Supporting information

Highly efficient synthesis of β-nitrate ester carboxamides through the ring-opening of 2-oxazolines

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1. General Information

All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All reagents and solvents were commercially available and used without any further purification unless specified. Proton (1H NMR) and carbon (13C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for 1H NMR: TMS = 0.00 ppm, for 13C NMR: CDCl3 = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. Analytical TLC was performed on precoated silica gel plates. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experimental Section

2.1 General Procedure for the synthesis of starting materials

2.1.1 Synthesis of 2-aryl oxazolines and 2-aryl oxazines

In a three-necked flask (100 mL), substituted benzonitrile (20 mmol), ZnCl2 (2.0 mmol) and chlorobenzene (35 mL) were added under Argon. 2-Aminoethanol or 3-aminopropanol (60 mmol) was added to the suspension via a syringe. The mixture was heated to reflux for 36 h. After refluxing for 36 hours, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. CH2Cl2 (250 mL) was added to the residue and washed with saturated NaHCO3 (150 mL) and H2O (150 mL). The aqueous fraction was extracted with CH2Cl2 (250 mL × 3). The combined organic phase was dried over Na2SO4, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel and further recrystallized from EtOAc/hexane to give colorless crystals.

2.1.2 Synthesis of N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide

Substituted 2-(4,5-dihydrooxazol-2-yl)aniline (5 mmol) and acid chloride (5.5 mmol) were added to a 100 mL flask and then dissolved with THF (20 mL). Et3N (7.5 mmol) was taken to the vigorously stirred solution via a syringe. The reaction was stirred at room temperature for 10 h and quenched with saturated NaHCO3. And then the mixture was extracted with EtOAc. Combined organic phase was washed with brine, dried over anhydrous Na2SO4, and concentrated under
reduced pressure. The crude product was further recrystallized from EtOAc/hexane to give colorless crystals of the product.

\[ \text{N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (1a)} \]
\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 13.01 (s, 1H), 8.97 (d, } J = 8.4 \text{ Hz, 1H), 8.14} - 8.03 (m, 2H), 7.88 (dd, } J = 7.9, 1.7 \text{ Hz, 1H), 7.57} - 7.43 (m, 4H), 7.09 (t, } J = 7.6 \text{ Hz, 1H), 4.38 (t, } J = 9.3 \text{ Hz, 2H), 4.16 (t, } J = 9.6 \text{ Hz, 2H); } ^1\text{C NMR (100 MHz, CDCl}_3) \delta 165.99, 164.84, 140.12, 135.24, 132.54, 131.56, 129.22, 128.49, 127.66, 122.31, 119.78, 113.49, 66.18, 54.60; \text{ HRMS (ESI-TOF) m/z Calcd for C}_{16}\text{H}_{14}\text{N}_2\text{O}_2 [M+H]^+: 267.1128, found: 267.1125. \]

\[ \text{N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-methylbenzamide (1b)} \]
\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 12.49 (s, 1H), 8.86 (d, } J = 8.4 \text{ Hz, 1H), 7.79} (dd, } J = 7.9, 1.4 \text{ Hz, 1H), 7.54 (d, } J = 8.5 \text{ Hz, 1H), 7.42 (t, } J = 8.6 \text{ Hz, 1H), 7.26 (t, } J = 7.9 \text{ Hz, 1H), 7.22} - 7.13 (m, 2H), 7.01 (t, } J = 7.9 \text{ Hz, 1H), 4.23 (t, } J = 9.5 \text{ Hz, 2H), 3.93 (t, } J = 9.5 \text{ Hz, 2H), 2.48 (s, 3H); } ^1\text{C NMR (100 MHz, CDCl}_3) \delta 168.60, 164.52, 140.04, 137.08, 136.66, 134.66, 131.28, 130.04, 129.17, 127.45, 125.69, 122.35, 119.64, 113.39, 66.10, 54.59, 20.28; \text{ HRMS (ESI-TOF) m/z Calcd for C}_{17}\text{H}_{16}\text{N}_2\text{O}_2[M+H]^+: 281.1285, found: 281.1290. \]

\[ \text{N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-4-methylbenzamide (1c)} \]
\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 12.95 (s, 1H), 8.96 (d, } J = 9.0 \text{ Hz, 1H), 7.98} (d, } J = 8.2 \text{ Hz, 2H), 7.88} (dd, } J = 7.9, 1.5 \text{ Hz, 1H), 7.51 (t, } J = 8.6 \text{ Hz, 1H), 7.29} (d, } J = 8.0 \text{ Hz, 2H), 7.09 (t, } J = 8.1 \text{ Hz, 1H), 4.39 (t, } J = 9.7 \text{ Hz, 2H), 4.18 (t, } J = 9.7 \text{ Hz, 2H), 2.42 (s, 3H); } ^1\text{C NMR (100 MHz, CDCl}_3) \delta 166.06, 164.89, 142.03, 140.29, 132.58, 132.53, 129.22, 127.72, 122.18, 119.81, 113.43, 66.19, 54.66, 21.45; \text{ HRMS (ESI-TOF) m/z Calcd for C}_{17}\text{H}_{16}\text{N}_2\text{O}_2[M+H]^+: 281.1285, found: 281.1292. \]
**N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-3,4-dimethoxybenzamide (1d)**

$^1$H NMR (400 MHz, CDCl$_3$) δ 12.92 (s, 1H), 8.96 (d, $J = 8.4$ Hz, 1H), 7.88 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.77 – 7.65 (m, 2H), 7.51 (t, $J = 8.6$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 4.40 (t, $J = 9.6$ Hz, 2H), 4.18 (t, $J = 9.3$ Hz, 2H), 3.98 (s, 3H), 3.95 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.51, 165.05, 151.86, 148.72, 140.33, 132.64, 129.27, 127.75, 122.10, 121.03, 119.61, 113.24, 110.60, 110.45, 66.13, 55.95, 55.83, 54.66; HRMS (ESI-TOF) m/z Calcd for C$_{18}$H$_{18}$N$_2$O$_4$ [M+H]$^+$: 327.1339, found: 327.1349.

**N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-fluorobenzamide (1e)**

$^1$H NMR (400 MHz, CDCl$_3$) δ 12.80 (s, 1H), 8.91 (d, $J = 8.3$ Hz, 1H), 7.95 (td, $J = 7.6$, 0.9 Hz, 1H), 7.65 – 7.42 (m, 2H), 7.21 – 7.07 (m, 2H), 4.36 (t, $J = 9.4$ Hz, 2H), 4.10 (t, $J = 9.5$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.24, 162.95 (d, $J_{C-F} = 1.8$ Hz), 160.02 (d, $J_{C-F} = 252.6$ Hz), 139.60, 132.86 (d, $J_{C-F} = 8.6$ Hz), 132.36, 131.06 (d, $J_{C-F} = 3.6$ Hz), 124.02 (d, $J_{C-F} = 12.8$ Hz), 122.74, 120.44, 116.39 (d, $J_{C-F} = 22.9$ Hz), 113.99, 66.22, 54.65; HRMS (ESI-TOF) m/z Calcd for C$_{16}$H$_{13}$FN$_2$O$_2$ [M+H]$^+$: 285.1034, found: 285.1045.

