Supporting Information

for Chiral *N,O*-acetal TMS ether; Stereoselective formation of *N*-acyliminium ion and application to the synthesis of β -amino acids

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General Experimental

Unless noted otherwise, all starting materials and reagents were obtained from commercial suppliers and were used without further purification. Tetrahydrofuran and Et₂O were distilled from sodium benzophenone ketyl. Dichloromethane, triethylamine, acetonitrile and pyridine were freshly distilled from calcium hydride. All solvents used for routine isolation of products and chromatography were reagent grade and glass distilled. Reaction flasks were dried at 100 °C. Air and moisture sensitive reactions were performed under an argon atmosphere. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck) with the indicated solvents. Thin-layer chromatography was performed using 0.25 mm silica gel plates (Merck). Melting points were measured on a Büchi melting point apparatus and are uncorrected. Optical rotations were measured with JASCO DIP-1000 digital polarimeter at ambient temperature using 100 mm cell of 2 mL capacity. Infrared spectra were recorded on a Perkin-Elmer 1710 FT-IR spectrometer. Mass spectra were obtained with VG Trio-2 GC-MS instrument. High resolution mass spectra were obtained with JEOL JMS-AX 505WA instrument. ¹H and ¹³C NMR spectra were recorded on either a JEOL JNM-GCX 400 or JEOL JNM-LA 300 spectrometer as solutions in deuteriochloroform (CDCl₃). Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane and are referenced to the deuterated solvent (CHCl₃). ¹H-NMR data were reported in the order of chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and/or multiple resonance), number of protons, and coupling constant in hertz (Hz).

Standard procedure for the preparation of *N,O*-acetal TMS ethers

To a solution of the amide **8** (600 mg, 2.9 mmol) in CH_2Cl_2 (14 mL) was added DIBAL (1.0 M solution in toluene, 3.5 mL, 3.5 mmol) dropwise at -78°C . After 1 h, the reaction mixture was treated with pyridine (0.94 mL, 11 mmol) and then TMSOTf (1.06 mL, 5.9 mmol). The mixture was stirred at -78°C for 10 min, and then slowly warmed to 0°C , quenched with 15% aqueous sodium potassium tartrate (10 mL), and diluted with Et_2O (30 mL). The resultant mixture was warmed to room temperature and stirred vigorously until two layers were completely separated. The mixture was extracted with Et_2O and the combined organic layers were washed with brine, dried over anhydrous MgSO_4 , and concentrated in reduced pressure. The residue was purified by flash column chromatography (10% EtOAc /hexanes) to afford 752 mg (92%) of *N,O*-acetal TMS ether **9** as a white solid.

(4*R*)-4-Phenyl-3-(1*S*)-1-[(trimethylsilyl)oxy]ethyl-1,3-oxazolan-2-one (**9a**)

Yield: 92% (isolated); white solid; m.p. $111\text{--}112^\circ\text{C}$; IR (thin film, neat) ν 1751 ($\text{C}=\text{O}$) cm^{-1} ; $[\alpha]_{\text{D}}^{25} = -74.4$ (c 0.2, CH_2Cl_2); ^1H -NMR (CDCl_3 , 300 MHz) δ 7.24 – 7.14 (m, 5H), 5.49 (q, 1H, $J = 6.1$ Hz), 4.68 (dd, 1H, $J = 9.2, 6.1$ Hz), 4.41 (t, 1H, $J = 8.8$ Hz), 3.94 (dd, 1H, $J = 9.2, 6.1$ Hz), 0.72 (d, 3H, $J = 6.1$ Hz), 0.00 (s, 9H); ^{13}C -NMR (CDCl_3 , 75 MHz) δ 158.4, 141.2, 129.1, 128.7, 127.0, 76.2, 71.0, 55.6, 23.9, 0.0.

