Supporting Information

Catalytic Asymmetric Hydrogenation using Homogeneous Chiral Nickel-Bisphosphine Complexes through DKR
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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 polarimeter. NMR spectra were recorded on a JEOL JNM GSX 400A and JNM ECP400 spectrometers, operating at 400 MHz for $^1$H-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.

I. Influence of Air and Moisture

We employed nickel acetate tetrahydrate as the catalyst precursor. We first examined the effects of moisture and air. As shown in Table S1, the hydrogenation without any care indicated the problem of reproducibility on the chemical yield (entries 1-3). Careful experiments revealed that the strict exclusion of both air and moisture was essential for smooth reaction (entries 6 and 7). Under this conditions, the reaction using 10% nickel catalyst completed in 6 h. The origin for the negative effect of water is unclear.

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a) Determined after N-benzylation. b) Estimated by $^1$H NMR spectra. c) Determined after N-benzylation by HPLC analysis.

Table S1
II. Experimental Procedures and Characterization of the Products

Typical procedure for Ni-catalyzed asymmetric hydrogenation

Methyl (2R,3R)-2-benzoylamino-3-hydroxy-3-phenylpropionate (5a)

1. Ni(OAc)$_2$ (5 mol%), (R,S)-ligand 3g (5 mol%) H$_2$ (100 atm), NaOAc (1.0 eq), TFE / AcOH (1/4, 0.2 M) MS3A, rt, 24 h

2. Bz$_2$O, Et$_3$N, THF

The reaction was carried out in a glass vessel placed in a stainless autoclave apparatus. A glass test tube was charged with Ni(OAc)$_2$·4H$_2$O (8.7 mg, 0.035 mmol), (R,S)-ferrocenyl ligand (3g, 24.9 mg, 0.035 mmol), the α-amino-β-keto ester hydrochloride (1, 161 mg, 0.70 mmol), sodium acetate (57.4 mg, 0.70 mmol), and molecular sieves 3A (70 mg), and then was flushed with argon. After trifluoroethanol (0.7 mL) and acetic acid (2.8 mL) was added, the resulting mixture was degassed by three freeze-thaw cycles. The glass test tube was transferred to a stainless steel autoclave in an argon-filled glove bag. The mixture was stirred at 25 °C under hydrogen pressure (100 atm) for 24 h. After hydrogen was carefully released, MeOH (3.5 mL) and aqueous HCl (1.4 mL, 1 M in H$_2$O) was added and the mixture was concentrated in vacuo to dryness below 40 °C. The resulting residue was dissolved in MeOH and the mixture was concentrated in vacuo. This operation was repeated three times. The residue was used for next step without any purification. Benzoic anhydride (158 mg, 0.70 mmol) followed by a solution of Et$_3$N (0.3 mL, 2.1 mmol) in THF (2.1 mL) were added dropwise to a solution of the above crude product in THF (3.5 mL) at 0 °C. After stirring the mixture at 25 °C for 12 h, the reaction was quenched with saturated aqueous NH$_4$Cl, and the mixture was extracted with EtOAc. The organic layer was washed with saturated aqueous NH$_4$Cl, saturated aqueous NaHCO$_3$, and brine, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to give the N-benzoyl derivative 6a (204 mg, 98%). The diastereomeric ratio was determined by $^1$H NMR. The enantiomeric excess was determined by chiral HPLC. 6a: colorless solids; 100% conversion yield and 91% isolated yield (two steps); anti:syn = >99:1, 92% ee; $[\alpha]_D^{18} -122.7$ (c 1.04, CHCl$_3$) for 92% ee; mp 130.5-131.5 °C (recrystallized from ethyl acetate-n-hexane); IR (KBr) 3338, 1744, 1644, 1525, 1229, 1173 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) 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), 6.67 (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); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 52.6, 59.4, 75.1, 125.9, 127.1, 128.0, 128.3, 128.6, 132.1, 133.0, 139.1; LR-FABMS (NBA) m/z : 300 (M+H$^+$). Anal. calcd for C$_{17}$H$_{17}$NO$_4$: C 68.21; H 5.72; N 4.68. Found: C 68.18; H 5.64; N 4.55. HPLC analysis using CHIRALPAK AD and n-hexane/i-PrOH (85/15, 0.5 mL/min), Retention time for (2S, 3S): 35.0 min [minor], (2R, 3R): 39.6 min [major].

