Supporting Information

Dynamic Kinetic Resolution Catalyzed by Ir-Axially Chiral Phosphine Catalyst: Asymmetric Synthesis of *Anti* Aromatic β -Hydroxy- α -amino Acid Esters

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Experimental Procedures and Characterization of the Products

General: Melting points were uncorrected. Infrared spectra were recorded on a JASCO FT/IR-230 Fourier transform infrared spectrometer. Optical rotations were measured on a JASCO P-1020 and DIP-140 polarimeters. NMR spectra were recorded on a JEOL JNM GSX 400A and JNM ECP400 spectrometers, operating at 400 MHz for ^1H -NMR and 100 MHz for ^{13}C -NMR. Chemical shifts are recorded in ppm from tetramethylsilane or chloroform as an internal standard. Mass spectra were obtained on a JEOL HX-110A spectrometer. The enantiomeric excess (ee) was determined by HPLC analysis. Reagents and solvent were purified by standard procedures.

Experimental Procedures for the α -Amino- β -keto Esters

General procedure of preparation of 2-*tert*-butoxycarbonylamino-3-oxo esters¹⁾

A solution of *t*-BuOK (1.12 g, 10 mmol) in THF (7 mL) was cooled to -70 °C under argon, and a solution of the Schiff base (10 mmol) in THF (4 mL) was added while maintaining the reaction temperature at -70 °C. After 30 min, this red solution of the Schiff base anion was added via cannula to a mechanically stirred solution of the acyl chloride (10 mmol) in THF (3 mL) at -70 °C. Half an hour after completion of addition, the reaction was quenched with aqueous HCl solution (10 mL, 3 N in H₂O), and the reaction mixture was concentrated to dryness under reduced pressure (<40 °C). Water was added to the residue and benzophenone was extracted with diethyl ether. The aqueous solution was concentrated to dryness under reduced pressure, stripped twice from methanol, the residue re-dissolved in anhydrous methanol and removal of white solids by filtration. The clear filtrate was concentrated *in vacuo* and the residue was used for the next step without further purification.

The residue was dissolved in THF (20 mL), and Boc₂O (10 mmol) and Et₃N (10 mmol) were added at 0 °C. After stirring the mixture for 3 h at 23 °C, the reaction was quenched with water and diluted with ethyl acetate (100 mL). The organic layer was washed with aqueous KHSO₄ (1N in

H₂O), saturated aqueous NaHCO₃, and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/4) to give the 2-*tert*-butoxycarbonylamino-3-oxo ester in moderate to excellent yield.

Methyl 2-*tert*-butoxycarbonylamino-3-oxo-3-phenylpropionate¹⁾

colorless solids: mp 95-96 °C (ethy acetate-hexane); IR (KBr) 3333, 2954, 1763, 1690, 1680, 1534, 1350, 1294, 1216, 1167, 1063 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.47 (s, 9H), 3.73 (s, 3H), 5.60-6.00 (m, 2H), 7.52 (dd, *J* = 7.2, 7.6 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 8.11 (d, *J* = 7.6, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 28.2, 53.1, 59.1, 80.6, 128.8, 129.4, 134.1, 134.3, 154.9, 167.6, 191.7. Anal. calcd for C₁₅H₁₉NO₅: C 61.42; H 6.53; N 4.78. Found: C 61.25; H 6.44; N 4.65.

Methyl 3-(4-benzyloxyphenyl)-2-*tert*-butoxycarbonylamino-3-oxopropionate

colorless solids: mp 100-101 °C (ethy acetate-hexane); IR (KBr) 3292, 2983, 1762, 1689, 1676, 1598, 1597, 1571, 1509, 1312, 1248, 1202, 1175, 996, 977, 839 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.46 (s, 9H), 3.72 (s, 3H), 5.15 (s, 2H), 5.90-6.00 (brs, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 7.20-7.45 (m, 5H), 8.10 (d, *J* = 8.8 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 28.2, 53.0, 58.8, 70.2, 80.5, 114.8, 127.1, 127.5, 128.3, 128.7, 132.0, 135.8, 155.0, 163.7, 167.9, 189.8; LR-FABMS (NBA) *m/z*: 400 (M+H⁺). Anal. calcd for C₂₂H₂₅NO₆: C 66.15; H 6.31; N 3.51. Found: C 66.00; H 6.33; N 3.47.

Methyl 3-(benzo[1,3]dioxol-5-yl)-2-*tert*-butoxycarbonylamino-3-oxopropionate

colorless solids: mp 103-104 °C (ethy acetate-hexane); IR (KBr) 3328, 2963, 1768, 1687, 1667, 1602, 1536, 1500, 1589, 1445, 1370, 1350, 1288, 1270, 1214, 1161, 1112, 11061, 1038 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.45 (s, 9H), 3.73 (s, 3H), 5.85-5.90 (brs, 2H), 6.08 (s, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 1.6 Hz, 2H), 7.78 (dd, *J* = 1.6, 8.4 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 28.2, 53.1, 58.8, 80.6, 102.1, 108.1, 108.8, 126.6, 128.8, 148.4, 153.0, 155.0, 167.8, 189.6. Anal. calcd for C₁₆H₁₉NO₇: C 56.97; H 5.68; N 4.15. Found: C 56.78; H 5.59; N 4.00.

