Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 4563–4572

TETRAHEDRON

Synthesis of sugar-based ethenyl ethers through a vinyl bis-sulfone methodology

Florence Chéry,[a] Matthieu Desroses,[a] Arnaud Tatibouët,[a] Ottorino De Lucchi[b] and Patrick Rollin[a,*]

[a]*Institut de Chimie Organique et Analytique, UMR CNRS 6005, Université d'Orléans, B.P. 6759, F-45067 Orléans, France*
[b]*Dipartimento di Chimica, Universita Ca'Foscari di Venezia, Dorsoduro 2137, I-30123 Venezia, Italy*

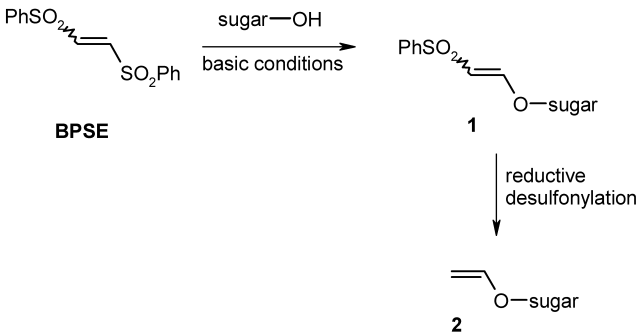
Received 7 February 2003; revised 25 March 2003; accepted 24 April 2003

Abstract—The recently devised route to ethenyl ethers—i.e. 1,2-bis(phenylsulfonyl)ethylene (BPSE)-mediated conversion of alcohols into β-alkoxyvinyl sulfones followed by reductive desulfonylation—has been applied in the carbohydrate field to the synthesis of a number of vinyl-functionalised monosaccharides, a number of which had not been prepared via alternative routes.

1. Introduction

Chiral auxiliaries based on carbohydrate template are gaining further interest and diffusion mostly as the result of their low cost and large availability.[1] Furthermore, the countless number of compounds that may arise from the activation of the many functional sites of the carbohydrate template is an added value over standard chiral auxiliaries, offering structural diversity for the solution of varied stereochemical challenges. In the field of asymmetric synthesis, sugar-based ethenyl ethers are particularly interesting chiral tools because of the versatile reactivity of the enol ether function and the importance of the derived products.[2a] For example, ethenyl ethers have been used as starting reagents for the preparation of pyrrolidines,[3] pyranes,[4–6] oxazoles[7] as well as β-lactams[8] and other families of molecules.[9]

Sugar-based ethenyl ethers—including vinyl glycosides—have been previously prepared by more than one route,[10] but still the interest for such chiral intermediates accounts for the development of additional synthetic methods. Herein we present an extension to diverse carbohydrate series of our recently devised[2] approach to ethenyl ethers, involving conversion of alcohols into β-alkoxyvinyl sulfones[11,12] followed by reductive desulfonylation (Scheme 1).



Scheme 1.

2. Results and discussion

Carbohydrates-derived β-alkoxyvinyl sulfones **1** were formed via the addition–elimination of a sugar alkoxide to 1,2-bis(phenylsulfonyl)ethylene (BPSE). Two basic reagents—NaH or LiHMDS—have been tested to effect *O*-deprotonation: the nature of the base involved to activate the carbohydrate hydroxyl group proved important in terms of yield, stereoselectivity and potential formation of acetal side-products (Scheme 2).

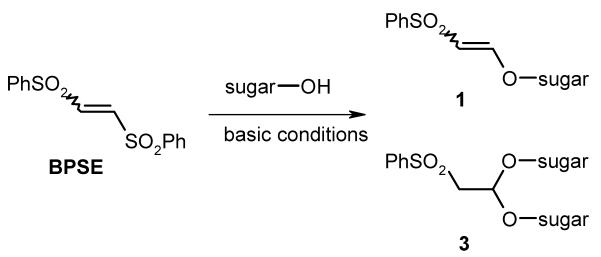
A typical behaviour can be observed in the D-galacto series: whereas the use of NaH in THF resulted in a mixture of mono- and bis-adducts **1a** and **3a**, respectively, LiHMDS selectively afforded a good yield of the expected β-alkoxyvinyl sulfone **1a**.

The formation of the tethered compound **3** is also dependent on the reactivity of the free hydroxyl group in the carbohydrate partner. Indeed, while unhindered primary

Keywords: carbohydrates; alkoxyvinylsulfones; ethenyl ethers; desulfonylation.

* Corresponding author. Tel.: +33-2-38-41-73-70; fax: +33-2-38-41-72-81; e-mail: patrick.rollin@univ-orleans.fr

0040–4020/03/$ - see front matter
doi:10.1016/S0040-4020(03)00661-6



Scheme 2.

Table 1.

Carbohydrate series	(*E*)-**1**[a]	(*Z*)-**1**[a]	**2**[b]
α-D-galactopyrano **a**	65	–	66
β-D-fructopyrano **b**	84	73	82
α-L-sorbofurano **c**	90	85	65
β-D-fructopyrano **d**	80	79	94 (64)
β-L-sorbopyrano **e**	78	85	93
α-D-altropyrano **f**	80	72	84
α-D-glucopyrano **g**	81	72	84
α-D-glucofurano **h**	83	81	60
β-D-psicopyrano **i**	93	73	55 (65)
α-D-mannofurano **j**	83	–	65

[a] Yields of isolated β-alkoxyvinyl sulfones.
[b] Yields of ethenyl ethers through desulfonylation using either sodium amalgam or (magnesium) in methanol.

alcohols—such as 1,2:3,4-di-*O*-isopropylidene-D-galacto-pyranose, the precursor to **1a**—can react to afford mixtures of mono- and bis-adducts, secondary or hindered primary alcohols selectively yield the β-alkoxyvinyl sulfones **1**. However, with a view to developing an alternative synthetic procedure towards sugar-based ethenyl ethers **2**, we optimised procedures and reaction conditions to selectively produce β-alkoxyvinyl sulfones **1** and no description of marginal type **3** compounds have been included in this paper.

Table 1 displays the broad range of monosaccharidic alcohols which have been subjected to the reaction sequence. This encompasses substrates bearing a primary (including pseudo-neopentylic), secondary (equatorial or axial) and anomeric hydroxyl groups,[13] selected with the aim of estimating the scope of the reaction. The entire set of compounds was successfully submitted to the reaction with BPSE and the resulting carbohydrate-based β-alkoxyvinyl sulfones **1** were obtained in high yields (even when scaling up the reaction to the gram-scale) and usually with complete retention of the *E*- or *Z*-configuration of the bis-sulfone precursor involved (Fig. 1).[14] In the case of **1a** and **1j** however, it must be noted that the *E*-stereoisomer was the exclusively isolated form, whatever the *E*- or *Z*-configuration of the starting BPSE reagent.

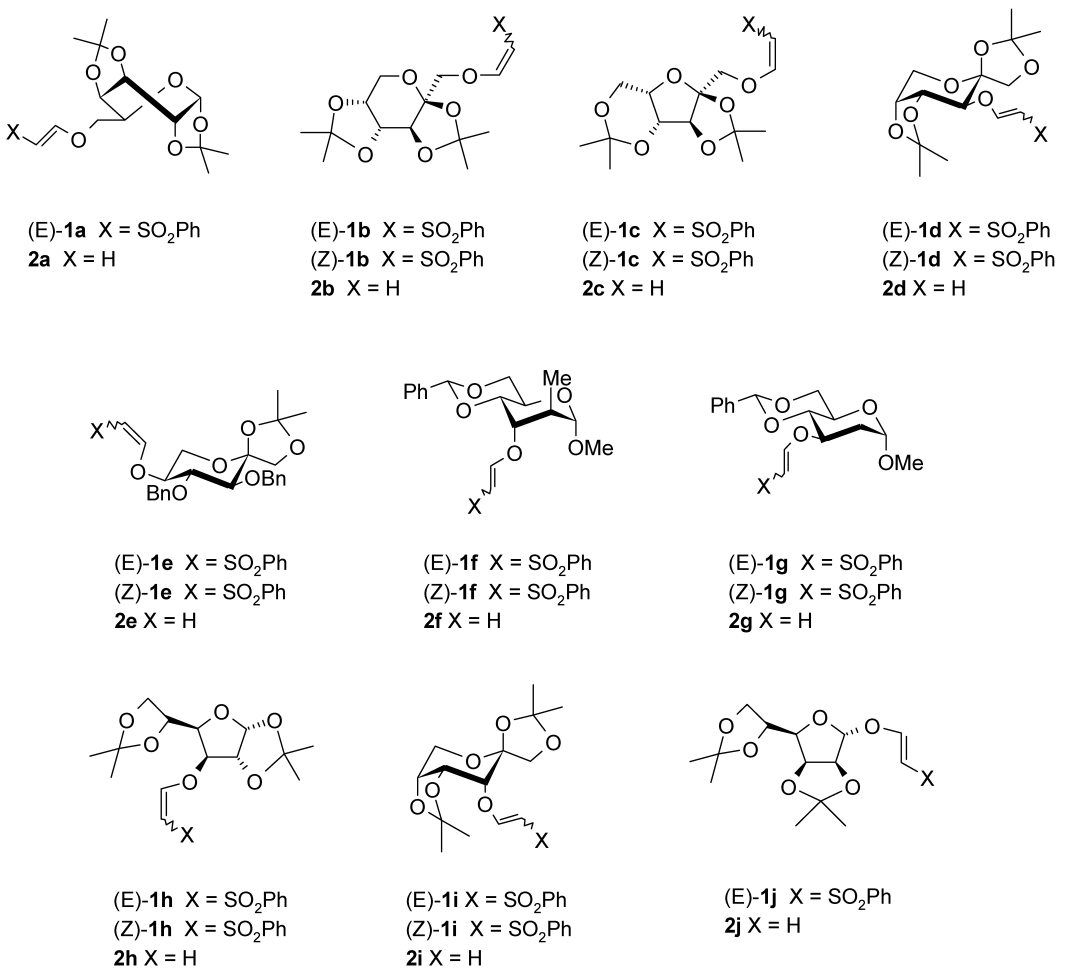
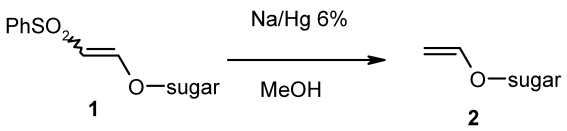


Figure 1.



Scheme 3.

The corresponding ethenyl ethers **2** (Fig. 1 and Table 1) were obtained from the above carbohydrate-based vinyl sulfones **1** through a reductive desulfonylation process (Scheme 3). Several reducing methodologies are indeed available for desulfonylation:[15] in many instances however, 6% sodium amalgam in methanol remains the most popular and general procedure because of the low cost, smooth reaction conditions and simplicity of the work-up and purification. The above conditions proved compatible with the sensitive character of the enol ethers produced mainly because they do not implicate acidic conditions and because the hydrophobic nature of the enol ethers allows an easy separation from the hydrophilic co-products.

An alternative approach was envisaged with the use of magnesium as the electron donor for desulfonylation in methanol (Table 1). The process was only explored on the D-fructo and D-psico epimers **1d** and **1i**: in both cases a different behaviour was observed, depending on the carbohydrate structure. Desulfonylation of **1d** was found much less efficient whereas **1i** was converted into the enol ether with a comparable yield.

The above results call for several observations. As described elsewhere,[14] the formation of product **1** can be accounted for a Michael-type addition of the nucleophilic alkoxide on the highly electrophilic double bond of BPSE, followed by a $E1_{cb}$ elimination of phenylsulfinate $PhSO_2^-$. The type **3** double adduct arises from a second Michael addition of the alkoxide on the β-alkoxyvinyl sulfone **1**. On the basis of such mechanistic considerations, a strongly nucleophilic, unhindered monosaccharide should indeed exhibit higher propensity to doubly add, eventually leading to **3**. A careful choice of the reaction conditions thus allows to direct the reaction towards the desired product.

