Carbohydrate-Based Spiro-1,3-oxazolidine-2-thiones: Stereoselective Approaches Using Aziridines and Epoxides

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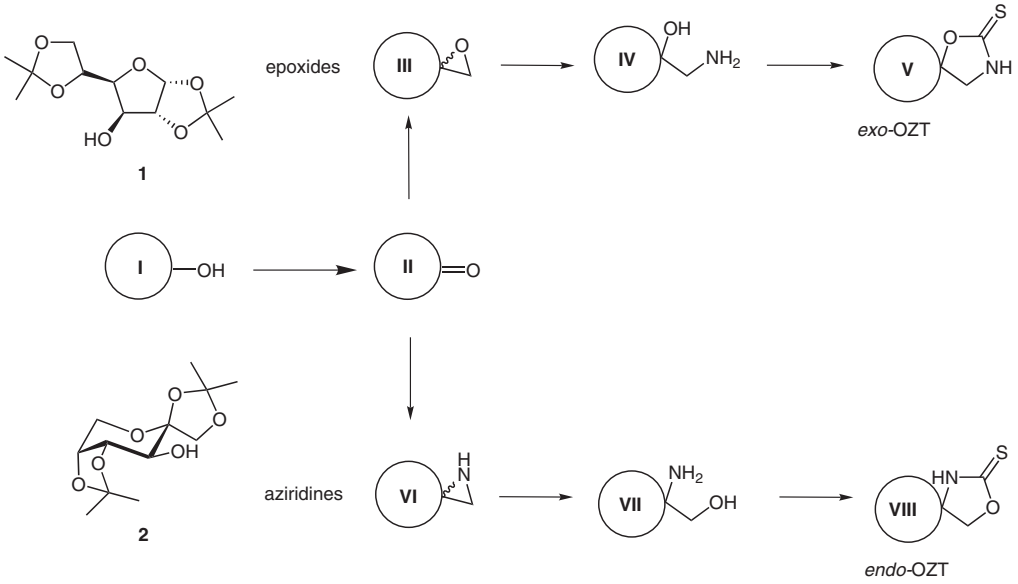
Abstract: D-glucose and D-fructose have been used as starting materials to prepare spiro-1,3-oxazolidine-2-thiones anchored on the third position of both carbohydrates. Following different approaches and depending on the carbohydrate template explored, stereoselective reactions have been developed via the formation of epoxides or aziridines.

Key words: azide, epoxide, spiro-compounds, chirality

Carbohydrate-derived chiral auxiliaries are useful templates in asymmetric reactions.[1] Various sugar series have been used for chiral induction: among the selected series, D-glucose[2] and D-fructose[3] are the most used, not only because they are among the cheapest sugars, but also due to the remarkable efficiency of their derivatives in chiral induction processes. Chiral 1,3-oxazolidin-2-ones are also recognised as major asymmetry inducers[4] and, more recently, 1,3-oxazolidine-2-thiones (OZTs) have emerged as useful alternatives on account of their enhanced possibilities. For example, depending on conditions, a stereoselective modulation of aldol reactions has been attained.[5] Connecting a broadly functionalisable OZT with a carbohydrate template might improve the chiral induction potential through geometric control of the rigid sugar backbone.

The purpose of this study was to explore the introduction of an OZT moiety onto the specific C-3 site of both 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) and 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**2**), taking advantage of the well-defined frame of both carbohydrate structures to generate all possible OZT-isomers. These spiroheterocyclic structures could be constructed according to a simplified sequence based on a key stereoselective approach from uloses **II** via epoxides **III** and aziridines **VI** (Scheme 1).

The *exo* spiro-OZTs could be produced through a standard reaction sequence (Scheme 1): a ketone **II**, readily obtained by oxidation[6] of a protected sugar **I**, is transformed into the epoxide **III** via the key step of the process, leading to both possible epimers. Completion of the sequence involves regioselective nitrogen introduction to afford the amino-alcohol **IV** and subsequent cyclisation to the *exo*-spiro-OZT **V**.



Scheme 1 Overview of *endo* and *exo* spiro-OZT formation

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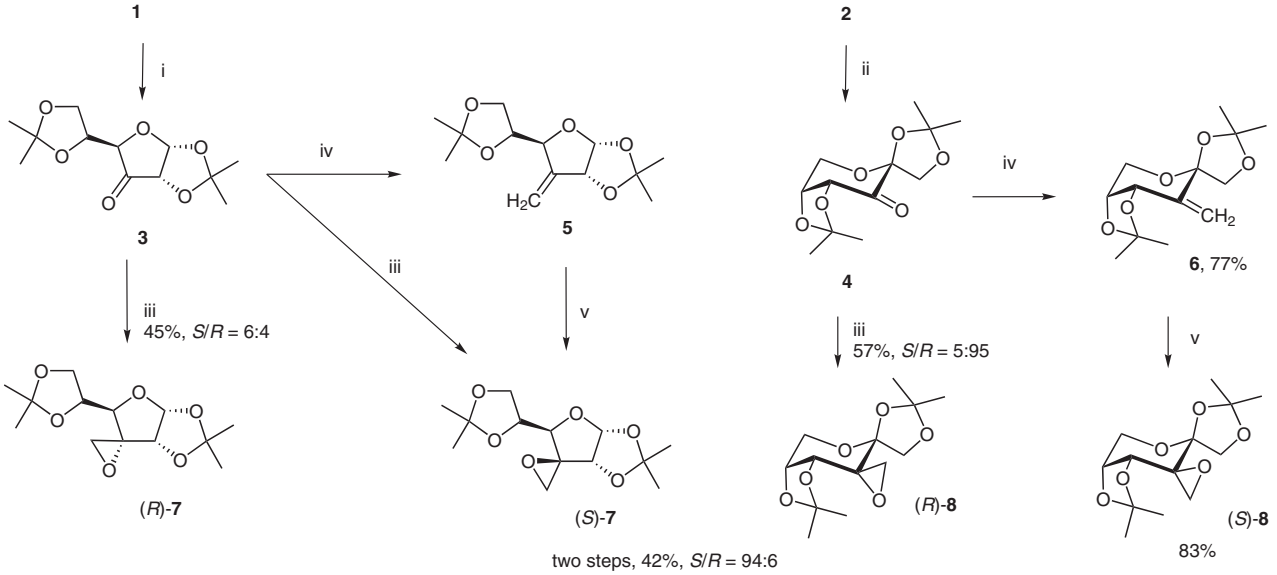
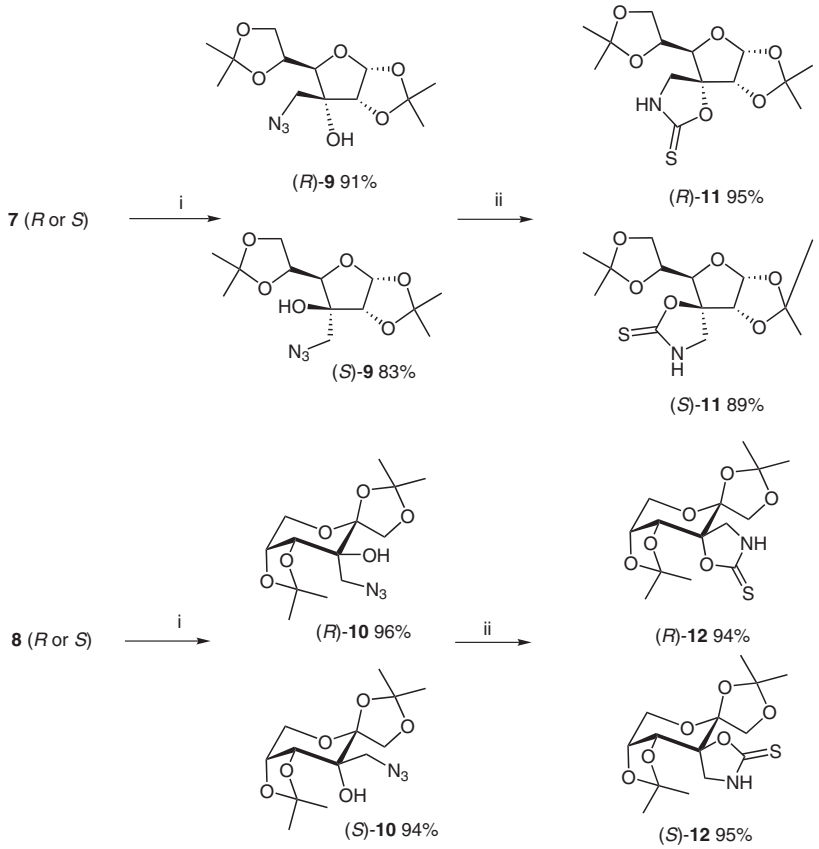


Scheme 2 Formation of epoxides. *Reagents and conditions*: (i) PDC, Ac_2O, CH_2Cl_2, 98%; (ii) $RuCl_3$, $NaIO_4$, K_2CO_3, $PhCH_2N(Et)_3Cl$, $CHCl_3$–H_2O; (iii) Me_3SOI, BuLi, THF; (iv) Ph_3PCH_2, THF; (v) MCPBA, $NaHCO_3$, CH_2Cl_2.

At first, a direct approach with the dimethylsulfoxonium methylide reagent was used to generate the epoxides (Scheme 2). As previously reported for ketone **3** (*t*-BuOK in *t*-BuOH, 50 °C),[7] a thermodynamic reaction was observed: despite the facial differentiation in favour of an attack on the upper face of the furanose ring, the methylene group was introduced on the lower face to selectively (*S*/*R* = 93:7) afford the epimer (*S*)-**7**. Reconsidering the reaction conditions (*n*-BuLi in THF, 0 °C) with the aim of favouring attack on the upper face, resulted in only a 45% yield of an epimeric mixture of epoxides (*S*/*R* = 6:4). Fortunately, epimers (*S*)-**7** and (*R*)-**7** could be readily separated by chromatography. When reacted under the above thermodynamic conditions, and at variance with previously reported data, ketone **4** afforded a mixture of epimeric epoxides **8** (*S*/*R* = 2:1) in only 35% yield, which could not

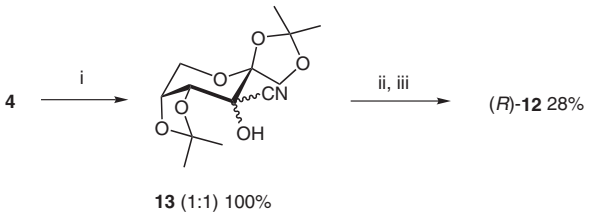


Scheme 3 Formations of *exo*-spiro-OZTs. *Reagents and conditions*: (i) NaN_3, NH_4Cl, DMF–H_2O (10:1); (ii) CS_2, Ph_3P, dioxane.

be separated.[7,8] Moving back to a kinetic approach to the reaction (*n*-BuLi in THF, –70 °C), we were pleased to observe a satisfactory 95:5 stereoselectivity in favour of epoxide (*R*)-**8**, while the global yield was raised to 57%.

However, considering the moderate yields obtained when using the sulfonium ylide approach with ketones **3** and **4**, we also explored a two-step route to the spiro-epoxides: (i) Wittig methylenation (ii) stereoselective *meta*-chloroperoxybenzoic acid (MCPBA) epoxidation (Scheme 2). Following such a protocol, ketone **3** afforded epoxide (*S*)-**7** in 42% overall yield and excellent selectivity (*S*/*R* = 94:6).[9] In comparison, the D-fructose-derived ketone **4** produced the corresponding epoxide (*S*)-**8** with a much better overall yield of 64%.[8] The Wittig methylenation step was optimised by using butyllithium in tetrahydrofuran at –78 °C to give a 77% yield of alkene **6**, whereas MCPBA epoxidation proceeded in 83% yield. All four isomers [(*S*)-**7**, (*R*)-**7** and (*S*)-**8**, (*R*)-**8**] – mostly obtained stereoselectively – were thus in our hands.

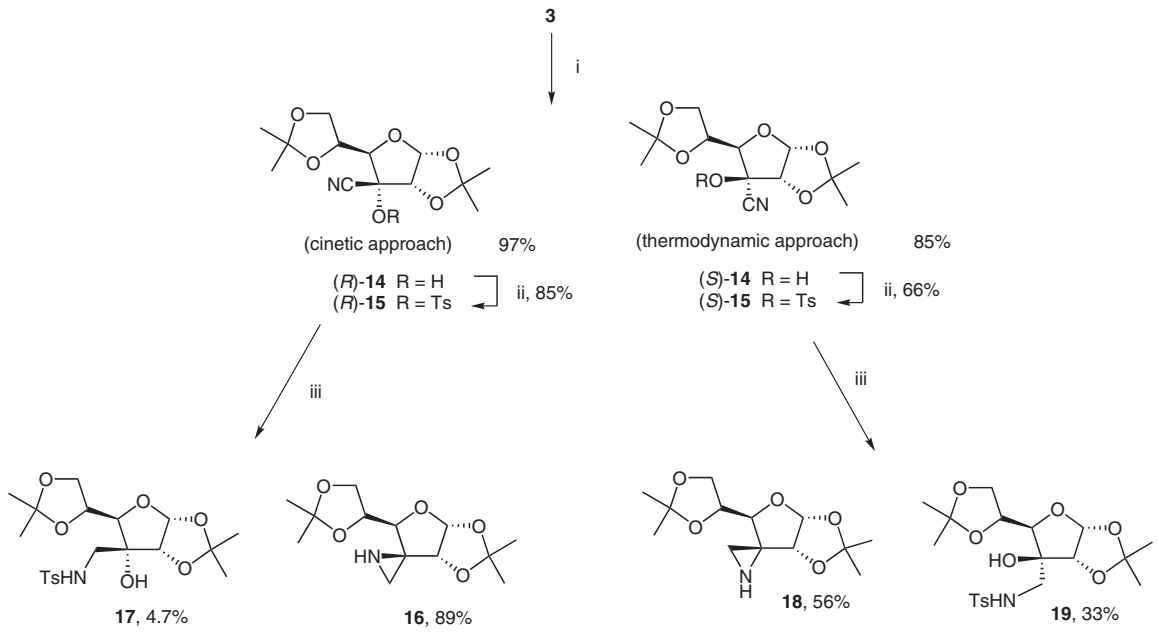
The above epoxides were then regioselectively cleaved by sodium azide under protic conditions (Scheme 3) to afford the corresponding azido-alcohols **9**[10] and **10** in excellent yields, ranging from 83% to 96%.