**4-chloro-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (1f)**

$^1$H NMR (400 MHz, CDCl$_3$) δ 13.04 (s, 1H), 8.93 (d, $J = 8.4$ Hz, 1H), 8.03 (d, $J = 8.5$ Hz, 2H), 7.90 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.52 (t, $J = 8.5$ Hz, 1H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.12 (t, $J = 7.6$ Hz, 1H), 4.43 (t, $J = 9.6$ Hz, 2H), 4.20 (t, $J = 9.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.05, 164.94, 139.99, 137.90, 133.75, 132.72, 129.31, 129.14, 128.82, 122.58, 119.84, 113.52, 66.29, 54.63; HRMS (ESI-TOF) m/z Calcd for C$_{16}$H$_{13}$ClN$_2$O$_2$ [M+H]$^+$: 301.0738, found: 301.0746.
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-4-(trifluoromethyl)benzamide (1g)

$^1$H NMR (400 MHz, CDCl$_3$) δ 13.16 (s, 1H), 8.93 (d, $J = 8.3$ Hz, 1H), 8.18 (d, $J = 8.2$ Hz, 2H), 7.89 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.52 (t, $J = 8.6$ Hz, 1H), 7.12 (t, $J = 8.1$ Hz, 1H), 4.41 (t, $J = 9.6$ Hz, 2H), 4.18 (t, $J = 9.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.00, 164.50, 139.76, 138.49, 133.15 (q, $J_{C-F} = 32.6$ Hz), 132.69, 129.32, 128.09, 125.55 (q, $J_{C-F} = 3.7$ Hz), 123.76 (q, $J_{C-F} = 270.9$ Hz), 122.79, 119.80, 113.59, 66.30, 54.55; HRMS (ESI-TOF) m/z Calcd for C$_{17}$H$_{13}$F$_3$N$_2$O$_2$ [M+H]$^+$: 335.1002, found: 335.1008.

\[
\begin{array}{c}
\text{N-(2-(4,5-dihydrooxazol-2-yl)phenyl)pivalamide (1h)}
\end{array}
\]

$^1$H NMR (400 MHz, CDCl$_3$) δ 12.22 (s, 1H), 8.80 (d, $J = 9.2$ Hz, 1H), 7.85 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.45 (t, $J = 8.7$ Hz, 1H), 7.05 (t, $J = 8.1$ Hz, 1H), 4.38 (t, $J = 9.7$ Hz, 2H), 4.15 (t, $J = 9.6$ Hz, 2H), 1.33 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 178.30, 164.65, 140.32, 132.43, 129.11, 121.87, 119.71, 113.28, 66.11, 54.64, 40.47, 27.71; HRMS (ESI-TOF) m/z Calcd for C$_{14}$H$_{18}$N$_2$O$_2$ [M+H]$^+$: 247.1441, found: 247.1448.

\[
\begin{array}{c}
\text{N-(2-(4,5-dihydrooxazol-2-yl)phenyl)thiophene-2-carboxamide (1i)}
\end{array}
\]

$^1$H NMR (400 MHz, CDCl$_3$) δ 13.07 (s, 1H), 8.85 (d, $J = 9.2$ Hz, 1H), 8.29 (d, $J = 9.5$ Hz, 1H), 7.98 – 7.82 (m, 2H), 7.53 (d, $J = 7.9$, 1.5 Hz, 1H), 7.78 (dd, $J = 7.7$, 1.0 Hz, 1H), 7.53 (dd, $J = 5.0$, 1.0 Hz, 1H), 7.49 (t, $J = 8.7$ Hz, 1H), 7.13 – 7.11 (m, 1H), 7.09 (t, $J = 8.1$ Hz, 1H), 4.41 (t, $J = 9.8$ Hz, 2H), 4.20 (t, $J = 9.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.92, 160.66, 141.08, 139.92, 132.61, 130.84, 129.21, 128.47, 127.71, 122.29, 119.61, 113.16, 66.25, 54.57; HRMS (ESI-TOF) m/z Calcd for C$_{14}$H$_{12}$N$_2$O$_2$S [M+H]$^+$: 273.0692, found: 273.0701.

\[
\begin{array}{c}
\text{N-(2-(4,5-dihydrooxazol-2-yl)phenyl)picolinamide (1j)}
\end{array}
\]

$^1$H NMR (400 MHz, CDCl$_3$) δ 13.64 (s, 1H), 9.02 (d, $J = 8.4$ Hz, 1H), 8.71 (d, $J = 4.6$ Hz, 1H), 8.29 (d, $J = 8.4$ Hz, 1H), 7.98 – 7.82 (m, 2H), 7.53 (t, $J = 8.6$ Hz, 1H), 7.49 – 7.41 (m, 1H), 7.13 (t, $J = 8.1$ Hz, 1H), 4.41 (t, $J = 9.7$ Hz, 2H), 4.26 (t, $J = 9.9$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.17, 163.97, 151.08, 148.42, 139.33, 137.23, 132.24, 129.34, 126.05, 122.81, 122.67, 120.17,
114.66, 66.24, 55.01; HRMS (ESI-TOF) m/z Calcd for C_{13}H_{13}N_{3}O_{2} [M+H]^+: 268.1081, found: 268.1071.

\[ \text{N-(2-(4,5-dihydrooxazol-2-yl)-5-methylphenyl)benzamide (1k)} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 13.00 (s, 1H), 8.82 (s, 1H), 8.19 - 8.01 (m, 2H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.61 - 7.40 (m, 3H), 6.92 (d, $J = 8.8$ Hz, 1H), 4.38 (t, $J = 9.7$ Hz, 2H), 4.17 (t, $J = 9.6$ Hz, 2H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.00, 164.92, 143.40, 139.98, 135.30, 131.55, 129.09, 128.51, 127.68, 123.32, 120.27, 119.08, 66.12, 54.57, 22.07; HRMS (ESI-TOF) m/z Calcd for C$_{17}$H$_{16}$N$_2$O$_2$ [M+H]^+: 281.1285, found: 281.1307.

\[ \text{N-(4-chloro-2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (1l)} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 12.94 (s, 1H), 8.95 (d, $J = 9.1$ Hz, 1H), 8.12 - 8.00 (m, 2H), 7.86 (d, $J = 2.5$ Hz, 1H), 7.58 - 7.42 (m, 4H), 4.56 - 4.32 (m, 2H), 4.21 (t, $J = 9.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.98, 163.96, 138.73, 134.91, 132.36, 131.80, 128.92, 128.59, 127.66, 127.32, 121.19, 114.78, 66.44, 54.75; HRMS (ESI-TOF) m/z Calcd for C$_{16}$H$_{13}$ClN$_2$O$_2$ [M+H]^+: 301.0738, found: 301.0745.

\[ \text{2-phenyl-4,5-dihydrooxazole (4a)} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 - 7.86 (m, 2H), 7.50 - 7.35 (m, 3H), 4.48 - 4.32 (m, 2H), 4.14 - 3.92 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.38, 131.07, 128.13, 127.94, 127.56, 67.38, 54.74; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_9$NO [M+H]^+: 148.0757, found: 148.0750.

\[ \text{2-(o-tolyl)-4,5-dihydrooxazole (4b)} \]
\( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.68 (d, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 7.15 (t, \( J = 7.4 \text{ Hz}, 1\text{H} \)), 7.12 – 6.97 (m, 2H), 4.13 (t, \( J = 9.5 \text{ Hz}, 2\text{H} \)), 3.87 (t, \( J = 9.5 \text{ Hz}, 2\text{H} \)), 2.45 (s, 3H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 164.40, 138.26, 130.73, 130.00, 129.34, 126.67, 125.07, 66.18, 54.90, 21.42; HRMS (ESI-TOF) m/z Calcd for C\(_{10}\)H\(_{11}\)NO [M+H]^+: 162.0913, found: 162.0911.