The addition–elimination reaction leading to **1** is a stereospecific process: *Z*-BPSE affords *Z*-β-alkoxyvinyl sulfones **1** while *E*-BPSE affords the *E* isomers. This observation is in agreement with the postulated mechanism and derives by the minimal reorganisation of the intermediate adduct to effect $PhSO_2^-$ elimination. The possibility of an elimination–addition process (first $PhSO_2^-$ base-promoted elimination, then addition of the alkoxide moiety) is to be ruled out because the above pathway would inevitably generate phenylsulfonyl acetylene as a common intermediate and thus the stereochemical outcome should result identical, starting either from the *Z*- or the *E*-BPSE isomers. It should be kept in mind, however, that the strongly basic conditions under which the reactions are carried out associated with the highly hindered situation of certain hydroxyl groups—strongly reducing their nucleophilicity—render the elimination–addition mechanism still possible in special cases. Furthermore, one should also take into account the fact that in any case, the *Z*-isomer being the kinetic product is thus susceptible of isomerisation to the thermodynamic *E*-isomer under the applied reaction conditions.

Nevertheless, the preceding considerations do not hold importance in view of the preparation of the related enol ethers, which are devoided of such stereochemical issues. The use of either *Z*- or *E*-forms in the desulfonylation process did not reveal detectable differences as they both led to the corresponding ethenyl ether under identical reaction conditions and in comparable yields.

3. Conclusion

We have developed a simple, efficient and upscalable synthetic pathway to carbohydrate-derived vinyl sulfones,[16,17] which in turn can be converted into the corresponding ethenyl ethers **2** overall representing a 2-step approach to sugar-based ethenyl ethers. These enantiomerically pure compounds can be envisaged as chiral reagents useful in the preparation of many diverse synthetic targets because of their high reactivity for example in inverse-electron cycloadditions,[18] Claisen rearrangements,[10d] *O*-glycosidation[19] or even *C*-glycosidation.[20]

4. Experimental

4.1. General methods

Solvents were dried and distilled by standard methods before use. All reagents were of commercial quality (Acros, Aldrich or Lancaster) and used without purification. Reactions were carried out under argon and monitored by TLC analysis with silica gel plate (Kieselgel $60F_{254}$, Merck). Compounds were visualised with UV light and charring after a 10% H_2SO_4 ethanolic solution spray. Column chromatography was performed on silica gel 60 M (0.036–0.063 mm, Merck). ^1H NMR (250 MHz) and ^{13}C NMR (62.6 MHz) spectra ($CDCl_3$, internal TMS) were recorded on a Bruker AVANCE DPX 250 spectrometer. Chemical shifts (δ) are reported in ppm downfield from TMS, coupling constants (J) are reported in Hz and refer to apparent peak multiplicity. Assignments are based on H,H- and C,H-COSY experiments. Mass spectra were obtained using Ion Spray® (IS) method with a API 300 Perkin–Elmer SCIEX spectrometer. HR-ESI-TOF-MS was performed on a Micromass LC TOF spectrometer. Optical rotations were measured in chloroform at 20°C with a Perkin–Elmer 410 polarimeter.

4.2. Synthesis of β-alkoxyvinyl sulfones 1a–j

To a stirred mixture containing (0.3 mmol) of the sugar, (0.3 mmol) of (*E*)- or (*Z*)-BPSE and a few crystals of Bu_4NBr, a freshly prepared THF solution of LiHMDS (0.3 mmol) was added at −78°C. The mixture was stirred overnight at room temperature, then quenched with water, extracted with EtOAc and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the product was purified by column chromatography on silica gel.

4.2.1. 1,2:3,4-Di-*O*-isopropylidene-6-*O*-[(*E*)-2′-(phenylsulfonyl)vinyl]-α-D-galactopyranose ((*E*)-1a). Obtained

from commercially available 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (850 mg) and (*E*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 9:1 and 8:2) afforded (*E*)-**1a** with 65% yield as a colourless gum, $\alpha_D=-60$ ($c=1.3$, $CHCl_3$). ^1H NMR δ 1.31 (s, 6H, *i*Prd), 1.41 (s, 3H, *i*Prd), 1.47 (s, 3H, *i*Prd), 3.93–4.09 (m, 3H, H-5, H-6a, H-6b), 4.19 (dd, 1H, H-4, $J_{3-4}=7.8$ Hz, $J_{4-5}=1.7$ Hz), 4.31 (dd, 1H, H-2, $J_{1-2}=5.2$ Hz, $J_{2-3}=2.6$ Hz), 4.60 (dd, 1H, H-3, $J_{2-3}=2.6$ Hz, $J_{3-4}=7.8$ Hz), 5.50 (d, 1H, H-1, $J_{1-2}=5.2$ Hz), 5.74 (d, 1H, H-2′, $J_{1'-2'}=12.4$ Hz), 7.61 (d, 1H, H-1′, $J_{1'-2'}=12.4$ Hz), 7.45–7.59 (m, 3H, H-Ar), 7.84–7.87 (m, 2H, *ortho*-H-$PhSO_2$). ^{13}C NMR δ 24.7, 25.3, 26.3 et 26.4 (4*Me), 66.5 (C-5), 70.7 (C-3), 70.9 (C-2), 71.0 (C-6), 71.1 (C-4), 96.6 (C-1), 107.6 (C-2′), 109.3 and 110.2 (2*C_{IV}–*i*Prd), 126.3 (2*CH–*ortho*-$PhSO_2$), 129.5 (2*CH–*meta*-$PhSO_2$), 133.1 (CH–*para*-$PhSO_2$), 142.8 (C_{IV}–$PhSO_2$), 161.1 (C-1′). IR (film): 2998 cm^{-1} (CH–Ar,=CH), 1615 cm^{-1} (C=C), 1384 cm^{-1}, 1133 cm^{-1} ($PhSO_2$), 1011 cm^{-1} (=C–OR). MS IS *m*/*z*=427.5 $[M+H]^+$, 444.5 $[M+NH_4]^+$, 449.5 $[M+Na]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1341.

4.2.2. 2,3:4,5-Di-*O*-isopropylidene-1-*O*-[(*E*)-2′-(phenylsulfonyl)vinyl]-β-D-fructopyranose ((*E*)-1b). Obtained from 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose[21] (150 mg) and (*E*)-BPSE; silica gel column chromatography (toluene/ethyl acetate 8:2) afforded (*E*)-**1b** with 84% yield as a colourless gum, $\alpha_D=-27$ ($c=2.0$, $CHCl_3$). ^1H NMR δ 1.27 (s, 3H, *i*Prd), 1.32 (s, 3H, *i*Prd), 1.43 (s, 3H, *i*Prd), 1.49 (s, 3H, *i*Prd), 3.72 (d, 1H, H-6b, $J_{5-6b}<0.5$ Hz, $J_{6a-6b}=13.0$ Hz), 3.89 (d, 1H, H-6a, $J_{5-6a}<0.5$ Hz, $J_{6a-6b}=13.0$ Hz), 3.95 (d, 1H, H-1b, $J_{1a-1b}=11.1$ Hz), 4.01 (d, 1H, H-1a, $J_{1a-1b}=11.1$ Hz), 4.22 (d, 1H, H-5, $J_{4-5}=7.8$ Hz, $J_{5-6a}=J_{5-6b}<0.5$ Hz), 4.29 (d, 1H, H-3, $J_{3-4}=2.5$ Hz), 4.59 (dd, 1H, H-4, $J_{3-4}=2.5$ Hz, $J_{4-5}=7.8$ Hz), 5.81 (d, 1H, H-2′, $J_{1'-2'}=12.1$ Hz), 7.50 (t, 2H, *meta*-H-$PhSO_2$, $J=7.4$ Hz), 7.56 (d, 1H, H-1′, $J_{1'-2'}=12.1$ Hz), 7.58 (t, 1H, *para*-H-$PhSO_2$, $J=7.4$ Hz), 7.87 (d, 2H, *ortho*-H-$PhSO_2$, $J=7.4$ Hz). ^{13}C NMR δ 24.4, 25.6, 26.3, 26.9 (4*Me), 61.7 (C-6), 70.2 (C-4), 70.5 (C-3), 70.9 (C-5), 73.5 (C-1), 101.6 (C-2), 108.5 (C-2′), 109.5 and 109.9 (2*C_{IV}–*i*Prd), 127.4 (2*CH–*ortho*-$PhSO_2$), 129.5 (2*CH–*meta*-$PhSO_2$), 133.4 (CH–*para*-$PhSO_2$), 142.8 (C_{IV}–$PhSO_2$), 161.7 (C-1′). IR (film): 2980, 2937 cm^{-1} (CH–Ar,=CH); 1630, 1612 cm^{-1} (C=C); 1383, 1143 cm^{-1} ($PhSO_2$); 1020, 979 cm^{-1} (=C–OR). MS IS *m*/*z*=427.5 $[M+H]^+$, 444.5 $[M+NH_4]^+$, 449.5 $[M+Na]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1340.

4.2.3. 2,3:4,5-Di-*O*-isopropylidene-1-*O*-[(*Z*)-2′-(phenylsulfonyl)vinyl]-β-D-fructopyranose ((*Z*)-1b). Obtained from 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose[21] (150 mg) and (*Z*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 8:2 and 7:3) afforded (*Z*)-**1b** with 73% yield as a colourless gum; $\alpha_D=+26$ ($c=3.6$, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 1.16 (s, 3H, Me), 1.36 (s, 3H, Me), 1.46 (s, 3H, Me), 1.47 (s, 3H, Me), 3.71 (d, 1H, H-6b, $J_{5-6b}<0.5$ Hz, $J_{6a-6b}=12.9$ Hz), 3.88 (d, 1H, H-1b, $J_{1a-1b}=12.5$ Hz), 3.91 (d, 1H, H-6a, $J_{5-6a}<0.5$ Hz, $J_{6a-6b}=12.9$ Hz), 4.17 (d, 1H, H-1a, $J_{1a-1b}=12.5$ Hz), 4.22 (d, 1H, H-5, $J_{4-5}=7.9$ Hz, $J_{5-6a}=J_{5-6b}<0.5$ Hz), 4.30 (d, 1H, H-3, $J_{3-4}=2.5$ Hz), 4.62 (dd, 1H, H-4, $J_{3-4}=2.5$ Hz, $J_{4-5}=7.9$ Hz), 5.52 (d, 1H, H-2′, $J_{1'-2'}=6.6$ Hz), 6.58 (d, 1H, H-1′, $J_{1'-2'}=6.6$ Hz), 7.50 (t, 2H, *meta*-H-$PhSO_2$, $J=7.6$ Hz), 7.5 (t, 1H, *para*-H-$PhSO_2$, $J=7.6$ Hz), 7.97 (d, 2H, *ortho*-H-$PhSO_2$, $J=7.6$ Hz). ^{13}C NMR δ 26.4, 26.5, 27.2, 28.5 (4*Me), 60.6 (C-6), 71.8 (C-1), 74.1, 76.1 (C-4, C-5), 82.6 (C-3), 103.3 (C-2), 108.7 (C-2′), 110.0 and 113.5 (2*C_{IV}–*i*Prd), 127.6 (2*CH–*ortho*-$PhSO_2$), 129.1 (2*CH–*meta*-$PhSO_2$), 133.3 (CH–*para*-$PhSO_2$), 143.3 (C_{IV}–$PhSO_2$), 155.6 (C-1′). IR (film): 3071, 3019, 2991, 2938 cm^{-1} (CH–Ar,=CH); 1630 cm^{-1} (C=C), 1144 cm^{-1} ($PhSO_2$), 997, 979 cm^{-1} (=C–OR). MS IS *m*/*z*=427.5 $[M+H]^+$, 444.5 $[M+NH_4]^+$, 449.5 $[M+Na]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1354.

