Supporting Information for

Visible light-driven photocatalytic generation of sulfonamidyl radicals for alkene hydroamination of unsaturated sulfonamides

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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. The solvents used were purified by distillation over the drying agents. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. $^1$H NMR spectra were recorded on 400/600 MHz spectrophotometers. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers (CDCl$_3$: 77.0 ppm). The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or Bruker Compact TOF mass spectrometer by ESI. Fluorescence spectra were collected on Cary Eclipse Fluorescence Spectrophotometer. Enantiomeric ratio (ee) values were determined by chiral HPLC with chiral OD-H, AD-H columns with hexane and i-PrOH as solvent.

2. Preparation and Spectral Data of the Substrates

2.1 General procedure for preparation of N-sulfonyl-O-buteryl hydroxylamines

\[
\begin{align*}
\text{R} & \quad \text{MgBr (1.2 eq.)} \quad \text{THF, 0°C to r.t.} \\
\text{R} & \quad \text{OH} \\
\text{R} & \quad \text{PPht$_3$(1.2 eq.), DEAD (1.2 eq.)} \quad \text{THF, 0°C to r.t., 16 h} \\
& \quad \text{Nphth}
\end{align*}
\]

To a solution of aldehyde (1.0 equiv) in THF (0.2 M) at 0 °C was added allylmagnesium bromide (1.0 M/THF, 1.2 equiv). After 2–4 h, the reaction medium was warmed to room temperature and a saturated aqueous solution of NH$_4$Cl was added. The two phases were separated, the aqueous layer was extracted twice with Et$_3$O (2 × 30 mL) and the combined organic layers were dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was filtered through silica gel to obtain
the desired alcohol.

To a solution of the previously synthesized alcohol (1 equiv) in THF (0.1 M) were added PPh₃ (1.2 equiv) and N-hydroxyphthalimide (1.2 equiv). The resulting mixture was cooled to 0 °C before DEAD (1.2 equiv) was added dropwise. After 30 mins at 0 °C, the reaction medium was allowed to reach room temperature. Until the reaction was completed, as monitored by TLC analysis, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford the desired product.

To a solution of the previously synthesized N-alkoxyphthalimides (1.0 equiv) in DCM (0.1 M) were added hydrazine monohydrate (6.0 equiv). After 2 h, the mixture was filtered through Celite and concentrated in vacuo.

The resulting hydroxylamine was dissolved in DCM (1 M), treated with pyridine (3.0 equiv) and p-TsCl (1.5 equiv) and stirred at r.t. until the reaction was completed, as monitored by TLC analysis. The mixture was quenched with water and extracted with DCM (2 × 30 mL). The organics were washed with 1 M HCl (20 mL), brine (20 mL), dried over Na₂SO₄ and concentrated in vacuo. Flash chromatography on SiO₂ (10–30% EtOAc in hexanes) gave N-tosyl hydroxylamine.

1a[1], 1b[2], 1f[1], 1g[1], 1h[2], 1j[1], 1n[3], 1o[1], 1q[7], 1t[7] are known compounds. Other N-sulfonyl-O-butenylnitroxylamines were prepared according to the above procedures.

2.2 Spectral data of N-sulfonyl-O-butenylnitroxylamines

N-sulfonyl-O-butenylnitroxylamines 1c

Yield of 1c: 36% as a white solid.¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.14 (s, 4H), 6.64 (s, 1H), 5.83 – 5.67 (m, 1H), 5.10 – 5.07 (m, 1H), 5.05 (d, J = 1.4 Hz, 1H), 4.98 (dd, J = 7.7, 6.3 Hz, 1H), 2.63 (m, 1H), 2.45 (s, 4H), 2.34 (s, 3H).¹³C NMR (100 MHz, CDCl₃) δ 144.8, 138.1, 136.5, 133.9, 133.8,
129.6, 129.1, 128.7, 117.5, 87.9, 39.5, 21.7, 21.2. M.P.: 97 – 98 °C. IR (in KBr): 3194, 2361, 1404, 1337, 1159, 738, 544 cm\(^{-1}\). HRMS (EI) for C\(_{18}H_{21}NO_3S\) [M+Na\(^+\)]: calcd 354.1140, found 354.1134.

\(N\)-sulfonyl-\(O\)-butenyl hydroxylamines 1d

Yield of 1d: 71% as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)

- 7.80 (d, \(J = 8.4\) Hz, 2H),
- 7.32 (d, \(J = 8.1\) Hz, 2H),
- 7.21 – 7.12 (m, 4H),
- 6.70 (s, 1H),
- 5.85 – 5.69 (m, 1H),
- 5.35 (dd, \(J = 8.0, 5.8\) Hz, 1H),
- 5.09 (d, \(J = 6.3\) Hz, 1H),
- 5.06 (s, 1H),
- 2.57 (m, 1H),
- 2.45 (s, 3H),
- 2.40 (dd, \(J = 14.0, 6.1\) Hz, 1H),
- 2.34 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\)

- 144.8,
- 138.1,
- 136.0,
- 133.9,
- 133.7,
- 130.4,
- 129.6,
- 128.7,
- 127.8,
- 126.1,
- 125.7,
- 117.6,
- 84.0,
- 39.4,
- 21.6,
- 19.3. M.P.: 118 – 119 °C. IR (in KBr): 3214, 1401, 1336, 1165, 732, 544 cm\(^{-1}\). HRMS (EI) for C\(_{18}H_{21}NO_3S\) [M+Na\(^+\)]: calcd 354.1140, found 354.1128.

