Supporting Information

Experimental Procedure:

***trans*-5-Bromo-4-alkoxy-2-oxazolidinones (4). General Procedure:** To a solution of 3-acetyl-2-oxazolone **3** (80 mmol) in the specified alcohols (160 ml) was added NBS (160 mmol) in dioxane (80 ml), and the mixture was stirred at room temperature for 14 h. Concentration of the mixture *in vacuo*, followed by chromatography on silica gel (hexane-AcOEt (9:1 to 8:2)) afforded 5-bromo-4-alkoxy derivatives.

***trans*-5-Bromo-4-methoxy-2-oxazolidinone (4; R=Me):** 78% yields as a colorless oil: ^{1}H-NMR (60 MHz, $CDCl_3$) δ 2.60 (3H, s),3.65 (3H, s), 5.82 (1H, s), 6.15 (1H, s).

***trans*-5-Bromo-4-*tert*-butoxy-2-oxazolidinone (4; R=^{t}Bu):** 77% yields as a colorless oil: ^{1}H-NMR (60 MHz, $CDCl_3$) δ 1.25 (9H, s), 2.55 (3H, s), 5.90 (1H, s), 6.05 (1H, s).

***trans*-4,5-Dialkoxy-2-oxazolidinones. General Procedure:** To a solution of 5-bromo-4-alkoxy derivatives **4** (0.8 mmol) in BnOH or MeOH (8.4 ml) was added ^{i}Pr$_2$NEt (5.0 mmol), and the mixture was stirred at room temperature for 12 h. The mixture was passed through a short silica gel column using AcOEt as the eluent. Concentration of the eluate *in vacuo*, followed by chromatography on silica gel (hexane-AcoEt (6:4)) afforded *trans*-4,5-dialkoxy derivatives.

***trans*-5-Benzyloxy-4-methoxy-2-oxazolidinone (5):** 62% yields as a colorless oil: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.32 (3H, s), 4.63 (1H, d, J = 11.0 Hz), 4.78 (2H, s), 4.89 (1H, d, J = 11.0 Hz), 5.34 (1H, s), 7.25-7.52 (5H, m).

***trans*-4-*tert*-Butoxy-5-methoxy-2-oxazolidinone (6):** 84% yields as colorless crystals, mp 83 °C (from hexane): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.25 (9H, s), 3.53 (3H, s), 4.95 (1H, s), 5.10 (1H, s), 6.65-6.73 (1H, br); Anal. Calcd for $C_8H_{15}NO_4$: C, 50.78; H, 7.99; N, 7.40. Found: C, 50.55; H, 7.80; N, 7.37.

(4*R*,5*S*)- and (4*S*,5*R*)-3-Mac-5-Benzyloxy-4-methoxy-2-oxazolidinones (7 and 8). To a solution of 5-benzyloxy-4-methoxy-2-oxazolidinone **5** (1.8 g, 7.9 mmol) in THF (79.2 ml) were added NaH (60% in oil, 0.6 g, 15.8 mmol) and Mac-Cl **11** (1.9 g, 9.5 mmol) at 0 °C, and the mixture was stirred at room temperature for 12 h. The usual work-up, followed by chromatography on silica gel (hexane-CH_2Cl_2 (3:7)) afforded **7** (1.4 g, 42%) and **8** (1.6 g, 49%) as colorless oils. **7**: $[\alpha]^{26}_D$ –144.8° (*c* 0.50, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.13 (3H, s), 1.26-1.30 (1H, m), 1.28 (3H, s), 1.65-1.69 (2H, m), 1.74-1.82 (1H, m), 1.85-1.91 (2H, m), 2.38-2.42 (1H, m), 3.13 (3H, s), 3.46 (3H, s), 4.36-4.39 (1H, m), 4.64 (1H, d, J = 11.6 Hz), 4.87 (1H, d, J = 11.6 Hz), 5.23 (1H, s), 5.44 (1H, s), 7.26-7.36 (5H, m). **8**: $[\alpha]^{26}_D$ +92.0° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.10 (3H, s), 1.23-1.31 (1H, m), 1.33 (3H, s), 1.63-1.78 (4H, m), 1.89-1.91 (1H, m), 2.24-2.28 (1H, m), 3.22 (3H, s), 3.44 (3H, s), 4.54-4.56 (1H, m), 4.64 (1H, d, J = 11.6 Hz), 4.88 (1H, d, J = 11.6 Hz), 5.23 (1H, s), 5.53 (1H, s), 7.34-7.40 (5H, m).

