Supplementary Information for

Transition-Metal-Free α-Arylation of Oxindoles via Visible-Light-Promoted Electron Transfer

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General Information

All reactions were performed under argon atmosphere using flame-dried glassware unless otherwise noted. CH$_3$CN was distilled over CaH$_2$ and rigorously degassed by freeze/pump/thaw. All reagents were commercially available and used without further purification unless indicated otherwise. Thin layer chromatographies were carried out on GF254 plates (0.25 mm layer thickness). Flash chromatography was performed with 200-300 mesh silica gels. Visualization of the developed chromatogram was performed by fluorescence quenching or by ceric ammonium molybdate, or KMnO$_4$ stain. Yields reported were for isolated, spectroscopically pure compounds.

$^1$H and $^{13}$C NMR spectra were recorded on Bruker Avance 400 and 600 MHz spectrophotometers. Chemical shifts (δ) are expressed in ppm, and J-values are given in Hz. The residual solvent protons ($^1$H) or the solvent carbons ($^{13}$C) were used as internal standards. ESIMS and HRESIMS were taken on Agilent 6540 Q-TOF spectrometer. UV-Vis measurements were carried out on a HITACHI U-4100 spectrophotometer. Cyclic voltammetry studies was carried out on a CHI 760E electrochemical workstation (Shanghai CH Instruments Co., China).

General Procedure for Visible-Light-Promoted α-Arylation of Oxindoles

To an oven dried 10 mL glass tube with a magnetic stirring bar was added oxindoles (0.2 mmol) and CsOH·H$_2$O (0.3 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. CH$_3$CN (1 mL) and (hetero)aryl halides (0.1 mmol) were carefully added under Argon. The reaction mixture was stirred under a household 23 W compact fluorescent light (CFL) bulb (the distance was about 7 cm) irradiation for the indicated time. Irradiation was stopped and the reaction was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether) on silica gel to afford the product.
Supplementary Figure 1. Experimental setup for visible-light-promoted α-arylation of oxindoles

Supplementary Figure 2. Emission spectra of the 23W CFL lamp. The emission spectra was recorded on a Fluorescence Spectrophotometer F-4500.

Supplementary Note 1. 1H NMR Spectroscopic Studies

The 1H NMR analysis was made on a solution containing 8 mg of 2a (0.05 mmol) and MOH (M = Cs⁺, K⁺ or Na⁺) (0.075 mmol) in 0.5 mL of CD₃CN. Under these conditions (Argon and solvent were rigorously degassed by freeze/pump/thaw), all the MOHs could efficiently deprotonate the oxindole and complete enolate formation of 2a was observed. Moreover, significant upfield peak shifting of aromatic hydrogens
were observed with the magnitude followed the order: Cs\(^+\) solution > K\(^+\) solution > Na\(^+\) solution. These results provided evidences that varying alkali metal cations affecting reactivity might be due to secondary effect in the charge transfer process.\(^1\)

**Supplementary Note 2. UV-Vis Spectroscopic Measurement**

The UV-Vis absorption spectra of acetonitrile solutions (0.1 M) of 1a, 2a, mixtures of 1a and 2a, mixtures of 1a and CsOH, mixtures of 2a and CsOH, and mixtures of 1a, 2a and CsOH were recorded on HITACHI U-4100 UV-Visible Spectrophotometer. The bathochromic shift to the visible spectral region is indicative of EDA complex formation.

**Supplementary Note 3. Determination of the Stoichiometry of the EDA Complex**

The stoichiometry of the EDA complex formed between iodobenzene 1a and the enolate of 2a (generated *in situ* by the deprotonation of 2a with 1.1 equiv CsOH) in CH\(_3\)CN was determined using the Job’s plot method. The Job’s plot was constructed by measuring the absorption at 470 nm of CH\(_3\)CN solutions of different ratios of iodobenzene 1a and the enolate of 2a, where the total concentration of the two components remained constant at 0.1 M. The maximum absorbance is obtained at 50% molar fraction, indicating that the stoichiometry of the EDA complex is 1:1.

**Supplementary Table 1.** Absorbance of 0.1 M CH\(_3\)CN solutions of different molar ratios of iodobenzene 1a and the enolate of 2a.

<table>
<thead>
<tr>
<th>entry</th>
<th>1a:the enolate of 2a ratio</th>
<th>molar fraction of the enolate of 2a (%)</th>
<th>absorbance at 470 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0:0.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.8:0.2</td>
<td>20</td>
<td>0.042</td>
</tr>
<tr>
<td>3</td>
<td>0.6:0.4</td>
<td>40</td>
<td>0.059</td>
</tr>
<tr>
<td>4</td>
<td>0.5:0.5</td>
<td>50</td>
<td>0.062</td>
</tr>
<tr>
<td>5</td>
<td>0.4:0.6</td>
<td>60</td>
<td>0.056</td>
</tr>
<tr>
<td>6</td>
<td>0.2:0.8</td>
<td>80</td>
<td>0.039</td>
</tr>
<tr>
<td>7</td>
<td>0.0:1.0</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>
Supplementary Figure 3. Job’s plot of iodobenzene 1a and the enolate of 2a in CH$_3$CN.

Supplementary Note 4. Long Wavelength Experiment.

To an oven dried 10 mL glass tube with a magnetic stirring bar was added 2a (32.2 mg, 0.2 mmol) and CsOH·H$_2$O (50.4 mg, 0.3 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. CH$_3$CN (1 mL) and iodobenzene 1a (20.4 mg, 0.1 mmol) were carefully added under Argon. The reaction mixture was stirred under a 45 W white LED lamp which equipped with a band-pass filter at 532 nm irradiation for 6h. Irradiation was stopped and the reaction was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether = 1:5) on silica gel to afford 3a as a colorless oil (16.1 mg, 68% yield).

Supplementary Note 5. Intramolecular Radical Clock Experiment

To an oven dried 10 mL glass tube with a magnetic stirring bar was added 2a
(32.2 mg, 0.2 mmol) and CsOH·H$_2$O (50.4 mg, 0.3 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. CH$_3$CN (1 mL) and compound 5 (28.8 mg, 0.1 mmol) were carefully added under Argon. The reaction mixture was stirred under a household 23 W compact fluorescent light (CFL) bulb irradiation for 8h. Irradiation was stopped and the reaction was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether = 1:100) on silica gel to afford 6 (6.5 mg, 40% yield). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.18 (d, $J = 7.4$, 1H), 7.12 (td, $J = 8.1$, 0.7, 1H), 6.84 (td, $J = 7.4$, 0.9, 1H), 6.77 (d, $J = 8.0$, 1H), 4.51 (t, $J = 9.1$, 1H), 4.37 (dd, $J = 9.0$, 5.1, 1H), 3.35 – 3.29 (m, 1H), 2.02 – 1.92 (m, 1H), 0.95 (d, $J = 6.8$, 3H), 0.87 (d, $J = 6.8$, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 160.4, 129.4, 128.1, 125.1, 120.1, 109.3, 73.8, 48.2, 31.7, 19.8, 18.4; HR-ESI-MS ($m/z$): calcd. for C$_{11}$H$_{15}$O $[M+H]^+$, 163.1117, found 163.1117.

