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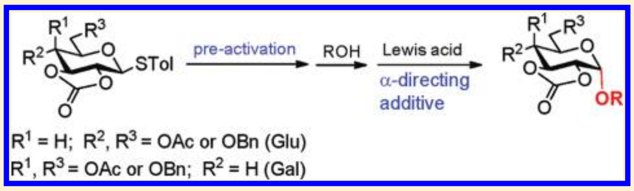
Lewis Acids as α-Directing Additives in Glycosylations by Using 2,3-O-Carbonate-Protected Glucose and Galactose Thioglycoside Donors Based on Preactivation Protocol

Yiqun Geng, Qi Qin, and Xin-Shan Ye*

State Key Laboratory of Natural and Biomimetic Drugs and School of Pharmaceutical Sciences, Peking University, Xue Yuan Road No. 38, Beijing 100191, China

Supporting Information

ABSTRACT: Catalytic or stoichiometric amounts of Lewis acids were found to be very effective α-directing additives in the stereoselective glycosylations of diverse 2,3-*O*-carbonate-protected glucose and galactose thioglycoside donors by preactivation protocol. The poor stereoselectivities of 4,6-di-*O*-acetyl-2,3-*O*-carbonate protected thioglycoside donors in glycosyl coupling reactions were greatly improved, and excellent α-stereoselectivities were achieved by the addition of 0.2 equiv of $BF_3{\cdot}OEt_2$. On the other hand, the β-selectivities of 4,6-di-*O*-benzyl-2,3-*O*-carbonate-protected thioglucoside donor toward glycosylations were reversed completely to the α-selectivities by the use of 1 equiv of $SnCl_4$, making the stereoselectivity controllable. Furthermore, the poor stereoselectivities of 4,6-di-*O*-benzyl-2,3-*O*-carbonate-protected thiogalactoside donor in glycosylations were also improved by using $SnCl_4$ as additive.



INTRODUCTION

Synthesis of oligosaccharides and glycoconjugates has a great demand for biological research as well as carbohydrate-based drug and vaccine discovery. Although much progress has been made in this field in the past decades,[1−4] there are still no general methods for the routine preparation of this type of compounds. The stereoselective introduction of a glycosidic bond is one of the key determinants.[5] The formation of α/β-anomers during glycosylations usually requires a time-consuming separation process, thus decreasing the efficiency of oligosaccharide assembly. Generally, the 1,2-*trans* glycosidic bond is constructed by the neighboring group participation of an acyl group at C-2 position of a glycosyl donor, while the formation of 1,2-*cis* linked glycosides remains a difficult task in many cases. The introduction of a nonparticipating neighboring group at C-2 position is insufficient to guarantee stereoselective *cis*-glycosylation reactions.

To improve the stereoselectivity (especially 1,2-*cis*-type) of glycosylation reactions, many strategies have been developed. These include the traditional methods such as anchimeric assistance, anomeric effect, in situ anomerization of α-halide,[6] heterogeneous catalysis,[7] and the solvent effects of nitriles[8,9] or ethers.[10] Recent progress in intramolecular aglycon delivery approach,[11,12] stereodirecting effects of the conformation-constraining protecting groups such as benzylidene,[13,14] oxazolidinone,[15,16] carbonate,[17−19] and the related mechanism studies,[20] as well as the participation of chiral auxiliary (*S*)-(phenylthiomethyl)benzyl ether through β-sulfonium ion intermediate[21] has been also very encouraging. However, there is still no general protocol to guarantee the stereoselectivities in one-pot multistep oligosaccharide assembly,[22] in which thioglycosides are usually employed as glycosyl donors.

The preactivation protocol,[23] which was developed as an effective strategy for iterative one-pot synthesis of oligosaccharides in this laboratory,[24] was found to have dramatic influences on the stereoselectivies of glycosylations. Our recent work showed that, using this protocol, either α- or β-stereoselective glycosylations of 2,3-*N*,*O*-oxazolidinone protected glucosamine and galactosamine thioglycoside donors can be modulated just by different additives,[15d,25] and highly α-selective glycosylations of 3,4-*O*-carbonate protected 2-deoxy- and 2,6-dideoxythioglycoside donors can be also performed.[19] Very recently, Mong and co-workers also reported DMF as a good modulator to effect α-glycosylation by preactivation procedure.[26] Combination of the conformation-constraining protecting group and preactivation protocol could be an effective approach to stereoselective glycosylations and might find wide applications to the oligosaccharide assembly.

Encouraged by the initial success in glucosamine, galactosamine, 2-deoxysugar, and 2,6-dideoxysugar donors, our next goal was to extend the preactivation-based stereoselective glycosylation protocol to glucose and galactose donors. We wanted to develop an effective method for stereoselective (especially α-selective) glycosylations of thioglucoside and thiogalactoside donors. Considering the significant role played by the conformation-constraining protecting groups, we decided to use 2,3-*O*-carbonate as a fixed protecting group in our thioglycoside donors, which was reported as an α-directing agent with solvent assistance by the Boons group in 2001.[17] A similar glycosyl donor was reported by the Crich group to show good β-selectivity in the absence of solvent effects.[18c]

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These interesting findings also inspired us to find a way to modulate the α/β selectivities of a single donor by changing additives, like the additive-controlled stereoselective glycosylations of glucosamine and galactosamine donors reported previously by us.[25b] Herein we report the Lewis acid mediated α-selective glycosylations of 2,3-*O*-carbonate-protected glucose and galactose thioglycoside donors based on preactivation protocol.

■ RESULTS AND DISCUSSION

First, a series of 2,3-*O*-carbonate protected thioglycoside donors **1−6** (Figure 1) were designed and prepared with different protecting groups at 4,6-OH positions, including the rigid benzylidene group, the electron-donating benzyl group, and the electron-withdrawing acetyl group. Among them, the similar structure of donor **3** was reported to show moderate to excellent β-selectivities toward glycosylations.[18c]

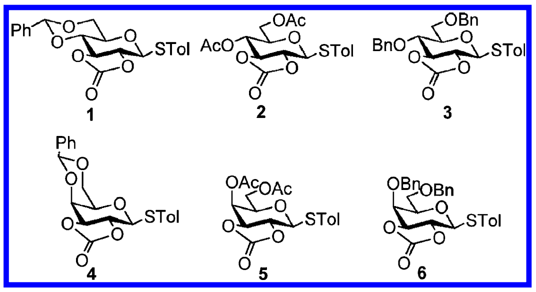
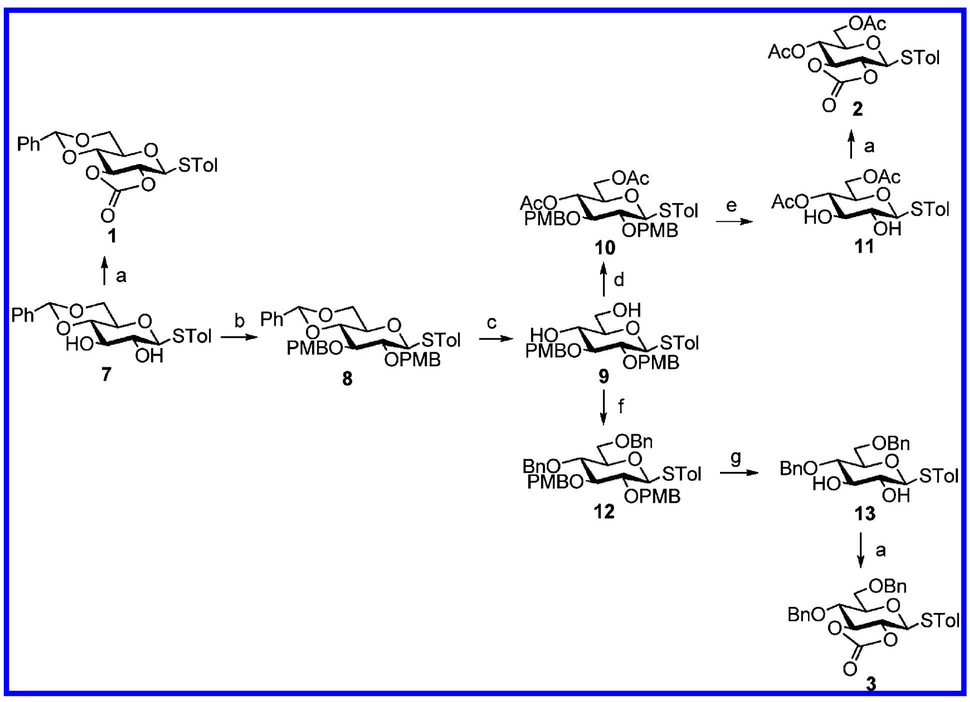


Figure 1. 2,3-*O*-Carbonate-protected glucose and galactose thioglycoside donors.

The synthesis of thioglucoside donors **1−3** started from the same glucose derivative **7**[27] (Scheme 1). Donor **1** was obtained through phosgenation of compound **7** in the presence of pyridine using dichloromethane (DCM) as solvent. Compound **7** was treated with sodium hydride (NaH) and *p*-methoxybenzyl chloride (PMBCl) to provide compound **8**. Removal of the benzylidene group in **8** under acidic conditions in DCM/MeOH (V/V, 1:1) afforded intermediate **9**, which was converted to compound **10** by acetylation and compound **12** by benzylation, respectively. Subsequently, the removal of *p*-methoxybenzyl groups of compound **10** and compound **12** followed by phosgenation led to 4,6-di-*O*-acetyl-2,3-*O*-carbonate protected thioglucoside donor **2** and 4,6-di-*O*-benzyl-2,3-*O*-carbonate protected donor **3**, respectively. It is worth mentioning that, in the synthetic routes of donors **2** and **3**, the *p*-methoxybenzyl group worked as a temporary protecting group and the precursor of carbonate group, which was somewhat unstable during the protecting group manipulations and was introduced to the target molecules in the last step. In the similar way, thiogalactoside donors **4−6** were prepared starting from galactose derivative **14**[28] (Scheme 2).

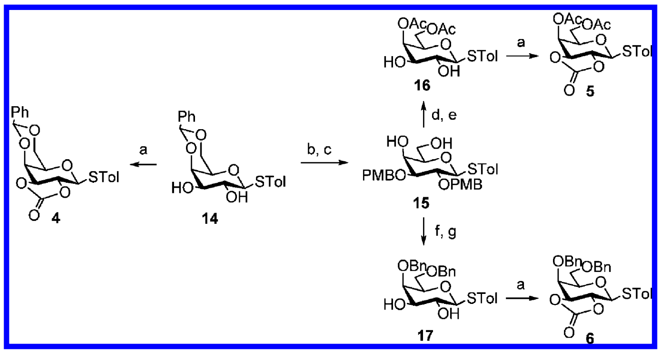
With glycosyl donors **1−6** in hand, we first investigated the influence of protecting groups at 4,6-OH positions on the stereochemical outcome toward glycosylations. A series of couplings of acceptor **18a**[29] with diverse donors **1−6** by preactivation protocol were carried out (Table 1). Benzenesulfinyl morpholine/triflic anhydride (BSM/Tf_2O),[30] diphenyl sulfoxide/triflic anhydride (Ph_2SO/Tf_2O),[31] or benzenesulfinyl piperidine/triflic anhydride (BSP/Tf_2O)[32] worked as the promoter system. It is worth mentioning that a preactivation procedure is necessary for all glycosylations because we found that none of donors **1−6** could be activated by the BSM (or Ph_2SO, BSP)/Tf_2O system when using nonpreactivation procedure. The promoter systems reacted preferentially with the acceptor alcohol due to the disarmed nature of such *trans*-carbonate-protected donors. Each donor was preactivated at low temperature in anhydrous dichloromethane under argon atmosphere, acceptor **18a** was then added to the reaction

Scheme 1. Preparation of Thioglucoside Donors 1−3[a]



[a]Reagents and conditions: (a) triphosgene, Py, CH_2Cl_2, 81% for **1**, 76% for **2**, 86% for **3**; (b) PMBCl, NaH, DMF, 88%; (c) *p*-TsOH, CH_2Cl_2/MeOH (1:1), 90%; (d) Ac_2O, Py, DMAP, 100%; (e) TFA, CH_2Cl_2, 97%; (f) BnBr, NaH, DMF, 94%; (g) DDQ, CH_2Cl_2/H_2O (10:1), 88%.

Scheme 2. Preparation of Thiogalactoside Donors 4–6[a]

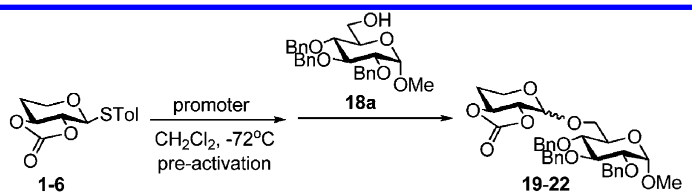


[a]Reagents and conditions: (a) triphosgene, Py, CH_2Cl_2, 83% for **4**, 75% for **5**, 83% for **6**; (b) PMBCl, NaH, DMF, 85%; (c) *p*-TsOH, CH_2Cl_2/MeOH (1:1), 90%; (d) Ac_2O, Py, DMAP, 100%; (e) TFA, CH_2Cl_2, 93%; (f) BnBr, NaH, DMF, 95%; (g) DDQ, CH_2Cl_2/H_2O (10:1), 86%.

mixture after the complete consumption of donor as indicated by TLC monitoring. After that, the reaction mixture was allowed to warm up to room temperature to accomplish the glycosidic bond formation. In each case, both the yield and the anomeric ratio were determined based on the isolated products. As shown in Table 1, 4,6-*O*-benzylidene protected donors **1** and **4** were not able to be activated by any promoters, even at room temperature (entries 1 and 4), due to the strong "disarming" effects of both benzylidene and carbonate groups.[18c] At −72 °C, 4,6-di-*O*-acetyl-protected donors **2** and **5** were completely activated only by Ph_2SO/Tf_2O,[33] which is nearly the most powerful promoter for the activation of thioglycoside donors. More reactive 4,6-*O*-benzyl protected donors **3** and **6** were fully activated by BSM/Tf_2O at −72 °C. The glycosylations of acceptor **18a** with donors **2**, **3**, **5**, and **6** went well with good yields but poor stereoselectivities except for donor **3**, which showed excellent *β*-selectivity. It seemed that even with closely related structures, donors with different protecting groups at 4,6-OH showed quite different stereoselectivities, which was consistent with the results reported by the Boons[17] and Crich groups.[18c] Under our preactivation protocol, the more important *α*-selectivity was not achieved as expected by using carbonate protecting groups.