(4*R*,5*S*)-5-Benzyloxy-4-methoxy-2-oxazolidinone [(+)-BMOx] (1a). To a solution of *N*-Mac-5-benzyloxy-4-methoxy-2-oxazolidinone **7** (3.3 mmol) in THF (32.5 ml) were added $LiBH_4$ (13.0 mmol) and MeOH (26.0 mmol) at -78 °C under an atmosphere of argon. After stirring at 0 °C for 4 h, the reaction was quenched by the addition of an *aqueous* saturated NH_4Cl solution (3.3 ml). The usual work-up, followed by chromatography on silica gel (hexane-AcOEt (6:4)) afforded 5-benzyloxy-4-methoxy-2-oxazolidinone **1a** in 77% yields as colorless crystals, mp 62.5 °C (from hexane): $[\alpha]^{26}_D$ +224.2° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.32 (3H, s), 4.64 (1H, d J = 11.60 Hz), 4.78 (1H, s), 4.90 (1H, d J = 11.60 Hz), 5.34 (1H, s), 7.14 (1H, s), 7.32-7.39 (5H, m); Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.17; H, 5.87; N, 6.27. Found: C, 59.02; H, 5.94; N, 6.37.

(4*S*,5*R*)-5-Benzyloxy-4-methoxy-2-oxazolidinone [(-)-BMOx] (1b). In a manner similar to the preparation of **1a**, this was obtained from **8** in 77% yields as colorless crystals, mp 62.0 °C (from hexane): $[\alpha]^{26}_D$ -227.2° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.32 (3H, s), 4.64 (1H, d J = 11.60 Hz), 4.78 (1H, s), 4.90 (1H, d J = 11.60 Hz), 5.34 (1H, s), 6.75 (1H, s), 7.33-7.39 (5H, m); Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.17; H, 5.87; N, 6.27. Found: C, 59.27; H, 5.91; N, 6.38.

(4*R*,5*S*)- and (4*S*,5*R*)-4-*tert*-Butoxy-5-methoxy-2-oxazolidinones (9 and 10) (Table 1, Entry 4). To a solution of the amino alcohol **12a** (9.5 mg, 0.04 mmol) and BH_3·THF (0.09 mmol) in THF (2.2 ml) was added a solution of 3-acetyl-4-*tert*-butoxy-5-methoxy-2-oxazolidinone **6** (100 mg, 0.4 mmol) and BH_3·THF (0.8 mmol) in THF (4.3 ml) at 0 °C under an atmosphere of argon. The deacetylation partially proceeded on stirring at 0 °C for 6 h and the mixture was then acidified with *3N* HCl. The usual work-up, followed by chromatography on silica gel (hexane-AcOEt (9:1 to 7:3)) afforded **9** (49.6 mg, 61%) as colorless crystals and **10** (38.8 mg, 39%) as a colorless oil. The deacetylated derivative **9** thus obtained (62%ee) was reacetylated with AcCl (0.4 mmol) and NaH (0.4 mmol) and the identical procedure for enantioselective deacetylation was repeated to give optically pure **9** in 38% yield. **9**: $[\alpha]^{30}_D$ +222.2° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.25 (9H, s), 3.53 (3H, s), 4.95 (1H, s), 5.10 (1H, s), 6.65-6.73 (1H, br).δ 1.31 (9H, s), 2.52 (3H, s), 3.53 (3H, s), 5.03 (1H, s), 5.50 (1H, s). Purification of the recovered **10** (80%ee) by a single recrystallization resulted in the optical purity above 99%ee (by HPLC on OD-H). **10**: $[\alpha]^{30}_D$ –221.4° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.31 (9H, s), 2.52 (3H, s), 3.53 (3H, s), 5.03 (1H, s), 5.50 (1H, s).

(4*R*,5*S*)-4,5-Dimethoxy-2-oxazolidinone [(+)-DMOx] (2a): To a solution of optically pure 4-*tert*-butoxy-5-methoxy-2-oxazolidinone (**9**) (0.5 mmol) in CH_2Cl_2 (5.3 ml) were added $BF_3{\cdot}OEt_2$ (0.2 mmol) and MeOH (5.3 mmol) in CH_2Cl_2 (1.0 ml), and the mixture was stirred at 35 °C for 6 h. The mixture was passed through a short silica gel column using AcOEt as the eluent. Concentration of the eluate *in vacuo*, followed by chromatography on silica gel (hexane-AcoEt (6:4)) afforded (+)-4,5-dimethoxy derivative (**2a**) in 95% yield as colorless crystals, mp 52 ℃ (from hexane): $[\alpha]^{28}_D$ +273.0° (*c* 0.20, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.36 (3H, s), 3.54 (3H, s), 4.72 (1H, s), 5.18 (1H, s), 7.27 (1H, brs); Anal. Calcd for $C_5H_9NO_4$: C, 40.82; H, 6.17; N, 9.52. Found: C, 40.59; H, 5.87; N, 9.40.

(4*S*,5*R*)-4,5-Dimethoxy-2-oxazolidinone [(-)-DMOx] (2b). Analogously, this was obtained from **10** in 95% yield as colorless crystals, mp 53 °C (from hexane): $[\alpha]^{28}_D$ –275.2° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.36 (3H, s), 3.54 (3H, s), 4.72 (1H, s), 5.18 (1H, s), 7.44 (1H, brs); Anal. Calcd for $C_5H_9NO_4$: C, 40.82; H, 6.17; N, 9.52. Found: C, 40.86; H, 6.02; N, 9.48.

