Supporting information for

An Efficient Synthesis and Ring Opening Reactions of *trans*- and *cis*-Oxazoline-5-carboxylates

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EXPERIMENTAL

General. NMR spectra were recorded with a JEOL spectrometer (JNM-LA 300) at 300 MHz (^{1}H NMR) and at 75 MHz (^{13}C NMR). Chemical shifts were given in ppm using TMS as internal standard. Mass spectra were obtained using a JEOL spectrometer (JMS AX505WA). Melting points were determined in open capillaries and are uncorrected. Flash chromatography was carried out with Merck silica gel 60 (230-400 mesh). Thin layer chromatography was carried out with Merck 60 F_{254} plates with 0.25 mm thickness. $CHCl_3$, CH_2Cl_2, and MeOH were distilled from CaH_2, and THF was distilled from sodium-benzophenone ketyl.

Isopropyl (2*R*,3*S*)-3-(Acetylamino)-2-hydroxy-3-phenylpropionate (2). The compound **2** was prepared in 81% yield according to the reported acetamide - based Sharpless aminohydroxylation protocol.[1] m.p. 111-112 ^{o}C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.29 (d, *J* = 6.2 Hz, 3H), 1.31 (d, *J* = 6.2 Hz, 3H), 2.01 (s, 3H), 3.26 (d, *J* = 3.8 Hz, 1H), 4.48 (dd, *J* = 2.0, 3.8 Hz, 1H), 5.11 (sept, *J* = 6.2 Hz, 1H), 5.56 (dd, *J* = 2.0, 9.2 Hz, 1H), 6.30 (br d, *J* = 9.2 Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.48, 21.65, 23.14, 54.31, 70.79, 73.25, 126.86, 127.74, 128.58, 138.88, 169.28, 172.40; HRMS (CI) m/z 266.1400 $(M+H)^+$, calcd for $C_{14}H_{20}N_1O_4$ 266.1392.

Isopropyl (2*R*,3*S*)-3-(Acetylamino)-2-(methanesulfonyloxy)-3-phenylpropionate (3). MsCl (645 mg, 5.65 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of **2** (1 g, 3.77 mmol) and Et_3N (1.05 mL, 7.54 mmol) in CH_2Cl_2 (25 mL) at 0 ^{o}C under N_2. After being stirred for 1 h at 0 ^{o}C, the reaction mixture was stirred for additional 2 h at room temperature. The reaction mixture was passed through a short silica gel plug (~10 cm^3) and further eluted with EtOAc (100 mL). The combined filtrate was concentrated under reduced pressure, and the crude product was recrystallized from EtOAc-hexane to afford **3** (1.2 g, 3.49 mmol, 93%) as a pale yellow solid. m.p. 116-117 ^{o}C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.27 (d, *J* = 6.2 Hz, 3H), 1.30 (d, *J* = 6.2 Hz, 3H), 2.05 (s, 3H), 2.75 (s, 3H), 5.11 (sept, *J* = 6.2 Hz, 1H), 5.18 (d, *J* = 2.8 Hz, 1H), 5.81 (dd, *J* = 2.8, 9.4 Hz, 1H), 6.34 (br d, *J* = 9.4 Hz, 1H), 7.20-7.50 (m, 5H); ^{13}C-NMR($CDCl_3$, 75MHz) δ 21.33, 21.56, 22.94, 38.40, 53.41, 70.90, 80.78, 126.60, 128.32,

(1) Bruncko, M.; Schlingloff, G.; Sharpless, K. B. *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 1483.

128.82, 136.91, 166.17, 169.40; HRMS (FAB) m/z 344.1175 $(M+H)^+$, calcd for $C_{15}H_{22}N_1O_6S_1$ 344.1168.

(4*S*,5*S*)-5-(Isopropoxycarbonyl)-2-methyl-4-phenyl-2-oxazoline (4). The compound **3** (300 mg, 0.874 mmol) and $KHCO_3$ (175 mg, 1.747 mmol) were dissolved in a mixture of acetone (8 mL) and water (3.2 mL). The resulting mixture was heated at 70 ^oC for 20 h with occasional swirling. The reaction mixture was then allowed to cool to room temperature, and the solvent was evaporated to dryness. The residue was treated with EtOAc (4 x 10 mL) and passed through a short silica gel plug. The combined filtrate was concentrated under reduced pressure, and purification of the residue by flash chromatography on silica gel (hexane- EtOAc, 4:3) afforded **4** (135 mg, 0.546 mmol, 62%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.60 (d, *J* = 6.4 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H), 2.21 (d, *J* = 1.5 Hz, 3H), 4.52 (sept, *J* = 6.4 Hz, 1H) 5.13 (d, *J* = 10.8 Hz, 1H), 5.48 (dd, *J* = 1.5, 10.8 Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C-NMR($CDCl_3$, 75MHz) δ 13.83, 20.70, 21.47, 69.04, 73.13, 80.80, 127.96, 128.05, 128.12, 136.97, 165.77, 167.66; HRMS (FAB) m/z 248.1284 $(M+H)^+$, calcd for $C_{14}H_{18}N_1O_3$ 248.1287.

