Supporting Information

Visible-light-promoted tandem radical difunctionalization of olefinic amides:
A direct access to NO₂-containing benzoxazines and oxazolines

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General Information
All the reagents and substrates were purchased from commercial suppliers with best quality and were used without further purification. All the solvents were distilled prior use according to the established procedures. The column chromatography was carried out using silica gel with 100-200 mesh size. $^1$H and $^{13}$C NMR spectra were measured in CDCl$_3$ with TMS as an internal standard. Chemical shifts ($\delta$) are reported in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). Data of the peaks are reported as follows: s, singlet; d, doublet, t, triplet; m, multiplet; dd, doublet of doublet; and so on. High-resolution mass spectra (HRMS) were collected by ESI-Q-TOF Premier mass spectrometer. Visible light irradiation was carried out using high-power blue LEDs Philips LUXEON® Rebel (9 W, $\lambda = 455 \pm 5$ nm). N-allylamides (4) were prepared according to the literature procedures.

Synthesis of N-Nitrosuccinimide (2): This compound was prepared according to the previously reported procedure.

\[ \begin{align*}
\text{N-Nitrosuccinimide (2): White solid, m.p. 88 °C.} \\
^1\text{H NMR (300 MHz, CDCl}_3\text{) } \delta 2.92 \text{ (s, 4H).} \\
^{13}\text{C NMR (75 MHz, CDCl}_3\text{) } \delta 168, 27.12. \text{ HRMS (ESI), calcd for C}_4\text{H}_4\text{N}_2\text{O}_4 [M]+ 144.0171, \text{ found 144.0170.}
\end{align*} \]

General experimental details
A 20-mL vial equipped with magnetic stir bar was charged with olefinic amides (0.5 mmol, 1.0 equiv.), N-Nitrosuccinimides (1.0 mmol, 2.0 equiv.) and Ru(bpy)$_3$(PF$_6$)$_2$ (3 mol%) and the mixture was degassed by “pump-freeze-thaw” cycles (x3) via a syringe needle. Then dry CH$_3$CN (3.0 mL) was injected under Ar and the resulting mixture was stirred at room temperature under 9 W blue LEDs for 7 h. After completion of the reaction (as indicated by TLC), the mixture was diluted by adding ethyl acetate and brine. The aqueous layer was extracted with ethyl acetate (x3) and combined organic layer was dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The crude products were further purified by filtration through short-pad of silica-gel column
chromatography using mixture of ethyl acetate and n-hexane. The identity and purity of the products was confirmed by spectroscopic analysis.

**Experimental characterization data for products**

![Structure 3a](image1)

4-methyl-4-(nitromethyl)-2-phenyl-4H-benzo[d][1,3]oxazine (3a): Yellow solid 81% (81 mg), m.p. 75-77 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97 (dt, $J = 6.9, 1.2$ Hz, 2H), 7.56 – 7.46 (m, 3H), 7.45 – 7.38 (m, 1H), 7.32 – 7.24 (m, 3H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 162.53, 141.34, 135.89, 132.49, 131.15, 129.12, 127.27, 125.11, 124.73, 84.41, 25.41. HRMS (ESI), calcd for C$_{16}$H$_{14}$N$_2$O$_3$ [M+H]$^+$ 283.1038, found 283.1039.

![Structure 3b](image2)

4-methyl-4-(nitromethyl)-2-(p-tolyl)-4H-benzo[d][1,3]oxazine (3b): Yellow oil 84% (78 mg) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.91 – 7.83 (m, 2H), 7.47 – 7.38 (m, 1H), 7.34 – 7.26 (m, 2H), 7.30 – 7.20 (m, 3H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 2.26 (s, 3H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 162.53, 141.89, 141.34, 135.89, 131.29, 129.39, 129.14, 128.12, 125.21, 125.00, 124.73, 84.40, 25.41, 21.42. HRMS (ESI), calcd for C$_{17}$H$_{16}$N$_2$O$_3$ [M+H]$^+$ 297.1194, found 297.1195.