Nucleophilic Substitution of 4-Methoxy Groups. General Procedure: A solution of 4,5-dimethoxy-2-oxazolidinones (**1b** and **2b**) (0.2 mmol) in THF (1.1 ml) and $BF_3{\cdot}OEt_2$ (1.8 mmol) was added to a suspension of LiCl (3.9 mmol; dried at 150 °C for 1 h under reduced pressure), CuCN (1.9 mmol) and organometals (R'Li or R'MgBr) (1.8 mmol) in THF (2.2 ml), which had previously been stirred at –30 °C under an argon atmosphere for 30 min. The mixture was then stirred at -30 °C for an additional 24 h. The reaction was quenched by the addition of a saturated *aqueous* NH_4Cl solution (2.2 ml). The usual work-up, followed by chromatography on silica gel (hexane-AcOEt (6:4)) afforded the *trans*-5-methoxy-4-substituted 2-oxazolidinones (**13a** and **13b**). No contamination with *cis*-isomers was verified by NMR-analysis.

(4*S*,5*R*)-5-Benzyloxy-4-butyl-2-oxazolidinone (13a; R'=Bu): 76% yields as a colorless oil: $[\alpha]^{30}_D$ -184.8° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 6.7 Hz), 1.21-1.34 (4H, m), 1.50-1.55 (2H, m), 3.60-3.62 (1H, m), 4.61 (1H, d, *J* = 11.6 Hz), 4.90 (1H, d, *J* = 11.6 Hz), 5.21 (1H, d, *J* = 2.4 Hz), 6.21 (1H, brs), 7.31-7.38 (5H, m); MS (FAB) *m*/*z*: 382 (MCs^+), 286, 250, 154, 133, 107; HRMS (FAB) Calcd for $C_{14}H_{19}NO_3Cs$ (MCs^+): *m*/*z* 382.0419, Found: *m*/*z* 382.0418.

(4*S*,5*R*)-5-Benzyloxy-4-*iso*-propyl-2-oxazolidinone (13a; R'=^{i}Pr): 76% yields as a colorless oil: $[\alpha]^{29}_D$ –190.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.88 (3H, d, *J* = 6.7 Hz), 0.92 (3H, d, *J* = 6.7 Hz), 1.68-1.74 (1H, m), 3.38-3.39 (1H, m), 4.63 (1H, d, *J* = 11.6 Hz), 4.90 (1H, d, *J* = 11.6 Hz), 5.25 (1H, d, *J* = 2.4 Hz), 6.38 (1H, brs), 7.31-7.38 (5H, m); MS (FAB) *m*/*z*: 368 (MCs^+), 286, 236, 133; HRMS (FAB) Calcd for $C_{13}H_{17}NO_3Cs$ (MCs^+): *m*/*z* 368.0263, Found: *m*/*z* 368.0293.

(4*S*,5*R*)-5-Benzyloxy-4-*tert*-butyl-2-oxazolidinone (13a; R'=^{t}Bu): 74% yields as a colorless oil: $[\alpha]^{30}_D$ –182.8° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.87 (9H, s), 3.35 (1H, q, *J* = 1.2 Hz), 4.64 (1H, dd, *J* = 4.9, 11.6 Hz), 4.90 (1H, d, *J* = 11.6 Hz), 5.27 (1H, d, *J* = 2.4 Hz), 6.59 (1H, brs), 7.31-7.38 (5H, m); MS (FAB) *m*/*z*: 382 (MCs^+), 286, 250, 206, 180, 154, 133; HRMS (FAB) Calcd for $C_{14}H_{19}NO_3Cs$ (MCs^+): *m*/*z* 382.0419, Found: *m*/*z* 382.0446.

(4*S*,5*R*)-5-Benzyloxy-4-phenyl-2-oxazolidinone (13a; R'=Ph): 80% yields as colorless crystals, mp 137 °C (from hexane): $[\alpha]^{29}_D$ –186.4° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.61 (1H, d, *J* = 11.6 Hz), 4.71 (1H, s), 4.95 (1H, d, *J* = 11.6 Hz), 5.36 (1H, d, *J* = 2.4 Hz), 5.54 (1H, brs), 7.29-7.42 (10H, m); Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.41; H, 5.66; N, 5.24.

