**Radical Addition Approach to Asymmetric Amine Synthesis:
Design, Implementation, and Comparison of Chiral *N*-Acylhydrazones**

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Supporting Information

Table of Contents

Materials and Methods	S2
Preparation and Analysis of Hydrazones (Compounds 3–8)	S2
Radical Addition to Hydrazones (Compounds 9–12)	S5
Stereochemical Proofs (Compounds 13–15)	S11
Acetone Hydrazone (Compound 16)	S13
References	S13
¹ H NMR Spectra of 9aK , 10aE , 11aC , and 16	S14
NMR Spectra of 2a , 13 , and 15 (for originals, see reference 16)	S19

Materials and Methods. Reactions employed oven- or flame-dried glassware under nitrogen unless otherwise noted. THF and toluene were distilled from sodium/benzophenone ketyl under argon. CH_2Cl_2 was distilled from CaH_2 under argon or nitrogen. Nitrogen was passed successively through columns of anhydrous CaSO_4 and R3-11 catalyst for removal of water and oxygen, respectively. All other materials were used as received or purified by standard procedures. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator. Flash chromatography columns were packed with 230-400 mesh silica gel as a slurry in the initial elution solvent. Gradient flash chromatography was conducted by adsorption of product mixtures on silica gel, packing over a short pad of clean silica gel as a slurry in hexane, and eluting with a continuous gradient from hexane to the indicated solvent. Radial chromatography refers to centrifugally accelerated thin-layer chromatography performed with a Chromatotron using commercially supplied rotors. Melting points are uncorrected. Nuclear magnetic resonance (NMR) data were obtained at operating frequencies of 500 MHz (^1H) and 125 MHz (^{13}C). Infrared spectra were recorded using a single beam FT-IR spectrophotometer by standard transmission methods or by use of an attenuated total reflectance (ATR) probe. Optical rotations were determined using a digital polarimeter operating at ambient temperature. Low resolution mass spectra were obtained using sample introduction by dip, liquid chromatography or gas chromatography. High resolution mass spectra and combustion analyses were obtained from external commercial and institutional services. Chromatographic diastereomer ratio analyses employed GCMS with 15 mL x 0.25 mm I.D X 0.25 μm F.T 5%-phenyl-95%-dimethylsiloxane column and helium as mobile phase or HPLC with Microsorb-MV Si 8 μm 100A or Chiralcel OD columns (2-propanol/hexane as mobile phase) or Chirex 3014 column (chloroform/hexane as mobile phase).

(S)-3-Amino-4-phenylmethyl-2-oxazolidinone (2a). To a solution of (S)-(-)-4-benzyl-2-oxazolidinone (**1a**) (3.50 g, 19.77 mmol) in THF (350 mL) was added *n*-BuLi (12.35 mL, 2.0 M in hexane, 24.7 mmol) at -78°C . After 1 h, *O*-(mesitylenesulfonyl)hydroxylamine [MtsONH₂, **CAUTION**¹] (5.53 g, 25.7 mmol) was added, and the reaction mixture was allowed to warm to room temperature. Concentration and gradient flash chromatography (hexane $\rightarrow$ 1:5 hexane/EtOAc) afforded **2a** as a pale yellow oil (2.85 g, 75% yield); $[\alpha]_D^{22} +72.8^\circ$ (*c* 3.7, CHCl_3); IR (film) 3339, 3215, 3061, 2921, 1762, 1625, 1454, 1230, 1091, 1025, 921 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.30 (dd, $J = 7.3, 7.3$ Hz, 2H), 7.23 (dd, $J = 7.3, 7.3$ Hz, 1H), 7.14 (d, $J = 7.3$ Hz, 2H), 4.14 (dd, $J = 7.5, 7.5$ Hz, 1H), 3.98-3.90 (m, 4H), 3.27 (dd, $J = 13.8, 3.6$ Hz, 1H), 2.70 (dd, $J = 13.6, 8.7$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.1, 135.5, 129.0, 128.7, 126.9, 66.0, 59.5, 37.3; MS (CI) m/z (relative intensity) 193 ($[\text{M}+\text{H}]^+$, 100%), 178 (100%); Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_2$: C, 62.49; H, 6.29; N, 14.57. Found: C, 62.05; H, 6.34; N, 14.27.²

Preparation of Hydrazones: General Procedure A: To a solution of **1** in THF (0.06 M) was added *n*-BuLi (2.5 M in hexane, 1.1 eq) at -78°C . After 40 min, MtsONH₂¹ (1.2 eq) was added, the reaction mixture was allowed to warm to room temperature, and the appropriate aldehyde (5 eq) was introduced. When the reaction was complete (TLC) the mixture was diluted with twice its volume of ether and partitioned between ether and water. The organic phase was dried over Na_2SO_4 and concentrated. Gradient flash chromatography (hexane $\rightarrow$ 3:1 hexane/EtOAc) furnished pure hydrazones as single C=N isomers (>98:2, ^1H NMR). (**Note:** Although this General Procedure A was used to obtain **4–8** as described below, we now recommend the alternative General Procedure B.)

Preparation of Hydrazones: General Procedure B. As described in detail elsewhere,³ hydrazones **3b–3e** were prepared by the following sequence: (i) NaH (or KH; 1.05 equiv), dioxane, reflux; (ii) *O*-(*p*-nitrobenzoyl)hydroxylamine (NbzONH₂; 1.05 equiv); (iii) aldehyde, *p*-TsOH, toluene.)

(S)-3-(Propylidene)amino-4-phenylmethyl-2-oxazolidinone (3a). From **1a** (400 mg, 2.26 mmol) and propionaldehyde by General Procedure A was obtained **3a** (425 mg, 81% yield) as a pale yellow oil; $[\alpha]_D^{25} +7.5^\circ$ (*c* 3.8, CHCl₃); IR (film) 3062, 2935, 2877, 1762, 1632, 1478, 1405, 1208, 1093, 930 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.98 (t, *J* = 5.2 Hz, 1H), 7.27–7.11 (m, 5H), 4.31 (dddd, *J* = 8.2, 8.2, 4.0, 4.0 Hz, 1H), 4.17 (dd, *J* = 8.8, 8.8 Hz, 1H), 4.02 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.16 (dd, *J* = 13.9, 3.7 Hz, 1H), 2.76 (dd, *J* = 13.9, 8.6 Hz, 1H), 2.37–2.34 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 157.3, 154.3, 135.2, 129.1, 128.7, 127.0, 65.6, 57.6, 37.1, 26.5, 10.5; MS (CI) *m/z* (relative intensity) 233 ([M+H]⁺, 100%), 232 (M, 7%); Anal. Calcd for C₁₃H₁₆N₂O₂: C, 67.22; H, 6.94; N, 12.06. Found: C, 66.98; H, 6.83; N, 12.06.

(S)-3-(Propylidene)amino-4-diphenylmethyl-2-oxazolidinone (3b). From **1b** (160 mg, 1.03 mmol) and propionaldehyde by General Procedure B was obtained **3b** (192 mg, 99% yield) as a pale yellow oil; $[\alpha]_D^{28} +32.3^\circ$ (*c* 0.65, CHCl₃); IR (film) 3493, 2982, 2913, 1753, 1495, 1410, 1222, 1091, 1030 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.82 (t, *J* = 4.35 Hz, 1H), 7.21–7.04 (m, 10H), 4.81 (ddd, *J* = 8.5, 6.1, 6.1 Hz, 1H), 4.38 (d, *J* = 6.4 Hz, 1H), 4.33 (dd, *J* = 8.7, 8.7 Hz, 1H), 4.06 (dd, *J* = 9.0, 5.6 Hz, 1H), 2.14–2.08 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 159.2, 154.7, 140.2, 139.1, 128.8 (2C), 128.7, 128.6, 127.4, 126.9, 64.9, 59.9, 53.1, 26.5, 10.2; MS (CI) *m/z* (relative intensity) 309.5 ([M+H]⁺, 100%); Anal. Calcd for C₁₉H₂₀N₂O₂: C, 74.00; H, 6.54; N, 9.08. Found: C, 73.82; H, 6.60; N, 8.85.

