Electronic Supplementary Information

Visible light-induced 3-sulfenylation of N-methylindoles with arylsulfonyl chlorides

Min Chen, Zhi-Tang Huang and Qi-Yu Zheng

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Chinese Academy of Sciences, Beijing 100190, China

Fax: +86 10 62554449; Tel: +86 10 62652811; E-mail: zhengqy@iccas.ac.cn

Content

1. General methods 2
2. Optimization of the reaction of N-methylindole with p-toluene sulfonyl chloride 2
3. The procedures for the synthesis of reactants 4
4. General procedure for the 3-sulfenylation of N-methylindoles with arylsulfonyl chlorides 5
5. Experimental data for the described substances 6
6. Controlled experiments for the mechanistic investigation 16
7. References 22
8. Copies of $^1$H, $^{13}$C NMR spectra and HRMS spectra 23
1. General methods

Unless specified noted, all reagents were purchased from commercial suppliers without further purification. All the solvents were treated according to general methods. Column chromatography was performed using 200-300 mesh silica gel (YanTai, China). $^1$H NMR spectra were recorded on BRUKER 400 (400 MHz) spectrophotometer. Chemical shifts ($\delta$) are reported in ppm from TMS as the internal standard (TMS 0 ppm). Data are reported as follows: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $dd$ = doublet of doublets, $m$ = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR spectra were recorded on BRUKER 400 (100 MHz) with complete proton decoupling spectrophotometer. Mass spectra were measured on a Micromass UK MS spectrometer (EI) or Bruker Apex IV FTMS (ESI).

2. Optimization of the reaction of $N$-methyldindole with $p$-toluene sulfonyl chloride

A 25 ml Schlenk tube equipped with stir-bar was charged with $p$-tolylsulfonyl chloride (2a, 1 mmol), photocatalyst (2% mol), additives (2 mmol, if it existed as solid). The system was evacuated 3 times and backfilled with Ar before $N$-methyldindoles (1a), solvent and other liquid additives were added by syringe. Then the vial was evacuated 3 times and backfilled with Ar again at -78 °C and slowly warmed to 40 °C. After given time 12 hours under 23 w fluorescent light, the reaction mixture was diluted with CH$_2$Cl$_2$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.
### Table S1  Evaluation of various parameters in the photoredox reaction

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Solvent</th>
<th>Ratio of 1a/2a</th>
<th>Additive</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>1</td>
<td></td>
<td>23%</td>
</tr>
<tr>
<td>2</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>1</td>
<td>K₂HPO₄</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>1</td>
<td>NaHCO₃</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>1</td>
<td>2,6-lutidine</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>1</td>
<td>TMEDA</td>
<td>Trace</td>
</tr>
<tr>
<td>6</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>1</td>
<td>i-Pr₂NEt</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>3</td>
<td></td>
<td>57%</td>
</tr>
<tr>
<td>8</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>2</td>
<td></td>
<td>26%</td>
</tr>
<tr>
<td>9</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>5</td>
<td></td>
<td>58%</td>
</tr>
<tr>
<td>10</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Ru(bpy)₃Cl₂</td>
<td>CH₃CN</td>
<td>3</td>
<td></td>
<td>55%</td>
</tr>
<tr>
<td>12</td>
<td>Ru(bpy)₃(PF₆)₂</td>
<td>CH₃CN</td>
<td>3</td>
<td></td>
<td>59%</td>
</tr>
<tr>
<td>13</td>
<td>Ru(bpy)₃(PF₆)₂</td>
<td>DMF</td>
<td>3</td>
<td></td>
<td>Trace</td>
</tr>
<tr>
<td>14</td>
<td>Ru(bpy)₃(PF₆)₂</td>
<td>DMSO</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Ru(bpy)₃(PF₆)₂</td>
<td>NMP</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Ru(bpy)₃(PF₆)₂</td>
<td>CH₃CN/DMF</td>
<td>3</td>
<td></td>
<td>Trace</td>
</tr>
<tr>
<td>17</td>
<td>Ru(bpy)₃(PF₆)₂</td>
<td>CH₃CN</td>
<td>3</td>
<td>4Å MS</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Ru(bpy)₃(PF₆)₂</td>
<td>CH₃CN</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* Unless otherwise specified, all reactions were carried out with 1a, 2a (1 mmol), photocatalyst (2% mol), under 23 W fluorescent light at 40 °C with atmosphere of Ar for 12 h. *b* Isolated yield. *c* Indoles were not involved in reactions. *d* At temperature of 20 °C. *e* Similar conversion as entry 7 indicated by TLC, but not isolated. *f* At temperature of 30 °C. *g* 10 mmol CH₃CN with 2.5 mmol DMF. *h* No light.
3. The procedure for the synthesis of reactants

