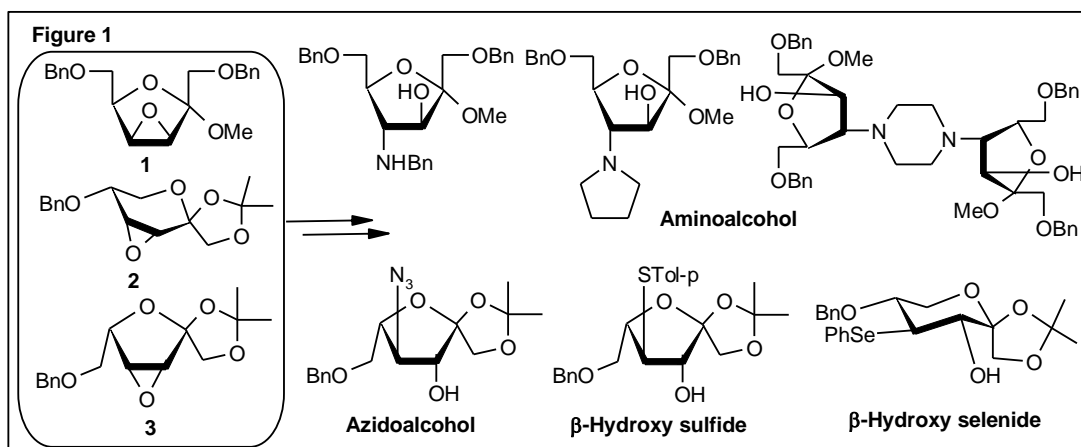


**Epoxides and Vinyl Selenones Derived from D-Fructose and L-Sorbose:
Synthesis and Synthetic Applications**

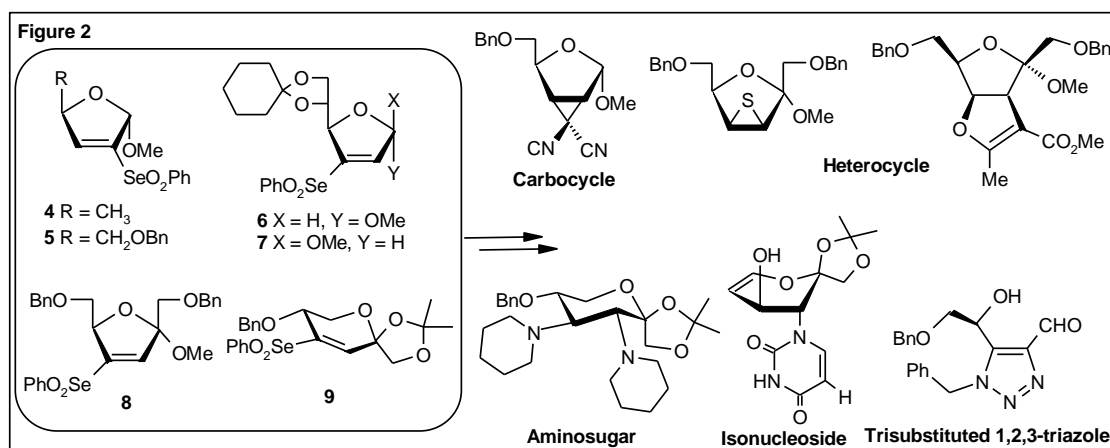
Carbohydrates are the most abundant organic compounds on earth, and represent the major portion of the annually renewable biomass. There is a need, therefore to develop appropriate methodology to convert carbohydrates into useful products, such as enantiopure building blocks for organic synthesis. Inexpensive sugars, such as D-glucose, D-ribose, D-xylose, D-galactose etc., available in large scale are widely used in chemical transformation as “chiral pool”. However, the non-food utilization of ton-scale accessible ketoses, namely D-fructose and L-sorbose are particularly modest as their chemistry is considerably complicated and less well understood. The main problem of using these ketoses sugars for organic transformation is that both the ketoses in solution exist in several cyclic and acyclic tautomeric forms. Under the circumstances, simple derivatization of partially protected D-fructose or L-sorbose usually generates a mixture of products. Consequently, there is a need to develop new methodologies for the conversion of D-fructose and L-sorbose into functionalized organic molecules.

Epoxides derived from D-glucose, D-ribose, D-xylose, D-galactose etc have been extensively opened by various nucleophiles to produce a plethora of modified sugar derivatives. We, therefore, decided to study the reaction patterns of epoxides synthesized from D-fructose and L-sorbose for the generation of a wide range of regioselectively functionalized sugar molecules. The relatively easily accessible epoxides **1**, **2** and **3** (Figure 1) were synthesized from D-fructose and L-sorbose in single isomeric forms. Reactions of these epoxides with different classes of nucleophiles afforded single diastereomeric aminoalcohols, azidoalcohols, β -hydroxy sulfides and β -hydroxy selenides (Figure 1).



It has been established in our laboratory that vinyl sulfone-modified carbohydrates react with a wide range of nucleophiles to afford a wide variety of modified sugar derivatives. However, removal of sulfone group from the products, in some cases is found to be problematic. Moreover endocyclic vinyl sulfone-modified carbohydrates were found to be less reactive with certain reagents than their terminal counterparts. We, therefore, assumed that the replacement of sulfone by selenone may solve these problems because of the great leaving ability of selenone functionality.

Thus, we initiated a study using vinyl selenones derived from D-fructose or L-sorbose where the rich chemistry of vinyl selenone and the in-built chirality of these carbohydrate molecules are expected to lead to the formation of enantiopure intermediates. As a starting point, we synthesized vinyl selenones **4-7** derived from D-xylose and D-glucose for a model study to understand the intricate chemistry of the sugar derived vinyl selenones. Applying similar synthetic strategy, vinyl selenones **8, 9** were synthesized from D-fructose (Figure 2). Surprisingly, L-sorbose, under similar reaction conditions, failed to produce vinyl selenone derivative. Although endocyclic vinyl selenones **4-7** on reactions with various organic azides afforded enantiomerically pure 1,4,5-trisubstituted 1,2,3-triazoles, the reaction did not work with vinyl selenones **8** and **9**. On the other hand, reactions of the model compound **5**, were successfully employed using **8** and **9** as the Michael acceptor for the generation of various carbocycles, heterocycles, aminosugars and isonucleosides (Figure 2).



Key words: Carbohydrates, Epoxides, Vinyl Selenones, Michael Acceptor, Enantiopure, Aminoalcohols, Azidoalcohols, Carbocycles, Heterocycles, Aminosugars, Isonucleosides, 1,2,3-triazoles.