A New Route to *exo*-Glycals Using the Ramberg−Bäcklund Rearrangement

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Dedicated to Professor Jean-François Normant on the occasion of his 65th birthday

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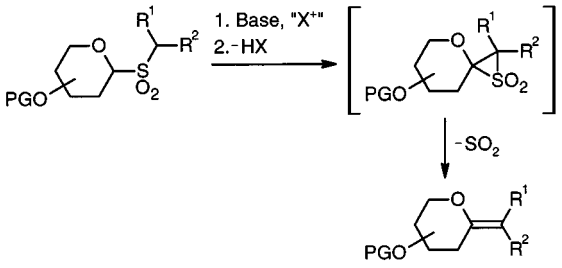
A new route to *exo*-glycals **4** is described in which glycosyl sulfones **3** are subjected to the Meyers variant of the Ramberg–Bäcklund rearrangement. The conversion of sulfones derived from glucose, galactose, mannose, cellobiose, and ribose into di-, tri-, and tetra-substituted alkenes is reported. Preliminary mechanistic studies of this process are also described.

Introduction

The discovery of the fundamental roles played by oligosaccharides, and their lipid and protein conjugates, at a molecular level has stimulated the enormous growth in carbohydrate research over the last three decades.[1] Crucial to the expansion of knowledge in this area has been the contribution of synthetic chemists in providing practical quantities of pure, naturally occurring carbohydrates and, perhaps more significantly, chemically modified mono- and oligosaccharides. Particularly useful in this context are *exo*-glycals (formally 2,5- or 2,6-anhydro-1-deoxy-hex- or -hept-1-enitols) which are not only valuable in biological investigations per se,[2] but are also important synthetic intermediates owing to the scope of the enol ether functional group for further elaboration.[3] Herein we present a novel synthetic route to *exo*-glycals employing the Ramberg−Bäcklund rearrangement[4,5] as the key step.

The methods for *exo*-glycal synthesis may be divided into two main categories: those in which the carbon skeleton is constructed first and then subjected to an elimination reaction,[6] and those in which unsaturation is incorporated during C−C bond formation such as in the olefination of sugar lactones using the Tebbe[7] or Petasis[8] reagent, or Wittig chemistry.[9] In a novel route recently reported by Tóth and Somsák,[10] 2,5- and 2,6-anhydroaldose tosylhydrazones are transformed, in a Bamford−Stevens reaction, into glycosylmethyl carbenes, which then undergo a spontaneous 1,2-hydrogen shift to give *exo*-methylenic sugar derivatives.

The ease of preparation and the chemical stability of alkyl and aryl thioglycosides, combined with their ready activation to the corresponding sulfonium species, has resulted in their routine application as glycosyl donors in *O*-glycoside synthesis.[11] The use of thioglycoside derivatives as precursors to glycosyl anions has also been extensively investigated, and is among the many approaches described in a recent review on this subject.[12] Due to the long-standing interest in sulfone and Ramberg−Bäcklund chemistry within our own research group,[13] we also recognised the potential of such compounds: we envisaged a thioglycoside *S*,*S*-dioxide (glycosyl sulfone) being subjected to a Ramberg−Bäcklund rearrangement to introduce an *exo*-C−C double bond at the anomeric position (Scheme 1). Initial studies established that this was indeed a feasible transformation, the scope of which appeared considerable with regard to both the saccharide and aglycon portions.[14] Shortly after we disclosed our own results, similar findings were reported by Belica and Franck.[15] In the following sections the synthesis of a variety of glycosyl sulfones and their conversion into *exo*-glycals are described.



Scheme 1. Generic representation of the transformation of glycosyl sulfones into *exo*-glycals via a Ramberg−Bäcklund rearrangement. PG = protecting group

Results and Discussion

Synthesis of Glycosyl Sulfones

Thioglycosides may be conveniently prepared from a variety of common glycosyl donors, for example from the

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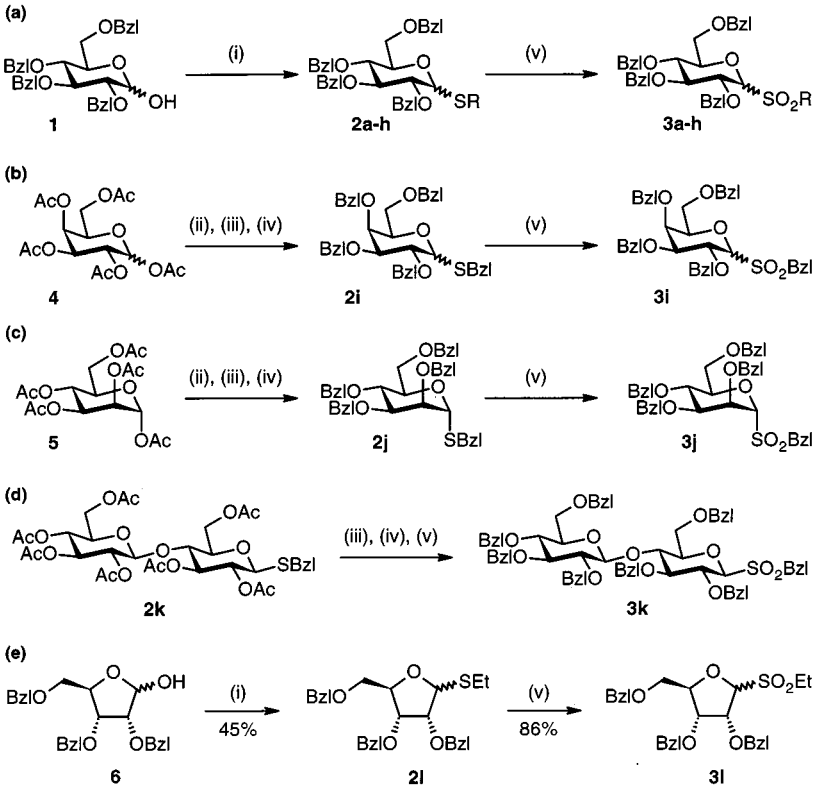
reaction of glycosyl esters with mercaptans in the presence of a Lewis acid such as $SnCl_4$,[16] by nucleophilic substitution of glycosyl halides[17] by thiolates or xanthate salts[18] or from hemiacetals using disulfides, and a trialkylphosphane in a Mitsunobu-like process.[19,20] Our initial studies, which were designed to explore the scope of the aglycon in our methodology, were conducted on benzyl-protected glucose derivatives (Scheme 2, a, and Table 1). Commencing with tetra-*O*-benzyl-D-glucose (**1**), thioglycosylation with a variety of thiols was accomplished using a modification of Suzaki's zinc triflate-mediated procedure[21] to prepare *S*-glycosides **2b−h** as mixtures of α- and β-anomers, which were separated and characterised individually. For the preparation of the methyl thioglycosides **2aα** and **2aβ**, the method reported by Landry and co-workers[19] using dimethyl disulfide was employed in order to avoid handling the toxic and volatile (b.p. 6 °C) methanethiol. We then extended the range of substrates in our study to include other monosaccharides. The thioglycosides **2i** and **2j** were prepared from peracetylated galactose (**4**) and mannose (**5**), respectively, by boron trifluoride-mediated thioglycosylation, followed by deacetylation and benzylation (Scheme 2, b and c). Thiocellobioside **2k** was prepared from the corresponding acetyl-protected glycosyl bromide according to the method of Durette and Shen,[22] and thioriboside **2l** was prepared from 2,3,5-tri-*O*-benzyl-D-ribofuranose[23] (**6**) by using Suzaki's method (Scheme 2, d and e).[21] Sulfur oxidation of these derivatives was achieved in most cases by reaction with Oxone® in aqueous acetone to give the corresponding sulfones **3**. For the more sterically demanding benzhydryl sulfide **2g**, peroxyacetic acid was required to obtain a satisfactory yield of the sulfone, and for the adamantyl derivative **2h**,[24] *meta*-chloroperoxybenzoic acid (mCPBA) was used as the oxidant.

Table 1. Summary of the thioglycosides and glycosyl sulfones synthesised according to Scheme 2; Cy = cyclohexyl; Adam = adamant-2-yl

Entry	Saccharide	Aglycon	Yield	
			2 (α/β)	**3**
a	D-Glucose	Me	71 (3:1)	82
b	D-Glucose	Et	47 (3:1)	80
c	D-Glucose	Pr	82 (3:1)	83
d	D-Glucose	Bzl	85 (2:1)	87
e	D-Glucose	*i*Pr	53 (4:1)	87
f	D-Glucose	Cy	68 (3:1)	85
g	D-Glucose	$CHPh_2$	76 (4:1)	73
h	D-Glucose	Adam[a]	–	69
i	D-Galactose	Bzl	42[b] (1:5)	84
j	D-Mannose	Bzl	41[c] (α only)	93
k	Cellobiose	Bzl	19[d] (β only)	95
l	D-Ribose	Et	45	86

[a] In this example adamant-2-yl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-glucopyranoside was used. [b] Overall yield from **4**. [c] Overall yield from **5**. [d] Overall yield from cellobiose octaacetate.



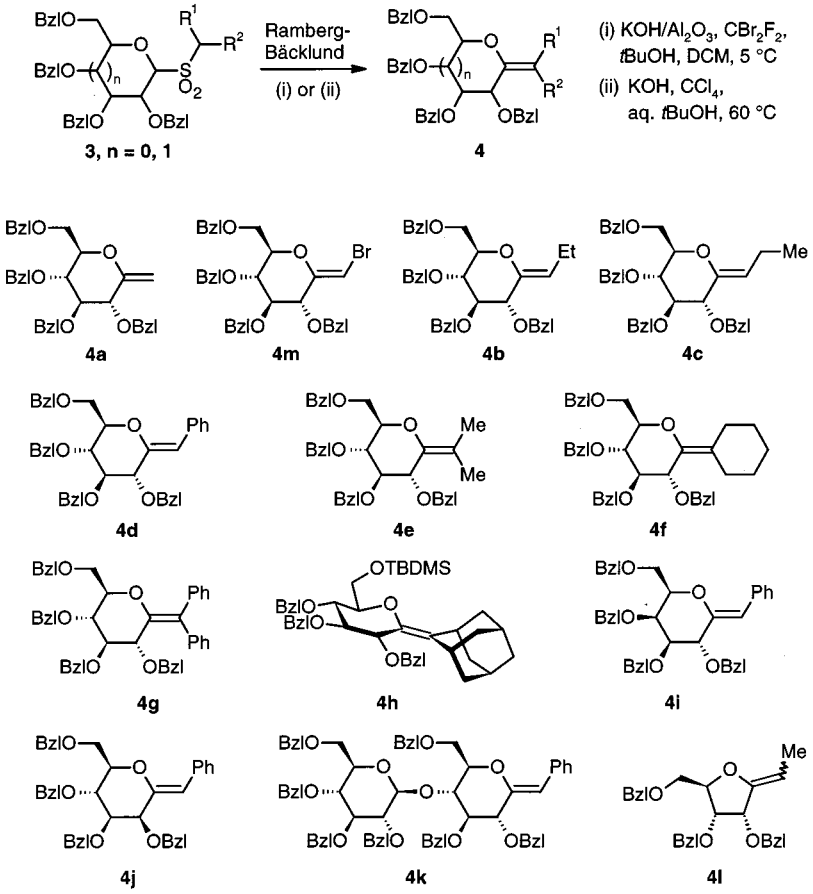
Scheme 2. (i) R ≠ Me, Me_3SiCl, $Zn(OTf)_2$, RSH, MeCN, 40 °C; R = Me, MeSSMe, $BF_3{\cdot}OEt_2$, MeCN; (ii) BzlSH, $BF_3{\cdot}OEt_2$, DCM; (iii) MeONa, MeOH; (iv) NaH, BzlBr, DMF; (v) R ≠ $CHPh_2$, Adam, Oxone,® acetone, H_2O, reflux; R = $CHPh_2$, H_2O_2, AcOH; R = Adam, mCPBA, $NaHPO_4$, DCM. Adam = adamant-2-yl, Bzl = benzyl; DCM = dichloromethane; mCPBA = *meta*-chloroperoxybenzoic acid

Ramberg−Bäcklund Rearrangement of Glycosyl Sulfones

Exposure of glycosyl sulfones **3a−l** to the tandem halogenation-Ramberg−Bäcklund conditions developed by Meyers[25] (KOH, CCl_4, aq. *t*BuOH, 60 °C) or Chan[26] (alumina-supported KOH, CBr_2F_2, *t*BuOH), in which α-sulfonyl halogenation occurs in situ, yielded *exo*-glycals in all cases, as shown in Scheme 3 and Table 2. When the rearrangement of **3a** was carried out using Chan's conditions, the *exo*-methylenic sugar **4a** was accompanied by 15−32% of vinyl bromide **4m** (R^1 = Br, R^2 = H), probably as a result of *gem*-dibromination of the starting material followed by Ramberg−Bäcklund rearrangement. No vinyl halide was detected when Meyers' Method was employed. The tri-substituted olefinic products **4b−d** and **4c−k** were obtained in good to excellent yield using Chan's procedure, with the (*Z*)-isomer predominating in most cases. Stereochemical assignment was based on the trend that the vinylic protons of (*Z*)-*exo*-glycals resonate at lower field in the ^{1}H NMR spectrum than those in the corresponding (*E*)-isomers.[27] The more sterically hindered tetra-substituted alkenes **4e−h** could only be formed under the more forcing Meyers conditions, and although the yields in these cases are significantly lower, the availability of fully substituted alkenes using this methodology, particularly the constrained adamantylidene derivative **4h**, is noteworthy. As expected from a stereospecific process, the stereochemistry of the olefin product is influenced by the configuration of the starting sulfone. Thus a higher proportion of the (*Z*)-alkene was obtained from the α-anomer **3dα** than from the β-anomer **3dβ**, perhaps reflecting the relative ease of formation of the (*pro*-*Z*) and (*pro*-*E*) episulfones in these cases.

As well as being useful intermediates, *exo*-glycals are of interest in their own right as tools for the study of glycosidase action[2] and, as such, must be accessible in their fully deprotected form. The hydrogenolytic conditions required for the cleavage of the benzyl ethers in products **4a−l** would also undoubtedly effect the reduction of the enol ether moiety, and hence a different protection strategy was examined (Scheme 4).

Acid-catalysed thioglycosylation of α-D-glucose pentaacetate, followed by oxidation, gave the known β-*S*-glycoside dioxide **8**.[28] Zemplén deacetylation and subsequent reprotection using *tert*-butyldimethylsilyl triflate/2,6-lutidine furnished the tetra-*O*-silylated sulfone **9** in excellent yield. Pleasingly, this material readily underwent Ramberg−Bäcklund rearrangement upon application of the Chan conditions to give a 69% yield of enol ether **10** as a 89:11 (*Z*)/(*E*) isomeric mixture. Smooth desilylation was then accomplished using tetra-*n*-butylammonium fluoride (TBAF) producing the desired tetraol **11**, which was converted into its crystalline tetraacetate derivative **12** {mp 112−113 °C. $[\alpha]_D^{20}$ = +109.8 (*c* = 1.0, $CHCl_3$)} for charac-

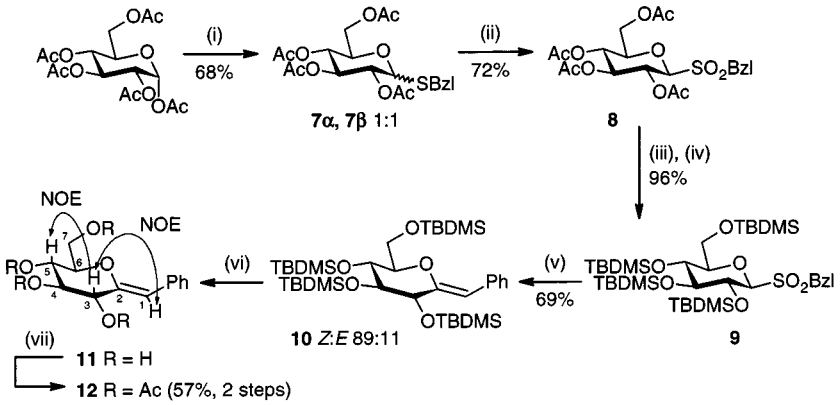


Scheme 3. The scope of the Ramberg−Bäcklund rearrangement of glycosyl sulfones

Table 2. Summary of Ramberg−Bäcklund rearrangements of glycosyl sulfones **3** to give *exo*-glycals **4**

Sulfone	Saccharide	R^1	R^2	α/β	Conditions	Yield of **4**	(*Z*)/(*E*)
3a	D-Glucose	H	H	3:1	(i)	54[a]	–
				3:1	(ii)	72	–
3b	D-Glucose	Me	H	4:1	(i)	75	80:20
3c	D-Glucose	Et	H	4:1	(i)	71	92:8
3d	D-Glucose	Ph	H	4:1	(i)	83	88:12
					(ii)	56	88:12
3dα	D-Glucose	Ph	H	α only	(i)	62[b]	94:6
3dβ	D-Glucose	Ph	H	β only	(i)	61	79:21
3e	D-Glucose	Me	Me	3:1	(ii)	51	–
3f	D-Glucose	cyclohexyl		4:1	(ii)	32	–
3g	D-Glucose	Ph	Ph	4:1	(i)	57	–
3h	D-Glucose	adamantyl		α only	(ii)	20	–
3i	D-Galactose	Ph	H	1:6	(i)	83	62:38
3j	D-Mannose	Ph	H	α only	(i)	94	(*Z*) only
3k	Cellobiose	Ph	H	β only	(i)	80	87:13
3l	D-Ribose	Me	H	β only	(i)	58	50:50

[a] When the reaction was carried out at 5 °C, vinyl bromide **4m** (R^1 = Br, R^2 = H) was obtained in 15% yield along with 54% of **4a**; the yield of **4m** could be increased to 32% (with 57% **4a**) when the reaction was conducted at room temp. [b] 97% based on recovered **3dα**.



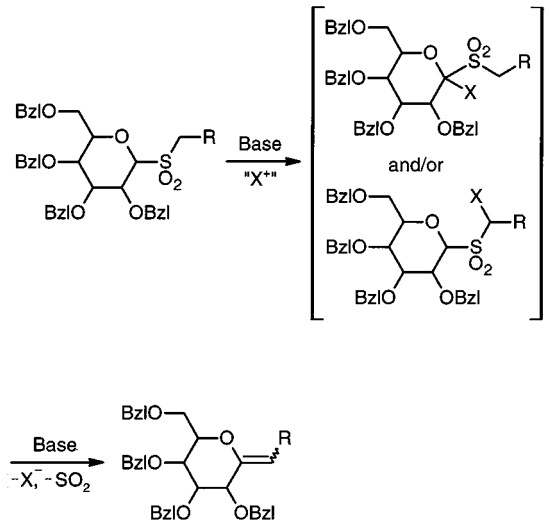
Scheme 4. (i) BzlSH, $SnCl_4$, DCM, −30 °C to room temp., 68%, then crystallisation of β-anomer; (ii) Oxone,® THF, MeOH, H_2O; (iii) MeONa, MeOH; (iv) TBDMSOTf, 2,6-lutidine, DCM; (v) KOH/Al_2O_3, CBr_2F_2, *t*BuOH, DCM, 5 °C to room temp., 69%; (vi) TBAF, THF; (vii) Ac_2O, DMAP, DCM, 64% over 2 steps. TBDMSOTf = *tert*-butyldimethylsilyl trifluoromethanesulfonate; TBAF = tetra-*n*-butylammonium fluoride; DMAP = 4-dimethylaminopyridine

terisation purposes. NMR spectroscopy of the *exo*-glycal **12** confirmed the presence of the *exo*-methine moiety {δ_H ($CDCl_3$) = 5.76, s; δ_C ($CDCl_3$) = 111.4} and the observation of mutual NOEs between the vinylic proton (1-H) and the allylic proton (3-H) suggests a (*Z*)-configuration about the double bond. Although this assignment cannot be made unequivocally in the absence of the other geometric isomer on which to conduct the complementary NOE experiments, the observed chemical shift for 1-H is very close ($\Delta\delta$ = 0.03) to that observed for the major isomer of benzylated analogue **4d**, which is believed to be (*Z*) on the basis of its resonance at higher field than the minor co-product. Additional evidence is presented by the results of hydroboration reactions involving **4d** which are discussed in the following paper.[3]

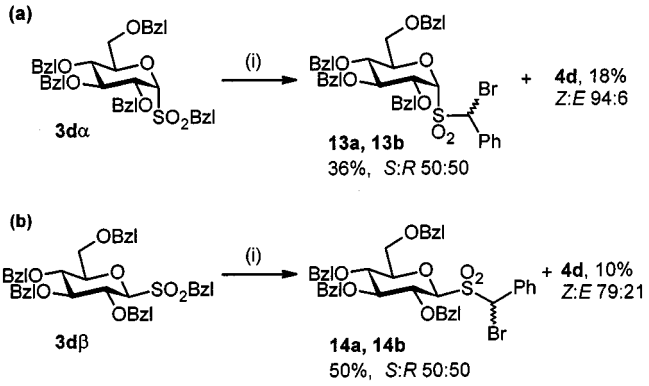
Mechanistic Studies

As these rearrangements were all carried out using one-pot procedures, one aspect of the chemistry was unclear: which of the two possible regioisomeric α-halosulfones was being formed during the in situ halogenation step of the reaction? Scheme 5 shows the two alternative pathways, either (or both) of which could be in operation. Although the formation of vinyl bromide **4m** from the reaction of methyl sulfone **3a** suggests that bromination occurs at the α′-position in this substrate at least, no direct evidence in support of the precise mechanism could be found. [When referring to 1-thioglycosides and their *S*,*S*-dioxide derivatives, C1 of the saccharide shall be denoted as the α-sulfonyl position and the corresponding site on the aglycon as α′.]

