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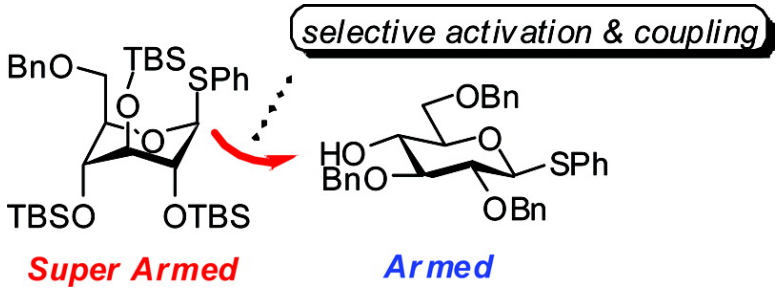

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"Super Armed" Glycosyl Donors: Conformational Arming of Thioglycosides by Silylation

Christian Marcus Pedersen, Lars Ulrik Nordstrøm, and Mikael Bols*,†

Contribution from the Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Received March 20, 2007; E-mail: bols@kemi.ku.dk

Abstract: Glycosyl donors protected with bulky silyl protective groups (*tert*-butyldimethylsilyl, TBS), on the 2-, 3-, and 4-OH groups were found to have superior reactivity compared with benzylated thioglucosides. The enhanced reactivity is explained by the stereoelectronic effects associated with the conformational change induced by the silylation. A TBS silylated thioglucoside donor has axial OR groups, whereas a benzylated thioglucoside has equatorial OR groups, leading to much more favorable charge−dipole interactions in the transition state. This concept could be used to create "super armed" glucosyl, mannosyl, rhamnosyl, and galactosyl donors, which could cross-couple with the armed acceptors, phenyl 2,3,4-tri-*O*-benzyl-β-D-thioglucoside or phenyl 2,3,6-tri-*O*-benzyl-β-D-thioglucoside, to give the corresponding armed disaccharides in good to excellent yields.

Introduction

Glycosylation reactions play a central role in carbohydrate chemistry. In order to facilitate synthesis of complex oligosaccharides a wide variety of glycosylation reactions have been developed.[1] Thioglycosides[2] have become one of the most popular donor types due to their easy preparation and stability toward carbohydrate manipulation reactions such as standard protection/deprotection reactions. It was noticed, since the early years of glycosylations, that the reactivity of carbohydrates depended on their substituents and their stereochemistry.[3] In the late 1980s Fraiser-Reid et al.[4] described the major difference in the reactivity between glycosyl donors having benzyl- and acyl-protecting groups, as the armed−disarmed concept: Benzylated donors are more reactive and termed "armed", whereas acetylated donors are less reactive and described as "disarmed". This concept has been widely explored most notably in "one pot" glycosylation reactions.[5] The armed−disarmed concept also covers other types of protecting groups such as acetals, which have been shown to be both electronic[6] and torsional[4] disarming. The influence of electronic effects on the reactivity at the anomeric center has also been used to solve other synthetic problems: Crich et al.[7] developed a stereoselective synthesis of β-mannosides which employs, as its key element, donors that have been disarmed by locking their conformation in $^4C_1$ conformer. Stable α-mannosyl triflates can be generated from these donors and cleanly substituted with inversion to give the β-mannoside.

Until recently the influence of stereochemistry on carbohydrate reactivity was poorly understood. However, under our study of substituent effects on the pK_a of piperidines[8] it was observed that axial hydroxyl groups were less electron withdrawing than the corresponding equatorial hydroxyl groups. The phenomenon is presumably caused by differences in charge−dipole interactions between a positive charge in the ring and an axial or equatorial C−O dipole.[9]

The concept of an axial polar substituent stabilizing a positive charge to a higher degree than the corresponding equatorial equivalent explains age-old observations[10,11] such as the increased propensity of methyl glycosides to undergo hydrolysis; the more axial hydroxyl groups they have, the relative ratio of hydrolysis rates between the methyl-galacto and -glucosides is

† Present address: M. Bols, Department of Chemistry, University of Copenhagen, 2100 Kbh Ø Copenhagen, Denmark.

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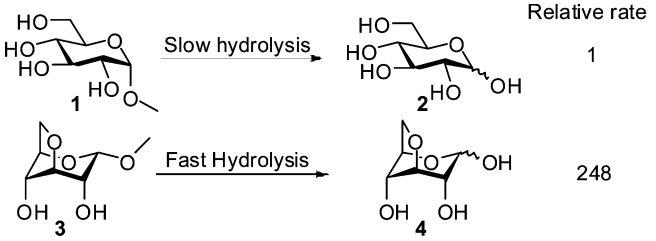

Figure 1. Influence of conformational changes in the hydrolysis of methyl-α-D-glucoside.

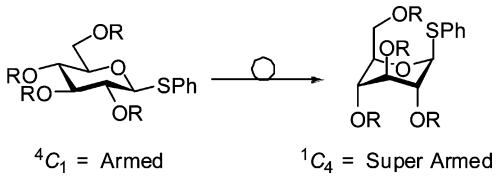

Figure 2. Conformational arming of thioglucosyl donor.

5 to 1. It also explains why the same tendency is observed in glycosylation reactions[12] where benzylated tolylthiogalactoside reacts with MeOH under NIS activation 6.4 times faster than the corresponding thioglycoside. It follows that forcing equatorial *O*-substituents into the axial position will make a carbohydrate derivative more reactive. Indeed, a conformationally restricted glycoside such as methyl 3,6-anhydroglucoside, which has all-axial hydroxyl groups, has been shown to hydrolyze much faster than its all-equatorial counterpart (Figure 1).[10f] The idea behind the present work was to investigate whether it was possible to arm glycosyl donors by forcing the oxygen substituents into an axial position (Figure 2). This could conceivably be achieved by bulky silyl protections groups. Interestingly, glycosylation with conformationally inverted donors has been carried out in the literature several times, typically for the purpose of obtaining stereoselectivity,[13] and though the reactivity of such donors has not been systematically investigated, there are some indications that they may be more reactive.[14−16]

In this work we have systematically investigated the reactivity of such "conformationally armed" glycosyl donors and carried out a number of glycosylation reactions with them. We find that they are considerably more reactive than benzylated (armed) donors.

Results and Discussion

Synthesis and Conformation. First we investigated a glucosyl donor, since it has all the ring hydroxyl groups equatorial and would give the largest effect upon change of conformation. Thus, changing a glucose derivative from the all-equatorial $^4C_1$ conformation to the all-axial $^1C_4$ conformation should make it "super armed".

Changing the conformation of glucose to $^1C_4$ conformation often involves locking of the pyranose ring with 2,4-restriction[17] and 3,6-[18] or 1,6-anhydrides. This approach gives the desired conformation, but not necessarily a useful glucosyl donor; difficulties in the activation of the 1,6-anhydride and the problems concerning "breaking" the 3,6-anhydride limit the usefulness of these structures for synthetic purposes.

The ring flip can also be achieved by introducing bulky silyl protecting groups,[19,20] such as TBS, TBDPS, or TIPS, which cannot be accommodated into a $^4C_1$ conformation and force the pyranose ring to an axial-rich conformation—ideally a $^1C_4$ conformation (Figure 3).

TBS groups have been popular hydroxyl protecting groups in carbohydrate chemistry[21] since their introduction by Corey.[22] The conformational changes observed when using bulky silyl protecting groups have been used to control the stereochemistry in C-glycosylation. When having $^4C_1$ restricted conformation, α selectivity was observed in radical reactions on the anomeric center, whereas $^1C_4$ conformation resulted in β selectivity.[23] Selectivities in reduction at the anomeric position have also been shown to greatly influence the conformation of the pyranose ring. Substrates in $^4C_1$ conformation resulted in β-products, while substrates in $^1C_4$ conformation gave α-products.[24]

Inspired from the examples above and the literature,[19,25] we prepared compound **8** as illustrated in Scheme 1.

Even though the conformation is a twisted boat[19] rather than the desired $^1C_4$ conformation, the oxygen substituents are perpendicular to the sugar ring, minimizing the unfavorable charge−dipole interactions between C−O bonds and a positive charge at C-1 or ring oxygen. When this glucosyl donor was applied to NIS-/TfOH-mediated glycosylation reactions with 1-octanol as an acceptor, none of the expected coupling product was observed—only the 1,6-anhydride **9**. To prevent this side reaction the 6-OH had to be protected with a more stable protective group.

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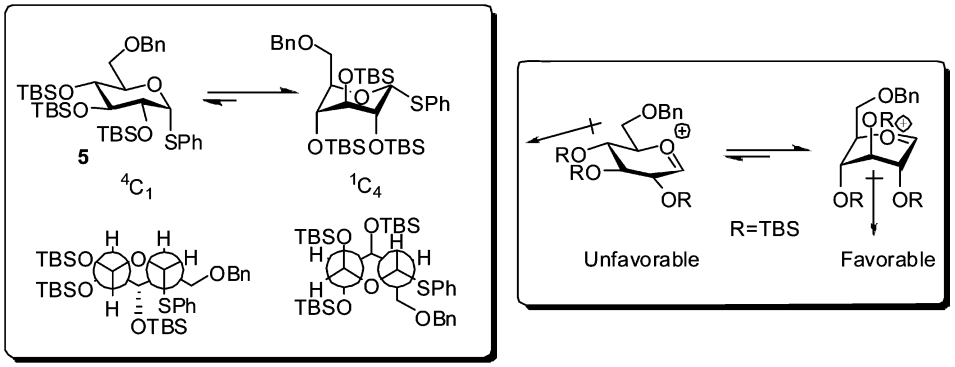


Figure 3. Ring flip caused by bulky hydroxy protection groups in α-thioglycoside and dipoles in $^4C_1$ and $^1C_4$ conformation respectively.

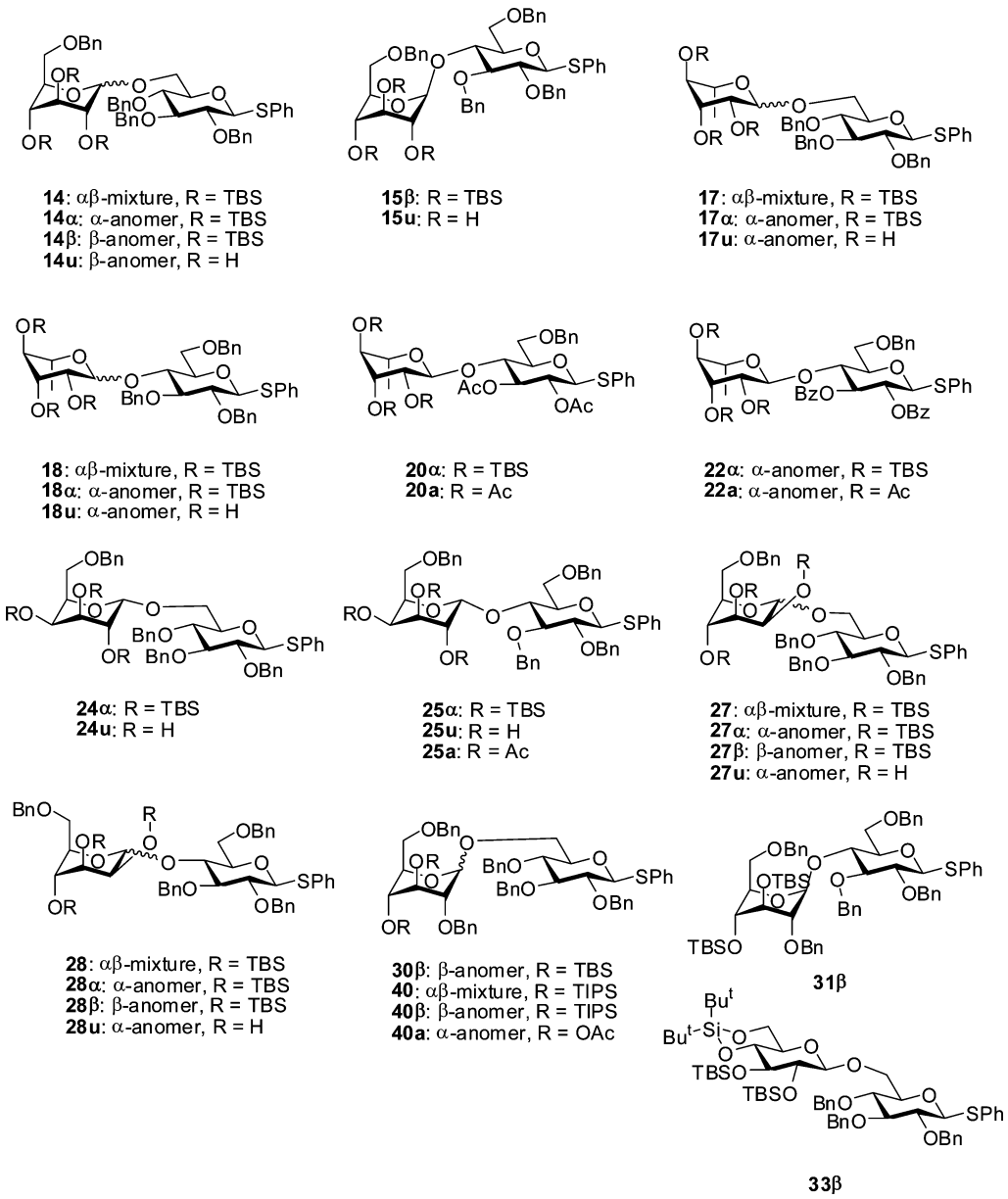


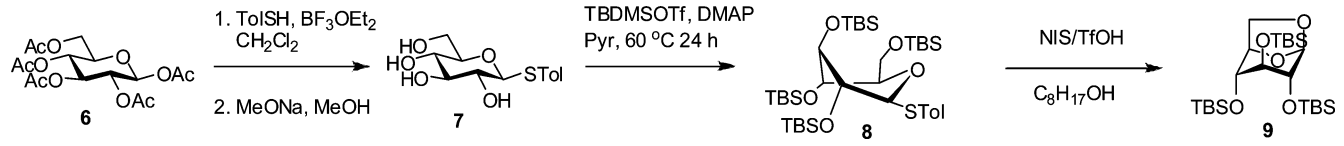
Figure 4. Products from the glycosylations together with desilylated and acetylated derivatives.

We chose 6-*O*-benzyl protection which was obtained from reductive opening of the 4,6-di-*O*-benzylidene-thioglucoside using TESH and TFA[26] followed by 2,3,4-*O*-protection with TBSOTf.

