1,2-*cis*-*C*-Glycoside Synthesis by Samarium Diiodide-Promoted Radical Cyclizations

Troels Skrydstrup,* Daniel Mazéas, Mohamed Elmouchir, Gilles Doisneau, Claude Riche, Angèle Chiaroni, and Jean-Marie Beau*

Dedicated to Professor Hans Paulsen on the occasion of his 75th birthday

Abstract: The samarium diiodide reduction of glycosyl pyridyl sulfones bearing a silicon-tethered unsaturated group at the C2–OH position leads to the stereospecific synthesis of 1,2-*cis*-*C*-glycosides in good yield after desilylation. These reactions proceed via an anomeric radical with subsequent 5-*exo* cyclization. Unlike the corresponding glycosyl phenyl sulfones, the pyridyl derivatives react instantaneously with samarium diiodide and do not require a cosolvent such as hexamethylphosphoramide (HMPA). Under these reaction conditions radical cyclization precedes the second reduction step. Examples of 5-*exo*-*trig* and -*dig* ring closures are given. The synthetic utility of this method was demonstrated by a short synthesis of methyl *C*-isomaltoside.

Keywords
aryl sulfones · glycosides · radical reactions · samarium

Introduction

With over 100 years of experience in *O*-glycosylation reactions involving cyclic oxonium ion intermediates, organic chemists are now able to construct almost any naturally occurring *O*-glycoside efficiently and stereoselectively by the judicious choice of certain factors such as the C2 functionality of the glycosyl donor, the C1-activating group, the promoter, or the type of solvent.[1]

In the last ten years *O*-glycoside mimics known as *C*-glycosides, in which the interglycosidic linkage has been replaced by a methylene group, have attracted considerable interest owing to their inherent stability to hydrolysis (chemical or enzymatic) and because their conformational preferences are similar to those of the corresponding parent *O*-glycoside,[2] suggesting their potential as biological tools.[3] However, no general synthetic strategy has yet been devised that provides facile and stereocontrolled access to a large body of such compounds by means of a simple set of rules as in *O*-glycoside synthesis. Most synthetic strategies were aimed towards a particular structure and hence are not applicable to the synthesis of other *C*-glycosides.[3]

In 1989, De Mesmaeker et al. provided a partial solution for a general approach to *C*-glycosides by employing intramolecular free-radical cyclizations for the stereocontrolled preparation of 1,2-*cis*-*C*-glycosides under mild conditions.[4] Although intermolecular addition of glycosyl anomeric radicals to olefins were known at the time, mainly through the work of Giese et al.,[5] α-*C*-glycosides are preferentially formed owing to a configurationally biased anomeric radical.[6] In addition, the fact that activated olefins are required to give acceptable coupling yields limits the applicability of this methodology. De Mesmaeker et al. suggested the use of a connector between the C2 hydroxyl group and the acceptor which, because of the geometric requirements for *cis*-ring fusion in tin-hydride-based 5-*exo*-radical cyclization, allows one to efficiently prepare α- or β-*C*-glycosides, depending on the configuration of the directing C2 hydroxyl group, even with unactivated olefins.[4] The Ciba-Geigy group has developed an acetal connection which, after cyclization, can be modified to liberate the linking hydroxyl functionality (Scheme 1a). This strategy was later refined by Stork et al., who used silicon as the tethering atom.[7] Radical cyclizations onto a dimethylsilyl-tethered phenylacetylene were investigated for series of sugars and gave the desired 1,2-*cis*-*C*-glycosides in high yield after removal of the tether (Scheme 1b). An interesting adaptation of the silicon-tethered approach was provided by Sinaÿ et al. for the synthesis of *C*-disaccharides by employing 8- and 9-*endo* radical cyclizations with the readily prepared silaacetal connectors.[8] These reactions (Scheme 1c) are surprisingly

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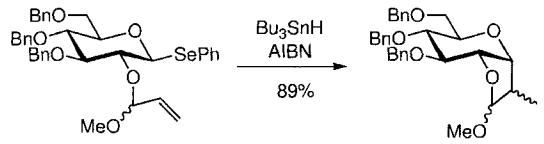
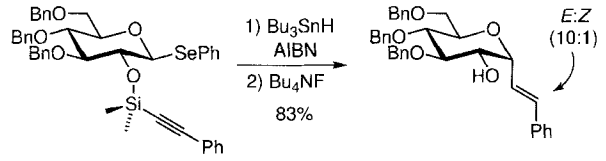
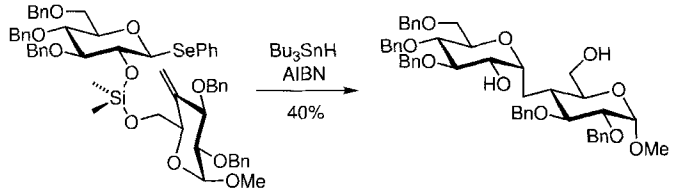
a) De Mesmaeker et al. [ref. 4]



b) Stork et al. [ref. 7]



c) Sinaÿ et al. [ref. 8]



Scheme 1. Previous *C*-glycoside syntheses by the tethering approach.

efficient in view of the medium-sized ring intermediates formed, although it is not always easy to predict the stereochemical outcome at the newly formed C–C bond. The efficiency and the stereochemistry at the anomeric center are critically dependent on the hydroxyl protecting groups of the acceptor and donor as well as the position of the silicon link.

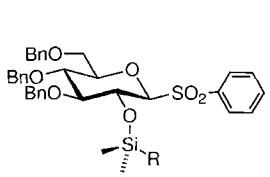
When we began these studies at the end of 1992, we decided to explore the Stork approach for the stereocontrolled construction of more complicated 1,2-*cis*-*C*-glycosides, and, in particular, whether it could be applied to the synthesis of *C*-disaccharides. Most of the above-mentioned intramolecular radical cyclizations use tributyltin-hydride-promoted reductions of selenoglycosides. This led us to explore other possibilities for the generation of an anomeric radical. In recent years, several groups have successfully used the one-electron reducing agent samarium diiodide to promote 5-*exo*-radical cyclization of suitably functionalized alkyl and aryl halides or ketones.[9, 10] Several reports on the applicability of SmI_2 for reductive desulfonation of alkyl aryl sulfones[11] suggested that this divalent lanthanide species may be suitable for the generation of an anomeric radical from a glycosyl aryl sulfone.[12]

Here we demonstrate that the silicon-tether approach is not only compatible with SmI_2-based radical cyclizations for the stereospecific synthesis of 1,2-*cis*-*C*-glycosides, but also a promising and simple alternative to the tin-hydride-based chemistry that avoids the sometimes tedious purification procedures of the latter. We then used this method for the first synthesis of a *C*-disaccharide by silicon-tethered 5-*exo* radical cyclization.[13]

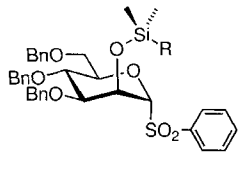
Results and Discussion

Scheme 2 outlines the principle of this strategy for the synthesis of *C*-glycosides starting from the appropriately functionalized glycosyl aryl sulfone **A**. It is well known that one-electron transfer to the LUMO of the aryl sulfone moiety results in cleavage of the anomeric C–S bond with liberation of an anomeric radical.[14] For efficient *C*-glycoside formation the rate of 5-*exo*-cyclization must be fast compared to the second, SmI_2-promoted electron-transfer step.[15] If this condition is fulfilled, the newly formed exocyclic carbon radical **B** will either abstract a hydrogen atom from the ether solvent (C=C) or undergo a second reduction to give an alkylsamarium species (C–C). In constrast, if the cyclization is inefficient, competing reduction of the anomeric radical leads to the glycosylsamarium species **C** with probable concomitant β-elimination of the C2 heteroatom to give the corresponding glycal.[12] Removal of the silicon tether should then be possible with previously published procedures for the cleavage of C–Si bonds.[16]

We examined the glucosyl and mannosyl phenyl sulfones **1** and **2** for three reasons. First, the *gluco* and *manno* series were

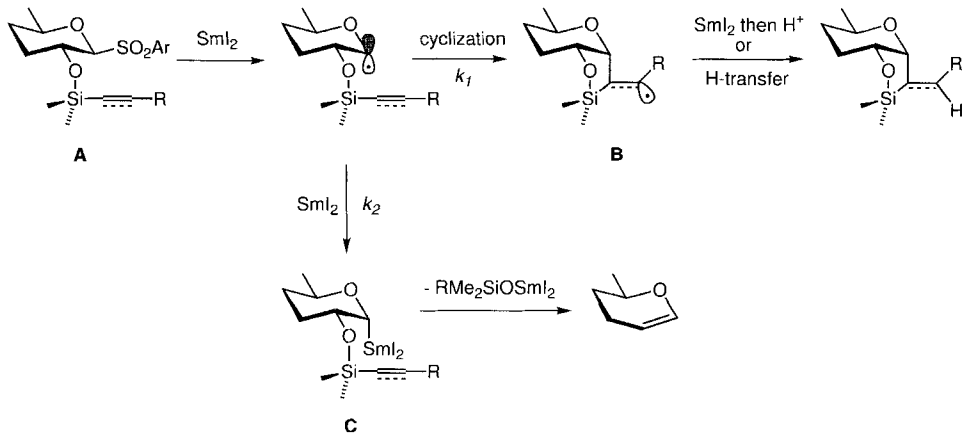


1a R = $CH{=}CH_2$
1b R = CCPh



2a R = $CH{=}CH_2$
2b R = CCPh

chosen for their opposing C2 configurations, which allow the efficiency of both α- and β-*C*-glycoside formation to be evaluated. Secondly, the differing degrees of unsaturation not only permitted a direct comparison of the efficiency of 5-*exo*-*trig* versus 5-*exo*-*dig* cyclization, but also with results obtained by



Scheme 2. Principle strategy for the synthesis of 1,2-*cis*-*C*-glycosides from glycosyl aryl sulfones.

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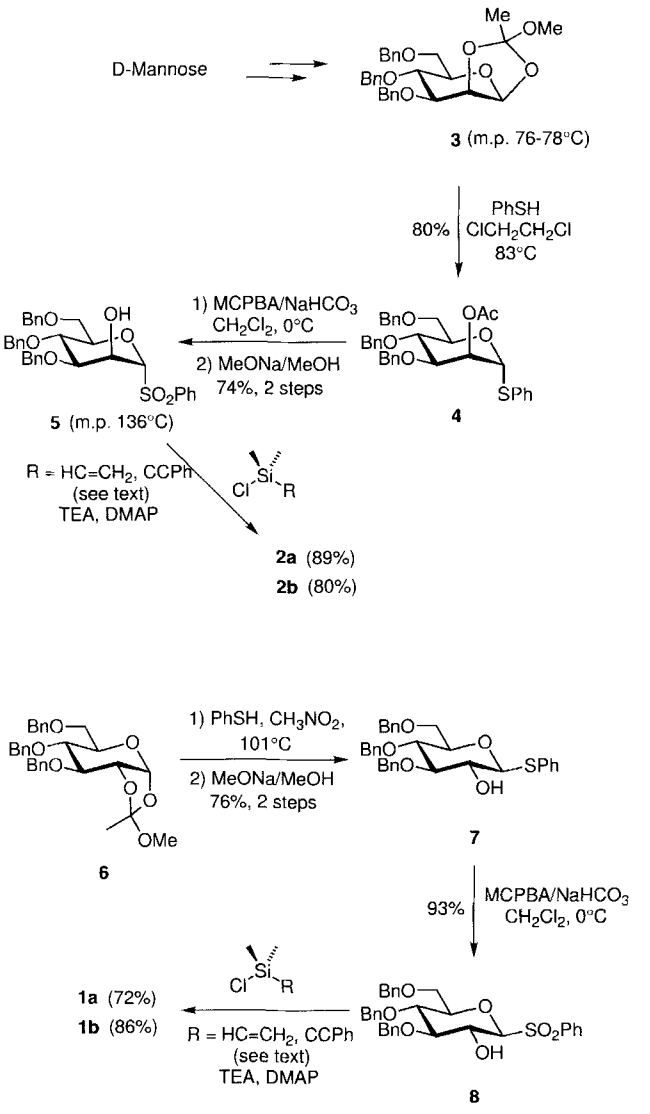
Stork et al.[7] for the tin hydride procedure. Finally, the phenyl sulfone group was chosen for ease of preparation and with regard to its previous use for the generation of C1 anions by reductive lithiation.[17]

Synthesis and cyclization studies with the glycosyl phenyl sulfones 1 and 2: The preparation of the desired glycosyl phenyl sulfones **1** and **2** started from the cyclic orthoesters **3** and **6** (Scheme 3).[18, 19] The mannosyl orthoester **3** is particularly convenient due to its high crystallinity and facile five-step preparation from mannose without purification in any of the intermediate steps. Treatment of **3** with thiophenol under Lewis acid catalysis ($BF_3 \cdot Et_2O$) in CH_2Cl_2 at 0 °C resulted in the formation of numerous products including the desired phenyl sulfide **4**.



Scheme 3. Preparation of glycosyl phenyl sulfones **1** and **2** from cyclic orthoesters **3** and **6**.

By simply refluxing a solution of the orthoester with 1.3 equivalents of thiophenol in 1,2-dichloroethane, an 80% yield of the phenyl thio-α-D-mannopyranoside **4** was obtained. Sulfide to sulfone oxidation was performed with *m*-chloroperoxybenzoic acid (MCPBA) in CH_2Cl_2 at 0 °C followed by deacetylation under standard conditions to give the crystalline mannosyl phenyl sulfone **5** (m.p. 136 °C) in 74% yield. The glucosyl phenyl sulfone **8** was prepared analogously from orthoester **6**. Compound **6** proved rather resistant to phenyl sulfide introduction by the above method and requires hot nitromethane rather than dichloroethane if good yields of the β-thioglucoside are to be obtained.

Treatment of **5** or **8** with dimethylvinylsilyl chloride and triethylamine (TEA) in CH_2Cl_2 at 20 °C required the presence of 4-dimethylaminopyridine (DMAP) for effective silylation to afford formation of acyclic precursors **1a** and **2a**. The silyl ethers were purified quickly on a silica gel column as some signs of acid instability were observed with all the silicon-tethered glycosyl aryl sulfones discussed below. Silylation of **5** or **8** with an alkynyldimethylaminosilane according to the procedure of Stork and Keitz[20] failed to introduce a tethered alkyne group and only led to the recovered alcohol. In a search for an alternative approach we found that rapid addition of a large excess of dimethyldichlorosilane (6 equiv) to a preformed solution of lithiated phenylalkyne in THF at −78 °C, followed by the removal of excess dichlorosilane in vacuo and subsequent treatment with a dichloromethane solution of **5** or **8** (0.3 equiv) in the presence of TEA and DMAP gave good yields of the silylated products **2b** and **1b**, respectively. The major by-products in these reactions were the dialkynyldimethylsilanes, which could easily be separated from the silyl ethers by chromatography, and in turn reconverted, particularly in the case of the more costly alkynes, to the liberated alkyne in high yields by simple subjection to tetrabutylammonium fluoride (TBAF) in THF. Although this approach does not solve the problem of selective silylation upon addition of the alkyne anion to dichlorodimethylsilane, it nevertheless provides a facile and rapid access to the required alkynylsilyl ethers.[21]

It has already been reported that for effective reduction of the phenyl sulfone group the addition of a THF solution of SmI_2 alone does not suffice, since the energy gap between the singly occupied HOMO of samarium diiodide and the $\sigma^*_{SO_2Ph}$ level is too large for efficient electron transfer (see Figure 1a).[11, 12] A cosolvent such as HMPA displaying a high affinity for the divalent metal cation is necessary for fast reduction.[22] The role of the complexing agent on the reducing power of SmI_2 has been discussed.[23] The higher reactivity was attributed to an in-

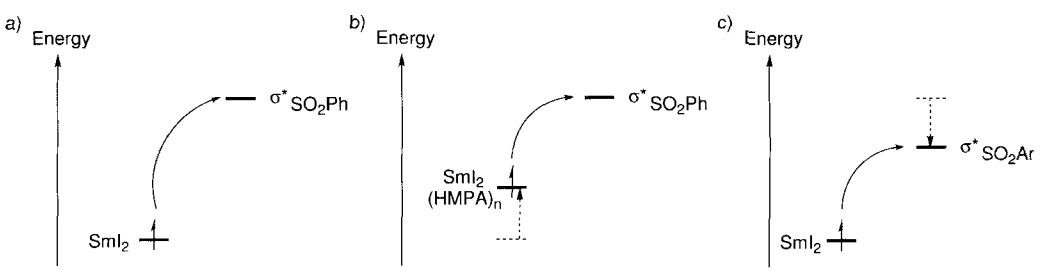


Figure 1. Effect of changing the SmI_2 HOMO and the aryl sulfone LUMO energy levels.

