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$SnCl_4$-catalyzed Solvent-free Acetolysis of 2,7-Anhydrosialic Acid Derivatives

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Abstract

Sialic acid-containing glycans are found in different sialic acid forms and a variety of glycosidic linkages in biologically active glycoconjugates. Hence, the preparation of suitably protected sialyl building blocks requires high attention in order to access glycans in pure form. In this line, various *C*-5 substituted 2,7-anhydrosialic acid derivatives bearing both electron donating and withdrawing protecting groups were synthesized and subjected to different Lewis acid-catalyzed solvent free ring opening reactions at room temperature in the presence of acetic anhydride. Among the various Lewis acids tested, the desired acetolysized products were obtained in moderate yields under a tin(IV)

chloride catalysis system. Our methodology can be extended to regioselective protecting group installation and manipulation towards a number of thiosialoside and halide donors.

Keywords: acetolysis; acetolysized products; 2,7-anhydrosialic acid; $SnCl_4$

Introduction

Sialic acids are the most prevalent monosaccharides which are found at the non-reducing ends of glycans, and are involved in many biologically important ligand-receptor interactions [1]. *N*-acetylneuraminic acid (Neu5Ac) is the most studied monosaccharide from the 50 derivatives of sialic acid that are found in nature. The most common glycosidic linkages of Neu5Ac in glycoconjugates are α(2→3) and α(2→6) to galactose, α(2→8) and α(2→9) in polysialic acids [2,3], fucosyl and galactosyl α(1→4) to Neu5Ac and intramolecularly *C*-7 oxygen linked to *C*-2 forming 2,7-anhydro-Neu5Ac (Figure 1A) [4,5]. Owing to the substantial role of sialic acids in biological systems, numerous synthetic methods have been described in literature [6-10]. 2,7-anhydro-Neu5Ac is the main prebiotic which is utilized as a sole carbon source for human gut commensal anaerobic bacterium and plays a key biological role in body fluid and secretions [11,12].

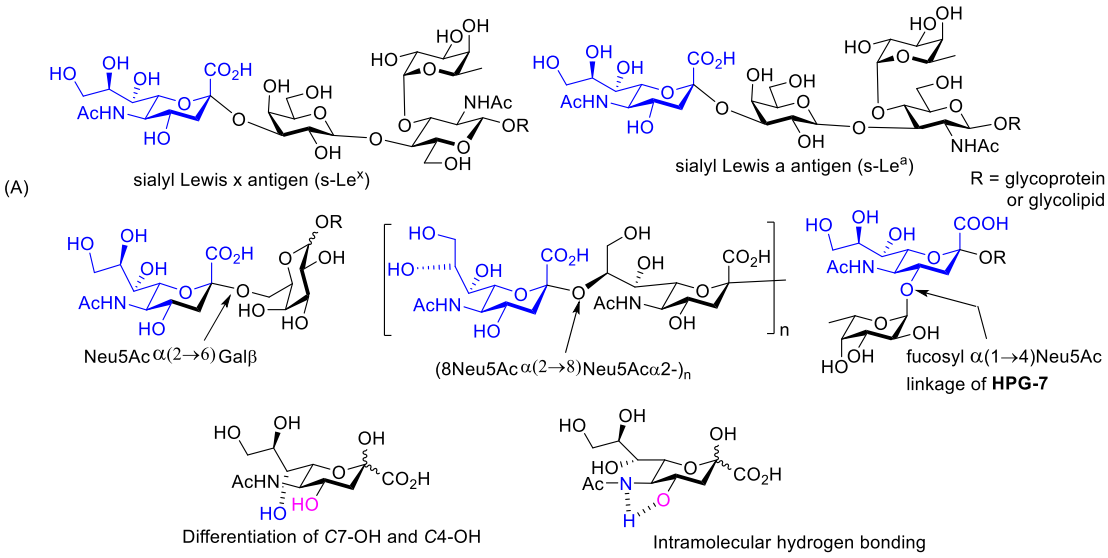
Upon cleaving the internal ketal ring and protection of 4-OH, further modifications at *C*-7 and sialylations at the *C*-2 positions can be conducted. To study substrate specificity of bacterial and human sialidases using the library of *C*-7-modified Neu5Ac, Chen *et al*. has described the systematic substitution of the 7-OH of Neu5Ac by -F, -OMe, -H, and -N_3 functional groups [13]. Additionally, De Meo and co-workers have reported the significant effect of *O*-substituents at *C*-7 on the reactivity of thiosialoside donors and on the anomeric stereoselectivity of chemical sialylation [14]. Thus, 2,7-anhydro-Neu5Ac can

serve as a promising building block for the chemical synthesis of gangliosides and other Neu5Ac containing glycans after its 2,7-anhydro backbone is opened. Representative structures of bacterial glycans containing sialic acid which can be chemically synthesized from sialyl donors are illustrated in Figure 1 (A) [2-4, 15].