However, based on our experiences in developing the additive-controlled stereoselective glycosylation strategy,[25b] there is still possibility for us to find suitable additives to improve the poor selectivities of such donors. So our next goal focused on looking for effective stereoselectivity-directing

Table 1. Glycosylations of Acceptor 18a with Various 2,3-*O*-Carbonate Protected Glycosyl Donors 1–6



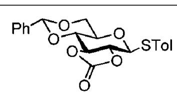
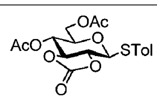
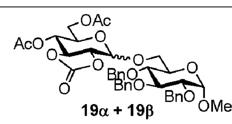
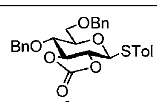
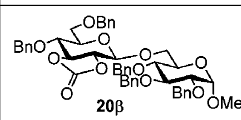
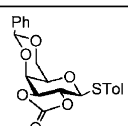
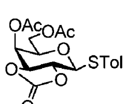
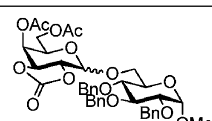
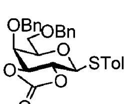
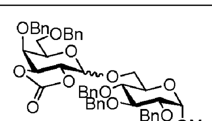
entry	donor	promoter	product	yield	α/β ratio
1	 **1**	BSM/Tf_2O BSP/Tf_2O Ph_2SO/Tf_2O	no activation	--	--
2	 **2**	Ph_2SO/Tf_2O	 **19α + 19β**	80%	1.5:1
3	 **3**	BSM/Tf_2O	 **20β**	86%	β only
4	 **4**	BSM/Tf_2O BSP/Tf_2O Ph_2SO/Tf_2O	no activation	--	--
5	 **5**	Ph_2SO/Tf_2O	 **21α + 21β**	81%	2:1
6	 **6**	BSM/Tf_2O	 **22α + 22β**	83%	1:1

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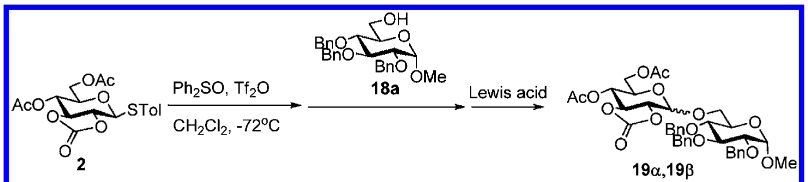
Table 2. Effects of Different Lewis Acids on the Stereochemical Outcome in the Glycosylation of Acceptor 18a with Donor 2



entry	Lewis acid	equiv.	α/β ratio	yield[a]
1	none		α/β = 1.5:1[b]	80%
2	$CuCl_2$	1-3	α/β = 1.5:1[c]	--[d]
3	$AuCl_3$	1-3	α/β = 1.5:1[c]	--[d]
4	$MnCl_2$	1-3	α/β = 1.5:1[c]	--[d]
5	$FeCl_3$	1-3	α/β = 1.5:1[c]	--[d]
6	$GaCl_3$	1	no product	
7	$TiCl_4$	1	no product	
8	$SnCl_4$	1	no product	
9	$AlCl_3$	1	no product	
10	$ZnCl_2$	1	α/β = 1:3[c]	--[d]
11		3	β only[b]	30-40%
12	$Cu(OTf)_2$,	1	α/β = 1:2[c]	--[d]
13	$La(OTf)_3$	1	α/β = 1.5:1[c]	--[d]
14	$Zn(OTf)_2$	1	α/β = 1.5:1[c]	--[d]
15	$Sc(OTf)_3$	1	α/β = 1.5:1[c]	--[d]
16	AgOTf	1	α/β = 1.5:1[c]	--[d]
17	$Hf(OTf)_4$	1	α/β = 3:1[b]	65%
18		2	α/β = 6:1[b]	60%
19		3	α/β = 15:1[b]	53%
20		5	α/β > 20:1[b]	48%
21	TMSOTf	1, 2, 5, 10	α/β = 1:1[c]	--[d]
22	$BF_3{\cdot}OEt_2$	2	α only[b]	51%
23		1	α only[b]	59%
24		0.5	α/β > 20:1[b]	67%
25		0.2	α/β > 20:1[b]	76%
26		0.1	α/β = 10:1[b]	78%
27	$AgBF_4$	2	α only[b]	50%
28		1	α only[b]	70%
29		0.5	α only[b]	71%
30		0.1-0.2	α/β > 20:1[b]	75%
31	$AgPF_6$	1	α only[b]	80%
32		0.5	α/β = 1:2[c]	--[d]
33		0.2	α/β = 1:1[c]	--[d]

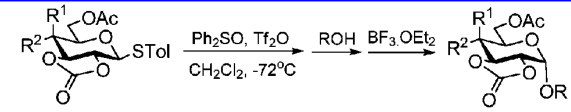
[a]The yield was determined on the basis of isolated products. [b]The anomeric ratio was determined by isolated products. [c]The anomeric ratio was determined by integration of ^{1}H NMR spectrum of the crude product. [d]The crude product was not isolated furthermore to give the yield.

additives in the glycosylation reactions of 2,3-*O*-carbonate-protected donors. In the beginning, the *β*-directing additive 2,4,6-tri-*tert*-butylpyrimidine (TTBP), *α*-directing additive thiophene, bifunctional additives TBAI, and dimethyl sulfide, which worked well in the stereoselective glycosylations of glucosamine and galactosamine donors,[25b] were checked. Unfortunately, they did not work at all in this case.

Our previous work and related mechanism studies by other research groups[34,35] suggested that the good *α*-selectivity of 2,3-*N*,*O*-oxazolidinone protected aminosugar donors arose from the in situ anomerization of *β*-glycosidic bonds under the mild acidic reaction conditions. Obviously, the same mild acidic conditions in the glycosylation of 2,3-*O*-carbonate-protected donor **2** was not enough to promote the anomerization process. We then decided to use Lewis acid as additive in this glycosylation reaction to assist the anomerization process from *β*-glycoside to its *α*-anomer. Some Lewis acids were screened, their effects on the stereochemical outcome in the coupling of **2** with **18a** were investigated, and the results are listed in Table 2. In each coupling reaction, Lewis acid was added after the preactivation of donor **2** by Ph_2SO/Tf_2O at −72 °C and the addition of acceptor **18a**. Fortunately, it was found that a catalytic amount of $BF_3{\cdot}OEt_2$ (entry 25) or $AgBF_4$ (entry 30) as well as 1 equiv of $AgPF_6$ (entry 31) significantly improved the stereoselectivity of this reaction, and excellent *α*-selectivity was realized. We also found that the yields were reduced when adding larger amounts of Lewis acid (entries 22−24, 27−29), but no hydrolysis products were observed under these conditions. The decrease of yields could probably arise from the degradation of the disaccharide.

Considering the high cost and sensibility to moisture of $AgBF_4$ or $AgPF_6$, we preferred $BF_3{\cdot}OEt_2$ as an effective *α*-directing

Table 3. $BF_3{\cdot}OEt_2$ as an Effective α-Directing Additive in the Glycosylations of a Series of Acceptors 18a−g with Donor 2 or 5



2: R^1 = H, R^2 = OAc
5: R^1 =OAc, R^2 = H

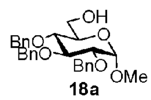
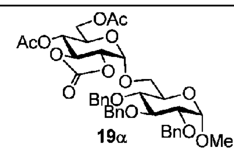
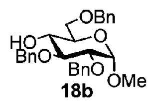
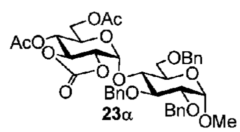
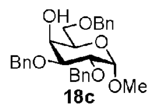
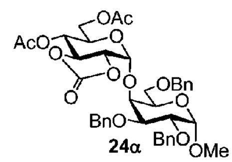
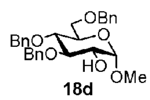
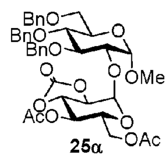
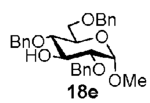
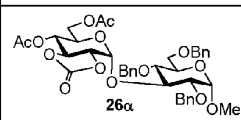
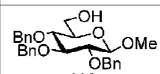
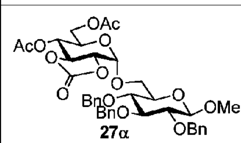
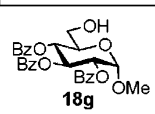
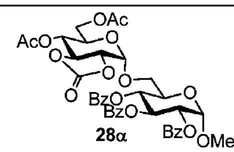
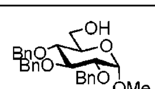
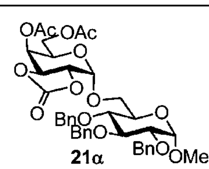
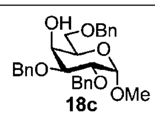
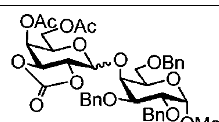
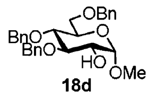
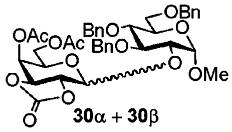
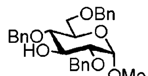
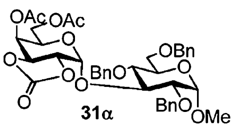
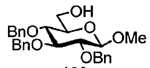
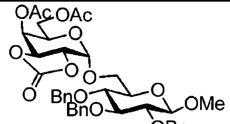
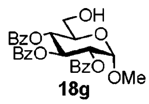
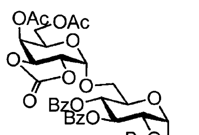
entry	donor	accepter	equiv.	product	α/β ratio	yield
1	**2**	 **18a**	0.2	 **19α**	α/β > 20:1	76%
2	**2**	 **18b**	0.2	 **23α**	α only	51% (75%)[a]
3	**2**	 **18c**	0[b]	 **24α**	α only	77%
4	**2**	 **18d**	2[c]	 **25α**	α/β > 20:1	70%
5	**2**	 **18e**	0.2	 **26α**	α only	78%
6	**2**	 **18f**	0.2	 **27α**	α only	75%
7	**2**	 **18g**	1[d]	 **28α**	α only	55%
8	**5**	 **18a**	0.2	 **21α**	α only	81%
9	**5**	 **18c**	0[b]	 **29α + 29β**	α/β = 15:1	75%

Table 3. continued

entry	donor	accepter	equiv.	product	α/β ratio	yield
10	**5**	 **18d**	2[c]	 **30α + 30β**	α/β = 5:1	68%
11	**5**	 **18e**	0.2	 **31α**	α only	77%
12	**5**	 **18f**	0.2	 **32α**	α only	76%
13	**5**	 **18g**	0.2	 **33α**	α only	60%

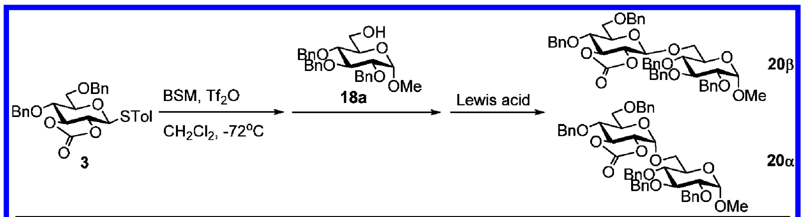
[a]Yield based on the recovery of the acceptor. [b]The reaction was carried out without adding $BF_3{\cdot}OEt_2$ as additive. [c]α-Selectivity was obtained by using 2 equiv of $BF_3{\cdot}OEt_2$ as additive. [d]α-Selectivity was obtained by using 1 equiv of $BF_3{\cdot}OEt_2$ as additive.

additive in the glycosylations of 2,3-*O*-carbonate-protected donors. The generality of such an additive on both glycosyl acceptors and donors was then checked. Either thioglucoside donor **2** or similar thiogalactoside donor **5** was preactivated in dry dichloromethane at −72 °C and reacted with a series of representative glycosyl acceptors **18a−g**[29,36−41] (Table 3). Generally, excellent α-selectivities were obtained in moderate to high yields by using $BF_3{\cdot}OEt_2$ as additive in the glycosylation reactions. In most cases, 0.2 equiv of $BF_3{\cdot}OEt_2$ was quite enough, except for the coupling of donor **2** or **5** with acceptor **18d** (2 equiv, entries 4 and 10) as well as the coupling of donor **2** with **18g** (1 equiv, entry 7). We reasoned that the good α-selectivities resulted from the Lewis acid-mediated anomerization of the β-glycosidic bonds to the α-linked ones, which are thermodynamically favored. That is, even α/β mixtures were obtained at first, β-linked disaccharides anomerized immediately through endocyclic C1−O5 bond cleavage assisted by Lewis acid $BF_3{\cdot}OEt_2$. It seemed that both 2,3-*O*-carbonate group and Lewis acid are determining factors in this case. It is worth mentioning that the β-configuration of the glycosidic bond at the anomeric carbon of acceptor **18f** was kept during the process of glycosylation and anomerization of new glycosidic bond (entries 6 and 12). Meanwhile, we realized that the cleavage of the exocyclic C−O bond, which is the glycosidic bond of the product, might occur competitively. This may be explained by the fact that the use of even catalytic amounts of $BF_3{\cdot}OEt_2$ in the coupling of donor **2** or **5** with acceptor **18c** led to disaccharide **24** or **29** (entries 3 and 9) in poor yield (less than 10%). The newly formed α-1,4-glycosidic bond in both cases might be sensitive to Lewis acid and easily cleaved. However, unlike the others, the α-selectivities of both glycosylations were good even without any additives, perhaps due to the less nucleophilic property of 4-OH in the acceptor or the in situ anomerization under the mild acidic reaction conditions.

One limitation of the 4,6-*O*-acetyl-protected donor was its lower reactivity due to the "disarming" effects of both acetyl groups and carbonate group. Thus, moderate yield was achieved in the coupling reaction of donor **2** with the less nucleophilic acceptor **18b** (entry 2, Table 3). Therefore, we decided to extend the Lewis acid-assisted α-selective glycosylation protocol to the more reactive 4,6-*O*-benzyl-protected donor **3**. According to our preliminary investigation (entry 3, Table 1), which is consistent with the reported work by Crich et al.,[18c] the glycosylation of donor **3** without any additive is β-selective. Hopefully the initially formed β-glycosidic bond could anomerize to the α-bond in the presence of proper Lewis acid, making the stereoselectivities of this donor toward glycosylations controllable just by modulating the additive.

