Supplementary Information

A Chiral Ferrocene-Tethered Ruthenium Diamine Catalyst

for Asymmetric Transfer Hydrogenation of Ketones

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Table of Content

1.General information and materials	3
2. General procedure for synthesizing Ru catalyst	3
3. General procedures for Ru-catalyzed asymmetric transfer hydrogenation of ketones	7
4. Analytical data of alcohol products from Ru-catalyzed ATH	8
5. References	.49
6. NMR Spectra	.50

1. General information and materials:

¹H, ¹³C and ¹⁹F NMR data were recorded on Bruker DRX500 or DRX400 NMR Spectrometer with CDCl₃ or DMSO as solvent. ¹³C NMR chemical shifts were obtained with ¹H decoupling. MS was measured on Agilent 1100 series LC/MSD, Thermo Fisher LTQ FT, Agilent 5973N and Waters Micromass G1540/GCT Premier spectrometers. High resolution mass spectra (HRMS) were recorded on a Bruker APEXIII 7.0 Tesla ESI-FT. Enantiomeric excesses were determined with Agilent Series HPLC using AD-3, OD-H, OD-3, OJ-H, OJ-3, IC, IC-3 chiral columns. Optical rotations were measured on a Rudolph-Autopol I instrument. All reagents were used as received from commercial sources, unless otherwise specified. All reactions and manipulations sensitive to moisture or air were performed in a nitrogen-filled glovebox or using standard Schlenk techniques, unless otherwise noted. Analytical thin-layer chromatography (TLC) was carried out with silica gel pre-coated glass plates (TLC-Silica gel GF254, coating thickness: 0.20-0.25 mm, particle size: 10-40 μ m). The TLC was visualized with a UV lamp (254 or 365 nm). Column chromatography was performed with silica gel (200-300 mesh).



2. General procedure for synthesizing Ru catalyst:

Synthesis of 1-2¹

Ferrocene formaldehyde (1-1) (2.14 g, 10 mmol, 1.0 equiv) was dissolved in dry trimethoxymethane (12 mL) and then PTSA (86 mg, 0.5 mmol, 5% equiv) was added. The resulting mixture was stirred at 80 °C overnight. K₂CO₃ (1.66 g, 12 mmol, 1.2 equiv) was added and the mixture was further stirred at room temperature (monitored by TLC). Upon completion of the reaction, the reaction

mixture was partitioned between ethyl acetate (30 mL) and water (20 mL). The organic layer was separated and the aqueous lay was extracted with EA (3×20 mL). The organic phases were combined, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure.

The above crude reside was dissolved in CHCl₃ (15 mL). Activated molecular sieves (4 Å) (6 g), (2*R*)-1,2,4-butanetriol² (0.89 mL, 10 mmol, 1.0 equiv), and (±)-CSA (116 mg, 0.5 mmol, 5% equiv) were added. After the reaction mixture being stirred at room temperature for 20 h, K₂CO₃ (1.66 g, 12 mmol, 1.2 equiv) was added and then the mixture was stirred for 20 minutes. After completion of the reaction, the mixture was partitioned between ethyl acetate (30 mL) and water (30 mL). The organic layer was separated and the aqueous lay was extracted with EA (3 × 20 mL). The organic phases were combined, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was firstly purified by recrystallization (-20 °C for 2-3 days), and then by silica gel column chromatography to give compound **1-2** (1.92 g, yellow solid, 64% yield). **¹H NMR** (500 MHz, Chloroform-*d*) δ 5.34 (s, 1H), 4.38 (s, 2H), 4.23 (s, 5H), 4.20 (s, 2H), 3.97 - 3.85 (m, 2H), 3.63 (dd, *J* = 24.3, 9.4 Hz, 2H), 2.12 (s, 1H), 1.81 (qd, *J* = 12.3, 4.8 Hz, 1H), 1.38 (d, *J* = 12.9 Hz, 1H); ¹³C **NMR** (126 MHz, Chloroform-*d*) δ 100.3, 86.2, 69.5, 69.0, 68.7, 67.2, 67.0, 66.6, 65.8, 26.9; **HRMS (MALDI)** calculated for [M, C₁₅H₁₈O₃Fe]⁺: 302.1510; found: 302.7454.

Synthesis of 1-3²: Alcohol 1-2 (1.81 g, 6 mmol, 1.0 equiv) was dissolved in dry THF (15 mL). NaH (360 mg, 60 wt%, 9 mmol, 1.5 equiv) was slowly added at 0 °C and the mixture was stirred for 1.5 hours. MeI (0.56 mL, 9 mmol, 1.5 equiv) was slowly added at 0 °C and the reaction mixture was allowed to warm to room temperature and stirred overnight. Upon complete conversion of substrate, the reaction was quenched with H₂O (20 mL). The mixture was extracted with EA (3×25 mL). The organic phases were combined, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (PE: EA = 15:1) to give compound 1-3 (1.8 g, auburn oil, 95% yield.). ¹H NMR (500 MHz, Chloroform-*d*) δ 5.37 (s, 1H), 4.41 - 4.07 (m, 9H), 4.05 - 3.84 (m, 2H), 3.61 - 3.49 (m, 1H), 3.43 (s, 3H), 1.85 - 1.69 (m, 1H), 1.48 (d, *J* = 12.4 Hz, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 100.2, 86.1, 76.2, 75.7, 69.0, 68.0, 67.9, 66.8, 66.8, 66.7, 59.6, 28.1; HRMS (MALDI) calculated for [M, C₁₆H₂₀O₃Fe]⁺: 316.1780; found: 316.7006.

Synthesis of 1-4³: An oven dried 100 mL three necked flask was charged with compound 1-3 (1.58 g, 5 mmol, 1.0 equiv). The system was evacuated under high vacuum and back-filled with N₂ for three times. Anhydrous THF (20 mL) was added and the mixture was cooled to 0 °C. *t*-BuLi (4.7 mL, 6 mmol, 1.2 equiv, 1.3 M in pentane) was added dropwise over 15 minutes and then the reaction was allowed to warm to room temperature and stirred for 2 h. The flask was put in an ice/water bath and 1,2-dibromotetrafluoroethane (0.9 mL, 7.5 mmol, 1.5 equiv) was added dropwise. After completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. Afterwards, the reaction was quenched with H₂O (30 mL). The mixture was extracted with DCM (3×25 mL). The organic phases were combined, washed once with saturated NaCl solution (20 mL), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure give crude compound 1-4 which was used in the next step without further purification (dark red oil).

Synthesis of 1a³: The crude compound 1-4 was dissolved in DCM (15 mL)/H₂O (5 mL) and PTSA (856 mg, 5 mmol, 1.0 equiv) was added. The mixture was stirred at room temperature until completion of the reaction. The reaction mixture was partitioned between DCM (15 mL) and water (10 mL). The organic layer was separated, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (PE: EA = 20:1) to give compound 1a (792 mg, dark red oil, 54% yield over two steps). ¹H NMR (500 MHz, Chloroform-*d*) δ 10.16 (s, 1H), 4.82 (d, *J* = 15.6 Hz, 2H), 4.59 (s, 1H), 4.32 (s, 5H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 193.2, 80.3, 75.8, 75.2, 72.4, 71.4, 66.8; HRMS (MALDI) calculated for [M, C₁₁H₉BrOFe]⁺: 292.9410; found: 292.5322.

