Supporting Information

Aminopolyols from Carbohydrates: Amination of Sugars and Sugar-Derived Tetrahydrofurans with Transaminases

Fabiana Subrizi, Laure Benhamou, John M. Ward, Tom D. Sheppard, and Helen C. Hailes*

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Author Contributions

H.H. Conceptualization: Lead; Investigation: Lead; Methodology: Supporting; Project administration: Lead; Supervision: Lead; Writing—original draft: Lead; Writing—review & editing: Lead
F.S. Conceptualization: Supporting; Investigation: Lead; Methodology: Lead; Writing—original draft: Lead
L.B. Investigation: Supporting; Methodology: Supporting; Writing—review & editing: Supporting
J.W. Conceptualization: Supporting; Investigation: Supporting; Methodology: Supporting; Supervision: Supporting; Writing—review & editing: Supporting
T.S. Investigation: Supporting; Methodology: Supporting; Supervision: Supporting; Writing—review & editing: Lead.
**Table of contents:**

I. General experimental and analytic methods S2
II. Analytical HPLC chromatograms S5
III. Supplementary Data and Figures S8
IV. Chemical syntheses and preparative scale biocatalytic reactions S15
V. NMR spectra S30
VI. References S47
I. General Experimental and analytic methods

The solvents and chemicals were purchased from Sigma-Aldrich or Fluorochem and were used as supplied. Column chromatography was carried out using BDH (40-63 μm) silica gel and analytical thin layer chromatography was carried out using Merck Kieselgel aluminium-backed plates coated with silica gel. Compounds were visualised using combinations of UV (254 nm) or potassium permanganate. $^1$H and $^{13}$C NMR spectra were recorded respectively at 400 MHz and 100 MHz on a Bruker Avance 400 spectrometer, 500 MHz and 125 MHz on a Bruker Avance 500 or at 600 MHz and 150 MHz on a Bruker Avance 600 spectrometer in the stated solvent. Chemical shifts (in ppm) are quoted relative to tetramethylsilane and referenced to residual protonated solvent. Coupling constants ($J$) are measured in Hertz (Hz) and multiplicities for $^1$H NMR coupling are shown as s (singlet), d (doublet), t (triplet), and m (multiplet). HPLC analyses were performed on an Agilent 1260 Infinity provided with a 1260 VWD detector. Infrared (IR) spectra were recorded on a Perkin-Elmer spectrum 100 FT-IR spectrometer as thin films. Mass spectra were obtained using either a VG70-SE or MAT 900XP spectrometer at the Department of Chemistry, University College London. All optical rotations were measured on a Perkin-Elmer 343 polarimeter with a path length of 1 dm.

Transaminase expression and preparation. Overnight cultures (10 mL) of the TAmS in E. coli from the UCL TAm library were prepared in 2xTY broth (16 g/L tryptone, 10 g/L yeast extract, 5 g/L NaCl) supplemented with kanamycin (50 μg/mL) and incubated overnight at 37 °C. Cells were subcultured using 1% v/v inoculum in 2 L shake flasks containing 500 mL of the same supplemented broth at 37 °C and 250 rpm. Transaminases were induced with 1 mM of IPTG when growing in the early exponential phase (OD$_{600}$ = 0.5 - 0.7), and the temperature was dropped to 30 °C until harvesting. Cells were harvested by centrifugation after 5 h of induction, and stored at −20 °C. When needed, the cell pellet after induction was resuspended in the appropriate buffer containing PLP at a 1:25 volume ratio (1 mL of the resuspension buffer per 25 mL of cell suspension) and sonicated (Soniprep 150 sonicator, MSE Sanyo Japan) on ice using 10 cycles of 10 s on, 10 s off at 10 Watts. The sonicated suspension was centrifuged at 12,000 rpm at 4 °C for 45 min to obtain the clarified lysate. The total protein concentration was determined using the Bradford method. TAm concentrations in the crude lysates were determined as 8.8 mg/mL Cv-
TAm, 8.0 mg/mL Rh-TAm, 9.6 mg/mL Mv-TAm, 6.4 mg/mL pQR2189, \[^{[1]}\] 4.8 mg/mL pQR2191, \[^{[1]}\] and 8.0 mg/mL pQR2208.\[^{[1]}\]

**Colorimetric screening.** The assay was performed in a 96 well-plate with a total volume of 200 μL containing 2-(4-nitrophenyl)ethan-1-amine hydrochloride 5 (25 mM) as amine donor, amine acceptor (10 mM), PLP (0.5 mM) and potassium phosphate buffer (100 mM, pH 8.0). The reaction was started by the addition of TAm clarified lysate (20 μL) containing the overexpressed TAm and the reaction was incubated at 30 °C and 500 rpm for 24 h. A positive control was performed using benzaldehyde or pyruvate as the amine acceptor as specified. Two negative controls were also performed, one without amine acceptor and another without enzyme. An orange/red coloration indicated that the TAms were active towards the selected aldehydes.

**MBA screening.** The assay was performed in an Eppendorf tube (500 μL total volume) containing (R)- or (S)-MBA (20 mM), PLP (2 mM), potassium phosphate buffer (100 mM, pH 8.0), amine acceptor (5 mM) and crude cell lysate (30 μL) containing the overexpressed TAm. After incubation at 30 °C and 350 rpm for the time specified, the reaction was stopped by the addition of 0.1% trifluoroacetic acid (TFA) in water (100 μL). Denatured protein was removed by centrifugation (4 °C, 12000 rpm, 10 min) and the supernatant diluted with water and analysed by analytical HPLC using an ACE 5-C18 300 column (150 × 4.6 mm) with UV detection at 250 nm. The concentration of acetophenone produced was determined using a linear gradient 15%–72% over 10 minutes at 1 mL min\(^{-1}\) (A = water with 0.1% of TFA and B = acetonitrile) with subtraction of a negative control without amine acceptor for all substrates. The acetophenone (ACP) produced eluted at a retention time of 8.8 min. Results were verified in duplicate or triplicate.

**Isopropylamine assay.** The assay was performed in an Eppendorf tube containing isopropylamine (250 mM, pH 8), PLP (2 mM), potassium phosphate buffer (100 mM, pH 8), amine acceptor (25 mM) and crude cell lysate (30 μL) containing the overexpressed TAm in a final volume of 500 μL. After incubation at 37 °C and 400 rpm, the reaction was stopped by the addition of 1% TFA in water (100 μL). Denatured protein was removed by centrifugation (4 °C, 13000 rpm, 10 min) and the supernatant analysed by analytical HPLC after derivatization with 9-fluorenylmethyl chloroformate (Fmoc-Cl).
Derivatization with Fmoc-Cl and analytical HPLC. 25 μL of reaction sample was diluted with 5 μL of milliQ water or quenched with 1% TFA and mixed with 70 μL of sodium borate buffer solution (7 mM, pH 8) and 70 μL of Fmoc-Cl (40 mM in acetonitrile), and then incubated at r.t. for 5 min. After this time the reaction was stopped by adding 80 μL of L-alanine (100 mM in water:acetonitrile 2:1). After 1 min the reaction mixture was centrifuged (25 °C, 13000 rpm, 10 min) and the supernatant was analysed by HPLC using an ACE 5-C18 column (150 × 4.6 mm). The mobile phase A consisted of trifluoroacetic acid 0.1% in MilliQ water and the mobile phase B was trifluoroacetic acid 0.1% in acetonitrile 80% and MilliQ water 20%. The gradient elution was performed from 0 to 55% of phase B and run at 0.8 mL/min for 10 min at 30 °C for 3a and from 40 to 60% of phase B and run at 0.8 mL/min for 20 min at 30 °C 3b and for 28 min for 3c and 3d. The eluted products were detected at 360 nm and quantitative analysis was performed by the integration of peak areas using the external standard method (standard concentrations from 5 mM to 25 mM).
II. Analytical HPLC chromatograms

**Figure S1.** Typical HPLC chromatogram of the Fmoc-derivatives of *anti-3a* and *syn-3a*. The retention times for *anti-3b* and *syn-3b* were the same.

