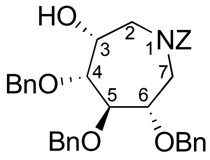
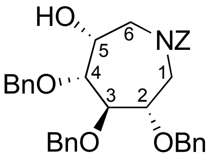
Note:

- **compounds with the nitrogen protected with a Z group appear as a mixture of rotamers due to the π bonding in the amide bond by NMR and these are indicated with normal and prime numbers)**
- **the numbering used to name the compounds is the following one:**



10

- **the numbering used to describe the NMR of the compounds is the following one by analogy with the parent sugar:**



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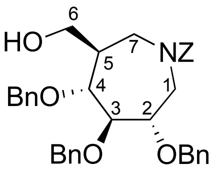
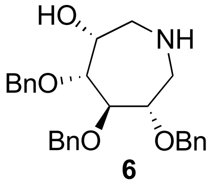


13

(3*R*,4*R*,5*R*,6*S*) -3-hydroxy-4,5,6-tribenzyloxyazepane **6**



6

To a stirred solution of azidolactol **5** (4.18 g, 8.80 mmol) in dry THF (35 mL) was added triphenyl phosphine (4.63 g, 17.65 mmol). The mixture was stirred at room temperature under argon atmosphere for 4 h by which time TLC (Cy/EtOAc, 2:1) showed a complete reaction. Evaporation under reduced pressure provided a crude product which was dissolved in AcOH (45 mL). $NaBH_3CN$ (1.54 g, 24.51 mmol) was added at 0 °C, and the reaction mixture was stirred at room temperature under argon for 6 h. The solvent was removed under reduced pressure and the residue was dissolved in EtOAc, washed with saturated aqueous $NaHCO_3$, water and brine. The organic layer was dried over $MgSO_4$ and concentrated. Purification by flash column chromatography (CH_2Cl_2/MeOH, 20:1) gave β-hydroxy azepane **6** (3.33 g, 87% yield) as an oil.

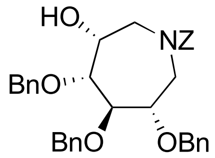
$[\alpha]_D$ + 1.0 (c = 0.97 in $CHCl_3$);

^{1}H NMR ($CDCl_3$, 400 MHz): 7.41-7.31 (m, 15H, 3×Ph), 4.74-4.54 (m, 6H, 3×CH_2Ph), 4.11 (m, 3H, H-5, NH, OH), 3.95 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 5.5 Hz, H-3), 3.79 (dd, 1H, $J_{4,5}$ = 1.2 Hz, $J_{3,4}$ = 5.5 Hz, H-4), 3.67 (app.dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{1a,2}$ = 6.5 Hz, H-2), 3.24 (dd, 1H, $J_{1a,2}$ = 6.5 Hz, $J_{1a,1b}$ = 14.5 Hz, H-1a), 3.21 (dd, 1H, $J_{5,6a}$ = 6.7 Hz, $J_{6a,6b}$ = 13.8 Hz, H-6a), 2.97 (app.d, 1H, $J_{1a,1b}$ = 14.5 Hz, H-1b), 2.91 (dd, 1H, $J_{5,6b}$ = 1.2 Hz, $J_{6a,6b}$ = 13.8 Hz, H-6b);

^{13}C NMR ($CDCl_3$, 100 MHz): 138.02, 137.74 and 136.95 (3×Cipso), 128.42-127.52 (15×C arom.), 84.99 (C-4), 81.82 (C-3), 78.00 (C-2), 72.83, 72.43 and 70.51 (3×CH_2Ph), 70.38 (C-5), 50.69 (C-6), 46.05 (C-1);

m/z (CI, NH_3): 434 ($M+H^+$, 100%); HRMS (CI, CH_4): Calcd for $C_{27}H_{32}O_4N$ ($M+H^+$): 434.2331; Found 434.2328.

