Supporting Information for

Synthesis of 2-Oxazolidinones by Direct Pd-catalyzed Oxidative Carbonylation of 2-Amino-1-alkanols

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Experimental Section

General Methods. Melting points are uncorrected. ^{1}H NMR spectra were run on $CDCl_3$ solutions with Me_4Si as internal standard and recorded at 300 MHz. Chemical shifts and coupling constants (J) are given in ppm (δ) and in Hz, respectively. IR spectra were taken on a FT-IR spectrometer. Mass spectra were obtained at 70 eV on a GC-MS apparatus. All reactions were analyzed by TLC on silica gel 60 F_{254} or by GLC using capillary columns with polymethylsilicone + 5% phenylsilicone as the stationary phase. Column chromatography was performed on silica gel 60 (70-230 mesh). Starting 2-aminoethanol **1a**, 1-amino-2-propanol **1b**, 2-amino-1-phenylethanol **1c**, 2-amino-1-propanol (alaninol) **1d**, (*R*)-2-amino-2-phenylethanol [(D)-2-phenylglycinol] **1e**, (*S*)-2-amino-3-methyl-1-butanol [(L)-valinol] **1f**, and (*S*)-2-amino-3-phenyl-1-propanol [(L)-

phenylalaninol] **1g** were commercially available and were used without further purification.

Typical procedure for oxidative carbonylation of 2-amino-1-alkanols 1a-1e. In a typical experiment, a 300 mL stainless steel autoclave with magnetic stirring was charged in the presence of air with PdI_2 (2.2 mg, $6.1 \cdot 10^{-3}$ mmol), KI (203 mg, 1.22 mmol) and a solution of **1** (12.2 mmol) in MeOH (24.4 mL). The autoclave was pressurized at room temperature with stirring with air (25 atm), CO (up to 30 atm) and O_2 (up to 60 atm of total pressure), and then heated at 100 °C with stirring for 15 h. After cooling, the autoclave was degassed and solvent removed by rotary evaporation. Crude products were easily purified by bulb-to-bulb distillation (**2a**, **2b**, **2d**) or column chromatography on silica gel using hexane-AcOEt = 7/3 as eluent (**2c**, **2e**). Spectroscopic properties for 2-oxazolidinone **2a** (0.90 g, 85% yield; colorless solid, mp 88-89 °C, lit.[1] 90-91 °C) agreed with those reported:[1,2,3] IR (KBr) 3269 (m, br), 1700 (s), 1256 (m), 1085 (w), 921 (w), 707 (m) cm^{-1}; ^1H NMR δ 6.61 (br s, 1 H, NH), 4.46 (t, J = 8.1, 2 H, CH_2O), 3.65 (t, J = 8.1, 2 H, CH_2N); MS *m/e* 87 (100, M^+), 59 (46). Spectroscopic properties for 5-methyl-2-oxazolidinone **2b** (1.13 g, 92%; colorless oil) agreed with those reported:[2,4] IR (neat) 3317 (s, br), 1735 (s), 1245 (m), 1074 (m), 971 (w) cm^{-1}; ^1H NMR δ 6.90 (br s, 1 H, NH), 4.84-4.72 (m, 1 H, OC*H*CH_3), 3.72 (t, J = 8.5, 1 H, NC*H*HCHCH_3), 3.21 (t, J = 7.8, 1 H, NCH*H*CHCH_3), 1.44 (d, J = 5.9, 3 H, Me); MS *m/e* 101 (M^+, 83), 86 (16), 73 (21), 58 (33), 57 (10), 56 (71). Spectroscopic