![Structure 3c](image3)
2-(4-methoxyphenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3c): Yellow oil 89% (81 mg). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.06 – 7.98 (m, 2H), 7.46 – 7.38 (m, 1H), 7.33 – 7.21 (m, 3H), 6.94 – 6.86 (m, 2H), 4.96 (d, $J$ = 14.2 Hz, 1H), 4.71 (d, $J$ = 14.2 Hz, 1H), 3.82 (s, 3H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 163.00, 162.56, 141.36, 135.91, 132.24, 129.94, 129.17, 125.13, 124.76, 114.53, 84.43, 55.38, 25.43. HRMS (ESI), calcd for C$_{17}$H$_{16}$N$_2$O$_4$ [M+H]$^+$ 313.1144, found 313.1145.

![Image of 3c](image)

4-methyl-4-(nitromethyl)-2-(4-nitrophenyl)-4H-benzo[d][1,3]oxazine (3d): Pale yellow solid 74% (71 mg), m.p. 80-82 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.28 – 8.20 (m, 2H), 8.11 – 8.03 (m, 2H), 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, $J$ = 14.2 Hz, 1H), 4.71 (d, $J$ = 14.2 Hz, 1H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 162.53, 148.49, 141.34, 135.89, 134.64, 131.26, 129.14, 125.11, 124.73, 124.01, 84.41, 25.41. HRMS (ESI), calcd for C$_{16}$H$_{13}$N$_3$O$_5$ [M+H]$^+$ 328.0889, found 328.0888.

![Image of 3d](image)

2-(4-chlorophenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3e): White solid 72% (85 mg), m.p. 118-120 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.89 – 7.81 (m, 2H), 7.44 – 7.41 (m, 1H), 7.39 – 7.35 (m, 2H), 7.32 – 7.22 (m, 3H), 4.96 (d, $J$ = 14.2 Hz, 1H), 4.71 (d, $J$ = 14.2 Hz, 1H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 162.53, 141.34, 136.70, 135.89, 133.23, 131.41, 129.51, 129.14, 125.21, 125.00, 124.14, 84.41, 25.41. HRMS (ESI), calcd for C$_{16}$H$_{13}$ClN$_2$O$_3$ [M+H]$^+$ 318.0585, found 318.0584.

![Image of 3e](image)
**2-(4-bromophenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3f):** White solid 76% (82 mg), m.p. 109-111 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.81 – 7.73 (m, 2H), 7.57 – 7.49 (m, 2H), 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, \(J = 14.2\) Hz, 1H), 4.71 (d, \(J = 14.2\) Hz, 1H), 1.79 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 162.53, 141.34, 135.89, 132.43, 131.81, 130.52, 129.14, 126.93, 125.11, 124.73, 84.41, 25.41. HRMS (ESI), calcd for C\(_{16}\)H\(_{13}\)BrN\(_2\)O\(_3\) [M+H]\(^+\) 362.0089, found 362.0088.

**4-methyl-4-(nitromethyl)-2-(4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazine (3g):** White solid 55% (53 mg), m.p. 95-97 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.89 – 7.81 (m, 2H), 7.78 – 7.70 (m, 2H), 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, \(J = 14.2\) Hz, 1H), 4.71 (d, \(J = 14.2\) Hz, 1H), 1.79 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 162.53, 141.34, 135.89, 132.43, 131.81, 130.52, 129.14, 126.93, 125.11, 124.73, 84.41, 25.41. HRMS (ESI), calcd for C\(_{17}\)H\(_{13}\)F\(_3\)N\(_2\)O\(_3\) [M+H]\(^+\) 351.0912, found 351.0911.

**2-(4-(tert-butyl)phenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3h):** Yellowish oil 82% (87 mg). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.88 – 7.80 (m, 2H), 7.64 – 7.56 (m, 2H), 7.46 – 7.38 (m, 1H), 7.32 – 7.22 (m, 3H), 4.96 (d, \(J = 14.2\) Hz, 1H), 4.71 (d, \(J = 14.2\) Hz, 1H), 1.79 (s, 3H), 1.33 (s, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 162.53, 155.35, 141.34, 135.89, 131.47, 129.14,
127.96, 126.12, 125.21, 125.00, 124.73, 84.41, 35.00, 31.09, 25.41. HRMS (ESI), calcd for C_{20}H_{22}N_{2}O_{3} [M+H]^+ 339.1664, found 339.1665.