The coupling of donor **3** with acceptor **18a** was chosen as the model reaction, and the effects of different Lewis acids on the stereochemical outcome were investigated (Table 4). First, Lewis acids such as $BF_3{\cdot}OEt_2$ (entries 2−5), $AgBF_4$ (entries 6−7), and $AgPF_6$ (entries 8−9), which were quite effective α-directing additives in the glycosylations of donor **2** or **5**, were checked. It was found that good α-stereoselectivity was obtained only when a large amount of $BF_3{\cdot}OEt_2$ was used, and the yield was moderate (entry 5). So we got a hint that the electron-donating effects of benzyl groups at 4,6-OH resulted in reduced tendency of anomerization from the initially formed disaccharide **20β** to its anomer **20α**. During the process of searching for a more powerful Lewis acid as our α-directing additive, we found that strong Lewis acids such as $TiCl_4$ (entries 10−11), $HfCl_4$ (entry 12), BCl_3 (entry 13), and $GaCl_3$ (entry 23) only gave rise to the cleavage of glycosidic bonds or debenzylation or decomposition of sugars but did not assist the anomerization process. Relatively mild ones such as SnF_4 (entry 18) and $BiCl_3$ (entry 24) had no effect at all. Only the addition of appropriate amount of $SnCl_4$ (entry 14) or $AlCl_3$ (entry 21) resulted in the total reversal of the β-stereoselectivity to α-stereoselectivity. Compared with $AlCl_3$,

Table 4. Effects of Different Lewis Acids on the Stereochemical Outcome in the Glycosylation of Acceptor 18a with Donor 3



entry	Lewis acid	equiv.	α/β ratio	yield
1	none	--	β only	86%
2	$BF_3 \cdot OEt_2$	0.2	β only	84%
3		2	α/β = 10:1	80%
4		5	α/β = 15:1	73%
5		10	α/β > 20:1	70%
6	$AgBF_4$	2	α/β = 1:1	81%
7		5	α/β = 1:1	75%
8	$AgPF_6$	2	α/β = 1:3	80%
9		5	α/β = 1:2	75%
10	$TiCl_4$	1	α/β mixture	--
11		3	α/β mixture with by-product	
12	$HfCl_4$	1-3	α/β mixture with by-product	
13	BCl_3	1	α/β mixture with by-product	
14	$SnCl_4$	1	α only	80%
15		0.5	α/β mixture	--
16	$SnCl_2$	1-5	α/β mixture	--
17	$SnBr_4$	1-3	α/β mixture	--
18	SnF_4	1	β only	85%
19	$AlCl_3$	1	α/β mixture	--
20		2	α/β mixture	--
21		5	α/β > 20:1	55%
22	$InCl_3$	1-5	α/β mixture	--
23	$GaCl_3$	1	no product	
24	$BiCl_3$	1	β only	83%

$SnCl_4$ performed better, with advantages of less influence on the coupling yield, fewer side reactions, and smaller amount needed.

Because of the good performance of its α-directing effect in the glycosylation of donor **3**, we next investigated the generality of $SnCl_4$ as additive. As we reasoned the total reversal of β-selectivity to α-selectivity may come from the endocyclic C−O bond cleavage assisted by $SnCl_4$, we slightly optimized the protocol this time. Acceptor was added after donor **3** was preactivated completely by BSM/Tf_2O at −72 °C, and then the reaction mixture was warmed slowly to accomplish the new glycosidic bond formation. After the full consumption of acceptor and the formation of disaccharide (usually at low temperature below −20 °C) as indicated by TLC monitoring, $SnCl_4$ (neat liquid) was then added to perform the anomerization process. As shown in Table 5, in most cases, 1−3 equiv of $SnCl_4$ worked well as an effective α-directing additive in the couplings of donor **3** with different acceptors **18a−g**. In this way, the stereochemical outcome of donor **3** toward glycosylations can be modulated by means of additive, that is, β-selectivity was obtained in the absence of $SnCl_4$ whereas α-selectivity was obtained in the presence of it.

However, this protocol did not work well in the coupling reactions of donor **3** with the 4-OH acceptors **18b** and **18c** (entries 4 and 6). No stereoselectivity was observed when even 5 equiv of $SnCl_4$ was used in the glycosylation of acceptor **18b** with donor **3**. In the case of acceptor **18c**, the presence of $SnCl_4$ only gave rise to the cleavage of glycosidic bond, leading to decomposition of the product.

Although the stereoselectivity was quite poor in the case of similar benzyl-protected thiogalactoside donor **6**, we want to use $SnCl_4$ as additive to improve the α-selectivity through the same anomerization mechanism, and the results are listed in Table 6. As expected, the additive worked well. Except for the coupling of donor **6** with the 4-OH acceptor **18b** (entries 3 and 4, from 1.5:1 without any additives to 3:1 with 3 equiv of $SnCl_4$), the stereoselectivities of all glycosylations were improved to good to excellent α-selectivities by using $SnCl_4$ as additive.

In the end, in order to support our assumption of the in situ anomerization process, β-disaccharide **19*β*** and **20*β*** were treated with a catalytic amount of $BF_3 \cdot OEt_2$ or a stoichiometric amount of $SnCl_4$ at −72 °C in dichloromethane, respectively (Scheme 3). The reaction mixture was allowed to warm up to room temperature, and an efficient anomerization was observed, providing the α-linked disaccharides **19*α*** and **20*α*** in around 85% yield. The experimental results demonstrated that the anomerization indeed occurred after the glycosylation, probably through an endocyclic C−O bond cleavage assisted by the Lewis acid.

■ CONCLUSION

In this context, we developed a Lewis acid mediated α-stereoselective glycosylation protocol of 2,3-*O*-carbonate-protected

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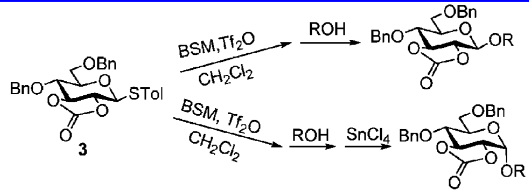
Table 5. Additive $SnCl_4$-Controlled Stereoselective Glycosylations of Different Acceptors 18a–g with Donor 3



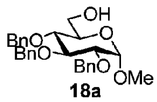
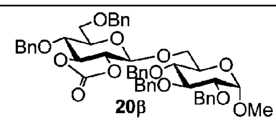
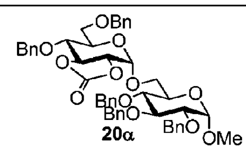
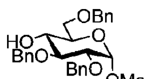
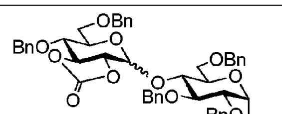
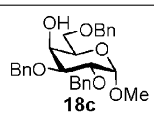
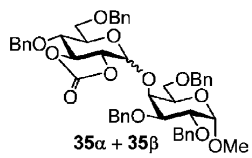
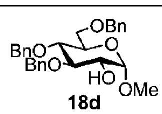
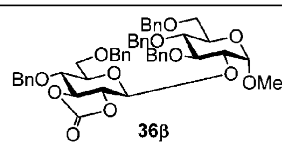
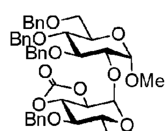
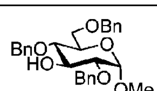
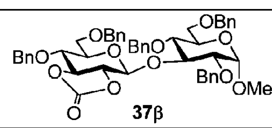
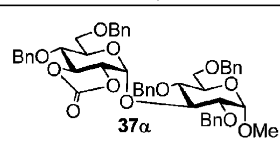
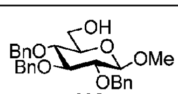
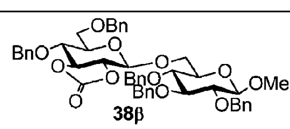
entry	ROH	equiv. of $SnCl_4$	product	α/β ratio	yield
1	 18a	0	 20β	β only	86%
2		1	 20α	α only	80%
3	 18b	0	 34α + 34β	α/β = 1:4	83%
4		1-5		α/β = 1:1	71% -80%
5	 18c	0	 35α + 35β	α/β = 1:10	85%
6		1	No product	--	--
7	 18d	0	 36β	β only	90%
8		3	 36α	α only	85%
9	 18e	0	 37β	β only	84%
10		3	 37α	α only	78%
11	 18f	0	 38β	β only	87%

Table 5. continued

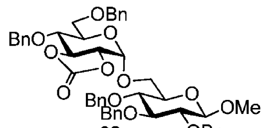
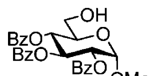
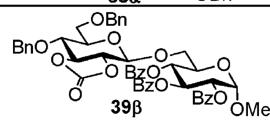
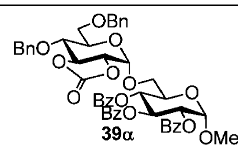
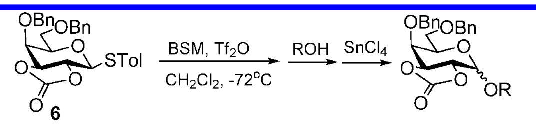
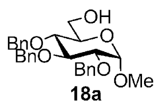
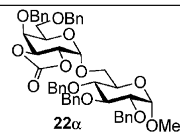
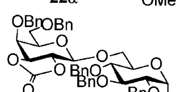
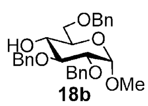
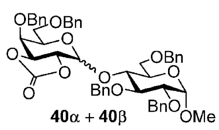
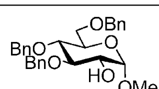
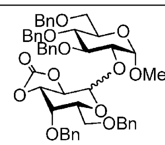
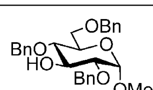
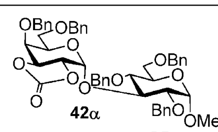
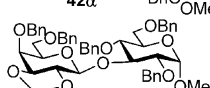
entry	ROH	equiv. of $SnCl_4$	product	α/β ratio	yield
12		1	 **38α**	α/β > 20:1	81%
13	 **18g**	0	 **39β**	α/β = 1:5	83%
14		1	 **39α**	α/β > 20:1	79%

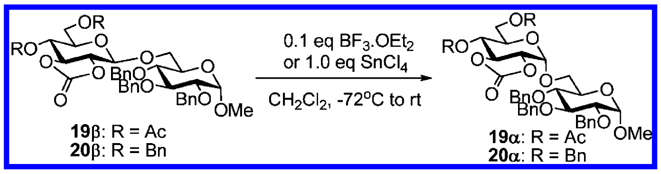
Table 6. $SnCl_4$-Mediated *α*-Selective Glycosylations of Different Acceptors 18a,b,d,e with Donor 6



entry	ROH	equiv.	product	α/β ratio	yield
1	 **18a**	0	 **22α**	α/β = 1:1	83%
2		1	 **22β**	α only	78%
3	 **18b**	0	 **40α + 40β**	α/β = 1.5:1	79%
4		1-3		α/β = 3:1	68-73%
5	 **18d**	0	 **41α + 41β**	α/β = 2:1	85%
6		3		α/β = 5:1	78%
7	 **18e**	0	 **42α**  **42β**	α/β = 1:2	82%
8		3		α/β > 20:1	71%

thioglucoside and thiogalactoside donors based on preactivation strategy. $BF_3 \cdot OEt_2$ was found to be an effective *α*-directing additive in the glycosylations of a series of representative acceptors with 4,6-di-*O*-acetyl-2,3-*O*-carbonate-protected thioglucoside donor **2** and thiogalactoside donor **5**. Poor stereoselectivities were greatly improved to nearly *α*-only selectivities by the addition of catalytic amount of $BF_3 \cdot OEt_2$. Meanwhile, the *β*-stereoselectivity of 4,6-di-*O*-benzyl-2,3-*O*-carbonate-protected thioglucoside donor **3** toward glycosylations with different acceptors was totally reversed to the *α*-selectivity by the use of stoichiometric Lewis acid $SnCl_4$ as additive, making the stereochemical outcome predictable and

Scheme 3. Anomerization Reaction of β-Disaccharides 19β and 20β



controllable. For the similar thiogalactoside donor **6**, poor stereoselectivities in glycosylations were also improved by adding $SnCl_4$. It was suggested that the good α-selectivities in all cases may come from one mechanism, that is, no matter what the initial stereoselectivities are, the newly formed β-glycosidic bonds in the glycosylations of such donors can anomerize to their thermodynamically more stable α-anomers, through the endocyclic C−O bond cleavage assisted by an appropriate Lewis acid. It is worth to mention that, the anomerization process relies on the conformation-constraining 2,3-*O*-carbonate group, just like the 2,3-*N*,*O*-oxazolidinone group in the glucosamine and galactosamine donors reported before. Further exploration of new additives which may modulate the stereoselectivity of glycosylations, and the extension of this protocol to other types of sugars is still under investigation.

■ EXPERIMENTAL SECTION

General Methods. All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Dichloromethane, pyridine, and DMF were distilled over calcium hydride. Methanol was distilled from magnesium. All reactions were carried out under anhydrous conditions with freshly distilled solvents, unless otherwise noted. Reactions were monitored by analytical thin-layer chromatography on silica gel 60 F_{254} precoated on aluminum plates. Spots were detected under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate. Solvents were evaporated under reduced pressure and below 40 °C (bath). Column chromatography was performed on silica gel (200−300 mesh). ^{1}H NMR spectra were recorded on a spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in deuterated chloroform. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Mass spectra were recorded using a spectrometer. Elemental analysis data were recorded on an elemental analyzer.

Preparation of 2,3-*O*-Carbonate-Protected Glycosyl Donors 1−6. *p-Tolyl 4,6-O-Benzylidene-2,3-O-carbonyl-1-thio-β-D-glucopyranoside (**1**).* Triphosgene (0.94 g, 3.21 mmol) in 5 mL of dichloromethane was added dropwise to a solution of *p*-tolyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[27] (2.00 g, 5.35 mmol) and pyridine (2.6 mL) in dichloromethane (25 mL) at −20 °C. The reaction mixture was stirred vigorously for 30 min at the same temperature. After consumption of the starting material by TLC detection, the reaction was quenched by satd NH_4Cl solution (20 mL) and extracted with dichloromethane (2 × 25 mL). The combined organic layer was dried, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/acetone, 6:1) to give **1** (1.73 g, 81%) as a foam: R_f = 0.2 (petroleum ether/ethyl acetate, 2:1); $[\alpha]_D$ −16.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.48 (m, 4H), 7.35−7.38 (m, 3H), 7.18 (d, 2H, *J* = 8.0 Hz), 5.55 (s, 1H), 4.89 (d, 1H, *J* = 9.6 Hz), 4.46 (dd, 1H, *J* = 10.0, 10.8 Hz), 4.40 (dd, 1H, *J* = 4.8, 10.8 Hz), 3.93 (dd, 1H, *J* = 8.4, 9.6 Hz), 3.88 (t, 1H, *J* = 10.0 Hz), 3.83 (dd, 1H, *J* = 9.6, 10.8 Hz), 5.57−3.61 (m, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 140.0, 136.0, 135.3, 130.0, 129.4, 128.4, 126.0, 124.7, 101.3, 83.6, 80.8, 78.3 (2C), 72.8, 68.2, 21.2; HRMS (ESI) calcd for $C_{21}H_{20}O_6SNa$ $[M + Na]^+$ 423.0873, found 423.0875.

