Supporting Information

Carbohydrate-based pseudo-dipeptides: New ligands for the highly enantioselective Ru-catalyzed transfer hydrogenation reaction

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SI. 1. General considerations. All reactions were carried out using standard Schlenk techniques under an atmosphere of argon. Solvents were purified and dried by standard procedures. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are relative to that of $SiMe_4$ as internal standard. ^{1}H and ^{13}C assignments were done based on ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC experiments.

SI. 2. Typical procedure for the preparation of ligands L1-L10. To a cooled solution (-15 °C) of the desired *N*-Boc-protected amino acid (1 mmol) in THF (2 mL) *N*-methylmorpholine (NMM, 1.15 mmol, 126 μL) and isobutylchloroformate (1.15 mmol, 150 μL) were slowly added. After 45 minutes, a solution of **2** (1 mmol, 323.4 mg) in THF (2 mL) was added and the resulting mixture was stirred at room temperature for 2 h. The crude mixture was purified by flash chromatography to produce the corresponding ligands as white solids.

L1: Yield: 382 mg, 73 %. ^{1}H NMR ($CDCl_3$), δ: 0.86 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$= 6.8 Hz), 0.91 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$= 7.2 Hz), 1.33 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.39 (s, 9H, CH_3, ^{t}Bu), 1.57 (s, 3H, CH_3), 2.07 (m, 1H, CH, ^{i}Pr), 2.89 (b, 1H, OH), 3.39 (m, 1H, H-6'), 3.59 (m, 1H, H-6), 3.80 (m, 1H, H-5), 3.87 (m, 2H, H-4 and CH), 4.34 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 3.6 Hz), 4,61 (s, 2H, CH_2, Bn), 5.18 (b, 1H, NH), 5.71 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.6 Hz), 6.49 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 16.6 (CH_3), 17.9 (CH_3, ^{i}Pr), 19.4 (CH_3, ^{i}Pr), 26.7 (CH_3), 26.9 (CH_3), 28.5 (CH_3, ^{t}Bu), 31.2 (CH, ^{i}Pr), 43.4 (C-6), 60.0 (CH), 67.2 (CH_2, Bn), 68.8 (C-5), 79.7 (C, ^{t}Bu), 79.9 (C-4), 82.8 (C-2), 83.4 (C-3), 104.2 (C-1), 113.2 (CMe_2), 127.8 (CH=), 127.9 (CH=), 128.4 (CH=), 138.1 (C), 155.9 (CO), 172.1 (CO). Anal. calcd (%) for $C_{27}H_{42}N_2O_8$: C 62.05, H 8.10, N 5.36; found: C 62.11, H 8.13, N 5.32.

L2: Yield: 400 mg, 81 %. ^{1}H NMR ($CDCl_3$), δ: 1.29 (d, 3H, CH_3, $^{3}J_{H\text{-}H}$= 6.8 Hz), 1.32 (s, 6H, CH_3), 1.39 (s, 9H, CH_3, ^{t}Bu), 1.56 (s, 3H, CH_3), 2.79 (b, 1H, OH), 3.32 (m, 1H, H-6'), 3.56 (m, 1H, H-6), 3.78 (m, 1H, H-5), 3.80 (m, 1H, H-4), 4.13 (m, 1H, CH), 4.33 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 3.6 Hz), 4.61 (m, 2H, CH_2, Bn), 5.37 (b, 1H, NH), 5.69 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.6 Hz), 6.60 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 16.4

(CH_3), 18.8 (CH_3), 26.5 (CH_3), 26.7 (CH_3), 28.2 (CH_3, ^{t}Bu), 43.4 (C-6), 60.4 (CH), 67.0 (CH_2, Bn), 68.7 (C-5), 79.6 (C-4), 79.7 (C, ^{t}Bu), 82.6 (C-2), 83.2 (C-3), 104.0 (C-1), 113.0 (CMe_2), 127.6 (CH=), 128.3 (CH=), 137.9 (C), 155.3 (CO), 171.1 (CO). Anal. calcd (%) for $C_{25}H_{38}N_2O_8$: C 60.71, H 7.74, N 5.66; found: C 60.79, H 7.79, N 5.62.

L3: Yield: 422 mg, 74 %. ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.35 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 3H, CH_3), 2.72 (b, 1H, OH), 3.01 (m, 2H, CH_2), 3.23 (m, 1H, H-6'), 3.53 (m, 1H, H-6), 3.66 (m, 1H, H-5), 3.82 (m, 1H, H-4), 4.39 (m, 1H, CH), 4.32 (d, 1H, H-2, $^3J_{2\text{-}1}$= 3.6 Hz), 4.59 (m, 2H, CH_2, OBn), 5.15 (b, 1H, NH), 5.65 (d, 1H, H-1, $^3J_{1\text{-}2}$= 3.6 Hz), 6.31 (b, 1H, NH), 7.1-7.4 (m, 10H, CH=). ^{13}C NMR ($CDCl_3$), δ: 18.8 (CH_3), 26.5 (CH_3), 26.7 (CH_3), 28.2 (CH_3, ^{t}Bu), 38.9 (CH_2), 43.6 (C-6), 60.4 (CH), 67.0 (CH_2, Bn), 68.7 (C-5), 75.9 (C, ^{t}Bu), 79.8 (C-4), 82.6 (C-2), 83.3 (C-3), 104.1 (C-1), 113.1 (CMe_2), 126.7 (CH=), 127.7 (CH=), 128.3 (CH=), 128.5 (CH=), 129.3 (CH=), 136.7 (C), 137.9 (C), 155.1 (CO), 171.1 (CO). Anal. calcd (%) for $C_{31}H_{42}N_2O_8$: C 65.24, H 7.42, N 4.91; found: C 65.13, H 7.40, N 4.87.

L4: Yield: 241 mg, 45 %. ^{1}H NMR ($CDCl_3$), δ: 0.92 (s, 9H, CH_3, ^{t}Bu), 1.31 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.38 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 3H, CH_3), 2.78 (b, 1H, OH), 3.41 (m, 1H, H-6'), 3.50 (m, 1H, H-6), 3.75 (m, 2H, H-5 and CH), 3.86 (m, 1H, H-4), 4.33 (d, 1H, H-2, $^3J_{2\text{-}1}$= 4.0 Hz), 4.60 (m, 2H, CH_2, Bn), 5.34 (b, 1H, NH), 5.68 (d, 1H, H-1, $^3J_{1\text{-}2}$= 4.0 Hz), 6.32 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 16.4 (CH_3), 26.5 (CH_3), 26.6 (CH_3, ^{t}Bu), 26.8 (CH_3), 28.3 (CH_3, ^{t}Bu), 34.5 (C, ^{t}Bu), 43.3 (C-6), 62.3 (CH), 67.0 (CH_2, Bn), 68.6 (C-5), 79.4 (C, ^{t}Bu), 79.8 (C-4), 82.7 (C-2), 83.3 (C-3), 104.0 (C-1), 113.0 (CMe_2), 127.6 (CH=), 127.7 (CH=), 128.3 (CH=), 137.9 (C), 155.5 (CO), 171.2 (CO). Anal. calcd (%) for $C_{28}H_{44}N_2O_8$: C 62.67, H 8.26, N 5.22; found: C 62.79, H 8.34, N 5.30.

L5: Yield: 241 mg, 45 %. ^{1}H NMR ($CDCl_3$), δ: 1.25 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.52 (s, 3H, CH_3), 2.89 (b, 1H, OH), 3.34 (m, 1H, H-6'), 3.52 (m, 1H, H-6), 3.71 (m, 1H, H-5), 3.80 (m, 1H, H-4), 4.32 (d, 1H, H-2, $^3J_{2\text{-}1}$= 3.6 Hz), 4.57 (m, 2H, CH_2, OBn), 5.09 (m, 1H, CH), 5.60 (d, 1H, H-1, $^3J_{1\text{-}2}$= 3.6 Hz), 5.92 (b, 1H, NH), 6.27 (b, 1H, NH), 7.2-7.4 (m, 10H, CH=). ^{13}C NMR ($CDCl_3$), δ: 16.3 (CH_3), 26.5

(CH_3), 26.7 (CH_3), 28.2 (CH_3, ^{t}Bu), 43.5 (C-6), 58.3 (CH), 67.0 (CH_2, Bn), 68.3 (C-5), 79.6 (C, ^{t}Bu), 79.8 (C-4), 82.5 (C-2), 83.2 (C-3), 104.0 (C-1), 113.2 (CMe_2), 124.9 (C), 127.1 (CH=), 127.7 (CH=), 127.8 (CH=), 128.1 (CH=), 128.3 (CH=), 128.9 (CH=), 137.8 (C), 155.1 (CO), 170.3 (CO). Anal. calcd (%) for $C_{30}H_{40}N_2O_8$: C 64.73, H 7.24, N 5.03; found: C 64.78, H 7.26, N 4.99.

L6: Yield: 402 mg, 78 %. ^{1}H NMR ($CDCl_3$), δ: 0.85 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 7.2 Hz), 0.89 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 7.2 Hz), 1.31 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.39 (s, 9H, CH_3, ^{t}Bu), 1.57 (s, 3H, CH_3), 2.02 (m, 1H, CH, ^{i}Pr), 2.72 (b, 1H, OH), 3.31 (m, 1H, H-6'), 3.59 (m, 1H, H-6), 3.77 (m, 1H, H-5), 3.86 (m, 2H, H-4 and CH), 4.33 (d, 1H, H-2, $^3J_{2\text{-}1}$= 3.6 Hz), 4.60 (m, 2H, CH_2, Bn), 5.19 (b, 1H, NH), 5.69 (d, 1H, H-1, $^3J_{1\text{-}2}$= 3.6 Hz), 6.45 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 16.3 (CH_3), 18.7 (CH_3, ^{i}Pr), 26.5 (CH_3), 26.7 (CH_3), 28.3 (CH_3, ^{t}Bu), 30.8 (CH, ^{i}Pr), 43.3 (C-6), 58.5 (CH), 67.0 (CH_2, Bn), 68.7 (C-5), 79.9 (C, ^{t}Bu), 82.6 (C-4), 83.2 (C-2), 83.3 (C-3), 104.1 (C-1), 113.1 (CMe_2), 127.6 (CH=), 127.7 (CH=), 128.3 (CH=), 138.0 (C), 155.9 (CO), 171.9 (CO). Anal. calcd (%) for $C_{27}H_{42}N_2O_8$: C 62.05, H 8.10, N 5.36; found: C 62.13, H 8.14, N 5.33.

