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Synthesis of Pyranoid and Furanoid Glycals from Glycosyl Sulfoxides by Treatment with Organolithium Reagents

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Dedicated to Prof. Serafín Valverde on the occasion of his 70th birthday

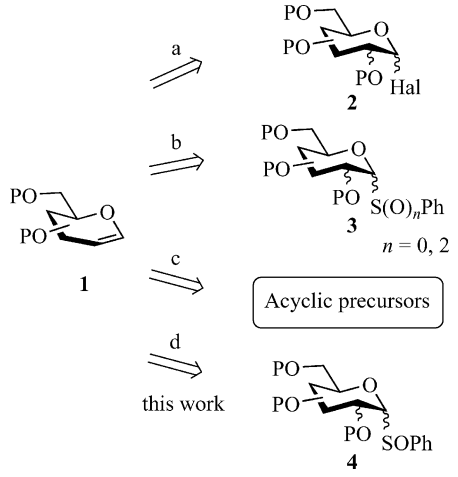
Keywords: Glycosyl sulfoxides / Organolithium reagents / Pyranoid glycals / Furanoid glycals / Sulfoxide ligand exchange

Glycosyl sulfoxides can be conveniently transformed into pyranoid or furanoid glycals by treatment with organolithium reagents. The more likely reaction pathway involves a sulfoxide/metal exchange reaction to generate a glycosyllithium derivative that undergoes β-elimination of its C-2 substituent.

Introduction

Over the past three decades a considerable amount of work has been devoted to the study of the synthesis and chemistry of pyranoid glycals (1,5-anhydro-2-deoxy-1-enitols) such as **1** (Scheme 1).[1] These carbohydrate derivatives are frequently employed as useful starting materials in the synthesis of oligosaccharide motifs,[2] C-glycosides,[3] C-nucleosides,[4] and other biologically important molecules.[5] More recently, glycals have also been shown to be excellent starting substrates for library development, thanks to their rigid structures and inherent stereochemical diversity. These attributes have been exploited in the synthesis of carbohydrate-based scaffolds,[6] and also in the preparation of molecules with distinct skeletal frameworks in diversity-oriented synthesis (DOS).[7]

Many synthetic approaches for the preparation of glycals have been devised.[8] The original Fischer–Zach method,[9] which uses zinc dust in acetic acid in the reductive elimination of acylated glycosyl bromides, has been one of the most popular methods for synthesizing glycals (Scheme 1a). It has been suggested that heterolytic cleavage of the carbon–halogen bond occurs under these acidic conditions, initially to give an anomeric carbocation that, after taking two electrons from the zinc atom, generates a transient carbanion that evolves through the splitting off of an acetate anion.[10] Other reducing agents used in this transformation with glycosyl halides include sodium and potassium metal,[11] sodium naphthalide,[11] zinc/silver graphite,[12] aluminum amalgam,[13] SmI_2,[14] potassium graphite,[15] lithium/ammonia,[16] chromium(II),[17,18] zinc/base,[19] cobalt(II),[20] and titanium(III).[21] A glucal derivative has also been prepared by introduction of a halogen atom at C-2, followed by a reductive elimination reaction in the opposite sense.[22] In spite of the ready availability of glycosyl halides, their rather sensitive natures have led to the consideration of the more stable 1-thio- and 1-sulfonylglycosyl derivatives (e.g., **3**, Scheme 1b) as glycal precursors. Compounds **3** are thus conveniently transformed into glycals when treated with lithium naphthalide,[23] chromium(II) complexes in aqueous medium,[24] or SmI_2.[14,25] In the last case, electron transfer to the glycosyl phenylsulfone to generate a 1-glycosyl radical has been proposed; a (glycosyl)samarium deriva-



Scheme 1. Strategies for the synthesis of pyranoid glycals; P = protecting group.

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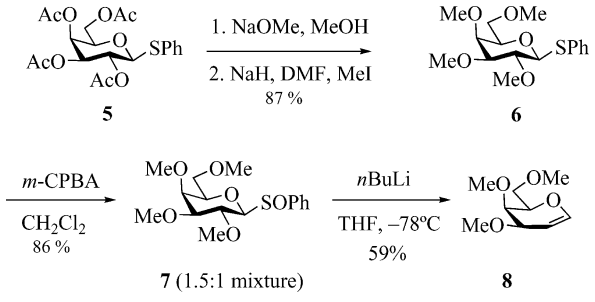
tive would then be formed,[14,25] with subsequent β-acetate elimination resulting in the formation of the expected glycal. Potassium graphite laminate (C_8K) has also been used to transform phenyl thioglycosides into glycals.[26] More recent strategies have focused on the use of acyclic derivatives as glycal precursors (Scheme 1c). In this context, strategies based on the hetero-Diels–Alder reaction,[27] ring-closing metathesis,[28] metal-promoted alkynol *endo* cycloisomerization,[29] and iodonium-mediated 6-*endo* cyclization followed by elimination,[30] have been described.

Earlier work in our group showed that glycosyl sulfoxides (e.g., **4**, Scheme 1d) can also be useful precursors in the preparation of glycals. In fact, some years ago we reported reactions between anomeric glycosyl sulfoxides and organolithium reagents as an efficient approach for the synthesis of pyranoid glycals.[31] The method was thought to occur by generation of a carbanion at the anomeric position, followed by β-elimination of the C-2 substituent.[32] In this paper we report our studies on the scope of this transformation in full, as well as its extension to the preparation of furanoid glycals. We also disclose our studies directed towards shedding light on the reaction pathway for this conversion.

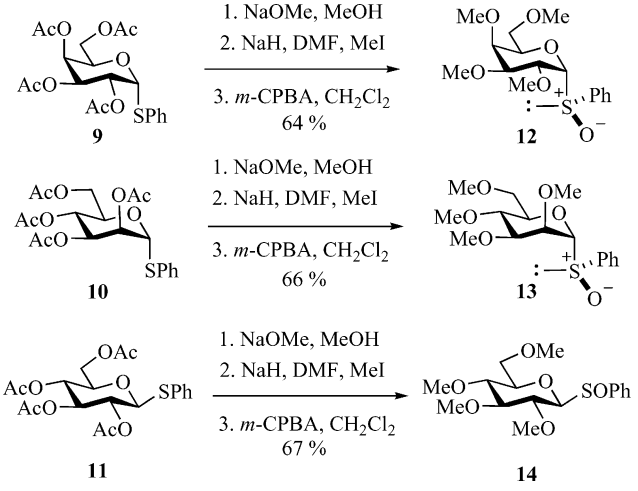
Results and Discussion

Our initial studies were carried out with galactose-derived sulfoxide **7**[33] (Scheme 2; 1.5:1 diastereomeric mixture with respect to the sulfur atom). Its synthesis was effected from the known tetraacetate **5**,[34] and involved three steps: Zemplèn deacetylation,[35] exhaustive methylation, and oxidation of the sulfide **6** with *m*-chloroperoxybenzoic acid (*m*-CPBA) at low temperature. Accordingly, treatment of galactosyl sulfoxide **7** with 3 equiv. of *n*BuLi[36] in THF at –78 °C for 20 min resulted in a clean reaction mixture[37] from which the protected galactal **8** could be isolated in 59% yield.



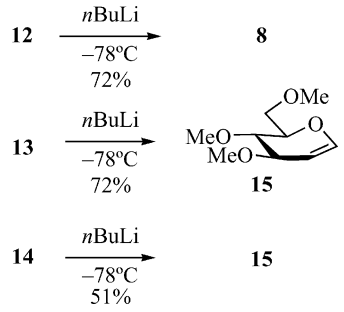
Scheme 2. Preparation of galactal derivative **8**.

We subsequently extended this reaction to a variety of glycosyl sulfoxides – **12**, **13**, **14** – with different stereochemical patterns (Scheme 3).[38] These sulfoxides were uneventfully prepared from D-galactose-, D-mannose-, and D-glucose-derived sulfides **9**, **10**, and **11**, respectively, in five steps. α-Galactopyranosyl sulfoxide **12** was chosen for purposes of comparison with β-galactopyranosyl sulfoxide **7**. Unlike β-glycopyranosyl sulfoxides **7** and **14**, which were obtained as diastereomeric mixtures, the corresponding α-glycopyranosyl sulfoxides **12** and **13** were obtained with excellent stereoselectivity upon oxidation of the parent thioglycosides. These results are in agreement with studies carried out by Crich and co-workers, who inferred that the stereoselectivity in the oxidation step is dictated predominantly by steric effects and the conformation imposed on the thioglycosides by the *exo*-anomeric effect.[39] In general, in α-thioglycosides the *pro-S* lone pair would be substantially hindered by the pyranose ring and by the axial hydrogen atoms, whereas the *pro-R* lone pair of the thioglycoside would be exposed to attack. In the case of β-thioglycosides the two lone pairs are sterically less differentiated, and mixtures of sulfoxides result.



Scheme 3. Preparation of glycosyl sulfoxides.

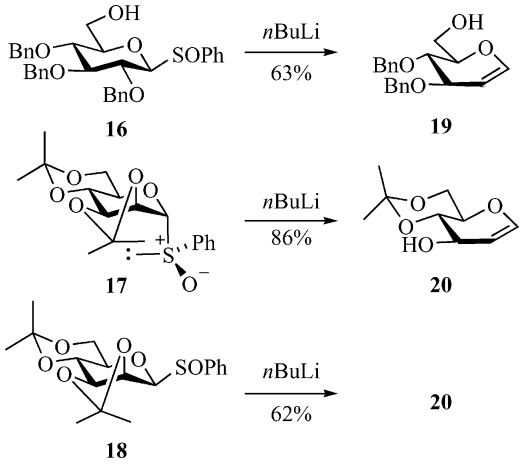
Treatment of sulfoxides **12**–**14** with *n*BuLi (3 equiv.) in THF at low temperature resulted in the exclusive formation of the expected glycal derivatives (Scheme 4). From the results in Schemes 2 and 4, it seems that α-sulfoxides, regardless of the relative orientation of the oxygen substituent at C-2, gave better yields than equatorial sulfoxides.



