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Wittig approach to carbohydrate-derived vinyl sulfides, new substrates for regiocontrolled ring-closure reactions

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Abstract—Reaction of methyl- and phenylthiomethylidene phosphoranes **1** and **2** with a variety of reducing sugars has been explored. Furano-type carbohydrates afforded with good yields the corresponding open-chain vinyl sulfides, whereas pyrano derivatives produced elimination compounds together with the expected vinyl sulfides, depending on the nature of the protective groups.
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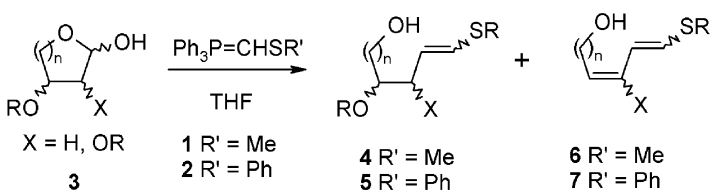
1. Introduction

Carbohydrate-derived open-chain vinyl sulfides have been recognized as useful intermediates for the synthesis of diverse carbohydrate mimics or derivatives.[1–5] Since vinyl sulfides can easily be converted into other interesting functionalities and/or selectively activated with various electrophiles,[6] formation of such carbohydrate building blocks appeared essential to be studied. Carbohydrate-based vinyl sulfides have previously been prepared using diverse methodologies including Vasella's fragmentation reaction,[1] Grignard reagent-induced Grob-type fragmentation[2] or various eliminative methodologies.[7] Whereas the Wittig reaction applied to reducing sugars has been routinely used in glycochemistry,[8] only a limited number of examples involving thiofunctionalized phosphoranylidene reagents have been reported.[5] We have therefore explored the applicability of the Wittig reaction to produce various vinyl sulfides in different carbohydrate series.

2. Results and discussion

A range of protected reducing sugars were prepared from commercially available precursors and reacted with phosphoranes **1** and **2** generated in situ, from their respective phosphonium salts precursors using *n*-butyllithium in anhydrous THF. The results for these Wittig condensations (Scheme 1) on lactols under standard conditions (THF, room temperature) are summarized in Table 1.

As a first observation, it appeared that pyrano- or furano-lactols containing one or more extra free hydroxyl groups—as for 4,6-*O*-benzylidene-D-glucopyranose or 2,3-*O*-isopropylidene-D-ribose—did not react correctly with either ylide **1** or **2** under standard conditions and applying heat to the reactions only resulted in complex mixtures of products. In contrast, Table 1 shows that lactols **3a–f** can react smoothly at room temperature with both ylides to deliver **4a–f** with good to excellent yields in the form of *E*/*Z* isomeric mixtures. Among the above lactols, only **3a** produced a small amount of a mixture of conjugated dienes **7a** resulting from base-induced α,β-elimination close to the anomeric group prior to Wittig reaction[9] (entry a, R=Ph). Due to the high complexity of their NMR spectra, all mixtures of such isomeric dienes further evocated in this paper were only characterized using HRMS.



X = H, OR
3

1 R' = Me
2 R' = Ph

4 R' = Me
5 R' = Ph

6 R' = Me
7 R' = Ph

Scheme 1. Standard Wittig reaction and elimination side-reaction.

Keywords: Carbohydrates; Wittig reaction; Vinyl sulfides; Ring-closure reaction.
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The apparent lack of coherence in *Z*/*E* selectivity observed during this process is usual for reactions of phosphoranylidene reagents with chiral lactols. Some authors have shown the influence of hydrogen bonding between the free hydroxyl group and the oxaphosphetane intermediate obtained from a stabilized phosphorane.[10]

In the case of compound **3c**, the Wittig reaction proved to be applicable in the presence of a pivaloyl protecting group to afford **4c** or **5c** in reasonable yield while also producing appreciable amounts of the de-acylated compounds **8** and **9**—isolated and characterized as their respective di-*O*-acetyl derivatives **10** and **11**—and of the bis-pivaloates **12** and **13** resulting from transesterification processes. Application of catalytic basic conditions (NaH 0.1 equiv., THF, RT, 5 h) to the vinyl sulfide **4c** also led to the formation of **8** and **12** (Scheme 2).

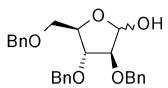
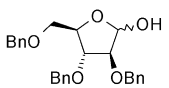
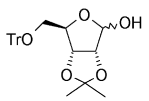
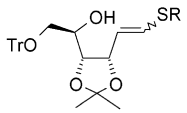
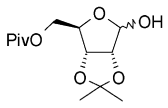
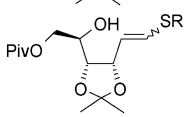
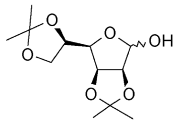
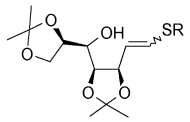
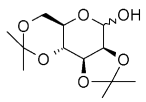
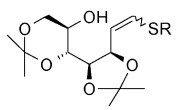
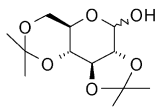
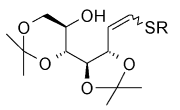
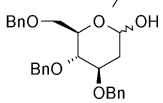
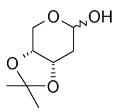
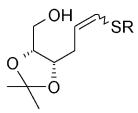
In some cases, direct purification was not effective, as with compound **5e** which could not be obtained exempt from triphenylphosphine oxide contamination. A subsequent acetylation (intermediate **14**)/deacetylation two-step sequence had to be applied to afford pure **5e** in excellent yield.

Considering all the results obtained, it clearly appeared that within the furano-lactol series, whatever the protecting group, the Wittig reaction was quite efficient. In only one case, a small amount of elimination product was obtained. In contrast, with pyrano derivatives, the condensation seemed to be much more complex. 2-Deoxy pyranoses **3g** and **3h** appeared more prone to elimination: 3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose **3g** quantitatively furnished mixtures of the elimination products **6g** or **7g**, whereas 4,5-*O*-isopropylidene-D-ribopyranose **3h** led to mixtures of the expected vinyl sulfides **4h** or **5h** and elimination products **6h** or **7h**. All our attempts to obtain **4g** under modified conditions were unsuccessful: either pretreatment of lactols by *n*-butyllithium in THF[11] or addition of tributyltin chloride[12] to the reaction mixture failed to prevent elimination.

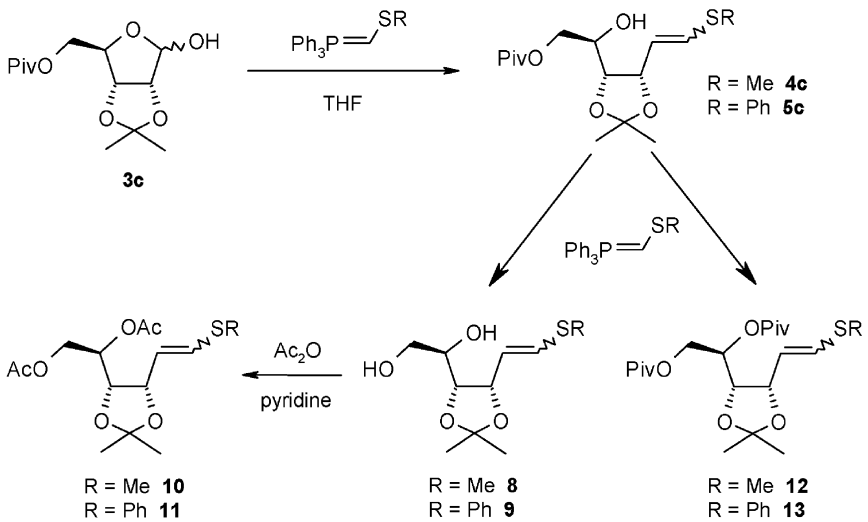
A similar outcome was obtained when starting from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose or 2,3,4,6-tetra-*O*-benzyl-D-mannopyranose, which are known for their low reactivity and their ability to eliminate or epimerize under such Wittig conditions.[9]

From the above results, it can be seen that furano-lactols

Table 1.

Entry	Reducing sugar **3**	Vinyl sulfides	**4**, R=Me **5**, R=Ph Yield (%)		**4**, R=Me **5**, R=Ph *E*/*Z* ratio		**6**, R=Me **7**, R=Ph Yield (%)	
a			96	77	>95/5	85/15	—	6
b			86	94	57/43	17/83	—	—
c			64[a]	57[b]	45/55	20/80	—	—
d			92	86	81/19	41/59	—	—
e			98	87[c]	4/96	13/87	—	—
f			75	71	19/81	5/95	—	—
g		—	—	—	—	—	96	95
h			64	62	75/25	40/60	23	18

[a] 23% of the 5,6-diol resulting from de-*O*-pivaloylation was also isolated as its diacetate derivative **10**.
[b] 28% of the 5,6-diol resulting from de-*O*-pivaloylation was also isolated as its diacetate derivative **11**.
[c] Yield including acetylation and deacetylation steps.



Scheme 2. Application to a 5-*O*-pivaloylated sugar.

constitute suitable substrates for the thio-functionalized phosphoranylidene-type Wittig reaction when no free hydroxyl is present. In the case of pyrano-lactols, protecting groups are critical to favor the Wittig reaction. To avoid the elimination process with alkoxy groups such as *O*-benzyl, cyclic ketals such as *O*-isopropylidene might be used and are less detrimental to the Wittig reaction.