However, on examination of the Ramberg−Bäcklund rearrangement of sulfone **3dα** using Chan's protocol we found that, by reducing the base stoichiometry from ca. 7.5 g·mmol^{-1} substrate to ca. 0.5 g·mmol^{-1} and shortening the reaction time from 20 h to 2 h, the intermediate α′-bromosulfone **13** could be isolated from the reaction mixture in 36% yield along with *exo*-glycal **4d** (18%) and unchanged starting material **3dα** (32%) (Scheme 6, a).



Scheme 5. Alternative pathways for the tandem halogenation-Ramberg–Bäcklund rearrangement of glycosyl sulfones involving regioisomeric halosulfones



Scheme 6. Isolation of α′-bromosulfones from the tandem bromination-Ramberg–Bäcklund rearrangements of **3dα** and **3dβ**; (i) 0.5 g·mmol^{-1} KOH/Al_2O_3, CBr_2F_2, *t*BuOH, DCM, 5 °C

^{1}H NMR spectroscopy revealed the halogenated material to be an equimolar mixture of the diastereoisomeric α′-bromosulfones **13a** and **13b**, which were separated by further column chromatography and characterised individually. Conclusive evidence came when one of the diastereoisomers was crystallised and X-ray diffraction provided unambiguous confirmation that bromination had indeed occurred at the exocyclic position, as shown in Figure 1. A similar procedure was followed for the β-glycosyl sulfone **3dβ** (Scheme 6, b) and here also a separable pair of diastereoisomeric bromides (**14a** and **14b**) was isolated, which displayed spectroscopic characteristics in full accordance with their assigned structures.

In order to provide further evidence for the involvement of these species in the tandem halogenation-Ramberg–Bäcklund process, the individual bromosulfones **13a**, **13b**, **14a**, and **14b** were treated with KOH/Al_2O_3 suspended in *t*BuOH, in the absence of any brominating agent,

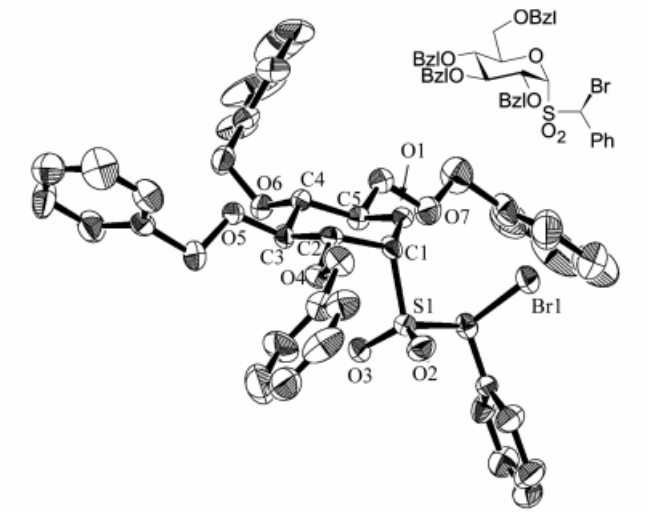
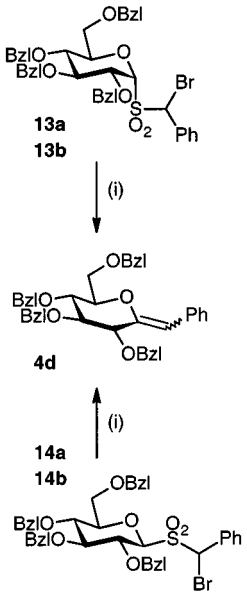


Figure 1. ORTEP representation of bromosulfone **13a**



Scheme 7. (i) 7.5 g·mmol^{-1} KOH/Al_2O_3, *t*BuOH, DCM, 5 °C; see Table 3 for yields

Table 3. Ramberg–Bäcklund rearrangements of isolated glycosyl α′-bromosulfones

Substrate	Yield of **9d**	(*Z*)/(*E*) ratio
13a	89%	89:11
13b	87%	89:11
14a	81%	45:55
14b	72%	45:55

and gave the expected *exo*-glycal **4d** as the sole product and in high yield (Scheme 7 and Table 3).

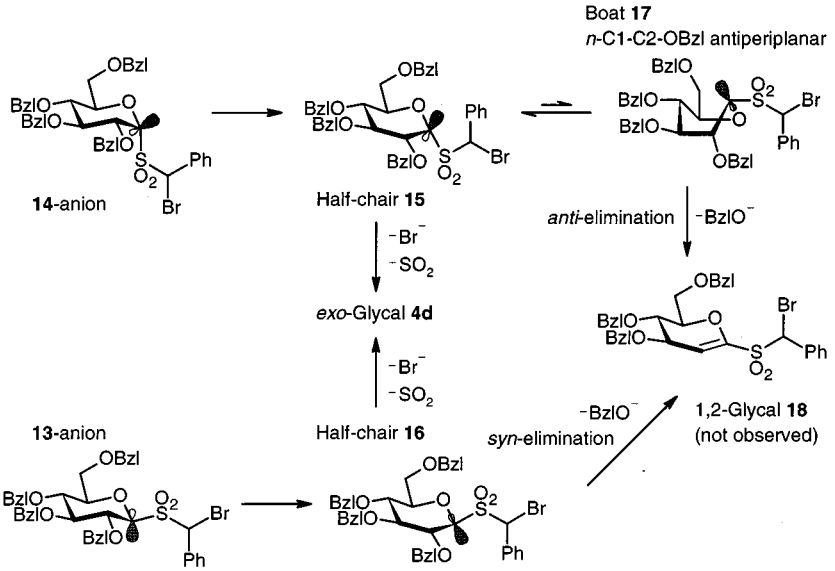
Although the yields and (*Z*)/(*E*) ratios of the alkene varied between the two anomers, the product mixtures obtained were unaffected by the configuration of the bromine-

bearing carbon, as shown in Table 3. This observation was initially surprising because episulfone formation and decomposition are both stereospecific processes. Closer examination by TLC, however, revealed that both diastereomeric pairs of bromosulfones suffer rapid epimerisation of the benzylic centre before any product is formed, and hence, for each anomer, the rearrangements commence from the same equilibrium mixture of epimers. The stereoselectivity of the Ramberg−Bäcklund rearrangements of these substrates must, therefore, be derived solely from the anomeric configuration. However, the fact that starting material was recovered from the rearrangement of α-anomer **3dα** with its C1 stereochemistry intact, suggests that inversion of this centre is not a factor in the selectivity.

It is also surprising to note that in neither case are the (*Z*)- and (*E*)-alkenes formed in the same ratio as in the tandem halogenation-Ramberg−Bäcklund rearrangement sequence. While the α-anomer still exhibits a high stereoselectivity in favour of the (*Z*)-alkene, the relative proportion of the (*E*)-isomer is increased by a factor of two. Even more unexpected is the fact that an essentially equimolar mixture of (*E*)- and (*Z*)-olefins was obtained from the reaction of the β-anomer, whereas before the product was significantly enriched in the (*Z*)-isomer. One possible explanation for the differing selectivities between the stepwise and tandem processes is that during the latter, α′-bromination may occur concurrently with deprotonation of the anomeric centre and, assuming that episulfone formation then occurs more rapidly than epimerisation of the bromine-bearing carbon, any diastereoselectivity in the initial bromination step will be preserved and conveyed to the alkene product. As already mentioned (vide supra) epimerisation of the benzylic centres of isolated bromides **13** and **14** occurs at a faster rate than 1,3-elimination to form the episulfone intermediate and, hence, some selectivity may be lost during the stepwise process.

Apart from its wide applicability, the most surprising feature of this methodology is the fact that, despite the probable formation of anomeric α-sulfonyl carbanion intermediates, we did not observe any direct evidence of β-elimination of the 2-alkoxy group to give 1,2-glycals, a process which has severely hampered C-1 anionic approaches to *C*-glycosylation. [Although no 1,2-glycals were isolated, β-elimination cannot be excluded as a contributory factor towards the low yielding transformations leading to *exo*-glycals **4f** and **4h**. In these examples the rate of episulfone formation may be sufficiently retarded that 1,2-glycal formation becomes a competing process.] Indeed a number of tactics, the most notable of which are described in Somsák's review,[12] have been implemented in *C*-glycoside synthesis in order to overcome unwanted β-elimination of the C2-substituent from glycosyl anions. Conceptually, these either involve the introduction of a group of poor nucleofugality at the 2-position, as demonstrated by the glycosyl dianion method,[29] or a reduction of the anionic character of the sugar nucleophile, most notably by the reductive samariation of glycosyl pyridyl sulfones in the absence of HMPA[30a,30b] and in the presence of catalytic amounts of NiI_2.[30c] In our Ramberg−Bäcklund process we believe that, although the substrates bear a moderately good leaving group[31] (benzyloxy or *tert*-butyldimethylsilyloxy), the glycosyl anion intermediate is intercepted intramolecularly by a γ-elimination process (episulfone formation) before β-elimination can occur.

It is likely that the formation of 1,2-glycal **18** in these systems would follow an E1cb mechanism since the substrates bear a relatively acidic α-sulfonyl hydrogen and a moderate leaving group. 1,2-Eliminations of HX from six-membered rings usually proceed from a conformation in which the C−H bond (or the derived nonbonding pair) and the nucleofuge are *anti*-periplanar, although Skrydstrup et al.[30a] have recently proposed that intermediate glycosyl sa-



Scheme 8. Conformational requirements for 1,3- and 1,2-elimination from glycosyl α′-bromosulfones leading to *exo*-glycals and 1,2-glycals respectively

marium(III) species, generated from the reduction of glycosyl pyridyl sulfones in the absence of HMPA, undergo an unprecedented *syn*-elimination to give 1,2-glycals. However, Scheme 8 illustrates that for either *syn*- or *anti*-elimination to occur, the predominant $^4C_1$ conformation of the glucose-derived molecules studied would be required to undergo a conformational change. In this rationale we assume that C1 deprotonation of the α′-bromosulfones **13** and **14** takes place while in the $^4C_1$ arrangement and that inversion of the α-sulfonyl carbanion does not occur. The latter assumption is supported by the isolation of the α-thioglycoside dioxide **3dα** from tandem halogenation Ramberg−Bäckund rearrangements with its anomeric configuration intact (Scheme 6, a).

The *trans* relationship between H−C(1) and BzlO−C(2) of **14** requires that, before 1,2-elimination can proceed, the derived carbanion must adopt the boat (or twist boat) conformation represented by **17** in which the *n*-C1−C2−OBzl dihedral angle approaches 180°. In attaining this geometry, the pyranose ring must pass through the half-chair **15**, and it is at this point that the process may be halted by the intervention of a competing process. The planarisation of the O5−C1−C2 portion of the heterocycle coincides with the conformation which leads to the episulfone-forming transition state, and hence 1,3-elimination predominates. In **13** the H−C(1) and BzlO−C(2) bonds are *cis* and hence a *syn*-elimination process may be possible from half-chair **16**. However, since episulfone formation also competes in determining the fate of this species, and considering the relative leaving group capabilities of bromide and benzyloxy, 1,3-elimination is likely to be preferred over 1,2-elimination. Further experiments to probe the mechanism of this process are currently in progress and the results will be reported in due course.

Conclusion

In summary, we have shown that readily available glycosyl sulfones can be converted into *exo*-glycals in a tandem halogenation-Ramberg−Bäcklund rearrangement. 1,1-Di-, tri-, and tetra-substituted alkene products derived from glucose, galactose, mannose, cellobiose, and ribose have been prepared in this way. It is believed that the α′-halosulfonyl intermediates formed in situ during this process preferentially undergo 1,3-elimination to give spiroepisulfones as opposed to 1,2-elimination. The elaboration of these *exo*-glycals is described in the accompanying paper.[3]

Experimental Section

General Remarks: Dichloromethane (DCM) was distilled from calcium hydride immediately prior to use. Light petroleum ether refers to the fraction boiling in the range 40−60 °C and was redistilled before use. Alumina-supported potassium hydroxide (KOH/Al_2O_3) was prepared according to Chan's procedure.[26] Reactions were monitored by TLC on silica gel 60 F_{254} (Merck) with detection by charring with 10% sulfuric acid in methanol followed by heating. Organic extracts were dried over anhydrous sodium sulfate and column chromatography was carried out using 33−64 (60 Å) silica gel (ICN). Melting points (m.p.) were determined with an Electrothermal IA9100 digital melting point apparatus and are uncorrected. Specific rotations were measured on a Jasco DIP-370 digital polarimeter and are expressed in units of 10^{-2} deg·cm^{-2}·g^{-1}. Mass spectrometry was carried out on a Fisons Analytical Autospec instrument using either chemical ionisation (CI) or fast atom bombardment (FAB) techniques; all high resolution mass spectral determinations are within 5 ppm of the calculated value. Elemental analyses were performed by Chemical Analytical Services Unit, University of Newcastle, UK using a Carlo Erba 1106 elemental analyser. NMR spectra were recorded on a Jeol EX270 spectrometer, operating at ^{1}H and ^{13}C frequencies of 270 and 67.9 MHz, respectively.

Methyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (2aα) and Methyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[32] (2aβ): To a suspension of the lactol **1**, (3.00 g, 5.55 mmol) in dry MeCN (30 mL) over activated 4 Å molecular sieves was added dimethyl disulfide (1.2 mL, 13.3 mmol), followed by tri-*n*-butylphosphane (3.36 mL, 13.5 mmol) and then boron trifluoride diethyl etherate (2.88 mL, 23.4 mmol) and the resulting solution was heated to 60 °C and stirred overnight. After cooling, the solvent was removed under reduced pressure and the residue was redissolved in DCM (100 mL), washed with satd. aq. $NaHCO_3$ (50 mL) then with water (30 mL), dried, and purified by flash column chromatography (light petroleum ether/EtOAc, 9:1→4:1) to afford the title compounds as a colourless oil (1.50 g, 71%, **2aα/2aβ**, 3:1). For characterisation purposes, the anomers were separated by further column chromatography (DCM/light petroleum ether, 1:1→4:1→1:0) to give first **2aα** which was recrystallised from MeOH to give fine needles, R_f = 0.34 (DCM); m.p. 57−58 °C. $[\alpha]_D^{20}$ = +106.7 (c = 1.0, $CHCl_3$); $\tilde{\nu}_{max}$/cm^{-1}: 3030, 2917, 1496, 1453, 1363, 1208, 1074; δ_H (270 MHz, $CDCl_3$): 2.05 (s, 3 H, SCH_3), 3.59−3.64 (m, 1 H, 2-H), 3.64, 3.76 (ABX, $J_{6A,6B}$ = 10.7, $J_{6A,5}$ = 1.7, $J_{6B,5}$ = 3.9 Hz, 2 H, 6-H_A, 6-H_B), 3.85−3.92 (m, 2 H, 3-H, 4-H), 4.10−4.16 (ddd, $J_{5,4}$ = 9.6, $J_{5,6B}$ = 3.9, $J_{5,6A}$ = 1.7 Hz, 1 H, 5-H), 4.47, 4.61 (AB, J = 12.1 Hz, 2 H, CH_2Ph), 4.46, 4.83 (AB, J = 10.9 Hz, 2 H, CH_2Ph), 4.64, 4.74 (AB, J = 11.6 Hz, 2 H, CH_2Ph), 4.76, 4.95 (AB, J = 10.9 Hz, 2 H, CH_2Ph), 5.32 (d, $J_{1,2}$ = 4.5 Hz, 1 H, 1-H), 7.12−7.15 (m, 2 H, 2 × arom. H), 7.24−7.40 (m, 18 H, 18 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 12.4 (SCH_3), 68.6, (C6), 72.3, 73.4, 75.0, 75.7 (4 × CH$_2$Ph), 70.3, 77.2, 79.6, 82.5, 84.4 (C1, C2, C3, C4, C5), 127.6, 127.7, 127.9, 128.0 (× 2), 128.4 (× 2) (arom. CH), 137.8, 137.9, 138.3, 138.7 (subst. arom. C); *m/z* (CI): 588 (20%, [M + NH_4]$^+$), 392 (100%). Further elution gave **2aβ** which was recrystallised from MeOH to afford fine needles, R_f = 0.24 (DCM); m.p. 69−70.5 °C, ref.[32] 64−66 °C. $[\alpha]_D^{20}$ = +9.7 (c = 1.0, $CHCl_3$), ref.[32] +9.4 (c = 0.79, $CHCl_3$).

General Procedure for the Preparation of Thioglycosides 2b−g and 2l From Lactols 1 and 6: Trimethylsilyl chloride (2.6 mmol) was added to a suspension containing the lactol (2 mmol), zinc(II) triflate (0.2 mmol), and thiol (1.3 mmol) in anhydrous MeCN (10 mL) at 20 °C, after which the mixture rapidly became homogeneous. The solution was then heated to 40 °C and stirred for 3−4 h. The solvent was removed in vacuo and the residue was purified by flash chromatography (gradient elution with light petroleum ether/EtOAc, 9:1→3:1) to afford the thioglycoside as a mixture of α- and β-anomers. Further column chromatography (elution with DCM/light petroleum ether, 4:1) followed by crystallisation, where possible, gave pure samples of each anomer for characterisation.

Ethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-glucopyranoside[33] (2bα): From 0.282 g of **1**. Yield: 0.103 g, 34%; fine needles (MeOH); R_f = 0.25 (DCM); m.p. 90−91 °C, ref.[33] 91 °C. $[\alpha]_D^{20}$ = +111.8 (*c* = 1.0, $CHCl_3$), ref.[33] +108 ($CHCl_3$).

Ethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[33,34] (2bβ): From 0.282 g of **1**. Yield: 0.40 g, 13%; fine needles (MeOH); R_f = 0.17 (DCM); m.p. 94−94.5 °C, ref.[33] 94 °C. $[\alpha]_D^{20}$ = +3.4 (*c* = 1.0, $CHCl_3$), ref.[34] +2.7 (*c* = 1.6, $CHCl_3$).

Propyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-glucopyranoside[35] (2cα): From 1.03 g of **1**. Yield: 0.70 g, 61%; colourless oil; R_f = 0.36 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = +110.0 (*c* = 1.0, $CHCl_3$), ref.[35] +84.1 (*c* = 1.0, $CHCl_3$).

Propyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (2cβ): From 1.03 g of **1**. Yield: 0.24 g, 21%; needles (MeOH); R_f = 0.36 (light petroleum ether/EtOAc, 4:1); m.p. 86.5−87 °C. $[\alpha]_D^{20}$ = +2.3 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3066, 3000, 1496, 1454, 1361, 1314, 1243, 1147, 1094; δ_H (270 MHz, $CDCl_3$): 1.00 (t, *J* = 7.3 Hz, 3 H, $SCH_2CH_2CH_3$), 1.69 (sext., *J* = 7.3 Hz, 2 H, $SCH_2CH_2CH_3$), 2.67, 2.76 (ABX_2, *J* = 12.6, 7.3 Hz, 2 H, $SCH_2CH_2CH_3$), 3.41−3.48 (m, 2 H, 2-H, 5-H), 3.57−3.77 (m, 4 H, 3-H, 4-H, 6-H_A, 6-H_B), 4.44 (d, *J* = 9.7 Hz, 1 H, 1-H), 4.54, 4.61 (AB, *J* = 12.1 Hz, 2 H, CH_2Ph), 4.57, 4.82 (AB, *J* = 10.7 Hz, 2 H, CH_2Ph), 4.74, 4.93 (AB, *J* = 10.2 Hz, 2 H, CH_2Ph), 4.84, 4.93 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 7.16−7.39 (m, 20 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 13.5 ($SCH_2CH_2CH_3$), 23.25 ($SCH_2CH_2CH_3$), 32.9 ($SCH_2CH_2CH_3$), 69.1 (C6), 73.35, 75.0, 75.4, 75.7 (4 × CH_2Ph), 77.9, 79.0, 81.8, 85.2, 86.6 (C1−C5), 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3 (× 2) (arom. CH), 137.9, 138.0, 138.2, 138.4 (subst. arom. C); *m/z* (CI): 616 (100%, $[M + NH_4]^+$); found $[M + NH_4]^+$ 616.3100. $C_{37}H_{42}O_5S{\cdot}NH_4$ requires 616.3097.

Benzyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (2dα): From 0.610 g of **1**. Yield: 0.28 g, 38%; fine needles (MeOH); R_f = 0.46 (DCM); m.p. 82.5−83.5 °C. $[\alpha]_D^{20}$ = +161.6 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 2914, 1497, 1453, 1363, 1074; δ_H (270 MHz, $CDCl_3$): 3.51−3.88 (m, 7 H, 2-H, 3-H, 4-H, 6-H_A, 6-H_B, SCH_2Ph), 4.16−4.19 (m, 1 H, 5-H), 4.40, 4.49 (AB, *J* = 11.6 Hz, 2 H, CH_2Ph), 4.46, 4.61 (AB, *J* = 12.1 Hz, 2 H, CH_2Ph), 4.46, 4.82 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.75, 4.93 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 5.22 (d, $J_{1,2}$ = 5.3 Hz, 1 H, 1-H), 7.12−7.36 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 33.3 (SCH_2Ph), 68.4 (C6), 71.7, 73.4, 75.0, 75.6 (4 × CH_2Ph), 70.7, 77.4, 78.9, 82.1, 82.7 (C1, C2, C3, C4, C5), 126.9, 127.5, 127.6 (× 2), 127.7, 127.8 (× 2), 127.9, 128.3 (× 2), 128.6, 128.8, 129.1 (arom. CH), 137.5, 137.8, 138.0, 138.2, 138.6 (subst. arom. C); *m/z* (CI): 664 (40%, $[M + NH_4]^+$), 108 (100%), 91(75%, $[C_7H_7]^+$); found C 76.20, H 6.50, S 5.12. $C_{41}H_{42}O_5S$ requires C, 76.13, H 6.55, S 4.96%.

Benzyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (2dβ): From 0.610 g of **1**. Yield: 0.09 g, 13%; fine needles (MeOH); R_f = 0.38 (DCM); m.p. 65−67 °C, ref.[18] 75.5−76 °C. $[\alpha]_D^{20}$ = −42.2 (*c* = 1.0, $CHCl_3$), ref.[18] −40.2 ($CHCl_3$); found C 75.93, H 6.50, S 4.97. $C_{41}H_{42}O_5S$ requires C, 76.13, H 6.55, S 4.96%.

Isopropyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-glucopyranoside[36] (2eα): From 1.64 g of of **1**. Yield: 0.77 g, 42%; needles (MeOH); R_f = 0.36 (light petroleum ether/EtOAc, 4:1); m.p. 87−88 °C. $[\alpha]_D^{20}$ = +102.2 (*c* = 1.0, $CHCl_3$), ref.[36] +90.4 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3005, 2867, 1497, 1454, 1364, 1152, 1073; δ_H (270 MHz, $CDCl_3$): 1.28, 1.31 [2 × d, *J* = 6.8 Hz, 6 H, $SCH(CH_3)_2$], 2.97 [hept., *J* = 6.8 Hz, 1 H, $SCH(CH_3)_2$], 3.59−3.68 (m, 2 H, 4-H, 6-H_A), 3.77 (dd, $J_{6B,6A}$ = 10.8, $J_{6B,5}$ = 3.6 Hz, 1 H, 6-H_B), 3.82−3.88 (m, 2 H, 2-H, 3-H), 4.22 (ddd, $J_{5,4}$ = 8, $J_{5,6B}$ = 3.6, $J_{5,6A}$ = 2.0 Hz, 1 H, 5-H), 4.43, 4.61 (AB, *J* = 12.1 Hz, 2 H, CH_2Ph), 4.46, 4.83 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.69 (A_2, 2 H, CH_2Ph), 4.76, 4.96 (AB, *J* = 10.7 Hz, 2 H, CH_2Ph), 5.42 (d, $J_{1,2}$ = 4.6 Hz, 1 H, 1-H), 7.11−7.37 (m, 20 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 23.5, 23.7 [$(CH_3)_2CHS$], 33.9 [$(CH_3)_2CHS$], 68.5 (C6), 72.4, 73.35, 75.0, 75.65 (4 × CH_2Ph), 70.4, 77.5, 79.5, 82.5, 82.6 (C1−C5), 127.5, 127.6, 127.6, 127.7, 127.8, 128.0, 128.1, 128.3, 128.35 (arom. CH), 137.9 (× 2), 138.3, 138.7 (subst. arom. C); *m/z* (CI): 616 (4%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$).

Isopropyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (2eβ): From 1.64 g of **1**. Yield: 0.29 g, 11%; needles (MeOH); R_f = 0.36 (light petroleum ether/EtOAc, 4:1); m.p. 86−87 °C. $[\alpha]_D^{20}$ = +4.6 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3006, 2868, 1497, 1454, 1360, 1210, 1154, 1065; δ_H (270 MHz, $CDCl_3$): 1.34, 1.37 [6 H, 2 × d, *J* = 6.8 Hz, $CH(CH_3)_2$], 3.48 [br. hept., *J* = 6.8 Hz, 1 H, $CH(CH_3)_2$], 3.40−3.49 (m, 2 H, 4-H, 5-H), 3.58 (t, *J* = 8.7 Hz, 1 H, 3-H), 3.64−3.77 (m, 3 H, 2-H, 6-H_A, 6-H_B), 4.51−4.62 (m, 4 H, 1-H, 3 × benzylic H), 4.72, 4.93 (AB, *J* = 10.7 Hz, 2 H, CH_2Ph), 4.82 (d, *J* = 10.9 Hz, 1 H, benzylic H), 4.84, 4.93 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 7.15−7.38 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 23.96, 24.00 [$(CH_3)_2CHS$], 35.5 [$(CH_3)_2CHS$], 69.2 (C6), 73.3, 75.0, 75.5, 75.7 (4 × CH_2Ph), 78.0, 79.0, 82.0, 84.6, 86.7 (C1−C5), 127.5, 127.6 (× 2), 127.7, 127.9, 128.1, 128.25, 128.35 (arom. CH), 138.0 (× 2), 138.2, 138.5 (subst. arom. C); *m/z* (CI): 616 (4%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found $[M + NH_4]^+$ 616.3092. $C_{37}H_{42}O_5S{\cdot}NH_4$ requires 616.3097.

Cyclohexyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (2fα): From 1.16 g of **1**. Yield: 0.70 g, 51%; needles (MeOH); R_f = 0.38 (light petroleum ether/EtOAc, 4:1); m.p. 89−90 °C. $[\alpha]_D^{20}$ = +115.3 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3006, 2933, 2856, 1454, 1207, 1072; δ_H (270 MHz, $CDCl_3$): 1.25−1.57, 1.65−1.80, 1.89−2.01 [m, 10 H, $SCH(CH_2)_5$], 2.70−2.79 [m, 1 H, $SCH(CH_2)_5$], 3.60−3.66 (m, 2 H, 4-H, 6-H_A), 3.77 (dd, $J_{6B,6A}$ = 10.6, $J_{6B,5}$ = 3.6 Hz, 1 H, 6-H_B), 3.82−3.88 (m, 2 H, 2-H, 3-H), 4.25 (ddd, $J_{5,4}$ = 9.9, $J_{5,6B}$ = 3.6, $J_{5,6A}$ = 7 Hz, 1 H, 5-H), 4.43, 4.61 (AB, *J* = 12.1 Hz, 2 H, CH_2Ph), 4.45, 4.83 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.69 (A_2, 2 H, CH_2Ph), 4.75, 4.96 (AB, *J* = 10.7 Hz, 2 H, CH_2Ph), 5.44 (d, $J_{1,2}$ = 4.8 Hz, 1 H, 1-H), 7.11−7.40 (20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 25.7 (× 2), 25.9, 33.6, 34.0 (5 × cyclohexyl CH_2), 42.5 (SCH on cyclohexyl), 68.5 (C6), 72.3, 73.3, 75.0, 75.6 (4 × CH_2Ph), 70.3, 77.5, 79.5, 82.4, 82.6 (C1−C5), 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 128.25, 128.3 (arom. CH), 137.9 (d), 138.3, 138.7 (subst. arom. C); *m/z* (CI): 656 (100%, $[M + NH_4]^+$); found $[M + NH_4]^+$ 656.3418. $C_{40}H_{46}O_5S{\cdot}NH_4$ requires 656.3418.

Cyclohexyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (2fβ): From 1.16 g of **1**. Yield: 0.23 g, 17%; fine needles (MeOH); R_f = 0.38 (light petroleum ether/EtOAc, 4:1); m.p. 90.5−91.5 °C. $[\alpha]_D^{20}$ = +4.3 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3006, 2933, 2856, 1454, 1207, 1072; δ_H (270 MHz, $CDCl_3$): 1.21−1.63 (m, 6 H, 4 × 3′-H, 2 × 4′-H), 1.76 (br. s, 2 H, 2 × 2′-H), 2.05 (br. d, *J* = 13.3 Hz, 2 H, 2 × 2′-H), 2.99 [tt, *J* = 10.2, 3.6 Hz, 1 H, $SO_2CH(CH_2)_5$], 3.42 (t, *J* = 8.7 Hz, 1 H, 4-H), 3.40−3.49 (m, 1 H, 5-H), 3.57 (t, *J* = 8.7 Hz, 1 H, 3-H), 3.65−3.77 (m, 3 H, 2-H, 6-H_A, 6-H_B), 4.51−4.62 (m, 4 H, 1-H, 3 × benzylic H), 4.72, 4.94 (AB, *J* = 10.2 Hz, 2 H, CH_2Ph), 4.82 (d, *J* = 10.9 Hz, 1 H, benzylic H), 4.83, 4.92 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 7.16−7.39 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 25.7, 25.9, 26.1, 34.05, 34.2 (5 × cyclohexyl CH_2), 43.8 (SCH on cyclohexyl), 69.3 (C6), 73.3, 75.0, 75.5, 75.7 (4 × CH_2Ph), 78.0, 79.0, 82.0, 84.4, 86.7 (C1−C5), 127.5, 127.6, 127.75, 127.9, 128.3, 128.4 (arom. CH), 138.0 (× 2), 138.2, 138.5 (subst. arom. C); *m/z* (CI): 656 (100%, $[M + NH_4]^+$).

Benzhydryl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (2gα): From 3.03 g of **1**. Yield: 2.52 g, 62%; colourless oil; R_f = 0.41 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = +162.3 (*c* = 2.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3005, 2869, 1496, 1453 1363, 1154, 1073; δ_H (270 MHz, $CDCl_3$): 3.55−3.62, 3.70, 3.77 (m, 4 H, 2-H, 4-H, 6H_A, 6-H_B), 3.89 (t, *J* = 9.2 Hz, 1 H, 3-H), 4.32 (br. d, *J* = 9.9 Hz, 1 H, 5-H), 4.39−4.54 (m, 4 H, 4 × benzylic H), 4.62 (d, *J* = 11.9 Hz, 1 H, benzylic H), 4.74, 4.94 (AB, *J* = 10.9 Hz, 2 H, C*H*$_2$Ph), 4.83 (d, *J* = 10.7 Hz, 1 H, benzylic H), 5.12 (d, $J_{1,2}$ = 5.6 Hz, 1 H, 1-H), 5.18 (s, 1 H, SC*H*Ph_2), 7.13−7.54 (m, 30 H, 6 × Ph); δ_C (67.9 MHz, $CDCl_3$): 51.1 (S*C*HPh_2), 68.7 (C6), 71.8, 73.4, 75.0, 75.7 (4 × *C*H_2Ph), 71.0, 77.5, 78.9, 82.6, 82.8 (C1−C5), 127.0, 127.3, 127.6 (× 2), 127.75, 127.85, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.7 (arom. CH), 137.6, 137.9, 138.2, 138.6, 141.1, 141.3 (subst. arom. C); *m*/*z* (CI): 740 (30%, $[M + NH_4]^+$), 574 (60%, $[M - CH(Ph)_2]^+$); found $[M + NH_4]^+$ 740.3411. $C_{47}H_{46}O_5S{\cdot}NH_4$ requires 740.3410.

Benzhydryl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (2gβ): From 3.03 g of **1**. Yield: 0.56 g, 14%; Colourless oil; R_f = 0.41 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = −23.3 (*c* = 0.9, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3005, 2868, 1496, 1453 1360, 1124, 1067; δ_H (270 MHz, $CDCl_3$): 3.18 (br. d, *J* = 8.7 Hz, 1 H, 5-H), 3.51−3.77 (m, 4 H, 2-H, 4-H, 6-H_A, 6-H_B), 4.06−4.09 (m, 1 H, 3-H), 4.51−4.89 (m, 9 H, 1-H, 4 × C*H*$_2$Ph), 5.58 (s, 1 H, SC*H*Ph_2), 7.13−7.47 (m, 30 H, 6 × Ph); δ_C (67.9 MHz, $CDCl_3$): 52.2 (Ph_2*C*HS), 68.6 (C6), 73.3, 74.9, 75.3, 75.7 (4 × *C*H_2Ph), 77.9, 78.8, 81.7, 83.65, 86.6 (C1−C5), 126.5, 127.1, 127.3, 127.5, 127.6, 127.7, 127.8, 127.8, 128.0, 128.15, 128.3, 128.4, 128.5, 128.7 (arom. CH), 138.0 (× 2), 138.2, 138.4, 140.6, 140.9 (subst. arom. C); *m*/*z* (CI): 740 (2%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found C 78.16, H 6.45, S 4.17. $C_{47}H_{46}O_5S$ requires C, 78.09, H 6.41, S 4.43%.

Ethyl 2,3,5-tri-*O*-benzyl-α-D-ribofuranoside (2lα): From 2.65 g of **6**. Yield: 0.42 g, 14%; pale yellow oil; R_f = 0.37 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = +90.7 (*c* = 1.3, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 2924, 1496, 1453, 1362, 1263, 1208, 1104, 1027; δ_H (270 MHz, $CDCl_3$): 1.31 (t, *J* = 7.5 Hz, 3 H, SCH_2CH_3), 2.79 (q, *J* = 7.5 Hz, 2 H, SCH_2CH_3), 3.55 (dd, *J* = 4, *J* = 11 Hz, 1 H), 3.60 (dd, *J* = 4, *J* = 11 Hz, 1 H), 3.93 (t, *J* = 6 Hz, 1 H) and 4.10 (t, *J* = 5 Hz, 1 H, 2-H, 3-H, 5-H_A, 5-H_B), 4.29−4.33 (m, 1 H, 4-H), 4.41−4.78 (m, 6 H, 3 × C*H*$_2$Ph), 5.49 (d, *J* = 5 Hz, 1 H, 1-H), 7.22−7.41 (m, 15 H, 3 × Ph); δ_C (67.9 MHz, $CDCl_3$): 14.9 (SCH_2CH_3), 25.0 (SCH_2CH_3), 69.1 (C5), 72.1, 72.4, 73.0 (3 × *C*H_2Ph), 76.8, 78.15, 80.2, 87.7 (C1−C4), 127.5, 127.6, 127.8, 128.0, 128.2 (arom. CH), 137.8, 137.9, 138.0 (subst. arom. C); *m*/*z* (CI): 482 (20%, $[M + NH_4]^+$), 420 (50%, $[M - EtSH]^+$), 290 (100%); found $[M + NH_4]^+$ 482.2362. $C_{28}H_{32}O_4S{\cdot}NH_4$ requires 482.2365.

Ethyl 2,3,5-Tri-*O*-benzyl-β-D-ribofuranoside (2lβ): From 2.65 g of **6**. Yield: 1.32 g, 45%; pale yellow oil; R_f = 0.34 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = −24.6 (*c* = 3.3, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 2925, 1496, 1453, 1361, 1263, 1207, 1121, 1096; δ_H (270 MHz, $CDCl_3$): 1.23 (t, *J* = 7.5 Hz, 3 H, SCH_2CH_3), 2.60, 2.69 (ABX_3, *J* = 12.0, 7.5 Hz, 2 H, SCH_2CH_3), 3.52−3.62 (m, 2 H, 5-H_A, 5-H_B), 3.87 (t, *J* = 4.4 Hz, 1 H, 2-H), 4.00 (t, *J* = 5.3 Hz, 1 H, 3-H), 4.28 (dt, *J* = 5.1 Hz, 1 H, 4.6, 4-H), 4.49, 4.57 (AB, *J* = 11.9 Hz, 2 H, C*H*$_2$Ph), 4.50, 4.57 (AB, *J* = 12.1 Hz, 2 H, C*H*$_2$Ph), 4.60, 4.67 (AB, *J* = 11.9 Hz, 2 H, C*H*$_2$Ph), 5.24 (d, $J_{1,2}$ = 3.9 Hz, 1 H, 1-H), 7.26−7.37 (m, 15 H, 3 × Ph); δ_C (67.9 MHz, $CDCl_3$): 15.0 (SCH_2CH_3), 24.9 (CH_3CH_2S), 70.8 (C5), 79.3 (× 2), 73.3 (3 × *C*H_2Ph), 78.1, 80.7, 81.6, 85.8 (C1−C4), 127.5, 127.6, 127.8, 128.0 (× 2), 128.3 (× 2), 128.4 (arom. CH), 137.6, 137.7, 138.15 (subst. arom. C); *m*/*z* (CI): 482 (100%, $[M + NH_4]^+$), 420 (70%, $[M - EtSH]^+$), 295 (85%); found $[M + NH_4]^+$ 482.2363. $C_{28}H_{32}O_4S{\cdot}NH_4$ requires 482.2365.

Adamant-2-yl 2,3,4-Tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-glucopyranoside (2h): A solution of 2-adamantyl 6-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-glucoside[24] (0.92 g, 2.07 mmol) in DMF (10 mL) was added to a slurry of sodium hydride (0.34 g, 60% w/w in mineral oil, 8.5 mmol) in DMF (5 mL) at 0 °C. After stirring at 0 °C for a further 10 minutes, the reaction was allowed to warm to room temp. over 1 h, after which it was recooled to 5 °C and benzyl bromide (1.00 mL, 8.42 mmol) added. The reaction mixture was maintained at 5 °C for 1 h and then allowed to warm to room temp. and was stirred overnight. After quenching with MeOH, the mixture was partitioned between water (50 mL) and toluene (50 mL). The organic layer was washed with water (5 × 20 mL), brine (20 mL), dried, and concentrated. The crude product was then purified by column chromatography (light petroleum ether/EtOAc, 19:1→9:1) to afford **2h** as a colourless oil (1.39 g, 94%); R_f = 0.41 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = +116.6 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 2856, 1496, 1454, 1072; δ_H (270 MHz, $CDCl_3$): 0.03, 0.04 [2 × s, 6 H, $Si(CH_3)_2$], 0.88 [s, 9 H, $SiC(CH_3)_3$], 1.50−1.63, 1.70−2.02 (m, 10 H, 5 × adamantyl CH_2), 2.05−2.30 (m, 4 H, 4 × adamantyl CH), 3.14 (br. s, 1 H, SCH of adamantyl), 3.49 (dd, $J_{4,5}$ = 9.9, $J_{4,3}$ = 8.3 Hz, 1 H, 4-H), 3.72−3.79 (m, 3 H, 2-H, 6-H_A, 6-H_B), 3.88 (t, *J* = 9.1 Hz, 1 H, 3-H), 4.13 (ddd, $J_{5,4}$ = 9.9, $J_{5,6}$ = 3.9, 2.7 Hz, 1 H, 5-H), 4.55 (A_2, 2 H, C*H*$_2$Ph), 4.67, 4.89 (AB, *J* = 11.1 Hz, 2 H, C*H*$_2$Ph), 4.77, 4.97 (AB, *J* = 10.7 Hz, 2 H, C*H*$_2$Ph), 5.31 (d, $J_{1,2}$ = 5.3 Hz, 1 H, 1-H), 7.22−7.41 (m, 15 H, 3 × Ph); δ_C (67.9 MHz, $CDCl_3$): −5.4, −5.2 [$(CH_3)_2Si$], 18.4 [$(CH_3)_3CSi$], 26.0 [$(CH_3)_3CSi$], 27.3, 27.6, 33.0, 34.2 (4 × adamantyl CH), 32.3, 32.5, 37.7, 38.7, 38.8 (5 × adamantyl CH_2), 51.9 (S*C*H of adamantyl), 62.65 (C6), 72.1, 74.3, 75.0 (3 × *C*H_2Ph), 72.5, 77.7, 80.1, 82.7, 83.6 (C1−C5), 127.4, 127.6, 127.8, 127.9 (× 2), 128.0, 128.1, 128.2, 128.4, 128.5, 128.8, 129.0 (arom. CH), 138.05, 138.35, 138.8 (subst. arom. C); *m*/*z* (FAB): 737 (10%, $[M + Na]^+$); found $[M + Na]^+$ 737.3679. $C_{43}H_{58}O_5SSi{\cdot}Na$ requires 737.3672.

Benzyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-galactopyranoside (2iα) and Benzyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (2iβ): Boron trifluoride diethyl etherate (3.40 mL, 26.8 mmol) was added to a solution of D-galactose pentaacetate (**4**) (3.83 g, 9.8 mmol) and benzyl mercaptan (1.5 mL, 12.8 mmol) in DCM (25 mL) at room temp. The reaction mixture was stirred for 20 h after which it was poured into water and extracted with DCM (2 × 50 mL). The combined organic parts were washed with water (2 × 50 mL), dried, and concentrated in vacuo. The residue was purified by column chromatography (light petroleum ether/EtOAc, 4:1→1:1) to give benzyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-galactopyranoside as a colourless oil (2.77 g, 62%). Zemplén deacetylation followed by *O*-benzylation under standard conditions (NaH, BzlBr, DMF) and purification by column chromatography (light petroleum ether/EtOAc, 19:1→9:1) afforded **2iα** as a colourless oil (0.62 g, 10% from **4**); R_f = 0.27 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = +148.2 (*c* = 0.9, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3029, 2865, 1496, 1454, 1100, 1070; δ_H (270 MHz, $CDCl_3$): 3.45−3.55 (m, 2 H, 6-H_A, 6-H_B), 3.63, 3.72 (AB, *J* = 13.8 Hz, 2 H, SC*H*$_2$Ph), 3.76−3.80 (m, 1 H, 3-H), 3.92 (br. d, *J* = 2.7 Hz, 1 H, 4-H), 4.21 (dd, $J_{2,3}$ = 9.9, $J_{2,1}$ = 5.6 Hz, 1 H, 2-H), 4.31 (br. t, *J* = 6.8 Hz, 1 H, 5-H), 4.41, 4.46 (AB, *J* = 11.9 Hz, 2 H, C*H*$_2$Ph), 4.48 (A_2, 2 H, C*H*$_2$Ph), 4.56, 4.92 (AB, *J* = 11.4 Hz, 2 H, C*H*$_2$Ph), 4.68, 4.81 (AB, *J* = 11.9 Hz, 2 H, C*H*$_2$Ph), 5.26 (d, $J_{1,2}$ = 5.6 Hz, 1 H, 1-H), 7.18−7.33 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 32.9 (S*C*H$_2$Ph), 69.1 (C6), 71.9, 73.4, 74.7 (4 × *C*H_2Ph), 69.9, 74.95, 75.8, 79.7, 82.1

(C1−C5), 126.5, 126.8, 127.4, 127.5, 127.5, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3 (× 2) 128.95, 129.1 (arom. CH), 138.0, 138.1, 138.4, 138.7 (subst. arom. C); *m/z* (CI): 664 (85%, [M + NH_4]$^+$), 108 (100%); found [M + NH_4]$^+$ 664.3100. $C_{41}H_{42}O_5S{\cdot}NH_4$ requires 664.3097. − Further elution gave **2iβ** as a colourless oil (3.65 g, 58% from **3**); R_f = 0.24 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = −34.9 (*c* = 3.1, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3028, 2866, 1495, 1455, 1098, 1070, 1027; δ_H (270 MHz, $CDCl_3$): 3.45−3.55 and 3.58−3.63 (2 × m, 4 H, 6-H_A, 6-H_B, SCH_2Ph), 3.81−3.98 (m, 4 H, 2-H, 3-H, 4-H, 5-H), 4.26 (d, $J_{1,2}$ = 9.7 Hz, 1 H, 1-H), 4.24, 4.49 (AB, *J* = 11.6 Hz, 2 H, CH_2Ph), 4.24, 4.49 (AB, *J* = 11.6 Hz, 2 H, CH_2Ph), 4.61, 4.94 (AB, *J* = 11.6 Hz, 2 H, CH_2Ph), 4.68 (A_2, 2 H, CH_2Ph), 4.70, 4.76 (AB, *J* = 10.2 Hz, 2 H, CH_2Ph), 7.20−7.33 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 34.0 (S*C*H_2Ph), 68.8 (C6), 72.7, 73.5, 74.5, 75.55 (4 × *C*H_2Ph), 73.7, 77.2, 78.25, 83.6, 84.0 (C1−C5), 126.9, 127.5, 127.6 (× 2), 127.8, 127.85, 128.1, 128.15, 128.2, 128.3, 128.4, 129.1 (arom. CH), 137.8, 138.0, 138.2, 138.3, 138.6 (subst. arom. C); *m/z* (CI): 664 (100%, [M + NH_4]$^+$); found [M + NH_4]$^+$ 664.3096. $C_{41}H_{42}O_5S{\cdot}NH_4$ requires 664.3097.

Benzyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-mannopyranoside (2jα): Boron trifluoride diethyl etherate (2.4 mL, 18.9 mmol) was added to a solution of D-mannose pentaacetate (**2**) (2.09 g, 5.4 mmol) and benzylmercaptan (0.8 mL, 6.8 mmol) in DCM (20 mL) at room temp. The reaction solution was stirred for 14 h, after which the solution was poured into water and extracted with DCM (2 × 50 mL). The combined organic extracts was washed with water (2 × 50 mL), dried, and concentrated. Purification by column chromatography (light petroleum ether/EtOAc, 4:1→1:1) followed by recrystallisation from ethanol afforded benzyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannoside[37] as fine needles (1.90 g, 78%); m.p. 138−139 °C, ref.[37] 137−138.5 °C. Zemplén deacetylation followed by *O*-benzylation under standard conditions (NaH, DMF then BzlBr) and purification by column chromatography (light petroleum ether/EtOAc, 19:1→9:1) afforded **2jα** as a colourless oil (41% from **5**); R_f = 0.38 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = +106.4 (*c* = 2.2, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3029, 2907, 1496, 1453, 1365, 1208, 1099, 1027; δ_H (270 MHz, $CDCl_3$): 3.64 (dd, $J_{6A,6B}$ = 10.8, $J_{6A,5}$ = 1.7 Hz, 1 H, 6-H_A), 3.67, 3.77 (AB, *J* = 13.3 Hz, 2 H, SCH_2Ph), 3.72 (dd, $J_{2,3}$ = 3.2, $J_{2,1}$ = 1.2 Hz, 1 H, 2-H), 3.77−3.84 (m, 3 H, 3-H, 5-H, 6-H_B), 4.03 (t, *J* = 9.0 Hz, 1 H, 4-H), 4.12 (ddd, $J_{5,4}$ = 9.0, $J_{5,6B}$ = 3.2, $J_{5,6A}$ = 1.7 Hz, 1 H, 5-H), 4.45−4.88 (m, 8 H, 4 × CH_2Ph), 5.28 (d, $J_{1,2}$ = 1.2 Hz, 1 H, 1-H), 7.13−7.37 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 34.6 (S*C*H_2Ph), 69.0 (C6), 71.6, 71.8, 73.2, 75.05 (4 × *C*H_2Ph), 72.2, 74.9, 75.65, 80.3, 80.65 (C2−C5), 127.0, 127.4, 127.5, 127.5, 127.7, 127.8, 128.2, 128.25, 128.4, 129.0 (arom. CH), 137.7, 137.8, 138.1, 138.3, 138.4 (subst. arom. C); *m/z* (CI): 664 (100%, [M + NH_4]$^+$); found [M + NH_4]$^+$ 664.3097. $C_{41}H_{42}O_5S{\cdot}NH_4$ requires 664.3097.

Benzyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (2k): A solution of benzyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside,[38] synthesised according to the method of Durette and Shen,[22] (0.300 g, 0.40 mmol) in MeOH (15 mL) was added a methanolic solution of sodium methoxide (25% w/w, 0.65 mL, 2.84 mmol) and the mixture was stirred for 20 h. Amberlyst 15 ion-exchange resin was then added until the pH of the solution became neutral, the resin was removed by filtration, the filtrate was evaporated in vacuo, triturated with DCM, and dried thoroughly under high vacuum to give a colourless oil (0.174 g) which was used without further purification. To a suspension of NaH (60% dispersion in oil, 0.168 g, 4.20 mmol) in anhydrous DMSO (10 mL) was slowly added a solution of the deacetylated thioglycoside (0.174 g) in DMSO (20 mL) and the mixture was stirred for 1 h. Benzyl bromide (0.67 mL, 5.63 mmol) was added with a syringe and the reaction was stirred overnight. After quenching excess NaH with methanol (10 mL) the reaction mixture was partitioned between DCM (50 mL) and water (30 mL) and the aqueous phase was further extracted with EtOAc (2 × 20 mL). The organic parts were washed with water (20 mL), brine (30 mL), dried, and concentrated in vacuo to give a pale yellow solid. The crude product was then purified by column chromatography (elution with light petroleum ether/EtOAc, 3:1) and recrystallised to give the **2k** as fine needles (0.212 g, 49%); R_f = 0.35 (light petroleum ether/EtOAc, 3:1); m.p. 125−127 °C. $[\alpha]_D^{20}$ = −15.2 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3029, 2907, 1496, 1454, 1362, 1216, 1122, 1069, 1049, 1029; δ_H (270 MHz, $CDCl_3$): 3.18−4.05 (m, 14 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_A, 6′-H_B, SCH_2Ph), 4.25 (d, $J_{1,2}$ = 9.5 Hz, 1 H, 1-H), 4.39−4.91 (m, 14 H, 1′-H, 13 × benzylic H), 5.09 (d, *J* = 11.4 Hz, 1 H, benzylic H), 7.15−7.37 (m, 40 H, 8 × Ph); δ_C (67.9 MHz, $CDCl_3$): 34.2 (S*C*H_2Ph), 68.2, 68.9 (C6, C6′), 73.2, 73.3, 74.8, 75.1, 75.2, 75.4, 75.6 (*C*H_2Ph), 75.0, 76.5, 78.0, 79.1, 81.0, 82.8, 83.3, 84.8, 84.9, (C1, C2, C3, C4, C5, C2′, C3′, C4′, C5′), 102.4 (C1′), 127.0, 127.2, 127.3, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.4 (× 2), 129.1 (arom. CH), 137.8, 138.1, 138.2 (× 2), 138.4, 138.6, 139.2 (subst. arom. C); *m/z* (FAB): 1101.5 (100%, [M + Na]$^+$), 181 (40%); found [M + Na]$^+$ 1101.4585. $C_{68}H_{70}O_{10}S{\cdot}Na$ requires 1101.4587; found C 75.67, H 6.44. $C_{68}H_{70}O_{10}S$ requires C, 75.67, H 6.54%.

General Procedure for the Oxidation of Thioglycosides to Glycosyl Sulfones: A solution of Oxone® (9 mmol) in water (25 mL) was added to a solution of the thioglycoside (2 mmol) in acetone (25 mL) and the mixture was stirred at reflux for 3 h. After cooling, the acetone was evaporated under reduced pressure and water (30 mL) added to the residue, which was then extracted with ether (3 × 50 mL), dried, and purified by flash chromatography (elution with light petroleum ether/EtOAc, 3:1).

Methyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (3aα): From 1.46 g of **2aα**. Yield: 1.26 g; 82%; R_f = 0.56 (light petroleum ether/EtOAc, 1:1); m.p. 77−78 °C. $[\alpha]_D^{20}$ = +65.9 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 2867, 1497, 1454, 1302 (SO_2), 1210, 1147 (SO_2), 1099; δ_H (270 MHz, $CDCl_3$): 2.94 (s, 3 H, SO_2CH_3), 3.59 (dd, $J_{4,5}$ = 9.9, $J_{4,3}$ = 7.5 Hz, 1 H, 4-H), 3.62, 3.72, (ABX, $J_{6A,6B}$ = 10.9, $J_{6A,5'}$ = 4.9, $J_{6B,5}$ = 2.2 Hz, 2 H, 6-H_A, 6-H_B), 4.12 (dd, $J_{2,3}$ = 8.2, $J_{2,1}$ = 5.8 Hz, 1 H, 2-H), 4.34−7.39 (m, 2 H, 3-H, 5-H), 4.46, 4.74 (AB, *J* = 11.2 Hz, 2 H, CH_2Ph), 4.47, 4.55 (AB, *J* = 11.9 Hz, 2 H, CH_2Ph), 4.72, 4.83 (AB, *J* = 11.4 Hz, 2 H, CH_2Ph), 4.72, 4.86 (AB, *J* = 11.2 Hz, 2 H, CH_2Ph), 4.88 (d, $J_{1,2}$ = 5.8 Hz, 1 H, 1-H), 7.13−7.17 (m, 2 H, 2 × arom. H), 7.24−7.40 (m, 18 H, 18 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 40.2 (SO_2CH_3), 68.7 (C6), 73.5, 74.0, 74.2, 74.9 (4 × *C*H_2Ph), 75.3, 76.6, 77.5, 79.8 (C2, C3, C4, C5), 89.0 (C1), 127.7, 127.8, 128.0, 128.2, 128.4 (× 2), 128.5 (arom. CH), 137.0, 137.7, 137.9, 138.1 (subst. arom. C); *m/z* (CI): 620 (100%, [M + NH_4]$^+$), 391 (40%); found C 69.75, H 6.33, S 5.48. $C_{35}H_{38}O_7S$ requires C, 69.74, H 6.35, S 5.32%.

Methyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (3aβ): From 0.66 g of **2aβ**. Yield: 0.59 g; 84%; R_f = 0.56 (light petroleum ether/EtOAc, 1:1); m.p. 107−110 °C. $[\alpha]_D^{20}$ = +33.8 (*c* = 1.0, $CHCl_3$); δ_H (270 MHz, $CDCl_3$): 2.95 (s, 3 H, SO_2CH_3), 3.58−3.83 (m, 5 H, 2-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.07 (t, *J* = 9.0 Hz, 1 H, 3-H) 4.36 (d, $J_{1,2}$ = 9.0 Hz, 1 H, 1-H), 4.54 (A_2, 2 H, CH_2Ph), 4.57, 4.81 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.78, 4.97 (AB, *J* = 9.9 Hz, 2 H, CH_2Ph), 4.88, 4.95 (AB, *J* = 10.9 Hz, 2 H,

CH_2Ph), 7.15−7.18 (m, 2 H, 2 × arom. H), 7.25−7.37 (m, 18 H, 18 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 39.0 (SO_2CH_3), 68.6 (C6), 73.4, 75.2, 75.4, 75.9 (4 × *C*H_2Ph), 76.5, 77.1, 79.8, 86.0 (C2, C3, C4, C5), 90.6 (C1), 127.6, 127.6, 127.8, 128.0 (× 2), 128.4, 128.5, 128.6 (arom. CH), 137.3, 137.5, 137.8, 138.1 (subst. arom. C); *m*/*z* (CI): 620 (100%, $[M + NH_4]^+$), 391 (25%); found C 69.60, H 6.38, S 5.41. $C_{35}H_{38}O_7S$ requires C, 69.74, H 6.35, S 5.32%.

Ethyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (3bα): From 0.425 g of **2bα**. Yield: 0.360 g; 80%; needles (MeOH); R_f = 0.16 (light petroleum ether/EtOAc, 3:1); m.p. 93.5−94 °C. $[\alpha]_D^{20}$ = +69.2 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3031, 2922, 1496, 1453, 1363, 1209, 1074, 1154 (SO_2), 1075, 1029; δ_H (270 MHz, $CDCl_3$): 1.35 (t, *J* = 7.5 Hz, 3 H, $SO_2CH_2CH_3$), 3.02, 3.18 (ABX_3, *J* = 13.8, 7.5 Hz, 2 H, $SO_2CH_2CH_3$), 3.58 (dd, $J_{4,5}$ = 10.0, $J_{4,3}$ = 7.8 Hz, 1 H, 4-H), 3.62, 3.71 (ABX, $J_{6A,6B}$ = 10.9, $J_{6A,5}$ = 4.5, $J_{6B,5}$ = 2.2 Hz, 2 H, 6-H_A, 6-H_B), 4.10 (dd, $J_{2,3}$ = 8.6, $J_{2,1}$ = 5.8 Hz, 1 H, 2-H), 4.36 (ddd, $J_{5,4}$ = 10.0, $J_{5,6A}$ = 4.5, $J_{5,6B}$ = 2.2 Hz, 1 H, 5-H), 4.43 (appt. t, $J_{3,4}$ = 7.8, $J_{3,2}$ = 8.6 Hz, 1 H, 3-H), 4.46, 4.55 (AB, *J* = 12.1 Hz, 2 H, CH_2Ph), 4.47, 4.76 (AB, *J* = 11.2 Hz, 2 H, CH_2Ph), 4.71, 4.89 (AB, *J* = 11.6 Hz, 2 H, CH_2Ph), 4.74, 4.85 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.92 (d, $J_{1,2}$ = 5.8 Hz, 1 H, 1-H), 7.13−7.17 (m, 2 H, 2 × arom. H), 7.23−7.35 (m, 16 H, 16 × arom. H), 7.37−7.41 (m, 2 H, 2 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 6.0 ($SO_2CH_2CH_3$), 46.6 ($SO_2CH_2CH_3$), 68.6, (C6), 73.4, 74.0, 74.4, 75.3 (4 × *C*H_2Ph), 75.2, 76.6, 77.8, 80.2, 86.9 (C1, C2, C3, C4, C5), 127.6, 127.7, 127.9, 128.1, 128.3, 128.4, 128.5 (arom. CH), 137.1, 137.6, 137.9, 138.2 (subst. arom. C); *m*/*z* (CI): 634 (100%, $[M + NH_4]^+$), 108 (35%), 91 (75%, $[C_7H_7]^+$).

Ethyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (3bβ): From 0.411 g of **2bβ**. Yield: 0.380 g; 88%; fine needles (MeOH); R_f = 0.16 (light petroleum ether/EtOAc, 4:1); m.p. 93−94 °C. $[\alpha]_D^{20}$ = +43.5 (*c* = 0.3, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3041, 2938, 1363, 1317 (SO_2), 1145 (SO_2), 1097, 1073; δ_H (270 MHz, $CDCl_3$): 1.38 (t, *J* = 7.5 Hz, 3 H, $SO_2CH_2CH_3$), 3.07, 3.17 (ABX_3, *J* = 14.1, 7.5 Hz, 2 H, $SO_2CH_2CH_3$), 3.55−3.72 (m, 4 H, 4-H, 5-H, 6-H_A, 6-H_B), 3.79 (t, *J* = 9.0 Hz, 1 H, 3-H), 4.11 (t, *J* = 9.2 Hz, 1 H, 2-H), 4.39 (d, $J_{1,2}$ = 9.2 Hz, 1 H, 1-H), 4.53 (A_2, 2 H, CH_2Ph), 4.56, 4.81 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.78, 4.00 (AB, *J* = 9.7 Hz, 2 H, CH_2Ph), 4.87, 4.95 (AB, *J* = 11.2 Hz, 2 H, CH_2Ph), 7.15−7.18 (m, 2 H, 2 × arom. H), 7.23−7.39 (m, 18 H, 18 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 6.1 ($SO_2CH_2CH_3$), 45.7 ($SO_2CH_2CH_3$), 68.6, (C6), 73.3, 75.1, 75.4, 75.9 (4 × *C*H_2Ph), 77.2 (× 2), 79.8, 86.1, 88.9 (C1, C2, C3, C4, C5), 127.6, 127.7 (× 2), 127.9 (× 2), 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, (arom. CH), 137.4, 137.6, 137.8, 138.1 (subst. arom. C); *m*/*z* (CI): 634 (100%, $[M + NH_4]^+$), 108 (45%), 91 (73%, $[C_7H_7]^+$); found C 70.03, H 6.42, S 5.14. $C_{36}H_{40}O_7S$ requires C, 70.11, H 6.54, S 5.20%.

Propyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (3cα): From 0.99 g of **2cα**. Yield: 0.87 g; 83%; needles (MeOH); R_f = 0.36 (light petroleum ether/EtOAc, 1:1); m.p. 97.5−98.0 °C. $[\alpha]_D^{20}$ = +73.1 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3088, 2870, 1360, 1314, 1146, 1135 (SO_2), 1028; δ_H (270 MHz, $CDCl_3$): 0.96 (t, *J* = 7.3 Hz, 3 H, $SO_2CH_2CH_2CH_3$), 1.84 (sext., *J* = 7.3 Hz, 2 H, $SO_2CH_2CH_2CH_3$), 2.97, 3.12 (ABX_2, *J* = 13.8, 7.3 Hz, 2 H, $SO_2CH_2CH_2CH_3$), 3.57 (dd, $J_{4,5}$ = 9.8, $J_{4,3}$ = 8.0 Hz, 1 H, 4-H), 3.61, 3.71 (ABX, $J_{6A,6B}$ = 10.7, $J_{6B,5}$ = 1.5, $J_{6A,5}$ = 4.9 Hz, 2 H, 6-H_A, 6-H_B), 4.10 (dd, $J_{2,3}$ = 8.5, $J_{2,1}$ = 6.1 Hz, 1 H, 2-H), 4.37 (ddd, $J_{5,4}$ = 9.8, $J_{5,6A}$ = 4.9, $J_{5,6B}$ = 1.5 Hz, 1 H, 5-H), 4.43 (t, *J* = 8.1 Hz, 1 H, 3-H), 4.46, 4.55, (AB, *J* = 12.1 Hz, 2 H, CH_2Ph), 4.47, 4.77 (AB, *J* = 11.1 Hz, 2 H, CH_2Ph), 4.72, 4.89 (AB, *J* = 11.4 Hz, 2 H, CH_2Ph), 4.75, 4.84 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.88 (d, $J_{1,2}$ = 6.1 Hz, 1 H, 1-H), 7.14−7.41 (20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 13.2 ($SO_2CH_2CH_2CH_3$), 15.15 ($SO_2CH_2CH_2CH_3$), 53.8 ($SO_2CH_2CH_2CH_3$), 68.7 (C6), 73.4, 74.0, 74.35, 75.1 (4 × *C*H_2Ph), 75.3, 76.7, 77.9, 80.2, 87.45 (C1−C5), 127.7, 127.8, 128.0, 128.1, 128.4, 128.5 (× 2) (arom. CH), 137.1, 137.7, 138.0, 138.2 (subst. arom. C); *m*/*z* (CI): 648 (100%, $[M + NH_4]^+$); found $[M + NH_4]^+$ 648.2999. $C_{37}H_{42}O_7S{\cdot}NH_4$ requires 648.2995.

Propyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (3cβ): From 0.96 g of **2cβ**. Yield: 0.73 g; 72%; colourless oil; R_f = 0.32 (light petroleum ether/EtOAc, 1:1). $[\alpha]_D^{20}$ = +26.8 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3088, 3065, 3041, 3006, 2870, 2933, 2877, 1355, 1318, 1141, 1139 (SO_2); δ_H (270 MHz, $CDCl_3$): 1.00 (t, *J* = 7.3 Hz, 3 H, $SO_2CH_2CH_2CH_3$), 1.77−1.96 (symm. m, 2 H, $SO_2CH_2CH_2CH_3$), 3.01, 3.11 (ABXY, *J* = 13.8, 9.7, 6.1 Hz, 2 H, $SO_2CH_2CH_2CH_3$), 3.50−3.72 (m, 4 H, 3-H, 4-H, 6-H_A, 6-H_B), 3.79 (br. t, *J* = 8.7 Hz, 1 H, 5-H), 4.10 (t, *J* = 9.2 Hz, 1 H, 2-H), 4.36 (d, $J_{1,2}$ = 9.2 Hz, 1 H, 1-H), 4.53 (A_2, 2 H, CH_2Ph), 4.57, 4.81 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.77, 4.99 (AB, *J* = 9.9 Hz, 2 H, CH_2Ph), 4.87, 4.95 (AB, *J* = 11.1 Hz, 2 H, CH_2Ph), 7.15−7.39 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 13.2 ($SO_2CH_2CH_2CH_3$); 15.2 ($SO_2CH_2CH_2CH_3$), 52.85 ($SO_2CH_2CH_2CH_3$), 68.6 (C6), 73.3, 75.1, 75.4, 75.85 (4 × *C*H_2Ph), 77.2 (× 2), 79.7, 86.1, 89.35 (C1−C5), 127.6 (× 2), 127.75, 127.9, 128.0 (× 2), 128.35, 128.4, 128.5, 128.6 (arom. CH), 137.4, 137.5, 137.8, 138.1 (subst. arom. C); *m*/*z* (CI): 648 (100%, $[M + NH_4]^+$); found $[M + NH_4]^+$ 648.3000. $C_{37}H_{42}O_7S{\cdot}NH_4$ requires 648.2995.

Benzyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (3dα): From 1.54 g of of **2dα**. Yield: 1.41 g; 87%; fine needles (MeOH); R_f = 0.20 (light petroleum ether/EtOAc, 3:1); m.p. 125−126.5 °C. $[\alpha]_D^{20}$ = +105.9 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3031, 2867, 1496, 1454, 1364, 1318 (SO_2), 1099; δ_H (270 MHz, $CDCl_3$): 3.51 (dd, *J* = 9.9, 8.2 Hz, 1 H, 4-H), 3.60, 3.72 (ABX, $J_{6A,6B}$ = 10.5, $J_{6A,5}$ = 5.3, $J_{6B,5}$ = 1.9 Hz, 2 H, 6-H_A, 6-H_B), 4.04 (dd, $J_{2,3}$ = 8.7, $J_{2,1}$ = 6.1 Hz, 1 H, 2-H), 4.11, (d, *J* = 13.8 Hz, 1 H, $SO_2CH_AH_BPh$), 4.43−4.64 (m, 7 H, $SO_2CH_AH_BPh$, 2 × CH_2Ph, 3-H, 5-H), 4.72−4.90 (m, 5 H, 2 × CH_2Ph, 1-H), 7.15−7.43 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 58.2 (*C*H_2Ph), 68.8 (C6), 73.4, 73.8, 74.5, 75.3 (4 × *C*H_2Ph), 75.1, 76.7, 77.9, 80.5, 85.7 (C1, C2, C3, C4, C5), 127.7, 127.8, 128.0 (× 2), 128.1, 128.3, 128.4, 128.6, 128.7, 131.0 (arom. CH), 137.1, 137.6, 137.9, 138.2 (subst. arom. C); *m*/*z* (CI): 696 (45%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found C 72.47, H 6.17, S 4.91. $C_{41}H_{42}O_7S$ requires C, 72.54, H 6.24, S 4.72%.

Benzyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (3dβ): From 1.00 g of **2dβ**. Yield: 0.74 g; 70%; colourless oil; R_f = 0.20 (light petroleum ether/EtOAc, 3:1). $[\alpha]_D^{20}$ = +0.3 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3031, 2867, 1496, 1454, 1364, 1318 (SO_2), 1099; δ_H (270 MHz, $CDCl_3$): 3.49−3.56 (m, 2 H, 2 × CH), 3.62−3.77 (m, 3 H, 5-H, 6-H_A, 6-H_B), 4.04−7.16 (m, 3 H, CH, SO_2CH_2Ph), 4.53, 4.80 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.54−7.59 (m, 3 H, CH, CH_2Ph), 4.71, 4.97 (AB, *J* = 9.7 Hz, 2 H, CH_2Ph), 4.80, 4.91 (AB, *J* = 11.1 Hz, 2 H, CH_2Ph), 7.14−7.36 (m, 23 H, 23 × arom. H), 7.46−7.49 (m, 2 H, 2 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 57.1 (SO_2CH_2Ph), 68.9 (C6), 73.4, 75.1, 75.4, 75.8 (4 × *C*H_2Ph), 76.8, 77.0, 79.4, 85.9, 86.5 (C1, C2, C3, C4, C5), 127.4, 127.5, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.6, 128.8, 128.9, 131.1 (arom. CH), 137.2, 137.5, 137.7, 138.0 (subst. arom. C); *m*/*z* (CI): 696 (45%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$).

Isopropyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (3eα): From 1.096 g of **2eα**. Yield: 1.12 g; 97%; fine needles (MeOH); R_f = 0.45 (light petroleum ether/EtOAc, 1:1); m.p. 105−106 °C. $[\alpha]_D^{20}$ = +81.2 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3006,

2871, 1497, 1454, 1364, 1314 (SO_2), 1207, 1143, 1095; δ_H (270 MHz, $CDCl_3$): 1.32, 1.35 [2 × d, J = 7.0 Hz, 6 H, $SO_2CH(CH_3)_2$], 3.44 [hept., J = 7.0 Hz, 1 H, $SO_2CH(CH_3)_2$], 3.58 (dd, $J_{4,5}$ = 9.9, $J_{4,3}$ = 8.5 Hz, 1 H, 4-H), 3.62, 3.70 (ABX, $J_{6A,6B}$ = 10.8, $J_{6B,5}$ = 2.2, $J_{6A,5}$ = 4.4 Hz, 2 H, 6-H_A, 6-H_B), 4.09 (dd, $J_{2,3}$ = 9.2, $J_{2,1}$ = 6.3 Hz, 1 H, 2-H), 4.38 (ddd, $J_{5,4}$ = 9.9, $J_{5,6A}$ = 4.4, $J_{5,6B}$ = 2.2 Hz, 1 H, 5-H), 4.45, 4.55 (AB, J = 12.1 Hz, 2 H, CH_2Ph), 4.48, 4.81 (AB, J = 11.1 Hz, 2 H, CH_2Ph), 4.52 (t, J = 9.0 Hz, 1 H, 3-H), 4.71, 4.89 (AB, J = 11.4 Hz, 2 H, CH_2Ph), 4.77, 4.93 (AB, J = 10.9 Hz, 2 H, CH_2Ph), 5.06 (d, J = 6.3 Hz, 1 H, 1-H), 7.14−7.44 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 13.3, 16.3 [$(CH_3)_2CHSO_2$], 51.7 [$(CH_3)_2CHSO_2$], 68.6 (C6), 73.4, 74.0, 74.6, 75.5 (4 × CH_2Ph), 75.3, 76.7, 78.3, 80.7, 84.85 (C1−C5), 127.6, 127.7, 127.8, 128.1, 128.3, 128.4 (× 2), 128.5 (arom. CH), 137.3, 137.7, 138.1, 138.4 (subst. arom. C); *m/z* (CI): 616 (40%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found $[M + NH_4]^+$ 648.3001. $C_{37}H_{42}O_7S{\cdot}NH_4$ requires 648.2995.

Isopropyl *S,S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (3eβ): From 0.98 g of **2cβ**. Yield: 0.90 g; 87%; amorphous solid; R_f = 0.45 (light petroleum ether/EtOAc, 1:1). $[\alpha]_D^{20}$ = +25.4 (c = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3006, 2874, 1497, 1454, 1361, 1328 (SO_2), 1310, 1210, 1145, 1097; δ_H (270 MHz, $CDCl_3$): 1.33, 1.41 [2 × d, J = 7.0 Hz, 6 H, $CH(CH_3)_2$], 3.48 [hept., J = 7.0 Hz, 1 H, $CH(CH_3)_2$], 3.54−3.62 (m, 3 H, 3-H, 4-H, 6-H_A), 3.69 (d, $J_{6B,6A}$ = 10.5 Hz, 1 H, 6-H_B), 3.80 (br. t, J = 8.7 Hz, 1 H, 5-H), 4.15 (t, J = 9.0 Hz, 1 H, 2-H), 4.47−4.52 (m, 3 H, 1-H, CH_2Ph), 4.55, 4.81 (AB, J = 11.1 Hz, 2 H, CH_2Ph), 4.77, 5.13 (AB, J = 9.9 Hz, 2 H, CH_2Ph), 4.87, 4.96 (AB, J = 11.1 Hz, 2 H, CH_2Ph), 7.15−7.40 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 13.1, 16.1 [$CH(CH_3)_2$], 51.0 [$CH(CH_3)_2$], 68.7 (C6), 73.25, 75.1, 75.4, 75.9 (4 × CH_2Ph), 77.2 (× 2), 79.8, 86.15, 87.5 (C1−C5), 127.6, 127.7, 127.9, 127.9, 128.0, 128.35, 128.45, 128.7 (arom. CH), 137.4, 137.55, 137.8, 138.1 (subst. arom. C); *m/z* (CI): 616 (4%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found C 70.75, H 6.78, S 4.87. $C_{37}H_{42}O_7S$ requires C, 70.45, H 6.71, S 5.08%.

Cyclohexyl *S,S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (3fα): From 1.40 g of **2fα**. Yield: 1.33 g; 90%; fine needles (MeOH); R_f = 0.42 (light petroleum ether/EtOAc, 1:1); m.p. 115−116 °C. $[\alpha]_D^{20}$ = +79.6 (c = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3011, 2938, 1454, 1302 (SO_2), 1216, 1143 (SO_2), 1096; δ_H (270 MHz, $CDCl_3$): 1.02−1.25, 1.47−1.64 (m, 6 H, 4 × 3′-H, 2 × 4′-H), 1.77 (br. d, J = 10.7 Hz, 1 H, 2′-H), 1.86 (br. d, J = 10.7 Hz, 1 H, 2′-H), 1.94 (br. d, J = 12.6 Hz, 2 H, 2 × 2′-H), 3.21 [tt, J = 12.1, 3.2 Hz, 1 H, $SO_2CH(CH_2)_5$], 3.54 (dd, $J_{4,5}$ = 9.9, $J_{4,3}$ = 8.5 Hz, 1 H, 4-H), 3.60, 3.71 (ABX, $J_{6A,6B}$ = 10.5, $J_{6A,5}$ = 5.1, $J_{6B,5}$ = 2.0 Hz, 2 H, 6-H_A, 6-H_B), 4.08 (dd, $J_{2,3}$ = 9.2, $J_{2,1}$ = 6.3 Hz, 1 H, 2-H), 4.40 (ddd, $J_{5,4}$ = 9.9, $J_{5,6A}$ = 5.1, $J_{5,6B}$ = 2.0 Hz, 1 H, 5-H), 4.44, 4.55 (AB, J = 11.6 Hz, 2 H, CH_2Ph), 4.44, 4.81 (AB, J = 11.1 Hz, 2 H, CH_2Ph), 4.53 (t, J = 9.0 Hz, 1 H, 3-H), 4.71, 4.93 (AB, J = 10.9 Hz, 2 H, CH_2Ph), 4.77, 4.87 (AB, J = 10.6 Hz, 2 H, CH_2Ph), 5.02 (d, $J_{1,2}$ = 6.3 Hz, 1 H, 1-H), 7.15−7.39 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 22.75, 24.8, 25.0, 25.1, 25.9 (5 × cyclohexyl CH_2), 59.7 (SO_2CH of cyclohexyl), 68.8 (C6), 73.4, 74.0, 74.5, 75.45 (4 × CH_2Ph), 75.2, 76.9, 78.4, 80.75, 84.6 (C1−C5), 127.6 (× 2), 127.75, 127.8, 128.0, 128.3, 128.35, 128.4, 128.5 (arom. CH), 137.3, 137.7, 138.1, 138.4 (subst. arom. C); *m/z* (CI): 688 (8%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found $[M + NH_4]^+$ 688.3288. $C_{40}H_{46}O_7S{\cdot}NH_4$ requires 688.3308.

Cyclohexyl *S,S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (3fβ): From 0.48 g of **2fβ**. Yield: 0.43 g; 85%; fine needles (MeOH); R_f = 0.42 (light petroleum ether/EtOAc, 1:1); m.p. 92−93 °C. $[\alpha]_D^{20}$ = +18.4 (c = 1.7, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3009, 2860, 1453, 1359, 1301 (SO_2), 1096, 1072; δ_H (270 MHz, $CDCl_3$): 1.03−1.32, 1.51−1.68 (m, 6 H, 4 × 3′-H, 2 × 4′-H), 1.76 (br. d, J = 12.8 Hz, 1 H, 2′-H), 1.94 (br. t, J = 12.8 Hz, 2 H, 2 × 2′-H), 2.20 (br. d, J = 12.8 Hz, 1 H, 2′-H), 3.26 [tt, J = 12.1, 3.4 Hz, 1 H, $SO_2CH(CH_2)_5$], 3.53−3.61 (m, 3 H, 3-H, 4-H, 6-H_A), 3.67 (d, $J_{6B,6A}$ = 10.2 Hz, 1 H, 6-H_B), 3.79 (br. t, J = 9.5 Hz, 1 H, 5-H), 4.15 (t, J = 9.2 Hz, 1 H, 2-H), 4.45 (d, 1 H, $J_{1,2}$ = 9.5 Hz, 1 H, 1-H), 4.51 (A_2, 2 H, CH_2Ph), 4.56, 4.81 (AB, J = 11.1 Hz, 2 H, CH_2Ph), 4.77, 5.02 (AB, J = 10.0 Hz, 2 H, CH_2Ph), 4.87, 4.96 (AB, J = 10.9 Hz, 2 H, CH_2Ph), 7.16−7.40 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 22.6, 24.8, 25.0, 25.1, 25.75 (5 × cyclohexyl CH_2), 58.9 (SO_2CH of cyclohexyl), 68.8 (C6), 73.35, 75.1, 75.4, 75.9 (4 × CH_2Ph), 77.15 (× 2), 79.75, 86.2, 87.2 (C1−C5), 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.4, 128.5, 128.7 (arom. CH), 137.5, 137.6, 137.8, 138.15 (subst. arom. C); *m/z* (CI): 688 (100%, $[M + NH_4]^+$); found C 71.67, H 6.86, S 4.69. $C_{40}H_{46}O_7S$ requires C, 71.62, H 6.91, S 4.78%.

Benzhydryl *S,S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (3gα): From 0.55 g of **2gα**. Yield: 0.052 g; 9%; colourless oil; R_f = 0.37 (light petroleum ether/EtOAc, 1:1). $[\alpha]_D^{20}$ = +112.3 (c = 0.8, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3005, 2868, 1496, 1453 1360, 1124, 1067; δ_H (270 MHz, $CDCl_3$): 3.07−3.13 (m, 1 H, 5-H), 3.52−3.63, 4.03−4.14 (m, 6 H, 1-H, 2-H, 3-H, 4-H, 6-H_A, 6-H_B), 4.52, 4.90 (AB, J = 11.1 Hz, 2 H, CH_2Ph), 4.59 (A_2, 2 H, CH_2Ph), 4.70, 4.99 (AB, J = 9.7 Hz, 2 H, CH_2Ph), 4.80 (A_2, 2 H, CH_2Ph), 5.76 (s, 1 H, $CHPh_2$), 7.12−7.15, 7.21−7.44 (m, 28 H, 28 × arom. CH), 7.63−7.66 (m, 2 H, 2 × arom. CH); δ_C (67.9 MHz, $CDCl_3$): 68.4 (C6), 73.3, 75.05, 75.5, 75.8 (4 × CH_2Ph), 69.9 (SO_2CHPh_2), 77.0, 77.1, 79.2, 86.0, 87.2, (C1−C5), 127.5, 127.7, 127.9, 128.1, 128.2, 128.35, 128.414 128.5, 128.65, 128.7, 128.8, 129.9, 130.1, 130.5.130.8 (arom. CH), 132.7, 137.2, 137.6, 137.8, 138.1 (subst. arom. C); *m/z* (FAB): 777 (80%, $[M + Na]^+$), 439 (100%); found $[M + Na]^+$ 777.2868. $C_{47}H_{46}O_7S{\cdot}Na$ requires 777.2862.

Benzyl *S,S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-galactopyranoside (3iα): From 1.85 g of **2iα**. Yield: 1.24 g; 64%; needles (MeOH); R_f = 0.34 (light petroleum ether/EtOAc, 4:1); m.p. 115−116 °C. $[\alpha]_D^{20}$ = +112.2 (c = 0.9, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3007, 2874, 1496, 1455, 1332 (SO_2), 1209, 1150 (SO_2), 1108; δ_H (270 MHz, $CDCl_3$): 3.46−3.59 (m, 3 H, 3-H, 6-H_A, 6-H_B), 3.74 (dd, $J_{2,3}$ = 9.0, $J_{2,1}$ = 5.8 Hz, 1 H, 2-H), 3.83 (br. d, $J_{4,3}$ = 2.4 Hz, 1 H, 4-H), 4.13−4.16 (m, 2 H, SO_2CH_2Ph), 4.41−4.78 (m, 8 H, 1-H, 5-H, 6 × benzylic H), 4.90 (d, J = 9.7 Hz, 1 H, benzylic H), 4.98 (d, J = 11.6 Hz, 1 H, benzylic H), 7.23−7.46 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 56.8 (SO_2CH_2Ph), 69.2 (C6), 73.1, 73.3, 74.5, 75.6 (4 × CH_2Ph), 73.65 (× 2), 78.4, 83.4, 88.05 (C1−C5); 127.5, 127.6, 127.7, 127.9, 128.2, 128.3, 128.5, 128.7, 128.8, 131.6 (arom. CH), 137.55, 137.6, 137.9, 138.2 (subst. arom. C); *m/z* (CI): 696 (5%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found C 72.52, H 6.16, S 4.57. $C_{41}H_{42}O_5S$ requires C, 72.54, H 6.24, S 4.72%.

Benzyl *S,S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (3iβ): From 0.67 g of **2jβ**. Yield: 0.58 g; 82%; colourless oil; R_f = 0.34 (light petroleum ether/EtOAc, 1:1). $[\alpha]_D^{20}$ = +1.9 (c = 0.9, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3031, 2872, 1496, 1454, 1318 (SO_2), 1126, 1101; δ_H (270 MHz, $CDCl_3$): 3.37, 3.73 (ABX, $J_{6A,6B}$ = 10.2, $J_{6A,5}$ = 3.6, $J_{6B,5'}$ Hz = 8.0 Hz, 2 H, 6-H_A, 6-H_A), 3.94 (br. s, 1 H, 4-H), 4.08 (d, J = 13.6 Hz, 1 H, $SO_2CH_AH_BPh$), 4.38−4.39, 4.55−4.79, 4.78−4.87 (m, 13 H, 1-H, 2-H, 3-H, 5-H, 4 × CH_2Ph, $SO_2CH_AH_BPh$), 7.15−7.49 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 57.9 (SO_2CH_2Ph), 69.0 (C6), 73.4, 73.7, 73.8, 74.2 (4 × CH_2Ph), 74.1, 75.0, 75.1, 77.5, 85.25 (4 × CH_2Ph), 127.6, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.4, 128.6, 128.7, 129.0, 129.3, 131.1 (arom. CH), 137.5, 137.7, 137.9, 138.3 (subst. arom. C); *m/z*

(CI): 696 (15%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found C 72.52, H 6.16, S 4.57. $C_{41}H_{42}O_7S$ requires C, 72.54, H 6.24, S 4.72%.

