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The Origin of High Stereoselectivity in Di-*tert*-butylsilylene-Directed α-Galactosylation

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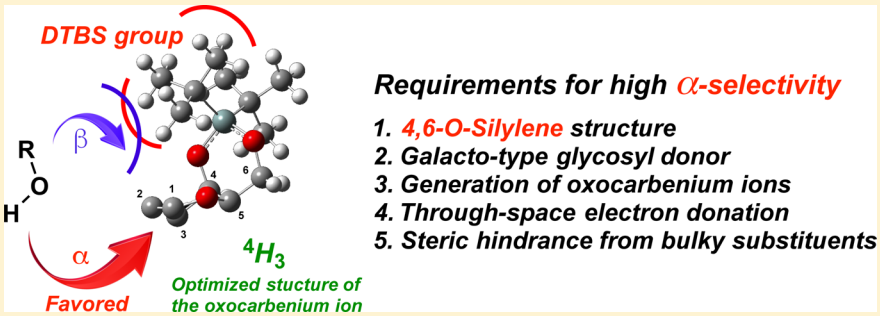
Supporting Information



ABSTRACT: The origin of the high α(1,2-*cis*)-stereoselectivity in the reaction of galactosyl and galactosaminyl donors with a di-*tert*-butylsilylene (DTBS) group with several nucleophiles has been elucidated by means of experimental and computational approaches. DTBS overcomes any other cyclic protecting groups examined to date and the β(1,2-*trans*)-directing effect due to the neighboring participation by CO groups at C2. Requirements for the α(1,2-*cis*)-stereoselectivity are as follows: (1) generation of an oxocarbenium ion; (2) a *galacto*-type glycosyl donor with a cyclic protecting group bridging O4 and O6 to form a six-membered ring; (3) through-space electron donation from O4 and O6 into the empty *p*-orbital of the anomeric carbon to stabilize the oxocarbenium intermediate; (4) steric hindrance due to bulky alkyl substituents on the cyclic protecting group to prevent nucleophilic attack from the β-face; and (5) a 4,6-*O*-silylene structure. Furthermore, it was found that the strong stereodirecting effect of the DTBS group was unique and specific among the various cyclic protecting groups examined.

INTRODUCTION

The pursuit of stereoselectivity in chemical glycosylation reactions is a key to success in the synthesis of glycoconjugates. To date, many factors in glycosylation have been identified that potentially affect the stereochemistry of glycoside product.[1] Among these factors, the presence of an acyl protecting group at the C2 position of the glycosyl donor is one of the most useful factors for forming 1,2-*trans*-glycosides.[2] Meanwhile, the synthesis of 1,2-*cis*-glycosides has been plagued by lower stereoselectivity due to a lack of reliable factors for controlling the glycosylation reaction. Hence, synthetic chemists have focused on developing methods for 1,2-*cis*-stereoselective glycosylation.[3] In particular, the formation of the α(1,2-*cis*)-glycosidic linkage between galactosamine and serine/threonine has garnered much attention because it is the core linkage of natural *O*-glycans in glycoproteins.[4] However, the construction of the α-*N*-acetylgalactosamine (α-GalNAc) linkage is usually difficult because the presence of the 2-acetamide group leads to the formation of the β(1,2-*trans*)-glycoside through neighboring group participation or the undesirable 1,2-oxazoline derivative through intramolecular cyclization. Thus, 2-azido-2-deoxy-galactosyl donors have been used in glycosylation reactions to maximize the anomeric effect, resulting in the formation of α-glycosides.[5] Although 2-azidogalactosaminyl (GalN) donors are useful for synthesizing glycans containing α-GalNAc, the glycosylation products are often α/β mixtures with moderate stereoselectivity. In 2003, we developed a di-*tert*-butylsilylene (DTBS)-directed α-stereoselective galactosylation[6] and found that both GalN and galactosyl donors bearing the DTBS group as a protecting group bridging the C4 and C6 positions gave unusual high α-stereoselectivity (Figure 1). Notably, this method was compatible with a wide variety of leaving groups, activator systems, reaction temperatures, solvent systems, and protecting groups (even in the presence of a neighboring acyl group at C2). High α-selectivity was almost

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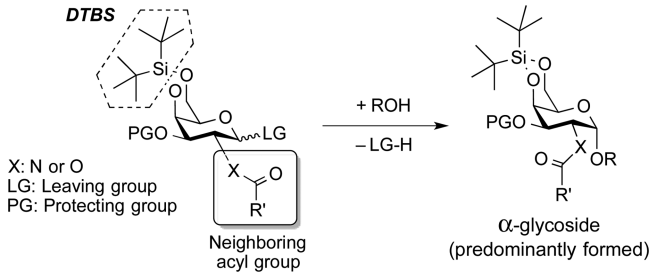

Figure 1. Outline of the DTBS-directed α-galactosylation.

completely independent of the nucleophile (the sugar acceptor), which could be an alcohol, either linear or sterically hindered, a phenol, Ser, Thr and partially protected monosaccharides.[7] Furthermore, DTBS-directed α-galactosylation was used to efficiently synthesize various α-GalNAc/Gal-containing glycans, such as α-GalNAc-Ser/Thr,[7] α-galactosyl ceramides,[8] isoglobotrihexosylceramide,[8] the α-tetrasaccharyl-Ser segment of glycophorin A,[7] *p*-nitrophenyl *O*-glycan cores,[9] 4-methylumbelliferyl T-antigen,[10] human ABO histo-blood group antigens,[11] and some gangliosides.[12] Also, glycosyl donors that are conformationally restricted by the DTBS group can be effective for a wide variety of stereoselective glycosylations, such as β-arabinofuranosylation,[13] β-galactofuranosylation,[14] α-sialylation,[15] and β-mannosylation.[16] These reports demonstrate that the DTBS group can serve as a factor for controlling glycosylation stereoselectivity. Several groups have reported theoretical and experimental studies regarding the ring restriction of glycosyl donors responsible for the reactivity of the donor and the stereochemical outcome of glycosylation.[17,18]

In previous papers, we proposed a reaction mechanism to explain the high α-stereoselectivity of the DTBS-directed reaction, which is summarized as follows (Figure 2). The previous X-ray crystallographic analysis of a DTBS-protected donor showed a six-membered ring composed of a 4,6-*O*-DTBS ketal moiety and a C4–C5–C6 bond in a nearly half-chair conformation, which resulted in the *tert*-butyl group being positioned close to the anomeric carbon, even in the ground state.[6] This implies that the steric effect of the DTBS group during the course of the glycosylation leads to the α-stereoselectivity. Furthermore, through-space electron donation[19] may contribute to the high α-stereoselectivity. Because of through-space electrostatic stabilization of the oxocarbenium ion by an axially oriented electronegative substituent at C4, the group on the C2 oxygen or nitrogen cannot interact effectively with the oxocarbenium ion in the intermediate. This lack of interaction, together with the steric effect of the DTBS group, results in the prominent α-stereoselectivity. However, this mechanism for the DTBS-directed α-galactosylation is still only a hypothesis and needs experimental verification. Therefore, to gain insight into the origin of the α-selectivity, we examined how the steric and electronic effects of the substituents on both O4 and O6 of the glycosyl donor influenced stereoselectivity. Here, we report a systematic study using experimental and computational approaches in combination to ascertain the origin of stereoselectivity in DTBS-directed α-galactosylation.

RESULTS AND DISCUSSION

In this study, we focused on the relationship between stereoselectivity and the magnitude of steric and electronic effects of substituents on O4/O6 of the glycosyl donor. For this purpose, we designed various GalN and glucosaminyl (GlcN) donors in which the only structural variation is the protecting groups on O4 and O6 (Figure 3). Selected protecting groups were a diisopropylsilylene group (less bulky than the DTBS group; **2**), various acetal groups that differed in bulkiness and electronic properties (**3**–**9**), cyclic groups that differed in ring size (**10**, **12**), and acyclic groups (**11**, **13**–**15**). Donors **1**–**16** were synthesized as outlined in Scheme 1. Starting from the known compound phenyl 2-deoxy-2-phthalimide-1-thio-β-D-galactopyranoside (**17**),[20] 4,6-*O*-benzylidene-protected donor **6** was prepared according to a typical acetalization procedure followed by benzylation at C3. Acidic hydrolysis then gave 4,6-diol product **18**, which was the common intermediate for synthesizing the other GalN donors. Compound **18** was transformed into GalN donors **1**–**15** using appropriate reaction conditions for each. For silylene-bridged donors, **18** was reacted with dialkylsilyl ditriflate in the presence of base, giving **1** (92%) and **2** (86%). Treatment of **18** with pivalaldehyde, dimethylacetal, or dimethoxymethane in the presence of camphorsulfonic acid (CSA) afforded alkylidene donors **3** (84%), **4** (92%), and **5** (84%), respectively. Substituted benzylidene donors were derived from **18** by treatment with 4-nitrobenzaldehyde or anisaldehyde dimethyl acetal under acidic conditions, affording **7** (94%) and **8** (89%), respectively. Similarly, the reaction of **18** with 2-chloroacetaldehyde diethyl acetal in the presence of camphorsulfonic acid afforded **9** in 74% yield. 1′,1′,3′,3′-Tetraisopropyldisiloxane (TIPDS)-protected donor was prepared by treating **18** with $TIPDSCl_2$ and imidazole in DMF, giving **10** in 88% yield. The reaction of **18** with *tert*-butyldimethylsilyl (TBS) triflate, imidazole along with 2,6-di-*tert*-butyl-4-methylpyridine as an acid scavenger gave acyclic 4,6-di-*O*-TBS-protected donor **11** in 96% yield. 4,6-*O*-Xylylene-protected donor **12** was prepared by the Williamson ether synthesis. Similarly, acyclic donors **13** and **14** were obtained in yield of 85% and 68%, respectively. The reaction of

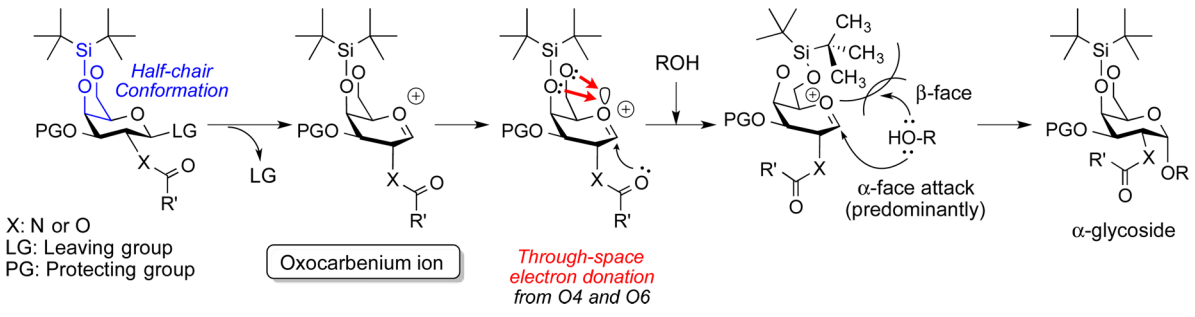

Figure 2. Plausible mechanism for the α-selectivity in DTBS-directed α-galactosylation.

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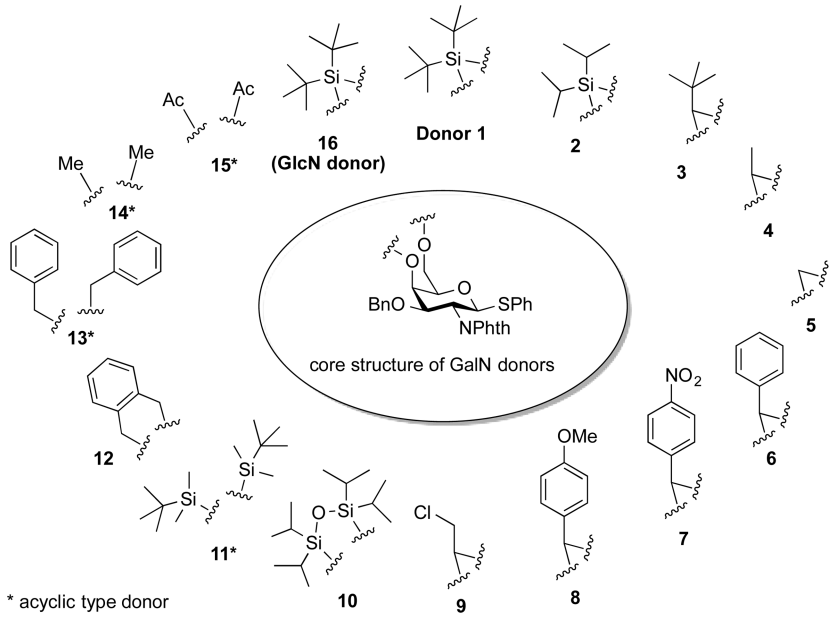

Figure 3. Structures of glycosyl donors used in this study.

18 with acetic anhydride in pyridine afforded 4,6-*O*-acetyl-protected donor **15** in quantitative yield. Meanwhile, glucosamine donor **16** bearing the DTBS group was prepared from the known glucosamine derivative **19**[21] in two steps. Hydrolysis of the benzylidene acetal under acidic conditions gave **20**, which was reacted with $DTBS(OTf)_2$ in pyridine to afford **16** in good yield. The glucosyl acceptor (**23**) was synthesized as follows and used in all the glycosylation experiments. The hydroxyl groups of the known 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-β-D-glucopyranoside **21**[22] were acetylated to give **22**, and subsequent reductive opening of the benzylidene acetal furnished 6-OH glucosyl acceptor **23** in 79% yield over the two steps.

Next, GalN/GlcN donors **1**−**16** and glucosyl acceptor **23** were used in glycosidation experiments to examine the relationship between substituents and stereoselectivity in relation to the cyclic protecting groups at C4 and C6 of the glycosyl donor. All glycosylation reactions were carried out using the NIS-TfOH promoter system[23] in CH_2Cl_2 at 0 °C. Moreover, almost all the glycosidations proceeded rapidly, requiring a reaction time less than 30 min. This high reactivity can be explained by Bols' work[18d] which found that the dihedral angle based on the exocyclic C5−O6 bond can strongly influence the reactivity of carbohydrates and *gg* conformer is the most reactive among *tg*, *gg*, and *gt* conformers. Specifically, the C5−O6 bond in the 4,6-*O*-ring-fused galactosyl donors must receive the imposition of the relatively reactive *gg* conformer. Figure 4 shows the results of glycosidation experiments. The α/β ratios were calculated from each of the isomers isolated after column chromatography.

Donor **1** bearing the DTBS group was glycosidated with acceptor **23** and the corresponding disaccharide **24** was obtained in 94% isolated yield with prominent α-selectivity. This result was consistent with our previous works.[6−12] Notably, the α-stereodirecting effect of the DTBS group overrides the effect of neighboring group participation, which has been reliably used for β(1,2-*trans*)-glycoside formation. We have attributed high α-stereoselectivity to steric effect arising from bulky *tert*-butyl substituents of the DTBS group. Thus, silylene-type donor **2** was examined, in which both *tert*-butyl substituents of **1** were replaced with less bulky isopropyl groups. The reaction gave glycosidated product **25** in 99% yield with 79:21 (α/β) stereoselectivity, which was lower than the α-stereoselectivity obtained with the *tert*-butyl groups. Thus, the bulk of the substituents in the silylene structure played a role in the observed stereoselectivity. Next, to assess the steric effect of substituents on the cyclic protecting group, cyclic acetal-type donors **3**−**5** were examined, the steric bulk of which decreased in the order of **3** (steric parameter E_s:E_{sCMe3} = −1.54)[24] to **4** (E_{sMe} = 0.00) and **5** (E_{sH} = 1.24). (*S*)-*tert*-Butylmethylidene donor **3** afforded the corresponding disaccharide **26** in 93% yield along with 36:64 (α/β) stereoselectivity. Similarly, (*S*)-ethylidene donor **4** and methylidene donor **5** were coupled with **23**, giving **27** in 85% yield (α/β = 29:71) and **28** in 74% yield (α/β = 16:84), respectively. These results strongly suggested that formation of the α-product could decrease as the steric bulk was decreased; in other words, the stereoselectivity was most likely to relate to the bulkiness of substituents at C4 and C6. Importantly, comparison of **1** with **3** showed the significance of the silylene structure for obtaining high α-selectivity, because both the compounds contained a *tert*-butyl substituent as a source of steric hindrance, but it was connected to silicon in **1** and carbon in **3**. This suggests that the spatial position of the *tert*-butyl group in the oxocarbenium intermediate and in the ground state might give rise to the stereoselectivity. On the basis of X-ray crystallographic data of the DTBS donor,[6] the *endo*-*tert*-butyl group in **1** is closer to the anomeric carbon compared to an *endo*-substituent of general cyclic acetal protecting groups. When **1** is activated to form the corresponding oxocarbenium intermediate, the *tert*-butyl group should move much closer to the anomeric carbon and prevent β-face nucleophilic attack by the glycosyl acceptor, leading to the observed α-selectivity. In contrast, the *tert*-butyl group in **3** is expected to be positioned far from the anomeric carbon in the oxocarbenium intermediate and would not sufficiently block the β-face. Next, we investigated the effect on stereoselectivity of the electronic environment at O4 and O6 of the glycosyl donor, because we

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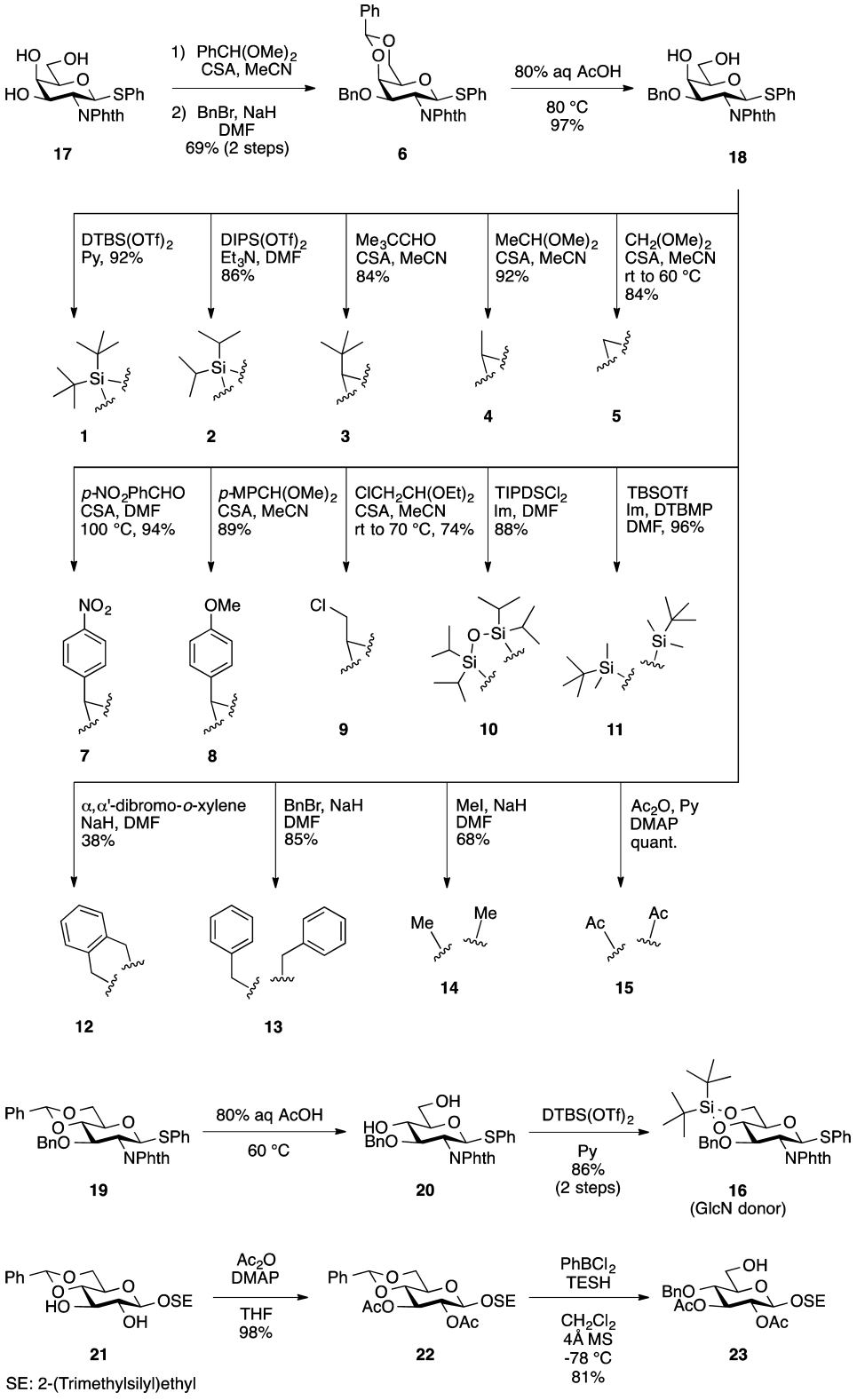
Scheme 1. Preparation of Glycosyl Donors (1−16) and Glucose Acceptor 23



expected through-space electron donation to contribute to the stereoselectivity. Glycosidation of benzylidene donor **6** with **23** proceeded smoothly and gave the corresponding disaccharide **29** in excellent yield with 13:87 (α/β) stereoselectivity. Aryl-substituted benzylidene-type donors, namely, **7** with an electron-withdrawing group (p-NO_2) and **8** with an electron-donating group (p-OMe), were then examined for their stereoselectivity. Donor **8** had clearly higher α-selectivity compared with the parent benzylidene donor **6**, whereas **7** showed no difference in stereoselectivity compared with **6**. These results could be a consequence of the different through-space stabilization of positive charge at the anomeric center affecting the position of substituents on the cyclic protecting group upon formation of the oxocarbenium intermediate stage.