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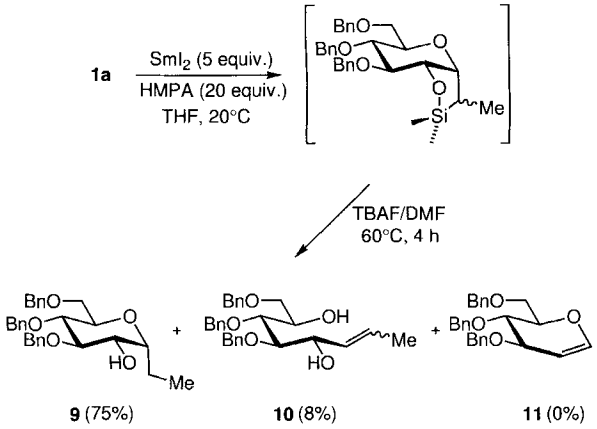
creased HOMO energy level compared with that of the uncomplexed reducing agent, which allows for the facile electron transfer to the phenyl sulfone LUMO (Figure 1b). That the phenylsulfinate obtained upon reduction probably undergoes competitive deoxygenation to the corresponding sulfenate with SmI_2/HMPA explains why an excess of SmI_2 (5–8 equiv) is required for effective desulfonylation.[11, 12]

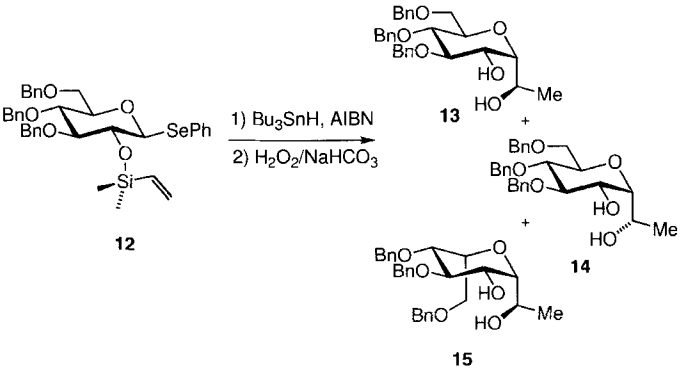
Addition of HMPA (20 equiv) to a 0.01 M solution of the glucosyl phenyl sulfone **1a** and SmI_2 (5 equiv) in THF led to rapid decolorization of the initially blue solution and formation of a colorless precipitate. Whereas TLC examination of the reaction mixture revealed severe streaking that suggested the hydrolytic instability of the cyclized compound, treatment of the crude product under the desilylation conditions reported by Stork (TBAF, DMF, 60 °C, 4 h)[16] afforded three new compounds (Scheme 4). The major product was the α-*C*-glucoside **9** (75% yield). In addition, two ring-opened products **10** were obtained as a mixture of (*E*) and (*Z*) isomers in 8% yield; they probably result from the desilylation process. These results and our inability to detect the tribenzylglucal **11** in this reaction suggested that the cyclization was highly efficient.



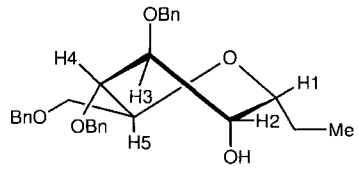
Scheme 4. Cyclization of **1a** and desilylation of the crude product to give α-*C*-glucoside **9** and (*E*) and (*Z*) isomers of **10**.

The question of whether the α-*C*-glucoside **9** was formed by a true 5-*exo* cyclization rather than by 6-*endo* ring closure arose from observations by Wilt et al. of the profound changes of *exo*/*endo* cyclization ratios for $SiMe_2$-substituted 5-hexenyl radicals in comparison to the all-carbon chain.[24] To clarify this point we prepared phenylselenide **12** and treated it with Bu_3SnH, followed by oxidation under conditions described by Tamao et al. (Scheme 5).[25] This afforded three new compounds **13**–**15**, all of which result from 5-*exo*-cyclization.[26]

Interestingly *C*-glucoside **9** did not possess the expected $^4C_1$ conformation, but rather that of a twist boat ($^0S_2$), as indicated by the coupling constants at $J_{H2,H3}$, $J_{H3,H4}$, and $J_{H4,H5}$ (Figure 2). This is in stark contrast to similar α-*C*-glucosides reported elsewhere, which were either perbenzylated or unprotected and all in a normal chair conformation.[27] Although we cannot explain this conformational deviation, it is possible that this phenomenon could reproduce itself with branched oligosaccharides containing an α-*C*-glucoside as the central unit (i.e., glycosylation of unprotected **9** at both the C3 and C4 positions



Scheme 5. Treatment of phenylselenide **12** with Bu_3SnH and followed by oxidation to give 5-*exo*-cyclized compounds **13**–**15**.



$J_{H1,H2}$ = 6.0 Hz $J_{H3,H4}$ = 5.2 Hz
$J_{H2,H3}$ = 3.4 Hz $J_{H4,H5}$ = 5.0 Hz

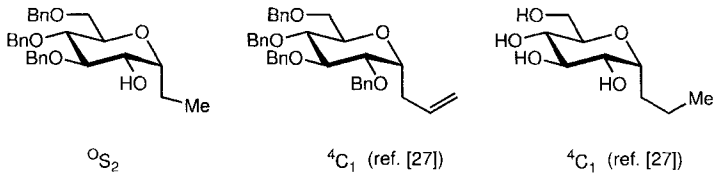
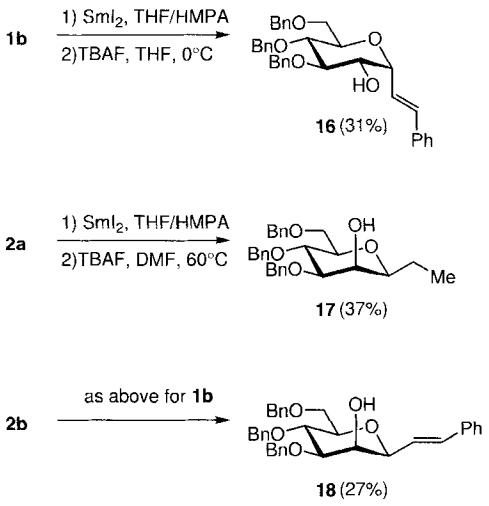


Figure 2. Conformational analysis of *C*-glucoside **9**.

could lead to a situation as for **9**, suggesting significant conformational differences between an *O*- and a mixed *C*,*O*-oligosaccharide).

We quickly found that this encouraging method was not generally applicable for the synthesis of other *C*-glycosides. For example, SmI_2-promoted cyclization of glucosyl phenyl sulfone **1b** led to a low yield (31%) of the (*E*)-2-phenylethenyl-*C*-glucoside **16** after desilylation (Scheme 6). In addition, extrapolation to the *manno* series with phenyl sulfones **2a** and **2b** was not efficient in that *C*-glycosides **17** and **18** were obtained in yields of only 37 and 27%, respectively (Scheme 6). The major byproduct in these reactions was glucal **11**, indicating that competitive reduction of the anomeric radical before cyclization was a major concern. The slow cyclization rates in the 5-*exo*-*dig* cyclizations compared to that of the 5-*exo*-*trig* can be explained by the deviation from an ideal approach trajectory of the anomeric radical to the C≡C triple bond.[28] A similar explanation can be invoked in the case of the inefficient β-*C*-mannoside formation by 5-*exo*-*dig* ring closure owing to the preference of the anomeric radical for a pseudoaxial orientation.[6]

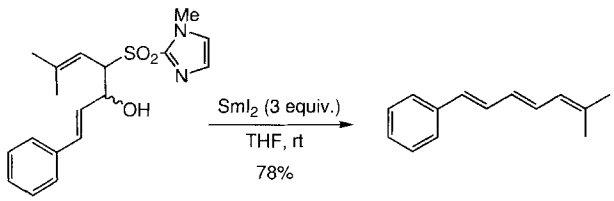
Samarium diiodide-promoted reduction of glycosyl aryl sulfones: Two options were available for rectifying the slow cyclization reactions of the above compounds. As the electron-transfer step



Scheme 6. The low yields obtained from SmI_2-promoted cyclization of glucosyl phenyl sulfone **1b** and mannosyl phenyl sulfones **2a** and **2b**.

from SmI_2 to the anomeric radical is concentration dependent (k_2 is a second-order rate constant, Scheme 2), the rate of this undesirable reduction step could be diminished by diluting the reaction mixture to favor radical cyclization. This, however, would render the approach impracticable for large-scale synthesis of *C*-glycosides. A second and potentially more interesting solution would be to retard the second electron transfer by changing the redox potential of SmI_2. Curran and Hasegawa have previously demonstrated that radical cyclizations promoted by SmI_2/HMPA can be significantly improved by using only two equivalents of HMPA,[15] although attempts along this line did not lead to any improvement in our case. An alternative approach would be to omit HMPA in these reductions, provided the LUMO energy level of the aryl sulfone is sufficiently lowered by chemical modification (Figure 1c).

Kende and Mendoga recently observed that desulfonylation of imidazolyl sulfone **19** can be performed with SmI_2 in the absence of an additive (Scheme 7), whereas the analogous



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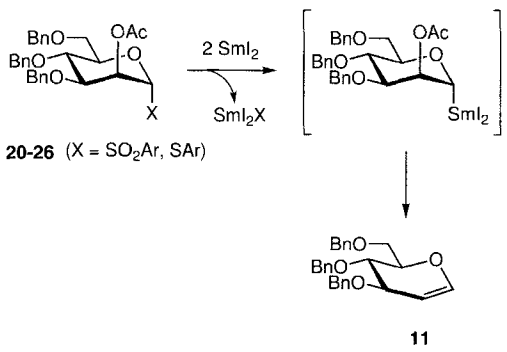
Scheme 7. Desulfonylation of imidazolyl sulfone **19** by SmI_2 alone.

phenyl sulfones were inert under identical conditions.[11a] Furthermore, electrochemical studies by Simonet and co-workers revealed that heteroatom-substituted alkylaryl sulfones have more positive reduction potentials E^0 than the parent alkyl phenyl sulfone.[29] These observations suggest that heterocycle substitution contributes significantly to the lowering of the aryl sulfone LUMO energy level.

A short study was therefore initiated with a series of mannosyl aryl sulfones and sulfides **20**–**26** in order to identify a suitable arene moiety for a high-yield *C*-glycosylation (Scheme 8).



Scheme 8. Reaction of the mannosyl aryl sulfones and sulfides **20**–**26**; efficacy and yields are compared in Table 1.

The glycosides **20**–**26** are ideal for this investigation as the efficacy of the SmI_2-induced electron-transfer reaction could easily be measured by the rate of SmI_2 consumption as well as the yield of glucal obtained from reduction of the intermediate C1 radical. Each mannosyl aryl sulfone was prepared in two steps starting from the mannosyl orthoester **3** by introduction of the thiol with or without Lewis acid assistance (see Experimental Section). For example, the 2-naphthalenethiol, 2-mercaptopyridine, and 2-mercaptopyrimidine required addition of mercuric bromide to catalyze the ring-opening of **3**.[12] Subsequent oxidation of the aryl sulfides with MCPBA led to high yields of the corresponding aryl sulfones in the case of **20**–**24**. The benzothiazolyl sulfone formed from the oxidation of sulfide **25** proved too hydrolytically unstable for isolation.

Each sulfone or sulfide was then treated with SmI_2, and the number of equivalents of SmI_2 consumed and the consumption rate were measured, as well as the yield of tribenzylglucal. The results are listed in Table 1. The large differences in reduction

Table 1. SmI_2-promoted reductive elimination of mannosyl aryl sulfones and sulfides [a].

	X	Equiv SmI_2 added (consumed)	Glucal **11** (%) [b]
1	-SO_2Ph **20**	5 (nd) [c]	< 5 [d]
2	-SO_2-2-naphth. **21**	5 (nd)	22 [d]
3	-SO_2-2-*N*-methylimid. **22**	3 (2)	76
4	-SO_2-2-pyridyl **23**	2.2 (2)	94
5	-SO_2-2-pyrimidyl **24**	2.2 (2)	72
6	-S-2-benzothiazolyl **25**	3 (nd) [e]	78
7	-S-2-pyridyl **26**	3 (nd) [e]	64

[a] All reactions were run at 20 °C by adding a 0.1 M THF solution of SmI_2 to a THF solution of the sulfone or sulfide. [b] Unless otherwise stated, yields are based on isolated chromatographically pure tribenzyl-D-glucal **11**. [c] nd = not determined. [d] Conversion to glucal after 24 h according to ^{1}H NMR analysis. [e] Reaction time 1.5 h.

rates upon treatment of the isocyclic aryl sulfones with SmI_2 compared with the heteroatom-substituted analogues are noteworthy. The former group (entries 1 and 2) reacted extremely slowly with SmI_2, as shown by the 5% reduction of the phenyl sulfone after 24 h. In contrast, the sulfones in entries 3–5, all possessing a nitrogen atom at position 2 of the aryl sulfone, consumed approximately two equivalents of SmI_2 instantaneously. Best yields of the glucal were obtained with the 2-pyridyl sulfone (94%, entry 4). Interesting and unexpected were

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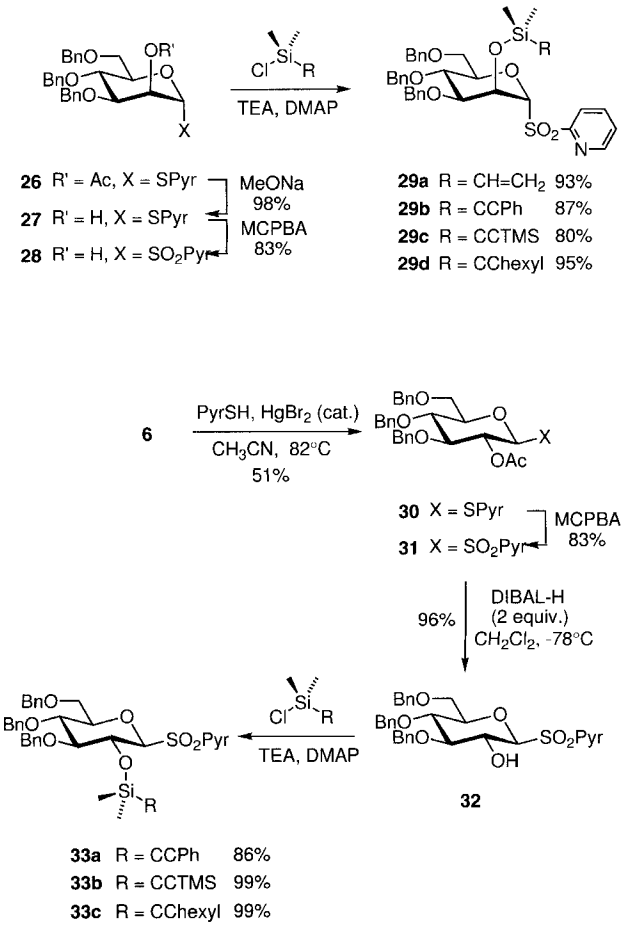
the high reactivities of the sulfides (entries 6 and 7) compared to the phenyl sulfone. These results indicated that the 2-pyridyl sulfone group was the ideal candidate for both its reactivity with SmI_2 and its ease of preparation.

Mannosyl pyridyl sulfide **26** was thus deacetylated to alcohol **27**, oxidized to sulfone **28** and then subjected to the above-described conditions for the introduction of four silicon-tethered unsaturated groups to give **29a–d** in high yields (Scheme 9).