Benzyl *S,S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyranoside (3jα): From 1.05 g of **2jα**. Yield: 1.02 g; 93%; colourless oil; R_f = 0.53 (light petroleum ether/EtOAc, 1:1). $[\alpha]_D^{20}$ = +66.3 (*c* = 2.3, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3031, 2867, 1496, 1454, 1366, 1314 (SO_2), 1110 (SO_2), 1027; δ_H (270 MHz, $CDCl_3$): 3.65−3.66 (m, 2 H, 6-H_A, 6-H_B), 3.88 (t, *J* = 8.2 Hz, 1 H, 4-H), 4.14 (dd, $J_{2,1}$ = 7.5, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 4.37−4.62 (m, 11 H, 3-H, 5-H, 9 × benzylic H), 4.75 (d, *J* = 9.9 Hz, 1 H, benzylic H), 4.75 (d, $J_{1,2}$ = 7.5 Hz, 1 H, 1-H), 7.13−7.39 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 56.6 (SO_2CH_2Ph), 69.3 (C6), 72.6, 73.0, 73.15, 74.2 (4 × CH_2Ph), 70.8, 73.85, 75.95, 79.0, 86.9 (5 × CH), 126.8, 127.3, 127.4, 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.3, 128.6, 128.8, 130.8, 130.9 (arom. CH), 137.1, 137.9, 137.95, 138.0 (subst. arom. C); *m/z* (CI): 696 (30%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found C 72.41, H 6.15, S 4.73. $C_{41}H_{42}O_7S$ requires C, 72.54, H 6.24, S 4.74%.

Benzhydryl *S,S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (3gβ): Hydrogen peroxide solution (1.2 mL, 35% in water, 12 mmol) was added slowly to a solution of **2gβ** (1.19 g, 1.65 mmol) in acetic acid (15 mL) at 0 °C. The reaction solution was then allowed to warm to room temp. and was stirred overnight. The solvent was removed in vacuo and the residue redissolved in DCM, washed with water (3 × 50 mL), dried, and concentrated. The crude product was purified by column chromatography (light petroleum ether/EtOAc, 4:1→1:1) to give **3gβ** as a colourless oil (0.91 g, 73%); R_f = 0.37 (light petroleum ether/EtOAc, 1:1). $[\alpha]_D^{20}$ = +26.4 (*c* = 1.7, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3005, 2868, 1496, 1453 1360, 1124, 1067; δ_H (270 MHz, $CDCl_3$): 3.28 (ddd, $J_{5,4}$ = 9.8, $J_{5,6A}$ = 6.0 Hz, $J_{5,6B}$ = 2.4, 1 H, 5-H), 3.45 (d, *J* = 9.7 Hz, 1 H, 1-H), 3.50 (t, *J* = 9.7 Hz, 1 H, 4-H), 3.63 (t, *J* = 9.7 Hz, 1 H, 3-H), 3.68−3.79 (m, 2 H, 6-H_A, 6-H_B), 4.05 (t, *J* = 9.5 Hz, 1 H, 2-H), 4.52, 4.79 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.62 (A_2, 2 H, CH_2Ph), 4.81, 4.92 (AB, *J* = 10.4 Hz, 2 H, CH_2Ph), 4.86 (A_2, 2 H, CH_2Ph), 5.71 (s, 1 H, $CHPh_2$), 7.13−7.45, 7.57−7.60 (m, 30 H, 6 × Ph); δ_C (67.9 MHz, $CDCl_3$): 67.1 (SO_2CHPh_2), 69.2 (C6), 73.4, 75.6, 76.4 (× 2) (4 × CH_2Ph), 76.6, 77.7, 79.8, 86.5, 87.4 (C1−C5), 127.5, 127.6, 127.8, 128.0, 128.1, 128.4, 128.6, 128.7, 129.0, 129.1, 129.5 (arom. CH), 133.9, 135.3, 137.85, 137.95, 138.1, 138.1 (subst. arom. C); *m/z* (FAB): 777 (80%, $[M + Na]^+$), 439 (100%).

Adamant-2-yl *S,S*-Dioxo-2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-glucopyranoside (3h): 3-Chloroperoxybenzoic acid (1.16 g, 57−86% purity, 3.83−5.78 mmol) was added portionwise to a stirred solution of **2h** (0.663 g, 0.93 mmol) in DCM (20 mL) containing Na_2HPO_4 (0.66 g, 4.65 mmol) at 0 °C. The reaction mixture was then stirred at room temp. for 2.5 h after which time it was diluted with ether (50 mL) and aq. $Na_2S_2O_3$ (0.1 M, 20 mL) and stirred for a further 0.5 h. The organic layer was separated and washed with aq. NaOH (1.0 M, 20 mL), water (50 mL), brine (50 mL), dried, and concentrated. The crude product was purified by column chromatography (light petroleum ether/EtOAc, 9:1→2:1) to afford **3hα** as a colourless syrup (0.481 g, 69%); R_f = 0.37 (light petroleum ether/EtOAc, 2:1). $[\alpha]_D^{20}$ = +70.9 (*c* = 0.6, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3011, 2862, 1453, 1363, 1301 (SO_2), 1096, 1073; δ_H (270 MHz, $CDCl_3$): 0.03, 0.04 [2 × s, 6 H, $Si(CH_3)_2$], 0.88 [s, 9 H, $SiC(CH_3)_3$], 1.55−1.77, 1.84−1.96 (m, 10 H, 5 × adamantyl CH_2), 2.35−2.65 (m, 4 H, 4 × adamantyl CH), 3.48 (br. s, 1 H, SO_2CH of adamantyl), 3.62 (dd, $J_{4,5}$ = 9.8, $J_{4,3}$ = 7.8 Hz, 1 H, 4-H), 3.78−3.85 (m, 2 H, 6-H_A, 6-H_B), 4.08 (dd, $J_{2,3}$ = 8.3, $J_{2,1}$ = 5.8 Hz, 1 H, 2-H), 4.21 (dt, $J_{5,4}$ = 9.8, $J_{5,6A}$ = $J_{5,6B}$ = 2.6 Hz, 1 H, 5-H), 4.46 (t, *J* = 8.0 Hz, 1 H, 3-H), 4.62, 4.79 (AB, *J* = 11.1 Hz, 2 H, CH_2Ph), 4.72, 4.85 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.72, 4.88 (AB, *J* = 11.4 Hz, 2 H, CH_2Ph), 4.96 (d, 1 H, $J_{1,2}$ = 5.8 Hz, 1-H), 7.24−7.44 (m, 15 H, 3 × Ph); δ_C (67.9 MHz, $CDCl_3$): −5.3, −5.1 [$(CH_3)_2Si$], 18.45 [$(CH_3)_3CSi$), 25.9 [$(CH_3)_3CSi$], 26.7, 27.4, 27.5, 28.65 (4 × adamantyl CH), 31.6, 32.1, 37.1, 38.9, 39.1 (5 × adamantyl CH_2), 62.2 (C6), 64.5 (SO_2CH of adamantyl), 73.9, 74.3, 75.0 (3 × CH_2Ph), 76.4, 77.2, 78.3, 80.3, 86.0 (C1−C5), 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6 (arom. CH), 137.5, 138.3, 138.35 (subst. arom. C); *m/z* (CI): 769 (30%, $[M + Na]^+$), 91 (100%, $[C_7H_7]^+$); found $[M + Na]^+$ 769.3573. $C_{43}H_{58}O_7SSi{\cdot}Na$ requires 769.3570.

Ethyl *S,S*-Dioxo-2,3,5-tri-*O*-benzyl-β-D-ribofuranoside (3lβ): From 0.62 g of **2lβ**. Yield: 0.57 g; 86%; colourless oil; R_f = 0.56 (light petroleum ether/EtOAc, 1:1). $[\alpha]_D^{20}$ = +39.9 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 2923, 1497, 1454, 1363, 1312 (SO_2), 1136 (SO_2), 1085, 1040; δ_H (270 MHz, $CDCl_3$): 1.34 (t, *J* = 7.5 Hz, 3 H, $SO_2CH_2CH_3$), 2.97, 3.08 (ABX_3, *J* = 14.7, 7.5 Hz, 2 H, $SO_2CH_2CH_3$), 3.58, 3.67 (ABX, $J_{5A,5B}$ = 10.9, $J_{5A,4}$ = 6.6, $J_{5B,4}$ = 2.9 Hz, 2 H, 5-H_A, 5-H_B), 4.00 (dd, $J_{3,2}$ = 8.3, $J_{3,4}$ = 5.1 Hz, 1 H, 3-H), 4.38 (d, *J* = 11.4 Hz, 1 H, benzylic H), 4.42−4.58 (m, 6 H, 2-H, 4-H, 4 × benzylic H), 4.70 (d, *J* = 11.9 Hz, 1 H, benzylic H), 4.93 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 7.22−7.41 (m, 15 H, 3 × Ph); δ_C (67.9 MHz, $CDCl_3$): 6.15 ($SO_2CH_2CH_3$), 44.0 ($SO_2CH_2CH_3$), 70.3 (C5), 72.3, 72.6, 73.2 (3 × CH_2Ph), 75.1, 78.35, 82.7, 93.7 (C1−C4), 127.6, 128.0, 128.15, 128.3, 128.4, 128.5 (arom. CH), 136.6, 137.1, 137.8 (subst. arom. C); *m/z* (CI): 514 (100%, $[M + NH_4]^+$); found C 67.42, H 6.59, S 6.52. $C_{28}H_{32}O_6S$ requires C, 67.72, H 6.49, S 6.46%.

Benzyl *S,S*-Dioxo-2,3,6-tri-*O*-benzyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (3k): To a solution of the thioglycoside **2k** (0.196 g, 0.182 mmol) in DCM (7 mL) was added Na_2HPO_4 (0.129 g, 0.91 mmol) followed by mCPBA (0.094 g, 0.54 mmol) and the reaction mixture was stirred overnight. The solution was then diluted with DCM (20 mL), washed with aq. $Na_2S_2O_3$ (1 M, 10 mL), aq. NaOH (1 M, 10 mL), brine (30 mL), and dried. The crude product obtained on evaporation of the solvent was chromatographed on silica (elution with light petroleum ether/EtOAc, 3:1) to give the **3k** as a colourless foam (0.190 g, 95%), R_f = 0.25 (light petroleum ether/EtOAc, 3:1). $[\alpha]_D^{20}$ = +7.9 (*c* = 1.5, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3031, 2909, 1496, 1401, 1361, 1334, 1314 (SO_2), 1214, 1149, 1121 (SO_2), 1071, 1029; δ_H (270 MHz, $CDCl_3$): 3.30−3.41 (m, 3 H, 5-H, 5′-H, 4-H), 3.50−3.68 (m, 5 H, 3-H, 6-H_A, 6-H_B, 2′-H, 4′-H), 3.76 (d, $J_{6',5'}$ = 3.4 Hz, 6′-H_A, 6′-H_B, 2 H), 3.94 (t, *J* = 9.2 Hz, 1 H, 3′-H), 4.03 (t, $J_{2,1}$ = 9.2 Hz, 1 H, 2-H), 4.14 (d, $J_{1,2}$ = 9.2 Hz, 1 H, 1-H), 4.14 (d, *J* = 13.6 Hz, 1 H, $SO_2CH_AH_BPh$), 4.37 (A_2, 2 H, CH_2Ph), 4.42−4.56 (m, 5 H, $SO_2CH_AH_BPh$, 2 × CH_2Ph), 4.67−4.92 (m, 8 H, 1′-H, 7 × benzylic H), 5.09 (d, *J* = 11.4 Hz, 1 H, benzylic H), 7.14−7.43 (m, 40 H, 8 × Ph); δ_C (67.9 MHz, $CDCl_3$): 57.0 (SO_2CH_2Ph), 68.0, 68.8 (C6, C6′), 73.2 (× 2), 74.9, 75.1, 75.2, 75.3, 75.7 (CH_2Ph), 75.0, 76.0, 76.2, 77.9, 79.6, 82.7, 84.0, 84.9, 87.1 (C1, C2, C3, C4, C5, C2′, C3′, C4′, C5′), 102.7 (C1′), 127.3, 127.4 (× 2), 127.5, 127.6, 127.7, 127.8, 128.1, 128.2, 128.3 (× 2), 128.4, 128.7 (× 2), 131.1 (arom. CH), 137.4, 137.8, 138.1, 138.3, 138.4, 138.8 (× 2), 139.2 (subst. arom. C); *m/z* (FAB): 1133.4 (100%, $[M + Na]^+$), 871 (20%); found $[M + Na]^+$ 1133.4487. $C_{68}H_{70}O_{12}S{\cdot}Na$ requires 1133.4486.

General Procedures for the Ramberg−Bäcklund Rearrangement of Glycosyl Sulfones. (i) Chan's Method: A solution of the glycosyl sulfone (0.3 mmol) in DCM (1 mL) was added to a vigorously stirred suspension of KOH/Al_2O_3 (25% w/w, 3 g) in *t*BuOH/DCM (10:1 mL) in a sealed flask, cooled to 5 °C, and CBr_2F_2 (10 mmol)

added dropwise over a period of 2 min. The mixture was allowed to warm to room temp. and was then stirred overnight or until the starting material had been consumed. The reaction mixture was then diluted with DCM (20 mL) in order to precipitate potassium *tert*-butoxide, filtered through Celite®, and the filtrate evaporated under reduced pressure. The crude product was purified by flash chromatography (elution with light petroleum ether/EtOAc, 4:1, with 1% Et_3N) to afford the *exo*-glycal.

(ii) Meyers Method: Powdered potassium hydroxide (3 g, 53.5 mmol) was added to a stirred mixture of *t*BuOH (6 mL) and water (1.5 mL) at 60 °C. After the base had dissolved, a solution of the glycosyl sulfone (0.3 mmol), in CCl_4 (6 mL) was added, and the biphasic mixture was stirred at 60 °C for 1 h. After cooling to room temp., the lower aqueous layer was removed and the organic phase was washed with brine, dried, and the solvent removed in vacuo. Purification by column chromatography (elution with light petroleum ether/EtOAc, 4:1 with 1% Et_3N) afforded the *exo*-glycal.

2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-deoxy-D-*gluco*-hept-1-enitol[7b,8] (4a) and (*Z*,*E*)-2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-bromo-1-deoxy-D-*gluco*-hept-1-enitol (4m). Chan's Method: From 0.108 g of **3a** (α/β = 3:1). Yield: 0.54 g of **4a**; 54%; fine needles (hexane); R_f = 0.31 (light petroleum ether/EtOAc, 4:1); m.p. 66.5−67 °C, ref.[8] 65−68 °C. $[\alpha]_D^{20}$ = +62.3 (*c* = 1.0, DCM), ref.[8] +58.4 (*c* = 1.0, DCM) and 0.017 g of **4m**; 15%; colourless oil; R_f = 0.61 (light petroleum ether/EtOAc, 4:1); δ_H (270 MHz, $CDCl_3$): (*Z*)-isomer: 3.59−3.78 (m, 3 H, 5-H, 7-H_A, 7-H_B), 3.88 (d, $J_{3,4}$ = 5.3 Hz, 1 H, 3-H), 3.97 (br. d, $J_{6,5}$ = 9.7 Hz, 1 H, 6-H), 4.34−4.68 (m, 9 H, 4 × CH_2Ph, 4-H), 5.46 (s, 1 H, 1-H), 7.07−7.32 (m, 20 H, 4 × Ph); (*E*)-isomer (selected data): 3.82 (td, *J* = 4.9, 1.7 Hz, 1 H, 6-H), 4.77−4.81 (m, 1 H, benzylic H), 5.86 (s, 1 H, 1-H), 7.15−7.39 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): (*Z*)-isomer: 68.3 (C7), 70.3, 73.4, 73.5, 74.0 (*C*H_2Ph), 77.2, 77.8, 83.75, 86.7 (C3, C4, C5, C6), 127.5, 127.75, 127.8, 127.95, 128.2, 128.3, 128.4, 128.5 (arom. CH), 137.3, 137.4, 137.8, 137.9, 138.2 (subst. arom. C), 151.05 (C2); *m*/*z* (CI): 582 (1%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found $[M + NH_4]^+$ 632.2012. $C_{35}H_{35}BrO_5{\cdot}NH_4$ requires 632.2012. *Meyers' Method*: From 0.100 g of **3a** (α/β = 3:1). Yield: 0.64 g 4a; 72%.

(*Z*,*E*)-3,7-Anhydro-4,5,6,8-tetra-*O*-benzyl-1,2-dideoxy-D-*gluco*-octit-2-enitol (4b). Chan's Method: From 0.205 g of **3b** (α/β = 4:1). Yield: 0.138 g of **4b**; 75% (*Z*/*E* = 80:20); colourless oil; R_f = 0.58 (light petroleum ether/EtOAc, 4:1); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 2958, 1662 (C=C), 1488, 1453, 1361, 1090, 1072; δ_H (270 MHz, $CDCl_3$): 1.68 (dd, *J* = 6.8, 1.5 Hz, 3 H, CH_3CH=), 3.64−3.83 (m, 5 H, 4-H, 5-H, 6-H, 8-H_A, 8-H_B), 3.89−3.94 (m, 1 H, 7-H), 4.50−4.87 (m, 8 H, 4 × CH_2Ph), 5.02 (qd, *J* = 6.0, 1.2 Hz, 1 H, 2-H, *Z* isomer), 7.14−7.37 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 9.7 (CH_3), 68.9 (C8), 72.4, 73.4, 74.2, 74.4 (4 × *C*H_2Ph), 77.8, 77.9, 79.2, 85.1 (C4−C7), 104.9 (C2), 127.3, 127.5, 127.6 (× 2), 127.7, 127.8, 127.9, 128.1, 128.3 (× 2), 128.4 (× 2), 128.5 (arom. CH), 138.0, 138.1, 138.3, 138.3 (subst. arom. C), 148.4 (C3); *m*/*z* (CI): 582 (1%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found $[M + NH_4]^+$ 582.3217. $C_{36}H_{38}O_5{\cdot}NH_4$ requires 582.3219.

(*Z*,*E*)-4,8-Anhydro-5,6,7,9-tetra-*O*-benzyl-1,2,3-trideoxy-D-*gluco*-non-3-entitol (4c). Chan's Method: From 0.201 g of **3c** (α/β = 4:1). Yield: 0.135 g; 75% (*Z*/*E* = 92:8); colourless oil; R_f = 0.59 (light petroleum ether/EtOAc, 4:1); $\tilde{\nu}_{max}/cm^{-1}$: 3006, 2964, 1603 (C=C), 1497, 1458, 1362, 1272, 1089; δ_H (270 MHz, $CDCl_3$): 0.90 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 2.05−2.14 (m, 2 H, CH_2CH$_3$), 3.57−3.74 (m, 5 H) 3.84 (d, *J* = 7.5 Hz, 1 H, 8-H), 4.41−4.85 (m, 8 H, 4 × CH_2Ph), 4.92 (br. t, *J* = 7.5 Hz, 1 H, 3-H, *Z*-isomer), 7.06−7.26 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 14.5 (C1), 17.7 (C2), 68.8 (C9), 73.2, 73.4, 74.4, 74.5 (4 × *C*H_2Ph), 77.7, 78.4, 79.3, 85.3 (C5−C8), 112.6 (C3), 127.3, 127.4, 127.5, 127.6, 127.7, 127.7, 127.8, 127.9, 128.05, 128.3 (× 2), 128.4 (arom. CH), 138.0, 138.1, 138.2, 138.4 (subst. arom. C), 147.45 (C4); *m*/*z* (CI): 582 (20%, $[M + NH_4]^+$), 457 (100%); found $[M + NH_4]^+$ 582.3211. $C_{37}H_{40}O_5{\cdot}NH_4$ requires 582.3219.

