Supporting Information

Photocatalyst-free hypervalent iodine reagent catalyzed
decarboxylative acylarylation of acrylamides with α-oxocarboxylic
acids driven by visible-light irradiation

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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 a Waters Micromass GCT instrument. High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

$\alpha$-Oxocarboxylic acids and acrylamides are prepared according to reported methods (J. Du, X. Zhang, L. Wang, Chem. Commun. 2015, 51, 4372–4375; A. J.-L. Ayitou, J. Sivaguru, Chem. Commun. 2011, 47, 2568–2570), and which must be recrystallized from ethanol/ethyl acetate before use. The chemicals and solvents were purchased from commercial suppliers either Aldrich (USA), or Shanghai Chemical Company (P. R. China). All the solvents were dried and freshly distilled in $N_2$ prior to use. Products were purified by flash chromatography on 200–300 mesh silica gels, $SiO_2$.

2. Typical procedure for the decarboxylative acylarylation of acrylamides with $\alpha$-oxocarboxylic acids

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with $N$-methyl-$N$-phenylmethacrylamide ($1a$, 35.0 mg, 0.20 mmol), 2-oxo-2-phenylacetic acid ($2a$, 45.0 mg, 0.30 mmol), BI-OAc (12.3 mg, 0.04 mmol), and PhCl (1.0 mL). The reaction vessel was exposed to blue LED (450–455 nm, 1.5 W) irradiation at room temperature in air with stirring for 12 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 3:1 to 15:1) to give the desired product $3a$ (43.5 mg, 78% yield).
3. Optimization of light source and solvent

Table S1. Screen of light source and solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>Light source</th>
<th>Solvent</th>
<th>Yield(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>blue LED (450–455 nm, 1.5 W)</td>
<td>PhCl</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>sunlight</td>
<td>PhCl</td>
<td>69</td>
</tr>
<tr>
<td>3</td>
<td>green LED (530–535 nm, 1.5 W)</td>
<td>PhCl</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>purple LED (400–405 nm, 1.5 W)</td>
<td>PhCl</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>red LED (695–700 nm, 1.5 W)</td>
<td>PhCl</td>
<td>Trace</td>
</tr>
<tr>
<td>6</td>
<td>white LED (8 W)</td>
<td>PhCl</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>UV (226 nm)</td>
<td>PhCl</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>blue LED (450–455 nm, 1.5 W)</td>
<td>PhBr</td>
<td>51</td>
</tr>
<tr>
<td>9</td>
<td>blue LED (450–455 nm, 1.5 W)</td>
<td>benzene</td>
<td>47</td>
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<td>10</td>
<td>blue LED (450–455 nm, 1.5 W)</td>
<td>DCE</td>
<td>50</td>
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<td>11</td>
<td>blue LED (450–455 nm, 1.5 W)</td>
<td>DCM</td>
<td>62</td>
</tr>
<tr>
<td>12</td>
<td>blue LED (450–455 nm, 1.5 W)</td>
<td>toluene</td>
<td>26</td>
</tr>
<tr>
<td>13</td>
<td>blue LED (450–455 nm, 1.5 W)</td>
<td>DMSO</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>blue LED (450–455 nm, 1.5 W)</td>
<td>CH(_3)CN</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: \(N\)-methyl-\(N\)-phenyl-methacrylamide (1a, 0.20 mmol), 2-oxo-2-phenylacetic acid (2a, 0.30 mmol), HIR (20 mol\%), solvent (1.0 mL) at room temperature under light irradiation in air for 12 h. \(^b\)Isolated yield.

4. Preliminary mechanistic study

(1) Free radical-trapping experiments

\[
\text{Ph} \quad \text{O} \quad \text{OH} + \text{O} \quad \text{N} \quad \text{TEMPO} \quad \xrightarrow{\text{BI-OAc, blue LED, PhCl, r.t., 12 h}} \text{Ph} \quad \text{O} \quad \text{N}
\]

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-oxo-2-phenylacetic acid (2a, 45.0 mg, 0.30 mmol), BI-OAc (12.3 mg, 0.04 mmol), TEMPO
(93.75 mg, 0.60 mmol) and PhCl (1.0 mL). The reaction vessel was exposed to blue LED (450–455 nm, 1.5 W) irradiation in air at room temperature with stirring for 12 h. After that, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 3:1 to 15:1) to give the trapping product 4 in 70% yield (54.8 mg). The following figure is the HRMS analysis of reaction mixture (Figure S1).

