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$_3$), $\delta$: 0.86 (d, 3H, CH$_3$, $^3$J$_{H-H}$= 6.8 Hz), 0.91 (d, 3H, CH$_3$, $^3$J$_{H-H}$= 7.2 Hz), 1.33 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$), 1.39 (s, 9H, CH$_3$, tBu), 1.57 (s, 3H, CH$_3$), 2.07 (m, 1H, CH, $^3$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$_{J=1}$= 3.6 Hz), 4.61 (s, 2H, CH$_2$, Bn), 5.18 (b, 1H, NH), 5.71 (d, 1H, H-1, $^3$J$_{J=2}$= 3.6 Hz), 6.49 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). $^{13}$C NMR (CDCl$_3$), $\delta$: 16.6 (CH$_3$), 17.9 (CH$_3$, $^1$Pr), 19.4 (CH$_3$, $^1$Pr), 26.7 (CH$_3$), 26.9 (CH$_3$), 28.5 (CH$_3$, tBu), 31.2 (CH, $^3$Pr), 43.4 (C-6), 60.0 (CH), 67.2 (CH$_2$, Bn), 68.8 (C-5), 79.7 (C, tBu), 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$_2$O$_8$: 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$_3$), $\delta$: 1.29 (d, 3H, CH$_3$, $^3$J$_{H-H}$= 6.8 Hz), 1.32 (s, 6H, CH$_3$), 1.39 (s, 9H, CH$_3$, tBu), 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$_{J=1}$= 3.6 Hz), 4.61 (m, 2H, CH$_2$, Bn), 5.37 (b, 1H, NH), 5.69 (d, 1H, H-1, $^3$J$_{J=2}$= 3.6 Hz), 6.60 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). $^{13}$C NMR (CDCl$_3$), $\delta$: 16.4
(CH₃), 18.8 (CH₃), 26.5 (CH₃), 26.7 (CH₃), 28.2 (CH₃, tBu), 43.4 (C-6), 60.4 (CH), 67.0
(CH₂, Bn), 68.7 (C-5), 79.6 (C-4), 79.7 (C, tBu), 82.6 (C-2), 83.2 (C-3), 104.0 (C-1),
113.0 (CMe₂), 127.6 (CH=), 128.3 (CH=), 137.9 (C), 155.3 (CO), 171.1 (CO). Anal.
calcd (%) for C₂₅H₃₈N₂O₈: C 60.71, H 7.74, N 5.66; found: C 60.79, H 7.79, N 5.62.

L₃: Yield: 422 mg, 74 %. ¹H NMR (CDCl₃), δ: 1.30 (s, 3H, CH₃), 1.32 (s, 3H, CH₃),
1.35 (s, 9H, CH₃, tBu), 1.55 (s, 3H, CH₃), 2.72 (b, 1H, OH), 3.01 (m, 2H, CH₂), 3.23 (m,
1H, H-6’), 3.53 (m, 1H, H-5), 3.66 (m, 1H, H-4), 4.39 (m, 1H, CH),
4.32 (d, 1H, H-2, ³J₂₋₁= 3.6 Hz), 4.59 (m, 2H, CH₂, OBn), 5.15 (b, 1H, NH), 5.65 (d,
1H, H-1, ³J₁₋₂= 3.6 Hz), 6.31 (b, 1H, NH), 7.1-7.4 (m, 10H, CH=). ¹³C NMR (CDCl₃),
δ: 18.8 (CH₃), 26.5 (CH₃), 26.7 (CH₃), 28.2 (CH₃, tBu), 38.9 (CH₂), 43.6 (C-6), 60.4
(CH), 67.0 (CH₂, Bn), 68.7 (C-5), 75.9 (C, tBu), 79.8 (C-4), 82.6 (C-2), 83.3 (C-3),
104.1 (C-1), 113.1 (CMe₂), 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

