Supporting Information

Decarboxylative Sulfenylation of Carboxylic Acids via Metallaphotoredox Catalysis

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General information

Unless otherwise noted, all the reagents were obtained commercially and used without further purification. Solvents used directly. Chromatographic purification of products was accomplished by column chromatography on silica gel (Qingdao Haiyang, 200-300 mesh). Thin layer chromatography (TLC) was performed on Jianqiang Weiye 0.2 mm silica gel plates. All NMR spectra were recorded on Bruker-400 MHz spectrometer and Bruker-500 MHz spectrometer. HRMS were measured on the Q-TOF6510 instruments. The light source for the reaction is 8W 450nm blue LED. Thermo Scientific Lumina Fluorescence Instrument was used for Emission Quenching Experiments.

Synthesis of the starting materials:

\[
\text{N-Cl} + \text{R-SH} \xrightarrow{\text{Et}_3\text{N}} \text{N-S-R} \qquad \text{14–85\% yield}
\]

To a solution of N-chlorosuccinimide (NCS; 1.0 equiv) in CH₂Cl₂ (5.0 mL for 2.0 mmol) was added thiophenol 1(1.0 equiv) and Et₃N (1.0 equiv) dropwise at 0 °C under argon. The resulting mixture was stirred at room temperature for 12 h. Upon completion, the reaction was quenched by the addition of a saturated aqueous NH₄Cl solution. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (2 × 10 mL, for 1.0 mmol). The combined organic extracts were washed with brine and dried with Na₂SO₄. After filtration, the mixture was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1).
**General Procedure for the Sulfur arylation of Carboxylic Acids**

A mixture of Boc-Pro-OH 1a (0.4 mmol), N-(Arylthio)succinimides 4a (0.2 mmol), PC-1 (1 mol%), Ni(acac)$_2$ (10 mol%), dtbpy (15 mol%), K$_2$HPO$_4$ (1.2 equiv), 1,4-dioxane (1 mL) was stirred at room temperature under irradiation with 8 W blue LED at N$_2$ atmosphere for 24 h. The organic layer was filtered on celite and evaporated under reduced pressure. The crude reaction mixture was purified by silica gel flash chromatography to afford the desired product.

**Optimization of the Photocatalyst and Solvent**

![Chemical structures](image)

<table>
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<th>Entry</th>
<th>PC</th>
<th>Solvent</th>
<th>T/°C</th>
<th>Time/h</th>
<th>Yield(%)</th>
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<td>6</td>
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<td>&lt;5</td>
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<tr>
<td>7</td>
<td>PC-1</td>
<td>1,4-dioxane</td>
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<td>&lt;5</td>
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<tr>
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*Table S1. Reaction conditions: a mixture of 1a (0.2 mmol), 4a (0.4 mmol), K$_2$HPO$_4$ (0.24 mmol), photocatalyst (0.002 mmol), in 1,4-dioxane (1 mL) was stirred at room temperature under irradiation of LED at N$_2$ atmosphere.*
Optimization of Metal and Ligand

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<th>entry</th>
<th>[M]</th>
<th>Ligand</th>
<th>T/°C</th>
<th>Time/h</th>
<th>Yield(%)</th>
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<td>65</td>
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<td>&lt;5</td>
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<td>r.t.</td>
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Table S2. Reaction conditions: a mixture of 1a (0.2 mmol), 4a (0.4 mmol), K₂HPO₄ (0.24 mmol), PC-1 (0.002 mmol), in 1,4-dioxane (1 mL) was stirred at room temperature under irridiation of LED at N₂ atmosphere.

Control Experiment
Table S3. Reaction conditions: a mixture of 1a (0.2 mmol), 4a (0.4 mmol), K$_2$HPO$_4$ (0.24 mmol), PC-1 (0.002 mmol), in 1,4-dioxane (1 mL) was stirred at room temperature under irradiation of LED at N$_2$ atmosphere.

Emission Quenching Experiments for PC-1

Emission intensities were recorded using a HITACHI F-4500 Fluorescence Spectrometer. All (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ solutions were excited at 380 nm and the emission intensity at 477 nm was observed. 1,4-dioxane was degassed with a stream of N$_2$ for 30 min and then moved to glove box. All the solutions were prepared in the glove box. In a typical experiment, the emission spectrum of a 5×10$^{-5}$ M solution of (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ in 1, 4-dioxane was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.
Figure S1. (Ir[dF(CF₃)ppy]₂(dtbpy))PF₆ Emission Quenching by Boc-Pro-O⁻.