L7: Yield: 240 mg, 50 %. ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 6H, CH_3), 1.39 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 3H, CH_3), 2.41 (b, 1H, OH), 3.25 (m, 1H, H-6'), 3.61 (m, 1H, H-6), 3.75 (m, 2H, CH_2), 3.78 (m, 1H, H-5), 3.86 (m, 1H, H-4), 4.32 (d, 1H, H-2, $^3J_{2\text{-}1}$= 3.6 Hz), 4.58(m, 2H, CH_2, Bn), 5.38 (b, 1H, NH), 5.68 (d, 1H, H-1, $^3J_{1\text{-}2}$= 3.6 Hz), 6.70 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 16.3 (CH_3), 26.5 (CH_3), 26.7 (CH_3), 28.3 (CH_3, ^{t}Bu), 43.4 (C-6), 44.0 (CH_2), 66.9 (CH_2, Bn), 68.7 (C-5), 79.7 (C-4), 79.9 (C, ^{t}Bu), 82.7 (C-2), 83.3 (C-3), 104.0 (C-1), 113.0 (CMe_2), 127.6 (CH=), 127.7 (CH=), 128.3 (CH=), 138.0 (C), 156.0 (CO), 169.9 (CO). Anal. calcd (%) for $C_{24}H_{36}N_2O_8$: C 59.98, H 7.55, N 5.83; found: C 60.01, H 7.58, N 5.85.

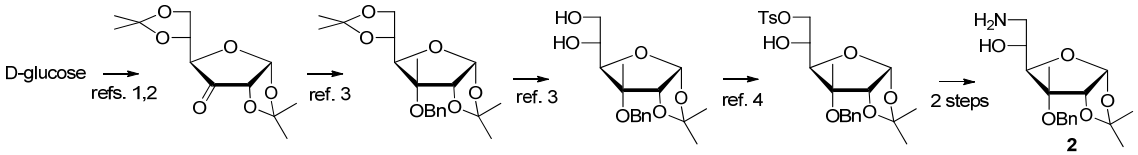
L8: Yield: 415 mg, 79 %. ^{1}H NMR ($CDCl_3$), δ: 0.87 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 6.8 Hz), 0.93 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 7.2 Hz), 1.28 (s, 3H, CH_3), 1.38 (s, 9H, CH_3, ^{t}Bu), 1.48 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 2.01 (m, 1H, CH, ^{i}Pr), 3.35 (m, 1H, H-6'), 3.67 (m, 1H, H-6), 3.82 (m, 1H, H-4), 3.91 (m, 1H, H-3), 4.01 (m, 1H, CH), 4.09 (m, 1H, H-5), 4.42 (d,

1H, H-2, $^{3}J_{2\text{-}1}$= 3.6 Hz), 4.52 (d, 1H, CH_2, Bn, $^{3}J_{2\text{-}1}$= 12.4 Hz), 4.65 (d, 1H, CH_2, Bn, $^{3}J_{2\text{-}1}$= 12.4 Hz), 5.24 (b, 1H, NH), 5.79 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.6 Hz), 6.82 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 15.4 (CH_3), 18.7 (CH_3, ^{i}Pr), 19.0 (CH_3, ^{i}Pr), 26.4 (CH_3), 27.0 (CH_3), 28.3 (CH_3, ^{t}Bu), 30.9 (CH, ^{i}Pr), 44.7 (C-6), 60.1 (CH), 65.2 (CH_2, Bn), 69.1 (C-5), 69.7 (C, ^{t}Bu), 75.7 (C-4), 83.4 (C-2), 84.6 (C-3), 104.4 (C-1), 112.0 (CMe_2), 126.7 (CH=), 127.4 (CH=), 128.3 (CH=), 138.7 (C), 155.9 (CO), 174.0 (CO). Anal. calcd (%) for $C_{27}H_{42}N_2O_8$: C 62.09, H 8.11, N 5.35; found: C 62.11, H 8.13, N 5.32.

L9: Yield: 392 mg, 77 %. ^{1}H NMR ($CDCl_3$), δ: 0.88 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$= 6.8 Hz), 0.95 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$= 7.2 Hz), 1.27 (s, 3H, CH_3), 1.39 (s, 9H, CH_3, ^{t}Bu), 1.42 (s, 3H, CH_3), 2.11 (m, 1H, CH, ^{i}Pr), 3.36 (b, 1H, OH), 3.62 (m, 1H, H-6'), 3.82 (m, 1H, H-6), 3.91 (m, 1H, H-5), 4.02 (m, 2H, H-4 and CH), 4.56 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 4.0 Hz), 4.58 (d, 1H, CH_2, Bn, ^{3}J= 10.6 Hz), 4.65 (d, 1H, CH_2, Bn, ^{3}J= 10.6 Hz), 5.16 (b, 1H, NH), 5.87 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 4.0 Hz), 6.71 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 18.7 (CH_3, ^{i}Pr), 19.2 (CH_3, ^{i}Pr), 26.2 (CH_3), 26.7 (CH_3), 28.4 (CH_3, ^{t}Bu), 30.9 (CH, ^{i}Pr), 44.1 (C-6), 60.0 (CH), 68.1 (CH_2, Bn), 71.8 (C, ^{t}Bu), 72.4 (C-5), 80.5 (C-4), 81.6 (C-2), 82.4 (C-3), 105.1 (C-1), 111.7 (CMe_2), 127.8 (CH=), 127.9 (CH=), 128.5 (CH=), 137.5 (C), 155.8 (CO), 172.0 (CO). Anal. calcd (%) for $C_{26}H_{40}N_2O_8$: C 61.44, H 7.97, N 5.56; found: C 61.40, H 7.93, N 5.51.

L10: Yield: 294 mg, 63 %. ^{1}H NMR ($CDCl_3$), δ: 1.34 (s, 3H, CH_3), 1.39 (s, 9H, CH_3, ^{t}Bu), 1.42 (s, 3H, CH_3), 2.49 (b, 1H, OH), 3.45 (m, 1H, H-6'), 3.65 (m, 1H, H-6), 3.86 (m, 1H, H-5), 3.92 (m, 1H, H-4), 3.99 (m, 1H, CH), 4.43 (d, 1H, H-2, $^{3}J_{2\text{-}1}$= 3.6 Hz), 4.62 (m, 2H, CH_2, Bn), 5.21 (b, 1H, NH), 5.79 (d, 1H, H-1, $^{3}J_{1\text{-}2}$= 3.6 Hz), 6.73 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 16.8 (CH_3), 26.4 (CH_3), 27.1 (CH_3), 28.3 (CH_3, ^{t}Bu), 43.9 (C-6), 44.3 (CH_2), 66.7 (CH_2, Bn), 68.9 (C-5), 79.4 (C-4), 79.7 (C, ^{t}Bu), 83.2 (C-2), 83.5 (C-3), 104.3 (C-1), 112.7 (CMe_2), 127.7 (CH=), 127.9 (CH=), 128.2 (CH=), 138.4 (C), 155.8 (CO), 171.2 (CO). Anal. calcd (%) for $C_{23}H_{34}N_2O_8$: C 59.24, H 7.41, N 5.97; found: C 59.21, H 7.35, N 6.00.

SI. 3. Synthesis of 6-amine-6-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-3-*O*-benzyl-α-allofuranose 2



The following intermediate compounds for the synthesis of **2** have been previously described: 1,2:5,6-*O*-di-isopropylidene-α-D-glucofuranose[1] (97% yield), 1,2:5,6-di-*O*-isopropylidene-α-D-ribo-hexofuranos-3-ulose[2] (84% yield), 1,2;5,6-*O*-di-isopropylidene-3-*C*-methyl-α-D-allofuranose[3] (95% yield), 3-*O*-benzyl-3-*C*-methyl-1,2;5,6-di-*O*-isopropylidene-α-D-allofuranose[3] (97% yield), 3-*O*-benzyl-3-*C*-methyl-1,2-*O*-isopropylidene-α-D-allofuranose[3] (83% yield) and 3-*O*-benzyl-3-*C*-methyl-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-allofuranose[4] (75% yield).

Synthesis of 6-azido-6-deoxy-1,2-O-isopropylidene-3-C-methyl-3-benzyl-α-allofuranose. To a solution of 3-*O*-benzyl-3-*C*-methyl-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-allofuranose (10 mmol, 4.78 g) in DMF (100 mL), sodium azide (12 mmol, 0.78 g) was added. The solution was stirred at 90 °C overnight. Then, DMF was removed by evaporation in vacuo and water (25 mL) was added. The mixture was extracted with dichloromethane (3 x 50 mL) and the organic phase dried over $MgSO_4$. The dried extract was evaporated and purified by flash chromatography (ethyl acetate/petroleum ether: 3/1) to give the corresponding azido-alcohol as a white solid. Yield: 2.86 g, 82 %. ^{1}H NMR ($CDCl_3$), δ: 1.36 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 2.81 (b, 1H, OH), 3.37 (dd, 1H, H-6', $^2J_{6'-6}$= 13.2 Hz, $^3J_{6'-5}$= 4.0 Hz), 3.48 (dd, 1H, H-6, $^2J_{6'-6}$= 13.2 Hz, $^3J_{6-5}$= 2.8 Hz), 3.89 (m, 1H, H-5), 3.98 (m, 1H, H-4), 4.39 (d, 1H, H-2, $^3J_{2-1}$= 3.6 Hz), 4.64 (d, 1H, CH_2, $^2J_{H-H}$= 6.8 Hz), 4.67 (d, 1H, CH_2, $^2J_{H-H}$= 6.8 Hz), 5.72 (d, 1H, H-1, $^3J_{1-2}$= 3.6 Hz), 7.2-7.4 (m, 5H, CH=).

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[3] M. M. Bio, F. Xu, M. Waters, J. M. Williams, K. A. Savary, C. J. Cowden, C. Yang, E. Buck, Z. J. Song, D. M. Tschaen, R. P. Volante, R. A. Reamer, E. J. J. Grabowski, *J. Org. Chem.* 2004, **69**, 6257.
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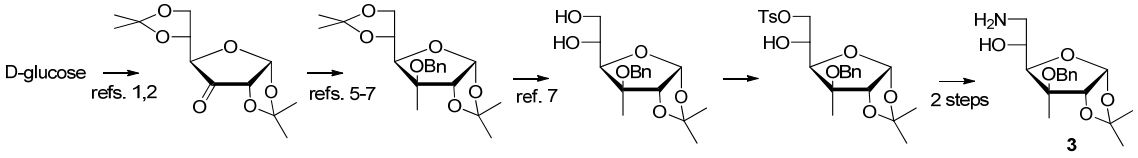
Synthesis of 6-amine-6-deoxy-1,2-O-isopropylidene-3-C-methyl-3-O-benzyl-α-allofuranose **2**. The corresponding azido-alcohol (1.74 g, 5 mmol) was dissolved in a mixture of tetrahydrofuran:water (30 mL, 4:1). Triphenylphosphine (3 g, 10.5 mmol) was then added and the mixture was stirred at room temperature overnight. Then, tetrahydrofuran was removed by evaporation in vacuo and the residue extracted twice with diethyl ether. The aqueous phase was concentrated in vacuo to give the **2** as a white solid. Yield: 1.34 g, 83 %. ^{1}H NMR ($CDCl_3$), δ: 1.34 (s, 3H, CH_3), 1.36 (s, 3H, CH_3-C3), 1.58 (s, 3H, CH_3), 2.41 (b, 3H, NH_2, OH), 2.65 (dd, 1H, H-6', $^{2}J_{6'-6}$= 12.8 Hz, $^{3}J_{6'-5}$= 4.4 Hz), 2.91 (dd, 1H, H-6, $^{2}J_{6'-6}$= 12.8 Hz, $^{3}J_{6-5}$= 2.0 Hz), 3.63 (m, 1H, H-5), 3.78 (m, 1H, H-4), 4.15 (d, 1H, H-2, $^{3}J_{2-1}$= 3.6 Hz), 4.61 (s, 2H, CH_2), 5.67 (d, 1H, H-1, $^{3}J_{1-2}$= 3.6 Hz), 7.2-7.4 (m, 5H, CH=). ^{13}C NMR ($CDCl_3$), δ: 16.5 (CH_3), 26.6 (CH_3), 26.9 (CH_3), 45.4 (C-6), 67.1 (CH_2, Bn), 70.4 (C-5), 79.4 (C-4), 82.8 (C-2), 83.4 (C-3), 104.2 (C-1), 113.1 (CMe_2), 127.8 (CH=), 128.3 (CH=), 128.6 (CH=), 138.2 (C).