\[ \text{N} \]
\[ \text{O} \]

2-(m-tolyl)-4,5-dihydrooxazole (4c)
\( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.64 (s, 1H), 7.60 (d, \( J = 7.0 \text{ Hz}, 1\text{H} \)), 7.16 – 7.06 (m, 2H), 4.17 (t, \( J = 9.5 \text{ Hz}, 2\text{H} \)), 3.83 (t, \( J = 9.5 \text{ Hz}, 2\text{H} \)), 2.20 (s, 3H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 164.10, 137.40, 131.46, 128.17, 127.65, 127.08, 124.70, 66.92, 54.28, 20.67; HRMS (ESI-TOF) m/z Calcd for C\(_{10}\)H\(_{11}\)NO [M+H]^+: 162.0913, found: 162.0909.

\[ \text{N} \]
\[ \text{O} \]

2-(p-tolyl)-4,5-dihydrooxazole (4d)
\( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.83 (d, \( J = 8.2 \text{ Hz}, 2\text{H} \)), 7.22 (d, \( J = 8.0 \text{ Hz}, 2\text{H} \)), 4.42 (t, \( J = 9.5 \text{ Hz}, 2\text{H} \)), 4.05 (t, \( J = 9.5 \text{ Hz}, 2\text{H} \)), 2.39 (s, 3H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 164.64, 141.55, 128.99, 128.03, 124.89, 67.43, 54.83, 21.51; HRMS (ESI-TOF) m/z Calcd for C\(_{10}\)H\(_{11}\)NO [M+H]^+: 162.0913, found: 162.0915.

\[ \text{N} \]
\[ \text{O} \]

2-(3,5-dimethylphenyl)-4,5-dihydrooxazole (4e)
\( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.57 (s, 2H), 7.11 (s, 1H), 4.42 (t, \( J = 9.6 \text{ Hz}, 2\text{H} \)), 4.04 (t, \( J = 9.5 \text{ Hz}, 2\text{H} \)), 2.34 (s, 6H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 164.55, 137.58, 132.62, 127.19, 125.58, 67.15, 54.53, 20.84; HRMS (ESI-TOF) m/z Calcd for C\(_{11}\)H\(_{13}\)NO [M+H]^+: 176.1070, found: 176.1072.
2-(4-(tert-butyl)phenyl)-4,5-dihydrooxazole (4f)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.6$ Hz, 2H), 4.34 (t, $J = 9.5$ Hz, 2H), 3.97 (t, $J = 9.4$ Hz, 2H), 1.26 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.59, 154.62, 127.87, 125.23, 124.81, 67.42, 34.88, 31.11; HRMS (ESI-TOF) m/z Calcd for C$_{13}$H$_{17}$NO [M+H]$^+$: 204.1383, found: 204.1380.

2-(4-methoxyphenyl)-4,5-dihydrooxazole (4g)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 4.39 (t, $J = 9.4$ Hz, 2H), 4.02 (t, $J = 9.4$ Hz, 2H), 3.83 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.27, 161.87, 129.73, 120.17, 113.55, 67.39, 55.23, 54.77; HRMS (ESI-TOF) m/z Calcd for C$_{10}$H$_{11}$NO$_2$ [M+H]$^+$: 178.0863, found: 178.0865.

2-(2-chlorophenyl)-4,5-dihydrooxazole (4h)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (dd, $J = 7.6$, 1.8 Hz, 1H), 7.28 (dd, $J = 8.0$, 1.1 Hz, 1H), 7.18 (td, $J = 7.7$, 1.8 Hz, 1H), 7.11 (td, $J = 7.5$, 1.3 Hz, 1H), 4.22 (t, $J = 9.6$ Hz, 2H), 3.92 (t, $J = 9.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.24, 132.63, 130.91, 130.66, 126.64, 125.89, 66.76, 54.74; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_8$ClNO [M+H]$^+$: 182.0367, found: 182.0363.

2-(3-chlorophenyl)-4,5-dihydrooxazole (4i)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (s, 1H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.12 (t, $J = 7.9$ Hz, 1H), 4.19 (t, $J = 9.6$ Hz, 2H), 3.84 (t, $J = 9.5$ Hz, 2H); $^{13}$C NMR (100 MHz,
CDCl$_3$ $\delta$ 162.59, 133.63, 130.55, 128.99, 128.95, 127.58, 125.66, 67.16, 54.38; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_8$ClNO [M+H]$^+$: 182.0367, found: 182.0370.

2-(4-chlorophenyl)-4,5-dihydrooxazole (4j)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J$ = 8.6 Hz, 2H), 7.39 (d, $J$ = 8.6 Hz, 2H), 4.44 (t, $J$ = 9.5 Hz, 2H), 4.06 (t, $J$ = 9.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.70, 137.37, 129.44, 128.57, 126.18, 67.71, 54.93; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_8$ClNO [M+H]$^+$: 182.0367, found: 182.0361.

2-(3,5-dichlorophenyl)-4,5-dihydrooxazole (4k)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 – 7.79 (m, 2H), 7.48 – 7.42 (m, 1H), 4.45 (td, $J$ = 9.6, 4.1 Hz, 2H), 4.07 (td, $J$ = 9.6, 3.7 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.42, 135.03, 131.06, 129.44, 128.57, 126.55, 68.00, 54.95; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_7$Cl$_2$NO [M+H]$^+$: 215.9977, found: 215.9980.

2-(4-bromophenyl)-4,5-dihydrooxazole (4l)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J$ = 8.6 Hz, 2H), 7.55 (d, $J$ = 8.7 Hz, 2H), 4.44 (t, $J$ = 9.5 Hz, 2H), 4.05 (t, $J$ = 9.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.84, 131.57, 129.65, 126.63, 125.91, 67.74, 54.95; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_8$BrNO [M+H]$^+$: 225.9862, found: 225.9857.
2-(4-iodophenyl)-4,5-dihydrooxazole (4m)
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.67 (d, $J = 8.6$ Hz, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 4.33 (t, $J = 9.5$ Hz, 2H), 3.95 (t, $J = 9.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.98, 137.52, 129.64, 127.16, 98.22, 67.72, 54.92; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_8$INO [M+H]$^+$: 273.9723, found: 273.9726.

![Structure of 2-(4-iodophenyl)-4,5-dihydrooxazole (4m)](image)

2-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (4n)
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, $J = 8.1$ Hz, 2H), 7.68 (d, $J = 8.2$ Hz, 2H), 4.48 (t, $J = 9.6$ Hz, 2H), 4.10 (t, $J = 9.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.44, 132.83 (q, $J_{C-F} = 32.6$ Hz), 131.03, 128.49, 125.27 (q, $J_{C-F} = 3.8$ Hz), 123.76 (q, $J_{C-F} = 272.5$ Hz), 67.86, 55.02; HRMS (ESI-TOF) m/z Calcd for C$_{10}$H$_8$F$_3$NO [M+H]$^+$: 216.0631, found: 216.0625.