(3*R*,4*R*,5*R*,6*S*)-*N*-Benzyloxycarbonyl-3-hydroxy-4,5,6-tribenzyloxyazepane **10**



10

To an ice-cold mixture of azepane **6** (0.75 g, 1.74 mmol) and $KHCO_3$ (3.36 g) in a H_2O/AcOEt solution (84 mL, 1:1, v/v) was added dropwise benzyl chloroformate (0.66 mL). The reaction mixture was stirred overnight at room temperature. The organic layer was then separated, washed with 1N aq. HCl and brine, dried with $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography (Cy/acetone, 4:1) afforded the carbamate derivative **10** as an oil (909 mg, 92% yield, R_f 0.23, Cy/acetone, 4:1).

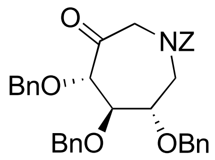
$[\alpha]_D$ - 10 (c = 0.99 in $CHCl_3$);

^{1}H NMR ($CDCl_3$, 400 MHz): 7.41-7.29 (m, 40H, 8×Ph), 5.19-5.09 (m, 4H, 4×NCOOCHPh), 4.86-4.46 (m, 12H, 6×CH_2Ph), 4.22 (br, 1H, H-5'), 4.17 (br, 1H, H-5), 4.07 (dd, 1H, $J_{5',6'a}$ = 4.6 Hz, $J_{6'a,6'b}$ = 13.6 Hz, H-6'a), 4.06-3.90 (m, 7H, H-1a, H-1'a, H-2, H-3, H-3', H-4, H-4'), 3.87 (dd, 1H, $J_{5,6a}$ = 4.3 Hz, $J_{6a,6b}$ = 13.9 Hz, H-6a), 3.73 (dt, 1H, $J_{1'a,2'}$ = $J_{2',3'}$ = 4.0 Hz, $J_{1'b,2'}$ = 9.8 Hz, H-2'), 3.58 (dd, 1H, $J_{1b,2}$ = 8.9 Hz, $J_{1a,1b}$ = 13.4 Hz, H-1b), 3.50 (dd, 1H, $J_{1'b,2'}$ = 9.8 Hz, $J_{1'a,1'b}$ = 14.2 Hz, H-1'b), 3.43 (dd, 1H, $J_{5,6b}$ = 9.2 Hz, $J_{6a,6b}$ = 13.9 Hz, H-6b), 3.36 (dd, 1H, $J_{5',6'b}$ = 8.6 Hz, $J_{6'a,6'b}$ = 13.6 Hz, H-6’b), 2.58 (d, 1H, J = 8.9 Hz, OH), 2.55 (br, 1H, OH’);

^{13}C NMR (CDCl$_3$, 100 MHz): 155.80 and 155.66 (2×C=O), 137.96, 137.88, 136.58 and 136.34 (8×Cipso), 128.46-127.54 (40×aromatic C), 82.76 and 82.22 (C-4 and C-4’), 80.24 and 79.96 (C-3’ and C-3), 79.88 and 77.98 (C-2’ and C-2), 72.96, 72.82, 72.70, 72.57, 72.00 and 71.79 (6×CH$_2$Ph), 68.68 and 68.59 (C-5’ and C-5), 67.47 and 67.14 (2×NCOO$\underline{C}$H$_2$Ph), 49.45 and 49.23 (C-6 and C-6’), 47.00 and 46.29 (C-1 and C-1’);

m/z (CI, NH$_3$): 568 (M+H$^+$, 55%), 585 (M+NH$_4$$^+$, 100%); HRMS (CI, CH$_4$): Calcd for $C_{35}H_{38}O_6N$ (M+H$^+$): 568.2699; Found 568.2695.

(4*S*,5*R*,6*S*)-*N*-Benzyloxycarbonyl-3-oxo-4,5,6-tribenzyloxyazepane **11**



11

To a stirred suspension of alcohol **10** (900 mg, 1.59 mmol) and 4Å molecular sieves (1.5 g) in dry CH$_2$Cl$_2$ (30 mL) was added PCC (1.05 g, 4.87 mmol) at room temperature under argon. After 4 h, the reaction mixture was directly poured onto a silica plug eluted with Cy/acetone (6:1) to give the corresponding ketone **11** as an oil (847 mg, 94% yield, R$_f$ 0.47, Cy/acetone, 3:1).

