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Supporting Information

Cinchona alkaloids derived NN ligand for ruthenium catalyzed asymmetric hydrogenation of

aromatic and α , β -unsaturated ketones

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1. General experimental details

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. HRMS was performed on a Waters Xevo G2-S Qtof instrument using electrospray ionization (ESI) techniques.

2.Synthesis of L8



To a solution of **L4** (90mg, 0.25mmol) in DMF (3mL) were added CH₃I (43mg, 0.3mmol) and K₂CO₃ (69mg, 0.5mmol) at room temperature. After stirring for 30min, the reaction was quenched with water (5 mL) and the aqueous layer was extracted with CH₂Cl₂ (5 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 (CH₂Cl₂/MeOH/ammonia water=20/1/0.1) to give the corresponding compound **L8** (81mg, 85.5% yield). Yellow solid, ¹H NMR (600 MHz, MeOD) δ 8.90 (d, *J* = 3.0 Hz, 1H), 8.49 – 8.59 (m, 1H), 8.12 (d, *J* = 3.0 Hz, 1H), 7.74 – 7.87 (m, 3H), 5.62 – 5.68 (m, 1H), 5.24 (d, *J* = 6.0 Hz, 1H), 5.14 (d, *J* = 3.0 Hz, 1H) 3.94 – 3.98(m, 1H), 3.59 – 3.76 (m, 3H), 3.45 – 3.47 (m, 3H), 2.82 – 2.87 (m, 1H), 2.36 – 2.40 (m, 1H), 2.02 – 2.14 (m, 3H), 1.82 (s, 1H), 1.23 – 1.44 (m, 8H), 1.07 – 1.16 (m, 1H), 0.80 – 0.91 (m, 4H). ¹³C NMR (150 MHz, MeOD) δ 149.86, 135.75, 130.02, 129.21, 127.63, 123.77, 123.20, 121.28, 116.46, 69.61, 60.52, 46.29, 37.47, 29.38, 29.17, 26.40, 23.40, 22.04, 12.88. HRMS (ESI) calcd. for C₂₄H₃₃N₃ [M+H]⁺:378.2904, found: 378.2903.

3. Details of catalytic study

3.1 General procedure for asymmetric hydrogenation

All reagents were of analytical grade and used as-received without further purification. The purity of hydrogen was over 99.99%. For asymmetric hydrogenation of acetophenone: Required amount of benzylidene-bis(tricyclohexylphosphine)-dichlororuthenium (3.7 mg, 0.0044 mmol), acetophenone (1.1144 mmol, 133.9 mg), **L4**(5.3 mg, 0.0145 mmol), Ba(OH)₂ (56.8 mg, 0.15 mmol) and ethanol (2 mL) were added to a 25 mL stainless autoclave and purged by three cycles of pressurization/venting with H₂. The required H₂ pressure (6.0 MPa) was then installed and the autoclave was wormed to the indicated temperature. The autoclave was cooled down after the indicated reaction time and the pressure was slowly released. The product was purified by silica gel chromatography using petroleum ether/ethylacetate (10/1) as eluent. The asymmetric hydrogenation of other substrates was similar to that of acetophenone.

The enantioselectivity values were analyzed by GC-9790 with a Beta-DEX TM 120 capillary column (df = 0.25 μ m, 0.25 mm i.d.×30 m) and LC-16 with Chirasil OD-H column (25 cm × 4.6 mm), Chirasil IA column (25 cm × 4.6 mm) and Chirasil IB 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 I with [α]_D²⁵ values reported in degrees at 25°C; concentration (c) is in g/100ml.

3.2 Characterization data of compounds



OH

(S)-1-Phenyl-ethanol (P1): Colorless oil; known compound^[3]; purified by silica gel

chromatography (petroleum ether/ethylacetate = 10:1),97.7% yield, 40 mg, 93.1% ee, *S* isomer; $[a]_D^{25} = -40.5$ (c=1.00 in CHCl₃) (lit. 3 $[a]_D^{20} = -42.6$ (c=1.0, CHCl₃)); ¹H NMR (600 MHZ, DMSO-*d*₆) δ 7.13 - 7.20 (m, 4H), 7.03 - 7.06 (m, 1H), 5.00 (d, *J* = 3.0 Hz, 1H), 4.55 - 4.59 (m, 1H), 1.17 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 147.88, 128.43, 126.95, 125.76, 68.60, 26.46.

(S)-1-(2-Fluoro-Phenyl)-ethanol (P2): Colorless oil; known compound^[4]; purified by

silica gel chromatography (petroleum ether/ethylacetate = 10:1),47.6% yield, 43 mg, 88.0% ee, *S* isomer; $[a]_D^{25} = -35.3$ (c=1.00 in CHCl₃) (lit. 4 $[a]_D^{20} = -43.4$ (c=0.9, CHCl₃)); ¹H NMR (400 MHZ, DMSO-*d*₆) δ 7.55 – 7.60 (m, 1H), 7.07 – 7.29 (m, 3H), 5.32 (s, 1H), 5.04 – 5.06 (m, 1H), 1.35 – 1.38 (m, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 160.58, 158.16, 134.59, 128.62, 127.38, 124.66, 115.32, 62.54, 25.12.