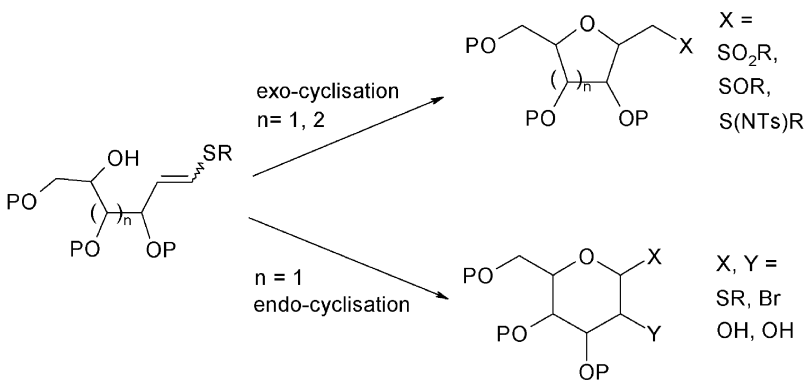
Vinyl sulfides are a functional class which has offered substantial applications in organic synthesis.[6] Deliberately stepping aside from standard solvolytic type C–S cleavages, which have previously been explored,[4,5a,13,14] we have undertaken a preliminary exploration of the ability of our multi-chiral vinyl sulfides to undergo regio- and stereoselective ring-closure: ring-formation via *endo*- or *exo*-cyclisation pathways can be achieved selectively, depending on the reaction conditions (Scheme 3). The *E*/*Z* mixtures of isomers should be considered in ring closing reactions, as *E* or *Z* isomers could produce opposite results in the stereochemical outcome.[15]

exo-Type cyclisations are under current development using a somewhat simple two-step procedure: oxidation of the sulfide moiety into sulfone—or another electron-withdrawing thio-function—followed by base-promoted intramolecular Michael addition led to *exo*-products.[16] This work opening a stereoselective access to novel thio-functionalized *C*-glycosides will shortly be published.[17]

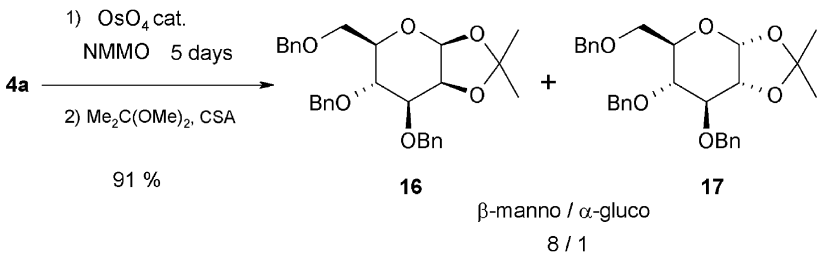
Various methodologies have been explored to perform *endo*-type cyclisation of the above vinyl sulfides: NBS-induced ring closure inspired by the pioneering work of Gallucci et al.[18] gave promising results which are being currently developed in the laboratory.[19] Osmium tetroxide assisted cyclisation has also been investigated: as an illustration, treatment of vinyl sulfide **4a** by a catalytic amount of OsO_4 using *N*-methyl morpholine as co-oxidant led to the diastereoselective formation of α-hydroxy lactols **15** which were characterized as their isopropylidene derivatives **16** and **17** (Scheme 4).[20] To our knowledge, this constitutes the first report on the osmylation of a vinyl sulfide derivative.

In order to clarify the mechanism of this process, the reaction medium was quenched and processed before completion. ^{1}H NMR spectroscopy of the crude allowed indirect follow-up of the reaction pathway.

At the early stage of the process, vinyl sulfone **18** was formed through the transient vinyl sulfoxide **19**.[21] This oxidative process was in competition with the fast direct osmylation of vinyl sulfide **4a** leading to a mixture of α- and



Scheme 3. Regioselective ring closures of the vinyl sulfides.



Scheme 4. Osmylation of vinyl sulfide **4a**.

β-lactols **15**. After 4 h reaction, **15** and **18** were the two sole components of the reaction mixture (4:6 ratio). In a second stage, the consumption of **18** was concomitant with the formation of lactols **15**. The kinetic of this transformation was quite slow due to electron deficiency of the double bond in sulfone **18**. After few days, lactols **15** had become essentially the sole product. With a view to better categorizing the process, osmium tetroxide oxidation was separately performed on vinyl sulfoxide **19** and vinyl sulfone **18**, which both similarly gave lactol **15** in a nearly quantitative yield. This led us to suggest the following mechanism for this oxidative ring-closing process (Scheme 5).

After the first oxidation stages, the resulting unstable *O*,*S*-hemiketal rearranged into the corresponding aldehyde, which is the tautomeric form of lactol **15**. Stereoselectivity of the reaction is therefore attributed to the osmylation step and is in complete agreement with Kishi's empirical rule for dihydroxylation of allylic alcohol derivatives.[22]

3. Conclusions

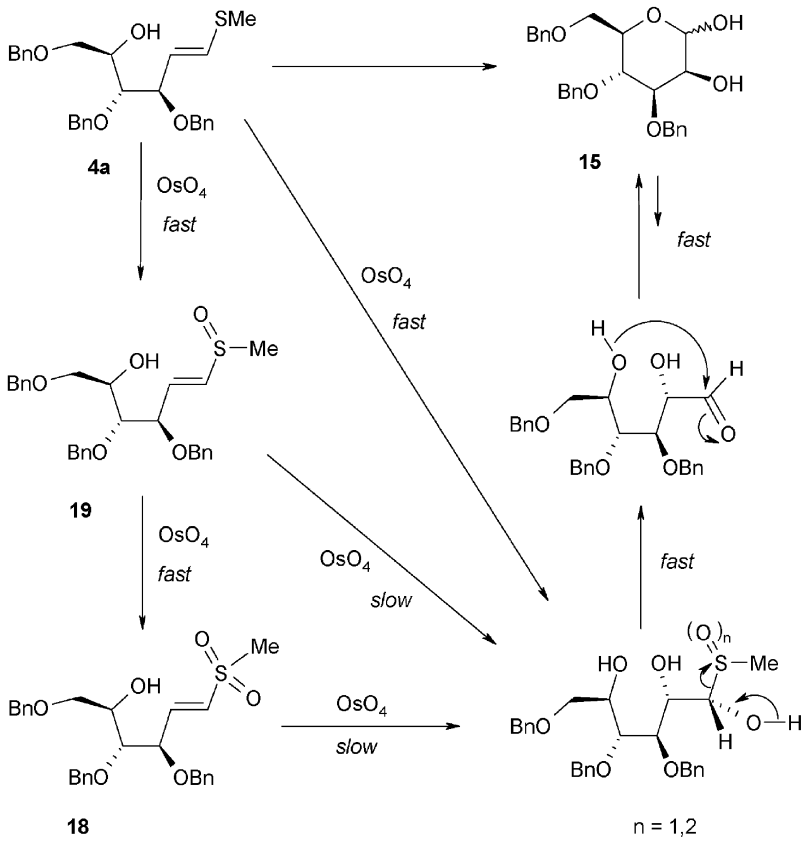
The synthesis of open-chain γ-hydroxy vinyl sulfides can efficiently be performed by treating suitably protected furano- or pyrano-lactols by thiofunctionalized phosphoranylidene reagents. The results for this Wittig reaction are more contrasted in the case of pyrano-lactols, depending on the protective groups.

Preliminary experiments allow to spot out the above vinyl sulfides as promising intermediates for the elaboration of stereoselectively functionalized carbohydrate mimics, and in particular new and selectively protected lactols.

4. Experimental

4.1. General methods

Melting points were determined on a Köfler hot-stage



Scheme 5. Proposed mechanism for the osmylation of vinyl sulfide **4a**.

apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX250 at 250 and 62.89 MHz, respectively. The chemical shifts (δ) are reported in ppm downfield from TMS as the internal standard. Coupling constants (J) are reported in Hz. Specific rotations were measured at 20 °C using a Perkin–Elmer polarimeter 141. HR-ESI-TOF-mass spectra were recorded on a Micromass LC TOF spectrometer. Evaporation was conducted in vacuo with a Büchi rotary evaporator. Analytical TLC was carried out on precoated silica gel 60F-254 plates (E. Merck) and spots were detected by UV light (254 nm) and by heat treatment with a 10:85:5 mixture of sulfuric acid, ethanol and water. Flash column chromatography was performed on Kieselgel 60 (230–400 mesh) silica gel (E. Merck). Methylthiomethyl triphenylphosphonium chloride was prepared from methylthiomethyl chloride.[23] Phenylthiomethyl triphenylphosphonium chloride was purchased from Lancaster.

4.2. Chemical procedure

4.2.1. General method for the synthesis of vinyl sulfides. A 1.6 M *n*-butyllithium solution in hexanes (2.19 mL, 3.5 mmol) was added slowly to an ice-cold suspension of 3.5 mmol methylthiomethyl or phenylthiomethyl triphenylphosphonium chloride in 10 mL dry THF. After 30 min stirring at room temperature, 1 mmol lactol was added. Non-solid lactols were solubilized in a small volume of dry THF prior to addition. The solution was stored at room temperature for 48 h, quenched with water (10 mL), extracted (3×10 mL ethyl acetate) then dried over $MgSO_4$. Evaporation of the solvents gave a brownish solid which was purified by flash column chromatography.