One way to obtain Neu5Ac-containing oligosaccharides with the desired regioselectivity is to regioselectively protect the Neu5Ac acceptor. Although Neu5Ac with free primary 9-OH is easy to obtain, there are only limited ways to distinguish the two secondary 4- and 7-OH groups (Figure 1A). In our previous report, we easily distinguished these alcohols by the selective protection of the 7-OH as 2,7-anhydro-Neu5Ac, leaving 4-OH free for glycosylation upon protection of the vicinal 8- and 9-OH as benzylidene or acetonide rings [5]. The formation of the [3.2.1] bicyclic backbone of 2,7-anhydro-Neu5Ac avoids not only installing protection groups at the *C*-2 and *C*-7 positions, but also the tedious anomeric isomers purification as it gives only the α-isomer. Besides, the configuration of the 4-OH and C-5 NHAc groups changed from equatorial to axial after the 2,7-anhydro backbone formation, which results in alleviation of hydrogen bonding, thus enhancing the reactivity of 4-OH group as acceptor (Figure 1B) [5].

Several chemical and enzymatic syntheses of 2,7-anhydro-Neu5Ac are currently developed [5, 16-18]. However, only a few synthetic applications of 2,7-anhydro-Neu5Ac are available in the literature. Previously, we successfully constructed the fucosyl *α*(1→4)Neu5Ac linkage of ganglioside HPG-7 using 2,7-anhydro-Neu5Ac derivatives as acceptor [5]. For utilization as selective sialidase inhibitors, Chen's and Juge's groups have reported one pot multienzyme synthetic protocol of 2,7-anhydro-Neu5Ac [11,12].

- Representative structures of bacterial glycans containing sialic acid.



- This work: Regio- and Chemoselective functionalization in the synthesis of sialic acid derivatives.

