Supporting Information for

Visible-Light-Driven Alkene Dicarboxylation with Formate and CO₂ Under Mild Conditions

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1. General information

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Solvents were generally dried over 4 Å molecular sieves. Unless otherwise indicated, all reactions were set up in glovebox in Schlenk tubes. Flash column chromatography was performed using silica gel 60 (200-300 mesh) or preparative thin layer chromatography. Reaction was monitored by thin layer chromatography (TLC) and was visualized by ultraviolet light (254 nm). Melting points were recorded using a SRS Melting Point thermometer. $^1$H and $^{13}$C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD spectrometer. Chemical shifts are reported parts per million (ppm) referenced to CDCl$_3$ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm), DMSO-$d_6$ (δ 2.50 ppm), CD$_3$OD (δ 3.31 ppm) for $^1$H NMR; CDCl$_3$ (δ 77.16 ppm), DMSO-$d_6$ (δ 40.00 ppm), CD$_3$OD (δ 49.00 ppm) for $^{13}$C NMR. Data for $^1$H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quarter; p = pentet; m = multiplet; br = broad), coupling constant (Hz), integration. Data for $^{13}$C NMR are reported in terms of chemical shift (δ, ppm). HRMS were obtained on SolariX 7.0T and Waters Micromass Q-Tof Premier mass spectrometer. CO$_2$ gas (Purity: 99.999%) was purchased from Air Liquide. The light source used for the photocatalyzed experiment was a 30 W blue LED strips, purchased from Xuzhou Ai Jia electronic technology Co. LTD. (China).
2. Optimization of the reaction conditions

An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with base (0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), photocatalyst (8.0 mg, 6.2 mol%), HAT (30 mol%), alkene (0.20 mmol, 1.0 equiv, if solid). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the alkene (0.2 mmol, if liquid) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO₂ for 10 times. Finally, the tube was placed under 30 W blue LEDs (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) and stirred for 24 h. Then, the mixture was quenched with H₂O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation and the yield of crude products was determined via ¹H NMR using CH₂Br₂ as internal standard.
Table S1. Screening of Basesa

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>2a [%]b</th>
<th>2aH [%]b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>11%</td>
<td>66%</td>
</tr>
<tr>
<td>2</td>
<td>CsF</td>
<td>23%</td>
<td>54%</td>
</tr>
<tr>
<td>3</td>
<td>Cs2CO3</td>
<td>40%</td>
<td>12%</td>
</tr>
<tr>
<td>4</td>
<td>KF</td>
<td>29%</td>
<td>36%</td>
</tr>
<tr>
<td>5</td>
<td>tBuOLi</td>
<td>42%</td>
<td>50%</td>
</tr>
<tr>
<td>6</td>
<td>CsOAc</td>
<td>38%</td>
<td>68%</td>
</tr>
<tr>
<td>7</td>
<td>NaOAc</td>
<td>44%</td>
<td>31%</td>
</tr>
<tr>
<td>8</td>
<td>KOAc</td>
<td>23%</td>
<td>34%</td>
</tr>
<tr>
<td>9</td>
<td>LiOAc</td>
<td>13%</td>
<td>40%</td>
</tr>
<tr>
<td>10</td>
<td>Na2CO3</td>
<td>24%</td>
<td>32%</td>
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<tr>
<td>11</td>
<td>K3PO4</td>
<td>44%</td>
<td>50%</td>
</tr>
<tr>
<td>12</td>
<td>KOH</td>
<td>27%</td>
<td>54%</td>
</tr>
<tr>
<td>13</td>
<td>Na3PO4</td>
<td>23%</td>
<td>52%</td>
</tr>
<tr>
<td>14</td>
<td>NaOCH3</td>
<td>23%</td>
<td>60%</td>
</tr>
<tr>
<td>15</td>
<td>DMAP</td>
<td>26%</td>
<td>34%</td>
</tr>
<tr>
<td>16</td>
<td>DBU</td>
<td>--</td>
<td>18%</td>
</tr>
<tr>
<td>17</td>
<td>Pyridine</td>
<td>8%</td>
<td>40%</td>
</tr>
<tr>
<td>18</td>
<td>1,10-phenanthroline</td>
<td>16%</td>
<td>18%</td>
</tr>
<tr>
<td>19a</td>
<td>Cs2CO3</td>
<td>59%</td>
<td>--</td>
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<tr>
<td>20d</td>
<td>K3PO4</td>
<td>64%</td>
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**Table S2. Screening of cooperative bases**

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<th>Entry</th>
<th>cooperative base</th>
<th>2a [%]</th>
<th>2aII [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>KPF₆</td>
<td>55%</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>KOPiv</td>
<td>31%</td>
<td>38%</td>
</tr>
<tr>
<td>3</td>
<td>KF</td>
<td>42%</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>K₃PO₄</td>
<td>91% (88%)</td>
<td>--</td>
</tr>
<tr>
<td>5c</td>
<td>K₂PO₄</td>
<td>74%</td>
<td>--</td>
</tr>
<tr>
<td>6d</td>
<td>K₃PO₄</td>
<td>65%</td>
<td>--</td>
</tr>
<tr>
<td>7e</td>
<td>K₃PO₄</td>
<td>71%</td>
<td>--</td>
</tr>
</tbody>
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*Reactions conditions: 1,1-diphenylethylene (0.2 mmol), 3DPAFIPN (6.2 mol%), DABCO (0.06 mmol), Cs₂CO₃ (0.6 mmol), additive (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine. Yield was determined by ¹H NMR with CH₂Br₂ as internal standard. Numbers in parentheses are referred to isolated yields.