(4*R*)-4-Phenyl-3-(1*S*)-1-[(trimethylsilyl)oxy]propyl-1,3-oxazolan-2-one (**9b**)

Yield: 93% (isolated); colorless oil; IR (thin film, neat) ν 1762 ($\text{C}=\text{O}$) cm^{-1} ; $[\alpha]_{\text{D}}^{25} = -86.5$ (c 1.0, CH_2Cl_2); ^1H -NMR (CDCl_3 , 300 MHz) δ 7.21 – 7.11 (m, 5H), 5.15 (t, 1H, $J = 6.8$ Hz), 4.81 (dd, 1H, $J = 9.3, 6.1$ Hz), 4.38 (t, 1H, $J = 9.0$ Hz), 3.96 (dd, 1H, $J = 8.8, 6.3$ Hz), 0.89 (m, 2H), 0.48 (t, 3H, $J = 7.3$ Hz), 0.00 (s, 9H); ^{13}C -NMR (CDCl_3 , 75 MHz) δ 158.6, 140.8, 129.1, 128.8, 127.2, 81.5, 71.0, 55.6, 29.9, 10.0, 0.0.

(4*R*)-4-Phenyl-3-(1*S*)-1-[(trimethylsilyl)oxy]pentyl-1,3-oxazolan-2-one (**9c**)

Yield: 87% (isolated); white solid; IR (thin film, neat) ν 1758 ($\text{C}=\text{O}$) cm^{-1} ; $[\alpha]_{\text{D}}^{25} = -70.4$ (c 0.4, CH_2Cl_2); ^1H -NMR (CDCl_3 , 300 MHz) δ 7.20 – 7.15 (m, 5H), 5.22 (t, 1H, $J = 6.1$ Hz), 4.81 (dd, 1H, $J = 9.2, 6.0$ Hz), 4.40 (t, 1H, $J = 8.8$ Hz), 3.99 (dd, 1H, $J = 8.6, 6.2$ Hz), 0.98 – 0.78 (m, 6H), 0.50 (t, 3H, $J = 7.0$ Hz), 0.00 (s, 9H); ^{13}C -NMR (CDCl_3 , 75 MHz) δ 158.6, 140.8, 129.0, 128.8,

127.3, 80.2, 70.9, 55.6, 36.4, 27.4, 22.1, 13.8, 0.0.

(4R)-4-Phenyl-3-(1S)-2-phenyl-1-[(trimethylsilyl)oxy]ethyl-1,3-oxazolan-2-one (9d)

Yield: 89% (isolated); white solid; m.p. 99–101 °C; IR (thin film, neat) ν 1756 (C=O) cm^{-1} ; $[\alpha]_{\text{D}}^{25} = -102.7$ (*c* 0.4, CH_2Cl_2); $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 7.49 – 7.44 (m, 5H), 7.31 – 7.24 (m, 3H), 7.07 (d, 2H, *J* = 6.1 Hz), 5.67 (dd, 1H, *J* = 9.5, 3.4 Hz), 5.16 (dd, 1H, *J* = 9.0, 6.3 Hz), 4.68 (t, 1H, *J* = 9.0 Hz), 4.26 (dd, 1H, *J* = 8.8, 6.3 Hz), 2.53 (dd, 1H, *J* = 13.4, 3.4 Hz), 2.32 (dd, 1H, *J* = 13.4, 9.8 Hz), 0.00 (s, 9H); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 158.8, 141.0, 137.8, 130.1, 129.7, 129.3, 128.6, 127.8, 127.0, 81.2, 71.4, 56.3, 44.1, 0.0.

(4R)-4-Phenyl-3-(1S)-1-[(trimethylsilyl)oxy]-4-pentenyl-1,3-oxazolan-2-one (9e)

Yield: 90% (isolated); white solid; IR (thin film, neat) ν 1747 (C=O) cm^{-1} ; $[\alpha]_{\text{D}}^{25} = -60.1$ (*c* 0.4, CH_2Cl_2); $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 7.22 – 7.13 (m, 5H), 5.40 – 5.23 (m, 2H), 4.81 (dd, 1H, *J* = 9.2, 6.3 Hz), 4.66 – 4.56 (m, 2H), 4.39 (t, 1H, *J* = 8.8 Hz), 3.99 (dd, 1H, *J* = 8.8, 6.1 Hz), 1.80 – 1.54 (m, 2H), 1.06 – 0.89 (m, 2H), 0.00 (s, 9H); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 158.5, 140.7, 137.3, 129.1, 128.8, 127.2, 114.9, 79.6, 70.9, 55.6, 35.8, 29.5, 0.0.

