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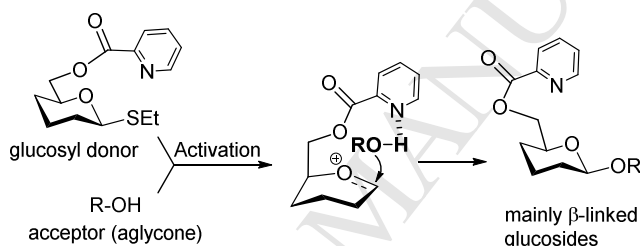
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Investigation of the H-bond-mediated aglycone delivery reaction in application to the synthesis of β -glucosides

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Abstract In an attempt to refine the H-bond-mediated Aglycone Delivery (HAD) glycosylation reaction reported herein is the synthesis of β -glucosides using an ethylthio glucoside donor equipped with the remote 6-*O*-picoloyl substituent. Upon examining various aliphatic, aromatic, and carbohydrate acceptors, it was determined that both electronic and steric factors may greatly affect the stereoselectivity of the HAD reaction with this donor.



Keywords: synthesis, stereoselectivity, glycosylation, oligosaccharides

Introduction

The chemical synthesis of glycans still faces many challenges and the biggest and most common problem is chemical glycosylation, the reaction of joining saccharide units via O-glycosidic linkages.¹⁻³ Due to the inherited mechanistic nature of this reaction, stereocontrol is often difficult to achieve.^{4,5} This results in the formation of undesired diastereomers, lowering yields and complicating purification. There are various conditions and methods currently used to control stereoselectivity.^{6,7} Among these is the hydrogen-bond-mediated aglycone delivery (HAD) method. First reported in 2012,⁸ the HAD method employs a glycosyl donor functionalized with a picoloyl (Pico) or similar moiety, a hydrogen bond accepting protecting group. This picoloyl group forms a hydrogen bond with the free hydroxyl of the glycosyl acceptor, forming an H-bonded donor-acceptor complex (Scheme 1). After addition of the promoter, the donor is activated without disrupting the H-bonded complex, and the acceptor is “delivered” to the anomeric position of the donor resulting in a facially preferential glycosidic bond formation that is *syn*-selective with respect to the picoloyl protecting group.

The HAD reaction has successfully been applied to α -glycosylation using 4-*O*-Pico donor⁸ and its utility was demonstrated by the synthesis of linear and branched α -glucans.⁹ Also mannosylation with the use of either 3- or 6-*O*-Pico donors proceeded with high β -

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