4-methyl-4-(nitromethyl)-2-(o-tolyl)-4H-benzo[d][1,3]oxazine (3i): Yellowish oil 66% (59 mg). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.71 (ddd, $J = 7.4, 1.2, 0.7$ Hz, 1H), 7.45 – 7.38 (m, 1H), 7.35 – 7.22 (m, 6H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 2.48 (d, $J = 0.5$ Hz, 3H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 161.03, 141.34, 137.35, 135.89, 134.61, 130.73, 129.24 (d, $J = 19.1$ Hz), 84.41, 25.41, 19.93. HRMS (ESI), calcd for C$_{17}$H$_{16}$N$_2$O$_3$ [M+H]$^+$ 297.1194, found 297.1193.

4-methyl-4-(nitromethyl)-2-(m-tolyl)-4H-benzo[d][1,3]oxazine (3j): Yellowish oil 78% (82 mg). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.87 (ddd, $J = 7.0, 2.2, 1.2$ Hz, 1H), 7.44 – 7.41 (m, 1H), 7.31 – 7.23 (m, 4H), 7.21 (t, $J = 2.2$ Hz, 1H), 7.16 (dd, $J = 7.9, 7.1$ Hz, 1H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 2.38 (d, $J = 0.8$ Hz, 3H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 162.59, 141.34, 139.07, 135.89, 134.09, 132.02, 129.04, 128.33, 125.21, 125.00, 124.73, 84.41, 25.41, 21.29. HRMS (ESI), calcd for C$_{17}$H$_{16}$N$_2$O$_3$ [M+H]$^+$ 297.1194, found 297.1193.
2-(3-chlorophenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3k): Yellowish oil 69% (66.5 mg). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.90 (t, $J = 2.3$ Hz, 1H), 7.85 (ddd, $J = 7.3$, 2.2, 1.2 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.37 – 7.21 (m, 4H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 135.89, 135.25, 132.69, 130.78, 129.06, 128.62, 125.21, 125.00, 124.73, 84.41, 25.41. HRMS (ESI), calcd for C$_{16}$H$_{13}$ClN$_2$O$_3$ [M+H]$^+ 318.0585$, found 318.0586.

4-methyl-4-(nitromethyl)-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazine (3l): Yellowish oil 75% (79 mg). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.61 (dd, $J = 5.7$, 1.8 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.32 – 7.23 (m, 3H), 7.06 (dd, $J = 5.4$, 1.8 Hz, 1H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 151.94, 141.34, 135.89, 130.70, 128.96, 127.83, 125.21, 125.00, 124.73, 84.41, 25.41. HRMS (ESI), calcd for C$_{14}$H$_{12}$N$_2$O$_3$S [M+H]$^+ 289.0602$, found 289.0604.

2-(furan-2-yl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3m): White solid 71% (76 mg), m.p. 92-95 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97 (t, $J = 1.7$ Hz, 1H), 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 7.14 (dd, $J = 4.4$, 1.6 Hz, 1H), 6.74 (dd, $J = 4.4$, 1.6 Hz, 1H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.46, 143.04, 141.06, 135.89, 129.14, 125.21, 125.00, 124.73, 118.83, 113.17, 84.40, 25.41. HRMS (ESI), calcd for C$_{14}$H$_{12}$N$_2$O$_4$ [M+H]$^+ 273.0831$, found 273.0830.
2,4-dimethyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3n): Yellowish oil 68% (55 mg). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.45 – 7.38 (m, 1H), 7.32 – 7.21 (m, 3H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 2.07 (s, 3H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 162.81, 142.72, 132.88, 128.92, 124.64, 123.42, 84.41, 25.41, 20.13. HRMS (ESI), calcd for C$_{11}$H$_{12}$N$_2$O$_3$ [M+H]$^+$ 221.0881, found 221.0882.