**Figure S1.** Analysis of reaction mixture by HRMS

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-oxo-2-phenylacetic acid (**2a**, 225 mg, 1.5 mmol), BHT (2,6-di-tert-butyl-4-methylphenol, 661.1 mg, 3.0 mmol), BI-OAc (61.2 mg, 0.20 mmol) and PhCl (4.0 mL). The reaction vessel was exposed to blue LED (450–455 nm) irradiation in air at room temperature with stirring for 12 h. After that, the mixture was concentrated to yield the crude product, which was further
purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 15:1 to 30:1) to give the trapping product 5 (K. Sun, X. Wang, G. Li, Z. Zhu, Y. Jiang, B. Xiao, Chem. Commun., 2014, 50, 12880–12883) in 31% isolated yield (150.7 mg) and 6 (A. M. Nicholas, P. Bozo, J. Am. Chem. Soc., 1968, 90, 4450–4453; M. Ochiai, A. Nakanishi, T. Ito, J. Org. Chem., 1997, 62, 4253–4259), which was identified by the HRMS analysis of reaction mixture (Figure S2).

**Figure S2.** HRMS analysis of reaction mixture

(2) Determination of the resulting CO₂ gas by FT-IR

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with N-methyl-N-phenyl-methacrylamide (1a, 35.0 mg, 0.20 mmol), 2-oxo-2-phenylacetic acid (2a, 45.0 mg, 0.30 mmol), BI-OAc (12.3 mg, 0.04 mmol), and PhCl (1.0 mL) under nitrogen atmosphere. The reaction vessel was exposed to blue LED (450–455 nm) irradiation at room temperature with stirring for 12 h. After completion of the reaction, the resulting gas from the
reaction mixture was directly determined by FT-IR analysis (Figure S3), and the concentration of CO₂ was found to be 1380.27 ppm.

![Figure S3. FT-IR analysis of the resulting gas by a Bruker Tensor 27 FT-IR](image)

(3) Typical procedure for the synthesis of 2a and the reaction of 2a with 1a

\[
\begin{align*}
\text{PhCOOH} + \text{BI-OAc} & \xrightarrow{\text{CHCl}_3, N_2 \text{ reflux}} \text{A, quantitative} \\
\text{1a} + \text{A} & \xrightarrow{\text{blue LED, PhCl}, \text{ r.t., 12 h}} \text{3a, 73%}
\end{align*}
\]

Under nitrogen atmosphere, a 25 mL oven-dried round bottomed flask equipped with a magnetic stirrer bar was charged with dry 2-oxo-2-phenylacetic acid (2a, 480.4 mg, 3.2 mmol), BI-OAc (917.8 mg, 3.0 mmol, for the preparation of BI-OAc, see: M. V. Vita, Waser, J. Org.
Lett., 2013, 15, 3246–3249) and anhydrous chloroform (3.0 mL). The mixture was refluxed for 30 min, and next the solvent was removed under vacuum to obtain a viscous fluid. Then the obtained viscous fluid was diluted with dry petroleum (5.0 mL) and cooled in −20 °C until white solid precipitated at the bottom of flask. The formed solid was filtrated and washed with cold, anhydrous CH$_3$CN, dried under vacuum and kept in dark, affording pure A in quantitative yield. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 8.01 (d, $J = 7.6$ Hz, 1H), 7.97–7.92 (m, 3H), 7.84 (m, $J = 8.4$ Hz, 1H), 7.76 (t, $J = 7.6$ Hz, 1H), 7.69 (t, $J = 7.6$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 189.17, 168.15, 166.55, 135.58, 134.91, 132.35, 132.00, 131.55, 130.82, 129.89, 129.74, 126.74, 120.87.

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 1a (35.0 mg, 0.20 mmol), A (79.2 mg, 0.20 mmol) and PhCl (1.0 mL). The reaction vessel was exposed to blue LED (450–455 nm, 1.5 W) irradiation in air at room temperature with stirring for 12 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 3:1 to 15:1) to give the desired product 3a in 73% yield (40.8 mg).