(*Z*,*E*)-2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-deoxy-1-phenyl-D-*gluco*-hept-1-enitol (4d). Chan's Method: From 0.104 g of **3d** (α/β = 4:1). Yield: 0.078 g; 83% (*Z*/*E* = 88:12); colourless oil; R_f = 0.30 (light petroleum ether/EtOAc, 3:1); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 2866, 1669 (C=C), 1495, 1453, 1088; δ_H (270 MHz, $CDCl_3$): (*Z*)-isomer, 3.76−3.91 (m, 4 H, 4-H, 5-H, 7-H_A, 7-H_B), 4.04 (br. d, $J_{3,4}$ = 4.6 Hz, 1 H, 3-H), 4.11 (ddd, $J_{6,5}$ = 9.7, $J_{6,7A}$ = 4.2, $J_{6,7B}$ = 1.9 Hz, 1 H, 6-H), 4.56, 4.77 (AB, *J* = 11.4 Hz, 2 H, CH_2Ph), 4.59, 4.66 (AB, *J* = 12.1 Hz, 2 H, CH_2Ph), 4.62, 4.79 (AB, *J* = 11.6 Hz, 2 H, CH_2Ph), 4.66, 4.79 (AB, *J* = 11.4 Hz, 2 H, CH_2Ph), 5.73 (s, 1 H, 1-H), 7.16−7.40 (m, 23 H, 23 × arom. H), 7.67−7.71 (m, 2 H, 2 × arom. H); (*E*)-isomer (selected data) 6.48 (s, 1 H, 1-H); δ_C (67.9 MHz, $CDCl_3$): (*Z*)-isomer, 69.1 (C7), 71.7, 73.5 (× 2), 74.0 (4 × *C*H_2Ph), 76.9, 77.8, 79.2, 84.5 (C3, C4, C5, C6), 109.5 (C1), 126.3, 127.6, 127.7, 127.8 (× 2), 127.9 (× 2), 128.1, 128.3, 128.4, 128.5, 128.7 (arom. CH), 135.1, 137.9, 138.1, 138.2 (subst. arom. C); *m*/*z* (CI): 630 (70%, $[M + NH_4]^+$), 612 (20%, $[M + H]^+$), 505 (85%), 415 (25%), 399 (35%), 91 (100%, $[C_7H_7]^+$). **Meyers' Method:** From 0.125 g **3d** (α/β = 4:1) was obtained 0.063 g **4d**; 56% (*Z*/*E* = 88:12).

3,7-Anhydro-4,5,6,8-tetra-*O*-benzyl-1,2-dideoxy-2-methyl-D-*gluco*-octit-2-enitol (4e). Meyers' Method: From 0.132 g of **3e** (α/β = 3:1). Yield: 0.061 g; 51%; colourless oil; R_f = 0.56 (light petroleum ether/EtOAc, 4:1); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 2958, 1662 (C=C), 1488, 1453, 1361, 1090, 1072; δ_H (270 MHz, $CDCl_3$): 1.60 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3), 3.66 (dd, $J_{6,7}$ = 9.9, $J_{6,5}$ = 5.3 Hz, 1 H, 6-H), 3.72−3.75 (m, 2 H, 8-H_A, 8-H_B), 3.91 (dd, $J_{5,4}$ = 8.1, $J_{5,6}$ = 5.3 Hz, 1 H, 5-H), 4.30 (ddd, $J_{7,6}$ = 9.9, $J_{7,8A}$ = 4.1 Hz, $J_{7,8B}$ = 2.4, 1 H, 7-H), 4.37 (d, *J* = 12.4 Hz, 1 H, benzylic H), 4.42 (d, *J* = 2.2 Hz, 1 H, 4-H), 4.49−4.68 (m, 7 H, 7 × benzylic H), 7.19−7.37 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 17.7, 18.9 [(*C*H_3)$_2$C=C], 69.5 (C8), 70.15, 72.2, 73.5, 73.8 (4 × *C*H_2Ph), 72.8, 74.7, 78.5, 83.25 (C4−C7), 114.25 (C2), 127.25, 127.4, 127.8, 128.0, 128.25, 128.4, 128.7, 128.75, 128.9, 129.0, 129.2, 129.4, 129.7, 129.8 (arom. CH), 138.4, 138.8, 138.9, 139.1 (subst. arom. C), 140.4 (C3); *m*/*z* (CI): 582 (1%, $[M + NH_4]^+$), 91 (100%, $[C_7H_7]^+$); found $[M + NH_4]^+$ 582.3217. $C_{37}H_{40}O_5{\cdot}NH_4$ requires 582.3219.

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosylidene cyclohexane (4f). Meyers' Method: From 0.174 g of **3f** (α/β = 4:1). Yield: 0.051 g; 32%; colourless oil; R_f = 0.52 (light petroleum ether/EtOAc, 4:1); $\tilde{\nu}_{max}/cm^{-1}$: 3030, 3009, 2960, 2936, 1665, 1492, 1451, 1361; δ_H (270 MHz, $CDCl_3$): 1.35−1.55 (br. s, 6 H, 2 × 3′-H, 2 × 4′-H, 2 × 5′-H), 1.91−2.04 (2 H, 2′-H_{ax}, 6′-H_{ax}), 2.20−2.38 (2 H, 2′-H_{eq}, 6′-H_{eq}), 3.59 (dd, $J_{4,5}$ = 9.9, $J_{4,3}$ = 5.6 Hz, 1 H, 4-H), 3.55−3.66 (m, 2 H, 6-H_A, 6-H_B), 3.84 (dd, $J_{3,4}$ = 5.6, $J_{3,2}$ = 2.2 Hz, 1 H, 3-H), 4.21 (dt, $J_{5,4}$ = 9.9, $J_{5,6}$ = 2.9 Hz, 1 H, 5-H), 4.29 (d, *J* = 12.1 Hz, 1 H, benzylic H), 4.37 (d, $J_{2,3}$ = 2.2 Hz, 1 H, 2-H), 4.42−4.62 (m, 7 H, 7 × benzylic H), 7.12−7.28 (m, 20 H, 4 × Ph); δ_C (67.9 MHz, $CDCl_3$): 26.7, 26.8, 27.4, 28.4, 28.9 (C=C(*C*H$_2$)$_5$], 68.9, 69.7, 71.7, 73.1, 73.3 (C6, 4 × *C*H_2Ph), 72.0, 74.4, 77.9, 82.9 (C2−C5), 122.6 (C=*C*(CH$_2$)$_5$], 127.3 127.5, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4 (arom. CH), 137.2 (C1), 138.0, 138.4, 138.5, 138.6 (subst. arom. C): *m*/*z* (CI): 622 (3%, $[M + NH_4]^+$), 90 (100%, $[C_7H_7]^+$); found $[M + NH_4]^+$ 605.3267. $C_{40}H_{44}O_5{\cdot}NH_4$ requires 605.3267.

2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-deoxy-1,1-diphenyl-D-*gluco*-hept-1-enitol (4g). Chan's Method: From 0.160 g of **3g** (α/β = 4:1). Yield: 0.061 g; 57%; colourless oil; R_f = 0.57 (light petroleum ether/EtOAc, 4:1); $\tilde{\nu}_{max}/cm^{-1}$: 3066, 2871, 1454, 1365, 1313, 1108, 1083, 1027; δ_H (270 MHz, $CDCl_3$): 3.79−3.90 (m, 4 H, 4-H, 5-H, 7-H_A, 7-H_B), 4.20, 4.62 (AB, J = 11.6 Hz, 2 H, CH_2Ph), 4.26, 4.34 (AB, J = 11.6 Hz, 2 H, CH_2Ph), 4.40 (br. s, 1 H, 3-H), 4.45, 4.51 (AB, J = 12.4 Hz, 2 H, CH_2Ph), 4.58, 4.66 (AB, J = 11.4 Hz, 2 H, CH_2Ph), 4.60−4.66 (m, 1 H, 6-H), 7.08−7.33, 7.44−7.48 (m, 30 H, 6 × Ph); δ_C (67.9 MHz, $CDCl_3$): 69.3, 69.6, 70.9, 73.05, 73.4 (C7, 4 × CH_2Ph), 72.7, 74.4, 78.3, 83.0 (C3−C6), 122.5 (C1), 126.1, 126.7, 127.2, 127.2, 127.4, 127.5, 127.8, 127.85, 127.9, 128.1, 128.2, 128.25, 128.35, 130.0, 130.2, 131.4 (arom. CH), 137.6, 138.0, 138.3, 138.7, 139.1, 140.5 (subst. arom. C), 144.95 (C2); *m*/*z* (CI): 706 (25%, $[M + NH_4]^+$), 108 (100%); found $[M + NH_4]^+$ 706.3539. $C_{47}H_{44}O_5{\cdot}NH_4$ requires 706.3532.

2-(2,3,4-Tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosylidene)-adamantane (4h). Meyers' Method: From 0.156 g of **3h**. Yield: 0.029 g; 20%; colourless oil; R_f = 0.67 (light petroleum ether/EtOAc, 4:1); $\tilde{\nu}_{max}/cm^{-1}$: 3032, 2925, 1676 (C=C), 1454, 1363, 1193, 1096, 1085; δ_H (270 MHz, $CDCl_3$): 0.098, 0.103 (2 × s, 6 H, 2 × CH_3Si), 0.92 [s, 9 H, $(CH_3)_3CSi$], 1.69−2.05 (m, 12 H, 5 × CH_2, 2 × CH, adamantyl), 2.52−2.58 (br. s, 1 H, allylic CH, adamantyl), 3.35−3.43 (br. s, 1 H, allylic CH, adamantyl), 3.73 (dd, $J_{4,5}$ = 9.9, $J_{4,3}$ = 6.0 Hz, 1 H, 4-H), 3.91−3.93 (m, 2 H, 6-H_A, 6-H_B), 3.95 (dd, $J_{3,4}$ = 6.0, $J_{3,2}$ = 1.9 Hz, 1 H, 3-H), 4.14−4.19 (m, 1 H, 5-H), 4.39, 4.69 (AB, J = 12.1 Hz, 2 H, CH_2Ph), 4.44 (d, $J_{2,3}$ = 1.9 Hz, 1 H, 2-H), 4.54, 4.62 (AB, J = 11.6 Hz, 2 H, CH_2Ph), 4.67, 4.76 (AB, J = 11.4 Hz, 2 H, CH_2Ph), 7.28−7.37 (m, 15 H, 3 × Ph); δ_C (67.9 MHz, $CDCl_3$): −5.4, −5.3 [$(CH_3)_2Si$], 18.3 [$(CH_3)_3CSi$], 25.9 [$(CH_3)_3CSi$], 28.2, 28.35, 29.2, 31.9 (4 × adamantyl CH), 37.1, 38.4, 38.8, 39.5, 39.75 (5 × adamantyl CH_2), 62.2 (C6), 68.9, 71.6, 73.5 (3 × CH_2Ph), 72.2, 75.0, 77.8, 83.9 (C2−C5), 127.4, 127.6, 127.9, 128.2, 128.3, 128.3 (arom. CH), 129.8 (O−C=*C*), 134.2 (C1), 138.15, 138.6, 138.75 (subst. arom. C); *m*/*z* (FAB): 703 (100%, [M + Na]$^+$); found $[M + Na]^+$ 769.3573. $C_{43}H_{56}O_5Si{\cdot}Na$ requires 769.3570.

(*Z*,*E*)-2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-deoxy-1-phenyl-D-*galacto*-hept-1-enitol (4i). Chan's Method: From 0.280 g of **3i** (α/β = 1:6). Yield: 0.210 g; 83% (*Z*/*E* = 62:38); colourless oil; R_f = 0.46 (light petroleum ether/EtOAc, 4:1); $\tilde{\nu}_{max}/cm^{-1}$: 3029, 2868, 1660 (C=C), 1496, 1454, 1364, 1312, 1108, 1096; δ_H (270 MHz, $CDCl_3$): 3.58−3.92, 4.01−4.15 (m, 6 H, 3-H, 4-H, 5-H, 6-H, 7-H_A, 7-H_B), 4.38−4.49 (m, 2 H, CH_2Ph), 4.62 (d, J = 11.6 Hz, 1 H, benzylic H), 4.69−4.82 (m, 4 H, 2 × CH_2Ph), 4.92 (d, J = 11.6 Hz, 1 H, benzylic H), 5.97 (s, 1 H, 1-H), 7.13−7.39, 7.67−7.70 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 69.2 (C7), 72.9, 73.2, 73.5, 74.0 (4 × CH_2Ph), 74.2, 77.3, 78.2, 81.4 (C3−C6), 110.8 (C1), 126.4, 127.0, 127.4, 127.5, 127.5, 127.6, 127.8, 127.9 (× 2), 128.1, 128.2, 128.3, 128.35, 128.8, 129.3, 129.6 (arom. CH), 135.0, 137.8, 138.0, 138.2, 138.4 (subst. arom. C), 150.1 (C2); *m*/*z* (CI): 630 (30%, M + $[NH_4]^+$), 108 (100%); found $[M + NH_4]^+$ 630.3218. $C_{41}H_{40}O_5{\cdot}NH_4$ requires 630.3219.

(*Z*)-2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-deoxy-1-phenyl-D-*manno*-hept-1-enitol (4j). Chan's Method: From 0.200 g of **3jα**. Yield: 0.17 g; 94%; colourless oil; R_f = 0.50 (light petroleum ether/EtOAc, 4:1); $\tilde{\nu}_{max}/cm^{-1}$: 3031, 2871, 1454, 1365, 1109, 1084, 1027; δ_H (270 MHz, $CDCl_3$): 3.72−3.91 (m, 4 H, 4-H, 6-H, 7-H_A, 7-H_B), 4.11 (d, J = 3.0 Hz, 1 H, 3-H) and 4.22 (t, J = 9.0 Hz, 1 H, 5-H), 4.48 (d, J = 12.5 Hz, 1 H, benzylic H), 4.55−4.72 (m, 5 H, 5 × benzylic H), 4.80 (d, J = 13.0 Hz, 1 H, benzylic H) and 4.99 (d, J = 10.0 Hz, 1 H, benzylic H), 5.57 (s, 1 H, 1-H), 7.18−7.70 (m, 25 H, 5 × Ph); δ_C (67.9 MHz, $CDCl_3$): 69.2, 69.8, 71.4, 73.3, 75.1 (C7, 4 × CH_2Ph), 74.3, 75.0, 79.7, 81.8 (C3−C6), 114.9 (C1), 127.1, 127.5, 127.6, 127.8, 127.9, 128.15, 128.3, 128.9 (arom. CH), 134.45, 138.06, 138.12, 138.34, 138.38 (subst. arom. C), 148.45 (C2); *m*/*z* (CI): 630 (35%, M + $[NH_4]^+$), 108 (100%); found C 80.01, H 6.61. $C_{41}H_{40}O_5$ requires C, 80.37, H 6.58%.

(*Z*,*E*)-1-Phenyl-2,6-anhydro-3,4,7-tri-*O*-benzyl-5-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-1-deoxy-D-gluco-hept-1-enitol (4k). Chan's Method: From 0.086 g of **3k**. Yield: 0.064 g; 80% (*Z*/*E* = 87:13); white solid; R_f = 0.39 (light petroleum ether/EtOAc, 3:1); $\tilde{\nu}_{max}/cm^{-1}$: 3029, 2909, 1660 (C=C), 1600 (C=C), 1496, 1454, 1210, 1181, 1150, 1071, 1028; δ_H (270 MHz, $CDCl_3$): 3.31−3.37 (m, 1 H), 3.44 (t, J = 9.0 Hz, 1 H), 3.55−3.73 (m, 6 H), 3.81 (br. s, 2 H), 3.96−4.02 (m, 2 H,), 4.14 (dd, J = 9.9 Hz, 1 H), 4.34−4.94 (m, 20 H), 5.51 (s, 1 H, 1-H, *Z*-isomer), 6.43 (s, 1 H, 1-H, *E*-isomer), 7.14−7.34 (m, 50 H, 50 × arom. H), 7.66−7.69 (m, 2 H, 2 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 68.6, 68.7 (C7, C6′), 70.4, 72.3, 73.2, 73.3, 74.9 (× 2), 75.6, (CH_2Ph), 74.8, 75.6, 77.7, 77.9, 78.6, 81.8, 82.4, 84.8 (C3, C4, C5, C6, C2′, C3′, C4′, C5′), 103.6 (C1′), 109.2 (C1), 126.1, 126.9, 127.3, 127.5 (× 2), 127.6, 127.7, 127.8 (× 2), 128.1, 128.2, 128.2, 128.3 (× 2), 128.6 (arom. CH), 129.0, 135.4, 137.9, 138.1, 138.2, 138.3, 138.5, 138.7 (subst. arom. C), 148.1 (C2); *m*/*z* (FAB): 1068 (95%, $[M + Na]^+$), 181 (100%); found $[M + Na]^+$ 1067.4707. $C_{68}H_{68}O_{10}{\cdot}Na$ requires 1067.4710.

(*Z*,*E*)-3,6-Anhydro-4,5,7-tri-*O*-benzyl-1,2-dideoxy-D-*ribo*-hept-2-enitol (4l). Chan's Method: From 0.152 g of **3l**. Yield: 0.138 g; 75% (*Z*/*E* = 50:50); colourless oil; R_f = 0.54 (light petroleum ether/EtOAc, 4:1); $\tilde{\nu}_{max}/cm^{-1}$: 3032, 2925, 2853, 1676 (C=C), 1496, 1454, 1363, 1259, 1193, 1085; δ_H (270 MHz, $CDCl_3$): 1.63, 1.67 (2 × d, J = 8 Hz, 6 H, 2 × CH_3CH=), 3.46−3.61 (m, 2 H), 3.73 (d, J = 8 Hz, 2 H), 3.91−4.00 (m, 2 H), 4.09 (d, J = 4 Hz, 1 H), 4.33−4.88 (m, 16 H), 5.06 (q, J = 7 Hz, 1 H, 2-H, *E*-isomer) 7.19−7.38 (m, 30 H, 3 × Ph); δ_C (67.9 MHz, $CDCl_3$): 9.9, 12.4 (2 × CH_3), 68.8, 69.0, 69.35, 70.1, 71.8, 72.2, 73.2, 73.25 (2 × C7, 6 × CH_2Ph), 71.4, 74.7, 76.9, 77.65, 79.8, 81.0 [2 × (C3−C5)], 97.5, 98.3 (2 × C2), 127.5 (× 2), 127.6, 127.75, 127.8, 127.9 (× 2), 128.2, 128.3 (arom. CH), 137.4, 137.5, 138.0 (× 2), 138.1, 138.3 (subst. arom. C), 152.2, 153.0 (2 × C3); found $[M + Na]^+$ 453.2057. $C_{28}H_{30}O_4{\cdot}Na$ requires 453.2066.

Benzyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside[39] (7β): Tin(IV) chloride (0.99 mL, 8.45 mmol) was added to a solution containing α-D-glucose pentaacetate (3.00 g, 7.69 mmol) and benzyl mercaptan (1.80 mL, 15.37 mmol) in dry DCM (150 mL) at −30 °C and the resulting mixture was allowed to warm to room temp. and was stirred overnight. The reaction was quenched with brine (30 mL), extracted with DCM (2 × 50 mL), the organic parts washed with satd. aq. $NaHCO_3$ (30 mL), then with brine (30 mL), and dried. The solvent was evaporated in vacuo and purified by flash chromatography (light petroleum ether/EtOAc, 3:1→1:1) to yield first an equimolar mixture of **7α** and **7β** as a colourless oil (2.39 g, 68%). Recrystallisation of the product mixture from ether gave pure **7β** as colourless needles (0.933 g, 27%), R_f = 0.45 (light petroleum ether/EtOAc, 1:1); m.p. 101.5−103 °C, ref.[39] 103−104 °C. $[\alpha]_D^{20}$ = −95.4 (*c* = 1.0, $CHCl_3$), ref.[39] −84.4 (*c* = 1.1, $CHCl_3$).

Benzyl *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside[28] (8): Oxone® (1.61 g, 2.62 mmol) was added to a solution of the thioglycoside **7β** (0.20 g, 0.44 mmol) in a mixture of THF, MeOH, and water (18:6:6 mL) at 5 °C and the mixture was stirred overnight at room temp. The bulk of the organic solvents was evaporated under reduced pressure and brine (50 mL) added to the residue which was then extracted with EtOAc (3 × 50 mL), washed

with water, dried, and concentrated in vacuo to give a white solid. Recrystallisation from MeOH furnished pure **8** as colourless needles (0.155 g, 72%), R_f = 0.32 (light petroleum ether/EtOAc, 1:1); m.p. 198−200 °C, ref.[28] 199 °C. $[\alpha]_D^{20}$ = −46.9 (*c* = 1.0, $CHCl_3$), ref.[28] −44.6 (*c* = 2, $CHCl_3$).

