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Synthesis of anomerically pure vinyl sulfone-modified pent-2-enofuranosides and hex-2-enopyranosides: a group of highly reactive Michael acceptors for accessing carbohydrate based synthons

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Abstract—Syntheses of the benzyl or the trityl protected α- and β-anomers of vinyl sulfone-modified pent-2-enofuranosides have been initiated by the ring opening of the suitably masked methyl α-*lyxo*furanosyl-epoxide or methyl β-*ribo*furanosyl-epoxide or by the nucleophilic displacement of the leaving groups in benzyl protected 3-*O*-tosyl *xylo*furanoside and 3-*O*-mesyl *ribo*furanoside by *p*-thiocresol. In case of the latter set of starting materials, α- and β-methyl glycosides formed in almost equal ratio only from the derivatives of D-xylose. For the synthesis of α- and β-anomers of vinyl sulfone-modified hex-2-enopyranosides, a D-glucose derivative was selected over a D-allose derivative as the starting material because the former almost exclusively produced the required methyl pyranosides whereas the latter produced a mixture. All sulfides were converted to vinyl sulfone-modified carbohydrates by the sequential application of oxidation, mesylation and base induced elimination reactions.

1. Introduction

The most common methods for the modification of monosaccharides involve reactions of various reagents with sugar derived epoxides, tosylates and ketones although several other minor methods are also reported.[1] Nucleophilic addition (Michael) to double bonds activated by electron withdrawing groups as part of carbohydrates could serve as a useful methodology for the functionalization of monosaccharides. Several examples of Michael addition of nucleophiles to hex-2-enose[2] and 3-nitro-hex-2-enopyranosides[3] have been reported.

During the course of our studies on the synthesis of carbohydrate modified monovinylsulfone[4] and bisvinylsulfone substituted nucleosides,[5] we envisaged that due to the high reactivities of vinyl sulfones towards a wide variety of nucleophiles, vinyl sulfone-modified carbohydrates could be utilized to generate numerous modified monosaccharides. Vinyl sulfone-modified carbohydrates are expected to offer several additional advantages for synthetic chemistry, which have been discussed in detail.[6] The reported anomers,[3i] methyl 2,3-dideoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfonyl-α-D-*erythro*-hex-2-enopyranoside **1α** and methyl 2,3-dideoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfonyl-

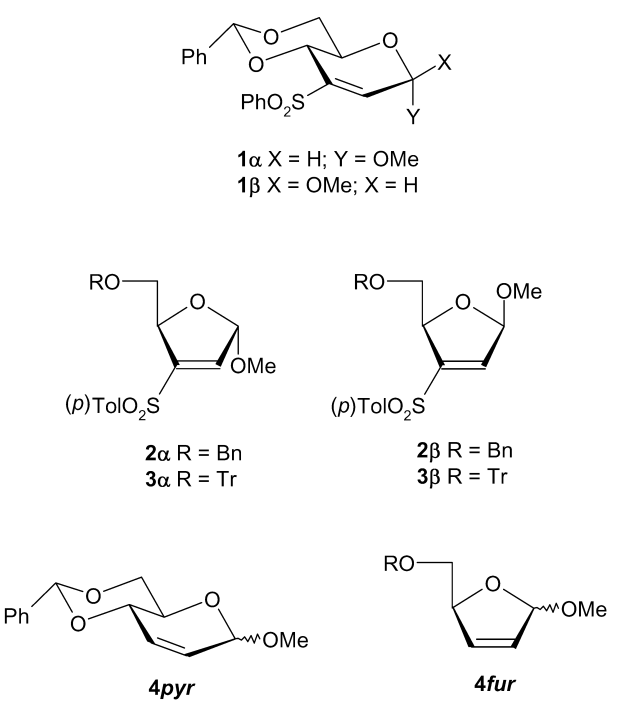

Figure 1.

Keywords: vinyl sulfone; pent-2-enopyranosides; hex-2-enopyranosides; Michael acceptors.
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β-D-*erythro*-hex-2-enopyranoside **1β** (Fig. 1) have been synthesized and subjected to reactions with various amines.[6a–d] The study has later been utilized for the synthesis of D-lividosamine (a component of aminoglycoside antibiotics) and its analogues.[6b] On the other hand, a facile route for the synthesis of new branched chain sugars has been designed recently by utilizing the directing effects of the anomeric configuration of vinyl sulfone-modified pent-2-enofuranosides and hex-2-enopyranosides.[6e]

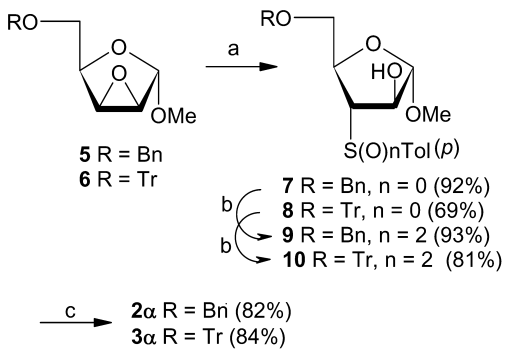
In order to broaden the scope of this study and also to gather information on the reaction patterns of endocyclic monovinylsulfones derived from pentofuranoses, we needed to develop a practical methodology for the synthesis of anomerically pure methyl 2,3-dideoxy-3-*C*-(*p*)-tolylsulfonyl-α-D-*erythro*-pent-2-enofuranoside (**2α** or **3α**) and methyl 2,3-dideoxy-3-*C*-(*p*)-tolylsulfonyl-β-D-*erythro*-pent-2-enofuranoside (**2β** or **3β**) (Fig. 1). Anomerically pure, vinyl sulfone-modified pent-2-enofuranoses were needed because we wanted to use the anomeric configuration as a tool to direct the diastereoselectivity of addition of nucleophiles to the 2-position of these enofuranoses. However, this particular requirement imposed greater restrictions on the choice of methodologies for the synthesis of compounds **1**, **2** and **3** starting from a single and easily accessible starting materials.

2. Results and discussion

A retrosynthetic analysis of the route to **1**, **2** and **3** necessitated the introduction of a tolylthio group at the C-3 position of a hexose or a pentose sugar, respectively. One of the easiest ways of forming a C-S bond would be the regioselective opening of epoxides derived from carbohydrates.[1c] It is also possible to introduce the *p*-tolylthio group at the C-3 position of a hexose or a pentose sugar by displacing the leaving group at the C-3 position of the easily accessible starting materials **17**, **26**, **32** or **38**. Synthesis of **1** or **2** and **3** via the addition of arylsulfenyl chloride to suitably protected methyl 2,3-dideoxy-D-hex-2-enopyranosides **4pyr** or methyl 2,3-dideoxy-D-pent-2-enofuranoside **4fur** (Fig. 1) as a method was ruled out because such an addition to the corresponding olefinic nucleoside derivatives was reported to produce a mixture of at least three diastereomers.[7]

2.1. Synthesis of 2 and 3 from epoxides derived from carbohydrates

The known *lyxo*-epoxides **5**[8] and **6**,[9] synthesized from D-xylose, were treated separately with the sodium salt of *p*-thiocresol in DMF at 80–90°C to furnish sulfide derivatives **7** and **8**, respectively in good to excellent yields. Compounds **7** and **8**, when oxidized separately with MMPP (magnesium monoperoxyphthalate) in MeOH generated the corresponding sulfone derivatives **9** and **10**, respectively in high yields. Compounds **9** and **10**, on treatment with mesyl chloride in pyridine separately, afforded smoothly the desired vinyl sulfone-modified carbohydrates **2α** and **3α**, respectively in 82 and 84% yields (Scheme 1). Similarly, the known *ribo*-epoxides **11**[10] and **12**[11] were treated separately with the sodium salt of *p*-thiocresol in DMF at 80–90°C to



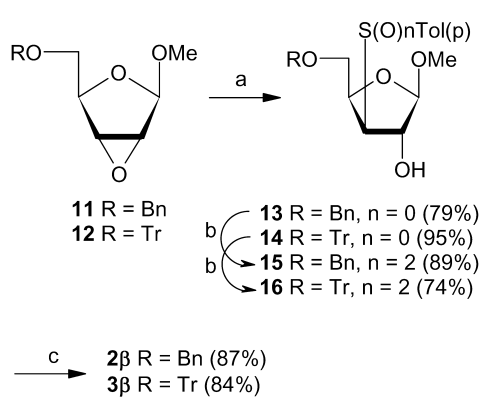
Scheme 1. *Reagents and conditions*: (a) *p*-Thiocresol, NaOMe, DMF, 80–90°C, 2.5–3 h; (b) MMPP, MeOH, room temperature, 2–3 h; (c) MsCl, Py., 0°C, 12–24 h.

afford sulfide derivatives **13** and **14**, respectively with *xylo*-configuration in high yields. Compounds **13** and **14** were converted to the corresponding vinyl sulfones **2β** and **3β** via sulfone derivatives **15** and **16** in the usual manner as described above (Scheme 2).

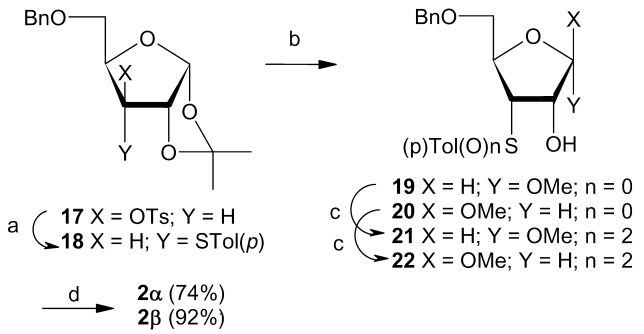
It should be noted that this route allows the synthesis of vinyl sulfone-modified pentofuranoses having the C-5 hydroxyl function masked with an acid labile trityl protecting group because the trityl group is introduced after the acid catalyzed methyl glycoside formation. However, separate synthesis of epoxides **5/6** and **11/12** increases the number of steps and therefore, it was necessary to devise different approaches towards the synthesis of vinyl sulfone-modified carbohydrates.

2.2. Synthesis of 2α and 2β from 3-*O*-tosylated D-*xylo*furanose

Compound **17**[12] was reacted with *p*-thiocresol in the presence of NaOMe in DMF at 120°C to produce sulfide derivative **18** with *ribo*-configuration in 59% yield. Compound **18** was deprotected and glycosylated in one step in the presence of conc. H_2SO_4 in MeOH to generate a mixture of two anomers **19** and **20** (1:10) in 78% yield. The anomers **19** and **20** were separated at this stage by chromatography and oxidized separately with MMPP in MeOH to the corresponding sulfones **21** and **22**, respectively in excellent yields. The sulfones **21** and **22**



Scheme 2. *Reagents and conditions*: (a) *p*-Thiocresol, NaOMe, DMF, 80–90°C, 2.5–3.0 h; (b) MMPP, MeOH, room temperature, 2.5–3.0 h; (c) MsCl. Py., 0°C, 12 h.



Scheme 3. *Reagents and conditions*: (a) *p*-Thiocresol, NaOMe, DMF, 115–120°C, 3.5–4.0 h, 59%; (b) MeOH, conc. H_2SO_4, 65–70°C, 3 h, 78%, (**19**:**20**=1:10); (c) MMPP, MeOH, room temperature, 3 h (**21**=94% and **22**=93%); (d) MsCl, Py., 0°C–room temperature, 18–24 h.

on treatment with mesyl chloride in pyridine afforded smoothly the desired vinyl sulfone-modified carbohydrates **2α** and **2β**, respectively in high yields (Scheme 3).

