

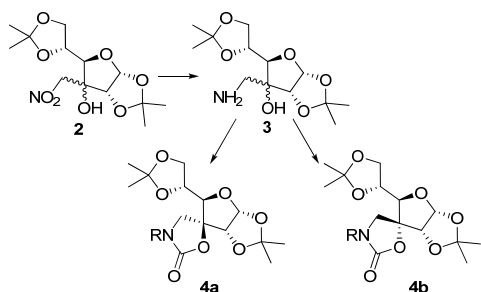
# Synthesis and Applications of Carbohydrate-based Amino Alcohols

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$\beta$ -Amino alcohol derivatives constitute a class of versatile intermediates in modern organic synthesis. Enantiomerically pure  $\beta$ -amino alcohol derivatives play an increasingly important role as chiral auxiliaries in organic synthesis [1]. Furthermore, only a few examples involve diacetone-D-glucose-based amino alcohols as chiral auxiliaries and catalysts. We report here the scalable synthesis of two diastereoisomeric series of oxazolidinone-carbohydrate conjugates with spiro-junction [3] and preliminary studies of their use as chiral auxiliaries. We also developed novel urea- and thiourea organocatalysts based on these sugar  $\beta$ -amino alcohols [2].

Commercially available diacetone-D-glucose was chosen as a convenient starting material for the preparation of *gluco*-furanose spirooxazolidinone **4a** (R = H) in seven steps with a combined yield of 36% on a 10 g scale (Scheme 1). Complementary spirooxazolidinone **4b** (R = H) with *allo*-configuration was obtained by the same general procedure.



Scheme 1. Obtaining the target compounds

To explore the scope and applicability of our approach, a small combinatorial library of novel *N*-alkyl-spirooxazolidinone derivatives was obtained with individual product yields of up to 99%.

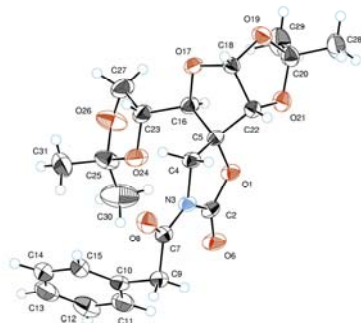


Figure 1. ORTEP representation of *N*-phenylacetyl derivative **4b** (R=Bn(O))

To study the diastereoselective alkylation at  $\alpha$ -position in resulting compounds **4a,b** (R = butyryl-, phenylacetyl-), the method of *N*-acylation with acylchlorides for both types of spirooxazolidinones was developed [4]. Relative configuration of *N*-phenylacetyl derivative with *allo*-configuration was confirmed by X-ray analysis (Figure 1). The selectivity of alkylation will be discussed.

Various molecular scaffolds have proven themselves as effective bidentate hydrogen bond donors. In this context, urea- and thiourea-derived catalysts are useful for many enantioselective transformations [5]. This fact attracted our attention to synthesize novel urea- and thiourea organocatalysts (**5**, **6**) using *allo*- and *gluco*-furanose derivatives (Figure 2).

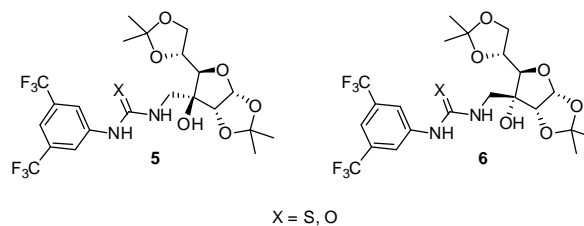


Figure 2. Novel urea- and thiourea organocatalysts using carbohydrate scaffolds

The addition of indole to *trans*- $\beta$ -nitrostyrene was used as the test reaction to explore the feasibility of the enantioselective Friedel-Crafts alkylation catalyzed by compounds **5** and **6**.

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