(4*S*,5*R*)-5-(Isopropoxycarbonyl)-2-methyl-4-phenyl-2-oxazoline (5). DBU (333 mg, 2.184 mmol) was added to a stirred solution of compound **3** (500 mg, 1.456 mmol) in dry $CHCl_3$ (15 mL) at room temperature, and the resulting solution was heated to reflux for 1 h. After being cooled to room temperature, the reaction mixture was passed through a short silica gel plug (~5 cm^3) and further eluted with EtOAc (50 mL). The combined filtrate was concentrated under reduced pressure, and purification of the residue by flash chromatography on silica gel (hexane-EtOAc, 3:1) afforded **5** (274 mg, 1.108 mmol, 76%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.31 (d, *J* = 6.2 Hz, 3H), 1.33 (d, *J* = 6.2 Hz, 3H), 2.19 (d, *J* = 1.5 Hz, 3H), 4.67 (d, *J* = 6.8 Hz, 1H), 5.10-5.25 (m, 2H), 7.20-7.45 (m, 5H); ^{13}C-NMR($CDCl_3$, 75MHz) δ 13.84, 21.70, 69.58, 74.38, 83.12, 126.27, 127.86, 128.75, 141.20, 165.14, 169.69; HRMS (FAB) m/z 248.1283 $(M+H)^+$, calcd for $C_{14}H_{18}N_1O_3$ 248.1287.

Isopropyl (2*S*,3*S*)-3-(Acetylamino)-2-azido-3-phenylpropionate (6). TMS-N_3 (0.8 mL) was added quickly to a solution of **5** (178 mg, 0.72 mmol) in dry MeOH (0.8 mL) in a 6 mL vial at 0 ^oC. The vial was closed tightly with a teflon disk lid, and the reaction mixture was heated at 70 ^oC for 1 d and at 80 ^oC for 1.5 d with occasional swirling. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane-EtOAc, 2:1) to afford **6** (188 mg, 0.648 mmol, 90%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.06 (d, *J* = 6.2 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H), 2.05 (s, 3H), 4.49 (d, *J* = 5.0 Hz, 1H), 4.95 (sept, *J* = 6.2 Hz, 1H), 5.53 (dd, *J* = 5.0, 8.4 Hz, 1H), 6.39 (br d, *J* = 8.4 Hz, 1H), 7.20-7.50 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.39, 21.57, 23.35, 53.76, 64.41, 70.30, 127.53, 128.50, 128.69, 136.53, 167.52, 169.41; HRMS (FAB) m/z 291.1462 $(M+H)^+$, calcd for $C_{14}H_{19}N_4O_3$ 291.1457.

Isopropyl (2*S*,3*S*)-3-(Acetylamino)-3-phenyl-2-(phenylthio)propionate (7). Thiophenol (0.2 mL) was added to a solution of **5** (60 mg, 0.243 mmol) in dry MeOH (0.2 mL) in a 6 mL vial at room temperature. The vial was closed tightly with a teflon disk lid and the reaction mixture was heated at 70 ^oC for 2 d with occasional swirling. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane-EtOAc, 3:2) to afford **7** (83 mg, 0.232 mmol, 96%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.87 (d, *J* = 6.2 Hz, 3H), 1.00 (d, *J* = 6.2 Hz, 3H), 2.12 (s, 3H), 4.01 (d, *J* = 4.4 Hz, 1H),

4.82 (sept, *J* = 6.2 Hz, 1H), 5.55 (dd, *J* = 4.4, 9.0 Hz, 1H), 7.15–7.45 (m, 9H), 7.45 - 7.55 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.25, 21.29, 23.38, 54.28, 55.65, 69.34, 126.31, 127.79, 128.46, 128.56, 129.17, 132.97, 133.42, 139.04, 169.76, 171.37; HRMS (FAB) m/z 358.1481 $(M+H)^+$, calcd for $C_{20}H_{24}N_1O_3S_1$ 358.1477.