Methyl 2-*tert*-butoxycarbonylamino-3-oxo-3-*p*-tolylpropionate

colorless solids: mp 104-105 °C (ethy acetate-hexane); IR (KBr) 3325, 2956, 1765, 1678, 1606, 1535, 1354, 1294, 1216, 1168, 1065, 830, 739 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.43 (s, 9H), 2.41 (s, 3H), 3.69 (s, 3H), 5.9-6.0 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 21.8, 28.2, 53.1, 59.0, 80.6, 129.5, 129.6, 131.6, 145.6, 155.0, 167.8, 191.1. Anal. calcd for C₁₆H₂₁NO₅: C 62.53; H 6.89; N 4.56. Found: C 62.14; H 6.79; N 4.45.

Methyl 2-*tert*-butoxycarbonylamino-3-oxo-3-*m*-tolylpropionate

colorless solids: mp 92-93 °C (ethy acetate-hexane); IR (KBr) 3337, 2983, 2952, 1760, 1681, 1528, 1349, 1292, 1211, 1161 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.46 (s, 9H), 2.43 (s, 3H), 3.71 (s, 3H), 5.90 (brd, *J* = 7.8 Hz, 1H), 5.96 (brd, *J* = 7.8 Hz, 1H), 7.3-7.5 (m, 2H), 7.90 (d, *J* = 7.2 Hz, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ 21.3, 28.2, 53.1, 59.1, 80.6, 126.7, 128.6, 129.9, 134.1, 135.2, 138.7, 155.0, 167.7, 191.9. Anal. calcd for C₁₆H₂₁NO₅: C 62.53; H 6.89; N 4.56. Found: C 62.53; H 6.83; N 4.50.

Methyl 2-*tert*-butoxycarbonylamino-3-(naphthalen-2-yl)-3-oxopropionate

colorless solids: mp 119.5-120.5 °C (ethy acetate-hexane); IR (KBr) 3435, 2977, 1757, 1707, 1675, 1626, 1488, 1435, 1280, 1154, 1059, 1002, 932, 854, 826, 758 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.47 (s, 9H), 3.72 (s, 3H), 5.97 (brd, *J* = 8.0 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 7.05-8.15 (m, 4H), 8.71 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ 28.2, 53.1, 59.1, 80.7, 124.3, 127.0, 127.8, 128.7, 129.2, 130.0, 131.4, 132.1, 132.3, 136.1, 155.0, 167.8, 191.7. Anal. calcd for C₁₉H₂₁NO₅: C 66.46; H 6.16; N 4.08. Found: C 66.21; H 6.12; N 4.04.

Methyl 3-(4-bromophenyl)-2-*tert*-butoxycarbonylamino-3-oxo-propionate

colorless solids: mp 98-99 °C (hexane); IR (KBr) 3326, 1768, 1676, 1586, 1533, 1353, 1295, 1215, 1164 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 1.45 (s, 9H), 3.73 (s, 3H), 5.80-5.95 (m, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.8 Hz, 2H); ^{13}C -NMR (100 MHz, CDCl_3) δ 28.1, 53.2, 59.0, 80.8, 129.8, 130.8, 132.1, 132.9, 154.9, 167.3, 191.0. Anal. calcd for $\text{C}_{15}\text{H}_{18}\text{BrNO}_5 \cdot 1/4 \text{C}_6\text{H}_{12}$: C 50.64; H 5.58; N 3.53. Found: C 50.67; H 5.74; N 3.27.

Methyl 2-*tert*-butoxycarbonylamino-3-oxo-3-(thiophen-2-yl)-propionate

colorless solids: mp 100-101 °C (ethy acetate-hexane); IR (KBr): 3340, 2952, 1762, 1690, 1659, 1530, 1412, 1360, 1346, 1299, 1058, 1029, 743 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 1.49 (s, 9H), 3.79 (s, 3H), 5.81 (brd, J = 8.0 Hz, 1H), 5.92 (brd, J = 8.0 Hz, 2H), 7.23 (dd, J = 4.4, 4.8 Hz, 1H), 7.80 (dd, J = 0.8, 4.8 Hz, 1H), 8.09 (d, J = 4.4 Hz, 1H); ^{13}C -NMR (100 MHz, CDCl_3) δ 28.2, 53.2, 60.0, 80.8, 128.6, 135.1, 136.1, 140.9, 154.9, 167.4, 184.0; LR-FABMS (NBA) m/z : 300 ($\text{M}+\text{H}^+$). Anal. calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_5\text{S}$: C 52.16; H 5.72; N 4.68. Found: C 52.05; H 5.60; N 4.64.

Methyl 2-*tert*-butoxycarbonylamino-3-(furan-2-yl)-3-oxopropionate

colorless solids: mp 103-104 °C (ethy acetate-hexane); IR (KBr) 3311, 3131, 2982, 1762, 1686, 1671, 1535, 1466, 1396, 1343, 1308, 1165, 1051, 1019, 773 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 1.46 (s, 9H), 3.76 (s, 3H), 5.73 (brd, J = 8.0 Hz, 1H), 5.84 (brd, J = 8.0 Hz, 2H), 6.62 (dd, J = 2.0, 4.0 Hz, 1H), 7.50 (d, J = 4.0 Hz, 1H), 7.71 (d, J = 2.0 Hz, 1H); ^{13}C -NMR (100 MHz, CDCl_3) δ 28.2, 53.2, 59.1, 80.7, 112.9, 121.0, 148.3, 150.3, 154.9, 167.3, 179.8. Anal. calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_6$: C 55.12; H 6.05; N 4.94. Found: C 54.89; H 6.08; N 4.91.

