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A Stereoselective Ring-Closing Glycosylation via Nonglycosylating Pathway

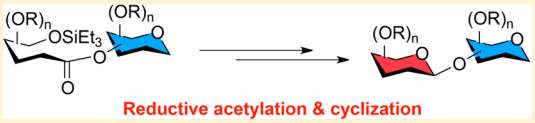
Han Liu[†] and Xuechen Li*[,†,‡]

[†]Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

[‡]State Key Laboratory of Synthetic Chemistry, University of Hong Kong, Hong Kong, PR China

Supporting Information

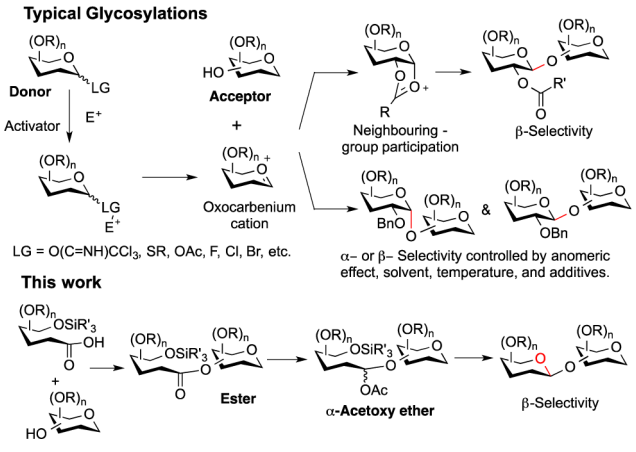
ABSTRACT: Two glycosyl partners were first coupled with as ester linkage, which upon reductive acetylation produced an α-acetoxy ether group. The subsequent activation with TfOH triggered the ring-closing process and provided the corresponding glycosidic bond in high β-selectivity without relying on neighboring group participation.



The past century has witnessed a great advance in chemical glycosylations, which have enabled the construction of complex oligosaccharides for biological and therapeutic applications.[1] Building on the first conceptual glycosylation by Koenigs and Knorr more than 100 years ago,[2] a plethora of modern methods have been developed.[3] Although these achievements have allowed carbohydrates with complex structures to be synthesized, if given enough time and resources, the development of new glycosylation methodologies leading to stereoselective construction of glycosidic linkages is still important in preparative carbohydrate chemistry.

The typical glycosylation methods involve a glycosyl donor (i.e., a sugar with a latent leaving group at the anomeric carbon) as an electrophile and an acceptor (e.g., a hydroxyl group from a partially protected sugar) as the nucleophilic counterpart (Scheme 1). Upon activation with a suitable promoter (e.g., Lewis acids), the anomeric latent leaving group undergoes anomeric substitution by the nucleophilic glycosyl acceptor to form a glycosidic linkage. Over the past decades, many latent leaving groups and the corresponding activators have been developed to serve as the glycosyl donor, including thioether,[4] sulfoxide,[5] halides,[6] trichloroacetoimidate,[7] *N*-phenyl trifluoroacetoimidate,[8] phosphate,[9] phosphite,[10] *o*-carboxyl benzoate,[11] *o*-alkynyl benzoate,[12] terminal alkenyl ether,[13] lactol,[14] glycal,[15] pyranones,[16] etc. Upon the glycosyl donor activation, the oxocarbenium cation is often considered to be the critical intermediate, which can be stabilized by the C2-*O* participating group (e.g., acyl groups) to produce 1,2-*trans* glycosidic linkage.[17] Without the C2-*O* participating group, the outcome of the resultant stereoselectivity is often complicated. Generally, although the kinetic anomeric effect will favor the formation of α-glycosides, the mixture of both α- and β-glycosides are often obtained, whose distribution is subjected to various effects from solvent, temperature, additives, glycosyl donor/promoter combination and the substrate structure.[18] New conceptual methods have emerged to control the anomeric stereoselectivity. Of particular significance, these methods include intramolecular aglycon delivery (IAD),[19] conformationally locked glycosyl donors,[20] and auxiliary-based glycosylation.[21]

Scheme 1. General Glycosylation Methods and Our Proposed Ring-Closing Glycosylation



In contrast to the traditional paradigm of chemical glycosylations, we reported herein a ring-closing glycosylation strategy, which resulted in high stereoselectivity without the aid of a C2-*O* participating group. As shown in Scheme 1, we conceived of the idea that if two glycosyl partners were first coupled with an ester bond, which, upon reduction and acetylation, would produce an α-acetoxy ether group, the subsequent activation with Lewis acids or Brønsted acids would trigger a ring-closing reaction to generate the corresponding glycosidic bond. To the best of our knowledge, a disaccharide synthesis via intramolecular cyclization from linear precursor is quite rare,[22,23] and the ring-closing glycosylation via an α-acetoxy ether has not been reported previously.

Our initial studies started with a model system, as illustrated in Scheme 2. The benzylated glucose **1** was readily converted into the corresponding acid via the activated amide **2**.[24] Esterification with 1.0 equiv of cyclohexanol was performed

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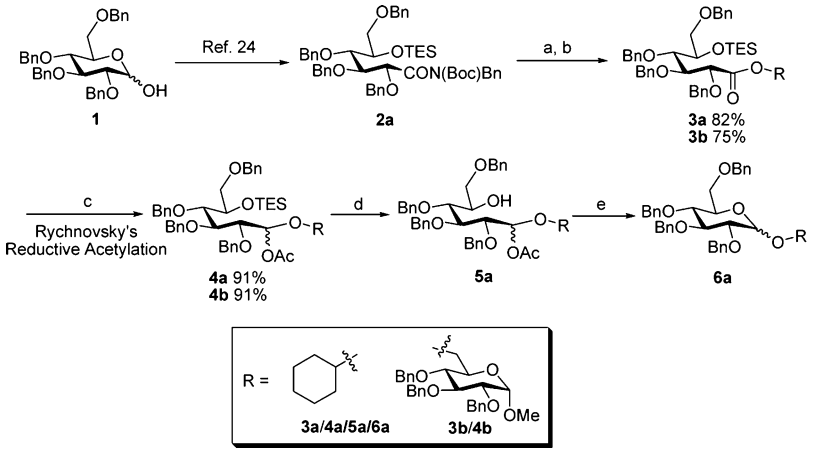
Scheme 2. Synthesis of Model Substrates and Attempt of Ring-Closing Glycosylation[a]



[a](a) 10 equiv of LiOH, 20 equiv of H_2O_2, THF/H_2O 4/1, 16 h; (b) 1 equiv of ROH, 2 equiv of DCC, 0.5 equiv of DMAP, CH_2Cl_2, 4 h; (c) (i) 2 equiv of DIBAL-H, CH_2Cl_2, −78 °C, 40 min; (ii) 3 equiv of pyridine, 2 equiv of DMAP, 6 equiv of Ac_2O, −78 °C, 10 h, and then 0 °C, 30 min. For details, see Supporting Information.

under DCC/DMAP condition to give ester **3a** in 82% yield. No epimerization was observed at C2-position during the coupling reaction when 0.5 equiv of DMAP was used. The desired α-acetoxy ether **4a** was successfully obtained via Rychnovsky's reductive acetylation reaction[25] in 91% yield as an inseparable mixture of diastereomers. A more advanced model **4b** containing a two-sugar skeleton was obtained in a similar way. It is noted that the compounds **4a**/**b** were quite stable for long time storage.

With the model substrates in hand, we set out to screen conditions for the cyclization. In our first attempt, the TES (triethylsilyl) group of **4a** was removed by TBAF, and the crude intermediate **5a** was treated with 1.0 equiv of nBu$_2$BOTf in DCM at −40 °C. The cyclized product was formed in 58% yield as 1:1 mixture of anomers. The selection of the TES group was quite critical, while the more stable TBDMS (*tert*-butyldimethylsilyl) group could not be easily removed under the same condition. Considering the significant decomposition during the desilylation step, we turned to explore a one-pot reaction, hoping for a more straightforward and efficient process. In an encouraging precedent, Mukaiyama and Kobayashi have reported that silylated alcohols could directly participate in the glycosylation with a glycosyl acetate donor.[26]

Thus, we envisaged that the TES protected hydroxyl group in **4a** could react with the acetoxy ether group intramolecularly. Gratifyingly, in the first round screening study, the ring-closing reaction of **4a** proceeded smoothly upon the treatment with various types of Lewis acids, affording **6a** with varied yields and stereoselectivities (entry 1−11, Table 1). Generally, nBu$_2$BOTf and TMSOTf gave better results than other Lewis acids in term of the isolated yield. To our surprise, a stoichiometric amount of strong Brønsted acid TfOH, which was usually considered to be destructive to the glycosidic bond, also gave good yields for the cyclization (entry 12−13, Table 1). Using DCM as solvent at lower temperature gave good yields, while other solvents and higher temperature led to partial decomposition. However, the stereoselectivity was not very obvious at this point, depending on the activator, solvent, temperature, and even the activator loading.

