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FULL PAPER

Synthesis and Glycosylation Properties of C6-silylated *Ido*- and *Gluco*-pyranosyl donors

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Abstract: Both stereoelectronic and steric interactions define the structure and reactivity of small molecules. Given its complexity, in carbohydrate chemistry, these interactions give rise to a variety of chemical behaviours that are often difficult to predict. Silyl groups are widely used as alcohol protecting groups and their study has provided insight on some very remarkable structure and reactivity features within carbohydrate chemistry. However, not much work has been put into the effect on reactivity of silyl groups directly attached to the sugar carbon chain. In this work, we have developed a synthetic methodology to obtain both D-glucosyl and L-idosyl donors containing a dimethylphenylsilyl group directly attached to C6. Glycosylation and competition experiments with different glycosyl acceptors have shown that this group is completely stable under glycosylation conditions and enhance reactivity beyond what a benzyl group attached to the sugar oxygen would do. Finally, we found adequate conditions for the protodesilylation of Si-containing glycosides to yield the 6-deoxy sugar analogue.

Introduction

Silicon (as other elements of group 14, e.g., germanium and tin) is relatively big in size and less electronegative than any non-metal (e.g., H, C, O, S). Consequently, a silyl group in organic chemistry can create electronic stabilizing interactions that can influence, or even determine, the reactivity and selectivity of the molecules of which they are part.[1] It has been known since the 1940s that silicon interactions decreases the leaving group departure rate at α-position, when comparing to a C atom, whereas placed in β- or γ-positions, it increases the rate, with the greatest enhancement being when placed in β-position, i.e., the β-silicon effect.[2,3] These β-silicon stabilizing interactions are maximized in an *anti*-periplanar arrangement;[4] γ-silicon interactions in a W-arrangement;[5] and δ-silicon interactions require an extended zig-zag pattern to maximize the through-bond interaction between the silyl group and the leaving group.[6]

The widespread use of silyl groups in organic chemistry has been possible due to the nature of σ bonds that they form with carbon or oxygen atoms, which are of similar bond strength as those between carbon and the same kind of atoms.[7] During the last decades, silyl groups have experienced an increasing use as protective groups for orthogonal strategies in carbohydrate chemistry,[8] where they are usually used to protect the sugar hydroxyl group by forming a silyloxy group. Silyl groups have also been used as a means in chain elongation in pentoses and hexoses to form heptoses or other derivatives (e.g., van Boom and co-workers[9–12] in the 1990s) due to their potential conversion into hydroxyl groups – what is known as the Tamao–Fleming oxidation.[13–16]

Another useful reaction replaces the silyl group by a hydrogen atom; this is known as a protodesilylation (or protiodesilylation). This reaction is particularly interesting in carbohydrate chemistry where the less common deoxy-sugars often are desired products. The reaction was developed by the Hurdlik group[17,18] and later modifications by the Roush group[19,20] broadened the scope and allowed much milder conditions when using a dimethylphenylsilyl group.

In carbohydrate chemistry, the influence of substituents on the reactivity of glycosyl donors has been known since the work of Paulsen and colleagues in the late 1970s.[21,22] However, the conceptualization of the phenomenon into the armed-disarmed concept[23] and its potential application was first described by Fraser-Reid and co-workers in 1990.[24,25] The direct correlation between the decreasing electron withdrawing abilities of the substituents and the increasing reactivity of the donors can be rationalized considering that, under the same circumstances, a more stable oxocarbenium ion (e.g., from an armed donor) will be more likely to be formed.

Glycosyl donors *O*-protected with silyl groups have shown increased reactivity in glycosylation reactions compared to the benzylated counterparts.[8] This increased reactivity is not only due to silyl groups being somewhat less electron withdrawing than benzyl, but also due to their bulkiness. When several silyl groups are attached to secondary alcohols on the pyranoside ring, a conformational change into an axially rich conformation can occur. Such conformational change influence the anomeric selectivity and dramatically increases the reactivity in glycosylation reactions compared to benzylated glycosyl donors, which are considered reactive (armed).[26]

Carbohydrates with the silyl groups directly attached to the carbon ring (C-Si bonded) have been much less explored. To the best of our knowledge, the reactivity of this kind of glycosides has not been studied, and there are only a handful of examples where these compounds have been prepared.

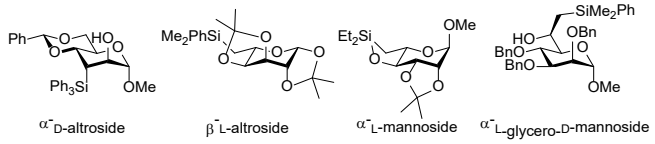


Figure 1. Among the few examples of carbohydrates with silyl groups directly attached to the carbon ring (C-Si bonded) found in the literature.

A few of these examples are shown in Figure 1. The preparation of D-altroside was described as a part of a work done in methodology development for preparation of sugars containing different elements of group 14; it was done by opening a C2–C3 epoxide.[27] Similar case for the L-altroside, which was prepared by a Rh-catalysed hydrosilation of a double bond.[28] The L-mannoside was formed by an Ir-catalysed C6–H activation.[29] In heptopyranoside, nucleophilic attack on a carbonyl group was used to form a new C–C bond, providing the sugar with a Si–C bond.[9]

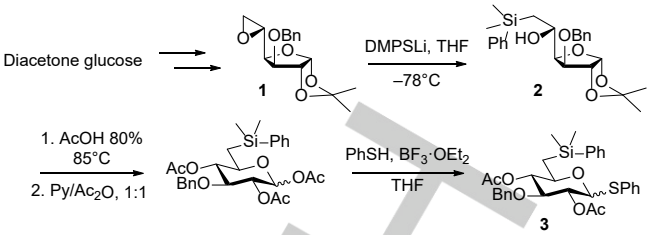
In this work, we have developed a synthetic methodology to obtain glycosyl donors containing a dimethylphenylsilyl group directly attached to C6, in both D-gluco and L-ido configurations. Glycosylation and competition experiments with these glycosyl donors against different acceptors have shown that the silyl group installed enhance reactivity beyond what a benzyl group attached to the sugar oxygen would do. Finally, we found adequate conditions for the protodesilylation of Si-containing glycosides to yield the 6-deoxy sugar analogue.

Results and Discussion

As the preferred silyl group for this study, the dimethylphenylsilyl group was chosen. This group is known to be reasonable stable in most of the common reaction conditions in carbohydrate chemistry and it can potentially be removed under relatively mild conditions, orthogonally to other functional groups in the carbohydrate.

For the synthesis of the glycosyl donors, two approaches for silyl group insertion were investigated. The first one being a regioselective ring-opening of an epoxide moiety by direct attack of a silyl lithium reagent; which leads to the D-*gluco* configuration. The second approach is a stereoselective nucleophilic attack on an aldehyde moiety by a Si-containing alkyl magnesium chloride, yielding the carbohydrate with the L-*ido* configuration.

For the first approach, D-glucose diacetonide was 3-*O*-benzylated in an excellent yield, followed by a regioselective deprotection of the 5,6-isopropylidene moiety under acidic conditions. The 5,6-anhydro sugar **1** was obtained via an intramolecular Mitsunobu reaction using standard conditions (DIAD and PPh_3) in a very good yield over two steps with retention of the *D-gluco*-configuration.[30]



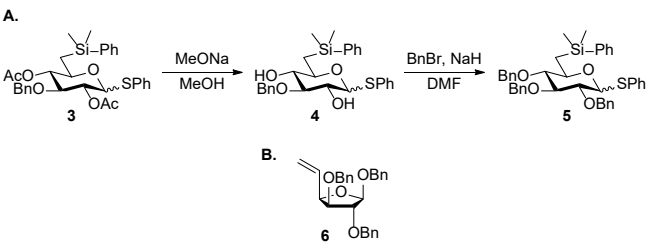
Scheme 1. Synthesis of donor **3**.

With epoxide **1** in hand, the silyl group was regioselectively attached to the sugar by epoxide opening (Scheme 1). To that purpose, dimethylphenylsilyl lithium (DMPSLi) was freshly prepared by treating chloro(dimethyl)phenylsilane with lithium under argon atmosphere. The resulting solution was added to the sugar (**1**) at −78°C.[31] The reaction was left at the low temperature and followed by TLC until completion – normally 3 to 4 h. As expected, the attack occurred on the least hindered carbon atom of the epoxide, i.e. C6, yielding exclusively the D-*gluco* product in very good yields (81%) on a half-gram scale. Uncompleted reactions, at larger scales, caused challenges in the separation of the product from the starting material and smaller scales were therefore preferred. The most convenient approach was therefore to use freshly prepared silyl lithium solutions and additions over a period of 30 to 60 min at −78°C (for 500 mg to 1 g of epoxide **1**) under an argon atm.

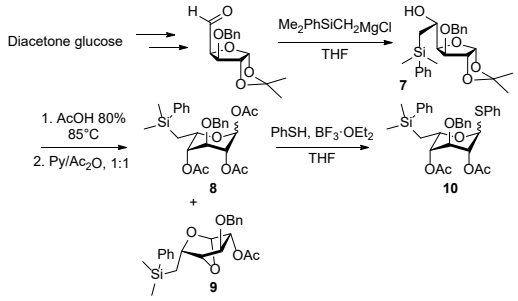
The 1,2-*O*-isopropylidene moiety was then removed by treating **2** with 80% acetic acid in water at 85°C, allowing the sugar to adapt the pyranose form. Acetylation and subsequent installation of the phenylsulfide moiety yielded glycosyl donor **3** as a mixture of anomers (α/β, 1:3) in a 72% yield over three steps.

With glycosyl donor **3** in hand, the 2,3,4-tri-*O*-benzyl counterpart **5** was synthesized (Scheme 2A). Thus, donor **3** was deacetylated under Zemplén conditions followed by benzylation via a Williamson ether synthesis for 60 to 90 min yielding glycosyl donor **5** in 89% yield over two steps. It is worth noting that performing the benzylation reaction for a longer time resulted in lower yields due to competing elimination reactions giving the terminal alkene **6** (Scheme 2B).

In order to access the L-*ido* configuration, 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose was prepared as previously described and then transformed into the aldehyde 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylo-pentodialdo-1,4-furanose by a Malaprade oxidation using $NaIO_4$ in DCM/H_2O (1:1) at 0°C, catalyzed by TBAB.[32]



Scheme 2. (A) Synthesis of donor **5**. (B) Side product after prolonged benzylation conditions.



Scheme 3. Synthesis of donor **10**.

With the aldehyde in hand, stereoselective nucleophilic addition of a Si-containing alkyl magnesium chloride was successfully accomplished yielding the desired *L-ido*-configuration in a L-ido/D-gluco ratio 97:3 (compounds **7** and **2**) in a 71% yield (Scheme 3).[33]

The stereochemistry of the addition on the aldehyde follows the Felkin–Ahn model, in which the stereochemistry of the attack is determined by the relative orientation of the groups attached to the α-carbonyl carbon atom (C4–C5 bond) (Figure 2).[34–37] Moreover, this stereochemical outcome is also compatible with the metal-ion of the nucleophile acting as a chelating agent between the carbonyl oxygen and the endocyclic oxygen atom.[38–40]

With silylated furanose **7** in hand, the same chemical transformations and conditions as in the D-gluco configuration were applied in order to obtain the desired L-idosyl donor **10**. Isopropylidene cleavage and subsequent acetylation furnished the product in 71% yield. Installation of the *S*-phenyl moiety was done in 68% yield, furnishing the desired L-idosyl donor **10** as an anomeric mixture (α/β, 2:1). Interestingly, after the isopropylidene cleavage and acetylation, side product **9** was obtained in 4% yield, presumably after dehydration of the α-anomer under acidic conditions, which is a sign of the higher reactivity as a consequence of introducing a C6-Si group.

Both anomers of the L-idosyl donor **10** were found to exhibit a $^1C_4$ conformation in agreement with the following data. First, a $^3J_{H\text{-}H} \lesssim$ 3 Hz suggested that vicinal protons atoms attached to the sugar ring are not coplanar to one another, and therefore, not axially oriented. Second, W-coupling constants ($^4J_{H2\text{-}H4}$ and, in the case of the α-anomer, also $^4J_{H1\text{-}H3}$) were measurable and in agreement with $^1J_{C1\text{-}H1}$ that indicates the orientation of H-1. This finding is especially relevant since axially oriented groups do not generally experience through-bond interactions with the developing positive charge that commonly forms during a glycosylation reaction as equatorially oriented groups do. This is usually translated into an increased reactivity for glycosyl donors with an axially rich conformation.[41,42]

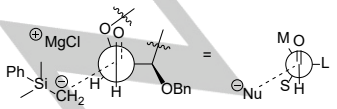
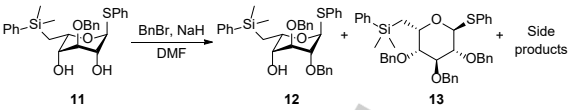


Figure 2. Stereochemistry of the addition over carbonyl (Felkin–Ahn model).

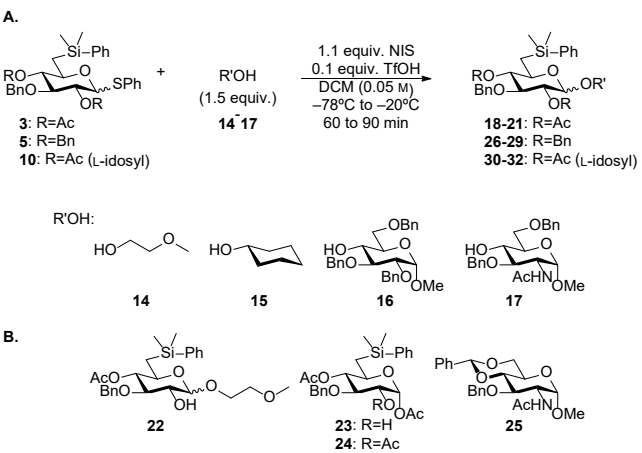


Scheme 4. Product profile of the benzylation of diol **11**.

With L-idosyl donor **10** in hand, attempts to obtain the tri-*O*-benzylated L-idolsyl donor **13** were done. Zemplén conditions applied to the L-idosyl donor **10** yielded diol **11** quantitatively. However, several attempts for the benzylation of the diol gave mixtures of products (Scheme 4), which seems to stem from the existence of competing elimination reactions of similar nature to the one observed in the benzylation of the D-glucosyl counterpart **4** on prolonged reaction times.

Applying standard benzylation conditions to α-L-idosyl diol **11** (BnBr, NaH, DMF, 0°C) gave, after 30 min reaction time, desired product **13** as well as 2-*O*-benzylated α-L-idosyl intermediate **12**. Together with them, three different terminal alkenes were also detected, which form at comparable rates as the desired product **13**. Other conditions for the benzylation were investigated; e.g. BnBr neat, TBAI with NaH; BnBr/DMF (1:1), TBAI with NaH; BnBr/toluene (1:1), TBAI with NaH; last, BnBr and Ag_2O in Cy/DCM (4:1). Disappointingly, all of them either yielded terminal alkenes at comparable rates to the rate of formation of the desired product **13** or gave uncompleted benzylation. Promoting the benzylation by silver(I) oxide in Cy/DCM (4:1) is supposed to minimize the formation of side products (e.g., undesired ethers), but the reaction stalls after alkylation of the least hindered alcohol, the 2-OH.[43]

While the L-idosyl donor **10** could be assigned to adopt a $^1C_4$ conformation, α-L-idosyl donor **13** (which was only obtained in small amounts) appeared to adopt a different conformation. First, $^3J_{H\text{-}H}$ ≈ 5-6 Hz, including $^3J_{H1\text{-}H2}$ = 4.8 Hz; indicate that the hydrogen atoms are closer to co-planarity (i.e. in an axial or pseudoaxial orientation), and therefore the functional groups, closer to an equatorial orientation. Second, W-couplings $^4J_{H2\text{-}H4}$ and $^4J_{H1\text{-}H3}$ are not observed, supporting an axial or pseudoaxial orientation of the hydrogen atoms.



Scheme 5. (A) Glycosylation reactions and acceptors. (B) Some of the side products identified during the glycosylation studies.

Table 1. Results of glycosylation studies.

Entry	Donor	Acceptor	Glycosylation products	Yield, % / α:β[b]
1	**3**	**14**	**18a, 18b**	82 / 16:84
2	**3**	**15**	**19a, 19b**	80 / 14:86
3	**3**	**16**	**20**	71 / Only β
4	**3**	**17**	**21**	38[a] / Only β
5	**5**	**14**	**26a, 26b**	88 / 52:48
6	**5**	**15**	**27a, 27b**	83 / 57:43
7	**5**	**16**	**28a, 28b**	67 / 65:35
8	**5**	**17**	**29a, 29b**	60[a] / 35:65
9	**10**	**14**	**30a, 30b**	81 / 91:9
10	**10**	**16**	**31**	58 / Only α
11	**10**	**17**	**32**	59[a] / Only α
12	**18b**	**14**	–	SM recovered

[a] Glycosylations with acceptor (0.67 equiv.) as a limiting reagent. [b] Ratio of anomers calculated from crude ^{1}H-NMR; normalized to 100.

