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Influence of Various Silyl Protecting Groups on Stereoselective 2-Deoxyrhamnosylation

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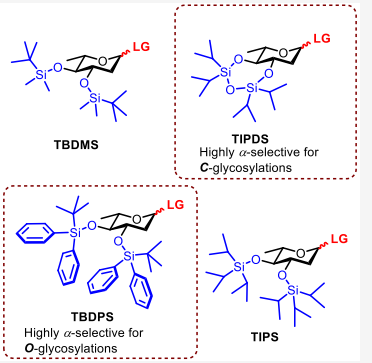
ABSTRACT: The influence of various silyl protecting groups on 2-deoxyrhamnosylation using 2-deoxyrhamnosyl acetates, thioglycosides, and (*p*-methoxyphenyl)vinylbenzoate (PMPVB) donors has been presented. *C*-Glycosylation reactions reveal that *tert*-butyldimethylsilyl (TBDMS), triisopropylsilyl (TIPS), and *tert*-butyldiphenylsilyl (TBDPS) silyl protected rhamnosyl oxocarbenium ions have no facial selectivity except for the conformationally ($^4H_3$) locked tetraisopropyldisiloxane (TIPDS) protected rhamnose donor, which provides complete α-selectivity. However, TBDPS protected rhamnosyl donors are found to be superior protecting groups for α-stereoselective *O*-glycosylation reactions with various acceptors. The observed results are found consistent across donors and donor activation conditions. Most importantly, the study was conducted at room temperature unlike the other energy-intensive low-temperature studies and was bound to have more practical utility. The outcomes have been explained using kinetic and thermodynamic analyses.



INTRODUCTION

2-Deoxy and 2,6-dideoxyhexoses are an important class of glycosides due to their presence in a wide range of natural products ranging from antibiotics to anticancer agents and in biologically active glycoconjugates.[1−3] These glycosides are more challenging to synthesize stereoselectively than their fully oxygenated analogues. The absence of any stereodirecting group adjacent to the anomeric center makes it difficult to form the glycosidic linkage in a stereoselective fashion and results in a mixture of anomers.[4−6] There are limited studies done on glycosylation of silyl protected 2,6-dideoxysugars.[7] Owing to the presence of 2-deoxyrhamnosides in natural products like mithramycin and landomycin families,[8] research efforts in achieving their stereoselective synthesis have increased in recent years. The fact that protecting groups play a significant role in carbohydrate reactivity[9] makes it more interesting for us to study the influence of the underexplored acid-labile silyl protecting groups on glycosylation with L-rhamnose-based sugar donors. Silyl protecting groups that are usually sterically hindered restrict access to several possible conformations and generally provide improved anomeric selectivity.[10] However, a comparative study on the stereoselective glycosylation of various silyl protected donors particularly for the synthesis of 2,6-dideoxy glycosides has not been reported and is highly desirable.

The tuning effect of various silyl protecting groups has been studied earlier on C2-benzoyl protected arabinofuranosyl donors by Yang and co-workers.[11] The group found the intriguing torsional strain imposed by the 3,5-*O*-di-*tert*-butylsilyl protecting group that presumably destabilizes the formation of the arabinofuranosyl oxocarbenium ion and hence decreases the reactivity of the corresponding thioglycoside donors. 2,6-Dideoxysugars are inherently more reactive than the corresponding 2,6-di-oxy counterparts. Furanosyl oxocarbenium ions are generally perceived to be relatively more stable or long-lived than the pyranosyl oxocarbenium ions and hence generally lead to less selective coupling reactions. Similar to furanoses, and unlike the fully oxygenated pyranoses, part of the high reactivity of 2,6-dideoxy donors could be attributed to the increased stability of the oxocarbenium ions. The absence of two electron-withdrawing oxygen atoms in the ring could decrease the destabilizing effect, which means the mechanism of glycosylation reactions of 2,6-dideoxysugars may proceed via dissociative mechanisms (S_N1). It is widely accepted that the mechanism of glycosylation is very complex and is controlled by several factors and is generally perceived to be somewhere in between the two extreme ends of the S_N1 and S_N2 continuum, depending on the protecting groups, solvent, temperature, and reactivity of the acceptor as well.[12] On the other hand, increasingly found pieces of evidence suggest the *O*-glycosylation reactions follow more associative mechanisms than dissociative ones.[13] However, most of the studies to understand the mechanistic aspects were carried out on the 2-oxysugars, and the corresponding 2-deoxy or 2,6-dideoxysugars were underexplored. The mechanism involved in the case of

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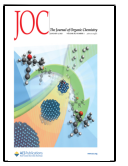

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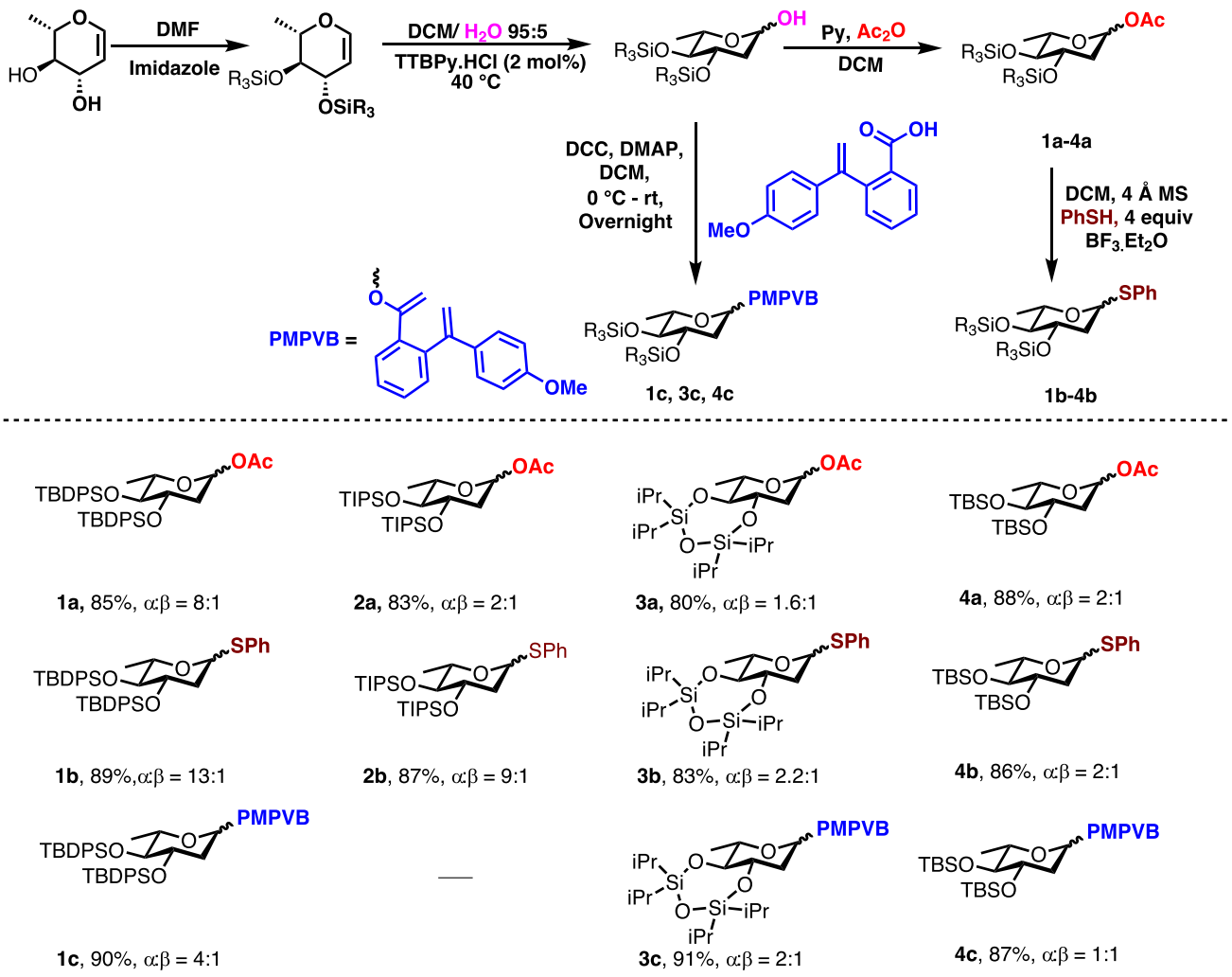
Table 1. Synthesis of Various Rhamanosyl Donors[a]



[a]Reaction conditions: The yield was determined after column purification. The anomeric ratio was determined by ^{1}H NMR spectral analysis of the crude reaction mixtures.

2,6-dideoxy sugar glycosylations may not obviously be correlated with the 2,6-oxy counterparts as there is a significant difference in their reactivity. 2,6-Dideoxy donors are generally very reactive, and in particular, the silyl protected donors, usually considered armed donors, are further more reactive. It is pertinent to understand the influence of the bulky silyl protecting groups not only on the reactivity of the 2,6-dideoxy donors but also on the facial selectivity of the corresponding oxocarbenium ions that would help us design better methods for the synthesis of natural products with a 2,6-dideoxy sugar backbone.

Previously, some of the silyl protecting groups were used for the synthesis of 2-deoxyrhamnosides, particularly via the corresponding glycals as donors.[7a,c,14] However, a systematic study of the effect of various silyl protecting groups on the selectivity of the corresponding donors under the reaction conditions and understanding the mechanistic reasons behind the observed outcome has not been carried out. Here, in this manuscript, we present a systematic study on the tuning effect of *tert*-butyldimethylsilyl (TBS), *tert*-butyldiphenylsilyl (TBDPS), triisopropylsilyl (TIPS), and the cyclic tetraisopropyldisiloxane (TIPDS) on the stereoselectivity of 2,6-dideoxy-L-rhamnosylation reactions utilizing the corresponding anomeric acetates, thioglycosides, and (*p*-methoxyphenyl)-vinylbenzoates (PMPVB) donors. Also, computational studies were performed to provide insights into the possible intermediates leading to the observed results.

RESULTS AND DISCUSSION

To test the influence of silyl protecting groups, we have chosen three different glycosylation methods using three different glycosyl donors, namely, the glycosyl acetates, thioglycosides, and the PMPVB donors, recently introduced by us. The synthesis of the three rhamnosyl donors has emanated from the free hydroxy L-rhamnal. The protection of free hydroxy L-rhamnal with the respective silyl chlorides in the presence of imidazole gave the corresponding silyl glycals, which were then converted to hemiacetals by employing the TTBPy·HCl catalyst system[15] recently developed by us. The various silyl protected L-rhamnals were converted to the corresponding glycosyl acetates **1a**−**4a** using the py/ Ac_2O method, whereas the PMPVB donors **1c**, **3c**, and **4c** have been synthesized via the *N*,*N*′-dicyclohexylcarbodiimide (DCC) coupling with 1-(*p*-methoxyphenyl)-vinylbenzoic acid (Table 1). The correspond-

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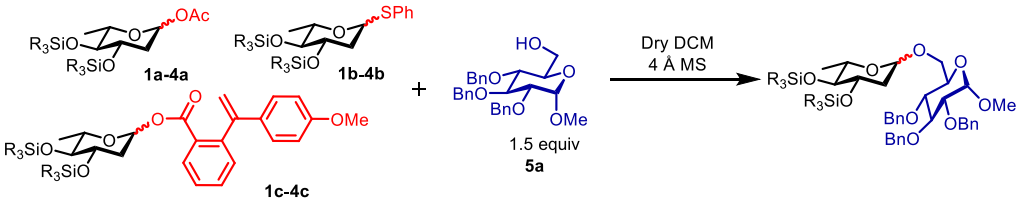
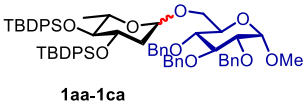
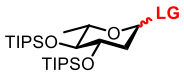
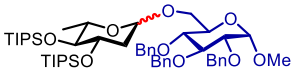
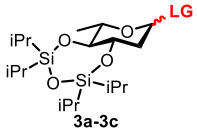
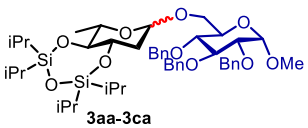
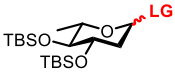
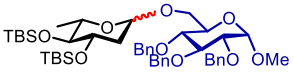
Table 2. Influence of Various Silyl Protecting Groups on Various Glycosylation Techniques[a]



Sl. No.	Donor	Product	LG = OAc[a]	LG = SPh[b]	LG = PMPVB[c]
1	 1a-1c	 1aa-1ca	**1aa**, 79%, $\alpha:\beta$ = 10:1	**1ba**, 83%, $\alpha:\beta$ =10:1	**1ca**, 81%, α-only[i] 79%, α-only[ii]
2	 2a-2b	 2aa-2ba	**2aa**, 72%, $\alpha:\beta$ = 8:1	**2ba**, 75%, $\alpha:\beta$ = 9:1	—
3	 3a-3c	 3aa-3ca	**3aa**, 80%, $\alpha:\beta$ = 3.6:1	**3ba**, 71%, $\alpha:\beta$ = 6:1	**3ca**, 78%, $\alpha:\beta$ = 4:1[i] 77%, $\alpha:\beta$ = 6:1[ii]
4	 4a-4c	 4aa-4ca	**4aa**, 75%, $\alpha:\beta$ = 1.2:1	**4ba**, 84%, $\alpha:\beta$ = 3:1	**4ca**, 76%, $\alpha:\beta$ = 3.5:1[i] 80%, $\alpha:\beta$ = 3.2:1[ii]

[a]Reaction conditions: (a) $BF_3{\cdot}Et_2O$, (b) NIS/TMSOTf, −40 °C, and (c) (i) 30 mol % Tf_2NH and (ii) 30 mol % TfOH.

ing thioglycosides **1b**−**4b** were obtained using the standard $BF_3{\cdot}Et_2O$ conditions (Table 1). The TBDPS protected L-rhamnosyl thioglycoside **1b** has been obtained in an $\alpha:\beta$ ratio of 13:1, whereas the TIPS protected donor **2b** was obtained in a 9:1 ratio. However, the other two silyl protected donors **3b** and **4b** were obtained in poor $\alpha:\beta$ ratios of 2.2:1 and 2:1 selectivity. The PMPVB donors **1c**, **3c**, and **4c** were obtained in 4:1, 2:1, and 1:1 $\alpha:\beta$ ratios, respectively. With all of the 11 donors in hand, we have chosen the 6-OH glucose **5a** as the acceptor to study the influence of the silyl protecting groups under three different glycosylation conditions ($BF_3{\cdot}Et_2O$ for acetates, NIS/TMSOTf for thioglycosides, and catalytic Tf_2NH or TfOH for PMPVB donors[16]), the results of which are tabulated in Table 2. Intriguingly, irrespective of the leaving group and the glycosylation method used, all of the TBDPS protected donors led to the coupled product in very high α-selectivity (Entry 1, Table 2), followed by the TIPS protected donors (Entry 2, Table 2). However, although the cyclic TIPDS and the TBS protected donors still led to α-selective products, they saw a huge drop in anomeric selectivity (Entries 3 and 4, Table 2). The drop is more with thioglycoside and PMPVB donors than with the glycosyl acetates. The presence of cyclic TIPDS protection is known to enhance α-selectivity for the glycosylation with 2-deoxyrhamnal donors.[14] However, our study shows that TBDPS protection is better in providing high selectivities in the direct synthesis of the disaccharides. After establishing the superiority of the TBDPS protecting group in rhamnosylation, and to examine the generality of our observation, various acceptors were subjected to glycosylation under NIS/TMSOTf catalyzed conditions with thioglycoside **1b** as the donor. Several examples of α-selective 2,6-dideoxy-*O*-glycosides were prepared (Table 3). Compounds **1bb** to **1bf** were obtained on reaction with commercially available non-carbohydrate alcohols in excellent yields as exclusive α-isomers (Table 3). The coupling with tertiary 1-adamantanol also proceeded well under the reaction conditions to provide glycoside **1bf** in 85% yield with 18:1 $\alpha:\beta$ selectivity. The primary sugar alcohols derived from glucose, galactose, and fructose were successfully coupled with donor **1b** to obtain compounds **1bg**, **1bl**−**n** with good yields and excellent α-selectivities. Similarly, the acetonide protected sterically congested secondary alcohols were also smoothly coupled with **1b** to furnish the disaccharides **1bh** and **1bi** in 74% and 78% yields, respectively. The Fmoc-protected methyl ester of serine **5j** and the threonine derivative **5k** was coupled with **1b** to provide the corresponding glycoamino acids **1bj**−**k** as only α products. Toward the end of the project, to showcase the orthogonality, we have synthesized trisaccharide **1apg** (Scheme 1). We have utilized mannose thioglycoside derived 6-OH acceptor **5p** under the $BF_3{\cdot}Et_2O$ condition to obtain the disaccharide **1ap** as an exclusive α-isomer, which in turn was used for another coupling under the NIS/TMSOTf condition to synthesize the trisaccharide **1apg** in one pot. Our desired trisaccharide was obtained in 70% yield as a 9.5:1 $\alpha:\beta$ mixture.

