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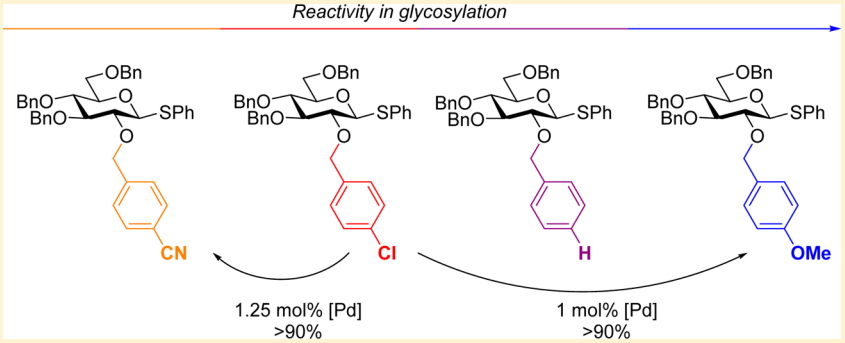
Remote Electronic Effects by Ether Protecting Groups Fine-Tune Glycosyl Donor Reactivity

Mads Heuckendorff, Lulu Teressa Poulsen, and Henrik H. Jensen*

Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark

Supporting Information



ABSTRACT: It was established that *para*-substituted benzyl ether protecting groups affect the reactivity of glycosyl donors of the thioglycoside type with the *N*-iodosuccinimide/triflic acid promoter system. Having electron donating *p*-methoxybenzyl ether (PMB) groups increased the reactivity of the donor in comparison to having electron withdrawing *p*-chloro (PClB) or *p*-cyanobenzyl ether (PCNB) protecting groups, which decreased the reactivity of the glycosyl donor relative to the parent benzyl ether (Bn) protected glycosyl donor. These findings were used to perform the first armed-disarmed coupling between two benzylated glucosyl donors by tuning their reactivity. In addition, the present work describes a highly efficient palladium catalyzed multiple cyanation and methoxylation of *p*-chlorobenzyl protected thioglycosides. The results of this paper regarding both the different electron withdrawing properties of various benzyl ethers and the efficient and multiple protecting group transformations are applicable in general organic chemistry and not restricted to carbohydrate chemistry.

INTRODUCTION

Efficient synthesis of oligosaccharides through chemical glycosylation remains a challenging task,[1] and investigation of effects that govern donor reactivity and stereochemical outcome continues to be performed in the hope of achieving some fundamental insight that eventually will lead to a general protocol for this intriguing reaction.[2] Since the early days of carbohydrate chemistry it has been known that protecting groups not only had an influence on the selectivity in glycosylation reactions,[3] but also affected the reactivity of glycosyl donors.[4,5] This difference in reactivity, the degree of so-called armament, can be synthetically useful[6−10] and provide oligosaccharides in a rapid fashion as especially showed by Wong and co-workers.[11]

Although generally agreed upon as being a challenging synthetic transformation, the glycosylation reaction is just another reaction within the field of organic chemistry and controlling its diastereoselectivity (anomeric selectivity) is a key issue.

Many scientists have offered much speculation when it comes to anomeric selectivity, but no rule seems to be available and widely known among experts in the field when it comes to reactions conducted without the use of participating protecting groups. Some text books[12] state that the axial glycoside will dominate as a consequence of the well-known anomeric effect, which has been brought into question since glycosylation, to a first approximation, must be under kinetic control.[13] There are many approaches for conducting a glycosylation reaction, which would fall into the category of being a "standard protocol", and the NIS/TfOH(cat) activation of a SPh thioglycoside donor initiated at −78 °C and allowed to warm to a higher temperature arguably belongs to this class. The slow warming of a reaction mixture is often used in organic chemistry for reactions in which diastereoselectivity is an issue to ensure as low a reaction temperature as possible. This, however, only makes sense when the kinetic product is the desired outcome.

The Hammett equation and values derived from the pK_a values of substituted benzoic acids are fundamental in physical organic chemistry, and linear free-energy relationships build on these have been widely used to interpret reaction mechanism in organic chemistry.[14] In actual fact, the Hammett constants, σ, have been found to correlate with pK_a of phenylacetic acids (ρ = 0.489) and β-phenylpropionic acids (ρ = 0.212). Since the effects cannot be explained by resonance it is believed to be an inductive effect.[15]

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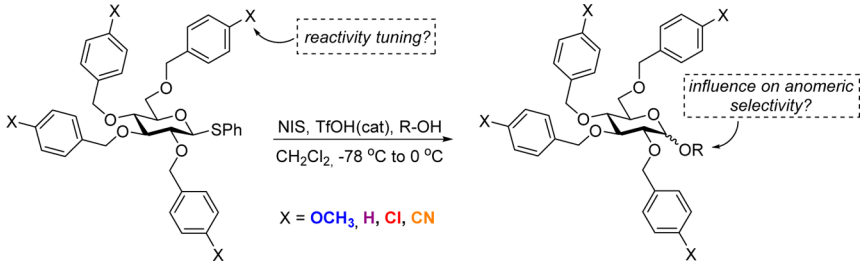
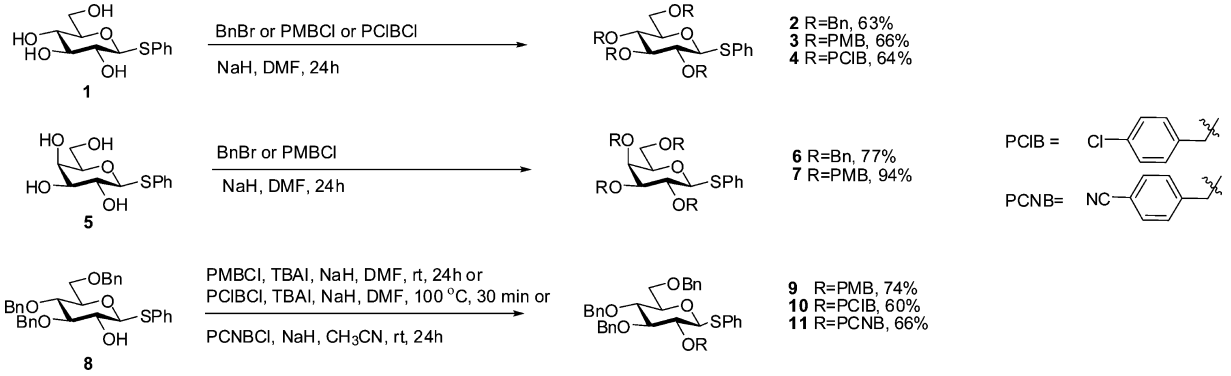
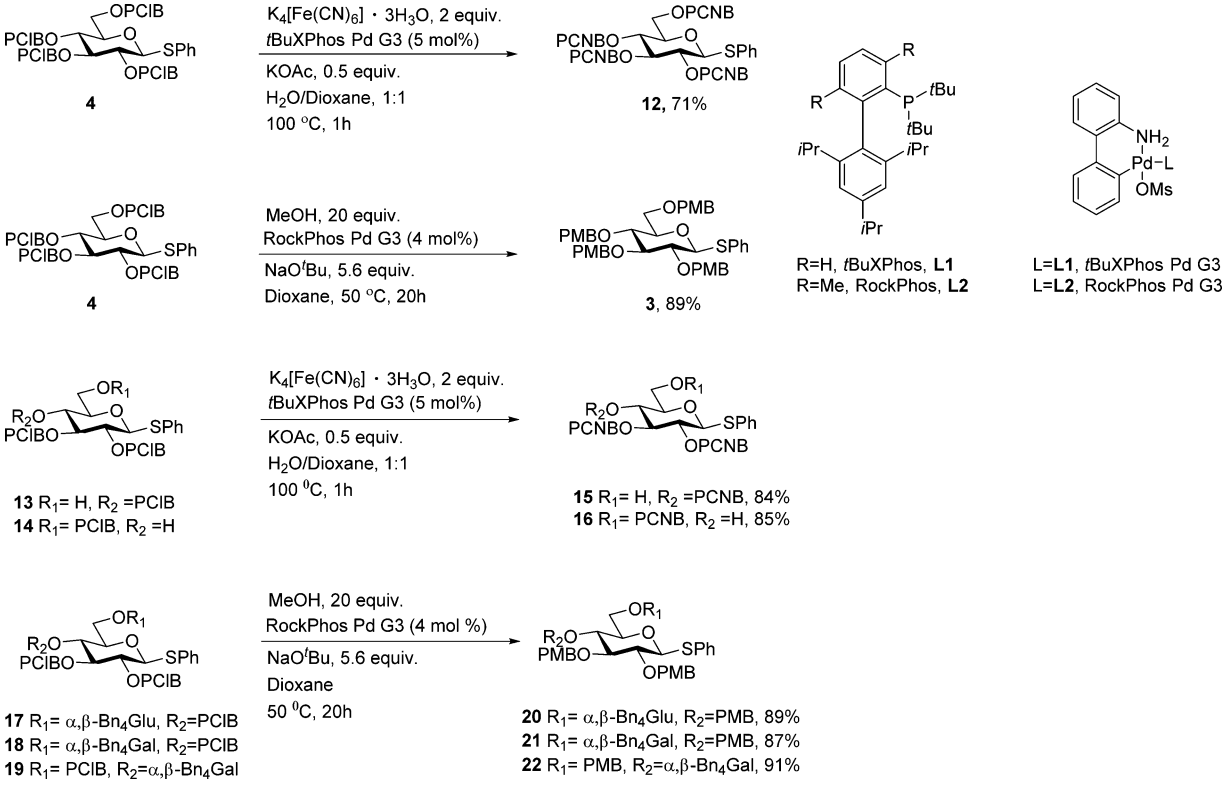
Scheme 1. Project Outline: Does the Nature of X Have an Influence on Glycosyl Donor Reactivity and Stereochemical Outcome?



