Supplementary Materials

General. ^{1}H and ^{13}C NMR were performed on a Bruker DRX500 (500.03 MHz) spectrometer using TMS and $CDCl_3$ as internal standards. High Resolution Mass Spectra (HRMS) were recorded on a JEOL HX110A instrument. Optical rotations were measured on a JASCO P-1010 polarimeter. Melting points (mp) are uncorrected and were obtained in open capillaries. All reagents and solvents, unless otherwise stated, are commercially available and were used as received. Unless otherwise stated, yields refer to isolated yields of products of greater than 95% purity as estimated by ^{1}H and ^{13}C NMR spectrometry. All new compounds were characterized by ^{1}H, and ^{13}C NMR and HRMS.

General Procedure for the Synthesis of 1-Phenyl-1-Propanol and 3-Methyl-1-Phenyl-1-Butanol. The reactions were conducted on 100 mmol scale. To a solution of aldehyde (propionaldehyde or iso-butaldehyde) (1eq) in 100 mL of anhydrous ethyl ether at –78°C, phenyl magnesium bromide (3M in Et_2O, 1.1 eq) was slowly added via a syringe. The reaction mixture was stirred for an hour at –78°C and overnight at room temperature. The reaction was quenched with saturated ammonium chloride at 0°C. The ether layer was separated from the aqueous layer. Then the aqueous layer was washed with ethyl ether (3 x 100 mL). The combined ether layer was washed with 5% $NaHCO_3$ (2 x 100 mL) and distilled water (2 x 100 mL). Then the ether solution was dried over anhydrous $MgSO_4$ and evaporated in vacuo to afford the crude product, which was purified by column chromatography with ethyl acetate/hexanes (3:7) as eluent.

1-Phenyl-1-Propanol Colorless oily liquid. Yield: 88%; ^{1}H-NMR($CDCl_3$) δ 0.84 (t, 3H, J = 6.8 Hz), 1.53-1.76 (m, 2H), 4.40 (t, 1H, J = 6.6 Hz), 7.10-7.30(m, 5H). ^{13}C-NMR ($CDCl_3$) δ 9.9, 31.6, 75.5, 125.8, 127.0, 127.7, 144.5. HRMS (FAB) $[M+H]^+$ calcd. for $C_9H_{12}O$ 137.0968, found 137.0971.

3-Methyl-1-Phenyl-1-Butanol Pale yellow oil. Yield: 81%; ^{1}H-NMR ($CDCl_3$) δ 0.9 (dd, 6H, J = 1.7 Hz, J = 6.3Hz), 1.40-1.55 (m, 1H), 1.60-1.83 (m, 2H), δ 4.70 (dd, 1H, J = 5.5 Hz, J = 7.8 Hz), 7.10-7.50 (m, 5H). ^{13}C-NMR ($CDCl_3$) δ 22.2, 23.0, 24.6, 48.2, 72.5, 125.8, 127.9, 128.3, 142.5. HRMS (FAB) $[M+H]^+$ calcd. for $C_{11}H_{16}O$ 165.1281, found 165.1277.

General Procedure for the Synthesis of Bromides 2b and 2c. To a solution of 20 mmole (1 eq.) of 1-phenyl-1-propanol or 3-methyl-1-phenyl-1-butanol in 100 mL of anhydrous ethyl ether and in Ar atmosphere, 2.1 mL (44 mmole, 2.2 eq.) of anhydrous pyridine was added via a syringe at –78 °C. After 5 minutes, 2.1 mL (22 mmole, 1.1 eq.) of phosphorus tribromide was slowly dropped into the solution in a period of one hour. Formation of white slurry was observed. The mixture was stirred for 2 hrs at –78 °C and overnight at room temperature. Completion of the reaction was monitored by TLC. The reaction was quenched by adding slowly a ice-water mixture with stirring at 0 °C, and the resulting mixture was stirred for 30 min at 0 °C. The ether layer was separated from the aqueous layer and the aqueous phase was washed with diethyl ether (2 x 150 mL). The combined ethyl ether solution was washed with ice-cold 85% phosphorus acid (50 mL), saturated sodium bicarbonate (2 x 100 mL) and water (2 x 100 mL). The ether solution was dried over anhydrous magnesium sulfate and evaporated *in vacuo* to afford product 2b or 2c. No further purification of compounds 2b or 2c was necessary.

2b: Pale yellow oil. Yield: 72%; ^{1}H-NMR ($CDCl_3$) δ 0.97(t, 3H, J = 7.5 Hz), 2.08-2.40 (m, 2H), 4.85 (t, 1H, J = 7.5 Hz), 7.15-7.35 (m, 5H). ^{13}C-NMR($CDCl_3$) δ 12.9, 33.1, 57.4, 127.1, 127.6, 128.1, 142.9. HRMS (FAB) $[M+H]^+$ calcd. for $C_9H_{11}Br$ 198.0044, found 198.0036.