Cl (S)-1-(2-Chloro-phenyl)-ethan-1-ol (P3): Colorless oil; known compound^[5]; purified by

silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 40.2% yield, 39 mg, 93.9% ee, *S* isomer; $[a]_D^{25} = -40.9$ (c = 1.00 in CHCl₃) (lit.5 $[a]_D^{20} = -56.8$ (c = 1.0, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.65 (d, *J* = 6.0 Hz, 1H), 7.34 - 7.37 (m, 2H), 7.23 - 7.26 (m, 1H), 5.38 (d, *J* = 2.0 Hz, 1H), 5.04 - 5.08 (m, 1H), 1.33 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 145.05, 130.76, 129.30, 128.59, 127.71, 127.36, 65.47, 24.77.

Br (S)-1-(2-Bromophenyl)-ethan-1-ol (P4): Colorless oil; known compound^[5]; purified by

silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 54.5% yield, 54mg, 84.2% ee, *S* isomer; $[a]_D^{25} = -31.9$ (c = 1.00 in CHCl₃) (lit.5 $[a]_D^{20} = -40.4$ (c = 1.0, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.65 – 7.69 (m, 1H), 7.53 (d , *J* = 6.0 Hz, 1H), 7.38 – 7.41 (m, 1H), 7.15 – 7.18 (m, 1H), 5.42 – 5.45 (m, 1H), 5.00 – 5.06 (m, 1H), 1.33 – 1.37 (m, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 146.61, 132.53, 128.95, 128.27, 127.65, 121.21, 67.88, 24.88.

F (S)-1-1-(4-Fluoro-phenyl)-ethanol (P5): Colorless oil; known compound^[7]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 96.2% yield, 43mg, 96.2% ee, *S* isomer;[a]_D²⁵ = - 29.0 (c = 1.00 in CHCl₃) (lit.7 [a]_D²⁰ = - 44.8 (c = 1.4, CHCl₃)); ¹H NMR (600 MHz, DMSO- d_6) δ 7.36 - 7.38 (m, 2H), 7.10 - 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.

CI OH

OH

OH

OH

(S)-1-(4-chloro-phenyl)-ethan-1-ol(P6): Colorless oil; known compound^[9]; purified

by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 96.6% yield, 64mg, 96.8% ee, *S* isomer;[a]_D²⁵ = - 46.3 (c = 1.00 in CHCl₃) (lit.9 [a]_D²⁰ = - 49.3 (c 1.0 (c = 1.0, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.36 (s, 4H), 5.29 (d, *J* = 3.0 Hz, 1H), 4.70 – 4.74 (m, 1H), 1.30 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 146.82, 131.39, 128.39, 127.65, 67.89, 26.29.



Br (S)-1-(4-bromo-phenyl)-ethan-1-ol(P7): Colorless oil; known compound^[10]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 87.1% yield, 77mg, 87.6% ee, *S* isomer; $[a]_D^{25} = -32.1$ (c = 1.00 in CHCl₃) (lit.10 $[a]_D^{24} = -33.4$ (c=0.60, CHCl₃)).¹H NMR (600 MHz, DMSO-*d*₆) δ 7.48 – 7.51 (m, 4H), 7.29 – 7.32 (m, 2H), 5.29 (d, *J* = 3.0 Hz, 1H), 4.68 – 4.72 (m, 1H), 1.30 (d, *J* = 3.0 Hz, 1H). ¹³C NMR (150 MHz, DMSO) δ 147.25, 131.31, 128.06, 119.86, 67.92, 26.27.

F₃C OH

OH

^{F₃C} (S)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (P8): Colorless oil; known compound^[9]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 20:1), 97.5% yield, 80mg, 97.4% ee, S isomer; $[a]_D^{25} = -27.0$ (c = 1.00 in CHCl₃) (lit.9 $[a]_D^{20} = -25.2$ (c = 1.0, CHCl₃)).¹H NMR (600 MHz, DMSO-*d*₆) δ 7.68 (d, *J* = 6.0 Hz, 2H), δ 7.58 (d, *J* = 3.0 Hz, 2H), 5.41 (d, *J* = 3.0 Hz, 1H), 4.81 – 4.85 (m, 1H), 1.35 (d, *J* = 6.0 Hz, 3H).¹³C NMR (150 MHz, DMSO-*d*₆) δ 152.61, 127.80, 127.59, 126.48, 125.78, 125.34, 124.98, 68.03, 26.22.

