Inverted regioselectivity of C–H amination: Unexpected oxidation at β- rather than γ-C–H

Filip J. Wyszynski, Amber L. Thompson and Benjamin G. Davis*

Department of Chemistry, University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, Oxford, UK, OX1 3TA

ben.davis@chem.ox.ac.uk

1. General Procedures S2
2. Synthesis of compounds **1**, **3** and **5** – **13** S3
3. Crystal data and structure refinement for compound **1** S12
4. References S17

1. General considerations

Proton nuclear magnetic resonance (δ_H) spectra were recorded on a Bruker DPX 200 (200 MHz), Bruker DPX 400 (400 MHz), Bruker DQX 400 (400 MHz) or Bruker AC 500 (500 MHz) spectrometer. Carbon nuclear magnetic resonance spectra were recorded on a Bruker DPX 200 (50 MHz), Bruker DQX 400 (100 MHz) spectrometer or on a Bruker AC 500 (125 MHz) with a ^{13}C cryoprobe (125 MHz). Spectra were fully assigned using a combination of ^{1}H, ^{13}C, COSY, HMQC, HMBC and DEPT 135. All chemical shifts were quoted on the δ- scale in ppm using residual solvent as the internal standard. Coupling constants (*J*) are reported in hertz (Hz).

Melting points were recorded on a Kofler hot block and are uncorrected. Infrared spectra were recorded on a Bruker Tensor 27 Fourier Transform spectrophotometer with absorption maxima recorded in wavenumbers (cm^{-1}). Specific rotations were measured on a Perkin Elmer 241 polarimeter with a pathlength of 1 dm with concentrations (*c*) given in g/100 mL and are reported with implied units of 10^{-1} deg cm^2 g^{-1}.

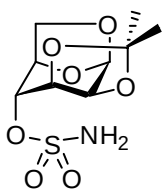
Low resolution mass spectra were recorded on an LCT Premier XE using electrospray ionization (ES). High resolution mass spectra were recorded by Dr. Robin Procter on a Bruker micrOTOF.

Thin layer chromatography (TLC) was carried out on Merk Kieselgel $60F_{254}$ precoated aluminium backed plates and visualized with a combination of the following: 254 nm UV lamp, aqueous $KMnO_4$ (5% $KMnO_4$ in 1 M NaOH), aqueous phosphomolybdic acid and Ce(IV) (2.5% phosphomolybdic acid hydrate, 1% cerium(IV) sulfate hydrate, and 6% H_2SO_4), ammonium molybdate (5% in 2M H_2SO_4), and/or sulfuric acid (2 M in ethanol/water 1:1).

Flash column chromatography was carried out with Fluka Kiegselgel 60 220-440 mesh silica gel. THF and DCM was dried through a column of Al_2CO_3. Remaining anhydrous solvents were purchased from Aldrich or Fluka and stored over molecular sieves (<0.005% H_2O). All other solvents were used as supplied (analytical or HPLC grade), without further purification. Distilled water was used for chemical reactions. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. Brine refers to a saturated solution of sodium chloride.

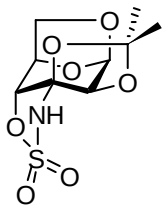
2. Synthesis of compounds 1, 3 and 5 – 13

1,6-Anhydro-2,3-*O*-isopropylidene-4-*O*-sulfamoyl-β-D-mannopyranose 1



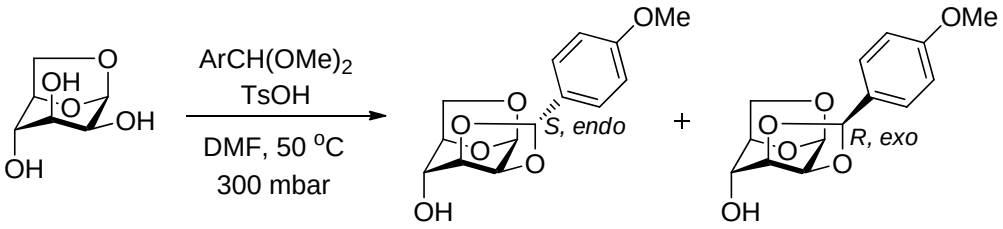
A flame dried flask was charged with DCM (2 mL) and cooled to 0 °C. Chlorosulfonyl isocyanate (700 μL, 8.15 mmol) was added, followed by dropwise addition of formic acid (300 μL, 8.15 mmol), which resulted in the formation of a white precipitate. After stirring for 17 h, the flask was cooled to -10 °C in a MeOH/ice bath. 1,6-Anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose[1] (659 mg, 3.25 mmol) was dissolved in dry DMA (2 mL) and transferred *via* cannula to the reaction flask. After 1 h, triethylamine (1.36 mL, 9.75 mmol) was added, upon which a heavy cream precipitate formed in the clear yellow solution. After stirring at room temperature for 1 h TLC (EtOAc/Petrol 1:1) showed a single product at R_f 0.5. The solvent was removed *in vacuo* and the residue dry loaded onto silica from MeOH. Flash chromatography (EtOAc/Petrol gradient elution: 9:11→1:0), afforded 1,6-anhydro-2,3-*O*-isopropylidene-4-*O*-sulfamoyl-β-D-mannopyranose **1** (730 mg, 2.60 mmol, 80%) as colourless crystals; Crystal Structure: The X-ray crystal structure of **1** was solved by Dr. Amber Thompson at the Oxford University Chemical Crystallography Laboratory. Crystal data and structural parameters can be found in section 3; $[\alpha]_D^{18}$ = -49, *c* = 2, MeOH; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.33, 1.55 (2 × s, 2 × 3 H, 2 × -C*H*$_3$), 3.78 (dd, $J_{6a,6b}$ = 7.4 Hz, $J_{6a,5}$ = 6.3 Hz, 1 H, H-6a), 4.05 (dd, $J_{6b,6a}$ = 7.4 Hz, $J_{6b,5}$ = 1.3 Hz, 1 H, H-6b), 4.07 (dd, $J_{2,3}$ = 6.3 Hz, $J_{2,1}$ = 2.8 Hz, 1 H, H-2), 4.19 (d, $J_{3,2}$ = 6.3 Hz, 1 H, H-3), 4.62 (dd, $J_{5,6a}$ = 6.3 Hz, $J_{5,6b}$ = 1.3 Hz, 1 H, H-5), 4.89 (br. s., 2 H, -N*H*$_2$), 4.95 (s, 1 H, H-4), 5.38 (d, $J_{1,2}$ = 2.8 Hz, 1 H, H-1); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 25.8, 25.9 (2 × -C(*C*H$_3$)$_2$), 64.5 (C-6), 71.6 (C-4), 72.1 (C-2), 73.5 (C-5), 73.8 (C-3), 99.2 (C-1), 110.2 (-*C*(CH$_3$)$_2$); IR (thin film) *v* : 3264 (br, N-H), 3268 (br, N-H), 2980 (m), 2360 (s), 2341 (m), 1373 (s, -SO_2NH_2), 1185 (s, -SO_2NH_2) cm^{-1}; MS *m/z* (ESI$^-$) : 280 [(M-H)$^-$, 100%], 316 [(M+^{35}Br)$^-$, 70%], 318 [(M+^{37}Br)$^-$, 40%]; HRMS *m/z* (ESI$^+$) : calc. for $C_9H_{13}NNaO_7S$ (M + Na)$^+$ = 302.0305. Found 302.0299;

3-Amino-1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose 3,4-sulfamidate 3