Synthesis of 1-5: An oven dried 50 mL Schlenk flask equipped with a magnetic stir bar was charged with **1a** (1.18 g, 4 mmol, 1.0 equiv), 4-methoxyphenylboronic acid (912 mg, 6 mmol, 1.5 equiv), $Pd(OAc)_2$ (90 mg, 0.4 mmol, 10% equiv), SPhos (197 mg, 0.48 mmol, 12% equiv), and K_3PO_4 (2.55 g, 12 mmol, 3.0 equiv). The system was evacuated under high vacuum and back-filled with N₂ for three times. Degassed THF (12 mL) and H₂O (3 mL) were added and the mixture was stirred at 60 °C for 12 h. The reaction mixture was cooled to rt, filtered through a layer of Celite and the solid was washed with ethyl acetate (3 × 5 mL). The filtrate was concentrated under reduced pressure and

the crude residue was purified by silica gel column chromatography (PE: EA = 6:1) to give the compound **1-5** (1.17 g, dark red viscous oil, 91% yield). ¹**H** NMR (500 MHz, Chloroform-*d*) δ 10.19 (s, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 4.97 (d, *J* = 2.3 Hz, 1H), 4.78 (s, 1H), 4.68 (d, *J* = 2.9 Hz, 1H), 4.24 (s, 5H), 3.85 (s, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 193.3, 159.0, 130.8, 127.9, 113.8, 92.8, 76.6, 74.6, 71.9, 71.1, 68.3, 55.5; **HRMS (MALDI)** calculated for [M, C₁₈H₁₆O₂Fe]⁺: 320.1690; found: 320.7240.

Synthesis of (*R*,*R*,*S_{Fe}*)-1b: Compound 1-5 (384 mg, 1.2 mmol, 1.0 equiv) and (1*R*, 2*R*)-N-(4-toluenesulfonyl)-1,2-diphenylethylenediamine (440 mg, 1.2 mmol, 1.0 equiv) were dissolved in MeOH (6 mL) and the reaction solution was stirred at 50 °C for 2 h. After the reaction mixture being cooled to room temperature, NaBH₄ (92 mg, 2.4 mmol, 2.0 equiv) was added and the mixture was stirred for additional 2 h. Upon completion of the reaction, the reaction was quenched with H₂O (20 mL). The mixture was extracted with DCM (3 × 20 mL). The organic phases were combined, washed once with saturated NaCl solution (20 mL), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (PE: EA = 4:1) to give compound (*R*,*R*,*S_{Fc}*)-1b (732 mg, yellow solid, 91% yield). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 6.6 Hz, 2H), 7.20 - 6.86 (m, 12H), 6.79 (d, *J* = 8.0 Hz, 2H), 4.44 (s, 1H), 4.28 (d, *J* = 31.5 Hz, 3H), 4.05 (s, 5H), 3.83 (s, 3H), 3.79 - 3.68 (m, 1H), 3.58 - 3.39 (m, 2H), 2.33 (s, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 158.2, 142.6, 138.1, 137.0, 130.0, 129.9, 129.1, 128.4, 128.0, 127.6, 127.5, 127.4, 127.3, 127.0, 113.5, 70.4, 69.9, 69.6, 67.4, 62.7, 55.3, 45.4, 21.5; HRMS (MALDI) calculated for [M, C₃₉H₃₈N₂O₃SFe]⁺: 670.6490; found: 670.5936.

Synthesis of Ru-1⁴: An oven dried 50 mL Schlenk tube was charged with compound (R,R, S_{Fc})-1b (537 mg, 0.8 mmol, 2.0 equiv) and dimeric Ru complex 1-6⁵ (258 mg, 0.4 mmol, 1.0 equiv). The system was evacuated under high vacuum and back-filled with N₂ for three times. Anhydrous PhCl (8 mL) was added under N₂ and the mixture was stirred at 60 °C for 1 h. Then the mixture was heated to 100 °C and stirred for additional 10 h. Upon completion of the reaction, the mixture was cooled to room temperature and filtered through a layer of Celite. The solid was washed with DCM (3 × 5 mL) and the filtrate was concentrated under reduced pressure. The crude Ru complex was

firstly purified by silica gel column chromatography (DCM: EA = 6:1, DCM: MeOH = 30:1) and then recrystallization in DCM/MTBE to give catalyst **Ru-1** (335 mg, brown solid, 52% yield). ¹**H NMR** (500 MHz, DMSO-*d*₆) δ 7.20 - 7.00 (m, 8H), 6.77 (d, *J* = 7.5 Hz, 2H), 6.70 - 6.59 (m, 2H), 6.55 (d, *J* = 7.2 Hz, 1H), 6.48 (s, 1H), 5.69 (s, 1H), 5.49 (s, 1H), 5.36 (s, 1H), 4.51 (s, 1H), 4.33 -4.20 (m, 7H), 4.16 - 3.99 (m, 4H), 3.80 (s, 3H), 2.18 (s, 3H); ¹³**C NMR** (126 MHz, DMSO-*d*₆) δ 145.5, 139.6, 138.0, 137.9, 137.4, 133.8, 132.7, 130.0, 129.7, 129.2, 129.0, 128.6, 128.4, 127.8, 126.7, 126.5, 126.1, 126.0, 90.1, 86.2, 83.9, 82.8, 82.7, 78.1, 70.8, 70.6, 70.5, 70.4, 68.2, 67.3, 66.3, 63.6, 57.0, 50.5, 21.2; **HRMS (MALDI)** calculated for [M-Cl, C₃₉H₃₇FeN₂O₃RuS]⁺: 770.7110; found: 770.5443; [M, C₃₉H₃₇ClFeN₂O₃RuS]⁺: 806.1610; found: 806.5259.

3. General procedures for Ru-catalyzed asymmetric transfer hydrogenation of ketones.

General procedure



Ketone (0.2 mmol, 1.0 equiv) and catalyst **Ru-1** (2 mol%) was added into a dry Schlenk tube equipped with a magnetic stir bar. The system was evacuated under high vacuum and back-filled with N_2 for three times. Anhydrous THF (1 mL) was added, followed by the addition of a mixture of HCOOH/TEA (5:2) (0.15 mL). The mixture was stirred at 60 °C for indicated time. After the reaction was completed, the mixture was concentrated under vacuum and purified by silica gel column chromatography to give the corresponding alcohol product. The ee values were determined by chiral HPLC. The ee values of product **51**, **7g** and **7h** were obtained by measuring the ees of their benzoylated derivatives by chiral HPLC.

Derivatization method⁶ of 5l, 7g and 7h for HPLC analysis



The chiral alcohol product was dissolved in DCM (1 mL) and then DMAP (1.2 equiv), TEA (2.0 equiv), and BzCl (1.2 equiv) was added sequentially. The mixture was stirred at room temperature. Upon completion, the mixture was concentrated under vacuum and the crude product was purified by silica gel column chromatography to give pure benzoylated product for chiral HPLC analysis.