![Structure of 2-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (4n)](image)

2-(1,1'-biphenyl)-4,5-dihydrooxazole (4o)
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.09 – 7.93 (m, 2H), 7.67 – 7.61 (m, 4H), 7.51 – 7.43 (m, 2H), 7.43 – 7.33 (m, 1H), 4.46 (t, $J = 9.6$ Hz, 2H), 4.09 (t, $J = 9.5$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.50, 143.95, 140.15, 128.84, 128.61, 127.85, 127.14, 126.98, 126.47, 67.62, 54.90; HRMS (ESI-TOF) m/z Calcd for C$_{15}$H$_{13}$NO [M+H]$^+$: 224.1070, found: 224.1075.

![Structure of 2-(1,1'-biphenyl)-4,5-dihydrooxazole (4o)](image)

2-(naphthalen-2-yl)-4,5-dihydrooxazole (4p)
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.44 (s, 1H), 8.04 (dd, $J = 8.6$, 1.7 Hz, 1H), 7.97 – 7.77 (m, 3H), 7.63 – 7.44 (m, 2H), 4.60 – 4.40 (m, 2H), 4.22 – 4.02 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.71, 134.64, 132.64, 128.88, 128.62, 128.09, 127.74, 127.46, 126.50, 124.99, 124.74, 67.66, 55.01; HRMS (ESI-TOF) m/z Calcd for C$_{13}$H$_{11}$NO [M+H]$^+$: 198.0913, found: 198.0915.

![Structure of 2-(naphthalen-2-yl)-4,5-dihydrooxazole (4p)](image)
2-(pyridin-4-yl)-4,5-dihydrooxazole (4q)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.80 – 8.61 (m, 2H), 7.91 – 7.65 (m, 2H), 4.48 (t, $J$ = 9.6 Hz, 2H), 4.11 (t, $J$ = 9.7 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.90, 150.22, 134.97, 121.82, 67.90, 55.06; HRMS (ESI-TOF) m/z Calcd for C$_8$H$_8$N$_2$O [M+H]$^+$: 149.0709, found: 149.0704.

2-(furan-2-yl)-4,5-dihydrooxazole (4r)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 – 7.50 (m, 1H), 6.95 (d, $J$ = 3.4 Hz, 1H), 6.49 (dd, $J$ = 3.4, 1.8 Hz, 1H), 4.41 (t, $J$ = 9.4 Hz, 2H), 4.06 (t, $J$ = 9.5 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.83, 145.03, 142.93, 114.05, 111.37, 67.62, 54.75; HRMS (ESI-TOF) m/z Calcd for C$_7$H$_7$NO$_2$ [M+H]$^+$: 138.0550, found: 138.0543.

2-(thiophen-2-yl)-4,5-dihydrooxazole (4s)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (dd, $J$ = 3.7, 1.0 Hz, 1H), 7.45 (dd, $J$ = 5.0, 1.1 Hz, 1H), 7.07 (dd, $J$ = 5.0, 3.7 Hz, 1H), 4.42 (t, $J$ = 9.5 Hz, 2H), 4.04 (t, $J$ = 9.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.26, 130.23, 129.63, 127.48, 67.94, 54.87; HRMS (ESI-TOF) m/z Calcd for C$_7$H$_7$NOS [M+H]$^+$: 154.0321, found: 154.0326.

2-phenyl-5,6-dihydro-4H-1,3-oxazine (4t)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.74 (m, 2H), 7.35 – 7.26 (m, 3H), 4.28 (t, $J$ = 5.5 Hz, 2H), 3.52 (t, $J$ = 5.9 Hz, 2H), 1.94 – 1.85 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.59, 133.95, 130.23, 127.93, 126.77, 65.11, 42.56, 21.82; HRMS (ESI-TOF) m/z Calcd for C$_{10}$H$_{11}$NO [M+H]$^+$: 162.0913, found: 162.0907.
2-(pyridin-3-yl)-4,5-dihydrooxazole (4u)

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.16 (d, $J = 1.2$ Hz, 1H), 8.71 (dd, $J = 4.9$, 1.6 Hz, 1H), 8.22 (dt, $J = 7.9$, 1.9 Hz, 1H), 7.36 (ddd, $J = 7.9$, 4.9, 0.8 Hz, 1H), 4.47 (t, $J = 9.5$ Hz, 2H), 4.10 (t, $J = 9.6$ Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.64, 151.95, 149.39, 135.44, 123.82, 123.15, 67.73, 54.93; HRMS (ESI-TOF) m/z Calcd for C$_8$H$_8$N$_2$O $[M+H]^+$: 149.0709, found: 149.0711.

2.1.3 Synthesis of N-(2-hydroxyethyl)benzamide

To an oven-dried flask, K$_3$PO$_4$ (900mg, 4.3 mmol, 0.3 equiv) and i-PrOH (10 mL) were added with methyl benzoate (1.78 mL, 14.2 mmol, 1 equiv) and ethanolamine (0.86 mL, 14.2 mmol, 1 equiv). The reaction mixture was stirred at 60 $^\circ$C for 22 h. The reaction mixture was allowed to cool to room temperature, EtOAc and water were added to the reaction mixture. The organic layer was separated and the aqueous layer was re-extracted with EtOAc. The combined organic layers were dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude mixture was purified via silica gel column chromatography to give the desired product as a white solid.

N-(2-hydroxyethyl)benzamide (6)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 – 7.71 (m, 2H), 7.49 – 7.43 (m, 1H), 7.41 – 7.30 (m, 2H), 7.08 (brs, 1H), 3.77 (t, $J = 5.0$ Hz, 2H), 3.62 – 3.45 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.68, 134.01, 131.58, 128.49, 126.94, 61.88, 42.77; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_{11}$NO$_2$ [M+H]$^+$: 166.0863, found: 166.0888.

2.2 General procedure for the synthesis of $\beta$-nitrate ester carboxamides.

In a 25 mL Schlenk tube, the corresponding aryl oxazolines 1 (0.2 mmol, 1.0 equiv), TBN (0.6 mmol, 3.0 equiv) and 2 mL 1,4-dioxane were added under O$_2$ atmosphere. The tube was sealed and the resulting solution was heated in 80 $^\circ$C oil bath with vigorous stirring for 16 h. Then the
reaction mixture was cooled to room temperature. The mixture was poured into water (10 mL) and extracted with ethyl acetate (20 mL × 3), the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and the solvent was evaporated under vacuum. The residue was purified by flash chromatography using EtOAc/hexanes (1:4) as eluent to afford the products.

2-(2-benzamidobenzamido)ethyl nitrate (3a)
$^1$H NMR (400 MHz, CDCl$_3$) δ 11.93 (s, 1H), 8.68 (d, $J = 8.2$ Hz, 1H), 8.03 – 7.93 (m, 2H), 7.57 – 7.44 (m, 5H), 7.19 (brs, 1H), 6.97 (t, $J = 8.0$ Hz, 1H), 4.66 (t, $J = 5.2$ Hz, 2H), 3.80 (q, $J = 5.5$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.66, 165.83, 139.64, 134.58, 132.78, 131.97, 128.79, 127.27, 126.99, 122.95, 121.52, 119.85, 71.33, 37.35; HRMS (ESI-TOF) m/z Calcd for C$_{16}$H$_{15}$N$_3$O$_5$ [M+H]$^+$: 330.1084, found: 330.1088.