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properties for 5-phenyl-2-oxazolidinone **2c** (1.57 g, 79%; pale yellow solid, mp 90-92 °C, lit.[1] 90-92 °C) agreed with those reported:[1,5,6] IR (KBr) 3277 (m, br), 1719 (s), 1241 (m), 1081 (w), 1072 (w), 697 (m) cm^{-1}; ^1H NMR δ 7.43-7.35 (m, 5 H on phenyl ring), 5.92 (br s, NH), 5.63 (t, *J* = 8.3, 1 H, OC*H*Ph), 3.99 (t, *J* = 8.3, 1 H, NC*H*HCHPh), 3.55 (t, *J* = 8.3, 1 H, NCH*H*CHPh); MS *m/e* 163 (24, M^+), 118 (16), 107 (100), 105 (15), 91 (23), 79 (58), 77 (26), 51 (19). Spectroscopic properties for 4-methyl-2-oxazolidinone **2d** (1.05 g, 85%; colorless oil) agreed with those reported:[7,8] IR (neat) 3299 (m, br), 1745 (s), 1407 (m), 1243 (m), 1033 (m), 939 (w) cm^{-1}; ^1H NMR δ 7.04 (br s, 1 H, NH), 4.50 (t, *J* = 8.1, 1 H, OC*H*HCHCH$_3$), 4.12-3.91 (m, 2 H, OCH*H*CHCH$_3$ + OCHHC*H*CH$_3$), 1.29 (d, *J* = 6.4, 3 H, Me); MS *m/e* 101 (24, M^+), 86 (100), 58 (30). Spectroscopic properties for (*R*)-4-phenyl-2-oxazolidinone **2e** (1.77 g, 89%; pale yellow solid, mp 131-132 °C, lit.[1] 132-133 °C) agreed with those reported:[1,9] IR (KBr) 3252 (m, br), 1745 (s), 1705 (s), 1236 (m), 1098 (w), 1039 (w), 1026 (w), 924 (w), 698 (m) cm^{-1}; ^1H NMR δ 7.45-7.32 (m, 5 H on phenyl ring), 5.80 (br s, 1 H, NH), 5.01-4.93 (m, 1 H, NC*H*Ph), 4.75 (t, *J* = 8.8, 1 H, OC*H*HCHPh), 4.20 (dd, *J* = 8.8, 7.1, 1 H, OCH*H*CHPh); MS *m/e* = 163 (M^+, 45), 133 (89), 103 (79), 104 (100), 91 (29), 78 (26), 77 (25), 51 (15).

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Typical procedure for oxidative carbonylation of 2-amino-1-alkanols 1f-1g. In a typical experiment, a 300 mL stainless steel autoclave with magnetic stirring was charged in the presence of air with PdI_2 (4.0 mg, 0.011 mmol), KI (369 mg, 2.22 mmol) and a solution of **1** (11.0 mmol) in MeOH (22.0 mL). The autoclave was pressurized at room temperature with stirring with air (25 atm), CO (up to 30 atm) and O_2 (up to 60 atm of total pressure), and then heated at 100 °C with stirring for 15 h. After cooling, the autoclave was degassed and solvent removed by rotary evaporation. Crude products were easily purified by column chromatography on silica gel using hexane-AcOEt = 7/3 as eluent. Spectroscopic properties for (*S*)-4-isopropyl-2-oxazolidinone **2f** (1.29 g, 91%; colorless solid, mp 69-70 °C, lit.[10] 71-72 °C) agreed with those reported:[10,11,12] IR (KBr) 3280 (m, br), 2964 (m), 2876 (w), 1751 (s), 1406 (w), 1390 (w), 1242 (m), 1016 (w), 938 (w) cm^{-1}; ^1H NMR δ 6.90 (br s, 1 H, NH), 4.45 (t, *J* = 8.8, 1 H, OC*H*HCH), 4.11 (dd, *J* = 8.8, 6.3, 1 H, OCH*H*CH), 3.70-3.57 (m, 1 H, NC*H*CH_2), 1.73 (oct, *J* = 6.8, 1 H, C*H*Me_2), 0.97 (d, *J* = 6.8, C*H*$_3$CHCH_3), 0.90 (d, *J* = 6.8, CH_3CHC*H*$_3$). MS *m/e* 129 (3, M^+), 87 (11), 86 (100), 85 (42), 58 (39). Spectroscopic properties for (*S*)-4-benzyl-2-oxazolidinone **2g** (1.52 g, 78%; colorless solid, mp 87-88 °C, lit.[6] 88-89 °C) agreed with those reported:[1,13] IR (KBr) 3267 (m, br), 1755 (s), 1705 (s), 1407 (w), 1251 (m), 1096 (w), 1021 (m), 937 (w), 705 (m) cm^{-1}; ^1H NMR δ 7.37-7.24 (m, 5 H on phenyl ring), 6.11 (br s, 1 H, NH), 4.42 (dd, *J* = 8.6, 8.0, 1 H, OC*H*HCH), 4.10 (dd, *J* = 8.6, 5.6, 1 H, OCH*H*CH), 3.94-3.85 (m, 1 H, NC*H*CH_2), 2.91-2.83 (m, 2 H, C*H*$_2$Ph); MS *m/e* 177 (4, M^+), 92 (100), 91 (94), 86 (97), 77 (11), 65 (33), 63 (12), 58 (30), 51 (18).

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