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A highly stereoselective construction of 1,2-*trans*-β-glycosidic linkages capitalizing on 2-azido-2-deoxy-D-glycosyl diphenyl phosphates as glycosyl donors

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Abstract—The scope of TMSOTf-promoted glycosidation of 2-azido-2-deoxyglycopyranosyl diphenyl phosphates is investigated. The 3,4,6-tri-*O*-benzyl-protected glucosyl and galactosyl donors and the 4,6-*O*-benzylidene-protected galactosyl donor each react with a range of acceptor alcohols in the presence of a stoichiometric amount of TMSOTf in propionitrile at −78 °C to afford 1,2-*trans*-β-linked disaccharides in high yields with α:β ratios ranging from 9:91 to 1:>99, regardless of the anomeric composition of the donor used. The use of propionitrile as a solvent at −78 °C has proven to be among the best choice for the highest levels of β-selectivity reported to date for this type of glycosidation. A plausible reaction mechanism, which features a large equilibrium preference for α-glycosyl-nitrilium ions over β-nitrilium ions, is proposed based on byproducts formed through their intermediacy and accounts for the observed excellent β-selectivities.

1. Introduction

The rapidly growing significance of glycosides and oligosaccharides as constituents of biologically important compounds such as antitumor antibiotics and glycoconjugates has mandated the rational design and development of stereocontrolled glycosidation reactions.[1] Since 2-acetamido-2-deoxy-D-glycopyranosides, mainly found in β-glycosidic linkage, are ubiquitous building blocks of glycolipids, glycoproteins, proteoglycans and peptidoglycans, numerous procedures for synthesizing 1,2-*trans*-β-linked 2-acetamido-2-deoxy-D-glycosides have been reported.[2] In terms of efficiency and practicality, direct glycosidation using 2-acetamido-2-deoxyglycosyl donors should constitute an ideal procedure for the stereocontrolled construction of these linkages. In practice, however, the reactions of these donors generally lead to the predominant formation of oxazoline derivatives via a neighboring group participation and subsequent elimination of an amide proton. Although oxazolines can react with acceptor alcohols in the presence of Brϕnsted or Lewis acids to afford 1,2-*trans*-glycosides with the natural 2-acetamido group (i.e. oxazoline method), the harsh reaction conditions for this conversion have precluded its wide application for synthesizing complex oligosaccharides.[3]

To overcome this problem, Lemieux and co-workers introduced the use of 2-deoxy-2-phthalimidoglycosyl donors as a reliable method for synthesizing 2-acetamido-2-deoxy-β-glycosides.[4] The phthalimido method generally gives high yields and virtually complete β-selectivity with most glycosyl acceptors as demonstrated with numerous complex oligosaccharide syntheses. However, removing the phthaloyl group requires basic conditions at elevated temperatures, which often cause the product to partially decompose. Therefore, a variety of different 2-amino protecting groups with an anchimeric assistance such as *N*-2,2,2-trichloroethoxycarbonyl (Troc),[5a–c] *N*-allyloxycarbonyl (Alloc),[5c] *N*-benzyloxycarbonyl (Cbz),[5c] *N*-trichloroacetyl (TCA),[5d] *N*-tetrachlorophthaloyl (TCP),[5e–g] *N*-dithiasuccinoyl (Dts),[5h,i] *N*,*N*-diacetyl,[5j] *N*-4,5-dichlorophthaloyl (DCPhth),[5k] *N*-dimethylmaleoyl (DMM),[5l] *N*,*N*-dibenzyl,[5m] and *N*-thiodiglycoloyl (TDG)[5n] have been investigated.

An alternative approach to 2-acetamido-2-deoxy-β-glycopyranosides involves using 2-azido-2-deoxyglycopyranosyl donors. Although the azido group as a latent amino functionality is incapable of neighboring group participation, modest to high levels of β-selectivity were observed with 2-azido-2-deoxyglycosyl trichloroacetimidates,[6–8] *S*-xanthates,[9] isopropenyl carbonate,[10] 2-pyridinecarboxylates,[11]

Keywords: 2-Azido-2-deoxyglycopyranosyl diphenyl phosphate; β-Selective glycosidation; α-Nitrilium ion.
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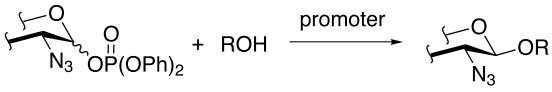
dibutyl phosphates,[12] and phenylthio glycosides.[13] Of these, glycosidation of 2-azido-2-deoxyglycosyl trichloroacetimidates in the presence of $BF_3 \cdot OEt_2$ in CH_2Cl_2–hexane[7] or in the presence of TMSOTf in acetonitrile[8] is the method of choice for a highly stereoselective construction of 2-azido-2-deoxy-β-glycosides.[14]

We recently developed glycosyl donors that incorporate various phosphorus-containing leaving groups. The glycosidations constitute mild and efficient methods for the highly stereocontrolled construction of 1,2-*trans*-β- and 1,2-*cis*-α-glycosidic linkages with or without a participating group at C2.[15] The exceptionally high levels of β-selectivity observed with 2,3,4,6-tetra-*O*-benzyl-protected glycosyl diphenyl phosphates,[15a] *N*,*N*,*N*′,*N*′-tetramethylphosphorodiamidates,[15d] and diethyl phosphites[15e] suggested that these leaving groups would also be promising candidates for constructing 2-azido-2-deoxy-β-glycosidic linkages. In this article, the scope, limitations, and mechanism of TMSOTf-promoted glycosidation of 2-azido-2-deoxyglycosyl diphenyl phosphates (Eq. (1)) are documented.[16] In addition, a comparative study with TMSOTf-promoted glycosidation of 2-azido-2-deoxyglycosyl trichloroacetimidates is described.



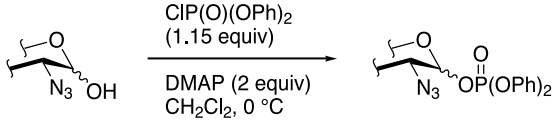
(1)

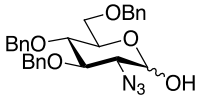
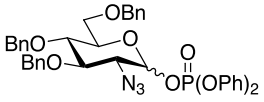
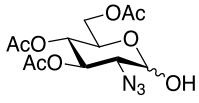
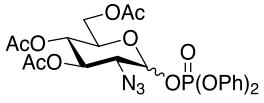
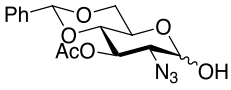
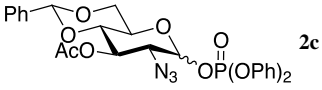
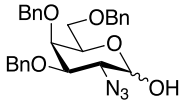
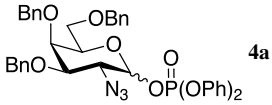
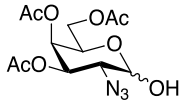
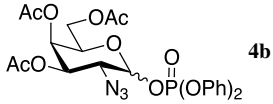
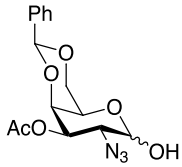
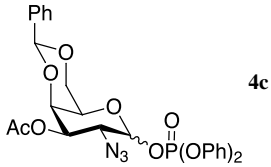
2. Results and discussion

2.1. Preparation of 2-azido-2-deoxy-D-glycosyl donors

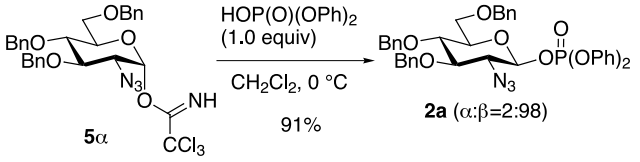
2-Azido-2-deoxy-D-glycosyl donors were prepared according to the standard procedures used for 2,3,4,6-tetra-*O*-benzyl-protected glycosyl donors. Application of Sabesan's phosphorylation method[17] [$ClP(O)(OPh)_2$, DMAP, CH_2Cl_2, 0 °C] to the corresponding glycopyranoses **1a–c** and **3a–c** afforded 2-azido-2-deoxyglycosyl diphenyl phosphates **2a–c** and **4a–c** in good to high yields (Table 1). Diphenyl phosphate **2a** with α:β ratio of 2:98 was obtained by coupling 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucosyl trichloroacetimidate (**5**α)[7b] with diphenyl phosphoric acid in CH_2Cl_2 at 0 °C (Eq. (2)).[18]

Table 1. Preparation of 2-azido-2-deoxyglycosyl diphenyl phosphates



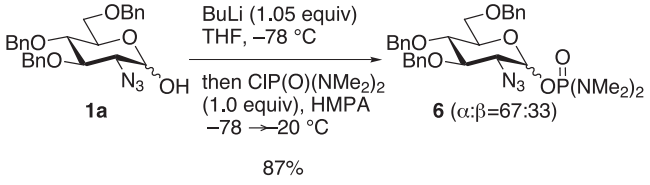
Entry	Glycopyranose	Phosphate	Yield %	α:β[a]
1	 **1a** (α:β=56:44)	 **2a**	97	72:28
2	 **1b** (α:β=61:39)	 **2b**	99	46:54
3	 **1c** (α:β=52:48)	 **2c**	99	31:69
4	 **3a** (α:β=68:32)	 **4a**	79	58:42
5	 **3b** (α:β=44:56)	 **4b**	97	24:76
6	 **3c** (α:β=63:37)	 **4c**	75	67:33

[a] Determined by 109 MHz ^{31}P NMR using 85% H_3PO_4 as an external standard.



(2)

Tetramethylphosphorodiamidate **6** was prepared by condensing a lithium alkoxide derived from **1a** with bis(dimethylamino)phosphorochloridate in THF-HMPA (Eq. (3)).[15d] On the other hand, 2-azido-2-deoxyglucosyl



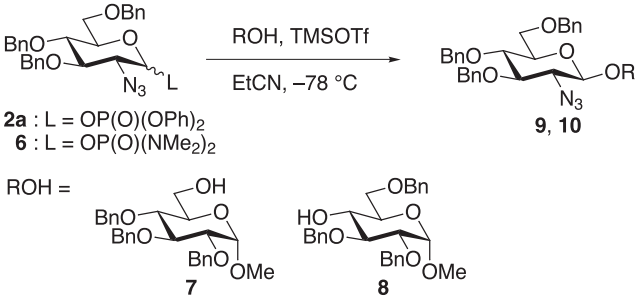
(3)

diethyl phosphite was inaccessible since it decomposed upon concentration in vacuo, although the reaction of **1a** with diethyl chlorophosphite and triethylamine proceeded in CH_2Cl_2 at 0 °C. The obtained 2-azido-2-deoxyglycosyl donors were purified by silica gel column chromatography, and stored without decomposition in the freezer (at −30 °C) for several months.

2.2. Reaction optimization

At the outset of this study, glycosidations of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucosyl diphenyl phosphate **2a** (α:β=72:28 or 2:98) and *N*,*N*,*N*′,*N*′-tetramethylphosphorodiamidate **6** (α:β=67:33) were explored with *O*-6- or *O*-4-unprotected glycosides **7** or **8** (1.1 equiv each) as highly reactive and less reactive acceptor alcohols, respectively (Table 2). The addition of a 1.0 M solution of TMSOTf (1.5 equiv) in CH_2Cl_2 to a cooled solution (−78 °C) of the donor and acceptor in propionitrile afforded a disaccharide and the α:β ratio was assayed by HPLC (Zorbax® Sil column). As expected from previous work,[15a] TMSOTf-promoted glycosidations of the diphenyl phosphate **2a** with **7** or **8** in propionitrile at −78 °C proceeded smoothly to give disaccharides **9** and **10** in high yields with excellent β-selectivities, regardless of the anomeric composition of the donor (entries 1–4) (Fig. 1). The reactions of phosphorodiamidate **6** under the same conditions exhibited virtually the same β-selectivities as those found with **2a** (entries 5 and 6), although longer reaction times were required. In either case, the reaction did not go to completion when a substoichiometric amount of TMSOTf was used. Upon further examining these reactions, we were somewhat surprised to find a small amount (5–7%) of the hydrolysis-prone α-imidate **11**, which has an R_f value comparable to disaccharide **9**, was produced as a byproduct when alcohol **7** was used as an acceptor (entries 1, 2 and 5). It must be mentioned that imidate byproducts such as **11** are formed regardless of the nature of 2-azido-2-deoxyglycosyl donors whenever the reactions with highly reactive *O*-6-unprotected glycoside alcohols are conducted in propionitrile (vide infra). Fortunately, their formation did not prevent the isolation of products since the imidates were

Table 2. TMSOTf-Promoted glycosidation of 2-azido-2-deoxyglycosyl donors **2a**[a] and **6**[b]



Entry	Donor		ROH	Time, h	Glycoside		
		α:β[c]				Yield, %	α:β[d]
1	**2a**	72:28	**7**	1.5	**9**	84[e]	1:99
2	**2a**	2:98	**7**	1.5	**9**	85[e]	1:99
3	**2a**	72:28	**8**	2	**10**	90	6:94
4	**2a**	2:98	**8**	2	**10**	92	7:93
5	**6**	67:33	**7**	2.5	**9**	81[e]	2:98
6	**6**	67:33	**8**	3	**10**	85	7:93

[a] Donor **2a**/ROH/TMSOTf molar ratio=1.0/1.1/1.5.
[b] Donor **6**/ROH/TMSOTf molar ratio=1.0/1.1/1.8.
[c] Determined by 109 MHz ^{31}P NMR using 85% H_3PO_4 as an external standard.
[d] The ratio was determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 13 or 17% AcOEt in hexane; flow rate 1.0 mL/min).
[e] α-Imidate **11** was obtained in 5–7% yield.

easily hydrolyzed upon an acidic aqueous work-up. The ^1H NOE between H1′ and CH_2 of ethyl group established the *anti* stereochemistry of **11**. In contrast, such a byproduct was not detected when less reactive alcohol **8** was used. While the phosphorodiamidate **6** has a greater shelf-stability than the diphenyl phosphate **2a**, we selected the phosphate method due to the ease in preparing this type of donor.

Examining solvents other than propionitrile for the reaction of diphenyl phosphate **2a** (α:β=72:28) with *O*-6-unprotected glycoside **7** showed that similar high levels of β-selectivity could be achieved in CH_2Cl_2 and toluene (Table 3, entries 1–5). A further solvent survey with *O*-4-unprotected glycoside **8** revealed that propionitrile was optimal for this glycosidation and has a beneficial effect on the stereoselectivity as well as the reaction rate (entries 6–8). Consistent with the proposal by Schmidt,[8] an

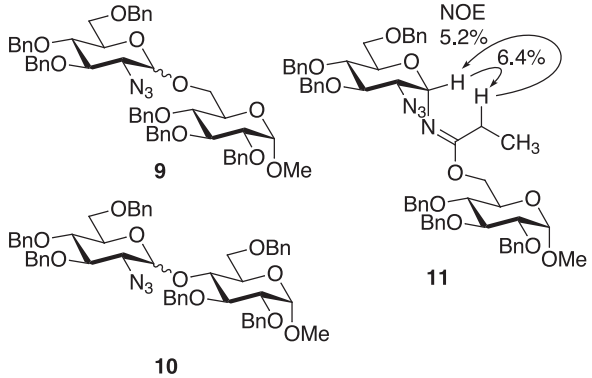
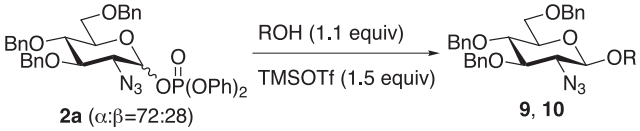


Figure 1. Products of glycosidation reactions of diphenyl phosphate **2a** with **7** and **8**.

Table 3. Effect of solvent in TMSOTf-promoted glycosidation of 2-azido-2-deoxyglycosyl diphenyl phosphate **2a**



2a (α:β=72:28) **9**, **10**

Entry	ROH	Solvent	Temp.[a] °C	Time, h	Glycoside		
						Yield, %	α:β[b]
1	**7**	EtCN	−78	1.5	**9**	84	1:99
2	**7**	CH_2Cl_2	−78	4	**9**	88	1:99
3	**7**	Toluene	−65	2	**9**	90	4:96
4	**7**	EtOAc	−65	2	**9**	89	11:89
5	**7**	Et_2O	−30	1	**9**	88	38:62
6	**8**	EtCN	−78	2	**10**	90	6:94
7	**8**	CH_2Cl_2	−78	8	**10**	84	10:90
8	**8**	Toluene	−65	8	**10**	81	24:76

[a] Temperature limit for smooth reaction.
[b] The ratio was determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 13% or 17% AcOEt in hexane; flow rate 1.0 mL/min).

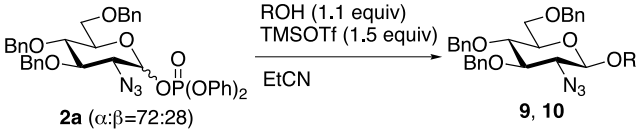
exceptionally high order of β-selectivity in propionitrile can be explained by the intermediacy of 2-azido-2-deoxy-α-D-glucosyl-nitrilium ion associated with triflate as a counter-ion (vide infra).

As expected the temperature profile of the glycosidation in propionitrile revealed a descending β-selectivity with ascending temperature (Table 4). The temperature effect was more pronounced with less reactive alcohol **8** (entries 4 vs 5) than with **7**.

2.3. Glycosidations of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxyglycosyl diphenyl phosphates 2a and 4a

With the optimal reaction conditions determined, glycosidations of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy glycosyl diphenyl phosphates **2a** (α:β=72:28) and **4a** (α:β=58:42) in the D-gluco and D-galacto series were explored with a range of suitably protected glycoside alcohols (Fig. 2). The results are compiled in Tables 5 and 6. In all cases,

Table 4. Temperature profile of TMSOTf-promoted glycosidation of 2-azido-2-deoxyglycosyl diphenyl phosphate **2a**



2a (α:β=72:28) **9**, **10**

Entry	ROH	Temp, °C	Time, h	Glycoside		
					Yield, %	α:β[a]
1	**7**	−78	1.5	**9**	84	1:99
2	**7**	−45	0.5	**9**	89	3:97
3	**7**	−10	0.1	**9**	92	8:92
4	**8**	−78	2	**10**	90	6:94
5	**8**	−45	0.5	**10**	88	13:87

[a] The ratio was determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 13% or 17% AcOEt in hexane; flow rate 1.0 mL/min).

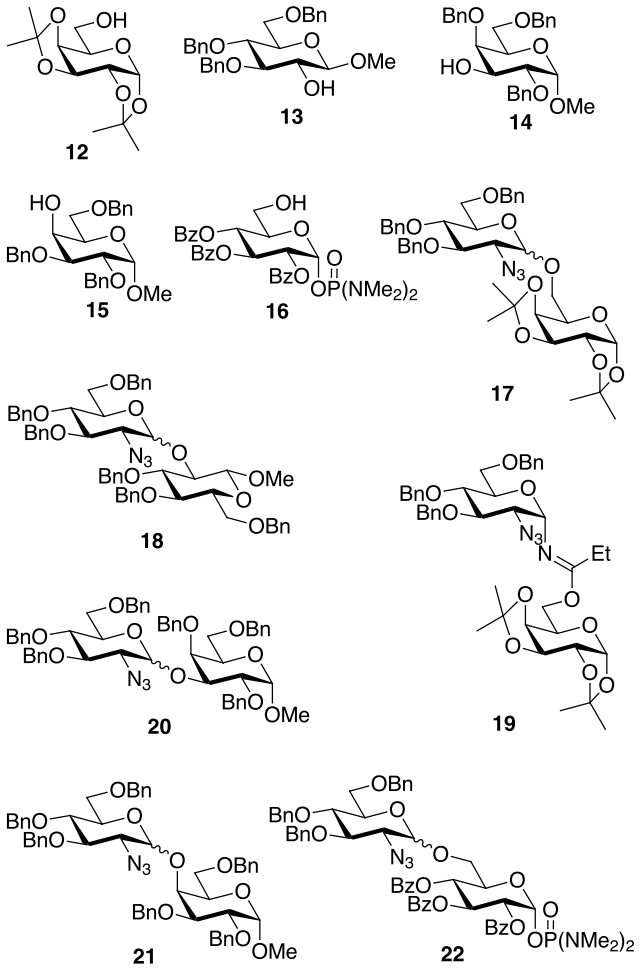
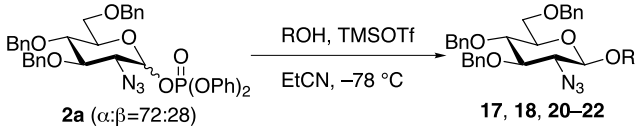


Figure 2. Acceptor alcohols and products in Table 5.

TMSOTf-promoted glycosidations in propionitrile at −78 °C offered a facile and high-yielding entry to 1,2-*trans*-β-linked disaccharides, wherein the α:β ratios ranged from 9:91 to 1:>99.

Table 5. TMSOTf-promoted glycosidation of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxyglucosyl diphenyl phosphate **2a** with acceptor alcohols[a,b]

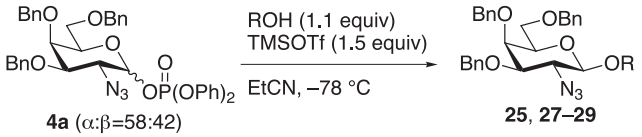


2a (α:β=72:28) **17**, **18**, **20–22**

Entry	ROH	Time, h	Glycoside		
				Yield, %	α:β[c]
1	**12**	1.5	**17**	79[d]	2:98
2	**13**	2	**18**	91	9:91
3	**14**	2	**20**	89	1:>99
4	**15**	2	**21**	90	5:95
5[e]	**16**	2	**22**	88	7:93[f]

[a] The reaction was carried out on 0.1 mmol scale.
[b] Donor **2a**/ROH/TMSOTf molar ratio=1.0/1.1/1.5 unless otherwise noted.
[c] The ratio was determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 17∼20% AcOEt in hexane or 14% THF in hexane; flow rate 1.0 mL/min), unless otherwise stated.
[d] α-Imidate **19** was obtained in 9% yield.
[e] The reaction was performed with 2.0 equiv of TMSOTf.
[f] Determined by 500 MHz ^{1}H NMR.

Table 6. TMSOTf-promoted glycosidation of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxygalactosyl diphenyl phosphate **4a** with acceptor alcohols[a]



4a (α:β=58:42) **25**, **27–29**

Entry	ROH	Time, h	Glycoside		
				Yield, %	α:β[b]
1	**7**	0.2	**25**	86[c]	4:96
2	**8**	0.5	**27**	90	4:96
3	**23**	0.3	**28**	81	6:94
4	**24**	0.5	**29**	86	8:92

[a] The reaction was carried out on 0.1 mmol scale.
[b] The ratio was determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 17% AcOEt in hexane or 17% THF in hexane; flow rate 1.0 mL/min).
[c] Propionate **26** was obtained in 5% yield.

Seeberger and co-workers reported that TMSOTf-promoted coupling of 2-azido-2-deoxyglucosyl dibutyl phosphate with glycoside alcohols **12** or **13** in acetonitrile at −40 °C produced disaccharides **17** and **18** in modest yields with α:β ratios of 1:5 and 1:4, respectively.[12] Clearly, the present method is superior to the dibutyl phosphate method in terms of product yield and stereoselectivity (Table 5, entries 1 and 2). Here again, a small amount (9%) of α-imidate byproduct **19** was detected when *O*-6-unprotected glycoside **12** was used. It is also noteworthy that glycosylation of *O*-3-unprotected galactose derivative **14** exclusively formed disaccharide **20**β, which corresponds to GlcNAcβ1→3Gal, a constituent of biologically important gangliosides such as sialyl Lewis^x (entry 3). Since the fully benzoylated glucosyl tetramethylphosphorodiamidate is unaffected at temperatures below −5 °C by these reaction conditions,[19] chemoselective glycosidation was uneventfully realized using *O*-6-unprotected glucosyl phosphorodiamidate **16** as a disarmed acceptor (entry 5). It is interesting to note that 2-azido-2-deoxygalactosyl diphenyl phosphate **4a** is even more reactive than the corresponding glucosyl donor **2a**, as manifested by much shorter reaction times (Table 6). When alcohols **7** and **8** were used, donor **4a** displayed somewhat lower and higher β-selectivities, respectively, than donor **2a**. In the former reaction, 5% of *O*-6-propionyl-protected glycoside **26**, due to the hydrolysis of the imidate byproduct (not shown), was obtained. The effectiveness of the present method was also demonstrated by synthesizing LacdiNAc equivalent **29**, which was achieved by glycosylation of *O*-4-unprotected glucosamine derivative **24** in 86% yield with an α:β ratio of 8:92 (entry 4) (Fig. 3).

2.4. Glycosidations of 3,4,6-tri-*O*-acetyl-2-azido-2-deoxyglycosyl diphenyl phosphates 2b and 4b

While 2-azido-3,4,6-tri-*O*-benzyl-2-deoxyglycosyl donors **2a** and **4a** performed well, attempts to employ 3,4,6-tri-*O*-acetyl-protected glycosyl donors **2b** and **4b** met with less success. 2-Azido-2-deoxyglucosyl diphenyl phosphate **2b** was activated by TMSOTf at −65 °C in propionitrile, but the reaction with alcohol **7** predominantly formed imidates **30** with an α:β ratio of 85:15 (Table 7, entry 1). Although some of the β-imidate partially decomposed during column

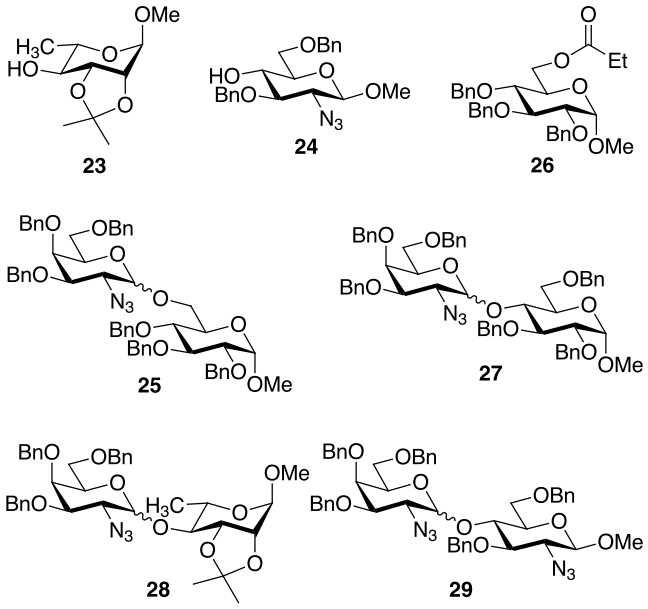
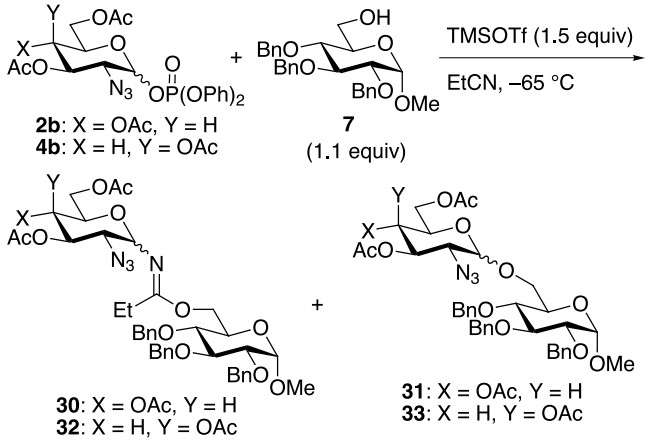


Figure 3. Acceptor alcohols and products in Table 6.

chromatography on silica gel, α-imidate **30**α was safely isolated in 79% yield. In this reaction, the corresponding disaccharide **31** with an α:β ratio of 14:86 was obtained in only 4% yield. Likewise, the reaction of 2-azido-2-deoxygalactosyl diphenyl phosphate **4b** with **7** afforded imidate **32** (α:β=88:12) as a major product, along with 9%

Table 7. TMSOTf-promoted glycosidation of 3,4,6-tri-*O*-acetyl-2-azido-2-deoxyglycosyl diphenyl phosphates **2b** and **4b** with alcohol **7**[a,b]



Entry	Donor	Time, h	Imidate		Glycoside		
				α:β[c]		Yield, %	α:β[c]
1	**2b**	4	**30**[d]	85:15	**31**	4	14:86
2	**4b**	3	**32**[e]	88:12	**33**	9	3:97

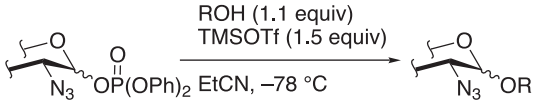
[a] The reaction was carried out on 0.1 mmol scale.
[b] The anomeric α:β ratio of the phosphates: **2b**, 46:54; **4b**, 24:76.
[c] The ratio was determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 29% AcOEt–THF (1:1) in hexane or 20% THF in hexane; flow rate 1.0 mL/min).
[d] Only α-imidate **30**α could be isolated in 79% yield after chromatographic separation.
[e] Only α-imidate **32**α could be isolated in 68% yield after chromatographic separation.

of disaccharide **33** (α:β=3:97), wherein the α-imidate **32α** was isolated in 68% yield (entry 2). These disappointing results are attributed to the electron-withdrawing effect of the ester functionality, which deactivates the anomeric reactivity of nitrilium ion intermediates and favors a nucleophilic attack by alcohol **7** on a nitrilium carbon leading to imidates **30** and **32** (vide infra). Although the fully acyl-protected 2-azido-2-deoxyglycosyl donors are not suitable for the present coupling reaction, other donors with partially acyl protection should not be excluded (vide infra).