(4R)-4-Phenyl-3-(1S)-1-[(trimethylsilyl)oxy]decyl-1,3-oxazolan-2-one (9f)

Yield: 81% (isolated); white solid; IR (thin film, neat) ν 1752 (C=O) cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 7.20 – 7.12 (m, 5H), 5.22 (t, 1H, *J* = 5.9 Hz), 4.81 (dd, 1H, *J* = 9.3, 6.1 Hz), 4.39 (t, 1H, *J* = 8.8 Hz), 3.99 (dd, 1H, *J* = 8.8, 6.1 Hz), 1.11 – 0.72 (m, 16H), 0.70 (t, 3H, *J* = 7.1 Hz), 0.00 (s, 9H); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 158.7, 140.8, 129.0, 128.7, 127.3, 80.2, 70.9, 55.6, 36.7, 31.9, 29.5, 29.4, 29.3, 29.0, 25.3, 22.8, 14.2, 0.0.

(4R)-4-Phenyl-3-(1S)-3-phenyl-1-[(trimethylsilyl)oxy]propyl-1,3-oxazolan-2-one (9g)

Yield: 83% (isolated); white solid; $[\alpha]_{\text{D}}^{25} = -37.9$ (*c* 0.4, CH_2Cl_2); IR (thin film, neat) ν 1758 (C=O) cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 7.45 – 7.28 (m, 5H), 7.22 – 7.10 (m, 3H), 6.84 (d, 2H, *J* = 6.2 Hz), 5.51 (t, 1H, *J* = 6.6 Hz), 5.06 (dd, 1H, *J* = 9.0, 6.1 Hz), 4.62 (t, 1H, *J* = 8.8 Hz), 4.22 (dd, 1H, *J* = 8.8, 6.1 Hz), 2.55 – 2.29 (m, 2H), 1.50 – 1.26 (m, 2H), 0.19 (s, 9H); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 158.7, 141.0, 140.7, 129.2, 128.9, 128.3, 128.2, 127.3, 125.9, 79.9, 71.0, 55.6, 38.0, 31.5, 0.0.

(4R,5S)-4,5-Diphenyl-3-(1S)-1-[(trimethylsilyl)oxy]propyl-1,3-oxazolan-2-one (14a)

Yield: 76% (isolated); colorless solid; m.p. 149–151 °C; IR (thin film, neat) ν 1754 (C=O) cm^{-1} ; $[\alpha]_{\text{D}}^{25} = 0.9$ (*c* 0.4, CH_2Cl_2); $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 6.97 – 6.69 (m, 10H), 5.52 (d, 1H, *J* = 8.3 Hz), 5.22 (dd, 1H, *J* = 8.3, 4.6 Hz), 4.94 (d, 1H, *J* = 8.3 Hz), 1.01–0.80 (m, 2H), 0.48 (t,

3H, $J = 7.3$ Hz), 0.00 (s, 9H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 157.8, 136.7, 134.3, 127.9, 127.72, 127.69, 127.6, 126.0, 81.2, 80.7, 60.0, 29.7, 10.1, 0.0.

(4*R*,5*S*)-4,5-Diphenyl-3-(1*R*)-1-[(trimethylsilyl)oxy]propyl-1,3-oxazolan-2-one (14b)

Yield: 9% (isolated); white solid; m.p. 111–112 °C; IR (thin film, neat) ν 1740 (C=O) cm^{-1} ; $[\alpha]_{\text{D}}^{25} = 21.7$ (c 0.4, CH_2Cl_2); ^1H -NMR (CDCl_3 , 300 MHz) δ 7.11 – 6.91 (m, 10H), 5.80 (d, 1H, $J = 8.1$ Hz), 5.32 (t, 1H, $J = 6.6$ Hz), 5.07 (d, 1H, $J = 7.8$ Hz), 1.92 – 1.69 (m, 2H), 0.97 (t, 3H, $J = 7.3$ Hz), 0.00 (s, 9H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 157.3, 135.9, 134.4, 128.1, 127.74, 127.72, 127.55, 126.0, 80.3, 80.2, 62.3, 28.8, 9.7, –0.2.

