STEREOSELECTIVE GLYCOSYLATIONS

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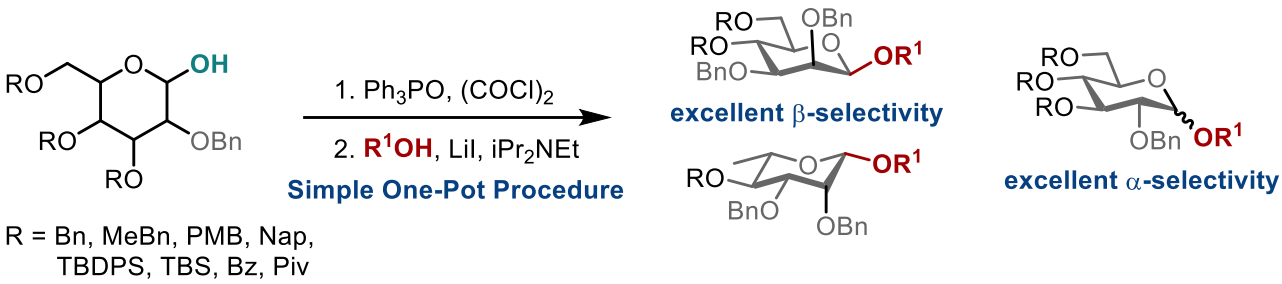
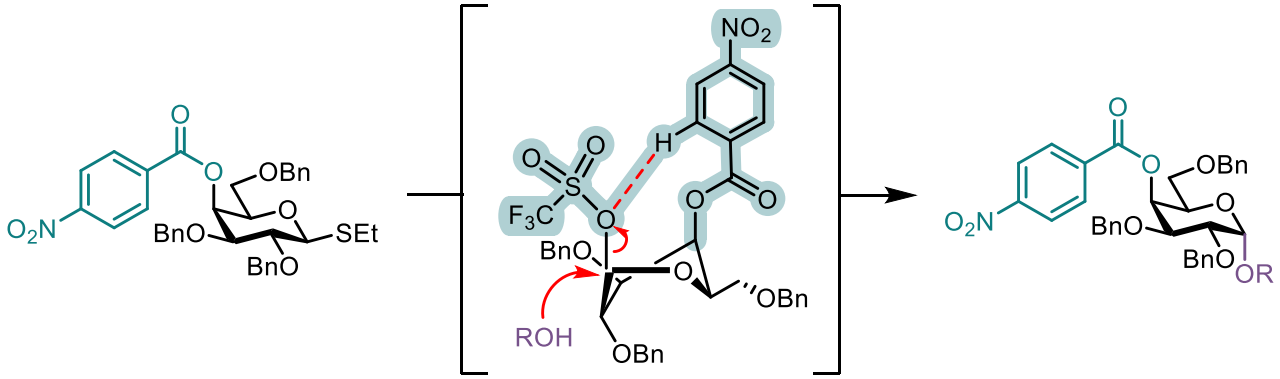
We will describe our efforts to develop stereoselective glycosylation reactions. We have adapted Denton's catalytic Appel methodology for the synthesis of glycosyl chlorides. The chlorides are first transformed *in situ* into iodides and then glycosides in a novel one-pot transformation of glycosyl hemiacetals to difficult-to-make β-mannosides and rhamnosides [1]. In contrast, the same protocol gives α-glucosides in high selectivity [2]. This selectivity switch will be discussed.

We have also investigated the role of remote substituents at the 4-position of galactosides and fucosides in influencing α/β-selectivity in glycosylations [3]. *para*-Nitrobenzoates gave high to excellent α-selectivity. The results of our mechanistic studies (experimental and computational) led us to propose that a non-classical hydrogen bond from the *ortho*-CH of benzoates to the β-triflate intermediate is important for the selectivity of the reactions of galactosides.





If time permits, results of our efforts to automate the synthesis of monosaccharide building blocks might be described.

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References:

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2. O. G. Popa, I. Pongener, D. A. Pepe, A. Chennaiah, E. M. McGarrigle *manuscript in preparation*.
3. a) K.E. Donaghy, D. A. Pepe, J. J. Ruddy, E. M. McGarrigle *manuscript submitted*; b) K.E. Donaghy, M. O'Neill, E. M. McGarrigle, *manuscript in preparation*.