2.5. Glycosidations of 2-azido-4,6-*O*-benzylidene-2-deoxyglycosyl diphenyl phosphates 2c and 4c

It is well documented that 4,6-*O*-benzylidene-protected glycosyl donors exhibit reduced reactivities[20] and different stereoselectivities[21] compared to the fully benzylated ones. Therefore, we were driven to investigate glycosidations of 2-azido-4,6-*O*-benzylidene-2-deoxyglycosyl diphenyl phosphates. 2-Azido-2-deoxyglucosyl donor **2c** was activated with TMSOTf at −45 °C in propionitrile, but the reaction with **7** gave disaccharide **35** in only 6% yield with an α:β ratio of 8:92 and considerable amounts of imidates **36** (α:β=91:9); the α-imidate **36α** was isolated in 84% yield (Table 8, entry 1). In stark contrast, 2-azido-2-deoxygalactosyl diphenyl phosphate **4c** underwent a smooth coupling with a range of alcohols even at −78 °C to provide disaccharides **37**, **39**, **40** in good yields with excellent β-selectivities (entries 2–4), although a small amount (10%) of α-imidate **38** was produced as a byproduct of the reaction with **7**. It is noteworthy that glycosylation of diol **34** produced 1,2-*trans*-β-linked disaccharide **40** with essentially perfect regioselectivity and excellent stereoselectivity (α:β=1:99 and 2:98) (entries 4 and 5).[22] The difference in reaction mode between these donors may be explained by considering that 2-azido-2-deoxyglucosyl donor **2c** is a *trans*-fused bicyclic compound whereas 2-azido-2-deoxygalactosyl donor **4c** has a relatively flexible, *cis*-decaline-like architecture (Fig. 4). The greater conformational rigidity of **2c** relative to **4c** would serve to torsionally disarm the nitrilium ion intermediate with respect to formation of the *O*-glycosidic linkage.[20,23]

Table 8. TMSOTf-promoted glycosidation of 2-azido-4,6-*O*-benzylidene-2-deoxyglycosyl diphenyl phosphates **2c** and **4c** with acceptor alcohols[a]



2c, **4c** → **35**, **37**, **39**, **40**

Entry	Donor	ROH	Time, h	Glycoside		
					Yield, %	α:β[b]
1[c]	**2c**[d]	**7**	4	**35**	6[e]	8:92
2	**4c**[f]	**7**	3	**37**	78[g]	3:97
3	**4c**[f]	**8**	3	**39**	90	4:96
4	**4c**[f]	**34**	2	**40**	80	1:99
5	**4c**[h]	**34**	2	**40**	82	2:98

[a] The reaction was carried out on 0.1 mmol scale.
[b] The ratio was determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 20 or 60% AcOEt in hexane; flow rate 1.0 mL/min).
[c] The reaction was carried out at −45 °C.
[d] α:β=31:69.
[e] α-Imidate **36α** was obtained in 84% yield.
[f] α:β=95:5.
[g] α-Imidate **38** was obtained in 10% yield.
[h] α:β=0:100.

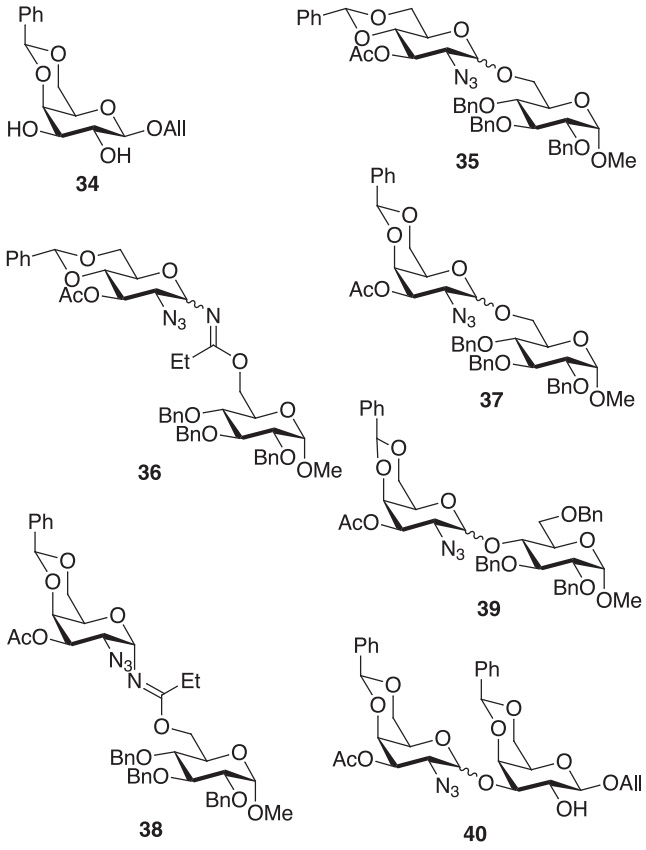
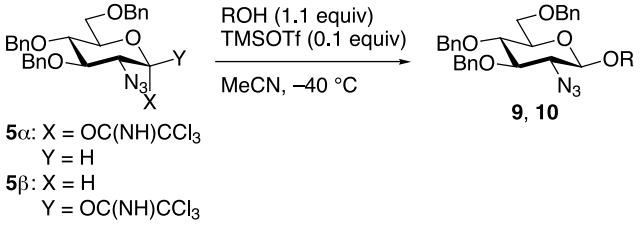


Figure 4. Acceptor alcohols and products in Table 8.

2.6. Comparative study

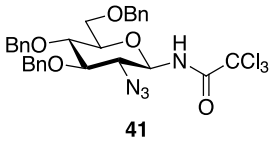
While high yields and excellent β-selectivities were achieved in the reactions of glycosyl diphenyl phosphates **2a**, **4a**, and **4c** with a range of acceptor alcohols, limitations of the phosphate method were recognized with donors **2b**, **2c**, and **4b**. To verify the effectiveness of the phosphate method, the scope of TMSOTf-promoted glycosidations of the corresponding trichloroacetimidates was examined. Although the exceptional power of the trichloroacetimidate method developed by Schmidt has been well demonstrated in numerous aminosugar-containing oligosaccharide syntheses,[24] a systematic investigation has yet to be described. The glycosidations were performed under frequently used conditions [cat. TMSOTf, acetonitrile, −40 °C].[8,22,24] Table 9 summarizes the results. TMSOTf (0.1 equiv)-catalyzed glycosidations of trichloroacetimidates **5α**[7b] or **5β**[25] with alcohols **7** and **8** proceeded to completion within 20 min, yielding high levels of β-selectivity similar to those of **2a** in propionitrile at −45 °C (entries 1 and 2 vs entry 2 in Table 4, and entries 3 and 4 vs entry 5 in Table 4). The stereochemical outcome observed was independent of the anomeric configuration of the donor similar to the phosphates. Somewhat surprisingly, evidence of the formation of imidate byproduct such as **11** could not be detected when alcohol **7** was used. Instead, a small amount

Table 9. TMSOTf-catalyzed glycosidation of 2-azido-2-deoxyglucosyl trichloroacetimidates **5**α and **5**β with alcohols **7** and **8** in acetonitrile[a]



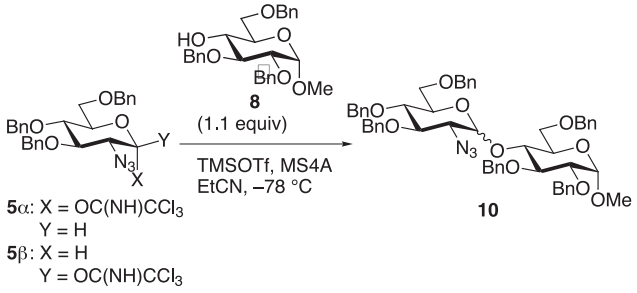
Entry	Donor	ROH	Time, h	Glycoside		
					Yield, %	α:β[b]
1	**5**α	**7**	0.1	**9**	82[c]	3:97
2	**5**β	**7**	0.1	**9**	85	3:97
3	**5**α	**8**	0.3	**10**	50[d]	10:90
4	**5**β	**8**	0.3	**10**	68[e]	11:89
5[f]	**5**α	**8**	0.3	**10**	51[g]	12:88
6[f]	**5**β	**8**	0.3	**10**	84	12:88

[a] The reaction was carried out on 0.1 mmol scale.
[b] The ratio was determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 17% AcOEt in hexane; flow rate 1.0 mL/min).
[c] β-Trichloroacetamide **41** was obtained in 4% yield.
[d] Amide **41** and lactol **1a** were obtained in 28% and 4% yields, respectively.
[e] Amide **41** and lactol **1a** were obtained in 10% and 5% yields, respectively.
[f] In the presence of MS4A.
[g] Amide **41** was obtained in 35% yield.



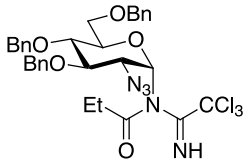
41

Table 10. TMSOTf-promoted glycosidation of 2-azido-2-deoxyglucosyl trichloroacetimidates **5**α and **5**β with alcohol **8** in propionitrile[a]



Entry	Donor	TMSOTf, equiv	Time, h	Glycoside **10**	
				Yield, %	α:β
1	**5**α	0.2	1	15	8:92[b]
2	**5**β	0.2	1	39	8:92[b]
3	**5**α	1.5	0.3	54[c]	7:93[d]
4	**5**β	1.5	0.3	85	9:91[d]

[a] The reaction was carried out on 0.1 mmol scale.
[b] Determined by 500 MHz ^{1}H NMR.
[c] Amidine **42** was obtained in 20% yield.
[d] Determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 17% AcOEt in hexane; flow rate 1.0 mL/min).



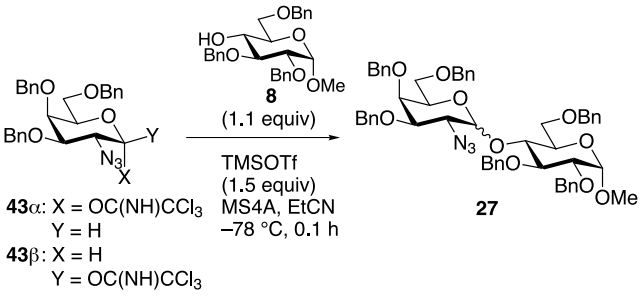
42

(4%) of β-trichloroacetamide **41** was obtained as a byproduct of the reaction of **5**α with **7** (entry 1), whereas **41** was not formed from **5**β (entry 2).[26] A moderate product yield in the reaction of **5**α with less reactive alcohol **8** was due to the formation of β-trichloroacetamide **41** (28%) and lactol **1a** (4%) (entry 3). The yield of byproduct **41** decreased to 10% with **5**β, thereby allowing a higher product yield (entry 4). A significant improvement in product yield (68→84%) was achieved when the reaction of **5**β with **8** was carried out in the presence of MS4A, whereas the beneficial effect was not observed with **5**α (entries 5 and 6). Although discrepancies between the behavior of α- and β-glycosyl trichloroacetimidates were observed in some cases,[27] the reason is currently unclear.

Next, glycosidation of trichloroacetimidates **5**α or **5**β with alcohol **8** in propionitrile at −78 °C were explored in order to determine whether the β-selectivity (α:β=12:88–10:90) observed in acetonitrile at −40 °C could be enhanced to the ratio (α:β=6:94) achieved with the phosphate method. Although the goal in terms of stereoselectivity could be virtually achieved using 0.2 equiv of TMSOTf, product yields were not preparatively useful (Table 10, entries 1 and 2). When using 1.5 equiv of TMSOTf, product yields from **5**α and **5**β were improved to 54 and 85%, respectively, without affecting the stereoselectivity (entries 3 and 4). α-Amidine byproduct **42** was obtained in 20% yield when **5**α was used, but β-trichloroacetamide **41** was not formed from either **5**α or **5**β. It is noteworthy that the formation of an amidine byproduct has not been reported in glycosidation reactions using trichloroacetimidates as glycosyl donors. It is also interesting that the reaction of **5**α with **8** in acetonitrile at −40 °C gave β-trichloroacetamide **41** as a major byproduct, whereas the same reaction in propionitrile at −78 °C afforded α-amidine **42** as a major one, but the reason is unclear. These results again demonstrated the superiority of donor **5**β over **5**α. From the results with **4a**, 2-azido-2-deoxygalactosyl trichloroacetimidates **43**α[7a] and **43**β[28] are anticipated to have greater reactivities than the corresponding glucosyl donors **5**α and **5**β. Indeed, the reactions with alcohol **8** in propionitrile at −78 °C in the presence of 1.5 equiv of TMSOTf proceeded to completion within 5 min (Table 11). Although virtually the same β-selectivities as those observed with phosphate **4a** were achieved, the product yields (48% from **43**α and 66% from **43**β) were unsatisfactory (Table 11 vs entry 2 in Table 6), due to the inevitable formation of β-trichloroacetamide **44** (37% from **43**α and 7% from **43**β) and α-amidine **45** (7% from **43**α and 7% from **43**β).

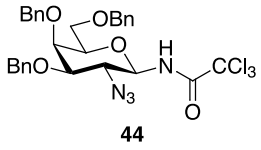
Two key findings emerged from this comparative study. (1) 2-Azido-2-deoxyglycosyl trichloroacetimidates generally exhibit higher reactivities than the corresponding diphenyl phosphates. (2) Only using β-imidates gives coupling products in good to high yields and with exceptionally

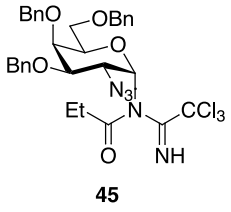
Table 11. TMSOTf-promoted glycosidation of 2-azido-2-deoxygalactosyl trichloroacetimidates **43**α and **43**β with alcohol **8** in propionitrile[a]



Entry	Donor	Glycoside **27**		**44**	**45**
		Yield, %	α:β[b]	Yield, %	Yield, %
1	**43**α	48	4:96	37	7
2	**43**β	66	4:96	7	7

[a] The reaction was carried out on 0.1 mmol scale.
[b] The ratio was determined by HPLC (column, Zorbax® Sil, 4.6×250 mm; eluent, 17% AcOEt in hexane; flow rate 1.0 mL/min).

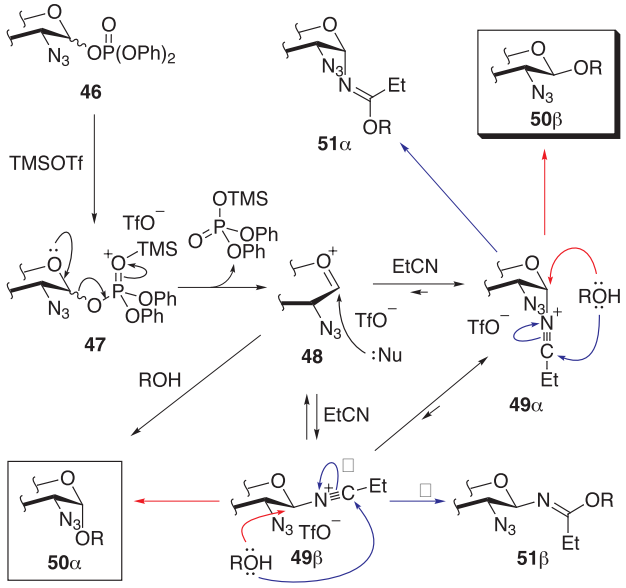




high levels of β-selectivity comparable to those found with an anomeric mixture of diphenyl phosphates, when the reactions are conducted in the presence of 1.5 equiv of TMSOTf in propionitrile at −78 °C.[29]

2.7. Mechanistic considerations

The beneficial effect of nitrile as a solvent on 1,2-*trans*-β-glycosidations without neighboring participation observed by Noyori and co-workers in 1984[30] is now a well-appreciated phenomenon in carbohydrate chemistry. In 1990 Fraser-Reid[31] and Schmidt[8] separately proposed that the β-selectivity could be given by an S_N2-like displacement at the anomeric carbon of kinetically formed α-nitrilium ion, which has been widely accepted.[32] It is evident that the so-called 'nitrile effect' plays a pivotal role in the TMSOTf-promoted glycosidations with 2-azido-2-deoxyglycosyl diphenyl phosphates since propionitrile at −78 °C is an excellent solvent for high levels of β-selectivity.[33] Scheme 1 outlines the possible reaction pathways. Diphenyl phosphate **46** is activated by silylation on the phosphoryl oxygen atom to cleave off the phosphate group, producing oxocarbenium ion **48** as a common intermediate. Intermediate **48** is rapidly trapped by propionitrile to form an anomeric mixture of nitrilium ions **49**α and **49**β associated with triflate as a counterion. In this step, the α-nitrilium ion **49**α preferentially forms over **49**β because of the stereoelectronically favored axial attack of propionitrile from the α-face.[34] In addition, **49**α benefits from anomeric stabilization.[35] On the kinetic and thermodynamic grounds, the equilibrium between these nitrilium ions would heavily lie to **49**α. The S_N2-like displacement by acceptor alcohols at the anomeric carbon of **49**α and **49**β affords glycosides **50**β and **50**α,

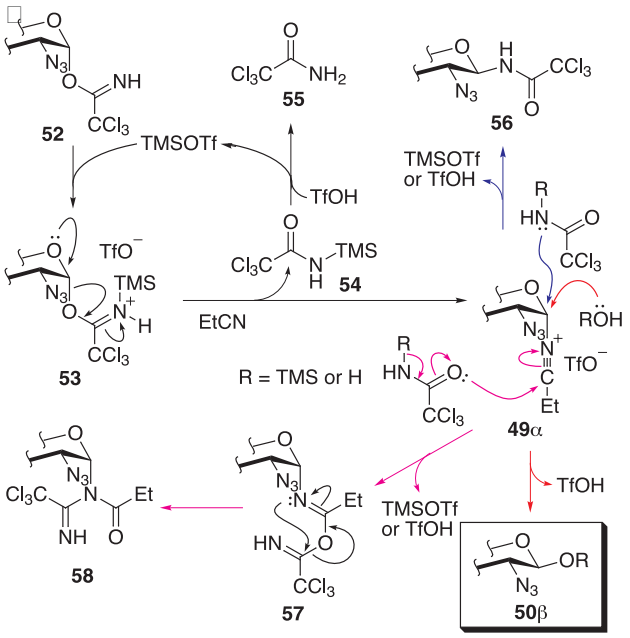


Scheme 1. A mechanistic rationale for TMSOTf-promoted glycosidation of 2-azido-2deoxyglycosyl diphenyl phosphates.

respectively, whereas capture of **49**α and **49**β by alcohols at the nitrilium carbon leads to the formation of imidate byproducts **51**α and **51**β, respectively. The chemoselectivity depends on the anomeric reactivity of glycosyl-nitrilium ions **49** influenced by the choice of protecting groups on 2-azido-2-deoxy-sugar components as well as the reactivity of acceptor alcohols, as is demonstrated by the foregoing experimental results. The exclusive formation of disaccharides was realized when the 3,4,6-tri-*O*-benzyl-protected glucosyl and galactosyl donors **2a** and **4a**, and the 4,6-*O*-benzylidene-protected galactosyl donor **4c** were used, although a small amount of imidates was produced as byproducts in the reaction with highly reactive *O*-6-unprotected glycoside alcohols. Hence, the high levels of β-selectivity observed here are attributed to a large equilibrium preference for **49**α as well as a high propensity of **49**α for an S_N2-like displacement.[6c] The stereochemical reaction course via a common oxocarbenium ion **48** is consistent with the fact that the stereoselectivities are irrespective of the anomeric configuration of the diphenyl phosphates used. Actually, it was found that glycosidation of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucosyl diphenyl phosphate **2a** ($\alpha:\beta = 2:98$) competes with the anomerization to α-phosphate via an internal return of the departing diphenyl phosphate group under the present reaction conditions. Of prime importance in terms of a mechanism is that only α-imidates **11**, **19**, and **38** were obtained as byproducts (5–10%) in the reaction of **2a** or **4c** with *O*-6-unprotected alcohols. Assuming that the much less stable β-nitrilium ion **49**β would have a reactivity comparable to **49**α toward the imidate formation, these results, along with the ^1H NMR analysis of the crude reaction mixture, which did not detect traces of β-imidates or their hydrolysates, provide evidence that α-nitrilium ion **49**α exclusively forms at least in these reactions. Along with the finding that the proportion of 1,2-*cis*-α-linked disaccharides slightly increased with less reactive alcohols compared to highly reactive ones, it seems likely that their formation would arise from the kinetically favored α-axial attack of alcohols

on the transient, solvent separated oxocarbenium ion **48** rather than the S_N2-like displacement of any **49**β. While the corresponding imidate byproduct could not be detected due to its increased hydrolytic lability for 3,4,6-tri-*O*-benzyl-protected galactosyl donor **4a**, highly efficient glycosidations of **4a** are also assumed to proceed in a similar manner as those of **2a** and **4c**. On the other hand, the behaviors of 3,4,6-tri-*O*-acetyl-protected glycosyl donors **2b** and **4b**, and 4,6-*O*-benzylidene-protected glucosyl donor **2c** are quite different from those of glycosyl donors **2a**, **4a** and **4c** mentioned above. Those reactions with alcohol **7** produced an anomeric mixture of imidates **30** (α:β=85:15), **32** (α:β=88:12), and **36** (α:β=91:9) as main products, along with small amounts of disaccharides **31**, **33**, and **35** with α:β ratios of 14:86, 3:97, and 8:92, respectively. It is interesting to note that the α:β ratios of imidates **30** and **36** in the D-gluco series are opposite to those of the corresponding disaccharides **31** and **35**, respectively. These relationships strongly suggest that glycosidations with electronically or torsionally disarmed 2-azido-2-deoxyglucosyl diphenyl phosphates proceed via an S_N2-like displacement, where the glucosyl-nitrilium ions **49** would be too stable to generate the solvent separated oxocarbenium ion **48**. However, this is not the case with 3,4,6-tri-*O*-acetyl-protected galactosyl diphenyl phosphate **4b** probably because the galactosyl nitrilium ions **49** may exhibit greater anomeric reactivities to allow for a dynamic equilibrium than the glucosyl counterparts.[20c,d]

Since TMSOTf-promoted glycosidations of 2-azido-2-deoxyglycosyl trichloroacetimidates exhibit essentially the same high β-selectivities as those found with diphenyl phosphates under identical conditions, the stereochemical reaction course seems to be analogous to that proposed with the phosphate method in Scheme 1. However, the product yields in the trichloroacetimidate method highly depends on the anomeric configuration of the starting donor and the reactivity of acceptor alcohols. Substantial amounts of β-trichloroacetamides and α-amidines were frequently obtained as byproducts when α-trichloroacetimidates were used as glycosyl donors. Although the striking difference between the behavior of α- and β-trichloroacetimidates currently cannot be explained, the formation of β-trichloroacetamides **56** and α-amidines **58** can be rationalized by the mechanism shown in Scheme 2. In glycosidations with trichloroacetimidates, the departing trichloroacetamide (**55**) and/or its TMS derivative **54** competes as a nucleophile with acceptor alcohols. No such reactions were observed in the phosphate method due to the low nucleophilicity of the diphenyl phosphate. The S_N2-like displacement by the amide nitrogen atom of **54** or **55** at the anomeric carbon of α-nitrilium ion **49**α leads to β-amides **56** with inversion of configuration, whereas the capture of **49**α by the amide oxygen atom of **54** or **55** at the nitrilium carbon followed by rearrangement produces α-amidines **58**. The stereocontrolled formation of β-amides **56** and α-amidines **58** again demonstrates the virtually exclusive intermediacy of α-nitrilium ion **49**α in glycosidations of the 3,4,6-tri-*O*-benzyl-protected glucosyl and galactosyl donors.



Scheme 2. Potential pathways in the TMSOTf-promoted glycosidation of 2-azido-2-deoxyglycosyl trichloroacetimidates.

3. Conclusion

The effectiveness of the diphenyl phosphate group as a leaving group of 2-azido-2-deoxyglycosyl donors has been demonstrated. We found that coupling of the 3,4,6-tri-*O*-benzyl-protected glucosyl and galactosyl donors and the 4,6-*O*-benzylidene-protected galactosyl donor with a range of glycoside alcohols in the presence of 1.5 equiv of TMSOTf in propionitrile at −78 °C proceeds smoothly to give 1,2-*trans*-β-linked disaccharides in high yields with α:β ratios ranging from 9:91 to 1:>99, regardless of the anomeric composition of the starting donor. The use of propionitrile as a solvent at −78 °C proved to be the best choice for the highest levels of β-selectivity reported to date for this type of glycosidation. However, limitations of the phosphate method were recognized for 3,4,6-tri-*O*-acetyl-protected glucosyl and galactosyl donors and 4,6-*O*-benzylidene-protected glucosyl donor. These results indicate that the properly choosing of protecting groups on 2-azido-2-deoxy-sugar components is crucial for the success in the present method. It has also been experimentally demonstrated that highly efficient and β-selective glycosidations proceed through intermediate α-glycosyl-nitrilium ions followed by an S_N2-like displacement, which is based on the finding that only α-imidates formed through their intermediate were small amounts of byproducts when highly reactive *O*-6-unprotected glycoside alcohols were used as a glycosyl acceptor. A comparative study with the corresponding trichloroacetimidates under the present reaction conditions demonstrated that similar high levels of β-selectivity are observed, but the phosphate method generally gives higher product yields than the trichloroacetimidate method. The latter method is frequently accompanied by side-products that originate from the departing trichloroacetamide, particularly when α-imidates are used. While the discrepancy in reaction mode between α- and β-trichloroacetimidates remains to be elucidated, only using β-trichloroacetimidates ensures a successful result. Thus, the present method would be a

potent alternative to Schmidt's trichloroacetimidate procedure.

4. Experimental

4.1. General

Melting points were determined on a Büchi 535 digital melting point apparatus and were uncorrected. Optical rotations were recorded on a JASCO P-1030 digital polarimeter. Infrared (IR) spectra were recorded on a JASCO FT/IR-5300 spectrophotometer and absorbance bands are reported in wavenumber (cm^{-1}). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker ARX500 (500 MHz) spectrometer with tetramethylsilane (δ_H 0.00) as an internal standard. Coupling constants (J) are reported in hertz (Hz). Abbreviations of multiplicity are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Data are presented as follows: chemical shift, multiplicity, coupling constants, integration and assignment. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on JEOL AL400 (100 MHz) or Bruker ARX500 (126 MHz) spectrometers with $CDCl_3$ (δ_C 77.0) as an internal standard. Phosphorus nuclear magnetic resonance (^{31}P NMR) spectra were recorded on JEOL EX270 (109 MHz) or Bruker ARX500 (202 MHz) spectrometers with H_3PO_4 (δ_P 0.00) as an external standard. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS HX110 spectrometer in the Center for Instrumental Analysis, Hokkaido University.