L₄: Yield: 241 mg, 45 %. ¹H NMR (CDCl₃), δ: 0.92 (s, 9H, CH₃, tBu), 1.31 (s, 3H,
CH₃), 1.32 (s, 3H, CH₃), 1.38 (s, 9H, CH₃, tBu), 1.55 (s, 3H, CH₃), 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, ³J₂₋₁= 4.0 Hz), 4.60 (m, 2H, CH₂, Bn), 5.34 (b, 1H, NH), 5.68 (d, 1H,
H-1, ³J₁₋₂= 4.0 Hz), 6.32 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ¹³C NMR (CDCl₃), δ: 16.4
(CH₃), 26.5 (CH₃), 26.6 (CH₃, tBu), 26.8 (CH₃), 28.3 (CH₃, tBu), 34.5 (C, tBu), 43.3 (C-6),
62.3 (CH), 67.0 (CH₂, Bn), 68.6 (C-5), 79.4 (C, tBu), 79.8 (C-4), 82.7 (C-2), 83.3
(C-3), 104.0 (C-1), 113.0 (CMe₂), 127.6 (CH=), 127.7 (CH=), 128.3 (CH=), 137.9 (C),
155.5 (CO), 171.2 (CO). Anal. calcd (%) for C₂₈H₄₄N₂O₈: C 62.67, H 8.26, N 5.22;
found: C 62.79, H 8.34, N 5.30.

L₅: Yield: 241 mg, 45 %. ¹H NMR (CDCl₃), δ: 1.25 (s, 3H, CH₃), 1.32 (s, 3H, CH₃),
1.37 (s, 9H, CH₃, tBu), 1.52 (s, 3H, CH₃), 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, ³J₂₋₁= 3.6 Hz), 4.57
(m, 2H, CH₂, OBn), 5.09 (m, 1H, CH), 5.60 (d, 1H, H-1, ³J₁₋₂= 3.6 Hz), 5.92 (b, 1H,
NH), 6.27 (b, 1H, NH), 7.2-7.4 (m, 10H, CH=). ¹³C NMR (CDCl₃), δ: 16.3 (CH₃), 26.5
(CH₃), 26.7 (CH₃), 28.2 (CH₃, tBu), 43.5 (C-6), 58.3 (CH), 67.0 (CH₂, Bn), 68.3 (C-5), 79.6 (C, tBu), 79.8 (C-4), 82.5 (C-2), 83.2 (C-3), 104.0 (C-1), 113.2 (CMe₂), 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 C₃₀H₄₀N₂O₈: C 64.73, H 7.24, N 5.03; found: C 64.78, H 7.26, N 4.99.

**L6:** Yield: 402 mg, 78 %. ¹H NMR (CDCl₃), δ: 0.85 (d, 3H, CH₃, ³Jₜ-H= 7.2 Hz), 0.89 (d, 3H, CH₃, ³Jₜ-H= 7.2 Hz), 1.31 (s, 3H, CH₃), 1.33 (s, 3H, CH₃), 1.39 (s, 9H, CH₃, tBu), 1.57 (s, 3H, CH₃), 2.02 (m, 1H, CH, ³Jt-P= 2.72 (b, 1H, OH), 3.31 (m, 1H, H-6'), 3.59 (m, 1H, H-6), 3.77 (m, 2H, H-4 and CH), 4.33 (d, 1H, H-2, ³J₂-₁= 3.6 Hz), 4.60 (m, 2H, CH₂, Bn), 5.19 (b, 1H, NH), 5.69 (d, 1H, H-1, ³J₁-₂= 3.6 Hz), 6.45 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ¹³C NMR (CDCl₃), δ: 16.3 (CH₃), 18.7 (CH₃), 26.5 (CH₃), 26.7 (CH₃), 28.3 (CH₃, tBu), 30.8 (CH, tBu), 43.3 (C-6), 58.5 (CH), 67.0 (CH₂, Bn), 68.7 (C-5), 79.9 (C, tBu), 82.6 (C-4), 83.2 (C-2), 83.3 (C-3), 104.1 (C-1), 113.1 (CMe₂), 127.6 (CH=), 127.7 (CH=), 128.3 (CH=), 138.0 (C), 155.9 (CO), 171.9 (CO). Anal. calcd (%) for C₂₇H₄₂N₂O₈: C 62.05, H 8.10, N 5.36; found: C 62.13, H 8.14, N 5.33.

