Direct α-Selective Glycosylations of Acetyl-Protected 2-Deoxy- and 2,6-Dideoxythioglycosides by Preactivation Protocol

Yin-Suo Lu,[a,b] Qin Li,[a,b] Yuan Wang,[a,b] Xin-Shan Ye*[a,b]

[a] The State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Xue Yuan Rd No. 38, Beijing 100191, P. R. of China

[b] School of Pharmaceutical Sciences, Peking University, Xue Yuan Rd No. 38, Beijing 100191, P. R. of China
Fax +86(10)62014949; E-mail: xinshan@bjmu.edu.cn

Received 4 March 2010

Dedicated to Professor Henry N. C. Wong on the occasion of his 60th birthday

Abstract: An efficient preactivation protocol for the highly α-stereoselective glycosylation of 2-deoxy- and 2,6-dideoxysugars has been developed using acetyl-protected 2-deoxy- and 2,6-dideoxythioglycosides as glycosyl donors. The approach allows a wide range of glycosyl acceptors and donors to be used.

Key words: preactivation, α-stereoselective glycosylation, 2-deoxyglycosides, 2,6-dideoxysugars, carbohydrate

2-Deoxyglycosides are essential constituents of a variety of biologically active natural products such as antitumor antibiotics.[1] The nonavailability of neighboring-group participation from substituents at the C-2 position and the enhanced conformational flexibility derived from the reduced number of substituents make it difficult to achieve glycosylation in a stereoselective manner. Furthermore, the lack of an electron-withdrawing C-2 substituent makes the resulting glycosides more acid labile. Strategies for the synthesis of 2-deoxyglycosides with good α- or β-anomeric selectivities rely frequently on indirect glycosylation. The indirect method involves the introduction of a temporary directing group at the C-2 position of the donor which is reductively removed after the glycosylation step has been completed.[2] Indirect approaches to 2-deoxyglycosides mainly exploit 1,2-migration,[3] introduce auxiliary groups at the C-2 position,[2] use 2,6-anhydro-2-thio sugars as donors,[4] or cyclize acyclic sulfanyl alkenes.[5] In some cases, glycals are used as donors.[6] These methods normally need a subsequent reduction step which might be not suitable for the construction of some complex natural products. Therefore, a direct strategy for the preparation of 2-deoxyglycopyranosyl linkages that uses 2-deoxyglycopyranosyl donors would be more efficient and practical than the indirect strategies. Although some direct methods such as glycosylation promoted by silver silicate,[7] I_2-Et_3SiH,[8] $AgPF_6$,[9] or polymer-bound iodate(I) complexes[10] have been used, other approaches have been explored, including the conformational assistance approach,[11] the use of *S*-(2-deoxyglycosyl)phosphorodithioates and 2-pyridylthioglycosides as donors,[12] and the anomeric O-alkylation/arylation method.[13] Phosphites, phosphoramidites, and (2-carboxy)benzyl have also been examined as leaving groups in the 2-deoxy systems.[14] Lewis acid or metal-catalyzed syntheses of 2-deoxyglycosides from glycals[15] have additionally been developed. Although β-anomeric selectivity of 2-deoxyglycosides is more difficult to achieve, the direct synthesis of 2-deoxyglycopyranosides from 2-deoxy-glycosyl donors, with high α-stereoselectivity, still remains an inconvenient task.