This result prompted us to conduct the second round screening using a more advanced substrate **4b** toward a real disaccharide. This time, all of the three selected activators

Table 1. Optimization of the Reaction Conditions of Intramolecular Glycosylation

entry	R	activator	equiv	solvent	temp (°C)	yield %[a] (α/β)[b]
1	**4a**	$Cu(OTf)_2$	0.5	DCM	20	75 (62:38)
2	**4a**	$Zn(OTf)_2$	0.5	DCM	20	52 (69:31)
3	**4a**	TMSOTf	1.0	DCM	−40	90 (65:35)
4	**4a**	TBSOTf	1.0	DCM	−40	77 (59:41)
5	**4a**	BF_3OEt_2	1.0	DCM	−40	69 (55:45)
6	**4a**	nBu$_2$BOTf	1.0	DCM	20	67 (43:57)
7	**4a**	nBu$_2$BOTf	1.0	DCM	−40	89 (81:19)
8	**4a**	nBu$_2$BOTf	0.1	DCM	−40	98 (34:66)
9	**4a**	nBu$_2$BOTf	1.0	TOL[c]	−40	34 (86:14)
10	**4a**	nBu$_2$BOTf	1.0	MeCN	−40	90 (60:40)
11	**4a**	nBu$_2$BOTf	0.1	THF	−40	56 (28:72)
12	**4a**	TfOH	1.0	DCM	20	76 (57:43)
13	**4a**	TfOH	1.0	DCM	−40	97 (59:41)
14	**4b**	nBu$_2$BOTf	1.0	DCM	−40	67 (38:62)
15	**4b**	nBu$_2$BOTf	0.1	DCM	−40	62 (38:62)
16	**4b**	TMSOTf	1.0	DCM	20	53 (22:78)
17	**4b**	TMSOTf	1.0	DCM	−40	88 (32:68)
18	**4b**	TfOH	1.0	DCM	20	83 (34:66)
19	**4b**	TfOH	1.0	DCM	−40	88 (33:67)

[a]Isolated yields. [b]The glycosylation products were identified, and the α/β ratio was determined by ^{1}H NMR of the crude reaction mixture. [c]Toluene.

(nBu$_2$BOTf, TMSOTf, and TfOH) gave a similar level of β-selectivity (β/α, ~ 2/1) (entry 14−19, Table 1), while TfOH provided higher yield at both −40 °C and room temperature. Thus, this activator was chosen in the following studies.

Having established the validity of this approach, we next sought to evaluate the efficiency of the glycosylation reaction for the construction of more complex disaccharides. A range of esters **3c**−**3i** were prepared from the glucose or galactose derived acids, which were esterified with acceptors having

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varied hydroxyl groups and protecting groups. In the reductive acetylation of the hindered esters, toluene was used as the solvent for the DIBAL-H reduction step, while DCM gave poor conversions. No significant stereoselectivity was observed in the reduction step, and the α- acetoxy ethers **4c**−**4i** were formed in moderate to good yields (41−89%) as mixture of diastereomers with varied ratios.

As shown in Figure 1, upon activation with TfOH in DCM, all the precursors **4c**−**4i** cyclized smoothly and gave rise to the

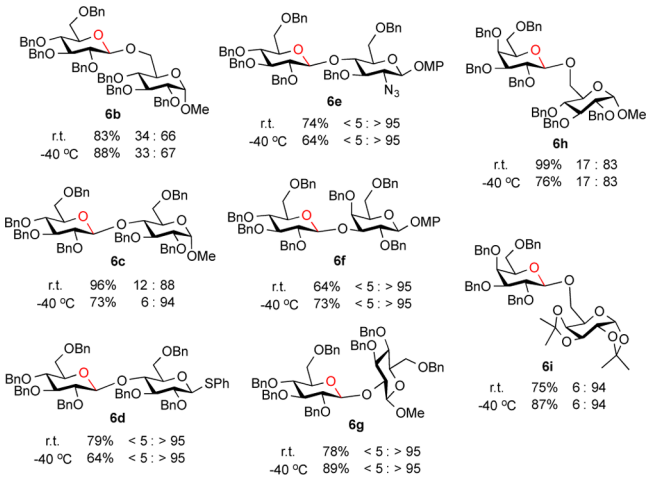


Figure 1. Scope of the ring-closing glycosylation. The isolated yield and α/β ratio are shown.

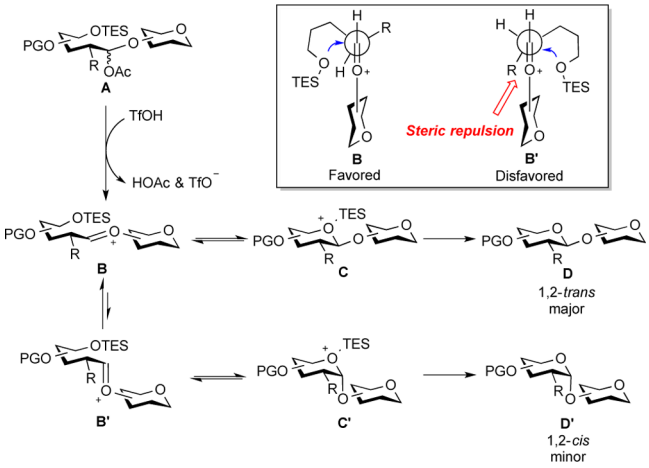
desired disaccharides **6c**−**6i** in good yields. Apart from the benzyl group, protecting groups such as OMP, azide, acetonide, and thioglycosides were compatible with our reaction conditions. The ester-type protecting groups would be potentially affected under the reductive acetylation condition. When other activators such as TMSOTf and nBu$_2$BOTf were used, only trace amount of products was obtained together with significant decomposition of the acetoxy ether.

To our delight, disaccharides **6c**−**6g** containing (1,4), (1,3), and (1,2) linkage gave much enhanced β-selectivity at both low and room temperature, compared to the model system. It appeared that the acceptor with hindered secondary alcohols promoted high stereoselectivity. Indeed, for **6h** and **6i** prepared from galactose-derived acid and primary C6-OH acceptors, significant β-selectivity was also achieved. No relationship between the stereoselectivity after the ring-closing glycosylation and the diastereomeric ratio of the acetoxy-ether group was observed. It is worthwhile to note that orthoester side-reactions, often occurring when C2-*O*-acyl donors were used to mediate the β-glycosylation,[27] unlikely took place under the current condition.

The postulated mechanism for the ring-closing glycosylation is shown in Scheme 3. As the stereoselectivity of our glycosylation was not associated with the diastereomeric ratio of the α-acetoxy ether group, the S_N2 pathway could be likely excluded. However, at this stage, we cannot rule out the possibility that the α-acetoxy ether rapidly racemized under the acidic conditions and only the most reactive diastereomer led to the β product.

To test the possibility that the desilylation takes place prior to the cyclization, the silylated ester **3b** (counterpart of α-acetoxy ether **4b** without the potential for the oxocarbenium cation generation) was subjected to the ring-closing glycosylation condition (1 equiv of TfOH in DCM at rt). The desilylation was observed, but the reaction was very slow with a 50% conversion after 1 h at room temperature. Thus, we conclude that it is more likely that the ring-closing precedes the desilylation.

Scheme 3. Postulated Mechanism of the Ring-Closing Glycosylation



Thus, we propose an oxocarbenium cation based cyclization. Upon activation of the acetoxy ether **A**, the oxocarbenium cation intermediate **B** is formed, in equilibrium with **B′** rotamer. Ring-closing glycosylation via **B** is more likely to avoid the steric repulsion between the acceptor part and the substituent at the C2-position. The nucleophilic attack of the C5-*O*-silylated oxygen to the cation lead to the cyclized intermediate **C**, which can be converted to the disaccharide product **D** via irreversible desilylation.

In summary, we developed a 3-step ring-closing glycosylation procedure that proceeds via the unconventional intramolecular pathway. This method involved coupling the two glycosyl counterparts via an ester linkage, which upon DIBAL-H mediated Rychnovsky's reductive acetylation afforded an α-acetoxy ether moiety; next, on the treatment with TfOH, the C5-*O*-silylated oxygen substituted the acetoxy ether to induce a ring-closing reaction, realizing the formation of the pyranosidic linkage. Interestingly, the β-pyranosides were produced with high selectivity from C2-*O*-benzyl donors without the aid of acyl groups for neighboring participation. This novel glycosylation offers an alternative concept for the design of chemical glycosylation procedure.

EXPERIMENTAL SECTION

General Procedure for the Preparation of Esters 3a−3i. To the solution of **2a,b** (1.0 equiv) in THF (0.1 mmol/4 mL), H_2O_2 (20 equiv) was added at 0 °C, followed by 1 M LiOH (aq., 10 equiv). The mixture was warmed gradually to rt and stirred at rt for 16 h. The mixture was diluted with ethyl acetate and neutralized by 10% citric acid (aq.) at 0 °C. The organic phase was separated and washed with water and brine. After being dried over Na_2SO_4, the solvent was removed under a vacuum, and the residue was purified by flash chromatography using *n*-hexane/ethyl acetate 5:1 to 2:1 as eluent. The corresponding acid was obtained in variable yields (>90% from **2a** and ~80% from **2b**) and directly used in the next step to avoid decomposition.

The acid (1.0 equiv) and alcohol (1.0 equiv) were dissolved in anhydrous DCM (1 mmol/10 mL). The mixture was cooled to 0 °C, then DCC (2.0 equiv) and DMAP (0.50 equiv) were added sequentially. The white precipitation can be observed within 10 min.

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The mixture was sitrred at rt for 4 h, and diluted with *n*-hexane. After filtration, the solution was concentrated under a vacuum, and the residue was purified by flash chromatography using *n*-hexane/ethyl acetate 10:1 to 5:1 as eluent to afford the pure esters **3a**−**i**.

*Cyclohexyl (2R,3S,4R,5R)-2,3,4,6-tetrabenzyloxy-5-triethylsiloxy-hexanoate (**3a**).* Yield 82% (178 mg, colorless oil, from 0.29 mmol acid): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.54−0.60 (m, 6H), 0.90 (t, J = 8.0 Hz, 9H), 1.16−1.34 (m, 5H), 1.49−1.52 (m, 1H), 1.62−1.69 (m, 3H), 1.83−1.86 (m, 1H), 3.43 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H), 3.71 (dd, J_1 = 9.6 Hz, J_2 = 4.8 Hz, 1H), 3.90 (dd, J_1 = 7.2 Hz, J_2 = 4.0 Hz, 1H), 4.00 (q, J = 4.8 Hz, 1H), 4.13 (dd, J_1 = 7.2 Hz, J_2 = 3.6 Hz, 1H), 4.27 (d, J = 3.6 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.48 (d, J = 11.6 Hz, 1H), 4.59 (d, J = 11.6 Hz, 1H), 4.71 (s, 2H), 4.73−4.77 (m, 1H), 4.82 (d, J = 11.2 Hz, 1H), 4.83 (d, J = 11.2 Hz, 1H), 7.23−7.39 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 5.1, 7.0, 23.9, 25.4, 31.7, 31.8, 72.0, 73.1, 73.3, 73.5, 73.7, 75.0, 75.4, 79.5, 80.8, 81.5, 137.6, 138.4, 138.9, 139.2, 170.1; ESI-TOF-HR-MS (m/z) Calcd for $C_{46}H_{60}O_7SiNa^+$ (M + Na^+) 775.4001, found 775.4011.