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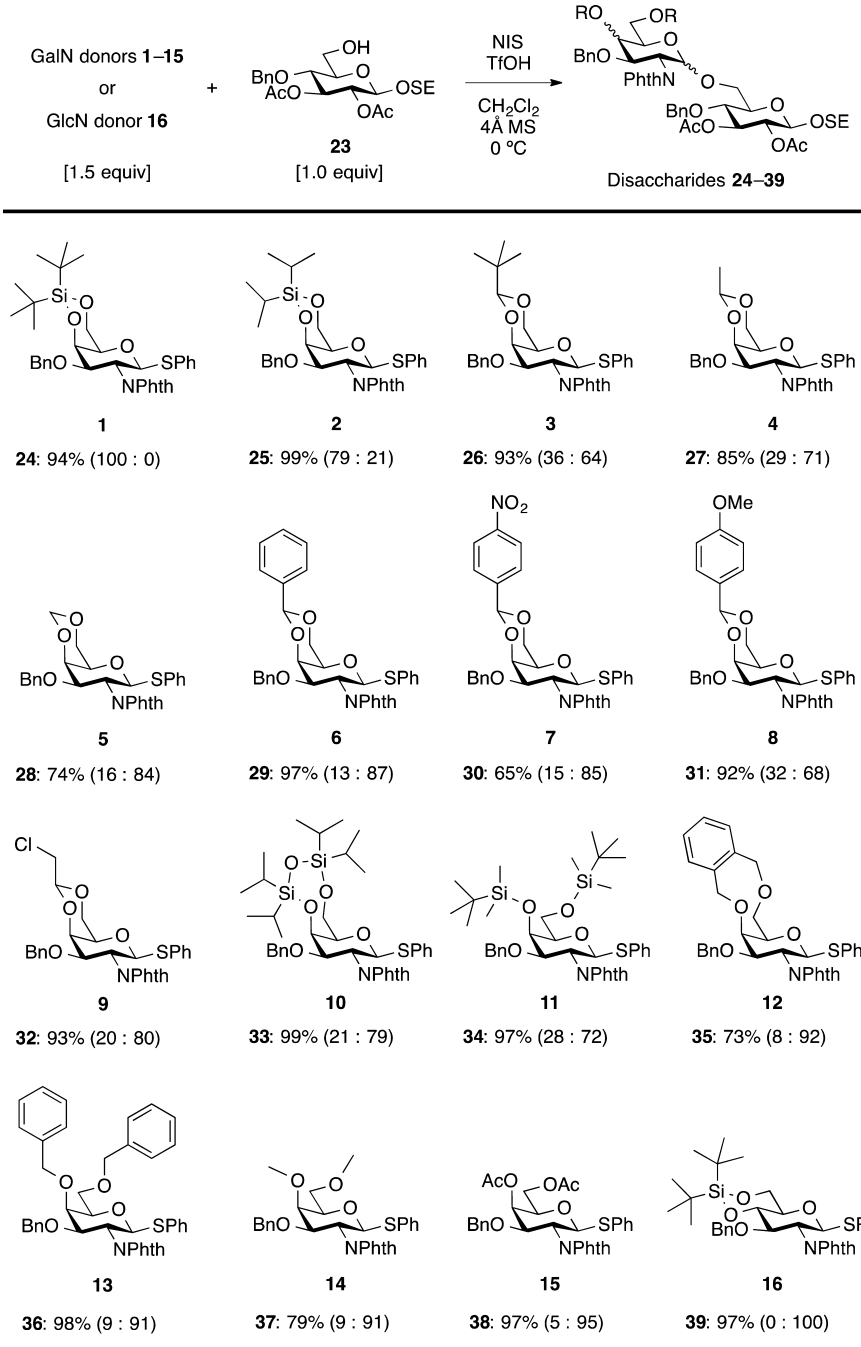

Figure 4. Glycosidation of GalN/GlcN donors **1**−**16** with glucosyl acceptor **23**. Percentages are isolated yields of the corresponding disaccharides obtained after column chromatography. Values in parentheses are α/β stereoselectivities calculated based on the yield of isolated isomers.

To further test this hypothesis, we designed donor **9** with electronegative chlorine atom on the ethylidene moiety; then, we compared the results with those for **4** (85% yield, α/β = 29:71). Decreased α-selectivity was observed for **9** (93% yield, α/β = 20:80), even though its chlorine atom (E_{sCH2Cl} − 0.24) is bulkier than the hydrogen atom (E_{sCH3} 0.00) on **4**. Next, to examine the stereoselectivity arising from ring size formed by cyclic protecting groups, donors **10** and **12** with larger ring sizes were investigated. First, donor **10** with a TIPDS group, which is bulkier than the DTBS group, was subjected to glycosidation with **23**, producing disaccharide **33** in 99% yield with 21:79 (α/β) stereoselectivity. This experiment eliminated the possibility that the α-selectivity was due to steric effects alone. Second, the glycosidation of xylylene-protected donor **12**, which contains a nine-membered ring, gave the β-linked disaccharide predominantly (α/β = 8:92). We then compared acyclic-type donors **11** and **13** with **10** and **12**, respectively. 4,6-Di-*O*-TBS-protected donor **11** gave stereoselectivity similar to that of **10**, and 4,6-di-*O*-Bn-protected donor **13** gave stereoselectivity nearly identical to that of **12**. In additional experiments, 4,6-di-*O*-Me-protected donor **14** with less steric bulk and donor **15** with acyl protecting groups on both O4 and O6 were examined. As expected based on reported findings in carbohydrate chemistry, both the donors showed a strong preference for the formation of the β-product. Finally, 4,6-*O*-DTBS-protected GlcN donor **16** was coupled with **23** under reaction conditions identical to those used with the GalN donors. The corresponding disaccharide **39** was obtained exclusively as the

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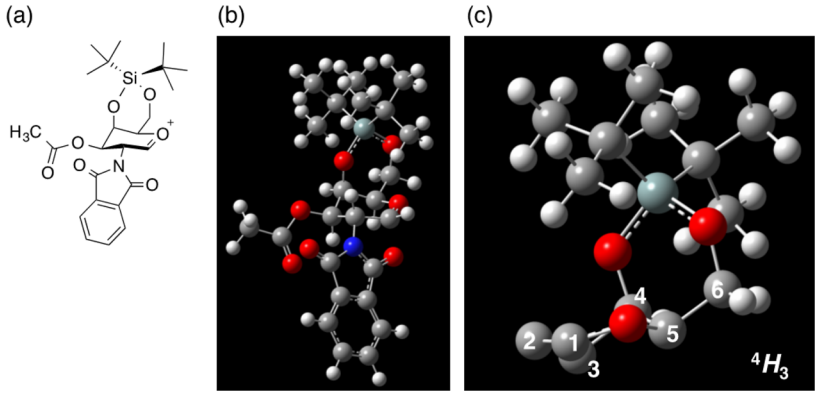

Figure 5. Optimized structure of the oxocarbenium intermediate liberated from a DTBS-protected galactosamine donor obtained by DFT calculations (M062X/6-31G*). (a) Chemical structure produced in ChemDraw. (b) Ball-and-stick representation of the whole structure (c) Ball-and-stick representation of the sugar ring in a partial structure.

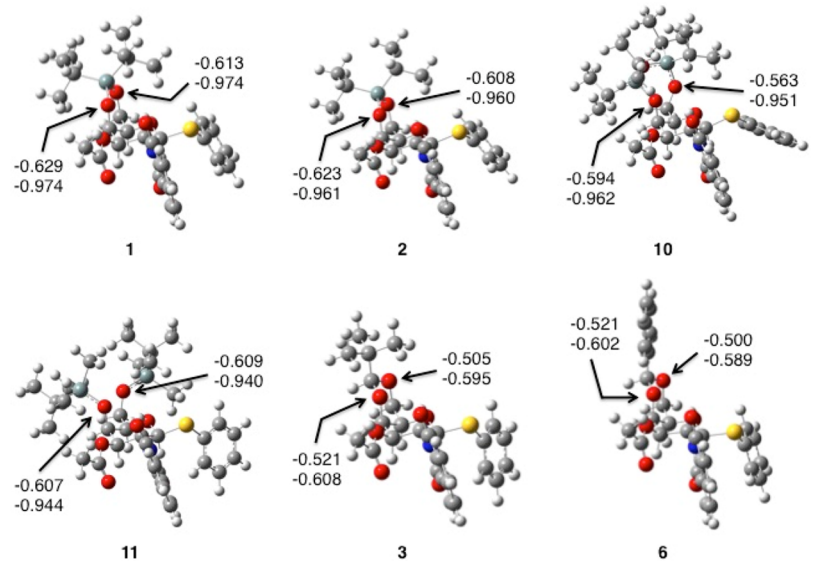

Figure 6. Calculated Mulliken charges (top numbers) and natural charges (bottom numbers) on O4 and O6 of glycosyl donors **1**, **2**, **3**, **6**, **10**, and **11**.

β-product with perfect stereoselectivity. From these experiments using donors **10**–**16**, we can conclude that just the presence of a silicon atom and a cyclic structure was not sufficient for α-selectivity. The requirements for marked α-selectivity were a silylene structure forming a six-membered ring and distinct steric hindrance due to bulky substituents.

Encouraged by the results of these experimental studies, we next shifted our attention to a computational study to examine the geometry of the postulated oxocarbenium intermediates. Density functional theory (DFT) calculations were performed to optimize the structures. Figure 5 shows the optimized structure of the oxocarbenium intermediate formed from phenyl 3-*O*-acetyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-phthalimide-1-thio-β-D-galactoside. The DFT-optimized geometry revealed that the sugar ring with the DTBS group at the C4 and C6 positions adopts the $^4H_3$ conformation in the oxocarbenium intermediate. We also calculated the Mulliken and natural charges on atoms in selected glycosyl donors, considering that the electronegativity of oxygen atoms at C4 and C6 might affect the through-space electron donation. As shown in Figure 6, oxygen atoms next to a silicon atom (**1**, **2**, **10**, and **11**) have a higher electron density compared with oxygen atoms next to a carbon atom (**3** and **6**). This result suggests the stronger through-space electron donation from oxygen atoms next to a silicon atom means that substituents on O4 and/or O6 are closer to the anomeric center, leading to increased formation of the α-product.

Taking together the experimental results and the computational results, we next propose an improved reaction mechanism for the DTBS-directed α-galactosylation (Figure 7). First, upon activation of the phenylthioglycoside under the NIS-TfOH promoter system, the buildup of positive charge on the sulfur atom requires electrons to be stabilized. When the sugar ring adopts the $^4C_1$ conformation, there is inefficient overlap to provide electron density from O5 to the C1 antibonding orbital. In contrast, when the ring adopts the $^{1,4}B$ conformation, the antiperiplanar electron pair on O5 can participate as in the E1 elimination reaction. Considering steric effects alone, there is not enough flexibility to provide access to the $^{1,4}B$ conformation from the $^4C_1$ conformation due to steric interactions between the pseudoaxial sulfonium ion and the bulky DTBS group. However, a conformational flip from the $^4C_1$ to the $^{1,4}B$ could be explained by stereoelectronic effects. Subsequent departure of the benzenesulfenyl iodide (ultimately giving PhSSPh and I_2) generates the oxocarbenium intermediate. Importantly, although typical pyranosyl oxocarbenium

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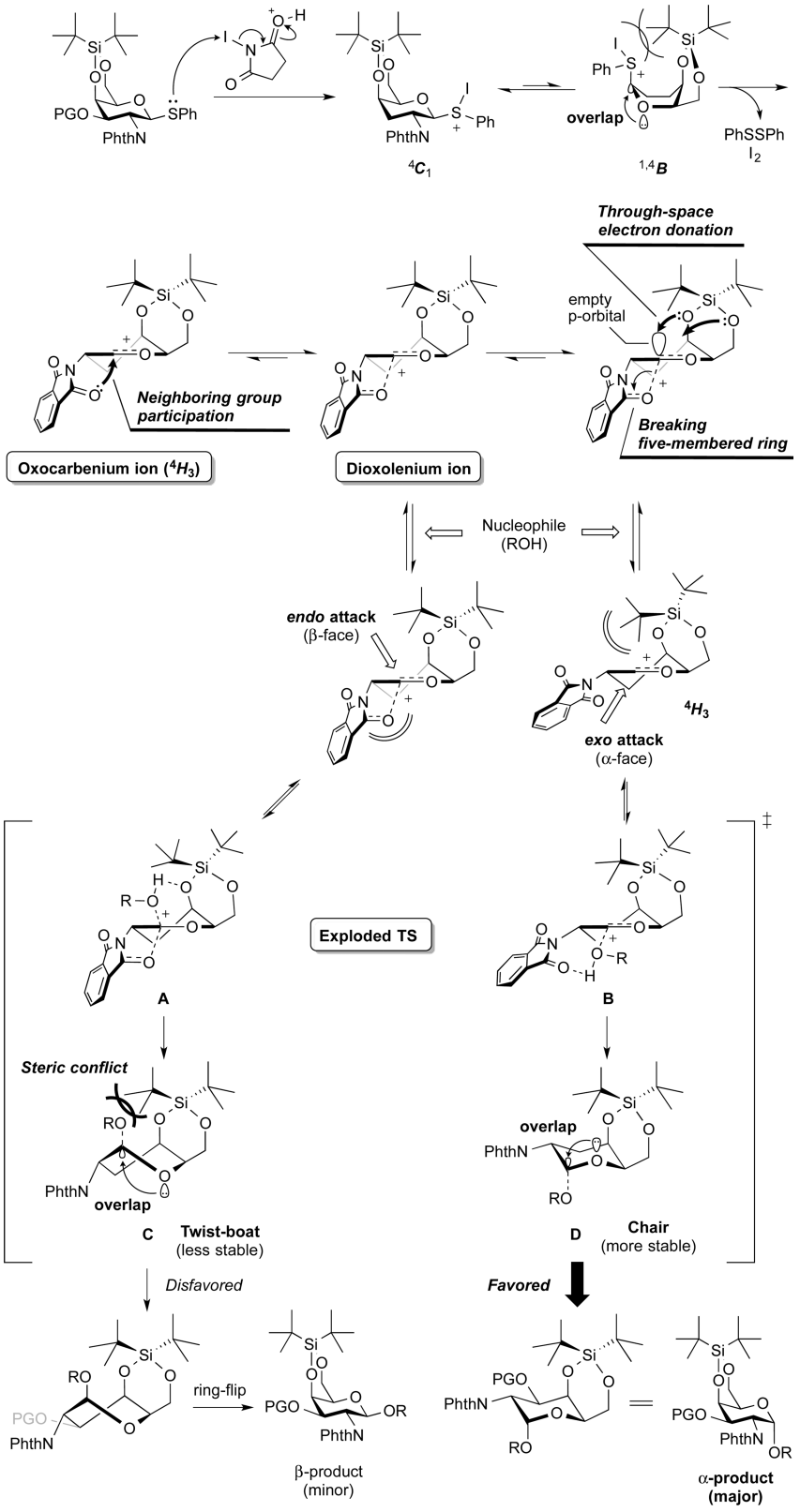

Figure 7. Proposed mechanism of DTBS-directed α-galactosylation.

intermediates can usually adopt a variety of conformations, such as ^4E, E_3, $^4H_3$, $^3H_4$, $^1S_5$, and $B_{2,5}$,[25] here the conformational freedom of the sugar ring is limited to the half-chair $^4H_3$ conformer because other conformers are unattainable because of the fused ring system formed by the DTBS group. Once the oxocarbenium intermediate is generated, the C2 phthalate group will interact with the electron-poor anomeric center through neighboring group participation, thus producing a dioxolenium ion. A preliminary computational study suggested that no reaction pathway could exist without neighboring group

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participation due to the phthalate group. Usually, 1,2-*trans* glycosides are produced by nucleophilic attack by an alcohol acceptor from β-face onto this sort of dioxolenium ion. In the DTBS-directed galactosylation, however, the dioxolenium ion would be cleaved by through-space electron donation because both O4 and O6 are in an axial orientation. In other words, the coplanar alignment of the O4−C4 and O6−C6 bonds with the empty p-orbital generated on C1 inevitably causes electrostatic attraction between the partially negatively charged oxygen atom of the C4 alkoxy groups and the positively charged carbon atom of the oxocarbenium ion. The Woerpel,[26] Bols,[27] and Crich[28] groups have independently reported the importance of the electrostatic effect of both the axially oriented C4 alkoxy and the exocyclic C5 alkoxymethyl groups in stabilizing the oxocarbenium ion. Breaking the five-membered ring in the dioxolenium ion would reform the oxocarbenium ion in the $^4H_3$ conformer, which can then undergo nucleophilic attack by the alcohol acceptor, predominantly from the *exo* side (α-face) because *endo* attack on the β-face is blocked by the substantial steric hindrance of the *tert*-butyl group. *Endo* or *exo* nucleophilic attack can determine the stereochemical outcome in the glycosylation. First, *endo* attack and *exo* attack generate the distinct exploded transition states **A** and **B**, respectively. Next, transition states **A** and **B** can access a twist-boat-like conformer (**C**) and a chairlike conformer (**D**), respectively, to maximize orbital overlap between the approaching alcohol acceptor and the developing lone pair on oxygen, resulting in glycosidated products where the resulting sp^3-hydridized orbitals are anticoplanar.[29] The chairlike conformer (**D**) is more stable than **C**, which is in a kinetically disfavored twist-boat-like conformation that must undergo a ring-flip to reach the more stable equatorial β-product. Moreover, **C** clearly suffers from unfavorable steric clash between the *tert*-butyl substituent and the incoming alcohol acceptor. Hence, the nucleophilic attack predominantly occurs via the pathway leading to the α-product. Importantly, the steric hindrance of the DTBS group can hamper the β-face approach of even the smallest alcohol, methanol, giving rise to predominantly the α-linked methylglycoside.[7] This study has demonstrated that the preferential formation of the $^4H_3$ oxocarbenium intermediate due to the conformational constraints imposed by the DTBS group and subsequent access to the kinetically stable chairlike transition state provide high stereoselectivity. Indeed, the powerful steric effect of the DTBS group is the most important factor in the observed α-selectivity. Whitfield and co-workers have reported that, to control the stereochemistry of glycosylations, glycosyl donors that can form face-discriminated cations and access only one ring conformation should be used.[30] Furthermore, they proposed that bridged donors are one possible approach. Our results support their account of stereoselective glycosylation.

