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Supporting Information

Iridium-catalyzed asymmetric transfer hydrogenation of aromatic ketones with cinchona alkaloid derived NNP ligand

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1. General information

Unless otherwise mentioned, all experiments were carried out under an atmosphere of argon or using standard Schlenk techniques. All the reagents and solvents were used as supplied commercially without further purification. Solvents were dried with standard procedures and degassed with N2. NMR spectra were recorded on a Bruker AVANCE 400 or 600 spectrometer. Chemical shifts are reported in ppm and coupling constants are given in Hz. High-resolution mass spectra (HRMS) were obtained on a Bruker MicroQTOF II instrument were recorded using electrospray ionization (ESI) techniques.

2. Synthesis of L11



Under argon, to a solution of 9-amino(9-deoxy)epicinchonidine (1.2mmol, 350mg) in 1,2-dichloroethane (10mL) was added 2-diarylphosphanylbenzaldehyde (1.5mmol, 525mg) and 4Å MS (4.0 g) at room temperature. After stirring for 24 h, the mixture was filtered and the filtrate was concentrated under reduced pressure to afford the solid residue. Subsequently, the solid residue was dissolved in anhydrous and oxygen free MeOH (6mL), and NaBH₄ (3.6mmol, 137mg) was added at 0 °C. The mixture was stirred at room temperature for 4h. The reaction was quenched with water (10mL) and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 3). The combined organic layers were dried over anhydrous sodium sulfate and filtered. The solvent was concentrated and the crude product was further purified by column chromatography on silica gel $(CH_2Cl_2/MeOH/ammonia water=20/1/0.1)$ to give the corresponding ligand L11 (white solid, 0.28) g, 38% yield). ¹H NMR (400MHz, CDCl₃): δ 8.90 (s, 1H), 8.23 (d, J = 2.0 Hz, 1H), 8.13 (d, J = 2.0 Hz, 1H), 7.84 (s, 1H), 7.70 - 7.72 (m, 1H),7.54 - 7.56 (m, 1H), 7.31 - 7.34 (m, 2H), 7.20 - 7.25 (m, 2H), 7.08 - 7.10 (m, 1H), 6.81 - 6.87 (m, 4H), 6.73 - 6.75 (m, 1H), 6.67 (s, 1H), 6.60 (s, 1H), 5.83 - 5.89 (m, 1H), 5.04 - 5.11 (m, 2H), 4.69 (d, J = 2.0 Hz, 1H), 3.93 - 4.07 (m, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 3.38 (d, J = 4.0 Hz, 1H), 2.87 (s, 1H), 2.72 (s, 2H), 2.17 (s, 1H), 1.51-1.55 (m, 1H), 1.39-1.43 (m, 2H), 1.26 - 1.31 (m, 2H), 1.12 - 1.16 (m, 1H), 0.85 - 0.90 (m, 1H), 0.70 (s, 1H). ¹³C NMR (100MHz, CDCl₃): *δ* 161.18, 150.57, 148.93, 148.13, 140.90, 133.89, 133.65, 130.29, 129.94, 129.09, 128.77, 126.99, 126.21, 125.11, 124.99, 124.80, 124.69, 122.90, 121.00, 120.79, 119.96, 114.05, 110.08, 62.36, 57.96, 55.53, 40.74, 31.91, 31.21, 29.68, 29.29, 27.58, 25.24, 22.67. ³¹P NMR (166MHz,

CDCl₃): δ -38.41. HRMS (ESI) calcd. for C₄₀H₄₂N₃O₂P [M+H]⁺: 628.3087, found: 628.3078.

3. General procedure for asymmetric transfer hydrogenation

All reagents were of analytical grade and used as-received without further purification. Under argon, to a tube were added [Ir(COD)CI]₂ (1 mg, 0.0015mmol) and L8 (3.7 mg, 0.006 mmol) in oxygen free *i*-PrOH (2 mL) at rt and the mixture was stirred at rt for 30 minutes. After which Cs₂CO₃ (13 mg, 0.004 mmol) and ketone (0.6 mmol) were added, and the reaction mixture was stirred at 82 °C for 3 h. The product was purified by silica gel chromatography using petroleum ether/ethylacetate as eluent. The enantioselectivity values were analyzed by GC-9790 with a Beta-DEXTM120 capillary column (df = 0.25 µm, 0.25 mm i.d.×30 m) and LC-16 with Chiralcel OD-H column (25 cm × 4.6 mm). The ee values of chiral alcohols were calculated from the equations enantioselectivity values (ee %) = |R-S|/|R+S|. Optical rotation was measured on the Rudolph Autopol with [α]_D²⁵ values reported in degrees at 25 °C; concentration (c) is in g/100ml.