General procedure for the synthesis of substituted N-alkylindoles.

\[
\begin{align*}
\text{R} & \quad \text{1. NaH, DMF} \quad \text{2. MeI} \\
\text{H} & \quad \text{R} \quad \text{N} \\
\end{align*}
\]

To a stirred solution of substituted 1H-indole (10 mmol) in dry DMF (25 mL), NaH (640 mg, 60% suspension in mineral oil, 16 mmol) was added portionwise under Ar atmosphere at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 30 min. After cooling to 0 °C, alkyl agents MeI (12 mmol) or benzyl bromide (12 mmol) was added dropwise to the solution, warming to room temperature. Water was added to quench the system when TLC indicated it was over (Caution!). The aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with water and brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give desired compound.

Procedure for the synthesis of tert-butyl 1H-indole-1-carboxylate.

\[
\begin{align*}
\text{H} & \quad \text{+ N,N-dimethylpyridin-4-amine (DMAP) + Boc anhydride (THF)} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

To the THF solution of 1H-indole (585 mg, 5 mmol), N,N-dimethylpyridin-4-amine (DMAP) (915 mg, 7.5 mmol) and Boc anhydride (2.18 g, 10 mmol) was added and the solution was stirred under room temperature. The reaction mixture was quenched by saturated sodium bicarbonate solution (20 mL) extracted by ethyl acetate (3 x 20 mL). Combined organic phase were washed by water, brine and dried over anhydrous Na₂SO₄, concentrated under vacuum. The residue was then purified by flash chromatography on silica gel.
4. General procedure for the 3-sulfenlylation of N-methylindoles with arylsulfonyl chlorides

A 25 ml Schlenk tube equipped with stir-bar was charged with arylsulfonyl chloride (if it was solid, 1 mmol), photocatalyst Ru(bpy)$_3$(PF$_6$)$_2$ (2% mol) and indole derivatives (if it was solid, 3 mmol). The system was evacuated 3 times and backfilled with Ar before solvent 2.5 ml CH$_3$CN and liquid reactants were added by syringe. Then the vial was evacuated 3 times and backfilled with Ar again at -78 °C and warmed to 40 °C. After given time under 23 w fluorescent light, the reaction mixture was diluted with CH$_2$Cl$_2$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.
5. Experimental data for the described substances

1,2-Dimethyl-1H-indole

Yielding the title compound as yellow solid in 80% yield. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.66 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 1H), 7.26-7.30 (m, 1H), 7.19-7.22 (m, 1H), 6.38 (s, 1H), 3.74 (s, 3H), 2.53 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 137.5, 136.9, 128.2, 120.6, 119.8, 119.4, 108.9, 99.7, 29.5, 12.9. The spectroscopic data are in accordance with those reported.$^1$

5-Methoxy-1-methyl-1H-indole

Yielding the title compound as white solid in 73% yield. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.24 (dd, $J = 2.4$, 10 Hz, 1H), 7.16 (dd, $J = 4.2$, 8.9 Hz, 1H), 7.02 (d, $J =$3.0 Hz, 1H), 6.93 (dt, $J = 2.4$, 9.1 Hz, 1H), 6.40 (d, $J =$3.0 Hz, 1H), 3.69 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 159.2, 156.9, 133.6, 130.6, 128.9, 128.8, 110.1, 110.0, 109.91, 109.85, 105.8, 105.5, 101.02, 100.97, 33.1. The spectroscopic data are in accordance with those reported.$^3$
Yielding the title compound as a white solid in 92% yield. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.21 (d, $J = 8.8$ Hz, 1H), 7.09 (d, $J = 2.2$ Hz, 1H), 7.01 (d, $J = 2.6$ Hz, 1H), 6.89 (d, $J = 2.3$, 8.8 Hz, 1H), 6.40 (d, $J = 2.6$ Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 154.2, 132.3, 129.5, 129.0, 112.0, 110.0, 102.7, 100.5, 56.0, 33.0. The spectroscopic data are in accordance with those reported.$^1$

![6-Fluoro-1-methyl-1H-indole](image)