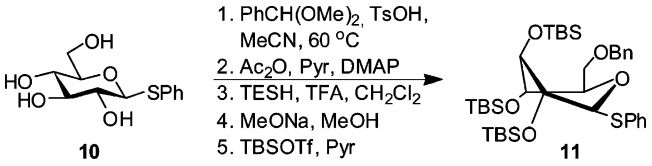
The conformation of the donor **11** was found to be in the same twisted boat conformation as donor **8**.

The α-anomer, donor **5**, was also synthesized and was likewise found to be in a twisted boat conformation rather than

Scheme 1. Preparation of Phenyl 2,3,4,6-Tetra-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-glucopyranoside (Tol = 4-CH_3Ph), and Attempted Glycosylation with *n*-Octanol



Scheme 2. Preparation of Phenyl 2,3,4-Tri-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl-thioglycoside



the $^1C_4$ conformation.[27] Both anomers are expected to be more reactive than conventional armed donors since the protected-ring hydroxyl groups are perpendicular to the pyranose ring as seen from Scheme 2.

Glycosylation. To test the donor, a set of armed donor/acceptors were prepared and used as acceptors in cross-coupling reactions with the conformationally armed donor (Scheme 3). The benzyl-protected thioglycosides **12** and **13** were chosen in order to have a comparable system, which is considered to be armed. These glucose donors are commonly used in glycosylation reactions and as test substrates.[12]

The initial studies of the glycosylation revealed a very fast activation (reaction) of the "super armed" donor as seen by the formation of iodine. The activation of the donor could be performed at −85 to −90 °C by addition of NIS[28] followed by a catalytical amount of TfOH. After a period (usually 1−2 h) at this temperature the reaction mixture was allowed to reach −55 °C over approximately 2 h, followed by quenching it with Et_3N at −55 °C to prevent activation of the acceptor or migration of TBS groups. For comparison the armed donors required a temperature of −60 to −65 °C to activate. Higher temperature led to a decline in stereoselectivity (Figure 4, Table 1).

Activator systems other than NIS/TfOH, such as NIS, NIS/TESOTf, or IDCP, did not give results as those of NIS/TfOH. NIS alone at RT resulted in a side reaction with succinimide as the acceptor. When using IDCP as activator only limited conversion was observed. The reaction appeared to be inhibited by formation of collidine since it could not be driven to completion by adding excess reagent. Since the NIS/TfOH system gave a clean activation and only limited deprotection of the silyl ethers, we continued with this activation method.

The anomeric stereochemistry was assigned on the basis of the $^3J_{H1,H2}$ coupling constants of the deprotected major product in the usual manner when sufficient resolution was available; otherwise the assignments were based on the $^1J_{CH}$ coupling constants.

To examine the influence of configuration as well as the mechanism of the glycosylation, the low-temperature conditions were applied to the α- and β-thioglucoside donors **5** and **11**. The activation of both donors occurred within 15 min as a color change from orange to dark red-purple was observed. The glycosylations afforded comparable good yields of the armed disaccharides **14** and **15** as well as similar stereoselectivity, as seen from Table 1, entries 1 and 2. The high reactivity of these twisted donors shows that it is not essential that the donor is in a $^1C_4$ conformation in order to be activated; the important point is presumably that the substituents are axial in the intermediate oxacarbenium ion. Furthermore the reactivities of the α- and β-thioglycoside donors are similar, as is the stereoselectivity of the NIS-/TfOH-mediated glycosylations compared with that of these donors. A common intermediate is therefore indicated, and this is most likely the glycosyl oxacarbenium ion.

A competition experiment with equal amounts of super armed donor **11** and armed donor phenylthio-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (**12a**) and the armed acceptor **12** was carried out (Scheme 4). In this case a 75% yield of **14** was obtained (α:β 1:4), whereas none of the coupling product between **12a** and **12** was seen.

The rapid reaction of the conformationally armed glycosyl donors **5** and **11** indicated similar enhancement of reactivity with other glycosyl donors. To investigate this, other donors were super armed in a similar manner (Scheme 5). TBDMS-protected thiorhamnoside **16**, thiogalactoside **23**, and thiomannoside **26** were prepared analogously to **5** and **11**. In the ideal $^1C_4$ conformation the manno- and rhamnosyl-donors **16** and **26** have axial hydroxyl groups in the 3- and 4-positions and should therefore be more reactive. The galactosyl donor **23**, however, has only one axial and one equatorial OR group in the 3- and 4-positions and is therefore not necessarily more reactive.

The ^1H NMR spectra of the **16**, **23**, and **26** donors were broad and complex since they exist in several conformers in slow equilibration. The spectra could be improved by heating the samples in DMSO to 100 °C so that the conformers gave one set of signals due to fast equilibration, or by cooling to −30 °C where the equilibration was slow and the different conformers gave sharper signals.

In the mannosyl donor **26** a 1:1 ratio of the two conformers was observed when the ^1H NMR spectra were recorded at −35 °C. With $^3J_{H1-H2}$ being 1.5 and 8.7 Hz this suggests an equatorial−equatorial and an axial−axial relationship between H1 and H2, respectively. When heating the sample to 100 °C, an intermediate coupling of $^3J_{H1-H2} = 6.6$ Hz is observed. When recording ^1H NMR of the rhamnosyl donor **16** at −25 °C, two conformers were observed, but this time the ratio was 1:4, favoring the conformation with an equatorial−equatorial relationship between H1 and H2 ($^3J_{H1-H2} = 1.6$ Hz). All the coupling constants in this conformation are very small, suggesting a conformation close to $^4C_1$ conformer, the flipped L-rhamnosyl donor. The minor conformation is having $^3J_{H1-H2} = 8.8$ Hz which suggests a more axial−axial relationship between H1 and H2. When heating **16** to 100 °C, an intermediate $^3J_{H1-H2}$ of 5.4 Hz is observed.

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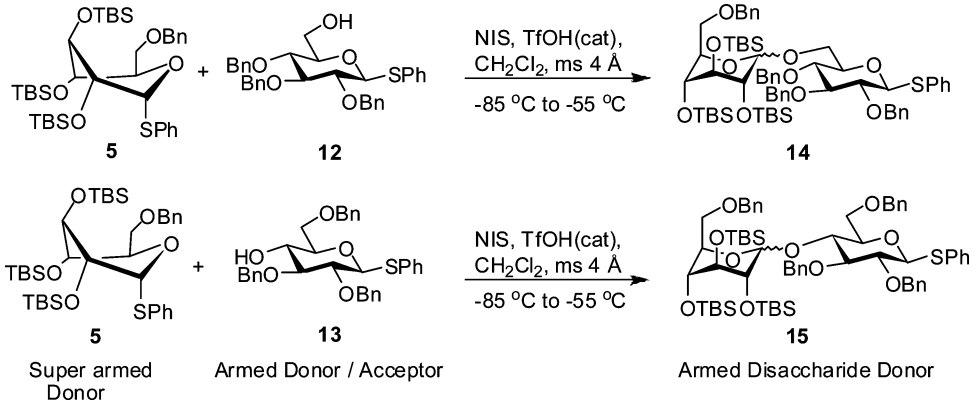
(27) Coupling constants show an almost axial relation between H4 and H5, whereas the other hydrogens only have small coupling constants.
(28) When adding NIS without TfOH, migration of the TBS protection groups was observed.

Scheme 3. Cross-Coupling between Super Armed Donor and Armed Donor/Acceptor (ms Is Molecular Sieves)



The conformation of the galactosyl donor **23** seems to be somewhat more complex even at low temperature. This might be due to several conformations in slow equilibrium. At 100 °C the ^{1}H NMR simplifies significantly, and one set of signals with $^3J_{H1-H2} = 4.9$ Hz can be observed in accordance with an equilibration becoming faster.

The three new donors were tested in glycosylation reactions with **12** and **13** (Table 3). The rhamnosyl donor **16** was very reactive and was readily activated below −80 °C. The reactions with both **12** and the more hindered **13** resulted in very good yields. The reactions gave a high α-selectivity,[29] which surprisingly increased upon raising the temperature; at approximately −60 °C, the α-anomer was the only observed product when coupling **16** and **13** and could be isolated in excellent yields. Such unusual behavior is most likely due to temperature influence on the conformational equilibria of donor or intermediates. The product gave a complex NMR spectrum even at high temperature since it existed in multiple conformers, even at high temperature. It was therefore deprotected in order to determine the stereochemistry.

When **16** was used in cross-coupling reactions with disarmed acceptors such as **19** and **21**, the yields were excellent, and the only products isolated were the α-anomers **20** and **22**, respectively.

The cross-coupling reactions of mannosyl donor **26** with **12** and **13** gave a similar high stereoselectivity and good yield as observed with **16** (Table 3). The α-selectivity was complete or, in the coupling with **12**, could be made complete by increasing the temperature, undoubtedly due to an influence of temperature on conformer equilibria. The products existed in multiple conformations, and it was not possible to obtain any information about the configuration from NMR studies. Therefore, the main products were subsequently deprotected and identified.

Under a number of different reaction conditions the galactosyl donor **23** gave good yields with the less sterically hindered acceptor **12** (Table 3), whereas the hindered acceptor **13** gave a poor yield of **25** together with a self-coupling product from **13** and a trisaccharide made from coupling **25** on **13**. The lower yields are clearly because **23** is less reactive than the other silylated donors, **5**, **11**, **16**, and **26**, presumably because the conformational change does not increase the number of axial OR groups significantly. Another explanation might be that the compound has little propensity for conformational change; it has been observed that 2,3-di-*O*-(*tert*-butyldimethylsilyl)-protected D-galactopyranoses are in the $^4C_1$ conformation.[30] However, Yamada et al.[31] recently showed that, in special cases, it is possible to flip the pyranose ring when having bulky silyl protection groups on O-2 and O-3 and a free hydroxyl group in the anomeric position. In all cases the α-anomer was the main product. This selectivity may arise from having a bulky TBS group on O-3 or O-4 shielding the "β side". A similar selectivity was obtained by Imamura et al.[32] when using di-*tert*-butylsilylene as a 4,6-O-protective group.

From the results obtained with the 3,4-*trans*-OTBS donors, **16** and **26**, one could suppose that it is only necessary to protect these two hydroxyl groups with bulky groups, since that is sufficient to induce the "ring flip". In order to investigate this the 3,4-di-*O*-TBS-protected glucose derivative[33] **29** was synthesized using the BDA protecting group method developed by Ley (Scheme 6).[34]

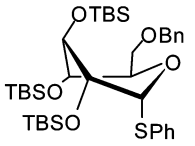
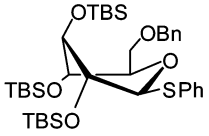
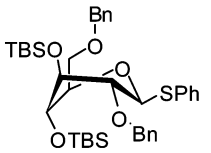
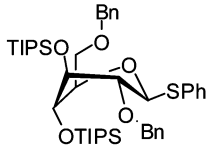
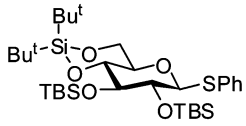
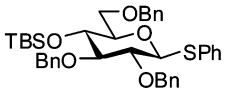
The conformation of the new donor could be determined from ^{1}H NMR to be an axial-rich twisted boat conformation. The donor **29** was applied to glycosylation reactions with **12** and **13** (Table 1) and showed greater reactivity than the armed acceptor/donor but nevertheless gave lower yields than the similar coupling with **11** either at low or high temperature. The stereoselectivity was excellent, giving only β-glycoside. The corresponding triisopropylsilyl (TIPS)-protected donor **39** was also made (Scheme 6) and investigated (Table 1). Coupling of **39** to **12** gave 77% of disaccharide **40**, showing that this TIPS-protected donor also is super armed.

Conformation or Silicon Effect? Although the above findings are in agreement with stereochemical substituent effects, it may nevertheless be argued that the silicon protective groups alone might have an activating effect. Thus, Gervay-Hague[35] has reported that a pertrimethylsilylated glucosyl donor was more reactive than the corresponding benzyl-protected donor. We therefore made a silyl-protected glucosyl donor **32** that was

(29) The stereochemistry of rhamnosides and mannosides was determined from the 1*J* CH of the deprotected major products.

(30) Totani, K.; Asano, S.; Takao, K.; Tadano, K. *Synlett* **2001**, 1772−1776; Tamai, T.; Asano, S.; Totani, K.; Takao, K.; Tadano, K. *Synlett* **2003**, 1865−1867; Asano, S.; Tamai, T.; Totani, K; Takao, K.; Tadano, K. *Synlett* **2003**, 2252−2254.
(31) Yamada, H.; Ikeda T. *Chem. Lett.* **2000**, *4*, 432−433.
(32) Imamura, A.; Ando, H.; Korogi, S.; Tanabe, G.; Muraoka, O.; Ishida, H.; Kiso, M. *Tetrahedron Lett.* **2003**, *44*, 6725−6728.
(33) Crich, D.; Jayalath, P. *J. Org. Chem.* **2005**, *70*, 7252−7259.
(34) (a) Hense, A.; Ley, S. V.; Osborn, H.; Owen, D. R.; Poisson, J.-F.; Warriner, S. L.; Wesson, K. E. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2023, (b) Montchamp, J.-L.; Tian, F.; Hart, M. E.; Frost, J. W. *J. Org. Chem.* **1996**, *61*, 3897. (c) Ley, S. V.; Baeschlin, D. K.; Dixon, D. J.; Foster, A. C.; Ince, S. J.; Priepke, H. W. M.; Reynolds, D. J. *Chem. Rev.* **2001**, *101*, 53.
(35) Du, W.; Gervay-Hague, J. *Org. Lett.* **2005**, *7*, 2063−2065.

Table 1. Glycosylation with Axial-Rich Glucosyl Donors

Donor	Acceptor	Activation Temperature / °C	Product	Yield[1]	α/β
 **5**	**12**	-85	**14**	86%	1:6
	13	-85	**15β**	63%	0:1
 **11**	**12**	-85	**14β**	78%	0:1
	12	-45	**14**	51%	2:9
	13	-85	**15β**	51%	0:1
	13	-78	**15β**	85%	0:1
 **29**	**12**	-45	**30β**	55%[#]	0:1
	12	-85	**30β**	37%[#]	0:1
	13	-45	**31β**	41%	0:1
	13	-85	**31β**	51%	0:1
 **39**	**12**	-78	**40**	77%	1:4
 **32**	**12**	-78	**33β**	7%	0:1
	13	-78	-	0%	
 **41**	**13**	-78	mixture	20%	

[1] All yields are isolated yields. The α/β ratio is of the isolated yield. *1.5 equiv of donor used. [#] TBS migration to acceptor occurring. The yield is based on reacting acceptor (subtracting TBS migration product).

restricted to $^4C_1$ conformation and compared it with the glucosyl donors **5** and **11** above (Scheme 7).