**Figure S1a.** Typical HPLC chromatogram of the biocatalytic reactions on 2a after Fmoc-derivatization. Retention times for the products *anti-3a* and *syn-3a* are labelled. The retention times for *anti-3b* and *syn-3b* were identical.
**Figure S2.** Typical HPLC chromatogram of the Fmoc-derivatives of anti-3c and syn-3c.

**Figure S2a.** Typical HPLC chromatogram of the biocatalytic reactions on 2c after Fmoc-derivatization. Retention times for the products anti-3c and syn-3c are labelled.
Figure S3. Typical HPLC chromatogram of the Fmoc-derivatives of anti-3d and syn-3d.

Figure S3a. Typical HPLC chromatogram of the biocatalytic reactions on 2d after FMOC-derivatization. Retention times for the products anti-3d and syn-3d are labelled.
III. Supplementary Data and Figures

Figure S4 Preliminary colorimetric assays on compound 2a showed high acceptance for almost all the 11 selected TAm. They are *Chromobacterium violaceum* TAm (Cv-TAm),[2] *Pseudomonas aeruginosa* TAm (Pa-TAm pQR426),[2] *Pseudomonas putida* TAm (Pp1-TAm pQR427),[4] *Dienococcus geothermalis* TAm (Dg-TAm pQR980),[5] *Rhodobacter sphaeroides* TAm (Rh-TAm),[6] *Mycobacterium vanbaalenii* TAm (Mv-TAm),[6] *Arthrobacter sp.* variant ArRMut11 (ArRMut11),[7] *Pseudomonas putida* TAm (Pp2-TAm pQR959),[8] *Rhospirillum rubrum* TAm (Rr-TAm pQR1017),[8] *Vibrio fluvialis* TAm (Vf-TAm),[9] *Saccharopolyspora erythraea* TAm (Se-TAm pQR805).[10] The assay was repeated in duplicate using 2-(4-nitrophenyl)ethan-1-amine 5 as amine donor: 5 (25 mM), 2a (10 mM), PLP (0.5 mM), TRIS-HCl buffer pH 8.0 (50 mM) and enzyme clarified lysate (20 uL), 24 h, 30 °C, 500 rpm. Benzaldehyde was used as a positive control (+) and buffer as a negative control (−).
**Figure S5.** Time course analysis (2 h and 24 h) towards 2a-d (5 mM) using 20 mM (S)-MBA (Cv-TAm and Rh-TAm) or 20 mM (R)-MBA (Mv-TAm) as amine donors, enzyme clarified lysate (1 mg/mL total protein), 24 h, 30 °C, 500 rpm. Blue (2a), Red (2b), Green (2c), and Purple (2d). The product acetophenone (ACP) was detected by HPLC analysis at 254 nm and used to determine % conversions. Background levels of acetophenone production were subtracted from the assay results in control reactions. All the reactions were performed in duplicate and average values are reported.
Figure S6. IPA Time course analysis towards 3c. Screening results for substrate 3c (25 mM) using 250 mM IPA as amine donors, enzyme clarified lysate (1 mg/mL), 24 h, 37 °C, 500 rpm. The product was detected by HPLC analysis after derivatization with Fmoc-Cl following the reported procedure in the experimental section and used to determine % yields.
**Figure S7.** Time course analysis experiment using $^1$H NMR spectroscopy over 48 h using 2e as starting material and Cv-TAm. 2e (37.5 mg, 0.25 mmol) was dissolved in 3.45 ml of potassium phosphate buffer (50 mM, pH 8, containing 2 mM PLP) and IPA 1 M (1.250 mL, freshly prepared in potassium phosphate buffer, pH adjusted to 8) was added. Finally, 0.3 mL of Cv-TAm were added and the solution stirred at 37 °C and 250 rpm in a shake flask incubator. Aliquots (0.5 ml) were taken at different time points and quenched with 0.1 mL of HCl 1% and freeze dried. The residue was then dissolved in D$_2$O and $^1$H NMR recorded. The signals at 3.8 ppm and 4.0 ppm are characteristic for syn-3e and anti-3e respectively.
**Figure S8.** Colorimetric assay on selected sugars (10 mM), using 5 as the amine donor (25 mM), DMSO (25% or 40% v/v) were indicated, PLP (0.5 mM), potassium phosphate buffer pH 8.0 (100 mM) and enzyme clarified lysate (1 mg/mL), 24 h, 350 rpm. Pyruvate was used as a positive control (+) and buffer as a negative control (-). Reactions were carried out at different pHs (6.5, 8, and 9.5) and temperatures (30 °C and 45 °C).
Figure S9. Colorimetric assay and conversions on selected sugars with pQR2191, using 5 or (S)-MBA as the amine donor, potassium phosphate buffer at pH 8.0, 24 h. Pyruvate was used as a positive control (+) and buffer as a negative control (-). Reactions were carried out at 30 °C or 45 °C as specified. [a] Control reaction without DMSO. It is noteworthy that the selected TAm pQR2191 performs well in 25% DMSO at 30 °C, as shown from the positive control with pyruvate (+), while the yield slightly decreased at 45 °C. Conversely, when sugars were used as substrates an increase in the conversion yields was observed at the higher temperature. Interestingly, the control reaction for D-ribose without DMSO showed lower conversion yields at both 30 °C or 45 °C. The conversion yields of D-ribose with pQR2191 also dropped when MeOH was used instead of DMSO.
Figure S10. Structures of selected sugars. Only the pyranose form is shown (where possible).
IV. Chemical syntheses and preparative scale biocatalytic reactions

**General procedure 1**

Amberlyst 15 (0.5 g/mmol) was added to a solution of hydrazone in water (C = 0.2 mol/L). The reaction was stirred at room temperature for 10 min before filtration on a sinter funnel (porosity 3). The resulting mixture was concentrated under vacuum and the resulting thick oil was lyophilised to afford the hydrate as a white foam.

(2S,3S,4S)-2-(Dihydroxymethyl)tetrahydrofuran-3,4-diol (anti-2a) and (2R,3S,4S)-2-(dihydroxymethyl)tetrahydrofuran-3,4-diol (syn-2a)

The THF-hydrate was obtained following the **General procedure 1** using Amberlyst 15 (7 g) and THF-hydrazone 1a (2.41 g, 13.8 mmol, d.r. = 50:50 (anti:syn)). After lyophilisation, the hydrate was isolated as a very hygroscopic white foam (1.59 g, 77%, d.r. = 80:20 (anti:syn)); $^1$H NMR (600 MHz, D$_2$O) $\tilde{\delta}$ = 5.16 (br d, $J = 7.2$, 1H, CH(OD)$_2$-syn), 5.04 (br d, $J = 4.7$, 1H, CH(OD)$_2$-anti), 4.47 (td, $J = 7.6$, 4.6, 1H, CH$_2$CH$_2$-syn), 4.37 4.26 (m, 2H, CH$_2$CH$_2$-anti, OCH$_2$CHCH$_2$-syn), 4.22 (br t, $J = 6.2$, 5.0, 1H, OCH$_2$CHCH$_2$-anti), 4.05 4.02 (m, 2H, CH/H$_2$-anti, CH/H$_2$-syn), 3.81 (dd, $J = 10.0$, 3.2, 1H, CH/H$_2$-anti), 3.78 (dd, $J = 7.2$, 3.7, 1H, CH(OD)$_2$CH$_2$-syn), 3.74 (dd, $J = 6.2$, 4.7, 1H, CH(OD)$_2$CH$_2$-anti), 3.71 (dd, $J = 8.6$, 7.6, 1H, CH/H$_2$-syn); $^{13}$C{ $^1$H} NMR (150 MHz, D$_2$O with MeOH standard) $\tilde{\delta}$ = 89.9 (CH(OD)$_2$-anti), 88.7 (CH(OD)$_2$-syn), 83.7 (CH(OD)$_2$CH$_2$-anti), 82.7 (CH(OD)$_2$CH$_2$-syn), 72.4 (OCH$_2$CH$_2$-anti), 72.2 (OCH$_2$-anti), 71.3 (OCH$_2$CHCH$_2$-anti), 71.3 (OCH$_2$CHCH$_2$-syn), 71.0 (OCH$_2$CH$_2$-syn), 70.3 (OCH$_2$-syn). Data in agreement with that previously reported.$^{[11]}$
(2R,3R,4R)-2-(Dihydroxymethyl)tetrahydrofuran-3,4-diol (anti-2b) and (2S,3R,4R)-2-(dihydroxymethyl)tetrahydrofuran-3,4-diol (syn-2b)