*p-Tolyl 4,6-O-Benzylidene-2,3-di-O-p-methoxybenzyl-1-thio-β-D-glucopyranoside (**8**).* Compound **7** (10.0 g, 26.7 mmol) was dissolved in dry DMF (100 mL) and stirred at −15 °C, and NaH (4.28 g, 107 mmol, 60% w/w in mineral oil) was added in three portions, followed by the dropwise addition of *p*-methoxybenzyl chloride (10.9 mL, 80.2 mmol). After being stirred for 30 min at −15 °C, the reaction mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was poured into ice-cooled water and extracted with dichloromethane (2 × 200 mL). The combined organic layer was dried, filtered, and concentrated under reduced pressure. The residue was purified through recrystallization in petroleum ether/ethyl acetate to give **8** (14.4 g, 88%) as a foam: R_f = 0.5 (petroleum ether/ethyl acetate, 2:1); $[\alpha]_D$ −2.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25−7.50 (m, 11H), 7.11 (d, 1H, *J* = 8.1 Hz), 6.82−6.90 (m, 4H), 5.57 (s, 1H), 4.86 (d, 1H, *J* = 10.8 Hz), 4.79 (d, 1H, *J* = 10.2 Hz), 4.73 (d, 1H, *J* = 9.9 Hz), 4.71 (d, 1H, *J* = 10.8 Hz), 4.66 (d, 1H, *J* = 9.6 Hz), 4.37 (dd, 1H, *J* = 5.1, 10.5 Hz), 3.81 (s, 3H), 3.78 (s, 3H), 3.68−3.81 (m, 2H), 3.65 (t, 1H, *J* = 9.3 Hz), 3.38−3.47 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 159.2, 138.0, 137.2, 132.9, 130.4, 130.2, 129.8, 129.71, 129.68, 129.1, 128.9, 128.2, 125.9, 113.73, 113.72, 101.0, 88.4, 82.6, 81.4, 80.0, 75.4, 74.9, 70.1, 68.6, 55.22, 55.17, 21.1; HRMS (ESI) calcd for $C_{36}H_{39}O_7S$ $[M + H]^+$ 615.2411, found 615.2436.

*p-Tolyl 2,3-Di-O-p-methoxybenzyl-1-thio-β-D-glucopyranoside (**9**).* *p*-TsOH (2.75 g, 16.0 mmol) was added to the solution of compound **8** (14.0 g, 22.8 mmol) in 200 mL of dichloromethane−methanol (v/v = 1:1). The reaction mixture was stirred at rt for 5 h, neutralized with Et_3N (2 mL), and concentrated to dryness under reduced pressure. The residue was purified by column chromatography (petroleum ether/acetone, 1:1) to give **9** (10.8 g, 90%) as a foam: R_f = 0.1 (petroleum ether/ethyl acetate, 1:1). Compound **9** was used for the next reaction directly.

*p-Tolyl 4,6-Di-O-acetyl-2,3-di-O-p-methoxybenzyl-1-thio-β-D-glucopyranoside (**10**).* To a stirred solution of compound **9** (5.00 g, 9.50 mmol) in pyridine (50 mL) with a catalytic amount of DMAP was added acetic anhydride (9.00 mL, 95.0 mmol) at 0 °C. The reaction mixture was warmed to room temperature, stirred for 3 h, and then concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give **10** (5.80 g, 100%) as a foam: R_f = 0.25 (petroleum ether/ethyl acetate, 1.5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, 2H, *J* = 8.1 Hz), 7.34 (d, 2H, *J* = 8.7 Hz), 7.09−7.18 (m, 4H), 6.84−6.90 (m, 4H), 4.99 (t, 1H, *J* = 9.6 Hz), 4.82 (d, 1H, *J* = 9.9 Hz), 4.75 (d, 1H, *J* = 11.1 Hz), 4.64 (d, 1H, *J* = 9.6 Hz), 4.57 (d, 1H, *J* = 11.4 Hz), 4.57 (d, 1H, *J* = 9.9 Hz), 4.20 (dd, 1H, *J* = 5.4, 12.0 Hz), 4.10 (dd, 1H, *J* = 2.7, 12.3 Hz), 3.81 (s, 3H), 3.79 (s, 3H), 3.61 (t, 1H, *J* = 9.0 Hz), 3.52−3.56 (m, 1H), 3.48 (t, 1H, *J* = 8.7 Hz), 2.34 (s, 3H), 2.08 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 169.6, 159.4, 159.2, 138.1, 132.9, 130.2, 130.0, 129.6, 129.4, 129.3, 113.84, 113.82, 87.8, 83.4, 80.2, 75.8, 75.2, 75.0, 69.8, 63.6, 55.3 (2C), 21.1, 20.8 (2C); HRMS (ESI) calcd for $C_{33}H_{38}O_9SNa$ $[M + Na]^+$ 633.2129, found 633.2147.

*p-Tolyl 4,6-Di-O-acetyl-1-thio-β-D-glucopyranoside (**11**).* TFA (20 mL) was added to the solution of compound **10** (5.80 g, 9.50 mmol) in 100 mL of dichloromethane at −20 °C. The reaction mixture was stirred at the same temperature for 30 min, diluted with dichloromethane, quenched with 100 mL of saturated $NaHCO_3$, and extracted with dichloromethane (2 × 120 mL). The combined organic layer was dried, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 1:2) to give **11** (3.41 g, 97%) as a foam: R_f = 0.1 (petroleum ether/ethyl acetate, 1:1.5). Compound **11** was used for the next reaction directly.

*p-Tolyl 4,6-Di-O-acetyl-2,3-O-carbonyl-1-thio-β-D-glucopyranoside (**2**).* Triphosgene (0.95 g, 3.24 mmol) in 5 mL of dichloromethane was added dropwise to the solution of compound **11** (2.00 g, 5.40 mmol) and pyridine (2.61 mL, 32.4 mmol) in dichloromethane (25 mL) at −20 °C. The reaction mixture was stirred vigorously for about 20−30 min at the same temperature. After most of the starting material was consumed by TLC detection, the reaction was quenched by satd NH_4Cl aqueous solution (20 mL) and extracted with dichloromethane (2 × 25 mL). The combined organic layer was dried, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 3:1 to 1:2) to give **2** (1.63 g, 76%) as a foam and the recovered starting material **11**. Compound **2**: R_f = 0.2 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ −8.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2H, *J* = 8.0 Hz), 7.16 (d, 2H, *J* = 8.0 Hz), 5.17 (t, 1H, *J* = 9.6 Hz), 4.83 (d, 1H, *J* = 9.2 Hz), 4.34 (t, 1H, *J* = 10.0 Hz), 4.29 (dd, 1H, *J* = 2.0, 12.4 Hz), 4.18 (dd, 1H, *J* = 4.4, 12.4 Hz), 3.81 (dd, 1H, *J* = 9.6, 11.2 Hz), 3.76 (td, 1H, *J* = 2.4, 4.4 Hz), 2.38 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 168.9, 152.2, 140.1, 135.6, 129.9, 124.2, 82.3, 81.9, 77.1, 75.6, 67.2, 61.6, 21.2, 20.7, 20.5; MS (ESI) 397 $[M + H]^+$. Anal. Calcd for $C_{18}H_{20}O_8S$: C, 54.54; H, 5.09. Found: C, 54.34; H, 5.07.

*p-Tolyl 4,6-Di-O-benzyl-2,3-di-O-p-methoxybenzyl-1-thio-β-D-glucopyranoside (**12**).* NaH (1.52 g, 38.0 mmol, 60% w/w in mineral oil) was added in two portions to the solution of compound **9** (5.00 g, 9.50 mmol) in DMF (60 mL) at −15 °C, followed by the dropwise addition of benzyl bromide (4.00 mL, 33.3 mmol). After being stirred for 30 min at the same temperature, the reaction mixture was warmed to room temperature, stirred for 3 h, then poured into ice-cooled water. The aqueous layer was extracted with dichloromethane (2 × 100 mL). The combined organic layer was dried, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 10:1) to give **12** (6.30 g, 94%) as a foam: R_f = 0.6 (petroleum ether/ethyl acetate, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, 2H, *J* = 8.0 Hz), 7.19−7.36 (m, 14H), 7.02 (d, 2H, *J* = 8.0 Hz), 6.82−6.89 (m, 4H), 4.84 (d, 1H, *J* = 10.8 Hz), 4.82 (d, 1H, *J* = 10.4 Hz), 4.77 (d, 1H, *J* = 10.4 Hz), 4.67 (d, 1H, *J* = 9.6 Hz), 4.56−4.60 (m, 3H), 4.52 (d, 1H, *J* = 12.0 Hz), 3.79 (s, 3H), 3.78 (s, 3H), 3.76 (d, 1H, *J* = 1.6 Hz), 3.71 (dd, 1H, *J* = 4.8, 10.8 Hz), 3.67 (t, 1H, *J* = 8.8 Hz), 3.60 (t, 1H, *J* = 9.2 Hz), 3.43−3.47 (m, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 159.2, 138.3, 138.1, 137.6, 132.6, 130.6, 130.3, 129.8, 129.6, 129.4, 128.4, 128.3, 127.8, 127.7, 127.6, 127.4, 113.8, 87.6, 86.4, 80.5, 79.0, 77.8, 75.4, 75.0, 73.3, 69.0, 55.23, 55.21, 21.1; HRMS (ESI) calcd for $C_{43}H_{46}O_7SNa$ $[M + Na]^+$ 729.2856, found 729.2859.

*p-Tolyl 4,6-Di-O-benzyl-1-thio-β-D-glucopyranoside (**13**).* Compound **12** (3.00 g, 4.25 mmol) was resolved in the mixed solution of dichloromethane (80 mL) and water (8 mL), followed by the addition of DDQ (5.79 g, 25.5 mmol) at room temperature. The reaction mixture was stirred for 1 h, quenched by 100 mL of saturated $NaHCO_3$, and extracted with dichloromethane (2 × 120 mL). The combined organic layer was dried, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 1.5:1) to give **13** (1.74 g, 88%) as a foam: R_f = 0.1 (petroleum ether/ethyl acetate, 1.5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, 2H, *J* = 8.1 Hz), 7.26−7.36 (m, 10H), 7.06 (d, 2H, *J* = 8.1 Hz), 4.77 (d, 1H, *J* = 11.1 Hz), 4.63 (d, 1H, *J* = 12.0 Hz), 4.62 (d, 1H, *J* = 11.4 Hz), 4.55 (d, 1H, *J* = 12.0 Hz), 4.43 (d, 1H, *J* = 9.9 Hz), 3.66−3.82 (m, 3H), 3.45−3.50 (m, 2H), 3.32 (t, 1H, *J* = 9.0 Hz), 2.68 (br.s, 1H), 2.60 (br.s, 1H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 138.2, 138.1, 133.5, 129.7, 128.5, 128.3, 128.0, 127.9, 127.7, 127.6, 87.8, 79.1, 78.1, 77.1, 74.6, 73.4, 71.9, 69.0, 21.1; HRMS (ESI) calcd for $C_{27}H_{30}O_5SNa$ $[M + Na]^+$ 489.1706, found 489.1713.

*p-Tolyl 4,6-Di-O-benzyl-2,3-O-carbonyl-1-thio-β-D-glucopyranoside (**3**).* Triphosgene (0.64 g, 2.20 mmol) in 3 mL of dichloromethane was added dropwise to the solution of compound **13** (1.70 g, 3.65 mmol) and pyridine (1.76 mL, 22.0 mmol) in dichloromethane (20 mL) at −20 °C. The reaction mixture was stirred vigorously for about 20 min. After the starting material was completely consumed by TLC detection, the reaction was quenched by 15 mL of satd NH_4Cl solution and extracted with dichloromethane (2 × 20 mL). The combined organic layer was dried, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 8:1) to give **3** (1.54 g, 86%) as a foam: R_f = 0.5 (petroleum ether/ethyl acetate, 2:1); $[\alpha]_D$ 2.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2H, *J* = 8.0 Hz), 7.22−7.37 (m, 10H), 7.06 (d, 2H, *J* = 8.0 Hz), 4.77 (d, 1H, *J* = 10.0 Hz), 4.76 (d, 1H, *J* = 11.6 Hz), 4.58 (d, 1H, *J* = 12.0 Hz), 4.50 (d, 2H, *J* = 11.6 Hz), 4.32 (dd, 1H, *J* = 10.0, 11.2 Hz), 3.87 (t, 1H, *J* = 9.6 Hz), 3.73−3.80 (m, 3H), 3.58−3.62 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 139.5, 138.0, 136.8, 135.2, 129.8, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6, 125.1, 85.4, 82.3, 80.1, 76.1, 73.6, 73.5, 72.9, 68.2, 21.2; HRMS (ESI) calcd for $C_{28}H_{28}O_6S$ Na $[M + Na]^+$ 515.1499, found 515.1500.

Donors **4**−**6** were prepared starting from galactoside derivative **14**,[28] following the same procedure as described in the preparation of donors **1**-**3**.

*p-Tolyl 4,6-O-Benzylidene-2,3-O-carbonyl-1-thio-β-D-galactopyranoside (**4**).* The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give **4** (83%) as a foam: R_f = 0.3 (petroleum ether/ethyl acetate, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58−7.60 (m, 2H), 7.27−7.41 (m, 5H), 7.15 (d, 1H, *J* = 7.8 Hz), 5.52 (s, 1H), 4.90 (d, 1H, *J* = 9.3 Hz), 4.58−4.59 (m, 1H), 4.41−4.50 (m, 2H), 4.35 (dd, 1H, *J* = 2.4, 10.4 Hz), 4.09 (dd, 1H, *J* = 1.5, 12.6 Hz), 3.64 (d, 1H, *J* = 1.2 Hz), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 139.6, 136.7, 135.8, 129.9, 129.5, 128.2, 126.4, 124.4, 100.7, 82.9, 81.1, 72.4, 71.7, 69.9, 69.7, 21.3; HRMS (ESI) calcd for $C_{21}H_{20}O_6SNa$ $[M + Na]^+$ 423.0873, found 423.0886.

*p-Tolyl 4,6-Di-O-acetyl-1-thio-β-D-galactopyranoside (**16**).* Through acetylation and removal of *p*-methoxybenzyl groups, compound **16** was prepared from the known compound **15**.[42] The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 1:1) to give **16** (93%, two steps) as a foam: R_f = 0.1 (petroleum ether/ethyl acetate, 1:1.5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, 2H, *J* = 7.8 Hz), 7.13 (d, 2H, *J* = 8.1 Hz), 5.34 (d, 1H, *J* = 3.0 Hz), 4.50 (d, 1H, *J* = 9.6 Hz), 4.16 (d, 2H, *J* = 6.9 Hz), 3.80−3.90 (m, 2H), 3.65 (t, 1H, *J* = 9.0 Hz), 2.58 (s, 1H), 2.56 (s, 1H), 2.35 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 170.6, 138.4, 133.0, 129.7, 128.2, 88.8, 74.7, 73.2, 69.6, 69.4, 62.2, 21.1, 20.7(2C); HRMS (ESI) calcd for $C_{17}H_{22}O_7SNa$ $[M + Na]^+$ 393.0978, found 393.0980.

