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Efficient Strategy for α-Selective Glycosidation of D-Glucosamine and Its Application to the Synthesis of a Bacterial Capsular Polysaccharide Repeating Unit Containing Multiple α-Linked GlcNAc Residues

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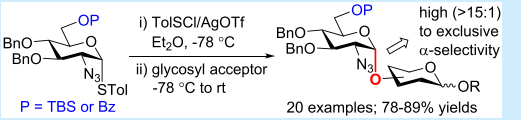
ABSTRACT: An efficient α-selective glycosylation method was developed for the synthesis of 2-deoxy-2-amino-D-glucosides based on synergetic α-directing effects of the TolSCl/AgOTf promotion system and the functional groups at the corresponding azido donor 6-*O*-position to exert steric β-shielding effect or remote participation in the glycosylation reaction. Its practicability was verified with a wide range of monosaccharide glycosyl acceptors and the first, one-pot synthesis of the challenging pentasaccharide repeating unit of an *Acinetobacter baumannii* K47 capsular polysaccharide.



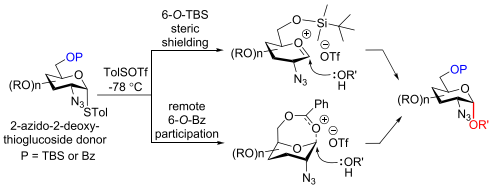
α-Linked 2-amino-2-deoxy-D-glucose or D-glucosamine (α-D-GlcN) and its *N*-acetyl derivative (α-D-GlcNAc) are key components in many natural polysaccharides and glycoconjugates.[1] For the synthesis of these biomolecules, stereoselective α-glycosidation of GlcN/GlcNAc is vital. However, in contrast to the facile synthesis of β-glucosaminosides, which can be readily achieved by taking advantage of the neighboring group participation effects, stereoselective construction of α-glucosaminosides is more difficult to achieve.

To address this issue, a variety of elegant strategies have been explored for α-selective glycosidation of GlcN. Typically, GlcN is converted into glycosyl donors with the 2-amino group protected by a nonparticipating functionality.[2] For instance, Kerns et al.[3] used oxazolidinone or its analogues[4,5] to protect the 2-*N*- and 3-*O*-positions of GlcN to promote α-glycosylation. The Nguyen group[6] employed a benzylidene group to protect the 2-amino group of GlcN, which enabled the donor-nickel catalyst coordination to further assist α-glycosylation. More often, the 2-amino group is converted into a nonparticipating azido group, which was first explored by Lemieux and Paulsen[7] over four decades ago, since the azido group is stable under both acidic and basic conditions and compatible with various glycosylation methods and orthogonal protecting tactics. In addition, an azido group can be easily transformed into amino and acetamido groups via selective reduction (and *N*-acetylation) at a later stage of the synthesis. Consequently, 2-azido derivatives of GlcN have been extensively studied for α-glycosylation. For example, both the Boons[8] and Hung[9] groups have used 2-azido-modified donors for stereoselective synthesis of α-D-glucosaminosides. In addition, 2-deoxy-2-azido-thioglucosides have been used as donors to effect more selective α-glycosylation.[10]

In spite of the above-mentioned progress, most of the current methods have either moderate stereoselectivity or limited application scope, and exclusive α-selectivity has been rarely realized.[2c,7−11] Therefore, more effective and broad strategies for stereoselective α-glycosidation of GlcN are demanded.

Inspired by the previous reports,[12] we have recently developed a highly selective α-glucosylation method based on the synergistic α-directing effects of the toluenesulfenyl chloride (TolSCl)-silver triflate (AgOTf) promotion system and the β-shielding or remote participation effect of protecting groups at the donor 6-*O*-position.[13] This method has exhibited broad applicability and great potential in one-pot synthesis of complex oligosaccharides.[13] Encouraged by this discovery, we explored here the stereoselective α-glycosidation of GlcN by a similar strategy. As shown in Scheme 1, we anticipated that the glycosidation of 2-azido-2-deoxy-thioglucosides with the 6-*O*-position protected by the bulky *t*-butyldimethylsilyl (TBS) or

Scheme 1. Proposed α-selective glycosylation reactions using 6-*O*-TBS and Bz protected 2-deoxy-2-azido-thioglucoside donors