(S)-3-(Propylidene)amino-4-isopropyl-2-oxazolidinone (3c). From **1c** (450 mg, 3.94 mmol) and propionaldehyde by General Procedure B was obtained **3c** (511 mg, 84% yield) as a pale yellow oil. Spectroscopic data were in good agreement with those previously reported.⁴

(S)-3-(Propylidene)amino-4-phenyl-2-oxazolidinone (3d). From **1d** (164 mg, 0.92 mmol) and propionaldehyde by General Procedure B was obtained **3d** (153 mg, 76 % yield) as a colorless oil; $[\alpha]_D^{22} +102.9^\circ$ (*c* 0.55, CHCl₃); IR (film) 3033, 2973, 1771, 1458, 1402, 1323, 1210, 1094, 1038 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.40–7.24 (m, 5H), 7.14 (t, *J* = 5.4 Hz, 1H), 5.17 (dd, *J* = 8.9, 5.9 Hz, 1H), 4.73 (t, *J* = 8.9 Hz, 1H), 4.11 (dd, *J* = 8.9, 5.8 Hz, 1H), 2.25–2.19 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 154.9, 153.1, 136.9, 129.4, 128.8, 125.9, 69.5, 58.9, 26.2, 10.7; MS (CI) *m/z* (relative intensity) 219.2 ([M+H]⁺, 100%); Anal. Calcd for C₁₂H₁₄N₂O₂: C, 66.04; H, 6.47; N, 12.84. Found: C, 66.36; H, 6.64 ; N, 12.50.

Propionaldehyde N-Acylhydrazone 3e. From **1e** (243 mg, 1.30 mmol) and propionaldehyde by General Procedure B was obtained **3e** (247 mg, 83% yield) as a pale yellow oil; $[\alpha]_D^{25} +118.0^\circ$ (*c* 0.7, CHCl₃); IR (film) 2970, 1770, 1400, 1365, 1200, 1110, 1040 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.13 (t, *J* = 5.0 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.29–7.18 (m, 3H), 5.47 (d, *J* = 7.2 Hz, 1H), 5.22 (ddd, *J* = 7.0, 7.0, 1.3 Hz, 1H), 3.28 (ABX, $\Delta\nu_{AB}$ = 51.6 Hz, *J*_{AB} = 17.9 Hz, *J*_{AX} = 6.5 Hz, *J*_{BX} = 0 Hz, 2H), 2.41–2.35 (m, 2H), 1.14 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 154.6, 153.3, 140.2, 138.4, 129.5, 127.5, 126.0, 125.4, 77.1, 64.3, 38.4, 26.5, 10.6; MS (CI) *m/z* (relative intensity) 231.5 ([M+H]⁺, 100%); Anal. Calcd for C₁₃H₁₄N₂O₂: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.63; H, 6.17; N, 11.95.

(S)-3-(2'-Methylpropylidene)amino-4-phenylmethyl-2-oxazolidinone (4). From **1a** (300 mg, 1.69 mmol) and isobutyraldehyde by General Procedure A was obtained **4** (291 mg, 70% yield) as a colorless solid; mp 43-45 °C; $[\alpha]_D^{30} +9.6^\circ$ (c 2.1, CHCl₃); IR (film) 3086, 3029, 2929, 2965, 1762, 1631, 1604, 1497, 1454, 1404, 1289, 1210, 1101, 1007, 923 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, *J* = 6.6 Hz, 1H), 7.30 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.24 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 4.35-4.30 (m, 1H), 4.21 (dd, *J* = 8.8, 8.8 Hz, 1H), 4.05 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.20 (dd, *J* = 13.8, 3.6 Hz, 1H), 2.80 (dd, *J* = 13.8, 8.7 Hz, 1H), 2.60 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 161.3, 154.4, 135.4, 129.2, 128.8, 127.1, 65.6, 57.9, 37.3, 32.2, 19.73, 19.65; MS (CI) *m/z* (relative intensity) 247 ([M+H]⁺, 100%), 246 (M, 21%); Anal. Calcd for C₁₄H₁₈N₂O₂: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.03; H, 7.37; N, 11.43.

(S)-3-(2,2-Dimethylpropylidene)amino-4-phenylmethyl-2-oxazolidinone (5). To a solution of **2a** (180 mg, 0.94 mmol) in toluene (10 mL) was added trimethylacetaldehyde (0.98 mL, 9.37 mmol) and a catalytic amount of *p*-toluenesulfonic acid. The mixture was stirred overnight at room temperature. Concentration and gradient flash chromatography (hexane → 3:1 hexane/EtOAc) afforded **5** (235 mg, 96% yield, 72% yield for two steps from **1**) as a colorless solid; mp 90.5-91.5 °C; $[\alpha]_D^{26} +11.7^\circ$ (c 1.6, CHCl₃); IR (film) 3060, 3030, 2954, 2867, 1760, 1629, 1498, 1434, 1417, 1248, 1088, 997, 922, 846 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.05 (s, 1H), 7.31 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.25 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 4.37-4.31 (m, 1H), 4.22 (dd, *J* = 8.8, 8.8 Hz, 1H), 4.05 (dd, *J* = 8.7, 5.9 Hz, 1H), 3.18 (dd, *J* = 13.8, 3.6 Hz, 1H), 2.83 (dd, *J* = 13.8, 8.5 Hz, 1H), 1.15 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 163.8, 154.3, 135.4, 129.2, 128.7, 127.0, 65.5, 58.0, 37.3, 35.4, 27.2; MS (CI) *m/z* (relative intensity) 261 ([M+H]⁺, 100%); Anal. Calcd for C₁₅H₂₀N₂O₂: C, 69.20; H, 7.74; N, 10.76. Found: C, 69.34; H, 7.72; N, 10.79.

(S)-3-(Cyclohexylmethylidene)amino-4-phenylmethyl-2-oxazolidinone (6). From **1a** (600 mg, 3.39 mmol) and cyclohexanecarboxaldehyde by General Procedure A was obtained **6** (630 mg, 65% yield) as a colorless solid; mp 53-55 °C; $[\alpha]_D^{25} +0.98^\circ$ (c 2.4, CHCl₃); IR (film) 3086, 3062, 2923, 2852, 1764, 1628, 1604, 1478, 1497, 1207, 1088, 971, 916, 893 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 11.5 Hz, 1H), 7.30 (dd, *J* = 7.1, 7.1 Hz, 2H), 7.24 (dd, *J* = 6.8, 6.8 Hz, 1H), 7.13 (d, *J* = 7.1 Hz, 2H), 4.20 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.05 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.18 (dd, *J* = 13.9, 3.7 Hz, 1H), 2.79 (dd, *J* = 13.9, 8.7 Hz, 1H), 2.38-2.24 (m, 1H), 1.85-1.64 (m, 5H), 1.34-1.22 (m, 5H), 4.35-4.29 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 160.4, 154.3, 135.4, 129.2, 128.8, 127.2, 65.6, 57.8, 41.6, 37.2, 30.1, 30.0, 25.9, 25.4; MS (CI) *m/z* (relative intensity) 287 ([M+H]⁺, 100%); Anal. Calcd for C₁₇H₂₂N₂O₂: C, 71.30; H, 7.74; N, 9.78. Found: C, 71.25; H, 7.80; N, 9.68.