(4*S*,5*R*)-4-Benzyl-5-benzyloxy-2-oxazolidinone (13a; R'=Bn): 90% yields as a colorless oil: $[\alpha]^{30}_D$ –183.4° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.75-2.79 (1H, m), 2.86-2.90 (1H, m), 3.39 (1H, d, *J* = 7.3 Hz), 4.58 (1H, d, *J* = 11.6 Hz), 4.87 (1H, d, *J* = 11.6 Hz), 5.31 (1H, d, *J* = 2.4 Hz), 5.34 (1H, brs), 7.13-7.14 (2H, m), 7.25-7.37 (8H, m); MS (FAB) *m*/*z*: 306 (MNa^+), 262, 202, 176, 135; HRMS (FAB) Calcd for $C_{17}H_{17}NO_3Na$ (MNa^+): *m*/*z* 306.1106, Found: *m*/*z* 306.1087.

(4*S*,5*R*)-4-Butyl-5-methoxy-2-oxazolidinone (13b; R'=Bu): 71% yields as a colorless oil: $[\alpha]^{30}_D$ -181.8° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.92 (3H, t, *J* = 6.7 Hz), 1.31-1.36 (4H, m), 1.53-1.58 (2H, m), 3.52 (3H, s), 3.52-3.55 (1H, m), 5.05 (1H, d, *J* = 2.5 Hz), 6.52-6.65 (1H, br); MS (FAB) *m*/*z*: 306 (MCs^+), 286, 174, 133, 107; HRMS (FAB) Calcd for $C_8H_{15}NO_3Cs$ (MCs^+): *m*/*z* 306.0106, Found: *m*/*z* 306.0076.

(4*S*,5*R*)-5-Methoxy-4-*iso*-propyl-2-oxazolidinone (13b; R'=^{i}Pr): 80% yields as a colorless oil: $[\alpha]^{28}_D$ –183.0° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.94 (3H, d, *J* = 6.1 Hz), 0.95 (3H, d, *J* = 6.1 Hz), 1.75 (1H, dq, *J* = 6.1, 6.7 Hz), 3.32 (1H, d, *J* = 6.7 Hz), 3.52 (3H, m), 5.09 (1H, d, *J* = 2.4 Hz), 6.77 (1H, brs); MS (FAB) *m*/*z*: 292 (MCs^+), 286, 180, 154, 133, 107; HRMS (FAB) Calcd for $C_7H_{13}NO_3Cs$ (MCs^+): *m*/*z* 291.9950, Found: *m*/*z* 291.9963.

(4*S*,5*R*)-4-*tert*-Butyl-5-methoxy-2-oxazolidinone (13b; R'=^{t}Bu): 71% yields as colorless crystals, mp 92 °C (from hexane): $[\alpha]^{27}_D$ –157.0° (*c* 0.20, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.92 (9H, s), 3.27 (1H, dd, *J* = 0.6, 2.4 Hz), 3.52 (3H, s), 5.11 (1H, d, *J* = 2.4 Hz), 6.91 (1H, brs); Anal. Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.37; H, 8.79; N, 8.15.

(4*S*,5*R*)-5-Methoxy-4-phenyl-2-oxazolidinone (13b;

R'=Ph): 72% yields as colorless crystals, mp 93 °C (from hexane): $[\alpha]^{27}_{D}$ –146.4° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.58-3.65 (1H, m), 3.60 (3H, s), 5.48 (1H, d, *J* = 1.2 Hz), 6.49 (1H, brs), 7.24-7.39 (5H, m); Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25. Found: C, 61.94; H, 5.60; N, 7.32.

(4*S*,5*R*)-4-Benzyl-5-methoxy-2-oxazolidinone (13b; R'=Bn): 83% yields as a colorless oil: $[\alpha]^{29}_{D}$ –180.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.75-2.79 (1H, m), 2.91-2.65 (1H, m), 3.49 (3H, s), 3.79-3.82 (1H, m), 5.15 (1H, d, *J* = 1.2 Hz), 5.33 (1H, brs), 7.26-7.49 (5H, m); MS (FAB) *m*/*z*: 340 (MCs^+), 312, 286, 208, 180, 133, 107; HRMS (FAB) Calcd for $C_{11}H_{13}NO_3Cs$ (MCs^+): *m*/*z* 339.9950, Found: *m*/*z* 340.0014.

(4*S*,5*R*)-4-Allyl-5-methoxy-2-oxazolidinone (13b; R'=Allyl): To a solution of (4*S*,5*R*)-4,5-dimethoxy-2-oxazolidinone **2b** (50.0 mg, 0.3 mmol) in CH_2Cl_2 (3.4 ml) were added allyltrimethylsilane (0.1 ml, 0.7 mmol) and $TiCl_4$ (0.01 ml, 0.1 mmol) at -50 °C under an atmosphere of argon. After stirring for 30 min, the reaction was quenched by the addition of MeOH (1.0 ml). Concentration of the mixture *in vacuo*, followed by chromatography on silica gel (hexane-AcoEt (7:3)) afforded **13b** (**R=Allyl**) (41.5 mg, 0.3 mmol, 78%) as a colorless oil: $[\alpha]^{28}_{D}$ –157.2° (*c* 0.50, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.27-2.38 (2H, m), 3.51 (3H, m), 3.63-3.65 (1H, m), 5.08 (1H, d, *J* = 2.4 Hz), 5.17-5.21 (2H, m), 5.69-5.77 (1H, m), 6.18 (1H, brs); MS (FAB) *m*/*z*: 290 (MCs^+), 180, 158, 133, 114; HRMS (FAB) Calcd for $C_7H_{11}NO_3Cs$ (MCs^+): *m*/*z* 289.9793, Found: *m*/*z* 289.9790.