$[\alpha]_D$ + 3 (c = 1.0 in CHCl$_3$);

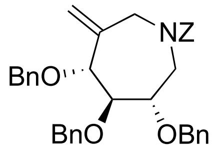
^{1}H NMR (CDCl$_3$, 400 MHz): 7.48-7.23 (m, 40H, 8×Ph), 5.29-5.11 (m, 4H, 4×NCOOCHPh), 4.90-4.83 (m, 3H, CHPh, H-6a), 4.77-4.56 (m, 8H, 6×CHPh, H-4, H-6’a), 4.53 (app.dd, 1H, $J_{1'a,2'}$ = 3.6 Hz, $J_{1'a,1'b}$ = 14.4 Hz, H-1’a), 4.50 (d, 1H, $J_{3',4'}$ = 4.7 Hz, H-4’), 4.49-4.23 (m, 5H, 4×CHPh, H-1a), 3.99 (t, 1H, $J_{2,3}$ = 4.8 Hz, H-3), 3.96 (t, 1H, $J_{2',3'}$ = 4.7 Hz, H-3’), 3.90 (d, 1H, $J_{6'a,6'b}$ = 18.6 Hz, H-6’b), 3.90-3.82 (m, 2H, H-2, H-2’), 3.84 (d, 1H, $J_{6a,6b}$ = 18.3 Hz, H-6b), 3.21 (dd, 1H, $J_{1b,2}$ = 2.3 Hz, $J_{1a,1b}$ = 14.5 Hz, H-1b), 3.50 (dd, 1H, $J_{1'b,2'}$ = 2.2 Hz, $J_{1'a,1'b}$ = 14.4 Hz, H-1’b);

^{13}C NMR (CDCl$_3$, 100 MHz): 204.18 and 204.05 (C-5’ and C-5), 156.11 and 155.97 (2×C=O), 137.75, 137.68, 137.40, 137.32, 136.96, 136.91, 136.15 and 136.05 (8×Cipso), 128.54-127.61 (40×aromatic C), 86.28 and 86.21 (C-4 and C-4’), 80.96 and 80.84 (C-3 and

C-3’), 76.90 and 76.67 (C-2’ and C-2), 72.90, 72.81, 72.46, 72.33, 71.88 and 71.77 (6×CH$_2$Ph), 67.90 and 67.73 (2×NCOO$\underline{\mathrm{C}}$H$_2$Ph), 55.15 and 55.11 (C-6 and C-6’), 46.17 and 46.02 (C-1’ and C-1);

m/z (CI, NH$_3$): 566 (M+H$^+$, 15%), 583 (M+NH$_4$$^+$, 100%); HRMS (CI, CH$_4$): Calcd for $C_{35}H_{36}O_6N$ (M+H$^+$): 566.2543; Found 566.2534.

(4*R*,5*S*,6*S*)-*N*-Benzyloxycarbonyl-3-methylene-4,5,6-tribenzyloxyazepan **12**



12

To a stirred solution of methyltriphenylphosphonium bromide (2.29 g, 6.41 mmol) in dry THF (20 mL) was added dropwise *n*-butyl lithium (2.4 mL of a 2.5 M solution in hexane) at 0 °C under argon atmosphere and the mixture was warmed to room temperature. After 0.5 h, the reaction mixture was cooled at 0 °C and a solution of ketone **11** (320 mg, 0.566 mmol) in dry THF (10 mL) was added dropwise. After stirring for 3 h at at 0 °C under argon, the reaction was quenched by slow addition of water and EtOAc. The organic layer was then separated, washed with water and brine, dried with MgSO$_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography (Cy/EtOAc, 8:1) afforded the exomethylene azepane **12** as an oil (248 mg, 78% yield, R$_f$ 0.23, Cy/EtOAc, 8:1). Further elution (Cy/EtOAc, 4:1) afforded the unreacted ketone **11** (31 mg, 10% recovered starting material).