(S)-3-(Benzylidene)amino-4-phenylmethyl-2-oxazolidinone (7). To a solution of **2a** (prepared from 3.56 mmol **1a** and used without purification) in toluene (70 mL) was added benzaldehyde (2.17 mL, 21.4 mmol) and a catalytic amount of *p*-toluenesulfonic acid. After heating at reflux for 1 hour, concentration and gradient flash chromatography (hexane → 3:1 hexane/EtOAc) afforded **7** (670 mg, 67% yield for two steps from **1a**). Using General Procedure B, the yield was 80%.³ Colorless solid; mp 95.6-95.7 °C; $[\alpha]_D^{25} -22.3^\circ$ (c 0.98, CHCl₃); IR (film) 3061, 3028, 2976, 2917, 1768, 1476, 1449, 1238, 1207, 1092, 940, 846 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.90 (s, 1H), 7.75-7.72 (m, 2H), 7.42-7.39 (m, 3H), 7.32 (dddd, *J* = 7.5, 7.5, 1.2, 1.2 Hz, 2H), 7.26 (dddd, *J* = 7.4, 7.4, 1.3, 1.3 Hz, 1H), 7.19 (ddd, *J* = 6.9, 1.5, 1.5 Hz, 2H), 4.47 (dddd, *J* = 9.1, 9.1, 5.5, 3.9 Hz, 1H), 4.30 (dd, *J* = 8.8, 8.8 Hz, 1H), 4.14 (dd, *J* = 8.9, 5.4 Hz, 1H), 3.31 (dd, *J* = 13.9, 3.8 Hz, 1H), 2.92 (dd, *J* = 13.9, 8.6 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 153.7, 150.8, 135.3, 134.4,

130.4, 129.3, 128.9, 128.6, 127.4, 127.2, 65.7, 58.3, 37.7; MS (CI) m/z (relative intensity) 281 ($[M+H]^+$, 100%); Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.91; H, 5.84; N, 9.98.

(S)-3-(Methoxycarbonylmethylidene)amino-4-phenylmethyl-2-oxazolidinone (8). To a solution of **2a** (prepared from 3.10 mmol **1a** and used without purification) in toluene (20 mL) was added methyl glyoxylate (300 mg, 3.41 mmol) and a catalytic amount of *p*-toluenesulfonic acid. The mixture was heated at reflux for 1 hour.

Concentration and gradient flash chromatography (hexane $\rightarrow$ 3:1 hexane/EtOAc) afforded **8** (580 mg, 71% yield for two steps from **1a**) as a colorless oil; $[\alpha]_D^{22} +32.9^\circ$ (*c* 0.9, $CHCl_3$); IR (film) 3029, 2953, 1786, 1717, 1593, 1455, 1283, 1202, 1173, 913 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.31–7.14 (m, 5H), 4.47 (dddd, $J = 8.4, 8.4, 4.8, 3.8$ Hz, 1H), 4.32 (dd, $J = 9.1, 8.2$ Hz, 1H), 4.18 (dd, $J = 9.1, 4.9$ Hz, 1H), 3.87 (s, 3H), 3.29 (dd, $J = 13.9, 3.7$ Hz, 1H), 2.88 (dd, $J = 13.9, 8.9$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 152.3, 134.4, 129.3, 129.0, 127.5, 65.9, 57.7, 52.5, 37.5; MS (CI) m/z (relative intensity) 263 ($[M+H]^+$, 85%), 231 (100%); Anal. Calcd for $C_{13}H_{14}N_2O_4$: C, 59.54; H, 5.38; N, 10.68. Found: C, 59.55; H, 5.47; N, 10.56.

Tin-Mediated Radical Addition to Hydrazones (Tables 2–4): General Procedure C. To a solution of the hydrazone in CH_2Cl_2 (ca. 0.25 M) was added $ZnCl_2$ (1 M in Et_2O , 2 eq). After 1 h at room temperature, the mixture was cooled to $-78^\circ C$, followed by addition of Et_3B (10 eq) and the appropriate alkyl iodide (10 eq). Bu_3SnH (0.25 M in CH_2Cl_2 , 5 eq) and O_2 (ca. 7 mL/mmol hydrazone) were introduced by syringe pump over ca. 5 h. The reaction mixture was allowed to warm slowly to room temperature. After 2 d, stannanes were removed by dilution with EtOAc, stirring overnight with excess KF, and filtration through a short pad of silica gel. Concentration and radial chromatography (hexane/EtOAc) afforded *N*-acylhydrazines **9–12**. Side products **9aA** and **9aB** were obtained in varying amounts in some experiments. For those *N*-acylhydrazines for which diastereomer ratios are reported, control experiments established that no change in the diastereomer ratios occurred prior to analysis. Diastereomer ratios were determined by comparison with authentic diastereomer mixtures prepared by an alternative route.⁶ Diastereomer ratios of **9aC–9aF** and **9eC** were determined by HPLC. Diastereomer ratios of *N*-acylhydrazines **12aC–12aF** were determined by GCMS. Diastereomer ratios of **9bC** and **9cC** were determined by integration of 1H NMR data obtained in the presence of the NMR shift reagent tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) europium(III) (Siever's reagent).

(S)-3-(1'-Propylamino)-4-phenylmethyl-2-oxazolidinone (9aA). Colorless oil; $[\alpha]_D^{23} +42.6^\circ$ (*c* 0.15, $CHCl_3$); IR (film) 3293, 3028, 2961, 1757, 1604, 1497, 1402, 1093 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.30 (dddd, $J = 7.0, 7.0, 1.1, 1.1$ Hz, 2H), 7.24 (dddd, $J = 7.3, 7.3, 1.2, 1.2$ Hz, 1H), 7.15 (ddd, $J = 6.8, 1.4, 1.4$ Hz, 2H), 4.13 (dd, $J = 8.6, 7.7$ Hz, 1H), 4.02–3.97 (m, 2H), 3.96–3.90 (m, 1H), 3.30 (dd, $J = 13.6, 3.7$ Hz, 1H), 3.00–2.93 (m, 1H), 2.91–2.85 (m, 1H), 2.64 (dd, $J = 13.5, 9.7$ Hz, 1H), 1.53 (m, apparent sextet, $J = 7.3$ Hz, 2H), 0.97 (dd, $J = 7.4, 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 135.9, 129.0, 128.9, 127.0, 66.2, 58.9, 52.7, 37.7, 21.3, 11.4; MS (CI) m/z (relative intensity) 235 ($[M+H]^+$, 100%); Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.39; H, 7.72; N, 11.75.

(S)-3-(3'-Pentylamino)-4-phenylmethyl-2-oxazolidinone (9aB). Colorless oil; $[\alpha]_D^{23} +33.5^\circ$ (*c* 0.21, $CHCl_3$); IR (film) 3291, 3028, 2963, 1758, 1604, 1454, 1239, 1088 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.32 (dddd, $J = 7.0, 7.0, 1.6, 1.6$ Hz, 2H), 7.25 (dddd, $J = 7.3, 7.3, 1.3, 1.3$ Hz, 1H), 7.16 (ddd, $J = 7.1, 1.5, 1.5$ Hz, 2H), 4.14 (dd, $J = 8.8, 7.6$ Hz, 1H), 4.03 (dd, $J = 8.9, 4.8$ Hz, 1H), 3.95 (d, $J = 3.8$ Hz, 1H), 3.92–3.87 (m, 1H), 3.34 (dd, $J = 13.5, 3.6$

Hz, 1H), 2.98-2.92 (m, 1H), 2.62 (dd, $J = 13.5, 10.0$ Hz, 1H), 1.53-1.45 (m, 4H), 1.00-0.94 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.6, 136.1, 129.1, 128.9, 127.0, 65.7, 61.5, 59.8, 37.0, 24.2, 24.1, 9.7, 9.1; MS (CI) m/z (relative intensity) 263 ($[\text{M}+\text{H}]^+$, 100%); Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_2$: C, 68.67; H, 8.45; N, 10.68. Found: C, 68.44; H, 8.42; N, 10.54.

(4*S*,3'*R*)-3-(2'-Methyl-3'-pentylamino)-4-phenylmethyl-2-oxazolidinone (9aC).