Column chromatography was carried out on Kanto silica gel 60 N (40–50 μm or 63–210 μm) or Wakogel C-200 (75–150 μm). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F_{254} plates. Visualization was accomplished with ultraviolet light and anisaldehyde or phosphomolybdic acid stain, followed by heating. HPLC analyses were performed on a JASCO PU-980 and UV-970 (detector, $\lambda=254$ nm). Retention times (t_R) and peak ratios were determined with a Shimadzu Chromatopac C-R6A. Hexane was HPLC grade, and filtered and degassed prior to use.

Reagents and solvents were purified by standard means or used as received unless otherwise noted. Dehydrated stabilizer free THF was purchased from Kanto Chemical Co., Inc. Dichloromethane and propionitrile were distilled from P_2O_5, and redistilled from calcium hydride prior to use. Molecular sieves 4 Å was finely ground in mortar and heated in vacuo at 220 °C for 12 h.

All reactions were conducted under an argon atmosphere. Lactols **1a**,[7b] **1b**,[7a] **3a**,[7a] **3b**[36] and **3c**[37] were prepared according to literature procedures. For full characterization, most of the authentic α-glycosides were prepared by glycosidations of diphenyl phosphates with acceptor alcohols in Et_2O at 0 °C, followed by chromatographic separation from the β-glycosides. Glycosides **31**, **33** and **35** were prepared by reactions of diphenyl phosphates with alcohol **7** in CH_2Cl_2 at −30 °C, followed by column chromatography.

4.2. Preparation of 2-azido-2-deoxy-D-glycosyl donors

4.2.1. Typical procedure for preparation of 2-azido-2-deoxyglycopyranosyl diphenyl phosphate: 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl diphenyl phosphate (2a). Diphenylphosphoryl chloride (0.55 mL, 2.66 mmol) was added to a stirred solution of **1a**[7b] (1.10 g, 2.31 mmol) and DMAP (564 mg, 4.62 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After 0.5 h, the reaction was quenched with crushed ice, followed by stirring at room temperature for 15 min. The mixture was poured into a two-layer mixture of Et_2O (20 mL) and saturated aqueous $NaHCO_3$ (20 mL), and the whole was extracted with AcOEt (40 mL). The organic layer was washed with brine (2× 20 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the pale yellow oil (1.70 g), which was purified by column chromatography (silica gel 30 g, 2:1 hexane/AcOEt with 2% Et_3N) to give diphenyl phosphate **2a** (1.59 g, 97%, $\alpha:\beta=72:28$) as a colorless oil. The anomeric $\alpha:\beta$ ratio of the diphenyl phosphate was determined by ^{31}P NMR.

Data for α-anomer (**2aα**): TLC $R_f=0.42$ (2:1 hexane/AcOEt); $[\alpha]_D^{14}=+38.1°$ (c 1.14, $CHCl_3$) ($\alpha:\beta=85:15$); IR (film) 3022, 2872, 2870, 2116, 1591, 1491, 1288, 1059, 1188, 966 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.35 (brd, $J=10.9$ Hz, 1H, H-6a), 3.61 (ddd, $J=3.4$, 9.8, 3.3 (J_{H-P}) Hz, 1H, H-2), 3.64 (dd, $J=1.0$, 10.9 Hz, 1H, H-6b), 3.79–3.85 (m, 2H, H-4, H-5), 3.88 (m, 1H, H-3), 4.43 (d, $J=11.1$ Hz, 1H, OC*H*Ph), 4.536 (d, $J=11.1$ Hz, 1H, OC*H*Ph), 4.537 (d, $J=10.9$ Hz, 1H, OC*H*Ph), 4.78 (d, $J=10.9$ Hz, 1H, OC*H*Ph), 4.82 (d, $J=10.7$ Hz, 1H, OC*H*Ph), 4.86 (d, $J=10.7$ Hz, 1H, OC*H*Ph), 5.98 (dd, $J=3.4$, 6.1 (J_{H-P}) Hz, 1H, H-1), 7.15–7.35 (m, 25H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 63.5 (d, $J_{C-P}=8.6$ Hz), 67.4, 73.2, 73.5, 75.1, 75.6, 80.0, 97.3 (d, $J_{C-P}=6.3$ Hz, C-1), 120.1 (d, $J_{C-P}=5.0$ Hz), 120.3 (d, $J_{C-P}=5.0$ Hz), 125.4, 125.5, 127.7, 127.77, 127.83, 127.9, 128.0, 128.1, 128.4, 128.45, 128.48, 129.7, 129.8, 137.6, 137.66, 137.70, 150.38 (d, $J_{C-P}=7.5$ Hz), 150.44 (d, $J_{C-P}=7.5$ Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ −13.3; FAB-HRMS m/z calcd for $C_{39}H_{39}N_3O_8P$ $(M+H)^+$ 708.2474, found 708.2476; Anal. calcd for: $C_{39}H_{38}N_3O_8P$: C, 66.19; H, 5.41; N, 5.94, found C, 66.06; H, 5.54; N, 5.82. Data for β-anomer (**2aβ**): TLC $R_f=0.38$ (2:1 hexane/AcOEt); $[\alpha]_D^{22}=+2.69°$ (c 1.33, $CHCl_3$) ($\alpha:\beta=5:95$); IR (film) 3022, 2872, 2870, 2116, 1591, 1491, 1288, 1059, 1188, 966 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.47–3.54 (m, 3H, H-2, H-4, H-5), 3.63 (dd, $J=1.7$, 11.1 Hz, 1H, H-6a), 3.73 (dd, $J=3.6$, 11.1 Hz, 1H, H-6b), 3.76 (t, $J=9.1$ Hz, 1H, H-3), 4.45 (d, $J=12.0$ Hz, 1H, OC*H*Ph), 4.55 (d, $J=12.0$ Hz, 1H, OC*H*Ph), 4.58 (d, $J=10.9$ Hz, 1H, OC*H*Ph), 4.78 (d, $J=10.9$ Hz, 1H, OC*H*Ph), 4.82 (d, $J=11.0$ Hz, 1H, OC*H*Ph), 4.86 (d, $J=11.0$ Hz, 1H, OC*H*Ph), 5.15 (dd, $J=7.3$, 7.3 (J_{H-P}) Hz, 1H, H-1), 7.16–7.34 (m, 25H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 66.5 (d, $J_{C-P}=9.2$ Hz), 67.9, 73.6, 75.0, 75.7, 75.9, 82.9, 98.2 (d, $J_{C-P}=5.5$ Hz, C-1), 120.1 (d, $J_{C-P}=5.0$ Hz), 120.5 (d, $J_{C-P}=5.0$ Hz), 125.5, 125.6, 127.68, 127.71, 127.8, 127.9, 128.0, 128.1, 128.4, 128.46, 128.48, 129.6, 129.8, 137.6, 137.7, 137.9, 150.3, (d, $J_{C-P}=7.5$ Hz), 150.5 (d, $J_{C-P}=7.5$ Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ −13.5; FAB-HRMS m/z calcd for $C_{39}H_{39}N_3O_8P$ $(M+H)^+$ 708.2474, found 708.2490.

4.2.2. 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-D-glucopyranosyl diphenyl phosphate (2b). The reaction was performed according to the typical procedure (10 mL CH_2Cl_2, 0 °C, 0.5 h) employing lactol **1b**[7a] (754 mg, 2.28 mmol), diphenylphosphoryl chloride (0.66 mL, 3.19 mmol), and DMAP (557 mg, 4.56 mmol). The crude product (1.53 g) was purified by column chromatography (silica gel 40 g, 1.5:1 hexane/AcOEt with 1% Et_3N) to give diphenyl phosphate **2b** (1.28 g, 99%, α:β=46:54) as a pale yellow syrup. TLC R_f=0.50 (1:1 hexane/AcOEt); $[\alpha]_D^{18}$=+48.0° (*c* 1.35, $CHCl_3$) (α:β=46:54); IR (film) 2116, 1753, 1591, 1489, 1188, 970 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.99 (s, 1.5H, CH_3CO), 2.02 (s, 1.5H, CH_3CO), 2.03 (s, 1.5H, CH_3CO), 2.04 (s, 1.5H, CH_3CO), 2.08 (s, 1.5H, CH_3CO), 2.10 (s, 1.5H, CH_3CO), 3.64 (m, 0.5H, H-2β), 3.72 (ddd, *J*=3.4, 10.4, 3.3 (J_{H-P}) Hz, 0.5H, H-2α), 3.76 (m, 0.5H, H-5β), 3.80 (dd, *J*=2.1, 12.6 Hz, 0.5H, H-6aα), 4.00 (dd, *J*=2.3, 12.5 Hz, 0.5H, H-6aβ), 4.03 (ddd, *J*=2.1, 3.9, 10.4 Hz, 0.5H, H-5α), 4.17 (dd, *J*=3.9, 12.6 Hz, 0.5H, H-6bα), 4.22 (dd, *J*=4.8, 12.5 Hz, 0.5H, H-6bβ), 5.02–5.11 (m, 1.5H, H-4α, H-3β, H-4β), 5.24 (dd, *J*=7.8, 7.8 (J_{H-P}) Hz, 0.5H, H-1β), 5.45 (dd, *J*=9.9, 10.4 Hz, 0.5H, H-3α), 6.01 (dd, *J*=3.4, 6.4 (J_{H-P}) Hz, 0.5H, H-1α), 7.20–7.38 (m, 10H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.36, 20.38, 20.41, 20.5, 60.8, 60.9 (d, J_{C-P}=8.9 Hz), 61.2, 63.9 (d, J_{C-P}=9.8 Hz), 67.4, 67.6, 69.7, 70.3, 72.4, 72.5, 96.1 (d, J_{C-P}=5.5 Hz, C-1α), 97.6 (d, J_{C-P}=5.0 Hz, C-1β), 119.88, 119.92, 120.0, 120.15, 120.19, 120.23, 120.3, 125.56, 125.62, 129.6, 129.7, 129.8, 150.0, 150.06, 150.10, 150.12, 150.15, 150.16, 169.36, 169.39, 169.5, 169.7, 170.2; ^{31}P NMR (109 MHz, $CDCl_3$) δ −13.6 (β), −13.2 (α); FAB-HRMS *m*/*z* calcd for $C_{24}H_{27}N_3O_{11}P$ $(M+H)^+$ 564.1383, found 564.1379; Anal. calcd for: $C_{24}H_{26}N_3O_{11}P$: C, 51.16; H, 4.65; N, 7.46, found C, 51.16; H, 4.71; N, 7.60.

4.2.3. 3-*O*-Acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-D-glucopyranose (1c). Tetrabutylammonium fluoride in THF (1.0 M, 2.50 mL, 2.50 mmol) was added to a stirred solution of *tert*-butyldimethylsilyl 3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside[38] (850 mg, 1.89 mmol) in THF (10 mL)—AcOH (0.16 mL) at 0 °C. After stirring for 15 min, saturated aqueous $NaHCO_3$ (3 mL) was added, and the whole was extracted with AcOEt (50 mL). The organic layer was successively washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (2× 10 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (1.02 g), which was purified by column chromatography (silica gel 30 g, 2:1 hexane/AcOEt) to give lactol **1c** (621 mg, 98%, α:β=52:48) as a white amorphous. The anomeric α:β ratio of the lactol was determined by ^1H NMR. TLC R_f=0.23 (2:1 hexane/AcOEt); $[\alpha]_D^{23}$=−7.49° (*c* 1.02, $CHCl_3$) (α:β=52:48); IR (KBr) 3468, 2868, 2112, 1726, 1452, 1371, 1259, 1095 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H, CH_3CO), 3.33 (dd, *J*=3.6, 10.3 Hz, 0.5H, H-2α), 3.37 (br, 0.5H, O*H*), 3.45 (dd, *J*=8.0, 10.0 Hz, 0.5H, H-2β), 3.49 (ddd, *J*=5.0, 9.6, 10.4 Hz, 0.5H, H-5β), 3.63 (dd, *J*=9.5, 9.6 Hz, 1H, H-4α, H-4β), 3.73 (dd, *J*=10.3, 10.4 Hz, 0.5H, H-6axα), 3.77 (dd, *J*=10.4, 10.6 Hz, 0.5H, H-6axβ), 3.97 (br, 0.5H, O*H*), 4.19 (ddd, *J*=5.0, 9.5, 10.3 Hz, 0.5H, H-5α), 4.28 (dd, *J*=5.0, 10.4 Hz, 0.5H, H-6eqα), 4.32 (dd, *J*=5.0, 10.6 Hz, 0.5H, H-6eqβ), 4.77 (d, *J*=8.0 Hz, 0.5H, H-1β), 5.17 (dd, *J*=9.5, 10.0 Hz, 0.5H, H-3β), 5.35 (brd, *J*=3.6 Hz, 0.5H, H-1α), 5.48 (s, 0.5H, C*H*Ph), 5.50 (s, 0.5H, C*H*Ph), 5.64 (dd, *J*=9.6, 10.3 Hz, 0.5H, H-3α), 7.34–7.38 (m, 3H, Ar-H), 7.40–7.45 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.8, 62.2, 62.7, 65.7, 66.5, 68.3, 68.8, 69.1, 71.3, 78.6, 79.4, 93.1 (C-1α), 96.6 (C-1β), 101.5, 101.7, 126.1, 126.2, 128.2, 129.2, 136.6, 136.8, 170.0, 170.1; FAB-HRMS *m*/*z* calcd for $C_{15}H_{18}N_3O_6$ $(M+H)^+$ 336.1196, found 336.1193.

4.2.4. 3-*O*-Acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl diphenyl phosphate (2c). The reaction was performed according to the typical procedure (8 mL, CH_2Cl_2, 0 °C, 0.5 h) employing lactol **1c** (621 mg, 1.85 mmol), diphenylphosphoryl chloride (0.50 mL, 2.41 mmol), and DMAP (476 mg, 3.90 mmol). The crude product (1.14 g) was purified by column chromatography (silica gel 40 g, 2:1 hexane/AcOEt with 1% Et_3N) to give diphenyl phosphates **2c**β (714 mg, 68%, white solid) and **2c**α (324 mg, 31%, colorless syrup). Data for α-anomer (**2c**α): mp 103.0–105.0 °C (AcOEt–hexane); TLC R_f=0.20 (2:1 hexane/AcOEt); $[\alpha]_D^{22}$=+48.1° (*c* 1.50, $CHCl_3$); IR (film) 2868, 2114, 1753, 1589, 1489, 1371, 1219, 1186, 954 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H, CH_3CO), 3.60–3.66 (m, 3H, H-2, H-4, H-6ax), 3.89–3.95 (m, 2H, H-5, H-6eq), 5.45 (s, 1H, C*H*Ph), 5.58 (t, *J*=9.9 Hz, 1H, H-3), 5.99 (dd, *J*=3.5, 6.5 (J_{H-P}) Hz, 1H, H-1), 7.21 (m, 2H, Ar-H), 7.25–7.31 (m, 4H, Ar-H), 7.35–7.42 (m, 9H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.6, 61.7 (d, J_{C-P}= 8.9 Hz), 64.6, 68.0, 68.9, 78.4, 96.9 (d, J_{C-P}=5.5 Hz, C-1), 101.1, 119.9 (d, J_{C-P}=5.0 Hz), 120.2 (d, J_{C-P}=5.0 Hz), 125.6, 126.0, 128.1, 129.1, 129.7, 129.8, 136.5, 150.1, (d, J_{C-P}=5.0 Hz), 150.2 (d, J_{C-P}=5.0 Hz), 169.4; ^{31}P NMR (109 MHz, $CDCl_3$) δ −13.0; FAB-HRMS *m*/*z* calcd for $C_{27}H_{27}N_3O_9P$ $(M+H)^+$ 568.1485, found 568.1467. Data for β-anomer (**2c**β): TLC R_f=0.39 (2:1 hexane/AcOEt); $[\alpha]_D^{22}$=−52.8° (*c* 1.50, $CHCl_3$); IR (film) 2868, 2114, 1755, 1589, 1489, 1371, 1219, 1186, 958 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.13 (s, 3H, CH_3CO), 3.56 (ddd, *J*= 4.9, 9.6, 10.2 Hz, 1H, H-5), 3.63 (m, 1H, H-2), 3.65 (dd, *J*= 9.6, 10.3 Hz, 1H, H-4), 3.67 (dd, *J*=10.2, 10.4 Hz, 1H, H-6ax), 4.23 (dd, *J*=4.9, 10.4 Hz, 1H, H-6eq), 5.22 (dd, *J*= 8.9, 10.3 Hz, 1H, H-3), 5.31 (dd, *J*=7.7, 7.9 (J_{H-P}) Hz, 1H, H-1), 5.46 (s, 1H, C*H*Ph), 7.20–7.27 (m, 6H, Ar-H), 7.34–7.41 (m, 9H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.5, 64.7 (d, J_{C-P}=8.8 Hz), 66.8, 67.7, 71.1 (d, J_{C-P}=1.1 Hz), 77.7, 98.0 (d, J_{C-P}=5.0 Hz, C-1), 101.4, 119.8 (d, J_{C-P}= 5.0 Hz), 120.1 (d, J_{C-P}=5.0 Hz), 125.5, 125.6, 125.9, 128.1, 129.0, 129.6, 129.7, 136.4, 150.05, (d, J_{C-P}= 6.3 Hz), 150.11 (d, J_{C-P}=6.3 Hz), 169.2; ^{31}P NMR (109 MHz, $CDCl_3$) δ −13.8; FAB-HRMS *m*/*z* calcd for $C_{27}H_{27}N_3O_9P$ $(M+H)^+$ 568.1485, found 568.1468; Anal. calcd for $C_{27}H_{26}N_3O_9P$: C, 57.15; H, 4.62; N, 7.40, found C, 57.22; H, 4.61; N, 7.49.

4.2.5. 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl diphenyl phosphate (4a). The reaction was performed according to the typical procedure (10 mL CH_2Cl_2, 0 °C, 0.5 h) with lactol **3a**[7a] (1.10 g, 2.31 mmol), diphenylphosphoryl chloride (0.63 mL, 3.02 mmol), and DMAP (567 mg, 4.63 mmol). The crude product (1.68 g) was purified by column chromatography (silica gel 40 g, 3:1 hexane/AcOEt with 2% Et_3N) to give diphenyl phosphate **4a** (1.30 g, 79%, α:β=58:42) as a colorless syrup. TLC

R_f=0.45 (α), 0.31 (β) (2:1 hexane/AcOEt); $[\alpha]_D^{22}$=+55.3° (*c* 1.50, $CHCl_3$) (α:β=90:10); IR (film) 3032, 2872, 2114, 1591, 1489, 1290, 1188, 958 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.28 (dd, *J*=5.4, 9.0 Hz, 0.6H, H-6aα), 3.39 (dd, *J*=2.7, 10.4 Hz, 0.4H, H-3β), 3.45 (dd, *J*=4.7, 8.5 Hz, 0.4H, H-6aβ), 3.56 (dd, *J*=8.1, 9.0 Hz, 0.6H, H-6bα), 3.58 (dd, *J*=8.0, 8.5 Hz, 0.4H, H-6bβ), 3.61 (dd, *J*=4.7, 8.0 Hz, 0.4H, H-5β), 3.86 (dd, *J*=2.5, 10.5 Hz, 0.6H, H-3α), 3.90 (dd, *J*=8.0, 10.4 Hz, 0.4H, H-2β), 3.92 (d, *J*=2.7 Hz, 0.4H, H-4β), 4.01 (dd, *J*=5.4, 8.1 Hz, 0.6H, H-5α), 4.05 (brs, 0.6H, H-4α), 4.10 (ddd, *J*=3.3, 10.5, 3.2 (J_{H-P}) Hz, 0.6H, H-2α), 4.36 (d, *J*=12.6 Hz, 0.6H, OC*H*Ph), 4.38 (d, *J*=12.6 Hz, 0.6H, OC*H*Ph), 4.39 (d, *J*=11.6 Hz, 0.4H, OC*H*Ph), 4.41 (d, *J*=11.6 Hz, 0.4H, OC*H*Ph), 4.52 (d, *J*=11.2 Hz, 0.6H, OC*H*Ph), 4.55 (d, *J*=11.4 Hz, 0.4H, OC*H*Ph), 4.64 (d, *J*=11.7 Hz, 0.4H, OC*H*Ph), 4.65 (d, *J*=11.4 Hz, 0.6H, OC*H*Ph), 4.69 (d, *J*=11.7 Hz, 0.4H, OC*H*Ph), 4.71 (d, *J*=11.4 Hz, 0.6H, OC*H*Ph), 4.85 (d, *J*=11.2 Hz, 0.6H, OC*H*Ph), 4.87 (d, *J*=11.4 Hz, 0.4H, OC*H*Ph), 5.09 (dd, *J*=8.0, 7.2 (J_{H-P}) Hz, 0.4H, H-1β), 5.94 (dd, *J*=3.3, 5.7 (J_{H-P}) Hz, 0.6H, H-1α), 7.11–7.39 (m, 25H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 59.4 (d, J_{C-P}=8.4 Hz), 63.1 (d, J_{C-P}=9.1 Hz), 67.4, 67.5, 71.5, 72.0, 72.4, 72.5, 73.30, 73.34, 74.2, 74.6, 74.8, 77.0, 77.2, 80.4 (d, J_{C-P}=2.4 Hz), 97.8 (d, J_{C-P}=5.9 Hz, C-1α), 98.3 (d, J_{C-P}=5.2 Hz, C-1β), 119.9 (d, J_{C-P}=5.0 Hz), 120.0 (d, J_{C-P}=5.0 Hz), 120.1 (d, J_{C-P}=5.0 Hz), 120.4 (d, J_{C-P}=5.0 Hz), 125.2, 125.3, 125.4, 125.5, 127.60, 127.64, 127.67, 127.73, 127.8, 127.86, 127.89, 128.15, 128.18, 128.3, 128.4, 129.4, 129.5, 129.6, 129.7, 137.08, 137.12, 137.5, 137.9, 138.0, 150.2 (d, J_{C-P}=7.5 Hz), 150.30 (d, J_{C-P}=7.5 Hz), 150.31 (d, J_{C-P}=7.5 Hz), 150.36 (d, J_{C-P}=7.5 Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ −13.32 (β), −13.25 (α); FAB-HRMS *m/z* calcd for $C_{39}H_{39}N_3O_8P$ $(M+H)^+$ 708.2474, found 708.2451; Anal. calcd for $C_{39}H_{38}N_3O_8P$: C, 66.19; H, 5.41; N, 5.94, found C, 66.35; H, 5.59; N, 5.85.

4.2.6. 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl diphenyl phosphate (4b). The reaction was performed according to the typical procedure (10 mL CH_2Cl_2, 0 °C, 0.5 h) with lactol **3b**[36] (994 mg, 3.00 mmol), diphenylphosphoryl chloride (0.81 mL, 3.90 mmol), and DMAP (953 mg, 7.80 mmol). The crude product (1.96 g) was purified by column chromatography (silica gel 40 g, 2:1 hexane/AcOEt) to give diphenyl phosphate **4b** (1.64 g, 97%, α:β=24:76) as a colorless syrup. Data for α-anomer (**4b**α): TLC R_f=0.58 (10:1 CH_2Cl_2/acetone); $[\alpha]_D^{24}$=+74.2° (*c* 1.50, $CHCl_3$); IR (film) 2116, 1753, 1591, 1489, 1371, 1226, 960 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.90 (s, 3H, CH_3CO), 2.07 (s, 3H, CH_3CO), 2.14 (s, 3H, CH_3CO), 3.86 (dd, *J*=6.4, 11.3 Hz, 1H, H-6a), 3.96 (ddd, *J*=3.3, 11.0, 3.2 (J_{H-P}) Hz, 1H, H-2), 4.06 (dd, *J*=6.8, 11.3 Hz, 1H, H-6b), 4.29 (dd, *J*=6.4, 6.8 Hz, 1H, H-5), 5.30 (dd, *J*=3.2, 11.0 Hz, 1H, H-3), 5.46 (brd, *J*=3.2 Hz, 1H, H-4), 6.04 (dd, *J*=3.3, 6.1 (J_{H-P}) Hz, 1H, H-1), 7.21 (m, 2H, Ar-H), 7.25–7.28 (m, 4H, Ar-H), 7.34–7.38 (m, 4H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.4, 20.47, 20.50, 57.4 (d, J_{C-P}=8.7 Hz), 60.8, 66.7, 68.4, 68.7, 96.7 (d, J_{C-P}=5.5 Hz, C-1), 120.0 (d, J_{C-P}=5.0 Hz), 120.2 (d, J_{C-P}=5.0 Hz), 125.60, 125.63, 129.7, 129.8, 150.2 (d, J_{C-P}=6.3 Hz), 150.3 (d, J_{C-P}=6.3 Hz), 169.6, 169.8, 170.1; ^{31}P NMR (109 MHz, $CDCl_3$) δ −13.1; FAB-HRMS *m/z* calcd for $C_{24}H_{27}N_3O_{11}P$ $(M+H)^+$ 564.1383, found 564.1368. Data for β-anomer (**4b**β): TLC R_f=0.42 (10:1 CH_2Cl_2/acetone); $[\alpha]_D^{24}$=+5.60° (*c* 1.50, $CHCl_3$); IR (film) 2116, 1753, 1591, 1489, 1371, 1226, 960 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.98 (s, 3H, CH_3CO), 2.05 (s, 3H, CH_3CO), 2.16 (s, 3H, CH_3CO), 3.82 (dd, *J*=8.2, 10.7 Hz, 1H, H-2), 3.97 (dt, *J*=0.6, 6.5 Hz, 1H, H-5), 4.02 (dd, *J*=6.5, 11.0 Hz, 1H, H-6a), 4.10 (dd, *J*=6.5, 11.0 Hz, 1H, H-6b), 4.87 (dd, *J*=3.3, 10.7 Hz, 1H, H-3), 5.24 (dd, *J*=8.2, 7.4 (J_{H-P}) Hz, 1H, H-1), 5.36 (dd, *J*=0.6, 3.3 Hz, 1H, H-4), 7.22 (m, 2H, Ar-H), 7.26–7.28 (m, 4H, Ar-H), 7.34–7.37 (m, 4H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.4, 20.5, 60.7, 61.0 (d, J_{C-P}=9.4 Hz), 65.9, 71.2 (d, J_{C-P}=1.6 Hz), 71.8, 98.1 (d, J_{C-P}=5.3 Hz, C-1), 120.0 (d, J_{C-P}=3.4 Hz), 120.3 (d, J_{C-P}=3.4 Hz), 125.6, 125.7, 129.7, 129.8, 150.2 (d, J_{C-P}=8.8 Hz), 150.3 (d, J_{C-P}=8.8 Hz), 169.5, 169.8, 170.2; ^{31}P NMR (109 MHz, $CDCl_3$) δ −13.5; FAB-HRMS *m/z* calcd for $C_{24}H_{27}N_3O_{11}P$ $(M+H)^+$ 564.1383, found 564.1385; Anal. calcd for: $C_{24}H_{26}N_3O_{11}P$: C, 51.16; H, 4.65; N, 7.46, found C, 51.02; H, 4.72; N, 7.47.