4.2.4. 2,3:4,6-Di-*O*-isopropylidene-1-*O*-[(*E*)-2′-(phenylsulfonyl)vinyl]-α-L-sorbofuranose ((*E*)-1c). Obtained from 2,3:4,6-di-*O*-isopropylidene-α-L-sorbofuranose[22] (150 mg) and (*E*)-BPSE; silica gel column chromatography (toluene/ethyl acetate 9:1 and 8:2) afforded (*E*)-**1c** with 90% yield as a colourless gum, $\alpha_D=-4$ ($c=3.7$, $CHCl_3$). ^1H NMR δ 1.27 (s, 3H, *i*Prd), 1.33 (s, 3H, *i*Prd), 1.41 (s, 3H, *i*Prd), 1.47 (s, 3H, *i*Prd), 3.91–4.13 (m, 5H, H-1a, H-1b, H-5, H-6a, H-6b), 4.34 (d, 1H, H-4, $J_{3-4}<0.5$ Hz, $J_{4-5}=2.3$ Hz), 4.40 (s, 1H, H-3, $J_{3-4}<0.5$ Hz), 5.83 (d, 1H, H-2′, $J_{1'-2'}=12.1$ Hz), 7.47–7.60 (m, 4H, H-1′, *meta*, *para*-H-$PhSO_2$), 7.87 (d, 2H, *ortho*-H-$PhSO_2$, $J=7.0$ Hz). ^{13}C NMR δ 18.9, 26.7, 27.8, 29.3 (4*Me), 60.5 (C-6), 71.8 (C-1), 73.0 (C-5), 73.3 (C-4), 84.6 (C-3), 97.8 (C-2), 103.3 (C-2′), 103.3 and 112.6 (2*C_{IV}–*i*Prd), 127.3 (2*CH–*ortho*-$PhSO_2$), 129.5 (2*CH–*meta*-$PhSO_2$), 133.2 (CH–*para*-$PhSO_2$), 142.7 (C_{IV}–$PhSO_2$), 161.5 (C-1′). IR (film): 3019, 2993, 2938 cm^{-1} (CH–Ar,=CH); 1630, 1612 cm^{-1} (C=C); 1384, 1143 cm^{-1} ($PhSO_2$); 969, 953 cm^{-1} (=C–OR). MS IS *m*/*z*=427.5 $[M+H]^+$, 444.5 $[M+NH_4]^+$, 449.5 $[M+Na]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1352.

4.2.5. 2,3:4,6-Di-*O*-isopropylidene-1-*O*-[(*Z*)-2′-(phenylsulfonyl)vinyl]-α-L-sorbofuranose ((*Z*)-1c). Obtained from 2,3:4,6-di-*O*-isopropylidene-α-L-sorbofuranose[22] (150 mg) and (*Z*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 7:3 and 6:4) afforded (*Z*)-**1c** with 85% yield as a colourless gum, $\alpha_D=+18$ ($c=3.0$, $CHCl_3$). ^1H NMR δ 1.08 (s, 3H, *i*Prd), 1.36 (s, 3H, *i*Prd), 1.41 (s, 3H, *i*Prd), 1.42 (s, 3H, *i*Prd), 3.89–4.09 (m, 3H, H-5, H-6a, H-6b), 4.05 (d, 1H, H-1b, $J_{1a-1b}=12.1$ Hz), 4.31 (d, 1H, H-1a, $J_{1a-1b}=12.1$ Hz), 4.34 (d, 1H, H-4, $J_{3-4}<0.5$ Hz, $J_{4-5}=2.8$ Hz), 4.35 (s, 1H, H-3, $J_{3-4}<0.5$ Hz), 5.51 (d, 1H, H-2′, $J_{1'-2'}=6.6$ Hz), 6.60 (d, 1H, H-1′, $J_{1'-2'}=6.6$ Hz), 7.49 (t, 2H, *meta*-H-$PhSO_2$, $J=7.4$ Hz), 7.58 (t, 1H, *para*-H-$PhSO_2$, $J=7.4$ Hz), 7.97 (d, 2H, *ortho*-H-$PhSO_2$, $J=7.4$ Hz). ^{13}C NMR δ 18.9, 26.5, 28.0, 29.4 (4*Me), 60.6 (C-6), 73.1, 73.2 (C-4, C-5), 74.2 (C-1), 84.1 (C-3), 97.7 (C-2), 107.4 (C-2′), 112.8 and 113.8 (2*C_{IV}–*i*Prd), 127.8 (2*CH–*ortho*-$PhSO_2$), 129.4 (2*CH–*meta*-$PhSO_2$), 133.3 (CH–*para*-$PhSO_2$), 142.9 (C_{IV}–$PhSO_2$), 157.8 (C-1′). IR (film): 2993, 2938 cm^{-1} (CH–Ar,=CH); 1632 cm^{-1} (C=C), 1384, 1144 cm^{-1} ($PhSO_2$); 1024, 973 cm^{-1} (=C–OR). MS IS *m*/*z*=427.5 $[M+H]^+$, 444.5 $[M+NH_4]^+$, 449.5 $[M+Na]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1338.

4.2.6. 1,2:4,5-Di-*O*-isopropylidene-3-*O*-[(*E*)-2′-(phenylsulfonyl)vinyl]-β-D-fructopyranose ((*E*)-1d). Obtained

from 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose[21] (150 mg) and (*E*)-BPSE; silica gel column chromatography (toluene/ethyl acetate 8:2 and 7:3) afforded (*E*)-**1d** with 80% yield as a colourless gum, α_D=+23 (*c*=2.2, $CHCl_3$). ^{1}H NMR δ 1.47 (s, 6H, *i*Prd), 1.48 (s, 3H, *i*Prd), 1.57 (s, 3H, *i*Prd), 3.96 (d, 1H, H-3, J_{3-4}=7.1 Hz), 3.99 (s, 2H, H-1a, H-1b), 4.05 (d, 1H, H-6b, J_{5-6b}<0.5 Hz, J_{6a-6b}=13.4 Hz), 4.13 (d, 1H, H-6a, J_{5-6a}=2.3 Hz, J_{6a-6b}=13, 4 Hz), 4.25 (dd, 1H, H-5, J_{4-5}=7.1 Hz, J_{5-6a}=2.3 Hz, J_{5-6b}<0.5 Hz), 4.31 (t, 1H, H-4, J_{3-4}=J_{4-5}=7.1 Hz), 5.93 (d, 1H, H-2′, $J_{1'-2'}$=11.7 Hz), 7.48–7.59 (m, 3H, *meta*, *para*-H-$PhSO_2$), 7.64 (d, 1H, H-1′, $J_{1'-2'}$=11.7 Hz), 7.87 (d, 2H, *ortho*-H-$PhSO_2$, *J*=7.6 Hz). ^{13}C NMR δ 26.3, 26.4, 26.8, 28.5 (4*Me), 60.8 (C-6), 71.9 (C-1), 75.1 (C-5), 75.6 (C-4), 82.1 (C-3), 103.4 (C-2), 109.6 (C-2′), 110.2 and 113.1 (2*C_{IV}–*i*Prd), 127.3 (2*CH–*ortho*-$PhSO_2$), 129.5 (2*CH–*meta*-$PhSO_2$), 133.2 (CH–*para*-$PhSO_2$), 142.6 (C_{IV}–$PhSO_2$), 160.9 (C-1′). IR (film): 2990cm^{-1}, 2947 cm^{-1} (CH–Ar,=CH); 1636 cm^{-1} (C=C), 1382, 1147 cm^{-1} ($PhSO_2$); 1031, 996 cm^{-1} (=C–OR). MS IS *m*/*z*=445.0 $[M+NH_4]^+$, 449.0 [M+Na]. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1345.

4.2.7. 1,2:4,5-Di-*O*-isopropylidene-3-*O*-[(*Z*)-2′-(phenylsulfonyl)vinyl]-β-D-fructopyranose ((*Z*)-1d). Obtained from 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose[21] (150 mg) and (*Z*)-BPSE; silica gel column chromatography (toluene/ethyl acetate 9:1 and 8:2) afforded (*E*)-**1d** with 79% yield as a colourless gum, α_D=−72 (*c*=3.2, $CHCl_3$). ^{1}H NMR δ 1.31 (s, 3H, *i*Prd), 1.49 (s, 3H, *i*Prd), 1.53 (s, 3H, *i*Prd), 1.59 (s, 3H, *i*Prd), 3.87 (d, 1H, H-3, J_{3-4}=7.2 Hz), 3.97 (d, 1H, H-1b, *J*=8.7 Hz), 4.06 (d, 1H, H-6b, J_{5-6b}<0.5 Hz, J_{6a-6b}=14.7 Hz), 4.09 (d, 1H, H-1a, *J*=8.7 Hz), 4.14 (d, 1H, H-6a, J_{5-6a}=6.0 Hz, J_{6a-6b}=14.7 Hz), 4.23 (m, 2H, H-4, H-5), 5.57 (d, 1H, H-2′, $J_{1'-2'}$=6.6 Hz), 6.83 (d, 1H, H-1′, $J_{1'-2'}$=6.6 Hz), 7.50 (t, 2H, *meta*-H-$PhSO_2$, *J*=7.2 Hz), 7.56 (t, 1H, *para*-H-$PhSO_2$, *J*=7.2 Hz), 8.02 (d, 2H, *ortho*-H-$PhSO_2$, *J*=7.2 Hz). ^{13}C NMR δ 26.4, 26.5, 27.2, 28.5 (4*Me), 60.6 (C-6), 71.8 (C-1), 74.1, 76.1 (C-4, C-5), 82.6 (C-3), 103.3 (C-2), 108.7 (C-2′), 110.0 and 113.5 (2*C_{IV}–*i*Prd), 127.6 (2*CH–*ortho*-$PhSO_2$), 129.1 (2*CH–*meta*-$PhSO_2$), 133.3 (CH–*para*-$PhSO_2$), 143.3 (C_{IV}CH–$PhSO_2$), 155.6 (C-1′). IR (film): 2988, 2937 cm^{-1} (CH–Ar,=CH); 1624 cm^{-1} (C=C); 1384, 1145 cm^{-1} ($PhSO_2$); 1022, 975 cm^{-1} (=C–OR). MS IS *m*/*z*=427.5 $[M+H]^+$, 444.5 $[M+NH_4]^+$, 448.5 $[M+Na]^+$, 465.5 $[M+K]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1354.

4.2.8. 3,4-Di-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-[(*E*)-2′-(phenylsulfonyl)vinyl]-β-L-sorbopyranose ((*E*)-1e). Obtained from 3,4-di-*O*-benzyl-1,2-*O*-isopropylidene-β-L-sorbopyranose[23] (150 mg) and (*E*)-BPSE; silica gel column chromatography (toluene/ethyl acetate 8:2 and 85:15) afforded (*E*)-**1e** with 78% yield as a colourless gum, α_D=−4 (*c*=3.7, $CHCl_3$). ^{1}H NMR δ 1.43 (s, 3H, *i*Prd), 1.47 (s, 3H, *i*Prd), 3.39 (d, 1H, J_{3-4}=9.2 Hz, H-3), 3.73–4.06 (m, 6H, H-1a, H-1b, H-4, H-5, H-6a, H-6b), 4.63 and 4.90 (2d, AB system, 2H, PhCH_2O, J_{gem}=11.3 Hz), 4, 66 and 4, 76 (2d, AB system, 2H, PhCH_2O, J_{gem}=10.3 Hz), 5.85 (d, 1H, H-2′, $J_{1'-2'}$=11.9 Hz), 7.25–7.33 (m, 10H, H-Ar), 7.44 (t, 2H, *meta*-H-$PhSO_2$, *J*=7.7 Hz), 7.55 (t, 1H, *para*-H-$PhSO_2$, *J*=7.7 Hz), 7.60 (d, 1H, H-1′, $J_{1'-2'}$=11.9 Hz), 7.79 (d, 2H, *ortho*-H-$PhSO_2$, *J*=7.7 Hz). ^{13}C NMR δ 26.4, 27.4 (2*Me), 60.4 (C-6), 71.7 (C-1), 78.2 (C-3), 75.9 (2*PhCH_2O), 82.3, 82.5 (C-4, C-5), 103.1 (C-2), 106.8 (2*C_{IV}–*i*Prd), 110.8 (C-2′), 125.2–127.4 (14*CH–Ar), 131.1 (CH–*para*-$PhSO_2$), 135.9 (2*C_{IV}–Ar), 140.5 (C_{IV}–$PhSO_2$), 158.8 (C-1′). IR (film): 3020, 2990 cm^{-1} (CH–Ar,=CH); 1627 cm^{-1} (C=C); 1384, 1142 cm^{-1} ($PhSO_2$); 1015 cm^{-1} (=C–OR). MS IS *m*/*z*=584.5 $[M+NH_4]^+$, 589.5 $[M+Na]^+$. HRMS: $C_{31}H_{34}O_8S$: calcd 566.1974; found 566.1983.

