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Substituent effects in endocyclic cleavage–recyclization anomerization reaction of pyranosides

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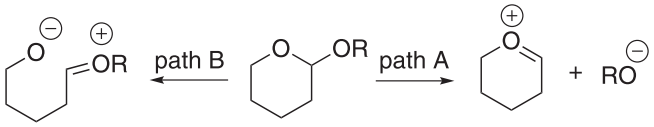
ABSTRACT

Pyranosides with 2,3-*trans* carbamate or 2,3-*trans* carbonate groups are anomerized under mild acidic conditions via endocyclic cleavage reaction. In order to understand the nature of the anomerization reaction via the endocyclic cleavage–recyclization process, the substituent effects at various positions were investigated.

1. Introduction

The reaction mechanism of acetal hydrolysis with its stereoelectronic aspects has received much attention as a fundamental issue in organic chemistry.[1] Since glycosides are acetals existing in living systems, the issue on glycosidic cleavage is also important in carbohydrate chemistry, biochemistry, and biotechnology. Since pyranosides are asymmetric acetals, there are two possibilities for their mode of C–O bond cleavage.[2] One is exocyclic cleavage, where the bond between the anomeric carbon and the exocyclic oxygen breaks giving a cyclic oxocarbenium ion (Scheme 1, path A). The cyclic oxocarbenium ion is assumed to be an important intermediate in glycosylation reactions, and a key species in carbohydrate science.[3] The other cleavage pattern is endocyclic cleavage, where the bond between the ring oxygen and the anomeric carbon is cleaved giving a linear cation (Scheme 1, path B). The endocyclic cleavage is less common in carbohydrate chemistry compared to the exocyclic cleavage. The mechanistic details of regioselectivity on the cleavage site of pyranosides are discussed extensively in the context of the stereoelectronic theory.[4] According to this theory, it is explained that, for glucosides in a $^4C_1$ chair form, the α-anomers preferentially proceed via an exocyclic pathway, whereas exocyclic cleavage in the β-anomers is energetically unfavorable unless a conformational change of the pyranoside ring is possible.[1d,5] For the β-pyranosides in a $^4C_1$ chair form, the exocyclic leaving group cannot depart easily because of lack of overlap with the electron orbital of the ring oxygen. It is also discussed that the β-pyranosides has to adopt twist boat or flattened chair conformations to be cleaved in an endocyclic manner. Thus, investigations into the cleavage patterns of pyranosides will be interesting not only to carbohydrate chemists but also to theoretical chemists studying stereoelectronic issues.



Scheme 1. Endocyclic cleavage versus exocyclic cleavage reactions.

Haworth reported as early as 1941 that 3,6-anhydro-methyl glucosides were hydrolyzed in the endocyclic cleavage mode.[6] Post and Karplus suggested the possibility of endocyclic cleavage in the hydrolysis of an oligosaccharide in lysozyme with molecular dynamics simulations.[7] These calculations were performed based on the X-ray crystallographic studies of lysozyme with an oligosaccharide substrate, wherein the conformation of *N*-acetylglucopyranoside was restricted to a $^4C_1$ chair form in the enzyme.[8] Inspired by the Post and Karplus hypothesis, several groups reported experimental evidence of conformationally locked sugar mimic

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compounds by capturing the cation generated in an endocyclic cleavage mode. For example, Franck succeeded in capturing the cation generated via endocyclic cleavage by an intramolecular aza-Diels–Alder reaction during alkyl β-acetal methanolysis.[9] Fraser-Reid demonstrated the presence of linear acetylium ions in acetic acid during acetolysis in the presence of ferric chloride.[10] Anslyn used a pseudosymmetric deuterium scrambling test to show that only a β-alkyl acetal locked in a *cis*-decalin type conformation underwent endocyclic cleavage in MeOH, with a 30% maximum ratio.[11] Deslongchamps and Dory investigated reaction pathways of the enzyme-catalyzed hydrolysis of glycosides based on quantum-mechanical calculations as well as experimental studies, showing endocyclic cleavage reactions.[12] Recently, systematic analyses on endocleavage of 6,1-anhydroglucopyranuronic acid were reported by Murphy.[13]

During the development of a glycosyl donor for the 1,2-*cis* glycosylation of 2-amino-2-deoxy sugar,[14,15] we found that pyranosides with a 2,3-*trans* carbamate group were quite easily anomerized under mild Lewis acidic conditions.[16,17] Crich and Oscarson also reported the same anomerization with 2,3-*trans* carbamate-carrying pyranosides.[18] We presented evidence that the anomerization was caused by an endocyclic cleavage reaction and subsequent recyclization of the pyranoside ring.[19] The generated linear cation was captured by intra- and inter-molecular Friedel–Crafts reactions, chloride addition, and reduction using Et_3SiH (Scheme 2). The anomerization reaction of pyranosides with 2,3-*trans* carbamate occurs at lower temperatures and milder conditions compared to other reported examples. Even the α-anomers are anomerized to the β-anomers, although higher (0 °C) temperature is required. Complete anomerization from the β- to the α-direction was observed in some cases.

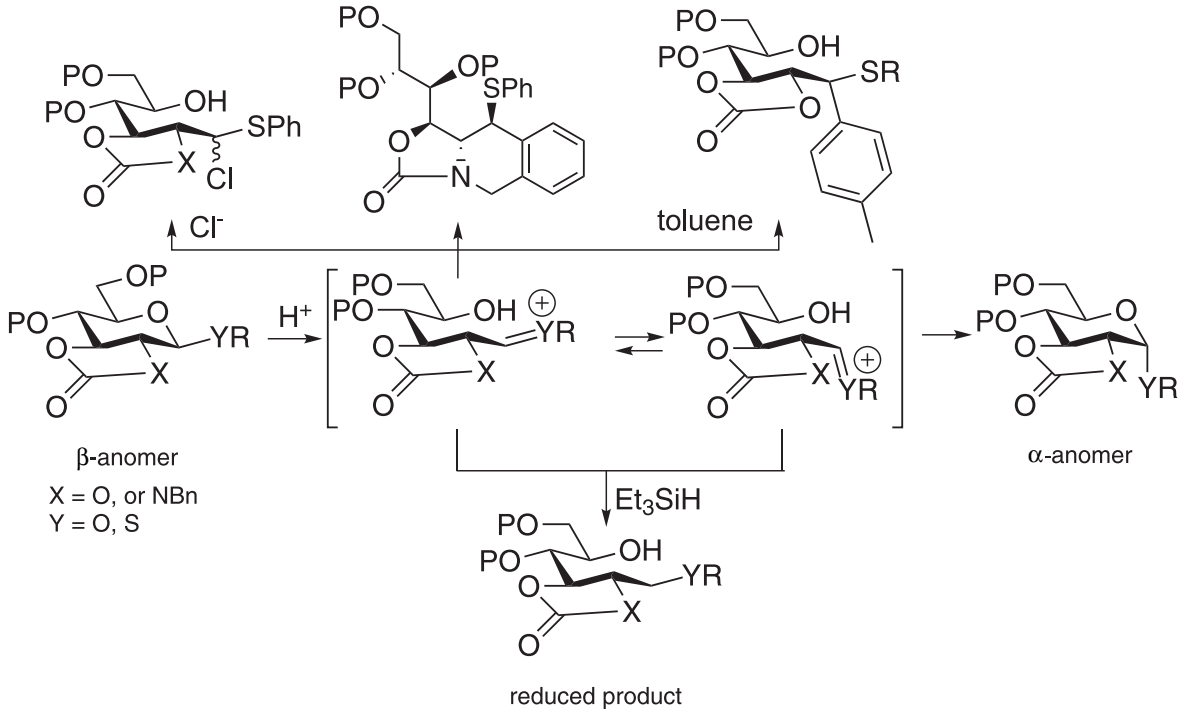
with 2,3-*trans* cyclic protecting group, inner strain caused by the fused rings distorting one ring by the force from the other is the primary factor enhancing the endocleavage reaction.[20b] The effect of the cyclic protecting group in restricting the pyranoside ring to a $^4C_1$ conformation is estimated to be a secondary factor.

In order to obtain further information aimed at the development of this endocyclic cleavage reaction for synthetic utility, we investigated substituent effects at the anomeric center, the 5-position, and the 2-position in the anomerization reaction.

2. Results and discussion

Reductive cleavage reaction of the benzylidene acetal group of a pyranoside with a 2,3-*trans* carbamate group **1a** was first carried out. When the reaction was performed at 0 °C for 30 min, anomerized α-thioglycoside **2a** and β-thioglycoside **3a** were obtained in 14% and 72% yields, respectively (entry 1, Table 1). No pyranose ring-opened diol **4a** was observed. After 6 h, β-glycoside **3a** was not obtained. Instead, α-glycoside **2a** (53%) and pyranoside-opened alcohol **4a** (11%) were obtained (entry 2). At room temperature, both α- and β-glycosides were obtained within 30 min (entry 3).

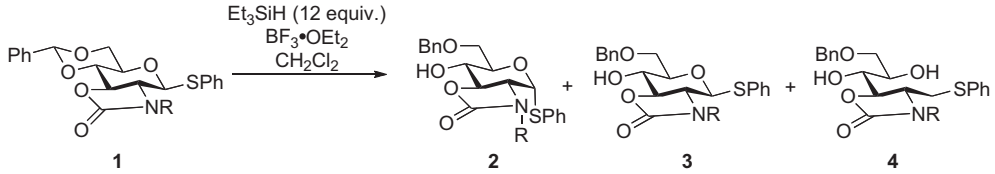
When the *N*-substituent was replaced with an electron-withdrawing *o*-nitrobenzyl group, the anomerization from the β-anomer to the α-anomer was suppressed. The β-thioglycoside **3b** was obtained in 87% yield and only a trace amount of α-glycoside **2b** was obtained at 0 °C after 30 min (entry 4). Even when the amount of $BF_3\cdot OEt_2$ was increased to 4 equiv, the α-glycoside was increased only up to 3% yield (entry 5). Similar to the *N*-benzylated substrate **1a**, the yield of α-glycoside **2b** was increased when the reaction was carried out at room temperature (entries 6 and 7). The



Scheme 2. Experimental evidence of endocyclic cleavage reaction.