(S)-1-1-p-Tolyl-ethanol (P9): Colorless oil; known compound^[5]; purified by silica gel

chromatography (petroleum ethe/ethylacetate = 20:1), 97.3% yield, 50mg, 92.8% ee, S isomer; $[a]_D^{25} = -46.7$ (c = 1.00 in CHCl₃) (lit.5 $[a]_D^{20} = -52.1$ (c = 1.0, CHCl₃)). ¹H NMR (400 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 144.91, 135.87, 129.00, 128.98, 125.76, 125.73, 68.50, 26.43, 21.12.

OH

(S)-1-(4-ethylphenyl)ethan-1-ol (P10): Colorless oil; known compound^[4]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 73.1% yield, 83mg, 98.8% ee, *S* isomer; $[a]_D^{25} = -40.8(c = 1.00 \text{ in CHCl}_3)$ (lit.4 $[a]_D^{20} = -50.1 (c = 1.0, CHCl_3)$). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.25 (d, *J* = 3.0 Hz, 2H), 7.13 (d, *J* = 6.0 Hz, 2H), 5.07 (d, *J* = 3.0 Hz, 1H), 4.68 - 4.70 (m, 1H), 2.55 - 2.58 (m, 2H), 1.31 (d, *J* = 3.0 Hz, 3H), 1.15 - 1.17 (m, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 145.15, 142.35, 127.78, 125.77, 68.45, 28.36, 26.41, 16.23.



CI

OH

(S)-1-(4-Methoxy-phenyl)-ethanol (P11): Colorless oil; known compound^[5]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 89.7% yield, 52mg, 96.2% ee, *S* isomer; $[a]_D^{25} = -35.8$ (c = 1.00 in CHCl₃) (lit.5 $[a]_D^{20} = -41.7$ (c = 1.0, CHCl₃)). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.31 – 7.35 (m, 2H), 6.90 – 6.94 (m, 2H), 5.12 – 5.14 (m, 1H), 4.74 – 4.78 (m, 1H), 3.75 – 3.76 (m, 3H), 1.37 – 1.41 (m, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 158.52, 139.89, 126.95, 126.94, 113.79, 68.28, 55.37, 55.35, 26.37, 26.35.

(S)-1-(3-chlorophenyl)ethan-1-ol (P12): Colorless oil; known compound^[5]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 96.7% yield, 118mg, 89.8% ee, *S* isomer; $[a]_D^{25} = -31.0$ (c = 1.00 in CHCl₃) (lit.5 $[a]_D^{20} = -40.4$ (c = 1.0, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.42 (s, 1H), 7.25 – 7.35 (m, 3H), 5.35 (d, *J* = 3 Hz, 1H), 4.74 – 4.78 (m, 1H),

1.35 (d, J = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO- d_6) δ 150.49, 133.36, 130.30, 126.83, 125.65, 124.43, 68.03, 26.21.



(S)-1-(3-bromophenyl)ethan-1-ol (P13) : Colorless oil; known compound^[6]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 73.0% yield, 107mg, 84.9% ee, *S* isomer; $[a]_D^{25} = -25.8$ (c = 1.00 in CHCl₃)(lit.6 $[a]_D^{20} = -28.87$ (c = 2.8, CHCl₃)); ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.65 – 7.68 (m, 1H), 7.26 – 7.45 (m, 3H), 5.42 (s, 1H), 4.84 (s, 1H), 1.41 – 1.46 (m, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 150.57, 130.52, 129.82, 128.68, 124.80, 122.25, 68.28, 26.21.



(S)-1-(3-(trifluoromethyl)phenyl)ethan-1-ol (P14): Colorless oil; known compound^[7]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 95.0% yield, 65mg, 91.4% ee, *S* isomer; $[a]_D^{25} = -19.7$ (c = 1.00 in CHCl₃) (lit.7 $[a]_D^{20} = -31$ (c = 1.95, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.71 (s, 1H), 7.65 (d, *J* = 3.0 Hz, 1H), 7.55 – 7.60 (m, 2H), 5.41 (d, *J* = 3.0 Hz, 1H), 4.82 – 4.86 (m, 1H), 1.37 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 149.31, 129.96, 129.49, 129.20, 125.77, 123.67, 122.14, 67.92, 26.24.



OH

(S)-1-(3-methoxyphenyl)ethan-1-ol (P15): Colorless oil; known compound^[8];

purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 96.6% yield, 63mg, 98.7% ee, *S* isomer; $[a]_D^{25} = -30.4$ (c = 1.00 in CHCl₃) (lit.8 $[a]_D^{20} = -42.1$ (c = 1.0, CHCl₃)); ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.22 - 7.26 (m, 1H), 6.93 - 7.00 (m, 2H), 6.78 - 6.82 (m, 1H), 5.18 - 5.23 (m, 1H), 4.72 - 4.78 (m, 1H), 3.76 - 3.77 (m, 3H), 1.34 - 1.38 (m, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 159.68, 149.66, 129.47, 118.02, 112.31, 111.33, 68.60, 55.30, 26.39.