2c. Colorless oil. Yield: 83%; ^{1}H-NMR ($CDCl_3$) δ 0.93 (d, 3H, J = 6.2 Hz), 1.00 (d, 3H, J = 6.9 Hz), 1.75-1.85 (m, 1H), 2.00-2.11 (m, 1H), 2.24-2.36 (m, 1H), 5.14 (dd, 1H, J = 7.0 Hz, J = 8.4 Hz), 7.20-7.50 (m, 5H). ^{13}C-NMR ($CDCl_3$) δ 21.8, 22.0, 26.6, 48.7, 53.9, 127.2, 128.1, 129.1, 139.0. HRMS (FAB) $[M+H]^+$ calcd. for $C_{11}H_{15}Br$ 226.0357, found 226.0340.

Reaction of Ni(II)-complex (*S*)(*S*,*R*)-1 with Bromides 2a-c. The reactions were conducted on 1-100 mmol scale. A 100 mL round-bottom flask with 10 mmole (1eq.) of (*S*)(*S*,*R*)-**1** and 4.0 g (100 mmole, 10eq.) of NaOH was purged with Ar and 20 mL of anhydrous DMF was added to dissolve the complex and the base. Then 25 mmole (2.5 eq.) of bromide **2a-c**, dissolved in 20 mL of anhydrous DMF, was dropped into the solution via a syringe. The reaction mixture was stirred under Ar and the reaction progress was monitored by TLC. Upon completion, the reaction was quenched by addition of 500 mL of icy water and the precipitated material was filtered off and dried *in vacuo.* The diastereomerically pure products were isolated by column chromatography on silica gel using acetone/hexanes 1/1 as an eluent.

Ni (II) Complex of Schiff Base of (*S*)-BPB [(*S*)-*o*-[*N*-(*N*-benzylprolyl)amino]-benzophenone [(*S*)-BPB] with (2*S*, 3*R*)-2, 3-Dimethylphenylalanine ((*S*)(2*S*,3*R*)-4a) R_f = 0.43 (acetone/hexanes, 1:1); m.p. 121-123 °C; $[\alpha]_D^{25}$ = + 2254 (*c* 0.01680, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 1.15 (s, 3H), 1.43 (d, 3H, *J* = 7.0 Hz), 1.49-1.56 (m, 1H), 1.94-2.03 (m, 2H), 2.11-2.22 (m, 2H), 3.02-3.05 (m, 1H), 3.25 (dd, 1H, *J* = 7.9 Hz, *J* = 9.3 Hz), 3.48 (d, 1H, *J* = 12.6 Hz), 3.47-3.51 (m, 1H), 4.27 (d, 1H, 12.6 Hz), 6.54-6.60 (m, 2H), 7.03-7.05 (m, 1H), 7.07-7.09 (m, 1H), 7.10-7.16 (m, 1H), 7.27-7.51 (m, 11H), 8.01 (d, 2H, *J* = 7.1 Hz), 8.22 (d, 1H, *J* = 8.4 Hz). ^{13}C-NMR ($CDCl_3$) δ 16.3, 22.9, 28.0, 30.2, 48.8, 57.3, 63.8, 69.9, 81.3, 120.1, 122.9, 127.1, 127.3, 127.6, 127.7, 127.8, 128.6, 129.2, 129.6, 130.9, 131.5, 131.8, 133.4, 133.9, 137.3, 142.3, 142.5, 171.8, 179.7, 180.3. HRMS (FAB) $[M+H]^+$ calcd. for $C_{36}H_{35}N_3O_3Ni$ 616.2110, found 616.2106.