SI. 4. Synthesis of 6-amine-6-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-3-*O*-benzyl-α-glucofuranose 3



The following intermediate compounds for the synthesis of **3** have been previously described: 1,2:5,6-*O*-di-isopropylidene-α-D-glucofuranose[1] (97% yield), 1,2:5,6-di-*O*-isopropylidene-α-D-ribo-hexofuranos-3-ulose[2] (84% yield), 3,3'-anhydro-3-*C*-hydroxymethyl-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose[5] (82% yield), 3-*C*-methyl-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose[6] (70% yield), 3-*O*-benzyl-3-*C*-methyl-1,2-*O*-isopropylidene-α-D-glucofuranose[7] (85% yield) and 3-*O*-Benzyl-3-*C*-methyl-1,2-*O*-isopropylidene-α-D-glucofuranose[7] (81% yield).

[5] T. Soler, A. Bachki, L. R. Falvello, F. Foubelo, M. Yus *Tetrahedron: Asymmetry* 2000, **11**, 493.
[6] Sk. Sahabuddin, R. Ghosh, B. Achari, S. B. Mandal, *Org. Biomol. Chem.* 2006, **4**, 551.
[7] S. Nishiyama, H. Toshima, H. Kanari, S. Yamamura, *Tetrahedron* 1988, **44**, 6315.

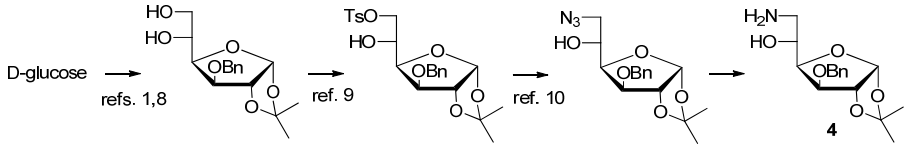
Synthesis of 3-O-benzyl-3-C-methyl-1,2-O-isopropylidene-6-O-tosyl-α-D-glucofuranose. A solution of *p*-toluenesulfonyl chloride (0.65 g, 3.4 mmol) in dichloromethane (2.3 mL) was slowly added to a cooled solution (0 ºC) of 3-*O*-Benzyl-3-*C*-methyl-1,2-*O*-isopropylidene-α-D-glucofuranose (1.1 g, 3.4 mmol) in pyridine (2.7 mL). The reaction was allowed to stir overnight. Then, water was added and the product was extracted with dichloromethane (3 x 100 mL) and once with a solution of HCl 0.1 M (100mL). The organic layer was dried over $MgSO_4$, evaporated to dryness and purified by flash chromatography (chloroform/acetone: 9/0.5) to produce the product as a white solid. Yield: 0.9 g, 56%. ^{1}H NMR ($CDCl_3$), δ: 1.32 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.86 (m, 1H), 4.07 (dd, 1H, H-6', $^2J_{6'-6}$= 10.4 Hz, $^3J_{6'-5}$= 7.2 Hz), 4.29 (m, 1H), 4.34 (dd, 1H, H-6, $^2J_{6'-6}$= 10.4 Hz, $^3J_{6-5}$= 4.8 Hz), 4.47 (d, 1H, H-2, $^3J_{2-1}$= 4.0 Hz), 4.55 (d, 1H, CH_2, $^2J_{H-H}$= 6.4 Hz), 4.64 (d, 1H, CH_2, $^2J_{H-H}$= 6.4 Hz), 5.78 (d, 1H, H-1, $^3J_{1-2}$= 4.0 Hz), 7.34 (m, 7H, CH=), 7.77 (d, 2H, *J*= 8.0 Hz).

Synthesis of 6-azido-6-deoxy-1,2-O-isopropylidene-3-C-methyl-3-benzyl-α-glucofuranose. A solution of 3-*O*-benzyl-3-*C*-methyl-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-allofuranose (0.9 g, 1.88 mmol) in DMF was treated with sodium azide as above described for 6-azido-6-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-3-benzyl-α-allofuranose. Yield: 0.6 g, 91%. ^{1}H NMR ($CDCl_3$), δ: 1.33 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 3.44 (b, 1H, OH), 3.46 (dd, 1H, H-6', $^2J_{6'-6}$= 12.4 Hz, $^3J_{6'-5}$= 6.4 Hz), 3.55 (dd, 1H, H-6, $^2J_{6'-6}$= 12.4 Hz, $^3J_{6-5}$= 3.2 Hz), 3.19 (m, 1H), 4.17 (m, 1H), 4.51 (d, 1H, H-2, $^3J_{2-1}$= 3.6 Hz), 4.57 (d, 1H, CH_2, $^2J_{H-H}$= 10.8 Hz), 4.63 (d, 1H, CH_2, $^2J_{H-H}$= 10.8 Hz), 5.84 (d, 1H, H-1, $^3J_{1-2}$= 3.6 Hz), 7.30 (m, 5H, CH=).

Synthesis of 6-amine-6-deoxy-1,2-O-isopropylidene-3-C-methyl-3-benzyl-α-glucofuranose **3.** The corresponding azido-alcohol (0.6 g, 1.72 mmol) was treated with triphenylphosphine as above described for **2**. Yield: 240 mg, 44%. ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 2.83 (b, 4H, NH_2, OH, H-6'), 3.06 (m, 1H, H-6), 3.91 (m, 1H, H-4), 4.05 (m, 1H, H-3), 4.47 (d, 1H, H-2, $^3J_{2-1}$= 4.0 Hz), 4.57 (m, 2H, CH_2), 5.84 (d, 1H, H-1, $^3J_{1-2}$= 4.0 Hz), 7.32 (m, 5H, CH=). ^{13}C NMR

($CDCl_3$), δ: 15.7 (CH_3), 26.6 (CH_3), 27.3 (CH_3), 44.5 (C-6), 65.4 (CH_2, Bn), 68.2 (C-5), 83.3 (C-2), 85.0 (C-4), 85.3 (C-3), 104.7 (C-1), 112.2 (CMe_2), 127.0 (CH=), 127.6 (CH=), 128.6 (CH=), 138.8 (C).

SI. 5. Synthesis of 6-amine-6-deoxy-1,2-*O*-isopropylidene-3-*O*-benzyl-α-glucofuranose 4



The following intermediate compounds for the synthesis of **4** have been previously described: 1,2:5,6-*O*-di-isopropylidene-α-D-glucofuranose[1] (97% yield), 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[8] (99% yield), 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[8] (98% yield), 3-*O*-benzyl-1,2-*O*-isopropylidene-6-tosyl-α-D-glucofuranose[9] (90% yield), 6-azido-6-deoxy-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[10] (81% yield).

Synthesis of 6-amine-6-deoxy-1,2-O-isopropylidene-3-C-methyl-3-benzyl-α-glucofuranose **4.** The corresponding azido-alcohol (2.4 g, 7.15 mmol) was treated with triphenylphosphine as above described for **2**. Yield: 1.79 g, 81%. For characterization details, see ref. 11.

SI. 6. Typical procedure for the ATH of ketones. The desired ligand (0.0055 mmol), catalyst precursor ($[RuCl_2(p\text{-cymene})_2]_2$) (0.0025 mmol), and LiCl (4.2 mg, 0.1 mmol) were treated under vacuum for 10 min. Under argon, substrate (1 mmol), propan-2-ol (2 mL) and THF (2.5 mmol) were sequentially added. The reaction was initiated by adding ^{i}PrONa (0.1M, 0.5 mL, 0.05 mmol) to the solution. After completion of the reaction the solution was filtered through a plug of silica and eluted with Et_2O,

[8] C. J. Schwörer, M. Oberthür, *Eur. J. Org. Chem.* 2009, 6129
[9] M. Morillo, V. Lequart, E. Grand, G. Goethals, A. Usubillaga, P. Villa, P. Martin, *Carbohydrate Res.* 2001, **314**, 281.
[10] J. Wang, J. Li, D. Tuttle, J. Y. Takemoto, C.-W. T. Chang, *Org. Lett.* 2002, **4**, 3997.
[11] M. Yamashita, C. Takahashi, K. Seo, *Heterocycles* 1993, **36**, 651.

and the solvents were evaporated. The products were analyzed by GC (CP Chirasil DEX CB).[12]

SI. 7. ATH results using **L2** and **L7**

Table SI.7. Ru-catalyzed asymmetric transfer hydrogenation reaction using ligands **L2** and **L7**[a]

Entry	Substrate	Ligand	% Conv (h)[b]	% ee[b]
1	**S2**	**L2**	100 (3)	>99 (*S*)
2[c]	**S2**	**L7**	98 (3)	99 (*S*)
3	**S3**	**L2**	99 (3)	99 (*S*)
4[c]	**S3**	**L7**	99 (3)	99 (*S*)
5	**S6**	**L2**	100 (3)	99 (*S*)
6[c]	**S6**	**L7**	100 (3)	>99 (*S*)
7	**S7**	**L2**	99 (3)	99 (*S*)
8[c]	**S7**	**L7**	95 (3)	99 (*S*)
9	**S10**	**L2**	78 (3)	99 (*S*)
10[c]	**S10**	**L7**	69 (3)	98 (*S*)

[a] Reaction conditions: substrate (1 equiv, 0.2M in 2-propanol/THF (1:1), $[RuCl_2(p\text{-cymene})]_2$ (0.25 mol% in Ru), ligand (0.55 mol%), NaO^iPr (5 mol%), LiCl (10 mol%) and at room temperature. [b] Conversion and enantiomeric excess was determined by GC. [c] Using 1 mol% of Ru.

[12] a) I. M. Pastor, P. Västilä, H. Adolfsson, *Chem. Eur. J.* 2003, **9**, 4031; b) A. Bøgevig, I. M. Pastor, H. Adolfsson, *Chem. Eur. J.* 2004, **10**, 294; c) J. Wettergren, A. Bøgevig, M. Portier, H. Adolfsson, *Adv. Synth. Catal.* 2006, **348**, 1277.