\(N\)-sulfonyl-\(O\)-butenyl hydroxylamines 1e

Yield of 1e: 68% as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)

- 7.78 (d, \(J = 8.0\) Hz, 2H),
- 7.32 (d, \(J = 7.9\) Hz, 2H),
- 7.24 (m, 2H),
- 7.01 (t, \(J = 8.5\) Hz, 2H),
- 6.81 – 6.68 (m, 1H),
- 5.72 (m, 1H),
- 5.08 (d, \(J = 1.4\) Hz, 1H),
- 5.07 – 4.98 (m, 2H),
- 2.63 (m, 1H),
- 2.45 (s, 4H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\)

- 162.6 (d, \(J = 246.6\) Hz),
- 144.9,
- 135.3,
- 133.6,
- 133.4,
- 129.6,
- 129.0 (d, \(J = 8.2\) Hz),
- 128.6,
- 117.9,
- 115.3 (d, \(J = 21.4\) Hz),
- 87.3,
- 39.5,
- 21.6. M.P.: 101 – 102 °C. IR (in KBr): 3220, 1403, 1341, 1165, 719, 538 cm\(^{-1}\). HRMS (EI) for C\(_{17}H_{18}FNO_3S\) [M+Na\(^+\)]: calcd 358.0889, found 358.0878.

\(N\)-sulfonyl-\(O\)-butenyl hydroxylamines 1i

Yield of 1i: 58% as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)

- 7.78 (d, \(J = 8.4\) Hz, 2H),
- 7.40 (d, \(J = 8.2\) Hz, 1H),
- 7.37 – 7.28 (m, 3H),
- 7.09 (dd, \(J = 8.2, 2.1\) Hz, 1H),
- 6.78 (s, 1H),
- 5.71 (m, 1H),
- 5.13 – 4.95 (m, 3H),
- 2.60 (m, 1H),
- 2.46 (s, 3H),
- 2.41 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\)

- 145.1,
- 140.0,
- 133.4,
- 132.8,
- 132.7,
- 132.3,
- 130.5,
- 129.7,
- 129.1,
- 128.7,
- 126.6,
- 118.4,
- 86.8,
- 39.5,
3209, 1404, 1343, 1135, 712, 527 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{17}$Cl$_2$NO$_3$S [M+Na]$^+$: calcd 408.0204, found 408.0191.

**N-sulfonyl-O-buteryl hydroxylamines 1k**

Yield of 1k: 36% as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (dd, $J$ = 8.4, 2.3 Hz, 5H), 7.72 (s, 1H), 7.51 – 7.45 (m, 2H), 7.37 (dd, $J$ = 8.5, 1.7 Hz, 1H), 7.30 (d, $J$ = 8.0 Hz, 2H), 6.78 – 6.67 (m, 1H), 5.78 (m, 1H), 5.18 (t, $J$ = 7.0 Hz, 1H), 5.13 – 5.05 (m, 2H), 2.73 (m, 1H), 2.59 – 2.50 (m, 1H), 2.43 (s, 3H). M.P.: 167 – 168 °C. IR (in KBr): 3208, 1640, 1401, 1166 cm$^{-1}$. HRMS (EI) for C$_{21}$H$_{21}$NO$_3$S [M+Na]$^+$: calcd 390.1140, found 390.1126.

**N-sulfonyl-O-buteryl hydroxylamines 1l**

Yield of 1l: 64% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J$ = 8.2 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 6.74 (s, 1H), 5.82 (dd, $J$ = 17.0, 10.2 Hz, 1H), 5.12 – 5.02 (m, 2H), 3.90 (q, $J$ = 5.7 Hz, 1H), 2.45 (s, 3H), 2.40 (m, 1H), 2.27 (m, 1H), 1.75 – 1.60 (m, 6H), 1.22 – 0.99 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.7, 134.9, 133.9, 129.6, 128.6, 117.0, 90.0, 39.2, 38.6, 28.6, 28.3, 26.5, 26.2, 26.1, 21.7. IR (in KBr): 3227, 2929, 2853, 1343, 1169, 722 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{25}$NO$_3$S [M+Na]$^+$: calcd 346.1453, found 346.1441.

**N-sulfonyl-O-buteryl hydroxylamines 1m**

Yield of 1m: 46% as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J$ = 8.1 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 7.26 (s, 0H), 6.72 (s, 1H), 5.78 (m, 1H), 5.07 (d, $J$ = 16.4 Hz, 1H), 4.08 (m, 1H), 2.45 (s, 3H), 2.39 – 2.30 (m, 1H), 1.47 (m, 3H), 1.27 (s, 12H), 0.89 (t, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.8, 134.2, 133.8, 129.6, 128.6, 117.4, 85.8, 37.1, 32.1, 31.9, 29.6, 29.5, 29.2, 25.2, 22.7, 21.7, 14.1. M.P.: 32 – 33 °C. IR (in KBr):
3224, 2927, 2856, 1401, 1337, 1168, 722 cm\(^{-1}\). HRMS (EI) for C\(_{19}\)H\(_{31}\)NO\(_3\)S [M+Na]\(^+\): calcd 376.1922, found 376.1909.

**N-sulfonyl-O-butenyldihydroxylamines 1n**

\(\text{Ts} \quad \text{O} \quad \text{NH} \quad \text{Ph} \quad \text{1n} \)

Yield of 1n: 66% as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (d, \(J = 7.8\) Hz, 2H), 7.33 (d, \(J = 7.9\) Hz, 2H), 7.11 (d, \(J = 7.9\) Hz, 1H), 5.74 (m, 1H), 5.07 (t, \(J = 13.7\) Hz, 2H), 4.04 (t, \(J = 6.7\) Hz, 2H), 2.44 (s, 3H), 2.36 (q, \(J = 6.8\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.8, 134.2, 133.4, 129.6, 128.5, 117.0, 76.2, 32.5, 21.6. HRMS (EI) for C\(_{11}\)H\(_{15}\)NO\(_3\)S [M+Na]\(^+\): calcd 264.0665, found 264.0657.

