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Synthesis of Vinyl Sulfoxide-Modified Pent-2-enofuranosides and Hex-2-enopyranosides and Preliminary Studies of Their Reactivity

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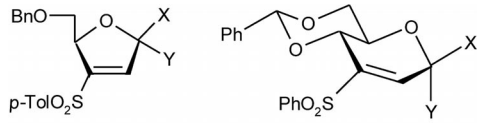
Vinyl sulfoxide-modified pent-2-enofuranosides and hex-2-enopyranosides have been synthesized by using a controlled oxidation of C-3-deoxy-C-3-thioaryl furanosides and pyranosides, respectively, followed by mesylation of the C-2-hydroxyl group and elimination. In the furanose system, both diastereomers were formed in almost equal ratio, whereas the pyranose ring imposed diastereoselectivity of oxidation of the sulfur atom to produce only S_s isomers in good overall yields. Vinyl sulfoxide-modified 2-enofuranosides were treated with $NaCH_2NO_2$ to obtain C-2 branched chain sugars. Furanosyl sulfoxides yielded products that were similar to the adducts obtained by treatment of the corresponding sulfones with nitromethane. The sulfinyl group in the pyranosides influenced the diastereoselectivity of addition to produce adducts that differed from the products obtained from the corresponding vinyl sulfones under similar reaction conditions.

Introduction

α,β-Unsaturated sulfoxides and vinyl sulfoxides in general are versatile intermediates and useful building blocks in synthetic chemistry because they are efficient partners in Diels–Alder reactions[1] and powerful Michael acceptors under radical or anionic conditions.[2] These compounds are also useful in asymmetric synthesis due to the presence of the sulfinyl group, which has been shown to be one of the most efficient chiral auxiliaries.[1a,2e,3] Attempts have been made in the past to combine the rich chemistry of vinyl sulfoxide with those of carbohydrates by replacing an endo- or exocyclic oxygen in a sugar system by a sulfoxide group; it was expected that a combination of the chiralities of sulfoxide sulfur and the inbuilt stereogenicity of carbohydrates would create a complex and versatile chiral controller that can be used in stereoselective synthesis.[4] Although there are a reasonably large number of publications on 5-thiopyranose monosaccharide *S*-oxides, anomeric glycopyranose sulfoxide, and, to a limited extent, on 6-deoxy-6-sulfinyl-D-monosaccharides, only a few examples have reported on sugars functionalized with sulfinyl substituents at C-2 or C-3 of carbohydrates.[4,5] We have established the usefulness of vinyl sulfone-modified carbohydrates **1** and **2** (Figure 1) and related compounds as intermediates in the synthesis of amino sugars,[6a–6e,6g,6h,6k,6p,6r] branched chain sugars,[6f,6i,6p] carbocycles,[6j,6n,6o,6q,6s] and N-, O-, an S-heterocycles.[6l,6m,6q,6s,7] However, the diastereoselectivity of addition reactions of vinyl sulfoxide-modified pent-2-enofuranosides and hex-2-enopyranosides have never been studied.[4] We reported the addition of carbon nucleophiles to the C-2 position of furanosides **1α/1β** and pyranosides **2α/2β** from a direction opposite to the disposition of the anomeric methoxy groups and concluded that the anomeric configurations of these Michael acceptors played a crucial role in determining the diastereoselectivity of addition of carbon nucleophiles.[6f] We therefore wanted to examine whether the sulfinyl group of a vinyl sulfoxide-modified carbohydrate could exert additional effects on the stereochemical outcome of the addition reaction to these Michael acceptors, particularly in view of the fact that sulfoxides are well-known as chiral auxiliaries.[3]



1α X = H, Y = OMe
1β X = OMe Y = H

2α X = H, Y = OMe
2β X = OMe, Y = H

Figure 1. Vinyl sulfone-modified pent-2-enofuranosides and hex-2-enopyranosides.

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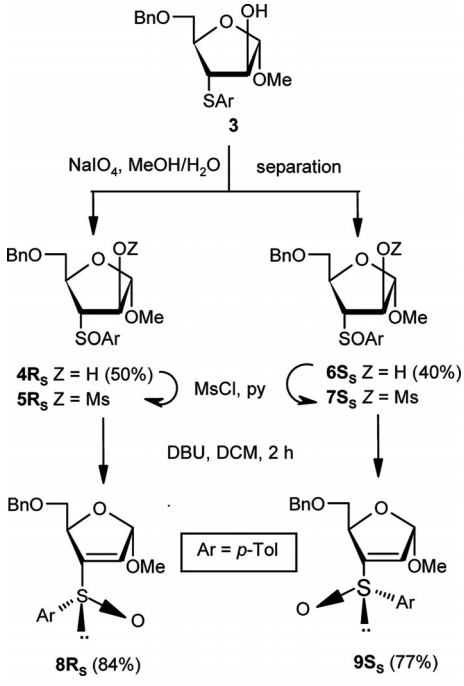
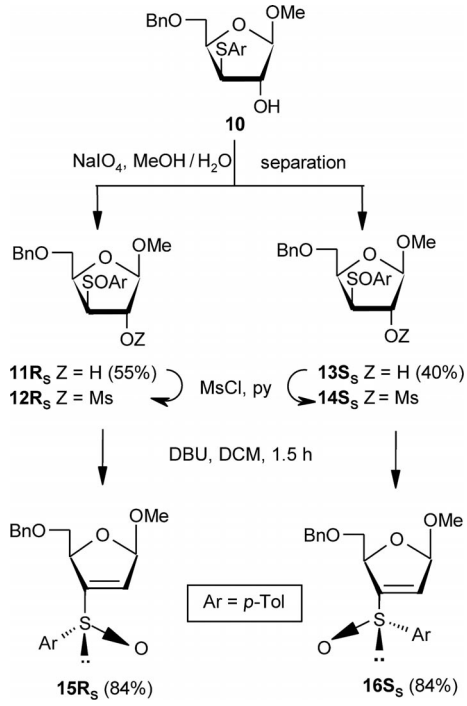
Results and Discussion

