Supporting Information

Photo-triggered Halodecarboxylation of Aliphatic Carboxylic Acids
via Cerium-Mediated ligand-to-metal-charge-transfer in water
Yan Xu, Panyi Huang, Yu Jiang, Chun Lv, Peixuan Li, Jiayang Wang, Bin Sun,* and Can Jin*

Page S1 General Information
Page S2-S4 Preparation of Substrate
Page S5 General procedure for decarboxylative halogenation
Page S6 Optimization of the reaction conditions
Page S7-S23 Characterization Data for the products
Page S24-S26 Application of the methodology
Page S27 Control experiments
Page S28-S30 UV-vis experiments
Page S31 Electron paramagnetic resonance (EPR) experiment
Page S32 KI-starch test
Page S33-S89 Copies of NMR Spectra
I. General Information

$^1$H NMR spectra were recorded at 400 MHz using TMS as internal standard, $^{13}$C NMR spectra were recorded at 100 MHz using TMS as internal standard. All chemical shifts were reported as δ values (ppm) relative to TMS and observed coupling constants ($J$) are given in Hertz (Hz). Mass spectra were measured with a HRMS-ESI instrument. The UV-Vis measurements were carried out using a UV-Vis spectrophotometer (ULN 2209003, MAPADA P6). The thin layer chromatography (TLC) was performed using glass plates covered with SiO$_2$. Spots were visualized by UV light irradiation or by staining of the TLC plate with iodine. Unless otherwise indicated, all reactions were carried out under air atmosphere at room temperature with magnetic stirring. All reagents were purchased from commercial source and without prior purification. Column chromatography was performed on silica gel (200-300 mesh) and the elution was performed with n-hexane/ethyl acetate.

The Material of the Irradiation Vessel
Manufacturer: Shenzhen Kelo Light Co., Ltd.
Model: Kelo A0100
Distance from the light source to the irradiation vessel: 2.0 cm

Figure S1. light setup and Broadband source.
II. Preparation of substrate

*General procedure for the synthesis of N-phthalimide carboxylic acid derivatives*¹

![Chemical structure](image1)

Reflux a solution of phthalic anhydride derivative (5 mmol) and amino acid (5 mmol) in acetic acid (20 mL) for 3 hours. Cool the reaction mixture to room temperature and then pour into ice water (50 mL). Stir the reaction mixture for 15 minutes. After that, a white crystalline product is obtained, filter the reaction mixture. Dry the reaction mixture in high vacuo to obtain the corresponding product.

*General procedure for the synthesis of N-sulfoylpiperidinic acid derivatives*²

![Chemical structure](image2)

Piperidine 4-carboxylic acid (646 mg, 5.00 mmol, 1.0 eq) was stirred with potassium carbonate (970 mg, 7.0 mmol, 1.4 eq) in water (5 mL) at room temperature until a clear solution was obtained. Solution of benzene sulfonyl chloride (6.5 mmol, 1.3 equiv) in THF (5 mL) was added with the aid of a dropping funnel within 15 min. After stirring for 15 min, the cooling bath was removed and the reaction mixture was stirred for 24 h. After that, the reaction mixture was diluted with EtOAc (20 mL) and 2 N HCl (20 mL). Then, poured into an extraction funnel, the organic phase was washed with brine (1 x 20 mL), dried over Na₂SO₄ and concentrated under reduced pressure. Dry the residues in high vacuo to obtain the corresponding product.

*General procedure for the synthesis of lithocolic acid derivative*³

![Chemical structure](image3)

Add acetic anhydride (26.43 mmol, 2.5 mL) dropwise to a solution of lithocholic (7.34 mmol, 2.764 g) and 4,4-dimethylaminopyridine (1.47 mmol, 180 mg) in CH₂Cl₂ (30 mL). Stir the reaction mixture at room temperature under nitrogen atmosphere for 1 h. Wash the mixture with HCl 1 N aqueous solution (3 x 30 mL), 5% NaHCO₃ solution (3 x 30 mL), saturated NaCl solution (3 x 20 mL) and water (1 x 20 mL). Dry the organic layer over Na₂SO₄ and concentrate. Purify the crude product by column chromatography (silica gel, cyclohexane/ethyl acetate, 8:2) to obtain lithocolic acid derivative.
General procedure for the synthesis of hyodeoxycholic acid derivative.⁴

Hyodeoxycholic acid (20.0 g, 51 mmol, 1 equiv.) was added into methanol (100 mL) and stirred at room temperature for 5 min. After all dissolved, sulfuric acid (2.5 mL) was slowly added into the reaction solution and the reaction was carried out for 18 hours at room temperature under nitrogen atmosphere. The mixture was concentrated to obtain yellow oil, which was extracted by ethyl acetate. After that, saturated NaHCO₃ solution was added to adjust the pH to neutral and washed combined organic layers with brine. The organic phase was concentrated to obtain 1 (20.7 g, 99%).

1 (10.2 g, 25 mmol, 1 equiv.), TsCl (14.1 g, 75 mmol, 3 equiv.), DMAP (0.305 g, 2.5 mmol, 0.1 equiv.) were dissolved in pyridine (50 mL). The mixture was placed in an ice bath and stirred for 48 hours under nitrogen atmosphere. Subsequently, 250 mL 10% HCl was added to the solution and then the white solid was precipitated, filtered under reduced pressure. The filter cake was washed with 5% HCl to neutral, and dried to obtain 2 (17.85 g, 99%).

2 (7.1 g, 10 mmol, 1 equiv.), KOH (0.729 g, 13 mmol, 1.3 equiv.) was dissolved in MeOH (50 mL). The mixture was stirred for 16 h at room temperature. Concentrated under reduced pressure. The mixture was purified by silica gel column to obtain 3 (6.8 g, 98%).
General procedure for the synthesis of 2,2-dimethyl-4-phenylbutanoic acid.\(^5\)

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{O} & \quad \text{COOH} \\
\text{LDA} & \quad \text{THF, -78 °C} \\
\text{KOH} & \quad \text{THF, reflux}
\end{align*}
\]

Methyl isobutyrate (10 mmol) and THF (20 mL) was added into an oven-dried 100 mL round-bottom flask and stirred at room temperature for 5 min. Submerge the flask in an acetone/dry ice bath (-78 °C) and stir the mixture vigorously for 5 minutes. Add LDA solution (20 ml, 0.5 M in THF, 10 mmol) dropwise to the mixture. Stir the mixture for 1 hours at -78 °C. Then, add corresponding halide (12 mmol) in THF (10 mL) dropwise to the mixture for 10 minutes. Remove the ice bath after stirring at -78 °C for 1 hour. Allow the mixture to stir for 8 hours at room temperature. After that, the reaction mixture was diluted with EtOAc and 1 M HCl (aq.). Dry the organic layer over Na\(_2\)SO\(_4\) and concentrate. Purify the crude product by column chromatography (silica gel, cyclohexane/ethyl acetate, 100:1) to obtain the ester (1.833 g, 89%).

Add a KOH solution (2.0 M in H\(_2\)O, 4.0 equiv.) to a solution of the alkylated ester (1.833 g, 1.0 equiv.) in THF (0.2 M) at room temperature for 12 h. After washing the aqueous phase with DCM twice, adjust the pH to 1-2 with 4 N HCl. Extract the aqueous layer with DCM. Dry the combined organic layers over Na\(_2\)SO\(_4\) and concentrate under reduced pressure to obtain 2,2-dimethyl-4-phenylbutanoic acid (1.505 g, 88%).
III. General procedure for decarboxylative halogenation

**Procedure A:** To a dried 8 mL vial was added acid (0.3 mmol), 1-bromopyrrolidine-2,5-dione (NBS) (1.0-1.5 equiv.), CeCl$_3$ (10 mol %), t-BuONa (30 mol %) in 3 mL H$_2$O under air atmosphere. The resulting solution was stirred under 100 W blue light for 6-12 h (25 °C). After that, the reaction mixture was diluted with DCM. Then, poured into an extraction funnel, the organic phase was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA as an eluent gave the product.

