2-trifluoroethyl)indolin-2-one (3m): $^1$H 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 C$_{13}$H$_{15}$F$_3$NO$_3$S (M + H$^+$): 322.0725, found: 322.0716.

1,3-dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carbonitrile (3n): $^1$H 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, 125.0 (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): $^1$H 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.; Thomoson, 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): $^1$H 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): $^1$H 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.; Thomoson, C. S.; Dolbier, Jr., W. R. Org. Lett. 2014, 16, 4594.

![Chemical structure of 5b](image)

acetyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5b): $^1$H 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 C$_{13}$H$_1_{2}$F$_3$NNaO$_2$ (M + Na$^+$): 294.0718, found: 294.0697.

![Chemical structure of 5c](image)

1-isopropyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5c): $^1$H 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):

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ -61.4, -61.9; HRMS calculated for C$_{14}$H$_{14}$F$_6$NO (M + H$^+$): 326.0980, found: 326.0982.

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

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ -61.5, -61.7; HRMS calculated for C$_{19}$H$_{16}$F$_6$NO (M + H$^+$): 388.1136, found: 388.1132.
3-butyl-1-methyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (5f):

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ -61.3, -61.6; HRMS calculated for C$_{16}$H$_{18}$F$_6$NO (M + H$^+$): 354.1293, found: 354.1288.

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

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ -61.2, -61.5; HRMS calculated for C$_{19}$H$_{15}$F$_6$NNaO (M + H$^+$): 410.0956, found: 410.0951.
3-(ethoxymethyl)-1-methyl-3-(2,2,2-trifluoroethyl)-5-(trifluoromethyl)indolin-2-one (5h): \(^1\)H 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 C\(_{15}\)H\(_{16}\)F\(_6\)NO (M + H\(^+\)): 356.1085, found: 356.1083.

\[
\text{F}_3\text{C} \backslash \text{Ar} \backslash \text{N} \backslash \text{CF}_3 \\
\text{5i} \quad (\text{Ar} = \text{Ph})
\]

4,4,4-trifluoro-N-methyl-2-phenyl-N-(4-(trifluoromethyl)phenyl)butanamide (5i): \(^1\)H 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 C\(_{18}\)H\(_{16}\)F\(_6\)NO (M + H\(^+\)): 376.1136, found: 376.1131.

\[
\text{F}_3\text{C} \backslash \text{Ar} \backslash \text{N} \backslash \text{CF}_3 \\
\text{5j} \quad (\text{Ar} = \rho\text{-Cl-Ph})
\]
2-(4-chlorophenyl)-4,4,4-trifluoro-N-methyl-N-(4-(trifluoromethyl)phenyl)butanamide (5j): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ -62.5, -65.1; HRMS calculated for C$_{18}$H$_{15}$ClF$_6$NO (M + H$^+$): 410.0746, found: 410.0740.

\[
\text{1,3-dimethyl-3-(2,2,2-trifluoroethyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (5k):} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ -61.6; HRMS calculated for C$_{11}$H$_{12}$F$_3$N$_2$O (M + H$^+$): 245.0902, found: 245.0820.

\[
\text{1-methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one (5l):} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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); $^{13}$C NMR (100 MHz, CDCl$_3$) 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 CF$_3$-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), CF$_3$SO$_2$Na 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.

$^1$H NMR and $^{13}$C NMR spectra data of compounds 7a-7d

2,4-dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2H,4H)-dione (7a): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (d, $J$ = 8.0 Hz, 1H), 7.67-7.65 (m, 1H), 7.51-7.47 (m, 1H), 7.41-7.39 (m, 1H), 7.38-7.36 (m, 1H), 7.19-7.17 (m, 1H), 7.11-7.09 (m, 2H), 7.08-7.06 (m, 1H), 7.05-7.03 (m, 1H), 7.02-7.00 (m, 1H), 6.99-6.97 (m, 1H), 6.96-6.94 (m, 1H), 6.93-6.91 (m, 1H), 5.12 (s, 2H), 4.72 (s, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 1.17 (s, 3H), 0.99 (s, 3H).
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.

![Image](7b)

### 2,4,6-trimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2$H$,4$H$)-dione (7b): $^1$H 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.

![Image](7c)

### 6-methoxy-2,4-dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2$H$,4$H$)-dione (7c): $^1$H 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.

![Chemical Structure](image)

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

$^1$H 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 switchng of the visible light irradiation

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

Figure (b). Time profile of visible-light-promoted trifluoromethylation/arylation of 1d with CF$_3$SO$_2$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 H\(_2\)SO\(_4\). 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 H\(_2\)SO\(_4\). 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.

\[
mol \text{Fe}^{2+} = \frac{(V*\Delta A)/(l*\varepsilon)}{(1*\varepsilon)}
\]

\[
= \frac{(0.00235L*0.381)/(1.000 \text{ cm}*11100 \text{ L mol}^{-1} \text{ cm}^{-1})}{(1.000 \text{ cm}*11100 \text{ L mol}^{-1} \text{ cm}^{-1})}
\]

\[
= 8.07 \times 10^{-8} \text{ mol}
\]

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

\[
\text{photo flux} = \frac{(mol \text{Fe}^{2+})/(\Phi*t*f)}{(1*\varepsilon)}
\]

\[
= \frac{(8.07 \times 10^{-8} \text{ mol})/(1.01*90 \text{ s}*0.9553)}{(1.000 \text{ cm}*11100 \text{ L mol}^{-1} \text{ cm}^{-1})}
\]

\[
= 9.29 \times 10^{-10} \text{ einstein/s}
\]

Where \(\Phi\) 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 \(9.29 \times 10^{-10}\) einstein s\(^{-1}\).
Determination of quantum yield:

![Chemical structure](image)

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 (λ = 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.

\[
\Phi = \frac{\text{(mol product)}}{\text{(photo flux} \times \text{t} \times \text{f)}}
\]

\[
= \frac{5.57 \times 10^{-6} \text{ mol}}{(9.29 \times 10^{-10} \text{ einstein/s} \times 1800 \text{ s} \times 1)} = 3.33
\]

Copies of $^1$H NMR and $^{13}$C NMR spectra
[Image of a chemical structure with N, O, Me, CF3, MeO, and 7c labels]

X: parts per Million - Proton

X: parts per Million - Carbon13