Scheme 4 Cyanohydrin approach to an OZT. *Reagents and conditions*: (i) NaCN, MeOH; (ii) LAH, THF; $CaCO_3$, $CSCl_2$, acetone–H_2O.

Direct cyclization to the corresponding OZTs **11** and **12** was effected following a one-pot protocol, which involved a modified Staudinger condensation and spontaneous cyclisation of the transient hydroxylated isothiocyanate.[11] A different approach involving cyanohydrin formation from the ketone was also explored in the D-fructo series (Scheme 4). A mixture of epimeric cyanohydrins **13** was quantitatively formed from ketone **4** – albeit without stereoselection. Chromatographic separation of (*R*)-**13** and (*S*)-**13** was straightforward and the former epimer was selected to exemplify the two-step transformation into OZT. Reduction of (*R*)-**13** by lithium aluminium hydride (LAH) led to the corresponding amino alcohol, which was further condensed with thiophosgene to afford OZT (*R*)-**12** in nearly 30% overall yield. Despite its shorter pathway, the cyanohydrin route to the OZTs was not exploited further, mainly because of the disappointing yields in the last two steps. The configuration of all spiro-OZTs was assigned through dedicated NOESY experiments, which showed the specific space relationships of the OZT methylene group with other hydrogens of the carbohydrate backbone.

The *endo* spiro-OZTs could be prepared through a reaction sequence similar to that applied for the *exo*-spiro-OZTs, with spiro-aziridine intermediates replacing the key spiro-epoxides (Scheme 1). Earlier approaches to the stereoselective preparation of spiro-aziridines involving cyanohydrin or azido-alcohol intermediates have already been disclosed, especially for D-gluco derivatives.[12] Testing cyanohydrin formation from ketones **3** and **4** under kinetic or thermodynamic conditions showed that only the D-gluco-related ketone **3** offered efficient stereoselectivity, in contrast to the D-fructo-related ketone **4**, for which no selectivity was observed; we therefore concentrated our efforts on the D-gluco series (Scheme 5).



Scheme 5 Aziridine formation in the D-gluco series. *Reagents and conditions*: (i) KCN, $NaHCO_3$, Et_2O, H_2O; (ii) TsCl, pyridine; (iii) LAH, Et_2O.

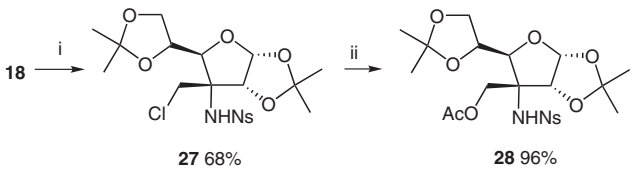
The cyanohydrins **14** were prepared according to the protocol described by Bourgeois.[12c] Under kinetic conditions ($NaHCO_3$, 0 °C, 10 min), (*R*)-**14**[12d] was obtained in nearly quantitative yield; in parallel, a modified procedure applied to **3** afforded the thermodynamic epimer (*S*)-**14**[12d] in 85% yield. The α-hydroxynitriles were further activated by O-tosylation to afford (*R*)-**15**[12e] in 85% yield and (*S*)-**15** in only 66% yield, respectively – a surprising result considering the steric difference between the two hydroxy groups.

Lithium aluminium hydride reduction of the cyano group in **15** caused spontaneous intramolecular cyclization. A highly selective reaction occurred with (*R*)-**15**, furnishing aziridine **16** in 90% yield, while by controlling the conditions, the competing tosyl migration leading to **17** was limited to 5% yield.

Applying the same reaction conditions to cyanohydrine (*S*)-**15** optimally afforded the corresponding aziridine **18** in 53% yield, together with its epimer **16** (3%) and sulfonamide **19** (32%). Formation of **16** suggested incomplete selectivity in the formation of (*S*)-**15**. Direct acetolysis of the aziridine **16** failed, even after *N*-Boc activation into carbamate **20**. As indicated in the literature, opening of a spiro-aziridine ring often requires stronger activation through N-sulfonylation.[13]

Testing both N-tosylation and N-nosylation showed the moderate reactivity of the aziridine, and afforded sulfonamides **21** and **22** in 49% and 60% yield, respectively (Scheme 6). In contrast, N-mesylation afforded sulfonamide **23** in 95% yield, thus suggesting a marked steric effect. The N-tosylated spiroaziridine **21** underwent both acetolysis and azidolysis to afford **24** and **25** with excellent yields, while the N-nosylated spiroaziridine **22** underwent acetate cleavage in moderate yield (58%) to produce **26**. The same reactions were applied to compound **18**, which showed a different behaviour: N-nosylation of this aziridine was followed by chloride ion counter-attack to provide the cleaved product **27** in 68% yield. Finally, nucleophilic displacement by acetate was realised to give a nearly quantitative yield of **28** (Scheme 7).

The final sequences were dedicated to the elaboration of the precursor β-amino alcohols to be converted into the OZTs. Compound **24** was efficiently de-O-acetylated using sodium methoxide to afford **29**; however, despite



27 68% **28** 96%

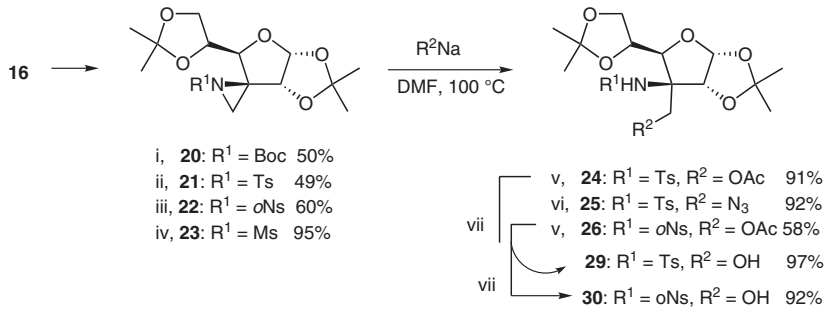
Scheme 7 Spontaneous aziridine **18** opening. *Reagents and conditions*: (i) *o*-NsCl, Et_3N, THF; (ii) AcONa, DMF, 100 °C.

many attempts at improvement, sodium naphthalenide N-desulfonylation could only be performed in poor yield. Tentative direct transformation of **24** into the OZT using thiophosgene under basic conditions failed.

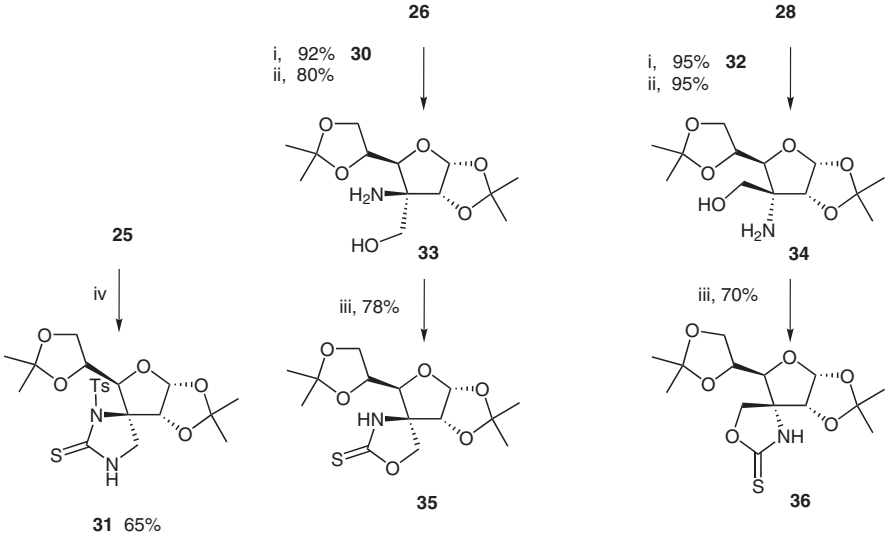
We then turned our attention to the N-nosylated epimers **26** and **28**, which were quantitatively de-O-acylated to **30** and **32**, then de-N-sulfonylated under standard thiolate deprotection conditions.[14] The resulting epimeric β-amino alcohols **33** and **34** were finally condensed with thiophosgene under basic conditions to yield the desired (*endo*-OZT) 1,3-oxazolidine-2-thiones **35** and **36** in 78 and 70% yield, respectively (Scheme 8).

The OZT formation was further explored by taking advantage of the azido group in derivative **25**. Applying the earlier modified Staudinger conditions to **25**,[11] a transient isothiocyanate was formed which spontaneously cyclized to furnish the spiro-1,3-imidazolidine-2-thione **31** in 65% yield (Scheme 8).

In conclusion, we have developed two general approaches to 1,3-oxazolidine-2-thiones clipped on standard carbohydrate templates. The epoxide approach could be realised in a stereoselective manner depending on the conditions used. On both templates, the epoxides (*S*)-**7** and (*S*)-**8** were obtained with very good stereoselectivity, whereas their epimeric counterparts proved more difficult to synthesize. Only the D-fructo derivative (*R*)-**8** could be obtained in reasonable yield and good stereoselectivity. The further sequences involving azide formation and modified Staudinger-aza-Wittig reaction were quite efficient. In contrast, spiro-aziridine formation only showed efficient selectivity with D-glucofurano derivatives. The D-fructopyrano cyanohydrins were formed without selectivity and lacked reactivity in O-sulfonyl activation. Following a three-step sequence, the furano spiro-aziridines **16** and **18** were prepared in 73% and 30% yield, respectively. Further steps to provide *endo*-spiro-OZTs were more



Scheme 6 Aziridine activations and opening. *Reagents and conditions*: (i) Boc_2O, THF; (ii) TsCl, DIPEA, THF; (iii) *o*-NsCl, Et_3N, THF; (iv) MsCl, Et_3N, THF; (v) AcONa, DMF, 100 °C; (vi) NaN_3, DMF, 100 °C; (vii) MeONa, MeOH.



Scheme 8 *endo*-OZT formation. *Reagents and conditions*: (i) MeONa, MeOH; (ii) PhSH, K_2CO_3, MeCN; (iii) Cl_2CS, $CaCO_3$; CS_2, Ph_3P, dioxane.

straightforward using a N-*ortho*-nosyl activation/protection system and resulted in the formation of the corresponding OZTs in overall 20% and 41%, respectively.

We have thus designed two approaches to the preparation of spiro-1,3-oxazolidine-2-thiones from D-glucose and D-fructose, either from epoxides or from aziridines, which can be prepared with a stereoselectivity that depends on the carbohydrate template used. All spiro-OZTs have been submitted to a chirality transfer study, the results of which will shortly be disclosed.

Solvents were dried and distilled by standard methods before use. All reagents were of commercial quality (Acros, Aldrich or Lancaster) and used without purification. Compounds were visualised with UV light and charring after a 10% H_2SO_4 ethanolic solution spray. Column chromatography was performed on silica gel 60 M (0.036–0.063 mm, Merck) using flash chromatographic elution techniques and TLC analysis with silica gel plates (Kieselgel $60F_{254}$, Merck). ^1H and ^{13}C NMR were recorded at 250 and 62.6 MHz, respectively, on a Bruker Avance DPX 250 spectrometer; chemical shifts (δ) are reported in ppm downfield from TMS or from residual solvent peak ($CDCl_3$); coupling constants (*J*) are reported in Hz and refer to apparent peak multiplicity. Low-resolution mass spectra were obtained using an Ionspray® (IS) method with an API 300 Perkin–Elmer SCIEX spectrometer. Optical rotations were measured at 20 °C with a Perkin–Elmer 341 polarimeter. IR spectra were recorded on a Perkin–Elmer Paragon 1000 PC spectrometer. HR-ESI-TOF-MS was performed on a Micromass LC TOF spectrometer. Microanalyses were performed on a Thermo Electron FlashEA 1112 analyser.

Me_3SOI Epoxidation of Uloses; General Procedure

n-BuLi (1.1 equiv) was carefully added to a solution of trimethylsulfoxonium iodide (1.2 equiv). When a clear solution was observed, a solution of ulose (1 equiv) in THF was added. When the reaction was complete, the resulting solution was hydrolysed through the addition of brine (10 mL). The aqueous layer was extracted with EtOAc (4 × 30 mL) and the combined organic layers were washed with brine (3 × 30 mL), dried over $MgSO_4$, and evaporated. The crude residue was purified by silica gel column chromatography.

3,7-Anhydro-3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose [(*R*)-7] [136522-01-5]

The ulofuranose **3** (218 mg, 0.84 mmol) in THF (7 mL) reacted for 2.5 h at 0 °C with a THF solution (7 mL) of the sulfoxonium ylide. Chromatography (PE–EtOAc, 4:1) afforded a 6:4 mixture of epimeric epoxides (*S*)-**7** and (*R*)-**7** (103 mg, 45% global yield). Selected analytical data for (*R*)-**7**:

$[\alpha]_D$ +74 (*c* 1.5, $CHCl_3$) [Lit.[7b] +85.6 (CH_2Cl_2)]; R_f = 0.24 (PE–EtOAc, 8:2).

IR (film): 1164, 1073, 1021 (epoxide C–O) cm^{-1}.