Standard procedure for $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed alkylation of *N,O*-acetal TMS ether with ketene silyl acetal

To a solution of *N,O*-acetal TMS ether **9a** (120 mg, 0.43 mmol) and ketene silyl acetal (1.5 – 2.0 equiv) in CH_2Cl_2 (2 mL) was added $\text{BF}_3 \cdot \text{OEt}_2$ (54 μL , 0.43 mmol) at –41 °C. After being stirred at the same temperature for 30 min, the mixture was quenched with triethylamine and concentrated in reduced pressure. The residue was purified by flash column chromatography to give an ester **10a** as a white solid (118 mg, 99%).

Ethyl (3*S*)-3-[(4*R*)-2-oxo-4-phenyl-1,3-oxazolan-3-yl]butanoate (10a)

Yield: 99% (isolated); **major** colorless oil; IR (thin film, neat) ν 1730 (C=O) cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.42 – 7.31 (m, 5H), 4.88 (dd, 1H, $J = 9.0, 6.8$ Hz), 4.54 (t, 1H, $J = 8.8$ Hz), 4.11 (dd, 1H, $J = 9.4, 7.1$ Hz), 4.08 (q, 2H, $J = 7.3$ Hz), 3.73 (m, 1H), 2.91 (dd, 1H, $J = 16.6, 8.5$ Hz), 2.22 (dd, 1H, $J = 16.3, 5.6$ Hz), 1.24–1.18 (m, 6H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 171.5, 156.9, 138.8, 129.13, 129.07, 127.4, 70.0, 61.0, 60.5, 47.1, 38.3, 18.1, 14.1; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_1\text{O}_4$: 277.1314, Found: 277.1322.

Ethyl (3*S*)-3-[(4*R*)-2-oxo-4-phenyl-1,3-oxazolan-3-yl]pentanoate (10b)

Yield: 98% (isolated); **major** colorless oil; IR (thin film, neat) ν 1746 (C=O) cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.37 – 7.32 (m, 5H), 4.79 (dd, 1H, $J = 9.0, 7.1$ Hz), 4.51 (t, 1H, $J = 9.0$ Hz), 4.14 (dd, 1H, $J = 8.8, 7.1$ Hz), 4.05 (q, 2H, $J = 7.1$ Hz), 3.54 (m, 1H), 2.66 (dd, 1H, $J =$

16.3, 8.8 Hz), 2.17 (dd, 1H, $J = 16.3, 5.3$ Hz), 1.72 – 1.51 (m, 2H), 1.18 (t, 3H, $J = 7.1$ Hz), 0.68 (t, 3H, $J = 7.6$ Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 171.8, 157.4, 138.7, 129.2, 129.1, 127.8, 70.0, 60.6, 60.5, 52.9, 36.9, 25.1, 14.1, 11.1; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{21}\text{N}_1\text{O}_4$: 291.1471, Found: 291.1505.

Ethyl (3S)-3-[(4R)-2-oxo-4-phenyl-1,3-oxazolan-3-yl]heptanoate (10c)

Yield: 87% (isolated); **major** colorless oil; IR (thin film, neat) ν 1747 (C=O) cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.37 – 7.28 (m, 5H), 4.78 (dd, 1H, $J = 9.0, 6.8$ Hz), 4.51 (t, 1H, $J = 8.8$ Hz), 4.14 (dd, 1H, $J = 8.8, 6.8$ Hz), 4.05 (q, 2H, $J = 7.1$ Hz), 3.62 (m, 1H), 2.67 (dd, 1H, $J = 8.8, 7.6$ Hz), 2.15 (dd, 1H, $J = 16.3, 5.4$ Hz), 1.66 – 1.54 (m, 2H), 1.18 (t, 3H, $J = 7.1$ Hz), 1.07 – 0.93 (m, 4H), 0.71 (t, 3H, $J = 6.8$ Hz); HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{25}\text{N}_1\text{O}_4$: 319.1784, Found: 319.1785.