Isopropyl (2*S*,3*S*)-3-(Acetylamino)-2-(acetylthio)-3-phenylpropionate (8). Thiolacetic acid (0.3 mL) was added to a solution of **5** (140 mg, 0.566 mmol) in dry THF (0.3 mL) in a 6 mL vial at room temperature. The vial was closed tightly with a teflon disk lid and the reaction mixture was heated at 70 °C for 12 h with occasional swirling. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane-EtOAc, 1:1) to afford **8** as a white solid. This was further purified by recrystallization (EtOAc-hexane) to afford **8** (143 mg, 0.442 mmol, 78%) as white needles. m.p. 155-157 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.95 (d, *J* = 6.2 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H), 2.10 (s, 3H), 2.38 (s, 3H), 4.62 (d, *J* = 4.4 Hz, 1H), 4.86 (sept, *J* = 6.2 Hz, 1H), 5.44 (dd, *J* = 4.4, 9.3 Hz, 1H), 7.18 (br d, *J* = 9.3 Hz, 1H), 7.22-7.35 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.29, 23.38, 30.26, 49.56, 54.25, 69.84, 126.40, 127.91, 128.60, 138.52, 169.65, 170.41, 192.64; HRMS (FAB) m/z 324.1278 $(M+H)^+$, calcd for $C_{16}H_{22}N_1O_4S_1$ 324.1270.

Isopropyl (2*R*,3*S*)-3-(Acetylamino)-2-(acetylthio)-3-phenylpropionate (9). A similar procedure described for **8** starting with **4** (135 mg, 0.546 mmol) gave **9** (94 mg, 0.291 mmol, 53%) as a white crystalline solid. m.p. 128-129 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.00 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H), 1.94 (s, 3H), 2.39 (s, 3H), 4.55 (d, *J* = 9.5 Hz, 1H), 4.83 (sept, *J* = 6.2 Hz, 1H), 5.46 (dd, *J* = 9.2, 9.5 Hz, 1H), 6.18 (br d, *J* = 9.2 Hz, 1H), 7.20-7.50 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.25, 21.32, 23.26, 30.34, 51.53, 54.87, 69.78, 127.26, 128.29, 128.68, 138.68, 167.99, 169.21, 195.20; HRMS (FAB) m/z 324.1264 $(M+H)^+$, calcd for $C_{16}H_{22}N_1O_4S_1$ 324.1270.

Methyl (2*R*,3*S*)-3-(Benzoylamino)-2-hydroxy-3-phenylpropionate (10). The compound **2** (500 mg, 1.89 mmol) was treated with 0.5 M HCl in MeOH (50 mL), and heated to reflux for 10 h. After removal of solvent under reduced pressure, the residue was treated again with 0.5 *M* HCl in MeOH (50 mL) and heated to reflux additional 10 h. After removal of solvent under reduced pressure, the residue was re-dissolved in fresh MeOH (2 x 30 mL) and re-evaptated. To this residue, dry CH_2Cl_2 (40 mL) was added and cooled to 0 °C. To this suspension was added Et_3N (1.31 mL, 9.40 mmol) in CH_2Cl_2 (5 mL) followed by BzCl (270 mg, 1.92 mmol) in CH_2Cl_2 (2 mL), and the reaction mixture was stirred for 1 h at 0 °C and for 1 h at room temperature. The reaction mixture was passed through a short silica gel plug (~10 cm^3) and further eluted with EtOAc(100 mL). The combined filtrate was concentrated under reduced pressure, and the residue was crystallized from EtOAc-hexane to afford **10** (480 mg, 1.60 mmol, 85%) as a off-white solid. An analytical sample was obtained by recrystallization ($CHCl_3$-hexane). m.p. 178-181 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.30 (d, *J* = 3.9 Hz, 1H), 3.85 (s, 3H), 4.64 (dd, *J* = 2.0, 3.9 Hz, 1H), 5.75 (dd, *J* = 2.0, 9.0 Hz, 1H), 6.99 (br d, *J* = 9.0 Hz, 1H), 7.20-7.60 (m, 8H), 7.70-7.85 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 53.28, 54.80, 73.20, 126.88, 127.04, 127.94, 128.63, 128.73, 131.76, 134.03, 138.66, 166.85, 173.38; HRMS (FAB) m/z 300.1240 $(M+H)^+$, calcd for $C_{17}H_{18}N_1O_4$ 300.1236.