Synthesis of α and β-Anomeric Vinyl Sulfoxide-Modified Pent-2-enofuranosides

Our synthesis of α and β-anomeric vinyl sulfoxide-modified pent-2-enofuranosides **8**R_S and **9**S_S (Scheme 1),[8] started from the reported[9] α-anomeric sugar sulfide **3**, which was oxidized to sulfoxides **4**R_S and **6**S_S with $NaIO_4$/MeOH/H_2O. The diastereomers were separated at this stage to obtain the sulfoxides in almost equal ratio. The hydroxyl groups of **4**R_S and **6**S_S were mesylated and the mesyl compounds **5**R_S and **7**S_S were directly treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dichloromethane to afford vinyl sulfoxides **8**R_S and **9**S_S, respectively, in excellent yields (Scheme 1). The β-anomeric sulfide **10**[9] was converted into the expected vinyl sulfoxide-modified carbohydrates **15**R_S and **16**S_S in a similar way via intermediates **11**R_S/**12**R_S and **13**S_S/**14**S_S, respectively (Scheme 2). It was quite clear that, for both α- and β-methyl furanosides **3** and **10**, there was virtually no selectivity of oxidation for the formation of **8/9** and **15/16**, respectively. However, the isomers were separated and the configurations at the sulfur of stereoisomers **8**R_S and **9**S_S were established on the basis of their ^{1}H NMR spectroscopic data. To establish the absolute configuration at the sulfoxide sulfur of vinyl sulfoxides **8/9** and **15/16**, we compared the ^{1}H NMR spectroscopic data of **8**R_S and **9**S_S with those reported for 2-aryl-3-sulfinyl-2,5-dihydrofurans.[10] In the reported data, the vinylic proton was used as an excellent tool for assigning the stereochemistry of the sulfur atom because of the highly deshielding effect induced by the sulfinyl oxygen on the vinylic hydrogen.[10] The chemical shift values of olefinic protons (H2) of the α-isomer were found at δ = 6.53 ppm for **8**R_S and δ = 6.36 ppm for **9**S_S. The olefinic proton (H2) of **8**R_S and H4 (δ = 4.47–4.57 ppm) were deshielded and shielded, respectively. The opposite phenomena occurred in the case of **9**S_S, in which the olefinic proton (H2) and H4 (δ = 4.94–4.97 ppm) were shielded and deshielded, respectively. According to the reported data,[10] the higher chemical shift value of the vinylic proton is possible if the sulfur oxygen was oriented towards the vinylic proton. Configurations of **15**R_S and **16**S_S were also established by comparing the chemical shift values of the olefinic protons (δ = 6.53 ppm for **15**R_S and δ = 6.25 ppm for **16**S_S) and the H4 protons (δ = 4.53 ppm for **15**R_S and δ = 4.88–4.90 ppm for **16**S_S).



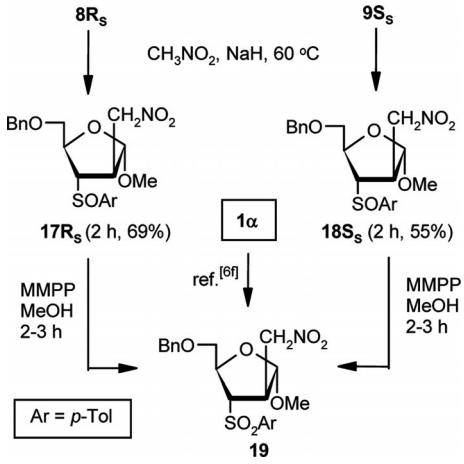
Scheme 1. Synthesis of α-anomeric vinyl sulfoxide-modified pent-2-enofuranosides.



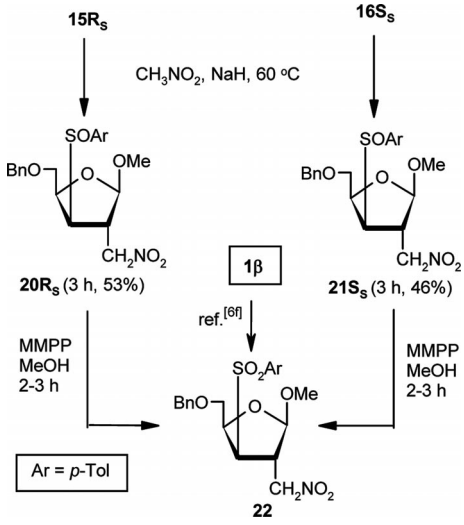
Scheme 2. Synthesis of β-anomeric vinyl sulfoxide-modified pent-2-enofuranosides.

Reactions of α and β-Anomeric Vinyl Sulfoxide-Modified Pent-2-enofuranosides with Nitromethane

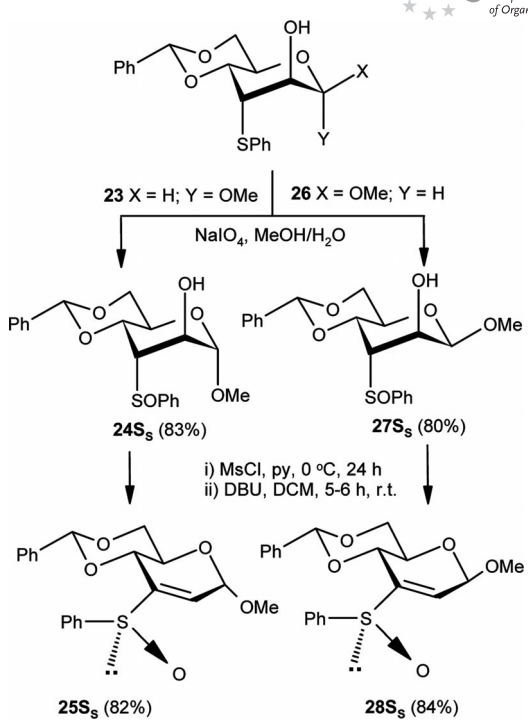
Compounds **8**R_S and **9**S_S were separately treated with nitromethane in the presence of sodium hydride to afford branched-chain sugars **17**R_S and **18**S_S, respectively. Oxidation of **17**R_S and **18**S_S afforded **19**, which was also obtained by reaction of vinyl sulfone **1α** with nitromethane[6f] under similar conditions (Scheme 3). The sodium salt of nitromethane was also treated with the β-anomeric vinyl sulfoxide-modified carbohydrates **15**R_S and **16**S_S to generate compounds **20**R_S and **21**S_S, respectively. Oxidation of **20**R_S and **21**S_S afforded **22**, which was also obtained by reaction of vinyl sulfone **1β** with nitromethane[6f] under similar conditions (Scheme 4).