Ethyl (3S)-3-[(4R)-2-oxo-4-phenyl-1,3-oxazolan-3-yl]-4-phenylbutanoate (10d)

Yield: 47% (isolated); **major** colorless oil; IR (thin film, neat) ν 1751 (C=O) cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.32 – 6.77 (m, 10H), 4.80 (t, 1H, $J = 8.8$ Hz), 4.40 (t, 1H, $J = 8.8$ Hz), 4.17 (dd, 1H, $J = 8.5, 5.1$ Hz), 4.00 (q, 2H, $J = 7.1$ Hz), 3.59 (m, 1H), 2.95 (dd, 1H, $J = 16.8, 9.5$ Hz), 2.86 (dd, 2H, $J = 8.0, 3.4$ Hz), 2.27 (dd, 1H, $J = 16.8, 4.6$ Hz), 1.14 (t, 3H, $J = 7.1$ Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 171.9, 157.1, 137.9, 137.8, 129.2, 129.14, 129.06, 128.6, 127.9, 126.6, 69.9, 61.8, 60.7, 52.6, 38.4, 35.5, 14.1; HRMS (EI) Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_1\text{O}_4$: 353.1627, Found: 353.1631.

Ethyl (3S)-3-[(4R)-2-oxo-4-phenyl-1,3-oxazolan-3-yl]-6-heptenoate (10e)

Yield: 96% (isolated); **major** colorless oil; IR (thin film, neat) ν 1746 (C=O) cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.37 – 7.28 (m, 5H), 5.52 – 5.41 (m, 1H), 4.82 – 4.75 (m, 3H), 4.51 (t, 1H, $J = 9.0$ Hz), 4.15 (dd, 1H, $J = 8.8, 6.8$ Hz), 4.05 (q, 2H, $J = 7.1$ Hz), 3.60 (m, 1H), 2.72 (dd, 1H, $J = 16.4, 6.9$ Hz), 2.18 (dd, 1H, $J = 16.3, 5.3$ Hz), 1.81 – 1.58 (m, 4H), 1.18 (t, 3H, $J = 7.1$ Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 171.6, 157.2, 138.5, 136.9, 129.2, 129.1, 127.8, 115.2, 69.9, 60.8, 60.6, 50.7, 36.8, 31.1, 30.4, 14.1; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{23}\text{N}_1\text{O}_4$: 317.1627, Found: 317.1623.

Ethyl (3S)-3-[(4R)-2-oxo-4-phenyl-1,3-oxazolan-3-yl]dodecanoate (10f)

Yield: 70% (isolated); **major** colorless oil; IR (thin film, neat) ν 1762 (C=O) cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.33 – 7.23 (m, 5H), 4.74 (dd, 1H, $J = 9.0, 6.8$ Hz), 4.47 (t, 1H, $J = 8.8$ Hz), 4.09 (dd, 1H, $J = 8.8, 6.7$ Hz), 4.01 (q, 2H, $J = 7.3$ Hz), 3.59 (m, 1H), 2.63 (dd, 1H, $J = 16.4, 8.8$ Hz), 2.11 (dd, 1H, $J = 16.4, 5.4$ Hz), 1.54 – 1.49 (m, 2H), 1.16 – 0.99 (m, 17H), 0.76 (t,

3H, $J = 6.8$ Hz); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 171.8, 157.3, 138.7, 129.2, 129.1, 127.9, 69.9, 60.6, 51.3, 37.1, 32.0, 31.8, 29.4, 29.3, 29.2, 29.0, 26.4, 22.6, 14.13, 14.09; HRMS (EI) Calcd for $\text{C}_{23}\text{H}_{35}\text{N}_1\text{O}_4$: 389.2366, Found: 389.2411.

Ethyl (3*S*)-3-[(4*R*)-2-oxo-4-phenyl-1,3-oxazolan-3-yl]-5-phenylpentanoate (10g)

Yield: 74% (isolated); **major** white solid; IR (thin film, neat) ν 1760 ($\text{C}=\text{O}$) cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.32 – 7.35 (m, 10H), 4.75 (dd, 1H, $J = 9.0, 6.8$ Hz), 4.44 (t, 1H, $J = 9.0$ Hz), 4.14 (dd, 1H, $J = 8.8, 6.8$ Hz), 4.04 (q, 2H, $J = 7.0$ Hz), 3.63 (m, 1H), 2.76 (dd, 1H, $J = 16.5, 8.6$ Hz), 2.36 (m, 2H), 2.20 (dd, 1H, $J = 16.5, 5.3$ Hz), 1.90 (m, 2H), 1.17 (t, 3H, $J = 7.1$ Hz); HRMS (EI) Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_1\text{O}_4$: 367.1784, Found: 367.1797.

