

Catalytic and Stereoselective Glycosylation with Glucosyl Thioformimidates

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A novel and efficient glycosyl donor having a *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate group at an anomeric position is easily prepared by the addition of anomeric hydroxy group of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose to *p*-trifluoromethylphenyl isothiocyanate, followed by treatment with *p*-trifluoromethylbenzyl bromide. Catalytic and stereoselective glycosylation of various glycosyl acceptors with the above glycosyl donor smoothly proceeds by using various protic and Lewis acid catalysts which interact with its nitrogen atom. Further, catalytic and highly 1,2-*cis* or 1,2-*trans* stereoselective and chemoselective glycosylation between two different "armed" and "disarmed" glycosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidates is also performed effectively in the presence of a catalytic amount of trifluoromethanesulfonic acid (TfOH) at −78 °C in ^{t}BuOMe or EtCN, respectively. These glycosylations are applied to successful one-pot sequential syntheses of trisaccharides.

Glycoconjugates of biological significance have stimulated synthetic activity of glycoside synthesis in the past years.[1] The classical glycosylation method introduced by Koenigs–Knorr in 1901[2] requires the formation of glycosyl donors by exchanging an anomeric hydroxy group with a bromine or chlorine atom and a glycosyl group transfer of thus formed donor to a glycosyl acceptor takes place by using an equimolar amount of heavy metal ion. Although the Koenigs–Knorr method has frequently been employed in glycosylations of various saccharides, it leaves some inherent problems: it is experimentally demanding and is certainly not very suited for large-scale preparation. Therefore, a more efficient method than the fundamental Koenigs–Knorr method and its modified versions has become a target for research on stereocontrolled glycoside synthesis including oligosaccharides during the past twenty years.[3] Various types of excellent glycosyl donors have been developed and are employed in the syntheses of saccharide chains in combination with suitable activators: these include thioglycosides,[4] glycosyl trichloroacetimidates,[5] glycosyl fluorides,[6] glycals,[7] glycosyl sulfoxide,[8] 4-pentenyl glycosides,[9] and glycosyl phosphites.[10]

Among the donors, glycosyl trichloroacetimidate reported by Schmidt et al. in 1980[5] is one of the most useful glycosyl donors. Various glycosyl trichloroacetimidates are prepared directly from 1-hydroxy sugars and trichloroacetonitrile as isolable glycosyl donors, and exhibit high glycosyl transfer potential upon treatment even with weak acid. Thus, glycosyl trichloroacetimidates have been widely employed in the synthesis of natural products. Because of their high reactivity, however, glycosyl trichloroacetimidates cannot be used as an acceptor in the glycosylation.

On the other hand, thioglycosides having an alkylthio or arylthio group at their anomeric position have recently attracted considerable attention.[4] Thioglycosides have some advantageous points as glycosyl donors because they are easily prepared and have high stability that can withstand most reaction conditions used in protecting group manipulations and glycosylations, while being activated effectively by thiophilic promoters. Therefore, thioglycosides are perfectly fitted for block synthesis of oligosaccharides, where stable oligosaccharide donors are prerequisite. However, since the reactivities of the thioglycosyl donors are generally low, their glycosylations of various acceptors require more than equimolar amounts of thiophilic reagents such as heavy metal salts, halonium, sulfonium and carbonium-type promoters.

In 1981, the use of glycosyl fluoride as a glycosyl donor was first reported from our laboratory.[11] Because of their enhanced stability, easy handling, and formation of saccharides in higher stereoselectivity compared with other glycosyl halides, glycosyl fluorides had since been utilized for effective glycosylation reactions. Recently, it was found that a catalytic amount of protic acids such as TfOH, $HClO_4$ and $HB(C_6F_5)_4$ effectively accelerated glycosylation reactions when glycosyl fluoride was used as a donor.[12] Now, it was planned to develop a new and highly reactive glycosyl donor so that it may effectively be employed for one-pot oligosaccharide synthesis in combination with glycosyl fluorides.

Further development of novel and efficient glycosyl donors having a new leaving group with two active cites, that is, imidate and alkylthio or arylthio linkages within the same leaving group, was thus planned. The planned donors were expected to be activated arbitrarily by choosing two different kinds of promoter: a) their imidate linkage by protic and Lewis acids; b) their thio linkage by thiophilic reagents (Scheme 1). Glycosylation using the planned ones will be effectively applied to the glycosylation of several useful glycosyl acceptors, e.g., glycosyl fluorides, thioglycosides, glycosyl trichloroacetimi-

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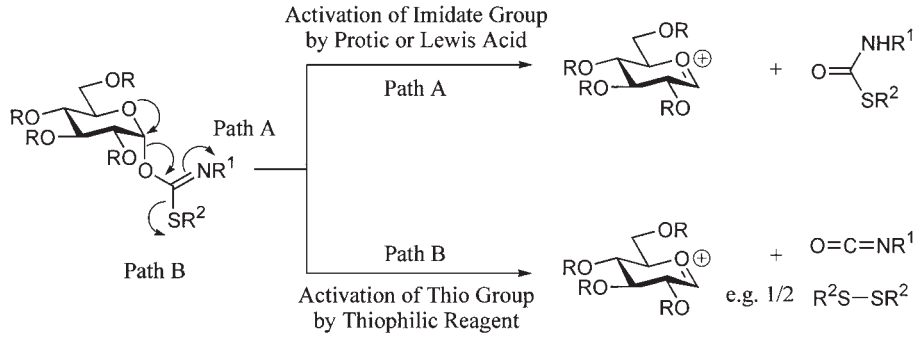
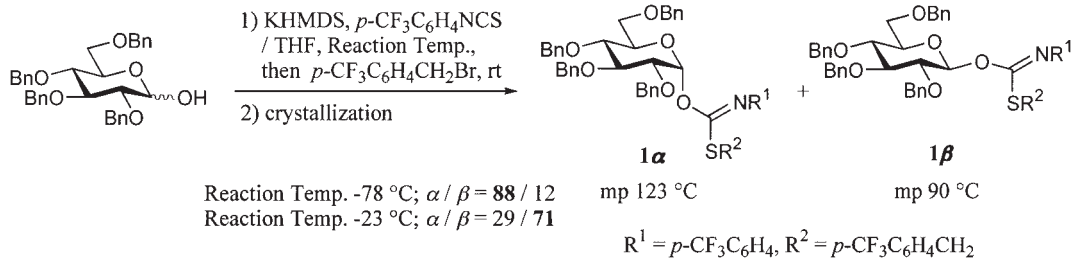


Scheme 1. Assumed mechanism for planned donor: Two possible activations using protic and Lewis acid or thiophilic reagent.



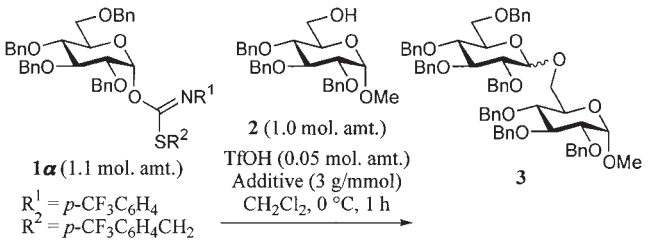
Scheme 2. Preparation of a newly devised glycosyl donor.

dates. In this paper, we would like to report on catalytic and stereoselective glycosylation in detail with a newly devised glycosyl donor via effective activation of a nitrogen atom of the leaving group by using various protic and Lewis acids. Further, catalytic, stereoselective and chemoselective glycosylation between two different "armed" and "disarmed" glycosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidates, which was then applied to one-pot sequential syntheses of trisaccharides is described.[13]

Results and Discussion

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (**1α**) was easily prepared in good yields with high α-stereoselectivity by a two-step procedure: 1) the addition of anomeric hydroxy group of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose[14] to *p*-trifluoromethylphenyl isothiocyanate using potassium bis(trimethylsilyl)amide (KHMDS) in THF at −78 °C and 2) subsequent treatment with *p*-trifluoromethylbenzyl bromide at −78 °C and raising the reaction temperature up to room temperature (Scheme 2). On the other hand, β-isomer of glucosyl thioformimidate **1β** was prepared predominantly by the addition to *p*-trifluoromethylphenyl isothiocyanate at −23 °C, followed by treatment with *p*-trifluoromethylbenzyl bromide at −23 °C and raising the reaction temperature up to room temperature. Similarly, glucosyl thioformimidates **1α** and **1β** were stereoselectively synthesized when potassium *t*-butoxide or potassium hydride was used. These isomers were purified just by recrystallization. Glucosyl thioformimidates **1α** and **1β** are stable compounds possessing higher melting points (**1α**: mp 123–124 °C, **1β**: mp 90–91 °C) compared with the corresponding glucosyl trichloroacetimidates (**19α**: mp 77 °C, **19β**: mp 72–73 °C).[5a] On the other hand, the glucosyl thioformimidate without having a substituent at *p*-positions of each phenyl group was too reactive and could not be isolated as crystalline form due to hydrolysis.

Table 1. Effect of Additives

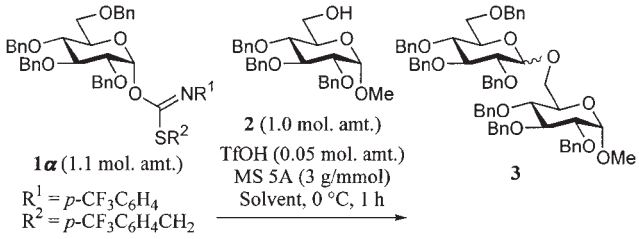


Entry	Additive	Yield/%	α/β[a)]
1	None	73	63/37
2	Drierite	98	64/36
3	MS3A	quant.	67/33
4	MS4A	quant.	66/34
5	MS5A	98	66/34

a) The α/β were determined by HPLC analysis.

In the first place, the reaction of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (**1α**) with methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**2**)[15] was tried in the presence of 0.05 molar amount of trifluoromethanesulfonic acid (TfOH) (Table 1). The reaction proceeded instantly in CH_2Cl_2 at 0 °C to give the corresponding disaccharide **3**[16] in 73% yield (entry 1). Next, the effect of various additives[17] was examined and disaccharide **3** was then obtained in quantitative yield along with an equimolar amount of co-product, *S*-*p*-trifluoromethylbenzyl-*N*-*p*-trifluoromethylphenylthiocarbamate, by using additives such as Drierite, MS 3A, 4A, 5A. Little influence of these additives on the stereoselectivity of glycosylation was observed.

Table 2. Effect of Solvents



Entry	Solvent	Yield / % (α / β)[a]	Entry	Solvent	Yield / % (α / β)[a]
1	CH_3CN	99 (11 / 89)	8	^{t}BuOMe	99 (88 / 12)
2	EtCN	quant. (14 / 86)	9	Et_2O	99 (86 / 14)
3[b]	^{t}BuCN	94 (25 / 75)	10	DME	quant. (82 / 18)
4	BTF	quant. (54 / 46)	11	THP	quant. (73 / 27)
5	Toluene	quant. (63 / 37)	12	$^i Pr_2O$	quant. (70 / 30)
6	CH_2Cl_2	98 (66 / 34)	13	$^n Bu_2O$	90 (65 / 35)
7	Fluorobenzene	68 (72 / 28)	14	THF	47 (42 / 58)

a) The α/β ratios were determined by HPLC analysis. b) The reaction was carried out at rt.

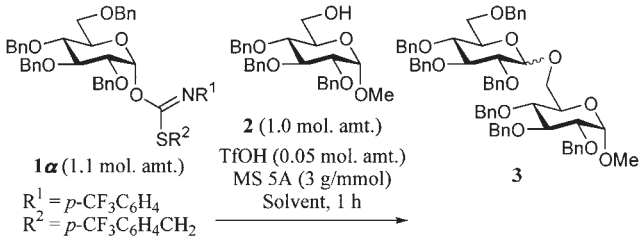
The stereoselectivity of glycosylations with donors having a non-participating protecting group at C-2 position is affected considerably by the nature of the solvent.[18] The effect of solvents on glycosylation of glycosyl thioformimidate **1α** with glycosyl acceptor **2** was thus studied. The reactions were carried out in various solvents by using 0.05 molar amount of TfOH for 1 h (these reactions were completed within ten minutes in almost all cases) at 0 °C (Table 2). As a result, the glycosylations proceeded instantly in all solvents except DMF, which worked as a weak base to prevent the effect of protic acid. Glycosylation proceeded in quantitative yield with 1,2-*trans* stereoselectivity when CH_3CN or EtCN was used as a solvent (entries 1,2). On the other hand, 1,2-*cis* glycoside was stereoselectively formed in quantitative yield when the same reaction was carried out in ^{t}BuOMe or Et_2O (entries 8,9). These results (α glycoside by ethereal solvents and β glycoside by nitrile solvents) coincide with the previous results obtained using other glycosyl donors.[18]

Next, the reactivity of this glycosyl donor **1α** was investigated. The glycosylation with this glycosyl donor **1α** proceeded smoothly even at lower temperatures (Table 3). It should be noted that 1,2-*trans* glycoside was formed in an almost perfectly controlled manner when the glycosylation was carried out in EtCN at −78 °C (entry 4, solvent: EtCN). This perfect 1,2-*trans* stereoselectivity may be controlled by the nature of solvent under kinetic condition. This glycosyl donor **1α** is highly reactive, similar to that of the corresponding glycosyl trichloroacetimidate **19α**.

Next, glycosylation using various protic acids was examined (Table 4). Methanesulfonic acid (MsOH) did not promote the reaction, even though 0.2 molar amount of the acid was used; however, the same reaction was effectively accelerated even when 0.01 molar amount of TfOH was used (entries 1–3). Nafion-H®,[19] that is perfluorinated alkanesulfonic acid-type resin, which exhibits the same acidity as TfOH, also accelerated the glycosylation (entry 4). It should be noted that 1,2-*trans* glycoside was formed in an almost perfectly controlled manner when HBF_4 was used as catalyst (entry 5). It is thought that the reaction proceeded via S_N2 reaction mechanism because HBF_4[20] is a milder acid than TfOH. Further, in situ generated strong protic acids[21] such as $HClO_4$ and $HB(C_6F_5)_4$ also proved to be effective. The reaction proceeded mainly via S_N1 type reaction mechanism (entries 6,7). When the reaction proceeded via S_N1 type reaction mechanism, it was considered that the stereoselectivity was dependent on the effect of counter anion [such as β-predominantly by $B(C_6F_5)_4^-$, α-predominantly by TfO^- or ClO_4^-] (entries 3,6,7).[6c,12c,d]

Next, glycosylation using various Lewis acids was investigated (Table 5). It was noted that 1,2-*trans* glycoside was formed in an almost perfectly controlled manner when $BF_3 \cdot Et_2O$ was used (entry 1). The reaction should have proceeded via S_N2 reaction mechanism similar to the case when HBF_4 was used. On the other hand, glycosylation proceeded mainly via S_N1 type reaction mechanism when stronger

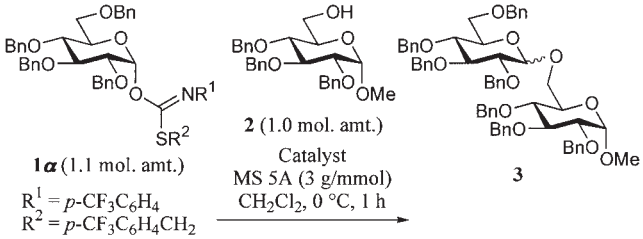
Table 3. Effect of Reaction Temperature



Entry	Temp./°C	Yield/%(α/β)[a]		
		EtCN	^{t}BuOMe	CH_2Cl_2
1	0	quant.(14/86)	quant.(88/12)	98(66/34)
2	−23	quant.(10/90)	97(85/15)	quant.(59/41)
3	−40	quant.(3/97)	97(74/26)	quant.(54/46)
4	−78	quant.(1/99)	95(52/48)	97(43/57)

a) The α/β ratios were determined by HPLC analysis.