### 6-Fluoro-1-methyl-1H-indole

Yielding the title compound as yellow oil in 75% yield. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.40 (dd, $J = 5.4$, 8.6 Hz, 1H), 6.82-6.86 (m, 2H), 6.73-6.78 (m, 1H), 6.33 (d, $J = 3.1$ Hz, 1H), 3.53 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 161.2, 158.8, 137.0, 136.9, 129.40, 129.36, 125.1, 121.7, 121.6, 108.3, 108.2, 101.3, 95.9, 95.6, 32.9. The spectroscopic data are in accordance with those reported.$^2$

![tert-Butyl 1H-indole-1-carboxylate](image)

### tert-Butyl 1H-indole-1-carboxylate

Yielding the title compound as a white solid in 100% yield. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.16 (d, $J = 5.4$ Hz, 1H), 7.57 (d, $J = 1.8$ Hz, 1H), 7.52 (d, $J = 4$ Hz, 1H), 7.29 (d, $J = 7.6$ Hz, 1H), 7.17 (d, $J = 7.5$ Hz, 1H), 6.52 (d, $J = 1.8$ Hz, 1H), 1.63 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 149.9, 135.3, 130.7, 125.9, 124.3, 122.7, 121.0, 115.3, 107.4, 83.6, 28.3. The spectroscopic data are in accordance with those reported.$^4$

![1-Benzyl-1H-indole](image)

### 1-Benzyl-1H-indole

Yielding the title compound as white solid in 94% yield. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.64 (d, $J = 7.7$ Hz, 1H), 7.22-7.30 (m, 4H), 7.14-7.18 (m, 1H), 7.09-7.12 (m, 4H), 6.54 (d, $J = 3.1$ Hz, 1H), 5.31 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 137.6, 136.4, 128.8, 128.7, 128.3, 127.6, 126.8, 121.7, 121.0, 119.6, 109.7, 101.7, 50.1. The spectroscopic data are in
1-Methyl-3-((p-tolylthio)-1H-indole

Prepared according to the general procedure from 1a (3 mmol), 2a (1 mmol), Ru(bpy)$_3$($\text{PF}_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (64% yield). M.p.: 122-123 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.60 (d, $J = 7.9$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.21–7.28 (m, 2H), 7.14 (t, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 8.2$ Hz, 2H), 6.95 (d, $J = 8.1$ Hz, 2H), 3.79 (s, 3H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.7, 136.2, 135.0, 134.7, 130.1, 129.6, 126.4, 122.7, 120.6, 120.0, 109.9, 101.5, 33.2, 21.0. IR (film, cm$^{-1}$): ν 1631, 1488, 1458, 740. HRMS (EI): Calcd for C$_{16}$H$_{15}$NS $[^{1}M]$: m/z 253.0925; found: 253.0928.

1-Methyl-3-((o-tolylthio)-1H-indole

Prepared according to the general procedure from 1a (3 mmol), 2-methylbenzene-1-sulfonyl chloride (1 mmol), Ru(bpy)$_3$($\text{PF}_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 24 hours to provide the title compound as a white solid in 44% yield. M.p.: 130-131 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.26-7.29 (m, 2H), 7.10-7.16 (m, 2H), 6.95 (t, $J = 7.2$ Hz, 1H), 6.87 (t, $J = 7.2$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 3.83 (s, 3H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.7, 137.7, 135.1, 134.3, 130.0, 129.8, 126.2, 125.3, 124.4, 122.6, 120.5, 119.8, 109.7, 100.3, 33.1, 19.9. IR (film, cm$^{-1}$): ν 1631, 1466. HRMS (EI): Calcd for C$_{16}$H$_{15}$NS $[^{1}M]$: m/z 253.0925; found: 253.0929.
1-Methyl-3-(m-tolylthio)-1H-indole

Prepared according to the general procedure from 1a (3 mmol), 3-methylbenzene-1-sulfonyl chloride (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (60% yield). M.p.: 87-88 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.61 (d, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 7.28 (t, $J = 8.2$ Hz, 2H), 7.15 (t, $J = 8.2$ Hz, 1H), 6.97-7.04 (m, 2H), 6.85 (t, $J = 7.1$ Hz, 2H), 3.82 (s, 3H), 2.21 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.5, 138.4, 137.6, 135.0, 130.0, 128.6, 126.5, 125.7, 123.0, 122.5, 120.5, 119.8, 109.7, 100.9, 33.1, 21.4. IR (film, cm$^{-1}$): v 1590, 1573, 1458. HRMS (EI): Calcd for C$_{16}$H$_{15}$NS [M]$^+$: m/z 253.0925; found: 253.0930

![Image 1](image1.png)