Scheme 4. Formation of glycals by treatment of pyranosyl sulfoxides with *n*BuLi (3 equiv.) in THF at –78 °C.

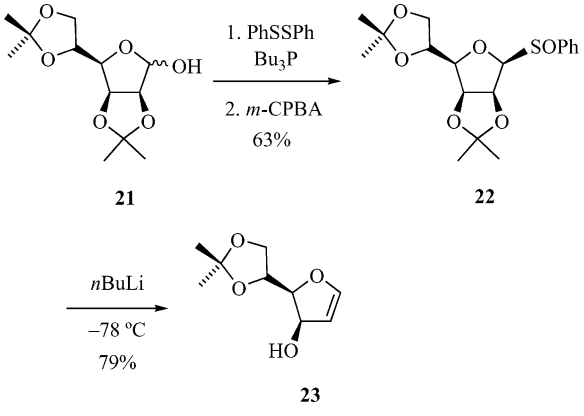
Since the methyl ether protecting groups in sulfoxides **8** and **12**–**14** are not synthetically very useful, we decided to test our procedure with glycosyl sulfoxides with more appealing protecting groups. Thus, by oxidation of the parent thioglycosides, we prepared the benzyl-protected β-D-gluco-

pyranosyl sulfoxide **16** and the isopropylidene-protected α- and β-D-mannopyranosyl sulfoxides **17** and **18** (Scheme 5). Treatment of sulfoxides **16**–**18** with *n*BuLi at –78 °C resulted in their conversion into glycal derivatives **19** and **20**. From the results shown in Schemes 2, 4, and 5, some conclusions could be drawn. The transformations of β-gluco sulfoxides **14** and **16**, and those of α-manno derivatives **13** and **17** (differing in the protecting groups) into the corresponding glycals seem to indicate that the leaving-group abilities of the substituents at C-2 play a significant role in the yields of the glycals obtained. Again, the results obtained in the preparation of glycal **20** from both α-manno and β-manno sulfoxides **17** and **18** (Scheme 5) appear to indicate that α-sulfoxides are more convenient starting materials for this transformation.



Scheme 5. Formation of glycals **19** and **20** by treatment of pyranosyl sulfoxides **16**–**18** with *n*BuLi in THF at –78 °C.

To extend the scope of this methodology further, we have evaluated its potential for the preparation of synthetically useful furanoid glycals (1,4-anhydro-2-deoxy-1-enitols).[40,41] Accordingly, furanosyl sulfoxide **22**, easily synthesized from hemiacetal **21** by thioglycosidation[26] followed by controlled oxidation, was chosen as our starting material (Scheme 6). To our delight, treatment of sulfoxide



Scheme 6. Formation of furanoid glycal **23** by treatment of furanosyl sulfoxides **22** with *n*BuLi (3 equiv.) in THF at –78 °C.

22 with *n*BuLi furnished, after column chromatography in the presence of 1% NEt_3,[42] the desired furanoid glycal **23** in 79% yield.

We also examined the effect of the organolithium reagent on the formation of the corresponding glycals. Our results, displayed in Table 1, seem to indicate that changes in the organolithium reagent have little or no effect in the formation of the target glycals (Table 1, compare Entries i–iii, iv–vii, viii–xi, xii–xv).

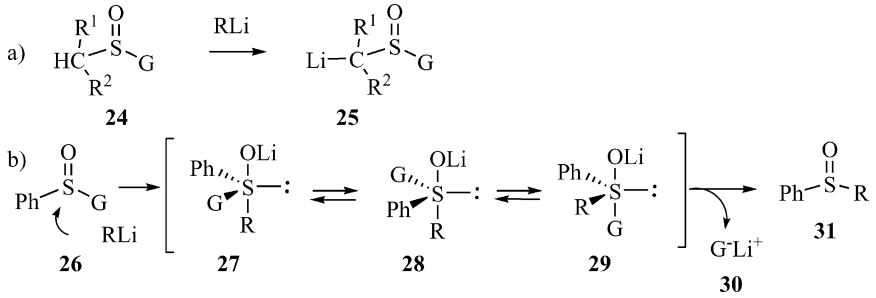
Table 1. Treatment of anomeric sulfoxides with organolithium reagents in THF at –78 °C.

Entry	Sulfoxide	RLi	Glycal	Yield
i	**7**	*n*BuLi	**8**	51%
ii	**7**	*t*BuLi	**8**	50%
iii	**7**	PhLi	**8**	50%
iv	**13**	*n*BuLi	**15**	72%
v	**13**	*t*BuLi	**15**	70%
vi	**13**	PhLi	**15**	74%
vii	**13**	MeLi	**15**	67%
viii	**17**	*n*BuLi	**20**	86%
ix	**17**	*t*BuLi	**20**	88%
x	**17**	PhLi	**20**	85%
xi	**17**	MeLi	**20**	83%
xii	**22**	*n*BuLi	**23**	79%
xiii	**22**	*t*BuLi	**23**	81%
xiv	**22**	PhLi	**23**	79%
xv	**22**	MeLi	**23**	85%

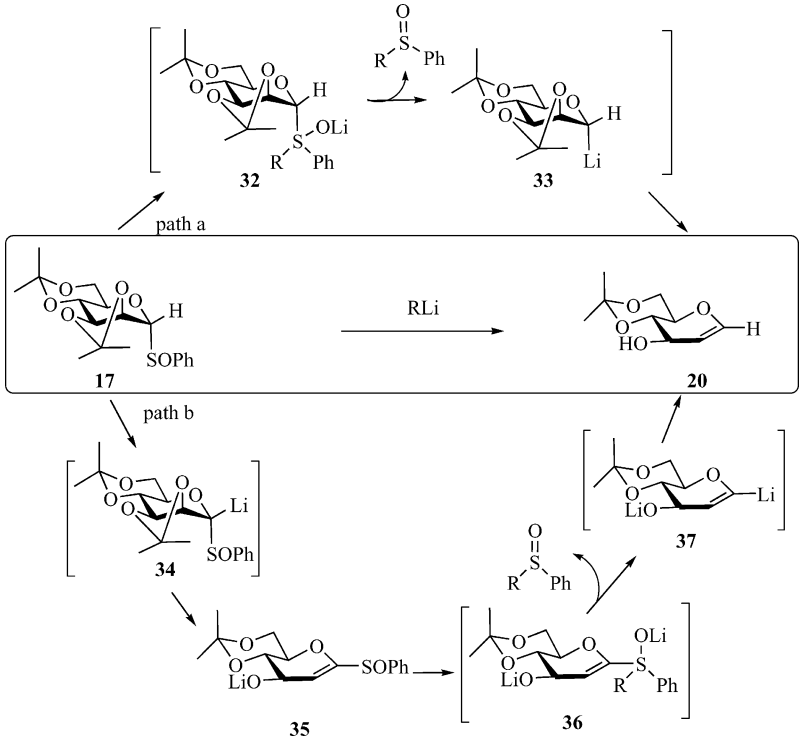
Mechanistic Considerations

During the course of these studies some mechanistic aspects drew our attention. It is known that a sulfoxide possessing a hydrogen atom on its α-carbon atom can give an α-sulfinyl carbanion upon treatment with organolithium reagents (e.g., **25**, Scheme 7a), and many examples of this reaction pathway have been reported.[43] On the other hand, Oae and co-workers have shown that alkyllithium reagents can also react with some sulfoxides to give anions (e.g., **30**, Scheme 7b) through a sulfoxide/metal exchange reaction (or sulfoxide/ligand exchange reaction).[44,45] In this case, the reaction involves the attack of the organolithium reagent on the sulfur atom of the sulfoxide to generate a pentacoordinate σ-sulfurane **27**, with the sulfur atom in the center of a trigonal bypyramid.[46] By way of a pseudorotation process different complexes can be formed, with the ligands occupying equatorial and apical positions (e.g., **28**, **29**). The complex that has the most electronegative group (G) occupying the apical position is the most stable and the one that undergoes bond rupture to generate the anion.[47]

According to these precedents, reactions of glycosyl sulfoxides to give glycals (e.g., **17** → **20**, Scheme 8) could take place by (at least) two reaction pathways (Scheme 8a, b). The first pathway would involve a direct sulfoxide/metal exchange reaction to give pentacoordinate species **32**, which could evolve by releasing a phenyl sulfoxide derivative and producing glycosyllithium compound **33** (Scheme 8, path a). This might then induce β-elimination of its C-2 substituent, leading to **20**. The second option (Scheme 8,



Scheme 7. Possible reaction pathways of reactions between sulfoxides and organolithium reagents.

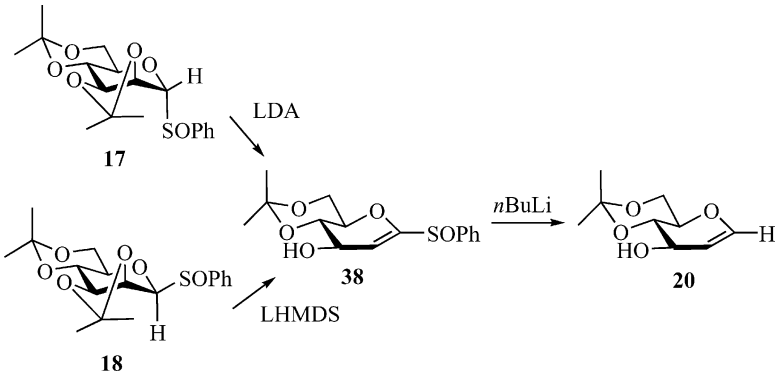


Scheme 8. Possible pathways for the transformation of sulfoxide **17** into glycal **20** mediated by organolithium reagents.