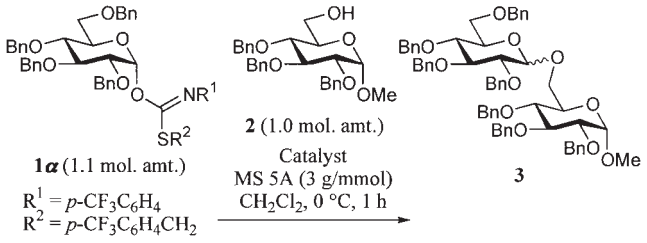
Table 4. Glycosylation Using Various Protic Acids



Entry	Catalyst	/10^{-2} mol. amt.	Yield/%	α/β[a]
1	MsOH	20	trace	—/—
2	TfOH	1	quant.	67/33
3	TfOH	5	98	66/34
4[b]	Nafion-H®	—	91	56/44
5	HBF_4	5	91	1/99
6	$HClO_4$	5	quant.	57/43
7	$HB(C_6F_5)_4$	5	quant.	23/77

a) The α/β ratios were determined by HPLC analysis. b) The reaction was carried out at room temperature for 18 h using 4 beads (7–9 mesh) of Nafion-H® (NR 50).

Table 5. Glycosylation Using Various Lewis Acids



Entry	Catalyst	/10^{-2} mol. amt.	Yield/%	α/β[a]
1	$BF_3 \cdot Et_2O$	5	91	1/99
2	TMSOTf	5	94	63/37
3	$AgB(C_6F_5)_4$	5	quant.	28/72
4	$AgClO_4$	5	quant.	63/37
5	$TrB(C_6F_5)_4$	5	99	31/69
6	$TrClO_4$	5	99	63/37
7[b]	$LiB(C_6F_5)_4$	20	97	37/63
8[b]	$LiClO_4$	20	99	63/37

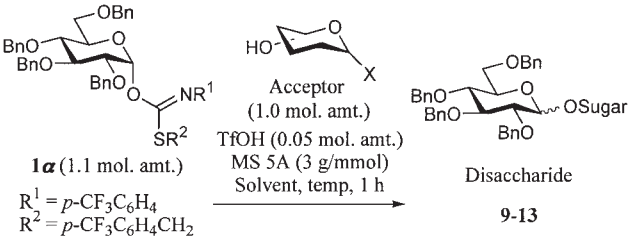
a) The α/β ratios were determined by HPLC analysis. b) These reaction proceeded at room temperature for 6 h.

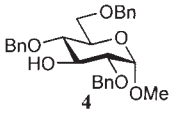
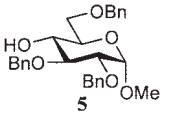
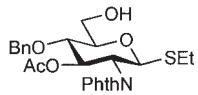
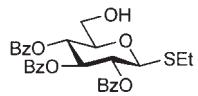
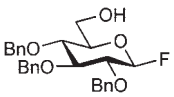
catalysts such as TMSOTf, $TrB(C_6F_5)_4$,[22] $TrClO_4$,[23] $AgB(C_6F_5)_4$,[24] $AgClO_4$[11] were used (entries 2–6). Its stereoselectivity was thought to be dependent on the effect of counter anion [β-predominantly by $B(C_6F_5)_4^-$, α-predominantly by TfO^- or ClO_4^-] as occurred when strongly protic acids such as $HB(C_6F_5)_4$, $HClO_4$ and TfOH were used. The weak Lewis acids such as lithium salts [$LiB(C_6F_5)_4$, $LiClO_4$] also promoted the reaction and gave glycoside in quantitative yield when the glycosylation was carried out in the presence of 0.2 molar amount of catalyst and MS 5A in CH_2Cl_2 at room temperature (entries 7,8).

Then, in order to extend the scope of stereoselective glycosylation using this glycosyl donor **1α**, glycosylation using various glycosyl acceptors such as **4**,[25] **5**,[26] **6**,[12d] **7**,[27] and **8** was tried (Table 6). α-Stereoselective glycosylations were performed in the presence of a catalytic amount of TfOH and MS 5A in ^{t}BuOMe at 0 °C. The desired disaccharides **9**–**12** were obtained in good to high yields with high α-stereoselectivities even when acceptors having secondary alcohol or anomeric thioglycosidic linkage were used (entries 1–4). It is especially worthwhile to note that the corresponding disaccharide **13** was obtained in high yield without damaging the "armed" glycosyl fluoride **8** (entry 5); therefore, the produced disaccharide **13** may be used for the next glycosylation by choosing a suitable reaction temperature. On the other hand, β-stereoselective glycosylations were performed in the presence of a catalytic amount of TfOH and MS 5A in EtCN at low temperature and the desired disaccharides **9**–**13** were also obtained in all cases in good to high yields with high β-stereoselectivities (entries 1–5). Thus, convenient methods for the stereoselective preparation of either α- or β-glycosides were established just by starting from the same glycosyl thioformimidate. These results indicated that the present method is quite useful for oligosaccharide synthesis.

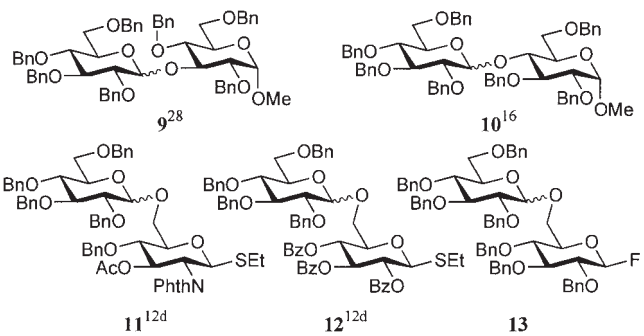
Next, application of glucosyl thioformimidates to the chemoselective glycosylation (so-called "armed-disarmed" glycosylation), which is a quite efficient oligosaccharide synthesis

Table 6. Stereoselective Glycosylation of Various Glycosyl Acceptors

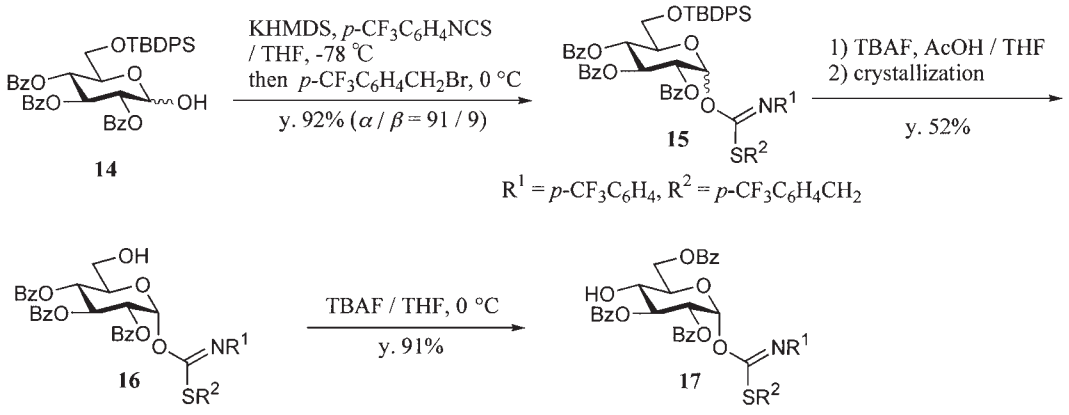


Entry	Acceptor	Yield/%(α/β)[a]	
		^{t}BuOMe, 0 °C	EtCN, −78 °C
1	 **4**	98 (**90**/10)	96 (5/**95**)[b]
2	 **5**	98 (**90**/10)	75 (16/**84**)[b,c]
3	 **6**	93 (**81**/19)	80 (2/**98**)
4	 **7**	95 (**89**/11)	98 (2/**98**)
5	 **8**	97 (**87**/13)	81 (2/**98**)

a) The α/β ratios were determined by HPLC analysis. b) The reactions were performed in the presence of 0.2 mol. amt. of TfOH. c) The reaction was carried out at −30 °C.



methodology, was attempted. Fraser-Reid et al. have firstly introduced "armed-disarmed" glycosylation strategy by using 4-pentenyl glycosides in 1988.[29] The chemoselective glycosylation is controlled by the properties that C-2 ethers (protected by electron donating group) activate ("arm") the anomeric center, while C-2 esters (protected by electron withdrawing group) deactivate ("disarm") this center. Concerning other glycosyl donors, e.g. glycals,[30] thioglycosides,[31] or glycosyl fluorides,[32] similar phenomena have been reported. However, "armed-disarmed" glycosylation using glycosyl trichloroacetimidates has not yet been reported. Therefore, the chemoselective glycosylation using glucosyl thioformimidates was



Scheme 3. Preparation of "disarmed" glucosyl thioformimidate acceptors.

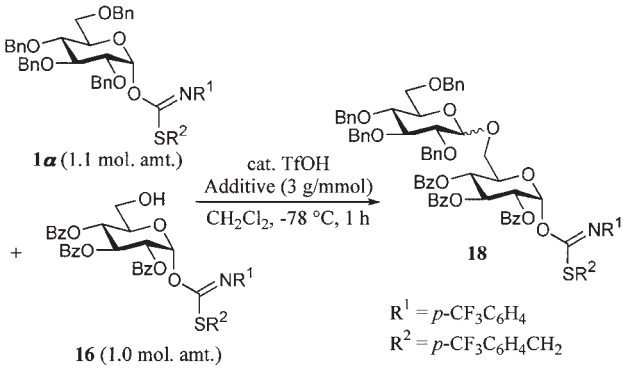
studied. "Disarmed" acceptor, 2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (**16**), was successfully prepared by two-step procedure from 2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-α,β-D-glucopyranose (**14**).[33] Transformation of **16** to 2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (**17**) by the migration of 4-benzoyl group was carried out by adding tetrabutylammonium fluoride (TBAF) in THF at 0 °C (Scheme 3).

Catalytic and chemoselective glycosylation between the "armed" glycosyl donor **1α** and the "disarmed" glycosyl acceptor **16** was examined in the presence of various additives (Table 7). The "armed-disarmed" chemoselective glycosylation proceeded smoothly in the coexistence of 0.05–0.1 molar amount of TfOH and MS 4A in CH_2Cl_2 at −78 °C and the desired disaccharide **18** was isolated in high yield without giving any damage to a reducing end of the acceptor (entries 7,8). The low yields of the desired disaccharide **18** shown in entries 2 and 4 are ascribed to the hydrolysis that took place in the usual work-up procedure of the initially formed **18**, in which a reactive leaving group still remained.

Next, the above glycosylation was tried in EtCN at −78 °C. The glycoside was formed in good yield with high 1,2-*trans* stereoselectivity, as expected (Table 8, entry 3). It is surprising to note that the glycoside was also formed in good yield with extremely high 1,2-*cis* stereoselectivity under kinetic conditions when ^{t}BuOMe was used as a solvent at −78 °C (entry 6).

Then, stereoselective glycosylations were tried under the same condition by using glucosyl trichloroacetimidate **19α**,[5a] a donor, with several acceptors (Table 9). In every case, high 1,2-*cis* stereoselectivity was achieved when glucosyl thioformimidate **1α**, was used as a donor (entries 1 vs 2, 3 vs 4, 5 vs 6). In addition, it was shown that the stereoselectivity of glycosylation was dependent on the nature of acceptors (**16**, **20**,[34] **2**), that is, the kind of leaving group at the anomeric position and the kind of protecting group at C-2, 3, 4 positions (entries 1 vs 3 vs 5, 2 vs 4 vs 6). A similar tendency was observed when β-isomer (**1β**, **19β**[5a]) was used (Table 10). It was considered that this high 1,2-*cis* stereoselectivity using glucosyl thioformimidate **1α** was an effect of in situ anomerization,[36] that is, the rate of anomerization of glucosyl thioformimidate from α-isomer to β-one appeared to be faster compared with that of

Table 7. Catalytic "Armed-Disarmed" Glycosylation



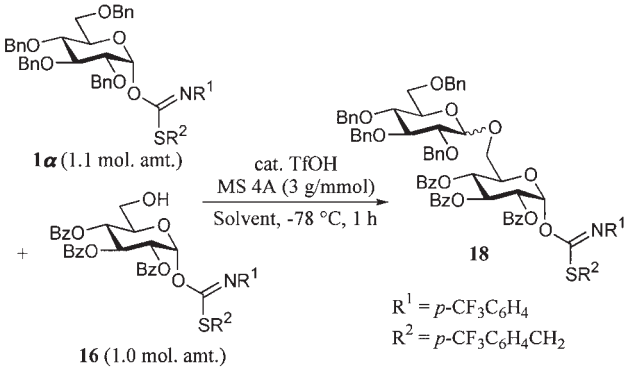
Entry	Additive	Cat. / 10^{-2} mol. amt.	Yield / % (α / β)[a)]	Recovery of **16**
1	MS 5A	5	77 (65 / 35)	14
2	MS 5A	10	trace	–
3	Drierite	5	51 (54 / 46)	14
4	Drierite	10	14 (40 / 60)	–
5	MS 3A	5	88 (66 / 34)	10
6	MS 3A	10	66 (61 / 39)	–
7	MS 4A	5	89 (66 / 34)	10
8	MS 4A	10	89 (65 / 35)	–

a) The α/β ratios were determined by HPLC analysis.

conventional glucosyl trichloroacetimidate **19α**. Thus, the reaction seemed to have proceeded by its β-isomer, which existed in rapid equilibrium with more stable α-isomer. Further, highly α-stereoselective glycosylation was observed when "disarmed" glucosyl thioformimidate **16** was used as an acceptor; this was probably because the above bulky leaving group prevented the acceptor from approaching the donor from the β-side.