**Procedure B:** To a dried 8 mL vial was added acid (0.3 mmol), 1-iodopyrrolidine-2,5-dione (NIS) (1.5 equiv.), CeCl$_3$ (10 mol %), t-BuONa (30 mol %) in 3 mL H$_2$O under air atmosphere. The resulting solution was stirred under 100 W blue light for 12 h (25 °C). After that, the reaction mixture was diluted with DCM. Then, poured into an extraction funnel, the organic phase was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA as an eluent gave the product.

**Procedure C:** To a dried 8 mL vial was added acid (0.3 mmol), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (TCCA) (0.5 equiv.), CeCl$_3$ (10 mol %), t-BuONa (30 mol %) in 3 mL H$_2$O under air atmosphere. The resulting solution was stirred under 100 W blue light for 12 h (25 °C). After that, the reaction mixture was diluted with DCM. Then, poured into an extraction funnel, the organic phase was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA as an eluent gave the product.

![Figure S2. 100 W blue LED light setup.](image-url)
IV. Optimization of the reaction conditions

Table S1. Photocatalyst and base screening

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviation from standard conditions</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>CeBr₃ as PC</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>Ce (SO₄)₂ as PC</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>5 mol % of CeCl₂</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>20 mol % of CeCl₃</td>
<td>84</td>
</tr>
<tr>
<td>6</td>
<td>CH₃ONa as base</td>
<td>46</td>
</tr>
<tr>
<td>7</td>
<td>K₂CO₃ as base</td>
<td>63</td>
</tr>
<tr>
<td>8</td>
<td>Cs₂CO₃ as base</td>
<td>32</td>
</tr>
<tr>
<td>9</td>
<td>10 mol % of t-BuONa</td>
<td>78</td>
</tr>
<tr>
<td>10</td>
<td>30 mol % of t-BuONa</td>
<td>82</td>
</tr>
<tr>
<td>11</td>
<td>1.0 equiv of t-BuONa</td>
<td>80</td>
</tr>
<tr>
<td>12</td>
<td>No base</td>
<td>trace</td>
</tr>
</tbody>
</table>

*a* Conditions: 3-Phthalimidopropionic acid (1) (0.2 mmol), NBS (1.5 equiv.), CeCl₃ (10 mol%), t-BuONa (30 mol %), H₂O (2 mL), room temperature, air atmosphere, 100W Blue LEDs, 12 h. 

*b* Determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Other parameter screening

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviation from standard conditions</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>CH₂CN as solvent</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>DCE as solvent</td>
<td>71</td>
</tr>
<tr>
<td>4</td>
<td>DMSO as solvent</td>
<td>59</td>
</tr>
<tr>
<td>5</td>
<td>400 nm light instead of 100W Blue LEDs</td>
<td>37</td>
</tr>
<tr>
<td>6</td>
<td>435 nm light instead of 100W Blue LEDs</td>
<td>69</td>
</tr>
<tr>
<td>7</td>
<td>475 nm light instead of 100W Blue LEDs</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td>Dark conditions</td>
<td>n.d.</td>
</tr>
<tr>
<td>9</td>
<td>No CeCl₃</td>
<td>n.d.</td>
</tr>
<tr>
<td>10</td>
<td>Nitrogen atmosphere</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

*a* Conditions: 3-Phthalimidopropionic acid (1) (0.2 mmol), NBS (1.5 equiv.), CeCl₃ (10 mol%), t-BuONa (30 mol %), H₂O (2 mL), room temperature, air atmosphere, 100W Blue LEDs, 12 h. 

*b* Determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. n.d. No detected.
V. Characterization Data for the products

2-(2-bromoethyl)isoindoline-1,3-dione

According to general procedure A: using 3-(1,3-dioxoisooindolin-2-yl)propanoic acid (0.3 mmol, 66 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 ml H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (62.5 mg, 82% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.89 – 7.83 (m, 2H), 7.76 – 7.70 (m, 2H), 4.10 (t, $J$ = 6.8 Hz 2H), 3.61 (t, $J$ = 7.3 Hz, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 167.77, 134.19, 131.87, 123.49, 39.32, 28.08.
(Known compound: ACS Omega. 2021, 6, 33846).

2-(bromomethyl)isoindoline-1,3-dione

According to general procedure A: using 2-(1,3-dioxoisooindolin-2-yl)acetic acid (0.3 mmol, 62 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 ml H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (54 mg, 75% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.93 – 7.85 (m, 4H), 4.96 (s, 2H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 167.83, 135.21, 132.00, 123.77, 60.61.

2-(3-bromopropyl)isoindoline-1,3-dione

According to general procedure A: using 4-(1,3-dioxoisooindolin-2-yl)butanoic acid (0.3 mmol, 70 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 ml H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (65 mg, 81% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.88 – 7.82 (m, 2H), 7.75 – 7.70 (m, 2H), 3.84 (t, $J$ = 6.8 Hz, 2H), 3.41 (t, $J$ = 6.7 Hz, 2H), 2.30 – 2.22 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 168.21, 134.03, 132.04, 123.32, 36.76, 31.66, 29.72.
(Known compound: SynOpen. 2017; 1, 173).

2-(4-bromobutyl)isoindoline-1,3-dione

According to general procedure A: using 4-(1,3-dioxoisooindolin-2-yl)butanoic acid (0.3 mmol, 70 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 ml H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (65 mg, 81% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.88 – 7.82 (m, 2H), 7.75 – 7.70 (m, 2H), 3.84 (t, $J$ = 6.8 Hz, 2H), 3.41 (t, $J$ = 6.7 Hz, 2H), 2.30 – 2.22 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 168.21, 134.03, 132.04, 123.32, 36.76, 31.66, 29.72.
(Known compound: SynOpen. 2017; 1, 173).
According to general procedure A: using 5-(1,3-dioxoisoindolin-2-yl) pentanoic acid (0.3 mmol, 74 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (62 mg, 73% yield).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.86 – 7.81 (m, 2H), 7.74 – 7.69 (m, 2H), 3.72 (t, $J$ = 6.7 Hz, 2H), 3.44 (t, $J$ = 6.3 Hz, 2H), 1.95 – 1.80 (m, 4H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 168.32, 133.95, 132.08, 123.24, 36.97, 32.69, 29.87, 27.25.


\[\text{\ chemfig{\cbrb{\cbrb{2-\text{\textit{5-bromopentyl}}-\text{isoindoline-1,3-dione}}}}}\]

According to general procedure A: using 6-(1,3-dioxoisoindolin-2-yl) hexanoic acid (0.3 mmol, 78 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as colorless oil (62 mg, 70% yield).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.78 – 7.73 (m, 2H), 7.67 – 7.62 (m, 2H), 3.62 (t, $J$ = 7.2 Hz, 2H), 3.32 (t, $J$ = 6.7 Hz, 2H), 1.88 – 1.79 (m, 2H), 1.69 – 1.60 (m, 2H), 1.47 – 1.38 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 168.23, 133.84, 132.08, 123.10, 37.59, 33.32, 32.15, 27.66, 25.35.