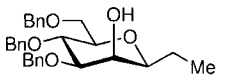
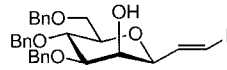
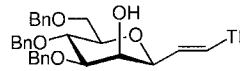
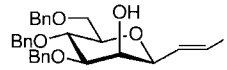
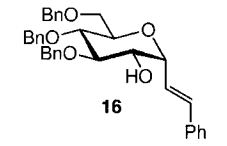
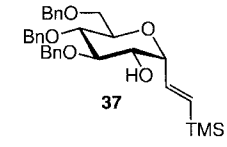
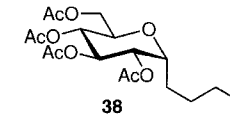


Scheme 9. Consecutive deacetylation and oxidation of mannosyl pyridyl sulfide **26** followed by introduction of four silicon-tethered unsaturated groups to give **29a–d**, and the analogous preparation of **33a–c** from starting material **6**.

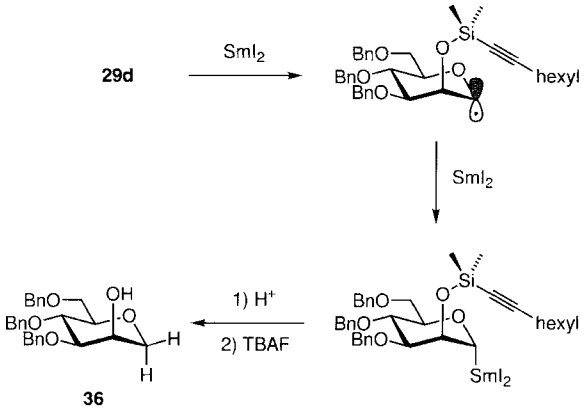
Analogously, the glucosyl pyridyl sulfones **33a–c** were prepared by mercuric bromide-catalyzed ring-opening of orthoester **6** to give pyridyl sulfide **30**, which was subsequently oxidized with MCPBA. Deacetylation of **31** with sodium methanolate in methanol led to low yields of the desired C2–OH liberated sugar **32**, possibly owing to competitive deprotonation of the acidic anomeric proton with concominant β-elimination. Treatment of **31** with DIBAL-H in CH_2Cl_2 at $-78\,^{\circ}C$ proved more effective in that it afforded **32** in 96% but also required two equivalents of the hydride for deacetylation, possibly due to coordination of one equivalent to the basic ring nitrogen. Finally, attachment of the silyl tethers gave **33a–c**.

Addition of SmI_2 over 30 min to a 0.01 M solution of **29a** at 20 °C led, after work-up and desilylation, to an 80% overall yield of the β-*C*-mannoside **17**—a 43% increase in yield compared to the phenyl sulfone **1a** (Table 2, entry 1). In addition,

Table 2. SmI_2-promoted radical cyclizations with glycosyl pyridyl sulfones.

	Pyridylsulfone	*C*-glycoside	Yield
1	**29a**	 **17**	80%
2	**29b**	 **18**	64% (*E*:*Z*, 10:1)
3	**29c**	 **34**	61% (*E*:*Z*, 10:1)
4	**29d**	 **35**	25%
5	**33a**	 **16**	76% (*E*:*Z*, >50:1)
6	**33b**	 **37**	78% (*E*:*Z*, >50:1)
7	**33c**	 **38**	52% 4 steps

we were not able to detect the formation of glucal **11**, which clearly indicates the efficiency of this cyclization. A nice feature of this procedure is that completion of the reaction is easily monitored by the persistance of the blue color of divalent samarium; hence these radical cyclizations are performed more or less as a titration. With the tethered activated alkynes **29b** and **29c**, good yields of the *C*-glycosides **18** and **34** were likewise obtained with (*E*):(*Z*) selectivities of approximately 10:1 (entries 2 and 3) paralleling the previous results reported by Stork with tributyltin hydride.[7] Only approximately 5% of the glucal was formed under these reaction conditions. On the other hand, *C*-glycosylation with an unactivated alkyne as in **29d** afforded **35** in a poor yield of 25% (entry 4), reflecting the combination of a slow 5-*exo*-*dig* cyclization and the axial-like orientation of the anomeric radical. Unexpectedly, it was not the elimination product which dominated in this reaction but rather the 1-deoxy sugar **36** (Scheme 10), isolated in a remarkably high yield of 60%. Two explanations were put forth for the formation of **36**. Because of a slow cyclization rate, the anomeric radical intermediate could be either quenched by hydrogen atom abstraction from solvent (THF), or reduced to give a possibly stable glycosyl organosamarium compound displaying a preference for protonation by solvent rather than β-elimination. The latter expla-

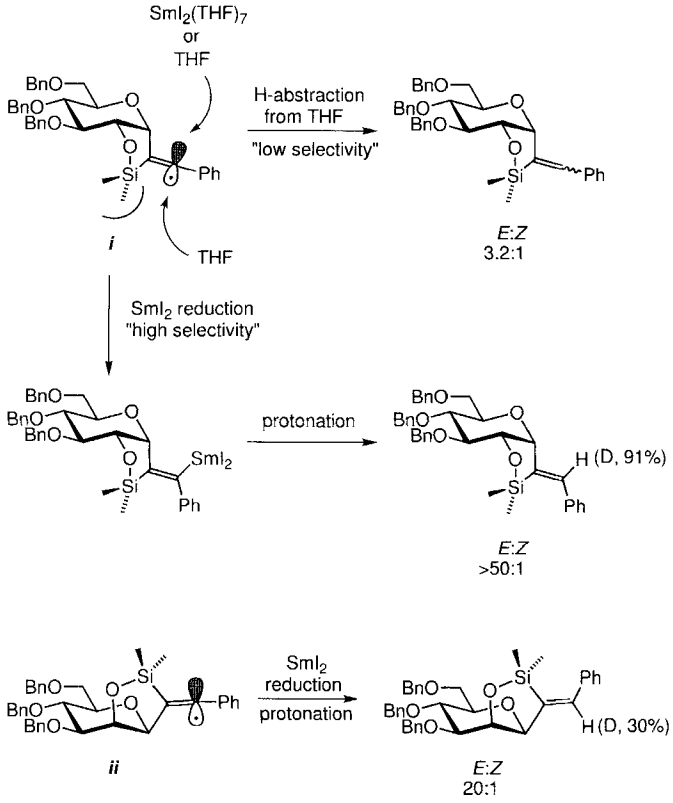


Scheme 10. Mechanistic explanation for the high (*E*) selectivity in the *gluco* series.

nation is indeed the correct one as we have subsequently reported that C2 OH-protected mannosyl pyridyl sulfones efficiently couple to carbonyl substrates with SmI_2 under Barbier conditions.[30] This example thus represents a possible limitation of SmI_2-promoted intramolecular *C*-glycosylations, independent of the aryl sulfone group employed.

Also unanticipated were the results obtained with the glucosyl pyridyl sulfones when treated with SmI_2 (Table 2, entries 5–7). In the case of **33a**, subjection to conditions identical to those used for **29** afforded a modest yield (51%) of the (*E*)- and (*Z*)-*C*-glycosides **16** in a ratio of 3.2:1. This (*E*):(*Z*) selectivity is considerably lower than the 10:1 ratio observed by Stork et al.[7] However, rapid addition of 5–8 equivalents of SmI_2 to an approximately 0.01 M solution of **33a** in THF led, after desilylation, to an improved 76% yield of **16** with an excellent (*E*):(*Z*) ratio of greater than 50:1. The glucal **11** was again a minor product, isolated in 5% yield. This result is tentatively explained in Scheme 11 by invoking the intermediacy of the stabilized vinylic radical ***i***.

Several groups have already reported on the competition between reduction of *gem*-substituted aryl or silyl alkenyl radicals by SmI_2 and hydrogen abstraction facilitated by the stabilizing effect of these substituents on intermediate vinylsamarium radicals. Inanaga et al. have shown that intermolecular coupling of carbonyls with aryl-substituted alkynes in the presence of CD_3OD leads to an approximately 50% incorporation of deuterium at the vinylic position.[31] A somewhat similar result was observed by Bennett and co-workers in SmI_2-induced intramolecular radical cyclizations, for which 18% deuterium incorporation was obtained with CH_3CH_2OD as the trapping agent.[9b] SmI_2-promoted cyclizations onto silylated alkynes led to the formation of deuterated products in the presence of D_2O.[9c] Hence, under slow addition of SmI_2 to **33a**, the low concentration of divalent samarium maintained would suggest that hydrogen abstraction from THF solvent by intermediate ***i*** is the major pathway. The abundance and small size of the THF molecule implies little preference in the direction of attack and therefore explains the low (*E*)/(*Z*) selectivities obtained. In contrast, higher concentrations of SmI_2 may lead to preferential reduction of the alkenyl radical to its anion. The large size of the heptacoordinate metal ion[32] enhances steric factors and results in the reduction of the alkenyl radical opposite to the bulky silicon tether and formation of a configurationally stable (*E*)-



Scheme 11. Pathways from stabilized vinylic radical ***i*** and vinyl radical ***ii*** and the resulting (*E*)/(*Z*) ratios.

alkenyl anion, which is subsequently protonated to give **16**. In order to prove this point, **33a** was subjected to rapid addition of SmI_2 (7 equiv) in the presence of six equivalents of CH_3OD, and the cyclized product was immediately desilylated. Isolation and analysis of the resulting alkenyl-*C*-glucoside revealed that 91% deuterium incorporation at the vinylic center had occurred, implying that the stabilized alkenyl radical is indeed reduced to its corresponding anion. To find out whether this event could occur in the *manno* series, **29b** was treated with SmI_2 and CH_3OD under similar conditions to those used for **33a**. In this case the major product was the 1-deoxy *manno*-derivative **36** (54%), which underlines the importance of the mode of SmI_2 addition for obtaining optimum yields of the *C*-glycoside. Nevertheless, the isolated alkenyl-*C*-mannoside showed an (*E*):(*Z*) ratio of 20:1, twice that observed in the case of the slow addition mode. In addition, an approximately 30% introduction of deuterium occurred at the vinylic position, again indicative of an anionic intermediate. However, we cannot explain the lower deuterium incorporation observed. No deuterium labeling was found when this experiment was repeated with slow addition, as would have been predicted, suggesting that under these conditions the vinyl radical ***ii*** (Scheme 11) is quenched by the ether solvent before it is reduced by SmI_2.

As expected, a similar result was obtained on fast addition of divalent samarium to the TMS-substituted alkyne **33b**, which gave the (*E*)-alkenyl-*C*-glucoside **37** in 78% yield (Table 2, entry 6). On the other hand, with the octyne derivative, a complex mixture of products was obtained. After exhaustive hydrogenation and acetylation, the tetraacetyl-α-*C*-glucoside **38** was obtained in a 53% overall yield from pyridyl sulfone **33c** (entry 7).

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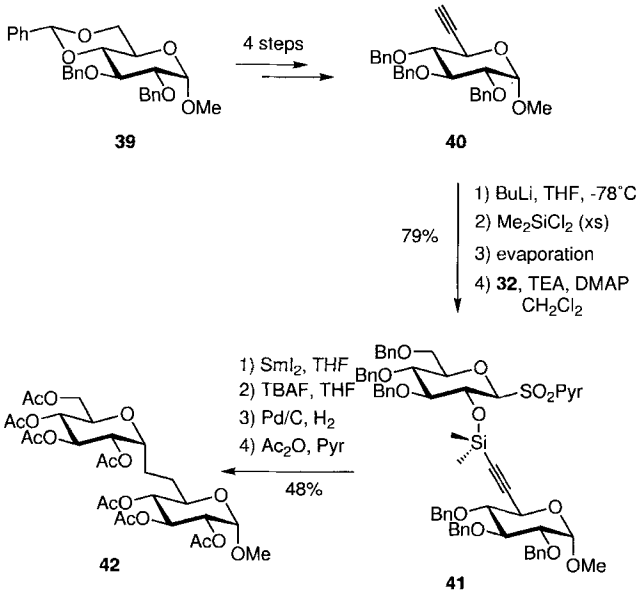
Finally, this radical cyclization strategem was adapted to the synthesis of a *C*-disaccharide, namely, methyl α-*C*-isomaltoside,[33] from alkyne **40**,[34] easily prepared in four steps from the benzylidene derivative **39**. Tethering to pyridyl sulfone **32** was achieved as described for **33** to provide the silaacetal **41** in 79% yield. SmI_2-promoted radical cyclization under the conditions for α-*C*-glucoside formation and then further transformation of the cyclic intermediate by desilylation, hydrogenation and peracetylation furnished the *C*-disaccharide as its crystalline peracetate **42** (M.p. 151–152 °C) in a 48% overall yield for four steps (Scheme 12). Again, it is interesting to note that



Scheme 12. Synthesis of methyl α-*C*-isomaltoside from alkyne **40**, itself prepared from the benzylidene derivative **39**.

the nonreducing sugar of *C*-disaccharide **42** has a normal $^4C_1$ chair conformation in solution in contrast to the methyl α-*C*-glucoside **9**, as indicated by their $^1H-^1H$ coupling constants. Confirmation of the structure of the heptaacetyl *C*-isomaltoside was provided by a single-crystal X-ray structure determination (Figure 3). This solid-state structure of **42** is interesting, as such

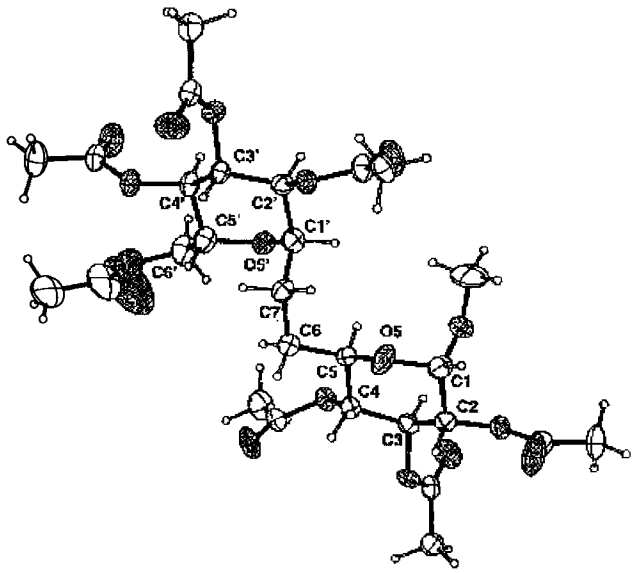


Figure 3. Single-crystal X-ray structure of the peracetylated *C*-isomaltoside **42**.

X-ray investigations of *C*-disaccharides are scarce, with only one other known structure, namely methyl *C*-gentiobioside, reported in the literature.[35] As in solution, both pyranose rings of **42** occupy the normal $^4C_1$ chair conformation in the solid state. The relative orientation of the two sugar units is represented by the torsion angles ϕ (O5′-C1′-C7′-C6), ψ (C1′-C7′-C6-C5) and Ω (C7′-C6-C5-O5) with values of +49°, +64°, and +62°, respectively. The ϕ value is in good agreement with that observed for the unprotected disaccharide in aqueous solution ($\phi = +50°$).[2b] However, ψ and Ω deviate significantly ($\psi = +165°$, $\Omega = +80°$) from the values for the solid-state conformation of **42**.

In conclusion, we have found that glycosyl pyridyl sulfones are quickly reduced by samarium diiodide in the absence of a cosolvent and that this combination may be exploited for the mild preparation of *C*-glycosides by radical cyclization. This procedure has certain advantages over the corresponding tin hydride method in that it avoids the use of toxic reagents and solvents such as tributyltin hydride, phenyl selenides, and benzene, as well as the often difficult purification procedures.

Experimental Section

General: Unless otherwise stated, all reactions were carried out under argon. THF was dried and freshly distilled over sodium/benzophenone. Dichloromethane was freshly distilled over P_2O_5. Acetonitrile was distilled over CaH_2. Reactions were monitored by thin-layer chromatography (TLC) analysis.