2-(2-(2-methylbenzamido)benzamido)ethyl nitrate (3b)
$^1$H NMR (400 MHz, CDCl$_3$) δ 11.26 (s, 1H), 8.63 (d, $J = 8.3$ Hz, 1H), 7.49 (d, $J = 7.3$ Hz, 1H), 7.46 – 7.37 (m, 2H), 7.29 (t, $J = 6.9$ Hz, 1H), 7.24 – 7.16 (m, 2H), 7.07 – 6.86 (m, 2H), 4.51 (t, $J = 5.1$ Hz, 2H), 3.64 (q, $J = 5.4$ Hz, 2H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.31, 168.49, 139.55, 136.80, 136.10, 132.86, 131.43, 130.43, 127.05, 126.86, 126.09, 123.07, 121.53, 119.92, 71.30, 37.24, 20.18; HRMS (ESI-TOF) m/z Calcd for C$_{17}$H$_{17}$N$_3$O$_5$ [M+H]$^+$: 344.1241, found: 344.1229.

2-(2-(4-methylbenzamido)benzamido)ethyl nitrate (3c)
$^1$H NMR (400 MHz, CDCl$_3$) δ 11.88 (s, 1H), 8.76 (d, $J = 8.3$ Hz, 1H), 7.91 (d, $J = 8.2$ Hz, 2H), 7.60 – 7.46 (m, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.06 (t, $J = 7.3$ Hz, 1H), 6.82 (brs, 1H), 4.67 (t, $J = 5.1$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.31, 168.49, 139.55, 136.80, 136.10, 132.86, 131.43, 130.43, 127.05, 126.86, 126.09, 123.07, 121.53, 119.92, 71.30, 37.24, 20.18; HRMS (ESI-TOF) m/z Calcd for C$_{17}$H$_{17}$N$_3$O$_5$ [M+H]$^+$: 344.1241, found: 344.1229.
5.0 Hz, 2H), 3.83 (q, J = 5.3 Hz, 2H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.64, 165.72, 142.48, 140.04, 133.09, 131.87, 129.47, 127.35, 126.73, 122.81, 121.68, 119.58, 71.43, 37.38, 21.53; HRMS (ESI-TOF) m/z Calcd for C$_{17}$H$_{17}$N$_3$O$_5$ [M+H]$^+$: 344.1241, found: 344.1251.

2-(2-(3,4-dimethoxybenzamido)benzamido)ethyl nitrate (3d)
$^1$H NMR (400 MHz, CDCl$_3$) δ 11.93 (s, 1H), 8.70 (d, J = 9.5 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.54 – 7.45 (m, 2H), 7.11 – 6.90 (m, 3H), 4.67 (t, J = 5.1 Hz, 2H), 3.98 (s, 3H), 3.96 (s, 3H), 3.82 (q, J = 5.5 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.70, 165.36, 152.09, 148.97, 139.98, 132.92, 127.22, 126.85, 122.70, 121.40, 120.20, 119.48, 71.34, 56.00, 55.95, 37.33; HRMS (ESI-TOF) m/z Calcd for C$_{18}$H$_{19}$N$_3$O$_7$ [M+H]$^+$: 390.1296, found: 390.1283.

2-(2-(2-fluorobenzamido)benzamido)ethyl nitrate (3e)
$^1$H NMR (400 MHz, CDCl$_3$) δ 11.52 (d, J = 8.3 Hz, 1H), 8.68 (d, J = 8.3 Hz, 1H), 8.06 (td, J = 7.8, 1.8 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.29 (td, J = 7.7, 1.1 Hz, 1H), 7.20 (ddd, J = 11.5, 8.3, 0.9 Hz, 1H), 7.11 (td, J = 7.8, 1.1 Hz, 1H), 6.76 (brs, 1H), 4.71 – 4.60 (m, 2H), 3.81 (q, J = 5.7 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.12, 162.30 (d, J$_{C-F}$ = 2.8 Hz), 160.30 (d, J$_{C-F}$ = 250.7 Hz), 138.75, 133.57 (d, J$_{C-F}$ = 9.0 Hz), 132.69, 131.59 (d, J$_{C-F}$ = 2.0 Hz), 126.80, 124.71 (d, J$_{C-F}$ = 3.5 Hz), 123.52, 122.59, 122.37 (d, J$_{C-F}$ = 11.9 Hz), 121.38, 116.49 (d, J$_{C-F}$ = 23.7 Hz), 71.45, 37.33; HRMS (ESI-TOF) m/z Calcd for C$_{16}$H$_{14}$FN$_3$O$_5$ [M+H]$^+$: 348.0990, found: 348.0979.

2-(2-(4-chlorobenzamido)benzamido)ethyl nitrate (3f)
$^1$H NMR (400 MHz, CDCl$_3$) δ 12.00 (s, 1H), 8.68 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.59 – 7.43 (m, 4H), 7.14 – 6.92 (m, 2H), 4.67 (t, J = 5.0 Hz, 2H), 3.82 (q, J = 5.3 Hz, 2H); $^{13}$C
NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 169.62, 164.67, 139.58, 138.27, 132.97, 132.96, 129.04, 128.73, 126.91, 123.09, 121.47, 119.57, 71.34, 37.36; HRMS (ESI-TOF) \textit{m/z} Calcd for C\textsubscript{16}H\textsubscript{14}ClN\textsubscript{3}O\textsubscript{5} [M+H]\textsuperscript{+}: 364.0695, found: 364.0698.

![Structure of 2-(2-(4-(trifluoromethyl)benzamido)benzamido)ethyl nitrate (3g)](attachment)

2-(2-(4-(trifluoromethyl)benzamido)benzamido)ethyl nitrate (3g)

\(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 12.10 (s, 1H), 8.64 (d, \(J = 8.5\) Hz, 1H), 8.03 (d, \(J = 8.1\) Hz, 2H), 7.70 (d, \(J = 8.2\) Hz, 2H), 7.48 – 7.39 (m, 2H), 7.03 – 6.87 (m, 2H), 4.60 (t, \(J = 5.0\) Hz, 2H), 3.75 (q, \(J = 5.4\) Hz, 2H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 169.59, 164.34, 139.58, 137.90, 133.49 (q, \(J_{\text{C-F}} = 32.7\) Hz), 133.13, 127.77, 126.88, 125.84 (q, \(J_{\text{C-F}} = 3.7\) Hz), 123.65 (q, \(J_{\text{C-F}} = 272.7\) Hz), 123.32, 121.52, 119.51, 71.33, 37.41; HRMS (ESI-TOF) \textit{m/z} Calcd for C\textsubscript{17}H\textsubscript{14}F\textsubscript{3}N\textsubscript{3}O\textsubscript{5} [M+H]\textsuperscript{+}: 398.0958, found: 398.0936.

![Structure of 2-(2-pivalamidobenzamido)ethyl nitrate (3h)](attachment)

2-(2-pivalamidobenzamido)ethyl nitrate (3h)

\(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 11.16 (s, 1H), 8.56 (d, \(J = 8.7\) Hz, 1H), 7.51 – 7.39 (m, 2H), 7.04 (t, \(J = 7.6\) Hz, 1H), 6.88 (brs, 1H), 4.66 (t, \(J = 5.0\) Hz, 2H), 3.80 (q, \(J = 5.3\) Hz, 2H), 1.32 (s, 9H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 177.97, 169.52, 139.95, 132.80, 126.67, 122.63, 121.69, 119.87, 71.34, 40.12, 37.40, 27.52; HRMS (ESI-TOF) \textit{m/z} Calcd for C\textsubscript{14}H\textsubscript{19}N\textsubscript{3}O\textsubscript{5} [M+H]\textsuperscript{+}: 310.1397, found: 310.1388.