$[\alpha]_D$ - 48 (c = 1.0 in CHCl$_3$);

^{1}H NMR (CDCl$_3$, 400 MHz): 7.40-7.29 (m, 40H, 8×Ph), 5.62 (app.d, 1H, $J_{6a,6b}$ = 0.87 Hz, H-6a), 5.56 (app.d, 1H, $J_{6'a,6'b}$ = 0.82 Hz, H-6’a), 5.41 (app.s, 1H, H-6b), 5.36 (app.s, 1H, H-6’b), 5.24-5.08 (m, 4H, 4×NCOOCHPh), 5.02-4.41 (m, 14H, 6×CH$_2$Ph, H-7a, H-7’a), 4.06 (app.dd, 1H, $J_{1'a,2'}$ = 3.1 Hz, $J_{1'a,1'b}$ = 14.2 Hz, H-1’a), 3.97 (d, 1H, $J_{3,4}$ = 8.7 Hz, H-4), 3.95 (d, 1H, $J_{3',4'}$ = 8.4 Hz, H-4’), 3.87 (app.dd, 1H, $J_{1a,2}$ = 3.1 Hz, $J_{1a,1b}$ = 14.3 Hz, H-1a), 3.84 (d, 1H, $J_{7'a,7'b}$ = 14.0 Hz, H-7‘b), 3.76 (d, 1H, $J_{7a,7b}$ = 14.2 Hz, H-7b), 3.66 (ddd, 1H, $J_{1'a,2'}$ = 3.5 Hz, $J_{2',3'}$ = 7.9 Hz, $J_{1'b,2'}$ = 10.6 Hz, H-2’), 3.57 (ddd, 1H, $J_{1a,2}$ = 3.3 Hz, $J_{2,3}$ = 8.0 Hz, $J_{1b,2}$ = 10.8 Hz, H-2), 3.52 (t, 1H, $J_{2',3'}$ = $J_{3',4'}$ = 8.2 Hz, H-3’), 3.47 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 8.5 Hz, H-3), 2.96 (dd, 1H, $J_{1'b,2'}$ = 10.6 Hz, $J_{1'a,1'b}$ = 14.2 Hz, H-1'b), 2.91 (dd, 1H, $J_{1b,2}$ = 10.8 Hz, $J_{1a,1b}$ = 14.3 Hz, H-1b);

^{13}C NMR ($CDCl_3$, 100 MHz): 155.51 and 154.96 (2×C=O), 142.01 and 141.68 (C-5 and C-5'), 138.78, 138.34, 138.26, 138.22, 138.18 and 136.18 (8×Cipso), 128.54-127.49 (40×aromatic C), 116.92 and 116.87 (C-6 and C-6'), 87.48 and 87.20 (C-3 and C-3'), 81.64 and 81.45 (C-4' and C-4), 80.80 and 80.35 (C-2 and C-2'), 76.03, 75.75, 72.86, 70.96 and 70.88 (6×CH_2Ph), 67.72 and 67.37 (2×$NCOOCH_2$Ph), 52.14 and 51.95 (C-7 and C-7'), 43.93 and 43.87 (C-1' and C-1);

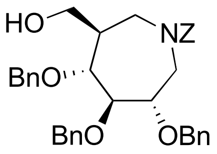
m/z (CI, NH_3): 564 ($M+H^+$, 100%), 581 ($M+NH_4^+$, 40%);

HRMS (CI, CH_4): Calcd for $C_{36}H_{38}O_5N$ ($M+H^+$): 564.2750, Found 564.2742.

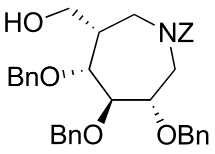
(3*R*,4*R*,5*S*,6*S*)-*N*-Benzyloxycarbonyl-3-hydroxymethyl-4,5,6-tribenzyloxyazepane **13**

and

(3*S*,4*R*,5*S*,6*S*)-*N*-Benzyloxycarbonyl-3-hydroxymethyl-4,5,6-tribenzyloxyazepane **14**



13



14

To a stirred solution of methyleneazepane **12** (100 mg, 0.178) in dry THF (2 mL) was added dropwise a 1 M solution of 9-BBN in THF (0.4 mL) at 0 °C under argon. The reaction mixture was kept at room temperature for 2 h and then EtOH (0.2 mL), 3 M aq. NaOH (0.3 mL) and a 35% solution of H_2O_2 (0.3 mL) were successively added dropwise. After stirring at room temperature for another 2 h, the reaction mixture was diluted with AcOEt, washed with 1M aq. HCl solution, water and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography (Cy/EtOAc, 4:1) afforded alcohol **13** as an oil (47 mg, 47% yield, R_f 0.30, Cy/EtOAc, 2:1) followed by alcohol **14** as an oil (31 mg, 30% yield, R_f 0.21, Cy/EtOAc, 2:1).