Scheme 3. Reactions of α-anomeric vinyl sulfoxide-modified pent-2-enofuranosides with nitromethane.



Scheme 4. Reactions of β-anomeric vinyl sulfoxide-modified pent-2-enofuranosides with nitromethane.



Scheme 5. Synthesis of α,β-anomeric vinyl sulfoxide-modified hex-2-enopyranosides.

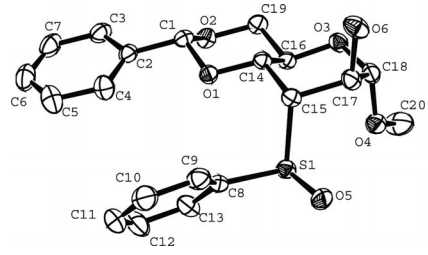


Figure 2. Crystal structure of compound **24*S*$_S$**.

Synthesis of α and β-Anomeric Vinyl Sulfoxide-Modified Hex-2-enopyranoside

Benzylidene protected α-anomeric sulfide **23**[9] (Scheme 5) was oxidized by using $NaIO_4$/MeOH/H_2O to afford, after purification, a single sulfoxide derivative **24*S*$_S$**. The hydroxyl group of **24*S*$_S$** was mesylated and the mesylated compound was treated with DBU in dichloromethane to afford a single compound **25*S*$_S$** (Scheme 5).

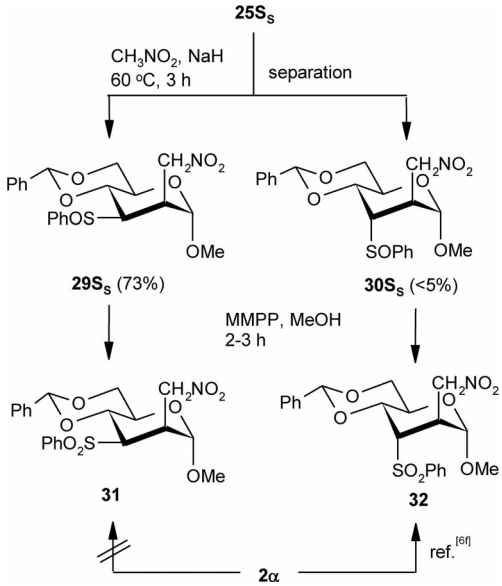
The structures of **24*S*$_S$** (Figure 2) and **25*S*$_S$** (see the Supporting Information) were unambiguously confirmed by X-ray analysis of their single crystals.

In the same way, β-anomeric sulfide **26** was converted into a single compound **28*S*$_S$** through intermediate **27*S*$_S$**. The chemical shift of the olefinic proton (δ = 6.52 ppm) of **25*S*$_S$** is comparable with that of **28*S*$_S$** (δ = 6.51 ppm). However, the structure of **28*S*$_S$** was established in an indirect way from X-ray analysis of a single crystal of one of its products (see below). It was clear from the analysis of the analytical data that both of the anomers afforded only one sulfur epimer.

Reactions of α and β-Anomeric Vinyl Sulfoxide-Modified Hex-2-enopyranosides with Nitromethane

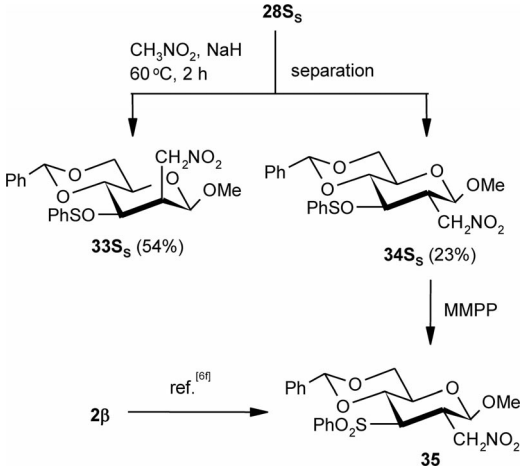
Compound **25*S*$_S$** was treated with nitromethane in the presence of sodium hydride to afford **29*S*$_S$** as the major compound. To unambiguously identify the configurations at C2 and C3 of **29*S*$_S$** it was oxidized to afford **31**; the latter compound differed from **32**, the addition product obtained from the reactions of **2α** with nitromethane.[6f] The stereochemistry of compound **31** was established on the basis of its single crystal X-ray crystal structure. Another isomer, obtained in less than 5% yield from the same reaction, was identified as **30*S*s** (Scheme 6) after oxidation to the known analogue **32**[6f] (mixed ^{1}H NMR spectroscopic analysis).

On the other hand, **28S$_S$** reacted similarly with nitromethane in the presence of sodium hydride to generate compounds **33*S*$_S$** and **34*S*$_S$** (Scheme 7). The oxidation product **35** of the minor compound **34*S*s** was identical (mixed ^{1}H NMR spectroscopic analysis) to the nitromethane adduct of **2β**.[6f] Structure of compound **33*S*$_S$** was confirmed by X-ray diffraction analysis of the single crystal.



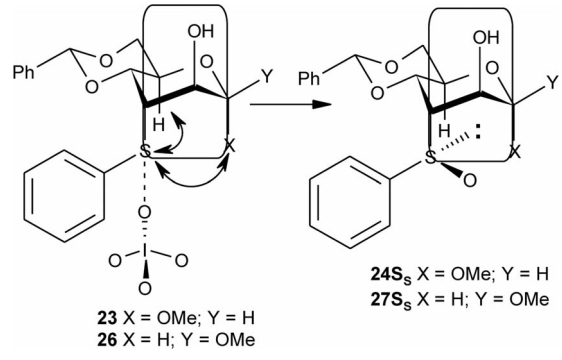
Scheme 6. Reactions of α-anomeric vinyl sulfoxide-modified hex-2-enopyranosides with nitromethane.

As mentioned above, the configuration of the sulfur center of **28*S*$_S$** was also indirectly confirmed from the crystal structure of **33*S*$_S$**.



Scheme 7. Reactions of β-anomeric vinyl sulfoxide-modified hex-2-enopyranosides with nitromethane.