Methyl 3-(4-benzyloxyphenyl-3-chloro)-2-*tert*-butoxycarbonylamino-3-oxopropionate

colorless solids: IR (KBr) 3376, 1755, 1682, 1592, 1525, 1496, 1165 cm^{-1} ; ^1H -NMR (400 MHz,

CDCl₃) δ 1.45 (s, 9H), 3.72 (s, 3H), 5.26 (s, 2H), 5.80-5.95 (m, 2H), 7.04 (d, J = 8.4 Hz, 1H), 7.33-7.48 (m, 5H), 8.01 (d, J = 8.8 Hz, 1H), 8.16 (d, J = 2.0 Hz, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ 28.2, 53.2, 58.8, 70.9, 80.7, 112.7, 123.9, 127.0, 127.7, 128.4, 128.8, 130.1, 131.7, 135.3, 154.9, 158.9, 167.5, 189.3. Anal. calcd for C₂₂H₂₄ClNO₆: C 60.90; H 5.58; N 3.23. Found: C 61.06; H 5.57; N 3.15.

General procedure of preparation of hydrochloric salt

To a solution of 2-*tert*-butoxycarbonylamino-3-oxo ester (5.5 mmol) in MeOH (5 mL) at 0 °C was added dropwise HCl (10 mL, 4 N in 1,4-dioxane). After stirring for 1 d at 23 °C, the mixture was concentrated *in vacuo*. The residue was triturated with diethyl ether and collected by filtration to afford the α -amino- β -keto ester hydrochloride.

Methyl 2-amino-3-oxo-3-phenylpropionate hydrochloride ²⁾

99% yield, colorless solids: IR (KBr) 3436, 3366, 2974, 1756, 1688, 1502, 1277, 1223, 1147, 943, 881, 750, 686 cm⁻¹; ¹H-NMR (400 MHz CD₃OD) δ 3.77 (s, 3H), 6.19 (s, 1H), 7.5 - 7.65 (m, 2H), 7.7-7.8 (m, 1H), 8.15-8.19 (m, 2H); ¹³C-NMR (100 MHz, CD₃OD) δ 54.6, 130.1, 131.0, 134.9, 136.3, 165.4, 190.0; LR-FABMS (NBA) m/z : 194 (M⁺-Cl).

Methyl 2-amino-3-(4-benzyloxyphenyl)-3-oxopropionate hydrochloride

99% yield, colorless solids: mp 163-170 °C (decomp, ethyl acetate-MeOH); IR (KBr): 3445, 2969, 1759, 1685, 1602, 1574, 1509, 1276, 1254, 1222, 1176 1143, 1118, 1075 cm⁻¹; ¹H-NMR (400 MHz, CD₃OD) δ 3.78 (s, 3H), 5.23 (s, 2H), 6.04 (s, 1H), 7.13-7.22 (m, 2H), 7.31-7.50 (m, 5H), 8.14 (d, J = 9.2 Hz, 2H); ¹³C-NMR (100 MHz, CD₃OD) δ 54.5, 58.4, 71.5, 116.2, 127.8, 128.7, 129.3, 129.7, 133.6, 137.7, 165.8, 166.0, 187.9; LR-FABMS (NBA) m/z : 300 (M⁺-Cl). Anal. calcd for C₁₇H₁₈ClNO₄·1/3H₂O: C 59.74; H 5.50; N 4.10. Found: C 59.99; H 5.46; N 4.02.

Methyl 2-amino-3-(benzo[1,3]dioxol-5-yl)-3-oxopropionate hydrochloride ²⁾

96% yield, colorless solids: IR (KBr) 3418, 2980, 1751, 1678, 1604, 1502, 1455, 1297, 1270, 1116, 1033 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz CD_3OD) δ 3.79 (s, 3H), 5.98 (s, 1H), 6.13 (s, 2H), 7.02 (d, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 1.6$ Hz, 1H), 7.83 (dd, $J = 1.6, 8.4$ Hz, 1H); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ 54.6, 58.5, 104.1, 109.3, 109.6, 128.8, 129.4, 150.0, 155.3, 165.6, 187.7; LR-FABMS (NBA) m/z : 238 ($\text{M}^+ - \text{Cl}$).

Methyl 2-amino-3-oxo-3-p-tolylpropionate hydrochloride ³⁾

94% yield, colorless solids: IR (KBr) 2995, 2826, 2626, 1739, 1685, 1604, 1505, 1434, 1276, 1220, 1179, 1074, 968, 942, 863 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz CD_3OD) δ 2.47 (s, 3H), 3.77 (s, 3H), 6.09 (s, 1H), 7.42 (d, $J = 8.0$ Hz, 2H), 8.05 (d, $J = 8.0$ Hz, 2H); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ 21.8, 54.5, 58.7, 130.7, 131.2, 132.4, 148, 0, 165.6, 189.3; LR-FABMS (NBA) m/z : 208 ($\text{M}^+ - \text{Cl}$).

Methyl 2-amino-3-oxo-3-m-tolylpropionate hydrochloride

97% yield, colorless solids, mp 163-165 $^{\circ}\text{C}$ (decomp., ethy acetate-MeOH); IR (KBr) 3004, 2813, 2626, 1989, 1737, 1685, 1434, 1274, 1228, 1167, 1072, 1030, 948, 889, 865, 785, 685 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ 2.45 (s, 3H), 3.81 (s, 3H), 6.11 (s, 1H), 7.4-7.6 (m, 2H), 7.9-8.0 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CD_3OD) δ 21.3, 54.6, 58.8, 128.3, 130.0, 131.2, 135.0, 137.0, 140.3, 165.5, 190.1. Anal. calcd for $\text{C}_{11}\text{H}_{14}\text{ClNO}_3$: C 54.22; H 5.79; N 5.75. Found: C 54.19; H 5.84; N 5.62.