**N-sulfonyl-O-butenyldihydroxylamines 1o**

\(\text{O} \quad \text{SO} \quad \text{O} \quad \text{NH} \quad \text{Ph} \quad \text{1o} \)

Yield of 1o: 50% as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.6\) Hz, 2H), 7.37 – 7.23 (m, 6H), 6.99 (d, \(J = 8.7\) Hz, 2H), 6.67 (s, 1H), 5.86 – 5.66 (m, 1H), 5.08 (d, \(J = 12.9\) Hz, 2H), 5.04 – 4.95 (m, 1H), 3.89 (s, 3H), 2.64 (m, 1H), 2.46 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.8, 139.6, 133.8, 130.9, 128.4, 128.3, 128.1, 127.1, 117.6, 114.2, 88.0, 55.7, 39.7. M.P.: 128 – 129 °C. IR (in KBr): 3212, 1596, 1336, 737, 555 cm\(^{-1}\). HRMS (EI) for C\(_{17}\)H\(_{19}\)NO\(_4\)S [M+Na]\(^+\): calcd 356.0932, found 356.0920.

**N-sulfonyl-O-butenyldihydroxylamines 1p**

\(\text{O} \quad \text{SO} \quad \text{O} \quad \text{NH} \quad \text{Ph} \quad \text{1p} \)

Yield of 1p: 73% as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.2\) Hz, 2H), 7.50 (d, \(J = 8.0\) Hz, 2H), 7.33 (d, \(J = 7.6\) Hz, 3H), 7.26 (s, 2H), 6.74 (s, 1H), 5.77 (m, 1H), 5.15 – 4.97 (m, 3H), 2.63 (m, 1H), 2.47 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.6, 139.3, 135.1, 133.7, 130.1, 129.4, 128.5, 128.5, 127.1, 117.8, 88.3, 39.7. M.P.: 118 – 119 °C. IR (in KBr): 3222, 2361, 1401, 1164, 773 cm\(^{-1}\). HRMS (EI) for C\(_{16}\)H\(_{16}\)ClNO\(_3\)S [M+Na]\(^+\): calcd 360.0437, found 360.0432.
**N-sulfonyl-O-butenyl hydroxylamines 1q**

Yield of 1q: 65% as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 7.8$ Hz, 2H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.54 (t, $J = 7.7$ Hz, 2H), 7.44 – 7.19 (m, 6H), 6.70 (s, 1H), 5.76 (m, 1H), 5.28 – 4.90 (m, 3H), 2.64 (m, 1H), 2.46 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.5, 136.7, 133.8, 133.7, 129.0, 128.7, 128.5, 128.3, 127.1, 117.7, 88.1, 39.6. HRMS (EI) for C$_{16}$H$_{17}$NO$_3$S [M+Na]$^+$: calcld 326.0821, found 326.0814.

**N-sulfonyl-O-butenyl hydroxylamines 1r**

Yield of 1r: 65% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (m, 5H), 6.70 (s, 1H), 5.77 (m, 1H), 5.14 – 4.99 (m, 3H), 3.02 (s, 3H), 2.71 (m, 1H), 2.52 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.3, 133.5, 128.5, 128.5, 127.2, 117.8, 87.9, 39.4, 37.1. M.P.: 70 – 71 °C. IR (in KBr): 3226, 1640, 1400, 1326, 1154, 763 cm$^{-1}$. HRMS (EI) for C$_{11}$H$_{15}$NO$_3$S [M+Na]$^+$: calcld 264.0670, found 264.0658.

**N-sulfonyl-O-butenyl hydroxylamines 1s**

Yield of 1s: 83% as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 7.9$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 6.90 (d, $J = 5.0$ Hz, 1H), 5.49 (m, 1H), 5.41 – 5.26 (m, 1H), 4.00 (t, $J = 6.7$ Hz, 2H), 2.45 (s, 3H), 2.28 (q, $J = 6.8$ Hz, 2H), 1.66 (d, $J = 6.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.8, 133.5, 129.6, 128.6, 127.7, 126.5, 76.8, 31.4, 21.7, 18.0. M.P.: 73 – 74 °C. IR (in KBr): 2361, 2340, 1930, 1403, 1164, 820 cm$^{-1}$. HRMS (EI) for C$_{12}$H$_{17}$NO$_3$S [M+Na]$^+$: calcld 278.0821, found 278.0824.

**2.3 Unsuccessful Substrates**
**N-sulfonyl-O-butenyl hydroxylamines 1u**

Yield of 1u: 73% as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 8.3$ Hz, 2H), 7.41 – 7.20 (m, 10H), 7.17 (dd, $J = 7.3$, 2.3 Hz, 2H), 6.66 (s, 1H), 5.33 (d, $J = 1.2$ Hz, 1H), 5.10 – 4.92 (m, 2H), 3.14 (dd, $J = 14.6$, 7.3 Hz, 1H), 2.80 (dd, $J = 14.6$, 6.5 Hz, 1H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.7, 143.6, 140.5, 139.6, 133.7, 129.6, 128.6, 128.4, 128.3, 127.6, 127.1, 126.2, 115.6, 87.2, 41.2, 21.7. HRMS (EI) for C$_{23}$H$_{23}$NO$_3$S$^{[M+Na]^+}$: calcd 416.1291, found 416.1286.

**N-sulfonyl-O-butenyl hydroxylamines 1v**

Yield of 1v: 78% as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 8.3$ Hz, 2H), 7.45 – 7.16 (m, 11H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.66 (s, 1H), 6.42 (d, $J = 15.8$ Hz, 1H), 6.24 (m, 1H), 5.14 (dd, $J = 8.8$, 5.2 Hz, 1H), 2.80 – 2.66 (m, 1H), 2.61 (m, 1H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.7, 139.8, 137.3, 133.5, 132.6, 129.6, 128.7, 128.6, 128.5, 128.3, 127.3, 127.0, 126.1, 125.8, 88.0, 39.3, 21.6. HRMS (EI) for C$_{23}$H$_{23}$NO$_3$S$^{[M+Na]^+}$: calcd 416.1291, found 416.1283.

