Bromodiethylsulfonium bromopentachloroantimonate (BDSB) as a novel activator for chemical glycosylation

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Abstract: Bromodiethylsulfonium bromopentachloroantimonate (BDSB) was recently reported as a novel source of highly electrophilic bromine. It was used to efficiently initiate cation-π cyclizations of polyene. Herein, chemical glycosylation of thioglycosides activated by BDSB is reported. Firstly, glycosyl donor (1), acting as electrophilic monomer, is synthesized over three steps. Commercially available β-D-glucose pentaacetate is subjected to anomeric displacement with thiol and protecting group manipulations to provide thioglycoside (1) in 26% overall yield. Next, synthesis of glycosyl acceptor (2) is accomplished in 50% overall yield. Methyl-α-D-glucopyranoside is selectively protected as benzyl ether at C2, C3, and C4 hydroxyl groups in three steps, leaving primary C6 hydroxyl as nucleophilic moiety. Finally, chemical glycosylation between glycosyl donor (1) and acceptor (2) activated by BDSB is examined. Several reaction conditions and parameters are investigated. It is found that treatment of reaction mixture with 1.5 equivalents of electrophilic BDSB in acetonitrile at −35 ºC to room temperature gives the desired O-linked disaccharide (3) in moderate yield and selectivity, 49% and 1:5 (α:β). However, applying BDSB in combination with stoichiometric silver triflate (AgOTf) provides the disaccharide (3) in 79% yield and exclusive β selectivity without using neighboring participation group at C2. Further mechanistic study of this novel BDSB activation and scope of substrates are in progress.

Keywords: Bromodiethylsulfonium bromopentachloroantimonate; Glycosylation; Thioglycosides