Ni (II) Complex of Schiff Base of (*S*)-BPB with (2*S*, 3*S*)-2, 3-Dimethylphenylalanine ((*S*)(2*S*,3*S*)-3a) R_f = 0.36 (acetone/hexanes, 1:1); m.p. 277-279 °C; $[\alpha]_D^{25}$ = +2095 (*c* 0.01250, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 0.67 (s, 3H), 1.66 (d, 3H, *J* = 6.7 Hz), 2.08-2.13 (m, 1H), 2.18-2.23 (m, 1H), 2.63-2.73 (m, 1H), 2.99-3.06 (m, 1H), 3.41-3.50 (m, 1H), 3.52-3.56 (m, 3H), 4.45 (d, 1H, *J* = 12.7 Hz), 4.85 (d, 1H, *J* = 7.7 Hz), 6.09-6.13 (m, 1H), 6.30-6.32 (m, 1H), 6.48-6.51 (m, 1H), 6.83-6.87 (m, 1H), 7.00-7.03 (m, 1H), 7.07-7.11 (m, 2H), 7.17-7.33 (m, 9H), 8.13 (d, 2H, *J* = 7.2 Hz), 8.21 (d, 1H, *J* = 8.7 Hz). ^{13}C-NMR ($CDCl_3$) δ 16.7, 20.6, 23.1, 30.5, 52.8, 56.6, 63.0, 70.6, 81.9, 120.0, 122.2, 125.9, 126.8, 127.0, 127.1, 127.6, 128.0, 128.3, 128.4, 128.5, 129.2, 129.6, 131.0, 131.5, 133.1, 133.5, 135.7, 139.6, 141.4, 169.7, 178.5, 179.4. HRMS (FAB) $[M+H]^+$ calcd. for $C_{36}H_{35}N_3O_3Ni$ 616.2110, found 616.2106.

Ni (II) Complex of Schiff Base of (*S*)-BPB with (2*S*, 3*S*)-3-Ethyl-2-methylphenylalanine ((*S*)(2*S*,3*S*)-3b) m.p. 236-238 °C; R_f = 0.60 (acetone/hexanes, 1:1); $[\alpha]_D^{25}$ = +2095 (*c* 0.01250, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 0.67 (s, 3H), 0.92 (t, 3H, *J* = 7.8 Hz), 1.89-1.95 (m, 1H), 2.08-2.14 (m, 1H), 2.19-2.23 (m, 1H), 2.34-2.39 (m, 1H), 2.66-2.73 (m, 1H), 3.03-3.08 (m, 1H), 3.46-3.60 (m, 3H), 3.58 (d, 1H, *J* = 12.5 Hz), 4.49 (d, 1H, *J* = 13.0 Hz), 4.81 (d, 1H, *J* = 7.3 Hz), 5.81-5.84 (m, 1H), 6.29 (d, 1H, *J* = 8.0 Hz), 6.51 (t, 1H, *J* = 7.3 Hz), 6.85-88 (m, 1H), 7.04 (t, 1H, *J* = 7.8 Hz), 7.07-7.08 (m, 1H), 7.13 (t, 1H, *J* = 7.5 Hz), 7.22-7.26 (m, 6H), 7.28-7.32 (m, 3H), 8.10 (d, 2H, *J* = 7.5 Hz), 8.20 (d, 1H, J = 8.5 Hz). ^{13}C-NMR($CDCl_3$) δ 13.0, 21.9, 23.4, 23.5, 30.8, 50.8, 61.4, 63.4, 61.4, 63.4, 70.9, 82.5, 120.4, 122.6, 126.3, 127.3, 127.4, 127.5, 128.1, 128.5, 128.7, 128.9, 129.6, 131.4, 131.9, 133.3, 133.9, 136.0, 137.4, 141.8, 170.0, 179.2, 179.7. HR MS (FAB) $[M+H]^+$ calcd. for $C_{37}H_{37}N_3O_3Ni$ 630.2267, found 630.2265.

Ni (II) Complex of Schiff Base of (*S*)-BPB with (2*S*, 3*R*)-3-*iso*-Butyl-2-methylphenylalanine ((*S*)(2*S*,3*R*)-4c) R_f = 0.50 (acetone/hexanes, 1:1); m.p. 246-248 °C; $[\alpha]_D^{25}$ = + 1650 (*c* 0.01244, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 0.56 (d, 3H, *J* = 6.4 Hz), 0.76 (d, 3H, *J* = 6.6 Hz), 1.01-1.06 (m, 1H), 1.18 (s, 3H), 1.49-1.56 (m, 3H), 2.00-2.20 (m, 3H), 2.43-2.44 (m, 1H), 3.07-3.10 (m, 1H), 3.22-3.25 (m, 1H), 3.30 (dd, 1H, *J* = 3.0 Hz , *J* = 12.5 Hz), 3.49 (d, 1H, *J* = 13.0 Hz), 4.31 (d, 1H, *J* = 13.0 Hz), 6.54-6.60 (m, 2H), 7.05-7.11 (m, 2H), 7.17-7.20 (m, 1H), 7.28-7.34 (m, 4H), 7.39-7.50 (m, 7H), 8.00 (d, 2H, *J* = 7.5 Hz), 8.22 (d, 1H, *J* = 8.5 Hz). ^{13}C-NMR ($CDCl_3$) δ 20.7, 23.1, 24.1, 25.0, 29.7, 30.4, 38.1, 52.5, 57.4, 63.9, 70.1, 81.7, 120.2, 122.9, 127.1, 127.4, 127.8, 128.3, 128.7, 129.2, 130.3, 131.1, 131.6, 131.9, 133.4, 134.0, 137.5, 140.2, 142.3, 171.9, 179.3, 180.4. HRMS (FAB) $[M+H]^+$ calcd. for $C_{39}H_{41}N_3O_3Ni$ 658.2580, found 658.2594.