The endocyclic cleavage in this series of compounds was investigated by density functional theory (DFT) calculations.[20] Transition state (TS) search calculations demonstrated that pyranosides carrying the cyclic protecting groups undergo endocyclic cleavage-induced anomerization reaction more easily than typical pyranosides.[20a] Further investigation concluded that, for glycosides electron-rich benzyl type NAP group[21] enhanced the reduction product. In the case of NAP-protected substrate **1c**, only the ring opened product **4c** was obtained even at 0 °C with 4 equiv of $BF_3\cdot OEt_2$ (entry 9) or at room temperature after 30 min (entry 10). The non-substituted substrate **1d**[17a] was submitted to the same standard reaction conditions as entry 1, but only the β-anomer

Table 1
Substituent effect on nitrogen of the carbamate group in endocyclic cleavage



Entry		R	$BF_3 \cdot OEt_2$ (equiv)	Temp (°C)	Period (h)	Product α	Yield (%) α	Product β	Yield (%) β	Product alcohol	Yield alcohol (%)
1	**1a**	Bn	2	0	0.5	**2a**	14	**3a**	72	**4a**	0
2	**1a**	Bn	2	0	6	**2a**	53	**3a**	0	**4a**	11
3	**1a**	Bn	2	rt	0.5	**2a**	49	**3a**	42	**4a**	5
4	**1b**	*o*-Nitrobenzyl	2	0	0.5	**2b**	Trace	**3b**	87	**4b**	0
5	**1b**	*o*-Nitrobenzyl	4	0	0.5	**2b**	3	**3b**	79	**4b**	0
6	**1b**	*o*-Nitrobenzyl	2	rt	0.5	**2b**	28	**3b**	55	**4b**	0
7	**1b**	*o*-Nitrobenzyl	2	rt	13	**2b**	8	**3b**	0	**4b**	34
8	**1c**	NAP	2	0	0.5	**2c**	11	**3c**	87	**4c**	0
9	**1c**	NAP	4	0	0.5	**2c**	0	**3c**	0	**4c**	68
10	**1c**	NAP	2	rt	0.5	**2c**	0	**3c**	0	**4c**	88
11	**1c**	NAP	2	rt	13	**2c**	0	**3c**	0	**4c**	83
12	**1d**	H	2	0	0.5	**2d**	0	**3d**	55	**4d**	0

3d[17a] was obtained in 55% yield (entry 12). From the above results, it was concluded that the *N*-substituent had a significant effect on the degree of anomerization caused by endocyclic cleavage.

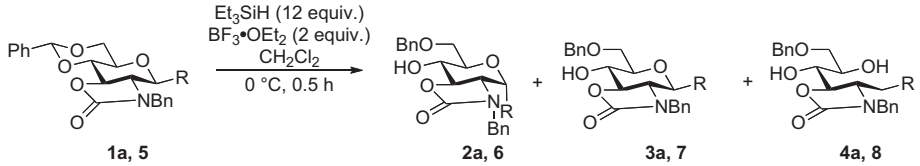
These results are explained as what follows: the cation generated by endocyclic cleavage under Lewis acidic conditions is captured by Et_3SiH giving pyranoside ring opened alcohol **4** (Scheme 2). It is clearly shown that the electron richness of the substituent on the nitrogen of the carbamate group affects the endocyclic cleavage. The electron-donating substituent increases the lifetime and population of the acyclic cation generated by endocyclic cleavage.

Next, the substituent effect at the sulfur of the thio group was investigated in the same manner (Table 2). The reaction conditions were chosen to be the same as in entry 1, Table 1. The 4-methoxyphenyl thioglycoside derivative **5b** more easily underwent anomerization than **1a** and **5a**[17i] (entry 3). On the other hand, thioglycoside **5c** with the electron-withdrawing substituent 4-methoxycarbonyl phenyl did not anomerize under the same conditions (entry 4). Similar to the substituent effect at the nitrogen atom of the carbamate, electron density at the thio group also affected the endocyclic cleavage reaction. The electronic properties at the anomeric site are supposed to influence on the stability of the acyclic cation, as well as on cyclic cation.

effect was observed for all of the Lewis acids, which worked as the promoter for anomerization (entries 1–4, 7, and 8). Although $FeCl_3$ has been known as a Lewis acid for anomerization of pyranosides,[23] when $FeCl_3$ was employed as a mediator for anomerization, the yield of α-thioglycoside **10**[20a] was reduced (entries 3 and 4). In addition to **9**[20a] and **10**, the chloride adduct of the endocyclic cation **11** was obtained in 34% yield in entry 3. Lewis acid $Cu(OTf)_2$ was recently reported as a useful Lewis acid for reductive benzylidene ring opening reactions.[24] However, in this reaction, $Cu(OTf)_2$ did not produce the α-anomer **10** in either CH_2Cl_2 or CH_3CN. The strong protic acid Tf_2NH[25] was also effective for anomerization, but the yields of both anomers were low and the bis-trifluoroimide adduct **12** was obtained in 41% yield in CH_2Cl_2 (entry 7) and 40% yield in CH_3CN (entry 8). The possible discussion on the difference of the reactivity is that the capability of the acid to the ring oxygen in terms of acidity and steric hindrance factors.

Next, the effect at the 5-position on the anomerization reaction was investigated. Substrates **14**–**16** were prepared from diol **13** (Scheme 3).[19] Selective tosylation was carried out by TsCl in pyridine and the tosylate was reduced by Bu_3SnH under typical conditions to generate the precursor to **14** in 85% yield. Subsequent acetylation gave 6-deoxy compound **14**. The selective trans-

Table 2
Substituent effect on the thio group in endocyclic cleavage



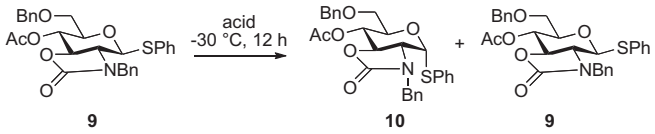
Entry		R	Product α	Yield (%) α	Product β	Yield (%) β	Product alcohol	Yield (%) alcohol
1	**1a**	SPh	**2a**	14	**3a**	72	**4a**	0
2	**5a**	STol	**6a**	trace	**7a**	66	**8a**	14
3	**5b**	OMP	**6b**	25	**7b**	37	**8b**	15
4	**5c**	4-$SPhCO_2Me$	**6c**	0	**7c**	65	**8c**	0

MP=4-methoxyphenyl.

Next, the Lewis acid and protic acid effect in the endocyclic cleavage reaction was investigated in CH_2Cl_2 and CH_3CN (Table 3). We previously reported that a CH_3CN solvent enhances the anomerization reaction.[22] The same tendency about the solvent

formation of the primary alcohol of diol **13** to the sulfide was carried out by the PhSSPh–Bu_3P combination. Subsequent methylation and acetylation gave compound **15** in 48% yield in three steps. For **16**, selective oxidation of the primary alcohol of **13**

Table 3
Lewis and protic acid effect in the anomerization reaction of pyranosides with 2,3-*trans* carbamate



Entry	Lewis acid	Solvent	**10** (%)	**9** (%)
1	BF_3•OEt_2	CH_2Cl_2	63	16
2	BF_3•OEt_2	CH_3CN	89	10
3	$FeCl_3$	CH_2Cl_2	24	25
4	$FeCl_3$	CH_3CN	36	6
5	$Cu(OTf)_2$	CH_2Cl_2	0	90
6	$Cu(OTf)_2$	CH_3CN	0	87
7	Tf_2NH	CH_2Cl_2	19	11
8	Tf_2NH	CH_3CN	20	2

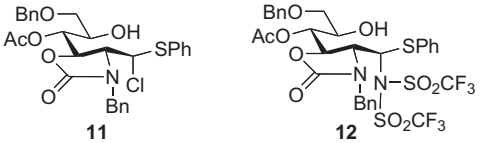
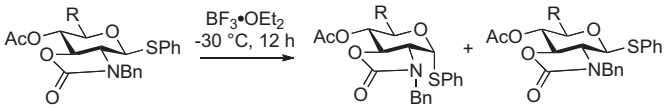
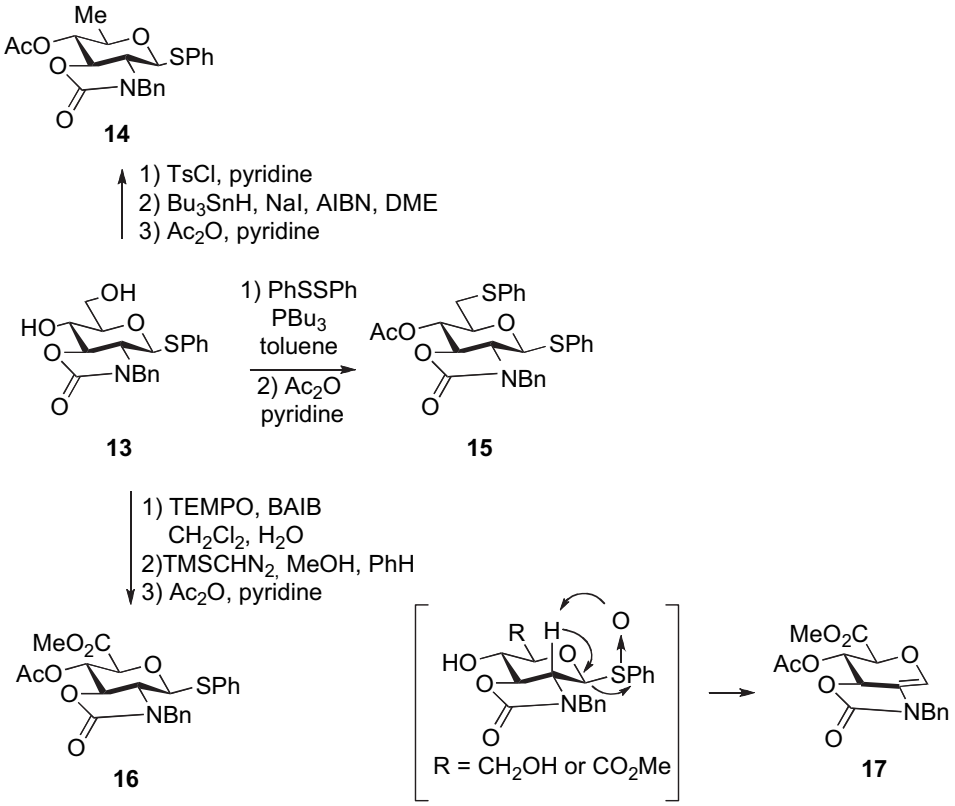


Table 4
Substitution effect at the 5-position on the anomerization reaction



Entry		R	Solvent	Product α	Yield (%) α	Product β	Yield (%) β
1	**14**	CH_3	CH_3CN	**19**	69	**14**	21
2	**14**	CH_3	CH_2Cl_2	**19**	88	**14**	16
3	**14**	CH_3	Toluene	**19**	32	**14**	60
4	**14**	CH_3	Et_2O	**19**	<1	**14**	99
5	**15**	CH_2SPh	CH_2Cl_2	**20**	21	**15**	66
6	**15**	CH_2SPh	Toluene	**20**	10	**15**	84
7	**15**	CH_2SPh	Et_2O	**20**	10	**15**	90
8	**16**	CO_2Me	CH_2Cl_2	**21**	34	**16**	57
9[a]	**18**	CH_2OAc	CH_3CN	**22**	41	**18**	9
10[a]	**18**	CH_2OAc	CH_2Cl_2	**22**	27	**18**	27
11[a]	**18**	CH_2OAc	Toluene	**22**	11	**18**	72
12[a]	**18**	CH_2OAc	Et_2O	**22**	0	**18**	86

[a] Entries 9–12 are cited from Ref. 22 for comparison.