The alternative procedure using the prior prepared nickel complex:

A glass test tube was charged with Ni(OAc)$_2$·4H$_2$O (1.3 mg, 0.005 mmol) and (R,S)-ferrocenyl ligand (3g, 3.8 mg,
0.005 mmol) in CH2Cl2 (0.5 mL). After degassed by three freeze-thaw cycles, the mixture was stirred at 50 °C for 45 min under an argon atmosphere. The resulting yellow solution was concentrated and dried in vacuo at rt for 20 min to give the yellow powder. The α-amino-β-keto ester hydrochloride (0.1 mmol), sodium acetate (8.3 mg, 0.1 mmol), molecular sieves 3A (10 mg), trifluoroethanol (0.1 mL) and acetic acid (0.4 mL) was added to the prepared yellow powder in an argon-filled glove bag. After the mixture was degassed by three freeze-thaw cycles, the glass test tube was transferred to a stainless steel autoclave in an argon-filled glove bag. The mixture was stirred at rt under hydrogen pressure (100 atm) for 24 h. After hydrogen was carefully released, MeOH (1 mL) and aqueous HCl (1 mL, 1 M in H2O) was added and the mixture was concentrated to dryness under reduced pressure below 40 °C. The resulting residue was dissolved in MeOH and the mixture was concentrated in vacuo. This cycle was repeated three times. The residue was used for next step without any purification. The conversion yield was estimated by 1H-NMR in DMSO-d6 of the crude product.

To a solution of the above residue in the THF (2 mL) at 0 °C was added benzoic anhydride (27.1 mg, 0.12 mmol) and dropwise a solution of Et3N (42 μL, 0.3 mmol) in THF (1 mL). After stirred at rt for 12 h, the reaction was quenched with saturated aqueous NH4Cl, and the mixture was diluted with EtOAc. The organic layer was washed with saturated aqueous NH4Cl, saturated aqueous NaHCO3, brine, dried over Na2SO4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to give N-benzoyl derivative.

**Methyl 2-benzoylamino-3-hydroxy-3-o-tolylpropionate (6b)**

Prepared according to the typical procedure. 6b: colorless solids; 100% conversion yield and 90% isolated yield (two steps), anti/syn = >99:1, 81% ee; [α]D17 –62.8 (c 1.28, CHCl3) for 81% ee; mp 123.5-124.5 °C; IR(ATR) 3356, 3065, 2952, 1739, 1639, 1578, 1521, 1486, 1436, 1365, 1211 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 2.42 (s, 3H), 3.45 (d, J = 5.6 Hz, 1H), 3.64 (s, 3H), 5.12 (dd, J = 3.6, 7.2 Hz, 1H), 5.50 (dd, J = 3.6, 5.2 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 7.18-7.23 (m, 3H), 7.38-7.41 (m, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.81 (t, J = 7.6 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 19.0, 52.3, 57.5, 71.7, 125.7, 125.8, 127.2, 128.0, 128.4, 128.7, 130.1, 130.6, 132.1, 133.3, 134.8, 137.2, 1436, 170.4. HR-FABMS (NBA): calcd for C18H19NO4 (M+H+): 314.1392. Found 314.1395.

HPLC analysis using CHIRALPAK AD-H and n-hexane/i-PrOH (85/15, 0.5 mL/min), Retention time 27.8 min [major], 31.4 min [minor].