SI. 8. GC separation conditions

(*rac*)-1-phenylethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

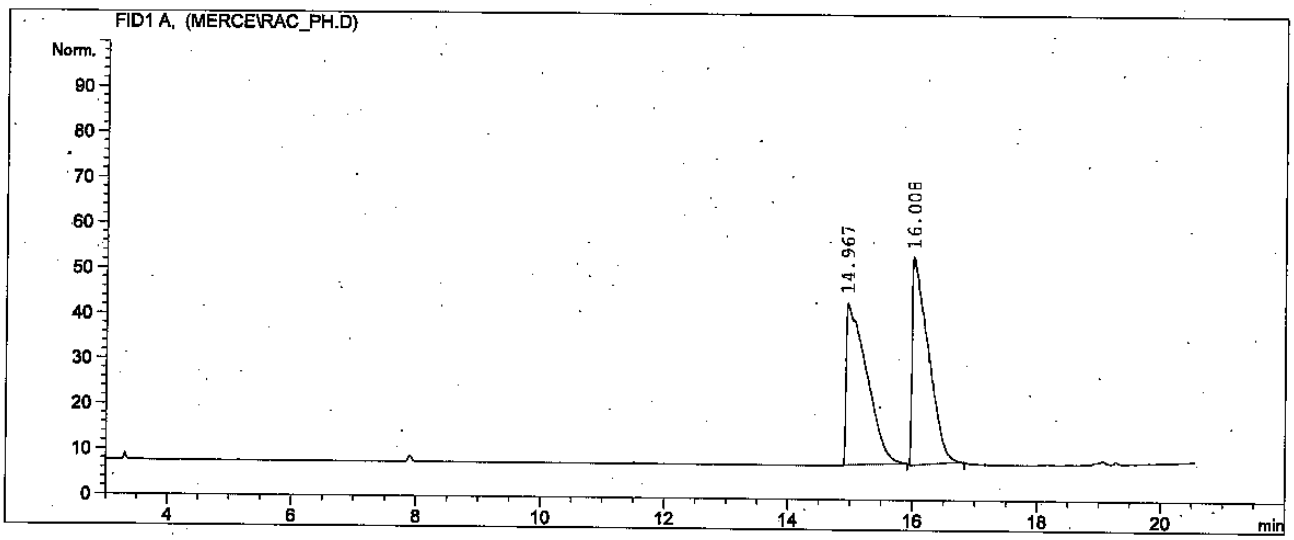
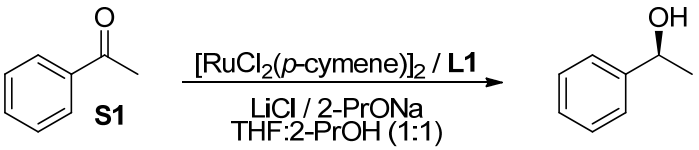
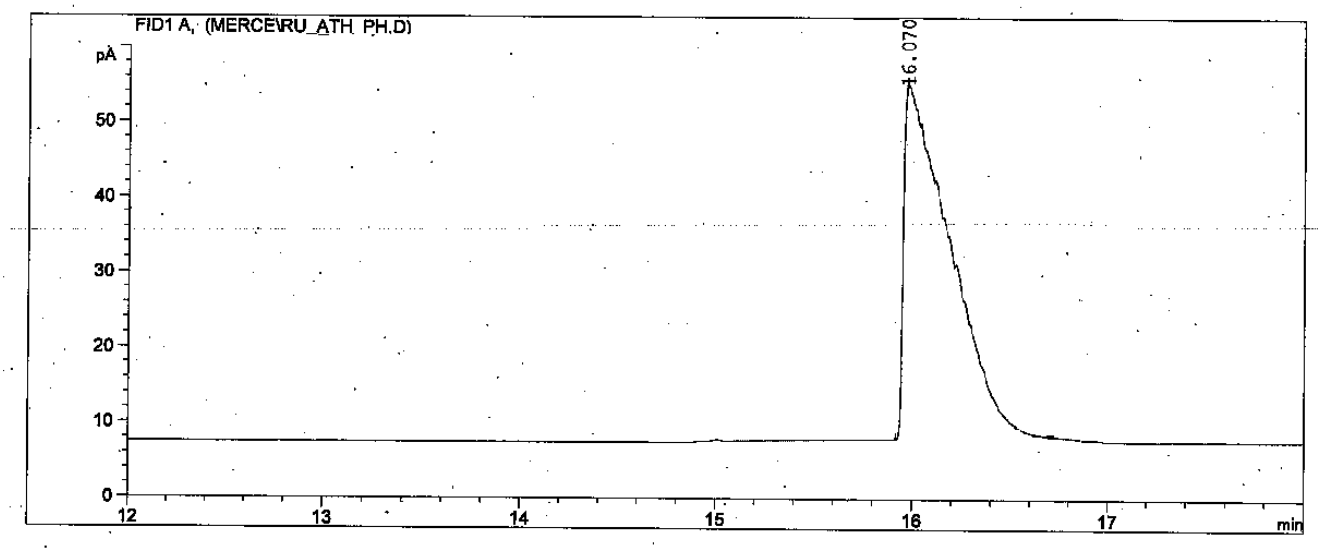


Table 1, entry 1. **(*S*)-1-phenylethanol**





(*rac*)-1-(*p*-tolyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

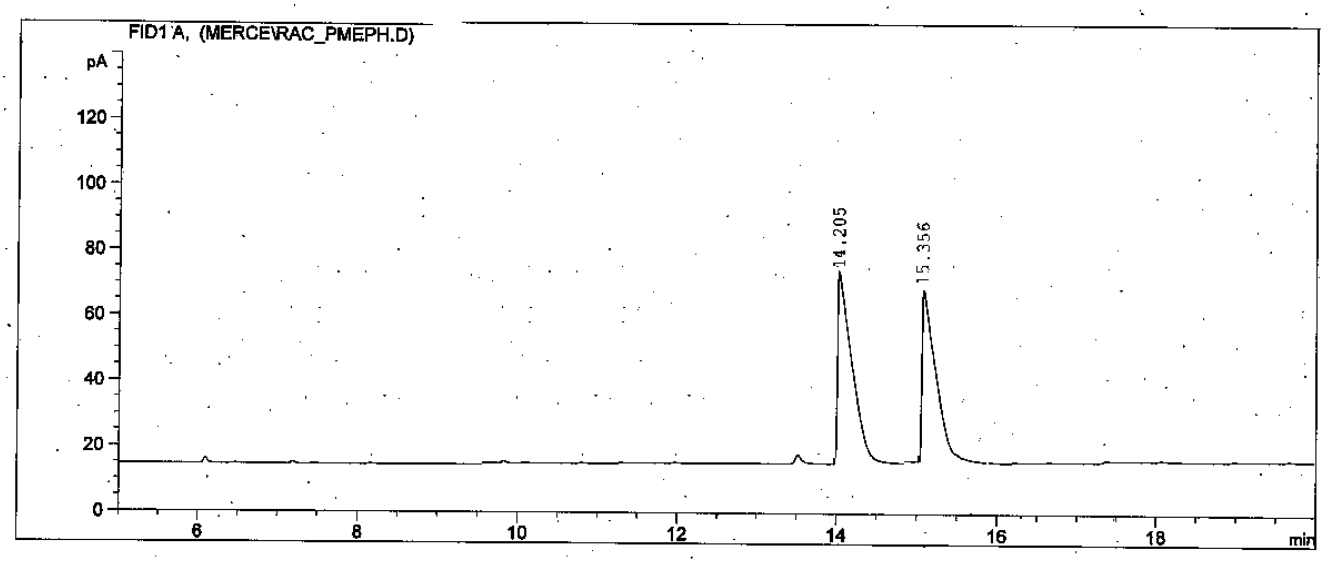
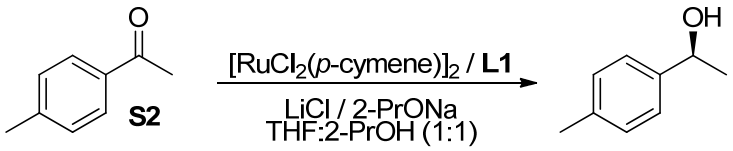
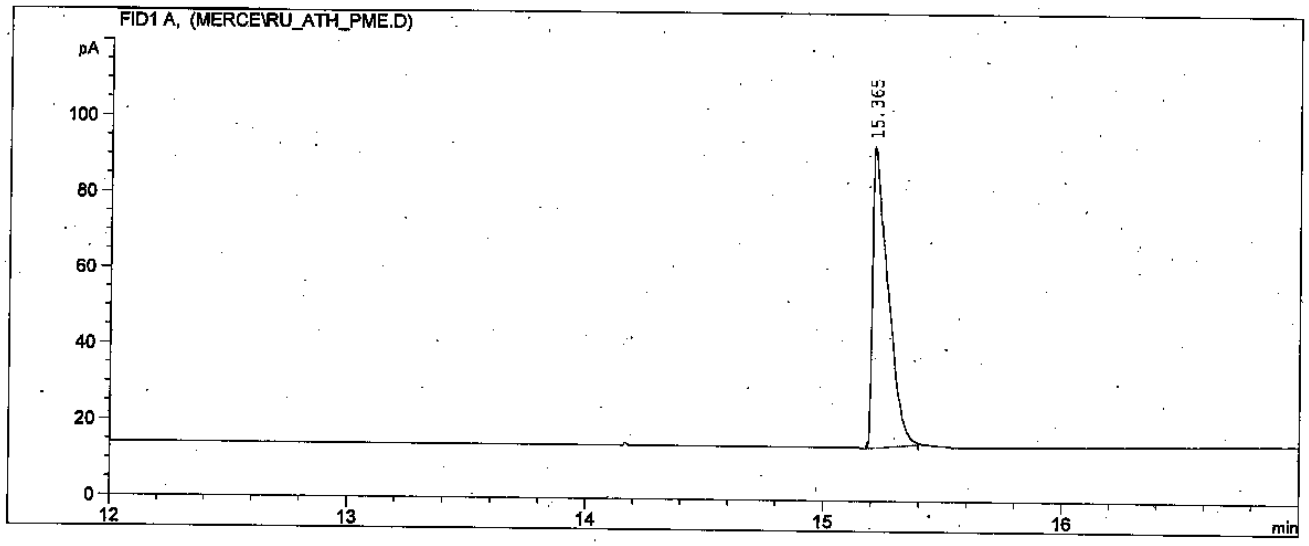


Figure 3. **(*S*)-1-(p-tolyl)ethanol**





(*rac*)- 1-(4-(trifluoromethyl)phenyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 20 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