*Methyl 2,3,4-O-tribenzyl-6-O-[(2R,3S,4R,5R)-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-α-D-glucopyranoside (**3b**).* Yield 75% (802 mg, colorless oil, from 0.96 mmol acid): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.54 (m, 6H), 0.87 (t, J = 8.0 Hz, 9H), 3.22 (s, 3H), 3.35 (dd, J_1 = 9.6 Hz, J_2 = 3.6 Hz, 1H), 3.40−3.44 (m, 2H), 3.70 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H), 3.73−3.76 (m, 1H), 3.91−3.96 (m, 2H), 3.98−4.01 (m, 1H), 4.14 (dd, J_1 = 7.2 Hz, J_2 = 3.6 Hz, 1H), 4.25 (dd, J_1 = 11.8 Hz, J_2 = 2.2 Hz, 1H), 4.30−4.34 (m, 2H), 4.39−4.44 (m, 4H), 4.48 (d, J = 10.8 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 11.2 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.68 (d, J = 11.2 Hz, 1H), 4.73 (d, J = 11.2 Hz, 1H), 4.76−4.83 (m, 4H), 4.95 (d, J = 11.2 Hz, 1H), 7.16−7.36 (m, 35H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 5.0, 7.0, 55.2, 63.3, 68.6, 71.8, 73.0, 73.2, 73.3, 73.4, 75.1, 75.2, 75.3, 75.7, 77.9, 79.3, 80.1, 80.5, 81.9, 97.9, 127.38, 127.40, 127.6, 127.76, 127.79, 127.89, 127.94, 128.0, 128.07, 128.11, 128.18, 128.25, 128.36, 128.41, 128.44, 128.5, 137.5, 138.0, 138.1, 138.3, 138.8, 138.9, 139.2, 170.5; ESI-TOF-HR-MS (m/z) Calcd for $C_{68}H_{80}O_{12}SiNa^+$ (M + Na^+) 1139.5311, found 1139.5307.

*Methyl 2,3,6-O-tribenzyl-4-O-[(2R,3S,4R,5R)-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-α-D-glucopyranoside (**3c**).* Yield 72% (284 mg, colorless oil, from 0.36 mmol acid): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.52−0.58 (m, 6H), 0.89 (t, J = 8.0 Hz, 9H), 3.33−3.44 (m, 3H), 3.37 (s, 3H), 3.62 (dd, J_1 = 9.6 Hz, J_2 = 3.6 Hz, 1H), 3.66 (dd, J_1 = 9.6 Hz, J_2 = 4.8 Hz, 1H), 3.78−3.80 (m, 1H), 3.83 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 1H), 3.95−4.02 (m, 2H), 4.12−4.20 (m, 3H), 4.27−4.30 (m, 2H), 4.40 (d, J = 12.2 Hz, 1H), 4.43 (d, J = 12.2 Hz, 1H), 4.52 (d, J = 11.2 Hz, 1H), 4.55−4.63 (m, 6H), 4.67 (d, J = 12.4 Hz, 1H), 4.70 (d, J = 12.4 Hz, 1H), 4.93 (d, J = 11.6 Hz, 1H), 5.16 (t, J = 9.6 Hz, 1H), 7.14−7.31 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 5.1, 7.1, 55.4, 68.8, 69.1, 71.0, 71.8, 73.0, 73.1, 73.3, 73.4, 73.5, 74.7, 74.8, 74.9, 79.0, 80.1, 81.5, 97.9, 127.17, 127.19, 127.3, 127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.38, 128.43, 128.6, 137.6, 137.9, 138.2, 138.4, 138.8, 138.9, 139.1, 170.2; ESI-TOF-HR-MS (m/z) Calcd for $C_{68}H_{80}O_{12}SiNa^+$ (M + Na^+) 1139.5311, found 1139.5322.

*Phenyl 2,3,6-O-tribenzyl-4-O-[(2R,3S,4R,5R)-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-1-thio-β-D-glucopyranoside (**3d**).* Yield 79% (305 mg, colorless oil, from 0.31 mmol acid): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.52−0.58 (m, 6H), 0.88 (t, J = 8.0 Hz, 9H), 3.39−3.47 (m, 2H), 3.52−3.64 (m, 4H), 3.72 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H), 3.88 (dd, J_1 = 7.2 Hz, J_2 = 4.0 Hz, 1H), 3.99 (q, J = 4.8 Hz, 1H), 4.16−4.19 (m, 3H), 4.26−4.29 (m, 2H), 4.41 (d, J = 12.0 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 11.2 Hz, 1H), 4.54−4.68 (m, 7H), 4.79 (d, J = 11.6 Hz, 1H), 4.86 (d, J = 10.4 Hz, 1H), 5.10 (t, J = 9.2 Hz, 1H), 7.15−7.29 (m, 38H), 7.54−7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 5.1, 7.1, 69.6, 71.0, 71.8, 72.9, 73.1, 73.2, 73.5, 74.8, 75.0, 75.1, 75.4, 77.9, 79.8, 80.2, 81.0, 81.7, 83.7, 87.5, 127.2, 127.28, 127.32, 127.45, 127.51, 127.6, 127.70, 127.74, 127.9, 127.98, 128.03, 128.2, 128.31, 128.35, 128.46, 128.51, 129.1, 131.8, 133.8, 137.6, 137.8, 138.2, 138.3, 138.5, 138.9, 139.1, 170.2; ESI-TOF-HR-MS (m/z) Calcd for $C_{73}H_{86}NO_{11}SSi^+$ (M + NH_4^+) 1212.5685, found 1212.5687.

*4-Methoxyphenyl 2-deoxy-2-azido-3,6-O-dibenzyl-4-O-[(2R,3S,4R,5R)-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-β-D-glucopyranoside (**3e**).* Yield 76% (321 mg, colorless oil, from 0.40 mmol acid): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.53−0.59 (m, 6H), 0.90 (t, J = 8.0 Hz, 9H), 3.33 (t, J = 9.6 Hz, 1H), 3.39−3.46 (m, 2H), 3.49−3.54 (m, 2H), 3.70−3.79 (m, 2H), 3.76 (s, 3H), 3.91 (dd, J_1 = 7.2 Hz, J_2 = 4.0 Hz, 1H), 4.01 (dd, J_1 = 9.2 Hz, J_2 = 5.2 Hz, 1H), 4.16−4.24 (m, 3H), 4.27−4.32 (m, 2H), 4.43 (d, J = 12.0 Hz, 1H), 4.47 (d, J = 12.0 Hz, 1H), 4.54−4.57 (m, 3H), 4.62−4.71 (m, 4H), 4.76 (d, J = 11.6 Hz, 1H), 5.07 (t, J = 9.2 Hz, 1H), 6.77 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 7.16−7.34 (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 5.1, 7.1, 55.8, 65.8, 69.3, 70.8, 71.9, 72.8, 73.1, 73.3, 73.5, 74.1, 74.2, 74.9, 75.1, 79.6, 80.1, 80.2, 81.7, 101.5, 114.7, 118.5, 127.36, 127.39, 127.5, 127.6, 127.7, 127.80, 127.84, 127.9, 128.0, 128.2, 128.3, 128.4, 128.50, 128.52, 137.5, 137.8, 138.3, 138.4, 138.8, 139.1, 151.2, 155.7, 170.2; ESI-TOF-HR-MS (m/z) Calcd for $C_{67}H_{77}N_3O_{12}SiNa^+$ (M + Na^+) 1166.5169, found 1166.5171.

*4-Methoxyphenyl 2,4,6-O-tribenzyl-3-O-[(2R,3S,4R,5R)-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-β-D-galactopyranoside (**3f**).* Yield 59% (288 mg, colorless oil, from 0.40 mmol acid): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.53−0.59 (m, 6H), 0.89 (t, J = 8.0 Hz, 9H), 3.04 (d, J = 2.8 Hz, 1H), 3.11 (dd, J_1 = 8.8 Hz, J_2 = 3.2 Hz, 1H), 3.42−3.49 (m, 2H), 3.56 (dd, J_1 = 9.6 Hz, J_2 = 6.0 Hz, 1H), 3.74 (s, 3H), 3.82 (dd, J_1 = 9.6 Hz, J_2 = 3.2 Hz, 1H), 3.97 (dd, J_1 = 10.4 Hz, J_2 = 8.0 Hz, 1H), 3.99−4.03 (m, 3H), 4.08−4.12 (m, 2H), 4.18 (d, J = 12.0 Hz, 1H), 4.31 (d, J = 12.0 Hz, 1H), 4.37 (d, J = 12.4 Hz, 1H), 4.40 (d, J = 12.4 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.52−4.55 (m, 2H), 4.60 (d, J = 11.6 Hz, 2H), 4.66 (d, J = 11.6 Hz, 1H), 4.78 (d, J = 10.4 Hz, 1H), 4.88 (d, J = 7.6 Hz, 1H), 4.93 (d, J = 11.6 Hz, 1H), 5.09 (dd, J_1 = 10.4 Hz, J_2 = 2.8 Hz, 1H), 6.77 (d, J = 9.2 Hz, 2H), 7.01 (d, J = 9.2 Hz, 2H), 7.09−7.34 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 5.2, 7.1, 55.7, 69.4, 72.4, 72.6, 73.4, 73.6, 74.1, 74.3, 74.4, 74.5, 74.6, 74.8, 74.9, 80.6, 81.0, 103.1, 114.6, 118.6, 127.4, 127.59, 127.62, 127.68, 127.69, 127.72, 127.8, 127.9, 128.07, 128.13, 128.2, 128.3, 128.36, 128.39, 128.5, 129.0, 137.8, 138.1, 138.2, 138.4, 138.6, 138.7, 151.5, 155.3, 170.3; ESI-TOF-HR-MS (m/z) Calcd for $C_{74}H_{84}O_{13}SiNa^+$ (M + Na^+) 1231.5573, found 1231.5593.