**N-sulfonyl-O-butenyl hydroxylamines 1w**

Yield of 1w: 82% as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 7.9$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 6.91 (s, 1H), 5.78 (m, 1H), 5.08 – 4.89 (m, 2H), 3.99 (t, $J = 6.6$ Hz, 2H), 2.45 (s, 3H), 2.07 (q, $J = 7.3$ Hz, 2H), 1.68 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.8, 137.6, 133.6, 129.7, 128.5, 115.1, 76.7, 29.9, 27.2, 21.6. HRMS (EI) for C$_{12}$H$_{17}$NO$_3$S$^{[M+Na]^+}$: calcd 278.0821, found 278.0812.
3. General Procedure and Spectral Data of the Products

3.1 General procedure for hydroamination of N-sulfonyl-O-butenyl hydroxylamines

\[ \overset{Ts}{\text{Ph}}\overset{\text{O}}{\text{NH}}\overset{\text{O}}{\text{Ph}} \xrightarrow{\text{[Ru(bpy)₃Cl₂·6H₂O} (2 mol%), K₂CO₃ (2.0 eq)}} \overset{\text{Ts}}{\text{O-NO}}\]

\[ 3 \text{ w blue LEDs, CHCl₃ (3 mL), R.T.} \]

1a (0.2 mmol, 63.5 mg), Ru(bpy)₃Cl₂·6H₂O (0.004 mmol) and K₂CO₃ (0.4 mmol, 55.3 mg) were dissolved in CHCl₃ (3.0 mL). Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 3W blue LEDs (450-460 nm) at room temperature about 12-24 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 200:1~50:1) directly to give the desired product 2a in 64% yield as a white solid.

3.2 Spectral data of the products

Product 2a

Yield of 2a: 64% as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 7.9 Hz, 2H), 7.30 (m, 7H), 5.02 (dd, J = 10.3, 5.8 Hz, 1H), 4.41 (q, J = 7.0 Hz, 1H), 2.75 (m, 1H), 2.44 (s, 3H), 2.00 (m, 1H), 1.52 (d, J = 6.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 136.8, 132.9, 129.7, 129.3, 128.6, 128.5, 126.8, 83.0, 57.0, 44.9, 22.0, 21.7. M.P.: 115 – 116 °C. IR (in KBr): 1596, 1354, 1162, 900, 703, 578 cm⁻¹. HRMS (EI) for C₁₇H₁₉NO₃S [M+H]⁺: calcd 318.1164, found 318.1153.

Product 2b

Yield of 2b: 58% as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 6.92 – 6.78 (m, 2H), 4.93 (dd, J = 10.4, 5.5 Hz, 1H), 4.49 – 4.32 (m, 1H), 2.68 (m, 1H), 2.44 (s, 3H), 1.99 (m,
1H), 1.53 (d, J = 6.2 Hz, 3H). $^1$H NMR (100 MHz, CDCl$_3$) $\delta$ 159.9, 144.8, 132.9, 129.6, 129.3, 128.4, 128.2, 113.9, 82.8, 57.1, 55.3, 44.6, 22.0, 21.6. M.P.: 127 – 128 °C. IR (in KBr): 3132, 2361, 1516, 1400, 1161, 580 cm$^{-1}$. HRMS (EI) for C$_{18}$H$_{21}$NO$_4$S [M+H]$^+$: calcd 348.1270, found 348.1254.

Product 2c

Yield of 2c: 71% as a white solid. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.94 – 7.84 (m, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.21 – 7.06 (m, 4H), 4.95 (dd, $J = 10.4$, 5.6 Hz, 1H), 4.47 – 4.33 (m, 1H), 2.70 (m, 1H), 2.43 (s, 3H), 2.32 (s, 3H), 1.99 (m, 1H), 1.52 (d, $J = 6.3$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 144.8, 138.6, 133.5, 132.8, 129.6, 129.3, 129.2, 126.8, 82.9, 57.0, 44.8, 22.0, 21.6, 21.1. M.P.: 121 – 122 °C. IR (in KBr): 3132, 2361, 1400, 1166 cm$^{-1}$. HRMS (EI) for C$_{18}$H$_{21}$NO$_3$S [M+H]$^+$: calcd 332.1320, found 332.1317.

Product 2d

Yield of 2d: 72% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.1$ Hz, 2H), 7.41 (dd, $J = 6.7$, 2.5 Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.19 – 7.14 (m, 2H), 7.11 (dd, $J = 6.3$, 2.7 Hz, 1H), 5.29 (dd, $J = 10.1$, 5.8 Hz, 1H), 4.47 (q, $J = 6.9$ Hz, 1H), 2.76 (m, 1H), 2.43 (s, 3H), 2.23 (s, 3H), 1.96 (m, 1H), 1.51 (d, $J = 6.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.8, 135.9, 134.9, 133.1, 130.3, 129.6, 129.2, 128.2, 126.2, 125.3, 79.8, 56.8, 43.2, 22.1, 21.6, 19.2. IR (in KBr): 2977, 2930, 2361, 1597, 1358, 1167, 670 cm$^{-1}$. HRMS (EI) for C$_{18}$H$_{21}$NO$_3$S [M+H]$^+$: calcd 332.1320, found 332.1308.

Product 2e

Yield of 2e: 67% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 7.25 (dd, $J = 8.5$, 5.2 Hz, 2H), 7.00 (t, $J = 8.5$ Hz, 2H), 5.01 (dd, $J = 10.3$, 5.7 Hz, 1H), 4.41 (q, $J = 7.0$ Hz, 1H), 2.74 (m, 1H), 2.44 (s, 3H), 2.09 – 1.86 (m, 1H), 1.52 (d, $J = 6.3$ Hz, 3H). $^{13}$C NMR (100
MHz, CDCl₃) δ 162.8 (d, J = 247.5 Hz), 144.9, 132.8, 132.5 (d, J = 3.5 Hz), 129.7, 129.2, 128.6 (d, J = 8.2 Hz), 115.5 (d, J = 21.9 Hz), 82.3, 56.9, 44.9, 22.0, 21.6. IR (in KBr): 3127, 2361, 1513, 1166, 582 cm⁻¹. HRMS (EI) for C₁₇H₁₈FNO₃S [M+H]^+: calcd 336.1070, found 336.1054.