We have previously made two intriguing findings regarding DTBS-directed α-galactosylation.[7] One is the exceptional case where β-selectivity (6:77, α/β ratio) is obtained by using glycosyl bromide donor with activation by insoluble silver silicate.[31] This remarkable result can be rationalized by an S_N2-like reaction mechanism. As illustrated in Figure 8, the reaction proceeds on insoluble silver silicate and the nucleophilic attack of the alcohol acceptor mainly occurs along an equatorial trajectory via an S_N2-like pathway where the oxocarbenium ion is formed but remains linked to silicate anionic surface, in such a way that the nucleophile (HO-R) can only attack by/through the β-face, predominantly forming the β-glycoside. This result

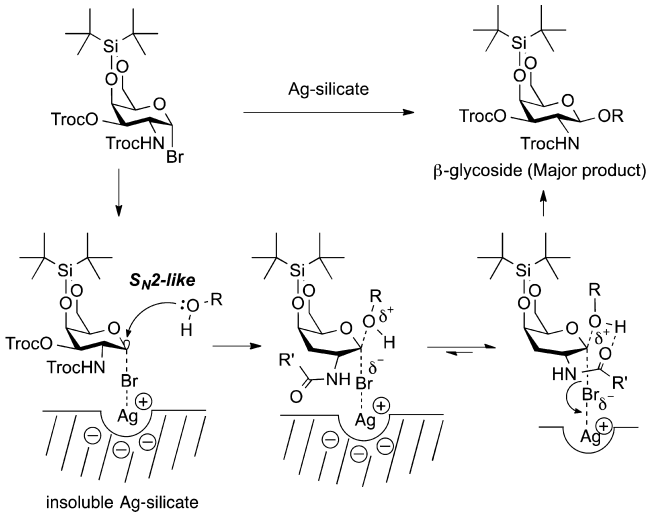

Figure 8. Proposed mechanism of β-selective glycosidation using a glycosyl bromide donor with activation by insoluble silver silicate.

suggests that the generation of the "distinct" oxocarbenium ion is required for the stereodirecting effect of the DTBS group.

Our second intriguing finding is the formation of 2-OH α-galactoside as a byproduct when 2-*O*-benzoyl-protected galactosyl donors were used. As expected, the DTBS-protected galactosyl donors gave predominantly α-glycosides in >70% yield. However, non-negligible amounts (~15%) of the corresponding 2-OH α-galactosides were also observed as byproducts (Figure 9). This phenomenon could be explained by a route involving the formation of an orthoester derivative. Usually, the benzoyl group is selected instead of the acetyl group to prevent the formation of the orthoester and it works well in most cases. However, coexistence of the benzoyl and DTBS group may make access of the alcohol acceptor to anomeric center at the oxocarbenium ion stage limited due to the steric clash, allowing for the nucleophilic attack at relatively less hindered carbonyl carbon on the benzoyl group at C2 to form the orthoester derivative. In addition, nucleophilic attack by the alcohol acceptor at the carbonyl carbon C2, giving the orthoester, could occur from the *exo* side because of the higher energy barrier to the *endo* attack.[30] Some of the orthoester formed could then be cleaved to the 2-OH oxocarbenium ion to release the benzoylated acceptor and form the 2-OH oxocarbenium ion, which is then glycosidated with the acceptor to furnish the 2-OH α-glycoside. We have not detected the benzoylated acceptor in the reaction mixture so far but the formation of orthoester derivatives has been actually observed. When 2-*O*-*benzyl*-protected DTBS-protected galactosyl donors were used, the corresponding α-glycosides were obtained in excellent yields without the formation of the 2-OH by-product.[32]

■ CONCLUSIONS

By experimental and computational studies, we have elucidated the origin of the α-selectivity in DTBS-directed α-galactosylation. Glycosidation experiments using various GalN donors, which differed in terms of only the protecting group at the C4 and C6 positions, demonstrated that the presence of the DTBS group was essential for strong α-selectivity. The following main requirements were found for α-selectivity. (1) Generation of the oxocarbenium ion:[33] A well-defined S_N1-like mechanism that produces the oxocarbenium ion results in the electron-

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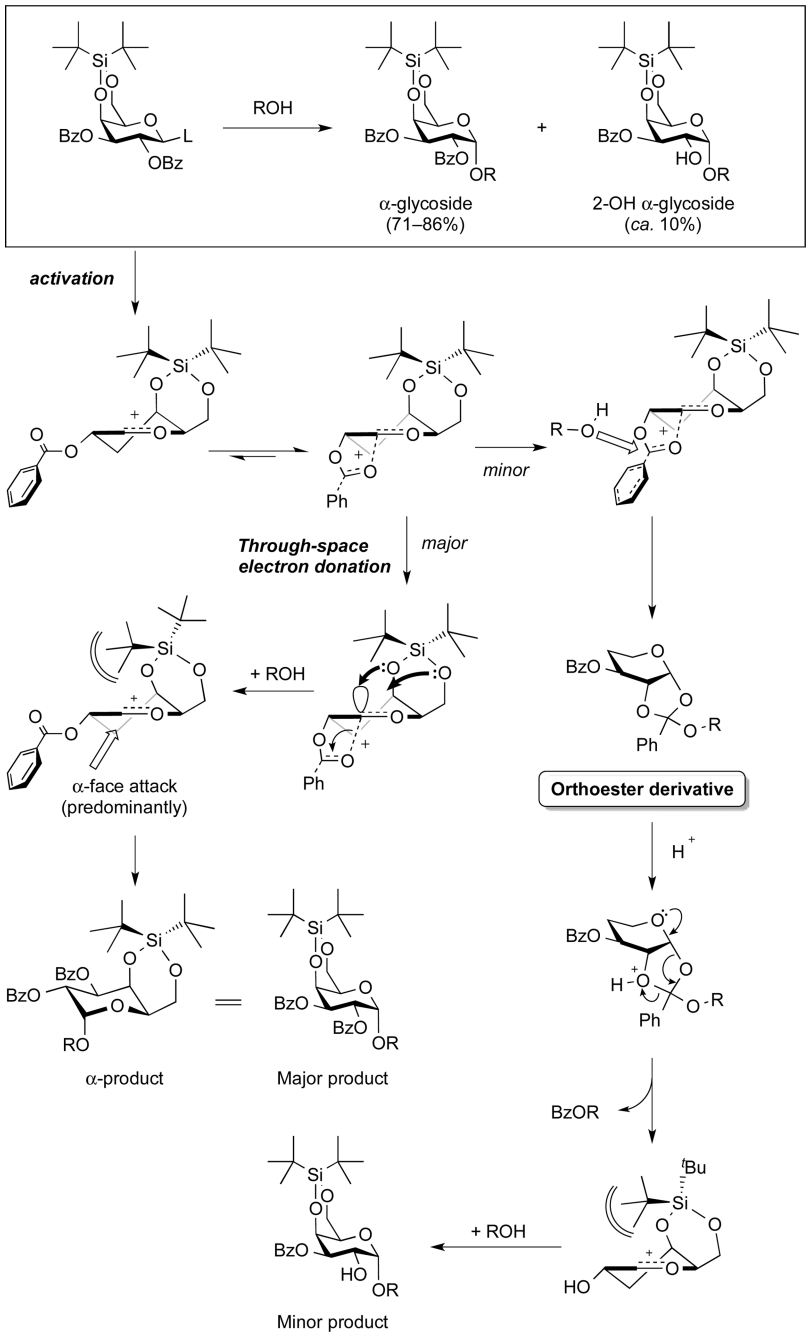

Figure 9. Proposed mechanism for the formation of 2-OH derivatives in DTBS-directed α-glycosidation using 2-*O*-benzoyl-protected galactosyl donors.

poor anomeric center necessary for modulating the stereoselectivity. (2) *Galacto*-type donors with cyclic protecting group bridging O4 and O6 to form six-membered ring: These donors preferentially adopt the $^4H_3$ conformation upon formation of the oxocarbenium ion, allowing for nucleophilic attack by the glycosyl acceptor preferentially from *exo* side (α-face) because of both stereoelectronic and steric effects. (3) Through-space electron donation: The axially oriented C4 alkoxy and the exocyclic C5 alkoxy groups exert a powerful electrostatic effect on the empty p-orbital that is formed after liberation of the leaving group, thus stabilizing the oxocarbenium ion. Moreover, the effect is strengthened by the C4−O4 and C6−O6 bonds being coplanar with the empty p-orbital. This effect is maximized when the donor has a cyclic protecting group enabling the formation of a six-membered ring. (4) Steric hindrance due to bulky alkyl substituents appended to cyclic protecting group: Steric bulk hinders nucleophilic attack on the β-face and also affects the stability in the transition state. (5) 4,6-*O*-Silylene structure: X-ray crystallographic analysis of the DTBS donor showed that one of the bulky alkyl groups in the silylene structure is positioned very close to the anomeric carbon, even in the ground state. The substituent can be positioned much closer to the anomeric carbon in the oxocarbenium intermediate, resulting in severe steric clash during the glycosylation (this is supported by the DFT calculations).

The DTBS group fulfills all these requirements well. These characteristics of the DTBS group may explain the high

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stereoselectivity of DTBS-directed α-galactosylation. Furthermore, of all the cyclic protecting groups examined, only the DTBS group provided strong α-selectivity. Thus, we suggest that the unique and specific effect of the DTBS group in α-selective galactosylation be called the "DTBS effect". Encouraged by the discovery of the DTBS effect, we are working on the development of stereoselective glycosylations using other ring-restricted glycosyl donors, the results of which will be reported in due course.

EXPERIMENTAL SECTION

General Procedure for Chemical Synthesis. All reactions were carried out under a positive pressure of argon unless otherwise noted. All chemicals were purchased from commercial suppliers and used as received without further purification. Molecular sieves were dried at 300 °C for 2 h in a muffle furnace prior to use. Solvents for reaction media were dried over molecular sieves and used without purification. Thin-layer chromatography (TLC) was performed on TLC plates (silica gel $60F_{254}$ on glass plate). Compounds were detected on TLC plates by either exposure to UV light (2536 Å) or development in 10% H_2SO_4 in ethanol followed by heating. Silica gel (80 mesh and 300 mesh) was used for flash column chromatography. The quantity of silica gel was usually 100 to 200-fold the weight of the crude sample to be purified. Solvent systems for chromatography are specified in volume ratios. Evaporation and concentration were carried out in vacuo. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400/500/600 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra are expressed in ppm (δ) relative to the Me_4Si signal adjusted to δ 0.00 ppm. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, td = triple doublet, m = multiplet and/or multiple resonances), coupling constant in hertz (Hz), integration, and position of the corresponding proton. ^{1}H–^{1}H COSY method was used to confirm the NMR peak assignments. High-resolution mass spectra (ESI-TOF MS) were obtained. Optical rotations were measured with a high-sensitivity polarimeter.

Computational Details. All DFT calculations were carried out in the GAUSSIAN09 software package.[34] We chose the M062X exchange-correlation functional[35] and the 6-31G* electronic basis set for calculations. Initial structures for the calculations were built with the aid of GaussView 5 visualization software.[36] To investigate the desired reactions, we constructed a six-membered ring as chairlike form in the initial structure. The geometries of complexes were fully optimized at the M062X/6-31G* level. We also performed normal-mode analysis to characterize the optimized structures and confirmed that all optimized structures have no imaginary frequencies.

Typical Procedure for Glycosidation Experiments. Molecular sieves, 4 Å (100 mg per 1 mL of solvent) were added to a mixture of the glycosyl donor (1.5 equiv with respect to the acceptor) and acceptor **23** in CH_2Cl_2 at room temperature. After stirring for 30 min, the mixture was cooled to 0 °C and *N*-iodosuccinimide (2.0 equiv with respect to the donor) and TfOH (0.2 equiv with respect to the donor) were added. The mixture was stirred for 30 min to 1 h while monitoring the reaction by TLC. Once all the acceptor was consumed, the reaction was quenched by the addition of saturated aq. $NaHCO_3$. The reaction mixture was diluted with $CHCl_3$ and filtered through Celite. The filtrate was then washed sequentially with saturated aq. $NaHCO_3$, saturated aq. $Na_2S_2O_3$, and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated. The resulting residue was purified by silica gel column chromatography to give the glycosylated products.

*Phenyl 3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylene-2-phthalimide-1-thio-β-D-galactopyranoside (**1**).* To a solution of **18** (200 mg, 0.407 mmol) in pyridine (2.0 mL) was added di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (223 μL, 0.611 mmol) at 0 °C. After stirring for 1 h at rt, the completion of the reaction was confirmed by TLC (1:3 EtOAc–*n*-hexane). The reaction was quenched by the addition of dry methanol at 0 °C. Solvents were removed by coevaporation with toluene, and then the residue was diluted with $CHCl_3$, washed with 2 M HCl, H_2O, satd. aq. $NaHCO_3$, and brine. The organic layer was subsequently dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:5 EtOAc–*n*-hexane) to give **1** (236 mg, 92%) as a colorless viscous compound. $[\alpha]_D$ + 112.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87–7.07 (m, 14 H, NPhth, 2 Ph), 5.54 (d, $J_{1,2}$ = 10.5 Hz, 1 H, 1-H), 4.87 (t, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 4.64 (d, J_{gem} = 12.3 Hz, 1 H, PhCH_2), 4.60 (d, $J_{3,4}$ = 2.7 Hz, 1 H, 4-H), 4.44 (d, 1 H, PhCH_2), 4.27 (dd, 1 H, 3-H), 4.25 (m, 2 H, 6a-H, 6b-H), 3.50 (s, 1 H, 5-H), 1.20, 1.07 (2 s, 18 H, 2 ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.4, 167.6, 137.9, 134.1, 133.9, 133.6, 132.0, 131.8, 128.8, 128.3, 127.6, 127.4, 123.6, 123.1, 84.9, 75.6, 75.2, 70.0, 69.4, 67.5, 50.7, 27.7, 27.6, 23.5, 20.8. HRMS (ESI-TOF) *m*/*z* calcd for $C_{35}H_{41}NO_6SSi$: 654.2316 $[M + Na]^+$, found 654.2318.

*Phenyl 3-O-benzyl-2-deoxy-4,6-O-diisopropylsilylene-2-phthalimide-1-thio-β-D-galactopyranoside (**2**).* To a solution of **18** (187 mg, 0.380 mmol) in DMF (3.8 mL) were added diisopropylsilyl bis(trifluoromethanesulfonate) (170 μL, 0.580 mmol) and triethylamine (370 μL, 2.66 mmol) at 0 °C. After stirring for 10 min at rt, the consumption of the starting material was confirmed by TLC (2:3 EtOAc–*n*-hexane). The reaction was quenched by the addition of dry methanol at 0 °C. Solvents were removed by coevaporation with toluene, and then the residue was diluted with $CHCl_3$, washed with H_2O and brine. The organic layer was subsequently dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:5 EtOAc–*n*-hexane) to give **2** (198 mg, 86%) as a colorless viscous compound. $[\alpha]_D$ + 108.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90–6.99 (m, 14 H, NPhth, 2 Ph), 5.53 (d, $J_{1,2}$ = 10.5 Hz, 1 H, 1-H), 4.80 (t, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 4.63 (d, J_{gem} = 12.4 Hz, 1 H, PhCH_2), 4.51 (d, $J_{3,4}$ = 2.7 Hz, 1 H, 4-H), 4.43 (d, 1 H, PhCH_2), 4.27–4.17 (m, 3 H, 3-H, 6a-H, 6b-H), 3.53 (s, 1 H, 5-H), 1.26–1.03 (m, 14 H, 2 ^{i}Pr); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.4, 167.4, 137.8, 134.0, 133.8, 132.9, 132.4, 131.7, 128.7, 128.2, 127.6, 127.6, 127.5, 123.6, 123.1, 84.4, 75.8, 75.3, 70.4, 69.2, 66.9, 50.7, 29.7, 17.1, 17.0, 16.9, 13.9, 12.7. HRMS (ESI-TOF) *m*/*z* calcd for $C_{33}H_{37}NO_6SSi$: 626.2003 $[M + Na]^+$, found 626.2002.

*Phenyl 3-O-benzyl-4,6-O-tert-butylmethylidene-2-deoxy-2-phthalimide-1-thio-β-D-galactopyranoside (**3**).* To a solution of **18** (50 mg, 0.105 mmol) in MeCN (349 μL) were added pivalaldehyde (46 μL, 0.418 mmol) and (±)-camphor-10-sulfonic acid (CSA) (5 mg, 21.0 μmol) at rt. After stirring for 7.5 h at rt as the reaction was monitored by TLC (1:2 EtOAc–*n*-hexane, 1:15 MeOH–$CHCl_3$), the reaction was quenched by the addition of triethylamine at 0 °C and the reaction mixture was then evaporated. The resulting residue was purified by silica gel column chromatography (1:5 EtOAc–*n*-hexane) to give **3** (49 mg, 84%) as a white foamy compound. $[\alpha]_D$ + 2.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.85–7.07 (m, 14 H, NPhth, 2 Ph), 5.53 (d, $J_{1,2}$ = 10.4 Hz, 1 H, 1-H), 4.70 (t, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 4.54 (d, J_{gem} = 12.4 Hz, 1 H, PhCH_2), 4.38 (d, 1 H, PhCH_2), 4.35 (dd, $J_{3,4}$ = 3.5 Hz, 1 H, 3-H), 4.27 (dd, J_{gem} = 12.2 Hz, $J_{5,6a}$ = 1.4 Hz, 1 H, 6a-H), 4.14 (s, 1 H, ^{t}BuC*H*<), 4.05 (d, 1 H, 4-H), 3.81 (dd, $J_{5,6b}$ = 1.7 Hz, 1 H, 6b-H), 3.49 (d, 1 H, 5-H), 0.99 (s, 9 H, ^{t}Bu); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.8, 167.0, 138.0, 134.0, 133.8, 132.8, 131.8, 131.8, 131.6, 128.7, 128.1, 127.7, 127.5, 127.3, 123.6, 123.1, 107.1, 83.0, 74.9, 72.1, 70.6, 69.2, 50.6, 35.2, 29.7, 24.7. HRMS (ESI-TOF) *m*/*z* calcd for $C_{32}H_{33}NO_6S$: 582.1921 $[M + Na]^+$, found 582.1922.

*Phenyl 3-O-benzyl-2-deoxy-4,6-O-ethylidene-2-phthalimide-1-thio-β-D-galactopyranoside (**4**).* To a solution of **18** (281 mg, 0.572 mmol) in MeCN (1.9 mL) were added dimethylacetal (182 μL, 1.72 mmol) and CSA (13 mg, 57.0 μmol) at rt. After stirring for 2.5 h at rt as the reaction was monitored by TLC (1:30 MeOH–$CHCl_3$), the reaction was quenched by the addition of triethylamine at 0 °C and the reaction mixture was then evaporated. The resulting residue was purified by silica gel column chromatography (1:2 → 2:3 EtOAc–*n*-hexane) to give **4** (273 mg, 92%) as a white foamy compound. $[\alpha]_D$ −105.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71–7.00 (m, 14 H, NPhth, 2 Ph), 5.54 (d, $J_{1,2}$ = 10.4 Hz, 1 H, 1-H), 4.75–4.68 (m, 2 H, 2-H, CH_3C*H*<), 4.59 (d, J_{gem} = 12.6 Hz, 1 H, PhCH_2), 4.37 (d, 1

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H, PhCH_2), 4.32 (dd, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 10.7 Hz, 1 H, 3-H), 4.23 (dd, $J_{5,6a}$ = 1.5 Hz, J_{gem} = 12.2 Hz, 1 H, 6a-H), 4.07 (d, 1 H, 4-H), 3.83 (dd, $J_{5,6b}$ = 1.2 Hz, 1 H, 6b-H), 3.48 (d, 1 H, 5-H), 1.46 (d, $J_{CH3CH<,CH3CH<}$ = 5.0 Hz, 3 H, CH_3CH<); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.5, 167.1, 137.6, 137.6, 134.0, 133.8, 132.8, 132.2, 131.8, 131.7, 128.7, 128.2, 128.0, 127.7, 127.7, 123.6, 123.1, 99.1, 83.5, 74.7, 72.1, 71.0, 70.1, 69.0, 50.7, 29.7, 21.1. HRMS (ESI-TOF) m/z calcd for $C_{29}H_{27}NO_6S$: 540.1451 $[M + Na]^+$, found 540.1453.