Next, this "armed-disarmed" chemoselective glycosylation was applied to one-pot sequential glycosylation. A one-pot se-

Table 8. Catalytic and Stereoselective "Armed-Disarmed" Glycosylation



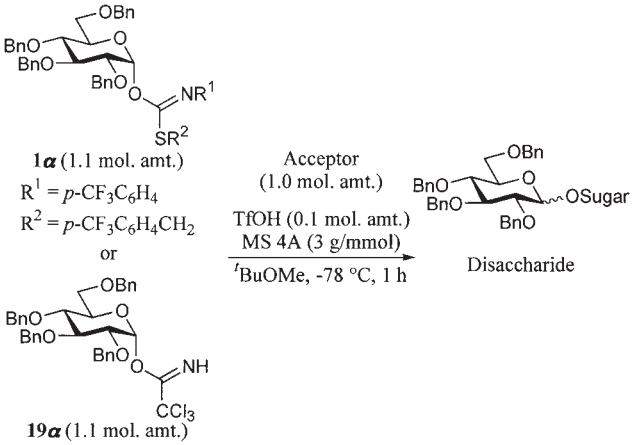
Entry	Solvent	Cat. / 10^{-2} mol. amt.	Yield / % (α / β)[a]	Recovery of **16**
1	EtCN	5	9 (2 / 98)	85
2	EtCN	10	42 (2 / 98)	56
3	EtCN	15	82 (4 / 96)	15
4	EtCN	20	77 (3 / 97)	–
5	^{t}BuOMe	5	77 (95 / 5)	19
6	^{t}BuOMe	10	93 (95 / 5)	–
7	^{t}BuOMe	15	80 (95 / 5)	–

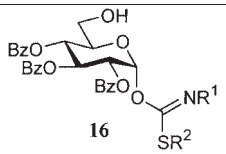
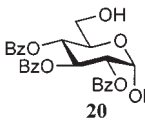
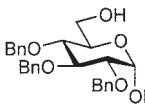
a) The α/β ratios were determined by HPLC analysis.

quential glycosylation method is one of the most promising strategies because of its efficiency in preparing saccharide-building blocks with less laborious purification processes. Therefore, chemical methods for one-pot syntheses of oligosaccharides have currently been introduced by many research groups.[37] Most of these methods, however, described β-stereoselective glycosylation by utilizing the assistance of the neighboring effect of 2-*O*-protecting group. Further, most of them were using orthogonal strategy that contained thioglycosides.[38] To our knowledge, only one catalytic true one-pot sequential glycosylation using phenyl sulfoxide sugars has been reported, by Kahne.[39] Also, no catalytic and highly α-stereoselective one-pot sequential glycosylations that fulfill requirements for the efficient synthesis of complex oligosaccharide have been reported, either. So, a catalytic and highly α-stereoselective one-pot sequential glycosylation using glucosyl thioformimidates was tried.

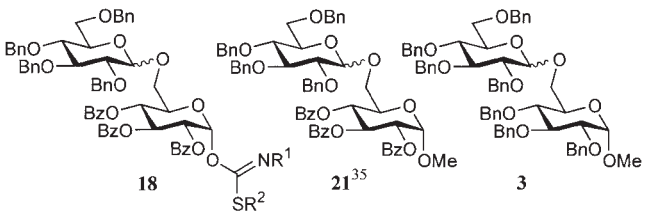
In the first step, the "armed-disarmed" chemoselective glycosylation between **1α** and **16** was tried in the presence of 0.1 molar amount of TfOH and MS 5A in ^{t}BuOMe at −78 °C. After **1α** was completely consumed, which was monitored by TLC, the second glycosylation was carried out to yield the trisaccharide **22**[12d] in high yield by addition of glucosyl acceptor **2** at −78 °C and then by a gradual raise in its temperature up to 0 °C. Formation of β-linkage in the second glycosylation was controlled by the assistance of a neighboring effect of the 2-*O*-benzoyl protecting group of the disaccharide donor. When glucosyl fluoride **8** was used as an acceptor, the desired trisaccharide **23** was also obtained in good yield without giving any damage to the reducing end of the acceptor (Scheme 4). In the

Table 9. Highly α-Stereoselective Glycosylation Using Both 'Armed' and 'Disarmed' Glycosyl Thioformimidates



Entry	Donor	Acceptor	Product	Yield/%(α/β)[a]
1	**1α**	 **16**	**18**	93(**95**/5)
2	**19α**			70(89/11)
3	**1α**	 **20**	**21**[35]	98(**89**/11)
4	**19α**			89(75/25)
5	**1α**	 **2**	**3**	97(**55**/45)
6	**19α**			99(25/75)

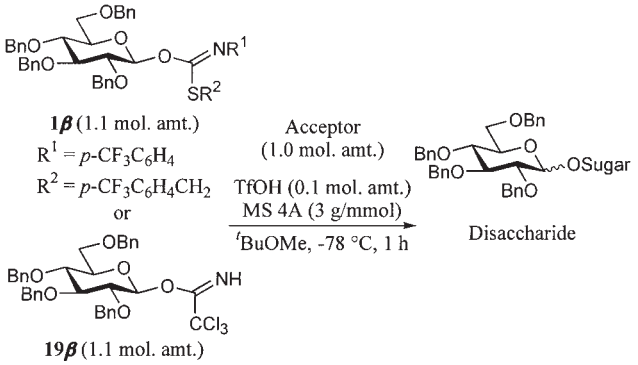
a) The α/β ratios were determined by HPLC analysis.

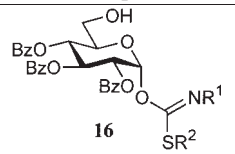
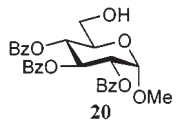
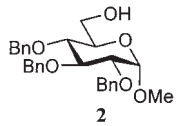


case of using glucosyl acceptor **17** having secondary alcohol at C-4 position, one-pot sequential glycosylation also proceeded by a similar procedure in CH_2Cl_2 to afford the aimed trisaccharide **25** in good yield with high α-stereoselectivity (Scheme 5).

Thus, simple and efficient highly α-stereoselective one-pot sequential glycosylations were achieved by using glucosyl thioformimidates in the presence of a catalytic amount of TfOH. The factors controlling high α-stereoselectivity were determined by the characteristic properties of thioformimidate groups contained both in glucosyl donor and acceptor. Therefore, it is noted that the glucosyl thioformimidates are useful both as a donor and an acceptor for the synthesis of α-linked oligosaccharide.

Table 10. Highly α-Stereoselective Glycosylation Using Both 'Armed' and 'Disarmed' Glycosyl Thioformimidates



Entry	Donor	Acceptor	Product	Yield/%(α/β)[a]
1	**1β**	 **16**	**18**	74(**92**/8)
2	**19β**			65(88/12)
3	**1β**	 **20**	**21**	95(**90**/10)
4	**19β**			97(78/22)
5	**1β**	 **2**	**3**	98(**86**/14)
6	**19β**			99(60/40)

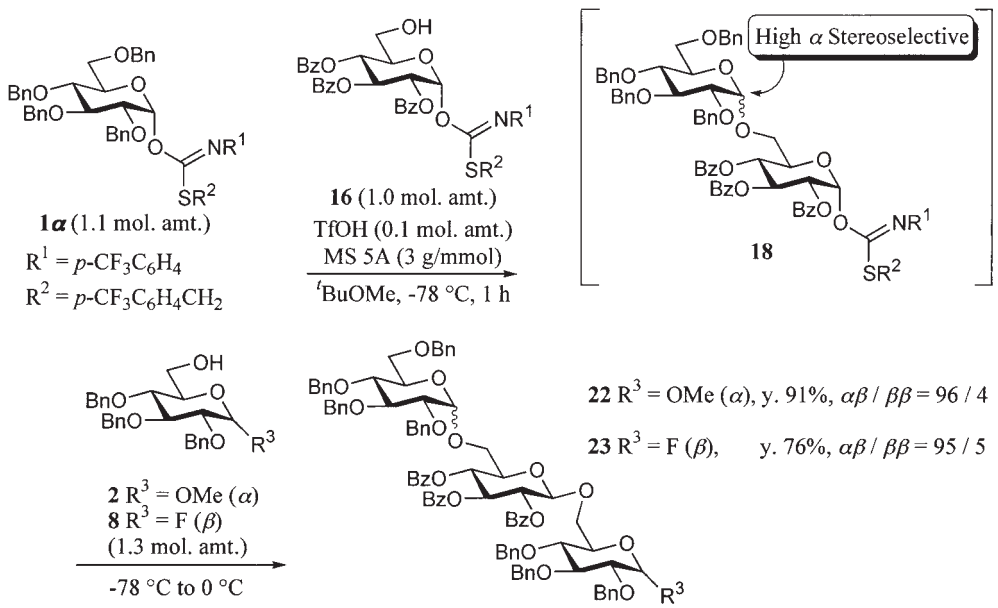
a) The α/β ratios were determined by HPLC analysis.

Conclusion

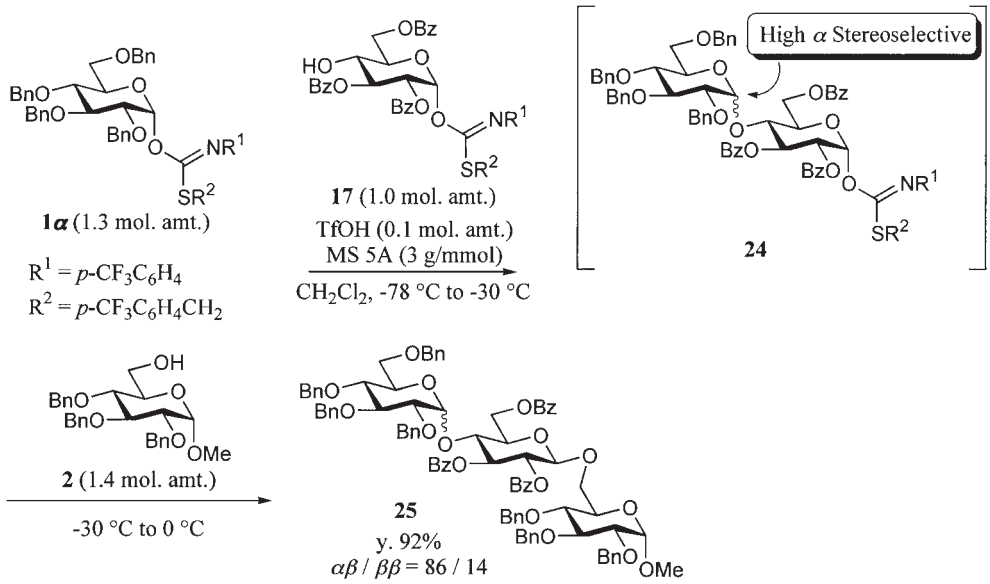
A novel and efficient glycosyl donor having a *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate function as a leaving group was developed. Catalytic and stereoselective glycosylations of the above glycosyl thioformimidate with various glycosyl acceptors were effectively performed. It is especially worthwhile to note that glycosylation of this glycosyl donor with reactive 'armed' glycosyl fluoride, an acceptor, proceeded in high yield without accompanying activation of glycosyl fluoride. Further, a catalytic, stereoselective and chemoselective glycosylation between two different "armed" and "disarmed" glycosyl thioformimidates was also effectively carried out in the presence of a catalytic amount of TfOH at −78 °C. Simple and efficient highly α-stereoselective one-pot sequential glycosylations were achieved by using glucosyl thioformimidates in the presence of a catalytic amount of TfOH according to the above method. The factors controlling high α-stereoselectivity were dependent on the characteristic properties of thioformimidate groups contained in both glucosyl donor and acceptor.

Experimental

General. All melting points were measured on a Yanaco MP-S3 micro melting point apparatus. Infrared spectra were recorded on a Horiba FT-300 infrared spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM EX270L (270MHz), a JEOL JNM-LA400 (400MHz), a JEOL JNM-LA500 (500MHz), or JEOL JNM-A500 (500MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to teteramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL JNM EX270L (68MHz), a JEOL JNM-LA400 (100MHz), a JEOL JNM-LA500 (125MHz), or JEOL JNM-A500 (125MHz) a spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane, with



Scheme 4. Catalytic one-pot trisaccharide (Glcα1–6Glcβ1–6Glc) synthesis using both 'armed' and 'disarmed' glycosyl thioformimidates.



Scheme 5. Catalytic one-pot trisaccharide (Glcα1–4Glcβ1–6Glc) synthesis using both 'armed' and 'disarmed' glycosyl thioformimidates.

the solvent resonance as the internal standard ($CDCl_3$; δ 77.0 ppm). High-resolution mass spectra were recorded on a Micromass Q-Tof2 instrument [ESI positive, 0.01 M (1 M = 1 mol dm^{-3}) $AcONH_4$ in H_2O/MeCN = 1:1] or a Micromass Q-Tof Ultima Global instrument (ESI positive, 0.1% $AcONH_4$ in H_2O/MeOH = 4:6 or 0.1% TFA in H_2O/MeCN = 1:1). High-performance liquid chromatography (HPLC) was carried out using a Hitachi LC-Organizer, L-4000 UV Detector, L-6200 Intelligent Pump, and D-2500 Chromato-Integrator with Shodex SIL-5B (normal phase: 120 Å, 5 μm, ϕ4.6 × 250 mm), YMC J'sphere ODS M80 (reverse phase: 80 Å, S-4 μm, 4.6 × 250 mmI.D.) and YMC-Pack Pro C18 AS-303 (reverse phase: 120 Å, S-5 μm, 4.6 × 250 mmI.D.). Optical rotations were recorded on a Jasco-P-1020 polarimeter. Analytical TLC was done on precoated (0.25 mm) silica gel 60 F_{254} plates (E. Merck). Thin-layer chromatography was performed on Wakogel B-5F. Column chromatography was performed on Silica gel 60 (Merck).

All reactions were carried out under argon atmosphere in dried glassware, unless otherwise noted. All reagents were purchased from Tokyo Kasei Kogyo, Kanto Chemical, Fluka or Aldrich and used without further purification, unless otherwise noted. Trifluoromethanesulfonic acid (TfOH: donated by Central Glass Co. Limited) was simply distilled and used for glycosylation. CH_2Cl_2, CH_3CN, EtCN, and ^{t}BuCN were distilled from P_2O_5 and then from CaH_2 and were stored over molecular sieves 4A. Toluene, fluorobenzene, and (trifluoromethyl)benzene (BTF) were distilled from P_2O_5 and were stored over molecular sieves 4A. ^{n}Bu$_2$O, ^{i}Pr$_2$O, and DME were distilled from CaH_2 and used immediately. DMF was distilled from CaH_2 under reduced pressure (pre-dried P_2O_5) and was stored over molecular sieves 4A. THP (distilled from $LiAlH_4$) was used immediately after distillation. Dry THF, ^{t}BuOMe, and Et_2O were purchased from Kanto Chemical. Powdered and pre-dried (at 260 °C/133 Pa, 6 h) molecular sieves 3A, 4A, and 5A were used in glycosylation reactions. Sufficiently crushed and pre-dried (at 260 °C/133 Pa, 6 h) Drierite from W. A. Hammond Drierite Company was used in the glycosylations.

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (1α): To a stirred solution of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose (1.00 g, 1.85 mmol) in THF (28 mL) was added a 0.5 M toluene solution of potassium bis(trimethylsilyl)amide (KHMDS) (4.44 mL, 2.22 mmol) at −78 °C. After the reaction mixture was stirred for 1 h at −78 °C, *p*-trifluoromethylphenyl isothiocyanate (453 mg, 2.23 mmol) in THF (1 mL) was successively added at −78 °C. After this reaction mixture was stirred for 30 min at −78 °C, *p*-trifluoromethylbenzyl bromide (533 mg, 2.23 mmol) in THF (1 mL) was added at −78 °C and then the reaction temperature was raised up to room temperature. The reaction mixture was quenched by adding saturated aqueous NH_4Cl (30 mL) at room temperature and the aqueous layer was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was washed with H_2O (30 mL) and brine (30 mL), and dried over Na_2SO_4. After filtration and evaporation, the resultant (α/β = 88/12) was recrystallized from hexane/EtOAc to afford the title compound **1α** (1.10 g, 66%, only α).