When **32** was reacted with **12**, only approximately 7% of coupling product **33** was observed (Table 1). The main products were the 1,6-anhydride **38**, formed from the acceptor **12**, together with the anomerized **32**. When coupling **32** with **13**, only **32**, as a mixture of anomers, was isolated.[36] These results clearly show that this donor is less reactive than the benzylated acceptor; it rather appears to be disarmed. The reactivity can be compared with the 4,6-di-*O*-acetal-protected glycosyl donors, which are considered as stereoelectronic and torsional disarmed.[6] The TBS group thus does not appear to have an intrinsic arming electronic effect.

Another experiment that supports this conclusion is when glycosylation of **13** is carried out with donor **41**, which has a single TBS group in the 4-position, the reaction is slow, and only 20% of the desired coupling products are observed (Table 1). This compound has a reactivity similar to that of the armed donor.

Conclusion

In this work we have expanded the armed−disarmed concept to contain "super armed" donors. This was achieved by forcing conformational changes in glycosyl donors by choice of protection groups. The rationale is that, when a donor with a

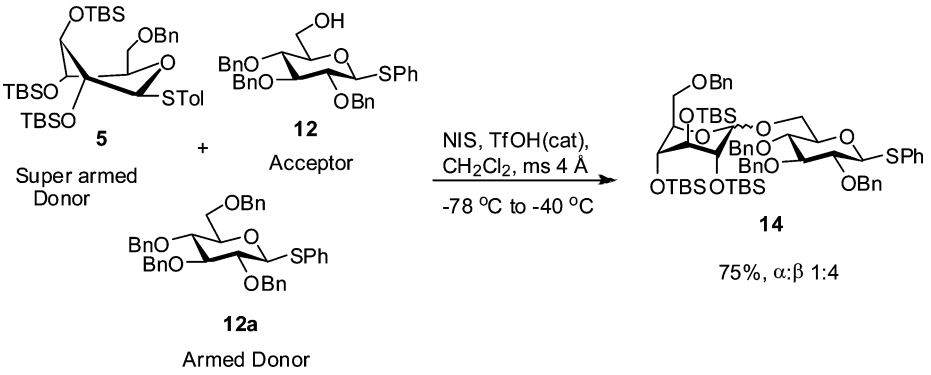
(36) Li, Z.; Gildersleeve, J. G. *J. Am. Chem. Soc.* **2006**, *128*, 11612−11619; Kartha, K. P. R.; Cura, P.; Aloui, M.; Readman, S. K.; Rutherford, T. J.; Field, R. A. *Tetrahedron Asymmetry* **2000**, *11*, 581−593.

Table 2. Coupling Constants in the Super Armed Donors

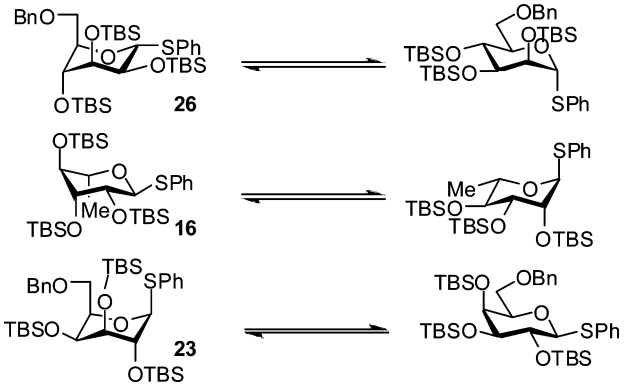
donor (T [°C])	δ (H1)/J_{1-2}(Hz)	δ(H2)/J_{2-3}(Hz)	δ(H3)/J_{3-4}(Hz)	δ(H4)/J_{4-5}(Hz)	δ(H5)/J_{5-6}(Hz)
5 (26)	5.61/4.2	4.10/3.6	3.89/≈ 0	3.79/8.6	4.39/2.1, 6.3
11 (50)	4.97/7.6	3.79/1.2	3.81/≈ 1.2[a]	3.84/2.1	3.98/6.6
23 (100)	4.96/4.9	4.09/5.4	3.82/2.1	4.25/4.2	4.05/7.8 (≈ 8)
26 (100)	5.23/6.6	4.06/≈ 0	3.86/≈ 0	3.87/4.0	3.92/≈ 5
(−30) major	5.27/8.7	4.37/8.3	3.62/9.9	3.84/1.6	3.97/2.0, 9.0
(−30) minor	5.27/1.5	4.14/1.7	3.74/1.7	3.71/4.8	4.03/2.8, 7.6
16 (100)	5.22/5.4	4.10/2.1	3.85/5.2	3.70/≈ 6.5	3.81/6.4
(−26) minor	5.22/5.4	3.90/2.1	3.67/≈1.9	3.43/4.8	3.75/6.6
(−26) major	5.18/1.5	4.07/≈ 0	3.75/≈ 0	3.76/≈ 6.8	3.98/6.3
29	5.04/8.3	3.46/3.2	3.87/4.7	3.77/3.9	3.89/5.8, 9.7
32	4.95/6.0	3.80/5.0	3.68/7.2	4.13/10.0	3.72/4.8, 10.0

[a] $J_{2-4} \approx 1.2$ Hz.

Scheme 4. Competition Experiment between Super Armed Donor and Armed Donor for the Same Acceptor (ms Is Molecular Sieves)



Scheme 5. Conformationally Armed Galactosyl, Rhamnosyl, and Mannosyl Donors



conformation rich on equatorial OR groups is altered to a more "axial-rich" conformation, it becomes significantly more reactive, since the axial substituents are less electron withdrawing. The method could be used to create "super armed" glucosyl, mannosyl, and rhamnosyl donors. The stereoselectivity could be controlled by temperature with the glucosyl donors giving mainly β at low temperature, while the galactosyl, mannosyl, and rhamnosyl donors were very α selective at −60 °C. The realization that carbohydrate donors can be "super armed" in this manner opens a number of exiting opportunities in the synthesis of complex carbohydrates and in the cross-couplings with acceptors of low reactivity.

Experimental Section

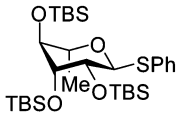
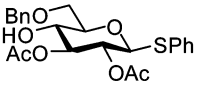
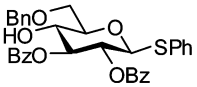
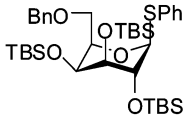
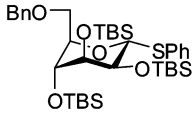
General. ^{13}C, ^{1}H, and H,H COSY NMR were recorded on a Varian Mercury 400 (400 MHz) NMR instrument. The spectra were referenced to solvent residues. MS was recorded on a Micromass LC-TOF instrument. Optical rotations were measured on a PE-314 polarimeter at 20 ± 1 °C. Chromatography was performed in Merck 60 silica. TLC was performed on Merck silica 60 E_{254}-coated glass plates and developed using Ce-mol (10 g of Ce(IV)SO_4 and 15 g of $(NH_4)_2MoO_4$ in 1 L of 10% H_2SO_4 med) or phosphomolybdic acid ($MoO_3-H_3PO_4$·H_2O 5% in EtOH) and subsequent heating.

***p*-Methylphenyl-2,3,4,6-tetra-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-glucopyranoside (8).**[19] *p*-Methylphenyl-1-thio-β-D-glycopyranoside (208 mg, 0.726 mmol) and 4-DMAP (20 mg, 0.16 mmol) were dissolved in pyridine (8 mL), and the solution was cooled to 0 °C. Then *tert*-butyldimethylsilyl triflate (1.5 mL, 6.5 mmol) was added, and the solution was stirred for 30 min at 0 °C and then for 68 h at room temperature. MeOH (3 mL) was added, and the solution was concentrated. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with aqueous $KHSO_4$ (10%, 2 × 50 mL) and sat. aqueous $NaHCO_3$ (50 mL). The solution was dried over $MgSO_4$ and concentrated under reduced pressure. The remaining solid was purified by column chromatography (eluent: pentane−toluene, 6:1) to give the fully protected compound **8** as a clear syrup (442 mg, 82%); $[\alpha]^{RT}_D$ −21.4° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.0 Hz, 2H, Ar*H*), 7.08 (d, 2H, Ar*H*), 4.97 (d, J = 7.6 Hz, 1H, H-1), 3.67 (dt, J 1.4 Hz, 2.8 Hz, 1H, H-4) 3.86 (d, J 2.8 Hz, 1H, H-3), 3.80−3.84 (m, 1H, H-5), 3.76−3.80 (m, H-2, 3H, 2 × H-6), 2.32 (s, 3H, ArCH_3), 0.92, 0.91, 0.90, 0.89 (4 s, 36H, C(CH_3)$_3$) 0.12, 0.11, 0.10, 0.09, 0.09, 0.07, 0.07 (7 s, 24H, Si(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 132.3, 130.7, 129.6, 86.7, 83.4, 78.1, 76.1, 70.2 (4C), 64.4, 26.0, 26.1, 26.1, 26.0, 21.2, 18.5, 18.3, 18.1, 18.0, −3.5, −4.0, −4.2, −4.2, −4.5, −4.5, −5.1; MS(ES) *m*/*z* calcd for $C_{37}H_{74}O_5SSi_4Na$: 765.4, *m*/*z* found: 765.3.

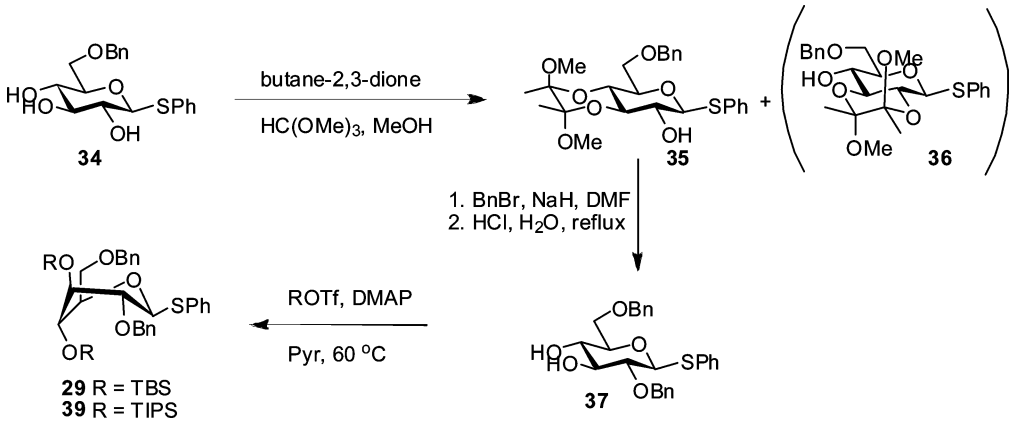
1,6-Anhydro-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (9):[37] ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.24 (s, 1H), 4.34 (d, J = 5.2 Hz, 1H) 4.08 (dd, J = 1.2 Hz, J = 6.8 Hz, 1H), 3.65 (t, 1H), 3.57−3.59 (m, 1H), 3.48 (d, J = 1.2 Hz, 1H), 3.42 (bs, 1H). 0.92, 0.90, 0.90 (3 × s, 27H), 0.02−0.14 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 102.21 (C), 76.53, 75.48, 72.98, 71.95, 64.58, 25.98, 25.94, 25.82,

(37) Chung, M.-K.; Schlaf, M. *J. Am. Chem. Soc.* **2005**, *127*, 18085−18092.

Table 3. Glycosylation with Axial-Rich Rhamnosyl, Mannosyl, and Galactosyl Donors

Donor	Acceptor	Activation Temperature / °C	Product	Yield[1]	α/β
 **16**	**12**	-85	**17**	79%	10:1
	13	-85	**18**	81%	3.6:1
	13	-75	**18**	84%	6.6:1
	13	-60	**18α**	90%	1:0
	 **19**	-78*	**20α**	78%	1:0
	 **21**	-78*	**22α**	95%	1:0
 **23**	**12**	-85	**24α**	73%[#]	1:0
	12	-40	**24α**	54%[#]	1:0
	12	-85	**24α**	39%	1:0
	13	-40	**25α**	42%[#]	1:0
	12	-78*	**24α**	70%	1:0
	13	-78*	**25α**	32%	1:0
 **26**	**12**	-85	**27**	68%	7:1
	12	-55	**27α**	65%[#]	1:0
	13	-78	**28α**	81%[#]	1:0
	13	-55	**28α**	80%[#]	1:0

Scheme 6. Preparation of Phenyl 3,4-Di-*O*-*tert*-butyl-dimethylsilyl-2,6-di-*O*-benzyl-thioglucoside **29**

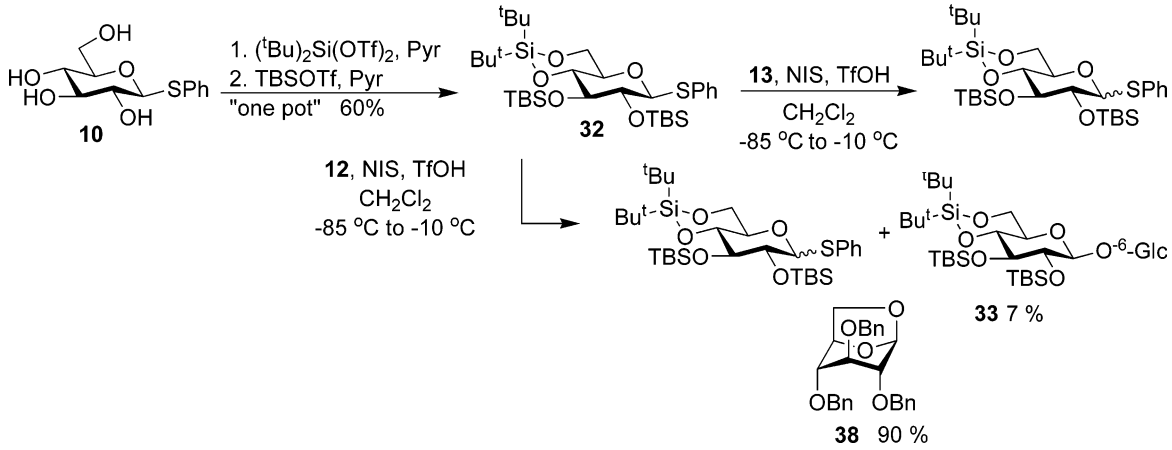


18.26, 18.17, 17.93, 1.17, −4.35, −4.40, −4.49, −4.62; MS(ES) *m*/*z* calcd for $C_{24}H_{52}O_5Si_3Na$: 527.3, *m*/*z* found: 527.4.