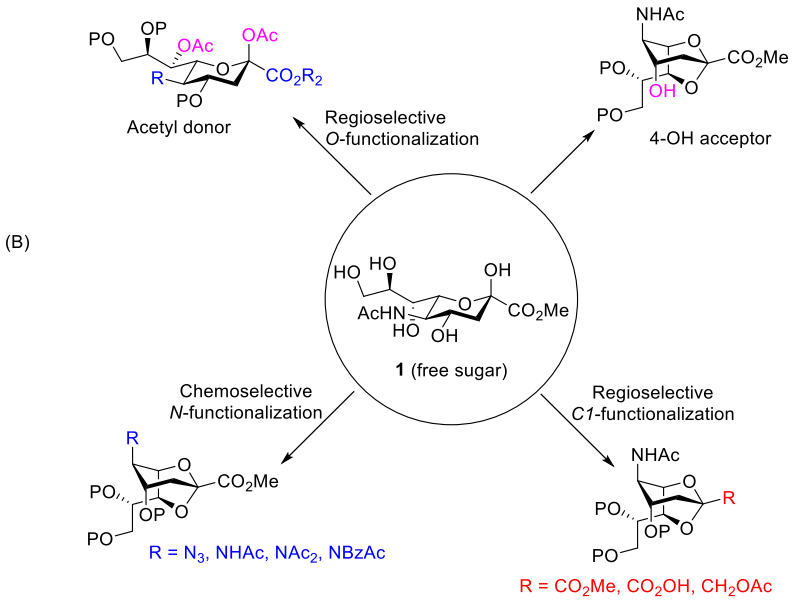


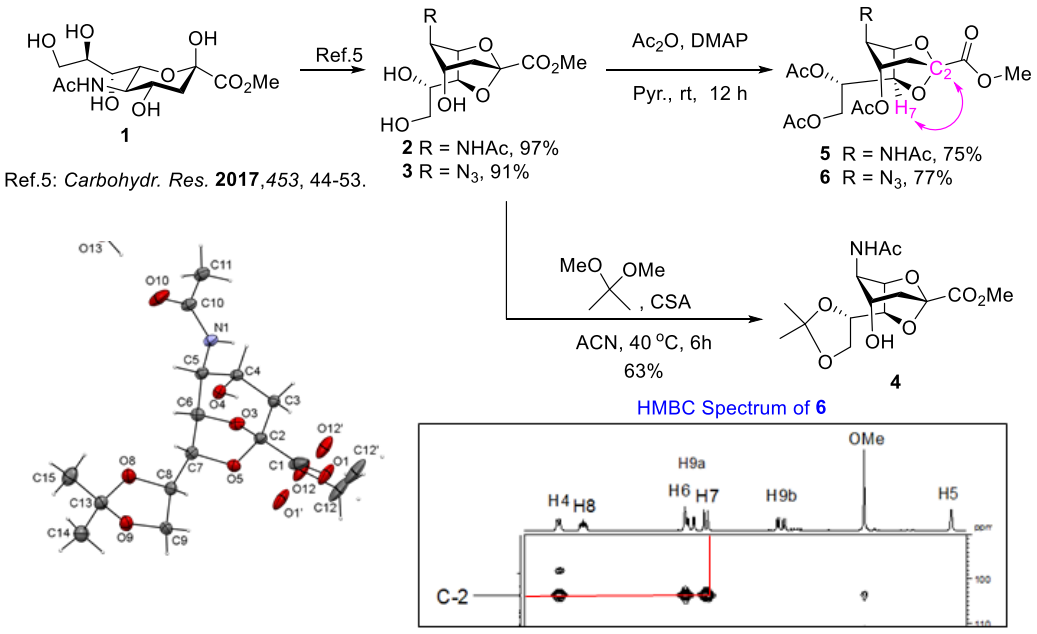
Figure 1: (A) Representative structures of bacterial glycans containing sialic acid; (B) Regio- and Chemoselective functionalization in the synthesis of sialic acid derivatives.

Our group has developed one-pot synthesis of several anhydrosugars via microwave (MW)-assisted intramolecular anomeric protection (iMAP) of silylated sugars as well as their ring opening protocols for the 1,6-anhydro rings [19-21]. Accordingly, D-galactosamine and D-allosamine derivatives were synthesized via the scandium (III) triflate ($Sc(OTf)_3$)-catalyzed ring opening of 1,6-anhydroglucosamine derivatives [19, 22]. However, there is a paucity of reports on the Lewis acid-catalyzed acetolysis of 2,7-anhydro backbone of the Neu5Ac. Thus, the aim of this study was to cleave the ring of the 2,7-anhydro derivatives with a choice of suitable Lewis acid as a catalyst, in order to utilize the acetolysized products as building blocks for the chemical synthesis of Neu5Ac-containg glycans.

Results and Discussion

It is known that $Sc(OTf)_3$ [19,22] and trimethylsilyl trifluoromethanesulfonate (TMSOTf) [23] in the presence of acetic anhydride (Ac_2O) as acetolysis agent were used to cleave the 1,6-anhydro ring. In these reactions, Ac_2O is used as both reactant and solvent, which can be easily removed in *vacuo*. Envisioned on these precedents, we applied an acetolysis procedure as a way to introduce acetate at *C*-2 and *C*-7 positions of Neu5Ac in order to prepare regioselectively protected glycosyl donors.

Our investigations began with the synthesis of 2,7-anhydro derivatives **2** and **3** following our previous procedure [5]. In order to characterize the formation of 2,7-anhydro skeleton, triol **2** was treated with 2,2-dimethoxypropane in the presence of a catalytic amount of camphorsulfonic acid (CSA) in acetonitrile (CH_3CN) and afforded the crystalized compound **4** in 63% yield (Scheme 1).