1α: White solid; mp 123–124 °C; R_f = 0.56 (hexane/EtOAc = 3/1); $[\alpha]_D^{27}$ + 61.3 (c = 0.75, $CHCl_3$); IR (KBr): 1612, 1327, 1157, 1119, 1072, 1003, 918, 748, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.61–3.82 (m, 6 H), 4.14 (d, J = 14.3 Hz, 1 H), 4.25 (d, J = 14.3 Hz, 1 H), 4.48 (d, J = 11.9 Hz, 1 H), 4.51 (d, J = 10.7 Hz, 1 H), 4.59 (d, J = 11.9 Hz, 1 H), 4.74 (d, J = 11.6 Hz, 1 H), 4.77 (d, J = 11.6 Hz, 1 H), 4.80 (d, J = 10.7 Hz, 1 H), 4.84 (d, J = 10.7 Hz, 1 H), 4.91 (d, J = 10.7 Hz, 1 H), 6.72 (brs, 1 H, H-1), 6.87 (d, J = 8.2 Hz, 2 H), 7.16–7.51 (m, 26 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 34.7, 68.1, 73.2, 73.4, 73.6, 75.3, 75.5, 76.8, 79.5, 81.3, 93.9 (C-1), 121.6, 125.67, 125.70, 126.20, 126.23, 127.74, 127.80, 127.85, 127.93, 127.97, 128.02, 128.04, 128.42, 128.55, 128.94, 137.75, 137.78, 137.99, 138.39, 140.75, 149.60, 156.01; HRMS: m/z calcd for $C_{50}H_{45}F_6NO_6SNa$ [M + Na]$^+$ 924.2769, found 924.2789.

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (1β): To a stirred solution of 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranose (1.00 g, 1.85 mmol) in THF (28 mL) was added a 0.5 M toluene solution of potassium bis(trimethylsilyl)amide (KHMDS) (4.44 mL, 2.22 mmol) at −23 °C. After the reaction mixture

was stirred for 1 h at −23 °C, *p*-trifluoromethylphenyl isothiocyanate (451 mg, 2.22 mmol) in THF (1 mL) was successively added at −23 °C. After this reaction mixture was stirred for 30 min at −23 °C, *p*-trifluoromethylbenzyl bromide (531 mg, 2.22 mmol) in THF (1 mL) was added at −23 °C and then the reaction temperature was raised up to room temperature. The mixture was quenched by adding saturated aqueous NH_4Cl (30 mL) at 0 °C and the aqueous layer was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was washed with H_2O (30 mL) and brine (30 mL), and dried over Na_2SO_4. After filtration and evaporation, the resultant ($\alpha/\beta = 29/71$) was purified in the following order: precipitation of the 1-OH sugar (217 mg, 22%, recovery of starting material) from hexane/EtOAc; **1α** (368 mg, 22%, $\alpha/\beta = 90/10$) from hexane; and finally, the title compound **1β** (301 mg, 18%, only β) from petroleum ether at 0 °C.

1β: White solid; mp 90–91 °C; $R_f = 0.56$ (hexane/EtOAc = 3/1); $[\alpha]_D^{27} + 25.4$ ($c = 0.67$, $CHCl_3$); IR (KBr): 1651, 1612, 1458, 1412, 1327, 1157, 1111, 1072, 1011, 903, 849, 741, 694 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 3.65–3.81 (m, 6 H), 4.07 (d, $J =$ 13.4 Hz, 1 H), 4.18 (d, $J = 13.4$ Hz, 1 H), 4.54 (d, $J = 11.9$ Hz, 1 H), 4.58 (d, $J = 10.7$ Hz, 1 H), 4.60 (d, $J = 11.2$ Hz, 1 H), 4.65 (d, $J = 11.9$ Hz, 1 H), 4.73 (d, $J = 11.2$ Hz, 1 H), 4.82 (d, $J = 10.7$ Hz, 1 H), 4.83 (d, $J = 10.7$ Hz, 1 H), 4.87 (d, $J = 10.7$ Hz, 1 H), 6.08 (brd, $J = 7.4$ Hz, 1 H, H-1), 6.87 (d, $J =$ 8.2 Hz, 2 H), 7.15–7.55 (m, 26 H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 34.9, 68.3, 73.4, 74.6, 74.9, 75.4, 75.5, 77.2, 80.9, 84.8, 96.9 (C-1), 121.4, 125.44, 125.50, 126.08, 126.13, 127.53, 127.64, 127.72, 127.76, 127.78, 127.81, 128.29, 128.32, 128.37, 128.38, 129.21, 137.73, 137.76, 138.03, 140.2, 149.3, 155.9; HRMS: m/z calcd for $C_{50}H_{45}F_6NO_6SNa$ $[M + Na]^+$ 924.2769, found 924.2809.

Glycosylation Using TfOH as Catalyst (The General Procedure). To a stirred suspension of additive (MS 3,4,5A or Drierite: 3 g/mmol), glycosyl donor **1α** or **β** (1.1 eq. of glycosyl acceptor), and glycosyl acceptor (25.0 mg) in an appropriate solvent (2.0 mL) was successively added a toluene solution of TfOH (ca. 0.10 mL) at temperatures ranging from 0 °C to −78 °C. The reaction mixture was stirred for 1 h at stated reaction temperature and was quenched by adding saturated aqueous $NaHCO_3$. The mixture was filtered through the pad of celite, and aqueous layer was extracted with CH_2Cl_2 (×3). The combined organic layer was washed with H_2O and brine, and dried over Na_2SO_4. After filtration and evaporation, the resultant was purified by thin-layer chromatography to afford the corresponding disaccharide.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-α-D-glucopyranoside (3): The title compound was synthesized from glycosyl donor **1α** or **1β** and glycosyl acceptor **2** according to the general procedure. The ratios were determined by HPLC analysis (hexane/EtOAc = 4/1). Separation of anomers was achieved by thin-layer chromatography (hexane/$CHCl_3$/acetone) for characterization purposes.

3α: White solid; mp 98–99 °C; $R_f = 0.31$ (hexane/$CHCl_3$/acetone = 5/4/1); $[\alpha]_D^{24} + 53.0$ ($c = 0.57$, $CHCl_3$); IR (KBr): 3032, 2916, 1458, 1365, 1103, 1072, 1034, 741, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.35 (s, 3 H), 3.44 (dd, $J = 9.5$, 3.4 Hz, 1 H), 3.52–3.56 (m, 2 H), 3.59–3.68 (m, 3 H), 3.71 (d, $J = 11.3$ Hz, 1 H), 3.76–3.79 (m, 2 H), 3.82 (dd, $J = 11.3$, 4.3 Hz, 1 H), 3.96 (dd, $J = 9.5$, 9.2 Hz, 1 H), 3.98 (dd, $J = 9.5$, 9.2 Hz, 1 H), 4.41 (d, $J = 12.2$ Hz, 1 H), 4.45 (d, $J = 11.0$ Hz, 1 H), 4.55 (d, $J = 3.4$ Hz, 1 H, H-1), 4.53–4.58 (m, 2 H), 4.62–4.69 (m, 3 H), 4.71 (d, $J = 11.9$ Hz, 1 H), 4.77 (d, $J = 11.0$ Hz, 1 H), 4.81 (d, $J = 10.7$ Hz, 1 H), 4.82 (d, $J = 11.0$ Hz, 1 H), 4.91 (d, $J = 11.6$ Hz, 1 H), 4.94 (d, $J = 10.7$ Hz, 1 H), 4.96 (d, $J = 11.0$ Hz, 1 H), 4.98 (d, $J = 3.7$ Hz, 1 H, H-1′), 7.10–7.14 (m, 2 H), 7.20–7.36 (m, 33 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1, 66.0, 68.5, 70.2, 70.3, 72.3, 73.3, 73.4, 74.85, 74.94, 75.5, 75.7, 77.6, 77.8, 80.0, 80.1, 81.6, 82.1, 97.2 (C-1′), 97.9 (C-1), 127.46, 127.50, 127.51, 127.55, 127.58, 127.68, 127.71, 127.80, 127.84, 127.94, 127.97, 127.98, 128.24, 128.27, 128.29, 128.33, 128.38, 138.0, 138.2, 138.40, 138.43, 138.5, 138.79, 138.81; HRMS: m/z calcd for $C_{62}H_{66}O_{11}\cdot NH_4$ $[M + NH_4]^+$ 1004.4949, found 1004.4942.

3β: White solid; mp 133–135 °C; $R_f = 0.28$ (hexane/$CHCl_3$/acetone = 5/4/1); $[\alpha]_D^{24} + 19.0$ ($c = 1.0$, $CHCl_3$); IR (KBr): 3032, 2916, 1458, 1358, 1111, 1065, 741, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.32 (s, 3 H), 3.42–3.46 (m, 1 H), 3.49 (dd, $J = 8.9$, 8.2 Hz, 1 H), 3.51 (dd, $J = 9.8$, 9.5 Hz, 1 H), 3.52 (dd, $J = 9.5$, 3.7 Hz, 1 H), 3.57 (dd, $J = 9.8$, 9.2 Hz, 1 H), 3.63 (dd, $J = 9.2$, 8.9 Hz, 1 H), 3.64–3.74 (m, 3 H), 3.81–3.85 (m, 1 H), 3.99 (dd, $J = 9.5$, 9.5 Hz, 1 H), 4.16–4.20 (m, 1 H), 4.34 (d, $J = 8.2$ Hz, 1 H, H-1′), 4.51 (d, $J = 11.0$ Hz, 1 H), 4.52–4.56 (m, 2 H), 4.57–4.61 (m, 2 H), 4.61 (d, $J = 3.7$ Hz, 1 H, H-1), 4.65 (d, $J = 11.9$ Hz, 1 H), 4.71 (d, $J = 11.0$ Hz, 1 H), 4.75 (d, $J = 11.0$ Hz, 1 H), 4.77–4.81 (m, 2 H), 4.80 (d, $J = 11.0$ Hz, 1 H), 4.90 (d, $J = 11.0$ Hz, 1 H), 4.96 (d, $J = 11.0$ Hz, 1 H), 4.97 (d, $J = 11.0$ Hz, 1 H), 7.14–7.22 (m, 6 H), 7.23–7.40 (m, 29 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.2, 68.5, 69.0, 69.8, 73.3, 73.4 (C×2), 74.9 (C×2), 75.0, 75.68, 75.71, 77.9, 78.0, 79.8, 82.0, 82.1, 84.8, 98.0 (C-1), 103.8 (C-1′), 127.5, 127.60, 127.65, 127.75, 127.85, 127.87, 127.91, 127.94, 127.96, 128.1, 128.33, 128.36, 128.39, 128.44, 138.08, 138.12, 138.2, 138.4, 138.5, 138.8; HRMS: m/z calcd for $C_{62}H_{66}O_{11}\cdot NH_4$ $[M + NH_4]^+$ 1004.4949, found 1004.4957.

2,3,4-Tri-*O*-benzyl-β-D-glucopyranosyl fluoride (8): To a stirred solution of 2,3,4-tri-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α(and/or β)-D-glucopyranosyl fluoride[40] (9.77 g, 14.1 mmol, $\alpha/\beta = 11/89$) in THF (70 mL) were added acetic acid (8.1 mL, 141 mmol) and a 1.0 M THF solution of tetrabutylammonium fluoride (TBAF) (70.5 mL, 70.5 mmol) at 0 °C. The reaction mixture was stirred for 7 h at room temperature. Then, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ and EtOAc, and the aqueous layer was extracted with EtOAc (×2). The combined organic layer was washed with H_2O and brine, and dried over $MgSO_4$. After filtration and evaporation, the resultant was purified by silica-gel column chromatography (hexane/EtOAc = 10/1 to 2/1), then further purified by recrystallization from hexane/EtOAc to afford the title compound **8** (3.43 g, 54%, $\alpha/\beta = 2/98$).

8: White solid; mp 112–113 °C; $R_f = 0.36$ (hexane/EtOAc = 2/1); $[\alpha]_D^{20} + 27.3$ ($c = 1.0$, $CHCl_3$); IR (KBr): 1496, 1458, 1404, 1358, 1311, 1111, 1065, 987, 903, 748, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.50–3.60 (m, 2 H), 3.66–3.76 (m, 3 H), 3.88 (dd, $J = 12.2$, 2.4 Hz, 1 H), 4.66 (d, $J = 11.0$ Hz, 1 H), 4.70 (d, $J = 11.0$ Hz, 1 H), 4.79 (d, $J = 11.0$ Hz, 1 H), 4.83 (d, $J = 11.0$ Hz, 1 H), 4.86 (d, $J = 11.0$ Hz, 1 H), 4.89 (d, $J = 11.0$ Hz, 1 H), 5.30 (dd, $J = 52.9$, 6.3 Hz, 1 H, H-1), 7.25–7.35 (m, 15 H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 61.5, 74.4 (d, $J =$ 2.2 Hz), 75.0, 75.27 (d, $J = 3.9$ Hz), 75.33, 76.3, 81.4 (d, $J = 21.8$ Hz), 83.2 (d, $J = 11.2$ Hz), 109.6 (d, $J = 216.3$ Hz, C-1), 127.67, 127.73, 127.87, 127.90, 127.93, 128.01, 128.32, 128.36, 128.41, 137.41, 137.56, 137.98; HRMS: m/z calcd for $C_{27}H_{29}FO_5\cdot NH_4$ $[M + NH_4]^+$ 470.2343, found 470.2345.

Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-α-D-glucopyranoside (9):

The title compound was synthesized from glycosyl donor **1α** and glycosyl acceptor **4** according to the general procedure. The ratios were determined by HPLC analysis (hexane/EtOAc = 4/1). Separation of anomers was achieved by thin-layer chromatography (hexane/acetone) for characterization purposes.

9α: colorless oil; $R_f = 0.58$ (hexane/acetone = 100/6, 2 times); ($[\alpha]_D^{23} + 59$ ($c = 0.68$, $CHCl_3$); IR (KBr): 2916, 1450, 1365, 1103, 1049, 741, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.31 (s, 3 H), 3.50–3.55 (m, 2 H), 3.56 (dd, $J = 9.2$, 3.4 Hz, 1 H), 3.57 (dd, $J = 9.5$, 3.4 Hz, 1 H), 3.58–3.63 (m, 1 H), 3.65–3.77 (m, 3 H), 3.78 (dd, $J = 10.1$, 8.5 Hz, 1 H), 4.06 (dd, $J = 9.5$, 9.2 Hz, 1 H), 4.26 (dd, $J = 9.2$, 8.5 Hz, 1 H), 4.28–4.35 (m, 1 H), 4.34 (d, $J = 12.2$ Hz, 1 H), 4.38 (d, $J = 11.3$ Hz, 1 H), 4.44 (d, $J = 11.9$ Hz, 1 H), 4.45 (d, $J = 11.0$ Hz, 1 H), 4.52 (d, $J = 11.6$ Hz, 1 H), 4.56–4.63 (m, 3 H), 4.63 (d, $J = 3.4$ Hz, 1 H, H-1), 4.67 (d, $J = 11.6$ Hz, 1 H), 4.68 (d, $J = 11.6$ Hz, 1 H), 4.80 (d, $J = 11.0$ Hz, 1 H), 4.83 (d, $J = 10.7$ Hz, 1 H), 4.90 (d, $J = 10.7$ Hz, 1 H), 4.94 (d, $J = 11.3$ Hz, 1 H), 5.59 (d, $J = 3.4$ Hz, 1 H, H-1′), 6.98–7.04 (m, 2 H), 7.08–7.36 (m, 33 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.0, 68.37, 68.44, 69.4, 70.2, 73.2, 73.3, 73.5, 74.8, 75.4, 76.6, 78.1, 78.5, 78.7, 79.6, 82.2, 97.3 (C-1′), 97.5 (C-1), 126.8, 127.2, 127.37, 127.40, 127.5, 127.61, 127.64, 127.71, 127.76, 127.83, 127.86, 128.06, 128.14, 128.21, 128.25, 128.31, 128.34, 128.7, 137.8, 138.0, 138.1, 138.3, 138.7, 138.8; HRMS: m/z calcd for $C_{62}H_{66}O_{11}\cdot NH_4$ $[M + NH_4]^+$ 1004.4949, found 1004.4935.