2-(tert-butyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3o): Yellowish oil 72% (68 mg). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.45 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 10H), 1.79 (s, 3H), 1.24 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 171.83, 141.34, 135.89, 129.14, 125.73, 124.73, 84.41, 35.68, 27.76, 25.41. HRMS (ESI), calcd for C$_{14}$H$_{18}$N$_2$O$_3$ [M+H]$^+$ 263.1351, found 263.1350.

2-cyclopropyl-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3p): Yellow oil 59% (46 mg). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 1.79 (s, 3H), 0.77 – 0.61 (m, 2H), 0.52 – 0.36 (m, 2H), 0.20 (p, $J = 5.5$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.68, 141.69, 134.83, 129.05, 124.83, 124.46, 84.41, 25.41, 15.85, 8.54. HRMS (ESI), calcd for C$_{13}$H$_{14}$N$_2$O$_3$ [M+H]$^+$ 247.1038, found 247.1039.
6-chloro-4-methyl-4-(nitromethyl)-2-phenyl-4H-benzo[d][1,3]oxazine (3q): Yellowish oil 67% (61 mg). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97 (dd, $J = 7.1, 1.7$ Hz, 2H), 7.58 – 7.44 (m, 3H), 7.42 – 7.37 (m, 1H), 7.34 – 7.26 (m, 2H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.2$ Hz, 1H), 1.79 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 162.53, 141.78, 132.48, 131.87, 131.15, 129.12, 128.99, 127.14, 125.45, 84.41, 25.41. HRMS (ESI), calcd for C$_{16}$H$_{13}$ClN$_2$O$_3$ [M+H]$^+$ 318.0585, found 318.0586.

4-(nitromethyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (3r): White solid 82% (87 mg), m.p. 102-105 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.99 – 7.94 (m, 2H), 7.58 – 7.47 (m, 7H), 7.44 – 7.40 (m, 1H), 7.33 – 7.23 (m, 3H), 7.18 (tt, $J = 6.3, 1.6$ Hz, 1H), 5.30 (d, $J = 14.8$ Hz, 1H), 5.05 (d, $J = 14.8$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 161.64, 143.47, 131.15, 129.82, 129.10, 128.28, 127.28, 126.52, 125.04, 124.21, 123.34, 88.52, HRMS (ESI), calcd for C$_{21}$H$_{16}$N$_2$O$_3$ [M+H]$^+$ 345.1194, found 345.1193.

4-(nitromethyl)-2-phenyl-4-(p-tolyl)-4H-benzo[d][1,3]oxazine (3s): White solid 78% (76.5 mg), m.p. 94-96 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.00 – 7.90 (m, 2H), 7.58 – 7.44 (m, 3H), 7.49 – 7.38 (m, 1H), 7.32 – 7.21 (m, 3H), 7.22 – 7.14 (m, 2H), 6.89 – 6.81 (m, 2H), 5.30 (d, $J = 14.8$ Hz, 1H), 5.05 (d, $J = 14.8$ Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 161.64,
143.95, 141.47, 137.34, 132.48, 131.15, 129.82, 128.99, 128.45, 126.91, 125.04, 124.21, 123.34, 88.52, 21.19. HRMS (ESI), calcd for C$_{22}$H$_{18}$N$_2$O$_3$ [M+H]$^+$ 359.1351, found 359.1352.

5-(nitromethyl)-2,5-diphenyl-4,5-dihydrooxazole (5a): Yellow oil 73% (71.5 mg). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.92 (dd, $J = 7.3$, 1.6 Hz, 2H), 7.58 – 7.47 (m, 3H), 7.39 (t, $J = 7.3$ Hz, 2H), 6.92 – 6.88 (m, 1H), 6.75 (dd, $J = 7.6$, 6.4 Hz, 2H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.5$ Hz, 1H), 4.10 (d, $J = 12.5$ Hz, 1H), 3.85 (d, $J = 12.4$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 160.88, 135.06, 131.15, 128.88, 127.92, 126.91, 126.55, 125.68, 87.26, 63.67. HRMS (ESI), calcd for C$_{16}$H$_{14}$N$_2$O$_3$ [M+H]$^+$ 283.1038, found 283.1037.