Scheme 2. Synthesis of Glycosyl Donors



Scheme 3. Palladium Catalyzed Cyanation and Methoxylation of *p*-Chlorobenzyl Protected Carbohydrates



The present paper describes for the first time that benzyl ether *p*-substituents indeed can be used to fine-tune the reactivity of thioglycoside glycosyl donors undergoing NIS/TfOH activation (Scheme 1). The results furthermore systematically show that the anomeric selectivity changes when varying the benzyl ether *p*-substituent indicative of a temperature effect on glycosylation outcome (vide infra).

Before this study, fully *p*-methoxybenzyl (PMB)[16] protected glycosyl donors have been used in glycosylations, when debenzylation by hydrogenolysis is not an option. *p*-Chlorobenzyl (PClB)[17] protecting groups have been reported

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Scheme 4. General Glycosylation Reaction with L-Menthol as Acceptor

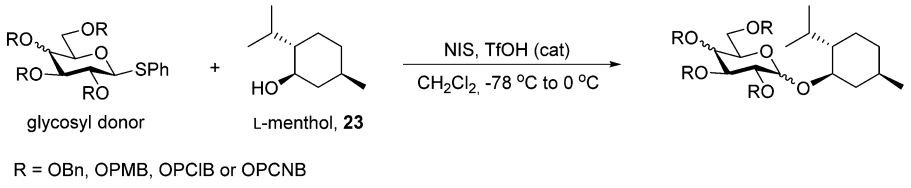
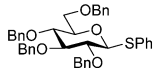
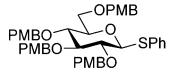
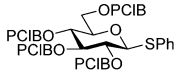
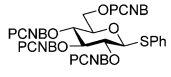
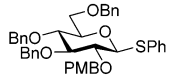
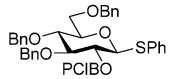
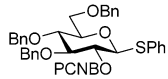
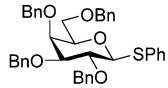
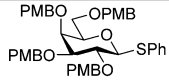


Table 1. Glycosylation Results with L-Menthol According to Scheme 4[c]

Entry	Donor	α/β	Yield[a]
1	 **2**	1/3	100%
2	 **3**	1/5	91%
3	 **4**	1/1.1 1/3[b]	81% 80%[b]
4	 **12**	1/1[b]	85%[b]
5	 **9**	1/4	93%
6	 **10**	1/4	90%
7	 **11**	1/4	72%
8	 **6**	1/7	93%
9	 **7**	1/6	59%

[a]Isolated yield after chromatography. [b]2 equiv of NIS. [c]Conditions: 1.1 equiv of NIS; 0.1 equiv of TfOH; −78 to 0 °C in CH_2Cl_2.

to render protected carbohydrates more prone to crystallize and to stabilize the sensitive fucopyranoside linkage. There are no reports describing the use of *p*-cyanobenzylated (PCNB) glycosyl donors. Lately, however, highly selective benzyl protected glycosyl donors with a 2-*O*-(*o*-cyanobenzyl) or a 2-*O*-(*o*-nitrobenzyl) group have been reported without the mention of their reactivity.[18]

RESULTS AND DISCUSSION

To investigate donor reactivity as a function of the benzyl ether *p*-substituent we started out by synthesizing eight different glycosyl donors. In the *gluco*-series perbenzylated (**2**), per-*O*-*p*-methoxybenzylated (**3**) and per-*O*-*p*-chlorobenzylated (**4**) phenyl thioglucosides were synthesized under standard benzylation conditions in DMF with NaH as the base giving the donors in reasonable yields (Scheme 2). In the *galacto*-series the perbenzylated (**6**) and per-*O*-*p*-methoxybenzylated (**7**) donors were prepared in a similar fashion in good yields. To investigate the effect of having only one *p*-substituted benzyl group; the 2-*O* position was chosen due to its proximity to the anomeric position. 2-*O*-PMB, 2-*O*-PClB and 2-*O*-PCNB (**9**–**11**, respectively) were synthesized from **8** under published[18] benzylation conditions.

Investigating the influence of multiple electron withdrawing cyano groups on glycosyl donor reactivity was also interesting, but the synthesis of a per-*O*-*p*-cyanobenzylated phenyl thioglucoside was not possible under the standard benzylation conditions as described in Scheme 2. The reaction proceeded sluggishly and the only isolable compound formed was the 6-*O*-*p*-cyanobenzylated product.