9β: colorless oil; $R_f = 0.52$ (hexane/acetone = 100/6, 2 times); $[\alpha]_D^{23} + 36$ ($c = 1.1$, $CHCl_3$); IR (KBr): 3024, 2908, 2870, 1458, 1365, 1041, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.31 (s, 3 H), 3.40–3.44 (m, 1 H), 3.47 (dd, $J = 8.9$, 7.9 Hz, 1 H), 3.52 (dd, $J = 9.5$, 3.7 Hz, 1 H), 3.59 (dd, $J = 9.8$, 8.9 Hz, 1 H), 3.60–3.65 (m, 1 H), 3.67 (dd, $J = 9.2$, 8.9 Hz, 1 H), 3.67–3.78 (m, 5 H), 4.37 (d, $J = 11.9$ Hz, 1 H), 4.39 (dd, $J = 9.5$, 8.9 Hz, 1 H), 4.44 (d, $J = 12.2$ Hz, 1 H), 4.48 (d, $J = 11.0$ Hz, 1 H), 4.49 (d, $J = 10.1$ Hz, 1 H), 4.50 (d, $J = 3.7$ Hz, 1 H, H-1), 4.50 (d, $J = 11.9$ Hz, 1 H), 4.58 (d, $J = 12.2$ Hz, 1 H), 4.60 (d, $J = 11.0$ Hz, 1 H), 4.65 (d, $J = 11.9$ Hz, 1 H), 4.82 (d, $J = 11.0$ Hz, 1 H), 4.86 (d, $J = 11.0$ Hz, 1 H), 4.89 (d, $J = 11.6$ Hz, 1 H), 4.99 (d, $J = 11.0$ Hz, 1 H), 5.04–5.09 (m, 2 H), 5.07 (d, $J = 7.9$ Hz, 1 H, H-1′), 7.10–7.36 (m, 33 H), 7.40–7.44 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1, 68.6, 68.9, 69.5, 73.3, 73.6, 74.7, 74.9, 75.0, 75.8, 76.0, 77.5, 78.3, 81.3, 83.2, 85.0, 97.8 (C-1), 102.6 (C-1′), 126.9, 127.2, 127.4, 127.51, 127.55, 127.7, 127.83, 127.86, 127.96, 127.98, 128.1, 128.2, 128.3, 128.4, 137.98, 138.01, 138.2, 138.5, 138.6, 138.7, 138.8; HRMS: m/z calcd for $C_{62}H_{66}O_{11}\cdot NH_4$ $[M + NH_4]^+$ 1004.4949, found 1004.4959.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-α-D-glucopyranoside (10): The title compound was synthesized from glycosyl donor **1α** and glycosyl acceptor **5** according to the general procedure. The ratios were determined by HPLC analysis (MeOH/H_2O = 20/1). Separation of anomers was achieved by thin-layer chromatography (hexane/$CHCl_3$/acetone) for characterization purposes.

10α: colorless oil; $R_f = 0.44$ (hexane/$CHCl_3$/acetone = 5/4/1); $[\alpha]_D^{24} + 47$ ($c = 0.87$, $CHCl_3$); IR (neat): 3032, 2924, 2862, 1450, 1365, 1149, 1095, 1041, 741, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.37 (s, 3 H), 3.37–3.42 (m, 1 H), 3.46–3.52 (m, 2 H), 3.59 (dd, $J = 8.9$, 3.7 Hz, 1 H), 3.64 (dd, $J = 9.8$, 9.2 Hz, 1 H), 3.65 (dd, $J = 9.5$, 2.7 Hz, 1 H), 3.68–3.73 (m, 1 H), 3.80–3.87 (m, 2 H), 3.90 (dd, $J = 9.5$, 9.2 Hz, 1 H), 4.04 (dd, $J = 9.2$, 8.9 Hz, 1 H), 4.09 (dd, $J = 8.9$, 8.9 Hz, 1 H), 4.28 (d, $J = 12.2$ Hz, 1 H), 4.42 (d, $J = 11.0$ Hz, 1 H), 4.47–4.63 (m, 6 H), 4.60 (d, $J = 3.4$ Hz, 1 H, H-1), 4.69 (d, $J = 11.9$ Hz, 1 H), 4.77 (d, $J = 10.7$ Hz, 1 H), 4.78 (d, $J = 10.7$ Hz, 1 H), 4.80 (d, $J = 11.3$ Hz, 1 H), 4.88 (d, $J = 10.7$ Hz, 1 H), 5.03 (d, $J = 11.3$ Hz, 1 H), 5.69 (d, $J = 3.7$ Hz, 1 H, H-1′), 7.08–7.10 (m, 2 H), 7.16–7.32 (m, 33 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1, 68.1, 69.0, 69.5, 70.9, 72.3, 73.1, 73.2, 73.3, 73.4, 74.4, 74.9, 75.5, 77.6, 79.4, 80.2, 82.0, 96.6 (C-1′), 97.7 (C-1), 126.7, 127.1, 127.2, 127.3, 127.46, 127.54, 127.60, 127.68, 127.79, 127.80, 127.9, 128.0, 128.19, 128.23, 128.27, 128.30, 128.4, 137.9, 138.0, 138.2, 138.5, 138.7, 138.9; HRMS: m/z calcd for $C_{62}H_{66}O_{11}\cdot NH_4$ $[M + NH_4]^+$ 1004.4949, found 1004.4952.

10β: White solid; mp 83–85 °C; $R_f = 0.40$ (hexane/$CHCl_3$/acetone = 5/4/1); $[\alpha]_D^{24} + 21$ ($c = 1.0$, $CHCl_3$); IR (KBr): 3016, 2916, 2870, 1450, 1357, 1049, 733, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.27–3.33 (m, 1 H), 3.36 (s, 3 H), 3.33–3.40 (m, 1 H), 3.44–3.52 (m, 3 H), 3.54 (dd, $J = 11.0$, 4.6 Hz, 1 H), 3.56–3.63 (m, 2 H), 3.68–3.73 (m, 1 H), 3.78–3.94 (m, 2 H), 3.96 (dd, $J = 9.8$, 9.2 Hz, 1 H), 4.38 (d, $J = 12.5$ Hz, 1 H), 4.38 (d, $J = 7.6$ Hz, 1 H, H-1′), 4.39 (d, $J = 11.3$ Hz, 1 H), 4.43 (d, $J = 12.5$ Hz, 1 H), 4.54–4.60 (m, 2 H), 4.57 (d, $J = 4.0$ Hz, 1 H, H-1), 4.60 (d, $J = 12.5$ Hz, 1 H), 4.74–4.83 (m, 6 H), 4.87 (d, $J = 11.0$ Hz, 1 H), 5.09 (d, $J = 11.3$ Hz, 1 H), 7.16–7.34 (m, 33 H), 7.39–7.43 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.3, 67.8, 69.0, 69.9, 73.31, 73.32, 73.6, 74.7, 74.9, 75.1, 75.3, 75.6, 76.6, 78.0, 78.8, 80.4, 82.8, 84.8, 98.4 (C-1), 102.5 (C-1′), 127.0, 127.3, 127.49, 127.55, 127.60, 127.72, 127.74, 127.75, 127.9, 128.0, 128.1, 128.2, 128.31, 128.33, 128.4, 137.8, 138.3, 138.4, 138.5, 139.6; HRMS: m/z calcd for $C_{62}H_{66}O_{11}\cdot NH_4$ $[M + NH_4]^+$ 1004.4949, found 1004.4932.

Ethyl 3-*O*-acetyl-4-*O*-benzyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl sulfide (11): The title compound was synthesized from glycosyl donor **1α** and glycosyl acceptor **6** according to the general procedure. The ratios were determined by HPLC analysis (hexane/EtOAc = 4/1). Separation of anomers was achieved by thin-layer chromatography (hexane/$CHCl_3$/acetone) for characterization purposes.

11α: foam; $R_f = 0.32$ (hexane/$CHCl_3$/acetone = 5/4/1); $[\alpha]_D^{27} + 36$ ($c = 1.2$, $CHCl_3$); IR (KBr): 2939, 1720, 1381, 1227, 1103, 1034, 741, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.14 (t, $J = 7.3$ Hz, 3 H), 1.68 (s, 3 H), 2.58 (dq, $J = 12.5$, 7.3 Hz, 1 H), 2.65 (dq, $J = 12.5$, 7.3 Hz, 1 H), 3.62–3.79 (m, 5 H), 3.83–3.94 (m, 4 H), 4.03 (dd, $J = 9.5$, 8.9 Hz, 1 H), 4.23 (dd, $J = 10.7$, 10.1 Hz, 1 H), 4.46 (d, $J = 12.2$ Hz, 1 H), 4.47 (d, $J = 10.7$ Hz, 1 H), 4.62 (d, $J = 12.2$ Hz, 1 H), 4.63 (d, $J = 11.6$ Hz, 1 H), 4.68 (d, $J = 11.6$ Hz, 1 H), 4.76–4.88 (m, 4 H), 5.03 (d, $J = 10.7$ Hz, 1 H), 5.13 (d, $J = 3.7$ Hz, 1 H, H-1′), 5.48 (d, $J = 10.7$ Hz, 1 H, H-1), 5.80 (dd, $J = 10.1$, 9.2 Hz, 1 H), 7.10–7.15 (m, 2 H), 7.20–7.40 (m, 21 H), 7.43–7.48 (m, 2 H), 7.66–7.76 (m, 2 H), 7.78–7.88 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.0, 20.5, 24.4, 54.5, 65.3, 68.5, 70.3, 72.7, 73.4, 73.9, 74.5, 75.0, 75.6, 76.4, 77.6, 79.2, 80.0, 80.9 (C-1), 81.9, 97.1 (C-1′), 123.5, 123.6, 127.56, 127.68, 127.73, 127.75, 127.84, 127.89, 127.94, 127.98, 128.02, 128.1, 128.29, 128.38, 128.43, 128.5, 131.3, 131.8, 134.0, 134.3, 137.99, 138.01, 138.3, 138.5, 138.8, 167.4, 167.8, 170.1; HRMS: m/z calcd for $C_{59}H_{61}NO_{12}S\cdot NH_4$ $[M + NH_4]^+$ 1025.4258, found 1025.4248.

11β: foam; $R_f = 0.26$ (hexane/$CHCl_3$/acetone = 5/4/1); $[\alpha]_D^{23} + 12$ ($c = 0.40$, $CHCl_3$); IR (KBr): 2924, 2854, 1743, 1720, 1458, 1381, 1227, 1095, 1065, 741, 702 cm^{-1}; ^1H NMR

(500 MHz, $CDCl_3$): δ 1.09 (t, $J = 7.3$ Hz, 3 H), 1.74 (s, 3 H), 2.55 (dq, $J = 12.2$, 7.3 Hz, 1 H), 2.60 (dq, $J = 12.2$, 7.3 Hz, 1 H), 3.40–3.46 (m, 1 H), 3.51 (dd, $J = 8.2$, 7.6 Hz, 1 H), 3.60–3.67 (m, 2 H), 3.68 (dd, $J = 9.8$, 9.8 Hz, 1 H), 3.72–3.75 (m, 2 H), 3.78 (dd, $J = 11.0$, 5.8 Hz, 1 H), 3.83 (dd, $J = 9.8$, 5.8 Hz, 1 H), 4.24 (d, $J = 11.0$ Hz, 1 H), 4.28 (dd, $J = 10.4$, 10.4 Hz, 1 H), 4.44 (d, $J = 7.6$ Hz, 1 H, H-1′), 4.49 (d, $J = 11.0$ Hz, 1 H), 4.55 (d, $J = 11.0$ Hz, 1 H), 4.56 (d, $J = 12.2$ Hz, 1 H), 4.58 (d, $J = 12.2$ Hz, 1 H), 4.66 (d, $J = 12.2$ Hz, 1 H), 4.80 (d, $J = 12.2$ Hz, 1 H), 4.81 (d, $J = 11.0$ Hz, 1 H), 4.82 (d, $J = 11.0$ Hz, 1 H), 4.95 (d, $J = 11.0$ Hz, 1 H), 5.01 (d, $J = 11.0$ Hz, 1 H), 5.48 (d, $J = 10.4$ Hz, 1 H, H-1), 5.83 (dd, $J = 10.1$, 8.9 Hz, 1 H), 7.14–7.20 (m, 4 H), 7.22–7.42 (m, 21 H), 7.68–7.75 (m, 2 H), 7.80–7.90 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.8, 20.5, 24.2, 54.3, 68.6, 68.8, 73.5, 74.1, 74.5, 74.8, 74.9, 75.0, 75.7, 77.1, 77.8, 78.9, 80.8 (C-1), 82.1, 84.7, 104.0 (C-1′), 123.5, 123.6, 127.48, 127.55, 127.58, 127.72, 127.79, 127.84, 127.9, 128.0, 128.32, 128.36, 128.39, 128.40, 131.3, 131.8, 134.0, 134.3, 137.8, 138.1, 138.2, 138.45, 138.53, 168.0, 168.2, 170.0; HRMS: m/z calcd for $C_{59}H_{61}NO_{12}S\cdot NH_4$ $[M + NH_4]^+$ 1025.4258, found 1025.4276.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-β-D-glucopyranosyl sulfide (12): The title compound was synthesized from glycosyl donor **1α** and glycosyl acceptor **7** according to the general procedure. The ratios were determined by HPLC analysis (hexane/EtOAc = 4/1). Separation of anomers was achieved by thin-layer chromatography (hexane/$CHCl_3$/acetone) for characterization purposes.

12α: foam; $R_f = 0.48$ (hexane/$CHCl_3$/acetone = 5/4/1); $[\alpha]_D^{24} + 39$ ($c = 1.6$, $CHCl_3$); IR (KBr): 2908, 1728, 1450, 1365, 1273, 1095, 1034, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13 (t, $J = 7.3$ Hz, 3 H), 2.64 (dq, $J = 12.2$, 7.3 Hz, 1 H), 2.70 (dq, $J = 12.2$, 7.3 Hz, 1 H), 3.54 (dd, $J = 9.5$, 3.4 Hz, 1 H), 3.54–3.60 (m, 2 H), 3.63 (dd, $J = 9.8$, 9.2 Hz, 1 H), 3.65 (dd, $J = 10.7$, 3.7 Hz, 1 H), 3.84–3.93 (m, 2 H), 3.95 (dd, $J = 9.5$, 9.2 Hz, 1 H), 4.05–4.12 (m, 1 H), 4.41 (d, $J = 12.2$ Hz, 1 H), 4.45 (d, $J = 11.0$ Hz, 1 H), 4.59 (d, $J = 12.2$ Hz, 1 H), 4.62 (d, $J = 12.2$ Hz, 1 H), 4.72 (d, $J = 3.4$ Hz, 1 H, H-1′), 4.75 (d, $J = 10.7$ Hz, 1 H), 4.77 (d, $J = 9.5$ Hz, 1 H, H-1), 4.77 (d, $J = 12.2$ Hz, 1 H), 4.81 (d, $J = 11.0$ Hz, 1 H), 4.92 (d, $J = 10.7$ Hz, 1 H), 5.46 (dd, $J = 9.5$, 9.5 Hz, 1 H), 5.46 (dd, $J = 9.5$, 9.5 Hz, 1 H), 5.86 (dd, $J = 9.5$, 9.5 Hz, 1 H), 7.10–7.15 (m, 2 H), 7.16–7.45 (m, 25 H), 7.46–7.54 (m, 2 H), 7.76–7.83 (m, 2 H), 7.90–7.93 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.7, 24.4, 66.9, 68.3, 69.8, 70.1, 70.8, 73.26, 73.35, 74.3, 74.8, 75.6, 77.4, 77.6, 80.0, 81.9, 83.6 (C-1), 97.1 (C-1′), 127.4, 127.5, 127.6, 127.7, 127.82, 127.88, 127.93, 128.0, 128.18, 128.25, 128.34, 128.4, 128.9, 129.3, 129.7, 129.86, 129.89, 133.16, 133.21, 133.4, 138.0, 138.3, 138.6, 138.9, 165.2, 165.8; HRMS: m/z calcd for $C_{63}H_{62}O_{13}S\cdot NH_4$ $[M + NH_4]^+$ 1076.4255, found 1076.4240.