(*S*)-1-Phenyl-ethanol (P1): colorless oil; known compound ^[1], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 90% ee, *S* isomer; $[a]_D^{25}$ = -50.0 (*c* = 1.00 in CHCl₃) (lit.1[a]_D^{20}= -42.6 (*c* = 1.00, CHCl₃)), ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.29-7.35 (m, 4H), 7.19-7.23 (m, 1H), 5.17 (d, *J* = 2.0 Hz, 1H), 4.68 - 4.74 (m, 1H), 1.32 (d, *J* = 4.0 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 147.81, 128.44, 126.97, 125.74, 68.55, 26.43.

(*S*)-1-o-Tolyl-ethanol (P2): colorless oil; known compound ^[2], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 96% ee, *S* isomer; $[a]_D^{25} = -60.8 (c = 1.00 in CHCl_3) (lit.2[a]_D^{20} = -62.8 (c = 1.09, CHCl_3)); ¹H NMR (400 MHz, CDCl_3) <math>\delta$ 7.44 (d, *J* = 4.0 Hz, 1H), 7.05-7.16 (m, 3H), 5.03-5.06 (m, 1H), 2.27 (s, 3H), 1.39 (d, *J* = 4.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl_3) δ 142.79, 133.20, 129.35, 126.15, 125.35, 123.43, 65.80, 22.90, 17.88.



OH

OH

(*S*)-1-(2-Methoxy-phenyl)-ethanol (P3): colorless oil; known compound^[5], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 99% ee, *S* isomer; $[a]_D^{25} = -18.0 \ (c = 1.00 \ in CHCl_3) \ (lit.5[a]_D^{20} = -28.7 \ (c = 1.24, CHCl_3)); {}^{1}H \ NMR \ (400 \ MHz, DMSO-d_6) \ \delta 7.42-7.44 \ (m, 1H), 7.17-7.21 \ (m, 1H), 6.91-6.95 \ (m, 2H), 4.98-5.01 \ (m, 2H), 3.77 \ (s, 3H), 1.25 \ (d, J = 4.0 \ Hz, 3H). {}^{13}C \ NMR \ (100 \ MHz, DMSO-d_6) \ \delta \ 155.71, 135.86, 127.87, 125.80, 120.70, 110.78, 62.84, 55.67, 25.13.$ OH

ΟН

OH

OH

OH

CI

F (*S*)-1-(2-Fluoro-phenyl)-ethanol (P4): colorless oil; known compound ^[3], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 89% ee, *S* isomer; $[a]_D^{25} = -37.9 \ (c = 1.00 \ in CHCl_3) \ (lit.3[a]_D^{20} = -43.4 \ (c = 0.90, CHCl_3); {}^{1}H \ NMR \ (400 \ MHz, DMSO-d_6) \delta 7.50-7.54 \ (m, 1H), 7.08-7.26 \ (m, 3H), 5.32 \ (d, J = 2.0 \ Hz, 1H), 4.96-5.01 \ (m, 1H), 1.33 \ (d, J = 4.0 \ Hz, 3H). {}^{13}C \ NMR \ (100 \ MHz, DMSO-d_6) \delta 160.51, 158.10, 134.35, 128.76, 127.42, 124.79, 115.40, 115.59, 62.47, 25.18.$

CI (S)-1-(2-Chlorophenyl)-ethan-1-ol (P5): colorless oil, known compound^[4], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 96% ee, *S* isomer; $[a]_D^{25} = -73.0 \ (c = 1.00 \ \text{in CHCl}_3) \ (\text{lit.4}[a]_D^{20} = -56.8 \ (c = 1.00, \text{CHCl}_3)); ^1\text{H NMR (400 MHz, DMSO-}d_6) \delta 7.60-7.63 \ (m, 1\text{H}), 7.34 - 7.37 \ (m, 2\text{H}), 7.23-7.27 \ (m, 1\text{H}), 5.40 \ (d, J = 2.0 \ \text{Hz}, 1\text{H}), 4.99-5.05 \ (m, 1\text{H}), 1.31 \ (d, J = 2.0 \ \text{Hz}, 3\text{H}). ^{13}\text{C NMR} \ (100 \ \text{MHz}, \text{DMSO-}d_6) \delta 144.97, 130.69, 129.32, 128.67, 127.78, 127.34, 65.43, 24.77.$

Br (*S*)-1-(2-Bromophenyl)-ethan-1-ol (P6): colorless oil, known compound^[4], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 94% ee, *S* isomer; $[a]_D^{25} = -64.0 \ (c = 1.00 \ in CHCl_3) \ (lit.4[a]_D^{20} = -40.4 \ (c = 1.00, CHCl_3)); {}^{1}H \ NMR \ (400 \ MHz, DMSO-d_6) \delta$ 7.59-7.62 (m, 1H), 7.52-7.54 (m, 1H), 7.38-7.41 (m, 1H), 7.15-7.19 (m, 1H), 5.43 (d , *J* = 2.0 Hz, 1H), 4.93-4,98 (m, 1H), 1.30 (d , *J* = 2.0 Hz, 3H). {}^{13}C \ NMR \ (100 \ MHz, DMSO-d_6) \delta 146.50, 132.55, 129.08, 128.36, 127.61, 121.11, 67.79, 24.86.