*p-Tolyl 4,6-Di-O-acetyl-2,3-O-carbonyl-1-thio-β-D-galactopyranoside (**5**).* The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 5:1) to give **5** (75%) as a foam: R_f = 0.3 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ −9.6 (*c* 2.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2H, *J* = 8.0 Hz), 7.16 (d, 2H, *J* = 8.0 Hz), 5,62 (dd, 1H, *J* = 1.2, 2.0 Hz), 4.90 (d, 1H, *J* = 9.6 Hz), 4.40 (dd, 1H, *J* = 2.4, 11.2 Hz), 4.30 (dd, 1H, *J* = 9.2, 11.2 Hz), 4.18 (d, 2H, *J* = 6.4 Hz), 4.04 (td, 1H, *J* = 1.2, 7.2 Hz), 2.37 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 169.1, 152.2, 139.6, 134.6, 129.8, 125.8, 84.5, 80.2, 75.5, 74.0, 65.5, 61.3, 21.2, 20.6, 20.4; MS (ESI) 397 $[M + H]^+$. Anal. Calcd for $C_{18}H_{20}O_8S$: C, 54.54; H, 5.09. Found: C, 54.28; H, 5.10.

*p-Tolyl 4,6-Di-O-benzyl-1-thio-β-D-galactopyranoside (**17**).* Through benzylation and removal of *p*-methoxybenzyl groups, compound **17** was prepared from the known intermediate **15**. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 1.5:1) to give **17** (82%, two steps) as a foam: R_f = 0.1 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ −5.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 2H, *J* = 8.0 Hz), 7.25−7.36 (m, 10H), 7.06 (d, 2H, *J* = 8.0 Hz), 4.72 (d, 1H, *J* = 11.6 Hz), 4.67 (d, 1H, *J* = 11.6 Hz), 4.53 (d, 1H, *J* = 11.6 Hz), 4.47 (d, 1H, *J* = 12.0 Hz), 4.44 (d, 1H, *J* = 9.2 Hz), 3.91 (d, 1H, *J* = 3.2 Hz), 3.59−3.73 (m, 5H), 2.51 (d, 1H, *J* = 8.0 Hz), 2.36−2.40 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.9, 137.8, 132.7, 129.6, 128.6, 128.4, 128.3, 127.8, 127.63, 127.56, 88.6, 77.5, 76.0, 75.3, 74.9, 73.5, 70.2, 68.5, 21.1; HRMS (ESI) calcd for $C_{27}H_{30}O_5SNa$ $[M + Na]^+$ 489.1706, found 489.1708.

*p-Tolyl 4,6-Di-O-benzyl-2,3-O-carbonyl-1-thio-β-D-galactopyranoside (**6**).* The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 8:1) to give **6** (83%) as a foam: R_f = 0.4 (petroleum ether/ethyl acetate, 2:1); $[\alpha]_D$ −11.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, 2H, *J* = 8.0 Hz), 7.25−7.35 (m, 8H), 7.19−7.21 (m, 2H), 7.10 (d, 2H, *J* = 8.0 Hz), 4.82 (d, 1H, *J* = 9.6 Hz), 4.75 (d, 1H, *J* = 12.0 Hz), 4.43−4.53 (m, 4H), 4.30 (dd, 1H, *J* = 2.0, 11.2 Hz), 4.22 (s, 1H), 3.80 (t, 1H, *J* = 6.0 Hz), 3.62−3.69 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

152.8, 139.1, 137.6, 137.1, 134.3, 129.8, 128.4, 128.3, 127.90, 127.86, 127.7, 127.6, 126.4, 84.4, 83.2, 78.2, 74.2, 73.60, 73.56, 71.9, 68.0, 21.2; MS (ESI) 515 [M + Na]$^+$. Anal. Calcd for $C_{28}H_{28}O_6S$: C, 68.27; H, 5.73. Found: C, 68.24; H, 5.62.

*General Procedure for the $BF_3 \cdot OEt_2$-Mediated α-Selective Glycosylations of Donor **2** or **5** with Acceptors **18a–g**.* Triflic anhydride (10.2 μL, 0.060 mmol, 1.4 equiv) was added to a stirred solution of **2** or **5** (22.2 mg, 0.056 mmol, 1.3 equiv), Ph_2SO (2.2 mg, 0.060 mmol, 1.4 equiv), and activated 4 Å molecular sieves (300 mg) in dichloromethane (3.0 mL) at −72 °C under nitrogen atmosphere. The reaction mixture was stirred for 3−5 min. After disappearance of donor detected by TLC, a solution of the acceptor alcohol **18a** (20.0 mg, 0.043 mmol, 1.0 equiv) or **18b−g** in dichloromethane (0.2 mL) was added dropwise to the preactivated system, followed by the addition of $BF_3 \cdot OEt_2$. The reaction mixture was stirred and slowly warmed to room temperature, and then quenched by Et_3N (0.1 mL). The precipitate was filtered off, and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel to give the disaccharides. The yields were calculated on the basis of the isolated products.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**19α**).* The coupling of donor **2** with acceptor **18a**[29] afforded **19α** (76%, α/β > 20:1) as a foam: R_f = 0.4 (petroleum ether/ethyl acetate, 1:1); $[\alpha]_D$ +23.6 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.38 (m, 15H), 5.35 (d, 1H, *J* = 2.8 Hz), 5.28 (t, 1H, *J* = 10.0 Hz), 5.00 (d, 1H, *J* = 10.8 Hz), 4.93 (d, 1H, *J* = 11.6 Hz), 4.80 (d, 2H, *J* = 11.2 Hz), 4.66 (d, 1H, *J* = 12.0 Hz), 4.60 (dd, 1H, *J* = 10.0, 11.6 Hz), 4.60 (d, 1H, *J* = 11.6 Hz), 4.56 (d, 1H, *J* = 3.6 Hz), 4.20 (dd, 1H, *J* = 2.8, 11.6 Hz), 4.14 (dd, 1H, *J* = 4.4, 12.4 Hz), 4.09 (td, 1H, *J* = 2.0, 12.4 Hz), 4.00 (t, 1H, *J* = 9.2 Hz), 3.87 (dd, 1H, *J* = 4.4, 11.6 Hz), 3.74−3.83 (m, 3H), 3.52 (dd, 1H, *J* = 3.6, 9.6 Hz), 3.46 (t, 1H, *J* = 9.6 Hz), 3.36 (s, 3H), 2.12 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 168.9, 152.7, 138.6, 138.1, 138.0, 128.5, 128.4, 128.1, 127.9, 127.8, 127.6, 98.1, 94.7, 82.0, 80.1, 76.8, 76.5, 75.7, 74.6, 73.5, 69.9 (2C), 68.1, 67.1, 61.2, 55.3, 20.6, 20.5; MS (ESI) 759 [M + Na]$^+$. Anal. Calcd for $C_{39}H_{44}O_{14}$: C, 63.58; H, 6.02. Found: C, 63.54; H, 6.02.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (**23α**).* The coupling of donor **2** with acceptor **18b**[36] afforded **23α** (51%) as a colorless glassy solid: R_f = 0.4 (petroleum ether/ethyl acetate, 1:1); $[\alpha]_D$ +25.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.34 (m, 15H), 5.86 (d, 1H, *J* = 3.2 Hz), 5.25 (t, 1H, *J* = 10.0 Hz), 5.04 (d, 1H, *J* = 10.4 Hz), 4.75 (d, 1H, *J* = 12.4 Hz), 4.73 (d, 1H, *J* = 10.4 Hz), 4.67 (t, 1H, *J* = 10.0 Hz), 4.63 (d, 1H, *J* = 12.0 Hz), 4.61 (d, 1H, *J* = 3.2 Hz), 4.60 (d, 1H, *J* = 12.0 Hz), 4.54 (d, 1H, *J* = 12.0 Hz), 4.14 (dd, 1H, *J* = 3.2, 11.6 Hz), 4.04 (dd, 1H, *J* = 3.6, 12.4 Hz), 3.96−4.00 (m, 1H), 3.80−3.84 (m, 3H), 3.74−3.77 (m, 1H), 3.67 (d, 2H, *J* = 2.0 Hz), 3.54 (dd, 1H, *J* = 3.6, 9.6 Hz), 3.41 (s, 3H), 2.10 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 168.8, 152.7, 138.3, 137.8 (2C), 128.53, 128.46, 128.4, 128.11, 128.06, 127.8, 127.6, 127.4, 97.8, 95.1, 81.2, 80.2, 76.4, 76.3, 75.3, 73.6, 73.3, 70.5, 69.3, 69.1, 68.0, 61.1, 55.5, 20.61, 20.56; HRMS (ESI) calcd for $C_{39}H_{45}O_{14}$ [M + H]$^+$ 737.2804, found 737.2803. Anal. Calcd for $C_{39}H_{44}O_{14}$: C, 63.58; H, 6.02. Found: C, 63.53; H, 6.17.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-galactopyranoside (**24α**).* The coupling of donor **2** with acceptor **18c**[37] in the absence of $BF_3 \cdot OEt_2$ afforded **24α** (77%) as a colorless oil: R_f = 0.3 (petroleum ether/ethyl acetate, 1:1); $[\alpha]_D$ +13.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25−7.42 (m, 15H), 5.27 (t, 1H, *J* = 10.0 Hz), 5.27 (d, 1H, *J* = 4.0 Hz), 4.83 (d, 1H, *J* = 12.0 Hz), 4.80 (d, 1H, *J* = 12.5 Hz), 4.77 (d, 1H, *J* = 12.5 Hz), 4.70 (d, 1H, *J* = 3.5 Hz), 4.70 (d, 1H, *J* = 11.0 Hz), 4.68 (dd, 1H, *J* = 10.5, 12.0 Hz), 4.51 (s, 2H), 4.22 (d, 1H, *J* = 3.0 Hz), 4.10−4.16 (m, 2H), 3.88−3.91 (m, 2H), 3.80−3.85 (m, 2H), 3.59 (t, 1H, *J* = 9.0 Hz), 3.48 (dd, 1H, *J* = 5.5, 9.0 Hz), 3.42 (dd, 1H, *J* = 2.0, 13.0 Hz), 3.36 (s, 3H), 2.12 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 168.9, 152.8, 138.1, 138.0, 137.3, 128.6, 128.48, 128.46, 128.1, 128.01, 127.95, 127.7, 98.3, 95.7, 77.2, 76.9, 76.0, 75.5, 73.5, 73.3, 73.0, 69.9, 67.74, 67.68, 66.7, 60.4, 55.5, 20.6; HRMS (ESI) calcd for $C_{39}H_{44}O_{14}Na$ [M + Na]$^+$ 759.2623, found 759.2625.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (**25α**).* The coupling of donor **2** with acceptor **18d**[38] afforded **25α** (70%, α/β > 20:1) as a colorless glassy solid: R_f = 0.5 (petroleum ether/ethyl acetate, 1:1); $[\alpha]_D$ +10.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.35 (m, 13H), 7.11−7.12 (m, 2H), 5.34 (d, 1H, *J* = 2.8 Hz), 5.24 (t, 1H, *J* = 10.0 Hz), 4.98 (d, 1H, *J* = 11.2 Hz), 4.87 (d, 1H, *J* = 3.6 Hz), 4.75−4.80 (m, 2H), 4.67 (d, 1H, *J* = 11.2 Hz), 4.64 (d, 1H, *J* = 12.0 Hz), 4.53 (d, 1H, *J* = 10.8 Hz), 4.51 (d, 1H, *J* = 12.0 Hz), 4.24 (dd, 1H, *J* = 2.8, 11.2 Hz), 3.84−4.02 (m, 5H), 3.67−3.79 (m, 4H), 3.42 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 168.8, 152.5, 138.2, 137.80, 137.76, 128.4, 127.9, 127.8, 127.7, 127.1, 96.5, 92.4, 80.0, 78.4, 76.74, 76.68, 76.6, 76.4, 75.4, 75.0, 70.3, 70.1, 68.2, 67.6, 60.7, 55.4, 20.6, 20.5; HRMS (ESI) calcd for $C_{39}H_{44}O_{14}K$ [M + K]$^+$ 775.2363, found 775.2362.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-α-D-glucopyranoside (**26α**).* The coupling of donor **2** with acceptor **18e**[39] afforded **26α** (78%) as a colorless glassy solid: R_f = 0.2 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +18.7 (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25−7.38 (m, 13H), 7.14−7.16 (m, 2H), 5.69 (d, 1H, *J* = 3.5 Hz), 5.22 (t, 1H, *J* = 10.0 Hz), 4.82 (d, 1H, *J* = 3.5 Hz), 4.73 (dd, 1H, *J* = 10.0, 11.5 Hz), 4.65 (d, 2H, *J* = 12.0 Hz), 4.62 (d, 1H, *J* = 11.5 Hz), 4.51 (d, 1H, *J* = 12.5 Hz), 4.50 (d, 1H, *J* = 11.5 Hz), 4.48 (d, 1H, *J* = 10.5 Hz), 4.10−4.21 (m, 3H), 3.86 (dd, 1H, *J* = 2.0, 13.0 Hz), 3.65−3.77 (m, 5H), 3.55 (dd, 1H, *J* = 3.5, 10.0 Hz), 3.38 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 168.9, 152.9, 137.5 (2C), 137.3, 128.6, 128.53, 128.45, 128.40, 128.3, 128.1, 127.9, 127.8, 127.6, 97.1, 94.4, 78.4, 77.5, 77.4, 76.9, 74.6, 73.7, 72.2, 69.9, 69.6, 67.8, 60.7, 55.1, 20.61, 20.58; HRMS (ESI) calcd for $C_{39}H_{44}O_{14}Na$ [M + Na]$^+$ 759.2623, found 759.2625.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**27α**).* The coupling of donor **2** with acceptor **18f**[40] afforded **27α** (75%) as a colorless glassy solid: R_f = 0.2 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +16.7 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.36 (m, 15H), 5.39 (d, 1H, *J* = 2.8 Hz), 5.31 (t, 1H, *J* = 10.0 Hz), 4.96 (d, 1H, *J* = 11.2 Hz), 4.91 (d, 1H, *J* = 10.8 Hz), 4.89 (d, 1H, *J* = 11.6 Hz), 4.78 (d, 1H, *J* = 11.2 Hz), 4.71 (d, 1H, *J* = 10.8 Hz), 4.65 (dd, 1H, *J* = 10.4, 11.6 Hz), 4.59 (d, 1H, *J* = 11.6 Hz), 4.31 (d, 1H, *J* = 7.6 Hz), 4.18−4.25 (m, 2H), 4.12 (dd, 1H, *J* = 2.0, 12.4 Hz), 3.87−3.91 (m, 2H), 3.82 (dd, 1H, *J* = 4.8, 11.6 Hz), 3.67 (t, 1H, *J* = 8.8 Hz), 3.55 (s, 3H), 3.46−3.47 (m, 2H), 3.41 (dd, 1H, *J* = 8.0, 9.2 Hz), 2.11 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 168.9, 152.7, 138.4, 138.3, 137.9, 128.5, 128.40, 128.39, 128.1, 127.99, 127.97, 127.9, 127.71, 127.68, 104.7, 94.5, 84.6, 82.2, 77.0. 76.9, 76.5, 75.6, 74.8, 74.7, 74.2, 70.0, 68.0, 67.0, 61.2, 57.1, 20.7, 20.5; HRMS (ESI) calcd for $C_{39}H_{44}O_{14}Na$ [M + Na]$^+$ 759.2623, found 759.2640.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-α-D-glucopyranoside (**28α**).* The coupling of donor **2** with acceptor **18g**[41] afforded **28α** (55%) as a foam: R_f = 0.3 (petroleum ether/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.99 (m, 4H), 7.54−7.87 (m, 2H), 7.43−7.53 (m, 2H), 7.36−7.42 (m, 5H), 7.28−7.32 (m, 2H), 6.16 (t, 1H, *J* = 9.6 Hz), 5.62 (t, 1H, *J* = 10.0 Hz), 5.33 (d, 1H, *J* = 3.2 Hz), 5.23−5.31 (m, 3H), 4.89 (dd, 1H, *J* = 10.0, 11.2 Hz), 3.92−4.35 (m, 6H), 3.81 (dd, 1H, *J* = 2.0, 11.2 Hz), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.1, 166.4, 165.3, 165.1, 152.7, 133.6, 133.4, 133.0, 129.9, 129.7, 129.6, 129.2, 129.1, 128.9, 128.8, 128.5, 128.2, 99.0, 94.9, 78.0, 76.8, 74.1, 72.7, 69.9, 68.0, 67.8, 65.9, 65.5, 62.0, 56.2, 20.7, 20.5; HRMS (ESI) calcd for $C_{39}H_{39}O_{17}$ [M + H]$^+$ 779.2182, found 779.2182.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**21α**).* The coupling of donor **5** with acceptor **18a** afforded **21α** (81%) as a colorless glassy solid: R_f = 0.4 (petroleum ether/ethyl acetate, 1:1); $[\alpha]_D$ +20.0 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.39 (m, 15H), 5.56 (s, 1H), 5.35 (d, 1H, *J* = 2.4 Hz), 5.00 (d, 1H, *J* = 10.8 Hz), 4.90 (d, 1H, *J* = 11.2 Hz), 4.80 (d, 1H, *J* = 10.8 Hz), 4.80 (d, 1H, *J* = 12.4 Hz), 4.66