**Table S3. Screening of HATs**

<table>
<thead>
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<th>Entry</th>
<th>HAT</th>
<th>2a [%]</th>
<th>2aII [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>quinuclidine</td>
<td>40%</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>Mesna</td>
<td>56%</td>
<td>20%</td>
</tr>
<tr>
<td>3</td>
<td>p-Toluenethiol</td>
<td>81%</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>2-Mercaptobenzoic Acid</td>
<td>77%</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Methyl Ester</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>L-Cysteine</td>
<td>50%</td>
<td>48%</td>
</tr>
<tr>
<td>6c</td>
<td>DABCO</td>
<td>65%</td>
<td>--</td>
</tr>
<tr>
<td>7d</td>
<td>DABCO</td>
<td>71%</td>
<td>--</td>
</tr>
</tbody>
</table>

*Reactions conditions: 1,1-diphenylethylene (0.2 mmol), 3DPAFIPN (6.2 mol%), HAT (0.06 mmol), Cs₂CO₃ (0.6 mmol), K₃PO₄ (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine. Yield was determined by ¹H NMR with CH₂Br₂ as internal standard. Numbers in parentheses are referred to isolated yields.
mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine.

Yield was determined by ¹H NMR with CH₂Br₂ as internal standard. 

**Table S4. Screening of photocatalysts**

<table>
<thead>
<tr>
<th>Entry</th>
<th>photocatalyst</th>
<th>2a [%]ᵇ</th>
<th>2aH [%]ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>3DPAFIPN</td>
<td>91% (88%)ᶜ</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>Ru(bpy)₃Cl₂</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>Ir(ppy)₂(dbbpy)(PF₆)</td>
<td>7%</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>[Ir(dF(CF₃)ppy)₂(dbbpy)]PF₆</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>[Ir(dF(Me)ppy)₂(dbbpy)]PF₆</td>
<td>20%</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>4DPAIPN</td>
<td>65%</td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>4CzIPN</td>
<td>39%</td>
<td>--</td>
</tr>
<tr>
<td>9ᵈ</td>
<td>3DPAFIPN</td>
<td>70%</td>
<td>--</td>
</tr>
<tr>
<td>10ᵉ</td>
<td>3DPAFIPN</td>
<td>86%</td>
<td>--</td>
</tr>
<tr>
<td>11ᶠ</td>
<td>3DPAFIPN</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>12ᵍ</td>
<td>3DPAFIPN</td>
<td>32%</td>
<td>28%</td>
</tr>
<tr>
<td>13ᵇ</td>
<td>3DPAFIPN</td>
<td>--</td>
<td>76%</td>
</tr>
<tr>
<td>14ˡ</td>
<td>3DPAFIPN</td>
<td>--</td>
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</tr>
</tbody>
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⁽ᵃ⁾Reaction conditions: 1,1-diphenylethylene (0.2 mmol), photocatalyst (6.2 mol%), DABCO (0.06 mmol), Cs₂CO₃ (0.6 mmol), K₃PO₄ (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine.

⁽ᵇ⁾Yield was determined by ¹H NMR with CH₂Br₂ as internal standard. 

⁽ᶜ⁾Isolated yield. 

⁽ᵈ⁾3DPAF (2.0 mol%). 

⁽ᵉ⁾3DPAFIPN (4.0 mol%). 

⁽ᶠ⁾In darkness. 

⁽ᵍ⁾Without DABCO. 

⁽ʰ⁾In N₂ atmosphere. 

⁽ᵢ⁾Without HCOOK.

**Table S5. Screening of solvents**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Slovent</th>
<th>2a [%]ᵇ</th>
<th>2aH [%]ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMF</td>
<td>15%</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>1,4-dioxane</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>16%</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>MeCN</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>DMA</td>
<td>17%</td>
<td>--</td>
</tr>
</tbody>
</table>

⁽ᵃ⁾Reaction conditions: 1,1-diphenylethylene (0.2 mmol), 3DPAFIPN (6.2 mol%), DABCO (0.06 mmol), Cs₂CO₃ (0.6 mmol), K₃PO₄ (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs (450 - 455 nm), rt, 24 h.
mmol), HCOOK (0.6 mmol) in slovent (2 mL), 1 atm CO$_2$, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine.

$^3$Yield was determined by $^1$H NMR with CH$_3$Br$_2$ as internal standard.

3. General procedure

An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K$_3$PO$_4$ (2.0 equiv, 0.4 mmol, 85.5 mg), Cs$_2$CO$_3$ (3.0 equiv, 0.6 mmol, 195.5 mg), HCOOK (3.0 equiv, 0.6 mmol, 50.5 mg), 3DPAFIPN (6.2 mol%, 8.0 mg, 3DPAFIPN was synthesized following the literature procedures$^1$), DABCO (30 mol%), alkene (0.20 mmol, 1.0 equiv, if solid). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the alkene (0.2 mmol, if liquid) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO$_2$ for 10 times. Finally, the tube was placed under 30 W blue LEDs ($\lambda = 450 - 455$ nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) and stirred for 24 h. Then, the mixture was quenched with H$_2$O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product 2. If there was traces of DMSO, extraction with H$_2$O.

An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K$_3$PO$_4$ (2.0 equiv, 0.4 mmol, 85.5 mg), Cs$_2$CO$_3$ (3.0 equiv, 0.6 mmol, 195.5 mg), HCOOK (3.0 equiv, 0.6 mmol, 50.5 mg), 3DPAFIPN (6.2 mol%, 8.0 mg),
DABCO (30 mol%, 6.8 mg), alkene (0.20 mmol, 1.0 equiv, if solid). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the alkene (0.2 mmol, if liquid) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO₂ for 10 times. Finally, the tube was placed under 30 W blue LEDs (\(\lambda = 450 - 455 \text{ nm} \), 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) and stirred for 24 h. Then, the mixture was quenched with H₂O and 2 mL of HCl (2 N), extracted with EtOAc three times, then concentrated in vacuo. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product 4.

2,2-diphenylsuccinic acid (2a)²

![Structure of 2,2-diphenylsuccinic acid (2a)](attachment:structure.png)

Product (2a) was obtained as a white solid (47.4 mg, 88%); R<sub>f</sub> = 0.4 (Petroleum ether : Acetone = 3 : 1); <sup>1</sup>H NMR (400 MHz, CD₃OD) \(\delta\) 7.35 - 7.32 (m, 4H), 7.27 - 7.18 (m, 6H), 3.50 (s, 2H). <sup>13</sup>C NMR (100 MHz, CD₃OD) \(\delta\) 176.6, 174.3, 144.4, 129.9, 128.8, 127.8, 58.5, 44.7.