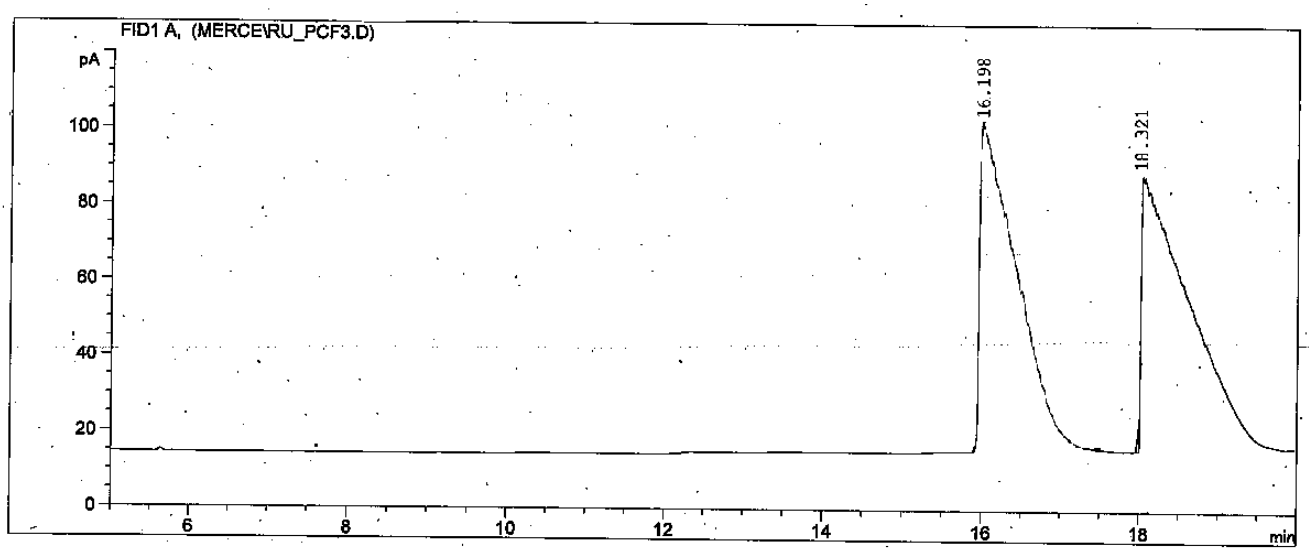
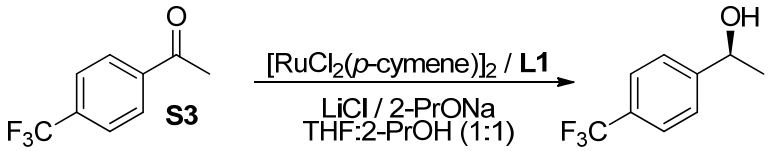
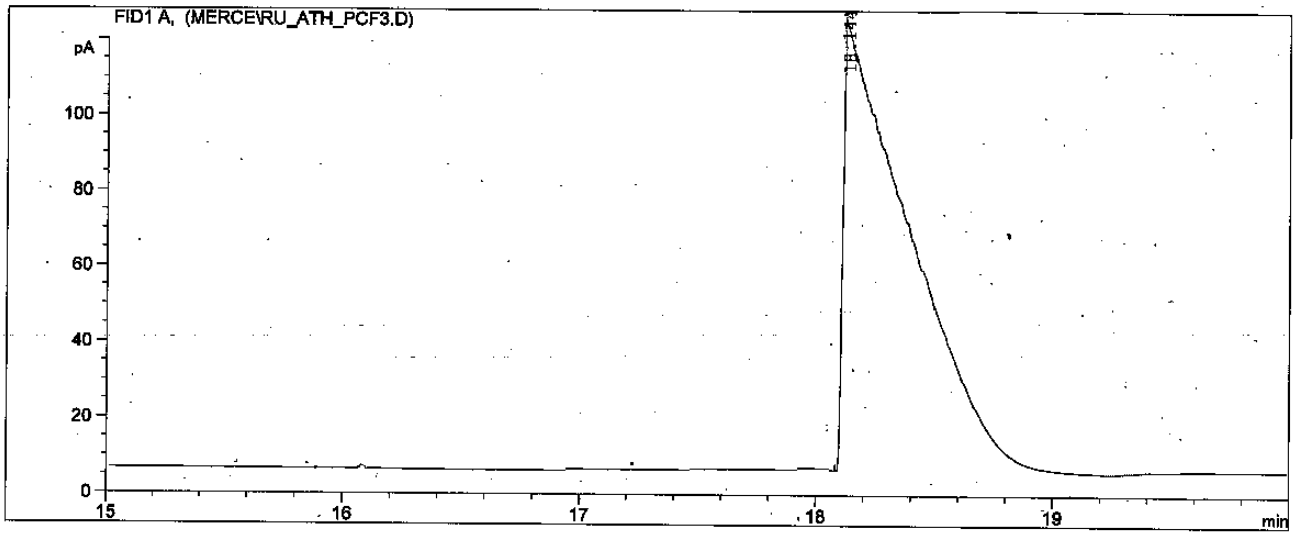


Figure 3. **(*S*)-1-(4-(trifluoromethyl)phenyl)ethanol**





(*rac*)-1-(4-fluorophenyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

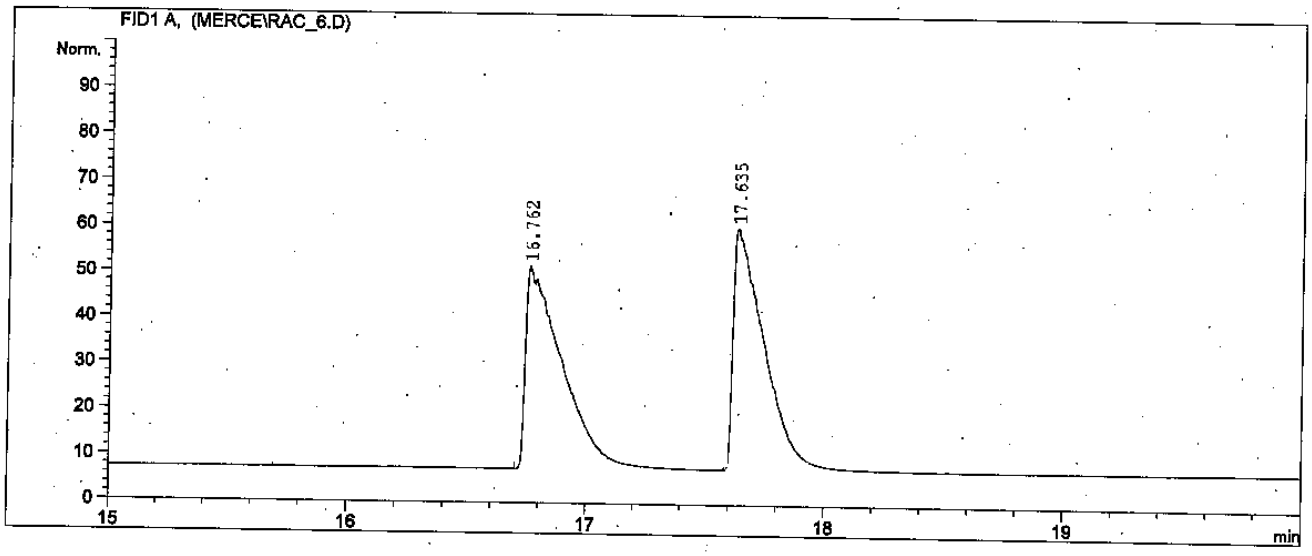
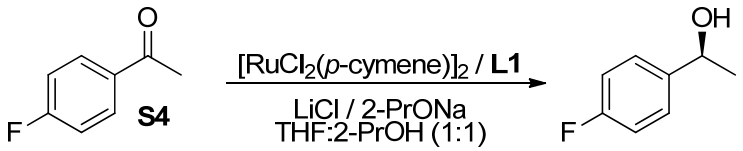
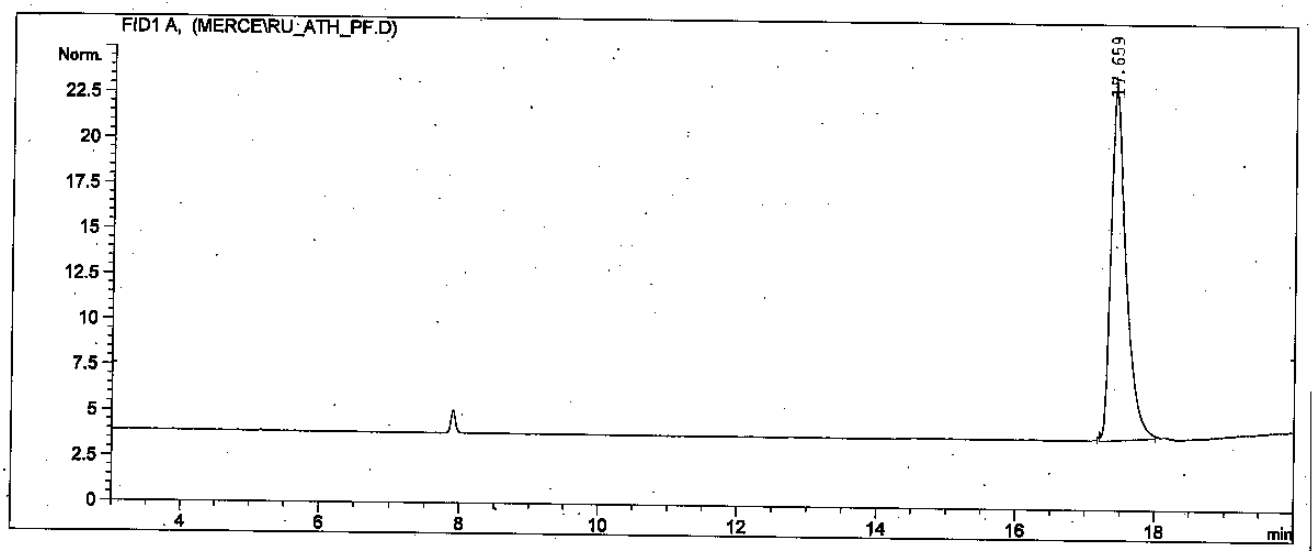