(Known compound: ChemPhysChem. 2013, 14, 390).

\[\text{\chemfig{\clb\Br\cbr{\Cl\text{\textit{1-(bromomethyl)-4-chlorobenzene}}}}}\]

According to general procedure A: using 2-(4-chlorophenyl) acetic acid (0.3 mmol, 51 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (50 mg, 81% yield).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.32 (s, 4H), 4.46 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 136.31, 134.32, 130.40, 129.02, 129.02, 32.43.


\[\text{\chemfig{\Br\Br\text{\textit{1-bromo-4-(bromomethyl)benzene}}}}}\]

According to general procedure A: using 2-(4-bromophenyl) acetic acid (0.3 mmol, 65 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (62 mg, 83% yield).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.50 (d, $J$ = 7.5 Hz, 2H), 7.29 (d, $J$ = 8.3 Hz, 2H), 4.46 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 136.80, 131.98, 130.68, 122.48, 32.40.
1-(bromomethyl)-4-nitrobenzene

According to general procedure A: using 2-(4-nitrophenyl) acetic acid (0.3 mmol, 54 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (45 mg, 70% yield).

$^1$H NMR (400 MHz, Chloroform-d) δ 8.23 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H), 4.54 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 147.67, 144.77, 129.93, 124.06, 30.94.

4-(bromomethyl)benzonitrile

According to general procedure A: using 2-(4-cyanophenyl) acetic acid (0.3 mmol, 49 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (41 mg, 69% yield).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.64 (d, J = 7.9 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H), 4.48 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 142.83, 132.60, 129.73, 118.38, 112.22, 31.50.

1-(bromomethyl)-4-(trifluoromethyl)benzene

According to general procedure A: using 2-(4-(trifluoromethyl) phenyl) acetic acid (0.3 mmol, 61 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (54 mg, 76% yield).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.63 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 4.53 (s, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 141.63, 130.51 (q, J = 32.6 Hz), 129.36, 125.79 (q, J = 3.7 Hz), 123.88 (q, J = 273.4 Hz), 31.81.

$^{19}$F NMR (376 MHz, Chloroform-d) δ -62.75.

2-(4-(bromomethyl)phenyl)isoindoline-1,3-dione

According to general procedure A: using 2-(4-(1,3-dioxoisoindolin-2-yl) phenyl) acetic acid (0.3 mmol, 84 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (53 mg, 56% yield).
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.99 (dd, $J = 5.6$, 2.9 Hz, 2H), 7.83 (dd, $J = 5.9$, 3.1 Hz, 2H), 7.56 (d, $J = 8.1$ Hz, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 4.55 (d, $J = 2.5$ Hz, 2H).

$^13$C NMR (101 MHz, Chloroform-$d$) $\delta$ 167.10, 137.49, 134.54, 131.68, 129.84, 126.70, 123.85, 32.59. (Known compound: *Green Chem.* 2011, 13, 928).

![1-(bromomethyl)-(tert-butyl)benzene](image1)

1-(bromomethyl)-(tert-butyl)benzene

According to general procedure A: using 2-(4-(tert-butyl) phenyl) acetic acid (0.3 mmol, 58 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (46 mg, 68% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.39 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 4.51 (s, 2H), 1.33 (s, 9H).

$^13$C NMR (101 MHz, Chloroform-$d$) $\delta$ 151.60, 134.79, 128.81, 125.81, 34.68, 33.67, 31.30. (Known compound: *Org. Lett.* 2013, 15, 2210).

![1-(bromomethyl)-3-nitrobenzene](image2)

1-(bromomethyl)-3-nitrobenzene

According to general procedure A: using 2-(3-nitrophenyl) acetic acid (0.3 mmol, 54 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (45 mg, 69% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.30 – 8.24 (m, 1H), 8.17 (d, $J = 8.5$ Hz, 1H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.54 (td, $J = 8.0$, 1.9 Hz, 1H), 4.54 (s, 2H).

$^13$C NMR (101 MHz, Chloroform-$d$) $\delta$ 148.37, 139.73, 135.02, 129.90, 123.94, 123.33, 31.13. (Known compound: *Green Chem.* 2008, 10, 232).

![2-(bromomethyl)naphthalene](image3)

2-(bromomethyl)naphthalene

According to general procedure A: using 2-(naphthalen-2-yl) acetic acid (0.3 mmol, 56 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (47 mg, 71% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.84 (q, $J = 4.1$ Hz, 4H), 7.51 (dd, $J = 8.2$, 4.7 Hz, 3H), 4.68 (s, 2H).

$^13$C NMR (101 MHz, Chloroform-$d$) $\delta$ 135.10, 133.18, 133.09, 128.80, 127.99, 127.88, 127.75, 126.79, 126.60, 126.50, 34.10. (Known compound: *J. Org. Chem.* 2006, 71, 8276).
According to general procedure A: using 2-([1,1'-biphenyl]-4-yl) acetic acid (0.3 mmol, 64 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (53 mg, 72% yield).

**1H NMR (400 MHz, Chloroform-d)** δ 7.61 – 7.56 (m, 4H), 7.47 (d, J = 7.2 Hz, 4H), 7.38 (d, J = 7.4 Hz, 1H), 4.56 (s, 2H).

**13C NMR (101 MHz, Chloroform-d)** δ 141.41, 140.45, 136.77, 129.52, 128.85, 127.57, 127.13, 33.41.


**5-(bromomethyl)-2-chloropyridine**

According to general procedure A: using 2-(6-chloropyridin-3-yl) acetic acid (0.3 mmol, 52 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as yellow solid (38 mg, 62% yield).

**1H NMR (400 MHz, Chloroform-d)** δ 8.39 (d, J = 2.9 Hz, 1H), 7.69 (dd, J = 8.0, 2.7 Hz, 1H), 7.32 (dd, J = 8.3, 2.1 Hz, 1H), 4.43 (s, 2H).

**13C NMR (101 MHz, Chloroform-d)** δ 151.32, 149.55, 139.43, 132.68, 124.49, 28.40.


**3-bromo-1-phenylpropan-1-one**

According to general procedure A: using 4-oxo-4-phenylbutanoic acid (0.3 mmol, 54 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as colorless oil (45 mg, 71% yield).

**1H NMR (400 MHz, Chloroform-d)** δ 7.99 – 7.93 (m, 2H), 7.63 – 7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 3.75 (t, J = 7.0 Hz 2H), 3.58 (t, J = 7.2 Hz, 2H).

**13C NMR (101 MHz, Chloroform-d)** δ 196.94, 136.29, 133.55, 128.75, 128.05, 41.56, 25.69.

(Known compound: Org. Lett. 2007, 9, 1323).
According to general procedure A: using 2-((3r,5r,7r)-adamantan-1-yl) acetic acid (0.3 mmol, 58 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (38 mg, 56% yield).

1H NMR (400 MHz, Chloroform-d) δ 3.15 (s, 2H), 2.04 – 1.95 (m, 3H), 1.71 – 1.60 (m, 6H), 1.56 (d, J = 3.1 Hz, 6H).

13C NMR (101 MHz, Chloroform-d) δ 48.48, 40.69, 36.70, 33.57, 28.37.

(1-bromo-2-methylpropan-2-yl)benzene

According to general procedure A: using 3-methyl-3-phenylbutanoic acid (0.3 mmol, 53 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (44 mg, 69% yield).

1H NMR (400 MHz, Chloroform-d) δ 7.50 – 7.41 (m, 4H), 7.37 – 7.30 (m, 1H), 3.68 (s, 2H), 1.58 (s, 6H).

13C NMR (101 MHz, Chloroform-d) δ 146.08, 128.43, 126.60, 125.90, 46.92, 39.22, 27.35.