Starting materials: The following starting materials were prepared according to literature procedures: 3,4,6,-tri-*O*-benzyl-β-D-mannose 1,2-(methyl orthoacetate) (**3**),[18] 3,4,6,-tri-*O*-benzyl-α-D-glucose 1,2-(ethyl orthoacetate) (**6**).[19]

Phenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (4): A solution of tribenzyl orthoester **3** (2.0 g, 3.94 mmol) and thiophenol (466 μL, 4.54 mmol) in 1,2-dichloroethane (10 mL) was heated under reflux for 12 h. After cooling, the solution was evaporated to dryness in vacuo, and the residue was purified by flash chromatography (60:1, toluene/acetone) to give the thioglycoside **4** as a colorless syrup (1.83 g, 80%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.50-7.18$ (m, 20H; 4Ph), 5.60 [dd, $^3J(H,H) = 3.0$, 1.9 Hz, 1H; H2], 5.52 [d, $^3J(H,H) = 1.9$ Hz, 1H; H1], 4.88 [d, $^3J(H,H) = 10.8$ Hz, 1H; CHPh], 4.72 [d, $^3J(H,H) = 11.4$ Hz, 1H; CHPh], 4.66 [d, $^3J(H,H) = 12.1$ Hz, 1H; CHPh], 4.57 [d, $^3J(H,H) = 11.4$ Hz, 1H; CHPh], 4.51 [d, $^3J(H,H) = 10.8$ Hz, 1H; CHPh], 4.47 [d, $^3J(H,H) = 12.1$ Hz, 1H; CHPh], 4.33 [ddd, $^3J(H,H) = 9.8$, 4.5, 2.1 Hz, 1H; H5], 4.00–3.91 [m, 2H; H3, H4], 3.85 [dd, $^3J(H,H) = 11.0$, 4.5 Hz, 1H; H6a], 3.72 [dd, $^3J(H,H) = 11.0$, 2.1 Hz, 1H; H6b], 2.13 (s, 3H; $COCH_3$).

3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl phenyl sulfone (5): *m*-Chloroperoxybenzoic acid (MCPBA) of 85% purity (740 mg, 3.7 mmol) was added to a stirred mixture of sulfide **4** (866 mg, 1.48 mmol) and sodium bicarbonate (915 mg, 11.1 mmol) in CH_2Cl_2 (8 mL) at 0 °C. The cold bath was removed and the mixture was stirred at 20 °C for 3 h, after which it was diluted with CH_2Cl_2 and washed consecutively with a 50% saturated solution of $Na_2S_2O_3$, saturated $NaHCO_3$, and brine. The organic phase was dried with Na_2SO_4 and concentrated to dryness in vacuo to give an oil, which was redissolved in MeOH (15 mL) and CH_2Cl_2 (2 mL). *NaOMe in MeOH (0.1 M*, 2 mL) was added and the solution was stirred for 3 h at 20 °C. The solution was neutralized by the addition of dry ice and evaporated to dryness in vacuo. The residue was partitioned between CH_2Cl_2 and water, and the organic phase was washed with water, dried with Na_2SO_4 and evaporated to dryness in vacuo to give a solid. Recrystallization from MeOH afforded **5** as colorless needles (633 mg, 74%). M.p. 136 °C; $[\alpha]_D^{25} = +100.1$ ($c = 1.0$, chloroform); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.94-7.20$ (m, 20H; 4Ph), 4.91 [d,

^3J(H,H) = 2.9 Hz, 1H; H1], 4.85 [dd, ^3J(H,H) = 2.9, 2.9 Hz, 1H; H2], 4.79 (s, 2H, CH_2Ph), 4.78 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.54 [ddd, ^3J(H,H) = 9.7, 4.0, 4.0 Hz, 1H; H5], 4.53 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.48 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.39 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.28 [dd, ^3J(H,H) = 7.8, 2.9 Hz, 1H, H3], 3.81 [dd, ^3J(H,H) = 9.7, 7.8 Hz, 1H; H4], 3.62 [m, 2H; H6a, H6b], 2.92 (brs, 1H; OH); MS (CI, NH_3): m/z = 592 [M^+ + 18], 450 [M^+ + 18 − $PhSO_2H$]; $C_{33}H_{34}O_7S$ (584.7): calcd C 68.97, H 5.96; found C 68.70, H 5.88.

Phenyl 3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (7): A solution of orthoester **6** (2.0 g, 3.84 mmol) and thiophenol (0.6 mL, 5.76 mmol) in nitromethane (5 mL) was heated under reflux for 4 h. The solution was cooled and evaporated to dryness in vacuo, and the residue obtained was then redissolved in MeOH/THF (1/1, 10 mL). K_2CO_3 (670 mg, 4.8 mmol) was added and the mixture was stirred for 12 h at 20 °C. The reaction mixture was diluted with CH_2Cl_2, washed twice with water, dried (Na_2SO_4), and evaporated to dryness in vacuo. Purification of the crude material by flash chromatography (hexane/EtOAc, 5:1) gave a colorless solid (76%). Recrystallization from MeOH gave colorless needles. M.p. 69 °C; $[\alpha]_D^{25}$ = −12.4 (c = 1.0, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.19 (m, 20H; 4Ph), 4.90 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.83 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.81 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 4.60 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.57 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 4.53 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.48 [d, ^3J(H,H) = 9.5 Hz, 1H; H1], 4.28 [dd, ^3J(H,H) = 11.1, 2.2 Hz, 1H; H6a], 3.81 [dd, ^3J(H,H) = 11.1, 4.2 Hz, 1H; H6b], 3.63–3.44 (m, 4H; H2, H3, H4, H5], 2.37 [d, ^3J(H,H) = 2.1 Hz, 1H; OH].

3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl phenyl sulfone (8); General procedure for sulfide to sulfone oxidation: MCPBA of approx. 85% purity (810 mg, 2.35 mmol) was added to a stirred mixture of sulfide **7** (510 mg, 0.94 mmol) and $NaHCO_3$ (592 mg, 7.05 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The cold bath was removed and stirring was continued for 3 h at 20 °C, after which the reaction mixture was diluted with CH_2Cl_2 and then washed consecutively with a 50% saturated solution of $Na_2S_2O_3$, saturated $NaCO_3$, and brine. The organic phase was dried with Na_2SO_4 and concentrated to dryness in vacuo. Flash chromatography (toluene/EtOAc, 19:2) gave **8** (500 mg, 93%) as a colorless solid. Recrystallization from MeOH afforded colorless needles. M.p. 74 °C; $[\alpha]_D^{25}$ = −6.4 (c = 1.0, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.13 (m, 20H; 4Ph), 5.01 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.80 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.78 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.52 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.42 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.37 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.31 [d, ^3J(H,H) = 9.7 Hz, 1H; H1], 3.97 [ddd, ^3J(H,H) = 9.7, 8.5, 1.8 Hz, 1H; H2], 3.69–3.59 [m, 3H, H3; H6a, H6b], 3.52–3.42 (m, 2H; H4, H5), 2.33 [d, ^3J(H,H) = 1.8 Hz, 1H; OH]; $C_{33}H_{34}O_7S$ (574.7): calcd C 68.97, H 5.96; found C 68.80, H 5.87.

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethylvinylsilyl)-α-D-mannopyranosyl phenyl sulfone (2a); General procedure for the dimethylvinylsilylation of C2-hydroxyglycosyl aryl sulfones: Dichloromethylvinylsilane (144 μL, 2.08 mmol) was added to a stirred solution of sulfone **5** (200 mg, 0.35 mmol) triethylamine (184 μL, 1.79 mmol), and DMAP (2 mg) in CH_2Cl_2 (4 mL) at 0 °C, after which the solution was warmed to 20 °C. After stirring for 1 h, the solution was diluted with CH_2Cl_2 and then washed with ice-cold water, dried with Na_2SO_4, and evaporated to dryness. The crude product was purified by flash chromatography to give 166 mg (72%) of **2a** as a colorless syrup. As **2a** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.18 (m, 20H; 4Ph), 6.16 [dd, ^3J(H,H) = 20.0, 15.0 Hz, 1H; SiCH=C], 6.02 [dd, ^3J(H,H) = 15.0, 4.4 Hz, 1H; *cis*-SiC=CH], 5.80 [dd, ^3J(H,H) = 20.0, 4.4 Hz, 1H; *trans*-SiC=CH], 4.96 [dd, ^3J(H,H) = 3.0, 3.0 Hz, 1H; H2], 4.83 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.81 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.75 [d, ^3J(H,H) = 3.0 Hz, 1H; H1], 4.73 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.54 [ddd, ^3J(H,H) = 9.0, 5.1, 2.4 Hz, 1H; H5], 4.54 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.49 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.39 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.23 [dd, ^3J(H,H) = 9.0, 3.0 Hz, 1H; H3], 3.91 [dd, ^3J(H,H) = 9.0, 9.0 Hz, 1H; H4], 3.67 [dd, ^3J(H,H) = 11.0, 2.4 Hz, 1H; H6a], 3.63 [dd, ^3J(H,H) = 11.0, 5.1 Hz, 1H; H6b], 0.31 (s, 6H; $SiMe_2$).

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethylvinylsilyl)-β-D-glucopyranosyl phenyl sulfone (1a): The dimethylvinylsilyl ether **1a** was prepared according to the general procedure outlined for **2a** to give the title compound as a colorless solid in 89% yield (203 mg) after flash chromatography (hexane/EtOAc, 3:1). As compound **1a** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.07 (m, 20H; 4Ph), 6.32 [dd, ^3J(H,H) = 20.6, 15.0 Hz, 1H; SiCH=C], 5.98 [dd, ^3J(H,H) = 15.0, 3.8 Hz, 1H; *cis*-SiC=CH], 5.79 [dd, ^3J(H,H) = 20.6, 3.8 Hz, 1H; *trans*-SiC=CH], 4.97 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.88 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.67 [d, ^3J(H,H) = 10.8 Hz, 1H; CHPh], 4.54 [d, ^3J(H,H) = 10.8 Hz, 1H; CHPh], 4.49 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.39 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.23 [dd, ^3J(H,H) = 9.0, 3.0 Hz, 1H; H3], 3.91 [dd, ^3J(H,H) = 9.0, 9.0 Hz, 1H; H4], 4.54 [ddd, ^3J(H,H) = 9.0, 5.1, 2.4 Hz, 1H; H5], 3.70–3.59 (m, 2H; H6a, H6b), 0.31 (s, 6H; $SiMe_2$).

3,4,6-Tri-*O*-benzyl-α-D-glucopyranosylethane (9): Phenyl sulfone **1a** (200 mg, 0.30 mmol) in THF (2 mL) was transferred through a cannula into a stirred solution of SmI_2 in THF (0.1 M, 15 mL, 1.5 mmol) under argon. HMPA (1.1 mL, 6.1 mmol) was then added, resulting in an immediate color change of the solution from blue to purple to brown and the formation of a white precipitate. After stirring for 20 min, saturated aqueous NH_4Cl and ether were added, after which the organic phase was washed with water and brine, dried with Na_2SO_4, and evaporated to dryness in vacuo. The residue was dissolved in dry DMF (8 mL), and a 1 M THF solution of Bu_4NF was added to the resulting solution. The solution was heated to 60 °C for 1 h, cooled to room temperature, diluted with ether, and washed five times with water and then brine. After drying with Na_2SO_4 and evaporation to dryness in vacuo the crude product was purified by flash chromatography (hexane/EtOAc 3:1) to give **9** as a white solid (105 mg, 75%). Recrystallization from pentane afforded colorless needles. M.p. 86–88 °C; $[\alpha]_D^{22}$ = +33.2 (c = 1.07, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.23 (m, 15H; 3Ph), 4.69 [d, ^3J(H,H) = 11.8 Hz, 1H; CHPh], 4.65 [d, ^3J(H,H) = 11.4 Hz, 1H; CHPh], 4.59 [d, ^3J(H,H) = 11.8 Hz, 1H; CHPh], 4.59 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.58 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.53 [d, ^3J(H,H) = 11.4 Hz, 1H; CHPh], 4.01 [ddd, ^3J(H,H) = 5.7, 5.2, 5.0 Hz, 1H; H5], 3.83 [dd, ^3J(H,H) = 10.3, 5.7 Hz, 1H; H6a], 3.82–3.72 (m, 2H; H1, H3), 3.73 [dd, ^3J(H,H) = 10.3, 5.0 Hz, 1H; H6b], 3.66 [ddd, ^3J(H,H) = 7.8, 6.0, 3.4 Hz, 1H; H2], 3.65 [dd, ^3J(H,H) = 5.0, 5.2 Hz, 1H; H4], 2.80 [d, ^3J(H,H) = 7.8 Hz, 1H; OH], 1.75–1.59 (m, 2H; CH_2), 0.97 [dd, ^3J(H,H) = 7.5, 7.5 Hz, 3H; CH_3]; MS (CI, NH_3): m/z = 480 [M^+ + 18], 463 [M^+ + 1]; $C_{29}H_{34}O_5$ (462.6): calcd C 75.30, H 7.41; found C 75.13, H 7.52.

Further elution of the column afforded an approx. 3:2 mixture of the (*E*) and (*Z*) olefins **10** (12 mg, 8%). Olefin **10** displayed characteristic signals in the ^{1}H NMR (300 MHz, $CDCl_3$) spectra at δ = 5.76–5.45 (m; vinylic protons), 1.68 [dd, ^3J(H,H) = 6.7, 1.5 Hz, 3H; CH_3 (*E*) isomer], 1.67 [dd, ^3J(H,H) = 4.9, 1.5 Hz, 3H; CH_3 (*Z*) isomer]; MS (CI, NH_3): m/z = 480 [M^+ + 18].

3,4,6-Tri-*O*-benzyl-β-D-mannopyranosylethane (17): The procedure employed for the synthesis of **9** was applied to phenyl sulfone **2a** and afforded the *C*-mannoside **17** as a colorless oil in 37% yield (26 mg) after flash chromatography (hexane/EtOAc, 3:1). $[\alpha]_D^{22}$ = −2.9 (c = 1.0, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.18 (m, 15H; 3Ph), 4.84 [d, ^3J(H,H) = 10.8 Hz, 1H; CHPh], 4.75 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.67 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.62 [d, ^3J(H,H) = 12.4 Hz, 1H; CHPh], 4.56 [d, ^3J(H,H) = 12.4 Hz, 1H; CHPh], 4.52 [d, ^3J(H,H) = 10.8 Hz, 1H; CHPh], 3.93 [brdd, ^3J(H,H) = 3.4, 3.2 Hz, 1H; H2], 3.75 [dd, ^3J(H,H) = 9.5, 9.1, 1H; H4], 3.75 [dd, ^3J(H,H) = 10.9, 2.0 Hz, 1H; H6a], 3.66 [dd, ^3J(H,H) = 10.9, 5.0 Hz, 1H; H6b], 3.58 [dd, ^3J(H,H) = 9.1, 3.2 Hz, 1H; H3], 3.39 [ddd, ^3J(H,H) = 9.5, 5.0, 2.0 Hz, 1H; H5], 3.21 [brdd, ^3J(H,H) = 7.5, 7.0 Hz, 1H; H1], 2.26 [d, ^3J(H,H) = 3.4, 1H; OH], 1.89–1.59 (m, 2H; CH_2), 0.97 [dd, ^3J(H,H) = 7.5, 7.0 Hz, 3H; CH_3]; MS (CI, NH_3): m/z = 480 [M^+ + 18], 463 [M^+ + 1]; $C_{29}H_{34}O_5$ (462.6): calcd C 75.30, H 7.41; found C 75.07, H 7.53.