(d, 1H, J = 12.0 Hz), 4.61 (dd, 1H, J = 2.4, 12.0 Hz), 4.59 (d, 1H, J = 11.6 Hz), 4.56 (d, 1H, J = 3.6 Hz), 4.55 (dd, 1H, J = 2.8, 12.0 Hz), 4.12 (dd, 1H, J = 5.6, 10.4 Hz), 3.97−4.06 (m, 3H), 3.73−3.85 (m, 3H), 3.51 (dd, 1H, J = 3.2, 9.6 Hz), 3.43 (t, 1H, J = 10.0 Hz), 3.36 (s, 3H), 2.14 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.1, 152.1, 138.6, 138.14, 138.06, 128.5, 127.9, 127.8, 127.6, 98.0, 95.6, 82.0, 80.1, 76.9, 75.7, 74.6, 74.2, 74.1, 73.5, 69.8, 68.3, 67.2, 66.6, 61.3, 55.3, 20.6, 20.5; HRMS (ESI) calcd for $C_{39}H_{45}O_{14}$ [M + H]$^+$ 737.2804, found 737.2804. Anal. Calcd for $C_{39}H_{44}O_{14}$: C, 63.58; H, 6.02. Found: C, 63.30; H, 6.17.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-galactopyranoside (**29α**).* The coupling of donor **5** with acceptor **18c** in the absence of $BF_3{\cdot}OEt_2$ afforded major product **29α** (75%, α/β = 15:1) as a colorless oil: R_f = 0.3 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +18.3 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.40 (m, 15H), 5.55 (s, 1H), 5.29 (d, 1H, J = 2.4 Hz), 4.76−4.81 (m, 3H), 4.67−4.73 (m, 3H), 4.47−4.54 (m, 3H), 4.37 (t, 1H, J = 7.6 Hz), 4.19 (d, 1H, J = 2.4 Hz), 3.94 (t, 1H, J = 10.8 Hz), 3.86−3.89 (m, 2H), 3.77 (dd, 1H, J = 3.2, 10.0 Hz), 3.58 (t, 1H, J = 9.2 Hz), 3.49 (dd, 1H, J = 5.6, 8.8 Hz), 3.41 (dd, 1H, J = 5.2, 11.2 Hz), 3.36 (s, 3H), 2.11 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.2, 153.0, 138.2, 138.0, 137.4, 128.6, 128.42, 128.39, 128.3, 128.01, 127.98, 127.9, 127.7, 127.6, 98.2, 96.6, 75.9, 75.3, 74.6, 74.1, 73.5, 73.3, 72.9, 68.0, 67.8, 66.8, 66.4, 60.3, 55.5, 20.56, 20.55; HRMS (ESI) calcd for $C_{39}H_{44}O_{14}Na$ [M + Na]$^+$ 759.2623, found 759.2625.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α- and β-D-galactopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (**30α** and **30β**).* The coupling of donor **5** with acceptor **18d** afforded a mixture of **30α** and **30β** (68%, α/β = 5:1). For **30α**: colorless glassy solid; R_f = 0.5 (petroleum ether/ethyl acetate, 1:1); $[\alpha]_D$ +30.0 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.37 (m, 13H), 7.15−7.17 (m, 2H), 5.34 (d, 1H, J = 2.8 Hz), 5.10 (s, 1H), 4.99 (d, 1H, J = 11.2 Hz), 4.86 (d, 1H, J = 3.6 Hz), 4.81 (d, 1H, J = 10.8 Hz), 4.67 (d, 1H, J = 11.6 Hz), 4.65 (d, 1H, J = 12.0 Hz), 4.50−4.56 (m, 3H), 4.40 (dd, 1H, J = 2.8, 12.0 Hz), 4.09−4.12 (m, 1H), 3.97−4.02 (m, 2H), 3.76−3.83 (m, 4H), 3.68−3.72 (m, 2H), 3.42 (s, 3H), 2.09 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.0, 152.6, 138.4, 137.78, 137.76, 128.6, 128.44, 128.41, 128.1, 128.0, 127.9, 127.8, 127.7, 96.4, 92.9, 80.4, 78.6, 75.8, 75.4, 75.0, 74.03, 73.96, 73.6, 70.3, 68.5, 68.2, 66.6, 61.0, 55.3, 20.6, 20.5; HRMS (ESI) calcd for $C_{39}H_{44}O_{14}Na$ [M + Na]$^+$ 759.2623, found 759.2626. For **30β**: foam; R_f = 0.4 (petroleum ether/ethyl acetate, 1:1); $[\alpha]_D$ +3.8 (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.38 (m, 13H), 7.15−7.17 (m, 2H), 5.58 (br.s, 1H), 5.02 (d, 1H, J = 8.0 Hz), 4.85 (d, 1H, J = 3.6 Hz), 4.85 (d, 2H, J = 10.8 Hz), 4.82 (d, 1H, J = 10.8 Hz), 4.63 (d, 1H, J = 12.0 Hz), 4.55 (dd, 1H, J = 4.4, 12.4 Hz), 4.51 (d, 1H, J = 11.2 Hz), 4.50 (d, 1H, J = 12.0 Hz), 4.20 (dd, 1H, J = 6.4, 11.6 Hz), 4.12 (dd, 1H, J = 2.8, 12.0 Hz), 4.07 (dd, 1H, J = 6.4, 11.2 Hz), 4.03 (t, 1H, J = 9.6 Hz), 3.93 (td, 1H, J = 1.2, 6.4 Hz), 3.65−3.79 (m, 5H), 3.42 (s, 3H), 2.16 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 169.1, 152.4, 138.1, 138.0, 137.8, 128.5, 128.4, 128.2, 127.9, 127.85, 127.80, 101.7, 99.1, 81.1, 81.0, 78.3, 77.8, 75.9, 75.5, 75.1, 73.5, 72.9, 70.1, 68.2, 65.2, 61.2, 55.2, 20.7, 20.5; HRMS (ESI) calcd for $C_{39}H_{44}O_{14}Na$ [M + Na]$^+$ 759.2623, found 759.2618.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-galactopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-α-D-glucopyranoside (**31α**).* The coupling of donor **5** with acceptor **18e** afforded **31α** (77% yield) as a colorless glassy solid: R_f = 0.2 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +47.8 (c 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.37 (m, 13H), 7.14 (d, 2H, J = 7.2 Hz), 5.70 (s, 1H), 5.34 (s, 1H), 4.76 (d, 1H, J = 3.2 Hz), 4.60−4.67 (m, 3H), 4.46−4.53 (m, 5H), 4.37 (t, 1H, J = 6.4 Hz), 4.15 (t, 1H, J = 7.6 Hz), 4.07 (dd, 1H, J = 6.4, 11.2 Hz), 3.65−3.77 (m, 5H), 3.55 (dd, 1H, J = 3.2, 10.0 Hz), 3.35 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.2, 153.0, 137.52, 137.46 (2C), 128.64, 128.57, 128.5, 128.43, 128.40, 128.1, 127.9, 127.8, 127.6, 97.3, 95.1, 78.5, 77.9, 76.5, 74.6, 74.33, 74.28, 73.7, 72.5, 69.9, 68.1, 67.9, 66.8, 61.1, 55.1, 20.6, 20.5; HRMS (ESI) calcd for $C_{39}H_{45}O_{14}$ [M + H]$^+$ 737.2804, found 737.2803. Anal. Calcd for $C_{39}H_{44}O_{14}$: C, 63.58; H, 6.02. Found: C, 63.43; H, 6.05.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**32α**).* The coupling of donor **5** with acceptor **18f** afforded **32α** (76% yield) as a colorless glassy solid: R_f = 0.25 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +17.0 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.36 (m, 15H), 5.58 (br.s, 1H), 5.42 (d, 1H, J = 2.4 Hz), 4.95 (d, 1H, J = 10.8 Hz), 4.91 (d, 1H, J = 11.2 Hz), 4.88 (d, 1H, J = 11.2 Hz), 4.78 (d, 1H, J = 10.8 Hz), 4.70 (d, 1H, J = 10.8 Hz), 4.66 (dd, 1H, J = 2.4, 12.0 Hz), 4.59 (d, 1H, J = 11.2 Hz), 4.58 (dd, 1H, J = 3.6, 12.0 Hz), 4.30 (d, 1H, J = 7.6 Hz), 4.08−4.17 (m, 2H), 4.02 (dd, 1H, J = 5.6, 10.0 Hz), 3.89 (d, 1H, J = 11.2 Hz), 3.80−3.84 (m, 1H), 3.64−3.69 (m, 1H), 3.54 (s, 3H), 3.45−3.47 (m, 2H), 3.41 (dd, 1H, J = 8.0, 9.2 Hz), 2.15 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 169.2, 152.8, 138.4, 138.3, 137.9, 128.5, 128.4, 128.1, 127.93, 127.86, 127.7, 104.6, 95.5, 84.6, 82.2, 76.9, 75.6, 74.8, 74.7, 74.3, 74.2, 74.1, 68.4, 67.2, 66.6, 61.2, 57.1, 20.6, 20.5; HRMS (ESI) calcd for $C_{39}H_{44}O_{14}Na$ [M + Na]$^+$ 759.2623, found 759.2629.

*Methyl (4,6-Di-O-acetyl-2,3-O-carbonyl-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-α-D-glucopyranoside (**33α**).* The coupling of donor **5** with acceptor **18g** afforded **33α** (60% yield) as a foam: R_f = 0.1 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +18.0 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, 2H, J = 7.6 Hz), 7.94 (d, 2H, J = 7.2 Hz), 7.88 (d, 2H, J = 7.6 Hz), 7.50−7.56 (m, 2H), 7.36−7.45 (m, 5H), 7.26−7.32 (m, 2H), 6.16 (t, 1H, J = 10.0 Hz), 5.68 (s, 1H), 5.65 (t, 1H, J = 10.0 Hz), 5.37 (d, 1H, J = 2.4 Hz), 5.24−5.30 (m, 2H), 5.01 (dd, 1H, J = 2.8, 12.0 Hz), 4.67 (dd, 1H, J = 2.8, 12.0 Hz), 4.26 (dd, 1H, J = 2.4, 10.0 Hz), 4.17 (t, 1H, J = 6.4 Hz), 4.06 (dd, 1H, J = 5.6, 11.2 Hz), 3.92−3.98 (m, 2H), 3.80 (dd, 1H, J = 1.6, 11.2 Hz), 3.48 (s, 3H), 2.16 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.2, 165.8, 165.7, 165.5, 152.8, 133.7, 133.4, 133.2, 129.9, 129.8, 129.7, 129.1, 129.0, 128.64, 128.57, 128.4, 128.3, 97.1, 95.6, 74.24, 74.18, 71.9, 70.3, 69.0, 68.7, 68.0, 67.0, 66.9, 61.5, 55.8, 20.5, 20.4; HRMS (ESI) calcd for $C_{39}H_{38}O_{17}Na$ [M + Na]$^+$ 801.2001, found 801.2010.