Methyl 2-amino-3-(naphthalen-2-yl)-3-oxopropionate hydrochloride ²⁾

91% yield, colorless solids: IR (KBr) 3440, 2819, 1739, 1688, 1622, 1594, 1502, 1434, 1280, 1236, 1174, 1008, 937, 811, 760 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CD_3OD) δ 3.75 (s, 3H), 6.30 (s, 1H), 7.6-7.75

(m, 2H), 7.9-8.15 (m, 4H), 8.82 (s, 1H); ^{13}C -NMR (100 MHz, CD_3OD) δ 54.6, 58.7, 125.0, 128.5, 129.0, 129.9, 131.0, 131.2, 132.2, 133.8, 134.3, 137.8, 165.6, 189.9. Anal. calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_3$: C 60.11; H 5.04; N 5.01. Found: C 59.95; H 5.19; N 4.92.

Methyl 2-amino-3-(4-bromo-phenyl)-3-oxopropionate hydrochloride

97% yield, colorless solids: mp 187-193 °C (decomp., ethy acetate-MeOH); IR (KBr) 2810, 1738, 1689, 1586, 1497, 1433, 1405, 1275, 1213, 1176, 1134, 1175, 966, 940, 864, 816, 764, 676 cm^{-1} ; ^1H -NMR (400 MHz, CD_3OD) δ 3.78 (s, 3H), 6.11 (s, 1H), 7.79 (m, 2H), 8.05 (m, 2H); ^{13}C -NMR (100 MHz, CD_3OD) δ 547, 589, 131.5, 132.6, 133.4, 133.9, 165.2, 189.3. Anal. calcd for $\text{C}_{10}\text{H}_{11}\text{BrClNO}_3$: C 38.93; H 3.59; N 4.54. Found: C 38.85; H 3.60; N 4.37.

Methyl 2-amino-3-(furan-2-yl)-3-oxopropionate hydrochloride ³⁾

99% yield, colorless solids: IR (KBr) 3430, 2973, 2637, 1752, 1679, 1590, 1570, 1504, 1464, 1404, 1285, 1252, 1155, 1088, 1079, 1036, 1023, 991, 951, 910, 876, 841, 769 cm^{-1} ; ^1H -NMR (400 MHz, CD_3OD) δ 3.82 (s, 3H), 5.78 (s, 1H), 6.80 (dd, J = 1.6, 4.0 Hz, 1H), 7.71 (d, J = 4.0 Hz, 1H), 8.00 (d, J = 1.6 Hz, 1H); ^{13}C -NMR (100 MHz, CD_3OD) δ 54.7, 58.4, 114.6, 124.1, 151.2, 151.3, 165.5, 177.1; LR-FABMS (NBA) m/z : 184 ($\text{M}^+ - \text{Cl}$).

Methyl 2-amino-3-oxo-3-(thiophen-2-yl)-propionate hydrochloride ³⁾

99% yield, colorless solids: IR (KBr): 3420, 2972, 1752, 1661, 1507, 1416, 1278, 1227, 1151, 1088, 1056, 735 cm^{-1} ; ^1H -NMR (400 MHz, CD_3OD) δ 3.83 (s, 3H), 5.94 (s, 1H), 7.33 (dd, J = 4.0, 4.8 Hz, 1H), 8.10 (d, J = 4.2 Hz, 1H), 8.22 (d, J = 4.0 Hz, 1H); ^{13}C -NMR (100 MHz, CD_3OD) δ 54.7, 59.2, 130.2, 138.4, 139.2, 141.3, 165.5, 182.0; LR-FABMS (NBA) m/z : 200 ($\text{M}^+ - \text{Cl}$).

Methyl 2-amino-3-(4-benzyloxyphenyl-3-chloro)-3-oxopropionate hydrochloride

95% yield, colorless solids: IR (KBr): 2839, 1739, 1685, 1592, 1506, 1284, 1215 cm^{-1} ; ^1H -NMR (400 MHz, CD_3OD) δ 3.78 (s, 3H), 5.33 (s, 2H), 6.11 (s, 1H), 7.32-7.50 (m, 6H), 8.13 (dd, J = 2.0, 8.8 Hz, 1H), 8.21 (d, J = 2.0 Hz, 1H); ^{13}C -NMR (100 MHz, CD_3OD) δ 54.6, 58.5, 72.2, 114.5, 124.7, 128.4, 128.5, 129.4, 129.7, 132.2, 132.8, 137.2, 161.0, 165.5, 187.5. Anal. calcd for $\text{C}_{10}\text{H}_{11}\text{BrClNO}_3$: C 55.15; H 4.63; N 3.78. Found: C 55.12; H 4.66; N 3.68.

General procedure for the anti-selective hydrogenation through dynamic kinetic resolution

Anti-selective hydrogenation

A mixture of $[\text{Ir}(\text{cod})\text{Cl}]_2$ (2.5 mg, 0.0037 mmol), (*S*)-MeO-BIPHEP (5.8 mg, 0.01 mmol), and NaI (2.3 mg, 0.015 mmol) in CH_2Cl_2 (1.0 mL) was degassed by three freeze-thaw cycles. The mixture was stirred for 10 min at 23 $^\circ\text{C}$ under argon atmosphere. The resulting yellow solution was concentrated and dried *in vacuo*. α -Amino- β -keto ester hydrochloride (0.25 mmol), acetic acid (1.2 mL) and sodium acetate (20.5 mg, 0.25 mmol) was added to the obtained yellow Ir catalyst and the resulting mixture was degassed by three freeze-thaw cycles. The mixture was stirred at 27-30 $^\circ\text{C}$ under hydrogen pressure (100 atm) for 96 h. The reaction mixture was concentrated to dryness under reduced pressure below 40 $^\circ\text{C}$. The obtained residue was dissolved in MeOH and the mixture was concentrated *in vacuo*, and this cycle was repeated five times. The residue was used for next step without any purification.