Powdered magnesium oxide (9.0 mg, 0.213 mmol) was flame dried under reduced pressure (1 mbar). 1,6-Anhydro-2,3-*O*-isopropylidene-4-*O*-sulfamoyl-β-D-mannopyranose **1** (26.0 mg, 0.093 mmol) was dissolved in dry THF (4 mL) and added *via* cannula. Iodobenzene diacetate (33 mg, 0.100 mmol) and Rh(II) acetate dimer (1.6 mg, 4 μmol, 0.04 eq) were added. After stirring the pale blue solution at room temperature for 5 h under N_2, TLC (acetone/toluene 1:4) showed spots at R_f 0.45 (product) and 0.3 (starting material). The reaction mixture was filtered through celite and washed with THF. Flash chromatography (acetone/toluene gradient: 1:9→1:4), afforded 3-amino-1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose 3,4-sulfamidate **3** (14 mg, 0.050 mmol, 54%) as a white amorphous solid which decomposed upon storage. Starting material was also recovered (12 mg, 0.042 mmol, 46%); $[\alpha]_D^{21}$ = -57, *c* = 0.7, MeOH; ^{1}H NMR (400 MHz, MeOD) δ ppm 1.47, 1.51 (2 x s, 2 x 3 H, 2 x -CH_3), 3.83 (dd, $J_{6a,6b}$ = 8.1 Hz, $J_{6a,5}$ = 6.3 Hz, 1 H, H-6a), 3.92 (dd, $J_{6b,6a}$ = 8.1 Hz, $J_{6b,5}$ = 1.3 Hz, 1 H, H-6b), 4.21 (d, $J_{2,1}$ = 3.5 Hz, 1 H, H-2), 4.74 (d, $J_{4,5}$ = 0.8 Hz, 1 H, H-4), 4.86 (ddd, $J_{5,6a}$ = 6.3 Hz, $J_{5,6b}$ = 1.3 Hz, $J_{5,4}$ = 0.8 Hz, 1 H, H-5), 5.46 (d, $J_{1,2}$ = 3.5 Hz, 1 H, H-1); ^{13}C NMR (100 MHz, MeOD) δ ppm 26.1, 26.6 (2 x -C(*C*H_3)$_2$), 65.0 (C-6), 72.3 (C-5), 80.3 (C-2), 83.4 (C-4), 92.5 (C-3, quaternary C by lack of signal in HSQC and DEPT, coupled to H-1, H-2, H-4, H-5 by HMBC), 98.4 (C-1), 113.6 (-*C*(CH$_3$)$_2$); IR (thin film) *v* : 3262 (br, N-H), 2970 (m), 2300 (s), 2321 (m) cm^{-1}; MS *m/z* (ESI$^-$) : 278 [(M-H)$^-$]; HRMS *m/z* (ESI$^+$) : calc. for $C_9H_{15}NNaO_7S$ (M + Na)$^+$ = 304.0461. Found 304.0462;

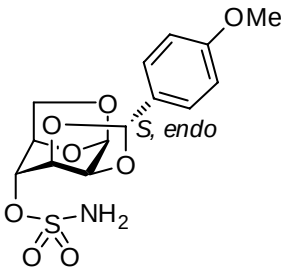
4-Methoxybenzylidene protection of 1,6-anhydro-β-D-mannopyranose[2, 3]



1,6-Anhydro-D-mannose (707 mg, 4.36 mmol) was dissolved in dry DMF (5 mL). *p*-Toluenesulfonic acid (12 mg, 0.088 mmol) and 4-methoxybenzaldehyde dimethyl acetal (720 μL, 4.78 mmol) were added. After stirring for 4 h at 50 °C under reduced pressure (300 mbar), TLC (EtOAc/Petrol 4:1) showed spots at R_f 0.7 (4-methoxybenzaldehyde derivatives) and R_f 0.4 (product). Triethylamine (1 mL) was added and the solvent removed *in vacuo*. Flash chromatography (EtOAc/Petrol 1:1), afforded 1,6-anhydro-2,3-*O*-(4-methoxybenzylidene)-β-D-mannopyranose (1.01 g, 3.92 mmol, 90%) as a mixture of 4-methoxybenzylidene isomers (*endo*/*exo* 2.3:1). This white solid was recrystallised

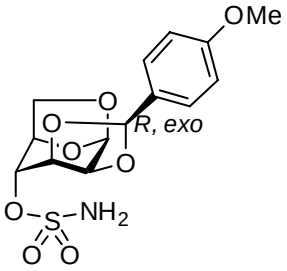
from acetone and petroleum ether to yield 1,6-anhydro-2,3-*O*-*endo*-(4-methoxybenzylidene)-β-D-mannopyranose (373 mg, 1.29 mmol, 31%) as white crystals. The orange mother liquor contained 1,6-anhydro-2,3-*O*-(4-methoxybenzylidene)-β-D-mannopyranose (630 mg, 2.63 mmol, 59%) as an *exo*-enriched mixture of 4-methoxybenzylidene isomers (*endo*/*exo* 1:2);

1,6-Anhydro-*endo*-2,3-*O*-(4-methoxybenzylidene)-4-*O*-sulfamoyl-β-D-mannopyranose 5



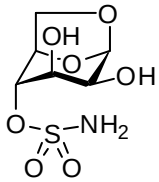
A flame dried flask was charged with DCM (5 mL) and cooled to 0 °C. Chlorosulfonyl isocyanate (326 μL, 2.68 mmol) was added, followed by dropwise addition of formic acid (100 μL, 2.68 mmol), which resulted in the formation of a white precipitate. After stirring for 16 h, the flask was cooled to -10 °C in a MeOH/ice bath. 1,6-Anhydro-*endo*-2,3-*O*-(4-methoxybenzylidene)-β-D-mannopyranose (300 mg, 1.07 mmol) was dissolved in dry DCM (10 mL) and triethylamine (750 μL, 5.35 mmol), and transferred *via* cannula to the reaction flask. After 1 h stirring at room temperature under N_2, TLC (EtOAc/Petrol 3:1) showed a single product at R_f 0.5. Triethylamine was added until the solution was no longer acidic. The solvent was removed *in vacuo* and the residue dry loaded onto silica from MeOH. Flash chromatography (EtOAc/Petrol gradient elution: 1:1→6:4) afforded 1,6-anhydro-*endo*-2,3-*O*-(4-methoxybenzylidene)-4-*O*-sulfamoyl-β-D-mannopyranose **5** (292 mg, 0.81 mmol, 76%) as a white amorphous solid; $[\alpha]_D^{18}$ = -26, *c* = 1, MeOH; ^{1}H NMR (400 MHz, MeOD) δ ppm 3.79 (s, 3 H, -OC*H*$_3$), 3.80 (dd, $J_{6b,6a}$ = 7.6 Hz, $J_{6b,5}$ = 6.6 Hz, 1 H, H-6b), 4.03 (dd, $J_{6a,6b}$ = 7.6 Hz, $J_{6a,5}$ = 1.3 Hz, 1 H, H-6a), 4.15 (dd, $J_{2,3}$ = 6.8 Hz, $J_{2,1}$ = 3.0 Hz, 1 H, H-2), 4.38 (app. dq, $J_{3,2}$ = 6.8 Hz, $J_{3,4}$ = 1.0 Hz, $^4J_{3,5}$ = 1.0 Hz, $^4J_{3,1}$ = 0.8 Hz, 1 H, H-3), 4.77 (app. t, $J_{4,5}$ = 1.0 Hz, $J_{4,3}$ = 1.0 Hz, 1 H, H-4), 4.79 (app. dq, $J_{5,6b}$ = 6.6 Hz, $J_{5,6a}$ = 1.3 Hz, $J_{5,4}$ = 1.0 Hz, $^4J_{5,3}$ = 1.0 Hz, 1 H, H-5), 5.44 (dd, $J_{1,2}$ = 3.0 Hz, $^4J_{1,3}$ = 0.8 Hz, 1 H, H-1), 5.71 (s, 1 H, ArC*H*-), 6.91 (d, *J* = 8.6 Hz, 2 x 1H, 2 x Ar-*H*), 7.59 (d, *J* = 8.6 Hz, 2 x 1H, 2 x Ar-*H*); ^{13}C NMR (100 MHz, MeOD) δ ppm 55.7 (-O*C*H$_3$), 65.3 (C-6), 72.4 (C-2), 75.2 (C-5), 77.2 (C-3), 77.3 (C-4), 100.1 (C-1), 105.6 (Ar*C*H-), 114.4 (2 C, 2 x Ar-*C*H), 129.7 (Ar-*C*), 130.3 (2 C, 2 x Ar-*C*H), 162.2 (Ar-*C*); IR (thin film) *v* : 3288 (br, N-H), 3272 (br, N-H), 2955 (s), 2930 (s), 2897 (s), 2858 (s), 1718 (s, C=C^{Ar}) 1363 (s, -SO_2NH_2), 1256 (s), 1185 (s, -SO_2NH_2) cm^{-1}; MS *m/z* (ESI$^-$) : 358 [(M-H)$^-$, 100%], 717 [(2M-H)$^-$, 80%]; HRMS *m/z* (ESI$^-$) : calc. for $C_{14}H_{16}NO_8S$ (M - H)$^-$ = 358.0602. Found 358.0603;