![Structure of 2-(2-(thiophene-2-carboxamido)benzamido)ethyl nitrate (3i)](attachment)

2-(2-(thiophene-2-carboxamido)benzamido)ethyl nitrate (3i)

\(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 11.94 (s, 1H), 8.60 (d, \(J = 8.0\) Hz, 1H), 7.66 (dd, \(J = 3.8, 1.1\) Hz, 1H), 7.49 (dd, \(J = 5.0, 1.1\) Hz, 1H), 7.46 – 7.40 (m, 2H), 7.08 (dd, \(J = 5.0, 3.8\) Hz, 1H), 6.98 (t, \(J = 8.1\) Hz, 1H), 6.81 (brs, 1H), 4.61 (t, \(J = 5.0\) Hz, 2H), 3.77 (q, \(J = 5.7\) Hz, 2H); \(^{13}\text{C}\) NMR (125 MHz,
CDCl$_3$ δ 169.65, 160.39, 140.24, 139.95, 133.22, 131.16, 128.64, 127.95, 126.72, 122.88, 121.48, 119.10, 71.35, 37.47; HRMS (ESI-TOF) m/z Calcd for C$_{14}$H$_{13}$N$_3$O$_5$S [M+H]$^+$: 336.0649, found: 336.0634.

2-(2-(picolinamido)benzamido)ethyl nitrate (3j)
$^1$H NMR (400 MHz, CDCl$_3$) δ 12.56 (s, 1H), 8.70 (d, $J$ = 8.4 Hz, 1H), 8.67 (d, $J$ = 4.7 Hz, 1H), 8.18 (d, $J$ = 7.8 Hz, 1H), 7.81 (td, $J$ = 7.7, 1.7 Hz, 1H), 7.48 – 7.36 (m, 3H), 7.00 (t, $J$ = 8.0 Hz, 1H), 6.84 (brs, 1H), 4.60 (t, $J$ = 5.0 Hz, 2H), 3.77 (q, $J$ = 5.6 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 168.99, 163.40, 150.32, 148.64, 138.72, 137.34, 132.66, 127.01, 126.32, 123.28, 122.61, 121.86, 121.63, 71.59, 37.39; HRMS (ESI-TOF) m/z Calcd for C$_{15}$H$_{14}$N$_4$O$_5$ [M+H]$^+$: 331.1037, found: 331.1029.

2-(2-benzamido-4-methylbenzamido)ethyl nitrate (3k)
$^1$H NMR (400 MHz, CDCl$_3$) δ 12.10 (s, 1H), 8.67 (s, 1H), 8.02 (d, $J$ = 7.7 Hz, 2H), 7.57 – 7.50 (m, 3H), 7.41 (d, $J$ = 8.0 Hz, 1H), 6.90 (d, $J$ = 8.0 Hz, 1H), 6.69 (brs, 1H), 4.66 (t, $J$ = 5.0 Hz, 2H), 3.83 (q, $J$ = 5.3 Hz, 2H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.62, 165.62, 144.29, 140.18, 134.79, 131.87, 128.77, 127.32, 126.56, 123.76, 121.98, 116.57, 71.51, 37.30, 21.94; HRMS (ESI-TOF) m/z Calcd for C$_{17}$H$_{17}$N$_3$O$_5$ [M+H]$^+$: 344.1241, found: 344.1229.

2-(2-benzamido-5-chlorobenzamido)ethyl nitrate (3l)
$^1$H NMR (400 MHz, CDCl$_3$) δ 11.86 (s, 1H), 8.79 (s, 1H), 8.00 (d, $J$ = 9.7 Hz, 1H), 8.00 (d, $J$ = 7.8 Hz, 2H), 7.61 – 7.48 (m, 5H), 6.71 (brs, 1H), 4.67 (t, $J$ = 4.9 Hz, 2H), 3.84 (q, $J$ = 5.2 Hz, 2H); $^{13}$C NMR
(125 MHz, CDCl₃) δ 168.50, 165.61, 138.75, 134.42, 133.04, 132.12, 128.85, 128.01, 127.38, 126.54, 123.17, 120.87, 71.19, 37.60; HRMS (ESI-TOF) m/z Calcd for C₁₆H₁₄ClN₃O₅ [M+H]⁺: 364.0695, found: 364.0681.

2-benzamidoethyl nitrate (5a)

¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.67 (m, 2H), 7.48 – 7.41 (m, 1H), 7.41 – 7.30 (m, 2H), 6.71 (brs, 1H), 4.57 (t, J = 5.1 Hz, 2H), 3.72 (q, J = 5.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.92, 133.60, 131.87, 128.61, 126.95, 71.76, 37.36; HRMS (ESI-TOF) m/z Calcd for C₉H₁₀N₂O₄ [M+H]⁺: 211.0713, found: 211.0714.

2-(2-methylbenzamido)ethyl nitrate (5b)

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.29 (m, 2H), 7.23 – 7.14 (m, 2H), 6.39 (brs, 1H), 4.62 (t, J = 5.1 Hz, 2H), 3.74 (q, J = 5.7 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.43, 136.12, 135.36, 131.06, 130.19, 126.65, 125.72, 71.67, 37.11, 19.67; HRMS (ESI-TOF) m/z Calcd for C₁₀H₁₂N₂O₄ [M+H]⁺: 225.0870, found: 225.0874.

2-(3-methylbenzamido)ethyl nitrate (5c)

¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 1H), 7.57 – 7.52 (m, 1H), 7.36 – 7.30 (m, 2H), 6.56 (brs, 1H), 4.65 (t, J = 5.1 Hz, 2H), 3.81 (q, J = 5.7 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.00, 138.57, 133.57, 132.65, 128.53, 127.69, 123.91, 71.86, 37.33, 21.31; HRMS (ESI-TOF) m/z Calcd for C₁₀H₁₂N₂O₄ [M+H]⁺: 225.0870, found: 225.0872.

2-(4-methylbenzamido)ethyl nitrate (5d)

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.49 (brs, 1H), 4.58 (t, J = 5.1 Hz, 2H), 3.73 (q, J = 5.5 Hz, 2H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.74, 142.43, 130.75, 129.30, 126.95, 71.89, 37.31, 21.45; HRMS (ESI-TOF) m/z Calcd for C₁₀H₁₂N₂O₄ [M+H]⁺: 225.0870, found: 225.0876.
2-(3, 5-dimethylbenzamido)ethyl nitrate (5e)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (s, 2H), 7.14 (s, 1H), 6.69 (brs, 1H), 4.63 (t, $J = 5.1$ Hz, 2H), 3.79 (q, $J = 5.6$ Hz, 2H), 2.33 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.24, 138.33, 133.55, 133.43, 124.70, 71.86, 37.25, 21.14; HRMS (ESI-TOF) m/z Calcd for C$_{11}$H$_{14}$N$_2$O$_4$ [M+H]$^+$: 239.1026, found: 239.1028.