4.2.9. 3,4-Di-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-[(*Z*)-2′-(phenylsulfonyl)vinyl]-β-L-sorbopyranose ((*Z*)-1e). Obtained from 3,4-di-*O*-benzyl-1,2-*O*-isopropylidene-β-L-sorbopyranose[23] (150 mg) and (*Z*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 7:3) afforded (*Z*)-**1e** with 85% yield as a colourless gum, α_D=+40 (*c*=3.0, $CHCl_3$). ^{1}H NMR δ 1.46 (s, 3H, *i*Prd), 1.59 (s, 3H, *i*Prd), 3.32 (d, 1H, H-3, J_{3-4}=8.7 Hz), 3.64 (d, 1H, H-6b, J_{5-6b}=5.3 Hz, J_{6a-6b}=10.2 Hz), 3.66–3.84 (m, 3H, H-4, H-5, H-6a), 3.80 (s, 1H, H-1b, *J*=8.5 Hz), 3.87 (s, 1H, H-1a, *J*=8.5 Hz), 4.32 and 4.62 (2d, AB system, 2H, PhCH_2O, J_{gem}=10.2 Hz), 4.60 and 4.90 (2d, AB system, 2H, PhCH_2O, J_{gem}=11.5 Hz), 5.57 (d, 1H, H-2′, $J_{1'-2'}$=6.4 Hz), 6.63 (d, 1H, H-1′, $J_{1'-2'}$=6.4 Hz), 7.14–7.37 (m, 10H, H-Ar), 7.48 (t, 2H, *meta*-H-$PhSO_2$, *J*=7.0 Hz), 7.56 (t, 1H, *para*-H-$PhSO_2$, *J*=7.0 Hz), 7.99 (d, 2H, *ortho*-H-$PhSO_2$, *J*=7.0 Hz). ^{13}C NMR δ 26.5, 27.6 (2*Me), 60.5 (C-6), 71.7 (C-1), 75.8, 75.9 (2*PhCH_2O), 78.2 (C-3), 82.6, 84.0 (C-4, C-5), 105.3 (C-2), 108.7 (C-2′), 112.9 (C_{IV}–*i*Prd), 126.3–129.1 (14*CH–Ar), 133.4 (CH–*para*-$PhSO_2$), 138.1 (2*C_{IV}–Ar), 143.2 (C_{IV}–$PhSO_2$), 155.9 (C-1′). IR (film): 3029, 2989, 2938, 2988 cm^{-1} (CH–Ar,=CH); 1624 cm^{-1} (C=C); 1383, 1144 cm^{-1} ($PhSO_2$); 1021 cm^{-1} (=C–OR). MS IS *m*/*z*=567.5 $[M+H]^+$, 584.5 $[M+NH_4]^+$, 589.5 $[M+Na]^+$, 605.5 $[M+K]^+$. HRMS: $C_{31}H_{34}O_8S$: calcd 566.1974; found 566.1979.

4.2.10. Methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-3-*O*-[(*E*)-2′-(phenylsulfonyl)vinyl]-α-D-altropyranoside ((*E*)-1f). Obtained from methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-α-D-altropyranoside[24] (150 mg) and (*E*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 7:3, 65:35 and 6:4) afforded (*E*)-**1f** with 80% yield as a colourless gum, α_D=+126 (*c*=2.0, $CHCl_3$). ^{1}H NMR δ 1.18 (d, 3H, Me, *J*=7.6 Hz), 2.38 (dq, 1H, H-2, J_{1-2}<0.5 Hz, J_{2-3}=1.9 Hz, *J*=7.6 Hz), 3.32 (s, 3H, OMe), 3.73 (t, 1H, H-6b, J_{5-6b}=J_{6a-6b}=9.8 Hz), 3.88 (dd, 1H, H-4, J_{3-4}=2.7 Hz, J_{4-5}=9.4 Hz), 4.14–4.31 (m, 3H, H-3, H-5, H-6a), 4.41 (s, 1H, H-1, J_{1-2}<0.5 Hz), 5.57 (s, 1H, H-7), 5.82 (d, 1H, H-2′, $J_{1'-2'}$=11.9 Hz), 7.31–7.37 (m, 5H, H-Ar), 7.44–7.51 (m, 3H, *meta*, *para*-H-$PhSO_2$), 7.56 (d, 1H, H-1′, $J_{1'-2'}$=11.9 Hz), 7.72 (d, 2H, *ortho*-H-Ar *Ph*SO_2, *J*=7.7 Hz). ^{13}C NMR δ 16.5 (Me), 38.9 (C-2), 55.7 (OMe), 58.7 (C-5), 69.7 (C-6), 75.5 (C-4), 82.0 (C-3), 102.4 (C-7), 102.6 (C-1), 107.6 (C-2′), 126.5–129.5 (9*CH–Ar), 132.9 (CH–*para*-$PhSO_2$), 137.4 (C_{IV}–Ar), 143.0 (C_{IV}–$PhSO_2$), 162.1 (C-1′). IR (film): 3035, 2980, 2926 cm^{-1} (CH–Ar,=CH); 1626 cm^{-1}, 1605 cm^{-1} (C=C); 1391, 1143 cm^{-1} ($PhSO_2$); 976, 953 cm^{-1} (=C–OR). MS IS *m*/*z*=415.5 $[M-OMe]^+$, 447.5 $[M+H]^+$, 464.5 $[M+NH_4]^+$, 469.5 $[M+Na]^+$, 485.5 $[M+K]^+$. HRMS: $C_{23}H_{26}O_7S$: calcd 446.1399; found 446.1404.

4.2.11. Methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-3-*O*-[(*Z*)-2′-(phenylsulfonyl)vinyl]-α-D-altropyranoside ((*Z*)-1f). Obtained from methyl 4,6-*O*-benzylidene-2-

deoxy-2-*C*-methyl-α-D-altropyranoside[24] (150 mg) and (*Z*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 7:3 and 6:4) afforded (*Z*)-**1f** with 72% yield as a colourless gum, α_D=+131 (*c*=3.3, $CHCl_3$). ^{1}H NMR δ 1.13 (d, 3H, Me, *J*=7.7 Hz), 2.39 (dq, 1H, H-2, J_{1-2}<0.5 Hz, J_{2-3}=1.9 Hz, *J*=7.7 Hz), 3.43 (s, 3H, OMe), 3.63 (t, 1H, H-6b, J_{5-6b}=J_{6a-6b}=9.8 Hz), 3.77 (dd, 1H, H-4, J_{3-4}=2.5 Hz, J_{4-5}=9.6 Hz), 3.99–4.10 (m, 2H, H-3, H-5), 4.43 (s, 1H, H-1, J_{1-2}<0.5 Hz), 5.41 (d, 1H, H-2′, $J_{1',2'}$=6.6 Hz), 5.45 (s, 1H, H-7), 6.48 (d, 1H, H-1′, $J_{1',2'}$=6.6 Hz), 7.26–7.34 (m, 5H, H-Ar), 7.39 (t, 2H, *meta*-H-$PhSO_2$, *J*=7.4 Hz), 7.49 (t, 1H, *para*-H-$PhSO_2$, *J*=7.4 Hz), 8.14 (d, 2H, *ortho*-H-$PhSO_2$, *J*=7.4 Hz). ^{13}C NMR δ 16.6 (Me), 39.1 (C-2), 55.6 (OMe), 58.5 (C-5), 69.5 (C-6), 75.4 (C-4), 83.7 (C-3), 102.6 (C-1, C-7), 106.2 (C-2′), 126.8–129.6 (9*CH–Ar), 132.9 (CH–*para*-$PhSO_2$), 137.7 (C_{IV}–Ar), 143.5 (C_{IV}–$PhSO_2$), 157.6 (C-1′). IR (film): 3037, 2956, 2938 cm^{-1} (CH–Ar,=CH); 1617 cm^{-1} (C=C); 1384 cm^{-1}, 1144 cm^{-1} ($PhSO_2$); 1014, 953 cm^{-1} (=C–OR). MS IS *m*/*z*=415.5 $[M-OMe]^+$, 447.5 $[M+H]^+$, 464.5 $[M+NH_4]^+$, 469.5 $[M+Na]^+$, 485.5 $[M+K]^+$. HRMS: $C_{23}H_{26}O_7S$: calcd 446.1399; found 446.1408.

4.2.12. Methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-[(*E*)-2′-(phenylsulfonyl)vinyl]-α-D-glucopyranoside ((*E*)-1g). Obtained from methyl 4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside[25] (150 mg) and (*E*)-BPSE; silica gel column chromatography (toluene/ethyl acetate 9:1 and 8:2) afforded (*E*)-**1g** with 81% yield as a colourless gum, α_D=−37 (*c*=2.0, $CHCl_3$). ^{1}H NMR δ 1.87 (ddd, 1H, H-2b, J_{1-2b}=3.4 Hz, J_{2a-2b}=13.2 Hz, J_{2b-3}=11.3 Hz), 2.30 (dd, 1H, H-2a, J_{1-2a}<0.5 Hz, J_{2a-2b}=13.2 Hz, J_{2a-3}=5.3 Hz), 3.33 (s, 3H, OMe), 3.63 (t, 1H, H-4, J_{3-4}=J_{4-5}=9.1 Hz), 3.75 (t, 1H, H-6b, J_{5-6b}=J_{6a-6b}=9.1 Hz), 3.83 (dt, 1H, H-5, J_{4-5}=9.1 Hz, J_{5-6a}=3.6 Hz, J_{5-6b}=9.1 Hz), 4.26 (dd, 1H, H-6a, J_{5-6a}=3.6 Hz, J_{6a-6b}=9.1 Hz), 4.48 (ddd, 1H, H-3, J_{2a-3}=5.3 Hz, J_{2b-3}=11.3 Hz, J_{3-4}=9.1 Hz), 4.81 (d, 1H, H-1, J_{1-2a}<0.5 Hz, J_{1-2b}=3.4 Hz), 5.53 (s, 1H, H-7), 5.80 (d, 1H, H-2′, $J_{1'-2'}$=11.9 Hz), 7.28–7.39 (m, 5H, H-Ar), 7.42–7.50 (m, 3H, *meta*, *para*-H-$PhSO_2$), 7.62 (d, 1H, H-1′, $J_{1'-2'}$=11.9 Hz), 7.71 (d, 2H, *ortho*-H-$PhSO_2$, *J*=7.5 Hz). ^{13}C NMR δ 35.8 (C-2), 55.3 (OMe), 63.1 (C-5), 69.1 (C-6), 78.2 (C-3), 81.9 (C-4), 101.1 (C-1), 102.0 (C-7), 108.3 (C-2′), 125.7–129.6 (9*CH–Ar), 133.0 (CH–*para*-$PhSO_2$), 137.3 (C_{IV}–Ar), 142.8 (C_{IV}–$PhSO_2$), 161.4 (C-1′). IR (film): 3031, 2930 cm^{-1} (CH–Ar,=CH); 1627 cm^{-1} (C=C); 1142 cm^{-1} ($PhSO_2$); 1005, 979 cm^{-1} (=C–OR). MS IS *m*/*z*=401.5 $[M-OMe]^+$, 433.5 $[M+H]^+$, 450.5 $[M+NH_4]^+$. HRMS: $C_{22}H_{24}O_7S$: calcd 432.1243; found 432.1234.