*Phenyl 3-O-benzyl-2-deoxy-4,6-O-methylidene-2-phthalimide-1-thio-β-D-galactopyranoside (**5**).* To a solution of **18** (200 mg, 0.407 mmol) in MeCN (814 μL) were added dimethoxymethane (2.53 mL, 28.5 mmol) and CSA (19 mg, 81.4 μmol) at rt. After stirring for 14 h at rt as the reaction was monitored by TLC (1:30 MeOH−$CHCl_3$), the reaction was warmed to 40 °C and the stirring was continued for 10 h at the same temperature. Then the reaction was warmed to 60 °C and the stirring was continued for 10 h at the same temperature. The reaction was quenched by the addition of triethylamine at 0 °C and the reaction mixture was then evaporated. The resulting residue was purified by silica gel column chromatography (1:1 EtOAc−*n*-hexane) to give **5** (173 mg, 84%) as a white foamy compound. $[\alpha]_D$ + 0.2 (*c* 4.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88−7.00 (m, 14 H, NPhth, 2 Ph), 5.56 (d, $J_{1,2}$ = 10.5 Hz, 1 H, 1-H), 5.28 (d, J_{gem} = 6.4 Hz, 1 H, CH_2O_2), 4.77−4.73 (m, 2 H, 2-H, CH_2O_2), 4.63 (d, J_{gem} = 12.6 Hz, 1 H, PhCH_2), 4.38−4.35 (m, 2 H, 3-H, PhCH_2), 4.23 (br dd, J_{gem} = 12.2 Hz, 1 H, 6a-H), 4.07 (d, $J_{3,4}$ = 3.3 Hz, 1 H, 4-H), 3.80 (dd, $J_{5,6b}$ = 1.5 Hz, 1 H, 6b-H), 3.53 (d, 1 H, 5-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.4, 167.1, 137.4, 134.0, 133.8, 132.7, 132.5, 131.7, 128.8, 128.2, 127.8, 127.7, 123.7, 123.1, 93.4, 84.2, 74.7, 72.3, 71.4, 70.9, 68.9, 50.9. HRMS (ESI-TOF) m/z calcd for $C_{28}H_{25}NO_6S$: 526.1295 $[M + Na]^+$, found 526.1295.

*Phenyl 3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimide-1-thio-β-D-galactopyranoside (**6**).* To a solution of **17** (14.3 g, 35.5 mmol) in MeCN (71.0 mL) were added benzaldehyde dimethyl acetal (BDA) (5.83 mL, 39.1 mmol) and CSA (411 mg, 1.77 mmol) at 0 °C. After stirring for 1.5 h at rt as the reaction was monitored by TLC (1:1 EtOAc−toluene), the reaction was quenched by the addition of triethylamine at 0 °C and the reaction mixture was then evaporated. The resulting residue was purified by silica gel column chromatography (1:3 → 1:1 EtOAc−toluene) to give the 4,6-*O*-benzylidenated product (15.4 g, 31.6 mmol), which was subsequently dissolved in DMF (158 mL). To the mixture was added BnBr (9.41 mL, 79.1 mmol) at rt. After cooling to 0 °C, NaH (60% in oil; 2.53 g, 63.3 mmol) was added to the mixture at the same temperature. After stirring for 2.5 h at rt as the reaction was monitored by TLC (2:3 EtOAc−*n*-hexane, 1:10 EtOAc−toluene), the reaction was quenched by the addition of triethylamine and satd. aq. NH_4Cl at 0 °C. The reaction mixture was coevaporated with toluene. The residue was diluted with EtOAc and washed with H_2O, satd. aq. $NaHCO_3$, and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (2:7 EtOAc−*n*-hexane) to give **6** (14.2 g, 69% over two steps) as a white foamy compound, which was then recrystallized from EtOAc−*n*-hexane system. mp = 211 to 216 °C. $[\alpha]_D$ + 48.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86−7.01 (m, 19 H, NPhth, 3 Ph), 5.58 (d, $J_{1,2}$ = 10.5 Hz, 1 H, 1-H), 5.51 (s, 1 H, PhCH<), 4.77 (t, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 4.59 (d, J_{gem} = 12.4 Hz, 1 H, PhCH_2), 4.42−4.37 (m, 3 H, 3-H, 6a-H, PhCH_2), 4.26 (d, $J_{3,4}$ = 3.2 Hz, 1 H, 4-H), 4.03 (d, J_{gem} = 11.9 Hz, 1 H, 6b-H), 3.60 (s, 1 H, 5-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.5, 167.0, 137.7, 134.0, 133.8, 133.3, 131.7, 131.7, 131.4, 129.0, 128.7, 128.1, 127.8, 127.6, 126.6, 123.6, 123.2, 123.1, 122.9, 101.2, 82.9, 74.7, 72.6, 70.9, 70.4, 70.1, 69.9, 69.5, 50.7, 50.5. HRMS (ESI-TOF) m/z calcd for $C_{34}H_{29}NO_6S$: 602.1608 $[M + Na]^+$, found 602.1606.

*Phenyl 3-O-benzyl-2-deoxy-4,6-O-(4-nitrobenzylidene)-2-phthalimide-1-thio-β-D-galactopyranoside (**7**).* To a solution of **18** (200 mg, 406 μmol) in DMF (810 μL) were added 4-nitrobenzaldehyde (307 mg, 2.03 mmol) and CSA (63 mg, 0.203 mmol) at rt. After stirring for 2 h at 100 °C as the reaction was monitored by TLC (1:1 EtOAc−*n*-hexane), the reaction mixture was evaporated. The resulting residue was purified by silica gel column chromatography (2:3 EtOAc−*n*-hexane) to give **7** (238 mg, 94%) as a colorless foamy compound. $[\alpha]_D$ + 43.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.24−7.01 (m, 18 H, Ar), 5.58 (d, $J_{1,2}$ = 10.4 Hz, 1 H, 1-H), 5.56 (s, 1 H, ArCH<), 4.70 (t, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 4.58 (d, J_{gem} = 12.7 Hz, 1 H, PhCH_2), 4.44−4.40 (m, 3 H, 3-H, 6a-H, PhCH_2), 4.27 (d, $J_{3,4}$ = 3.2 Hz, 1 H, 4-H), 4.05 (dd, $J_{5,6b}$ = 1.5 Hz, J_{gem} = 12.2 Hz, 1 H, 6b-H), 3.64 (s, 1 H, 5-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.5, 167.1, 148.3, 144.0, 137.5, 134.1, 133.9, 133.6, 131.7, 131.2, 128.7, 128.2, 128.1, 127.8, 127.7, 123.7, 123.4, 123.2, 99.6, 83.0, 74.6, 72.7, 71.2, 69.9, 69.6, 50.7. HRMS (ESI-TOF) m/z calcd for $C_{34}H_{28}N_2O_8S$: 647.1459 $[M + Na]^+$, found 647.1459.

*Phenyl 4,6-O-anisylidene-3-O-benzyl-2-deoxy-2-phthalimide-1-thio-β-D-galactopyranoside (**8**).* To a solution of **18** (300 mg, 610 μmol) in MeCN (1.2 mL) were added anisaldehyde dimethyl acetal (153 μL, 915 μmol) and CSA (14 mg, 61.0 μmol) at rt. After stirring for 4 h at rt as the reaction was monitored by TLC (1:1 EtOAc−*n*-hexane), the reaction was quenched by the addition of triethylamine at 0 °C. The reaction mixture was then evaporated. The resulting residue was purified by silica gel column chromatography (1:100 acetone−$CHCl_3$) to give **8** (331 mg, 89%) as a colorless foamy compound. $[\alpha]_D$ + 63.3 (*c* 4.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87−6.89 (m, 18 H, Ar), 5.58 (d, $J_{1,2}$ = 10.4 Hz, 1 H, 1-H), 5.46 (s, 1 H, ArCH<), 4.76 (t, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 4.58 (d, J_{gem} = 12.7 Hz, 1 H, PhCH_2), 4.40−4.36 (m, 3 H, 3-H, 6a-H, PhCH_2), 4.25 (d, $J_{3,4}$ = 3.2 Hz, 1 H, 4-H), 4.18 (dd, $J_{5,6b}$ = 1.5 Hz, J_{gem} = 12.2 Hz, 1 H, 6b-H), 3.84 (s, 3 H, OMe), 3.59 (d, 1 H, 5-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.6, 167.1, 160.2, 137.8, 134.0, 133.8, 133.4, 131.8, 131.7, 131.5, 130.5, 128.7, 128.2, 128.0, 127.9, 127.6, 123.6, 123.1, 113.6, 101.2, 83.0, 74.8, 72.7, 71.0, 70.2, 69.5, 55.4, 50.7. HRMS (ESI-TOF) m/z calcd for $C_{35}H_{31}NO_7S$: 632.1713 $[M + Na]^+$, found 632.1714.

*Phenyl 3-O-benzyl-4,6-O-(2-chloroethylidene)-2-deoxy-2-phthalimide-1-thio-β-D-galactopyranoside (**9**).* To a solution of **18** (49 mg, 100 μmol) in MeCN (500 μL) were added 2-chloroacetaldehyde diethyl acetal (23 μL, 150 μmol) and CSA (5 mg, 20.0 μmol) at rt. After stirring for 20 h at rt as the reaction was monitored by TLC (1:2 EtOAc−*n*-hexane, 1:15 MeOH−$CHCl_3$), the reaction was warmed to 70 °C and the stirring was continued for 7 h at the same temperature. The reaction was quenched by the addition of triethylamine at 0 °C and the reaction mixture was then evaporated. The resulting residue was purified by silica gel column chromatography (2:3 EtOAc−*n*-hexane) to give **9** (41 mg, 74%) as a white foamy compound. $[\alpha]_D$ + 0.1 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89−7.07 (m, 14 H, NPhth, 2 Ph), 5.53 (d, $J_{1,2}$ = 10.4 Hz, 1 H, 1-H), 4.74 (dd, $J_{ClCH2CH<,ClCH2CH<}$ = 3.7, 6.0 Hz, 1 H, ClCH_2CH<), 4.65 (t, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H), 4.57 (d, J_{gem} = 12.6 Hz, 1 H, PhCH_2), 4.40 (d, 1 H, PhCH_2), 4.36 (dd, $J_{3,4}$ = 3.4 Hz, 1 H, 3-H), 4.30 (dd, $J_{5,6a}$ = 1.4 Hz, J_{gem} = 12.3 Hz, 1 H, 6a-H), 4.09 (d, 1 H, 4-H), 3.87 (dd, $J_{5,6b}$ = 1.6 Hz, 1 H, 6b-H), 3.66, 3.60 (2 dd, J_{gem} = 11.5 Hz, 2 H, ClCH_2CH<), 3.53 (d, 1 H, 5-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.5, 167.1, 137.5, 134.1, 133.9, 133.1, 131.8, 131.7, 131.7, 128.7, 128.2, 128.0, 127.8, 127.7, 123.7, 123.2, 100.4, 83.5, 74.5, 72.4, 71.1, 69.9, 69.2, 50.6, 44.0. HRMS (ESI-TOF) m/z calcd for $C_{29}H_{26}ClNO_6S$: 574.1062 $[M + Na]^+$, found 574.1065.

*Phenyl 3-O-benzyl-2-deoxy-2-phthalimide-4,6-O-1′,1′,3′,3′-tetraisopropyldisiloxanylidene-1-thio-β-D-galactopyranoside (**10**).* To a solution of **18** (301 mg, 0.612 mmol) in DMF (6.1 mL) were added 1,3-dichloro-1′,1′,3′,3′-tetraisopropyldisiloxane (215 μL, 0.671 mmol), imidazole (183 mg, 2.68 mmol) at 0 °C. After stirring for 1 h at rt as the reaction was monitored by TLC (2:7 EtOAc−*n*-hexane), the reaction was quenched by the addition of dry methanol at 0 °C. The reaction mixture was coevaporated with toluene and then diluted with $CHCl_3$, washed with satd. aq. $NaHCO_3$ and brine. The organic layer was subsequently dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:10 EtOAc−*n*-hexane, 1:6 diethyl ether−*n*-hexane) to give **10** (380 mg, 88%) as a colorless viscous compound. $[\alpha]_D$ + 53.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71−6.81 (m, 14 H, NPhth, 2 Ph), 5.45 (d, $J_{1,2}$ = 10.1 Hz, 1 H, 1-H), 4.62 (t, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 4.46 (d, J_{gem} = 11.9 Hz, 1 H, PhCH_2), 4.33 (br d, 1 H, 4-H), 4.18 (br dd, 1 H, 3-H), 4.12 (d, 1 H, PhCH_2), 3.82−3.77 (m, 2 H,

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6a-H, 6b-H), 3.66 (m, 1 H, 5-H), 1.02−0.90 (m, 28 H, 4 ^{i}Pr); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.4, 167.2, 137.5, 133.8, 133.6, 132.2, 132.1, 131.7, 128.6, 128.0, 127.7, 127.5, 127.4, 123.3, 123.0, 83.2, 77.8, 71.9, 65.0, 59.3, 50.8, 17.5, 17.4, 17.3, 17.2, 17.2, 17.1, 16.9, 14.0, 13.2, 12.7, 12.5. HRMS (ESI-TOF) m/z calcd for $C_{39}H_{51}NO_7SSi_2$: 756.2817 $[M + Na]^+$, found 756.2817.

*Phenyl 3-O-benzyl-4,6-di-O-tert-butyldimethylsilyl-2-deoxy-2-phthalimide-1-thio-β-D-galactopyranoside (**11**).* To a solution of **18** (201 mg, 0.409 mmol) in DMF (2.7 mL) were added *tert*-butyldimethylsilyl trifluoromethanesulfonate (560 μL, 2.44 mmol), imidazole (222 mg, 3.26 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (251 mg, 1.22 mmol) at 0 °C. After stirring for 135 min at rt as the reaction was monitored by TLC (1:3 EtOAc−*n*-hexane), the reaction was quenched by the addition of dry methanol at 0 °C. The reaction mixture was diluted with EtOAc, washed with H_2O, satd. aq. $NaHCO_3$, and brine. The organic layer was subsequently dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:10 EtOAc−*n*-hexane) to give **11** (281 mg, 96%) as a colorless viscous compound. $[\alpha]_D$ + 37.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71−6.80 (m, 14 H, NPhth, 2 Ph), 5.45 (d, $J_{1,2}$ = 10.1 Hz, 1 H, 1-H), 4.58 (t, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 4.50 (d, J_{gem} = 11.9 Hz, 1 H, PhCH_2), 4.16 (d, $J_{3,4}$ = 1.8 Hz, 1 H, 4-H), 4.11 (d, 1 H, PhCH_2), 4.07 (dd, 1 H, 3-H), 3.71−3.70 (m, 2 H, 6a-H, 6b-H), 3.50 (br t, $J_{5,6b}$ = 6.4 Hz, $J_{5,6a}$ = 6.9 Hz, 1 H, 5-H), 0.83 (s, 18 H, 2 ^{t}Bu), 0.03−0.00 (m, 12 H, 2 $SiMe_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.5, 167.1, 137.4, 133.8, 133.6, 132.4, 131.9, 131.7, 128.6, 128.0, 127.6, 127.4, 127.4, 123.3, 123.1, 82.9, 79.9, 78.0, 72.1, 66.9, 61.6, 50.7, 26.0, 25.9, 18.5, 18.2, −4.3, −5.1, −5.3, −5.3. HRMS (ESI-TOF) m/z calcd for $C_{39}H_{53}NO_6SSi_2$: 742.3024 $[M + Na]^+$, found 742.3024.

*Phenyl 3-O-benzyl-2-deoxy-2-phthalimide-1-thio-4,6-O-xylylene-β-D-galactopyranoside (**12**).* To a solution of **18** (100 mg, 0.203 mmol) in DMF (2.0 mL) was added α,α′-dibromo-*o*-xylene (134 mg, 0.509 mmol) at rt. After cooling to 0 °C, NaH (60% in oil; 20 mg, 0.505 mmol) was added to the mixture at 0 °C. After stirring for 1 h at rt as the reaction was monitored by TLC (2:3 EtOAc−*n*-hexane), the reaction was quenched by the addition of triethylamine and satd. aq. NH_4Cl at 0 °C. The reaction mixture was coevaporated with toluene. The residue was diluted with EtOAc and washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:3 EtOAc−*n*-hexane) to give **12** (46 mg, 38%) as a colorless viscous compound. $[\alpha]_D$ + 32.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88−7.63 (m, 4 H, Phth), 7.34−7.00 (m, 14 H, 3 Ar), 5.48 (d, $J_{1,2}$ = 10.5 Hz, 1 H, 1-H), 5.20 (d, J_{gem} = 12.5 Hz, 1 H, ArCH_2), 5.03 (d, 1 H, ArCH_2), 4.92 (d, J_{gem} = 11.5 Hz, 1 H, ArCH_2), 4.84 (d, 1 H, ArCH_2), 4.76 (t, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 4.61 (d, J_{gem} = 12.5 Hz, 1 H, ArCH_2), 4.28 (dd, $J_{3,4}$ = 3.0 Hz, 1 H, 3-H), 4.23 (d, 1 H, ArCH_2), 4.11 (d, 1 H, 4-H), 4.09 (dd, $J_{5,6a}$ = 6.0 Hz, J_{gem} = 11.0 Hz, 1 H, 6a-H), 3.78 (t, $J_{5,6b}$ = 6.5 Hz, 1 H, 5-H), 3.72 (dd, 1 H, 6b-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.3, 167.5, 137.5, 137.0, 136.5, 133.9, 133.8, 132.9, 132.1, 131.7, 130.8, 130.5, 128.7, 128.6, 128.5, 128.2, 127.6, 127.5, 123.5, 123.1, 84.2, 77.6, 76.7, 75.6, 74.6, 71.1, 71.0, 70.5, 51.8. HRMS (ESI-TOF) m/z calcd for $C_{35}H_{31}NO_6S$: 616.1764 $[M + Na]^+$, found 616.1765.

*Phenyl 3,4,6-tri-O-benzyl-2-deoxy-2-phthalimide-1-thio-β-D-galactopyranoside (**13**).* To a solution of **18** (200 mg, 0.407 mmol) in DMF (2.0 mL) was added BnBr (194 μL, 1.63 mmol) at rt. After cooling to 0 °C, NaH (60% in oil; 49 mg, 1.22 mmol) was added to the mixture at 0 °C. After stirring for 2 h at rt as the reaction was monitored by TLC (2:3 EtOAc−*n*-hexane), the reaction was quenched by the addition of dry MeOH at 0 °C. The reaction mixture was coevaporated with toluene. The residue was diluted with EtOAc and washed with H_2O and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:5 EtOAc−*n*-hexane) to give **13** (233 mg, 85%) as a colorless viscous compound. $[\alpha]_D$ + 86.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84−7.65 (m, 4 H, Phth), 7.39−6.96 (m, 20 H, 4 Ph), 5.56 (d, $J_{1,2}$ = 10.5 Hz, 1 H, 1-H), 4.96 (d, J_{gem} = 12.5 Hz, 1 H, PhCH_2), 4.84 (t, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 4.59 (d, J_{gem} = 11.5 Hz, 1 H, PhCH_2), 4.57 (d, 1 H, PhCH_2), 4.48 (d, J_{gem} = 12.0 Hz, 1 H, PhCH_2), 4.43 (d, 1 H, PhCH_2), 4.35 (dd, $J_{3,4}$ = 2.5 Hz, 1 H, 3-H), 4.29 (d, 1 H, PhCH_2), 4.07 (d, 1 H, 4-H), 3.81 (t, $J_{5,6a}$ = $J_{5,6b}$ = 6.5 Hz, 1 H, 5-H), 3.69 (d, 2 H, 6a-H, 6b-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.3, 167.4, 140.9, 138.5, 137.9, 137.5, 133.9, 133.7, 132.9, 131.8, 131.7, 128.8, 128.6, 128.5, 128.5, 128.3, 128.3, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.9, 123.4, 123.1, 84.0, 77.6, 77.5, 74.4, 73.5, 72.2, 71.4, 68.8, 65.2, 51.6. HRMS (ESI-TOF) m/z calcd for $C_{41}H_{37}NO_6S$: 694.2234 $[M + Na]^+$, found 694.2233.