^1H NMR: δ = 1.32, 1.37, 1.40, 1.63 (4 × s, 12 H, 4 × CH_3), 2.99 (d, J_{7b-7a} = 5.0 Hz, 1 H, H-7b), 3.39 (d, 1 H, H-7a), 3.86–4.10 (m, 3 H, H-5, H-6b, H-6a), 4.25 (d, J_{4-5} = 6.9 Hz, 1 H, H-4), 4.43 (d, J_{2-1} = 4.1 Hz, 1 H, H-2), 5.87 (d, 1 H, H-1).

^{13}C NMR: δ = 25.3, 26.7, 26.9, 27.1 (4 × CH_3), 50.5 (C-7), 64.5 (C-3), 67.2 (C-6), 75.3 (C-5), 75.8 (C-4), 80.6 (C-2), 103.9 (C-1), 110.1, 113.8 (2 × C_{IV}).

MS (IS): *m*/*z* = 290.5 $[M + NH_4]^+$, 295.5 $[M + Na]^+$, 327.5 [M + MeOH + Na]$^+$, 567.5 $[2M + Na]^+$.

3,7-Anhydro-3-*C*-hydroxymethyl-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose [(*R*)-8] [78136-24-0]

A solution of the ylide in THF (240 mL) was carefully added to a cooled (–78 °C) solution of the ulopyranose **4** (4.0 g, 15.5 mmol) in THF. The mixture was stirred and slowly allowed to come to r.t. overnight. Column chromatography (PE–EtOAc, 4:1) afforded epoxide (*R*)-**8** as a colourless oil that crystallized on standing.

Yield: 2.4 g (57%); mp 42–44 °C; $[\alpha]_D$ –120 (*c* 1.2, $CHCl_3$) [Lit.[7b] –120 (CH_2Cl_2)]; R_f = 0.36 (PE–EtOAc, 8:2).

IR (film): 1239, 1090, 1013 (epoxide C–O) cm^{-1}.

^1H NMR: δ = 1.30, 1.31, 1.49, 1.51 (4 × s, 12 H, 4 × CH_3), 2.66 (d, J_{7b-7a} = 5.7 Hz, 1 H, H-7b), 3.20 (d, 1 H, H-7a), 3.77 (d, J_{6b-6a} = 13.2 Hz, 1 H, H-6b), 3.84 (dd, J_{6a-5} = 1.6 Hz, 1 H, H-6a), 4.02 (d, J_{4-5} = 7.5 Hz, 1 H, H-4), 4.04 (d, J_{1b-1a} = 9.2 Hz, 1 H, H-1b), 4.20 (d, 1 H, H-1a), 4.37 (d, J_{5-4} = 7.5 Hz, 1 H, H-5).

^{13}C NMR: δ = 25.2, 26.1, 26.2, 26.3 (4 × CH_3), 48.8 (C-7), 56.6 (C-3), 64.0 (C-6), 73.7 (C-1), 75.2 (C-5), 76.0 (C-4), 103.5 (C-2), 110.5, 111.0 (2 × C_{IV}).

MS (IS): *m*/*z* = 273.0 $[M + H]^+$, 290.5 $[M + NH_4]^+$, 295.5 $[M + Na]^+$.

MCPBA Epoxidation; General Procedure

The *exo*-methylene (**5** or **6**) in 1,2-DCE was treated with MCPBA (2.5 equiv) at 70 °C. After cooling, the mixture was diluted with CH_2Cl_2 (40 mL). The organic layer was taken and successively washed with a sat. aq Na_2SO_4 (10 mL), NaOH (0.2 M, 3 × 10 mL), H_2O (10 mL) then brine (10 mL). After drying the combined organic extracts over $MgSO_4$ and concentration under vacuum, the residue was purified by column chromatography on silica gel.

3,7-Anhydro-3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose [(*S*)-7] [53270-27-2]

The *exo*-methylene **5** (121 mg, 0.47 mmol) was treated with MCPBA in 1,2-DCE (4.5 mL). Column chromatography (PE–EtOAc, 4:1) afforded a 93:7 ratio of epoxides (*S*)-**7** (84 mg) and (*R*)-**7** (6 mg) with 70% global yield, as colourless oils.[9d,10]

$[\alpha]_D$ +47 (*c* 1.2, $CHCl_3$) [Lit.[7b] +55.5 (CH_2Cl_2)]; R_f = 0.59 (PE–EtOAc, 8:2).

IR (film): 1164, 1071, 1022 (C–O epoxide) cm^{-1}.

^{1}H NMR: δ = 1.31, 1.33, 1.40, 1.56 (4 × s, 12 H, 4 × CH_3), 3.09 (d, $J_{7a–7b}$ = 4.8 Hz, 1 H, H-7a), 3.16 (d, $J_{7b–7a}$ = 4.8 Hz, 1 H, H-7b), 3.96–4.11 (m, 3 H, H-5, H-6a, H-6b), 4.28 (d, $J_{2–1}$ = 3.9 Hz, 1 H, H-2), 4.37 (d, $J_{4–5}$ = 6.9 Hz, 1 H, H-4), 5.95 (d, $J_{1–2}$ = 3.9 Hz, H-1).

^{13}C NMR: δ = 25.4, 26.6, 26.9, 27.1 (4 × CH_3), 46.4 (C-7), 65.2 (C-3), 67.1 (C-6), 73.1 (C-5), 76.6 (C-4), 84.7 (C-2), 104.3 (C-1), 109.7 (C_{IV}), 112.7 (C_{IV}).

MS (IS): *m*/*z* = 273.0 $[M + H]^+$, 290.5 $[M + NH_4]^+$, 295.5 $[M + Na]^+$, 305.5 [M + MeOH + H]$^+$, 327.5 [M + MeOH + Na]$^+$, 567.5 $[2M + Na]^+$.

3,7-Anhydro-3-*C*-hydroxymethyl-1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose [(*S*)-8] [78136-25-1][8]

The *exo*-methylene **6** (661 mg, 2.58 mmol) was treated with MCPBA in 1,2-DCE (26 mL). Column chromatography (PE–EtOAc, 85:15) afforded epoxide (*S*)-**8**.

Yield: 583 mg (83%); solid; mp 93–95 °C; $[\alpha]_D$ –105 (*c* 1.1, $CHCl_3$) [Lit.[8] –119 (MeOH)]; R_f = 0.42 (PE–EtOAc, 8:2).

IR (film): 1187, 1093, 1067, 1022 (epoxide C–O) cm^{-1}.

^{1}H NMR: δ = 1.33, 1.39, 1.49, 1.51 (4 × s, 12 H, 4 × CH_3), 2.81 (d, $J_{7b–7a}$ = 4.9 Hz, 1 H, H-7b), 2.88 (d, 1 H, H-7a), 3.88 (dd, $J_{6b–6a}$ = 13.1 Hz, $J_{6b–5}$ = 0.7 Hz, 1 H, H-6b), 3.97–4.13 (m, 4 H, H-6a, H-4, H-1a, H-1b), 4.43 (dd, $J_{5–4}$ = 7.4 Hz, 1 H, H-5).

^{13}C NMR: δ = 25.0, 25.8, 26.2, 26.4 (4 × CH_3), 47.4 (C-7), 56.4 (C-3), 63.3 (C-6), 74.1 (C-1), 74.5 (C-5), 75.0 (C-4), 103.0 (C-2), 110.6, 110.9 (2 × C_{IV}).

MS (IS): *m*/*z* = 273.0 $[M + H]^+$, 290.5 $[M + NH_4]^+$, 295.0 $[M + Na]^+$.

Azidolysis of Epoxides; General Procedure

The epoxides in a DMF–H_2O (10:1 v/v) solution were reacted with NaN_3 (furano series: 4 equiv, pyrano series: 3 equiv) and NH_4Cl (furano series: 5 equiv, pyrano series: 8 equiv) at 80 °C. When the reaction was complete, the reaction medium was diluted with H_2O (20 mL) and extracted with EtOAc (5 × 40 mL). The combined organic phases were washed with brine (3 × 20 mL), dried over $MgSO_4$, and evaporated. The crude residue was purified by silica gel column chromatography.

3-*C*-Azidomethyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose [(*R*)-9]

The epoxide (*R*)-**7** (178 mg, 0.65 mmol) was treated with NaN_3 and NH_4Cl in DMF–H_2O (6.5 mL) for 140 min. Chromatography (PE–EtOAc, 4:1) afforded the azido-alcohol (*R*)-**9**.

Yield: 187 mg (91%); solid; mp 128–129 °C; $[\alpha]_D$ –28 (*c* 1.0, $CHCl_3$); R_f = 0.47 (PE–EtOAc, 8:2).

IR (film): 3543 (OH), 2108 (N_3) cm^{-1}.

^{1}H NMR: δ = 1.37 (s, 6 H, 2 × CH_3), 1.47, 1.60 (2 × s, 6 H, 2 × CH_3), 2.96 (s, 1 H, OH), 3.07 (d, $J_{7b–7a}$ = 13.2 Hz, 1 H, H-7b), 3.80 (d, $J_{4–5}$ = 8.2 Hz, 1 H, H-4), 3.83 (d, 1 H, H-7a), 3.92 (m, 1 H, H-5), 4.09 (m, 2 H, H-6a, H-6b), 4.57 (d, $J_{2–1}$ = 3.9 Hz, 1 H, H-2), 5.75 (d, 1 H, H-1).

^{13}C NMR: δ = 25.3, 26.6, 26.6, 26.8 (4 × CH_3), 52.0 (C-7), 68.0 (C-6), 73.1 (C-5), 80.3 (C-3), 80.4 (C-4), 81.6 (C-2), 103.7 (C-1), 110.1, 112.9 (2 × C_{IV}).

MS (IS): *m*/*z* = 316.5 $[M + H]^+$, 333.5 $[M + NH_4]^+$, 338.5 $[M + Na]^+$, 370.5 [M + MeOH + Na]$^+$.

HRMS-ES: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{21}N_3O_6Na$: 338.1328; found: 338.1320.

3-*C*-Azidomethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose [(*S*)-9] [880486-64-6][10]

The epoxide (*S*)-**7** (210 mg, 0.77 mmol) was treated with NaN_3 and NH_4Cl in DMF–H_2O (6.5 mL) for 140 min. Chromatography (PE–EtOAc, 4:1) afforded the azido-alcohol (*S*)-**9**.

Yield: 192 mg (83%); colourless oil.

HRMS-ES: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{21}N_3O_6Na$: 338.1328; found: 338.1333.

3-*C*-Azidomethyl-1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose [(*S*)-10]

The epoxide (*S*)-**8** (279 mg, 1.02 mmol) was treated with NaN_3 and NH_4Cl in DMF–H_2O (7.5 mL) for 3 h. Chromatography (PE–EtOAc, 4:1) afforded the azido-alcohol (*S*)-**10**.

Yield: 304 mg (94%); solid; mp 89–91 °C; $[\alpha]_D$ –105 (*c* 1.1, $CHCl_3$); R_f = 0.45 (PE–EtOAc, 8:2).

IR (film): 3536 (OH), 2106 (N_3) cm^{-1}.

^{1}H NMR: δ = 1.31, 1.42, 1.43, 1.47 (4 × s, 12 H, 4 × CH_3), 2.95 (s, 1 H, OH), 3.38 (d, $J_{7a–7b}$ = 12.8 Hz, 1 H, H-7b), 3.52 (d, 1 H, H-7a), 3.75 (d, $J_{6a–6b}$ = 12.6 Hz, 1 H, H-6b), 3.89 (d, $J_{1a–1b}$ = 10.1 Hz, 1 H, H-1b), 4.15 (d, 1 H, H-1a), 4.18 (dd, $J_{6a–5}$ = 2.4 Hz, 1 H, H-6a), 4.29 (dd, $J_{5–4}$ = 7.6 Hz, 1 H, H-5), 4.44 (d, 1 H, H-4).

^{13}C NMR: δ = 24.7, 25.6, 26.1, 26.6 (4 × CH_3), 54.5 (C-7), 63.3 (C-6), 72.5 (C-1), 72.5 (C-5), 73.6 (C-3), 74.1 (C-4), 104.4 (C-2), 109.6, 110.4 (2 × C_{IV}).

MS (IS): *m*/*z* = 333.5 $[M + NH_4]^+$, 338.5 $[M + Na]^+$.

HRMS-ES: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{21}N_3O_6Na$: 338.1328; found: 338.1331.

3-*C*-Azidomethyl-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose [(*R*)-10]

The epoxide (*R*)-**8** (1.1 g, 4.04 mmol) was treated with NaN_3 and NH_4Cl in DMF–H_2O (31 mL) for 3 h. Chromatography (PE–EtOAc, 4:1) afforded the azido-alcohol (*R*)-**10**.

Yield: 1.22 g (96%); white solid; mp 68–69 °C; $[\alpha]_D$ –99 (*c* 1.2, $CHCl_3$); R_f = 0.52 (PE–EtOAc, 8:2).

IR (film): 3496 (OH), 2106 (N_3) cm^{-1}.

^{1}H NMR: δ = 1.40, 1.41, 1.47, 1.61 (4 × s, 12 H, 4 × CH_3), 2.89 (s, 1 H, OH), 3.36 (s, 2 H, H-7a, H-7b), 3.98 (d, $J_{1a–1b}$ = 9.6 Hz, 1 H, H-1b), 4.09–4.28 (m, 4 H, H-4, H-5, H-6a, H-6b), 4.51 (d, 1 H, H-1a).

^{13}C NMR: δ = 25.3, 25.6, 26.1, 26.4 (4 × CH_3), 54.9 (C-7), 59.8 (C-6), 71.4 (C-5), 72.0 (C-3), 72.5 (C-1), 73.7 (C-4), 105.6 (C-2), 109.4, 112.6 (2 × C_{IV}).

MS (IS): *m*/*z* = 333.5 $[M + NH_4]^+$, 338.5 $[M + Na]^+$.