The moderate yield of the *ribo*-product **18** can be partly explained on the basis of the repulsion caused by the 1,2-*O*-isopropylidene group to the incoming nucleophile.[13] Although at this stage the less efficient conversion of **17** to **18** was acceptable, the major drawback of this methodology was the unacceptable ratio of **19** and **20** (1:10) in the mixture. The lower ratio of α-anomer **19** in the mixture of **19** and **20** contributed to the poor overall yield of the vinyl sulfone derivative **2α**.

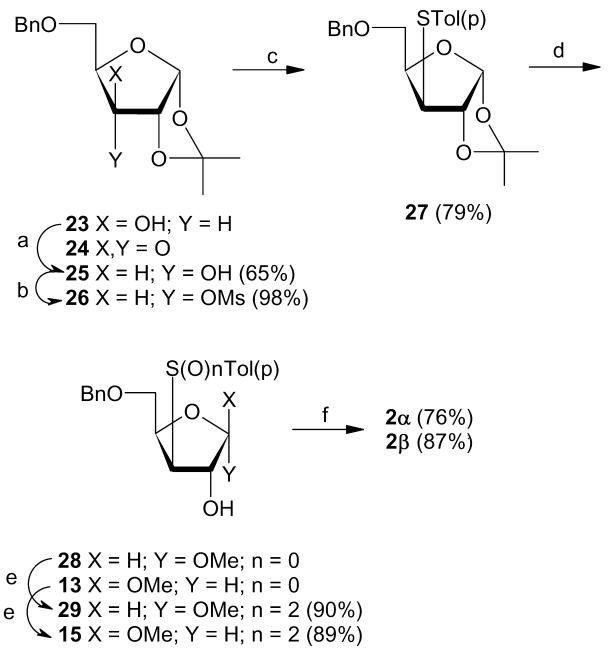
2.3. Synthesis of 2α and 2β from 3-*O*-mesylated D-*ribo*furanose

An examination of the percentage compositions of methyl furanosides of D-ribose, D-arabinose, D-xylose and D-lyxose revealed that the ratios of α- and β-furanosides present in equilibrium were 1:3.4, 3.1:1, 1:1.5 and only α-isomer, respectively.[14] Thus, the pattern of glycosylation of various pentose sugars dictated us to select a D-*xylo*-derivative based strategy for the synthesis of an anomeric mixture close to the ideal ratio of 1:1.

5-*O*-Benzyl-1,2-*O*-isopropylidene-3-*O*-mesyl-α-D-*ribo*-furanose **26**, which had been synthesized from a known compound **23**[15] (via oxidation-reduction followed by mesylation), was subjected to nucleophilic displacement by *p*-thiocresol in the presence of NaOMe in DMF to generate a sulfide derivative **27** with *xylo*-configuration in 79% yield.

Compound **27** was deprotected and glycosylated in the presence of conc. H_2SO_4 in MeOH in one step to afford a mixture of both α- and β-anomers **28** and **13** (1.5:1) in excellent yields. Compounds **28** and **13** were separated at this stage by flash chromatography. On treatment with MMPP in MeOH, compounds **28** and **13** produced the corresponding sulfones **29** and **15**, respectively in excellent yields. Compound **15** on treatment with mesyl chloride in pyridine smoothly generated the desired vinyl sulfone **2β** in 87% yield whereas **29** generated the desired vinyl sulfone **2α** in good yield (Scheme 4).

Compound **27** on methanolysis produced a mixture of



Scheme 4. *Reagents and conditions*: (a) (i) $(COCl)_2$,DMSO, CH_2Cl_2, Et_3N, −60°C, 1.5 h; (ii) LAH, THF, 0°C–room temperature, 3.5–4 h; (b) MsCl, Py., 0°C, 24 h; (c) NaSTol (*p*), DMF, 145°C, 3 h; (d) MeOH, conc. H_2SO_4, 65–70°C, 3 h, 89% (**28**:**13**=1.5:1); (e) MMPP, MeOH, room temperature, 3 h; (f) MsCl, Py., 0°C–room temperature, 24 h.

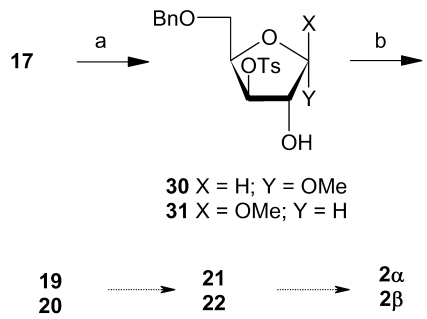
anomers **28** and **13** in a ratio 1.5:1. Although this ratio was acceptable for the synthesis of both the anomers **2α** and **2β**, the overall yield again dropped due to the addition of two synthetic steps for converting *xylo*-derivative **23** to *ribo*-derivative **25** via a two-step oxidation-reduction process. We therefore, looked for yet another route for the synthesis of **2α** and **2β**.

2.4. Synthesis of 2α and 2β from 3-*O*-tosylated methyl D-*xylo*furanosides

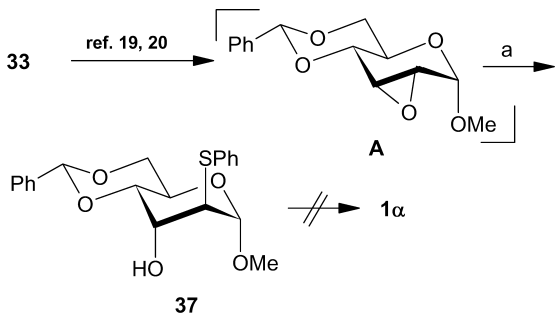
It was possible to circumvent all the shortcomings mentioned above by first converting the *xylo*-tosylate derivative **17** to an anomeric mixture of **30** and **31**. Compound **17** was therefore treated with conc. H_2SO_4 in MeOH to produce an anomeric mixture of **30** and **31** in a ratio of 1:1.3 (α:β) in 89% yield. In the absence of any steric hindrance exhibited by **17**, the nucleophilic displacement of the tosyl group of the mixture of **30** and **31** by *p*-thiocresol proceeded smoothly at elevated temperature to afford a mixture of 3-deoxy-3-*C*-(*p*)-tolylsulfide-D-*ribo*furanosides **19** and **20** in 94% yield. Compounds **19** and **20** were separated and converted to the desired vinyl sulfone-modified carbohydrates **2α** and **2β**, respectively in the usual manner described above (Scheme 5).

2.5. Synthesis of 1α and 1β from 3-*O*-tosylated D-*gluco*furanose

For accessing relatively large amount of anomerically pure **1α** and **1β** through a shorter route, we applied the glycosylation driven strategy, which was successfully utilized in the synthesis of **2α** and **2β**, for the selection of starting sugar for the synthesis of **1α** and **1β**. It has been reported that the equilibrium mixture of methyl-D-allosides



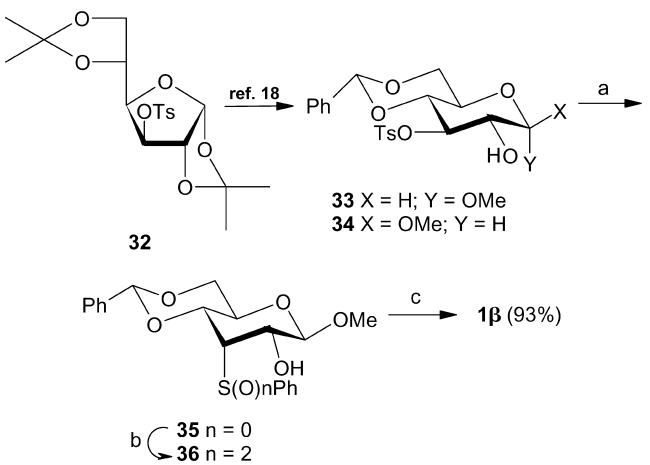
Scheme 5. *Reagents and conditions*: (a) MeOH, conc. H_2SO_4, 65–70°C, 3 h, 89% (**30**:**31**=1:1.3); (b) *p*-Thiocresol, NaOMe, DMF, 115–120°C, 3.5–4.0 h, 94%.



Scheme 7. *Reagents and conditions*: (a) PhSH, NaOMe, DMF, 135–140°C, 2 h, 39%.

in MeOH, contained more than 30% of furanosides[16] whereas D-glucose produced[14] methyl-D-pyranosides almost exclusively. Although the reported ratio of α- and β-anomers were not close to the ideal value of 1:1, in this case it was more important to get the methyl pyranosides without any contamination of the corresponding furanosides. This observation prompted us to study the feasibility of using the known tosylate **32** as the starting material.[17]

The known tosylate **32**[17] was considered as a suitable starting material[17] because it could be easily converted to a mixture of **33** and **34** (via deprotection, glycosylation followed by benzylidenation) in a ratio 1:1.5.[18] The anomers were separated by column chromatography. The β-anomer **34** was reacted with thiophenol in the presence of NaOMe in DMF to afford sulfide derivative **35**. Compound **35**, on oxidation with MMPP in MeOH produced the sulfone **36**. Compound **36** under mesylation condition generated smoothly the desired vinyl sulfone **1β** in overall 79% yield (in 3 steps from **34**) (Scheme 6). The α-anomer **33**, when treated with the sodium salt of thiocresol, produced an undesired sulfide derivative **37**. Since it was reported[19] that **33** very easily formed the epoxide **A**, it is logical to conclude that under the reaction conditions *altro*-derivative **37** was formed[20] along with some other unidentified products (Scheme 7). No further study was carried out on



Scheme 6. *Reagents and conditions*: (a) PhSH, NaOMe, DMF, 135–140°C, 2.5–3 h, 90%; (b) MMPP, MeOH, room temperature, 3 h, 95%; (c) MsCl, Py., 0°C–room temperature, 4 h.

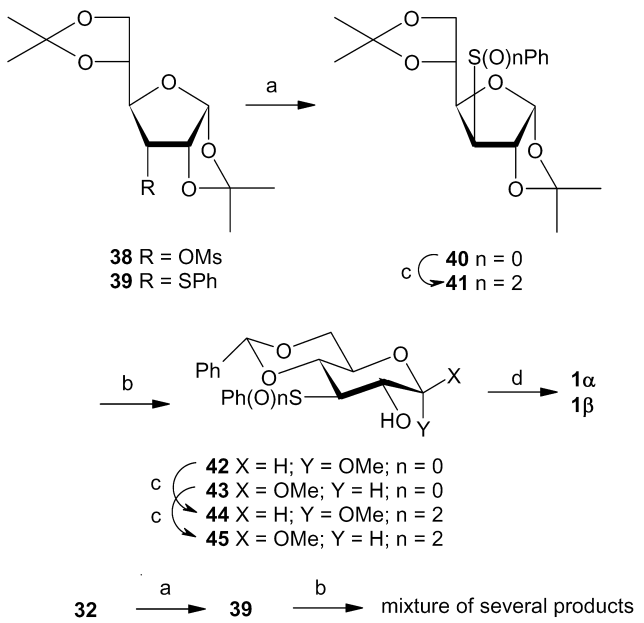
this reaction sequence because it was not possible to synthesize the desired vinyl sulfone **1α** from **37**.