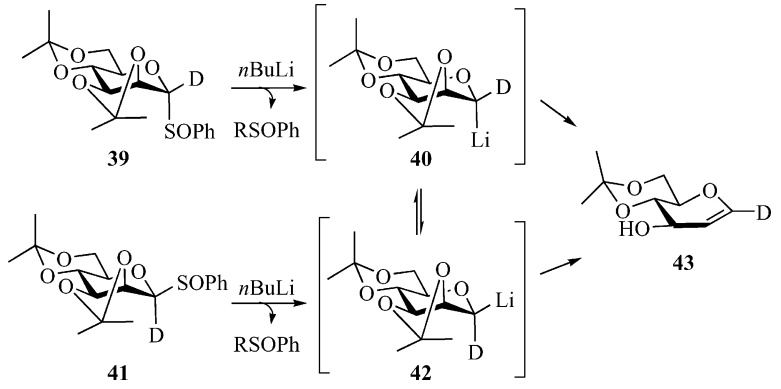
path b) would entail a combination of both of the processes outlined in Scheme 7: initially, the alkyllithium reagent could abstract the acidic hydrogen atom on the anomeric carbon atom to give the α-sulfinyl carbanion **34**, which could then evolve to the vinyl sulfoxide **35** by β-elimination of the substituent at C-2. This could then undergo a sulfoxide/metal exchange reaction (as in Scheme 7b) to give glycal **20** via the pentacoordinate α-sulfurane **36** and release of vinyllithium species **37**, which would subsequently be protonated to glycal **20**. Indeed, we have observed that compound **38** (obtained from either **17** or **18**, on treatment with LHMDS or LDA,[48] respectively) reacted with *n*BuLi, in THF at –78 °C to yield glycal **20** (Scheme 9). On the other hand, Milne and Kocienski have reported sulfoxide/metal exchange reactions of α-benzenesulfinyl enol ethers (related to **38**) with *t*BuLi, in Et_2O/THF at –78 °C, to give α-lithiated glycals.[49]

In order to gain some mechanistic insight into this transformation, we prepared the deuterated compounds **39** and **41**[50] (Scheme 10), as analogues of sulfoxides **17** and **18**, respectively, with deuterium at their anomeric positions.[51] Treatment of **39** with *n*BuLi (3 equiv., THF, –78 °C) gave C-1-deuterated glycal **43** exclusively. Likewise, treatment of β-sulfoxide **41** with *n*BuLi also resulted in the formation of **43**. From these results, the second mechanistic option (Scheme 8, path b) could be ruled out, since it would have implied the disappearance of the deuterium atom on the glycal. By corollary, we believe that a direct ligand-exchange mechanism, involving the presence of glycosyllithium intermediates (e.g., **40**, **42**, Scheme 10), which also explains the presence of deuterium in the glycal (Scheme 8, path a), is responsible for the transformation.

Along similar lines, the generation of glycosyllithium derivatives[52] in reactions between glycosyl sulfoxides and



Scheme 9. Reaction of C-1-deuterated glycosyl sulfoxides with *n*BuLi to give deuterated glycal **20**.



Scheme 10. Reactions of deuterated sulfoxides **39** and **41** with *n*BuLi.

organolithium reagents has been applied in carbohydrate chemistry. Fernández-Mayoralas and co-workers elegantly exploited it in their approach to C-glycosides from glycosyl sulfoxides.[53]

Conclusions

We have described a general method for the transformation of glycosyl sulfoxides into glycols, involving treatment of the former compounds with organolithium reagents. The process is believed to take place through a direct ligand-exchange mechanism that generates anomeric glycosyllithium species, which trigger β-elimination of the substituent at C-2. A variety of organolithium reagents can be used to effect this transformation without major changes in the observed yields. The procedure can be applied to the preparation either of pyranoid or furanoid glycals. This methodology, when applied to 2,3-*O*-isopropylidene derivatives (e.g., **17**, **18**, **22**, **39**, **41**), represents a valuable route to synthetically useful fully protected furanoid and pyranoid glycal derivatives in which the allylic 3-OH group is unprotected.[54]

Experimental Section

General Remarks: All reactions were performed in dry flasks fitted with glass stoppers or rubber septa under a positive pressure of Ar, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred by syringe or stainless steel cannula. Optical rotations were determined for solutions in chloroform. Flash column chromatography was performed on 230–400 mesh silica gel. Thin-layer chromatography was conducted on Kieselgel 60 F254 (Merck). Spots were first observed under UV irradiation (254 nm) and then by charring with a solution of aqueous H_2SO_4 (20%, 200 mL) in AcOH (800 mL). Anhydrous $MgSO_4$ or Na_2SO_4 were used to dry organic solutions during workup, and evaporation of the solvents was performed under vacuum with a rotary evaporator. Optical rotations were measured at 20 °C. Solvents were dried and purified by standard methods. Unless otherwise noted, ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 MHz and 50 MHz, respectively. Chemical shifts are expressed in ppm (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ = 7.25 ppm).

Phenyl 2,3,4,6-Tetra-*O*-methyl-1-thio-β-D-galactopyranoside (6): A solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside[34] (5 g, 11.3 mmol) in MeOH (55 mL) was treated with freshly prepared NaOMe (619 mg, 11.3 mmol) and stirred for 10 h. The reaction mixture was then neutralized with Amberlite H^+ resin, filtered, and concentrated. The residue was then dried under high vacuum and dissolved in DMF (75 mL), cooled to 0 °C, and treated portionwise with NaH (60%, 3.61 g, 90.4 mmol, 8 equiv.). After 30 min, methyl iodide (4.2 mL, 67.8 mmol, 6 equiv.) was added by syringe over 5 min. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was carefully quenched with water, diluted with Et_2O, washed with H_2O, dried, and concentrated. The product was then purified by flash chromatography (20% EtOAc/hexane) to afford **6**[55] as a col-

orless oil (3.22 g, 87%), $[\alpha]_D$ = –23.9 (*c* = 1.05, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.50–7.55 (m, 2 H), 7.20–7.30 (m, 3 H), 4.50 (d, *J* = 9.6 Hz), 3.70 (d, *J* = 3.0 Hz, 1 H), 3.58 (s, 3 H), 3.56 (s, 3 H), 3.45–3.65 (m, 3 H), 3.52 (s, 3 H), 3.41 (m, 1 H), 3.36 (s, 3 H), 3.20 (dd, *J* = 3.1, 9.2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 134.7, 131.5, 128.9, 127.2, 87.8, 86.0, 79.4, 77.0, 75.3, 70.9, 61.2, 61.0, 59.1, 58.2 ppm. MS (EI): *m*/*z* (%) = 328.1 $[M]^+$. $C_{16}H_{24}O_5S$ (328.12): calcd. C 58.51, H 7.37, S 9.76; found C 58.65, H 7.49, S 9.60.

2,3,4,6-Tetra-*O*-methyl-1-(phenylsulfinyl)-β-D-galactopyranoside (7): A solution of compound **6** (205 mg, 0.62 mmol) in dichloromethane (10 mL) was cooled to –78 °C, and then *m*-CPBA (173 mg, 0.65 mmol) was added. After 5 h of stirring, the reaction mixture was diluted with CH_2Cl_2, and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (20% EtOAc/hexane) to afford a mixture (1.5:1) of sulfoxides **7** (183 mg, 86%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.70 (m, 5 H), 4.20 (d, *J* = 8.9 Hz, 1 H_{major}), 3.97 (t, *J* = 8.9 Hz, 1 H_{minor}), 3.83 (t, *J* = 9.7 Hz, 1 H_{min}), 3.70 (d, *J* = 9.7 Hz, 1 H_{minor}) 3.20–3.65 (m, 5 H), 3.73 (s, 3 H_{minor}), 3.55 (s, 3 H_{minor}), 3.53 (s, 3 H_{minor}), 3.50 (s, 3 H_{major}), 3.48 (s, 3 H_{major}), 3.46 (s, 3 H_{major}), 3.37 (s, 3 H_{major}), 3.14 (s, 3 H_{major}) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 141.7, 140.5, 131.2, 129.1, 129.0, 125.6, 125.2, 96.6, 94.2, 88.6, 86.1, 78.7, 78.0, 75.2, 75.1, 74.8, 74.7, 71.0, 70.6, 61.6, 61.4, 60.5, 59.5, 59.4, 59.3, 58.4, 58.2 ppm. MS (EI): *m*/*z* = 345.3 $[M]^+$. $C_{16}H_{24}O_6S$ (344.13): calcd. C 55.80, H 7.02, S 9.31; found C 55.60, H 6.90, S 9.15.