To decipher the involvement of oxocarbenium ions in *O*-glycosylation reactions, we wish to understand the facial selectivities of the various silyl protected oxocarbenium ions. To that effect, we performed the *C*-glycosylation reactions on four rhamnosyl acetate donors under $BF_3{\cdot}Et_2O$ conditions (Table 4), as it is widely accepted that the weakly nucleophilic C-nucleophiles usually react via a dissociative mechanism.[17] Particularly, π-nucleophile allylTMS is not nucleophilic enough to undergo an S_N2-type displacement reaction. In addition, C-nucleophiles that react irreversibly also reveal the kinetic

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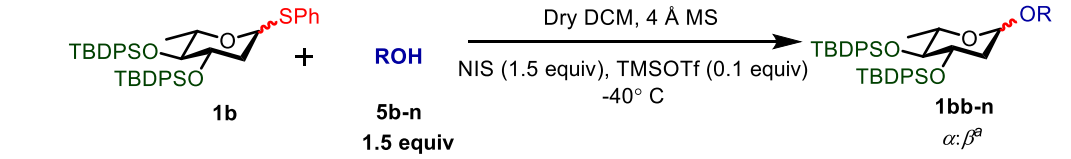
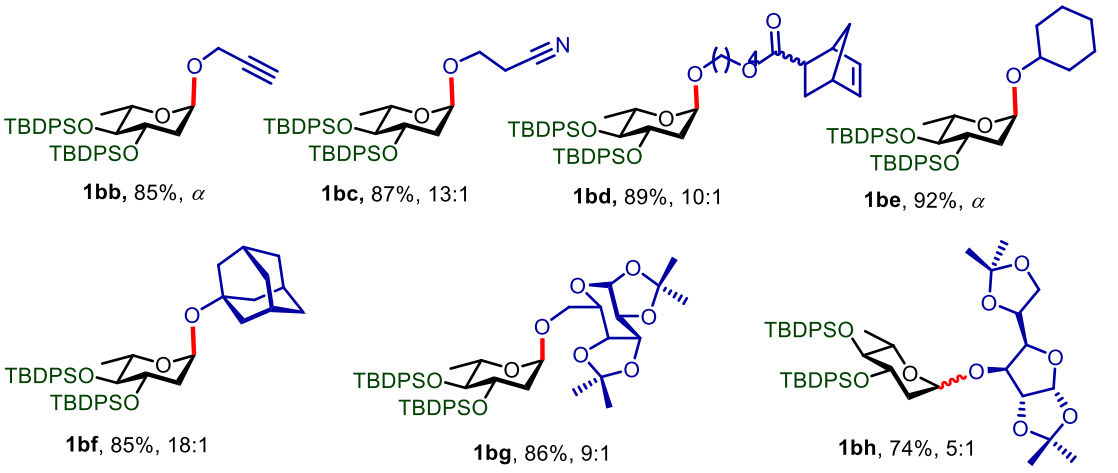
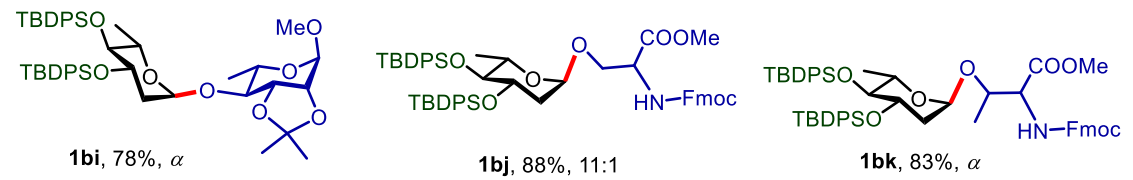
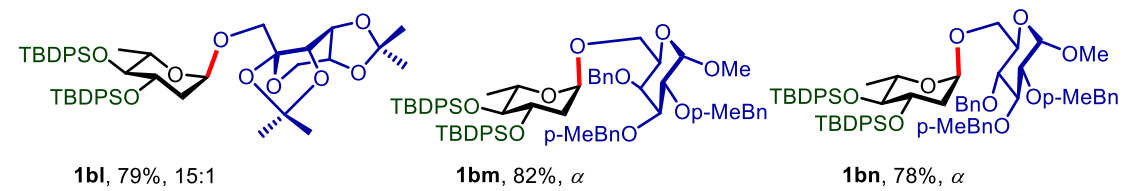
Table 3. Glycosylation of TBDPS Protected L-Rhamnosyl Donor with Various Glycosyl Acceptors[a]



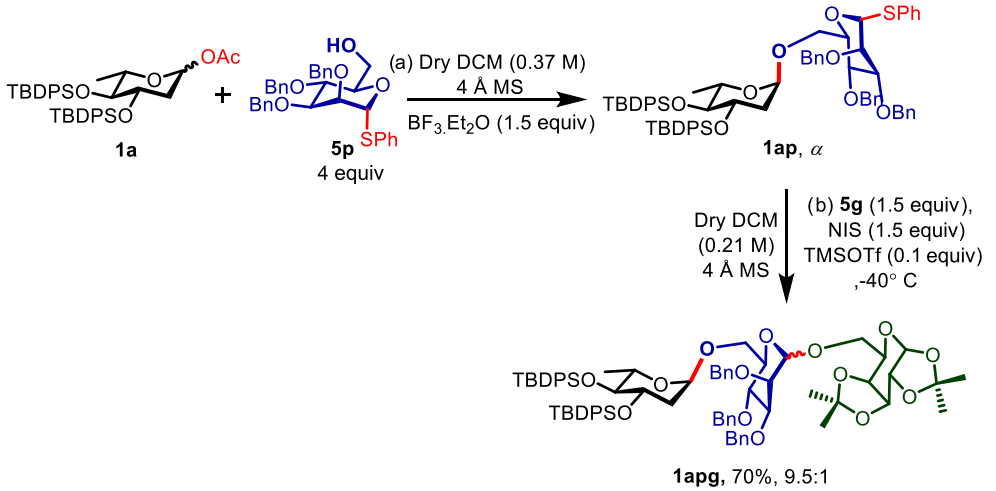






[a]Reaction conditions: The anomeric ratio was determined using ^{1}H NMR spectroscopy.

Scheme 1. Stereoselective Synthesis of the Trisaccharide 1apg



control over the anomeric selectivity. Intriguingly, in contrast to the *O*-glycosylation reactions, the anomeric selectivities in *C*-glycosylation reactions with allylTMS as the nucleophile led to very poor facial selectivities. The TBDPS protected donor

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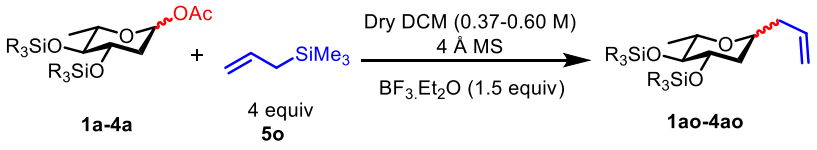
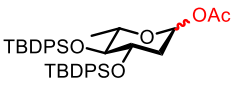
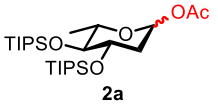
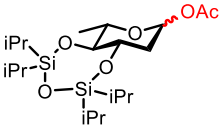
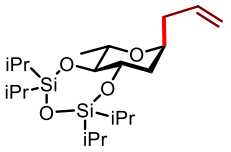
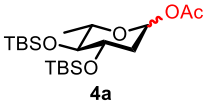
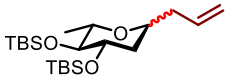
Table 4. Influence of the Silyl Protecting Group on C-Glycosylation Reactions



Sl No.	Donor	Product (α:β)[a]
1	 **1a**	 **1ao**, 89%, α:β= 1.1:1[b]
2	 **2a**	 **2ao**, 88%, α:β= 1.5:1
3	 **3a**	 **3ao**, 82%, α
4	 **4a**	 **4ao**, 86%, α:β= 2:1[b]

[a]Reaction conditions: Anomeric ratios are determined using ^{1}H NMR spectroscopy. [b]Anomeric ratios are determined by high-performance liquid chromatography (HPLC).

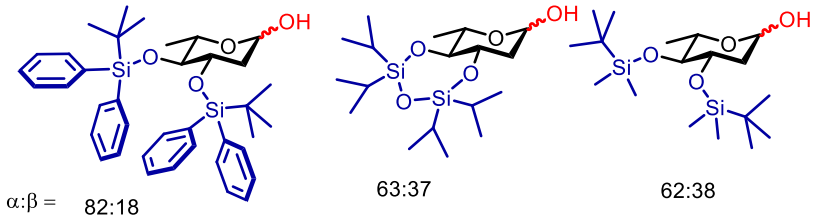


Figure 1. Equilibrium anomeric ratios of various silyl protected 2-deoxy L-rhamnopyranoses.[15] Reproduced from [*Org. Lett.* 2020, *22*, 2191−2195]. Copyright [2020] American Chemical Society.

1a along with TIPS and TBS protected donors (**2a** and **4a**, respectively) gave a mixture of products (**1ao**, **2ao**, and **4ao**, respectively), whereas the cyclic TIPDS protecting group **3a** led to the exclusive formation of the α-allyl product **3ao** (entries 1 and 4, Table 4). These experiments demonstrate that presumably the oxocarbenium ions are not the probable intermediates in the *O*-glycosylation reactions. Also, these studies demonstrate that the cyclic TIPDS protecting group is the best for the stereoselective *C*-glycosylation of L-rhamnoses. Interestingly, the anomeric ratios of the silyl protected rhamnosyl anomeric acetals at equilibrium (Figure 1),[15] though not exactly matching with the observed selectivities in the *O*-glycosylation reactions, follow a similar trend, with the α isomer more populated in the case of the TBDPS protected hemiacetal. The equilibrium studies decipher the role of the thermodynamic factor in the observed selectivities. However, one cannot rule out the associative mechanisms involving the displacement of reactive intermediates like the generally invoked contact ion-pairs or covalent glycosyl triflates under kinetic conditions leading to the high selectivities. To have better insights into the stereoselective glycosylation, particularly with the TBDPS protecting group, we performed density functional theory (DFT) studies using the B97-D3 DFT functional with the Grimme D3BJ dispersion correction and the 6-31++G** basis set. The relative energies of the oxocarbenium ions and the corresponding rhamnosyl triflates have been calculated (refer to the Supporting Information, SI, for more details). It was found that the $^4H_3$ conformation of the oxocarbenium ion **I2** is 9.4 kcal/mol more stable than the $^3H_4$ conformation **I1**. Hence, it is safe to assume that the $^4H_3$ conformation **I2** is the dominant conformation in determining the stereoselectivity. The computational studies also reveal that the β and α attack of the triflate anion on the $^4H_3$ and $^3H_4$ conformers of the oxocarbenium ions led to almost similar energy triflate intermediates **I3** (−3.6 kcal/mol) and **I5** (−4.6 kcal/mol). In addition, the lowest energy or the most stable intermediate is the axial β-triflate and hence is assumed to be more populated than the equatorial triflates (Figure 2). Also,

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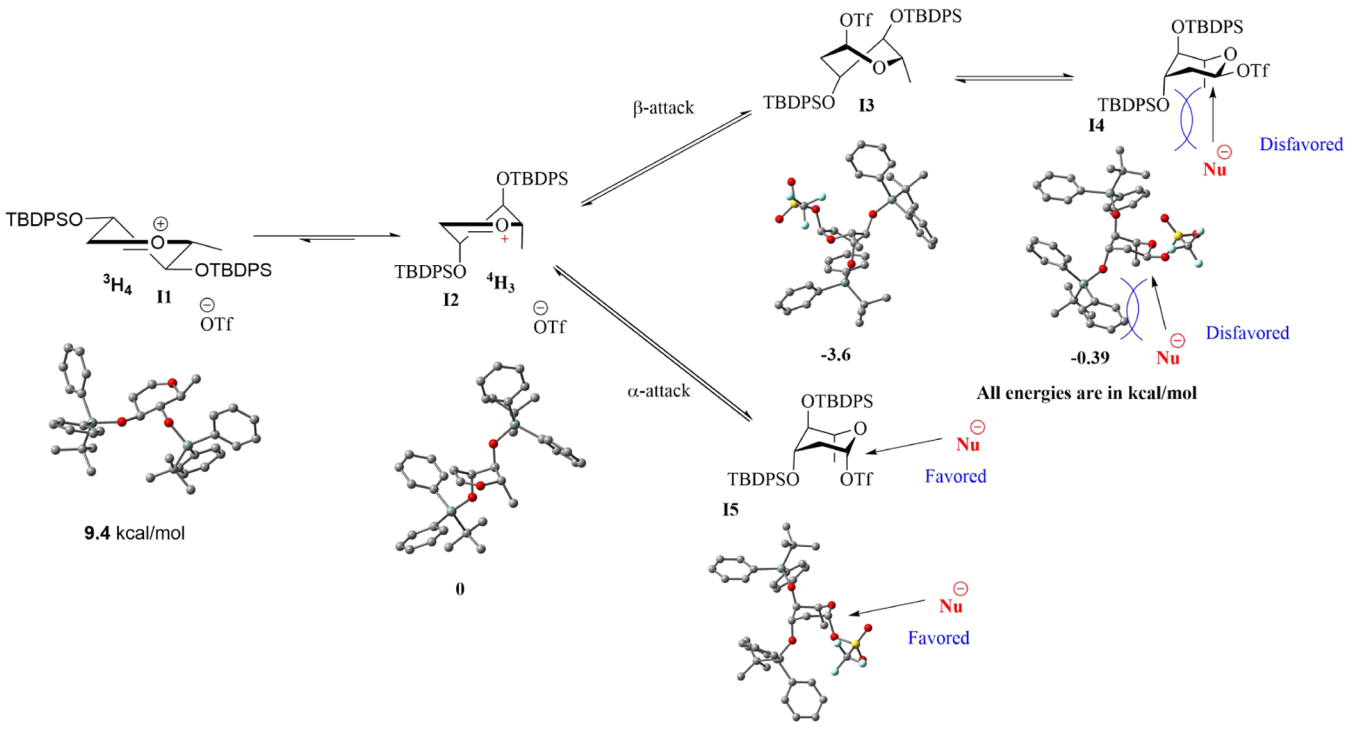

Figure 2. DFT calculations of the B97-D3 DFT functional with the Grimme D3BJ dispersion correction and the 6-31++G** basis set to determine the relative energies of the reactive intermediates.