The THF-hydrate was obtained following the General procedure 1 using Amberlyst 15 (7 g) and THF-hydrazone 1b (2.22 g, 12.7 mmol, d.r. = 80:20 (anti: syn)). After lyophilisation, the hydrate 2b was isolated as a hygroscopic white foam (1.54 g, 79%, d.r. = 90:10 (anti: syn)). ¹H NMR (600 MHz, D₂O)  δ = 5.09 (br d, J = 7.3, 1H, CH(OD)₂-syn), 4.97 (d, J = 4.8, 1H, CH(OD)₂-anti), 4.42 (td, J = 7.4, 4.6, 1H, OCH₂CH₃), 4.24 ± 4.20 (m, 2H, OCH₂CH₃syn, CH₂CHCH₃syn), 3.94 (2H, m, CH₂CHCH₃), 4.00 ± 3.94 (2H, m, CHH₂OCH₃, CHH₂OCH₃), 3.75 (dd, J = 10.0, 3.2, 1H, CHH₂OCH₃), 3.72 (dd, J = 7.3, 3.7, 1H, CH(OD)₂CH₃), 3.68 (dd, J = 6.1, 4.8, 1H, CH(OD)₂CH₃), 3.66 ± 3.61 (m, 1H, CHH₂OCH₃); ¹³C {¹H} NMR δ = (150 MHz, D₂O) 90.4 (CH(OD)₂-anti), 89.2 (CH(OD)₂-syn), 84.1 (CH(OD)₂CH₃), 83.3 (CH(OD)₂CH₃), 73.0 (OCH₂CH₃), 72.7 (OCH₂CH₃), 71.9 (CH₂CHCH₃), 71.8 (CH₂CHCH₃), 71.5 (OCH₂CH₃), 70.7 (OCH₂-syn); Characterization data was the same as for 2a.

(2S,3S,4R)-2-(Dihydroxymethyl)tetrahydrofuran-3,4-diol (anti-2c) and (2R,3S,4R)-2-(dihydroxymethyl)tetrahydrofuran-3,4-diol (syn-2c)

The THF-hydrate was obtained following the General procedure 1 using Amberlyst 15 (7 g) and THF-hydrazone 1c (2.12 g, 12.1 mmol, d.r. = 55:45 (anti: syn)). After lyophilisation, the hydrate 2e was isolated as a hygroscopic white foam (1.66 g, 91%, d.r. = 60:40 (anti: syn)). ¹H NMR (600 MHz, D₂O)  δ = 5.07 (br d, J = 7.5, 1H, CH(OD)₂-syn), 5.00 (d, J = 6.5, 1H, CH(OD)₂-anti), 4.26 (br d, J = 4.0, 1H, OCH₂CH₃), 4.19 ± 4.17 (m, 1H, OCH₂CH₃), 4.16 (br d, J = 4.0, 1H, CH₂CHCH₃), 4.15 ± 4.11 (m, 2H, CH₂CHCH₃, OCHH₂OCH₃), 3.97 (dd, J = 10.2, 4.0, 1H,
OCH\textsubscript{H}H\textsubscript{anti}), 3.86\textsubscript{1} 3.81 (m, 2H, OCH\textsubscript{H}'\textsubscript{anti}, CH(OD)\textsubscript{2}CH\textsubscript{syn}), 3.73 (br d, \(J = 10.2, 1H, OCH\textsubscript{H}H\textsubscript{syn}), 3.62 (dd, \(J = 6.5, 3.0, 1H, CH(OD)\textsubscript{2}CH\textsubscript{anti})); \(^{13}\)C\{\(^{1}H\)\} NMR (150 MHz, D\textsubscript{2}O with MeOH standard)

\[ \bar{\delta} = 89.6 \ (CH(OD)\textsubscript{2}antii), 88.6 \ (CH(OD)\textsubscript{2}syn), 87.7 \ (CH(OD)\textsubscript{2}CH\textsubscript{anti}), 82.1 \ (CH(OD)\textsubscript{2}CH\textsubscript{syn}), 78.1 \ (OCH\textsubscript{2}CHCH\textsubscript{anti}), 76.9 \ (CH\textsubscript{2}CH\textsubscript{anti}), 76.6 \ (CH\textsubscript{2}CH\textsubscript{syn}), 75.9 \ (OCH\textsubscript{2}CHCH\textsubscript{syn}), 73.4 \ (OCH\textsubscript{2}syn), 73.2 \ (OCH\textsubscript{2}ani); FT-IR (ATR) \text{v/cm}^{-1} = 3324 \text{ br,} 2934, 1421; HRMS (ES-) found [M-H\textsubscript{2}O+Cl]^{-} 167.0112; C\textsubscript{8}H\textsubscript{8}O\textsubscript{3}Cl requires 167.0111.

\((2R,3R,4R,5S)-2-(Dihydroxymethyl)-5-methyltetrahydrofuran-3,4-diol \ (anti-2d) \ and \ (2S,3R,4R,5S)-2-(dihydroxymethyl)-5-methyltetrahydrofuran-3,4-diol \ (syn-2d)\)

The THF-hydrate was obtained following the **General procedure 1** using Amberlyst 15 (13 g) and the THF-hydrazone 1d (5.00 g, 26.6 mmol, d.r. = 60:40 (anti:syn)). After lyophilisation, the THF-hydrate was isolated as a hygroscopic white foam (3.23 g, 81%, d.r. = 70:30 (anti:syn)). \(^{1}\)H NMR (600 MHz, D\textsubscript{2}O) \(\bar{\delta} = 5.10 \) (br d, \(J = 7.2, 1H, CH(OD)\textsubscript{2}syn), 5.02 (d, \(J = 5.6, 1H, CH(OD)\textsubscript{2}anti)), 4.12\textsubscript{1} 4.09 (m, 2H, CH\textsubscript{2}CHCH\textsubscript{syn}, CH(OD)\textsubscript{2}CH\textsubscript{anti}), 3.89 (app. quint, \(J = 6.4, 1H, CH\textsubscript{3}CH\textsubscript{anti}), 3.84\textsubscript{1} 3.78 (m, 2H, CH\textsubscript{3}CH\textsubscript{syn}, CH(OD)\textsubscript{2}CHCH\textsubscript{syn}), 3.78\textsubscript{1} 3.72 (m, 2H, CH\textsubscript{3}CHCH\textsubscript{anti}, CH(OD)\textsubscript{2}CH\textsubscript{syn}), 3.67 (app. t, \(J = 5.7, 1H, CH(OD)\textsubscript{2}CHCH\textsubscript{anti}), 1.31 (d, \(J = 6.3, 3H, CH\textsubscript{3}CH\textsubscript{syn}), 1.24 (d, \(J = 6.4, 3H, CH\textsubscript{3}CH\textsubscript{anti}); \(^{13}\)C\{\(^{1}H\)\} NMR (150 MHz, D\textsubscript{2}O with MeOH standard) \(\bar{\delta} = 89.9 \) (CH(OD)\textsubscript{2}anti), 88.6 (CH(OD)\textsubscript{2}syn), 84.0 (CH(OD)\textsubscript{2}CH\textsubscript{anti}), 82.9 (CH(OD)\textsubscript{2}CH\textsubscript{syn}, 81.9 (CH\textsubscript{3}CHCH\textsubscript{anti}, 81.7 (OCH\textsubscript{3}syn), 78.8 (CH\textsubscript{3}CH\textsubscript{syn}), 77.7 (CH(OD)\textsubscript{2}CHCH\textsubscript{anti}), 77.5 (CH\textsubscript{3}CHCH\textsubscript{syn}, 18.5 (CH\textsubscript{3}syn), 17.7 (CH\textsubscript{3}anti); FT-IR (ATR) \text{v/cm}^{-1} = 3319\text{ br,} 2926\text{s,} 1448\text{m}; HRMS (ES+) found [M+Na]^{+} 187.0585; C\textsubscript{8}H\textsubscript{12}O\textsubscript{3}Na requires 187.0582.
Boc-amines 4a-d synthesis. Compounds 4a-d were prepared following the General procedure 2.