Large Scale Reaction Procedure:

An oven-dried reaction tube (250 mL) containing a stirring bar was cooled to room temperature. The tube was then introduced in a glovebox, where it was charged with K₃PO₄ (2.0 equiv, 2.0 mmol, 425 mg), Cs₂CO₃ (3.0 equiv, 3.0 mmol, 977.5 mg), HCOOK (3.0 equiv, 3.0 mmol, 252.5 mg), 3DPAFIPN (6.0 mol%, 38.9 mg), DABCO (30 mol%, 34 mg). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (10 mL, 0.1 M) and 1,1-diphenylethylene (1.0 mmol, 1.0 equiv, 181 mg) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO₂ for 10 times. Finally, the tube was placed under 30 W blue LEDs (\(\lambda = 450 - 455 \text{ nm} \), 3.0 cm - 4.5 cm away from the LEDs, with a fan to cool the
reaction temperature which was about 42 °C) and stirred for 52 h. Then, the mixture was quenched with H₂O and 10 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product in 88% yield (238 mg).

2-phenyl-2-(o-tolyl)succinic acid (2b)

Product (2b) was obtained as a white solid (43.7 mg, 77%); Rf = 0.5 (Petroleum ether : Acetone = 3 : 1); ¹H NMR (400 MHz, CD₃OD) δ 7.51 - 7.47 (m, 1H), 7.40 - 7.37 (m, 2H), 7.26 - 7.15 (m, 5H), 7.09 - 7.07 (m, 1H), 3.62 (d, J = 15.6 Hz, 1H), 3.41 (d, J = 15.6 Hz, 1H), 1.86 (s, 3H). ¹³C NMR (100 MHz, CD₃OD) δ 176.1, 174.4, 143.7, 141.7, 138.9, 133.5, 130.0, 129.7, 128.8, 128.3, 127.7, 126.4, 58.7, 45.0, 22.0.

2-(2-fluorophenyl)-2-phenylsuccinic acid (2c)
Product (2c) was obtained as a colorless oil (42 mg, 73%); R$_f$ = 0.5 (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) δ 7.45 - 7.24 (m, 7H), 7.09 - 6.97 (m, 2H), 3.58 (2H, ABq, $J$ = 17.2 Hz). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 176.0, 174.2, 162.3 (d, $J$ = 246 Hz), 141.8, 132.5 (d, $J$ = 3.6 Hz), 131.4 (d, $J$ = 10.8 Hz), 130.2 (d, $J$ = 9.0 Hz), 129.2, 129.0, 128.2, 124.2 (d, $J$ = 3.3 Hz), 116.7 (d, $J$ = 23.2 Hz), 56.6, 41.6 (d, $J$ = 3.0 Hz). $^{19}$F NMR (376 MHz, CD$_3$OD) δ -109.5.

2-phenyl-2-(m-tolyl)succinic acid (2d)

Product (2d) was obtained as a white solid (42 mg, 74%); mp: 151-152 °C; R$_f$ = 0.5 (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) δ 7.34 - 7.31 (m, 2H), 7.27 - 7.20 (m, 3H), 7.17 - 7.10 (m, 3H), 7.05 - 7.03 (m, 1H), 3.47 (2H, ABq, $J$ = 16.8 Hz), 2.27 (s, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 176.7, 174.4, 144.5, 144.4, 138.4, 130.5, 130.0, 128.71, 128.68, 128.5, 127.8, 126.8, 58.4, 44.8, 21.6. HRMS (ESI) m/z calcd for C$_{17}$H$_{15}$O$_4$ - (M-H)$^-$ 283.0976; found 283.0967.

2-phenyl-2-(3-(trifluoromethyl)phenyl)succinic acid (2e)$^2$

Product (2e) was obtained as a white solid (41 mg, 62%); R$_f$ = 0.4 (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) δ 7.52 (s, 1H), 7.35 - 7.29 (m, 2H), 7.24 - 7.20 (m, 1H), 7.15 - 7.03 (m, 5H), 3.46 (d, $J$ = 16.4 Hz, 1H), 3.19 (d, $J$ = 16.8 Hz, 1H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 176.0, 174.0, 145.9, 144.0, 134.2, 130.9 (q,
$J = 31.6 \text{ Hz}$, 129.4, 129.31, 129.28, 128.4, 127.4 (q, $J = 3.9 \text{ Hz}$), 125.7 (q, $J = 270 \text{ Hz}$), 124.5 (q, $J = 3.8 \text{ Hz}$), 58.5, 44.5. $^{19}$F NMR (376 MHz, CD$_3$OD) δ -64.0.

2-phenyl-2-(p-tolyl)succinic acid (2f)

Product (2f) was obtained as a white solid (35 mg, 62%); $R_f = 0.3$ (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) δ 7.34 - 7.31 (m, 2H), 7.26 - 7.19 (m, 5H), 7.08 - 7.06 (m, 2H), 3.46 (2H, ABq, $J = 16.4 \text{ Hz}$), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 176.8, 174.4, 144.6, 141.5, 137.6, 129.9, 129.7, 129.4, 128.7, 127.7, 58.2, 44.8, 20.9.

2,2-di-p-tolylsuccinic acid (2g)

Product (2g) was obtained as a white solid (42 mg, 70%); mp: 117-118 °C; $R_f = 0.5$ (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.43 (br, 2H), 7.16 - 7.14 (m, 4H), 7.07 - 7.05 (m, 4H), 3.34 (s, 2H), 2.25 (s, 6H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 174.2, 171.9, 140.6, 135.5, 128.4, 128.2, 56.0, 43.5, 20.5. HRMS (ESI) m/z calcd for C$_{18}$H$_{17}$O$_4$- (M-H)$^-$ 297.1132; found 297.1122.