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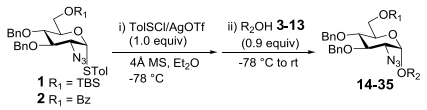
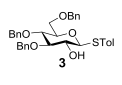
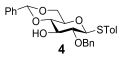
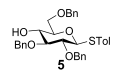
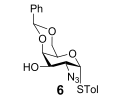
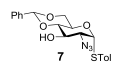
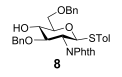
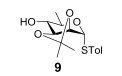
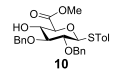
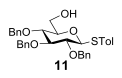
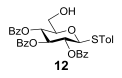
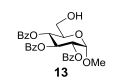
the participating benzoyl (Bz) group would facilitate α-selectivity because β-facial attack by the glycosyl acceptor at the glycosyl triflates formed from preactivation of the donor with TolSCl and AgOTf would be shielded due to either steric hindrance or remote group participation.[13a]

In natural products, GlcN or GlcNAc is α-linked to different positions of various sugars, such as Glc$^{O\text{-}2}$,[14] Glc$^{O\text{-}3}$,[15] Glc$^{O\text{-}4}$,[16] GalNAc$^{O\text{-}3}$,[17] GlcNAc$^{O\text{-}3}$,[18] GlcNAc$^{O\text{-}4}$,[19] D-Rha$^{O\text{-}4}$,[20] GlcA$^{O\text{-}4}$,[21] etc. Accordingly, we prepared monosaccharides **3**-**13**[22] as glycosyl acceptors (Table 1) to examine the glycosylation reactions utilizing 6-*O*-TBS and Bz-protected 2-deoxy-2-azido-thioglucosides **1** and **2** (see the SI for their preparation),[23] both of which were designed as α-configuration with an expectation to get the more comparable results. All of the glycosylation reactions were carried out with the preactivation protocol;[24] that is, after the donor was activated with TolSCl/AgOTf (1.0 equiv relative to the donor) in diethyl ether at −78 °C, the acceptor was added at the same temperature. Subsequently, the reaction mixture was slowly warmed to room temperature in 1.5 h and stirred for another 15 min.

Table 1. Glycosylation of Various Monosaccharides with 1 and 2



Entry	R_2OH	Products	Yield[a]	α:β[b]
1	 **3**	R = TBS **14** R = Bz **15**	80% 81%	α-only α-only
2	 **4**	R = TBS **16** R = Bz **17**	86% 84%	α-only α-only
3	 **5**	R = TBS **18** R = Bz **19**	81% 83%	>19:1 15:1
4	 **6**	R = TBS **20** R = Bz **21**	86% 83%	α-only α-only
5	 **7**	R = TBS **22** R = Bz **23**	82% 82%	α-only α-only
6	 **8**	R = TBS **24** R = Bz **25**	78% 84%	>19:1 α-only
7	 **9**	R = TBS **26** R = Bz **27**	81% 85%	α-only >19:1
8	 **10**	R = TBS **28** R = Bz **29**	87% 89%	α-only α-only
9	 **11**	R = TBS **30** R = Bz **31**	80% 84%	5:1 3:1
10	 **12**	R = TBS **32** R = Bz **33**	87% 85%	>19:1 >19:1
11	 **13**	R = TBS **34** R = Bz **35**	87% 88%	>19:1 16:1

[a]Based on isolated yields. [b]α:β anomeric ratios were determined by ^{1}H NMR analysis of reaction mixture.

The results in Table 1 indicated clearly that the reactions of **1** and **2** with all secondary alcohols (entries 1−8), regardless of the sugar species and protecting groups, proceeded smoothly to afford the desired products in very high yields (78−89%) and outstanding (α:β > 15:1) to exclusive (α-only) α-selectivity. However, the reactions of **1** and **2** with more reactive **11** containing a primary alcohol gave significantly lower α-selectivity (α:β = 5:1 and 3:1, respectively, Table 1, entry 9) but good yields. Considering that glycosyl acceptors with less nucleophilic hydroxyl groups are less reactive but can usually afford more stereoselective outcomes,[25] we utilized the Bz-protected analogue **12** of **11** as an acceptor for the glycosylation. Delightfully, a significant improvement in α-selectivity (α:β > 19:1) was observed for the reaction between **12** and **1** or **2** (Table 1, entry 10). Similar results were obtained with Bz-protected acceptor **13** having an α-anomeric configuration (α:β > 16:1, Table 1, entry 11). The azido groups in products **14**-**35** can be readily converted into free amino or acetamino groups through chemoselective azido reduction and *N*-acetylation, as demonstrated in the synthesis of a very complex oligosaccharide described below. Consequently, a convenient, reliable and efficient strategy was established for exclusive or highly selective α-glycosylation of various glycosyl acceptors using donors **1** and **2**.