*Phenyl 3-O-benzyl-2-deoxy-4,6-di-O-methyl-2-phthalimide-1-thio-β-D-galactopyranoside (**14**).* To a solution of **18** (300 mg, 0.610 mmol) in DMF (6.1 mL) were added iodomethane (191 μL, 3.05 mmol), NaH (60% in oil; 97 mg, 2.44 mmol) at 0 °C. After stirring for 1 h at rt as the reaction was monitored by TLC (1:1 EtOAc−*n*-hexane), the reaction was quenched by the addition of satd. aq. NH_4Cl and triethylamine at 0 °C. The reaction mixture was coevaporated with toluene and then diluted with $CHCl_3$, washed with H_2O, satd. aq. $NaHCO_3$, and brine. The organic layer was subsequently dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:2 EtOAc−*n*-hexane) to give **14** (224 mg, 68%) as a colorless foamy compound. $[\alpha]_D$ + 109.8 (*c* 2.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86−6.97 (m, 14 H, NPhth, 2 Ph), 5.51 (d, $J_{1,2}$ = 10.6 Hz, 1 H, 1-H), 4.71 (t, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 4.65 (d, J_{gem} = 12.2 Hz, 1 H, PhCH_2), 4.35−4.29 (m, 2 H, 3-H, PhCH_2), 3.81 (d, $J_{3,4}$ = 2.7 Hz, 1 H, 4-H), 3.74−3.66 (m, 2 H, 5-H, 6a-H), 3.62 (s, 3 H, OMe), 3.58 (dd, $J_{5,6b}$ = 5.4 Hz, J_{gem} = 9.2 Hz, 1 H, 6b-H), 3.56 (s, 3 H, OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.3, 167.4, 137.5, 134.0, 133.8, 133.3, 131.9, 131.7, 128.7, 128.2, 127.7, 127.6, 127.4, 123.5, 123.1, 84.4, 74.4, 71.3, 70.7, 61.4, 59.3, 51.7. HRMS (ESI-TOF) m/z calcd for $C_{29}H_{29}NO_6S$: 542.1608 $[M + Na]^+$, found 542.1612.

*Phenyl 4,6-di-O-acetyl-3-O-benzyl-2-deoxy-2-phthalimide-1-thio-β-D-galactopyranoside (**15**).* To a solution of **18** (150 mg, 0.305 mmol) in pyridine (1.5 mL) were added acetic anhydride (288 μL, 3.05 mmol), DMAP (3.7 mg, 30.5 μmol) at 0 °C. After stirring for 30 min at rt as the reaction was monitored by TLC (2:3 EtOAc−*n*-hexane), the reaction was quenched by the addition of dry methanol at 0 °C. The reaction mixture was coevaporated with toluene and then diluted with $CHCl_3$, washed with 2 M HCl, H_2O, satd. aq. $NaHCO_3$, and brine. The organic layer was subsequently dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:3 EtOAc−*n*-hexane) to give **15** (176 mg, quant) as a colorless viscous compound. $[\alpha]_D$ + 130.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86−6.89 (m, 14 H, NPhth, 2 Ph), 5.61 (d, $J_{3,4}$ = 3.0 Hz, 1 H, 4-H), 5.55 (d, $J_{1,2}$ = 10.5 Hz, 1 H, 1-H), 4.56 (d, J_{gem} = 12.0 Hz, 1 H, PhCH_2), 4.52 (t, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 4.34 (dd, 1 H, 3-H), 4.25−4.21 (m, 3 H, 6a-H, 6b-H, PhCH_2), 4.02 (t, $J_{5,6a}$ = $J_{5,6b}$ = 6.5 Hz, 1 H, 5-H), 2.18, 2.06 (2 s, 6 H, 2 Ac); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.3, 170.3, 167.8, 167.2, 137.0, 134.0, 133.8, 132.3, 132.2, 131.5, 131.4, 128.6, 128.0, 127.9, 127.7, 127.6, 123.4, 123.2, 83.9, 74.7, 73.4, 71.0, 65.6, 62.3, 51.3, 20.7, 20.6. HRMS (ESI-TOF) m/z calcd for $C_{31}H_{29}NO_8S$: 598.1506 $[M + Na]^+$, found 598.1507.

*Phenyl 3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylene-2-phthalimide-1-thio-β-D-glucopyranoside (**16**).* Compound **19** (283 mg, 0.488 mmol) was dissolved in 80% aq. AcOH (4.9 mL) and the solution was stirred for 2 h at 60 °C as the reaction was monitored by TLC (1:1 EtOAc−*n*-hexane). The reaction mixture was evaporated, then diluted with $CHCl_3$, washed with H_2O, satd. aq. Na_2CO_3, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The resulting residue was roughly purified by silica gel column chromatography (2:1 EtOAc−*n*-hexane) to give crude mixture mainly containing **20**. The residue was then dissolved in pyridine (4.9 mL). To the solution was added $DTBS(OTf)_2$ (174 μL, 0.537 mmol) at 0 °C. After stirring for 1 h as the reaction was monitored by TLC (1:2 EtOAc−*n*-hexane), the reaction was quenched by the addition of dry methanol at 0 °C. The reaction mixture was coevaporated with toluene and then diluted with $CHCl_3$, washed with 2 M HCl, H_2O, satd. aq. $NaHCO_3$, and brine. The organic layer was subsequently

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dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:5 EtOAc−*n*-hexane) to give **16** (293 mg, 86%) as a colorless foamy compound. $[\alpha]_D$ + 52.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87−6.86 (m, 14 H, NPhth, 2 Ph), 5.59 (d, $J_{1,2}$ = 10.1 Hz, 1 H, 1-H), 4.83 (d, J_{gem} = 12.3 Hz, 1 H, PhCH_2), 4.60 (d, 1 H, PhCH_2), 4.26−4.13 (m, 3 H, 2-H, 6a-H, 6b-H), 4.05 (dd, $J_{2,3}$ = 8.3 Hz, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 3.97 (t, $J_{4,5}$ = 10.3 Hz, 1 H, 4-H), 3.65−3.60 (m, 1 H, 5-H), 1.09, 1.06 (2 s, 18 H, 2 ^{t}Bu); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.9, 167.2, 138.0, 134.0, 133.8, 132.7, 131.9, 131.7, 128.9, 128.2, 128.1, 128.0, 127.4, 123.6, 123.3, 84.0, 79.1, 78.1, 74.6, 74.3, 66.4, 54.4, 27.5, 27.1, 22.7, 20.0. HRMS (ESI-TOF) *m*/*z* calcd for $C_{35}H_{41}NO_6SSi$: 654.2316 $[M + Na]^+$, found 654.2317.

*2-(Trimethylsilyl)ethyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranoside (**22**).* To a solution of 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**21**) (4.69 g, 12.7 mmol) in THF (63.5 mL) was added Ac_2O (3.6 mL, 38.1 mmol) at rt. After cooling to 0 °C, DMAP (160 mg, 1.31 mmol) was added to the mixture at the same temperature. After stirring for 1 h at rt as the reaction was monitored by TLC (2:3 EtOAc−*n*-hexane), the reaction was quenched by the addition of dry MeOH at 0 °C. The reaction mixture was diluted with $CHCl_3$ and washed with 2 M HCl, satd. aq. $NaHCO_3$, and brine. The organic layer was subsequently dried over Na_2SO_4, filtered, and concentrated. The resulting residue was crystallized from EtOAc−*n*-hexane system to give **22** (5.75 g, 98%) as a white crystalline solid. mp = 133 to 135 °C. $[\alpha]_D$ − 81.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45−7.26 (m, 5 H, Ph), 5.50 (s, 1 H, PhC*H*<), 5.31 (t, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 4.99 (t, $J_{1,2}$ = 8.7 Hz, 1 H, 2-H), 4.59 (d, 1 H, 1-H), 4.37 (dd, $J_{5,6a}$ = 5.0 Hz, J_{gem} = 10.5 Hz, 1 H, 6a-H), 3.98 (m, 1 H, $Me_3SiCH_2CH_2$), 3.81 (t, $J_{5,6b}$ = 5.0 Hz, 1 H, 6b-H), 3.70 (t, $J_{4,5}$ = 10.3 Hz, 1 H, 4-H), 3.61−3.45 (m, 2 H, 5-H, $Me_3SiCH_2CH_2$), 2.06 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 1.02−0.86 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2, 169.5, 136.8, 129.1, 128.2, 126.1, 101.5, 100.9, 78.4, 72.4, 72.0, 68.6, 67.8, 66.3, 20.8, 20.8, 18.0, −1.4. HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{32}O_8Si$: 475.1759 $[M + Na]^+$, found 475.1759.

*2-(Trimethylsilyl)ethyl 2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**23**).* To a solution of **22** (3.00 g, 6.63 mmol) in CH_2Cl_2 (66.0 mL) was added 4 Å MS (3.00 g). After cooling to −78 °C and stirring for 1 h at the same temperature, dichlorophenylborane (2.0 mL, 15.4 mmol) and triethylsilane (3.3 mL, 20.7 mmol) were added to the mixture at −78 °C. After stirring for 35 min as the reaction was monitored by TLC (1:2 EtOAc−*n*-hexane), the reaction was quenched by the addition of triethylamine at −78 °C. The reaction mixture was filtered through Celite and washed with $CHCl_3$. The filtrate was washed with satd. aq. $NaHCO_3$ and brine. The organic layer was subsequently dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by silica gel column chromatography (1:4 EtOAc−*n*-hexane) to give **23** (2.45 g, 81%) as a white powder. $[\alpha]_D$ − 47.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36−7.25 (m, 5 H, Ph), 5.23 (t, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 4.85 (t, $J_{1,2}$ = 8.0 Hz, 1 H, 2-H), 4.64 (d, J_{gem} = 11.4 Hz, 1 H, PhCH_2), 4.60 (d, 1 H, PhCH_2), 4.51 (d, 1 H, 1-H), 3.99−3.88 (m, 2 H, $Me_3SiCH_2CH_2$, 6a-H), 3.78−3.70 (m, 2 H, 6a-H, 4-H), 3.54 (m, 1 H, $Me_3SiCH_2CH_2$), 3.43 (m, 1 H, 5-H), 2.02 (s, 3 H, Ac), 1.93 (m, 4 H, Ac, OH), 0.97−0.84 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2, 169.6, 137.5, 128.5, 128.0, 128.0, 100.2, 75.5, 75.1, 75.0, 74.8, 72.1, 67.7, 61.5, 20.8, 20.7, 18.0, −1.4. HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{34}O_8Si$: 477.1915 $[M + Na]^+$, found 477.1911.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylene-2-phthalimide-α-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**24**).* The glycosidation of **1** (75 mg, 0.119 mmol) with **23** (67 mg, 0.147 mmol) in CH_2Cl_2 (2.0 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:4 EtOAc−*n*-hexane) to give **24** (80 mg, 94%) as a colorless viscous compound. $[\alpha]_D$ + 79.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04−7.28 (m, 14 H, NPhth, 2 Ph), 5.16 (dd, $J_{3,4}$ = 2.7 Hz, $J_{2,3}$ = 11.5 Hz, 1 H, 3-H^{GalN}), 5.10 (m, 2 H, 1-H^{GalN}, 3-H^{Glc}), 4.96 (dd, $J_{1,2}$ = 3.2 Hz, 1 H, 2-H^{GalN}), 4.78−4.69 (m, 4 H, PhCH_2), 4.59 (d, 1 H, 4-H^{GalN}), 4.28−4.24 (m, 2 H, 1-H^{Glc}, 2-H^{Glc}), 4.20−4.13 (m, 2 H, 6a-H^{GalN}, 6b-H^{GalN}), 3.98 (dd, $J_{5,6a}$ = 2.3 Hz, J_{gem} = 11.9 Hz, 1 H, 6a-H^{Glc}), 3.81 (t, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4-H^{Glc}), 3.66 (dd, 1 H, H-6b^{Glc}), 3.61 (d, 1 H, 5-H^{GalN}), 3.58 (m, 1 H, $Me_3SiCH_2CH_2$), 3.32−3.24 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 2.00 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.19, 1.11 (2 s, 18 H, 2 ^{t}Bu), 0.77−0.61 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2, 169.2, 169.0, 168.6, 138.6, 138.3, 134.3, 133.7, 132.5, 131.1, 128.3, 127.8, 127.7, 127.6, 127.5, 123.4, 122.9, 99.9, 99.8, 77.2, 75.8, 75.2, 74.8, 74.1, 72.2, 72.1, 70.5, 70.0, 67.9, 67.3, 66.5, 50.9, 29.7, 27.6, 27.3, 23.4, 20.8, 20.8, 17.6, −1.4. HRMS (ESI-TOF) *m*/*z* calcd for $C_{51}H_{69}NO_{14}Si_2$: 998.4149 $[M + Na]^+$, found 998.4150.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-2-deoxy-4,6-O-diisopropylsilylene-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**25**).* The glycosidation of **2** (135 mg, 0.224 mmol) with **23** (67 mg, 0.147 mmol) in CH_2Cl_2 (3.7 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (2:9 EtOAc−*n*-hexane) to give **25*α*** (111 mg, 79%) and **25*β*** (29 mg, 21%) as a colorless viscous compound. **25*α***: $[\alpha]_D$ + 79.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04−7.28 (m, 14 H, NPhth, 2 Ph), 5.16 (dd, $J_{3,4}$ = 2.8 Hz, $J_{2,3}$ = 11.4 Hz, 1 H, 3-H^{GalN}), 5.12 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H^{GalN}), 5.08 (t, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 1 H, 3-H^{Glc}), 4.94 (dd, 1 H, 2-H^{GalN}), 4.76−4.69 (m, 4 H, PhCH_2), 4.46 (d, 1 H, 4-H^{GalN}), 4.26 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H^{Glc}), 4.22 (t, 1 H, 2-H^{Glc}), 4.15−4.08 (m, 2 H, 6a-H^{GalN}, 6b-H^{GalN}), 3.97 (dd, $J_{5,6a}$ = 2.7 Hz, J_{gem} = 12.4 Hz, 1 H, 6a-H^{Glc}), 3.79 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H^{Glc}), 3.67 (dd, 1 H, 6b-H^{Glc}), 3.61 (s, 1 H, 5-H^{GalN}), 3.59 (m, 1 H, $Me_3SiCH_2CH_2$), 3.31−3.24 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 2.00 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.22−1.12 (m, 14 H, 2 ^{i}Pr), 0.78−0.62 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2, 169.2, 168.9, 168.6, 138.6, 138.2, 134.3, 133.7, 132.5, 132.3, 131.1, 129.9, 129.3, 128.4, 128.2, 127.7, 127.7, 127.5, 123.4, 123.0, 99.9, 99.7, 77.2, 75.7, 75.1, 74.7, 74.0, 72.5, 72.0, 71.0, 70.0, 67.9, 66.6, 66.5, 50.8, 29.6, 28.5, 20.8, 20.7, 17.5, 17.1, 17.0, 16.6, 13.9, 12.4, −1.5. HRMS (ESI-TOF) *m*/*z* calcd for $C_{49}H_{65}NO_{14}Si_2$: 970.3836 $[M + Na]^+$, found 970.3838. **25*β***: $[\alpha]_D$ + 14.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83−7.10 (m, 14 H, NPhth, 2 Ph), 5.28 (d, $J_{1,2}$ = 8.7 Hz, 1 H, 1-H^{GalN}), 5.13 (t, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3-H^{Glc}), 4.80−4.73 (m, 2 H, 2-H^{Glc}, 2-H^{GalN}), 4.65 (d, J_{gem} = 12.4 Hz, 1 H, PhCH_2), 4.48−4.38 (m, 4 H, 4-H^{GalN}, 3 PhCH_2), 4.37 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H^{Glc}), 4.30−4.23 (m, 3 H, 6a-H^{GalN}, 6b-H^{GalN}, 3-H^{GalN}), 4.02 (dd, J_{gem} = 10.5 Hz, 1 H, 6a-H^{Glc}), 3.86−3.78 (m, 2 H, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 3.53 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H^{Glc}), 3.50−3.40 (m, 3 H, 5-H^{Glc}, 5-H^{GalN}, $Me_3SiCH_2CH_2$), 2.01 (s, 3 H, Ac), 1.91 (s, 3 H, Ac), 1.28−1.10 (m, 14 H, 2 ^{i}Pr), 0.96−0.72 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.1, 169.6, 168.6, 167.5, 138.0, 137.5, 133.9, 133.7, 131.8, 131.7, 128.3, 128.2, 127.8, 127.6, 123.4, 123.0, 99.7, 98.2, 77.2, 76.3, 75.1, 75.0, 74.7, 74.6, 72.1, 71.6, 70.6, 69.2, 66.8, 66.7, 51.4, 31.9, 29.7, 29.3, 22.7, 20.8, 17.7, 17.1, 17.0, 16.9, 14.1, 12.7, 1.0, 0, −1.3. HRMS (ESI-TOF) *m*/*z* calcd for $C_{49}H_{65}NO_{14}Si_2$: 970.3836 $[M + Na]^+$, found 970.3840.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-4,6-O-tert-butylmethylidene-2-deoxy-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**26**).* The glycosidation of **3** (92 mg, 0.165 mmol) with **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:10 → 1:5 EtOAc−*n*-hexane) to give **26*α*** (33 mg, 33%) and **26*β*** (60 mg, 60%) as a colorless viscous compound. **26*α***: $[\alpha]_D$ + 57.7 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.01−7.28 (m, 14 H, NPhth, 2 Ph), 5.30 (dd, $J_{3,4}$ = 3.3 Hz, $J_{2,3}$ = 11.7 Hz, 1 H, 3-H^{GalN}), 5.17 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H^{GalN}), 5.05 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.83 (dd, 1 H, 2-H^{GalN}), 4.74−4.67 (m, 4 H, 2 PhCH_2), 4.25 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{Glc}), 4.14−4.10 (m, 3 H, 4-H^{GalN}, 6a-H^{GalN}, 2-H^{Glc}), 3.98 (d, $J_{5,6a}$ = 3.0 Hz, 1 H, 5-H^{GalN}), 3.95 (dd, $J_{5,6a}$ = 2.4 Hz, J_{gem} = 12.2 Hz, 1 H, 6a-H^{Glc}), 3.76−3.71 (m, 2 H, 6b-H^{GalN}, 4-H^{Glc}), 3.68−3.61 (m, 2 H, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 3.43 (s, 1 H, ^{t}BuC*H*<), 3.30−