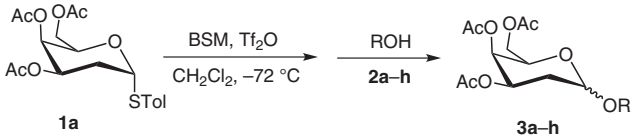
In recent years, 'preactivation' as a new glycosylation approach has attracted considerable interest.[16] 'Preactivation' was developed as an effective method for the iterative one-pot synthesis of oligosaccharides in Huang's laboratory as well as in our own group.[17] Very recently, when this protocol was applied to the glycosylations of oxazolidinone-protected glucosamine donors[18] and carbonate-protected deoxyglycosyl donors,[19,20] stereoselective coupling reactions were realized. In the synthesis of 2-deoxysugars and 2,6-dideoxysugars, this approach enjoyed a large scope in terms of glycosyl acceptors and donors, and the α-selectivity of glycosylations was good to excellent. By comparison with the routine (non-preactivation) glycosylation approach, it was found that the preactivation protocol played an important role in the outcomes and stereochemistry of glycosylations. And it was presumed that the conformational constraint of 3,4-*O*-carbonate in glycosyl donors appeared to enhance α-selectivity. In order to investigate how much the 3,4-*O*-carbonate group might have influenced the glycosylation results, we used acetyl-protected 2-deoxythioglycosides and 2,6-dideoxythioglycosides as glycosyl donors to perform glycosylations by preactivation protocol, and herein we report the high α-selectivity results by the use of these simple glycosyl donors.

The 'preactivation' approach was conducted in a manner where the glycosyl donor was completely activated and consumed (by TLC detection) prior to the addition of a glycosyl acceptor. First, 2-deoxy-galactopyranosyl donor was examined. The combination of benzenesulfinyl morpholine (BSM)[21] and triflic anhydride (Tf_2O) was used as the promoter system in the preactivation operations. Thus, the triacetyl-protected thioglycoside **1a** was preactivated at –72 °C in anhydrous dichloromethane using BSM–Tf_2O. After disappearance of donor **1a** (TLC detection in around ten minutes), the acceptor **2a** was added to the reaction mixture. Fortunately, the coupling reaction of **1a** and **2a** exhibited complete α-selectivity and proceeded as

SYNLETT 2010, No. 10, pp 1519–1524
Advanced online publication: 19.05.2010
DOI: 10.1055/s-0029-1219943; Art ID: W03610ST

shown in Table 1 (entry 1).[22] Next, our investigation was expanded to other glycosyl acceptors **2b–h**, and the results are listed in Table 1. As displayed, all the glycosylations proceeded very smoothly in high yields and with excellent α-selectivity except glycosyl acceptors **2g** and **2h**, in which the 6-OH was exposed (Table 1, entries 7 and 8). The α-anomers were identified by their ^{1}H NMR coupling constants for the anomeric protons or the coupling constants for the axial protons at the C-2 position of deoxysugars ($J_{1,2}$ = 3.0–4.0 Hz). It was found that donor **1a** coupled with diverse glycosyl acceptors, including pyranosides as well as furanosides. The glycosyl acceptors **2a** and **2b**, which differ only in their anomeric configurations, provided the same excellent α-stereoselectivity during the glycosylations (Table 1, entries 1 and 2). It was shown that the α-selectivity of acceptors **2f** and **2h** were better than that of acceptors **2e** and **2g** (Table 1, entry 5 vs. entry 6, entry 7 vs. entry 8). One might therefore conclude that the acceptors with lower reactivity can improve the stereoselectivity of the glycosylations.[23]