2,3,4,6-Tetra-*O*-methyl-1-[(*R*)-phenylsulfinyl]-α-D-galactopyranoside (12): A solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-galactopyranoside[34] (1 g, 2.26 mmol) in MeOH (11 mL) was treated with freshly prepared NaOMe (124 mg, 2.23 mmol) and stirred for 8 h. The reaction mixture was then neutralized with Amberlite H^+ resin, filtered, and concentrated. The residue was then dried under high vacuum and dissolved in DMF (15 mL), cooled to 0 °C, and treated portionwise with NaH (60%, 722 mg, 18.1 mmol, 8 equiv.). After 30 min, methyl iodide (840 μL, 13.6 mmol, 6 equiv.) was added by syringe over 5 min. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was carefully quenched with water, diluted with Et_2O, washed with H_2O, dried, and concentrated. The product was then purified by flash chromatography (20% EtOAc/hexane) to afford phenyl 2,3,4,6-tetra-*O*-methyl-1-thio-α-D-galactopyranoside[55] as a colorless oil (615 mg, 83%), $[\alpha]_D$ = –235.0 (*c* = 1.33, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.50–7.55 (m, 2 H), 7.20–7.30 (m, 3 H), 5.78 (d, *J* = 5.5 Hz), 4.40 (t, *J* = 6.8 Hz, 1 H), 3.97 (dd, *J* = 5.5, 10.2 Hz, 1 H), 3.77 (d, *J* = 2.9 Hz, 1 H), 3.64–3.38 (m, 3 H), 3.59 (s, 3 H), 3.55 (s, 3 H), 3.52 (s, 3 H), 3.36 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 134.6, 131.3, 128.7, 127.1, 90.4, 89.5, 84.9, 80.5, 78.6, 72.2, 59.2, 59.0, 58.0, 57.6 ppm. MS (EI): *m*/*z* = 328.0 $[M]^+$. $C_{16}H_{24}O_5S$ (328.12): calcd. C 58.51, H 7.37, S 9.76; found C 58.80, H 7.60, S 9.48. A solution of the above sulfide (610 mg, 1.86 mmol) in dichloromethane (20 mL) was cooled to –78 °C. *m*-CPBA (561 mg, 1.95 mmol) was then added. After 5 h of stirring, the reaction mixture was diluted with CH_2Cl_2 and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (35% EtOAc/hexane) to afford the diastereomerically pure sulfoxide **12** (496 mg, 78%), $[\alpha]_D$ = +13.4 (*c* = 0.57, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.65–7.70 (m, 2 H), 7.45–7.55 (m, 3 H), 4.50 (d, *J* = 2.1 Hz, 1 H), 4.41 (dd, *J* = 2.1, 3.0 Hz, 1 H), 4.21 (dd, *J* = 4.1, 6.8 Hz, 1 H), 3.95 (dd, *J* = 3.0, 6.8 Hz, 1 H), 3.49–3.51 (m, 2 H), 3.43–3.56 (m, 1 H), 3.48 (s, 3 H), 3.46 (s, 3 H), 3.38 (s, 3 H), 3.26 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 141.8, 131.1, 128.8, 124.6, 101.1, 85.8, 85.5, 84.4, 78.5, 71.6, 59.1, 58.0, 57.4 ppm. MS (EI): *m*/*z* = 345.1 $[M]^+$. $C_{16}H_{24}O_6S$ (344.13): calcd. C 55.80, H 7.02, S 9.31; found C 56.03, H 7.03, S 9.02.

2,3,4,6-Tetra-*O*-methyl-1-[(*R*)-phenylsulfinyl]-α-D-mannopyranoside (13): A solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside[34] (2 g, 4.5 mmol) in MeOH (22 mL) was treated with freshly prepared NaOMe (248 mg, 4.5 mmol) and stirred for 10 h. The reaction mixture was then neutralized with Amberlite H^+ resin, filtered, and concentrated. The residue was then dried under high vacuum and dissolved in DMF (30 mL), cooled to 0 °C, and treated portionwise with NaH (60%, 1.4 g, 36.1 mmol, 8 equiv.). After 30 min, methyl iodide (1.8 mL, 27.1 mmol, 6 equiv.) was added by syringe over 5 min. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was carefully quenched with water, diluted with Et_2O, washed with H_2O, dried, and concentrated. The product was then purified by flash chromatography (20% EtOAc/hexane) to afford phenyl 2,3,4,6-tetra-*O*-methyl-1-thio-α-D-mannopyranoside[56] as a colorless, viscous oil (1.25 g, 85%), $[\alpha]_D$ +128.6 (*c* = 4.6, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.54–7.51 (m, 2 H), 7.35–7.20 (m, 3 H), 5.68 (d, *J* = 1.5 Hz, 1 H), 4.15–4.09 (m, 1 H), 3.86 (dd, *J* = 3.1, 1.7 Hz, 1 H), 3.71–3.49 (m, 4 H), 3.57 (s, 3 H), 3.55 (s, 3 H), 3.48 (s, 3 H), 3.41 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 134.6, 131.0, 129.0, 127.2, 84.6, 81.5, 78.7, 76.2, 72.1, 71.2, 60.7, 59.1, 58.1, 57.7 ppm. $C_{16}H_{24}O_5S$ (328.42): calcd. C 58.51, H 7.37, S 9.76; found C 58.52, H 7.39, S 9.71. A solution of the above sulfide (710 mg, 2.16 mmol) in dichloromethane (30 mL) was cooled to –78 °C. *m*-CPBA (683 mg, 2.37 mmol) was then added. After 5 h of stirring, the reaction mixture was diluted with CH_2Cl_2, and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (35% EtOAc/hexane) to afford the diastereomerically pure sulfoxide **13**[56] (580 mg, 78%), $[\alpha]_D$ = –54.2 (*c* = 0.44, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.62–7.59 (m, 2 H), 7.49–7.45 (m, 3 H), 4.48 (d, *J* = 1.7 Hz, 1 H), 4.12 (dd, *J* = 3.4, 1.9 Hz, 1 H), 3.86 (ddd, *J* = 10.0, 5.1, 2.0 Hz, 1 H), 3.76 (dd, *J* = 9.3, 3.4 Hz, 1 H), 3.56–3.44 (m, 3 H), 3.50 (s, 3 H), 3.48 (s, 3 H), 3.28 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 141.6, 131.2, 129.0, 124.2, 94.8, 80.8, 77.2, 75.2, 73.4, 71.3, 60.5, 59.1, 58.1, 57.7 ppm. $C_{16}H_{24}O_6S$ (344.42): calcd. C 55.80, H 7.02, S 9.31; found C 55.73, H 6.98, S 9.19.

Phenyl 2,3,4,6-Tetra-*O*-methyl-1-(phenylsulfinyl)-β-D-glucopyranoside (14): A solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside[34] (5 g, 11.3 mmol) in MeOH (55 mL) was treated with freshly prepared NaOMe (619 mg, 11.3 mmol) and stirred for 10 h. The reaction mixture was then neutralized with Amberlite H^+ resin, filtered, and concentrated. The residue was then dried under high vacuum and dissolved in DMF (75 mL), cooled to 0 °C, and treated portionwise with NaH (60%, 3.61 g, 90.4 mmol, 8 equiv.). After 30 min, methyl iodide (4.2 mL, 67.8 mmol, 6 equiv.) was added by syringe over 5 min. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was carefully quenched with water, diluted with Et_2O, washed with H_2O, dried, and concentrated. The product was then purified by flash chromatography (20% EtOAc/hexane) to afford phenyl 2,3,4,6-tetra-*O*-methyl-1-thio-β-D-glucopyranoside (3.18 g, 86%), m.p. 69–70 °C, $[\alpha]_D$ = –24.9 (*c* = 1.25, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.50–7.55 (m, 2 H), 7.20–7.35 (m, 3 H), 4.48 (d, *J* = 9.8 Hz, 1 H), 3.50–3.66 (m, 3 H), 3.65 (s, 3 H), 3.60 (s, 3 H), 3.53 (s, 3 H), 3.38 (s, 3 H), 3.24–3.28 (m, 1 H), 3.19 (t, *J* = 8.6 Hz, 1 H),

3.04 (dd, J = 8.6, 9.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 134.5, 132.2, 129.2, 127.7, 89.1, 87.8, 83.1, 79.8, 71.8, 61.3, 61.2, 60.8, 59.8 ppm. MS (EI): m/z = 328.1 $[M]^+$. $C_{16}H_{24}O_5S$ (328.12): calcd. C 58.51, H 7.37, S 9.76; found C 58.81, H 7.62, S 9.96. A solution of the above sulfide (3.0 g, 9.14 mmol) in dichloromethane (60 mL) was cooled to –78 °C. *m*-CPBA (2.76 g, 9.6 mmol) was then added. After 5 h of stirring, the reaction mixture was diluted with CH_2Cl_2, and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (35% EtOAc/hexane) to afford a 1:1 diastereomeric mixture of sulfoxides **13** (2.45 g, 78%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.45–7.70 (m, 10 H), 4.22 (d, J = 10.0 Hz, 2 H), 3.00–3.80 (m, 12 H), 3.75 (s, 3 H), 3.67 (s, 3 H), 3.59 (s, 3 H), 3.50 (s, 3 H), 3.49 (s, 3 H), 3.43 (s, 3 H), 3.36 (s, 3 H), 3.08 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 141.2, 140.0, 131.3, 129.1, 129.0, 125.6, 125.1, 96.2, 93.6, 88.9, 88.7, 80.7, 79.7, 79.5, 79.3, 72.3, 71.5, 71.4, 71.2, 61.9, 61.2, 60.9, 60.8, 60.6, 60.0, 59.8, 59.7 ppm. MS (EI): m/z = 345.1 $[M]^+$. $C_{16}H_{24}O_6S$ (344.13): calcd. C 55.80, H 7.02, S 9.31; found C 55.52, H 6.82, S 9.08.

2,3,4-Tri-*O*-benzyl-1-(phenylsulfinyl)-β-D-glucopyranoside (16): A solution of phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[57] (450 mg, 0.83 mmol) in CH_2Cl_2 (20 mL) was treated at –78 °C with *m*-CPBA (60%, 250 mg, 0.87 mmol). After 2 h, the reaction mixture was diluted with CH_2Cl_2 and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (40% EtOAc/hexane) to afford a mixture of sulfoxides (3:1, 361 mg, 78%), from which the major isomer could be characterized, $[\alpha]_D$ = –82.8 (c = 0.99, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.20–7.70 (m, 20 H), 4.95 (d, J = 1.7 Hz, 2 H), 4.61–4.85 (m, 2 H), 4.08 (dd, J = 9.8, 9.3 Hz, 1 H), 3.94 (d, J = 9.8 Hz, 1 H), 3.81 (t, J = 9.3 Hz, 1 H), 3.62 (t, J = 9.3 Hz, 1 H), 3.48–3.55 (m, 2 H), 3.18–3.23 (m, 1 H), 2.25 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 139.8, 138.4, 137.7, 131.5 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 125.2, 96.5, 86.5, 80.6, 77.9, 77.6, 76.1, 75.9, 75.4, 62.1 ppm. MS (EI): m/z = 433.2 $[M – SOPh]^+$. $C_{33}H_{34}O_6S$ (558.21): C 70.95, H 6.13, S 5.74; found C 71.23, H 6.28, S 5.58.