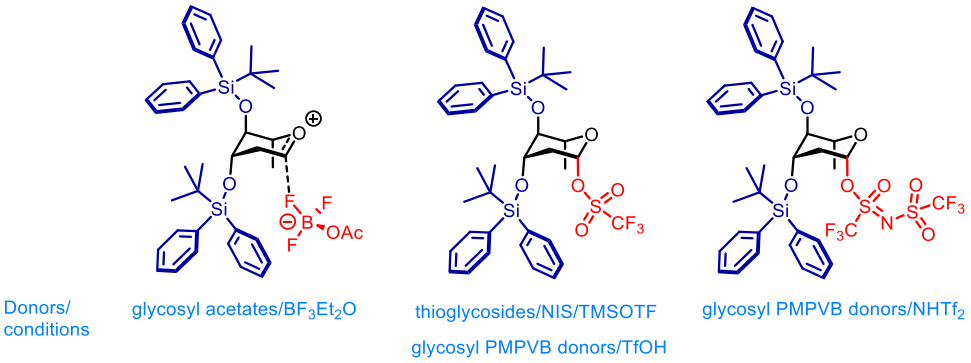

Figure 3. Possible intermediates in the α-selective glycosylations using various donors.

the nucleophilic attack on the equatorial triflate is more sterically hindered than the attack on the axial triflates (Figure 2). Hence, we presume that the attack of the nucleophilic alcohol on the dominant β-triflates leads to the observed high α-selectivities. Although calculations were done using triflate as the anion, Figure 3 represents the possible axial intermediates undergoing the S_N2 reaction under various conditions from the respective donors. The erosion of selectivity in other cases could be due to the relatively less steric shielding around the α-triflate intermediates unlike the TBDPS donors. The TIPDS protected oxocarbenium ion is restricted to only the $^3H_4$ conformation due to the conformation locking, and the α-attack of the *C*-nucleophile is the dominant pathway as it directly leads to the chair conformation product.

CONCLUSIONS

In conclusion, it is observed that the OTBDPS protecting group provided better stereoselectivity than OTBS, OTIPS, and cyclic OTIPDS groups on L-rhamnose donors in *O*-glycosylation reactions irrespective of the donor leaving group and the activation conditions used. While the anomeric equilibrium ratios of the corresponding hemiacetals point to the thermodynamic origins of the α-products, the DFT calculations along with the *C*-glycosylation reactions reveal that the high selectivities observed could be due to the S_N2 displacement of the corresponding axial intermediates (Figure 3). Also, the study reveals that the cyclic TIPDS protected rhamnose donors are superior in providing excellent α-selective *C*-glycosylation reactions with allyltrimethylsilane presumably *via* an S_N1 mechanism. As an application of this study, stereoselective synthesis of several 2-deoxy L-rhamnosides was achieved. Several non-carbohydrate acceptors, primary and secondary sugar acceptors, and also amino acid-derived acceptors were used in this study. Moreover, a trisaccharide consisting of rhamnose, mannose, and galactose in a stereoselective fashion emanating from the TBDPS protected rhamnosyl donor has also been synthesized. The present systematic study on the influence of silyl protecting groups on 2-deoxy-rhamnosides could have widespread

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applications not only in the stereoselective synthesis of rhamnose-based oligosaccharides but also in general.

EXPERIMENTAL SECTION

General Information. All solvents used were of commercial grade for the reaction without further purification. Reagents were purchased from Sigma-Aldrich, Merck, Spectrochem, Alfa Aesar, and Loba and used without further purification.

Analysis. Reactions were monitored by thin-layer chromatography (TLC) on a Kieselgel 60 F254 (Merck). Detection was done by examination under UV light (254 nm) and by charring with 10% sulfuric acid in water. Purification was performed by ultrahigh-performance liquid chromatography (UHPLC) using a column [particle size: (μ) 12; Dim: (mm) 250 × 10] in both the reverse phase and the normal phase using silica gel [Merck, 60−120 mesh]. Extracts were concentrated in vacuo using a Büchi rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.7 mmHg (oil pump) at room temperature. ^{1}H- and ^{13}C{^{1}H} NMR were recorded on Bruker 600, 500, and 400 MHz spectrometers using $CDCl_3$ as the solvent. Chemical shift values are reported in ppm with the solvent as the internal standard ($CDCl_3$: δ 7.26 for ^{1}H, δ 77.16 for ^{13}C{^{1}H}). Data are reported as follows: chemical shifts (δ), multiplicity (s, singlet; d, doublet; dd, double of doublet; ddd, doublet of doublet of doublets; dt, doublet of triplet; t, triplet; td, triplet of doublet; q, quartet; m, multiplet), etc., coupling constants J (Hz), and integration. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. High-resolution mass measurements were performed using an Agilent Technologies high-resolution mass spectrometer QTOF 6520. The diastereomeric ratio was calculated from crude NMR. Specific rotation was recorded in Autopol II S2, the unit of the specific rotation is (deg·mL)/(g·dm), and concentration c is given in g/100 mL.

*Synthesis of Anomeric Acetate Glycosyl Donors. Synthesis of 2,6-Dideoxy-3,4-O-bis-(t-butyldiphenylsilyl)-2-deoxy-α,β-L-rhamnopyranosyl-1-acetate (**1a**).* TBDPSCl (3.03 mL, 11.523 mmol, 3 equiv) was added to a solution of 3,4-dihydro-L-rhamnal (500 mg, 3.841 mmol, 1.0 equiv) and imidazole (785 mg, 11.523 mmol, 3 equiv) in dimethylformamide (DMF) (20 mL). After the reaction mixture was allowed to stir at room temperature for 12 h, most of the reaction solvent was removed under reduced pressure. The residue was dissolved with dichloromethane (DCM) and then washed with saturated aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in an ethyl acetate (EA)/hexane solvent system to give the glycal as a white solid. R_f = 0.5 (50% cyclohexane in hexane), amount = 1.78 g, yield = 76%. Spectroscopic data are in agreement with the reported data.[7a]

The synthesized 3,4-di-*O*-*tert*-butyldiphenylsilyl-L-rhamnal (500 mg, 0.82 mmol, 1.0 equiv) and the catalyst 2,4,6-tri-*tert*-butylpyridinium hydrochloride (5 mg, 0.0164 mmol, 2 mol %) were taken in a round-bottomed flask and the flask was then filled with dry DCM and water in a 95:5 ratio (10 mL). The mixtures were stirred and heated at 40 °C (using an oil bath) in the sealed flask until the reaction was determined to be complete by either TLC or NMR analysis of the crude material. The reaction mixture was quenched by water (20 mL), and it was extracted with DCM, dried over Na_2SO_4, concentrated in vacuo, and then purified by silica gel column chromatography to obtain the product as a colorless crystalline solid. R_f = 0.5 in 20% EA/hexane, eluent = 10% EA in hexane, amount = 412 mg, yield = 80%. Spectroscopic data are in agreement with the reported data.[15]

The synthesized 3,4-di-*O*-*tert*-butyldiphenylsilyl-L-rhamnopyranose (500 mg, 0.80 mmol, 1.0 equiv) was taken in DCM, and to it, pyridine (96 μL, 1.20 mmol, 1.5 equiv) and Ac_2O (115 μL, 1.20 mmol, 1.5 equiv) were added, keeping in an ice bath. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched by water (20 mL) and it was extracted with DCM, dried over Na_2SO_4, concentrated in vacuo, and then purified by silica gel column chromatography to get the product **1a** as a colorless oil. R_f = 0.8 in 20% EA/hexane, eluent = 5% EA in hexane, amount = 454 mg, yield = 85%. Selectivity α/β = 8:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.52 (m, 4H), 7.50−7.46 (m, 4H), 7.42−7.37 (m, 4H), 7.36−7.29 (m, 4H), 7.27−7.22 (m, 4H), 6.24 (dd, J = 8.5, 3.6 Hz, 1H), 4.10 (d, J = 3.1 Hz, 1H), 3.96−3.90 (m, 1H), 3.57 (t, J = 3.0 Hz, 1H), 2.07 (s, 1H), 1.93 (ddd, J = 13.3, 8.6, 2.7 Hz, 1H), 1.73 (dt, J = 13.6, 3.8 Hz, 1H), 1.18 (d, J = 7.0 Hz, 3H), 0.96 (s, 9H), 0.94 (s, 9H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.9, 135.9 (2C), 135.8 (2C), 133.7, 133.5, 133.4 (2C), 129.9, 129.8 (4C), 127.7 (3C), 89.4, 74.9, 73.9, 71.9, 32.8, 27.0 (2C), 21.5, 19.3, 19.2, 17.9. HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{40}H_{50}O_5Si_2Na$ 689.3094; found 689.3096. $[\alpha]_D^{22}$ = −25 (c 0.79, $CHCl_3$).

*Synthesis of 2,6-Dideoxy-3,4-O-bis-(triisopropylsilyl)-2-deoxy-α,β-L-rhamnopyranosyl-1-acetate (**2a**).* TIPSCl (2.22 mL, 11.523 mmol, 3 equiv) was added to a solution of 3,4-dihydro-L-rhamnal (500 mg, 3.841 mmol, 1.0 equiv) and imidazole (785 mg, 11.523 mmol, 3 equiv) in DMF (20 mL). After the reaction mixture was allowed to stir at room temperature for 12 h, most of the reaction solvent was removed under reduced pressure. The residue was dissolved with DCM and then washed with saturated aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in an ethyl acetate/hexane solvent system to give the glycal as a colorless oil. R_f = 0.5 (50% cyclohexane in hexane), amount = 1.43 g, yield = 84%. Spectroscopic data are in agreement with the reported data.[18]

The synthesized 3,4-di-*O*-triisopropylsilyl-L-rhamnal (500 mg, 1.13 mmol, 1.0 equiv) and the catalyst 2,4,6-tri-*tert*-butylpyridinium hydrochloride (7 mg, 0.0225 mmol, 2 mol %) were taken in a round-bottomed flask, and the flask was then filled with dry DCM and water in a 95:5 ratio (10 mL). The mixtures were stirred and heated at 40 °C (using an oil bath) in a sealed flask until the reaction was determined to be complete by either TLC or NMR analysis of the crude material. The reaction mixture was quenched by water (20 mL), and it was extracted with DCM, dried over Na_2SO_4, concentrated in vacuo, and then purified by silica gel column chromatography to get the product 2,6-dideoxy-3,4-*O*-bis-(triisopropylsilyl)-2-deoxy-α,β-L-rhamnopyranose as a colorless oil. R_f = 0.5 in 20% EA/hexane, eluent = 10% EA in hexane, amount = 416 mg, yield = 80%. Selectivity α/β = 2.7:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (td, J = 7.7, 2.7 Hz, 2.7H), 5.11−5.08 (m, 1H), 4.41 (d, J = 9.3 Hz, 1H), 4.16−4.12 (m, 2.7H), 4.12−4.08 (m, 3.7H), 3.83 (qd, J = 7.1, 3.2 Hz, 1H), 3.75−3.74 (m, 1H), 3.59 (t, J = 3.0 Hz, 2.7H), 2.88 (d, J = 6.9 Hz, 2.7H), 2.31 (dt, J = 13.6, 3.3 Hz, 1H), 1.98 (ddd, J = 12.9, 8.0, 3.1 Hz, 2.7H), 1.90−1.86 (m, 2.7H), 1.84−1.79 (m, 1H), 1.50 (d, J = 7.2 Hz, 3H), 1.41 (d, J = 7.1 Hz, 8H), 1.09 (dt, J = 5.4, 4.4 Hz, 166H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 92.9, 88.5, 75.1, 73.9, 73.6, 73.0, 72.0, 36.9, 34.6, 29.9, 21.4, 18.4, 18.3 (4C), 17.9, 13.0, 12.8 (2C), 12.7.

The synthesized 3,4-di-*O*-triisopropylsilyl-L-rhamnopyranose (500 mg, 1.08 mmol, 1.0 equiv) was taken in DCM, and to it, pyridine (132 μL, 1.63 mmol, 1.5 equiv) and Ac_2O (154 μL, 1.63 mmol, 1.5 equiv) were added, keeping in an ice bath. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched by water (20 mL) and it was extracted with DCM, dried over Na_2SO_4, concentrated in vacuo, and then purified by silica gel column chromatography to get the product **2a** as a colorless oil. R_f = 0.8 in 20% EA/hexane, eluent = 5% EA in hexane, amount = 453 mg, yield = 83%. Selectivity α/β = 2:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.19 (dd, J = 7.0, 3.3 Hz, 2H), 6.03 (t, J = 4.0 Hz, 1H), 4.12 (dt, J = 9.9, 5.1 Hz, 2H), 4.00 (dd, J = 9.2, 4.6 Hz, 1H), 3.98−3.93 (m, 2H), 3.87 (qd, J = 7.0, 3.3 Hz, 1H), 3.70−3.68 (m, 1H), 3.57 (t, J = 4.5 Hz, 2H), 2.33 (dt, J = 14.0, 4.2 Hz, 1H), 2.13 (ddd, J = 13.2, 7.0, 3.2 Hz, 2H), 2.08 (s, 6H), 2.05 (s, 3H), 1.87 (ddd, J = 13.2, 5.9, 3.4 Hz, 2H), 1.81 (dt, J = 14.0, 4.4 Hz, 1H), 1.47 (d, J = 7.1 Hz, 3H), 1.41 (d, J = 6.9 Hz, 6H), 1.10−1.05 (m, 130H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.3, 169.9, 90.9, 89.9, 75.0, 74.8, 74.7, 73.4, 71.8, 69.5, 34.6, 33.1, 29.9, 21.6, 21.4, 19.9, 18.4 (2C), 18.3 (3C), 18.0, 13.1, 13.0, 12.8. HRMS (ESI) m/z: [M + K]$^+$ calcd for $C_{26}H_{54}O_5Si_2K$ 541.3147; found 541.3133. $[\alpha]_D^{22}$ = −20 (c 0.70, $CHCl_3$).

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*Synthesis of 2,6-Dideoxy-3,4-O-(tetraisopropyldisiloxane)-1,3-diyl-α,β-L-rhamnopyranosyl-1-acetate (**3a**).* TIPDSCl (1.85 mL, 5.762 mmol, 1.5 equiv) was added to a solution of 3,4-dihydro-L-rhamnal (500 mg, 3.841 mmol, 1.0 equiv) and imidazole (785 mg, 11.523 mmol, 3 equiv) in DMF (20 mL). After the reaction mixture was allowed to stir at room temperature for 12 h, most of the reaction solvent was removed under reduced pressure. The residue was dissolved with DCM and then washed with saturated aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the glycal as a colorless oil. R_f = 0.5 (50% cyclohexane in hexane), amount = 1.15 g, yield = 82%.