Figure S1. (Ir[dF(CF₃)ppy]₂(dtbpy))PF₆ Ru(bpy)₃(SbF₆)₂ emission quenching with Boc-Pro-O⁻ and 4a; I₀ and I represent the intensities of the emission in the absence and presence of the quencher. Emission Quenching by Boc-Pro-O⁻, kq = 3.50 × 10³ mol⁻¹ L. 
Characterization Data

Yield: 83%.\(^2\) \(\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3) \delta 7.50 (d, J = 20.2 \text{ Hz, 2H}), 7.29 (s, 3\text{H}), 5.43 – 5.22 (m, 1\text{H}), 3.52 – 3.21 (m, 2\text{H}), 2.24 – 1.95 (m, 3\text{H}), 1.88 (d, J = 3.4 \text{ Hz, 1H}), 1.39 (d, J = 46.4 \text{ Hz, 9H}).\)

Yield: 99%.\(^2\) \(\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3) \delta 7.52 – 7.34 (m, 2\text{H}), 7.27 (s, 2\text{H}), 5.30 (d, J = 57.4 \text{ Hz, 1H}), 3.36 (d, J = 58.6 \text{ Hz, 2H}), 2.24 – 1.95 (m, 3\text{H}), 1.90 (dd, J = 7.4, 2.8 \text{ Hz, 1H}), 1.38 (d, J = 38.2 \text{ Hz, 9H}).\)

Yield: 97%.\(^2\) \(\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3) \delta 7.46 – 7.29 (m, 4\text{H}), 5.31 (d, J = 58.3 \text{ Hz, 1H}), 3.51 – 3.23 (m, 2\text{H}), 2.24 – 1.96 (m, 3\text{H}), 1.95 – 1.84 (m, 1\text{H}), 1.38 (d, J = 39.6 \text{ Hz, 9H}).\)

Yield: 68%.\(^2\) \(\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3) \delta 7.48 (d, J = 26.9 \text{ Hz, 2H}), 6.98 (d, J = 6.8 \text{ Hz, 2H}), 5.26 (d, J = 51.1 \text{ Hz, 1H}), 3.49 – 3.20 (m, 2\text{H}), 2.04 (dd, J = 49.1, 17.5 \text{ Hz, 3H}), 1.87 (d, J = 6.6 \text{ Hz, 1H}), 1.37 (d, J = 35.8 \text{ Hz, 9H}).\)
Yield: 82%.\textsuperscript{2} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.32 (d, \textit{J} = 14.9 Hz, 2H), 7.18 (t, \textit{J} = 7.4 Hz, 1H), 7.09 (d, \textit{J} = 7.7 Hz, 1H), 5.46 – 5.21 (m, 1H), 3.52 – 3.21 (m, 2H), 2.32 (s, 3H), 2.05 (t, \textit{J} = 9.6 Hz, 3H), 1.88 (d, \textit{J} = 4.0 Hz, 1H), 1.39 (d, \textit{J} = 41.4 Hz, 9H).

Yield: 97%.\textsuperscript{2} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.50 – 7.31 (m, 2H), 7.10 (d, \textit{J} = 6.1 Hz, 2H), 5.40 – 5.13 (m, 1H), 3.50 – 3.17 (m, 2H), 2.32 (s, 3H), 2.02 (d, \textit{J} = 7.8 Hz, 3H), 1.84 (d, \textit{J} = 14.1 Hz, 1H), 1.39 (d, \textit{J} = 41.9 Hz, 9H).

Yield: 87%.\textsuperscript{2} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.50 – 7.36 (m, 2H), 7.16 (d, \textit{J} = 7.0 Hz, 2H), 5.39 – 5.22 (m, 1H), 3.53 – 3.22 (m, 2H), 2.88 (dt, \textit{J} = 13.2, 6.5 Hz, 1H), 2.07 (ddd, \textit{J} = 23.8, 17.1, 9.7 Hz, 3H), 1.89 (d, \textit{J} = 6.6 Hz, 1H), 1.37 (d, \textit{J} = 56.0 Hz, 9H), 1.23 (d, \textit{J} = 6.9 Hz, 6H).