To verify the practicability of this new glycosylation method, we applied it to one-pot assembly of the pentasaccharide repeating unit **37** (Figure 1) of an *Acinetobacter baumannii* K47 capsular polysaccharide (CPS).[26] Compound **37**, which contained three α-linked GlcNAc residues and a branching α-GalNAc motif, represents a notable synthetic challenge. To date, there has been no reported synthesis of this oligosaccharide. In our designed synthetic target **37**, a free amino group is attached to the glycan downstream end to facilitate its conjugation with other molecules for biological studies, such as anti-*A. baumannii* K47 vaccine development.

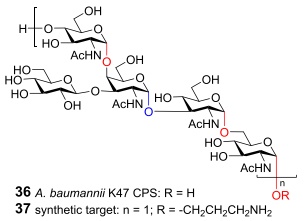


Figure 1. Structure of *A. baumannii* K47 CPS and the synthetic target **37**.

Our synthetic plan for **37** is outlined in Scheme 2. We projected that pentasaccharide **38** as the fully protected form of **37** could be constructed from building blocks **1**, **39**, and **40** through preactivation-based iterative one-pot glycosylation.[24] The 6-*O*-TBS and -Bz groups in **1** and **39** were expected to secure α-selective glycosylations. In turn, trisaccharide **39** would be prepared from α-selective glycosylation of **42** with **41**.

Our synthesis commenced with the preparation of mono- and disaccharide building blocks **41**−**43** (see the SI for their preparation). Next, preactivation-based glycosylation of **41** with **42**[27] was achieved using promoter TolSCl/AgOTf at −40 °C with DCM−Et_2O (v/v, 10:1) as the solvent (Scheme 3).

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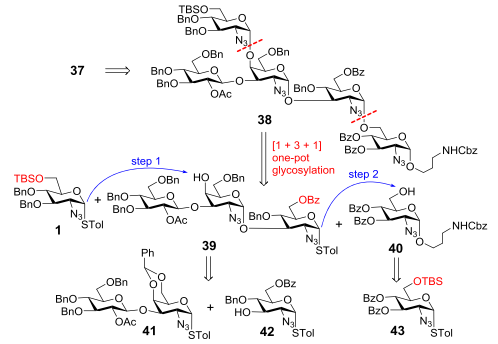
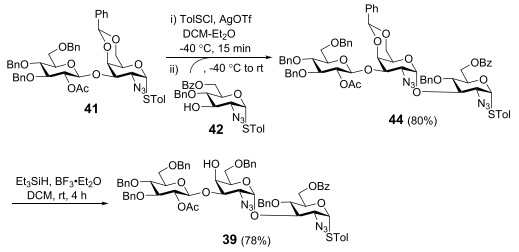
Scheme 2. Retrosynthesis of the Target Molecule 37



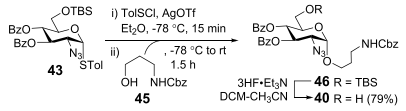
Scheme 3. Synthesis of Trisaccharide Building Block 39



Only the α-product **44** was obtained from this reaction in an 80% yield, and the resultant new α-glycosyl linkage was verified by the small anomeric coupling constant of GalN-2 ($J_{H1',2'}$ = 3.5 Hz) in its ^{1}H NMR spectrum. It is worth noting that the reaction at −78 °C gave only a low yield (<10% yield) of **44** because **41** was less reactive and was not effectively activated at too low temperature. Subsequently, the benzylidene ring in **44** was regioselectively opened by reaction with triethylsilane (Et_3SiH) in the presence of boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$) to afford **39** in a 78% yield.

Similarly, preactivation of **43** with TolSCl/AgOTf at −78 °C followed by reaction with primary alcohol **45** provided **46** in a moderate α-selectivity (α:β = 9:1), and the isomers were easily separated after desilylation with 3HF·Et_3N to give pure **40** ($J_{H1,2}$ = 3.5 Hz) in 79% yield for two steps (Scheme 4). In