^{CF₃} (*S*)-1-(2-Trifluoromethyl-phenyl)-ethanol (P7): colorless oil, known compound^[6], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 95% ee, *S* isomer; $[a]_D^{25} = -67.4$ (*c* = 1.00 in CHCl₃) (lit.6 $[a]_D^{20} = -39.1$ (*c* = 1.44, CHCl₃)); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 4.0 Hz, 1H), 7.57-7.62 m, 2H), 7.35-7.38 (m, 1H), 5.31- 5.36 (m, 1H), 1.49 (d, *J* = 4.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.01, 131.37, 126.33, 126.06, 125.61, 125.31, 124.72, 124.37, 124.32, 124.26, 124.20, 122.00, 64.68, 64.66, 24.41.

(*S*)-1-(3-chlorophenyl)ethan-1-ol (P8): colorless oil, known compound^[4], purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1), 99% yield, 87% ee, *S* isomer; [a]_D²⁵ = -49.3 (*c* = 1.00 in CHCl₃) (lit.4[a]_D²⁰= -40.4 (*c* = 1.00, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.40 (s, 1H), 7.33 - 7.35 (m, 1H), 7.26 - 7.30 (m, 2H), 5.30 (d, *J* = 1.5 Hz, 1H), 4.72 - 4.75 (m, 1H), 1.32 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 150.52, 133.27, 130.37, 126.85, 125.63, 124.47, 67.95, 26.24.



(*S*)-1-(3-bromophenyl)ethan-1-ol (P9): Colorless oil, known compound^[8], purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1), 99% yield, 87% ee, *S* isomer; $[a]_D^{25} = -31.8$ (*c* = 1.00 in CHCl₃) (lit.8[a]_D^{20} = -28.8 (*c* = 2.80, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.53 (s, 1H), 7.41 (d, *J* = 3.0 Hz, 1H), 7.34 (d, *J* = 3.0 Hz, 1H), 7.27 - 7.29 (m, 1H), 5.31 (d, *J* = 3.0 Hz, 1H), 4.70 - 4.73 (m, 1H), 1.32 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 150.71, 130.72, 129.76, 128.52, 124.87, 121.95, 67.90, 26.26.



(*S*)-1-(3-(trifluoromethyl)phenyl)ethan-1-ol (P10): colorless oil, known compound^[11], purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1), 99% yield, 84% ee, *S* isomer; $[a]_D^{25}$ = -18.0 (*c* = 1.00 in CHCl₃) (lit.11[a]_D²⁰= -31 (*c* = 1.95, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.69 (s, 1H), 7.65 (d, *J* = 3.0 Hz, 1H), 7.54 - 7.59 (m, 2H), 5.39 (d, *J* = 3.0 Hz, 1H), 4.81 - 4.85 (m, 1H), 1.35 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 149.31, 129.98, 129.52, 125.77, 123.97, 123.70, 122.15, 67.91, 26.26.



(*S*)-1-(3-methoxyphenyl)ethan-1-ol (P11): colorless oil; known compound^[7], purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1), 98% yield, 90% ee, *S* isomer; $[a]_D^{25} = -39.2$ (*c* = 1.00 in CHCl₃) (lit.7[a]_ D^{20} = -42.1 (*c* = 1.00, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.21-7.23 (m, 1H), 6.91 (d, *J* = 6.0Hz, 2H), 6.78 (d, *J* = 6.0Hz, 1H), 5.15 (d, *J* = 3.0Hz, 1H), 4.68-4.71 (m, 1H), 3.75 (s, 1H), 1.32 (d, *J* = 3.0Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 159.62, 149.65, 129.47, 117.99, 112.33, 111.30, 68.48, 55.35, 26.42.



F (*S*)-1-(4-Fluoro-phenyl)-ethanol (P12): colorless oil, known compound^[9], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 98% yield, 81% ee *S* isomer; $[a]_D^{25} = -53.5$ (*c* = 1.00 in CHCl₃) (lit.9 $[a]_D^{20} = -44.8$ (*c* = 1.40, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.36 - 7.38 (m, 2H), 7.11 - 7.14(m, 2H), 5.20 (d, *J* = 3.0 Hz, 1H), 4.70 - 4.74 (m, 1H), 1.31 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 162.23, 160.63, 143.99, 127.64, 127.59, 115.14, 115 .00, 67.91, 26.43.