2.6. Synthesis of 1α and 1β from 3-*O*-mesylated D-*allo*furanose

To overcome the aforementioned problems and to have an easy access to both **1α** and **1β** through a single intermediate we studied another sequence of reactions using two possible starting materials **39** and **40** which were obtained by displacing the leaving groups of **32** and **38**, respectively by sodium thiophenolate. Here also, for reasons discussed above, the *gluco*-derivative **40** was the starting material of choice over the *allo*-derivative **39** because methanolysis of the latter generated more than six products as reported.[16] The known mesylated *allo*-derivative **38**[21] was treated with thiophenol in the presence of NaOMe in DMF to afford sulfide derivative **40** with *gluco*-configuration. Compound **40** was deprotected and glycosylated in a single operation by using acetyl chloride and MeOH to afford a mixture of 3-deoxy-3-phenylsulfide-hexopyranosides which were collected as the benzylidene derivatives **42** and **43** in a ratio 2.2:1 in good yields. The anomers **42** and **43** were separated on silica gel column and were converted separately to the corresponding sulfones **44** and **45** in excellent yields using MMPP in MeOH. In an alternative approach, compound **40** was oxidized with MMPP in MeOH to the corresponding sulfone **41** in excellent yield. Compound **41** was deprotected and glycosylated in the presence of acetyl chloride and MeOH in one step to generate a mixture of anomeric sulfones, which were collected as the benzylidene *gluco*-derivatives **44** and **45**, respectively in good yields in a ratio 1:1.8. The anomers were separated by column chromatography. Compounds **44** and **45** were mesylated separately and the mesylated derivatives on treatment with DBU produced the desired vinyl sulfone-modified hex-2-enopyranosides **1α** and **1β**, respectively in excellent yields (Scheme 8).

2.7. Structural elucidation

The regio- and stereospecificities of attack of sodium thiocresolate to C-3 positions of **5/6** and **11/12** were determined by the configurations of the epoxide rings and the anomeric configurations. It was, therefore a foregone conclusion that the α-*lyxo*-epoxides **5/6** would produce *arabino*-derivatives **7/8** and the β-*ribo*-epoxides would generate *xylo*-derivatives **13/14**. Similarly, backside attack



Scheme 8. *Reagents and conditions*: (a) PhSH, NaOMe, DMF, 120–125°C, 2–4 h, **40**=80% and **39**=90%; (b) (i) CH_3COCl, anhydr. MeOH, reflux, 24 h; (ii) 1,1-dimethoxytoluene, *p*-TSA, DMF, 100°C, 1 h, **42**+**43**=71% (2.2:1) and **44**+**45**=75% (1:1.8) (in two steps); (c) MMPP, MeOH, room temperature, 2–3 h, **41**=94%, **44**=92%, **45**=90%; (d) (i) MsCl, Py., 0°C, 12 h; (ii) DBU, CH_2Cl_2, room temperature, 15 min, **1α**=96%, **1β**=96% (in two steps).

of sodium thiocresolate at the C-3 positions of **17**, **26** and **30/31** would afford products **18**, **27** and **19/20**, respectively. In a similar fashion, **38** produced the *gluco*-derivative **40**.

However, additional support for the structures, especially the relationships between H-1 and H-2 protons came from the analysis of the ^{1}H NMR spectrum. It is well documented in the literature[22] that for methyl α-D-pentofuranosides with D-*ribo*- and D-*xylo*-configurations, a coupling constant ($J_{1,2}$) value of 4.0–4.7 Hz is the characteristic of a *cis*-arrangement for H-1 and H-2 and for methyl β-D-pentofuranoside series with D-*ribo*- and D-*xylo*-configurations, a coupling constant ($J_{1,2}$) value of 0.0–2.0 Hz implies a *trans*-arrangement of H-1 and H-2. Therefore, by comparing $J_{1,2}$ values of our compounds with those of the reported compounds, **19** (3.9 Hz) and **21** (4.9 Hz) were regarded as possessing α-*ribo*-configurations and **28** (4.4 Hz)/**29** (4.4 Hz) as having α-*xylo*-configurations. Similarly, by comparing the $J_{1,2}$ values of the corresponding β-series, compounds **20** (0.0 Hz), **22** (0.0 Hz) were concluded as having β-*ribo*-configurations and **13** (2.3 Hz), **15** (2.3 Hz), **14** (2.4 Hz) and **16** (3.0 Hz) as β-*xylo*-configurations. Furthermore, for methyl α-D-pentofuranosides with *arabino*- and *lyxo*-configurations, a coupling constant ($J_{1,2}$) value of 0.0–3.0 Hz indicated the *trans*-orientation of H-1 and H-2. For β-series, a value of 3.0–5.0 Hz is characteristic of a *cis*-arrangement for H-1 and H-2. Thus, configurations of compounds **7** (0.0 Hz), **8** (0.0 Hz), **9** (0.0 Hz), and **10** (2.0 Hz) were assigned as having α-*arabino*-configurations.

It is also evident from literature[22] that the chemical shifts of the methyl groups of methyl α-D-*ribo*furanosides as well as α-D-*xylo*furanosides with free OH groups at C-2 position (δ 3.44–3.47) were always more downfield than the corresponding values of methyl β-D-*ribo*furanosides and β-D-*xylo*furanosides (δ 3.25–3.36). In the case of our compounds, in a pair of anomers like **19** (δ 3.49)/**20** (δ 3.34), **21** (δ 3.49)/**22** (δ 3.26), **28** (δ 3.50)/**13** (δ 3.36) and **29** (δ 3.45)/**15** (δ 3.41) α-methoxy protons always appeared at a more downfield region. Interestingly, in the same pair of anomers the C-1 carbons of α-anomers **19**, **21**, **28** and **29** (δ 101.2–103.2) appeared at a more upfield region than those of β-anomers **20**, **22**, **13** and **15** (δ 108.4–110.2). This observation is in agreement with the report[22e] that the chemical shift values of C-1 ranging from δ 100.2–100.9 are characteristic of α-*xylo*-configurations and those of β-*xylo*-derivatives have their values ranging from δ 107.8–109.8.

In the case of the pyranosyl compounds, **35** was the product of the substitution reactions as expected, the undesired *altro*-derivative **37** was obtained through a reported[19,20] sequence of reactions. In the case of **42** and **43**, C-S bonds at C-3 and the *gluco*-configurations of the compounds were predecided by selecting a starting thiosugar **40** which was obtained from the known mesylate **38**.

It is reported[3,6a,23] that for methyl 4,6-*O*-(phenylmethylene)-α-D-hexopyranosides with D-*gluco*-and D-*allo*-configurations, a coupling constant ($J_{1,2}$) value of 3.3–3.8 Hz is the characteristic of equatorial H-1/axial H-2 arrangements. For β-series, in general a relatively large value of $J_{1,2}$ (6.6–8.5 Hz) is characteristic of axial H-1/axial H-2 arrangement.[22f,g] Compounds **42** (3.5 Hz) and **44** (3.4 Hz) are concluded as having α-*gluco*-configuration and **43** (7.3 Hz) and **45** (6.9 Hz) are regarded as possessing β-*gluco*-configuration. Similarly, by comparison, it was inferred that compound **37** (0.0 Hz) is having α-*altro*-configuration and compounds **35** (8.3 Hz) and **36** (8.3 Hz) are having β-*allo*-configurations.

It is also evident from literature[22] that in general α-anomeric methyl glycofuranosides show high and positive optical rotation values while β-anomeric methyl glycosides render either very small positive or negative values. In our case, methyl α-D-*ribo*furanosides, **18** (+100.1), **19** (+145.1), **21** (+100.9) and **26** (+88.2) have shown positive rotations and the corresponding β-intermediates **20** (−40.5) and **22** (−50.0) showed negative rotations. Methyl α-D-*xylo*furanosides **28** (+163.7) and **29** (+236.8) are having higher optical rotations than the corresponding β-intermediates **13** (+16.1) and **15** (+17.2), respectively. Similarly, benzylated or tritylated α-anomeric compounds **7** (+128.8)/**8** (+74.2) and **9** (+95.2)/**10** (+81.7) with *arabino*-configuration were showing higher rotation values than the β-anomeric *xylo*furanosides **13** (+16.1)/**14** (+56.9) and **15** (+17.2)/**16** (+40.9) as expected from the literature. Among 1,2-*O*-isopropylidene derivatives, intermediates with *xylo*-configuration **17** (−26.1) and **27** (−31.0) showed negative rotations whereas compounds **18** (+100.1) and **26** (+88.2) with *ribo*-configuration showed positive rotations. In the case of benzyl protected vinyl sulfone-modified carbohydrates, the α-anomer **2α** (+5.9) is having higher rotation than the corresponding β-isomer **2β** (−16.2) whereas the tritylated α-anomer **3α** (+17.1) is having slightly higher rotation than the β-anomer **3β** (+11.4).[24]

3. Conclusion

Both α- and β-anomers of vinyl sulfone-modified pent-2-enofuranosides **2** and **3** have been synthesized for the first time using epoxides derived from carbohydrates as starting materials as well as by taking advantage of the formation of α- and β-methyl glycosides in almost equal ratio only from derivatives of D-xylose. In the synthesis of α- and β-anomers of vinyl sulfone-modified hex-2-enopyranosides, a D-glucose derivative was selected over a D-allose compound as the starting material because the former almost exclusively produced the required methyl pyranosides. Compounds **1α** and **1β** have been synthesized earlier[6a] in a total of 15 steps from D-glucose (7 steps for **1α**, and 8 steps for **1β** each). The present method makes use of common intermediates up to compounds **44** and **45**, thereby drastically reducing the overall purification steps. Although overall yields for both the methods are comparable, methyl β-D-*gluco*pyranoside, which has been used in the earlier synthesis,[6a] is far too expensive as a starting material to be used in a large-scale multi-step synthesis.

4. Experimental

4.1. General methods

Melting points were determined in open-end capillary tubes and are uncorrected. Carbohydrates and other fine chemicals were obtained from commercial suppliers and are used without purification. Solvents were dried and distilled following the standard procedures.[25] TLC was carried out on precoated plates (Merck silica gel 60, f_{254}) and the spots were visualized with UV light or by charring the plate dipped in 5% H_2SO_4–MeOH solution. Column chromatography was performed on silica gel (60–120 or 230–400 mesh). ^{1}H NMR spectra were recorded at Bruker AC 200, MSL 300 or DRX 500 MHz in $CDCl_3$ using the residual $CHCl_3$ as standard. ^{13}C NMR spectra were recorded at 50.3 and 75 MHz in $CDCl_3$ using the triplet centered at δ 77.27 as the standard. Optical rotations were recorded at 589 nm.

4.2. General procedure for the synthesis of 7, 8, 13 and 14

To a well stirred solution of **5**, **6**, **11** or **12** in DMF (4 mL/mmol) were added *p*-thiocresol (5 equiv.) and NaOMe (4 equiv.) and the mixture was heated at 80–90°C for 2.5–3.5 h with stirring. After completion of the reaction (TLC), the reaction mixture was poured into saturated solution of NaCl (60 mL/mmol) and the product was extracted with EtOAc. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a gummy residue. The residue was purified over silica gel column to obtain the title compound.

4.3. General procedure for the MMPP oxidation

To a well-stirred solution of the arylsulfide furanoses or pyranoses in distilled MeOH (20 mL/mmol) was added MMPP (5 equiv.) and the mixture was stirred for 2–3 h. After completion of the reaction (TLC), the solid mass was filtered off through celite bed. The filtrate was evaporated to dryness under reduced pressure and the solid residue thus obtained was dissolved in saturated $NaHCO_3$. The aqueous solution was washed with EtOAc (4×30 mL). The combined organic layers were dried over anhydr. Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to obtain the sulfones **9**, **10**, **15**, **16**, **21**, **22**, **29**, **36**, **41**, **44** and **45**.