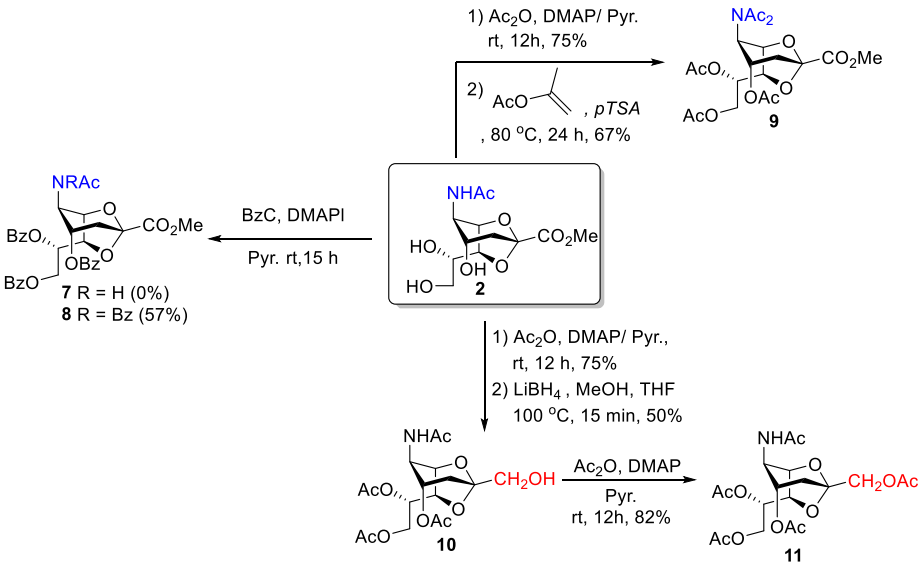


Scheme 1: The concise synthesis of 2,7-anhydrosialic acid derivatives **2-6**

The X-ray single crystal structure of **4** clearly showed that the *C*-5 NHAc and 4-OH groups are oriented as a *trans*-diaxial configuration. This enhances the nucleophilicity of 4-OH due to the absence of hydrogen bonding between these groups. After confirming of the structure of **4** by X-ray crystallography, compounds **2** and **3** were acetylated with Ac_2O in pyridine to give **5** [5] and **6** in 75 and 77% yields, respectively (Scheme 1), and the compatibility of acetyl protecting group with the Lewis acids during acetolysis reactions was tested. The structure of compound **6** was confirmed by using NMR analysis. The HMBC spectrum of **6** showed downfield shift of H-4 and illustrated three bond away correlation with *C*-2 like that of H-7 and H-6.

Furthermore, the *C*-1 and *C*-5 positions of compound **2** were functionalized over certain steps in order to open the 2,7-anhydro bridge. Accordingly, the *per*-*O*-benzoylation of **2** with benzoyl chloride in pyridine produced compounds **8** in a moderate

yield (57%). On the other hand, introducing an additional *N*-acetyl moiety to **5** using isopropenyl acetate and *p*-toluenesulfonic acid (*p*-TSA) afforded **9** in a 67% yield (Scheme 2).



Scheme 2: *N*-functionalization and *C*-1 functionalization of **2**

Wong and co-workers reported the major effect of the carboxyl group on the anomeric reactivity of sialic acid compared with the side-chain protecting groups. Hence, we converted the carboxylate esters of **5** in to *O*-acetyl protected hydroxymethyl group **9** in order to increase its reactivity by reducing the steric hinderance and destabilizing the effect of the electron withdrawing carboxyl group on anomeric center (Scheme 2) [24]. Consequently, reduction of the ester derivative of **5** with $LiBH_4$ in MeOH and tetrahydrofuran (THF) followed by acetylation of hydroxymethyl group provided **11** in an 82% yield.

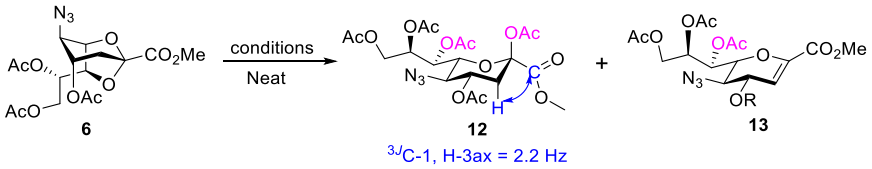
After getting the 2,7-anhydrosialic acid derevatives (**5-11**) in hand, they were subjected to various Lewis acid-catalyzed ring opening reaction. Inline this, $Sc(OTf)_3$,