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethyl(phenylethynyl)silyl)-β-D-glucopyranosyl phenyl sulfone (1b); General procedure for the dimethylalkynylsilylation of C2-hydroxyglycosyl aryl sulfones: BuLi in hexanes (1.5 M, 1.0 mL, 1.5 mmol) was added to a stirred solution of phenylacetylene (189 μL, 1.72 mmol) in THF (6 mL) at −78 °C. After 10 min, Me_2SiCl_2 (550 μL, 4.5 mmol) was added quickly, followed by stirring for 30 min at −78 °C and then warming to 20 °C. The solution was evaporated almost to dryness, after which CH_2Cl_2 (5 mL) and TEA (240 μL, 1.72 mmol) were added, followed by

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sulfone **8** (200 mg, 0.35 mmol) and DMAP (3 mg). The reaction mixture was stirred for 1 h and then washed three times with water, dried (Na_2SO_4), and evaporated to dryness. Purification of the residue by flash chromatography (hexane/EtOAc, 6:1) afforded **1b** as a colorless syrup (234 mg, 86%). As **1b** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01–7.09 (m, 25H; 5Ph), 5.20 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.93 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.79 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.54 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.45–4.40 (m, 2H; H1, H2), 4.38 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.33 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 3.75–3.60 (m, 2H; H3, H4), 3.60 [dd, ^3J(H,H) = 11.3, 4.6 Hz, 1H; H6a], 3.52 [dd, ^3J(H,H) = 11.3, 2.1 Hz, 1H; H6b], 3.44 [ddd, ^3J(H,H) = 9.6, 4.6, 2.1 Hz, 1H; H5], 0.59 (s, 3H; SiMe), 0.49 (s, 3H; SiMe).

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethyl(phenylethynyl)silyl]-α-D-mannopyranosyl phenyl sulfone (2b): The dimethyl(phenylethynyl)silyl ether **2b** was prepared according to the general procedure outlined for **1b** to give the title compound as a colorless syrup in 80% yield (150 mg) after flash chromatography (hexane/EtOAc, 3:1). As **2b** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83–7.15 (m, 25H; 5Ph), 5.24 [dd, ^3J(H,H) = 2.2, 2.2 Hz, 1H; H2], 5.04 [d, ^3J(H,H) = 2.2 Hz, 1H; H1], 4.91 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.82 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.73 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.63 [ddd, ^3J(H,H) = 9.6, 5.0, 2.6 Hz, 1H; H5], 4.53 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.46 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.39 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.31 [dd, ^3J(H,H) = 8.7, 2.2 Hz, 1H; H3], 3.91 [dd, ^3J(H,H) = 9.6, 7.8 Hz, 1H; H4], 3.67 [dd, ^3J(H,H) = 11.3, 5.0 Hz, 1H; H6a], 3.63 [dd, ^3J(H,H) = 11.3, 2.6 Hz, 1H; H6b], 0.40 (s, 3H; SiMe), 0.38 (s, 3H; SiMe).

2-Pyridyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (26); General procedure for the preparation of glycosyl aryl sulfones by mercury(II) bromide catalysis: A mixture of orthoester **3** (5.0 g, 9.9 mmol), 2-mercaptopyridine (1.2 g, 10.8 mmol) and mercuric bromide (350 mg, 0.97 mmol) in acetonitrile (50 mL) was heated under reflux for 2 h, after which the reaction mixture was evaporated to dryness. CH_2Cl_2 and water were added, and the organic phase was washed with saturated $NaHCO_3$ and brine, and then evaporated to dryness. Purification of the residue by flash chromatography (heptane/EtOAc, 3:1) afforded **26** as a colorless solid (4.5 g, 78%). Recrystallization from ether/heptane afforded colorless needles. M.p. 83 °C; $[\alpha]_D^{22}$ = +102.0 (c = 0.98, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.47 [dd, ^3J(H,H) = 4.8, 2.0 Hz, 1H; pyr), 7.49 [ddd, ^3J(H,H) = 7.8, 7.8, 2.0 Hz, 1H; pyr], 7.35–7.16 (m, 16H; 3Ph, pyr), 7.04 [ddd, ^3J(H,H) = 7.8, 4.8, 1.0 Hz, 1H; pyr], 6.40 [d, ^3J(H,H) = 1.9 Hz, 1H; H1], 5.64 [dd, ^3J(H,H) = 3.0, 1.9 Hz, 1H; H2], 4.88 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.74 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.63 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.56 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.52 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.44 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.11 [ddd, ^3J(H,H) = 9.2, 4.2, 2.0 Hz, 1H; H5], 4.00 [dd, ^3J(H,H) = 9.2, 9.2 Hz, 1H; H4], 3.92 [dd, ^3J(H,H) = 9.2, 3.0 Hz, 1H; H3], 3.83 [dd, ^3J(H,H) = 11.0, 4.2 Hz, 1H; H6a], 3.68 [dd, ^3J(H,H) = 11.0, 2.0 Hz, 1H; H6b], 2.19 (s, 3H; $COCH_3$); MS (CI, NH_3): m/z = 586 [M^+ + 1], 475 [M^+ + 1 − pyrSH], 112 [pyrSH$_2$]; $C_{34}H_{35}O_6NS$ (617.7): calcd C 69.72, H 6.02, N 2.39; found C 69.37, H 6.24, N 2.53.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl 2-pyridyl sulfone (23): The pyridyl sulfone **23** was prepared according to the general procedure outlined for **8**, which gave the title compound as a colorless syrup in 99% yield (2.11 g) after flash chromatography (heptane/EtOAc, 1:1). $[\alpha]_D^{22}$ = +70.0 (c = 0.98, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.77 [dd, ^3J(H,H) = 4.9, 1.9 Hz, 1H; pyr], 8.07 [brd, ^3J(H,H) = 7.9 Hz, 1H; pyr], 7.78 [ddd, ^3J(H,H) = 7.9, 7.9, 1.9 Hz, 1H; pyr], 7.50 [brdd, ^3J(H,H) = 7.9, 4.9 Hz, 1H; pyr], 7.39–7.18 (m, 15H; 3Ph), 6.24 [dd, ^3J(H,H) = 3.7, 2.0 Hz, 1H; H2], 5.49 [d, ^3J(H,H) = 2.0 Hz, 1H; H1], 4.86 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.80 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.63 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.54 [ddd, ^3J(H,H) = 10.0, 4.6, 2.4 Hz, 1H; H5], 4.49 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.47 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.37 [dd, ^3J(H,H) = 8.8, 3.7 Hz, 1H; H3], 4.31 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.00 [dd, ^3J(H,H) = 10.0, 8.8 Hz, 1H; H4], 3.63 [dd, ^3J(H,H) = 11.1, 4.6 Hz, 1H; H6a], 3.57 [dd, ^3J(H,H) = 11.1, 2.4 Hz, 1H; H6b], 2.15 (s, 3H; $COCH_3$); MS (CI, NH_3): m/z = 618 [M^+ + 1], 475 [M^+ + 1 − pyrSO$_2$H], 112 [pyrSH$_2$]; $C_{34}H_{35}O_8NS$ (617.7): calcd C 66.11, H, 5.71, N 2.27; found C 66.47, H 6.02, N 2.33.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl β-naphthyl sulfone (21): The procedure employed for the synthesis of **26** was adopted starting from orthoester **3** and afforded the naphthylsulfide as a colorless syrup in 61% yield (1.15 g) after flash chromatography (cyclohexane/EtOAc, 10:1). $[\alpha]_D^{22}$ = +83.6 (c = 0.78, dichloromethane); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.00–7.17 (m, 22H; 3Ph, naphth), 5.70 [d, ^3J(H,H) = 1.7 Hz, 1H; H1], 5.67 [dd, ^3J(H,H) = 2.2, 1.7 Hz, 1H; H2], 4.92 [d, ^3J(H,H) = 10.6 Hz, 1H; CHPh], 4.78 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.75 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.62 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.53 [d, ^3J(H,H) = 10.6 Hz, 1H; CHPh], 4.47 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.41 [ddd, ^3J(H,H) = 9.3, 4.6, 2.1 Hz, 1H; H5], 4.03 [dd, ^3J(H,H) = 9.3, 9.3 Hz, 1H; H4], 3.99 [dd, ^3J(H,H) = 9.3, 2.2 Hz, 1H; H3], 3.89 [dd, ^3J(H,H) = 10.8, 4.6 Hz, 1H; H6a], 3.75 [dd, ^3J(H,H) = 10.8, 2.1 Hz, 1H; H6b], 2.18 (s, 3H; $COCH_3$); $C_{39}C_{38}O_6S$ (634.8): calcd C 73.79, H 6.03; found C 73.76, H 6.21.

The naphthyl sulfone **21** was prepared according to the general procedure outlined for **8** from the corresponding sulfide and afforded the title compound as a colorless syrup in 87% yield (1.05 g) after flash chromatography (cyclohexane/EtOAc, 4:1). $[\alpha]_D^{22}$ = +30.0 (c = 1.1, dichloromethane); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.50 (brs, 1H; naphth) 7.92–7.17 (m, 21H; 3Ph, naphth), 6.26 [dd, ^3J(H,H) = 3.6, 2.0 Hz, 1H; H2], 4.94 [d, ^3J(H,H) = 2.0 Hz, 1H; H1], 4.89 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.82 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.73 [ddd, ^3J(H,H) = 9.7, 3.5, 3.5 Hz, 1H; H5], 4.66 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.53 [d, ^3J(H,H) = 11.8 Hz, 1H; CHPh], 4.48 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.44 [dd, ^3J(H,H) = 9.0, 3.6 Hz, 1H; H3], 4.36 [d, ^3J(H,H) = 11.8 Hz, 1H; CHPh], 3.87 [dd, ^3J(H,H) = 9.7, 9.0 Hz, 1H; H4], 3.67 [m, 2H; H6a, H6b], 2.14 (s, 3H; $COCH_3$); $C_{39}C_{38}O_8S$ (666.8): calcd C 70.25, H 5.74; found C 70.11, H 6.01.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl *N*-methylimidazolyl sulfone (22): The procedure employed for the synthesis of **4** was adopted starting from orthoester **3** and affording the *N*-methylimidazolylsulfide as a colorless syrup in 43% yield (100 mg) after flash chromatography (hexane/EtOAc, 3:1). $[\alpha]_D^{22}$ = +72.2 (c = 1.21, dichloromethane); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.37 [d, ^3J(H,H) = 5.2 Hz, 1H; imid), 7.38–7.10 (m, 16H; 3Ph), 6.86 [d, ^3J(H,H) = 5.2 Hz, 1H; imid], 6.64 [d, ^3J(H,H) = 2.1 Hz, 1H; H1], 5.64 [dd, ^3J(H,H) = 3.1, 2.1 Hz, 1H; H2], 4.87 [d, ^3J(H,H) = 10.7 Hz, 1H; CHPh], 4.73 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.67 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.56 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.50 [d, ^3J(H,H) = 10.7 Hz, 1H; CHPh], 4.45 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.10–4.00 (m, 2H; H3, H4], 3.90 [ddd, ^3J(H,H) = 9.5, 3.6, 1.5 Hz, 1H; H5], 3.86 [dd, ^3J(H,H) = 10.7, 3.6 Hz, 1H; H6a], 3.68 [dd, ^3J(H,H) = 10.7, 1.5 Hz, 1H; H6b], 2.46 (s, 3H; NCH_3], 2.22 (s, 3H; $COCH_3$); $C_{33}H_{36}O_6N_2S$ (588.7): calcd C 67.33, H 6.16; found C 67.63, H 6.03.

The imidazolyl sulfone **22** was prepared according to the general procedure outlined for **8** from the corresponding sulfide to give the title compound as a colorless syrup in 88% yield (92 mg) after flash chromatography (cyclohexane/EtOAc, 1:1). $[\alpha]_D^{22}$ = +48.9 (c = 0.88, dichloromethane); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.72 [d, ^3J(H,H) = 5.1 Hz, 1H; imid], 7.36–7.13 (m, 16H; 3Ph, imid), 6.24 [dd, ^3J(H,H) = 3.8, 1.7 Hz, 1H; H2], 5.78 [d, ^3J(H,H) = 1.7 Hz, 1H; H1], 4.85 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.79 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.62 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.54 [ddd, ^3J(H,H) = 10.0, 4.0, 2.1 Hz, 1H; H5], 4.52 [d, ^3J(H,H) = 12.2 Hz, 1H; CHPh], 4.45 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.40 [dd, ^3J(H,H) = 9.1, 3.8 Hz, 1H; H3], 4.31 [d, ^3J(H,H) = 12.2 Hz, 1H; CHPh], 3.96 [dd, ^3J(H,H) = 10.0, 9.1 Hz, 1H; H4], 3.68 [dd, ^3J(H,H) = 11.2, 4.0 Hz, 1H; H6a], 3.52 [dd, ^3J(H,H) = 11.2, 2.1 Hz, 1H; H6b], 2.65 (s, 3H; NCH_3); 2.19 (s, 3H; $COCH_3$); $C_{34}H_{36}O_8N_2S$ (620.7): calcd C 63.85, H 5.85; found C 64.15, H 5.72.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl 2-pyrimidyl sulfone (24): The procedure employed for the synthesis of **26** was applied to orthoester **3** and afforded the pyrimidyl sulfide as a colorless syrup in 97% yield (113 mg) after flash chromatography (cyclohexane/EtOAc, 2:1). $[\alpha]_D^{22}$ = +77.2 (c = 1.0, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.47 [d, ^3J(H,H) = 4.7 Hz, 2H; pyrim], 7.39–7.17 (m, 16H; 3Ph, pyrim), 6.62 [d, ^3J(H,H) = 2.2 Hz, 1H; H1], 5.66 [dd, ^3J(H,H) = 2.9, 2.1 Hz, 1H; H2], 4.90 [d, ^3J(H,H) = 10.6 Hz, 1H; CHPh], 4.77 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.68 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.60 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.54 [d, ^3J(H,H) = 10.6 Hz, 1H; CHPh], 4.48 [d, ^3J(H,H) = 12.0 Hz,

1H; CHPh], 4.41–3.91 (m, 3H; H3, H4, H5), 3.88 [dd, ^3J(H,H) = 10.8, 3.2 Hz, 1H; H6a], 3.71 [dd, ^3J(H,H) = 10.8, 3.2 Hz, 1H; H6b], 2.23 (s, 3H; $COCH_3$); $C_{33}C_{34}O_6N_2S \cdot H_2O$ (586.7 + H_2O): calcd C 65.98, H 6.04; found C 65.84, H 6.01.

The pyrimidyl sulfone **24** was prepared according to the general procedure outlined for **8** from the corresponding sulfide to give the title compound as a colorless syrup in 69% yield (80 mg) after flash chromatography (pentane/EtOAc, 3:2). $[\alpha]_D^{22} = +55.6$ ($c = 1.0$, dichloromethane); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.90$ [d, ^3J(H,H) = 5.0 Hz, 2H; pyrim], 7.47 [t, ^3J(H,H) = 5.0 Hz, 1H; pyrim], 7.37–7.16 (m, 16H; 3Ph), 6.24 [dd, ^3J(H,H) = 3.7, 1.7 Hz, 1H; H2], 5.77 [d, ^3J(H,H) = 1.7 Hz, 1H; H1], 4.87 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.81 [d, ^3J(H,H) = 11.1 Hz, 1H; CHPh], 4.65 [d, ^3J(H,H) = 11.1 Hz, 1H; CHPh], 4.55 [ddd, ^3J(H,H) = 10.0, 4.4, 2.1 Hz, 1H; H5], 4.52 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.48 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.41 [dd, ^3J(H,H) = 9.3, 3.7 Hz, 1H; H3], 4.31 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 3.95 [dd, ^3J(H,H) = 10.0, 9.3 Hz, 1H; H4], 3.67 [dd, ^3J(H,H) = 11.0, 4.4 Hz, 1H; H6a], 3.54 [dd, ^3J(H,H) = 11.0, 2.1 Hz, 1H; H6b], 2.18 (s, 3H; $COCH_3$); $C_{33}H_{34}O_8N_2S$ (618.7): calcd C 64.06, H 5.54; found C 63.77, H 5.64.