Cl⁷ (S)-1-(4-chlorophenyl)ethan-1-ol (P13): colorless oil, known compound^[8], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 93% ee, S isomer; $[a]_D^{25} = -40.4$ (c= 1.00 in CHCl₃) (lit.8 $[a]_D^{20} = -36.2$ (c = 2.20, CHCl₃)); ¹H NMR (400 MHz,

DMSO- d_6) δ 7.36 (s, 4H), 5.29 (d, J = 2.0 Hz, 1H), 4.74 – 4.70 (m, 1H), 1.30 (d, J = 2.0 Hz, 3H). ¹³C NMR (100 MHz, DMSO- d_6) δ 146.81, 131.39, 128.39, 127.65, 67.89, 26.29.



Br' (*S*)-1-(4-bromophenyl)ethan-1-ol (P14): colorless oil, known compound^[8], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 86% ee, *S* isomer; $[a]_D^{25} = -28.3$ (*c* = 1.00 in CHCl₃). (lit.8[$a]_D^{20} = -28.1$ (*c* = 2.20, CHCl₃)); ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.65 – 7.48 (m, 2H), 7.30 (d, *J* = 4.0 Hz, 2H), 5.29 (d, *J* = 2 Hz, 1H), 4.72 – 4.68 (m, 1H), 1.30 (d, *J* = 2.0 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 142.25, 131.30, 128.06, 119.86, 67.92, 26.26.



H₃C (*S*)-1-1-p-Tolyl-ethanol (P15): colorless oil, known compound^[4], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 96% yield, 88% ee, *S* isomer; [a]_D²⁵ = -66.1 (*c* = 1.00 in CHCl₃) (lit.4[a]_D²⁰= -52.1 (*c* = 1.00, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.23 (d, *J* = 3.0 Hz, 2H), 7.12 (d, *J* = 3.0 Hz, 2H), 5.07 (d, *J* = 3.0 Hz, 1H), 4.66 - 4.70 (m, 1H), 2.28 (s, 3H), 1.31 (d, *J* = 3.0 Hz, 3H) . ¹³C NMR (150 MHz, DMSO-*d*₆) δ 144.87, 135.86, 128.97, 125.69, 68.37, 26.45, 21.13.



(*S*)-1-(4-Methoxy-phenyl)-ethanol (P16): colorless oil, known compound^[4], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 88% yield, 85% ee, *S* isomer; $[a]_D^{25} = -39.7$ (*c* = 1.00 in CHCl₃) (lit.4[a]_D²⁰= -41.7 (*c* = 1.00, CHCl₃)); ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.25 (d, *J* = 6.0 Hz, 2H), 6.86 (d, *J* = 4.0 Hz, 2H), 5.06 (d, *J* = 2.0 Hz, 1H), 4.65 - 4.66 (m, 1H), 3.72 (s, 3H), 1.29 (d, *J* = 4.0 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 158.42, 139.84, 126.90, 113.80, 68.11, 55.49, 26.41.



(*S*)-1-(4-ethylphenyl)ethan-1-ol (P17): colorless oil; known compound^[3], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 91% ee, *S* isomer; $[a]_D^{25} = -47.8$ (*c* = 1.00 in CHCl₃) (lit.3[$a]_D^{20} = -50.1$ (*c* = 1.00, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.25 (d, *J* = 3.0 Hz, 2H), 7.14 (d, *J* = 6.0 Hz, 2H), 5.07 (d, *J* = 3.0 Hz, 1H), 4.67 - 4.70 (m, 1H), 2.55 - 2.59 (m, 2H), 1.31 (d, *J* = 3.0 Hz, 3H), 1.15 - 1.18 (m, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 145.13, 142.36, 127.76, 125.76, 68.40, 28.32, 26.41, 16.24.



(S)-1-(3,4-dimethoxyphenyl)ethan-1-ol (P18): Colorless oil, known compound^[13], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 98% yield, 84% ee, *S* isomer; $[a]_D^{25} = -28.3$ (*c* = 1.00 in CHCl₃) (lit.13 $[a]_D^{20} = -37.3$ (*c* = 1.09, CHCl₃)); ¹H

NMR (600 MHz, DMSO- d_6) δ 6.95 (m, 1H), 6.83 - 6.88 (m, 2H), 5.05 (d, J = 3.0 Hz, 1H), 4.64 - 4.68 (m, 1H), 3.74 (d, J = 6.0 Hz, 3H), 1.31 (d, J = 3.0 Hz, 1H). ¹³C NMR (150 MHz, DMSO- d_6) δ 148.97, 147.94, 140.53, 117.65, 111.98, 109.78, 68.34, 56.03, 26.45.