**Methyl (2R, 3R)-2-benzoylamino-3-hydroxy-3-m-tolylpropionate (6c)**

Prepared according to the typical procedure. 6c: colorless solids; 88% conversion yield and 83% isolated yield
Methyl (2R, 3R)-2-benzoylamino-3-(3-fluorophenyl)-3-hydroxypropionate (6d)

Prepared according to the typical procedure. 6d: colorless solids; 100% conversion yield and 88% isolated yield (two steps), anti:syn = >99:1, 89% ee; [α]D18 = −113.3 (c 0.81, CHCl3) for 93% ee; mp 111-112 °C; IR(KBr) 3304, 1747, 1719, 1645, 1541, 1337, 1273, 1219 cm⁻¹; ¹H NMR (400 MHz, CDCl3) δ 2.31 (s, 3H), 3.78 (s, 3H), 4.42 (d, J= 5.6 Hz, 1H), 5.21 (dd, J= 4.0, 5.6 Hz, 1H), 5.34 (dd, J= 4.0, 6.8 Hz, 1H), 6.87 (brd, J= 6.8 Hz, 1H), 7.00-7.11 (m, 3H, Ar-H), 7.19-7.25 (m, 1H, Ar-H), 7.42-7.56 (m, 3H, Ar-H), 7.73-7.76 (m, 2H, Ar-H); 1H NMR (400 MHz, CDCl3) δ 2.31 (s, 3H), 3.78 (s, 3H), 4.42 (d, J= 5.6 Hz, 1H), 5.21 (dd, J= 4.0, 5.6 Hz, 1H), 5.34 (dd, J= 4.0, 6.8 Hz, 1H), 6.87 (brd, J= 6.8 Hz, 1H), 7.00-7.11 (m, 3H, Ar-H), 7.19-7.25 (m, 1H, Ar-H), 7.42-7.56 (m, 3H, Ar-H), 7.73-7.76 (m, 2H, Ar-H); 13C NMR (100 MHz, CDCl3) 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; LR-FABMS (NBA) m/z: 314 (M+H+). Anal. calcd for C18H19NO4: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.71; H, 6.01; N, 4.37.

HPLC analysis using CHIRALCEL OD-H and n-hexane/i-PrOH (90/10, 0.4 mL/min), Retention time for (2R,3R) : 41.7 min [major], for (2S,3S) : 54.1 min [minor].

Methyl (2R, 3R)-2-benzoylamino-3-(3-chlorophenyl)-3-hydroxypropionate (6e)

Prepared according to the typical procedure. 6e: colorless solids; 100% conversion yield and 91% isolated yield (two steps), anti:syn = >99:1, 92% ee; [α]D18 = −99.3 (c 0.95, CHCl3) for 92% ee; mp 132-133 °C; IR (KBr) 3905, 3306, 1742, 1645, 1578, 1534, 1438, 1272 cm⁻¹; ¹H NMR (400 MHz, CDCl3) δ 3.78 (s, 3H), 4.81 (d, J= 5.6 Hz, 1H), 5.19 (dd, J= 3.2, 6.8 Hz, 1H), 5.36 (br, 1H), 6.95 (d, J= 8 Hz, 1H), 7.14-7.16 (m, 1H), 7.23-7.29 (m, 3H), 7.44 (t, J= 8 Hz, 2H), 7.52-7.56 (m, 1H), 7.74-7.76 (m, 2H); ¹³C NMR (100 MHz, CDCl3) δ 52.8, 59.5, 74.6, 113.0 (d, J= 22.3 Hz), 114.9 (d, J= 20.6 Hz), 121.5 (d, J= 3.2 Hz), 127.1, 128.7, 129.8 (d, J= 8.2 Hz), 132.3, 132.8, 141.9 (d, J= 6.6 Hz), 162.8 (d, J= 245 Hz), 168.7, 169.7. HR-FABMS (NBA): calcd for C17H17ClNO4 (M+H+): 334.0846. Found 334.0817.