2-Benzothiazolyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (25): The procedure employed for the synthesis of **4** was adopted starting from orthoester **3** and afforded the sulfide **25** as a colorless syrup in 70% yield (266 mg) after flash chromatography (cyclohexane/EtOAc, 5:1). $[\alpha]_D^{22} = +114.1$ ($c = 0.85$, dichloromethane); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.96$ [d, ^3J(H,H) = 8.4 Hz, 1H; benzothiaz], 7.79 [d, ^3J(H,H) = 8.4 Hz, 1H; benzothiaz], 7.51–7.17 (m, 17H; 3Ph, benzothiaz), 6.34 [d, ^3J(H,H) = 1.7 Hz, 1H; H1], 5.67 [dd, ^3J(H,H) = 3.4, 1.7 Hz, 1H; H2], 4.90 [d, ^3J(H,H) = 10.6 Hz, 1H; CHPh], 4.77 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.70 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.60 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.54 [d, ^3J(H,H) = 10.6 Hz, 1H; CHPh], 4.48 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.17 [ddd, ^3J(H,H) = 9.6, 3.7, 1.9 Hz, 1H; H5], 4.08 [dd, ^3J(H,H) = 9.6, 8.7 Hz, 1H; H4], 3.92 [dd, ^3J(H,H) = 8.7, 3.0 Hz, 1H; H3], 3.90 [dd, ^3J(H,H) = 11.0, 3.7 Hz, 1H; H6a], 3.73 [dd, ^3J(H,H) = 11.0, 1.9 Hz, 1H; H6b], 2.23 (s, 3H; $COCH_3$); $C_{36}C_{35}O_6NS_2$ (641.8): calcd C 67.37, H 5.50; found C 67.18, H 5.51.

General procedure for glucal formation from the mannosyl aryl sulfones and sulfides: Two to five equivalents (see Table 1) of a 0.1 M solution of SmI_2 in THF was added to a stirred and well degassed solution of the mannosyl aryl sulfone or sulfide (0.16 mmol) in THF (5 mL). After consumption of the sulfone or sulfide (see Table 1 for reaction time), saturated aqueous NH_4Cl and CH_2Cl_2 were added, after which the organic phase was washed with water and brine, dried with Na_2SO_4, and evaporated to dryness in vacuo. The residue was purified by flash chromatography (cyclohexane/EtOAc, 5:1) to give glucal **11** as a colorless solid.

2-Pyridyl 3,4,6-Tri-*O*-benzyl-1-thio-α-D-mannopyranoside (27): A mixture of acetate **26** (4.1 g, 7.0 mmol) and K_2CO_3 (967 mg, 7.0 mmol) in methanol (200 mL) was stirred at 0 °C for 2 h. The reaction mixture was diluted with CH_2Cl_2 and washed with water several times and then dried with Na_2SO_4 and evaporated to dryness in vacuo. The residue was purified by flash chromatography (1:1, heptane/EtOAc) to give **27** as a colorless syrup (3.76 g, 98%). $[\alpha]_D^{22} = +177.0$ ($c = 1.0$, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.45$ [dd, ^3J(H,H) = 5.0, 2.0 Hz, 1H; pyr], 7.48 [ddd, ^3J(H,H) = 7.8, 7.8, 2.0 Hz, 1H; pyr], 7.39–7.18 [m, 16H; 3Ph, pyr], 7.05 [br dd, ^3J(H,H) = 7.8, 5.0 Hz, 1H; pyr], 6.33 [d, ^3J(H,H) = 2.1 Hz, 1H; H1], 4.84 [d, ^3J(H,H) = 10.8 Hz, 1H; CHPh], 4.75 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.69 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.60 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.54 [d, ^3J(H,H) = 10.8 Hz, 1H; CHPh], 4.44 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.29 [ddd, ^3J(H,H) = 3.0, 2.9, 2.1 Hz, 1H; H2], 4.10 [ddd, ^3J(H,H) = 9.8, 4.3, 2.1 Hz, 1H; H5], 3.98 [dd, ^3J(H,H) = 9.8, 9.0 Hz, 1H; H4], 3.87 [dd, ^3J(H,H) = 9.0, 3.0 Hz, 1H; H3], 3.78 [dd, ^3J(H,H) = 11.0, 4.3 Hz, 1H; H6a], 3.66 [dd, ^3J(H,H) = 11.0, 2.1 Hz, 1H; H6b], 2.03 [d, ^3J(H,H) = 2.9 Hz, 1H; OH]; MS (CI, NH_3): $m/z = 544$ [$M^+ + 1$], 450 [$M^+ + 18 -$ pyrSH], 432 [$M^+ + 18 -$ pyrSH $- H_2O$], 342 [$M^+ + 18 -$ pyrSH $-$ BnOH], 112 [pyrSH$_2$]; $C_{34}H_{35}O_6NS$ (543.7): calcd C 70.69, H 6.12, N 2.58; found C 70.78, H 5.84, N 2.29.

3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl 2-pyridyl sulfone (28): The procedure employed for the synthesis of **8** was adopted for sulfide **27** and afforded the sulfone **28** as a colorless syrup in 85% yield (3.75 g) after flash chromatography (heptane/EtOAc, 4:3). $[\alpha]_D^{22} = +111.0$ ($c = 1.02$, chloroform); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 8.13$ [dd, ^3J(H,H) = 5.8, 2.0 Hz, 1H; pyr], 7.89 [dd, ^3J(H,H) = 7.9, 1.1 Hz, 1H; pyr], 7.29–7.08 (m, 15H; 3Ph), 6.82 [ddd, ^3J(H,H) = 7.9, 7.9, 2.0 Hz, 1H; pyr], 6.43 [ddd, ^3J(H,H) = 7.9, 5.8, 1.1 Hz, 1H; pyr], 6.09 [d, ^3J(H,H) = 2.2 Hz, 1H; H1], 5.23 [ddd, ^3J(H,H) = 3.5, 2.2, 2.1 Hz, 1H; H2], 4.88 [ddd, ^3J(H,H) = 9.7, 4.4, 2.9 Hz, 1H; H5], 4.83 [d, ^3J(H,H) = 11.7 Hz, 1H; CHPh], 4.55 [dd, ^3J(H,H) = 8.4, 3.5 Hz, 1H; H3], 4.50 [d, ^3J(H,H) = 11.7 Hz, 1H; CHPh], 4.48 [d, ^3J(H,H) = 11.4 Hz, 1H; CHPh], 4.42 [d, ^3J(H,H) = 11.4 Hz, 1H; CHPh], 4.29 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.13 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.05 [dd, ^3J(H,H) = 9.7, 8.4 Hz, 1H; H4], 3.61 [dd, ^3J(H,H) = 11.5, 4.4 Hz, 1H; H6a], 3.57 [dd, ^3J(H,H) = 11.5, 2.9 Hz, 1H; H6b], 2.97 [d, ^3J(H,H) = 2.1 Hz, 1H; OH]; MS (CI, NH_3): $m/z = 576$ [$M^+ + 1$], 450 [$M^+ + 18 -$ pyrSH], 433 [$M^+ + 1 -$ pyrSH]; $C_{32}H_{33}O_7NS$ (575.7): C 66.76, H 5.78, N 2.43; found C 66.54, H 5.77, N 2.51.

2-Pyridyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (30): The pyridyl sulfide **30** was prepared according to the general procedure outlined for **26** to give the title compound as a colorless solid in 70% yield (3.22 g) after flash chromatography (heptane/EtOAc, 3:1). Recrystallization from heptane/EtOAc afforded colorless needles. M.p. 95–97 °C; $[\alpha]_D^{22} = +10.4$ ($c = 0.9$, dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.42$ [dd, ^3J(H,H) = 5.2, 2.5 Hz, 1H; pyr], 7.46 [ddd, ^3J(H,H) = 7.8, 7.8, 2.5 Hz, 1H; pyr], 7.35–7.17 [m, 16H; 3Ph, pyr], 7.01 [dd, ^3J(H,H) = 7.8, 5.2 Hz, 1H; pyr], 5.57 [d, ^3J(H,H) = 10.6 Hz, 1H; H1], 5.20 [dd, ^3J(H,H) = 10.6, 8.7 Hz, 1H; H2], 4.82 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.81 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 4.71 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.58 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 4.57 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.47 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 3.81 [dd, ^3J(H,H) = 8.7, 8.7 Hz, 1H; H3], 3.79–3.68 [m, 3H; H4, H6a, H6b], 3.66 [ddd, ^3J(H,H) = 9.6, 4.3, 2.3 Hz, 1H; H5], 1.94 (s, 3H; $COCH_3$); $C_{34}H_{35}O_6NS$ (585.7): calcd C 69.72, H 6.02, N 2.39; found C 69.62, H 6.00, N 2.48.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl 2-pyridyl sulfone (31): The procedure employed for the synthesis of **8** was adopted for sulfide **30** and afforded the sulfone **31** as a colorless solid in 83% yield (790 mg) after flash chromatography (heptane/EtOAc, 2:1). Recrystallization from heptane/EtOAc afforded colorless needles. M.p. 127 °C; $[\alpha]_D^{22} = -18.6$ ($c = 1.0$, dichloromethane); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.72$ [dd, ^3J(H,H) = 5.0, 1.7 Hz, 1H; pyr], 8.09 [br d, ^3J(H,H) = 7.1 Hz, 1H; pyr], 7.83 [ddd, ^3J(H,H) = 7.1, 7.1, 1.7 Hz, 1H; pyr], 7.46–7.10 (m, 16H; 3Ph, pyr), 5.70 [dd, ^3J(H,H) = 9.7, 8.8 Hz, 1H; H2], 4.90 [d, ^3J(H,H) = 9.7 Hz, 1H; H1], 4.83 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.79 [d, ^3J(H,H) = 11.1 Hz, 1H; CHPh], 4.73 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.57 [d, ^3J(H,H) = 11.1 Hz, 1H; CHPh], 4.30 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.22 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 3.80 [dd, ^3J(H,H) = 8.8, 8.8 Hz, 1H; H3], 3.66 [dd, ^3J(H,H) = 9.7, 8.8 Hz, 1H; H4], 3.57 [dd, ^3J(H,H) = 11.6, 4.6 Hz, 1H; H6a], 3.52 [dd, ^3J(H,H) = 11.6, 2.6 Hz, 1H; H6b], 3.49 [ddd, ^3J(H,H) = 9.7, 4.6, 2.6 Hz, 1H; H5], 2.04 (s, 3H; $COCH_3$); IR: $\tilde{\nu} = 2880, 1755, 1325$ cm^{-1}; $C_{34}H_{35}O_8NS$ (617.7): calcd C 66.11, H 5.71, N 2.27; found C 65.85, H 5.82, N 2.39.

3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl 2-pyridyl sulfone (32): A 1.0 M solution of DIBAL-H (8.5 mL, 8.5 mmol) was added to a stirred solution of acetate **31** (2.29 g, 3.71 mmol) in CH_2Cl_2 (80 mL) at −78 °C. After stirring for 30 min, the solution was quenched with saturated aqueous NH_4Cl and then allowed to warm to 20 °C. The mixture was filtered through Celite, washed with water and brine, and then dried (Na_2SO_4) and evaporated to dryness in vacuo. The residue was purified by flash chromatography (2:1, heptane/EtOAc) to give **32** as a colorless syrup (2.05 g, 96%). $[\alpha]_D^{22} = -16.2$ ($c = 0.9$, dichloromethane); IR (neat): $\tilde{\nu} = 3540$ (s), 2920 (s), 1345 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.75$ [dd, ^3J(H,H) = 4.9, 2.2 Hz, 1H; pyr], 8.01 [d, ^3J(H,H) = 7.7 Hz, 1H; pyr], 7.83 [dd, ^3J(H,H) = 7.1, 1.7 Hz, 1H; pyr], 7.50–7.02 (m, 16H; 3Ph, pyr), 5.09 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.86 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.84 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.73 [d, ^3J(H,H) = 9.7 Hz, 1H; H1], 4.57 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.39 [dd, ^3J(H,H) = 9.7, 8.7 Hz, 1H; H2], 4.33 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.28 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 3.75 [dd, ^3J(H,H) = 8.7, 8.7 Hz, 1H; H3], 3.75 [ddd, ^3J(H,H) = 8.7, 4.0, 2.5 Hz, 1H; H5], 3.68 (s, 1H; OH], 3.63–3.50 (m, 3H; H4, H6a, H6b); $C_{32}H_{33}O_7NS$ (575.7): calcd C 66.76, H 5.78, N 2.43; found C 66.71, H 5.88, N 2.48.

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3,4,6-Tri-*O*-benzyl-2-*O*-(dimethylvinylsilyl)-α-D-mannopyranosyl 2-pyridyl sulfone (29a): The dimethylvinylsilyl ether **29a** was prepared according to the general procedure outlined for **2a**, which afforded the title compound as a colorless syrup in 93% yield (394 mg) after flash chromatography (heptane/EtOAc, 5:2). As compound **29a** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, C_6D_6): δ = 8.20 [dd, ^3J(H,H) = 4.6, 1.9 Hz, 1H; pyr], 7.93 [brd, ^3J(H,H) = 7.9 Hz, 1H; pyr], 7.42–7.10 (m, 15H; 3Ph), 6.87 [ddd, ^3J(H,H) = 7.9, 7.8, 1.9 Hz, 1H; pyr], 6.47 [brdd, ^3J(H,H) = 7.8, 4.6 Hz, 1H; pyr], 6.30 [dd, ^3J(H,H) = 20.3, 14.9 Hz, 1H; SiCH=C], 6.03 [d, ^3J(H,H) = 1.8 Hz, 1H; H1], 6.00 [dd, ^3J(H,H) = 14.9, 3.5 Hz, 1H; *cis*-SiC=CH], 5.86 [dd, ^3J(H,H) = 20.3, 3.8 Hz, 1H; *trans*-SiC=CH], 5.45 [dd, ^3J(H,H) = 3.0, 1.8 Hz, 1H; H2], 5.00 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.94 [ddd, ^3J(H,H) = 9.9, 4.7, 2.4 Hz, 1H; H5], 4.70 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.69 [dd, ^3J(H,H) = 9.1, 3.0 Hz, 1H; H3], 4.63 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.58 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.35 [dd, ^3J(H,H) = 9.9, 7.5 Hz, 1H; H4], 4.30 [d, ^3J(H,H) = 12.2 Hz, 1H; CHPh], 4.12 [d, ^3J(H,H) = 12.2 Hz, 1H; CHPh], 3.64 [dd, ^3J(H,H) = 11.0, 4.7 Hz, 1H; H6a], 3.59 [dd, ^3J(H,H) = 11.0, 2.4 Hz, 1H; H6b], 0.33 (s, 6H; $2SiMe_2$).

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethyl(phenylethynyl)silyl)-α-D-mannopyranosyl 2-pyridyl sulfone (29b): The dimethyl(phenylethynyl)silyl ether **29b** was prepared according to the general procedure outlined for **1b** to give the title compound as a colorless syrup in 87% yield (200 mg) after flash chromatography (heptane/EtOAc, 3:1). As **29b** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, C_6D_6): δ = 8.13 [dd, ^3J(H,H) = 4.7, 1.7 Hz, 1H; pyr], 7.94 [dd, ^3J(H,H) = 7.2, 1.5 Hz, 1H; pyr], 7.75–6.99 (m, 20H; 4Ph), 6.88 [ddd, ^3J(H,H) = 7.5, 7.2, 1.7 Hz, 1H; pyr], 6.48 [ddd, ^3J(H,H) = 7.5, 4.7, 1.5 Hz, 1H; pyr], 6.36 [d, ^3J(H,H) = 2.1 Hz, 1H; H1], 5.86 [dd, ^3J(H,H) = 3.0, 2.1 Hz, 1H; H2], 5.04 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 5.01 [ddd, ^3J(H,H) = 9.8, 4.6, 2.4 Hz, 1H; H5], 4.88 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.80 [dd, ^3J(H,H) = 8.8, 3.1 Hz, 1H; H3], 4.68 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.61 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.37 [dd, ^3J(H,H) = 9.8, 8.8 Hz, 1H; H4], 4.34 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.15 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 3.68 [dd, ^3J(H,H) = 11.3, 4.6 Hz, 1H; H6a], 3.62 [dd, ^3J(H,H) = 11.2, 2.4 Hz, 1H; H6b], 0.52 (s, 3H; $SiCH_3$), 0.48 (s, 3H; $SiCH_3$).

