SUPPORTING INFORMATION

A convenient method for the conversion of *N*-acyl oxazolidinones to hydroxamic acids

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Experimental Procedures. Tetrahydrofuran was distilled from sodium-benzophenone prior to use. Flash chromatography was performed using EM Science silica gel 60 (230-400 mesh). Melting points were determined using the Fisher-Johns melting point apparatus. All glassware was oven dried, assembled hot, and cooled under a stream of dry nitrogen before use. Reactions with air sensitive materials were carried out by standard syringe techniques.

¹H NMR were recorded on a Varian Unity/Inova-500 NB (500 MHz), or a Varian Mercury-300 (300 MHz). Chemical shifts are reported in parts per million (ppm) down field from TMS, using residual CDCl₃ (7.27 ppm) as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublets of doublets, m = multiplet, b = broad), coupling constant(s) and integration. ¹³C NMR were recorded on a Varian Unity/Inova-500 NB (125 MHz) or a Varian Mercury-300 (75 MHz) spectrometers using broad band proton decoupling. Chemical shifts are reported in parts per million (ppm) down field from TMS, using the middle resonance of CDCl₃ (77.0 ppm) as an internal standard. Rotations were recorded on a JASCO-DIP-370 instrument. Elemental analyses were performed in house on a Perkin Elmer Series II CHNS/O Analyzer 2400. High-resolution mass spectra (HRMS) [EI+] were obtained at the Mass spectrometry Laboratory, University of South Carolina, Columbia, SC or at the Ohio State University, Columbus, OH.

Starting Imides: The starting materials used in this study are known compounds and were prepared through standard procedures.

Compound (3).¹

Compound (6).²

Compound (8a).³

Compound (8b).⁴

Compound (8c).⁵

Compound (8d).⁶

Compound (8e).⁷

4-oxo-4-(2-oxo-oxazolidin-3-yl)-butyric acid methyl ester (8f).

¹H NMR (CDCl₃, 300 MHz): δ 2.67 (t, J = 6 Hz, 2H), 3.23 (t, J = 6.6 Hz, 2H), 3.69 (s, 3H), 4.02 (t, J = 8.1 Hz, 2H), 4.43 (t, J = 8.1, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 28.1, 30.5, 42.6, 52.0, 62.4, 153.8, 172.1, 173.0.

General procedure for the conversion of *N*-benzoyl oxazolidinone to *N*-benzyloxybenzamide (4).

N-Benzoyl oxazolidinone **3/6** (0.1 mmol), lanthanide triflate (0.03 mmol) were mixed and dissolved in dry tetrahydrofuran (1 mL) under N₂. To the solution *O*-

benzylhydroxylamine (0.2 mmol) was added and the reaction mixture was stirred at RT for 1 h. Reaction was quenched by addition 1M HCl (1 mL). Tetrahydrofuran was removed under vacuum and the aqueous layer was extracted with dichloromethane (3x5 mL). Organic extracts were combined, dried over anhydrous sodium sulfate and solvent was removed using a rotary evaporator. The residue was purified by column chromatography on silica gel using 15% ethyl acetate in hexanes as eluent to afford *O*-benzyloxybenzamide **4** as a crystalline solid. m.p. 104-105 °C; Lit.⁸ m.p.103-104 °C.

General procedure for the conversion of *N*-acyl oxazolidinones to hydroxamide derivatives using hydroxylamine hydrochloride.

N-acyl oxazolidinone (0.1 mmol), samarium triflate (0.018g, 0.03 mmol) and hydroxylamine hydrochloride (0.028g, 0.4 mmol, dried by heating under vacuum before use) were mixed in dry tetrahydrofuran (0.5 mL) under N₂. To the mixture triethylamine (0.34g, 0.053 mL, 0.38 mmol) was added and the reaction mixture was stirred at RT for 3 days. Reaction was quenched by addition 1M HCl (1 mL). Tetrahydrofuran was removed under vacuum and the aqueous layer was extracted with ethyl acetate (3x5 mL). Organic extracts were combined, dried on anhydrous sodium sulfate and solvent was removed using a rotary evaporator. Residue was purified by column chromatography on silica gel using ethyl acetate in hexanes as eluent to afford hydroxamide derivatives.