Phenyl 6-*O*-Benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-1-thio-*β*-D-glucopyranoside (11). Phenyl 6-*O*-benzyl-1-thio-*β*-D-glucopyranoside (0.713 g, 1.96 mmol), and 4-DMAP (40 mg) were dissolved in pyridine 20 mL, and the solution was cooled to 0 °C. *tert*-Butyldimethylsilyl triflate (3.17 g, 12 mmol) was added to the reaction mixture, and it was heated to 60 °C. After 24 h the reaction was quenched with MeOH, diluted with EtOAc, and washed with water, HCl (1 M), and brine. The organic phase was dried over $MgSO_4$ and concentrated to give a pale-yellow syrup which was purified by column chromatography (CH_2Cl_2−pentane, 1:4 then 1:1) to give the title product **11** as a colorless syrup (1.313 g, 95%); $[\alpha]^{RT}_D$ −28.3° (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.1 Hz, 2H), 7.33−7.17 (m, 8H), 4.97 (d, J = 7.6 Hz, 1H), 4.57 (d, J = 11.9 Hz, 1H), 4.53 (d, J = 11.9 Hz, 1H), 3.98 (broad dt, J = 2.1, 6.6 Hz, 1H), 3.84 (ddd, $J \approx$ 1.2, 1.2, 4.2 Hz, 1H), 3.81 (dd, $J \approx$ 1.2, 1.2 Hz, 1H), 3.79 (dd, $J \approx$ 1.2 Hz, 7.6Hz, 1H), 3.69 (d, J = 6.6 Hz, 2H), 0.89 (2 × s, 18H), 0.87 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.07 (2 × s, 6H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 135.9, 130.2, 128.8, 128.3, 127.7, 127.5, 126.4, 86.5, 81.8, 77.7, 75.7, 73.4, 71.6, 71.0, 26.1, 25,9, 18,2, 18,1, 18,0, −3.9, −4.0, 4.2 (2C), −4.4, −4.7; HRMS(ES) *m*/*z* calcd for $C_{37}H_{64}O_5Si_3Na$: 727.3680, *m*/*z* found: 727.3683.

Phenyl 6-*O*-Benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-glucopyranoside (5). Phenyl 6-*O*-benzyl-1-thio-α-D-glucopyranoside (1.07 g, 2.96 mmol) and 4-DMAP (40 mg) were dissolved in pyridine 30 mL, and the solution was cooled to 0 °C. *tert*-Butyldimethylsilyl triflate (4.68 g, 17.7 mmol) was added to the reaction mixture, and it was heated to 60 °C. After 24 h the reaction was quenched with MeOH, diluted with EtOAc, and washed with water, HCl (1 M), and brine. The organic phase was dried over $MgSO_4$ and concentrated to give a pale-yellow syrup which was purified by column chromatography (CH_2Cl_2−pentane, 1:4 then 1:1) to give a colorless syrup (1.721 g, 83%); $[\alpha]^{RT}_D$ +117.9° (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (m, 2H), 7.35−7.18 (m, 8H), 5.61 (d, J = 4.2 Hz, 1H), 4.62 (d, J = 12.1 Hz, 1H), 4.59 (d, J = 12.1 Hz, 1H), 4.39 (ddd, J = 2.1 Hz, 6.4

Scheme 7. Synthesis of $^4C_1$ Conformationally Restricted Glucosyl Donor **32**



Hz, 8.5 Hz, 1H), 4.10 (bt, J = 3.6 Hz, 1H), 3.89 (bd, J = 3.6 Hz, 1H), 3.79 (bd, J = 8.6 Hz, 1H), 3.75 (dd, J = 2.1 Hz, 11.2 Hz, 1H), 3.66 (dd, J = 6.3 Hz, 11.1 Hz, 1H), 1.03, 0.90, 0.90 (3 s, 18H), 0.26, 0.18, 0.15, 0.13, 0.12, 0.07 (6 s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 136.6, 131.6, 128.7, 128.3, 127.7, 127.3, 126.6, 87.2, 76.4, 73.6, 73.2, 73.0, 72.8, 70.3, 26.2, 26.1, 25.9, 18.4, 18.2, 18.0, −3.4, −3.5, −3.8, −4.2, −4.8, −4.9; HRMS(ES) *m*/*z* calcd for $C_{37}H_{64}O_5Si_3Na$: 727.3680, *m*/*z* found: 727.3709.

Phenyl 6-*O*-Benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (26). Phenyl 6-*O*-benzyl-1-thio-α-D-mannopyranoside (1.500 g, 4.14 mmol) yielded 1.638 g (56%) of **26** as a colorless oil following the procedure above; $[\alpha]^{RT}_D$ +104.1 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 100 °C): δ 7.49 (m, 2H), 7.36−7.14 (m, 8H), 5.23 (d, J = 6.6 Hz), 4.49 (s, 2H), 4.06 (d, J = 6.6 Hz, 1H), 3.92 (dd, $J \approx$ 4, 5 Hz, 1H), 3.87 (bd, $J \approx$ 4 Hz, 1H), 3.86 (bs, 1H), 3.62 (bd, $J \approx$ 5 Hz, 2H), 0.93 (s, 9H), 0.91 (s, 1H), 0.89 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 6H), 0.07 (s, 3H).

^{1}H NMR (400 MHz, (CD_3Cl, −30 °C, A = $^4C_1$ conformation, B = $^1C_4$ conformation): δ 7.56 (m, 2H), 7.18−7.16 (m, 8H), 5.27 (d, J = 1.5 Hz, 0.59H, A), 5.27 (d, J = 8.7 Hz, 0.41H, B), 4.63 (d, J = 12.0 Hz, 0.59H, A), 4.54 (d, J = 11.8 Hz, 0.41H, B), 4.49 (d, J = 11.8 Hz, 0.41H, B), 4.46 (d, J = 12.0 Hz, 0.59H, A), 4.37 (dd, J = 8.3, 8.7 Hz, 0.59H, A), 4.14 (dd, J = 1.5 Hz, 1.7 Hz, 0.59H, A), 4.03 (ddd, J = 2.8, 4.8, 7.6 Hz, 0.41H, B), 3.99 (t, J = 9.1, 0.59H, A), 3.97 (ddd, J = 1.6, 2.0, 9.1 Hz, 0.41H, B), 3.88 (dd, J = 2.0, 8.9 Hz, 0.41H, B), 3.84 (dd, J = 1.8, 9.9 Hz, 0.41H, B), 3.77 (dd, J = 2.0 Hz, 4.7 Hz, 0.59H, A), 3.74 (dd, $J \approx$ 1.7, 1.7 Hz, 0.41H, B), 3.72 (dd, J = 1.7, 4.8 Hz, 0.41H, B), 3.64 (dd, J = 8.3, 9.9 Hz, 0.59H, A), 3.59 (dd, J = 2.8, 10.7 Hz, 0.41H, B), 0.92, 0.90, 0.84, 0.81, 0.78 (5 s, 27H), 0.16, 0.12, 0.10, 0.07, 0.06, 0.04, 0.03, 0.01, −0.05 (9 s, 18H); *m*/*z* calcd for $C_{37}H_{64}O_5SSi_3Na$: 727.3680, *m*/*z* found: 727.3692.

Phenyl 6-*O*-Benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactopyranoside (23). Phenyl 6-*O*-benzyl-1-thio-β-D-galactopyranoside (530 mg, 1.46 mmol) yielded 593 mg (58%) of **23** as a colorless oil following the procedure above; $[\alpha]^{RT}_D$ −63.4° (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 100 °C): δ 7.48 (d, J = 7.0 Hz, 2H), 7.31−7.19 (m, 8H), 4.96 (d, J = 4.9 Hz, 1H), 4.51 (d, J = 12.1 Hz, 1H), 4.46 (d, J = 12.1, 1H), 4.25 (dd, J = 2.1, 4.2 Hz, 1H), 4.20 (bm, 1H), 4.09 (t, J = 5.4 Hz, 1H), 4.05 (ddd, $J \approx$ 3.6, 4.2, 7.8 Hz, 1H), 3.82 (dd, J = 2.1, 5.4 Hz, 1H), 3.71 (dd, J = 3.6, 10.7 Hz, 1H), 0.96 (s, 9H), 0.91 (s, 18H), 0.15 (s, 3H), 0.13 (s, 3H), 0.13 (s, 2H), 0.11 (s, 3H), 0.08 (s, 3H).

^{1}H NMR (400 MHz, (CD_3Cl, −41 °C): δ 7.64 (d, J = 7.1 Hz, 1H), 7.48 (d, J = 7.1 Hz, 1H), 7.42−7.09 (m, 8H), 5.11 (s, 0.5H, B), 5.01 (t, J = 10.6 Hz, 0.5H, A H_2), 4.62 (d, J = 11.8 Hz, 0.5H, $PhCH_2$), 4.60 (d, J = 10.6, 0.5H, A H_1), 4.57 (d, J = 12.0 Hz, 0.5H, $PhCH_2$), 4.52 (d, J = 12 Hz, 0.5H, $PhCH_2$), 4.44 (d, J = 11.8 Hz, 0.5H, $PhCH_2$), 4.30 (dd, J = 2.3 Hz, 6.7 Hz, 0.5H), 4.23 (dd, J = 7.8 Hz, 8.8 Hz, 0.5H), 4.10 (d, J = 3.6 Hz, 0.5H), 4.04−4.01 (m, 1H), 3.74−3.61 (m, 3H), 3.57 (d, J = 8.8 Hz, 0.5H), 0.91, 0.85, 0.83 (3 s, 27H), 0.19, 0.14, 0.11, 0.10, 0.07, 0.05, 0.04, 0.03, 0.02, 0.01 (10 s, 18H); HRMS-(ES) *m*/*z* calcd for $C_{37}H_{64}O_5SSi_3Na$: 727.3680, *m*/*z* found: 727.3685.

Phenyl 6-Deoxy-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-1-thio-α-L-mannopyranoside (16). Phenyl 6-deoxy-1-thio-α-1-mannopyranoside (1.594 g, 6.22 mmol) was dissolved in pyridine (8 mL), and DMAP (100 mg) was added. The reaction mixture was stirred, and *tert*-butyldimethylsilyl triflate (8.2 g, 31 mmol) was added slowly by syringe. The reaction was heated to 50 °C and stirred overnight. After cooling to 0 °C in an ice bath, MeOH was added, and the mixture was diluted with EtOAc, washed with water, HCl (1 M), $NaHCO_3$ (sat.), and finally brine followed by concentration in vacuo to give a crude syrup, which was purified by flash chromatography (pentane to pentane−CH_2Cl_2, 5:1) to give the title product as a colorless syrup (3.812 g, 99%).

$[\alpha]^{RT}_D$ −99.4° (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 100 °C): δ 7.45 (m, 2H), 7.35 (m, 2H), 7.28 (m, 1H), 5.22 (d, J = 5.4 Hz, 1H), 4.10 (dd, J = 2.1 Hz, J = 5.4 Hz, 1H), 3.85 (dd, J = 2.1 Hz, 5.2 Hz, 1H), 3.81 (dq, J = 6.4, 6.5 Hz, 1H), 3.70 (dd, $J \approx$ 5.2, 6.5 Hz, 1H), 1.22 (d, J = 6.4 Hz, 1H), 0.93 (s, 9H), 0.93 (s, 18H), 0.14 (2s, 6H), 0.13 (s, 6H), 0.12 (s, 3H), 0.11 (s, 3H); ^{1}H NMR (400 MHz, ($CDCl_3$, −50 °C): δ 7.49 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.3 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 5.28 (d, J = 4.6 Hz, 1H), 4.25−3.59 (m, 4H) 1.28 (d, J = 6.4 Hz, 3H), 0.96 (bs, 9H), 0.95 (bs, 18H), 0.16 (s, 3H), 0.15 (s, 3H), 0.14 (bs, 6H), 0.13 (s, 3H), 0.11 (s, 3H); HRMS-(ES) *m*/*z* calcd for $C_{30}H_{58}O_4SSi_3Na$: 621.3261, *m*/*z* found: 621.3261.

Phenyl 4,6-Di-*O*-(di-*tert*-butylsilylene)-2,3-di-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-glucopyranoside (32). To a solution of the tetraol **10** (880 mg, 3.23 mmol) in pyridine (5 mL) was slowly added bis-*tert*-butylsilyl ditrifluoromethanesulfonate (1.18 mL, 3.23 mmol) at 0 °C. After stirring overnight at RT, TLC (EtOAc−MeOH, 10:1) showed full conversion, and the mixture was cooled to 0 °C where TBSOTf (2.2 mL, 9.69 mmol) was added slowly by syringe. After stirring additional 24 h the reaction mixture was quenched by addition of MeOH, diluted with EtOAc, and washed with 1 M HCl (aq), water, and finally brine; dried ($MgSO_4$), and concentrated in vacuo to give a yellow syrup which was further purified by flash chromatography (pentane−CH_2Cl_2, 10:1 to 5:1) to give a colorless syrup (1.212 g, 55%) and the mono-TBDMS-protected product (608 mg, 36%); $[\alpha]^{RT}_D$ −53.1° (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.48−7.46 (m, 2H), 7.33−7.23 (m, 3H), 4.95 (d, 1H, J = 6.0 Hz); 4.15 (t, J = 4.8 Hz, 1H); 4.13 (dd, J = 7.2, 10.0 Hz, 1H); 3.89 (t, J = 10.0 Hz, 1H); 3.80 (dd, J = 5.0, 6.0 Hz, 1H); 3.72 (dt, J = 4.8, 10.0 Hz, 1H); 3.68 (dd, J = 5.0, 7.2 Hz, 1H); 1.07(s, 9H); 1.00 (s, 9H), 0.97(s, 9H), 0.94(s, 9H), 0.29 (2 s, 6H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.76, 131.41, 129.03, 127.29, 88.79, 79.89, 78.49, 76.04, 72.02, 67.01, 27.71, 27.31, 26.48, 26.38, 22.93, 20.10, 18.35, 18.31,

−2.56, −2.84, −3.17, −3.21; HRMS(ES) *m*/*z* calcd for $C_{32}H_{60}O_5SSi_3Na$: 663.3367, *m*/*z* found: 663.3392.