*Methyl 3,4,6-O-tribenzyl-2-O-[(2R,3S,4R,5R)-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-β-D-glucopyranoside (**3g**).* Yield 70% (271 mg, colorless oil, from 0.35 mmol acid): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.52−0.58 (m, 6H), 0.89 (t, J = 8.0 Hz, 9H), 3.20 (s, 3H), 3.40 (dd, J_1 = 9.6 Hz, J_2 = 5.2 Hz, 1H), 3.44−3.47 (m, 1H), 3.54 (t, J = 9.2 Hz, 1H), 3.68−3.75 (m, 4H), 3.89 (dd, J_1 = 7.2 Hz, J_2 = 4.0 Hz, 1H), 4.01 (q, J = 4.8 Hz, 1H), 4.08 (d, J = 11.2 Hz, 1H), 4.16 (dd, J_1 = 7.2 Hz, J_2 = 3.2 Hz, 1H), 4.22 (d, J = 7.6 Hz, 1H), 4.24 (d, J = 3.2 Hz, 1H), 4.42 (s, 2H), 4.52 (d, J = 10.8 Hz, 1H), 4.54 (d, J = 10.8 Hz, 1H), 4.60−4.77 (m, 9H), 5.19 (dd, J_1 = 9.2 Hz, J_2 = 8.4 Hz, 1H), 7.12−7.14 (m, 2H), 7.20−7.33 (m, 33H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 5.1, 7.1, 56.1, 68.8, 72.2, 72.6, 73.2, 73.4, 73.5, 73.7, 74.6, 75.01, 75.04, 75.2, 75.3, 77.9, 79.4, 80.4, 81.8, 83.2, 101.4, 127.3, 127.4, 127.5, 127.7, 127.8, 127.88, 127.92, 127.94, 128.07, 128.10, 128.12, 128.17, 128.25, 128.5, 137.7, 137.9, 138.2, 138.3, 138.4, 138.8, 139.3, 169.1; ESI-TOF-HR-MS (m/z) Calcd for $C_{68}H_{80}O_{12}SiNa^+$ (M + Na^+) 1139.5311, found 1139.5307.

*Methyl 2,3,4-O-tribenzyl-6-O-[(2R,3S,4S,5R)-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-α-D-glucopyranoside (**3h**).* Yield 38% (117 mg, colorless oil, from 0.27 mmol acid): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.52−0.59 (m, 6H), 0.89 (t, J = 8.0 Hz, 9H), 3.25 (s, 3H), 3.41 (t, J = 8.4 Hz, 1H), 3.44 (dd, J_1 = 9.6 Hz, J_2 = 5.6 Hz, 1H), 3.51 (dd, J_1 = 9.2 Hz, J_2 = 6.4 Hz, 1H), 3.56 (dd, J_1 = 9.2 Hz, J_2 = 6.0 Hz, 1H), 3.78−3.83 (m, 1H), 3.91 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 3.96 (t, J = 9.2 Hz, 1H), 4.22 (dt, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 4.25−4.34 (m, 4H), 4.38 (d, J = 5.6 Hz, 1H), 4.39 (d, J = 9.2 Hz, 1H), 4.44−4.51 (m, 4H), 4.54 (d, J = 12.4 Hz, 1H), 4.58 (d, J = 12.4 Hz, 1H), 4.59 (d, J = 11.2 Hz, 1H), 4.66 (d, J = 11.2 Hz, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.79 (d, J = 10.8 Hz, 1H), 4.81 (d, J = 11.2 Hz, 2H), 4.97 (d, J = 10.8 Hz, 1H), 4.18−4.34 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 5.6, 7.2, 55.3, 63.7, 68.6, 71.4, 72.0, 72.8, 72.9, 73.2, 73.5, 73.6, 75.2, 75.8, 77.9, 78.5, 79.2, 80.2, 82.1, 98.0, 127.3, 127.38, 127.44, 127.6, 127.7, 127.8, 127.96, 128.00, 128.05, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6,

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137.9, 138.0, 138.2, 138.3, 138.6, 138.8, 139.0, 171.7; ESI-TOF-HR-MS (m/z) Calcd for $C_{68}H_{80}O_{12}SiNa^+$ (M + Na^+) 1139.5311, found 1139.5301.

*6-O-[(2R,3S,4S,5R)-2,3,4,6-Tetrabenzyloxy-5-triethylsiloxyhexanoyl]-1,2;3,4-O-diisopropylidene-α-D-galactopyranoside (**3i**).* Yield 61% (162 mg, colorless oil, from 0.29 mmol acid): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.55−0.61 (m, 6H), 0.91 (t, J = 8.0 Hz, 9H), 1.24 (s, 3H), 1.30 (s, 3H), 1.39 (s, 3H), 1.46 (s, 3H), 3.50−3.58 (m, 2H), 3.92 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 4.04 (dt, J_1 = 6.4 Hz, J_2 = 1.6 Hz, 1H), 4.17 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 4.21−4.32 (m, 5H), 4.34 (d, J = 11.2 Hz, 1H), 4.38 (d, J = 12.4 Hz, 1H), 4.43−4.47 (m, 2H), 4.47 (d, J = 12.0 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.56 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 4.63 (d, J = 11.2 Hz, 1H), 4.69 (d, J = 11.2 Hz, 1H), 4.89 (d, J = 11.2 Hz, 1H), 5.52 (d, J = 5.2 Hz, 1H), 7.20−7.32 (m, 18H), 7.36−7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 5.5, 7.2, 24.6, 25.0, 26.0, 26.1, 63.6, 65.6, 70.5, 70.7, 70.9, 71.5, 71.9, 72.7, 73.1, 73.7, 78.1, 78.4, 79.1, 96.3, 108.8, 109.6, 127.3, 127.5, 127.6, 127.7, 127.9, 128.18, 128.22, 128.25, 128.32, 128.4, 137.9, 138.2, 138.6, 138.9, 171.6; ESI-TOF-HR-MS (m/z) Calcd for $C_{52}H_{68}O_{12}SiNa^+$ (M + Na^+) 935.4372, found 935.4360.

General Procedure for the Preparation of α-Acetoxy Ethers 4a−4i. The esters **3a**−**i** (1.0 equiv) were dissolved in anhydrous DCM or toluene (**3a**,**b** in DCM and **3c**−**i** in toluene, 0.1 mmol/1 mL). The mixture was cooled to −78 °C, and DIBAL-H (1.0 M in hexane, 2.0 equiv) was added dropwise. The mixture was stirred at −78 °C for 60−100 min (60 min for **3a**,**b** and 100 min for **3c**−**i**). At this stage, the solution of pyridine (3.0 equiv) and DMAP (2.0 equiv) in DCM (0.1 mmol ester/1 mL) was added dropwise at −78 °C via cannular, followed by Ac_2O (6.0 equiv). The mixture was stirred at −78 °C for 10 h, and at 0 °C for 30 min. The reaction was quenched by saturated NH_4Cl (aq.) at 0 °C, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The residue was purified by flash chromatography using *n*-hexane/ethyl acetate 10:1 to 5:1 as eluent. The desired α-acetoxy ethers **4a**−**i** were obtained as mixture of diastereomers.

*(2R,3S,4R,5R)-1-Cyclohexyloxy-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexyl acetate (**4a**).* Yield 91% (187 mg, colorless oil, from 0.26 mmol **3a**) as the 1.8:1 mixture of two inseparable diastereomers: ^{1}H NMR (500 MHz, $CDCl_3$, mixture of isomers) δ = 0.49−0.57 (m, 6H), 0.83−0.88 (m, 9H), 1.05−1.28 (m, 6H), 1.39−1.44 (m, 1H), 1.54−1.76 (m, 3H), 1.88 (s, 1.1H, minor isomer), 1.89 (s, 1.9 H, major isomer), 3.35−3.39 (m, 0.36H, minor isomer), 3.42 (dd, J_1 = 10.0 Hz, J_2 = 6.0 Hz, 0.64H, major isomer), 3.45 (dd, J_1 = 10.0 Hz, J_2 = 5.5 Hz, 0.36H, minor isomer), 3.53−3.59 (m, 0.64H, major isomer), 3.64−3.69 (m, 2H), 3.75 (q, J = 5.5 Hz, 1H), 3.82 (t, J = 5.5 Hz, 0.64H, major isomer), 3.87 (dd, J_1 = 5.5 Hz, J_2 = 4.5 Hz, 0.36 H, minor isomer), 3.98−4.02 (m, 1H), 4.36−4.41 (m, 2H), 4.49 (d, J = 11.0 Hz, 0.64H, major isomer), 4.55−4.69 (m, 4.36H), 4.74 (d, J = 11.5 Hz, 0.36H, minor isomer), 4.79 (d, J = 11.5 Hz, 0.64H, major isomer), 6.15 (d, J = 5.0 Hz, 0.64H, major isomer), 6.21 (d, J = 6.5 Hz, 0.36H, minor isomer), 7.12−7.25 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$, mixture of isomers) δ = 5.27, 5.28, 7.1, 21.47, 21.53, 24.0, 24.1, 24.4, 25.66, 25.68, 32.0, 32.3, 33.4, 33.6, 72.58, 72.60, 73.3, 74.08, 74.13, 74.4, 74.46, 74.53, 74.6, 75.0, 75.1, 78.2, 78.3, 78.9, 79.8, 80.7, 81.0, 81.2, 95.4, 95.6, 127.3, 127.35, 127.37, 127.45, 127.51, 127.53, 127.7, 127.78, 127.82, 127.9, 128.0, 128.1, 128.21, 128.24, 128.29, 128.33, 128.4, 128.5, 138.56, 138.59, 138.7, 138.9, 139.1, 139.2, 170.6, 170.9; ESI-TOF-HR-MS (m/z) Calcd for $C_{48}H_{64}O_8SiNa^+$ (M + Na^+) 819.4263, found 819.4259.