4.2.13. Methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-[(*Z*)-2′-(phenylsulfonyl)vinyl]-α-D-glucopyranoside ((*Z*)-1g). Obtained from methyl 4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside[25] (150 mg) and (*Z*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 7:3 and 6:4) afforded (*Z*)-**1g** with 72% yield as a colourless gum, α_D=−27 (*c*=2.9, $CHCl_3$). ^{1}H NMR δ 1.88 (ddd, 1H, H-2b, J_{1-2b}=3.6 Hz, J_{2a-2b}=13.2 Hz, J_{2b-3}=9.8 Hz), 2.21 (dd, 1H, H-2a, J_{1-2a}<0.5 Hz, J_{2a-2b}=13.2 Hz, J_{2a-3}=5.3 Hz), 3.29 (t, 1H, H-4, J_{3-4}=J_{4-5}=9.8 Hz), 3.29 (s, 3H, OMe), 3.62–3.75 (m, 2H, H-5, H-6b), 4.18–4.28 (m, 2H, H-3, H-6a), 4.79 (d, 1H, H-1, J_{1-2a}<0.5 Hz, J_{1-2b}=3.6 Hz), 5.30 (s, 1H, H-7), 5.55 (d, 1H, H-2′, $J_{1'-2'}$=6.4 Hz), 6.63 (d, 1H, H-1′, $J_{1'-2'}$=6.4 Hz), 7.26–7.39 (m, 5H, H-Ar), 7.42 (t, 2H, *meta*-H-$PhSO_2$, *J*=7.7 Hz), 7.53 (t, 1H, *para*-H-$PhSO_2$, *J*=7.7 Hz), 7.96 (d, 2H, *ortho*-H-$PhSO_2$, *J*=7.7 Hz). ^{13}C NMR δ 37.6 (C-2), 57.1 (OMe), 64.6 (C-5), 71.0 (C-6), 81.2 (C-3), 83.8 (C-4), 100.6 (C-1), 103.4 (C-7), 109.8 (C-2′), 128.1–131.3 (9*CH–Ar), 134.9 (CH–*para*-$PhSO_2$), 139.1 (C_{IV}–Ar), 145.1 (C_{IV}–$PhSO_2$), 158.2 (C-1′). IR (film): 3025, 2937 cm^{-1} (CH–Ar,=CH); 1620 cm^{-1} (C=C); 1384, 1144 cm^{-1} ($PhSO_2$); 1000, 979 cm^{-1} (=C–OR). MS IS *m*/*z*=401.5 $[M-OMe]^+$, 433.5 $[M+H]^+$, 450.5 $[M+NH_4]^+$. HRMS: $C_{22}H_{24}O_7S$: calcd 432.1243; found 432.1232.

4.2.14. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(*E*)-2′-(phenylsulfonyl)vinyl]-α-D-glucofuranose ((*E*)-1h). Obtained from commercially available 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (150 mg) and (*E*)-BPSE; silica gel column chromatography (toluene/ethyl acetate 8:2 and 7:3) afforded (*E*)-**1h** with 83% yield as a colourless gum, α_D=−41 (*c*=3.0, $CHCl_3$). ^{1}H NMR δ 1.29 (s, 3H, *i*Prd), 1.30 (s, 3H, *i*Prd), 1.41 (s, 3H, *i*Prd), 1.50 (s, 3H, *i*Prd), 3.97 (d, 1H, H-6b, J_{5-6b}=3.8 Hz, J_{6a-6b}=7.9 Hz), 4.06–4.17 (m, 3H, H-4, H-5, H-6a), 4.47 (s, 1H, H-3, J_{2-3}<0.5 Hz, J_{3-4}<0.5 Hz), 4.57 (d, 1H, H-2, J_{1-2}=3.8 Hz, J_{2-3}<0.5 Hz), 5.88 (d, 1H, H-1, J_{1-2}=3.8 Hz), 5.90 (d, 1H, H-2′, $J_{1'-2'}$=12.5 Hz), 7.57 (d, 1H, H-1′, $J_{1'-2'}$=12.5 Hz), 7.49–7.63 (m, 3H, *meta*, *para*-H-$PhSO_2$), 7.89 (d, 2H, *ortho*-H-$PhSO_2$, *J*=7.4 Hz). ^{13}C NMR δ 25.5, 26.5, 26.9, 27.2 (4*Me), 67.8 (C-6), 71.9 (C-5), 80.7 (C-4), 82.8 (C-2), 85.2 (C-3), 105.5 (C-1), 109.4 (C-2′), 110.0 and 112.9 (2*C_{IV}–*i*Prd), 127.4 (2*CH–*ortho*-$PhSO_2$), 129.5 (2*CH–*meta*-$PhSO_2$), 133.3 (CH–*para*-$PhSO_2$), 142.9 (C_{IV}–$PhSO_2$), 160.0 (C-1′). IR (film): 2988 cm^{-1} (CH–Ar,=CH); 1630, 1610 cm^{-1} (C=C); 1374, 1145 cm^{-1} ($PhSO_2$); 1023 cm^{-1} (=C–OR). MS IS *m*/*z*=427.5 $[M+H]^+$, 444.5 $[M+NH_4]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1345.

4.2.15. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(*Z*)-2′-(phenylsulfonyl)vinyl]-α-D-glucofuranose ((*Z*)-1h). Obtained from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (150 mg) and (*Z*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 8:2 and 7:3) afforded (*Z*)-**1h** with 81% yield as a colourless gum, α_D=+3 (*c*=2.2, $CHCl_3$). ^{1}H NMR δ 1.19 (s, 3H, *i*Prd), 1.28 (s, 3H, *i*Prd), 1.25 (s, 3H, *i*Prd), 1.47 (s, 3H, *i*Prd), 3.54 (dt, 1H, H-5, J_{4-5}=9.1 Hz, J_{5-6a}=J_{5-6b}=5.0 Hz), 3.84 (d, 1H, H-6b, J_{5-6b}=5.0 Hz, J_{6a-6b}=8.7 Hz), 3.92 (d, 1H, H-6a, J_{5-6a}=5.0 Hz, J_{6a-6b}=8.7 Hz), 3.98 (dd, 1H, H-4, J_{3-4}=2.6 Hz, J_{4-5}=9.1 Hz), 4.37 (d, 1H, H-3, J_{2-3}<0.5 Hz, J_{3-4}=2.6 Hz), 4.43 (d, 1H, H-2, J_{1-2}=3.8 Hz, J_{2-3}<0.5 Hz), 5.70 (d, 1H, H-2′, $J_{1',2'}$=6.2 Hz), 5.86 (d, 1H, H-1, J_{1-2}=3.8 Hz), 6.60 (d, 1H, H-1′, $J_{1'-2'}$=6.2 Hz), 7.51 (t, 2H, *meta*-H-$PhSO_2$, *J*=7.2 Hz), 7.61 (t, 1H, *para*-H-$PhSO_2$, *J*=7.2 Hz), 7.94 (d, 2H, *ortho*-H-$PhSO_2$, *J*=7.2 Hz). ^{13}C NMR δ 25.4, 25.6, 27.0, 27.1 (4*Me), 67.9 (C-6), 71.7 (C-5), 81.0 (C-4), 83.2 (C-2), 87.8 (C-3), 105.6 (C-1), 109.7 (C-2′), 109.8 and 112.9 (2*C_{IV}–*i*Prd), 128.1 (2*CH–*ortho*-$PhSO_2$), 129.1 (2*CH–*meta*-$PhSO_2$), 133.3 (CH–*para*-$PhSO_2$), 142.8 (C_{IV}–$PhSO_2$), 155.4 (C-1′). IR (film): 2987 cm^{-1} (CH–Ar,=CH); 1625 (C=C); 1384, 1145 cm^{-1} ($PhSO_2$);

1023 cm^{-1} (=C–OR). MS IS m/z=427.5 $[M+H]^+$, 444.5 $[M+NH_4]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1340.

4.2.16. 1,2:4,5-Di-*O*-isopropylidene-3-*O*-[(*E*)-2′-(phenylsulfonyl)vinyl]-β-D-psicopyranose ((*E*)-1i). Obtained from 1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose[26] (500 mg) and (*E*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 3:2) afforded (*E*)-**1i** with 93% yield as a colourless gum, α_D=−115 (c=1.0, $CHCl_3$). ^1H NMR δ 1.30 (s, 3H, *i*Prd), 1.32 (s, 3H, *i*Prd), 1.43 (s, 3H, *i*Prd), 1.45 (s, 3H, *i*Prd), 3.83 (s, 2H, H-6), 3.93 (d, 1H, H-1b, J_{1a-1b}=9.3 Hz), 4.19 (d, 1H, H-3, J_{3-4}=3.2 Hz), 4.22 (d, 1H, H-1a, J_{1a-1b}=9.3 Hz), 4.31 (d, 1H, H-5, J_{5-4}=7.2 Hz), 4.56 (dd, 1H, H-4, J_{3-4}=3.2 Hz, J_{4-5}=7.2 Hz), 5.99 (d, 1H, H-1′, $J_{1'-2'}$=11.6 Hz), 7.45–7.6 (m, 4H, H-2′, *meta*, *para*-H-$PhSO_2$), 7.85–7.95 (m, 2H, *ortho*-H-$PhSO_2$). ^{13}C NMR δ 25.1, 25.7, 26.1, 26.4 (4*Me), 62.6 (C-1), 71.9, 72.0 (C-3 or C-5), 73.3 (C-6), 80.8 (C-4), 104.2 (C-2), 109.4 (C-2′), 110.6 and 110.8 (2*C_{IV}–*i*Prd), 127.0 (*ortho*-$PhSO_2$), 129.3 (*meta*-$PhSO_2$), 133.0 (*para*-$PhSO_2$), 142.3 (C_{IV}–$PhSO_2$), 161.2 (C-1′). IR (film): 3064, 2992 et 2934 cm^{-1} (=CH et CH–Ar); 1737 et 1618 cm^{-1} (C=C); 1446 cm^{-1} ($PhSO_2$); 1012 cm^{-1} (=C–OR). MS IS m/z=444.5 $[M+NH_4]^+$, 449.5 $[M+Na]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1339.