Procedure for gram scale reaction



Ru-1 (4.0 mg, 0.025 mol%) was added to a 50 mL Schlenk tube under N₂. Then distilled acetophenone (2.4 g, 20 mmol, 1.0 equiv), 1 mL dry THF, and 4 mL degassed HCOOH/TEA (5:2) azeotrope were added. The mixture was stirred at 60 °C for 24 hours and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give alcohol **3a** in 83% yield and 97% ee.

4. Analytical data of alcohol products from Ru-catalyzed ATH

(*R*)-1-Phenylethanol (3a) 7

Colorless oil, 95% yield, 98% ee; $[\alpha]_D^{25}$: 44.7 (c = 0.51, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.41 - 7.32 (m, 4H), 7.32 - 7.24 (m, 1H), 4.90 (q, *J* = 6.5 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 145.9, 128.6,

127.6, 125.5, 70.6, 25.3; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-H column (hexane : isopropanol = 95 : 5, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 10.8 min (major), t_R = 13.1 min (minor).



(*R*)-1-(4-Nitrophenyl) Ethanol (3b)⁹

Colorless oil, 95% yield, 90% ee; $[\alpha]_D^{25}$: 26.7 (c = 2.47, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 5.6 Hz, 2H), 7.53 (d, *J* = 5.6 Hz, 2H), 5.01 (q, *J* = 8.6, 7.3 Hz, 1H), 2.12 (s, 1H), 1.50 (d, *J* = 3.5 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 153.2, 147.2, 126.2, 123.9, 69.6, 25.6; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 90 : 10, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 25.3 min (minor), t_R = 27.3 min (major).





(*R*)-1-(4-Methoxyphenyl) Ethanol $(3c)^7$









(*R*)-1-(2-Methylphenyl) Ethanol $(3d)^7$



MHz, Chloroform-*d*) δ 143.9, 134.3, 130.5, 127.3, 126.5, 124.6, 66.9, 24.1, 19.1; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak AD-3 column (hexane : isopropanol = 97 : 3, flow rate = 0.6 mL/min, T = 20 °C, λ = 210 nm), t_R = 26.0 min (major), t_R = 29.9 min (minor).



(R)-1-(4-Bromophenyl) Ethanol (3e)⁸



Chloroform-*d*) δ 144.9, 131.7, 127.3, 121.3, 69.9, 25.4; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak IC column (hexane : isopropanol = 96 : 4, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 10.3 min (major), t_R = 11.0 min (minor).



(R)-1-(3-Bromophenyl) Ethanol (3f)⁷

 $\begin{array}{c} \begin{array}{l} \label{eq:Br} {\sf OH} \\ \mbox{Br} \\ \mbox{Hz, Chloroform-}d) \ \delta \ 7.52 \ ({\rm s}, \ 1{\rm H}), \ 7.39 \ ({\rm d}, \ J=7.8 \ {\rm Hz}, \ 1{\rm H}), \ 7.27 \ ({\rm d}, \ J=7.5 \ {\rm Hz}, \ 1{\rm H}), \ 7.20 \ ({\rm t}, \ J=7.7 \ {\rm Hz}, \ 1{\rm H}), \ 4.83 \ ({\rm q}, \ J=6.3 \ {\rm Hz}, \ 1{\rm H}), \ 2.30 \ ({\rm s}, \ 1{\rm H}), \ 1.46 \ ({\rm d}, \ J=7.5 \ {\rm Hz}, \ 1{\rm H}), \ 5.20 \ ({\rm s}, \ 1{\rm H}), \ 5$

J = 9.7 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 148.2, 130.5, 130.2, 128.7, 124.1, 122.7,

69.8, 25.3; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-3 column (hexane : isopropanol = 95 : 5, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 10.7 min (minor), t_R = 12.0 min (major).



(R)-1-(2-Bromophenyl) Ethanol (3g)¹⁰



¹³C NMR (126 MHz, Chloroform-*d*) δ 144.7, 132.8, 128.9, 128.0, 126.8, 121.8, 69.3, 23.7; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-3 column (hexane : isopropanol = 95 : 5, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 9.0 min (major), t_R = 9.8 min (minor).



(R)-1-(4-Bromophenyl)-2-Phenylethanol (3h)⁸





(R)-5-Methoxy-1-Indenol (3i)⁷

Colorless oil, 95% yield, 96% ee; $[a]_D^{25}$: -20.6 (c = 1.69, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.9 Hz, 1H), 6.79 (dd, *J* = 5.8, 2.5 Hz, 2H), 5.19 (dd, *J* = 6.6, 4.5 Hz, 1H), 3.80 (s, 3H), 3.05 (ddd, *J* = 16.1, 8.5, 5.5 Hz, 1H), 2.79 (ddd, *J* = 15.5, 8.4, 5.9 Hz, 1H), 2.47 (dddd, *J* = 13.6, 8.5, 6.7, 5.4 Hz, 1H), 1.96 (dddd, *J* = 13.2, 8.5, 5.9, 4.6 Hz, 1H), 1.78 (s, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 158.9, 138.7, 131.3, 130.2, 113.4, 112.6, 67.7, 55.3, 32.5, 29.7, 18.7; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak IC column (hexane : isopropanol = 95 : 5, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 18.6 min (minor), t_R = 20.9 min (major).



(*R*)-6-Methoxy-1,2,3,4-Tetrahydronaphthalen-1-ol $(3j)^7$

Colorless oil, 95% yield, 98% ee; $[\alpha]_D^{25}$: -18.1 (c = 3.01, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.3 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 4.74 (t, *J* = 3.2 Hz, 1H), 3.79 (s, 3H), 2.84 - 2.75 (m, 1H), 2.75 - 2.65 (m, 1H), 2.00 - 1.87 (m, 3H), 1.77 (qd, *J* = 10.7, 8.2, 3.2 Hz, 2H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 160.3, 145.4, 137.4, 125.2, 113.1, 109.9, 76.0, 55.5, 36.4, 30.1; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-H column (hexane : isopropanol = 96 : 4, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 24.9 min (minor), t_R = 27.9 min (major).



(*R*)- 1,2,3,4-Tetrahydro-1-Naphthol $(3k)^7$

Colorless oil, 91% yield, 98% ee; $[\alpha]_{D}^{25}$: -30.7 (c = 2.15, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.43 (dt, *J* = 6.6, 2.0 Hz, 1H), 7.20 (dq, *J* = 7.7, 3.1, 2.6 Hz, 2H), 7.11 (dt, *J* = 6.0, 1.9 Hz, 1H), 4.78 (t, *J* = 4.0 Hz, 1H), 2.83 (dt, *J* = 17.0, 5.6 Hz, 1H), 2.73 (dt, *J* = 17.0, 6.8 Hz, 1H), 2.03 - 1.93 (m, 2H), 1.91 (ddd, *J* = 10.5, 7.8, 5.4 Hz, 1H), 1.82 - 1.73 (m, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 138.9, 137.2, 129.1, 128.8, 127.7, 126.3, 68.2, 32.4, 29.4, 18.9; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak IC column (hexane : isopropanol = 96 : 4, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 10.1 min (minor), t_R = 11.5 min (major).