5-(nitromethyl)-5-phenyl-2-(p-tolyl)-4,5-dihydrooxazole (5b): Yellow oil 78% (82 mg). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.87 (d, $J = 7.9$ Hz, 2H), 7.51 (dd, $J = 7.6$, 1.5 Hz, 2H), 7.24 (dd, $J = 7.8$, 0.9 Hz, 2H), 6.94 – 6.86 (m, 1H), 6.79 – 6.70 (m, 2H), 4.96 (d, $J = 14.2$ Hz, 1H), 4.71 (d, $J = 14.4$ Hz, 1H), 4.10 (d, $J = 12.5$ Hz, 1H), 3.85 (d, $J = 12.4$ Hz, 1H), 2.26 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 160.88, 141.89, 135.06, 129.34, 127.92, 127.25, 126.91, 125.68, 87.26, 63.67, 21.42. HRMS (ESI), calcd for C$_{17}$H$_{16}$N$_2$O$_3$ [M+H]$^+$ 297.1194, found 297.1193.

2-(4-methoxyphenyl)-5-(nitromethyl)-5-phenyl-4,5-dihydrooxazole (5c): Yellow oil 81% (85 mg). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.02 (d, $J = 8.3$ Hz, 2H), 7.51 (dd, $J = 7.6$, 1.4 Hz, 2H), 6.94 – 6.86 (m, 3H), 6.79 – 6.70 (m, 2H), 4.96 (d, $J = 14.3$ Hz, 1H), 4.71 (dd, $J = 14.5$, 0.7 Hz, 1H), 3.85 (d, $J = 12.4$ Hz, 1H), 3.69 (s, 3H). HRMS (ESI), calcd for C$_{22}$H$_{18}$N$_2$O$_3$ [M+H]$^+$ 359.1351, found 359.1352.
4.10 (d, J = 12.5 Hz, 1H), 3.85 (d, J = 12.5 Hz, 1H), 3.82 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 162.98, 160.88, 135.06, 127.90, 126.91, 125.68, 114.58, 87.26, 63.67, 55.35. HRMS (ESI), calcd for C$_{17}$H$_{16}$N$_2$O$_3$ [M+H]$^+$ 313.1144, found 313.1143.

5-(4-bromophenyl)-5-(nitromethyl)-5-phenyl-4,5-dihydrooxazole (5d): Yellow oil 83% (86 mg). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.55 – 7.49 (m, 4H), 6.92 – 6.88 (m, 1H), 6.75 (dd, J = 7.6, 6.5 Hz, 2H), 4.96 (d, J = 14.1 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 4.10 (d, J = 12.5 Hz, 1H), 3.85 (d, J = 12.6 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 160.88, 135.06, 132.41, 129.17, 127.92, 126.92, 125.68, 87.26, 63.67. HRMS (ESI), calcd for C$_{16}$H$_{13}$BrN$_2$O$_3$ [M+H]$^+$ 362.0089, found 362.0088.

5-(nitromethyl)-2-phenyl-5-(p-tolyl)-4,5-dihydrooxazole (5e): Yellow oil 82% (81 mg). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.92 (dd, J = 7.3, 1.6 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.43 – 7.30 (m, 14H), 7.14 – 7.08 (m, 2H), 4.96 (d, J = 14.2 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 4.10 (d, J = 12.6 Hz, 1H), 3.85 (d, J = 12.6 Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 160.88, 137.11, 134.61, 131.15, 129.22, 128.88, 126.55, 124.08, 87.26, 63.67, 21.19. HRMS (ESI), m/z calcd for C$_{17}$H$_{16}$N$_2$O$_3$ [M+H]$^+$ 297.1194, found 297.1195.