HPLC analysis using CHIRALCEL OD-H and n-hexane/i-PrOH (85/15, 0.4 mL/min), Retention time for (2R,3R) : 23.7 min [major], for (2S,3S) : 39.1 min [minor].
(2R,3R) : 23.8 min [major], for (2S,3S) : 37.2 min [minor].

**Methyl (2R, 3R)-2-benzoylamino-3-(3-bromo-phenyl)-3-hydroxypropionate (6f)**

1. Ni(OAc)₂ (5 mol%), (R,S)-ligand 3g (5 mol%) H₂ (100 atm), NaOAc (1.0 eq), TFE / AcOH (1/4, 0.2 M) MS3A, rt, 24 h
2. Bz₂O, Et₃N, THF

Prepared according to the typical procedure. 6f: colorless solids. 100% conversion yield and 91% isolated yield (two steps). *anti:syn = > 99:1, 92% ee; [α]D¹¹₈ = -90.2 (c 0.82, CHCl₃) for 92% ee; mp 122.5-123.5 °C; IR (ATR) 3285, 2918, 1722, 1642, 1535, 1435, 1268 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 3.82 (s, 3H), 4.73 (d, J = 5.6 Hz, 1H), 5.21 (dd, J = 3.2, 6.4 Hz, 1H), 5.38 (dd, J = 3.2, 5.2 Hz, 1H), 6.91 (brd, J = 6.0 Hz, 1H), 7.20 (d, J = 5.2 Hz, 2H), 7.41-7.49 (m, 4H), 7.54-7.58 (m, 1H), 7.75-7.78 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 52.8, 59.5, 75.2, 125.8, 127.2, 128.7, 129.2, 129.9, 131.2, 132.3, 132.8, 141.5, 168.9, 169.6. HR-FABMS (NBA): calcd for C₁₇H₁₆BrNO₄ (M+H⁺): 378.0341. Found 378.0336.

HPLC analysis using CHIRALCEL OD-H and n-hexane/i-PrOH (85/15, 0.4 mL/min), Retention time for (2R,3R) : 25.0 min [major], (2S,3S) : 38.8 min [minor].

**Methyl (2R, 3R)-2-benzoylamino-3-(3-bromo-phenyl)-3-hydroxypropionate (6g)**

1. Ni(OAc)₂ (5 mol%), (R,S)-ligand 3g (5 mol%) H₂ (100 atm), NaOAc (1.0 eq), TFE / AcOH (1/4, 0.2 M) MS3A, rt, 24 h
2. Bz₂O, Et₃N, THF

Prepared according to the typical procedure. 6g: colorless solids; 86% conversion yield and 82% isolated yield (two steps), *anti:syn = > 99:1, 93% ee; [α]D¹¹₈ = -116.6 (c 0.61, CHCl₃) for 93% ee; mp 122-123 °C; IR(KBr) 3319, 1740, 1645, 1539, 1324, 1264 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) 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), 7.10-7.20 (m, 4H), 7.40-7.60 (m, 3H), 7.70-7.80 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃) 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-FABMS (NBA) m/z: 314 (M+H⁺). Anal. calcd for C₁₈H₁₉NO₄: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.83; H, 6.17; N, 4.38.

HPLC analysis using CHIRALCEL OD-H and n-hexane/i-PrOH (85/15, 0.5 mL/min), Retention time for (2R,3R) : 25.8 min [major], (2S,3S) : 34.4 min [minor].