***N*-*tert*-Butoxycarbonylation. General Procedure:** To a solution of 4-substituted-2-oxazolidinones **13a**, **b** (0.2 mmol) in CH_2Cl_2 (3.4 ml) were added NEt_3 (0.7 mmol), $(Boc)_2O$ (0.2 mmol) and DMAP (0.03 mmol) at 0 °C and the mixture was stirred at room temperature for 2 h. The mixture was then passed through a short silica gel column using AcOEt as the eluent. Concentration of the eluate *in vacuo*, followed by chromatography on silica gel (hexane-AcoEt (19:1)) afforded the *N*-Boc derivatives **14a**, **b**, quantitatively.

(4*S*,5*R*)-5-Benzyloxy-3-*tert*-butoxycarbonyl-4-butyl-2-oxazolidinone (14a; R'=Bu): a colorless oil: $[\alpha]^{30}_{D}$ –102.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.3 Hz), 1.20-1.37 (4H, m), 1.51-1.61 (2H, m), 1.53 (9H, s), 1.77-1.83 (1H, m), 4.02-4.05 (1H, m), 4.61 (1H, d, *J* = 11.6 Hz), 4.98 (1H, d, *J* = 11.6 Hz), 5.11 (1H, s), 7.34-7.40 (5H, m); MS (FAB) *m*/*z*: 372 (MNa^+), 316, 294, 272, 176, 153; HRMS (FAB) Calcd for $C_{19}H_{27}NO_5Na$ (MNa^+): *m*/*z* 372.1787, Found: *m*/*z* 372.1805.

(4*S*,5*R*)-5-Benzyloxy-3-*tert*-butoxycarbonyl-4-*iso*-propyl-2-oxazolidinone (14a; R'=^{i}Pr): a colorless oil: $[\alpha]^{29}_{D}$ –109.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.85 (3H, d, *J* = 6.7 Hz), 0.92 (3H, d, *J* = 6.7 Hz), 1.53 (9H, s), 2.21-2.27 (1H, m), 3.99 (1H, dd, *J* = 1.2, 3.1 Hz), 4.62 (1H, d, *J* = 11.6 Hz), 4.88 (1H, d, *J* = 11.6 Hz), 5.13 (1H, d, *J* = 1.2 Hz), 7.32-7.40 (5H, m); MS (FAB) *m*/*z*: 358 (MNa^+), 302, 280, 258, 214, 176, 153; HRMS (FAB) Calcd for $C_{18}H_{25}NO_5Na$ (MNa^+): *m*/*z* 358.1631, Found: *m*/*z* 358.1613.

(4*S*,5*R*)-5-Benzyloxy-3-*tert*-butoxycarbonyl-4-*tert*-butyl-2-oxazolidinone (14a; R'=^{t}Bu): a colorless oil: $[\alpha]^{29}_{D}$ –108.2° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.90 (9H, s), 1.54 (9H, s), 3.98 (1H, s), 4.63 (1H, dd, *J* = 11.6 Hz), 4.87 (1H, d, *J* = 11.6 Hz), 5.16 (1H, s), 7.33-7.39 (5H, m); MS (FAB) *m*/*z*: 372 (MNa^+), 294, 272, 214, 173, 153, 124; HRMS (FAB) Calcd for $C_{19}H_{27}NO_5Na$ (MNa^+): *m*/*z* 372.1787, Found: *m*/*z* 372.1803.

(4*S*,5*R*)-5-Benzyloxy-3-*tert*-butoxycarbonyl-4-phenyl-2-oxazolidinone (14a; R'=Ph): a colorless oil: $[\alpha]^{29}_{D}$ –132.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.31 (9H, s), 4.60 (1H, d, *J* = 11.0 Hz), 4.92 (1H, d, *J* = 11.0 Hz), 5.02 (1H, d, *J* = 1.8 Hz), 5.25 (1H, d, *J* = 1.2 Hz), 7.23-7.41 (10H, m); MS (FAB) *m*/*z*: 392 (MNa^+), 336, 292, 202, 176, 153; HRMS (FAB) Calcd for $C_{21}H_{23}NO_5Na$ (MNa^+): *m*/*z* 392.1474, Found: *m*/*z* 392.1489.