**Supplementary Note 6. Quantum Yield Measurement**

**Determination of the Photon Flux:**

The photon flux of the LED setup was determined by standard ferrioxalate actinometry.[2] A 0.15 M ferrioxalate solution was prepared by dissolving 2.21 g of potassium ferrioxalate trihydrate in 30 mL of 0.05 M H$_2$SO$_4$. A buffered phenanthroline solution was prepared by dissolving 50 mg of 1,10-phenanthroline 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 LED setup, 2.0 mL of the ferrioxalate solution was placed in a quartz cuvette (l = 1.0 cm). The cuvette was placed 10 cm from an 18W blue LED lamp ($\lambda_{\text{max}}$ at 455 nm) and irradiated for 30 s. After irradiation, 0.5 mL of the 1,10-phenanthroline solution was added to the cuvette. The mixture was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the 1,10-phenanthroline. The absorbance of the solution was measured at 510 nm. The
absorbance of a non-irradiated sample was also measured. Conversion was calculated using:

\[ \text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \]

Where \( V \) is the total volume (0.0025 L) of the solution after addition of 1,10-phenanthroline, \( \Delta A \) is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, \( l \) is the path length (1.0 cm), and \( \varepsilon \) is the molar absorptivity at 510 nm (11,100 L mol\(^{-1}\) cm\(^{-1}\)).

The photon flux can be calculated using:

\[ \text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f} \]

Where \( \Phi \) is the quantum yield for the ferrioxalate actinometer (a reported value of 0.85 for a 0.15 M solution at \( \lambda = 458 \) nm was used in the calculations), \( t \) is the time (30 s), and \( f \) is the fraction of absorbed light at \( \lambda = 455 \) nm, where \( f = 1 - 10^{-A} \).

The absorbance \((A)\) of the ferrioxalate solution at \( \lambda = 455 \) nm was measured by UV/Vis spectroscopy to be 0.901, therefore \( f = 0.8744 \). The photon flux was calculated (average of three experiments) to be \( 8.54 \times 10^{-9} \) einstein s\(^{-1}\).

Sample calculation:

\[
\text{mol } Fe^{2+} = \frac{0.0025 \text{ L} \cdot 0.849}{1.000 \text{ cm} \cdot 11100 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}} = 1.91 \times 10^{-7} \text{ mol}
\]

\[
\text{photon flux} = \frac{1.91 \times 10^{-7} \text{ mol}}{0.85 \cdot 30.0 \text{ s} \cdot 0.8744} = 8.57 \times 10^{-9} \text{ einstein s}^{-1}
\]

Determination of the Quantum Yield:

To a quartz cuvette (path length, \( l = 1 \) cm) equipped with a magnetic stir bar was
added 2a (32.2 mg, 0.2 mmol) and CsOH·H$_2$O (50.4 mg, 0.3 mmol). The cuvette was purged with Argon before being sealed with a septum. CH$_3$CN (1 mL) and iodobenzene 1a (20.4 mg, 0.1 mmol) were carefully added under Argon and the cuvette was further sealed with parafilm. The cuvette was positioned 10 cm away from an 18 W blue LED lamp ($\lambda_{\text{max}}$ at 455 nm) and the reaction was irradiated for 1200 s (20 min). The yield was determined by $^1$H NMR, using diphenylacetonitrile as a standard, to be (average of three experiments) 43% ($4.3 \times 10^{-5}$ mol).

The quantum yield (Φ) was then calculated using:

$$\Phi = \frac{\text{mol product}}{\text{photon flux} \cdot t \cdot f}$$

Where $t$ is the time (1200 s) and $f$ is the fraction of light absorbed by the reaction mixture at $\lambda = 455$ nm, where $f = 1 - 10^{-A}$ (the absorbance of the reaction mixture (A) was determined by UV/Vis spectroscopy to be 0.207, thus $f = 0.3791$). The photon flux of the LED setup was determined using standard ferrioxalate actinometry to be $8.54 \times 10^{-9}$ einstein s$^{-1}$.

$$\Phi = \frac{4.3 \times 10^{-5}}{8.54 \times 10^{-9} \cdot 1200 \cdot 0.3791} = 11.1$$

**Supplementary Note 7. Cyclic Voltammetry Experiments**

Tetrabutylammonium hexafluorophosphate (378 mg, 1.0 mmol) and 1a (20.4 mg, 0.1 mmol) were dissolved in dry acetonitrile (10 mL) and the solution was vigorously bubbled with N$_2$ for 5 minutes prior to the measurement. The reduction potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a KCl saturated Ag/AgCl reference electrode at 0.1 V/s scan rate. A completely irreversible reduction wave was observed with $E_{p}^{\text{red}} = -2.31$ V vs. Ag/Ag$^+$ in CH$_3$CN.
**Supplementary Figure 4.** The cyclic voltammogram of 1a vs Ag/Ag⁺ in acetonitrile at 0.1V/s.

The cyclic voltammetry of 3a was also carried out, using the same experimental conditions and concentrations. No reduction waves were detected for 3a in the range -2.80 – 0 V.

**Supplementary Figure 5.** The cyclic voltammogram of 3a vs Ag/Ag⁺ in acetonitrile at 0.1V/s.

**Supplementary Note 8. Gram Scale Experiment**

\[
\begin{align*}
1\text{a} + 2\text{a} & \xrightarrow{hv, \text{CsOH}} 3\text{a} & (81\%) \\
3\text{a} + 7 & \xrightarrow{g \text{scale}} 8 & (4\%) \\
\end{align*}
\]
To an oven dried 100 mL round-bottom flask with a magnetic stirring bar was added 2a (1.61 g, 10 mmol) and CsOH·H$_2$O (2.52 g, 15 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. CH$_3$CN (25 mL) and Iodobenzene 1a (1.02 g, 5 mmol) were carefully added under Argon. The reaction mixture was stirred under four household 23 W compact fluorescent light (CFL) bulbs irradiation for 24 h. Irradiation was stopped and the reaction was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether = 1:5) on silica gel to afford 3a as a colorless oil (0.96 g, 81% yield), 7 as a colorless oil (63.1 mg, 4% yield), and 8 as a colorless oil (33.5 mg, 2% yield).