Benzoyl protection

To a mixture of the above residue in THF (3 mL) and H_2O (0.3 mL) at 0 $^\circ\text{C}$ was added dropwise benzoyl chloride (35.2 mg, 0.25 mmol) and TEA (75.9 mg, 0.75 mmol). After stirring for 1 h at 23 $^\circ\text{C}$, the reaction mixture was diluted with water and ethyl acetate. The organic layer was washed with aqueous hydrochloric acid (1 N in H_2O), saturated aqueous NaHCO_3 and brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give α -benzoylamino- β -hydroxy ester.

Boc protection

To a mixture of the above residue in 1,4-dioxane (1.5 mL) and H_2O (0.15 mL) at 0 $^\circ\text{C}$ was added $(\text{Boc})_2\text{O}$ (43.6 mg, 0.25 mmol) and NaHCO_3 (63 mg, 0.75 mmol). After stirring for 1 h at 23 $^\circ\text{C}$,

the reaction mixture was diluted with ethyl acetate. The organic layer was washed with aqueous KHSO₄ (1 N in H₂O), saturated aqueous NaHCO₃ and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give α -*tert*-butoxycarbonylamino- β -hydroxy ester.

Methyl (2*S*, 3*S*)-2-benzoylamino-3-hydroxy-3-phenylpropionate⁴⁾

colorless solids, 82 % yield, anti:syn = >99:1 (judged by ¹H-NMR), 90%ee; mp 130.5-131.5 °C (ethyl acetate-hexane); [α]_D²⁵ +127.8 (c 0.93, CHCl₃) for 90% ee; IR (KBr) 3338, 1744, 1644, 1525, 1229, 1173, 693 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 3.79 (s, 3H), 4.56 (d, *J* = 5.6 Hz, 1H), 5.24 (dd, *J* = 3.6, 6.8 Hz, 1H), 5.40 (dd, *J* = 3.6, 5.6 Hz, 1H), 6.87 (brd, 1H), 7.2-7.4 (m, 5H), 7.4-7.5 (m, 2H), 7.5-7.6 (m, 1H), 7.7-7.8 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 52.6, 59.4, 75.1, 125.9, 127.1, 128.0, 128.3, 128.6, 132.1, 133.0, 139.1; LR-FABMASS (NBA) *m/z*: 300 (M+H⁺). Anal. calcd for C₁₇H₁₇NO₄: C 68.21; H 5.72; N 4.68. Found: C 68.18; H 5.64; N 4.55. The enantiomeric purity was determined to be 90%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 85/15, flow rate = 1.0 mL/min). Retention time: 8.6 min for (2*R*,3*R*), 12.0 min for (2*S*,3*S*).

Methyl (2*S*, 3*S*)-2-benzoylamino-3-(4-benzyloxy-phenyl)-3-hydroxypropionate

colorless solids, 88% yield, anti:syn = >99:1 (judged by ¹H-NMR), 95%ee; [α]_D²³ -66.7 (c 0.97, CHCl₃) for 95% ee; IR (KBr) 3428, 3374, 1720, 1695, 1524, 1239, 1173, 1026 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.43 (s, 9H), 3.70 (s, 3H), 3.81 (brs, 1H), 4.69 (brs, 1H), 5.05 (s, 2H), 5.13 (brs, 1H), 5.25 (brd, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.30-7.45 (m, 5H); ¹³C-NMR (100 MHz, CDCl₃) δ 28.2, 52.5, 59.6, 69.9, 74.7, 80.6, 114.6, 127.3, 127.5, 128.0, 131.4, 136.8, 156.3, 158.6, 170.4. Anal. calcd for C₂₂H₂₇NO₆: C 65.82; H 6.78; N 3.49. Found: C 65.78; H 6.74; N 3.45. The enantiomeric purity was determined to be 95%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 75/25, flow rate = 0.5 mL/min). Retention time: 24.3 min for (2*R*,3*R*), 28.0 min for (2*S*,3*S*).

Methyl (2*S*, 3*S*)-3-(benzo[1,3]dioxol-5-yl)-2-benzoylamino-3-hydroxypropionate⁶⁾

colorless solids. 80% yield, anti:syn = 98:2 (judged by $^1\text{H-NMR}$), 93%ee; mp 113-114.5 °C (ethyl acetate-hexane); $[\alpha]_{\text{D}}^{23} +111.3$ (c 0.96, CHCl_3) for 93% ee; IR(KBr) 3404, 2896, 1743, 1644, 1529, 1504, 1488, 1443, 1246, 1036 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.80 (s, 3H), 4.57 (d, J = 5.2 Hz, 1H), 5.19 (dd, J = 3.6, 6.8 Hz, 1H), 5.31 (m, 1H), 5.94 (s, 2H), 6.67-6.80 (m, 3H), 6.89 (brd, J = 6.8, 1H), 7.46 (dd, J = 7.2, 8.0 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.77 (dd, J = 1.6, 8.0 Hz, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 52.8, 59.5, 75.2, 101.1, 106.5, 108.1, 119.4, 127.2, 128.7, 132.2, 132.9, 133.0, 147.4, 147.8, 168.8, 169.9. Anal. calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_6$: C 62.97; H 4.99; N 4.08. Found: C 62.63; H 5.23; N 3.83. The enantiomeric purity was determined to be 93%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 75/25, flow rate = 0.5 mL/min). Retention time: 16.5 min for (2*R*,3*R*), 22.4 min for (2*S*,3*S*).