Product 2f

Yield of 2f: 62% as a colorless oil.¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.21 (d, J = 8.4 Hz, 2H), 5.03 (dd, J = 10.1, 5.8 Hz, 1H), 4.42 (q, J = 7.0 Hz, 1H), 2.80 – 2.69 (m, 1H), 2.44 (s, 3H), 1.94 (m, 1H), 1.51 (d, J = 6.4 Hz, 3H).¹³C NMR (100 MHz, CDCl₃) δ 145.0, 135.4, 134.4, 132.8, 129.7, 129.2, 128.7, 128.1, 82.2, 56.9, 44.9, 22.0, 21.7. IR (in KBr): 3125, 2361, 1359, 1166, 1091, 582 cm⁻¹. HRMS (EI) for C₁₇H₁₈ClNO₃S [M+H]^+: calcd 352.0774, found 352.0760.

Product 2g

Yield of 2g: 59% as a colorless oil.¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 5.02 (dd, J = 10.1, 5.9 Hz, 1H), 4.42 (q, J = 7.1 Hz, 1H), 2.79 – 2.72 (m, 1H), 2.44 (s, 3H), 1.93 (m, 1H), 1.50 (d, J = 6.4 Hz, 3H).¹³C NMR (100 MHz, CDCl₃) δ 145.0, 136.0, 132.8, 131.7, 129.7, 129.3, 128.4, 82.3, 56.9, 45.0, 22.0, 21.7. IR (in KBr): 3130, 2361, 1596, 1401, 1166, 816 cm⁻¹. HRMS (EI) for C₁₇H₁₈BrNO₃S [M+H]^+: calcd 396.0269, found 396.0257.

Product 2h

Yield of 2h: 69% as a white solid.¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.16 (dd, J = 9.9, 6.1 Hz, 1H), 4.46 (q, J = 7.0 Hz, 1H), 2.87 – 2.79 (m, 1H), 2.45 (s,
3H), 1.95 (m, 1H), 1.50 (d, \( J = 6.4 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 145.1, 141.3, 132.8, 130.7 (d, \( J = 32.6 \) Hz), 129.7, 129.3, 126.8, 125.5 (q, \( J = 3.8 \) Hz), 123.9 (q, \( J = 270 \) Hz), 82.1, 56.8, 45.1, 22.0, 21.7. M.P.: 84 – 85 °C. IR (in KBr): 3130, 2361, 1400, 1167, 1129, 1067 cm\(^{-1}\). HRMS (EI) for \( \text{C}_{18}\text{H}_{18}\text{F}_{3}\text{N}_{3}\text{O}_{3}\text{S} \ [\text{M+H}]^+ \): calcd 386.1038, found 386.1028.

Product 2i

Yield of 2i: 60% as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.87 (d, \( J = 8.0 \) Hz, 2H), 7.40 – 7.33 (m, 4H), 7.11 (d, \( J = 8.2 \) Hz, 1H), 5.05 (dd, \( J = 9.9, 6.0 \) Hz, 1H), 4.43 (q, \( J = 6.9 \) Hz, 1H), 2.78 (m, 1H), 2.45 (s, 3H), 1.92 (m, 1H), 1.49 (d, \( J = 6.4 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 145.1, 137.4, 132.7, 132.7, 132.5, 130.5, 129.7, 129.2, 128.5, 125.9, 81.6, 56.7, 44.9, 22.0, 21.7. IR (in KBr): 2978, 2930, 2361, 1359, 1166, 673 cm\(^{-1}\). HRMS (EI) for \( \text{C}_{17}\text{H}_{17}\text{Cl}_{2}\text{N}_{3}\text{O}_{3}\text{S} \ [\text{M+H}]^+ \): calcd 386.0384, found 386.0374.

Product 2j

Yield of 2j: 53% as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.89 (d, \( J = 8.0 \) Hz, 2H), 7.34 (d, \( J = 8.0 \) Hz, 2H), 7.29 (d, \( J = 5.0 \) Hz, 1H), 7.02 (d, \( J = 3.5 \) Hz, 1H), 6.95 (dd, \( J = 5.0, 3.6 \) Hz, 1H), 5.38 (dd, \( J = 9.7, 6.1 \) Hz, 1H), 4.48 (q, \( J = 6.8 \) Hz, 1H), 2.83 (m, 1H), 2.43 (s, 3H), 2.10 (m, 1H), 1.53 (d, \( J = 6.4 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 144.9, 139.2, 132.9, 129.7, 129.2, 127.1, 126.7, 126.5, 78.8, 56.8, 44.8, 22.0, 21.7. M.P.: 97 – 98 °C. IR (in KBr): 3100, 2361, 1400, 1349, 1163, 589 cm\(^{-1}\). HRMS (EI) for \( \text{C}_{15}\text{H}_{17}\text{NO}_{3}\text{S}_{2} \ [\text{M+H}]^+ \): calcd 324.0728, found 324.0714.

Product 2k

Yield of 2k: 51% as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.91 (d, \( J = 8.0 \) Hz, 2H), 7.79 (dd, \( J = 8.9, 4.5 \) Hz, 3H), 7.74 (s, 1H), 7.47 (dd, \( J = 6.3, 3.2 \) Hz, 2H), 7.38 (dd, \( J = 8.5, 1.7 \) Hz, 1H), 7.34 (d, \( J = 8.0 \) Hz, 2H), 5.22 (dd, \( J = 10.1, 5.8 \) Hz,
1H), 4.47 (q, $J = 7.0$ Hz, 1H), 2.82 (m, 1H), 2.43 (s, 3H), 2.09 (m, 1H), 1.55 (d, $J = 6.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.9, 134.2, 133.3, 133.0, 132.9, 129.7, 129.3, 128.4, 127.9, 127.7, 126.3, 126.1, 124.1, 83.2, 57.0, 45.0, 22.1, 21.7. M.P.: 142–143 °C. IR (in KBr): 3132, 2340, 1400, 1160, 823 cm$^{-1}$. HRMS (EI) for C$_{21}$H$_{21}$NO$_3$S [M+H]$^+$: calcd 368.1320, found 368.1311.