Figure 3. **(*S*)-1-(4-fluorophenyl)ethanol**





(*rac*)- 1-(4-methoxyphenyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

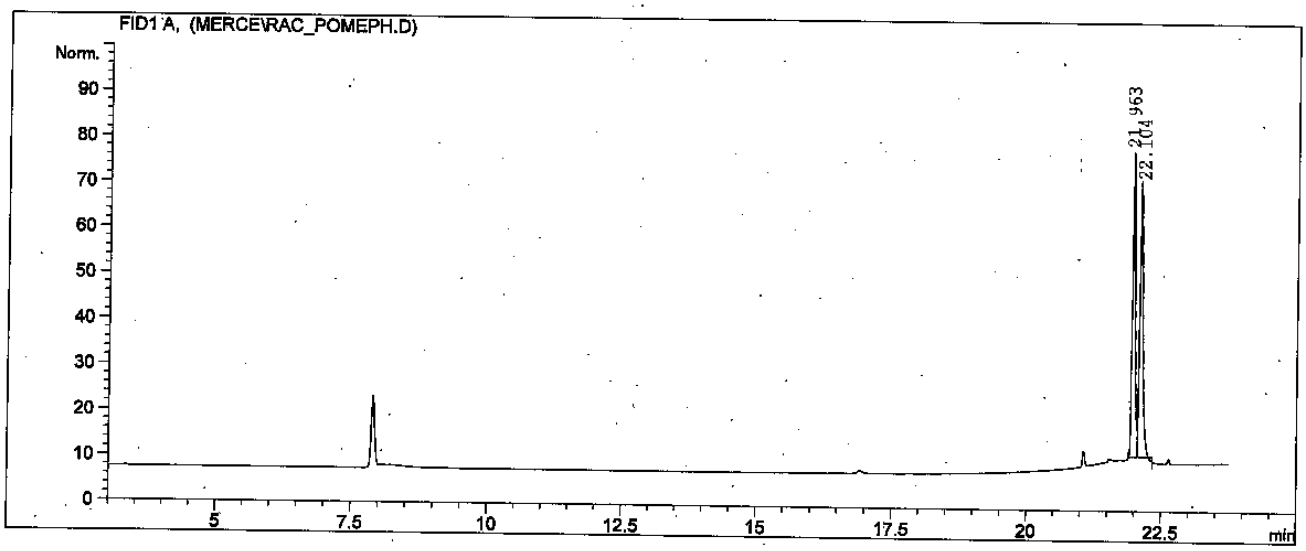
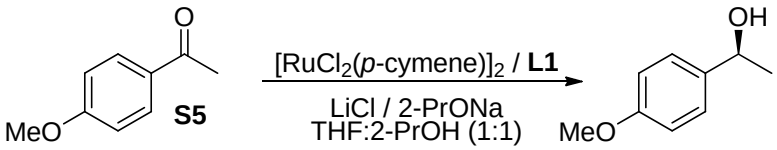
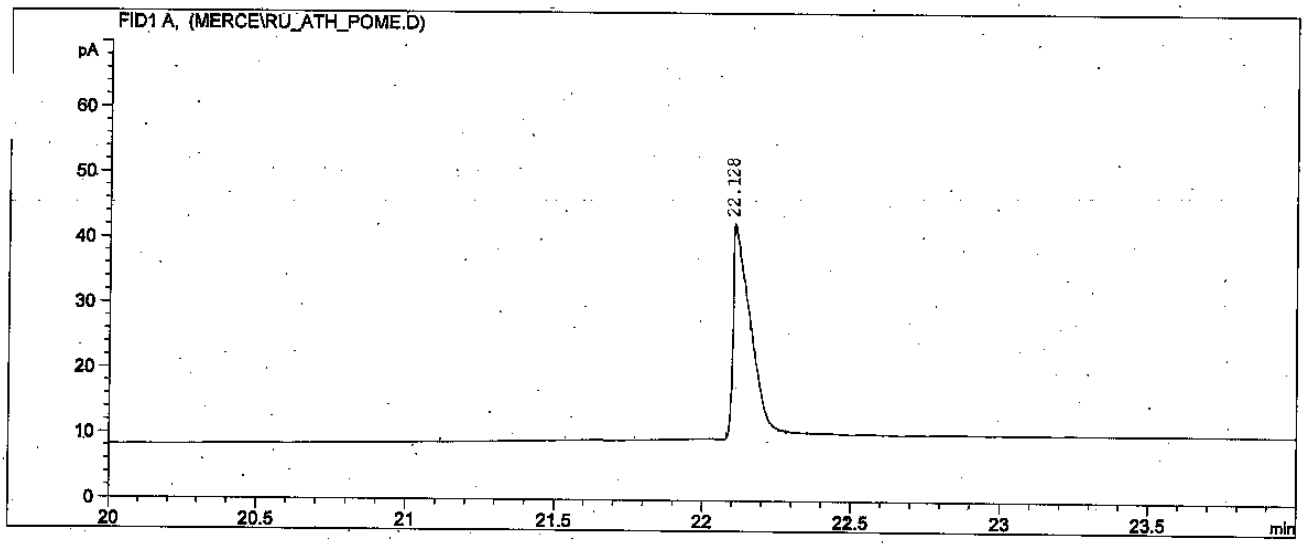


Figure 3. **(*S*)- 1-(4-methoxyphenyl)ethanol**





(*rac*)- 1-(naphthalen-2-yl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

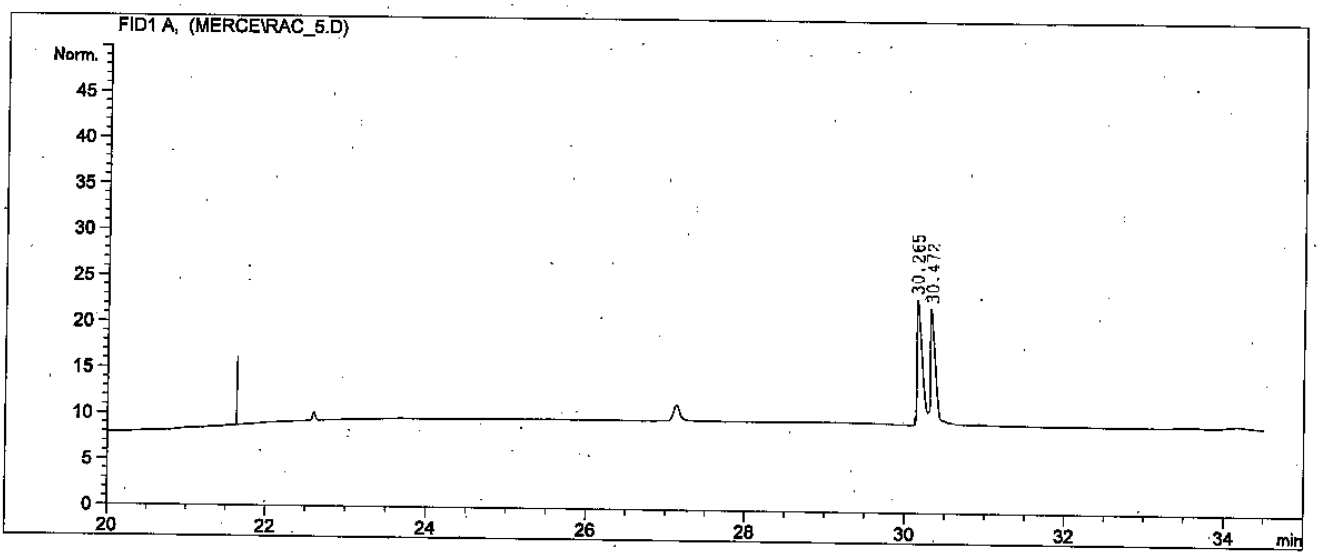
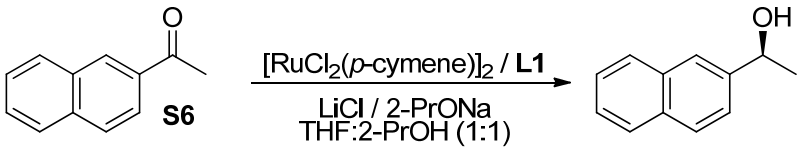
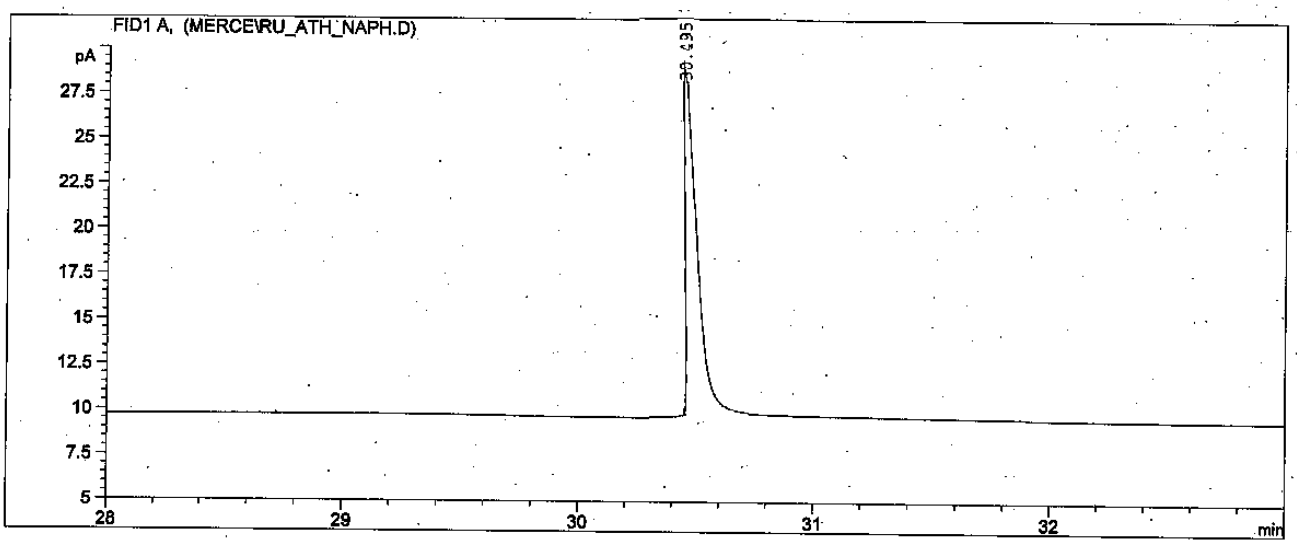