*General Procedure for the $SnCl_4$-Modulated α/β-Selective Glycosylations of Donor **3** or **6** with Acceptors **18a–g**.* **Protocol A** (in the absence of $SnCl_4$): Triflic anhydride (9.50 μL, 0.056 mmol, 1.3 equiv) was added to a stirred solution of **3** or **6** (25.4 mg, 0.052 mmol, 1.2 equiv), BSM (11.8 mg, 0.056 mmol, 1.3 equiv), and activated 4 Å molecular sieves (300 mg) in dichloromethane (3.0 mL) at −72 °C under nitrogen atmosphere. The reaction mixture was stirred for 3−5 min. After the disappearance of donor detected by TLC, a solution of the acceptor alcohol **18a** (20.0 mg, 0.043 mmol, 1.0 equiv) or **18b−g** in dichloromethane (0.2 mL) was added dropwise to the preactivated system. The reaction mixture was stirred and slowly warmed to room temperature, and then quenched by Et_3N (0.1 mL). The precipitate was filtered off and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel to give the disaccharides. **Protocol B** (in the presence of $SnCl_4$): Triflic anhydride (9.50 μL, 0.056 mmol, 1.3 equiv) was added to a stirred solution of **3** or **6** (25.4 mg, 0.052 mmol, 1.2 equiv), BSM (11.8 mg, 0.056 mmol, 1.3 equiv), and activated 4 Å molecular sieves (300 mg) in dichloromethane (3.0 mL) at −72 °C under nitrogen atmosphere. The reaction mixture was stirred for 3−5 min. After the disappearance of donor detected by TLC, a solution of the acceptor alcohol **18a** (20.0 mg, 0.043 mmol, 1.0 equiv) or **18b−g** in dichloromethane (0.2 mL) was added dropwise to the preactivated system. The reaction was monitored by TLC. $SnCl_4$ (1−3 equiv) was added after disappearance of the acceptor at about −40 °C to −20 °C. The reaction mixture was warmed up to room temperature to accomplish the anomerization process, and then quenched by Et_3N (0.1 mL). The precipitate was filtered off and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel to give the disaccharides.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**20β**).* The coupling of donor **3** with acceptor **18a** by protocol A afforded **20β** (86% yield) as a foam: R_f = 0.3 (petroleum ether/ethyl acetate, 1.5:1). Compound **20β** is a known compound, and its spectroscopic data coincide with the previous report.[18c]

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**20α**).* The coupling of donor **3** with acceptor **18a** by protocol B afforded **20α** (80% yield) as a colorless glassy solid: R_f = 0.25 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +21.0 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.37 (m, 25H), 5.32 (d, 1H, J = 2.8 Hz), 4.99 (d, 1H, J = 10.8 Hz), 4.90 (d, 1H, J = 11.6 Hz), 4.80 (d, 1H, J = 4.0 Hz), 4.76−4.79 (m, 2H), 4.63−4.70 (m, 2H), 4.53−4.59 (m, 3H), 4.47 (d, 1H, J = 11.2 Hz), 4.42 (d, 1H, J = 12.0 Hz), 4.12 (dd, 1H, J = 2.8, 11.6 Hz), 3.96−4.01 (m, 2H), 3.66−3.84 (m, 5H), 3.51−3.57 (m, 2H), 3.48 (t, 1H, J = 8.0 Hz), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 138.6, 138.1 (2C), 137.7, 137.0, 128.5, 128.42, 128.39, 128.37, 128.1, 128.03, 127.96, 127.92, 127.89, 127.79, 127.75, 127.7, 127.6, 98.0, 95.0, 82.0, 80.12, 80.07, 77.2, 75.7, 74.7, 74.5, 73.5 (2C), 72.8, 72.4, 69.9, 67.4, 66.7, 55.2; HRMS (ESI) calcd for $C_{49}H_{52}O_{12}K$ $[M + K]^+$ 871.3090, found 871.3095.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α- and β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (**34α** and **34β**).* The coupling of donor **3** with acceptor **18b** by either protocol A or protocol B afforded a mixture of **34α** and **34β**. Both of them are known compounds, and their spectroscopic data coincide with the previous report.[18c]

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α- and β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-galactopyranoside (**35α** and **35β**).* The coupling of donor **3** with acceptor **18c** by protocol A afforded an inseparable anomeric mixture of **35α** and **35β** (85% yield, α/β = 1:10) as a colorless glassy solid, and the anomeric ratio was determined by integration of the ^{1}H NMR spectrum: R_f = 0.4 (petroleum ether/ethyl acetate, 1.5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.40 (m, 30H), 5.29 (d, 0.1H, J = 3.2 Hz, H-$1_{\alpha}'$), 5.16 (d, 1H, J = 7.2 Hz, H-$1_{\beta}'$), 4.94 (d, 1H, J = 11.6 Hz), 4.83 (d, 1H, J = 12.0 Hz), 4.77 (d, 1H, J = 11.6 Hz), 4.79 (d, 1H, J = 12.0 Hz), 4.62 (t, 1H, J = 3.6 Hz), 4.61 (d, 1H, J = 11.6 Hz), 4.47−4.51 (m, 3H), 4.43 (d, 1H, J = 12.0 Hz), 4.34 (d, 1H, J = 12.0 Hz), 4.19−4.23 (m, 1H), 3.85−4.01 (m, 7H), 3.62−3.68 (m, 2H), 3.54−3.59 (m, 2H), 3.36−3.38 (m, 1H), 3.37 (s, 3H), 3.35 (s, 0.3H); HRMS (ESI) calcd for $C_{49}H_{52}O_{12}Na$ $[M + Na]^+$ 855.3351, found 855.3359.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (**36β**).* The coupling of donor **3** with acceptor **18d** by protocol A afforded **36β** (90% yield) as a foam: R_f = 0.3 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +13.8 (c 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.38 (m, 23H), 7.15−7.17 (m, 2H), 4.99 (d, 1H, J = 4.0 Hz), 4.89 (d, 1H, J = 7.6 Hz), 4.86 (d, 1H, J = 10.8 Hz), 4.85 (d, 1H, J = 11.2 Hz), 4.81 (d, 1H, J = 10.8 Hz), 4.78 (d, 1H, J = 11.6 Hz), 4.62 (d, 1H, J = 12.0 Hz), 4.56 (d, 1H, J = 12.0 Hz), 4.52 (d, 1H, J = 11.2 Hz), 4.50 (d, 1H, J = 12.4 Hz), 4.49 (d, 1H, J = 12.0 Hz), 4.47 (d, 1H, J = 12.0 Hz), 4.11−4.13 (m, 2H), 4.01 (t, 1H, J = 9.2 Hz), 3.93−3.98 (m, 1H), 3.63−3.79 (m, 7H), 3.52 (ddd, 1H, J = 2.0, 4.0, 8.4 Hz), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 138.2, 138.0, 137.9, 137.7, 136.7, 128.5, 128.43, 128.37, 128.1, 128.0, 127.9, 127.80, 127.77, 127.71, 127.66, 100.6, 99.3, 83.3, 81.2, 80.5, 77.8, 77.7, 77.0, 75.9, 75.0, 73.7, 73.6, 73.5, 72.9, 70.1, 68.3, 68.1, 55.2; HRMS (ESI) calcd for $C_{49}H_{53}O_{12}$ $[M + H]^+$ 833.3532, found 833.3532. Anal. Calcd for $C_{49}H_{52}O_{12}$: C, 70.66; H, 6.29. Found: C, 70.38; H, 6.14.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (**36α**).* The coupling of donor **3** with acceptor **18d** by protocol B afforded **36α** (85% yield) as a foam: R_f = 0.15 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +27.1 (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.34 (m, 18H), 7.07−7.18 (m, 7H), 5.34 (d, 1H, J = 2.8 Hz), 4.87 (d, 1H, J = 3.6 Hz), 4.73−4.86 (m, 5H), 4.63 (d, 1H, J = 12.0 Hz), 4.51 (d, 1H, J = 12.0 Hz), 4.50 (d, 2H, J = 11.6 Hz), 4.44 (d, 1H, J = 11.2 Hz), 4.33 (d, 1H, J = 12.4 Hz), 4.18 (dd, 1H, J = 2.8, 11.6 Hz), 4.04 (t, 1H, J = 9.6 Hz), 3.97 (t, 1H, J = 9.2 Hz), 3.82−3.87 (m, 2H), 3.73−3.78 (m, 2H), 3.65−3.70 (m, 2H), 3.50 (dd, 1H, J = 2.8, 11.2 Hz), 3.41 (s, 3H) 3.39−3.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 138.0, 137.9, 137.8, 137.7, 137.2, 128.4, 128.3, 127.92, 127.89, 127.87, 127.8, 127.72, 127.67, 127.6, 96.6, 92.6, 80.19, 80.15, 78.2, 76.6, 75.9, 74.9, 74.5, 73.5, 73.4, 72.8, 72.6, 70.2, 68.2, 67.0, 55.3; HRMS (ESI) calcd for $C_{49}H_{52}O_{12}K$ $[M + K]^+$ 871.3090, found 871.3082.