Ethyl (3*S*)-3-[(4*R*,5*S*)-2-oxo-4,5-diphenyl-1,3-oxazolan-3-yl]pentanoate (15a)

Yield: 89% (isolated); white solid; IR (thin film, neat) ν 1755 ($\text{C}=\text{O}$) cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.23 – 6.91 (m, 10H), 5.79 (d, 1H, $J = 8.3$ Hz), 5.05 (d, 1H, $J = 8.3$ Hz), 4.07 (q, 2H, $J = 7.1$ Hz), 3.75 (m, 1H), 2.73 (dd, 1H, $J = 16.3, 8.3$ Hz), 2.21 (dd, 1H, $J = 16.4, 5.9$ Hz), 1.89 – 1.58 (m, 2H), 1.21 (t, 3H, $J = 7.3$ Hz), 0.83 (t, 3H, $J = 7.6$ Hz); ^{13}C -NMR (CDCl_3 , 75 MHz) δ 171.6, 157.3, 135.5, 134.7, 128.4, 128.3, 128.1, 127.8, 127.6, 125.8, 79.8, 65.2, 60.6, 53.6, 37.0, 25.4, 14.1, 11.2.

Ethyl (3*R*)-3-[(4*R*,5*S*)-2-oxo-4,5-diphenyl-1,3-oxazolan-3-yl]pentanoate (15b)

Yield: 56% (isolated); colorless needle; IR (thin film, neat) ν 1751 ($\text{C}=\text{O}$) cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.02 – 6.87 (m, 10H), 5.77 (d, 1H, $J = 8.0$ Hz), 5.01 (d, 1H, $J = 8.0$ Hz), 4.05 (2H, qd, $J = 7.3, 1.9$ Hz), 3.94 (m, 1H), 2.73 (dd, 1H, $J = 14.9, 5.6$ Hz), 2.55 (dd, 1H, $J = 15.1, 8.8$ Hz), 1.14 (m, 1H), 0.97 (t, 3H, $J = 7.3$ Hz), 0.84 (m, 1H), 0.50 (t, 3H, $J = 7.3$ Hz).

(3S)-3-[(4R)-2-Oxo-4-phenyl-1,3-oxazolan-3-yl]pentanoic acid (11**)**

To a solution of ester **10b** (74 mg, 0.25 mmol) in THF–H₂O (1:1) (3 mL) was added LiOH·H₂O (3 equiv), and the mixture was stirred for 3 h. The solution was acidified with 1N HCl, and extracted with EtOAc. Organic layer was washed with H₂O and brine, and concentrated in reduced pressure. The crude product **11** (66 mg, 99%) was used for next step without further purification.

Yield: 99% (crude); white solid; IR (thin film, neat) ν 1738 (C=O) cm^{-1} ; ¹H-NMR (CDCl₃, 300 MHz) δ 7.85 (bs, 1H), 7.40 – 7.35 (m, 5H), 4.85 (dd, 1H, J = 8.8, 7.1 Hz), 5.89 (t, 1H, J = 8.8 Hz), 4.20 (dd, 1H, J = 8.6, 7.1 Hz), 3.60 (m, 1H), 2.71 (dd, 1H, J = 16.6, 8.6 Hz), 2.24 (dd, 1H, J = 16.3, 5.3 Hz), 1.67 (m, 2H), 0.72 (t, 3H, J = 7.6 Hz); HRMS (EI) Calcd for C₁₄H₁₇N₁O₄: 263.1158, Found: 263.1191.