2-(4-methoxyphenyl)-2-phenylsuccinic acid (2h)

Product (2h) was obtained as a white solid (45 mg, 75%); $R_f = 0.5$ (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) δ 7.34 - 7.32 (m, 2H), 7.27 - 7.18 (m,
5H), 6.82 - 6.79 (m, 2H), 3.75 (s, 3H), 3.46 (2H, ABq, \( J = 16.4 \) Hz). 13C NMR (100 MHz, CD3OD) δ 176.9, 174.4, 159.8, 144.7, 136.4, 131.0, 129.9, 128.7, 127.8, 114.1, 57.9, 55.6, 44.9.

2,2-bis(4-methoxyphenyl)succinic acid (2i)

![structure](image)

Product (2i) was obtained as a colorless oil (48 mg, 74%); \( R_f = 0.5 \) (Petroleum ether : Acetone = 3 : 1); 1H NMR (400 MHz, CD3OD) δ 7.25 - 7.22 (m, 4H), 6.83 - 6.79 (m, 4H), 3.77 (s, 6H), 3.41 (s, 2H). 13C NMR (100 MHz, CD3OD) δ 177.2, 174.5, 159.8, 136.7, 131.0, 114.0, 57.3, 55.6, 45.1. HRMS (ESI) m/z calcd for C18H17O6- (M-H)- 329.1031; found 329.1018.

2-(4-fluorophenyl)-2-phenylsuccinic acid (2j)

![structure](image)

Product (2j) was obtained as a white solid (45 mg, 78%); \( R_f = 0.5 \) (Petroleum ether : Acetone = 3 : 1); 1H NMR (400 MHz, CD3OD) δ 7.38 - 7.32 (m, 4H), 7.30 - 7.20 (m, 3H), 7.00 - 6.94 (m, 2H), 3.55 (d, \( J = 16.4 \) Hz, 1H), 3.42 (d, \( J = 16.4 \) Hz, 1H). 13C NMR (100 MHz, CD3OD) δ 176.4, 174.2, 162.9 (d, \( J = 243.5 \) Hz), 144.4, 140.5 (d, \( J = 3.4 \) Hz), 132.1 (d, \( J = 7.9 \) Hz), 129.6, 129.0, 128.0, 115.2 (d, \( J = 21.3 \) Hz), 58.0, 44.7. 19F NMR (376 MHz, CD3OD) δ -118.3.

2-(3,4-dimethoxyphenyl)-2-phenylsuccinic acid (2k)
Product (2k) was obtained as a colorless oil (29.8 mg, 72%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^1H NMR (400 MHz, CD_3OD) δ 7.36 - 7.34 (m, 2H), 7.28 - 7.19 (m, 3H), 6.97 (s, 1H), 6.88 - 6.82 (m, 2H), 3.80 (s, 3H), 3.69 (s, 3H), 3.47 (s, 2H). ^13C NMR (100 MHz, CD_3OD) δ 176.8, 174.3, 149.6, 149.5, 144.6, 137.2, 129.9, 128.8, 127.8, 122.4, 114.9, 112.1, 58.2, 56.4, 44.9. HRMS (ESI) m/z calcd for C_{18}H_{17}O_6 (M-H)^- 329.1031; found 329.1018.

2-phenyl-2-(thiophen-3-yl)succinic acid (2l)

Product (2l) was obtained as a white solid (30 mg, 55%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^1H NMR (400 MHz, CD_3OD) δ 7.37 - 7.30 (m, 4H), 7.25 - 7.21 (m, 4H), 7.03 - 7.00 (m, 1H), 6.92 - 6.90 (m, 1H), 3.66 (d, J = 16.8 Hz, 1H), 3.47 (d, J = 16.8 Hz, 1H). ^13C NMR (100 MHz, CD_3OD) δ 175.9, 174.3, 147.8, 129.1, 128.4, 128.3, 127.6, 126.7, 126.3, 56.0, 45.6.

2-butyl-2-phenylsuccinic acid (2m)

Product (2m) was obtained as a white solid (31 mg, 63%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^1H NMR (400 MHz, CD_3OD) δ 7.37 - 7.30 (m, 4H), 7.25 - 7.21 (m, 1H), 3.20 (d, J = 16.0 Hz, 1H), 3.02 (d, J = 16.0 Hz, 1H), 2.24 - 2.09 (m, 2H), 1.20 - 1.01 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). ^13C NMR (100 MHz, CD_3OD) δ 178.6, 174.7, 143.2, 129.4, 127.9, 127.4, 52.8, 40.0, 38.9, 18.6, 14.8.
2-methyl-2-phenylsuccinic acid (2n)

Product (2n) was obtained as a white solid (25 mg, 60%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^1H NMR (400 MHz, CD_3OD) δ 7.42 - 7.40 (m, 2H), 7.35 - 7.31 (m, 2H), 7.26 - 7.22 (m, 1H), 3.21 (d, J = 16.4 Hz, 1H), 2.82 (d, J = 16.4 Hz, 1H), 1.69 (s, 3H). ^13C NMR (100 MHz, CD_3OD) δ 178.8, 174.7, 144.7, 129.5, 128.0, 126.8, 49.2, 44.3, 24.0.

2-(3-cyanophenyl)-2-methylsuccinic acid (2o)

Product (2o) was obtained as a white solid (31 mg, 68%); mp: 140-141 °C; R_f = 0.4 (Petroleum ether : Acetone = 3 : 1); ^1H NMR (400 MHz, CD_3OD) δ 7.78 - 7.74 (m, 2H), 7.64 - 7.62 (m, 1H), 7.54 - 7.50 (m, 1H), 3.15 (d, J = 16.8 Hz, 1H), 2.93 (d, J = 16.8 Hz, 1H), 1.72 (s, 3H). ^13C NMR (100 MHz, CD_3OD) δ 177.8, 174.1, 146.3, 132.5, 131.8, 131.0, 130.6, 119.7, 113.5, 44.0, 23.8. HRMS (ESI) m/z calcd for C_{12}H_{10}NO_4^-(M-H) - 232.0615; found 232.0605.