(±)-1,3-dimethyl-3-((1-methyl-2-oxoindolin-3-yl)methyl)indolin-2-one (7): $^1$H NMR (600 MHz, CDCl$_3$): δ 7.19 (d, $J = 7.3$, 1H), 7.16 (d, $J = 7.3$, 1H), 7.08-7.05 (m, 2H), 6.99-6.94 (m, 2H), 6.37-6.35 (m, 2H), 3.33 (d, $J = 7.1$, 1H), 2.96 (dd, $J = 14.8$, 7.3, 1H), 2.79 (d, $J = 14.8$, 1H), 2.67 (s, 6H), 1.30 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 180.6, 177.3, 144.4, 143.3, 130.8, 127.7, 125.9, 125.5, 125.2, 121.5, 121.4, 107.2, 46.8, 43.8, 35.2, 26.4, 25.8; HR-ESI-MS (m/z): calcd. for C$_{20}$H$_{21}$N$_2$O$_2$ [M + H]$^+$, 321.1598, found 321.1599.

(±)-1,1',3,3'-tetramethyl-[3,3'-biindoline]-2,2'-dione (8): $^1$H NMR (400 MHz, CDCl$_3$): δ 7.06 (d, $J = 7.5$, 2H), 7.04 – 6.99 (m, 2H), 6.82 (t, $J = 7.6$, 2H), 6.45 (d, $J = 7.8$, 2H), 3.09 (s, 6H), 1.75 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 178.2, 142.6, 131.1, 128.1, 122.8, 121.8, 107.4, 51.1, 25.7, 16.1; calcd. for C$_{20}$H$_{20}$N$_2$O$_2$Na [M + Na]$^+$, 343.1417, found 343.1418.
Identification of Compounds

(±)-1,3-dimethyl-3-phenylindolin-2-one (3a)

Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3a as a colorless oil (X = I, 21.1 mg, 85% yield; X = Br, 12.1 mg, 51% yield; X = Cl, 8.1 mg, 34% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.37 – 7.21 (m, 6H), 7.19 (d, $J$ = 7.3, 1H), 7.10 (t, $J$ = 7.5, 1H), 6.92 (d, $J$ = 7.8, 1H), 3.24 (s, 3H), 1.79 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 179.5, 143.3, 140.8, 134.8, 128.6, 128.1, 127.3, 126.7, 124.2, 122.8, 108.3, 52.2, 26.5, 23.8; HR-ESI-MS (m/z): calcd. for C$_{16}$H$_{16}$NO [M + H]$^+$, 238.1226, found 238.1230.

(±)-3-(4-methoxyphenyl)-1,3-dimethylindolin-2-one (3b)

Prepared according to the general procedure using 4-iodoanisole (23.4 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3b as a colorless oil (X = I, 20.0 mg, 75% yield; X = Br, 17.9 mg, 67% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.32 (t, $J$ = 7.7, 1H), 7.22 (d, $J$ = 8.7, 2H), 7.19 (d, $J$ = 7.6, 1H), 7.10 (t, $J$ = 7.5, 1H), 6.91 (d, $J$ = 7.8, 1H), 6.82 (d, $J$ = 8.6, 2H), 3.76 (s, 3H), 3.23 (s, 3H), 1.76 (s, 3H); $^{13}$C NMR
(±)-1,3-dimethyl-3-(p-tolyl)indolin-2-one (3c)

Prepared according to the general procedure using 4-iodotoluene (21.8 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3c as a colorless oil (X = I, 17.6 mg, 70% yield; X = Br, 12.6 mg, 50% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33 (t, $J$ = 7.7, 1H), 7.21 – 7.17 (m, 3H), 7.16 – 7.05 (m, 3H), 6.92 (d, $J$ = 7.8, 1H), 3.24 (s, 3H), 2.30 (s, 3H), 1.78 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 179.6, 143.3, 137.8, 137.0, 135.0, 129.3, 128.1 126.5, 124.2, 122.8, 108.3, 51.9, 26.5, 23.7, 21.0; HR-ESI-MS ($m/z$): calcd. for C$_{17}$H$_{17}$NO$_2$Na [M + Na]$^+$, 274.1206, found 274.1202.

(±)-3-(4-acetylphenyl)-1,3-dimethylindolin-2-one (3d)

Prepared according to the general procedure using 4-acetyliodobenzene (24.6 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 2 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3d as a colorless oil (X = I, 18.3 mg, 70% yield; X = Br, 12.6 mg, 50% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37 (t, $J$ = 7.7, 1H), 7.24 – 7.17 (m, 3H), 7.16 – 7.05 (m, 3H), 6.93 (d, $J$ = 7.8, 1H), 3.28 (s, 3H), 2.30 (s, 3H), 2.03 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 179.6, 143.3, 137.8, 137.0, 135.0, 129.3, 128.1 126.5, 124.2, 122.8, 108.3, 51.9, 26.5, 23.7, 21.0; HR-ESI-MS ($m/z$): calcd. for C$_{17}$H$_{17}$NO$_2$Na [M + Na]$^+$, 274.1206, found 274.1202.
chromatography (acetone/petroleum ether 1:3) to afford the product 3d as a colorless oil (X = I, 23.7 mg, 85% yield; X = Br, 24.3 mg, 87% yield; X = Cl, 15.9 mg, 57% yield). 1H NMR (400 MHz, CDCl3): δ 7.88 (d, J = 8.2, 2H), 7.40 (d, J = 8.2, 2H), 7.35 (t, J = 7.8, 1H), 7.17 (d, J = 7.3, 1H), 7.11 (t, J = 7.4, 1H), 6.95 (d, J = 7.8, 1H), 3.25 (s, 3H), 2.56 (s, 3H), 1.81 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 197.7, 178.7, 146.1, 143.2, 136.0, 134.1, 128.6, 128.5, 127.0, 124.2, 123.0, 108.6, 52.3, 26.7, 26.6, 23.7; HR-ESI-MS (m/z): calcd. for C18H17NO2Na [M + Na]+, 302.1151, found 302.1154.