4.2.2. 1-(*E*)-3,4,6-Tri-*O*-benzyl-1,2-dideoxy-1-methylthio-D-*arabino*-hex-1-enitol (4a). Prepared from commercial 2,3,5-tri-*O*-benzyl-D-arabinofuranose **3a**. Eluent: petroleum ether–ethyl acetate 85:15; yellow oil; $[\alpha]_D$=+30 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 3H, MeS), 3.54–3.62 (m, 3H, H-4, H-6a, H-6b), 4.01 (m, 1H, H-5), 4.11 (dd, 1H, J_{2-3}=8.1 Hz, J_{3-4}=3.9 Hz, H-3), 4.34 (d, 1H, J_{gem}=11.9 Hz, CH_2Ph), 4.47–4.65 (m, 5H, CH_2Ph), 5.43 (dd, 1H, J_{1-2}=15.3 Hz, H-2), 6.28 (d, 1H, H-1), 7.22–7.37 (m, 15H, H_{Ar}). ^{13}C NMR: δ 14.8 (MeS), 70.8 (C-5 and CH_2Ph), 71.4 (C-6), 73.8, 74.6 (CH_2Ph), 80.2 (C-3), 81.4 (C-4), 121.5 (C-1), 130.4 (C-2), 128.2, 128.3, 128.5, 128.6, 128.8, 128.9, 138.4, 138.5, 138.6 (C_{Ar}). HRMS: $C_{28}H_{32}O_4S$ calcd. 464.2021; found 464.2032.

4.2.3. 3,4,6-Tri-*O*-benzyl-1,2-dideoxy-1-phenylthio-D-*arabino*-hex-1-enitols (5a). Prepared from commercial 2,3,5-tri-*O*-benzyl-D-arabinofuranose **3a**. Eluent: petroleum ether–ethyl acetate 85:15; colorless oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 2.73–2.83 (m, 1H, OH), 3.54–3.62 (m, 3H, H-4, H-6a, H-6b), 4.01 (m, 1H, H-5), 4.16 (ddd, 1H, J_{1-3}=0.6 Hz, J_{2-3}=7.5 Hz, J_{3-4}=3.5 Hz, H-3), 4.34 and 4.63 (2d, 2H, J_{gem}=11.2 Hz, CH_2Ph), 4.48 (s, 2H, CH_2Ph), 4.52 and 4.58 (2d, 2H, J_{gem}=11.4 Hz, CH_2Ph), 5.84 (dd, 1H, J_{1-2}=15.4 Hz, H-2), 6.42 (dd, 1H, H-1), 7.22–7.47 (m, 20H, H_{Ar}); *Z* isomer: δ 2.96 (m, 1H, OH), 3.54–3.62 (m, 2H, H-6a, H-6b), 3.69 (dd, 1H, J_{3-4}=3.8 Hz, J_{4-5}=6.6 Hz, H-4), 4.01 (m, 1H, H-5), 4.35–4.78 (m, 7H, H-3, 3×CH_2Ph), 5.95 (dd, 1H, J_{1-2}=9.7 Hz, J_{2-3}=9.7 Hz, H-2), 6.50 (dd, 1H, J_{1-3}=0.6 Hz, H-1), 7.22–7.47 (m, 20H, H_{Ar}). ^{13}C NMR: *E* isomer: δ 70.3 (C-5), 70.9 (CH_2Ph), 71.0 (C-6), 73.4, 74.3 (CH_2Ph), 79.4 (C-3), 80.7 (C-4), 128.0 (C-1), 128.5 (C-2), 127.2, 127.7, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 134.4, 137.8, 138.1 (C_{Ar}); *Z* isomer (selected peaks): δ 70.7 (C-5), 71.1 (CH_2Ph), 71.2 (C-6), 73.4, 74.1 (CH_2Ph), 75.9 (C-3), 80.4 (C-4). HRMS: $C_{33}H_{34}O_4S$ calcd. 526.2178; found 526.2183.

4.2.4. 1,2-Dideoxy-3,4-*O*-isopropylidene-1-methylthio-6-*O*-trityl-D-*ribo*-hex-1-enitols (4b). Prepared from 2,3-*O*-isopropylidene-5-*O*-trityl-D-ribofuranose **3b**.[24] Eluent: petroleum ether–ethyl acetate 90:10; colorless oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.32 (s, 6H, Me_2C), 2.17 (s, 3H, SMe), 2.64 (m, 1H, OH), 3.25–3.42 (m, 2H, H-6a, H-6b), 3.68–3.85 (m, 1H, H-5), 4.03–4.24 (m, 1H, H-4), 4.71 (dd, 1H, J_{2-3}=7.8 Hz, J_{3-4}=6.7 Hz, H-3), 5.47 (dd, 1H, J_{1-2}=14.9 Hz, H-2), 6.35 (dd, 1H, H-1), 7.12–7.52 (m, 5H, HAr); *Z* isomer: δ 1.32, 1.35 (2s, 2×3H, Me_2C), 2.17 (s, 3H, SMe), 2.64 (m, 1H, OH), 3.25–3.42 (m, 2H, H-6a, H-6b), 3.68–3.85 (m, 1H, H-5), 4.03–4.24 (m, 1H, H-4), 5.06 (dd, 1H, J_{2-3}=9.2 Hz, J_{3-4}=6.4 Hz, H-3), 5.61 (dd, 1H, J_{1-2}=9.4 Hz, H-2), 6.16 (dd, 1H, H-1), 7.12–7.52 (m, 5H, HAr). ^{13}C NMR: *E* isomer: δ 14.4 (MeS), 25.3, 27.8 (2*Me), 65.1 (C-6), 69.2 (C-5), 77.9 (C-4), 78.6 (C-3), 86.7 (*C*Ph_3), 108.4 (C_{IV}-iPrd), 120.0 (C-2), 127.0, 127.8, 128.6 (C_{Ar}), 129.2 (C-1), 143.8 (C_{Ar}); *Z* isomer: δ 17.4 (MeS), 25.3, 27.7 (2*Me), 65.1 (C-6), 69.8 (C-5), 74.7 (C-3), 77.8 (C-4), 86.6 (*C*Ph_3), 108.6 (C_{IV}-iPrd), 123.6 (C-2), 127.0, 127.8, 128.6 (C_{Ar}), 131.9 (C-1), 143.8 (C_{Ar}). HRMS: $C_{29}H_{32}O_4S$ calcd 476.2021; found 476.2013.

4.2.5. 1,2-Dideoxy-3,4-*O*-isopropylidene-1-phenylthio-6-*O*-trityl-D-*ribo*-hex-1-enitols (5b). Prepared from 2,3-*O*-isopropylidene-5-*O*-trityl-D-ribofuranose **3b**.[24] Eluent: petroleum ether–ethyl acetate 90:10; colorless oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.33, 1.36 (2s, 2×3H, Me_2C), 2.50 (m, 1H, OH), 3.32–3.37 (m, 2H, H-6a, H-6b), 3.62–3.75 (m, 1H, H-5), 4.14 (dd, 1H, J_{3-4}=8.7 Hz, J_{4-5}=6.3 Hz, H-4), 4.74 (dd, 1H, J_{2-3}=7.0 Hz, H-3), 5.92 (dd, 1H, J_{1-2}=15.1 Hz, H-2), 6.49 (dd, 1H, H1); *Z* isomer: δ 1.36, 1.37 (2s, 2×3H, Me_2C), 2.34 (m, 1H, OH), 3.32–3.37 (m, 2H, H-6a, H-6b), 3.72–3.85 (m, 1H, H-5), 4.24 (dd, 1H, J_{3-4}=8.1 Hz, J_{4-5}=6.5 Hz, H-4), 5.20 (dd, 1H, J_{2-3}=8.7 Hz, H-3), 5.83 (dd, 1H, J_{1-2}=9.3 Hz, H-2), 6.45 (dd, 1H, H-1), 7.22–7.37 (m, 15H, H_{Ar}). ^{13}C NMR: *E* isomer (selected peaks): δ 21.6, 27.9 (2*Me), 65.2 (C-6), 69.3 (C-5), 78.1 (C-4), 78.4 (C-3), 86.9 (*C*Ph_3), 109.0 (C_{IV}-iPrd), 125.4 (C-2), 130.0 (C-1); *Z* isomer (selected peaks): δ 25.5, 27.9 (2*Me), 65.0 (C-6), 69.9 (C-5), 75.0 (C-3), 78.1 (C-4), 86.9 (*C*Ph_3), 109.0 (C_{IV}-iPrd), 126.9 (C-2), 128.5 (C-1). HRMS: $C_{34}H_{34}O_4S$ calcd 538.2178; found 538.2190.

4.2.6. 1,2-Dideoxy-3,4-*O*-isopropylidene-1-methylthio-6-*O*-pivaloyl-D-*ribo*-hex-1-enitols (4c). Reaction of 2,3-*O*-isopropylidene-5-*O*-pivaloyl-D-ribofuranose **3c**[25] with phosphorane **1** afforded a mixture of **4c**, a de-*O*-acylated compound **8** and its di-*O*-pivaloylated derivative **12** that could easily be separated using standard flash column chromatography. Due to its contamination with reaction side-products including triphenylphosphine oxide, **8** could not be satisfactorily characterized: it was therefore, peracetylated under standard procedure to give pure **10**.