(4*S*,5*S*)-5-(Methoxycarbonyl)-2,4-diphenyl-2-oxazoline (11). Tf_2O (255 mg, 0.904 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a stirred solution of **10** (180 mg, 0.601 mmol)

and DMAP (220 mg, 1.801 mmol) in CH_2Cl_2 (20 mL) at -30 ^oC under N_2. After being stirred for 1 h at -30 ^oC, the reaction mixture was warmed to room temperature. The reaction mixture was passed through a short silica gel plug (~5 cm^3) and further eluted with EtOAc-hexane (1:1, 30 mL). The combined filtrate was concentrated under reduced pressure, and purification of the residue by flash chromatography on silica gel (hexane-EtOAc, 6:1) afforded **11** (142 mg, 0.504 mmol, 84%) as a white solid. m.p. 92.5-93.5 ^oC; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.21 (s, 3H), 5.39 (d, *J* = 10.8 Hz, 1H), 5.75 (d, *J* = 10.8 Hz, 1H), 7.20-7.60 (m, 8H), 8.05-8.20 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 51.57, 73.51, 81.10, 126.75, 127.76, 128.11, 128.16, 128.46, 128.72, 131.96, 136.90, 164.78, 168.49; HRMS (FAB) m/z 282.1126 $(M+H)^+$, calcd for $C_{17}H_{16}N_1O_3$ 282.1130.

Methyl (2*R*,3*S*)-2-(Acetylthio)-3-(benzoylamino)-3-phenylpropionate (12). Thiolacetic acid (0.3 mL) was added to the **11** (120 mg, 0.427 mmol) in a 6 mL vial at room temperature. The vial was closed tightly with a teflon disk lid and the reaction mixture was heated at 70 ^oC for 12 h and at 80 ^oC for 1 d with occasional swirling. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane-EtOAc, 5:2) to afford **12** (102 mg, 0.285 mmol, 67%) as a off-white solid. m.p. 117-118 ^oC; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.37 (s, 3H), 3.60 (s, 3H), 4.74 (d, *J* = 9.2 Hz, 1H), 5.69 (dd, *J* = 8.8, 9.2 Hz, 1H), 7.01 (br d, *J* = 8.8 Hz, 1H), 7.25-7.60 (m, 8H), 7.65-7.80 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 30.33, 51.16, 52.88, 55.35, 126.96, 127.06, 128.37, 128.61, 128.78, 131.72, 133.71, 138.60, 166.36, 169.06, 195.37; HRMS (FAB) m/z 358.1120 $(M+H)^+$, calcd for $C_{19}H_{20}N_1O_4S_1$ 358.1113.

Methyl (2*R*,3*S*)-3-(Benzoylamino)-2-(methanesulfonyloxy)-3-phenylpropionate (13). MsCl (114 mg, 1.00 mmol) in THF (1 mL) was added dropwise to a stirred solution of **10** (200 mg, 0.668 mmol) and Et_3N (186 μL, 1.334 mmol) in THF (10 mL) at 0 ^oC under N_2. After being stirred for 30 min at 0 ^oC, the reaction mixture was stirred for additional 1 h at room temperature. After removal of solvent under reduced pressure, the residue was suspended in EtOAc (10 mL) and passed through a short silica gel plug (~3 cm^3) and further eluted with EtOAc (50 mL). The combined filtrate was concentrated under reduced pressure, and the crude product was crystallized from EtOAc-hexane to afford **13** (218 mg, 0.578 mmol, 86%) as a white solid. m.p. 127.5-128.5 ^oC; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.81 (s, 3H), 3.83 (s, 3H), 5.35 (d, *J* = 2.7 Hz, 1H), 5.99 (dd, *J* = 2.7, 9.2 Hz, 1H), 6.90 (br d, *J* = 9.2 Hz, 1H), 7.25-7.60 (m, 8H), 7.75-7.90 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 38.67, 53.30, 54.02, 80.22, 126.57, 127.13, 128.58, 128.75, 129.03, 132.07, 133.57, 136.62, 166.92, 167.38; HRMS (FAB) m/z 378.1022 $(M+H)^+$, calcd for $C_{18}H_{20}N_1O_6S_1$ 378.1011.