General procedure for the conversion of *N*-acyl oxazolidinones to *N,O*-dimethylhydroxamide derivatives.

N-acyl oxazolidinone (0.1 mmol), samarium triflate (0.018 g, 0.03 mmol) and *N,O*-dimethylhydroxylamine hydrochloride (0.039 g, 0.4 mmol) were mixed in dry tetrahydrofuran (0.5 mL) under N₂. To the mixture triethylamine (0.34 g, 0.053 mL, 0.38 mmol) was added and the reaction mixture was stirred at RT for 3 days. Reaction was quenched by addition 1M HCl (1 mL). Tetrahydrofuran was removed under vacuum and the aqueous layer was extracted with dichloromethane (3x5 mL). Organic extracts were combined, dried on anhydrous sodium sulfate and solvent was removed under using a

rotary evaporator. Residue was purified by column chromatography on silica gel using ethyl acetate in hexanes as eluent to afford *N,O*-dimethylhydroxamide derivatives.

Procedure for the conversion of *N*-benzoyl oxazolidinone to hydroxybenzamide using *O*-(tetrahydro-2H-pyran-2-yl)hydroxylamine

N-Benzoyl oxazolidinone **6** (0.1 g, 0.52 mmol), samarium triflate (0.094 g 0.16 mmol) *O*-(tetrahydro-2H-pyran-2-yl)hydroxylamine (0.12 g, 1.04 mmol) were mixed and dissolved in dry tetrahydrofuran (3 mL) under N_2 and the reaction mixture was stirred at RT for 1 h. Reaction was quenched by addition 1M HCl (2 mL). Tetrahydrofuran was removed under vacuum and the aqueous layer was extracted with ethyl acetate (3x5 mL). Organic extracts were combined, dried on anhydrous sodium sulfate and solvent was removed using a rotary evaporator. Residue was column chromatographed on silica gel using 50% ethyl acetate in hexanes as eluent to afford impure *N*-hydroxybenzamide as a white crystalline solid that was further purified by washing with dichloromethane:hexanes (1:10, 3x5 mL). Yield 0.50 g (70%).

Procedure for the conversion of *N*-benzoyl oxazolidinone to *N*-(4-methoxybenzyloxy)benzamide.

N-Benzoyl oxazolidinone **6** (0.1 g, 0.52 mmol), samarium triflate (0.094 g 0.16 mmol) 4-methoxybenzylhydroxylamine (0.158 g, 1.04 mmol) were mixed and dissolved in dry tetrahydrofuran (3 mL) under N_2 and the reaction mixture was stirred at RT for 1 h. Reaction was quenched by addition 1M HCl (2 mL). Tetrahydrofuran was removed under vacuum and the aqueous layer was extracted with ethyl acetate (3x5 mL). Organic extracts were combined, dried on anhydrous sodium sulfate and solvent was removed using a rotary evaporator. Residue was purified by column chromatography on silica gel using 15% ethyl acetate in hexanes as eluent to afford *N*-(4-methoxybenzyloxy)benzamide as a crystalline solid. Yield 0.10 g (75%).

General procedure for the conversion of *N*-acyl oxazolidinones to *O*-benzylhydroxamide derivatives.

N-Acyl oxazolidinone **8a-f** (0.1 mmol), samarium triflate (0.018 g, 0.03 mmol) were mixed and dissolved in dry tetrahydrofuran (0.2-1 mL) under N_2 . To the solution *O*-benzylhydroxylamine (0.2-0.5 mmol) was added and the reaction mixture was stirred at RT for 1-5 h. Reaction was quenched by addition of 1M HCl (1 mL). Tetrahydrofuran was removed under vacuum and the aqueous layer was extracted with dichloromethane (3x5 mL). Organic extracts were combined, dried over anhydrous sodium sulfate and solvent was removed using a rotary evaporator. The residue was purified by column

chromatography on silica gel using ethyl acetate in hexanes as eluent to afford *O*-benzylhydroxamide derivatives **9a-f**.