*Methyl (4,6-di-O-benzyl-2,3-O-carbonyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-α-D-glucopyranoside (**37β**).* The coupling of donor **3** with acceptor **18e** by protocol A afforded **37β** (84% yield) as a glassy solid: R_f = 0.3 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +13.6 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.36 (m, 25H), 5.32 (d, 1H, J = 7.6 Hz), 5.00 (d, 1H, J = 11.2 Hz), 4.76 (d, 1H, J = 11.2 Hz), 4.72 (d, 1H, J = 11.6 Hz), 4.60 (d, 1H, J = 12.0 Hz), 4.58 (d, 1H, J = 4.0 Hz), 4.54 (d, 1H, J = 12.0 Hz), 4.50 (d, 1H, J = 11.2 Hz), 4.44 (d, 1H, J = 12.0 Hz), 4.27 (d, 1H, J = 12.0 Hz), 4.41 (d, 1H, J = 11.2 Hz), 4.31 (d, 1H, J = 12.0 Hz), 4.27 (t, 1H, J = 9.2 Hz), 4.14 (dd, 1H, J = 9.6, 11.2 Hz), 4.01−4.06 (m, 2H), 3.57−3.72 (m, 7H), 3.48 (td, 1H, J = 2.8, 8.4 Hz), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 138.6, 138.0, 137.9, 137.5, 136.8, 128.6, 128.5, 128.33, 128.27, 128.2, 128.14, 128.08, 128.0, 127.8, 127.64, 127.58, 127.5, 127.4, 99.9, 97.4, 83.7, 80.31, 80.26, 78.5, 75.7, 74.7, 73.8, 73.6, 73.43, 73.36, 73.0, 69.8, 68.4, 67.9, 55.2; MS (ESI) 855 $[M + Na]^+$. Anal. Calcd for $C_{49}H_{52}O_{12}$: C, 70.66; H, 6.29. Found C, 70.52; H, 6.26.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-α-D-glucopyranoside (**37α**).* The coupling of donor **3** with acceptor **18e** by protocol B afforded **37α** (78% yield) as a glassy solid: R_f = 0.25 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +18.9 (c 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13−7.36 (m, 25H), 5.70 (d, 1H, J = 3.2 Hz), 4.78−4.83 (m, 1H), 4.76 (d, 1H, J = 12.0 Hz), 4.75 (d, 1H, J = 2.8 Hz), 4.69 (d, 1H, J = 10.8 Hz), 4.64 (d, 1H, J = 12.0 Hz), 4.44−4.54 (m, 6H), 4.27 (d, 1H, J = 12.0 Hz), 4.11−4.16 (m, 2H), 4.03 (d, 2H, J = 6.0 Hz), 3.75 (dd, 1H, J = 2.8, 10.4 Hz), 3.64−3.73 (m, 3H), 3.49 (dd, 1H, J = 3.6, 10.0 Hz), 3.31−3.37 (m, 2H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 137.9, 137.52, 137.49, 137.4, 137.1, 128.8, 128.6, 128.5, 128.44, 128.36, 128.3, 128.1, 128.0, 127.91, 127.85, 127.8, 127.7, 127.6, 97.2, 94.7, 80.4, 78.5, 77.7, 77.5, 74.7, 74.6, 73.7, 73.3, 72.8, 72.7, 72.1, 69.7, 68.0, 66.9, 55.1; HRMS (ESI) calcd for $C_{49}H_{56}NO_{12}$ $[M + NH_4]^+$ 850.3797, found 850.3795. Anal. Calcd for $C_{49}H_{52}O_{12}$: C, 70.66; H, 6.29. Found: C, 70.38; H, 6.32.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**38β**).* The coupling of donor **3** with acceptor **18f** by protocol A afforded **38β** (87% yield) as a colorless glassy solid: R_f = 0.4 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +8.0 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.34 (m, 25H), 4.93 (d, 1H, J = 11.2 Hz), 4.90 (d, 1H, J = 11.6 Hz), 4.88 (d, 1H, J = 11.2 Hz), 4.77 (d, 2H, J = 12.0 Hz), 4.76 (d, 1H, J = 7.2 Hz), 4.69 (d, 1H, J = 10.8 Hz), 4.58 (d, 1H, J = 11.6 Hz), 4.55 (d, 1H, J = 10.0 Hz), 4.51 (d, 1H, J = 11.2 Hz), 4.49 (d, 1H, J = 12.0 Hz), 4.31 (d, 1H, J = 7.6 Hz), 4.21 (dd, 1H, J = 9.6, 11.6 Hz), 4.14 (d, 1H, J = 11.2 Hz), 4.03 (dd, 1H, J = 8.0, 12.0 Hz), 3.95 (t, 1H, J = 9.2 Hz), 3.63−3.70 (m, 4H), 3.57 (s, 3H), 3.38−3.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 138.48, 138.45, 138.2, 137.8, 136.8, 128.5, 128.43, 128.41, 128.35, 128.14, 128.07, 128.0, 127.83, 127.78, 127.75, 127.63, 127.60, 104.7, 100.0, 84.6, 83.4, 82.3, 77.93, 77.88, 77.2, 75.6, 74.9, 74.7, 74.5, 74.0, 73.6, 72.9, 68.8, 68.2, 57.2; HRMS (ESI) calcd for $C_{49}H_{56}NO_{12}$ $[M + NH_4]^+$ 850.3797, found 850.3796.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**38α**).* The coupling of donor **3** with acceptor **18f** by protocol B afforded **38α** (81% yield, α/β > 20:1) as a colorless glassy solid: R_f = 0.35 (petroleum ether/ethyl acetate, 1.5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.35 (m, 25H), 5.37 (d, 1H, J = 2.8 Hz), 4.94 (d, 1H, J = 10.8 Hz), 4.90 (d, 1H, J = 11.2 Hz), 4.87 (d, 1H, J = 12.0 Hz), 4.78 (d, 2H, J = 10.0 Hz), 4.71 (dd, 1H, J = 10.0, 12.0 Hz), 4.69 (d, 1H, J = 11.2 Hz), 4.59 (d, 1H, J = 12.4 Hz), 4.57 (d, 1H, J = 11.2 Hz), 4.47 (d, 1H, J = 12.8 Hz), 4.44 (d, 1H, J = 12.4 Hz), 4.29 (d, 1H, J = 8.0 Hz), 4.16 (dd, 1H, J = 3.2, 12.0 Hz), 4,01 (t, 1H, J = 9.2 Hz), 3.61−3.88 (m, 7H), 3.50 (s, 3H), 3.45 (d, 2H, J = 9.6 Hz), 3.40 (t, 1H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 138.4 (2C), 137.9, 137.7, 137.1, 128.44, 128.42, 128.40, 128.38, 128.1, 128.0, 127.91, 127.87, 127.85, 127.7, 127.6, 104.6, 94.4, 84.6, 82.2, 80.1, 77.2, 77.1, 75.6, 74.8, 74.5, 74.3, 73.5, 72.7, 72.2, 67.4, 66.6, 57.1; HRMS (ESI) calcd for $C_{49}H_{56}NO_{12}$ $[M + NH_4]^+$ 850.3797, found 850.3799.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-α-D-glucopyranoside (**39β**).* The coupling of donor **3** with acceptor **18g** by protocol A afforded major product **39β** (83% yield, α/β = 1:5) as a foam: R_f = 0.25 (petroleum ether/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−7.98 (m, 4H), 7.86 (d, 2H, J = 7.2 Hz), 7.49−7.52 (m, 2H), 7.34−7.43 (m, 5H), 7.26−7.33 (m, 10H), 7.22−7.24 (m, 2H), 6.17 (t, 1H, J = 10.0 Hz), 5.46 (t, 1H, J = 10.0 Hz), 5.22−5.27 (m, 1H), 5.24 (d, 1H, J = 3.6 Hz), 4.93 (d, 1H, J = 7.6 Hz), 4.78 (d, 1H, J = 11.2 Hz), 4.56 (d, 1H, J = 12.4 Hz), 4.51 (d, 1H, J = 11.2 Hz), 4.46 (d, 1H, J = 12.4 Hz), 4.27−4.34 (m, 2H), 4.04 (dd, 1H, J = 2.0, 11.6 Hz), 3.99 (dd, 1H, J = 7.6, 11.6 Hz), 3.95 (t, 1H, J = 9.2 Hz), 3.82 (dd, 1H, J = 6.8, 11.6 Hz), 3.66−3.73 (m, 2H), 3.57−3.61 (m, 1H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 165.4, 153.4, 137.8, 136.8, 133.5, 133.3, 133.1, 129.91, 129.87, 129.6, 129.2, 129.1, 128.8, 128.4, 128.3, 128.12, 128.10, 127.7, 100.0, 96.8, 83.2, 78.0, 73.9, 73.5, 72.9, 72.0, 70.3, 69.7, 69.0, 68.4, 68.1, 55.6; HRMS (ESI) calcd for $C_{49}H_{47}O_{15}$ [M + H]$^+$ 875.2910, found 875.2910.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-α-D-glucopyranoside (**39α**).* The coupling of donor **3** with acceptor **18g** by protocol B afforded **39α** (79% yield, α/β > 20:1) as a foam: R_f = 0.3 (petroleum ether/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.99 (m, 2H), 7.86−7.92 (m, 4H), 7.48−7.53 (m, 2H), 7.23−7.44 (m, 17H), 6.14 (t, 1H, J = 10.0 Hz), 5.57 (t, 1H, J = 10.0 Hz), 5.29 (d, 1H, J = 2.8 Hz), 5.26 (d, 1H, J = 3.6 Hz), 5.22 (t, 1H, J = 3.6 Hz), 4.87 (dd, 1H, J = 9.6, 11.6 Hz), 4.81 (d, 1H, J = 11.6 Hz), 4.52 (d, 1H, J = 12.0 Hz), 4.50 (d, 1H, J = 12.0 Hz), 4.39 (d, 1H, J = 12.0 Hz), 4.23−4.27 (m, 1H), 4.18 (dd, 1H, J = 3.2, 12.0 Hz), 4.02 (t, 1H, J = 9.2 Hz), 3.95 (dd, 1H, J = 5.6, 11.2 Hz), 3.73−3.78 (m, 2H), 3.67 (dd, 1H, J = 3.2, 10.8 Hz), 3.53 (dd, 1H, J = 2.0, 10.8 Hz), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (2C), 165.3, 153.5, 137.7, 137.1, 133.5, 133.4, 133.1, 129.93, 129.89, 129.7, 129.6, 129.1, 129.0, 128.7, 128.5, 128.44, 128.40, 128.3, 128.0, 127.8, 97.0, 94.7, 80.1, 77.1, 74.6, 73.5, 72.8, 72.6, 72.0, 70.3, 69.2, 68.2, 67.3, 67.0, 55.7; HRMS (ESI) calcd for $C_{49}H_{50}NO_{15}$ [M + NH_4]$^+$ 892.3180, found 892.3183.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**22α**).* The coupling of donor **6** with acceptor **18a** by protocol B afforded **22α** (78% yield) as a colorless glassy solid: R_f = 0.4 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +15.0 (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.37 (m, 25H), 5.30 (d, 1H, J = 2.8 Hz), 4.99 (d, 1H, J = 10.8 Hz), 4.88 (d, 1H, J = 11.2 Hz), 4.79 (d, 1H, J = 10.8 Hz), 4.79 (d, 1H, J = 12.0 Hz), 4.78 (d, 1H, J = 11.2 Hz), 4.73 (dd, 1H, J = 2.8, 12.0 Hz), 4.65 (d, 1H, J = 12.0 Hz), 4.63 (dd, 1H, J = 2.0, 12.0 Hz), 4.58 (d, 1H, J = 11.2 Hz), 4.54 (d, 1H, J = 3.6 Hz), 4.52 (d, 1H, J = 11.6 Hz), 4.46 (d, 1H, J = 11.6 Hz), 4.40 (d, 1H, J = 11.6 Hz), 4.20 (s, 1H), 3.99 (t, 1H, J = 9.2 Hz), 3.89 (t, 1H, J = 6.4 Hz), 3.74 (dd, 1H, J = 4.8, 12.0 Hz), 3.79 (s, 1H), 3.71−3.76 (m, 1H), 3.58 (dd, 1H, J = 3.6, 8.8 Hz), 3.50−3.53 (m, 2H), 3.44 (t, 1H, J = 9.6 Hz), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 138.6, 138.1, 137.6, 137.1, 128.5, 128.42, 128.38, 128.1, 128.0, 127.91, 127.85, 127.74, 127.69, 127.6, 98.0, 95.6, 82.0, 80.1, 77.1, 75.7, 74.8, 74.5, 73.9, 73.5, 72.9, 70.6, 69.9, 67.9, 66.9, 55.2; HRMS (ESI) calcd for $C_{49}H_{56}NO_{12}$ [M + NH_4]$^+$: 850.3797, found 850.3796. Anal. Calcd for $C_{49}H_{52}O_{12}$: C, 70.66; H, 6.29. Found: C, 70.40; H, 6.43.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α- and β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (**40α** and **40β**).* The coupling of donor **6** with acceptor **18b** by protocol B afforded a mixture of **40α** and **40β** (73% yield, α/β = 3:1), both of them are colorless glassy solids. For **40α**: R_f = 0.4 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +5.0 (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.34 (m, 23H), 7.18−7.0 (m, 2H), 5.85 (d, 1H, J = 3.2 Hz), 4.99 (d, 1H, J = 10.4 Hz), 4.76 (d, 1H, J = 2.8 Hz), 4.75 (d, 2H, J = 10.8 Hz), 4.70 (dd, 1H, J = 3.2, 12.0 Hz), 4.62 (d, 2H, J = 12.0 Hz), 4.58 (d, 1H, J = 3.2 Hz), 4.53 (d, 1H, J = 12.0 Hz), 4.48 (d, 1H, J = 11.6 Hz), 4.40 (d, 1H, J = 12.0 Hz), 4.34 (d, 1H, J = 12.0 Hz), 4.28 (d, 1H, J = 11.6 Hz), 4.08 (s, 1H), 3.96 (t, 1H, 8.8 Hz), 3.76−3.84 (m, 3H), 3.58−3.65 (m, 2H), 3.52 (dd, 1H, J = 3.2, 9.6 Hz), 3.45 (t, 1H, 7.6 Hz), 3.40 (s, 3H), 3.35−3.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 138.3, 138.1, 137.9, 137.6, 137.0, 128.5, 128.44, 128.37, 128.3, 128.13, 128.11, 128.08, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 97.8, 96.0, 81.4, 80.1, 75.7, 75.4, 74.1, 73.9, 73.5, 73.3, 73.1, 72.9, 71.2, 69.3, 69.2, 68.0, 55.4; HRMS (ESI) calcd for $C_{49}H_{52}O_{12}$Na [M + Na]$^+$ 855.3351, found 855.3358. For **40β**: R_f = 0.3 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ −1.3 (c 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.21 (m, 5H), 7.25−7.35 (m, 20H), 4.86 (d, 1H, J = 10.8 Hz), 4.78 (d, 1H, J = 10.8 Hz), 4.78 (d, 1H, J = 13.2 Hz), 4.77 (d, 1H, J = 12.4 Hz), 4.73 (d, 1H, J = 11.2 Hz), 4.62 (d, 1H, J = 12.0 Hz), 4.59 (d, 1H, J = 3.6 Hz), 4.50 (d, 1H, J = 11.2 Hz), 4.49 (d, 1H, J = 7.6 Hz), 4.37 (dd, 1H, J = 8.0, 12.0 Hz), 4.30 (d, 1H, J = 12.0 Hz), 4.29 (d, 1H, J = 11.6 Hz), 4.22 (d, 1H, J = 11.6 Hz), 4.06 (s, 1H), 3.80−3.89 (m, 3H), 3.71 (d, 1H, J = 9.6 Hz), 3.60 (dd, 1H, J = 1.6, 10.8 Hz), 3.50 (dd, 1H, J = 3.6, 9.2 Hz), 3.46 (t, 1H, J = 8.4 Hz), 3.43 (dd, 1H, J = 2.4, 12.0 Hz), 3.35−3.40 (m, 1H), 3.37 (s, 3H), 3.20 (dd, 1H, J = 4.8, 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 139.2, 138.1, 137.8, 137.7, 137.3, 128.8, 128.5, 128.42, 128.39, 128.10, 128.05, 128.02, 127.97, 127.9, 127.84, 127.81, 127.7, 127.5, 127.2, 100.6, 98.4, 80.9, 79.9, 79.0, 78.1, 76.1, 75.3, 74.9, 73.8, 73.6, 73.4, 71.4, 69.3, 67.5, 67.1, 55.3; HRMS (ESI) calcd for $C_{49}H_{56}NO_{12}$ [M + NH_4]$^+$ 850.3797, found 850.3796. Anal. Calcd for $C_{49}H_{52}O_{12}$: C, 70.66; H, 6.29. Found: C, 70.38; H, 6.40.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α- and β-D-galactopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (**41α** and **41β**).* The coupling of donor **6** with acceptor **18d** by protocol B afforded a mixture of **41α** and **41β** (78% yield, α/β = 5:1), both of them as colorless glassy solids. For **41α**: R_f = 0.4 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +17.6 (c 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.36 (m, 23H), 7.12−7.14 (m, 2H), 5.32 (d, 1H, J = 2.8 Hz), 4.92 (d, 1H, J = 11.2 Hz), 4.86 (d, 1H, J = 3.6 Hz), 4.78 (d, 1H, J = 10.8 Hz), 4.70−4.75 (m, 3H), 4.63 (d, 1H, J = 12.0 Hz), 4.49−4.53 (m, 3H), 4.45 (d, 1H, J = 11.2 Hz), 4.38 (d, 1H, J = 12.0 Hz), 4.32 (d, 1H, J = 12.0 Hz), 4.01−4.05 (m, 1H), 3.98 (t, 1H, J = 8.8 Hz), 3.84 (dd, 1H, J = 3.6, 10.0 Hz), 3.81 (br.s, 1H), 3.74−3.77 (m, 2H), 3.65−3.70 (m, 2H), 3.47 (dd, 1H, J = 6.0, 9.6 Hz), 3.38−3.42 (m, 1H), 3,41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 138.5, 138.0, 137.88, 137.85, 137.1, 128.41, 128.39, 128.3, 128.1, 127.9, 127.8, 127.74, 127.65, 127.6, 127.5, 96.6, 93.1, 80.8, 78.4, 77.1, 75.8, 75.6, 74.9, 74.3, 73.8, 73.6, 73.1, 72.9, 70.5, 70.3, 68.3, 67.8, 55.3; HRMS (ESI) calcd for $C_{49}H_{52}O_{12}$Na [M + Na]$^+$ 855.3351, found 855.3356. For **41β**: R_f = 0.3 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +2.7 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.38 (m, 23H), 7.14−7.16 (m, 2H), 4.94 (d, 1H, J = 8.0 Hz), 4.86 (d, 1H, J = 10.8 Hz), 4.84 (d, 1H, J = 10.8 Hz), 4.82 (d, 1H, J = 3.6 Hz), 4.82 (d, 1H, J = 9.6 Hz), 4.79 (d, 1H, J = 11.2 Hz), 4.65 (dd, 1H, J = 8.0, 12.0 Hz), 4.62 (d, 1H, J = 11.6 Hz), 4.53 (d, 1H, J = 12.0 Hz), 4.50 (d, 1H, J = 11.6 Hz), 4.49 (d, 1H, J = 12.0 Hz), 4.46 (d, 1H, J = 12.0 Hz), 4.43 (d, 1H, J = 12.0 Hz), 4.16 (brs, 1H), 4.02 (dd, 1H, J = 2.4, 12.0 Hz), 4.01 (t, 1H, J = 9.6 Hz), 3.72−3.78 (m, 3H), 3.60−3.68 (m, 4H), 3.53 (dd, 1H, J = 4.8, 8.4 Hz), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 138.3, 138.1, 137.9, 137.4, 137.0, 128.51, 128.45, 128.4, 128.2, 128.13, 128.12, 128.0, 127.9, 127.8, 127.73, 127.71, 101.6, 99.3, 81.4, 81.3, 80.1, 77.9, 75.8, 75.05, 75.01, 73.9, 73.6, 73.5, 71.4, 70.1, 68.4, 67.7, 55.2; HRMS (ESI) calcd for $C_{49}H_{52}O_{12}$Na [M + Na]$^+$ 855.3351, found 855.3353.

*Methyl (4,6-Di-O-benzyl-2,3-O-carbonyl-α-D-galactopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-α-D-glucopyranoside (**42α**).* The coupling of donor **6** with acceptor **18e** by protocol B afforded **42α** (71% yield, α/β > 20:1) as a foam: R_f = 0.45 (petroleum ether/ethyl acetate, 1.5:1); $[\alpha]_D$ +9.1 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.35 (m, 23H), 7.11−7.14 (m, 2H), 5.68 (d, 1H, J = 3.2 Hz), 4.75 (dd, 1H, J = 3.2, 12.0 Hz), 4.74 (d, 1H, J = 11.2 Hz), 4.68 (d, 1H, J = 11.6 Hz), 4.65 (d, 1H, J = 12.4 Hz), 4.65 (dd, 1H, J = 2.4, 14.8 Hz), 4.64 (d, 1H, J = 3.2 Hz), 4.61 (d, 1H, J = 12.0 Hz), 4.53 (d, 1H, J = 12.0 Hz), 4.51 (d, 1H, J = 11.2 Hz), 4.50 (d, 1H, J = 12.0 Hz), 4.44 (d, 1H, J = 10.8 Hz), 4.36 (d, 1H, J = 11.6 Hz), 4.31 (d, 1H, J = 11.6 Hz), 4.25 (t, 1H, J = 7.2 Hz), 4.11−4.16 (m, 2H), 3.75 (dd, 1H, J = 2.4, 10.8 Hz), 3.63−3.71 (m, 3H), 3.48−3.53 (m, 3H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 138.0, 137.7, 137.5 (2C), 137.3, 128.6, 128.48, 128.46, 128.41, 128.39, 128.3, 128.2, 128.10, 128.05, 128.0, 127.9, 127.8, 127.7, 127.6, 97.5, 95.5, 78.5, 78.2, 77.5, 77.2, 74.6 (2C), 73.9, 73.7, 73.11 (2C), 73.05, 70.1, 69.8, 68.0, 67.5, 55.0; HRMS (ESI) calcd for $C_{49}H_{52}O_{12}Na$ $[M + Na]^+$ 855.3351, found 855.3355.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xinshan@bjmu.edu.cn.

Notes

The authors declare no competing financial interest.

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