Cl (S)-1-(2,4-dichlorophenyl)ethan-1-ol (P19): colorless oil, known compound^[9], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 88% ee, S isomer; $[a]_D^{25} = -48.7$ (c = 1.00 in CHCl₃) (lit.9 $[a]_D^{20} = -21.6$ (c = 0.50, CHCl₃)); ¹H NMR (600 MHz, DMSO- d_6) δ 7.62 (d, J = 6.0 Hz, 1H), 7.52 (d, J = 3.0 Hz, 1H), 7.43 - 7.45 (m, 1H), 5.47 (d, J = 3.0 Hz, 1H), 4.97 - 5.01 (m, 1H), 1.30 (d, J = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO- d_6) δ 144.17, 132.20, 131.55, 128.84, 128.70, 127.98, 65.15, 24.56.



OH

^{CF₃} (*S*)-1-(3,5-Bis-trifluoromethyl-phenyl)-ethanol (P20): colorless oil, known compound^[14], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 80% ee, *S* isomer; $[a]_D^{25}$ = -17.0 (*c* = 1.00 in CHCl₃) (lit.14[$a]_D^{20}$ = -24 (*c* = 1.00, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.04 (s, 2H), 7.95 (s, 2H), 5.62 (d, *J* = 3.0 Hz, 1H), 4.93 - 4.97 (m, 1H), 1.39 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 151.4, 130.16-130.59 (CF₃), 126.55, 124.84, 123.03, 120.70, 67.44, 26.04.

(S)-1-Phenyl-butan-1-ol (P21): colorless oil, known compound^[2], purified by silica

gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 92% ee, *S* isomer; $[a]_D^{25} = -57.8$ (*c* = 1.00 in CHCl₃) (lit.2[a]_D²⁰= - 44.2 (*c* = 0.99, CHCl₃)); ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.31 (d, *J* = 2.0 Hz, 4H), 7.18 - 7.24 (m, 1H), 5.12 (d, *J* = 2.0 Hz, 1H), 4.48 - 4.53 (m, 1H), 1.47 - 1.64 (m, 2H), 1.20 - 1.37 (m, 2H), 0.84 - 0.87 (m, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 146.90, 128.37, 127.00, 126.23, 72.50, 42.03, 19.00, 14.36.



(*S*)-2-methyl-1-phenylpropan-1-ol (P22): colorless oil, purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 99% ee, *S* isomer; $[a]_D^{25} = -33.2$ (*c* = 1.00 in CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.2 (m, 5H), 4.27 (d, *J* = 2.0 Hz, 1H), 1.90-1.85 (m, 3H), 0.92 (d, *J* = 4.0 Hz, 3H), 0.72 (d, *J* = 2.0 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 142.59, 127.14, 126.37, 125.54, 79.00, 34.20, 17.95, 17.23.



(S)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol (P23): white solid, known compound^[11], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99%

yield, 98% ee, *S* isomer; $[a]_D^{25} = -32.7$ (*c* = 1.00 in CHCl₃) (lit.11 $[a]_D^{20} = -30.3$ (*c*=1.00, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.44 (d, *J* = 3.0 Hz, 1H), 7.13 - 7.16 (m, 1H), 7.05 - 7.09 (m, 2H), 5.17 (s, 1H), 4.74 (d, *J* = 6.0 Hz, 1H), 2.80 - 2.83 (m, 1H), 2.65 - 2.69 (m, 1H), 1.87 - 1.95 (m, 2H), 1.70 - 1.75 (m, 2H), 1.49 - 1.52 (m, 1H), 1.24 - 1.27 (m, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 146.18, 140.58, 129.27, 126.58, 126.06, 125.0, 71.99, 37.74, 35.46, 27.89.

OH

CL

Br∖

OH

(*S*)-1-(Thiophen-2-yl)-ethan-1-ol (P24): colorless oil; known compound^[11], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 85% yield, 85% ee, *S* isomer; [a]_D²⁵ = -15.6 (c = 1.00 in CHCl₃) (lit.11[a]_D²⁰= -44.5 (c = 1.65, CHCl₃)); ¹H NMR (400 MHz, DMSO- d_6) δ 7.35(d, J = 2.0 Hz, 1H), 6.91 - 6.95 (m, 2H), 5.50 (d, J = 2.0 Hz, 1H), 4.91 - 4.97 (m, 1H), 1.41 (d, J = 4.0 Hz, 3H). ¹³C NMR (100 MHz, DMSO- d_6) δ 152.40, 126.94, 124.25, 122.75, 64.86, 26.40.