4-bromo-1-(4-fluorophenyl)butan-1-one

According to general procedure A: using 5-(4-fluorophenyl)-5-oxopentanoic acid (0.3 mmol, 63 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as colorless oil (64 mg, 88% yield).

1H NMR (400 MHz, Chloroform-d) δ 8.06 – 7.97 (m, 2H), 7.19 – 7.10 (m, 2H), 3.55 (t, J = 6.3 Hz, 2H), 3.16 (t, J = 6.9 Hz, 2H), 2.37 – 2.26 (m, 2H).

13C NMR (101 MHz, Chloroform-d) δ 197.21, 165.85 (d, J = 254.9 Hz), 133.18 (d, J = 3.0 Hz), 130.68 (d, J = 9.4 Hz), 115.78 (d, J = 21.9 Hz), 36.46, 33.59, 26.79.
19F NMR (376 MHz, Chloroform-d) δ -104.93.
(Known compound: Green Chem. 2020, 22, 4357).

4-bromo-1-((4-chlorophenyl)sulfonyl)piperidine

According to general procedure A: using 1-((4-chlorophenyl) sulfonyl) piperidine-4-carboxylic acid (0.3 mmol, 91 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent:
According to general procedure A: using 1-((4-bromophenyl) sulfonyl) piperidine-4-carboxylic acid (0.3 mmol, 104 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (84 mg, 73% yield).

**1H NMR (400 MHz, Chloroform-d)** δ 7.69 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 4.31 – 4.24 (m, 1H), 3.24 – 3.10 (m, 4H), 2.25 – 2.13 (m, 2H), 2.09 – 1.97 (m, 2H).

**13C NMR (101 MHz, Chloroform-d)** δ 135.59, 132.48, 129.02, 127.97, 47.51, 43.60, 34.61.


According to general procedure A: using 1-((4-fluorophenyl) sulfonyl) piperidine-4-carboxylic acid (0.3 mmol, 86 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (75 mg, 78% yield).

**1H NMR (400 MHz, Chloroform-d)** δ 7.85 (d, J = 5.0 Hz, 2H), 7.29 (d, J = 10.4 Hz, 2H), 4.37 – 4.28 (m, 1H), 3.28 – 3.15 (m, 4H), 2.30 – 2.18 (m, 2H), 2.15 – 2.05 (m, 2H).

**13C NMR (101 MHz, Chloroform-d)** δ 165.26 (d, J = 255.3 Hz), 132.37 (d, J = 9.3 Hz), 116.48 (d, J = 22.5 Hz), 47.64, 43.59, 34.56.

**19F NMR (376 MHz, Chloroform-d)** δ -104.82.


According to general procedure A: using 1-((4-nitrophenyl) sulfonyl) piperidine-4-carboxylic acid (0.3 mmol, 94 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (65 mg, 62% yield).

**1H NMR (400 MHz, Chloroform-d)** δ 8.40 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 4.36 – 4.29 (m, 1H), 3.32 – 3.16 (m, 4H), 2.25 – 2.03 (m, 4H).
$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 150.28, 142.55, 128.70, 124.49, 47.29, 43.36, 34.43.

**HRMS:** C$_{11}$H$_{12}$BrN$_2$O$_4$S [M-H]$^-$; calculated: 346.9701, found: 346.9694.

![Structure](image)

(4-bromopiperidin-1-yl)(phenyl)methanone

According to general procedure A: using 1-benzoylpiperidine-4-carboxylic acid (0.3 mmol, 70 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (58 mg, 72% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.47 – 7.34 (m, 5H), 4.43 (tt, $J = 7.4$, 3.7 Hz, 1H), 3.67 (t, $J = 114.5$ Hz, 4H), 2.25 – 1.86 (m, 4H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 170.49, 135.72, 129.76, 128.54, 126.85, 48.77.

(Known compound: *Org. Lett.* 2011, 13, 2138).

![Structure](image)

tert-butyl 4-bromo-4-methylpiperidine-1-carboxylate

According to general procedure A: using 1-(tert-butoxycarbonyl)-4-methylpiperidine-4-carboxylic acid (0.3 mmol, 73 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as colorless oil (62 mg, 74% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 4.12 – 3.85 (m, 2H), 3.13 (t, $J = 12.5$ Hz, 2H), 1.97 (d, $J = 14.4$ Hz, 2H), 1.84 (s, 3H), 1.54 (td, $J = 13.4$, 12.0, 4.1 Hz, 2H), 1.42 (s, 9H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 154.63, 79.67, 67.82, 41.55, 35.01, 28.43. (one carbon signal is overlapped)


![Structure](image)

methyl 4-bromobicyclo[2.2.2]octane-1-carboxylate

According to general procedure A: using 4-(methoxycarbonyl) bicyclo [2.2.2] octane-1-carboxylic acid (0.3 mmol, 64 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (60 mg, 81% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) δ 3.63 (s, 3H), 2.37 – 2.14 (m, 6H), 2.00 – 1.91 (m, 6H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 177.12, 62.16, 51.89, 36.87, 36.83, 31.17.

(3r,5r,7r)-1-bromoadamantane

According to general procedure A: using (3r,5r,7r)-adamantane-1-carboxylic acid (0.3 mmol, 52 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (54 mg, 83% yield).

¹H NMR (400 MHz, Chloroform-d) δ 2.37 (d, J = 3.0 Hz, 6H), 2.13 – 2.07 (m, 3H), 1.73 (t, J = 3.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d) δ 66.67, 49.35, 35.56, 32.62.


(1R,3S,5S,7S)-5-bromoadamantan-2-one

According to general procedure A: using (1S,3R,5S,7S)-4-oxoadamantane-1-carboxylic acid (0.3 mmol, 58 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (52 mg, 76% yield).

¹H NMR (400 MHz, Chloroform-d) δ 2.73 – 2.42 (m, 8H), 2.26 (s, 1H), 2.12 – 1.96 (m, 4H).

¹³C NMR (101 MHz, Chloroform-d) δ 214.44, 59.94, 49.07, 49.00, 47.79, 37.52, 31.30.

(Known compound: Org. Lett. 2010, 12, 332).

(3-bromo-3-methylbutyl)benzene

According to general procedure A: 2,2-dimethyl-4-phenylbutanoic acid (0.3 mmol, 58 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (49 mg, 72% yield).

¹H NMR (400 MHz, Chloroform-d) δ 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 2.91 – 2.84 (m, 2H), 2.14 – 2.07 (m, 2H), 1.84 (s, 6H).

¹³C NMR (101 MHz, Chloroform-d) δ 141.62, 128.51, 128.45, 126.01, 67.55, 49.47, 34.31, 32.93.

(Known compound: Science. 2022, 376, 410).

(3-(1-bromoethyl)phenyl)(phenyl)methanone

According to general procedure A: using ketoprofen (0.3 mmol, 76 mg), 1-bromopyrrolidine-2,5-dione
(0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as yellow oil (70 mg, 81% yield).

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\text{)} \delta 7.88 (s, 1H), 7.81 (d, J = 7.6 Hz, 2H), 7.69 (t, J = 7.6 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.54 – 7.44 (m, 3H), 5.25 (q, J = 7.0 Hz, 1H), 2.07 (d, J = 6.8 Hz, 3H) \]

\[ ^13C \text{ NMR (101 MHz, Chloroform-}d\text{)} \delta 196.18, 143.67, 137.98, 137.32, 132.65, 130.87, 130.08, 130.05, 128.71, 128.40, 128.23, 48.40, 26.76. \]


4-(1-bromoethyl)-2-fluoro-1,1'-biphenyl

According to general procedure A: using flurbiprofen (0.3 mmol, 73 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (61 mg, 73% yield).