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3.25 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.98 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 0.98 (s, 9 H, ^{t}Bu), 0.79−0.65 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.6, 170.6, 170.2, 170.1, 140.1, 139.7, 135.6, 135.1, 133.8, 132.5, 132.2, 130.1, 129.8, 129.6, 129.1, 129.0, 128.9, 124.6, 124.5, 108.5, 101.5, 101.1, 77.1, 76.6, 76.2, 75.5, 73.8, 73.5, 72.4, 72.3, 70.6, 69.5, 68.0, 67.7, 64.7, 53.0, 40.1, 36.5, 31.7, 31.0, 30.3, 26.0, 25.1, 24.3, 22.2, 22.1, 18.9, 15.4, 12.3, 1.3. HRMS (ESI-TOF) m/z calcd for $C_{48}H_{61}NO_{14}Si$: 926.3754 $[M + Na]^+$, found 926.3758. **26*β***: $[\alpha]_D$ − 5.0(*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84−7.14 (m, 14 H, NPhth, 2 Ph), 5.34 (d, $J_{1,2}$ = 8.7 Hz, 1 H, 1-H^{GalN}), 5.13 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.79−4.71 (m, 2 H, 2-H^{GalN}, 2-H^{Glc}), 4.60−4.57 (m, 2 H, PhCH_2), 4.47−4.38 (m, 4 H, 3-H^{GalN}, 1-H^{Glc}, PhCH_2), 4.21 (dd, $J_{5,6a}$ = 2.0 Hz, J_{gem} = 12.2 Hz, 1 H, 6a-H^{GalN}), 4.18 (s, 1 H, ^{t}BuC*H*<), 4.06 (dd, $J_{5,6b}$ = 1.2 Hz, 1 H, 6b-H^{GalN}), 4.01 (d, $J_{3,4}$ = 3.3 Hz, 1 H, 4-H^{GalN}), 3.92 (dd, $J_{5,6a}$ = 5.1 Hz, J_{gem} = 11.2 Hz, 1 H, 6a-H^{Glc}), 3.85−3.81 (m, 2 H, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 3.54 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H^{Glc}), 3.50−3.43 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 3.40 (s, 1 H, 5-H^{GalN}), 2.00 (s, 3 H, Ac), 1.90 (s, 3 H, Ac), 1.04 (s, 9 H, ^{t}Bu), 0.84−0.77 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.4, 170.9, 139.4, 138.9, 135.2, 135.1, 133.1, 129.7, 129.5, 129.4, 129.3, 129.2, 128.8, 128.6, 124.7, 124.4, 108.2, 101.1, 99.0, 77.5, 76.4, 76.1, 75.9, 75.3, 73.4, 73.1, 71.8, 70.2, 68.3, 68.3, 66.5, 52.7, 36.5, 26.0, 25.8, 24.0, 22.1, 19.0, 18.8, 15.4, 1.3. HRMS (ESI-TOF) m/z calcd for $C_{48}H_{61}NO_{14}Si$: 926.3754 $[M + Na]^+$, found 926.3755.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-2-deoxy-4,6-O-ethylidene-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**27**).* The glycosidation of **4** (85 mg, 0.165 mmol) with **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:3 EtOAc−*n*-hexane) to give **27*α*** (23 mg, 24%) and **27*β*** (59 mg, 61%) as a colorless viscous compound. **27*α***: $[\alpha]_D$ + 56.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.00−7.28 (m, 14 H, NPhth, 2 Ph), 5.30 (dd, $J_{3,4}$ = 3.9 Hz, $J_{2,3}$ = 11.7 Hz, 1 H, 3-H^{GalN}), 5.17 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H^{GalN}), 5.05 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.89 (dd, 1 H, 2-H^{GalN}), 4.77−4.65 (m, 5 H, PhCH_2, CH_3CH<), 4.25 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{Glc}), 4.15−4.06 (m, 2 H, 6a-H^{GalN}, 2-H^{Glc}), 3.96−3.93 (m, 2 H, 4-H^{GalN}, 6a-H^{Glc}), 3.77−3.72 (m, 2 H, 6b-H^{Glc}, 4-H^{Glc}), 3.67−3.60 (m, 2 H, 6b-H^{GalN}, $Me_3SiCH_2CH_2$), 3.47 (s, 1 H, 5-H^{GalN}), 3.29−3.25 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.98 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 1.57 (d, $J_{CH3CH<,CH3CH<}$ = 5.0 Hz, 3 H, CH_3CH<), 0.76−0.66 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.6, 170.6, 170.2, 170.1, 140.0, 139.6, 135.7, 135.2, 133.8, 130.7, 130.4, 129.8, 129.5, 129.1, 129.0, 128.9, 124.7, 124.6, 101.6, 101.1, 100.4, 77.1, 76.6, 76.1, 75.5, 74.1, 73.5, 72.7, 72.4, 70.4, 68.0, 67.8, 64.3, 52.9, 31.0, 29.9, 22.4, 22.2, 22.1, 18.9, 1.3. HRMS (ESI-TOF) m/z calcd for $C_{45}H_{55}NO_{14}Si$: 884.3284 $[M + Na]^+$, found 884.3281. **27*β***: $[\alpha]_D$ + 2.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.85−7.04 (m, 14 H, NPhth, 2 Ph), 5.31 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H^{GalN}), 5.10 (t, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 1 H, 3-H^{Glc}), 4.76−4.61 (m, 4 H, 2-H^{GalN}, CH_3CH<, 2-H^{Glc}, PhCH_2), 4.47−4.38 (m, 5 H, 3-H^{GalN}, 1-H^{Glc}, PhCH_2), 4.21 (d, J_{gem} = 11.8 Hz, 1 H, 6a-H^{GalN}), 4.05−4.02 (m, 2 H, 4-H^{GalN}, 6a-H^{Glc}), 3.88 (dd, $J_{5,6b}$ = 1.4 Hz, 1 H, 6b-H^{GalN}), 3.81 (m, 1 H, $Me_3SiCH_2CH_2$), 3.76−3.73 (m, 1 H, 5-H^{Glc}), 3.46−3.40 (m, 3 H, 4-H^{Glc}, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 3.38 (s, 1 H, 5-H^{GalN}), 1.99 (s, 3 H, Ac), 1.88 (s, 3 H, Ac), 1.49 (d, $J_{CH3CH<,CH3CH<}$ = 5.0 Hz, 3 H, CH_3CH<), 0.86−0.74 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.4, 170.9, 169.9, 168.7, 139.1, 138.7, 135.2, 135.0, 133.1, 133.0, 129.7, 129.4, 129.2, 129.2, 128.9, 128.9, 124.8, 124.3, 101.0, 100.5, 99.4, 78.6, 77.7, 76.4, 76.2, 75.9, 75.3, 73.5, 73.4, 72.4, 70.1, 68.4, 68.1, 68.0, 53.3, 22.3, 22.1, 19.0, 1.3. HRMS (ESI-TOF) m/z calcd for $C_{45}H_{55}NO_{14}Si$: 884.3284 $[M + Na]^+$, found 884.3284.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-2-deoxy-4,6-O-methylidene-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**28**).* The glycosidation of **5** (82 mg, 0.165 mmol) and **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:3 EtOAc−*n*-hexane) to give **28*α*** (11 mg, 12%) and **28*β*** (58 mg, 62%) as a colorless viscous compound. **28*α***: $[\alpha]_D$ + 60.0 (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.00−7.25 (m, 14 H, NPhth, 2 Ph), 5.32−5.28 (m, 2 H, 3-H^{GalN}, CH_2O_2), 5.18 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H^{GalN}), 5.06 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.91 (dd, $J_{2,3}$ = 11.7 Hz, 1 H, 2-H^{GalN}), 4.76−4.69 (m, 5 H, CH_2O_2, PhCH_2), 4.25 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{Glc}), 4.16 (t, 1 H, 2-H^{Glc}), 4.10 (d, J_{gem} = 12.3 Hz, 1 H, 6a-H^{GalN}), 3.97−3.93 (m, 2 H, 4-H^{GalN}, 6a-H^{Glc}), 3.78−3.59 (m, 4 H, 6b-H^{GalN}, 4-H^{Glc}, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 3.52 (s, 1 H, 5-H^{GalN}), 3.30−3.24 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.99 (s, 3 H, Ac), 1.97 (s, 3 H, Ac), 0.78−0.63 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.6, 170.6, 170.2, 170.0, 139.7, 136.7, 135.7, 135.2, 133.8, 132.4, 129.8, 129.8, 129.6, 129.1, 129.0, 124.7, 124.6, 101.7, 101.2, 94.8, 77.1, 76.6, 76.1, 75.5, 74.1, 73.5, 72.9, 72.3, 70.4, 68.0, 67.8, 65.2, 52.8, 22.2, 22.1, 18.9, 1.3. HRMS (ESI-TOF) m/z calcd for $C_{44}H_{53}NO_{14}Si$: 870.3128 $[M + Na]^+$, found 870.3127. **28*β***: $[\alpha]_D$ + 4.8 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83−7.01 (m, 14 H, NPhth, 2 Ph), 5.30 (d, $J_{1,2}$ = 8.6 Hz, 1 H, 1-H^{GalN}), 5.28 (d, J_{gem} = 6.4 Hz, 1 H, CH_2O_2), 5.09 (t, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, 1 H, 3-H^{Glc}), 4.76−4.63 (m, 4 H, 2-H^{GalN}, CH_2O_2, 2-H^{Glc}, PhCH_2), 4.46−4.34 (m, 4 H, 1-H^{Glc}, PhCH_2), 4.29 (dd, $J_{3,4}$ = 3.5 Hz, $J_{2,3}$ = 11.1 Hz, 1 H, 3-H^{GalN}), 4.20 (d, J_{gem} = 12.2 Hz, 1 H, 6a-H^{GalN}), 4.01−3.99 (m, 2 H, 4-H^{GalN}, 6a-H^{Glc}), 3.85−3.72 (m, 3 H, 6b-H^{GalN}, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 3.46−3.36 (m, 4 H, 5-H^{GalN}, 4-H^{Glc}, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 1.98 (s, 3 H, Ac), 1.87 (s, 3 H, Ac), 0.84−0.73 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.4, 170.9, 169.9, 168.6, 138.8, 138.8, 135.2, 135.0, 133.1, 133.0, 129.7, 129.5, 129.2, 129.0, 128.9, 124.8, 124.3, 101.0, 99.5, 94.7, 77.7, 76.4, 76.4, 76.2, 75.8, 75.4, 73.6, 73.4, 72.8, 70.1, 68.9, 68.4, 53.3, 22.1, 19.7, 1.3. HRMS (ESI-TOF) m/z calcd for $C_{44}H_{53}NO_{14}Si$: 870.3128 $[M + Na]^+$, found 870.3126.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**29**).* The glycosidation of **6** (101 mg, 0.174 mmol) and **23** (53 mg, 0.117 mmol) in CH_2Cl_2 (2.9 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:3 EtOAc−*n*-hexane) to give **29*α*** (14 mg, 13%) and **29*β*** (91 mg, 84%) as a colorless viscous compound. **29*α***: $[\alpha]_D$ + 68.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01−7.27 (m, 19 H, NPhth, 3 Ph), 5.46 (s, 1 H, PhC*H*<), 5.39 (dd, $J_{3,4}$ = 3.2 Hz, $J_{2,3}$ = 11.9 Hz, 1 H, 3-H^{GalN}), 5.02 (d, $J_{1,2}$ = 3.2 Hz, 1 H, 1-H^{GalN}), 5.07 (t, $J_{3,4}$ = 9.4 Hz, $J_{2,3}$ = 9.7 Hz, 1 H, 3-H^{Glc}), 4.94 (dd, 1 H, 2-H^{GalN}), 4.81−4.72 (m, 4 H, 2 PhCH_2), 4.25 (m, 2 H, 1-H^{Glc}, 6a-H^{GalN}), 4.18−4.12 (m, 2 H, 4-H^{GalN}, 2-H^{Glc}), 3.99−3.94 (m, 2 H, 6a-H^{Glc}, 6b-H^{GalN}), 3.76 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H^{Glc}), 3.68 (br d, 1 H, 6b-H^{Glc}), 3.63 (m, 1 H, $Me_3SiCH_2CH_2$), 3.56 (s, 1 H, 5-H^{GalN}), 3.31−3.24 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.98 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 0.80−0.63 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2, 169.2, 168.8, 138.8, 138.3, 137.7, 134.3, 133.8, 132.5, 131.1, 128.9, 128.6, 128.5, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 126.3, 123.3, 123.2, 100.9, 100.2, 99.8, 85.8, 75.8, 75.2, 74.8, 74.5, 74.1, 73.2, 72.1, 71.3, 71.1, 69.6, 66.6, 66.4, 63.1, 51.6, 29.7, 20.8, 20.8, 17.6, 0, −1.4, −2.1. HRMS (ESI-TOF) m/z calcd for $C_{50}H_{57}NO_{14}Si$: 946.3441 $[M + Na]^+$, found 946.3441. **29*β***: $[\alpha]_D$ + 21.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85−7.06 (m, 19 H, NPhth, 3 Ph), 5.54 (s, 1 H, PhC*H*<), 5.36 (d, $J_{1,2}$ = 8.7 Hz, 1 H, 1-H^{GalN}), 5.11 (m, 1 H, 3-H^{Glc}), 4.80−4.74 (m, 2 H, 2-H^{GalN}, 2-H^{Glc}), 4.63 (d, J_{gem} = 12.4 Hz, 1 H, PhCH_2), 4.50 (d, J_{gem} = 13.2 Hz, 1 H, PhCH_2), 4.47 (d, 1 H, PhCH_2), 4.45−4.36 (m, 3 H, 3-H^{GalN}, 6a-H^{GalN}, PhCH_2), 4.35 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H^{Glc}), 4.24 (d, $J_{3,4}$ = 2.8 Hz, 1 H, 4-H^{GalN}), 4.11−4.04 (m, 2 H, 6b-H^{GalN}, 6a-H^{Glc}), 3.86−3.80 (m, 2 H, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 3.49−3.42 (m, 4 H, 4-H^{Glc}, 5-H^{Glc}, 5-H^{GalN}, $Me_3SiCH_2CH_2$), 2.00 (s, 3 H, Ac), 1.88 (s, 3 H, Ac), 0.96−0.72 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.1, 169.6, 168.6, 167.4, 137.9, 137.7, 137.4, 133.9, 133.7, 131.8, 131.7, 128.9, 128.4, 128.2, 128.1, 127.9, 127.8, 127.6, 127.5, 126.4, 123.5, 123.0, 101.1, 99.7, 98.1, 76.3, 75.0, 74.8, 74.6, 74.1, 72.6, 72.0, 71.0, 69.3,

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67.1, 66.8, 66.5, 51.9, 36.3, 20.7, 17.7, −1.3. HRMS (ESI-TOF) m/z calcd for $C_{50}H_{57}NO_{14}Si$: 946.3441 $[M + Na]^+$, found 946.3439.

*2-(Trimethylsilyl)ethyl [3-O-benzyl-2-deoxy-4,6-O-(4-nitrobenzylidene)-2-phthalimide-D-galactopyranosyl]-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**30**).* The glycosidation of **7** (103 mg, 0.165 mmol) and **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (2:3 EtOAc−*n*-hexane) to give **30α** (9 mg, 10%) and **30β** (56 mg, 55%) as a colorless viscous compound. **30α**: $[\alpha]_D$ + 92.5 (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.28−7.24 (m, 18 H, NPhth, Ar), 5.48 (s, 1 H, ArC*H*<), 5.39 (dd, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 11.7 Hz, 1 H, 3-H^{GalN}), 5.16 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H^{GalN}), 5.04 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.86 (dd, 1 H, 2-H^{GalN}), 4.80−4.69 (m, 4 H, PhCH_2), 4.26−4.22 (m, 2 H, 6a-H^{GalN}, 1-H^{Glc}), 4.15 (d, 1 H, 4-H^{GalN}), 4.10 (dd, $J_{1,2}$ = 8.0 Hz, 1 H, 2-H^{Glc}), 3.97−3.93 (m, 2 H, 6a-H^{Glc}, 6b-H^{GalN}), 3.73 (t, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H^{Glc}), 3.66 (dd, $J_{5,6b}$ = 1.9 Hz, J_{gem} = 12.2 Hz, 1 H, 6b-H^{Glc}), 3.61 (m, 1 H, $Me_3SiCH_2CH_2$), 3.57 (s, 1 H, 5-H^{GalN}), 3.29−3.22 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.96 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 0.77−0.61 (m, 2 H, $Me_3SiCH_2CH_2$), −0.02 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz,, $CDCl_3$) δ = 170.3, 169.3, 168.8, 148.3, 143.1, 138.7, 138.3, 134.4, 134.0, 132.4, 131.1, 128.5, 128.3, 127.8, 127.8, 127.7, 127.6, 127.4, 123.4, 123.3, 100.2, 99.9, 99.2, 75.8, 75.3, 74.8, 74.1, 73.4, 72.1, 71.5, 71.1, 69.7, 66.7, 66.5, 62.9, 51.5, 29.7, 20.8, 20.8, 17.6, −1.3. HRMS (ESI-TOF) m/z calcd for $C_{50}H_{56}N_2O_{16}Si$: 991.3291 $[M + Na]^+$, found 991.3287. **30β**: $[\alpha]_D$ + 29.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.26−7.06 (m, 18 H, NPhth, Ar), 5.60 (s, 1 H, ArC*H*<), 5.37 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H^{GalN}), 5.11 (m, 1 H, 3-H^{Glc}), 4.77−4.70 (m, 2 H, 2-H^{GalN}, 2-H^{Glc}), 4.63 (d, J_{gem} = 12.6 Hz, 1 H, PhCH_2), 4.50−4.36 (m, 6 H, 3-H^{GalN}, 6a-H^{GalN}, 1-H^{Glc}, PhCH_2), 4.27 (d, $J_{3,4}$ = 3.4 Hz, 1 H, 4-H^{GalN}), 4.12 (dd, $J_{5,6b}$ = 1.3 Hz, J_{gem} = 12.2 Hz, 1 H, 6b-H^{GalN}), 4.04 (d, J_{gem} = 11.1 Hz, 1 H, 6a-H^{Glc}), 3.85−3.77 (m, 2 H, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 3.54 (s, 1 H, 5-H^{GalN}), 3.50−3.42 (m, 3 H, 4-H^{Glc}, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 2.00 (s, 3 H, Ac), 1.88 (s, 3 H, Ac), 0.86−0.74 (m, 2 H, $Me_3SiCH_2CH_2$), −0.01 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.1, 169.6, 168.6, 167.5, 160.1, 148.3, 144.1, 137.7, 137.4, 134.0, 133.9, 131.7, 131.6, 128.4, 128.2, 127.9, 127.9, 127.8, 127.6, 127.5, 123.6, 123.4, 123.1, 99.8, 99.4, 98.2, 76.3, 75.0, 74.8, 74.6, 74.0, 72.8, 72.0, 71.3, 69.4, 67.1, 67.0, 66.6, 52.0, 20.8, 17.8, −1.3. HRMS (ESI-TOF) m/z calcd for $C_{50}H_{56}N_2O_{16}Si$: 991.3291 $[M + Na]^+$, found 991.3295.