(4) Determination of the resulting H$_2$ gas by GC

A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with $N$-methyl-$N$-phenyl-methacrylamide (1a, 175.1 mg, 1.0 mmol), 2-oxo-2-phenylacetic acid (2a, 225.2 mg, 1.5 mmol), BI-OAc (61.2 mg, 0.20 mmol), and PhCl (3.0 mL) under vacuum. The reaction vessel was exposed to blue LED (450–455 nm, 1.5 W) irradiation at room temperature with stirring for 12 h.

During the reaction, the resulting gas from the reaction mixture was directly determined
by GC analysis (Figure S4).

**Figure S4.** Determination of the resulting $\text{H}_2$ gas by GC
5. Characterization data for the products

3a:\textsuperscript{[1]}\textsuperscript{[1]} H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.84 (d, \(J = 7.6\) Hz, 2H), 7.52 (t, \(J = 7.2\) Hz, 1H) 7.40 (t, \(J = 7.6\) Hz, 2H), 7.28–7.25 (m, 1H), 7.15 (d, \(J = 7.2\) Hz, 1H), 6.99 (t, \(J = 7.6\) Hz, 1H), 6.91 (d, \(J = 7.6\) Hz, 1H), 3.75–3.64 (m, 2H), 3.32 (s, 3H), 1.46 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 196.01, 180.46, 143.75, 136.31, 133.62, 133.02, 128.36, 127.84, 127.73, 122.04, 121.67, 108.03, 45.92, 45.20, 26.33, 24.79.

3b:\textsuperscript{[1]}\textsuperscript{[1]} H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.86 (d, \(J = 7.6\) Hz, 2H), 7.53 (t, \(J = 7.2\) Hz, 1H), 7.41 (t, \(J = 7.6\) Hz, 2H), 7.06 (d, \(J = 8.0\) Hz, 1H), 6.96 (s, 1H), 6.80 (d, \(J = 8.0\) Hz, 1H), 3.74–3.64 (m, 2H), 3.30 (s, 3H), 2.28 (s, 3H), 1.44 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 196.10, 180.52, 141.47, 136.40, 133.77, 133.13, 131.57, 128.47, 128.07, 128.00, 122.71, 107.86, 46.03, 45.32, 26.48, 25.02, 21.13.

3c:\textsuperscript{[1]}\textsuperscript{[1]} H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.84 (d, \(J = 7.6\) Hz, 2H), 7.51 (t, \(J = 7.2\) Hz, 1H), 7.39 (t, \(J = 7.6\) Hz, 2H), 6.82–6.76 (m, 3H), 3.73 (s, 3H), 3.68–3.67 (m, 2H), 3.29 (s, 3H), 1.44 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 196.07, 180.22, 155.75, 137.45, 136.36, 135.20, 133.17, 128.49, 127.97, 111.47, 109.95, 108.30, 55.70, 45.99, 45.70, 26.54, 24.97.
3d: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.85 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 6.81–6.75 (m, 3H), 3.97–3.92 (m, 2H), 3.72–3.62 (m, 2H), 3.29 (s, 3H), 1.43 (s, 3H), 1.36 (t, J = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 196.05, 180.25, 155.05, 137.36, 136.34, 135.15, 133.17, 128.48, 127.97, 112.10, 110.55, 108.29, 63.96, 46.00, 45.67, 26.54, 24.98, 14.88. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{20}$H$_{22}$NO$_3$: 324.1600, Found: 324.1604.

3e:$^{[1]}$H NMR (400 MHz, CDCl$_3$) δ: 7.85 (d, J = 7.6 Hz, 2H), 7.56–7.52 (m, 1H), 7.42 (t, J = 7.6 Hz, 2H), 6.98–6.90 (m, 2H), 6.84–6.81 (m, 1H), 3.69 (s, 2H), 3.31 (s, 3H), 1.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 195.92, 180.23, 159.13 (d, J = 238.5 Hz), 139.81 (d, J = 2.0 Hz), 136.16, 135.46 (d, J = 7.8 Hz), 133.34, 128.56, 127.96, 113.84 (d, J = 23.2 Hz), 110.16 (d, J = 24.7 Hz), 108.51 (d, J = 8.2 Hz), 45.97, 45.72 (d, J = 1.8 Hz), 26.61, 24.80.