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\text{)} \delta 7.60 – 7.54 (m, 2H), 7.51 – 7.39 (m, 4H), 7.34 – 7.27 (m, 2H), 5.24 (q, J = 7.0 Hz, 1H), 2.10 (d, J = 6.9 Hz, 3H) \]

\[ ^13C \text{ NMR (101 MHz, Chloroform-}d\text{)} \delta 159.54 (d, J = 249.2 Hz), 144.49 (d, J = 7.2 Hz), 135.23, 130.95 (d, J = 3.8 Hz), 129.13, 128.96 (d, J = 2.9 Hz), 128.51, 127.90, 47.94, 26.63. \]

\[ ^19F \text{ NMR (376 MHz, Chloroform-}d\text{)} \delta -117.04. \]


2-((1-(bromomethyl)cyclohexyl)methyl)isoindoline-1,3-dione

According to general procedure A: using 2-(1-((1,3-dioxoisoindolin-2-yl) methyl) cyclohexyl) acetic acid (0.3 mmol, 91 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as colorless oil (62 mg, 61% yield).

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\text{)} \delta 7.89 – 7.83 (m, 2H), 7.76 – 7.70 (m, 2H), 3.70 (s, 2H), 3.53 (s, 2H), 1.72 – 1.60 (m, 4H), 1.58 – 1.43 (m, 2H), 1.41 – 1.24 (m, 4H) \]

\[ ^13C \text{ NMR (101 MHz, Chloroform-}d\text{)} \delta 169.09, 134.05, 131.99, 123.34, 45.55, 41.35, 39.07, 32.46, 25.51, 21.36. \]

2-((4-bromocyclohexyl)(methyl)isoindoline-1,3-dione

According to general procedure A: using 4-((1,3-dioxoisoinolin-2-yl) methyl) cyclohexane-1-carboxylic acid (0.3 mmol, 86 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as colorless oil (72 mg, 72% yield).

¹H NMR (400 MHz, Chloroform-d) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 4.58 (p, J = 3.5 Hz, 0.62 H) (major), 4.00 – 3.93 (m, 0.40) (minor), 3.61 (d, J = 7.3 Hz, 1.32H) (major), 3.52 (d, J = 7.1 Hz, 1H), 2.36 – 2.26 (m, 1H), 2.14 – 2.05 (m, 1H), 1.94 – 1.69 (m, 4H), 1.62 – 1.52 (m, 2H), 1.28 – 1.09 (m, 1H).

¹³C NMR (101 MHz, Chloroform-d) δ 168.62 (major), 168.57 (minor), 134.03 (minor), 133.97 (major), 132.00 (major), 131.93 (minor), 123.31 (minor), 123.27 (major), 53.67, 51.36, 43.35 (major), 43.30 (minor), 37.17, 36.04, 35.62, 33.96, 31.31, 25.40.

HRMS: C₁₅H₁₇BrNO₂ [M+H]⁺; calculated: 322.0442, found: 322.0440.

According to general procedure A: using monomethylsuccinate (0.3 mmol, 77 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (68 mg, 78% yield).

¹H NMR (400 MHz, Chloroform-d) δ 4.74 (td, J = 10.8, 4.0 Hz, 1H), 3.58 (t, J = 6.7 Hz, 2H), 2.89 (t, J = 6.9 Hz, 2H), 2.04 – 1.83 (m, 2H), 1.72 – 1.64 (m, 2H), 1.55 – 1.32 (m, 2H), 1.30 – 1.15 (m, 1H), 1.11 – 0.96 (m, 2H), 0.92 – 0.87 (m, 6H), 0.76 (d, J = 7.0 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 170.09, 46.96, 40.85, 38.13, 34.20, 31.40, 26.26, 23.36, 22.01, 20.76, 16.28.

HRMS: C₁₃H₂₁BrNaO₂ [M+Na]⁺; calculated: 313.0779, found: 313.0775.

1-bromo-4-((4-bromo-4-methylpentyl)oxy)-2,5-dimethylbenzene

According to general procedure A: using gemfibrozil (0.3 mmol, 99 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O.
Purification by flash column chromatography (elucent: PE/EA = 100:1) gave the title compound as colorless oil (69 mg, 63% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.28 (s, 1H), 6.70 (s, 1H), 3.98 (t, $J = 6.1$ Hz, 2H), 2.36 (s, 3H), 2.18 (s, 3H), 1.91 – 1.84 (m, 2H), 1.81 – 1.76 (m, 2H), 1.29 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 156.18, 135.68, 133.70, 126.27, 114.74, 113.75, 82.51, 68.49, 34.47, 24.00, 23.91, 22.89, 15.51.

HRMS: C$_{15}$H$_{21}$Br$_2$O$_3$ [M+HCOO]$^-$; calculated: 408.9837, found: 408.9832.

According to general procedure A: using 3-acetyllithocholic acid (0.3 mmol, 126 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), $t$-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (elucent: PE/EA = 50:1) gave the title compound as white solid (96 mg, 71% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 4.72 (tt, $J = 11.6$, 6.3, 5.5 Hz, 1H), 3.55 – 3.44 (m, 1H), 3.42 – 3.29 (m, 1H), 2.06 – 1.92 (m, 5H), 1.89 – 1.77 (m, 4H), 1.71 – 1.65 (m, 1H), 1.61 – 1.35 (m, 10H), 1.29 – 1.20 (m, 3H), 1.18 – 1.00 (m, 6H), 0.92 (s, 6H), 0.66 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 170.65, 74.40, 56.51, 56.13, 42.86, 41.89, 40.41, 40.16, 39.34, 35.78, 35.11, 35.04, 34.60, 32.26, 32.10, 28.25, 27.02, 26.65, 26.32, 24.17, 23.35, 21.51, 20.83, 18.11, 12.04.


2-(2-iodoethyl)isoindoline-1,3-dione

According to general procedure B: using 3-(1,3-dioxoisindolin-2-yl) propanoic acid (0.3 mmol, 66 mg), 1-iodopyrrolidin-2,5-dione (0.45 mmol, 101 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (elucent: PE/EA = 50:1) gave the title compound as white solid (70 mg, 78% yield).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.93 – 7.82 (m, 2H), 7.79 – 7.69 (m, 2H), 4.08 (t, $J = 7.2$ Hz, 2H), 3.40 (t, $J = 7.3$ Hz, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 167.67, 134.26, 131.85, 123.55, 40.06.


tert-butyl 3-iodoazetidine-1-carboxylate

According to general procedure B: using 1-(tert-butoxycarbonyl) azetidine-3-carboxylic acid (0.3
mmol, 60 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (54 mg, 63% yield).

¹H NMR (400 MHz, Chloroform-d) δ 4.66 – 4.58 (m, 2H), 4.49 – 4.41 (m, 1H), 4.30 – 4.23 (m, 2H), 1.42 (s, 9H).

¹³C NMR (101 MHz, Chloroform-d) δ 155.57, 80.13, 61.56, 28.32, 2.63.

(Known compound: *Org. Lett.* 2019, 21, 2285).

According to general procedure B: using 1-(tert-butoxycarbonyl) pyrrolidine-3-carboxylic acid (0.3 mmol, 65 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (56 mg, 63% yield).

¹H NMR (400 MHz, Chloroform-d) δ 4.44 – 4.27 (m, 1H), 3.87 – 3.72 (m, 1.41H), 3.72 – 3.62 (m, 0.58H), 3.61 – 3.50 (m, 1H), 3.47 – 3.35 (m, 1H), 2.34 – 2.13 (m, 2H), 1.46 (s, 9H).