(R)-3,4-Dihydro-2H-1-Benzopyran-4-ol $(3l)^7$

White solid, 99% yield, >99% ee; $[\alpha]_D^{25}$: 68.3 (c = 2.84, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.6 Hz, 1H), 7.21 (dd, *J* = 8.4, 7.2 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.80 (t, *J* = 4.0 Hz, 1H), 4.27 (dd, *J* = 9.1, 3.1 Hz, 2H), 2.19 - 2.08 (m, 1H), 2.04 (dq, *J* = 14.4, 3.6 Hz, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 154.7, 129.8, 129.8, 124.4, 120.7, 117.2, 63.4, 62.0, 30.9; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-H column (hexane : isopropanol = 96 : 4, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 19.6 min (minor), t_R = 23.9 min (major).



(*R*)-1-(2-Naphthyl) Ethanol $(3m)^7$



143.3, 133.4, 133.0, 128.4, 128.0, 127.8, 126.3, 125.9, 123.9, 123.9, 70.6, 25.3; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-H column (hexane : isopropanol = 90 : 10, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 16.5 min (minor), t_R = 21.6 min (major).



(*R*)-Naphthyl-1-Ethanol $(3n)^7$

HO Colorless oil, 99% yield, 98% ee; $[\alpha]_D^{25}$: 53.8 (c = 3.30, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 7.1 Hz, 1H), 7.51 (dq, *J* = 15.0, 7.6, 7.1 Hz, 3H), 5.66 (q, *J* = 6.6 Hz, 1H), 1.67 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 141.4, 133.9, 130.3, 129.0, 128.0, 126.1, 125.6, 125.6, 123.3, 122.1, 67.2, 24.5; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-H column (hexane : isopropanol = 90 : 10, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 10.9 min (minor), t_R = 18.6 min (major).



[(*R*)-1-Hydroxyethyl] Ferrocene (30)⁷



Red solid, 99% yield, 98% ee; $[\alpha]_D^{25}$: -27.0 (c = 4.17, CHCl₃); ¹H NMR (500 MHz, Chloroform-d) δ 4.55 (d, J = 7.0 Hz, 1H), 4.27 - 4.04 (m, 9H), 1.86 (s, 1H), 1.44 (d, J = 6.3 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 94.9, 68.4, 68.1, 68.0, 66.3, 66.2, 65.7, 23.9; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak IC-3 column (hexane : isopropanol = 97 : 3, flow rate = 1 mL/min, T = 20 °C, λ = 210

nm), $t_R = 22.8 \text{ min (minor)}, t_R = 28.4 \text{ min (major)}.$



(R)-2-(1-Hydroxyethyl) Pyridine (3p)¹¹



isopropanol = 97 : 3, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 16.8 min (major), t_R = 20.0 min (minor).



(*R*)-1-(3-Pyridyl) Ethanol $(3q)^9$

Colorless oil, 92% yield, 90% ee; $[\alpha]_D^{25}$: 38.5 (c = 1.60, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 41.5 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 5.7 Hz, 1H), 4.92 (q, *J* = 6.6 Hz, 1H), 1.49 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 148.3, 147.1, 141.6, 133.7, 123.8, 67.9, 25.3; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-H column (hexane : isopropanol = 90 : 10, flow rate = 1 mL/min, T = 20 °C, λ = 254 nm), t_R = 9.2 min (minor), t_R = 11.8 min (major).



(*R*)-1-(2-Thienyl) Ethanol $(3r)^7$

OH Colorless oil, 94% yield, 98% ee; $[a]_D^{25}$: 24.7 (c = 1.63, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.27 - 7.21 (m, 1H), 7.01 - 6.93 (m, 2H), 5.14 (q, *J* = 6.5, 5.6 Hz, 1H), 2.02 (br, 1H), 1.61 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 150.0, 126.8, 124.6, 123.3, 66.4, 25.4; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak IC-3 column (hexane : isopropanol = 97 : 3, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 20.9 min (minor), t_R = 23.4 min (major).





(*R*)-1-Phenyl-1-Butanol (3s)⁷





(R)-1-Phenyl-1-Cyclohexyl-Mathanol (3t)⁷



Colorless oil, 28% yield, 76% ee; $[\alpha]_D^{25}$: 29.6 (c = 0.32, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.41 - 7.23 (m, 5H), 4.37 (d, *J* = 7.2 Hz, 1H), 2.04 - 1.95 (m, 1H), 1.81 - 1.71 (m, 2H), 1.67 - 1.56 (m, 2H), 1.39 - 1.34 (m, 1H), 1.29 - 0.86 (m, 6H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 143.7, 128.3, 127.6, 126.8, 79.5, 45.1,

29.4, 29.0, 26.5, 26.2, 26.1; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-3 column (hexane : isopropanol = 95 : 5, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), $t_R = 9.6 \text{ min}$ (minor), $t_R = 11.6 \text{ min}$ (major).



#	Time	Area	Height	Width	Area%	Symmetry
1	9.55	804.5	53.2	0.2204	11.618	0.562
2	11.621	6119.6	327.2	0.2722	88.382	0.511

(R)-2-Methyl-1-Phenyl-1-Propanol (3u)⁷



¹³C NMR (126 MHz, Chloroform-*d*) δ 143.7, 128.2, 127.4, 126.7, 80.0, 35.3, 19.0, 18.4; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-3 column (hexane : isopropanol = 95 : 5, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 9.0 min (minor), t_R = 10.7 min (major).



(R)-1,2,3,4-Tetrahydro-6-Methoxy-2-Naphthalenol (5a)¹²



Colorless oil, 98% yield, 96% ee; $[\alpha]_D^{25}$: 45.6 (c = 3.07, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.00 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.71 (dd, J = 8.5, 2.7 Hz, 1H), 6.64 (d, J = 2.6 Hz, 1H), 4.16 - 4.12 (m, 1H), 3.78 (s, 3H), 3.06 - 2.99 (m, 1H), 2.97 - 2.89 (m, 1H), 2.82 (dt, J = 16.6, 7.5 Hz, 1H), 2.74 - 2.65 (m, 1H), 2.07 - 2.00 (m, 1H), 1.86 - 1.76 (m, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 158.0, 136.9, 130.5, 126.4, 113.3, 112.4, 67.6, 55.4, 37.8, 31.5, 27.4; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 96 : 4, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 35.7 min (major), t_R = 45.5 min (minor).



(R)-5-Methoxy-1,2,3,4-Tetrahydronahthalen-2-ol (5b)¹²



"OH

White solid, 99% yield, 94% ee; $[\alpha]_D^{25}$: 54.1 (c = 2.94, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.14 - 7.08 (m, 1H), 6.69 (dd, *J* = 17.0, 7.9 Hz, 2H), 4.17-4.08 (m, 1H), 3.82 (s, 3H), 3.06 (d, *J* = 12.7 Hz, 1H), 2.91 (dt, *J* = 17.9,

5.8 Hz, 1H), 2.76 (dd, *J* = 16.2, 8.1 Hz, 1H), 2.70 - 2.61 (m, 1H), 2.11 - 2.02 (m, 1H), 1.83 - 1.75 (m, 1H), 1.73 - 1.67 (m, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 157.2, 135.7, 126.6, 124.6, 121.8, 107.3, 67.2, 55.4, 38.5, 31.2, 21.3; The enantiomeric excess was determined by chiral HPLC

analysis on Chiralpak OJ-3 column (hexane : isopropanol = 96 : 4, flow rate = 1 mL/min, T = 20 °C, $\lambda = 210$ nm), t_R = 20.4 min (major), t_R = 22.5 min (minor).