(4*S*,5*R*)-4-Benzyl-5-benzyloxy-3-*tert*-butoxycarbonyl-2-oxazolidinone (14a; R'=Bn): a colorless oil: $[\alpha]^{30}_{D}$ –121.8° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.58 (9H, s), 2.71 (1H, dd, *J* = 3.7, 9.4 Hz), 3.27 (1H, dd, *J* = 3.7, 9.4 Hz), 4.30-4.48 (1H, m), 4.63 (1H, d, *J* = 11.6 Hz), 4.88 (1H, d, *J* = 11.6 Hz), 5.13 (1H, s), 7.08-7.12 (2H, m), 7.26-7.32 (8H, m); MS (FAB) *m*/*z*: 406 (MNa^+), 346, 306, 246, 214, 176, 153; HRMS (FAB) Calcd for $C_{22}H_{25}NO_5Na$ (MNa^+): *m*/*z* 406.1631, Found: *m*/*z* 406.1636.

(4*S*,5*R*)-3-*tert*-Butoxycarbonyl-4-butyl-5-methoxy-2-oxazolidinone (14b; R'=Bu): a colorless oil: $[\alpha]^{29}_{D}$ –76.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.93 (3H, t, *J* = 6.7 Hz), 1.28-1.41 (4H, m), 1.54 (9H, s), 1.61-1.67 (1H, m), 1.78-1.82 (1H, m), 3.51 (3H, s), 3.97 (1H, q, *J* = 4.3 Hz), 4.95 (1H, s); MS (FAB) *m*/*z*: 296 (MNa^+), 274, 240, 218, 196, 174, 156, 137, 120, 107; HRMS (FAB) Calcd for $C_{13}H_{23}NO_5Na$ (MNa^+): *m*/*z* 296.1474, Found: *m*/*z* 296.1471.

(4*S*,5*R*)-3-*tert*-Butoxycarbonyl-5-methoxy-4-*iso*-propyl-2-oxazolidinone (14b; R'=^{i}Pr): a colorless oil: $[\alpha]^{28}_{D}$ –85.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.90 (3H, d, *J* = 6.7 Hz), 1.00 (3H, d, *J* = 6.7 Hz), 1.54 (9H, s), 2.23-2.27 (1H, m), 3.51 (3H, s), 3.92 (1H, d, *J* = 4.8 Hz), 4.98 (1H, s); MS (FAB) *m*/*z*: 282 (MNa^+), 226, 204, 184, 138; HRMS (FAB) Calcd for $C_{12}H_{21}NO_5Na$ (MNa^+): *m*/*z* 282.1317, Found: *m*/*z* 282.1338.

(4*S*,5*R*)-3-*tert*-Butoxycarbonyl-4-*tert*-butyl-5-methoxy-2-oxazolidinone (14b; R'=^{t}Bu): a colorless oil: $[\alpha]^{28}_{D}$

–78.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.96 (9H, s), 1.54 (9H, s), 3.50 (3H, s), 3.91 (1H, s), 5.02 (1H, s); MS (FAB) *m*/*z*: 296 (MNa^+), 240, 218, 196, 176, 138; HRMS (FAB) Calcd for $C_{13}H_{23}NO_5Na$ (MNa^+): *m*/*z* 296.1474, Found: *m*/*z* 296.1482.

(4*S*,5*R*)-3-*tert*-Butoxycarbonyl-5-methoxy-4-phenyl-2-oxazolidinone (14b; R'=Ph): a colorless oil: $[\alpha]^{28}_D$ –52.0° (*c* 0.20, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.32 (9H, s), 3.53 (3H, s), 4.94 (1H, s), 5.07 (1H, d, *J* = 1.8 Hz), 7.25-7.27 (2H, m) , 7.36-7.42 (3H, m); MS (FAB) *m*/*z*: 316 (MNa^+), 294, 238, 216, 154, 118; HRMS (FAB) Calcd for $C_{15}H_{19}NO_5Na$ (MNa^+): *m*/*z* 316.1161, Found: *m*/*z* 316.1199.

(4*S*,5*R*)-4-Benzyl-3-*tert*-butoxycarbonyl-5-methoxy-2-oxazolidinone (14b; R'=Bn): a colorless oil: $[\alpha]^{27}_D$ –73.8° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.58 (9H, s), 2.74-2.79 (1H, m), 3.24-3.27 (1H, m), 3.37 (3H, s), 4.26 (1H, d, *J* = 10.4 Hz), 4.96 (1H, s), 7.18-7.35 (5H, m); MS (FAB) *m*/*z*: 330 (MNa^+), 274, 252, 230, 173, 137, 115; HRMS (FAB) Calcd for $C_{16}H_{21}NO_5Na$ (MNa^+): *m*/*z* 330.1318, Found: *m*/*z* 330.1322.

