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Supporting Information

Visible-light-induced and iron-catalyzed methylation of N-arylacrylamides with dimethyl sulfoxide: A convenient access to 3-ethyl-3-methyl oxindoles

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1. General considerations

All $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as $\delta$ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, $J$, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

$N$-Arylacrylamides were prepared according to the reported methods. The chemicals and solvents were purchased from commercial suppliers either from Aldrich (USA) or Shanghai Chemical Company (China) without further purification. All the solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO$_2$.

2. The control experiments

2.1 Free radical-trapping experiment

\[ \text{FeSO}_4 \cdot 7\text{H}_2\text{O} (15 \text{ mol } \%), \text{H}_2\text{O}_2 (3 \text{ equiv}), \text{TEMPO (2.0 equiv)}, \text{3 W White LED, rt, 2 h.} \]

$N$-Arylacrylamide (1a, 0.20 mmol), DMSO (2, 1.0 mL), FeSO$_4$·7H$_2$O (0.03 mmol), H$_2$O$_2$ (0.60 mmol) and 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 0.40 mmol), were added in an oven-dried reaction vessel equipped with magnetic stirring bar. Then the reaction vessel was irradiated using 3 W White LED under air atmosphere at room temperature for 2 h. After the reaction was stopped, no desired product 3a was detected by TLC and HPLC-HRMS, indicating that the reaction was completely inhibited. Meanwhile, a methyl radical (Me·) trapping product 4 was observed through HPLC-HRMS analysis of the reaction solution, which was shown in Figure S1.
2.2 Free radical-trapping experiment

N-Arylacrylamide (1a, 0.20 mmol), DMSO (2, 1.0 mL), FeSO\(_4\)-7H\(_2\)O (0.03 mmol), H\(_2\)O\(_2\) (0.60 mmol), were added in an oven-dried reaction vessel equipped with magnetic stirring bar. The reaction vessel was irradiated using 3 W White LED for 20 minutes, then 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 0.40 mmol) was added, under air atmosphere at room temperature the reaction continues for 1 h. After the reaction was stopped, the desired product 3a was obtained in 18% yields. Meanwhile, a radical trapping product 5 was observed through HPLC-HRMS analysis of the reaction solution, which was shown in Figure S2.

Figure S1 HRMS analysis of TEMPO with a methyl radical (Me·) trapping product 4

Figure S2 HRMS analysis of TEMPO with a methyl radical trapping product 5
2.3 The isotopic labeling experiments

\[
\begin{align*}
\text{N-Arylacrylamide} & \quad (1a, 0.20 \text{ mmol}) \quad \text{DMSO-}d_6 \quad (1.0 \text{ mL}) \quad \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \quad (0.03 \text{ mmol}) \quad \text{and} \quad \text{H}_2\text{O}_2 \quad (0.60 \text{ mmol}) \\
\end{align*}
\]

was added to an oven-dried reaction vessel equipped with magnetic stirring bar. Then the reaction vessel was irradiated using 3 W White LED under air atmosphere at room temperature for 2 h. After the reaction was completed, the reaction solution was extracted with EtOAc (2×5.0 mL). The organic layers were combined, dried over Na$_2$SO$_4$, and concentrated under reduced pressure to yield crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give the product $d_6$-3a as a colorless liquid in 76% yield. The $^1$H NMR analysis of $d_6$-3a was shown in Figure S3.

**Figure S3** $^1$H NMR analysis of 3a and $d_6$-3a
3. $^1$H and $^{13}$C NMR spectra of the products
4. References