4.4. General procedure for the formation of 1, 2, 3

To a well stirred solution of the arylsulfonyl furanoses or pyranoses in pyridine (5 mL/mmol) was added mesyl chloride (4–6 equiv.) in pyridine (1 mL/mmol of MsCl) dropwise at 0°C under nitrogen. After completion of the addition, the reaction mixture was kept at +4°C. After 24 h (TLC), the reaction mixture was poured into ice-cold water (10 mL/mmol of sugar) and aqueous layer was extracted with $CHCl_3$ (3×20 mL). The combined organic layers were dried over anhydr. Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The crude material was purified over silica gel column to get any of the title compounds.

4.4.1. Methyl 5-*O*-benzyl-2,3-dideoxy-3-*C*-(*p*)-tolylsulfonyl-α-D-*erythro*-pent-2-enofuranoside 2α. Compound **9** (0.48 g, 1.232 mmol) was converted to **2α** following the general procedure described above (0.38 g, 82%). Eluent: EtOAc:pet ether (1:9). Brown gum. $[\alpha]_D^{25}$=+5.9 (*c* 0.927, $CHCl_3$). IR ($CHCl_3$): 3444, 2358, 1953, 1892, 1776, 1724, 1596 cm^{-1}.^{1}H NMR: δ 7.78 (2H, d, *J*=8.3 Hz, aromatic), 7.30 (7H, m, aromatic), 6.59 (1H, s), 5.88 (1H, d, *J*=4.4 Hz), 5.13 (1H, m), 4.44 (2H, s, $PhCH_2$), 3.85 (1H, dd, *J*=10.7, 2.4 Hz), 3.60 (1H, dd, *J*=10.7, 4.4 Hz), 3.39 (3H, s, OMe), 2.42 (3H, s, aromatic Me).^{13}C NMR: δ 147.2, 137.0, 145.3, 138.1, 136.4, 130.1, 128.3, 127.5, 107.5 (C-1), 83.6, 73.3 (CH_2), 70.3 (CH_2), 54.6 (OMe), 21.6 (aromatic Me). MS: *m*/*z* (EI) 326 (0.4M$^+$−48), 251 (3), 236 (23), 219 (6), 139 (9), 105 (17), 91 (100), 77 (33), 65 (48). Anal. calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.91; S, 8.56. Found: C, 64.48; H, 5.90; S, 8.67.

4.4.2. Methyl 2,3-dideoxy-3-*C*-(*p*)-tolylsulfonyl-5-*O*-trityl-α-D-*erythro*-pent-2-enofuranoside 3α. Compound **10** (3.14 g, 5.77 mmol) was converted to **3α** following the general procedure described above (2.56 g, 84%). Eluent: EtOAc:pet ether (1:4). Colorless hygroscopic gum. $[\alpha]_D^{26}$=+17.1 (*c* 1.07, $CHCl_3$). IR ($CHCl_3$): 4214, 3479, 2401, 1596, 1490 cm^{-1}. ^{1}H NMR: δ 7.52 (2H, d, *J*=8.3 Hz, aromatic); 7.2 (17H, m, aromatic), 6.56 (1H, s, H-2), 5.90 (1H, d, *J*=4.4 Hz, H-1), 5.02 (1H, m), 3.43 (1H, dd, *J*=10.7, 2.4 Hz), 3.30 (3H, s, OMe), 3.08 (1H, dd, *J*=10.8, 4.9 Hz), 2.32 (3H, s, aromatic Me). ^{13}C NMR: δ 147.5, 145.2, 143.9, 137.3, 136.3, 130.0, 128.8, 128.1, 127.8, 127.1, 107.5 (C-1), 86.9, 83.8, 64.7 (CH_2), 54.2 (OMe), 21.7 (aromatic Me). MS: *m*/*z* (EI) 449 (<2), 243 (100), 165 (66), 91 (30). Anal. calcd for $C_{32}H_{30}O_5S.1H_2O$: C, 70.57; H, 5.54. Found: C, 70.60; H, 5.76.

4.4.3. Methyl 5-*O*-benzyl-2,3-dideoxy-3-*C*-(*p*)-tolylsulfonyl-β-D-*erythro*-pent-2-enofuranoside 2β. Compound **15** (0.25 g, 0.637 mmol) was converted to **2β** following the general procedure described above (0.21 g, 87%).

Eluent: EtOAc:pet ether (1:3). Brown gum. IR ($CHCl_3$): 1722, 1596, 1494 cm^{-1}. $[\alpha]_D^{26}=-16.2$ (*c* 1.004, $CHCl_3$). ^1H NMR: δ 7.75 (2H, d, *J*=8.3 Hz, aromatic), 7.30 (7H, m, aromatic), 6.60 (1H, s), 5.72 (1H, s), 4.95 (1H, d, *J*=6.3 Hz), 4.47 (2H, s, $PhCH_2$), 3.83 (1H, dd, *J*=10.7, 2.4 Hz), 3.50 (1H, m), 3.42 (3H, s, OMe), 2.43 (3H, s, aromatic Me). ^{13}C NMR: δ 147.6, 136.6, 145.3, 138.2, 136.3, 130.0, 128.3, 127.5, 107.3 (C-1), 83.4, 73.2 (CH_2), 72.0 (CH_2), 55.3 (OMe), 21.6 (aromatic Me). MS: *m/z* (EI) 250 ($6M^+-124$), 236 ($91M^+-138$), 218 ($13M^+-156$), 139 (16), 105 (17), 91 (100), 77 (30), 65 (46). Anal. calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.91; S, 8.56. Found: C, 64.41; H, 6.36; S, 8.81.

4.4.4. Methyl 2,3-dideoxy-3-*C*-(*p*)-tolylsulfonyl-5-*O*-trityl-β-D-*erythro*-pent-2-enofuranoside 3β. Compound **16** (0.46 g, 0.838 mmol) was converted to **3β** following the general procedure described earlier (0.37 g, 84%). Eluent: EtOAc:pet ether (1:4). White needle shaped crystal. Mp: 131–132°C. $[\alpha]_D^{26}=+11.4$ (*c* 1.012, $CHCl_3$). IR (Nujol): 3097, 3051, 3028, 1593, 1490, 1463, 1448, 1377 cm^{-1}. ^1H NMR: δ 7.53 (2H, d, *J*=8.3 Hz, aromatic), 7.42 (6H, dd, *J*=8.3, 2.4 Hz, aromatic), 7.34–7.25 (9H, m, aromatic), 7.17 (2H, d, *J*=7.8 Hz, aromatic), 6.64 (1H, t, *J*=1.5, 1.4 Hz, H-2), 5.78 (1H, s, H-1), 5.00 (1H, d, *J*=6.8 Hz), 3.48 (3H, s, OMe), 3.37 (1H, dd, *J*=10.3, 2.0 Hz), 3.09 (1H, dd, *J*=10.3, 6.8 Hz), 2.41 (3H, s, aromatic Me). ^{13}C NMR: δ 147.4, 145.1, 143.9, 136.9, 136.2, 130.1, 128.9, 128.0, 127.1, 107.7 (C-1), 86.7, 83.7, 66.0 (CH_2), 55.9, 21.7 (aromatic Me). MS: *m/z* (EI) 526 ($0.1M^+$), 494 (0.1), 450 (0.8), 449 (0.9), 267 (0.9), 243 (100), 165 (36), 91 (16), 77 (9). Anal. calcd for $C_{32}H_{30}O_5S$: C, 72.98; H, 5.73. Found: C, 73.12; H, 5.72.

4.4.5. Methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfide-α-D-*arabino*furanoside 7. Compound **5** (0.57 g, 2.43 mmol) was converted to **7** following the general procedure described above (0.81 g, 92%). Eluent: EtOAc:pet ether (1:4). Brown oil. $[\alpha]_D^{26}=+128.8$ (*c* 1.00, $CHCl_3$). IR (neat on KBr plate): 3438, 3062, 3030, 2866, 2833, 1596, 1494, 1454, 1400 cm^{-1}. ^1H NMR: δ 7.30 (7H, m, aromatic), 7.06 (2H, d, *J*=8.3 Hz, aromatic), 4.92 (1H, s, H-1), 4.61 (1H, d, *J*=12.2 Hz), 4.48 (1H, d, *J*=11.8 Hz), 4.42 (1H, m), 4.13 (1H, d, *J*=10.0 Hz), 3.77 (1H, dd, *J*=10.7, 2.0 Hz), 3.56 (1H, d, *J*=9.8 Hz), 3.44 (2H, m), 3.38 (3H, s, OMe), 2.29 (3H, s, aromatic Me). ^{13}C NMR: δ 137.2, 136.6, 131.1, 129.5, 128.1, 127.5, 109.4 (C-1), 82.9, 81.0, 73.0 (CH_2), 69.4 (CH_2), 54.6 (OMe), 52.9, 20.6 (aromatic Me). MS: *m/z* (EI) 360 ($9M^+$), 328 (2), 221 (1), 189 (1), 179 (3), 165 (5), 124 (39), 91 (100). Anal. calcd for $C_{20}H_{24}O_4S$: C, 66.64; H, 6.70; S, 8.89. Found: C, 66.34; H, 7.34: S, 8.89.

4.4.6. Methyl 3-deoxy-3-*C*-(*p*)-tolylsulfide-5-*O*-trityl-α-D-*arabino*furanoside 8. Compound **6** (5.1 g, 13.13 mmol) was converted to **8** following the general procedure described above (4.61 g, 69%). Eluent: EtOAc:pet ether (3:7). Colorless gum. $[\alpha]_D^{25}=+74.2$ (*c* 1.09, $CHCl_3$). IR ($CHCl_3$): 3442, 2831, 1666, 1492 cm^{-1}. ^1H NMR: δ 7.28 (17H, m, aromatic), 6.98 (2H, d, *J*=8.3 Hz, aromatic), 4.99 (1H, s, H-1), 4.15 (2H, a broad hump), 3.56 (1H, dd, *J*=10.3, 2.5 Hz), 3.39 (3H, s, OMe), 3.35 (1H, m), 3.05 (1H, dd, *J*=11.3, 4.0 Hz), 2.80 (1H, d, *J*=2.5 Hz, OH), 2.27 (3H, s, aromatic Me). ^{13}C NMR: δ 143.5, 136.8, 131.4, 131.2, 129.7, 128.6, 127.8, 127.0, 109.4, 87.1, 83.1, 81.3, 63.8 (CH_2), 54.9 (OMe), 53.5, 20.9 (aromatic Me). MS: *m/z* (EI) 512 ($4M^+$), 270 (2), 259 (2), 251 (3), 244 (8), 243 (100). Anal. calcd for $C_{32}H_{32}O_4S.1H_2O$: C, 72.43; H, 6.07; S, 6.04. Found: C, 72.25; H, 6.45; S, 5.73.

4.4.7. Methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfonyl-α-D-*arabino*furanoside 9. Compound **7** (0.59 g, 1.652 mmol) was converted to **9** following the general procedure described above (0.6 g, 93%). Eluent: EtOAc:pet ether (1:4). Brown gum. $[\alpha]_D^{26}=+95.2$ (*c* 1.00, $CHCl_3$). IR (Neat on KBr plate): 3481, 3062, 3030, 2925, 1596, 1494, 1454, 1402, 1363 cm^{-1}. ^1H NMR: δ 7.73 (2H, d, *J*=8.3 Hz, aromatic), 7.29 (7H, m, aromatic), 4.86 (1H, s, H-1), 4.48 (5H, m), 3.69 (2H, m), 3.33 (1H, dd, *J*=11.3 (10.8), 3.9 (3.4) Hz), 3.25 (3H, s, OMe), 2.39 (3H, s, aromatic Me). ^{13}C NMR: δ 144.9, 137.3, 134.9, 129.6, 128.3, 128.1, 127.5, 108.9, 77.2, 77.0, 73.1 (CH_2), 71.0, 69.4 (CH_2), 54.5 (OMe), 21.2 (aromatic Me). MS: *m/z* (EI) 392 ($<1.0M^+$), 343 (0.3), 301 (0.4), 271 (0.6), 262 (1.2), 243 (0.9), 205 (4), 155 (7), 107 (32), 92 (14), 91 (100). Anal. calcd for $C_{20}H_{24}O_6S.0.25H_2O$: C, 60.50; H, 6.21; S, 8.07. Found: C, 60.43; H, 6.46; S, 8.21.