Exo-enriched 1,6-anhydro-2,3-_O_-(4-methoxybenzylidene)-4-_O_-sulfamoyl-β-D-mannopyranose 6



A flame dried flask was charged with DCM (10 mL) and cooled to 0 °C. Chlorosulfonyl isocyanate (684 μL, 5.62 mmol) was added, followed by dropwise addition of formic acid (212 μL, 5.62 mmol) which resulted in the formation of a white precipitate. After stirring for 16 h, the flask was cooled to -10 ºC in a MeOH/ice bath. An *exo*-enriched isomeric mixture of 1,6-anhydro-2,3-*O*-(4-methoxybenzylidene)-β-D-mannopyranose (630 mg, 2.25 mmol) was dissolved in dry DCM (10 mL) and triethylamine (1.57 mL, 11.25 mmol), and transferred via cannula to the reaction flask. After 2 h stirring at room temperature under N_2, TLC (EtOAc/Petrol 3:1) showed spots at R_f 0.5 (product) and R_f 0 ($Et_3NHOOCH$ salts). Triethylamine was added until the solution was no longer acidic. The solvent was removed *in vacuo* and the residue dry loaded onto silica from MeOH. Flash chromatography (EtOAc/Petrol gradient elution: 1:1→7:3), afforded *exo*-enriched 1,6-anhydro-2,3-*O*-(4-methoxybenzylidene)-4-*O*-sulfamoyl-β-D-mannopyranose **6** (373 mg, 1.04 mmol, 46%) as an orange oil (*endo*/*exo* 1:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 3.81 (s, 3 H, -OC*H*$_3$), 3.84 (dd, $J_{6b,6a}$ = 7.8 Hz, $J_{6b,5}$ = 5.8 Hz, 1 H, H-6b), 4.13 (dd, $J_{6a,6b}$ = 7.8 Hz, $J_{6a,5}$ = 1.0 Hz, 1 H, H-6a), 4.39 (d, $J_{3,2}$ = 6.0 Hz, 2 H, H-3), 4.43 (dd, $J_{2,3}$ = 6.0 Hz, $J_{2,1}$ = 2.7 Hz, 1 H, H-2), 4.82 (m, 2 × 1H, H-4, H-5), 5.57 (d, $J_{1,2}$ = 2.7 Hz, 1 H, H-1), 6.28 (s, 1 H, ArC*H*-), 6.91 (d, *J* = 8.8 Hz, 2 x 1H, 2 x Ar-*H*), 7.33 (d, *J* = 8.8 Hz, 2 x 1H, 2 x Ar-*H*), shifts were assigned from a spectrum of an inseparable mixture of isomers, enriched in the *exo* isomer; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 55.3 (-O*C*H$_3$), 65.0 (C-6), 73.2 (C-2), 73.6 (C-5), 75.4 (C-3), 77.4 (C-4), 99.7 (C-1), 105.5 (Ar*C*H-), 113.9 (2 C, 2 x Ar-*C*H), 127.6 (2 C, 2 x Ar-*C*H), 130.7 (Ar-*C*), 160.4 (Ar-*C*), shifts were assigned from a spectrum of an inseperable mixture of isomers, enriched in the *exo* isomer; MS *m/z* (ESI$^-$) : 358 [(M-H)$^-$, 100%], 717 [(2M-H)$^-$, 80%]; HRMS *m/z* (ESI$^-$) : calc. for $C_{14}H_{16}NO_8S$ (M - H)$^-$ = 358.0602. Found 358.0603;

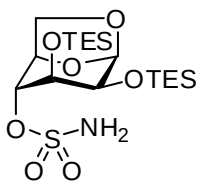
1,6-Anhydro-4-_O_-sulfamoyl-β-D-mannopyranose 7



A mixture of 1,6-anhydro-2,3-*O*-isopropylidene-4-*O*-sulfamoyl-β-D-mannopyranose isomers (754 mg, 2.68 mmol) was dissolved in TFA/H_2O 4:1 (8 mL). After stirring at room temperature for 18 h, TLC (MeOH/EtOAc 1:49) showed a single product at R_f 0.25. Removal of solvent *in vacuo* afforded 1,6-anhydro-4-*O*-sulfamoyl-β-D-mannopyranose **7** (646 mg, 2.68 mmol, 100%) as an off white amorphous solid; $[\alpha]_D^{18}$ = -77, *c* = 0.8, MeOH; ^{1}H NMR (400 MHz, MeOD) δ ppm 3.58 (dd, $J_{2,3}$ = 5.5 Hz, $J_{2,1}$ = 2.0 Hz, 1 H, H-2), 3.70 (dd,

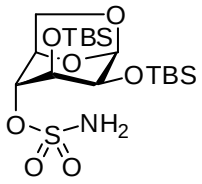
$J_{6b,6a}$ = 7.3 Hz, $J_{6b,5}$ = 6.1 Hz, 1 H, H-6b), 4.06 (app. dq, $J_{3,2}$ = 5.5 Hz, $^4J_{3,5}$ = 1.8 Hz, $J_{3,4}$ = 1.8 Hz, $^4J_{3,1}$ = 1.7 Hz, 1 H, H-3), 4.25 (dd, $J_{6a,6b}$ = 7.3 Hz, $J_{6a,5}$ = 0.8 Hz, 1 H, H-6a), 4.55 (t, $J_{4,5}$ = 1.8 Hz, $J_{4,3}$ = 1.8 Hz, 1 H, H-4), 4.68 (app. ddt, $J_{5,6b}$ = 6.1 Hz, $^4J_{5,3}$ = 1.8 Hz, $J_{5,4}$ = 1.8 Hz, $J_{5,6a}$ = 0.8 Hz, 1 H, H-5), 5.28 (dd, $J_{1,2}$ = 2.0 Hz, $^4J_{1,3}$ = 1.7 Hz, 1 H, H-1); ^{13}C NMR (100 MHz, MeOD) δ ppm 65.7 (C-6), 67.7 (C-2), 70.3 (C-3), 75.5 (C-5), 80.5 (C-4), 103.2 (C-1); IR (thin film) *v* : 3282 (br, N-H, O-H), 1362 (s, -SO_2NH_2), 1181 (s, -SO_2NH_2) cm^{-1}; MS *m/z* (ESI$^-$) : 240 [(M-H)$^-$, 50%], 354 [(M+TFA-H)$^-$, 100%], 481 [(2M-H)$^-$, 80%]; (ESI$^+$) : 305 [(M+MeCN+Na)$^+$, 60%], 505 [(2M+ Na)$^+$, 100%]; HRMS *m/z* (ESI$^-$) : calc. for $C_6H_{10}NO_7S$ (M - H)$^-$ = 240.0183. Found 240.0191;