Vinyl sulfide **4c**. Eluent: petroleum ether–ethyl acetate 80:20; yellowish oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.24 (s, 9H, Me_3C), 1.36, 1.47 (2s, 2×3H, Me_2C), 2.33 (m, 1H, OH), 2.29 (s, 3H, SMe), 3.75–3.92 (m, 1H, H-5), 4.01–4.21 (m, 3H, H-6b, H-5, H-4), 4.30–4.43 (m, 1H, H-6a), 5.08 (ddd, 1H, J_{2-3}=8.8 Hz, J_{3-4}=6.0 Hz, J_{1-3}=0.9 Hz, H-3), 5.70 (dd, 1H, J_{1-2}=15.1 Hz, H-2), 6.35 (dd, 1H, H-1); *Z* isomer: δ 1.23 (s, 9H, Me_3C), 1.37, 1.47 (2s, 2×3H, Me_2C), 2.33 (m, 1H, OH), 2.31 (s, 1H, SMe), 3.75–3.92 (m, 1H, H-5), 4.01–4.21 (m, 3H, H-6b, H-5, H-4), 4.30–4.43 (m, 1H, H-6a), 4.76 (ddd, 1H, J_{2-3}=7.3 Hz, J_{3-4}=6.0 Hz, J_{1-3}=1.0 Hz, H-3), 5.51 (dd, 1H, J_{1-2}=15.1 Hz, H-2), 6.35 (dd, 1H, H-1). ^{13}C NMR: *E* isomer: δ 14.7 (MeS), 25.4, 27.8 (2*Me), 27.3 (Me_3C), 39.0 (CMe_3), 66.7 (C-6), 69.5 (C-5), 77.4 (C-4), 78.6 (C-3), 109.2 (C_{IV}-iPrd), 119.7 (C-2), 132.6 (C-1), 179.2 (CO); *Z* isomer: δ 17.6 (MeS), 25.4, 27.8 (2*Me), 27.3 (Me_3C), 39.0 (CMe_3), 65.5 (C-6), 69.1 (C-5), 74.7 (C-3), 77.7 (C-4), 108.9 (C_{IV}-iPrd), 123.4 (C-2), 130.2 (C-1), 179.0 (CO). HRMS: $C_{15}H_{26}O_5S$ calcd 318.1501; found 318.1497.

4.2.7. 5,6-Di-*O*-acetyl-1,2-dideoxy-3,4-*O*-isopropylidene-1-methylthio-D-*ribo*-hex-1-enitols (10). Obtained from acetylation of raw **8**. Eluent: petroleum ether–ethyl acetate 90:10; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.37, 1.48 (2s, 2×3H, Me_2C), 2.02, 2.06 (2s, 2×3H, CH_3CO), 2.23 (s, 3H, SMe), 4.04–4.16 (m, 1H, H-6b), 4.25 (dd, 1H, J_{3-4}=9.0 Hz, J_{4-5}=6.4 Hz, H-4), 4.47–4.62 (m, 1H, H-6a), 4.75 (ddd, 1H, J_{2-3}=8.2 Hz, J_{3-4}=6.1 Hz, J_{1-3}=0.9 Hz, H-3), 4.95–5.13 (m, 1H, H-5), 5.25 (dd, 1H, J_{1-2}=14.7 Hz, H-2), 6.43 (dd, 1H, H-1); *Z* isomer: δ 1.39, 1.48 (2s, 2×3H, Me_2C), 2.02, 2.06 (2s, 2×3H, CH_3CO), 2.29 (s, 3H, SMe), 4.04–4.16 (m, 1H, H-6b), 4.30 (dd, 1H, J_{3-4}=8.3 Hz, J_{4-5}=6.4 Hz, H-4), 4.47–4.62 (m, 1H, H-6a), 4.95–5.13 (m, 2H, H-3, H-5), 5.56 (dd, 1H, J_{1-2}=9.8 Hz, H-2), 6.20 (dd, 1H, H-1). ^{13}C NMR: *E* isomer: δ 14.1 (MeS), 20.8, 21.1 (CH_3CO), 25.1, 27.6 (2*Me), 63.3 (C-6), 69.3 (C-5), 75.4 (C-4), 81.6 (C-3), 109.0 (C_{IV}-iPrd), 122.8 (C-1), 130.9 (C-2), 169.9, 170.8 (CO); *Z* isomer: δ 17.5 (MeS), 20.8, 20.9 (CH_3CO), 25.2, 27.6 (2*Me), 63.3 (C-6), 69.7 (C-5), 74.5 (C-3), 75.3 (C-4), 109.2 (C_{IV}-iPrd), 117.8 (C-1), 132.4 (C-2), 170.0, 170.8 (CO). HRMS: $C_{14}H_{22}O_6S$ calcd 318.1137; found 318.1124.

4.2.8. 1,2-Dideoxy-3,4-*O*-isopropylidene-1-methylthio-5,6-di-*O*-pivaloyl-D-*ribo*-hex-1-enitols (12). Eluent: petroleum ether–ethyl acetate 85:15; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.16 (s, 9H, Me_3C), 1.20 (s, 9H, Me_3C), 1.25 (s, 3H, Me_2C), 1.36 (s, 3H, Me_2C), 2.23 (s, 3H, SMe), 4.09 (dd, 1H, J_{6a-6b}=12.3 Hz, J_{5-6b}=5.1 Hz, H-6b), 4.27 (dd, 1H, J_{4-5}=9.4 Hz, J_{3-4}=6.3 Hz, H-4), 4.51 (dd, 1H, J_{5-6a}=2.2 Hz, H-6a), 4.70 (ddd, J_{2-3}=8.4 Hz, J_{1-3}=0.6 Hz, H-3), 5.01–5.17 (m, 1H, H-5), 5.25 (dd, 1H, J_{1-2}=15.0 Hz, H-2), 6.39 (dd, 1H, H-1); *Z* isomer: δ 1.17 (s, 9H, Me_3C), 1.20 (s, 9H, Me_3C), 1.38 (s, 3H, Me_2C), 1.48 (s, 3H, Me_2C), 2.27 (s, 3H, SMe), 4.09 (dd, 1H, J_{6a-6b}=12.3 Hz, J_{5-6b}=5.1 Hz, H-6b), 4.28 (dd, 1H, J_{2-3}=7.9 Hz, J_{3-4}=6.3 Hz, H-4), 4.37 (dd, 1H, J_{5-6a}=2.3 Hz, H-6a), 5.01–5.17 (m, 2H, H-3, H-5), 5.57 (dd, 1H, J_{1-2}=9.7 Hz, J_{2-3}=8.8 Hz, H-2), 6.39 (dd, 1H, H-1). ^{13}C NMR ($CDCl_3$): *E* isomer: δ 14.2 (MeS), 25.3 (Me_2C), 27.1 (2*Me_3C), 27.8 (Me_2C), 38.9 (2*Me_3C), 63.8 (C-6), 68.1 (C-5), 75.6 (C-4), 78.8 (C-3), 109.0 (C_{IV}-iPrd), 122.2 (C-1), 133.4 (C-2), 176.6, 177.0 (CO); *Z* isomer: δ 17.6 (MeS), 25.2 (Me_2C), 27.1 (2*Me_3C), 27.8 (Me_2C), 39.0 (2*Me_3C), 63.5 (C-6), 69.6 (C-5), 74.3 (C-3), 75.5 (C-4), 109.1 (C_{IV}-iPrd), 124.1 (C-1), 131.6 (C-2), 176.6, 177.0 (CO). HRMS: $C_{20}H_{34}O_6S$ calcd 402.2076; found 402.2068.

4.2.9. 1,2-Dideoxy-3,4-*O*-isopropylidene-1-phenylthio-6-*O*-pivaloyl-D-*ribo*-hex-1-enitols (5c). Reaction of 2,3-*O*-isopropylidene-5-*O*-pivaloyl-D-ribofuranose **3c**[25] with phosphorane **2** afforded a mixture of **5c**, a de-*O*-acylated compound **9** and its di-*O*-pivaloylated derivative **13** that could easily be separated using standard flash column chromatography. Due to its contamination with reaction side-products including triphenylphosphine oxide, **9** could not be satisfactorily characterized: it was therefore peracetylated under standard procedure to give pure **11**.

Vinyl sulfide **5c**. Eluent: petroleum ether–ethyl acetate 80:20; yellowish oil. ^{1}H NMR ($CDCl_3$): *E* isomer: 1.23 (s, 9H, Me_3C), 1.35, 1.46 (2s, 2×3H, Me_2C), 2.37 (m, 1H, OH), 3.77–3.95 (m, 1H, H-5), 4.02–4.24 (m, 3H, H-4, H-5, H-6b), 4.33–4.42 (m, 1H, H-6a), 4.78 (dd, 1H, J_{2-3}=J_{3-4}=6.6 Hz, H-3), 5.92 (dd, 1H, J_{1-2}=14.9 Hz, H-2), 6.57 (dd, 1H, H-1), 7.18–7.42 (m, 5H, HAr); *Z* isomer: δ 1.23 (s, 9H, Me_3C), 1.39, 1.50 (2s, 2×3H, Me_2C), 2.37 (m, 1H, OH), 3.75–3.92 (m, 1H, H-5), 4.12–4.21 (m, 3H, H-4, H-5, H-6b), 4.30–4.43 (m, 1H, H-6a), 5.23 (dd, 1H, J_{2-3}=J_{3-4}=7.7 Hz, H-3), 5.91 (dd, 1H, J_{1-2}=9.6 Hz, H-2), 6.52 (dd, 1H, H-1), 7.18–7.42 (m, 5H, HAr). ^{13}C NMR: *E* isomer: δ 25.4, 27.9 (2*Me), 27.3 (Me_3C), 66.9 (C-6), 69.0 (C-5), 77.6 (C-3), 77.8 (C-4), 109.2 (C_{IV}-iPrd), 127.1 (C_{Ar}), 127.2 (C-1), 127.7 (C-2), 129.2, 130.2, 134.6 (C_{Ar}), 179.1 (CO); *Z* isomer: δ 25.4, 27.9 (2*Me), 27.3 (Me_3C), 66.7 (C-6), 69.5 (C-5), 74.8 (C-3), 78.1 (C-4), 109.3 (C_{IV}-iPrd), 126.7 (C-1), 129.1 (C-2), 127.1, 129.2, 129.8, 135.3 (C_{Ar}), 179.1 (CO). HRMS: $C_{20}H_{28}O_5S$ calcd 380.1657; found 380.1670.