4.4.8. Methyl 3-deoxy-3-*C*-(*p*)-tolylsulfonyl-5-*O*-trityl-α-D-*arabino*furanoside 10. Compound **8** (3.82 g, 7.460 mmol) was converted to **10** following the general procedure described above (3.31 g, 81%). Eluent: EtOAc: pet ether (3:7). White needle shaped solid. Mp: 70–71°C. $[\alpha]_D^{25}=+81.7$ (*c* 1.01, $CHCl_3$). IR ($CHCl_3$): 3479, 1637, 1596, 1492 cm^{-1}. ^1H NMR: δ 7.62 (2H, d, *J*=8.3 Hz, aromatic), 7.29 (17H, m, aromatic), 5.03 (1H, d, *J*=2.0 Hz, H-1), 4.64 (1H, m), 4.49 (1H, m), 3.80 (1H, m), 3.45 (1H, dd, *J*=10.8, 2.0 Hz), 3.37 (3H, s, OMe), 2.73 (2H, m), 2.42 (3H, s, aromatic Me). ^{13}C NMR: δ 145.1, 143.7, 135.3, 130.0, 128.7, 128.5, 127.9, 127.2, 109.0, 86.9, 77.3, 71.4, 63.9 (CH_2), 55.3, 21.7 (aromatic Me). MS: *m/z* (EI) 287 (1), 259 (1), 244 (6), 243 (100), 228 (3), 165 (19). Anal. calcd for $C_{32}H_{32}O_6S.1H_2O$: C, 68.31; H, 5.72; S, 5.69. Found: C, 68.01; H, 5.62; S, 6.78.

4.4.9. Methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfide-β-D-*xylo*furanoside 13. Compound **11** (0.44 g, 1.851 mmol) was converted to **13** following the general procedure described above (0.53 g, 79%). Eluent: EtOAc:pet ether (1:9). Brown gum. $[\alpha]_D^{30}=+16.1$ (*c* 1.04, $CHCl_3$). IR (neat): 3425, 3062, 3031, 2923, 2862 cm^{-1}. ^1H NMR: δ 7.28 (7H, m, aromatic), 7.03 (2H, d, *J*=8.3 Hz, aromatic), 4.81 (1H, d, *J*=1.9 Hz, H-1), 4.60 (1H, m), 4.54 (2H, s, $PhCH_2$), 4.25 (1H, dd, *J*=4.9, 1.9 Hz), 3.76–3.63 (3H, 2×m), 3.36 (3H, s, OMe), 3.25 (1H, broad hump, OH), 2.27 (3H, s, aromatic Me). ^{13}C NMR: δ 138.0, 136.0, 132.2, 130.3, 129.7, 128.1, 127.7, 127.4, 109.4 (C-1), 81.1, 79.9, 73.1 (CH_2), 71.2 (CH_2), 55.3 (OMe), 54.7, 20.8 (aromatic Me). MS: *m/z* (EI) 360 ($11M^+$), 328 (11), 149 (20), 135 (15), 124 (41), 91 (100). Anal. calcd for $C_{20}H_{24}O_4S$: C, 66.64; H, 6.70; S, 8.89. Found: C, 66.32; H, 7.24; S, 8.81.

4.4.10. Methyl 3-deoxy-3-*C*-(*p*)-tolylsulfide-5-*O*-trityl-β-D-*xylo*furanoside 14. Compound **12** (1.3 g, 3.37 mmol) was converted to **14** following the general procedure described above (1.64 g, 95%). Eluent: EtOAc:pet ether (1:9). White plate shaped solid. Mp: 114–115°C. $[\alpha]_D^{26}=+56.9$ (*c* 1.008,

$CHCl_3$). IR ($CHCl_3$): 4212, 3608, 3431, 2399, 1492, 1448 cm^{-1}. ^1H NMR: δ 7.51 (6H, d, J=6.8 Hz, aromatic), 7.25 (10H, m, aromatic), 7.02 (3H, dd, J=26.3, 7.8 Hz, aromatic), 4.88 (1H, d, J=2.4 Hz, H-1), 4.57–4.49 (1H, m), 4.35 (1H, bs), 3.58 (1H, t, J=6.9, 5.8 Hz), 3.43 (3H, s, OMe), 3.41–3.32 (2H, m), 2.65 (1H, J=4.4 Hz, OH), 2.25 (3H, s, aromatic Me). ^{13}C NMR: δ 144.2, 137.1, 132.1, 131.4, 129.9, 129.0, 127.8, 127.4, 109.6 (C-1), 87.1, 88.9, 81.2, 65.3 (CH_2), 55.9, 55.6, 21.1 (aromatic Me). MS: *m/z* (EI) 512 ($2M^+$), 269 (30), 243 (100). Anal. calcd for $C_{32}H_{32}O_4S$: C, 74.97; H, 6.28; S, 6.25. Found: C, 75.00; H, 6.21; S, 6.22.

4.4.11. Methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfonyl-β-D-*xylo*furanoside 15. Compound **13** (0.4 g, 1.11 mmol) was converted to **15** following the general procedure described above (0.39 g, 89%). Eluent: EtOAc:pet ether (3:7). Brown gum. $[\alpha]_D^{27}$=+17.2 (*c* 1.10, $CHCl_3$). IR ($CHCl_3$): 3479, 3087, 3062, 3029, 2927, 2869 cm^{-1}. ^1H NMR: δ 7.75 (2H, d, J=8.0 Hz, aromatic), 7.31 (7H, m, aromatic), 4.87 (1H, d, J=2.3 Hz, H-1), 4.74 (1H, dd, J=8.0, 2.0 Hz), 4.58 (2H, s, $PhCH_2$), 4.48 (1H, m), 3.91 (3H, m), 3.41 (3H, s, OMe), 3.00 (1H, bs, OH), 2.42 (3H, s, aromatic Me). ^{13}C NMR: δ 144.9, 137.8, 136.2, 129.7, 128.0, 127.5, 127.3, 110.2 (C-1), 78.1, 76.2, 73.1 (CH_2), 71.3, 69.8 (CH_2), 55.6 (OMe), 21.2 (aromatic Me). MS: *m/z* (EI) 392 (<$1M^+$), 360 (6), 205 (9), 187 (9), 155 (20), 139 (22), 107 (33), 99 (32), 99 (100). Anal. calcd for $C_{20}H_{24}O_6S$: C, 61.20; H, 6.16. Found: C, 61.37; H, 5.89.

4.4.12. Methyl 3-deoxy-3-*C*-(*p*)-tolylsulfonyl-5-*O*-trityl-β-D-*xylo*furanoside 16. Compound **14** (1.38 g, 2.69 mmol) was converted to **16** following the general procedure described above (1.08 g, 74%). Eluent: EtOAc:pet ether (1:3). White needle shaped solid. Mp: 74–75°C. $[\alpha]_D^{26}$=+40.9 (*c* 1.00, $CHCl_3$). IR (Nujol): 3469, 1596, 1490, 1463, 1448, 1377 cm^{-1}. ^1H NMR: δ 7.51–7.20 (19H, a broad multiplet, aromatic), 4.94 (1H, d, J=3.0 Hz, H-1), 4.75 (1H, dd, J=2.5(3.0), 7.8(8.3) Hz), 4.34 (1H, m), 3.83 (1H, t, J=58.3, 7.8 Hz), 3.42–3.64 (2H, m), 3.46 (3H, s, OMe), 2.82 (1H, bs, OH), 2.43 (3H, s, aromatic Me). ^{13}C NMR: δ 145.8, 144.5, 136.7, 130.7, 129.5, 128.6, 128.4, 127.6, 110.9, 87.5, 79.2, 77.2, 72.2, 64.5 (CH_2), 56.8, 21.8 (aromatic Me). MS: *m/z* (EI) 544 ($1M^+$), 470 (2), 405 (2), 360 (3), 243 (100). Anal. calcd for $C_{32}H_{32}O_6S.2H_2O$: C, 66.18; H, 6.24; S, 5.52. Found: C, 66.28; H, 6.30; S, 5.93.

4.4.13. 5-*O*-Benzyl-3-deoxy-1,2-*O*-isopropylidene-3-*C*-(*p*)-tolylsulfide-α-D-*ribo*furanose 18. To a well stirred solution of NaOMe (1.98 g, 36.79 mmol) in DMF (40 mL) was added *p*-thiocresol (5.7 g, 45.99 mmol) and the mixture was stirred for 0.5 h. A solution of **17** (3.99 g, 9.19 mmol) in DMF (20 mL) was added and the reaction mixture was then heated at 120°C. After 4 h, the mixture was cooled to room temperature and poured into brine (150 mL) solution. The aqueous phase was extracted with EtOAc (5×30 mL). The combined organic phases were dried over anhydr. Na_2SO_4, filtered and the filtrate was concentrated to dryness under reduced pressure. Purification of the crude product on silica gel using EtOAc:pet ether (1:19) yielded **18** (2.08 g, 59%). Brown gum. $[\alpha]_D^{26}$=+100.1 (*c* 1.02, $CHCl_3$). IR ($CHCl_3$): 1492, 1454, 1384 cm^{-1}. ^1H NMR: δ 7.28 (9H, m, aromatic); 5.84 (1H, d, J=3.4 Hz, H-1), 4.80 (1H, t, J=3.9 Hz), 4.37 (2H, d, J=2.9 Hz, $PhCH_2$), 4.16 (1H, m), 3.80 (1H, dd, J=11.2, 1.5 Hz), 3.53 (2H, m), 2.32 (3H, s, aromatic Me), 1.56 (3H, s, Me), 1.37 (3H, s, Me). ^{13}C NMR: δ 137.9, 137.0, 131.9, 129.6, 128.0, 127.3, 111.8, 104.1, 81.3, 73.1 ($PhCH_2$), 67.6 (CH_2), 50.7, 26.5 (Me), 26.3 (Me), 20.8 (aromatic Me). MS: *m/z* (EI) 386 ($18M^+$), 328 (20), 207 (33), 163 (20), 123 (75), 91 (100). Anal. calcd for $C_{22}H_{26}O_4S$: C, 68.36; H, 6.77; S, 8.29. Found: C, 68.25; H, 6.87; S, 8.62.

4.4.14. Methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfide-α-D-*ribo*furanoside 19 and methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfide-β-D-*ribo*furanoside 20. A solution of **18** (2.08 g, 5.39 mmol) and conc. H_2SO_4 (1 mL) in dry MeOH (30 mL) was heated under reflux in an inert atmoshphere. After 3.5 h, the reaction mixture was cooled to room temperature and neutralized by $BaCO_3$. The mixture was evaporated to dryness under reduced pressure and the residue was triturated with EtOAc (3×40 mL). The mixture was filtered through celite and the combined filtrates were concentrated to dryness under reduced pressure. Purification of the gummy residue over silica gel using EtOAc:pet ether (4:21) furnished a mixture of **19** and **20** (1.52 g, 78%). Compound **19** and **20** were isolated as colorless thick gum.