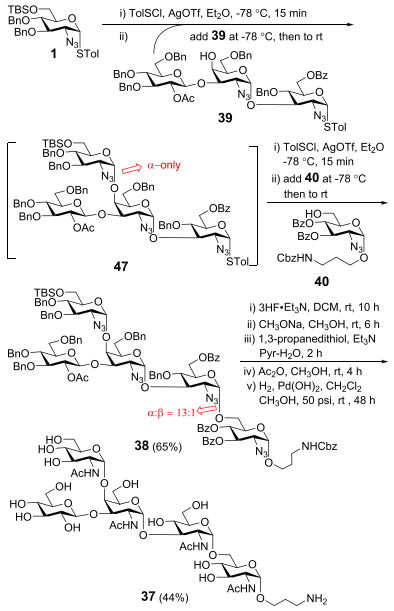
Scheme 4. Synthesis of Building Block 40



addition, we also carried out this glycosylation by the conventional procedure; that is, **43** and **45** were mixed in diethyl ether before AgOTf and TolSCl were added at −78 °C, and the reaction was kept at room temperature for 15 min. The latter gave essentially the same stereoselectivity and yield as the former.

After building blocks **1**, **39**, and **40** were available, we moved on to perform one-pot synthesis of pentasaccharide **37** (Scheme 5). Thus, after **1** was preactivated with TolSCl/AgOTf in diethyl ether at −78 °C within 15 min, trisaccharide **39** was added at the same temperature. The reaction mixture was allowed to warm to room temperature in 1.5 h and was stirred for another 15 min to accomplish the first glycosylation. This reaction afforded the desired α-isomer **47** only, which was proved by the NMR spectrum (GlcN-3: $J_{H1'',2''}$ = 3.0 Hz) of

Scheme 5. One-pot Assembly of the Synthetic Target 37



the product isolated from a fraction of the reaction mixture. Thereafter, **40** was glycosylated with **47** by means of the same preactivation procedure to provide **38**. For each glycosylation, 1.0 equiv of TolSCl/AgOTf (relative to the donor) was employed. Pure pentasaccharide **38** (GlcN: $J_{H1',2'}$ = 3.5 Hz, GlcN: $J_{H1''',2'''}$ = 3.5 Hz) was isolated from the reaction mixture in an impressive 65% overall yield together with a very small amount of the β isomer (α:β = 13:1) that was generated from the second glycosylation step.

Full deprotection of **38** was accomplished by a five-step protocol. First, the TBS group was chemoselectively removed with 3HF·Et_3N at room temperature. This was followed by removal of the acyl groups with CH_3ONa. Next, all four azido groups were readily converted into acetamido groups by a one-pot two-step procedure including reduction of the azido groups with 1,3-propanedithiol and then selective *N*-acetylation of the resultant free amines with acetic anhydride in CH_3OH. The intermediate was purified with a Sephadex LH-20 column and then subjected to $Pd(OH)_2$/C-catalyzed hydrogenolysis in CH_2Cl_2 and CH_3OH (1:5) to remove all of the benzyl groups and to remove the Cbz group concurrently. This mixed solvent could dissolve both of the starting material and the product well. Finally, the synthetic target **37** was obtained in a 44% overall yield after purification with a Sephadex G-15 column using H_2O as the eluent and lyophilization. Its structure was verified with 1D and 2D NMR and HR MS data.

In summary, a new, efficient, and highly stereoselective strategy was developed for the construction of α-GlcN linkages with 2-deoxy-2-azido-thioglucosides as glycosyl donors. It was proposed that the high α-selectivity was due to combined α-directing effects of the TolSCl/AgOTf promotion system to facilitate the formation of an oxonium triflate intermediate and protecting groups at the donor 6-*O*-position to shield the β-face, leading to favorable attack by aglycones from the α-face. This mechanism was supported by the observation that less reactive aglycones afforded better α-selectivity (Table 1). Further study to reveal the exact mechanism are currently ongoing in our laboratory. The new glycosylation method was

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Org. Lett. XXXX, XXX, XXX−XXX

proved to be efficient, versatile, and broadly useful and compatible with various protecting groups, as evidenced by the examples in Table 1. Furthermore, due to its robustness and high stereoselectivity, this glycosylation method should be also suitable for one-pot carbohydrate synthesis. As a proof of principle, it was employed to synthesize the pentasaccharide repeating unit **37** of *A. baumannii* K47 CPS that contained multiple α-linked GlcNAc residues via one-pot [1 + 3 + 1] glycosylation. It represented the first total synthesis of this highly challenging pentasaccharide. All of the glycosylation reactions proceeded smoothly to form α-glycosidic linkages in excellent yields and stereoselectivity. Thus, the new glycosylation method should be applicable to the synthesis of various complex oligosaccharides containing α-linked GlcN or GlcNAc residues.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00101.

Synthetic procedures, analytical data, and NMR and MS spectra of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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