12β: foam; $R_f = 0.42$ (hexane/$CHCl_3$/acetone = 5/4/1); $[\alpha]_D^{23} + 7.4$ ($c = 1.0$, $CHCl_3$); IR (KBr): 3062, 2862, 1728, 1597, 1450, 1365, 1273, 1072, 741, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13 (t, $J = 7.3$ Hz, 3 H), 2.63 (dq, $J = 12.2$, 7.3 Hz, 1 H), 2.68 (dq, $J = 12.2$, 7.3 Hz, 1 H), 3.38–3.46 (m, 2 H), 3.56–3.68 (m, 4 H), 3.87 (dd, $J = 11.6$, 7.9 Hz, 1 H), 4.04–4.15 (m, 2 H), 4.43 (d, $J = 12.2$ Hz, 1 H), 4.50 (d, $J = 7.6$ Hz, 1 H, H-1′), 4.51 (d, $J = 11.0$ Hz, 1 H), 4.54 (d, $J = 12.2$ Hz, 1 H), 4.70 (d, $J = 11.0$ Hz, 1 H), 4.75 (d, $J = 10.1$ Hz, 1 H, H-1), 4.77 (d, $J = 11.0$ Hz, 1 H), 4.80 (d, $J = 11.0$ Hz, 1 H), 4.91 (d, $J = 11.0$ Hz, 1 H), 5.00 (d, $J = 11.0$ Hz, 1 H), 5.42 (dd, $J = 10.1$, 9.5 Hz, 1 H), 5.51 (dd, $J = 10.1$, 9.5 Hz, 1 H), 5.89 (dd, $J = 9.5$, 9.5 Hz, 1 H), 7.12–7.16 (m, 2 H), 7.22–7.45 (m, 25 H), 7.47–7.52 (m, 2 H), 7.78–7.83 (m, 2 H), 7.88–7.97 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.7, 24.2, 68.6, 68.9, 70.0, 70.7, 73.5, 74.2, 74.7, 74.8, 75.0, 75.7, 77.6, 78.4, 82.2, 83.6 (C-1), 84.5, 103.9 (C-1′), 127.58, 127.65, 127.72, 127.77, 127.86, 127.92, 128.27, 128.34, 128.36, 128.42, 128.81, 128.85, 129.2, 129.7, 129.8, 133.18, 133.23, 133.5, 138.06, 138.08, 138.5, 138.6, 165.2, 165.4, 165.8; HRMS: m/z calcd for $C_{63}H_{62}O_{13}S\cdot NH_4$ $[M + NH_4]^+$ 1076.4255, found 1076.4265.

2,3,4-Tri-*O*-benzyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-β-D-glucopyranosyl fluoride (13): The title compound was synthesized from glycosyl donor **1α** and glycosyl acceptor **8** according to the general procedure. The ratios were determined by HPLC analysis (hexane/EtOAc = 4/1). Separation of anomers was achieved by thin-layer chromatography (hexane/$CHCl_3$/EtOAc) for characterization purposes.

13α: White solid; mp 94–95 °C; $R_f = 0.37$ (hexane/$CHCl_3$/EtOAc = 5/3/1); $[\alpha]_D^{26} + 61.1$ ($c = 1.0$, $CHCl_3$); IR (neat): 1458, 1365, 1103 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.30–3.38 (m, 1 H), 3.49–3.79 (m, 10 H), 3.90 (t, $J = 9.2$ Hz, 1 H), 4.36 (d, $J = 12.2$ Hz, 1 H), 4.40 (d, $J = 11.0$ Hz, 1 H), 4.51 (d, $J = 12.2$ Hz, 2 H), 4.58 (d, $J = 11.0$ Hz, 1 H), 4.63 (d, $J = 12.2$ Hz, 1 H), 4.66 (d, $J = 12.2$ Hz, 1 H), 4.679 (d, $J = 11.0$ Hz, 1 H), 4.684 (d, $J = 11.0$ Hz, 1 H), 4.72 (d, $J = 11.0$ Hz, 1 H), 4.76 (d, $J = 11.0$ Hz, 1 H), 4.79 (d, $J = 11.0$ Hz, 1 H), 4.80 (d, $J = 11.0$ Hz, 1 H), 4.90 (d, $J = 11.0$ Hz, 1 H), 4.93 (d, $J = 3.4$ Hz, 1 H, H-1′), 5.14 (dd, $J = 7.0$, 53.1 Hz, 1 H, H-1), 7.05–7.31 (m, 35 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 65.9, 68.5, 70.3, 72.5, 73.4, 74.5, 74.8 (d, $J = 5.2$ Hz), 74.93, 74.96, 75.4, 75.5, 76.8, 77.6, 80.1, 81.6 (d, $J = 21.7$ Hz), 81.7, 83.4 (d, $J = 11.4$ Hz), 97.5 (C-1′), 109.8 (d, $J = 215.2$ Hz, C-1), 127.48, 127.55, 127.60, 127.65, 127.76, 127.79, 127.80, 127.82, 127.84, 127.98, 128.06, 128.28, 128.31, 128.34, 128.40, 137.8, 138.0, 138.3, 138.4, 138.8; HRMS: m/z calcd for $C_{61}H_{63}FO_{10}\cdot NH_4$ $[M + NH_4]^+$ 992.4749, found 992.4741.

13β: White solid; mp 143–144 °C; $R_f = 0.30$ (hexane/$CHCl_3$/EtOAc = 5/3/1); $[\alpha]_D^{25} + 25.2$ ($c = 1.0$, $CHCl_3$); IR (KBr): 1458, 1365, 1103 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.42–3.44 (m, 1 H), 3.50 (t, $J = 7.6$ Hz, 1 H), 3.54–3.72 (m, 9 H), 4.21–4.22 (m, 1 H), 4.38 (d, $J = 7.6$ Hz, 1 H, H-1′), 4.52–4.55 (m, 3 H), 4.60 (d, $J = 12.2$ Hz, 1 H), 4.69 (d, $J = 11.0$ Hz, 1 H), 4.72 (d, $J = 11.0$ Hz, 1 H), 4.76 (d, $J = 10.1$ Hz, 1 H), 4.80 (d, $J = 11.0$ Hz, 1 H), 4.82 (d, $J = 11.0$ Hz, 2 H), 4.84 (d, $J = 11.0$ Hz, 1 H), 4.87 (d, $J = 11.0$ Hz, 1 H), 4.93 (d, $J = 11.0$ Hz, 1 H), 4.98 (d, $J = 11.0$ Hz, 1 H), 5.26 (dd, $J = 6.4$, 52.8 Hz, 1 H, H-1), 7.16–7.35 (m, 35 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 68.6, 68.9, 73.5, 74.3, 74.6 (d, $J = 4.1$ Hz), 74.8, 75.0, 75.3, 75.7, 77.1, 77.8, 81.5 (d, $J = 22.8$ Hz), 82.0, 83.4 (d, $J = 11.4$ Hz), 84.7, 104.0 (C-1′), 109.7 (d, $J = 216.2$ Hz, C-1), 127.50, 127.54, 127.56, 127.67, 127.69, 127.74, 127.80, 127.84, 127.88, 127.93, 128.02, 128.08, 128.34, 128.38, 128.42, 137.7, 137.9, 138.1, 138.19, 138.24, 138.5, 138.6; HRMS: m/z calcd for $C_{61}H_{63}FO_{10}\cdot NH_4$ $[M + NH_4]^+$ 992.4749, found 992.4759.

2,3,4-Tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (15): To a stirred solution of 2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-α,β-D-glucopyranose (**14**) (5.83 g, 7.98 mmol) in THF (100 mL) was added a 0.5 M toluene solution of potassium bis(trimethylsilyl)amide (KHMDS) (0.5 M

in toluene, 19.1 mL, 9.57 mmol) at −78 °C. After the reaction mixture was stirred for 0.5 h at −78 °C, *p*-trifluoromethylphenyl isothiocyanate (2.01 g, 9.57 mmol) in THF (10 mL) was successively added at −78 °C. After this reaction mixture was stirred for 30 min at −78 °C, *p*-trifluoromethylbenzyl bromide (2.29 g, 9.57 mmol) in THF (10 mL) was added at −78 °C and then the reaction temperature was raised up to room temperature. The reaction mixture was quenched by adding saturated aqueous NH_4Cl (200 mL) at 0 °C and the aqueous layer was extracted with CH_2Cl_2 (300 mL ×3). The combined organic layer was washed with H_2O (300 mL) and brine (300 mL), and dried over $MgSO_4$. After filtration and evaporation, the resultant was purified by silica-gel column chromatography (hexane/EtOAc = 8/1) to afford the title compound **15** (8.03 g, 92%, $\alpha/\beta = 91/9$).

15: foam; $R_f = 0.46$ (hexane/EtOAc = 3/1); $[\alpha]_D^{23} + 58.6$ ($c = 1.1$, $CHCl_3$); IR (neat): 1736, 1643, 1605, 1327, 1265, 1165, 1119, 1072, 1018, 710 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, major isomer): δ 1.04 (s, 9 H), 3.74–3.80 (m, 2 H), 3.83–3.86 (m, 1 H), 4.33 (d, $J = 14.3$ Hz, 1 H), 4.44 (d, $J = 14.3$ Hz, 1 H), 5.54 (dd, $J = 10.1$, 3.7 Hz, 1 H), 5.80 (t, $J = 10.1$ Hz, 1 H), 6.10 (t, $J = 10.1$ Hz, 1 H), 6.58 (d, $J = 8.2$ Hz, 2 H), 7.04 (brs, 1 H, H-1), 7.14–7.71 (m, 25 H), 7.88 (d, $J = 7.3$ Hz, 2 H), 7.94 (d, $J = 7.3$ Hz, 2 H), 7.97 (d, $J = 7.0$ Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$, major isomer): δ 19.2, 26.6, 34.8, 61.8, 67.8, 70.3, 71.1, 73.4, 93.0 (C-1), 121.03, 125.60, 125.66, 125.82, 125.87, 126.04, 127.36, 127.48, 128.19, 128.24, 128.43, 128.52, 128.62, 128.66, 128.81, 129.03, 129.40, 129.48, 129.49, 129.58, 129.62, 132.51, 133.15, 133.20, 133.48, 135.25, 135.34, 135.42, 140.54, 140.56, 140.58, 148.71, 148.73, 155.17, 164.7, 165.1, 165.8; HRMS: *m/z* calcd for $C_{59}H_{51}F_6NO_9SSiNa$ $[M + Na]^+$ 1114.2856, found 1114.2850.

2,3,4-Tri-*O*-benzoyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (16): To a stirred solution of 2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (**15**) (1.44 g, 1.32 mmol, $\alpha/\beta = 91/9$) in THF (7 mL) were added acetic acid (0.76 mL, 13.2 mmol) and a 1.0 M THF solution of tetrabutylammonium fluoride (TBAF) (6.6 mL, 6.60 mmol) at 0 °C. The reaction mixture was stirred for 7 h at room temperature. Then, it was quenched by adding saturated aqueous $NaHCO_3$ at 0 °C and the aqueous layer was extracted with CH_2Cl_2 (×3). The combined organic layer was washed with H_2O and brine, and dried over Na_2SO_4. After filtration and evaporation, the resultant was purified by silica-gel column chromatography (hexane/EtOAc = 5/1 to 3/1), then further purified by crystallization from petroleum ether/THF to afford the title compound **16** (0.59 g, 52%, only α).

16: White solid; mp 120–121 °C; $R_f = 0.32$ (hexane/EtOAc = 2/1); $[\alpha]_D^{15} + 81.9$ ($c = 1.0$, $CHCl_3$); IR (KBr): 1728, 1643, 1605, 1450, 1419, 1335, 1281, 1250, 1158, 1111, 1072, 1018, 895, 849, 795, 710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.65–2.69 (m, 1 H), 3.61–3.65 (m, 2 H), 3.72–3.77 (m, 1 H), 4.32 (d, $J = 14.6$ Hz, 1 H), 4.49 (d, $J = 14.6$ Hz, 1 H), 5.54 (dd, $J = 10.3$, 3.4 Hz, 1 H), 5.56 (dd, $J = 10.0$, 9.8 Hz, 1 H), 6.19 (dd, $J = 10.3$, 10.0 Hz, 1 H), 6.65 (d, $J = 8.1$ Hz, 2 H), 6.98 (brd, $J = 3.4$ Hz, 1 H, H-1), 7.32–7.67 (m, 15 H), 7.86–8.15 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.9, 60.6, 68.5, 69.6, 70.8, 72.8, 92.9 (C-1), 121.2, 125.87, 125.90, 126.12, 126.16, 126.36, 128.29, 128.45, 128.58, 128.67, 128.76, 129.69, 129.79, 129.85, 133.51, 133.79, 133.92, 140.8, 148.8, 155.5, 165.3, 166.0, 166.2; HRMS: *m/z* calcd for $C_{43}H_{33}F_6NO_9SNa$ $[M + Na]^+$ 876.1678, found 876.1691.

2,3,6-Tri-*O*-benzoyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (17): To a stirred solution of 2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (**16**) (100 mg, 0.117 mmol) in THF (4 mL) was added a 1.0 M THF solution of tetrabutylammonium fluoride (TBAF) (0.13 mL, 0.13 mmol) at 0 °C. The reaction mixture was stirred for 20 min at 0 °C. Then, it was quenched by adding H_2O at 0 °C and the aqueous layer was extracted with CH_2Cl_2 (×2). The combined organic layer was washed with H_2O and brine, and dried over Na_2SO_4. After filtration and evaporation, the resultant was purified by thin-layer chromatography (hexane/EtOAc) to afford the title compound **17** (90.6 mg, 91%).