4.2.7. 3-*O*-Acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranosyl diphenyl phosphate (4c). The reaction was performed according to the typical procedure (6 mL CH_2Cl_2, 0 °C, 0.5 h) employing lactol **3c**[37] (350 mg, 1.04 mmol), diphenylphosphoryl chloride (0.28 mL, 1.36 mmol), and DMAP (254 mg, 2.08 mmol). The crude product (530 mg) was purified by column chromatography (silica gel 25 g, 2:1→1:1 hexane/AcOEt with 1% Et_3N) to give diphenyl phosphates **4c**α (295 mg, 50%) and **4c**β (147 mg, 25%) as white amorphous. Data for α-anomer (**4c**α): TLC R_f=0.44 (1:1 hexane/AcOEt); $[\alpha]_D^{24}$=+152.5° (*c* 1.50, $CHCl_3$); IR (KBr) 3069, 2922, 2116, 1747, 1591, 1489, 1224, 1188, 958, 756 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H, CH_3CO), 3.66 (brs, 1H, H-5), 3.83 (dd, *J*=1.0, 13.0 Hz, 1H, H-6a), 3.95 (dd, *J*=0.9, 13.0 Hz, 1H, H-6b), 4.20 (ddd, *J*=3.2, 11.0, 3.2 (J_{H-P}) Hz, 1H, H-2), 4.42 (brd, *J*=5.4 Hz, 1H, H-4), 5.23 (dd, *J*=3.3, 11.0 Hz, 1H, H-3), 5.46 (s, 1H, C*H*Ph), 6.10 (dd, *J*=3.2, 6.0 (J_{H-P}) Hz, 1H, H-1), 7.18 (m, 2H, Ar-H), 7.25–7.38 (m, 11H, Ar-H), 7.46 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.8, 57.0 (d, J_{C-P}=8.6 Hz), 64.3, 68.3, 69.4, 72.6, 97.6 (d, J_{C-P}=5.0 Hz, C-1), 100.6, 120.0 (d, J_{C-P}=5.0 Hz), 120.2 (d, J_{C-P}=5.0 Hz), 125.4, 125.5, 126.0, 128.1, 129.1, 129.67, 129.72, 137.1, 150.2, (d, J_{C-P}=4.4 Hz), 150.3 (d, J_{C-P}=4.4 Hz), 170.2; ^{31}P NMR (202 MHz, $CDCl_3$) δ −12.9; FAB-HRMS *m/z* calcd for $C_{27}H_{27}N_3O_9P$ $(M+H)^+$ 568.1485, found 568.1501; Anal. calcd for: $C_{27}H_{26}N_3O_9P$: C, 57.15; H, 4.62; N, 7.40, found C, 57.20; H, 4.64; N, 7.39. Data for β-anomer (**4c**β): TLC R_f=0.28 (1:1 hexane/AcOEt); $[\alpha]_D^{26}$=+73.8° (*c* 1.50, $CHCl_3$); IR (KBr) 3069, 2905, 2118, 1749, 1591, 1491, 1371, 1294, 1186, 1087 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.12 (s, 3H, CH_3CO), 3.56 (brs, 1H, H-5), 3.95 (dd, *J*=1.3, 12.5 Hz, 1H, H-6a), 4.00 (dd, *J*=8.2, 10.8 Hz, 1H, H-2), 4.17 (dd, *J*=1.2, 12.5 Hz, 1H, H-6b), 4.34 (d, *J*=3.3 Hz, 1H, H-4), 4.78 (dd, *J*=3.3, 10.8 Hz, 1H, H-3), 5.25 (dd, *J*=8.2, 6.7 (J_{H-P}) Hz, 1H, H-3), 5.49 (s, 1H, C*H*Ph), 7.18 (m, 2H, Ar-H), 7.24–7.43 (m, 11H, Ar-H), 7.51 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.8, 60.5 (d, J_{C-P}=10.1 Hz), 67.0, 68.3, 72.0, 72.2 (d, J_{C-P}=1.5 Hz), 98.2 (d, J_{C-P}=5.0 Hz, C-1), 100.8, 120.0 (d, J_{C-P}=5.0 Hz), 120.7 (d, J_{C-P}=5.0 Hz), 125.5, 126.2, 128.2, 129.2, 129.6, 129.7, 137.4, 150.2 (d, J_{C-P}=6.3 Hz), 150.3 (d, J_{C-P}=7.5 Hz),

170.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ −13.1; FAB-HRMS *m/z* calcd for $C_{27}H_{27}N_3O_9P$ $(M+H)^+$ 568.1485, found 568.1470.

4.2.8. 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl diphenyl phosphate (2a) (α:β=2:98). Diphenyl phosphate (207 mg, 0.83 mmol) was added to a stirred solution of **5**α[7b] (514 mg, 0.83 mmol) in CH_2Cl_2 (7 mL) at 0 °C. After 0.1 h, the mixture was poured into a two-layer mixture of Et_2O (5 mL) and saturated aqueous $NaHCO_3$ (5 mL), and the whole was extracted with AcOEt (30 mL). The organic layer was successively washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (2×10 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the pale yellow oil (735 mg), which was purified by column chromatography (silica gel 15 g, 2:1 hexane/AcOEt with 2% Et_3N) to give diphenyl phosphate **2a** (507 mg, 86%, α:β=2:98) as a colorless oil. The anomeric α:β ratio of the product was determined by ^{31}P NMR.

4.2.9. 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl *N*,*N*,*N*′,*N*′-tetramethylphosphorodiamidate (6). Butyllithium in hexane (1.56 M, 0.3 mL, 0.468 mmol) was added to a stirred solution of **1a** (212 mg, 0.446 mmol) in THF (5.0 mL) at −78 °C. After 15 min, a solution of bis(dimethylamino)phosphoryl chloride (0.067 mL, 0.450 mmol) in HMPA (0.5 mL) was added, and the mixture was allowed to warm to −20 °C over 30 min. After stirring at this temperature for 2 h, the reaction was quenched with crushed ice, followed by stirring at 0 °C for 30 min. The mixture was poured into a two-layer mixture of Et_2O (5 mL) and saturated aqueous $NaHCO_3$ (5 mL), and the whole was extracted with AcOEt (20 mL). The organic layer was washed with brine (2×10 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the yellow residue (301 mg), which was purified by column chromatography (silica gel 8 g, 1:1→1:2 hexane/AcOEt) to give diamidate **6** (238 mg, 87%, α:β=67:33) as a colorless oil. The anomeric α:β ratio of the product was determined by ^{31}P NMR. TLC R_f=0.31 (AcOEt); $[\alpha]_D^{22}$=+13.9° (*c* 1.27, $CHCl_3$) (α:β=67:33); IR ($CHCl_3$) 3034, 2932, 2114, 1454, 1305, 1215, 995 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.62 (d, J_{H-P}=10.1 Hz, 4.2H, N(C*H*$_3$)$_2$), 2.63 (d, J_{H-P}=10.4 Hz, 1.8H, N(C*H*$_3$)$_2$), 2.66 (d, J_{H-P}=10.2 Hz, 4.2H, N(C*H*$_3$)$_2$), 2.69 (d, J_{H-P}=10.3 Hz, 1.8H, N(C*H*$_3$)$_2$), 3.44–3.52 (m, 0.9H, H-2β, H-3β, H-5β), 3.61 (ddd, *J*=3.4, 10.1, 1.4 (J_{H-P}) Hz, 0.7H, H-2α), 3.64–3.69 (m, 1H, H-6aα, H-6aβ), 3.71–3.79 (m, 2H, H-4α, H-6bα, H-4β, H-6bβ), 3.88 (dd, *J*=9.0, 10.1 Hz, 0.7H, H-3α), 3.94 (ddd, *J*=1.8, 3.1, 10.0 Hz, 0.7H, H-5α), 4.49 (d, *J*=12.0 Hz, 0.7H, OC*H*Ph), 4.51 (d, *J*=12.1 Hz, 0.3H, OC*H*Ph), 4.561 (d, *J*=12.1 Hz, 0.3H, OC*H*Ph), 4.562 (d, *J*=10.7 Hz, 0.7H, OC*H*Ph), 4.60 (d, *J*=10.9 Hz, 0.3H, OC*H*Ph), 4.61 (d, *J*=12.0 Hz, 0.7H, OC*H*Ph), 4.80 (d, *J*=10.9 Hz, 0.3H, OC*H*Ph), 4.81 (d, *J*=10.7 Hz, 0.7H, OC*H*Ph), 4.83 (d, *J*=10.3 Hz, 0.3H, OC*H*Ph), 4.86 (d, *J*=10.8 Hz, 0.7H, OC*H*Ph), 4.87 (d, *J*=10.3 Hz, 0.3H, OC*H*Ph), 4.90 (d, *J*=10.8 Hz, 0.7H, OC*H*Ph), 5.00 (dd, *J*=7.5, 7.6 (J_{H-P}) Hz, 0.3H, H-1β), 5.75 (dd, *J*=3.4, 7.9 (J_{H-P}) Hz, 0.7H, H-1α), 7.10–7.17 (m, 3H, Ar-H), 7.26–7.38 (m, 12H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 36.3, 36.36, 36.41, 36.45, 36.48, 64.2 (d, J_{C-P}=7.3 Hz), 67.2 (d, J_{C-P}=7.9 Hz), 68.2, 68.3, 72.7, 73.5, 73.6, 75.0, 75.2, 75.3, 75.5, 75.6, 77.4, 77.9, 80.4, 83.0, 93.5 (d, J_{C-P}=4.0 Hz, C-1α), 96.1 (d, J_{C-P}=4.5 Hz, C-1β), 127.66, 127.72, 127.8, 127.88, 127.91, 128.06, 128.11, 128.3, 128.4, 128.45, 128.47, 137.7, 137.76, 137.81, 137.87, 137.94; ^{31}P NMR (109 MHz, $CDCl_3$) δ 19.41 (α), 20.01 (β); FAB-HRMS *m/z* calcd for $C_{31}H_{41}N_5O_6P$ $(M+H)^+$ 610.2795, found 610.2795.

4.3. Glycosidations of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxyglucosyl diphenyl phosphate 2a

4.3.1. Typical procedure for glycosidation of 2-azido-2-deoxyglucopyranosyl donors: methyl 4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (10). TMSOTf in CH_2Cl_2 (1.0 M, 0.15 mL, 0.15 mmol) was added to a stirred solution of diphenyl phosphate **2a** (α:β=72:28) (70.8 mg, 0.10 mmol) and alcohol **8** (51.1 mg, 0.11 mmol) in EtCN (1.5 mL) at −78 °C. After stirring at this temperature for 2 h, the reaction was quenched with Et_3N (0.1 mL). The reaction mixture was poured into a two-layer mixture of AcOEt (2 mL) and $NaHCO_3$ (3 mL), and the whole was extracted with AcOEt (20 mL). The organic layer was successively washed with saturated aqueous $NaHCO_3$ (5 mL) and brine (2×5 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product (108.9 mg), from which an anomeric mixture of disaccharide **10** (82.6 mg, 90%, α:β=6:94) was obtained as a colorless oil after column chromatography (silica gel 6 g, 5:1 hexane/AcOEt). The anomeric ratio of the disaccharide was determined by HPLC analysis [column, Zorbax® Sil, 4.6×250 mm; eluent, 7:1 hexane/AcOEt; flow rate, 1.0 mL/min; detection, 254 nm; t_R (α-anomer)=56.6 min, t_R (β-anomer)=63.5 min]. The α- and β-glycosides were separated by flash column chromatography with 6:1 hexane/AcOEt.

The following work-up may be employed in those cases where the highly reactive primary alcohol (**7** or **12**) was used as an acceptor. It serves only to remove the imidate as its hydrolyzed product. After the reaction was quenched with Et_3N (0.1 mL), the mixture was diluted with AcOEt (20 mL). The whole was successively washed with 10% aqueous HCl (5 mL), H_2O (5 mL), saturated aqueous $NaHCO_3$ (5 mL) and brine (2×5 mL), and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo to yield the crude product containing propionated acceptor alcohol.

Data for β-anomer (**10**β): TLC R_f=0.49 (2:1 hexane/AcOEt); $[\alpha]_D^{15}$=−11.4° (*c* 1.09, $CHCl_3$); IR ($CHCl_3$) 3009, 2910, 2870, 2112, 1496, 1454, 1361, 1277, 1087, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18 (ddd, *J*=1.7, 4.3, 9.6 Hz, 1H, H-5′), 3.24 (dd, *J*=8.9, 9.8 Hz, 1H, H-3′), 3.31 (dd, *J*=8.0, 9.8 Hz, 1H, H-2′), 3.38 (s, 3H, OC*H*$_3$), 3.47–3.50 (m, 2H, H-2, H-6′a), 3.59 (dd, *J*=8.9, 9.6 Hz, 1H, H-4′), 3.62 (dd, *J*=1.7, 11.1 Hz, 1H, H-6′b), 3.70 (dd, *J*=1.6, 10.9 Hz, 1H, H-6a), 3.78 (ddd, *J*=1.6, 3.2, 9.8 Hz, 1H, H-5), 3.89 (dd, *J*=8.9, 9.5 Hz, 1H, H-3), 3.92 (dd, *J*=3.2, 10.9 Hz, 1H, H-6b), 3.96 (dd, *J*=8.9, 9.8 Hz, 1H, H-4), 4.26 (d, *J*=8.0 Hz, 1H, H-1′), 4.35 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.40 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.47 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.54 (d, *J*=11.0 Hz, 1H, OC*H*Ph), 4.58 (d, *J*=

12.1 Hz, 1H, OC*H*Ph), 4.59 (d, J=3.6 Hz, 1H, H-1), 4.67 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.74 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.76 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.781 (d, J=11.4 Hz, 1H, OC*H*Ph), 4.782 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.82 (d, J=10.7 Hz, 1H, OC*H*Ph), 5.02 (d, J=11.4 Hz, 1H, OC*H*Ph), 7.17–7.36 (m, 30H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.3, 66.9, 68.2, 68.6, 69.7, 73.3, 73.47, 73.51, 74.7, 75.19, 75.24, 75.4, 77.9, 79.1, 80.3, 83.3, 98.3 (C-1), 100.9 (C-1′), 127.0, 127.4, 127.5, 127.65, 127.67, 127.70, 127.72, 127.8, 127.95, 127.98, 128.1, 128.2, 128.3, 128.36, 128.42, 128.5, 137.8, 137.9, 138.0, 138.3, 138.4, 139.5; FAB-HRMS m/z calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4083; Anal. calcd for: $C_{55}H_{59}N_3O_{10}$: C, 71.64; H, 6.45; N, 4.56, found C, 71.45; H, 6.45; N, 4.55. Data for α-anomer (**10α**): TLC R_f=0.54 (2:1 hexane/AcOEt); $[\alpha]_D^{15}=+39.1°$ (c 0.78, $CHCl_3$); IR ($CHCl_3$) 3013, 2910, 2870, 2112, 1602, 1454, 1361, 1221, 1049, 713 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.27 (dd, J=3.9, 10.4 Hz, 1H, H-2′), 3.34 (brd, J=11.0 Hz, 1H, H-6′a), 3.38 (s, 3H, OCH_3), 3.52 (dd, J=1.4, 11.0 Hz, 1H, H-6′b), 3.57 (dd, J=3.6, 9.6 Hz, 1H, H-2), 3.65 (dd, J=1.9, 11.0 Hz, 1H, H-6a), 3.66–3.70 (m, 2H, H-4′, H-5′), 3.72 (dd, J=4.3, 11.0 Hz, 1H, H-6b), 3.79 (ddd, J=1.9, 4.3, 10.0 Hz, 1H, H-5), 3.86 (m, 1H, H-3′), 3.91 (dd, J=8.6, 10.0 Hz, 1H, H-4), 4.08 (dd, J=8.6, 9.6 Hz, 1H, H-3), 4.25 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.45 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.49 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.50 (s, 2H, OCH_2Ph), 4.61 (d, J=3.6 Hz, 1H, H-1), 4.62 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.74 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.75 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.83 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.85 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.86 (d, J=10.7 Hz, 1H, OC*H*Ph), 5.10 (d, J=10.7 Hz, 1H, OC*H*Ph), 5.73 (d, J=3.9 Hz, 1H, H-1′), 7.12 (m, 2H, Ar-H), 7.20–7.35 (m, 28H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.3, 63.3, 67.9, 69.3, 69.5, 71.4, 73.27, 73.31, 73.5, 74.9, 75.0, 75.3, 78.1, 80.1, 80.5, 82.0, 97.69 (C-1′), 97.73 (C-1), 127.2, 127.4, 127.45, 127.53, 127.66, 127.71, 127.8, 127.9, 128.1, 128.26, 128.32, 128.4, 128.5, 137.8, 137.9, 138.0, 138.1, 138.2, 138.7; FAB-HRMS m/z calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4083.

4.3.2. Methyl 6-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 1.5 h) employing diphenyl phosphate **2a** (70.8 mg, 0.10 mmol), alcohol **7** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **9** (77.0 mg, 84%, α:β=1:99) was obtained as a white solid from the crude product (108.7 mg) after flash column chromatography (silica gel 6 g, 6:1 hexane/AcOEt with 1% Et_3N), along with α-imidate **11** (5.3 mg, 5%) as a colorless oil. The anomeric ratio of the disaccharide was determined by HPLC analysis [column, Zorbax® Sil, 4.6×250 mm; eluent, 5:1 hexane/AcOEt; flow rate, 1.0 mL/min; detection, 254 nm; t_R (β-anomer)=24.1 min, t_R (α-anomer)=34.7 min]. The α- and β-glycosides were separated by flash column chromatography with 3:1 hexane/Et_2O. Data for β-anomer (**9β**): TLC R_f=0.46 (2:1 hexane/AcOEt), 0.30 (1:1 hexane/Et_2O); mp 119.0–120.0 °C (colorless fine needles from AcOEt–hexane); $[\alpha]_D^{19}=-5.27°$ (c 1.15, $CHCl_3$); IR ($CHCl_3$) 3009, 2930, 2868, 2112, 1496, 1454, 1359, 1265, 1222, 1068, 763 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.37 (m, 1H, H-5′), 3.38 (s, 3H, OCH_3), 3.40 (dd, J=8.7, 9.8 Hz, 1H, H-3′), 3.45 (dd, J=7.7, 9.8 Hz, 1H, H-2′), 3.55 (dd, J=3.5, 9.6 Hz, 1H, H-2), 3.575 (dd, J=8.7, 9.4 Hz, 1H, H-4′), 3.576 (dd, J=8.9, 10.0 Hz, 1H, H-4), 3.64–3.71 (m, 3H, H-6a, H-6′a, H-6′b), 3.81 (ddd, J=1.6, 4.3, 10.0 Hz, 1H, H-5), 4.00 (dd, J=8.9, 9.6 Hz, 1H, H-3), 4.12 (dd, J=1.6, 10.9 Hz, 1H, H-6b), 4.16 (d, J=7.7 Hz, 1H, H-1′), 4.51 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.55 (d, J=12.4 Hz, 1H, OC*H*Ph), 4.57 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.62 (d, J=3.5 Hz, 1H, H-1), 4.65 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.66 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.77–4.80 (m, 3H, OC*H*Ph×3), 4.84 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.86 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.93 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.98 (d, J=11.0 Hz, 1H, OC*H*Ph), 7.17 (m, 2H, Ar-H), 7.24–7.36 (m, 28H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.2, 66.4, 68.4, 68.7, 69.7, 73.4, 74.8, 75.0, 75.2, 75.6, 75.7, 77.75, 77.79, 79.8, 82.1, 83.3, 98.2 (C-1), 102.1 (C-1′), 127.5, 127.59, 127.63, 127.7, 127.8, 127.85, 127.87, 128.0, 128.06, 128.14, 128.3, 128.35, 128.42, 128.44, 137.9, 138.1, 138.2, 138.4, 138.8; FAB-HRMS m/z calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4080; Anal. calcd for: $C_{55}H_{59}N_3O_{10}$: C, 71.64; H, 6.45; N, 4.56, found C, 71.67; H, 6.44; N 4.49. Data for α-anomer (**9α**): TLC R_f=0.44 (2:1 hexane/AcOEt), 0.26 (1:1 hexane/Et_2O); $[\alpha]_D^{24}=+84.7°$ (c 1.18, $CHCl_3$); IR (film) 3030, 2922, 2106, 1496, 1454, 1359, 1207, 1049, 736 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.33 (dd, J=3.5, 10.1 Hz, 1H, H-2′), 3.37 (s, 3H, OCH_3), 3.51–3.55 (m, 2H, H-2, H-6′a), 3.56 (dd, 1H, J=9.2, 9.4 Hz, H-4), 3.63 (dd, J=3.3, 10.7 Hz, H-6′b), 3.67–3.71 (2H, m, H-6a, H-4′), 3.74–3.78 (2H, m, H-5, H-5′), 3.83 (dd, J=4.6, 11.4 Hz, 1H, H-6b), 3.92 (dd, J=8.8, 10.1 Hz, 1H, H-3′), 4.00 (t, J=9.2 Hz, 1H, H-3), 4.43 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.49 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.56–4.61 (m, 3H, H-1, OC*H*Ph×2), 4.66 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.78 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.79 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.80 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.83 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.86 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.94 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.98 (d, J=10.9 Hz, 1H, OC*H*Ph), 5.01 (d, J=3.5 Hz, 1H, H1′), 7.13 (m, 2H, Ar-H), 7.24–7.37 (m, 28H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 63.5, 66.4, 68.1, 69.9, 70.7, 73.4, 73.5, 74.9, 75.2, 75.8, 77.2, 77.7, 78.2, 79.8, 80.0, 82.0, 97.9 (C-1), 98.2 (C-1′), 127.5, 127.6, 127.7, 127.76, 127.80, 128.0, 128.1, 128.29, 128.31, 128.4, 137.7, 137.8, 137.95, 138.04, 138.2, 138.6; FAB-HRMS m/z calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4109.

Data for methyl 6-*O*-[1-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)iminopropyl]-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**11**): TLC R_f=0.49 (2:1 hexane/AcOEt); $[\alpha]_D^{20}=+47.5°$ (c 0.40, $CHCl_3$); IR (film) 3030, 2922, 2106, 1664, 1496, 1454, 1359, 1211, 1089 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (t, J=7.6 Hz, 3H, CH_2CH_3), 2.36 (dq, J=14.6, 7.6 Hz, 1H, C*H*CH$_3$), 2.38 (dq, J=14.6, 7.6 Hz, 1H, C*H*CH$_3$), 3.37 (s, 3H, OCH_3), 3.52 (dd, J=4.1, 10.0 Hz, 1H, H-2′), 3.54 (dd, J=3.6, 9.5 Hz, 1H, H-2), 3.56 (dd, J=1.7, 10.7 Hz, 1H, H-6′a), 3.62 (dd, J=9.0, 10.0 Hz, 1H, H-4), 3.73 (dd, J=3.5, 10.7 Hz, 1H, H-6′b), 3.78 (dd, J=9.0, 9.9 Hz, 1H, H-4′), 3.87 (ddd, J=1.8, 4.1, 10.0 Hz, 1H, H-5), 4.00 (dd, J=9.0, 9.5 Hz, 1H, H-3), 4.08 (ddd, J=1.7, 3.5, 9.9 Hz, 1H, H-5′), 4.09 (dd, J=9.0, 10.0 Hz, 1H, H-3′), 4.23 (dd, J=4.1, 12.3 Hz, 1H, H-6a), 4.30 (dd, J=1.8, 12.3 Hz, 1H, H-6b), 4.46 (d, J=

12.2 Hz, 1H, OC*H*Ph), 4.51 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.59 (d, J=10.6 Hz, 1H, OC*H*Ph), 4.60 (d, J=3.6 Hz, 1H, H-1), 4.62 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.66 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.73 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.789 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.790 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.80 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.82 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.84 (d, J=10.6 Hz, 1H, OC*H*Ph), 4.97 (d, J=10.8 Hz, 1H, OC*H*Ph), 5.20 (d, J=4.1 Hz, 1H, H-1′), 7.12–7.18 (m, 3H, Ar-H), 7.22–7.37 (m, 27H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.7, 22.9, 55.1, 64.2, 64.7, 68.7, 71.2, 73.4, 73.5, 75.09, 75.14, 75.2, 75.9, 77.8, 78.9, 80.0, 80.9, 82.1, 83.2 (C-1′), 98.1 (C-1), 127.6, 127.68, 127.74, 127.76, 127.79, 127.87, 127.91, 128.0, 128.1, 128.35, 128.41, 128.5, 137.9, 138.0, 138.07, 138.13, 138.2, 138.7, 168.8; FAB-HRMS *m/z* calcd for $C_{58}H_{65}N_4O_{10}$ $(M+H)^+$ 977.4700, found 977.4721.

4.3.3. 6-*O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (17).[12a] The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 1.5 h) employing diphenyl phosphate **2a** (70.8 mg, 0.10 mmol), alcohol **12** (28.6 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **17** (56.8 mg, 79%, α:β=2:98) was obtained as a colorless oil from the crude product (91.4 mg) after column chromatography (silica gel 8 g, 7:1 hexane/AcOEt with 1% Et_3N), along with α-imidate **19** (7.2 mg, 9%) as a colorless syrup. The anomeric ratio of the product was determined by HPLC analysis [eluent, 6:1 hexane/THF; flow rate, 1.0 mL/min; t_R (α-anomer)=8.9 min, t_R (β-anomer)=9.6 min]. The α- and β-glycosides were separated by flash column chromatography with 30:1 toluene/acetone. Data for β-anomer (**17**β): TLC R_f=0.39 (3:1 hexane/AcOEt), 0.49 (10:1 toluene/acetone); $[\alpha]_D^{16}$=−47.9° (c 2.45, $CHCl_3$) (α:β=2:98); IR (film) 2986, 2906, 2110, 1454, 1381, 1211, 1070 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (s, 3H, CC*H*$_3$), 1.33 (s, 3H, CC*H*$_3$), 1.44 (s, 3H, CC*H*$_3$), 1.54 (s, 3H, CC*H*$_3$), 3.40–3.44 (m, 3H, H-2′, H-4′, H-5′), 3.63 (m, 1H, H-3′), 3.70 (dd, J=4.1, 11.1 Hz, 1H, H-6′a), 3.73 (dd, J=2.2, 11.1 Hz, 1H, H-6′b), 3.79 (m, 1H, H-6a), 4.04–4.09 (m, 2H, H-5, H-6b), 4.28 (dd, J=1.2, 7.8 Hz, 1H, H-4), 4.31 (dd, J=2.4, 5.0 Hz, 1H, H-2), 4.41 (m, 1H, H-1′), 4.53 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.54 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.60 (dd, J=2.4, 7.8 Hz, 1H, H-3), 4.61 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.78 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.79 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.89 (d, J=10.8 Hz, 1H, OC*H*Ph), 5.54 (d, J=5.0 Hz, 1H, H-1), 7.16 (m, 2H, Ar-H), 7.25–7.36 (m, 13H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 24.4, 25.0, 25.97, 26.02, 66.4, 67.6, 68.5, 68.8, 70.5, 70.7, 71.2, 73.5, 74.96, 75.02, 75.5, 77.7, 83.1, 96.3 (C-1), 102.4 (C-1′), 108.7, 109.3, 127.6, 127.76, 127.79, 127.82, 128.0, 128.35, 128.38, 128.41, 138.0, 138.06, 138.08; FAB-HRMS *m/z* calcd for $C_{39}H_{47}N_3O_{10}Na$ $(M+Na)^+$ 740.3159, found 740.3195; Anal. calcd for: $C_{39}H_{47}N_3O_{10}$: C, 65.26; H, 6.60; N, 5.85, found C, 65.26; H, 6.60; N, 5.83. Data for α-anomer (**17**α): TLC R_f=0.41 (3:1 hexane/AcOEt), 0.53 (10:1 toluene/acetone); $[\alpha]_D^{17}$=+42.2° (c 0.49, $CHCl_3$); IR ($CHCl_3$) 2924, 2106, 1454, 1381, 1255, 1070 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (s, 3H, CC*H*$_3$), 1.34 (s, 3H, CC*H*$_3$), 1.43 (s, 3H, CC*H*$_3$), 1.53 (s, 3H, CC*H*$_3$), 3.33 (dd, J=3.5, 10.3 Hz, 1H, H-2′), 3.66 (dd, J=1.8, 10.8 Hz, 1H, H-6′a), 3.72 (dd, J=6.7, 10.3 Hz, 1H, H-6a), 3.73–3.80 (m, 2H, H-4′, H-6′b), 3.81 (dd, J=6.4, 10.3 Hz, 1H, H-6b), 3.88 (m, 1H, H-5′), 3.98–4.01 (m, 2H, H-5, H-3′), 4.31 (dd, J=2.3, 5.0 Hz, 1H, H-2), 4.32 (dd, J=1.8, 8.0 Hz, 1H, H-3), 4.48 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.53 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.61 (dd, J=2.3, 8.0 Hz, 1H, H-3), 4.64 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.79 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.85 (d, J=11.5 Hz, 1H, OC*H*Ph), 4.87 (d, J=11.5 Hz, 1H, OC*H*Ph), 4.99 (d, J=3.5 Hz, 1H, H-1′), 5.51 (d, J=5.0 Hz, 1H, H-1), 7.16 (m, 2H, Ar-H), 7.24–7.37 (m, 13H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 24.4, 24.9, 26.0, 26.1, 63.4, 66.2, 66.9, 68.2, 70.6, 70.66, 70.69, 70.8, 73.5, 74.9, 75.3, 78.3, 79.9, 96.3 (C-1), 98.3 (C-1′), 108.6, 109.3, 127.70, 127.73, 127.8, 127.9, 128.0, 128.38, 128.43, 137.9, 138.1; FAB-HRMS *m/z* calcd for $C_{39}H_{47}N_3O_{10}Na$ $(M+Na)^+$ 740.3159, found 740.3134.