3f:$^{[1]}$H NMR (400 MHz, CDCl$_3$) δ: 7.86 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 8.4 Hz, 1H), 7.11 (s, 1H), 6.84 (d, J = 8.4 Hz, 1H), 3.71 (s, 2H), 3.32 (s, 3H), 1.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 195.82, 180.11, 142.52, 136.05, 135.57, 133.39, 128.58, 127.98, 127.72, 127.46, 122.31, 109.06, 46.07, 45.43, 26.59, 24.86.
$3g$: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.86 (d, $J = 7.6$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.44–7.38 (m, 3H), 7.24 (s, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 3.70 (s, 2H), 3.31 (s, 3H), 1.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 195.79, 179.99, 143.03, 136.04, 135.97, 133.39, 130.63, 128.58, 127.98, 125.00, 114.78, 109.60, 46.10, 45.38, 26.57, 24.89.

$3h$: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.85 (d, $J = 7.6$ Hz, 2H), 7.58–7.52 (m, 2H), 7.43–7.40 (m, 3H), 6.70 (d, $J = 8.0$ Hz, 1H), 3.70 (s, 2H), 3.30 (s, 3H), 1.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 195.80, 179.83, 143.72, 136.64, 136.35, 136.02, 133.40, 130.47, 128.58, 128.00, 110.26, 84.68, 46.12, 45.19, 26.53, 24.93.

$3i$: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.84 (d, $J = 7.6$ Hz, 2H), 7.52 (t, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 6.97 (t, $J = 7.2$ Hz, 2H), 6.86 (t, $J = 7.2$ Hz, 1H), 3.74–3.64 (m, 2H), 3.60 (s, 3H), 2.63 (s, 3H), 1.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 196.19, 181.38, 141.62, 136.43, 134.39, 133.11, 131.60, 128.46, 127.96, 122.06, 119.73, 119.51, 46.34, 44.65, 29.83, 25.50, 19.13.
3j: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.87 (d, $J = 8.0$ Hz, 2H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.44–7.41 (m, 7H), 7.15–7.09 (m, 2H), 7.00 (t, $J = 7.2$ Hz, 1H), 3.80–3.69 (m, 2H), 2.85 (s, 3H), 1.51 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 196.19, 181.73, 140.85, 139.23, 136.45, 134.82, 133.16, 130.85, 128.50, 127.99, 127.51, 125.49, 121.50, 120.71, 46.49, 44.67, 30.55, 25.45. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{24}$H$_{22}$NO$_2$: 356.1651, Found: 356.1654.

3k+3k’ (3 : 2):$^{[2]}$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.86–7.81 (m, 3.31H), 7.52 (t, $J = 7.6$ Hz, 1.76H), 7.40 (t, $J = 7.6$ Hz, 3.45H), 7.16 (t, $J = 7.6$ Hz, 1.09H), 7.03 (d, $J = 7.2$ Hz, 0.62H), 6.80 (d, $J = 7.2$ Hz, 0.69H), 6.75 (d, $J = 7.6$ Hz, 2.58H), 4.00–3.95 (m, 1.00H), 3.73–3.62 (m, 2.47H), 3.31 (s, 1.95H), 3.28 (s, 3.10H), 2.38 (s, 2.01H), 2.31 (s, 3.04H), 1.50 (s, 3.00H), 1.44 (s, 2.02H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 196.33, 196.24, 180.91, 180.47, 144.09, 143.89, 137.85, 136.41, 136.21, 133.15, 133.13, 132.77, 130.79, 130.40, 128.49, 128.48, 127.98, 127.94, 127.66, 124.78, 122.65, 121.53, 109.20, 106.00, 46.12. 46.02, 45.09, 45.01, 26.52, 26.43, 25.01, 22.90, 21.83, 18.25.
3l: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.85 (d, $J = 8.0$ Hz, 2H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 6.99–6.92 (m, 2H), 3.95–3.79 (m, 2H), 3.76–3.65 (m, 2H), 1.45 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 196.00, 180.16, 142.88, 136.44, 134.01, 133.11, 128.47, 127.98, 127.75, 121.94, 108.33, 45.96, 45.28, 34.76, 25.06, 12.38.

3m: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.90 (d, $J = 7.6$ Hz, 2H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.45–7.42 (m, 4H), 7.35–7.33 (m, 2H), 7.16–7.13 (m, 2H), 6.97 (t, $J = 7.2$ Hz, 1H), 6.72 (d, $J = 8.0$ Hz, 1H), 5.08–4.95 (m, 2H), 3.84–3.74 (m, 2H), 1.51 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 195.88, 180.62, 142.63, 136.26, 134.81, 133.79, 133.29, 133.23, 128.90, 128.78, 128.55, 128.04, 127.75, 122.39, 121.69, 109.14, 45.90, 45.35, 43.36, 25.67. HRMS (ESI) ([M+H]$^+$) Calcd. For C$_{24}$H$_{21}$ClNO$_2$: 390.1261, Found: 390.1259.