Ni (II) Complex of Schiff Base of (*S*)-BPB with (2*S*, 3*S*)-3-*iso*-Butyl-2-methylphenylalanine ((*S*)(2*S*,3*S*)-3c) R_f = 0.57 (acetone/hexanes, 1:1); m.p. 129-131 °C; $[\alpha]_D^{25}$ = +1710 (*c* 0.02498, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 0.72 (s, 3H), 0.92 (d, 3H, *J* = 6.5 Hz), 0.98 (d, 3H, *J* = 6.5 Hz), 1.36-1.42 (m, 1H), 2.02-2.20 (m, 4H), 2.61-2.68 (m, 1H), 3.00-3.05 (m, 1H), 3.39-3.44 (m, 1H), 3.49-3.53 (m, 1H), 3.59-3.65 (m, 2H), 4.49 (d, 1H, *J* = 12.7 Hz), 4.98 (d, 1H, *J* = 7.5 Hz), 5.38-5.41 (m, 1H), 6.29-6.31 (m, 1H), 6.49-6.52 (m, 1H), 6.92-695 (m, 1H), 7.02-7.32 (m, 12H), 8.10 (d, 2H, *J* = 7.9 Hz), 8.21 (d, 1H, *J* = 8.7 Hz). ^{13}C-NMR ($CDCl_3$) δ 21.1, 22.8, 23.8, 24.1, 25.8, 31.0, 39.0, 56.1, 57.0, 63.6, 70.9, 82.1, 120.3, 122.4, 126.3, 127.2, 127.4, 127.6, 128.0, 128.2, 128.6, 128.7, 128.8, 129.7, 131.4, 131.9, 133.3, 133.9, 136.2, 137.5, 141.8, 170.5, 179.3, 179.8. HRMS (FAB) $[M+H]^+$ calcd. for $C_{39}H_{41}N_3O_3Ni$ 658.2580, found 658.2574.

Decomposition of Ni (II)-complexes. A solution of **3** (1 eq.) in 20 mL of MeOH was slowly dropped into a mixture of 20 mL of 3 *N* HCl (6 eq.) and MeOH (1:1) at 70 °C. When the red color disappeared, the solution was evaporated to dryness and the solid residue was dissolved in water (3 x 50 mL) and evaporated again to remove HCl. The solid residue was treated with 100 mL of concentrated ammonium hydroxide and 100 mL of water and evaporated to dryness. The resulting material was dissolved in 100 mL of water and extracted with 100 mL of $CHCl_3$. (Sometimes, part of the product stayed in the interface between the aqueous phase and organic phase due to the limited solubility of the product in water. The undissolved product was filtered and washed with water and $CHCl_3$. Then this part of product was combined with the rest of product obtained later. Also the washings were combined with the filtrate.) The $CHCl_3$ layer was separated from the aqueous layer and the aqueous layer was washed with $CHCl_3$ (2 x 50 mL). The chloroform layers was dried over anhydrous $MgSO_4$ and evaporated to recover chiral ligand (*S*)-**6**. The aqueous layer was evaporated *in vacuo*, the resultant material was dissolved in minimal amount of ethanol/water 1v:1v and the solution was applied to Dowex 50X2 100 ion-exchange column. First, the column was washed with water until the eluent showed a neutral pH. Then, the column was washed with 1:4 water/concentrated ammonium hydroxide to yield a solution of **5**, which was evaporated to give the solid amino acids. If necessary, a mixture of 2:3:5 concentrated ammonium hydroxide/ ethanol/water could be used as eluent.

(2*S*, 3*S*)-2, 3-Dimethylphenylalanine (5a) Yield: 87%; m.p. 263-265 °C; $[\alpha]_D^{25} = -31.42$ (*c* 0.3472, MeOH) [lit.[6] –31.7 42 (*c* 0.3472, MeOH)]; ^{1}H-NMR(d_6-DMSO/DCl) δ 0.94 (d, 3H, *J* = 5.4 Hz), 1.07 (s, 3H), 2.95 (q, 1H, *J* = 5.6 Hz), 6.84-6.91 (m, 5H). ^{13}C-NMR (d_6-DMSO/DCl) δ 17.7, 22.0, 47.5, 66.2, 131.0, 131.6, 132.2, 141.0, 174.6. HRMS (FAB) [M+H]+ calcd. for $C_{11}H_{15}NO_2$ 194.1181, found 194.1186.