4.2.17. 1,2:4,5-Di-*O*-isopropylidene-3-*O*-[(*Z*)-2′-(phenylsulfonyl)vinyl]-β-D-psicopyranose ((*Z*)-1i). Obtained from 1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose[26] (200 mg) and (*Z*)-BPSE; silica gel column chromatography (petroleum ether/ethyl acetate 1:1) afforded (*Z*)-**1i** with 73% yield as a colourless gum, α_D=−153 (c=1.0, $CHCl_3$). ^1H NMR δ 1.30 (s, 3H, *i*Prd), 1.35 (s, 3H, *i*Prd), 1.38 (s, 3H, *i*Prd), 1.43 (s, 3H, *i*Prd), 3.76 (d, 2H, H-6, J_{6-5}=1.6 Hz), 3.81 (d, 1H, H-1b, J_{1a-1b}=9.7 Hz), 3.91 Hz (d, 1H, H-1a), 4.02 (d, 1H, H-3, J_{3-4}=2.8 Hz), 4.24 (d, 1H, H-5, J_{5-4}=7.2 Hz), 4.42 (dd, 1H, H-4, J_{3-4}=2.8 Hz, J_{4-5}=7.2 Hz), 5.53 (d, 1H, H-2′, $J_{1'-2'}$=6.6 Hz), 6.58 (d, 1H, H-1′), 7.43–7.5 (m, 4H, H-2′, *meta*, *para*-H-$PhSO_2$), 7.96 (d, 2H, *ortho*-H-$PhSO_2$). ^{13}C NMR δ 25.2, 26.0, 26.1, 26.4 (4*Me), 62.8 (C-1), 71.7 (C-4), 71.9 (C-6), 73.2 (C-5), 81.1 (C-3), 104.1 (C-2), 108.8 (C-2′), 110.3 and 110.5 (2*C_{IV}–*i*Prd), 128.4 (CH–*ortho*-$PhSO_2$), 129.4 (CH–*meta*-$PhSO_2$), 129.9 (CH–*para*-$PhSO_2$), 142.2 (C_{IV}–$PhSO_2$), 155.4 (C-1′). IR (film): 3098, 2992, 2934, 2894 cm^{-1} (CH–Ar,=CH); 1635 cm^{-1} (C=C); 1447 and 1374 cm^{-1} ($PhSO_2$); 1006 et 960 cm^{-1} (=COR). MS IS m/z=449.5 $[M+Na]^+$. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1337.

4.2.18. [(*E*)-2′-(Phenylsulfonyl)vinyl] 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranoside ((*E*)-1j). Obtained from commercially available 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (150 mg) and either (*E*) or (*Z*)-BPSE; silica gel column chromatography (toluene/ethyl acetate 8:2 and 7:3) afforded (*E*)-**1j** with 83% yield as a colourless gum, α_D=+7 (c=1.9, $CHCl_3$). ^1H NMR δ 1.28 (s, 3H, *i*Prd), 1.31 (s, 3H, *i*Prd), 1.35 (s, 3H, *i*Prd), 1.41 (s, 3H, *i*Prd), 3.87 (dd, 1H, H-6b, J_{5-6b}=4.5 Hz, J_{6a-6b}=8.7 Hz), 3.90 (dd, 1H, H-4, J_{3-4}=3.4 Hz, J_{4-5}=8.7 Hz), 4.01 (dd, 1H, H-6a, J_{5-6a}=6.2 Hz, J_{6a-6b}=8.7 Hz), 4.33 (ddd, 1H, H-5, J_{4-5}=8.7 Hz, J_{5-6a}=6.2 Hz, J_{5-6b}=4.5 Hz), 4.43 (d, 1H, H-2, J_{1-2}<0.5 Hz, J_{2-3}=5.9 Hz), 4.78 (dd, 1H, H-3, J_{2-3}=5.9 Hz, J_{3-4}=3.4 Hz), 5.34 (s, 1H, H-1, J_{1-2}<0.5 Hz), 5.89 (d, 1H, H-2′, $J_{1'-2'}$=12.1 Hz), 7.44–7.55 (m, 4H, H-1′, *meta*, *para*-H-$PhSO_2$), 7.82 (d, 2H, *ortho*-H-$PhSO_2$ J=7.1 Hz). ^{13}C NMR δ 25.2, 25.8, 26.2 et 27.2 (4*Me), 66.9 (C-6), 72.9 (C-5), 79.5 (C-3), 82.5 (C-4), 82.5 (C-4), 84.9 (C-2), 107.5 (C-1), 109.7 (C-2′), 113.2 and 113.8 (2*C_{IV}–*i*Prd), 127.3 (2*CH–*ortho*-$PhSO_2$), 129.6 (2*CH–*meta*-$PhSO_2$), 133.4 (CH–*para*-$PhSO_2$), 146.8 (C_{IV}CH–$PhSO_2$), 156.9 (C-1′). IR (film): 3068, 2987, 2939 cm^{-1} (CH–Ar,=CH); 1632, 1612 cm^{-1} (C=C); 1375, 1144 cm^{-1} ($PhSO_2$); 990 cm^{-1} (=C–OR). MS IS m/z=427.5 $[M+H]^+$, 444.5 $[M+NH_4]^+$, 449.5 [M+Na]. HRMS: $C_{20}H_{26}O_8S$: calcd 426.1348; found 426.1356.

4.3. Desulfonylation reaction: synthesis of vinyl ethers 2

To a solution of the β-alkoxyvinyl sulfone **1** (0.5 mmol) in anhydrous MeOH (5 mL) 6% Na/Hg amalgam (8 g) and crystalline $NaH_2PO_4{\cdot}2H_2O$ (4 g) were added. The reaction mixture was stirred at room temperature while monitoring the consumption of the sulfone by TLC. After completion (1–2 h), the reaction mixture was filtered over a Celite pad. After removal of the solvent under reduced pressure, the product was purified by silica gel column chromatography.

4.3.1. 1,2:3,4-Di-*O*-isopropylidene-6-*O*-vinyl-α-D-galactopyranose[27] (2a). Desulfonylation of (*E*)-**1a** gave, after chromatography (petroleum ether/ethyl acetate 9:1 and 8:2), a 66% yield of ethenyl ether **2a** in the form of a colourless gum, α_D=−65 (c=2.7, $CHCl_3$). ^1H NMR δ 1.32 (s, 3H, *i*Prd), 1.34 (s, 3H, *i*Prd), 1.45 (s, 3H, *i*Prd), 1.53 (s, 3H, *i*Prd), 3.83 (dd, 1H, H-6b, J_{5-6b}=6.8 Hz, J_{6a-6b}=10.2 Hz), 3.88 (dd, 1H, H-6a, J_{5-6a}=5.3 Hz, J_{6a-6b}=10.2 Hz), 4.01 (dd, 1H, H-2′$_Z$, $J_{1'-2'Z}$=6.8 Hz, $J_{2'E-2'Z}$=1.9 Hz), 4.05 (ddd, 1H, H-5, J_{4-5}=7.5 Hz, J_{5-6a}=5.3 Hz, J_{5-6b}=6.8 Hz), 4.22 (dd, 1H, H-2′$_E$, $J_{1'-2'E}$=14.3 Hz, $J_{2'E-2'Z}$=1.9 Hz), 4.26 (dd, 1H, H-4, J_{3-4}=7.8 Hz, J_{4-5}=7.5 Hz), 4.32 (dd, 1H, H-2, J_{1-2}=5.1 Hz, J_{2-3}=2.5 Hz), 4.62 (dd, 1H, H-3, J_{2-3}=2.5 Hz, J_{3-4}=7.8 Hz), 5.54 (d, 1H, H-1, J_{1-2}=5.1 Hz), 6.49 (dd, 1H, H-1′, $J_{1'-2'E}$=14.3 Hz, $J_{1'-2'Z}$=6.8 Hz). ^{13}C NMR δ 24.8, 25.3, 26.3 and 26.4 (4*Me), 66.5 (C-5), 66.9 (C-6), 70.9 (C-2), 71.1 (C-3), 71.4 (C-4), 87.2 (C-2′), 96.7 (C-1), 109.1 and 109.8 (2*C_{IV}–*i*Prd), 151.9 (C-1′). IR (film): 2980, 2948 cm^{-1} (=CH_2); 1618 cm^{-1} (C=C); 992cm^{-1}, 973 cm^{-1} (=C–OR). MS IS m/z=287.5 $[M+H]^+$, 304.5 $[M+NH_4]^+$, 309.5 $[M+Na]^+$.

4.3.2. 2,3:4,5-Di-*O*-isopropylidene-1-*O*-vinyl-β-D-fructopyranose (2b). Desulfonylation of (*E*)-**1b** gave, after chromatography (petroleum ether/ethyl acetate 9:1 and 8:2), a 82% yield of ethenyl ether **2b** in the form of a colourless gum, α_D=−20 (c=2.8, $CHCl_3$). ^1H NMR δ 1.35 (s, 3H, *i*Prd), 1.42 (s, 3H, *i*Prd), 1.48 (s, 3H, *i*Prd), 1.55 (s, 3H, *i*Prd), 3.76 (d, 1H, H-6b, J_{5-6b}<0.5 Hz, J_{6a-6b}=11.9 Hz), 3.78 (d, 1H, H-1b, J_{1a-1b}=10.8 Hz), 3.85 (d, 1H, H-1a, J_{1a-1b}=10.8 Hz), 3.93 (d, 1H, H-6a, J_{5-6a}<0.5 Hz, J_{6a-6b}=11.9 Hz), 4.03 (dd, 1H, H-2′$_Z$, $J_{1'-2'Z}$=6.6 Hz, $J_{2'E-2'Z}$=2.1 Hz), 4.24 (dd, 1H, H-2′$_E$, $J_{1'-2'E}$=14.1 Hz, $J_{2'E-2'Z}$=2.1 Hz), 4.25 (d, 1H, H-5, J_{4-5}=8.1 Hz, J_{5-6a}=J_{5-6b}<0.5 Hz), 4.39 (d, 1H, H-3, J_{3-4}=2.8 Hz), 4.62 (dd, 1H, H-4, J_{3-4}=2.8 Hz, J_{4-5}=8.1 Hz), 6.46 (dd, 1H, H-1′, $J_{1'-2'E}$=14.1 Hz, $J_{1'-2'Z}$=6.6 Hz). ^{13}C NMR δ 24.4, 25.6,

26.2, 29.6 (4*Me), 61.4 (C-6), 70.1 (C-1), 70.4 (C-4), 71.3 (C-3), 71.4 (C-5), 87.7 (C-2′), 102.3 (C-2), 109.2 and 109.3 (2*C_{IV}–*i*Prd), 152.3 (C-1′). IR (film): 2990, 2937 cm^{-1} (=CH_2); 1638, 1616 cm^{-1} (C=C). MS IS *m*/*z*=287.0 $[M+H]^+$, 304.5 $[M+NH_4]^+$, 309.5 $[M+Na]^+$. HRMS: $C_{14}H_{22}O_6$: calcd 286.1416; found 286.1425.

4.3.3. 2,3:4,5-Di-*O*-isopropylidene-1-*O*-vinyl-α-L-sorbofuranose (2c). Desulfonylation of (*E*)-**1c** gave, after chromatography (petroleum ether/ethyl acetate 9:1 and 8:2) a 65% yield of ethenyl ether **2c** in the form of a colourless gum, α_D=+1 (*c*=2.1, $CHCl_3$). ^{1}H NMR δ 1.37 (s, 3H, *i*Prd), 1.41 (s, 3H, *i*Prd), 1.43 (s, 3H, *i*Prd), 1.51 (s, 3H, *i*Prd), 3.92 (d, 1H, H-1b, J_{1a-1b}=11.1 Hz), 3.98–4.05 (m, 4H, H-1a, H-6a, H-6b, H-2′$_Z$), 4.12 (d, 1H, H-5, J_{4-5}=2.1 Hz), 4.26 (dd, 1H, H-2′$_E$, $J_{1'-2'E}$=14.0 Hz, $J_{2'E-2'Z}$=2.1 Hz), 4.34 (d, 1H, H-4, J_{3-4}<0.5 Hz, J_{4-5}=2.1 Hz), 4.87 (s, 1H, H-3, J_{3-4}<0.5 Hz), 6.48 (dd, 1H, H-1′, $J_{1'-2'E}$=14.0 Hz, $J_{1'-2'Z}$=6.6 Hz). ^{13}C NMR δ 18.9, 26.7, 27.9, 29.3 (4*Me), 60.6 (C-6), 68.4 (C-1), 72.6 (C-5), 73.5 (C-4), 84.6 (C-3), 87.6 (C-2′), 97.7 (C-2), 112.9 and 113.6 (2*C_{IV}–*i*Prd), 152.2 (C-1′). IR (film): 2990, 2938 cm^{-1} (=CH_2); 1621 cm^{-1} (C=C); 991, 975 cm^{-1} (=C–OR). MS IS *m*/*z*=287.0 $[M+H]^+$, 304.0 $[M+NH_4]^+$, 309.5 $[M+Na]^+$. HRMS: $C_{14}H_{22}O_6$: calcd 286.1416; found 286.1426.