*2-(Trimethylsilyl)ethyl (4,6-O-anisylidene-3-O-benzyl-2-deoxy-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**31**).* The glycosidation of **8** (101 mg, 0.165 mmol) and **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (2:3 EtOAc−*n*-hexane) to give **31α** (26 mg, 29%) and **31β** (56 mg, 63%) as a colorless viscous compound. **31α**: $[\alpha]_D$ + 98.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96−6.90 (m, 18 H, NPhth, Ar), 5.37 (s, 1 H, ArC*H*<), 5.33 (dd, $J_{3,4}$ = 3.0 Hz, $J_{2,3}$ = 11.5 Hz, 1 H, 3-H^{GalN}), 5.15 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H^{GalN}), 5.02 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.89 (dd, 1 H, 2-H^{GalN}), 4.74 (d, J_{gem} = 12.0 Hz, 1 H, PhCH_2), 4.69 (t, J_{gem} = 11.5 Hz, 2 H, PhCH_2), 4.68 (d, 1 H, PhCH_2), 4.20 (m, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{Glc}), 4.17 (dd, $J_{5,6a}$ = 1.5 Hz, J_{gem} = 12.5 Hz, 1 H, 6a-H^{GalN}), 4.11−4.07 (m, 2 H, 4-H^{GalN}, 2-H^{Glc}), 3.92 (dd, $J_{5,6a}$ = 2.5 Hz, J_{gem} = 12.0 Hz, 1 H, 6a-H^{Glc}), 3.88 (dd, $J_{5,6b}$ = 1.5 Hz, 1 H, 6b-H^{GalN}), 3.81 (s, 3 H, OMe), 3.72 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H^{Glc}), 3.63 (dd, $J_{5,6b}$ = 2.0 Hz, 1 H, 6b-H^{Glc}), 3.59 (m, 1 H, $Me_3SiCH_2CH_2$), 3.51 (s, 1 H, 5-H^{GalN}), 3.26−3.20 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.93 (s, 3 H, Ac), 1.91 (s, 3 H, Ac), 0.75−0.59 (m, 2 H, $Me_3SiCH_2CH_2$), −0.05 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.2, 169.2, 168.8, 160.0, 138.8, 138.3, 134.3, 133.8, 132.4, 131.1, 130.3, 128.4, 128.1, 127.7, 127.7, 127.6, 127.5, 123.3, 123.1, 113.5, 100.8, 100.2, 99.8, 75.7, 75.2, 74.8, 74.1, 73.1, 72.1, 71.2, 71.1, 69.5, 66.6, 66.4, 63.1, 55.3, 51.6, 20.8, 20.7, 17.5, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{51}H_{59}NO_{15}Si$: 976.3546 $[M + Na]^+$, found 976.3545. **31β**: $[\alpha]_D$ + 13.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83−6.89 (m, 18 H, NPhth, Ar), 5.48 (s, 1 H, ArC*H*<), 5.33 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H^{Glc}), 5.09 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.77−4.72 (m, 2 H, 2-H^{GalN}, 2-H^{Glc}), 4.60 (d, J_{gem} = 12.5 Hz, 1 H, PhCH_2), 4.48 (d, J_{gem} = 11.0 Hz, 1 H, PhCH_2), 4.44 (d, 1 H, PhCH_2), 4.40 (dd, $J_{3,4}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1 H, 3-H^{GalN}), 4.38 (d, 1 H, PhCH_2), 4.35 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{GalN}), 4.31 (dd, $J_{5,6a}$ = 1.0 Hz, J_{gem} = 12.0 Hz, 1 H, 6a-H^{GalN}), 4.20 (d, 1 H, 4-H^{GalN}), 4.04 (dd, $J_{5,6b}$ = 1.5 Hz, 1 H, 6b-H^{GalN}), 4.03 (d, J_{gem} = 10.5 Hz, 1 H, 6a-H^{Glc}), 3.84−3.78 (m, 5 H, 6b-H^{Glc}, $Me_3SiCH_2CH_2$, OMe), 3.49−3.40 (m, 4 H, 5-H^{GalN}, 4-H^{Glc}, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.97 (s, 3 H, Ac), 1.86 (s, 3 H, Ac), 0.85−0.71 (m, 2 H, $Me_3SiCH_2CH_2$), −0.02 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.0, 169.6, 168.6, 167.4, 160.0, 137.9, 137.5, 133.9, 133.7, 131.8, 131.7, 130.4, 128.4, 128.1, 127.9, 127.8, 127.8, 127.5, 127.5, 123.5, 123.0, 113.5, 101.0, 99.8, 98.1, 76.3, 75.1, 74.8, 74.5, 74.1, 72.6, 72.0, 71.0, 69.2, 67.0, 66.8, 66.5, 55.3, 51.9, 20.7, 17.7, −1.3. HRMS (ESI-TOF) m/z calcd for $C_{51}H_{59}NO_{15}Si$: 976.3546 $[M + Na]^+$, found 976.3544.

*2-(Trimethylsilyl)ethyl [3-O-benzyl-4,6-O-(2-chloroethylidene)-2-deoxy-2-phthalimide-D-galactopyranosyl]-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**32**).* The glycosidation of **9** (91 mg, 0.165 mmol) and **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:2 EtOAc−*n*-hexane) to give **32α** (18 mg, 17%) and **32β** (74 mg, 73%) as a colorless viscous compound. **32α**: $[\alpha]_D$ + 12.5 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96−7.22 (m, 14 H, NPhth, 2 Ph), 5.28 (dd, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 11.7 Hz, 1 H, 3-H^{GalN}), 5.10 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H^{GalN}), 5.01 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.78 (dd, 1 H, 2-H^{GalN}), 4.73−4.62 (m, 5 H, PhCH_2, ClCH_2C*H*<), 4.20 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{Glc}), 4.10−4.06 (m, 2 H, 6a-H^{GalN}, 2-H^{Glc}), 3.92−3.88 (m, 2 H, 4-H^{GalN}, 6a-H^{Glc}), 3.73−3.55 (m, 6 H, 6b-H^{Glc}, ClCH_2, 4-H^{Glc}, 6b-H^{GalN}, $Me_3SiCH_2CH_2$), 3.42 (s, 1 H, 5-H^{GalN}), 3.25−3.20 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.93 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 0.74−0.59 (m, 2 H, $Me_3SiCH_2CH_2$), −0.05 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.2, 169.2, 168.8, 138.6, 138.3, 134.4, 133.9, 132.5, 131.1, 128.5, 128.3, 128.2, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 123.4, 123.3, 100.6, 100.2, 99.9, 75.8, 75.3, 74.8, 74.1, 73.0, 72.1, 71.5, 70.8, 69.3, 66.7, 66.5, 62.9, 51.4, 44.0, 20.8, 20.8, 17.6, −1.3. HRMS (ESI-TOF) m/z calcd for $C_{45}H_{54}ClNO_{14}Si$: 918.2894 $[M + Na]^+$, found 918.2895. **32β**: $[\alpha]_D$ + 43.0 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84−7.06 (m, 14 H, NPhth, 2 Ph), 5.28 (d, $J_{1,2}$ = 8.6 Hz, 1 H, 1-H^{GalN}), 5.08 (t, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, 1 H, 3-H^{Glc}), 4.74−4.71 (m, 2 H, 2-H^{Glc}, ClCH_2C*H*<), 4.64 (dd, $J_{2,3}$ = 11.1 Hz, 1 H, 2-H^{GalN}), 4.58 (d, J_{gem} = 12.5 Hz, 1 H, PhCH_2), 4.44−4.33 (m, 5 H, 3-H^{GalN}, 1-H^{Glc}, PhCH_2), 4.25 (dd, $J_{5,6a}$ = 0.9 Hz, J_{gem} = 11.9 Hz, 1 H, 6a-H^{GalN}), 4.03−4.00 (m, 2 H, 4-H^{GalN}, 6a-H^{Glc}), 3.89 (dd, $J_{5,6b}$ = 1.5 Hz, 1 H, 6b-H^{GalN}), 3.75 (m, 1 H, $Me_3SiCH_2CH_2$), 3.75−3.72 (m, 1 H, 6b-H^{Glc}), 3.70−3.63 (m, 2 H, ClCH_2), 3.46−3.40 (m, 4 H, 5-H^{GalN}, 4-H^{Glc}, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.97 (s, 3 H, Ac), 1.86 (s, 3 H, Ac), 0.90−0.71 (m, 2 H, $Me_3SiCH_2CH_2$), −0.01 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.1, 169.6, 168.6, 167.4, 137.7, 137.4, 134.0, 133.8, 131.8, 131.7, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 123.6, 123.0, 100.6, 99.8, 98.2, 76.4, 75.1, 74.9, 74.6, 73.9, 72.5, 72.1, 71.2, 69.0, 67.1, 66.9, 66.7, 51.9, 44.0, 20.8, 17.8, −1.3. HRMS (ESI-TOF) m/z calcd for $C_{45}H_{54}ClNO_{14}Si$: 918.2894 $[M + Na]^+$, found 918.2893.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-2-deoxy-2-phthalimide-4,6-O-1′,1′,3′,3′-tetraisopropyldisiloxanylidene-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**33**).* The glycosidation of **10** (211 mg, 0.287 mmol) with **23** (87 mg, 0.191 mmol) in CH_2Cl_2 (4.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:9 EtOAc−*n*-hexane) to give **33α** (44 mg, 21%) and **33β** (161 mg, 78%) as a colorless viscous compound. **33α**: $[\alpha]_D$ + 98.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97−7.17 (m, 14 H, NPhth, 2 Ph), 5.20 (dd, $J_{3,4}$ = 2.3 Hz, $J_{2,3}$ = 11.5 Hz, 1 H, 3-H^{GalN}), 5.06 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H^{GalN}), 5.04 (t, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3-H^{Glc}), 4.90 (dd, 1 H, 2-H^{GalN}), 4.78−4.65 (m, 4 H, PhCH_2), 4.58 (br d, 1 H, 4-H^{GalN}), 4.24 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H^{Glc}), 4.10 (t, 1 H, 2-H^{Glc}), 4.03−3.80 (m, 4 H, 5-H^{GalN}, 6a-H^{GalN}, 6b-H^{GalN}, 6a-H^{Glc}), 3.75 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H^{Glc}), 3.66−3.61 (m, 2 H, 6b-H^{Glc},

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$Me_3SiCH_2CH_2$), 3.31−3.25 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.97 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 1.31−0.90 (m, 28 H, 4 ^{i}Pr), 0.80−0.63 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.3, 169.2, 169.1, 168.8, 138.1, 138.0, 134.3, 133.9, 133.7, 132.4, 131.2, 128.7, 128.5, 128.0, 127.8, 127.8, 127.3, 123.2, 123.0, 100.0, 99.7, 77.7, 77.6, 75.5, 75.2, 74.9, 74.3, 73.3, 72.1, 71.7, 70.5, 66.5, 66.2, 65.1, 59.5, 51.5, 29.7, 20.8, 17.6, 17.5, 17.3, 17.2, 14.3, 13.3, 12.8, 12.6, 1.0, 0, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{55}H_{79}NO_{15}Si_3$: 1100.4650 $[M + Na]^+$, found 1100.4651. **33*β***: $[\alpha]_D$ + 18.5 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78−6.96 (m, 14 H, NPhth, 2 Ph), 5.30 (d, $J_{1,2}$ = 8.7 Hz, 1 H, 1-H^{GalN}), 5.11 (t, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 1 H, 3-H^{Glc}), 4.77 (dd, $J_{1,2}$ = 7.8 Hz, 1 H, 2-H^{Glc}), 4.71 (dd, $J_{2,3}$ = 11.0 Hz, 1 H, 2-H^{GalN}), 4.60 (d, J_{gem} = 11.9 Hz, 1 H, $PhCH_2$), 4.51 (d, J_{gem} = 11.0 Hz, 1 H, $PhCH_2$), 4.40 (d, $J_{3,4}$ = 2.3 Hz, 1 H, 4-H^{GalN}), 4.39 (d, 1 H, $PhCH_2$), 4.27 (dd, 1 H, 3-H^{GalN}), 4.24 (d, 1 H, $PhCH_2$), 3.99 (br dd, J_{gem} = 10.1 Hz, 1 H, 6a-H^{Glc}), 3.89−3.75 (m, 4 H, 6a-H^{GalN}, 5-H^{GalN}, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 3.67 (dd, $J_{5,6b}$ = 5.5 Hz, 1 H, 6b-H^{GalN}), 3.48 (t, 1 H, 4-H^{Glc}), 3.46−3.41 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.99 (s, 3 H, Ac), 1.89 (s, 3 H, Ac), 1.28−0.72 (m, 30 H, 4 ^{i}Pr, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.1, 169.6, 168.6, 167.7, 137.6, 137.5, 133.6, 133.6, 131.8, 128.3, 128.0, 127.8, 127.7, 127.4, 123.2, 123.0, 99.7, 97.8, 76.2, 76.1, 75.1, 74.5, 74.0, 72.1, 71.9, 66.9, 65.5, 65.4, 64.8, 59.3, 51.5, 20.7, 17.7, 17.6, 17.4, 17.3, 17.3, 17.2, 17.2, 17.2, 17.1, 16.9, 14.1, 13.2, 12.7, 12.5, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{55}H_{79}NO_{15}Si_3$: 1100.4650 $[M + Na]^+$, found 1100.4654.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-4,6-di-O-tert-butyldimethylsilyl-2-deoxy-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**34**).* The glycosidation of **11** (101 mg, 0.140 mmol) with **23** (43 mg, 94.0 μmol) in CH_2Cl_2 (2.3 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:5 EtOAc−*n*-hexane) to give **34*α*** (27 mg, 27%) and **34*β*** (70 mg, 70%) as a colorless viscous compound. **34*α***: $[\alpha]_D$ + 56.0 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97−7.17 (m, 14 H, NPhth, 2 Ph), 5.11 (dd, $J_{3,4}$ = 1.8 Hz, $J_{2,3}$ = 11.9 Hz, 1 H, 3-H^{GalN}), 5.09 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H^{GalN}), 5.05 (t, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 1 H, 3-H^{Glc}), 4.93 (dd, 1 H, 2-H^{GalN}), 4.79, 4.71 (2 d, J_{gem} = 11.4 Hz, 2 H, $PhCH_2$), 4.78, 4.66 (2 d, J_{gem} = 11.0 Hz, 2 H, $PhCH_2$), 4.36 (br s, 1 H, 4-H^{GalN}), 4.24 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1-H^{Glc}), 4.19 (t, 1 H, 2-H^{Glc}), 4.06 (dd, $J_{5,6a}$ = 0.9 Hz, J_{gem} = 13.3 Hz, 1 H, 6a-H^{Glc}), 3.92 (br t, $J_{5,6b}$ = 6.4 Hz, $J_{5,6a}$ = 6.8 Hz, 1 H, 5-H^{GalN}), 3.84−3.79 (m, 3 H, 4-H^{Glc}, 6a-H^{GalN}, 6b-H^{GalN}), 3.67 (dd, $J_{5,6b}$ = 1.8 Hz, J_{gem} = 12.8 Hz, 1 H, 6b-H^{Glc}), 3.60 (m, 1 H, $Me_3SiCH_2CH_2$), 3.29−3.22 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.99 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 0.96 (s, 18 H, 2 ^{t}Bu), 0.76−0.58 (m, 2 H, $Me_3SiCH_2CH_2$), 0.13−0.00 (m, 21 H, 2 $SiMe_2$, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2, 169.2, 169.1, 168.8, 138.2, 134.3, 133.6, 132.5, 131.1, 128.5, 128.1, 128.0, 127.8, 127.4, 127.2, 123.4, 123.0, 100.3, 99.7, 77.2, 75.5, 75.0, 74.9, 74.3, 74.2, 72.8, 72.1, 71.7, 67.5, 66.5, 66.4, 62.3, 51.4, 26.0, 25.9, 20.8, 20.8, 18.6, 18.2, 17.6, −1.4, −4.1, −4.9, −5.2, −5.3. HRMS (ESI-TOF) m/z calcd for $C_{55}H_{81}NO_{14}Si_3$: 1086.4857 $[M + Na]^+$, found 1086.4856. **34*β***: $[\alpha]_D$ + 4.0 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79−6.94 (m, 14 H, NPhth, 2 Ph), 5.32 (d, $J_{1,2}$ = 8.7 Hz, 1 H, 1-H^{GalN}), 5.10 (t, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 1 H, 3-H^{Glc}), 4.77 (dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 9.2 Hz, 1 H, 2-H^{Glc}), 4.71 (dd, $J_{2,3}$ = 11.0 Hz, 1 H, 2-H^{GalN}), 4.65 (d, J_{gem} = 11.9 Hz, 1 H, $PhCH_2$), 4.51 (d, J_{gem} = 11.0 Hz, 1 H, $PhCH_2$), 4.37 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H^{Glc}), 4.36 (d, 1 H, $PhCH_2$), 4.27 (br d, 1 H, 4-H^{GalN}), 4.24 (d, 1 H, $PhCH_2$), 4.18 (dd, $J_{3,4}$ = 2.3 Hz, 1 H, 3-H^{GalN}), 4.04 (dd, $J_{5,6a}$ = 1.8 Hz, J_{gem} = 11.5 Hz, 1 H, 6a-H^{Glc}), 3.86−3.78 (m, 3 H, 6a-H^{GalN}, 6b-H^{Glc}, $Me_3SiCH_2CH_2$), 3.70 (dd, $J_{5,6b}$ = 5.5 Hz, $J_{5,6a}$ = 9.6 Hz, 1 H, 5-H^{GalN}), 3.53−3.40 (m, 4 H, 4-H^{Glc}, 5-H^{Glc}, 6b-H^{GalN}, $Me_3SiCH_2CH_2$), 1.99 (s, 3 H, Ac), 1.87 (s, 3 H, Ac), 0.99, 0.94 (2 s, 18 H, 2 ^{t}Bu), 0.87−0.72 (m, 2 H, $Me_3SiCH_2CH_2$), 0.16−0.00 (m, 21 H, 2 $SiMe_2$, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.1, 169.6, 168.7, 137.6, 137.6, 133.6, 133.5, 131.7, 128.3, 128.0, 127.7, 127.6, 127.4, 123.2, 123.0, 99.7, 97.9, 77.0, 76.3, 75.7, 75.1, 74.5, 72.2, 72.1, 66.9, 66.5, 65.6, 61.2, 51.6, 29.7, 26.2, 26.1, 26.0, 25.9, 20.7, 20.7, 18.6, 18.2, 17.7, −1.3, −4.3, −4.9, −5.3. HRMS (ESI-TOF) m/z calcd for $C_{55}H_{81}NO_{14}Si_3$: 1086.4857 $[M + Na]^+$, found 1086.4852.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-2-deoxy-2-phthalimide-4,6-O-xylylene-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**35**).* The glycosidation of **12** (98 mg, 0.165 mmol) with **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (2:5 EtOAc−*n*-hexane) to give **35*α*** (7 mg, 7%) and **35*β*** (73 mg, 70%) as a colorless viscous compound. **35*α***: $[\alpha]_D$ + 79.2 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.01−7.13 (m, 18 H, NPhth, Ar), 5.28 (dd, $J_{3,4}$ = 3.0 Hz, $J_{2,3}$ = 12.0 Hz, 1 H, 3-H^{GalN}), 5.20 (d, J_{gem} = 12.5 Hz, 1 H, $ArCH_2$), 5.08 (d, $J_{1,2}$ = 4.0 Hz, 1 H, 1-H^{GalN}), 5.05 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.98 (d, 1 H, $ArCH_2$), 4.97 (d, J_{gem} = 12.0 Hz, 1 H, $ArCH_2$), 4.93 (dd, 1 H, 2-H^{GalN}), 4.91 (d, 1 H, $ArCH_2$), 4.73−4.68 (m, 4 H, $ArCH_2$), 4.24 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{Glc}), 4.21−4.17 (m, 2 H, 4-H^{GalN}, 2-H^{Glc}), 4.04 (m, 1 H, 6a-H^{GalN}), 4.00−3.97 (m, 2 H, 5-H^{GalN}, 6a-H^{Glc}), 3.77 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H^{Glc}), 3.71 (dd, $J_{5,6b}$ = 8.0 Hz, J_{gem} = 11.0 Hz, 1 H, 6b-H^{GalN}), 3.63 (dd, $J_{5,6b}$ = 1.5 Hz, J_{gem} = 12.0 Hz, 1 H, 6b-H^{Glc}), 3.57 (m, 1 H, $Me_3SiCH_2CH_2$), 3.27−3.21 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 2.00 (s, 3 H, Ac), 1.95 (s, 3 H, Ac), 0.76−0.60 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.3, 169.2, 169.0, 168.8, 138.3, 138.0, 136.9, 136.7, 135.8, 134.3, 133.7, 132.5, 131.1, 130.8, 130.6, 129.0, 128.6, 128.5, 128.3, 128.2, 127.9, 127.9, 127.5, 127.4, 123.5, 123.1, 100.1, 99.8, 79.2, 75.5, 75.1, 75.0, 74.9, 74.2, 72.9, 72.5, 72.1, 71.0, 70.2, 70.1, 66.7, 66.5, 52.3, 20.8, 17.6, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{51}H_{59}NO_{14}Si$: 960.3597 $[M + Na]^+$, found 960.3595. **35*β***: $[\alpha]_D$ − 46.2 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.82−6.99 (m, 18 H, NPhth, Ar), 5.22 (d, J_{gem} = 13.0 Hz, 1 H, $ArCH_2$), 5.18 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H^{GalN}), 5.07 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 5.04 (d, 1 H, $ArCH_2$), 4.92 (d, J_{gem} = 11.5 Hz, 1 H, $ArCH_2$), 4.81 (d, 1 H, $ArCH_2$), 4.72 (dd, $J_{1,2}$ = 8.0 Hz, 1 H, 2-H^{Glc}), 4.67 (dd, $J_{2,3}$ = 11.0 Hz, 1 H, 2-H^{GalN}), 4.61 (d, J_{gem} = 12.5 Hz, 1 H, $ArCH_2$), 4.37 (d, J_{gem} = 11.5 Hz, 1 H, $ArCH_2$), 4.33 (d, 1 H, $ArCH_2$), 4.32 (d, 1 H, 1-H^{Glc}), 4.23 (dd, $J_{3,4}$ = 3.0 Hz, 1 H, 3-H^{GalN}), 4.22 (d, 1 H, $ArCH_2$), 4.10 (dd, $J_{5,6a}$ = 3.5 Hz, J_{gem} = 8.5 Hz, 1 H, 6a-H^{GalN}), 4.06 (d, 1 H, 4-H^{GalN}), 3.94 (dd, $J_{5,6a}$ = 1.5 Hz, J_{gem} = 11.0 Hz, 1 H, 6a-H^{Glc}), 3.78 (m, 1 H, $Me_3SiCH_2CH_2$), 3.74−3.68 (m, 2 H, 5-H^{GalN}, 6b-H^{GalN}), 3.65 (dd, $J_{5,6b}$ = 5.0 Hz, 1 H, 6b-H^{Glc}), 3.44−3.36 (m, 3 H, 4-H^{Glc}, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.97 (s, 3 H, Ac), 1.86 (s, 3 H, Ac), 0.84−0.70 (m, 2 H, $Me_3SiCH_2CH_2$), −0.02 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.0, 169.5, 168.4, 167.6, 137.5, 137.4, 137.1, 136.4, 133.8, 133.6, 131.7, 131.6, 130.9, 130.5, 128.7, 128.5, 128.3, 128.2, 127.8, 127.7, 127.5, 127.4, 123.3, 123.0, 99.7, 98.2, 76.2, 76.0, 75.7, 75.1, 74.6, 74.4, 74.4, 73.7, 72.0, 71.2, 70.6, 70.5, 67.0, 66.9, 52.8, 20.7, 17.7, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{51}H_{59}NO_{14}Si$: 960.3597 $[M + Na]^+$, found 960.3597.