**General procedure 2**

THF-hydrazone (1 eq.) was dissolved in a mixture of iPrOH:H₂O (2:1, c = 0.05 mol/L). The solution was degassed with 3 vacuum/argon cycles before the addition of di-tert-butyl dicarbonate (2.5 eq.) and Pd(OH)₂ (20% on carbon, 0.02 eq.). The resulting mixture was then degassed with 3 vacuum/hydrogen cycles before hydrogen was bubbled for 5 minutes directly into the solution. The reaction was stirred under hydrogen atmosphere (1 atm.) at room temperature for 24 h before filtration through a pad of Celite. The filtrate was then concentrated under reduced pressure and the crude residue was purified by flash column chromatography using a gradient of petroleum ether 40-60:acetone (1:0 to 1:1) to give the Boc-amine.

**tert-Butyl (((2R,3S,4S)-3,4-dihydroxytetrahydrofuran-2-yl)methyl)carbamate (anti-4a)**

The protected amine was obtained by following **General procedure 2** using the THF-hydrazone *anti*-1a (250 mg, 1.44 mmo), di-tert-butyl dicarbonate (0.84 mL, 3.59 mmol) and Pd(OH)₂ (20% on carbon; 200 mg, 0.29 mmol) in a mixture of iPrOH:H₂O (3 mL). After purification by column chromatography, the product was isolated as a colourless oil (125 mg, 38%, *anti* only); [α] +34 (c 0.9, MeOH), lit [α] +32 (c 1.0, MeOH),[12] ¹H NMR (600 MHz, CDCl₃) 5.01 (s, 1H, NH), 4.24 (br s, 1H, OCH₂CH), 4.10 (dd, J = 10.1, 4.8, 1H, OCH₂H), 3.91/ 3.82 (m, 1H, NCH₂CHCH), 3.81/ 3.75 (m, 2H, OCHH', NCH₂CH), 3.43/ 3.32 (m, 1H, NCH₂), 3.11 (s, 2H, OH), 2.01 (s, 2H, OH), 1.41 (s, 9H, 3 x CH₃); ¹³C¹H NMR (151 MHz, CDCl₃) 157.0 (C=O), 80.6 (NCH₂CH), 80.1 (C(CH₃)), 73.2 (OCH₂), 73.0 (NCH₂CHCH), 71.2 (OCH₂CH), 41.9 (NCH₂), 28.5 (CH₃) ppm;
FT-IR (ATR) $\nu$/cm$^{-1}$ = 3339, 2975, 2931, 1682, 1520; HRMS (CI) calcd for C$_{10}$H$_{20}$NO$_{5}$ [M+H]$^+$ 234.1336 found 234.1336.

tert-Butyl (((2S,3R,4R)-3,4-dihydroxytetrahydrofuran-2-yl)methyl)carbamate (anti-4b)

The protected amine was obtained by following General procedure 2 using the THF-hydrazone anti-1b (50 mg, 0.29 mmol), di-tert-butyl dicarbonate (165 µL, 0.72 mmol) and Pd(OH)$_2$ (20% on carbon, 40 mg, 0.06 mmol) in a mixture of iPrOH:H$_2$O (2 mL). After purification by column chromatography, the product was isolated as a colourless oil (41 mg, 61%, anti only); $\delta$ -28 (c 0.8, MeOH); $^1$H NMR (600 MHz, CDCl$_3$) 5.18 (br s, 1H, NH), 4.21 (br td, 1H, OCH$_2$CH$_2$), 4.10 (dd, $J$ = 10.1, 4.8, 1H, OCHH$_{\text{anti}}$), 3.86–3.80 (m, 1H, NCH$_2$CHCH$_2$), 3.79–3.74 (m, 2H, OCHH$_{\text{syn}}$, NCH$_2$CH$_2$), 3.66 (br s, 2H, 2 x OH), 3.45–3.25 (m, 1H, NCH$_2$), 1.41 (s, 9H, 3 x CH$_3$); $^{13}$C[$^1$H] NMR (151 MHz, CDCl$_3$) 157.0 (C=O), 80.6 (NCH$_2$CH), 80.1 (C(CH$_3$)), 73.2 (OCH$_2$), 73.0 (NCH$_2$CHCH$_2$), 71.2 (OCH$_2$CH), 41.9 (NCH$_2$), 28.5 (CH$_3$) ppm; FT-IR (ATR) $\nu$/cm$^{-1}$ = 3339, 2975, 2932, 1682, 1520; HRMS (CI) calcd for C$_{10}$H$_{20}$NO$_{5}$ [M+H]$^+$ 234.1336, found 234.1335.

tert-Butyl (((2R,3S,4R)-3,4-dihydroxytetrahydrofuran-2-yl)methyl)carbamate (anti-4c) and tert-butyl (((2S,3S,4R)-3,4-dihydroxytetrahydrofuran-2-yl)methyl)carbamate (syn-4c)