***N*-Benzyloxybenzamide (4).**

m.p. 104-105 °C Lit.⁸ m.p.103-104 °C; ¹H NMR (CDCl₃, 500 MHz): δ 5.01 (s, 2H), 7.41 (m, 6H), 7.49 (m, 2H), 7.67 (m, 2H), 8.61(b, 1H); ¹³C NMR (CD₃OD, 75 MHz): δ 81.9, 131.0, 132.3, 132.4, 132.5, 133.3, 135.9, 136.0, 139.7, 171.0.

***N*-Hydroxybenzamide (7) (R = R₁ = H).**

m.p. 126-127 °C; Lit.⁹ 125-128 °C; ¹H NMR (CD₃OD, 300 MHz): δ 7.47 (m, 2H), 7.51 (m, 1H), 7.73 (m, 2H); ¹³C NMR (CD₃OD, 75 MHz): δ 130.9, 132.4, 135.6, 136.3, 171.0.

***N*-(4-methoxybenzyloxy)benzamide (7) (R = H, R₁ = CH₂C₆H₄-OMe).**

m.p. 120-121°C; Lit.¹⁰ 121-122°C. ¹H NMR (CDCl₃, 400 MHz): δ 3.77 (s, 3H), 4.93 (s, 2H), 6.85 (d, J = 8.4 Hz, 2H), 7.34 (m, 4H), 7.46 (m, 1H), 7.66 (m, 2H), 9.01 (b, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 55.5, 78.9, 114.2, 127.3, 127.7, 128.8, 131.3, 132.1, 160.2. HRMS Calcd for C₁₅H₁₅NO₃Na⁺ 280.09444; Found: 280.09356.

***N*-Methoxy-*N*-methylbenzamide (7)** ($R = R_1 = \text{Me}$).¹¹

¹H NMR (CDCl₃, 300 MHz): δ 3.36 (s, 3H), 3.55 (s, 3H), 7.42 (m, 3H), 7.66 (m, 2H).

***N*-Benzyloxy-3-phenylpropionamide (9a).**

¹H NMR (CD₃OD, 300 MHz): δ 2.33 (t, $J = 7.2$ Hz, 2H), 2.89 (t, $J = 7.5$ Hz, 2H), 4.70 (s, 2H), 7.29 (m, 10H); ¹³C NMR (CD₃OD, 75 MHz): δ 35.3, 38.4, 81.8, 130.1, 132.2, 132.3, 132.4, 133.2, 139.6, 144.5, 174.6; Anal. Calcd for C₁₆H₁₇NO₂: C, 75.29; H, 6.66; N, 5.49; Found: C, 75.45; H, 6.89; N, 5.33.

***N*-Benzyloxy-4-methylpentanamide (9b).**

¹H NMR (CDCl₃, 300 MHz): δ 0.86 (d, $J = 6.3$ Hz, 6H), 1.51 (m, 3H), 2.02 (b, 2H), 4.89 (s, 2H), 7.37 (m, 5H), 8.32 (b, 1H); ¹³C NMR (CD₃OD, 75 MHz): δ 25.4, 31.5, 34.6, 38.3, 81.6, 132.2, 132.4, 133.1, 139.7, 175.9; Anal. Calcd for C₁₃H₁₉NO₂: C, 70.59; H, 8.60; N, 6.33; Found: C, 70.55; H, 8.51; N, 6.24.

3-Benzyloxycarbamoyl-4-phenylbutanoic acid *tert.* butyl ester (9c).

^1H NMR (CDCl_3 , 300 MHz): δ 1.40 (s, 9H), 2.37 (dd, $J = 3.3, 16.2$ Hz, 1H), 2.40 (m, 1H), 2.67 (m, 2H), 2.95 (m, 1H), 4.60 (d, $J = 11.4$ Hz, 1H), 4.77 (d, $J = 11.4$ Hz, 1H), 7.16-7.32 (m, 10H), 8.15 (b, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 28.3, 37.4, 38.3, 42.3, 78.5, 81.5, 126.9, 128.7, 128.8, 129.4, 129.6, 135.5, 138.8, 171.8, 172.4; $[\alpha]_{\text{D}}^{25}$ 17.6 (c 1, CHCl_3); Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_4$: C, 71.54; H, 7.32; N, 3.79; Found: C, 71.33; H, 7.17; N, 3.57.