**Methyl (2R, 3R)-2-benzoylamino-3-(4-tert-butylphenyl)-3-hydroxypropionate (6h)**

1. Ni(OAc)₂ (5 mol%), (R,S)-ligand 3g (5 mol%) H₂ (100 atm), NaOAc (1.0 eq), TFE / AcOH (1/4, 0.2 M) MS3A, rt, 24 h
2. Bz₂O, Et₃N, THF

Prepared according to the typical procedure. 6h: colorless solids; 100% conversion yield and 90% isolated yield (two steps), *anti:syn = > 99:1, 92% ee; [α]D¹¹₈ = -98.4 (c 1.52, CHCl₃) for 92% ee; mp 77-78 °C; IR(KBr) 3432,
2965, 1719, 1526, 1490, 1436, 1281 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.30 (s, 9H), 3.79 (s, 3H), 4.36 (d, \(J = 5.6\) Hz, 1H), 5.23 (dd, \(J = 3.6, 7.2\) Hz, 1H), 5.36 (dd, \(J = 3.6, 5.6\) Hz, 1H), 6.86 (d, \(J = 7.2\) Hz, 1H), 7.18-7.20 (m, 2H), 7.36-7.38 (m, 3H), 7.74-7.76 (m, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 31.3, 34.5, 52.7, 59.4, 75.0, 125.3, 125.6, 127.2, 128.6, 132.1, 133.2, 135.9, 151.1, 168.6, 170.1. HR-FABMS (NBA): calcd for C\(_{21}\)H\(_{26}\)NO\(_4\) (M+H\(^{+}\)): 356.1862. Found 356.1827.

HPLC analysis using CHIRALPAK AD-3 and \(n\)-hexane/i-PrOH (85/15, 0.5 mL/min), Retention time for (2\(S\),3\(S\)) : 29.2 min [minor], for (2\(R\),3\(R\)) : 42.1 min [major].

Methyl (2\(S\), 3\(S\))-2-benzoylamino-3-(4-benzyloxyphenyl)-3-hydroxypropionate (6i)

Prepared according to the typical procedure. 6i: colorless solids; 100% conversion yield and 94% isolated yield (two steps), \(\text{anti:syn} = >99\%\); \([\alpha\]\(_D\))\(^{18}\) –92.9 (c 1.03, CHCl\(_3\)) for 91% ee; mp 108-110 °C; IR(KBr) 3323, 1743, 1642, 1515, 1246 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.78 (s, 3H), 4.44 (d, \(J = 5.2\) Hz, 1H), 5.04 (s, 2H), 5.21 (dd, \(J = 3.6, 6.8\) Hz, 1H), 5.34 (dd, \(J = 3.6, 5.2\) Hz, 1H), 6.86 (d, \(J = 6.8\) Hz, 1H), 6.93 (d, \(J = 8.8\) Hz, 2H), 7.19 (d, \(J = 8.8\) Hz, 2H), 7.26-7.75 (m, 8H), 7.75 (d, \(J = 7.2\) Hz, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 52.7, 59.5, 70.0, 75.0, 114.7, 127.2, 127.5, 128.0, 128.6, 128.7, 131.4, 132.2, 133.1, 136.8, 158.7, 168.6, 170.1; LR-FABMS (NBA) m/z: 406 (M+H\(^{+}\)). Anal. calcd for C\(_{24}\)H\(_{23}\)NO\(_5\): C, 71.10; H, 7.72; N, 3.45. Found: C, 70.71; H, 5.75; N, 3.41.

HPLC analysis using CHIRALCEL OD-H and \(n\)-hexane/i-PrOH (65/35, 0.4 mL/min), Retention time for (2\(R\),3\(R\)) : 26.8 min [major], for (2\(S\),3\(S\)) : 33.5 min [minor];

Methyl (2\(R\),3\(R\))-2-benzoylamino-3-(4-nitrophenyl)-3-hydroxypropionate (6j)