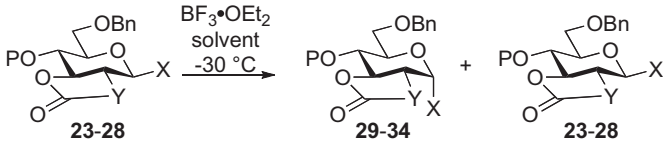
Scheme 3. Preparation of 5-position modified substrates.

was achieved by TEMPO-iodosobenzene diacetate in CH_2Cl_2/H_2O.[26] During the oxidation reaction, elimination of the sulfenyl group occurred as a side reaction to give **17**. The side reaction may have occurred by sulfide oxidation and subsequent [2,3]-sigmatropic rearrangement though the sulfoxide, although the intermediate sulfoxide was not isolated.

Then, anomerization was then conducted with the prepared compounds **14**, **15**, and **16** (Table 4). In the case of CH_3-substituted **14**, the enhancement in CH_3CN was not observed (entries 1–3). The anomerization was slightly enhanced compared to the glucosamine derivative **18**. In Et_2O, only a trace amount of anomerization product was produced (entry 4). In the case of SPh-substituted substrate **15**, the anomerization tendency was reduced. These phenomena are explained by the steric hindrance around O5 that blocks the approach of the Lewis acids to O5 for the endocyclic cleavage reaction.

It is well known that aryl pyranosides are difficult to anomerize, although the reason is not clear.[1] In order to test the efficacy of 2,3-*trans* carbamate and 2,3-*trans* carbonate groups for anomerization, the anomerization reaction of aryl pyranosides with 2,3-*trans* carbamate and 2,3-*trans* carbonate groups was investigated. A reported solvent effect for the anomerization reaction[22] was observed with thiophenyl glycoside **23** and *O*-methyl glycoside **24** (Table 5, entries 1–5). However, in the case of phenyl glycoside with 2,3-*trans* carbonate **25**, no anomerization was observed in CH_2Cl_2 or CH_3CN at −30 °C after 12 h (entries 6 and 7), whereas at 0 °C, partial anomerization occurred in CH_3CN (entry 8). More electron-donating 4-methoxyphenyl glycosides **26**–**28** were also not anomerized at −30 °C (entries 9 and 10), but the α-anomer **32** was obtained in 56% yield at 0 °C in the case of 2,3-*trans* carbonate carrying pyranoside **26** (entry 11). Similarly, pyranosides with 2,3-*trans* carbamates **27** and **28** were not anomerized at −30 °C (entries 12 and 13). In these substrates and conditions, again, the anomeric site considerably influences on the reactivity. These results suggest that electronic properties at the anomeric site are essential to discuss the nature of the reactivity of anomerization.

Table 5
Anomerization of aryl pyranosides with 2,3-*trans* carbamate and 2,3-*trans* carbonate group



Entry		X	Y	P	Solvent	Temp (°C)	Product α	Yield (%) α	Product β	Yield (%) β
1[a]	**23**	SPh	O	Ac	CH_3CN	−30	**29**	62	**23**	10
2[a]	**23**	SPh	O	Ac	CH_2Cl_2	−30	**29**	46	**23**	14
3[a,b]	**24**	OMe	O	Ac	CH_3CN	−30	**30**	71	**24**	5
4[a,b]	**24**	OMe	O	Ac	CH_2Cl_2	−30	**30**	33	**24**	47
5[a]	**24**	OMe	O	Ac	CH_3CN	−30	**30**	86	**24**	0
6	**25**	OPh	O	Ac	CH_3CN	−30	**31**	0	**25**	96
7	**25**	OPh	O	Ac	CH_2Cl_2	−30	**31**	0	**25**	90
8	**25**	OPh	O	Ac	CH_3CN	0	**31**	23	**25**	77
9	**26**	OMP	O	Bn	CH_3CN	−30	**32**	0	**26**	71
10	**26**	OMP	O	Bn	CH_2Cl_2	−30	**32**	0	**26**	75
11	**26**	OMP	O	Bn	CH_3CN	0	**32**	56	**26**	33
12	**27**	OMP	NH	Ac	CH_2Cl_2	−30	**33**	0	**27**	98
13	**28**	OMP	NBn	Ac	CH_2Cl_2	−30	**34**	0	**28**	94

MP=4-methoxyphenyl.
[a] Entries 9–12 are cited from Ref. 22 for comparison.
[b] Reaction period 1.5 h.

3. Conclusion

Here, we report the substituent effects at the nitrogen of the carbamate group, at the 5-position of the pyranoside, and at the anomeric position in the anomerization reaction via endocyclic cleavage reaction. The present study suggests that electronic properties of substituent at these sites, the acidity and the size of the Lewis acid, and solvents influence the reactivity of the anomerization reaction. These factors are supposed most likely to contribute to increasing the inner strain and/or to stabilizing the intermediate cation. The conformational distribution of the pyranoside ring is expected to be varied as the results of complex interactions between these factors. The conformational properties directly influence the stereoelectronic effect. Still, there is a possibility that other factors influencing the reactivity of anomerization exist. Further experimental and theoretical investigations on property–reactivity relationships will give better understanding of the mechanistic details on the anomerization reaction. This knowledge will enhance the synthetic utility of this endocyclic cleavage-induced anomerization reaction.

4. Experimental section

4.1. General

^1H and ^{13}C NMR spectra were recorded at ambient temperature (23–24 °C) in $CDCl_3$ using JEOL EX 400 MHz or JEOL JNM-ECP 500 MHz spectrometer. Chemical shifts are reported in parts per million relative to internal tetramethylsilane (δ=0.00 ppm) for ^1H and $CDCl_3$ (δ=77.00 ppm) for ^{13}C NMR spectra. Optical rotations were measured with a JASCO DIP-310 polarimeter. Melting points (not corrected) were measured with a YANACO micro melting point apparatus. Silica gel 60 N (spherical, neutral, Kanto Chemical Co., Inc, Tokyo) was used for flash column (40–100 μm) and open column (100–200 μm) chromatography. Silica gel 60 F_{254} (E. Merck) was used for analytical and preparative thin-layer chromatography.

4.2. Typical procedure for preparation of 1 and 5

*4.2.1. Phenyl N-benzyl-2-amino-4,6-O-benzylidene-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**1a**)*[16,27]. To an ice-cold mixture of phenyl *N*-trichloroethoxycarbonyl-2-amino-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (2.20 g, 4.11 mmol) and benzyl bromide (0.98 mL, 8.22 mmol) in DMF (40 mL) was added NaH (0.2 g, 8.22 mmol). After stirring the mixture for 30 min on the ice-water bath, the reaction mixture was warmed up to room temperature and stirred for 30 min. The mixture was quenched by addition of Et_3N (1.5 mL), diluted with EtOAc, poured into satd aqueous NH_4Cl, and extracted with EtOAc. The combined organic extracts were washed with water and brine, dried (Na_2SO_4), filtered, and concentrated. The crystalline residue was crystallized from EtOAc/hexane to give **1a** (1.88 g, 96%) as a colorless crystal. ^1H NMR δ: 7.47–7.26 (m, 15H, aromatic *H*), 5.59 (s, 1H, acetal–PhC*H*), 4.85 (d, $J_{1,2}$=10.0 Hz, 1H, H-1), 4.83 and 4.78 (d, *J*=15.5 Hz, 1H each, N–CH_2Ph), 4.32 (t, $J_{2,3}$=10.5 Hz, 1H, H-3), 4.32 (dd, $J_{5,6a}$=5.0 Hz, $J_{6a,6b}$=10.5 Hz, 1H, H-6a), 4.04 (dd, $J_{3,4}$=10.0 Hz, $J_{4,5}$=8.5 Hz, 1H, H-4), 3.90 (t, $J_{5,6b}$=10.0 Hz, 1H, H-6b), 3.57 (dddd, 1H, H-5), 3.52 (dd, 1H, H-2); ^{13}C NMR δ 158.8 (oxazolidinone, *C*=O), 136.4, 136.3, 132.6, 131.7, 129.3, 129.2, 128.7, 128.3, 128.0, 127.6 and 126.1 (aromatic *C*), 101.4 (acetal–*C*HPh), 87.7 (C-1), 78.9 (C-3), 78.4 (C-4), 72.8 (C-5), 68.2 (C-6), 61.5 (C-2), 47.7 (N–*C*H_2Ph); mp 216–217 °C; $[\alpha]_D^{24}$ −72 (*c*

1.0, $CHCl_3$); Anal. Calcd for $C_{27}H_{25}NO_5S$: C, 68.19; H, 5.30; N, 2.95. Found: C, 68.15; H, 5.17; N, 2.88.

*4.2.2. Phenyl N-o-nitrobenzyl-2-amino-4,6-O-benzylidene-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**1b**).* ^{1}H NMR δ 8.10 (d, *J*=8.0 Hz, 1H), 7.59 (t, *J*=7.2 Hz, 1H), 7.36–7.06 (m, 12H), 5.62 (s, 1H), 5.23 (d, *J*=17.6 Hz, 1H), 5.00 (d, *J*=17.6 Hz, 1H), 4.73 (d, *J*=10.0 Hz, 1H), 4.00 (t, *J*=10.8 Hz, 1H), 4.35 (dd, *J*=10.4, 4.8 Hz, 1H), 4.08 (t, *J*=10.0 Hz, 1H), 3.92 (t, *J*=10.0 Hz, 1H), 3.61 (m, 1H), 3.53 (t, *J*=10.0 Hz, 1H); ^{13}C NMR δ 158.4, 147.9, 136.1, 133.6, 133.5, 132.1, 130.8, 129.2, 129.0, 128.6, 128.2, 128.0, 127.7, 126.0, 125.2, 101.4, 86.7, 70.0, 78.2, 77.2, 72.8, 68.3, 62.4, 46.3; $[\alpha]_D^{rt}$ −7.5 (*c* 0.40, $CHCl_3$); HRMS calcd for $[C_{27}H_{24}N_2O_7S+Na]^+$ 543.1202, found 543.1175.