*Methyl 2,3,4-O-tribenzyl-6-O-[(2R,3S,4R,5R)-1-acetoxy-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-α-D-glucopyranoside (**4b**).* Yield 91% (529 mg, colorless oil, from 0.50 mmol **3b**) as the 10.6:1 mixture of two inseparable diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$, mixture of isomers) δ = 0.57−0.63 (m, 6H), 0.90 (t, J = 7.6 Hz, 0.78H, minor isomer), 0.91 (t, J = 8.0 Hz, 8.22H, major isomer), 1.80 (s, 2.74H, major isomer), 1.90 (s, 0.26H, minor isomer), 3.26 (s, 2.74H, major isomer), 3.28 (s, 0.26H, minor isomer), 3.40 (dd, J_1 = 9.6 Hz, J_2 = 3.6 Hz, 1H), 3.46 (dd, J_1 = 9.6 Hz, J_2 = 5.6 Hz, 1H), 3.55 (dd, J_1 = 10.0 Hz, J_2 = 8.8 Hz, 1H), 3.61−3.68 (m, 2.74H), 3.74−3.77 (m, 0.26H, minor isomer), 3.81−3.98 (m, 5H), 4.04−4.07 (m, 1H), 4.40−4.44 (m, 2H), 4.48 (d, J = 3.6 Hz, 1H), 4.53−4.86 (m, 11H), 4.94 (d, J = 11.2 Hz, 1H), 6.19 (d, J = 6.8 Hz, 0.09H, minor isomer), 6.24 (d, J = 6.4 Hz, 0.91H, major isomer), 7.17−7.32 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$, selected peaks of major isomer) δ = 5.1, 7.1, 21.1, 55.1, 68.3, 69.5, 72.3, 73.3, 73.4, 74.0, 74.3, 74.7, 75.0, 75.2, 75.6, 77.6, 79.8, 80.2, 80.5, 82.0, 97.1, 98.0, 127.3, 127.4, 127.48, 127.52, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.17, 128.24, 128.28, 128.35, 128.39, 128.5, 138.2, 138.4, 138.5, 138.7, 139.06, 139.11, 139.3, 171.0; ESI-TOF-HR-MS (m/z) Calcd for $C_{70}H_{84}O_{13}SiNa^+$ (M + Na^+) 1183.5573, found 1183.5568.

*Methyl 2,3,6-O-tribenzyl-4-O-[(2R,3S,4R,5R)-1-acetoxy-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-α-D-glucopyranoside (**4c**).* Yield 57% (168 mg, colorless oil, from 0.25 mmol **3c**) as the 1.3:1 mixture of two inseparable diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$, mixture of isomers) δ = 0.53−0.59 (m, 2.61H, minor isomer), 0.60−0.66 (m, 3.39H, major isomer), 0.91 (t, J = 8.0 Hz, 3.91H, minor isomer), 0.94 (t, J = 8.0 Hz, 5.09H, major isomer), 1.55 (s, 1.70H, major isomer), 1.69 (s, 1.30H, minor isomer), 3.29 (s, 1.70H, major isomer), 3.37 (s, 1.30H, minor isomer), 3.48−3.54 (m, 3H), 3.64−3.73 (m, 3H), 3.76−3.82 (m, 3H), 3.91 (t, J = 6.0 Hz, 0.57H, major isomer), 3.97−4.06 (m, 1.43H), 4.11−4.16 (m, 1H), 4.28 (d, J = 12.4 Hz, 0.57H, major isomer), 4.35 (d, J = 10.4 Hz, 0.43H, minor isomer), 4.40 (d, J = 12.4 Hz, 0.57H, major isomer), 4.42−4.45 (m, 2H), 4.48−4.62 (m, 6H), 4.65 (d, J = 10.0 Hz, 0.57H, major isomer), 4.69−4.84 (m, 2.86H), 4.89−4.92 (m, 2H), 6.32 (d, J = 6.4 Hz, 0.57H, major isomer), 6.62 (d, J = 2.8 Hz, 0.43H, minor isomer), 7.08−7.32 (m, 33.57H), 7.39−7.41 (m, 1.43H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of isomers) δ = 5.2, 5.4, 7.1, 7.2, 21.0, 21.1, 55.3, 55.4, 67.9, 68.9, 69.6, 70.3, 72.3, 73.0, 73.2, 73.30, 73.34, 73.4, 73.6, 73.7, 73.8, 74.3, 74.4, 74.6, 74.9, 75.3, 75.7, 77.9, 78.4, 78.5, 79.4, 79.8, 80.0, 80.1, 80.5, 80.8, 81.39, 81.44, 96.8, 97.6, 98.0, 98.1, 126.8, 127.0, 127.1, 127.2, 127.28, 127.30, 127.32, 127.34, 127.4, 127.49, 127.51, 127.6, 127.66, 127.68, 127.69, 127.8, 127.86, 127.93, 128.12, 128.13, 128.19, 128.21, 128.23, 128.27, 128.33, 128.35, 128.4, 128.46, 128.47, 128.49, 138.1, 138.2, 138.3, 138.40, 138.44, 138.48, 138.52, 138.9, 139.10, 139.15, 139.2, 139.6, 170.3, 170.5; ESI-TOF-HR-MS (m/z) Calcd for $C_{70}H_{84}O_{13}SiNa^+$ (M + Na^+) 1183.5573, found 1183.5565.

*Phenyl 2,3,6-O-tribenzyl-4-O-[(2R,3S,4R,5R)-1-acetoxy-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-1-thio-β-D-glucopyranoside (**4d**).* Yield 84% (131 mg, colorless oil, from 0.13 mmol **3d**) as the 2.3:1 mixture of two inseparable diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$, mixture of isomers) δ = 0.48−0.64 (m, 6H), 0.89 (t, J = 8.0 Hz, 6.27H, major isomer), 0.92 (t, J = 8.0 Hz, 2.73H, minor isomer), 1.57 (s, 0.91H, minor isomer), 1.75 (s, 2.09H, major isomer), 3.25−3.28 (m, 0.30H, minor isomer), 3.41−3.54 (m, 3H), 3.64−3.85 (m, 6.40H), 3.91 (t, J = 6.4 Hz, 0.30H, minor isomer), 3.95 (dd, J_1 = 7.2 Hz, J_2 = 3.6 Hz, 0.70H, major isomer), 4.04 (q, J = 4.8 Hz, 0.30H, minor isomer), 4.11−4.17 (m, 1H), 4.34 (d, J = 12.0 Hz, 0.30H, minor isomer), 4.39−4.44 (m, 2.70H), 4.47−4.66 (m, 7H), 4.69−4.86 (m, 4H), 4.90 (d, J = 12.0 Hz, 0.70H, major isomer), 4.96 (d, J = 11.2 Hz, 0.30H, minor isomer), 6.34 (d, J = 6.0 Hz, 0.30H, minor isomer), 6.56 (d, J = 3.2 Hz, 0.70H, major isomer), 7.06−7.37 (m, 38H), 7.52−7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of isomers) δ = 5.2, 5.4, 7.1, 7.2, 21.0, 21.1, 68.5, 69.0, 72.3, 72.9, 73.2, 73.3, 73.36, 73.38, 73.42, 73.8, 74.05, 74.09, 74.2, 74.5, 74.7, 74.9, 75.0, 75.2, 75.6, 75.9, 78.0, 78.4, 78.6, 78.7, 79.3, 79.5, 80.1, 80.6, 80.86, 80.90, 81.5, 85.2, 86.0, 87.4, 87.5, 96.8, 97.3, 126.8, 127.20, 127.25, 127.3, 127.4, 127.48, 127.51, 127.6, 127.67, 127.74, 127.8, 127.88, 127.92, 128.15, 128.24, 128.3, 128.35, 128.38, 128.41, 128.97, 129.04, 131.8, 131.9, 133.8, 134.1, 138.0, 138.17, 138.21, 138.3, 138.4, 138.5, 138.62, 138.65, 138.75, 138.82, 139.03, 139.06, 139.2, 170.4, 170.5; ESI-TOF-HR-MS (m/z) Calcd for $C_{75}H_{90}NO_{12}SSi^+$ (M + NH_4^+) 1256.5953, found 1256.5945.