N O
\[
\text{CH}_3
\]
\[
\text{CH}_3
\]

(±)-4-(1,3-dimethyl-2-oxoindolin-3-yl)benzonitrile (3e)

Prepared according to the general procedure using 4-iodobenzonitrile (22.9 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H2O (50.4 mg, 0.3 mmol), and CH3CN (1 mL). Time of irradiation: 2 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:4) to afford the product 3e as a colorless oil (X = I, 22.3 mg, 85% yield; X = Br, 20.2 mg, 77% yield). 1H NMR (400 MHz, CDCl3): δ 7.58 (d, J = 8.4, 2H), 7.43 (d, J = 8.4, 2H), 7.37 (td, J = 7.6, 1.5, 1H), 7.22 – 7.10 (m, 2H), 6.95 (d, J = 7.8, 1H), 3.25 (s, 3H), 1.79 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 178.2, 146.1, 143.2, 133.4, 132.3, 128.8, 127.7, 124.2, 123.2, 118.7, 111.2, 108.7, 52.3, 26.7, 23.8; HR-ESI-MS (m/z): calcd. for C17H16N2ONa [M + Na]+, 285.0998, found 285.1006.
(±)-3-(4-benzoylphenyl)-1,3-dimethylindolin-2-one (3f)

Prepared according to the general procedure using 4-bromobenzophenone (26.1 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H2O (50.4 mg, 0.3 mmol), and CH3CN (1 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product 3f as a colorless oil (X = Br, 27.3 mg, 80% yield). 1H NMR (400 MHz, CDCl3): δ 7.78 (d, J = 7.3, 2H), 7.73 (d, J = 8.4, 2H), 7.57 (t, J = 7.4, 1H), 7.49 – 7.42 (m, 4H), 7.40 – 7.32 (m, 1H), 7.20 (d, J = 7.2, 1H), 7.13 (t, J = 7.5, 1H), 6.95 (d, J = 7.8, 1H), 3.27 (s, 3H), 1.83 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 196.2, 178.8, 145.4, 143.2, 137.5, 136.5, 134.2, 132.5, 130.3, 130.1, 128.5, 128.3, 126.7, 124.2, 123.0, 108.6, 52.4, 26.6, 23.8; HR-ESI-MS (m/z): calcd. for C23H19NO2Na [M + Na]+, 364.1308, found 364.1329.

(±)-3-(3-methoxyphenyl)-1,3-dimethylindolin-2-one (3g)

Prepared according to the general procedure using 3-iodoanisole (23.4 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H2O (50.4 mg, 0.3 mmol), and CH3CN (1 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3g as a colorless oil (X = I, 21.4 mg, 80% yield; X = Br, 11.5 mg, 43% yield). 1H NMR (400 MHz, CDCl3): δ 7.32 (td, J = 7.7, 1.0, 1H), 7.24 – 7.16 (m, 2H), 7.09 (t, J = 7.5, 1H), 6.92 – 6.87 (m, 3H), 6.78 (dd, J = 7.4, 1.7, 1H), 3.76 (s, 3H), 3.24 (s, 3H), 1.77 (s, 3H); 13C NMR (100 MHz,
CDCl₃): δ 179.3, 159.6, 143.2, 142.4, 134.7, 129.5, 128.1, 124.2, 122.8, 119.1, 113.2, 112.0, 108.3, 55.2, 52.1, 26.5, 23.7; HR-ESI-MS (m/z): calcd. for C₁₇H₁₇NO₂Na [M + Na]⁺, 290.1151, found 290.1150.

(±)-1,3-dimethyl-3-(m-tolyl)indolin-2-one (3h)
Prepared according to the general procedure using 3-iodotoluene (21.8 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3h as a colorless oil (X = I, 18.3 mg, 73% yield; X = Br, 12.3 mg, 49% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.32 (td, J = 7.7, 1.2, 1H), 7.19 – 7.17 (m, 2H), 7.12 – 7.06 (m, 4H), 6.92 (d, J = 7.8, 1H), 3.25 (s, 3H), 2.30 (s, 3H), 1.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 179.6, 143.2, 140.7, 138.2, 135.1, 128.4, 128.1, 127.3, 124.2, 123.7, 122.8, 108.3, 52.1, 26.5, 23.7, 21.6; HR-ESI-MS (m/z): calcd. for C₁₇H₁₇NO₂Na [M + Na]⁺, 274.1202, found 274.1203.

(±)-3-(3-acetylphenyl)-1,3-dimethylindolin-2-one (3i)
Prepared according to the general procedure using 3-iodoacetophenone (24.6 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel
chromatography (acetone/petroleum ether 1:3) to afford the product 3i as a colorless oil (X = I, 22.6 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.94 (d, $J = 1.6$, 1H), 7.83 (d, $J = 7.7$, 1H), 7.51 – 7.46 (m, 1H), 7.41 – 7.31 (m, 2H), 7.21 – 7.15 (m, 1H), 7.11 (t, $J = 7.5$, 1H), 6.94 (d, $J = 7.8$, 1H), 3.26 (s, 3H), 2.56 (s, 3H), 1.82 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.0, 179.0, 143.2, 141.5, 137.4, 134.2, 131.6, 128.8, 128.5, 127.4, 126.4, 124.1, 123.1, 108.6, 52.1, 26.7, 26.6, 24.0; HR-ESI-MS ($m/z$): calcd. for C$_{18}$H$_{17}$NO$_2$Na [M + Na]$^+$, 302.1151, found 302.1151.

![3j](image)

(±)-3-(2-methoxyphenyl)-1,3-dimethylindolin-2-one (3j)

Prepared according to the general procedure using 2-iodoanisole (23.4 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3j as a colorless oil (X = I, 12.0 mg, 45% yield; X = Br, 5.6 mg, 21% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58 (dd, $J = 7.7$, 1.1, 1H), 7.30 – 7.19 (m, 2H), 7.04 (t, $J = 7.3$, 1H), 6.93 (t, $J = 7.4$, 1H), 6.89 – 6.84 (m, 2H), 6.75 (d, $J = 8.1$, 1H), 3.41 (s, 3H), 3.32 (s, 3H), 1.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 181.1, 157.0, 143.6, 135.7, 129.8, 128.8, 127.6, 127.3, 122.2, 120.9, 112.0, 107.4, 55.9, 49.8, 26.4, 23.4; HR-ESI-MS ($m/z$): calcd. for C$_{17}$H$_{17}$NO$_2$Na [M + Na]$^+$, 290.1151, found 290.1153.