1,6-Anhydro-2,3-bis-O-(triethylsilyl)-4-O-sulfamoyl-β-D-mannopyranose 8



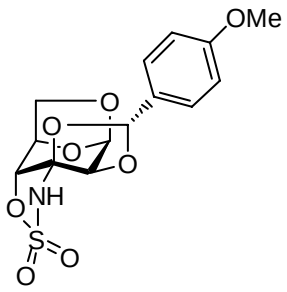
1,6-Anhydro-4-*O*-sulfamoyl-β-D-mannopyranose **7** (51 mg, 0.212 mmol) and imidazole (182 mg, 2.67 mmol) were dissolved in dry DMA (420 μL). Chlorotriethylsilane (300 μL, 1.78 mmol) was then added. After stirring for 18 h at room temperature, TLC (EtOAc/Petrol 1:4) showed a single spot at R_f 0.2 (product). The solution was diluted with H_2O (5 mL). The aqueous layer was extracted with DCM (3 × 5 mL) and the combined organic layers washed with sat. aq. $NaHCO_3$ (5 mL) and brine (5 mL), before being dried over $MgSO_4$. Flash chromatography (EtOAc/Petrol gradient: 3:14→3:7) afforded 1,6-anhydro-2,3-bis-*O*-(triethylsilyl)-4-*O*-sulfamoyl–β-D-mannopyranose **8** (36 mg, 0.077 mmol, 36%) as a white amorphous solid; $[\alpha]_D^{18}$ = -55, *c* = 1.0, MeOH; ^{1}H NMR (400 MHz, MeOD) δ ppm 0.69 (m, 12 H, 6 × -OSiC*H*$_2$CH$_3$), 1.01 (m, 18 H, 6 × -OSiCH$_2$C*H*$_3$), 3.68 (m, 2 H, H-2, H-6b), 4.17 (m, 1 H, H-3), 4.31 (dd, $J_{6a,6b}$ = 7.1 Hz, $J_{6a,5}$ = 0.8 Hz, 1 H, H-6a), 4.47 (app t, $J_{4,3}$ = 2.0 Hz, $J_{4,5}$ = 2.0 Hz, 1 H, H-4), 4.65 (app d, $J_{5,6b}$ = 5.4 Hz, $J_{5,6a}$ = 0.8 Hz, $J_{5,4}$ = 2.0 Hz, 1 H, H-5), 5.22 (dd, $J_{1,2}$ = 1.7, $^4J_{1,3}$ = 1.2 Hz, 1 H, H-1); ^{13}C NMR (100 MHz, MeOD) δ ppm 4.8 (6 × 1C, 6 × -OSi*C*H$_2$CH$_3$), 6.2 (3 × 1C, 3 × -OSiCH$_2$*C*H$_3$), 6.3 (3 × 1C, 3 × -OSiCH$_2$*C*H$_3$), 64.9 (C-6), 69.4 (C-2), 72.1 (C-3), 74.3 (C-5), 80.2 (C-4), 102.7 (C-1); IR (thin film) *v* : 3350 (br, N-H), 3271 (br, N-H), 2955 (s), 2911 (m), 2877 (s), 1373 (s, -SO_2NH_2), 1185 (s, -SO_2NH_2) cm^{-1}; MS *m/z* (ESI$^-$) : 468 [(M-H)$^-$, 100%]; (ESI$^+$) : 487 [(M+NH$_4$)$^+$, 30%], 492 [(M+Na)$^+$, 100%], 533 [(M+MeCN+Na)$^+$, 70%]; HRMS *m/z* (ESI$^-$) : calc. for $C_{18}H_{39}NNaO_7SSi_2$ (M + Na)$^+$ = 492.1878. Found 492.1878;

1,6-Anhydro-2,3-bis-*O*-(*tert*-butyldimethylsilyl)-4-*O*-sulfamoyl–β-D-mannopyranose 9



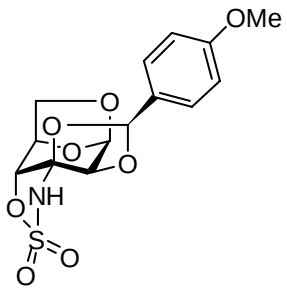
1,6-Anhydro-4-*O*-sulfamoyl-β-D-mannopyranose **7** (48 mg, 0.20 mmol) and imidazole (207 mg, 3.03 mmol) were dissolved in dry DMA (400 µL). *tert*-Butyldimethylchlorosilane (304 mg, 2.02 mmol) was then added. After stirring for 48 h at room temperature, TLC (EtOAc/Petrol 1:4) showed spots at R_f 0.6 (trisilylated product) and 0.2 (disilylated product). The yellow suspension was diluted with water (10 mL), extracted with DCM (3 × 10 mL) and the combined organic layers washed with sat. aq. $NaHCO_3$ (10 mL) and brine (10 mL), before being dried over $MgSO_4$. Flash chromatography (EtOAc/Petrol gradient: 1:4→1:2) afforded 1,6-anhydro-2,3-bis-*O*-(*tert*-butyldimethylsilyl)-4-*O*-(*N*-*tert*-butyldimethylsilyl)sulfamoyl–β-D-mannopyranose (62 mg, 0.105 mmol, 53%) as a white amorphous solid and 1,6-anhydro-2,3-bis-*O*-(*tert*-butyldimethylsilyl)-4-*O*-sulfamoyl–β-D-mannopyranose **9** (10 mg, 0.020 mmol, 10%) as a white amorphous solid. Subsequently, the major trisilylated product (62 mg, 0.105 mmol) was dissolved in TFA/THF/H_2O 1:10:5 (5.4 mL) at 0 °C. After stirring at room temperature for 90 min, TLC (EtOAc/Petrol 3:7) showed a single product at R_f 0.25. Removal of solvent *in vacuo* followed by flash chromatography (EtOAc/Petrol 3:7) afforded further disilylated **9** (39 mg, 0.083 mmol, 79%) as a white amorphous solid, giving a combined yield of 1,6-anhydro-2,3-bis-*O*-(*tert*-butyldimethylsilyl)-4-*O*-sulfamoyl–β-D-mannopyranose of 51% (49 mg, 0.103 mmol) from diol **7**; $[\alpha]_D^{18}$ = -53, *c* = 1.5, $CHCl_3$; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.11, 0.12, 0.13, 0.13 (4 × s, 4 × 3 H, 4 × -OSiC*H*$_3$), 0.92, 0.94 (2 × s, 2 × 9 H, 6 × -CH_3^{tBu}), 3.71 (dd, $J_{2,3}$ = 4.8 Hz, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 3.77 (dd, $J_{6b,6a}$ = 7.3 Hz, $J_{6b,5}$ = 5.9 Hz, 1 H, H-6b), 4.13 (dq, $J_{3,2}$ = 4.8 Hz, $J_{3,4}$ = 1.9 Hz, $^4J_{3,5}$ = 1.8 Hz, $^4J_{3,1}$ = 1.4 Hz, 1 H, H-3), 4.34 (dd, $J_{6a,6b}$ = 7.3 Hz, $J_{6a,5}$ = 1.0 Hz, 1 H, H-6a), 4.53 (td, $J_{4,3}$ = 1.9 Hz, $J_{4,5}$ = 1.0 Hz, 1 H, H-4), 4.69 (app d, $J_{5,6b}$ = 5.9 Hz, $^4J_{5,3}$ = 1.8 Hz, $J_{5,6a}$ = 1.0 Hz, $J_{5,4}$ = 1.0 Hz, 1 H, H-5), 5.04 (s, 2 H, -N*H*$_2$), 5.31 (dd, $J_{1,2}$ = 1.5 Hz, $^4J_{1,3}$ = 1.4 Hz, 1 H, H-1); ^{13}C NMR (100 MHz, CDCl) δ ppm -5.0, -4.8, -4.8, -4.0 (4 × -Si*C*H_3), 18.0, 18.4 (2 × -Si*C*$(CH_3)_3$), 25.8, 26.1 (2 × 3 C, 6 × -SiC($C$$H_3$)$_3$), 64.8 (C-6), 68.9 (C-2), 71.2 (C-3), 73.7 (C-5), 81.2 (C-4), 102.5 (C-1); IR (thin film) *v* : 3290 (br, N-H), 3271 (br, N-H), 2955 (s), 2930 (s), 2897 (s), 2858 (s), 1563 (m), 1472 (m), 1363 (s, -SO_2NH_2) cm^{-1}; MS *m/z* (ESI$^-$) : 468 [(M-H)$^-$, 80%], 582 [(M+TFA-H)$^-$, 100%]; (ESI$^+$) : 487 [(M+NH_4)$^+$, 80%], 492 [(M+Na)$^+$, 100%], 533 [(M+MeCN+Na)$^+$, 90%]; HRMS *m/z* (ESI$^-$) : calc. for $C_{18}H_{38}NO_7SSi_2$ (M - H)$^-$ = 468.1913. Found 468.1910;