The protected amine was obtained by following General procedure 2 using the THF-hydrazone 1c (250 mg, 1.44 mmol, d.r. = 55:45 (anti:syn)), di-tert-butyl dicarbonate (0.84 mL, 3.59 mmol) and Pd(OH)$_2$ (20% on carbon, 200 mg, 0.29 mmol) in a mixture of iPrOH:H$_2$O (3 mL). After purification by column chromatography, the product was isolated as a colourless oil (142 mg, 42%, d.r. = 55:45 (anti:syn)); $^1$H NMR (600 MHz, CDCl$_3$) $\tilde{\delta}$ = 5.15 (br s, 1H, NH$_{\text{anti}}$), 5.07 (br s, 1H, NH$_{\text{syn}}$), 4.80 (s, 1H, OH$_{\text{syn}}$), 4.34 (br s, 1H, OCH$_2$CH$_{\text{syn}}$), 4.24 (br s, 1H, OCH$_2$CH$_{\text{anti}}$), 4.19 (dd, $J$ = 9.8, 4.1, 1H, OCHH$_{\text{syn}}$), 4.05–4.01 (m, 1H, OCHH$_{\text{anti}}$), 3.97–3.90 (m, 1H, NCH$_2$CHCH$_{\text{syn}}$), 3.79–3.76 (m, 3H, NCH$_2$CH), 3.05–3.01 (m, 1H, NCH$_2$CHCH$_{\text{anti}}$), 2.88–2.85 (m, 1H, NCH$_2$CHCH$_{\text{syn}}$), 2.48–2.42 (m, 1H, NCH$_2$CH), 2.27–2.21 (m, 1H, NCH$_2$CH), 1.39–1.32 (s, 9H, 3 x CH$_3$).
3.90i 3.84 (m, 2H, NCH$_2$CH$_{syn}$, NCH$_2$CHCH$_{anti}$), 3.82 (br d, J = 9.7, 1H, OCH$_2$H$_{anti}$), 3.74 (br d, J = 9.8, 1H, NCH$_2$CH$_{anti}$), 3.70 (br d, J = 9.8, 1H, OCHH$_{syn}$), 3.65i 3.53 (m, 1H, NCH$_2$H$_{syn}$), 3.45i 3.35 (m, 2H, NCH$_2$-anti), 3.30 (brs, 1H, OH$_{anti}$), 3.16 (dt, J = 14.3, 4.7, 1H, NCHH$_{syn}$), 2.67 (br s, 1H, OH$_{anti}$), 1.96 (br s, 1H, OH$_{syn}$), 1.43 (s, 18H, C(CH$_3$)$_3$-anti, C(CH$_3$)$_3$-syn; $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$) $\ddot{u}$ = 157.7 (C=O)$_{syn}$, 157.1 (C=O)$_{anti}$, 84.0 (NCH$_2$CH$_{anti}$), 80.86 (NCH$_2$CHCH$_{anti}$), 80.83 (C(CH$_3$)$_3$), 80.2 (C(CH$_3$)$_3$), 79.4 (NCH$_2$CH$_{syn}$), 77.7 (OCH$_2$CH$_{anti}$), 77.3 (OCH$_2$CH$_{syn}$ with CDCl$_3$), 76.3 (NCH$_2$CHCH$_{syn}$), 73.9 (OCH$_2$-syn), 73.1 (OCH$_2$-anti), 42.1 (NCH$_2$-anti), 38.6 (NCH$_2$-syn), 28.5 (C(CH$_3$)$_3$-anti), 28.4 (C(CH$_3$)$_3$-syn) ppm; FT-IR (ATR) $\nu$/cm$^{-1}$ = 3332, 2976, 2932, 1679, 1522; HRMS (CI) calcd for C$_{10}$H$_{20}$NO$_3$ [M+H]$^+$ 234.1336 found 234.1334.

**tert-Butyl-(((2R,3R,4R,5S)-3,4-dihydroxy-5-methyltetrahydrofuran-2-yl)methyl)carbamate (anti-4d) and tert-butyl-(((2S,3R,4R,5S)-3,4-dihydroxy-5-methyltetrahydrofuran-2-yl)methyl)carbamate (syn-4d)**

The protected amine was obtained by following General procedure 2 using the THF-hydrazone 1d (290 mg, 1.50 mmol, d.r. = 60:40 (anti:syn)), di-tert-butyl dicarbonate (0.88 mL, 3.85 mmol) and Pd(OH)$_2$ (20% on carbon, 215 mg, 0.3 mmol) in a mixture of iPrOH:H$_2$O (3 mL). After purification by column chromatography, the product was isolated as a colourless oil (117 mg, 30%, d.r. = 60:40 (anti:syn)); $^1$H NMR (600 MHz, CD$_3$OD) $\ddot{u}$ = 3.95i 3.91 (m, 1H, NCH$_2$CHCH$_{syn}$), 3.91i 3.86 (m, 1H, NCH$_2$CH$_{syn}$), 3.85i 3.76 (m, 3H, CH$_3$CH$_{anti}$, CH$_2$CHCH$_{anti}$, NCH$_2$H$_{anti}$), 3.72i 3.66 (m, 2H, CH$_3$CH$_{syn}$, CH$_2$CHCH$_{syn}$), 3.64 (br t, J = 7.6, 1H, NCH$_2$CH$_{anti}$), 3.39 (dd, J = 14.1, 6.4, 1H, NCHH$_{syn}$), 3.29i 3.20 (m, 2H, NCH$_2$-anti), 3.16 (dd, J = 14.0, 6.3, 1H, NCHH$_{anti}$), 1.44 (s, 18H, C(CH$_3$)$_3$-syn, C(CH$_3$)$_3$-anti), 1.28 (d, J = 6.4, 3H, CH$_3$-syn), 1.26 (d, J = 6.3, 3H, CH$_3$-anti); $^{13}$C{$^1$H} NMR (151 MHz, CD$_3$OD) $\ddot{u}$ = 158.9 (CO$_{syn}$), 158.6 (CO$_{anti}$), 84.6 (CH$_3$CH$_{syn}$ or CH$_3$CHCH$_{syn}$), 84.1 (NCH$_2$CHCH$_{anti}$), 82.9 (NCH$_2$CH$_{anti}$ or CH$_3$CHCH$_{anti}$), 82.4 (CH$_3$CH$_{syn}$ or CH$_3$CHCH$_{syn}$), 81.3 (NCH$_2$CH$_{syn}$), 80.4 (NCH$_2$CH$_{anti}$ or CH$_3$CHCH$_{anti}$), 80.3 (C(CH$_3$)$_3$); 80.1 (C(CH$_3$)$_3$), 79.9 (CH$_3$CH$_{anti}$), 79.3 (NCH$_2$CHCH$_{syn}$), 43.5 (NCH$_2$-anti), 40.7 (NCH$_2$-syn), 28.73
Amines 3a-d synthesis. Compounds 3a-d were prepared following the General procedure 3.

General procedure 3

The protected amine was dissolved in a solution of HCl in MeOH (0.5 M) and heated at 40 °C for 4 hours. The reaction mixture was then evaporated to dryness. The residue was washed with Et<sub>2</sub>O and dried under high vacuum to give the ammonium salt.

(2R,3S,4S)-2-(Aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (3a)

The amine hydrochloride salt was obtained by following the General procedure 3 using the Boc-amine anti-4a (179 mg, 0.77 mmol, 1 eq.) and HCl in MeOH (4.6 mL, C = 0.5 mol/L, 2.30 mmol, 3 eq.). After evaporation of the volatiles under vacuum the amine salt was obtained as a white solid (129 mg, quant. anti only); mp = 173 - 175 °C (dec.); [α]<sub>D</sub> + 55 (c 0.4, MeOH); <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD) δ = 4.17 (m, 1H, OCH<sub>2</sub>CH), 4.10 (dd, J = 9.9, 4.4, 1H, OCH/H); 3.93 (m, 2H, NCH<sub>2</sub>CH, NCH<sub>2</sub>CHCH<sub>2</sub>), 3.78 (dd, J = 9.9, 2.3, 1H, OCH/H); 3.21 (dd, J = 13.0, 2.9, 1H, NCH/H); 2.96 (dd, J = 13.0, 8.7, 1H, NCH/H); <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>OD) δ = 78.7 (NCH<sub>2</sub>CH), 75.3 (NCH<sub>2</sub>CHCH), 74.6 (OCH<sub>2</sub>), 72.3 (OCH<sub>2</sub>CH), 43.2 (NCH<sub>2</sub>) ppm; FT-IR (ATR) ν/cm<sup>−1</sup> = 3444, 3233, 3142, 3000, 2941, 2884, 1586, 1515, 1474, 1458; HRMS (ESI) calcd for C<sub>5</sub>H<sub>12</sub>NO<sub>3</sub> [M-Cl]<sup>+</sup> 134.0812, found 134.0811.
(2S,3R,4R)-2-(Aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (3b)

\[ \text{HCl}_2N\]

\[ \text{O} \]

\[ \text{H}\]

\[ \text{OH} \]

\[ \text{OH} \]