Table 1 Glycosylation of Donor **1a** with Various Acceptors by Preactivation



1a **3a–h**

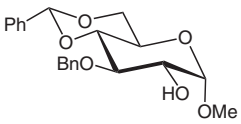
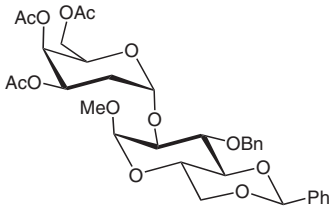
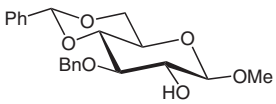
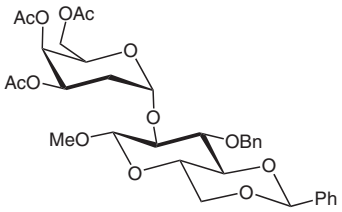
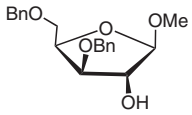
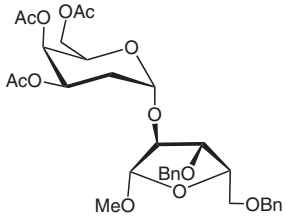
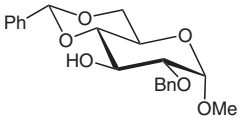
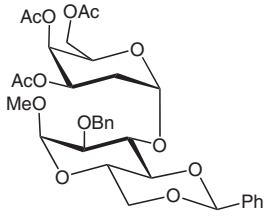
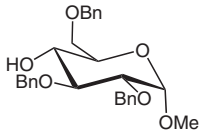
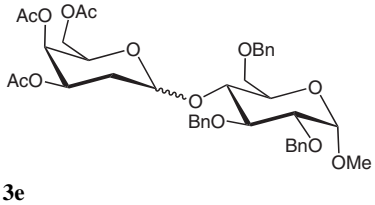
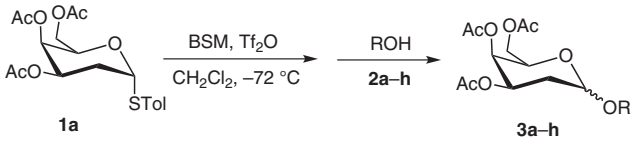
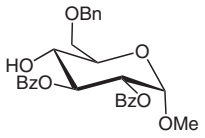
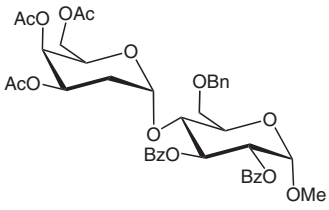
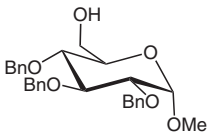
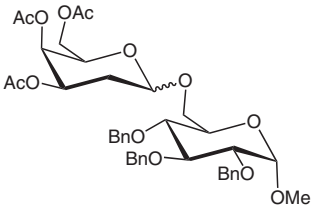
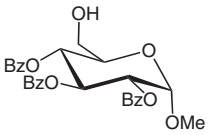
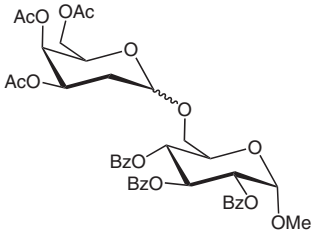
Entry	Donor	Acceptor	Product	Yield (%)	Ratio α/β
1	**1a**	 **2a**	 **3a**	84	α only
2	**1a**	 **2b**	 **3b**	93	α only
3	**1a**	 **2c**	 **3c**	91	α only
4	**1a**	 **2d**	 **3d**	87	α only
5	**1a**	 **2e**	 **3e**	86	8:1

Table 1 Glycosylation of Donor **1a** with Various Acceptors by Preactivation (continued)



1a **3a–h**

Entry	Donor	Acceptor	Product	Yield (%)	Ratio α/β
6	**1a**	 **2f**	 **3f**	87	α only
7	**1a**	 **2g**	 **3g**	85	2:1
8	**1a**	 **2h**	 **3h**	91	4:1[a]

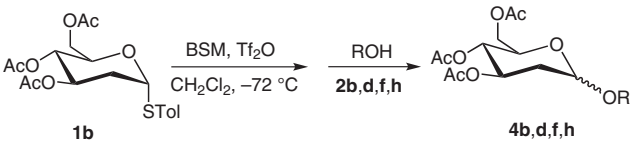
[a] Determined from ^{1}H NMR spectrum.

Encouraged by the results described above, we then synthesized donor **1b** in order to extend the scope of our methodology. Methyl glycosides **2b**,**d**,**f**,**h**, in which the 2-OH, 3-OH, 4-OH, and 6-OH were exposed, respectively, were again used as the glycosyl acceptors. The glycosylations were conducted under the above-mentioned preactivation conditions, and the results are listed in Table 2. The glycosyl acceptors **2d** and **2f** proceeded with excellent α-selectivity (Table 2, entries 2 and 3), whereas the α-selectivity of the coupling reaction of **2b** and **1b** was just moderate (Table 2, entry 1).