Phenyl 2,6-di-*O*-Benzyl-3,4-di-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-glucopyranoside (29). To a solution of the phenyl 2,6-di-*O*-benzyl-1-thio-β-D-glucopyranoside (1.110 g, 2.53 mmol) and DMAP (40 mg) in pyridine (6 mL) was slowly added TBSOTf (2.33 mL, 10.1 mmol) at 0 °C. The mixture was heated to 60 °C. After 14 h the reaction was quenched with MeOH, diluted with EtOAc, and washed with 1 M HCl (aq), water, and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to give a yellow oil which was purified by flash chromatography to give the title product **29** as a colorless syrup (1.350 g, 80%); $[\alpha]^{RT}_D$ −17.9° (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.48−7.45 (m, 2H), 7.32−7.12 (m, 13H), 5.04 (d, *J* = 8.3 Hz, 1H); 4.71 (d, *J* = 11.4 Hz, 1H); 4.60 (d, *J* = 11.4 Hz, 1H); 4.54 (d, *J* = 11.9 Hz, 1H); 4.47 (d, *J* = 11.9 Hz, 1H); 3.89 (ddd, *J* = 3.9, 5.8, 6.7 Hz, 1H); 3.87 (dd, *J* = 3.2, 4.7 Hz, 1H); 3.77 (dd, *J* = 3.9, 4.7 Hz, 1H), 3.69 (dd, *J* = 5.8, 9.8 Hz, 1H); 3.63 (dd, *J* = 6.7, 9.8 Hz, 1H); 3.46 (dd, *J* = 3.2, 8.3 Hz, 1H); 0.83 (s, 9H); 0.81 (s, 9H); 0.04(s, 3H); 0.02(s, 3H); 0.00(s, 3H); −0.05(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.4, 135.0, 131.0, 128.8, 128.3, 128.2, 127.6 (2C), 127.5, 127.5, 126.8, 84.8, 81.7, 81.4, 76.0, 73.3, 73.1, 71.2, 71.2, 26.1, 26.0, 18.1, 18.0, −3.6, −3.7, −4.1, −4.3. HRMS(ES) *m*/*z* calcd for $C_{38}H_{56}O_5SSi_2Na$: 703.3285, *m*/*z* found: 703.3304.

Phenyl 2,6-Di-*O*-di-benzyl-3,4-di-*O*-di-(tri-isopropyl-silyl)-1-thio-β-D-glucopyranoside (39). To a solution of the diol **37** (400 mg, 0.884 mmol) in DMF (4 mL) and 2,6-lutidine (4 mL) was added TIPSCl (682 mg, 3.5 mmol, 0.76 mL) followed by AgOTf (454 mg, 1.77 mmol). The mixture was heated to 60 °C overnight, cooled to 0 °C, and quenched by MeOH. The crude mixture was diluted with EtOAc and washed HCl (1 M), $NaHCO_3$ (sat.), water (four times), and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to give a crude product which was purified by flash chromatography (pentane−EtOAc, 50:1 to 10:1) to give 598 mg of **39** (88%) as a colorless syrup; $[\alpha]^{RT}_D$ −3.0° (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.53 (m, 2H), 7.38−7.19 (m, 13H), 5.28 (d, *J* = 8.6 Hz, 1H), 4.90 (d, *J* = 11.2 Hz, 1H), 4.63 (d, *J* = 11.2 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.27 (d, *J* = 3.2 Hz, 1H), 4.21 (t, *J* = 6.9 Hz, 1H), 4.16 (d, *J* = 3.3 Hz, 1H), 3.76 (d, *J* = 6.9 Hz, 2H), 3.67 (d, *J* = 8.5 Hz, 1H), 1.08−1.00 (m, 42H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 138.4, 134.8, 131.2, 128.8, 128.3, 128.0, 127.9, 127.7, 127.5, 127.3, 126.9, 83.6, 82.7, 82.4, 75.8, 73.4, 73.4, 71.7, 70.8, 18.2, 18.2, 18.1, 18.1, 12.4, 12.3. HRMS(ES) *m*/*z* calcd for $C_{44}H_{68}O_5SSi_2Na$: 710.3832, *m*/*z* found: 710.3867.

Phenyl 2,3,6-tri-*O*-tri-benzyl-4-*O*-(*tert*-butyldimethyl-silyl)-1-thio-β-D-glucopyranoside (41): $[\alpha]^{RT}_D$ −15.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.62 (m, 2H), 7.37−7.21 (m, 18H), 5.02 (d, *J* = 11.7 Hz, 1H), 4.91 (d, *J* = 10.1 Hz, 1H), 4.79 (d, *J* = 11.7 Hz, 1H), 4.75 (d, *J* = 9.2 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 10.1 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 3.83 (dd, *J* = 1.9, 10.6 Hz, 1H), 3.70 (d, *J* = 9.4 Hz, 1H), 3.67 (dd, *J* = 6.4, 10.7 Hz, 1H), 3.55 (dd, *J* = 8.6 Hz, 9.5 Hz, 1H), 3.53 (m, 1H), 3.50 (ddd, *J* = 1.9 Hz, 6.0 Hz, 9.3 Hz, 1H), 0.91 (s, 9H), 0.06 (s, 3H), 0.0 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 138.5, 137.9, 134.3, 131.6, 129.0, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 127.3, 127.2, 126.8, 87.6, 86.8, 81.5, 80.5, 75.3, 75.2, 73.4, 70.9, 69.6, 26.0, 18.1, −3.6, −4.5. HRMS(ES) *m*/*z* calcd for $C_{39}H_{48}O_5SSiK$: 695.2629, *m*/*z* found: 695.2690.

General Procedure for NIS/TfOH Activated Cross-Couplings. Equivalent amounts of the glycosyl donor and acceptor were co-evaporated with toluene three times followed by drying under vacuum. Then powdered 4 Å molecular sieves and dichloromethane were added, and the mixture was stirred under argon atmosphere for 2 h at RT, followed by cooling to −85 °C where NIS (1.1 equiv) and a catalytical amount of TfOH (5 μL) were added. The reaction was stirred 1 h at −85 °C and allowed to reach −50 to −60 °C where it was quenched by addition of Et_3N. The mixture was diluted with EtOAc and filtered through Celite. The organic phase was washed with $NaHSO_3$ and brine, dried ($MgSO_4$), and concentrated in vacuo to give a crude product which was purified further by flash chromatography (pentane:EtOAc, 25:1 to 10:1).

General Procedure for Deprotection of the TBDMS Groups. The disaccharide was dissolved in THF (approximately 30 mg per mL) and 10 equiv of TBAF (1 M in THF) was added. The reaction was followed by TLC (pentane−EtOAc), and when finished, it was concentrated in vacuo and purified by flash chromatography (CH_2Cl_2−EtOAc, 3:1 to 1:1). When necessary, the crude product was acetylated (pyridine−Ac_2O, 1:1 and DMAP (cat.)) and purified by flash chromatography (pentane−EtOAc, 3:1 to 1:1).

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (14α): $[\alpha]^{RT}_D$ +23.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.36−7.16 (m, 23H), 4.88 (d, *J* = 3.2 Hz,, 1H), 4.86−4.81 (m, 3H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.74 (d, *J* = 10.8 Hz, 1H), 4.70 (d, *J* = 10.1 Hz, 1H), 4.63 (d, *J* = 9.8 Hz, 1H), 4.45 (d, *J* = 12.2 Hz, 1H), 4.33 (d, *J* = 12.3 Hz, 1H), 4.15 (dd, *J* = 4.1 Hz, 11.1 Hz, 1H), 4.08 (td, *J* = 3.9 Hz, 8.3 Hz, 1H), 3.86 (d, *J* = 4.4 Hz, 1H), 3.83 (dd, *J* = 2.0 Hz, 4.4 Hz, 1H), 3.76 (m, 2H), 3.67 (t, *J* = 9.3 Hz, 1H), 3.65 (t, *J* = 8.7 Hz, 1H), 3.48−3.38 (m, 4H), 0.90 (s, 9H), 0.86 (s, 9H), 0.75 (s, 9H), 0.11 (s, 3H), 0.08 (s, 9H), 0.03 (s, 3H), −0.09 (s, 3H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.8, 138.7, 138.4, 138.2, 134.5, 131.7, 129.0, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6 (2C), 127.6, 127.3, 127.3, 97.0, 87.9, 86.8, 81.2, 78.9, 77.9, 76.2, 75.6, 75.5, 75.0, 73.6, 73.1, 72.8, 71.7, 69.7, 66.9, 26.3, 26.1, 26.1, 18.5, 18.1, 18.0, −3.2, −3.5, −3.9, −3.9, −4.4, −4.6; HRMS(ES) *m*/*z* calcd for $C_{64}H_{92}O_{10}SSi_3Na$: 1159.5617, *m*/*z* found: 1159.5625.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (14β): $[\alpha]^{RT}_D$ + 6.0° (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.57−7.55 (m, 2H), 7.37−7.17 (m, 23H), 4.88 (d, *J* = 8.9 Hz, 1H), 4.87 (d, *J* = 8.9 Hz, 1H), 4.81 (m, 2H), 4.71 (d, *J* = 6.1 Hz, 1H), 4.70 (d, *J* = 9.7 Hz, 1H), 4.66 (d, *J* = 9.8 Hz, 1H), 4.61 (d, *J* = 11.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.02 (t, *J* = 6.6 Hz, 1H), 4.00 (d, *J* = 9.3 Hz, 1H), 3.85 (m, 1H), 3.78 (d, *J* = 3.8 Hz, 1H), 3.71−3.59 (m, 5H), 3.46 (dd, *J* = 8.9 Hz, 9.7 Hz, 1H), 3.42 (t, *J* = 9.3 Hz, 1H), 0.89 (s, 9H), 0.86 (s, 9H), 0.84 (s, 9H), 0.10 (s, 3H), 0.6 (s, 3H), 0.04 (s, 6H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.6, 138.3, 138.1, 134.7, 131.3, 129.0, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.6, 127.5, 127.0, 103.1, 87.5, 86.9, 81.0, 80.4, 79.3, 78.9, 78.6, 77.2, 75.9, 73.3, 71.8, 71.0, 69.6, 26.1, 26.1, 26.0, 18.2, 18.2, 18.0, −3.9, −4.2, −4.4, −4.5, −4.7, −4.8; HRMS(ES) *m*/*z* calcd for $C_{64}H_{92}O_{10}SSi_3Na$: 1159.5617, *m*/*z* found: 1159.5621.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-benzyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (14u): $[\alpha]^{RT}_D$ −3.4° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.54 (m, 2H), 7.40−7.24 (m, 23H), 4.91 (d, *J* = 10.1 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.74 (d, *J* = 10.1 Hz, 1H), 4.72 (d, *J* = 9.9 Hz, 1H, H_1), 4.62 (d, *J* = 11.0 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.30 (d, *J* = 7.8 Hz, 1H, H_1'), 4.12 (bd, *J* = 10.1 Hz), 3.48 (dd, *J* = 8.9 Hz, 9.7 Hz, 1H), 3.37 (t, *J* = 7.8 Hz, 1H), 3.76−3.41 (m, 9H), 3.00 (bs, 3H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.4, 138.0, 137.9, 137.8, 133.8, 131.8, 129.2, 128.63, 128.60, 128.57, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 103.1 (J_{CH} = 154.2), 87.8, 86.7, 81.2, 78.5, 78.2, 76.2, 76.0, 75.7, 75.2, 74.3, 73.8, 73.3, 71.8, 70.4, 68.5; HRMS(ES) *m*/*z* calcd for $C_{46}H_{50}O_{10}SNa$: 817.3022, *m*/*z* found: 817.3004.

Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (15β): $[\alpha]^{RT}_D$ −15.5° (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.52−7.49 (m, 2H), 7.36−7.05 (m, 23H), 5.05 (d, *J* = 10.3 Hz, 1H), 4.84 (d, *J* = 6.7 Hz, 1H), 4.74 (s, 2H), 4.63 (d, *J* = 10.3 Hz, 1H), 4.60 (d, *J* = 9.9 Hz, 1H) 4.55 (d, *J* = 11.8 Hz, 1H), 4.49 (d, *J* = 11.8 Hz,