*4.2.3. Phenyl N-naphtyl-2-amino-4,6-O-benzylidene-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**1c**).* ^{1}H NMR δ 7.83–7.78 (m, 4H), 7.50–7.15 (m, 5H), 7.25–7.15 (m, 8H), 5.57 (s, 1H), 4.98 (d, *J*=15.6 Hz, 1H), 4.92 (d, *J*=15.6 Hz, 1H), 4.85 (d, *J*=9.6 Hz, 1H), 4.35 (t, *J*=10.8 Hz, 1H), 4.29 (dd, *J*=4.8, 10.4 Hz, 1H), 4.02 (t, *J*=8.8 Hz, 1H), 3.86 (t, *J*=10.4 Hz, 1H), 3.83–3.51 (m, 2H); ^{13}C NMR δ 158.7, 136.2, 133.6, 133.2, 132.7, 132.4, 131.5, 129.1, 129.0, 128.6, 128.5, 128.2, 127.7, 127.5, 126.9, 126.2, 126.0, 125.8, 101.4, 87.8, 79.0, 78.4, 72.8, 68.3, 61.6, 48.0; $[\alpha]_D^{24}$ −38.4 (*c* 0.5, $CHCl_3$); HRMS calcd for $[C_{31}H_{27}NO_5S+Na]^+$ 548.1508, found 548.1498.

*4.2.4. Tolyl N-benzyl-2-amino-4,6-O-benzylidene-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**5a**)*[17i]. ^{1}H NMR δ 7.44–7.29 (m, 10H), 7.15 (d, *J*=8.0 Hz, 2H), 7.09 (d, *J*=8.0 Hz, 2H), 5.57 (s, 1H), 4.84–4.74 (m, 3H), 4.32–4.27 (m, 2H), 4.01 (t, *J*=8.4 Hz, 1H), 3.87 (t, *J*=10.4 Hz, 1H), 3.53 (m, 1H), 3.52 (d, *J*=10.8 Hz, 1H), 3.48 (d, *J*=10.8 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR δ 158.7, 139.0, 136.2, 133.0. 129.8, 129.1, 128.6, 128.1, 127.9, 127.7, 127.5, 125.9, 101.3, 88.0, 78.9, 78.4, 77.2, 72.8, 68.3, 61.6, 47.8, 21.3; $[\alpha]_D^{24}$ −54.8 (*c* 1.22, $CHCl_3$); HRMS calcd for $[C_{28}H_{27}NO_5S+Na]^+$ 512.1502, found 512.1501.

*4.2.5. 4-Methoxylphenyl N-benzyl-2-amino-4,6-O-benzylidene-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**5b**).* ^{1}H NMR δ 7.44–7.26 (m, 10H), 7.17 (d, *J*=8.8 Hz, 2H), 6.78 (d, *J*=8.8 Hz, 2H), 5.56 (s, 1H), 4.84 (d, *J*=15.6 Hz, 1H), 4.76 (d, *J*=15.6 Hz, 1H), 4.69 (d, *J*=10.0 Hz, 1H), 4.31–4.26 (m, 2H), 4.00 (t, *J*=8.8 Hz, 1H), 3.87 (t, *J*=10.4 Hz, 1H), 3.79 (s, 3H), 3.49–3.44 (m, 2H); ^{13}C NMR δ 160.4, 158.8, 136.4, 136.3, 135.5, 129.2, 128.6, 128.2, 127.9, 127.5, 126.0, 121.5, 114.6, 101.3, 88.2, 78.9, 78.4, 72.7, 68.3, 61.6, 55.4, 47.8; $[\alpha]_D^{24}$ −60.5 (*c* 0.58, $CHCl_3$); Anal. Calcd for $C_{28}H_{27}NO_6S$: C, 66.52; H, 5.56; N, 2.85. Found C, 66.26; H, 5.56, N, 2.85.

*4.2.6. 4-Methoxycarbonylphenyl N-benzyl-2-amino-4,6-O-benzylidene-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**5c**).* ^{1}H NMR δ 7.92 (d, *J*=8.4 Hz, 2H), 7.45–7.26 (m, 12H), 5.58 (s, 1H), 4.93 (d, *J*=9.6 Hz, 1H), 4.78 (d, *J*=15.6 Hz, 1H), 4.73 (d, *J*=15.6 Hz, 1H), 4.37–4.30 (m, 2H), 4.05 (t, *J*=8.8 Hz, 1H), 3.91 (s, 3H), 3.91–3.86 (m, 2H), 3.56 (m, 1H), 3.54 (t, *J*=10.0 Hz, 1H); ^{13}C NMR δ 166.0, 158.5, 137.8, 136.1, 135.9, 130.6, 130.1, 129.7, 129.2, 128.6, 128.2, 127.8, 127.6, 125.9, 101.4, 86.7, 78.6, 78.3, 73.0, 68.2, 52.4, 47.9; $[\alpha]_D^{24}$ −48.1 (*c* 0.59, $CHCl_3$); Anal. Calcd for $C_{29}H_{27}NO_7S$; C, 65.28; H, 5.10; N, 2.62. Found C, 65.30; H, 5.21; N, 2.73.

4.3. General procedure for anomerization reaction of 1 and 5 (Tables 1 and 2)

To a solution of **1** or **5** (1 equiv) and Et_3SiH (12 equiv) in CH_2Cl_2 (0.077 M), $BF_3{\cdot}OEt_2$ (2 equiv) was added at 0 °C or room temperature. After certain reaction period, the reaction was quenched with satd $NaHCO_3$ and the mixture was extracted with EtOAc. The combined layers were washed with brine and dried over Na_2SO_4. After concentration, the residue was purified by preparative TLC.

*4.3.1. Phenyl N-benzyl-2-amino-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-α-D-glucopyranoside (**2a**).* ^{1}H NMR δ 7.50–7.24 (m, 15H, aromatic *H*), 5.37 (d, *J*=4.5 Hz, 1H), 4.79 (d, *J*=15.0 Hz, 1H N–CH_2Ph), 4.17 (d, *J*=15.0 Hz, 1H), 4.60 (d, *J*=12.0 Hz, 1H, CH_2Ph), 4.50 (d, *J*=12.0 Hz *CH*$_2$Ph), 4.36 (dd, *J*=12.0, *J*=9.5 Hz, 1H), 4.14 (m, *J* 1H), 4.02 (ddd, *J*=9.5, 9.5, 3.0 Hz, 1H), 3.78 (dd, *J*=4.5, 10.5 Hz, 1H), 3.70 (dd, *J*=10.5, 4.0 Hz, 1H), 3.50 (dd, *J*=12.0, 4.5 Hz, 1H), 2.71 (d, *J*=3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 137.5, 134.4, 132.9, 131.9, 129.1, 129.0, 128.9, 128.5, 128.4, 127.9 and 127.7, 84.9, 78.4, 73.6, 73.0, 69.4, 68.7, 59.6, 47.8; mp 118–119 °C; $[\alpha]_D^{22}$ +210 (*c* 1.0, $CHCl_3$); Anal. Calcd for $C_{27}H_{27}NO_5S$: C, 67.90; H, 5.70; N, 2.93. Found: C, 67.96; H, 5.64; N, 2.85.

*4.3.2. Phenyl N-benzyl-2-amino-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**3a**).* ^{1}H NMR δ: 7.40–7.22 (m), 4.77 (d, *J*=9.0 Hz, 1H, H-1), 4.74 (s, 2H), 4.58 (d, *J*=11.5 Hz, 1H), 4.55 (d, *J*=11.5 Hz, 1H), 4.07 (t, *J*=10.5 Hz, 1H), 4.01 (dddd, *J*=10.5 Hz, 10.3, *J*=8.0, 2.5 Hz, 1H), 3.79 (dd, *J*=5.0 Hz, *J*=10.0 Hz, 1H), 3.76 (dd, *J*=10.0, 5.0, 1H), 3.56 (m, 1H), 3.41 (dd, *J*=10.5, 9.0 Hz, 1H, H-2), 2.97 (d, *J*=2.5 Hz, 1H, 4-O*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 137.5, 136.2, 132.4, 132.3, 129.1, 128.6, 128.5, 128.4, 128.2, 127.9, 127.7 and 127.6, 86.7, 82.4, 79.6, 73.7, 69.7, 69.1, 60.1, 47.6; mp 125–126 °C; $[\alpha]_D^{22}$ −77 (*c* 1.0, $CHCl_3$); Anal. Calcd for $C_{27}H_{27}NO_5S$: C, 67.90; H, 5.70; N, 2.93. Found: C, 67.89; H, 5.56; N, 2.84.

*4.3.3. Phenyl N-o-nitrobenzyl-2-amino-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-α-D-glucopyranoside (**2b**).* ^{1}H NMR δ 7.86 (d, *J*=8.0 Hz, 1H), 7.61 (d, *J*=7.6 Hz, 1H), 7.50 (t, *J*=6.8 Hz, 1H), 7.35–7.15 (m, 11H), 5.34 (d, *J*=4.4 Hz, 1H), 4.95 (d, *J*=16.0 Hz, 1H), 4.58 (d, *J*=16.0 Hz, 1H), 4.54 (d, *J*=12.4 Hz, 1H), 4.45 (d, *J*=12.0 Hz, 1H), 4.34 (t, *J*=9.6 Hz, 1H), 4.08–4.02 (m, 2H), 3.78–3.64 (m, 3H), 2.85 (br s, 1H); ^{13}C NMR δ 158.7, 148.5, 137.3, 133.3, 132.3, 131.6, 131.3, 130.4, 128.9, 128.8, 128.4, 127.8, 127.8, 127.6, 124.8, 85.1, 78.6, 73.7, 72.9, 69.8, 61.7, 45.0; $[\alpha]_D^{rt}$ +88.3 (*c* 0.5, $CHCl_3$); HRMS calcd for $[C_{27}H_{26}N_2O_7S+Na]^+$ 545.1353, found 545.1347.

*4.3.4. Phenyl N-o-nitrobenzyl-2-amino-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**3b**).* ^{1}H NMR δ 8.09 (d, *J*=8.0 Hz, 1H), 7.58–7.09 (m, 13H), 5.19 (d, *J*=17.2 Hz, 1H), 4.92 (d, *J*=17. 2 Hz, 1H), 4.64 (d, *J*=9.6 Hz, 1H), 4.60 (d, *J*=12.0 Hz, 1H), 4.56 (d, *J*=12.0 Hz, 1H), 4.18–4.07 (m, 2H), 3.85–3.75 (m, 2H), 3.59 (m, 1H), 3.44 (t, *J*=10.4 Hz, 1H); ^{13}C NMR δ 159.0, 147.8, 137.4, 133.6, 133.5, 131.8, 131.4, 129.1, 128.9, 128.3, 128.2, 127.8, 127.8, 127.7, 127.6, 125.0, 85.6, 82.6, 79.8, 73.7, 69.5, 68.6, 61.0, 46.0; $[\alpha]_D^{rt}$ −30.3 (*c* 0.57, $CHCl_3$); HRMS calcd for $[C_{27}H_{26}N_2O_7S+Na]^+$ 545.1358, found 545.1384.