Methyl (2*S*, 3*S*)-2-benzoylamino-3-hydroxy-3-*p*-tolylpropionate

colorless solid; 81% yield, anti:syn = >99:1 (judged by $^1\text{H-NMR}$), 94%ee; mp 122-123 °C (ethyl acetate-hexane); $[\alpha]_{\text{D}}^{25} +124$ (c 0.93, CHCl_3) for 94% ee; IR (KBr) 3319, 1741, 1645, 1539, 1324, 1264, 1054, 1023, 821, 709, 692, 535 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.33 (s, 3H), 3.78 (s, 3H), 4.45 (d, J = 5.6 Hz, 1H), 5.23 (dd, J = 3.2, 6.8 Hz, 1H), 5.35 (dd, J = 3.2, 5.6 Hz, 1H), 6.87 (brd, J = 6.8 Hz, 1H), 7.1-7.2 (m, 4H), 7.4-7.6 (m, 3H), 7.7-7.8 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 21.1, 52.7, 59.5, 75.2, 125.8, 127.2, 128.7, 129.0, 132.1, 133.1, 136.0, 137.8, 168.6, 170.0; LR-FABMASS (NBA) m/z : 314 ($\text{M}+\text{H}^+$). Anal. calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_4$: C 68.99; H 6.11; N 4.47. Found: C 68.83; H 6.17; N 4.38. The enantiomeric purity was determined to be 94%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 75/25, flow rate = 0.5 mL/min). Retention time: 12.6 min for (2*R*,3*R*), 16.2 min for (2*S*,3*S*).

Methyl (2*S*, 3*S*)-2-benzoylamino-3-hydroxy-3-*m*-tolylpropionate

colorless solid; 93% yield, anti:syn = >99:1 (judged by $^1\text{H-NMR}$), 87%ee; mp 111-112 °C (diethyl ether-hexane); $[\alpha]_{\text{D}}^{24} +110.9$ (c 0.99, CHCl_3) for 87% ee; IR (KBr) 3304, 1747, 1719, 1645, 1541,

1337, 1273, 1219, 1203, 1043, 692 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.31 (s, 3H), 3.96 (s, 3H), 4.42 (d, $J = 5.6$ Hz, 1H), 5.21 (dd, $J = 4.0, 6.8$ Hz, 1H), 5.34 (dd, $J = 4.0, 5.6$ Hz, 1H), 6.87 (brd, $J = 6.8$ Hz, 1H), 7.00-7.11 (m, 3H), 7.19-7.25 (m, 1H), 7.42-7.56 (m, 3H), 7.73-7.76 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 21.4, 52.6, 59.4, 75.2, 122.9, 126.6, 127.1, 128.2, 128.6, 128.9, 132.1, 133.2, 138.0, 139.0, 168.6, 170.0. Anal. calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_4$: C 68.99; H 6.11; N 4.47. Found: C 68.71; H 6.01; N 4.37. The enantiomeric purity was determined to be 87%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 85/15, flow rate = 0.5 mL/min). Retention time: 16.9 min for (2*R*,3*R*), 20.9 min for (2*S*,3*S*).

Methyl (2*S*, 3*S*)-2-benzoylamino-3-hydroxy-3-(naphthalen-2-yl)-propionate

colorless solid; 95% yield, anti:syn = 98:2 (judged by $^1\text{H-NMR}$), 86%ee; mp 134-136 $^{\circ}\text{C}$ (ethyl acetate-hexane); $[\alpha]_{\text{D}}^{23} +102.6$ (c 1.02, CHCl_3) for 86% ee; IR (KBr) 3333, 1741, 1646, 1523, 1488, 1437, 1363, 1217, 712, 479 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.77 (s, 3H), 4.68 (brd, $J = 6.0$ Hz, 1H), 5.32 (dd, $J = 3.2, 6.8$ Hz, 1H), 5.50-5.58 (m, 1H), 6.92 (brd, $J = 6.8$ Hz, 1H), 7.37-7.55 (m, 6H), 7.73-7.84 (m, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 52.7, 59.6, 75.4, 123.7, 125.1, 126.1, 126.2, 127.2, 128.0, 128.1, 128.7, 132.2, 133.0, 133.1, 133.2, 136.6, 168.7, 169.9; LR-FABMS (NBA) m/z : 350 ($\text{M}+\text{H}^+$). Anal. calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_4$: C 72.19; H 5.48; N 4.01. Found: C 71.92; H 5.78; N 4.27. The enantiomeric purity was determined to be 86%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 75/25, flow rate = 0.5 mL/min). Retention time: 16.5 min for (2*R*,3*R*), 20.1 min for (2*S*,3*S*).