Data for 6-*O*-[1-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)iminopropyl]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**19**): TLC R_f=0.43 (3:1 hexane/AcOEt); $[\alpha]_D^{24}$=+4.68° (c 0.28, $CHCl_3$); IR (film) 2924, 2106, 1658, 1462, 1213, 1072 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (t, J=7.6 Hz, 3H, CH_2CH_3), 1.32 (s, 6H, CC*H*$_3$×2), 1.44 (s, 3H, CC*H*$_3$), 1.50 (s, 3H, CC*H*$_3$), 2.34 (dq, J=15.0, 7.6 Hz, 1H, C*H*CH$_3$), 2.38 (dq, J=15.0, 7.6 Hz, 1H, C*H*CH$_3$), 3.57 (dd, J=4.2, 10.0 Hz, 1H, H-2′), 3.58 (dd, J=1.8, 10.8 Hz, 1H, H-6′a), 3.74 (dd, J=3.5, 10.8 Hz, 1H, H-6′b), 3.78 (t, J=9.5 Hz, 1H, H-4′), 4.05 (ddd, J=1.6, 5.3, 7.1 Hz, 1H, H-5), 4.10 (dd, J=9.5, 10.0 Hz, 1H, H-3′), 4.10–4.14 (m, 2H, H-6a, H-5′), 4.27 (dd, J=1.6, 7.9 Hz, 1H, H-4), 4.31 (dd, J=2.4, 5.0 Hz, 1H, H-2), 4.33 (dd, J=5.3, 11.2 Hz, 1H, H-6b), 4.47 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.53 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.60 (dd, J=2.4, 7.9 Hz, 1H, H-3), 4.62 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.82 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.85 (d, J=11.7 Hz, 1H, OC*H*Ph), 4.89 (d, J=11.7 Hz, 1H, OC*H*Ph), 5.22 (d, J=4.2 Hz, 1H, H-1′), 5.55 (d, J=5.0 Hz, 1H, H-1), 7.17 (m, 2H, Ar-H), 7.24–7.38 (m, 13H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.7, 23.0, 24.4, 25.0, 26.0, 26.1, 29.7, 64.0, 65.0, 66.1, 68.7, 70.7, 71.2, 71.3, 73.5, 75.0, 75.3, 79.0, 80.8, 83.4 (C-1′), 96.3 (C-1), 108.6, 109.5, 127.65, 127.70, 127.76, 127.80, 127.9, 128.1, 128.3, 128.38, 128.43, 138.0, 138.1, 138.2, 168.0; FAB-HRMS *m/z* calcd for $C_{42}H_{53}N_4O_{10}$ $(M+H)^+$ 773.3762, found 773.3770.

4.3.4. Methyl 2-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (18).[12b] The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 2 h) employing diphenyl phosphate **2a** (70.8 mg, 0.10 mmol), alcohol **13** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **18** (83.6 mg, 91%, α:β=9:91) was obtained as a colorless oil from the crude product (107.4 mg) after column chromatography (silica gel 5 g, 5:1 hexane/AcOEt). The anomeric ratio of the product was determined by HPLC analysis [eluent, 5:1 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (α-anomer)=12.6 min, t_R (β-anomer)=16.3 min]. The α- and β-glycosides were separated by flash column chromatography with 6:1 hexane/AcOEt. Data for β-anomer (**18**β):[12b] TLC R_f=0.61 (2:1 hexane/AcOEt); mp 83.5–84.5 °C (colorless needles from AcOEt–hexane); $[\alpha]_D^{28}$=−17.9° (c 1.00, $CHCl_3$); IR (KBr) 3030, 2908,

2868, 2112, 1496, 1452, 1359, 1269, 1062, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.34 (m, 1H, H-5′), 3.39 (dd, J= 9.1, 9.5 Hz, 1H, H-3′), 3.46 (dd, J=8.1, 9.5 Hz, 1H, H-2′), 3.48 (s, 3H, OCH_3), 3.49 (m, 1H, H-5), 3.64–3.78 (m, 7H, H-3, H-4, H-6a, H-6b, H-4′, H-6′a, H-6′b), 3.80 (dd, J=7.2, 8.9 Hz, 1H, H-2), 4.37 (d, J=7.2 Hz, 1H, H-1), 4.53–4.59 (m, 4H, OC*H*Ph×4), 4.61–4.66 (m, 2H, OC*H*Ph×2), 4.71 (d, J=8.1 Hz, 1H, H-1′), 4.78 (d, J=10.5 Hz, 1H, OC*H*Ph), 4.79 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.81 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.85 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.89 (d, J= 10.6 Hz, 1H, OC*H*Ph), 4.95 (d, J=10.6 Hz, 1H, OC*H*Ph), 7.16–7.19 (m, 4H, Ar-H), 7.22–7.38 (m, 26H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.3, 66.6, 68.3, 68.8, 73.5, 73.6, 74.8, 75.0, 75.2, 75.3, 75.4, 77.8, 78.3, 78.9, 83.4, 85.1, 101,1 (C-1′), 102.4 (C-1), 127.5, 127.6, 127.65, 127.67, 127.72, 127.77, 127.81, 127.90, 127.94, 128.0, 128.3, 128.4, 137.9, 138.0, 138.2, 138.3, 138.4; FAB-HRMS m/z calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4072; Anal. calcd for: $C_{55}H_{59}N_3O_{10}$: C, 71.64; H, 6.45; N, 4.56, found C, 71.58; H, 6.49; N, 4.61. Data for α-anomer (**18**α):[12b] TLC R_f=0.66 (2:1 hexane/AcOEt); $[\alpha]_D^{28}$ = +67.4° (c 1.00, $CHCl_3$); IR (film) 3030, 2918, 2864, 2104, 1496, 1454, 1359, 1211, 1126, 1055, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.26 (d, J=1.6 Hz, 2H, H-6′), 3.34 (dd, J=3.7, 10.4 Hz, 1H, H-2′), 3.48 (ddd, J=2.0, 3.7, 9.4 Hz, 1H, H-5), 3.57 (s, 3H, OCH_3), 3.61 (dd, J=9.0, 9.2 Hz, 1H, H-3), 3.64–3.76 (m, 5H, H-2, H-4, H-6a, H-6b, H-4′), 3.91 (dd, J=8.9, 10.4 Hz, 1H, H-3′), 3.98 (m, 1H, H-5′), 4.28 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.38 (d, J= 7.4 Hz, 1H, H-1), 4.43 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.53 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.55 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.56 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.64 (d, J= 12.2 Hz, 1H, OC*H*Ph), 4.72 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.74 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.79 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.85 (d, J=11.3 Hz, 1H, OC*H*Ph), 4.87 (d, J= 11.3 Hz, 1H, OC*H*Ph), 4.91 (d, J=10.8 Hz, 1H, OC*H*Ph), 5.58 (d, J=3.7 Hz, 1H, H-1′), 7.06–7.08 (m, 4H, Ar-H), 7.12–7.18 (m, 3H, Ar-H), 7.22–7.36 (m, 23H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.2, 63.3, 67.6, 68.5, 70.4, 73.4, 73.5, 74.8, 74.9, 75.3, 75.8, 76.3, 77.2, 78.1, 78.5, 80.0, 83.1, 96.7 (C-1′), 104.5 (C-1), 127.4, 127.50, 127.54, 127.6, 127.68, 127.73, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 137.69, 137.72, 137.8, 137.91, 137.94, 138.3; FAB-HRMS m/z calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4110.

4.3.5. Methyl 3-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (20). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 2 h) employing diphenyl phosphate **2a** (70.8 mg, 0.10 mmol), alcohol **14** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **20** (81.7 mg, 89%, α:β=1:>99) was obtained as a colorless oil from the crude product (108.5 mg) after column chromatography (silica gel 6 g, 5:1 hexane/AcOEt). The anomeric ratio of the product was determined by HPLC analysis [eluent, 5:1 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (α-anomer)=29.9 min, t_R (β-anomer)=36.3 min]. The α- and β-glycosides were separated by flash column chromatography with 20:1 toluene/AcOEt. Data for β-anomer (**20**β): TLC R_f=0.42 (2:1 hexane/AcOEt), 0.28 (10:1 toluene/AcOEt); $[\alpha]_D^{16}$ = −7.13° (c 1.17, $CHCl_3$); IR ($CHCl_3$) 3024, 2914, 2870, 2112, 1454, 1358, 1273, 1091 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.32 (s, 3H, OCH_3), 3.38–3.43 (m, 3H, H-2′, H-4′, H-5′), 3.48 (dd, J= 6.6, 9.5 Hz, 1H, H-6a), 3.51 (dd, J=6.2, 9.5 Hz, 1H, H-6b), 3.66–3.71 (m, 2H, H-3′, H-6′a), 3.74 (dd, J=3.9, 11.0 Hz, 1H, H-6′b), 3.93 (dd, J=6.2, 6.6 Hz, 1H, H-5), 4.00 (brd, J=3.0 Hz, 1H, H-4), 4.06 (dd, J=3.6, 10.1 Hz, 1H, H-2), 4.19 (dd, J=3.0, 10.1 Hz, 1H, H-3), 4.38 (d, J=11.8 Hz, 1H, OC*H*Ph), 4.46 (d, J=11.8 Hz, 1H, OC*H*Ph), 4.49 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.57–4.61 (m, 5H, H-1, OC*H*Ph×4), 4.73 (m, 1H, H-1′), 4.80 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.81 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.88 (d, J= 10.9 Hz, 1H, OC*H*Ph), 4.90 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.95 (d, J=11.4 Hz, 1H, OC*H*Ph), 7.18 (m, 2H, Ar-H), 7.20–7.38 (m, 26H, Ar-H), 7.42 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.3, 67.1, 68.5, 69.1, 69.2, 73.4, 73.5, 73.6, 74.7, 75.05, 75.14, 75.5, 77.2, 77.4, 77.7, 83.0, 98.3 (C-1), 102.7 (C-1′), 127.5, 127.59, 127.64, 127.7, 127.79, 127.82, 127.84, 127.9, 128.2, 128.3, 128.35, 128.40, 128.42, 128.5, 137.95, 138.03, 138.10, 138.12, 138.4, 138.7; FAB-HRMS m/z calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4136; Anal. calcd for: $C_{55}H_{59}N_3O_{10}$: C, 71.64; H, 6.45; N, 4.56, found C, 71.67; H, 6.49; N, 4.56. Data for α-anomer (**20**α): TLC R_f=0.44 (2:1 hexane/AcOEt), 0.33 (10:1 toluene/AcOEt); $[\alpha]_D^{24}$ = +66.5° (c 0.95, $CHCl_3$); IR ($CHCl_3$) 3022, 2914, 2870, 2112, 1454, 1358, 1209, 1091 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.33 (s, 3H, OCH_3), 3.50–3.57 (m, 4H, H-6a, H-6b, H-2′, H-6′a), 3.62 (dd, J=2.8, 11.1 Hz, 1H, H-6′b), 3.79 (dd, J=9.4, 9.6 Hz, 1H, H-4′), 3.90 (dd, J=6.5, 6.6 Hz, 1H, H-5), 3.99-4.03 (m, 2H, H-2, H-4), 4.05 (dd, J=9.4, 9.8 Hz, 1H, H-3′), 4.16–4.19 (m, 2H, H-3, H-5′), 4.35 (d, J=11.9 Hz, 1H, OC*H*Ph), 4.41 (d, J=11.9 Hz, 1H, OC*H*Ph), 4.489 (d, J=11.9 Hz, 1H, OC*H*Ph), 4.490 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.562 (d, J=11.7 Hz, 1H, OC*H*Ph), 4.564 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.60 (d, J=11.9 Hz, 1H, OC*H*Ph), 4.70 (d, J= 3.6 Hz, 1H, H-1), 4.72 (d, J=11.7 Hz, 1H, OC*H*Ph), 4.77 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.82 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.87 (d, J=10.8 Hz, 1H, OC*H*Ph), 5.06 (d, J= 11.2 Hz, 1H, OC*H*Ph), 5.21 (d, J=3.5 Hz, 1H, H-1′), 7.11 (m, 2H, Ar-H), 7.18–7.20 (m, 3H, Ar-H), 7.22–7.35 (m, 25H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.2, 63.7, 68.1, 68.8, 69.0, 70.5, 73.3, 73.4, 74.4, 74.7, 74.8, 75.1, 75.3, 78.3, 80.2, 94.7 (C-1′), 98.4 (C-1), 127.5, 127.55, 127.62, 127.71, 127.74, 127.8, 128.0, 128.1, 128.2, 128.25, 128.28, 128.36, 128.39, 137.87, 137.92, 138.1, 138.3, 138.6; FAB-HRMS m/z calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4097.

4.3.6. Methyl 4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-galactopyranoside (21). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 2 h) employing diphenyl phosphate **2a** (70.8 mg, 0.10 mmol), alcohol **15** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **21** (82.5 mg, 90%, α:β=5:95) was obtained as a colorless oil from the crude product (100.6 mg) after column chromatography (silica gel 8 g, 4:1 hexane/AcOEt). The anomeric ratio of the product was determined by HPLC analysis [eluent, 4:1 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (α-anomer)=12.4 min, t_R (β-anomer)=15.5 min]. The α- and β-glycosides were separated by flash column

chromatography with 15:1 toluene/AcOEt. Data for β-anomer (**21**β): TLC R_f=0.46 (2:1 hexane/AcOEt), 0.34 (10:1 toluene/AcOEt); $[\alpha]_D^{19}$=+3.32° (*c* 0.74, $CHCl_3$); IR ($CHCl_3$) 3020, 2930, 2868, 2114, 1454, 1358, 1277, 1089 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.27 (ddd, *J*=1.9, 3.9, 9.9 Hz, 1H, H-5′), 3.34 (dd, *J*=8.8, 9.8 Hz, 1H, H-3′), 3.37 (s, 3H, OC*H*$_3$), 3.40 (dd, *J*=7.6, 9.8 Hz, 1H, H-2′), 3.58–3.65 (m, 4H, H-6a, H-4′, H-6′a, H-6′b), 3.73 (dd, *J*=4.7, 10.5 Hz, 1H, H-6b), 3.90–3.94 (m, 2H, H-3, H-5), 4.13 (dd, *J*=3.7, 10.1 Hz, 1H, H-2), 4.16 (brd, *J*=3.0 Hz, 1H, H-4), 4.37 (d, *J*=12.0 Hz, 1H, OC*H*Ph), 4.44 (d, *J*=12.0 Hz, 1H, OC*H*Ph), 4.48 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.52 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.54 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.64 (d, *J*=3.7 Hz, 1H, H-1), 4.67 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.69 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.73 (d, *J*=7.6 Hz, 1H, H-1′), 4.77–4.80 (m, 2H, OC*H*Ph×2), 4.84 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.91 (d, *J*=10.8 Hz, 1H, OC*H*Ph), 4.92 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 7.15 (m, 2H, Ar-H), 7.24–7.37 (m, 28H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.3, 66.6, 68.9, 69.4, 70.2, 73.2, 73.4, 73.5, 73.8, 74.3, 74.8, 75.0, 75.5, 76.6, 77.7, 78.4, 83.1, 98.8 (C-1), 101.6 (C-1′), 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.80, 127.82, 127.9, 128.0, 128.2, 128.27, 128.32, 128.36, 128.42, 128.44, 137.9, 138.05, 138.14, 138.58, 138.61, 138.9; FAB-HRMS *m/z* calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4102; Anal. calcd for: $C_{55}H_{59}N_3O_{10}$: C, 71.64; H, 6.45; N, 4.56, found C, 71.68; H, 6.55; N, 4.55. Data for α-anomer (**21**α): TLC R_f=0.43 (2:1 hexane/AcOEt), 0.40 (10:1 toluene/AcOEt); $[\alpha]_D^{18}$=+44.5° (*c* 0.21, $CHCl_3$); IR ($CHCl_3$) 3018, 2930, 2870, 2114, 1454, 1358, 1277, 1089 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.03 (dd, *J*=1.7, 11.1 Hz, 1H, H-6′a), 3.28 (dd, *J*=2.0, 11.1 Hz, 1H, H-6′b), 3.35 (dd, *J*=3.6, 9.2 Hz, 1H, H-2′), 3.36 (s, 3H, OC*H*$_3$), 3.54 (dd, *J*=10.4, 12.9 Hz, 1H, H-5), 3.75 (dd, *J*=9.4, 10.1 Hz, 1H, H-4′), 3.83–3.92 (m, 5H, H-2, H-3, H-6a, H-6b, H-3′), 4.18 (d, *J*=12.2 Hz, 1H, OC*H*Ph), 4.20 (d, *J*=2.9 Hz, 1H, H-4), 4.23 (ddd, *J*=1.7, 2.0, 10.1 Hz, 1H, H-5′), 4.43 (d, *J*=12.2 Hz, 1H, OC*H*Ph), 4.46 (d, *J*=12.2 Hz, 1H, OC*H*Ph), 4.52 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.55 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.69–4.74 (m, 4H, H-1, OC*H*Ph×3), 4.77 (d, *J*=11.9 Hz, 1H, OC*H*Ph), 4.80–4.82 (m, 2H, OC*H*Ph×2), 4.86 (d, *J*=10.6 Hz, 1H, OC*H*Ph), 4.94 (d, *J*=3.6 Hz, 1H, H-1′), 7.13 (m, 2H, Ar-H), 7.17–7.37 (m, 28H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.4, 64.1, 67.3, 67.5, 68.9, 70.7, 73.16, 73.19, 73.3, 73.6, 74.8, 74.9, 75.27, 75.33, 78.2, 80.4, 98.5, 98.6, 127.4, 127.5, 127.6, 127.66, 127.73, 127.8, 127.95, 127.99, 128.03, 128.26, 128.31, 128.33, 128.4, 128.5, 137.6, 137.9, 138.1, 138.2, 138.4, 138.7; FAB-HRMS *m/z* calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4136.

4.3.7. 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl *N*,*N*,*N*′,*N*′-tetramethylphosphorodiamidate (22). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 2 h) employing diphenyl phosphate **2a** (70.8 mg, 0.10 mmol), alcohol **16** (68.9 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.20 mL, 0.20 mmol). An anomeric mixture of disaccharide **22** (95.0 mg, 88%, α:β=7:93) was obtained as a colorless oil from the crude product (126.0 mg) after column chromatography (silica gel 8 g, 1:2 hexane/AcOEt). The anomeric ratio of the product was determined by ^1H NMR [integration of H1′, β-anomer (4.27 ppm), α-anomer (4.94 ppm)]. The α- and β-glycosides were separated by flash column chromatography with 1:2 hexane/AcOEt. Data for β-anomer (**22**β): TLC R_f=0.37 (1:3 hexane/AcOEt); $[\alpha]_D^{16}$=+2.06° (*c* 1.66, $CHCl_3$); IR ($CHCl_3$) 3018, 2978, 2114, 1730, 1452, 1358, 1107, 947 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.61 (d, J_{H-P}=10.4 Hz, 6H, N(C*H*$_3$)$_2$), 2.71 (d, J_{H-P}=10.1 Hz, 6H, N(C*H*$_3$)$_2$), 3.34 (dd, *J*=7.9, 9.8 Hz, 1H, H-2′), 3.36 (ddd, *J*=2.2, 4.1, 9.8 Hz, 1H, H-5′), 3.44 (dd, *J*=8.9, 9.8 Hz, 1H, H-3′), 3.58 (dd, *J*=8.9, 9.8 Hz, 1H, H-4′), 3.62 (dd, *J*=2.2, 11.2 Hz, 1H, H-6′a), 3.65 (dd, *J*=4.1, 11.2 Hz, 1H, H-6′b), 3.76 (dd, *J*=5.1, 11.1 Hz, 1H, H-6a), 4.14 (dd, *J*=2.5, 11.1 Hz, 1H, H-6b), 4.27 (d, *J*=7.9 Hz, 1H, H-1′), 4.45 (d, *J*=12.2 Hz, 1H, OC*H*Ph), 4.48 (ddd, *J*=2.5, 5.1, 10.1 Hz, 1H, H-5), 4.540 (d, *J*=12.2 Hz, 1H, OC*H*Ph), 4.541 (d, *J*=10.9 Hz, 1H, OC*H*Ph), 4.78 (d, *J*=10.9 Hz, 1H, OC*H*Ph), 4.79 (d, *J*=10.8 Hz, 1H, OC*H*Ph), 4.89 (d, *J*=10.8 Hz, 1H, OC*H*Ph), 5.39 (ddd, *J*=3.3, 10.3, 1.5 (J_{H-P}) Hz, 1H, H-2), 5.72 (dd, *J*=9.7, 10.2 Hz, 1H, H-4), 6.15 (dd, *J*=3.3, 8.1 (J_{H-P}) Hz, 1H, H-1), 6.19 (dd, *J*=9.7, 10.3 Hz, 1H, H-3), 7.16 (m, 2H, Ar-H), 7.25–7.52 (m, 22H, Ar-H), 7.87 (m, 2H, Ar-H), 7.94–7.97 (m, 4H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 36.4 (d, J_{C-P}=3.8 Hz), 36.5 (d, J_{C-P}=4.0 Hz), 66.3, 68.2, 68.4, 69.2, 70.0, 70.8, 71.5 (d, J_{C-P}=6.4 Hz), 73.4, 74.9, 75.1, 75.6, 77.6, 83.2, 92.0 (d, J_{C-P}=3.9 Hz, C-1), 102.1 (C-1′), 127.6, 127.7, 127.79, 127.84, 128.0, 128.29, 128.32, 128.33, 128.38, 128.42, 128.95, 129.03, 129.1, 129.7, 129.8, 129.9, 133.16, 133.22, 133.4, 137.87, 137.89, 138.0, 165.2, 165.4, 165.9; ^{31}P NMR (109 MHz, C_6D_6) δ 19.7; FAB-HRMS *m/z* calcd for $C_{58}H_{63}N_5O_{14}P$ $(M+H)^+$ 1084.4109, found 1084.4150; Anal. calcd for: $C_{58}H_{62}N_5O_{14}P$: C, 64.26; H, 5.76; N, 6.46, found C, 64.33; H, 5.83; N, 6.41. Data for α-anomer (**22**α): TLC R_f=0.25 (1:3 hexane/AcOEt); $[\alpha]_D^{17}$=+84.8° (*c* 1.13, $CHCl_3$); IR ($CHCl_3$) 3026, 2934, 2114, 1730, 1452, 1278 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.60 (d, J_{H-P}=10.1 Hz, 6H, N(C*H*$_3$)$_2$), 2.69 (d, J_{H-P}=10.0 Hz, 6H, N(C*H*$_3$)$_2$), 3.35 (dd, *J*=3.6, 10.2 Hz, 1H, H-2′), 3.45 (dd, *J*=1.4, 10.9 Hz, 1H, H-6′a), 3.58 (dd, *J*=3.2, 10.9 Hz, 1H, H-6′b), 3.65–3.72 (m, 3H, H-6a, H-4′, H-5′), 3.92 (dd, *J*=5.0, 11.3 Hz, 1H, H-6b), 4.02 (dd, *J*=8.4, 10.2 Hz, 1H, H-3′), 4.37 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.48 (ddd, *J*=1.9, 5.0, 10.3 Hz, 1H, H-5), 4.50 (d, *J*=11.1 Hz, 1H, OC*H*Ph), 4.51 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.80 (d, *J*=11.1 Hz, 1H, OC*H*Ph), 4.86 (d, *J*=11.3 Hz, 1H, OC*H*Ph), 4.88 (d, *J*=11.3 Hz, 1H, OC*H*Ph), 4.94 (d, *J*=3.6 Hz, 1H, H-1′), 5.38 (ddd, *J*=3.4, 10.3, 1.5 (J_{H-P}) Hz, 1H, H-2), 5.72 (dd, *J*=9.8, 10.3 Hz, 1H, H-4), 6.13 (dd, *J*=3.4, 8.1 (J_{H-P}) Hz, 1H, H-1), 6.16 (dd, *J*=9.8, 10.3 Hz, 1H, H-3), 7.18 (m, 2H, Ar-H), 7.24–7.50 (m, 22H, Ar-H), 7.87 (m, 2H, Ar-H), 7.93–7.95 (m, 4H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 36.4 (d, J_{C-P}=3.5 Hz), 36.6 (d, J_{C-P}=3.6 Hz), 63.4, 66.7, 68.1, 68.7, 70.1, 70.5, 70.8, 71.5 (d, J_{C-P}=6.5 Hz), 73.4, 74.9, 75.4, 78.2, 80.0, 92.2 (d, J_{C-P}=3.9 Hz, C-1), 98.4 (C-1′), 127.6, 127.7, 127.8, 128.1, 128.29, 128.33, 128.34, 128.38, 128.44, 128.9, 129.0, 129.1, 129.7, 129.8, 129.9, 133.2, 133.3, 133.4, 137.8, 138.0, 138.2, 165.0, 165.4, 166.0; ^{31}P NMR (109 MHz, C_6D_6) δ 19.4; FAB-HRMS *m/z* calcd for $C_{58}H_{63}N_5O_{14}P$ $(M+H)^+$ 1084.4109, found 1084.4100.