Glycosylation Studies: The three new glycosyl donors (**3**, **5**, **10**) were subjected to glycosylation conditions in the presence of four different glycosyl acceptors (**14**-**17**) to determine scope and limitation in terms of selectivity, reactivity and yield (Scheme 5A).

As for the acceptors, **14** was chosen as a primary alcohol; **15**, as an unhindered secondary alcohol; **16**, as an example of a protected sugar; and **17**, to challenge the glycosyl donor, since this acceptor is known for its low reactivity. This low reactivity is due to the formation of an intermolecular hydrogen-bonding network by means of the amide. This network increases the steric hindrance, which renders the hydroxyl groups poor nucleophiles.[44]

Glycosyl donor **3** with acceptors **14** and **15** shows a clear β selectivity (α/β, 16:84 and 14:86, respectively) (Entries 2 and 3, Table 1). Despite this good selectivity, the amount of α-product obtained is still higher than expected from the acetyl neighbouring group participation in the reaction. A hypothesis that accounts for this observation is that the extra stabilization of the oxocarbenium ion provided by the silyl group reduces the energy gap between the acetoxonium and the oxocarbenium ion. This reduction would increase the amount of glycosyl product that forms by direct attack on the latter, which would give both α and β products. Yields for the reaction were very good (81% and 80%, resp.), even if acetyl α-glycoside **24** forms and partial deacetylation at 2-OH in all species occurs during the glycosylation (acetyl transfer is a well-known side reaction during glycosylations)[45]. Upon acetylation of the 2-OHs, the ratio between glycosyl product (**18** and **19**) and side product **24** was 94:6 and 91:9, respectively. D-Glucoside **24** was isolated in a 5% yield from glycosylation with acceptor **14**.

As it can be observed, using an unhindered secondary alcohol (**15**) as an acceptor instead of a primary alcohol (**14**) does not seem to affect the course of the reaction significantly.

With D-glucoside **16** as an acceptor (Entry 3, Table 1), only β anomer **20** was obtained in a 71% yield. In addition, acetyl α-D-glucoside **24** was found on ^{1}H-NMR (**20**/**24,** 96:4). The stereoselectivity of the reaction suggests that the size of acceptor **16** makes the glycosylation α-D-glucosyl product kinetically inaccessible.

With challenging acceptor **17** (Entry 4, Table 1), donor **3** was used in excess (0.67 equiv. of acceptor) in order to achieve a reasonable yield, albeit still low. Thus, β-glycoside **21** was isolated in 38 % yield as the only anomer of the desired product. From the anomeric region of the crude ^{13}C-NMR (85-105 ppm), remaining acceptor **17** as well as acetyl α-D-glucosides **23** and **24** were identified. Together with them, benzylidene acetal **25** was also found. This side product might form from a radical oxidation of the benzylic position followed by benzylidene formation due to the presence of NIS or I_2 (see Supporting Information).[46]

In order to determine whether the reaction is happening under kinetic control, an anomerization experiment was performed. Hereby, β-glycosyl product **18b** was treated under the NIS/TfOH conditions used for the glycosylations studies (including 1.5 equiv. of acceptor **14**). The unmodified starting material was fully recovered (Entry 12, Table 1) indicating that the glycosyl products in these experiments are formed irreversibly, i.e., the product profile is determined by the rate at which the products form (kinetic control), not by their stability (thermodynamic control).

Glycosyl donor **5** with acceptor **14** (Entry 5, Table 2) gave a clean reaction, but no selectivity. The yield of **26a** and **26b** combined was 88%. With secondary alcohol **15** (Entry 6, Table 2), it also resulted in a clean glycosylation, in this case with a low α-selectivity (α/β, 57:43 - **27a**/**27b**). The anomers could not be separated, and the yield was 83%.

With D-glucoside **16** as an acceptor (Entry 7, Table 1), α-selectivity increased until 65:35 (**28a**/**28b**) and products were isolated in a 67% yield. It seems that as the bulkiness of the acceptor increases, the α product is formed more favourably.

With challenging acceptor **17** (Entry 8, Table 1), the reaction resulted in a complex mixture of products as observed previously. Desired products **29** were isolated in a 60 % yield (acceptor as a limiting reagent) in a α/β ratio, 35:65. Benzylidene acetal **25** was again identified.

Glycosyl donor **10** with acceptor **14** (Entry 9, Table 1) resulted in a clean reaction, with an α/β ratio of 9:91 (**30a**/**30b**) in 81% yield.

Glycosylation of acceptor **16** (Entry 10, Table 1) gave exclusively the α-glycosyl product **30** in 58% yield, and 46% of acceptor was recovered. Despite the obtained yield, no other major peaks were found on the crude NMR spectra.

Glycosylation of challenging acceptor **17** (Entry 11, Table 1) gave the desired α-glycosyl product **32** as well as the benzylidene acetal **25**, isolated in 59% and 10%, respectively (see Supporting Information).

Competition Experiments: In order to shed light on the effect caused by a silyl group attached to C6 on the reactivity of glycosyl donors, a pair of competition experiments were performed (Scheme 6).

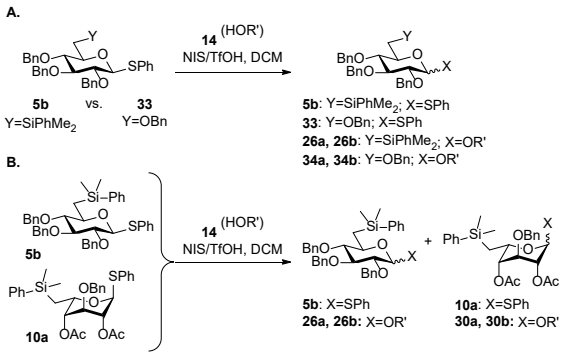
Two glycosyl donors (1 equiv. per donor) were set to compete under glycosylation conditions, using 5 equiv. of acceptor.

In the first experiment, silylated β-D-glucosyl donor **5b** was competing against Si-free analogue **33**[47], which was synthesised from D-glucose pentaacetate (Scheme 6A).

The experiment showed that for each molecule of Si-free glycosyl donor **33** that reacted, 1.6 molecules of the silylated donor **5b** reacted, which can solely be attributed to the substitution of the *O*-Bn group by the silyl group. The α/β ratio of silylated glycosylation products was 56:44 (**26a**/**26b**), which is in agreement with the ratio observed during the glycosylation experiments (52:48). The

α/β ratio of Si-free glycosylation products was interestingly 35:65 (**34a**/**34b**). No anomerization of the glycosyl donors (**5b** or **33**) was observed (see Supporting Information).

In the second experiment, silylated β-D-glucosyl donor **5b** was set to compete against silylated α-L-idosyl donor **10a** (Scheme 6B).

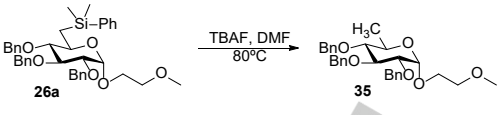


Scheme 6. Competition experiments. (A) Silylated vs. free-Si donor. (B) D-Gluco vs. L-ido donor.

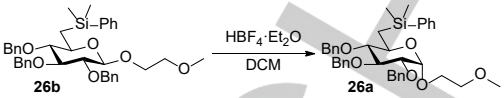
The experiment showed that for each molecule of L-idosyl donor **10a** that reacted, 1.2 molecules of the D-glucosyl donor **5b** reacted. The D-glucosyl donor **5b** has three equatorially oriented benzyl groups and is the β anomer, while the L-idosyl donor **10a** has two acetyl and one benzyl group, all axially oriented, and is the α anomer. The axial rich conformation of L-idosyl donor **10a** increases the reactivity of the otherwise more disarmed donor, making it of comparable reactivity to the armed benzylated D-glucosyl donor **33** – which is in agreement with the almost 2-fold reactivity enhancement of L-idosides comparing to D-glucosides found previously by the Wong group.[48] The α/β ratio of D-glucosyl products was 57:43 (**26a**/**26b**), which is also in agreement with the α/β ratio 52:48 and 56:44 observed during the glycosylation experiments and the previous competition experiment, respectively. The α/β ratio of L-idosyl glycosylation products was 88:12 (**30a**/**30b**), in agreement with the 91:9 observed during the glycosylation experiments. No anomerization of the glycosyl donors was observed (see Supporting Information).

Desilylation Studies: With the access to silylated glycosides, the focus was turned to developing methodologies to convert the silyl group into other functionalities.

With that purpose, silylated α-D-glucoside **26a** was treated overnight with TBAF in DMF at 80°C. After workup, desired glycoside **35** was obtained as a pure colourless solid in a 79% yield (Scheme 7).[20] When using acetylated glycosides as starting material, partial deacetylation was observed as a competing reaction. Tamao-Fleming oxidation was also investigated. Despite a number of publications reporting a Hg-free, two-pot methodology for the oxidation of a Me_2PhSi–C bond in heterocyclic molecules, attempts in different substrates did not bear the desired product (see Supporting Information).[16] Vincent and colleagues accomplished this transformation on carbohydrates by the use of mercuric salts.[33]



Scheme 7. Desilylation reaction.



Scheme 8. Anomerization reaction.

Interestingly, complete and clean anomerization of glycoside **26b** was observed upon less than 5 min of treatment with $HBF_4{\cdot}OEt_2$ (2 equiv.) in DCM at 0°C (Scheme 8). Upon this observation, and given that $HBF_4{\cdot}OEt_2$ is both a Brønsted–Lowry acid and a Lewis acid, two samples of **26b** were prepared and one of them was treated with TfOH and the other with $BF_3{\cdot}OEt_2$ in DCM at 0°C. While it did not occur as neatly as with $HBF_4{\cdot}OEt_2$, the Brønsted–Lowry acid seems to induce the anomerization to some extent, whereas the Lewis acid did not convert the starting material.

Conclusion

In this work, we have described two stereoselective methodologies to attach a silyl group to C-6 in hexoses, in order to obtain Si-containing D-glucosyl and L-idosyl donors. It has been shown that these glycosyl donors are completely stable under glycosylation conditions and react to give glycosyl products in good to excellent yields; they are also stable under several established transformations in carbohydrate chemistry. These glycosyl donors exhibit a selectivity in glycosylation that is comparable to that observed for the Si-free analogues. Competition experiments have shown that a silyl group in C-6 increases the reactivity of the molecule of which they form part, but only slightly. Finally, a methodology for a clean substitution of the silyl group by a H atom has also been described.

Experimental Section

General procedure A (for glycosylations with acceptors 14, 15 and 16). To an oven-dried 10-mL flask, glycosyl donor (100 mg) and glycosyl acceptor (1.5 equiv.) were added and dried under vacuum overnight. Under argon atmosphere, 4Å molecular sieves and dichloromethane (for a 0.05 M in donor) were added. When reagents were dissolved, NIS (1.1 equiv) was added and, within 5 seconds, the flask was submerged into an acetone–dry-ice bath at −78°C. TfOH (0.1 equiv) was added by syringe. The dry ice was removed from the bath and the temperature was let rise from −78°C to −35/−25°C over 60 to 90 min. When the reaction mixture acquired a full red–violet colour (from iodine in dichloromethane)—approx. at −40°C—, a TLC was taken. If the reaction was completed, the temperature was allowed to rise additional 10°C and quenched by 0.2 to 0.4 mL of Et_3N. The molecular sieves were removed by filtration through diatomite and the filtrate was diluted in EtOAc (20 mL). The solution was washed with water (20 mL), 1 M HCl(aq) (20 mL), 10% $Na_2S_2O_3$(aq) (20 mL), water (20 mL) and brine (20 mL) and then dried over $MgSO_4$(s). After concentration over reduced pressure, the crude was purified by flash silica column chromatography.

General procedure B (for glycosylations with 17). To an oven-dried 10-mL flask, glycosyl donor (40 mg) and glycosyl acceptor (0.67 equiv.) were added and dried under vacuum overnight. Under an argon atmosphere, 4Å molecular sieves and dichloromethane (for a 0.05 M in donor) were added. When reagents were dissolved, NIS (1.1 equiv) was added and, within 5 seconds, the flask was submerged into an acetone–dry-ice bath at −78°C. TfOH (0.1 equiv) was added by syringe. The dry ice was removed from the bath and the temperature was let rise from −78°C to 0°C over 60 to 90 min and then kept at 0°C for 4 to 5 h. The reaction was quenched by 0.2 to 0.4 mL of Et_3N. The molecular sieves were removed by filtration through diatomite and the filtrate was diluted in EtOAc (20 mL). The solution was washed with water (20 mL), 1 M HCl(aq) (20 mL), 10% $Na_2S_2O_3$(aq) (20 mL), water (20 mL) and brine (20 mL) and then dried over $MgSO_4$(s). After concentration over reduced pressure, the crude was purified by flash silica column chromatography.

General procedure for competition experiments. To an oven-dried, 10-mL flask, glycosyl donor A (0.10 mmol) and glycosyl donor B (0.10 mmol; 1 equiv) were added and dried under vacuum overnight. Under an argon atmosphere, 4Å molecular sieves and dichloromethane (for a 0.05 M in donor) were added. Acceptor (5 equiv) was then added. When the donors and acceptors were dissolved, NIS (1 equiv) was added and, within 5 seconds, the flask was submerged into an acetone dry-ice bath at −78°C. TfOH (0.1 equiv) was added by syringe. The dry ice was removed from the acetone bath and the temperature was allowed to rise from −78°C to −25/−15°C over 90 to 120 min. When the reaction mixture acquired a full red–violet colour (from iodine in dichloromethane)—approx. at −40°C—, a TLC was taken. Then, the temperature was allowed to rise additional 10°C, where it was quenched by adding 0.2 to 0.4 mL of Et_3N. The molecular sieves were removed by filtration through diatomite and the filtrate was diluted in EtOAc (20 mL). The solution was washed with water (20 mL), 1 M HCl(aq) (20 mL), 10% $Na_2S_2O_3$(aq) (20 mL), water (20 mL) and brine (20 mL) and then dried over $MgSO_4$(s). After concentration over reduced pressure, the products ratio was determined by ^{1}H NMR.

5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (1). To a 250-mL flask, diacetone D-glucose (10 g, 38.4 mmol), benzyl chloride (4.6 mL, 40.3 mmol) and dry DMF (100 mL) were added. The mixture was stirred at 0°C for 15 min and 60 % NaH(s) (1.61 g, 40.3 mmol) was added in several portions under vigorous stirring. After 60 min, the temperature was allowed to rise and the mixture was stirred for 3 h until no starting material was longer present. To quench the reaction, water (5 mL) was added dropwise preventing vigorous bubbling. An additional amount of water (95 mL) was added and the mixture was extracted with EtOAc (3 × 150 mL). The organic layers were combined and washed with water (2 × 150 mL) and brine (2 × 150 mL) and then dried over $MgSO_4$(s). After concentration over reduced pressure, the residue was purified by column chromatography (P.E./EtOAc, 3:1) yielding a colourless syrup (12.4 g, 35.4 mmol, 92 % yield).

To a 250-mL flask, 3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (12.4 g, 35.4 mmol) and acetic acid/water (85:15, 100 mL) were added. The mixture was stirred overnight until starting material has disappeared on TLC. Then, it was concentrated under reduced pressure and co-evaporated twice with toluene yielding crude 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose as an orange-brown syrup.

To a 500-mL flask, the crude 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose, diisopropyl azodicarboxylate (DIAD) (9.7 mL, 46.8 mmol), PPh_3 (12.9 g, 46.8 mmol) and toluene (200 mL) were added. The reaction was refluxed in an oil bath for 3 h. After concentration at reduced pressure, the residue was purified by column chromatography (P.E./EtOAc, 4:1) yielding 5,6-anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) (8.00 g; 77% over two steps) as a pale yellow syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H; *H*C$_{Ar}$), 5.95 (d, *J* = 3.7 Hz, 1H; H-1), 4.72 (d, *J* = 11.9 Hz, 1H; C*H*H, Bn-3), 4.65 (d, *J* = 11.9 Hz, 1H; CH*H*, Bn-3), 4.63 (d, *J* = 3.7 Hz, 1H; H-2), 4.08 (d, *J* = 3.2 Hz, 1H; H-3), 3.76 (dd, *J* = 7.2, 3.2 Hz, 1H; H-4), 3.30 (ddd, *J* = 7.2, 3.8, 2.6 Hz, 1H; H-5), 2.91 (dd, *J* = 5.1, 3.8 Hz, 1H; H-6a), 2.77 (dd, *J* = 5.1, 2.6 Hz, 1H; H-6b), 1.45 (s, 3H; C*H*$_3$C), 1.31 (s, 3H; C*H*$_3$C). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4 (*C*$_{Ar,q}$), 128.5 (2×*C*$_{Ar}$H), 128.0 (*C*$_{Ar}$H), 127.6 (2×*C*$_{Ar}$H), 111.9 (*C*(CH$_3$)$_2$), 105.4 (*C*-1), 82.7 (*C*-2), 82.1 (*C*-3), 81.7 (*C*-4), 72.4 (*C*H$_2$, Bn-3), 48.3 (*C*-5), 47.0 (*C*-6), 26.9 (*C*H$_3$C), 26.3 (*C*H$_3$C). The analytical data matches the one reported in the literature.[30]

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-6-dimethylphenylsilyl-α-D-glucofuranose (2).