(R)-7-Methoxy-1,2,3,4-Tetrahydronahthalen-2-ol (5c)¹²

MeO , OH White solid, 90% yield, 93% ee; $[\alpha]_{D}^{25}$: 33.1 (c = 2.89, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.01 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.70 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.62 (d, *J* = 2.5 Hz, 1H), 4.19 - 4.10 (m, 1H), 3.78 (s, 3H), 3.06 (d, *J* = 12.3 Hz, 1H), 2.89 (dt, *J* = 16.9, 5.8 Hz, 1H), 2.77 (td, *J* = 15.7, 8.2 Hz, 2H), 2.09 - 1.99 (m, 1H), 1.84 - 1.75 (m, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 157.8, 135.5, 129.6, 127.8, 114.0, 112.5, 67.3, 55.4, 38.7, 31.8, 26.2; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 90 : 10, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 15.0 min (major), t_R = 20.0 min (minor).



(*R*)-7-Chloro-1,2,3,4-Tetrahydronahthalen-2-ol (5d)¹²

Cloreless oil, 97% yield, 90% ee; $[\alpha]_D^{25}$: 41.8 (c = 3.03, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.11 - 7.05 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 1H), 4.20 - 4.11 (m, 1H), 3.03 (dd, *J* = 16.4, 5.0 Hz, 1H), 2.93 (dt, *J* = 17.2, 5.9 Hz, 1H), 2.85 - 2.74 (m, 1H), 2.71 (dd, *J* = 16.3, 7.6 Hz, 1H), 2.08 - 1.97 (m, 1H), 1.87 - 1.75 (m, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 137.6, 132.7, 131.6, 130.9, 128.5, 126.1, 67.0, 37.8, 31.1, 26.8; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 96 : 4, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 19.2 min (major), t_R = 22.1 min (minor).



(R)-6-Bromo-1,2,3,4-Tetrahydronahthalen-2-ol (5e)¹³

 $\begin{array}{l} \textbf{OH} \quad \text{Yellow oil, 94\% yield, 91\% ee; } [\textbf{a}]_{\textbf{D}}^{\textbf{25}} : 44.3 \ (\text{c} = 1.10, \text{CHCl}_3); \ ^1\textbf{H} \ \textbf{NMR} \\ (500 \ \text{MHz, Chloroform-}d) \ \delta \ 7.28 - 7.18 \ (\text{m}, 2\text{H}), \ 6.94 \ (\text{d}, J = 8.0 \ \text{Hz}, 1\text{H}), \\ 4.19 - 4.09 \ (\text{m}, 1\text{H}), \ 3.01 \ (\text{d}, J = 16.3 \ \text{Hz}, 1\text{H}), \ 2.93 \ (\text{dt}, J = 17.2, \ 5.9 \ \text{Hz}, 1\text{H}), \ 2.79 \ (\text{dt}, J = 16.2, \ 7.3 \ \text{Hz}, 1\text{H}), \ 2.69 \ (\text{dd}, J = 16.4, \ 7.5 \ \text{Hz}, 1\text{H}), \ 2.06 - 1.97 \ (\text{m}, 1\text{H}), \ 1.87 - 1.78 \ (\text{m}, 2\text{H}); \ ^{13}\textbf{C} \ \textbf{NMR} \ (126 \ \text{MHz}, \ \text{Chloroform-}d) \ \delta \ 138.1, \ 133.3, \ 131.4, \ 131.2, \ 129.0, \ 119.6, \ 66.9, \ 37.9, \ 31.1, \ 26.7; \ \text{The} \ \text{enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 97 : 3, flow rate = 0.8 \ \text{mL/min}, \ T = 20 \ ^{\circ}\text{C}, \ \lambda = 210 \ \text{nm}), \ t_{\text{R}} = 32.8 \ \text{min} \ (\text{major}), \ t_{\text{R}} = 38.4 \ \text{min} \ (\text{minor}). \end{array}$



(R)-8-Bromo-1,2,3,4-Tetrahydronahthalen-2-ol (5f)¹³

Br Colorless oil, 95% yield, 97% ee; $[\alpha]_D^{25}$: 30.1 (c = 2.80, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 4.24 - 4.16 (m, 1H), 3.14 (dd, *J* = 17.2, 5.1 Hz, 1H), 2.98 (dt, *J* = 17.0, 5.8 Hz, 1H), 2.88 - 2.78 (m, 1H), 2.70 (dd, *J* = 17.2, 7.1 Hz, 1H), 2.05 - 1.95 (m, 1H), 1.86 - 1.80 (m, 1H), 1.78 (s, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 138.5, 134.1, 130.2, 127.9, 127.2, 125.9, 67.2, 39.2, 30.8, 27.4; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 97 : 3, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 23.2 min (major), t_R = 28.6 min (minor).



(R)-6,8-Difluoro-1,2,3,4-Tetrahydronahthalen-2-ol (5g)¹⁴



White solid, 99% yield, 94% ee; $[\alpha]_{D}^{25}$: 34.8 (c = 3.31, CHCl₃); ¹H NMR "OH (500 MHz, Chloroform-*d*) δ 6.62 (tt, *J* = 9.1, 2.6 Hz, 2H), 4.19 (qd, *J* = 5.2, 2.5 Hz, 1H), 3.04 - 2.90 (m, 2H), 2.79 (dt, J = 16.2, 7.2 Hz, 1H), 2.61 (dd, J = 16.9, 7.1 Hz, 1H), 2.07 - 1.95 (m, 1H), 1.88 - 1.79 (m, 1H); ¹³C NMR (126 MHz, Chloroform*d*) δ 161.9 (t, *J* = 11.8 Hz), 159.9, 139.3 (d, *J* = 6.3 Hz), 117.4 (d, *J* = 3.6 Hz), 110.5 (dd, *J* = 20.4, 3.5 Hz), 100.9 (t, J = 25.7 Hz), 66.0, 30.7 (d, J = 3.2 Hz), 30.5, 26.6; ¹⁹F NMR (376 MHz, Chloroform-d) δ -114.6, -114.8; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 96 : 4, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), $t_R = 13.2 \text{ min}$ (major), $t_R = 15.3 \text{ min}$ (minor).



(R)-6,8-Dichloro-1,2,3,4-Tetrahydronahthalen-2-ol (5h)¹⁵



White solid, 96% yield, 92% ee; $[\alpha]_D^{25}$: 30.8 (c = 3.85, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 2.1 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 4.19 (qd, *J* = 8.2, 6.8, 2.9 Hz, 1H), 3.07 (dd, *J* = 17.4, 5.2 Hz, 1H),

2.94 (dt, J = 17.2, 6.1 Hz, 1H), 2.77 (ddd, J = 17.0, 8.4, 5.8 Hz, 1H), 2.65 (dd, J = 17.4, 6.9 Hz, 1H), 1.96 (qd, J = 6.1, 2.6 Hz, 1H), 1.86 - 1.73 (m, 1H); ¹³**C NMR** (126 MHz, Chloroform-*d*) δ 139.5, 135.4, 131.8, 131.1, 127.1, 126.6, 66.5, 35.8, 30.4, 26.9; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 96 : 4, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 14.0 min (major), t_R = 16.6 min (minor).