*4-Methoxyphenyl 2-deoxy-2-azido-3,6-O-dibenzyl-4-O-[(2R,3S,4R,5R)-1-acetoxy-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-β-D-glucopyranoside (**4e**).* Yield 74% (123 mg, colorless oil, from 0.14 mmol **3e**) as the 6.1:1 mixture of two inseparable diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$, mixture of isomers) δ = 0.52−0.66 (m, 6H), 0.91 (t, J = 8.0 Hz, 7.73H, major isomer), 0.96 (t, J = 8.0 Hz, 1.27H, minor isomer), 1.63 (s, 0.42H, minor isomer), 1.79 (s, 2.58H, major isomer), 3.26−3.33 (m, 0.28H, minor isomer), 3.39−

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3.46 (m, 1.72H, major isomer), 3.54 (dd, J_1 = 10.0 Hz, J_2 = 6.0 Hz, 1H), 3.61−3.72 (m, 3H), 3.75 (s, 0.42H, minor isomer), 3.76 (s, 2.58H, major isomer), 3.79−3.86 (m, 3.86H), 3.95 (dd, J_1 = 6.8 Hz, J_2 = 3.6 Hz, 1H), 4.03−4.07 (m, 0.14H, minor isomer), 4.13−4.16 (m, 1H), 4.30−4.40 (m, 0.56H, minor isomer), 4.42 (s, 1.72H, major isomer), 4.45−4.60 (m, 5H), 4.62−4.71 (m, 2.72H), 4.74−4.84 (m, 2.84H), 4.94 (d, J = 11.2 Hz, 0.14H, minor isomer), 6.34 (d, J = 6.4 Hz, 0.14H, minor isomer), 6.50 (d, J = 3.2 Hz, 0.86H, major isomer), 6.76 (d, J = 8.8 Hz, 0.28H, minor isomer), 6.79 (d, J = 8.8 Hz, 1.72H, major isomer), 7.01 (d, J = 8.8 Hz, 0.28H, minor isomer), 7.03 (d, J = 8.8 Hz, 1.72H, major isomer), 7.13−7.43 (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$, selected peaks of major isomer) δ = 5.4, 7.2, 21.1, 55.8, 65.7, 68.7, 72.9, 73.4, 73.5, 73.8, 73.9, 74.1, 74.3, 74.97, 75.04, 78.3, 79.4, 81.5, 82.4, 97.3, 101.7, 114.7, 118.7, 127.3, 127.4, 127.5, 127.59, 127.64, 127.7, 127.8, 127.9, 128.2, 128.25, 128.28, 128.38, 128.42, 138.2, 138.4, 138.5, 138.8, 139.0, 151.3, 155.7, 170.3; ESI-TOF-HR-MS (m/z) Calcd for $C_{69}H_{85}N_4O_{13}Si^+$ (M + NH_4^+) 1205.5882, found 1205.5878.

*4-Methoxyphenyl 2,4,6-O-tribenzyl-3-O-[(2R,3S,4R,5R)-1-acetoxy-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-β-D-galactopyranoside (**4f**).* Yield 84% (154 mg, colorless oil, from 0.15 mmol **3f**) as the 2.3:1 mixture of two inseparable diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$, mixture of isomers) δ = 0.55−0.66 (m, 6H), 0.95 (t, J = 8.0 Hz, 6.27H, major isomer), 0.96(t, J = 8.0 Hz, 2.73H, minor isomer), 1.59 (s, 2.09H, major isomer), 2.04 (s, 0.91H, minor isomer), 3.47 (dd, J_1 = 10.0 Hz, J_2 = 6.4 Hz, 0.30H, minor isomer), 3.52−3.57 (m, 1.40H), 3.59−3.73 (m, 2.60H), 3.77−3.81 (m, 0.70H, major isomer), 3.79 (s, 0.91H, minor isomer), 3.80 (s, 2.09H, major isomer), 3.85−4.05 (m, 5H), 4.11−4.14 (m, 0.30H, minor isomer), 4.15 (dd, J_1 = 7.2 Hz, J_2 = 3.2 Hz, 0.70H, major isomer), 4.20 (dd, J_1 = 9.6 Hz, J_2 = 3.2 Hz, 0.30H, minor isomer), 4.23−4.27 (m, 0.70H, major isomer), 4.40−4.50 (m, 5H), 4.58−4.68 (m, 2.40H), 4.73−4.78 (m, 1.70H), 4.81−4.87 (m, 3.30H), 4.91 (d, J = 10.4 Hz, 0.30H, minor isomer), 4.92 (d, J = 10.8 Hz, 1H), 4.97 (d, J = 12.0 Hz, 1H), 5.11 (d, J = 11.6 Hz, 0.30H, minor isomer), 6.27 (d, J = 2.0 Hz, 0.70H, major isomer), 6.61 (d, J = 5.6 Hz, 0.30H, minor isomer), 6.79 (d, J = 9.2 Hz, 0.61H, minor isomer), 6.82 (d, J = 9.2 Hz, 1.39H, major isomer), 6.99 (d, J = 9.2 Hz, 0.61H, minor isomer), 7.04 (d, J = 9.2 Hz, 1.39H, major isomer), 7.09−7.44 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of isomers) δ = 5.2, 5.3, 7.16, 7.21, 21.0, 21.5, 55.7, 68.91, 68.94, 72.6, 73.0, 73.3, 73.37, 73.39, 73.5, 73.6, 73.7, 73.8, 73.9, 74.3, 74.4, 74.5, 74.9, 74.97, 75.03, 75.1, 75.6, 75.7, 78.0, 78.1, 78.4, 79.5, 80.4, 80.5, 80.9, 81.5, 81.8, 82.3, 95.7, 98.6, 102.9, 103.3, 114.5, 118.36, 118.44, 127.2, 127.30, 127.32, 127.4, 127.48, 127.55, 127.59, 127.66, 127.71, 127.78, 128.85, 127.90, 127.94, 128.11, 128.14, 128.16, 128.19, 128.21, 128.26, 128.34, 128.37, 128.40, 128.5, 138.1, 138.3, 138.41, 138.44, 138.5, 138.6, 138.7, 138.79, 138.85, 138.90, 139.0, 139.3, 151.5, 151.8, 155.16, 155.19, 170.6, 171.5; ESI-TOF-HR-MS (m/z) Calcd for $C_{76}H_{92}NO_{14}Si^+$ (M + NH_4^+) 1270.6287, found 1270.6275.

*Methyl 3,4,6-O-tribenzyl-2-O-[(2R,3S,4R,5R)-1-acetoxy-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-β-D-glucopyranoside (**4g**).* Yield 41% (69 mg, colorless oil, from 0.14 mmol **3g**) as the 7.6:1 mixture of two partially separable diastereomers. The major diastereomer can be obtained in pure form: ^{1}H NMR (400 MHz, $CDCl_3$, selected peaks of major isomer) δ = 0.52−0.63 (m, 6H), 0.90 (t, J = 8.0 Hz, 9H), 1.68 (s, 3H), 3.26 (s, 3H), 3.31−3.35 (m, 1H), 3.47 (t, J = 9.2 Hz, 1H), 3.50 (dd, J_1 = 10.0 Hz, J_2 = 6.0 Hz, 1H), 3.57 (t, J = 9.2 Hz, 1H), 3.66 (dd, J_1 = 10.8 Hz, J_2 = 4.4 Hz, 1H), 3.68−3.73 (m, 2H), 3.76−3.81 (m, 2H), 3.93 (dd, J_1 = 6.4 Hz, J_2 = 4.0 Hz, 1H), 3.97 (dd, J_1 = 6.4 Hz, J_2 = 3.6 Hz, 1H), 4.08 (d, J = 8.0 Hz, 1H), 4.16 (dt, J_1 = 5.6 Hz, J_2 = 2.0 Hz, 1H), 4.40 (s, 2H), 4.50 (d, J = 10.4 Hz, 1H), 4.53 (d, J = 12.4 Hz, 1H), 4.61 (d, J = 12.4 Hz, 1H), 4.69−4.82 (m, 7H), 4.90 (d, J = 11.2 Hz, 1H), 4.99 (d, J = 11.2 Hz, 1H), 6.42 (d, J = 4.4 Hz, 1H), 7.11−7.13 (m, 2H), 7.20−7.37 (m, 33H); ^{13}C NMR (100 MHz, $CDCl_3$, selected peaks of major isomer) δ = 5.4, 7.2, 21.0, 56.7, 68.8, 72.8, 73.3, 73.5, 73.6, 73.7, 74.9, 75.0, 75.19, 75.21, 75.7, 77.8, 79.2, 80.8, 80.9, 81.0, 84.0, 96.8, 103.7, 127.30, 127.34, 127.49, 127.52, 127.6, 127.67, 127.72, 127.77, 127.81, 127.85, 127.91, 128.02, 128.05, 128.26, 128.28, 128.32, 128.4, 128.5, 138.21, 138.24, 138.4, 138.8, 138.95, 139.02, 139.1, 170.7; ESI-TOF-HR-MS (m/z) Calcd for $C_{70}H_{88}NO_{13}Si^+$ (M + NH_4^+) 1178.6025, found 1178.6028.

*Methyl 2,3,4-O-tribenzyl-6-O-[(2R,3S,4S,5R)-1-acetoxy-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-α-D-glucopyranoside (**4h**).* Yield 87% (99 mg, colorless oil, from 0.10 mmol **3h**) as a single diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.55−0.62 (m, 6H), 0.91 (t, J = 8.0 Hz, 9H), 1.76 (s, 3H), 3.31 (s, 3H), 3.46 (dd, J_1 = 9.6 Hz, J_2 = 3.6 Hz, 1H), 3.53−3.59 (m, 2H), 3.61−3.64 (m, 1H), 3.65 (dd, J_1 = 9.6 Hz, J_2 = 4.8 Hz, 1H), 3.67−3.71 (m, 1H), 3.86−3.97 (m, 4H), 4.05 (dd, J_1 = 6.8 Hz, J_2 = 3.2 Hz, 1H), 4.21−4.24 (m, 1H), 4.41 (d, J = 12.0 Hz, 1H), 4.47 (d, J = 12.0 Hz, 1H), 4.54 (d, J = 3.6 Hz, 1H), 4.58−4.64 (m, 4H), 4.67−4.75 (m, 5H), 4.80 (d, J = 10.0 Hz, 1H), 4.83 (d, J = 10.0 Hz, 1H), 4.95 (d, J = 10.8 Hz, 1H), 6.21 (d, J = 6.4 Hz, 1H), 7.21−7.34 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 5.5, 7.2, 21.0, 55.2, 68.1, 69.6, 72.4, 72.6, 72.8, 73.2, 73.5, 73.7, 74.2, 75.0, 75.8, 77.6, 78.2, 78.5, 79.7, 80.3, 82.2, 97.0, 98.1, 127.31, 127.35, 127.5, 127.58, 127.60, 127.62, 127.7, 127.8, 127.9, 128.1, 128.30, 128.33, 128.38, 128.43, 128.48, 128.51, 138.28, 138.32, 138.5, 139.00, 139.02, 139.1, 171.0; ESI-TOF-HR-MS (m/z) Calcd for $C_{70}H_{88}NO_{13}Si^+$ (M + NH_4^+) 1178.6025, found 1178.6022.