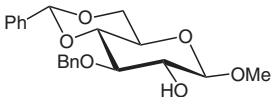
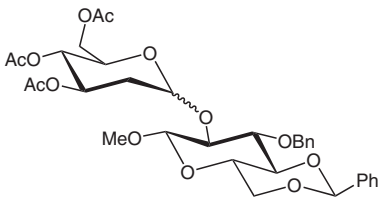
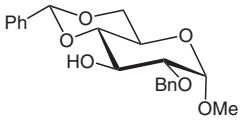
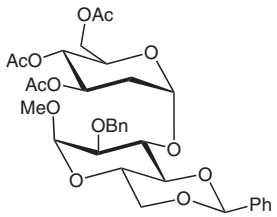
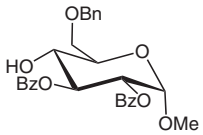
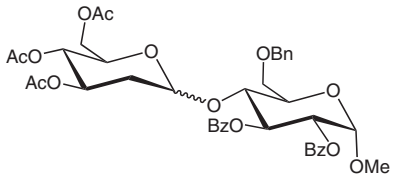
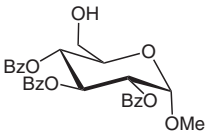
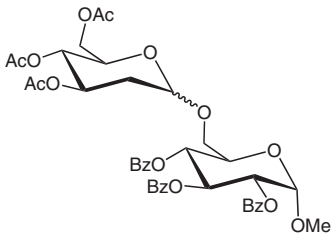
2,6-Dideoxysugars are also found in a plethora of biologically important natural products.[1] To further check the effectiveness of our method, the construction of 2,6-dideoxyglycosyl linkages was investigated. For this purpose, the acetyl-protected thioglycoside donor **1c** was synthesized, and monosaccharide building blocks **2a**,**b**,**d**,**e**,**h** were chosen as the glycosyl acceptors. The glycosyl coupling reactions between donor **1c** and acceptors **2a**,**b**,**d**,**e**,**h** by the preactivation protocol were carried out. The results are listed in Table 3. As shown, the glycosyl acceptors **2a** and **2d** displayed excellent α-selectivity (Table 3, entries 1 and 3), whereas the glycosyl acceptors **2b** and **2e** exhibited moderate α-selectivity (Table 3, entries 2 and 4). And the acceptor **2h** in which the 6-OH was exposed showed poor α-selectivity towards glycosylation (Table 3, entry 5).

Comparing with the results we reported previously,[19] it can be concluded that the 3,4-*O*-carbonate group did influence the glycosylation results by enhancing the α-selectivity. The high α-selectivity observed might originate from the species formed as intermediates after preactivation. Once activated, the glycosyl donor becomes an oxacarbenium ion, which can be trapped by triflate anion to give either α-triflate or β-triflate intermediate.[20b] As a result of the higher reactivity of the acetyl-protected thioglycosides than the cyclocarbonate derivatives,[24] both α-triflate and β-triflate intermediates formed from acetyl-protected thioglycosides will undergo glycosylation faster. By lowering the reactivity of glycosyl acceptors,[16c,23,25] they might prefer to undergo an S_N2-like reaction with the more reactive β-triflate intermediate, resulting in the formation of α-glycosides. This process might shift the anomerization equilibrium from the α- to β-triflate intermediate. This might also explain why the higher ste-

Table 2 Glycosylation of Donor **1b** with Various Acceptors by Preactivation



1b **4b,d,f,h**

Entry	Donor	Acceptor	Product	Yield (%)	Ratio α/β
1	**1b**	 **2b**	 **4b**	91	5.3:1
2	**1b**	 **2d**	 **4d**	67	α only
3	**1b**	 **2f**	 **4f**	92	12:1
4	**1b**	 **2h**	 **4h**	86	2:1[a]

[a] Determined from ^{1}H NMR spectrum.