¹³C NMR (101 MHz, Chloroform-d) δ [154.27, 154.12], [79.78, 79.72], [57.39, 57.06], [45.07, 44.75], [38.39, 37.61], 28.48, 19.97.

(Known compound: *Org. Lett.* 2019, 21, 2285).

According to general procedure B: using 5-(tert-butoxy)-4-((tert-butoxycarbonyl) amino)-5-oxopentanoic acid (0.3 mmol, 91 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (71 mg, 62% yield).

¹H NMR (400 MHz, Chloroform-d) δ 5.22 – 4.98 (m, 1H), 4.23 – 4.10 (m, 1H), 3.20 – 3.08 (m, 2H), 2.43 – 2.27 (m, 1H), 2.19 – 2.07 (m, 1H), 1.45 (s, 9H), 1.43 (s, 9H).

¹³C NMR (101 MHz, Chloroform-d) δ 170.59, 155.34, 82.49, 79.98, 54.98, 37.66, 28.32, 27.99, -0.44.

BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (58 mg, 72% yield).

¹H NMR (400 MHz, Chloroform-d) δ 4.69 – 4.60 (m, 0.64H) (major), 4.21 – 4.06 (m, 0.38H) (minor), 3.68 (d, J = 16.7 Hz, 3H), 2.43 – 2.38 (m, 1H), 2.17 – 1.88 (m, 4H), 1.88 – 1.49 (m, 4H).

¹³C NMR (101 MHz, Chloroform-d) δ 175.63 (minor), 175.19 (major), 51.75 (major), 51.74 (minor), 41.49 (minor), 41.39 (major), 38.78, 35.88, 32.61, 30.63, 28.06, 26.15.


According to general procedure B: using tetrahydro-2H-thiopyran-4-carboxylic acid 1,1-dioxide (0.3 mmol, 54 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (59 mg, 76% yield).

¹H NMR (400 MHz, Chloroform-d) δ 4.66 (p, J = 4.2 Hz, 1H), 3.43 – 3.29 (m, 2H), 3.08 – 2.94 (m, 2H), 2.48 (q, J = 4.4 Hz, 4H).

¹³C NMR (101 MHz, Chloroform-d) δ 50.36, 35.33, 24.62.

(Known compound: PCT Int. Appl. 2011, 2011128455).

According to general procedure B: using camphorsulfonic acid (0.3 mmol, 59 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as white solid (65 mg, 77% yield).

¹H NMR (400 MHz, Chloroform-d) δ 2.53 – 2.38 (m, 2H), 1.88 – 1.79 (m, 1H), 1.75 – 1.67 (m, 1H), 1.20 (s, 3H), 1.00 (s, 3H), 0.86 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 177.52, 56.43, 49.58, 40.70, 30.13, 18.86, 17.50, 10.62.

(Known compound: PCT Int. Appl. 2015, 2015068159).

According to general procedure B: using (R)-3-((1,3-dioxoisindolin-2-yl) methyl)-5-methylhexanoic acid (0.3 mmol, 87 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as yellow oil (85 mg, 76% yield).
According to general procedure B: using 3α, 6α-tos-hyodeoxycholic acid (0.3 mmol, 210 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as white solid (143 mg, 61% yield).

**$^1$H NMR (400 MHz, Chloroform-$d$)** δ 7.78 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 7.9$ Hz, 2H), 7.34 (t, $J = 8.0$ Hz, 4H), 4.78 (dt, $J = 12.3$, 4.9 Hz, 1H), 4.29 (tt, $J = 11.1$, 4.6 Hz, 1H), 3.29 (td, $J = 9.2$, 3.6 Hz, 1H), 3.08 (q, $J = 8.4$ Hz, 1H), 2.46 (s, 6H), 2.04 – 1.90 (m, 2H), 1.84 – 1.68 (m, 4H), 1.66 – 1.59 (m, 2H), 1.54 – 1.36 (m, 6H), 1.33 – 1.16 (m, 6H), 1.15 – 1.02 (m, 4H), 0.88 (d, $J = 6.1$ Hz, 3H), 0.80 (s, 3H), 0.61 (s, 3H).

**$^{13}$C NMR (101 MHz, Chloroform-$d$)** δ 144.71, 144.68, 134.49, 134.47, 129.85, 129.81, 127.62, 127.54, 81.76, 55.82, 55.66, 46.32, 42.93, 40.10, 39.60, 39.45, 37.03, 36.15, 34.83, 34.81, 32.09, 27.98, 27.40, 26.46, 23.90, 22.90, 21.71, 21.69, 20.52, 17.76, 11.99, 5.12.

**HRMS:** C$_{37}$H$_{52}$INO$_6$ [M+Na]$^+$; calculated: 805.2069, found: 805.2069.

**48**

According to general procedure C: using 5-(4-fluorophenyl)-5-oxopentanoic acid (0.3 mmol, 63 mg), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (0.15 mmol, 35 mg), CeCl$_3$ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H$_2$O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as yellow oil (43 mg, 72% yield).

**$^1$H NMR (400 MHz, Chloroform-$d$)** δ 8.05 – 7.96 (m, 2H), 7.13 (t, $J = 8.6$ Hz, 2H), 3.67 (t, $J = 6.2$ Hz, 2H), 3.15 (t, $J = 7.0$ Hz, 2H), 2.22 (p, $J = 6.6$ Hz, 2H).

**$^{13}$C NMR (101 MHz, Chloroform-$d$)** δ 197.34, 165.82 (d, $J = 254.9$ Hz), 133.19 (d, $J = 3.0$ Hz), 130.66 (d, $J = 9.2$ Hz), 115.76 (d, $J = 21.8$ Hz), 44.64, 35.19, 26.69.

**$^{19}$F NMR (376 MHz, Chloroform-$d$)** δ -105.03. 
(Known compound: *J. Am. Chem. Soc.* 2022, 144, 13895).
According to general procedure C: using 4-(methoxycarbonyl) bicyclo [2.2.2] octane-1-carboxylic acid (0.3 mmol, 64 mg), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (0.15 mmol, 35 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE/EA = 30:1) gave the title compound as colorless oil (42 mg, 69% yield).

\(^1\)H NMR (400 MHz, Chloroform-d) δ 3.63 (s, 3H), 2.10 – 2.01 (m, 6H), 1.98 – 1.90 (m, 6H).

\(^{13}\)C NMR (101 MHz, Chloroform-d) δ 177.07, 66.23, 51.86, 37.51, 35.54, 30.36.


\(\text{Cl}\)

\(\text{O}\)

\(\text{methyl}\)

\(\text{5-chloropentanoate}\)

According to general procedure C: using 6-methoxy-6-oxohexanoic acid (0.3 mmol, 48 mg), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (0.15 mmol, 35 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (28 mg, 62% yield).

\(^1\)H NMR (400 MHz, Chloroform-d) δ 3.67 (s, 3H), 3.54 (t, \(J = 6.3\) Hz, 2H), 2.35 (t, \(J = 6.7\) Hz, 2H), 1.87 – 1.72 (m, 4H).

\(^{13}\)C NMR (101 MHz, Chloroform-d) δ 173.63, 51.61, 44.45, 33.18, 31.84, 22.23.


\(\text{Cl}\)

\(\text{C}\)

\(\text{Cl}\)

\(\text{52}\)

\((1\text{-chloro-2-methylpropan-2-yl)}\text{benzene}\)

According to general procedure C: using 6-methoxy-6-oxohexanoic acid (0.3 mmol, 54 mg), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (0.15 mmol, 35 mg), CeCl₃ (0.03 mmol, 7.4 mg), t-BuONa (0.09 mmol, 8.6 mg) and 3 mL H₂O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (31 mg, 61% yield).
\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.45 – 7.35 (m, 4H), 7.31 – 7.26 (m, 1H), 3.70 (s, 2H), 1.48 (s, 6H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 146.03, 128.35, 126.50, 125.93, 56.36, 39.80, 26.45.