The amine hydrochloride salt was obtained by following the General procedure 3 using the Boc-amine anti-4b (179 mg, 0.77 mmol) and HCl in MeOH (4.6 mL, c = 0.5 mol/L, 2.30 mmol). After evaporation of the volatiles under vacuum the amine salt was obtained as a colourless oil (109 mg, Quant., anti only); mp = 175 - 176 °C (dec.); \[ \text{H} \] 49 (c 0.5, MeOH), lit \[ \text{H} \] 57 (c 1.56, H₂O)[11]; ¹H NMR (600 MHz, CD₃OD) \( \tilde{\delta} = 4.17 i 4.13 \) (m, 1H, OCH₂CH), 4.10 (dd, \( J = 9.9, 4.6, 1H, OCH'H \)), 3.91i 3.88 (m, 1H, NCH₂CH), 3.85 (dd, \( J = 7.7, 4.8, 1H, NCH₂CHCH \)), 3.78 (dd, \( J = 9.9, 2.4, 1H, OCH'H' \)) 3.22 (dd, \( J = 13.0, 2.9, 1H, NCH'H \)), 2.97 (dd, \( J = 13.0, 8.7, 1H, NCH'H' \)); ¹³C[¹H] NMR (151 MHz, CD₃OD) \( \tilde{\delta} = 78.7 \) (NCH₂CH), 75.3 (NCH₂CHCH), 74.6 (OCH₂), 72.3 (OCH₂CH), 43.2 (NCH₂); FT-IR (ATR) \( \nu/cm^{-1} = 3445, 3234, 3144, 2999, 2940, 2913; 1587, 1515 \); HRMS (CI) calc for C₈H₁₃NO₃ [M-Cl]⁺ 134.0812 found 134.0811.

(2R,3S,4R)-2-(Aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (anti-3c) and (2S,3S,4R)-2-(aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (syn-3c)

\[ \text{HCl}_2N\]

\[ \text{O} \]

\[ \text{H}\]

\[ \text{OH} \]

\[ \text{OH} \]

The amine hydrochloride salt was obtained by following the General procedure 3 using the Boc-amine 4c (152 mg, 0.65 mmol, 1 eq., d.r. = 59:41 (anti:syn)) and HCl in MeOH (4.0 mL, C = 0.5 mol/L, 1.95 mmol, 3 eq.). After evaporation of the volatiles under vacuum the amine salt was obtained as a colourless oil (109 mg, Quant., d.r. = 59:41 (anti:syn)); ¹H NMR (600 MHz, CD₃OD) \( \tilde{\delta} = 4.20 i 4.17 \) (m, 1H, OCH₂CH₃), 4.17i 4.10 (m, 4H, OCH₂CH₃, OCHH₃, NCH₂CH₃, NCH₂CHCH₃), 4.02 (dd, \( J = 9.7, 3.6, 1H, OCHH'₃ \)), 3.97i 3.91 (m, 2H, NCH₂CH₃, NCH₂CHCH₃), 3.89 (d, \( J = 9.7, 1H, OCHH'₃ \)), 3.72 (d, \( J = 8.7, 1H, OCHH₃ \)), 3.21 (br d, \( J = 4.7, 2H, NCH₂₃ \)), 3.15 (d, \( J = 5.8, 2H, NCH₂₂ \)); ¹³C[¹H] NMR (151 MHz, CD₃OD) \( \tilde{\delta} = 83.3 \).
(NCH₂CH₃), 80.7 (NCH₂CHCH₃), 79.0 (CH₃), 78.6 (CH₃), 78.2 (OCH₂CH₃), 77.1 (CH₃), 75.6 (OCH₂CH₃), 74.9 (OCH₂CH₃), 42.7 (NCH₂CH₃), 40.5 (NCH₂CH₃) ppm. FT-IR (ATR) v/cm⁻¹ = 3246, 2921, 1605, 1501, 1456; HRMS (ESI) calcd for C₅H₁₂NO₃ [M·Cl]⁺ 134.0812 found 134.0812.

(2R,3R,4R,5S)-2-(Aminomethyl)-5-methyltetrahydrofuran-3,4-diol hydrochloride (anti-3d) and (2S,3R,4R,5S)-2-(aminomethyl)-5-methyltetrahydrofuran-3,4-diol hydrochloride (syn-3d)

The amine hydrochloride salt was obtained by following the General procedure 3 using the Boc-amine 4d (120 mg, 0.48 mmol, d.r. = 60:40 (anti:syn)) and HCl in MeOH (3.0 mL, c = 0.5 mol/L, 1.45 mmol). After evaporation of the volatiles under vacuum the amine salt was obtained as a colourless oil (86 mg, 96%, antisy:n = 63:37); ¹H NMR (600 MHz, CD₃OD) û = 4.13 (m, 1H, NCH₂CH₃), 4.09 (dd, J = 4.4, 2.0, 1H, NCH₂CHCH₃), 3.99 (td, J = 8.7, 4.4, 1H, NCH₂CH₃), 3.95 (br quint, J = 12.2, 1H, CH₃CH₃), 3.86 (m, 1H, NCH₂CHCH₃), 3.83 (m, 1H, CH₃CH₃), 3.75 (m, 1H, CH₃CHCH₃), 3.72 (dd, J = 3.8, 2.1, 1H, CH₃CHCH₃), 3.24 (m, 2H, NCH₂CH₃), 3.16 (m, 2H, NCH₂CH₃), 1.34 (m, 3H, CH₃), 1.32 (m, 3H, CH₃); ¹³C{¹H} NMR (151 MHz, CD₃OD) û = 84.7 (OCH₂CH₃), 83.6 (OCH₂CH₃), 82.9 (CH₃CH₃), 81.4 (CH₃CH₃), 80.8 (NCH₂CH₃), 80.3 (NCH₂CH₃), 77.3 (NCH₂CH₃), 42.7 (NCH₂CH₃), 40.6 (NCH₂CH₃), 19.5 (CH₃), 19.2 (CH₃) ppm; FT-IR (ATR) v/cm⁻¹ = 3238, 2969, 2920, 1605, 1493, 1451; HRMS (ESI) calcd for C₅H₁₂NO₃ [M·Cl]⁺ 148.0968 found 148.0968.
General procedure 4: Preparative scale biocatalytic reactions on substrates 2a-d

The enzymatic reactions were performed using a total volume of 20 mL or 40 mL, containing IPA (250 mM) as amine donor, and the aldehydes 2a-d (50 mM, 1 mmol or 2 mmol) as amine acceptor, PLP (2 mM), potassium phosphate buffer pH 8.0 (50 mM), clarified cell lysate of Cv-TAm or Rh-TAm (1.5 or 3 ml) at 37 °C and 250 rpm for 24 h in a falcon tube. The reaction mixture was basified with NaOH to pH 12 and centrifuged. The supernatant was freeze dried to remove water and excess IPA and the yellow residue dissolved in methanol to prepare the Boc-amine following the General procedure 3. Boc₂O (1.2 equiv.) was added at room temperature and the reaction mixture was stirred for 24 h. Methanol was removed under reduced pressure and the residue dissolved in EtOAc and filtered through celite. After evaporation to dryness, a pale yellow oil corresponding to the Boc-derived compound was obtained and further purified with silica column chromatography with a gradient of petroleum ether 40-60:acetone (1:0 to 1:1). The Boc deprotection was carried out in MeOH-HCl 0.5 M at 40 °C.