(3S)-3-[(Benzyloxy)carbonyl]aminopentanoic acid (12**)**

To a solution of acid **11** (66 mg, 0.25 mmol), in THF (20 mL) and *t*-BuOH (3 mL) was added lithium (18 mg, 2.6 mmol, 10 equiv). The reaction mixture was cooled to –78 °C, and then NH₃ (30 mL) was added by condensation. The resulting deep-blue solution was stirred at –78 °C for 30 min, and then NH₄Cl (500 mg) was added. The reaction mixture was allowed to warm to room temperature, concentrated to about 5 mL by evaporation at reduced pressure. After sequential addition of aqueous 2N Na₂CO₃ (5 mL) and CbzCl (128 mg, 0.75 mmol), the mixture was stirred for 18 h and then concentrated at the reduced pressure. The resulting aqueous solution was extracted with CH₂Cl₂ and the organic layer was dried over MgSO₄. After evaporation of the solvent at reduced pressure, the residue was purified by flash column chromatography (15% EtOAc/hexanes) to give the carbamate **12** (52 mg, 82%) as a white solid. Yield: 82% (isolated); white solid; IR (thin film, neat) ν 3320 (OH), 1695 (C=O) cm^{-1} ; $[\alpha]_D^{25}$ = –26.3 (c 0.1, CH₂Cl₂); ¹H-NMR (CDCl₃, 300 MHz) δ 7.29 – 7.24 (m, 5H), 5.27 (bs, 1H), 5.03 (s, 2H), 3.83 (bs, 1H), 2.53 (d, 2H, J = 3.4 Hz), 1.58 – 1.48 (m, 2H), 0.87 (t, 3H, J = 7.1 Hz); ¹³C-NMR (CDCl₃, 75 MHz) δ 176.5, 156.0, 136.4, 128.5, 128.1, 128.06, 66.8, 53.4, 49.5, 38.4, 27.4, 10.5.

Selected data of X-ray Crystallographic Analysis
for (4*R*,5*S*)-4,5-Diphenyl-3-(1*S*)-1-[(trimethylsilyl)oxy]propyl-1,3-oxazolan-2-one (14a**)**

An ORTEP drawing of **14a** with 30% thermal ellipsoids. Single crystal X-ray data were collected on an Enraf-Nonius CCD single crystal X-ray diffractometer at room temperature using graphite-monochromated MoK α radiation ($\lambda=0.71073\text{\AA}$). The structures were solved by direct methods (SHELXS-97), and refined against all F^2 data (SHELXS-97). Crystal data for **14a**: C₂₁H₂₇NO₃Si, $M = 369.53$, orthorhombic, space group $P2_12_12_1$, $a = 9.2287(3)$, $b = 9.9625(3)$, $c = 23.3118(6)$ $\text{\AA}$, $V = 2143.31(11)$ $\text{\AA}^3$, $Z = 4$, $\rho_c = 1.145\text{g/cm}^3$, $\mu = 0.128\text{mm}^{-1}$, $T = 293(2)$ K, $F(000) = 792$, A total of 6910 reflections were collected, 3874 unique ($R_{\text{int}} = 0.0269$), Flack's parameter = 0.00(19), $R1 = 0.0522$, $wR2 = 0.1128$ ($I > 2\sigma(I)$), GOF = 1.102.

ppm

180

160

140

120

100

80

60

40

20

171.525

156.975

138.821

129.130

129.066

127.428

127.033

77.320

77.001

76.684

70.045

61.041

60.493

47.072

38.270

18.128

14.058

ppm

180

160

140

120

100

80

60

40

20

ppm

171.760

157.385

138.693

129.204

129.113

127.836

127.331

77.320

77.002

76.685

69.953

60.624

60.504

52.941

36.857

25.109

14.128

11.120

ppm

180

160

140

120

100

80

60

40

20

0

171.928

157.112

137.862

137.755

129.202

129.143

129.066

128.564

127.878

126.591

77.319

77.203

77.001

76.684

69.928

61.819

60.715

52.605

38.430

35.507

14.134

1.008

ppm

180

160

140

120

100

80

60

40

20

171.786

157.303

138.738

129.197

129.104

127.873

77.319

77.001

76.684

69.910

60.600

51.340

37.082

31.969

31.838

29.399

29.323

29.223

28.966

26.366

22.639

14.136

14.088