*4.3.5. 5-[(1R,2R)-1,2-Dihydroxy-3-(phenylmethoxy)propyl]-3-(phenylmethyl)-4-[(phenylthio)methyl]-2-oxazolidinone (**4a**).* ^{1}H NMR δ 7.34–7.20 (m, 15H), 4.71–4.62 (m, 2H), 4.55 (s, 2H), 4.02 (s, 2H), 4.02 (d, *J*=15.2 Hz, 1H), 3.85–3.80 (m, 2H), 3.70–3.69 (m, 2H), 3.52 (t, *J*=8.0 Hz, 1H), 3.15 (d, *J*=12.4 Hz, 1H), 2.89 (dd, *J*=8.4, 14.4 Hz, 1H), 2.56 (d, *J*=8.4 Hz, 1H), 2.47 (d, *J*=8.4 Hz, 1H); ^{13}C NMR δ 157.4, 137.3, 135.0, 134.1, 130.0, 129.1, 128.7, 128.4, 128.0, 127.9, 127.8, 127.7, 126.9, 77.6, 77.2, 73.6, 73.4, 71.3, 70.0, 55.5, 46.5, 36.3; $[\alpha]_D^{24}$ −21.2 (*c* 0.5, $CHCl_3$); HRMS calcd for $[C_{27}H_{29}NO_5S+Na]^+$ 502.1659, found 502.1670.

*4.3.6. Tolyl N-benzyl-2-amino-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-α-D-glucopyranoside (**6a**).* ^{1}H NMR δ 7.33–7.25 (m, 12H), 7.09 (d, *J*=8.0 Hz, 2H), 5.31 (d, *J*=4.8 Hz, 1H), 4.79 (d, *J*=14.8 Hz, 1H), 4.59 (d, *J*=12.0 Hz, 1H), 4.49 (d, *J*=12.0 Hz, 1H), 4.35 (t, *J*=12.0 Hz, 1H), 4.18–4.14 (m, 2H), 4.00 (t, *J*=9.2 Hz, 1H), 3.77 (dd, *J*=10.0, 4.4 Hz, 1H), 3.70 (dd, *J*=10.4, 3.6 Hz, 1H), 3.48 (dd, *J*=10.4, 4.4 Hz, 1H), 2.80 (br s, 1H), 2.34 (s, 3H); ^{13}C NMR δ 158.3, 138.1, 137.3, 134.3, 132.4, 129.8, 128.9, 128.8, 128.0, 128.4, 128.3, 127.8, 127.6,

85.3, 78.4, 77.2, 73.6, 72.9, 69.6, 68.8, 59.5, 47.8, 21.3; $[\alpha]_D^{24}$ +30.5 (*c* 1.0, $CHCl_3$); HRMS calcd for $[C_{28}H_{29}NO_5S+Na]^+$ 502.1117, found 502.1113.

*4.3.7. Tolyl N-benzyl-2-amino-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**7a**).* ^1H NMR δ 7.39–7.21 (m, 12H), 7.02 (d, *J*=7.6 Hz, 1H), 4.73 (s, 2H), 4.69 (d, *J*=9.2 Hz, 1H), 4.57 (d, *J*=12.0 Hz, 1H), 4.53 (d, *J*=12.0 Hz, 1H), 4.04 (t, *J*=10.4 Hz, 1H), 3.98 (m, 1H), 3.76 (m, 2H), 3.52 (m, 1H), 3.37 (t, *J*=10.8 Hz, 1H), 3.17 (br s, 1H), 2.31 (s, 3H); ^{13}C NMR δ 159.1, 138.6, 137.3, 136.1, 132.8, 129.7, 128.5, 128.3, 128.3, 128.0, 127.3, 127.6, 127.4, 87.0, 82.4, 79.5, 77.2, 73.7, 69.8, 69.2, 60.2, 47.6, 21.3; $[\alpha]_D^{24}$ −66.7 (*c* 0.81, $CHCl_3$); HRMS calcd for $[C_{28}H_{29}NO_5S+Na]^+$ 514.1659, found 514.1662.

*4.3.8. 4-Methoxyphenyl N-benzyl-2-amino-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-α-D-glucopyranoside (**6b**).* ^1H NMR δ 7.34–7.25 (m, 12H), 6.78 (d, *J*=8.4 Hz, 2H), 5.22 (d, *J*=4.4 Hz, 1H), 4.78 (d, *J*=14.8 Hz, 1H), 4.58 (d, *J*=11.6 Hz, 1H), 4.50 (d, *J*=11.6 Hz, 1H), 4.37 (t, *J*=11.2 Hz, 1H), 4.21–4.17 (m, 2H), 3.97 (m, 1H), 3.78 (s, 3H), 3.77–3.76 (m, 2H), 3.47 (dd, *J*=11.6, 4.4 Hz, 1H), 3.04 (br s, 1H); ^{13}C NMR δ 159.8, 158.4, 137.4, 134.8, 134.4, 128.8, 128.3, 128.2, 127.7, 127.6, 122.6, 114.6, 85.7, 78.4, 77.2, 73.6, 72.9, 69.6, 68.9, 59.6, 55.4, 47.9; $[\alpha]_D^{24}$ +17.7 (*c* 0.90, $CHCl_3$); Anal. Calcd for $C_{28}H_{29}NO_6S$; C, 66.25; H, 5.76; N, 2.76. Found C, 66.31; H, 5.82; N, 2.89.

*4.3.9. 4-Methoxyphenyl N-benzyl-2-amino-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**7b**).* ^1H NMR δ 7.40–7.25 (m, 10H), 7.23 (d, *J*=8.8 Hz, 2H), 6.73 (d, *J*=8.8 Hz, 2H), 4.77 (d, *J*=15.6 Hz, 1H), 4.72 (d, *J*=15.6 Hz, 1H), 4.62 (d, *J*=9.2 Hz, 1H), 4.57 (d, *J*=12.0 Hz, 1H), 4.54 (d, *J*=12.0 Hz, 1H), 4.04 (t, *J*=10.4 Hz, 1H), 3.98 (m, 1H), 3.76 (s, 5H), 3.50 (m, 1H), 3.35 (t, *J*=10.4 Hz, 1H), 3.06 (br s, 1H); ^{13}C NMR δ 160.0, 159.1, 137.3, 126.2, 135.3, 128.5, 128.4, 128.0, 127.8, 127.6, 127.4, 122.0, 114.5, 87.3, 82.4, 70.3, 77.2, 73.7, 69.9, 69.3, 60.2, 55.4, 47.6; $[\alpha]_D^{24}$ −68.7 (*c* 1.21, $CHCl_3$); HRMS calcd for $[C_{28}H_{29}NO_6S+Na]^+$ 530.1608, found 530.1611.

*4.3.10. 4-Methoxycarbonylphenyl N-benzyl-2-amino-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**7c**).* ^1H NMR δ 7.86 (d, *J*=8.8 Hz, 2H), 7.36–7.24 (m, 12H), 4.85 (d, *J*=9.6 Hz, 1H), 4.69 (s, 2H), 4.57 (d, *J*=11.6 Hz, 1H), 4.53 (d, *J*=11.6 Hz, 1H), 4.09 (t, *J*=10.0 Hz, 1H), 4.02 (m, 1H), 3.90 (s, 3H), 3.76 (d, *J*=4.4 Hz, 2H), 3.60 (m, 1H), 3.43 (t, *J*=10.8 Hz, 1H); ^{13}C NMR δ 166.2, 159.0, 138.6, 135.8, 130.3, 130.0, 129.3, 128.6, 128.4, 128.0, 127.9, 127.6, 127.6, 85.6, 82.4, 79.9, 77.2, 73.7, 69.5, 69.0, 60.1, 52.3, 47.7; $[\alpha]_D^{24}$ −76.9 (*c* 0.42, $CHCl_3$); Anal. Calcd for $C_{29}H_{29}NO_7S$; C, 65.03; H, 5.46; N, 2.62. Found C, 65.09; H, 5.50, N; 2.77.

4.4. General procedure for anomeization of 9 with various acids (Table 3)

To a solution of **9** (1 equiv) in CH_2Cl_2 (0.077 M), an acid (2 equiv) was added at −30 °C. After 12 h, the reaction was quenched with satd $NaHCO_3$. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine and dried over Na_2SO_4. After concentration, the residue was purified by preparative TLC.

*4.4.1. (1R)-1-((4R,5R)-3-Benzyl-2-oxo-4-((R)-phenylthio(1,1,1-trifluoro-N-(trifluoromethylsulfonyl)methylsulfonamido)methyl)oxazolidin-5-yl)-3-(benzyloxy)-2-hydroxypropyl acetate (**12**).* ^1H NMR δ 7.34–7.08 (m, 14H), 6.99 (d, *J*=7.6 Hz, 1H), 5.12 (dd, *J*=5.2, 2.8 Hz, 1H), 5.02 (m, 1H), 4.59 (d, *J*=11.6 Hz, 1H), 4.54 (d, *J*=11.6 Hz, 1H), 4.28 (m, 1H), 4.24 (d, *J*=2.8 Hz, 1H), 4.22 (d, *J*=18.8 Hz, 1H), 4.10 (d, *J*=18.8 Hz, 1H), 3.96 (dd, *J*=5.6, 2.4 Hz, 1H), 3.89 (dd, *J*=10.4, 2.4 Hz, 1H), 3.77 (dd, *J*=10.4, 4.0 Hz, 1H); ^{13}C NMR δ 170.0, 156.1, 137.0, 134.9, 131.2, 131.4, 129.8, 128.7, 128.5, 128.4, 128.0, 127.9, 127.9, 126.9, 126.5, 77.2, 76.8, 73.8, 72.0, 71.9, 69.1, 57.3, 50.7, 42.8, 21.2.

*4.4.2. Phenyl N-benzyl-2-amino-4-O-acetyl-2-N,3-O-carbonyl-2,6-O-dideoxy-1-thio-β-D-glucopyranoside (**14**).* To a solution of diol **13** (1.83 g, 4.72 mmol) in pyridine (20 mL), TsCl (1.17 g, 6.14 mmol) was added at 0 °C. The mixture was stirred at room temperature overnight. After evaporation of the solvent, the residue was partitioned between EtOAc and satd $NaHCO_3$. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the extract over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography to give the 6-tosylate (2.03 g, 80%). To the suspension of tosylate (0.64 g, 1.18 mmol) and NaI (355 mg, 2.37 mmol) in DME (10 mL), Bu_3SnH (0.53 mL, 1.95 mmol) was added. Then, AIBN (20 mg) was added. The mixture was refluxed for 4 h under N_2 atmosphere. After cooling the mixture to room temperature, aqueous 10% KF was added. After filtration the mixture through Celite, the aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the mixture over Na_2SO_4, the solvent was evaporated. The residue was dissolved in pyridine (10 mL) and Ac_2O (3 mL) was added. After 1 h, the mixture was concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 7:3) to give the product **14** (0.40 g, 91%).