The procedure for the synthesis of **3a** was similar to the procedure of **1a** with 2,6-dideoxy-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-L-rhamnal to get the product as a colorless oil. R_f = 0.8 in 20% EA/hexane, eluent = 5% EA in hexane, amount = 1.32 g, overall yield = 80%. Selectivity α/β = 1.6:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.14 (d, J = 2.5 Hz, 1H), 5.73 (d, J = 10.1 Hz, 1.6H), 3.99−3.95 (m, 1H), 3.79−3.75 (m, 1.6H), 3.71 (dq, J = 12.4, 6.2 Hz, 1H), 3.40 (dq, J = 12.3, 6.1 Hz, 1.6H), 3.31−3.26 (m, 2.6H), 2.21−2.18 (m, 1.6H), 2.12 (d, J = 5.7 Hz, 1H), 2.10 (s, 7.8H), 1.86−1.81 (m, 1H), 1.76 (dd, J = 23.0, 11.5 Hz, 1.6H), 1.34 (d, J = 6.1 Hz, 4.8H), 1.29 (d, J = 6.2 Hz, 3H), 1.09−0.92 (m, 73H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.8, 169.4, 92.1, 92.0, 79.6, 79.2, 73.6, 73.4, 71.2, 70.7, 38.6, 37.4, 21.3, 21.2, 18.2, 18.1, 17.7 (2C), 17.5 (4C), 17.4 (3C), 17.3, 13.0 (2C), 12.4 (3C). HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{40}O_6Si_2Na$ 455.2261; found 455.2261. $[\alpha]_D^{22}$ = −22 (c 0.79, $CHCl_3$).

*Synthesis of 2,6-Dideoxy-3,4-di-O-tert-butyldimethylsilyl-α,β-L-rhamnopyranosyl-1-acetate (**4a**).* TBDMSCl (1.74 g, 11.523 mmol, 3 equiv) was added to a solution of 3,4-dihydro-L-rhamnal (500 mg, 3.841 mmol, 1.0 equiv) and imidazole (785 mg, 11.523 mmol, 3 equiv) in DMF (20 mL). After the reaction mixture was allowed to stir at room temperature for 12 h, most of the reaction solvent was removed under reduced pressure. The residue was dissolved with DCM and then washed with saturated aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the glycal as a colorless oil. R_f = 0.5 (50% cyclohexane in hexane), amount = 1.1 g, yield = 80%.

The procedure for the synthesis of **4a** was similar to the procedure of **1a** with 2,6-dideoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-L-rhamnal to get the product as a colorless oil. R_f = 0.8 in 20% EA/hexane, eluent = 5% EA in hexane, amount = 1.42 g, overall yield = 88%. Selectivity α/β = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10−6.08 (m, 1H), 5.70 (dd, J = 9.8, 2.4 Hz, 2H), 3.92 (ddd, J = 10.8, 8.1, 4.5 Hz, 1H), 3.72−3.66 (m, 3H), 3.38 (tt, J = 12.7, 6.3 Hz, 2H), 3.19 (dt, J = 11.4, 8.4 Hz, 3H), 2.16 (dd, J = 4.7, 2.4 Hz, 1H), 2.13−2.11 (m, 2H), 2.10 (s, 6H), 2.08 (s, 3H), 1.80−1.73 (m, 1H), 1.72−1.64 (m, 2H), 1.29 (d, J = 6.3 Hz, 6H), 1.24 (d, J = 6.4 Hz, 3H), 0.91−0.89 (m, 58H), 0.12−0.07 (m, 38H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.8, 169.5, 92.1, 91.6, 77.9, 77.3, 73.9, 72.5, 71.9, 70.5, 39.2, 38.2, 26.4, 26.3, 26.2 (2C), 25.8, 21.3, 21.3, 18.9, 18.8, 18.4 (2C), 18.2 (2C), −2.7 (2C), −3.0, −3.8, −3.9, −4.1, −4.3, −4.6. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{42}O_5Si_2Na$ 441.2468; found 441.2467. $[\alpha]_D^{22}$ = −22 (c 0.77, $CHCl_3$).

General Procedure A for the Glycosylation Reaction Using Acetate Donors. Anomeric acetate donor (0.075−0.24 mmol, 1.0 equiv) was taken in dry DCM, and activated 4 Å MS was added to it at 0 °C under an argon atmosphere. The glycosyl acceptor (0.3−0.96 mmol, 4.0 equiv) was added to it, and the reaction mixture was allowed to stir under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel and then quenched by water (20 mL for a 0.075 mmol donor); then, it was extracted with DCM (3 × 15 mL for a 0.075 mmol donor), dried over Na_2SO_4, concentrated in vacuo, and then purified by column chromatography (Merck 60−120 mesh, 7 gm) and using HPLC (Hypersil Gold C18, I = 214 nm).

*Synthesis of Thioglycosyl Donors Using General Procedure A. Synthesis of Phenyl-2,6-dideoxy-3,4-bis-O-[(1,1-dimethylethyl)-diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside (**1b**).* General procedure **A** was followed by taking 2,6-dideoxy-3,4-*O*-bis-(*t*-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl-1-acetate **1a** (100 mg, 0.15 mmol, 1.0 equiv) in dry DCM (4 mL, 0.37 M), and thiophenol (66 mg, 61 μL, 0.6 mmol, 4.0 equiv) was added to it; then, the reaction mixture was allowed to stir under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (32 mg, 28 μL, 0.22 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel and washed with DCM and the excess thiophenol was quenched with a 5% NaOH solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the thioglycoside **1b** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 96 mg, yield = 89%. Selectivity α/β = 18:1. α-Anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.53 (m, 4H), 7.49−7.20 (m, 21H), 5.47 (dd, J = 11.2, 2.8 Hz, 1H), 4.03−3.97 (m, 2H), 3.51 (s, 1H), 2.12 (ddd, J = 13.7, 11.4, 5.7 Hz, 1H), 1.69 (d, J = 13.7 Hz, 1H), 1.23 (d, J = 7.1 Hz, 3H), 0.95 (s, 9H), 0.91 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.9, 135.8 (2C), 134.6, 133.8, 133.5 (2C), 133.3, 131.5, 129.9, 129.8 (4C), 128.8, 127.8 (2C), 127.7, 127.0, 75.4, 75.2, 72.5, 71.7, 34.0, 27.1, 27.0, 19.3 (2C), 17.1. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{44}H_{52}O_3Si_2SNa$ 739.3073; found 739.3059. $[\alpha]_D^{22}$ = −32 (c 66, $CHCl_3$).

*Synthesis of Phenyl-2,6-dideoxy-3,4-O-bis-(triisopropylsilyl)-2-deoxy-1-thio-α,β-L-arabino-hexapyranoside (**2b**).* The procedure for the synthesis of **2b** was similar to the procedure of **1b** with 2,6-dideoxy-3,4-*O*-bis-(triisopropylsilyl)-2-deoxy-α,β-L-rhamnopyranosyl-1-acetate **2a** (100 mg, 0.20 mmol, 1.0 equiv) as the starting material, thiophenol (88 mg, 82 μL, 0.80 mmol, 4.0 equiv) as the acceptor, and $BF_3{\cdot}Et_2O$ (43 mg, 37 μL, 0.30 mmol, 1.5 equiv) as the catalyst in dry DCM (4 mL, 0.5 M) to get the product **2b** as a colorless oil. R_f = 0.5 in 10% EA/hexane, eluent = 3% EA in hexane, amount = 96 mg, yield = 87%. Selectivity α/β = 9:1. α-Anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46−7.44 (m, 1H), 7.32−7.26 (m, 1H), 7.21−7.18 (m, 2H), 7.13 (ddd, J = 7.3, 3.7, 1.1 Hz, 1H), 5.37 (dd, J = 10.2, 2.8 Hz, 1H), 4.05 (qd, J = 7.0, 2.4 Hz, 1H), 4.01 (dd, J = 6.8, 3.4 Hz, 1H), 3.51 (t, J = 3.0 Hz, 1H), 2.22 (ddd, J = 13.1, 8.3, 2.8 Hz, 1H), 1.81−1.77 (m, 1H), 1.37 (d, J = 7.1 Hz, 3H), 1.03−0.95 (m, 46H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 137.1, 134.8, 131.4, 131.0, 129.2, 128.8, 128.7, 126.9, 75.8, 75.6, 72.9, 71.7, 35.2, 32.1, 31.0, 29.9, 29.8, 29.5, 22.8, 18.6, 18.5 (2C), 18.4, 18.3 (4C), 17.2, 14.3, 13.8, 12.8, 12.7. HRMS (ESI) m/z: $[M + K]^+$ calcd for $C_{30}H_{56}O_3SSi_2K$ 591.3126; found 591.3116. $[\alpha]_D^{22}$ = −32 (c 0.60, $CHCl_3$).

*Synthesis of Phenyl-2,6-dideoxy-3,4-O-[1,1,3,3-tetrakis(1-methylethyl)-1,3-disiloxanediyl]-1-thio-α,β-L-arabino-hexapyranoside (**3b**).* The procedure for the synthesis of **3b** was similar to the procedure of **1b** with 2,6-dideoxy-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-L-rhamnopyranosyl-1-acetate **3a** (100 mg, 0.21 mmol, 1.0 equiv) as the starting material, thiophenol (91 mg, 85 μL, 0.83 mmol, 4.0 equiv) as the acceptor, and $BF_3{\cdot}Et_2O$ (44 mg, 38 μL, 0.31 mmol, 1.5 equiv) as the catalyst in dry DCM (4 mL, 0.52 M) to get the product **3b** as a colorless oil. R_f = 0.5 in 10% EA/hexane, eluent = 3% EA in hexane, amount = 93 mg, yield = 83%. Selectivity α/β = 2.2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.56 (m, 2H), 7.42−7.38 (m, 5H), 7.31−7.13 (m, 13H), 5.50 (d, J = 5.5 Hz, 2.2H), 4.73 (dd, J = 12.1, 1.8 Hz, 1H), 4.07 (dq, J = 9.1, 6.2 Hz, 2.2H), 3.93 (ddd, J = 11.6, 8.2, 5.1 Hz, 2.2H), 3.66 (ddd, J = 11.0, 7.8, 5.4 Hz, 1H), 3.28−3.26 (m, 1H), 3.20 (td, J = 8.9, 2.6 Hz, 3.2H), 2.23 (dd, J = 13.3, 5.2 Hz, 3.2H), 2.06 (ddd, J = 13.7, 11.6, 5.7 Hz, 2.2H), 1.78 (dd, J = 24.1, 12.1 Hz, 1H), 1.29 (d, J = 5.9 Hz, 3H), 1.22 (d, J = 6.2 Hz, 7H), 1.04−0.88 (m, 92H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 137.1, 135.5, 134.7, 132.4, 131.2, 131.1, 129.2, 129.0 (2C), 128.7, 127.3, 127.1, 84.1, 82.2, 80.3, 79.3, 76.6, 75.2, 72.1, 69.3, 59.6, 40.0, 39.4, 30.9, 18.5, 18.0, 17.8, 17.6, 17.5 (2C), 17.4 (4C), 13.1, 13.0 (2C), 12.4 (2C), 12.3. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for

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$C_{24}H_{42}O_4SSi_2NH_4$ 500.2686; found 500.2686. $[\alpha]_D^{22} = -32$ (*c* 0.60, $CHCl_3$).

*Synthesis of Phenyl-2,6-dideoxy-3,4-bis-O-tert-butyldimethylsilyl-1-thio-α,β-L-arabino-hexapyranoside (**4b**).* The procedure for the synthesis of **4b** was similar to the procedure of **1b** with 2,6-dideoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-L-rhamnopyranosyl-1-acetate **4a** (100 mg, 0.24 mmol, 1.0 equiv) as the starting material, thiophenol (105 mg, 99 μL, 0.96 mmol, 4.0 equiv) as the acceptor, and $BF_3{\cdot}Et_2O$ (51 mg, 44 μL, 0.36 mmol, 1.5 equiv) as the catalyst in dry DCM (4 mL, 0.6 M) to get the product **4b** as a colorless oil. R_f = 0.5 in 10% EA/hexane, eluent = 3% EA in hexane, amount = 96 mg, yield = 86%. Selectivity α/β = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.46 (ddd, *J* = 5.0, 3.7, 2.0 Hz, 4H), 7.32−7.21 (m, 9H), 5.51 (dd, *J* = 5.3, 2.3 Hz, 2H), 4.79 (dd, *J* = 12.0, 1.9 Hz, 1H), 4.08 (dq, *J* = 12.9, 6.4 Hz, 2H), 3.95−3.90 (m, 2H), 3.66 (ddd, *J* = 11.0, 8.1, 4.9 Hz, 1H), 3.30 (tt, *J* = 12.4, 6.2 Hz, 1H), 3.18 (dt, *J* = 15.0, 8.3 Hz, 3H), 2.25 (tdd, *J* = 12.5, 4.6, 2.1 Hz, 3H), 2.06−1.99 (m, 2H), 1.76 (dd, *J* = 23.8, 12.0 Hz, 1H), 1.30 (d, *J* = 3.5 Hz, 3H), 1.25 (d, *J* = 6.4 Hz, 6H), 0.92 (s, 18H), 0.91 (s, 18H), 0.90 (s, 9H), 0.89 (s, 9H), 0.13−0.07 (m, 39H). Other spectroscopic data are in agreement with the reported data.[19]

General Procedure B for the Synthesis of PMPVB Donors. In an oven-dried RB, a solution of hemiacetal (1.0 equiv), 2-(1-(4-methoxyphenyl)vinyl)benzoic acid (1.2 equiv), and 4-dimethylaminopyridine (DMAP) (0.2 equiv) in dry DCM was taken followed by the addition of *N*,*N*′-dicyclohexylcarbodiimide (DCC) (2 equiv) at 0 °C. The resulting mixture was stirred overnight at room temperature. The reaction was monitored by TLC; after completion of the reaction, the mixture was diluted with DCM and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated in a rotavapor. The compound was purified through column chromatography to afford the PMPVB donor.[14]

*Synthesis of PMPVB Donors Using General Procedure B. Synthesis of 2,6-Dideoxy-3,4-O-Bis-(t-butyldiphenylsilyl)-2-deoxy-α,β-L-rhamnopyranosyl-1-(1-(4-methoxyphenyl)vinyl)benzoate (**1c**).* General procedure **B** was followed for the synthesis of the rhamanosyl donor 2,6-dideoxy-3,4-*O*-Bis-(*t*-butyldiphenylsilyl)-2-deoxy-α,β-L-rhamnopyranosyl-1-(1-(4-methoxyphenyl)vinyl)benzoate (**1c**) by taking 2,6-dideoxy-3,4-di-*O*-*tert*-butyldiphenylsilyl-L-rhamnopyranose (150 mg, 0.24 mmol) to obtain a sticky compound and was purified through column chromatography (R_f = 0.3 in 5% EA/hexane, eluent = 3% EA in hexane). Amount = 186 mg, yield = 90% (α/β = 4:1). α-Anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 9.9 Hz, 6H), 7.44 (d, *J* = 8.2 Hz, 3H), 7.40 (d, *J* = 4.3 Hz, 2H), 7.36 (dd, *J* = 9.7, 6.7 Hz, 4H), 7.30 (dd, *J* = 7.7, 2.6 Hz, 4H), 7.25−7.17 (m, 6H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.16 (dd, *J* = 7.7, 4.6 Hz, 1H), 5.57 (s, 1H), 5.06 (s, 1H), 4.01 (d, *J* = 3.7 Hz, 1H), 3.77−3.63 (m, 4H), 3.52 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.75−1.69 (m, 1H), 1.63 (dt, *J* = 14.7, 5.0 Hz, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.92−0.88 (m, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 159.2, 148.5, 143.0, 135.8, 135.7 (2C), 133.7, 133.6, 133.5, 133.4, 133.3, 131.5, 131.4, 130.9, 130.0, 129.7 (2C), 129.6, 128.1, 127.6 (2C), 127.5, 127.3, 113.5, 112.4, 75.3, 73.7, 71.9, 55.2, 32.0, 29.7, 26.9 (2C), 19.2, 19.1, 18.3. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{34}H_{52}O_6Si_2Na$ 635.3195; found 635.3189.