*2-(Trimethylsilyl)ethyl (3,4,6-tri-O-benzyl-2-deoxy-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**36**).* The glycosidation of **13** (111 mg, 0.165 mmol) with **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:3 EtOAc−*n*-hexane) to give **36*α*** (10 mg, 9%) and **36*β*** (90 mg, 80%) as a colorless viscous compound. **36*α***: $[\alpha]_D$ + 76.0 (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94−7.19 (m, 24 H, NPhth, 4 Ph), 5.27 (dd, $J_{3,4}$ = 2.5 Hz, $J_{2,3}$ = 11.5 Hz, 1 H, 3-H^{GalN}), 5.07 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H^{GalN}), 5.00 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.94−4.91 (m, 2 H, 2-H^{GalN}, $PhCH_2$), 4.74 (d, J_{gem} = 11.0 Hz, 1 H, $PhCH_2$), 4.71 (d, J_{gem} = 11.5 Hz, 1 H, $PhCH_2$), 4.66−4.63 (m, 2 H, $PhCH_2$), 4.55 (d, J_{gem} = 11.5 Hz, 1 H, $PhCH_2$), 4.49, 4.42 (2 d, J_{gem} = 12.0 Hz, 2 H, $PhCH_2$), 4.18 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{Glc}), 4.14−4.10 (m, 3 H, 4-H^{GalN}, 2-H^{Glc}, 6a-H^{GalN}), 3.98 (dd, $J_{5,6a}$ = 2.5 Hz, J_{gem} = 12.5 Hz, 1 H, 6a-H^{Glc}), 3.70 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H^{Glc}), 3.64−3.57 (m, 3 H, 6b-H^{Glc}, 5-H^{GalN}, 6b-H^{GalN}), 3.53 (m, 1 H, $Me_3SiCH_2CH_2$), 3.24−3.17 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.93 (s, 3 H, Ac), 1.89 (s, 3 H, Ac), 0.71−0.55 (m, 2 H, $Me_3SiCH_2CH_2$), −0.06 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.2, 169.3, 169.0, 168.8, 138.5, 138.1, 138.1, 138.0, 134.3, 133.7, 132.5, 131.2, 128.5, 128.4, 128.3, 128.2, 127.9,

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127.8, 127.8, 127.7, 127.6, 127.5, 123.4, 123.1, 100.0, 99.8, 77.6, 75.6, 75.1, 75.0, 74.7, 74.2, 73.9, 73.5, 72.8, 72.1, 71.3, 70.2, 69.0, 66.6, 66.5, 52.2, 20.8, 20.8, 17.6, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{57}H_{65}NO_{14}Si$: 1038.4067 $[M + Na]^+$, found 1038.4069. **36*β***: $[\alpha]_D$ + 6.0 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.83−6.99 (m, 24 H, NPhth, 4 Ph), 5.28 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H^{GalN}), 5.10 (m, 1 H, 3-H^{Glc}), 4.99 (d, J_{gem} = 11.5 Hz, 1 H, PhCH_2), 4.79−4.75 (m, 2 H, 2-H^{GalN}, 2-H^{Glc}), 4.64 (d, 1 H, PhCH_2), 4.60 (d, J_{gem} = 12.5 Hz, 1 H, PhCH_2), 4.50, 4.46 (2 d, J_{gem} = 12.0 Hz, 2 H, PhCH_2), 4.42 (d, J_{gem} = 11.0 Hz, 1 H, PhCH_2), 4.36 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H^{Glc}), 4.35−4.30 (m, 3 H, 3-H^{GalN}, PhCH_2), 4.08 (d, $J_{3,4}$ = 2.5 Hz, 1 H, 4-H^{GalN}), 4.03 (d, J_{gem} = 10.5 Hz, 1 H, 6a-H^{Glc}), 3.81 (m, 1 H, $Me_3SiCH_2CH_2$), 3.78−3.64 (m, 4 H, 5-H^{GalN}, 6a-H^{GalN}, 6b-H^{GalN}, 6b-H^{Glc}), 3.47−3.39 (m, 3 H, 4-H^{Glc}, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.99 (s, 3 H, Ac), 1.87 (s, 3 H, Ac), 0.86−0.72 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.0, 169.5, 168.5, 167.6, 138.5, 137.9, 137.6, 137.4, 133.7, 133.6, 131.7, 128.4, 128.3, 128.2, 128.2, 128.1, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 123.3, 123.0, 99.7, 98.3, 77.2, 76.3, 75.1, 74.5, 74.4, 73.6, 73.4, 72.1, 71.9, 71.5, 68.4, 66.8, 52.7, 20.7, 20.7, 17.6, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{57}H_{65}NO_{14}Si$: 1038.4067 $[M + Na]^+$, found 1038.4067.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-2-deoxy-4,6-di-O-methyl-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**37**).* The glycosidation of **14** (86 mg, 0.165 mmol) with **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:2 EtOAc−*n*-hexane) to give **37*α*** (7 mg, 7%) and **37*β*** (69 mg, 72%) as a colorless viscous compound. **37*α*:** $[\alpha]_D$ + 5.2 (*c* 1.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.94−7.18 (m, 14 H, NPhth, 2 Ph), 5.23 (dd, $J_{3,4}$ = 2.6 Hz, $J_{2,3}$ = 11.7 Hz, 1 H, 3-H^{GalN}), 5.06 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H^{GalN}), 5.00 (t, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, 1 H, 3-H^{Glc}), 4.82 (dd, 1 H, 2-H^{GalN}), 4.75 (d, J_{gem} = 10.9 Hz, 1 H, PhCH_2), 4.70 (d, J_{gem} = 11.4 Hz, 1 H, PhCH_2), 4.64 (d, 1 H, PhCH_2), 4.63 (d, 1 H, PhCH_2), 4.19 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{Glc}), 4.13 (t, 1 H, 2-H^{Glc}), 4.04 (br t, 1 H, 5-H^{GalN}), 3.98 (dd, $J_{5,6a}$ = 2.3 Hz, J_{gem} = 12.1 Hz, 1 H, 6a-H^{GalN}), 3.84 (d, 1 H, 4-H^{GalN}), 3.71 (t, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H^{Glc}), 3.64−3.49 (m, 7 H, 6b-H^{GalN}, 6a-H^{Glc}, 6b-H^{Glc}, OMe, $Me_3SiCH_2CH_2$), 3.34 (s, 3 H, OMe), 3.24−3.18 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 1.93 (s, 3 H, Ac), 1.89 (s, 3 H, Ac), 0.70−0.55 (m, 2 H, $Me_3SiCH_2CH_2$), −0.05 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.3, 169.3, 169.0, 168.8, 138.1, 138.0, 134.3, 133.8, 132.5, 131.2, 128.5, 128.3, 128.0, 127.9, 127.8, 127.6, 123.4, 123.1, 100.0, 99.8, 77.6, 75.6, 75.1, 75.0, 75.0, 74.2, 73.7, 72.1, 71.3, 71.2, 70.0, 66.6, 66.5, 61.2, 59.2, 52.1, 20.8, 17.6, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{45}H_{57}NO_{14}Si$: 886.3441 $[M + Na]^+$, found 886.3440. **37*β*:** $[\alpha]_D$ − 12.3 (*c* 2.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.78−7.01 (m, 14 H, NPhth, 2 Ph), 5.21 (d, $J_{1,2}$ = 8.6 Hz, 1 H, 1-H^{GalN}), 5.08 (m, 1 H, 3-H^{Glc}), 4.73 (dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H^{Glc}), 4.65 (d, J_{gem} = 12.1 Hz, 1 H, PhCH_2), 4.61 (dd, $J_{2,3}$ = 11.1 Hz, 1 H, 2-H^{GalN}), 4.40 (d, J_{gem} = 11.0 Hz, 1 H, PhCH_2), 4.35−4.32 (m, 3 H, 1-H^{Glc}, PhCH_2), 4.26 (dd, $J_{3,4}$ = 2.9 Hz, 1 H, 3-H^{GalN}), 3.99 (dd, $J_{5,6a}$ = 0.5 Hz, J_{gem} = 11.0 Hz, 1 H, 6a-H^{GalN}), 3.80−3.75 (m, 2 H, 4-H^{GalN}, $Me_3SiCH_2CH_2$), 3.70−3.66 (m, 3 H, 6b-H^{GalN}, 6a-H^{Glc}, 6b-H^{Glc}), 3.62 (s, 3 H, OMe), 3.55 (dd, 1 H, 5-H^{GalN}), 3.45−3.37 (m, 6 H, 4-H^{Glc}, 5-H^{Glc}, OMe, $Me_3SiCH_2CH_2$), 1.97 (s, 3 H, Ac), 1.86 (s, 3 H, Ac), 0.84−0.70 (m, 2 H, $Me_3SiCH_2CH_2$), −0.01 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.1, 169.6, 166.4, 165.9, 146.8, 137.4, 137.0, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 99.9, 98.4, 76.1, 74.9, 74.7, 74.6, 73.3, 72.8, 71.9, 71.5, 70.3, 67.8, 67.3, 63.7, 51.5, 20.8, 20.8, 17.9, −1.3. HRMS (ESI-TOF) m/z calcd for $C_{45}H_{57}NO_{14}Si$: 886.3441 $[M + Na]^+$, found 886.3439.

*2-(Trimethylsilyl)ethyl (4,6-di-O-acetyl-3-O-benzyl-2-deoxy-2-phthalimide-D-galactopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**38**).* The glycosidation of **15** (95 mg, 0.165 mmol) with **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:3 EtOAc−*n*-hexane) to give **38*α*** (5 mg, 5%) and **38*β*** (94 mg, 92%) as a colorless viscous compound. **38*α***: $[\alpha]_D$ + 111.5 (*c* 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.96−7.16 (m, 14 H, NPhth, 2 Ph), 5.68 (d, $J_{3,4}$ = 3.0 Hz, 1 H, 4-H^{GalN}), 5.32 (dd, $J_{2,3}$ = 11.5 Hz, 1 H, 3-H^{GalN}), 5.10 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H^{GalN}), 5.02 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.75 (d, J_{gem} = 10.0 Hz, 1 H, PhCH_2), 4.69, 4.66 (2 d, J_{gem} = 11.5 Hz, 2 H, PhCH_2), 4.62 (dd, 1 H, 2-H^{GalN}), 4.48 (d, 1 H, PhCH_2), 4.21 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H^{Glc}), 4.20−4.16 (m, 2 H, 5-H^{GalN}, 6a-H^{GalN}), 4.11 (dd, $J_{5,6b}$ = 9.0 Hz, J_{gem} = 13.0 Hz, 1 H, 6b-H^{GalN}), 4.06 (dd, 1 H, 2-H^{Glc}), 3.95 (dd, $J_{5,6a}$ = 2.5 Hz, J_{gem} = 12.0 Hz, 1 H, 6a-H^{Glc}), 3.68−3.64 (m, 2 H, 4-H^{Glc}, 6b-H^{Glc}), 3.59 (m, 1 H, $Me_3SiCH_2CH_2$), 3.26−3.21 (m, 2 H, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 2.16 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 1.90 (s, 3 H, Ac), 0.76−0.60 (m, 2 H, $Me_3SiCH_2CH_2$), −0.04 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.5, 170.4, 170.2, 169.2, 168.9, 168.6, 138.1, 137.5, 134.5, 134.0, 132.3, 131.0, 128.5, 128.3, 128.2, 127.9, 127.9, 127.7, 123.4, 123.2, 99.8, 99.7, 77.6, 75.5, 75.3, 74.9, 74.2, 72.1, 71.2, 70.5, 67.4, 66.7, 66.5, 66.3, 62.5, 52.1, 20.9, 20.8, 20.8, 20.7, 17.6, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{47}H_{57}NO_{16}Si$: 942.3339 $[M + Na]^+$, found 942.3338. **38*β***: $[\alpha]_D$ + 18.8 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.81−6.90 (m, 14 H, NPhth, 2 Ph), 5.59 (d, $J_{3,4}$ = 3.0 Hz, 1 H, 4-H^{GalN}), 5.28 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H^{GalN}), 5.10 (t, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, 3-H^{Glc}), 4.76 (dd, $J_{1,2}$ = 8.0 Hz, 1 H, 2-H^{Glc}), 4.59 (d, J_{gem} = 12.0 Hz, 1 H, PhCH_2), 4.46 (dd, $J_{2,3}$ = 11.0 Hz, 1 H, 2-H^{GalN}), 4.38−4.29 (m, 4 H, 1-H^{Glc}, 3-H^{GalN}, PhCH_2), 4.27−4.19 (m, 3 H, 6a-H^{GalN}, 6b-H^{GalN}, PhCH_2), 4.04 (d, J_{gem} = 11.0 Hz, 1 H, 6a-H^{Glc}), 3.96 (t, $J_{5,6a}$ = $J_{5,6b}$ = 6.5 Hz, 1 H, 5-H^{GalN}), 3.83 (m, 1 H, $Me_3SiCH_2CH_2$), 3.69 (dd, $J_{5,6b}$ = 4.5 Hz, J_{gem} = 11.0 Hz, 1 H, 6b-H^{Glc}), 3.46−3.41 (m, 3 H, 4-H^{Glc}, 5-H^{Glc}, $Me_3SiCH_2CH_2$), 2.22 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.87 (s, 3 H, Ac), 0.88−0.74 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 176.3, 170.4, 170.4, 170.0, 169.5, 168.1, 167.4, 137.2, 137.1, 133.9, 133.9, 133.7, 132.2, 131.5, 131.5, 129.8, 129.3, 128.3, 128.1, 127.9, 127.8, 127.8, 127.6, 127.6, 123.3, 123.1, 99.8, 98.2, 77.2, 76.2, 75.0, 74.5, 74.4, 72.9, 72.0, 71.2, 71.1, 67.4, 67.0, 65.5, 62.0, 52.6, 28.5, 20.8, 20.7, 20.6, 17.7, −1.4. HRMS (ESI-TOF) m/z calcd for $C_{47}H_{57}NO_{16}Si$: 942.3339 $[M + Na]^+$, found 942.3340.

*2-(Trimethylsilyl)ethyl (3-O-benzyl-2-deoxy-4,6-O-di-tert-butylsilylene-2-phthalimide-β-D-glucopyranosyl)-(1→6)-2,3-di-O-acetyl-4-O-benzyl-β-D-glucopyranoside (**39**).* The glycosidation of **16** (104 mg, 0.165 mmol) with **23** (50 mg, 0.111 mmol) in CH_2Cl_2 (2.8 mL) was performed according to the typical procedure. The glycosylated products were purified by silica gel column chromatography (1:20 → 1:5 EtOAc−toluene) to give **39** (105 mg, 97%) as a colorless viscous compound. $[\alpha]_D$ + 2.3 (*c* 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.80−6.86 (m, 14 H, Phth, 2 Ph), 5.34 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H^{GlcN}), 5.08 (t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3-H^{Glc}), 4.85 (d, J_{gem} = 12.5 Hz, 1 H, PhCH_2), 4.76 (dd, $J_{1,2}$ = 8.0 Hz, 1 H, 2-H^{Glc}), 4.61 (d, 1 H, PhCH_2), 4.36 (d, 1 H, 1-H^{Glc}), 4.31 (d, J_{gem} = 11.0 Hz, 1 H, PhCH_2), 4.29 (d, 1 H, PhCH_2), 4.24 (dd, $J_{5,6a}$ = 5.0 Hz, J_{gem} = 10.5 Hz, 1 H, 6a-H^{GlcN}), 4.19 (dd, $J_{2,3}$ = 10.0 Hz, 1 H, 2-H^{GlcN}), 4.13 (t, $J_{3,4}$ = 9.0 Hz, 1 H, 3-H^{GlcN}), 4.08 (t, $J_{4,5}$ = 9.0 Hz, 1 H, 4-H^{GlcN}), 4.00 (t, $J_{5,6b}$ = 10.0 Hz, 1 H, 6b-H^{GlcN}), 3.96 (dd, $J_{5,6a}$ = 1.5 Hz, J_{gem} = 11.5 Hz, 1 H, 6a-H^{Glc}), 3.84 (m, 1 H, $Me_3SiCH_2CH_2$), 3.69 (dd, $J_{5,6b}$ = 5.5 Hz, 1 H, 6b-H^{Glc}), 3.58 (m, 1 H, 5-H^{GlcN}), 3.47−3.42 (m, 2 H, $Me_3SiCH_2CH_2$, 4-H^{Glc}), 3.38 (m, 1 H, 5-H^{Glc}), 1.99 (s, 3 H, Ac), 1.87 (s, 3 H, Ac), 1.11, 1.08 (2 s, 18 H, 2 ^{t}Bu), 0.86−0.75 (m, 2 H, $Me_3SiCH_2CH_2$), 0.00 (s, 9 H, $Me_3SiCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.1, 169.6, 138.2, 137.3, 133.8, 131.6, 129.0, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 127.3, 123.2, 99.8, 98.2, 79.3, 76.2, 75.1, 74.6, 74.5, 74.1, 72.0, 70.4, 67.3, 67.1, 66.4, 55.2, 27.5, 27.1, 22.7, 20.8, 20.7, 20.0, 17.8, −1.3. HRMS (ESI-TOF) m/z calcd for $C_{51}H_{69}NO_{14}Si_2$: 998.4149 $[M + Na]^+$, found 998.4150.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01685.

^1H and ^{13}C NMR spectra of all new compounds; tables of atom coordinates and absolute energies to document the theoretical calculations (PDF)

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Notes

The authors declare no competing financial interest.

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