**L7:** Yield: 240 mg, 50 %. ¹H NMR (CDCl₃), δ: 1.31 (s, 6H, CH₃), 1.39 (s, 9H, CH₃, tBu), 1.55 (s, 3H, CH₃), 2.41 (b, 1H, OH), 3.25 (m, 1H, H-6'), 3.61 (m, 1H, H-6), 3.75 (m, 2H, CH₂), 3.78 (m, 1H, H-5), 3.86 (m, 1H, H-4), 4.32 (d, 1H, H-2, ³J₂-₁= 3.6 Hz), 4.58(m, 2H, CH₂, Bn), 5.38 (b, 1H, NH), 5.68 (d, 1H, H-1, ³J₁-₂= 3.6 Hz), 6.70 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). ¹³C NMR (CDCl₃), δ: 16.3 (CH₃), 26.5 (CH₃), 26.7 (CH₃), 28.3 (CH₃, tBu), 43.4 (C-6), 44.0 (CH₂), 66.9 (CH₂, Bn), 68.7 (C-5), 79.7 (C-4), 79.9 (C, tBu), 82.7 (C-2), 83.3 (C-3), 104.0 (C-1), 113.0 (CMe₂), 127.6 (CH=), 127.7 (CH=), 128.3 (CH=), 138.0 (C), 156.0 (CO), 169.9 (CO). Anal. calcd (%) for C₂₄H₃₆N₂O₈: C 59.98, H 7.55, N 5.83; found: C 60.01, H 7.58, N 5.85.