*Synthesis of 2,6-Dideoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-α,β-L-rhamnopyranosyl-1-(1-(4-methoxyphenyl)vinyl)-benzoate (**3c**).* General procedure **B** was followed for the synthesis of the rhamanosyl donor 2,6-dideoxy-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-L-rhamnopyranosyl-1-(1-(4-methoxyphenyl)vinyl)benzoate (**3c**) by taking 2,6-dideoxy-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-L-rhamnopyranose (100 mg, 0.25 mmol) to obtain a sticky compound and was purified through column chromatography (R_f = 0.4 in 5% EA/hexane, eluent = 2% EA in hexane). Amount = 146 mg, yield = 91% (α/β = 1:2). α-Anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 9.5 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.85−6.70 (m, 2H), 6.12 (d, *J* = 3.5 Hz, 1H), 5.63 (s, 1H), 5.08 (s, 1H), 3.81−3.78 (m, 1H), 3.77 (s, 3H), 3.47−3.36 (m, 1H), 3.20 (t, *J* = 8.8 Hz, 1H), 2.12−2.02 (m, 1H), 1.77 (m, 1H), 1.12 (d, *J* = 6.2 Hz, 3H), 1.09−0.97 (m, 28H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.8, 158.3, 147.4, 141.8, 131.9, 130.5, 130.3, 130.0, 129.0, 127.1, 126.5, 112.6, 111.2, 91.9, 78.3, 70.3, 69.7, 54.1, 36.3, 28.7, 16.8, 16.6, 16.4, 16.3 (3C), 16.2, 11.9, 11.8, 11.3, 11.2.

β-Anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 5.65−5.58 (m, 2H), 5.13 (s, 1H), 3.76 (s, 3H), 3.67 (ddd, *J* = 12.5, 8.0, 5.3 Hz, 1H), 3.30 (dt, *J* = 12.3, 5.9 Hz, 1H), 3.22 (t, *J* = 8.4 Hz, 1H), 1.99−1.91 (m, 1H), 1.60 (q, *J* = 11.6 Hz, 1H), 1.29 (d, *J* = 6.1 Hz, 3H), 1.04 (ddt, *J* = 23.0, 10.2, 3.9 Hz, 28H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.4, 159.3, 148.6, 143.4, 133.3, 132.0, 131.3, 130.2, 127.9, 127.5, 113.5, 112.5, 92.5, 79.2, 73.6, 73.2, 55.2, 38.1, 18.0, 17.6, 17.4 (2C), 17.3 (2C), 17.2, 13.0, 12.8, 12.3. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{34}H_{51}O_7Si_2$ 627.3168; found 627.3173

*Synthesis of 2,6-Dideoxy-3,4-di-O-tertiary-butyldimethylsilyl-α,β-L-rhamnopyranosyl-1-(1-(4-methoxyphenyl)vinyl)benzoate (**4c**).* General procedure **B** was followed for the synthesis of the rhamanosyl donor 2,6-dideoxy-3,4-di-*O*-tertiary-butyldimethylsilyl-α,β-L-rhamnopyranosyl-1-(1-(4-methoxyphenyl)vinyl)benzoate (**4c**) by taking 2,6-dideoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-L-rhamnopyranose (200 mg, 0.53 mmol) to obtain as a sticky compound and was purified through column chromatography (R_f = 0.71 in 5% EA/hexane, eluent = 1.5% EA in hexane). Amount = 284 mg, yield = 87% (α/β = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.50 (ddt, *J* = 9.0, 5.1, 1.9 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33−7.15 (m, 6H), 6.85−6.75 (m, 4H), 6.10−6.04 (m, 1H), 5.63 (s, 1H), 5.64−5.56 (m, 2H), 5.08 (d, *J* = 3.6 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.73−3.64 (m, 1H), 3.60 (tt, *J* = 11.2, 4.8 Hz, 1H), 3.43−3.34 (m, 1H), 3.34−3.26 (m, 1H), 3.11 (q, *J* = 8.2 Hz, 2H), 2.07 (m, 1H), 1.96 (ddd, *J* = 12.5, 4.7, 2.6 Hz, 1H), 1.71 (m, 1H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.05 (d, *J* = 6.3 Hz, 3H), 0.95−0.78 (m, 36H), 0.10−0.03 (m, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.9, 165.9, 159.4 (2C), 148.8, 148.4, 143.5, 133.4, 133.0, 132.0, 131.6, 131.5, 131.3, 131.1, 130.5, 130.3, 130.1, 128.3, 128.1, 127.6, 113.8, 113.7, 112.4, 93.2, 92.2, 77.8, 73.8, 72.7, 71.8, 70.6, 55.3 (2C), 38.9, 38.2, 29.9, 26.4, 26.3, 26.2, 18.9, 18.6, 18.4, 18.3, 18.2, 1.2, −2.7 (2C), −3.0, −3.1, −3.8, −3.9, −4.1, −4.2. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{54}H_{60}O_6Si_2Na$ 883.3821; found 883.3813.

*Glycosylation Using General Procedure A. Synthesis of Methyl-2,3,4-tri-O-benzyl-6-O-(3,4-di-O-tert-butyldiphenylsilyl-2,6-dideoxy-α-L-rhamnosyl)-α,β-D-glucopyranoside (**1aa**).* General procedure **A** was followed by taking the glycosyl donor 2,6-dideoxy-3,4-*O*-bis-(*t*-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl-1-acetate **1a** (50 mg, 0.075 mmol, 1.0 equiv) and the glycosyl acceptor **5a** (140 mg, 0.3 mmol, 4.0 equiv), and then, the reaction mixture was allowed to stir in dry DCM (2 mL, 0.37 M) under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (16 mg, 14 μL, 0.11 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel, washed with DCM, and quenched with a sat. $NaHCO_3$ solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the product **1aa** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 63 mg, yield = 79%. Selectivity α/β = 10:1. α-Anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.53 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.37−7.17 (m, 28H), 5.00−4.95 (m, 2H), 4.84−4.78 (m, 3H), 4.67 (d, *J* = 12.2 Hz, 1H), 4.61 (d, *J* = 3.5 Hz, 1H), 4.50 (d, *J* = 10.7 Hz, 1H), 4.11 (d, *J* = 1.4 Hz, 1H), 4.02−3.97 (m, 2H), 3.89−3.83 (m, 1H), 3.77 (dd, *J* = 10.0, 3.3 Hz, 1H), 3.61 (dd, *J* = 11.1, 4.8 Hz, 1H), 3.56−3.53 (m, 2H), 3.48 (t, *J* = 9.5 Hz, 1H), 3.35 (s, 3H), 1.90 (ddd, *J* = 13.3, 7.9, 2.6 Hz, 1H), 1.69−1.63 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.87 (s, 9H). Other spectroscopic data are in agreement with the reported data.[7a]

*Synthesis of Methyl-2,3,4-tri-O-benzyl-6-O-(3,4-di-O-triisopropylsilyl-2,6-dideoxy-α,β-L-rhamnosyl)-α-D-glucopyranoside (**2aa**).* General procedure **A** was followed by taking the glycosyl donor 2,6-dideoxy-3,4-*O*-bis-(triisopropylsilyl)-2-deoxy-α,β-L-rhamnopyranosyl-1-acetate **2a** (50 mg, 0.10 mmol, 1.0 equiv) and the glycosyl

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acceptor **5a** (186 mg, 0.4 mmol, 4.0 equiv), and then, the reaction mixture was allowed to stir in dry DCM (2 mL, 0.5 M) under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (21 mg, 19 μL, 0.15 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel, washed with DCM, and quenched with a sat. $NaHCO_3$ solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the product **2aa** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 65 mg, = 72%. Selectivity α/β = 7:1. α-Anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.25 (m, 15H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.90 (dd, *J* = 5.6, 3.1 Hz, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.79 (dd, *J* = 13.4, 11.7 Hz, 2H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.58 (dd, *J* = 18.2, 7.2 Hz, 2H), 4.07 (t, *J* = 7.4 Hz, 1H), 4.01−3.97 (m, 2H), 3.87−3.82 (m, 1H), 3.79 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.53 (ddd, *J* = 16.5, 8.9, 4.6 Hz, 2H), 3.47 (dd, *J* = 10.4, 5.6 Hz, 2H), 3.36 (s, 3H), 2.10 (ddd, *J* = 13.0, 6.0, 3.5 Hz, 1H), 1.75 (ddd, *J* = 13.0, 6.7, 3.1 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.06 (dd, *J* = 14.7, 10.3 Hz, 42H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 139.0, 138.4 (2C), 128.6, 128.5 (2C), 128.3, 128.2, 128.1, 128.0 (2C), 127.9, 127.8, 127.7, 98.0, 96.0, 82.2, 80.1, 78.3, 75.9, 75.1, 73.5, 72.5, 72.1, 70.3, 66.8, 55.1, 36.2, 29.9, 18.5 (2C), 18.4 (3C), 18.3 (3C), 13.4, 13.3 (2C), 13.1, 12.4, 12.3. HRMS (ESI) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{52}H_{82}O_9Si_2NH_4$ 924.5841; found 924.5845. $[\alpha]_D^{22}$ = −42 (*c* 0.60, $CHCl_3$).

*Synthesis of Methyl-2,3,4-tri-O-benzyl-6-O-(2,6-deoxy)-3,4-O-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl-α,β-L-erythro-hexapyranosyl)-α-D-glucopyranoside (**3aa**).* General procedure **A** was followed by taking the glycosyl donor 2,6-dideoxy-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-L-rhamnopyranosyl-1-acetate **3a** (50 mg, 0.11 mmol, 1.0 equiv) and the glycosyl acceptor **5a** (204 mg, 0.44 mmol, 4.0 equiv), and then, the reaction mixture was allowed to stir in dry DCM (2 mL, 0.55 M) under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (23 mg, 20 μL, 0.17 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel, washed with DCM, and quenched with a sat. $NaHCO_3$ solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the product **3aa** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 77 mg, yield = 80%. Selectivity α/β = 3.6:1. α-Anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.27 (m, 15H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.89 (d, *J* = 11.1 Hz, 1H), 4.82 (d, *J* = 6.3 Hz, 1H), 4.80 (d, *J* = 7.5 Hz, 1H), 4.77 (d, *J* = 3.2 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 3.5 Hz, 1H), 4.54 (d, *J* = 11.0 Hz, 1H), 3.97 (ddd, *J* = 11.8, 8.3, 5.7 Hz, 1H), 3.88 (dd, *J* = 10.6, 1.0 Hz, 1H), 3.81−3.77 (m, 1H), 3.73−3.60 (m, 2H), 3.51 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.42−3.36 (m, 1H), 3.36 (s, 3H), 3.22 (dd, *J* = 11.6, 5.9 Hz, 1H), 2.08 (dd, *J* = 13.1, 5.2 Hz, 1H), 1.70−1.62 (m, 1H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.07−0.95 (m, 29H). Other spectroscopic data are in agreement with the reported data.[15]

*Synthesis of Methyl-2,3,4-tri-O-benzyl-6-O-(3,4-di-O-tertiary-butyldimethylsilyl-2,6-dideoxy-α,β-L-rhamnosyl)-α-D-glucopyranoside (**4aa**).* General procedure **A** was followed by taking the glycosyl donor 2,6-dideoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-L-rhamnopyranosyl-1-acetate **4a** (50 mg, 0.12 mmol, 1.0 equiv) and the glycosyl acceptor **5a** (223 mg, 0.48 mmol, 4.0 equiv), and then, the reaction mixture was allowed to stir in dry DCM (2 mL, 0.6 M) under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (26 mg, 22 μL, 0.18 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel, washed with DCM, and quenched with a sat. $NaHCO_3$ solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the product **4aa** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 80 mg, yield = 75%. Selectivity α/β = 1.3:1. α-Anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.27 (m, 30H), 4.98 (dd, *J* = 10.8, 5.7 Hz, 2H), 4.87 (t, *J* = 10.3 Hz, 2H), 4.84−4.78 (m, 4H), 4.71 (d, *J* = 2.0 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 2H), 4.63 (d, *J* = 3.5 Hz, 1H), 4.57 (d, *J* = 3.5 Hz, 1H), 4.54 (d, *J* = 11.0 Hz, 1H), 4.49 (dd, *J* = 9.7, 1.6 Hz, 1H), 4.23 (dd, *J* = 11.0, 3.1 Hz, 1H), 3.99 (dt, *J* = 13.2, 9.3 Hz, 2H), 3.94−3.89 (m, 1H), 3.86 (d, *J* = 10.9 Hz, 1H), 3.78 (dd, *J* = 9.8, 6.3 Hz, 1H), 3.72 (d, *J* = 9.8 Hz, 1H), 3.67 (d, *J* = 8.7 Hz, 1H), 3.65−3.57 (m, 3H), 3.55−3.49 (m, 2H), 3.39 (t, *J* = 5.4 Hz, 1H), 3.36 (s, 3H), 3.36 (s, 3H), 3.23−3.16 (m, 1H), 3.11 (q, *J* = 8.5 Hz, 2H), 2.18−2.14 (m, 1H), 2.05 (dd, *J* = 12.5, 3.9 Hz, 1H), 1.60 (ddd, *J* = 23.9, 11.4, 8.1 Hz, 1H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.17 (d, *J* = 6.4 Hz, 3H), 0.90−0.88 (m, 38H), 0.09−0.05 (m, 27H). Other spectroscopic data are in agreement with the reported data.[15]

*Synthesis of Allyl-1,2,3,5,8-pentadeoxy-6,7-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-α,β-L-arabino-non-1-enitol (**1aoαβ**).* General procedure **A** was followed by taking the glycosyl donor 2,6-dideoxy-3,4-*O*-bis-(*t*-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl-1-acetate **1a** (50 mg, 0.075 mmol, 1.0 equiv) and the glycosyl acceptor **5o** (34 mg, 43 μL, 0.3 mmol, 4.0 equiv), and then, the reaction mixture was allowed to stir in dry DCM (2 mL, 0.37 M) under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (16 mg, 14 μL, 0.11 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel, washed with DCM, and quenched with a sat. $NaHCO_3$ solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the product **1ao** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 43 mg, yield = 89%. α- and β-Anomers were isolated in HPLC. Selectivity α/β = 1.1:1.

*Synthesis of Allyl-1,2,3,5,8-pentadeoxy-6,7-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-α-L-arabino-non-1-enitol (**1aoα**).* Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, *I* = 254 nm) tR = 12.730 min. The compound obtained was a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56−7.55 (m, 2H), 7.52−7.51 (m, 2H), 7.47 (d, *J* = 6.9 Hz, 2H), 7.43−7.21 (m, 14H), 5.84 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.11−5.05 (m, 2H), 4.12−4.08 (m, 1H), 3.98 (d, *J* = 2.0 Hz, 1H), 3.85 (q, *J* = 7.2 Hz, 1H), 3.51 (d, *J* = 2.7 Hz, 1H), 2.30 (dt, *J* = 12.9, 6.4 Hz, 1H), 2.18 (dt, *J* = 13.8, 7.0 Hz, 1H), 1.79−1.75 (m, 1H), 1.32 (d, *J* = 13.5 Hz, 1H), 1.23 (d, *J* = 7.3 Hz, 3H), 0.97 (s, 9H), 0.93 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 135.9 (2C), 135.8 (2C), 135.1, 134.2, 133.8, 133.6, 129.8 (2C), 129.7 (2C), 127.7 (2C), 127.6 (2C), 116.7, 74.7, 71.5, 70.6, 63.2, 40.7, 33.4, 27.1, 27.0, 19.3, 19.2, 16.6. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{41}H_{52}O_3Si_2Na$ 671.3353; found 671.3356. $[\alpha]_D^{22}$ = 0.02 (*c* 0.1, $CHCl_3$).