Yield: 71%.\textsuperscript{2} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.51 – 7.33 (m, 2H), 6.83 (d, \textit{J} = 7.4 Hz, 2H), 5.19 (dd, \textit{J} = 47.7, 4.8 Hz, 1H), 3.78 (s, 3H), 3.48 – 3.17 (m, 2H), 2.16 – 1.90 (m, 3H), 1.90 – 1.77 (m, 1H), 1.38 (d, \textit{J} = 35.6 Hz, 9H).
Yield: 53%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 7.3$ Hz, 2H), 7.28 (d, $J = 6.9$ Hz, 2H), 7.25 – 7.19 (m, 1H), 5.08 (dd, $J = 10.4$, 5.1 Hz, 1H), 4.71 (d, $J = 10.1$ Hz, 1H), 2.03 (dq, $J = 13.3$, 6.7 Hz, 1H), 1.32 (s, 9H), 1.05 (dd, $J = 6.7$, 4.8 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 154.89, 133.44, 132.74, 128.86, 127.28, 79.72, 64.88, 33.86, 28.23, 19.49, 18.24. HRMS (ESI, m/z) calcd for C$_{15}$H$_{23}$NO$_2$S [M+Na]$^+$ 304.1347, found 304.1353.

Yield: 42%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 7.3$ Hz, 3H), 7.32 (dt, $J = 15.7$, 4.8 Hz, 3H), 4.91 (s, 1H), 4.59 (d, $J = 6.3$ Hz, 2H), 1.40 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.94, 133.85, 131.66, 129.14, 127.35, 80.19, 45.82, 28.28. HRMS (ESI, m/z) calcd for C$_{15}$H$_{17}$NO$_2$S [M+Na]$^+$ 262.0878, found 262.0878.

Yield: 53%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 6.8$ Hz, 2H), 7.35 – 7.27 (m, 6H), 7.25 (s, 2H), 5.43 (d, $J = 8.8$ Hz, 1H), 4.72 (d, $J = 9.2$ Hz, 1H), 3.08 (ddd, $J = 20.4$, 14.1, 6.8 Hz, 2H), 1.30 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 154.47, 133.71, 132.24, 128.98, 127.95, 80.07, 58.25, 35.64, 30.74, 28.25, 15.59. HRMS (ESI, m/z) calcd for C$_{19}$H$_{23}$NO$_2$S [M+Na]$^+$ 352.1347, found 352.1348.

Yield: 74%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 6.2$ Hz, 2H), 7.30 (d, $J = 7.0$ Hz, 2H), 7.28 (d, $J = 6.9$ Hz, 2H), 7.25 – 7.19 (m, 1H), 5.08 (dd, $J = 10.4$, 5.1 Hz, 1H), 4.71 (d, $J = 10.1$ Hz, 1H), 2.03 (dq, $J = 13.3$, 6.7 Hz, 1H), 1.32 (s, 9H), 1.05 (dd, $J = 6.7$, 4.8 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 154.89, 133.44, 132.74, 128.86, 127.28, 79.72, 64.88, 33.86, 28.23, 19.49, 18.24. HRMS (ESI, m/z) calcd for C$_{15}$H$_{23}$NO$_2$S [M+Na]$^+$ 304.1347, found 304.1353.
Hz, 3H), 5.23 (d, J = 8.3 Hz, 1H), 4.75 (d, J = 9.6 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.10 (s, 3H), 2.07 – 1.87 (m, 2H), 1.34 (s, 9H). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.48 (s, 2H), 7.28 (s, 3H), 5.91 (d, J = 133.1 Hz, 1H), 4.19 – 3.69 (m, 1H), 3.30 (td, J = 13.1, 2.8 Hz, 1H), 2.06 – 1.79 (m, 3H), 1.78 – 1.58 (m, 2H), 1.53 – 1.37 (m, 1H), 1.22 (d, J = 74.8 Hz, 9H).

Yield: 90%. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.54 – 7.47 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H), 5.65 (dd, J = 7.2, 4.0 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.98 – 3.92 (m, 1H), 2.43 – 2.31 (m, 1H), 2.07 – 1.93 (m, 2H), 1.93 – 1.81 (m, 1H).