We presume that the conformationally preferred orientation of the phenyl moiety of the of Ph–S group in compounds **23** and **26** are comparable to the orientation of the methyl group of cyclohexyl methyl ether; in the latter case, the methyl group in the chair conformer of the molecule is known to move away from the six-membered ring to accommodate the 1,3-diaxial interactions.[11] This is also evident from the orientation of the thiophenyl group in the crystal structure of the sulfoxide **24*S*$_S$** (Figure 2) and other pyranosyl compounds. DFT computations established that sulfides are oxidized mainly with IO_4^- under normal experimental conditions. During the process, oxygen atoms of the periodates attack the sulfides in a direction perpendicular to the plane of the C–S–C atoms, and the S···O···I atoms are in a linear arrangement in the very early transition state.[12] We presume that in such a scenario IO_4^- would also approach the sulfur atom of the PhS group from a direction perpendicular to the planes comprised of –S–C3–C1–O– (methoxy oxygen) for the α-anomer **23** and –S–C3–C1–H– for the β-anomer **26**, affording only S_S stereoisomers in both cases (Scheme 8). Such a positioning of the phenyl group of SPh is not possible in the case of furanosides **3** or **10** because of the pseudoaxial and pseudoequatorial nature of bonds in five-membered rings and, therefore, there is no selectivity in the approach of IO_4^- towards the sulfur. It is also evident from the reaction patterns of vinyl sulfoxide-modified furanosides **3** or **10** that the directing effect of the anomeric methoxy group dominated over the same of sulfoxides, which resulted in the formation of *arabino*- and *xylo*-analogues **17*R*$_S$/18*S*$_S$** and **20*R*$_S$/21*S*$_S$**, respectively, as expected (Schemes 3 and 4). The dominance of the α-anomeric methoxy group over the directing effect of sulfoxide is also evident in the addition of the carbon nucleophile from the β-face of pyranosides **25*S*$_S$** (Scheme 6). However, in contrast to the formation of **32** from **2*α***,[6f] it is plausible that the stereoelectronic repulsion between sulfoxide and methoxy groups forced the sulfoxide group to occupy the equatorial position, affording **29*S*$_S$** as the major product (Scheme 6). With the exception of the minor product **30*S*$_S$**, all other pyranosyl sulfoxide adducts **29*S*$_S$**, **33*S*$_S$**, and **34*S*$_S$** have their sulfoxide groups in equatorial positions, presumably to avoid stereoelectronic interactions. It was reported earlier that vinyl sulfone **2β** reacted with either carbon or nitrogen nucleophiles to exclusively produce *gluco*-analogues in which all functional groups at C1–C5 occupy equatorial positions.[6a,6f] Although the formation of **34*S*$_S$** followed the same trend, the delivery of the carbanion from the β-face of **28*S*$_S$** affording **33*S*$_S$** is probably the sole example of the directing effect of sulfoxide among the vinyl sulfones-modified carbohydrates reported in this study.



Scheme 8. Plausible mode of attack of IO_4^- for the diastereoselective oxidation of the sulfur atoms of **23** and **26**.

Conclusions

In the case of furanosyl systems, the sugar component did not have any influence on the oxidation of sulfides to

sulfoxides. The chirality of the sulfoxide group did not have much influence on the reaction patterns of vinyl sulfoxide-modified pent-2-enofuranosides. On the other hand, the pyranosyl moiety contributed to the selective formation of only one of the diastereomers during oxidation, and vinyl sulfoxide-modified hex-2-enopyranosides significantly influenced the outcome of carbon nucleophile addition to these Michael acceptors. The formation of compound **29*S*$_S$** indicated the influence the sulfoxide has on the protonation pattern of the C-3 carbanion generated after the addition of nitromethane nucleophile at C-2 of **25*S*$_S$** (Scheme 6). The formation of **33*S*$_S$** was unexpected because no such compound was obtained when vinyl sulfone **2β** was treated with nitromethane under similar conditions (Scheme 7). We have therefore been successful in identifying the directing effect of sulfoxide in the case of vinyl sulfoxide-modified carbohydrates. Research is in progress on the usefulness of some of these vinyl sulfoxide-modified carbohydrates as Michael acceptors, partners in Diels–Alder reactions, and as chiral auxiliaries.

Experimental Section

General Methods: Reactions were conducted either under a nitrogen atmosphere or in open air. Carbohydrates and other fine chemicals were obtained from commercial suppliers and were used without purification. Solvents were dried and distilled following the standard procedures. TLC was carried out on precoated silica gel plates and the spots were visualized either with UV light or by charring the plate dipped in 5% H_2SO_4/MeOH solution. Column chromatography was performed on silica gel (230–400 mesh). ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, using $CDCl_3$ as the solvent. DEPT experiments were carried out to identify the methylene carbons. Optical rotations were recorded at 589 nm.

General Procedure for the Synthesis of Sulfoxides: To a well-stirred solution of sulfide (1 equiv.) in MeOH (10 mL/mmol) was added $NaIO_4$ (1.2 eq/mmol) in H_2O (5 mL/mmol), and the mixture was stirred for 4–6 h at room temperature. The mixture was then evaporated to dryness under reduced pressure and the residue was partitioned between aqueous saturated $NaHCO_3$ and EtOAc (3× 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to give a residue, which was purified over silica gel to afford the required sulfoxide.

General Procedure for the Synthesis of Mesylated Compounds: To a well-stirred solution of sulfoxide (1 equiv.) in pyridine (5 mL/mmol) was added methanesulfonyl chloride (4 equiv.) in pyridine (1 mL/mmol of MsCl) dropwise at 0 °C under N_2. After completion of the addition, the reaction mixture was kept at +4 °C for 24 h (reaction monitored by TLC analysis). The reaction mixture was poured into aqueous saturated $NaHCO_3$ and the product was extracted with EtOAc (3× 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to give a residue, which was purified over silica gel to afford the title compound.

General Procedure for the Synthesis of Pentosyl and Hexosyl Vinyl Sulfoxides: The mesylated compound (1 equiv.) was treated with DBU (2 equiv./mmol) in anhydrous CH_2Cl_2 (10 mL/mmol) at ambient temperature for 5–6 h. The solvent was evaporated under reduced pressure and the resulting residue was purified over silica gel to afford pentosyl and hexosyl vinyl sulfoxide.