HRMS-ES: *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{21}N_3O_6Na$: 338.1328; found: 338.1324.

Conversion of Azido-Alcohols into Spiro-oxazolidinethiones; General Procedure

The azido-alcohol in anhydrous 1,4-dioxane was treated with CS_2 (19 equiv) and Ph_3P (1.1 equiv), overnight at 70 °C. After evaporation of the solvent, the residue was purified by column chromatography on silica gel.

1,2:5,6-Di-*O*-isopropylidene-3,5′-spiro(1′,3′-oxazolidine-2′-thione)-α-D-allofuranose [(*R*)-11] [908848-39-5]

The azido-alcohol (*R*)-**9** (1.163 g, 3.7 mmol) in dioxane (71 mL) was treated with CS_2 and Ph_3P. Chromatography (PE–EtOAc, 2:3) afforded the OZT (*R*)-**11**.

Yield: 1.16 g (95%); solid; mp 197–199 °C; $[\alpha]_D$ +94 (*c* 1.0, $CHCl_3$); R_f = 0.10 (PE–EtOAc, 8:2).

IR (film): 3314 (NH), 1533, 1184 (O–CS–N) cm^{-1}.

^1H NMR: δ = 1.33, 1.38, 1.48, 1.63 (4 × s, 12 H, 4 × CH_3), 3.56 (d, $J_{7a–7b}$ = 10.4 Hz, 1 H, H-7b), 4.02 (dd, $J_{6a–6b}$ = 11.8 Hz, $J_{6b–5}$ = 6.0 Hz, 1 H, H-6b), 4.10 (d, 1 H, H-7a), 4.10–4.20 (m, 2 H, H-6a, H-5), 4.23 (d, $J_{4–5}$ = 8.2 Hz, 1 H, H-4), 4.59 (d, $J_{2–1}$ = 3.3 Hz, 1 H, H-2), 5.75 (d, 1 H, H-1).

^{13}C NMR: δ = 25.3, 26.6, 26.8, 26.9 (4 × CH_3), 47.9 (C-7), 68.2 (C-6), 73.8 (C-5), 77.3 (C-4), 84.0 (C-2), 91.4 (C-3), 103.1 (C-1), 110.5, 114.7 (2 × C_{IV}), 188.7 (CS).

MS (IS): *m*/*z* = 332.5 $[M + H]^+$, 349.5 $[M + NH_4]^+$, 354.5 $[M + Na]^+$, 386.5 [M + MeOH + Na]$^+$, 663.5 [2M + H]$^+$, 685.5 [2M + Na]$^+$.

HRMS-ES: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{21}NO_6SNa$: 354.0987; found: 354.1004.

Anal. Calcd for $C_{14}H_{21}NO_6S$: C, 50.74; H, 6.39; N, 4.23; S, 9.68. Found: C, 50.94; H, 6,39; N, 4.24; S, 9.28.

1,2:5,6-Di-*O*-isopropylidene-3,5′-spiro(1′,3′-oxazolidine-2′-thione)-α-D-glucofuranose [(*S*)-11] [908848-40-8]

The azido-alcohol (*S*)-**9** (95 mg, 0.3 mmol) in dioxane (7.5 mL) was treated with CS_2 and Ph_3P. Chromatography (PE–EtOAc, 7:3) afforded the OZT (*S*)-**11**.

Yield: 89 mg (89%); solid; mp 136–138 °C; $[\alpha]_D$ +39 (*c* 1.2, $CHCl_3$); R_f = 0.52 (PE–EtOAc, 8:2).

IR (film): 3222 (NH), 1534, 1162 (O–CS–N) cm^{-1}.

^1H NMR: δ = 1.31 (s, 6 H, 2 × CH_3), 1.43, 1.51 (2 × s, 6 H, 2 × CH_3), 3.94 (d, $J_{7a–7b}$ = 10.4 Hz, 1 H, H-7b), 3.96 (d, $J_{4–5}$ = 8.2 Hz, 1 H, H-4), 4.00 (d, 1 H, H-7a), 4.03 (dd, $J_{6a–6b}$ = 8.7 Hz, $J_{6b–5}$ = 5.0 Hz, 1 H, H-6b), 4.15 (dd, $J_{6a–5}$ = 6.2 Hz, 1 H, H-6a), 4.38 (m, 1 H, H-5), 4.63 (d, $J_{2–1}$ = 3.7 Hz, 1 H, H-2), 5.96 (d, 1 H, H-1), 8.30 (s, 1 H, NH).

^{13}C NMR: δ = 25.1, 26.4 (2 × CH_3), 26.8 (2 × CH_3), 46.0 (C-7), 67.5 (C-6), 72.5 (C-5), 81.1 (C-4), 83.5 (C-2), 94.3 (C-3), 104.8 (C-1), 110.0, 113.2 (2 × C_{IV}), 188.1 (CS).

MS (IS): *m*/*z* = 332.5 $[M + H]^+$, 349.5 $[M + NH_4]^+$, 354.5 $[M + Na]^+$, 386.5 [M + MeOH + Na]$^+$, 663.5 [2M + H]$^+$, 685.5 [2M + Na]$^+$.

HRMS-ES: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{21}NO_6SH$: 332.1167; found: 332.1167.

Anal. Calcd for $C_{14}H_{21}NO_6S$: C, 50.74; H, 6.39; N, 4.23; S, 9.68. Found: C, 50.61; H, 6.39; N, 4.20; S, 9.15.

1,2:4,5-Di-*O*-isopropylidene-3,5′-spiro(1′,3′-oxazolidine-2′-thione)-β-D-fructopyranose [(*S*)-12]

The azido-alcohol (*S*)-**10** (1.3 g, 4.12 mmol) in dioxane (90 mL) was treated with CS_2 and Ph_3P. Chromatography (PE–EtOAc, 7:3) afforded the OZT (*S*)-**12**.

Yield: 1.29 g (95%); solid; mp 134–136 °C; $[\alpha]_D$ –127 (*c* 1.0, $CHCl_3$); R_f = 0.33 (PE–EtOAc, 8:2).

IR (film): 3198 (NH), 1549, 1182 (O–CS–N) cm^{-1}.

^1H NMR: δ = 1.32, 1.42 (2 × s, 6 H, 2 × CH_3), 1.47 (br s, 6 H, 2 × CH_3), 3.61 (d, $J_{7a–7b}$ = 10.5 Hz, 1 H, H-7b), 3.87 (d, $J_{6a–6b}$ = 13.1 Hz, 1 H, H-6b), 3.91 (d, $J_{7b–7a}$ = 10.5 Hz, 1 H, H-7a), 3.96 (d, $J_{1a–1b}$ = 9.9 Hz, 1 H, H-1b), 4.05 (d, 1 H, H-1a), 4.22 (dd, $J_{6a–5}$ = 2.7 Hz, 1 H, H-6a), 4.42 (dd, $J_{5–4}$ = 7.3 Hz, $J_{5–6a}$ = 2.7 Hz, 1 H, H-5), 4.58 (d, 1 H, H-4), 8.22 (s, 1 H, NH).

^{13}C NMR: δ = 24.6, 25.6, 25.9, 26.2 (4 × CH_3), 48.1 (C-7), 62.5 (C-6), 72.1 (C-1), 72.9 (C-5), 74.5 (C-4), 87.8 (C-3), 104.0 (C-2), 110.1, 112.1 (2 × C_{IV}), 188.5 (CS).

MS (IS): *m*/*z* = 332.5 $[M + H]^+$, 349.0 $[M + NH_4]^+$, 354.0 $[M + Na]^+$, 370.0 [M + K]$^+$.

Anal. Calcd for $C_{14}H_{21}NO_6S$: C, 50.74; H, 6.39; N, 4.23; S, 9.68. Found: C, 50.47; H, 6,33; N, 4.26; S, 9.35.

1,2:4,5-Di-*O*-isopropylidene-3,5′-spiro(1′,3′-oxazolidine-2′-thione)-β-D-psicopyranose [(*R*)-12]

The azido-alcohol (*R*)-**10** (192 mg, 0.61 mmol) in dioxane (12 mL) was treated with CS_2 and Ph_3P. Chromatography (PE–EtOAc, 1:1) afforded the OZT (*R*)-**12**.

Yield: 190 mg (94%); solid; mp 203–205 C; $[\alpha]_D$ –52 (*c* 1.0, $CHCl_3$); R_f = 0.13 (PE–EtOAc, 8:2).

IR (film): 3296 (NH), 1544, 1164 (O–CS–N) cm^{-1}.

^1H NMR (500 MHz): δ = 1.36, 1.41, 1.48, 1.66 (4 × s, 12 H, 4 × CH_3), 3.65 (d, $J_{7b–7a}$ = 10.5 Hz, 1 H, H-7b), 3.78 (d, 1 H, H-7a), 4.12 (d, $J_{1a–1b}$ = 10.0 Hz, 1 H, H-1b), 4.16 (d, 1 H, H-1a), 4.20 (dd, $J_{6a–6b}$ = 13.0 Hz, $J_{6b–5}$ = 3.0 Hz, 1 H, H-6b), 4.26 (m, 2 H, H-4, H-5), 4.30 (d, 1 H, H-6a), 8.09 (s, 1 H, NH).

^{13}C NMR: δ = 25.2, 25.8, 26.0, 26.5 (4 × CH_3), 49.6 (C-7), 60.6 (C-6), 71.0 (C-5), 72.1 (C-1), 75.2 (C-4), 85.9 (C-3), 104.8 (C-2), 110.9, 113.0 (2 × C_{IV}), 188.7 (CS).

MS (IS): *m*/*z* = 332.5 $[M + H]^+$, 349.0 $[M + NH_4]^+$, 354.0 $[M + Na]^+$, 370.0 [M + K]$^+$.

Anal. Calcd for $C_{14}H_{21}NO_6S$: C, 50.74; H, 6.39; N, 4.23; S, 9.68. Found: C, 50.59; H, 6.37; N, 4.22; S, 9.31.

3-*C*-Cyano-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose [(*S*)-14] [43179-08-4]

Ulose **3** (5.07 g, 19.6 mmol) in an ice-cold solution of Et_2O (50 mL) and H_2O (10 mL), was treated with $NaHCO_3$ (3.3 g, 39.2 mmol) for 10 min with stirring at 0 °C. The solution was added dropwise to aq KCN (5 mL, 1.34 g, 20.6 mmol). The mixture was stirred 20 min then diluted with sat. aq $NaHCO_3$ (20 mL). The aqueous layer was extracted with Et_2O (3 × 30 mL) and the combined organic phases were washed with brine (1 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo to give the cyanohydrin (*S*)-**14**.

Yield: 5.42 g (97%); gum; $[\alpha]_D$ +16 (*c* 0.85, $CHCl_3$); R_f = 0.67 (PE–EtOAc, 7:3).

IR (film): 3381 (OH), 1633 (CN) cm^{-1}.

^1H NMR: δ = 1.40 (s, 6 H, 2 × CH_3), 1.48, 1.61 (2 × s, 6 H, 2 × CH_3), 3.66 (s, 1 H, OH), 3.85 (d, $J_{4–5}$ = 8.8 Hz, 1 H, H-4), 4.03 (dd, $J_{6a–6b}$ = 9.1 Hz, $J_{6b–5}$ = 4.2 Hz, 1 H, H-6b), 4.20 (dd, $J_{6a–5}$ = 6.1 Hz, 1 H, H-6a), 4.42 (m, 1 H, H-5), 4.80 (d, $J_{2–1}$ = 3.5 Hz, 1 H, H-2), 5.92 (d, 1 H, H-1).

^{13}C NMR: δ = 24.9, 26.5, 26.7, 26.8 (4 × CH_3), 67.5 (C-6), 75.1 (C-5), 77.2 (C-3), 79.7 (C-4), 82.2 (C-2), 104.1 (C-1), 110.6, 114.8 (2 × C_{IV}), 117.3 (CN).

MS (IS): *m*/*z* = 259.5 $[M – CN]^+$, 308.5 $[M + Na]^+$.

3-*C*-Cyano-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose [(*R*)-14] [52290-80-9]

A solution of KCN (1.35 g, 20.7 mmol) in H_2O (12 mL) was added dropwise to a solution of ulose **3** (5.1 g, 19.7 mmol) in Et_2O (60

mL). After 7 h at r.t., the mixture was diluted with sat. aq $NaHCO_3$ (20 mL). The aqueous layer was extracted with Et_2O (3 × 30 mL) and the combined organic layers were washed with brine (1 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo to give the crude cyanohydrin (*R*)-**14**.

Yield: 4.82 g (85%); solid; mp 91–93 °C; $[\alpha]_D$ +46 (*c* 1.14, $CHCl_3$); R_f = 0.64 (PE–EtOAc, 7:3).

IR (film): 3374 (OH), 1633 (CN) cm^{-1}.

^1H NMR: δ = 1.37, 1.39, 1.55, 1.58 (4 × s, 12 H, 4 × CH_3), 4.09 (dd, $J_{6a–6b}$ = 9.1 Hz, $J_{6b–5}$ = 4.4 Hz, 1 H, H-6b), 4.20 (dd, $J_{6a–5}$ = 6.0 Hz, 1 H, H-6a), 4.20 (d, $J_{4–5}$ = 6.9 Hz, 1 H, H-4), 4.33 (m, 2 H, H-5, OH), 4.58 (d, $J_{2–1}$ = 3.5 Hz, 1 H, H-2), 5.95 (d, 1 H, H-1).

^{13}C NMR: δ = 25.1, 26.6, 26.7, 26.9 (4 × CH_3), 67.1 (C-6), 73.2 (C-5), 75.3 (C-3), 82.5 (C-4), 85.7 (C-2), 105.2 (C-1), 110.9, 113.8 (2 × C_{IV}), 116.9 (CN).