3n: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.90 (d, $J = 7.6$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.33 (d, $J = 7.6$ Hz, 2H), 7.18–7.11 (m, 4H), 6.94 (t, $J = 7.2$ Hz, 1H), 6.77 (d,
$J = 7.6$ Hz, 1H), 5.09–4.92 (m, 2H), 3.81–3.71 (m, 2H), 2.34 (s, 3H), 1.51 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 195.93, 180.59, 142.94, 137.02, 136.39, 133.78, 133.22, 133.19, 129.40, 128.51, 128.04, 127.70, 127.29, 122.15, 121.69, 109.33, 45.81, 45.39, 43.74, 25.49, 21.13. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{25}$H$_{24}$NO$_2$: 370.1807, Found: 370.1808.

3o: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.91 (d, $J = 7.6$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.30–7.25 (m, 3H), 7.17–7.10 (m, 3H), 6.96 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 7.6$ Hz, 1H), 5.09–4.95 (m, 2H), 3.84–3.73 (m, 2H), 2.37 (s, 3H), 1.53 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 195.86, 180.64, 143.00, 138.39, 136.40, 136.21, 133.81, 133.20, 128.57, 128.53, 128.18, 128.05, 128.03, 127.73, 124.31, 122.18, 121.67, 109.34, 45.84, 45.40, 43.95, 25.56, 21.48. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{25}$H$_{24}$NO$_2$: 370.1807, Found: 370.1809.

3p: $^{[1]}$H NMR (400 MHz, CDCl$_3$) δ: 7.75 (d, $J = 7.6$ Hz, 2H), 7.26–7.19 (m, 3H), 7.14 (d, $J = 7.2$ Hz, 1H), 6.98 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 3.74–3.61 (m, 2H), 3.33 (s, 3H) 2.38 (s, 3H) 1.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 195.60, 180.58, 143.86, 143.75, 133.81, 133.73, 129.05, 127.98, 127.69, 122.01, 121.63, 108.02, 45.79, 45.19, 26.35, 24.82, 21.51.
**3q**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.78 (d, $J = 8.0$ Hz, 2H), 7.27–7.21 (m, 3H), 7.14 (d, $J = 7.2$ Hz, 1H), 6.98 (t, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 3.75–3.62 (m, 2H), 3.33 (s, 3H), 2.67 (q, $J = 7.6$ Hz, 2H), 1.45 (s, 3H), 1.23 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 195.63, 180.58, 150.02, 143.75, 134.04, 133.73, 128.09, 127.87, 127.69, 122.01, 121.64, 108.02, 45.82, 45.19, 28.79, 26.35, 24.83, 15.04. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{20}$H$_{22}$NO$_2$: 308.1651, Found: 308.1658.

**3r**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.83 (d, $J = 8.4$ Hz, 2H), 7.27–7.24 (m, 1H), 7.14 (d, $J = 7.2$ Hz, 1H), 6.98 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 2H), 3.84 (s, 3H), 3.71–3.59 (m, 2H), 3.32 (s, 3H), 1.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 194.47, 180.62, 163.39, 143.73, 133.80, 130.15, 129.42, 127.66, 121.99, 121.64, 113.50, 108.01, 55.33, 45.56, 45.23, 26.34, 24.84.

**3s**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.89–7.85 (m, 2H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.14 (d, $J = 7.2$ Hz, 1H), 7.07 (t, $J = 8.4$ Hz, 2H), 6.99 (t, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 3.71–3.61 (m, 2H), 3.32 (s, 3H), 1.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 194.53, 180.48, 165.75 (d, $J = 253.5$ Hz), 143.83, 133.62, 132.81 (d, $J = 3.0$ Hz), 130.63 (d, $J = 9.3$ Hz),
127.91, 122.19, 121.73, 115.60 (d, $J = 21.7$ Hz), 108.19, 45.92, 45.29, 26.46, 24.94.