Figure 3. **(*S*)- 1-(naphthalen-2-yl)ethanol.**





(*rac*)- 1-(3-methoxyphenyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

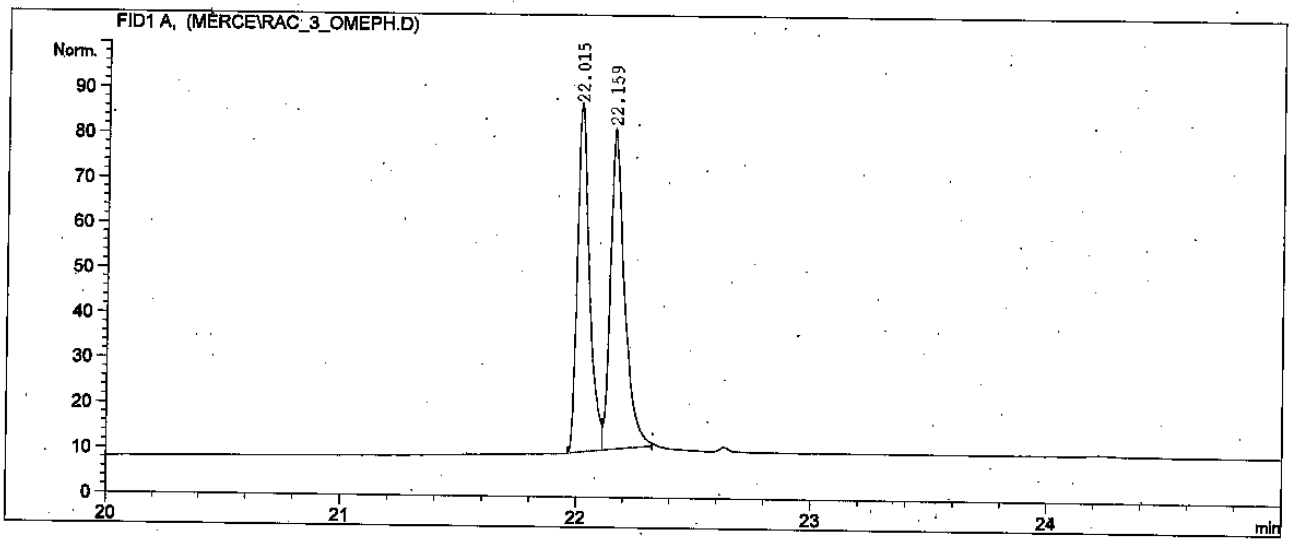
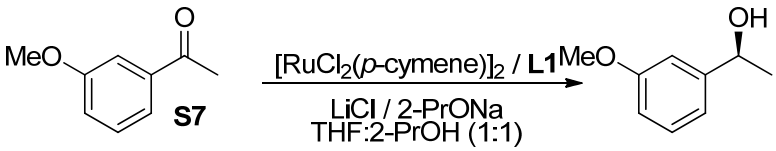
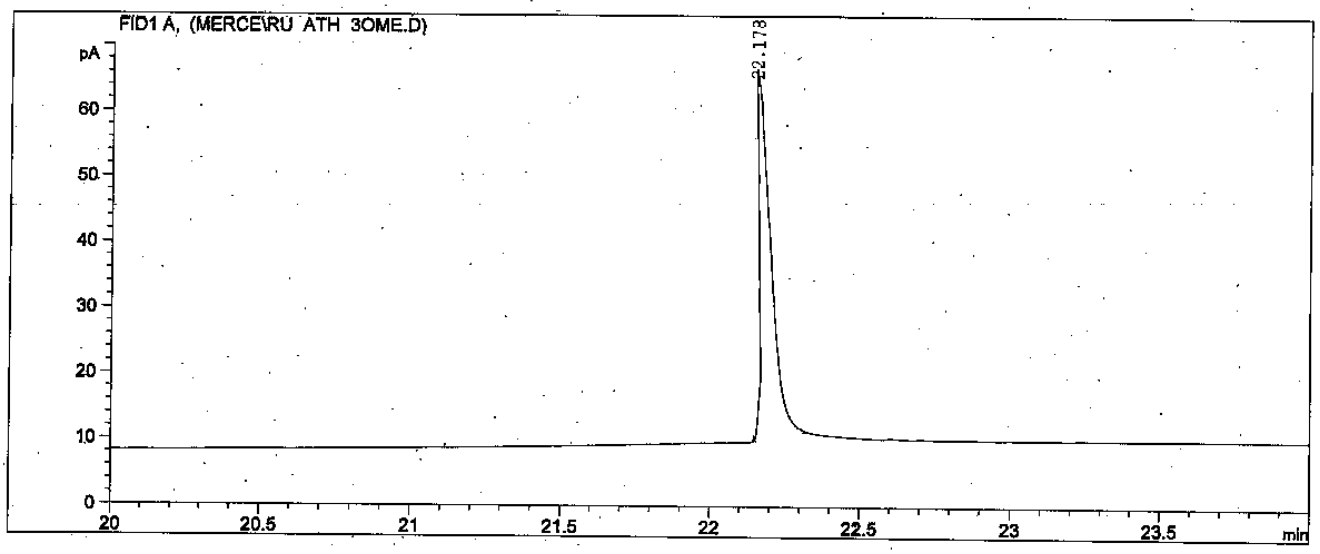


Figure 3. **(*S*)- 1-(3-methoxyphenyl)ethanol**





(*rac*)-1-(*m*-tolyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

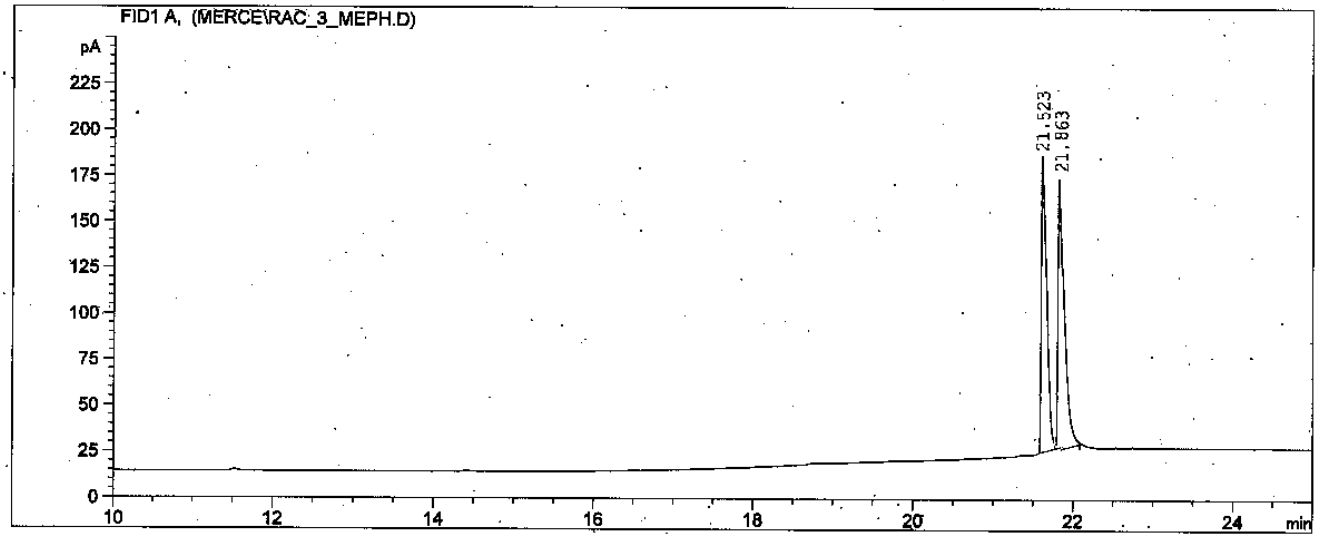
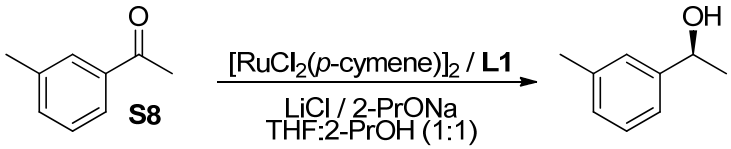
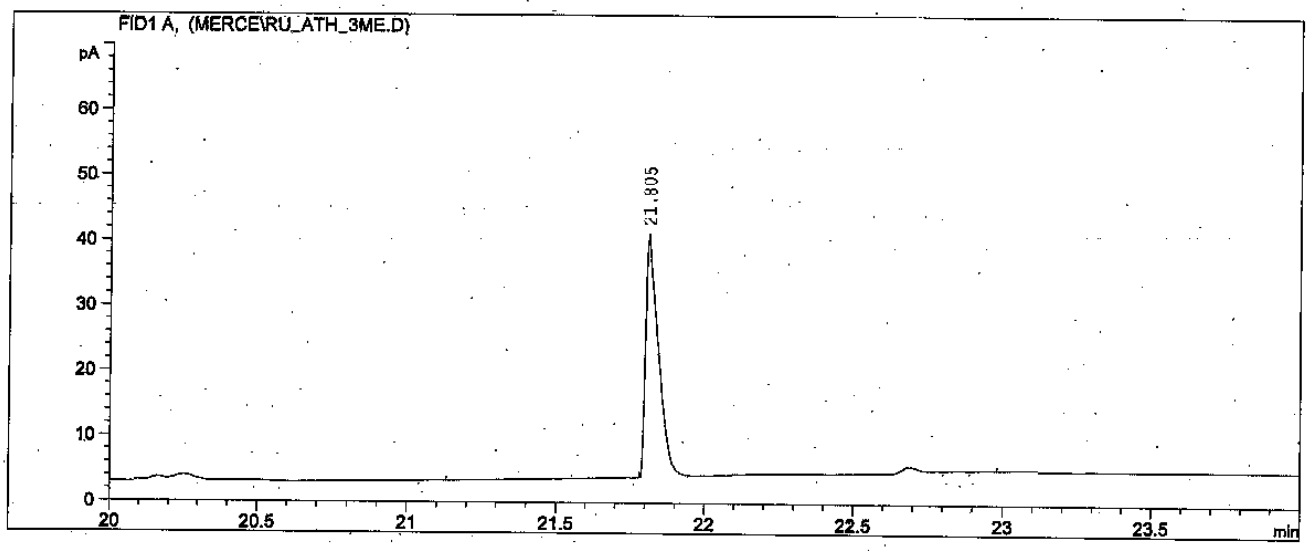