2-(4-(tert-butyl)benzamido)ethyl nitrate (5f)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J = 8.5$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 6.47 (brs, 1H), 4.66 (t, $J = 5.1$ Hz, 2H), 3.82 (q, $J = 5.6$ Hz, 2H), 1.34 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.67, 155.52, 130.70, 126.79, 125.62, 71.91, 37.31, 34.96, 31.11; HRMS (ESI-TOF) m/z Calcd for C$_{13}$H$_{18}$N$_2$O$_4$ [M+H]$^+$: 267.1339, found: 267.1391.

2-(4-methoxybenzamido)ethyl nitrate (5g)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 8.8$ Hz, 2H), 6.94 (d, $J = 8.8$ Hz, 2H), 6.39 (brs, 1H), 4.66 (t, $J = 5.1$ Hz, 2H), 3.86 (s, 3H), 3.81 (q, $J = 5.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.24, 162.50, 128.81, 125.83, 113.86, 71.99, 55.44, 37.31; HRMS (ESI-TOF) m/z Calcd for C$_{10}$H$_{12}$N$_2$O$_5$ [M+H]$^+$: 241.0819, found: 241.0815.

2-(2-chlorobenzamido)ethyl nitrate (5h)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 – 7.50 (m, 1H), 7.40 – 7.24 (m, 3H), 6.89 (brs, 1H), 4.64 (t, $J = 5.2$ Hz, 2H), 3.76 (q, $J = 5.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.06, 134.30, 131.40, 130.50, 130.08, 129.64, 126.94, 71.32, 37.21; HRMS (ESI-TOF) m/z Calcd for C$_8$H$_6$ClN$_2$O$_4$ [M+H]$^+$: 245.0324, found: 245.0325.
2-(3-chlorobenzamido)ethyl nitrate (5i)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (s, 1H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.48 (d, $J = 9.0$ Hz, 1H), 7.36 (t, $J = 7.9$ Hz, 1H), 6.93 (brs, 1H), 4.65 (t, $J = 5.1$ Hz, 2H), 3.80 (q, $J = 5.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.77, 135.36, 134.69, 131.84, 129.92, 127.30, 125.10, 71.54, 37.47; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_9$ClN$_2$O$_4$ [M+H]$^+$: 245.0324, found: 245.0323.

2-(4-chlorobenzamido)ethyl nitrate (5j)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J = 8.6$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 6.68 (brs, 1H), 4.65 (t, $J = 5.0$ Hz, 2H), 3.80 (q, $J = 5.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.92, 138.15, 131.98, 128.87, 128.43, 71.64, 37.46; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_9$ClN$_2$O$_4$ [M+H]$^+$: 245.0324, found: 245.0320.

2-(3,5-dichlorobenzamido)ethyl nitrate (5k)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 1.8$ Hz, 2H), 7.49 (t, $J = 1.8$ Hz, 1H), 6.80 (brs, 1H), 4.65 (t, $J = 5.0$ Hz, 2H), 3.81 (q, $J = 5.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.47, 136.42, 135.54, 131.73, 125.66, 71.41, 37.61; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_8$Cl$_2$N$_2$O$_4$ [M+Na]$^+$: 300.9753, found: 300.9740.

2-(4-bromobenzamido)ethyl nitrate (5l)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 8.6$ Hz, 2H), 7.57 (d, $J = 8.6$ Hz, 2H), 6.69 (brs, 1H), 4.65 (t, $J = 5.0$ Hz, 2H), 3.80 (q, $J = 5.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.96, 132.40, 131.88, 128.57, 126.66, 71.63, 37.46; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_9$BrN$_2$O$_4$ [M+H]$^+$: 288.9818, found: 288.9817.
2-(4-iodobenzamido)ethyl nitrate (5m)

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.78 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 8.2$ Hz, 2H), 6.68 (brs, 1H), 4.65 (t, $J = 4.9$ Hz, 2H), 3.80 (q, $J = 5.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.10, 137.88, 132.98, 128.53, 99.01, 71.64, 37.46; HRMS (ESI-TOF) m/z Calcd for C$_9$H$_9$IN$_2$O$_4$ [M+H]$^+$: 336.9680, found: 336.9672.

2-(4-(trifluoromethyl)benzamido)ethyl nitrate (5n)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 8.1$ Hz, 2H), 7.67 (d, $J = 8.1$ Hz, 2H), 4.66 (t, $J = 5.0$ Hz, 2H), 3.82 (q, $J = 5.4$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.85, 136.89, 133.54 (q, $J_{C,F} = 33.0$ Hz), 127.48, 125.65 (q, $J_{C,F} = 3.9$ Hz), 123.49 (q, $J_{C,F} = 272.8$ Hz), 71.49, 37.57; HRMS (ESI-TOF) m/z Calcd for C$_{10}$H$_9$F$_3$N$_2$O$_4$ [M+H]$^+$: 279.0587, found: 279.0603.

2-([1,1'-biphenyl]-4-carboxamido)ethyl nitrate (5o)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 8.3$ Hz, 2H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.64 – 7.59 (m, 2H), 7.52 – 7.45 (m, 2H), 7.44 – 7.36 (m, 1H), 6.56 (brs, 1H), 4.69 (t, $J = 5.0$ Hz, 2H), 3.85 (q, $J = 5.5$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.49, 144.75, 139.79, 132.21, 128.93, 128.10, 127.51, 127.32, 127.18, 71.86, 37.42; HRMS (ESI-TOF) m/z Calcd for C$_{15}$H$_{14}$N$_2$O$_4$ [M+Na]$^+$: 309.0846, found: 309.0855.

2-(2-naphthamido)ethyl nitrate (5p)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (s, 1H), 7.95 – 7.80 (m, 4H), 7.62 – 7.52 (m, 2H), 6.66 (brs, 1H), 4.71 (t, $J = 5.1$ Hz, 2H), 3.89 (q, $J = 5.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.83, 134.88, 132.52, 130.79, 128.95, 128.65, 127.91, 127.77, 127.62, 126.92, 123.36, 71.89, 37.49; HRMS (ESI-TOF) m/z Calcd for C$_{13}$H$_{12}$N$_2$O$_4$ [M+Na]$^+$: 283.0689, found: 283.0695.
2-(isonicotinamido)ethyl nitrate (5q)
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.70 (d, \(J = 6.0\) Hz, 2H), 7.56 (d, \(J = 6.1\) Hz, 2H), 6.68 (brs, 1H), 4.61 (t, \(J = 5.1\) Hz, 2H), 3.78 (q, \(J = 5.7\) Hz, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.86, 150.59, 140.81, 120.88, 71.37, 37.58; HRMS (ESI-TOF) m/z Calcd for C\(_9\)H\(_8\)N\(_3\)O\(_4\) [M+H]\(^+\): 212.0666, found: 212.0669.

2-(furan-2-carboxamido)ethyl nitrate (5r)
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 – 7.42 (m, 1H), 7.15 (d, \(J = 3.5\) Hz, 1H), 6.74 (brs, 1H), 6.52 (dd, \(J = 3.5, 1.7\) Hz, 1H), 4.64 (t, \(J = 5.1\) Hz, 2H), 3.80 (q, \(J = 5.6\) Hz, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.57, 147.21, 144.26, 114.91, 112.27, 71.72, 36.43; HRMS (ESI-TOF) m/z Calcd for C\(_7\)H\(_8\)N\(_2\)O\(_5\) [M+H]\(^+\): 201.0506, found: 201.0501

2-(thiophene-2-carboxamido)ethyl nitrate (5s)
\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.56 (d, \(J = 2.8\) Hz, 1H), 7.50 (d, \(J = 4.7\) Hz, 1H), 7.07 (t, \(J = 4.0\) Hz, 1H), 6.67 (brs, 1H), 4.64 (t, \(J = 5.1\) Hz, 2H), 3.78 (q, \(J = 5.2\) Hz, 2H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 162.38, 137.99, 130.52, 128.61, 127.72, 71.69, 37.36; HRMS (ESI-TOF) m/z Calcd for C\(_7\)H\(_8\)N\(_2\)O\(_4\)S [M+H]\(^+\): 217.0278, found: 217.0265.