3-methyl-2,2-diphenylsuccinic acid (2p)

Product (2p) was obtained as a white solid (30 mg, 53%); mp: 138-139 °C; R_f = 0.4 (Petroleum ether : Acetone = 2 : 1); ^1H NMR (400 MHz, CD_3OD) δ 7.40 - 7.22 (m, 10H), 4.15 (q, J = 7.2 Hz, 1H), 1.12 (d, J = 7.2 Hz, 3H). ^13C NMR (100 MHz, CD_3OD) δ 177.8, 177.3, 143.0, 141.7, 132.5, 130.7, 128.8, 128.1, 127.8, 127.7, 63.5, 45.2, 15.2.
HRMS (ESI) m/z calcd for C₁₇H₁₆O₄Na⁺ (M+Na)⁺ 307.0941; found 307.0942.

2-(2,2-diphenylvinyl)succinic acid (2qa)

Product (2qa) was obtained as a white solid (22 mg, 37%); mp: 172-173 °C; Rf = 0.3 (Petroleum ether : Acetone = 2 : 1); ¹H NMR (400 MHz, CD₃OD) δ 7.43 - 7.33 (m, 3H), 7.28 - 7.18 (m, 7H), 6.04 (d, J = 10.8 Hz, 1H), 3.59 - 3.53 (m, 1H), 2.81 - 2.75 (m, 1H), 2.54 - 2.49 (m, 1H). ¹³C NMR (100 MHz, CD₃OD) δ 176.7, 174.9, 146.5, 143.3, 140.6, 130.9, 129.4, 129.2, 128.6, 128.4, 126.1, 43.7, 37.9. HRMS (ESI) m/z calcd for C₁₈H₁₈O₄Na⁺ (M+Na)⁺ 319.0941; found 319.0942.

(E)-2,2-diphenylhex-3-enedioic acid (2qb)

Product (2qb) was obtained as a white solid (10 mg, 17%); mp: 155-156 °C; Rf = 0.4 (Petroleum ether : Acetone = 2 : 1); ¹H NMR (400 MHz, CD₃OD) δ 7.32 - 7.24 (m, 6H), 7.20 - 7.18 (m, 4H), 6.58 (d, J = 15.8 Hz, 1H), 5.07 - 5.00 (m, 1H), 3.13 (dd, J = 7.0, 0.8 Hz, 2H). ¹³C NMR (100 MHz, CD₃OD) δ 177.2, 175.4, 143.1, 138.8, 130.6, 128.8, 128.1, 127.1, 65.2, 38.8. HRMS (ESI) m/z calcd for C₁₈H₁₈O₄- (M-H)- 295.0976; found 295.0961.

2-(tert-butoxycarbonyl)-2-methylsuccinic acid (2r)

Product (2r) was obtained as a white solid (35 mg, 76%); Rf = 0.5 (Petroleum ether :
Acetone = 3 : 1); $^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ 3.01 (2H, ABq, $J = 17.2$ Hz), 1.54 (s, 3H), 1.46 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.8, 175.6, 172.0, 83.9, 51.2, 40.1, 27.6, 21.9.

2-((cyclohexyloxy)carbonyl)-2-methylsuccinic acid (2s)$^2$

![2-((cyclohexyloxy)carbonyl)-2-methylsuccinic acid (2s)](image)

Product (2s) was obtained as a white solid (42 mg, 82%); $R_f = 0.3$ (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 4.84 - 4.78 (m, 1H), 2.97 (d, $J = 16.8$ Hz, 1H), 2.83 (d, $J = 17.2$ Hz, 1H), 1.80 - 1.70 (m, 4H), 1.53 - 1.44 (m, 6H), 1.42 - 1.29 (m, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 174.6, 173.9, 172.4, 74.7, 52.8, 40.9, 32.0, 26.5, 24.2, 20.8.

2-benzyl-2-(methoxycarbonyl)succinic acid (2t)

![2-benzyl-2-(methoxycarbonyl)succinic acid (2t)](image)

Product (2t) was obtained as a white solid (21 mg, 40%); mp: 134-135 °C; $R_f = 0.4$ (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.29 - 7.21 (m, 3H), 7.12 - 7.10 (m, 2H), 3.73 (s, 3H), 3.38 (dd, $J = 31.6$, 14.0 Hz, 2H), 2.76 (dd, $J = 44.0$, 17.6 Hz, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 174.1, 172.9, 172.5, 137.4, 131.1, 129.4, 128.2, 57.7, 53.1, 39.5, 37.3. HRMS (ESI) m/z calcd for C$_{13}$H$_{13}$O$_6^-$ (M-H)$^-$ 265.0718; found 265.0708.

2-phenylsuccinic acid (4a)$^3$

![2-phenylsuccinic acid (4a)](image)

Product (4a) was obtained as a white solid (28 mg, 72%); $R_f = 0.3$ (Petroleum ether : Acetone = 2 : 1); $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.35 - 7.25 (m, 5H), 4.01 (dd, $J = 197
10.0, 5.2 Hz, 1H), 3.10 (dd, J = 16.8, 10.4 Hz, 1H), 2.62 (dd, J = 16.8, 5.2 Hz, 1H).

$^{13}$C NMR (100 MHz, CD$_3$OD) δ 176.6, 175.2, 139.9, 129.8, 128.9, 128.5, 48.7, 38.7.

**2-(o-tolyl)succinic acid (4b)**

Product (4b) was obtained as a white solid (30 mg, 72%); $R_f = 0.5$ (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) δ 7.23 - 7.11 (m, 4H), 4.32 (dd, J = 10.0, 5.2 Hz, 1H), 3.08 (dd, J = 17.2, 10.0 Hz, 1H), 2.57 (dd, J = 16.8, 5.2 Hz, 1H), 2.42 (s, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 176.8, 175.4, 138.3, 137.4, 131.7, 128.3, 127.6, 127.4, 44.2, 38.1, 19.8.