**Product 2l**

Yield of 2l: 72% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 7.9$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 4.16 (q, $J = 7.1$ Hz, 1H), 3.62 (m, 1H), 2.45 (s, 3H), 2.36 (m, 1H), 1.83 (d, $J = 13.5$ Hz, 1H), 1.63 (m, 5H), 1.42 (d, $J = 6.4$ Hz, 4H), 1.22 – 1.10 (m, 3H), 0.95 – 0.86 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.7, 132.8, 129.5, 129.2, 85.7, 56.6, 40.9, 40.7, 29.9, 28.9, 26.1, 25.7, 25.4, 21.9, 21.6. IR (in KBr): 2930, 2361, 1360, 1167, 673, 585 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{25}$NO$_3$S [M+H]$^+$: calcd 324.1633, found 324.1620.

**Product 2m**

Yield of 2m: 68% as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 7.9$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 4.21 (q, $J = 7.0$ Hz, 1H), 3.93 (dd, $J = 10.6$, 5.7 Hz, 1H), 2.45 (s, 4H), 1.59 – 1.49 (m, 2H), 1.42 (d, $J = 6.3$ Hz, 4H), 1.24 (s, 13H), 0.88 (t, $J = 6.7$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.7, 133.0, 129.6, 129.2, 81.7, 56.5, 42.7, 32.8, 31.8, 29.4, 29.2, 26.1, 22.6, 22.0, 21.6, 14.1. M.P.: 42 – 43 °C. IR (in KBr): 2929, 2361, 1400, 1167, 672, 579 cm$^{-1}$. HRMS (EI) for C$_{19}$H$_{31}$NO$_3$S [M+H]$^+$: calcd 354.2103, found 354.2092.

**Product 2n**

Yield of 2n: 77% as white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 4.31 (q, $J = 6.5$ Hz, 1H), 4.00 – 3.92 (m, 2H), 2.44 (s, 3H), 2.34 (m, 1H), 1.96 – 1.89 (m, 1H), 1.38 (d, $J = 6.5$ Hz, 3H).
Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.8, 133.0, 129.6, 129.2, 69.7, 55.5, 36.4, 21.7, 21.5. M.P.: 78 – 79 °C. IR (in KBr): 3133, 2361, 1400, 1167 cm$^{-1}$. HRMS (EI) for C$_{11}$H$_{15}$NO$_3$S [M+H]$^+$: calcd 242.0851, found 242.0841.

**Product 2o**

Yield of 2o: 61% as white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 8.9$ Hz, 2H), 7.30 (d, $J = 4.9$ Hz, 5H), 7.00 (d, $J = 8.9$ Hz, 2H), 5.01 (dd, $J = 10.2$, 5.8 Hz, 1H), 4.38 (q, $J = 7.1$ Hz, 1H), 3.87 (s, 3H), 2.74 (m, 1H), 2.00 (m, 1H), 1.52 (d, $J = 6.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.9, 136.8, 131.4, 128.6, 128.5, 127.1, 126.8, 114.3, 82.9, 57.0, 55.6, 45.0, 22.0. M.P.: 110 – 111 °C. IR (in KBr): 3105, 2361, 1593, 1262, 1154, 552 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{19}$NO$_4$S [M+H]$^+$: calcd 334.1113, found 334.1104.

**Product 2p**

Yield of 2p: 64% as white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 8.3$ Hz, 2H), 7.51 (d, $J = 8.3$ Hz, 2H), 7.43 – 7.26 (m, 5H), 5.14 (dd, $J = 10.3$, 5.8 Hz, 1H), 4.46 (m, 1H), 2.80 (m, 1H), 2.02 (m, 1H), 1.53 (d, $J = 6.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.5, 136.5, 134.6, 130.6, 129.3, 128.8, 128.6, 126.8, 83.3, 56.8, 44.9, 22.0. M.P.: 130 – 131 °C. IR (in KBr): 3132, 2361, 1399, 1161, 1057, 760 cm$^{-1}$. HRMS (EI) for C$_{16}$H$_{16}$ClNO$_3$S [M+H]$^+$: calcd 338.0618, found 338.0606.

**Product 2q**

Yield of 2q: 64% as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J = 7.6$ Hz, 2H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.54 (t, $J = 7.7$ Hz, 2H), 7.29 (q, $J = 7.0$ Hz, 6H), 5.00 (dd, $J = 10.5$, 5.7 Hz, 1H), 4.43 (q, $J = 7.0$ Hz, 1H), 2.75 (m, 1H), 2.01 (q, $J = 10.2$ Hz, 1H), 1.53 (d, $J = 6.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.5, 135.8, 133.8, 129.2, 129.0, 128.7,
128.5, 126.8, 83.1, 57.0, 44.9, 22.0. IR (in KBr): 3121, 2361, 1359, 1168, 692, 599 cm$^{-1}$. HRMS (EI) for C$_{16}$H$_{17}$NO$_3$S [M+H]$^+$: calcd 304.1007, found 304.0996.

**Product 2r**

Yield of 2r: 73% as white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (m, 5H), 5.49 (dd, $J$ = 10.0, 6.1 Hz, 1H), 4.58 – 4.41 (m, 1H), 3.13 (s, 3H), 2.88 (m, 1H), 2.02 (m, 1H), 1.47 (d, $J$ = 6.4 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.8, 128.8, 128.7, 126.9, 83.8, 54.7, 44.9, 38.1, 22.1. M.P.: 68 – 69 °C. IR (in KBr): 3130, 2361, 1340, 1325, 1154, 765, 540 cm$^{-1}$. HRMS (EI) for C$_{11}$H$_{15}$NO$_3$S [M+Na]$^+$: calcd 264.0670, found 264.0667.