From **3a** (32 mg, 0.138 mmol) and 2-iodopropane by General Procedure C was obtained **9aC** (23 mg, 60% yield, S,R/S,S = 99:1) as a colorless solid. HPLC retention time 11.3 min; mp 75-76 °C; $[\alpha]_{\text{D}}^{26} + 38.3^\circ$ (c 0.65, CHCl_3); IR (film) 3296, 3089, 3026, 2960, 2927, 1779, 1604, 1491, 1392, 1368, 1252, 1082, 953, 833 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.29 (dd, $J = 7.2, 7.2$ Hz, 2H), 7.23 (dd, $J = 7.4, 7.4$ Hz, 1H), 7.13 (d, $J = 7.2$ Hz, 2H), 4.09 (dd, $J = 8.6, 8.6$ Hz, 1H), 4.00 (dd, $J = 8.8, 4.9$ Hz, 2H), 3.89-3.84 (m, 1H), 3.32 (dd, $J = 13.4, 3.5$ Hz, 1H), 2.75 (m, apparent quartet, $J = 6.1$ Hz, 1H), 2.59 (dd, $J = 13.4, 10.0$ Hz, 1H), 1.83 (m, apparent octet, $J = 4.8$ Hz, 1H), 1.52-1.44 (m, 1H), 1.43-1.35 (m, 1H), 0.98-0.92 (m, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.6, 136.1, 129.1, 128.9, 127.0, 65.8, 59.7, 37.0, 28.2, 21.5, 18.4, 17.9, 10.2; MS (CI) m/z (relative intensity) 277 ($[\text{M}+\text{H}]^+$, 100%), 276 (M, 8%); HRMS (FAB+) calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_2\text{Li}$: 283.1998. Found: 283.1993.

(4*S*,1'*R*)-3-(1'-Cyclopentyl-1'-propylamino)-4-phenylmethyl-2-oxazolidinone

[(*S,R*)-9aD]. From **3a** (34 mg, 0.146 mmol) and iodocyclopentane by General Procedure

C was obtained (**(*S,R*)-9aD**) (26 mg, 59% yield, S,R/S,S = 96:4) as a colorless oil. HPLC retention time 8.8 min; $[\alpha]_{\text{D}}^{26} + 17.8^\circ$ (c 1.4, CHCl_3); IR (film) 3306, 3062, 3027, 2953, 2869, 1758, 1604, 1497, 1454, 1399, 1238, 1217, 1092, 1005, 894 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.30 (dd, $J = 7.2, 7.2$ Hz, 2H), 7.23 (dd, $J = 7.4, 7.4$ Hz, 1H), 7.14 (d, $J = 7.2$ Hz, 2H), 4.11 (dd, $J = 8.7, 8.7$ Hz, 1H), 4.04-4.00 (m, 2H), 3.87 (dddd, $J = 10.1, 7.3, 3.6, 3.6$ Hz, 1H), 3.34 (dd, $J = 13.4, 3.3$ Hz, 1H), 2.94-2.90 (m, 1H), 2.58 (dd, $J = 13.4, 10.1$ Hz, 1H), 1.94-1.79 (m, 2H), 1.78-1.72 (m, 1H), 1.69-1.41 (m, 7H), 1.28-1.20 (m, 1H), 0.98 (dd, $J = 7.4, 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.2, 136.2, 129.1, 128.9, 127.0, 65.4, 64.8, 59.9, 40.5, 36.7, 29.4, 25.6, 25.4, 23.1, 8.2; MS (CI) m/z (relative intensity) 303 ($[\text{M}+\text{H}]^+$, 100%), 193 (100%); Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_2$: C, 71.47; H, 8.67; N, 9.26. Found: C, 71.57; H, 8.84; N, 9.16.

(4*S*,1'*R*)-3-(1'-Cyclohexyl-1'-propylamino)-4-phenylmethyl-2-oxazolidinone

[(*S,R*)-9aE]. From **3a** (91 mg, 0.392 mmol) and iodocyclohexane by General Procedure

C was obtained (**(*S,R*)-9aE**) (35 mg, 28% yield, S,R/S,S = 97:3) as a colorless oil. HPLC retention time 8.5 min; $[\alpha]_{\text{D}}^{26} + 38.6^\circ$ (c 0.4, CHCl_3); IR (film) 3299, 3027, 2926, 2852, 1759, 1604, 1497, 1453, 1398, 1238, 1086, 1029, 893.3 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.32 (dddd, $J = 7.6, 7.6, 1.3, 1.3$ Hz, 2H), 7.25 (dddd, $J = 7.4, 7.4, 1.3, 1.3$ Hz, 1H), 7.16 (ddd, $J = 7.0, 1.3, 1.3$ Hz, 2H), 4.13 (dd, $J = 8.8, 7.6$ Hz, 1H), 4.06 (d, $J = 4.5$ Hz, 1H), 4.03 (dd, $J = 8.9, 4.9$ Hz, 1H), 3.89 (dddd, $J = 13.6, 8.3, 4.8, 3.6$ Hz, 1H), 3.35 (dd, $J = 13.4, 3.5$ Hz, 1H), 2.77 (m, apparent quintet, $J = 5.3$ Hz, 1H), 2.62 (dd, $J = 13.4, 10.1$ Hz, 1H), 1.80-1.70 (m, 5H), 1.58-1.44 (m, 3H), 1.28-1.09 (m, 5H), 0.98 (dd, $J = 7.4, 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.6, 136.1, 129.1, 128.9, 127.0, 65.7, 65.3, 59.9, 38.6, 37.0, 29.1, 28.6, 26.7, 26.6, 21.8, 10.1; MS (CI) m/z (relative intensity) 317 ($[\text{M}+\text{H}]^+$, 73%), 193 (100%); Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_2$: C, 72.12; H, 8.92; N, 8.85. Found: C, 72.16; H, 8.83; N, 8.58.

(4*S*,3'*R*)-3-(2',2'-Dimethyl-3'-pentylamino)-4-phenylmethyl-2-oxazolidinone

[(*S,R*)-9aF]. From **3a** (35 mg, 0.150 mmol) and 2-iodo-2,2-dimethylpropane by General Procedure C was obtained (**(*S,R*)-9aF**) (24 mg, 54% yield, S,R/S,S = 95:5) as colorless oil. HPLC retention time 7.5 min; $[\alpha]_{\text{D}}^{26} + 23.4^\circ$ (c 2.6, CHCl_3); IR (film) 3316, 3087, 3028,

2960, 2872, 1757, 1604, 1498, 1397, 1237, 1198, 1087, 1030, 945, 836 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.32 (dddd, $J = 7.1, 7.1, 1.4, 1.4$ Hz, 2H), 7.25 (dddd, $J = 7.4, 7.4, 1.3, 1.3$ Hz, 1H), 7.16 (ddd, $J = 7.2, 1.4, 1.4$ Hz, 2H), 4.15 (d, $J = 4.3$ Hz, 1H), 4.11 (dd, $J = 8.9, 7.5$ Hz, 1H), 4.03 (dd, $J = 8.9, 4.1$ Hz, 1H), 3.93 (dddd, $J = 10.0, 6.3, 3.7, 3.7$ Hz, 1H), 3.36 (dd, $J = 13.5, 3.5$ Hz, 1H), 2.71 (m, apparent quartet, $J = 4.7$ Hz, 1H), 2.62 (dd, $J = 13.5, 10.0$ Hz, 1H), 1.73-1.64 (m, 1H), 1.48-1.40 (m, 1H), 1.05 (dd, $J = 7.6, 7.6$ Hz, 3H), 1.00 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.3, 136.1, 129.1, 128.8, 126.9, 69.6, 65.4, 60.3, 36.7, 34.2, 26.8, 23.0, 13.6; MS (CI) m/z (relative intensity) 291 ($[\text{M}+\text{H}]^+$, 53%), 193 (100%); Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_2$: C, 70.31; H, 9.02; N, 9.65. Found: C, 70.17; H, 9.01; N, 9.65.

(4S,3'R)-3-(5'-Methyl-3'-hexanamino)-4-phenylmethyl-2-oxazolidinone (9aG).