**L8:** Yield: 415 mg, 79 %. ¹H NMR (CDCl₃), δ: 0.87 (d, 3H, CH₃, ³Jₜ-H= 6.8 Hz), 0.93 (d, 3H, CH₃, ³Jₜ-H= 7.2 Hz), 1.28 (s, 3H, CH₃), 1.38 (s, 9H, CH₃, tBu), 1.48 (s, 3H, CH₃), 1.52 (s, 3H, CH₃), 2.01 (m, 1H, CH, ³Jt-P= 2.35 (m, 1H, H-6'), 3.67 (m, 1H, NH), 3.82 (m, 1H, H-6'), 3.91 (m, 1H, H-3), 4.01 (m, 1H, CH), 4.09 (m, 1H, H-5), 4.42 (d,
1H, H-2, $^3J_{2,1}= 3.6$ Hz), 4.52 (d, 1H, CH₂, Bn, $^3J_{2,1}= 12.4$ Hz), 4.65 (d, 1H, CH₂, Bn, $^3J_{2,1}= 12.4$ Hz), 5.24 (b, 1H, NH), 5.79 (d, 1H, H-1, $^3J_{1,2}= 3.6$ Hz), 6.82 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). $^{13}$C NMR (CDCl₃), δ: 15.4 (CH₃), 18.7 (CH₃, iPr), 19.0 (CH₃, iPr), 26.4 (CH₃), 27.0 (CH₃), 28.3 (CH₃, tBu), 30.9 (CH, iPr), 44.7 (C-6), 60.1 (CH), 65.2 (CH₂, Bn), 69.1 (C-5), 69.7 (C, tBu), 75.7 (C-4), 83.4 (C-2), 84.6 (C-3), 104.4 (C-1), 112.0 (CMe₂), 126.7 (CH=), 127.4 (CH=), 128.3 (CH=), 138.7 (C), 155.9 (CO), 174.0 (CO). Anal. calcd (%) for C₂₇H₄₂N₂O₈: 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 (CDCl₃), δ: 0.88 (d, 3H, CH₃, iPr, $^3J_{H-H}= 6.8$ Hz), 0.95 (d, 3H, CH₃, iPr, $^3J_{H-H}= 7.2$ Hz), 1.27 (s, 3H, CH₃), 1.39 (s, 9H, CH₃, tBu), 1.42 (s, 3H, CH₃), 2.11 (m, 1H, CH, iPr), 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, $^3J_{2,1}= 4.0$ Hz), 4.58 (d, 1H, CH₂, Bn, $^3J= 10.6$ Hz), 4.65 (d, 1H, CH₂, Bn, $^3J= 10.6$ Hz), 5.16 (b, 1H, NH), 5.87 (d, 1H, H-1, $^3J_{1,2}= 4.0$ Hz), 6.71 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). $^{13}$C NMR (CDCl₃), δ: 18.7 (CH₃, iPr), 19.2 (CH₃, iPr), 26.2 (CH₃), 26.7 (CH₃), 28.4 (CH₃, tBu), 30.9 (CH, iPr), 44.1 (C-6), 60.0 (CH), 68.1 (CH₂, Bn), 71.8 (C, tBu), 72.4 (C-5), 80.5 (C-4), 81.6 (C-2), 82.4 (C-3), 105.1 (C-1), 111.7 (CMe₂), 127.8 (CH=), 127.9 (CH=), 128.5 (CH=), 137.5 (C), 155.8 (CO), 172.0 (CO). Anal. calcd (%) for C₂₆H₄₀N₂O₈: 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 (CDCl₃), δ: 1.34 (s, 3H, CH₃), 1.39 (s, 9H, CH₃, tBu), 1.42 (s, 3H, CH₃), 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, $^3J_{2,1}= 3.6$ Hz), 4.62 (m, 2H, CH₂, Bn), 5.21 (b, 1H, NH), 5.79 (d, 1H, H-1, $^3J_{1,2}= 3.6$ Hz), 6.73 (b, 1H, NH), 7.2-7.4 (m, 5H, CH=). $^{13}$C NMR (CDCl₃), δ: 16.8 (CH₃), 26.4 (CH₃), 27.1 (CH₃), 28.3 (CH₃, tBu), 43.9 (C-6), 44.3 (CH₂), 66.7 (CH₂, Bn), 68.9 (C-5), 79.4 (C-4), 79.7 (C, tBu), 83.2 (C-2), 83.5 (C-3), 104.3 (C-1), 112.7 (CMe₂), 127.7 (CH=), 127.9 (CH=), 128.2 (CH=), 138.4 (C), 155.8 (CO), 171.2 (CO). Anal. calcd (%) for C₂₃H₃₄N₂O₈: 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\(_3\)), \(\delta\): 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, \(2J_{6,5} = 13.2\) 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, \(2J_{2,1} = 3.6\) Hz), 4.64 (d, 1H, CH\(_2\), \(2J_{1,2} = 6.8\) Hz), 4.67 (d, 1H, CH\(_2\), \(2J_{1,2} = 6.8\) Hz), 5.72 (d, 1H, H-1, \(3J_{1,2} = 3.6\) Hz), 7.2-7.4 (m, 5H, CH=).

\(^1\) K. P. R. Kartha, *Tetrahedron Lett.* 1986, 27, 3415
Synthesis of 6-amine-6-deoxy-1,2-O-isopropylidene-3-C-methyl-3-O-benzyl-\(\alpha\)-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\(_3\)), \(\delta\): 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\(_3\)), \(\delta\): 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-\(\alpha\)-glucofuranose 3