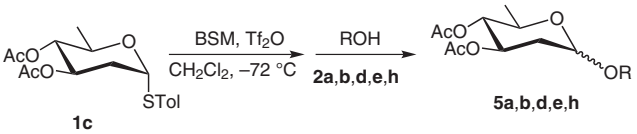
reoselectivity was achieved when less reactive acceptors were employed.

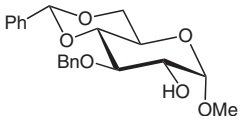
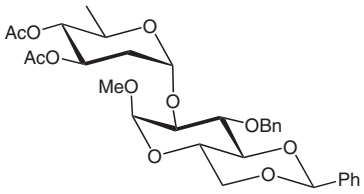
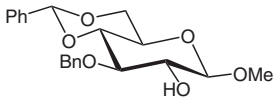
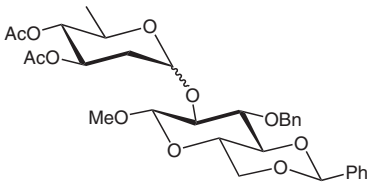
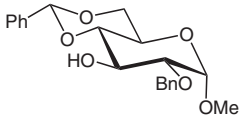
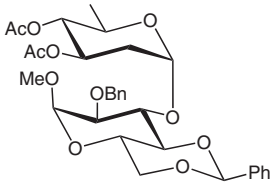
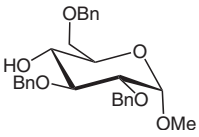
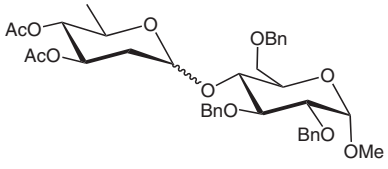
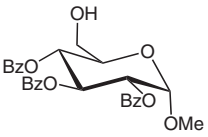
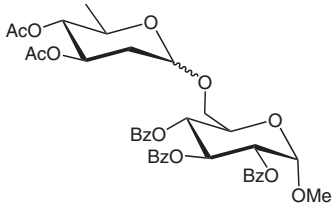
When the above-mentioned glycosylation reactions were performed at –72 °C in CH_2Cl_2 preactivated by the BSM–Tf_2O system in the presence of a hindered base 2,4,6-tri-*tert*-butylpyrimidine (TTBP), we obtained the glycosylating products in the same yields and the same α/β ratios as that of glycosylation in the absence of TTBP. These results appeared to exclude the possibility that the α-selective glycosylation in the absence of TTBP may be due to the in situ β → α anomerization under acidic conditions.[26,27]

Recently, Boons and co-workers published their investigation on direct and stereoselective synthesis of α-linked 2-deoxyglycosides by $BF_3{\cdot}OEt_2$-promoted activation of trichloroacetimidate glycosyl donors having a participating (*S*)-(phenylthiomethyl)benzyl moiety at C-6, whereas 2,6-dideoxyglycosides could be prepared by allyl glycosyl donors.[28] Although several same disaccharides were prepared independently in Boons' and our own work and both of the results were good, our method enjoyed using the same type of simple glycosyl donors, and the glycosylations were conducted in the same promoter system. In addition, among the various glycosyl donors, thioglycosides that we used are one type of the most enduring and widely used donors due to their stability, accessibility, and compatibility, and they can be activated by a variety of methods.[29]

In conclusion, a new simple and efficient method for highly α-stereoselective glycosylations of 2-deoxysugars and 2,6-dideoxysugars using acetyl-protected thioglycosides as donors has been uncovered. To the best of our knowledge, these glycosyl donors are the simplest thioglycoside

Table 3 Glycosylation of Donor **1c** with Various Acceptors by Preactivation



Entry	Donor	Acceptor	Product	Yield (%)	Ratio α/β
1	**1c**	 **2a**	 **5a**	57	α only
2	**1c**	 **2b**	 **5b**	85	4.7:1
3	**1c**	 **2d**	 **5d**	73	α only
4	**1c**	 **2e**	 **5e**	86	5:1
5	**1c**	 **2h**	 **5h**	82	1.5:1[a]

[a] Determined from ^{1}H NMR spectrum.

donors that have been used in the stereoselective construction of deoxyglycosides. Due to the good α-stereoselectivity obtained and the advantages of thioglycosides, it is expected that the disclosed method might be a concise and efficient supplement in the synthesis of α-linked 2-deoxyglycopyranose-containing complex structures with important biological functions. Further extension of this protocol to β-selective glycosylations is still under investigation.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China, and '863' grant from the Ministry of Science and Technology of China.