MS (IS): *m*/*z* = 286.5 $[M + H]^+$, 303.5 $[M + NH_4]^+$, 308.5 $[M + Na]^+$, 340.5 $[M + MeOH + Na]^+$.

3-*C*-Cyano-1,2:5,6-di-*O*-isopropylidene-3-*O*-(*p*-toluene-4-sulfonyl)-α-D-allofuranose [(*R*)-15] [55052-95-4]

TsCl (8.73 g, 45.8 mmol) was added to a solution of (*R*)-**14** (5.46 g, 19.1 mmol) in pyridine (30 mL) cooled to –50 °C. The mixture was allowed to warm up slowly (80 h) to r.t., then the reaction was quenched through the addition of ice (50 g). The resulting aqueous layer was extracted with $CHCl_3$ (5 × 50 mL) and the combined organic phase was washed with HCl (1M, 2 × 100 mL), then with sat. aq $NaHCO_3$ (2 × 100 mL) and with brine (100 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo to give the crude tosylate (*R*)-**15**.

Yield: 7.13 g (85%); solid; mp 82–85 °C; $[\alpha]_D$ +42 (*c* 1.39, $CHCl_3$); R_f = 0.77 (PE–EtOAc, 7:3).

IR (film): 1598 (CN), 1455 cm^{-1}.

^1H NMR: δ = 1.25, 1.31, 1.41, 1.57 (4 × s, 12 H, 4 × CH_3), 2.47 (s, 3 H, CH_3-Ar), 3.98 (dd, $J_{6a–6b}$ = 8.8 Hz, $J_{6b–5}$ = 4.1 Hz, 1 H, H-6b), 4.07 (d, $J_{4–5}$ = 7.8 Hz, 1 H, H-4), 4.10 (dd, $J_{6a–5}$ = 5.7 Hz, 1 H, H-6a), 4.23 (m, 1 H, H-5), 5.13 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 5.93 (d, 1 H, H-1), 7.36 (d, J_{vic} = 8.2 Hz, 2 H, ArH), 7.90 (d, 2 H, ArH).

^{13}C NMR: δ = 21.6 (CH_3-Ar), 25.0, 26.3, 26.5, 26.9 (4 × CH_3), 66.9 (C-6), 74.2 (C-5), 79.6 (C-4), 79.8 (C-3), 82.5 (C-2), 104.1 (C-1), 110.0, 114.6 (2 × C_{IV}), 113.7 (CN), 128.2 (2 × C-Ar), 129.5 (2 × C-Ar), 133.6 (C_{IV-Me}), 145.5 (C_{IV-SO2}).

MS (IS): *m*/*z* = 440.5 $[M + H]^+$, 457.5 $[M + NH_4]^+$, 462.5 $[M + Na]^+$, 494.5 $[M + MeOH + Na]^+$.

3-*C*-Cyano-1,2:5,6-di-*O*-isopropylidene-3-*O*-(*p*-toluene-4-sulfonyl)-α-D-glucofuranose [(*S*)-15]

TsCl (12.43 g, 65.2 mmol) and a catalytic amount of DMAP were added to a solution of (*S*)-**14** (4.65 g, 16.3 mmol) in pyridine (30 mL) at 0 °C. The mixture was then heated at 70 °C for 16 h. After cooling to r.t., the reaction was quenched with ice. After separation, the aqueous layer was extracted with $CHCl_3$ (5 × 50 mL) and the combined organic phase was washed with aq HCl (1M, 2 × 100 mL), then with sat. aq $NaHCO_3$ (2 × 100 mL) and brine (100 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Silica gel column chromatography (PE–EtOAc, 4:1) afforded (*S*)-**15**.

Yield: 4.72 g (66%); colourless syrup; $[\alpha]_D$ –34 (*c* 2.58, $CHCl_3$); R_f = 0.66 (PE–EtOAc, 8:2).

IR (film): 1598 (CN), 1455 cm^{-1}.

^1H NMR: δ = 1.19, 1.33, 1.38, 1.57 (4 × s, 12 H, 4 × CH_3), 2.46 (s, 3 H, CH_3-Ar), 3.94 (dd, $J_{6a–6b}$ = 9.1 Hz, $J_{6b–5}$ = 4.1 Hz, 1 H, H-6b), 4.03 (dd, $J_{6a–5}$ = 5.7 Hz, 1 H, H-6a), 4.17 (m, 1 H, H-5), 4.24 (d, $J_{4–5}$ = 7.9 Hz, 1 H, H-4), 5.24 (d, $J_{2–1}$ = 3.6 Hz, 1 H, H-2), 6.01 (d, 1 H, H-1), 7.37 (d, J_{vic} = 8.2 Hz, 2 H, ArH), 7.90 (d, 2 H, ArH).

^{13}C NMR: δ = 21.9 (CH_3-Ar), 25.1, 26.1 (2 × CH_3), 26.7 (2 × CH_3), 66.9 (C-6), 71.8 (C-5), 81.4 (C-3), 83.8 (C-4), 84.0 (C-2), 105.4 (C-1), 110.2, 114.4 (2 × C_{IV}), 111.9 (CN), 128.6 (2 × C-Ar), 129.8 (2 × C-Ar), 133.0 (C_{IV-Me}), 146.1 (C_{IV-SO2}).

MS (IS): *m*/*z* = 440.5 $[M + H]^+$, 457.5 $[M + NH_4]^+$, 462.5 $[M + Na]^+$, 494.5 $[M + MeOH + Na]^+$.

Formation of Spiro-Aziridines; General Procedure

To a cooled (–15 °C) and vigorously stirred suspension of LAH (4.3 equiv) in Et_2O, a solution of the sulfonylated cyanohydrine (1 equiv) in Et_2O was added dropwise. The reaction was maintained at low temperature for 30 min, then allowed to reach r.t. and the reaction mixture was cooled again in an ice-bath and quenched with ice. EtOAc (30 mL) was added and the resulting emulsion was filtered over a Celite® pad and the cake was washed with EtOAc (4 × 60 mL). The aqueous layer was further extracted with EtOAc and the combined organic phase was washed with brine, dried over $MgSO_4$ then evaporated. The crude product was purified by column chromatography on silica gel.

3-*C*-Aminomethyl-3,7-anhydro-1,2:4,5-di-*O*-isopropylidene-α-D-glucofuranose (16)

The tosylated cyanohydrin (*R*)-**15** (2.0 g, 4.55 mmol) dissolved in Et_2O (25 mL) was treated with LAH (0.75 g, 19.56 mmol) suspended in Et_2O (25 mL) at –30 °C. The reaction was quenched with ice (100 g) and EtOAc (30 mL) and the organic layer was taken. Chromatography (PE–EtOAc, 2:3) afforded the spiro-aziridine **16**. The faster moving side-product **17** was also isolated.

Yield: 1.10 g (89%); colourless oil; $[\alpha]_D$ +44 (*c* 0.72, $CHCl_3$); R_f = 0.22 (PE–EtOAc, 45:55).

IR (film): 3382 (NH), 1644 (C–N) cm^{-1}.

^1H NMR: δ = 1.24, 1.26, 1.31, 1.49 (4 × s, 12 H, 4 × CH_3), 1.97 (s, 1 H, H-7b), 2.02 (s, 2 H, H-7a, NH), 3.87 (m, 1 H, H-5), 3.93 (dd, $J_{6a–6b}$ = 8.8 Hz, $J_{6b–5}$ = 4.7 Hz, 1 H, H-6b), 4.05 (dd, $J_{6a–5}$ = 6.4 Hz, 1 H, H-6a), 4.18 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 4.25 (d, $J_{4–5}$ = 8.2 Hz, 1 H, H-4), 5.84 (d, 1 H, H-1).

^{13}C NMR: δ = 24.8, 26.3, 26.4, 26.7 (4 × CH_3), 29.3 (C-7), 46.0 (C-3), 67.3 (C-6), 74.1 (C-5), 77.2 (C-4), 86.9 (C-2), 104.0 (C-1), 109.3, 111.6 (2 × C_{IV}).

MS (IS): *m*/*z* = 272.5 $[M + H]^+$, 304.5 $[M + MeOH + H]^+$.

HRMS-ES: *m*/*z* calcd for $C_{13}H_{21}NO_5H$: 272.1498; found: 272.1484.

3-*C*-*p*-Toluenesulfonamidomethyl-1,2:4,5-di-*O*-isopropylidene-α-D-allofuranose (17)

Yield: 95 mg (4.7%); white solid; mp 177–179 °C; $[\alpha]_D$ +44 (*c* 1.23, $CHCl_3$); R_f = 0.60 (PE–EtOAc, 45:55).

IR (film): 3443 (NH), 3290 (OH), 1336, 1161 (SO_2) cm^{-1}.

^1H NMR: δ = 1.28, 1.33, 1.35, 1.57 (4 × s, 12 H, 4 × CH_3), 2.43 (s, 3 H, CH_3-Ar), 3.04 (br s, 1 H, OH), 3.07 (dd, $J_{7a–7b}$ = 13.0 Hz, $J_{7b–NH}$ = 9.4 Hz, 1 H, H-7b), 3.23 (dd, $J_{7a–NH}$ = 3.8 Hz, 1 H, H-7a), 3.75 (d, $J_{4–5}$ = 7.2 Hz, 1 H, H-4), 3.89 (dd, $J_{6a–6b}$ = 11.3 Hz, $J_{6b–5}$ = 8.8 Hz, 1 H, H-6b), 3.98–4.07 (m, 2 H, H-5, H-6a), 4.59 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 5.15 (dd, 1 H, NH), 5.75 (d, 1 H, H-1), 7.32 (d, J_{vic} = 8.2 Hz, 2 H, ArH), 7.74 (d, 2 H, ArH).

^{13}C NMR: δ = 21.6 (CH_3-Ar), 25.1, 26.5, 26.7 (4 × CH_3), 44.1 (C-7), 67.5 (C-6), 72.9 (C-5), 78.9 (C-4), 80.3 (C-3), 80.8 (C-2), 103.5 (C-1), 110.0, 112.7 (2 × C_{IV}), 127.1 (2 × C-Ar), 129.9 (2 × C-Ar), 136.8 (C_{IV-Me}), 143.7 (C_{IV-SO2}).

MS (IS): *m*/*z* = 444.5 $[M + H]^+$, 461.5 $[M + NH_4]^+$, 466.5 $[M + Na]^+$, 909.5 $[2M + Na]^+$.

3-*C*-Aminomethyl-3,7-anhydro-1,2:4,5-di-*O*-isopropylidene-α-D-allofuranose (18)

Tosylated cyanohydrin (*S*)-**15** (362 mg, 0.82 mmol) dissolved in Et_2O (5 mL) was treated with LAH (134 mg, 3.53 mmol) in Et_2O (5 mL) at –15 °C. The reaction was quenched with ice (50 g) and EtOAc (20 mL) and the organic layer was taken. Chromatography (PE–EtOAc, 1:1) afforded the spiro-aziridine **18**, the spiro-aziridine **16** (8 mg, 3.6% yield) and the tosylamide **19**.

Yield: 125 mg (56%); colourless oil; $[\alpha]_D$ +71 (*c* 1.72, $CHCl_3$); R_f = 0.19 (PE–EtOAc, 45:55).

IR (film): 3300 (NH), 1643 (C–N) cm^{-1}.

^1H NMR: δ = 1.30, 1.34, 1.38, 1.60 (4 × s, 12 H, 4 × CH_3), 1.81 (s, 1 H, H-7b), 2.10 (s, 1 H, NH), 2.37 (s, 1 H, H-7a), 3.91 (m, 1 H, H-5), 3.94 (dd, $J_{6a–6b}$ = 8.8 Hz, $J_{6b–5}$ = 4.7 Hz, 1 H, H-6b), 4.10 (dd, $J_{6a–5}$ = 6.0 Hz, 1 H, H-6a), 4.17 (d, $J_{4–5}$ = 8.2 Hz, 1 H, H-4), 4.26 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 5.84 (d, 1 H, H-1).

^{13}C NMR: δ = 25.3 (CH_3), 26.4 (C-7), 26.8 (CH_3), 27.0 (2 × CH_3), 46.9 (C-3), 68.4 (C-6), 75.5 (C-5), 82.6 (C-4), 84.1 (C-2), 104.3 (C-1), 110.0, 112.9 (2 × C_{IV}).

MS (IS): *m*/*z* = 272.5 $[M + H]^+$, 304.5 $[M + MeOH + H]^+$, 543.5 $[2M + H]^+$.

HRMS-ES: *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{21}NO_5H$: 272.1498; found: 272.1497.

3-*C*-*p*-Toluenesulfonamidomethyl-1,2:4,5-di-*O*-isopropylidene-α-D-glucofuranose (19)

Yield: 122 mg (33%); solid; $[\alpha]_D$ +33 (*c* 1.19, $CHCl_3$); mp 153–155 °C; R_f = 0.62 (PE–EtOAc, 45:55).

IR (film): 3443 (NH), 3238 (OH), 1324, 1162 (SO_2) cm^{-1}.

^1H NMR: δ = 1.26, 1.33, 1.35, 1.42 (4 × s, 12 H, 4 × CH_3), 2.43 (s, 3 H, CH_3-Ar), 3.24 (dd, $J_{7a–7b}$ = 13.8 Hz, $J_{7b–NH}$ = 5.8 Hz, 1 H, H-7b), 3.32 (dd, $J_{7a–NH}$ = 7.5 Hz, 1 H, H-7a), 3.47 (br s, 1 H, OH), 3.67 (d, $J_{4–5}$ = 8.8 Hz, 1 H, H-4), 3.96 (dd, $J_{6a–6b}$ = 8.8 Hz, $J_{6b–5}$ = 5.0 Hz, 1 H, H-6b), 4.11 (dd, $J_{6a–5}$ = 6.3 Hz, 1 H, H-6a), 4.23–4.33 (m, 1 H, H-5), 4.38 (d, $J_{2–1}$ = 3.5 Hz, 1 H, H-2), 5.71 (dd, 1 H, NH), 5.84 (d, 1 H, H-1), 7.32 (d, J_{vic} = 8.2 Hz, 2 H, ArH), 7.76 (d, 2 H, ArH).