(4*S*,5*R*)-5-(Methoxycarbonyl)-2,4-diphenyl-2-oxazoline (14). DBU (127 mg, 0.834 mmol) was added to a stirred solution of compound **13** (210 mg, 0.556 mmol) in dry $CHCl_3$ (10 mL) at room temperature, and the resulting solution was heated to reflux for 2 h. After being cooled to room temperature, the reaction mixture was passed through a short silica gel plug (~3 cm^3) and further eluted with EtOAc (50 mL). The combined filtrate was concentrated under reduced pressure, and purification of the residue by flash chromatography on silica gel (hexane-EtOAc, 6:1) afforded **14** (150 mg, 0.533 mmol, 96%) as a colorless oil (*trans*-oxazoline **14** : *cis*-oxazoline **11** = 25 : 1 by ^{1}H NMR analysis). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.87 (s, 3H), 4.92 (d, *J* = 6.4 Hz, 1H), 5.45 (d, *J* = 6.4 Hz, 1H), 7.20-7.60 (m, 8H), 8.05-8.15 (m, 2H); ^{13}C-NMR

($CDCl_3$, 75 MHz) δ 52.74, 74.62, 83.13, 126.46, 126.76, 128.04, 128.45, 128.71, 128.85, 131.93, 141.09, 163.99, 170.63; HRMS (FAB) m/z 282.1125 $(M+H)^+$, calcd for $C_{17}H_{16}N_1O_3$ 282.1130.

Methyl (2*S*,3*S*)- 2-(Acetylthio)-3-(benzoylamino)-3-phenylpropionate (15). Thiolacetic acid (0.3 mL) was added to a solution of **14** (130 mg, 0.462 mmol) in dry THF (0.3 mL) in a 6 mL vial at room temperature. The vial was closed tightly with a teflon disk lid and the reaction mixture was heated at 70 °C for 12 h with occasional swirling. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane-EtOAc, 5:2) to afford **15** (120 mg, 0.336 mmol, 72%) as a sticky oil, which slowly crystallized on standing. m.p. 105-106 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.40 (s, 3H), 3.62 (s, 3H), 4.81 (d, *J* = 4.0 Hz, 1H), 5.65 (dd, *J* = 4.0, 9.2 Hz, 1H), 7.25-7.60 (m, 8H), 7.80-7.95 (m, 2H), 8.12 (br d, *J* = 9.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 30.23, 49.14, 52.84, 54.92, 126.28, 127.11, 128.04, 128.68, 128.74, 131.79, 133.93, 138.51, 166.74, 171.75, 192.50; HRMS (FAB) m/z 358.1112 $(M+H)^+$, calcd for $C_{19}H_{20}N_1O_4S_1$ 358.1113.

Methyl (2*S*,3*S*)-2-Azido-3-(benzoylamino)-3-phenylpropionate (16a). The compound **6** (150 mg, 0.517 mmol) in a 6 mL vial was treated with a solution of 6 *N* HCl-dioxane (4.5 mL, 2:1). The vial was closed tightly with a teflon disk lid and the reaction mixture was heated at 90 °C for 12 h with occasional swirling. The reaction mixture was transferred into a single-necked round bottom flask (25 mL), and solvent was evaporated to dryness. The resulting white solid was treated with 0.5*M* HCl in MeOH (15 mL) and heated to reflux for 2.5 h. After removal of solvent under reduced pressure, the residue was re-dissolved in fresh MeOH (2 x 15 mL) and re-evaporated. To this residue, dry CH_2Cl_2 (15 mL) was added and cooled to 0 °C. To this suspension was added Et_3N (288 μL, 2.067 mmol) in CH_2Cl_2 (1 mL) followed by BzCl (80 mg, 0.568 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was stirred for 1 h at 0 °C and for 1 h at room temperature. The reaction mixture was passed through a short silica gel plug (~3 cm^3) and further eluted with EtOAc (50 mL). The combined filtrate was concentrated under reduced pressure, and purification of the residue by flash chromatography on silica gel (hexane-EtOAc, 3:1) afforded **16a** as a white solid. This was further purified by recrystallization (EtOAc-hexane) to afford **16a** (120 mg, 0.370 mmol, 72%) as a white crystalline solid. m.p. 123-124 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.71 (s, 3H), 4.65 (d, *J* = 4.7 Hz, 1H), 5.75 (dd, *J* = 4.7, 8.2 Hz, 1H), 7.09 (br d, *J* = 8.2 Hz, 1H), 7.28- 7.60 (m, 8H), 7.75–7.90 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 52.80, 54.42, 64.61, 127.10, 127.31, 128.65, 128.71, 128.90, 131.94, 133.80, 136.51, 166.82, 168.70; HRMS (FAB) m/z 325.1298 $(M+H)^+$, calcd for $C_{17}H_{17}N_4O_3$ 325.1301.