References and Notes

(1) (a) Kirschning, A.; Bechthold, A. F.-W.; Rohr, J. *Top. Curr. Chem.* **1997**, *188*, 1. (b) Weymouth-Wilson, A. C. *Nat. Prod. Rep.* **1997**, *14*, 99. (c) Butler, M. S. *J. Nat. Prod.* **2004**, *67*, 2141.

(2) (a) Tavecchia, P.; Trumtel, M.; Veyrieres, A.; Sinaÿ, P. *Tetrahedron Lett.* **1989**, *30*, 2533. (b) Perez, M.; Beau,

J.-M. *Tetrahedron Lett.* **1989**, *30*, 75. (c) Roush, W. R.; Bennett, C. E. *J. Am. Chem. Soc.* **1999**, *121*, 3541. (d) Blanchard, N.; Roush, W. R. *Org. Lett.* **2003**, *5*, 81. (e) Roush, W. R.; Sebesta, D. P.; James, R. A. *Tetrahedron* **1997**, *53*, 8837. (f) Thiem, J.; Schottmer, B. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 555. (g) Marzabadi, C. H.; Franck, R. W. *Tetrahedron* **2000**, *56*, 8385.

(3) (a) Nicolaou, K. C.; Ladduwahetty, T.; Randall, J. L.; Chucholowski, A. *J. Am. Chem. Soc.* **1986**, *108*, 2466. (b) Zuurmond, H. M.; van der Klein, P. A. M.; van der Marel, G. A.; van Boom, J. H. *Tetrahedron Lett.* **1992**, *33*, 2063.

(4) Toshima, K.; Mukaiyama, S.; Nozaki, Y.; Inokuchi, H.; Nakata, M.; Tatsuta, K. *J. Am. Chem. Soc.* **1994**, *116*, 9042.

(5) Rodríguez, M. A.; Boutureira, O.; Matheu, M. I.; Díaz, Y.; Castillón, S. *Eur. J. Org. Chem.* **2007**, 2470.

(6) (a) Lemieux, R. U.; Morgan, A. R. *Can. J. Chem.* **1964**, *42*, 1473. (b) Muller, T.; Schneider, R.; Schmidt, R. R. *Tetrahedron Lett.* **1994**, *35*, 4763.

(7) Binkley, R. W.; Koholic, D. J. *J. Org. Chem.* **1989**, *54*, 3577.

(8) Tanaka, H.; Yoshizawa, A.; Takahashi, T. *Angew. Chem. Int. Ed.* **2007**, *46*, 2505.

(9) Lear, M. J.; Yoshimura, F.; Hirama, M. *Angew. Chem. Int. Ed.* **2001**, *40*, 946.

(10) Jaunzems, J.; Sourkouni-Argirusi, G.; Jesberger, M.; Kirschning, A. *Tetrahedron Lett.* **2003**, *44*, 637.

(11) Toshima, K.; Nozaki, Y.; Tatsuta, K. *Tetrahedron Lett.* **1991**, *32*, 6887.

(12) (a) Bielawska, H.; Michalska, M. *J. Carbohydr. Chem.* **1991**, *10*, 107. (b) Laupichler, L.; Sajus, H.; Thiem, J. *Synthesis* **1992**, 1133. (c) Mereyala, H. B.; Kulkarni, V. R.; Ravi, D.; Sharma, G. V. M.; Rao, B. V.; Reddy, G. B. *Tetrahedron* **1992**, *48*, 545.

(13) Morris, W. J.; Shair, M. D. *Org. Lett.* **2009**, *11*, 9.