General Procedure for the Synthesis of Sulfones from Sulfoxides: To a well-stirred solution of sulfoxide (1 equiv.) in anhydrous MeOH (10 mL/mmol) was added magnesium monoperoxyphthalate hexahydrate (1.2 equiv./mmol), and the mixture was stirred at room temperature under N_2. After 2–3 h, the mixture was evaporated to dryness under reduced pressure and the residue was dissolved in aqueous saturated $NaHCO_3$. The aqueous layer was washed with EtOAc (3× 10 mL) and the combined organic layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to give a residue that was purified over silica gel to afford sulfones in 40–62% yields.

Compound 4*R*$_S$ and 6*S*$_S$: Compound **3** (2 g, 5.56 mmol) was converted into sulfoxides **4*R*$_S$** and **6*S*s** by following the general procedure described above and the products were separated by column chromatography.

Compound 4*R*$_S$: Yield 1.05 g (50%); $[\alpha]_D^{26}$ = –1.01 (*c* = 0.30, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 2.42 (s, 3 H), 3.14 (d, *J* = 2.8 Hz, 1 H), 3.39 (s, 3 H), 3.55 (dd, *J* = 1.6, 10.4 Hz, 1 H), 3.66 (d, *J* = 11.6 Hz, 1 H), 3.86–3.91 (m, 2 H), 4.59 (dd, *J* = 11.6, 28.8 Hz, 2 H), 4.86 (s, 2 H), 7.26–7.36 (m, 7 H), 7.59 (d, *J* = 8.4 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.4, 54.4, 71.1 (CH_2), 73.4, 73.7 (CH_2), 75.6, 78.3, 108.7, 125.1, 127.9, 128.1, 128.6, 130.1, 136.6, 139.7, 142.4 ppm; HRMS (ESI+): calcd for $C_{20}H_{24}O_5SNa$ [M + Na]$^+$ 399.1242; found 399.1234.

Compound 6*S*$_S$: Yield 0.83 g (40%); $[\alpha]_D^{26}$ = +186.28 (*c* = 0.20, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 2.38 (s, 3 H), 2.61 (d, *J* = 10.4 Hz, 1 H), 3.26–3.27 (m, 1 H), 3.37–3.40 (m, 4 H), 3.54 (d, *J* = 10.0 Hz, 1 H), 3.89 (s, 1 H), 4.34 (d, *J* = 12 Hz, 1 H), 4.63 (d, *J* = 10.0 Hz, 1 H), 4.98 (s, 1 H), 7.19–7.34 (m, 7 H), 7.51 (d, *J* = 7.6 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.5, 54.8, 69.2 (CH_2), 73.0, 73.4 (CH_2), 75.3, 76.2, 109.6, 125.1, 127.9 (2× C), 128.5, 130.1, 136.8, 139.9, 142.6 ppm; HRMS (ESI+): calcd for $C_{20}H_{24}O_5SNa$ [M + Na]$^+$ 399.1242; found 399.1248.

Compound 8*R*$_S$: Compound **4*R*$_S$** (0.75 g, 1.99 mmol) was converted into **5*R*$_S$** by following the general procedure described above. Compound **5*R*s** (0.385 g, 0.85 mmol) was directly converted into **8*R*$_S$** (0.255 g, 84%) by following the general procedure described above. $[\alpha]_D^{26}$ = –97.14 (*c* = 0.06, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 2.38 (s, 3 H), 3.35 (s, 3 H), 3.46–3.50 (m, 1 H), 3.56–3.59 (m, 1 H), 4.47–4.57 (m, 3 H), 5.88 (d, *J* = 3.6 Hz, 1 H), 6.53 (s, 1 H), 7.22–7.39 (m, 7 H), 7.46 (d, *J* = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.4, 54.2, 71.1 (CH_2), 73.6 (CH_2), 82.2, 107.9, 125.9, 127.9, 128.0, 128.4, 128.7, 130.2, 137.3, 138.5, 142.6, 153.8 ppm; HRMS (ESI+): calcd for $C_{20}H_{22}O_4SNa$ [M + Na]$^+$ 381.1137; found 381.1131.

Compound 9*S*$_S$: Compound **6*S*$_S$** (0.63 g, 1.68 mmol) was converted into **7*S*$_S$** by following the general procedure described above. Compound **7*S*$_S$** (0.645 g, 1.42 mmol) was directly converted into **9*S*$_S$** (0.391 g, 77%) by following the general procedure described above. $[\alpha]_D^{26}$ = +57.86 (*c* = 0.34, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 2.41 (s, 3 H), 3.35 (s, 3 H), 3.51–3.55 (m, 1 H), 3.76 (dd, *J* = 2.4, 10.4 Hz, 1 H), 4.49 (dd, *J* = 12.0, 28.8 Hz, 2 H), 4.94–4.97 (m, 1 H), 5.87 (d, *J* = 4.0 Hz, 1 H), 6.36 (s, 1 H), 7.26–7.35 (m, 7 H), 7.49 (d, *J* = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.4, 54.5, 70.9 (CH_2), 73.2 (CH_2), 83.5, 107.6, 124.8, 127.5, 127.6, 128.2, 130.1, 133.0, 137.9, 139.0, 142.1, 149.4 ppm; HRMS (ESI+): calcd for $C_{20}H_{22}O_4SNa$ [M + Na]$^+$ 381.1137; found 381.1145.

Compounds 11R$_S$ and 13S$_S$: Compound **10** (1.0 g, 2.78 mmol) was converted into sulfoxides by following the general procedure described above.

Compound 11R_S: Yield 0.57 g (55%); $[\alpha]_D^{26}$ = –100.84 (c = 0.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H), 2.93 (s, 1 H), 3.42 (s, 3 H), 3.45–3.47 (m, 1 H), 3.61–3.65 (m, 1 H), 3.79 (t, J = 8.4 Hz, 1 H), 4.28 (q, J = 5.6, 12.4 Hz, 1 H), 4.54 (d, J = 11.2 Hz, 1 H), 4.62 (d, J = 11.2 Hz, 1 H), 4.84 (d, J = 8.0 Hz, 1 H), 4.88 (s, 1 H), 7.24–7.37 (m, 7 H), 7.53 (d, J = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.4, 56.0, 70.3 (CH_2), 71.7, 73.6 (CH_2), 76.7, 77.4, 109.9, 124.8, 127.9, 128.1, 128.4, 130.0, 137.4, 140.2, 142.0 ppm; HRMS (ESI+): calcd for $C_{20}H_{24}O_5SNa$ [M + Na]$^+$ 399.1242; found 399.1234.