(*R*)-1,2,3,4-Tetrahydronaphthalen-2-ol (5i)¹²

White solid, 97% yield, 90% ee; [α]_D²⁵: 54.3 (c = 2.54, CHCl₃); ¹H NMR (500 MHz, Chloroform-d) δ 7.17 - 7.06 (m, 4H), 4.17 (dd, J = 9.1, 5.1 Hz, 1H), 3.11 (d, J = 16.2 Hz, 1H), 2.97 (dt, J = 17.1, 5.7 Hz, 1H), 2.91 - 2.74 (m, 1H), 2.78 (dd, J = 16.2, 7.6 Hz, 1H), 2.08 (dd, J = 12.9, 6.0 Hz, 1H), 1.92 - 1.80 (m, 2H); ¹³C NMR (126 MHz, Chloroform-d) δ 135.7, 134.3, 129.6, 128.7, 126.1, 126.0, 67.4, 38.5, 31.6, 27.1; The enantiomeric excess was

determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 97 : 3, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 24.4 min (major), t_R = 27.5 min (minor).



3,4-Dihydro-2H-1-Benzopyran-3-ol (5j)¹⁶

White solid, 93% yield, 40% ee; $[\alpha]_D^{25}$: 6.2 (c = 1.72, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.17 - 7.00 (m, 2H), 6.94 - 6.76 (m, 2H), 4.25 (d, *J* = 5.4 Hz, 1H), 4.16 - 3.97 (m, 2H), 3.10 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.80 (dd, *J* = 16.5, 4.5 Hz, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 153.9, 130.6, 127.7, 121.2, 119.4, 116.7, 69.8, 63.4, 33.6; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 96 : 4, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 37.0 min (minor), t_R = 40.4 min (major).


(R)-1-Phenyl-2-Butanol (5k)¹⁷

Colorless oil, 94% yield, 25% ee; $[a]_{D}^{25}$: -9.7 (c = 1.80, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.38 - 7.19 (m, 5H), 3.77 (ddp, *J* = 11.8, 7.8, 4.2, 3.7 Hz, 1H), 2.91 - 2.78 (m, 1H), 2.74 - 2.58 (m, 1H), 1.65 - 1.50 (m, 2H), 1.01 (dt, *J* = 15.1, 7.4 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 138.8, 129.5, 128.6, 126.5, 74.2, 43.7, 29.7, 10.2; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-H column (hexane : isopropanol = 95 : 5, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 7.3 min (minor), t_R = 9.6 min (major).



(S)-1-Cyclohexyl-Ethanol (51)⁹



0.91 (m, 2H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 72.4, 45.2, 28.8, 28.5, 26.6, 26.4, 26.3, 20.5.



isopropanol = 100 : 0, flow rate = 0.8 mL/min, T = 20 °C, λ = 225 nm), t_R = 13.3 min (minor), t_R = 14.2 min (major)



cis-1-Ethyl-1,2,3,4-tetrahydro-2-naphthalenol (7a)



Colorless oil, 94% yield, 91% ee, >20:1 dr.; $[\alpha]_D^{25}$: 42.2 (c = 2.45, CHCl₃); ¹H NMR (500 MHz, Chloroform-d) δ 7.23 - 7.07 (m, 4H), 4.23 (dt, J = 7.8, 3.9 Hz, 1H), 3.08 - 2.94 (m, 1H), 2.89 - 2.77 (m, 1H), 2.69 (dt, J = 10.4, 5.5 Hz, 1H), 2.08 - 1.88 (m, 2H), 1.90 - 1.80 (m, 1H), 1.77 - 1.62 (m, 1H), 1.08 (t, J = 7.5 Hz, 3H); ¹³C

NMR (126 MHz, Chloroform-*d*) δ 138.9, 135.7, 128.9, 128.9, 126.2, 125.6, 68.6, 45.8, 28.1, 26.6, 22.6, 12.6; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 96 : 4, flow rate = 0.8 mL/min, T = 20 °C, λ = 210 nm), t_R = 12.0 min (major, *cis*), $t_R = 12.6$ min (minor, *trans*), $t_R = 13.0$ min (minor, *trans*), $t_R = 15.9$ min (minor,



cis-1,2,3,4-Tetrahydro-5-methoxy-1-methyl-2-naphthalenol (7b)



White solid, 94% yield, 94% ee; >20:1 dr.; $[\alpha]_{D}^{25}$: 49.3 (c = 2.51, CHCl₃); ¹**H NMR** (500 MHz, Chloroform-*d*) δ 7.15 (t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 4.10 (dt, *J* = 9.9, 4.1 Hz, 1H), 3.81 (s, 3H), 3.08 - 2.99 (m, 1H), 2.89 (dt, *J* = 18.1, 5.8 Hz, 1H), 2.66 (dt, *J* = 17.9, 7.9 Hz, 1H),

2.02 - 1.83 (m, 2H), 1.29 (d, J = 7.1 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 157.1, 141.8, 126.6, 124.1, 121.1, 107.3, 70.1, 55.4, 38.7, 26.7, 21.5, 16.7; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 97 : 3, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 22.7 min (minor, *trans*), t_R = 23.5 min (major, *cis*), t_R = 25.5 min (minor, *cis*).



cis-1,2,3,4-Tetrahydro-5-methoxy-1-ethyl-2-naphthalenol (7c)



White solid, 96% yield, 90% ee; >20:1 dr.; [*α*]_D²⁵: 39.4 (c = 3.01, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.17 - 7.09 (m, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 5.5 Hz, 1H), 4.23 - 4.15 (m, 1H), 3.82 (s, 3H), 2.91 - 2.79 (m, 1H), 2.77 - 2.65 (m, 2H), 2.07 - 1.94 (m, 1H), 1.93 - 1.78 (m, 2H), 1.67 - 1.57

(m, 1H), 1.06 (t, J = 7.3 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 157.3, 140.4, 126.1, 124.2, 121.3, 107.5, 68.6, 55.4, 45.9, 27.2, 22.9, 20.9, 12.8; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-H column (hexane : isopropanol = 95 : 5, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 11.8 min (minor, *cis*), t_R = 13.9 min (major, *cis*).



cis-1,2,3,4-Tetrahydro-5-methoxy-1-(n-propyl)-2-naphthalenol (7d)

White solid, 95% yield, 93% ee; >20:1 dr.; $[\alpha]_{D}^{25}$: 41.9 (c = 3.37, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.13 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 4.16 (dt, *J* = 9.0, 4.0 Hz, 1H), 3.82 (s, 3H), 2.92 - 2.67 (m, 3H), 2.04 - 1.87 (m, 2H), 1.79 (dq, *J* = 11.1, 4.8, 3.6 Hz, 1H), 1.51 (hept, *J* = 8.2, 7.2 Hz, 3H), 0.96 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 157.2, 140.8, 126.1, 124.2, 121.3, 107.4, 68.9, 55.3, 44.1, 32.4, 27.0, 21.3, 21.1, 14.6; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 96 : 4, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 15.6 min (minor, *trans*), t_R = 17.6 min (minor, *cis*), t_R = 20.9 min (major, *cis*).



cis-1,2,3,4-Tetrahydro-7-methoxy-1-methyl-2-naphthalenol (7e)