![3k](image)

(±)-2-(1,3-dimethyl-2-oxoindolin-3-yl)benzonitrile (3k)
Prepared according to the general procedure using 2-bromobenzonitrile (18.2 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH-H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3k as a colorless oil (X = Br, 9.2 mg, 35% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J$ = 8.0, 1H), 7.72 – 7.62 (m, 1H), 7.57 (d, $J$ = 7.6, 1H), 7.39 – 7.33 (m, 2H), 7.03 (t, $J$ = 7.5, 1H), 6.96 (d, $J$ = 7.8, 1H), 6.89 (d, $J$ = 7.3, 1H), 3.34 (s, 3H), 1.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 178.6, 144.2, 143.4, 135.1, 134.0, 132.8, 128.9, 128.1, 127.9, 123.0, 116.8, 111.9, 108.8, 52.3, 26.5, 24.3; HR-ESI-MS ($m/z$): calcd. for C$_{17}$H$_{14}$N$_2$O$_2$Na [M + Na]$^+$, 285.0998, found 285.0992.

(±)-1,3-dimethyl-3-(naphthalen-2-yl)indolin-2-one (3l)

Prepared according to the general procedure using 2-iodonaphthalene (25.4 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH-H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3l as a colorless oil (X = I, 22.4 mg, 78% yield; X = Br, 14.6 mg, 51% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 – 7.74 (m, 4H), 7.46 – 7.44 (m, 2H), 7.37 – 7.35 (m, 2H), 7.22 (d, $J$ = 7.3, 1H), 7.12 (t, $J$ = 7.5, 1H), 6.96 (d, $J$ = 7.8, 1H), 3.28 (s, 3H), 1.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 179.5, 143.3, 138.1, 134.9, 133.2, 132.5, 128.4, 128.2, 128.1, 127.5, 126.1, 126.0, 125.3, 124.9, 124.3, 122.9, 108.4, 52.3, 26.6, 23.6; HR-ESI-MS ($m/z$): calcd. for C$_{20}$H$_{18}$NO [M + H]$^+$, 288.1383, found 288.1389.
(±)-1,3-dimethyl-3-(phenanthren-9-yl)indolin-2-one (3m)

Prepared according to the general procedure using 9-iodophenanthrene (30.4 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3m as a colorless oil (X = I, 25.3 mg, 75% yield; X = Br, 18.5 mg, 55% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.67 (d, J = 8.3, 1H), 8.63 (d, J = 7.8, 1H), 8.12 (s, 1H), 7.97 (d, J = 7.5, 1H), 7.70 – 7.58 (m, 2H), 7.49 (t, J = 7.6, 1H), 7.32 (t, J = 7.7, 1H), 7.23 (d, J = 7.8, 1H), 7.07 (d, J = 7.8, 1H), 6.95 – 6.86 (m, 3H), 3.46 (s, 3H), 1.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 180.4, 142.3, 136.5, 133.4, 131.3, 130.6, 130.3, 129.0, 128.1, 128.0, 127.1, 126.8, 126.7, 126.1, 124.3, 123.3, 123.2, 122.8, 122.4, 108.8, 52.6, 27.2, 26.8; HR-ESI-MS (m/z): calcd. for C₂₄H₁₉NONa [M + Na]⁺, 360.1359, found 360.1368.

(±)-3-(anthracen-2-yl)-1,3-dimethylindolin-2-one (3n)

Prepared according to the general procedure using 2-idoanthracene (30.4 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3n as a colorless
oil (X = I, 21.2 mg, 63% yield). $^1$H NMR (600 MHz, CDCl$_3$): δ 8.36 (s, 1H), 8.34 (s, 1H), 7.98 – 7.94 (m, 2H), 7.92 (s, 1H), 7.89 (d, $J = 9.0$, 1H), 7.44 (s, 1H), 7.42 (s, 1H), 7.35 (td, $J = 7.8$, 1.1, 1H), 7.31 (dd, $J = 8.9$, 1.6, 1H), 7.23 (d, $J = 6.8$, 1H), 7.12 (t, $J = 7.5$, 1H), 6.95 (d, $J = 7.8$, 1H), 3.28 (s, 3H), 1.92 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 179.4, 143.4, 137.5, 134.7, 131.9, 131.8, 131.4, 130.8, 128.8, 128.3, 128.2, 126.5, 125.8, 125.4, 125.3, 124.7, 124.3, 122.9, 108.4, 52.5, 26.6, 23.4; HR-ESI-MS ($m/z$): calcd. for C$_{24}$H$_{19}$NONa [M + Na]$^+$, 360.1359, found 360.1360.

$(\pm)$-3-(9H-fluoren-2-yl)-1,3-dimethylindolin-2-one (3o)

Prepared according to the general procedure using 2-iodofluorene (29.2 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3o as a colorless oil (X = I, 14.0 mg, 43% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.73 (d, $J = 7.5$, 1H), 7.68 (d, $J = 8.0$, 1H), 7.52 – 7.50 (m, 2H), 7.39 – 7.27 (m, 4H), 7.23 (d, $J = 7.4$, 1H), 7.12 (t, $J = 7.5$, 1H), 6.95 (d, $J = 7.8$, 1H), 3.84 (s, 2H), 3.27 (s, 3H), 1.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 179.7, 143.6, 143.4, 143.3, 141.3, 140.9, 139.3, 135.2, 128.1, 126.7, 125.3, 125.0, 124.3, 122.9, 119.9, 119.8, 108.4, 52.3, 37.0, 26.6, 24.0; HR-ESI-MS ($m/z$): calcd. for C$_{23}$H$_{20}$NO [M + H]$^+$, 326.1539, found 326.1541.
(±)-1,3-dimethyl-3-(pyridin-3-yl)indolin-2-one (3p)

Prepared according to the general procedure using 3-iodopyridine (20.5 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product 3p as a colorless oil (X = I, 19.5 mg, 82% yield; X = Br, 18.6 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.51 – 8.49 (m, 2H), 7.75 – 7.69 (m, 1H), 7.36 (td, J = 7.7, 1.2, 1H), 7.29 – 7.19 (m, 2H), 7.13 (t, J = 7.5, 1H), 6.95 (d, J = 7.8, 1H), 3.25 (s, 3H), 1.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 178.6, 148.5, 148.2, 143.2, 136.5, 134.6, 133.3, 128.6, 124.2, 123.4, 123.1, 108.7, 50.6, 26.6, 23.8; HR-ESI-MS (m/z): calcd. for C₁₅H₁₅N₂O [M + H]⁺, 239.1179, found 239.1181.