Compound 13S_S: Compound **10** (1.0 g, 2.78 mmol) was converted into **13S_S** (0.42 g, 40%) by following the general procedure described above. $[\alpha]_D^{26}$ = +58.86 (c = 0.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 1.39 (s, 1 H), 2.42 (s, 3 H), 3.35–3.38 (m, 1 H), 3.41 (s, 3 H), 3.86 (s, 1 H), 3.97–4.02 (m, 1 H), 4.12 (dd, J = 2.8, 10.4 Hz, 1 H), 4.68 (d, J = 1.6 Hz, 2 H), 4.79–4.80 (m, 2 H), 7.26–7.43 (m, 7 H), 7.61 (d, J = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.5, 55.3, 70.2 (CH_2), 73.4 (CH_2), 74.0, 76.5, 79.4, 108.9, 125.6, 127.6, 127.8, 128.3, 130.0, 130.2, 138.0, 138.9, 142.6 ppm; HRMS (ESI+): calcd for $C_{20}H_{24}O_5SNa$ [M + Na]$^+$ 399.1242; found 399.1241.

Compound 15R_S: Compound **11R_S** (1.19 g, 3.16 mmol) was converted into **12R_S** by following the general procedure described above. Compound **12R_S** (1.30 g, 2.86 mmol) was directly converted into **15R_S** (0.865 g, 84%) by following the general procedure described above. $[\alpha]_D^{26}$ = –188.43 (c = 0.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3 H), 3.41 (s, 3 H), 3.52–3.56 (m, 1 H), 3.61–3.64 (m, 1 H), 4.39 (t, J = 6.0 Hz, 1 H), 4.53 (dd, J = 11.6, 19.6 Hz, 2 H), 5.73 (s, 1 H), 6.53 (s, 1 H), 7.22–7.39 (m, 7 H), 7.43 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.4, 54.9, 72.6 (CH_2), 73.6 (CH_2), 82.3, 108.4, 125.6, 127.9, 128.0, 128.4, 128.8, 130.1, 137.4, 138.8, 142.4, 154.2 ppm. HRMS (ESI+): calcd for $C_{20}H_{22}O_4SNa$ [M + Na]$^+$ 381.1137; found 381.1138.

Compound 16S_S: Compound **13S_S** (0.56 g, 1.49 mmol) was converted into **14S_S** by following the general procedure described above. Compound **14S_S** (0.50 g, 1.10 mmol) was directly converted into **16S_S** (0.331 g, 84%) by following the general procedure described above. $[\alpha]_D^{26}$ = +93.69 (c = 0.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 2.41 (s, 3 H), 3.41 (s, 3 H), 3.49–3.53 (m, 1 H), 3.69 (dd, J = 3.2, 10.4 Hz, 1 H), 4.48 (dd, J = 12.0, 18.4 Hz, 2 H), 4.88–4.90 (m, 1 H), 5.69 (s, 1 H), 6.25 (s, 1 H), 7.26–7.35 (m, 7 H), 7.50 (s, J = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.4, 55.1, 72.5 (CH_2), 73.2 (CH_2), 83.3, 107.7, 125.1, 127.5, 127.6, 128.2, 130.1, 132.0, 137.9, 138.5, 142.4, 150.5 ppm; HRMS (ESI+): calcd for $C_{20}H_{22}O_4SNa$ [M + Na]$^+$ 381.1137; found 381.1120.

General Procedure for Nitromethane Addition: To a well-stirred solution of NaH (8 equiv.) in DMF (5 mL/mmol) or 1,4-dioxane (5 mL/mmol) was added nitromethane (11 equiv.) and the mixture was stirred for 0.5 h at ambient temperature under an inert atmosphere. The appropriate vinyl sulfone-modified carbohydrate (1 equiv.) was added and the mixture was stirred for 2–3 h at 50–60 °C. The reaction mixture was then partitioned between aqueous saturated $NaHCO_3$ and EtOAc (3 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to give a residue that was purified over silica gel to afford the title compound.

Compound 17R_S: Compound **8R_S** (0.50 g, 1.39 mmol) was converted into **17R_S** (0.41 g, 69%) by following the general procedure described above. $[\alpha]_D^{26}$ = –32.99 (c = 0.09, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 2.43 (s, 3 H), 2.71–2.75 (m, 1 H), 3.04–3.06 (m, 1 H), 3.39 (s, 3 H), 3.42–3.45 (m, 1 H), 3.82–3.89 (m, 2 H), 4.29–4.35 (m, 1 H), 4.49 (d, J = 12 Hz, 1 H), 4.57 (d, J = 11.6 Hz, 1 H), 4.74–4.75 (m, 1 H), 4.88 (s, 1 H), 7.26–7.38 (m, 7 H), 7.56 (d, J = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.5, 46.0, 54.8, 66.3, 70.4 (CH_2), 73.6 (CH_2), 74.5 (CH_2), 78.4, 105.6, 124.9, 127.8 (2× C), 128.4, 130.2, 137.5, 139.2, 142.8 ppm; HRMS (ESI+): calcd for $C_{21}H_{25}O_6NSNa$ [M + Na]$^+$ 442.1300; found 442.1307.

Compound 18S_S: Compound **9S_S** (0.40 g, 1.11 mmol) was converted into **18S_S** (0.26 g, 55%) by following the general procedure described above. $[\alpha]_D^{26}$ = +210.51 (c = 0.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H), 2.76 (dd, J = 3.2, 10.8 Hz, 1 H), 3.03–3.06 (m, 1 H), 3.39 (s, 3 H), 3.41–3.45 (m, 1 H), 3.49–3.54 (m, 1 H), 4.06–4.07 (m, 1 H), 4.13 (dd, J = 4.8, 13.6 Hz, 1 H), 4.26–4.33 (m, 2 H), 4.52 (d, J = 12.0 Hz, 1 H), 5.01 (s, 1 H), 7.21–7.26 (m, 4 H), 7.31–7.38 (m, 3 H), 7.48 (d, J = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.4, 44.5, 55.1, 66.7, 68.3 (CH_2), 73.4 (CH_2), 75.2 (CH_2), 76.1, 106.3, 124.6, 127.8, 127.9, 128.5, 130.2, 137.2, 139.1, 142.7 ppm; HRMS (ESI+): calcd for $C_{21}H_{25}NO_6SNa$ [M + Na]$^+$ 442.1300; found 442.1302.