Prepared according to the typical procedure. 6j: colorless solids. 100% conversion yield and 80% isolated yield (two steps), \(\text{anti:syn} = >99\%\); \([\alpha\]\(_D\))\(^{18}\) –95.8 (c 0.57, CHCl\(_3\)) for 91% ee; mp 145.5-146.5 °C; IR (ATR) 3298, 2918, 1738, 1638, 1603, 1579, 1517, 1489, 1431, 1346, 1227 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.85 (s, 3H), 5.11 (d, \(J = 6.4\) Hz, 1H), 5.24 (dd, \(J = 3.2, 6.0\) Hz, 1H), 5.52 (dd, \(J = 3.2, 6.0\) Hz, 1H), 6.95 (brd, \(J = 6.0\) Hz, 1H), 7.45-7.49(m, 4H), 7.56-7.59 (m, 1H), 7.75-7.77 (m, 2H), 8.18-8.20 (m, 2H); \(^1\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 53.2, 59.9, 74.9, 123.5, 126.9, 127.2, 128.9, 132.3, 132.6, 146.7, 147.7, 169.0, 169.3. HR-FABMS (NBA): calcd for C\(_{17}\)H\(_{17}\)N\(_2\)O\(_6\) (M+H\(^{+}\)): 345.1087. Found 345.1079.

HPLC analysis using CHIRALPAK AD-H and \(n\)-hexane/i-PrOH (65/35, 0.5 mL/min), Retention time for (2\(S\),3\(S\)) : 20.6 min [minor], for (2\(R\),3\(R\)) : 22.1 min [major];
Methyl 2-benzoylamino-3-(4-carbomethoxyphenyl)-3-hydroxypropionate (6k)

1. Ni(OAc)$_2$ (5 mol%), (R,S)-ligand 3g (5 mol%) H$_2$ (100 atm), NaOAc (1.0 eq), TFE / AcOH = 1 : 4 (0.2 M), MS3A, rt, 48 h
2. Bz$_2$O, Et$_3$N, THF

Prepared according to the typical procedure. 6k: colorless solids; 100% conversion yield and 82% isolated yield (two steps), $\text{anti:} \text{syn} = >99:1$, 88% ee; $[\alpha]_D^{18} = -112.7$ (c 1.00, CHCl$_3$) for 88% ee; mp 150-151.5 °C; IR (ATR) 3465, 2924, 1741, 1716, 1643, 1578, 1521, 1491, 1434, 1272 cm$^{-1}$; $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.82 (s, 3H), 3.91 (s, 3H), 4.91 (d, $J$ = 6.0 Hz, 1H), 5.25 (dd, $J$ = 3.2, 6.4 Hz, 1H), 5.47 (dd, $J$ = 3.2, 5.6 Hz, 1H), 6.90 (brd, $J$ = 7.2 Hz, 1H), 7.31 (d, $J$ = 8.0 Hz, 2H), 7.44 (t, $J$ = 7.6 Hz, 2H), 7.55 (d, $J$ = 8.4 Hz, 2H), 7.99 (d, $J$ = 8.4 Hz, 2H); 13C-NMR (100 MHz, CDCl$_3$) $\delta$ 52.1, 52.9, 59.7, 75.2, 125.9, 127.1, 128.8, 129.6, 129.9, 132.4, 132.7, 144.3, 166.8, 168.9, 169.5. HR-FABMS (NBA): calcd for C$_{19}$H$_{19}$NO$_6$ (M+H$^+$): 358.1291. Found 358.1263.

HPLC analysis using CHIRALPAK AD-H and $n$-hexane/i-PrOH (75/25, 0.5 mL/min), Retention time 34.0 min [major], 37.6 min [minor];

Methyl (2R,3R)-3-(benzo[1,3]dioxol-5-yl)-2-benzoylamino-3-hydroxypropionate (6l)

1. Ni(OAc)$_2$ (10 mol%), (R,S)-ligand 3g (10 mol%) H$_2$ (100 atm), NaOAc (1.0 eq), TFE / AcOH = 1 : 4 (0.2 M), MS3A, rt, 4 days
2. Bz$_2$O, Et$_3$N, THF