**2-(2-methoxyphenyl)succinic acid (4c)**

Product (4c) was obtained as a white solid (35 mg, 78%) (42 mg, 94%, note: the reaction temperature is 40 to 45°C); mp: 177-178 °C; $R_f = 0.5$ (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) δ 7.27 - 7.23 (m, 1H), 7.18 - 7.16 (m, 1H), 6.98 - 6.92 (m, 1H), 6.92 - 6.88 (m 1H), 4.35 (dd, J = 9.6, 5.2 Hz, 1H), 3.83 (s, 3H), 3.01 (dd, J = 16.8, 9.6 Hz, 1H), 2.52 (dd, J = 16.8, 5.2 Hz, 1H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 177.0, 175.7, 158.3, 129.8, 128.4, 121.7, 112.1, 56.0, 43.2, 37.5. HRMS (ESI) m/z calcd for C$_{11}$H$_{11}$O$_5$ (M-H)$^-$ 223.0612; found 223.0602.

**2-(2-chlorophenyl)succinic acid (4d)**

Product (4d) was obtained as a white solid (22 mg, 48%); $R_f = 0.5$ (Petroleum ether :
Acetone = 3 : 1; \( ^1 \)H NMR (400 MHz, CD\(_3\)OD) \( \delta \) 7.44 - 7.41 (m, 1H), 7.35 - 7.24 (m, 3H), 4.56 (dd, \( J = 10.0, 5.2 \) Hz, 1H), 3.05 (dd, \( J = 17.2, 10.0 \) Hz, 1H), 2.61 (dd, \( J = 16.8, 4.8 \) Hz, 1H). \( ^{13} \)C NMR (100 MHz, CD\(_3\)OD) \( \delta \) 175.7, 174.9, 137.7, 134.9, 130.9, 130.1, 130.0, 128.5, 45.4, 37.6.

2-(3-methoxyphenyl)succinic acid (4e)\(^5\)

Product (4e) was obtained as a white solid (35 mg, 78%); \( R_f = 0.5 \) (Petroleum ether : Acetone = 3 : 1); \( ^1 \)H NMR (400 MHz, CD\(_3\)OD) \( \delta \) 7.25 - 7.21 (m, 1H), 6.89 - 6.81 (m, 3H), 3.99 (dd, \( J = 10.0, 5.2 \) Hz, 1H), 3.77 (s, 3H), 3.09 (dd, \( J = 16.8, 10.0 \) Hz, 1H), 2.62 (dd, \( J = 16.8, 5.2 \) Hz, 1H). \( ^{13} \)C NMR (100 MHz, CD\(_3\)OD) \( \delta \) 176.5, 175.2, 161.3, 141.2, 130.8, 121.0, 114.6, 113.9, 55.6, 48.6, 38.7.

2-(3-chlorophenyl)succinic acid (4f)\(^3\)

Product (4f) was obtained as a white solid (33 mg, 73%); \( R_f = 0.5 \) (Petroleum ether : Acetone = 3 : 1); \( ^1 \)H NMR (400 MHz, CD\(_3\)OD) \( \delta \) 7.35 - 7.24 (m, 4H), 4.02 (dd, \( J = 10.0, 5.6 \) Hz, 1H), 3.09 (dd, \( J = 16.8, 9.6 \) Hz, 1H), 2.65 (dd, \( J = 16.8, 5.6 \) Hz, 1H). \( ^{13} \)C NMR (100 MHz, CD\(_3\)OD) \( \delta \) 175.9, 174.8, 142.1, 135.5, 131.3, 129.1, 128.6, 127.4, 48.3, 38.4.

2-(3-cyanophenyl)succinic acid (4g)
Product (4g) was obtained as a white solid (31 mg, 71%); mp: 180-181 °C; R_f = 0.3 (Petroleum ether : Acetone = 3 : 1); ¹H NMR (400 MHz, CD₃OD) δ 7.70 - 7.63 (m, 3H), 7.53 - 7.49 (m, 1H), 4.11 (dd, J = 9.2, 5.6 Hz, 1H), 3.12 (dd, J = 17.2, 9.6 Hz, 1H), 2.69 (dd, J = 16.8, 5.6 Hz, 1H). ¹³C NMR (100 MHz, CD₃OD) δ 175.5, 174.7, 141.6, 133.9, 132.8, 132.3, 130.9, 119.5, 113.7, 48.4, 38.2. HRMS (ESI) m/z calcd for C₁₁H₈NO₄ (M-H) - 218.0459; found 218.0446.

2-((p-tolyl)succinic acid (4h)²

Product (4h) was obtained as a white solid (25 mg, 62%); R_f = 0.4 (Petroleum ether : Acetone = 3 : 1); ¹H NMR (400 MHz, CD₃OD) δ 7.20 - 7.12 (m, 4H), 3.97 (dd, J = 10.0, 5.2 Hz, 1H), 3.08 (dd, J = 17.2, 10.4 Hz, 1H), 2.59 (dd, J = 16.8, 5.2 Hz, 1H), 2.30 (s, 3H). ¹³C NMR (100 MHz, CD₃OD) δ 176.8, 175.2, 138.3, 136.8, 130.4, 128.7, 48.2, 38.8, 21.1.

2-(4-methoxyphenyl)succinic acid (4i)⁶

Product (4i) was obtained as a white solid (25 mg, 56%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ¹H NMR (400 MHz, CD₃OD) δ 7.24 - 7.21 (m, 2H), 6.89 - 6.85 (m, 2H), 3.95 (dd, J = 10.0, 5.2 Hz, 1H), 3.76 (s, 3H), 3.07 (dd, J = 17.2, 10.0 Hz, 1H), 2.59 (dd, J = 17.2, 5.2 Hz, 1H). ¹³C NMR (100 MHz, CD₃OD) δ 176.9, 175.3, 160.5, 131.7, 129.9, 115.1, 55.7, 47.8, 38.8.
2-(4-fluorophenyl)succinic acid (4j)$^2$

Product (4j) was obtained as a white solid (25.5 mg, 60%); R$_f$ = 0.3 (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.39 (br, 2H), 7.35 - 7.31 (m, 2H), 7.17 - 7.13 (m, 2H), 3.91 (dd, $J$ = 10.0, 5.2 Hz, 1H), 2.94 (dd, $J$ = 17.2, 10.4 Hz, 1H), 2.57 - 2.53 (m, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 174.0, 172.6, 161.4 (d, $J$ = 242 Hz), 134.9 (d, $J$ = 3.0 Hz), 129.8 (d, $J$ = 8.1 Hz), 115.4 (d, $J$ = 21.1 Hz), 46.1, 37.4. $^{19}$F NMR (376 MHz, DMSO) δ -115.6.