1-Methyl-3-(phenylthio)-1H-indole

Prepared according to the general procedure from 1a (3 mmol), benzenesulfonyl chloride (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (66% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (d, $J = 7.9$ Hz, 1H), 7.36 (d, $J = 8.2$ Hz, 1H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.08-7.17 (m, 5H), 7.00-7.04 (m, 1H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.9, 137.8, 135.2, 130.0, 128.8, 126.0, 124.9, 122.8, 120.7, 119.9, 109.9, 100.8, 33.3. The spectroscopic data are in accordance with those reported.$^5$

![Image 2](image2.png)

3-((4-Fluorophenyl)thio)-1-methyl-1H-indole

Prepared according to the general procedure from 1a (3 mmol), 4-fluorobenzene-1-sulfonyl chloride (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (68% yield). M.p.: 56-58 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58 (d, $J = 7.9$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 7.27 (t, $J = 6.5$ Hz, 2H), 7.15 (t, $J = 7.2$ Hz, 1H), 7.05-7.08 (m, 2H), 6.84 (t, $J = 8.7$ Hz, 2H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.3, 159.9, 137.8, 135.1, 134.8, 134.7, 129.8, 128.03, 128.0, 127.3, 123.0, 122.5, 120.5, 119.8, 109.7, 100.9, 33.1, 21.4. IR (film, cm$^{-1}$): v 1590, 1573, 1458. HRMS (EI): Calcd for C$_{16}$H$_{15}$NS [M]$^+$: m/z 253.0925; found: 253.0930

![Image 3](image3.png)
3-((4-Chlorophenyl)thio)-1-methyl-1H-indole

Prepared according to the general procedure from 1a (3 mmol), 4-chlorobenzene-1-sulfonyl chloride (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (68% yield). M.p.: 137-138°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J = 7.9$ Hz, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 7.29 (d, $J = 7.7$ Hz, 2H), 7.16 (t, $J = 7.4$ Hz, 1H), 7.09 (d, $J = 8.6$ Hz, 2H), 7.00 (t, $J = 8.6$ Hz, 2H), 3.83 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.5, 137.8, 135.3, 130.6, 129.8, 128.9, 127.2, 122.9, 120.9, 119.8, 110.0, 100.4, 33.3. IR (film, cm$^{-1}$): ν 1656, 1628, 1508, 1470. HRMS (EI): Calcd for C$_{15}$H$_{12}$ClNS [M]$^+$: $m/z$ 273.0379; found: 273.0382

3-((4-bromophenyl)thio)-1-methyl-1H-indole

Prepared according to the general procedure from 1a (3 mmol), 4-bromobenzene-1-sulfonyl chloride (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (63% yield). M.p.: 170-171°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J = 8$ Hz, 1H), 7.38 (d, $J = 8.2$ Hz, 1H), 7.28-7.32 (m, 2H), 7.23-7.25 (m, 2H), 7.17 (t, $J = 7.5$ Hz, 1H), 6.94 (t, $J = 8.6$Hz, 2H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.2, 137.8, 135.3, 131.8, 129.7, 127.5, 122.9, 120.9, 119.8, 118.4, 110.0, 100.1, 33.3. IR (film, cm$^{-1}$): ν 1504, 1472. HRMS (EI): Calcd for C$_{15}$H$_{12}$BrNS [M]$^+$: $m/z$ 316.9877; found: 316.9877; C$_{15}$H$_{12}$BrNS [M]$^+$: $m/z$ 318.9853; found: 318.9856
3-((4-Methoxyphenyl)thio)-1-methyl-1H-indole

Prepared according to the general procedure from 1a (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (58% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62 (d, $J$ = 7.9 Hz, 1H), 7.23-7.34 (m, 3H), 7.10-7.16 (m, 3H), 6.72 (d, $J$ = 8.8 Hz, 2H), 3.79 (s, 3H), 3.71 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.8, 137.5, 134.5, 130.1, 129.8, 128.5, 122.5, 120.4, 119.8, 114.5, 109.7, 102.5, 55.4, 33.1. The spectroscopic data are in accordance with those reported.$^5$