White solid, 99% yield, 92% ee; >20:1 dr.; [α]_D²⁵: 36.9 (c = 2.62, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.01 (d, *J* = 8.2 Hz, 1H), 6.73 - 6.69 (m, 2H), 4.14 - 4.08 (m, 1H), 3.79 (s, 3H), 3.00 (p, *J* = 6.7

Hz, 1H), 2.90 (dt, J = 17.0, 6.0 Hz, 1H), 2.77 (dt, J = 16.3, 7.7 Hz, 1H), 2.02 - 1.93 (m, 1H), 1.92 - 1.84 (m, 1H), 1.30 (d, J = 7.2 Hz, 3H); ¹³**C** NMR (126 MHz, Chloroform-*d*) δ 157.9, 141.5, 129.6, 127.3, 113.7, 112.1, 70.3, 55.4, 38.8, 27.7, 26.3, 16.6; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OJ-3 column (hexane : isopropanol = 93 : 7, flow rate = 0.8 mL/min, T = 20 °C, $\lambda = 210$ nm), t_R = 17.1 min (minor, *trans*), t_R = 17.8 min (major, *cis*), t_R = 19.1 min (minor, *cis*), t_R = 25.9 min (minor, *trans*).



cis-1,2,3,4-Tetrahydro-7-methoxy-1-ethyl-2-naphthalenol (7f)



Colorless oil, 95% yield, 90% ee; [α]_D²⁵: 23.4 (c = 0.63, CHCl₃); ¹H
NMR (500 MHz, Chloroform-d) δ 7.02 (d, J = 8.2 Hz, 1H), 6.76 - 6.68 (m, 2H), 4.25 - 4.17 (m, 1H), 3.79 (s, 3H), 2.98 - 2.87 (m, 1H), 2.80 -

2.71 (m, 1H), 2.68 - 2.60 (m, 1H), 2.02 - 1.95 (m, 1H), 1.94 - 1.88 (m, 1H), 1.88 - 1.79 (m, 1H), 1.68 (dq, J = 13.8, 7.3 Hz, 1H), 1.08 (t, J = 7.5 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 157.6, 140.1, 129.6, 127.7, 114.1, 112.0, 68.5, 55.4, 45.9, 28.3, 25.6, 22.6, 12.7; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-H column (hexane : isopropanol = 95 : 5, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 12.3 min (minor), t_R = 14.3 min (major).



(1S, 2S)-2-Hydroxycyclopentane-1-Carbonitrile (7g)¹⁸

 $\begin{array}{l} \underset{\text{HO}}{\overset{\text{CN}}{\longrightarrow}} \quad \text{Light yellow oil, 95\% yield, 60\% ee, >20:1 dr.; } [\alpha] \mathbf{p}^{25}: 3.0 (c = 2.21, \text{CHCl}_3); {}^{1}\text{H} \\ \underset{\text{NMR}}{\overset{\text{HO}}{\longrightarrow}} \quad \underset{\text{NMR}}{\overset{\text{CN}}{\longrightarrow}} \quad \text{NMR (500 MHz, Chloroform-d) } \delta 4.46 - 4.38 (m, 1H), 2.74 (td, J = 8.8, 4.6 \text{ Hz}, 1H), \\ 2.20 (s, 1H), 2.14 - 2.01 (m, 2H), 2.04 - 1.56 (m, 4H); {}^{13}\text{C NMR (126 MHz, Chloroform-d) } \delta 120.5, 73.3, 36.7, 33.7, 28.0, 22.1; The absolute configuration of$ **7g** $was assigned by comparing the optical rotation value with reported data. [16] \end{array}$

$$\begin{array}{l} \underset{l}{\overset{\mbox{\footnotesize Light yellow oil, 60\% ee, >20:1 dr.; }^{1}\mbox{\footnotesize H} \mbox{\scriptsize NMR} (500 \mbox{\scriptsize MHz, Chloroform-}d) \ \delta \ 8.09 \ (d, \ J=7.9 \ Hz, 2H), \ 7.58 \ (t, \ J=7.4 \ Hz, 1H), \ 7.46 \ (t, \ J=7.6 \ Hz, 2H), \ 5.49 \ (td, \ J=5.9, \ 3.4 \ Hz, 1H), \ 3.11 \ (td, \ J=7.9, \ 5.6 \ Hz, 1H), \ 2.25 \ -2.11 \ (m, \ 3H), \ 2.07 \ -1.96 \ (m, \ 2H), \ .216 \$$

1.82 - 1.72 (m, 1H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 165.9, 133.5, 129.9, 129.7, 128.6, 119.1, 75.2, 34.3, 31.6, 29.3, 22.3. The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak OD-3 column (hexane : isopropanol = 97 : 3, flow rate = 0.8 mL/min, T = 20 °C, λ = 230

nm), $t_R = 14.4 \text{ min (minor, trans)}, t_R = 16.4 \text{ min (minor, trans)}, t_R = 19.1 \text{ min (minor, cis)}, t_R = 21.5 \text{ min (major, cis)}.$



cis-1,5-Anhydro-3-cyano-2,3-dideoxy-threo-pentitol (7h)

 $\begin{array}{c} \underset{l}{\text{HO}} & \text{White solid, 93\% yield, 99\% ee, >20:1 dr.; } [a]_{D}^{25}: 11.3 (c = 2.36, CHCl_{3}); {}^{1}\text{H NMR} \\ & \text{(500 MHz, Chloroform-d) } \delta \ 3.99 - 3.79 (m, 2H), 3.78 - 3.55 (m, 3H), 3.11 - 3.01 (m, 1H), 2.31 (s, 1H), 2.21 - 2.09 (m, 1H), 1.99 - 1.81 (m, 1H); {}^{13}\text{C NMR} (126 \text{ MHz}, Chloroform-d) \\ \delta \ 119.5, 70.1, 65.1, 64.6, 33.2, 25.9. \end{array}$

EXAMPLE CINCULAR Light yellow oil, 99% ee, >20:1 dr.; ¹H NMR (500 MHz, Chloroform-*d*) δ 8.08 (d, BZO,,, J = 6.9 Hz, 2H), 7.63 - 7.56 (m, 1H), 7.46 (d, J = 7.7 Hz, 2H), 5.16 (dt, J = 7.9, 4.3 Hz, 1H), 3.94 - 3.76 (m, 4H), 3.42 (q, J = 4.9 Hz, 1H), 2.24 - 2.03 (m, 2H); ¹³C

NMR (126 MHz, Chloroform-*d*) δ 165.5, 133.8, 130.1, 128.7, 128.5, 118.3, 66.9, 66.3, 64.6, 31.1, 27.3; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak IC-3 column (hexane : isopropanol = 92 : 8, flow rate = 0.8 mL/min, T = 20 °C, λ = 230 nm), t_R = 35.0 min (minor, *cis*), t_R = 39.4 min (major, *cis*), t_R = 46.8 min (minor, *trans*), t_R = 55.0 min (minor, *trans*).