1H), 4.42 (d, J = 11.8 Hz, 1H), 4.35 (d, J = 11.8 Hz, 1H), 3.94 (dd, J = 8.7 Hz, 9.2 Hz, 1H), 3.93−3.90 (m, 2H), 3.86 (dd, J = 10.5 Hz, 1.6 Hz, 1H), 3.74 (bd, J = 2.9 Hz, 1H), 3.67 (dd, J = 10.7 Hz, 5.9 Hz, 1H), 3.60 (t, J = 9.3 Hz, 1H), 3.59 (t, J = 8.8 Hz, 1H), 3.59 (d, J = 6.2 Hz, 1H), 3.47 (dd, J = 9.1 Hz, 5.1 Hz, 1H), 3.46 (m, 1H), 3.42 (dd, J = 9.8 Hz, 8.8 Hz, 1H), 0.86 (s, 9H), 0.81(s, 9H), 0.80(s, 9H), 0.05 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H), −0.01 (s, 3H), −0.06 (s, 3H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.9, 138.7, 138.6, 138.5, 133.9, 132.0, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 100.6, 87.3, 85.1, 81.2, 80.2, 79.6, 79.3, 78.7, 75.7, 75.6, 75.2, 73.3, 73.3, 71.2, 70.7, 68.9, 26.1, 26.0, 25.9, 25.9, 25.7, 18.0, 18.0, 17.9, −3.5, −3.6, −4.4, −4.5, −4.7, −4.9; HRMS(ES) *m*/*z* calcd for $C_{64}H_{92}O_{10}SSi_3Na$: 1159.5617, *m*/*z* found: 1159.5640.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-benzyl-*β*-D-glucopyranosyl)-1-thio-*β*-D-glucopyranoside (15u): $[\alpha]^{RT}_D$ −6.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.48 (m, 2H), 7.29−7.09 (m, 23H), 4.90 (d, J = 11.4 Hz, 1H), 4.75 (d, J = 9.4 Hz, 1H), 4.75 (d, J = 10.3 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 10.3 Hz, 1H), 4.55 (d, J = 8.0 Hz, 1H), 4.54 (d, J = 7.3 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.30 (s, 2H), 3.95 (t, J = 9.5 Hz, 1H), 3.90 (dd, J = 3.5 Hz, 11.8 Hz, 1H), 3.72 (dd, J = 1.8 Hz, 11.7 Hz, 1H), 3.60 (t, J = 8.8 Hz, 1H), 3.43 (t, J = 9.1 Hz, 1H), 3.40 (t, J = 9.2 Hz, 1H), 3.40−3.31 (m, 4H), 3.22 (dd, J = 8.0 Hz, 8.8 Hz, 1H), 3.11 (ddd, J = 5.1 Hz, 5.2 Hz, 9.3 Hz, 1H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 139.0, 137.9, 137.6, 137.5, 133.4, 132.4 (2 C), 129.0, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.4, 126.9, 103.2 (J_{CH} = 160.3 Hz), 87.7, 85.7, 80.8, 78.7, 76.8, 76.2, 75.6, 75.1, 74.6, 73.8, 73.7, 73.5, 72.4, 70.7, 68.5; HRMS(ES) *m*/*z* calcd for $C_{46}H_{50}O_{10}SNa$: 817.3022, *m*/*z* found: 817.3027.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl)-1-thio-*β*-D-glucopyranoside (27α): $[\alpha]^{RT}_D$ 23.9° (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.57 (bd, J = 7.5 Hz, 2H), 7.39 (m, 2H), 7.36−7.21 (m, 21H), 4.95−4.62 (m, 7.2H), 4.51 (m, 1.6H), 4.36 (m, 1.0H), 4.12 (m, 0.9H), 4.03−3.87 (m, 2.3H), 3.78 (m, 1H), 3.72−3.61 (m, 4H), 3.48 (m, 3.5H), 0.97−0.79 (m, 27H), 0.22−0.10 (m, 18H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.8, 138.8, 138.6, 138.4, 131.9 (b), 128.9−127.4 (multiple peaks), 101.6 (b), 88.2 (b), 87.0 (b), 81.7 (b), 79.1 (b), 78.3 (b), 75.8 (3 peaks), 75.5 (3 peaks), 75.0 (b), 73.1 (3 peaks), 70.3 (b), 26.2 (b), 18.4 (2C), 18.0, −3.9 (b) −4.0, −4.6 (b); HRMS(ES) *m*/*z* calcd for $C_{64}H_{92}O_{10}SSi_3Na$: 1159.5617, *m*/*z* found: 1159.5623.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-benzyl-α-D-mannopyranosyl)-1-thio-*β*-D-glucopyranoside (27u): $[\alpha]^{RT}_D$ +21.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.55 (d, J = 7.1 Hz, 2H), 7.42−7.22 (m, 23H), 4.92 (2d, J = 10.9 Hz, 2H), 4.91 (d, J = 3.5 Hz, 1H), 4.90 (d, J = 10.1 Hz, 1H), 4.84 (d, J = 10.9 Hz, 1H), 4.73 (d, J = 10.3 Hz, 1H), 4.64 (d, J = 9.7 Hz, 1H), 4.60 (d, J = 11.0 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 3.96 (bs, 1H), 3.91−3.61 (m, 8H), 3.53−3.46 (m, 2H) 3.47 (dd, J = 8.6 Hz, 9.2 Hz, 1H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.3, 138.0, 138.0, 137.8, 133.6, 132.2, 129.1, 128.6, 128.6, 128.5, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 100.2 (J_{CH} = 169.3 Hz), 87.4, 86.8, 80.9, 78.3, 77.8, 75.9, 75.5, 75.2, 73.8, 71.8, 70.4 (2C), 70.1, 69.8, 66.8; HRMS(ES) *m*/*z* calcd for $C_{46}H_{50}O_{10}SNa$:: 817.3022, *m*/*z* found: 817.3035.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-*β*-D-mannopyranosyl)-1-thio-*β*-D-glucopyranoside (27*β*): $[\alpha]^{RT}_D$ 83.5° (*c* 0.63, $CHCl_3$); HRMS(ES) *m*/*z* calcd for $C_{64}H_{92}O_{10}SSi_3Na$: 1159.5617, *m*/*z* found: 1159.5614.

Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl)-1-thio-*β*-D-glucopyranoside (28α): $[\alpha]^{RT}_D$ 37.9° (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.57 (m, 2H), 7.31−7.17 (m, 23H), 5.24 (bd, J = 6.5 Hz, 1H), 5.06 (bd, J = 11.4 Hz, 1H), 4.78 (bd, J = 10.4, 1H), 4.75 (bd, J = 11.4 Hz, 1H), 4.70 (d, J = 9.8 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 4.55−4.46 (bm, 3H), 4.45 (d, J = 11.8 Hz, 1H), 3.98 (bd, J = 11.0 Hz, 1H), 3.93 (bt, J = 9.3 Hz, 1H), 3.81 (bd, J = 6.6 Hz, 1.3H), 3.81 (bd, J = 6.6 Hz, 1.4H), 3.76−3.62 (m, 4.4H), 3.60−3.50 (m, 2.9H), 3.45 (bt, J = 9.1 Hz, 1H), 0.88, 0.84, 0.72 (3 bs, 27H), 0.07, 0.05, 0.03, −0.01, −0.04, −0.15 (6 bs, 18H); ^{13}C NMR (400 MHz, $CDCl_3$, 50 °C): δ 139.0, 138.6, 138.2, 134.6, 131.8 (b), 129.0, 128.4, 127.8−126.8 (multiple peaks), 98.3 (b), 87.7, 87.6, 87.4 (b), 81.5 (b), 79.5 (b), 76.4 (b), 75.5 (b), 74.9 (b), 73.6, 73.5, 72.6 (b), 72.2 (b), 71.1 (b), 70.1 (b), 26.4 (b), 25.9 (b), 18.7 (b), 18.2 (b), 18.0, −3.7 (b), −4.0 (b), −4.7 (b); HRMS(ES) *m*/*z* calcd for $C_{64}H_{92}O_{10}SSi_3Na$: 1159.5617, *m*/*z* found: 1159.562.

^{1}H NMR (400 MHz, $(CD_3)_2SO$, 100 °C): δ 7.53 (m, 2H), 7.33−7.19 (m, 23H), 5.17 (d, J = 6.1 Hz, 1H), 4.95 (d, J = 9.5 Hz, 1H), 4.90 (d, J = 11.8 Hz, 1H), 4.76 (d, J = 10.9 Hz, 2H), 4.57 (d, J = 11.0 Hz, 1H), 4.50−4.47 (3 d, 3H), 3.91−3.85 (m, 3H), 3.83−3.77 (m, 3H), 3.73−3.66 (m, 2H), 3.64−3.56 (m, 3H), 3.49 (dd, J = 8.9 Hz, 9.0 Hz, 1H), 0.91, 0.87, 0.78 (3 s, 27H), 0.08 (bs, 6H), 0.07, 0.04, 0.03, −0.04 (4 s, 12H).

Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(6-*O*-benzyl-α-D-mannopyranosyl)-1-thio-*β*-D-glucopyranoside (28u): $[\alpha]^{RT}_D$ +5.4° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.50 (m, 2H), 7.32−7.12 (m, 23H), 5.20 (d, J = 1.5 Hz, 1H), 4.91 (d, J = 11.1 Hz, 1H), 4.86 (d, J = 10.4 Hz, 1H), 4.60 (d, J = 10.4 Hz, 1H), 4.59 (d, J = 9.7 Hz, 1H), 4.55 (d, J = 11.1 Hz, 1H), 4.46 (d, J = 11.9 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.36 (d, J = 12.0 Hz, 1H), 3.73 (dd, J = 2.0 Hz, 11.1 Hz, 1H), 3.71 (t, J = 9.1 Hz, 1H), 3.68−3.61 (m, 4H), 3.59 (m, 1H), 3.55 (t, J = 8.8 Hz, 1H), 3.55 (dd, J = 4.2 Hz, 10. 0 Hz, 1H), 3.48 (dd, J = 4.7 Hz, 10.0 Hz, 1H), 3.44 (dd, J = 8.8 Hz, 9.6 Hz, 1H), 3.40 (ddd, J = 2.0 Hz, 5.2 Hz, 9.7 Hz, 1H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.5, 138.2, 137.9, 137.8, 133.8, 132.0, 129.0, 128.7, 128.6, 128.4, 128.3, 128.0, 128.0, 128.0, 127.9, 127.8, 127.6, 127.6, 127.6, 101.2 (J_{C1-H1} = 172 Hz), 87.5, 87.1, 81.1, 78.7, 75.8, 75.5, 75.3, 73.8, 73.4, 71.4, 71.0, 70.7, 70.6, 69.7, 69.5; HRMS(ES) *m*/*z* calcd for $C_{46}H_{50}O_{10}SNa$: 817.3022, *m*/*z* found: 817.3039.

Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-*β*-D-mannopyranosyl)-1-thio-*β*-D-glucopyranoside (28*β*): $[\alpha]^{RT}_D$ +91.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.63 (m, 2H), 7.43−7.16 (m, 23H), 5.63 (bs, 1H), 5.37 (m, 1H), 5.14−4.47 (m, 8H), 4.35−3.39 (m, 12H), 1.32−0.80 (m, 27H), 0.24−0.14 (m, 18H); HRMS(ES) *m*/*z* calcd for $C_{64}H_{92}O_{10}SSi_3Na$: 1159.5617, *m*/*z* found: 1159.5660.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-D-galactopyranosyl)-1-thio-*β*-D-glucopyranoside (24α): $[\alpha]^{RT}_D$ +32.4° (*c* 2.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C): δ 7.52 (m, 2H), 7.40−7.18 (m, 23H), 4.94 (d, J = 2.8 Hz, 1H), 4.90 (d, J = 11.2 Hz, 1H), 4.90 (d, J = 10.5 Hz, 1H), 4.87 (d, J = 11.2 Hz, 1H), 4.83 (d, J = 10.6 Hz, 1H), 4.77 (m, 1H), 4.74 (d, J = 10.3 Hz, 1H), 4.63 (d, J = 9.8 Hz, 1H), 4.50 (s, 2H), 4.13−4.05 (m, 2H), 4.05−4.00 (m, 2H), 3.98 (bdd, J = 3.5 Hz, 11.4 Hz, 1H), 3.82 (dd, J = 1.6 Hz, 11.6 Hz, 1H), 3.75−3.64 (m, 3H), 3.60 (dd, J = 5.3 Hz, 10.1 Hz, 1H), 3.47 (dd, J = 8.6 Hz, 9.8 Hz, 1H), 3.46 (m, 1H), 0.96, 0.92, 0.91 (3 s, 27H), 0.14, 0.13, 0.12, 0.05 (4 s, 18H); ^{13}C NMR (400 MHz, $CDCl_3$, 50 °C): δ 139.0, 138.7, 138.6, 138.4, 134.7, 132.1, 132.0, 132.0, 128.9 (b), 128.4 (b), 128.4 (b), 128.3 (b), 128.0 (b), 127.7 (b), 127.5 (b), 127.4 (b), 127.4 (b), 99.0 (b), 88.4, 88.3, 87.0 (b), 81.5 (b), 81.5 (b), 79.4 (b), 79.3 (b), 78.1 (b), 75.6, 75.5, 75.1, 73.3, 72.7 (b), 70.9 (b), 69.2 (b), 66.7 (b), 26.6 (b), 26.2 (b), 18.8, 18.7, 18.5, −3.4 (b), −3.8 (b), −3.8 (b), −4.0 (b), −4.6 (b); HRMS(ES) *m*/*z* calcd for $C_{64}H_{92}O_{10}SSi_3Na$: 1159.5617, *m*/*z* found: 1159.5623.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-benzyl-α-D-galactopyranosyl)-1-thio-*β*-D-glucopyranoside (24u): $[\alpha]^{RT}_D$ +40.9 (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C): δ 7.48 (m, 2H), 7.40−7.20 (m, 23H), 4.95 (d, J = 3.7 Hz, 1H, H_1), 4.91 (d, J = 10.9 Hz, 1H), 4.90 (d, J = 10.3 Hz, 1H), 4.85 (d, J = 10.9 Hz, 1H), 4.83 (d, J = 10.9 Hz, 1H), 4.73 (d, J = 10.3 Hz, 1H), 4.71 (d, J = 9.9 Hz, 1H, H_1'), 4.57 (d, J = 10.9 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.50 (d, J = 12.0 Hz, 1H), 3.91 (bd, J = 5.5 Hz, 1H), 3.88 (dd, J = 5.0 Hz, 10.4 Hz, 1H), 3.82

(dd, J = 5.9 Hz, 6.2 Hz, 1H), 3.82 (dd, J = 3.9 Hz, 9.7 Hz, 1H), 3.74 (dd, J = 1.6 Hz, 10.8 Hz, 1H), 3.71 (t, J = 8.5 Hz, 1H), 3.69 (dd, J = 4.6 Hz, 10.4 Hz, 1H), 3.63 (dd, J = 4.9 Hz, 5.5 Hz, 1H), 3.62 (bd, J = 8.5 Hz, 1H), 3.50 (m, 1H), 3.48 (dd, J = 8.9 Hz, 9.6 Hz, 1H), 3.45 (dd, J = 8.9 Hz, 9.5 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$, 50 °C): δ 138.3, 137.9, 137.8, 137.7, 133.6, 131.5, 129.1, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.6, 99.2 (J_{C-H} = 170 Hz), 87.1, 86.7, 81.1, 78.2, 77.9, 75.9, 75.6, 75.1, 73.7, 71.3, 70.3, 70.1, 69.8, 68.8, 67.4; HRMS(ES) m/z calcd for $C_{46}H_{50}O_{10}SNa$: 817.3022, m/z found: 817.3008.

Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (25α): $[\alpha]^{RT}_D$ 23.2° (c 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.55 (m, 2H), 7.43−7.09 (m, 23H), 5.24 (d, J = 2.5 Hz, 0.22H, a), 5.10 (s, 0.78H, b), 4.85 (d, J = 12.2 Hz, 1H), 4.79 (d, J = 12.2 Hz, 1H), 4.79 (d, J = 9.9 Hz, 1H), 4.67 (d, J = 9.8 Hz, 1H), 4.59 (d, J = 11.7 Hz, 1H), 4.56 (d, J = 12.2 Hz, 1H), 4.53 (d, J = 12.2 Hz, 1H), 4.50 (d, J = 11.6 Hz, 1H), 4.47 (d, J = 9.9 Hz, 1H), 4.29 (d, J = 1.50 Hz, 0.22H, a), 4.21 (dd, J = 2.5 Hz, 5.8 Hz, 0.78H, b), 4.15 (bd, J = 11.0 Hz, 0.78H, b), 4.06 (m, 0.78H, b), 3.89 (m, 0.22H, a), 3.80, 3.68 (m, 2H), 3.69−3.63 (m, 1.3H), 3.60 (t, J = 8.7 Hz, 0.78H, b), 3.59−3.56 (m, 1H), 3.52 (bddd, J = 1.7 Hz, 7.9 Hz, 9.7 Hz, 0.78H, b), 3.45 (dd, J = 8.8 Hz, 9.6 Hz, 0.78H, b), 3.40 (t, J = 4.9 Hz, 0.22H, a), 3.30 (dd, J = 8.4 Hz, 9.4 Hz, 0.22H, a), 0.88, 0.87, 0.85 (3 s, 6H, a), 0.86, 0.85 (2 s, 14H, b), 0.64 (s, 7H), 0.08, 0.07, 0.05, 0.04, 0.01, 0.00, −0.06, −0.18 (8 s, 18H); ^{13}C NMR (400 MHz, (50 °C, $CDCl_3$): δ 139.0, 138.8, 138.8, 137.9, 134.5, 131.4, 128.9, 128.5, 128.4 (3C), 128.3, 128.3, 127.8, 127.7, 127.7, 127.6, 127.3, 127.2, 126.7, 93.8 (broad), 87.5, 86.6, 81.1, 79.4, 76.6 (broad), 75.4 (broad), 75.0 (broad), 74.6 (broad), 74.4 (broad), 73.4, 73.1, 72.5 (broad), 70.7, 67.6 (broad), 66.4 (broad), 26.1, 25.9, 25.8, 18.3, 18.2, 17.9, −4.1, −4.1, −4.5, −4.7, −4.8, −4.9; HRMS(ES) m/z calcd for $C_{64}H_{92}O_{10}SSi_3Na$: 1159.5617, m/z found: 1159.5604.