1-Methyl-3-(naphthalen-1-ylthio)-1H-indole

Prepared according to the general procedure from 1a (3 mmol), naphthalene-1-sulfonyl chloride (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (45% yield). M.p.: 150-151°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.47 (d, $J$ = 8.4 Hz, 1H), 7.81 (d, $J$ = 8.1 Hz, 1H), 7.48-7.59 (m, 4H), 7.36 (t, $J$ = 9.4 Hz, 2H), 7.28 (t, $J$ = 8.1Hz, 1H), 7.13 (t, $J$ = 7.7 Hz, 2H), 6.94 (t, $J$ = 7.3 Hz, 1H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.9, 136.9, 135.5, 133.9, 130.9, 130.0, 128.7, 126.2, 126.1, 125.9, 125.3, 124.2, 123.4, 122.8, 120.7, 120.0, 110.0, 100.0, 33.3. IR (film, cm$^{-1}$): $\nu$ 1655, 1560, 1508. HRMS (ESI): Calcd for C$_{19}$H$_{15}$NS [M+H]$^+$: m/z 290.0998; found: 290.0997

1-Methyl-3-(thiophen-2-ylthio)-1H-indole

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012
Prepared according to the general procedure from 1a (3 mmol), thiophene-2-sulfonyl chloride (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (45% yield). M.p.: 70-71 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 7.8$ Hz, 1H), 7.17-7.29 (m, 4H), 7.10-7.12 (m, 1H), 7.07 (d, $J = 3.4$ Hz, 1H), 6.82-6.84 (m, 1H), 3.72 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.7, 137.4, 133.9, 129.8, 129.4, 127.4, 127.3, 122.7, 120.6, 119.7, 109.9, 104.7, 33.2. IR (film, cm$^{-1}$): ν 1508, 1454, 741. HRMS (EI): Calcd for C$_{13}$H$_{11}$NS$_2$ [M]+: m/z 245.0333; found: 245.0336.

![4a](image)

5-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1H-indole

Prepared according to the general procedure from 5-fluoro-1-methyl-1H-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (2h, 1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (65% yield). M.p.: 91-92 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32 (s, 1H), 7.23-7.28 (m, 2H), 7.11 (d, $J = 8.8$ Hz, 2H), 7.00 (dt, $J = 2.4$, 9 Hz, 2H), 6.73 (d, $J = 8.8$ Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.9, 158.1, 157.6, 136.1, 134.3, 130.7, 130.6, 129.7, 128.8, 114.7, 111.3, 111.1, 110.7, 110.6, 105.0, 104.8, 102.8, 55.5, 33.5. IR (film, cm$^{-1}$): ν 1631, 1592, 1490. HRMS (ESI): Calcd for C$_{16}$H$_{14}$FNSO [M+H]$^+$: m/z 288.0858; found: 288.0854

![4b](image)

3-((4-Methoxyphenyl)thio)-1,5-dimethyl-1H-indole

Prepared according to the general procedure from 1,5-dimethyl-1H-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (2h, 1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a yellow oil (61% yield). M.p.: 91-92 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41 (s, 1H), 7.20-7.22
(m, 2H), 7.06-7.10 (m, 3H), 6.70 (d, J = 8.8 Hz, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 2.41 (s, 3H); ^13^C NMR (100 MHz, CDCl₃): δ 157.7, 136.0, 134.7, 130.4, 130.1, 129.9, 128.2, 124.2, 119.3, 114.6, 109.4, 101.5, 55.4, 33.1, 21.5. HRMS (ESI): Calcd for C₁₇H₁₇NSO [M+H]^+: m/z 284.1109; found: 284.1104.

5-Methoxy-3-((4-methoxyphenyl)thio)-1-methyl-1H-indole

Prepared according to the general procedure from 5-methoxy-1-methyl-1H-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (2h, 1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (47% yield). M.p.: 97-98 °C. ^1^H NMR (400 MHz, CDCl₃): δ 7.25 (s, 1H), 7.22 (d, J = 9.2 Hz, 1H), 7.09 (d, J = 1.9 Hz, 2H), 7.05 (d, J = 2.4 Hz, 1H), 6.90 (d, J = 2.4, 1.0 Hz, 1H), 6.73 (d, J = 1.9 Hz, 1H), 6.71 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H); ^13^C NMR (100 MHz, CDCl₃): δ 157.9, 155.2, 135.2, 132.8, 130.7, 130.4, 128.3, 114.7, 113.2, 110.7, 101.7, 101.2, 56.0, 55.5, 33.4. IR (film, cm$^{-1}$): ν 1610, 1490. HRMS (ESI): Calcd for C$_{17}$H$_{17}$NO$_2$S [M+H]^+: m/z 300.1058; found: 300.1056.