Methyl (2*S*,3*S*)-2-Azido-3-(*tert*-butoxycarbonylamino)-3-phenylpropionate (16b). The compound **6** (163 mg, 0.561 mmol) in a 6 mL vial was treated with a solution of 6 *N* HCl-dioxane (4.5 mL, 2:1). The vial was closed tightly with a teflon disk lid and the reaction mixture was heated at 90 °C for 12 h with occasional swirling. The reaction mixture was transferred into a single-necked round bottom flask (25 mL), and solvent was evaporated to dryness. The resulting white solid was treated with 0.5 *M* HCl in MeOH (15 mL) and heated to reflux for 2.5 h. After removal of solvent under reduced pressure, the residue was re-dissolved in fresh MeOH (2 x 15 mL) and re-evaptated. To this residue, dry CH_2Cl_2 (10 mL) was added and cooled to 0 °C. To this suspension was added Et_3N (196 μL, 1.406 mmol) in CH_2Cl_2 (1 mL) followed by Boc_2O (184 mg, 0.842 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was stirred for 1 h at

0 ^{o}C and for 24 h at room temperature. The reaction mixture was passed through a short silica gel plug (~3 cm^3) and further eluted with EtOAc (50 mL). The combined filtrate was concentrated under reduced pressure, and purification of the residue by flash chromatography on silica gel (hexane-EtOAc, 6:1) afforded **16b** as a white solid. This was further purified by recrystallization (hexane) to afford **16b** (129 mg, 0.403 mmol, 72%) as white needles. m.p. 93-94 ^{o}C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.44 (s, 9H), 3.69 (s, 3H), 4.50 (br d, *J* = 4.1 Hz, 1H), 5.23 (br s, 1H), 5.38 (br s, 1H), 7.20-7.40 (m, 5H); ^{13}C-NMR($CDCl_3$, 75MHz) δ 28.32, 52.66, 55.67, 65.22, 80.42, 127.23, 128.51, 128.75, 136.83, 154.78, 168.48; HRMS (FAB) m/z 321.1564 $(M+H)^+$, calcd for $C_{15}H_{21}N_4O_4$ 321.1562.

Methyl (2*S*,3*S*)-2-Amino-3-(benzoylamino)-3-phenylpropionate (17a). 10% Pd/C catalyst (20 mg) was added to a stirred solution of **16a** (100 mg, 0.303 mmol) in EtOAc (12 mL). The mixture was hydrogenated at atmospheric H_2 (balloon) at room temperature for 30 h and filtered through short silica gel plug (~3 cm^3). After removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane-EtOAc, 1:5) to afford **17a** (88 mg, 0.295 mmol, 96%) as a white solid. m.p. 114.5-117 ^{o}C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.75 (br s, 2H), 3.70 (s, 3H), 3.94 (d, *J* = 4.4 Hz, 1H), 5.65 (dd, *J* = 4.4, 8.4 Hz, 1H), 7.20–7.60 (m, 8H), 7.69 (br d, *J* = 8.4 Hz, 1H), 7.80-7.95 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 52.16, 54.76, 58.23, 126.85, 127.07, 128.08, 128.59, 128.62, 131.62, 134.26, 137.46, 166.35, 173.50; HRMS (FAB) m/z 299.1392 $(M+H)^+$, calcd for $C_{17}H_{19}N_2O_3$ 299.1396.

Methyl (2*S*,3*S*)-2-Amino-3-(*tert*-butoxycarbonylamino)-3-phenylpropionate (17b). 10% Pd/C catalyst (22 mg) was added to a stirred solution of **16b** (110 mg, 0.343 mmol) in EtOAc (10 mL). The mixture was hydrogenated at atmospheric H_2 (balloon) at room temperature for 24 h and filtered through short silica gel plug (~3 cm^3). After removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane-EtOAc, 1:1) to afford **17b** (98 mg, 0.333 mmol, 97%) as a white solid. m.p. 97-98 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz, 50 ^{o}C) δ 1.40 (s, 9H), 1.47 (br s, 2H), 3.66 (s, 3H), 3.81 (d, *J* = 4.6 Hz, 1H), 5.08 (br s, 1H), 5.76 (br d, *J* = 6.8 Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.29, 51.96, 56.07, 58.51, 79.59, 126.70, 127.80, 128.42, 137.88, 155.01, 173.58; HRMS (FAB) m/z 295.1657 $(M+H)^+$, calcd for $C_{15}H_{23}N_2O_4$ 295.1658.