2,3:4,6-Bis-*O*-isopropylidene-1-[(*R*)-phenylsulfinyl]-α-D-mannopyranoside (17): Phenyl 1-thio-α-D-mannopyranoside[34] (3.1 g, 12.1 mmol) and *p*-toluenesulfonic acid (pTsOH) monohydrate (200 mg, 10%) were dissolved in acetone (20 mL), and the solution was then treated with 2,2-dimethoxypropane (11 mL, 87 mmol). After the mixture had been stirred for 7 h, solid Na_2CO_3 was added, and the reaction mixture was filtered through a Celite® pad and concentrated. The residue was then purified by flash chromatography (10% EtOAc/hexane) to afford phenyl 2,3:4,6-bis-*O*-isopropylidene-1-thio-α-D-mannopyranoside (3.83 g, 90%), m.p. 128–129 °C, $[\alpha]_D$ = +171.0 (c = 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.48–7.58 (m, 2 H), 7.25–7.35 (m, 3 H), 5.77 (s, 1 H), 4.38 (d, J = 5.7 Hz, 1 H), 4.21 (dd, J = 5.7, 8.0 Hz, 1 H), 4.01 (dt, J = 10.1, 5.9 Hz, 1 H), 3.83 (dd, J = 8.0, 10.1 Hz, 1 H), 3.69–3.79 (m, 2 H), 1.56 (s, 3 H), 1.51 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 132.8, 132.2, 129.1, 127.9, 109.7, 99.7, 84.5, 76.4, 74.8, 72.9, 62.6, 61.7, 29.0, 28.2, 26.2, 18.7 ppm. MS (EI): m/z = 352.1 $[M]^+$. $C_{18}H_{24}O_5S$ (352.45): calcd. C 61.34, H 8.86, S 9.10; found C 61.62, H 7.13, S 8.99. A solution of the above sulfide (991 mg, 2.81 mmol) in CH_2Cl_2 (60 mL) was treated at –78 °C with *m*-CPBA (60%, 888 mg, 3.1 mmol). After 2 h, the reaction mixture was diluted with CH_2Cl_2, and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (20% EtOAc/hexane) to afford diastereomerically pure sulfoxide **17** (879 mg, 85%), $[\alpha]_D$ = –84.2 (c = 0.68, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.20–7.60 (m, 5 H), 4.78 (s, 1 H), 4.77 (d, J = 5.3 Hz, 1 H), 4.33 (m, 1 H), 3.88–3.93 (m, 1 H), 3.73–3.81 (m, 2 H), 3.63–3.70 (m, 1 H), 1.49 (s, 6 H), 1.43 (s, 3 H), 1.32 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 141.1, 131.5, 129.2, 124.3, 109.2, 99.7, 95.6, 74.6, 71.8, 70.4, 67.2, 61.4, 28.7, 27.9, 25.8, 18.6 ppm. MS (EI): m/z = 368 $[M]^+$. $C_{18}H_{24}O_6S$ (368.44): C 58.68, H 6.57, S 8.70; found C 58.81, H 6.77, S 8.52.

2,3:4,6-Bis-*O*-isopropylidene-1-(phenylsulfinyl)-β-D-mannopyranoside (18): Phenyl 1-thio-β-D-glucopyranoside[34] (300 mg, 1.17 mmol) and *p*TsOH monohydrate (30 mg) were dissolved in acetone (5 mL), and the solution was then treated with 2,2-dimethoxypropane (1.6 mL, 13 mmol). After the mixture had been stirred for 7 h, solid Na_2CO_3 was added, and the reaction mixture was filtered through a Celite® pad and concentrated. The residue was then purified by flash chromatography (10% EtOAc/hexane) to afford phenyl 2,3:4,6-bis-*O*-isopropylidene-1-thio-β-D-mannopyranoside (334 mg, 81%), m.p. 139–141 °C, $[\alpha]_D$ = –1.0 (c = 0.63, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.50–7.60 (m, 2 H), 7.25–7.35 (m, 3 H), 5.10 (d, J = 2.4 Hz, 1 H), 4.47 (dd, J = 2.4, 5.3 Hz, 1 H), 4.09 (dd, J = 5.3, 8.0 Hz, 1 H), 3.81–3.96 (m, 3 H), 3.18 (dt, J = 5.9, 9.9 Hz, 1 H), 1.62 (s, 3 H), 1.52 (s, 3 H), 1.42 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 134.6, 131.2, 129.0, 127.7, 110.6, 99.7, 84.7, 76.7, 76.2, 72.5, 69.8, 61.8, 29.0, 28.3, 26.3, 18.9 ppm. MS (EI): m/z = 352.1 $[M]^+$. $C_{18}H_{24}O_5S$ (352.45): calcd. C 61.34, H 8.86, S 9.10; found C 61.09, H 7.01, S 9.40. A solution of the above sulfide (210 mg, 0.59 mmol) in CH_2Cl_2 (20 mL) was treated at –78 °C with *m*-CPBA (60%,186 mg, 0.65 mmol). After 2 h, the reaction mixture was diluted with CH_2Cl_2 and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (20% EtOAc/hexane) to afford a diastereomeric mixture of sulfoxides **18** (184 mg, 85%), from which the major isomer could be characterized (unassigned stereochemistry), $[\alpha]_D$ = +30.6 (c = 0.60, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70–7.75 (m, 5 H), 7.45–7.55 (m, 3 H), 4.70 (dd, J = 2.5, 5.1 Hz, 1 H), 4.25 (d, J = 2.5 Hz, 1 H), 4.10 (dd, J = 5.1, 8.0 Hz, 1 H), 3.85 (dd, J = 8.0, 10.1 Hz, 1 H), 3.70–3.67 (m, 2 H), 3.00 (ddd, J = 7.3, 8.1, 10.1 Hz, 1 H), 1.65 (s, 3 H), 1.49 (s, 3 H), 1.46 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 142.0, 131.6, 128.8, 125.2, 110.9, 99.8, 92.4, 76.1, 72.4, 71.7, 70.7, 61.3, 28.7, 28.3, 26.3, 18.7 ppm. MS (EI): m/z = 368 $[M]^+$. $C_{18}H_{24}O_6S$ (368.44): C 58.68, H 6.57, S 8.70; found C 58.30, H 6.68, S 8.63.

General Procedure for the Glycal Formation: A solution of the glycosyl sulfoxide (1 mmol) in dry THF was cooled to –78 °C and then treated with the corresponding organolithium reagent (3 equiv.). After stirring for 30 min, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl. After partitioning between water and diethyl ether, the organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography.

1,5-Anhydro-3,4,6-tri-*O*-methyl-2-deoxy-D-*lyxo*-hex-1-enitol (8): Sulfoxide **7** (160 mg, 0.49 mmol) was treated with *n*BuLi (918 μL, 1.6 M solution in hexane, 1.47 mmol) as base as described in the General Procedure to give **8**[58] (55 mg, 59%), $[\alpha]_D$ = +15.0 (c = 0.81, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.25 (d, J = 6.1 Hz, 1 H), 4.83 (dd, J = 6.1, 2.1 Hz, 1 H), 3.40–4.17 (m, 5 H), 3.53 (s, 3 H), 3.42 (s, 3 H), 3.39 (s, 3 H) ppm.

1,5-Anhydro-3,4,6-tri-*O*-methyl-2-deoxy-D-*arabino*-hex-1-enitol (15): Sulfoxide **13** (100 mg, 0.3 mmol) was treated with *n*BuLi (562 μL, 1.6 M solution in hexane, 0.9 mmol) as base as described in the General Procedure to give **15**[59] (40 mg, 72%). In a different experiment and by the same procedure, sulfoxide **14** (121 mg, 0.35 mmol) was also converted into glycal **15** (51 mg, 51%), $[\alpha]_D$ = +17.0 (*c* = 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.31 (d, *J* = 6.1 Hz, 1 H), 4.83 (dd, *J* = 6.1, 2.1 Hz, 1 H), 3.36–3.95 (m, 5 H), 3.54 (s, 3 H), 3.42 (s, 3 H), 3.40 (s, 3 H) ppm. $C_9H_{16}O_4$ (188.10): calcd. C 57.43, H 8.57; found C 57.37, H 8.23.

1,5-Anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (19): Sulfoxide **16** (94 mg, 0.49 mmol) was treated with *n*BuLi (1.2 mL 1.6 M solution in hexane, 1.96 mmol, 4 equiv.) as base as described in the General Procedure to give **19**[60] (35 mg, 63%), $[\alpha]_D$ = –102.0 (*c* = 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.20–7.50 (m, 10 H), 6.41 (dd, *J* = 6.1, 1.2 Hz, 1 H), 4.61–5.07 (m, 5 H), 4.26 (m, 1 H), 3.62 (t, *J* = 9.3 Hz, 1 H), 3.80–4.00 (m, 4 H), 2.04 (m, 1 H) ppm. $C_{20}H_{22}O_4$ (326.15): calcd. C 73.60, H 6.79; found C 73.46, H 6.53.