Prepared according to the typical procedure. 6l: colorless solids; 100% conversion yield and 90% isolated yield (two steps), $\text{anti:} \text{syn} = >99:1$, 89% ee; $[\alpha]_D^{18} = -94.9$ (c 1.32, CHCl$_3$) for 89% ee; mp 113-114.5 °C (recrystallized from ethyl acetate-$n$-hexane); IR (ATR) 3852, 3376, 2982, 1733, 1646, 1578, 1505, 1486, 1443, 1374 cm$^{-1}$; $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$ 1.28 (3H, t, $J$ = 7.2 Hz), 4.22 (2H, q, $J$ = 7.2 Hz), 4.73 (1H, br), 5.14 (1H, dd, $J$ = 3.6 Hz), 5.29 (1H, s), 5.92 (2H, s), 6.73 (2H, s), 6.79 (1H, s), 6.98 (1H, d, $J$ = 7.2 Hz), 7.41-7.46 (2H, m), 7.51-7.55 (1H, m), 7.75-7.77 (2H, m); 13C-NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 59.6, 62.2, 75.1, 101.0, 106.6, 108.0, 119.4, 127.2, 128.7, 132.2, 133.0, 147.3, 147.7, 168.7, 169.4. HR-FABMS (NBA): calcd for C$_{19}$H$_{19}$NO$_6$ (M+H$^+$): 358.1291. Found 358.1279.

HPLC analysis using CHIRALCEL OD-H and $n$-hexane/i-PrOH (75/25, 0.3 mL/min), Retention time for (2R,3R) : 38.7 min [major], (2S,3S) : 52.1 min [minor].

Methyl (2R,3R)-2-benzoylamino-3-hydroxy-3-(naphthalen-2-yl)-propionate (6m)

1. Ni(OAc)$_2$ (5 mol%), (R,S)-ligand 3g (5 mol%) H$_2$ (100 atm), NaOAc (1.0 eq), TFE / AcOH (1/4, 0.2 M), MS3A, rt, 24 h
2. Bz$_2$O, Et$_3$N, THF

Prepared according to the typical procedure. 6m: colorless solids; 100% conversion yield and 92% isolated yield (two steps), $\text{anti:} \text{syn} = >99:1$, 90% ee; $[\alpha]_D^{18} = -115.1$ (c 0.99, CHCl$_3$) for 90% ee; mp 134-136 °C (recrystallized from ethyl acetate-$n$-hexane); IR (ATR) 3465, 2924, 1741, 1716, 1643, 1578, 1521, 1491, 1434, 1272 cm$^{-1}$; $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.82 (s, 3H), 3.91 (s, 3H), 4.91 (d, $J$ = 6.0 Hz, 1H), 5.25 (dd, $J$ = 3.2, 6.4 Hz, 1H), 5.47 (dd, $J$ = 3.2, 5.6 Hz, 1H), 6.90 (brd, $J$ = 7.2 Hz, 1H), 7.31 (d, $J$ = 8.0 Hz, 2H), 7.44 (t, $J$ = 7.6 Hz, 2H), 7.55 (d, $J$ = 8.4 Hz, 2H), 7.99 (d, $J$ = 8.4 Hz, 2H); 13C-NMR (100 MHz, CDCl$_3$) $\delta$ 52.1, 52.9, 59.7, 75.2, 101.0, 106.6, 108.0, 119.4, 127.2, 128.7, 132.2, 133.0, 133.1, 147.3, 147.7, 168.7, 169.4. HR-FABMS (NBA): calcd for C$_{19}$H$_{19}$NO$_6$ (M+H$^+$): 358.1291. Found 358.1279. 

HPLC analysis using CHIRALPAK AD-H and $n$-hexane/i-PrOH (75/25, 0.5 mL/min), Retention time 34.0 min [major], 37.6 min [minor];
from ethyl acetate-\textit{n}-hexane); IR (KBr) \(3333, 1741, 1523, 1488, 1437, 1363\) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 52.7, 59.6, 75.4, 123.7, 125.1, 126.1, 126.2, 128.0, 128.1, 128.7, 133.0, 133.1, 133.2, 136.6, 168.7, 169.9; LR-FABMS (NBA) \(m/z\) 350 (M\(^{+}\)H\(^{+}\)). Anal. calcd for C\(_{21}\)H\(_{19}\)NO\(_4\) \(\cdot\) 1/2 H\(_2\)O: C, 70.38; H, 5.62; N, 3.91. Found: C, 68.28; H, 6.18; N, 4.37.