(±)-1,3-dimethyl-3-(quinolin-5-yl)indolin-2-one (3q)

Prepared according to the general procedure using 5-bromoquinoline (20.8 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product 3q as a colorless oil (X = Br, 22.2 mg, 77% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.76 (dd, J = 4.1, 1.2, 1H), 8.10 (d, J = 8.4, 1H), 7.90 (d, J = 7.2, 1H), 7.83 – 7.73 (m, 1H), 7.33 (t, J = 7.7, 1H), 7.25 (d, J = 8.4, 1H), 7.12 – 7.03 (m, 2H), 6.96 (t, J = 7.5, 1H), 6.84 (d, J = 7.4, 1H), 3.44 (s, 3H), 1.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 180.0, 149.5, 149.1, 142.0, 136.4, 135.7, 132.0, 130.5, 128.7, 128.3, 126.8, 126.7, 123.4, 123.1, 121.1, 108.9, 52.3, 26.8, 26.7; HR-ESI-MS (m/z): calcd. for C₁₉H₁₇N₂O [M + H]⁺, 289.1335, found 289.1344.
(±)-3-(isoquinolin-5-yl)-1,3-dimethylindolin-2-one (3r)

Prepared according to the general procedure using 5-bromoisoquinoline (20.8 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product 3r as a colorless oil (X = Br, 21.3 mg, 74% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.18 (s, 1H), 8.20 (d, J = 6.2, 1H), 8.05 (d, J = 7.3, 1H), 7.95 (d, J = 8.2, 1H), 7.69 (t, J = 7.8, 1H), 7.35 (t, J = 7.7, 1H), 7.08 (d, J = 7.8, 1H), 6.97 (t, J = 7.5, 1H), 6.82 (d, J = 7.3, 1H), 6.68 (d, J = 6.2, 1H), 3.45 (s, 3H), 1.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 179.8, 153.5, 143.5, 142.2, 135.9, 134.7, 134.2, 130.3, 129.5, 128.6, 128.4, 126.7, 123.4, 123.0, 116.6, 108.9, 52.2, 26.8, 26.4; HR-ESI-MS (m/z): calcd. for C₁₉H₁₇N₂O [M + H]^⁺, 289.1335, found 289.1343.

(±)-1,3-dimethyl-3-(thiophen-3-yl)indolin-2-one (3s)

Prepared according to the general procedure using 3-iodothiophene (21.0 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3s as a colorless oil (X = I, 15.8 mg, 65% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.33 (t, J = 7.7, 1H), 7.30 – 7.24 (m, 2H), 7.15 – 7.03 (m, 3H), 6.90 (d, J = 7.8, 1H), 3.23 (s, 3H), 1.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 178.7, 143.1, 141.6, 134.2, 128.3, 126.5, 126.1,
123.9, 122.8, 121.5, 108.3, 50.0, 26.5, 24.5; HR-ESI-MS (m/z): calcd. for C_{14}H_{13}NOSNa [M + Na]^+, 266.0610, found 266.0612.

(±)-3-(benzo[b]thiophen-7-yl)-1,3-dimethylindolin-2-one (3t)
Prepared according to the general procedure using 7-bromobenzothiophene (21.3 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H_2O (50.4 mg, 0.3 mmol), and CH_3CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3t as a colorless oil (X = Br, 16.1 mg, 55% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, J = 7.9, 1H), 7.64 (d, J = 7.5, 1H), 7.45 (t, J = 7.7, 1H), 7.36 (t, J = 7.5, 1H), 7.24 (d, J = 5.5, 1H), 7.17 (d, J = 5.5, 1H), 7.01 – 6.95 (m, 3H), 3.36 (s, 3H), 1.94 (s, 3H); ^13C NMR (100 MHz, CDCl_3): δ 178.5, 144.1, 140.7, 137.7, 134.2, 133.6, 128.6, 126.2, 124.5, 124.0, 123.9, 123.5, 123.2, 123.0, 108.4, 52.6, 26.6, 23.8; HR-ESI-MS (m/z): calcd. for C_{18}H_{15}NOSNa [M + Na]^+, 316.0767, found 316.0772.

(±)-3-(benzofuran-5-yl)-1,3-dimethylindolin-2-one (3u)
Prepared according to the general procedure using 5-bromobenzofuran (19.7 mg, 0.1 mmol), 2a (32.2 mg, 0.2 mmol), CsOH·H_2O (50.4 mg, 0.3 mmol), and CH_3CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 3u as a colorless
oil (X = Br, 14.1 mg, 51% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57 (dd, $J = 11.9$, 1.9, 2H), 7.40 (d, $J = 8.7$, 1H), 7.34 (td, $J = 7.7$, 1.1, 1H), 7.24 – 7.17 (m, 2H), 7.11 (t, $J = 7.5$, 1H), 6.94 (d, $J = 7.8$, 1H), 6.70 (d, $J = 1.3$, 1H), 3.26 (s, 3H), 1.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 179.8, 145.4, 143.2, 135.3, 128.1, 127.5, 124.2, 123.2, 122.8, 119.3, 111.3, 108.4, 106.8, 52.1, 26.5, 24.2; HR-ESI-MS ($m/z$): calcd. for C$_{18}$H$_{15}$NO$_2$Na [M + Na]$^+$, 300.0995, found 300.1003.

$^{4a}$

(±)-3-methyl-3-phenylindolin-2-one (4a)

Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), 3-methylindolin-2-one (29.4 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:4) to afford the product 4a as a colorless oil (15.2 mg, 68% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.23 (s, 1H), 7.36 – 7.21 (m, 6H), 7.14 (d, $J = 7.4$, 1H), 7.06 (t, $J = 7.5$, 1H), 6.96 (d, $J = 7.8$, 1H), 1.82 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 181.6, 140.5, 140.2, 135.5, 128.6, 128.1, 127.3, 126.6, 124.5, 122.8, 110.0, 52.6, 23.5; HR-ESI-MS ($m/z$): calcd. for C$_{15}$H$_{13}$NONa [M + Na]$^+$, 246.0889, found 246.0888.

$^{4b}$

(±)-1-allyl-3-methyl-3-phenylindolin-2-one (4b)

Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1
mmol), 1-allyl-3-methylindolin-2-one (37.4 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product $4b$ as a colorless oil (21.3 mg, 81% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34 – 7.22 (m, 6H), 7.19 (d, $J$ = 7.3, 1H), 7.08 (t, $J$ = 7.5, 1H), 6.91 (d, $J$ = 7.8, 1H), 5.90 – 5.78 (m, 1H), 5.27 – 5.15 (m, 2H), 4.39 – 4.33 (m, 2H), 1.81 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 179.2, 142.4, 134.9, 131.5, 128.6, 128.0, 127.3, 126.6, 124.3, 122.8, 117.5, 109.2, 52.1, 42.4, 23.9; HR-ESI-MS ($m/z$): calcd. for C$_{18}$H$_{17}$NONa [M + Na]$^+$, 286.1202, found 286.1197.

