STEREOSELECTIVE 1,2-*CIS*-GLUCOSYLATIONS

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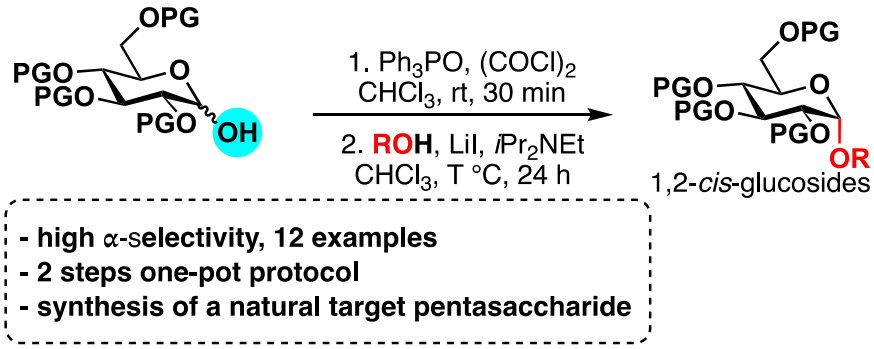
Oligosaccharide synthesis, consisting of multiple glycosylation steps, poses many difficulties with respect to regio- and stereoselectivity [1]. Depending on the reaction conditions, 1,2-*cis*- or 1,2-*trans*-glycosides can be obtained, of which the former are usually more difficult to synthesize. Previously, the McGarrigle group reported access to 1,2-*cis*-glycosides, by treatment of the glycosyl hemiacetal donor with Denton's catalytic Appel conditions [2,3], followed by reaction with LiI, *i*Pr$_2$NEt and the acceptor [4]. This procedure was successfully applied to the stereoselective synthesis of β-mannosides and β-rhamnosides.
In contrast to β-mannosides and β-rhamnosides, we will describe how glucosyl hemiacetal donors give α-glucosides under the same protocol (Scheme 1). A range of glucosyl hemiacetal donors and acceptors have been tested. Optimization studies were required to prevent unwanted elimination of the glycosyl iodide intermediate to form the corresponding glucal side product. Changing the rate of addition of base *i*Pr$_2$NEt was found to limit the formation of the side product, affording an increase in the acceptor conversion, and still with an excellent α selectivity. To demonstrate the usefulness of the method, a target pentasaccharide containing four α-linkages was also synthesized using these conditions [5].



Scheme 1. Reaction conditions for the synthesis of α-glucosides.

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