Phenyl 2,3,4-tri-*O*-benzyl-4-*O*-(6-*O*-benzyl-α-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (25u): $[\alpha]^{RT}_D$ +25.5 (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.58 (m, 2H), 7.41−7.20 (m, 23H), 5.24 (d, J = 3.7 Hz, 1H), 5.00 (d, J = 11.0 Hz, 1H), 4.96 (d, J = 10.2 Hz, 1H), 4.71 (d, J = 11.0 Hz, 1H), 4.65 (d, J = 9.4 Hz, 1H), 4.65 (d, J = 11.0 Hz, 1H), 4.59 (d, J = 11.8 Hz, 1H), 4.53 (d, J = 11.9 Hz, 1H), 4.50 (d, J = 11.8 Hz, 1H), 4.49 (d, J = 11.9 Hz, 1H), 3.98 (m, 1H), 3.94 (dd, J = 5.5 Hz, 5.7 Hz, 1H), 3.91 (dd, J = 4.1 Hz, 10.9 Hz, 1H), 3.88 (t, J = 9.2 Hz, 1H), 3.78 (dd, J = 1.7 Hz, 10.9 Hz, 1H), 3.70−3.62 (m, 3H), 3.62 (t, J = 8.7 Hz, 1H), 3.57 (t, J = 8.7 Hz, 1H), 3.48 (dd, J = 3.1 Hz, 10.0 Hz, 1H), 3.44 (bd, J = 9.5 Hz, 1H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.4, 137.9, 137.6, 137.3, 133.6, 132.1, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3 (2 C), 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 100.8, 87.4, 85.2, 81.1, 79.3, 76.5, 75.5, 75.1, 73.8, 73.3, 71.0, 70.2, 70.1, 70.1, 69.5, 68.8; HRMS(ES) m/z calcd for $C_{46}H_{50}O_{10}SNa$: 817.3022, m/z found: 817.3051.

Phenyl 2,3,4-tri-*O*-benzyl-4-*O*-(6-*O*-benzyl-2,3,4-tri-*O*-acetyl-α-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (25a): $[\alpha]^{RT}_D$ +26.7 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.57 (m, 2H), 7.40−7.14 (m, 23H), 5.72 (d, J = 3.6 Hz, 1H), 5.50 (dd, J = 1.2, 3.1 Hz, 1H), 5.30 (dd, J = 3.1, 11.0 Hz, 1H), 5.23 (dd, J = 3.6, 11.0 Hz, 1H), 4.93 (d, J = 11.1 Hz, 1H), 4.91 (d, J = 10.3 Hz, 1H), 4.67 (d, J = 10.3 Hz, 1H), 4.65 (d, J = 11.1 Hz, 1H), 4.62(d, J = 9.7 Hz, 1H), 4.62 (d, J = 12.1 Hz, 1H), 4.57 (d, J = 12.1 Hz, 1H), 4.44 (d, J = 11.9 Hz, 1H), 4.20 (bt, $J \approx$ 6 Hz, 1H), 4.18 (d, J = 11.9 Hz, 1H), 4.03 (t, J = 9.1 Hz, 1H), 3.89 (dd, J = 4.1, 11.2 Hz, 1H), 3.79 (dd, J = 1.9, 11.2 Hz, 1H), 3.71 (t, J = 8.6 Hz, 1H), 3.55 (dd, J = 8.7, 9.7 Hz, 1H), 3.53 (m, 1H), 3.34 (dd, $J \approx$ 6, 9 Hz, 1H), 3.31 (dd, $J \approx$ 6, 9 Hz, 1H), 2.00 (s, 3H), 1.96 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 170.2, 170.1, 170.1, 138.5, 138.1, 137.9, 137.7, 133.7, 132.1, 129.0, 128.5, 128.5, 128.5, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.2, 96.3, 87.4, 86.4, 81.1, 78.8, 75.2, 74.8, 73.5, 73.4, 73.4, 69.2, 68.5, 68.0, 67.8, 67.7, 67.5, 20.8 (2C), 20.7; HRMS(ES) m/z calcd for $C_{52}H_{56}O_{13}SNa$: 943.3339, found 943.3337.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-deoxy-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-L-mannopyranosyl)-1-thio-β-D-glucopyranoside (17α): $[\alpha]^{RT}_D$ −16.2° (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.56 (bd, J = 6.9 Hz, 2H), 7.42−7.15 (m, 18H), 4.90 (d, J = 11.0 Hz, 1H), 4.89 (bd, J = 9.2 Hz, 1H), 4.90−4.83 (m, 1H), 4.84 (d, J = 11.2 Hz, 1H), 4.71 (d, J = 10.3 Hz, 1H), 4.62 (d, J = 9.7 Hz, 1H), 4.58 (d, J = 9.7 Hz, 1H), 3.97 (bm, 2H), 3.91 (dd, J = 2.2 Hz, 3.0 Hz, 1H), 3.78 (bm, 1H), 3.70 (t, J = 8.7 Hz, 1H), 3.70 (m, 1H), 3.59 (bm, 1H), 3.55−3.33 (m, 3H), 1.21 (d, J = 6.2 Hz, 3H), 0.95−0.90 (bm, 18H), 0.90 (s, 9H), 0.17−0.05 (m, 18H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.8, 138.4, 138.3, 134.0 (b), 132.3 (b), 129.0−127.5 (multiple peaks), 100.8 (b), 87.6, 87.4, 87.0 (b), 81.3 (b), 79.0 (b), 78.3 (b), 75.8, 75.7, 75.6, 75.5, 75.4, 75.3, 75.2, 75.1, 75.0, 73.6 (b), 71.2 (b), 26.3 (b), 26.0 (b), 18.9 (b), 18.4, 18.3 (b), −2.4(b), −3.8 (b) −3.9, −4.0; HRMS(ES) m/z calcd for $C_{57}H_{86}O_9SSi_3Na$: 1053.5198, m/z found: 1053.5175.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-deoxy-α-L-mannopyranosyl)-1-thio-β-D-glucopyranoside (17u): $[\alpha]^{RT}_D$ −15.8° (c 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.55 (m, 2H), 7.40 (m, 2H), 7.37−7.18 (m, 16H), 4.92 (d, J = 10.9 Hz, 1H), 4.90 (d, J = 10.1 Hz, 1H), 4.85 (2 d, $J \approx$ 11 Hz, 2H), 4.73 (d, J = 11.0 Hz, 1H), 4.72 (bs, 1H, H_1), 4.66 (d, J = 9.8 Hz, 1H, H_1'), 4.57 (d, J = 11.1 Hz, 1H), 3.94 (bd, J = 9.8 Hz, 1H), 3.89 (bs, 1H), 3.83 (dd, J = 3.2 Hz, 9.4 Hz, 1H), 3.74 (dd, J = 6.5 Hz, 9.3 Hz, 1H), 3.71 (bd, J = 8.8 Hz, 1H), 3.55 (bdd, J = 4.4 Hz, 6.4 Hz, 1H), 3.53−3.44 (m, 4H), 1.30 (d, J = 6.2 Hz, 3H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.0, 137.7, 137.6, 133.3, 131.7, 128.7, 128.2, 128.2, 128.2, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 99.6 (J_{CH} = 167.5 Hz), 87.1, 86.5, 80.7, 78.1, 76.5, 75.6, 75.2, 74.8, 72.9, 71.5, 70.6, 67.8, 65.9, 17.3: HRMS(ES) m/z calcd for $C_{39}H_{44}O_9SNa$: 711.2604, m/z found: 711.2604.

Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(6-deoxy-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-L-mannopyranosyl)-1-thio-β-D-glucopyranoside (18α): $[\alpha]^{RT}_D$ −32.3° (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.56 (d, J = 6.8 Hz, 2H), 7.40−7.10 (m, 18H), 5.08 (d, J = 10.4 Hz, 1H), 4.92 (d, J = 7.3 Hz, 1H), 4.78 (d, J = 10.2 Hz, 1H), 4.74 (d, J = 10.4 Hz, 1H), 4.74 (d, J = 10.4 Hz, 1H), 4.63 (d, J = 9.8 Hz, 1H), 4.59 (d, J = 11.9 Hz, 1H), 4.55 (d, J = 11.9 Hz, 1H), 3.99 (t, J = 9.5 Hz, 1H), 3.88 (dd, J = 2.1 Hz, 7.6 Hz, 1H), 3.85−3.75 (m, 4H), 3.69 (m, 1H), 3.60 (t, J = 9.0 Hz, 1H), 3.49−3.40 (m, 2H), 1.09 (d, J = 6.85 Hz, 3H), 0.91, 0.86, 0.85 (3 s, 27H), 0.11, 0.08, 0.07, 0.07, 0.04, 0.02 (6 s, 18H); ^{13}C NMR (400 MHz, ($CDCl_3$): δ 138.8, 138.7, 138.5, 133.6, 132.3, 128.9, 128.5, 128.4, 128.3 (2 C), 128.2, 127.8, 127.6, 127.5 (2C), 127.3, 96.8, 87.2, 85.4, 80.2, 80.0, 76.9, 76.6, 76.1, 75.5, 74.0, 74.0, 73.3, 71.5, 68.5, 26.3, 25.9, 25.8, 18.5, 18.3, 18.2, 18.0, −3.9, −4.0, −4.3, −4.3, −4.4, −4.7; HRMS(ES) m/z calcd for $C_{57}H_{86}O_9SSi_3Na$: 1053.5198, m/z found: 1053.5217.

Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(6-deoxy-α-L-mannopyranosyl)-1-thio-β-D-glucopyranoside (18u): $[\alpha]^{RT}_D$ −26.5 (c 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.49 (m, 2H), 7.30−7.15 (m, 18H), 4.90 (d, J = 11.0 Hz, 1H), 4.90 (bs, 1H, H_1), 4.82 (d, J = 10.1 Hz, 1H), 4.67 (d, J = 11.0 Hz, 1H), 4.59 (d, J = 10.1 Hz, 1H), 4.58 (d, J = 9.1 Hz, 1H, H_1'), 4.54 (d, J = 11.9 Hz, 1H), 4.48 (d, J = 11.9 Hz, 1H), 3.80 (t, J = 9.15 Hz, 1H), 3.71−3.67 (m, 2H), 3.66 (bs, 1H), 3.59 (dd, J = 3.9 Hz, 11.1 Hz, 1H), 3.53−3.45 (m, 3H), 3.32 (ddd, J = 2.7 Hz, 3.0 Hz, 9.5 Hz, 1H), 3.22 (dd, J = 9.2 Hz, 9.6 Hz, 1H), 0.87 (d, J = 6.1 Hz, 3H); ^{13}C− NMR (400 MHz, ($CDCl_3$): δ 138.5, 138.0, 137.9, 133.8, 132.2, 129.1, 128.6 (3 C), 128.5, 128.4, 128.1, 128.1, 127.9, 127.7, 127.6, 100.1 (J_{CH} = 167 Hz), 87.8, 85.0, 81.3, 79.3, 75.5, 75.4, 75.0, 73.8, 73.5, 71.8, 71.0, 69.1, 68.6, 17.4; HRMS(ES) m/z calcd for $C_{39}H_{44}O_9SNa$: 711.2604, m/z found: 711.2623.

Phenyl 2,3-Di-*O*-benzoyl-6-*O*-benzyl-4-*O*-(6-deoxy-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-L-mannopyranosyl)-1-thio-β-D-glucopyranoside (22α). The standard procedure was followed with the exception that 1.5 equiv of donor was used.

The reaction mixture was purified by flash chromatography (EtOAc−pentane 1:25) to give the title product as a clear oil, 194 mg (95%); $[\alpha]^{RT}_D$ −12.1 (*c* 1.0, $CHCl_3$); HRMS(ES) *m*/*z* calcd for $C_{57}H_{82}O_{11}SSi_3Na$: 1081.4683 found 1081.4792.

Due to poor resolution in the NMR caused by multiple conformation the purified product (149 mg, 0.157 mmol) was deprotected with TBAF (1 mL, 1 mmol) in THF (1 mL). The crude reaction mixture was concentrated in vacuo, dissolved in pyridine (1 mL) and Ac_2O (1 mL), and left over night. After concentration in vacuo the crude product was purified by flash chromatography (EtOAc−pentane, 1:4 to 1:1) to give the desired product quantitatively as a colorless solid.

Phenyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-4-*O*-(6-deoxy-2,3,4-tri-*O*-acetyl-α-L-mannopyranosyl)-1-thio-*β*-D-glucopyranoside (22a): $[\alpha]^{RT}_D$ +3.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): *δ* 7.91 (m, 4H), 7.48 (m), 7.38−7.23 (m, 12H), 5.71 (t, *J* = 9.4 Hz, 1H), 5.33 (t, *J* = 9.6 Hz, 1H), 5.18 (dd, *J* = 1.9 Hz, 3.3 Hz, 1H), 5.13 (dd, *J* = 3.3 Hz, 10.1 Hz, 1H), 4.93 (bd, *J* = 1.8 Hz, 1H), 4.90 (d, *J* = 10.0 Hz, 1H), 4.89 (t, *J* = 10.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.22 (t, *J* = 9.5 Hz, 1H), 3.90 (bs, 2H), 3.74 (ddd, *J* = 2.2 Hz, 2.5 Hz, 9.7 Hz, 1H), 3.63 (dq, *J* = 6.2 Hz, 9.9 Hz, 1H), 2.05 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 0.58 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (400 MHz, ($CDCl_3$): *δ* 170.3, 170.1, 170.0, 165.9, 165.3, 138.3, 133.4, 133.4, 133.3, 132.0, 130.0, 130.0, 129.6, 129.5, 129.0, 128.5, 128.4, 128.4, 127.7, 98.8 (J_{CH} = 172 Hz), 86.0, 79.3, 76.0, 75.3, 73.4, 71.1, 70.7, 70.0, 69.0, 68.4, 67.4, 21.0, 20.9, 20.9, 16.9; HRMS(ES) *m*/*z* calcd for $C_{45}H_{46}O_{14}SNa$: 865.2506 found 865.2503.