Methyl (2*S*, 3*S*)-2-benzoylamino-3-(4-bromo-phenyl)-3-hydroxypropionate

colorless solid; 87% yield, anti:syn = >99:1 (judged by $^1\text{H-NMR}$), 75%ee; mp 148-149.5 $^{\circ}\text{C}$ (ethyl acetate-hexane); $[\alpha]_{\text{D}}^{25} +97.0$ (c 0.99, CHCl_3) for 75% ee; IR (KBr) 3373, 1742, 1641, 1523, 1488, 1205, 1079, 723, 712, 565 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.81 (s, 3H), 4.81 (d, $J = 5.6$ Hz, 1H), 5.21 (dd, $J = 2.8, 6.4$ Hz, 1H), 5.37 (dd, $J = 2.8, 5.6$ Hz, 1H), 6.90 (brd, $J = 6.4$ Hz, 1H), 7.15 (dd, $J = 1.2, 8.8$ Hz, 2H), 7.4-7.6 (m, 5H), 7.75 (dd, $J = 1.2, 8.8$ Hz, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 52.8, 59.5, 74.9, 122.0, 127.1, 127.7, 128.7, 131.4, 132.3, 132.7, 138.2, 168.8, 169.6. Anal. calcd for $\text{C}_{17}\text{H}_{16}\text{BrNO}_4$: C 53.99; H 4.26; N 3.70. Found: C 53.89; H 4.30; N 3.57. The enantiomeric

purity was determined to be 75%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 75/25, flow rate = 0.5 mL/min). Retention time: 12.6 min for (2*R*,3*R*), 19.9 min for (2*S*,3*S*).

Methyl (2*S*, 3*S*)-2-benzoylamino-3-hydroxy-3-(thiophen-2-yl)-propionate

colorless solid; 75% yield, anti : syn = >99:1 (judged by $^1\text{H-NMR}$), 92%ee; mp 129-130 °C (ethyl acetate-hexane); $[\alpha]_{\text{D}}^{24} +84.2$ (c 1.03, CHCl_3) for 92% ee; IR (KBr) 3408, 3354, 1727, 1643, 1526, 1279, 1023, 698 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.83 (s, 3H), 4.96 (d, $J = 5.2$ Hz, 1H), 5.30 (dd, $J = 3.2, 6.8$ Hz, 1H), 5.66-5.69 (m, 1H), 6.89-7.05 (m, 3H), 7.24-7.27 (m, 1H), 7.46 (dd, 2H, $J = 7.2, 7.6$ Hz), 7.55 (d, 2H, $J = 7.6$ Hz), 7.81 (d, $J = 7.2$ Hz, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 3.0, 59.4, 72.2, 124.3, 125.3, 126.7, 127.2, 128.7, 132.3, 132.9, 142.4, 169.1, 169.4. Anal. calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_4\text{S}$: C 59.00; H 4.95; N 4.59. Found: C 58.83; H 4.93; N 4.41. The enantiomeric purity was determined to be 92%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 75/25, flow rate = 0.5 mL/min). Retention time: 13.0 min for (2*R*,3*R*), 17.1 min for (2*S*,3*S*).

Methyl (2*S*, 3*S*)-2-benzoylamino-3-furan-2-yl-3-hydroxypropionate

colorless amorphous; 74% yield, anti:syn = >99:1 (judged by $^1\text{H-NMR}$), 88%ee; $[\alpha]_{\text{D}}^{25} +48.3$ (c 1.00, CHCl_3) for 88% ee; IR (KBr) 3240, 2979, 1746, 1714, 1505, 1367, 1164 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.45 (s, 9H), 3.76 (s, 3H), 3.80-3.90 (brs, 1H), 4.76 (brs, 1H), 5.18 (brs, 2H), 5.37 (brs, 1H), 6.30-6.35 (m, 2H), 7.36 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 28.2, 52.7, 58.1, 69.5, 80.7, 107.6, 110.2, 141.4, 152.5, 156.4, 170.1. Anal. calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_6$: C 54.73; H 6.71; N 4.91. Found: C 54.53; H 6.63; N 4.75. The enantiomeric purity was determined to be 88%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 90/10, flow rate = 0.5 mL/min). Retention time: 37.1 min for (2*R*,3*R*), 42.2 min for (2*S*,3*S*).

Methyl 2-benzoylamino-3-(4-benzyloxyphenyl-3-chloro)-3-hydroxypropionate

colorless solid; 72% yield, anti:syn = >99:1 (judged by $^1\text{H-NMR}$), 88% ee; $[\alpha]_{\text{D}}^{25} -82.8$ (c 1.02, CHCl_3) for 88% ee; IR (KBr) 3312, 1742, 1643, 1639, 1525, 1228 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.77 (s, 3H), 4.71 (d, J = 5.2 Hz, 1H), 5.13 (s, 2H), 5.17 (dd, J = 3.6, 7.2 Hz, 1H), 5.30 (dd, J = 3.6, 5.6 Hz, 1H), 6.88-6.95 (m, 2H), 7.29-7.60 (m, 9H), 7.44-7.77 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 52.9, 59.5, 70.7, 74.5, 113.6, 123.1, 125.2, 127.0, 127.2, 128.0, 128.6, 128.7, 132.2, 132.6, 132.8, 136.3, 153.9, 168.9, 169.7. Anal. calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_5$: C 65.53; H 5.04; N 3.18. Found: C 65.26; H 5.03; N 3.16. The enantiomeric purity was determined to be 88%ee by HPLC analysis with a chiral stationary phase column, Daicel Chiralcel OD-H (hexane/2-propanol = 65/35, flow rate = 0.5 mL/min). Retention time: 14.0 min for (2*S*,3*S*), 18.7 min for (2*R*,3*R*).