*Synthesis of Allyl-1,2,3,5,8-pentadeoxy-6,7-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-β-L-arabino-non-1-enitol (**1aoβ**).* Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, *I* = 254 nm) tR = 13.537 min. The compound obtained was a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77−7.73 (m, 4H), 7.64−7.63 (m, 2H), 7.57−7.55 (m, 2H), 7.42−7.28 (m, 11H), 5.43 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 4.82 (d, *J* = 10.1 Hz, 1H), 4.76 (dd, *J* = 17.1, 1.4 Hz, 1H), 4.15 (ddd, *J* = 9.7, 7.1, 5.5 Hz, 1H), 3.65 (t, *J* = 7.3 Hz, 1H), 3.37−3.33 (m, 1H), 3.17−3.13 (m, 1H), 2.04 (dt, *J* = 13.0, 6.4 Hz, 1H), 1.79 (dt, *J* = 14.0, 7.1 Hz, 1H), 1.57 (dd, *J* = 5.3, 2.3 Hz, 1H), 1.10 (dt, *J* = 13.0, 10.4 Hz, 1H), 1.00 (s, 9H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 136.1 (2C), 135.9, 135.8, 135.7, 135.0, 134.8, 134.3, 134.2, 129.6, 129.5 (2C), 127.7 (2C), 127.5, 117.0, 79.7, 77.0, 75.8, 73.5, 40.1, 39.5, 27.4, 27.3, 20.4, 19.9, 19.3. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{41}H_{52}O_3Si_2Na$ 671.3353; found 671.3356. $[\alpha]_D^{22}$ = 0.02 (*c* 0.1, $CHCl_3$).

*Synthesis of Allyl-1,2,3,5,8-pentadeoxy-6,7-bis-O-(triisopropylsilyl)-2-deoxy-α,β-L-arabino-non-1-enitol (**2aoαβ**).* General procedure **A** was followed by taking the glycosyl donor 2,6-dideoxy-3,4-*O*-bis-(triisopropylsilyl)-2-deoxy-α,β-L-rhamnopyranosyl-1-acetate **2a** (50 mg, 0.10 mmol, 1.0 equiv) and the glycosyl acceptor **5o** (46 mg, 64 μL, 0.40 mmol, 4.0 equiv), and then, the reaction mixture was allowed to stir in dry DCM (2 mL, 0.5 M) under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (22 mg, 19 μL, 0.15 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel, washed

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with DCM, and quenched with a sat. $NaHCO_3$ solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the product **2ao** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 43 mg, yield = 88%. Selectivity α/β = 1.3:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (dddt, J = 20.6, 17.2, 10.2, 7.0 Hz, 2.3H), 5.09 (d, J = 6.9 Hz, 1H), 5.06−5.02 (m, 3.3H), 4.03−4.01 (m, 3.6H), 3.77 (ddd, J = 11.0, 7.7, 5.0 Hz, 1H), 3.61 (d, J = 2.7 Hz, 1H), 3.41−3.36 (m, 1H), 3.33 (t, J = 8.1 Hz, 1H), 3.26−3.21 (m, 1H), 2.32 (ddd, J = 21.1, 13.4, 6.3 Hz, 2.3H), 2.16 (tt, J = 14.0, 6.9 Hz, 2.3H), 2.04 (ddd, J = 12.7, 4.8, 1.5 Hz, 1H), 1.89−1.84 (m, 1.3H), 1.47 (d, J = 13.3 Hz, 1.3H), 1.41 (d, J = 7.3 Hz, 5H), 1.29 (d, J = 6.2 Hz, 3H), 1.20−1.13 (m, 2H), 1.13−0.99 (m, 97H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 135.3, 134.8, 117.0, 116.6, 79.4, 75.6, 75.3, 74.3, 71.7, 70.5, 63.1, 40.7, 40.4, 34.0, 19.3, 18.8, 18.6, 18.5, 18.3 (2C), 18.2, 16.7, 14.1, 14.0, 12.6, 12.4. HRMS (ESI) m/z: $[M + K]^+$ calcd for $C_{27}H_{56}O_3Si_2K$ 523.3405; found 523.3393. $[\alpha]_D^{22}$ = 0.02 (c 0.1, $CHCl_3$).

*Synthesis of Allyl-1,2,3,5,8-pentadeoxy-6,7-bis-O-[1,1,3,3-tetrakis(1-methylethyl)-1,3-disiloxanediyl]-α-L-arabino-non-1-enitol (**3ao**).* General procedure **A** was followed by taking the glycosyl donor 2,6-dideoxy-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-L-rhamnopyranosyl-1-acetate **3a** (50 mg, 0.11 mmol, 1.0 equiv) and the glycosyl acceptor **5o** (50 mg, 70 μL, 0.44 mmol, 4.0 equiv), and then, the reaction mixture was allowed to stir in dry DCM (2 mL, 0.55 M) under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (23 mg, 20 μL, 0.17 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel, washed with DCM, and quenched with a sat. $NaHCO_3$ solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the product **3ao** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 39 mg, yield = 82%. Selectivity α. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77 (ddt, J = 17.0, 10.1, 7.1 Hz, 1H), 5.11−5.07 (m, 2H), 3.98 (dd, J = 14.0, 7.2 Hz, 1H), 3.86 (ddd, J = 11.7, 8.3, 5.2 Hz, 1H), 3.47 (dq, J = 9.1, 6.1 Hz, 1H), 3.21 (t, J = 8.7 Hz, 1H), 2.53 (ddd, J = 14.4, 7.8, 6.9 Hz, 1H), 2.32−2.27 (m, 1H), 1.92 (dd, J = 13.4, 5.1 Hz, 1H), 1.81 (ddd, J = 13.4, 11.7, 6.1 Hz, 1H), 1.26 (d, J = 6.1 Hz, 3H), 1.09−0.93 (m, 28H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 135.0, 117.1, 80.7, 72.6, 71.9, 69.4, 36.1, 35.9, 18.8, 17.7, 17.6 (2C), 17.5, 17.4 (2C), 13.1 (2C), 12.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{43}O_4Si_2$ 415.2700; found 415.2688. $[\alpha]_D^{22}$ = 0.02 (c 0.1, $CHCl_3$).

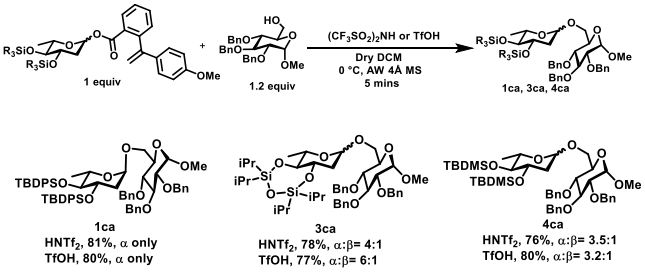
*Synthesis of Allyl-1,2,3,5,8-pentadeoxy-6,7-bis-O-tert-butyldimethylsilyl-α,β-L-arabino-non-1-enitol (**4aoαβ**).* General procedure **A** was followed by taking the glycosyl donor 2,6-dideoxy-3,4-di-*O*-*tert*-butyldimethylsilyl-L-rhamnopyranosyl-1-acetate **4a** (50 mg, 0.12 mmol, 1.0 equiv) and the glycosyl acceptor **5o** (55 mg, 76 μL, 0.48 mmol, 4.0 equiv), and then, the reaction mixture was allowed to stir in dry DCM (2 mL, 0.6 M) under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (26 mg, 22 μL, 0.18 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel, washed with DCM, and quenched with a sat. $NaHCO_3$ solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to give the product **4aoαβ** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 45 mg, yield = 86%. α- and β-Anomers were isolated in HPLC. Selectivity α/β = 2:1.

*Synthesis of Allyl-1,2,3,5,8-pentadeoxy-6,7-bis-O-tert-butyldimethylsilyl-α-L-arabino-non-1-enitol (**4aoα**).* Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 7.71 min. The compound obtained was a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 5.08 (dd, J = 17.2, 1.6 Hz, 1H), 5.04 (dd, J = 10.2, 0.8 Hz, 1H), 3.98−3.93 (m, 1H), 3.84−3.80 (m, 2H), 3.30−3.29 (m, 1H), 2.34 (dt, J = 13.4, 6.6 Hz, 1H), 2.17 (dt, J = 14.0, 6.8 Hz, 1H), 1.82 (ddd, J = 12.9, 9.5, 3.0 Hz, 1H), 1.44 (ddd, J = 13.3, 4.4, 2.8 Hz, 1H), 1.34 (d, J = 7.1 Hz, 3H), 0.90 (d, J = 1.6 Hz, 18H), 0.07−0.05 (m, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 135.3, 116.6, 74.3, 73.2, 70.5, 65.0, 39.7, 34.7, 26.1, 26.0, 18.3, 18.2, 17.4, 1.2, −4.3, −4.4, −4.5, −4.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{45}O_3Si_2$ 401.2907; found 401.2906. $[\alpha]_D^{22}$ = −43 (c 0.52, $CHCl_3$).

*Synthesis of Allyl-1,2,3,5,8-pentadeoxy-6,7-bis-O-tert-butyldimethylsilyl-β-L-arabino-non-1-enitol (**4aoβ**).* Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 9.25 min. The compound obtained was a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, J = 17.1, 10.2, 7.0 Hz, 1H), 5.06 (dd, J = 20.6, 5.1 Hz, 2H), 3.61 (ddd, J = 11.3, 8.1, 4.9 Hz, 1H), 3.39−3.35 (m, 1H), 3.20−3.16 (m, 1H), 3.09 (t, J = 8.5 Hz, 1H), 2.32 (dt, J = 13.0, 6.4 Hz, 1H), 2.15 (dt, J = 14.0, 6.8 Hz, 1H), 1.93 (ddd, J = 13.0, 4.8, 1.7 Hz, 1H), 1.34 (dd, J = 24.2, 11.4 Hz, 1H), 1.23 (d, J = 6.2 Hz, 3H), 0.90 (s, 9H), 0.90 (s, 9H), 0.08 (t, J = 8.5 Hz, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 134.8, 117.0, 78.7, 74.9, 74.7, 41.1, 40.2, 26.5, 26.3, 19.2, 18.6, 18.3, 1.2, −2.5, −2.7, −3.7, −3.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{45}O_3Si_2$ 401.2907; found 401.2906. $[\alpha]_D^{22}$ = −43 (c 0.52, $CHCl_3$).

General Procedure C for Glycosylation Reactions Using Thioglycoside Donors. The glycosyl donor **1b** (0.070 mmol, 1.0 equiv) and the glycosyl acceptor (0.105 mmol, 1.5 equiv) were taken in a round-bottomed flask (10 mL). The starting materials were coevaporated thrice with toluene in a rotary evaporator and dried under vacuum. The flask was then filled with dry DCM (2 mL for 0.070 mmol donor, 0.35 M) and activated 4 Å MS and was allowed to stir at 0 °C under an argon atmosphere. NIS (23 mg, 0.105 mmol, 1.5 equiv) was added to the reaction, and it was allowed to stir for 30 min at −40 °C under argon, followed by addition of TMSOTf (1.3 μL, 0.1 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was quenched by water (20 mL for 0.070 mmol of donor) and filtered through a sintered funnel; then, it was extracted with DCM (3 × 15 mL for 0.070 mmol of donor), dried over Na_2SO_4, concentrated in vacuo, and purified by column chromatography (Merck 60−120 mesh, 7 gm) and using HPLC (Hypersil Gold C18, I = 214 nm).

General Procedure D for Glycosylation Reactions Using PMPVB Donors. In an oven-dried round-bottom flask, activated acid-washed (AW) 4 Å molecular sieves (3.0 g/mmol) were taken followed by a rhamanosyl donor (1 equiv) and an acceptor (1.2 equiv) in dry DCM (0.03 M) under an Ar atmosphere at room temperature and stirred for 60 min. Then, the RB was cooled to 0 °C and triflic acid or triflamide was added ($(CF_3SO_2)_2NH$) (30 mol %). The reaction was monitored by TLC. The reaction was completed within 5 min. Et_3N was added to quench the reaction. The reaction mixture was worked up with water, washed with brine, dried using Na_2SO_4, and concentrated in a rotavapor. The resulting reaction mixture was purified through column chromatography to afford the product.[16a]



*Scope of Derivatives Using General Procedure C. Synthesis of 1-Propargyl-2,6-dideoxy-3,4-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-α-L-arabino-hexapyranoside (**1bb**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor propargyl alcohol **5b** (6 mg, 6 μL, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bb** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 39 mg, yield = 85%. Selectivity α. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 6.9 Hz, 2H), 7.51 (d, J = 7.0 Hz, 2H), 7.46 (dd, J = 14.6, 7.0 Hz, 4H), 7.41−7.35 (m, 4H), 7.31 (dd, J = 13.2, 7.2 Hz, 4H), 7.23 (dd, J = 16.0, 8.0 Hz, 4H), 5.19 (dd, J = 8.3, 3.7 Hz, 1H), 4.29 (qd, J = 15.7, 2.3 Hz, 2H),

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4.08 (d, J = 2.4 Hz, 1H), 3.88 (td, J = 10.7, 6.7 Hz, 1H), 3.55 (d, J = 2.6 Hz, 1H), 1.88 (ddd, J = 13.4, 8.4, 2.5 Hz, 1H), 1.74−1.71 (m, 1H), 1.13 (d, J = 6.9 Hz, 3H), 0.94 (s, 9H), 0.91 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 135.9 (3C), 135.8, 133.9, 133.7, 133.6, 133.5, 129.8 (2C), 129.7, 127.7 (4C), 93.4, 79.9, 74.7, 74.1, 73.1, 72.4, 54.7, 33.6, 30.2, 29.9, 27.0 (2C), 19.3, 19.2, 18.2, 14.3. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{43}H_{58}O_4Si_2Na$ 717.3771; found 717.3775. $[\alpha]_D^{22}$ = −7 (c 0.5, $CHCl_3$).

*Synthesis of 2-Cyanoethyl-2,6-dideoxy-3,4-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-α-L-arabino-hexapyranoside (**1bc**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor 3-hydroxypropionitrile **5c** (7.5 mg, 7 μL, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bc** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 41 mg, yield = 87%. Selectivity α. ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.46 (dd, J = 13.2, 7.5 Hz, 4H), 7.42−7.36 (m, 4H), 7.34−7.29 (m, 4H), 7.27−7.22 (m, 4H), 4.96 (dd, J = 8.1, 3.8 Hz, 1H), 4.10 (s, 1H), 3.92 (dt, J = 10.2, 6.3 Hz, 1H), 3.87−3.82 (m, 1H), 3.67 (dt, J = 10.1, 6.9 Hz, 1H), 3.55 (s, 1H), 2.61 (td, J = 6.5, 3.9 Hz, 2H), 1.86 (ddd, J = 13.5, 8.2, 2.4 Hz, 1H), 1.72 (dt, J = 13.6, 3.6 Hz, 1H), 1.10 (d, J = 6.9 Hz, 3H), 0.95 (s, 9H), 0.92 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 135.9 (3C), 135.8, 133.9, 133.8, 133.7, 133.6, 129.9, 129.8 (2C), 127.8 (2C), 127.7 (2C), 95.6, 74.9, 72.9, 72.3, 62.8, 33.5, 27.1, 27.0, 19.4, 19.3 (2C), 18.4. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{42}H_{55}O_4NSi_2Na$ 732.3880; found 732.3888. $[\alpha]_D^{22}$ = −4 (c 1.3, $CHCl_3$).