17: White solid; mp 185–187 °C; $R_f = 0.42$ (hexane/EtOAc = 2/1); $[\alpha]_D^{20} + 80.9$ ($c = 1.0$, $CHCl_3$); IR (KBr): 3464, 1728, 1635, 1612, 1327, 1273, 1165, 1119, 1065, 1018, 849, 710 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.31 (d, $J = 4.3$ Hz, 1 H), 3.73–3.75 (m, 1 H), 3.89 (dt, $J = 4.3$, 9.8 Hz, 1 H), 4.31 (d, $J = 14.6$ Hz, 1 H), 4.43 (d, $J = 14.6$ Hz, 1 H), 4.49 (dd, $J = 12.5$, 2.1 Hz, 1 H), 4.77 (dd, $J = 12.5$, 3.7 Hz, 1 H), 5.44 (dd, $J = 10.4$, 3.6 Hz, 1 H), 5.78 (dd, $J = 10.4$, 9.8 Hz, 1 H), 6.60 (d, $J = 8.2$ Hz, 2 H), 6.89 (brd, $J = 3.6$ Hz, 1 H, H-1), 7.38–7.64 (m, 15 H), 7.93 (d, $J = 7.6$ Hz, 2 H), 8.01 (d, $J = 7.9$ Hz, 2 H), 8.10 (d, $J = 7.9$ Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 34.9, 62.8, 68.4, 70.4, 72.6, 73.0, 92.9 (C-1), 121.1, 125.86, 125.90, 125.94, 126.00, 128.38, 128.41, 128.51, 128.67, 128.80, 129.11, 129.67, 129.74, 129.80, 133.47, 133.62, 140.37, 140.39, 148.75, 155.29, 165.28, 166.67, 167.02; HRMS: *m/z* calcd for $C_{43}H_{33}F_6NO_9SNa$ $[M + Na]^+$ 876.1678, found 876.1680.

2,3,4-Tri-*O*-benzoyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-α-D-glucopyranosyl *p*-trifluoromethylbenzylthio-*N*-*p*-trifluoromethylphenylformimidate (18): The title compound was synthesized from glycosyl donor **1α** or **1β** and glycosyl acceptor **16** according to the general procedure. The ratios were determined by HPLC analysis (hexane/EtOAc = 6/1). Separation of anomers was achieved by thin-layer chromatography (toluene/CH_3CN) for characterization purposes.

18α: colorless oil; $R_f = 0.57$ (toluene/MeCN = 9/1); $[\alpha]_D^{22} + 75.4$ ($c = 1.59$, $CHCl_3$); IR (neat): 1736, 1643, 1605, 1458, 1327, 1265, 1165, 1111, 1072, 1018 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.43 (dd, $J = 10.7$, 1.7 Hz, 1 H), 3.53–3.57 (m, 3 H), 3.62 (t, $J = 9.3$ Hz, 1 H), 3.70–3.73 (m, 1 H), 3.80 (dd, $J = 11.5$, 5.9 Hz, 1 H), 3.98 (t, $J = 9.3$ Hz, 1 H), 4.09–4.15 (m, 1 H), 4.34 (d, $J = 12.2$ Hz, 1 H), 4.39–4.45 (m, 3 H), 4.53 (d, $J = 12.2$ Hz, 1 H), 4.62 (d, $J = 12.2$ Hz, 1 H), 4.72 (d, $J = 3.4$ Hz, 1 H, H-1′), 4.76 (d, $J = 12.2$ Hz, 1 H), 4.78 (d, $J = 11.0$ Hz, 1 H), 4.79 (d, $J = 10.7$ Hz, 1 H), 4.94 (d, $J = 11.0$ Hz, 1 H), 5.49 (dd, $J = 10.2$, 3.7 Hz, 1 H), 5.68 (t, $J = 10.2$ Hz, 1 H), 6.12 (t, $J = 10.2$ Hz, 1 H), 6.59 (d, $J = 8.1$ Hz, 2 H), 6.98 (br, 1 H, H-1), 7.09–7.59 (m, 35 H), 7.89–7.95 (m, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 35.0, 66.4, 68.0, 68.4, 70.1, 70.2, 71.1, 71.7, 73.2, 73.3, 75.0, 75.7, 77.2, 80.0, 81.8, 92.9 (C-1), 97.5 (C-1′), 121.2, 125.64, 125.72, 125.78, 125.91, 125.96, 126.09, 126.12, 127.43, 127.48, 127.53, 127.74, 127.80, 127.87, 128.14, 128.21, 128.26, 128.31, 128.33, 128.52, 128.55, 128.59, 128.65, 128.91, 129.64, 129.71, 129.72, 137.7, 138.1, 138.2, 138.7, 140.3, 148.70, 148.72, 155.5, 164.8, 165.1, 165.8; HRMS: *m/z* calcd for $C_{77}H_{67}F_6NO_{14}SNa$ $[M + Na]^+$ 1398.4084, found 1398.4080.

18β: colorless oil; $R_f = 0.54$ (toluene/MeCN = 9/1); $[\alpha]_D^{22} + 45.6$ ($c = 0.78$, $CHCl_3$); IR (neat): 1736, 1605, 1458, 1327, 1265, 1165, 1111, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.39–3.45 (m, 2 H), 3.54–3.67 (m, 4 H), 3.79 (dd, $J = 11.2$, 6.8 Hz, 1 H),

4.13 (dd, $J = 11.2$, 2.9 Hz, 1 H), 4.29–4.33 (m, 1 H), 4.38 (s, 2 H), 4.43 (d, $J = 12.2$ Hz, 1 H), 4.44 (d, $J = 7.8$ Hz, 1 H, H-1′), 4.48 (d, $J = 11.0$ Hz, 1 H), 4.53 (d, $J = 12.2$ Hz, 1 H), 4.58 (d, $J = 10.7$ Hz, 1 H), 4.73 (d, $J = 11.0$ Hz, 1 H), 4.79 (d, $J = 10.7$ Hz, 1 H), 4.88 (d, $J = 10.7$ Hz, 1 H), 5.00 (d, $J = 10.7$ Hz, 1 H), 5.54 (dd, $J = 10.5$, 3.7 Hz, 1 H), 5.60 (t, $J = 10.5$ Hz, 1 H), 6.17 (t, $J = 10.5$ Hz, 1 H), 6.40 (d, $J = 8.1$ Hz, 2 H), 7.02 (brs, 1 H, H-1), 7.11–7.62 (m, 35 H), 7.88–7.94 (m, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 35.0, 68.3, 68.5, 68.9, 70.1, 71.0, 72.0, 73.4, 74.75, 74.78, 75.0, 75.7, 77.2, 82.1, 84.4, 92.8 (C-1), 103.8 (C-1′), 121.0, 121.9, 122.1, 125.6, 125.70, 125.76, 125.81, 125.85, 126.06, 126.09, 127.47, 127.52, 127.54, 127.65, 127.77, 127.82, 128.21, 128.23, 128.26, 128.30, 128.40, 128.46, 128.52, 128.61, 128.85, 128.92, 129.07, 129.55, 129.61, 129.70, 130.03, 133.3, 133.5, 133.6, 137.9, 138.2, 138.3, 140.22, 140.25, 148.47, 148.49, 155.2, 165.1, 165.7; HRMS: m/z calcd for $C_{77}H_{67}F_6NO_{14}SNa$ $[M + Na]^+$ 1398.4084, found 1398.4057.

2,3,4-Tri-*O*-benzoyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-α-D-glucopyranosyl methoxide (21): The title compound was synthesized from glycosyl donor **1α** or **1β** and glycosyl acceptor **20** according to the general procedure. The ratios were determined by HPLC analysis (hexane/EtOAc = 4/1). Separation of anomers was achieved by thin-layer chromatography (hexane/EtOAc) for characterization purposes.

21α: colorless oil; $R_f = 0.32$ (hexane/EtOAc = 2/1); $[\alpha]_D^{26} + 73.4$ ($c = 1.12$, $CHCl_3$); IR (neat): 1730, 1281, 1259, 1101 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.43 (s, 3 H), 3.50 (dd, $J = 10.7$, 1.8 Hz, 1 H), 3.53 (dd, $J = 9.5$, 3.4 Hz, 1 H), 3.58 (dd, $J = 11.0$, 2.1 Hz, 1 H), 3.61–3.64 (m, 2 H), 3.83–3.87 (m, 2 H), 3.96 (dd, $J = 9.5$, 9.5 Hz, 1 H), 4.30–4.33 (m, 1 H), 4.38 (d, $J = 11.9$ Hz, 1 H), 4.45 (d, $J = 11.0$ Hz, 1 H), 4.54 (d, $J = 11.9$ Hz, 1 H), 4.62 (d, $J = 12.2$ Hz, 1 H), 4.73 (d, $J = 3.4$ Hz, 1 H, H-1′), 4.76 (d, $J = 12.2$ Hz, 1 H), 4.77 (d, $J = 11.0$ Hz, 1 H), 4.81 (d, $J = 11.0$ Hz, 1 H), 4.90 (d, $J = 11.0$ Hz, 1 H), 5.20 (d, $J = 3.7$ Hz, 1 H, H-1), 5.21 (dd, $J = 12.2$, 3.7 Hz, 1 H), 5.52 (dd, $J = 10.1$, 9.8 Hz, 1 H), 6.14 (dd, $J = 12.2$, 9.8 Hz, 1 H), 7.12–7.53 (m, 29 H), 7.86 (d, $J = 7.3$ Hz, 2 H), 7.94 (d, $J = 7.3$ Hz, 2 H), 7.98 (d, $J = 7.3$ Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$): δ 55.6, 66.6, 68.1, 68.5, 69.6, 70.1, 70.5, 72.2, 73.1, 73.3, 74.8, 75.5, 77.5, 79.8, 81.7, 96.6 (C-1 or 1′), 97.1 (C-1′ or 1), 127.35, 127.39, 127.49, 127.64, 127.81, 127.85, 128.12, 128.20, 128.27, 128.82, 128.91, 129.08, 129.53, 129.78, 132.92, 133.21, 137.71, 138.20, 138.38, 138.67, 165.04, 165.60, 165.63.

21β: White solid; mp 132–133 °C; $R_f = 0.37$ (hexane/EtOAc = 2/1); $[\alpha]_D^{24} + 38.8$ ($c = 1.52$, $CHCl_3$); IR (KBr): 1728, 1452, 1279, 1174, 1099, 1070, 1026 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.38 (s, 3 H), 3.43–3.48 (m, 2 H), 3.58–3.65 (m, 4 H), 3.81 (dd, $J = 11.0$, 7.6 Hz, 1 H), 4.13 (dd, $J = 11.0$, 2.0 Hz, 1 H), 4.36–4.40 (m, 1 H), 4.43 (d, $J = 12.2$ Hz, 1 H), 4.47 (d, $J = 7.9$ Hz, 1 H, H-1′), 4.51 (d, $J = 11.0$ Hz, 1 H), 4.52 (d, $J = 12.2$ Hz, 1 H), 4.69 (d, $J = 11.0$ Hz, 1 H), 4.77 (d, $J = 11.0$ Hz, 1 H), 4.80 (d, $J = 11.0$ Hz, 1 H), 4.91 (d, $J = 11.0$ Hz, 1 H), 5.06 (d, $J = 11.0$ Hz, 1 H), 5.21 (d, $J = 3.7$ Hz, 1 H, H-1), 5.26 (dd, $J = 10.4$, 3.7 Hz, 1 H), 5.48 (t, $J = 10.4$ Hz, 1 H), 6.18 (t, $J = 10.4$ Hz, 1 H), 7.14–7.49 (m, 29 H), 7.85 (d, $J = 7.0$ Hz, 2 H), 7.93 (d, $J = 7.3$ Hz, 2 H), 7.97 (d, $J = 7.3$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 68.6, 68.8, 69.0, 69.9, 70.5, 72.1, 73.4, 74.8, 74.88, 74.94, 75.6, 77.6, 82.3, 84.5, 96.8 (C-1), 104.0 (C-1′), 127.52, 127.63, 127.69, 127.83, 127.90, 128.16, 128.22, 128.29, 128.31, 128.34, 128.35, 128.38, 128.90, 129.06, 129.22, 129.63, 129.86, 129.89, 133.02, 133.30, 133.36, 138.08, 138.46, 138.59, 165.43, 165.73, 165.80.

6-*O*-[2′,3′,4′-Tri-*O*-benzoyl-6′-*O*-(2″,3″,4″,6″-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl methoxide (22): To a stirred suspension of MS 5A (88 mg), **1α** (29.1 mg, 0.032 mmol) and **16** (25.0 mg, 0.029 mmol) in ^{t}BuOMe (2.0 mL) was added a toluene solution (ca. 0.1 mL) of TfOH (0.48 mg, 3.2 μmol) at −78 °C. After the reaction mixture was stirred for 1 h, **2** (17.7 mg, 0.038 mmol) was added at −78 °C and then the reaction temperature was raised gradually up to 0 °C. Then, this reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ at 0 °C. The mixture was filtered through the pad of celite, and the aqueous layer was extracted with CH_2Cl_2 (×3). The combined organic layer was washed with brine and dried over Na_2SO_4. After filtration and evaporation, the resultant was purified by thin-layer chromatography (hexane/EtOAc = 3/1) to afford the title compound **22** (39.0 mg, 91%, $\alpha\beta/\beta\beta = 96/4$). The ratios were determined by HPLC analysis (hexane/EtOAc = 3/1). Separation of anomers was achieved by thin-layer chromatography (hexane/EtOAc) for characterization purposes.

22αβ: foam; $R_f = 0.5$ (hexane/EtOAc = 6/4); $[\alpha]_D^{23} + 23$ ($c = 2.4$, $CHCl_3$); IR (KBr): 2931, 2908, 2862, 1736, 1450, 1365, 1265, 1095, 741, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.03 (s, 3H), 3.34–3.43 (m, 2 H), 3.51 (dd, $J = 9.8$, 3.4 Hz, 1 H), 3.52–3.58 (m, 1 H), 3.58–3.66 (m, 4 H), 3.73 (dd, $J = 10.7$, 3.4 Hz, 1 H), 3.78–3.83 (m, 1 H), 3.83 (dd, $J = 9.5$, 9.2 Hz, 1 H), 3.87 (dd, $J = 11.3$, 6.7 Hz, 1 H), 3.91 (dd, $J = 9.8$, 9.2 Hz, 1 H), 4.01–4.07 (m, 1 H), 4.10 (d, $J = 10.4$ Hz, 1 H), 4.20 (d, $J = 11.3$ Hz, 1 H), 4.35 (d, $J = 12.2$ Hz, 1 H), 4.38 (d, $J = 11.3$ Hz, 1 H), 4.44 (d, $J = 11.3$ Hz, 1 H), 4.45 (d, $J = 3.7$ Hz, 1 H, H-1), 4.54 (d, $J = 12.2$ Hz, 1 H), 4.56 (d, $J = 12.2$ Hz, 1 H), 4.59 (d, $J = 12.2$ Hz, 1 H), 4.65 (d, $J = 11.3$ Hz, 1 H), 4.69 (d, $J = 12.2$ Hz, 1 H), 4.71 (d, $J = 10.4$ Hz, 1 H), 4.71 (d, $J = 10.4$ Hz, 1 H), 4.72 (d, $J = 3.4$ Hz, 1 H, H-1″), 4.76 (d, $J = 7.9$ Hz, 1 H, H-1′), 4.80 (d, $J = 11.3$ Hz, 1 H), 4.86 (d, $J = 10.4$ Hz, 1 H), 4.87 (d, $J = 10.4$ Hz, 1 H), 5.48 (dd, $J = 9.8$, 9.8 Hz, 1 H), 5.53 (dd, $J = 9.5$, 7.9 Hz, 1 H), 5.83 (dd, $J = 9.8$, 9.5 Hz, 1 H), 6.99 (d, $J = 7.0$ Hz, 2 H), 7.08–7.13 (m, 2 H), 7.14–7.43 (m, 39 H), 7.48 (dd, $J = 7.9$, 7.9 Hz, 1 H), 7.79 (d, $J = 7.9$ Hz, 2 H), 7.87 (d, $J = 7.9$ Hz, 2 H), 7.92 (d, $J = 7.9$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 54.9, 67.1, 67.8, 68.4, 69.4, 69.8, 70.2, 71.9, 73.0, 73.1, 73.36, 73.40, 74.5, 74.8, 75.4, 75.5, 77.1, 77.4, 79.7, 80.1, 81.75, 81.82, 97.3 (C-1″), 97.9 (C-1), 100.8 (C-1′), 127.30, 127.37, 127.47, 127.55, 127.62, 127.79, 127.80, 127.83, 127.87, 128.02, 128.08, 128.18, 128.24, 128.27, 128.30, 128.4, 128.8, 128.9, 129.2, 129.7, 129.8, 133.0, 133.1, 133.3, 138.1, 138.25, 138.28, 138.43, 138.8, 164.8, 165.1, 165.8; HRMS: m/z calcd for $C_{89}H_{88}O_{19}\cdot NH_4$ $[M + NH_4]^+$ 1478.6264, found 1478.6271.