Compound **13**:

$[\alpha]_D$ - 5 (c = 1.0 in $CHCl_3$);

^{1}H NMR ($CDCl_3$, 400 MHz): 7.43-7.20 (m, 40H, 8×Ph), 5.26-5.15 (m, 4H, 4×NCOOCHPh), 4.92-4.39 (m, 12H, 6×CH_2Ph), 4.05 (dd, 1H, $J_{1'a,2'}$ = 2.3 Hz, $J_{1'a,1'b}$ = 14.0 Hz, H-1'a), 3.98 (dd, 1H, $J_{5,7a}$ = 5.2 Hz, $J_{7a,7b}$ = 14.4 Hz, H-7a), 3.94 (app.d, 1H, $J_{1a,1b}$ = 14.1 Hz, H-1a), 3.91 (dd, 1H, $J_{3',4'}$ = 4.2 Hz, $J_{2',3'}$ = 6.4 Hz, H-3'), 3.84 (dd, 1H, $J_{3,4}$ = 4.1 Hz, $J_{2,3}$ = 6.3 Hz, H-3), 3.82 (ddd, 1H, $J_{1'a,2'}$ = 2.3 Hz, $J_{2',3'}$ = 6.4 Hz, $J_{1'b,2'}$ = 9.6 Hz, H-2'), 3.79 (dd, 1H, $J_{3',4'}$ = 4.2 Hz, $J_{4',5'}$ = 7.2 Hz, H-4'), 3.74 (dd, 1H, $J_{3,4}$ = 4.1 Hz, $J_{3,4}$ = 6.7 Hz, H-4), 3.72 (dd, 1H, $J_{5',7'a}$ = 6.0 Hz, $J_{7'a,7'b}$ = 14.2 Hz, H-7'a), 3.64 (ddd, 1H, $J_{1a,2}$ = 2.7 Hz, $J_{2,3}$ = 6.3 Hz, $J_{1b,2}$ = 10.1 Hz, H-2), 3.63 (m, 4H, H-6a, H-6'a, H-6b, H-6'b), 3.47 (dd, 1H, $J_{5',7'b}$ = 3.2 Hz, $J_{7'a,7'b}$ = 14.2 Hz, H-7'b), 3.43 (dd, 1H, $J_{1'b,2'}$ = 9.6 Hz, $J_{1'a,1'b}$ = 14.0 Hz, H-1'b), 3.76 (dd, 1H, $J_{5,7b}$ = 3.2 Hz, $J_{7a,7b}$ = 14.4 Hz, H-7b), 3.34 (dd, 1H, $J_{1b,2}$ = 10.1 Hz, $J_{1a,1b}$ = 14.1 Hz, H-1b), 3.32 (br., 1H, OH), 2.52 (app. t, 1H, J = 6.3 Hz, OH'), 2.41 (m, 1H, H-5), 2.33 (m, 1H, H-5');

^{13}C NMR ($CDCl_3$, 100 MHz): 156.66 and 155.81 (2×C=O), 138.21, 138.08, 137.97, 137.79, 136.33 and 136.15 (8×Cipso), 128.58-127.43 (40×aromatic C), 85.50 and 84.89 (C-3 and C-3'), 82.73 and 81.71 (C-2 and C-2'), 79.65 and 78.62 (C-4' and C-4), 73.85, 73.58, 72.99, 72.74, 71.85 and 71.80 (6×CH_2Ph), 67.90 and 67.44 (2×NCOOCH_2Ph), 61.95 and 60.85 (C-6' and C-6), 45.46 and 44.91 (C-1 and C-1'), 44.35 and 44.17 (C-5 and C-5'), 43.91 and 43.45 (C-7' and C-7);

m/z (CI, NH_3): 582 (M+H$^+$, 100%); HRMS (CI, CH_4): Calcd for $C_{36}H_{40}O_6N$ (M+H$^+$): 582.2856, Found 582.2863.