Compound 20R_S: Compound **15R_S** (0.50 g, 1.39 mmol) was converted into **20R_S** (0.30 g, 53%) by following the general procedure described above. $[\alpha]_D^{26}$ = –132.81 (c = 0.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3 H), 2.75–2.79 (m, 1 H), 3.04 (dd, J = 2.8, 10.4 Hz, 1 H), 3.38 (s, 4 H), 3.44–3.47 (m, 1 H), 4.19 (d, J = 12 Hz, 1 H), 4.36 (d, J = 12 Hz, 1 H), 4.51–4.52 (m, 1 H), 4.68–4.74 (m, 1 H), 4.88 (d, J = 4.0 Hz, 1 H), 5.10–5.16 (m, 1 H), 7.05–7.35 (m, 9 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.3, 46.1, 56.1, 63.3, 71.8 (CH_2), 72.4 (CH_2), 72.9 (CH_2), 73.0, 105.0, 123.8, 127.5, 127.6, 128.3, 130.0, 136.7, 137.7, 141.7 ppm; HRMS (ESI+): calcd for $C_{21}H_{25}NO_6SNa$ [M + Na]$^+$ 442.1300; found 442.1309.

Compound 21S_S: Compound **16S_S** (0.45 g, 1.25 mmol) was converted into **21S_S** (0.24 g, 46%) by following the general procedure described above. $[\alpha]_D^{26}$ = +1.23 (c = 0.13, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 2.44 (s, 3 H), 2.50–2.53 (m, 1 H), 3.17–3.20 (m, 1 H), 3.40 (s, 3 H), 3.60 (dd, J = 5.6, 13.2 Hz, 1 H), 3.91–4.00 (m, 1 H), 4.04–4.08 (m, 1 H), 4.26 (dd, J = 2.8, 10.4 Hz, 1 H), 4.69–4.73 (m, 3 H), 4.84 (d, J = 2.0 Hz, 1 H), 7.26–7.42 (m, 7 H), 7.62 (d, J = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.5, 46.3, 55.5, 69.3, 70.0 (CH_2), 73.6 (CH_2), 74.1 (CH_2), 79.6, 106.0, 125.6, 127.7, 127.9, 128.4, 130.4, 137.9, 138.8, 143.3 ppm; HRMS (ESI+): calcd for $C_{21}H_{25}NO_6SNa$ [M + Na]$^+$ 442.1300; found 442.1317.

Compound 24S_S: Compound **23** (2.0 g, 5.15 mmol) was converted into **24S_S** (1.73 g, 83%) by following the general procedure described above. $[\alpha]_D^{26}$ = +192.56 (c = 0.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 3.54 (s, 3 H), 3.74–3.80 (m, 1 H), 3.89 (s, 1 H), 4.33–4.38 (m, 3 H), 4.49 (d, J = 5.6 Hz, 1 H), 4.74–4.75 (m, 1 H), 4.80 (s, 1 H), 5.32 (s, 1 H), 7.00 (d, J = 7.2 Hz, 2 H), 7.19–7.37 (m, 6 H), 7.69 (d, J = 7.6 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 55.1, 61.0, 66.0, 66.4, 69.2 (CH_2), 75.0, 101.0, 101.7, 125.9, 126.9, 127.8, 131.3, 136.5, 145.2 ppm; HRMS (ESI+): calcd for $C_{20}H_{23}O_6S$ [M + H]$^+$ 391.1365; found 391.1323.

Compound 25S_S: Compound **24S_S** (0.64 g, 1.64 mmol) was mesylated by following the general procedure. The crude mesylate was converted into vinyl sulfoxide **25S_S** (0.50 g, 82%) by following the general procedure described above. $[\alpha]_D^{26}$ = +77.08 (c = 0.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 3.49 (s, 3 H), 3.67–3.74 (m, 2 H), 4.00–4.06 (m, 1 H), 4.29–4.32 (m, 1 H), 5.07 (s, 1 H), 5.29 (s, 1 H), 6.52–6.53 (m, 1 H), 7.41–7.52 (m, 8 H), 7.52–7.67 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 56.3, 63.8, 69.1 (CH_2), 74.3, 96.8, 101.8, 124.7, 125.3, 126.6, 128.4, 129.3 (2× C), 131.7, 136.7, 142.2, 147.2 ppm; HRMS (ESI+): calcd for $C_{20}H_{21}O_5S$ [M + H]$^+$ 373.1110; found 373.1073.

Compound 27S_S: Compound **26** (2.0 g, 5.15 mmol) was converted into **27S_S** (1.67 g, 80%) by following the general procedure de-

scribed above. $[\alpha]_D^{26}$ = +45.29 (*c* = 0.19, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 3.67 (s, 3 H), 3.78–3.85 (m, 2 H), 3.91–3.97 (m, 1 H), 4.01–4.03 (m, 1 H), 4.35–4.41 (m, 1 H), 4.48–4.52 (m, 1 H), 5.20 (d, *J* = 8.4 Hz, 1 H), 5.51 (s, 1 H), 5.82 (d, *J* = 10.8 Hz, 1 H), 7.40–7.47 (m, 8 H), 7.66 (d, *J* = 6.4 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 57.4, 65.3, 65.8, 69.0 (CH_2), 74.8, 76.7, 101.8, 103.3, 124.9, 126.1, 128.3, 129.3, 129.4, 131.3, 136.5, 144.4 ppm; HRMS (ESI+): calcd for $C_{20}H_{23}O_6S$ $[M + H]^+$ 391.1215; found 391.1237.

Compound 28*S*$_S$: Compound **27*S*$_S$** (1.7 g, 5.15 mmol) was mesylated by following the general procedure. The crude mesylate was converted into vinyl sulfoxide **28*S*$_S$** (1.36 g, 84%) by following the general procedure described above. $[\alpha]_D^{26}$ = –4.18 (*c* = 0.11, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 3.48 (s, 3 H), 3.74–3.79 (m, 1 H), 3.84–3.90 (m, 2 H), 4.30–4.33 (m, 1 H), 5.32 (s, 1 H), 5.49 (s, 1 H), 6.51 (s, 1 H), 7.41–7.52 (m, 8 H), 7.67–7.69 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 55.5, 68.7 (CH_2), 69.9, 74.1, 99.9, 101.7, 125.6, 125.8, 125.9, 128.4, 129.1 (2× C), 131.8, 136.6, 141.9, 147.9 ppm; HRMS (ESI+): calcd for $C_{20}H_{21}O_5S$ $[M + H]^+$ 373.1110; found 373.1120.