Compound **19** (0.05 g, 2.6%). Brown gum. $[\alpha]_D^{26}$=+145.1 (*c* 1.024, $CHCl_3$). IR ($CHCl_3$): 3523, 1492 cm^{-1}. ^1H NMR: δ 7.31 (7H, m, aromatic), 7.08 (2H, d, J=8.3 Hz, aromatic), 4.97 (1H, d, J=3.9 Hz), 4.53 (2H, m, $PhCH_2$), 4.39 (1H, m), 4.25 (1H, m), 3.61 (3H, m), 3.49 (3H, s, OMe), 3.2 (1H, d, J=9.8 Hz, OH), 2.33 (3H, s, aromatic Me).^{13}C NMR: δ 138.3, 137.3, 132.7, 131.7, 130.0, 128.6, 127.8, 103.2 (C-1), 82.9, 73.8 (CH_2), 71.9, 70.4 (CH_2), 55.5 (OMe), 52.8, 21.2 (aromatic Me). MS: *m/z* (EI) 360 ($3M^+$), 328 (2), 163 (4), 124 (38), 91 (100). Anal. calcd for $C_{20}H_{24}O_4S$: C, 66.64; H, 6.70; S, 8.89. Found: C, 66.90; H, 6.72; S, 9.05.

Compound **20** (1.07 g, 55%). Brown gum. $[\alpha]_D^{26}$=−40.5 (*c* 1.01, $CHCl_3$). IR ($CHCl_3$): 3444, 1951, 1888, 1598 cm^{-1}. ^1H NMR: δ 7.35 (7H, m, aromatic), 7.11 (2H, d, J=7.9 Hz, aromatic), 4.98 (1H, s, H-1), 4.64 (2H, s, $PhCH_2$), 4.17 (1H, m), 3.98 (1H, dd, J=3.9, 1.4 Hz), 3.71 (4H, m), 3.34 (3H, s, OMe), 2.90 (1H, d, J=1.5 Hz, OH), 2.33 (3H, s, aromatic Me). ^{13}C NMR: δ 138.5, 138.0, 132.1, 130.2, 129.9, 128.5, 127.6, 108.4 (C-1), 81.7, 74.9, 73.4 (CH_2), 71.8 (CH_2), 54.7 (OMe), 53.5, 21.1 (aromatic Me). MS: *m/z* (EI) 360 ($13M^+$), 328 (4), 124 (23), 123 (18), 91 (100). Anal. calcd for $C_{20}H_{24}O_4S$: C, 66.64; H, 6.70; S, 8.89. Found: C, 66.80; H, 7.00; S, 8.82.

4.4.15. Methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfonyl-α-D-*ribo*furanoside 21. Compound **19** (0.05 g, 0.127 mmol) was converted to **21** following the general procedure described above (0.04 g, 94%). Eluent: EtOAc: pet ether (3:7). Brown gum. $[\alpha]_D^{26}$=+100.9 (*c* 1.006, $CHCl_3$). IR ($CHCl_3$): 4214, 3531, 2401, 2343, 1730, 1596 cm^{-1}. ^1H NMR: δ 7.77 (2H, d, J=8.3 Hz, aromatic), 7.31 (7H, m, aromatic), 4.95 (1H, d, J=4.9 Hz, H-1), 4.72 (1H, dq, J=2.9, 2.0 Hz), 4.59 (1H, d, J=12.2 Hz, PhCH), 4.46 (1H, d, J=12.2 Hz, PhCH), 4.33–4.45 (1H, m), 3.93 (1H, m), 3.65 (1H, dd, J=10.7, 1.9 Hz), 3.45–3.52 (5H, m), 2.43 (3H, s, aromatic Me). ^{13}C NMR: δ 144.8, 137.8, 136.9,

129.6, 128.7, 128.4, 127.7, 101.9 (C-1), 76.1, 73.5 (CH_2), 72.1, 69.5 (CH_2), 62.9, 55.3 (OMe), 21.6 (aromatic Me). MS: *m/z* (EI) 360 ($0.6M^+-O_2$), 205 (6.7), 175 (1.3), 155 (4.0), 139 (4.3), 117 (2.0), 91 (100). Anal. calcd for $C_{20}H_{24}O_6S$: C, 61.20; H, 6.16; S, 8.17. Found: C, 61.21; H, 6.23; S, 8.09.

4.4.16. Methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfonyl-β-D-*ribo*furanoside 22. Compound **20** (0.95 g, 2.64 mmol) was converted to **22** following the general procedure described above (0.96 g, 93%). Eluent: EtOAc:pet ether (1:3). Brown needle shaped solid. Mp: 79–80°C. $[\alpha]_D^{26}=-50.0$ (*c* 1.00, $CHCl_3$). IR ($CHCl_3$): 4214, 3479, 2401, 1596 cm^{-1}. ^1H NMR: δ 7.80 (2H, d, *J*=8.1 Hz, aromatic), 7.32 (7H, m, aromatic), 4.93 (1H, m), 4.84 (1H, s, H-1), 4.54 (2H, d, *J*=5.5 Hz, $PhCH_2$), 4.15 (1H, t, *J*=4.3 Hz), 3.87 (2H, m), 3.72 (1H, dd, *J*=10.7, 2.2 Hz), 3.52 (1H, dd, *J*=10.7, 5.5 Hz), 3.26 (3H, s, OMe), 2.45 (3H, s, aromatic Me). ^{13}C NMR: δ 145.5, 138.1, 136.4, 130.0, 128.2, 127.5, 108.4 (C-1), 77.1, 75.5, 73.3 (CH_2), 72.0 (CH_2), 65.1, 54.4 (OMe), 21.6 (aromatic Me). MS: *m/z* (EI) 360 ($0.5M^+-$MeOH), 271 (0.3), 243 (0.4), 205 (10), 155 (6), 107 (10), 91 (100). Anal. calcd for $C_{22}H_{24}O_6S$: C, 61.20; H, 6.16; S, 8.17. Found: C, 61.06; H, 6.38; S, 8.47.

4.4.17. Methyl 5-*O*-benzyl-2,3-dideoxy-3-*C*-(*p*)-tolylsulfonyl-α-D-*erythro*-pent-2-enofuranoside 2α. Compound **21** (0.38 g, 0.977 mmol) was converted to **2α** following the general procedure described above (0.27 g, 74%). The reaction mixture was kept at +4°C for 12 h and then it was stirred for 8 h at ambient temperature.

4.4.18. Methyl 5-*O*-benzyl-2,3-dideoxy-3-*C*-(*p*)-tolylsulfonyl-β-D-*erythro*-pent-2-enofuranoside 2β. Compound **22** (0.369 g, 0.941 mmol) was converted to **2β** following the general procedure described above (0.32 g, 92%).

4.4.19. 5-*O*-Benzyl-1,2-*O*-isopropylidene-3-*O*-mesyl-α-D-*ribo*furanose 26. To a stirred solution of **25** (0.32 g, 1.14 mmol) was added a solution of mesyl chloride (0.3 mL, 3.42 mmol) in dry pyridine (10 mL) dropwise at 0°C under nitrogen atmosphere. After completion of addition, the reaction mixture was kept at +4°C for 24 h. The reaction mixture was worked up as per the procedure mentioned for **17** to obtain an oil which was purified over silica gel using EtOAc:pet ether (1:4) to afford **26** (0.4 g, 98%). Brown oil. $[\alpha]_D^{26}=+88.2$ (*c* 1.07, $CHCl_3$). IR ($CHCl_3$): 3446, 2343, 1417, 1373, 1365 cm^{-1}. ^1H NMR: δ 7.43–7.26 (5H, m), 5.85 (1H, d, *J*=3.9 Hz, H-1), 4.87 (1H, m), 4.77 (1H, t, *J*=3.9 (4.4) Hz), 4.65 (1H, d, *J*=12.2 Hz), 4.56 (1H, d, *J*=11.7 Hz), 4.26 (1H, dt, *J*=3.4 (3.8), 3.0 Hz), 3.76 (1H, dd, *J*=11.7, 2.4 Hz), 3.65 (1H, dd, *J*=11.7, 3.4 Hz), 3.05 (3H, s, OMe), 1.58 (3H, s, Me), 1.38 (3H, s, Me). ^{13}C NMR: δ 137.7, 128.5, 127.8, 113.5, 104.1, 77.3, 76.6, 75.8, 73.7 (CH_2), 67.0 (CH_2), 38.3, 26.6. MS: *m/z* (EI) 358 ($14M^+$), 343 (6), 237 (7), 179 (23), 175 (13), 151 (14), 107 (22), 91 (100), 85 (18). Anal. calcd for $C_{16}H_{22}O_7S$: C, 53.62; H, 6.18; S, 8.94. Found: C, 53.62; H, 6.17; S, 8.72.

4.4.20. 5-*O*-Benzyl-3-deoxy-1,2-*O*-isopropylidene-3-*C*-(*p*)-tolylsulfide-α-D-*xylo*furanose 27. Compound **26** (2.84 g, 7.93 mmol) was converted to **27** following a procedure for the synthesis of **18**. The reaction mixture was heated at 135–140°C for 2.5–3 h (2.43 g, 79%). Eluent: EtOAc:pet ether (1:21). Brown gum. $[\alpha]_D^{30}=-31.0$ (*c* 1.00, $CHCl_3$). IR ($CHCl_3$): 2985, 2931, 1496 cm^{-1}. ^1H NMR: δ 7.36 (7H, m, aromatic), 7.14 (2H, d, *J*=7.8 Hz, aromatic), 5.94 (1H, d, *J*=3.4 Hz, H-1), 4.70–4.53 (4H, m), 3.83 (2H, d, *J*=5.9 Hz, $PhCH_2$), 3.76 (1H, d, *J*=3.9 Hz), 2.53 (3H, s, aromatic Me), 1.53 (3H, s, Me), 1.29 (3H, s, Me). ^{13}C NMR: δ 137.9, 136.8, 130.8 129.8, 128.1, 127.6, 111.5, 104.7, 85.2, 77.9, 73.3 (CH_2), 69.2 (CH_2), 54.2, 26.5, 26.2, 20.8 (aromatic Me). MS: *m/z* (EI) 386 ($19M^+$), 233 (10), 207 (24), 205 (10), 178 (20), 139 (14), 124 (14), 123 (40), 107 (14), 99 (16), 91 (100). Anal. calcd for $C_{22}H_{26}O_4S$: C, 68.36; H, 6.77; S, 8.29. Found: C, 68.03; H, 7.23; S, 8.29.