4.2.10. 5,6-Di-*O*-acetyl-1,2-dideoxy-3,4-*O*-isopropylidene-1-phenylthio-D-*ribo*-hex-1-enitols (11). Obtained from acetylation of raw **9**. Eluent: petroleum ether–ethyl acetate 90:10; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.37, 1.47 (2s, 2×3H, Me_2C), 2.03, 2.07 (2s, 2×3H, CH_3CO), 4.11 (dd, 1H, J_{6a-6b}=12.4 Hz, J_{5-6b}=4.9 Hz, H-6b), 4.27 (dd, 1H, J_{3-4}=8.9 Hz, J_{4-5}=6.2 Hz, H-4), 4.55 (dd, 1H, J_{5-6a}=2.6 Hz, H-6a), 4.75 (ddd, 1H, J_{2-3}=7.25 Hz, J_{1-3}=1.1 Hz, H-3), 4.95 (ddd, 1H, H-5), 5.66 (dd, 1H, J_{1-2}=15.2 Hz, H-2), 6.43 (dd, 1H, H-1), 7.20–7.47 (m, 5H, HAr); *Z* isomer: δ 1.42, 1.51 (2s, 2×3H, Me_2C), 2.04, 2.08 (2s, 2×3H, CH_3CO), 4.12 (dd, 1H, J_{6a-6b}=12.6 Hz, J_{5-6b}=5.8 Hz, H-6b), 4.35 (dd, 1H, J_{3-4}=8.5 Hz, J_{4-5}=6.2 Hz, H-4), 4.56 (dd, 1H, J_{5-6a}=2.6 Hz, H-6a), 5.04 (ddd, 1H, H-5), 5.19 (ddd, 1H, J_{2-3}=9.2 Hz, J_{1-3}=0.9 Hz, H-3), 5.77 (dd, 1H, J_{1-2}=9.4 Hz, H-2), 6.46 (dd, 1H, H-1), 7.20–7.47 (m, 5H, HAr). ^{13}C NMR ($CDCl_3$): *E* isomer: δ 22.9, 23.0 (CH_3CO), 27.3, 29.7 (2*Me), 65.0 (C-6), 71.4 (C-5), 77.4 (C-4), 79.9 (C-3), 111.3 (C_{IV}-iPrd), 126.1 (C-1), 130.8 (C-2), 129.2, 131.3, 131.6, 137.0 (C_{Ar}), 171.7, 172.0 (CO); *Z* isomer: δ 23.0, 23.2 (CH_3CO), 27.4, 29.7 (2*Me), 65.3 (C-6), 71.7 (C-5), 76.6 (C-3), 77.4 (C-4), 111.5 (C_{IV}-iPrd), 127.8 (C-1), 131.0 (C-2), 129.4, 131.3, 132.7, 138.9 (C_{Ar}), 171.7, 172.0 (CO). HRMS: $C_{19}H_{24}O_6S$ calcd 380.1293; found 380.1301.

4.2.11. 1,2-Dideoxy-3,4-*O*-isopropylidene-1-phenylthio-5,6-di-*O*-pivaloyl-D-*ribo*-hex-1-enitols (13). Eluent: petroleum ether–ethyl acetate 92:8; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.17 (s, 9H, Me_3C), 2.21 (s, 3H, Me_2C), 1.26 (s, 3H, Me_2C), 1.37 (s, 3H, Me_2C), 4.12 (dd, 1H, J_{6a-6b}=12.2 Hz, J_{6a-5}=5.3 Hz, H-6b), 4.27–4.38 (m, 1H, H-4), 4.45–4.57 (m, 1H, H-6a), 4.71 (dd, 1H, J_{2-3}=7.5 Hz, J_{3-4}=6.3 Hz, H-3), 4.96–5.05 (m, 1H, H-5), 5.66 (dd, 1H, J_{1-2}=14.9 Hz, H-2), 6.50 (d, 1H, H-1), 7.20–7.48 (m, 5H, HAr); *Z* isomer: δ 1.17 (s, 9H, Me_3C), 2.21 (s, 9H, Me_2C), 1.41 (s, 3H, Me_2C), 1.51 (s, 3H, Me_2C), 4.12 (dd, 1H, J_{6a-6b}=12.2 Hz, J_{6a-5}=5.3 Hz, H-6b), 4.27–4.38 (m, 1H, H-4), 4.52 (dd, J_{6a-5}=2.4 Hz, H-6a), 5.15 (m, 2H, H-3, H-5), 5.78 (dd, 1H, J_{1-2}=9.6 Hz, H-2), 6.45 (dd, 1H, J_{1-3}=0.6 Hz, H-1), 7.20–7.48 (m, 5H, HAr). ^{13}C NMR ($CDCl_3$): *E* isomer: δ 25.5 (Me_2C), 27.2 (2^*Me_3C), 27.8 (Me_2C), 38.9 (2^*CMe_3), 63.2 (C-6), 69.3 (C-5), 75.5 (C-4), 78.2 (C-3), 109.2 (C_{IV}-iPrd), 124.5 (C-2), 127.4, 129.5, 130.1 (C_{Ar}), 129.5 (C-1), 134.2 (C_{Ar}); *Z* isomer: δ 25.5 (Me_2C), 27.2 (2^*Me_3C), 27.8 (Me_2C), 38.9 (2^*CMe_3), 63.5 (C-6), 69.5 (C-5), 74.3 (C-3), 75.7 (C-4), 109.4 (C_{IV}-iPrd), 124.9 (C-2), 127.2, 129.3, 129.8 (C_{Ar}), 130.8 (C-1), 135.1 (C_{Ar}). HRMS: $C_{25}H_{36}O_6S$ calcd 464.2232; found 464.2221.

4.2.12. 1,2-Dideoxy-3,4,6,7-di-*O*-isopropylidene-1-methylthio-D-*manno*-hept-1-enitols (4d). Prepared from commercial 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose **3d**. Eluent: petroleum ether–ethyl acetate 85:15; yellowish oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.35, 1.40, 1.52 (3s, 4×3H, Me_2C), 2.22 (d, 1H, OH, J_{OH-5}=7.4 Hz), 2.29 (s, 3H, SMe), 3.45 (ddd, 1H, J_{5-6}=7.4 Hz, J_{4-5}=1.4 Hz, H-5), 3.95–4.12 (m, 3H, H-6, H-7a, H-7b), 4.34 (dd, 1H, J_{3-4}=7.5 Hz, H-4), 4.78 (dd, 1H, J_{2-3}=8.5 Hz, H-3), 5.62 (dd, 1H, J_{1-2}=14.9 Hz, H-2), 6.47 (dd, 1H, H-1); *Z* isomer: δ 1.35, 1.40, 1.42, 1.53 (4s, 4×3H, Me_2C), 2.13 (d, 1H, OH, J_{OH-5}=7.4 Hz), 2.31 (s, 3H, SMe), 3.40 (ddd, 1H, J_{5-6}=7.6 Hz, J_{4-5}=1.2 Hz, H-5), 3.95–4.12 (m, 3H, H-6, H-7a, H-7b), 4.44 (dd, 1H, J_{3-4}=7.5 Hz, H-4), 5,11 (ddd, 1H, J_{2-3}=8.7 Hz, J_{1-3}=0.9 Hz, H-3), 5.83 (dd, 1H, J_{1-2}=9.6 Hz, H-2), 6.22 (dd, 1H, H-1). ^{13}C NMR: *E* isomer: δ 14.4 (MeS), 24.5, 25.3, 26.7, 26.9 (4^*Me), 67.1 (C-7), 70.7 (C-5), 76.2 (C-6), 76.2 (C-4), 79.2 (C-3), 108.2, 109.4 (2^*C_{IV}-iPrd), 119.4 (C-2), 132.4 (C-1); *Z* isomer: 17.5 (MeS), 24.4, 25.4, 26.6, 26.9 (4^*Me), 66.8 (C-7), 70.4 (C-5), 74.7 (C-3), 76.1 (C-6), 76.6 (C-4), 108.6, 109.3 (2^*C_{IV}-iPrd), 124.7 (C-2), 131.5 (C-1). HRMS: $C_{14}H_{24}O_5S$ calcd 304.1344; found 304.1349.