4.4. Glycosidations of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxygalactosyl diphenyl phosphate 4a

4.4.1. Methyl 6-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (25).[9] The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 0.2 h) employing diphenyl phosphate **4a** (70.8 mg, 0.10 mmol), alcohol **7** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **25** (79.4 mg, 86%, α:β=4:96) was obtained as a white solid from the crude product (108.0 mg) after column chromatography (silica gel 7 g, 5:1 hexane/AcOEt), along with propionate **26** (2.7 mg, 5%) as a colorless oil. The anomeric ratio of **25** was determined by HPLC analysis [eluent, 5:1 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (α-anomer)=20.5 min, t_R (β-anomer)=27.2 min]. The α- and β-glycosides were separated by flash column chromatography with 6:1 hexane/AcOEt. Data for β-anomer (**25**β):[9] mp 93.5–94.5 °C (colorless needles from AcOEt–hexane); TLC R_f=0.42 (2:1 hexane/AcOEt); $[\alpha]_D^{23}$=+0.79° (*c* 1.00, $CHCl_3$); IR (KBr) 3030, 2912, 2856, 2110, 1496, 1454, 1358, 1284, 1105, 1062 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.29 (dd, *J*=2.8, 10.4 Hz, 1H, H-3′), 3.36 (s, 3H, OC*H*$_3$), 3.44 (dd, *J*=6.1, 7.7 Hz, 1H, H-5′), 3.51–3.55 (m, 3H, H-2, H-4, H-6′a), 3.61 (dd, *J*=7.7, 9.9 Hz, 1H, H-6′b), 3.64 (dd, *J*=5.0, 10.9 Hz, 1H, H-6a), 3.79 (ddd, *J*=1.8, 5.0, 10.1 Hz, 1H, H-5), 3.85 (dd, *J*=8.2, 10.4 Hz, 1H, H-2′), 3.87 (m, 1H, H-4′), 3.98 (t, *J*=9.3 Hz, 1H, H-3), 4.07 (dd, *J*=1.8, 10.9 Hz, 1H, H-6b), 4.09 (d, *J*=8.2 Hz, 1H, H-1′), 4.40 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.43 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.53 (d, *J*=11.3 Hz, 1H, OC*H*Ph), 4.60 (d, *J*=3.5 Hz, 1H, H-1), 4.639 (d, *J*=11.3 Hz, 1H, OC*H*Ph), 4.640 (d, *J*=12.2 Hz, 1H, OC*H*Ph), 4.66 (d, *J*=11.7 Hz, 1H, OC*H*Ph), 4.70 (d, *J*=11.7 Hz, 1H, OC*H*Ph), 4.77 (d, *J*=12.2 Hz, 1H, OC*H*Ph), 4.80 (d, *J*=10.0 Hz, 1H, OC*H*Ph), 4.86 (d, *J*=11.3 Hz, 1H, OC*H*Ph), 4.90 (d, *J*=11.1 Hz, 1H, OC*H*Ph), 4.97 (d, *J*=10.0 Hz, 1H, OC*H*Ph), 7.24–7.38 (m, 30H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.1, 63.2, 68.27, 68.34, 69.8, 72.2, 72.4, 73.4, 73.52, 73.53, 74.6, 74.8, 75.7, 77.8, 79.9, 80.9, 82.1, 98.0 (C-1), 102.5 (C-1′), 127.5, 127.6, 127.8, 127.85, 127.86, 128.0, 128.05, 128.13, 128.2, 128.3, 128.42, 128.44, 128.5, 137.6, 137.8, 138.2, 138.4, 138.5, 138.8; FAB-HRMS *m*/*z* calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4093; Anal. calcd for: $C_{55}H_{59}N_3O_{10}$: C, 71.64; H, 6.45; N, 4.56, found C, 71.62; H, 6.51; N 4.55. Data for α-anomer (**25**α):[9] TLC R_f=0.48 (2:1 hexane/AcOEt); $[\alpha]_D^{21}$=+83.3° (*c* 1.00, $CHCl_3$); IR (film) 3030, 2916, 2108, 1496, 1454, 1358, 1259, 1159, 1095 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.33 (s, 3H, OC*H*$_3$), 3.49 (dd, *J*=6.1, 9.2 Hz, 1H, H-6′a), 3.51 (dd, *J*=9.0, 9.9 Hz, 1H, H-4), 3.53 (dd, *J*=3.6, 9.6 Hz, 1H, H-2), 3.56 (dd, *J*=7.9, 9.2 Hz, 1H, H-6′b), 3.69 (dd, *J*=1.2, 11.2 Hz, 1H, H-6a), 3.75 (ddd, *J*=1.2, 4.9, 9.9 Hz, 1H, H-5), 3.80 (dd, *J*=4.9, 11.2 Hz, 1H, H-6b), 3.83 (dd, *J*=3.5, 10.7 Hz, 1H, H-2′), 3.89 (dd, *J*=2.5, 10.7 Hz, 1H, H-3′), 3.93 (dd, *J*=6.1, 7.9 Hz, 1H, H-5′), 3.992 (br, 1H, H-4′), 3.994 (dd, *J*=9.0, 9.6 Hz, 1H, H-3), 4.37 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.44 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.53 (d, *J*=11.3 Hz, 1H, OC*H*Ph), 4.56 (d, *J*=11.0 Hz, 1H, OC*H*Ph), 4.58 (d, *J*=3.6 Hz, 1H, H-1), 4.649 (d, *J*=11.4 Hz, 1H, OC*H*Ph), 4.654 (d, *J*=12.0 Hz, 1H, OC*H*Ph), 4.71 (d, *J*=11.4 Hz, 1H, OC*H*Ph), 4.78 (d, *J*=12.0 Hz, 1H, OC*H*Ph), 4.80 (d, *J*=10.8 Hz, 1H, OC*H*Ph), 4.87 (d, *J*=11.3 Hz, 1H, OC*H*Ph), 4.88 (d, *J*=11.0 Hz, 1H, OC*H*Ph), 4.980 (d, *J*=10.8 Hz, 1H, OC*H*Ph), 4.982 (d, *J*=3.5 Hz, 1H, H-1′), 7.22–7.39 (m, 30H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.0, 59.8, 66.7, 68.6, 69.6, 69.9, 72.0, 73.35, 73.37, 73.39, 74.8, 74.9, 75.7, 76.6, 77.9, 80.0, 82.0, 97.9, 98.6, 127.6, 127.65, 127.66, 127.71, 127.72, 127.8, 127.87, 127.90, 128.0, 128.06, 128.07, 128.2, 128.36, 128.40, 128.5, 137.5, 137.9, 138.1, 138.27, 138.29, 138.8; FAB-HRMS *m*/*z* calcd for $C_{55}H_{59}N_3O_{10}Na$ $(M+Na)^+$ 944.4098, found 944.4079.

Data for methyl 2,3,4-tri-*O*-benzyl-6-*O*-propionyl-α-D-glucopyranoside (**26**): TLC R_f=0.45 (2:1 hexane/AcOEt); $[\alpha]_D^{25}$=+27.1° (*c* 1.00, $CHCl_3$); IR (film) 3030, 2918, 1738, 1454, 1190, 1072 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.11 (t, *J*=7.7 Hz, 3H, CH_2CH_3), 2.30 (m, 2H, CH_2CH_3), 3.36 (s, 3H, OC*H*$_3$), 3.47 (dd, *J*=8.9, 10.1 Hz, 1H, H-4), 3.53 (dd, *J*=3.5, 9.6 Hz, 1H, H-2), 3.82 (ddd, *J*=3.0, 3.9, 10.1 Hz, 1H, H-5), 4.01 (dd, *J*=8.9, 9.6 Hz, 1H, H-3), 4.26 (dd, *J*=3.9, 12.0 Hz, 1H, H-6a), 4.29 (dd, *J*=3.0, 12.0 Hz, 1H, H-6b), 4.56 (d, *J*=10.8 Hz, 1H, OC*H*Ph), 4.60 (d, *J*=3.5 Hz, 1H, H-1), 4.66 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.79 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.83 (d, *J*=10.8 Hz, 1H, OC*H*Ph), 4.88 (d, *J*=10.8 Hz, 1H, OC*H*Ph), 5.00 (d, *J*=10.8 Hz, 1H, OC*H*Ph), 7.26–7.36 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 9.0, 27.3, 55.1, 62.8, 68.6, 73.3, 75.0, 75.7, 77.4, 79.9, 82.0, 97.9 (C-1), 127.6, 127.8, 127.87, 127.92, 127.94, 128.0, 128.3, 128.38, 128.39, 137.8, 138.0, 138.5, 174.0; FAB-HRMS *m*/*z* calcd for $C_{31}H_{36}O_7Na$ $(M+Na)^+$ 543.2359, found 543.2333; Anal. calcd for: $C_{31}H_{36}O_7$: C, 71.52; H 6.97, found C, 71.40; H, 6.93.

4.4.2. Methyl 4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (27).[10] The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 0.5 h) employing diphenyl phosphate **4a** (70.8 mg, 0.10 mmol), alcohol **8** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **27** (82.8 mg, 90%, α:β=4:96) was obtained as a colorless oil from the crude product (110.6 mg) after column chromatography (silica gel 5 g, 5:1 hexane/AcOEt). The anomeric ratio of the product was determined by HPLC analysis [eluent, 5:1 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (α-anomer)=15.3 min, t_R (β-anomer)=22.8 min]. The α- and β-glycosides were separated by flash column chromatography with 6:1 hexane/AcOEt. Data for β-anomer (**27**β):[10] TLC R_f=0.49 (2:1 hexane/AcOEt); $[\alpha]_D^{25}$=−3.12° (*c* 2.51, $CHCl_3$); IR (film) 3030, 2868, 2112, 1496, 1454, 1361, 1099 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.13 (dd, *J*=2.8, 10.3 Hz, 1H, H-3′), 3.21 (dd, *J*=5.2, 8.2 Hz, 1H, H-5′), 3.30 (dd, *J*=5.2, 9.2 Hz, 1H, H-6′a), 3.37 (s, 3H, OC*H*$_3$), 3.47 (dd, *J*=3.7, 9.4 Hz, 1H, H-2), 3.48 (dd, *J*=8.2, 9.2 Hz, 1H, H-6′b), 3.70 (dd, *J*=1.5, 10.9 Hz, 1H, H-6a), 3.74 (dd, *J*=8.1, 10.3 Hz, 1H, H-2′), 3.76 (m, 1H, H-5), 3.849 (dd, *J*=8.9, 9.4 Hz, 1H, H-4), 3.852 (brd, *J*=2.8 Hz, 1H, H-4′), 3.91 (dd, *J*=9.3, 9.4 Hz, 1H, H-3), 3.94 (dd, *J*=3.2, 10.9 Hz, 1H, H-6b), 4.14 (d, *J*=8.1 Hz, 1H, H-1′), 4.22 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.33 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.43 (d, *J*=12.0 Hz, 1H, OC*H*Ph), 4.50 (d, *J*=11.3 Hz, 1H, OC*H*Ph), 4.58 (d, *J*=3.7 Hz, 1H, H-1), 4.61 (d, *J*=11.7 Hz, 1H, OC*H*Ph), 4.62 (d, *J*=

12.1 Hz, 1H, OC*H*Ph), 4.66 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.68 (d, J=11.7 Hz, 1H, OC*H*Ph), 4.74 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.80 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.88 (d, J=11.3 Hz, 1H, OC*H*Ph), 4.96 (d, J=10.7 Hz, 1H, OC*H*Ph), 7.13–7.38 (m, 30H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.2, 63.8, 67.9, 68.3, 69.7, 72.1, 73.2, 73.3, 73.4, 73.6, 74.7, 75.4, 76.7, 79.1, 80.1, 81.0, 98.3 (C-1), 101.2 (C-1′), 127.5, 127.62, 127.64, 127.68, 127.71, 127.76, 127.78, 127.83, 127.86, 127.91, 127.93, 128.0, 128.2, 128.32, 128.34, 128.4, 137.6, 138.0, 138.4, 138.6, 139.4; FAB-HRMS m/z calcd for $C_{55}H_{60}N_3O_{10}$ $(M+H)^+$ 922.4278, found 922.4290; Anal. calcd for: $C_{55}H_{59}N_3O_{10}$: C, 71.64; H, 6.45; N, 4.56, found C, 71.42; H, 6.54; N, 4.52. Data for α-anomer (**27**α):[10] TLC R_f=0.55 (2:1 hexane/AcOEt); $[\alpha]_D^{23}$=+47.5° (c 0.35, $CHCl_3$); IR (film) 3030, 2868, 2112, 1496, 1454, 1361, 1099 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.38 (s, 3H, OC*H*$_3$), 3.39 (m, 1H, H-6′a), 3.47 (dd, J=8.0, 8.6 Hz, 1H, H-6′b), 3.55 (dd, J=3.5, 9.6 Hz, 1H, H-2), 3.63 (dd, J=4.0, 11.1 Hz, 1H, H-6a), 3.66 (dd, J=2.2, 11.1 Hz, 1H, H-6b), 3.76–3.85 (m, 5H, H-4, H-5, H-2′, H-3′, H-5′), 3.96 (brs, 1H, H-4′), 4.05 (dd, J=8.4, 9.6 Hz, 1H, H-3), 4.23 (d, J=11.7 Hz, 1H, OC*H*Ph), 4.30 (d, J=11.7 Hz, 1H, OC*H*Ph), 4.43 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.49 (d, J=11.3 Hz, 1H, OC*H*Ph), 4.56 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.58 (d, J=3.5 Hz, 1H, H-1), 4.60 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.61 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.66 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.75 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.81 (d, J=11.3 Hz, 1H, OC*H*Ph), 4.87 (d, J=10.6 Hz, 1H, OC*H*Ph), 5.06 (d, J=10.6 Hz, 1H, OC*H*Ph), 5.70 (d, J=2.8 Hz, 1H, H-1′), 7.20–7.39 (m, 30H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.3, 59.5, 68.5, 69.5, 69.7, 70.0, 72.1, 73.0, 73.1, 73.3, 73.5, 73.7, 74.8, 75.0, 80.4, 81.9, 97.7, 98.1, 127.39, 127.42, 127.67, 127.73, 127.8, 127.9, 128.0, 128.16, 128.21, 128.24, 128.3, 128.35, 128.37, 128.47, 128.49, 137.6, 137.8, 138.0, 138.2, 138.4, 138.6; FAB-HRMS m/z calcd for $C_{55}H_{60}N_3O_{10}$ $(M+H)^+$ 922.4278, found 922.4301.

4.4.3. Methyl 4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (28). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 0.3 h) employing diphenyl phosphate **4a** (70.8 mg, 0.10 mmol), alcohol **23** (24.0 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **28** (55.0 mg, 81%, α:β=6:94) was obtained as a colorless oil from the crude product (82.5 mg) after column chromatography (silica gel 7 g, 7:1 hexane/AcOEt). The anomeric ratio of the product was determined by HPLC analysis [eluent, 5:1 hexane/THF; flow rate, 1.0 mL/min; t_R (α-anomer)=6.3 min, t_R (β-anomer)=7.4 min]. The α- and β-glycosides were separated by flash column chromatography with 8:1 hexane/AcOEt. Data for β-anomer (**28**β): TLC R_f=0.57 (2:1 hexane/AcOEt); $[\alpha]_D^{24}$=−33.8° (c 1.47, $CHCl_3$); IR (film) 2934, 2112, 1454, 1367, 1221, 1091, 1022 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (d, J=5.6 Hz, 3H, H-6), 1.33 (s, 3H, CC*H*$_3$), 1.44 (s, 3H, CC*H*$_3$), 3.34 (dd, J=3.0, 10.4 Hz, 1H, H-3′), 3.36 (s, 3H, OC*H*$_3$), 3.47 (m, 1H, H-5′), 3.53 (dd, J=5.3, 9.1 Hz, 1H, H-6′a), 3.60–3.66 (m, 3H, H-4, H-5, H-6′b), 3.73 (dd, J=8.1, 10.4 Hz, 1H, H-2′), 3.86 (d, J=3.0 Hz, 1H, H-4′), 4.09 (d, J=5.6 Hz, 1H, H-2), 4.25 (dd, J=5.6, 5.8 Hz, 1H, H-3), 4.42 (d, J=11.9 Hz, 1H, OC*H*Ph), 4.45 (d, J=11.9 Hz, 1H, OC*H*Ph), 4.57 (d, J=11.4 Hz, 1H, OC*H*Ph), 4.67 (d, J=12.6 Hz, 1H, OC*H*Ph), 4.70 (d, J=12.6 Hz, 1H, OC*H*Ph), 4.71 (d, J=8.1 Hz, 1H, H-1′), 4.84 (s, 1H, H-1), 4.89 (d, J=11.4 Hz, 1H, OC*H*Ph), 7.25–7.39 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.7, 26.4, 27.8, 54.8, 63.4, 64.1, 68.4, 72.6, 73.48, 73.50, 74.7, 76.0, 78.2, 78.5, 80.7, 97.9 (C-1), 100.5 (C-1′), 109.2, 127.6, 127.75, 127.78, 127.83, 128.1, 128.2, 128.4, 128.5, 137.76, 137.80, 138.5; FAB-HRMS m/z calcd for $C_{37}H_{46}N_3O_9$ $(M+H)^+$ 676.3236, found 676.3252; Anal. calcd for: $C_{37}H_{45}N_3O_9$: C, 65.76; H, 6.71; N, 6.22, found C, 65.65; H, 6.69; N, 6.17. Data for α-anomer (**28**α): TLC R_f=0.63 (2:1 hexane/AcOEt); $[\alpha]_D^{23}$=+80.8° (c 0.99, $CHCl_3$); IR (film) 2986, 2934, 2112, 1496, 1454, 1367, 1221, 1091 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (s, 3H, CC*H*$_3$), 1.34 (d, J=6.3 Hz, 3H, H-6), 1.37 (s, 3H, CC*H*$_3$), 3.32 (dd, J=6.4, 10.1 Hz, 1H, H-4), 3.35 (s, 3H, OC*H*$_3$), 3.50 (dd, J=4.6, 8.4 Hz, 1H, H-6′a), 3.67 (dd, J=8.4, 9.5 Hz, 1H, H-6′b), 3.69 (dq, J=10.1, 6.3 Hz, 1H, H-5), 3.89 (dd, J=3.4, 10.7 Hz, 1H, H-2′), 3.95 (dd, J=2.5, 10.7 Hz, 1H, H-3′), 4.07–4.10 (m, 2H, H-2, H-3), 4.16 (brs, 1H, H-4′), 4.24 (dd, J=4.6, 9.5 Hz, 1H, H-5′), 4.40 (d, J=11.9 Hz, 1H, OC*H*Ph), 4.50 (d, J=11.9 Hz, 1H, OC*H*Ph), 4.57 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.64 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.72 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.83 (s, 1H, H-1), 4.89 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.98 (d, J=3.4 Hz, 1H, H-1′), 7.24–7.40 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.5, 26.4, 27.9, 54.8, 60.1, 64.8, 67.5, 69.0, 71.9, 73.1, 73.5, 74.9, 76.0, 76.9, 80.4, 97.9, 98.8, 109.1, 127.5, 127.8, 127.9, 128.0, 128.2, 128.45, 128.49, 137.6, 138.0, 138.6; FAB-HRMS m/z calcd for $C_{37}H_{46}N_3O_9$ $(M+H)^+$ 676.3234, found 676.3232.

4.4.4. Methyl 2-azido-4-*O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl)-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (29). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 0.5 h) employing diphenyl phosphate **4a** (70.8 mg, 0.10 mmol), alcohol **24** (43.9 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **29** (73.7 mg, 86%, α:β=8:92) was obtained as a colorless oil from the crude product (100.3 mg) after column chromatography (silica gel 6 g, 30:1 toluene/AcOEt). The anomeric ratio of the product was determined by HPLC analysis [eluent, 5:1 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (α-anomer)=10.2 min, t_R (β-anomer)=14.8 min]. The α- and β-glycosides were separated by flash column chromatography with 30:1 toluene/AcOEt. Data for β-anomer (**29**β): TLC R_f=0.53 (2:1 hexane/AcOEt), 0.53 (10:1 toluene/AcOEt); $[\alpha]_D^{22}$=−39.7° (c 0.93, $CHCl_3$); IR (film) 3030, 2868, 2110, 1496, 1454, 1361, 1280, 1059 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.15 (dd, J=2.8, 10.4 Hz, 1H, H-3′), 3.23 (dd, J=5.1, 8.4 Hz, 1H, H-5′), 3.29 (dd, J=5.1, 9.0 Hz, 1H, H-6′a), 3.35 (dd, J=7.6, 9.8 Hz, 1H, H-2), 3.38 (dd, J=8.3, 9.8 Hz, 1H, H-3), 3.43 (ddd, J=1.2, 3.5, 9.8 Hz, 1H, H-5), 3.48 (dd, J=8.4, 9.0 Hz, 1H, H-6′b), 3.55 (s, 3H, OC*H*$_3$), 3.75 (dd, J=8.2, 10.4 Hz, 1H, H-2′), 3.80 (dd, J=1.2, 11.1 Hz, 1H, H-6a), 3.87 (d, J=2.8 Hz, 1H, H-4′), 3.92 (dd, J=3.5, 11.1 Hz, 1H, H-6b), 4.01 (dd, J=8.3, 9.8 Hz, 1H, H-4), 4.12 (d, J=7.6 Hz, 1H, H-1), 4.23 (d, J=11.8 Hz, 1H, OC*H*Ph), 4.25 (d, J=8.2 Hz, 1H, H-1′), 4.32 (d, J=11.8 Hz, 1H, OC*H*Ph), 4.47 (d, J=12.1 Hz, 1H,

OC*H*Ph), 4.51 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.62 (d, J=11.8 Hz, 1H, OC*H*Ph), 4.65 (d, J=10.3 Hz, 1H, OC*H*Ph), 4.68 (d, J=11.8 Hz, 1H, OC*H*Ph), 4.69 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.89 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.98 (d, J=10.3 Hz, 1H, OC*H*Ph), 7.12–7.38 (m, 25H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 57.1, 63.8, 65.8, 67.7, 68.0, 72.20, 72.22, 73.2, 73.3, 73.4, 74.8, 74.9, 75.3, 76.1, 80.8, 81.4, 101.1 (C-1′), 102.8 (C-1), 127.4, 127.5, 127.66, 127.74, 127.8, 127.9, 128.0, 128.2, 128.3, 128.35, 128.39, 128.5, 137.6, 137.9, 138.1, 138.2, 138.6; FAB-HRMS m/z calcd for $C_{48}H_{53}N_6O_9$ $(M+H)^+$ 857.3874, found 857.3879; Anal. calcd for: $C_{48}H_{52}N_6O_9$: C, 67.27; H, 6.12; N, 9.81, found C, 67.36; H, 6.15; N, 9.89. Data for α-anomer (**29**α): TLC R_f=0.59 (2:1 hexane/AcOEt), 0.67 (10:1 toluene/AcOEt); $[\alpha]_D^{22}=+27.4°$ (c 1.07, $CHCl_3$); IR (film) 3030, 2868, 2110, 1496, 1454, 1361, 1280, 1059 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.39–3.42 (m, 2H, H-2, H-6′a), 3.46 (dd, J=6.4, 9.0 Hz, 1H, H-6′b), 3.49 (m, 1H, H-5), 3.51 (dd, J=9.1, 9.5 Hz, 1H, H-3), 3.57 (s, 3H, OCH_3), 3.66 (dd, J=5.0, 11.0 Hz, 1H, H-6a), 3.74 (dd, J=2.3, 11.0 Hz, 1H, H-6b), 3.76 (dd, J=2.3, 10.9 Hz, 1H, H-3′), 3.81 (dd, J=3.7, 10.9 Hz, 1H, H-2′), 3.83 (dd, J=9.1, 9.2 Hz, 1H, H-4), 3.86 (t, J=6.4 Hz, 1H, H-5′), 3.95 (brs, 1H, H-4′), 4.22 (d, J=8.0 Hz, 1H, H-1), 4.28 (d, J=11.7 Hz, 1H, OC*H*Ph), 4.36 (d, J=11.7 Hz, 1H, OC*H*Ph), 4.46 (d, J=12.4 Hz, 1H, OC*H*Ph), 4.49 (d, J=11.3 Hz, 1H, OC*H*Ph), 4.572 (d, J=12.4 Hz, 1H, OC*H*Ph), 4.574 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.64 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.80 (d, J=11.3 Hz, 1H, OC*H*Ph), 4.84 (d, J=10.4 Hz, 1H, OC*H*Ph), 5.00 (d, J=10.4 Hz, 1H, OC*H*Ph), 5.63 (d, J=3.7 Hz, 1H, H-1′), 7.21–7.39 (m, 25H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 57.0, 59.5, 66.7, 68.5, 69.6, 70.2, 72.0, 72.9, 73.3, 73.4, 73.5, 74.6, 74.76, 74.78, 83.7, 97.9 (C-1′), 102.9 (C-1), 127.5, 127.6, 127.7, 127.78, 127.80, 127.9, 128.2, 128.3, 128.4, 128.49, 128.51, 137.5, 137.7, 137.8, 138.2, 138.3; FAB-HRMS m/z calcd for $C_{48}H_{53}N_6O_9$ $(M+H)^+$ 857.3874, found 857.3863.

4.5. Glycosidations of 3,4,6-tri-*O*-acetyl-2-azido-2-deoxyglycosyl diphenyl phosphates 2b and 4b

4.5.1. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[1-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-glucopyranosyl)iminopropyl]-α-D-glucopyranoside (30). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −65 °C, 4 h) employing diphenyl phosphate **2b** (56.3 mg, 0.10 mmol), alcohol **7** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). A mixture of imidate **30** and disaccharide **31** (79.7 mg) was obtained as a colorless oil from the crude product (106.9 mg) after short column chromatography (silica gel 3 g, 2:1 hexane/AcOEt with 1% Et_3N). The anomeric ratio of the products was determined by HPLC analysis [eluent, 5:1:1 hexane/AcOEt/THF; flow rate, 1.0 mL/min; t_R (**30**α)=9.6 min, t_R (**31**α)=10.3 min, t_R (**31**β)=11.1 min, t_R (**30**β)=11.8 min]. The mixture was purified by flash column chromatography (silica gel 6 g, 3:1 hexane/AcOEt with 1% Et_3N) to give α-imidate **30**α (65.5 mg, 79%) as a colorless oil, along with an anomeric mixture of disaccharide **31** (3.4 mg, 4%, α:β=14:86) as a colorless oil. The α- and β-glycosides of disaccharide **31** were separated by flash column chromatography with 15:1 toluene/acetone. Data for α-anomer (**30**α): TLC R_f=0.46 (1:1 hexane/AcOEt); $[\alpha]_D^{23}=+87.7°$ (c 2.01, $CHCl_3$); IR (film) 2922, 2106, 1751, 1660, 1454, 1367, 1228, 1049 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (t, J=7.6 Hz, 3H, CH_2CH_3), 2.01 (s, 3H, CH_3CO), 2.06 (s, 3H, CH_3CO), 2.08 (s, 3H, CH_3CO), 2.35 (q, J=7.6 Hz, 2H, CH_2CH_3), 3.41 (s, 3H, OCH_3), 3.52 (dd, J=4.1, 10.2 Hz, 1H, H-2′), 3.55 (dd, J=3.5, 9.6 Hz, 1H, H-2), 3.61 (dd, J=8.9, 10.1 Hz, 1H, H-4), 3.90 (ddd, J=1.5, 4.0, 10.1 Hz, 1H, H-5), 3.95 (m, 1H, H-6a), 4.01 (dd, J=8.9, 9.6 Hz, 1H, H-3), 4.22–4.26 (m, 3H, H-6b, H-5′, H-6′a), 4.42 (dd, J=1.7, 12.3 Hz, 1H, H-6′b), 4.60 (d, J=3.5 Hz, 1H, H-1), 4.61 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.67 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.81 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.84 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.85 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.99 (d, J=10.8 Hz, 1H, OC*H*Ph), 5.08 (t, J=9.6 Hz, 1H, H-4′), 5.22 (d, J=4.1 Hz, 1H, H-1′), 5.63 (dd, J=9.6, 10.2 Hz, 1H, H-3′), 7.26–7.38 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.6, 20.6, 20.69, 20.73, 23.0, 55.2, 62.1, 62.2, 64.6, 68.0, 68.7, 69.2, 71.4, 73.4, 75.1, 75.8, 77.6, 80.0, 82.0, 83.0 (C-1′), 98.1 (C-1), 127.6, 127.8, 127.9, 128.0, 128.06, 128.11, 128.39, 128.44, 137.9, 138.1, 138.6, 169.7, 169.9, 170.3, 170.6; FAB-HRMS m/z calcd for $C_{43}H_{53}N_4O_{13}$ $(M+H)^+$ 833.3609, found 833.3600; Anal. calcd for: $C_{43}H_{52}N_4O_{13}$: C, 62.01; H, 6.30; N, 6.73, found C, 61.85; H, 6.23; N, 6.64. Data for β-anomer (**30**β): TLC R_f=0.40 (1:1 hexane/AcOEt); $[\alpha]_D^{21}=+9.07°$ (c 0.45, $CHCl_3$); IR (film) 2924, 2112, 1751, 1657, 1454, 1365, 1230, 1047 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (t, J=7.4 Hz, 3H, CH_2CH_3), 2.01 (s, 3H, CH_3CO), 2.02 (s, 3H, CH_3CO), 2.09 (s, 3H, CH_3CO), 2.34 (dq, J=14.6, 7.4 Hz, 1H, C*H*CH_3), 2.36 (dq, J=14.6, 7.4 Hz, 1H, C*H*CH_3), 3.37 (s, 3H, OCH_3), 3.515 (dd, J=8.4, 9.4 Hz, 1H, H-2′), 3.523 (dd, J=9.0, 10.1 Hz, 1H, H-4), 3.54 (dd, J=3.6, 9.5 Hz, 1H, H-2), 3.75 (ddd, J=2.1, 5.6, 9.7 Hz, 1H, H-5′), 3.87 (ddd, J=1.8, 4.7, 10.1 Hz, 1H, H-5), 4.01 (dd, J=9.0, 9.5 Hz, 1H, H-3), 4.09 (dd, J=2.1, 12.3 Hz, 1H, H-6′a), 4.18 (dd, J=5.6, 12.3 Hz, 1H, H-6′b), 4.30 (dd, J=1.8, 12.2 Hz, 1H, H-6a), 4.42 (dd, J=4.7, 12.2 Hz, 1H, H-6b), 4.51 (d, J=8.4 Hz, 1H, H-1′), 4.56 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.61 (d, J=3.6 Hz, 1H, H-1), 4.67 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.80 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.82 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.87 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.99 (d, J=10.8 Hz, 1H, OC*H*Ph), 5.00 (dd, J=8.2, 9.7 Hz, 1H, H-4′), 5.04 (dd, J=8.2, 9.4 Hz, 1H, H-3′), 7.26–7.37 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.8, 20.6, 20.68, 20.74, 23.9, 55.1, 62.6, 64.6, 65.8, 68.8, 73.0, 73.4, 73.7, 75.1, 75.9, 78.0, 80.0, 82.1, 87.8 (C-1′), 98.0 (C-1), 127.7, 127.8, 127.88, 127.93, 128.07, 128.09, 128.41, 128.43, 128.5, 138.1, 138.2, 138.7, 169.7, 170.1, 170.6, 171.9; FAB-HRMS m/z calcd for $C_{43}H_{53}N_4O_{13}$ $(M+H)^+$ 833.3609, found 833.3580.