2-(4-cyanophenyl)succinic acid (4k)$^2$

Product (4k) was obtained as a white solid (28 mg, 65%); R$_f$ = 0.4 (Petroleum ether : Acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) δ 7.71 - 7.69 (m, 2H), 7.54 - 7.52 (m, 2H), 4.15 - 4.11 (m, 1H), 3.16 - 3.10 (m, 1H), 2.72 - 2.66 (m, 1H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 175.3, 174.6, 145.5, 133.6, 130.2, 119.5, 112.3, 48.6, 48.4.

2-(1,1'-biphenyl)-4-yl)succinic acid (4l)$^2$

Product (4l) was obtained as a white solid (36 mg, 66%); R$_f$ = 0.5 (Petroleum ether : acetone = 3 : 1); $^1$H NMR (400 MHz, CD$_3$OD) δ 7.60 - 7.57 (m, 4H), 7.43 - 7.39 (m, 4H), 7.34 - 7.30 (m, 1H), 4.07 (dd, $J$ = 10.0, 5.2 Hz, 1H), 3.14 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.67 (dd, $J$ = 16.8, 5.2 Hz, 1H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 176.6, 175.2, 141.9, 141.7, 138.9, 129.9, 129.4, 128.4, 128.3, 127.9, 48.3, 38.7.
4. Mechanistic Experiments

Radical clock experiment

\[
\begin{array}{c}
\text{Ph} - \text{C} - \text{Ph} \\
\text{CO}_2 \\
\text{DMSO (0.1 M), blue LEDs, rt, 24 h then HCl} \\
\rightarrow \\
\text{Ph} - \text{C} - \text{Ph} \\
\end{array}
\]

4-(2-(1-phenylvinyl)cyclopropyl)-1,1'-biphenyl was synthesized following the literature procedures\(^7\). An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K$_3$PO$_4$ (85.5 mg, 0.4 mmol, 2.0 equiv), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%), DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the 4-(2-(1-phenylvinyl)cyclopropyl)-1,1'-biphenyl (44.1 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO$_2$ for 10 times. Finally, the tube was placed under 30 W blue LEDs (\(\lambda = 450 - 455\) nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred for 24 h. Then, the mixture was quenched with H$_2$O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product 6 as a colorless oil; \(R_t = 0.4\) (Petroleum ether : ethyl acetate = 1 : 1); \(^1\)H NMR (400 MHz, CD$_3$OD) \(\delta\) 7.39 - 7.17 (m, 11.5H), 7.10 - 7.08 (m, 2H), 5.84 (t, \(J = 7.4\) Hz, 0.33H), 5.58 (t, \(J = 7.3\) Hz, 1H), 3.76 (t, \(J = 7.7\) Hz, 0.33H), 3.59 - 3.54 (m, 1H), 3.50 - 3.42 (m, 0.6H), 3.32 - 3.25 (m, 2.31H), 3.01 - 2.94 (m, 0.33H), 2.72 - 2.64 (m, 1.31H), 2.48 - 2.41 (m, 1H). \(^{13}\)C NMR (100 MHz, CD$_3$OD) \(\delta\) 177.1, 177.1, 175.2, 175.1, 143.6, 140.9, 140.5, 140.2, 137.6, 136.1, 129.8, 129.6, 129.5, 129.5, 129.4, 129.2, 129.1, 129.1, 129.1, 128.3, 128.2, 128.1, 128.0, 127.0, 52.9, 52.6, 36.7, 34.0. HRMS (ESI) m/z calcd for C$_{19}$H$_{18}$NaO$_4$ (M+Na)$^+$ 333.1097; found 333.1096.
Reactions in the presence of D₂O

An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K₃PO₄ (85.5 mg, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (195.5 mg, 0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%), DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, D₂O (40 mg, 10 equiv), the degassed anhydrous DMSO (2 mL, 0.1 M) and the 1a (36.05 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO₂ for 10 times. Finally, the tube was placed under 30 W blue LEDs (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred for 24 h. Then, the mixture was quenched with H₂O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product 2aH-DH (30 mg, 65%). ¹H NMR (400 MHz, CD₃OD) δ 7.27 - 7.23 (m, 8H), 7.19 - 7.13 (m, 2H), 4.50 (t, J = 8.0 Hz, 0.51H), 3.05 - 3.03 (m, 2H). ¹³C NMR (100 MHz, CD₃OD) δ 175.7, 145.3, 145.2, 129.5, 128.5, 128.7, 127.4, 48.5, 41.5, 41.4.

An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K₃PO₄ (85.5 mg, 0.4 mmol, 2.0 equiv), Cs₂CO₃ (195.5 mg, 0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%),
DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, D₂O (80 mg, 20 equiv), the degassed anhydrous DMSO (2 mL, 0.1 M) and the 1a (36.05 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with N₂ for 10 times. Finally, the tube was placed under 30 W blue LEDs (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred for 24 h. Then, the mixture was quenched with H₂O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation and the yield of crude products was determined via ¹H NMR using CH₂Br₂ as internal standard.

![Figure S1. Reaction in the presence of D₂O.](image)

**The reaction in the absence of HCOOK**

An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was
charged with K$_3$PO$_4$ (85.5 mg, 0.4 mmol, 2.0 equiv), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%), DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the 1a (36.05 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO$_2$ for 10 times. Finally, the tube was placed under 30 W blue LEDs ($\lambda = 450 - 455$ nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred at ambient temperature for 24 h. Then, the mixture was quenched with H$_2$O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation and the yield of crude products was determined via $^1$H NMR using CH$_2$Br$_2$ as internal standard.