6-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1H-indole

Prepared according to the general procedure from 6-fluoro-1-methyl-1H-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (2h, 1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (46% yield). M.p.: 96-97 °C. ^1^H NMR (400 MHz, CDCl₃): δ 7.51 (dd, J = 5.4, 8.6 Hz, 1H), 7.26 (s, 1H), 7.11 (d, J = 8.7 Hz, 2H), 7.00 (dd, J = 1.9, 9.5 Hz, 1H), 6.86-6.91 (m, 1H), 6.73 (d, J = 8.7 Hz, 2H), 3.74 (s, 3H), 3.72 (s, 3H); ^13^C NMR (100 MHz, CDCl₃): δ 161.6, 159.2, 157.9, 137.6, 137.5, 134.64, 134.62, 129.6, 128.7, 126.1, 120.8, 120.7, 114.5, 110.7, 101.2, 56.0, 55.5, 33.4. IR (film, cm$^{-1}$): ν 1610, 1490. HRMS (ESI): Calcd for C$_{17}$H$_{17}$NO$_2$S [M+H]^+: m/z 300.1058; found: 300.1056.

3-((4-Methoxyphenyl)thio)-1,2-dimethyl-1H-indole

Prepared according to the general procedure from 1,2-dimethyl-1H-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (2h, 1 mmol), Ru(bpy)₃(PF₆)₂ (0.02 mmol) and CH₃CN (2.5 mL) under visible light irradiation 48 hours to provide the title compound as a white solid (46% yield). M.p.: 96-97 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.19-7.24 (m, 1H), 7.10-7.14 (m, 1H), 7.02 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 2.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 157.8, 142.6, 137.3, 130.6, 130.0, 128.0, 121.9, 120.6, 119.2, 114.7, 109.2, 100.0, 55.6, 30.5, 11.1. IR (film, cm⁻¹): ν 1650, 1630, 1491, 1466. HRMS (ESI): Calcd for C₁₇H₁₇NSO [M+H]^+: m/z 284.1109; found: 284.1105.

1-Benzyl-3-((4-methoxyphenyl)thio)-1H-indole

Prepared according to the general procedure from 1-benzyl-1H-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (2h, 1 mmol), Ru(bpy)₃(PF₆)₂ (0.02 mmol) and CH₃CN (2.5 mL) under visible light irradiation 24 hours to provide the title compound as a white solid (44% yield). M.p.: 99-100 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.63 (d, J = 7.8 Hz, 1H), 7.36 (s, 1H), 7.27-7.31 (m, 4H), 7.18-7.21 (m, 1H), 7.11-7.15 (m, 5H), 6.73 (d, J = 8.8 Hz, 2H), 5.31 (s, 2H), 3.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 157.8, 137.2, 136.7, 133.9, 130.0, 129.8, 128.9, 128.5, 127.9, 127.0, 122.7, 120.6, 119.9, 114.5, 110.2, 103.3, 55.4, 50.4. IR (film, cm⁻¹): ν 1589, 1488, 1450. HRMS (ESI): Calcd for C₂₂H₁₉NSO [M+H]^+: m/z 346.1266; found: 346.1258.
3-(p-Tolylthio)-1H-indole

Prepared according to the general procedure from 1H-indole (4 mmol), 4-methylbenzene-1-sulfonyl chloride (2a, 1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mmol) and CH$_3$CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (33% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.35 (s, 1H), 7.61 (d, $J$ = 7.9 Hz, 1H), 7.47 (d, $J$ = 2.3 Hz, 1H), 7.43 (d, $J$ = 8.2 Hz, 1H), 7.26 (t, $J$ = 7.6 Hz, 1H), 7.15 (t, $J$ = 7.5 Hz, 1H), 7.03 (d, $J$ = 8.0 Hz, 2H), 6.97 (d, $J$ = 8.0 Hz, 2H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 136.7, 135.7, 134.8, 130.6, 129.7, 129.3, 126.5, 123.1, 121.0, 119.9, 111.7, 21.0. The spectroscopic data are in accordance with those reported.$^6$
6. Controlled experiments for the mechanistic investigation

A. Synthesis of 1-methyl-3-tosyl-1H-indole and its reaction under reaction photocatalysis condition

To a solution of 1-methyl-3-(p-tolylthio)-1H-indole (3a, 1 mmol) in dry CH₂Cl₂ (25 ml) at 0 °C, 10 ml CH₂Cl₂ solution of m-CPBA (3 mmol) was added dropwise. After 10 mins, the solution warmed to r.t. and its color got darker with time. When 3a was consumed indicated by TLC, the reaction mixture was washed by Na₂SO₃, NaHCO₃ and brine successively, and dried over anhydrous MgSO₄. The residue was available by concentrated under vacuum, which was purified by Column chromatography on silica gel giving desired compound in 80 % yield. ¹H NMR (400 MHz, CDCl₃): δ 7.88-7.93 (m, 3H), 7.72 (s, 1H), 7.20-7.29 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 143.4, 140.9, 137.5, 133.7, 129.8, 126.9, 124.4, 123.7, 122.5, 120.0, 115.6, 110.5, 33.7, 21.6. MS [M⁺]: m/z 285. The spectroscopic data are in accordance with those reported.⁷