4.2.13. 1,2-Dideoxy-3,4,6,7-di-*O*-isopropylidene-1-phenylthio-D-*manno*-hept-1-enitols (5d). Prepared from commercial 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose **3d**. Eluent: petroleum ether–ethyl acetate 85:15; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.35, 1.40, 1.51 (3s, 4×3H, Me_2C), 2.14 (d, 1H, OH, J_{OH-5}=7.7 Hz), 3.45 (ddd, 1H, J_{5-6}=7.7 Hz, J_{4-5}=1.5 Hz, H-5), 3.95–4.15 (m, 3H, H-6, H-7a, H-7b), 4.36 (dd, 1H, J_{3-4}=7.3 Hz, H-4), 4.78 (dd, 1H, J_{2-3}=8.3 Hz, H-3), 6.02 (dd, 1H, J_{1-2}=15.1 Hz, H-2), 6.57 (dd, 1H, H-1); 7.20–7.41 (m, 5H, HAr); *Z* isomer: δ 1.36), 1.42, 1.44, 1.55 (4s, 4×3H, Me_2C), 2.18 (d, 1H, OH, J_{OH-5}=7.7 Hz), 3.44 (ddd, 1H, J_{5-6}=7.7 Hz, J_{4-5}=0.8 Hz, H-5), 3.97–4.15 (m, 3H, H-6, H-7a, H-7b), 4.51 (dd, 1H, J_{3-4}=7.7 Hz, H-4), 5.24 (ddd, 1H, J_{2-3}=7.8 Hz, J_{3-4}=7.7 Hz, H-3), 6.07 (dd, 1H, J_{1-2}=9.5 Hz, H-2), 6.49 (dd, 1H, H-1); 7.20–7.41 (m, 5H, HAr). ^{13}C NMR: *E* isomer: δ 24.4, 25.5, 26.7, 27.1 (4^*Me), 67.0 (C-7), 70.6 (C-5), 74.7 (C-3), 76.2 (C-6), 76.5 (C-4), 108.9, 109.5 (2^*C_{IV}-iPrd), 127.2 (C-2), 128.1 (C_{Ar}), 128.2 (C-1), 129.3, 129.6, 135.0 (C_{Ar}),; *Z* isomer: δ 24.6, 25.4, 26.8, 26.9 (4^*Me), 67.2 (C-7), 70.7 (C-5), 76.2 (C-6), 76.9 (C-4), 78.6 (C-3), 108.7, 109.5 (2^*C_{IV}-iPrd), 126.5 (C-2), 130.4 (C-1), 127.4, 129.3, 130.6, 134.4 (C_{Ar}). HRMS: $C_{19}H_{26}O_5S$ calcd 366.1501; found 366.1511.

4.2.14. 1,2-Dideoxy-3,4,5,7-di-*O*-isopropylidene-1-methylthio-D-*manno*-hept-1-enitols (4e). Prepared from 2,3:4,6-di-*O*-isopropylidene-D-mannopyranose **3e**.[26] Eluent: petroleum ether–ethyl acetate 85:15; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.38, 1.42, 1.48, 1.53 (4s, 4×3H, Me_2C), 2.27 (s, 3H, SMe), 3.52–3.69 (m, 2H, H-5, H-7b), 3.85–3.98 (m, 2H, H-6, H-7a), 4.39 (dd, 1H, J_{3-4}=7.0 Hz, J_{4-5}=1.3 Hz, H-4), 4.79 (dd, 1H, J_{2-3}=6.7 Hz, H-3), 5.76 (dd, 1H, J_{1-2}=14.9 Hz, H-2), 6.17 (dd, 1H, H-1); *Z* isomer: δ 1.39, 1.40, 1.42, 1.53 (4s, 4×3H, Me_2C), 2.31 (s, 3H, SMe), 2.92–3.05 (m, 1H, OH), 3.43 (dd, 1H, J_{5-6}=8.9 Hz, J_{4-5}=1.5 Hz, H-5), 3.55–3.67 (m, 1H, H-7b), 3.78–3.93 (m, 2H, H-6, H-7a), 4.48 (dd, 1H, J_{3-4}=7.2 Hz, H-4), 5.12 (ddd, 1H, J_{2-3}=7.7 Hz, J_{1-3}=1.3 Hz, H-3,), 5.76 (dd, 1H, J_{1-2}=9.8 Hz, H-2), 6.17 (dd, 1H, H-1). ^{13}C NMR: δ *E* isomer: 14.3 (MeS), 21.1, 26.0, 26.4, 28.6 (4^*Me), 60.5 (C-7), 62.7 (C-6), 73.0 (C-5), 75.7 (C-4), 79.0 (C-3), 98.6, 109.3 (2^*C_{IV}-iPrd), 118.8 (C-2), 131.9 (C-1); *Z* isomer: δ 17.5 (MeS), 19.2, 26.0, 26.4, 28.6 (4^*Me), 62.8 (C-6), 64.9 (C-7), 73.0 (C-5), 74.7 (C-3), 75.1 (C-4), 98.6, 109.4 (2^*C_{IV}-iPrd), 124.5 (C-2), 130.9 (C-1). HRMS: $C_{14}H_{24}O_5S$ calcd 304.1344; found 304.1331.

4.2.15. 1,2-Dideoxy-3,4,5,7-di-*O*-isopropylidene-1-phenylthio-D-*manno*-hept-1-enitols (5e). Reaction of **3e** with phosphorane **2** afforded **5e** contaminated with side-products including triphenylphosphine oxide; the crude mixture was first acetylated under standard procedure to give pure 6-*O*-acetyl-1,2-dideoxy-3,4,5,7-di-*O*-isopropylidene-1-phenylthio-D-*manno*-hept-1-enitols **14**. Eluent: petroleum ether–ethyl acetate 90:10; colorless oil. ^{1}H NMR (C_6D_6): *E* isomer: δ 1.24 (s, 3H, Me_2C), 1.29 (s, 3H, Me_2C), 1.35 (s, 3H, Me_2C), 1.60 (s, 3H, Me_2C), 1.59 (s, 3H, CH_3CO), 3.54 (dd, 1H, J_{7a-7b}=12.0 Hz, J_{6-7b}=6.0 Hz, H-7b), 3.70 (dd, 1H, J_{4-5}=1.3 Hz, J_{5-6}=8.5 Hz, H-5), 4.07 (dd, 1H, J_{6-7a}=4.5 Hz, H-7a), 4.19 (dd, 1H, J_{3-4}=7.2 Hz, H-4), 4.59 (dd, 1H, J_{2-3}=7.9 Hz, H-3), 5.34 (ddd, 1H, H-6), 6.12 (dd, 1H, J_{1-2}=15.1 Hz, H-2), 6.32 (d, 1H, H-1), 7,22–7,42 (m, 5H, HAr); *Z* isomer: δ 1.23 (s, 3H, Me_2C), 1.29 (s, 3H, Me_2C), 1.30 (s, 3H, Me_2C), 1.55 (s, 3H, Me_2C), 1.59 (s, 3H, CH_3CO), 3.50 (dd, 1H, J_{7a-7b}=11.9 Hz, J_{6-7b}=6.2 Hz, H-7b), 3.70 (dd, 1H, J_{4-5}=1.0 Hz, J_{5-6}=8.0 Hz, H-5), 4.02 (dd, 1H, J_{6-7a}=5.0 Hz, H-7a), 4.44 (dd, 1H, J_{3-4}=7.2 Hz, H-4), 5.25 (ddd, 1H, H-6), 5.35 (dd, 1H, J_{2-3}=6.2 Hz, H-3), 6.09 (dd, 1H, J_{1-2}=9.5 Hz, H-2), 6.15 (d, 1H, H-1), 7,22–7,42 (m, 5H, HAr). ^{13}C NMR (C_6D_6): *E* isomer: δ 20.5, 21.0, 26.1, 26.8 (Me_2C), 62.4 (C-7), 68.0 (C-6), 70.2 (C-5), 76.9 (C-4), 78.6 (C-3), 99.7, 109.7 (C_{IV}-iPrd), 127.36 (C_{Ar}), 125.0 (C-2), 126.3 (C-1), 129.5, 130.8, 132.4 (C_{Ar}), 169.5 (CO); *Z* isomer: δ 20.5, 21.0, 26.7, 27.0 (Me_2C), 62.4 (C-6), 67.6 (C-7), 70.3 (C-5), 75.2 (C-3), 76.4 (C-4), 99.6, 109.9 (C_{IV}-iPrd), 126.1 (C-2), 127.1, 129.5, 129.6 (C_{Ar}), 129.9

(C-1), 135.6 (C_{Ar}), 169.5 (CO). HRMS: $C_{21}H_{28}O_6S$ calcd 408.1606; found 408.1599.