(2R,3S,4S)-2-(Aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (anti-3a) and (2S,3S,4S)-2-(aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (syn-3a)

The aldehyde 2a (300 mg, 2.00 mmol) was subjected to the General procedure 4 using Rh-TAm (3 mL) in a total volume of 40 mL, quenched with NaOH and the denatured protein removed by centrifugation. The supernatant was freeze dried and the residue dissolved in MeOH (8 mL). To this solution was added Boc₂O (550 mg, 2.4 mmol) and the reaction was stirred at room temperature for 24 h. After work up as described in the General procedure 3 the purification by column chromatography afforded compound 4a as a pale yellow oil (330 mg, 71%, anti:syn
90:10). An aliquot (200 mg, 0.86 mmol) was deprotected in MeOH-HCl (0.5 M, 6 mL) for 16 h, and the solvent removed under reduced pressure to give the 2-(aminomethyl)tetrahydrofuran-3,4-diol hydrochloride 3a (145 mg, quant., anti:syn 90:10). The characterisation data for the anti isomer was identical to 3a synthesised above.

(2S,3R,4R)-2-(Aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (anti-3b) and (2R,3R,4R)-2-(aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (syn-3b)

The aldehyde 2b (150 mg, 1.00 mmol) was subjected to the General procedure 4 using Cv-TAm (1.5 mL) in a total volume of 20 mL, quenched with NaOH and the denatured protein removed by centrifugation. The supernatant was freeze dried and the residue dissolved in MeOH (2 mL). To this solution was added Boc₂O (275 mg, 1.2 mmol) and the reaction was stirred at room temperature for 24 h. After work up as described in the general procedure the purification by column chromatography afforded compound 4b as a clear oil (177 mg, 76%, anti:syn 90:10). This was deprotected in MeOH-HCl (0.5 M, 3 mL) for 16 h, and the solvent removed under reduced pressure to give the 2-(aminomethyl)tetrahydrofuran-3,4-diol hydrochloride 3b (127 mg, quant, anti:syn 90:10). The characterisation data for the anti isomer was identical to 3b synthesised above.

(2R,3S,4R)-2-(Aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (anti-3c) and (2S,3S,4R)-2-(aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (syn-3c)

The aldehyde 2c (150 mg, 1.00 mmol) was subjected to the General procedure 4 using Rh-TAm (1.5 mL) in a total volume of 20 mL, quenched with NaOH and the denatured protein removed by centrifugation. The supernatant was freeze dried and the residue dissolved in MeOH (2 mL). To this solution was added Boc₂O (275 mg, 1.2 mmol) and the reaction was stirred at room temperature for 24 h. After work up as described in the general procedure the purification by column chromatography afforded compound 4c as a colourless oil (160 mg, 69%, anti:syn 55:45). An
aliquot (100 mg, 0.43 mmol) was deprotected in MeOH-HCl (0.5 M, 3 mL) for 16 h, and the solvent removed under reduced pressure to give the 2-(aminomethyl)tetrahydrofuran-3,4-diol hydrochloride 3e (72 mg, quant, anti:syn 60:40). The characterisation data was identical to 3e synthesised above.

2R,3R,4R,5S)-2-(Aminomethyl)-5-methyltetrahydrofuran-3,4-diol hydrochloride (anti-3d) and (2S,3R,4R,5S)-2-(aminomethyl)-5-methyltetrahydrofuran-3,4-diol hydrochloride (syn-3d)

The aldehyde 2d (328 mg, 2.00 mmol) was subjected to the General procedure 4 using Rh-TAm (3 mL) in a total volume of 40 mL, quenched with NaOH and the denatured protein removed by centrifugation. The supernatant was freeze dried and the residue dissolved in MeOH (8 mL). To this solution was added Boc₂O (550 mg, 2.4 mmol) and the reaction was stirred at room temperature for 24 h. After work up as described in the general procedure the purification by column chromatography afforded compound 4d as a colourless oil (290 mg, 58%, anti:syn 70:30). This was deprotected in MeOH-HCl (0.5 M, 8 mL) for 16 h, and the solvent removed under reduced pressure to give the 2-(aminomethyl)-5-methyltetrahydrofuran-3,4-diol hydrochloride 3d (213 mg, quant, anti:syn 70:30). The characterisation data was identical to 3d synthesised above.

General procedure 5: Preparative scale biocatalytic reactions on aldose sugar substrates (L-arabinose and D-xylene) with IPA

The enzymatic reactions were performed using a total volume of 30 mL, containing IPA (250 mM) as amine donor, sugar substrate (25 mM, 0.75 mmol), PLP (2 mM), potassium phosphate buffer pH 8.0 (50 mM), clarified cell lysate of Rh-TAm (2 mL) at 30 °C and 250 rpm. After 4 h, another aliquot of clarified cell lysate of Rh-TAm (2 mL) was added together with 5 mg of PLP. After 48 h the reaction mixture was quenched with MeOH and centrifuged (10 min, 4000 rpm).
supernatant was basified to pH 12 with NaOH and concentrated to remove excess IPA. The yellow residue was redissolved in water (50 mL, pH adjusted to 8.0), loaded on to a Dowex 50WX8 ion-exchange resin, and washed several times with water (100 mL) to remove excess salt. The amine product was then eluted with 28% aq NH$_3$ (60 mL) and the eluent was concentrated under reduced pressure. The off-white residue obtained was resuspended in 1 M HCl and concentrated to dryness to give the amine salt as a single isomer.

1-Amino-1-deoxy-L-arabinitol hydrochloride (7)

L-arabinose was subjected to the General Procedure 5 and 1-amino-1-deoxy-L-arabinitol hydrochloride 7 was obtained as a solid (58.6 mg, 42%); $^1$H NMR (700 MHz, D$_2$O) $\tilde{\delta}$ = 4.22 (td, $J$ = 6.5, 1.8, 1H, CH$_2$N), 3.89 (dd, $J$ = 11.9, 2.9, 1H, CH/O), 3.80 (ddd, $J$ = 8.9, 6.0, 2.9, 1H, CHCH$_2$O), 3.72 (dd, $J$ = 11.9, 6.0, 1H, CH/CHOH), 3.60 (dd, $J$ = 8.9, 1.8, 1H, CHCHCH), 3.24 (d, $J$ = 6.5, 1H, CH/HN); $^{13}$C NMR (176 MHz, D$_2$O with MeOH standard) $\tilde{\delta}$ = 71.3 (CHCH$_2$OH), 70.7 (CHCHCH), 66.5 (CHCH$_2$N), 62.9 (CH$_2$OH), 42.7 (CH$_2$N) ppm; Mp 126 ± 2 °C (with decomposition); HRMS (ESI+) calcd for C$_5$H$_{14}$NO$_4$ [M+H]$^+$ 152.0917 found 152.0914. Characterisation data was in agreement with the literature.$^{[13]}$

1-Amino-1-deoxy-D-xylitol hydrochloride (8)

D-xylose was subjected to the General Procedure 5 and 1-amino-1-deoxy-D-xylitol hydrochloride 8 was obtained as a solid (95% purity by $^1$H NMR - NH$_4$Cl present) (117.5 mg, 79%). A batch of material was re-purified with the Dowex resin to give the hydrochloric salt for further NMR analysis; $^1$H NMR (700 MHz, D$_2$O) $\tilde{\delta}$ = 4.09 (dt, $J$ = 9.3, 3.5, 1H, CHCH$_2$N), 3.88 (ddd, $J$ = 11.9, 2.9, 1H, CHCH$_2$O), 3.78 (dd, $J$ = 11.9, 4.3, 1H, CH/OH), 3.73 $\tilde{\delta}$ 3.69 (m, 2H,
CH3OH and CH2CH3), 3.29 (dd, J = 13.1, 3.2, 1H, CH2N), 3.21 (dd, J = 13.1, 9.3, 1H, CH2N); 13C NMR (176 MHz, D2O with MeOH standard) ǚ = 71.6 (CH2OH and CH2CH), 67.9 (CH2N), 62.5 (CH2OH), 42.1 (CH2N) ppm; Mp 110 ± 2 °C (with decomposition), HRMS (ESI+) calcd for C5H14NO4 [M+H]+ 152.0917 found 152.0914.