1,5-Anhydro-4,6-*O*-isopropylidene-2-deoxy-D-*arabino*-hex-1-enitol (20): Sulfoxide **17** (101 mg, 0.27 mmol) was treated with *n*BuLi (506 μL, 1.6 M solution in hexane, 0.81 mmol) as base as described in the General Procedure to give **20**[60] (44 mg, 86%). In a different experiment and by the same procedure, sulfoxide **18** (177 mg, 0.48 mmol) was also converted into glycal **20** (56 mg, 62%), $[\alpha]_D$ = –19.0 (*c* = 1.2, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.31 (dd, *J* = 6.1, 1.2 Hz, 1 H), 4.75 (dd, *J* = 6.2, 2.0 Hz, 1 H), 4.36 (m, 1 H), 3.70–4.00 (m, 4 H), 2.10 (d, *J* = 4.4 Hz, 1 H), 1.55 (s, 3 H), 1.45 (s, 3 H) ppm. ^1H NMR (C_6D_6, 300 MHz): δ = 6.18 (dd, *J* = 6.1, 1.2 Hz, 1 H), 4.68 (dd, *J* = 6.2, 1.8 Hz, 1 H), 4.36 (m, 1 H), 3.70–4.00 (m, 4 H), 2.10 (d, *J* = 4.4 Hz, 1 H), 1.55 (s, 3 H), 1.45 (s, 3 H) ppm.

2,3:5,6-Di-*O*-isopropylidene-1-(phenylsulfinyl)-β-D-mannofuranose (22): A solution of phenyl 2,3:5,6-di-*O*-isopropylidene-1-thio-β-D-mannofuranose[26] (500 mg, 1.42 mmol) in CH_2Cl_2 (20 mL) was treated at –55 °C with *m*-CPBA (60%, 463 mg, 1.56 mmol). After 2 h, the reaction mixture was diluted with CH_2Cl_2 and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (40% EtOAc/hexane) to afford a 5:1 mixture of sulfoxides (470 mg, 90%), from which the major isomer (unassigned) could be characterized, $[\alpha]_D$ = +102.4 (*c* = 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.72 (m, 2 H), 7.48 (m, 3 H), 5.12 (dd, *J* = 6.0, 4.2 Hz, 1 H), 4.85 (dd, *J* = 6.0, 4.2 Hz, 1 H), 4.38 (m, 1 H), 4.23 (d, *J* = 4.2 Hz, 1 H), 4.00 (dd, *J* = 8.7, 6.3 Hz, 1 H), 3.88 (dd, *J* = 8.7, 4.2 Hz, 1 H), 3.65 (dd, *J* = 6.3, 4.2 Hz, 1 H), 1.62 (s, 3 H), 1.39 (s, 3 H), 1.32 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 141.7, 131.4, 128.7, 125.3, 114.5, 109.1, 97.5, 82.8, 80.5, 80.2, 72.8, 66.0, 26.6, 25.5, 25.1, 24.3 ppm. MS (EI): *m*/*z* = 369.2 $[M + Na]^+$. $C_{18}H_{24}O_6S$ (368.13): calcd. C 58.68, H 6.57, S 8.70; found C 58.51, H 6.31, S 8.59.

1,4-Anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (23): Sulfoxide **22** (300 mg, 0.81 mmol) was treated with *n*BuLi as base as described in the General Procedure to give **23**[26] (119 mg, 79%), $[\alpha]_D$ = –78.9 (*c* = 1.0, $CHCl_3$). ^1H NMR (C_6D_6, 300 MHz): δ = 6.57 (d, *J* = 2.7 Hz, 1 H), 5.23 (t, *J* = 2.7 Hz, 1 H), 4.91 (dd, *J* = 6.6, 2.7 Hz, 1 H), 4.49 (ddd, *J* = 7.8, 6.3, 5.1 Hz, 1 H), 4.17–4.12 (m, 1 H), 4.15 (dd, *J* = 8.7, 6.3 Hz, 1 H), 4.00 (dd, *J* = 8.7, 5.1 Hz, 1 H), 2.19 (br. s, 1 H), 1.45 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 150.3, 109.3, 103.9, 84.7, 72.8 (×2), 66.8, 26.8, 25.1 ppm.

1,5-Anhydro-4,6-*O*-isopropylidene-1-(phenylsulfinyl)-2-deoxy-D-*arabino*-hex-1-enitol (38): A solution of **17** (900 mg, 2.45 mmol) in dry THF (11 mL) was cooled to –78 °C and then treated with lithium diisopropylamide (12 mL, 0.8 M solution in THF, 9.78 mmol). After stirring for 30 min, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl. After partitioning between water and diethyl ether, the organic layer was dried with $MgSO_4$ and concentrated. The residue was then purified by flash chromatography (50% EtOAc/hexane) to give sulfoxide **38** (580 mg, 76%), $[\alpha]_D$ = –128.0 (*c* = 0.35, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.65–7.80 (m, 2 H), 7.45–7.60 (m, 3 H), 5.74 (d, *J* = 2.2 Hz, 1 H), 4.47 (m, 1 H), 3.65–3.90 (m, 4 H), 3.10 (s, 1 H), 1.44 (s, 3 H), 1.40 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 156.2, 131.7, 129.7, 125.9, 124.4, 106.9, 100.5, 73.0, 71.2, 69.1, 61.6, 29.3, 19.5 ppm. MS (EI): *m*/*z* = 311.1 $[M + 1]^+$. $C_{15}H_{18}O_5S$ (310.09): calcd. C 58.05, H 5.85, S 10.33; found C 57.89, H 5.13, S 9.97.

1-Deuterio-2,3:4,6-bis-*O*-isopropylidene-1-(phenylsulfinyl)-α-D-mannopyranoside (39) and 1-Deuterio-2,3:4,6-bis-*O*-isopropylidene-1-(phenylsulfinyl)-β-D-mannopyranoside (41): A solution of 2,3:4,6-bis-*O*-isopropylidene-D-mannono-1,5-lactone[60] (254 mg, 0.98 mmol) in THF (20 mL) was cooled to 0 °C, and a cold solution of $NaBD_4$ (82 mg, 1.96 mmol) in D_2O (800 μL) was added dropwise.[61] The mixture was stirred for 20 min and then poured into cold, saturated $NaHCO_3$ solution (20 mL), stirred for 1 h, and extracted with CH_2Cl_2 (2×15 mL), and the extract was washed with water (2×15 mL), dried with $MgSO_4$, and concentrated. The residue was then purified by flash chromatography (30% EtOAc/hexane) to give the corresponding 1-deuteriomannopyranose (220 mg, 86%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.19–4.22 (m, 2 H), 3.74–3.90 (m, 4 H), 2.76 (m, 1 H), 1.56 (s, 3 H), 1.52 (s, 3 H), 1.44 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 109.4, 99.7, 92.2, 76.2, 74.6, 72.7, 62.0, 61.4, 28.9, 28.0, 26.0, 18.7 ppm. MS (EI): *m*/*z* = 246.1 $[M – 15]^+$. A solution of the above deuteriomannopyranose (220 mg, 0.84 mmol) in dry dichloromethane (15 mL) was treated with PhSSPh (200 mg, 0.92 mmol) and Bu_3P (211 μL, 1.68 mmol). After 24 h, the reaction mixture was diluted with CH_2Cl_2 and washed with water and brine. The organic layer was then dried with $MgSO_4$, filtered, and concentrated under vacuum. The residue was filtered through a short pad of silica gel to provide a mixture of anomers (β/α = 4:1) of phenyl 1-deuterio-2,3:5,6-di-*O*-isopropylidene-1-thio-D-mannofuranose (236 mg, 80%), which were separated by careful flash chromatography (15% EtOAc/hexane). α-Anomer: $[\alpha]_D$ = +91.9 (*c* = 0.56, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.48–7.65 (m, 2 H), 7.25–7.35 (m, 3 H), 4.38 (d, *J* = 5.4 Hz, 1 H), 4.19 (dd, *J* = 5.4 Hz, 1 H), 4.02 (dt, *J* = 5.7, 9.9 Hz, 1 H), 3.83 (dd, *J* = 7.9, 9.9 Hz, 1 H), 3.69–3.79 (m, 2 H), 1.56 (s, 3 H), 1.51 (s, 3 H), 1.45 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 132.8, 132.2, 129.1, 127.9, 109.7, 99.7, 84.5, 76.4, 74.8, 72.9, 62.6, 61.7, 29.0, 28.2, 26.2, 18.7 ppm. MS (EI): *m*/*z* = 353.1 $[M]^+$. β-Anomer: $[\alpha]_D$ = –119.6 (*c* = 0.69, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.48–7.60 (m, 2 H), 7.25–7.35 (m, 3 H), 4.44 (d, *J* = 5.3 Hz, 1 H), 4.07 (dd, *J* = 5.3, 8.0 Hz, 1 H), 3.79–3.93 (m, 3 H), 3.16 (dt, *J* = 6.2, 9.7 Hz, 1 H), 1.60 (s, 3 H), 1.50 (s, 3 H), 1.40 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 134.5, 131.0, 128.9, 127.6, 110.4, 99.6, 84.7, 76.6, 76.0, 72.4, 69.6, 61.7, 28.9, 28.2, 26.2, 16.7 ppm. MS (EI): *m*/*z* = 353.1 $[M]^+$. A solution of phenyl 1-deuterio-2,3:5,6-di-*O*-isopropylidene-1-thio-α-D-mannopyranose (50 mg, 0.14 mmol) in CH_2Cl_2 (2 mL) was treated at –55 °C with *m*-CPBA (60%,46.3 mg, 0.156 mmol). After 2 h, the reaction mixture was diluted with CH_2Cl_2 and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with

Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (20% EtOAc/hexane) to afford a diastereomerically pure sulfoxide **39** (44 mg, 85%), $[\alpha]_D$ = –32.7 (*c* = 0.3, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.20–7.60 (m, 5 H), 4.77 (d, *J* = 5.3 Hz, 1 H), 4.33 (m, 1 H), 3.88–3.93 (m, 1 H), 3.73–3.81 (m, 2 H), 3.63–3.70 (m, 1 H), 1.49 (s, 6 H), 1.43 (s, 3 H), 1.32 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 141.1, 131.5, 129.2, 124.3, 109.2, 99.7, 95.6, 74.6, 71.8, 70.4, 67.2, 61.4, 28.7, 27.9, 25.8, 18.6 ppm. MS (EI): *m*/*z* = 369 $[M]^+$. A solution of phenyl 1-deuterio-2,3:5,6-di-*O*-isopropylidene-1-thio-β-D-mannopyranose (50 mg, 0.14 mmol) in CH_2Cl_2 (2 mL) was treated at –55 °C with *m*-CPBA (60%, 46.3 mg, 0.156 mmol). After 2 h, the reaction mixture was diluted with CH_2Cl_2 and sequentially washed with $Na_2S_2O_3$ (20%) and saturated $NaHCO_3$ solutions. The organic layer was then dried with Na_2SO_4, concentrated in vacuo, and subjected to purification by flash chromatography (20% EtOAc/hexane) to afford a diastereomeric mixture of sulfoxides **41** (46 mg, 86%), from which the major isomer could be characterized (unassigned stereochemistry), $[\alpha]_D$ = +20.3 (*c* = 0.83, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.70–7.75 (m, 5 H), 7.45–7.55 (m, 3 H), 4.70 (d, *J* = 5.1 Hz, 1 H), 4.10 (m, 1 H), 3.85 (dd, *J* = 8.0, 10.1 Hz, 1 H), 3.70–3.67 (m, 2 H), 3.00 (ddd, *J* = 7.3, 8.0, 10.1 Hz, 1 H), 1.65 (s, 3 H), 1.51 (s, 3 H), 1.46 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 131.7, 128.8, 125.2, 110.9, 99.8, 92.4, 76.1, 72.4, 71.7, 70.7, 61.3, 28.7, 28.3, 26.3, 18.7 ppm.

1,5-Anhydro-2-deoxy-4,6-*O*-isopropylidene-1-*C*-deuterio-D-*arabino*-hex-1-enitol (43): Sulfoxide **36** (30 mg, 0.081 mmol) was treated with *n*BuLi (150 μL, 1.6 M solution in hexane, 0.24 mmol) as base as described in the General Procedure to give **43** (12 mg, 80%). In a different experiment, sulfoxide **39** (17 mg, 0.05 mmol) was also converted into glycal **43** (7 mg, 76%) by the same procedure, $[\alpha]_D$ = –4.4 (*c* = 0.31, $CHCl_3$). ^1H NMR (C_6D_6, 300 MHz): δ = 4.68 (d, *J* = 1.8 Hz, 1 H), 4.27–4.30 (m, 1 H), 3.67–3.93 (m, 4 H), 2.03 (d, *J* = 4.4 Hz, 1 H), 1.48 (s, 3 H), 1.39 (s, 3 H) ppm. ^{13}C NMR (C_6D_6, 50 MHz): δ = 169.0, 105.9, 100.6, 86.3, 74.6, 74.0, 67.5, 27.4, 25.3 ppm. MS (EI): *m*/*z* = 187.2 $[M]^+$.

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[1] a) R. J. Ferrier, J. O. Hoberg, *Adv. Carbohydr. Chem. Biochem.* **2003**, *58*, 55–107; b) R. J. Ferrier, *Top. Curr. Chem.* **2001**, *215*, 153–175; c) R. J. Ferrier, O. A. Zubkov, *Org. React.* **2003**, *62*, 569–736; d) B. Fraser-Reid, *Acc. Chem. Res.* **1975**, *8*, 192–201; e) B. Fraser-Reid, *Acc. Chem. Res.* **1985**, *18*, 347–354; f) R. J. Ferrier, *Adv. Carbohydr. Chem. Biochem.* **1969**, 199–266.

[2] a) S. J. Danishefsky, M. T. Bilodeau, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1380–1419; b) J. Thiem, M. Gerken, *J. Org. Chem.* **1985**, *50*, 954–958; c) J. Y. Roberge, X. Beebe, S. J. Danishefsky, *J. Am. Chem. Soc.* **1998**, *120*, 3915–3927.

[3] a) D. E. Levy, in *The Organic Chemistry of Sugars* (Ed.: P. Fügedi, D. E. Levy), CRC Press, Boca Raton, FL, **2006**, pp. 269–348; b) M. H. D. Postema in *C-Glycoside Synthesis*, CRC Press, Boca Raton, FL, **1995**; c) J.-M. Beau, T. Gallagher, *Top. Curr. Chem.* **1997**, *187*, 1–54; d) R. Csuk, M. Schaade, C. Krieger, *Tetrahedron* **1996**, *52*, 6397–6408.

[4] M. D. Erion, R. M. Rydzewski, *Nucleosides Nucleotides* **1997**, *16*, 315–317.

[5] A. G. Tolstikov, G. A. Tolstikov, *Russ. Chem. Rev.* **1993**, *62*, 579–601.

[6] Selected contributions: a) U. Hünger, J. Ohnsmann, H. Kunz, *Angew. Chem. Int. Ed.* **2004**, *43*, 1104–1107; b) M. J. Sofia, R. Hunter, T. Y. Chan, A. Vaughan, R. Dulina, H. M. Wang, D. Gange, *J. Org. Chem.* **1998**, *63*, 2802–2803; c) R. Hirschmann, K. C. Nicolaou, S. Pietranico, E. M. Leahy, J. Salvino, B. Arison, M. A. Cichy, P. G. Spoors, W. C. Shakespeare, P. A. Sprengeler, P. Hamley, A. B. Smith III, J. T. Reisine, K. Raynor, L. Maechler, C. Donaldson, W. Vale, R. M. Freidinger, M. R. Cascieri, C. D. Strader, *J. Am. Chem. Soc.* **1993**, *115*, 12550–12568.

[7] a) A. R. Yeager, G. K. Min, J. A. Porco Jr, S. E. Schaus, *Org. Lett.* **2006**, *8*, 5065–5068; b) P. Arya, R. Joseph, Z. Gan, B. Rakic, *Chem. Biol.* **2005**, *12*, 163–180; c) H. Kubota, J. Lim, K. M. Depew, S. L. Schreiber, *Chem. Biol.* **2002**, *9*, 265–276.

[8] L. Somsák, *Chem. Rev.* **2001**, *101*, 81–135.

[9] E. Fischer, E. K. Zach, *Sitzungsber. Kl. Preuss. Akad. Wiss.* **1913**, *27*, 311–317.

[10] A. Wisniewski, E. Skorupova, R. Walczyna, J. Sokołowsky, D. Głód, *Pol. J. Chem.* **1991**, *65*, 875–881.

[11] S. J. Eitelman, R. H. Hall, A. Jordaan, *J. Chem. Soc. Perkin Trans. 1* **1978**, 595–600.

[12] R. Csuk, A. Fürstner, B. I. Glänzer, H. Weidmann, *J. Chem. Soc., Chem. Commun.* **1986**, 1149–1150.

[13] S. Jain, S. N. Suryawanshi, D. S. Bhakuni, *Ind. J. Chem.* **1987**, *26b*, 866–867.

[14] P. de Pouilly, A. Chénedé, J.-M. Mallet, P. Sinaÿ, *Bull. Soc. Chim. Fr.* **1993**, *130*, 256–265.

[15] A. Fürstner, H. Weidmann, *J. Carbohydr. Chem.* **1988**, *7*, 773–783.

[16] a) R. E. Ireland, C. S. Wilcox, S. Thaisrivongs, *J. Org. Chem.* **1978**, *43*, 786–787; b) R. E. Ireland, S. Thaisrivongs, N. Vanier, C. S. Wilcox, *J. Org. Chem.* **1980**, *45*, 48–61.

[17] a) G. Kovács, J. Gyarmati, L. Somsák, K. Micskei, *Tetrahedron Lett.* **1996**, *37*, 1293–1296; b) G. Kovács, K. Tóth, Z. Dinya, L. Somsák, K. Micskei, *Tetrahedron* **1999**, *55*, 5253–5264; c) G. Kovács, K. Micskei, L. Somsák, *Carbohydr. Res.* **2001**, *35*, 225–228.

[18] J. H. P. Pollon, G. Llewellyn, J. M. Williams, *Synthesis* **1989**, 758–759.

[19] L. Somsàk, I. Németh, *J. Carbohydr. Chem.* **1993**, *12*, 679–684.

[20] C. L. Forbes, R. W. Franck, *J. Org. Chem.* **1999**, *64*, 1424–1425.

[21] a) R. P. Spencer, J. Schwartz, *Tetrahedron* **2000**, *56*, 2103–2112; b) T. Hanssen, K. Daasbjerg, T. Skrydstrup, *Tetrahedron Lett.* **2000**, *41*, 8645.

[22] D. J. Chambers, G. R. Evans, A. J. Fairbanks, *Tetrahedron: Asymmetry* **2003**, *14*, 1767–1769.

[23] A. Fernández-Mayoralas, A. Marra, M. Trumtel, A. Veyriëres, P. Sinaÿ, *Tetrahedron Lett.* **1989**, *30*, 2537–2540.

[24] K. Micskei, Z. Juhász, Z. R. Ratkovic, L. Somsák, *Tetrahedron Lett.* **2006**, *47*, 6117–6120.

[25] D. Urban, T. Skrydstrup, J.-M. Beau, *J. Org. Chem.* **1998**, *63*, 2507–2516.

[26] A. Fürstner, *Liebigs Ann. Chem.* **1993**, 1211–1217.

[27] R. R. Schmidt, *Acc. Chem. Res.* **1986**, *19*, 250–259.

[28] a) D. Calimente, M. H. D. Postema, *J. Org. Chem.* **1999**, *64*, 1770–1771; b) M. H. D. Postema, D. Calimente, *Tetrahedron Lett.* **1999**, *40*, 4755–4759; c) B. Schmidt, H. Wildemann, *Eur. J. Org. Chem.* **2000**, 3145–3163; d) M. H. D. Postema, D. Calimente, L. Liu, T. L. Behrmann, *J. Org. Chem.* **2000**, *65*, 6061–6068; e) B. Schmidt, A. Biernat, *Org. Lett.* **2008**, *10*, 105–108.