Figure 3. **(*S*)-1-(m-tolyl)ethanol**





(*rac*)- 1-(2-methoxyphenyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

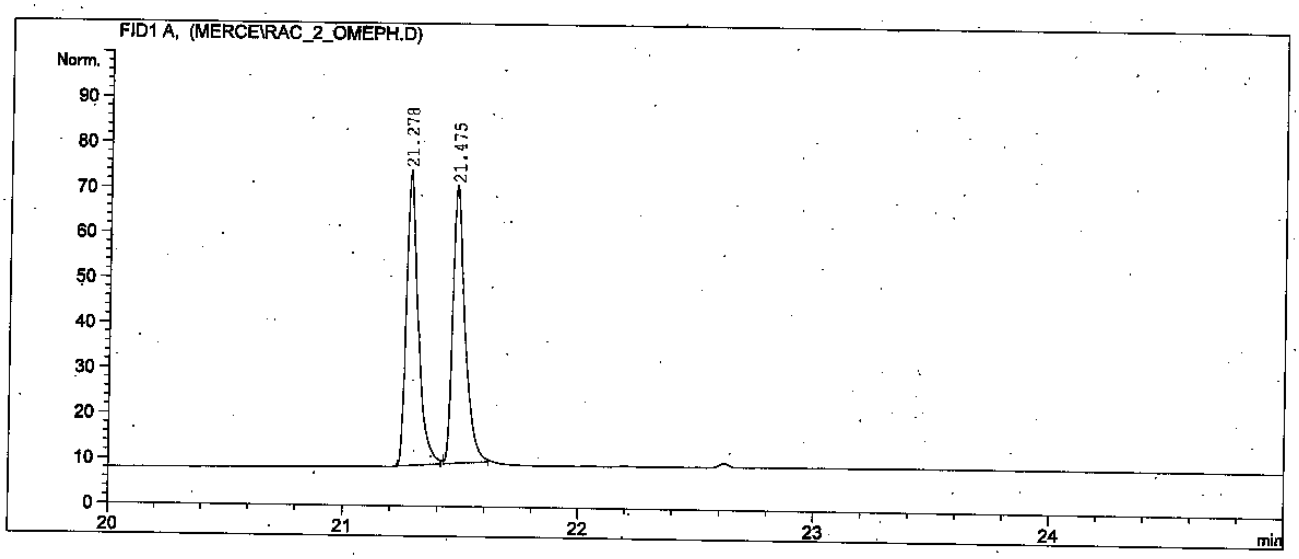
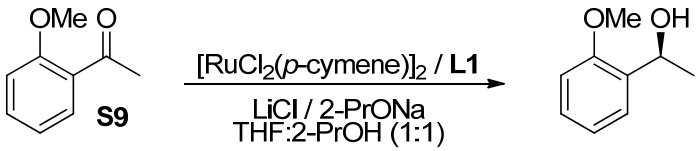
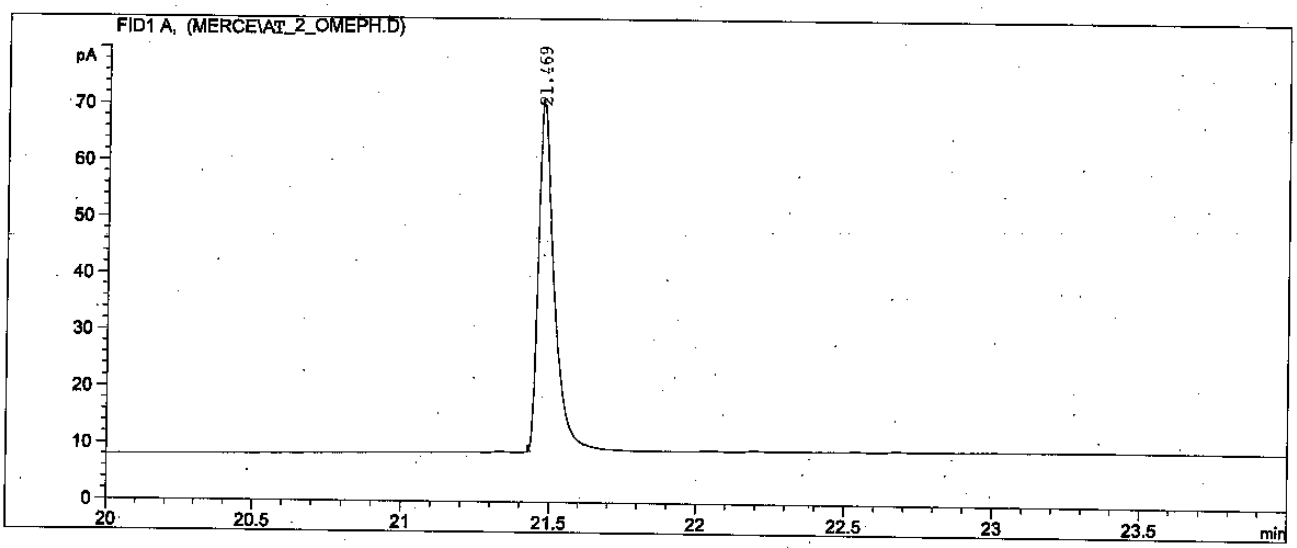


Figure 3. **(*S*)- 1-(2-methoxyphenyl)ethanol**





(*rac*)-1-(*o*-tolyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

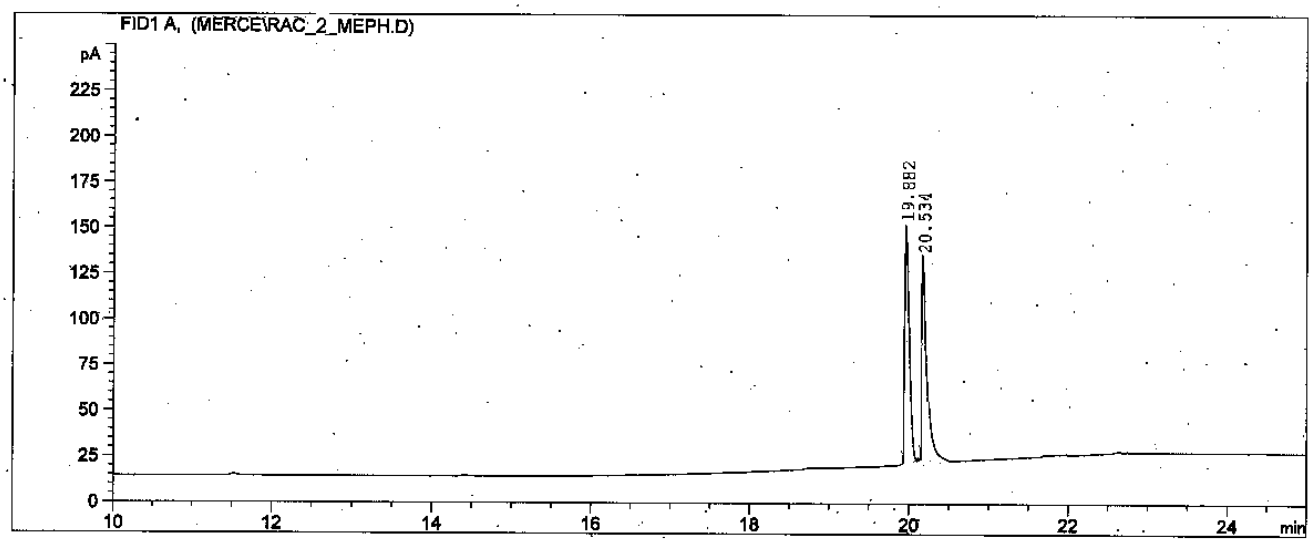
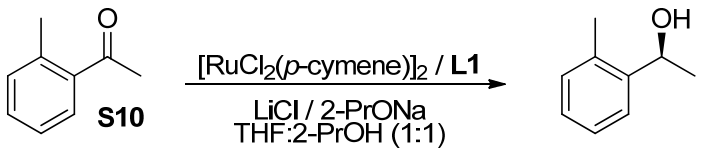
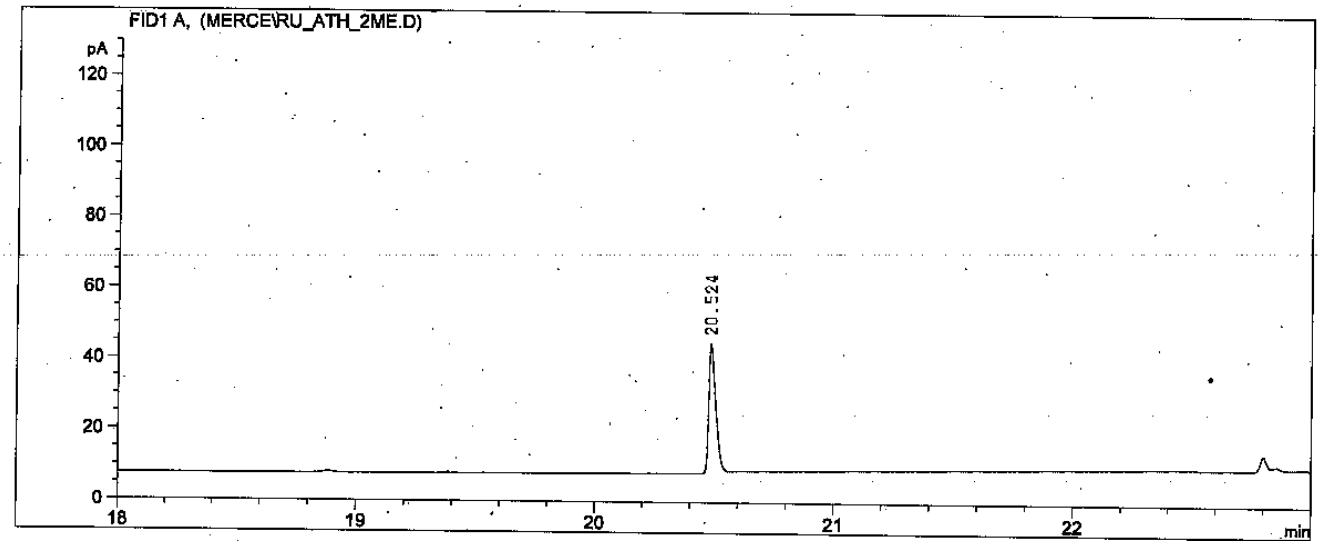


Figure 3. **(*S*)-1-(*o*-tolyl)ethanol**





(*rac*)- 1-phenylpropan-1-ol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min^{-1} to 180 °C and hold for 20 min)

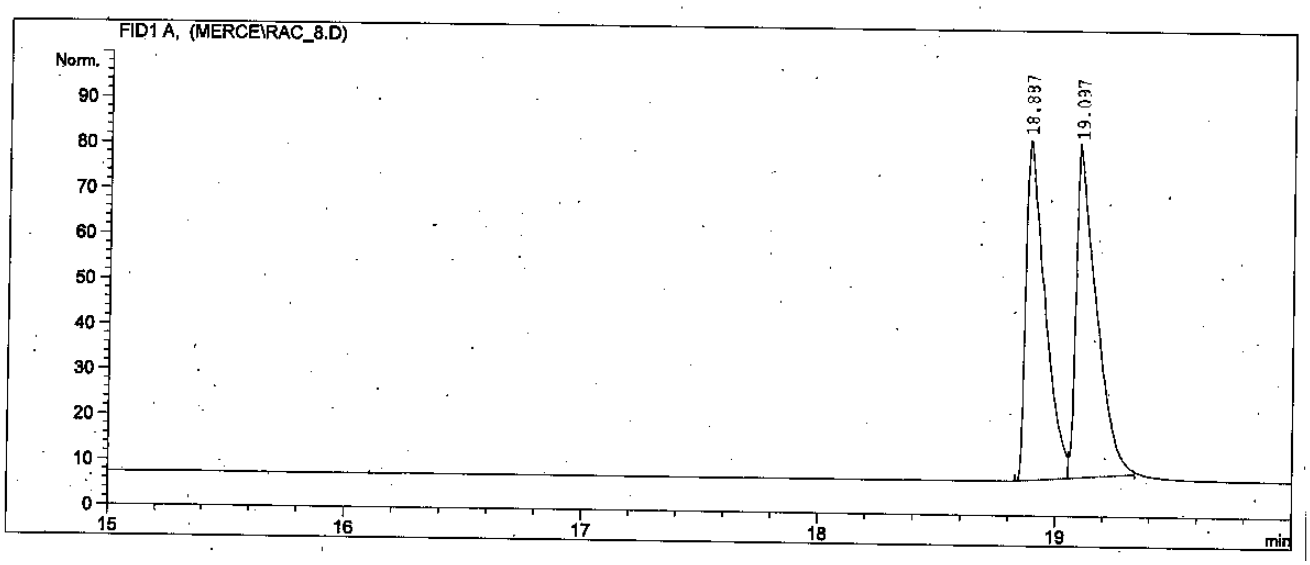


Figure 3. **(*S*)- 1-phenylpropan-1-ol.**