^{13}C NMR: δ = 21.6 (CH_3-Ar), 25.2, 26.4, 26.8, 27.1 (4 × CH_3), 45.5 (C-7), 67.8 (C-6), 72.0 (C-5), 80.3 (C-4), 82.6 (C-3), 86.4 (C-2), 104.6 (C-1), 109.7, 112.7 (2 × C_{IV}), 127.2 (2 × C-Ar), 129.9 (2 × C-Ar), 136.5 (C_{IV-Me}), 143.9 (C_{IV-SO2}).

MS (IS): *m*/*z* = 444.5 $[M + H]^+$, 461.5 $[M + NH_4]^+$, 466.5 $[M + Na]^+$, 909.5 $[2M + Na]^+$.

3,7-Anhydro-3-*C*-*t*-butoxycarboxamidomethyl-1,2:4,5-di-*O*-isopropylidene-α-D-glucofuranose (20)

$(Boc)_2O$ (280 μL, 1.3 mmol, 3.5 equiv) was added to a solution of the spiro-aziridine **16** (101 mg, 0.37 mmol) in THF (3 mL). After 24 h at r.t., the solvent was removed in vacuo and the crude product was purified by chromatography (PE–EtOAc, 4:1) to afford the carbamate **20**.

Yield: 69 mg (50%); solid; mp 120–122 °C; $[\alpha]_D$ +1 (*c* 1.06, $CHCl_3$); R_f = 0.42 (PE–EtOAc, 9:1).

IR (film): 1718 (C=O) cm^{-1}.

^1H NMR: δ = 1.31, 1.33, 1.40 (3 × s, 9 H, 3 × CH_3), 1.47 (s, 9 H, *t*Bu), 1.57 (s, 3 H, CH_3), 2.48 (s, 1 H, H-7b), 2.66 (s, 1 H, H-7a), 4.01–4.12 (m, 3 H, H-5, H-6a, H-6b), 4.23 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 4.28 (d, $J_{4–5}$ = 6.0 Hz, 1 H, H-4), 5.93 (d, 1 H, H-1).

^{13}C NMR: δ = 25.2, 26.6, 26.9, 27.1 (4 × CH_3), 28.1 (3 × CH_3-*t*Bu), 29.8 (C-7), 50.9 (C-3), 66.5 (C-6), 74.1 (C-5), 77.4 (C-4), 82.2 (C_{IV-tBu}), 83.0 (C-2), 104.5 (C-1), 109.5, 112.7 (2 × C_{IV}), 159.7 (CO).

MS (IS): *m*/*z* = 372.5 $[M + H]^+$, 389.5 $[M + NH_4]^+$, 761.0 $[2M + NH_4]^+$, 765.5 $[2M + Na]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{29}NO_7Na$: 394.1842; found: 394.1846.

3,7-Anhydro-3-*C*-*p*-toluenesulfonamidomethyl-1,2:4,5-di-*O*-isopropylidene-α-D-glucofuranose (21)

A solution of **16** (105 mg, 0.39 mmol) in THF (4 mL) was treated with TsCl (184 mg, 0.97 mmol, 2.5 equiv) and DIPEA (202 μL, 1.16 mmol, 3 equiv) at r.t. overnight, then heated at 80 °C for 2 h. The product was hydrolysed with H_2O (50 mL), extracted with CH_2Cl_2 (4 × 20 mL), and the organic phase was washed successively with HCl (1 M, 2 × 50 mL), sat. aq $NaHCO_3$ (3 × 20 mL) and brine (2 × 20 mL), then dried over $MgSO_4$ and concentrated in vacuo. Chromatography (PE–EtOAc, 85:15) afforded **21**.

Yield: 80 mg (49%); white solid; mp 94–95 °C; $[\alpha]_D$ –6 (*c* 0.73, $CHCl_3$); R_f = 0.56 (PE–EtOAc, 8:2).

IR (film): 1455 (Ar), 1328 (SO_2) cm^{-1}.

^1H NMR: δ = 1.25 (s, 3 H, CH_3), 1.37 (s, 6 H, 2 × CH_3), 1.57 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3-Ar), 2.61 (s, 1 H, H-7b), 3.11 (s, 1 H, H-7a), 3.95–4.13 (m, 3 H, H-5, H-6a, H-6b), 4.32 (d, $J_{4–5}$ = 6.0 Hz, 1 H, H-4), 5.28 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 5.98 (d, 1 H, H-1), 7.34 (d, J_{vic} = 8.0 Hz, 2 H, ArH), 7.82 (d, 2 H, ArH).

^{13}C NMR: δ = 21.8 (CH_3-Ar), 25.3, 26.6, 26.8, 27.0 (4 × CH_3), 33.8 (C-7), 56.1 (C-3), 66.6 (C-6), 73.7 (C-5), 77.2 (C-4), 80.6 (C-2), 104.8 (C-1), 109.5, 112.8 (C_{IV}), 127.7 (2 × C-Ar), 129.9 (2 × C-Ar), 136.6 (C_{IV-Me}), 144.9 (C_{IV-SO2}).

MS (IS): *m*/*z* = 426.5 $[M + H]^+$, 443.5 $[M + NH_4]^+$, 448.5 $[M + Na]^+$, 475.5 $[M + MeOH + NH_4]^+$, 868.5 $[2M + NH_4]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{27}NO_7SNa$: 448.1406; found: 448.1395.

3,7-Anhydro-3-*C*-*o*-nitrobenzenesulfonamidomethyl-1,2:4,5-di-*O*-isopropylidene-α-D-glucofuranose (22)

Et_3N (737 μL, 5.30 mmol) and *o*-nosyl chloride (878 mg, 3.96 mmol) were successively added to a cooled (ice-bath) THF solution (13 mL) of **16** (359 mg, 1.32 mmol). After stirring at r.t. for 36 h, the mixture was diluted with H_2O (120 mL) and extracted with CH_2Cl_2 (4 × 30 mL). The combined organic phase was washed with H_2O (3 × 20 mL), brine (2 × 20 mL), then dried over $MgSO_4$ and concentrated in vacuo. Chromatography (PE–EtOAc, 75:25) afforded **22**.

Yield: 362 mg (60%); pale-yellow solid; mp 67–70 °C; $[\alpha]_D$ –77 (*c* 0.96, $CHCl_3$); R_f = 0.74 (PE–EtOAc, 6:4).

IR (film): 1546 (NO_2), 1342 (SO_2).

^1H NMR: δ = 1.24, 1.36, 1.38, 1.57 (4 × s, 12 H, 4 × CH_3), 2.96 (s, 1 H, H-7b), 3.33 (s, 1 H, H-7a), 3.95–4.10 (m, 3 H, H-5, H-6a, H-6b), 4.32 (d, $J_{4–5}$ = 6.3 Hz, 1 H, H-4), 5.15 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 6.05 (d, 1 H, H-1), 7.70–7.85 (m, 3 H, ArH), 8.15–8.20 (m, 1 H, ArH).

^{13}C NMR: δ = 26.4, 26.7 (2 × CH_3), 26.8 (2 × CH_3), 36.5 (C-7), 58.1 (C-3), 66.5 (C-6), 73.5 (C-5), 77.4 (C-4), 81.4 (C-2), 104.6 (C-1), 109.5 (C_{IV}), 112.9 (C_{IV}), 124.8 (ArC-3), 130.7 (ArC-6), 132.6 (ArC-4), 134.7 (ArC-5), 141.6 (ArC-1), 148.2 (ArC-2).

MS (IS): *m*/*z* = 457.5 $[M + H]^+$, 474.5 $[M + NH_4]^+$, 479.5 $[M + Na]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{24}N_2O_9SNa$: 479.1100; found: 479.1078.

3,7-Anhydro-3-*C*-methanesulfonamidomethyl-1,2:4,5-di-*O*-isopropylidene-α-D-glucofuranose (23)

Et_3N (271 μL, 1.95 mmol) and MsCl (110 μL, 1.42 mmol) were successively added dropwise to a cooled (–30 °C) solution of **16** (151

mg, 0.56 mmol) in THF (5 mL). The mixture was stirred overnight while slowly reaching r.t., then diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (4 × 30 mL). The combined organic phase was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. Chromatography (PE–EtOAc, 7:3) afforded **23**.

Yield: 186 mg (95%); white solid; mp 123–125 °C; $[\alpha]_D$ –14 (*c* 1.13, $CHCl_3$); R_f = 0.74 (PE–EtOAc, 6:4).

IR (film): 1325, 1153 (SO_2) cm^{-1}.

^1H NMR: δ = 1.31, 1.34, 1.39, 1.55 (4 × s, 12 H, 4 × CH_3), 2.76 (s, 1 H, H-7b), 3.05 (s, 1 H, H-7a), 3.15 (s, 3 H, CH_3SO_2), 4.02–4.14 (m, 3 H, H-5, H-6a, H-6b), 4.23 (d, $J_{4–5}$ = 7.2 Hz, 1 H, H-4), 5.10 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 5.95 (d, 1 H, H-1).

^{13}C NMR: δ = 25.2, 26.4 (2 × CH_3), 26.8 (2 × CH_3), 34.2 (C-7), 41.9 (CH_3SO_2), 55.5 (C-3), 66.8 (C-6), 73.5 (C-5), 77.3 (C-4), 80.6 (C-2), 104.8 (C-1), 109.5, 112.7 (2 × C_{IV}).

MS (IS): *m*/*z* = 350.0 $[M + H]^+$, 367.5 $[M + NH_4]^+$, 372.5 $[M + Na]^+$, 716.5 $[2M + NH_4]^+$, 721.5 $[2M + Na]^+$.

HRMS-ES: *m*/*z* [M + Na] calcd for $C_{14}H_{23}NO_7SNa$: 372.1093; found: 372.1095.

Ring-Opening of Aziridines; General Procedure

AcONa (10 equiv) or NaN_3 (6 equiv) was added to a DMF solution of N-sulfonylated spiro-aziridine. The mixture was stirred at r.t. (NaN_3) or heated at 100 °C (AcONa). After complete conversion, the mixture was diluted with H_2O (150 mL) then extracted with EtOAc (4 × 40 mL). The combined organic phase was washed with brine (3 × 60 mL), dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by silica gel column chromatography.

3-*C*-Acetoxymethyl-3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-*N*-*p*-toluenesulfonamido-α-D-glucofuranose (24)

The N-sulfonylated aziridine **21** (306 mg, 0.72 mmol) was treated with AcONa in DMF (13 mL) for 2.5 h. Chromatography (PE–EtOAc, 75:25) afforded the acetylated derivative **24**.

Yield: 317 mg (91%); gum; $[\alpha]_D$ +14 (*c* 0.73, $CHCl_3$); R_f = 0.32 (PE–EtOAc, 7:3).

IR (film): 3265 (NH), 1739 (COO), 1496, 1455 (Ar), 1335, 1162 (SO_2) cm^{-1}.

^1H NMR: δ = 1.29, 1.30, 1.38, 1.47 (4 × s, 12 H, 4 × CH_3), 1.87 (s, 3 H, CH_3CO_2), 2.43 (s, 3 H, CH_3-Ar), 3.75 (d, $J_{4–5}$ = 8.2 Hz, 1 H, H-4), 3.90 (dd, $J_{6a–6b}$ = 8.5 Hz, J_{6b-5} = 4.7 Hz, 1 H, H-6b), 4.04 (dd, J_{6a-5} = 6.3 Hz, 1 H, H-6a), 4.05–4.15 (m, 1 H, H-5), 4.17 (d, $J_{7a–7b}$ = 11.9 Hz, 1 H, H-7b), 4.51 (d, 1 H, H-7a), 5.11 (d, $J_{2–1}$ = 3.5 Hz, 1 H, H-2), 5.22 (s, 1 H, NH), 5.74 (d, 1 H, H-1), 7.31 (d, J_{vic} = 8.3 Hz, 2 H, ArH), 7.79 (d, 2 H, ArH).

^{13}C NMR: δ = 20.8 (*C*H_3COO), 21.6 (*C*H_3-Ar), 25.0, 26.4, 26.6, 26.8 (4 × CH_3), 63.8 (C-7), 67.9 (C-6), 70.8 (C-3), 73.0 (C-5), 82.4 (C-4), 82.8 (C-2), 105.1 (C-1), 110.1, 112.5 (2 × C_{IV}), 127.1 (2 × C-Ar), 129.7 (2 × C-Ar), 139.5 (C_{IV-Me}), 143.7 (C_{IV-SO2}), 170.7 (COO).

MS (IS): *m*/*z* = 486.5 $[M + H]^+$, 503.5 $[M + NH_4]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{31}NO_9SNa$: 508.1617; found: 508.1616.

3-*C*-Azidomethyl-3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-*N*-*p*-toluenesulfonamido-α-D-glucofuranose (25)

Compound **21** (0.3 g, 0.70 mmol) was treated with NaN_3 in DMF (13 mL) for 3.5 h. Chromatography (PE–EtOAc, 4:1) afforded the azide **25**.

Yield: 305 mg (93%); colourless oil; $[\alpha]_D$ +29 (*c* 0.96, $CHCl_3$); R_f = 0.63 (PE–EtOAc, 7:3).

IR (film): 3264 (NH), 2107 (N_3), 1496, 1455 (Ar), 1335, 1161 (SO_2) cm^{-1}.