Ethyl (3R,4R)-3-hydroxy-1-(phenylmethyl)-4-piperidinecarboxylate (7i)¹⁹

CO₂Et Colorless oil, 97% yield, 85% ee, >20:1 dr.; $[\alpha]_D^{25}$: 32.0 (c = 4.83, CHCl₃); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.36 - 7.19 (m, 5H), 4.17 (td, *J* = 13.9, 13.4, 6.4 Hz, 3H), 3.57 - 3.46 (m, 2H), 3.08 (br, 1H), 2.90 (dt, *J* = 49.7, 11.0 Hz, 2H), 2.40 - 1.67 (m, 5H), 1.24 (dt, *J* = 14.0, 7.2 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 173.3, 137.8, 129.1, 128.4, 127.3, 66.6, 62.6, 60.7, 59.1, 52.2, 45.7, 22.4, 14.3; The enantiomeric excess was determined by chiral HPLC analysis on Chiralpak IC column (hexane : isopropanol = 95 : 5, flow rate = 1 mL/min, T = 20 °C, λ = 210 nm), t_R = 22.9 min (minor, *cis*), t_R = 25.2 min (major, *cis* and *trans*), t_R = 29.1 min (minor, *trans*). The dr value was determined by ¹H NMR spectrum and the absolute configuration of **7i** was assigned by comparing the optical rotation value with reported data.^[17]



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6. NMR Spectra



1-2-¹³C NMR (126 MHz, Chloroform-*d*)



1-3-¹H NMR (500 MHz, Chloroform-*d*)



1-3-¹³C NMR (126 MHz, Chloroform-*d*)



1a-¹H NMR (500 MHz, Chloroform-*d*)



1a-13C NMR (126 MHz, Chloroform-d)



1-5-¹H NMR (500 MHz, Chloroform-*d*)



1-5-¹³C NMR (126 MHz, Chloroform-d)





(R,R,S_{Fc}) -1b-¹H NMR (500 MHz, Chloroform-*d*)





Ru-1-¹H NMR (500 MHz, DMSO-*d*₆)



Ru-1-¹³C NMR (126 MHz, DMSO-*d*₆)



3a-¹H NMR (500 MHz, Chloroform-*d*)



3a-13C NMR (126 MHz, Chloroform-d)



3b-¹H NMR (500 MHz, Chloroform-*d*)



3b-¹³C NMR (126 MHz, Chloroform-*d*)



3c-¹H NMR (500 MHz, Chloroform-*d*)



3d-¹H NMR (500 MHz, Chloroform-*d*)



3d-13C NMR (126 MHz, Chloroform-d)



3e-¹H NMR (500 MHz, Chloroform-*d*)



3e-13C NMR (126 MHz, Chloroform-d)



3f-¹H NMR (500 MHz, Chloroform-*d*)



3f-¹³C NMR (126 MHz, Chloroform-*d*)



3g-¹H NMR (500 MHz, Chloroform-*d*)



3g-¹³C NMR (126 MHz, Chloroform-*d*)



3h-¹H NMR (500 MHz, Chloroform-*d*)



3h-¹³C NMR (126 MHz, Chloroform-*d*)



3i-¹H NMR (500 MHz, Chloroform-*d*)



3i-¹³C NMR (126 MHz, Chloroform-d)



3j-¹H NMR (500 MHz, Chloroform-*d*)





3k-1H NMR (500 MHz, Chloroform-d)



3k-13C NMR (126 MHz, Chloroform-d)



3I-¹H NMR (500 MHz, Chloroform-*d*)



3I-¹³C NMR (126 MHz, Chloroform-d)



3m-¹H NMR (500 MHz, Chloroform-*d*)



3m-¹³C NMR (126 MHz, Chloroform-d)



3n-¹H NMR (500 MHz, Chloroform-*d*)



3n-¹³C NMR (126 MHz, Chloroform-*d*)



30-¹H NMR (500 MHz, Chloroform-*d*)



30-¹³C NMR (126 MHz, Chloroform-*d*)



3p-¹H NMR (500 MHz, Chloroform-*d*)





f1 (ppm)

3q-¹H NMR (500 MHz, Chloroform-*d*)



3q-¹³C NMR (126 MHz, Chloroform-*d*)


3r-¹H NMR (500 MHz, Chloroform-*d*)



3r-¹³C NMR (126 MHz, Chloroform-*d*)



3s-¹H NMR (500 MHz, Chloroform-*d*)



3s-13C NMR (126 MHz, Chloroform-d)



3t-¹H NMR (500 MHz, Chloroform-d)



3t-13C NMR (126 MHz, Chloroform-d)



3u-¹H NMR (500 MHz, Chloroform-*d*)



3u-¹³C NMR (126 MHz, Chloroform-d)



5a-¹H NMR (500 MHz, Chloroform-d)



5a-13C NMR (126 MHz, Chloroform-d)



5b-¹H NMR (500 MHz, Chloroform-*d*)



5b-13C NMR (126 MHz, Chloroform-d)



5c-¹H NMR (500 MHz, Chloroform-*d*)





5d-¹H NMR (500 MHz, Chloroform-*d*)



5d-13C NMR (126 MHz, Chloroform-d)



5e-1H NMR (500 MHz, Chloroform-d)



5e-13C NMR (126 MHz, Chloroform-d)



5f-¹H NMR (500 MHz, Chloroform-*d*)



5f-¹³C NMR (126 MHz, Chloroform-d)



5g-¹H NMR (500 MHz, Chloroform-*d*)



5g-¹³C NMR (126 MHz, Chloroform-d)



5g-¹⁹F NMR (376 MHz, Chloroform-*d*)



5h-¹H NMR (500 MHz, Chloroform-*d*)







5i-¹H NMR (500 MHz, Chloroform-d)



5i-¹³C NMR (126 MHz, Chloroform-d)



5j-¹H NMR (500 MHz, Chloroform-*d*)



5j-¹³C NMR (126 MHz, Chloroform-d)



5k-¹H NMR (500 MHz, Chloroform-*d*)



5k-13C NMR (126 MHz, Chloroform-d)



5l-¹H NMR (500 MHz, Chloroform-d)



5l-¹³C NMR (126 MHz, Chloroform-*d*)



5l-Bz-¹H NMR (500 MHz, Chloroform-d)



5I-Bz-13C NMR (126 MHz, Chloroform-d)



7a-1H NMR (500 MHz, Chloroform-d)





7b-¹H NMR (500 MHz, Chloroform-*d*)



7b-13C NMR (126 MHz, Chloroform-d)







7c-13C NMR (126 MHz, Chloroform-d)



7d-¹H NMR (500 MHz, Chloroform-*d*)



7d-13C NMR (126 MHz, Chloroform-d)



7e-1H NMR (500 MHz, Chloroform-d)



7e-13C NMR (126 MHz, Chloroform-d)







7f-13C NMR (126 MHz, Chloroform-d)



7g-¹H NMR (500 MHz, Chloroform-*d*)



7g-¹³C NMR (126 MHz, Chloroform-d)



7g-Bz-¹H NMR (500 MHz, Chloroform-*d*)



7g-Bz-¹³C NMR (126 MHz, Chloroform-*d*)



7h-¹H NMR (500 MHz, Chloroform-*d*)



7h-13C NMR (126 MHz, Chloroform-d)



7h-Bz-¹H NMR (500 MHz, Chloroform-*d*)



7h-Bz-¹³C NMR (126 MHz, Chloroform-d)



7i-¹H NMR (500 MHz, Chloroform-d)



7i-¹³C NMR (126 MHz, Chloroform-d)