OH (S)-2-methyl-1-phenylpropan-1-ol (P16): Colorless oil; known compound^[10]; 85.2%

yield, 50mg, 98.2% ee, *S* isomer; $[a]_D^{25} = -39.8$ (c = 1.00 in CHCl₃) (lit.10 $[a]_D^{24} = -41.1$ (c =1.24, CHCl₃)). ¹H NMR (600 MHz, DMSO) δ 7.06 – 7.09 (m, 4H), 6.96 – 7.00 (m, 1H), 4.86 – 4.87 (m, 1H), 4.01 – 4.04 (m, 1H), 1.56 – 1.61 (m, 1H), 0.63 – 0.65 (m, 3H), 0.52 – 0.53 (m, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 145.55, 128.08, 126.97, 126.95, 78.04, 35.49, 19.54, 18.41.

(S)-1-Phenyl-butan-1-ol (P17): Colorless oil; known compound^[7]; purified by silica

gel chromatography (petroleum ethe/ethylacetate = 20:1), 93.4% yield, 28mg, 90.7% ee, *S* isomer; $[a]_D^{25} = -40.0$ (c = 1.00 in CHCl₃) (lit.7 $[a]_D^{20} = -44.2$ (c = 0.99, CHCl₃)). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.29 - 7.32 (m, 4H), 7.20 - 7.22 (m, 1H), 5.10 (d, *J* = 3.0 Hz, 1H), 1.50 - 1.64 (m, 2H),

1.22 – 1.38 (m, 2H), 0.86 – 0.88 (m, 3H). 13 C NMR (150 MHz, DMSO- d_6) δ 146.99, 128.35, 126.97, 126.24, 72.50, 42.08, 19.02, 14.37.

Cl (S)-1-(2,4-dichlorophenyl)ethan-1-ol (P18): Colorless oil; known compound^[13]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 20:1), 58.2% yield, 49mg, 84.4 % ee, *S* isomer; $[a]_D^{25} = -46.0$ (c = 1.00 in CHCl₃) (lit.13 $[a]_D^{20} = -21.6$ (c = 0.5, CHCl₃)). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.67 (d, *J* = 3.0 Hz, 1H), 7.46 (d, *J* = 1.2 Hz, 1H), 7.41 – 7.42 (m, 1H), 5.49 (d, *J* = 2.1 Hz, 1H), 5.03 – 5.07 (m, 1H), 1.34 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 144.14, 132.21, 131.57, 128.75, 128.62, 127.83, 65.21, 24.49.



OH

Cl⁽³⁾ (S)-1-(3,4-dichlorophenyl)ethan-1-ol (P19): Colorless oil; known compound^[12]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 96.8% yield, 98mg, 83.4 % ee, *S* isomer; $[a]_D^{25} = -37.2$ (c = 1.00 in CHCl3) (lit.12 $[a]_D^{20} = -33.0$ (c=0.30, CHCl₃)). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.55 – 7.57 (m, 2H), 7.32 – 7.34 (m, 1H), 5.39 (d, *J* = 3.0 Hz, 1H), 4.71 – 4.75 (m, 1H), 1.32 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 149.12, 131.15, 130.70, 129.30, 127.81, 126.19, 67.40, 26.07.



CF₃ (S)-1-(3,5-Bis-trifluoromethyl-phenyl)-ethanol (P20): White solid, mp: 53.4-54.8°C; known compound^[16]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 84.5% yield, 99mg, 75.8% ee, *S* isomer; $[a]_D^{25} = -12.8$ (c = 1.00 in CHCl₃) (lit.16 $[a]_D^{20} = -20.4$ (c =1.0, CHCl₃)). ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.02 (s, 2H), 7.91 (s, 1H), 5.61 (d, *J* = 2.3 Hz, 1H), 4.92 - 4.96 (m, 1H), 1.38 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 151.39, 130.82, 130.60, 130.38, 130.17, 126.50, 124.82, 123.01, 121.21, 120.61, 67.44, 25.99.



OH

(S)-1-(3,4-dimethoxyphenyl)ethan-1-ol (P21): Colorless oil; known compound^[11]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 5:1), 50.0% yield, 28mg, 81.1% ee, *S* isomer; $[a]_D^{25} = -42.7$ (c = 1.00 in CHCl₃) (lit.11 $[a]_D^{20} = -37.3$ (c = 1.09, CHCl₃)). ¹H NMR (600 MHz, DMSO-*d*₆) δ 6.98 (s, 1H), 6.85 - 6.88 (m, 2H), 5.09 (d, *J* = 3.0 Hz, 1H), 4.68 - 4.72 (m, 1H), 3.74 (d, *J* = 9.0 Hz, 6H), 1.34 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 149.04, 148.02, 140.55, 117.69, 111.96, 109.79, 68.47, 55.96, 55.79, 26.39.