copper(II) triflate ($Cu(OTf)_2$) and $SnCl_4$-catalyzed acetolysis of *N*-Ac_2 and *N*-BzAc derevatives (**9** and **8**) did not afford the desired acetolysized products. In the course of these reactions, the functional groups of *N*-BzAc in **8** and *N*-Ac_2 in **9** were hydrolyzed back to **7** and **5**, respectively; whereas compound **7** afforded an unidentifiable mixture of compounds. Similarly, the 2,7-anhydro backbone of **11** was not cleaved under the above conditions, and results in either recovered starting material or unidentifiable mixtures. Differently, ring opening reactions of **6** with $BF_3.OEt_2$, TMSOTf, $Sc(OTf)_3$ and $SnCl_4$ in Ac_2O afforded glycal **13** (Table 1, entries 1 to 4). None of these conditions was successful for the acetolysis of these 2,7-anhydro derivatives, although they worked for the 1,6-anhydro sugars [19,22,23]. Adding 10 equivalent of acetic acid (HOAc) to suppress the 2,3-elimination reaction failed to give the desired compound **12**. Due to the absence of a hydrogen bond, the azido-protected glycal **13** can be used as acceptor for reactions at its *C*-4- and *C*-8-OH groups [25, 26]. Moreover, it is used as sialyl donor in α-selective glycosylation reactions [24].

Next, acetolysis of 2,7-anhydro derivative **6** was examined with $SnCl_4$ as catalyst under neat condition and provided the expected *β*-ring-opened product **12** in moderate yield (Table 1, entries 5). This acetolysis reaction results in regioselecitve actylation on *O*-7 and *O*-2 inline with the principles of green chemistry.

It is known that anomeric acetates can be transformed smoothly in to thioglycoside [10, 24] and sialyl halide [27] donors when treated with a thiol in the presence of triflic acid or boron trifluoride etherate ($BF_3.Et_2O$) and HCl, respectively.

Table 1: Optimization of Ring Opening Reaction (**6**)



Entry	Conditions	T (°C)	Time (h)	Product, yield	
				12	**13**
1	$BF_3.OEt_2$ (cat.)/Ac_2O	100	19	---	15%[a]
2	TMSOTf (cat.)/Ac_2O	70	20	--	13%[a]
3[b]	TMSOTf (cat.)/Ac_2O	70	11	--	20%[a]
4	$Sc(OTf)_3$ (cat.)/Ac_2O	100	2	--	7%[a]
5	$SnCl_4$ (cat.)/Ac_2O	rt	20	54%	34%

[a]The reaction cannot totally consume. [b]With 10 equiv. of AcOH

Through comparison with the reported mechanism of $Sc(OTf)_3$-catalyzed acetolysis of the 1,6-anhydro-β-hexopyranoses [22], we proposed a pleausible mechanism for the acetolysis of 2,7-anhydro-Neu5Ac derivative **15** (Figure 2). First, Ac_2O is activated by $SnCl_4$ forming a polarized complex **14**. Next, the *O*7 atom 7 of **15** captures the acylium ion from **14** to afford an unstable species **17** and their counter ion **16**. The *C*2-*O*7 bond of this positively charged intermediate **17** rapidly undergoes a bond cleavage to generate a sialyl cation **18**, which was then attacked by the nucleophile **16** from the beta face to provide the desired acetolysized products **20** and the original $SnCl_4$. On other hand, abstraction of H-3 by the nucleophile **16** afforded the 2,3-elimination product **19**.