Data for methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-glucopyranosyl)-α-D-glucopyranoside (**31**). Data for β-anomer (**31**β): TLC R_f=0.40 (1:1 hexane/AcOEt), 0.52 (5:1 toluene/acetone); $[\alpha]_D^{17}=-1.41°$ (c 1.58, $CHCl_3$); IR (film) 2930, 2112, 1753, 1454, 1365, 1228, 1049 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01 (s, 3H, CH_3CO), 2.04 (s, 3H, CH_3CO), 2.08 (s, 3H, CH_3CO), 3.38 (s, 3H, OCH_3), 3.52 (dd, J=9.2, 10.1 Hz, 1H, H-4), 3.52–3.55 (m, 2H, H-2, H-2′), 3.57 (ddd, J=2.4, 3.6, 9.5 Hz, 1H, H-5′), 3.70 (dd, J=4.7, 10.9 Hz, 1H, H-6a), 3.82 (ddd, J=1.7, 4.7, 10.1 Hz, 1H, H-5), 4.00 (dd, J=9.2, 9.3 Hz, 1H, H-3), 4.090 (dd, J=1.7, 10.9 Hz, 1H, H-6b), 4.094 (dd, J=

2.4, 12.1 Hz, 1H, H-6′a), 4.22 (dd, J=3.6, 12.1 Hz, 1H, H-6′b), 4.23 (d, J=8.1 Hz, 1H, H-1′), 4.61 (d, J=3.5 Hz, 1H, H-1), 4.62 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.65 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.79 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.82 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.94 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.96–5.00 (m, 3H, H-3′, H-4′, OC*H*Ph), 7.26–7.37 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.5, 20.61, 20.63, 55.3, 61.8, 63.8, 68.4, 68.7, 69.7, 71.7, 72.6, 73.4, 74.8, 75.7, 77.6, 79.8, 82.0, 98.2 (C-1), 102.0 (C-1′), 127.6, 127.7, 127.90, 127.93, 128.1, 128.2, 128.35, 128.43, 128.5, 138.1, 138.3, 138.7, 169.5, 169.9, 170.5; FAB-HRMS *m/z* calcd for $C_{40}H_{47}N_3O_{13}Na$ $(M+Na)^+$ 800.3007, found 800.3033; Anal. calcd for: $C_{40}H_{47}N_3O_{13}$: C, 61.77; H, 6.09; N, 5.40, found C, 61.64; H, 6.08; N, 5.31. Data for α-anomer (**31**α): TLC R_f=0.42 (1:1 hexane/AcOEt), 0.56 (5:1 toluene/acetone); $[\alpha]_D^{20}=+119.6°$ (*c* 1.28, $CHCl_3$); IR (film) 3030, 2932, 2108, 1751, 1454, 1367, 1226, 1047 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H, CH_3CO), 2.03 (s, 3H, CH_3CO), 2.08 (s, 3H, CH_3CO), 3.30 (dd, J=3.4, 10.7 Hz, 1H, H-2′), 3.39 (s, 3H, OCH_3), 3.53 (dd, J=3.5, 9.8 Hz, 1H, H-2), 3.54 (dd, J=8.7, 10.2 Hz, 1H, H-4), 3.68 (m, 1H, H-6a), 3.77–3.81 (m, 2H, H-5, H-6b), 3.92 (ddd, J=2.2, 4.3, 10.1 Hz, 1H, H-5′), 3.99 (dd, J=2.2, 12.5 Hz, 1H, H-6′a), 4.01 (dd, J=8.7, 9.8 Hz, 1H, H-3), 4.15 (dd, J=4.3, 12.5 Hz, 1H, H-6′b), 4.59 (d, J=3.5 Hz, 1H, H-1), 4.62 (d, J=11.5 Hz, 1H, OC*H*Ph), 4.66 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.78 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.81 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.97 (d, J=11.5 Hz, 1H, OC*H*Ph), 4.99 (d, J=11.2 Hz, 1H, OC*H*Ph), 5.00 (dd, J=9.4, 10.1 Hz, 1H, H-4′), 5.04 (d, J=3.4 Hz, 1H, H-1′), 5.40 (dd, J=9.4, 10.7 Hz, 1H, H-3′), 7.26–7.37 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.57, 20.64, 20.7, 55.2, 61.0, 61.7, 66.7, 67.5, 68.5, 69.9, 70.3, 73.4, 74.9, 75.7, 77.5, 80.0, 82.0, 97.95 (C-1′), 98.04 (C-1), 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.37, 128.42, 138.1, 138.3, 138.7, 169.6, 169.9, 170.5; FAB-HRMS *m/z* calcd for $C_{40}H_{47}N_3O_{13}Na$ $(M+Na)^+$ 800.3007, found 800.3034.

4.5.2. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[1-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl)iminopropyl]-α-D-glucopyranoside (32). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −65 °C, 3 h) employing diphenyl phosphate **4b** (56.3 mg, 0.10 mmol), alcohol **7** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). A mixture of imidate **32** and disaccharide **33** (80.3 mg) was obtained as a colorless oil from the crude product (102.4 mg) after short column chromatography (silica gel 3 g, 2:1 hexane/AcOEt with 1% Et_3N). The anomeric ratio of the products was determined by HPLC analysis [eluent, 4:1 hexane/THF; flow rate, 1.0 mL/min; t_R (**32**α)=19.3 min, t_R (**33**α)=21.7 min, t_R (**33**β)=26.6 min, t_R (**32**β)=30.4 min]. The mixture was purified by flash column chromatography (silica gel 6 g, 4:1 hexane/acetone with 1% Et_3N) to give α-imidate **32**α (56.4 mg, 68%) as a colorless oil, along with an anomeric mixture of disaccharide **33** (6.8 mg, 9%, α:β=3:97) as a white solid. The α- and β-glycosides of disaccharide **33** were separated by flash column chromatography with 1:1 hexane/Et_2O. Data for α-anomer (**32**α): TLC R_f=0.47 (1:1 hexane/AcOEt); $[\alpha]_D^{22}=+72.7°$ (*c* 1.50, $CHCl_3$); IR (film) 2916, 2108, 1751, 1662, 1454, 1371, 1228, 1078 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (t, J=7.6 Hz, 3H, CH_2CH_3), 1.99 (s, 3H, CH_3CO), 2.05 (s, 3H, CH_3CO), 2.15 (s, 3H, CH_3CO), 2.35 (q, J=7.6 Hz, 2H, CH_2CH_3), 3.40 (s, 3H, OCH_3), 3.55 (dd, J=3.6, 9.6 Hz, 1H, H-2), 3.60 (dd, J=9.0, 10.0 Hz, 1H, H-4), 3.81 (dd, J=4.0, 10.8 Hz, 1H, H-2′), 3.88 (ddd, J=1.6, 4.3, 10.0 Hz, 1H, H-5), 3.97 (dd, J=6.8, 11.3 Hz, 1H, H-6′a), 4.01 (dd, J=9.0, 9.6 Hz, 1H, H-3), 4.04 (dd, J=6.6, 11.3 Hz, 1H, H-6′b), 4.23 (dd, J=4.3, 12.1 Hz, 1H, H-6a), 4.36 (dd, J=1.6, 12.1 Hz, 1H, H-6b), 4.39 (ddd, J=0.7, 6.6, 6.8 Hz, 1H, H-5′), 4.59 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.61 (d, J=3.6 Hz, 1H, H-1), 4.68 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.81 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.83 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.85 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.99 (d, J=10.7 Hz, 1H, OC*H*Ph), 5.24 (d, J=4.0 Hz, 1H, H-1′), 5.44 (dd, J=0.7, 3.3 Hz, 1H, H-4′), 5.47 (dd, J=3.3, 10.8 Hz, 1H, H-3′), 7.26–7.38 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.6, 20.6, 20.66, 20.70, 23.0, 55.2, 58.6, 62.0, 64.5, 67.0, 68.0, 68.7, 69.3, 73.4, 75.2, 75.8, 77.7, 80.0, 82.0, 83.4 (C-1′), 98.1 (C-1), 127.6, 127.8, 127.9, 128.00, 128.02, 128.1, 128.4, 128.5, 138.0, 138.1, 138.7, 169.8, 170.0, 170.1, 170.3; FAB-HRMS *m/z* calcd for $C_{43}H_{53}N_4O_{13}$ $(M+H)^+$ 833.3609, found 833.3626; Anal. calcd for: $C_{43}H_{52}N_4O_{13}$: C, 62.01; H, 6.30; N, 6.73, found C, 61.95, H, 6.14, N, 6.69. Data for β-anomer (**32**β): TLC R_f=0.45 (1:1 hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (dd, J=7.0, 7.3 Hz, 3H, CH_2CH_3), 2.01 (s, 3H, CH_3CO), 2.06 (s, 3H, CH_3CO), 2.15 (s, 3H, CH_3CO), 2.35 (dq, J=14.4, 7.3 Hz, 1H, C*H*CH$_3$), 2.38 (dq, J=14.4, 7.0 Hz, 1H, C*H*CH$_3$), 3.38 (s, 3H, OCH_3), 3.545 (dd, J=3.6, 9.7 Hz, 1H, H-2), 3.546 (dd, J=8.9, 9.9 Hz, 1H, H-4), 3.80 (dd, J=8.3, 10.9 Hz, 1H, H-2′), 3.88 (ddd, J=2.1, 4.5, 9.9 Hz, 1H, H-5), 3.94 (dd, J=6.5, 6.7 Hz, 1H, H-5′), 4.01 (dd, J=8.9, 9.7 Hz, 1H, H-3), 4.10 (dd, J=6.5, 11.4 Hz, 1H, H-6′a), 4.12 (dd, J=6.7, 11.4 Hz, 1H, H-6′b), 4.35 (dd, J=2.1, 12.1 Hz, 1H, H-6a), 4.39 (dd, J=4.5, 12.1 Hz, 1H, H-6b), 4.50 (d, J=8.3 Hz, 1H, H-1′), 4.57 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.61 (d, J=3.6 Hz, 1H, H-1), 4.67 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.80 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.82 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.85 (dd, J=3.4, 10.9 Hz, 1H, H-3′), 4.86 (d, J=10.7 Hz, 1H, OC*H*Ph), 4.98 (d, J=10.7 Hz, 1H, OC*H*Ph), 5.38 (d, J=3.4 Hz, 1H, H-4′), 7.25–7.37 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.8, 20.6, 20.66, 20.68, 23.8, 55.1, 61.8, 62.8, 64.7, 66.8, 68.7, 71.3, 72.5, 73.4, 75.2, 75.9, 78.1, 80.1, 82.1, 88.3 (C-1′), 98.0 (C-1), 127.67, 127.69, 127.9, 128.06, 128.08, 128.38, 128.42, 128.5, 138.1, 138.2, 138.7, 169.9, 170.2, 170.4, 171.8; FAB-HRMS *m/z* calcd for $C_{43}H_{53}N_4O_{13}$ $(M+H)^+$ 833.3609, found 833.3614.

Data for methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl)-α-D-glucopyranoside (**33**).[9] Data for β-anomer (**33**β):[9] TLC R_f=0.42 (1:1 hexane/AcOEt), 0.24 (1:3 hexane/Et_2O); mp 145.0–146.0 °C (colorless needles from AcOEt–hexane); $[\alpha]_D^{24}=-9.46°$ (*c* 1.00, $CHCl_3$); IR (KBr) 3032, 2926, 2114, 1751, 1454, 1369, 1242, 1076 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01 (s, 3H, CH_3CO), 2.04 (s, 3H, CH_3CO), 2.11 (s, 3H, CH_3CO), 3.39 (s, 3H, OCH_3), 3.53 (dd, J=8.8, 10.2 Hz, 1H, H-4), 3.54 (dd, J=3.5, 9.6 Hz, 1H, H-2), 3.70 (dd, J=4.8, 11.0 Hz, 1H, H-6a), 3.72 (dd, J=8.1, 10.9 Hz, 1H, H-2′), 3.77 (dd, J=6.8, 7.0 Hz, 1H, H-5′), 3.83 (ddd, J=1.5, 4.5, 10.2 Hz, 1H, H-5), 4.01 (dd, J=8.8, 9.6 Hz, 1H, H-3), 4.07–4.14 (m, 3H, H-6b, H-6′a, H-6′b), 4.22 (d, J=8.1 Hz, 1H, H-1′), 4.62 (d, J=3.5 Hz,

1H, H-1), 4.63 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.65 (d, J=12.4 Hz, 1H, OC*H*Ph), 4.76 (dd, J=3.3, 10.9 Hz, 1H, H-3′), 4.80 (d, J=12.4 Hz, 1H, OC*H*Ph), 4.82 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.94 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.99 (d, J=10.9 Hz, 1H, OC*H*Ph), 5.30 (d, J=3.3 Hz, 1H, H-4′), 7.27–7.37 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.56, 20.58, 20.61, 55.3, 60.9, 61.1, 66.3, 68.8, 69.7, 70.6, 71.3, 73.4, 75.7, 77.7, 79.8, 82.0, 98.2 (C-1), 102.4 (C-1′), 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.4, 128.45, 128.46, 138.1, 138.3, 138.7, 169.8, 170.0, 170.3; FAB-HRMS m/z calcd for $C_{40}H_{47}N_3O_{13}Na$ $(M+Na)^+$ 800.3007, found 800.2985; Anal. calcd for: $C_{40}H_{47}N_3O_{13}$: C, 61.77; H, 6.09; N, 5.40, found C, 61.75; H, 6.09; N, 5.30. Data for α-anomer (**33**α):[9] TLC R_f=0.43 (1:1 hexane/AcOEt), 0.31 (1:3 hexane/Et_2O); $[\alpha]_D^{25}=+96.4°$ (c 1.01, $CHCl_3$); IR (film) 2928, 2110, 1751, 1454, 1371, 1228, 1074 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.98 (s, 3H, CH_3CO), 2.05 (s, 3H, CH_3CO), 2.12 (s, 3H, CH_3CO), 3.38 (s, 3H, OCH_3), 3.51 (dd, J=9.0, 9.9 Hz, 1H, H-4), 3.52 (dd, J=3.5, 9.7 Hz, 1H, H-2), 3.62 (dd, J=3.4, 11.2 Hz, 1H, H-2′), 3.70 (m, 1H, H-6a), 3.75–3.79 (m, 2H, H-5, H-6b), 3.96–4.02 (m, 2H, H-3, H-6′a), 4.05 (dd, J=6.0, 10.9 Hz, 1H, H-6′b), 4.09 (dd, J=6.0, 6.9 Hz, 1H, H-5′), 4.59 (d, J=3.5 Hz, 1H, H-1), 4.61 (d, J=11.3 Hz, 1H, OC*H*Ph), 4.66 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.79 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.81 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.94 (d, J=11.3 Hz, 1H, OC*H*Ph), 4.99 (d, J=10.9 Hz, 1H, OC*H*Ph), 5.06 (d, J=3.6 Hz, 1H, H-1′), 5.28 (dd, J=3.3, 11.2 Hz, 1H, H-3′), 5.39 (brd, J=3.3 Hz, 1H, H-4′), 7.26–7.37 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.5, 20.6, 55.2, 57.5, 61.6, 66.6, 66.7, 67.6, 68.0, 69.9, 73.4, 74.9, 75.7, 77.6, 80.0, 82.0, 97.9, 98.1, 127.6, 127.7, 127.85, 127.94, 128.1, 128.3, 128.4, 138.1, 138.2, 138.6, 169.7, 169.9, 170.2; FAB-HRMS m/z calcd for $C_{40}H_{47}N_3O_{13}Na$ $(M+Na)^+$ 800.3007, found 800.3007.

4.6. Glycosidations of 2-azido-4,6-*O*-benzylidene-2-deoxyglycosyl diphenyl phosphates 2c and 4c

4.6.1. Methyl 6-*O*-(3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (35). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −45 °C, 4 h) employing diphenyl phosphate **2c** (56.7 mg, 0.10 mmol), alcohol **7** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). A mixture of disaccharide **35** and imidate **36** (80.3 mg) was obtained as a colorless oil from the crude product (104.6 mg) after short column chromatography (silica gel 3 g, 3:1 hexane/AcOEt with 1% Et_3N). The anomeric ratio of the products was determined by HPLC analysis [eluent, 4:1 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (**36**α)=17.4 min, t_R (**35**β)=21.5 min, t_R (**36**β)=25.4 min, t_R (**35**α)=30.6 min]. The mixture was purified by flash column chromatography (silica gel 8 g, 5:1 hexane/AcOEt with 1% Et_3N) to give α-imidate **36** (70.4 mg, 84%) as a white amorphous, along with an anomeric mixture of disaccharide **35** (5.0 mg, 6%, α:β=8:92) as a white solid. The α- and β-glycosides of disaccharide **35** were separated by flash column chromatography with 6:1 hexane/AcOEt. Data for β-anomer (**35**β): TLC R_f=0.38 (2:1 hexane/AcOEt); mp 149.0–149.5 °C (colorless needles from AcOEt–hexane); $[\alpha]_D^{23}=-35.5°$ (c 1.01, $CHCl_3$); IR (film) 2928, 2112, 1753, 1454, 1369, 1222, 1095 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (s, 3H, CH_3CO), 3.38 (s, 3H, OCH_3), 3.41 (ddd, J=5.0, 9.4, 10.1 Hz, 1H, H-5′), 3.53 (dd, J=8.0, 9.8 Hz, 1H, H-2′), 3.54 (dd, J=3.5, 9.4 Hz, 1H, H-2), 3.56 (dd, J=9.1, 9.3 Hz, 1H, H-4), 3.59 (dd, J=9.4, 9.7 Hz, 1H, H-4′), 3.75 (dd, J=4.2, 10.4 Hz, 1H, H-6a), 3.76 (dd, J=10.1, 10.5 Hz, 1H, H-6′ax), 3.80 (ddd, J=1.4, 4.2, 9.3 Hz, 1H, H-5), 4.01 (dd, J=9.1, 9.4 Hz, 1H, H-3), 4.08 (dd, J=1.4, 10.4 Hz, 1H, H-6b), 4.30 (dd, J=5.0, 10.5 Hz, 1H, H-6′eq), 4.35 (d, J=8.0 Hz, 1H, H-1′), 4.61 (d, J=3.5 Hz, 1H, H-1), 4.64 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.65 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.80 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.83 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.95 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.99 (d, J=10.9 Hz, 1H, OC*H*Ph), 5.15 (dd, J=9.7, 9.8 Hz, 1H, H-3′), 5.46 (s, 1H, C*H*Ph), 7.28–7.36 (m, 18H, Ar-H), 7.41 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.8, 55.3, 64.8, 66.4, 68.4, 68.8, 69.6, 71.3, 73.4, 74.9, 75.7, 77.6, 78.5, 79.7, 82.0, 98.2 (C-1), 101.5, 102.4 (C-1′), 127.6, 127.77, 127.80, 127.9, 128.0, 128.15, 128.23, 128.4, 128.45, 128.49, 129.1, 136.7, 138.1, 138.2, 138.7, 169.7; FAB-HRMS m/z calcd for $C_{43}H_{47}N_3O_{11}Na$ $(M+Na)^+$ 804.3109, found 804.3135; Anal. calcd for: $C_{43}H_{47}N_3O_{11}$: C, 66.06; H, 6.06; N, 5.37, found C, 65.94; H, 6.13; N, 5.27. Data for α-anomer (**35**α): TLC R_f=0.32 (2:1 hexane/AcOEt); mp 152.0–153.0 °C (colorless fine needles from AcOEt/hexane); $[\alpha]_D^{21}=+106.9°$ (c 0.76, $CHCl_3$); IR (film) 2926, 2112, 1753, 1454, 1369, 1222, 1095 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (s, 3H, CH_3CO), 3.21 (dd, J=3.6, 10.4 Hz, 1H, H-2′), 3.39 (3H, s, OCH_3), 3.54 (dd, J=3.5, 9.7 Hz, 1H, H-2), 3.55 (dd, J=8.9, 10.5 Hz, 1H, H-5), 3.58 (dd, J=9.5, 9.8 Hz, 1H, H-4′), 3.69 (m, 1H, H-6a), 3.70 (dd, J=10.2, 10.3 Hz, 1H, H-6′ax), 3.77–3.83 (m, 2H, H-5, H-6b), 3.91 (ddd, J=4.9, 9.8, 10.2 Hz, 1H, H-5′), 4.01 (dd, J=8.9, 9.7 Hz, 1H, H-3), 4.20 (dd, J=4.9, 10.3 Hz, 1H, H-6′eq), 4.59 (d, J=3.5 Hz, 1H, H-1), 4.63 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.65 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.77 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.82 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.95 (d, J=11.2 Hz, 1H, OC*H*Ph), 4.99 (d, J=11.0 Hz, 1H, OC*H*Ph), 5.02 (d, J=3.6 Hz, 1H, H-1′), 5.48 (s, 1H, C*H*Ph), 5.53 (dd, J=9.5, 10.4 Hz, 1H, H-3′), 7.26–7.36 (m, 18H, Ar-H), 7.42 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.9, 55.3, 61.8, 62.7, 66.9, 68.7, 68.8, 69.9, 73.5, 75.1, 75.7, 77.5, 79.5, 80.0, 82.1, 98.1 (C-1), 99.1 (C-1′), 101.7, 127.5, 127.86, 127.87, 127.93, 128.1, 128.2, 128.37, 128.43, 128.5, 129.1, 136.9, 138.1, 138.8, 169.7; FAB-HRMS m/z calcd for $C_{43}H_{47}N_3O_{11}Na$ $(M+Na)^+$ 804.3109, found 804.3134.

Data for methyl 6-*O*-[1-(3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)iminopropyl]-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**36**α): TLC R_f=0.40 (2:1 hexane/AcOEt); $[\alpha]_D^{20}=+81.0°$ (c 2.30, $CHCl_3$); IR (film) 2926, 2106, 1753, 1660, 1454, 1369, 1224, 1095 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (t, J=7.6 Hz, 3H, CH_2CH_3), 2.15 (s, 3H, CH_3CO), 2.35 (q, J=7.6 Hz, 2H, CH_2CH_3), 3.397 (dd, J=4.2, 10.0 Hz, 1H, H-2′), 3.399 (s, 3H, OCH_3), 3.52 (dd, J=3.6, 9.7 Hz, 1H, H-2), 3.63 (dd, J=8.8, 10.5 Hz, 1H, H-4), 3.64–3.70 (m, 2H, H-4′, H-6′ax), 3.88 (ddd, J=1.6, 4.1, 10.5 Hz, 1H, H-5), 4.00 (dd, J=8.8, 9.7 Hz, 1H, H-3), 4.14–4.20 (m, 2H, H-5′, H-6′eq), 4.23 (dd, J=4.1, 12.3 Hz, 1H, H-6a), 4.53 (dd, J=1.6, 12.3 Hz, 1H, H-6b), 4.617 (d, J=10.5 Hz, 1H, OC*H*Ph), 4.619 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.64 (d, J=3.6 Hz, 1H, H-1), 4.74

(d, J=12.1 Hz, 1H, OC*H*Ph), 4.83 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.84 (d, J=10.5 Hz, 1H, OC*H*Ph), 4.97 (d, J=10.8 Hz, 1H, OC*H*Ph), 5.21 (d, J=4.2 Hz, 1H, H-1′), 5.52 (s, 1H, C*H*Ph), 5.76 (dd, J=9.5, 10.0 Hz, 1H, H-3′), 7.23 (m, 1H, Ar-H), 7.25–7.36 (m, 17H, Ar-H), 7.44 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.7, 20.9, 23.0, 55.2, 62.7, 63.3, 64.4, 68.9, 69.2, 69.8, 73.2, 75.2, 75.8, 77.6, 80.1, 80.3, 82.1, 84.1 (C-1′), 97.9 (C-1), 101.5, 126.1, 127.6, 127.79, 127.83, 128.0, 128.1, 128.2, 128.38, 128.40, 128.5, 129.0, 137.1, 138.0, 138.2, 138.7, 169.7, 170.4; FAB-HRMS m/z calcd for $C_{46}H_{53}N_4O_{11}$ $(M+H)^+$ 837.3711, found 837.3727; Anal. calcd for: $C_{46}H_{52}N_4O_{11}$: C, 66.02; H, 6.26; N, 6.69, found C, 65.90; H, 6.27; N, 6.66.

4.6.2. Methyl 6-*O*-(3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (37).[9] The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 3 h) employing diphenyl phosphate **4c** (56.7 mg, 0.10 mmol), alcohol **7** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **37** (60.6 mg, 78%, α:β=3:97) was obtained as a white solid from the crude product (98.4 mg) after column chromatography (silica gel 6 g, 40:1→30:1 CH_2Cl_2/AcOEt with 0.5% Et_3N), along with α-imidate **38** (8.5 mg, 10%) as a colorless oil. The anomeric ratio of the product was determined by HPLC analysis [eluent, 4:1 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (α-anomer)=29.5 min, t_R (β-anomer)=79.6 min]. The α- and β-glycosides were separated by flash column chromatography with 4:1 hexane/AcOEt. Data for β-anomer (**37**β):[9] TLC R_f=0.20 (2:1 hexane/AcOEt), 0.40 (10:1 CH_2Cl_2/AcOEt); mp 149.0–150.0 °C (colorless fine needles from AcOEt–hexane); $[\alpha]_D^{23}=+31.1°$ (c 1.01, $CHCl_3$); IR (KBr) 3032, 2918, 2114, 1745, 1454, 1367, 1246, 1059 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H, CH_3CO), 3.37 (brs, 1H, H-5′), 3.39 (s, 3H, OCH_3), 3.53 (dd, J=8.2, 10.1 Hz, 1H, H-4), 3.55 (dd, J=3.6, 9.7 Hz, 1H, H-2), 3.71 (dd, J=5.1, 11.1 Hz, 1H, H-6a), 3.85 (ddd, J=1.7, 5.1, 10.1 Hz, 1H, H-5), 3.95 (dd, J=8.0, 10.7 Hz, 1H, H-2′), 3.99–4.02 (m, 2H, H-3, H-6′a), 4.16 (dd, J=1.7, 11.1 Hz, 1H, H-6b), 4.23 (d, J=8.0 Hz, 1H, H-1′), 4.27–4.29 (m, 2H, H-4′, H-6′b), 4.62 (d, J=3.6 Hz, 1H, H-1), 4.64 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.65 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.68 (dd, J=3.5, 10.7 Hz, 1H, H-3′), 4.78 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.82 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.93 (d, J=11.1 Hz, 1H, OC*H*Ph), 4.99 (d, J=11.0 Hz, 1H, OC*H*Ph), 5.48 (s, 1H, C*H*Ph), 7.25–7.38 (m, 18H, Ar-H), 7.47 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.9, 55.3, 60.3, 66.3, 68.6, 68.8, 69.9, 72.5, 72.6, 73.4, 74.9, 75.7, 77.9, 79.9, 82.1, 98.1 (C-1), 100.9, 102.5 (C-1′), 126.2, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.36, 128.44, 129.1, 137.5, 138.1, 138.4, 138.8, 170.5; FAB-HRMS m/z calcd for $C_{43}H_{47}N_3O_{11}Na$ $(M+Na)^+$ 804.3108, found 804.3094; Anal. calcd for: $C_{43}H_{47}N_3O_{11}$: C, 66.06; H, 6.06; N, 5.37, found C, 66.07; H, 5.92; N, 5.41. Data for α-anomer (**37**α):[9] TLC R_f=0.34 (2:1 hexane/AcOEt), 0.53 (10:1 CH_2Cl_2/AcOEt); $[\alpha]_D^{22}=+153.1°$ (c 1.00, $CHCl_3$); IR (KBr) 3032, 2914, 2110, 1745, 1496, 1454, 1371, 1228, 1145, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H, CH_3CO), 3.38 (s, 3H, OCH_3), 3.52–3.56 (m, 2H, H-2, H-4), 3.56 (brs, 1H, H-5′), 3.70 (m, 1H, H-6a), 3.77–3.81 (m, 2H, H-5, H-6b), 3.88 (d, J=12.5 Hz, 1H, OC*H*Ph), 3.90 (dd, J=3.1, 11.0 Hz, 1H, H-2′), 4.01 (t, J=9.2 Hz, 1H, H-3), 4.13 (d, J=12.5 Hz, 1H, OC*H*Ph), 4.38 (d, J=3.1 Hz, 1H, H-4′), 4.59 (d, J=3.6 Hz, 1H, H-1), 4.60 (d, J=11.6 Hz, 1H, OC*H*Ph), 4.66 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.79 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.81 (d, J=10.9 Hz, 1H, OC*H*Ph), 4.96 (d, J=11.6 Hz, 1H, OC*H*Ph), 4.99 (d, J=10.9 Hz, 1H, OC*H*Ph), 5.12 (d, J=3.1 Hz, 1H, H-1′), 5.22 (dd, J=3.1, 11.0 Hz, 1H, H-3′), 5.47 (s, 1H, C*H*Ph), 7.27–7.36 (m, 18H, Ar-H), 7.47 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.9, 55.1, 57.2, 62.3, 66.6, 69.0, 69.3, 69.9, 73.3, 73.4, 74.8, 75.7, 77.8, 80.0, 82.0, 98.0 (C-1), 98.6 (C-1′), 100.7, 126.1, 127.56, 127.63, 127.9, 128.0, 128.07, 128.14, 128.3, 128.4, 129.0, 137.5, 138.1, 138.4, 138.7, 170.5; FAB-HRMS m/z calcd for $C_{43}H_{47}N_3O_{11}Na$ $(M+Na)^+$ 804.3108, found 804.3093.