4.4.21. Methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfide-α-D-*xylo*furanoside 28 and methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfide-β-D-*xylo*furanoside 13. A solution of **27** (2.43 g, 6.29 mmol) and conc. H_2SO_4 (1 mL) in dry MeOH (70 mL) was heated under reflux. After 2.5 h, the reaction mixture was worked up as described for **19** and **20**. The anomers were separated on silica gel using EtOAc:pet ether (1:3) to give **28** and **13**. Compound **28** (1.2 g, 53%). Yellowish gum. $[\alpha]_D^{30}=+163.7$ (*c* 1.13, $CHCl_3$). IR (neat): 3487, 3062, 3024, 2916, 1862 cm^{-1}. ^1H NMR: δ 7.37 (7H, m, aromatic), 7.10 (2H, d, *J*=8.3 Hz, aromatic), 4.98 (1H, d, *J*=4.4 Hz, H-1), 4.60 (1H, m), 4.60 (2H, d, *J*=11.2 Hz, $PhCH_2$), 4.29 (1H, dd, *J*=8.0, 4.6 Hz), 3.78 (2H, d, *J*=3.9 Hz), 3.65 (1H, t, *J*=7.8 Hz), 3.50 (3H, s, OMe), 2.76 (1H, bs, OH), 2.34 (3H, s, aromatic Me).^{13}C NMR: δ 137.7, 136.0, 132.3, 130.2, 129.4, 128.0, 127.3, 127.1, 101.2 (C-1), 77.4, 76.3, 72.9 (CH_2), 70.2 (CH_2), 55.0 (OMe), 54.0, 20.5 (aromatic Me). MS: *m/z* (EI) 360 ($13M^+$), 159 (11), 149 (11), 124 (100), 91 (61). Anal. calcd for $C_{20}H_{24}O_4S$: C, 66.64; H, 6.70. Found: C, 66.57; H, 7.07. Compound **13** (0.81 g, 36%).

4.4.22. Methyl 5-*O*-benzyl-3-deoxy-3-*C*-(*p*)-tolylsulfonyl-α-D-*xylo*furanoside 29. Compound **28** (0.62 g, 1.72 mmol) was converted to **29** following the general procedure described above (0.61 g, 90%). Eluent: EtOAc:pet ether (3:7). White needle shaped solid. Mp: 127–128°C. $[\alpha]_D^{27}=+236.8$ (*c* 1.00, $CHCl_3$). IR ($CHCl_3$): 3487, 2954, 2923, 2854 cm^{-1}. ^1H NMR: δ 7.79 (2H, d, *J*=7.8 Hz, aromatic), 7.36 (7H, m, aromatic), 4.98 (1H, d, *J*=4.4 Hz, H-1), 4.62 (4H, m), 4.09 (2H, m), 3.74 (1H, t, *J*=7.8 Hz), 3.45 (3H, s, OMe), 3.00 (1H, bs, OH), 2.42 (3H, s, aromatic Me). ^{13}C NMR: δ 145.1, 138.2, 136.6, 129.9, 129.0, 128.0, 127.9, 101.3 (C-1), 76.6, 73.9, 73.6 (CH_2), 69.7 (CH_2), 69.4, 55.6 (OMe), 21.7 (aromatic Me). MS: *m/z* (EI) 392 ($<1M^+$), 360 ($5M^+-O_2$), 115 (10), 139 (11), 107 (10), 99 (16), 99 (100). Anal. calcd for $C_{20}H_{24}O_6S$: C, 61.20; H, 6.16. Found: C, 61.07; H, 6.05.

4.4.23. Methyl 5-*O*-benzyl-2,3-dideoxy-3-*C*-(*p*)-tolylsulfonyl-α-D-*erythro*-pent-2-enofuranoside 2α. Compound **29** (0.5 g, 1.27 mmol) was converted to **2α** following the general procedure (0.36 g, 76%).

Compound **19** *from* **30**. Compound **30** (1.71 g, 4.196 mmol) was converted to **19** following a procedure described for the synthesis of **18**. The reaction mixture was heated at 115–120°C for 3.5 h (1.33 g, 88%).

Compound **20** *from* **31**. Compound **31** (1.15 g, 3.705 mmol) was converted to **20** following a procedure described for the synthesis of **18**. The reaction mixture was heated at 115–120°C for 3 h (1.11 g, 83%).

Compounds **19** *and* **20** *from the mixture of* **30** *and* **31**. A mixture of compounds **30** and **31** (3.99 g, 9.19 mmol) was converted to the mixture of **19** and **20** following the procedure described for the synthesis of **18** (2.09 g, 94%).

4.4.24. Methyl 3-deoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfide-β-D-*allo*pyranoside 35. To a well stirred solution of NaOMe (0.506 g, 9.38 mmol) in DMF (10 mL) was added dropwise thiophenol (1.2 mL, 11.726 mmol) under nitrogen at ambient temperature. After 15 min, **34** (0.98 g, 2.345 mmol) in DMF (20 mL) was added into the mixture and the mixture was heated at 135–140°C. After 2 h, the mixture was cooled to room temperature, poured into brine (150 mL) and the aqueous phase was extracted with EtOAc (4×40 mL). The combined extracts were dried over anhydr. Na_2SO_4, filtered and the filtrate was evaporated to dryness under reduced pressure to get the crude material. Purification of the crude material over silica gel using EtOAc:pet ether (1:4) produced the title compound (0.79 g, 90%). White solid. Mp: 133–134°C. $[\alpha]_D^{26}=-40.5$ (*c* 1.00, $CHCl_3$). IR ($CHCl_3$): 3475, 3018, 2401, 2358 cm^{-1}. ^1H NMR: δ 7.59 (2H, m, aromatic), 7.39 (5H, m, aromatic), 7.24 (3H, t, *J*=3.4 Hz, aromatic), 5.60 (1H, s, PHCH), 4.40 (2H, m), 4.02 (5H, m), 3.60 (3H, s, OMe), 3.12 (1H, d, *J*=8.8 Hz, OH). ^{13}C NMR: δ 137.4, 135.7, 132.8, 129.1, 128.2, 127.6, 126.4, 103.3, 101.5, 78.6, 70.4, 69.1 (CH_2), 65.4, 57.9, 57.3 (OMe). MS: *m/z* (EI) 374 ($6M^+$), 233 (2), 187 (3), 159 (9), 129 (20), 107 (100), 91 (75). Anal. calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.91. Found: C, 63.98; H, 5.81.

4.4.25. Methyl 3-deoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfonyl-β-D-*allo*pyranoside 36. Compound **35** (0.58 g, 1.54 mmol) was converted to **36** following the general procedure described above (0.59 g, 95%). Eluent: EtOAc:pet ether (3:7). Brownish needle shaped solid. Mp: 129–130°C. $[\alpha]_D^{26.5}=-46.3$ (*c* 1.00, $CHCl_3$). IR ($CHCl_3$): 3450, 3427, 3016, 1448 cm^{-1}. ^1H NMR: δ 7.76 (2H, d, *J*=7.8 Hz, aromatic), 7.23 (8H, a series of m, aromatic), 5.22 (1H, s, PhCH), 5.11 (1H, d, *J*=8.3 Hz, H-1), 4.87 (1H, broad hump), 4.74 (1H, m), 4.35 (1H, q), 4.18 (1H, t, *J*=4.9 Hz), 3.85 (1H, broad hump), 3.68 (1H, q), 3.57 (3H, s, OMe), 3.54 (1H, m). ^{13}C NMR: δ 140.9, 136.1, 133.4, 128.7, 128.5, 128.3, 127.7, 125.9, 101.1 (C-1), 77.1, 76.3, 72.4, 69.3 (CH_2), 63.8, 63.2, 56.9 (OMe). MS: *m/z* (EI) 233 (7), 187 (6), 159 (10), 127 (30), 107 (100), 91 (38), 77 (57). Anal. calcd for $C_{20}H_{22}O_7S$ C, 59.10; H, 5.45; S, 7.88. Found: C, 58.97; H, 5.66; S, 7.86.

4.4.26. Methyl 2,3-dideoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfonyl-β-D-*erythro*-hex-2-enopyranoside 1β. Compound **36** (0.59 g, 1.472 mmol) was converted to **1β** following the general procedure described above (0.53 g, 93%). The reaction mixture was stirred for 4 h allowing it to warm up from 0°C to room temperature. Eluent: EtOAc:pet ether (2:3).

4.4.27. Methyl 2-deoxy-4,6-*O*-(phenylmethylene)-2-*C*-phenylsulfide-α-D-*altro*pyranoside 37. Compound **33** (0.17 g, 0.407 mmol) was converted to **37** following a procedure reported for **35** (0. 06 g, 39%). Eluent: EtOAc:pet ether (1:4). Colorless gum. IR ($CHCl_3$): 3500, 2360, 2331, 1671, 1583 cm^{-1}. ^1H NMR: δ 7.32 (10H, m, aromatic), 5.61 (1H, s, PhCH), 4.81 (1H, s, H-1), 4.22 (3H, m), 4.04 (1H, dd, *J*=9.8, 3.0 Hz), 3.81 (1H, t, *J*=8.3 Hz), 3.58 (1H, d, *J*=2.4 Hz), 3.35 (3H, s, OMe), 3.09 (1H, d, *J*=5.8 Hz, OH). ^{13}C NMR: δ 137.3, 133.9, 131.0, 129.4, 129.1, 128.2, 127.6, 126.3, 102.2, 101.3, 76.4, 69.1 (CH_2), 68.8, 58.6, 55.7 (OMe), 51.6. MS: *m/z* (EI) 374 ($36M^+$), 343 (4), 165 (88), 152 (88), 123 (42), 105 (82), 91 (100), 77 (90). Anal. calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.91; S, 8.56. Found: C, 63.90; H, 6.23; S, 8.27.

4.4.28. 3-Deoxy-1,2:5,6-di-*O*-isopropylidene-3-*C*-phenylsulfide-α-D-*allo*furanose 39. Compound **32** (10.72 g, 25.88 mmol) was converted to **39** following the procedure reported for **35** (8.23 g, 90%). The reaction mixture was heated at 125°C for 4 h. Eluent: EtOAc:pet ether (1:9). Colorless needle shaped solid. Mp: 84–85°C. IR (Nujol): 1647, 1461 cm^{-1}. ^1H NMR: δ 7.50 (2H, d, *J*=5.9 Hz, aromatic), 7.28 (3H, m, aromatic), 5.81 (1H, d, *J*=3.4 Hz, H-1), 4.77 (1H, t, *J*=4.4, 3.9 Hz), 4.17–4.45 (2H, m), 4.04 (1H, t, *J*=6.8, 9.3 Hz), 3.92 (1H, t, *J*=7.9, 6.8 Hz), 3.29 (1H, dd, *J*=9.8, 4.4 Hz), 1.58 (3H, s, Me), 1.37 (3H, s, Me), 1.30 (6H, s, 2×Me). ^{13}C NMR: δ 143.8, 132.0, 129.0, 127.4, 112.3, 109.6, 104.1, 81.7, 80.6, 75.7, 65.1 (CH_2), 52.5, 26.7, 26.5, 26.1. MS: *m/z* (E1) 352 ($27M^+$), 337 (13), 193 (100), 109 ($76M^+-PhS$). Anal. calcd for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86. Found: C, 61.26; H, 7.17.

4.4.29. 3-Deoxy-1,2:5,6-di-*O*-isopropylidene-3-*C*-phenylsulfide-α-D-*gluco*furanose 40. Compound **38** (2.35 g, 6.96 mmol) was converted to **40** following a procedure reported for **35** (1.98 g, 80%). The reaction mixture was heated at 125°C for 2 h. Eluent: EtOAc:pet ether (4%–10%). Brown solid. Mp: 75–76°C. $[\alpha]_D^{26}=-31.3$ (*c* 1.06, $CHCl_3$). IR ($CHCl_3$): 2889, 2434, 2401, 1944, 1868, 1583, 1481, 1454, 1375 cm^{-1}. ^1H NMR: δ 7.43 (2H, dd, *J*=8.3, 1.5 Hz, aromatic), 7.40–7.19 (3H, m, aromatic), 5.89 (1H, d, *J*=3.4 Hz, H-1), 4.62 (1H, d, *J*=3.5 Hz, H-2), 4.45–4.30 (2H, m), 4.16 (1H, dd, *J*=8.2, 5.5 Hz), 4.03 (1H, dd, *J*=8.8, 4.4 Hz), 3.90 (1H, d, *J*=3.4 Hz), 1.52 (3H, s, Me), 1.45 (3H, s, Me), 1.36 (3H, s, Me), 1.27 (3H, s, Me). ^{13}C NMR: δ 134.0, 130.3 129.2, 126.8, 111.9, 109.5, 105.0, 85.4, 80.0, 73.8, 67.7 (CH_2), 53.6, 26.9 (Me), 26.7 (Me), 26.3 (Me), 25.3 (Me). MS: *m/z* (EI) 352 ($30M^+$), 337 (29), 193 (58), 164 (25), 101 (100). Anal. calcd for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86; S, 9.09. Found: C, 61.66; H, 7.66; S, 9.53.