Yield: 72%. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.42 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 5.58 (dd, J = 7.2, 3.9 Hz, 1H), 4.03 (dd, J = 15.4, 7.9 Hz, 1H), 3.95 (td, J = 8.1, 4.1 Hz, 1H), 2.39 – 2.31 (m, 4H), 2.07 – 1.92 (m, 2H), 1.87 (qdd, J = 8.0, 6.7, 5.0 Hz, 1H).

Yield: 67%. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.47 – 7.41 (m, 2H), 7.28 – 7.24 (m, 2H), 5.60 (dd, J = 7.2, 3.9 Hz, 1H), 4.05 – 3.99 (m, 1H), 3.96 (td, J = 8.1, 4.1 Hz, 1H), 2.37
(ddddd, J = 14.8, 12.8, 12.2, 7.6 Hz, 1H), 2.07 – 1.92 (m, 2H), 1.92 – 1.83 (m, 1H).

Yield: 26%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.13 (s, 1H), 7.63 (d, \(J = 7.7\) Hz, 1H), 7.44 (s, 1H), 7.35 (dd, \(J = 17.0, 5.7, 1.2\) Hz, 3H), 7.30 – 7.24 (m, 4H), 7.23 – 7.18 (m, 1H), 4.24 (s, 2H), 1.65 (s, 9H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 149.69, 136.61, 130.20, 129.03, 126.60, 124.74, 124.47, 122.72, 119.43, 116.55, 115.45, 83.81, 29.76, 28.33. HRMS (ESI, m/z) calcd for C\(_{20}\)H\(_{21}\)NO\(_2\)S [M+Na]\(^+\) 362.1185, found 362.1191.

References

Supplementary spectra
Chemical Formula: C_{15}H_{23}NO_2S
Exact Mass: 281.14495
Molecular Weight: 281.41400
m/z: 281.14495 (100.0%), 282.14830 (16.2%), 283.14075 (4.5%), 283.15166 (1.2%)
Elemental Analysis: C, 64.02; H, 8.24; N, 4.98; O, 11.37; S, 11.39
HRMS (ESI, m/z) calculated for $\text{C}_{15}\text{H}_{23}\text{NO}_{2}\text{S} \ [\text{M+Na}]^+ 304.1347$, found 304.1353.
$5b$
HRMS (ESI, m/z) calcd for C_{15}H_{17}NO_{2}S [M+Na]^+ 262.0878, found 262.0878.
Chemical Formula: C_{19}H_{23}NO_{2}S
Exact Mass: 329.14495
Molecular Weight: 329.45800
m/z: 329.14495 (100.0%), 330.14830 (20.5%), 331.14075 (4.5%), 331.15166 (2.0%)
Elemental Analysis: C, 69.27; H, 7.04; N, 4.25; O, 9.71; S, 9.73

HRMS (ESI, m/z) caleld for C_{19}H_{23}NO_{2}S [M+Na]^+ 352.1347, found 352.1348.
5d
Chemical Formula: C$_{15}$H$_{23}$NO$_2$S$_2$
Exact Mass: 313.11702
Molecular Weight: 313.47400
m/z: 313.11702 (100.0%), 314.12038 (16.2%), 315.11282 (4.5%), 315.11282 (4.5%), 316.11617 (1.5%), 315.12373 (1.2%)
Elemental Analysis: C, 57.47; H, 7.40; N, 4.47; O, 10.21; S, 20.45

HRMS (ESI, m/z) calcd for C$_{15}$H$_{23}$NO$_2$S$_2$ [M+Na]$^+$ 330.1068, found 330.1064.
Chemical Formula: C$_{20}$H$_{21}$NO$_2$S

Exact Mass: 339.12930

Molecular Weight: 339.45300

m/z: 339.12930 (100.0%), 340.13265 (21.6%), 341.12510 (4.5%), 341.13601 (2.2%)

Elemental Analysis: C, 70.77; H, 6.24; N, 4.13; O, 9.43; S, 9.44

HRMS (ESI, m/z) calcd for C$_{20}$H$_{21}$NO$_2$S [M+Na]$^+$ 362.1185, found 362.1191.