![Image of $4c$]

$^{(\pm)}$-1-benzyl-3-methyl-3-phenylindolin-2-one ($4c$)

Prepared according to the general procedure using iodobenzene $1a$ (20.4 mg, 0.1 mmol), 1-benzyl-3-methylindolin-2-one (47.4 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product $4c$ as a colorless oil (22.5 mg, 72% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32 – 7.21 (m, 11H), 7.18 (d, $J$ = 8.6, 2H), 7.05 (t, $J$ = 7.5, 1H), 6.79 (d, $J$ = 7.7, 1H), 4.94 (q, $J$ = 15.7, 2H), 1.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 179.6, 142.3, 140.8, 136.0, 135.0, 128.8, 128.6, 128.0, 127.6, 127.3, 127.2, 126.7, 124.2, 122.8, 109.4, 52.2, 43.9, 23.8; HR-ESI-MS ($m/z$): calcd. for C$_{22}$H$_{19}$NONa [M + Na]$^+$, 336.1359, found 336.1364.
(±)-1-(methoxymethyl)-3-methyl-3-phenylindolin-2-one (4d)

Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), 1-(methoxymethyl)-3-methylindolin-2-one (38.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 4d as a colorless oil (20.3 mg, 76% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.22 (m, 6H), 7.20 (d, J = 6.8, 1H), 7.14 – 7.11 (m, 2H), 5.20 – 5.12 (m, 2H), 3.31 (s, 3H), 1.83 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 180.1, 141.4, 140.7, 134.4, 128.6, 128.3, 127.4, 126.6, 124.4, 123.4, 109.8, 71.5, 56.2, 52.5, 24.0; HR-ESI-MS (m/z): calcd. for C₁₇H₁₇NO₂Na [M + Na]⁺, 290.1151, found 290.1152.

(±)-3-butyl-1-methyl-3-phenylindolin-2-one (4e)

Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), 3-butyl-1-methylindolin-2-one (40.6 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 4e as a colorless oil (22.9 mg, 82% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.39 – 7.22 (m, 7H), 7.12 (t, J = 7.5, 1H), 6.90 (d, J = 6.8, 1H), 3.23 (s, 3H), 2.37 (td, J = 12.8, 4.5, 1H), 2.19 (td, J = 12.9, 4.1, 1H), 1.36 – 1.17 (m, 2H), 1.17 – 0.98 (m, 1H), 0.93 – 0.71 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 178.7, 144.0, 140.4, 132.5, 128.5, 128.1, 127.2, 126.9, 124.8, 122.6, 108.2, 56.7, 37.8, 26.7, 26.4, 22.8, 13.8; HR-
ESI-MS (m/z): calcd. for C_{19}H_{21}NONa [M + Na]^+, 302.1515, found 302.1519.

(±)-1-methyl-3-phenyl-3-(3-phenylpropyl)indolin-2-one (4f)
Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), 1-methyl-3-(3-phenylpropyl)indolin-2-one (53 mg, 0.2 mmol), CsOH·H_2O (50.4 mg, 0.3 mmol), and CH_3CN (1 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 4f as a colorless oil (27.3 mg, 80% yield). \(^1\)H NMR (400 MHz, CDCl_3): \(\delta\) 7.37 – 7.26 (m, 5H), 7.25 – 7.14 (m, 5H), 7.13 – 7.03 (m, 3H), 6.88 (d, \(J = 7.8\), 1H), 3.21 (s, 3H), 2.61 (ddd, \(J = 14.9, 9.3, 5.9\), 1H), 2.57 – 2.48 (m, 1H), 2.48 – 2.38 (m, 1H), 2.23 (td, \(J = 12.9, 4.0\), 1H), 1.53 – 1.39 (m, 1H), 1.38 – 1.13 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl_3): \(\delta\) 178.6, 143.9, 141.8, 140.2, 132.1, 128.5, 128.4, 128.3, 128.2, 127.2, 126.9, 125.8, 124.8, 122.6, 108.3, 56.6, 37.6, 36.0, 26.4; HR-ESI-MS (m/z): calcd. for C_{24}H_{23}NONa [M + Na]^+, 364.1672, found 364.1681.

(±)-3-(2-methoxyethyl)-1-methyl-3-phenylindolin-2-one (4g)
Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), 3-(2-methoxyethyl)-1-methylindolin-2-one (41 mg, 0.2 mmol), CsOH·H_2O (50.4 mg, 0.3 mmol), and CH_3CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 4g as a colorless oil (22.5 mg, 80% yield). \(^1\)H NMR (400 MHz,
CDCl$_3$: $\delta$ 7.38 – 7.21 (m, 7H), 7.12 (t, $J = 7.5$, 1H), 6.91 (d, $J = 7.8$, 1H), 3.22 (s, 3H), 3.19 – 3.12 (m, 2H), 3.11 (s, 3H), 2.84 (dt, $J = 13.5$, 7.9, 1H), 2.40 (ddd, $J = 13.3$, 7.4, 4.6, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 178.5, 144.1, 140.2, 131.5, 128.6, 128.3, 127.3, 126.7, 125.0, 122.5, 108.3, 68.9, 58.6, 54.5, 37.0, 26.5; HR-ESI-MS ($m/z$): calcd. for C$_{18}$H$_{19}$NO$_2$Na [M + Na]$^+$, 304.1308, found 304.1311.

Methyl (±)-methyl(2-(1-methyl-2-oxo-3-phenylindolin-3-yl)ethyl)carbamate (4h)
Prepared according to the general procedure using iodo benzene 1a (20.4 mg, 0.1 mmol), methyl methyl(2-(1-methyl-2-oxoindolin-3-yl)ethyl)carbamate (52.4 mg, 0.2 mmol), CsOH·H$_2$O (50.4 mg, 0.3 mmol), and CH$_3$CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 4h as a colorless oil (24.7 mg, 73% yield). $^1$H NMR (400 MHz, CDCl$_3$): (rotameric mixture)$^{[4]}$ $\delta$ = 7.44 – 7.20 (m, 7H), 7.15 (t, $J = 7.4$, 1H), 6.92 (d, $J = 6.7$, 1H), 3.60 (brs, 1.4H), 3.58 (brs, 1.6H), 3.23 (s, 3H), 3.10 – 2.90 (m, 2H), 2.81 (brs, 1.6H), 2.78 (brs, 1.4H), 2.71 – 2.54 (m, 1H), 2.54 – 2.30 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): (rotameric mixture) $\delta$ 177.8, 156.6, 143.7, 139.7, 131.3, 128.6, 128.5, 127.5, 126.7, 124.7, 122.8, 108.5, 54.9, 52.6, 45.5, 45.0, 35.3, 34.7, 34.1, 26.5; HR-ESI-MS ($m/z$): calcd. for C$_{20}$H$_{22}$N$_2$O$_3$Na [M + Na]$^+$, 361.1523, found 361.1526.