In 2000, Seeberger and Buchwald and co-workers published a paper wherein *p*-halobenzyl ethers underwent Hartwig–Buchwald amination using a variety of amines and $Pd(dba)_2$ or $Pd(OAc)_2$ as catalysts to arrive at an electron rich and hence more Lewis acid labile benzyl ether protecting group.[19]

The momentous progress witnessed in recent years in the area of palladium catalysis driven by developments of highly active palladium ligands and palladium precatalysts have paved the way for new and mild reactions.[20] In 2013, the Buchwald group published a safe method for performing cyanation of aryl chlorides, using $K_4[Fe(CN)_6]\cdot 3H_2O$ and a palladium precatalyst system (*t*BuXPhos Pd G3); having broad substrate scope, low catalyst loading and reaction times around 1 h at 100 °C.[21] Subjecting tetra-*p*-chlorobenzylated compound **4** to slightly modified conditions gave the per-*O*-*p*-cyanobenzylated glucosyl donor **12** in 71% yield (92% for each cyano substitution) (see Scheme 3).[22] Delighted by the effective palladium catalyzed cyanation, we moved on to perform cyanation of *p*-chlorobenzyl protected acceptors **13** and **14** with a free 4- or 6-OH, respectively. The free OH groups did not hamper the reactions, and the two desired compounds **15** and **16** were obtained in satisfactory yields of 85% and 84% (95% and 94%, respectively for each cyano substitution). Next, our attention was lead to another Buchwald publication, in which palladium

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catalyzed methoxylation of aryl chlorides under very mild conditions was described.[23] To investigate the methoxylation reaction on *p*-chlorobenzyl ethers the tetra-*O*-*p*-chlorobenzylated compound **4** was again chosen as substrate. Upon treatment of **4** with 20 equiv of methanol (5 equiv per chloride), 5.6 equiv of NaO^{t}Bu (1.4 equiv per chloride) and 4 mol % (1 mol % per chloride) of the precatalyst system *t*BuBrettphos Pd G3 or RockPhos Pd G3 in dioxane the per-*O*-*p*-methoxybenzylated donor **3** was obtained in 89% (97% for each methoxy substitution). To further expand the method, we subjected the three disaccharides **17**, **18** and **19** (vide infra) bearing three PClB groups to the same conditions giving the products in around 90% yields. The high yield obtained with low catalyst loading is a testament to the high turnover frequency of this system. The mild methoxylation reaction is highly recommendable and would allow a late stage introduction of PMB groups by masking them as acid stable PClB groups.

Glycosylation and Determination of Donor Reactivity in Competition Experiments. With the glycosyl donors in hand, we started out to compare their reactivity in glycosylation reactions. Standard activation conditions using NIS/TfOH-(cat)[7] were chosen in a nonparticipating solvent, CH_2Cl_2, using L-menthol (**23**) as an easily handled nonhygroscopic acceptor. Since it can be difficult to find an appropriate reaction temperature under which a given glycosylation takes place, the reaction mixture was cooled to −78 °C prior to the addition of catalyst (TfOH). The temperature was then allowed to slowly increase to 0 °C over several hours (Scheme 4). No reaction throughout this study was found to take place at −78 °C, but all reactions were found to have completed before reaching 0 °C. (Anomeric ratios were measured by comparison of integral intensities of the anomeric protons and anomeric carbons from ^{1}H NMR and ^{13}C NMR spectra of crude reaction mixtures.)

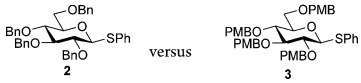
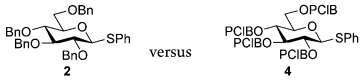
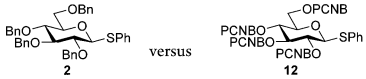
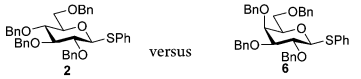
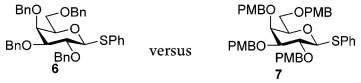
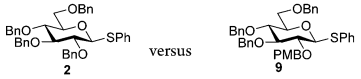
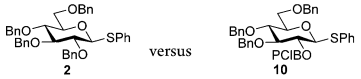
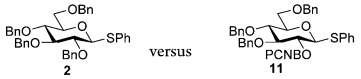
As can be seen from Table 1, the reactions gave good yields and comparable β-selectivities for donor **2** and **3** (Entry 1 and 2). The per-*O*-*p*-chlorobenzylated donor **4**, however, was almost unselective, which could be a result of a sluggish reaction due to the near equimolar amounts of donor and promoter. Reaction completion for glycosylation with donor **4** was attained more easily with 2 equiv of NIS resulting in an increased β-selectivity (α/β 1:3) of the reaction to a level close to that observed for the donors **2** and **3** (α/β 1:3 and 1:5, respectively). The increased amount of NIS (2 equiv) was also used for activation of per-*p*-*O*-cyanobenzyl protected donor **12** (Entry 4) in an unselective reaction (α/β 1:1).

The remaining glucosyl donors (**9**−**11**) bearing three unmodified benzyl ether protecting groups, but substituted benzyl ethers (PMB, PClB and PCNB, respectively) as protection of O-2 also gave good to excellent chemical yields of the menthyl glucosides with very similar β-selectivity with only slight excess (1.1 equiv) of NIS as promoter. Identical conditions also provided the galactoside products with per-*O*-benzyl and per-*O*-*p*-methoxybenzyl ether protecting groups from donors **6** and **7**.

Having established that all glycosyl donors gave high yields under the applied glycosylation conditions, we went on to investigate their reactivity by performing competition experiments between pairs of thioglycosides. This was undertaken by having 1 equiv of each donor to compete for 1 equiv of NIS in the presence of excess acceptor, L-menthol (5 equiv). Prior to the reactions, the donors were mixed and a ^{13}C NMR spectrum with a high signal-to-noise ratio was recorded of the mixture to ensure that the donors were present in a 1:1 ratio by comparing the anomeric (C-1) signals.[24] After ended reaction and workup a new ^{13}C NMR was recorded of the crude reaction mixture and the anomeric signals of the unreacted donors were again integrated and compared. It was thereby possible to obtain a ratio of donors before and after reaction that shows how much of each donor has been consumed during the reaction and thus how reactive the donors are compared to each other.

As seen from Table 2, the benzyl ether *p*-substituent significantly influences the reactivity of the glycosyl donor. As

Table 2. Competition Experiments Conducted with 5 equiv of L-Menthol (23)[a]

Entry	Competing donors	Integrals after reaction (reciprocal)
1		1:0.45 (2.2:1)
2		1:3 (0.33:1)
3		1:7 (0.14:1)
4		1:0.14 (7:1)
5		1:0.4 (2.5:1)
6		1:0.67 (1.5:1)
7		1:1.2 (0.83:1)
8		1:1.6 (0.63:1)

[a]Conditions: 1 equiv of NIS; 0.1 equiv of TfOH in CH_2Cl_2, −78 to 0 °C. Before reaction anomeric carbons integrals were 1.0:1.0.

expected from the Hammett constants the diminished electron withdrawing ability of four PMB ethers renders donor **3** more reactive than **2** (Table 2, Entry 1) by causing less destabilization to the oxacarbenium ion-like transition state during donor activation. From the integrals it is apparent that twice as much of the PMB donor (**3**) is consumed during the reaction, when compared to the benzylated donor (**2**) giving a 2.2:1 anomeric ratio of unreacted donors. This means that donor **3** is at least 2.2 times more reactive than **2**.[25] Furthermore, both the tetra-*O*-PClB donor (**4**) and especially the tetra-*O*-PCNB donor

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(**12**) are less reactive than the benzylated donor (**2**) as expected (Table 2, Entry 2 and Entry 3). The reactivity difference between the two *gluco*-configured donors, the benzylated donor **2** and the tetra-*O*-PCNB donor (**12**) was furthermore found to correspond to the reactivity difference between **2** and its *galacto*-configured congener **6** (Table 2, Entry 4).

