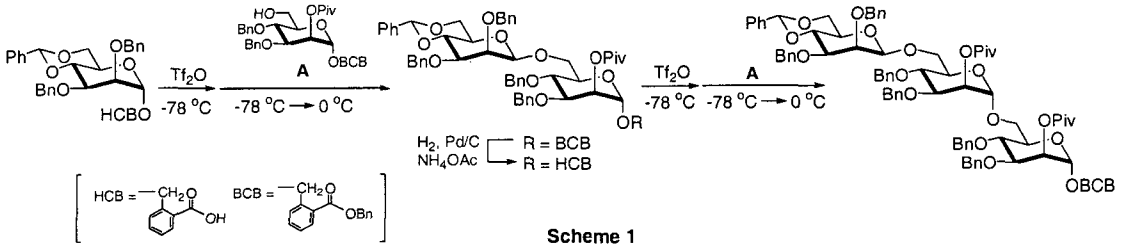
[S4-3] [4/19/2002(Friday) 10:50-11:15/Hall B]

Oligosaccharide Synthesis with Novel HCB Glycosides and Related Glycosyl Donors

Kwan Soo Kim,* Yong Joo Lee, Jin Park, Jin Hwan Kim, Yong Sung Seo, and Sung-Soo Kang

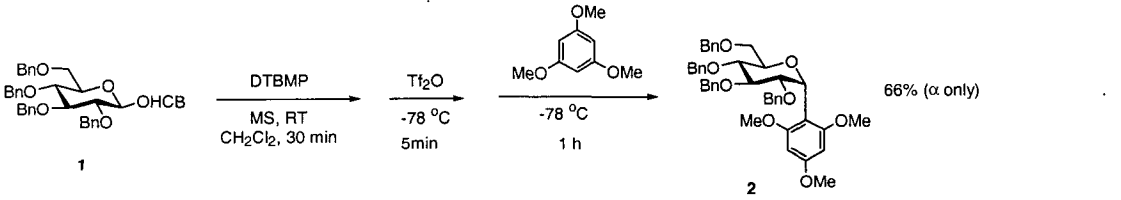
Department of Chemistry, Yonsei University, Seoul 1220-749, Korea

Oligosaccharides have been recognized as mediators of complex cellular events.[1] The procurement of sufficient quantities of chemically defined oligosaccharides is essential for the study of their detailed biological functions and for the development of oligosaccharide-based anticancer vaccines and drugs. However, it is difficult to obtain pure, structurally defined oligosaccharides from biological sources because the biosynthetic pathway for oligosaccharides affords significant product microheterogeneity.[2] A great deal of effort has been devoted to the development of efficient and stereoselective glycosylation methodologies for the construction of complex oligosaccharides.[3,4] Devising new glycosyl donors and developing new activating systems for existing donors have led to major advances in this field. We have previously reported 2-(hydroxycarbonyl)benzyl (HCB) glycosides as a novel type of glycosyl donors for highly efficient β-mannopyranosylation and oligosaccharide synthesis by latent-active glycosylation (Scheme 1).[5]



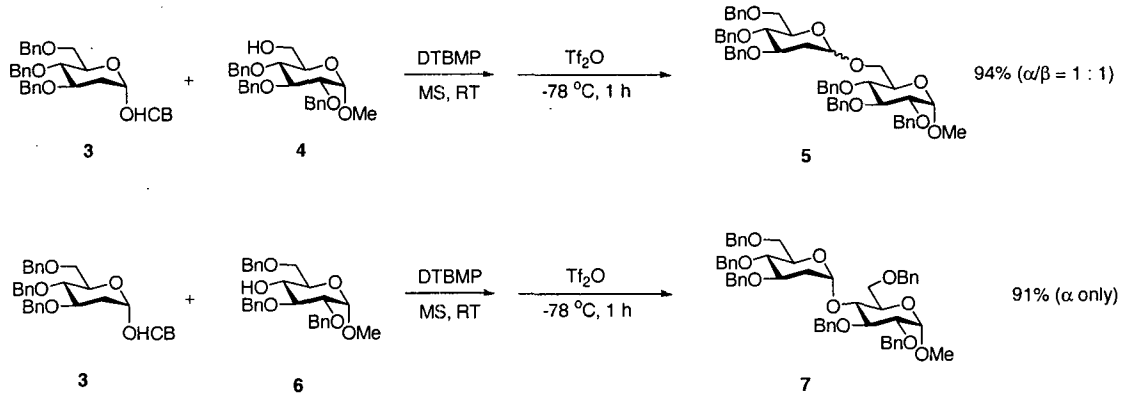
Scheme 1

We applied this HCB methodology to the synthesis of *C*-glycosides and 2-deoxyglucosides. *C*-Glycosylation of HCB glucopyranoside **1** with trimethoxybenzene afforded only the α-anomer of the *C*-glycoside **2** in 66% yield (Scheme 2). Discussion on the minor product in this *C*-glycosylation will be given in the lecture.



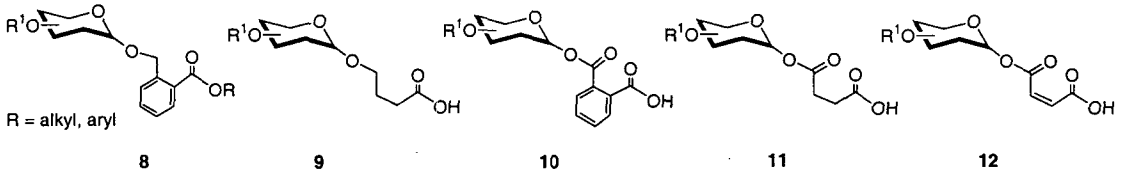
Scheme 2

Glycosylation of HCB 2-deoxyglucoside **3** with the primary alcohol **4** afforded a 1:1 mixture of α- and β-disaccharides **5** in 94% yield (Scheme 3). On the other hand, the glycosylation of **3** with the secondary alcohol **6** gave exclusively the α-disaccharide **7** in 91% yield. Glycosylation of **3** with other glycosyl accepters exhibited the similar stereoselectivity. 4,6-*O*-Benzylidene-protected HCB 2-deoxyglucosides, on the other hand showed different reactivity and stereoselectivity from the 3,4,5-benzyl-protected **3**.



Scheme 3

Related glycosyl donors **8~12** were prepared and their reactivities and stereoselectivities were examined in the glycosylation reactions. Mechanism, scope, and limitation of the HCB glycosides and related glycosides in the glycosylation reaction will be discussed in the lecture.



References

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