From **3a** (50.5 mg, 0.218 mmol) and isobutyl iodide (0.25 mL, 2.2 mmol) by General Procedure C was obtained **9aB** (6.7 mg, 12% yield) and **9aG** (5.7 mg, 6% yield) as a colorless oil; $[\alpha]_D^{25} +19.5^\circ$ (c 0.85, CHCl_3); IR (film) 3299, 3028, 2958, 2872, 1758, 1497, 1454, 1399, 1238, 1091, 1030, 743, 702 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.32 (dd, $J = 7.6, 7.6$ Hz, 2H), 7.25 (dd, $J = 7.4, 7.4$ Hz, 1H), 7.16 (d, $J = 7.0$ Hz, 2H), 4.14 (dd, $J = 8.2, 8.2$ Hz, 1H), 4.03 (dd, $J = 8.9, 4.4$ Hz, 1H), 3.92-3.87 (m, 1H), 3.97 (br s, 1H), 3.35 (dd, $J = 13.5, 3.4$ Hz, 1H), 3.12-3.03 (m, 1H), 2.60 (dd, $J = 13.4, 10.1$ Hz, 1H), 1.82-1.73 (m, 1H), 1.58-1.42 (m, 2H), 1.29 (dd, $J = 6.9, 6.9$ Hz, 2H), 0.99-0.94 (m, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.5, 136.1, 129.1, 128.9, 127.0, 65.6, 60.1, 58.4, 41.1, 36.8, 25.4, 24.9, 23.1, 22.7, 8.9; MS (CI) m/z (relative intensity) 291 ($[\text{M}+\text{H}]^+$, 100%); Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_2$: C, 70.31; H, 9.02; N, 9.65. Found: C, 70.21; H, 8.97; N, 9.55.

(4S,1'R)-3-(1'-Ethyl-3'-butenylamino)-4-phenylmethyl-2-oxazolidinone (9aH).

From **3a** (66.6 mg, 0.287 mmol) and allyl iodide (0.26 mL, 2.8 mmol) by General Procedure C was obtained **9aH** (5.7 mg, 7% yield) as a colorless oil. This material was identified by comparison with a known sample.⁵

Tin-Free Radical Addition Using InCl_3 with Triethylborane Initiation (Table 5): General Procedure D. The standard method for tin-mediated radical addition (General Procedure C) was employed, with the following modifications: InCl_3 was substituted for ZnCl_2 , and Bu_3SnH was omitted.

(4S,2'R)-3-(1'-Chloro-2'-butanamino)-4-phenylmethyl-2-oxazolidinone (9aI).

From **3a** (48 mg, 0.21 mmol) and chloriodomethane (0.15 mL, 2.07 mmol) by General Procedure D was obtained **9aI** (19 mg, 33% yield) as colorless oil. $[\alpha]_D^{27} +44.9^\circ$ (c 3.4, CHCl_3); IR (film) 3286, 3028, 2966, 2878, 1758, 1497, 1400, 1240, 1217, 1091, 1207, 745, 702 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.31 (dd, $J = 8.0, 8.0$ Hz, 2H), 7.25 (dd, $J = 7.9, 7.9$ Hz, 1H), 7.16 (d, $J = 7.6$ Hz, 2H), 4.13 (dd, $J = 8.6, 8.6$ Hz, 1H), 4.03 (dd, $J = 8.9, 5.8$ Hz, 1H), 3.93-3.88 (m, 1H), 4.25-3.85 (br s, 1H), 3.62 (ABX, $\Delta\nu_{\text{AB}} = 28$ Hz, $J_{\text{AB}} = 11.4$ Hz, $J_{\text{AX}} = 4.6$ Hz, $J_{\text{BX}} = 4.9$ Hz, 2H), 3.41 (dd, $J = 13.4, 3.6$ Hz, 1H), 3.24 (dddd, $J = 5.5, 5.5, 5.5, 5.5$ Hz, 1H), 2.63 (dd, $J = 13.3, 10.1$ Hz, 1H), 1.70-1.56 (m, 2H), 1.01 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.0, 135.8, 129.0, 128.9, 127.1, 66.2, 61.3, 59.7, 45.5, 37.1, 23.4, 9.8; MS (CI) m/z (relative intensity) 283 ($[\text{M}+\text{H}]^+$, 100%); Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}_2\text{Cl}$: C, 59.47; H, 6.77; N, 9.91. Found: C, 59.69; H, 6.82; N, 9.80.

Photolytic Tin-Mediated Radical Addition (Table 6): Hydrazines 9aB and 9aK (General Procedure E).

To a solution of hydrazone **3a** (60 mg, 0.26 mmol) and InCl_3 (132 mg, 0.60 mmol) in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (2 mL/2 mL) was added EtI (41 μL , 0.52 mmol), $(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3$ (102 mg, 0.31 mmol) and acetone (95 μL , 1.30 mmol) and the mixture was irradiated for 18 h under N_2 . Stannanes were removed by dilution with EtOAc, stirring overnight with excess KF, and filtration through a short pad of silica gel. Concentration

and gradient flash chromatography (hexane to hexane/EtOAc 3:1) afforded **9aB** (17 mg, 25% yield) and **9aK** (7 mg major isomer, 4 mg minor isomer, 14% yield). **(4S,3'R)-3-(2'-Ethoxy-3'-pentanamino)-4-phenylmethyl-2-oxazolidinone 9aK (major diastereomer)**: Colorless oil; $[\alpha]_D^{23} +20.0^\circ$ (c 0.35, CHCl_3); IR (film) 3283, 3028, 2972, 2934, 2876, 1757, 1498, 1454, 1402, 1381, 1288, 1238, 1216, 1090, 1004, 746, 701 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.12 (m, 5H), 4.14 (dd, $J = 8.7, 8.7$ Hz, 1H), 4.04 (dd, $J = 9.4, 3.8$ Hz, 1H), 3.99-3.92 (m, 1H), 3.69-3.60 (m, 2H), 3.58-3.49 (m, 1H), 3.37 (dd, $J = 13.9, 4.5$ Hz, 1H), 3.13 (ddd, $J = 6.8, 6.8, 3.4$ Hz, 1H), 2.63 (dd, $J = 13.6, 9.8$ Hz, 1H), 1.64-1.52 (m, 1H), 1.52-1.39 (m, 1H), 1.23 (dd, $J = 7.2, 7.2$ Hz, 3H), 1.17 (d, $J = 6.4$ Hz, 3H), 0.98 (dd, $J = 7.2, 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.0, 136.2, 129.2, 128.4, 126.9, 74.7, 65.4, 64.1, 62.3, 59.6, 36.6, 21.8, 15.6, 14.3, 10.6; MS (CI) m/z (relative intensity) 307 ($[\text{M}+\text{H}]^+$, 100%); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3$: 306.1943. Found: 306.1942. **9aK (minor diastereomer)**. Colorless oil; $[\alpha]_D^{23} +4.2^\circ$ (c 0.80, CHCl_3); IR (film) 3299, 3028, 2972, 2931, 1760, 1455, 1400, 1288, 1238, 1100, 1030, 743, 702 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.39-7.12 (m, 5H), 4.13 (dd, $J = 8.7, 8.7$ Hz, 1H), 4.03 (dd, $J = 9.1, 4.5$ Hz, 1H), 3.97-3.89 (m, 1H), 3.71-3.61 (m, 1H), 3.49 (m, apparent quintet, $J = 6.0$ Hz, 1H), 3.44-3.32 (m, 2H), 3.05 (ddd, $J = 6.4, 4.9, 4.9$ Hz, 1H), 2.62 (dd, $J = 13.6, 10.2$ Hz, 1H), 1.74-1.60 (m, 1H), 1.53-1.41 (m, 1H), 1.30-1.17 (m, 6H), 0.98 (dd, $J = 7.2, 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.2, 136.1, 129.1, 128.9, 127.0, 74.6, 65.5, 63.7, 63.4, 59.7, 36.9, 21.0, 15.6, 15.2, 8.6; MS (CI) m/z (relative intensity) 307 ($[\text{M}+\text{H}]^+$, 100%); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3$: 306.1943. Found: 306.1942.