(S)-1-(naphthalen-2-yl)ethan-1-ol (P22): White solid ,Mp: 70.6-71.4°C; known compound^[14]; purified by silica gel chromatography (petroleum ethe/ethylacetate = 10:1), 96.9%

yield, 68mg, 91.1% ee, *S* isomer; $[a]_D^{25} = -43.5$ (c = 1.00 in CHCl₃) (lit.14 $[a]_D^{20} = -38.5$ (c =1.0, CHCl₃)). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.87 - 7.92 (m, 4H), 7.48 - 7.56 (m, 3H), 5.34 (d, *J* = 3.0 Hz, 1H), 4.91 - 4.95 (m, 1H), 1.45 (d, *J* = 3.0 Hz, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 145.43, 133.37, 132.61, 128.16, 128.00, 127.94, 126.41, 125.86, 124.86, 123.68, 68.65, 26.32.

26mg, 63.9 % ee, S isomer; $[a]_D^{25} = -14.0$ (c = 1.00 in CHCl₃) (lit.17 $[a]_D^{25} = -16.1$ (c = 0.88, CHCl₃)). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.32 - 7.33 (m, 1H), 7.17 - 7.22 (m, 3H), 5.21 (d, *J* = 3 Hz, 1H), 5.02 - 5.05 (m, 1H), 2.88 - 2.92 (m, 1H), 2.67 - 2.73 (m, 1H), 2.29 - 2.34 (m, 1H), 1.73 - 1.79 (m, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 146.87, 142.98, 127.78, 126.59, 124.87, 124.63, 74.84, 35.95, 29.73.



(S)-4-phenylbut-3-en-2-ol (P24): Light yellow oil, known compound^[18]; 98.0 %

yield, 64mg, 68.9 % ee, *S* isomer; $[a]_{D}^{20} = -12.2$ (c = 1.00 in CHCl₃).¹H NMR (400 MHz, DMSO-*d*₆) δ 7.41(d, *J* = 4 Hz, 2H), 7.30 - 7.34 (m, 2H), 7.20 - 7.24 (m, 1H), 6.51 (d, *J* = 8 Hz, 1H), 6.29 - 6.34 (m, 1H), 4.91 (d, *J* = 2 Hz, 1H), 4.29 - 4.33 (m, 1H), 1.22 (d, *J* = 4 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 137.41, 136.02, 129.11, 127.69, 127.65, 126.66, 67.15, 24.35.



(S)-4-(4-fluorophenyl)but-3-en-2-ol (P25): Colorless oil; known compound^[18];

97.5% yield, 71mg, 66.3% ee, *S* isomer; $[a]_D^{20} = -9.833$ (c = 1.00 in CHCl₃). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.46 (s, 2H), 7.13 – 7.17 (m, 2H), 6.51 (d, *J* = 8 Hz, 1H), 6.26 (d, *J* = 8 Hz, 1H), 4.91 (s, 1H), 4.30 (s, 1H), 1.22 (d, *J* = 4 Hz, 3H).¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.02, 160.63, 135.93, 135.90, 133.99, 133.95, 128.51, 128.43, 126.43, 115.97, 115.61, 67.10, 24.30.



Br (S)-4-(4-bromophenyl)but-3-en-2-ol (P26): Light yellow solid, known compound^[18]; 90.5 % yield, 90.0mg, 65.1 % ee, *S* isomer; $[a]_D^{20} = -7.7$ (c = 1.00 in CHCl₃). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.50 (d, *J* = 4 Hz, 2H), 7.38 (d, *J* = 4 Hz, 2H), 6.49 (d, *J* = 8 Hz, 1H), 6.33 - 6.38 (m, 1H), 4.94 (d, *J* = 2 Hz, 1H), 4.28 - 4.32 (m, 1H), 1.21 (d, *J* = 4 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 137.12, 136.71, 131.95, 128.71, 126.40, 120.56, 67.00, 24.21.



(S)-4-(p-tolyl)but-3-en-2-ol (P27): Light yellow solid, known compound^[18];

71.5 % yield, 51mg, 69.0 % ee, *S* isomer; $[a]_D^{20} = -6.2$ (c = 1.00 in CHCl₃). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.25 (d, *J* = 4 Hz, 2H), 7.08 (d, *J* = 4 Hz, 2H), 6.41 (d, *J* = 8 Hz, 1H), 6.16 - 6.22 (m, 1H),

4.81 – 4.83 (m, 1H), 4.22 – 4.27 (m, 1H), 2.23 (s, 3H) 1.16 (d, J = 2 Hz, 3H). ¹³C NMR (100 MHz, DMSO- d_6) δ 136.90, 134.93, 134.61, 129.69, 127.58, 126.58, 67.21, 24.37, 21.27.