4.3.4. 1,2:4,5-Di-*O*-isopropylidene-3-*O*-vinyl-β-D-fructopyranose (2d). Desulfonylation of (*E*)-**1d** gave, after chromatography (petroleum ether/ethyl acetate 9:1 and 8:2), a 94% yield of ethenyl ether **2d** in the form of a colourless gum, α_D=−145 (*c*=3.1, $CHCl_3$). ^{1}H NMR δ 1.37 (s, 3H, *i*Prd), 1.42 (s, 3H, *i*Prd), 1.51 (s, 3H, *i*Prd), 1.56 (s, 3H, *i*Prd), 3.78 (d, 1H, H-3, J_{3-4}=7.2 Hz), 3.94–4.11 (m, 4H, H-1a, H-1b, H-6b, H-2′$_Z$), 4.14 (dd, 1H, H-6a, J_{5-6a}=2.8 Hz, J_{6a-6b}=13.4 Hz), 4.23 (dd, 1H, H-5, J_{3-4}=7.2 Hz, J_{5-6a}=2.8 Hz, J_{5-6b}<0.5 Hz), 4.31 (t, 1H, H-4, J_{3-4}=J_{4-5}=7.2 Hz), 4.46 (d, 1H, H-2′$_E$, $J_{1'-2'E}$=13.8 Hz, $J_{2'E-2'Z}$<0.5 Hz), 6.45 (dd, 1H, H-1′, $J_{1'-2'E}$=13.8 Hz, $J_{1'-2'Z}$=6.4 Hz). ^{13}C NMR δ 26.2, 26.5, 27.2, 28.5 (4*Me), 60.6 (C-6), 71.8 (C-1), 74.1 (C-5), 76.6 (C-4), 78.1 (C-3), 90.1 (C-2′), 106.7 (C-2), 111.5 and 114.7 (2*C_{IV}–*i*Prd), 152.4 (C-1′). IR (film): 2988, 2936, 2889 cm^{-1} (=CH_2); 1637, 1636 cm^{-1} (C=C); 1027 cm^{-1}, 991, 976 cm^{-1} (=C–OR). MS IS *m*/*z*=287.0 $[M+H]^+$, 309.5 $[M+Na]^+$, 325.0 $[M+K]^+$. HRMS: $C_{14}H_{22}O_6$: calcd 286.1416; found 286.1418.

4.3.5. 3,4-Di-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-vinyl-β-L-sorbopyranose (2e). Desulfonylation of (*E*)-**1e** gave, after chromatography (petroleum ether/ethyl acetate 9:1 and 8:2), a 93% yield of ethenyl ether **2e** in the form of a colourless gum, α_D=−32 (*c*=2.7, $CHCl_3$). ^{1}H NMR δ 1.43 (s, 3H, *i*Prd), 1.48 (s, 3H, *i*Prd), 3.37 (d, 1H, H-3, J_{3-4}=8.1 Hz), 3.69–3.93 (m, 6H, H-1a, H-1b, H-4, H-5, H-6a, H-6b), 4.06 (d, 1H, H-2′$_Z$, $J_{1'-2'Z}$=6.2 Hz, $J_{2'E-2'Z}$<0.5 Hz), 4.43 (d, 1H, H-2′$_E$, $J_{1'-2'E}$=13.8 Hz, $J_{2'E-2'Z}$<0.5 Hz), 4.61 and 4.96 (2d, AB system, 2H, Ph*CH*$_2$O, J_{gem}=11.5 Hz), 4.73 and 4.85 (2d, AB system, 2H, Ph*CH*$_2$O, J_{gem}=10.4 Hz), 6.40 (dd, 1H, H-1′, $J_{1-2'E}$=13.8 Hz, $J_{1-2'Z}$=6.2 Hz), 7.25–7.35 (m, 10H, H-Ar). ^{13}C NMR δ 26.6, 27.6 (2*Me), 60.9 (C-6), 71.9 (C-1), 75.8, 75.9 (2*Ph*CH*$_2$O), 78.1 (C-3), 79.3, 83.2 (C-4, C-5), 89.5 (C-2′), 103.7 (C-2), 110.9 (C_{IV}–*i*Prd), 128.2–128.9 (10*CH–Ar), 136.8, 137.1 (2*C_{IV}–Ar), 151.9 (C-1′). IR (film): 3061, 3031 cm^{-1} (CH–Ar), 2988, 2938, 2888 cm^{-1} (=CH_2); 1635 cm^{-1} (C=C); 973 cm^{-1} (=C–OR). MS IS *m*/*z*=449.5 $[M+Na]^+$. HRMS: $C_{25}H_{30}O_6$: calcd 426.2042; found 426.2029.

4.3.6. Methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-3-*O*-vinyl-α-D-altropyranoside (2f). Desulfonylation of (*E*)-**1f** gave, after chromatography (petroleum ether/ethyl acetate 9:1 and 8:2), a 84% yield of ethenyl ether **2e** in the form of a colourless gum, α_D=+102 (*c*=2.8, $CHCl_3$). ^{1}H NMR δ 1.17 (d, 3H, Me, *J*=7.7 Hz), 2.43 (dq, 1H, H-2, J_{1-2}<0.5 Hz, J_{2-3}=2.3 Hz, *J*=7.7 Hz), 3.37 (s, 3H, OMe), 3.75 (dd, 1H, H-6b, J_{5-6b}=2.5 Hz, J_{6a-6b}=11.9 Hz), 3.83 (dd, 1H, H-4, J_{3-4}=2.3 Hz, J_{4-5}=9.4 Hz), 4.02 (dd, 1H, H-2′$_Z$, $J_{1'-2'Z}$=6.6 Hz, $J_{2'E-2'Z}$=1.3 Hz), 4.06 (t, 1H, H-3, J_{2-3}=J_{3-4}=2.3 Hz), 4.26–4.38 (m, 3H, H-5, H-6a, H-2′$_E$), 4.42 (s, 1H, H-1, J_{1-2}<0.5 Hz), 5.55 (s, 1H, H-7), 6.39 (dd, 1H, H-1′, $J_{1'-2'E}$=14.3 Hz, $J_{1'-2'Z}$=6.6 Hz), 7.46–7.50 (m, 5H, H-Ar). ^{13}C NMR δ 16.6 (Me), 38.1 (C-2), 55.8 (OMe), 58.8 (C-5), 69.9 (C-6), 76.2 (C-4), 77.1 (C-3), 89.4 (C-2′), 103.5 (C-7), 104.0 (C-1), 127.6 (2*CH–Ar), 129.4 (2*CH–Ar), 130.3 (CH–Ar), 138.7 (C_{IV}–Ar), 153.0 (C-1′). IR (film): 3015, 2974, 2936, 2886, 2838 cm^{-1} (CH–Ar,=CH_2); 1637, 1616 cm^{-1} (C=C); 1015, 948 cm^{-1} (=C–OR). MS IS *m*/*z*=324.0 $[M+NH_4]^+$, 329.0 $[M+Na]^+$, 345.0 $[M+K]^+$. HRMS: $C_{17}H_{22}O_5$: calcd 306.1467; found 306.1457.

4.3.7. Methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-vinyl-α-D-glucopyranoside (2g). Desulfonylation of (*E*)-**1g** gave, after chromatography (petroleum ether/ethyl acetate 9:1 and 8:2), a 84% yield of ethenyl ether **2g** in the form of a colourless gum, α_D=+66 (*c*=2.8, $CHCl_3$). ^{1}H NMR δ 1.79 (ddd, 1H, H-2b, J_{1-2b}=3.6 Hz, J_{2a-2b}=13.4 Hz, J_{2b-3}=11.3 Hz), 2.32 (dd, 1H, H-2a, J_{1-2a}<0.5 Hz, J_{2a-2b}=13.4 Hz, J_{2a-3}=5.1 Hz), 3.33 (s, 3H, OMe), 3.65 (t, 1H, H-4, J_{3-4}=J_{4-5}=8.9 Hz), 3.76–3.88 (m, 2H, H-5, H-6b), 4.00 (dd, 1H, H-2′$_Z$, $J_{1-2'Z}$=6.4 Hz, $J_{2'E-2'Z}$=1.5 Hz), 4.24–4.33 (m, 2H, H-3, H-6a), 4.38 (dd, 1H, H-2′$_E$, $J_{1'-2'E}$=14.1 Hz, $J_{2'E-2'Z}$=1.5 Hz), 4.80 (d, 1H, H-1, J_{1-2a}<0.5 Hz, J_{1-2b}=3.6 Hz), 5.58 (s, 1H, H-7), 6.41 (dd, 1H, H-1′, $J_{1'-2'E}$=14.1 Hz, $J_{1'-2'Z}$=6.4 Hz), 7.46–7.50 (m, 5H, H-Ar). ^{13}C NMR δ 36.1 (C-2), 55.2 (OMe), 63.2 (C-5), 69.5 (C-6), 74.6 (C-3), 83.2 (C-4), 89.9 (C-2′), 99.9 (C-1), 101.8 (C-7), 126.8 (2*CH–Ar), 129.2 (2*CH–Ar), 129.9 (CH–Ar), 138.4 (C_{IV}–Ar), 152.4 (C-1′). IR (film): 3018, 2936, 2867 cm^{-1} (CH–Ar,=CH_2); 1636 cm^{-1} (C=C); 1018cm^{-1}, 981 cm^{-1} (=C–OR). MS IS *m*/*z*=293.0 $[M+H]^+$, 310.0 $[M+NH_4]^+$, 315.0 $[M+Na]^+$, 331.0 $[M+K]^+$. HRMS: $C_{16}H_{20}O_5$: calcd 292.1311; found 292.1300.

4.3.8. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-vinyl-α-D-glucofuranose[8b] (2h). Desulfonylation of (*E*)-**1h** gave, after chromatography (petroleum ether/ethyl acetate 9:1 and 8:2), a 60% yield of ethenyl ether **2h** in the form of a colourless gum, α_D=−32 (*c*=2.1, $CHCl_3$). ^{1}H NMR δ 1.31 (s, 3H, *i*Prd), 1.34 (s, 3H, *i*Prd), 1.43 (s, 3H, *i*Prd), 1.51 (s, 3H, *i*Prd), 4.02 (d, 1H, H-6b, J_{5-6b}=5.3 Hz, J_{6a-6b}=8.5 Hz), 4.09 (d, 1H, H-6a, J_{5-6a}=5.7 Hz, J_{6a-6b}=8.5 Hz), 4.15 (dd, 1H, H-2′$_Z$, $J_{1'-2'Z}$=6.8 Hz, $J_{2'E-2'Z}$=2.3 Hz), 4.18 (dt, 1H,

J_{3-4}=2.9 Hz, J_{4-5}=4.5 Hz, H-4), 4.27–4.33 (m, 1H, H-5), 4.34 (d, 1H, H-3, J_{2-3}<0.5 Hz, J_{3-4}=2.9 Hz), 4.39 (dd, 1H, H-2′$_E$, $J_{1'-2'E}$=14.3 Hz, $J_{2'E-2'Z}$=2.3 Hz), 4.58 (d, 1H, H-2, J_{1-2}=3.6 Hz, J_{2-3}<0.5 Hz), 5.88 (d, 1H, H-1, J_{1-2}= 3.6 Hz), 6.39 (dd, 1H, H-1′, $J_{1'-2'E}$=14.3 Hz, $J_{1'-2'Z}$= 6.8 Hz). ^{13}C NMR δ 24.9, 25.5, 26.3, 27.3 (4*Me), 67.3 (C-6), 73.3 (C-5), 79.8 (C-3), 81.4 (C-4), 85.2 (C-2), 92.5 (C-2′), 105.6 (C-1), 109.7 and 113.3 (2*C$_{IV}$–*i*Prd), 148.2 (C-1′). IR (film): 2987, 2937 cm^{-1} (=CH$_2$); 1639, 1621 cm^{-1} (C=C); 1075 cm^{-1}, 1021, 963 cm^{-1} (=C–OR). MS IS *m*/*z*=287.0 [M+H]$^+$, 304.0 [M+NH$_4$]$^+$, 309.0 [M+Na]$^+$, 325.0 [M+K]$^+$.