^1H NMR δ 7.34–7.12 (m, 10H), 4.95 (t, *J*=8.8 Hz, 1H), 4.69–4.67 (m, 3H), 4.06 (t, *J*=10.8 Hz, 1H), 3.53 (m, 1H), 3.44 (t, *J*=7.2 Hz, 1H), 2.05 (s, 3H), 1.23 (d, *J*=6.0 Hz, 3H); ^{13}C NMR δ 169.2, 158.6, 135.8, 132.4, 131.9, 129.0, 128.9, 128.6, 128.4, 128.0, 127.5, 86.5, 80.0, 75.8, 71.9, 60.1, 47.6, 20.9, 17.8; $[\alpha]_D^{24}$ −54.5 (*c* 1.39, $CHCl_3$); HRMS calcd for $[C_{22}H_{23}NO_5+Na]^+$ 436.1189 found 436.1191.

*4.4.3. Phenyl N-benzyl-2-amino-4-O-acetyl-2-N,3-O-carbonyl-2,6-dideoxy-6-phenylthio-1-thio-β-D-glucopyranoside (**15**).* To a solution of diol **13** (361.5 mg, 0.934 mmol) in toluene (5 mL), PBu_3 (0.47 mmol, 1.88 mmol), and PhSSPh (408 mg, 1.88 mmol) were added at room temperature. After overnight, the mixture was evaporated and the residue was purified by silica gel column chromatography (hexane/EtOAc 7:3) to give the sulfide (445 mg, quant.). The sulfide (445 mg, 0.934 mmol) was dissolved in pyridine (2 mL), and Ac_2O (1 mL) was added. After stirring the mixture for 2 h, the volatile materials were removed in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc 4:1) to give the product **15** (233 mg, 48%, two steps); ^1H NMR δ 7.40–7.18 (m, 15H), 5.20 (t, *J*=8.8 Hz, 1H), 4.75 (s, 2H), 4.73 (d, *J*=10.0 Hz, 1H), 4.10 (t, *J*=10.8 Hz, 1H), 3.64 (m, 1H), 3.52 (t, *J*=9.6 Hz, 1H), 3.15 (dd, *J*=14.0, 2.8 Hz, 1H), 3.08 (dd, *J*=14.0, 8.0 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR δ 169.1, 158.4, 153.7, 135.6, 132.7, 132.1, 131.8, 129.6, 129.5, 129.1, 128.9, 128.9, 128.8, 128.6, 128.5, 128.1, 127.6, 126.4, 87.1, 79.7, 78.3, 70.3, 60.5, 60.4, 47.7, 36.1, 20.8; $[\alpha]_D^{24}$ 3.3 (*c* 0.90, $CHCl_3$); Anal. Calcd for $C_{28}H_{27}NO_5S_2$: C, 64.47, H, 5.22, N, 2.69. Found C, 64.33, H, 5.26, N, 2.63.

*4.4.4. Phenyl N-benzyl-2-amino-4-O-acetyl-6-carbomethoxy-2-N,3-O-carbonyl-2,6-dideoxy-1-thio-β-D-glucopyranoside (**16**).* To a suspension of diol **13** (0.60 g, 1.69 mmol) in CH_2Cl_2 (2.5 mL) and H_2O (0.5 mL), iodosobenzene diacetate (BAIB) (1.40 g, 4.23 mmol) and TEMPO (100 mg, 0.64 mmol) was added at room temperature. After 30 min, the mixture was diluted with $CHCl_3$ and 1 M HCl. The aqueous layer was extracted with $CHCl_3$. The combined layers were washed with brine and dried over Na_2SO_4. After filtration, the solvent was removed in vacuo. The residue was roughly purified by silica gel column chromatography ($CHCl_3$/EtOAc 4:1 to $CHCl_3$/MeOH 9:1). The residue was dissolved in PhH (5 mL) and MeOH (5 mL), $TMSCHN_2$ (4.0 M in hexane) was added until the color of reaction mixture became yellow. After evaporation, the residue was

dissolved in pyridine (5 mL) and Ac_2O (3 mL) was added. After 1 h, volatile material was evaporated. The crude was purified by preparative TLC (toluene/EtOAc 4:1) to give product **16** (432 mg, 56%, three steps) together with glycal **17** (170 mg, 26%, three steps) ^{1}H NMR δ 7.32–7.22 (m, 10H), 5.42 (dd, J=10.0, 6.4 Hz, 1H), 4.86 (d, J=9.6 Hz, 1H), 4.74 (d, J=15.6 Hz, 1H), 4.59 (d, J=15.6 Hz, 1H), 4.19 (t, J=11.6 Hz, 1H), 4.09 (m, 2H), 3.74 (s, 3H), 3.63 (m, 1H), 2.05 (s, 3H); ^{13}C NMR δ 169.31, 169.41, 158.25, 135.93, 132.73, 131.50, 129.08, 128.68, 128.65, 127.94, 127.68, 87.45, 77.63, 69.42, 59.62, 53.08, 47.81, 20.56; $[\alpha]_D^{24}$ −136.0 (c 2.0, $CHCl_3$); HRMS calcd for $[C_{23}H_{23}NO_7S+Na]^+$ 480.1087, found 480.1096. glycal **17**; ^{1}H NMR δ 7.34–7.22 (m, 5H), 5.90 (d, J=2.8 Hz, 1H), 5.33 (t, J=9.6 Hz, 1H), 4.73 (d, J=14.8 Hz, 1H), 4.65 (t, J=10.4 Hz, 1H), 4.27 (d, J=9.2 Hz, 1H), 4.07 (d, J=14.8 Hz, 1H), 4.06 (m, 1H), 3.68 (s, 3H), 3.55 (dd, J=11.2, 2.8 Hz, 1H), 2.06 (s, 3H), ^{13}C NMR δ 168.85, 166.18, 157.14, 133.42, 129.16, 128.77, 128.65, 87.21, 72.82, 72.41, 68.12, 60.75, 53.29, 48.12, 20.59; $[\alpha]_D^{24}$ +15.0 (c 1.0, $CHCl_3$).

4.5. General procedure for anomerization of 14–16 and 18 (Table 4)

To a solution of β-anomer (1 equiv) in solvent (0.077 M), $BF_3\cdot OEt_2$ (2 equiv) was added at −30 °C. After 12 h, the reaction was quenched with satd $NaHCO_3$. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine and dried over Na_2SO_4. After concentration, the residue was purified by preparative TLC.

*4.5.1. Phenyl N-benzyl-2-amino-4-O-acetyl-2-N,3-O-carbonyl-2,6-O-dideoxy-1-thio-α-D-glucopyranoside (**19**).* ^{1}H NMR δ 7.41–7.21 (m, 10H), 5.31 (d, J=4.8 Hz, 1H), 4.95 (t, J=9.2 Hz, 1H), 4.80 (d, J=14.8 Hz, 1H), 4.39 (dd, J=12.0, 10.4 Hz, 1H), 4.19 (m, 1H), 4.13 (d, J=14.8 Hz, 1H), 3.56 (dd, J=12.0, 4.4 Hz, 1H), 2.11 (s, 3H), ^{13}C NMR δ 169.2, 157.9, 134.0, 132.7, 131.6, 129.1, 128.9, 128.7, 128.3, 127.9, 84.6, 75.8, 72.9, 68.8, 60.1, 47.9, 20.9, 17.0; $[\alpha]_D^{24}$ +172.8 (c 1.13, $CHCl_3$); Anal. Calcd for $C_{22}H_{23}NO_5$: C, 63.90, H, 5.61, N, 3.39. Found C, 63.84, H, 5.62, N, 3.34.

*4.5.2. Phenyl N-benzyl-2-amino-4-O-acetyl-2-N,3-O-carbonyl-2,6-dideoxy-6-phenylthio-1-thio-α-D-glucopyranoside (**20**).* ^{1}H NMR δ 7.47–7.17 (m, 15H), 5.34 (d, J=4.8 Hz, 1H), 5.16 (t, J=9.2 Hz, 1H), 4.79 (d, J=14.8 Hz, 1H), 4.37 (t, J=10.0 Hz, 1H), 4.32 (m, 1H), 4.15 (d, J=15.8 Hz, 1H), 3.58 (dd, J=12.0, 4.4 Hz, 1H), 3.16 (dd, J=14.0, 2.8 Hz, 1H), 3.09 (dd, J=14. 0, 8.0 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR δ 169.0, 157.8, 137.3, 134.4, 132.2, 129.0, 128.8, 128.7, 128.2, 128.2, 127.9, 127.7, 127.6, 85.8, 74.2, 73.5, 70.1, 68.3, 66.1, 56.1, 48.2, 20.8; $[\alpha]_D^{24}$ +255.3 (c 1.0 $CHCl_3$); Anal. Calcd for $C_{28}H_{27}NO_5S_2$: C, 64.47, H, 5.22, N, 2.69. Found C, 64.11, H, 5.32, N, 2.63.

*4.5.3. Phenyl N-benzyl-2-amino-4-O-acetyl-6-carbometoxy-2-N,3-O-carbonyl-2,6-dideoxy-1-thio-α-D-glucopyranoside (**21**).* ^{1}H NMR δ 7.32–7.18 (m, 10H), 5.40 (d, J=4.4 Hz, 1H), 5.30 (t, J=9.2 Hz, 1H), 4.75 (d, J=14.8 Hz, 1H), 4.60 (d, J=9.6 Hz, 1H), 4.41 (t, J=12.0 Hz, 1H), 4.12 (d, J=14.8 Hz, 1H), 3.67 (s, 3H), 3.61 (dd, J=12.0, 4.8 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR δ 169.1, 167.2, 157.6, 131.8129.3, 129.2, 128.8, 128.7, 128.6, 128. 3, 85.5, 74.8, 70.8, 69.5, 59.5, 53.1, 48.0, 20.6.