*6-O-[(2R,3S,4S,5R)-1-Acetoxy-2,3,4,6-tetrabenzyloxy-5-triethylsiloxyhexanoyl]-1,2;3,4-O-diisopropylidene-α-D-galactopyranoside (**4i**).* Yield 83% (140 mg, colorless oil, from 0.17 mmol **3i**) as the >20:1 mixture of two inseparable diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$, selected peaks of major isomer) δ = 0.57−0.64 (m, 6H), 0.93 (t, J = 8.0 H, 9H), 1.21 (s, 3H), 1.30 (s, 3H), 1.35 (s, 3H), 1.51 (s, 3H), 1.93 (s, 3H), 3.57 (dd, J_1 = 9.6 Hz, J_2 = 6.8 Hz, 1H), 3.65 (dd, J_1 = 9.6 Hz, J_2 = 4.4 Hz, 1H), 3.68−3.73 (m, 2H), 3.86 (dd, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 1H), 3.90−3.93 (m, 1H), 3.95 (dd, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 1H), 4.04 (dd, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 1H), 4.20 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 4.21−4.26 (m, 1H), 4.29 (dd, J_1 = 4.8 Hz, J_2 = 2.4 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.49 (d, J = 12.0 Hz, 1H), 4.56 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 4.61 (s, 2H), 4.66 (d, J = 12.0 Hz, 1H), 4.70 (d, J = 11.6 Hz, 1H), 4.72 (d, J = 11.6 Hz, 1H), 4.73 (d, J = 11.6 Hz, 1H), 5.49 (d, J = 5.2 Hz, 1H), 6.24 (d, J = 6.4 Hz, 1H), 7.20−7.38 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$, selected peaks of major isomer) δ = 5.5, 7.2, 21.2, 24.6, 25.0, 26.1, 26.2, 66.3, 67.5, 70.7, 70.8, 72.6, 72.7, 73.0, 73.3, 73.8, 74.2, 78.1, 78.8, 79.4, 96.4, 96.7, 108.7, 109.4, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.30, 128.33, 128.4, 138.4, 139.0, 139.07, 139.10, 170.8; ESI-TOF-HR-MS (m/z) Calcd for $C_{54}H_{76}NO_{13}Si^+$ (M + NH_4^+) 974.5080, found 974.5081.

General Procedure for Intramolecular Glycosylation. The α-acetoxy ether **4a−i** (1.0 equiv) was dissolved in DCM (0.010 mmol/1 mL), and molecular sieves 4 Å (100 mg/1 mL DCM) were added. The mixture was stirred at rt for 1 h, and then the temperature was adjusted to the designated value (rt or −40 °C). TfOH (1.0 equiv) was added, and the mixture was stirred at the same temperature for 0.5 h (at rt) to 2 h (at −40 °C). The reaction was quenched by Et_3N, and the product was purified by flash chromatography on silica gel using *n*-hexane/ethyl acetate 6:1 to 4:1 as eluent. The desired disaccharides **6a−i** were obtained as mixture of α/β anomers. The α/β ratio was determined by ^{1}H NMR of the mixture. The ratios and yields under different temperatures are shown in Figure 1.

*Cyclohexyl 2,3,4,6-O-tetrabenzyl-β-D-glucopyranoside (**6a**).* ^{1}H NMR (400 MHz, $CDCl_3$, β-anomer) δ = 1.22−1.33 (m, 3H), 1.39−1.54 (m, 3H), 1.72−1.78 (m, 2H), 1.92−2.03 (m, 2H), 3.45 (dd, J_1 = 8.8 Hz, J_2 = 8.0 Hz, 1H), 3.45−3.48 (m, 1H), 3.54 (t, J = 9.2 Hz, 1H), 3.61−3.67 (m, 2H), 3.68−3.72 (m, 1H), 3.74 (dd, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1H), 4.51 (d, J = 8.0 Hz, 1H), 4.53 (d, J = 11.2 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.71 (d, J = 10.8 Hz, 1H), 4.78 (d, J = 11.2 Hz, 1H), 4.82 (d, J = 10.8 Hz, 1H), 4.92 (d, J = 10.8 Hz, 1H), 5.00 (d, J = 10.8 Hz, 1H), 7.16−7.18 (m, 2H), 7.24−7.36 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, β-anomer) δ = 24.1, 24.2, 25.8, 32.2, 33.9, 69.3, 73.5, 74.9, 75.0, 75.1, 75.8, 78.1, 82.4, 85.0, 102.1, 127.66, 127.70, 127.77, 127.82, 127.9, 128.0, 128.2, 128.4, 128.46, 128.49, 128.52, 138.2, 138.4, 138.6, 138.8.[28]

*Methyl 2,3,4-O-tribenzyl-6-O-(2,3,4,6-O-tetrabenzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**6b**).* ^{1}H NMR (400 MHz, $CDCl_3$, β-anomer) δ = 3.32 (s, 3H), 3.41−3.45 (m, 1H), 3.46−3.53 (m, 3H), 3.56 (t, J = 9.2 Hz, 1H), 3.63 (t, J = 9.0 Hz, 1H), 3.66−3.74 (m, 3H),

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3.81−3.84 (m, 1H), 3.99 (t, J = 9.2 Hz, 1H), 4.18 (dd, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1H), 4.35 (d, J = 7.6 Hz, 1H), 4.49−4.54 (m, 3H), 4.56 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 3.6 Hz, 1H), 4.65 (d, J = 12.4 Hz, 1H), 4.71 (d, J = 11.2 Hz, 1H), 4.75 (d, J = 11.2 Hz, 1H), 4.76−4.82 (m, 4H), 4.91 (d, J = 10.8 Hz, 1H), 4.96 (d, J = 10.8 Hz, 1H), 4.97 (d, J = 11.2 Hz, 1H), 7.15−7.35 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$, β-anomer) δ = 55.3, 68.7, 69.1, 69.9, 73.49, 73.54, 75.0, 75.1, 75.8, 75.9, 78.0, 78.1, 78.8, 82.1, 82.2, 84.9, 98.2, 103.9, 127.6, 127.67, 127.71, 127.74, 127.8, 127.9, 127.98, 128.01, 128.04, 128.08, 128.10, 128.3, 128.46, 128.49, 128.52, 128.6, 138.18, 138.23, 138.3, 138.4, 138.5, 138.6, 138.9.[29]

*Methyl 2,3,6-O-tribenzyl-4-O-(2,3,4,6-O-tetrabenzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**6c**).* ^{1}H NMR (400 MHz, $CDCl_3$, β-anomer) δ = 3.28−3.31 (m, 1H), 3.34−3.38 (m, 1H), 3.36 (s, 3H), 3.44−3.50 (m, 3H), 3.54 (dd, J_1 = 10.8 Hz, J_2 = 4.4 Hz, 1H), 3.57−3.62 (m, 2H), 3.70−3.72 (m, 1H), 3.82−3.85 (m, 1H), 3.85 (t, J = 9.6 Hz, 1H), 3.97 (t, J = 9.6 Hz, 1H), 4.36−4.40 (m, 3H), 4.44 (d, J = 12.0 Hz, 1H), 4.54−4.61 (m, 4H), 4.72−4.82 (m, 6H), 4.87 (d, J = 10.8 Hz, 1H), 5.09 (d, J = 11.6 Hz, 1H), 7.17−7.30 (m, 33H), 7.40−7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, β-anomer) δ = 55.4, 68.0, 69.1, 70.1, 73.5, 73.7, 74.9, 75.0, 75.3, 75.5, 75.7, 76.7, 78.2, 79.0, 80.5, 82.9, 85.0, 98.5, 102.6, 127.2, 127.4, 127.61, 127.64, 127.68, 127.74, 127.8, 127.9, 128.08, 128.10, 128.12, 128.2, 128.3, 128.4, 128.6, 138.0, 138.4, 138.5, 138.68, 138.72, 139.7.[29]

*Phenyl 2,3,6-O-tribenzyl-4-O-(2,3,4,6-O-tetrabenzyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (**6d**).* ^{1}H NMR (400 MHz, $CDCl_3$, β-anomer) δ = 3.31−3.41 (m, 3H), 3.44 (t, J = 9.2 Hz, 1H), 3.54−3.59 (m, 2H), 3.62−3.66 (m, 2H), 3.70 (dd, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1H), 3.75 (dd, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1H), 3.85 (dd, J_1 = 10.8 Hz, J_2 = 4.4 Hz, 1H), 4.04 (t, J = 9.6 Hz, 1H), 4.39 (s, 2H), 4.46 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 7.6 Hz, 1H), 4.54 (d, J = 10.8 Hz, 1H), 4.56 (d, J = 11.6 Hz, 1H), 4.63 (d, J = 9.6 Hz, 1H), 4.69−4.75 (m, 4H), 4.78−4.82 (m, 3H), 4.89 (d, J = 10.8 Hz, 1H), 5.14 (d, J = 11.2 Hz, 1H), 7.15−7.36 (m, 38H), 7.54−7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, β-anomer) δ = 68.3, 69.0, 73.3, 73.4, 75.0, 75.2, 75.5, 75.6, 75.8, 76.6, 78.1, 79.4, 80.2, 82.9, 85.06, 85.11, 87.5, 102.7, 127.4, 127.50, 127.53, 127.6, 127.7, 127.82, 127.84, 127.9, 128.0, 128.1, 128.2, 128.35, 128.38, 128.43, 128.47, 128.50, 129.0, 132.2, 133.8, 138.30, 138.32, 138.4, 138.48, 138.54, 138.7, 139.2.[30]