3-Amino-1,6-anhydro-2,3-*endo*-*O*-(4-methoxybenzylidene)-β-D-mannopyranose 3,4-sulfamidate 10



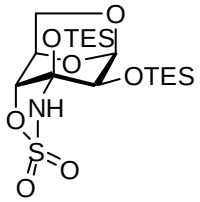
Powdered magnesium oxide (9.0 mg, 0.218 mmol) was flame dried under reduced pressure (1 mbar). 1,6-Anhydro-*endo*-2,3-*O*-(4-methoxybenzylidene)-4-*O*-sulfamoyl-β-D-mannopyranose **5** (34 mg, 0.094 mmol) was dissolved in dry 1,4-dioxane (470 μL) and added *via* syringe. Iodobenzene diacetate (33 mg, 0.103 mmol) and Rh(II) acetate dimer (2.0 mg, 4.7 μmol, 0.05 eq) were added. After stirring the pale blue solution under N_2 at room temperature for 1 h and 45 °C for a further 90 min, TLC (EtOAc/Petrol 1:1) showed a single product at R_f 0.5. The reaction mixture was filtered through celite and washed with 1,4-dioxane, and the filtrate concentrated *in vacuo*. Flash chromatography (EtOAc/Petrol 2:3), afforded 3-amino-1,6-anhydro-2,3-*endo*-*O*-(4-methoxybenzylidene)-β-D-mannopyranose 3,4-sulfamidate **10** (31 mg, 0.087 mmol, 92%) as a white foam which decomposed upon storage; $[\alpha]_D^{21}$ = -41, *c* = 0.5, MeOH; ^{1}H NMR (400 MHz, DMSO-d^6) δ ppm 3.77 (s, 3 H, -OC*H*$_3$), 3.85 (dd, $J_{6b,6a}$ = 8.3 Hz, $J_{6b,5}$ = 6.3 Hz, 1 H, H-6b), 3.92 (dd, $J_{6a,6b}$ = 8.3 Hz, $J_{6a,5}$ = 1.5 Hz, 1 H, H-6a), 4.21 (d, $J_{2,1}$ = 3.8 Hz, 1 H, H-2), 4.95 (d, $J_{4,5}$ = 0.7 Hz, 1 H, H-4), 4.98 (ddd, $J_{5,6b}$ = 6.3 Hz, $J_{5,6a}$ = 1.5 Hz, $J_{5,4}$ = 0.7 Hz, 1 H, H-5), 5.75 (d, $J_{1,2}$ = 3.8 Hz, 1 H, H-1), 5.80 (s, 1 H, ArC*H*-), 6.98 (d, *J* = 8.7 Hz, 2 H, 2 x 1H, 2 x Ar-*H*), 7.54 (d, *J* = 8.7 Hz, 2 H, 2 x 1H, 2 x Ar-*H*), 9.80 (br. s., 1 H, -N*H*); ^{13}C NMR (100 MHz, DMSO-d^6) δ ppm 55.2 (-O*C*H$_3$), 64.8 (C-6), 71.3 (C-5), 77.4 (C-2), 82.4 (C-4), 91.5 (C-3, quaternary C by absence from DEPT, HSQC), 97.1 (C-1), 102.9 (Ar*C*H-), 113.7 (2 C, 2 x Ar-*C*H), 127.1 (Ar-*C*), 129.3 (2 C, 2 x Ar-*C*H), 160.7 (Ar-*C*); IR (thin film) *v* : 3280 (br, N-H), 2965 (s), 2933 (s), 2890 (s), 1713 (s, C=C^{Ar}); MS *m/z* (ESI$^-$) : 356 [(M-H)$^-$, 100%]; HRMS *m/z* (ESI$^-$) : calc. for $C_{14}H_{14}NO_8S$ (M - H)$^-$ = 356.0440. Found 356.0442;

Exo-enriched 3-amino-1,6-anhydro-2,3-_O_-(4-methoxybenzylidene)-β-D-mannopyranose 3,4-sulfamidate 11



Powdered magnesium oxide (14.0 mg, 0.346 mmol) was flame dried under reduced pressure (1 mbar). An *exo*-enriched isomeric mixture (*exo*/*endo* 2:1) of 1,6-anhydro-2,3-*O*-(4-methoxybenzylidene)-4-*O*-sulfamoyl-β-D-mannopyranose (54 mg, 0.150 mmol) was dissolved in dry 1,4-dioxane (750 μL) and added *via* syringe. Iodobenzene diacetate (53 mg, 0.165 mmol) and Rh(II) acetate dimer (3.3 mg, 7.5 μmol, 0.05 eq) were added. After stirring the pale blue solution under N_2 at room temperature for 3 h and 45 °C for a further 2 h, TLC (EtOAc/Petrol 3:2) showed a single product at R_f 0.6 (product). The reaction mixture was filtered through celite and washed with 1,4-dioxane, and the filtrate concentrated *in vacuo*. Flash chromatography (EtOAc/Petrol 1:1), afforded *exo*-enriched 3-amino-1,6-anhydro-2,3-*O*-(4-methoxybenzylidene)-β-D-mannopyranose 3,4-sulfamidate (24 mg, 0.067 mmol, 49%) as a white foam (*exo*/*endo* 2:1); ^{1}H NMR (400 MHz, MeOD-d^4) δ ppm 3.81 (s, 3 H, -OC*H*$_3$), 3.89 (dd, $J_{6b,6a}$ = 8.2 Hz, $J_{6b,5}$ = 4.3 Hz, 1 H, H-6b), 4.10 (dd, $J_{6b,6a}$ = 8.2 Hz, $J_{6b,5}$ = 0.9 Hz, 1 H, H-6a), 4.46 (d, $J_{2,1}$ = 3.0 Hz, 2 H, H-2), 4.96 (m, 3 H, H-4, H-5), 5.65 (d, $J_{1,2}$ = 33.8 Hz, 1 H, H-1), 6.29 (s, 1 H, ArC*H*-), 6.94 (d, *J*=8.8 Hz, 2 H, 2 x 1H, 2 x Ar-*H*), 7.42 (d, *J*=8.8 Hz, 3 H, 2 x 1H, 2 x Ar-*H*), 7.97 (s, 1 H, -N*H*), shifts were assigned from a spectrum of an inseperable mixture of isomers, enriched in the *exo* isomer; ^{13}C NMR (100 MHz, MeOD-d^4) δ ppm 54.8 (-O*C*H$_3$), 65.6 (C-6), 72.4 (C-5), 81.3 (C-2), 83.4 (C-4), 92.1 (C-3, quaternary C by absence from DEPT, HSQC), 99.7 (C-1), 108.1 (Ar*C*H-), 113.7 (2 C, 2 x Ar-*C*H), 128.6 (2 C, 2 x Ar-*C*H), 129.6, 163.9 (2 x 1 C, 2 x Ar-*C*), shifts were assigned from a spectrum of an inseperable mixture of isomers, enriched in the *exo* isomer; MS *m/z* (ESI$^-$) : 356 [(M-H)$^-$, 100%];