A solution of **14** (409 mg, 1 mmol) in 5 mL methanol was treated at RT by sodium methoxide (1 M in methanol, 50 μL, 0.05 equiv.). The reaction mixture was let to stand for 4 h then quenched by silica gel and the solvent was removed in vacuo. The residue was purified by flash column chromatography (petroleum ether–ethyl acetate 70:30) to afford a diastereomeric mixture of vinyl sulfides **5e** (348 mg, 95%). NMR spectra were recorded in C_6D_6 due to the slow isomerisation in chloroform of **5e** into the more stable **5d** through *O*-isopropylidene migration promoted by traces of HCl in commercial $CDCl_3$. ^{1}H NMR (C_6D_6): *E* isomer: δ 1.23, 1.38, 1.65 (3s, 4×3H, Me_2C), 2.01 (m, 1H, OH), 3.43–3.54 (m, 2H, H-5, H-7b), 3.78 (dd, 1H, J_{7a-7b}=11.3 Hz, J_{6-7a}=5.5 Hz, H-7a), 3.85–3.90 (m, 1H, H-6), 4.42 (dd, 1H, J_{4-5}=1.3 Hz, J_{3-4}=7.2 Hz, H-4), 4.61 (dd, 1H, J_{2-3}=J_{1-3}=7.5 Hz, H-3), 6.15 (dd, 1H, J_{1-2}=15.1 Hz, H-2), 6.33 (d, 1H, H-2), 7.20–7.41 (m, 5H, HAr); *Z* isomer: δ 1.27, 1.38, 1.46, 1.69 (4s, 4×3H, Me_2C), 2.50 (m, 1H, OH), 3.51–3.62 (m, 2H, H-5, H-7b), 3.87 (dd, 1H, J_{7a-7b}=11.0 Hz, J_{6-7a}=5.2 Hz, H-7a), 3.96–4.08 (m, 1H, H-6), 4.75 (dd, 1H, J_{4-5}=1.0 Hz, J_{3-4}=7.5 Hz, H-4), 5.48 (ddd, 1H, J_{2-3}=7.7 Hz, J_{1-3}=1.2 Hz, H-3), 6.13–6.25 (m, 2H, H-1, H-2), 7.20–7.41 (m, 5H, HAr). ^{13}C NMR: *E* isomer: δ 19.2, 26.2, 26.9, 28.7 (4*Me), 63.3 (C-6), 65.2 (C-7), 73.3 (C-5), 76.3 (C-4), 78.8 (C-3), 98.8, 109.5 (2*C_{IV}-iPrd), 127.9 (C-2), 128,3 (C-1), 127.3, 129.5, 130.7, 134.8 (C_{Ar}); *Z* isomer: δ 19.2, 26.1, 26.9, 28.9 (4*Me), 63.2 (C-6), 65.3 (C-7), 73.6 (C-5), 75.4 (C-3), 76.1 (C-4), 98.7, 109.8 (2*C_{IV}-iPrd), 126.1 (C-2), 130.0 (C-1), 127.0, 129.4, 129.6, 135.8 (C_{Ar}). HRMS: $C_{19}H_{26}O_5S$ calcd 366.1501; found 366.1498.

4.2.16. 1,2-Dideoxy-3,4,5,7-di-*O*-isopropylidene-1-methylthio-D-*gluco*-hept-1-enitols (4f). Prepared from 2,3:4,6-di-*O*-isopropylidene-D-glucopyranose **3f**.[27] Eluent: petroleum ether–ethyl acetate 90:10; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.38–1.51 (m, 12H, 2Me_2C), 2.27 (s, 3H, SMe), 3.55–3.68 (m, 2H, H-5, H-7b), 3.80–4.02 (m, 3H, H-4, H-6, H-7a), 4.62 (dd, 1H, J_{2-3}=9.0 Hz, J_{3-4}=8.5 Hz, H-3), 5.33 (dd, 1H, J_{1-2}=14.9 Hz, H-2), 6.43 (dd, 1H, H-1); *Z* isomer: δ 1.42, 1.44, 1.50 (3s, 4×3H, Me_2C), 2.29 (s, 3H, MeS), 2.92 (m, 1H, OH), 3.55–3.68 (m, 2H, H-5, H-7b), 3.80–3.95 (m, 2H, H-6, H-7a), 4.02 (dd, 1H, J_{3-4}=8.2 Hz, J_{4-5}=2.3 Hz, H-4), 5.00 (dd, 1H, J_{2-3}=8.5 Hz, H-3), 5.56 (dd, 1H, J_{1-2}=9.4 Hz, H-2), 6.22 (d, 1H, H-1). ^{13}C NMR: *E* isomer: δ 14.4 (MeS), 19.6, 26.5, 27.2, 28.2 (4*Me), 63.7 (C-6), 64.6 (C-7), 71.1 (C-5), 77.2 (C-3), 79.3 (C-4), 99.0, 109.2 (2*C_{IV}-iPrd), 125.9 (C-2), 130.9 (C-1); *Z* isomer: δ 17.5 (MeS), 19.5, 26.3, 27.3, 28.4 2 (4*Me), 63.6 (C-6), 64.6 (C-7), 71.3 (C-5), 72.6 (C-3), 79.2 (C-4), 99.0, 109.7 (2*C_{IV}-iPrd), 124.7 (C-2), 133.3 (C-1). HRMS: $C_{14}H_{24}O_5S$ calcd 304.1344; found 304.1351.

4.2.17. 1,2-Dideoxy-3,4,5,7-di-*O*-isopropylidene-1-phenylthio-D-*gluco*-hept-1-enitols (5f). Prepared from 2,3:4,6-di-*O*-isopropylidene-D-glucopyranose **3f**.[27] Eluent: petroleum ether–ethyl acetate 90:10; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer (selected peaks): δ 4.62 (dd, 1H, J_{2-3}=6.9 Hz, J_{3-4}=8.3 Hz, H-3), 5.80 (dd, 1H, J_{1-2}=15.1 Hz, H-2), 6.54 (dd, 1H, H-1); *Z* isomer: δ 1.44 (s, 3×3H, Me_2C), 1.53 (s, 3H, Me_2C), 2.39 (m, 1H, OH), 3.64–3.74 (m, 2H, H-5, H-7b), 3.89–3.99 (m, 2H, H-6, H-7a), 4.10 (dd, 1H, J_{3-4}=8.2 Hz, J_{4-5}=2.5 Hz, H-4), 5.13 (dd, 1H, J_{2-3}=9.1 Hz, H-3), 5.78 (dd, 1H, J_{1-2}=9.4 Hz, H-2), 6.48 (d, 1H, H-1), 7.22–7.42 (m, 5H, HAr). ^{13}C NMR: *Z* isomer: δ 19.6, 26.5, 27.3, 28.4 (4*Me), 63.9 (C-6), 64.6 (C-7), 71.4 (C-5), 72.8 (C-3), 79.4 (C-4), 99.2, 109.2 (2*C_{IV}-iPrd), 128.0 (C-2), 129.8 (C-1), 127.1, 129.3, 135.5, 139.7 (C_{Ar}). HRMS: $C_{19}H_{26}O_5S$ calcd 366.1501; found 366.1507.

4.2.18. 1,2,3-Trideoxy-3,4-*O*-isopropylidene-1-methylthio-D-*erythro*-hex-1-enitols (4h). Prepared from 2-deoxy-3,4-*O*-isopropylidene-D-ribopyranose **3h**.[28] Eluent: petroleum ether–ethyl acetate 90:10; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.37 (s, 1H, Me_2C), 1.48 (s, 3H, Me_2C), 2.24 (s, 3H, SMe), 2.25–2.51 (m, 2H, H-3a, H-3b), 3.61–3.72 (m, 2H, H-6a, H-6b), 4.13–4.28 (m, 2H, H-4, H-5), 5.41 (ddd, 1H, J_{1-2}=15.1 Hz, J_{2-3a}=7.5 Hz, J_{2-3b}=6.3 Hz, H-2), 6.12 (ddd, 1H, J_{1-3a}=J_{1-3b}=1.3 Hz, H-1); *Z* isomer: δ 1.37 (s, 3H, Me_2C), 1.48 (s, 3H, Me_2C), 2.29 (s, 3H, SMe), 2.25–2.51 (m, 2H, H-3a, H-3b), 3.61–3.72 (m, 2H, H-6a, H-6b), 4.13–4.28 (m, 2H, H-4, H-5), 5.57 (ddd, 1H, J_{1-2}=9.4 Hz, J_{2-3a}=8.2 Hz, J_{2-3b}=6.6 Hz, H-2), 6.12 (ddd, 1H, J_{1-3a}=J_{1-3b}=1.5 Hz, H-1). ^{13}C NMR: *E* isomer: δ 14.9 (MeS), 25.5, 28.2 (2*Me), 33.2 (C-3), 61.7 (C-6), 76.1, 78.0 (C-4 and C-5), 108.4 (C_{IV}-iPrd), 121.6 (C-2), 127.1 (C-1); *Z* isomer: δ 17.1 (MeS), 25.5, 28.2 (2*Me), 29.4 (C-3), 61.7 (C-6), 76.6, 77.8 (C-4 and C-5), 108.4 (C_{IV}-iPrd), 123.5 (C-2), 129.6 (C-1). HRMS: $C_{10}H_{18}O_3S$ calcd 218.0977; found 218.0988.

4.2.19. 1,2,3-Trideoxy-3,4-*O*-isopropylidene-1-phenylthio-D-*erythro*-hex-1-enitols (5h). Prepared from 2-deoxy-3,4-*O*-isopropylidene-D-ribopyranose **3h**.[28] Eluent: petroleum ether–ethyl acetate 90:10; yellow oil. ^{1}H NMR ($CDCl_3$): *E* isomer: δ 1.38 (s, 3H, Me_2C), 1.50 (s, 3H, Me_2C), 1.97 (m, 1H, OH), 2.32–2.58 (m, 2H, H-3a, H-3b), 3.61–3.76 (m, 2H, H-6a, H-6b), 4.13–4.35 (m, 2H, H-4, H-5), 5.95 (ddd, 1H, J_{1-2}=15.0 Hz, J_{2-3a}=7.3 Hz, J_{2-3b}=6.5 Hz, H-2), 6.28 (ddd, 1H, J_{1-3a}=J_{1-3b}=1.2 Hz, H-1), 7.18–7.42 (m, 5H, HAr); *Z* isomer: δ 1.37 (s, 3H, Me_2C), 1.49 (s, 3H, Me_2C), 1.86–2.08 (m, 1H, OH), 2.32–2.58 (m, 2H, H-3a, H-3b), 3.61–3.76 (m, 2H, H-6a, H-6b), 4.13–4.35 (m, 2H, H-4, H-5), 5.87 (ddd, 1H, J_{1-2}=9.5 Hz, J_{2-3a}=J_{2-3b}=7.3 Hz, H-2), 6.34 (ddd, 1H, J_{1-3}=1.4 Hz, H-1), 7.18–7.42 (m, 5H, HAr). ^{13}C NMR: *E* isomer: δ 28.2, 29.6 (2*Me), 33.2 (C-3), 61.8 (C-6), 76.3, 77.9 (C-4 and C-5), 108.6 (C_{IV}-iPrd), 126.0 (C-1), 127.8 (C-2), 126.7, 129.1, 129.3 (C_{Ar}); *Z* isomer: δ 25.5, 28.2 (2*Me), 33.2 (C-3), 61.7 (C-6), 76.2, 77.8 (C-4 and C-5), 108.5 (C_{IV}-iPrd), 124.8 (C-1), 131.0 (C-2), 126.6, 129.1, 129.2, 135.9 (C_{Ar}). HRMS: $C_{15}H_{20}O_3S$ calcd 280.1133; found 280.1124.