4.3.9. 1,2:4,5-Di-*O*-isopropylidene-3-*O*-vinyl-β-D-psicopyranose (2i). Desulfonylation of (*E*)-**1i** gave, after chromatography (petroleum ether/ethyl acetate 6:4), a 55% yield of ethenyl ether **2i** in the form of a colourless gum, α_D=−127 (*c*=1.0, CHCl$_3$). ^{1}H NMR δ 1.35 (s, 3H, *i*Prd), 1.40 (s, 3H, *i*Prd), 1.47 (s, 3H, *i*Prd), 1.51 (s, 3H, *i*Prd), 3.78 (dd, 1H, H-6b, J_{6a-6b}=13.5 Hz, J_{6b-5}=1.2 Hz), 3.84 (dd, 1H, H-6a, J_{6a-5}=1.9 Hz), 3.96 (d, 1H, H-1b, J_{1a-1b}=9.1 Hz), 4.01 (d, 1H, H-3, J_{3-4}=2.8 Hz), 4.07 (dd, H-2′$_Z$, $J_{2'E-2'Z}$=2.2 Hz, $J_{1'-2'Z}$=6.3 Hz), 4.27–4.33 (m, 1H, H-5), 4.34 (d, 1H, H-1a, J_{1a-1b}=9.1 Hz), 4.48–4.55 (dd, 1H, H-2′*E*, $J_{1'-2'E}$=13.8 Hz), 4.56 (dd, 1H, H-4, J_{4-5}=7.2 Hz), 6.33 (dd, 1H, H-1′, $J_{1'-2'E}$=13.8 Hz). ^{13}C NMR δ 24.0, 25.1, 25.2 et 25.3 (4*Me), 61.4 (C-6); 70.8 (C-1); 71.4 (C-4); 72;4 (C-5); 75;5 (C-3); 89.1 (C-2′); 103.5 (C-2); 109.0 and 109.3 (2*C$_{IV}$–*i*Prd), 151.0 (C-1′). MS IS *m*/*z*=287.0 [M+H]$^+$. HRMS: $C_{14}H_{22}O_6$: calcd 286.1416; found 286.1421.

4.3.10. Vinyl 2,3:5,6-di-*O*-isopropylidène-α-D-mannofuranoside (2j). Desulfonylation of (*E*)-**1j** gave, after chromatography (petroleum ether/ethyl acetate 9:1 and 8:2), a 65% yield of ethenyl ether **2j** in the form of a colourless gum, α_D=+50 (*c*=2.0, CHCl$_3$). ^{1}H NMR δ 1.34 (s, 3H, *i*Prd), 1.38 (s, 3H, *i*Prd), 1.45 (s, 3H, *i*Prd), 1.48 (s, 3H, *i*Prd), 3.96 (dd, 1H, H-4, J_{3-4}=3.4 Hz, J_{4-5}=8.3 Hz), 4.01 (dd, 1H, H-6b, J_{5-6b}=4.5 Hz, J_{6a-6b}=8.7 Hz), 4.16 (dd, 1H, H-6a, J_{5-6a}=6.2 Hz, J_{6a-6b}=8.7 Hz), 4.18 (dd, 1H, H-2′$_Z$, $J_{1'-2'Z}$=6.4 Hz, $J_{2'E-2'Z}$=1.7 Hz), 4.39 (ddd, 1H, H-5, J_{4-5}=8.3 Hz, J_{5-6a}=6.2 Hz, J_{5-6b}=4.5 Hz), 4.47 (dd, 1H, H-2′$_E$, $J_{1'-2'E}$=14.0 Hz, $J_{2'E-2'Z}$=1.7 Hz), 4.69 (d, 1H, H-2, J_{1-2}<0.5 Hz, J_{2-3}=5.7 Hz), 4.82 (dd, 1H, H-3, J_{2-3}= 5.7 Hz, J_{3-4}=3.4 Hz), 5.27 (s, 1H, H-1, J_{1-2}<0.5 Hz), 6.34 (dd, 1H, H-1′, $J_{1'-2'E}$=14.0 Hz, $J_{1'-2'Z}$=6.4 Hz). ^{13}C NMR δ 24.9, 25.5, 26.3, 27.3 (4*Me), 67.3 (C-6), 73.3 (C-5), 79.8 (C-3), 81.4 (C-4), 85.2 (C-2), 92.5 (C-2′), 105.6 (C-1), 109.7, 113.3 (2*C$_{IV}$–*i*Prd), 148.2 (C-1′). IR (film): 2987, 2939 cm^{-1} (CH–Ar,=CH$_2$); 1643, 1625 cm^{-1} (C=C); 1020, 987, 945 cm^{-1} (=C–OR). MS IS *m*/*z*=287.0 [M+H]$^+$, 304.0 [M+NH$_4$]$^+$, 309.0 [M+Na]$^+$, 325.0 [M+K]$^+$. HRMS: $C_{14}H_{22}O_6$: calcd 286.1416; found 286.1427.

Acknowledgements

The authors wish to thank Professor P. Andrew Evans (University of Delaware) for useful comments on their work.

References

1. Hultin, P. G.; Earle, M. A.; Sudharshan, M. *Tetrahedron* **1997**, *53*, 14823–14870.
2. (a) Cabianca, E.; Chéry, F.; Rollin, P.; Cossu, S.; De Lucchi, O. *Synlett* **2001**, 1962–1964. (b) Desroses, M.; Chéry, F.; Tatibouët, A.; De Lucchi, O.; Rollin, P. *Tetrahedron: Asymmetry* **2002**, *13*, 2535–2539. (c) Okimoto, Y.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1590–1591.
3. Denmark, S. E.; Hurd, A. R. *J. Org. Chem.* **1998**, *63*, 3045–3050, and references cited therein.
4. (a) Dujardin, G.; Rossignol, S.; Molato, S.; Brown, E. *Tetrahedron* **1994**, *50*, 9037–9050. (b) Dujardin, G.; Rossignol, S.; Brown, E. *Synthesis* **1998**, *5*, 763–770, and references cited therein.
5. De Gaudenzi, L.; Apparao, S.; Schmidt, R. R. *Tetrahedron* **1990**, *46*, 277–290.
6. Clark, J. S.; Kettle, J. G. *Tetrahedron* **1999**, *55*, 8231–8248.
7. (a) Boa, A. N.; Booth, S. E.; Dawkins, D. A.; Jenkins, P. R.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1277–1278. (b) Boa, A. N.; Dawkins, D. A.; Hergueta, A. R.; Jenkins, P. R. *J. Chem. Soc., Perkin Trans. 1* **1994**, 953–960.
8. (a) Kaluźa, Z.; Abramski, W.; Belźecki, C.; Grodner, J.; Mostowicz, D.; Urbański, R.; Chmielewski, M. *Synlett* **1994**, *7*, 539–541. (b) Kaluźa, Z.; Furman, B.; Patel, M.; Chmielewski, M. *Tetrahedron: Asymmetry* **1994**, *5*, 2179–2186. (c) Chmielewski, M.; Kaluźa, Z.; Furman, B. *J. Chem. Soc., Chem. Commun.* **1996**, 2689–2696.
9. (a) Markó, I. E.; Evans, G. R. *Tetrahedron Lett.* **1994**, *35*, 2771–2774. (b) Ganz, I.; Kunz, H. *Synthesis* **1994**, *12*, 1353–1358. (c) Bayón, P.; de March, P.; Figueredo, M.; Font, J. *Tetrahedron* **1998**, *54*, 15691–15700. (d) Godage, H. Y.; Fairbanks, A. J. *Tetrahedron Lett.* **2000**, *41*, 7589–7593. (e) Vallin, K. S. A.; Larhed, M.; Johansson, K.; Hallberg, A. *J. Org. Chem.* **2000**, *65*, 4537–4542. (f) Crousse, B.; Bégué, J.-P.; Bonnet-Delpon, D. *J. Org. Chem.* **2000**, *65*, 5009–5013.
10. (a) Perrine, T. D.; Glaudemans, C. P. J.; Ness, R. K.; Kyle, J.; Fletcher, H. G., Jr. *J. Org. Chem.* **1967**, *32*, 664–669. (b) Cottier, L.; Descotes, G. *Synthesis* **1979**, 711–713. (c) Rollin, P.; Verez-Bencomo, V.; Sinaÿ, P. *Synthesis* **1984**, 134–135. (d) de Raadt, A.; Ferrier, R. *J. Carbohydr. Res.* **1992**, *216*, 93–107. (e) Edathil, J.; Nguyen, J.; Hughes, K.; Boyko, W. J.; Giuliano, R. M. *J. Carbohydr. Chem.* **2001**, *20*, 81–85. (f) Handerson, S.; Schlaf, M. *Org. Lett.* **2002**, *4*, 407–409.
11. (a) McCombie, S. W.; Shankar, R. B.; Ganguly, A. K. *Tetrahedron Lett.* **1985**, *26*, 6301–6304. (b) Pelter, A.; Ward, R. S.; Little, G. M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2775–2790.
12. Evans, P. A.; Manangan, T. *J. Org. Chem.* **2000**, *65*, 4523–4528.
13. The sole mannofuranoside case (compounds **1j** and **2j**) is fully described in the present paper.
14. Meek, J. S.; Fowler, J. S. *J. Org. Chem.* **1968**, *33*, 985–991.
15. Najera, C.; Yus, M. *Tetrahedron* **1999**, *55*, 10547–10658.
16. Vinyl sulfones can find many interesting applications e.g. as radical acceptors; see Ref. 12 and literature cited.
17. We are currently investigating the Michael-acceptor character of compounds **1**.
18. Choudhury, A.; Franck, R. W.; Gupta, R. B. *Tetrahedron Lett.* **1989**, *37*, 4921–4924.
19. (a) Marra, A.; Esnault, J.; Veyrières, A.; Sinaÿ, P. *J. Am. Chem. Soc.* **1992**, *114*, 6354–6360. (b) Boons, G. J.; Heskamp,

B.; Hout, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2845–2847. (c) Boons, G. J.; Isles, S. *J. Org. Chem.* **1996**, *61*, 4262–4271.
20. Godage, H. Y.; Fairbanks, A. J. *Tetrahedron Lett.* **2000**, *41*, 7589–7593.
21. Kang, J.; Lim, G. J.; Yoon, S. K.; Kim, M. Y. *J. Org. Chem.* **1995**, *60*, 564–577.
22. Lichtenthaler, F. W. *Carbohydr. Res.* **1998**, *313*, 69–89.
23. Tatibouët, A.; Lefoix, M.; Nadolny, J.; Martin, O. R.; Rollin, P.; Yang, Y.; Holman, G. D. *Carbohydr. Res.* **2001**, *333*, 327–334.
24. Jones, K.; Woods, W. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 537–545.
25. Yoshisuke, T.; Makoto, N.; Yoko, I. *Chem. Pharm. Bull.* **1991**, *39*, 1983–1989.
26. Prisbe, E. J.; Smejkal, J.; Verheyden, J. P. H.; Moffatt, J. G. *J. Org. Chem.* **1976**, *41*, 1836–1846.
27. Klein, J.; Blumenberg, K. *Makromol. Chem. Rapid Commun.* **1986**, *7*, 621–625.