H₃CO (S)-4-(4-methoxyphenyl)but-3-en-2-ol (P28): White solid, known compound^[18]; 54.0 % yield, 42mg, 70.5 % ee, S isomer; $[a]_D^{20} = -18.5$ (c = 1.00 in CHCl₃). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.34 (d, *J* = 4 Hz, 2H), 6.88 (d, *J* = 4 Hz, 2H), 6.43 (d, *J* = 8 Hz, 1H), 6.11 – 6.17 (m, 1H), 4.82 (d, *J* = 2 Hz, 1H), 4.25 – 4.29 (m, 1H), 3.74 (s, 3H) 1.20 (d, *J* = 2 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 159.07, 133.64, 129.98, 127.86, 127.27, 114.50, 67.28, 55.58, 24.36.

4. NMR spectra



















































S34









5. HPLC and GC chromatograms of alcohol products

(±)-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): Colorless oil; 89.2% yield, 93.1 % ee, S isomer; $[a]_D^{25} = -40.5$ (c = 1.00 in CHCl₃). The enantiomeric excess was determined by GC equipped with a chiral θ -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]	[%]
1	11.887	8190	3.462
2	12.294	228338	96.538

(±)-1-(2-Fluoro-phenyl)-ethanol(P2): 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(P2): Colorless oil; 47.6 % yield, 88.0 % ee, S isomer; $[a]_D^{25} = -35.3$ (c = 1.00 in CHCl₃). 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.



39299

94.021

S40	

12.230

2

(±)-1-(2-Chlorophenyl)-ethan-1-ol(P3): 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.



[min]

(S)-1-(2-Chlorophenyl)-ethan-1-ol(P3): Colorless oil; 40.2 % yield, 93.9 % ee, S isomer; $[a]_D^{25} = -40.9$ (c = 1.00 in CHCl₃). 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: 125°C; inlet pressure = 0.06 MPa.



Peak	Retention time	Area	Area
	[min]	[uv*s]	[%]
1	29.692	1720	3.038
2	36.885	54902	96.962

(±)-1-(2-Bromophenyl)-ethan-1-ol(P4): 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(P4): Colorless oil; 54.5 % yield, 84.2 % ee, S isomer; $[a]_D^{25} = -31.9$ (c = 1.00 in CHCl₃). 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: 130°C; inlet pressure = 0.06 MPa.



[min]

Peak	Retention time	Area	Area
	[min]	[uv*s]	[%]
1	42.897	4522	7.906
2	56.135	52673	92.094

(±)-1-(4-Fluoro-phenyl)-ethanol(P5): 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(P5): Colorless oil; 82.7 % yield, 96.1 % ee, S isomer; $[a]_D^{25} = -29.0$ (c = 1.00 in CHCl₃). The enantiomeric excess 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.



Peak	Retention time	Area	Area
	[min]	[uv*s]	[%]
1	17.906	732	1.957
2	19.289	36682	98.043

(±)-1-(4-chloro-phenyl)-ethan-1-ol(P6): 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-chloro-phenyl)-ethan-1-ol(P6): Colorless oil; 96.6% yield, 96.8% ee, S isomer; $[a]_D^{25} = -46.3$ (c = 1.00 in CHCl₃). 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: 130 °C; inlet pressure =

0.06MPa





Peak	Retention time	Area	Area
	[min]	[uv*s]	[%]
1	27.401	3924	1.641
2	28.878	232302	98.359

(±)-1-(4-bromo-phenyl)-ethan-1-ol(P7): 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-(4-bromo-phenyl)-ethan-1-ol(P7): Colorless oil; 87.1% yield, 87.6% ee, S isomer; $[a]_D^{25} = -32.1$ (c = 1.00 in CHCl₃); The enantiomeric excess were determined by GC equipped with a chiral θ -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]	[%]
1	23.060	2597	6.208
2	24.231	39236	93.792

(±)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (P8): 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-(trifluoromethyl)phenyl)ethan-1-ol (P8): Colorless oil; 97.5% yield, 97.4% ee, S isomer; $[a]_{D}^{25} = -27.0$ (c = 1.00 in CHCl₃). 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	20.446	3854	1.298
2	22.438	293026	98.702

(±)-1-p-Tolyl-ethanol(P9): 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 = 0.08 MPa.



(S) -1-p-Tolyl-ethanol(P9): Colorless oil; 90.3 % yield, 92.8% ee, S isomer; $[a]_D^{25} = -46.7$ (c = 1.00 in CHCl₃). 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]	[%]
1	17.563	4164	3.583
2	18.706	112058	96.417

(±)-1-(4-ethylphenyl)ethan-1-ol(10): 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(P10): Colorless oil; 73.1 % yield, 98.8 % ee, S isomer; $[a]_D^{25} = -40.8$ (c = 1.00 in CHCl₃). 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.