4.2.20. 3,4,6-Tri-*O*-benzyl-1,2-*O*-isopropylidene-β-D-mannopyranose (16) and 3,4,6-tri-*O*-benzyl-1,2-*O*-isopropylidène-α-D-glucopyranose (17). Vinyl sulfide **4a** (300 mg, 0.647 mmol) was dissolved in a 3:1 mixture of acetone and water (4 mL). A 2.5% solution of OsO_4 in *t*BuOH was added (363 μL, 0.05 equiv.), followed by a 1:1 mixture of *N*-methylmorpholine *N*-oxide (1.33 mL, 10 equiv.). The resulting dark solution was stirred at room temperature during 3 days. The reaction mixture was then cooled to 0 °C and quenched by the addition of a saturated

solution of $NaHSO_3$ (3 mL). The resulting solution was stirred during 10 min at RT, then extracted by AcOEt (3×5 mL) and the organic phases were dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was purified by flash column chromatography (petroleum ether–ethyl acetate 70:30 then 20:80) to afford a mixture of lactols **15** that could not be satisfactorily characterized, due to the anomeric equilibrium of both *gluco* and *manno* lactols. To overcome this problem, the yellowish oil was dissolved in 2,2-dimethoxypropane (5 mL) and CSA was added (15 mg, 0.1 equiv.). The solution was stirred overnight then quenched by a saturated solution of $NaHCO_3$ (5 mL) and extracted with AcOEt (3×5 mL). Organic phases were dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was purified by flash column chromatography (petroleum ether–ethyl acetate 85:15) to afford 32 mg (10%) of **17** then 257 mg of **16** (81%).

Isomer **17**. Colorless oil; $[\alpha]_D$=+35 (*c* 1.0, $CHCl_3$) (lit.[20a] +37.3, *c*=2.9, $CHCl_3$, lit.[20b] +39.4, *c*=1.0, $CHCl_3$). Spectroscopic data were identical to previous description.[20b] ^{1}H NMR ($CDCl_3$): 1.36 and 1.54 (2s, 2×3H, Me_2C), 3.63–3.67 (m, 2H, H-6a and H-6b), 3.71 (dd, 1H, H-4, J_{3-4}=3.8 Hz, J_{4-5}=9.6 Hz), 3.86–3.98 (m, 2H, H-3 and H-5), 4.26 (dd, 1H, H-2, J_{1-2}=4.9 Hz, J_{2-3}=4.2 Hz), 4.39 (d, 1H, CH_2Ph, J_{gem}=11.5 Hz), 4.49 (d, 1H, CH_2Ph, J_{gem}=12.2 Hz), 4.54–4.65 (m, 3H, CH_2Ph), 4.71 (d, 1H, CH_2Ph, J_{gem}=11.9 Hz), 5.64 (d, 1H, H-1), 7.15–7.43 (m, 15H, H_{Ar}) ^{13}C NMR ($CDCl_3$): δ 26.1 and 27.1 (Me_2C); 69.4 (C-6); 70.5 (C-5); 72.1, 73.1 and 73.5 (CH_2Ph); 75.3 (C-4); 75.9 (C-2); 79.4 (C-3); 97.5 (C-1); 109.2 (CMe_2); 127.7, 127.9, 128.0, 128.1, 128.2, 128.5, 128.6, 138.0, 138.1 and 138.9 (CAr).

Isomer **16**. White solid; $[\alpha]_D$=+38 (*c* 1.0, $CHCl_3$); mp (Et_2O) 106–108 °C. ^{1}H NMR ($CDCl_3$): δ 1.38 and 1.62 (2s, 2×3H, Me_2C), 3.37 (ddd, 1H, H-5, J_{4-5}=9.5 Hz, J_{5-6a}=4.0 Hz, J_{5-6b}=2.4 Hz), 3.37–3.81 (m, 3H, H-3, H-6a and H-6b), 3.99 (dd, 1H, J_{3-4}=9.5 Hz), 4.19 (dd, 1H, H-2, J_{1-2}=2.0 Hz, J_{5-6a}=3.7 Hz), 4.53 (d, 1H, CH_2Ph, J_{gem}=12.2 Hz), 4.54–4.67 (m, 2H, CH_2Ph), 4.78 (s, 1H, CH_2Ph), 4.90 (d, 1H, CH_2Ph, J_{gem}=10.9 Hz), 5.15 (d, 1H, H-1), 7.17–7.43 (m, 15H, H_{Ar}) ^{13}C NMR ($CDCl_3$): δ 25.9 and 28.1 (Me_2C); 69.0 (C-6); 72.1 and 73.3 (CH_2Ph); 74.2 (C-5); 74.5 (C-4); 75.2 (CH_2Ph); 76.5 (C-2); 79.0 (C-3); 97.3 (C-1); 112.2 (CMe_2); 127.4, 127.5, 127.7, 127.9, 128.0, 143.2 and 143, 6 (CAr). HRMS: $C_{30}H_{34}O_6$ calcd 490.2355; found 490.2343.

4.2.21. 1(*E*)-3,4,6-Tri-*O*-benzyl-1,2-dideoxy-1-methylsulfonyl-D-*arabino*-hex-1-enitol (18). To an ice-cold solution of vinyl sulfide **4a** (464 mg, 1.00 mmol) in dry CH_2Cl_2 (10 mL), dry *m*-CPBA (518 mg, 3.0 equiv.) was added and the reaction mixture was warmed slowly to RT. After 4 h stirring at this temperature, the mixture was cooled to 0 °C and quenched by a saturated solution of $NaHSO_3$ (10 mL). The resulting biphasic mixture was vigorously stirred during 10 min, then extracted by CH_2Cl_2 (3×20 mL). The organic phases were pooled, washed with a saturated solution of $NaHCO_3$ (3×5 mL) then dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was purified by flash column chromatography (petroleum ether–ethyl acetate 65:35) to afford the desired vinyl sulfone **18** (452 mg, 91%) as a colorless oil; $[\alpha]_D$=+21 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.70–2.85 (s, 1H, OH), 3.55–3.68 (m, 3H, H-4, H-6a, H-6b), 3.90–4.00 (m, 1H, H-5), 4.39–4.44 (m, 1H, H-3), 4.45–4.63 (m, 6H, CH_2Ph), 6.65 (dd, 1H, J_{1-2}=15.3 Hz, J_{1-3}=1.6 Hz, H-1), 7,00 (dd, 1H, J_{2-3}=4.4 Hz, H-2), 7.17–7.48 (m, 15H, HAr). ^{13}C NMR ($CDCl_3$): δ 42.7 ($MeSO_2$), 70.2 (C-5), 71.4 (C-6), 73.8, 74.6 (CH_2Ph), 77.7 (C-3), 79.8 (C-4), 128.1, 128.2, 128.4, 128.6, 128.7 (C_{Ar}), 131.1 (C-1), 137.2, 137.6, 137.8 (C_{Ar}), 145.4 (C-2). HRMS: $C_{28}H_{32}O_6S$ calcd 496.1919; found 496.1923.

4.2.22. 1(*E*)-3,4,6-Tri-*O*-benzyl-1,2-dideoxy-1-methylsulfinyl-D-*arabino*-hex-1-enitols (19). To an ice-cold solution of vinyl sulfide **4a** (1.00 g, 2.16 mmol) in dry CH_2Cl_2 (20 mL), dry *m*-CPBA (373 mg, 1.0 equiv.) was added and the reaction mixture was warmed slowly to RT. After 20 h stirring at this temperature, a saturated solution of $NaHCO_3$ (20 mL) was carefully added. The reaction medium was extracted by CH_2Cl_2 (3×20 mL) and the organic phases were dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was purified by flash column chromatography (petroleum ether–ethyl acetate 30:70) to afford a 1:1 mixture of *S*-epimers of vinyl sulfoxides **19** (894 mg, 86%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.47, 2.51 (2s, MeSO), 3.52–3.68 (m, H-4, H-6a, H-6b), 3.89–4.05 (m, H-5), 4.36–4.67 (m, H-3, CH_2Ph), 6.50–6.57 (m, H-1, H-2), 7.16–7.38 (m, HAr). ^{13}C NMR ($CDCl_3$): δ 40.6, 40.7 (MeSO), 70.2 (C-5), 70.9 (C-6), 72.4, 72.6, 73.6, 74.3, 74.5 (CH_2Ph), 78.3 (C-3), 80.0 (C-4), 128.0, 128.2, 128.3, 128.4, 128.5, 128.6 (C_{Ar}), 135.8, 136.3, 136.4, 136.5 (C-1, C-2), 137.5, 137.5, 137.8, 137.9, 138.0 (C_{Ar}). HRMS: $C_{28}H_{32}O_5S$ calcd 480.1970; found 480.1981.

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