(4S,2'S)-3-(2'-Butanamino)-4-phenylmethyl-2-oxazolidin-one (9aJ). From **3a** (60

mg, 0.26 mmol) and iodomethane (161 μL , 2.6 mmol) by General Procedure E **9aJ** (6 mg, 9% yield) as colorless oil. $[\alpha]_D^{26} +49.2^\circ$ (c 0.65, CHCl_3); IR (film) 3288, 3028, 2966, 2877, 1758, 1498, 1454, 1399, 1218, 1088, 745, 703 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.32 (dd, $J = 7.1, 7.1$ Hz, 2H), 7.25 (dd, $J = 7.2, 7.2$ Hz, 1H), 7.16 (d, $J = 7.0$ Hz, 2H), 4.15 (dd, $J = 8.3, 8.3$ Hz, 1H), 4.03 (dd, $J = 8.8, 5.3$ Hz, 1H), 3.93-3.88 (m, 1H), 4.30-3.70 (br s, 1H), 3.33 (dd, $J = 13.5, 3.6$ Hz, 1H), 3.19-3.10 (m, 1H), 2.62 (dd, $J = 13.4, 9.9$ Hz, 1H), 1.60-1.57 (m, 1H), 1.41-1.32 (m, 1H), 1.08 (d, $J = 6.4$ Hz, 3H), 0.95 (dd, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.8, 136.0, 129.1, 128.8, 127.0, 66.0, 59.7, 56.0, 37.3, 27.5, 18.0, 9.7; MS (CI) m/z (relative intensity) 249 ($[\text{M}+\text{H}]^+$, 100%); Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_2$: C, 67.71; H, 8.12; N, 11.28. Found: C, 67.79; H, 8.09; N, 11.22.

(4S,3'R)-3-(2'-Methyl-3'-pentylamino)-4-diphenylmethyl-2-oxazolidinone (9bC).

From **3b** (29 mg, 0.094 mmol) and 2-iodopropane by General Procedure C was obtained **9bC** (5 mg, 15% yield, S,R/S,S >98:2, minor diastereomer not detected by ^1H NMR) as a colorless crystalline solid. mp 114-115 $^\circ\text{C}$; $[\alpha]_D^{23} +51.1^\circ$ (c 0.7, CHCl_3); IR (film) 3316, 3029, 2961, 1756, 1495, 1454, 1405, 1219, 1091 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.33-7.14 (m, 10H), 4.58 (d, $J = 5.8$ Hz, 1H), 4.57-4.54 (m, 1H), 4.37 (dd, $J = 9.0, 8.2$ Hz, 1H), 4.22 (dd, $J = 9.1, 3.4$ Hz, 1H), 3.61 (d, $J = 3.3$ Hz, 1H), 2.74-2.70 (m, 1H), 1.77-1.70 (m, 1H), 1.34-1.27 (m, 1H), 1.24-1.11 (m, 1H), 0.81 (d, $J = 6.9$ Hz, 3H), 0.78 (d, $J = 6.9$ Hz, 3H), 0.72 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.0, 140.8, 139.2, 128.9 (2C), 128.7, 128.3, 127.4, 127.0, 64.4, 64.2, 59.4, 51.5, 28.1, 21.4, 18.0, 17.7, 10.3; MS (CI) m/z (relative intensity) 353.7 ($[\text{M}+\text{H}]^+$, 100%); Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2$: C, 74.97; H, 8.01; N, 7.95. Found: C, 74.85; H, 8.06; N, 7.74.

(4S,3'R)-3-(2'-Methyl-3'-pentylamino)-4-isopropyl-2-oxazolidinone (9cC). From **3c**

(147 mg, 0.80 mmol) and 2-iodopropane by General Procedure C was obtained **9cC** (28 mg, 16% yield) as a colorless oil. IR (film) 3300, 2962, 1757, 1465, 1399, 1220, 1090 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.21 (dd, $J = 8.8, 8.7$ Hz, 1H), 4.05 (dd, $J = 9.0, 4.2$ Hz, 1H), 3.89 (br s, 1H), 3.69-3.66 (m, 1H), 2.76-2.73 (m, apparent q, $J = 5.2$ Hz, 1H), 2.30-2.22 (m, 1H), 1.82-1.76 (m, 1H), 1.49-1.36 (m, 2H), 0.97-0.88 (m, 12H), 0.85 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (125 MHz,

CDCl_3) δ 158.6, 65.1, 62.3, 61.8, 28.2, 27.4, 21.6, 18.1, 18.0, 17.7, 14.9, 10.1; MS (CI) m/z (relative intensity) 229.2 ($[\text{M}+\text{H}]^+$, 100%); Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_2$: C, 63.12; H, 10.59; N, 12.27. Found: C, 63.09; H, 10.69; N, 12.11. Diastereomers of **9cC** were not resolved by ^1H NMR or any of the chromatographic methods attempted, including several chiral HPLC columns. Thus the diastereomer ratio was not available.

(4S,3'R)-3-(2'-Methyl-3'-pentylamino)-4-phenyl-2-oxazolidinone (9dC). From **3d** (83 mg, 0.40 mmol) and 2-iodopropane by General Procedure C was obtained **9dC** (35 mg, 35% yield, S,R/S,S = 94:6) as a colorless oil. $[\alpha]_{\text{D}}^{23} +32.0^\circ$ (c 0.3, CHCl_3); IR (film) 3304, 2922, 1761, 1459, 1391, 1240, 1086, 1039 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.44-7.33 (m, 5H), 4.81 (dd, J = 8.4, 6.4 Hz, 1H), 4.61 (dd, J = 8.8, 8.7 Hz, 1H), 4.24 (dd, J = 8.8, 6.4 Hz, 1H), 2.54-2.51 (m, 1H), 1.67-1.62 (m, 1H), 1.44-1.39 (m, 1H), 1.38-1.27 (m, 2H), 0.83 (d, J = 6.9 Hz, 3H), 0.77 (d, J = 6.8 Hz, 3H), 0.71 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.3, 137.2, 129.1 (2C), 127.5, 68.5, 64.4, 61.4, 28.3, 20.9, 18.2, 17.2, 10.2; MS (CI) m/z (relative intensity) 263.1 ($[\text{M}+\text{H}]^+$, 100%), 219.0 (20%); Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_2$: C, 68.67; H, 8.45; N, 10.68. Found: C, 68.89; H, 8.43; N, 10.51.

(4S,3'R)-3-(2'-Methyl-3'-pentylamino)-4-phenyl-2-oxazolidinone (9eC). From **3e** (131 mg, 0.57 mmol) and 2-iodopropane by General Procedure C was obtained **9eC** (80 mg, 50% yield, S,R/S,S = 95:5) as a colorless oil. $[\alpha]_{\text{D}}^{23} -28.9^\circ$ (c 0.4, CHCl_3); IR (film) 3304, 3031, 2961, 1753, 1462, 1381, 1201, 1106, 1035 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, J = 7.5 Hz, 1H), 7.35-7.25 (m, 3H), 5.25-5.21 (m, 1H), 5.09 (d, J = 6.9 Hz, 1H), 4.02 (br s, 1H), 3.33 (ABX, $\Delta\nu_{\text{AB}}$ = 32.2 Hz, J_{AB} = 17.5 Hz, J_{AX} = 6.1 Hz, J_{BX} = 0 Hz, 2H), 2.94-2.91 (m, 1H), 1.88-1.82 (m, 1H), 1.63-1.50 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.91 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.5, 140.2, 138.3, 129.5, 127.2, 126.1, 125.3, 76.5, 65.6, 64.9, 38.9, 28.2, 21.7, 18.2, 18.1, 10.1; MS (CI) m/z (relative intensity) 275.4 ($[\text{M}+\text{H}]^+$, 100%); Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_2$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.85; H, 8.10; N, 10.08.