(*S*)-1-(5-Methyl-thiophen-2-yl)-ethan-1-ol (P25): light yellow oil, known compound^[10], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 90% ee, S isomer; $[a]_D^{25}$ = -16.7 (*c* = 1.00 in CHCl₃) (lit.10 $[a]_D^{20}$ = -41.8 (*c* = 1.00, CHCl₃)); ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.68 (d, *J* = 2.0 Hz, 2H), 6.60 (d, *J* = 2.0 Hz, 1H), 5.37 (d, *J* = 2.0 Hz, 1H), 4.82 - 4.85 (m, 1H), 2.38 (s, 1H), 1.37 (d, *J* = 4.0 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 149.83, 137.50, 124.91, 122.52, 64.89, 26.22, 15.49.

(*S*)-1-(5-Chlorothiophen-2-yl)-ethan-1-ol (P26): light yellow oil, known compound^[12], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 96% yield, 80% ee, *S* isomer; $[a]_D^{25}$ = -17.3 (*c*=1.00 in CHCl₃) (lit.12 $[a]_D^{20}$ = -11.4 (*c* = 1.00, CHCl₃)); ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.93(d, *J* = 2.0 Hz, 1H), 6.77 (d, *J* = 2.0 Hz, 1H), 5.68 (d, *J* = 2.0 Hz, 1H), 4.83 - 4.89 (m, 1H), 1.38 (d, *J* = 4.0 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 152.01, 126.68, 126.30, 122.30, 65.02, 25.91.

(*S*)-1-(5-Bromothiophen-2-yl)-ethan-1-ol (P27): colorless oil, known compound^[12], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 80% ee, *S* isomer; $[a]_D^{25} = -11.6$ (*c* = 1.00 in CHCl₃) (lit.12 $[a]_D^{20} = -9.5$ (*c* = 1.00, CHCl₃)); ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.03 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 5.67 (d, *J* = 4.0 Hz, 1H), 4.85 - 4.90 (m, 1H), 1.38 (d, *J* = 4.0 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 154.70, 130.21, 123.37, 109.37, 65.06, 25.96.

(*S*)-1-(Thiophen-2-yl)-propan-1-ol (P28): light yellow oil, known compound^[11], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 99% ee, *S* isomer; $[a]_D^{25} = -16.0$ (c = 1.00 in CHCl₃) (lit.11 $[a]_D^{20} = -22.1$ (c = 0.90, CHCl₃)); ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 2.0 Hz, 1H), 6.94 - 6.96 (m, 2H), 4.81 - 4.84 (m, 1H), 2.13 (s, 1H), 1.83 - 1.90 (m, 2H), 0.94 - 0.97 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.83, 124.76, 122.65, 121.96, 69.92, 30.41, 8.34.

(*S*)-1-(Furan-2-yl)-ethan-1-ol (P29): colorless oil, known compound^[9], purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99%yield, 93% ee, *S* isomer; $[a]_D^{25} = -12.0 \ (c = 1.00 \ in CHCl_3) \ (lit.9[a]_D^{20} = -31.2 \ (c = 0.50, CHCl_3)); {}^{1}H \ NMR \ (400 \ MHz, CDCl_3); \delta$ 7.37 (d, *J* = 2.0 Hz, 1H), 6.33 (d, *J* = 2.0 Hz, 1H), 6.22 (d, *J* = 2.0 Hz, 1H), 4.85 - 4.90 (m, 1H), 2.08 (s, 1H), 1.54 (d, *J* = 4.0 Hz, 3H). {}^{13}C \ NMR \ (100 \ MHz, CDCl_3) \ \delta \ 157.63, 141.91, 110.13, 105.11, 63.62, 21.27.

(*S*)-1-(5-methylfuran-2-yl)ethan-1-ol (P30): colorless oil; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 69% yield, 81% ee, *S* isomer; $[a]_D^{25} = -7.4$ (*c* = 1.00 in CHCl₃). ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.06 (s, 1H), 5.95 (s, 1H), 5.12 (s, 1H), 4.60 (s, 1H), 2.23 (d, *J* = 2.0 Hz, 3H), 1.32 - 1.35 (m, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 157.66, 150.41, 106.43, 105.66, 62.16, 22.43, 13.75. HRMS: [M+Na]⁺ calcd for C₇H₁₀NaO₂ 149.0573, found 149.0575.

(*R*)-1-phenyl-ethanol (P31): colorless oil; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 95% yield, 82% ee, *R* isomer; $[a]_D^{25} = +38.1$ (*c* = 1.00 in CHCl₃) (lit.15 $[a]_D^{20} = +41.9$ (*c* = 1.10, CHCl₃)).

(*R*)-1-o-Tolyl-ethanol (P32): colorless oil; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 96% yield, 98% ee, *R* isomer; $[a]_D^{25} = +74.3$ (*c* = 1.00 in CHCl₃) (lit.16 $[a]_D^{20} = +79.8$ (*c* = 1.00, CHCl₃)).