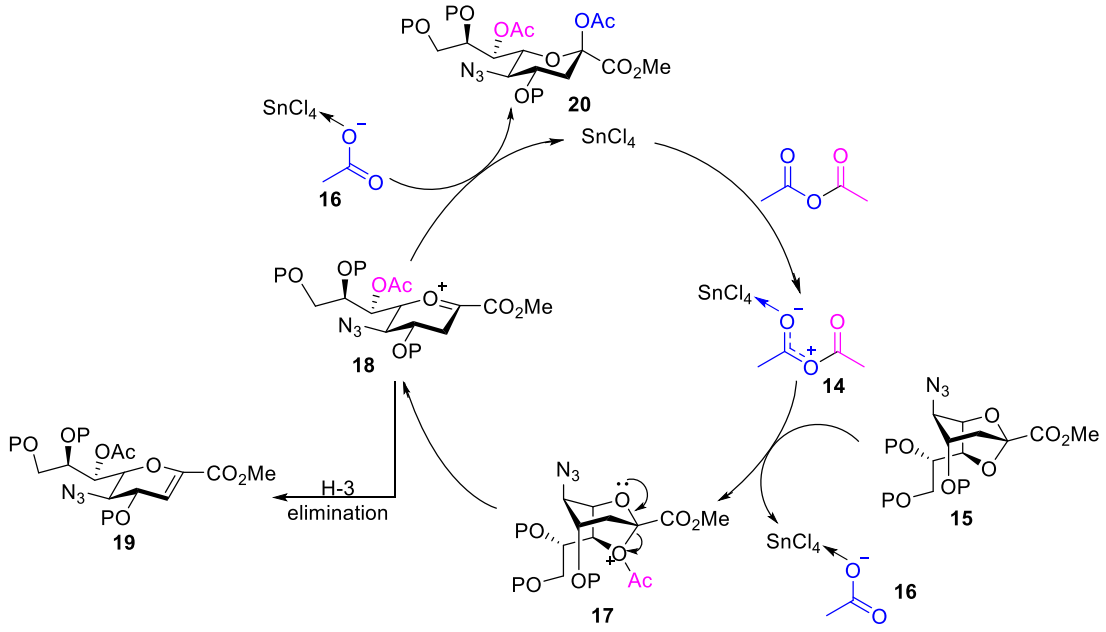


Figure 2: Mechanism of $SnCl_4$-catalyzed acetolysis of 2,7-anhydro derivatives **15**

To substantiate the reaction mechanism, acetolysis of 2,7-anhydro derivatives **5** and **21** were examined with $SnCl_4$ as catalyst (Table 2). With the substrate **21**, the expected product **22** was successfully isolated in good yield (66%) accompanied by 27% of the 2,3-elimination product **23** (Table 2, entry 2) similar to per-*O*-acetylated **6,** which gave glycal **13** in 34% yield. The ring opening reaction of **21** occurred faster than **6**; this might be attributed to the presence of three electron-donating methyl groups in it.

The cleavage of the intramolecular glycosidic bond of **5** and **21** was confirmed by NMR spectroscopic data; H-7 of compounds **12** and **22** shifted to downfield region due to the presence of acetyl group at *O*-7 which was introduced after the cleaving of the 2,7-anhydro skeleton; it also showed no correlation with *C*-2, but exhibited a three bond away correlation with the quaternary C of the acetyl group at *O*-7 (Figure 3). The anomeric configuration of the acetolysized products was identified by the three-bond coupling

constant of C1-C2-C3-Hax (^{3J}C-1, H-3ax, 1.6-2.2 Hz, see SI) and indicated the β-anomer [9, 10].

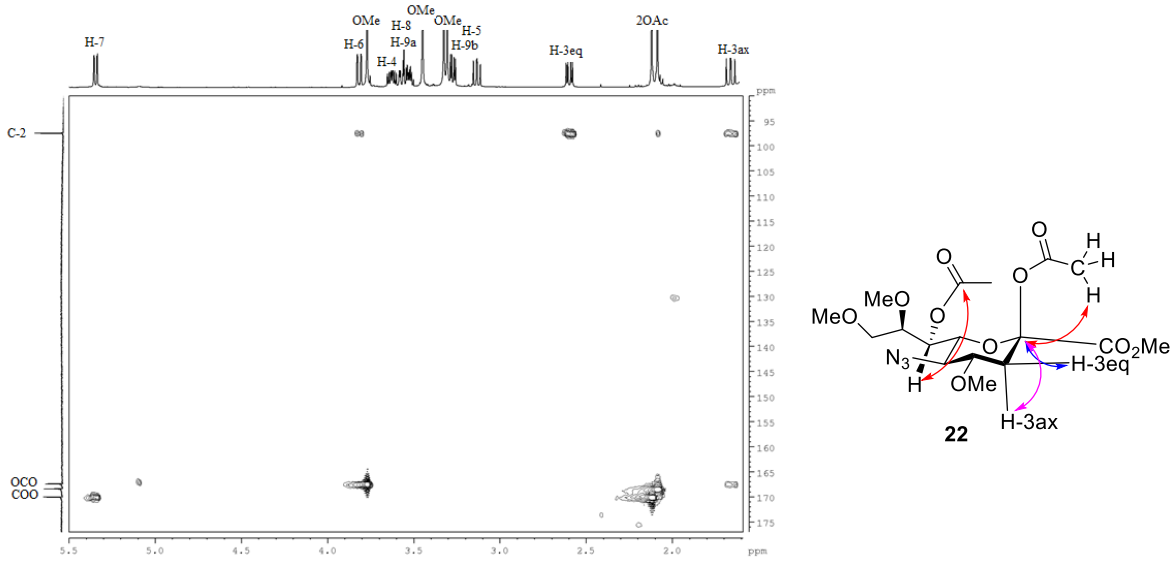
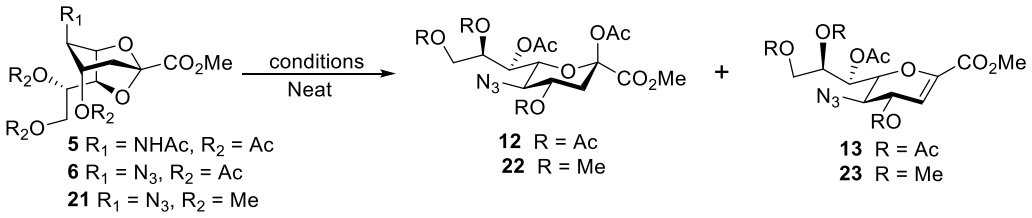