Compound 29*S*$_S$: Compound **25*S*$_S$** (0.20 g, 0.54 mmol) was converted into **29*S*$_S$** (0.17 g, 73%) by following the general procedure described above. $[\alpha]_D^{26}$ = +84.93 (*c* = 0.15, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 3.42 (s, 3 H), 3.51–3.54 (m, 1 H), 3.60–3.64 (m, 1 H), 3.78–3.83 (m, 1 H), 3.88–3.91 (m, 1 H), 4.12 (t, *J* = 10.4 Hz, 1 H), 4.19–4.22 (m, 1 H), 4.68 (s, 1 H), 4.73–4.80 (m, 1 H), 5.39 (dd, *J* = 2.4, 14.8 Hz, 1 H), 5.48 (s, 1 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 7.20–7.33 (m, 6 H), 7.48 (d, *J* = 7.2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 41.8, 55.2, 59.3, 64.0, 69.2 (CH_2), 71.3, 72.3 (CH_2), 98.8, 101.6, 124.2, 126.1, 127.8, 128.7, 128.9, 130.2, 136.3, 141.84 ppm; HRMS (ESI+): calcd for $C_{21}H_{24}NO_7S$ $[M + H]^+$ 434.1273; found 434.1249.

Compound 31: Compound **29*S*$_S$** (0.10 g, 0.24 mmol) was converted into **31** (0.06 g, 62%) by oxidation by following the general procedure. ^1H NMR ($CDCl_3$): δ = 3.36 (s, 3 H), 3.51–3.62 (m, 1 H), 3.75–3.78 (m, 2 H), 3.92–3.94 (m, 2 H), 4.15–4.18 (m, 1 H), 4.68–4.74 (m, 2 H), 5.12–5.23 (m, 1 H), 5.51 (s, 1 H), 7.05–7.44 (m, 8 H), 7.71 (d, *J* = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 38.8, 55.6, 60.5, 64.3, 69.2 (CH_2), 72.3 (CH_2), 75.4, 99.3, 102.6, 126.5, 128.3, 128.9, 129.1, 129.6, 133.9, 136.3, 140.9 ppm; $C_{21}H_{23}NO_8S$ (449.47): calcd. C 56.12, H 5.16, N 3.12; found C 56.33, H 4.98, N 3.20.

Compound 33*S*$_S$: Compound **28*S*$_S$** (0.20 g, 0.54 mmol) was converted into **33*S*$_S$** (0.126 g, 54%) by following the general procedure described above. ^1H NMR ($CDCl_3$): δ = 3.28 (dd, *J* = 5.2, 10.8 Hz, 1 H), 3.46 (s, 3 H), 3.48–3.54 (m, 1 H), 3.79–3.87 (m, 2 H), 4.07 (t, *J* = 10 Hz, 1 H), 4.28 (dd, *J* = 4.8, 10.8 Hz, 1 H), 4.65–4.66 (m, 1 H), 4.91 (dd, *J* = 8, 15.2 Hz, 1 H), 5.10–5.14 (m, 1 H), 5.50 (s, 1 H), 6.98 (d, *J* = 7.2 Hz, 2 H), 7.21–7.36 (m, 6 H), 7.48 (d, *J* = 7.2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 41.4, 56.8, 62.4, 68.9 (CH_2), 69.0, 69.9 (CH_2), 71.6, 101.5, 102.1, 124.2, 126.1, 127.8, 128.7, 129.0, 130.4, 136.2, 141.9 ppm; $C_{21}H_{23}NO_7S$ (433.48): calcd. C 58.19, H 5.35, N 3.23; found C 58.23, H 5.48, N 3.46.

Compound 34*S*$_S$: Compound **28*S*$_S$** (0.20 g, 0.54 mmol) was converted into **34*S*$_S$** (0.054 g, 23%) by following the general procedure described above. $[\alpha]_D^{26}$ = +59.05 (*c* = 0.04, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 2.59–2.60 (m, 1 H), 3.44–3.55 (m, 2 H), 3.56 (s, 3 H), 3.78 (t, *J* = 10.4 Hz, 1 H), 4.06 (t, *J* = 9.6 Hz, 1 H), 4.28 (dd, *J* = 4.8, 10.8 Hz, 1 H), 4.63 (d, *J* = 8.4 Hz, 1 H), 5.13–5.16 (m, 2 H), 5.42 (s, 1 H), 6.95 (d, *J* = 7.2 Hz, 2 H), 7.20–7.34 (m, 6 H), 7.52–7.55 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$): δ = 40.7, 57.5, 60.8, 67.6, 68.8 (CH_2), 72.4, 72.9 (CH_2), 101.2, 101.9, 124.3, 125.9, 127.8, 128.9, 130.5, 136.2, 140.4 ppm; HRMS (ESI+): calcd for $C_{21}H_{24}NO_7S$ $[M + H]^+$ 434.1273; found 434.1257.

CCDC-884993 (for **24*S*s**), -885022 (for **25*S*s**), -885023 (for **31**), and -885024 (for **33*S*s**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of all new compounds and ORTEP drawings of compounds **25*S*s**, **31** and **33*S*s**.

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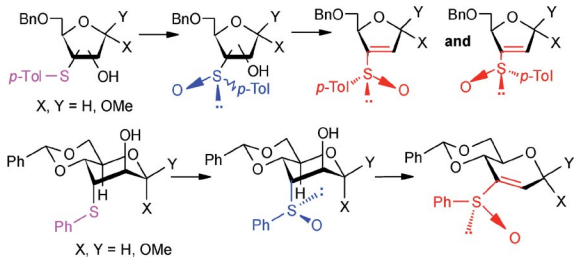

Oxidation of furanosyl sulfides to sulfoxides afforded both diastereomers. The chirality of the sulfoxide group did not greatly influence the addition patterns of vinyl sulfoxide-modified pent-2-enofuranosides. Oxidation of pyranosyl sulfide gave only one diastereomer and the modified hex-2-enopyranosides significantly influenced the outcome of carbon nucleophile addition to these Michael acceptors.

Keywords: Carbohydrates / Sulfur / Sulfoxides / Chiral auxiliaries / Diastereoselectivity / Oxidation