*4.5.4. Phenyl 4-O-acetyl-6-O-benzyl-2-O,3-O-carbonyl-4-β-D-glucopyranoside (**25**).* To a solution of phenyl 4,6-*O*-benzylidene-β-D-glucopyranoside[28] (3.44 g, 10.0 mmol) in Et_3N (6 mL) and CH_2Cl_2 (20 mL), triphosgene (1.48 g, 5.00 mol) was added in some portion at −20 °C. After 2 h, the reaction was quenched with satd $NaHCO_3$ and the aqueous layer was extracted with $CHCl_3$. The combined layers were washed with brine and dried over Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography ($CHCl_3$/EtOAc 4:1–1:1) to give the pyranoside with 2,3-*trans* carbonate. Then, the benzylidene product (2.05 g, 5.54 mmol) was suspended in CH_2Cl_2 (30 mL) and Et_3SiH (6 mL) was added. $BF_3\cdot OEt_2$ (1.36 mL, 11.1 mmol) was added at 0 °C. After 1 h, the reaction was quenched with satd $NaHCO_3$ and extracted with $CHCl_3$. The combined layers were washed with brine and concentrated. The residue was dissolved in pyridine (10 mL) and Ac_2O (5 mL) was added. After stirring the mixture for 1 h, the volatile reagents were evaporated in vacuo. The residue was purified by silica gel column chromatography ($CHCl_3$/EtOAc 4:1) to give the product **25** (1.89 mg, 46%, three steps).

^{1}H NMR δ 7.25–7.24 (m, 7H), 7.07–7.03 (m, 3H), 5.40 (d, J=7.2 Hz, 1H), 5.35 (t, J=9.2 Hz, 1H), 4.52 (d, J=11.6 Hz, 1H), 4.46–4.32 (m, 3H), 3.44 (m, 1H), 3.63 (m, 2H), 2.00 (s, 3H); ^{13}C NMR δ 169.0, 155.9, 152.6, 137.3, 129.6, 128.3, 127.8, 127.7, 123.5, 117.1, 97.7, 79.5, 77.3, 73.6, 68.7, 68.4, 20.6; $[\alpha]_D^{24}$ −64 (c 1.0, $CHCl_3$); HRMS calcd for $[C_{22}H_{22}O_8+Na]^+$ 447.1207, found 437.1209.

*4.5.5. Phenyl 4-O-acetyl-6-O-benzyl-2-O,3-O-carbonyl-α-D-glucopyranoside (**31**).* ^{1}H NMR δ 7.33–7.26 (m, 7H), 7.12–7.08 (m, 3H), 5.86 (d, J=2.8 Hz, 1H), 5.54 (t, J=9.6 Hz, 1H), 4.99 (t, J=11.2 Hz, 1H), 4.59 (d, J=12.0 Hz, 1H), 4.44 (d, J=12.0 Hz, 1H), 4.43 (t, J=9.6 Hz, 1H), 3.97 (m, 1H), 3.61–3.52 (m, 2H); ^{13}C NMR δ 169.6, 155.6, 152.6, 137.1, 129.7, 128.3, 127.8, 127.8123.7, 116.9, 93.5, 77.2, 76.6, 73.6, 72.0, 68.2, 67.1, 20.7; $[\alpha]_D^{24}$ 67.4 (c 0.65 $CHCl_3$); HRMS calcd for $[C_{22}H_{22}O_8+Na]^+$ 447.1207, found 447.1212.

*4.5.6. 4-Methoxyphenyl 2-O,3-O-carbonyl-4,6-O-dibenzyl-β-D-glucopyranoside (**26**).* To a solution of 4-methoxyphenyl 4,6-*O*-dibenzyl-β-D-glucopyranoside[29] (2.00 g, 4.29 mmol) in Et_3N (2 mL) and CH_2Cl_2 (20 mL), triphosgene (450 mg, 1.52 mol) was added in some portion at −20 °C. After 2 h, the reaction was quenched with satd $NaHCO_3$ and the aqueous layer was extracted with $CHCl_3$. The combined layers were washed with brine and dried over Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography ($CHCl_3$/EtOAc 4:1–1:1) to give the pyranoside with 2,3-*trans* carbonate **26** (1.59 g, 75%).

^{1}H NMR δ 7.34–7.25 (m, 10H), 7.02 (d, J=8.8 Hz, 2H), 6.80 (d, J=8.8 Hz, 2H), 5.23 (d, J=7.6 Hz, 1H), 4.80 (d, J=11.2 Hz, 1H), 4.56 (t, J=12.8 Hz, 1H), 4.50 (d, J=11.2 Hz, 1H), 4.37 (dd, J=11.6, 8.8 Hz, 1H), 4.26 (dd, J=11.2, 7.2 Hz, 1H), 4.02 (t, J=9.2 Hz , 1H), 3.75 (s, 3H), 3.78–3.71 (m, 4H); ^{13}C NMR δ 169.2, 158.5, 149.0, 135.8, 135.6, 132.8, 129.6, 129.0, 128.9, 128.6, 128.5, 128.1, 127.6, 126.5, 87.0, 79.7, 78.2, 70.2, 60.4, 47.6, 36.0, 20.7; $[\alpha]_D^{24}$ −11.5 (c 0.92, $CHCl_3$); HRMS calcd for $[C_{28}H_{28}O_8+Na]^+$515.1676, found 515.1680.

*4.5.7. 4-Methoxyphenyl-2-amino-4-O-acetyl 6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**27**).* From 4-methoxyphenyl-2-amino-4,6-*O*-benzylidene-2-*N*,3-*O*-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside,[30] **27** was prepared by a similar procedure as **25**.

^{1}H NMR δ 7.30–7.26 (m, 5H), 6.99 (d, J=9.2 Hz, 2H), 6.80 (d, J=9.2 Hz, 2H), 5.35 (dd, J=10.0, 8.4 Hz, 1H), 5.24 (s, 1H), 5.09 (d, J=8.0 Hz, 1H), 4.55 (d, J=12.0 Hz, 1H), 4.49 (d, J=12.0 Hz, 1H), 4.24 (t, J=12.0 Hz, 1H), 3.84–3.79 (m, 2H), 3.76 (s, 3H), 3.67–3.63 (m, 2H); 2.02 (s, 3H); ^{13}C NMR δ 169.1, 158.1, 155.6, 149.9, 137.4, 128.3, 127.7, 118.4, 114.6, 100.3, 79.2, 77.2, 76.7, 73.6, 68.8, 68.3, 59.2, 55.7, 20.8; $[\alpha]_D^{rt}$ −50 (c 1.4, $CHCl_3$); HRMS calcd for $[C_{23}H_{25}NO_8+Na]^+$ 466.1478, found 466.1472.

*4.5.8. 4-Methoxyphenyl-N-benzyl-2-amino-4-O-acetyl-6-O-benzyl-2-N,3-O-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**28**).* Compound **28** was prepared in a similar manner as **1a** and **25** from 4-methoxyphenyl *N*-trichloroethoxycarbonyl-2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside.

^{1}H NMR δ 7.41–7.22 (m, 10H), 6.86 (d, J=8.8 Hz, 2H), 6.76 (d, J=8.8 Hz, 2H), 5.25 (dd, J=10.0, 8.0 Hz, 1H), 5.09 (d, J=7.2 Hz, 1H), 4.61 (d, J=15.2 Hz, 1H), 4.51 (d, J=10.8 Hz, 1H), 4.50–4.43 (m, 3H),

4.16 (t, J=2.0 Hz, 1H), 3.79 (m, 1H), 3.76 (s, 3H), 3.70–3.59 (m, 3H), 2.01 (s, 3H); ^{13}C NMR δ 169.1, 158.2, 155.6, 149.8, 137.4, 135.5, 128.6, 128.6, 128.2, 127.6, 118.4, 114.5, 100.6, 77.2, 76.9, 76.8, 73.6, 68.9, 68.5, 60.5, 55.7, 48.3, 20.8; $[\alpha]_D^{24}$ −38.8 (c 0.84, $CHCl_3$); HRMS calcd for $[C_{30}H_{31}NO_8+Na]^+$ 556.1947, found 556.1957.

*4.5.9. Phenyl 4-O-acetyl-6-O-benzyl-2-O,3-O-carbonyl-α-D-glucopyranoside (**31**).* ^{1}H NMR δ 7.33–7.26 (m, 7H), 7.12–7.08 (m, 3H), 5.86 (d, J=2.8 Hz, 1H), 5.54 (t, J=9.6 Hz, 1H), 4.99 (t, J=11.2 Hz, 1H), 4.59 (d, J=12.0 Hz, 1H), 4.44 (d, J=12.0 Hz, 1H), 4.43 (t, J=9.6 Hz, 1H), 3.97 (m, 1H), 3.61–3.52 (m, 2H); ^{13}C NMR δ 169.6, 155.6, 152.6, 137.1, 129.7, 128.3, 127.8, 127.8, 123.7, 116.9, 93.5, 77.2, 76.6, 73.6, 72.0, 68.2, 67.1, 20.7; $[\alpha]_D^{24}$ +30.5 (c 1.0, $CHCl_3$), 67.4 (c 0.65, $CHCl_3$); HRMS calcd for $[C_{22}H_{22}O_8+Na]^+$ 447.1207, found 447.1212.

*4.5.10. 4-Methoxyphenyl-2-O,3-O-carbonyl-4,6-O-dibenzyl-α-D-glucopyranoside (**32**).* ^{1}H NMR δ 7.24–7.18 (m, 10H), 6.96 (d, J=9.2 Hz, 2H), 6.75 (d, J=9.2 Hz, 2H), 5.66 (d, J=2.0 Hz, 1H), 4.97 (t, J=11.6 Hz, 1H); 4.76 (d, J=10.8 Hz, 1H), 4.53 (d, J=12.0 Hz, 1H), 4.46 (d, J=11.2 Hz, 1H), 4.39 (d, J=12.4 Hz, 1H), 4.24 (dd, J=11.6, 2 Hz, 1H), 4.07 (d, J=9.2 Hz, 1H), 3.86 (m, 1H), 3.70 (s, 3H), 3.72–3.60 (m, 4H); ^{13}C NMR δ 155.7, 153.4, 129.7, 137.5, 136.8, 128.4, 128.4, 128.1, 128.0, 127.8, 118.3, 115.7, 94.3, 80.2, 76.9, 74.4, 73.5, 73.0, 72.9, 67.4, 55.6; $[\alpha]_D^{24}$ +30.5 (c 1.0, $CHCl_3$), 124 (c 1.05, $CHCl_3$); HRMS calcd for $[C_{21}H_{21}O_7+Na]^+$ 408.1180, found 408.1178.