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethyl(trimethylsilylethynyl)silyl)-α-D-mannopyranosyl 2-pyridyl sulfone (29c): The dimethyl(trimethylsilylethynyl)silyl ether **29c** was prepared according to the general procedure outlined for **1b** to give the title compound as a colorless syrup in 80% yield (195 mg) after flash chromatography (heptane/EtOAc, 3:1). As **29c** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, C_6D_6): δ = 8.25 [dd, ^3J(H,H) = 4.7, 1.7 Hz, 1H; pyr], 7.95 [dd, ^3J(H,H) = 7.5, 1.5 Hz, 1H; pyr], 7.51–7.11 (m, 15H; 3Ph), 6.88 [ddd, ^3J(H,H) = 7.5, 7.5, 1.7 Hz, 1H; pyr], 6.50 [ddd, ^3J(H,H) = 7.5, 4.7, 1.5 Hz, 1H; pyr], 6.25 [d, ^3J(H,H) = 2.3 Hz, 1H; H1], 5.91 [dd, ^3J(H,H) = 3.1, 2.3 Hz, 1H; H2], 5.03 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.97 [ddd, ^3J(H,H) = 9.9, 4.8, 2.5 Hz, 1H; H5], 4.90 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.79 [dd, ^3J(H,H) = 9.2, 3.1 Hz, 1H; H3], 4.68 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.59 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.31 [dd, ^3J(H,H) = 9.9, 9.2 Hz, 1H; H4], 4.31 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.13 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 3.66 [dd, ^3J(H,H) = 11.3, 4.8 Hz, 1H; H6a], 3.59 [dd, ^3J(H,H) = 11.3, 2.5 Hz, 1H; H6b], 0.46 (s, 3H; $SiCH_3$), 0.38 (s, 3H; $SiCH_3$), 0.33 (s, 9H; $SiMe_3$).

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethyl(1-octynyl)silyl]-α-D-mannopyranosyl 2-pyridyl sulfone (29d): The dimethyl(hexylethynyl)silyl ether **29d** was prepared according to the general procedure outlined for **1b** to give the title compound as a colorless syrup in 95% yield (235 mg) after flash chromatography (heptane/EtOAc, 3:1). As **29d** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, C_6D_6): δ = 8.21 [dd, ^3J(H,H) = 4.7, 1.7 Hz, 1H; pyr), 7.94 [dd, ^3J(H,H) = 7.5, 1.5 Hz, 1H; pyr], 7.50–7.10 (m, 15H; 3Ph), 6.84 [ddd, ^3J(H,H) = 7.5, 7.5, 1.7 Hz, 1H; pyr], 6.46 [ddd, ^3J(H,H) = 7.5, 4.7, 1.5 Hz, 1H; pyr], 6.30 [d, ^3J(H,H) = 1.9 Hz, 1H; H1], 5.82 [dd, ^3J(H,H) = 3.5, 1.9 Hz, 1H; H2], 5.03 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.98 [ddd, ^3J(H,H) = 9.9, 4.6, 2.7 Hz, 1H; H5], 4.91 [d, ^3J(H,H) = 11.4 Hz, 1H; CHPh], 4.79 [dd, ^3J(H,H) = 9.4, 3.5 Hz, 1H; H3], 4.67 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.58 [d, ^3J(H,H) = 11.4 Hz, 1H; CHPh], 4.32 [dd, ^3J(H,H) = 9.9, 9.4 Hz, 1H; H4], 4.30 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.12 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 3.65 [dd, ^3J(H,H) = 11.3, 4.6 Hz, 1H; H6a], 3.59 [dd, ^3J(H,H) = 11.3, 2.7 Hz, 1H; H6b], 2.27 (t, ^3J(H,H) = 7.3 Hz, 2H; $CCCH_2$], 1.62–1.14 (m, 8H; $4CH_2$), 0.88 [t, ^3J(H,H) = 6.7 Hz, 3H; CH_3], 0.46 (s, 3H; $SiCH_3$), 0.38 (s, 3H; $SiCH_3$).

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethyl(phenylethynyl)silyl]-β-D-glucopyranosyl 2-pyridyl sulfone (33a): The dimethyl(phenylethynyl)-silyl ether **33a** was prepared according to the general procedure outlined for **1b** to give the title compound as a colorless syrup in 86% yield (220 mg) after flash chromatography (heptane/EtOAc, 2:1). As **33a** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 [brd, ^3J(H,H) = 5.0 Hz, 1H; pyr], 8.06 [brd, ^3J(H,H) = 7.9 Hz, 1H; pyr], 7.79 [ddd, ^3J(H,H) = 7.9, 7.9, 1.7 Hz, 1H; pyr], 7.41–7.06 (m, 21H; 4Ph, pyr), 5.03 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.89 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.89 [d, ^3J(H,H) = 9.7 Hz, 1H; H1], 4.67 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.56 [dd, ^3J(H,H) = 9.7, 8.7 Hz, 1H; H2], 4.49 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.22 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.14 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 3.73 [dd, ^3J(H,H) = 8.7, 8.7 Hz, 1H; H3], 3.57 [dd, ^3J(H,H) = 9.0, 8.7 Hz, 1H; H4], 3.51–3.37 (m, 3H; H5, H6a, H6b), 0.58 (s, 3H; $SiCH_3$), 0.46 (s, 3H; $SiCH_3$).

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethyl(trimethylsilylethynyl)silyl]-β-D-glucopyranosyl 2-pyridyl sulfone (33b): The dimethyl(trimethylsilylethynyl)silyl ether **33b** was prepared according to the general procedure outlined for **1b** to give the title compound as a colorless syrup in 99% yield (253 mg) after flash chromatography (heptane/EtOAc, 3:1). As compound **33b** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (brd, ^3J(H,H) = 5.0 Hz, 1H; pyr), 7.98 [brd, ^3J(H,H) = 8.0 Hz, 1H; pyr], 7.72 [ddd, ^3J(H,H) = 8.0, 8.0, 1.7 Hz, 1H; pyr], 7.42–7.03 (m, 16H; 3Ph, pyr), 5.23 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 4.81 [d, ^3J(H,H) = 9.1 Hz, 1H; H1], 4.80 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 4.62 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.44 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.42 [dd, ^3J(H,H) = 9.1, 8.7 Hz, 1H; H2], 4.16 [d, ^3J(H,H) = 11.8 Hz, 1H; CHPh], 4.08 [d, ^3J(H,H) = 11.8 Hz, 1H; CHPh], 3.67 [dd, ^3J(H,H) = 8.7, 8.4 Hz, 1H; H3], 3.53–3.31 (m, 4H; H4, H5, H6a, H6b), 0.51 (s, 3H; $SiCH_3$), 0.38 (s, 3H; $SiCH_3$), 0.02 (s, 9H; $SiMe_3$).

3,4,6-Tri-*O*-benzyl-2-*O*-[dimethyl(1-octynyl)silyl]-β-D-glucopyranosyl 2-pyridyl sulfone (33c): The dimethyl(hexylethynyl)silyl ether **33c** was prepared according to the general procedure outlined for **1b** to give the title compound as a colorless syrup in 99% yield (257 mg) after flash chromatography (heptane/EtOAc, 3:1). As **33c** showed signs of facile hydrolysis of the O–Si bond, it was immediately used in the subsequent reduction step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 [brd, ^3J(H,H) = 5.1 Hz, 1H; pyr], 8.06 [brd, ^3J(H,H) = 8.0 Hz, 1H; pyr], 7.80 [ddd, ^3J(H,H) = 8.0, 8.0, 1.7 Hz, 1H; pyr], 7.47–7.09 (m, 16H; 3Ph, pyr), 5.26 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.89 [d, ^3J(H,H) = 9.3 Hz, 1H; H1], 4.88 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.70 [d, ^3J(H,H) = 11.1 Hz, 1H; CHPh], 4.53 [dd, ^3J(H,H) = 9.3, 8.7 Hz, 1H; H2], 4.51 [d, ^3J(H,H) = 11.1 Hz, 1H; CHPh], 4.23 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 4.15 [d, ^3J(H,H) = 12.0 Hz, 1H; CHPh], 3.73 [dd, ^3J(H,H) = 8.7, 8.7 Hz, 1H; H3], 3.58 [dd, ^3J(H,H) = 9.3, 8.7 Hz, 1H; H4], 3.52–3.38 [m, 3H; H5, H6a, H6b], 2.04 [t, ^3J(H,H) = 7.3 Hz, 2H; $CCCH_2$], 1.45–1.14 (m, 8H; $4CH_2$), 0.88 [t, ^3J(H,H) = 7.3 Hz, 3H; CH_3], 0.54 (s, 3H; $SiCH_3$), 0.39 (s, 3H; $SiCH_3$).

3,4,6-Tri-*O*-benzyl-β-D-mannopyranosylethane (17) from 29a: A solution of SmI_2 in THF (0.1 M, 6.5 mL, 0.65 mmol) was added over 40 min by syringe to a well-degassed solution of **29a** (172 mg, 0.26 mmol) in THF (26 mL) at 20 °C. Saturated aqueous NH_4Cl and CH_2Cl_2 were added, and the organic phase was washed twice with water and brine, dried (Na_2SO_4), and then evaporated to dryness in vacuo. The residue was redissolved in DMF (15 mL) and a 1.0 M solution of Bu_4NF in THF (1.04 mL, 1.04 mmol) was added. The solution was stirred for 3 h at 60 °C, after which CH_2Cl_2 and water were added. The organic phase was washed twice with water and brine, dried (Na_2SO_4), and then concentrated to dryness in vacuo. Purification of the residue by flash chromatography (heptane/EtOAc, 3:1) afforded **17** (96 mg, 80%).

2-Phenyl-1-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)ethylene (18); general procedure for the preparation of alkenyl β-*C*-mannosides: A solution of SmI_2 in THF (0.1 M, 3.4 mL, 0.34 mmol) was added over a period of 30 min by syringe to a well-degassed solution of **29b** (59.5 mg, 0.081 mmol) in THF (8 mL) at 20 °C. Saturated aqueous NH_4Cl was added, and the mixture was extracted twice with CH_2Cl_2. The combined organic phases were washed twice with water, dried (Na_2SO_4), and evaporated to dryness in vacuo. The residue was redissolved in THF (3 mL), cooled to 0 °C, and Bu_4NF in THF (1.0 M, 165 μL, 0.165 mmol) was added. After stirring for 30 min, water and CH_2Cl_2 were added, and the organic phase was washed twice with water, dried (Na_2SO_4), and evaporated to dryness in vacuo. Flash chromatography (heptane/EtOAc, 9:1) gave first glucal **11** (1.7 mg, 5%) and then **18** as a colorless syrup (28 mg, 64%, (*E*):(*Z*) = 10:1). The (*E*)/(*Z*) mixture was separated by column chromatography. (*E*) isomer: $[\alpha]_D^{22} = +4.0$ (*c* = 1.23, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.21 (m, 20H; 4Ph), 6.74 [d, ^3J(H,H) = 16.1 Hz, 1H; C=CHPh], 6.40 [dd, ^3J(H,H) = 16.1, 6.2 Hz, 1H; CH=CPh], 4.89 [d, ^3J(H,H) = 10.8 Hz, 1H; CHPh], 4.78 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.70 [d, ^3J(H,H) = 11.9 Hz, 1H; CHPh], 4.66 [d, ^3J(H,H) = 12.7 Hz, 1H; CHPh], 4.58 [d, ^3J(H,H) = 12.7 Hz, 1H; CHPh], 4.57 [d, ^3J(H,H) = 10.8 Hz, 1H; CHPh], 4.10 [brd, ^3J(H,H) = 6.2 Hz, 1H; H1], 4.09 [d, ^3J(H,H) = 3.2 Hz, 1H; H2], 3.89 [dd, ^3J(H,H) = 9.6, 9.1, 1H; H4], 3.81 [dd, ^3J(H,H) = 10.8, 2.3 Hz, 1H; H6a], 3.77 [dd, ^3J(H,H) = 10.8, 4.5 Hz, 1H; H6b], 3.70 [dd, ^3J(H,H) = 9.1, 3.2 Hz, 1H; H3], 3.54 [ddd, ^3J(H,H) = 9.6, 4.5, 2.3 Hz, 1H; H5], 2.40 (brs, 1H; OH); MS (CI, isobutene): *m*/*z* = 537 [M^+ + 1], 519 [M^+ + 1 − H_2O], 429 [M^+ + 1 − BnOH], 411 [M^+ + 1 − BnOH − H_2O]; HR-MS (CI, CH_4) ($C_{35}H_{36}O_5$): calcd for [M^+ + 1] 537.2642, found 537.2591; calcd for [M^+ + 1 − H_2O] 519.2536, found 519.2533. (*Z*) isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.77 [d, ^3J(H,H) = 11.6 Hz, 1H; C=CHPh], 6.13 [dd, ^3J(H,H) = 11.6, 8.8 Hz, 1H; CH=CPh].

1-(3,4,6-Tri-*O*-benzyl-β-D-mannopyranosyl)-2-trimethylsilylethylene (34): The *C*-mannoside **34** was prepared according to the general procedure outlined for **18** to give the title compound as a colorless syrup in 61% yield (46 mg) after flash chromatography (heptane/EtOAc, 9:1, (*E*)/(*Z*) = 13:1) and glucal **11** (1.6 mg, 3%). The (*E*)/(*Z*) mixture was separated by column chromatography. (*E*) isomer: $[\alpha]_D^{22} = +3.0$ (*c* = 1.04, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.18 (m, 15H; 3Ph), 6.15 [dd, ^3J(H,H) = 19.1, 3.7 Hz, 1H; CH=CTMS], 6.07 [d, ^3J(H,H) = 19.1 Hz, 1H; C=CHTMS], 4.88 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 4.78 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.68 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.64 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.58 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.54 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 4.08 [brdd, ^3J(H,H) = 3.1, 3.0 Hz, 1H; H2], 3.91 [brd, ^3J(H,H) = 3.7 Hz, 1H; H1], 3.83 [dd, ^3J(H,H) = 9.5, 9.2, 1H; H4], 3.78 [dd, ^3J(H,H) = 10.9, 2.2 Hz, 1H; H6a], 3.72 [dd, ^3J(H,H) = 10.9, 4.8 Hz, 1H; H6b], 3.64 [dd, ^3J(H,H) = 9.2, 3.1 Hz, 1H; H3], 3.48 [ddd, ^3J(H,H) = 9.5, 4.8, 2.2 Hz, 1H; H5], 2.23 [d, ^3J(H,H) = 3.0 Hz, 1H; OH], 0.11 (s, 9H; $SiMe_3$); MS (CI, isobutene): *m*/*z* = 533 [M^+ + 1], 515 [M^+ + 1 − H_2O]; HR-MS (CI, CH_4) ($C_{32}H_{40}O_5Si$): calcd for [M^+ + 1] 533.2724, found 533.2704. (*Z*) isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.52 [dd, ^3J(H,H) = 14.5, 7.4 Hz, 1H; CHC→CTMS], 5.84 [brd, ^3J(H,H) = 14.5 Hz, 1H; C=CHTMS].

2-(1-Octynyl)-1-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)ethylene (35): The *C*-mannoside **35** was prepared according to the general procedure outlined for **18** to give the title compound as a colorless syrup in 25% yield (11 mg) after flash chromatography (heptane/EtOAc, 9:1) as the (*E*) isomer, glucal **11** (3.7 mg, 11%), and the 1-deoxy derivative **36** (21 mg, 60%).