Synthesis of dimethyl(phenyl)silyl lithium. To a 25-mL two-necked flask, Li(s) (0.15 g, 21.4 mmol, 12.5 equiv) was added. Under argon, the solid was rinsed with three volumes of petroleum ether to remove mineral oil. Then, THF (6 mL) was added and the mixture was cooled in a water–ice bath. Chloro(dimethyl)phenylsilane (1.46 mL, 8.55 mmol, 5 equiv) was added dropwise over 30 s. After 6 h, the temperature was allowed to rise and the maroon mixture was stirred overnight under argon.

To a 50-mL flask, 5,6-anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) (0.5 g, 1.71 mmol) and THF (7 mL) were added. The mixture was cooled down to −78°C in an acetone–dry-ice bath. Then, the freshly prepared dimethyl(phenyl)silyl lithium in THF was transfer under argon and added dropwise to the mixture by syringe pump over 30 min (15 mL/h). The mixture was stirred under argon at −78°C over 3 h. To quench the reaction, NH_4Cl(aq) (4 mL) was added and then brine (50 mL). The product was extracted with EtOAc (3 × 50 mL) and dried over $MgSO_4$(s). After concentration over reduced pressure, the residue was purified by column chromatography (PE/EtOAc, 4:1) yielding the product (**2**) as a pale yellow syrup (0.59 g, 1.38 mmol, 81 % yield). R_f 0.53 (PE/EtOAc, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.29 (m, 10H; *H*C$_{Ar}$), 5.97 (d, *J* = 3.9 Hz, 1H; H-1), 4.72 (d, *J* = 11.8 Hz, 1H; C*H*H, Bn-3), 4.62 (d, *J* = 3.9 Hz, 1H, H-2), 4.46 (d, *J* = 11.8 Hz, 1H; CH*H*, Bn-3), 4.10 (dddd, *J* = 10.3, 7.3, 6.4, 4.2 Hz, 2H; H-5), 4.04 (d, *J* = 3.4 Hz, 1H; H-3), 3.92 (dd, *J* = 6.4, 3.4 Hz, 1H; H-4), 2.27 (d, *J* = 7.3 Hz, 1H; O*H*), 1.46 (s, 3H; C*H*$_3$C), 1.33 (s, 3H; C*H*$_3$C), 1.18 (dd, *J* = 14.8, 4.2 Hz, 1H; H-6a), 1.03 (dd, *J* = 14.8, 10.3 Hz, 1H; H-6b), 0.35 (s, 3H; C*H*$_3$Si), 0.33 (s, 3H; C*H*$_3$Si).^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3 (*C*$_{Ar,q}$), 136.9 (*C*$_{Ar,q}$), 133.7 (2×*C*$_{Ar}$H), 129.0 (*C*$_{Ar}$H), 128.9 (2×*C*$_{Ar}$H), 128.5 (*C*$_{Ar}$H), 128.3 (2×*C*$_{Ar}$H), 127.9 (2×*C*$_{Ar}$H), 111.7 (*C*(CH$_3$)$_2$), 105.2 (*C*-1), 84.1 (*C*-4), 82.2 (*C*-3), 82.1 (*C*-2), 71.9 (CH$_2$, Bn-3), 67.8 (*C*-5), 26.9 (*C*H$_3$C), 26.4 (*C*H$_3$C), 22.5 (*C*-6), −1.8 (*C*H$_3$Si), −2.3 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{24}H_{32}KNaO_5Si$: 451.1917; found: 451.1921.

Phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranosides (3a, 3b). To a 250-mL flask, 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-6-dimethylphenylsilyl-α-D-glucofuranose (**2**) (4.03 g, 9.40 mmol) and acetic acid/water (4:1, 100 mL) was added. The mixture was stirred in an oil bath at 80°C overnight. After concentration under reduced pressure and co-evaporation twice with toluene, the residue was used in the next reaction. To the crude, acetic anhydride/pyridine (1:1, 100 mL) was added, and the mixture was stirred overnight at RT. After concentration over reduced pressure and co-evaporation twice with toluene, the residue was used in the next reaction.

To a 250-mL flask, the crude acetyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-D-glucopyranoside and dichloromethane (100 mL) were added. The mixture was cooled down to 0°C in a water-ice bath. Thiophenol (1.2 mL, 11.28 mmol, 1.2 equiv) and boron trifluoride etherate (1.2 mL, 9.40 mmol, 1 equiv) were added. The mixture was stirred for 5 h while the temperature was allowed to rise. To quench the reaction, $NaHCO_3$(aq) (10 mL) was added. After separation and drying over $MgSO_4$(s), the reaction mixture was directly concentrated under reduced pressure and co-evaporation twice with toluene. The residue was purified by column chromatography (30:1, toluene/acetone) yielding a yellow syrup (3.81 g; α/β, 24:76; 72 % over three steps).

Phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-α-D-glucopyranoside (3a). R_f 0.36 (PE/EtOAc, 6:1); $[\alpha]_D^{25}$ +94.4° (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.18 (m, 15H; *H*C$_{Ar}$), 5.93

(d, *J* = 5.6, 1H; H-1), 5.03 (dd, *J* = 10.1, 5.6, 1H; H-2), 4.88 (dd, *J* = 9.7, 9.2, 1H; H-4), 4.75 (d, *J* = 11.8, 1H; C*H*H, Bn-3), 4.62 (d, *J* = 11.8, 1H; CH*H*, Bn-3), 4.26 (ddd, *J* = 9.7, 8.7, 4.7, 1H; H-5), 3.79 (dd, *J* = 10.1, 9.2, 1H; H-3), 2.05 (s, 3H; C*H*$_3$CO), 1.96 (s, 3H; C*H*$_3$CO), 1.7 – 1.4 (m, 2H; H-6a; H-6b), 0.17 (s, 3H; C*H*$_3$Si), 0.14 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1 (*C*=O), 169.9 (*C*=O), 139.3 ($C_{Ar,q}$), 138.3 ($C_{Ar,q}$), 134.4 ($C_{Ar,q}$-S), 133.7 (2×C_{ArH}), 130.1 (2×C_{ArH}), 129.2 (2×C_{ArH}), 129.0 (C_{ArH}), 128.6 (2×C_{ArH}), 127.9 (C_{ArH}), 127.8 (2×C_{ArH}), 127.8 (2×C_{ArH}), 127.0 (C_{ArH}), 85.4 (*C*-1), 77.9 (*C*-3), 75.9 (*C*-4), 74.9 (*C*H$_2$, Bn-3), 73.6 (*C*-2), 69.7 (*C*-5), 21.1 (*C*H$_3$CO), 21.1 (*C*H$_3$CO), 18.9 (C-6), −1.7 (*C*H$_3$Si), −2.7 (*C*H$_3$Si). HR-MS: [*M*+K]$^+$ calcd for $C_{13}H_{36}KO_6SSi$: 603.1639; found: 603.1621.

Phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-β-D-glucopyranoside (3b). R_f 0.40 (PE/EtOAc, 6:1); $[\alpha]_D^{25}$ +26.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.18 (m, 15H; *H*C$_{Ar}$), 5.00 (dd, *J* = 10.3, 9.0 Hz, 1H; H-2), 4.86 (dd, *J* = 9.6 Hz, 9.4 Hz,1H; H-4), 4.57 – 4.51 (m, 3H; 2×C*H*H, Bn-3; H-1), 3.59 (dd, *J* = 9.6, 9.0 Hz, 1H; H-3), 3.32 (ddd, *J* = 11.0, 9.4, 3.0 Hz, 1H; H-5), 2.02 (s, 3H; C*H*$_3$CO), 1.95 (s, 3H; C*H*$_3$CO), 1.05 (dd, *J* = 14.9, 11.0 Hz, 1H; H-6a), 0.95 (dd, *J* = 14.9, 3.0 Hz, 1H; H-6b), 0.25 (s, 3H; C*H*$_3$Si), 0.24 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7 (*C*=O), 169.3 (*C*=O), 138.7 ($C_{Ar,q}$), 138.0 ($C_{Ar,q}$), 133.8 (2×C_{ArH}), 133.6 (2×C_{ArH}), 132.2 ($C_{Ar,q}$-S), 129.1 (2×C_{ArH}), 129.1 (C_{ArH}), 128.5 (2×C_{ArH}), 128.4 (C_{ArH}), 128.0 (2×C_{ArH}), 127.9 (C_{ArH}), 127.9 (2×C_{ArH}), 87.0 (*C*-1), 81.6 (*C*-3), 77.0 (*C*-5), 75.3 (*C*-4), 73.8 (*C*H$_2$, Bn-3), 71.8 (*C*-2), 21.1 (*C*H$_3$CO), 21.1 (*C*H$_3$CO), 19.1 (*C*-6), −1.6 (*C*H$_3$Si), −2.5 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{31}H_{36}NaO_6SSi$: 587.1900; found: 587.1900.

Phenyl 3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranosides (4a, 4b). To a 50-mL flask, phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**3**) (0.62 g, 1.10 mmol) and dry MeOH (25 mL) were added. To the solution, NaOH (4.4 mg, 0.11 mmol) was added. The mixture was stirred overnight at room temperature. To quench the reaction, acidic ion-exchange resin was rinsed in methanol and added in small portions to the reaction mixture until neutral pH was observed. After filtration, the solution was concentrated under reduced pressure, yielding a colourless syrup that was used directly in the next reaction.

Phenyl 3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-α-D-glucopyranoside (4a). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H; *H*C$_{Ar}$), 7.42 – 7.23 (m, 16H; *H*C$_{Ar}$), 5.54 (d, *J* = 5.4 Hz, 1H; H-1), 5.02 (d, *J* = 11.4 Hz, 1H; C*H*H, Bn), 4.76 (d, *J* = 11.4 Hz, 1H; CH*H*, Bn), 4.12 (ddd, *J* = 10.2, 9.0, 3.2 Hz, 1H; H-5), 3.96 (ddd, *J* = 9.6, 8.6, 5.4 Hz, 1H; H-2), 3.34 (dd, *J* = 9.6, 8.9 Hz, 1H; H-3), 3.24 (ddd, *J* = 9.0, 8.9, 2.5 Hz, 1H; H-4), 2.35 (d, *J* = 8.6 Hz, 1H; O*H*-2), 2.19 (d, *J* = 2.5 Hz, 1H; O*H*-4), 1.47 (dd, *J* = 14.9, 3.2 Hz, 1H; H-6a), 1.04 (dd, *J* = 14.9, 10.2 Hz, 1H; H-6b), 0.27 (s, 3H; C*H*$_3$Si), 0.26 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6 ($C_{Ar,q}$), 138.5 ($C_{Ar,q}$), 135.0 ($C_{Ar,q}$-S), 133.7 (2×C_{ArH}), 130.9 (2×C_{ArH}), 129.3 (2×C_{ArH}), 129.0 (C_{ArH}), 128.9 (2×C_{ArH}), 128.2 (C_{ArH}), 128.2 (2×C_{ArH}), 127.8 (2×C_{ArH}), 127.3 (C_{ArH}), 91.8 (*C*-1), 83.4 (*C*-3), 76.1 (*C*-4), 75.2 (*C*H$_2$, Bn), 72.7 (*C*-2), 72.0 (*C*-5), 19.3 (*C*-6), −1.7 (*C*H$_3$Si), −2.2 (*C*H$_3$Si).

Phenyl 3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-β-D-glucopyranoside (4b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 6H; *H*C$_{Ar}$), 7.37 – 7.15 (m, 18H; *H*C$_{Ar}$), 4.98 (d, *J* = 11.6 Hz, 1H; C*H*H, Bn), 4.71 (d, *J* = 11.6 Hz, 1H; CH*H*, Bn), 4.40 (d, *J* = 9.7 Hz, 1H; H-1), 3.46 (ddd, *J* = 9.7, 8.6, 1.9 Hz, 1H; H-2), 3.30 (dd, *J* = 8.7, 8.6 Hz, 1H; H-3), 3.25 (ddd, *J* = 10.5, 9.0, 3.0 Hz, 1H; H-5), 3.19 (ddd, *J* = 9.0, 8.7, 2.4 Hz, 1H; H-4), 2.48 (d, *J* = 1.9 Hz, 1H; O*H*-2), 2.17 (d, *J* = 2.4 Hz, 1H; O*H*-4), 1.39 (dd, *J* = 14.9, 3.0 Hz, 1H; H-6a), 1.00 (dd, *J* = 14.9, 10.5 Hz, 1H; H-6b), 0.30 (s, 3H; C*H*$_3$Si), 0.30 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1 ($C_{Ar,q}$), 138.6 ($C_{Ar,q}$), 133.8 (2×C_{ArH}), 133.8 (2×C_{ArH}), 131.5 ($C_{Ar,q}$-S), 129.2 (2×C_{ArH}), 129.0 (C_{ArH}), 128.8 (2×C_{ArH}), 128.5 (C_{ArH}), 128.2 (2×C_{ArH}), 128.1 (C_{ArH}), 127.8 (2×C_{ArH}), 89.3 (*C*-1), 85.1 (*C*-3), 78.4 (*C*-5), 75.6 (*C*-4), 74.9 (*C*H$_2$, Bn), 73.0 (*C*-2), 19.6 (*C*-6), −1.6 (C*H*$_3$Si), −2.2 (C*H*$_3$Si).

Phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (5a, 5b). To a 100-mL flask, phenyl 3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**4**) (528 mg, 1.10 mmol), benzyl bromide (0.40 mL, 3.30 mmol, 3 equiv) and dry dimethylformamide (24 mL) were added. The mixture was cooled to 0°C in a water-ice bath. To the mixture, 60% NaH (132 mg, 3.30 mmol) was added in one portion. The reaction mixture was stirred at 0°C and monitored by TLC, since elimination-products may form at prolonged reaction times. After 60 min the reaction was completed. To quench the reaction, water (2 mL) was added dropwise, avoiding intense bubbling. Then, an additional amount of water (23 mL) was added and the mixture was extracted with EtOAc (3 × 75 mL). The organic layers were combined and washed with water (2 × 40 mL) and brine (2 × 40 mL). After drying over $MgSO_4$(s), the mixture was concentrated to dryness over reduced pressure. The residue was purified by column chromatography (40:1 to 20:1, PE/EtOAc) yielding a colourless syrup (647 mg; 89% over two steps)

Phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-α-D-glucopyranoside (5a). R_f 0.27 (PE/EtOAc, 19:1)**;** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.17 (m, 25H; *H*C$_{Ar}$), 5.62 (d, *J* = 5.3 Hz, 1H; H-1), 4.24 (ddd, *J* = 10.5, 9.3, 2.7 Hz, 1H; H-5), 3.85 (dd, *J* = 9.8, 5.3 Hz, 1H; H-2), 3.79 (dd, *J* = 9.8, 8.6 Hz, 1H; H-3), 3.16 (dd, *J* = 9.3, 8.6 Hz, 1H; H-4), 1.44 (dd, *J* = 14.9, 2.7 Hz, 1H; H-6a), 0.92 (dd, *J* = 14.9, 10.5 Hz, 1H; H-6b), 0.15 (s, 3H; C*H*$_3$Si), 0.10 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0 – 126.3 [aromatic C atoms], 87.0 (*C*-1), 84.6 (*C*-4), 82.5 (*C*-3), 80.2 (*C*-2), 75.9 (*C*H$_2$, Bn), 75.6 (*C*H$_2$, Bn), 72.7 (*C*H$_2$, Bn), 70.8 (*C*-5), 19.3 (*C*-6), −1.8 (*C*H$_3$Si), −2.5 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{41}H_{44}NaO_4SSi$: 683.2627; found: 683.2645.

Phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-β-D-glucopyranoside (5b). R_f 0.32 (PE/EtOAc, 19:1); $[\alpha]_D^{25}$ +44.8° (*c* 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H; *H*C$_{Ar}$), 7.41 – 7.37 (m, 3H; *H*C$_{Ar}$), 7.36 – 7.23 (m, 20H; *H*C$_{Ar}$), 4.90 (d, *J* = 10.3 Hz, 1H; C*H*H, Bn-a), 4.87 (d, *J* = 10.9 Hz, 1H; C*H*H, Bn-b), 4.86 (d, *J* = 10.9 Hz, 1H; C*H*H, Bn-c), 4.82 (d, *J* = 10.9 Hz, 1H; CH*H*, Bn-b), 4.74 (d, *J* = 10.3 Hz, 1H; CH*H*, Bn-a), 4.67 (d, *J* = 10.9 Hz, 1H; CH*H*, Bn-c), 4.59 (d, *J* = 9.8 Hz, 1H; H-1), 3.59 (dd, *J* = 8.8, 8.8 Hz, 1H; H-3), 3.47 (dd, *J* = 9.8, 8.8 Hz, 1H; H-2), 3.26 (dd, *J* = 11.0, 9.1, 2.5 Hz, 1H; H-5), 3.20 (dd, *J* = 9.1, 8.8 Hz, 1H; H-4), 1.37 (dd, *J* = 14.7, 2.5 Hz, 1H; H-6a), 0.93 (dd, *J* = 14.7, 11.0 Hz, 1H; H-6b), 0.22 (s, 3H; C*H*$_3$Si), 0.20 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0 ($C_{Ar,q}$), 138.6 ($C_{Ar,q}$), 138.3 ($C_{Ar,q}$), 138.2 ($C_{Ar,q}$), 133.8 (2×C_{ArH}), 133.6 ($C_{Ar,q}$-S), 132.9 (2×C_{ArH}), 129.1 (2×C_{ArH}), 128.9 (C_{ArH}), 128.6 (4×C_{ArH}), 128.5 (2×C_{ArH}), 128.3 (2×C_{ArH}), 128.1 (2×C_{ArH}), 128.0 (2×C_{ArH}), 128.0 (C_{ArH}), 128.0 (C_{ArH}), 127.9 (C_{ArH}), 127.8 (C_{ArH}), 127.8 (2×C_{ArH}), 88.6 (*C*-1), 86.7 (*C*-3), 84.4 (*C*-4), 81.4 (*C*-2), 78.0 (*C*-5), 75.9 (*C*H$_2$, Bn), 75.6 (*C*H$_2$, Bn), 75.6 (*C*H$_2$, Bn), 19.5 (*C*-6), −1.6 (*C*H$_3$Si), −2.5 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{41}H_{44}NaO_4SSi$: 683.2627; found: 683.2645.

Benzyl 2,3-di-*O*-benzyl-5,6-dideoxy-β-D-xylo-hex-5-enofuranoside (6). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H; *H*C$_{Ar}$), 7.48 – 7.20 (m, 28H; *H*C$_{Ar}$), 6.04 (ddd, *J* = 17.2, 10.3, 7.8 Hz, 1H; H-5), 5.39 (ddd, *J* = 17.2, 1.6, 1.1 Hz, 1H; H-6a), 5.32 (ddd, *J* = 10.3, 1.6, 0.8 Hz, 1H; H-6b), 5.07 (d, *J* = 4.3 Hz, 1H; H-1), 4.85 (d, *J* = 12.3 Hz, 1H; C*H*H, Bn), 4.74 – 4.68 (m, 1H; H-4), 4.66 – 4.54 (m, 5H; 5×C*H*H Bn), 4.38 (dd, *J* = 6.9, 6.0 Hz, 1H; H-3), 4.06 (dd, *J* = 6.0, 4.3 Hz, 1H; H-2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2 ($C_{Ar,q}$), 137.9 ($C_{Ar,q}$), 137.8 ($C_{Ar,q}$), 134.3 (*C*-5), 133.7, 133.1, 129.2, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7 [aromatic C atoms], 118.7 (*C*-6), 98.2 (*C*-1), 83.8 (*C*-2), 82.7 (*C*-3), 78.9 (*C*-4), 72.5 (*C*H$_2$ Bn), 72.4 (*C*H$_2$ Bn), 69.1 (*C*H$_2$ Bn). HR-MS: [*M*+Na]$^+$ calcd for $C_{27}H_{28}NaO_4$: 439.1885; found: 439.1889.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-6-dimethylphenylsilyl-α-L-idofuranose (7). To a 1-L flask, 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (10.81 g, 34.83 mmol), tetrabutylammonium chloride (0.97 g, 3.48 mmol) and DCM/H_2O (1:1, 400 mL) were added. In order to prevent periodate decomposition, the mixture was excluded from light by covering the flask with aluminium foil. After cooling down the mixture to 0°C in a

water-ice bath, sodium periodate (8.96 g, 41.80 mmol) was added in three portions over 30 min. The mixture was stirred for 150 min. After this, the aqueous layer was extracted with DCM (3 × 100 mL). The organic layers were combined, washed with water (2 × 80 mL) and brine (80 mL) and dried over $MgSO_4$. After concentration over reduced pressure, the residue was stored at 0°C and used in the next reaction without further purification.

To a 50-mL flask, dry magnesium (119 mg, 4.81 mmol) was added and it was mechanically activated overnight by dry stirring under an argon atmosphere. To the dry metal, dry THF (10.5 mL) was added and then (chloromethyl)dimethylphenylsilane (855 mg, 4.49 mmol) was added dropwise. The reaction mixture was refluxed for 90 min, allowed to cool down to room temperature and then to 0°C in an ice-water bath. 3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-xylo-pentodialdo-1,4-furanose (0.5 g, 4.492 mmol) in THF (7.30 mL) was added dropwise over 45 min. Once the addition was done, the mixture was stirred for 2 h. To quench the reaction, water (1 mL) was added. After filtration over a pad of diatomite, NH_4Cl(aq) (25 mL) was added, the mixture was extracted with DCM (3 × 30 mL). The organic layers were combined, washed with brine (3 × 30 mL) dried over $MgSO_4$(s) and concentrated under reduced pressure. The residue was purified by column chromatography (toluene/acetone, 24:1) yielding a yellowish syrup (546 mg, 1.27 mmol; 71 %; L-ido/D-gluco, 97:3). R_f 0.17 (toluene/acetone, 24:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H; *H*C$_{Ar}$), 7.37 – 7.20 (m, 8H; *H*C$_{Ar}$), 5.96 (d, *J* = 3.8 Hz, 1H; H-1), 4.67 (d, *J* = 11.8 Hz, 1H; C*H*H, Bn), 4.63 (d, *J* = 3.8 Hz, 1H; H-2), 4.40 (d, *J* = 11.8 Hz, 1H; CH*H*, Bn), 4.11 (ddd, *J* = 11.0, 6.4, 3.3, 1.9 Hz, 1H; H-5), 3.97 (dd, *J* = 6.4, 3.4 Hz, 1H; H-4), 3.90 (d, *J* = 3.4 Hz, 1H; H-3), 2.54 (dd, *J* = 2.2, 1.9 Hz, 1H; O*H*), 1.47 (s, 3H; C*H*$_3$C), 1.32 (s, 3H; C*H*$_3$C), 1.05 (dd, *J* = 14.4, 11.0 Hz, 1H; H-6a), 0.83 (ddd, *J* = 14.4, 3.3, 2.2 Hz, 1H; H-6b), 0.35 (s, 3H; C*H*$_3$Si), 0.33 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6 (*C*$_{Ar,q}$), 136.9 (*C*$_{Ar,q}$), 133.8 (2×*C*$_{Ar}$H), 128.9 (*C*$_{Ar}$H), 128.7 (2×*C*$_{Ar}$H), 128.3 (*C*$_{Ar}$H), 128.1 (2×*C*$_{Ar}$H), 127.8 (2×*C*$_{Ar}$H), 111.9 (*C*(CH$_3$)$_2$), 105.1 (*C*-1), 85.6 (*C*-4), 82.3 (*C*-3, C-2), 71.9 (*C*H$_2$, Bn), 68.1 (*C*-5), 26.9 (C*H*$_3$CO), 26.5 (C*H*$_3$CO), 20.2 (*C*-6), −1.5 (C*H*$_3$Si), −2.3 (C*H*$_3$Si).

Phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-L-idopyranosides (10a, 10b). This product was synthesised as mixture of anomers in a 3-step procedure equivalent to the one used to obtain the D-gluco isomers (**3a**, **3b**) from **2**. In this case, using **7** as a starting material.

Acetyl 2,4-di-*O*-Acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-α-L-idopyranoside (8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H; *H*C$_{Ar}$), 7.40 – 7.22 (m, 12H; *H*C$_{Ar}$), 5.99 (d, *J* = 1.8 Hz, 1H; H-1), 4.97 (ddd, *J* = 2.8, 1.8, 0.9 Hz, 1H; H-2), 4.65 (d, *J* = 11.8 Hz, 1H; C*H*H, Bn), 4.62 (d, *J* = 11.8 Hz, 1H; CH*H,* Bn), 4.57 (ddd, *J* = 2.6, 1.7, 0.9 Hz, 1H; H-4), 4.19 (ddd, *J* = 9.3, 5.3, 1.7 Hz, 1H; H-5), 3.80 (dd, *J* = 2.8 Hz, 1H; H-3), 2.12 (s, 3H; C*H*$_3$CO), 2.10 (s, 3H; C*H*$_3$CO), 2.06 (s, 3H; C*H*$_3$CO), 1.33 (dd, *J* = 14.8, 9.3 Hz, 1H), 0.96 (dd, *J* = 14.8, 5.3 Hz, 1H), 0.34 (s, 3H; C*H*$_3$Si), 0.31 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4 (*C*=O), 170.1 (*C*=O), 168.9 (*C*=O), 138.5 (*C*$_{Ar,q}$), 137.2 (*C*$_{Ar,q}$), 133.7 (2×*C*$_{Ar}$H), 129.2 (*C*$_{Ar}$H), 128.6 (2×*C*$_{Ar}$H), 128.2 (*C*$_{Ar}$H), 128.0 (2×*C*$_{Ar}$H), 127.8 (2×*C*$_{Ar}$H), 90.2 (*C*-1), 73.9 (*C*-3), 72.7 (*C*H$_2$, Bn), 72.0 (*C*-5), 69.5 (*C*-4), 66.6 (*C*-2), 21.1 (*C*H$_3$CO), 21.0 (*C*H$_3$CO), 21.0 (*C*H$_3$CO), 18.1 (*C*-6), −2.0 (*C*H$_3$Si), −2.8 (*C*H$_3$Si).

1,4-Anhydro-2-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-β-L-idopyranose (9). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H; *H*C$_{Ar}$), 7.39 – 7.22 (m, 12H; *H*C$_{Ar}$), 5.35 (d, *J* = 1.2 Hz, 1H; H-1), 4.62 (d, *J* = 11.9 Hz, 1H; C*H*H Bn), 4.61 (d, *J* = 1.7 Hz, 1H; H-4), 4.47 (dd, *J* = 7.9, 7.0 Hz, 1H; H-5), 4.44 (d, *J* = 11.9 Hz, 1H; CH*H* Bn), 4.18 (d, *J* = 4.9 Hz, 1H; H-3), 3.78 (ddd, *J* = 4.9, 1.7, 1.2 Hz, 1H; H-2), 1.55 (s, 3H; C*H*$_3$CO), 1.14 (dd, *J* = 14.4, 7.9 Hz, 1H; H-6a), 0.96 (dd, *J* = 14.4, 7.0 Hz, 1H; H-6b), 0.35 (s, 3H; C*H*$_3$Si), 0.32 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2 (*C*=O), 138.9 (*C*$_{Ar,q}$), 137.5 (*C*$_{Ar,q}$), 133.8 (2×*C*$_{Ar}$H), 129.2 (*C*$_{Ar}$H), 128.6 (2×*C*$_{Ar}$H), 128.1 (*C*$_{Ar}$H), 128.0 (2×*C*$_{Ar}$H), 127.9 (2×*C*$_{Ar}$H), 102.5 (*C*-1), 82.6 (*C*-2), 80.2 (*C*-3), 79.0 (*C*-4), 73.0 (*C*H$_2$, Bn), 71.4 (*C*-5), 22.0 (*C*-6), 21.1 (*C*H$_3$CO), −1.8 (*C*H$_3$Si), −2.5 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{23}H_{28}NaO_5Si$: 435.1604; found: 435.1615.

Phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-α-L-idopyranoside (10a). R_f 0.29 (PE/EtOAc, 5:1); $[\alpha]_D^{25}$ −99.6° (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.17 (m, 15H; *H*C$_{Ar}$), 5.56 (bs, 1H; H-1), 5.17 (ddd, *J* = 2.6, 1.2, 1.0 Hz, 1H; H-2), 4.82 (ddd, *J* = 8.7, 6.0, 1.3 Hz, 1H; H-5), 4.80 (d, *J* = 12.1 Hz, 1H; C*H*H, Bn), 4.65 (d, *J* = 12.1 Hz, 1H; CH*H*, Bn), 4.64 – 4.62 (m, 1H; H-4), 3.75 (ddd, *J* = 3.0, 2.6, 1.2 Hz, 1H; H-3), 2.07 (s, 3H; C*H*$_3$CO), 2.07 (s, 3H; C*H*$_3$CO), 1.27 (dd, *J* = 14.8, 8.7 Hz, 1H; H-6a), 1.03 (dd, *J* = 14.8, 6.0 Hz, 1H; H-6b), 0.28 (s, 3H; C*H*$_3$Si), 0.27 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4 (*C*=O), 169.7 (*C*=O), 138.8 (*C*$_{Ar,q}$), 137.5 (*C*$_{Ar,q}$), 137.0 (*C*$_{Ar,q}$), 133.7 (2×*C*$_{Ar}$H), 129.9 (2×*C*$_{Ar}$H), 129.2 (*C*$_{Ar}$H), 129.0 (2×*C*$_{Ar}$H), 128.6 (2×*C*$_{Ar}$H), 128.0 (2×*C*$_{Ar}$H), 127.9 (*C*$_{Ar}$H), 127.6 (2×*C*$_{Ar}$H), 126.8 (*C*$_{Ar}$H), 85.9 (*C*-1; $^1J_{C1\text{-}H1}$ = 165.0 Hz, characteristic of an axially oriented group on C-1), 72.4 (*C*H$_2$, Bn), 72.0 (*C*-3), 70.4 (*C*-4), 69.2 (*C*-2), 65.0 (*C*-5), 21.2 (*C*H$_3$CO), 21.0 (*C*H$_3$CO), 18.1 (*C*-6), −2.0 (*C*H$_3$Si), −2.7 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{31}H_{36}NaO_6SSi$: 587.1900; found: 587.1890.

Phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-β-L-idopyranoside (10b). R_f 0.33 (PE/EtOAc, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H; *H*C$_{Ar}$), 7.39 – 7.23 (m, 13H; *H*C$_{Ar}$), 5.16 (d, *J* = 1.8 Hz, 1H; H-1), 5.06 (ddd, *J* = 2.4, 1.8, 1.0 Hz, 1H; H-2), 4.67 (d, *J* = 12.0 Hz, 1H; C*H*H, Bn), 4.63 (d, *J* = 12.0 Hz, 1H; CH*H*, Bn), 4.57 (ddd, *J* = 2.8, 1.5, 1.0 Hz, 1H; H-4), 3.95 (ddd, *J* = 9.1, 5.5, 1.5 Hz, 1H; H-5), 3.78 (dd, *J* = 2.8, 2.4 Hz, 1H; H-3), 2.13 (s, 3H; C*H*$_3$CO), 2.07 (s, 3H; C*H*$_3$CO), 1.33 (dd, *J* = 14.8, 9.1 Hz, 1H; H-6a), 0.97 (dd, *J* = 14.8, 5.5 Hz, 1H; H-6b), 0.22 (s, 3H; C*H*$_3$Si), 0.19 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5 (*C*=O), 170.3 (*C*=O), 138.5 (*C*$_{Ar,q}$), 137.4 (*C*$_{Ar,q}$), 134.1 (*C*$_{Ar,q}$-S), 133.6 (2×*C*$_{Ar}$H), 132.3 (2×*C*$_{Ar}$H), 129.2 (*C*$_{Ar}$H), 129.2 (2×*C*$_{Ar}$H), 128.6 (2×*C*$_{Ar}$H), 128.1 (*C*$_{Ar}$H), 128.0 (2×*C*$_{Ar}$H), 127.9 (*C*$_{Ar}$H), 127.8 (2×*C*$_{Ar}$H), 84.7 (*C*-1; $^1J_{C1\text{-}H1}$ = 155.2 Hz, characteristic of an equatorially oriented group on C-1), 73.4 (*C*-5), 73.3 (*C*-3), 72.7 (*C*H$_2$, Bn), 69.6 (*C*-2), 69.4 (*C*-4), 21.1 (*C*H$_3$CO), 21.0 (*C*H$_3$CO), 18.5 (*C*-6), −1.8 (*C*H$_3$Si), −2.7 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{31}H_{36}NaO_6SSi$: 587.1900; found: 587.1891.

