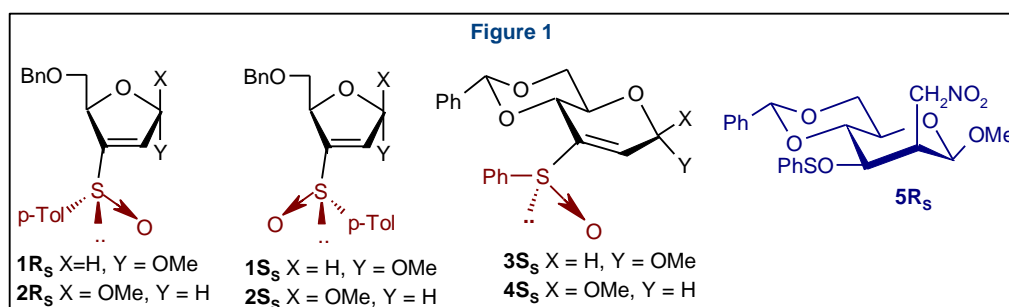


## ABSTRACT

### Syntheses and Reactivities of Vinyl Sulfoxide-Modified Carbohydrates, Vinyl Sulfone- and Vinyl Sulfoxide-Modified Tetrahydrofurans

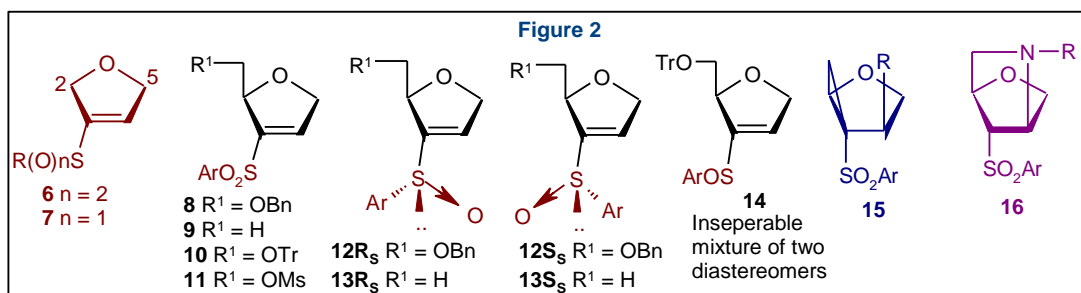
Vinyl sulfones and vinyl sulfoxides are versatile intermediates and useful building blocks in synthetic chemistry because they have the potential to undergo Michael addition reactions with various nucleophiles and also cycloaddition reactions. Additionally  $\alpha$ ,  $\beta$ -unsaturated sulfoxides are known as efficient chiral auxiliaries in asymmetric synthesis.

Attempts have been made in the past to combine the chiralities of sulfoxide sulfur and 'in-built' stereogenicity of carbohydrates to create a complex and versatile chiral controller in a stereoselective synthesis. The usefulness of vinyl sulfone-modified carbohydrates and related compounds as intermediates for the synthesis of amino sugars, branched chain sugars, carbocycles and heterocycles prompted us to look into the synthesis and reactivities of vinyl sulfoxide-modified carbohydrates. Therefore, we have synthesized  $\alpha$ - and  $\beta$ -anomeric vinyl sulfoxide modified-pent-2-enofuranosides **1R<sub>S</sub>**/**1S<sub>S</sub>** and **2R<sub>S</sub>**/**2S<sub>S</sub>** (Figure 1) respectively. We have also synthesized  $\alpha$ - and  $\beta$ -anomeric vinyl sulfoxide-modified hex-2-enopyranosides **3S<sub>S</sub>** and **4S<sub>S</sub>** (Figure 1) respectively. We have studied the reaction patterns of these Michael acceptors with various nucleophiles. From these studies it emerges that the directing effect of anomeric methoxy group dominated over that of sulfoxides, which resulted into the formation of *arabino*- and *xylo*- analogues after Michael addition of nucleophiles to **1R<sub>S</sub>**/**1S<sub>S</sub>** and **2R<sub>S</sub>**/**2S<sub>S</sub>** (Figure 1). The dominance of the  $\alpha$ -anomeric methoxy group over the directing effect of sulfoxide group is also evident in the addition of nucleophiles in case of **3S<sub>S</sub>**. The formation of **5R<sub>S</sub>** from vinyl sulfoxide **4S<sub>S</sub>** (Figure 1) is the sole example of the directing effect of sulfoxide amongst the vinyl sulfoxide-modified carbohydrates reported in this study.



## ABSTRACT

2,5-Dihydro-3-(alkyl/aryl)-sulfonyl/sulfinyl furans **6/7** (Figure 2) also represent the basic structures of a new class of cyclic Michael acceptors with high potential as synthetic intermediates. The cyclic Michael acceptors are functionalized to make them useful starting materials for the preparation of lignans, porphyrins and a wide range of synthetic intermediates. A perusal of literature reveals that the synthetic strategies for accessing these novel classes of Michael acceptors are not so straightforward. This information prompted us to synthesize vinyl sulfone- and vinyl sulfoxide-modified tetrahydrofurans **8-14** (Figure 2) from easily available carbohydrates. We also subjected these compounds to reaction with various nucleophiles. On the basis of the information gathered from these studies we concluded that even in the absence of any group at C-5,  $-\text{CH}_2\text{R}$  group at C-2 alone



was capable of imposing the diastereoselectivity in the Michael addition of nucleophiles. It was also evident that irrespective of steric bulk present at C-2 position of these vinyl sulfones or vinyl sulfoxides, nucleophiles attacked the C-4 carbon center from the  $\beta$ -face of the furan ring. The reaction patterns of various nucleophiles with vinyl sulfoxide modified tetrahydrofurans **12-14** (Figure 2) clearly prove that in these systems the stereoelectronic effects of  $-\text{CH}_2\text{R}$  ( $\text{R} = \text{OBn}, \text{H}, \text{OTr}$ ) group at C-2 and/or the thermodynamic stability of the Michael adducts suppressed the influence of sulfoxides as chiral auxiliaries. A mesylated vinyl sulfone **11** was also used as an intermediate for the synthesis of a new class of bicyclic heterocycles like **15-16** (Figure 2).

*Key words:* Vinyl Sulfone, Vinyl Sulfoxide, Carbohydrates, Tetrahydrofurans, Modified Tetrahydrofurans, Michael Addition, Chiral Auxiliary, Diastereoselectivity, Fused Bicyclic Heterocycles.