3-Benzyloxycarbamoyl-5-methylhexanoic acid *tert.* butyl ester (9d).

^1H NMR (CDCl_3 , 500 MHz): δ 0.84 (dd, $J = 6.5, 14$ Hz, 6H), 1.12 (m, 1H), 1.41 (s, 9H), 1.49 (m, 1H), 1.66 (m, 1H), 2.28 (dd, $J = 3, 17$ Hz, 1H), 2.41 (m, 1H), 2.60 (dd, $J = 7, 10$ Hz, 1H), 4.89 (s, 2H), 7.36-7.43 (m, 5H), 8.36 (b, 1H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 22.1, 23.3, 25.8, 28.3, 37.9, 38.2, 41.2, 78.4, 81.4, 128.8, 128.9, 129.5, 135.7, 172.1, 173.8; $[\alpha]_{\text{D}}^{25}$ -10.6 (c 0.96, CHCl_3); Anal. Calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_4$: C, 68.05; H, 8.65; N, 4.18; Found: C, 68.29; H, 8.59; N, 4.05.

(1-Benzyloxycarbamoyl-2-phenylethyl)carbamic acid *tert.* butyl ester (9e).¹²

¹H NMR (CDCl₃, 300 MHz): δ 1.38 (s, 9H), 3.03 (m, 2H), 4.16 (dd, J = 7, 8 Hz, 1H), 4.67 (d, J = 11 Hz, 1H), 4.81 (d, J = 10.5 Hz, 1H), 5.05 (b, 1H), 7.19-7.32 (m, 10H), 8.53 (b, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 28.5, 38.5, 53.9, 78.6, 80.7, 127.3, 128.8, 128.9, 129.0, 129.5, 129.6, 135.1, 136.5, 155.71, 169.0; [α]_D²⁵ -26.4 (c 1.1, CHCl₃); Anal. Calcd for C₂₁H₂₆N₂O₄: C, 68.11; H, 7.03; N, 7.57; Found: C, 68.01; H, 7.02; N, 7.44.

***N*-Benzyloxysuccinamic acid methyl ester (9f).**

¹H NMR (CD₃OD, 300 MHz): δ 2.33 (t, J = 6.9 Hz, 1H), 2.61 (t, J = 6.9 Hz, 2H), 3.66 (s, 3H), 4.82 (s, 2H), 7.38 (m, 5H); ¹³C NMR (CD₃OD, 75 MHz): δ 31.1, 32.5, 55.0, 81.7, 132.2, 132.4, 133.1, 139.7, 174.1, 177.2; HRMS (CH₄ CI) M⁺H Calc. 238. 1079; Found: 238.1081.

[1-(Methoxymethylcarbamoyl)-2-phenylethyl]carbamic acid *tert.* butyl ester (9g).¹³

¹H NMR (CDCl₃, 300 MHz): δ 1.38 (s, 9H), 2.86 (dd, J = 7.5, 13.5 Hz, 3H), 3.05 (dd, J = 6.0, 13.5 Hz, 1H), 3.16 (s, 3H), 3.65 (s, 3H), 4.95 (b, 1H), 5.17 (s, 1H), 7.2-7.3

(m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 28.5, 32.3, 39.1, 51.7, 61.8, 79.8, 127.0, 128.6, 129.7, 136.8, 155.4, 172.5.

***N*-Hydroxy-3-phenylpropionamide (9h).**

^1H NMR (CDCl_3 , 500 MHz): δ 2.37 (t, J = 8 Hz, 2H), 2.89 (t, J = 8 Hz, 2H), 7.10-7.23 (m, 5H), 8.16 (b, 1H); ^{13}C NMR (CDCl_3 , 125MHz): δ 31.5, 35.0, 126.8, 128.5, 128.9, 140.2, 171.2; HRMS [EI] Calc. 165.0790; Found; 165.0795.

References and Footnotes

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