HPLC analysis using CHIRALPAK AD-H and \(n\)-hexane/\(i\)-PrOH (75/25, 0.5 mL/min), Retention time for (2\(S\),3\(S\)) : 27.9 min [minor], for (2\(R\),3\(R\)) : 29.5 min [major];

\textbf{Methyl (2\(R\),3\(S\))-2-benzoylamino-3-hydroxy-3-(thiophen-2-yl)-propionate (6\(n\))}

\begin{center}
\includegraphics[width=0.5	extwidth]{methyl-2-benzoylamino-3-hydroxy-3-(thiophen-2-yl)-propionate.png}
\end{center}

Prepared according to the typical procedure. 6\(n\): colorless solids; 100% conversion yield and 79% isolated yield (two steps), \textit{anti}:\textit{syn} = >99:1, 95% ee; \([\alpha]_D^{18} = -78.2\) (c 1.02, CHCl\(_3\)) for 95% ee; mp 129-130 °C (recrystallized from ethyl acetate-\textit{n}-hexane); IR (KBr) 3408, 3354, 1727, 1643, 1526, 1279 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 53.0, 59.4, 72.2, 124.3, 125.3, 126.7, 127.2, 128.7, 132.3, 132.9, 142.4, 169.1, 169.4. HR-FABMS (NBA) calcd for C\(_{15}\)H\(_{15}\)NO\(_4\)S: 306.0800 (M\(^{+}\)H\(^{+}\)). Found: 306.0785. Anal. calcd for C\(_{15}\)H\(_{15}\)NO\(_4\)S: C, 59.00; H, 4.95; N, 4.59. Found: C, 58.83; H, 4.93; N, 4.41.

HPLC analysis using CHIRALCEL OD-H and \(n\)-hexane/\(i\)-PrOH (75/25, 0.3 mL/min), Retention time for (2\(R\),3\(S\)) : 28.7 min [major], for (2\(S\),3\(R\)) : 36.2 min [minor];

\textbf{Methyl (2\(R\),3\(S\))-2-benzoylamino-3-hydroxy-3-(cyclohexyl)-propionate (6\(o\))}

\begin{center}
\includegraphics[width=0.5	extwidth]{methyl-2-benzoylamino-3-hydroxy-3-(cyclohexyl)-propionate.png}
\end{center}

Prepared according to the typical procedure. 6\(o\): colorless solids; 16% isolated yield (2 steps), \textit{anti}:\textit{syn} = >99:1, 81% ee; mp 94-97 °C; IR (KBr) 3548, 3493, 3281, 2927, 2854, 1739, 1630, 1542, 1363, 1230, 1209 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.97-1.30 (m, 5H), 1.42-1.51 (m, 1H), 1.65-1.84 (m, 4H), 2.03-2.06 (m, 1H), 2.94 (d, \(J = 8.4\) Hz, 1H), 3.68 (dt, \(J = 3.2, 8.8\) Hz, 1H), 4.07 (dd, \(J = 3.2, 7.6\) Hz, 1H), 7.18 (d, \(J = 7.2\) Hz, 1H), 7.44-7.47 (m, 2H), 7.51-7.56 (m, 1H), 7.82-7.84 (m, 2H). Anal. calcd for C\(_{17}\)H\(_{23}\)NO\(_4\): C, 66.86; H 7.59; N 4.59. Found: C 66.68; H 7.49; N 4.55.

HPLC analysis using CHIRALCEL OD-H and \(n\)-hexane/\(i\)-PrOH (85/15, 0.5 mL/min), Retention time for (2\(R\),3\(R\)) : 11.0 min [major], (2\(S\),3\(S\)) : 15.2 min [minor].