22ββ: foam; $R_f = 0.6$ (hexane/EtOAc = 6/4); $[\alpha]_D^{23} - 0.72$ ($c = 0.74$, $CHCl_3$); IR (KBr): 2924, 1736, 1450, 1365, 1095, 1072, 741, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.11 (s, 3H), 3.31 (dd, $J = 9.8$, 8.9 Hz, 1 H), 3.35–3.43 (m, 3 H), 3.50–3.62 (m, 4 H), 3.62–3.68 (m, 2 H), 3.81 (dd, $J = 9.5$, 8.9 Hz, 1 H), 3.89 (dd, $J = 11.9$, 8.5 Hz, 1 H), 4.00–4.09 (m, 3 H), 4.11 (d, $J = 11.0$ Hz, 1 H), 4.32 (d, $J = 11.0$ Hz, 1 H), 4.42 (d, $J = 12.2$ Hz, 1 H), 4.48 (d, $J = 11.0$ Hz, 1 H), 4.48 (d, $J = 3.4$ Hz, 1 H, H-1), 4.52 (d, $J = 7.3$ Hz, 1 H, H-1″), 4.54 (d, $J = 12.2$ Hz, 1 H), 4.57 (d, $J = 12.2$ Hz, 1 H), 4.64 (d, $J = 12.2$ Hz, 1 H), 4.66 (d, $J = 8.2$ Hz, 1 H, H-1′), 4.68–4.76 (m, 3 H), 4.76 (d, $J = 11.0$ Hz, 1 H), 4.85 (d, $J = 11.0$ Hz, 1 H), 4.86 (d, $J = 11.0$ Hz, 1 H), 4.94 (d, $J = 11.0$ Hz, 1 H), 5.39 (dd, $J = 9.8$, 9.5 Hz, 1 H), 5.53 (dd, $J = 9.8$, 8.2 Hz, 1 H),

5.84 (dd, $J = 9.8$, 9.5 Hz, 1 H), 6.90–6.96 (m, 2 H), 7.06–7.14 (m, 2 H), 7.14–7.44 (m, 39 H), 7.47–7.53 (m, 1 H), 7.79 (dd, $J = 8.5$, 1.2 Hz, 2 H), 7.85 (d, $J = 8.2$ Hz, 2 H), 7.91 (dd, $J = 8.2$, 1.2 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.0, 67.9, 68.6, 69.4, 70.0, 71.9, 73.0, 73.3, 73.5, 74.6, 74.8, 74.9, 75.4, 75.5, 77.2, 77.6, 79.7, 81.8, 82.1, 84.7, 98.0 (C-1), 100.8 (C-1′), 103.9 (C-1″), 127.31, 127.37, 127.45, 127.56, 127.67, 127.73, 127.77, 127.82, 127.85, 128.09, 128.11, 128.20, 128.25, 128.31, 128.4, 128.8, 129.1, 129.7, 129.8, 133.0, 133.2, 133.5, 138.06, 138.17, 138.22, 138.5, 138.8, 164.8, 165.4, 165.8; HRMS: m/z calcd for $C_{89}H_{88}O_{19}\cdot NH_4$ $[M + NH_4]^+$ 1478.6264, found 1478.6262.

6-*O*-[2′,3′,4′-Tri-*O*-benzoyl-6′-*O*-(2″,3″,4″,6″-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (23): To a stirred suspension of MS 5A (88 mg), **1α** (29.1 mg, 0.032 mmol) and **16** (25.0 mg, 0.029 mmol) in ^{t}BuOMe (2.0 mL) was added a toluene solution (ca. 0.1 mL) of TfOH (0.48 mg, 3.2 μmol) at −78 °C. After the reaction mixture was stirred for 1 h, **8** (17.2 mg, 0.038 mmol) was added at −78 °C and then the reaction temperature was raised gradually up to 0 °C. Then, this reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ at 0 °C. The mixture was filtered through the pad of celite, and aqueous layer was extracted with CH_2Cl_2 (×3). The combined organic layer was washed with brine, and dried over Na_2SO_4. After filtration and evaporation, the resultant was purified by thin-layer chromatography (hexane/EtOAc = 3/1 and toluene/CH_3CN = 19/1) to afford the title compound **23** (32.1 mg, 76%, $\alpha\beta/\beta\beta = 95/5$). The ratios were determined by HPLC analysis (hexane/EtOAc = 3/1). Separation of anomers was achieved by thin-layer chromatography (hexane/EtOAc) for characterization purposes.

23αβ: colorless oil; $R_f = 0.28$ (hexane/EtOAc = 2/1); $[\alpha]_D^{21}$ + 30.7 ($c = 0.80$, $CHCl_3$); IR (neat): 1736, 1605, 1497, 1450, 1365, 1265, 1103, 741, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.10 (d, $J = 9.5$ Hz, 1 H), 3.35–3.41 (m, 2 H), 3.46 (t, $J = 9.5$ Hz, 1 H), 3.56 (dd, $J = 9.5$, 3.4 Hz, 1 H), 3.59–3.61 (m, 2 H), 3.66 (t, $J = 9.2$ Hz, 1 H), 3.70–3.72 (m, 2 H), 3.86–3.93 (m, 2 H), 3.97 (t, $J = 9.2$ Hz, 1 H), 4.04–4.07 (m, 1 H), 4.15 (d, $J = 9.8$ Hz, 1 H), 4.20 (d, $J = 11.0$ Hz, 1 H), 4.36 (d, $J = 11.0$ Hz, 1 H), 4.41 (d, $J = 10.7$ Hz, 1 H), 4.42 (d, $J = 12.5$ Hz, 1 H), 4.59–4.82 (m, 12 H), 4.94 (d, $J = 11.0$ Hz, 1 H), 5.45 (t, $J = 9.8$ Hz, 1 H), 5.53 (dd, $J = 9.8$, 7.9 Hz, 1 H), 5.84 (t, $J = 9.8$ Hz, 1 H), 6.93–7.51 (m, 44 H), 7.80 (d, $J = 7.9$ Hz, 2 H), 7.89 (d, $J = 7.9$ Hz, 2 H), 7.93 (d, $J = 7.9$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 66.4, 67.2, 68.4, 69.8, 70.1, 72.0, 73.1, 73.3, 73.5, 73.9, 74.3, 74.5, 74.8, 75.1, 75.6, 76.3, 77.5, 80.1, 81.4 (d, $J = 20.7$ Hz), 81.9, 83.2 (d, $J = 11.4$ Hz), 96.8 (C-1″), 100.8 (C-1′), 109.6 (d, $J = 215.2$ Hz, C-1), 127.30, 127.46, 127.54, 127.67, 127.74, 127.77, 127.81, 127.87, 128.02, 128.23, 128.26, 128.30, 128.37, 128.39, 128.88, 128.96, 129.24, 129.73, 129.87, 133.03, 133.12, 133.36, 137.89, 137.92, 138.18, 138.31, 138.34, 138.68, 138.92, 164.84, 165.10, 165.80; HRMS: m/z calcd for $C_{88}H_{85}FO_{18}\cdot NH_4$ $[M + NH_4]^+$ 1466.6064, found 1466.6093.

23ββ: colorless oil; $R_f = 0.35$ (hexane/EtOAc = 2/1); $[\alpha]_D^{21}$ + 4.4 ($c = 1.06$, $CHCl_3$); IR (neat): 1736, 1605, 1497, 1458, 1365, 1265, 1095, 741, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.27–3.29 (m, 1 H), 3.35–3.48 (m, 5 H), 3.56–3.66 (m, 5 H), 3.90 (dd, $J = 11.3$, 7.9 Hz, 1 H), 4.05–4.12 (m, 3 H), 4.16 (d, $J = 10.7$ Hz, 1 H), 4.38 (d, $J = 11.0$ Hz, 1 H), 4.44 (d, $J = 12.2$ Hz, 1 H), 4.51 (d, $J = 11.0$ Hz, 1 H), 4.546 (d, $J = 12.2$ Hz, 1 H), 4.552 (d, $J = 7.9$ Hz, 1 H, H-1′ or 1″), 4.62 (d, $J = 10.7$ Hz, 1 H), 4.64 (d, $J = 10.7$ Hz, 1 H), 4.70 (d, $J = 11.3$ Hz, 1 H), 4.71 (d, $J = 11.0$ Hz, 1 H), 4.75–4.79 (m, 4 H), 4.85 (d, $J = 11.0$ Hz, 1 H), 4.96 (dd, $J = 52.5$, 6.4 Hz, 1 H, H-1), 4.97 (d, $J = 11.3$ Hz, 1 H), 5.42 (t, $J = 9.8$ Hz, 1 H), 5.54 (dd, $J = 9.8$, 7.9 Hz, 1 H), 5.86 (t, $J = 9.8$ Hz, 1 H), 6.94 (t, $J = 3.4$ Hz, 2 H), 7.13–7.42 (m, 41 H), 7.49 (t, $J = 7.3$ Hz, 1 H), 7.81 (d, $J = 7.9$ Hz, 2 H), 7.89 (d, $J = 8.9$ Hz, 2 H), 7.91 (d, $J = 8.2$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 67.6, 68.6, 68.7, 70.0, 71.9, 72.9, 73.4, 74.32 (d, $J = 6.2$ Hz), 74.38, 74.46, 74.63, 74.69, 74.76, 74.80, 75.2, 75.6, 76.6, 77.7, 81.3 (d, $J = 21.7$ Hz), 82.3, 83.2 (d, $J = 11.4$ Hz), 84.5, 101.0 (C-1′ or 1″), 103.9 (C-1″ or 1′), 109.7 (d, $J = 216.2$ Hz, C-1), 127.47, 127.54, 127.60, 127.65, 127.70, 127.77, 127.82, 127.87, 128.11, 128.20, 128.28, 128.31, 128.41, 128.43, 128.86, 129.21, 129.75, 129.85, 133.1, 133.2, 133.4, 137.8, 138.2, 138.29, 138.32, 138.6, 165.0, 165.4, 165.8; HRMS: m/z calcd for $C_{88}H_{85}FO_{18}\cdot NH_4$ $[M + NH_4]^+$ 1466.6064, found 1466.6072.

6-*O*-[2′,3′,6′-Tri-*O*-benzoyl-4′-*O*-(2″,3″,4″,6″-tetra-*O*-benzyl-α(and/or β)-D-glucopyranosyl)-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl methoxide (25): To a stirred suspension of MS 5A (176 mg), **1α** (68.7 mg, 0.076 mmol) and **17** (50.0 mg, 0.059 mmol) in CH_2Cl_2 (2.0 mL) was added a toluene solution (ca. 0.1 mL) of TfOH (1.14 mg, 7.6 μmol) at −78 °C. The reaction mixture was stirred for 2.5 h, during which the reaction temperature was raised gradually up to −30 °C. After **1α** was completely consumed, **2** (38.1 mg, 0.082 mmol) was added at −30 °C and then the reaction temperature was slowly raised up to 0 °C. Then, this reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ at 0 °C. The mixture was filtered through a pad of celite, and aqueous layer was extracted with CH_2Cl_2 (×3). The combined organic layer was washed with brine and dried over Na_2SO_4. After filtration and evaporation, the resultant was purified by thin-layer chromatography (hexane/EtOAc = 3/1 and hexane/$CHCl_3$/acetone = 10/10/1) to afford the title compound **25** (78.5 mg, 92%, $\alpha\beta/\beta\beta = 86/14$). The ratios were determined by HPLC analysis (MeOH/H_2O = 20/1).

25αβ: colorless oil; $R_f = 0.35$ (hexane/EtOAc = 2/1); $[\alpha]_D^{18}$ + 23.7 ($c = 0.91$, $CHCl_3$); IR (neat): 1728, 1605, 1497, 1450, 1365, 1265, 1095, 1072, 918, 741, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, major isomer): δ 3.16 (s, 3H), 3.22 (dd, $J = 3.4$, 9.8 Hz, 1 H), 3.32 (t, $J = 9.2$ Hz, 1 H), 3.40 (dd, $J = 3.4$, 9.8 Hz, 1 H), 3.48–3.52 (m, 2 H), 3.57 (dd, $J = 3.4$, 11.0 Hz, 1 H), 3.66 (d, $J = 9.5$ Hz, 2 H), 3.80–3.91 (m, 5 H), 4.08 (d, $J = 8.9$ Hz, 1 H), 4.14 (d, $J = 12.5$ Hz, 1 H), 4.16 (t, $J = 9.2$ Hz, 1 H), 4.25 (d, $J = 11.0$ Hz, 1 H), 4.31 (d, $J = 12.2$ Hz, 1 H), 4.38 (d, $J = 11.0$ Hz, 1 H), 4.46 (d, $J = 11.0$ Hz, 1 H), 4.474 (d, $J = 3.4$ Hz, 1 H, H-1 or 1″), 4.475 (d, $J = 12.2$ Hz, 1 H), 4.56–4.59 (m, 2 H), 4.67 (d, $J = 11.0$ Hz, 1 H), 4.69–4.72 (m, 4 H), 4.75 (d, $J = 11.3$ Hz, 1 H), 4.82 (d, $J = 3.4$ Hz, 1 H, H-1″ or 1), 4.84 (d, $J = 11.0$ Hz, 1 H), 4.87 (d, $J = 11.0$ Hz, 1 H), 5.54 (dd, $J = 7.6$, 9.2 Hz, 1 H), 5.83 (t, $J = 9.2$ Hz, 1 H), 7.02–7.47 (m, 43 H), 7.57 (t, $J = 7.0$ Hz, 1 H), 7.86 (d, $J = 7.3$ Hz, 2 H), 7.97 (d, $J = 7.3$ Hz, 2 H), 8.02 (d, $J = 7.0$ Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$, major isomer): δ 54.9, 63.4, 68.19, 68.23, 69.5, 71.8, 72.0, 72.9, 73.3, 73.5, 73.6, 74.1, 74.7, 74.8, 75.5, 77.5, 79.1, 79.8, 81.4, 81.9, 97.9 (C-1 or 1″), 99.8 (C-1″ or 1), 101.2 (C-1′), 127.44, 127.47, 127.54, 127.58, 127.60, 127.66, 127.70, 127.85, 127.88, 127.90, 127.95, 128.07, 128.26, 128.30, 128.38, 128.40, 129.27, 129.72, 129.76, 129.81, 129.87, 129.96, 132.97, 133.01, 133.05, 137.83, 138.11, 138.16, 138.31, 138.68, 138.81, 165.2, 165.6, 165.9; HRMS: m/z calcd for $C_{89}H_{88}O_{19}\cdot NH_4$ $[M + NH_4]^+$ 1478.6264, found 1478.6304.

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