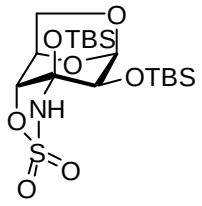
3-Amino-1,6-anhydro-2,3-bis-_O_-(triethylsilyl)-β-D-mannopyranose 3,4-sulfamidate 12



1,6-Anhydro-2,3-bis-*O*-(triethylsilyl)-4-*O*-sulfamoyl–β-D-mannopyranose **8** (36 mg, 0.077 mmol) was dissolved in dry 1,4-dioxane (390 μL). Powdered magnesium oxide was flame dried under reduced pressure (1 mbar) and a sample (7.1 mg, 0.176 mmol) added to the solution. Iodobenzene diacetate (27 mg, 0.085 mmol) and Rh(II) acetate dimer (1.7 mg, 3.9 μmol, 0.05 eq) were added. After stirring the solution under Ar at room temperature for 2 h, the reaction was heated to 45 °C for 3 h, upon which

TLC (EtOAc/Petrol 3:7) showed a product at R_f 0.5, alongside remaining starting material at R_f 0.3. The reaction mixture was concentrated *in vacuo*. Flash chromatography (EtOAc/Petrol gradient: 1:9→3:7) afforded 3-amino-1,6-anhydro-2,3-bis-*O*-(triethylsilyl)-β-D-mannopyranose 3,4-sulfamidate **12** (7 mg, 0.015 mmol, 19%) as a white amorphous solid which decomposed rapidly upon storage. Starting material **8** was also recovered (5 mg, 0.011 mmol, 14%); $[\alpha]_D^{22}$ = -42, *c* = 0.5, $CHCl_3$; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.71 (m, 12 H, 6 × -OSiCH_2CH$_3$), 1.00 (m, 18 H, 6 × -OSiCH$_2$CH_3), 3.88 (dd, $J_{6b,6a}$ = 7.6 Hz, $J_{6b,5}$ = 5.9 Hz, 1 H, H-6b), 3.91 (d, $J_{2,1}$ = 1.5 Hz, 1 H, H-2), 4.14 (dd, $J_{6a,6b}$ = 7.6 Hz, $J_{6a,5}$ = 1.0 Hz, 1 H, H-6a), 4.50 (d, $J_{4,5}$ = 1.8 Hz, 1 H, H-4), 4.80 (m, 2 H, H-5, N-H), 5.34 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 4.9 (3 × 1C, 3 × -OSi*C*H$_2$CH$_3$), 5.9 (3 × 1C, 3 × -OSi*C*H$_2$CH$_3$), 6.7 (3 × 1C, 3 × -OSiCH$_2$*C*H$_3$), 6.9 (3 × 1C, 3 × -OSiCH$_2$*C*H$_3$), 65.3 (C-6), 71.6 (C-5), 75.5 (C-2), 85.5 (C-4), 89.7 (C-3, quaternary C by absence from DEPT, HSQC), 101.5 (C-1); IR (thin film) *v* : 3258 (br, N-H), 2948 (s), 2929 (s), 2891 (s), 2867 (s), 1470 (m); MS *m/z* (ESI$^-$) : 466 [(M-H)$^-$, 100%]; HRMS *m/z* (ESI$^-$) : calc. for $C_{18}H_{36}NO_7SSi$ (M – H)$^-$ = 466.1751. Found 466.1749;

3-Amino-1,6-anhydro-2,3-bis-*O*-(*tert*-butyldimethylsilyl)-β-D-mannopyranose 3,4-sulfamidate 13



Powdered magnesium oxide (4.5 mg, 0.113 mmol) was flame dried under reduced pressure (1 mbar). 1,6-Anhydro-2,3-bis-*O*-(*tert*-butyldimethylsilyl)-4-*O*-sulfamoyl−β-D-mannopyranose **9** (23 mg, 0.049 mmol) was dissolved in dry DCM (245 μL) and added *via* syringe. Iodobenzene diacetate (17 mg, 0.054 mmol) and Rh(II) acetate dimer (1.1 mg, 2.5 μmol, 0.05 eq) were added. After stirring the solution under Ar at room temperature for 4 h, TLC (EtOAc/Petrol 3:7) showed a single product at R_f 0.5 (product). The reaction mixture was concentrated *in vacuo*. Flash chromatography (EtOAc/Petrol gradient: 3:14→3:7) afforded 3-amino-1,6-anhydro-2,3-bis-*O*-(*tert*-butyldimethylsilyl)-β-D-mannopyranose 3,4-sulfamidate **13** (14 mg, 0.03 mmol, 61%) as a clear amorphous solid; $[\alpha]_D^{22}$ = -63, *c* = 0.5, $CHCl_3$; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.18, 0.19, 0.22, 0.26 (4 × s, 4 × 3 H, 4 × -OSiCH_3), 0.92, 0.96 (2 × s, 2 × 9 H, 6 × -CH$_3^{tBu}$), 3.88 (dd, $J_{6b,6a}$ = 7.7 Hz, $J_{6b,5}$ = 5.7 Hz, 1 H, H-6b), 3.93 (d, $J_{2,1}$ = 1.4 Hz, 1 H, H-2), 4.18 (dd, $J_{6a,6b}$ = 7.7, $J_{6a,5}$ = 0.8 Hz, 1 H, H-6a), 4.50 (d, $J_{4,5}$ = 1.5 Hz, 1 H, H-4), 4.81 (ddd, $J_{5,6b}$ = 5.7 Hz, $J_{5,6a}$ = 0.8 Hz, $J_{5,4}$ = 1.5 Hz, 1 H, H-5), 4.85 (s, 1 H, N-H), 5.35 (d, $J_{1,2}$ = 1.4 Hz, 1 H, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm -4.5, -3.9, -3.3, -2.8 (4 × -Si*C*H$_3$), 18.1, 18.3 (2 × -Si*C*(CH$_3$)$_3$), 25.7, 26.0 (2 × 3 C, 6 × -SiC(*C*H$_3$)$_3$), 65.3 (C-6), 71.7 (C-5), 76.1 (C-2), 84.8 (C-4), 89.8 (C-3, quaternary C by absence from DEPT, HSQC), 101.6 (C-1); IR (thin film) *v* : 3273 (br, N-H),