The following intermediate compounds for the synthesis of 3 have been previously described: 1,2:5,6-O-di-isopropylidene-\(\alpha\)-D-glucofuranose\(^{1}\) (97% yield), 1,2:5,6-di-O-isopropylidene-\(\alpha\)-D-ribo-hexofuranos-3-ulose\(^{2}\) (84% yield), 3,3'-anhydro-3-C-hydroxymethyl-1,2;5,6-di-O-isopropylidene-\(\alpha\)-D-glucofuranose\(^{3}\) (82% yield), 3-C-methyl-1,2;5,6-di-O-isopropylidene-\(\alpha\)-D-glucofuranose\(^{4}\) (70% yield), 3-O-benzyl-3-C-methyl-1,2-O-isopropylidene-\(\alpha\)-D-glucofuranose\(^{5}\) (85% yield) and 3-O-Benzyl-3-C-methyl-1,2-O-isopropylidene-\(\alpha\)-D-glucofuranose\(^{6}\) (81% yield).


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 °C) 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 MgSO₄, 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%. 1H NMR (CDCl₃), δ: 1.32 (s, 3H, CH₃), 1.49 (s, 3H, CH₃), 1.54 (s, 3H, CH₃), 2.44 (s, 3H, CH₃), 3.86 (m, 1H), 4.07 (dd, 1H, H-6', 2J₆'-6= 10.4 Hz, 3J₆'-5= 7.2 Hz), 4.29 (m, 1H), 4.34 (dd, 1H, H-6, 2J₆'-6= 10.4 Hz, 3J₆-5= 4.8 Hz), 4.47 (d, 1H, H-2, 3J₂₋₁= 4.0 Hz), 4.55 (d, 1H, CH₂, 2J₂₋₁= 6.4 Hz), 4.64 (d, 1H, CH₂, 3J₆.₅-H= 6.4 Hz), 5.78 (d, 1H, H-1, 3J₁₂= 4.0 Hz), 7.34 (m, 7H, CH=). 13C NMR

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%. 1H NMR (CDCl₃), δ: 1.33 (s, 3H, CH₃), 1.53 (s, 3H, CH₃), 1.57 (s, 3H, CH₃), 3.44 (b, 1H, OH), 3.46 (dd, 1H, H-6', 2J₆'-6= 12.4 Hz, 3J₆'-5= 6.4 Hz), 3.55 (dd, 1H, H-6, 2J₆'-6= 12.4 Hz, 3J₆-5= 3.2 Hz), 3.19 (m, 1H), 4.17 (m, 1H), 4.51 (d, 1H, H-2, 3J₂₋₁= 3.6 Hz), 4.57 (d, 1H, CH₂, 2J₂₋₁= 10.8 Hz), 4.63 (d, 1H, CH₂, 2J₆.₅-H= 10.8 Hz), 5.84 (d, 1H, H-1, 3J₁₂= 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%. 1H NMR (CDCl₃), δ: 1.31 (s, 3H, CH₃), 1.51 (s, 3H, CH₃), 1.55 (s, 3H, CH₃), 2.83 (b, 4H, NH₂, 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, 3J₂₋₁= 4.0 Hz), 4.57 (m, 2H, CH₂), 5.84 (d, 1H, H-1, 3J₁₂= 4.0 Hz), 7.32 (m, 5H, CH=). 13C NMR
(CDCl₃), δ: 15.7 (CH₃), 26.6 (CH₃), 27.3 (CH₃), 44.5 (C-6), 65.4 (CH₂, Bn), 68.2 (C-5), 83.3 (C-2), 85.0 (C-4), 85.3 (C-3), 104.7 (C-1), 112.2 (CMe₂), 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-glucofuranose¹ (97% yield), 3-O-benzyl-1,2-O-isopropylidene-α-D-glucofuranose² (99% yield), 3-O-benzyl-1,2-O-isopropylidene-α-D-glucofuranose⁸ (98% yield), 3-O-benzyl-1,2-O-isopropylidene-6-tosyl-α-D-glucofuranose⁹ (90% yield), 6-azido-6-deoxy-3-O-benzyl-1,2-O-isopropylidene-α-D-glucofuranose¹⁰ (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 ([RuCl₂(p-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 iPrONa (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 Et₂O.