**Product 2s**

Yield of 2s: 53% as white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, $J$ = 7.3 Hz, 2H), 7.34 (d, $J$ = 7.7 Hz, 2H), 4.15 (m, 1H), 4.08 – 3.90 (m, 2H), 2.44 (s, 3H), 2.33 (m, 1H), 2.03 – 1.86 (m, 1H), 1.72 (m, 1H), 1.64 – 1.45 (m, 2H), 1.02 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.8, 133.3, 129.6, 129.1, 69.9, 60.8, 34.3, 28.7, 21.7, 10.8. M.P.: 81 – 82 °C. IR (in KBr): 2362, 2341, 1637, 1400, 1166, 816 cm$^{-1}$. HRMS (EI) for C$_{12}$H$_{17}$NO$_3$S [M+Na]$^+$: calcd 278.0821, found 278.0826.

**Product 3**

Yield of 3: 95% as white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J$ = 7.8 Hz, 2H), 7.38 – 7.18 (m, 8H), 5.48 (d, $J$ = 5.8 Hz, 1H), 4.60 (d, $J$ = 8.7 Hz, 1H), 3.44 (p, $J$ = 6.5 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 1H), 1.89 (m, 1H), 1.67 (d, $J$ = 14.7 Hz, 1H), 1.10 (d, $J$ = 6.4 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.1, 143.3, 137.7, 129.6, 128.6, 127.8, 127.2, 125.6, 73.2, 49.3, 45.7, 22.2, 21.5. M.P.: 151 – 152 °C. IR (in KBr): 3533, 3277, 2976, 1312, 1158, 1088, 668 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{21}$NO$_3$S [M+H]$^+$: calcd 342.1140, found 342.1134.
4. Optimization of the Reaction Conditions

4.1 Impact of the base\textsuperscript{d}

\[
\begin{array}{|c|c|c|c|}
\hline
\text{entry} & \text{base} & \text{loading of base (eq.)} & \text{yield}^{b} (%) \\
\hline
1 & \text{NaOH} & 1.5 & 32 \\
2 & \text{K}_2\text{CO}_3 & 1.5 & 61 \\
3 & \text{NaHCO}_3 & 1.5 & 9 \\
4 & \text{Cs}_2\text{CO}_3 & 1.5 & 42 \\
5 & \text{tBuOK} & 1.5 & 43 \\
6 & \text{K}_2\text{HPO}_4 & 1.5 & 53 \\
7 & \text{DBU} & 1.5 & 38 \\
8 & \text{TMG} & 1.5 & 50 \\
9 & \text{K}_3\text{PO}_4 & 1.5 & 20 \\
10 & \text{LiOH} & 1.5 & 55 \\
11' & \text{Na}_2\text{CO}_3 & 1.5 & 49 \\
12' & \text{Li}_3\text{CO}_3 & 1.5 & \text{trace} \\
13' & \text{CsHCO}_3 & 1.5 & 39 \\
14 & \text{Na}_2\text{HPO}_4 & 1.5 & 8 \\
15 & \text{KOH} & 1.5 & 32 \\
16 & \text{KHCO}_3 & 1.5 & 31 \\
17' & \text{K}_2\text{CO}_3 & 1.0 & 58 \\
18' & \text{K}_2\text{CO}_3 & 2.0 & 69 \\
19' & \text{K}_2\text{CO}_3 & 2.0 & 59 \\
19' & \text{K}_2\text{CO}_3 & 2.5 & 59 \\
\hline
\end{array}
\]

\( ^{d}\text{Reaction conditions: 1a (0.10 mmol), } [\text{Ru(bpy)}_3\text{Cl}_2\text{H}_2\text{O} (2 \text{ mol\%})]\), base, 1.5 mL of CHCl\textsubscript{3}, 24 h, 3 W blue LEDs and r.t. \( ^{b}\text{Yield determined by } ^{1}\text{H NMR using 1,3,5-trimethoxybenzene as internal standard.} \)

4.2 Impact of photocatalyst \textsuperscript{a}

\[
\begin{array}{|c|c|c|c|}
\hline
\text{entry} & \text{photocatalyst} & \text{base} & \text{yield}^{d} (%) \\
\hline
1 & \text{Mes-AcrClO}_4 & \text{K}_2\text{CO}_3 & \text{trace} \\
\hline
\end{array}
\]
4.3 Impact of the photocatalyst loading

```
Ph
O
\[\text{Ts} \quad \text{O}^\text{\text{-NH}} \quad \text{Ts} \]
\[\text{Ph} \quad \text{O} \quad \text{O} \quad \text{O} \]

1a

\[\text{[Ru(bpy)_3]Cl}_2\cdot6\text{H}_2\text{O (x mol\%)} \quad \text{K}_2\text{CO}_3 (2.0 eq.), rt.} \]
\[\text{CHCl}_3 (1.5 \text{ mL}), 12 \text{ h}} \quad 3 \text{ W blue LEDs}

2a
```

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<tr>
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<td>8</td>
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“Reaction conditions: 1a (0.10 mmol), [Ru(bpy)_3]Cl2•6H2O (x mol%), K2CO3 (2.0 eq.), 1.5 mL of CHCl3, 24 h, 3 W blue LEDs and r.t. “Yield was determined by 1H NMR using 1,3,5-trimethoxybenzene as internal standard.

4.4 Impact of the solvent

```
Ph
O
\[\text{Ts} \quad \text{O}^\text{\text{-NH}} \quad \text{Ts} \]
\[\text{Ph} \quad \text{O} \quad \text{O} \quad \text{O} \]

1a

\[\text{[Ru(bpy)_3]Cl}_2\cdot6\text{H}_2\text{O (2 mol\%)} \quad \text{K}_2\text{CO}_3 (2.0 eq.), rt.} \]
\[\text{solvent (1.5 mL), 12 h}} \quad 3 \text{ W blue LEDs}

2a
```

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</table>

“Reaction conditions: 1a (0.10 mmol), [Ru(bpy)_3]Cl2•6H2O (2 mol%), K2CO3 (2.0 eq.), K2CO3 (2.0 eq.), 1.5 mL of CHCl3, 24 h, 3 W blue LEDs and r.t. "Yield was determined by 1H NMR using 1,3,5-trimethoxybenzene as internal standard.
5. Synthetic Utility of the Methodology

5.1 Sun-light driven reaction

1a (63.5 mg, 0.2 mmol), [Ru(bpy)_3]Cl_2•6H_2O (3.0 mg, 0.002 mol), K_2CO_3 (55.3 mg, 0.4 mmol) were dissolved in CHCl_3 (3.0 mL). Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times) under argon atmosphere. After that, the solution was stirring under sun light for 6 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 50:1) directly to give the desired product 2a in 65% isolated yield as a white solid.