Data for methyl 6-*O*-[1-(3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranosyl)iminopropyl]-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**38**): TLC R_f=0.34 (2:1 hexane/AcOEt); $[\alpha]_D^{22}=+104.2°$ (c 0.31, $CHCl_3$); IR (film) 3032, 2908, 2108, 1743, 1662, 1454, 1373, 1228, 1095 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (t, J=7.6 Hz, 3H, CH_2CH_3), 2.15 (s, 3H, CH_3CO), 2.36 (q, J=7.6 Hz, 2H, CH_2CH$_3$), 3.39 (s, 3H, OCH_3), 3.55 (dd, J=3.6, 9.6 Hz, 1H, H-2), 3.59 (dd, J=8.9, 10.1 Hz, 1H, H-4), 3.87 (ddd, J=1.7, 4.5, 10.1 Hz, 1H, H-5), 3.92 (brs, 1H, H-5′), 3.94 (dd, J=1.6, 12.6 Hz, 1H, H-6′a), 4.01 (dd, J=8.9, 9.6 Hz, 1H, H-3), 4.09 (dd, J=4.0, 10.9 Hz, 1H, H-2′), 4.12 (dd, J=1.5, 12.6 Hz, 1H, H-6′b), 4.20 (dd, J=4.5, 12.2 Hz, 1H, H-6a), 4.36 (dd, J=1.7, 12.2 Hz, 1H, H-6b), 4.43 (d, J=3.5 Hz, 1H, H-4′), 4.59 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.60 (d, J=3.6 Hz, 1H, H-1), 4.67 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.81 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.84 (d, J=10.8 Hz, 1H, OC*H*Ph), 4.86 (d, J=11.0 Hz, 1H, OC*H*Ph), 4.99 (d, J=10.8 Hz, 1H, OC*H*Ph), 5.33 (d, J=4.0 Hz, 1H, H-1′), 5.41 (dd, J=3.5, 10.9 Hz, 1H, H-3′), 5.50 (s, 1H, C*H*Ph), 7.26–7.39 (m, 18H, Ar-H), 7.51 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.8, 21.1, 22.9, 55.2, 58.3, 62.9, 64.4, 68.8, 69.5, 70.7, 73.4, 73.7, 75.2, 75.9, 77.9, 80.0, 82.1, 83.6 (C-1′), 98.2 (C-1), 100.8, 126.2, 127.66, 127.73, 127.9, 127.97, 128.04, 128.1, 128.2, 128.4, 128.5, 129.0, 137.7, 138.1, 138.2, 138.7, 169.4, 170.6; FAB-HRMS m/z calcd for $C_{46}H_{53}N_4O_{11}$ $(M+H)^+$ 837.3711, found 837.3692.

4.6.3. Methyl 4-*O*-(3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (39). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 3 h) employing diphenyl phosphate **4c** (56.7 mg, 0.10 mmol), alcohol **8** (51.1 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **39** (70.1 mg, 90%, α:β=4:96) was obtained as a colorless oil from the crude product (97.7 mg) after column chromatography (silica gel 6 g, 15:1 toluene/AcOEt). The anomeric ratio of the product was determined by HPLC analysis [eluent, 4:1 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (α-anomer)=28.6 min, t_R (β-anomer)=60.0 min]. The α- and β-glycosides were separated by flash column chromatography with 3:1 hexane/AcOEt. Data for β-anomer (**39**β): TLC R_f=0.23 (2:1 hexane/AcOEt), 0.21 (5:1 toluene/AcOEt); $[\alpha]_D^{27}=+24.2°$ (c 1.17, $CHCl_3$); IR (film) 3032, 2903, 2114, 1747, 1454, 1367, 1232, 1047, 912 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H,

CH_3CO), 2.97 (brs, 1H, H-5′), 3.39 (s, 3H, OCH_3), 3.53 (dd, J=3.6, 9.4 Hz, 1H, H-2), 3.72 (dd, J=1.6, 10.8 Hz, 1H, H-6a), 3.78 (m, 1H, H-5), 3.81 (dd, J=8.1, 10.7 Hz, 1H, H-2′), 3.85 (dd, J=1.7, 12.5 Hz, 1H, H-6′a), 3.92 (dd, J=9.0, 9.4 Hz, 1H, H-3), 3.98 (dd, J=9.0, 9.8 Hz, 1H, H-4), 3.99 (dd, J=2.5, 10.8 Hz, 1H, H-6b), 4.192 (dd, J=1.0, 12.5 Hz, 1H, H-6′b), 4.194 (d, J=3.7 Hz, 1H, H-4′), 4.25 (d, J=8.1 Hz, 1H, H-1′), 4.42 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.47 (dd, J=3.7, 10.7 Hz, 1H, H-3′), 4.60 (d, J=3.6 Hz, 1H, H-1), 4.63 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.72 (d, J=12.1 Hz, 1H, OC*H*Ph), 4.78 (d, J=10.6 Hz, 1H, OC*H*Ph), 4.81 (d, J=12.1 Hz, 1H, OC*H*Ph), 5.10 (d, J=10.6 Hz, 1H, OC*H*Ph), 5.46 (s, 1H, C*H*Ph), 7.17–7.22 (m, 3H, Ar-H), 7.25–7.35 (m, 13H, Ar-H), 7.45–7.47 (m, 4H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.9, 55.3, 60.9, 66.2, 68.2, 68.6, 69.7, 72.5, 72.8, 73.4, 73.6, 75.9, 77.4, 79.2, 80.3, 98.3 (C-1), 100.9, 101.2 (C-1′), 127.8, 127.9, 128.06, 128.08, 128.10, 128.11, 128.2, 128.35, 128.40, 128.5, 129.0, 137.7, 138.0, 138.4, 139.1, 170.4; FAB-HRMS *m/z* calcd for $C_{43}H_{48}N_3O_{11}$ $(M+H)^+$ 782.3289, found 782.3281; Anal. calcd for: $C_{43}H_{47}N_3O_{11}$: C, 66.06; H, 6.06; N, 5.37, found C, 65.94; H, 6.13; N, 5.27. Data for α-anomer (**39**α): TLC R_f=0.35 (2:1 hexane/AcOEt), 0.38 (5:1 toluene/AcOEt); $[\alpha]_D^{24}=+99.5°$ (*c* 1.24, $CHCl_3$); IR (film) 3032, 2908, 2110, 1743, 1496, 1454, 1369, 1228, 1143, 1101, 1039 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H, CH_3CO), 3.40 (s, 3H, OCH_3), 3.54 (brs, 1H, H-5′), 3.57 (dd, J=3.5, 9.6 Hz, 1H, H-2), 3.61 (dd, J=1.2, 12.6 Hz, 1H, H-6′a), 3.63 (dd, J=1.4, 11.2 Hz, 1H, H-6a), 3.75 (dd, J=4.2, 11.2 Hz, 1H, H-6b), 3.80 (ddd, J=1.4, 4.2, 9.8 Hz, 1H, H-5), 3.85 (dd, J=3.6, 11.2 Hz, 1H, H-2′), 3.87 (brd, J=12.6 Hz, 1H, H-6′b), 3.94 (dd, J=8.7, 9.8 Hz, 1H, H-4), 4.08 (dd, J=8.7, 9.6 Hz, 1H, H-3), 4.29 (d, J=3.3 Hz, 1H, H-4′), 4.53 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.59 (d, J=12.2 Hz, 1H, OC*H*Ph), 4.60 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.61 (d, J=3.5 Hz, 1H, H-1), 4.73 (d, J=12.0 Hz, 1H, OC*H*Ph), 4.85 (d, J=10.9 Hz, 1H, OC*H*Ph), 5.10 (d, J=10.9 Hz, 1H, OC*H*Ph), 5.20 (dd, J=3.3, 11.2 Hz, 1H, H-3′), 5.38 (s, 1H, C*H*Ph), 5.85 (d, J=3.6 Hz, 1H, H-1′), 7.26–7.38 (m, 18H, Ar-H), 7.43 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.0, 55.3, 57.0, 62.7, 69.0, 69.1, 69.45, 69.48, 73.1, 73.3, 73.4, 73.5, 74.8, 80.6, 81.9, 97.8, 98.0, 100.6, 126.1, 127.3, 127.36, 127.39, 127.7, 128.0, 128.1, 128.2, 128.3, 128.48, 128.50, 129.0, 137.5, 137.9, 138.0, 138.7, 170.5; FAB-HRMS *m/z* calcd for $C_{43}H_{48}N_3O_{11}$ $(M+H)^+$ 782.3289, found 782.3306.

4.6.4. Allyl 3-*O*-(3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-D-galactopyranosyl)-4,6-*O*-benzylidene-β-D-galactopyranoside (40).[22b]

The glycosidation was performed according to the typical procedure [1.55 mL EtCN–CH_2Cl_2 (30:1), −78 °C, 2 h] employing diphenyl phosphate **4c** (56.7 mg, 0.10 mmol), alcohol **34** (33.9 mg, 0.11 mmol), and TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol). An anomeric mixture of disaccharide **40** (50.1 mg, 80%, α:β=1:99) was obtained as a colorless film from the crude product (87.4 mg) after column chromatography (silica gel 6 g, 5:1 toluene/AcOEt). The anomeric ratio of the product was determined by HPLC analysis [eluent, 1:1.5 hexane/AcOEt; flow rate, 1.0 mL/min; t_R (α-anomer)=9.4 min, t_R (β-anomer)=14.6 min]. The α- and β-glycosides were separated by flash column chromatography with 1:1 hexane/AcOEt. Data for β-anomer (**40**β):[22b] TLC R_f=0.36 (1:3 hexane/AcOEt), 0.36 (3:1 toluene/acetone); $[\alpha]_D^{21}=+24.2°$ (*c* 1.00, $CHCl_3$); IR (KBr) 3514, 2870, 2116, 1745, 1454, 1369, 1236, 1051, 916 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (s, 3H, CH_3CO), 3.03 (br, 1H, O*H*), 3.40 (brs, 1H, H-5), 3.46 (brs, 1H, H-5′), 3.86 (dd, J=3.5, 10.0 Hz, 1H, H-3), 3.99 (dd, J=8.0, 10.8 Hz, 1H, H-2′), 4.03 (dd, J=1.5, 12.5 Hz, 1H, H-6′a), 4.05 (dd, J=1.1, 12.5 Hz, 1H, H-6a), 4.11 (dd, J=7.8, 10.0 Hz, 1H, H-2), 4.14 (m, 1H, C*H*CH=CH_2), 4.27 (brd, J=12.5 Hz, 1H, H-6′b), 4.28 (d, J=3.6 Hz, 1H, H-4′), 4.31 (brd, J=12.5 Hz, 1H, H-6b), 4.37 (d, J=7.8 Hz, 1H, H-1), 4.38 (d, J=3.5 Hz, 1H, H-4), 4.42 (m, 1H, C*H*CH=CH_2), 4.73 (dd, J=3.6, 10.8 Hz, 1H, H-3′), 4.98 (1H, d, J=8.0 Hz, H-1′), 5.20 (1H, dd, J=0.9, 10.6 Hz, CH_2CH=C*H*), 5.32 (1H, dd, J=1.2, 17.3 Hz, CH_2CH=C*H*), 5.49 (s, 1H, C*H*Ph), 5.57 (s, 1H, C*H*Ph), 5.95 (m, 1H, CH_2CH=CH_2), 7.28–7.37 (m, 6H, Ar-H), 7.49 (m, 2H, Ar-H), 7.54 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 60.1, 66.2, 66.6, 68.9, 69.0, 69.9, 70.2, 71.9, 72.5, 75.9, 78.9, 100.5, 100.7, 101.6 (C-1), 102.0 (C-1′), 117.8, 126.06, 126.09, 127.9, 128.1, 128.5, 129.0, 133.7, 137.4, 137.6, 170.3; FAB-HRMS *m/z* calcd for $C_{31}H_{36}N_3O_{11}$ $(M+H)^+$ 626.2350, found 626.2353; Anal. calcd for: $C_{31}H_{35}N_3O_{11}$: C, 59.51; H, 5.64; N, 6.72, found C, 59.32; H, 5.64; N, 6.62. Data for α-anomer (**40**α): TLC R_f=0.55 (1:3 hexane/AcOEt), 0.44 (3:1 toluene/acetone); $[\alpha]_D^{23}=+165.1°$ (*c* 0.36, $CHCl_3$); IR (film) 3510, 2922, 2864, 2110, 1743, 1452, 1369, 1244, 1049 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H, CH_3CO), 2.63 (br, 1H, O*H*), 3.44 (brs, 1H, H-5), 3.80 (dd, J=3.7, 9.8 Hz, 1H, H-3), 3.93 (dd, J=3.4, 11.2 Hz, 1H, H-2′), 3.98 (dd, J=7.8, 9.8 Hz, 1H, H-2), 4.04 (dd, J=1.1, 12.6 Hz, 1H, H-6′a), 4.11 (dd, J=1.1, 12.5 Hz, 1H, H-6a), 4.14 (m, 1H, C*H*CH=CH_2), 4.19 (brs, 1H, H-5′), 4.24 (dd, J=1.2, 12.6 Hz, 1H, H-6′b), 4.32 (d, J=3.7 Hz, 1H, H-4), 4.36 (d, J=7.8 Hz, 1H, H-1), 4.37 (dd, J=1.3, 12.5 Hz, 1H, H-6b), 4.44 (dddd, J=1.0, 1.1, 5.1, 12.7 Hz, 1H, C*H*CH=CH_2), 4.50 (d, J=3.3 Hz, 1H, H-4′), 5.23 (dd, J=1.0, 11.1 Hz, 1H, CH_2CH=C*H*), 5.30 (d, J=3.4 Hz, 1H, H-1′), 5.32 (m, 1H, CH_2CH=C*H*), 5.40 (dd, J=3.3, 11.2 Hz, 1H, H-3′), 5.52 (s, 1H, C*H*Ph), 5.58 (s, 1H, C*H*Ph), 5.96 (dddd, J=5.1, 6.0, 11.1, 17.1 Hz, 1H, CH_2CH=CH_2), 7.30–7.40 (m, 6H, Ar-H), 7.49 (m, 2H, Ar-H), 7.55 (m, 2H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.0, 56.7, 62.8, 66.7, 69.1, 69.2, 69.4, 70.0, 72.3, 73.5, 76.8, 95.8 (C-1′), 100.7, 101.0, 101.9 (C-1), 118.0, 126.1, 126.2, 128.0, 128.2, 128.8, 129.1, 133.8, 137.6, 170.4; FAB-HRMS *m/z* calcd for $C_{31}H_{36}N_3O_{11}$ $(M+H)^+$ 626.2350, found 626.2372.

4.7. Comparative study

4.7.1. TMSOTf-catalyzed glycosidation of 2-azido-2-deoxyglucopyranosyl trichloroacetimidate 5α with alcohol 8 in acetonitrile (Table 9, entry 5).

The glycosidation was performed according to the typical procedure (1.5 mL MeCN, −40 °C, 0.3 h) employing trichloroacetimidate **5**α[7b] (62.0 mg, 0.10 mmol), alcohol **8** (51.1 mg, 0.11 mmol), TMSOTf (1.0 M in CH_2Cl_2, 0.015 mL, 0.015 mmol), and pulverized molecular sieves 4 Å (60 mg). An anomeric mixture of disaccharide **10** (47.2 mg, 51%, α:β=12:88) was obtained as a white solid from the crude product (118.5 mg) after column chromatography (silica gel 6 g, 5:1 hexane/AcOEt with 1% Et_3N),

along with β-trichloroacetamide **41** (21.7 mg, 35%) as a white solid.

Data for *N*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)trichloroacetamide (**41**):[26b] TLC R_f=0.59 (2:1 hexane/AcOEt); mp 129.5–131.0 °C (colorless needles from Et_2O–hexane); $[\alpha]_D^{23}=-3.79°$ (*c* 1.00, $CHCl_3$); IR (KBr) 3360, 3032, 2893, 2108, 1699, 1520, 1454, 1363, 1277, 1128, 1060 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.46 (dd, *J*=9.4, 9.6 Hz, 1H, H-2), 3.54 (ddd, *J*=1.8, 2.9, 10.2 Hz, 1H, H-5), 3.62 (dd, *J*=8.9, 9.6 Hz, 1H, H-3), 3.71 (dd, *J*=1.8, 11.0 Hz, 1H, H-6a), 3.75 (dd, *J*=2.9, 11.0 Hz, 1H, H-6b), 3.79 (dd, *J*=8.9, 10.2 Hz, 1H, H-4), 4.49 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.56 (d, *J*=10.9 Hz, 1H, OC*H*Ph), 4.60 (d, *J*=12.1 Hz, 1H, OC*H*Ph), 4.80 (d, *J*=10.9 Hz, 1H, OC*H*Ph), 4.88 (s, 2H, OCH_2Ph), 4.97 (dd, *J*=9.3, 9.4 Hz, 1H, H-1), 7.08 (d, *J*=9.3 Hz, 1H, N*H*), 7.15 (m, 2H, Ar-H), 7.25–7.35 (m, 13H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 65.8, 67.8, 73.6, 75.0, 75.7, 77.0, 77.2, 80.4 (C-1), 83.8, 92.0, 127.7, 127.89, 127.90, 128.0, 128.05, 128.14, 128.45, 128.51, 137.4, 137.5, 137.7, 161.7; FAB-HRMS *m/z* calcd for $C_{29}H_{30}N_4O_5Cl_3$ $(M+H)^+$ 619.1282, found 619.1271; Anal. calcd for: $C_{29}H_{29}N_4O_5Cl_3$: C, 56.19; H, 4.72; N, 9.04, found C, 56.04; H, 4.62; N, 8.89.

4.7.2. TMSOTf-promoted glycosidation of 2-azido-2-deoxyglucopyranosyl trichloroacetimidate 5α with alcohol 8 in propionitrile (Table 10, entry 3). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 0.3 h) employing trichloroacetimidate **5α**[7b] (62.0 mg, 0.10 mmol), alcohol **8** (51.1 mg, 0.11 mmol), TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol), and pulverized molecular sieves 4 Å (60 mg). An anomeric mixture of disaccharide **10** (49.6 mg, 54%, α:β=7:93) was obtained as a colorless oil from the crude product (125.4 mg) after column chromatography (silica gel 6 g, 5:1 hexane/AcOEt with 1% Et_3N), along with α-amidine **42** (13.6 mg, 20%) as a colorless oil.

Data for *N*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-*N*-(2,2,2-trichloro-1-iminoethyl)propionamide (**42**): TLC R_f=0.50 (2:1 hexane/AcOEt); $[\alpha]_D^{22}=-11.4°$ (*c* 1.61, $CHCl_3$); IR ($CHCl_3$) 3020, 2926, 2868, 2118, 1635, 1577, 1221, 1070 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.25 (dd, *J*=7.4, 7.5 Hz, 3H, CH_2CH_3), 2.61 (m, 2H, CH_2CH_3), 3.61 (brd, *J*=10.8 Hz, 1H, H-6a), 3.66 (m, 1H, H-5), 3.76 (dd, *J*=3.4, 10.8 Hz, 1H, H-6b), 3.79 (dd, *J*=8.2, 9.4 Hz, 1H, H-4), 3.82 (dd, *J*=8.2, 9.5 Hz, 1H, H-3), 3.89 (dd, *J*=4.9, 9.5 Hz, 1H, H-2), 4.47 (d, *J*=12.0 Hz, 1H, OC*H*Ph), 4.54 (d, *J*=10.9 Hz, 1H, OC*H*Ph), 4.59 (d, *J*=12.0 Hz, 1H, OC*H*Ph), 4.80 (d, *J*=10.9 Hz, 1H, OC*H*Ph), 4.92 (d, *J*=10.3 Hz, 1H, OC*H*Ph), 4.94 (d, *J*=10.3 Hz, 1H, OC*H*Ph), 5.46 (d, *J*=4.9 Hz, 1H, H-1), 7.16 (m, 2H, Ar-H), 7.26–7.36 (m, 13H, Ar-H), 11.0 (br, 1H, N*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.6, 26.9, 62.0, 68.0, 72.0, 73.6, 75.1, 76.1, 77.6, 78.8, 81.3, 95.8, 127.7, 127.86, 127.91, 128.0, 128.1, 128.2, 128.45, 128.50, 128.6, 137.2, 137.4, 137.5, 174.5, 179.8; FAB-HRMS *m/z* calcd for $C_{32}H_{35}N_5O_5Cl_3$ $(M+H)^+$ 674.1704, found 674.1691; Anal. calcd for: $C_{32}H_{34}N_5O_5Cl_3$: C, 56.94; H, 5.08; N, 10.39; Cl, 15.76, found: C, 57.34; H, 5.18; N, 10.31; Cl, 15.41.

4.7.3. TMSOTf-promoted glycosidation of 2-azido-2-deoxygalactopyranosyl trichloroacetimidate 43α with alcohol 8 in propionitrile (Table 11, entry 1). The glycosidation was performed according to the typical procedure (1.5 mL EtCN, −78 °C, 0.1 h) employing trichloroacetimidate **43α**[7a] (62.0 mg, 0.10 mmol), alcohol **8** (51.1 mg, 0.11 mmol), TMSOTf (1.0 M in CH_2Cl_2, 0.15 mL, 0.15 mmol), and pulverized molecular sieves 4 Å (60 mg). An anomeric mixture of disaccharide **27** (43.8 mg, 48%, α:β=4:96) was obtained as a white solid from the crude product (123.4 mg) after column chromatography (silica gel 6 g, 5:1 hexane/AcOEt with 1% Et_3N), along with β-trichloroacetamide **44** (23.0 mg, 37%) and α-amidine **45** (4.5 mg, 7%) as colorless oils.

Data for *N*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)trichloroacetamide (**44**): TLC R_f=0.59 (2:1 hexane/AcOEt); $[\alpha]_D^{24}=+21.1°$ (*c* 1.20, $CHCl_3$); IR (film) 3323, 3032, 2872, 2114, 1724, 1520, 1454, 1361, 1286, 1101 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.56 (dd, *J*=2.8, 9.8 Hz, 1H, H-3), 3.56–3.61 (m, 2H, H-6a, H-6b), 3.68 (t, *J*=6.6 Hz, 1H, H-5), 3.86 (dd, *J*=9.5, 9.8 Hz, 1H, H-2), 4.00 (brd, *J*=2.8 Hz, 1H, H-4), 4.43 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.47 (d, *J*=11.8 Hz, 1H, OC*H*Ph), 4.57 (d, *J*=11.1 Hz, 1H, OC*H*Ph), 4.69 (d, *J*=11.6 Hz, 1H, OC*H*Ph), 4.74 (d, *J*=11.6 Hz, 1H, OC*H*Ph), 4.87 (d, *J*=11.1 Hz, 1H, OC*H*Ph), 4.91 (dd, *J*=9.3, 9.5 Hz, 1H, H-1), 7.07 (d, *J*=9.3 Hz, 1H, N*H*), 7.27–7.40 (m, 15H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 62.5, 67.7, 71.9, 72.4, 73.5, 75.0, 75.5, 80.4 (C-1), 81.6, 92.0, 127.87, 127.92, 128.1, 128.3, 128.35, 128.44, 128.5, 137.1, 137.5, 137.9, 161.6; FAB-HRMS *m/z* calcd for $C_{29}H_{30}N_4O_5Cl_3$ $(M+H)^+$ 619.1282, found 619.1276; Anal. calcd for: $C_{29}H_{29}N_4O_5Cl_3$: C, 56.19; H, 4.72; N, 9.04, found C, 55.98; H, 4.69; N, 8.93.

Data for *N*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-*N*-(2,2,2-trichloro-1-iminoethyl)propionamide (**45**): TLC R_f=0.43 (2:1 hexane/AcOEt); $[\alpha]_D^{20}=+4.32°$ (*c* 1.05, $CHCl_3$); IR (film) 3342, 3032, 2874, 2118, 1637, 1574, 1454, 1367, 1211, 1080 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.22 (t, *J*=7.5 Hz, 3H, CH_2CH_3), 2.55 (dq, *J*=15.3, 7.5 Hz, 1H, $CHCH_3$), 2.59 (dq, *J*=15.3, 7.5 Hz, 1H, $CHCH_3$), 3.50 (dd, *J*=6.1, 9.2 Hz, 1H, H-6a), 3.56 (dd, *J*=7.1, 9.2 Hz, 1H, H-6b), 3.76–3.79 (m, 2H, H-3, H-5), 4.02 (brs, 1H, H-4), 4.34 (dd, *J*=5.1, 10.5 Hz, 1H, H-2), 4.40 (d, *J*=11.7 Hz, 1H, OC*H*Ph), 4.45 (d, *J*=11.7 Hz, 1H, OC*H*Ph), 4.51 (d, *J*=11.2 Hz, 1H, OC*H*Ph), 4.77 (d, *J*=10.6 Hz, 1H, OC*H*Ph), 4.79 (d, *J*=10.6 Hz, 1H, OC*H*Ph), 4.57 (d, *J*=11.2 Hz, 1H, OC*H*Ph), 5.44 (d, *J*=5.1 Hz, 1H, H-1), 7.24–7.42 (m, 15H, Ar-H), 11.0 (br, 1H, N*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.5, 26.9, 58.2, 68.2, 70.8, 72.5, 72.7, 73.6, 75.0, 78.8, 79.0, 95.9, 127.85, 127.91, 128.0, 128.1, 128.2, 128.4, 128.5, 128.6, 136.8, 137.4, 137.9, 174.4, 180.1; ESI-HRMS *m/z* calcd for $C_{32}H_{34}N_5O_5Cl_3Na$ $(M+Na)^+$ 696.1523, found 696.1537.

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