Cl (*R*)-1-(2-Chlorophenyl)-ethan-1-ol (P33): colorless oil, purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 95%ee, *R* isomer; $[a]_D^{25}$ = +62.5 (*c* = 1.00 in CHCl₃) (lit.16[a]_D^{20}= +66.8 (*c* = 1.00, CHCl₃)).

 CF_3 (*R*)-1-(2-Trifluoromethyl-phenyl)-ethanol (P34): colorless oil, purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1), 99% yield, 99%ee, *R* isomer; $[a]_D^{25} = +26.5$ (*c* = 1.00 in CHCl₃) (lit.17[a]_D²⁰= +25.8 (*c* = 1.00, CHCl₃)).

Reference:

ΟН

ΟН

ΟН

OH

ОH

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4.NMR spectra











































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5. Chiral analysis:

(±)-1-Phenylethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; injector temprature: 250 °C; detector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.08 MPa.



(S)-1-Phenylethanol (P1): 90% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.08 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	13.375	5825	4.822
3	13.917	114988	95.178

(±)-1-o-Tolyl-ethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



(S)-1-o-Tolyl-ethanol (P2): 96% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	21.546	1917	2.128
3	24.548	76834	97.872

(±)-1-(2-Methoxy-phenyl)-ethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



(S)-1-(2-Methoxy-phenyl)-ethanol (P3): 99% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	34.624	34	0.072
2	36.157	46910	99.927

(±)-1-(2-Fluoro-phenyl)-ethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.08 MPa.



(S)-1-(2-Fluoro-phenyl)-ethanol (P4): 89% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.08 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	9.565	4813	5.345
3	9.954	78798	94.655

(±)-1-(2-Chlorophenyl)-ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



(S)-1-(2-Chlorophenyl)-ethan-1-ol (P5): 96% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



(±)-1-(2-Bromophenyl)-ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130 °C; inlet pressure = 0.06 MPa.



(*S*)-1-(2-Bromophenyl)-ethan-1-ol (P6): 94% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	47.195	1837	3.128
2	62.486	56881	96.872

(±)-1-(2-Trifluoromethyl-phenyl)-ethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(S)-1-(2-Trifluoromethyl-phenyl)-ethanol (P7): 95% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	47.195	1418	2.713
2	62.486	50836	97.287

(±)-1-(3-chlorophenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130°C; inlet pressure = 0.08 MPa.



(*S*)-1-(3-chlorophenyl)ethan-1-ol (P8): 87% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130 °C; inlet pressure = 0.08 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	23.100	1700	6.184
2	24.351	25797	93.816

(±)-1-(3-bromophenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 140 °C; inlet pressure = 0.08 MPa.



(*S*)-1-(3-bromophenyl)ethan-1-ol (P9): 87% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 140 °C; inlet pressure = 0.08 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	23.964	4035	6.446
3	24.798	52885	93.554

(±)-1-(3-(trifluoromethyl)phenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(S)-1-(3-(trifluoromethyl)phenyl)ethan-1-ol (P10): 84% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(±)-1-(3-methoxyphenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



(S)-1-(3-methoxyphenyl)ethan-1-ol (P11): 90% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	46.748	12020	4.891
3	48.393	219940	95.109

(±)-1-(4-Fluoro-phenyl)-ethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(*S*)-1-(4-Fluoro-phenyl)-ethanol (P12): 81% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	20.224	13053	9.572
3	21.730	123309	90.428

(±)-1-(4-chlorophenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130 °C; inlet pressure = 0.06 MPa.



(S)-1-(4-chlorophenyl)ethan-1-ol (P13): 93% ee (S) isomer. The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	26.344	3164	3.361
2	28.097	104868	96.639

(±)-1-(4-bromophenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature:140 °C; inlet pressure = 0.08 MPa.



(S)-1-(4-bromophenyl)ethan-1-ol (P14): 86% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 140 °C; inlet pressure = 0.08 MPa.



(±)-1-p-Tolyl-ethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.08 MPa.



(*S*)-1-p-Tolyl-ethanol (P15): 88% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.08 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	19.515	9688	5.732
3	20.793	159318	94.268

(±)-1-(4-Methoxy-phenyl)-ethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



(*S*)-1-(4-Methoxy-phenyl)-ethanol (P16): 88% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	48.443	12140	6.265
3	50.258	150780	93.735

(±)-1-(4-ethylphenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



(S)-1-(4-ethylphenyl)ethan-1-ol (P17): 91% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	27.427	4501	4.726
2	28.540	82160	95.274

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(±)-1-(3,4-dimethoxyphenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 135 °C; inlet pressure = 0.1 MPa.