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and the solvents were evaporated. The products were analyzed by GC (CP Chirasil DEX CB).\textsuperscript{12}

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

**Table SI.7.** Ru-catalyzed asymmetric transfer hydrogenation reaction using ligands L2 and L7\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Ligand</th>
<th>% Conv (h)\textsuperscript{b}</th>
<th>% ee\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S2</td>
<td>L2</td>
<td>100 (3)</td>
<td>&gt;99 (S)</td>
</tr>
<tr>
<td>2\textsuperscript{c}</td>
<td>S2</td>
<td>L7</td>
<td>98 (3)</td>
<td>99 (S)</td>
</tr>
<tr>
<td>3</td>
<td>S3</td>
<td>L2</td>
<td>99 (3)</td>
<td>99 (S)</td>
</tr>
<tr>
<td>4\textsuperscript{c}</td>
<td>S3</td>
<td>L7</td>
<td>99 (3)</td>
<td>99 (S)</td>
</tr>
<tr>
<td>5</td>
<td>S6</td>
<td>L2</td>
<td>100 (3)</td>
<td>99 (S)</td>
</tr>
<tr>
<td>6\textsuperscript{c}</td>
<td>S6</td>
<td>L7</td>
<td>100 (3)</td>
<td>&gt;99 (S)</td>
</tr>
<tr>
<td>7</td>
<td>S7</td>
<td>L2</td>
<td>99 (3)</td>
<td>99 (S)</td>
</tr>
<tr>
<td>8\textsuperscript{c}</td>
<td>S7</td>
<td>L7</td>
<td>95 (3)</td>
<td>99 (S)</td>
</tr>
<tr>
<td>9</td>
<td>S10</td>
<td>L2</td>
<td>78 (3)</td>
<td>99 (S)</td>
</tr>
<tr>
<td>10\textsuperscript{c}</td>
<td>S10</td>
<td>L7</td>
<td>69 (3)</td>
<td>98 (S)</td>
</tr>
</tbody>
</table>

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

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

\[
\begin{align*}
\text{S1} & \quad \text{[RuCl}_2\text{(cymene)}\text{]}_2 / \text{L1} \\
& \quad \text{LiCl / 2-PrONa} \\
& \quad \text{THF/2-PrOH (1:1)} \\
\end{align*}
\]
(rac)-1-(p-tolyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min 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

\[
\begin{align*}
\text{F}_{3}\text{C} & \quad \text{S3} \\
\text{O} & \quad \text{[RuCl}_{2}(p\text{-cymene})]_2 / \text{L1} \\
\text{LiCl} / 2\text{-PrONa} & \quad \text{THF-2-PrOH (1:1)} \\
& \quad \text{F}_{3}\text{C}
\end{align*}
\]
(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

```
F
\[\text{S4} \quad \text{[RuCl}_6\text{(p-cymene)}]\text{b} / L1 \quad \text{LiCl/2-PrONa} \quad \text{THF/2-PrOH (1:1)} \quad \text{OH} \quad \text{F} \]
```
(rac)-1-(4-methoxyphenyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min 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 to 180 °C and hold for 20 min)

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

![Chemical structure and graph](image)
(rac)-1-(3-methoxyphenyl)ethanol. (CP Chirasil DEX CB, Hold 110 °C for 15 min, rate 10 °C/min 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

\[
\begin{align*}
\text{S8} & \quad \text{[RuCl}_2\text{(p-cymene)}_2/L1} \\
\text{LiCl/2-PrONa} & \quad \text{THF/2-PrOH (1:1)} \\
\end{align*}
\]
(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)

![Graph for rac-1-(2-methoxyphenyl)ethanol](image)

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

![Graph for (S)-1-(2-methoxyphenyl)ethanol](image)
*(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.

\[
\text{[RuCl}_2(\text{o-cymene})]_2 / \text{L1} \\
\text{LiCl / 2-ProNa} \\
\text{THF:2-ProOH (1:1)}
\]

S11