VI. Application of the methodology

**Gram-scale synthesis**

![Chemical structure of compounds](image)

In a dry 100 mL round-bottom flask was added 3-(1,3-dioxoisoindolin-2-yl) propanoic acid (5 mmol), 1-bromopyrrolidine-2,5-dione (7.5 mmol) in 20 mL H$_2$O under air atmosphere. The resulting solution was stirred for 12 h at room temperature under 100W Blue lights. On completion, the resulting solution was diluted with DCM (30 mL). Then, poured into an extraction funnel, the organic phase was washed with brine (1 x 20 mL), dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA (100/1) as eluent gave the compound 37 as white solid (0.889 g, 70% yield).

Figure S3. 100 W blue LED light setup for gram-scale reaction.
Synthesis of drug

In a dry 100 mL round-bottom flask were added 4-bromo-1-(4-fluorophenyl) butan-1-one 20 (1 mmol, 1.0 equiv.), 4-(4-chlorophenyl) piperidin-4-ol (1.5 mmol, 1.5 equiv.), NaI (15 mg, 0.1 mmol, 0.1 equiv), K$_2$CO$_3$ (207 mg, 1.5 mmol, 1.5 equiv.), and anhydrous MeCN (20 mL) in an N$_2$ glovebox. The vial was sealed and transferred out of glovebox. The reaction mixture was reflux for 4 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the desired product haloperidol 51 (271 mg, 72%) (eluent: PE/EA = 1/1): yellow solid.

In a dry 100 mL round-bottom flask were added 4-bromo-1-(4-fluorophenyl) butan-1-one 20 (1 mmol, 1.0 equiv.), 1-(pyridin-2-yl) piperazine (1.5 mmol, 1.5 equiv.), NaI (15 mg, 0.1 mmol, 0.1 equiv), K$_2$CO$_3$ (207 mg, 1.5 mmol, 1.5 equiv.), and anhydrous MeCN (20 mL) in an N$_2$ glovebox. The vial was sealed and transferred out of glovebox. The reaction mixture was reflux for 4 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the desired product azaperone 52 (242 mg, 74%) (eluent: PE/EA = 1/1): yellow solid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.07 – 7.99 (m, 2H), 7.43 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.19 – 7.11 (m, 2H), 3.00 (t, $J$ = 7.0 Hz, 2H), 2.85 – 2.75 (m, 2H), 2.54 – 2.38 (m, 4H), 2.07 – 1.95 (m, 4H), 1.72 – 1.65 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 198.39, 165.63 (d, $J$ = 254.5 Hz), 146.94, 133.68 (d, $J$ = 3.0 Hz), 132.73, 130.69 (d, $J$ = 9.2 Hz), 128.37, 126.11, 115.62 (d, $J$ = 21.9 Hz), 71.08, 57.85, 49.33, 38.38, 36.26, 21.90.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -105.65.

(Known compound: ACS Catal. 2020, 10, 7543).
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.17 (dd, $J = 4.9, 1.9$ Hz, 1H), 8.00 (dd, $J = 8.6, 5.4$ Hz, 2H), 7.52 - 7.41 (m, 1H), 7.12 (t, $J = 8.5$ Hz, 2H), 6.68 - 6.55 (m, 2H), 3.51 (t, $J = 5.0$ Hz, 4H), 3.01 (t, $J = 7.0$ Hz, 2H), 2.57 (t, $J = 5.0$ Hz, 4H), 2.48 (t, $J = 7.1$ Hz, 2H), 2.00 (p, $J = 7.0$ Hz, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 198.39, 165.66 (d, $J = 254.3$ Hz), 159.49, 147.97, 137.44, 130.67 (d, $J = 9.2$ Hz), 115.63 (d, $J = 21.8$ Hz), 113.31, 107.06, 57.70, 52.89, 45.06, 36.13, 21.42.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -105.58.

VII. Control experiments

(a) 

(b) 

(c) 

(d) 

The reaction was completely inhibited by free radical inhibitors, and the radical adducts was detected by HRMS ((M+H) $^+$ =331.2022)

Figure S4. HRMS data of TEMPO adduct
VIII. UV-visible absorption Spectra

UV-Vis experiments were performed to analyse the ligand-to-metal-charge-transfer (LMCT) process between cerium catalyst and alkyl carboxylic acids. For verification, \((\text{n-Bu}_4\text{N})_2\text{Ce}^{IV}\text{Cl}_6\) was chosen as a Ce(IV) source according to one reported by Zuo et al. In order to ensure the solubility, acetonitrile (similar yield to the model reaction) was selected as the solvent.

Preparation of a stock solution (solution A): In a glass vial equipped with a teflon-coated stirring bar and a septum, \((\text{n-Bu}_4\text{N})_2\text{Ce}^{IV}\text{Cl}_6\) (25.1 mg, 0.03 mmol) were dissolved in MeCN (3 mL). Dilute 66 µL of the above solution to 6 mL to obtain solution A.

Preparation of a stock solution (solution B): In a glass vial equipped with a teflon-coated stirring bar and a septum, \((\text{n-Bu}_4\text{N})_2\text{Ce}^{IV}\text{Cl}_6\) (25.1 mg, 0.03 mmol) and 1-adamantane carboxylic acid (54.1 mg, 0.3 mmol) were dissolved in MeCN (3 mL). Dilute 66 µL of the above solution to 6 mL to obtain solution B.

UV-Visible absorption spectra of solution A

UV-Vis spectra were recorded after irradiation the cuvette solution A with 100 W blue LED light.

![Figure S5. UV-Visible spectra of a solution of \((\text{n-Bu}_4\text{N})_2\text{Ce}^{IV}\text{Cl}_6\) without acid after irradiation with 100 W blue LED light.](image)

As shown in Figure S5, in the absence of acid, Ce(IV) \((\lambda_{\text{max}} \approx 380 \text{ nm})\) absorbance hardly changed with the increase of irradiation time.
UV-Visible absorption spectra of solution B

UV-Vis spectra were recorded after irradiation the cuvette solution B with 100 W blue LED light.

Figure S6. UV-Visible spectra of a solution of \((n-\text{Bu}_4\text{N})_2\text{Ce}^{\text{IV}}\text{Cl}_6\) with acid after irradiation with 100 W blue LED light.

When the 100 W blue LED was switched-on, the fast consumption of Ce\text{IV} (\(\lambda_{\text{max}} \approx 380\) nm) was observed and the absorbance of Ce\text{III} (\(\lambda_{\text{max}} \approx 330\) nm) gradually increases, which demonstrated that in the presence of carboxylic acid, the Ce\text{IV} was rapidly reduced to Ce\text{III} after gradually increasing the illumination time.
In order to investigate the effect of the strong oxidant TCCA on the reaction, the following UV-VIS experiments were performed.

Preparation of a stock solution (solution C): In a glass vial equipped with a teflon-coated stirring bar and a septum, CeCl$_3$ (7.4 mg, 0.03 mmol) were dissolved in H$_2$O (3 mL). Dilute 66 µL of the above solution to 6 mL to obtain solution C.

Preparation of a stock solution (solution D): In a glass vial equipped with a teflon-coated stirring bar and a septum, TCCA (34.9 mg, 0.15 mmol) were dissolved in H$_2$O (3 mL). Dilute 66 µL of the above solution to 6 mL to obtain solution D.