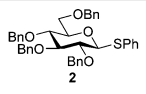
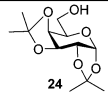
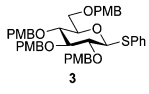
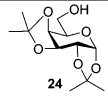
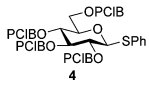
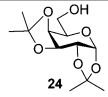
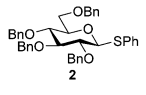
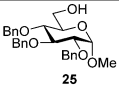
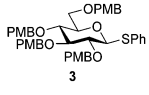
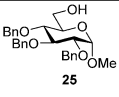
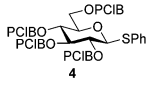
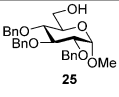
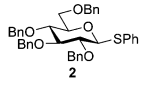
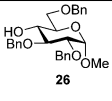
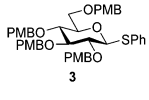
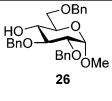
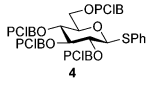
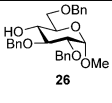
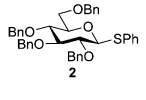
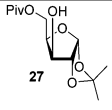
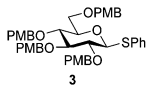
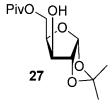
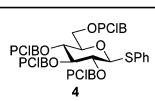
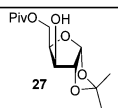
The competition experiment between donor **2** and **6** (Entry 4) enables a comparison of the method used in this paper to reactivity differences known from the literature. The established ratio of unreacted *gluco*:*galacto* donor being 7:1 is fully in accordance with observation by Wong and co-workers, who observed a 6.4 fold difference in RRV's between galactosyl and glucosyl donors.[9] From other glycosylation and hydrolysis studies a comparable rate difference has also been observed.[26] The difference in reactivity between per-*O*-benzyl and per-*O*-PMB was also compared in the *β*-*galacto*-series (**6** and **7**, Entry 5) giving a similar result as in the *gluco*-series (**2** and **3**, Entry 1). From Table 2 (Entry 6−8) it is evident that glucosyl donors having only one *p*-substituted benzyl present on the O-2 and unsubstituted benzyl ethers on O-3, O-4 and O-6 have an altered reactivity compared to the tetra-*O*-benzyl protected donor (**2**). The trend is the same as seen for the per-*O*-p-substituted donors **3**, **4** and **12**; a PMB-ether (**9**) increases reactivity, while PClB- (**10**) and especially PCNB-ethers (**11**) decrease thioglycoside reactivity. The differences in reactivity between the parent donor (**2**) and the singly altered donors (**9**−**11**) are reduced when compared to the fully altered donors (**3**, **4** and **12**) as would be expected, but the magnitude, however modest, is still remarkably easy observed.

Anomeric Selectivity. Enticed by the relatively high *β*-selectivity in glycosylation with L-menthol, as described in Table 1, we set out to investigate if this was an effect of the acceptor or whether the used conditions generally offered a majority of *β*-anomeric product for the Bn, PMB and PClB protected donors (**2**, **3** and **4**) in glycosylation reactions with a range of acceptors. As can be seen from the results listed in Table 3, comparable yields and selectivity were obtained for the reactive acceptors **24** and **25** as those obtained in reaction with L-menthol (**23**).

Glycosylation with per-*O*-benzyl and per-*O*-PMB donors (**2** and **3**) gave identical or very similar glycosylation outcomes with regards to anomeric selectivity in reaction with acceptors **24**−**27** (Table 3).[27] The more reactive acceptors **3**, **24** and **25** gave a moderate *β*-selectivity, whereas the selectivity seemed to drop for reactions with the more sterically hindered secondary alcohols **26** and **27**. For the xylofuranose acceptor **27** (Entry 10−12) a reversed stereoselectivity was obtained for all three donors and mostly *α*-products were isolated. Glycosylation of a similar xylofuranose based acceptor with bulky 5-*O*-TBDPS or 5-*O*-TBDMS have previously been reported to give high *α*-selectivity.[28] We speculate that the reversed selectivity is due to steric reasons; the result underscores how glycosylation selectivities can be very acceptor dependent.

Commenting on anomeric selectivity and the origin thereof must always be done with utmost caution,[13] but a glycosylation reaction must, at least initially, give the kinetic product as the major product. The kinetic product could be the same as the thermodynamic product (expected to be the axial glycoside) or the kinetic product could undergo anomerization to the thermodynamic product. A certain trend, however, seems evident in that the less reactive PClB donor **4**, in comparison to the donors **2** and **3**, returns a lower level of *β*-glycoside product. This is furthermore in agreement with the results shown in Table 1 including those of the PCNB protected donor **12**. The eroding *β*-selectivity could be a result of (i) higher degree of postglycosylation anomerization for the PClB and PCNB

Table 3. Glycosylation Results with Carbohydrate Based Acceptor[c]

Entry	Donor	Acceptor	α/β	Yield[a]
1	 **2**	 **24**	1/4	74%
2	 **3**	 **24**	1/4	90%
3	 **4**	 **24**	1/2[b]	88%[b]
4	 **2**	 **25**	1/4	86%
5	 **3**	 **25**	1/4	68%
6	 **4**	 **25**	1/3[b]	86%[b]
7	 **2**	 **26**	1/1.2	89%
8	 **3**	 **26**	1/1.3	68%
9	 **4**	 **26**	2/1[b]	100%[b]
10	 **2**	 **27**	7/1	88%
11	 **3**	 **27**	7/1	58%
12	 **4**	 **27**	9/1[b]	87%[b]

[a]Isolated yield after chromatography. [b]2 equiv of NIS. [c]Conditions: 1.1 equiv of NIS; 0.1 equiv of TfOH; −78 to 0 °C in CH_2Cl_2.

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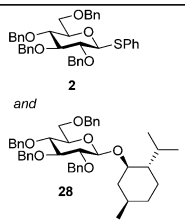
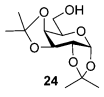
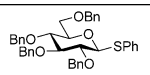
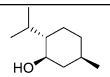
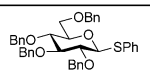
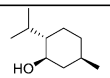
protected donors, (ii) the reaction undergoing a different path with respect to mechanism and conformational preferences,[29] or (iii) the less reactive donors undergoing glycosylation at a higher temperature resulting in a smaller degree of selectivity. To shed light on the origin of the changing selectivity when going to less reactive donors, a series of experiments were conducted.

(i) First, addressing the possibility of anomerization of the glycoside product under the reaction conditions postglycosylation was studied (Table 4). A glycosylation was carried out as previously described between donor **2** and acceptor **24** but in the presence of menthyl β-glucoside **28**. After the reaction **28** could be reisolated in near quantitative yield as the β-anomer (Table 4, Entry 1). Next, the glycosylation between **2** and L-menthol (**23**) was carried out as earlier (Table 1), but by letting the reaction mixture warm to ambient temperature (Table 4, Entry 2). The outcome with regards to both anomeric selectivity and yield was identical to that found for the experiment described in Table 1, Entry 1, where the reaction was quenched at 0 °C. These experiments show that no anomerization occurs for the menthyl glycoside under the glycosylation conditions and between 0 °C and ambient temperature. Performing the reaction at ambient temperature, however, resulted in an unselective reaction yielding a 1:1 anomeric product ratio. This result is in accordance with the fact that the yield of the kinetic product will be expected to drop at elevated temperatures (Table 4, Entry 3).

Table 4. Investigation of the Level of Post-glycosylation Anomerization[c]

Entry	Temperature	Donor	Acceptor	α/β	Yield[a]
1	-78 °C to 0 °C	 2 and 28	 24	β only[b]	97%
2	-78 °C to r.t.	 2	 23	1/3	100%
3	r.t. (isothermal)	 2	 23	1/1	93%

[a]Isolated yield after chromatography. [b]Refers to L-menthyl glucoside **28**. [c]Conditions: 1.1 equiv of NIS; 0.1 equiv of TfOH.