Compound **14**:

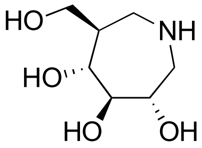
$[\alpha]_D$ - 9 (c = 1.0 in $CHCl_3$);

^{1}H NMR ($CDCl_3$, 400 MHz): 7.40-7.28 (m, 40H, 8×Ph), 5.22-5.06 (m, 4H, 4×NCOOCHPh), 4.83-4.37 (m, 12H, 6×CH_2Ph), 4.20 (dd, 1H, $J_{1'a,2'}$ = 4.0 Hz, $J_{1'a,1'b}$ = 13.6 Hz, H-1'a), 4.06-3.95 (m, 7H, H-1a, H-2', H-3, H-3', H-4, H-4', H-7a), 3.92 (dd, 1H, $J_{5',7'a}$ = 3.6 Hz, $J_{7'a,7'b}$ = 14.0 Hz, H-7'a), 3.81 (dt, 1H, $J_{1a,2}$ = $J_{2,3}$ = 3.8 Hz, $J_{1b,2}$ = 9.7 Hz, H-2), 3.68 (dd, 1H, $J_{5,6a}$ = 5.7 Hz, $J_{6a,6b}$ = 10.9 Hz, H-6a), 3.67-3.53 (m, 3H, H-6'a, H-6b, H-6'b), 3.52 (dd, 1H, $J_{1b,2}$ = 9.7 Hz, $J_{1a,1b}$ = 14.0 Hz, H-1b), 3.46 (dd, 1H, $J_{1'b,2'}$ = 9.7 Hz, $J_{1'a,1'b}$ = 13.6 Hz, H-1'b), 3.26 (dd, 1H, $J_{5',7'b}$ = 5.4 Hz, $J_{7'a,7'b}$ = 14.0 Hz, H-7'b), 3.23 (dd, 1H, $J_{5,7b}$ = 4.9 Hz, $J_{7a,7b}$ = 13.9 Hz, H-7b), 2.40-2.27 (m, 2H, H-5, H-5'), 1.97 (br., 1H, OH'), 1.75 (br., 1H, OH);

^{13}C NMR ($CDCl_3$, 100 MHz): 156.76 and 155.70 (2×C=O), 138.36, 138.16, 138.06, 138.04, 137.87, 137.82, 136.88 and 136.56 (8×Cipso), 128.45-127.56 (40×aromatic C), 80.80 and

79.84 (C-2 and C-2'), 80.03 and 79.44 (C-3 and C-3'), 78.75 and 78.54 (C-4' and C-4), 72.14, 72.12, 72.06, 71.99, 71.88 and 71.65 (6×CH_2Ph), 67.31 and 66.90 (2×$NCOOCH_2Ph$), 63.98 and 63.37 (C-6' and C-6), 47.75 and 47.26 (C-1' and C-1), 45.51 and 45.36 (C-7 and C-7'), 41.48 and 41.40 (C-5' and C-5);
HRMS (CI, CH_4) : Calcd for $C_{36}H_{40}O_6N$ ($M+H^+$): 582.2856, Found 582.2845.

(3*R*,4*R*,5*S*,6*S*)-3-hydroxymethyl-4,5,6-trihydroxyazepane **15**

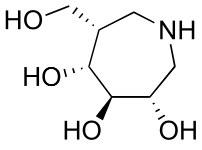


15

To a solution of compound **13** (37 mg, 0.064 mmol) in MeOH (3.7 mL) and 1 M HCl aq. solution (0.13 mL) was added 10% Pd/C (42 mg). The suspension was hydrogenated at room temperature overnight, and then filtered through a 0.45 μM rotilabo® filter eluted with CH_3OH and concentrated to afford tetrol **15** (14 mg, quant. yield) as an oil.