![Reaction Scheme](image)

A 25 ml Schlenk tube equipped with stir-bar was charged with 1-methyl-3-tosyl-1H-indole (0.3 mmol), photocatalyst Ru(bpy)₃(PF₆)₂ (2% mol). The system was evacuated 3 times and backfilled with Ar before solvent 2.5 ml CH₃CN were added by springe. Then the vial was evacuated 3 times and backfilled with Ar again at -78 °C and warmed to 40 °C. After 24 hours under 23 w fluorescent light, TLC indicated no new product generated.

![Reaction Scheme](image)

At the same time, a 25 ml Schlenk tube equipped with stir-bar was charged with 1-methyl-3-tosyl-1H-indole (0.3 mmol), photocatalyst Ru(bpy)₃(PF₆)₂ (2% mol). The system
was evacuated 3 times and backfilled with Ar before solvent 2.5 ml CH₃CN and
\(N\)-methylinldole were added by springe. Then the vial was evacuated 3 times and backfilled
with Ar again at -78 °C and slowly warmed to 40 °C. After 24 hours under 23 w fluorescent
light, TLC indicated no new product generated.

\[ \text{Ru(bpy)}_3(\text{PF}_6)_2 \rightarrow \text{no reaction} \]

**B. The reaction of 4-methylbenzene-1-sulfinic chloride with \(N\)-methylinldole**

According to literature, to the 9 ml aqueous solution of NaOH (3.6 g), 35 ml aqueous solution
of Na₂SO₃ (6.8 g) was added. The \(p\)-toluene sulfonyl chloride (7.65 g) was added to the above
mixed solution portionwise. Then the reaction system was stirred for 3 hours at 70 °C. The
precipitated sodium salt of 4-methyl-benseneulfonic acid after placed in the fridge was
filtered cold, dissolved in water, and hydrolyzed with concentrated hydrochloric acid. The
precipitation was filtered and washed by cold water. \(^1\)H NMR (CDCl₃): \(\delta \) 2.40 (s, 3H), 7.29 (d,
\(J = 8.0\) Hz, 2H), 7.58 (d, \(J = 8.0\) Hz, 2H), 9.35-9.45 (m, 1H). The spectroscopic data are in
accordance with those reported.⁸

\[
\text{Na}_2\text{SO}_3 + \text{NaOH} + \text{SO}_2\text{Cl}_2 \rightarrow \text{HCl} \rightarrow \text{S-OH} \\
1. 70^\circ \text{C, water} \rightarrow \text{HCl} \\
2. \text{HCl} \rightarrow \text{S-OH}
\]

To the solution of 0.8 ml thionyl chloride in 50 ml dry ether, 1 g 4-methyl-benzensulfinic
acid was added portionwise under Ar atmosphere. The reaction mixture was stirred for 3
hours at room, and then excess of thionyl chloride was removed by rotavapor. The obtained
residue was dissolved in 50 ml x 3 hexane and concentrated on rotavapor. No further
purification was done and the obtained product was used under standard photocatalysis
reaction condition. A 25 ml Schlenk tube equipped with stir-bar was charged with
photocatalyst Ru(bpy)₃(PF₆)₂ (18 mg, 0.02 mmol). The system was evacuated 3 times and
backfilled with Ar before 2.5 ml CH₃CN, \(p\)-toluene sulfonyl chloride (1mmol) and
\(N\)-methylinldole were added by springe. Then the vial was evacuated 3 times and backfilled
with Ar again at -78 °C and warmed to 40 °C. After 12 hours under 23 w fluorescent light, the
reaction mixture was diluted with CH$_2$Cl$_2$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product in 63% yield.