(S)-1-(3,4-dimethoxyphenyl)ethan-1-ol (P18): 84% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 135 °C; inlet pressure = 0.1 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	48.256	12593	7.860
3	49.150	147302	91.940

(±)-1-(2,4-dichlorophenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 150 °C; inlet pressure = 0.08 MPa.



(S)-1-(2,4-dichlorophenyl)ethan-1-ol (P19): 88% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 150 °C; inlet pressure = 0.08 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	19.190	5320	5.895
2	23.010	84920	94.105

(±)-1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(S)-1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol (P20): 80% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	9.025	195706	90.256
2	10.121	21339	9.744

(±)-1-Phenyl-butan-1-ol: The racemate was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 99:1; flow rate = 0.5 mL/min; UV detection at 254 nm.



(S)-1-Phenyl-butan-1-ol (P21): 92% ee (S). The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 99:1; flow rate = 0.5 mL/min; UV detection at 254 nm.



Peak	Processed	Retention	Peak Area	Peak Hight	Peak Area
	Channel	Time (min)	(mAU*s)	(mAU)	(%)
1	PDA 254 nm	43.942	416509	4326	3.792
2	PDA 254 nm	49.866	10567814	80238	96.208

(±)- **2-methyl-1-phenylpropan-1-ol:** The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature:115 °C; inlet pressure = 0.06 MPa.



(S)-2-methyl-1-phenylpropan-1-ol (P22): 99% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(±)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 160 °C; inlet pressure = 0.08 MPa.



(*S*)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol (P23): 98% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 160 °C; inlet pressure = 0.08 MPa.



(±)-1-(Thiophen-2-yl)-ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(S)-1-(Thiophen-2-yl)-ethan-1-ol (P24): 85% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	16.705	1935	7.934
3	17.488	22449	92.066

(±)-1-(5-Methyl-thiophen-2-yl)-ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(S)-1-(5-Methyl-thiophen-2-yl)-ethan-1-ol (P25): 90% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	24.057	5099	4.843
3	25.712	100183	95.157

(±)-1-(5-Chlorothiophen-2-yl)-ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130 °C; inlet pressure = 0.08 MPa.



(S)-1-(5-Chlorothiophen-2-yl)-ethan-1-ol (P26): 80% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130 °C; inlet pressure = 0.08 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	20.189	2614	10.408
3	21.517	22498	89.592

(±)-1-(5-Bromothiophen-2-yl)-ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂ ; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130 °C; inlet pressure = 0.08 MPa.



(S)-1-(5-Bromothiophen-2-yl)-ethan-1-ol (P27): 80% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 130 °C; inlet pressure = 0.08 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	30.533	5445	9.638
3	32.473	49649	90.362

(±)-1-(Thiophen-2-yl)-propan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(s)-1-(Thiophen-2-yl)-propan-1-ol (P28): 99% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	28.081	211	0.429
2	29.044	51796	99.571

(±)-1-(Furan-2-yl)-ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 75 °C; inlet pressure = 0.06 MPa.



(*S*)-1-(Furan-2-yl)-ethan-1-ol (P29): 93% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 75 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
1	30.246	1286	3.363
2	31.426	36945	96.637
(±)-1-(5-methylfuran-2-yl)ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂ ; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 80 °C; inlet pressure = 0.06 MPa.



(*S*)-1-(5-methylfuran-2-yl)ethan-1-ol (P30): 81% ee (S). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂ ; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 80 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	41.978	2938	9.697
3	43.163	27359	90.303

(±)-1-Phenylethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; injector temprature: 250 °C; detector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.08 MPa.



(*R*)-1-Phenylethanol (P1): 82% ee (R). The enantiomeric excess was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.08 MPa.



(±)-1-o-Tolyl-ethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



(*R*)-1-o-Tolyl-ethanol (P2): 98% ee (R). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25 μ m, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



peak	Retention time	Area	%Area
	[min]	[uv*s]	
2	22.149	112636	99.1
3	26.225	1124	0.9

(±)-1-(2-Chlorophenyl)-ethan-1-ol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



(*R*)-1-(2-Chlorophenyl)-ethan-1-ol (P33): 95% ee (R). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 125 °C; inlet pressure = 0.06 MPa.



45.684

2

810

2.5

(±)-1-(2-Trifluoromethyl-phenyl)-ethanol: The racemate was determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa.



(*R*)-1-(2-Trifluoromethyl-phenyl)-ethanol (P34): 99% ee (R). The enantiomeric excess were determined by GC equipped with a chiral β -DEXTM120 (df = 0.25µm, 0.25 mm i.d.×30 m, fused silica capillary column); carrier gas: H₂; detector temperature: 250 °C; injector temperature: 250 °C; column temperature: 115 °C; inlet pressure = 0.06 MPa



12.637

2

1117

0.7