Preparation of a stock solution (solution E): In a glass vial equipped with a teflon-coated stirring bar and a septum, CeCl$_3$ (7.4 mg, 0.03 mmol), TCCA (34.9 mg, 0.15 mmol) were dissolved in H$_2$O (3 mL). The solution was stirred for 10 h at room temperature. Dilute 66 µL of the above solution to 6 mL to obtain solution E.

UV-Visible absorption spectra of solution C, solution D and solution E

Figure S7. UV-Visible spectra of a solution C, solution D and solution E

As show in Figure S7, no absorption of Ce$^{IV}$ ($\lambda_{max} \approx 380$ nm) was observed at 380 nm. Thus, it could be speculated that Ce$^{III}$ cannot be oxidized to Ce$^{IV}$ by TCCA.
IX. Electron paramagnetic resonance (EPR) experiment

In order to determine the active species of oxygen involved in the present reaction, 5,5-dimethylpyrrole-N-oxide (DMPO) were employed to capture $\text{O}_2^\cdot$ ($g = 2.0069$).

To a dried 8 mL vial was added 3-(1,3-dioxoisoindolin-2-yl) propanoic acid (0.3 mmol), 1-bromopyrrolidine-2,5-dione (NBS) (1.0-1.5 equiv.), CeCl$_3$ (10 mol %), $t$-BuONa (30 mol %), DMPO (5,5-dimethyl-1-pyrrole N-oxide, 15 μL) in 3 mL H$_2$O under air atmosphere. The resulting solution was stirred under 100 W blue light for 30 min (25 °C). After that, the solution sample was taken out into a small tube and analyzed by EPR. As show in Figure S6, there was a strong characteristic signal of $\text{O}_2^\cdot$ adduct with DMPO when the DMPO was added into model reaction.

![Figure S8](image-url)

**Figure S8.** Electron spin resonance (ESR) spectra of DMPO with $\text{O}_2^\cdot$
X. KI-starch test for the detection of hydrogen peroxide ($H_2O_2$) in the reaction

It was anticipated that $H_2O_2$ may be one of the reasonable by-products of the photo-induced halodecarboxylation reaction, which was confirmed by KI/starch test.

To a dried 8 mL vial was added 3-(1,3-dioxoisoindolin-2-yl) propanoic acid (0.3 mmol), 1-bromopyrrolidin-2,5-dione (NBS) (1.0-1.5 equiv.), CeCl$_3$ (10 mol %), $t$-BuONa (30 mol %) in 3 mL $H_2O$ under air atmosphere. The resulting solution was stirred under 100 W blue light for 12 h ($25 ^\circ C$). After that, the KI-starch paper was immersed in the reaction solution and quickly turned into dark purple colour (Figure S7), which confirms the formation of $H_2O_2$.

![Figure S9](image)

**Figure S9.** Detection of hydrogen peroxide ($H_2O_2$) using KI-starch paper

Reference:

XI. Copied of NMR spectra

$^1$H NMR of compound 2

$^{13}$C NMR of compound 2
$^1$H NMR of compound 3

$^{13}$C NMR of compound 3
$^1$H NMR of compound 4

$^{13}$C NMR of compound 4
$^1$H NMR of compound 5

$^{13}$C NMR of compound 5
$^1$H NMR of compound 7

$^{13}$C NMR of compound 7
$^{1}H$ NMR of compound 8

$^{13}C$ NMR of compound 8
$^1$H NMR of compound 9

$^{13}$C NMR of compound 9
\( ^1\text{H NMR of compound 10} \)

\( \text{Br}^- \)

\( \text{N} \)

\( ^1\text{C NMR of compound 10} \)

\( -142.35 \)

\( -132.60 \)

\( -123.75 \)

\( -118.78 \)

\( -112.22 \)

\( -31.39 \)
$^1$H NMR of compound 11

$^{13}$C NMR of compound 11
\( ^{19}\text{F} \text{NMR of compound 11} \)

\[ \text{Structure Image} \]

\( ^{1}\text{H} \text{NMR of compound 12} \)

\[ \text{Structure Image} \]
$^{13}\text{C}$ NMR of compound 12

$^1\text{H}$ NMR of compound 13
$^{13}$C NMR of compound 13

$^1$H NMR of compound 14
$^{13}$C NMR of compound 14

$^1$H NMR of compound 15
$^{13}$C NMR of compound 15

$^1$H NMR of compound 16
$^{13}$C NMR of compound 16

$^1$H NMR of compound 17
$^{13}$C NMR of compound 17

$^1$H NMR of compound 18
$^{13}$C NMR of compound 18

$^1$H NMR of compound 19
$^{13}$C NMR of compound 19

$^{1}$H NMR of compound 20
$^{13}$C NMR of compound 20

$^1$H NMR of compound 21

S52
$^{13}$C NMR of compound 21

$^{19}$F NMR of compound 21
$^1$H NMR of compound 22

$^{13}$C NMR of compound 22
$^1$H NMR of compound 23

$^{13}$C NMR of compound 23
$^1$H NMR of compound 24

$^{13}$C NMR of compound 24
$^{19}$F NMR of compound 24

$^1$H NMR of compound 25
$^{13}$C NMR of compound 25

$^1$H NMR of compound 26
$^{13}$C NMR of compound 26

$^1$H NMR of compound 27
$^{13}$C NMR of compound 27

$^1$H NMR of compound 28
$^{13}$C NMR of compound 29

$^{1}$H NMR of compound 30
$^{13}$C NMR of compound 30

$^1$H NMR of compound 31
$^{13}$C NMR of compound 31

H NMR of compound 32
$^{13}$C NMR of compound 32

$^1$H NMR of compound 33
\[ \text{\[^{13}C\ \text{NMR of compound 33}} \]

\[ \text{\[^{19}F\ \text{NMR of compound 33}} \]
$^1$H NMR of compound 34

$^{13}$C NMR of compound 34
$^1$H NMR of compound 35

$^{13}$C NMR of compound 35
$^1$H NMR of compound 36

$^{13}$C NMR of compound 36
$^1$H NMR of compound 37

$^{13}$C NMR of compound 37
$^1$H NMR of compound 38

$^{13}$C NMR of compound 38
$^1$H NMR of compound 39

$^{13}$C NMR of compound 39
$^1$H NMR of compound 41

$^{13}$C NMR of compound 41
$^1$H NMR of compound 42

$^{13}$C NMR of compound 42
$^1$H NMR of compound 43

$^{13}$C NMR of compound 43
$^1$H NMR of compound 44

$^{13}$C NMR of compound 44
$^{1}$H NMR of compound 45

$^{13}$C NMR of compound 45
$^1$H NMR of compound 46

$^{13}$C NMR of compound 46
H NMR of compound 47

\begin{figure}
\centering
\includegraphics[width=\textwidth]{hnmr}
\caption{H NMR spectrum of compound 47.}
\end{figure}

C NMR of compound 47

\begin{figure}
\centering
\includegraphics[width=\textwidth]{cmr}
\caption{C NMR spectrum of compound 47.}
\end{figure}
$^1$H NMR of compound 48

$^{13}$C NMR of compound 48
$^{19}\text{F NMR of compound 48}$

$^{1}\text{H NMR of compound 49}$
$^{13}$C NMR of compound 49

$^1$H NMR of compound 50
$^{13}$C NMR of compound 50

$^1$H NMR of compound 51
$^{13}\text{C NMR of compound 51}$

$^{1}\text{H NMR of compound 52}$
$^{13}$C NMR of compound 52

$^1$H NMR of compound 53
$^1$H NMR of compound 54

$^{13}$C NMR of compound 54
$^{19}$F NMR of compound 54