(4*S*,5*R*)-4-Allyl-3-*tert*-butoxycarbonyl-5-methoxy-2-oxazolidinone (14b; R'=Allyl): a colorless oil: $[\alpha]^{27}_D$ –68.8° (*c* 0.50, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.55 (9H, s), 2.37-2.43 (1H, m), 2.58-2.63 (1H, m), 3.50 (3H, m), 4.06-4.08 (1H, m), 4.98 (1H, s), 5.12-5.23 (2H, m), 5.68-5.76 (1H, m); MS (FAB) *m*/*z*: 390 (MCs^+), 286, 224, 202, 154, 133; HRMS (FAB) Calcd for $C_{12}H_{19}NO_5Cs$ (MCs^+): *m*/*z* 390.0318, Found: *m*/*z* 390.0304.

***N*-*tert*-Butoxycarbonyl-α-amino Aldehydes (15). General Procedure:** A solution of *N*-Boc derivatives **14a** (0.2 mmol) in MeOH (4.5 ml) in the presence of Pd-C (50 mg) under a hydrogen atmosphere was stirred at room temperature for 2 h. The catalyst was filtered off and the filtrate evaporated *in vacuo*, followed by chromatography on silica gel (hexane-AcoEt (8:2)) to afford the *N*-Boc-α-amino aldehydes **15**. An optical purity above 99%ee was verified by HPLC analysis on OD-H or by oxidation with $KMnO_4$ to *N*-Boc α-amino acids.

(2*S*)-2-*tert*-Butoxycarbonylaminohexanal ((*S*)-*N*-Boc-leucinal) (15; R'=Bu): 87% yields as a colorless oil: $[\alpha]^{20}_D$ –30.6° (*c* 1.00, MeOH); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.91 (3H, t, *J* = 7.3 Hz), 1.34-1.49 (6H, m), 1.46 (9H, s), 4.22 (1H, brs), 5.03 (1H, brs), 9.58 (1H, brs).

(2*S*)-2-*tert*-Butoxycarbonylamino-3-methylbutanal ((*S*)-*N*-Boc-valinal) (15; R'=^{i}Pr): 80% yields as a colorless oil: $[\alpha]^{20}_D$ –11.6° (*c* 1.00, MeOH); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.95 (3H, d, *J* = 6.7 Hz), 1.03 (3H, d, *J* = 6.7 Hz), 1.45 (9H, s), 2.28 (1H, brs), 4.24 (1H, brs), 5.09 (1H, brs), 9.64 (1H, brs).

(2*S*)-2-*tert*-Butoxycarbonylamino-3,3-dimethylbutanal ((*S*)-*N*-Boc-*tert*-leucinal) (15; R'=^{t}Bu): 97% yields as colorless crystals: $[\alpha]^{28}_D$ –4.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.98 (9H, s), 1.38 (9H, s), 4.10 (1H, brs), 5.07 (1H, brs), 9.76 (1H, brs).

(2*S*)-2-*tert*-Butoxycarbonylamino-2-phenylacetaldehyde ((*S*)-*N*-Boc-phenylglycinal) (15; R'=Ph): 81% yields as colorless crystals: $[\alpha]^{20}_D$ –2.9° (*c* 3.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.43 (9H, s), 5.32 (1H, brs), 5.74 (1H, brs), 7.23-7.42 (5H, m), 9.58 (1H, brs).

(2*S*)-2-*tert*-Butoxycarbonylamino-3-phenylpropional ((*S*)-*N*-Boc-phenylalaninal) (15; R'=Bn): 81% yields as colorless crystals: $[\alpha]^{20}_D$ –36.0° (*c* 1.00, MeOH); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.43 (9H, s), 3.12 (1H, d, *J* = 6.7 Hz), 4.43 (1H, brs), 5.04 (1H, brs), 7.16-7.18 (2H, m), 7.24-7.33 (3H, m), 9.54 (1H, brs).

***N*-*tert*-Butoxycarbonyl-α-amino Acid Methyl Ester (16). Typical procedure for $KMnO_4$ oxidation: Methyl (2*S*)-2-*tert*-Butoxycarbonylaminohexanoate (*N*-Boc-(*S*)-leucine methyl ester) (16; R'=Bu):** To a solution of (4*S*,5*R*)-3-*tert*-butoxycarbonyl-4-butyl-5-methoxy-2-oxazolidinone (**14b**; **R'=Bu**) (120 mg, 0.4 mmol) in *t*-BuOH (8.8 ml)-H_2O (4.4 ml) were added $KMnO_4$ (140 mg, 0.9 mmol) and KOH (120 mg, 2.2 mmol). After vigorous stirring at room temperature for 1 h, the reaction was quenched with aqueous formaldehyde (0.22 ml) at 0 °C, acidified with citric acid and extracted with AcOEt (100 ml × 4). The combined extracts were evaporated *in vacuo* to give the *N*-Boc-α-amino acid, which was treated with diazomethane. Column chromatography on silica gel (hexane-AcOEt (9:1)) afforded **16** (**R'=Bu**) (86.4 mg, 80%) as a colorless oil: $[\alpha]^{29}_D$ +11.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 6.7 Hz), 1.26-1.36 (4H, m), 1.45 (9H, s), 1.58-1.66 (1H, m), 1.75-1.82 (1H, m), 3.74 (3H, s), 4.25-4.32 (1H, m), 4.95-5.02 (1H, br); MS (FAB) *m*/*z*: 378 (MCs^+), 286, 190, 154, 133, 107; HRMS (FAB) Calcd for $C_{12}H_{23}NO_4Cs$ (MCs^+): *m*/*z* 378.0681, Found: *m*/*z* 378.0649.