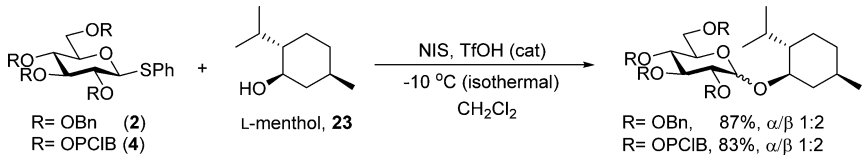
(ii) Next, the stereochemical outcome of glycosylations performed under isothermal conditions at a temperature at which activation of both donors were rapid was investigated (Scheme 5). Benzylated donor **2** and PClB protected donor **4** were accordingly reacted separately with L-menthol as acceptor (NIS/10 mol % TfOH, CH_2Cl_2) in the same cold bath at −10 °C. This resulted in an identical α/β-ratio (1:2) suggesting that the donors (**2** and **4**) are highly alike and react through the same conformation despite their different reactivity.

Collectively, the results of Table 4 and Scheme 5 show that the anomeric outcome of the conducted glycosylations (Table 1 and Table 3) are a result of the reaction's intrinsic selectivity and not a result of a postglycosylation anomerization reaction. In general, the benzylated donors were found to be β-selective and not α-selective as often claimed in literature.[12] Furthermore, the observed eroding β-selectivity going from the benzylated donor over PClB to PCNB protected donors must be a result of the reaction temperatures as mentioned under (iii), which is generally accepted, but to the best of our knowledge not previously studied in detail for glycosylations.[30] The established α/β 1:2-selectivty at −10 °C is in between the selectivity of the reactions carried out at ambient temperature (α/β 1:1) and between −78 °C to 0 °C over approximately 3 h (α/β 1:3) as would be expected. Another glycosylation involving donor **2** and acceptor **23** (not shown) was carried out between −78 °C to −40 °C, which resulted in an improved α/β ratio of 1:5.

These findings underline the importance of temperature control during glycosylation and how the selectivity can be significantly improved in favor of the kinetic product by cooling. Conducting glycosylations at rising temperatures could benefit from considering the gradient with which the temperature climbs.

Armed-Disarmed Glycosylation. Having investigated reactivity and selectivity of the glycosyl donors, we moved on to explore the possibility of performing chemoselective activation and thereby conducting armed-disarmed-type couplings. The experiments were performed by taking 1 equiv of donor to 1 equiv of thioglycoside acceptor, activating as previously described (Scheme 4). A successful coupling would be indicative of a sufficiently large reactivity difference between the two reaction partners, while the failure to produce a disaccharide in acceptable yield would suggest the opposite. As seen from Table 5, Entry 1−2, benzyl and PMB protected donors (**2** and **3**, respectively) successfully gave the disaccharide products in reaction with 6-OH-PClB acceptor **13** with a level of β-selectivity previously found for reactive primary acceptors (Table 3). To the best of our knowledge, the reaction of **2** and **3** with the primary acceptor **13** are the first armed disarmed-type couplings between two benzylated donors and acceptors.

Scheme 5. Glycosylation with Acceptor 23 under Isothermal Conditions Gives Identical Anomeric Selectivity



R= OBn (**2**)
R= OPClB (**4**)

L-menthol, **23**

R= OBn, 87%, α/β 1:2
R= OPClB, 83%, α/β 1:2

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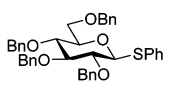
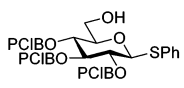
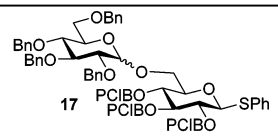
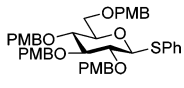
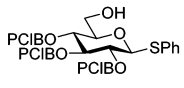
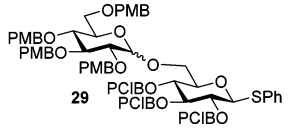
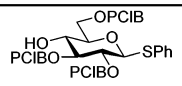
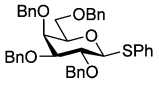
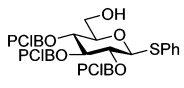
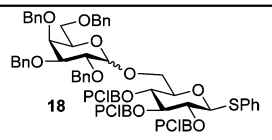
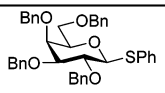
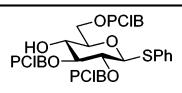
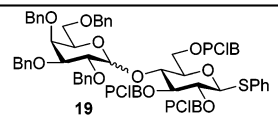
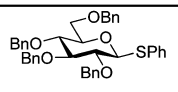
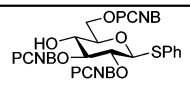
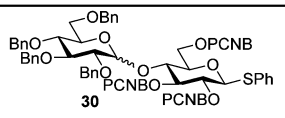
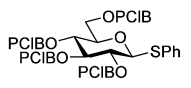
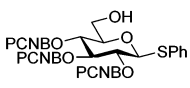
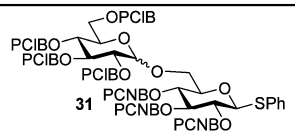
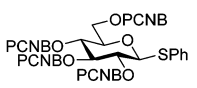
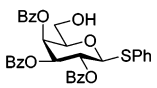
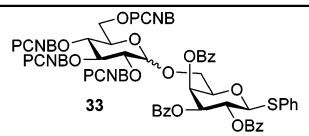
Table 5. Glycosylation by Chemoselective Activation[a]

Entry	Donor	Acceptor	Product	α/β	Yield
1	 **2**	 **13**	 **17**	1/4	65%
2	 **3**	 **13**	 **29**	1/3	66%
3	**2 or 3**	 **14**	No disaccharide product observed	-	0%
4	 **6**	 **13**	 **18**	1/1	80%
5	 **6**	 **14**	 **19**	3/1	57%
6	 **2**	 **16**	 **30**	3/1	46%
7	 **4**	 **15**	 **31**	1/2	49%
8	 **12**	 **32**	 **33**	2/1	79%

[a]Conditions: 1 equiv of both NIS, donor and acceptor; 0.1 equiv of TfOH; −78 to 0 °C in CH_2Cl_2.

The same glucosyl donors (**2** and **3**) failed to give a useful result in reaction with the more sterically hindered 4-OH-PClB acceptor **14** (Entry 3). A reason for this could be that **14** is more reactive than **13** thereby diminishing the reactivity gap between **2**/**3** and **14**. In actual fact, Koeller and Wong[9c] have reported that OH is an accelerating substituent compared to OBn and Withers and co-workers have shown that alterations at C-4 have greater influence on hydrolysis rates than alterations on C-6.[26d]

Compared to the glucosyl donors **2** and **3**, the more reactive galactosyl counterpart **6** smoothly made the glycosylation possible on both the 6-OH and 4-OH of the PClB protected acceptors **13** and **14**, respectively (Entry 4 and Entry 5).

The reactivity difference between benzyl and PCNB protected glucosyl donors were found to be sufficient to allow for a 4-OH glycosylation in reaction with **2** and acceptor **16** (Entry 6). Also the PClB donor **4** was found to be able to provide disaccharide **31** in coupling with the more disarmed PCNB protected acceptor (**15**) carrying a free primary alcohol (Entry 7). Again, the reaction resulted in predominant formation of the *β*-anomer (*α*/*β* 1:2) but with a diminished degree of selectivity as previously found for the PClB donor.