**3t:** [2] $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.77 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H) 7.28–7.24 (m, 1H), 7.14 (d, $J = 7.2$ Hz, 1H). 6.99 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 3.70–3.60 (m, 2H), 3.31 (s, 3H), 1.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 194.82, 180.31, 143.71, 139.55, 134.54, 133.42, 129.28, 128.71, 127.84, 122.11, 121.63, 108.10, 45.82, 45.14, 26.35, 24.80.

**3u:** [1] $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.70 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.14 (d, $J = 7.2$ Hz, 1H). 6.99 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 3.69–3.59 (m, 2H), 3.31 (s, 3H), 1.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 195.02, 180.28, 143.70, 134.93, 133.39, 131.70, 129.37, 128.28, 127.84, 122.11, 121.62, 108.10, 45.82, 45.14, 26.35, 24.80.

**3v:** [1] $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.75 (d, $J = 8.0$ Hz, 2H), 7.27–7.24 (m, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 7.2$ Hz, 1H). 6.98 (t, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 3.74–3.61 (m, 2H), 3.32 (s, 3H), 2.38 (s, 3H), 1.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$:
**3w:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.51 (d, $J = 7.6$ Hz, 1H), 7.33–7.16 (m, 4H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.2$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 3.65–3.51 (m, 2H), 3.22 (s, 3H), 2.11 (s, 3H), 1.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 200.54, 180.22, 143.70, 137.67, 137.47, 133.26, 131.47, 131.01, 128.08, 127.81, 125.29, 122.09, 121.94, 108.06, 49.01, 45.67, 26.26, 24.77, 20.40.

**3x:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.47 (dd, $J = 8.4$ Hz, 1.2 Hz, 1H), 7.27–7.23 (m, 2H), 7.13 (d, $J = 7.2$ Hz, 1H), 6.97 (t, $J = 7.2$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 5.97 (s, 2H), 3.67–3.55 (m, 2H), 3.31 (s, 3H), 1.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 194.09, 180.64, 151.79, 148.07, 143.85, 133.84, 131.31, 127.79, 124.25, 122.11, 121.72, 108.12, 107.73, 107.71, 101.80, 45.72, 45.36, 26.43, 24.92. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{19}$H$_{18}$NO$_4$: 324.1236, Found: 324.1236.
$3y$: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.96–7.91 (m, 2H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.41–7.38 (m, 1H), 7.26–7.22 (m, 2H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 3.83–3.63 (m, 2H), 3.15 (s, 3H), 1.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 200.81, 180.25, 143.77, 135.61, 133.68, 133.22, 132.37, 129.72, 128.11, 127.97, 127.60, 127.16, 126.32, 125.48, 124.14, 122.30, 122.16, 108.24, 49.68, 46.01, 26.28, 24.81.

$3z$: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.41 (s, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.88–7.81 (m, 3H), 7.61–7.52 (m, 2H), 7.29–7.25 (m, 1H), 7.20 (d, $J = 7.2$ Hz, 1H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.92 (d, $J = 8.0$ Hz, 1H), 3.91–3.78 (m, 2H), 3.34 (s, 3H), 1.51 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 196.09, 180.65, 143.89, 135.57, 133.78, 133.76, 132.39, 129.70, 129.53, 128.50, 128.34, 127.87, 127.74, 126.78, 123.66, 122.20, 121.87, 108.17, 46.12, 45.44, 26.47, 24.93.

$3aa$: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.02 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 7.6$ Hz, 2H), 7.78
(s, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 3.83–3.71 (m, 2H), 3.36 (s, 3H), 1.45 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 195.84, 180.90, 166.50, 148.16, 136.04, 133.84, 133.31, 130.62, 128.52, 127.96, 124.37, 122.65, 107.60, 60.73, 46.27, 44.95, 26.65, 24.96, 14.36.

4: $^{[4]}$ $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.07 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 1.81–1.44 (m, 6H), 1.27 (s, 6H), 1.12 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 166.34, 132.85, 129.73, 129.54, 128.45, 60.38, 39.07, 31.97, 20.85, 17.01.

5: $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.05 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.07 (s, 2H), 5.14 (s, 1H), 4.22 (s, 2H), 1.43 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 198.32, 152.71, 136.94, 135.99, 132.97, 128.60, 128.56, 126.18, 124.97, 45.23, 34.30, 30.27. HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{22}$H$_{29}$O$_2$: 325.2168, Found: 325.2170.

6. References

7. $^1$H and $^{13}$C NMR spectra of the products

![NMR spectra](image-url)