Methyl (±)-(2-(1,5-dimethyl-2-oxo-3-phenylindolin-3-yl)ethyl)(methyl)carbamate (4i)
Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), methyl (2-(1,5-dimethyl-2-oxoindolin-3-yl)ethyl)(methyl)carbamate (55.2 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 4i as a colorless oil (26.4 mg, 75% yield). ¹H NMR (600 MHz, CDCl₃): (rotameric mixture) δ 7.44 – 7.19 (m, 5H), 7.19 – 7.01 (m, 2H), 6.81 – 6.77 (m, 1H), 3.60 (brs, 3H), 3.21 (brs, 3H), 3.06-2.97 (m, 2H), 2.81 (brs, 1.5H), 2.78 (brs, 1.5H), 2.68-2.59 (m, 1H), 2.54 – 2.27 (m, 4H); ¹³C NMR (150 MHz, CDCl₃): (rotameric mixture) δ 156.7, 147.2, 141.3, 139.9, 132.3, 131.5, 128.6, 127.4, 126.7, 125.5, 108.1, 52.5, 45.0, 35.2, 34.5, 26.5, 21.2; HR-ESI-MS (m/z): calcd. for C₂₁H₂₄N₂O₃Na [M + Na]+, 375.1679, found 375.1682.

Methyl (±)-(2-(5-methoxy-1-methyl-2-oxo-3-phenylindolin-3-yl)ethyl)(methyl)carbamate (4j)

Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), methyl (2-(5-methoxy-1-methyl-2-oxoindolin-3-yl)ethyl)(methyl)carbamate (58.4 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and CH₃CN (1 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product 4j as a colorless oil (23.2 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃): (rotameric mixture) δ 7.46 – 7.18 (m, 5H), 6.92-6.85 (m, 3H), 3.81 (brs, 3H), 3.61 (brs, 3H), 3.20 (brs, 3H), 3.04 – 2.94 (m, 2H), 2.82 (brs, 1.8H), 2.78 (brs, 1.2H), 2.73 – 2.60 (m, 1H), 2.50 – 2.30 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): (rotameric mixture) δ 177.5, 156.6, 156.2, 139.7, 137.3, 132.8, 128.6, 127.4, 126.7, 112.6, 112.3, 108.7, 55.9, 55.3, 52.6, 45.5, 45.0, 35.2, 34.5, 34.1, 26.5;
Methyl (±)-(2-(2-oxo-3-phenylindolin-3-yl)ethyl)carbamate (4k)

Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), methyl (2-(2-oxoindolin-3-yl)ethyl)carbamate (46.8 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and DMSO (1 mL). Time of irradiation: 10 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:3) to afford the product 4k as a colorless oil (14.3 mg, 46% yield). ¹H NMR (600 MHz, CDCl₃): δ 8.16 (s, 1H), 7.36 (d, J = 7.5, 2H), 7.33 – 7.28 (m, 3H), 7.28 – 7.23 (m, 2H), 7.11 (t, J = 7.4, 1H), 6.95 (d, J = 7.6, 1H), 4.77 (s, 1H), 3.57 (s, 3H), 3.12 – 3.02 (m, 2H), 2.71 – 2.64 (m, 1H), 2.49 – 2.43 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 180.8, 156.8, 140.8, 139.6, 132.1, 128.7, 128.5, 127.5, 126.7, 125.1, 123.0, 110.4, 55.7, 52.0, 37.5, 37.1; HR-ESI-MS (m/z): calcd. for C₁₈H₁₈N₂O₃Na [M + Na]⁺, 333.1210, found 333.1211.

(±)-3-(2-hydroxyethyl)-3-phenylindolin-2-one (4l)

Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), 3-(2-hydroxyethyl)indolin-2-one (35.4 mg, 0.2 mmol), CsOH·H₂O (50.4 mg, 0.3 mmol), and DMSO (1 mL). Time of irradiation: 10 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:2.5) to afford the product 4l as a colorless oil (12.1 mg, 48% yield). ¹H NMR (600 MHz, CDCl₃): δ
9.02 (s, 1H), 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 (d, \( J = 8.3 \), 1H), 7.20 (td, \( J = 7.7, 1.0, 1H \)), 7.15 (d, \( J = 7.4, 1H \)), 7.08-7.04 (m, 1H), 6.89 (d, \( J = 7.7, 1H \)), 3.58 – 3.52 (m, 1H), 3.46 – 3.40 (m, 1H), 2.84 – 2.80 (m, 1H), 2.42 – 2.38 (m, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \( \delta \) 181.8, 141.2, 140.1, 132.5, 128.7, 128.4, 127.4, 126.7, 124.9, 122.7, 110.5, 59.3, 55.5, 39.8; HR-ESI-MS (m/z): calcd. for C\(_{16}\)H\(_{16}\)NO\(_2\) [M + H]\(^+\), 254.1176, found 254.1175.

(±)- 4-(2-oxo-3-phenylindolin-3-yl)butanoic acid (4m)

Prepared according to the general procedure using iodobenzene 1a (20.4 mg, 0.1 mmol), 4-(2-oxoindolin-3-yl)butanoic acid (43.8 mg, 0.2 mmol), CsOH·H\(_2\)O (67.2 mg, 0.4 mmol), and DMSO (1 mL). Time of irradiation: 10 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:2) to afford the product 4m as a colorless oil (11.5 mg, 39% yield). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 8.68 (s, 1H), 7.36 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 7.20 (d, \( J = 7.4, 1H \)), 7.10 (d, \( J = 7.5, 1H \)), 6.97 (d, \( J = 7.7, 1H \)), 2.47 – 2.41 (m, 1H), 2.35 – 2.25 (m, 3H), 1.57 – 1.53 (m, 1H), 1.36 – 1.32 (m, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \( \delta \) 140.8, 139.6, 132.4, 128.6, 128.4, 127.5, 126.8, 125.1, 122.9, 110.3, 57.0, 36.8, 33.7, 20.0; HR-ESI-MS (m/z): calcd. for C\(_{18}\)H\(_{17}\)NO\(_3\)Na [M + Na]\(^+\), 318.1101, found 318.1102.

References


NMR Spectral Data
N\text{OCH}_3\text{CH}_3

3e

CN

N\text{OCH}_3\text{CH}_3

3e
57
\[ \text{NOCH}_3 \quad 4e \]

\[ \text{NOCH}_3 \quad 4e \]
N\text{OCH}_3^{4f}

\text{CH}_3^{4f}