2957 (s), 2933 (s), 2899 (s), 2856 (s), 1560 (m), 1465 (m) cm^{-1}; MS *m/z* (ESI^-) : 466 [$(M-H)^-$, 100%]; HRMS *m/z* (ESI^-) : calc. for $C_{18}H_{36}NO_7SSi_2$ $(M - H)^-$ = 466.1756. Found 466.1745;

3. Crystal data and structure refinement for compound 1

Table S1: Crystal data and structure refinement

Oxford University Chemical Crystallography Laboratory Identification code	5940
Empirical formula	C9 H15 N1 O7 S1
Formula weight	281.29
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P 1
Unit cell dimensions	a = 6.0756(2) Å α = 80.5318(12)°. b = 6.6423(2) Å β = 84.2434(12)°. c = 7.3505(2) Å γ = 89.0269(12)°.
Volume	291.120(15) $Å^3$
Z	1
Density (calculated)	1.604 Mg/m^3
Absorption coefficient	0.306 mm^{-1}
F(000)	148
Crystal size	0.40 × 0.25 × 0.24 mm^3
Theta range for data collection	5.483 to 27.494°
Index ranges	-7<=h<=7, -8<=k<=8, -9<=l<=9
Reflections collected	6964
Independent reflections	2545 [R(int) = 0.034]
Completeness to theta = 26.944°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.93 and 0.86
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2545 / 3 / 170
Goodness-of-fit on F^2	1.0079
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR2 = 0.0567
R indices (all data)	R1 = 0.0238, wR2 = 0.0570
Absolute structure parameter	-0.02(4)
Largest diff. peak and hole	0.20 and -0.24 $e.Å^{-3}$

Table S2: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$).

	x	y	z	U(eq)[a]
S(1)	5470(1)	5488(1)	3347(1)	17
O(2)	6667(2)	6972(2)	2000(2)	25
O(3)	3453(2)	6076(2)	4285(2)	27
N(4)	7041(2)	4484(2)	4857(2)	19
O(5)	4993(2)	3601(2)	2357(2)	16
C(6)	3972(2)	3950(2)	614(2)	15
C(7)	1559(2)	4577(2)	924(2)	16
O(8)	399(2)	2948(2)	2178(2)	17
C(9)	91(2)	1510(2)	985(2)	17
O(10)	-563(2)	2670(2)	-665(2)	19
C(11)	356(3)	4696(2)	-823(2)	19
C(12)	2299(2)	400(2)	696(2)	15
C(13)	4215(2)	1870(2)	-23(2)	14
O(14)	4130(2)	2120(2)	-1991(2)	16
C(15)	3523(2)	161(2)	-2387(2)	17
O(16)	2290(2)	-845(2)	-713(2)	18
C(17)	5585(3)	-1070(2)	-2788(2)	24
C(18)	2047(3)	484(2)	-3941(2)	23

[a] U(eq) is defined as one third of the trace of the orthogonalized Uij tensor;

Table S3 Bond lengths (Å) for **1**

S(1)-O(2)	1.4284(11)	C(11)-H(111)	0.965
S(1)-O(3)	1.4259(11)	C(11)-H(112)	1.003
S(1)-N(4)	1.5921(12)	C(12)-C(13)	1.5276(18)
S(1)-O(5)	1.5930(10)	C(12)-O(16)	1.4277(16)
N(4)-H(41)	0.90(2)	C(12)-H(121)	0.979
N(4)-H(42)	0.87(2)	C(13)-O(14)	1.4350(15)
O(5)-C(6)	1.4622(16)	C(13)-H(131)	0.97
C(6)-C(7)	1.5227(18)	O(14)-C(15)	1.4404(16)
C(6)-C(13)	1.5300(18)	C(15)-O(16)	1.4432(17)
C(6)-H(61)	0.99	C(15)-C(17)	1.515(2)
C(7)-O(8)	1.4438(16)	C(15)-C(18)	1.5081(19)
C(7)-C(11)	1.530(2)	C(17)-H(171)	0.992
C(7)-H(71)	0.979	C(17)-H(172)	0.988
O(8)-C(9)	1.4251(17)	C(17)-H(173)	0.976
C(9)-O(10)	1.4147(16)	C(18)-H(181)	1.007
C(9)-C(12)	1.5327(18)	C(18)-H(182)	0.999
C(9)-H(91)	1.003	C(18)-H(183)	0.985
O(10)-C(11)	1.4483(17)		

Table S4 Bond angles (°) for **1**

O(2)-S(1)-O(3)	118.91(7)	O(10)-C(11)-H(112)	109.9
O(2)-S(1)-N(4)	110.04(7)	H(111)-C(11)-H(112)	112.4
O(3)-S(1)-N(4)	108.49(7)	C(9)-C(12)-C(13)	112.49(11)
O(2)-S(1)-O(5)	107.49(6)	C(9)-C(12)-O(16)	111.96(11)
O(3)-S(1)-O(5)	108.79(6)	C(13)-C(12)-O(16)	103.22(10)
N(4)-S(1)-O(5)	101.75(6)	C(9)-C(12)-H(121)	109
S(1)-N(4)-H(41)	118.4(13)	C(13)-C(12)-H(121)	110.5
S(1)-N(4)-H(42)	109.7(13)	O(16)-C(12)-H(121)	109.5
H(41)-N(4)-H(42)	114.3(18)	C(6)-C(13)-C(12)	114.59(11)
S(1)-O(5)-C(6)	119.67(8)	C(6)-C(13)-O(14)	109.68(10)
O(5)-C(6)-C(7)	111.03(11)	C(12)-C(13)-O(14)	101.99(10)
O(5)-C(6)-C(13)	102.57(10)	C(6)-C(13)-H(131)	110.1
C(7)-C(6)-C(13)	112.05(11)	C(12)-C(13)-H(131)	111.4
O(5)-C(6)-H(61)	108.9	O(14)-C(13)-H(131)	108.7
C(7)-C(6)-H(61)	111.7	C(13)-O(14)-C(15)	106.32(10)
C(13)-C(6)-H(61)	110.1	O(14)-C(15)-O(16)	105.45(10)
C(6)-C(7)-O(8)	108.16(10)	O(14)-C(15)-C(17)	109.85(12)
C(6)-C(7)-C(11)	112.49(12)	O(16)-C(15)-C(17)	109.08(11)
O(8)-C(7)-C(11)	102.51(11)	O(14)-C(15)-C(18)	108.95(11)
C(6)-C(7)-H(71)	110.9	O(16)-C(15)-C(18)	109.48(12)
O(8)-C(7)-H(71)	107.4	C(17)-C(15)-C(18)	113.69(12)
C(11)-C(7)-H(71)	114.7	C(15)-O(16)-C(12)	109.36(10)
C(7)-O(8)-C(9)	102.00(10)	C(15)-C(17)-H(171)	110.1
O(8)-C(9)-O(10)	105.63(10)	C(15)-C(17)-H(172)	110.9
O(8)-C(9)-C(12)	107.19(11)	H(171)-C(17)-H(172)	109
O(10)-C(9)-C(12)	113.24(11)	C(15)-C(17)-H(173)	111.3
O(8)-C(9)-H(91)	107.3	H(171)-C(17)-H(173)	108.3
O(10)-C(9)-H(91)	109.9	H(172)-C(17)-H(173)	107.2
C(12)-C(9)-H(91)	113.1	C(15)-C(18)-H(181)	105.8
C(9)-O(10)-C(11)	107.24(10)	C(15)-C(18)-H(182)	107.2
C(7)-C(11)-O(10)	103.52(11)	H(181)-C(18)-H(182)	110.6
C(7)-C(11)-H(111)	109.3	C(15)-C(18)-H(183)	105.5
O(10)-C(11)-H(111)	109.4	H(181)-C(18)-H(183)	114.2
C(7)-C(11)-H(112)	112	H(182)-C(18)-H(183)	112.8