5.2 Gram-scale reaction

1c (1.66 g, 5.0 mmol), [Ru(bpy)_3]Cl_2•6H_2O (37.5 mg, 0.001 mol), K_2CO_3 (1.38 g, 2.0 eq.) were dissolved in CHCl_3 (40 mL). Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~3 cm from a 3 W blue LEDs (×2) at room temperature about 48 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel.
(petroleum ether/ethyl acetate 50:1) directly to give the desired product 2c in 60% isolated yield as a white solid.

5.3 Synthesis of amino alcohol\textsuperscript{[4]}

![Reaction Scheme]

To a solution of 2a (63.5 mg, 0.2 mmol) in satd aq solution of NH$_4$Cl (2 mL) was added zinc (260 mg, 20 equiv). The mixture was stirred in a sealed vial at 100 °C. After 24 h at 100 °C, the reaction was cooled to r.t. and then evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/EtOAc 10:1 to 1:1) afforded 3 as a white solid (63.9 mg, 95% yield).

5.4 Preliminary attempts to remove the Ts group of 2a

(a) ![Reaction Scheme]

To a 10 mL flame-dried round schlenk tube were added 2a (31.7 mg, 0.1 mmol), Mg (24.0 mg, 1.0 mmol) in dry MeOH (2 mL). The mixture was stirred in microwave for 1.5h. However, there is no desired product as confirmed by $^1$H NMR.

(b) ![Reaction Scheme]

To a 10 mL flame-dried round schlenk tube were added 2a (31.7 mg, 0.1 mmol), NaOH (8.0 mg, 0.2 mmol) in dry MeOH (2 mL). The mixture was stirred in a sealed vial at 90 °C. After 12 h at 90 °C, the reaction was cooled to r.t.. However, there is no desired product as confirmed by $^1$H NMR analysis of the mixture.
2a (31.7 mg, 0.1 mmol) was dissolved in 1.2 mL of 98% H₂SO₄ and stirred for 1 h at room temperature. After completion of reaction, the solution was diluted with 20 mL of EA and neutralized with saturated sodium bicarbonate at 0 °C for 30 min, followed by extraction with EA. However, there is no desired product as confirmed by ¹H NMR analysis of the mixture.

6. Mechanism Investigation

6.1 The control experiments

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6.2 Luminescence quenching experiments

Fluorescence spectra were collected on Cary Eclipse Fluorescence Spectrophotometer. All Ru(bpy)₃Cl₂·6H₂O solutions were excited at 452 nm and the emission intensity at 616 nm was observed. In a typical experiment, the emission spectrum of a 4×10⁻⁶ M solution of Ru(bpy)₃Cl₂·6H₂O in DMF was collected. The decrease of Ru(bpy)₃²⁺ luminescence couldn’t be observed in the presence of substrate 1a. Under basic condition (K₂CO₃ 100mM), a significant decrease of Ru(bpy)₃²⁺ luminescence was successfully observed in the presence of 1a. These results
suggested that it was the nitrogen anion of N-sulfonyl-O-buteryl hydroxylamine instead of C=C double bond that quenched the excited photocatalyst *Ru(bpy)₃²⁺.

6.3 Deuterium labeling experiment

1a (0.2 mmol, 63.5 mg), K₂CO₃ (0.4 mmol, 55.3 mg), 4Å MS and Ru(bpy)₃Cl₂·6H₂O (0.004 mmol) were dissolved in solvent (3.0 mL). Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 3W blue LEDs (450-460 nm) at room temperature about 24 h. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 50:1) directly to give rise to a mixture of 2a and 2a’ in 29% yield with 6:1 ratio as a white solid. This finding indicates that the reaction media served as hydrogen source⁵, and the hydrogen atom transfer process should be the rate limiting step.

6.4 Trapping experiments with TEMPO
1a (0.2 mmol, 63.5 mg), K$_2$CO$_3$ (0.4 mmol, 55.3 mg), TEMPO (2.0 eq.) and Ru(bpy)$_3$Cl$_2$•6H$_2$O (0.004 mmol) were dissolved in CHCl$_3$ (3.0 mL). Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 3W blue LEDs (450-460 nm) at room temperature about 24 h. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 50:1) directly to give the desired product 2a as a white solid. When the TEMPO (2.0 eq.) was added to the reaction mixture under current conditions, the formation of 2a was totally inhibited, indicating the involvement of carbon-centred radical intermediate, which should be formed after the radical of nitrogen-centred radical.

6.5 Enantioselective version\cite{6}

(R)-1b (69.5 mg, 0.2 mmol), [Ru(bpy)$_3$]Cl$_2$•6H$_2$O (3.0 mg, 0.002 mol), K$_2$CO$_3$ (55.3 mg, 0.4 mmol) were dissolved in CHCl$_3$ (3.0 mL). Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times) under argon atmosphere. After that, the solution was stirred under 3 w blue LEDs for 24 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1) directly to give the desired product ($3R$, $5R$)-2b in 57% isolated yield as a white solid with 99% ee. $[\alpha]_D^{25} = -38.2$ (c = 1.00 in CHCl$_3$); >99% ee, determined by HPLC analysis (Chiralpak OD column, hexane/i-PrOH, 90:10 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), $t_R$ (major) = 12.22 min, $t_R$ (minor) = 13.73 min.
References


7. X-Ray structures of 2a and (3R, 5R)-2b
8. $^1$H NMR and $^{13}$C NMR Spectra of the Substrates and Products
9. HPLC Data of Product

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(3R, 5R)-2b

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