(4S,3'S)-3-(2'-Methyl-3'-pentylamino)-4-phenylmethyl-2-oxazolidinone (10aB). From **4** (86 mg, 0.35 mmol) and ethyl iodide (0.28 mL, 3.5 mmol) by General Procedure C was obtained unreacted **4** (75.4 mg, 88%) and ethyl adduct **10aB** (5.8 mg, 6% yield) as colorless oil. This material was identified by comparison with a known sample.⁶

(4S,1'R)-3-(1'-Cyclohexyl-2'-methyl-1'-propylamino)-4-phenylmethyl-2-oxazolidinone (10aE). From **4** (40 mg, 0.16 mmol) and cyclohexyl iodide (0.21 mL, 1.60 mmol) by General Procedure C was obtained unreacted **4** (31 mg, 77%) and cyclohexyl adduct **10aE** (5 mg, 9% yield) as colorless oil. $[\alpha]_{\text{D}}^{23} +11.35^\circ$ (c 0.37, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.13 (m, 5H), 4.09-4.02 (m, 3H), 3.94-3.90 (m, 1H), 3.34 (dd, J = 13.4, 3.4 Hz, 1H), 2.63-2.56 (m, 2H), 1.95-1.88 (m, 1H), 1.82-1.74 (m, 3H), 1.68-1.65 (m, 1H), 1.48-1.44 (m, 1H), 1.34-1.14 (m, 6H), 1.04 (d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H); ^{13}C NMR (500 MHz, CDCl_3) δ 158.3, 136.2, 129.1, 128.9, 129.0, 69.1, 65.4, 59.6, 39.1, 36.6, 31.1, 29.7, 28.8, 27.0, 26.8, 26.6, 20.2, 19.0.

(4S,1'S)-3-(1'-Cyclohexyl-1'-propylamino)-4-phenylmethyl-2-oxazolidinone (11aB). From **5** (60 mg, 0.21 mmol) and ethyl iodide (0.17 mL, 2.1 mmol) by General Procedure C was obtained unreacted **5** (37 mg, 61%) and ethyl adduct **11aB** (10 mg, 15% yield) as colorless oil. This material was identified by comparison with a known sample.⁶

(4*S*,1'*S*)-3-(1'-Cyclohexyl-2'-methyl-1'-propylamino)-4-phenylmethyl-2-

oxazolidinone (11aC). From **5** (58 mg, 0.20 mmol) and isopropyl iodide (0.20 mL, 2.0 mmol) by General Procedure C was obtained unreacted **5** (46 mg, 79%) and cyclohexyl adduct **11aC** (6 mg, 9% yield) as colorless oil. $[\alpha]_D^{20} +16.6^\circ$ (*c* 0.53, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.13 (m, 5H), 4.08 (dd, *J* = 8.8, 7.4 Hz, 1H), 4.02-4.00 (m, 2H), 3.92-3.86 (m, 1H), 3.35 (dd, *J* = 13.4, 3.4 Hz, 1H), 2.61-2.56 (m, 2H), 1.94-1.87 (m, 1H), 1.80-1.65 (m, 4H), 1.52-1.48 (m, 1H), 1.27-1.13 (m, 6H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 158.3, 136.2, 129.1, 128.9, 127.0, 69.1, 65.4, 59.5, 39.7, 36.7, 30.7, 29.8, 28.5, 27.1, 26.9, 26.8, 20.7, 18.9.

(4*S*,1'*S*)-3-(2'-Methyl-1'-phenyl-1'-propylamino)-4-phenylmethyl-2-

oxazolidinone [(*S,S*)-12aC]. From **7** (47 mg, 0.168 mmol) and 2-iodopropane by General Procedure C was obtained (*S,S*)-**12aC** (23 mg, 42% yield, *S,S/S,R* = 99:1) as a colorless solid. GCMS retention time 6.2 min; mp 91-93 °C; $[\alpha]_D^{26} -18.2^\circ$ (*c* 0.8, CHCl₃); IR (film) 3309, 3062, 3028, 2960, 2873, 1755, 1604, 1492, 1454, 1402, 1238, 1092, 1029, 917 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, *J* = 8.0, 2H), 7.34 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.24 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.19 (dd, *J* = 7.0, 7.0 Hz, 1H), 6.97 (d, *J* = 7.6, 2H), 4.52 (s, 1H), 3.90 (d, *J* = 7.8 Hz, 1H), 3.79 (dd, *J* = 8.8, 3.9 Hz, 1H), 3.73 (dd, *J* = 8.5, 8.5 Hz, 1H), 3.22 (dd, *J* = 13.4, 3.4 Hz, 1H), 3.05 (dddd, *J* = 10.7, 7.4, 3.5, 3.5 Hz, 1H), 2.46 (dd, *J* = 13.4, 10.0 Hz, 1H), 2.04-1.94 (m, 1H), 1.10 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 157.7, 141.3, 136.0, 129.1, 128.7, 128.1, 127.6, 126.9, 70.6, 65.6, 58.1, 36.6, 32.4, 19.8, 19.1; MS (CI) *m/z* (relative intensity) 325 ([*M*+*H*]⁺, 6%), 193 (100%), 133 (27%); Anal. Calcd for C₂₀H₂₄N₂O₂: C, 74.04; H, 7.46; N, 8.63. Found: C, 74.24; H, 7.62; N, 8.48.

(4*S*,1'*S*)-3-(1'-Cyclopentyl-1'-phenylmethylamino)-4-phenylmethyl-2-

oxazolidinone [(*S,S*)-12aD]. From **7** (42 mg, 0.150 mmol) and iodocyclopentane by General Procedure C was obtained (*S,S*)-**12aD** (31 mg, 59% yield, *S,S/S,R* = 96:4) as a colorless oil. GCMS retention time 5.5 min; $[\alpha]_D^{26} -11.7^\circ$ (*c* 1.1, CHCl₃); IR (film) 3302, 3061, 3027, 2953, 2868, 1756, 1603, 1489, 1403, 1289, 1007, 922 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.42 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.36 (dd, *J* = 7.1, 7.1 Hz, 2H), 7.29 (dddd, *J* = 7.4, 7.4, 1.4, 1.4 Hz, 1H), 7.25 (dddd, *J* = 7.0, 7.0, 1.5, 1.5 Hz, 2H), 7.20 (dddd, *J* = 7.3, 7.3, 1.1, 1.1 Hz, 1H), 6.96 (d, *J* = 7.1 Hz, 2H), 4.54 (s, 1H), 3.93 (d, *J* = 9.8 Hz, 1H), 3.80 (dd, *J* = 8.8, 4.1 Hz, 1H), 3.75 (dd, *J* = 7.8, 7.8 Hz, 1H), 3.21 (dd, *J* = 13.4, 3.3 Hz, 1H), 2.99 (dddd, *J* = 10.0, 7.3, 3.7, 3.7 Hz, 1H), 2.46 (dd, *J* = 13.4, 10.0 Hz, 1H), 2.17 (m, apparent sextet, *J* = 8.5 Hz, 1H), 2.07-1.99 (m, 1H), 1.80-1.73 (m, 1H), 1.69-1.54 (m, 3H), 1.49-1.41 (m, 1H), 1.36-1.29 (m, 1H), 1.15-1.07 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 157.6, 142.6, 136.0, 129.1, 128.7, 128.3, 128.2, 127.6, 126.8, 70.2, 65.6, 58.1, 44.6, 36.5, 30.2, 30.1, 25.7, 24.9; MS (CI) *m/z* (relative intensity) 351 ([*M*+*H*]⁺, 11%), 193 (100%); Anal. Calcd for C₂₂H₂₆N₂O₂: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.29; H, 7.53; N, 7.83.