[min]

Peak	Retention time	Area	Area
	[min]	[uv*s]	[%]
1	26.120	2661	0.605
2	26.802	437151	99.395

(±)-1-(4-Methoxy-phenyl)-ethanol(P11): 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(P11): Colorless oil; 86.7 % yield, 95.3% ee, S isomer; $[a]_D^{25} = -35.8(c = 1.00 \text{ in CHCl}_3)$. 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: 125 °C; inlet pressure = 0.06 MPa.



Peak	Retention time	Area	Area
	[min]	[uv*s]	[%]
1	44.479	996	2.356
2	46.240	41259	97.644

(±)-1-(3-chlorophenyl)ethan-1-ol (P12): 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-(3-chlorophenyl)ethan-1-ol (P12): Colorless oil; 96.7% yield, 89.8% ee, S isomer; $[a]_D^{25} = -31.0$ (c = 1.00 in CHCl₃);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: 130 °C; inlet pressure = 0.08 MPa



Peak	Retention time	Area	Area	
	[min]	[uv*s]	[%]	
1	20.834	5093	5.070	
2	21.730	95352	94.930	

(±)-1-(3-bromophenyl)ethan-1-ol (P13) : 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(P13): Colorless oil; 73.0 % yield, 84.8 % ee, S isomer; $[a]_D^{25} = -25.8$ (c = 1.00 in CHCl₃). 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.



[min]

Peak	Retention time	Area	Area	
	[min]	[uv*s]	[%]	
1	21.509	9649	7.580	
2	22.113	117652	92.420	

(±)-1-(3-(trifluoromethyl)phenyl)ethan-1-ol(P14): 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-(trifluoromethyl)phenyl)ethan-1-ol(P14): Colorless oil; 95.0 % yield, 92.2 % ee, S isomer; $[a]_D^{25} = -19.7$ (c = 1.00 in CHCl₃). 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	15.910	6467	3.891	
2	16.710	159724	96.109	

(±)-1-(3-methoxyphenyl)ethan-1-ol(P15): 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(P15): Colorless oil; 96.6 % yield, 98.8 % ee, S isomer; $[a]_D^{25} = -30.4$ (c = 1.00 in CHCl₃). 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.



[min]

Peak	Retention time	Area	Area	
	[min]	[uv*s]	[%]	
1	43.777	1706	0.624	
2	45.027	271609	99.376	

(±)-2-methyl-1-phenylpropan-1-ol (P16): 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)-2-methyl-1-phenylpropan-1-ol (P16): Colorless oil; 85.2% yield, 98.2% ee, S isomer; $[a]_D^{25} = -39.8$ (c = 1.00 in CHCl₃). 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.



[min]

Peak	Retention time	Area	Area	
	[min]	[uv*s]	[%]	
1	39.477	932	0.917	
2	40.136	100704	99.083	

(±)-1-Phenyl-butan-1-ol(P17): 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(P17): Colorless oil; 93.4 % yield, 90.7% ee, S isomer; $[a]_D^{25} = -40.5$ (c = 1.00 in CHCl₃). The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 95:5; flow rate = 0.5 mL/min; UV detection at 254 nm. mV



reak	Channel	Time (min)	(mAU*s)	(mAU)	(%)
1	PDA 254 nm	42.006	360322	4018	4.669
2	PDA 254 nm	46.900	7356467	69195	95.331

(±)-1-(2,4-dichlorophenyl)ethan-1-ol(P18): 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: 150 °C; inlet pressure = 0.08 MPa.



(S)-1-(2,4-dichlorophenyl)ethan-1-ol(P18): Colorless oil; 99 % yield,84.3 % ee, S isomer; $[a]_D^{25} = -46.0$ (c = 1.00 in CHCl₃). 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	18.753	4250	7.831	
2	54.464	50025	92.169	

(±)-1-(3,4-dichlorophenyl)ethan-1-ol (P19): 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: 150 °C; inlet pressure = 0.08 MPa.



(S)-1-(3,4-dichlorophenyl)ethan-1-ol (P19): Colorless oil; 96.8% yield, 83.4 % ee, S isomer; $[a]_D^{25}$ = - 37.2 (c = 1.00 in CHCl₃). 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: 150 °C; inlet pressure = 0.08 MPa.



Peak	Retention time	Area	Area	
	[min]	[uv*s]	[%]	
1	24.914	21425	8.308	
2	25.657	236464	91.692	

(±)-1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol(P20): The racemate was determined by GC equipped with a chiral θ -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-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol(P20): White solid, Mp: 53.4 - 54.8 °C ; 84.5 % yield, 75.8 % ee, S isomer; $[a]_D^{25} = -12.797$ (c = 1.00 in CHCl₃). 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	9.639	217798	87.897
2	10.802	29990	12.103

(±)-1-(3,4-dimethoxyphenyl)ethan-1-ol(P21): 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 = 0.1 MPa.