Phenyl 2,3-Di-*O*-acetyl-6-*O*-benzyl-4-*O*-(6-deoxy-2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-L-mannopyranosyl)-1-thio-*β*-D-glucopyranoside (20α). The standard procedure was followed with the exception that 1.5 equiv of donor was used.

The reaction mixture was purified by flash chromatography (EtOAc−pentane 1:25) to give the title product as a clear oil-172 mg (78%); $[\alpha]^{RT}_D$ −52.3 (*c* 1.0, $CHCl_3$); HRMS(ES) *m*/*z* calcd for $C_{47}H_{78}O_{11}SSi_3Na$: 957.4470 found 957.4500.

Due to poor resolution in the NMR caused by multiple conformations the purified product (149 mg, 0.157 mmol) was deprotected with TBAF (1 mL, 1 mmol) in THF (1 mL). The crude reaction mixture was concentrated in vacuo, dissolved in pyridine (1 mL) and Ac_2O (1 mL), and left over night. After concentration in vacuo the crude product was purified by flash chromatography (EtOAc− pentane 1:4 to 1:1) to give the desired product quantitatively as a colorless solid.

Phenyl 2,3-di-*O*-acetyl-6-*O*-benzyl-4-*O*-(6-deoxy-2,3,4-tri-*O*-acetyl-α-L-mannopyranosyl)-1-thio-*β*-D-glucopyranoside (20a): $[\alpha]^{RT}_D$ −48.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): *δ* 7.48 (m, 2H), 7.33−7.22 (m, 8H), 5.21 (t, *J* = 9.2 Hz, 1H), 5.17−5.13 (m, 2H), 5.02 (t, *J* = 9.7 Hz, 1H), 4.85 (t, *J* = 9.2 Hz, 1H), 4.85 (bs, 1H), 4.67 (d, *J* = 10.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 3.93 (t, *J* = 9.5 Hz, 1H), 3.87−3.78 (m, 3H), 3.57 (ddd, *J* = 1.7 Hz, 3.2 Hz, 9.7 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.02 (s, 6H), 1.97 (s, 3H), 1.14 (d, *J* = 6.2 Hz, 3H); ^{13}C− NMR (400 MHz, ($CDCl_3$): *δ* 170.2, 170.1, 170.0, 169.9, 169.5, 138.2, 133.2, 131.6, 128.9, 128.3, 127.5, 127.5, 99.4, 85.3, 78.6, 76.5, 75.3, 73.2, 70.7, 70.6, 69.8, 69.0, 68.3, 67.6, 21.1, 20.9, 20.8, 20.8, 18.5, 17.3; HRMS(ES) *m*/*z* calcd for $C_{35}H_{42}O_{14}SNa$: 741.2193 found 741.2186.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,6-di-*O*-benzyl-3,4-di-*O*-*tert*-butyldimethylsilyl-*β*-D-glucopyranosyl)-1-thio-*β*-D-glucopyranoside (30*β*): $[\alpha]^{RT}_D$ +14.1° (*c* 1.87, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): *δ* 7.55 (m, 2H), 7.39−7.13 (m, 28H), 4.89 (d, *J* = 10.4 Hz, 1H), 4.86 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 11.4 Hz), 4.79 (d, *J* = 11.0 Hz), 4.72 (d, *J* = 6.8 Hz, 1H, H_1), 4.71 (d, *J* = 10.5 Hz, 1H), 4.70 (d, *J* = 11.3 Hz, 1H), 4.67 (d, *J* = 9.8 Hz, 1H, H_1'), 4.58 (d, *J* = 12.2 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 11.3 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 4.14 (dd, *J* = 1.6 Hz, 10.8 Hz, 1H), 3.80 (dd, *J* = 4.5 Hz, 5.1 Hz, 1H), 3.77 (bdd, *J* = 5.2 Hz, 6.4 Hz, 1H), 3.71 (t, *J* = 9.7 Hz, 1H), 3.70 (bt, *J* = 9 Hz, 1H), 3.65 (t, *J* = 9 Hz, 1H), 3.65−3.55 (m, 3H), 3.47 (bd, *J* = 9.5 Hz, 1H), 4.42 (bd, *J* = 9.0 Hz, 1H), 3.39 (dd, *J* = 4.2 Hz, 6.7 Hz, 1H), 0.89, 0.84 (2 s, 18H), 0.08, 0.06, 0.05, 0.04 (4 s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 139.0, 138.6, 138.5, 138.2, 138.1, 134.4, 131.5, 128.9, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.5, 127.4, 127.2, 127.1, 102.7, 87.4, 86.8, 83.0, 80.9, 78.7, 78.7, 78.2, 76.6, 75.8, 75.5, 74.9, 73.4, 73.1, 71.8, 71.1, 68.7, 26.3, 26.0, 18.3, 18.1, −3.3, −3.4, −3.8, −4.1; HRMS(ES) *m*/*z* calcd for C65H84O10SSi2Na: 1135.5221, *m*/*z* found: 1135.5253.

Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,6-di-*O*-benzyl-3,4-di-*O*-*tert*-butyldimethylsilyl-*β*-D-glucopyranosyl)-1-thio-*β*-D-glucopyranoside (31*β*): $[\alpha]^{RT}_D$ −9.8° (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): *δ* 7.61 (m, 2H), 7.46−7.17 (m, 28H), 5.15 (d, *J* = 10.6 Hz, 1H), 4.93 (d, *J* = 7.1 Hz, 1H, H_1), 4.86 (d, *J* = 10.4 Hz, 1H), 4.82 (d, *J* = 10.4 Hz, 1H), 4.79 (d, *J* = 10.7 Hz, 1H), 4.74 (s, 2H), 4.69 (d, *J* = 9.8 Hz, 1H, H_1'), 4.54 (d, *J* = 12.1 Hz, 1H), 4.51 (d, *J* = 11.0 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 12.1 Hz, 1H), 3.96 (dd, *J* = 9.4 Hz, 9.5 Hz, 1H), 3.92 (dd, *J* = 2.6 Hz, 4.4 Hz, 1H), 3.90−3.85 (m, 2H), 3.83 (dd, *J* = 2.9 Hz, 6.0 Hz, 1H), 3.74 (dd, *J* = 9.3 Hz, *J* = 10.5 Hz, 1H) 3.72 (dd, *J* = 10.0 Hz, 11.6 Hz, 1H), 3.69 (t, *J* = 8.9 Hz, 1H), 3.51 (dd, *J* = 9.0 Hz, 9.6 Hz, 1H), 3.46 (dt, *J* = 1.8 Hz, 5.0 Hz, 1H), 3.45 (m, 1H), 3.42 (dd, *J* = 2.6 Hz, 4.5 Hz, 1H), 0.92, 0.91 (2 s, 18H), 0.13 (s, 6H), 0.12, 0.07 (2 s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 139.1, 138.7, 138.7, 138.6, 138.4, 134.1, 131.9 (2 C), 128.9, 128.4 (2C), 128.3 (2 C), 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 127.4, 127.4, 127.4, 127.3, 101.5, 87.4, 85.0, 84.5, 80.4, 79.9, 79.5, 76.9, 76.0, 75.6, 75.6, 73.3, 73.2, 73.1, 71.2, 70.9, 68.7, 26.0, 26.0, 18.1, 18.0, −3.7, −3.9, −4.1, −4.3; HRMS(ES) *m*/*z* calcd for $C_{65}H_{84}O_{10}SSi_2Na$: 1135.5221, *m*/*z* found: 1135.5266.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-*tert*-butyldimethylsilyl-4,6-di-*O*-di-*tert*-butyl-silylene-*β*-D-glucopyranosyl)-1-thio-*β*-D-glucopyranoside (33*β*): $[\alpha]^{RT}_D$ +34.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): *δ* 7.54 (m, 2H), 7.40−7.23 (m, 18H), 4.92 (d, *J* = 10.3 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 11.0 Hz, 1H), 4.76 (d, *J* = 3.6 Hz, 1H, H_1), 4.73 (d, *J* = 10.3 Hz, 1H), 4.66 (d, *J* = 9.8 Hz, 1H, H_1'), 4.65 (d, *J* = 11.0 Hz, 1H), 4.09 (d, *J* = 4.9 Hz, 1H), 3.84 (t, *J* = 8.4 Hz, 1H), 3.82−3.78 (m, 2H), 3.79 (t, *J* = 8.9 Hz, 1H), 3.71 (t, *J* = 8.8 Hz, 1H), 3.71 (dd, *J* = 1.4 Hz, 11.1 Hz, 1H), 3.65 (bt, *J* = 8.8 Hz, 1H), 3.57 (dd, *J* = 3.6 Hz, 8.7 Hz, 1H), 4.58 (m, 1H), 3.50 (dd, *J* = 2.8 Hz, 8.9 Hz, 1H), 3.47 (dd, *J* = 3.0 Hz, 8.9 Hz, 1H), 1.04 (s, 9H), 0.94 (s, 9H), 0.93 (s, 9H), 0.88 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H), 0.12 (s, 1H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 138.5, 138.1, 138.1, 134.8, 131.2, 129.0, 128.5, 128.5, 128.4, 128.3, 128.0, 127.8, 127.8, 127.8, 127.7, 127.2, 100.1, 87.9, 86.9, 81.0, 78.8, 78.6, 78.3, 77.3, 75.8, 75.5, 75.1, 74.6, 74.4, 67.7, 67.1, 66.5, 27.7, 27.2, 26.5, 26.4, 22.8, 19.9, 18.4, 18.2, −2.9, −3.1, −3.4, −3.7; HRMS(ES) *m*/*z* calcd for $C_{24}H_{52}O_5Si_3Na$: 1095.5604, *m*/*z* found: 1095.5321.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,6-di-*O*-benzyl-3,4-di-*O*-tri-isopropylsilyl-*β*-D-glucopyranosyl)-1-thio-*β*-D-glucopyranoside (40*β*): $[\alpha]^{RT}_D$ −3.3° (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): *δ* 7.55 (m, 2H), 7.40−7.13 (m, 28H), 4.98 (d, *J* = 6.5 Hz, 1H, H_1), 4.90 (d, *J* = 10.3 Hz, 1H), 4.88 (d, *J* = 10.9 Hz), 4.82 (d, *J* = 12.0 Hz), 4.82 (d, *J* = 10.3 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 10.3 Hz, 1H), 4.70 (d, *J* = 9.7 Hz, 1H, H_1'), 4.59 (d, *J* = 11.0 Hz, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.19 (dd, *J* = 1.6 Hz, 10.4 Hz, 1H), 4.14 (m, 2H), 4.07 (bd, *J* = 3.1 Hz, 1H), 3.75 (dd, *J* = 7.3 Hz, 9.3 Hz, 1H), 3.72 (m, 1H), 3.69 (dd, *J* = 2.8 Hz, 6.6 Hz, 1H), 3.64 (ddd, *J* = 1.7 Hz, 6.5 Hz, 9.6 Hz, 1H), 3.58 (bd, *J* = 10.0 Hz, 1H), 3.57 (bd, *J* = 10.0 Hz, 1H), 3.50 (dd, *J* = 1.4 Hz, 10.0 Hz, 1H), 3.48 (dd, *J* = 1.4 Hz, 10.0 Hz, 1H) 1.06 (bs, 21H), 1.01 (bs, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 139.1, 138.6, 138.5, 138.2, 138.1, 134.5, 131.1, 128.9, 128.5 (2 C), 128.4, 128.3 (2 C), 128.0, 127.9 (3 C), 127.8 (2 C), 127.7, 127.5, 127.5, 127.0, 126.9, 102.2, 87.3, 86.9, 83.4, 80.9 (2 C), 78.7, 78.3, 76.7, 75.9, 75.5, 75.0, 73.4, 73.0, 71.7, 71.1, 68.8, 18.3, 18.2, 18.1, 18.1, 12.4, 12.3 HRMS-(ES) *m*/*z* calcd for $C_{71}H_{96}O_{10}SSi_2Na$: 1219.6160, *m*/*z* found: 1219.6141.

Due to inseparable impurities in the fraction with the α-anomer, it was deprotected and acetylated followed by purification using flask chromatography (pentane−EtOAC, 5:1 to 3:1).

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,6-di-*O*-benzyl-3,4-di-*O*-acetyl-α-D-glucopyranosyl)-1-thio-*β*-D-glucopyranoside (40a): $[\alpha]^{RT}_{D}$ +48.0 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.55 (m, 2H), 7.45 (m, 2H), 7.35−7.10 (m, 28H), 5.40 (t, J = 9.8 Hz, 1H), 5.00 (t, J = 10.1 Hz, 1H), 4.98 (d, J = 3.4 Hz, 1H), 4.82 (d, J = 11.3 Hz, 1H), 4.79 (d, J = 11.2 Hz, 1H), 4.73 (d, J = 11.1 Hz, 1H), 4.70 (d, J = 10.1 Hz, 1H), 4.67 (d, J = 12.5 Hz, 1H), 4.61 (d, J = 11.4 Hz, 1H), 4.57 (d, J = 9.9 Hz, 1H), 4.56 (d, J = 12.5 Hz, 1H), 4.51 (d, J = 10.3 Hz, 1H), 4.50 (d, J = 12.1 Hz, 1H), 4.33 (d, J = 12.1 Hz, 1H), 3.92 (ddd, J = 2.8 Hz, 3.5 Hz, 10.2 Hz, 1H), 3.76 (dd, J = 4.6 Hz, 11.5 Hz, 1H), 3.71 (dd, J = 1.3 Hz, 11.5 Hz, 1H), 3.58 (m, 2H), 3.51 (dd, J = 3.6 Hz, 10.0 Hz, 1H), 3.44 (bm, 1H), 3.40 (dd, J = 2.6 Hz, 11.0 Hz, 1H), 3.32 (dd, J = 4.1 Hz, 11.0 Hz, 1H), 3.15 (dd, J = 8.5 Hz, 9.7 Hz, 1H), 1.94 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 169.9, 138.7, 138.4, 138.2, 138.2, 137.9, 134.5, 131.5, 129.3, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.1, 128.0 (2 C), 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 97.2, 88.4, 86.8, 81.2, 78.9, 77.6, 76.9, 75.8, 75.7, 75.2, 73.5, 72.5, 72.3, 69.3, 68.3, 68.1, 66.7, 21.1, 20.8; HRMS(ES) *m*/*z* calcd for $C_{57}H_{60}O_{12}SK$: 1007.3443, *m*/*z* found: 1007.3465.

Supporting Information Available: Spectra of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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