Benzyl *S*,*S*-Dioxo-1-thio-2,3,4,6-tetra-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranoside (9): A methanolic solution of sodium methoxide (25% w/w, 0.02 mL, 0.1 mmol) was added to a solution of the sulfone **8** (0.50 g, 1.03 mmol) in MeOH (20 mL) and the mixture was stirred for 2 h. Amberlyst 15 ion-exchange resin was then added until the pH of the solution became neutral, the resin was removed by filtration and the filtrate evaporated in vacuo, triturated with DCM, and dried thoroughly under high vacuum to give a colourless oil which was used in the next step without further purification. A suspension of the crude, deprotected sulfone (0.324 g) in DCM (3 mL) was treated with 2,6-lutidine (0.95 mL, 8.1 mmol) followed by *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.4 mL, 6.1 mmol) and the mixture was stirred for 6 h. The solvent was evaporated under reduced pressure and the residue was partitioned between ether (100 mL) and brine (75 mL). A further extraction with ether (2 × 50 mL), followed by washing with 5% aq. $CuSO_4$ (2 × 30 mL), satd. aq. $NaHCO_3$, then with brine (30 mL), drying, and column chromatography on neutral alumina (light petroleum ether/EtOAc, 9:1) afforded **9** as a colourless oil (0.761 g, 96% over two steps), R_f = 0.53 (light petroleum ether/EtOAc, 4:1). $[\alpha]_D^{20}$ = −32.3 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 2928, 2858, 1472, 1463, 1361, 1330 (SO_2), 1259 (C-Si), 1152 (SO_2), 1105; δ_H (270 MHz, $CDCl_3$): 0.06 (× 2), 0.07, 0.10, 0.12, 0.13 (× 2), 0.17 [8 × s, 24 H, 4 × $Si(CH_3)_2$], 0.83, 0.88, 0.94, 0.95 [4 × s, 36 H, 4 × $SiC(CH_3)_3$], 3.66−3.71 (m, 1 H, 5-H), 3.75−3.87 (m, 4 H, 3-H, 4-H, 6-H_A, 6-H_B), 4.14, 4.49 (AB, *J* = 13.6 Hz, 2 H, SO_2CH_2Ph), 4.29 (br. d, $J_{2,1}$ = 6.0 Hz, 1 H, 2-H), 4.38 (d, $J_{1,2}$ = 6.0 Hz, 1 H, 1-H), 7.36−7.39 (m, 3 H, 3 × arom. H), 7.44−7.48 (m, 2 H, 2 × arom. H); δ_C (67.9 MHz, $CDCl_3$): −5.3, −5.2, −5.1, −4.9, −4.4, −4.2, −4.1, −3.0 [4 × $Si(CH_3)_2$], 17.8 (× 2), 18.0, 18.4 [4 × $SiC(CH_3)_3$], 25.7, 25.8 (× 2), 25.9, 26.0 [4 × $SiC(CH_3)_3$], 56.4 (C6), 64.1 (SO_2CH_2Ph), 69.7, 70.2, 77.2, 82.8, 89.1 (C1, C2, C3, C4, C5), 128.0 (subst. arom. C) 128.6 (× 2), 128.7), 131.0 (× 2), (arom. CH); *m*/*z* (FAB): 798 (40%, $[M + Na]^+$), 487 (20%), 329 (50%); found $[M + Na]^+$ 797.4126. $C_{37}H_{74}O_7SSi_4$·Na requires 797.4130.

(*Z*,*E*)-2,6-Anhydro-1-deoxy-3,4,5,7-tetra-*O*-(*tert*-butyldimethylsilyl)-1-phenyl-D-*gluco*-hept-1-enitol (10): To a solution of the sulfone **9** (0.30 g, 0.39 mmol) in DCM (1 mL) was added *t*BuOH (5 mL) followed by KOH/Al_2O_3 (25% w/w, 4 g) and the mixture was cooled to 5 °C. The flask was sealed with a septum and 3 aliquots of CBr_2F_2 (1 mL, 10.9 mmol each) were added over a period of 3 h. and the mixture was stirred overnight. Usual workup gave the crude product which was purified by flash chromatography (elution with light petroleum ether/EtOAc, 9:1) to give **10** as a colourless oil (0.190 g, 69%, *Z*/*E* = 89:11), R_f = 0.39 (light petroleum ether, Al_2O_3). $[\alpha]_D^{20}$ = +36.9 (*c* = 1.2, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 2929, 2858, 1662 (C=C), 1473, 1463, 1389, 1362, 1374, 1257 (C-Si), 1162, 1101; δ_H (270 MHz, $CDCl_3$): 0.10, 0.11, (× 2), 0.12, (× 3) 0.14, 0.15 [5 × s, 24 H, 4 × $Si(CH_3)_2$], 0.84, 0.90, 0.91, 0.92 [4 × s, 36 H, 4 × $SiC(CH_3)_3$], 3.79−3.85 (m, 2 H, 4-H, 7-$H_{A'}$), 3.96 (br. d, *J* = 9.2 Hz, 1 H, 5-H), 3.98 (dd, $J_{7B,7A}$ = 11.4, $J_{7B,6}$ = 1.7 Hz, 1 H, 7-H_B), 4.11 (dd, $J_{3,4}$ = 3.2, $^4J_{3,1}$ = 1 Hz, 1 H, 3-H), 4.25 (ddd, $J_{6,5}$ = 9.2, $J_{6,7A}$ = 4.1, $J_{6,7B}$ = 1.7 Hz, 1 H, 6-H), 5.21 (s, 1 H, 1-H), 7.12 (tt, J_{ortho} = 7.3, J_{meta} = 1.2 Hz, 1 H, *para*-arom. H), 7.24−7.29 (m, 2 H, 2 × *meta*-arom. H), 7.63−7.67 (m, 2 H, 2 × *ortho* arom. H); δ_C (67.9 MHz, $CDCl_3$): −5.4 (× 2), −5.0, −4.9, −4.6, −4.4, −3.9 (× 2) [4 × $Si(CH_3)_2$], 17.9 (× 2), 18.0, 18.2 [4 × $SiC(CH_3)_3$], 25.7 (× 2), 25.8, (× 2) [4 × $SiC(CH_3)_3$], 62.3 (C7), 72.6, 74.8, 77.2, 77.6 (C3, C4, C5, C6), 106.4 (C1), 125.2, 127.8 (× 2), 128.3 (× 2) (arom. CH), 136.5 (subst. arom. C), 151.6 (C2); *m*/*z* (FAB): 731.5 (40%, $[M + Na]^+$), 445 (20%), 176 (100%); found $[M + Na]^+$ 731.4349. $C_{37}H_{72}O_5Si_4$·Na requires 731.4355.

(*Z*)-2,6-Anhydro-3,4,5,7-tetra-*O*-acetyl-1-deoxy-1-phenyl-D-*gluco*-hept-1-enitol (12): A THF solution of tetra-*n*-butylammonium fluoride (1 M, 2.20 mL, 2.20 mmol) was slowly added to a solution of the alkene **10** (0.19 g, 0.27 mmol) in THF (15 mL) at 5 °C and the resultant yellow solution was stirred for 1 h at room temp. The solution was then treated with Ac_2O (0.20 mL, 2.1 mmol) and DMAP (0.010 g, 0.08 mmol) and stirred for 2 h. The solvent was removed in vacuo and the residue chromatographed on a short alumina column (elution with light petroleum ether/EtOAc, 4:1) to afford **12** as a white crystalline solid (0.065 g, 57% over two steps), R_f = 0.38 (light petroleum ether/EtOAc, 1:1); m.p. 112−113 °C. $[\alpha]_D^{20}$ = +109.8 (*c* = 1.0, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3025, 2930, 1755 (C=O), 1676 (C=C), 1495, 1449, 1371, 1220, 1040; δ_H (270 MHz, $CDCl_3$): 2.07 (× 2), 2.13, 2.18 (12 H, 4s, CH_3CO), 4.12 (m, 1 H, 6-H), 4.27−4.39 (m, 2 H, 7-H_A, 7-H_B), 5.16−5.24 (m, 2 H, 4-H, 5-H), 5.53−5.56 (m, 1 H, 3-H), 5.76 (d, $J_{1,3}$ = 0.5 Hz, 1 H, 1-H), 7.20−7.35 (m, 3 H, 2 × arom. H), 7.60−7.64 (m, 2 H, 2 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 20.6, 20.7 (× 2), 20.9 (CH_3CO), 62.3 (C7), 68.7, 70.2, 73.4, 75.1 (C3, C4, C5, C6), 111.4 (C1), 127.3, 128.3, 129.0 (arom. CH), 133.8 (subst. arom. C), 145.6 (C2), 169.0, 169.4, 169.8, 170.6 (CH_3CO); *m*/*z* (CI): 438 (75%, $[M + NH_4]^+$), 378 (30%), 361 (27%), 301 (100%), 243 (30%); found $[M + NH_4]^+$ 420.1423. $C_{21}H_{24}O_9$·NH_4 requires 420.1420; found C 59.49, H 5.84. $C_{21}H_{24}O_9$ requires C, 59.99, H 5.75%.

(*S*)-(Phenylbromomethyl) *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (13a) and (*R*)-(Phenylbromomethyl) *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (13b): A solution of the sulfone **3dα** (0.250 g, 0.39 mmol) in DCM (2 mL) was added to a vigorously stirred suspension of KOH/Al_2O_3 (25% w/w, 0.5 g) in *t*BuOH/DCM (8:2 mL) at 5 °C followed after 10 min by 3 aliquots of CBr_2F_2 (1 mL, 10.9 mmol each). The mixture was stirred for 30 min before the addition of more KOH/Al_2O_3 (1.1 g in 3 portions) and CBr_2F_2 (5 mL, 43.8 mmol in 2 portions). After a further 90 min the reaction was diluted with DCM, filtered through Celite®, and the filtrate concentrated in vacuo. Column chromatography of the residue (light petroleum ether/EtOAc, 5:1) gave three fractions. The first contained **4d** as a colourless oil (0.039 g, 22%, *Z*/*E* = 94:6). The second fraction contained the α-bromosulfone (0.080 g, 36%, 1:1 mixture of diastereomers) which was further purified by column chromatography (elution with DCM/light petroleum ether 5:1) to give **13a** as a colourless oil (0.040 g), R_f = 0.41 (DCM). $[\alpha]_D^{20}$ = +78.0 (*c* = 1.8, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3031, 2926, 1496, 1454, 1362, 1329 and 1147 (SO_2), 1103; δ_H (270 MHz, $CDCl_3$): 3.44 (dd, $J_{4,5}$ = 10.2, $J_{4,3}$ = 8.5 Hz, 1 H, 4-H), 3.53, 3.79 (ABX, $J_{6A,6B}$ = 10.4, $J_{6A,5}$ = 6.8, $J_{6B,5}$ = 1.7 Hz, 2 H, 6-H_A, 6-H_B), 4.15 (dd, $J_{2,3}$ = 9.0, $J_{2,1}$ = 6.3 Hz, 1 H, 2-H), 4.43 (t, *J* = 8.5 Hz, 1 H, 3-H), 4.48, 4.81 (AB, *J* = 9.7 Hz, 2 H, CH_2Ph), 4.50−4.60 (m, 3 H, 5-H, CH_2Ph), 4.72, 4.94 (AB, *J* = 11.6 Hz, 2 H, CH_2Ph), 4.74, 4.87 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 5.62 (d, $J_{1,2}$ = 6.3 Hz, 1 H, 1-H), 6.23 [s, 1 H, CH(Br)Ph], 7.16−7.37 (m, 23 H, 23 × arom. H), 7.42−7.44 (m, 2 H, 2 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 58.7 [SO_2CH(Br)Ph], 69.0 (C6), 73.5, 74.0, 74.7, 75.6 (4 × CH_2Ph), 75.7, 76.8, 78.2, 80.8, 85.6 (C1, C2, C3, C4, C5), 127.7 (× 2), 127.8, 128.0, 128.4 (× 2), 128.6, 129.3, 130.3, 130.7 (arom. CH), 137.1, 137.6, 137.8, 138.1 (subst. arom. C); *m*/*z* (FAB): 781 (25%, $[M + Na]^+$), 779 (21%, $[M + Na]^+$), 545 (20%), 439 (55%), 91 (100%, $[C_7H_7]^+$); found $[M + Na]^+$ 779.1650. $C_{41}H_{41}BrO_7S$·Na

requires 779.1654. − Further elution gave **13b** as a waxy solid (0.030 g), R_f = 0.37 (DCM). $[\alpha]_D^{20}$ = +95.1 (*c* = 0.7, $CHCl_3$); δ_H (270 MHz, $CDCl_3$): 3.47 (dd, $J_{4,5}$ = 10.1, $J_{4,3}$ = 9.0 Hz, 1 H, 4-H), 3.56, 3.73 (ABX, $J_{6A,6B}$ = 10.8, $J_{6A,5}$ = 5.6, $J_{6B,5}$ = 1.7 Hz, 2 H, 6-H_A, 6-H_B), 3.97 (dd, $J_{2,3}$ = 9.3, $J_{2,1}$ = 6.6 Hz, 1 H, 2-H), 4.43−4.49 (m, 1 H, 5-H), 4.49 (t, *J* = 8.7 Hz, 1 H, 3-H), 4.50, 4.80 (AB, *J* = 11.2 Hz, 2 H, CH_2Ph), 4.51−4.61 (m, 2 H, CH_2Ph), 4.66, 4.77 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.79, 4.90 (AB, *J* = 10.7 Hz, 2 H, CH_2Ph), 4.96 (d, $J_{1,2}$ = 6.3 Hz, 1 H, 1-H), 6.09 [s, 1 H, C*H*(Br)Ph], 7.14−7.18 (m, 2 H, 2 × arom. H), 7.24−7.39 (m, 21 H, 21 × arom. H), 7.56−7.60 (m, 2 H, 2 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 63.1 [SO_2*C*H(Br)Ph], 68.7 (C6), 73.5, 74.5, 74.6, 75.6 (4 × *C*H_2Ph), 75.6, 76.8, 78.5, 80.9, 85.6 (C1, C2, C3, C4, C5), 127.7 (× 2), 127.9, 128.0, 128.2, 128.4 (× 2), 128.5, 128.6, 130.3, 130.4, (arom. CH), 131.4 [subst. arom. C of CH(Br)Ph], 136.9, 137.5, 137.9, 138.2 (subst. arom. C); found $[M + NH_4]^+$ 779.1650. $C_{41}H_{41}BrO_7S{\cdot}NH_4$ requires 779.1654. The third fraction contained recovered **3dα** (0.064 g, 32%) which showed identical R_f, ^{1}H NMR and mass spectroscopic data to that already described for this compound.

(Phenylbromomethyl) *S*,*S*-Dioxo-2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (14a and 14b): A solution of the sulfone **3dβ** (0.090 g, 0.133 mmol) in DCM (1 mL) was added to a vigorously stirred suspension of KOH/Al_2O_3 (25% w/w, 0.5 g) in *t*BuOH/DCM (6:2 mL) at 5 °C followed after 10 min by 3 aliquots of CBr_2F_2 (0.5 mL, 5.47 mmol each) at intervals of 10 min. The reaction mixture was diluted with DCM, filtered through Celite®, and the filtrate concentrated in vacuo. Column chromatography of the residue (elution with light petroleum ether/EtOAc, 5:1) gave three main fractions. The first contained **4d** as a colourless oil (0.008 g, 10%, *Z*/*E* = 79:21). The second fraction contained **14** (0.050 g, 50%, 1:1 mixture of diastereomers) which was further purified by column chromatography (DCM/light petroleum ether 5:1) to give the more mobile diastereomer **14a** as a colourless oil (0.042 g), R_f = 0.44 (DCM). $[\alpha]_D^{20}$ = +17.5 (*c* = 1.8, $CHCl_3$); $\tilde{\nu}_{max}/cm^{-1}$: 3031, 2922, 1496, 1454, 1344 and 1154 (SO_2), 1094; δ_H (270 MHz, $CDCl_3$): 3.24 (ddd, $J_{5,4}$ = 9.5, $J_{5,6A}$ = 6.1, $J_{5,6B}$ = 1.9 Hz, 1 H, 5-H), 3.47 (appt. t, $J_{4,3}$ = 8.7, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.57 (t, *J* = 8.7 Hz, 1 H, 3-H), 3.59−3.63 (m, 1 H, 6-H_A), 3.68 (dd, $J_{6B,6A}$ = 10.7, $J_{6B,5}$ = 1.9 Hz, 1 H, 6-H_B), 3.93 (d, $J_{1,2}$ = 9.5 Hz, 1 H, 1-H), 4.10 (appt. t, $J_{2,3}$ = 8.7, $J_{2,1}$ = 9.5 Hz, 1 H, 2-H), 4.51, 4.77 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.53, 4.62 (AB, *J* = 11.9 Hz, 2 H, CH_2Ph), 4.71, 4.97 (AB, *J* = 9.5 Hz, 2 H, CH_2Ph), 4.77, 4.89 (AB, *J* = 11.2 Hz, 2 H, CH_2Ph), 6.07 [s, 1 H, C*H*(Br)Ph], 7.11−7.14 (m, 2 H, 2 × arom. H), 7.21−7.41 (m, 21 H, 21 × arom. H), 7.61−7.65 (m, 2 H, 2 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 61.9 [SO_2*C*H(Br)Ph], 68.7 (C6), 73.4, 75.2, 75.7, 75.9 (4 × *C*H_2Ph), 77.0, 77.5, 79.2, 85.7, 85.8, (C1, C2, C3, C4, C5), 127.5, 127.8, 128.0, 128.1, 128.5 (× 2) 128.8 128.9, 130.4, 130.5 (arom. CH), 131.1 [subst. arom. C of CH(Br)Ph], 136.9, 137.4, 137.6, 137.9 (subst. arom. C); found $[M + NH_4]^+$ 779.1648. $C_{41}H_{41}BrO_7S{\cdot}NH_4$ requires 779.1654. − Further elution gave the less mobile diastereomer **14b** as a colourless oil (0.019 g), R_f = 0.33 (DCM). $[\alpha]_D^{20}$ = −9.8 (*c* = 0.9, $CHCl_3$); δ_H (270 MHz, $CDCl_3$): 3.63−3.85 (m, 5 H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.05 (t, *J* = 9.2 Hz, 1 H, 2-H), 4.53, 4.64 (AB, *J* = 12.1 Hz, 2 H, CH_2Ph), 4.59, 4.82 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.71, 4.89 (AB, *J* = 9.9 Hz, 2 H, CH_2Ph), 4.86, 4.94 (AB, *J* = 10.9 Hz, 2 H, CH_2Ph), 4.97 (d, $J_{1,2}$ = 9.2 Hz, 1 H, 1-H), 6.05 [s, 1 H, C*H*(Br)Ph], 7.16−7.20 (m, 2 H, 2 × arom. H), 7.25−7.44 (m, 21 H, 21 × arom. H), 7.61−7.64 (m, 2 H, 2 × arom. H); δ_C (67.9 MHz, $CDCl_3$): 58.7 [SO_2*C*H(Br)Ph], 68.5 (C6), 73.2, 75.2, 75.4, 75.9 (4 × *C*H_2Ph), 77.2, 77.5, 79.9, 86.1, 87.7 (C1, C2, C3, C4, C5), 127.6, 127.7, 127.8 (× 2), 128.0, 128.4, 128.5, 128.6, 128.8, 131.1 (arom. CH), 130.7 [subst. arom. C of CH(Br)Ph], 137.2, 137.6, 137.8, 138.1 (subst. arom. C); found $[M + Na]^+$ 779.1658. $C_{41}H_{41}BrO_7S{\cdot}Na$ requires 779.1654.

X-ray Crystallographic Study of 13a: $C_{41}H_{41}BrO_7S$, *M*w = 757.73, *T* = 293(2) K, Mo-K_α radiation, λ = 0.71073 Å, orthorhombic, space group $P2_12_12_1$, *a* = 16.049(4), *b* = 23.479(13), *c* = 10.284(9) Å; α = β = γ = 90°; *V* = 3875(4) Å^3, *Z* = 4, D_c = 1.299 g·cm^{-3}, *F*(000) = 1576, crystal size 0.7 × 0.4 × 0.4 mm. MSC Rigaku AFC6S four-circle diffractometer, 2.35 < θ < 25, 3855 collected reflections, of which 3827 were unique and 1735 having $F_0 > 4\sigma(F_0)$ being regarded as observed. An empirical absorption correction based on 10 azimuthal scans (T_{min} = 0.950, T_{max} = 1.000) was applied to the data. The structure was solved by direct methods using SHELXS-86[40] and refined by full-matrix least-squares on F^2 with SHELXL-97[41] No restraints or constraints were used. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions using a riding model with C_{sp^2}−H = 0.93 Å, $C_{sp^3}(CRH_2)$−H = 0.97 Å, $C_{sp^3}(CHR_2)$−H = 0.98 Å. Isotropic *U* values for hydrogen atoms were calculated as 1.2 multiplied by the equivalent isotropic displacement parameter for the atom to which the hydrogen is attached. Full-matrix least-squares refinement based on F^2 gave *R*1 = 0.1671, *wR*2 = 0.1842 for all data and a goodness of fit, GooF = *S* = 1.007 for 451 parameters. A weighting scheme with $w = 1/[\sigma^2(F_0^2) + (0.0873P)^2 + 02.7367P]$, where $P = [\max(I_{obs},0) + 2F_c^2]/3$ was applied at the end of the refinement. The final absolute structure parameter[42] was 0.01(3), i.e. it is less than 1 s.u. from zero, indicating the absolute configuration of the structure is correct. The final Fourier difference synthesis showed the largest peak and hole to be 0.271 and −0.402 e·Å^{-3}. The following quantities are given in the information for the structure and were calculated as follows: goodness of fit (GooF = *S*) was calculated by using the formula: $\{\Sigma[w(F_0^2 - F_c^2)^2]/(n - p)\}^2$, where *p* = number of parameters, *n* = number of data. *R*-Factors were calculated using the formulae: $R1 = [\Sigma(||F_o| - |F_c||)^{1/2}]/\Sigma|F_o|$; $wR2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

CCDC-174420 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax (internat.): +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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