$[\alpha]_D + 25$ (c = 1.1 in CH_3OH);
^1H NMR (D_2O, 400 MHz): 4.07 (ddd, 1H, $J_{1a,2}$ = 2.4 Hz, $J_{2,3}$ = $J_{1b,2}$ = 7.0 Hz, H-2), 3.82 (dd, 1H, $J_{5,6a}$ = 3.6 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6a), 3.74 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 6.8 Hz, H-3), 3.70 (dd, 1H, $J_{5,6b}$ = 6.2 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6b), 3.59 (dd, 1H, $J_{3,4}$ = 6.8 Hz, $J_{4,5}$ = 9.9 Hz, H-4), 3.48 (dd, 1H, $J_{5,7a}$ = 2.2 Hz, $J_{7a,7b}$ = 14.0 Hz, H-7a), 3.37 (dd, 1H, $J_{1a,2}$ = 2.4 Hz, $J_{1a,1b}$ = 13.9 Hz, H-1a), 3.31 (dd, 1H, $J_{1b,2}$ = 7.0 Hz, $J_{1a,1b}$ = 13.9 Hz, H-1b), 3.09 (dd, 1H, $J_{5,7b}$ = 10.2 Hz, $J_{7a,7b}$ = 14.0 Hz, H-7b), 2.19 (m, 1H, H-5);
^{13}C NMR (D_2O, 100 MHz): 78.25 (C-3), 73.70 (C-4), 67.57 (C-2), 61.34 (C-6), 46.02 (C-1), 45.54 (C-7), 40.80 (C-5);
m/z (CI, CH_4): 178 ($M+H^+$, 100%); HRMS (CI, CH_4): Calcd for $C_7H_{16}O_4N$ ($M+H^+$): 178.1079, Found 178.1074.

(3*S*,4*R*,5*S*,6*S*)-3-hydroxymethyl-4,5,6-trihydroxyazepane **16**



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To a solution of compound **14** (30 mg, 0.052 mmol) in MeOH (3 mL) and 1 M HCl aq. solution (0.1 mL) was added 10% Pd/C (32 mg). The suspension was hydrogenated at room temperature overnight, and then filtered through a 0.45 µM rotilabo® filter eluted with CH_3OH and concentrated to afford tetrol **16** (12 mg, quant. yield) as an oil.

$[\alpha]_D$ - 13 (c = 1.0 in CH_3OH);
^{1}H NMR (D_2O, 400 MHz): 4.08-4.05 (m, 2H, H-2, H-4), 3.98 (t, 1H, $J_{2,3} = J_{3,4} = 4.6$ Hz, H-3), 3.64 (dd, 1H, $J_{5,6a} = 6.9$ Hz, $J_{6a,6b} = 11.2$ Hz, H-6a), 3.60 (dd, 1H, $J_{5,6b} = 6.9$ Hz, $J_{6a,6b} = 11.2$ Hz, H-6b), 3.43 (dd, 1H, $J_{1a,2} = 2.0$ Hz, $J_{1a,1b} = 14.1$ Hz, H-1a), 3.38 (dd, 1H, $J_{1b,2} = 6.5$ Hz, $J_{1a,1b} = 14.1$ Hz, H-1b), 3.29 (dd, 1H, $J_{7a,7b} = 13.2$ Hz, $J_{5,7a} = 15.6$ Hz, H-7a), 3.27 (app.dd, 1H, $J_{5,7b} = 9.1$ Hz, $J_{7a,7b} = 13.2$ Hz, H-7b), 2.43 (app.ddt, 1H, $J_{5,6a} = J_{5,6b} = 6.9$ Hz, $J_{5,7b} = 9.1$ Hz, $J_{5,7a} = 15.6$ Hz, H-5);
^{13}C NMR (D_2O, 100 MHz): 74.09 (C-3), 72.09 (C-4), 70.33 (C-2), 62.04 (C-6), 45.45 (C-1), 42.87 (C-7), 36.26 (C-5);
m/z (CI, CH_4): 178 ($M+H^+$, 100%);
HRMS (CI, CH_4): Calcd for $C_7H_{16}O_4N$ ($M+H^+$): 178.1079, Found 178.1075.