Preparative scale biocatalytic reactions for D-fructose with IPA to give the 2-amino-2-deoxy-D-mannitol hydrochloride (9)

The enzymatic reaction was performed using a total volume of 30 mL, containing IPA (250 mM) as amine donor, and D-fructose (25 mM, 0.75 mmol), PLP (2 mM), potassium phosphate buffer pH 8.0 (50 mM), clarified cell lysate of Mt-TAm (3.6 mL) at 45 °C and 250 rpm for 48 h. The reaction mixture was quenched with MeOH and centrifuged (10 min, 4000 rpm). The supernatant was basified to pH 12 with NaOH and concentrated to remove excess IPA. The yellow residue was redissolved in water (50 mL, pH adjusted to 8.0), loaded on to a Dowex 50WX8 ion-exchange resin, and washed several times with water (100 mL) to remove excess salt. The amine product was then eluted with 28% aq NH3 (60 mL) and the eluent was concentrated under reduced pressure. The off-white residue obtained was resuspended in 1 M HCl and concentrated to dryness to give the amine salt as a single isomer (67 mg, 40%); 1H NMR (600 MHz, D2O) ǚ = 4.21 (dd, J = 5.0, 1.8, 1H, CH2N), 4.01 (dd, J = 12.3, 4.5, 1H, CH2CHN), 3.86 (dd, J = 12.3, 3.0, 1H, CH2CHN), 3.84 (dd, J = 12.0, 1.8, 1H, CH2CHOH), 3.79 (ddd, J = 8.5, 6.0, 3.0, 1H, CH2CH2OH), 3.69 (dd, J = 12.0, 6.0, 1H, CH2CHOH), 3.68 (dd, J = 8.5, 1.8, 1H, CH2CH2OH), 3.64–3.54 (m, 1H, CHN); 13C NMR (151 MHz, D2O with MeOH standard) ǚ = 71.0 (CH2OH), 70.6 (CH2CH2OH), 66.9 (CH2N), 63.0 (CH2CHOH), 58.7 (CH2N), 56.1 (CHN) ppm; HRMS (ESI+) calcd for C6H16NO5 [M-Cl]+ 182.1028 found 182.1027. Characterisation data was in agreement with the literature.[14]
Preparative scale biocatalytic reactions for D-fructose with IPA to give the 2-amino-2-deoxy-D-glucitol hydrochloride (epi-9)

The enzymatic reaction was performed using a total volume of 30 mL, containing IPA (250 mM) as amine donor, and D-fructose (25 mM, 0.75 mmol), PLP (2 mM), potassium phosphate buffer pH 8.0 (50 mM), 25% v/v DMSO, clarified cell lysate of the enzyme cloned from pQR2191 (3.6 mL) at 45 °C and 250 rpm for 48 h. The reaction mixture was quenched with MeOH and centrifuged (10 min, 4000 rpm). The supernatant was basified to pH 12 with NaOH and concentrated to remove excess IPA. The yellow residue was redissolved in water (50 mL, pH adjusted to 8.0), loaded on to a Dowex 50WX8 ion-exchange resin, and washed several times with water (100 mL) to remove excess salt. The amine product was then eluted with 28% aq NH₃ (60 mL) and the eluent was concentrated under reduced pressure. The off-white residue obtained was resuspended in 1 M HCl and concentrated to dryness to give the amine salt as a single isomer (31.8 mg, 21%); 'H NMR (600 MHz, D₂O) δ = 4.10 (dd, J = 6.7, 1.3, 1H, CH/CHN), 3.88 (dd, J = 12.0, 4.2, 1H, CH/CHN), 3.84 (dd, J = 12.0, 2.8, 1H, CH/CHOH), 3.77 (dd, J = 12.0, 6.6, 1H, CH/CHN), 3.76 (dd, J = 9.0, 1.2, 1H, CH/CH₂OH), 3.67 (dd, J = 12.0, 6.0, 1H, CH/CHOH), 3.64 (dd, J = 8.5, 1.8, 1H, CH/CHCH₂OH), 3.56~3.50 (m, 1H, CH/N); ¹³C NMR (151 MHz, D₂O with MeOH standard) δ = 70.9 (CHCH₂OH), 70.6 (CHCHCH₂OH), 66.1 (CHCHN), 62.9 (CH₂CHOH), 59.0 (CH₂CHN), 55.5 (CHN) ppm; HRMS (ES+) calcd for C₆H₁₆NO₅ [M-Cl]+ 182.1028 found 182.1027.
V. NMR spectra

(2S,3S,4S)-2-(Dihydroxymethyl)tetrahydrofuran-3,4-diol (anti-2a) and (2R,3S,4S)-2-(dihydroxymethyl)tetrahydrofuran-3,4-diol (syn-2a)
(2R,3R,4R)-2-(Dihydroxymethyl)tetrahydrofuran-3,4-diol (anti-2b) and (2S,3R,4R)-2-(dihydroxymethyl)tetrahydrofuran-3,4-diol (syn-2b)
(2S,3S,4R)-2-(Dihydroxymethyl)tetrahydrofuran-3,4-diol \textit{(anti-2c)} and (2R,3S,4R)-2-(dihydroxymethyl)tetrahydrofuran-3,4-diol \textit{(syn-2c)}

[Diagram of molecular structures]

\[ f_1 \text{ (ppm)} \]

\[ 2LB117-W \]
(2R,3R,4R,5S)-2-[(Dihydroxymethyl)-5-methyltetrahydrofuran-3,4-diol \(\text{anti-2d}\) and \(\text{syn-2d}\)]
tert-Butyl (((2R,3S,4S)-3,4-dihydroxytetrahydrofuran-2-yl)methyl)carbamate (4a)

BocCHN

HO

HO
*tert*-Butyl ((2S,3R,4R)-3,4-dihydroxytetrahydrofuran-2-yl)methyl carbamate (4b)
tert-Butyl (((2R,3S,4R)-3,4-dihydroxytetrahydrofuran-2-yl)methyl)carbamate (anti-4c) and tert-butyl (((2S,3S,4R)-3,4-dihydroxytetrahydrofuran-2-yl)methyl)carbamate (syn-4c)
tert-Butyl-(((2R,3R,4R,5S)-3,4-dihydroxy-5-methyltetrahydrofuran-2-yl)methyl)carbamate (anti-4d) and tert-butyl-(((2S,3R,4R,5S)-3,4-dihydroxy-5-methyltetrahydrofuran-2-yl)methyl)carbamate (syn-4d)
(2R,3S,4S)-2-(Aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (3a)
(2S,3R,4R)-2-(Aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (3b)
(2R,3S,4R)-2-(Aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (anti-3c) and (2S,3S,4R)-2-(aminomethyl)tetrahydrofuran-3,4-diol hydrochloride (syn-3c)
(2R,3R,4R,5S)-2-(Aminomethyl)-5-methyltetrahydrofuran-3,4-diol hydrochloride (anti-3d) and (2S,3R,4R,5S)-2-(aminomethyl)-5-methyltetrahydrofuran-3,4-diol hydrochloride (syn-3d)
1-Amino-1-deoxy-L-arabinitol hydrochloride\textsuperscript{(13)} (7)
1-Amino-1-deoxy-D-xylitol hydrochloride (8)
1-Amino-1-deoxy-D-xylitol hydrochloride (8)
with NH₄Cl removed (¹H NMR, 400 MHz)
2-Amino-2-deoxy-D-mannitol hydrochloride (9)
2-Amino-2-deoxy-\text{-}D\text{-}glucitol hydrochloride (\textit{epi-9})
VI. References

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