(S)-1-(3,4-dimethoxyphenyl)ethan-1-ol(P21): Colorless oil; 50 % yield, 81.1 % ee, S isomer; $[a]_D^{25}$ = - 42.7 (c = 1.00 in CHCl₃). 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 = 0.1 MPa.



[min]

Peak	Retention time	Area	Area	
	[min]	[uv*s]	[%]	
1	62.292	11849	9.464	
2	63.563	104456	90.536	

(±)-1-(naphthalen-2-yl)ethan-1-ol(P22): 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-(naphthalen-2-yl)ethan-1-ol(P22): White solid Mp: 70.6 - 71.4 °C; 99 % yield, 91.1 % ee, S isomer; $[a]_D^{25} = -43.5$ (c = 1.00 in CHCl₃). 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: 140 °C; inlet pressure = 0.08 MPa.



Peak	Retention time	Area	Area	
	[min]	[uv*s]	[%]	
1	80.022	8409	4.428	
2	82.340	181517	95.572	

(±)-2,3-dihydro-1H-inden-1-ol (P23): The racemate was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 97:3; flow rate = 1.0 mL/min; UV detection at 254nm.



(S)-2,3-dihydro-1H-inden-1-ol (P23): White solid, Mp: 53.4 - 54.8 °C ; 51.4 % yield, 63.9 % ee, S isomer; $[a]_D^{25} = -14.0$ (c = 1.00 in CHCl₃). The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 97:3; flow rate = 1.0 mL/min; UV detection at 254nm.





Peak	Processed	Retention	Peak Area	Peak Hight	Peak Area
	Channel	Time (min)	(mAU*s)	(mAU)	(%)
1	PDA 254 nm	13.297	913124	36451	81.974
2	PDA 254 nm	15.182	200791	7331	18.026

(±)-4-phenylbut-3-en-2-ol (P24): The racemate was determined by HPLC on Chiralcel IB-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254nm.



(S)-4-phenylbut-3-en-2-ol (P24):Yellowish oil; 98.0 % yield, 68.9 % ee, S isomer; $[a]_D^{20} = -12.2$ (c = 1.00 in CHCl₃). The racemate was determined by HPLC on Chiralcel IB-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254nm.



(±)-4-(4-fluorophenyl)but-3-en-2-ol (P25): The racemate was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 254nm.



(S)-4-(4-fluorophenyl)but-3-en-2-ol (P25): Colorless oil; 97.5% yield, 66.3% ee, S isomer; $[a]_D^{20} = -$ 9.833 (c = 1.00 in CHCl₃). The racemate was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 254 nm.



(±)-4-(4-bromophenyl)but-3-en-2-ol (P26): The racemate was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 254 nm. mV



(S)-4-(4-bromophenyl)but-3-en-2-ol (P26): Yellowish solid, 90.5 % yield, 65.1 % ee, S isomer; $[a]_D^{20} = -7.7$ (c = 1.00 in CHCl₃). The racemate was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 254nm.



Peak	Processed	Retention	Peak Area	Peak Hight	Peak Area
	Channel	Time (min)	(mAU*s)	(mAU)	(%)
1	PDA 254 nm	28.621	4897254	88668	17.195
2	PDA 254 nm	31.411	23584261	392302	82.805

(±)-4-(p-tolyl)but-3-en-2-ol (P27): The racemate was determined by HPLC on Chiralcel IB-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 254nm.



(S)-4-(p-tolyl)but-3-en-2-ol (P27): Yellowish solid, 71.5 % yield, 69.0 % ee, S isomer; $[a]_D^{20} = -6.2$ (c = 1.00 in CHCl₃). The racemate was determined by HPLC on Chiralcel IB-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 254nm.



Peak	Processed	Retention	Peak Area	Peak Hight	Peak Area
	Channel	Time (min)	(mAU*s)	(mAU)	(%)
1	PDA 254 nm	23.184	3355537	81076	15.325
2	PDA 254 nm	26.971	18540835	408344	84.675

(±)-4-(4-methoxyphenyl)but-3-en-2-ol (P28): The racemate was determined by HPLC on Chiralcel IB-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 254nm.



(S)-4-(4-methoxyphenyl)but-3-en-2-ol (P28): White solid, 54.0 % yield, 70.5 % ee, S isomer; $[a]_D^{20} = -18.5$ (c = 1.00 in CHCl₃). The racemate was determined by HPLC on Chiralcel IB-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 254nm.



Peak	Processed	Retention	Peak Area	Peak Hight	Peak Area
	Channel	Time (min)	(mAU*s)	(mAU)	(%)
1	PDA 254 nm	32.909	2338908	45892	14.748
2	PDA 254 nm	37.433	13520603	233418	85.252

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