Table S5 Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	18(1)	17(1)	17(1)	-7(1)	-3(1)	0(1)
O(2)	34(1)	19(1)	23(1)	-1(1)	-6(1)	-8(1)
O(3)	23(1)	34(1)	28(1)	-17(1)	-4(1)	8(1)
N(4)	18(1)	24(1)	16(1)	-6(1)	-3(1)	0(1)
O(5)	18(1)	16(1)	15(1)	-6(1)	-5(1)	-1(1)
C(6)	16(1)	17(1)	14(1)	-4(1)	-4(1)	-2(1)
C(7)	17(1)	15(1)	16(1)	-2(1)	-1(1)	0(1)
O(8)	15(1)	18(1)	17(1)	-3(1)	1(1)	-1(1)
C(9)	16(1)	18(1)	16(1)	-2(1)	-3(1)	-3(1)
O(10)	15(1)	21(1)	22(1)	-1(1)	-7(1)	-2(1)
C(11)	17(1)	18(1)	22(1)	-2(1)	-6(1)	1(1)
C(12)	17(1)	15(1)	14(1)	-3(1)	-2(1)	-3(1)
C(13)	13(1)	17(1)	11(1)	-3(1)	-1(1)	0(1)
O(14)	19(1)	16(1)	13(1)	-4(1)	-2(1)	-3(1)
C(15)	20(1)	16(1)	15(1)	-4(1)	-2(1)	-3(1)
O(16)	24(1)	17(1)	15(1)	-4(1)	-2(1)	-6(1)
C(17)	27(1)	24(1)	22(1)	-9(1)	-1(1)	4(1)
C(18)	27(1)	24(1)	18(1)	-4(1)	-9(1)	-3(1)

Table S6 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(41)	6430(30)	3660(30)	5870(30)	26
H(42)	8220(30)	3980(30)	4310(30)	26
H(61)	4840	4992	-278	18
H(71)	1423	5799	1511	19
H(91)	-1140	575	1602	20
H(111)	-829	5677	-786	23
H(112)	1397	5002	-1982	21
H(121)	2598	-449	1866	17
H(131)	5622	1258	272	15
H(171)	6537	-1153	-1757	36
H(172)	6438	-444	-3953	36
H(173)	5215	-2457	-2928	36
H(181)	776	1344	-3519	35
H(182)	2931	1240	-5057	36
H(183)	1618	-894	-4106	34

Table S7 Hydrogen bonds for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(41)...O(14)#1	0.90(2)	2.13(2)	3.006(2)	163
N(4)-H(42)...O(8)#2	0.87(2)	2.14(2)	2.977(2)	160
C(7)-H(71)...O(3)	0.98	2.52	3.137(2)	121
C(13)-H(131)...O(10)#2	0.97	2.5	3.201(2)	129
C(18)-H(181)...O(10)	1.01	2.47	3.276(2)	137
C(18)-H(182)...O(5)#3	1	2.5	3.492(2)	171

Symmetry transformations used to generate equivalent atoms:
#1: x,y,z+1 #2: x+1,y,z #3: x,y,z-1

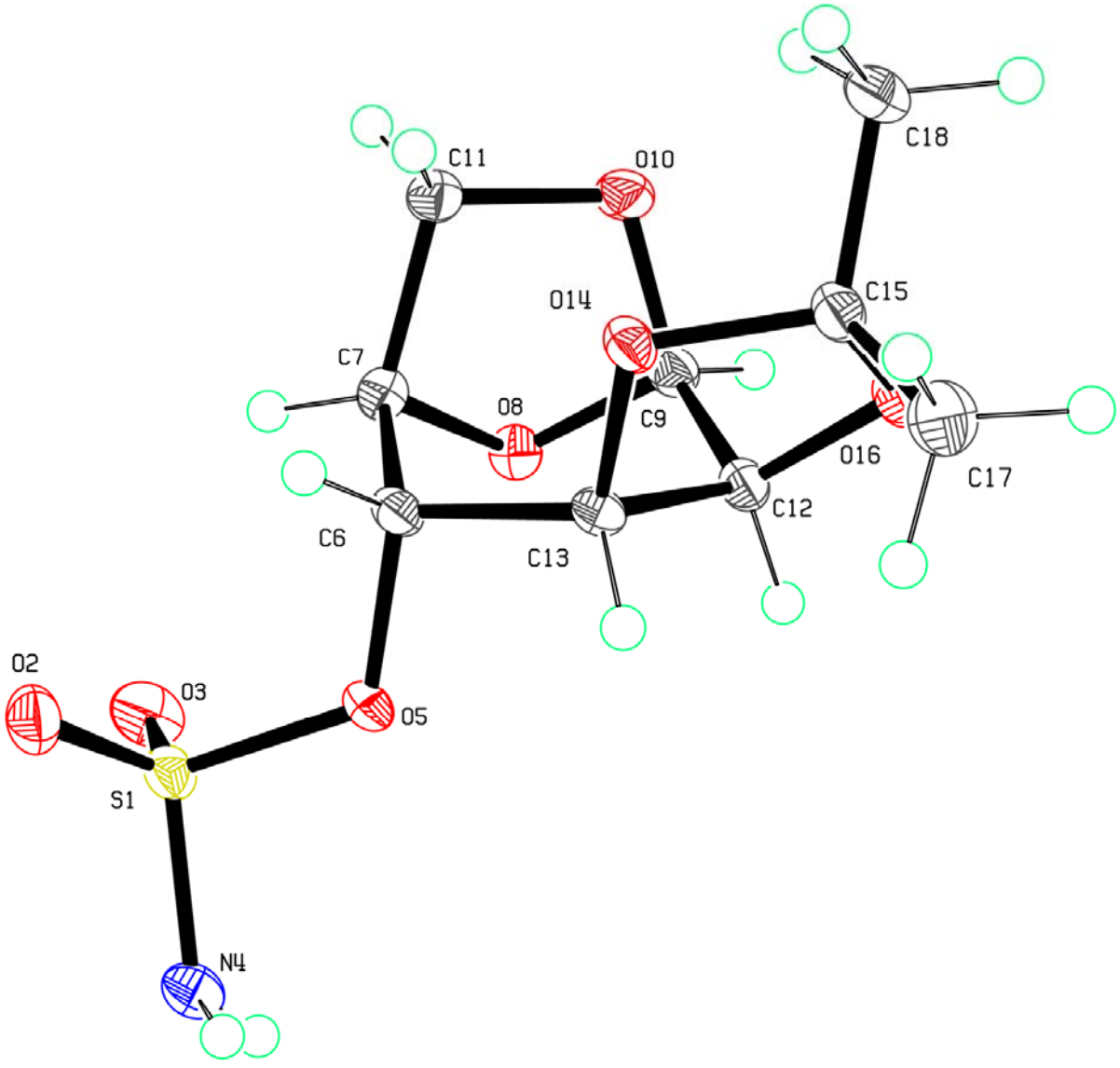


Fig. S1 ORTEP representation of compound **1**, created in ORTEP-3 v2.02[4]

4. References

1. M. Georges and B. Fraser-Reid, *Carbohydr. Res.*, 1984, **127**, 162.
2. M. López de la Paz, G. Ellis, M. Pérez, J. Perkins, J. Jiménez-Barbero and C. Vicent, *Eur. J. Org. Chem.*, 2002, **2002**, 840.
3. M. Kloosterman, M. P. d. Nijs and J. H. v. Boom, *Recl.: J. R. Neth. Chem. Soc.*, 1984, **103**, 243.
4. L. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.