C. GC-MS

The reaction of 1a with 2a under standard condition was carried out, and the residue of reaction mixture under vacuum was analyzed by GC-MS. (S-1) After the desired product obtained by column chromatography, the remained fraction eluted by ethyl acetate was also analyzed by GC-MS. (S-2) We found that besides of the desired product, byproduct $m/z$ 287, $m/z$ 294, and $m/z$ 382 were detected. With the $^1$H NMR of byproduct $m/z$ 294, we deduced it may be addition product of N-methylindole. Moreover, it was hard to purify the product of byproduct $m/z$ 382, for it became symmetrical trimers when recrystallized. In S-3, we tried to explain the reaction routines.
The routine D was referred to the similar example: A. Berlin et al. *Tetrahedron*, 1996, 52, 7947-7960.
7. **References**

8. Copies of $^1$H, $^{13}$C NMR spectra and HRMS spectra

1,2-Dimethyl-$^1$H-indole
1,5-Dimethyl-1H-indole

![NMR Spectrum of 1,5-Dimethyl-1H-indole](image)

**NMR Spectra:**
- **1H NMR:**
  - Peak at 2.8 ppm: 1H (4.22 Hz, 1H, CH2)
  - Peak at 3.6 ppm: 1H (4.22 Hz, 1H, CH2)
  - Peak at 7.5 ppm: 1H (1H, CH)

**Assignments:**
- CH2 at 2.8 ppm: 1H (4.22 Hz, 1H, CH2)
- CH2 at 3.6 ppm: 1H (4.22 Hz, 1H, CH2)
- CH at 7.5 ppm: 1H (1H, CH)

**References:**
- Bruker NMR instrument details
- Experimental conditions: 500 MHz, DMSO-d6

**Supplementary Material:**
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012
5-Fluoro-1-methyl-1H-indole
5-Methoxy-1-methyl-1H-indole
6-Fluoro-1-methyl-1H-indole

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012
**tert-Butyl 1H-indole-1-carboxylate**
1-Benzyl-1H-indole
1-Methyl-3-(p-tolylthio)-1H-indole (3a)
1-Methyl-3-(p-tolylthio)-1H-indole (3a)

Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

<table>
<thead>
<tr>
<th>Minimum:</th>
<th>Maximum:</th>
<th>RA</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>Score</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>255.0979</td>
<td>253.0928</td>
<td>253.0925</td>
<td>0.3</td>
<td>1.1</td>
<td>10.0</td>
<td>1</td>
<td>C16 H15 N S</td>
<td></td>
</tr>
</tbody>
</table>
1-Methyl-3-(o-tolylthio)-1H-indole (3b)
1-Methyl-3-(o-tolylthio)-1H-indole (3b)
1-Methyl-3-(m-tolylthio)-1H-indole (3c)
1-Methyl-3-\((m\)-tolylthio\)-1\(H\)-indole (3c)
1-Methyl-3-(phenylthio)-1H-indole (3d)
3-((4-Fluorophenyl)thio)-1-methyl-1H-indole (3e)
3-((4-Fluorophenyl)thio)-1-methyl-1H-indole (3e)
3-((4-Chlorophenyl)thio)-1-methyl-1H-indole (3f)
3-((4-Chlorophenyl)thio)-1-methyl-1H-indole (3f)
3-((4-bromophenyl)thio)-1-methyl-1H-indole (3g)
3-((4-bromophenyl)thio)-1-methyl-1H-indole (3g)
3-((4-Methoxyphenyl)thio)-1-methyl-1H-indole (3h)
1-Methyl-3-(naphthalen-1-ylthio)-1H-indole (3i)
1-Methyl-3-(naphthalen-1-ylthio)-1H-indole (3i)
1-Methyl-3-(thiophen-2-ylthio)-1H-indole (3j)
1-Methyl-3-(thiophen-2-ylthio)-1H-indole (3j)
5-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1H-indole (4a)
5-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1H-indole (4a)
3-((4-Methoxyphenyl)thio)-1,5-dimethyl-1H-indole (4b)
3-((4-Methoxyphenyl)thio)-1,5-dimethyl-1H-indole (4b)
5-Methoxy-3-((4-methoxyphenyl)thio)-1-methyl-1H-indole (4c)
5-Methoxy-3-((4-methoxyphenyl)thio)-1-methyl-1H-indole (4c)
6-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1H-indole (4d)
6-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1H-indole (4d)
3-((4-Methoxyphenyl)thio)-1,2-dimethyl-1H-indole (4e)
3-((4-Methoxyphenyl)thio)-1,2-dimethyl-1H-indole (4e)
1-Benzyl-3-((4-methoxyphenyl)thio)-1H-indole (4f)
1-Benzyl-3-((4-methoxyphenyl)thio)-1H-indole (4f)
3-(p-Tolylthio)-1H-indole (4g)
1-Methyl-3-tosyl-1H-indole
4-Methylbenzene-1-sulfinic chloride
MS spectrum of