To this stage, the present results have shown that glycosyl donor reactivity can be modulated by employment of different benzyl ethers and that the strongly electron withdrawing CN-group was found to be the least reactive. To investigate whether

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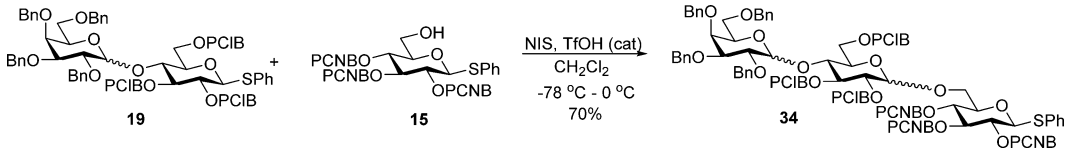
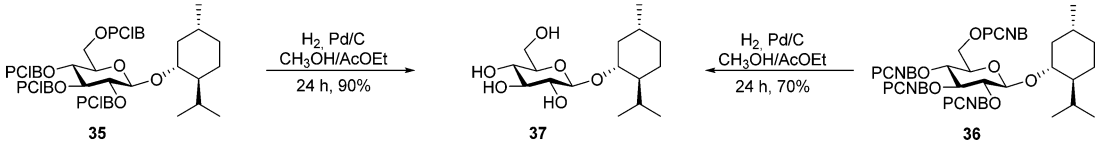
Scheme 6. Synthesis of Trisaccharide 30



Scheme 7. Debenzylation of PClB and PCNB Groups by Catalytic Hydrogenolysis



the least reactive donor in this study thus far, i.e., per-*O*-PCNB donor **12** was still more reactive than a classically (ester protected) disarmed donor, a coupling between tri-*O*-benzoylated acceptor **32** was attempted, which yielded the disaccharide **33** in 79% (Entry 8). This demonstrates that reactivity tuning with a benzyl ether *p*-substituent takes advantage of a previously unexploited area of the reactivity continuum.

In the elegant study by Wong and co-workers[9] it was noted that disaccharides generally are less reactive than their monosaccharide counterparts suggesting a lowering of reactivity as a function of carrying another glycosyl residue relative to a hydroxyl. An attempt to synthesize a trisaccharide, coupling between disaccharide donor **20**, **21** or **22** and PClB protected acceptor **13** failed, while disaccharide **19** effectively reacted with the 6-OH PCNB acceptor **15** giving **34** in 70% yield (Scheme 6).

Deprotection of PClB and PCNB Groups. Given the results found in this study some synthetic utility could be obtained in certain cases by fine-tuning donor reactivity as shown. PClB ethers have previously been used in rare cases but the PCNB group is not well-described. The PClB protecting group could be cleaved in a two-step process by first converting the Cl to OCH_3 in a palladium catalyzed reaction as described, followed by a standard PMB-deprotection step. Direct conversion by catalytic hydrogenolysis has been described previously for the PClB protecting group,[31] but not for the PCNB counterpart. To confirm previous results for the PClB removal and explore the possibility of catalytic hydrogenolysis as a means to remove the PCNB group, reactions were carried out on the menthyl glucosides **35** and **36**. Both were found smoothly to give the tetra-ol **37** under standard conditions (Scheme 7).

CONCLUSION

In conclusion, we have described the synthesis of several different glycosyl donors of the thioglycoside type bearing different benzyl ether protecting groups. For the preparation it was found that modern and commercially available palladium precatalysts and ligands efficiently preform the conversion of multiple PClB groups into either PMB or PCNB groups. This reaction can be expected to be generally applicable in organic synthesis.

Furthermore, it was found that the electron withdrawing power of the often used benzyl ether protecting group changes as a function of its aromatic *p*-substituent despite the absence of conjugative contact with the ether oxygen atom. This effect becomes measurable in NIS/TfOH promoted glycosylation reactions with tetra-*O*-benzylated thioglycoside donors where the order of reactivity follows the trend established by the Hammett constants (OCH_3 > H > Cl > CN). Remarkably, also donors having only one *p*-substituted (OCH_3, Cl or CN) benzyl ether on O-2, while having unmodified 3,4,6-tri-*O*-benzyl groups, were found to have a measurable change in reactivity. The reactivity tuning effects were in certain cases powerful enough to allow for chemoselective activation of the more reactive glycosyl donors over less reactive ones, which made it possible to synthesize a trisaccharide using the armed-disarmed approach.

Temperature is generally accepted as a parameter that influences the stereochemical outcome of a glycosylation reaction. As many others, we have in this study added the promoter (TfOH) at −78 °C where no color change is observed, and therefore, no reaction took place until the temperature was allowed to climb. Under these conditions we observed the slower reacting donors carrying PClB and PCNB protecting groups to give less of the major β-anomeric product than the more reactive Bn and PMB protected donors in reaction with good nucleophiles like L-menthol and primary alcohols. We demonstrated that no post glycosylation anomerization occurred and therefore concluded that the varying β-selectivity must be a consequence of the reaction temperature, which, in turn, depends on the reactivity of the donor.

EXPERIMENTAL SECTION

General Remarks. All reagents were used as purchased without further purification. Dry solvents were taken from a solvent purification system. Glassware used for water-free reactions were dried for 12 h at 120 °C before use. Columns were packed with silica gel 60 (230−400 mesh) as the stationary phase. TLC plates were visualized by 10% H_2SO_4 in EtOH and heating until spots appeared. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal. High-resolution mass spectral (HRMS) data were obtained on an electrospray (ES) mass spectrometer analyzing time-of-flight. NMR assignments were based on DEPT-135, COSY and HSQC NMR experiments.

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside. β-D-Glucose pentaacetate (10 g, 25.6 mmol, 1.0 equiv) was dissolved in anhydrous CH_2Cl_2 (50 mL). Thiophenol (5.3 mL, 51.2 mmol, 2.0 equiv) and $BF_3{\cdot}OEt_2$ (9.6 mL, 76.8 mmol, 3.0 equiv) were added at 0 °C. A color change from colorless to pink was observed after stirring for 18 h at rt. The reaction was quenched with sat. aq. $NaHCO_3$ until gas development ceased. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. Recrystallization of the resulting residue from Et_2O instantly yielded thioglycoside as white

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flocculent crystals. 10.9 g, 96%, R_f 0.68 (EtOAc/pentane 2:1) $[\alpha]_D^{RT}$ −20.4 (*c* 1.0, $CHCl_3$), lit. −19.2.[32] mp 118.5−119.0 °C, lit. 118 °C.[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.52−7.47 (m, 2H, Ar*H*), 7.37−7.27 (m, 3H, Ar*H*), 5.22 (t, *J* 9.3 Hz, 1H, H3), 5.04 (t, *J* 9.8 Hz, 1H, H4), 4.98 (dd, *J* 10.1, 9.2 Hz, 1H, H2), 4.71 (d, *J* 10.1 Hz, 1H, H1), 4.26−4.15 (m, 2H, $H6_a$, $H6_b$), 3.75−3.75 (m, 1H, H5), 2.09 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.99 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 170.7, 170.3, 169.5, 169.4 (C═O), 133.2, 131.8, 129.1, 128.6 (Ar), 85.9 (C1), 75.9 (C5), 74.1 (C3), 70.1 (C2), 68.3 (C4), 62.3 (C6), 20.9 (CH_3), 20.9 (CH_3), 20.8 (CH_3), 20.7 (CH_3). HRMS (ES): Calcd for $C_{20}H_{24}O_9SNa^+$ 463.1033; found 463.1034. Spectral values were in accordance with those reported in ref 32.

Phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (2). To a stirred solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (21.8 g, 49.7 mmol) in MeOH a catalytic amount of Na(s) was added until a pH-value of 10 was reached. The reaction mixture was stirred for 30 h at rt, then neutralized with DOWEX Acidic Cation Exchanger Resin in MeOH. The resin was filtered off by suction and the product mixture was concentrated in vacuo. The product (13 g) was dissolved in anhydrous DMF (60 mL) and cooled to 0 °C. NaH (60% (w/w) dispersion in mineral oil, 15.9 g, 397 mmol) was added and the solution became a slurry. BnBr (35.5 mL, 298 mmol) was then added dropwise to the suspension due to vigorous gas development. The resulting mixture was stirred for 24 h before the reaction mixture was cautiously transferred into a large volume of H_2O at 0 °C in which a minor amount of the crude product precipitated. The aqueous phase was extracted with DCM (2 × 300 mL), dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (pentane/EtOAc 4:1) to afford the product as white crystals. 19.9 g, 63%, R_f 0.66 (pentane/EtOAc 5:1). $[\alpha]_D^{RT}$ + 3.2 (*c* 1.0, $CHCl_3$). lit. 3.[34] mp: 91.5−92.5 °C. lit. 91−92 °C.[34] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.57−7.52 (m, 2H, Ar*H*), 7.37−7.14 (m, 23H, Ar*H*), 4.86 (d, *J* 10.9 Hz, 1H, C*H*HPh), 4.85 (d, *J* 10.2 Hz, 1H, C*H*HPh), 4.81 (d, *J* 10.8 Hz, 1H, CH*H*Ph), 4.79 (d, *J* 10.8 Hz, 1H, C*H*HPh), 4.69 (d, *J* 10.3 Hz, 1H, CH*H*Ph) 4.63 (d, *J* 9.8 Hz, 1H, H1), 4.57 (d, *J* 12.0 Hz, 1H, C*H*HPh), 4.55 (d, *J* 10.8 Hz, 1H, CH*H*Ph), 4.50 (d, *J* 12.0 Hz, 1H, CH*H*Ph) 3.75 (dd, *J* 9.8 Hz, 1H, H6a), 3.72−3.64 (m, 2H, H6b, H3/H4), 3.61 (t, *J* 9.2 Hz, 1H, H3/H4) 3.50−3.44 (m, 1H, H5), 3.47 (dd, *J* 9.5 Hz, 8.6 Hz, 1H, H2). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.4, 138.3, 138.0, 133.8, 132.0, 128.9, 128.5, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5 (Ar), 87.5 (C1), 86.8 (C3/C4), 80.6 (C2/C5), 79.1 (C2/C5), 77.8 (C3/C4), 75.9 (CH_2Ph), 75.5 (CH_2Ph), 75.1 (CH_2Ph), 73.5 (CH_2Ph), 69.0 (C6). HRMS (ES): Calcd for $C_{40}H_{40}O_5SNa^+$ 655.2494; found 655.2488. Spectral values were in accordance with those reported in ref 18.

Phenyl 2,3,4,6-tetra-*O*-(*p*-methoxybenzyl)-1-thio-β-D-glucopyranoside (3). To a stirred solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (2.7 g, 6.1 mmol, 1.0 equiv) in MeOH a catalytic amount of Na(s) was added until a pH-value of 10 was reached. After stirring for 4 h at rt the reaction mixture was neutralized with DOWEX Acidic Cation Exchanger Resin in MeOH. The resin was filtered off and the mixture was concentrated in vacuo. The crude deacetylated thioglycoside was dissolved in anhydrous DMF (50 mL) and NaH (60% w/w) dispersion in mineral oil, (1.22 g, 30.5 mmol) was added at 0 °C. *p*-Methoxybenzyl chloride (4.1 mL, 30.5 mmol) was added dropwise and the cloudy mixture was allowed to reach rt. After stirring for 3 1/2 h at rt the reaction mixture was heated to 100 °C and stirred for further 2 h to ensure completion. The yellow mixture was quenched by pouring it into H_2O (0 °C, 200 mL) upon which the crude product precipitated and was filtered off by suction. The filtrate was extracted with Et_2O (× 3) and the combined organic phases were washed with H_2O (× 5), dried over Na_2SO_4 and concentrated in vacuo leaving a white solid. Recrystallization of the combined crude products from Et_2O afforded the product as white flocculent crystals. 3.02 g, 66%, R_f 0.31 (pentane/EtOAc 1:1). $[\alpha]_D^{RT}$ + 9.6 (*c* 1.0, $CHCl_3$), lit. + 12.5.[35] mp: 121−123 °C, lit. 122.0−122.5 °C.[35] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.53−7.47 (m, 2H, Ar*H*), 7.25 (d, *J* 8.2 Hz, 2H, Ar*H*), 7.21−7.12 (m, 7H, Ar*H*), 7.02 (d, *J* 8.2 Hz, 2H, Ar*H*), 6.83−6.72 (m, 8H, Ar*H*), 4.79−4.68 (m, 1H, C*H*HAr), 4.76 (d, *J* 10.9 Hz, 1H, C*H*HAr), 4.71 (d, *J* 10.5 Hz, 1H, CH*H*Ar), 4.66 (d, *J* 10.5 Hz, 1H, C*H*HAr), 4.59 (d, *J* 10.4 Hz, 1H, CH*H*Ar), 4.56 (d, *J* 10.0 Hz, 1H, H1), 4.50−4.36 (m, 1H, CH*H*Ar), 4.47 (d, *J* 11.6 Hz, 1H, C*H*HAr), 4.39 (d, *J* 11.6, 8.9 Hz, 1H, CH*H*Ar), 3.75−3.70 (m, 12H, 4×OCH_3), 3.66 (d, *J* 10.2 Hz, 1H, H6a), 3.62−3.54 (m, 2H, H6b, H3/H4), 3.50 (t, *J* 9.3 Hz, 1H, H4/H3), 3.39 (t, *J* 9.3 Hz, 1H, H2), 3.39−3.35 (m, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.5, 159.4, 159.4, 159.3, 134.1, 132.0, 130.9, 130.5, 130.4, 130.4, 130.0, 129.7, 129.5, 129.5, 129.0, 127.5, 114.0, 114.0, 114.0, 113.9 (Ar), 87.6 (C1), 86.7 (C3/C4), 80.8 (C2), 79.3 (C5), 77.7 (C3/C4), 75.6 (CH_2Ar), 75.2 (CH_2Ar), 74.8 (CH_2Ar), 73.2 (CH_2Ar), 68.8 (C6), 55.4 (4×OCH_3). HRMS (ES): Calcd for $C_{44}H_{48}O_9SNH_4^+$ 770.3357; found 770.3361. Spectral values were in accordance with those reported in ref 35.