Phenyl 2,3-di-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-α-L-idopyranoside (12).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H; *H*C$_{Ar}$), 7.46 – 7.14 (m, 22H; *H*C$_{Ar}$), 5.59 (bs, 1H; H-1), 4.69 (ddd, *J* = 8.3, 6.6, 1.2 Hz, 1H; H-5), 4.64 – 4.60 (m, 2H; 2×C*H*H Bn), 4.53 (d, *J* = 11.8 Hz, 1H; C*H*H, Bn), 4.48 (d, *J* = 12.2 Hz, 1H; C*H*H, Bn), 3.87 (ddd, *J* = 2.9, 1.4, 1.2 Hz, 1H; H-3), 3.81 (ddd, *J* = 3.1, 3.1, 1.3 Hz, 1H; H-2), 3.41 (dddd, *J* = 11.7, 3.4, 1.9, 1.5 Hz, 1H; H-4), 3.21 (d, *J* = 11.7 Hz, 1H; OH), 1.42 (dd, *J* = 14.8, 8.3 Hz, 1H; H-6a), 1.19 (dd, *J* = 14.8, 6.5 Hz, 1H; H-6b), 0.31 (s, 3H; C*H*$_3$Si), 0.29 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6 (*C*$_{Ar,q}$), 138.0 (*C*$_{Ar,q}$), 137.8 (*C*$_{Ar,q}$), 136.9 (*C*$_{Ar,q}$), 133.7 (2×*C*$_{Ar}$H), 129.6 (2×*C*$_{Ar}$H), 129.0 (2×*C*$_{Ar}$H), 128.9 (*C*$_{Ar}$H), 128.7 (2×*C*$_{Ar}$H), 128.6 (2×*C*$_{Ar}$H), 128.3 (*C*$_{Ar}$H), 128.0 (2×*C*$_{Ar}$H), 127.9 (*C*$_{Ar}$H), 127.8 (2×*C*$_{Ar}$H), 127.7 (2×*C*$_{Ar}$H), 126.5 (*C*$_{Ar}$H), 85.9 (*C*-1), 76.0 (*C*-3), 73.8 (*C*-2), 72.4 (*C*H$_2$, Bn), 72.0 (*C*H$_2$, Bn), 70.0 (*C*-4), 67.0 (*C*-5), 17.9 (*C*-6), −1.9 (*C*H$_3$Si), −2.2 (*C*H$_3$Si).

Phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-α-L-idopyranoside (13).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 4H; *H*C$_{Ar}$), 7.41 – 7.17 (m, 25H; *H*C$_{Ar}$), 5.35 (d, *J* = 4.8 Hz, 1H; H-1), 4.74 (d, *J* = 11.5 Hz, 1H; Bn-a), 4.64 (d, *J* = 11.7 Hz, 1H; Bn-b), 4.59 (d, *J* = 11.5 Hz, 1H; Bn-a), 4.54 (d, *J* = 11.9 Hz, 1H; Bn-c), 4.52 (d, *J* = 11.7 Hz, 1H; Bn-b), 4.46 (ddd, *J* = 10.5, 4.3, 3.4 Hz, 1H; H-5), 4.37 (d, *J* = 11.9 Hz, 1H; Bn-c), 3.74 (dd, *J* = 5.7, 5.4 Hz, 1H; H-3), 3.59 (dd, *J* = 5.4, 4.8 Hz, 1H; H-2), 3.31 (dd, *J* = 5.7, 3.4 Hz, 1H; H-4), 1.38 (dd, *J* = 15.2, 10.5 Hz, 1H; H-6a), 1.07 (dd, *J* = 15.2, 4.3 Hz, 1H; H-6b), 0.20 (s, 3H; C*H*$_3$Si), 0.20 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5 (*C*$_{Ar,q}$), 138.3 (*C*$_{Ar,q}$), 138.2 (*C*$_{Ar,q}$), 138.1 (*C*$_{Ar,q}$), 135.8 (*C*$_{Ar,q}$-S), 133.8 (2×*C*$_{Ar}$H), 130.9 (2×*C*$_{Ar}$H), 129.0, 128.6, 128.4, 128.3, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.7, 126.9 [aromatic C atoms], 84.6 (*C*-1), 78.1 (*C*-4), 77.7 (*C*-2), 76.2 (*C*-3), 73.8 (*C*H$_2$,

Bn), 73.6 (CH_2, Bn), 72.8 (CH_2, Bn), 69.3 (*C*-5), 15.4 (*C*-6), −1.9 (CH_3Si), −2.9 (CH_3Si).

2-Methoxyethyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-D-glucopyranosides (18a, 18b). General procedure A with phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**3**) (100 mg, 0.178 mmol), 2-methoxyethanol (**14**) (21 µL, 0.266 mmol), NIS (46 mg, 0.195 mmol) and TfOH (1.6 µL, 0.017 mmol). After the work-up and before the column chromatography, overnight acetylation of the crude mixture with Ac_2O/pyridine (1:1, v/v). The procedure afforded 77 mg (82%; α/β, 16:84) of **18a** and **18b** after flash silica column chromatography (toluene/acetone, 30:1 to 15:1).

2-Methoxyethyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-α-D-glucopyranoside (18a). R_f 0.39 (toluene/acetone, 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.21 (m, 10H; *H*C_{Ar}), 4.99 (d, *J* = 3.8 Hz, 1H; H-1), 4.84 (dd, *J* = 9.6, 9.4 Hz, 1H; H-4), 4.76 (dd, *J* = 10.0, 3.8 Hz, 1H; H-2), 4.69 (d, *J* = 11.8 Hz, 1H; C*H*H, Bn-3), 4.57 (d, *J* = 11.8 Hz, 1H; CH*H*, Bn-3), 3.90 (dd, *J* = 10.0, 9.6, 1H; H-3), 3.87 (ddd, *J* = 10.5, 9.4, 3.5 Hz, 1H; H-5), 3.44 – 3.33 (m, 4H; 4×C*H*, aglyc.), 3.32 (s, 3H; CH_3O), 2.03 (s, 3H; CH_3CO), 1.96 (s, 3H; CH_3CO), 1.08 (dd, *J* = 14.9, 3.5 Hz, 1H; H-6a), 1.02 (dd, *J* = 14.9, 10.5 Hz, 1H; H-6b), 0.35 (s, 3H; CH_3Si), 0.28 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3 (*C*=O), 170.0 (*C*=O), 139.1 ($C_{Ar,q}$), 138.7 ($C_{Ar,q}$), 133.7 (2×C_{Ar}H), 129.1 (C_{Ar}H), 128.5 (2×C_{Ar}H), 127.9 (2×C_{Ar}H), 127.7 (C_{Ar}H), 127.5 (2×C_{Ar}H), 95.9 (*C*-1), 77.3 (*C*-3), 76.4 (*C*-4), 74.8 (CH_2, Bn-3), 73.9 (*C*-2), 71.5 (CH_2), 67.6 (*C*-5), 67.5 (CH_2), 59.1 (CH_3O), 21.2 (CH_3CO), 21.0 (CH_3CO), 19.0 (*C*-6), −0.9 (CH_3Si), −2.4 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{28}H_{38}NaO_8Si$: 553.2234; found: 553.2219.

2-Methoxyethyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-β-D-glucopyranoside (18b). R_f 0.35 (toluene/acetone, 9:1); $[\alpha]_D^{25}$ −7.3° (*c* 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.19 (m, 10H, *H*C_{Ar}), 5.02 (dd, *J* = 9.6, 8.0 Hz, 1H; H-2), 4.90 (dd, *J* = 9.4, 9.4 Hz, 1H; H-4), 4.57 (d, *J* = 11.7 Hz, 1H; C*H*H, Bn-3) , 4.54 (d, *J* = 11.7 Hz, 1H; CH*H*, Bn-3), 4.29 (d, *J* = 8.0 Hz, 1H; H-1), 3.82 – 3.76 (m, 1H; C*H*, aglyc.), 3.58 (dd, *J* = 9.6, 9.4 Hz, 1H; H-3), 3.51 – 3.45 (m, 3H; 3×C*H*, aglyc.), 3.39 (ddd, *J* = 10.9, 9.4, 3.2 Hz, 1H; H-5), 3.33 (s, 3H; CH_3O), 1.98 (s, 3H; CH_3CO), 1.98 (s, 3H; CH_3CO), 1.09 (dd, *J* = 14.9, 10.9 Hz, 1H; H-6a), 1.01 (dd, *J* = 14.9, 3.2 Hz, 1H; H-6b), 0.35 (s, 3H; CH_3Si), 0.31 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8 (*C*=O), 169.4 (*C*=O), 138.9 ($C_{Ar,q}$), 138.1 ($C_{Ar,q}$), 133.7 (2×C_{Ar}H), 129.1 (C_{Ar}H), 128.5 (2×C_{Ar}H) , 128.0 (2×C_{Ar}H) , 128.0 (2×C_{Ar}H), 127.9, (C_{Ar}H), 101.3 (*C*-1), 80.0 (*C*-3), 75.5 (*C*-4), 73.4 (CH_2, Bn-3), 72.9 (*C*-2), 72.3 (*C*-5) , 71.7 (CH_2) , 68.8 (CH_2) , 59.2 (CH_3O), 21.1 (CH_3CO) , 21.0 (CH_3CO), 18.6 (*C*-6), −1.4 (CH_3Si), −2.3 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{28}H_{38}NaO_8Si$: 553.2234; found: 553.2236.

Cyclohexyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-D-glucopyranosides (19a, 19b). General procedure A with phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**3**) (101 mg, 0.178 mmol), cyclohexanol (**15**) (29 µL, 0.267 mmol), NIS (46 mg, 0.196 mmol) and TfOH (1.6 µL, 0.018 mmol). After the work-up and before the column chromatography, overnight acetylation of the crude mixture with Ac_2O/pyridine (1:1, v/v). The procedure afforded 79 mg (80%; α/β, 14:86) of **19a** and **19b** after flash silica column chromatography (toluene/acetone, 40:1 to 30:1).

Cyclohexyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-α-D-glucopyranoside (19a). R_f 0.28 (toluene/acetone, 30:1); $[\alpha]_D^{25}$ +19.2° (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.20 (m, 10H, *H*C_{Ar}), 5.07 (d, *J* = 3.8 Hz, 1H; H-1), 4.83 (dd, *J* = 9.5, 9.5 Hz, 1H; H-4), 4.73 (dd, *J* = 10.1, 3.8 Hz, 1H; H-2), 4.71 (d, *J* = 11.9 Hz, 1H; C*H*H, Bn-3), 4.58 (d, *J* = 11.9 Hz, 1H; CH*H*, Bn-3), 3.93 (ddd, *J* = 10.6, 9.6, 3.5 Hz, 1H; H-5), 3.90 (dd, *J* = 10.1, 9.4 Hz, 1H; H-3), 3.38 – 3.31 (m, 1H; OC*H*, Cy), 2.03 (s, 3H; CH_3CO), 1.96 (s, 3H; CH_3CO), 1.71 – 1.12 (m, 10H; CH_2, Cy), 1.07 (dd, *J* = 14.9, 3.5 Hz, 1H; H-6a), 1.01 (dd, *J* = 14.9, 10.6 Hz, 1H; H6-b), 0.33 (s, 3H; CH_3Si), 0.27 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4 (*C*=O), 170.0 (*C*=O), 139.3 ($C_{Ar,q}$), 138.7 ($C_{Ar,q}$), 133.6 (2×C_{Ar}H), 129.0 (C_{Ar}H), 128.5 (2×C_{Ar}H), 127.9 (2×C_{Ar}H), 127.7 (C_{Ar}H), 127.5 (2×C_{Ar}H), 93.0 (*C*-1), 77.3 (*C*-3), 76.7 (*C*-4), 74.7 (OCH, Cy), 74.7 (CH_2, Bn-3), 74.2 (*C*-2), 67.6 (*C*-5), 33.1 (CH_2, Cy), 30.9 (CH_2, Cy), 25.7 (CH_2, Cy), 24.0 (CH_2, Cy), 23.6 (CH_2, Cy), 21.2 (CH_3CO), 21.0 (CH_3CO), 19.2 (*C*-6), −1.0 (CH_3Si), −2.5 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{31}H_{42}NaO_7Si$: 577.2598; found: 577.2586.

Cyclohexyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-β-D-glucopyranoside (19b). R_f 0.24 (toluene/acetone, 30:1); $[\alpha]_D^{25}$ −3.0° (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.20 (m, 10H; *H*C_{Ar}), 5.00 (dd, *J* = 9.8, 8.0 Hz, 1H; H-2), 4.91 (dd, *J* = 9.6, 9.3 Hz, 1H; H-4), 4.55 (s, 2H, CH_2, Bn-3), 4.28 (d, *J* = 8.0 Hz, 1H; H-1), 3.57 (dd, *J* = 9.8, 9.3 Hz, 1H; H-3), 3.55 – 3.44 (m, 1H, OC*H*, Cy), 3.36 (ddd, *J* = 11.0, 9.6, 2.9 Hz, 1H; H-5), 1.98 (s, 3H; CH_3CO), 1.97 (s, 3H; CH_3CO), 1.79 – 1.35 (m, 10H; CH_2, Cy), 1.10 (dd, *J* = 14.9, 11.0 Hz, 1H; H-6a), 1.02 (dd, *J* = 14.9, 2.9 Hz, 1H; H-6b), 0.35 (s, 3H; CH_3Si), 0.29 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8 (*C*=O), 169.2 (*C*=O), 138.9 ($C_{Ar,q}$), 138.2 ($C_{Ar,q}$), 133.7 (2×C_{Ar}H), 129.1 (C_{Ar}H), 128.5 (2×C_{Ar}H), 128.0 (2×C_{Ar}H), 127.9 (2×C_{Ar}H), 127.8 (C_{Ar}H), 99.2 (*C*-1), 80.1 (*C*-3), 76.7 (OCH, Cy), 75.5 (*C*-4), 73.1 (C-2; CH_2, Bn-3), 72.1 (*C*-5), 33.2 (CH_2, Cy), 31.3 (CH_2, Cy), 25.7 (CH_2, Cy), 23.8 (CH_2, Cy), 23.5 (CH_2, Cy), 21.2 (CH_3CO), 21.0 (CH_3CO), 18.6 (*C*-6), −1.3 (CH_3Si), −2.4 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{31}H_{42}NaO_7Si$: 577.2598; found: 577.2586.

Methyl 2',4'-di-*O*-acetyl-3'-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-β-D-glucopyranosyl-(1'→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (20). General procedure A with phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**3**) (101 mg, 0.178 mmol), methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**16**) (124 mg, 0.267 mmol), NIS (46 mg, 0.196 mmol) and TfOH (1.6 µL, 0.018 mmol). The procedure afforded 116 mg (71%) of **20** after flash silica column chromatography (PE/EtOAc, 2:1). R_f 0.28 (PE/EtOAc, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.20 (m, 25H, *H*C_{Ar}), 4.95 (d, *J* = 10.9 Hz, 1H; C*H*H, Bn), 4.92 (dd, *J* = 9.6, 8.0 Hz, 1H; H-2'), 4.84 (dd, *J* = 9.5, 9.4 Hz, 1H; H-4'), 4.83 (d, *J* = 11.9 Hz, 1H; C*H*H, Bn), 4.75 – 4.69 (m, 3H; C*H*H, Bn), 4.59 (d, *J* = 3.7 Hz, 1H; H-1), 4.52 (d, *J* = 11.5 Hz, 1H; C*H*H, Bn), 4.48 (d, *J* = 11.5 Hz, 1H; C*H*H, Bn), 4.35 (d, *J* = 12.1 Hz, 1H; C*H*H, Bn), 4.15 (d, *J* = 8.0 Hz, 1H; H-1'), 3.82 – 3.76 (m, 2H; H-3; H-4), 3.68 (dd, *J* = 10.6, 2.6 Hz, 1H; H-6a), 3.55 (ddd, *J* = 7.2, 2.6, 2.1 Hz, 1H; H-5), 3.50 (dd, *J* = 10.6, 2.1 Hz, 1H, H-6b), 3.45 – 3.41 (m, 1H; H-2), 3.38 (s, 3H; CH_3O), 3.23 (dd, *J* = 9.5, 9.5 Hz, 1H; H-3'), 3.19 (dd, *J* = 10.5, 9.5 2.5 Hz, 1H; H-5'), 2.01 (s, 3H; CH_3CO), 1.89 (s, 3H; CH_3CO), 0.89 (dd, *J* = 15.1, 2.5 Hz, 1H; H-6a'), 0.83 (dd, *J* = 15.1, 10.5 Hz, 1H; H-6b'), 0.29 (s, 3H; CH_3Si), 0.19 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8 (*C*=O), 168.9 (*C*=O), 139.4 ($C_{Ar,q}$), 139.3 ($C_{Ar,q}$), 138.5 ($C_{Ar,q}$), 138.2 ($C_{Ar,q}$), 137.5 ($C_{Ar,q}$), 133.7 (2×C_{Ar}H), 129.1 (C_{Ar}H), 129.0 (2×C_{Ar}H), 128.7 (2×C_{Ar}H), 128.6 (2×C_{Ar}H), 128.5 (2×C_{Ar}H), 128.5 (2×C_{Ar}H), 128.3 (2×C_{Ar}H), 128.2 (C_{Ar}H), 128.1 (2×C_{Ar}H), 128.0 (2×C_{Ar}H), 127.9 (C_{Ar}H), 127.8 (C_{Ar}H), 127.7 (2×C_{Ar}H), 127.3 (C_{Ar}H), 99.6 (*C*-1'), 99.0 (*C*-1), 80.4 (*C*-3'), 80.1 (*C*-3), 78.1 (*C*-2), 75.9 (CH_2, Bn), 75.7 (*C*-4), 75.4 (C-4'), 74.0 (CH_2, Bn), 73.7 (CH_2, Bn), 73.5 (*C*-2'), 73.4 (CH_2, Bn), 71.7 (*C*-5'), 70.2 (*C*-5), 67.4 (*C*-6), 55.5 (CH_3O), 21.2 (CH_3CO), 21.0 (CH_3CO), 17.9 (*C*-6'), −1.2 (CH_3Si), −2.9 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{53}H_{62}NaO_{12}Si$: 941.3908; found: 941.3882.