(4*S*,1'*S*)-3-(1'-Cyclohexyl-1'-phenylmethylamino)-4-phenylmethyl-2-

oxazolidinone [(*S,S*)-12aE]. From **7** (79 mg, 0.282 mmol) and iodocyclohexane by General Procedure C was obtained (*S,S*)-**12aE** (32 mg, 30% yield, *S,S/S,R* = 99:1) as a colorless oil. GCMS retention time 9.7 min; $[\alpha]_D^{26} -16.2^\circ$ (*c* 0.55, CHCl₃); IR (film) 3309, 3027, 2925, 2852, 1755, 1695, 1603, 1490, 1403, 1219, 1028, 893 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.39 (d, *J* = 7.0, 2H), 7.35 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.30 (d, *J* = 6.8 Hz, 1H), 7.26 (dd, *J* = 7.0, 7.0 Hz, 2H), 7.20 (dd, *J* = 7.1, 7.1 Hz, 1H), 6.98 (d, *J* = 7.1 Hz, 2H), 4.59 (s, 1H), 3.95 (d, *J* = 7.0 Hz, 1H), 3.81 (dd, *J* = 8.9, 4.0 Hz, 1H), 3.74 (dd, *J* = 7.9, 7.9 Hz, 1H), 3.22 (dd, *J* = 13.4, 3.1 Hz, 1H), 3.07-3.02 (m, 1H), 2.47 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.03 (d, *J* = 12.4 Hz, 1H), 1.81 (d, *J* = 13.2 Hz,

Stereochemical Proof of 9aC by Chemical Correlation

S11

135.4, 129.8, 129.0, 128.9, 128.5, 128.3, 127.3, 126.6, 70.4, 68.1, 67.6, 65.8, 61.0, 58.9, 39.7, 36.8, 31.4, 22.9, 21.9, 21.7, 19.9, 18.2, 12.2, 12.0; MS (CI) m/z (relative intensity) 381 ($[M+H]^+$, 56%), 297 (65%), 105 (100%); Anal. Calcd for $C_{23}H_{28}N_2O_3$: C, 72.06; H, 7.42; N, 7.36. Found: C, 72.60; H, 7.49; N, 7.36.²

14 **(R)-2-Methylpent-3-yl benzamide (14).** To a solution of **13** (20.9 mg, 0.055 mmol) in THF (0.7 mL) and HMPA (30 μ l) at -78°C was added SmI_2 (0.25 M in THF) until the solution turned deep blue. After 5 min, TLC indicated complete conversion. The mixture was partitioned between CH_2Cl_2 and brine, and the organic phase was dried over Na_2SO_4 . Concentration and flash chromatography afforded **1a** (9.5 mg, 97% yield) and **14** (11.2 mg, 99% yield) as a colorless solid; mp $116\text{--}117^\circ\text{C}$; $[\alpha]_D^{26} + 10.2^\circ$ (c 0.24, CHCl_3); IR (film) 3292, 3059, 2960, 2938, 2873, 1633, 1578, 1542, 1491, 1460, 1368, 1158, 985 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.74 (ddd, $J = 6.9, 1.5, 1.5$ Hz, 2H), 7.47 (dddd, $J = 7.3, 7.3, 1.4, 1.4$ Hz, 1H), 7.41 (dddd, $J = 7.1, 7.1, 1.4, 1.4$ Hz, 2H), 5.77 (br s, 1H), 3.97–3.91 (m, 1H), 1.89–1.80 (m, 1H), 1.70–1.62 (m, 1H), 1.45–1.36 (m, 1H), 0.96–0.93 (m, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.5, 135.3, 131.2, 128.6, 126.8, 56.1, 31.8, 25.3, 19.4, 17.9, 10.6; MS (CI) m/z (relative intensity) 206 ($[M+H]^+$, 100%); Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.98; H, 9.24; N, 6.71.

Stereochemical Proof of **12aF** by Crystallography

15 **Benzamide 15.** To a solution of (*S,S*)-**12aF** (33 mg, 0.098 mmol) in THF (1.0 mL) was added $n\text{-BuLi}$ (2 M in pentane, 0.098 mL, 0.195 mmol) at -78°C , followed after 40 min by addition of benzoyl chloride (23 μ l, 0.195 mmol). After warming to room temperature, the mixture was partitioned between CH_2Cl_2 and brine, and the organic phase was dried over Na_2SO_4 . Concentration and gradient flash chromatography (hexane $\rightarrow$ 3:1 hexane/EtOAc) afforded **15** (35 mg, 81% yield), which exhibited line broadening in ^1H NMR spectra due to restricted amide bond rotation. Recrystallization from 95% EtOH and 3:1 hexane/EtOAc afforded colorless orthorhombic crystals; mp $199\text{--}199.5^\circ\text{C}$; $[\alpha]_D^{27} + 47.7^\circ$ (c 0.65, CHCl_3); IR (film) 3064, 3028, 2962, 1775, 1668, 1447, 1397, 1199, 1109, 1029, 912 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.79 (s, 1H), 7.69 (d, $J = 7.3$ Hz, 2H), 7.47–7.37 (m, 7H), 7.08–7.03 (m, 3H), 6.17 (s, 2H), 4.16 (s, 1H), 3.80–3.62 (m, 2H), 3.50–3.40 (m, 1H), 2.69–2.60 (m, 1H), 1.65–1.50 (m, 1H), 1.27 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 174.6, 156.1, 141.3, 136.5, 134.2, 130.5, 130.2, 128.7, 128.3, 127.4, 127.1, 81.4, 67.6, 59.2, 37.1, 36.8, 29.1; MS (CI) m/z (relative intensity) 443 ($[M+H]^+$, 33%), 297 (100%); Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_3$: C, 75.99; H, 6.83; N, 6.33. Found: C, 75.32; H, 6.89; N, 6.24.² The assigned structure was further confirmed by x-ray crystallography.

(S)-3-(2-Propylidene)amino-4-phenylmethyl-2-oxazolidinone (16). From **3a** (60 mg, 0.259 mmol) and 2-iodopropane, by General Procedure E, photolytic radical addition in the presence of acetone gave the isopropyl adduct **9aC** (36 mg, 50% yield) and **16** (20 mg, 33% yield) as a colorless oil; $[\alpha]_D^{25}$ -65.9° (c 0.94, CHCl_3); IR (film) 3061, 3028, 2999, 2921, 1764, 1643, 1395, 1365, 1219, 1094, 1044 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.31-7.13 (m, 5H), 4.36-4.29 (m, 1H), 4.25 (dd, apparent t, J = 8.5 Hz, 1H), 4.04 (dd, apparent t, J = 9.0 Hz, 1H), 3.15 (dd, J = 13.7, 4.1 Hz, 1H), 2.73 (dd, J = 13.6, 8.9 Hz, 1H), 2.12 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.7, 154.6, 135.5, 129.1, 128.7, 127.0, 66.6, 60.6, 38.4, 25.2, 20.7; MS (CI) m/z (relative intensity) 233 ($[\text{M}+\text{H}]^+$, 43%), 193 (100%). The ^1H NMR spectrum was identical to an authentic sample prepared from **2a** and acetone.

References and Notes

- (1) **CAUTION:** *O*-(Mesitylenesulfonyl)hydroxylamine (MtsONH_2) shows a tendency toward exothermic spontaneous decomposition during its preparation and storage. Although most of the work described here was conducted using MtsONH_2 , we have discontinued use of this compound in favor of the alternative amination reagent *O*-(*p*-nitrobenzoyl)hydroxylamine (NbzONH_2), which gives similar results in the amination of oxazolidinones. Another viable alternative is *O*-(diphenylphosphinoyl)hydroxylamine (DppONH_2).
- (2) Slight deviation from theory was noted in combustion analyses of **2a**, **13**, and **15**. Unfortunately, samples for further analysis were not available at the time of manuscript preparation.
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500 MHz ^1H NMR Spectrum of **9aK** (major diastereomer)

500 MHz ^1H NMR Spectrum of **9aK** (minor diastereomer)

19-1-159 H
2/12/05

500 MHz ^1H NMR Spectrum of **10aE**

500 MHz ^1H NMR Spectrum of **11aC**

500 MHz ^1H NMR Spectrum of **16**