^1H NMR: δ = 1.28, 1.31, 1.39, 1.50 (4 × s, 12 H, 4 × CH_3), 2.43 (s, 3 H, CH_3-Ar), 3.59 (d, $J_{7a–7b}$ = 12.9 Hz, 1 H, H-7b), 3.70 (d, 1 H, H-7a), 3.77 (d, $J_{4–5}$ = 8.2 Hz, 1 H, H-4), 3.92 (dd, $J_{6a–6b}$ = 8.5 Hz, $J_{6b–5}$ = 4.7 Hz, 1 H, H-6b), 4.05 (dd, $J_{6a–5}$ = 6.3 Hz, 1 H, H-6a), 4.15 (m, 1 H, H-5), 5.02 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 5.34 (s, 1 H, NH), 5.76 (d, 1 H, H-1), 7.32 (d, J_{vic} = 8.2 Hz, 2 H, ArH), 7.83 (d, 2 H, ArH).

^{13}C NMR: δ = 21.6 (CH_3-Ar), 24.9, 26.2 (2 × CH_3), 26.6 (2 × CH_3), 53.5 (C-7), 67.8 (C-6), 71.2 (C-3), 73.1 (C-5), 82.1 (C-4), 82.7 (C-2), 105.0 (C-1), 110.1, 112.5 (2 × C_{IV}), 127.0 (2 × C-Ar), 129.8 (2 × C-Ar), 139.3 (C_{IV-Me}), 143.8 (C_{IV-SO2}).

MS (IS): *m*/*z* = 469.5 $[M + H]^+$, 486.5 $[M + NH_4]^+$, 491.5 $[M + Na]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{28}N_4O_7SNa$: 491.1576; found: 491.1568.

3-*C*-Acetoxymethyl-3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-*N*-*o*-nitrobenzenesulfonamido-α-D-glucofuranose (26)

The N-sulfonylated aziridine **23** (356 mg, 0.78 mmol) was treated with AcONa in DMF (10 mL) for 80 min. Chromatography (PE–EtOAc, 75:25) afforded the acetylated derivative **26**.

Yield: 235 mg (58%); pale-yellow oil; $[\alpha]_D$ +22 (*c* 0.65, $CHCl_3$); R_f = 0.40 (PE–EtOAc, 6:4).

IR (film): 3356 (NH), 1743 (COO), 1542 (NO_2), 1359 (SO_2) cm^{-1}.

^1H NMR: δ = 1.29, 1.35, 1.38, 1.51 (4 × s, 12 H, 4 × CH_3), 1.76 (s, 3 H, CH_3COO), 3.83 (d, $J_{4–5}$ = 8.5 Hz, 1 H, H-4), 3.86 (dd, $J_{6a–6b}$ = 8.5 Hz, $J_{6b–5}$ = 5.3 Hz, 1 H, H-6b), 3.95 (dd, $J_{6a–5}$ = 6.3 Hz, 1 H, H-6a), 4.05 (m, 1 H, H-5), 4.31 (d, $J_{7a–7b}$ = 12.2 Hz, 1 H, H-7b), 4.52 (d, 1 H, H-7a), 5.23 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 5.98 (d, 1 H, H-1), 6.08 (s, 1 H, NH), 7.74–7.80 (m, 2 H, ArH), 7.90–7.95 (m, 1 H, ArH), 8.10–8.20 (m, 1 H, ArH).

^{13}C NMR: δ = 20.5 (*C*H_3CO_2), 25.1, 26.4, 26.5, 26.8 (4 × CH_3), 63.7 (C-7), 67.9 (C-6), 71.4 (C-3), 72.6 (C-5), 82.8 (C-4), 83.7 (C-2), 105.0 (C-1), 110.3, 112.9 (2 × C_{IV}), 125.5 (ArC-3), 130.4 (ArC-6), 133.2 (ArC-4), 133.7 (ArC-5), 136.2 (ArC-1), 147.8 (ArC-2), 170.0 (COO).

MS (IS): *m*/*z* = 534.5 $[M + NH_4]^+$, 549.5 [M + MeOH + H]$^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{28}N_2O_{11}SNa$: 539.1312; found: 539.1308.

De-O-acetylation; General Procedure

A solution of MeONa (0.8 equiv) in MeOH was added to a cooled solution of the acetylated compound in MeOH. After the transformation, Amberlite® IR120 was added to neutrality, the solution was filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography.

3-Deoxy-3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-3-*N*-*p*-toluenesulfonamido-α-D-glucofuranose (29)

Compound **24** (316 mg, 0.65 mmol) was methanolated in MeOH (10 mL) for 1.5 h. Chromatography (PE–EtOAc, 3:2) afforded the alcohol **29**.

Yield: 280 mg (97%); solid; mp 57–60 °C; $[\alpha]_D$ +10 (*c* 0.20, $CHCl_3$); R_f = 0.51 (PE–EtOAc, 6:4).

IR (film): 3455 (NH, OH), 1455 (Ar), 1331, 1161 (SO_2) cm^{-1}.

^1H NMR: δ = 1.25, 1.29, 1.40, 1.46 (4 × s, 12 H, 4 × CH_3), 2.43 (s, 3 H, CH_3-Ar), 3.34 (dd, $J_{OH–7b}$ = 11.6 Hz, $J_{OH–7a}$ = 2.8 Hz, 1 H, OH), 3.70 (dd, $J_{7a–7b}$ = 12.2 Hz, 1 H, H-7b), 3.76–3.83 (m, 2 H, H-4, H-7a), 3.93–4.02 (m, 3 H, H-5, H-6a, H-6b), 5.06 (d, $J_{2–1}$ = 3.5 Hz, H-2), 5.66 (s, 1 H, NH), 5.82 (d, 1 H, H-1), 7.32 (d, J_{vic} = 8.2 Hz, 2 H, ArH), 7.79 (d, 2 H, ArH).

^{13}C NMR: δ = 21.5 (CH_3-Ar), 24.9, 26.0 (2 × CH_3), 26.4 (2 × CH_3), 62.3 (C-7), 67.8 (C-6), 70.2 (C-3), 71.6 (C-5), 83.8 (C-4, C-2),

104.6 (C-1), 110.2, 112.3 (2 × C_{IV}), 127.0 (2 × C-Ar), 129.6 (2 × C-Ar), 139.3 ($C_{IV\text{-}Me}$), 143.7 ($C_{IV\text{-}SO2}$).

MS (IS): *m*/*z* = 444.5 $[M + H]^+$, 461.5 $[M + NH_4]^+$, 466.5 $[M + Na]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{29}NO_8SNa$: 466.1512; found: 466.1498.

3-Deoxy-3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-3-*N*-*o*-nitrobenzenesulfonamido-α-D-glucofuranose (30)

Compound **26** (404 mg, 0.78 mmol) in MeOH (9 mL) was methanolated for 3 h. Chromatography (PE–EtOAc, 1:1) afforded the alcohol **30**.

Yield: 342 mg (92%); pale-yellow amorphous solid; $[\alpha]_D$ +14 (*c* 0.70, $CHCl_3$); R_f = 0.35 (PE–EtOAc, 6:4).

IR (film): 3436 (NH), 3322 (OH), 1539 (NO_2), 1360 (SO_2) cm^{-1}.

^1H NMR: δ = 1.26, 1.33, 1.38, 1.50 (4 × s, 12 H, 4 × CH_3), 3.34 (dd, $J_{OH–7b}$ = 11.6 Hz, $J_{OH–7a}$ = 2.8 Hz, 1 H, OH), 3.81–4.00 (m, 6 H, H-4, H-6a, H-6b, H-5, H-7a, H-7b), 5.19 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 6.01 (d, 1 H, H-1), 6.24 (s, 1 H, NH), 7.72–7.77 (m, 2 H, ArH), 7.87–7.92 (m, 1 H, ArH), 8.12–8.18 (m, 1 H, ArH).

^{13}C NMR: δ = 25.0, 26.1 (2 × CH_3), 26.6 (2 × CH_3), 61.9 (C-7), 68.1 (C-6), 71.3 (C-5), 71.8 (C-3), 83.9 (C-4), 85.2 (C-2), 104.8 (C-1), 110.6, 112.7 (2 × C_{IV}), 125.3 (ArC-3), 130.7 (ArC-6), 132.9 (ArC-4), 133.6 (ArC-5), 136.1 (ArC-1), 147.7 (ArC-2).

MS (IS): *m*/*z* = 475.5 $[M + H]^+$, 492.5 $[M + NH_4]^+$, 524.5 $[M + MeOH + NH_4]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{26}N_2O_{10}SNa$: 497.1206; found: 497.1202.

3-Deoxy-3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-3-*N*-*o*-nitrobenzenesulfonamido-α-D-allofuranose (32)

Compound **28** (1.4 g, 2.71 mmol) was methanolated in MeOH (30 mL) for 4.5 h. Chromatography (PE–EtOAc, 1:1) afforded the alcohol **32**.

Yield: 1.22 g (95%); white solid; $[\alpha]_D$ +18 (*c* 0.22, $CHCl_3$); mp 117–119 °C; R_f = 0.36 (PE–EtOAc, 1:1).

IR (film): 3353 (NH, OH), 1542 (NO_2), 1359 (SO_2) cm^{-1}.

^1H NMR: δ = 1.10, 1.12, 1.38, 1.56 (4 × s, 12 H, 4 × CH_3), 2.73 (br s, 1 H, OH), 3.76 (d, $J_{4–5}$ = 9.4 Hz, 1 H, H-4), 3.82–4.01 (m, 3 H, H-6b, H-7a, H-7b), 4.13–4.28 (m, 2 H, H-6a, H-5), 4.85 (d, $J_{2–1}$ = 3.5 Hz, 1 H, H-2), 5.71 (d, 1 H, H-1), 6.29 (s, 1 H, NH), 7.67–7.73 (m, 2 H, ArH), 7.88–7.94 (m, 1 H, ArH), 8.15–8.20 (m, 1 H, ArH).

^{13}C NMR: δ = 25.1 (CH_3), 26.3 (2 × CH_3), 26.4 (CH_3), 63.5 (C-7), 68.5 (C-6), 69.0 (C-3), 72.8 (C-5), 81.5 (C-4), 82.2 (C-2), 104.7 (C-1), 110.7, 112.2 (2 × C_{IV}), 125.1 (ArC-3), 130.8 (ArC-6), 132.2 (ArC-4), 132.9 (ArC-5), 136.8 (ArC-1), 147.4 (ArC-2).

MS (IS): *m*/*z* = 475.5 $[M + H]^+$, 492.5 $[M + NH_4]^+$, 524.5 $[M + MeOH + NH_4]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{26}N_2O_{10}SNa$: 497.1206; found: 497.1218.

3-*C*-Chloromethyl-3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-*N*-*o*-nitrobenzenesulfonamido-α-D-allofuranose (27)

A cooled solution (–78 °C) of spiro-aziridine **18** (745 mg, 2.74 mmol) in CH_2Cl_2 (40 mL), was treated with Et_3N (1.3 mL, 9.35 mmol) and *o*-nitrobenzenesulfonyl chloride (1.03 g, 4.65 mmol) and allowed to slowly come to r.t. overnight. After dilution with CH_2Cl_2 (50 mL), the organic phase was washed with H_2O (2 × 100 mL), then brine (1 × 50 mL), dried over $MgSO_4$ and concentrated in vacuo. Chromatography (PE–EtOAc, 75:25) afforded **27**.

Yield: 921 mg (68%); pale-yellow solid; mp 66–68 °C; $[\alpha]_D$ +111 (*c* 0.85, $CHCl_3$); R_f = 0.56 (PE–EtOAc, 6:4).

IR (film): 3347 (NH), 1542 (NO_2), 1357 (SO_2) cm^{-1}.

^1H NMR: δ = 1.07, 1.19, 1.40, 1.57 (4 × s, 12 H, 4 × CH_3), 3.80 (d, $J_{4–5}$ = 9.7 Hz, 1 H, H-4), 3.87 (dd, $J_{6a–6b}$ = 8.8 Hz, $J_{6b–5}$ = 5.6 Hz, 1 H, H-6b), 3.89 (d, $J_{7a–7b}$ = 12.2 Hz, 1 H, H-7b), 4.05 (d, 1 H, H-7a), 4.20 (dd, J_{6a-5} = 6.3 Hz, 1 H, H-6a), 4.28–4.39 (m, 1 H, H-5), 4.91 (d, $J_{2–1}$ = 3.5 Hz, 1 H, H-2), 5.80 (d, 1 H, H-1), 6.30 (s, 1 H, NH), 7.67–7.73 (m, 2 H, ArH), 7.87–7.93 (m, 1 H, ArH), 8.13–8.17 (m, 1 H, ArH).

^{13}C NMR: δ = 25.0, 26.3 (2 × CH_3), 26.4 (2 × CH_3), 43.6 (C-7), 68.3 (C-3), 68.4 (C-6), 72.6 (C-5), 82.9 (C-4), 83.4 (C-2), 105.3 (C-1), 110.8, 112.7 (2 × C_{IV}), 125.1 (ArC-3), 130.7 (ArC-6), 132.2 (ArC-4), 132.9 (ArC-5), 137.0 (ArC-1), 147.3 (ArC-2).

MS (IS): *m*/*z* = 494.0 $[M + H]^+$, 510.5 $[M + NH_4]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{25}ClN_2O_9SNa$: 515.0867; found: 515.0853.

3-*C*-Acetoxymethyl-3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-*N*-*o*-nitrobenzenesulfonamido-α-D-allofuranose (28)

Compound **27** (1.42 g, 2.88 mmol) in DMF (40 mL) was treated with anhydrous AcONa (2.03 g, 24.7 mmol) at r.t. for 105 min. After hydrolysis with H_2O (350 mL), the resulting solution was extracted with EtOAc (4 × 80 mL). The combined organic phases were washed with brine (3 × 100 mL), dried over $MgSO_4$ then concentrated in vacuo. Chromatography (PE–EtOAc, 1:1) afforded acetate **28**.