[29] a) F. E. McDonald, M. M. Gleason, *J. Am. Chem. Soc.* **1996**, *118*, 6648–6659; b) F. E. McDonald, J. L. Bowman, *Tetrahedron Lett.* **1996**, *37*, 4675–4678; c) F. E. McDonald, H. Y. H. Zhu, *Tetrahedron* **1997**, *53*, 11061–11068; d) F. E. McDonald, *Chem. Eur. J.* **1999**, *5*, 3103–3106; e) F. E. McDonald, K. S. Reddy, Y. Díaz, *J. Am. Chem. Soc.* **2000**, *122*, 4304–4309; f) B. M. Trost, Y. H. Rhee, *J. Am. Chem. Soc.* **2003**, *125*, 7482–7483; g) P. Wipf, T. H. Graham, *J. Org. Chem.* **2003**, *68*, 8798–

8807; h) B. Weyershausen, K. H. Dötz, *Eur. J. Inorg. Chem.* **1999**, 1057–1066; i) K. A. Parker, W. Chang, *Org. Lett.* **2003**, *5*, 3891–3893.
[30] O. Boutureira, M. A. Rodríguez, M. I. Matheu, Y. Díaz, S. Castillón, *Org. Lett.* **2006**, *8*, 673–675.
[31] M. Casillas, A. M. Gómez, J. C. López, S. Valverde, *Synlett* **1996**, 628–630.
[32] a) M. Casillas, Ph. D. Thesis, Universidad de Alcalá de Henares Madrid, **1999**; b) A. M. Gómez, M. Casillas, S. Mantecón, S. Valverde, J. C. López, *XVIIIth International Carbohydrate Symposium*, Milan, Italy, **1996**, BP 228, Book of Abstracts, p. 481.
[33] J. Gildersleeve, R. A. Pascal, D. Khane, *J. Am. Chem. Soc.* **1998**, *120*, 5961–5969.
[34] R. J. Ferrier, R. H. Furneaux, *Carbohydr. Res.* **1976**, *52*, 63–68.
[35] G. Zemplèn, A. Kunz, *Ber. Dtsch. Chem. Ges.* **1923**, *56*, 1705–1710.
[36] No thorough study directed towards the optimization of the number of equivalents of the organolithium reagent involved in this transformation has been carried out. According to our proposed mechanism, only 1 equiv. of organolithium reagent will be required for the transformation of fully alkylated sulfoxides into glycals, whereas 2,3-isopropylidene-protected sulfoxides will require a second equivalent of organolithium reagent to react with the acetone liberated in the process (see A. Klemer, G. Rodemeyer, *Chem. Ber.* **1974**, *107*, 2612–2614). However, we have observed that the use of 3 equiv. of organolithium reagent works reasonably well in all instances. Sulfoxide **16**, bearing a free hydroxy group, was treated with 4 equiv. of *n*BuLi for its transformation into glycal **19** (see Experimental Section).
[37] The TLC of the final reaction mixture showed only one spot corresponding to the final glycal **8**, but compound **8** could only be isolated in 59% yield.
[38] P. Wipf, J. T. Reeves, *J. Org. Chem.* **2001**, *66*, 7910–7914.
[39] D. Crich, J. Mataka, S. Sun, D. J. Wink, K.-C. Lam, A. L. Rheingold, *Chem. Commun.* **1998**, 2763–2764.
[40] Furanoid glycals in synthesis: a) A. Choudhury, M. E. Pierce, D. Nguyen, L. Storace, L. Confalone, *Tetrahedron Lett.* **2005**, *46*, 8099–8102; b) M. Tingoli, B. Panuzi, F. Santacroce, *Tetrahedron Lett.* **1999**, *40*, 9329–9332; c) R. S. Coleman, M. L. Madaras, *J. Org. Chem.* **1998**, *63*, 5700–5703.
[41] Preparation of furanoid glycals: a) F. Bravo, M. Kassou, Y. Díaz, S. Castillón, *Carbohydr. Res.* **2001**, *336*, 83–97; b) Z.-X. Wang, L. I. Wiebe, J. Balzarini, E. de Clerk, E. E. Knaus, *J. Org. Chem.* **2000**, *65*, 9214–9219; c) B. Schmidt, H. Wildemann, *Eur. J. Org. Chem.* **2000**, 3145–3164; d) F. Bravo, M. Kassou, S. Castillón, *Tetrahedron Lett.* **1999**, *40*, 1187–1190; e) M. A. Cameron, S. B. Cush, R. P. Hammer, *J. Org. Chem.* **1997**, *62*, 9065–9069; f) J. A. Walker II, J. J. Chen, D. S. Wise, L. B. Townsend, *J. Org. Chem.* **1996**, *61*, 2219–2221; g) M. Kassou, S. Castillón, *Tetrahedron Lett.* **1994**, *35*, 5513–5516.
[42] No furan formation from glycal **23** was observed. We believe that the presence of Et_3N (1%) in the eluent mixture for the column chromatography plays a key role in this respect.
[43] S. Patai, Z. Rappoport *The synthesis of sulphones, sulphoxides, and cyclic sulphides*, John Wiley and Sons, Chichester, **1994**, pp. 180–181.
[44] a) S. Oae, *Organic Sulfur Chemistry*, CRC Press, Boca Raton, FL, **1991**; b) S. Oae, Y. Uchida, *Acc. Chem. Res.* **1991**, *24*, 2001–2008.
[45] a) P. R. Blakemore, M. S. Burge, M. A. Sephton, *Tetrahedron Lett.* **2007**, *48*, 3999–4002, and references cited therein; b) T. Satoh, N. Hanaki, N. Yamada, T. Asano, *Tetrahedron* **2000**, *56*, 6223–6234; c) T. Satoh, S. Kobayashi, S. Nakanishi, K. Horiguchi, S. Irisa, *Tetrahedron* **1999**, *55*, 2515–2528.
[46] J. G. Tillet, *Chem. Rev.* **1976**, *76*, 747–772.
[47] S. Oae, T. Kawai, N. Furukawa, *Tetrahedron Lett.* **1984**, *25*, 69–72.
[48] B. Giese, M. Hoch, C. Lamberth, R. R. Schmidt, *Tetrahedron Lett.* **1988**, *29*, 1375–1378.
[49] a) J. E. Milne, P. J. Kocienski, *Synthesis* **2003**, 584–592; b) J. E. Milne, P. J. Kocienski, J. Alonso, *Chem. Commun.* **2002**, 426–427.
[50] The 1-deuterioglycosyl sulfoxides **39** and **41** were prepared from the corresponding lactone by a sequence of reactions involving $NaBD_4$ reduction, thioglycosylation [PhSSPh, $P(n\text{Bu})_3$], and *m*-CPBA oxidation.
[51] For a previous mechanistic study on the formation of glycals under strongly basic conditions using deuteration as a probe, see: T. M. Davis, T. L. Lowary, *Carbohydr. Res.* **2000**, *324*, 210–217.
[52] See, for example: a) V. Wittman, H. Kessler, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1091–1093; b) F. Burkhart, M. Hoffman, H. Kessler, *Tetrahedron Lett.* **1998**, *39*, 7699–7702; c) P. Lesimple, J.-M. Beau, *Bioorg. Med. Chem.* **1994**, *2*, 1319–1330; d) P. Lesimple, J.-M. Beau, P. Sinaÿ, *Carbohydr. Res.* **1987**, *171*, 289–300.
[53] a) M. Carpintero, I. Nieto, A. Fernández-Mayoralas, *J. Org. Chem.* **2001**, *66*, 1768–1774; b) M. Carpintero, C. Jaramillo, A. Fernández-Mayoralas, *Eur. J. Org. Chem.* **2000**, 1285–1296; c) C. Jaramillo, G. Corrales, A. Fernández-Mayoralas, *Tetrahedron Lett.* **1998**, *39*, 7783–7786.
[54] a) J. C. López, A. M. Gómez, B. Fraser-Reid, *J. Org. Chem.* **1995**, *60*, 3871–3878; b) A. M. Gómez, J. C. López, B. Fraser-Reid, *J. Org. Chem.* **1995**, *60*, 3859–3870; c) J. C. López, A. M. Gómez, S. Valverde, B. Fraser-Reid, *J. Org. Chem.* **1995**, *60*, 3851–3858; d) J. C. López, B. Fraser-Reid, *J. Chem. Soc., Chem. Commun.* **1992**, 94–96; e) J. C. López, B. Fraser-Reid, *J. Am. Chem. Soc.* **1989**, *111*, 3450–3452; f) A. M. Gómez, M. Casillas, S. Valverde, J. C. López, *Chem. Commun.* **1996**, 2357–2358.
[55] P. Li, L. Sun, D. W. Landry, K. Zhao, *Carbohydr. Res.* **1995**, *275*, 179–184.
[56] P. Wipf, J. T. Reeves, *J. Org. Chem.* **2001**, *66*, 7910–7914.
[57] P. J. Pfäffli, S. H. Hixson, L. Anderson, *Carbohydr. Res.* **1972**, *23*, 195–206.
[58] R. Kuhn, H. H. Baer, *Chem. Ber.* **1955**, *88*, 1537–1543.
[59] E. L. Hirst, C. S. Woolvin, *J. Chem. Soc.* **1931**, 1131–1137.
[60] A. Bandzoizi, M. Lakhrissi, Y. Chapleur, *J. Chem. Soc. Perkin Trans. 1* **1992**, 1471–1473.
[61] L. A. Berven, S. G. Withers, *Carbohydr. Res.* **1986**, *156*, 282–285.

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