*Synthesis of 4-Hydroxybutyl-bicyclo[2.2.1]hept-5-ene-2-carboxylate-2,6-dideoxy-3,4-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-α-L-arabino-hexapyranoside (**1bd**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor **5d** (22 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bd** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 50 mg, yield = 89%. Selectivity α. ^1H NMR (500 MHz, $CDCl_3$) δ 7.57−7.56 (m, 2H), 7.52−7.450 (m, 2H), 7.49−7.45 (m, 4H), 7.37 (dd, J = 13.2, 5.9 Hz, 1H), 7.30 (dt, J = 12.0, 6.0 Hz, 1H), 7.25−7.22 (m, 4H), 6.14 (dd, J = 5.6, 2.9 Hz, 1H), 6.10 (dd, J = 5.5, 3.0 Hz, 1H), 4.92 (dd, J = 8.1, 3.5 Hz, 1H), 4.11 (t, J = 6.4 Hz, 3H), 3.88−3.84 (m, 1H), 3.78 (dt, J = 9.6, 6.3 Hz, 1H), 3.55 (t, J = 3.1 Hz, 1H), 3.41 (dt, J = 9.6, 6.3 Hz, 1H), 3.04 (s, 1H), 2.91 (s, 1H), 2.22 (dd, J = 10.1, 4.4 Hz, 1H), 1.93 (dt, J = 11.8, 4.0 Hz, 1H), 1.85 (ddd, J = 13.5, 8.2, 2.7 Hz, 1H), 1.74−1.63 (m, 8H), 1.12 (d, J = 6.9 Hz, 3H), 0.94 (s, 9H), 0.92 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.3, 138.1, 135.8 (3C), 135.7, 134.0, 133.9, 133.7, 133.6, 129.7, 129.6 (2C), 127.6 (2C), 127.5, 94.6, 74.8, 72.7, 72.5, 67.4, 64.4, 46.7, 46.4, 43.3, 41.7, 33.9, 32.0, 30.4, 30.1, 29.7, 29.4, 27.0, 26.9, 26.4, 25.6, 22.7, 19.3, 19.1, 18.2, 14.1. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for $C_{50}H_{64}O_6Si_2NH_4$ 834.4585; found 834.4575. $[\alpha]_D^{22}$ = −4 (c 1.3, $CHCl_3$).

*Synthesis of Cyclohexyl-2,6-dideoxy-3,4-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-α-L-arabino-hexapyranoside (**1be**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor cyclohexanol **5e** (11 mg, 11 μL, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1be** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 44 mg, yield = 92%. Selectivity α. ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 6.8 Hz, 2H), 7.51 (d, J = 6.8 Hz, 2H), 7.47 (t, J = 7.5 Hz, 4H), 7.41−7.34 (m, 4H), 7.30 (dd, J = 13.0, 7.3 Hz, 4H), 7.25 (dt, J = 15.4, 5.5 Hz, 4H), 5.10 (dd, J = 8.3, 3.3 Hz, 1H), 4.08 (d, J = 3.0 Hz, 1H), 3.92−3.88 (m, 1H), 3.58 (td, J = 9.3, 4.4 Hz, 1H), 3.53 (t, J = 2.9 Hz, 1H), 1.92 (d, J = 11.7 Hz, 1H), 1.87 (ddd, J = 13.2, 8.3, 2.6 Hz, 2H), 1.74−1.71 (m, 2H), 1.65−1.62 (m, 1H), 1.55−1.53 (m, 1H), 1.39−1.19 (m, 6H), 1.14 (d, J = 6.9 Hz, 3H), 0.94 (s, 9H), 0.91 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 135.9 (2C), 135.8 (2C), 134.0, 133.9, 133.6 (2C), 129.8, 129.7, 129.6, 127.7 (2C), 127.6 (2C), 92.1, 74.7, 72.9, 72.7, 34.6, 34.0, 32.2, 27.0 (2C), 25.9, 24.5, 24.4, 19.34 19.2, 18.2. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{44}H_{58}O_4Si_2Na$ 729.3771; found 729.3805. $[\alpha]_D^{22}$ = −4 (c 1.3, $CHCl_3$).

*Synthesis of 1-Adamantanyl-2,6-dideoxy-3,4-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-α-L-arabino-hexapyranoside (**1bf**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor 1-adamantanol **5f** (16 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bf** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 46 mg, yield = 85%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 14.677 min. Selectivity α/β = 18:1. ^1H NMR (500 MHz, $CDCl_3$) δ 7.59−7.57 (m, 2H), 7.51−7.50 (m, 2H), 7.47−7.44 (m, 4H), 7.40−7.33 (m, 4H), 7.29 (td, J = 7.4, 3.4 Hz, 4H), 7.24−7.20 (m, 4H), 5.37 (dd, J = 8.7, 2.9 Hz, 1H), 4.08 (d, J = 2.8 Hz, 1H), 3.97 (qd, J = 7.0, 3.1 Hz, 1H), 3.53 (t, J = 2.7 Hz, 1H), 2.12 (s, 3H), 1.89 (ddd, J = 13.2, 8.8, 2.6 Hz, 1H), 1.79 (q, J = 11.6 Hz, 6H), 1.65−1.59 (m, 6H), 1.49−1.45 (m, 1H), 1.20 (d, J = 7.1 Hz, 3H), 0.95 (s, 9H), 0.92 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.0 (2C), 135.9 (2C), 134.1 (2C), 133.9, 133.7, 129.8, 129.7, 129.6, 127.7 (3C), 127.6, 86.6, 74.0, 73.9 (2C), 73.2, 42.8, 36.6, 35.7, 30.9, 27.1 (2C), 19.4, 19.2, 18.0. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{49}H_{66}O_4Si_2Na$ 797.4397; found 797.4399. $[\alpha]_D^{22}$ = −74 (c 0.73, $CHCl_3$).

*Synthesis of 6-O-(3,4-O-Bis-(t-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoside (**1bg**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)-diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor **5g** (27 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bg** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 52 mg, yield = 86%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 11.797 min. Selectivity α. ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 7.0 Hz, 2H), 7.49−7.44 (m, 6H), 7.37 (qd, J = 11.8, 5.9 Hz, 4H), 7.29 (dd, J = 15.1, 7.6 Hz, 4H), 7.23 (dt, J = 11.1, 7.6 Hz, 4H), 5.53 (d, J = 5.0 Hz, 1H), 4.99 (dd, J = 7.8, 3.6 Hz, 1H), 4.61 (dd, J = 7.9, 2.2 Hz, 1H), 4.31 (dd, J = 4.9, 2.3 Hz, 1H), 4.25 (dd, J = 8.0, 1.4 Hz, 1H), 4.09 (d, J = 3.0 Hz, 1H), 3.97 (t, J = 5.4 Hz, 1H), 3.91 (dd, J = 10.5, 5.5 Hz, 1H), 3.87−3.83 (m, 1H), 3.63 (dd, J = 10.4, 6.8 Hz, 1H), 3.53 (t, J = 3.2 Hz, 1H), 1.87 (ddd, J = 13.3, 8.0, 2.6 Hz, 1H), 1.75−1.71 (m, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.34 (s, 6H), 1.10 (d, J = 6.9 Hz, 3H), 0.93 (s, 9H), 0.91 (s, 9H). Other spectroscopic data are in agreement with the reported data.[15]

*Synthesis of 3-O-(3,4-O-Bis-(t-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl)-1,2:5,6-Di-O-isopropylidene-α-D-glucofuranose (**1bh**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)-diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor **5h** (27 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bh** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 45 mg, yield = 74%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 12.193 min. Selectivity α/β = 5:1. α-Anomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 6.9 Hz, 2H), 7.52−7.48 (m, 6H), 7.37 (t, J = 7.7 Hz, 4H), 7.33−7.27 (m, 6H), 7.24−7.21 (m, 2H), 5.82 (d, J = 3.5 Hz, 1H), 4.91 (dd, J = 7.1, 4.5 Hz, 1H), 4.37−4.34 (m, 1H), 4.31 (t, J = 3.9 Hz, 2H), 4.25−4.20 (m, 1H), 4.12−4.08 (m, 2H), 4.00 (dd, J = 8.1, 6.4 Hz, 1H), 3.84−3.81 (m, 1H), 3.59 (s, 1H), 1.76 (ddd, J = 9.4, 7.5, 2.4 Hz, 1H), 1.66 (dt, J = 13.8, 4.3 Hz, 1H), 1.49 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.06 (d, J = 6.6 Hz, 3H), 0.93 (s, 18H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 135.9 (3C), 135.8, 134.2, 133.9, 133.7 (2C), 129.8 (4C), 127.7 (2C), 111.9, 108.7, 105.4, 93.4, 82.9, 81.1, 77.3, 76.0, 73.2, 72.5, 72.1, 66.9, 33.9,

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27.1 (2C), 27.0, 26.8, 26.5, 25.4, 19.4, 19.3, 18.6. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for $C_{50}H_{66}O_9Si_2NH_4$ 884.4589; found 884.4587. $[\alpha]_D^{22} = -68$ (c 0.75, $CHCl_3$).

*Synthesis of Methyl-6-deoxy-4-O-(3,4-O-bis-(t-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl)-2,3-O-isopropylidene-α-L-rhamnopyranoside (**1bi**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)-diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor **5i** (23 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bi** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 45 mg, yield = 78%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 9 min. Selectivity α. ^{1}H NMR (500 MHz, D_2O) δ 7.57 (d, J = 7.5 Hz, 4H), 7.51 (d, J = 7.1 Hz, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.40−7.22 (m, 12H), 5.50 (dd, J = 8.3, 3.7 Hz, 1H), 4.86 (s, 1H), 4.14−4.09 (m, 3H), 3.85−3.80 (m, 1H), 3.63−3.57 (m, 2H), 3.52 (s, 1H), 3.37 (s, 3H), 1.85−1.79 (m, 1H), 1.76 (dt, J = 13.1, 3.2 Hz, 1H), 1.57 (s, 3H), 1.50 (s, 3H), 1.34 (d, J = 3.8 Hz, 6H), 1.08 (d, J = 6.9 Hz, 3H), 0.96 (s, 9H), 0.90 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.0, 135.9 (2C), 134.2, 133.9, 133.8, 133.7, 129.8, 129.7 (3C), 127.7 (3C), 127.6, 109.3, 98.2, 94.1, 79.0, 77.6, 76.3, 74.7, 72.9, 72.6, 64.7, 54.9, 34.0, 28.2, 27.0 (2C), 26.6, 19.4, 19.3, 18.1, 17.7. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for $C_{48}H_{64}O_8Si_2NH_4$ 842.4483; found 842.4484. $[\alpha]_D^{22} = -75$ (c 0.60, $CHCl_3$).

*Synthesis of Methyl-fmoc-serine-(3,4-O-bis-(t-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl)-2,3-O-isopropylidene-α-L-rhamnopyranoside (**1bj**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)-diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor **5j** (36 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bj** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 58 mg, yield = 88%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 10.543 min. Selectivity α/β = 11:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.4 Hz, 2H), 7.64−7.61 (m, 2H), 7.57 (d, J = 6.9 Hz, 2H), 7.52−7.47 (m, 7H), 7.38 (dt, J = 14.6, 7.3 Hz, 7H), 7.28 (ddd, J = 12.9, 11.0, 6.5 Hz, 8H), 5.65 (d, J = 8.4 Hz, 1H), 4.86 (dd, J = 6.9, 3.8 Hz, 1H), 4.51 (dd, J = 8.8, 4.0 Hz, 1H), 4.47−4.45 (m, 1H), 4.37 (dd, J = 10.4, 7.4 Hz, 1H), 4.25 (t, J = 7.1 Hz, 1H), 4.16 (dd, J = 9.9, 3.0 Hz, 1H), 4.10 (s, 1H), 3.76 (s, 3H), 3.72 (t, J = 5.8 Hz, 1H), 3.65 (dd, J = 9.8, 2.9 Hz, 1H), 3.58−3.56 (m, 1H), 1.82−1.76 (m, 1H), 1.68−1.63 (m, 1H), 1.07 (d, J = 6.7 Hz, 3H), 0.93 (s, 9H), 0.93 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.9, 156.3, 144.1, 144.0, 141.5, 135.9 (2C), 135.8, 134.1, 133.8, 133.7, 129.9, 129.8 (2C), 127.9, 127.8, 127.7 (2C), 127.2, 125.3, 120.1, 95.3, 75.6, 72.4, 72.4, 67.3, 67.1, 54.6, 52.6, 47.4, 27.1, 27.0, 19.4, 19.2, 18.5. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for $C_{57}H_{65}NO_8Si_2NH_4$ 965.4592; found 965.4595. $[\alpha]_D^{22} = -71$ (c 0.77, $CHCl_3$).

*Synthesis of Methyl-fmoc-threonine-(3,4-O-bis-(t-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl)-2,3-O-isopropylidene-α-L-rhamnopyranoside (**1bk**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)-diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor **5k** (37 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bk** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 56 mg, yield = 83%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 254 nm) tR = 11.720 min. Selectivity α. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.65−7.62 (m, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.53−7.48 (m, 5H), 7.39−7.24 (m, 17H), 5.62 (d, J = 9.0 Hz, 1H), 4.93 (dd, J = 7.3, 3.4 Hz, 1H), 4.45 (dd, J = 10.4, 7.3 Hz, 1H), 4.39 (dd, J = 10.1, 7.3 Hz, 2H), 4.32 (d, J = 9.0 Hz, 1H), 4.27 (t, J = 7.1 Hz, 1H), 4.10 (s, 1H), 3.71 (s, 3H), 3.69−3.66 (m, 1H), 3.56 (s, 1H), 1.79−1.75 (m, 1H), 1.62 (d, J = 11.3 Hz, 1H), 1.16 (d, J = 6.2 Hz, 3H), 1.08 (d, J = 6.7 Hz, 3H), 0.94 (s, 9H), 0.93 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 171.2, 156.9, 144.2, 144.0, 141.5, 135.9, 135.8 (2C), 134.0, 133.6, 129.9, 129.8 (2C), 129.7, 127.8 (2C), 127.7 (2C), 127.2, 125.3 (2C), 120.1, 92.3, 75.4, 72.6, 72.5, 71.3, 67.3, 59.2, 52.4, 47.4, 34.2, 27.0 (2C), 19.4, 19.2, 18.2, 16.8. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for $C_{58}H_{67}NO_8Si_2NH_4$ 979.4749; found 979.4746. $[\alpha]_D^{22} = -66$ (c 0.61, $CHCl_3$).