Methyl (2*S*)-2-*tert*-Butoxycarbonylamino-3-methylbutanoate (*N*-Boc-(*S*)-valine methyl ester) (16; R'=^{i}Pr): Similarly, this was prepared in 85% yields as a colorless oil: $[\alpha]^{27}_D$ +12.6° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, d, *J* = 6.7 Hz), 0.96 (3H, d, *J* = 6.7 Hz), 1.45 (9H, s), 2.09-2.16 (1H, m), 3.74 (3H, s), 4.20-4.25 (1H, m), 4.99-5.06 (1H, br); MS (FAB) *m*/*z*: 364 (MCs^+), 312, 286, 232, 176, 154, 133; HRMS (FAB) Calcd for $C_{11}H_{21}NO_4Cs$ (MCs^+): *m*/*z* 364.0525, Found: *m*/*z* 364.0522.

Typical procedure for PDC oxidation: Methyl (2*S*)-2-*tert*-Butoxycarbonylamino-3,3-dimethylbutanoate (*N*-Boc-(*S*)-*tert*-leucine methyl ester) (16; R'=^{t}Bu): To a solution of (4*S*,5*R*)-3-*tert*-butoxycarbonyl-4-*tert*-butyl-5-methoxy-2-oxazolidinone (**14b**; **R'=^{t}Bu**) (0.18 g, 0.7 mmol) in DMF (6.6 ml) were

added PDC (1.5 g, 4.0 mmol), MeOH (0.2 ml, 4.0 mmol) and KOH (0.1 g, 2.0 mmol) at room temperature, and the mixture was stirred for 36 h. The resulting nmixture was then passed through a short silica gel column using AcOEt as the eluent. Concentration of the eluate *in vacuo*, followed by chromatography on silica gel (hexane-CH_2Cl_2 (2:8)) afforded **16** (**R'=^{t}Bu**) (160 mg, 98%) as a colorless oil: $[\alpha]^{27}_D$ +10.4° (*c* 1.00, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.97 (9H, s), 1.44 (9H, s), 3.72 (3H, s), 4.08-4.12 (1H, br), 5.07-5.12 (1H, br); MS (FAB) *m*/*z*: 378 (MCs^+), 312, 286, 246, 190, 146, 133; HRMS (FAB) Calcd for $C_{12}H_{23}NO_4Cs$ (MCs^+): *m*/*z* 378.0681, Found: *m*/*z* 378.0676.

Methyl (2*S*)-2-*tert*-Butoxycarbonylamino-2-phenylacetate (*N*-Boc-(*S*)-phenylglycine methyl ester) (16; R'=Ph): According to the above procedure, this was obtained in 100% yields as colorless crystals, mp 105 ℃ (from hexane): $[\alpha]^{30}_D$ –134.7° (*c* 1.47, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.43 (9H, s), 3.72 (3H, s), 5.17-5.79 (2H, m), 7.37 (5H, s); Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.54; H, 7.39; N, 5.33.

Methyl (2*S*)-2-*tert*-Butoxycarbonylamino-3-phenylpropionate (*N*-Boc-(*S*)-phenylalanine methyl ester) (16; R'=Bn): Similarly, this was prepared in 70% yields as a colorless oil: $[\alpha]^{27}_D$ –51.4° (*c* 1.72, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.40 (9H, s), 3.09 (2H, d, *J* = 5.4 Hz), 3.71 (3H, s), 4.61 (1H, m), 4.97 (1H, br), 7.24-7.33 (5H, m).

Methyl (2*S*)-2-*tert*-Butoxycarbonylamino-4-pentenoate (*N*-Boc-(*S*)-allylglycine methyl ester) (16; R'=Allyl): Similarly, this was prepared in 100% yields as a colorless oil: $[\alpha]^{27}_D$ –18.2° (*c* 1.81, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.42 (9H, s), 2.50 (2H, t, *J* = 6.0 Hz), 3.73 (3H, s), 4.35-4.41 (1H, m), 4.88-6.18 (4H, m); MS (CI, *i*-C_4H_{10}) *m*/*z*: 459 ($2MH^+$), 230 (MH^+), 174; HRMS (CI, *i*-C_4H_{10}) Calcd for $C_{11}H_{20}NO_4$ (MH^+): *m*/*z* 230.1392, Found: *m*/*z* 230.1404.