3-benzamidopropyl nitrate (5t)
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 – 7.73 (m, 2H), 7.56 – 7.49 (m, 1H), 7.48 – 7.42 (m, 2H), 6.42 (brs, 1H), 4.58 (t, \(J = 6.2\) Hz, 2H), 3.59 (q, \(J = 6.5\) Hz, 2H), 2.14 – 2.05 (m, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.81, 134.09, 131.69, 128.65, 126.81, 71.12, 36.80, 27.15; HRMS (ESI-TOF) m/z Calcd for C\(_{10}\)H\(_{12}\)N\(_2\)O\(_4\) [M+H]\(^+\): 225.0870, found: 225.0873.
2-(nicotinamido)ethyl nitrate (5u)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.02 (d, $J = 1.7$ Hz, 1H), 8.71 (dd, $J = 4.8$, 1.5 Hz, 1H), 8.15 (dt, $J = 8.0$, 2.0 Hz, 1H), 7.55 (brs, 1H), 7.40 (dd, $J = 7.9$, 4.9 Hz, 1H), 4.67 (t, $J = 5.0$ Hz, 2H), 3.82 (q, $J = 5.5$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.12, 152.30, 147.86, 135.41, 129.60, 123.64, 71.57, 37.43; HRMS (ESI-TOF) m/z Calcd for C$_8$H$_9$N$_3$O$_4$ [M+H]$^+$: 212.0666, found: 212.0668.
2.3 The single crystal X-ray diffraction study of 3a

CCDC 1523402 (3a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

Crystal Data and Structure Refinement for 3a

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\[ w^{-1} = \frac{1}{\sigma^2(F_0)^2 + (0.0384P)^2 + 0.1747P}, \text{ where } P = (F_0^2 + 2F_c^2)/3; \]
2.4 Electrospray Ionization-Time-of-Flight-Mass Spectrometry (ESI-TOF-MS) of compound 7 and byproduct C.

Figure 1. HRMS spectrum of compound 7

Figure 2. HRMS spectrum of byproduct C
3. References

4. $^1$H and $^{13}$C NMR spectra

$N$-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (1a)
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-methylbenzamide (1b)
$N$-(2-(4,5-dihydrooxazol-2-yl)phenyl)-4-methylbenzamide (1c)
$N$-(2-(4,5-dihydrooxazol-2-yl)phenyl)-3,4-dimethoxybenzamide (1d)
$N$-(2-(4,5-dihydro-1,2-oxazol-2-yl)phenyl)-2-fluorobenzamide (1e)
4-chloro-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (1f)
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-4-(trifluoromethyl)benzamide (1g)
$N$-(2-(4,5-dihydrooxazol-2-yl)phenyl)pivalamide (1h)
$N-(2-(4,5$-dihydrooxazol-2-$y$l)phenyl)thiophene-2-carboxamide (1i)$
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)picolinamide (1j)
N-(2-(4,5-dihydrooxazol-2-yl)-5-methylphenyl)benzamide (1k)
N-(4-chloro-2-(4,5-dihydrooxazol-2-yl)phenyl)benzamide (II)
2-phenyl-4,5-dihydrooxazole (4a)
2-(o-tolyl)-4,5-dihydrooxazole (4b)
2-(m-tolyl)-4,5-dihydrooxazole (4c)
2-(p-tolyl)-4,5-dihydrooxazole (4d)
2-(3,5-dimethylphenyl)-4,5-dihydrooxazole (4e)
2-(4-(tert-butyl)phenyl)-4,5-dihydrooxazole (4f)
2-(4-methoxyphenyl)-4,5-dihydrooxazole (4g)
2-(2-chlorophenyl)-4,5-dihydrooxazole (4h)
2-(3-chlorophenyl)-4,5-dihydrooxazole (4i)
2-(4-chlorophenyl)-4,5-dihydrooxazole (4j)
2-(3,5-dichlorophenyl)-4,5-dihydrooxazole (4k)
2-(4-bromophenyl)-4,5-dihydrooxazole (4l)
2-(4-iodophenyl)-4,5-dihydrooxazole (4m)
2-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (4n)
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2-(naphthalen-2-yl)-4,5-dihydrooxazole (4p)
2-(pyridin-4-yl)-4,5-dihydrooxazole (4q)
2-(furan-2-yl)-4,5-dihydrooxazole (4r)
2-(thiophen-2-yl)-4,5-dihydrooxazole (4s)
2-phenyl-5,6-dihydro-4H-1,3-oxazine (4t)
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N-(2-hydroxyethyl)benzamide (6)
2-(2-benzamidobenzamido)ethyl nitrate (3a)
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2-(2-(4-methylbenzamido)benzamido)ethyl nitrate (3c)
2-(2-(3,4-dimethoxybenzamido)benzamido)ethyl nitrate (3d)
2-(2-(2-fluorobenzamido)benzamido)ethyl nitrate (3e)
2-(2-(4-chlorobenzamido)benzamido)ethyl nitrate (3f)
2-(2-(4-(trifluoromethyl)benzamido)benzamido)ethyl nitrate (3g)
2-(2-pivalamidobenzamido)ethyl nitrate (3b)
2-(2-(thiophene-2-carboxamido)benzamido)ethyl nitrate (3i)
2-(2-(picolinamido)benzamido)ethyl nitrate (3j)
2-(2-benzamido-4-methylbenzamido)ethyl nitrate (3k)
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2-benzamidoethyl nitrate (5a)
2-(2-methylbenzamido)ethyl nitrate (5b)
2-(3-methylbenzamido)ethyl nitrate (5c)
2-(4-methylbenzamido)ethyl nitrate (5d)
2-(3, 5-dimethylbenzamido)ethyl nitrate (5e)
2-(4-(tert-butyl)benzamido)ethyl nitrate (5f)
2-(4-methoxybenzamido)ethyl nitrate (5g)
2-(2-chlorobenzamido)ethyl nitrate (5h)
2-(3-chlorobenzamido)ethyl nitrate (5i)
2-(4-chlorobenzamido)ethyl nitrate (5j)
2-(3,5-dichlorobenzamido)ethyl nitrate (5k)
2-(4-bromobenzamido)ethyl nitrate (5I)
2-(4-iodobenzamido)ethyl nitrate (5m)
2-(4-(trifluoromethyl)benzamido)ethyl nitrate (5n)
2-([1,1'-biphenyl]-4-carboxamido)ethyl nitrate (5o)
2-(2-naphthamido)ethyl nitrate (5p)
2-(isonicotinamido)ethyl nitrate (5q)
2-(furan-2-carboxamido)ethyl nitrate (5r)
2-(thiophene-2-carboxamido)ethyl nitrate (5s)
3-benzamidopropyl nitrate (5t)
2-(nicotinamido)ethyl nitrate (5u)