5-(4-methoxyphenyl)-5-(nitromethyl)-2-phenyl-4,5-dihydrooxazole (5f): Yellow oil 71% (69 mg). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.92 (dd, J = 7.3, 1.6 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.42 –
7.36 (m, 2H), 6.82 (d, J = 8.5 Hz, 2H), 4.96 (d, J = 14.3 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 4.10 (d, J = 12.5 Hz, 1H), 3.85 (d, J = 12.5 Hz, 1H), 3.82 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 160.88, 158.88, 132.16, 131.15, 128.88, 126.55, 126.06, 113.71, 87.26, 63.67, 55.35. HRMS (ESI), calcd for C$_{17}$H$_{16}$N$_2$O$_4$ [M+H]$^+$ 313.1144, found 313.1145.

$^{5g}$

5-(4-chlorophenyl)-5-(nitromethyl)-2-phenyl-4,5-dihydrooxazole ($^{5g}$): Yellow oil 82% (87 mg). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.92 (dd, J = 7.3, 1.6 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.42 – 7.32 (m, 4H), 7.30 – 7.25 (m, 2H), 4.96 (d, J = 14.1 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 4.10 (d, J = 12.6 Hz, 1H), 3.85 (d, J = 12.5 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 160.88, 134.12, 132.74, 131.15, 128.88, 128.36, 126.66, 87.26, 63.67. HRMS (ESI), calcd for C$_{16}$H$_{13}$ClN$_2$O$_3$ [M+H]$^+$ 318.0585, found 318.0584.

$^{5h}$

5-(nitromethyl)-5-phenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole ($^{5h}$): Yellow oil 35% (42 mg). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.92 (dd, J = 7.3, 1.6 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.43 – 7.34 (m, 2H), 4.61 (d, J = 13.7 Hz, 1H), 4.36 (d, J = 13.9 Hz, 1H), 3.75 (d, J = 12.3 Hz, 1H), 3.50 (d, J = 12.3 Hz, 1H), 1.50 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.10, 131.14, 128.87, 126.54, 94.36, 87.58, 70.93, 23.49. HRMS (ESI), calcd for C$_{11}$H$_{12}$N$_2$O$_3$ [M+H]$^+$ 221.0881, found 221.0882.

$^{5i}$

5-(nitromethyl)-5-phenyl-2-(thiophen-2-yl)-4,5-dihydrooxazole ($^{5i}$): Yellow oil 65% (72 mg). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.61 (dd, J = 5.7, 1.8 Hz, 1H), 7.51 (dd, J = 7.6, 1.5 Hz, 2H), 7.44 (t, J = 5.6 Hz, 1H), 7.06 (dd, J = 5.4, 1.8 Hz, 1H), 6.94 – 6.86 (m, 1H), 6.75 (dd, J = 7.6, 6.5 Hz,
2H), 4.96 (d, J = 14.1 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 1.90 (d, J = 12.5 Hz, 1H), 1.60 (d, J = 12.4 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.95, 135.06, 130.70, 127.92, 127.83, 126.91, 126.40, 125.68, 125.62, 87.31, 62.31. HRMS (ESI), calcd for C$_{14}$H$_{12}$N$_2$O$_3$S [M+H]$^+$ 288.0569, found 288.0568.

References


Figure S1. $^1$H NMR spectra of 2 in CDCl$_3$. 