Yield: 1.426 g (96%); solid; mp 138–140 °C; $[\alpha]_D$ +80 (*c* 0.81, $CHCl_3$); R_f = 0.42 (PE–EtOAc, 1:1).

IR (film): 3348 (NH), 1746 (COO), 1542 (NO_2), 1360 (SO_2) cm^{-1}.

^1H NMR: δ = 1.14, 1.18, 1.35, 1.54 (4 × s, 12 H, 4 × CH_3), 1.97 (s, 3 H, CH_3COO), 3.76 (d, $J_{4–5}$ = 9.1 Hz, 1 H, H-4), 3.79 (dd, $J_{6a–6b}$ = 8.2 Hz, $J_{6b–5}$ = 5.3 Hz, 1 H, H-6b), 4.00–4.10 (m, 1 H, H-5), 4.14 (dd, $J_{6a–5}$ = 6.3 Hz, 1 H, H-6a), 4.28 (d, $J_{7a–7b}$ = 11.9 Hz, 1 H, H-7b), 4.41 (d, 1 H, H-7a), 4.81 (d, $J_{2–1}$ = 3.5 Hz, 1 H, H-2), 5.68 (d, 1 H, H-1), 6.32 (s, 1 H, NH), 7.64–7.70 (m, 2 H, ArH), 7.84–7.90 (m, 1 H, ArH), 8.10–8.17 (m, 1 H, ArH).

^{13}C NMR: δ = 20.6 (CH_3COO), 25.1 (CH_3), 26.3 (3 × CH_3), 63.0 (C-7), 67.3 (C-6), 68.7 (C-3), 72.8 (C-5), 82.0 (C-4), 82.3 (C-2), 104.7 (C-1), 110.6, 112.5 (2 × C_{IV}), 125.0 (ArC-3), 130.5 (ArC-6), 132.3 (ArC-4), 132.8 (ArC-5), 137.1 (ArC-1), 147.3 (ArC-2), 170.1 (*C*OO).

MS (IS): *m*/*z* = 517.5 $[M + H]^+$, 534.5 $[M + NH_4]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{28}N_2O_{11}SNa$: 539.1312; found: 539.1316.

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-3,5′-spiro(1′-*N*-*p*-toluenesulfonyl-1′,3′-imidazolidine-2′-thione)-α-D-glucofuranose (31)

An anhydrous 1,4-dioxane (5 mL) solution containing CS_2 (280 μL, 4.7 mmol), azide **25** (115 mg, 0.25 mmol) and Ph_3N (71 mg, 0.27 mmol) was heated for 2 h at 85 °C. After removal of the solvent, the crude product was purified by chromatography (PE–EtOAc, 7:3) to afford the imidazolidinethione **31**.

Yield: 79 mg (65%); solid; mp 102–105 °C; $[\alpha]_D$ –43 (*c* 1.1, $CHCl_3$); R_f = 0.56 (PE–EtOAc, 6:4).

IR (film): 3374 (NH), 1534, 1259 (N–CS–N), 1494, 1455 (Ar), 1322, 1165 (SO_2) cm^{-1}.

^1H NMR: δ = 1.22, 1.37, 1.38, 1.51 (4 × s, 12 H, 4 × CH_3), 2.44 (s, 3 H, CH_3-Ar), 3.53 (d, $J_{7a–7b}$ = 11.3 Hz, 1 H, H-7b), 3.90 (d, $J_{4–5}$ = 8.8 Hz, 1 H, H-4), 3.94 (dd, $J_{6a–6b}$ = 8.5 Hz, $J_{6b–5}$ = 6.0 Hz, 1 H, H-6b), 4.04 (dd, $J_{6a–5}$ = 6.0 Hz, 1 H, H-6a), 4.07 (d, $J_{7b–7a}$ = 11.3 Hz, 1 H, H-7a), 4.18 (dt, 1 H, H-5), 5.33 (d, $J_{2–1}$ = 3.8 Hz, 1 H, H-2), 6.21 (d, 1 H, H-1), 6.99 (s, 1 H, NH), 7.30 (d, J_{vic} = 8.2 Hz, 2 H, ArH), 8.02 (d, 2 H, ArH).

^{13}C NMR: δ = 21.8 (CH_3-Ar), 25.1, 26.2, 26.6, 26.9 (4 × CH_3), 47.9 (C-7), 68.0 (C-6), 72.9 (C-5), 81.3 (C-4), 85.4 (C-3), 86.8 (C-2), 106.3 (C-1), 110.0, 111.8 (2 × C_{IV}), 129.1 (2 × ArC), 129.8 (2 × ArC), 136.3 ($C_{IV\text{-}Me}$), 145.1 ($C_{IV\text{-}SO2}$), 180.9 (CS).

MS (IS): *m*/*z* = 485.5 $[M + H]^+$, 502.5 $[M + NH_4]^+$.

HRMS-ES: *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{28}N_2O_7S_2$: 485.1416; found: 485.1424.

N-Deprotection of *o*-Nitrobenzenesulfonamides; General Procedure

A solution of the sulfonamide with thiophenol (3 equiv) and anhydrous K_2CO_3 (4 equiv) in MeCN was heated at 60 °C overnight. After cooling to r.t., the mixture was filtered on a silica gel pad, which was then rinsed with MeOH. The combined organic phase was concentrated in vacuo and the crude product was purified by column chromatography on silica gel.

3-Amino-3-deoxy-3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (33)

The sulfonamide **30** (138 mg, 0.29 mmol) in MeCN (5 mL) was treated with thiophenol (90 μL, 0.88 mmol) and K_2CO_3 (161 mg, 1.16 mmol). Chromatography (CH_2Cl_2–MeOH, 19:1) afforded the amino-alcohol **33**.

Yield: 67 mg (80%); solid; mp 106–107 °C; $[\alpha]_D$ +26 (*c* 0.42, $CHCl_3$).

IR (film): 3456 (NH_2, OH), 1599 (NH_2) cm^{-1}.

^{1}H NMR: δ = 1.31, 1.36, 1.43, 1.52 (4 × s, 12 H, 4 × CH_3), 1.99 (br s, 3 H, OH, NH_2), 3.70–3.85 (m, 2 H, H-7a, H-7b), 3.81 (d, J_{4-5} = 8.8 Hz, 1 H, H-4), 4.00–4.09 (m, 1 H, H-5), 4.10–4.22 (m, 2 H, H-6a, H-6b), 4.28 (d, J_{2-1} = 3.8 Hz, 1 H, H-2), 5.84 (d, 1 H, H-1).

^{13}C NMR: δ = 25.2, 26.4, 26.7, 27.0 (4 × CH_3), 64.4 (C-7), 65.2 (C-3), 68.3 (C-6), 72.4 (C-5), 82.9 (C-4), 87.9 (C-2), 104.5 (C-1), 109.9, 112.6 (2 × C_{IV}).

MS (IS): *m*/*z* = 290.5 $[M + H]^+$, 322.5 $[M + MeOH + H]^+$.

HRMS-ES: *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{24}NO_6$: 290.1604; found: 290.1604.

3-Amino-3-deoxy-3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (34)

The sulfonamide **32** (1.206 g, 2.54 mmol) in MeCN (42 mL) was treated with thiophenol (835 μL, 8.13 mmol) and K_2CO_3 (1.58 g, 11.43 mmol). Chromatography (CH_2Cl_2–MeOH, 96:4) afforded the amino-alcohol **34**.

Yield: 695 mg (95%); colourless oil; $[\alpha]_D$ +18 (*c* 0.22, $CHCl_3$).

IR (film): 3372 (NH_2, OH), 1586 (NH_2) cm^{-1}.

^{1}H NMR: δ = 1.34 (s, 6 H, 2 × CH_3), 1.44, 1.56 (2 × s, 6 H, 2 × CH_3), 2.20 (br s, 3 H, OH, NH_2), 3.39 (d, J_{7a-7b} = 11.0 Hz, 1 H, H-7b), 3.72 (d, J_{4-5} = 9.1 Hz, 1 H, H-4), 3.73 (d, 1 H, H-7a), 3.89 (dd, J_{6a-6b} = 8.5 Hz, J_{6b-5} = 5.0 Hz, 1 H, H-6b), 3.98–4.06 (m, 1 H, H-5), 4.12 (dd, J_{6a-5} = 6.0 Hz, 1 H, H-6a), 4.58 (d, J_{2-1} = 3.8 Hz, 1 H, H-2), 5.76 (d, 1 H, H-1).

^{13}C NMR: δ = 25.2, 26.3, 26.8, 26.9 (4 × CH_3), 61.9 (C-7), 64.4 (C-3), 68.8 (C-6), 73.5 (C-5), 81.9 (C-4), 82.9 (C-2), 104.0 (C-1), 109.8, 112.2 (2 × C_{IV}).

MS (IS): *m*/*z* = 290.5 $[M + H]^+$, 322.5 $[M + MeOH + H]^+$.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{23}NO_6Na$: 312.1423; found: 312.1426.

Conversion of Amino Alcohols into Spiro-oxazolidinethiones; General Procedure

The β-amino alcohol, $CaCO_3$ and thiophosgene were dissolved in H_2O–acetone (1:1), and stirred at r.t. overnight. The mixture was filtered over a Celite® pad, which was then washed with acetone. After evaporation of the solvent, the residue was purified by chromatography on silica gel.

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-3,4′-spiro(1′,3′-oxazolidine-2′-thione)-α-D-glucofuranose (35)

The amino alcohol **33** (142 mg, 0.49 mmol) was treated with thiophosgene (94 μL, 1.23 mmol) and $CaCO_3$ (428 mg, 4.27 mmol) in H_2O–acetone (1:1, 10 mL). Chromatography (PE–EtOAc, 65:35) afforded the *endo*-spiro-OZT **35**.

Yield: 127 mg (78%); solid; mp 71–74 °C; $[\alpha]_D$ +13 (*c* 1.16, $CHCl_3$); R_f = 0.48 (PE–EtOAc, 65:35).

IR (film): 3148 (NH), 1520, 1164 (O-CS-N) cm^{-1}.

^{1}H NMR: δ = 1.29, 1.31, 1.40, 1.47 (4 × s, 12 H, 4 × CH_3), 3.79 (d, J_{4-5} = 8.8 Hz, 1 H, H-4), 3.95 (dd, J_{6a-6b} = 8.5 Hz, J_{6b-5} = 4.7 Hz, 1 H, H-6b), 4.12 (dd, J_{6a-5} = 6.3 Hz, 1 H, H-6a), 4.15–4.25 (m, 1 H, H-5), 4.53 (d, J_{2-1} = 3.5 Hz, 1 H, H-2), 4.74 (d, J_{7a-7b} = 9.6 Hz, 1 H, H-7b), 4.86 (d, 1 H, H-7a), 5.85 (d, 1 H, H-1), 9.48 (s, 1 H, NH).

^{13}C NMR: δ = 25.0, 26.3, 26.6, 26.8 (4 × CH_3), 67.8 (C-6), 72.3 (C-7), 72.4 (C-3), 73.0 (C-5), 80.0 (C-4), 84.7 (C-2), 104.2 (C-1), 110.1, 113.1 (2 × C_{IV}), 190.1 (CS).

MS (IS): *m*/*z* = 332.5 $[M + H]^+$, 349.0 $[M + NH_4]^+$.

Anal. Calcd for $C_{14}H_{21}NO_6S$: C, 50.74; H, 6.39; N, 4.23; S, 9.68. Found: C, 51.01; H, 6.44; N, 4.10; S, 9.25.

HRMS-ES: *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{22}NO_6S$: 332.1168; found: 332.1177.

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-3,4′-spiro(1′,3′-oxazolidine-2′-thione)-α-D-allofuranose (36)

The amino alcohol **34** (53 mg, 0.183 mmol) was treated with thiophosgene (38 μL, 0.5 mmol) and $CaCO_3$ (165 mg, 1.65 mmol) in H_2O–acetone (1:1, 3.5 mL). Chromatography (PE–EtOAc, 3:2) afforded the the *endo*-spiro-OZT **36**.

Yield: 43 mg (70%); solid; mp 242–244 °C; $[\alpha]_D$ +116 (*c* 1.04, $CHCl_3$); R_f = 0.38 (PE–EtOAc, 6:4).

IR (film): 3266 (NH), 1504, 1163 (O–CS–N) cm^{-1}.

^{1}H NMR: δ = 1.33, 1.35, 1.46, 1.58 (4 × s, 12 H, 4 × CH_3), 3.85 (d, J_{4-5} = 7.9 Hz, 1 H, H-4), 3.97 (dd, J_{6a-6b} = 11.6 Hz, J_{6b-5} = 6.9 Hz, 1 H, H-6b), 4.13–4.21 (m, 2 H, H-6a, H-5), 4.36 (d, J_{7a-7b} = 9.7 Hz, 1 H, H-7b), 4.50 (d, J_{2-1} = 3.8 Hz, 1 H, H-2), 4.87 (d, 1 H, H-7a), 5.74 (d, 1 H, H-1), 7.68 (s, 1 H, NH).

^{13}C NMR: δ = 25.0, 26.4, 26.6, 26.8 (4 × CH_3), 68.4 (C-6), 70.8 (C-3), 73.0 (C-7), 73.4 (C-5), 78.1 (C-4), 84.6 (C-2), 103.1 (C-1), 110.5, 113.9 (2 × C_{IV}), 189.4 (CS).

MS (IS): *m*/*z* = 332.5 $[M + H]^+$, 349.0 $[M + NH_4]^+$.

Anal. Calcd for $C_{14}H_{21}NO_6S$: C, 50.74; H, 6.39; N, 4.23; S, 9.68. Found: C, 50.64; H, 6.34; N, 4.16; S, 9.32.

HRMS-ES: *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{21}NO_6SNa$: 354.0987; found: 354.0976.

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