(14) (a) Ito, Y.; Ogawa, T. *Tetrahedron Lett.* **1987**, *28*, 2723. (b) Li, H.; Chen, M.; Zhao, K. *Tetrahedron Lett.* **1997**, *38*, 6143. (c) Kim, K. S.; Park, J.; Lee, Y. J.; Seo, Y. S. *Angew. Chem. Int. Ed.* **2003**, *42*, 459.

(15) (a) Yadav, J. S.; Reddy, B. V. S.; Reddy, K. B.; Satyanarayana, M. *Tetrahedron Lett.* **2002**, *43*, 7009. (b) Sherry, B. D.; Loy, R. N.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 4510.

(16) (a) Wang, Y.; Ye, X.-S.; Zhang, L.-H. *Org. Biomol. Chem.* **2007**, *5*, 2189. (b) Crich, D.; Sun, S. *J. Org. Chem.* **1996**, *61*, 4506. (c) Crich, D.; Sun, S. *J. Org. Chem.* **1997**, *62*, 1198. (d) Codée, J. D. C.; Van den Bos, L. J.; Litjens, R. E. J. N.; Overkleeft, H. S.; Van Boom, J. H.; Van der Marel, G. A. *Org. Lett.* **2003**, *5*, 1947. (e) Yamago, S.; Yamada, T.; Maruyama, T.; Yoshida, J.-I. *Angew. Chem. Int. Ed.* **2004**, *43*, 2145. (f) Nguyen, H. M.; Poole, J. L.; Gin, D. Y. *Angew. Chem. Int. Ed.* **2001**, *40*, 414. (g) Huang, L.; Wang, Z.; Li, X.; Ye, X.-S.; Huang, X. *Carbohydr. Res.* **2006**, *341*, 1669. (h) Huang, L.; Huang, X. *Chem. Eur. J.* **2007**, *13*, 529.

(17) Huang, X.; Huang, L.; Wang, H.; Ye, X.-S. *Angew. Chem. Int. Ed.* **2004**, *43*, 5221.

(18) (a) Geng, Y.; Zhang, L.-H.; Ye, X.-S. *Chem. Commun.* **2008**, 597. (b) Geng, Y.; Zhang, L.-H.; Ye, X.-S. *Tetrahedron* **2008**, *64*, 4949. For the use of oxazolidinone functionality, also see, for example: (c) Benakli, K.; Zha, C.; Kerns, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 9461. (d) Boysen, M.; Gemma, E.; Lahmann, M.; Oscarson, S. *Chem. Commun.* **2005**, 3044. (e) Manabe, S.; Ishii, K.; Ito, Y. *J. Am. Chem. Soc.* **2006**, *128*, 10666.

(19) Lu, Y.-S.; Li, Q.; Zhang, L.-H.; Ye, X.-S. *Org. Lett.* **2008**, *10*, 3445.

(20) For the use of carbonate functionality, also see, for example: (a) Crich, D.; Jayalath, P. *J. Org. Chem.* **2005**, *70*, 7252. (b) Crich, D.; Vinod, A. U.; Picione, J. *J. Org. Chem.* **2003**, *68*, 8453. (c) Cotarca, L.; Delogu, P.; Nardelli, A.; Sunjic, V. *Synthesis* **1996**, 553.

(21) Wang, C.; Wang, H.; Huang, X.; Zhang, L.-H.; Ye, X.-S. *Synlett* **2006**, 2846.