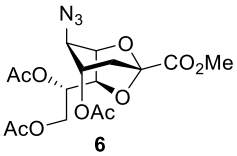
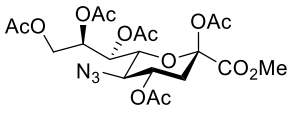
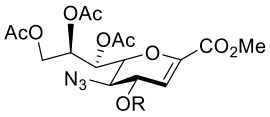
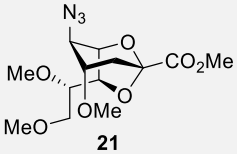
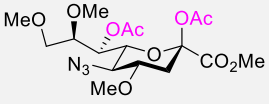
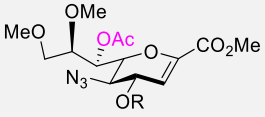
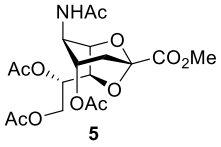
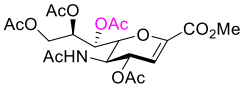
Figure 3: HMBC spectrum of **22**

Next, $SnCl_4$-catalyzed acetolysis reaction was evaluated with a 2,7-anhydro derivative **5**; however, the reaction did not take place. On the other hand, only a known glycal **24** was obtained in 44% moderate yield in the $Sn(OTf)_2$ catalysis system (Table 2, entry 3). The deriving force for the formation of a 2,3-dehydro derivative **24** might be attributed to the presence of a destabilizing electron withdrawing carboxyl group flanking *C*-2 and the lack of a participating auxiliary at *C*-3 of **5**. Glycal **24** is widely used for α-sialylation by utilizing neighboring group participation and site-selective fluorination at *C*-3 [9, 28]. Moreover, it is the main precursor in the synthsis of inhibitors for *N*-acetylneuraminidases of different source [29]. The ring opening of **5** was not a trivial one since it has a sterically hindered quaternary anomeric center, unlike the tertiary *C*-1 anomeric center of 1,6-anhydro sugars. Furthermore, $SnCl_4$ or $Sn(OTf)_2$ might form a

coordination bond with the carbonyl oxygen of the *C*-5 NHAc group and the *O*-6 in the hexapyranosyl ring; this inturn, retarded the ring opening reaction. The anchimeric participation of the NHAc group in stabilizing the axial conformation of the sialyl cation could also affect the cleavage of the ring [9].

Table 2: Substantiation of the reaction mechanism



Entry	Donor	Ring opening Product	Glycal
1	 **6**	 **12** (54%)	 **13** (34%)
2	 **21**	 **22** (66%)	 **23** (27%)
3	 **5**	--	 **24** (44%)

Conclusion

In conclusion, an acetolysis reaction was carried out by considering various parameters such as Lewis acid types and amount (both catalytic and stoichiometric),

solvent, acetolysis agent, reaction time and temperatures were unsuccessful with 2,7-anhydro derivatives bearing NHAc, *N*Ac$_2$ and *N*AcBz groups at its *C*-5 position. We have successfully developed a convenient route to conduct the $SnCl_4$-catalyzed acetolysis of 5-azido-protected 2,7-anhydro derivatives. The acetolysized products can be further transformed into regioselectively protected thiosialoside and sialyl halide donors in order to serve as an alternative building blocks for the synthesis of sialic acid-containing glycans.

Supporting Information. Experimental part and spectroscopic data for compounds described herein in PDF file. Additionally, the X-ray data of compound **4** is also available in PDF file.

Acknowledgement

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