4.4.30. 3-Deoxy-1,2:5,6-di-*O*-isopropylidene-3-*C*-phenylsulfonyl-α-D-*gluco*furanose 41. Compound **40** (0.2 g, 0.565 mmol) was converted to **41** following the general procedure described above (0.2 g, 94%). Eluent: EtOAc:pet ether (1:3). Colorless needle shaped solid. Mp: 158–159°C. $[\alpha]_D^{27}=-0.5$ (*c* 1.02, $CHCl_3$). IR ($CHCl_3$): 2358, 2341, 1595, 1585, 1448 cm^{-1}. ^1H NMR: δ 7.96 (2H, d, *J*=6.9 Hz, aromatic), 7.74–7.56 (3H, m, aromatic), 5.96 (1H, d, *J*=3.9 Hz, H-1), 4.96 (1H, d, *J*=3.5 Hz, H-2), 4.83–4.73 (1H, m), 4.31 (1H, dd, *J*=8.8, 4.8 Hz), 4.18 (1H, dd, *J*=8.8, 5.9 Hz), 4.02 (1H, dd, *J*=8.8, 4.9 Hz), 3.87 (1H, d, *J*=4.8 Hz), 1.49 (3H, s, Me), 1.35 (3H, s, Me), 1.29 (3H, s, Me), 1.21 (3H, s, Me). ^{13}C NMR: δ 139.6, 134.2, 129.5,

128.5, 112.4, 109.7, 105.0, 81.3, 80.2, 72.6, 69.9, 68.0 (CH_2), 26.7, 26.8, 26.4, 25.2. MS: *m/z* (EI) 369 (12), 311 (7), 141 (17), 125 (13), 101 (100), 77 (28). Anal. calcd for $C_{18}H_{24}O_7S$: C, 56.23; H, 6.28; S, 8.34. Found: C, 56.19; H, 6.90; S, 8.62.

4.4.31. Methyl 3-deoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfide-α-D-*gluco*pyranoside 42 and Methyl 3-deoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfide-β-D-*gluco*pyranoside 43. Acetyl chloride (0.2 mL, 2.451 mmol) was added drop-wise to a well stirred solution of **40** (0.173 g, 0.491 mmol) in anhydr. MeOH at an ambient temperature and the mixture was heated under reflux. After 24 h, the reaction mixture was neutralized with $BaCO_3$. The mixture was concentrated to dryness under reduced pressure to get a solid mass. The solid was triturated with EtOAc (30 mL) and the liquid was decanted. The process was repeated four times. The combined organic layers was passed through a celite bed. The filtrate was then concentrated to dryness under reduced pressure to get a mixture of methyl 3-deoxy-3-*C*-phenylsulfide-α- and -β-D-glucopyranosides. To a well stirred solution of the anomers (0.14 g, 0.491 mmol) in DMF (10 mL) was added a catalytic amount *p*-TSA and 1,1-dimethyl toluene (0.15 mL, 0.982 mmol) and the mixture was heated at 100°C with stirring under reduced pressure. After 1 h, the reaction mixture was neutralized with pyridine. Excess DMF and other volatile matters were removed under reduced pressure. The residue thus obtained was dissolved in saturated $NaHCO_3$ solution and the aqueous phase was extracted with EtOAc (4×20 mL). Combined organic layers after usual work up generated solid material which on purification over silica gel using EtOAc:pet ether (1:3) produced a mixture of **42** and **43** (0.131 g, 71%). Compounds **42** and **43** were finally separated over silica gel using a mixture of acetone:chloroform:pet ether (7:7:86).

Compound **42** (0.08 g, 44%). Cotton-like white solid. Mp: 129–130°C. $[\alpha]_D^{27}=+19.2$ (*c* 1.00, $CHCl_3$). IR ($CHCl_3$): 3444, 2725, 2360, 2324, 1456, 1373 cm^{-1}. ^1H NMR: δ 7.57–7.21 (10H, series of m, aromatic), 5.41 (1H, s, PhCH), 4.77 (1H, d, *J*=3.5 Hz, H-1), 4.20 (1H, dd, *J*=10.2, 4.9 Hz), 3.88–3.81 (1H, m), 3.57 (1H, t, *J*=10.3 Hz), 3.50–3.41 (1H, m), 3.41 (3H, s, OMe), 3.28 (1H, t, *J*=10.3 Hz), 3.19 (1H, t, *J*=10.3 Hz), 2.72 (1H, d, *J*=6.3 Hz, OH). ^{13}C NMR: δ 137.3, 135.2, 131.3, 128.9, 128.6, 126.2, 101.6, 99.5, 78.5, 69.7, 69.0 (CH_2), 64.4, 55.4 (OMe), 52.4. MS: *m/z* (EI) 374 (72M^+), 237 (13), 165 (15), 129 (29), 107 (100), 91 (41), 77 (25). Anal. calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.91. Found: C, 64.17; H, 6.37.

Compound **43** (0.03 g, 16%). Brown needle shaped solid. Mp: 84–85°C. $[\alpha]_D^{27}=-116.3$ (*c* 0.92, $CHCl_3$). IR ($CHCl_3$): 3502, 2360, 2331, 1471, 1452, 1386, 1365, 1217 cm^{-1}. ^1H NMR: δ 7.60–7.25 (10H, m, aromatic), 5.45 (1H, s, PhCH), 4.36 (1H, d, *J*=7.3 Hz, H-1), 4.31 (1H, dd, *J*=10.3, 4.4 Hz), 3.65 (1H, t, *J*=10.2 Hz), 3.55 (3H, s, OMe), 3.52–3.40 (1H, m), 3.34–3.01 (4H, m). ^{13}C NMR: δ 137.3, 135.6, 130.6, 129.2, 128.8, 128.4, 126.2, 105.4, 101.6, 77.9, 71.2, 69.5, 68.8 (CH_2), 57.4, 54.5. MS: *m/z* (EI) 374 (65M^+), 187 (13), 159 (11), 129 (21), 107 (100), 91 (84), 77 (52). Anal. calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.91; S, 8.56. Found: C, 64.33; H, 5.81; S, 8.95.

4.4.32. Methyl 3-deoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsufonyl-α-D-*gluco*pyranoside 44. Compound **42** (0.13 g, 0.35 mmol) was converted to **44** following the general procedure described above (0.13 g, 92%). White needle shaped solid. Mp: 104–105°C. $[\alpha]_D^{27}=+37.8$ (*c* 0.98, $CHCl_3$). IR ($CHCl_3$): 3504, 2401, 2360, 23443, 1448, 1365 cm^{-1}. ^1H NMR: δ 7.81 (2H, d, *J*=8.3 Hz, aromatic), 7.50 (1H, t, *J*=8.0 Hz, aromatic), 7.30 (5H, m, aromatic), 7.10 (2H, d, *J*=7.3 Hz, aromatic), 5.44 (1H, s, PhCH), 4.87 (1H, d, *J*=3.4 Hz, H-1), 4.50–4.41 (2H, m), 4.23 (1H, dd, *J*=9.3, 3.9 Hz), 3.94–3.69 (4H, m), 3.48 (3H, s, OMe). ^{13}C NMR: δ 140.6, 136.5, 133.9, 129.3, 128.9, 128.8, 128.2, 126.4, 102.0, 98.9, 76.2, 69.4 (CH_2), 67.3, 65.9, 62.6, 55.6. MS: *m/z* (EI) 406 (<1M^+), 405 (1), 375 (<1), 233 (20), 187 (12), 159 (14), 127 930), 107 (100), 91 (34), 77 (60). Anal. calcd for $C_{20}H_{22}O_7S$: C, 59.10; H, 5.45. Found: C, 59.30; H, 5.48.

4.4.33. Methyl 3-deoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsufonyl-β-D-*gluco*pyranoside 45. Compound **43** (0.07 g, 0.181 mmol) was converted to **45** following the general procedure described above (0.07 g, 90%). Pale brown solid. Mp: 145–146°C. $[\alpha]_D^{27}=-78.6$ (*c* 1.00, $CHCl_3$). IR ($CHCl_3$): 3502, 2401, 2360, 2331, 1448, 1365 cm^{-1}. ^1H NMR: δ 7.83 (2H, d, *J*=6.9 Hz, aromatic), 7.54 (1H, t, *J*=7.3 Hz, aromatic), 7.31 (5H, m, aromatic), 7.10 (2H, dd, *J*=7.8, 1.9 Hz, aromatic), 5.40 (1H, s, PhCH), 4.45 (1H, d, *J*=6.9 Hz, H-1), 4.30 (1H, dd, *J*=10.8, 4.8 Hz), 4.18 (1H, dd, *J*=9.8, 7.3 Hz), 3.89–3.43 (5H, m), 3.60 (3H, s, OMe). ^{13}C NMR: δ 140.0, 136.5, 134.0, 129.4, 129.1, 128.9, 128.2, 126.3, 104.7, 101.7, 75.8, 69.2, 69.0 (CH_2), 68.5, 67.7, 57.6. MS: *m/z* (EI) 265 (3), 233 (8), 187 (8), 159 (10), 127 (30), 107 (100), 91 (31), 77 (77). Anal. calcd for $C_{20}H_{22}O_7S$: C, 59.10; H, 5.45. Found: C, 58.88; H, 5.66.

4.4.34. Methyl 3-deoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfonyl-α-D-*gluco*pyranoside 44 and Methyl 3-deoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfonyl-β-D-*gluco*pyranoside 45. Compound **41** (0.21 g, 0.557 mmol) was converted to an anomeric mixture of **44** and **45** (0.17 g, 75%) following the procedure described for **42** and **43**. The anomers **44** (0.02 g, 11%) and **45** (0.05 g, 28%) were separated on silica gel. Eluent: acetone:chloroform:pet ether (1:1:8).

4.4.35. Methyl 2,3-dideoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfonyl-α-D-*erythro*-hex-2-enopyranoside 1α. To a well stirred solution of **44** (0.09 g, 0.214 mmol) in pyridine (2 mL) at 0°C was added drop-wise mesyl chloride (0.1 mL, 1.071 mmol) in pyridine (3 mL) and the mixture was left at +4°C. After 15 h the reaction mixture was worked up as described in the general procedure. A solution of the crude material in CH_2Cl_2 (10 mL) was treated with DBU (2 equiv.) for 15 min. Excess solvent was removed under reduced pressure. Purification of the crude residue over silica gel using EtOAc:pet ether (2:3) furnished **1α** as a solid (0.08 g, 96%).

4.4.36. Methyl 2,3-dideoxy-4,6-*O*-(phenylmethylene)-3-*C*-phenylsulfonyl-β-D-*erythro*-hex-2-enopyranoside 1β. Compound **45** (0.05 g, 0.120 mmol) was converted to **1β** following the procedure described for **1α** (0.045 g, 96%).

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