(22) **Typical Glycosylation Procedure**
Triflic anhydride (11.0 μL, 0.061 mmol) was added to a stirred solution of *p*-methylphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-α-D-galactopyranoside (**1a**, 30.0 mg, 0.076 mmol), benzenesulfinyl morpholine (BSM, 12.9 mg, 0.061 mmol), and 4 Å MS (350 mg, activated powder) in CH_2Cl_2 (3.0 mL) at –72 °C under nitrogen atmosphere. The reaction mixture was stirred for 10 min. After loss of **1a** detected by TLC, a solution of methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**2a**, 18.8 mg, 0.051 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to the reaction mixture. The mixture was stirred for 30 min, and the reaction was quenched by Et_3N (8.0 μL). The precipitate was filtered off, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (PE–EtOAc, 2.5:1) to give methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-α-D-glucopyranoside (**3a**, 27.6 mg, 84% yield) as a foam. R_f = 0.35 (PE–EtOAc, 1.5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (dd, 2 H, *J* = 2.0, 7.5 Hz), 7.40–7.33 (m, 7 H), 7.29–7.27 (m, 1 H), 5.60 (s, 1 H), 5.37 (ddd, 1 H, *J* = 3.0, 5.0, 12.5 Hz), 5.15 (d, 1 H, *J* = 3.0 Hz), 5.14 (d, 1 H, *J* = 3.5 Hz), 4.93 (d, 1 H, *J* = 10.5 Hz), 4.89 (d, 1 H, *J* = 3.5 Hz), 4.71 (d, 1 H, *J* = 10.5 Hz), 4.36 (t, 1 H, *J* = 6.5 Hz), 4.31 (dd, 1 H, *J* = 4.5, 10.0 Hz), 3.98 (t, 1 H, *J* = 9.5 Hz), 3.90 (dd, 1 H, *J* = 6.5, 11.0 Hz), 3.87–3.74 (m, 4 H), 3.65 (t, 1 H, *J* = 9.5 Hz), 3.43 (s, 3 H), 2.13–2.08 (m, 4 H), 2.00 (s, 3 H), 1.96–1.92 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.13, 170.23, 169.79, 138.06, 137.26, 128.96, 128.54, 128.47, 128.25, 127.86, 125.95, 101.27, 97.12, 94.10, 82.71, 76.85, 75.74, 73.45, 69.00, 66.61, 65.87, 62.25, 61.87, 55.23, 29.86, 20.81, 20.70. MS (ESI-TOF, positive): *m/z* = 667 $[M + Na]^+$. Anal. Calcd for $C_{33}H_{40}O_{13}$: C, 61.48; H, 6.25. Found: C, 61.65; H, 6.40.

(23) (a) Burgey, C. S.; Vollerthun, R.; Fraser-Reid, B. *J. Org. Chem.* **1996**, *61*, 1609. (b) Mootoo, D. R.; Konradsson, P.; Udodong, U.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1988**, *110*, 5583.

(24) Zhu, T.; Boons, G.-J. *Org. Lett.* **2001**, *3*, 4201; and references cited therein.

(25) (a) Crich, D.; Sun, S. *Tetrahedron* **1998**, *54*, 8321. (b) Crich, D.; Smith, M. *J. Am. Chem. Soc.* **2001**, *123*, 9015. (c) Kim, K. S.; Kim, J. H.; Lee, Y. J.; Lee, Y. J.; Park, J. *J. Am. Chem. Soc.* **2001**, *123*, 8477. (d) Tanada, S.-I.; Takashima, M.; Tokimoto, H.; Fujimoto, Y.; Tanaka, K.; Fukase, K. *Synlett* **2005**, 2325. (e) Codee, J. D. C.; Krock, L.; Castagner, B.; Seeberger, P. H. *Chem. Eur. J.* **2008**, *14*, 3987. (f) Crich, D.; Sharma, I. *Org. Lett.* **2008**, *10*, 4731. (g) Crich, D.; Li, L.-F. *J. Org. Chem.* **2009**, *74*, 773; and references cited therein.

(26) Manabe, S.; Ishii, K.; Hashizume, D.; Koshino, H.; Ito, Y. *Chem. Eur. J.* **2009**, *15*, 6894.

(27) Lin, S.-C.; Chao, C.-S.; Chang, C.-C.; Mong, K.-K. T. *Tetrahedron Lett.* **2010**, *51*, 1910.

(28) Park, J.; Boltje, T. J.; Boons, G.-J. *Org. Lett.* **2008**, *10*, 4367.

(29) Xiong, D.-C.; Zhang, L.-H.; Ye, X.-S. *Adv. Synth. Catal.* **2008**, *350*, 1696; and references cited therein.