*4-Methoxyphenyl 2-deoxy-2-azido-3,6-O-dibenzyl-4-O-(2,3,4,6-O-tetrabenzyl-β-D-glucopyranosyl)-1-β-D-glucopyranoside (**6e**).* ^{1}H NMR (400 MHz, $CDCl_3$, β-anomer) δ = 3.34 (dd, J_1 = 9.6 Hz, J_2 = 3.2 Hz, 1H), 3.39−3.43 (m, 3H), 3.54−3.65 (m, 4H), 3.68−3.74 (m, 2H), 3.75 (s, 3H), 3.83 (dd, J_1 = 10.8 Hz, J_2 = 4.0 Hz, 1H), 4.06 (t, J = 9.2 Hz, 1H), 4.40 (s, 2H), 4.44 (d, J = 12.0 Hz, 1H), 4.50 (d, J = 7.6 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 10.8 Hz, 1H), 4.66 (d, J = 8.4 Hz, 1H), 4.74−4.83 (m, 5H), 4.89 (d, J = 11.2 Hz, 1H), 5.10 (d, J = 11.2 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 7.17−7.30 (m, 28H), 7.42−7.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, β-anomer) δ = 55.7, 65.8, 67.9, 69.0, 73.38, 73.43, 75.0, 75.1, 75.17, 75.22, 75.5, 75.8, 76.4, 78.1, 81.1, 82.9, 85.0, 101.6, 102.7, 114.6, 118.8, 127.5, 127.58, 127.61, 127.7, 127.8, 127.87, 127.90, 127.93, 128.26, 128.34, 128.4, 128.5, 138.1, 138.3, 138.4, 138.5, 138.59, 138.62, 151.3, 155.7; ESI-TOF-HR-MS (m/z) Calcd for $C_{61}H_{63}N_3O_{11}Na^+$ (M + Na^+) 1036.4355, found 1036.4355.

*4-Methoxyphenyl 2,4,6-O-tribenzyl-3-O-(2,3,4,6-O-tetrabenzyl-β-D-glucopyranosyl)-1-β-D-galactopyranoside (**6f**).* ^{1}H NMR (400 MHz, $CDCl_3$, β-anomer) δ = 3.38−3.40 (m, 1H), 3.48 (t, J = 8.0 Hz, 1H), 3.58 (dd, J_1 = 9.2 Hz, J_2 = 6.4 Hz, 1H), 3.61−3.71 (m, 6H), 3.74 (s, 3H), 3.98 (dd, J_1 = 9.6 Hz, J_2 = 3.2 Hz, 1H), 4.02−4.03 (m, 1H), 4.09 (dd, J_1 = 9.6 Hz, J_2 = 7.6 Hz, 1H), 4.39 (d, J = 11.6 Hz, 1H), 4.45 (d, J = 11.6 Hz, 1H), 4.50 (d, J = 12.4 Hz, 1H), 4.55−4.63 (m, 3H), 4.72 (d, J = 12.0 Hz, 1H), 4.79−4.88 (m, 5H), 4.92 (d, J = 7.6 Hz, 1H), 4.98 (d, J = 11.2 Hz, 1H), 5.05 (d, J = 11.2 Hz, 1H), 5.07 (d, J = 11.2 Hz, 1H), 6.77 (d, J = 9.2 Hz, 2H), 7.01 (d, J = 9.2 Hz, 2H), 7.16−7.32 (m, 33H), 7.38−7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, β-anomer) δ = 55.7, 68.9, 69.1, 73.4, 73.7, 74.0, 74.7, 74.9, 75.0, 75.16, 75.17, 75.8, 76.2, 78.0, 79.3, 80.0, 82.8, 84.7, 103.2, 103.9, 114.5, 118.6, 127.5, 127.6, 127.68, 127.71, 127.8, 127.9, 128.0, 128.1, 128.25, 128.32, 128.34, 128.48, 128.51, 138.1, 138.2, 138.3, 138.4, 138.5, 138.7, 138.8, 151.7, 155.2; ESI-TOF-HR-MS (m/z) Calcd for $C_{68}H_{74}NO_{12}^+$ (M + NH_4^+) 1096.5206, found 1096.5210.

*Methyl 3,4,6-O-tribenzyl-2-O-(2,3,4,6-O-tetrabenzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**6g**).* ^{1}H NMR (400 MHz, $CDCl_3$, β-anomer) δ = 3.36−3.39 (m, 1H), 3.46−3.52 (m, 2H), 3.50 (s, 3H), 3.57 (t, J = 9.2 Hz, 1H), 3.63−3.76 (m, 7H), 3.86 (t, J = 8.0 Hz, 1H), 4.40 (d, J = 7.6 Hz, 1H), 4.54−4.58 (m, 4H), 4.63 (d, J = 12.0 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.72 (d, J = 11.2 Hz, 1H), 4.74 (d, J = 10.4 Hz, 1H), 4.77−4.81 (m, 3H), 4.86 (d, J = 10.8 Hz, 1H), 4.89 (d, J = 11.6 Hz, 1H), 4.90 (d, J = 7.6 Hz, 1H), 4.97 (d, J = 11.2 Hz, 1H), 7.14−7.36 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$, β-anomer) δ = 56.2, 68.8, 69.0, 73.6, 73.7, 75.0, 75.05, 75.06, 75.09, 75.3, 75.7, 78.0, 78.2, 78.3, 82.8, 85.0, 85.6, 102.4, 102.5, 127.5, 127.61, 127.62, 127.66, 127.71, 127.8, 127.88, 127.91, 127.98, 128.03, 128.2, 128.3, 128.4, 128.48, 128.50, 128.54, 138.1, 138.2, 138.3, 138.4, 138.5, 138.67, 138.73; ESI-TOF-HR-MS (m/z) Calcd for $C_{62}H_{66}O_{11}Na^+$ (M + Na^+) 1009.4497, found 1009.4491.

*Methyl 2,3,4-O-tribenzyl-6-O-(2,3,4,6-O-tetrabenzyl-β-D-galactopyranosyl)-α-D-glucopyranoside (**6h**).* ^{1}H NMR (400 MHz, $CDCl_3$, β-anomer) δ = 3.29 (s, 3H), 3.46 (t, J = 10.0 Hz, 1H), 3.47−3.52 (m, 3H), 3.54−3.63 (m, 3H), 3.80−3.89 (m, 3H), 3.97 (t, J = 9.2 Hz, 1H), 4.14 (d, J = 10.4 Hz, 1H), 4.30 (d, J = 7.6 Hz, 1H), 4.39 (d, J = 11.6 Hz, 1H), 4.43 (d, J = 11.6 Hz, 1H), 4.50 (d, J = 11.2 Hz, 1H), 4.57 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 2.8 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.69−4.78 (m, 6H), 4.91−4.97 (m, 3H), 7.15−7.35 (m, 35H); ^{13}C NMR (100 MHz, $CDCl_3$, β-anomer) δ = 55.3, 68.66, 68.74, 70.0, 73.0, 73.4, 73.5, 73.6, 74.7, 74.9, 75.3, 75.8, 78.2, 79.4, 80.0, 82.1, 82.4, 98.0, 104.3, 127.5, 127.57, 127.63, 127.8, 127.9, 128.0, 128.06, 128.10, 128.2, 128.3, 128.39, 128.43, 128.45, 128.54, 138.0, 138.3, 138.5, 138.6, 138.8, 138.9, 139.0.[29]

*6-O-(2,3,4,6-O-Tetrabenzyl-β-D-galactopyranosyl)-1,2;3,4-O-diisopropylidene-α-D-galactopyranoside (**6i**).* ^{1}H NMR (400 MHz, $CDCl_3$, β-anomer) δ = 1.30 (s, 6H), 1.43 (s, 3H), 1.48 (s, 3H), 3.48−3.58 (m, 4H), 3.69 (dd, J_1 = 10.4 Hz, J_2 = 7.6 Hz, 1H), 3.82 (dd, J_1 = 9.6 Hz, J_2 = 7.6 Hz, 1H), 3.88 (d, J = 2.8 Hz, 1H), 4.06−4.09 (m, 1H), 4.13 (dd, J_1 = 10.4 Hz, J_2 = 3.6 Hz, 1H), 4.21 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 4.30 (dd, J_1 = 4.8 Hz, J_2 = 2.4 Hz, 1H), 4.39 (d, J = 12.0 Hz, 1H), 4.41 (d, J = 7.6 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.57 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 4.60 (d, J = 11.6 Hz, 1H), 4.70 (d, J = 12.0 Hz, 1H), 4.73 (d, J = 10.8 Hz, 1H), 4.78 (d, J = 12.0 Hz, 1H), 4.92 (d, J = 11.6 Hz, 1H), 5.05 (d, J = 10.8 Hz, 1H), 5.56 (d, J = 4.8 Hz, 1H), 7.23−7.36 (m, 18H), 7.43−7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, β-anomer) δ = 24.5, 25.2, 26.10, 26.14, 67.5, 68.8, 69.7, 70.6, 70.9, 71.6, 73.2, 73.4, 73.6, 73.7, 74.6, 74.9, 79.2, 82.0, 96.5, 104.8, 108.7, 109.4, 127.4, 127.6, 127.9, 128.0, 128.2, 128.4, 128.50, 128.52, 128.7, 138.0, 138.75, 138.77, 139.1.[31]

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds **3a−i**, **4a−i**, and **6a−i**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: 852 2857 1586. Tel: 852 2219 4992. E-mail: xuechenl@hku.hk.

Notes

The authors declare no competing financial interest.

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