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Figure S2. $^{13}$C NMR spectra of 2 in CDCl$_3$. 
**Figure S3.** $^1$H NMR spectra of 3a in CDCl$_3$. 
Figure S4. $^{13}$C NMR spectra of 3a in CDCl$_3$. 
Figure S5. $^1$H NMR spectra of 3b in CDCl$_3$. 
Figure S6. $^{13}$C NMR spectra of 3b in CDCl$_3$. 
Figure S7. $^1$H NMR spectra of 3c in CDCl$_3$. 
Figure S8. $^{13}$C NMR spectra of 3c in CDCl$_3$. 
Figure S9. $^1$H NMR spectra of 3d in CDCl$_3$. 
Figure S10. $^{13}$C NMR spectra of 3d in CDCl$_3$. 
Figure S11. $^1$H NMR spectra of $3e$ in CDCl$_3$. 
Figure S12. $^{13}$C NMR spectra of 3e in CDCl$_3$. 
Figure S13. $^1$H NMR spectra of 3f in CDCl$_3$. 
Figure S14. $^{13}$C NMR spectra of 3f in CDCl$_3$. 
Figure S15. $^1$H NMR spectra of 3g in CDCl$_3$. 
Figure S16. $^13$C NMR spectra of 3g in CDCl$_3$. 
Figure S17. $^1$H NMR spectra of 3h in CDCl$_3$. 
Figure S18. $^{13}$C NMR spectra of 3h in CDCl$_3$. 
Figure S19. $^1$H NMR spectra of 3i in CDCl$_3$. 
Figure S20. $^{13}$C NMR spectra of 3i in CDCl$_3$. 
Figure S21. $^1$H NMR spectra of 3j in CDCl$_3$. 
Figure S22. $^{13}$C NMR spectra of 3j in CDCl$_3$. 
Figure S23. $^1$H NMR spectra of 3k in CDCl$_3$. 
Figure S24. $^{13}$C NMR spectra of 3k in CDCl$_3$. 
Figure S25. $^1$H NMR spectra of 3l in CDCl$_3$. 
Figure S26. $^{13}$C NMR spectra of 3l in CDCl$_3$. 
Figure S27. $^1$H NMR spectra of 3m in CDCl$_3$. 
Figure S28. $^{13}$C NMR spectra of 3m in CDCl$_3$. 
Figure S29. $^1$H NMR spectra of 3n in CDCl$_3$. 
Figure S30. $^{13}$C NMR spectra of 3n in CDCl$_3$. 
Figure S31. $^1$H NMR spectra of 3o in CDCl$_3$. 
Figure S32. $^{13}$C NMR spectra of 3o in CDCl$_3$. 

\[ \text{Figure S32: }^{13}\text{C NMR spectra of 3o in CDCl}_3. \]
Figure S33. $^1$H NMR spectra of 3p in CDCl$_3$. 
Figure S34. $^{13}$C NMR spectra of 3p in CDCl$_3$. 
Figure S35. $^1$H NMR spectra of 3q in CDCl$_3$. 
Figure S36. $^{13}$C NMR spectra of 3q in CDCl$_3$. 
Figure S37. $^1$H NMR spectra of 3r in CDCl$_3$. 
Figure S38. $^{13}$C NMR spectra of 3r in CDCl$_3$. 
Figure S39. $^1$H NMR spectra of 3s in CDCl$_3$. 
Figure S40. $^{13}$C NMR spectra of 3s in CDCl$_3$. 
Figure S41. $^1$H NMR spectra of 5a in CDCl$_3$. 
Figure S42. $^{13}$C NMR spectra of 5a in CDCl$_3$. 
Figure S43. $^1$H NMR spectra of 5b in CDCl$_3$. 
Figure S44. $^{13}$C NMR spectra of 5b in CDCl$_3$. 
Figure S45. $^1$H NMR spectra of 5c in CDCl$_3$. 
Figure S46. $^{13}$C NMR spectra of 5c in CDCl$_3$. 
Figure S47. $^1$H NMR spectra of 5d in CDCl$_3$. 
Figure S48. $^{13}$C NMR spectra of 5d in CDCl$_3$. 
Figure S49. $^1$H NMR spectra of 5e in CDCl$_3$. 
Figure S50. $^{13}$C NMR spectra of 5e in CDCl$_3$. 
Figure S51. $^1$H NMR spectra of 5f in CDCl$_3$. 
Figure S52. $^{13}$C NMR spectra of 5f in CDCl$_3$. 
Figure S53. $^1$H NMR spectra of 5g in CDCl$_3$. 
Figure S54. $^{13}$C NMR spectra of $5g$ in CDCl$_3$. 
Figure S55. $^1$H NMR spectra of 5h in CDCl$_3$. 
Figure S56. $^{13}$C NMR spectra of 5h in CDCl$_3$. 
Figure S57. $^{13}$C NMR spectra of 5i in CDCl$_3$. 
Figure S58. $^{13}$C NMR spectra of 5i in CDCl$_3$.

Figure S59. Pictorial diagram of reaction setup.