Figure S2. The reaction in the absence of HCOOK.

$^{13}$C-labelling experiment using commercially available H$^{13}$COONa

An oven-dried Schlenk t tube (25 mL) containing a stirring bar was cooled to room
temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K$_3$PO$_4$ (85.5 mg, 0.4 mmol, 2.0 equiv), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol, 3.0 equiv), H$^{13}$COONa (40.8 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%), DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the 1a (36.05 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO$_2$ for 10 times. Finally, the tube was placed under 30 W blue LEDs ($\lambda = 450 - 455$ nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred for 24 h. Then, the mixture was quenched with H$_2$O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired products 2a+(2aa/2ab)+2ac (37 mg, 68%) $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.34 - 7.19 (m, 5H), 3.49 (s, 1H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 176.6, 174.3, 144.5, 129.9, 128.8, 127.8, 58.5, 49.6, 44.7.

![Chemical Structures](image)

**Figure S3.** The products were detected by HR-MS.
Fluorescence spectra were collected on Edinburgh FS5 spectrofluorimeter. Samples for the quenching experiments were prepared in a 4 mL glass cuvette with a septum screw cap. 3DPAFIPN was irradiated at 420 nm and the emission intensity at 550 nm was observed. In a typical experiment, the emission spectrum of a $5.0 \times 10^{-5}$ M solution of 3DPAFIPN in DMSO was collected.

**Stern-Volmer fluorescence quenching experiments**

DABCO: A stock solution of DABCO (56.1 mg, 0.5 mmol) in 5 ml of DMSO was prepared. Then, different amounts of this stock solution were added to a solution of the 3DPAFIPN in DMSO ($5.0 \times 10^{-5}$ M).

HCOOK: A stock solution of HCOOK (42.1 mg, 0.5 mmol) in 10 ml of DMSO was prepared. Then, different amounts of this stock solution were added to a solution of the 3DPAFIPN in DMSO ($5.0 \times 10^{-5}$ M).
1a: A stock solution of 1a (90.1 mg, 0.5 mmol) in 5 ml of DMSO was prepared. Then, different amounts of this stock solution were added to a solution of the 3DPAFIPN in DMSO (5.0 × 10⁻⁵ M).

Figure S5. Stern-Volmer quenching by HCOOK.

Figure S6. Stern-Volmer quenching by 1a.
5. References


6. Copies of $^1$H and $^{13}$C NMR spectra

$^1$H NMR and $^{13}$C NMR spectra of 2a
$^{1}H$ NMR and $^{13}C$ NMR spectra of 2b
$\text{HOOC}_\text{Ph}$

$^{1}H$ NMR and $^{13}C$ NMR, DEPT-135°, $^{19}F$ NMR spectra of 2c
H NMR and $^{13}$C NMR spectra of 2d

![NMR spectra](image-url)
$^1$H NMR and $^{13}$C NMR, DEPT-135°, $^{19}$F NMR spectra of 2e
$^1$H NMR and $^{13}$C NMR of 2f
$^1$H NMR and $^{13}$C NMR spectra of 2g
$^1\text{H NMR and } ^{13}\text{C NMR spectra of 2h}$
$^1$H NMR and $^{13}$C NMR spectra of 2i
$^{1}H$ NMR and $^{13}C$ NMR, DEPT-135°, $^{19}F$ NMR spectra of 2j
$^{1}$H NMR and $^{13}$C NMR spectra of 2k
$^{1}H$ NMR and $^{13}C$ NMR spectra of 2l
\[ \text{HOOC} - C_4H_9 \] 
\[ \text{Ph} \] 
\[ \text{COOH} \] 
\[ ^1H \text{ NMR and } ^{13}C \text{ NMR spectra of 2m} \]
$^{1}H$ NMR and $^{13}C$ NMR spectra of 2n

![Diagram of molecular structure and NMR spectra]
$^1$H NMR and $^{13}$C NMR spectra of 2o
$^{1}H$ NMR and $^{13}C$ NMR spectra of 2p
$^1$H NMR and $^{13}$C NMR spectra of 2qₐ
$^{1}H$ NMR and $^{13}C$ NMR spectra of 2q$_b$
$\text{H NMR and }^{13}\text{C NMR spectra of 2r}$
$\text{COOH}$

$\text{COOH}$

$\text{CyO}$

$\text{Me}$

$\text{H NMR and }^{13}\text{C NMR of 2s}$
$^1$H NMR and $^{13}$C NMR spectra of 2t
$^1$H NMR and $^{13}$C NMR spectra of 4a

[Diagram of NMR spectra]
$^{1}$H NMR and $^{13}$C NMR spectra of 4b
$^{1}H$ NMR and $^{13}C$ NMR spectra of 4c
$^1$H NMR and $^{13}$C NMR spectra of 4d
$^1$H NMR and $^{13}$C NMR spectra of 4e
$^1$H NMR and $^{13}$C NMR spectra of 4f
$^1H$ NMR and $^{13}C$ NMR spectra of 4g
$^1$H NMR and $^{13}$C NMR spectra of 4h
$^{1}$H NMR and $^{13}$C NMR spectra of 4i
$\text{COOH}$

$\text{COOH}$

$\text{F}$

$\text{H NMR and } ^{13}\text{C NMR, DEPT-135\textdegree, } ^{19}\text{F NMR spectra of 4j}$
$^1$H NMR and $^{13}$C NMR spectra of 4k
$^1$H NMR and $^{13}$C NMR spectra of 4l
$^1$H NMR and $^{13}$C NMR spectra of 6
$^1$H NMR and $^{13}$C NMR spectra of 2a$_{H}$-DH
$^1$H NMR and $^{13}$C NMR spectra of 2a+(2aa/2ab)+2ac