Preparation of protected 3-methoxytyrosine

Methyl (2*R*, 3*R*)-3-(4-benzyloxyphenyl)-2-*tert*-butoxycarbonylamino-3-methoxypropionate

To a mixture of proton sponge (1.58 g, 7.4 mmol), trimethyloxonium tetrafluoroborate (1.09 g, 7.4 mmol), and 4 Å molecular sieve (90 mg) in CH_2Cl_2 (3 mL) at 0 °C was added dropwise a solution of the alcohol (150 mg, 0.37 mmol) in CH_2Cl_2 (1 mL) under argon atmosphere. After stirring at rt for 6 h, the mixture was diluted with ethyl acetate and filtered. The filtrate was washed with aqueous KHSO_4 (1N in H_2O), saturated aqueous NaHCO_3 , and brine. The organic extracts were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/3 to 1/2) to give the methyl ester (78 mg, 0.19 mmol, 51%) as a colorless amorphous and the starting material (61 mg, 0.15 mmol, 41%).

$[\alpha]_{\text{D}}^{24} -59.2$ (c 0.20, CHCl_3), $[\alpha]_{\text{D}}^{24} -36.7$ (c 0.96, MeOH); IR (ATR) 2930, 1713, 1610, 1508, 1239, 1158 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.39 (s, 9H), 3.29 (s, 3H), 3.65 (s, 3H), 4.46 (brd, 1H), 4.57 (m, 1H), 5.06 (s, 2H), 5.09 (brd, 1H), 6.97 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 7.26-7.44 (m, 5H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 28.2, 57.3, 58.3, 70.0, 77.2, 79.9, 83.2, 114.7, 127.4, 128.0, 128.1, 128.6, 129.1, 136.8, 155.1, 158.8, 171.0. Anal. calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_6$: C, 66.49; H, 7.04; N, 3.37. Found: C 66.25; H 6.90; N 3.10.

(2*R*, 3*R*)-3-(4-benzyloxyphenyl)-2-*tert*-butoxycarbonylamino-3-methoxypropionic acid ⁷⁾

To a solution of the ester (78 mg, 0.19 mmol) in THF (1.6 mL) and H₂O (0.4 mL) at 0 °C was added lithium hydroxide monohydrate (16 mg, 0.38 mmol). After stirring at 23 °C for 5 h, the reaction mixture was acidified with citric acid (5% in H₂O) and extracted with ethyl acetate. The organic extracts were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 4/1) to give the carboxylic acid as colorless solids (72 mg, 0.18 mmol, 94%).

$[\alpha]_D^{22}$ -46.6 (*c* 0.96, MeOH); mp 106-109 °C; IR (KBr) 3359, 2981, 1722, 1512, 1242 cm⁻¹;

¹H-NMR (400 MHz, CDCl₃) δ 1.36 (s, 9H), 3.32 (s, 3H), 4.35 (brd, 1H) 4.52 (m, 1H), 5.06 (s, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = # Hz, 2H), 7.33-7.44 (m, 5H); ¹³C-NMR (100 MHz, CDCl₃) δ 28.2, 57.3, 58.2, 70.0, 80.3, 82.9, 114.8, 127.5, 128.0, 128.4, 128.6, 128.8, 136.8, 155.3, 159.0, 174.2.

Anal. calcd for C₂₂H₂₇NO₆·2/3H₂O: C 63.91; H 6.91; N 3.39. Found: C 63.77; H 6.82; N 3.39.

Hydrogenation of 3-Oxo-3-phenylpropionic acid ethyl ester

Hydrogenation was carried out for 48 h according to the general procedure described above using 3-oxo-3-phenylpropionic acid ethyl ester in place of the α-amino-β-keto ester hydrochloride. After removal of the volatiles, the NMR analysis of the residue showed no desired product and recovery of the starting material.

Hydrogenation of α-amino acetophenone

Hydrogenation was carried out according to the general procedure described above using α-amino acetophenone in place of the α-amino-β-keto ester hydrochloride. After removal of the volatiles, the crude product was benzoylated with benzoyl chloride and triethylamine in THF and condensed *in vacuo*. The residue was purified on silica gel chromatography to give 2-amino-1-phenylethanol in 11 % yield with 8 % ee, which was judged by HPLC analysis.⁸

Hydrogenation of 2-Benzoylamino-3-oxo-3-phenylpropionic acid methyl ester

(i) Method (A):

Hydrogenation was carried out according to the general procedure described above using 2-benzoylamino-3-oxo-3-phenylpropionic acid methyl ester in place of the α -amino- β -keto ester hydrochloride. After removal of the volatiles, the NMR analysis of the residue showed no desired product and recovery of the starting material.

(ii) Method (B):

Hydrogenation was carried out by using the Ir-(*S*)-MeOBIPHEP catalyst (prepared by mixing of [Ir(cod)Cl]₂ (2.5 mg, 0.0037 mmol) and (*S*)-MeOBIPHEP (5.8 mg, 0.01 mmol) in CH₂Cl₂ (1.0 mL) prior to the hydrogenation) and 2-benzoylamino-3-oxo-3-phenylpropionic acid methyl ester (74 mg, 0.25 mmol) in CH₂Cl₂ (3 mL). After removal of the volatiles, the NMR analysis of the residue showed a 1:1 mixture of *anti*- and *syn*-2-benzoylamino-3-hydroxy-3-phenylpropionic acid methyl esters containing the unchanged starting material, which were separated on silica gel column chromatography to give the *anti*-product (7.5 mg) and the *syn*-one (3 mg) in 10% and 4% yields, respectively. The enantiomeric excess of the *anti* product was 17%ee by HPLC analysis. The products were confirmed by comparisons to the authentic samples.

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