Methyl 2',4'-di-*O*-acetyl-3'-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-β-D-glucopyranosyl-(1'→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (21). General procedure B with phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**3**) (41 mg, 0.073 mmol), methyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (**17**) (20 mg, 0.049 mmol), NIS (19 mg, 0.080 mmol) and TfOH (0.7 µL, 0.007 mmol). The procedure afforded 16 mg (38%) of **21** after flash silica column chromatography (toluene/acetone, 2:1). R_f 0.25 (toluene/acetone, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H, *H*C_{Ar}), 7.38 – 7.24 (m, 16H, *H*C_{Ar}), 7.24 – 7.19 (m, 2H, *H*C_{Ar}), 5.12 (d, *J* = 8.4 Hz, 1H; N*H*), 4.96 (dd, *J* = 9.6, 8.0 Hz, 1H; H-2'), 4.89 (d, *J* = 12.5 Hz, 1H; C*H*H, Bn), 4.84 (dd, *J* = 9.4, 9.4 Hz, 1H; H-4'), 4.77 (d, *J* = 3.6 Hz, 1H; H-1), 4.74 (d, *J* = 12.1 Hz, 1H; C*H*H, Bn), 4.55 – 4.50 (m, 3H; 3×C*H*H, Bn), 4.41 (d, *J* = 12.1 Hz, 1H; C*H*H, Bn), 4.21 (d, *J* = 8.0 Hz, 1H; H-1'), 4.10

(ddd, *J* = 10.4, 8.4, 3.6 Hz, 1H; H-2), 3.88 (dd, *J* = 9.6, 8.6 Hz, 1H; H-4), 3.71 (dd, *J* = 10.7, 3.2 Hz, 1H; H-6a), 3.55 (dd, *J* = 10.7, 2.0 Hz, 1H; H-6b), 3.51 (ddd, *J* = 9.6, 3.2, 2.0 Hz, 1H; H-5), 3.44 (dd, *J* = 10.4, 8.6 Hz, 1H; H-3), 3.30 (dd, *J* = 9.6, 9.4 Hz; H-3'), 3.29 (s, 3H; CH_3O), 3.22 (ddd, *J* = 10.6, 9.4, 2.2 Hz, 1H; H-5'), 1.99 (s, 3H; CH_3CO), 1.92 (s, 3H; CH_3CO), 1.83 (s, 3H; CH_3CON), 0.93 (dd, *J* = 15.1, 2.2 Hz, 1H; H-6a'), 0.84 (dd, *J* = 15.1, 10.6 Hz, 1H; H-6b'), 0.34 (s, 3H; CH_3Si), 0.25 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0 (*C*=O), 169.8 (*C*=O), 169.2 (*C*=O), 139.3 ($C_{Ar,q}$), 139.1 ($C_{Ar,q}$), 138.2 ($C_{Ar,q}$), 137.8 ($C_{Ar,q}$), 133.7 (2×C_{Ar}H), 129.1 (C_{Ar}H), 128.7 (2×C_{Ar}H), 128.7 (2×C_{Ar}H), 128.5 (2×C_{Ar}H), 128.4 (2×C_{Ar}H), 128.4 (2×C_{Ar}H), 128.1 (C_{Ar}H), 128.0 (2×C_{Ar}H), 127.9 (C_{Ar}H), 127.7 (2×C_{Ar}H), 127.6 (C_{Ar}H), 126.1, 99.8 (*C*-1'), 98.3 (*C*-1), 80.3 (*C*-3'), 77.5 – 76.8 (*C*-3), 76.5 (*C*-4), 75.6 (*C*-4'), 74.6 (CH_2, Bn), 73.9 (CH_2, Bn), 73.7 (*C*-2'; CH_2, Bn), 71.9 (*C*-5'), 70.9 (*C*-5), 67.5 (*C*-6), 55.3 (CH_3O), 52.6 (*C*-2), 23.5 (CH_3CON), 21.2 (CH_3CO), 21.0 (CH_3CO), 18.2 (*C*-6'), −1.3 (CH_3Si), −2.9 (CH_3Si).

Acetyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-α-D-glucopyranoside (24). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 2H; *H*C_{Ar}), 7.39 – 7.18 (m, 8H; *H*C_{Ar}), 6.23 (d, *J* = 3.8 Hz, 1H; H-1), 5.00 (dd, *J* = 10.0, 3.8 Hz, 1H; H-2), 4.90 (dd, *J* = 9.7, 9.5 Hz, 1H; H-4), 4.66 (d, *J* = 11.8 Hz, 1H; Bn), 4.57 (d, *J* = 11.8 Hz, 1H; Bn), 3.85 – 3.79 (m, 1H; H-5), 3.82 (dd, *J* = 10.0, 9.5 Hz, 1H; H-3), 1.98 (s, 3H; CH_3CO), 1.97 (s, 3H; CH_3CO), 1.97 (s, 3H; CH_3CO), 1.01 – 0.98 (m, 2H; H-6a, H-6b), 0.31 (s, 3H; CH_3Si), 0.25 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8 (*C*=O), 169.7 (*C*=O), 169.1 (*C*=O), 138.7 ($C_{Ar,q}$), 138.3 ($C_{Ar,q}$), 133.8 (2×C_{Ar}H), 129.0 (C_{Ar}H), 128.5 (2×C_{Ar}H), 127.9 (2×C_{Ar}H), 127.9 (C_{Ar}H), 127.6 (2×C_{Ar}H), 89.3 (*C*-1), 75.6 (*C*-4), 74.6 [one out of *C*-3, *C*-5], 72.0 (*C*-2), 70.4 [one out of *C*-5, *C*-3], 21.1 (CH_3CO), 20.9 (CH_3CO), 20.8 (CH_3CO), 19.0 (*C*-6), −1.4 (CH_3Si), −2.8 (CH_3Si).

Methyl 2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (25). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.12 (m, 10H; *H*C_{Ar}), 5.60 (s, 1H; C*H*O$_2$Ph), 5.32 (d, *J* = 9.2 Hz, 1H; N*H*), 4.91 (d, *J* = 12.2 Hz, 1H; C*H*H, Bn), 4.70 (d, *J* = 3.8 Hz, 1H; H-1), 4.66 – 4.61 (m, 1H, CH*H*, Bn), 4.30 – 4.27 (m, 1H; H-6a), 4.27 (ddd, *J* = 10.1, 9.2, 3.8 Hz, 1H; H-2), 3.81 – 3.62 (m, 4H; H-3; H-4; H-5; H-6b), 3.35 (s, 3H; CH_3O). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9 (*C*=O), 138.7 ($C_{Ar,q}$), 137.5 ($C_{Ar,q}$), 129.1, 128.5, 128.4, 128.2, 127.8, 126.1 [aromatic C atoms], 101.4 (*C*HO_2Ph), 99.3 (*C*-1), 82.9, 76.0 [two out of *C*-3, *C*-4, *C*-5], 74.1 (CH_2, Bn), 69.2 (*C*-6), 62.8 [one out of *C*-3, *C*-4, *C*-5], 55.3 (CH_3O), 52.6 (*C*-2), 23.6 (CH_3CO).

2-Methoxyethyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-D-glucopyranosides (26a, 26b). General procedure A with phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**5**) (101 mg, 0.152 mmol), 2-methoxyethanol (**14**) (18 µL, 0.228 mmol), NIS (40 mg, 0.167 mmol) and TfOH (1.4 µL, 0.015 mmol). The procedure afforded 84 mg (88%; α/β, 52:48) of **26a** and **26b** after flash silica column chromatography (petroleum ether/EtOAc, 7:1 to 4:1).

2-Methoxyethyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-α-D-glucopyranoside (26a). R_f 0.24 (PE/EtOAc, 7:1); $[\alpha]_D^{25}$ +37.2° (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.15 (m, 20H; *H*C_{Ar}), 4.90 (d, *J* = 10.8 Hz, 1H; C*H*H, Bn-a), 4.84 (d, *J* = 11.0 Hz, 1H; C*H*H, Bn-b), 4.71 (d, *J* = 10.8 Hz, 1H; CH*H*, Bn-a), 4.71 (d, *J* = 3.6 Hz, 1H; H-1), 4.65 (d, *J* = 12.0 Hz, 1H; C*H*H, Bn-c), 4.61 (d, *J* = 12.0 Hz, 1H; CH*H*, Bn-c), 4.58 (d, *J* = 11.0 Hz, 1H; CH*H*, Bn-b), 3.86 (dd, *J* = 9.8, 8.9 Hz, 1H; H-3), 3.76 (ddd, *J* = 11.0, 9.4, 2.6 Hz, 1H; H-5), 3.45 – 3.30 (m, 4H; 4×C*H*H, aglyc.), 3.43 (dd, *J* = 9.8, 3.6 Hz, 1H; H-2), 3.26 (s, 3H; CH_3O), 3.04 (dd, *J* = 9.4, 8.9 Hz, 1H; H-4), 1.40 (dd, *J* = 14.8, 2.6 Hz, 1H; H-6a), 0.78 (dd, *J* = 14.8, 11.0 Hz, 1H; H-6b), 0.26 (s, 3H; CH_3Si), 0.21 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5 ($C_{Ar,q}$), 139.1 ($C_{Ar,q}$), 138.6 ($C_{Ar,q}$), 138.6 ($C_{Ar,q}$), 133.7, 128.9, 128.5, 128.5, 128.5, 128.1, 128.1, 128.0, 127.9, 127.8, 127.6 [11 peaks; 4 signals C_{Ar}H, 8 signals 2×C_{Ar}H], 97.0 (*C*-1), 85.3 (*C*-4), 81.7 (*C*-3), 80.4 (*C*-2), 75.7 (CH_2, Bn), 75.5 (CH_2, Bn), 72.7 (CH_2, Bn), 71.9 (CH_2, aglyc.), 68.8 (*C*-5), 67.0 (CH_2, aglyc.), 59.1 (CH_3O), 19.7 (*C*-6), −1.0 (CH_3Si), −2.3 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{38}H_{46}NaO_6Si$: 649.2961; found: 649.2958.

2-Methoxyethyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-β-D-glucopyranoside (26b). R_f 0.32 (PE/EtOAc, 7:1); $[\alpha]_D^{25}$ +3.1° (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H; *H*C_{Ar}), 7.35 – 7.21 (m, 18H; *H*C_{Ar}), 4.94 (d, *J* = 10.9 Hz, 1H; C*H*H, Bn-a), 4.87 (d, *J* = 10.9 Hz, 1H; C*H*H, Bn-b), 4.85 (d, *J* = 11.0 Hz, 1H; C*H*H, Bn-c), 4.73 (d, *J* = 10.9 Hz, 1H; CH*H*, Bn-b), 4.66 (d, *J* = 10.9 Hz, 1H; CH*H*, Bn-a), 4.63 (d, *J* = 11.0 Hz, 1H; CH*H*, Bn-c), 4.26 (d, *J* = 7.7 Hz, 1H; H-1), 3.86 (ddd, *J* = 9.5, 5.1, 2.8 Hz, 1H; C*H*HCH$_2$, aglyc.), 3.57 – 3.49 (m, 4H; 3×C*H*, aglyc.; H-3), 3.42 (dd, *J* = 9.3, 7.7 Hz, 1H; H-2), 3.34 (s, 3H; CH_3O), 3.33 (ddd, *J* = 11.2, 9.2, 2.5 Hz, 1H; H-5), 3.17 (dd, *J* = 9.2, 8.9 Hz, 1H; H-4), 1.41 (dd, *J* = 14.8, 2.5 Hz, 1H; H-6a), 0.93 (dd, *J* = 14.8, 11.2 Hz, 1H; H-6b), 0.31 (s, 3H; CH_3Si), 0.29 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3 ($C_{Ar,q}$), 138.8 ($C_{Ar,q}$), 138.8 ($C_{Ar,q}$), 138.4 ($C_{Ar,q}$), 133.7, 129.0, 128.5, 128.5, 128.4, 128.3, 128.1, 128.1, 127.9, 127.7 [aromatic C atoms], 103.9 (*C*-1), 84.5 (*C*-3), 84.3 (*C*-4), 82.6 (*C*-2), 75.8 (CH_2, Bn-b), 75.5 (CH_2, Bn-c), 74.8 (CH_2, Bn-a), 73.2 (*C*-5), 71.8 (CH_2, aglyc.), 69.2 (CH_2, aglyc.), 59.1 (CH_3O), 18.9 (*C*-6), −1.3 (CH_3Si), −2.2 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{38}H_{46}NaO_6Si$: 649.2961; found: 649.2964.

Cyclohexyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-D-glucopyranosides (27a, 27b). General procedure A with phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**5**) (100 mg, 0.152 mmol), cyclohexanol (**15**) (24 µL, 0.227 mmol), NIS (40 mg, 0.167 mmol) and TfOH (1.4 µL, 0.015 mmol). The procedure afforded 82 mg (83%; α/β, 57:43) of **27a** and **27b** after flash silica column chromatography (toluene/acetone, 40:1). R_f 0.50 (PE/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.25 (m, 20H, *H*C_{Ar}–α; 20H, *H*C_{Ar}–β), 4.99 – 4.63 (m, 6H, Bn–α; 6H, Bn–β), 4.87 (d, *J* = 3.6 Hz, 1H; H-1–α), 4.37 (d, *J* = 7.8 Hz, 1H; H-1–β), 3.96 (dd, *J* = 9.8, 8.9 Hz, 1H; H-3–α), 3.89 (ddd, *J* = 11.2 Hz, 9.3 Hz, 2.4 Hz, 1H; H-5–α), 3.59 (dddd, *J* = 9.2 Hz, 9.2 Hz, 3.8 Hz, 3.8 Hz, 1H; OC*H*, Cy–β), 3.53 (dd, *J* = 9.3, 8.9 Hz, 1H; H-3–β), 3.50 (dd, *J* = 9.8, 3.6 Hz, 1H; H-2–α), 3.43 (m, 1H; OC*H*, Cy–α), 3.42 (dd, *J* = 9.3, 7.8 Hz; H-2–β), 3.33 (ddd, *J* = 11.3 Hz, 9.2 Hz, 2.5 Hz, 1H; H-5–β), 3.21 (dd, *J* = 9.2, 8.9 Hz, 1H; H-4–β), 3.12 (dd, *J* = 9.3, 8.9 Hz, 1H; H-4–α), 1.47 (dd, *J* = 14.8, 2.4 Hz; H-6a–α), 1.44 (dd, *J* = 14.8, 2.5 Hz; H-6a–β), 1.94 – 1.12 (m, 20H; CH_2, Cy–α; CH_2, Cy–β), 0.96 (dd, *J* = 14.8, 11.3, Hz, 1H; H-6b–β), 0.84 (dd, *J* = 14.8, 11.2, 1H; H-6b–α), 0.33 (s, 3H; CH_3Si), 0.31 (s, 3H; CH_3Si), 0.31 (s, 3H; CH_3Si), 0.28 (s, 3H; CH_3Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6 ($C_{Ar,q}$), 139.3 ($C_{Ar,q}$), 139.1 ($C_{Ar,q}$), 138.9 ($C_{Ar,q}$), 138.8 ($C_{Ar,q}$), 138.6 ($C_{Ar,q}$), 138.5 ($C_{Ar,q}$), 138.5 ($C_{Ar,q}$), 133.7 (C_{Ar}H), 133.6 (C_{Ar}H), 129.0 (C_{Ar}H), 128.9 (C_{Ar}H), 128.6 (C_{Ar}H), 128.5 (C_{Ar}H), 128.5 (C_{Ar}H), 128.5 (C_{Ar}H), 128.3 (C_{Ar}H), 128.2 (C_{Ar}H), 128.2 (C_{Ar}H), 128.2 (C_{Ar}H), 128.1 (C_{Ar}H), 127.9 (C_{Ar}H), 127.7 (C_{Ar}H), 127.7 (C_{Ar}H) [aromatic C atoms], 101.1 (*C*-1–β), 93.4 (C-1–α), 85.7 (C-4–α), 84.7 (C-3–β), 84.4 (C-4–β), 82.7 (C-2–β), 81.8 (C-3–α), 80.4 (C-2–α), 76.6 (O*C*H, Cy–β), 75.8 (Bn), 75.6 (Bn), 75.7 (Bn), 75.5 (Bn), 75.0 (Bn), 73.9 (O*C*H, Cy–α), 73.1 (C-5–β), 73.0 (Bn), 68.8 (C-5–α), 33.8 (*C*H$_2$, Cy), 33.2 (*C*H$_2$, Cy), 31.6 (*C*H$_2$, Cy), 31.0 (*C*H$_2$, Cy), 25.8 (*C*H$_2$, Cy), 25.8 (*C*H$_2$, Cy), 24.6 (*C*H$_2$, Cy), 24.3 (*C*H$_2$, Cy), 24.2 (*C*H$_2$, Cy), 24.0 (*C*H$_2$, Cy), 19.8 (C-6–α), 18.9 (C-6–β), −1.1 (CH_3Si–α), −1.3 (CH_3Si–β), −2.3 (CH_3Si–β), −2.4 (CH_3Si–α).