***C*-Mannoside 35**: $[\alpha]_D^{22} = +3.1$ (*c* = 0.32, dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.16 (m, 15H; 3Ph), 5.83 [ddd, ^3J(H,H) = 15.7, 6.5, 6.5 Hz, 1H; C=CHhexyl], 5.65 [dddd, ^3J(H,H) = 15.7, 6.0, 1.3, 1.3 Hz, 1H; CH=Chexyl], 4.87 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 4.77 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.68 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.63 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.56 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.53 [d, ^3J(H,H) = 10.9 Hz, 1H; CHPh], 3.98 [d, ^3J(H,H) = 3.4, 3.1 Hz, 1H; H2], 3.88 [d, ^3J(H,H) = 6.0 Hz, 1H; H1], 3.82 [dd, ^3J(H,H) = 9.8, 9.0, 1H; H4], 3.76 [dd, ^3J(H,H) = 10.8, 2.3 Hz, 1H; H6a], 3.71 [dd, ^3J(H,H) = 10.8, 4.4 Hz, 1H; H6b], 3.62 [dd, ^3J(H,H) = 9.0, 3.1 Hz, 1H; H3], 3.45 [ddd, ^3J(H,H) = 9.8, 4.4, 2.3 Hz, 1H; H5], 2.27 (brs, 1H; OH), 2.08 (m, 2H; C=CCH_2), 1.46–1.36 (m, 8H; 4CH_2), 0.89 [t, ^3J(H,H) = 7.0 Hz, 3H; CH_3]; MS (CI, isobutene): *m*/*z* = 545 [M^+ + 1], 527 [M^+ + 1 − H_2O], 437 [M^+ + 1 − BnOH], 419 [M^+ + 1 − BnOH − H_2O]; HR-MS (CI, CH_4) ($C_{35}H_{44}O_5$): calcd for [M^+ + 1 − H_2O] 527.3163, found 527.3164.

1-Deoxy derivative 36: $[\alpha]_D^{22} = -5.3$ (*c* = 0.53, dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.17 (m, 15H; 3Ph), 4.85 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.74 [d, ^3J(H,H) = 11.7 Hz, 1H; CHPh], 4.68 [d, ^3J(H,H) = 11.7 Hz, 1H; CHPh], 4.61 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.54 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.53 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.09 [dd, ^3J(H,H) = 12.7, 2.1 Hz, 1H; $H1_{ax}$], 4.02 (brs, 1H; H2], 3.77 [dd, ^3J(H,H) = 9.8, 8.9, 1H; H4], 3.73 [dd, ^3J(H,H) = 10.7, 2.4 Hz, 1H; H6a], 3.66 [dd, ^3J(H,H) = 10.7, 5.2 Hz, 1H; H6b], 3.61 [dd, ^3J(H,H) = 8.9, 3.5 Hz, 1H; H3], 3.46 [dd, ^3J(H,H) = 12.7 Hz, 1H; $H1_{eq}$], 3.38 [ddd, ^3J(H,H) = 9.8, 5.2, 2.4 Hz, 1H; H5], 2.52 (brs, 1H; OH); MS (CI, isobutene): *m*/*z* = 435 [M^+ + 1]; HR-MS (CI, CH_4) ($C_{27}H_{30}O_4$): calcd for [M^+ + 1] 435.2172, found 435.2139.

2-Phenyl-1-(3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)ethylene (16); General procedure for the preparation of alkenyl α-*C*-glucosides: A solution of SmI_2 in THF (0.1 M, 11 mL, 1.1 mmol) was added quickly to a stirred solution of **33a** (106 mg, 0.14 mmol) in THF (21 mL) at 20 °C. After stirring for 10 min, saturated aqueous NH_4Cl was added, and the mixture was extracted twice with CH_2Cl_2. The combined organic phases were washed twice with water, dried (Na_2SO_4), and evaporated to dryness in vacuo. The residue was redissolved in THF (5 mL), cooled to 0 °C, and 1.0 M Bu_4NF in THF (285 μL, 0.285 mmol) was added. After stirring for 30 min, water and CH_2Cl_2 were added, and the organic phase was washed twice with water, dried (Na_2SO_4), and evaporated to dryness in vacuo. Flash chromatography (heptane/EtOAc, 7:2) gave first glucal **11** (3 mg, 5%) and then **16** as a colorless syrup (58 mg, 76%). $[\alpha]_D^{22} = +38.7$ (*c* = 0.92, dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.28 (m, 20H; 4Ph), 6.73 [dd, ^3J(H,H) = 16.2, 1.9 Hz, 1H; C=CHPh], 6.42 [dd, ^3J(H,H) = 16.2, 5.8 Hz, 1H; CH=CPh], 4.78 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.70 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.67 [d, ^3J(H,H) = 11.5 Hz, 1H; CHPh], 4.63 [ddd, ^3J(H,H) = 5.8, 4.7, 1.9 Hz, 1H; H1], 4.61 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.56 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.52 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.07 [ddd, ^3J(H,H) = 6.8, 5.1, 3.5 Hz, 1H; H5], 3.85 [dd, ^3J(H,H) = 6.8, 4.7 Hz, 1H; H2], 3.81 [dd, ^3J(H,H) = 10.4, 5.1 Hz, 1H; H6a], 3.74 [dd, ^3J(H,H) = 6.8, 6.8, 1H; H4], 3.72 [dd, ^3J(H,H) = 10.4, 3.5 Hz, 1H; H6b], 3.68 [dd, ^3J(H,H) = 6.8, 6.8 Hz, 1H; H3], 2.77 (brs, 1H; OH); MS (CI, isobutene): *m*/*z* = 537 [M^+ + 1], 519 [M^+ + 1 − H_2O], 429 [M^+ + 1 − BnOH], 411 [M^+ + 1 − BnOH − H_2O]; HR-MS (CI, CH_4) ($C_{35}H_{36}O_5$): calcd for [M^+ + 1] 537.2642, found 537.2591; calcd for [M^+ + 1 − H_2O] 519.2536, found 519.2533.

1-(3,4,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-2-trimethylsilylethylene (37): The *C*-glucoside **37** was prepared according to the general procedure outlined for **16** to give the title compound as a colorless syrup in 78% yield (69.5 mg) after flash chromatography (heptane/EtOAc, 8:1). $[\alpha]_D^{22} = +58.0$ (*c* = 1.28, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.22 (m, 15H; 3Ph), 6.24 [dd, ^3J(H,H) = 19.2, 4.1 Hz, 1H; CH=CTMS], 6.11 [dd, ^3J(H,H) = 19.2, 1.7 Hz, 1H; C=CHTMS], 4.79 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.71 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.68 [d, ^3J(H,H) = 11.6 Hz, 1H; CHPh], 4.64 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.59 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.55 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.47 [ddd, ^3J(H,H) = 4.6, 4.1, 1.7 Hz, 1H; H1], 4.04 [ddd, ^3J(H,H) = 9.2, 5.2, 4.0 Hz, 1H; H5], 3.83 [dd, ^3J(H,H) = 10.4, 5.2 Hz, 1H; H6a], 3.81 [ddd, ^3J(H,H) = 7.5, 5.8, 4.6 Hz, 1H; H2], 3.74 [dd, ^3J(H,H) = 10.4, 4.0 Hz, 1H; H6b], 3.72–3.65 (m, 2H; H3, H4), 2.68 [d, ^3J(H,H) = 5.8 Hz, 1H; OH], 0.13 (s, 9H; $SiMe_3$); MS (CI, isobutene): *m*/*z* = 533 [M^+ + 1], 515 [M^+ + 1 − BnOH], 425 [M^+ + 1 − BnOH], 407 [M^+ + 1 − BnOH − H_2O]; HR-MS (CI, CH_4) ($C_{32}H_{40}O_5Si$): calcd for [M^+ + 1] 533.2724, found 533.2684.

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyloctane (38): The *C*-glucoside **38** was first prepared from **33c** (130 mg, 0.175 mmol) according to the general procedure outlined for **16**. After desilylation, the residue was dissolved in MeOH (10 mL) and AcOH (2 mL), and 5% palladium on activated carbon (30 mg) was added. The mixture was stirred for 12 h under an atmosphere of hydrogen, after which it was filtered through Celite and evaporated to dryness. The residue was dissolved in pyridine (10 mL) and Ac_2O (5 mL) with DMAP (1 mg) and left overnight. Evaporation and coevaporation with toluene afforded a syrup which was purified by flash chromatography (heptane/EtOAc, 3:1) to give **38** as a colorless solid (41 mg, 53%). Recrystallization from heptane/EtOAc gave colorless needles. M.p. 57–58 °C;

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$[\alpha]_D^{22} = +64.0$ ($c = 1.04$, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.31$ [dd, ^3J(H,H) = 9.6, 9.6 Hz, 1H; H3], 5.06 [dd, ^3J(H,H) = 9.6, 5.8 Hz, 1H; H2], 4.97 [dd, ^3J(H,H) = 9.6, 9.6 Hz, 1H; H4], 4.21 [dd, ^3J(H,H) = 12.0, 5.2 Hz, 1H; H6a], 4.10 [ddd, ^3J(H,H) = 11.5, 5.8, 3.3 Hz, 1H; H1], 4.08 [dd, ^3J(H,H) = 12.0, 2.7 Hz, 1H; H6b], 3.80 [ddd, ^3J(H,H) = 9.6, 5.2, 2.7 Hz, 1H; H5], 2.08 (s, 3H; $COCH_3$), 2.05 (s, 3H; $COCH_3$), 2.03 (s, 3H; $COCH_3$), 2.01 (s, 3H; $COCH_3$), 1.53–1.23 (m, 14H; $7CH_2$), 0.88 [t, ^3J(H,H) = 7.0 Hz, CH_3]; MS (CI, NH_3): $m/z = 480$ [$M^+ + 18$], 463 [$M^+ + 1$]; $C_{22}H_{36}O_9$ (444.5): calcd C 59.45, H 8.16; found C 59.53, H 8.25.

Tethered disaccharide 41: The alkynylsilyl ether **41** was prepared according to the general procedure outlined for **1b** to give the title compound as a colorless syrup in 79% yield (140 mg) after flash chromatography (heptane/EtOAc, 2:1). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 8.24$ [brd, ^3J(H,H) = 4.9 Hz, 1H; pyr], 7.93 [brd, ^3J(H,H) = 7.7 Hz, 1H; pyr], 7.62–7.05 (m, 30H; 6Ph), 6.89 [ddd, ^3J(H,H) = 7.7, 7.7, 1.8 Hz, 1H; pyr], 6.48 [ddd, ^3J(H,H) = 7.7, 4.8, 1.3 Hz, 1H; pyr], 5.38 [d, ^3J(H,H) = 11.1 Hz, 1H; CHPh], 5.34 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 5.19 [d, ^3J(H,H) = 9.3 Hz, 1H; H1′], 5.02 [d, ^3J(H,H) = 11.2 Hz, 1H; CHPh], 4.95 [d, ^3J(H,H) = 11.1 Hz, 1H; CHPh], 4.93 [dd, ^3J(H,H) = 9.3, 8.7 Hz, 1H; H2′], 4.93 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.87 [d, ^3J(H,H) = 11.3 Hz, 1H; CHPh], 4.59 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.59 [d, ^3J(H,H) = 9.9 Hz, 1H; H5], 4.58 [d, ^3J(H,H) = 3.4 Hz, 1H; H1], 4.56 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.44 [d, ^3J(H,H) = 12.1 Hz, 1H; CHPh], 4.34 [d, ^3J(H,H) = 11.0 Hz, 1H; CHPh], 4.11 [dd, ^3J(H,H) = 9.3, 9.0 Hz, 1H; H3], 4.09 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 4.01 [d, ^3J(H,H) = 12.3 Hz, 1H; CHPh], 3.82 [dd, ^3J(H,H) = 9.9, 9.0 Hz, 1H; H4], 3.67 [dd, ^3J(H,H) = 9.3, 8.7 Hz, 1H; H3′], 3.51 [dd, ^3J(H,H) = 9.3, 3.4 Hz, 1H; H2], 3.47 [dd, ^3J(H,H) = 9.6, 9.3 Hz, 1H; H4′], 3.35 [dd, ^3J(H,H) = 11.6, 4.8 Hz, 1H; H6a′], 3.29 [dd, ^3J(H,H) = 11.6, 2.1 Hz, 1H; H6b′], 3.24 [dd, ^3J(H,H) = 9.6, 4.8, 2.1 Hz, 1H; H5′], 3.04 (s, 3H; OCH_3), 0.82 (s, 3H; $SiCH_3$), 0.70 (s, 3H; $SiCH_3$).

Methyl α-D-*C*-isomaltoside heptaacetate (42): The procedure outlined for the preparation of **38** was followed to give the title compound as a colorless solid in 48% yield (19 mg) after flash chromatography (heptane/EtOAc, 3:2 to 2:3). Recrystallization from heptane/EtOAc gave colorless needles. M.p. 151–152 °C; $[\alpha]_D^{22} = +124.0$ ($c = 0.51$, chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.44$ [dd, ^3J(H,H) = 10.2, 9.8 Hz, 1H; H3], 5.32 [dd, ^3J(H,H) = 9.9, 9.2 Hz, 1H; H3′], 5.07 [dd, ^3J(H,H) = 9.9, 6.0 Hz, 1H; H2′], 4.97 [dd, ^3J(H,H) = 9.2, 9.2 Hz, 1H; H4′], 4.91 [d, ^3J(H,H) = 3.7 Hz, 1H; H1], 4.85 [dd, ^3J(H,H) = 9.8, 9.8 Hz, 1H; H4], 4.84 [dd, ^3J(H,H) = 10.2, 3.7 Hz, 1H; H2], 4.24 [dd, ^3J(H,H) = 12.3, 5.3 Hz, 1H; H6a′], 4.15 [ddd, ^3J(H,H) = 12.2, 6.0, 3.5 Hz, 1H; H1], 4.02 [dd, ^3J(H,H) = 12.3, 2.6 Hz, 1H; H6b′], 3.80 [ddd, ^3J(H,H) = 9.2, 5.3, 2.6 Hz, 1H; H5′], 3.78 (m, 1H; H5), 3.40 (s, 3H; OCH_3), 2.09 (s, 3H; $COCH_3$), 2.07 (s, 3H; $COCH_3$), 2.05 (s, 3H; $COCH_3$), 2.04 (s, 6H; 2 $COCH_3$), 2.03 (s, 3H; $COCH_3$), 2.01 (s, 3H; $COCH_3$), 2.00 (m, 1H; CH), 1.66–1.42 (m, 3H; CH_2, CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.2$, 169.9, 169.6, 169.2, 96.8, 72.4, 72.2, 71.3, 70.6, 70.2, 69.0, 68.6, 67.9, 62.4, 55.6, 26.5, 20.8, 20.6; MS (CI, isobutene): $m/z = 649$ [$M^+ + 1$], 617 [$M^+ + 1 -$ MeOH]; HR-MS (CI, CH_4) ($C_{28}H_{40}O_{17}$): calcd for [$M^+ + 1 -$ MeOH] 617.2081, found 617.2083.

X-Ray crystallographic analysis of 42: Crystal data: $C_{28}H_{40}O_{17}$, $M_r = 648.61$, colorless crystal of $0.07 \times 0.10 \times 0.20$ mm, triclinic, space group $P1$, $Z = 1$, $a = 5.535(5)$, $b = 11.223(8)$, $c = 14.442(10)$ Å, $\alpha = 109.13(8)$, $\beta = 89.75(3)$, $\gamma = 97.17(3)°$, $V = 840(1)$ Å^3, $\rho_{calcd} = 1.28$ g cm^{-3}, $F(000) = 344$, $\lambda(Cu_{K\alpha}) = 1.5418$ Å, $\mu = 0.87$ mm^{-1}.

Intensity data were measured on a Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation and the θ–2θ scan technique up to $\theta = 60°$ at 20 °C. Of the 3019 collected reflections ($-6 \le h \le 6$, $-12 \le k \le 11$, $-9 \le l \le 16$), 2446 were unique ($R_{int} = 0.023$) of which 1598 were considered as observed [$I \ge 2.5\sigma(I)$]. Cell parameters were refined from 25 well-centered reflexions with $8.8 \ge \theta \ge 24.7°$. The structure was solved by direct methods with SHELXS86 (G. M. Sheldrick, **1986**, SHELXS86, Program for the solution of crystal structures, Univ. of Göttingen, Germany), and refined by full-matrix least-squares with SHELX76[2] by minimization of the function $\sum w(Fo - |Fc|)$ (G. M. Sheldrick, **1976**, SHELX76, Program for crystal structure determination, Univ. of Cambridge, England). The hydrogen atoms, located in difference Fourier maps, were fitted at theoretical positions [d(C–H) = 1.00 Å]. They were assigned an isotropic thermal factor equivalent to that of the bonded carbon atom, plus 10%. Convergence was reached at $R = 0.044$ and $R_w = 0.058$. The residual electron density in the final difference map was located between -0.19 and 0.16 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100198. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

Received: December 23, 1996 [F563]

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