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References and notes

1. (a) Cordes, E. H. *Prog. Phys. Org. Chem.* **1967**, *4*, 1–44; (b) Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581–603; (c) van Eikeren, P. *J. Org. Chem.* **1980**, *45*, 4641–4645; (d) Kirby, A. J. *Acc. Chem. Res.* **1984**, *17*, 305–311; (e) Jones, G.; Kirby, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 444–445; (f) Bennet, A. J.; Sinnott, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 7287–7294; (g) Sinnott, M. L. *Adv. Phys. Org. Chem.* **1988**, *24*, 113–204; (h) Ratclife, A. J.; Mootoo, D. R.; Andrews, C. W.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1989**, *111*, 7661–7662; (i) Sinnott, M. L. *Chem. Rev.* **1990**, *90*, 1171–1202; (j) Sugiura, M.; Hagio, H.; Hirabayashi, R.; Kobayashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 12510–12517 and references therein; (k) Deslongchamps, G.; Deslongchamps, P. *Org. Biomol. Chem.* **2011**, *9*, 5321–5333.
2. (a) Guidon, Y.; Anderson, P. C. *Tetrahedron Lett.* **1987**, *28*, 2485–2488; (b) MacPhail, D. R.; Lee, J. R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1992**, *114*, 1905–1906; (c) Franck, R. W. *Bioorg. Chem.* **1992**, *20*, 77–88; (d) Liras, J. L.; Anslyn, E. V. Molecular Design and Bioorganic Catalysis In. *NATO SAI Ser.*; Wilcox, C. S., Hamilton, A. D., Eds.; Kluwer Academic: Boston, MA, 1996; Vol. 478, pp 1–14; (e) Horenstein, N. A. *Adv. Phys. Org. Chem.* **2006**, *41*, 275–314; (f) Mikkola, S.; Oivanen, M. *ARKIVOC* **2008**, 39–53.
3. (a) Crich, D.; Chandrasekara, N. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 5386–5389; (b) Galonić, D. P.; Gin, D. Y. *Nature* **2007**, *446*, 1000–1007; (c) Boltje, T. J.; Buskas, T.; Boons, G.-J. *Nat. Chem.* **2009**, *1*, 611–622; (d) Walvoort, M. T. C.; Dinkelaar, J.; van den Bos, L. J.; Lodder, G.; Overkleeft, H. S.; Codée, J. D. C.; Van der Marel, G. A. *Carbohydr. Res.* **2010**, *345*, 1252–1263.
4. (a) Deslongchamps, P. *Pure Appl. Chem.* **1993**, *65*, 1161–1178; (b) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983; (c) Kirby, A. J. *Stereoelectronic Effects*; Oxford University: USA, 1996.
5. (a) Gorenstein, D. G.; Findlay, J. B.; Luxon, B. A.; Kar, D. *J. Am. Chem. Soc.* **1977**, *99*, 3473–3479; (b) Hosie, L.; Marshall, P. J.; Sinnott, M. L. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1121–1131.
6. Haworth, W. N.; Owen, L. N.; Smith, F. *J. Chem. Soc.* **1941**, 88–102.
7. Post, C. B.; Karplus, M. *J. Am. Chem. Soc.* **1986**, *108*, 1317–1319.
8. Later, half-chair conformation of pyranoside in hen egg-white lysozyme by high-resolution crystallographic analyses were reported, see; (a) Chipman, D. M.; Sharon, N. *Science* **1969**, *165*, 454–465; (b) Ford, L. O.; Johnson, L. N.; Machin, P. A.; Phillips, D. C.; Tjian, R. *J. Mol. Biol.* **1974**, *88*, 349–371; (c) Strynadka, N. C. J.; James, M. N. G. *J. Mol. Biol.* **1991**, *220*, 401–424; (d) Hadfield, A. T.; Harvey, D. J.; Archer, D. B.; MacKenzie, D. A.; Jeenes, D. J.; Radford, S. E.; Lowe, G.; Dobson, C. M.; Johnson, L. N. *J. Mol. Biol.* **1994**, *243*, 856–872.
9. Gupta, R. B.; Franck, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 6554–6556.
10. McPhail, D. R.; Lee, J. R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1992**, *113*, 1905–1906.
11. (a) Liras, J. L.; Anslyn, E. V. *J. Am. Chem. Soc.* **1994**, *116*, 2645–2646; (b) Liras, J. L.; Lynch, V. M.; Anslyn, E. V. *J. Am. Chem. Soc.* **1997**, *119*, 8191–8200.
12. Deslongchamps, P.; Li, S.; Dory, Y. L. *Org. Lett.* **2004**, *6*, 505–508.
13. O'Brien, C.; Poláková, M.; Pitt, N.; Tosin, M.; Murphy, P. V. *Chem.—Eur. J.* **2007**, *13*, 902–909.
14. For reviews of 1,2-*cis* glycosylation; (a) Demchenko, A. V. *Curr. Org. Chem.* **2003**, *7*, 35–79; (b) Demchenko, A. V. *Synlett* **2003**, 1225–1240; (c) Fairbanks, A. J. *Synlett* **2003**, 1945–1958.
15. Other examples of 1,2-*cis* amino glycoside preparation; (a) Kochetkov, N. K.; Klimov, E. M.; Malysheva, N. N.; Demchenko, A. V. *Carbohydr. Res.* **1993**, *242*, C7–C10; (b) Winterfeld, G. A.; Schmidt, R. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2654–2657; (c) Imamura, A.; Ando, H.; Korogi, S.; Tanabe, G.; Muraoka, O.; Ishida, H.; Kiso, M. *Tetrahedron Lett.* **2003**, *44*, 6725–6728; (d) Bongat, A. F. G.; Demchenko, A. V. *Carbohydr. Res.* **2007**, *342*, 374–406; (e) Park, J.; Kawatkar, S.; Kim, J.-H.; Boons, G.-J. *Org. Lett.* **2007**, *9*, 1959–1962; (f) Koshiba, M.; Suzuki, N.; Arihara, R.; Tsuda, T.; Nambu, H.; Nakamura, S.; Hashimoto, S. *Chem.—Asian J.* **2008**, *3*, 1664–1677; (g) Ryan, D. A.; Gin, D. Y. *J. Am. Chem. Soc.* **2008**, *130*, 15228–15229; (h) Wei, G.; Lv, X.; Du, Y. *Carbohydr. Res.* **2008**, *343*, 3096–3099; (i) Ajayi, K.; Thakur, V. V.; Lapo, R. C.; Knapp, S. *Org. Lett.* **2010**, *12*, 2630–2633.
16. Manabe, S.; Ishii, K.; Ito, Y. *J. Am. Chem. Soc.* **2006**, *128*, 10666–10667.
17. For synthetic utility of 2,3-*trans* carbamate donor; (a) Benakli, K.; Zha, C.; Kerns, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 9461–9462; (b) Kerns, R. J.; Zha, C.; Benakli, K.; Liang, Y.-Z. *Tetrahedron Lett.* **2003**, *44*, 8069–8072; (c) Wei, P.; Kerns, R. J. *Tetrahedron Lett.* **2005**, *46*, 6901–6905; (d) Wei, P.; Kerns, R. J. *J. Org. Chem.* **2005**, *70*, 4195–4198; (e) Bohn, M. L.; Colombo, M. I.; Stortz, C. A.; Rúveda, E. A. *Carbohydr. Res.* **2006**, *341*, 1096–1104; (f) Manabe, S.; Ishii, K.; Ito, Y. *J. Org. Chem.* **2007**, *72*, 6107–6115; (g) Geng, Y.; Zhang, L.-H.; Ye, X.-S. *Chem. Commun.* **2008**, 597–599; (h) Geng, Y.; Zhang, L.-H.; Ye, X.-S. *Tetrahedron* **2008**, *64*, 4949–4958; (i) Manabe, S.; Ishii, K.; Ito, Y. *Trends Glycosci. Glycotech.* **2008**, *20*, 187–202; (j) Lu, Y.-S.; Li, Q.; Wang, Y.; Ye, X.-S. *Synlett* **2010**, 1519–1524; (k) Manabe, S.; Ishii, K.; Ito, Y. *Eur. J. Org. Chem.* **2011**, 497–516; (l) Manabe, S.; Aihara, Y.; Ito, Y. *Chem. Commun.* **2011**, 9720–9722.
18. (a) Crich, D.; Vinod, A. U. *J. Org. Chem.* **2005**, *70*, 1291–1296; (b) Boysen, M.; Gemma, E.; Lahmann, M.; Oscarson, S. *Chem. Commun.* **2005**, 3044–3046; (c) Olsson, J. D. M.; Eriksson, L.; Lahmann, M.; Oscarson, S. *J. Org. Chem.* **2008**, *73*, 7181–7188.
19. Manabe, S.; Ishii, K.; Hashizume, D.; Koshino, H.; Ito, Y. *Chem.—Eur. J.* **2009**, *15*, 6894–6901.
20. (a) Satoh, H.; Hutter, J.; Luthi, P.-H.; Manabe, S.; Ishii, K.; Ito, Y. *Eur. J. Org. Chem.* **2009**, 1127–1131; (b) Satoh, H.; Manabe, S.; Ito, Y.; Lüthi, H. P.; Laino, T.; Hutter, J. *J. Am. Chem. Soc.* **2011**, *133*, 5610–5619.
21. Gaunt, M. J.; Yu, J.; Spencer, J. B. *J. Org. Chem.* **1998**, *63*, 4172–4173.
22. Manabe, S.; Ito, Y. *Tetrahedron Lett.* **2009**, *50*, 4827–4829.
23. Ikemoto, N.; Kim, O. K.; Lo, L. C.; Satyanarayana, V.; Chang, M.; Nakanishi, K. *Tetrahedron Lett.* **1992**, *33*, 4295–4298.
24. Shie, C.-R.; Tzeng, Z.-H.; Kulkarni, S. S.; Uang, B.-J.; Hsu, C.-Y.; Hung, S.-C. *Angew. Chem., Int. Ed.* **2005**, *44*, 1665–1668.
25. (a) Foropoulos, J., Jr.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720–3723; (b) Juhasz, M.; Hoffmann, S.; Stoyanov, E.; Kim, K.-C.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5352–5355; (c) Sun, J.; Kozmin, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 13512–13513; (d) Payette, J. N.; Yamamoto, H. *J. Am. Chem. Soc.* **2007**, *129*, 9536–9537.
26. Epp, J. B.; Widlanski, T. S. *J. Org. Chem.* **1999**, *64*, 293–295.
27. For pyranoside with N-alkyl 2,3-trans carbamate preparation from 2-amino carbamate; Takahashi, S.; Inoue, H.; Kuzuhara, H. *J. Carbohydr. Chem.* **1995**, *14*, 273–285.
28. Reeves, R. *J. Am. Chem. Soc.* **1948**, *70*, 3963–3964.
29. Liu, C.; Skogman, F.; Cai, Y.; Lowary, T. L. *Carbohydr. Res.* **2007**, *32*, 2818–2825.
30. Matsuzaki, Y.; Fujita, S.; Ishikawa, K. **2006**, JP2006143694.