Methyl 2',3',4'-tri-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-D-glucopyranosyl-(1'→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosides (28a, 28b). General procedure A with phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**5**) (74 mg, 0.112 mmol), methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**16**) (78 mg, 0.168 mmol), NIS (29 mg, 0.132 mmol) and TfOH (1.0 µL, 0.011 mmol). The procedure afforded 76 mg (67%; α/β, 65:35) of **28a** and **28b** after flash silica column chromatography (PE/EtOAc, 4:1).

Methyl 2',3',4'-tri-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-α-D-glucopyranosyl-(1'→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (28a). R_f 0.33 (PE/EtOAc, 4:1); $[\alpha]_D^{25}$ +34.2° (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.27 (m, 35H; *H*C_{Ar}), 5.55 (d, *J* = 3.4 Hz, 1H; H-1'), 5.09 (d, *J* = 11.9 Hz, 1H; C*H*H, Bn), 4.94 (d, *J* = 11.2 Hz, 1H; C*H*H, Bn), 4.85 – 4.63 (m, 5H; C*H*H, Bn), 4.76 (d, *J* = 12.1 Hz, 1H; C*H*H, Bn), 4.67 – 4.65 (m, 1H; H-1), 4.60 (d, *J* = 11.9 Hz, 1H; C*H*H, Bn), 4.57 (d, *J* = 11.9 Hz, 1H; C*H*H, Bn), 4.54 (d, *J* = 12.2 Hz, 1H; C*H*H, Bn), 4.46 (d, *J* = 12.1 Hz, 1H;

C*H*H, Bn), 4.04 (dd, *J* = 9.5, 8.5 Hz, 1H; H-3), 3.87 – 3.79 (m, 2H; H-5; H-5'), 3.83 (dd, *J* = 9.9, 8.8 Hz; H-3'), 3.75 (dd, *J* = 10.0, 8.5 Hz, 1H; H-4), 3.63 (dd, *J* = 10.4, 2.0 Hz, 1H; H-6a), 3.57 (dd, *J* = 9.5, 3.5 Hz, 1H; H-2), 3.45 – 3.41 (m, 1H; H6b), 3.44 (s, 3H; C*H*$_3$O), 3.38 (dd, *J* = 9.9, 3.5 Hz, 1H; H-2'), 3.12 (dd, *J* = 9.5, 8.8 Hz, 1H; H-4'), 1.44 (dd, *J* = 14.9, 4.0 Hz, 1H; H-6a'), 0.97 (dd, *J* = 14.9, 9.1 Hz, 1H; H-6b'), 0.35 (s, 3H; C*H*$_3$Si), 0.32 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8 (*C*$_{Ar,q}$), 139.2 (*C*$_{Ar,q}$), 138.9 (*C*$_{Ar,q}$), 138.8 (*C*$_{Ar,q}$), 138.2 (*C*$_{Ar,q}$), 138.2 (*C*$_{Ar,q}$), 138.2 (*C*$_{Ar,q}$), 133.8, 129.0, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.7, 127.6, 127.6, 127.1, 126.8 [aromatic C atoms], 97.7 (*C*-1), 95.1 (*C*-1'), 85.0 (*C*-4'), 82.2 (*C*-3), 81.5 (*C*-3'), 80.3 (*C*-2'), 80.1 (*C*-2), 75.5 (*C*H$_2$, Bn), 75.3 (*C*H$_2$, Bn), 74.3 (*C*H$_2$, Bn), 73.4 (*C*H$_2$, Bn), 73.4 (*C*H$_2$, Bn), 73.0 (*C*H$_2$, Bn), 72.0 (*C*-4), 70.0, 69.6 [*C*-5, *C*-5'], 69.4 (*C*-6), 55.2 (*C*H$_3$O), 20.1 (*C*-6'), −0.8 (*C*H$_3$Si), −1.6 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{63}H_{70}NaO_{10}Si$: 1037.4636; found: 1037.4627.

Methyl 2',3',4'-tri-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-β-D-glucopyranosyl-(1'→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (28b). *R*$_f$ 0.43 (PE/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.20 (m, 35H; *H*C$_{Ar}$), 5.03 (d, *J* = 11.0 Hz, 1H; C*H*H, Bn), 4.93 (d, *J* = 11.2 Hz, 1H; C*H*H, Bn), 4.88 – 4.69 (m, 8H; C*H*H, Bn), 4.63 (d, *J* = 3.7 Hz, 1H; H-1), 4.62 (d, *J* = 11.9 Hz; C*H*H, Bn), 4.38 (d, *J* = 12.1 Hz, 1H; C*H*H, Bn), 4.23 (d, *J* = 7.0 Hz, 1H; H-1'), 3.91 (dd, *J* = 10.1, 9.1 Hz, 1H; H-4), 3.81 (dd, *J* = 9.7, 9.1 Hz, 1H; H-3), 3.77 (dd, *J* = 10.8, 2.9 Hz, 1H; H-6a), 3.54 (ddd, *J* = 10.1, 2.9, 1.6 Hz, 1H; H-5), 3.49 (dd, *J* = 9.7, 3.7 Hz, 1H; H-2), 3.45 – 3.40 (m, 1H; H-6b), 3.41 (s, 3H; C*H*$_3$O), 3.38 – 3.30 (m, 2H; H-2'; H-4'), 3.24 (ddd, *J* = 11.1, 9.1, 1.5 Hz, 1H; H-5'), 3.16 (dd, *J* = 8.8 Hz, 1H; H-3'), 1.40 (dd, *J* = 14.8, 1.5 Hz, 1H; H-6a'), 0.78 (dd, *J* = 14.8, 11.1 Hz, 1H; H-6b'), 0.31 (s, 3H; C*H*$_3$Si), 0.24 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8 (*C*$_{Ar,q}$), 139.7 (*C*$_{Ar,q}$), 138.9 (*C*$_{Ar,q}$), 138.8 (*C*$_{Ar,q}$), 138.7 (*C*$_{Ar,q}$), 138.6 (*C*$_{Ar,q}$), 137.6 (*C*$_{Ar,q}$), 133.8 (2×*C*$_{Ar}$H), 128.9 (*C*$_{Ar}$H), 128.7 (2×*C*$_{Ar}$H), 128.6 (2×*C*$_{Ar}$H), 128.6 (2×*C*$_{Ar}$H), 128.5 (2×*C*$_{Ar}$H), 128.5 (2×*C*$_{Ar}$H), 128.5 (2×*C*$_{Ar}$H), 128.3 (2×*C*$_{Ar}$H), 128.0 (*C*$_{Ar}$H), 128.0 (2×*C*$_{Ar}$H), 128.0 (2×*C*$_{Ar}$H), 127.9 (2×*C*$_{Ar}$H), 127.9 (2×*C*$_{Ar}$H), 127.8 (*C*$_{Ar}$H), 127.8 (2×*C*$_{Ar}$H), 127.8 (*C*$_{Ar}$H), 127.7 (*C*$_{Ar}$H), 127.6 (*C*$_{Ar}$H), 127.2 (*C*$_{Ar}$H), 101.8 (*C*-1'), 98.8 (*C*-1), 84.6, 84.5, 83.5 [*C*-2'; *C*-3'; *C*-4'], 80.6 (*C*-3), 78.2 (*C*-2), 75.8, 75.7, 75.5, 75.3 [3×*C*H$_2$, Bn; *C*-4], 74.9 (*C*H$_2$, Bn), 73.8 (*C*H$_2$, Bn), 73.7 (*C*H$_2$, Bn), 72.8 (*C*-5'), 70.3 (*C*-5), 67.6 (*C*-6), 55.4 (*C*H$_3$O), 18.4 (*C*-6'), −1.2 (*C*H$_3$Si), −2.7 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{63}H_{70}NaO_{10}Si$: 1037.4636; found: 1037.4627.

Methyl 2',3',4'-tri-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-D-glucopyranosyl-(1'→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosides (29a, 29b). General procedure B with phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-D-glucopyranoside (**5**) (48 mg, 0.072 mmol), methyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (**17**) (20 mg, 0.048 mmol), NIS (19 mg, 0.079 mmol) and TfOH (0.7 µL, 0.007 mmol). The procedure afforded 30 mg (60%; α/β, 35:65) of **29a** and **29b** after flash silica column chromatography (PE/acetone, 7:3).

Methyl 2',3',4'-tri-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-α-D-glucopyranosyl-(1'→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (29a). *R*$_f$ 0.28 (PE/acetone, 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H; *H*C$_{Ar}$), 7.40 – 7.17 (m, 28H; *H*C$_{Ar}$), 5.47 (d, *J* = 9.3 Hz, 1H; N*H*), 5.41 (d, *J* = 3.5 Hz, 1H; H-1'), 4.91 (d, *J* = 11.2 Hz, 1H; C*H*H, Bn), 4.84 (d, *J* = 10.8 Hz, 1H; C*H*H, Bn), 4.73 (d, *J* = 3.6 Hz, 1H; H-1), 4.71 – 4.43 (m, 8H; C*H*H, Bn), 4.37 (ddd, *J* = 10.2, 9.3, 3.6 Hz, 1H; H-2), 3.87 – 3.75 (m, 5H; H-3; H-4; H-5; H-3'; H-5'), 3.61 (dd, *J* = 10.5, 2.3 Hz, 1H; H-6a), 3.54 (dd, *J* = 10.5, 5.6 Hz, 1H; H-6b), 3.40 – 3.36 (m, 1H; *H*-2'), 3.36 (s, 3H; C*H*$_3$O), 3.09 (dd, *J* = 9.1 Hz, 1H; H-4'), 1.87 (s, 3H; C*H*$_3$CO), 1.42 (dd, *J* = 15.0, 4.0 Hz, 1H; H-6a'), 0.96 (dd, *J* = 15.0, 8.7 Hz, 1H; H-6b'), 0.29 (s, 3H; C*H*$_3$Si), 0.26 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9 (*C*=O), 139.5 (*C*$_{Ar,q}$), 138.9 (*C*$_{Ar,q}$), 138.7 (*C*$_{Ar,q}$), 138.4 (*C*$_{Ar,q}$), 138.3 (*C*$_{Ar,q}$), 138.0 (*C*$_{Ar,q}$), 133.8, 129.2, 128.5, 128.5, 128.5, 128.5, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6 [aromatic C atoms], 98.1 (*C*-1), 95.7 (*C*-1'), 84.8 (*C*-4'), 81.4, 80.0, 79.9 [*C*-2'; two out of *C*-3, *C*-4, *C*-3', *C*-5'], 75.5 (*C*H$_2$, Bn), 75.4 (*C*H$_2$, Bn), 73.4 (*C*H$_2$, Bn), 72.7 (*C*H$_2$, Bn), 71.8 [one out of *C*-3, *C*-4, *C*-3', *C*-5'], 70.8, 70.7 [*C*-5; *C*H$_2$, Bn], 70.3 [one out of *C*-3, *C*-4, *C*-3', *C*-5'], 69.2 (*C*-6), 55.1 (*C*H$_3$O), 51.0 (*C*-2), 23.6 (*C*H$_3$CO), 19.9 (*C*-6'), −0.9 (*C*H$_3$Si), −1.5 (*C*H$_3$Si).

Methyl 2',3',4'-tri-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-β-D-glucopyranosyl-(1'→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (29b). *R*$_f$ 0.22 (PE/acetone, 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H; *H*C$_{Ar}$), 7.39 – 7.18 (m, 28H; *H*C$_{Ar}$), 5.18 (d, *J* = 8.3 Hz, 1H; N*H*), 4.95 (d, *J* = 12.4 Hz, 1H; C*H*H, Bn), 4.88 (d, *J* = 11.1 Hz, 1H; C*H*H, Bn), 4.86 – 4.82 (m, 2H; 2×C*H*H, Bn), 4.80 (d, *J* = 3.7 Hz, 1H; H-1), 4.79 – 4.73 (m, 2H; 2×C*H*H, Bn), 4.66 (d, *J* = 11.2 Hz, 1H; C*H*H, Bn), 4.62 (d, *J* = 12.1 Hz, 1H; C*H*H, Bn), 4.55 (d, *J* = 12.4 Hz, 1H; C*H*H, Bn), 4.40 (d, *J* = 12.1 Hz, 1H; C*H*H, Bn), 4.28 (d, *J* = 7.5 Hz, 1H; H-1'), 4.14 (ddd, *J* = 10.8, 8.3, 3.7 Hz, 1H; H-2), 3.98 (dd, *J* = 10.1, 8.8 Hz, 1H; H-4), 3.82 (dd, *J* = 10.9, 3.2 Hz, 1H; H-6a), 3.53 (ddd, *J* = 10.1, 3.2, 2.4 Hz, 1H; H-5), 3.51 – 3.47 (m, 1H; H-6b), 3.46 (dd, *J* = 10.8, 8.8 Hz, 1H; H-3), 3.42 – 3.34 (m, 2H; H-3'; H-2'), 3.32 (s, 3H; C*H*$_3$O), 3.23 (ddd, *J* = 10.9, 9.0, 1.7 Hz, 1H; H-5'), 3.13 (dd, *J* = 9.0, 8.7 Hz, 1H; H-4'), 1.86 (s, 3H; C*H*$_3$CO), 1.38 (dd, *J* = 14.9, 1.7 Hz, 1H; H-6a'), 0.72 (dd, *J* = 14.9, 10.9 Hz, 1H; H-6b'), 0.31 (s, 3H; C*H*$_3$Si), 0.26 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8 (*C*=O), 139.6 (*C*$_{Ar,q}$), 139.5 (*C*$_{Ar,q}$), 138.8 (*C*$_{Ar,q}$), 138.7 (*C*$_{Ar,q}$), 138.6 (*C*$_{Ar,q}$), 138.0 (*C*$_{Ar,q}$), 133.8 (2×*C*$_{Ar}$H), 128.9 (*C*$_{Ar}$H), 128.6 (2×*C*$_{Ar}$H), 128.5 (*C*$_{Ar}$H), 128.5 (2×*C*$_{Ar}$H), 128.5 (2×*C*$_{Ar}$H), 128.4 (2×*C*$_{Ar}$H), 128.4 (2×*C*$_{Ar}$H), 128.3 (2×*C*$_{Ar}$H), 128.2 (2×*C*$_{Ar}$H), 128.0 (2×*C*$_{Ar}$H), 127.9 (2×*C*$_{Ar}$H), 127.9 (2×*C*$_{Ar}$H), 127.8 (2×*C*$_{Ar}$H), 127.8 (*C*$_{Ar}$H), 127.7 (*C*$_{Ar}$H), 127.7 (*C*$_{Ar}$H), 127.5 (*C*$_{Ar}$H), 102.0 (*C*-1'), 98.4 (*C*-1), 84.7, 84.6 [2 peaks: C-3'; C-4'], 83.6 (*C*-2'), 77.8 (*C*-3), 76.4 (*C*-4), 75.7 (*C*H$_2$, Bn), 75.3 (*C*H$_2$, Bn), 75.1 (*C*H$_2$, Bn), 74.4 (*C*H$_2$, Bn), 73.6 (*C*H$_2$, Bn), 72.9 (*C*-5'), 70.8 (*C*-5), 67.7 (*C*-6), 55.3 (*C*H$_3$O), 52.8 (*C*-2), 23.5 (*C*H$_3$CO), 18.5 (C-6'), −1.4 (*C*H$_3$Si), −2.7 (*C*H$_3$Si).

2-Methoxyethyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-L-idopyranosides (30a, 30b). General procedure A with phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-L-idopyranoside (**10**) (68 mg, 0.120 mmol), 2-methoxyethanol (**14**) (14 µL, 0.181 mmol), NIS (31 mg, 0.132 mmol) and TfOH (1.1 µL, 0.012 mmol). The procedure afforded 51 mg (81%; α/β, 93:7) of **30a** and **30b** after flash silica column chromatography (PE/EtOAc, 7:3).