*Synthesis of 1-O-(3,4-O-Bis-(t-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl)-2,3:4,5-Di-O-isopropylidene-α-D-fructopyranose (**1bl**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor **5l** (27 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bl** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 49 mg, yield = 79%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 8 min. Selectivity α/β = 15:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 6.1 Hz, 2H), 7.50−7.46 (m, 6H), 7.38 (d, J = 5.9 Hz, 4H), 7.31 (s, 4H), 7.25 (s, 4H), 5.00 (s, 1H), 4.61 (d, J = 7.0 Hz, 1H), 4.43 (s, 1H), 4.23 (d, J = 7.3 Hz, 1H), 4.12 (s, 1H), 3.91 (d, J = 12.5 Hz, 1H), 3.85 (s, 1H), 3.79 (d, J = 11.0 Hz, 1H), 3.73 (d, J = 13.0 Hz, 1H), 3.63 (d, J = 11.2 Hz, 1H), 3.58 (s, 1H), 1.86−1.82 (m, 1H), 1.73 (d, J = 12.6 Hz, 1H), 1.52 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.29 (s, 3H), 1.10 (d, J = 5.5 Hz, 3H), 0.92 (s, 18H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.0, 135.9, 135.8 (2C), 134.1 (2C), 133.9, 133.7, 129.8, 129.7 (3C), 127.7 (3C), 127.6, 109.3, 109.1, 108.7, 108.6, 103.2, 102.9, 95.8, 75.6, 72.5, 72.2, 71.3, 71.2, 71.0, 70.4, 70.2, 70.1, 68.6, 65.8, 61.5, 61.2, 34.0, 27.1, 27.0 (2C), 26.7, 26.6, 26.1, 25.9, 25.7, 25.5, 24.3, 19.4, 19.2, 18.4. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for $C_{51}H_{70}O_9Si_2NH_4$ 900.4902; found 900.4900. $[\alpha]_D^{22} = -59$ (c 0.66, $CHCl_3$).

*Synthesis of Methyl-6-O-(3,4-O-bis-(t-butyldiphenylsilyl)-2-deoxy-α-L-rhamnopyranosyl)-2,3-di-O-p-methylbenzyl-4-O-benzyl-D-galactopyranoside (**1bm**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor **5m** (52 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bm** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 49 mg, yield = 82%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 10.740 min. Selectivity α. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 6.9 Hz, 2H), 7.48−7.43 (m, 6H), 7.39−7.20 (m, 22H), 7.16 (d, J = 7.7 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 4.94 (dd, J = 11.1, 5.9 Hz, 2H), 4.82−4.80 (m, 2H), 4.69 (d, J = 11.5 Hz, 1H), 4.64 (dd, J = 11.1, 8.5 Hz, 3H), 4.08 (s, 1H), 4.00 (dd, J = 10.0, 3.5 Hz, 1H), 3.91 (dd, J = 10.1, 2.5 Hz, 1H), 3.86 (s, 1H), 3.81 (ddd, J = 12.9, 11.1, 6.2 Hz, 2H), 3.72 (dd, J = 10.3, 5.5 Hz, 1H), 3.58−3.53 (m, 1H), 3.52 (s, 1H), 3.33 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H), 1.84−1.80 (m, 1H), 1.64 (s, 1H), 1.08 (d, J = 6.9 Hz, 3H), 0.92 (s, 9H), 0.90 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 138.9, 137.4, 137.2, 136.1, 135.9 (2C), 135.8, 135.7, 134.0, 133.8, 133.7 (2C), 129.8, 129.7 (3C), 129.2, 129.1, 128.4 (2C), 128.3, 127.7 (4C), 127.6 (2C), 98.9, 95.3, 79.2, 76.3, 75.6, 74.8, 74.5, 73.6, 73.3, 73.0, 72.4, 69.9, 67.4, 55.3, 34.1, 27.1, 27.0, 21.3, 19.4, 19.2, 18.2. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for $C_{68}H_{82}O_9Si_2NH_4$ 1116.5841; found 1116.5846. $[\alpha]_D^{22} = -62$ (c 0.79, $CHCl_3$).

*Synthesis of Methyl-6-O-(3,4-O-bis-(t-butyldiphenylsilyl)-2-deoxy-α-L-rhamnopyranosyl)-2,3-di-O-p-methylbenzyl-4-O-benzyl-D-glucopyranoside (**1bn**).* General procedure **C** was followed by taking the glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (50 mg, 0.070 mmol, 1.0 equiv) and the glycosyl acceptor **5n** (52 mg, 0.105 mmol, 1.5 equiv) at −40 °C to get the product **1bn** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 47 mg, yield = 78%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 12.037 min. Selectivity α. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.1 Hz, 2H), 7.44 (t, J = 7.4 Hz, 5H), 7.38−7.30 (m, 4H), 7.30−7.17 (m, 18H), 7.15−7.12 (m, 4H), 4.95 (dd, J = 11.0, 4.8 Hz, 2H), 4.83 (d, J = 10.7 Hz, 1H), 4.78−4.75 (m, 2H), 4.62 (d, J = 12.1 Hz, 1H), 4.56 (d, J = 3.4 Hz, 1H), 4.48 (d,

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J = 10.8 Hz, 1H), 4.11 (d, J = 1.2 Hz, 1H), 3.97 (t, J = 9.5 Hz, 2H), 3.89−3.83 (m, 1H), 3.76 (dd, J = 9.9, 4.1 Hz, 1H), 3.59 (dd, J = 11.0, 5.0 Hz, 1H), 3.54−3.49 (m, 2H), 3.45 (t, J = 9.5 Hz, 1H), 3.33 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 1.89 (ddd, J = 13.3, 8.2, 2.3 Hz, 1H), 1.66 (dt, J = 13.6, 3.7 Hz, 1H), 1.09 (d, J = 6.8 Hz, 3H), 0.90 (s, 9H), 0.87 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.5, 137.7, 137.3, 136.1, 135.9 (2C), 135.8, 135.7, 135.4, 134.0, 133.8 (2C), 133.7, 129.8, 129.7, 129.2 (2C), 128.5, 128.4, 128.2, 128.2, 127.9, 127.7 (2C), 127.6, 98.2, 95.8, 82.1, 79.8, 78.1, 75.7, 75.3, 75.1, 73.3, 72.5 (2C), 70.3, 66.9, 55.1, 34.0, 27.0 (2C), 21.3 (2C), 19.3, 19.2, 18.4. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for $C_{68}H_{82}O_9Si_2NH_4$ 1116.5841; found 1116.5842. $[\alpha]_D^{22}$ = −77 (c 0.70, $CHCl_3$).

*Synthesis of Phenyl-2,3,4-tri-O-benzyl-6-O-(3,4-O-bis-(t-butyldiphenylsilyl)-2-deoxy-α-L-rhamnopyranosyl)-β-D-thioglucopyranoside (**1ap**).* General procedure **A** was followed by taking the glycosyl donor 2,6-dideoxy-3,4-*O*-bis-(*t*-butyldiphenylsilyl)-2-deoxy-L-rhamnopyranosyl-1-acetate **1a** (50 mg, 0.075 mmol, 1.0 equiv) and the glycosyl acceptor **5p** (163 mg, 0.3 mmol, 4.0 equiv), and then, the reaction mixture was allowed to stir in DCM (2 mL) under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (16 mg, 14 μL, 0.11 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel, washed with DCM, and quenched with a sat. $NaHCO_3$ solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by column chromatography in the ethyl acetate/hexane solvent system to get the product **1ap** as a colorless oil. R_f = 0.5 (10% hexane in ethyl acetate), amount = 69 mg, yield = 79%. Selectivity α. ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 6.9 Hz, 2H), 7.46 (dd, J = 13.6, 6.6 Hz, 7H), 7.37−7.21 (m, 29H), 5.57 (d, J = 1.0 Hz, 1H), 4.98 (dd, J = 7.7, 4.0 Hz, 1H), 4.90 (d, J = 10.8 Hz, 1H), 4.73 (d, J = 12.4 Hz, 1H), 4.62−4.54 (m, 4H), 4.32−4.30 (m, 1H), 4.13−4.08 (m, 2H), 4.00−3.99 (m, 1H), 3.93 (t, J = 9.4 Hz, 1H), 3.89−3.84 (m, 2H), 3.68 (dd, J = 10.8, 6.2 Hz, 1H), 3.55−3.53 (m, 1H), 1.91 (ddd, J = 13.5, 7.8, 2.6 Hz, 1H), 1.78−1.74 (m, 1H), 1.07 (d, J = 6.8 Hz, 3H), 0.89 (s, 9H), 0.89 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.6, 138.4, 138.1, 136.0 (2C), 135.9, 135.8, 134.4, 134.0, 133.9 (2C), 133.7, 132.3, 129.8, 129.7 (2C), 129.1, 128.5 (3C), 128.1, 128.0 (2C), 127.9, 127.8, 127.7 (2C), 127.6 (2C), 96.0, 85.9, 80.3, 76.3, 75.7, 75.5, 75.3, 72.9, 72.7, 72.2, 72.0 (2C), 67.3, 33.9, 29.9, 27.1, 27.0, 22.8, 19.4, 19.2, 18.6. HRMS (ESI) m/z: $[M + K]^+$ calcd for $C_{71}H_{80}O_8SSi_2K$ 1187.4750; found 1187.4745. $[\alpha]_D^{22}$ = −70 (c 0.65, $CHCl_3$).

*Synthesis of Trisaccharide (**1apg**).* General procedure **C** was followed by taking the glycosyl donor **1ap** (50 mg, 0.043 mmol, 1.0 equiv) and the glycosyl acceptor **5g** (17 mg, 0.064 mmol, 1.5 equiv) in DCM (2 mL) at −40 °C to get the product **1apg** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 41 mg, yield = 70%. Repurification was done using HPLC (Hypersil Gold C18, water/acetonitrile = 0/100, flow rate = 5.0 mL/min, I = 214 nm) tR = 11.027 min. Selectivity αα/αβ = 9.5:1. αα-Anomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 6.8 Hz, 2H), 7.46 (t, J = 6.6 Hz, 6H), 7.39 (d, J = 7.1 Hz, 2H), 7.35−7.19 (m, 25H), 5.52 (d, J = 5.0 Hz, 1H), 5.01 (dd, J = 6.8, 2.4 Hz, 2H), 4.87 (d, J = 10.7 Hz, 1H), 4.73 (q, J = 12.6 Hz, 2H), 4.61−4.57 (m, 3H), 4.52 (d, J = 10.7 Hz, 1H), 4.31 (dd, J = 4.9, 2.3 Hz, 1H), 4.16−4.12 (m, 2H), 4.08 (d, J = 9.6 Hz, 1H), 3.95 (t, J = 6.2 Hz, 1H), 3.91−3.87 (m, 2H), 3.81−3.76 (m, 2H), 3.70−3.66 (m, 2H), 3.54−3.53 (m, 1H), 1.93 (ddd, J = 13.4, 7.9, 2.5 Hz, 1H), 1.77−1.73 (m, 1H), 1.50 (s, 3H), 1.43 (s, 3H), 1.32 (d, J = 1.7 Hz, 6H), 1.10 (d, J = 6.8 Hz, 3H), 0.91 (s, 9H), 0.89 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 137.7, 137.6, 137.4, 134.8 (2C), 134.7, 134.6, 132.9, 132.9, 132.7, 132.6, 128.6, 128.5 (3C), 127.3, 126.9, 126.8, 126.6 (2C), 126.5 (2C), 126.4, 108.3, 107.5, 96.3, 95.4, 94.8, 79.0, 74.5, 74.1, 74.1, 73.7, 71.6, 71.3, 71.0 (3C), 69.9, 69.7 (2C), 66.2, 64.3, 32.8, 25.9, 25.9, 25.2, 25.0, 23.9, 23.6, 18.2, 18.1, 17.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{79}H_{102}O_{14}Si_2H$ 1331.6886; found 1331.6713. $[\alpha]_D^{22}$ = −42 (c 0.31, $CHCl_3$).

*Gram-Scale Synthesis of Compounds **1b** and **1bb**.*

*Gram-Scale Synthesis of Phenyl-2,6-dideoxy-3,4-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside (**1b**).* 3,4-Di-*O*-*tert*-butyldiphenylsilyl-L-rhamnopyranose was synthesized in the gram scale using the TTBPy·HCl catalyst system.[14] The synthesized anomeric hemiacetal (1.5 g, 2.4 mmol, 1.0 equiv) was taken in DCM, and to it, pyridine (393 μL, 3.6 mmol, 1.5 equiv) and Ac_2O (157 μL, 3.6 mmol, 1.5 equiv) were added, keeping in an ice bath. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched by water (40 mL) and it was extracted with DCM, dried over Na_2SO_4, and then concentrated in vacuo and purified by silica gel column chromatography to get the product **1a** as a colorless liquid with 81% yield, amount = 1.3 g.

2,6-Dideoxy-3,4-*O*-bis-(*t*-butyldiphenylsilyl)-2-deoxy-α,β-L-rhamnopyranosyl-1-acetate **1a** (1.95 mmol, 1.0 equiv) was taken in dry DCM, and activated 4 Å MS was added to it at 0 °C under an argon atmosphere. The glycosyl acceptor thiophenol (198 mg, 183 μL, 7.8 mmol, 4.0 equiv) was added to it, and the reaction mixture was allowed to stir under argon for 30 min followed by addition of $BF_3{\cdot}Et_2O$ (97 mg, 85 μL, 2.9 mmol, 1.5 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was filtered through a sintered funnel and washed with DCM (3 × 30 mL), and excess thiophenol was quenched with a 5% NaOH solution. After workup, the organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography (Merck 60−120 mesh, 20 gm) eluted with hexane/EA. Anomeric thioglycoside **1b** was isolated as a colorless oil, R_f = 0.5 (10% hexane in ethyl acetate), amount = 1.08 g, yield = 77%, selectivity α/β = 18:1. Along with the expected product **1b**, a trace amount of anomeric hemiacetal was also isolated during column purification, amount = 73 mg, yield = 6%.

*Gram-Scale Synthesis of 1-Propargyl-2,6-dideoxy-3,4-bis-O-[(1,1-dimethylethyl)diphenylsilyl]-α-L-arabino-hexapyranoside (**1bb**).* The glycosyl donor phenyl 2,6-dideoxy-3,4-bis-*O*-[(1,1-dimethylethyl)diphenylsilyl]-1-thio-α,β-L-arabino-hexapyranoside **1b** (1 g, 1.39 mmol, 1.0 equiv) and the glycosyl acceptor propargyl alcohol **5b** (119 mg, 119 μL, 2.09 mmol, 1.5 equiv) were taken in a round-bottomed flask (50 mL). The starting materials were coevaporated thrice with toluene in a rotary evaporator and dried under vacuum. The flask was then filled with dry DCM (20 mL) and activated 4 Å MS and was allowed to stir at 0 °C under an argon atmosphere. NIS (458 mg, 2.09 mmol, 1.5 equiv) was added to the reaction, and it was allowed to stir for 30 min at −40 °C under argon, followed by addition of TMSOTf (26 μL, 0.1 equiv). After complete consumption of the starting material (monitored by TLC), the reaction mixture was quenched by water (20 mL) and filtered through a sintered funnel; then, it was extracted with DCM (3 × 30 mL), dried over Na_2SO_4, concentrated in vacuo, and then purified by column chromatography (Merck 60−120 mesh, 20 gm) to get the product **1bb** as a colorless liquid. R_f = 0.4 in 10% EA/hexane, eluent = 5% EA in hexane, amount = 749 mg, yield = 81%, selectivity α. Along with the expected product **1bb**, a trace amount of anomeric hemiacetal was also isolated during column purification of the crude reaction mixture, amount = 35 mg, yield = 4%.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online supporting information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.2c02285.

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Spectroscopic data for all new compounds, 2D NMR spectra, HPLC chromatograms, and DFT calculations (PDF)

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Notes

The authors declare no competing financial interest.

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