2-Methoxyethyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-α-L-idopyranoside (30a). *R*$_f$ 0.22 (PE/EtOAc, 3:1); [α]$_D^{25}$ −64.1° (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H; *H*C$_{Ar}$), 7.37 – 7.25 (m, 8H; *H*C$_{Ar}$), 4.93 (ddd, *J* = 2.9, 1.6, 0.9 Hz, 1H; H-2), 4.79 (bs, 1H; H-1), 4.71 (d, *J* = 12.0 Hz, 1H; C*H*H, Bn), 4.66 – 4.65 (m, 1H; H-4), 4.60 (d, *J* = 12.0 Hz, 1H; CH*H*, Bn), 4.45 (ddd, *J* = 8.5, 6.4, 1.8 Hz, 1H; H-5), 3.68 (ddd, *J* = 11.0, 4.6, 4.5 Hz, 1H; C*H*, aglyc.), 3.66 – 3.64 (m, 1H; H-3), 3.52 (ddd, *J* = 11.0, 5.8, 4.4 Hz, 1H; C*H*, aglyc.), 3.46 – 3.43 (m, 2H; 2×C*H*, aglyc.), 3.32 (s, 3H; C*H*$_3$O), 2.07 (s, 3H; C*H*$_3$CO), 2.05 (s, 3H; C*H*$_3$CO), 1.22 (dd, *J* = 14.8, 8.5 Hz, 1H; H-6a), 1.04 (dd, *J* = 14.8, 6.4 Hz, 1H; H-6b), 0.34 (s, 3H; C*H*$_3$Si), 0.33 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4 (*C*=O), 169.7 (*C*=O), 138.6 (*C*$_{Ar,q}$), 138.1 (*C*$_{Ar,q}$), 133.7 (2×*C*$_{Ar}$H), 129.2 (*C*$_{Ar}$H), 128.4 (2×*C*$_{Ar}$H), 128.0 (2×*C*$_{Ar}$H), 127.7 (*C*$_{Ar}$H), 127.5 (2×*C*$_{Ar}$H), 98.6 (*C*-1; $^1J_{C1\text{-}H1}$ = 168.2 Hz, characteristic of an axially oriented group on C-1), 73.1 (*C*-3), 71.9 (*C*H$_2$, Bn), 71.7 (*C*H$_2$, aglyc.), 70.9 (*C*-4), 67.6 (*C*H$_2$, aglyc.), 67.4 (*C*-2), 63.6 (*C*-5), 59.3 (*C*H$_3$O), 21.2 (*C*H$_3$CO), 21.1 (*C*H$_3$CO), 18.0 (*C*-6), −1.7 (*C*H$_3$Si), −2.6 (*C*H$_3$Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{28}H_{38}NaO_8Si$: 553.2234; found: 553.2220.

2-Methoxyethyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-β-L-idopyranoside (30b). *R*$_f$ 0.14 (PE/EtOAc, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H; *H*C$_{Ar}$), 7.38 – 7.24 (m, 8H; *H*C$_{Ar}$), 4.95 (ddd, *J* = 2.9, 1.6, 0.9 Hz, 1H; H-2), 4.77 (d, *J* = 1.6 Hz, 1H; H-1), 4.66 (d, *J* = 11.8 Hz, 1H; C*H*H, Bn), 4.62 (d, *J* = 11.8 Hz, 1H; CH*H*, Bn), 4.57 (ddd, *J* = 2.5, 1.6, 0.9 Hz, 1H; H-4), 4.03 (ddd, *J* = 9.4, 5.0, 1.6 Hz, 1H; H-5), 3.95 (ddd, *J* = 10.6, 4.7, 3.6 Hz, 1H; C*H*HCH$_2$, aglyc.), 3.78 (dd, *J* = 2.9, 2.5 Hz, 1H; H-3), 3.62 (ddd, *J* = 10.6, 7.2, 3.9 Hz, 1H; CH*H*CH$_2$, aglyc.), 3.64 – 3.48 (m, 2H; 2×C*H*, aglyc.), 3.35 (s, 3H; C*H*$_3$O), 2.09 (s, 3H; C*H*$_3$CO), 2.05 (s, 3H; C*H*$_3$CO), 1.35 (dd, *J* = 14.9, 9.4 Hz, 1H; H-6a), 0.98 (dd, *J* = 14.9, 5.0 Hz, 1H; H-6b), 0.35 (s, 3H; C*H*$_3$Si), 0.33 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6 (*C*=O), 170.4 (*C*=O), 138.6 (*C*$_{Ar,q}$),

137.5 ($C_{Ar,q}$), 133.7 (2×C_{Ar}H), 129.3 (C_{Ar}H), 128.6 (2×C_{Ar}H), 128.1 (C_{Ar}H), 128.1 (2×C_{Ar}H), 127.7 (2×C_{Ar}H), 98.0 (*C*-1; $^1J_{C1\text{-}H1}$ = 158.1 Hz, characteristic of an equatorially oriented group on C-1), 74.1 (*C*-3), 72.7 (CH_2, Bn), 71.7 (CH_2, aglyc.), 70.8 (*C*-5), 70.0 (*C*-4), 69.0 (CH_2, aglyc.), 67.3 (*C*-2), 59.3 (CH_3O), 21.3 (CH_3CO), 21.0 (CH_3CO), 18.0 (*C*-6), −1.7 (CH_3Si), −2.4 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{28}H_{38}NaO_8Si$: 553.2234; found: 553.2220.

Methyl 2',4'-di-*O*-acetyl-3'-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-α-L-idopyranosyl-(1'→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (31). General procedure A with phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-L-idopyranoside (**10**) (102 mg, 0.180 mmol), methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**17**) (126 mg, 0.270 mmol), NIS (47 mg, 0.198 mmol) and TfOH (1.6 µL, 0.018 mmol). The procedure afforded 95 mg (58%) of **31** after flash silica column chromatography (toluene/acetone, 19:1). R_f 0.27 (PE/EtOAc, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (m, 2H; *H*C$_{Ar}$), 7.35 – 7.19 (m, 23H; *H*C$_{Ar}$), 5.05 (m, 1H; H-1'), 4.85 – 4.81 (m, 2H; H3'; C*H*H, Bn-a), 4.78 (d, *J* = 11.1 Hz, 1H; CH*H*, Bn-a), 4.67 (d, *J* = 12.0 Hz, 1H; C*H*H, Bn-b), 4.62 (d, *J* = 11.9 Hz, 1H; C*H*H, Bn-c), 4.59 (d, *J* = 11.9 Hz, 1H; CH*H*, Bn-c), 4.58 – 4.53 (m, 4H; H-1; H-2'; H-5'; CH*H*, Bn-b), 4.44 (s, 2H; 2×C*H*, Bn-d), 3.86 (dd, *J* = 9.1, 9.0 Hz, 1H; H-4), 3.82 (dd, *J* = 9.2, 9.0 Hz, 1H; H-3), 3.72 (dd, *J* = 10.7, 3.7 Hz, 1H; H-6a), 3.69 (ddd, *J* = 9.1, 3.7, 1.7 Hz, 1H; H-5), 3.64 (ddd, *J* = 3.0, 1.1, 1.1 Hz, 1H; H-4'), 3.59 (dd, *J* = 10.7, 1.7 Hz, 1H; H-6b), 3.49 (dd, *J* = 9.2, 3.6 Hz, 1H; H-2), 3.36 (s, 3H; C*H*$_3$O), 1.94 (s, 3H; C*H*$_3$CO), 1.91 (s, 3H; C*H*$_3$CO), 1.03 (dd, *J* = 14.7, 7.3 Hz, 1H; H-6a'), 0.87 (dd, *J* = 14.7, 8.1 Hz, 1H; H-6b'), 0.20 (s, 3H; *C*H$_3$Si), 0.19 (s, 3H; *C*H$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5 (*C*=O), 169.7 (*C*=O), 139.4 ($C_{Ar,q}$), 139.3 ($C_{Ar,q}$), 138.3 ($C_{Ar,q}$), 138.2 ($C_{Ar,q}$), 137.9 ($C_{Ar,q}$), 133.7, 129.2, 129.0, 128.5, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.2 [aromatic C atoms], 98.2 (*C*-1), 97.7 (*C*-1'), 80.8 (*C*-4), 80.0 (*C*-2), 75.1 (CH_2, Bn), 74.6 (*C*-3), 73.6, 73.3, 73.3 [*C*-4'; 2×CH_2, Bn], 72.4 (CH_2, Bn), 70.2, 70.2 [*C*-5; *C*-2' *or* *C*-5'], 68.9 (*C*-6), 67.8 (*C*-3'), 64.3 [C-2' *or* C-5'], 55.4 (CH_3O), 21.1 (CH_3CO), 21.0 (CH_3CO), 17.7 (*C*-6), −1.5 (CH_3Si), −2.2 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{53}H_{62}NaO_{12}Si$: 941.3908; found: 941.3878.

Methyl 2',4'-di-*O*-acetyl-3'-*O*-benzyl-6'-deoxy-6'-dimethylphenylsilyl-α-L-idopyranosyl-(1'→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (32). General procedure B with phenyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-1-thio-L-idopyranoside (**10**) (43 mg, 0.075 mmol), methyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (**17**) (21 mg, 0.051 mmol), NIS (20 mg, 0.083 mmol) and TfOH (0.7 µL, 0.008 mmol). The procedure afforded 21 mg (46%) of **32** after flash silica column chromatography (toluene/acetone, 12:1 to 2:1). R_f 0.30 (toluene/acetone, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H; *H*C$_{Ar}$), 7.35 – 7.21 (m, 16H; *H*C$_{Ar}$), 7.17 – 7.12 (m, 2H; *H*C$_{Ar}$), 5.02 (d, *J* = 9.0 Hz, 1H; N*H*), 5.01 – 5.00 (m, 1H; H-1'), 4.91 – 4.89 (m, 1H; H-2'), 4.67 (d, *J* = 3.7 Hz, 1H; H-1), 4.65 – 4.61 (m, 2H; H-4'; C*H*H, Bn-b), 4.64 (d, *J* = 12.2 Hz, 1H; C*H*H, Bn-a), 4.61 (d, *J* = 11.8 Hz, 1H; CH*H*, Bn-b), 4.56 (ddd, *J* = 8.5, 6.9, 1.8 Hz, 1H; H-5'), 4.54 (d, *J* = 12.1 Hz, 1H; C*H*H, Bn-c), 4.50 (d, *J* = 12.1 Hz, 1H; CH*H*, Bn-c), 4.40 (d, *J* = 12.2 Hz, 1H; CH*H*, Bn-a), 4.15 (ddd, *J* = 10.5, 9.0, 3.7 Hz, 1H; H-2), 3.93 (dd, *J* = 9.5, 8.9 Hz, 1H; H-4), 3.76 (dd, *J* = 10.8, 3.6 Hz, 1H; H-6a), 3.71 – 3.65 (m, 2H; H-3'; H-5), 3.64 (dd, *J* = 10.8, 1.9 Hz, 1H; H-6b), 3.54 (dd, *J* = 10.5, 8.9 Hz, 1H; H-3), 3.30 (s, 3H; C*H*$_3$O), 1.98 (s, 3H; C*H*$_3$CO), 1.97 (s, 3H; C*H*$_3$CO), 1.69 (s, 3H; C*H*$_3$CON), 1.16 (dd, *J* = 14.6, 6.9 Hz, 1H; H-6b'), 1.09 (dd, *J* = 14.6, 8.5 Hz, 1H; H-6b'), 0.27 (s, 3H; C*H*$_3$Si), 0.26 (s, 3H; C*H*$_3$Si). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4 (*C*=O), 169.8 (*C*=O), 169.7 (*C*=O), 138.9 ($C_{Ar,q}$), 138.8 ($C_{Ar,q}$), 138.4 ($C_{Ar,q}$), 137.8 ($C_{Ar,q}$), 133.7 (2×C_{Ar}H), 129.1 (C_{Ar}H), 128.5 (6×C_{Ar}H), 128.4 (2×C_{Ar}H), 128.0 (2×C_{Ar}H), 127.9 (C_{Ar}H), 127.8 (2×C_{Ar}H), 127.7 (C_{Ar}H), 127.6 (2×C_{Ar}H), 127.5 (C_{Ar}H), 98.4 (*C*-1), 97.6 (*C*-1'), 78.4 (*C*-3), 75.1 (*C*-4), 74.3 (CH_2, Bn-a), 73.4 (C-3'), 73.3 (CH_2, Bn-c), 72.6 (CH_2, Bn-b), 71.1 (*C*-5), 70.2 (*C*-4'), 68.7 (*C*-6), 68.3 (*C*-2'), 64.6 (*C*-5'), 55.2 (CH_3O), 52.4 (*C*-2), 23.4 (CH_3CON), 21.1 (CH_3CO), 21.0 (CH_3CO), 17.8 (*C*-6'), −1.7 (CH_3Si), −2.4 (CH_3Si). HR-MS: [*M*+Na]$^+$ calcd for $C_{53}H_{62}NaO_{12}Si$: 941.3908; found: 941.3878.

2-Methoxyethyl 2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranoside (35). To a 10-mL flask, 2-methoxyethyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-dimethylphenylsilyl-α-D-glucopyranoside (**26a**) (35 mg, 0.056 mmol) and dry DMF (2 mL) were added. To this solution, 1 M TBAF in THF (0.39 mL, 0.90 mmol) was added. The mixture was stirred at 80°C overnight. After cooling down to room temperature, 1 M HCl(aq) (10 mL) was added and extracted with EtOAc (3 × 10 mL). The organic layers were combined and washed with water, 1 M HCl(aq) and brine. After drying over $MgSO_4$(s), the mixture was concentrated to dryness over reduced pressure. The desired product was obtained pure as a colourless syrup without further purification (22 mg; 79%). R_f 0.27 (PE/EtOAc, 5:1); $[\alpha]_D^{25}$ +31.3° (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 18H), 5.00 (d, *J* = 10.8 Hz, 1H; C*H*H, Bn-a), 4.90 (d, *J* = 10.9 Hz, 1H; C*H*H, Bn-b), 4.82 (d, *J* = 10.8 Hz, 1H; CH*H*, Bn-a), 4.78 (d, *J* = 12.0 Hz, 1H; C*H*H, Bn-c), 4.77 (d, *J* = 3.6 Hz; H-1), 4.69 (d, *J* = 12.0 Hz, 1H; CH*H*, Bn-c), 4.63 (d, *J* = 10.9 Hz, 1H; CH*H*, Bn-b), 3.98 (dd, *J* = 9.6, 9.0 Hz, 1H; H-3), 3.82 (dq, *J* = 9.6, 6.2 Hz, 1H; H-5), 3.75 (ddd, *J* = 11.2, 5.5, 4.2 Hz, 1H; C*H*H, aglyc.), 3.66 (ddd, *J* = 11.2, 5.1, 5.1 Hz, 1H; CH*H*, aglyc.), 3.60 (m, 2H; 2×C*H*, aglyc.), 3.54 (dd, *J* = 9.6, 3.6 Hz, 1H; H-2), 3.39 (d, *J* = 1.5 Hz, 3H; C*H*$_3$O), 3.13 (dd, *J* = 9.6, 9.0 Hz, 1H; H-4), 1.24 (d, *J* = 6.2 Hz, 3H; C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1 ($C_{Ar,q}$), 138.5 ($C_{Ar,q}$), 138.5 ($C_{Ar,q}$), 128.5 (4×C_{Ar}H), 128.5 (2×C_{Ar}H), 128.2 (2×C_{Ar}H), 128.1 (4×C_{Ar}H), 127.9 (C_{Ar}H), 127.9 (C_{Ar}H), 127.7 (C_{Ar}H), 97.1 (*C*-1), 84.0, 81.9, 80.5, 75.8, 75.5, 73.0, 71.9, 66.9, 66.8 [9 peaks: C-2; C-3; C-4; C-5; 3×*C*H$_2$, Bn; 2×*C*H$_2$, aglyc.], 59.1 (*C*H$_3$O), 18.0 (*C*-6). HR-MS: [*M*+Na]$^+$ calcd for $C_{30}H_{36}NaO_6$: 515.2410; found: 515.2398.

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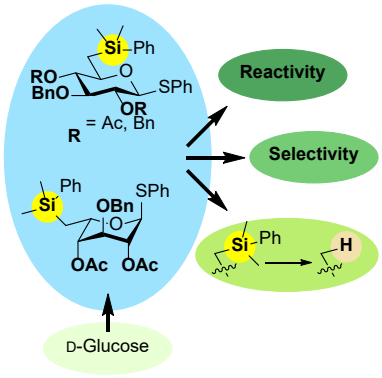
Entry for the Table of Contents



To study the influence of a silyl group on the reactivity and selectivity of glycosyl donors, two synthetic routes have been developed to obtain both D-glucosyl and L-idosyl donors with a silyl group attach to C6. The glycosylation and competition studies show that it enhances reactivity beyond what an *O*-benzyl group on C6 would do. In order to access C6-deoxy sugars, an efficient protodesilylation methodology is also described.