Phenyl 2,3,4,6-tetra-*O*-(*p*-chlorobenzyl)-1-thio-β-D-glucopyranoside (4). Phenyl 1-thio-β-D-glucopyranoside (0.1 g, 0.37 mmol) was dissolved in 2 mL of dry DMF. The solution was cooled to 0 °C and added NaH (60% in mineral oil, 0.12 g, 3.0 mmol), TBAI (0.27 g, 0.74 mmol) and *p*-chlorobenzyl chloride (0.48 g, 3.0 mmol). The mixture was allowed to reach rt. and stirred overnight, then quenched by adding a saturated aqueous solution of ammonium chloride. The mixture was diluted with EtOAc and washed five times with water, once with aqueous 10% $Na_2S_2O_3$ solution then brine. The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was recrystallized from CH_2Cl_2 and pentane. Yield: 181 mg, 64%. R_f: 0.52 (pentane/EtOAc 9:1). $[\alpha]_D^{RT}$ + 14.4 (*c* 1, $CHCl_3$). mp 138−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.56 (d, *J* 7.7 Hz, 2H, Ar*H*), 7.39−7.22 (m, 15H, Ar*H*), 7.15 (d, *J* 8.0 Hz, 2H, Ar*H*), 7.08 (d, *J* 7.9 Hz, 2H, Ar*H*), 4.87 (d, *J* 10.5 Hz, 1H, C*H*HAr), 4.80 (d, *J* 11.5 Hz, 1H, C*H*HAr), 4.75 (d, *J* 11.5 Hz, 1H, CH*H*Ar), 4.72 (d, *J* 11.5 Hz 1H, C*H*HAr), 4.66 (d, *J* 9.4 Hz, 1H, H1), 4.64 (d, *J* 10.5 Hz, 1H, CH*H*Ar), 4.59 (d, *J* 12.1 Hz, 1H, C*H*HAr), 4.54 (d, *J* 11.5 Hz, 1H, CH*H*Ar), 4.50 (d, *J* 12.1 Hz, 1H, CH*H*Ar), 3.76 (d, *J* 10.7 Hz, 1H, H6a), 3.70 (dd, *J* 10.7, 4.1 Hz, 1H, H6b), 3.68−3.58 (m, 2H, H3, H5), 3.52−3.44 (m, 2H, H2, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 136.8, 136.7, 136.5, 133.8, 133.8, 133.7, 133.6, 133.5, 131.9, 129.5, 129.1, 129.1, 129.1, 128.9, 128.7, 128.7, 128.7, 127.7 (Ar), 87.6 (C1), 86.7, 80.9, 79.1, 77.8, 75.0 (CH_2Ar), 74.7 (CH_2Ar), 74.2 (CH_2Ar), 72.8 (CH_2Ar), 68.9 (C6). HRMS (ES): calcd. for $C_{40}H_{36}{}^{35}Cl_3{}^{37}ClO_5SNH_4^+$ 788.1346; found 788.1387.

Phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (6). A solution of phenyl 1-thio-β-D-galactopyranoside (6.33 g, 23.2 mmol) in 60 mL of dry DMF was cooled to 0 °C and added NaH (60% (w/w) dispersion in mineral oil, 7.44 g, 186 mmol). BnBr (16.6 mL, 139 mmol) was added dropwise to the suspension due to vigorous gas development. The mixture was stirred overnight and quenched by methanol before diluted with Et_2O and washed five times with water then brine. The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The crude compound was crystallized from ethanol giving the product as white crystals. 11.3 g, 77%, R_f 0.8 (pentane/EtOAc 5:1). $[\alpha]_D^{RT}$ + 26 (*c* 1.0, $CHCl_3$). lit. + 1.[36] mp: 89−90 °C. lit. 88−89 °C.[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.59−7.54 (m, 2H, Ar*H*), 7.41−7.27 (m, 20H, Ar*H*), 7.21−7.15 (m, 3H, Ar*H*), 4.97 (d, *J* 11.5 Hz, 1H, C*H*HPh), 4.81−4.68 (m, 4H, CH_2Ph, H1), 4.64 (d, *J* 9.7 Hz, 1H, CH*H*Ph), 4.60 (d, *J* 11.5 Hz, 1H, CH*H*Ph), 4.47 (d, *J* 11.7 Hz, 1H, C*H*HPh), 4.42 (d, *J* 11.7 Hz, 1H, CH*H*Ph), 3.98 (d, *J* 2.5 Hz, 1H, H4), 3.93 (t, *J* 9.4 Hz, 1H, H2), 3.68−3.56 (m, 4H, H3, H5, H6). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.8, 138.4, 138.3, 137.9, 134.2, 131.6, 128.9, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.8, 127.6, 127.6, 127.1 (Ar), 87.8 (C1), 84.2, 77.4 (CH_2Ph), 75.7 (CH_2Ph), 74.5 (CH_2Ph), 73.6 (C4), 72.8 (CH_2Ph), 68.8 (C6). HRMS (ES): Calcd for $C_{40}H_{40}O_5SNH_4^+$ 650.2935; found 650.2943. Spectral values were in accordance with those reported in ref 37.

Phenyl 2,3,4,6-tetra-*O*-(*p*-methoxybenzyl)-1-thio-β-D-galactopyranoside (7). To a stirred solution of phenyl 1-thio-β-D-galactopyranoside (2.5 g, 9.2 mmol) in 50 mL of dry DMF was cooled to 0 °C and added NaH (60% (w/w) dispersion in mineral oil, 1.84 g, 46 mmol). *p*-Methoxybenzyl chloride (6.24 mL, 46 mmol) was added dropwise and the mixture was allowed to reach rt. After stirring for 3 h

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at rt. the reaction mixture was heated to 100 °C and stirred for further 1 h to ensure completion. The yellow mixture was cooled and the reaction was quenched by adding methanol. The mixture was diluted with EtOAc and washed five times with water then brine. The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified by flash column chromatography (pentane as eluent with a gradient of EtOAc) giving the product as a white solid. 6.51 g, 94%, R_f 0.3 (pentane/EtOAc 3:1). $[\alpha]_D^{RT}$ + 10.6 (*c* 1.0, $CHCl_3$), mp: 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.61−7.53 (m, 2H, Ar*H*), 7.36−7.29 (m, 3H, Ar*H*), 7.27−7.17 (m, 7H, Ar*H*), 6.95−6.82 (m, 8H, Ar*H*), 4.89 (d, *J* 11.2 Hz, 1H, C*H*HAr), 4.73 (d, *J* 9.8 Hz, 1H, C*H*HAr), 4.70−4.65 (m, 3H, Ar*H*), 4.63 (d, *J* 9.7 Hz, 1H, H1), 4.55 (d, *J* 11.2 Hz, 1H, CH*H*Ar), 4.42 (d, *J* 11.3 Hz, 1H, C*H*HAr), 4.35 (d, *J* 11.3 Hz, 1H, CH*H*Ar), 3.96−3.87 (m, 2H), 3.86−3.79 (m, 12H, CH_3), 3.64−3.52 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.4, 159.4, 159.3, 159.2, 134.5, 131.5, 131.1, 130.7, 130.6, 130.1, 129.7, 129.6, 129.3, 128.9, 127.1, 113.9, 113.9, 113.7, 113.7 (Ar), 88.0 (C1), 84.1, 77.2, 76.9, 75.4 (CH_2Ar), 74.1(CH_2Ar), 73.3(CH_2Ar), 73.2, 72.5 (CH_2Ar), 68.7 (C6), 55.4 (CH_3). HRMS (ES): Calcd for $C_{44}H_{48}O_9SNH_4^+$ 770.3357; found 770.3370.

Phenyl 3,4,6-tri-benzyl-2-*O*-(*p*-methoxybenzyl)-1-thio-β-D-glucopyranoside (9). Phenyl 3,4,6-tri-benzyl-1-thio-β-D-glucopyranoside[18] (0.50 g, 0.92 mmol) was dissolved in 10 mL of dry DMF. The solution were added NaH (0.060 g, 1.4 mmol), TBAI (0.50 g, 1.4 mmol) and *p*-methoxybenzyl chloride (0.19 mL, 1.4 mmol). The mixture was stirred overnight and quenched by addition of a saturated aqueous solution of ammonium chloride. The mixture was diluted with EtOAc and washed five times with water, once with aqueous 10% $Na_2S_2O_3$ solution then brine. The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The crude compound was purified by flash column chromatography with pentane as eluent with a gradient of EtOAc giving the product as a white solid. Yield: 451 mg, 74%. R_f: 0.3 (pentane/EtOAc 9:1). $[\alpha]_D^{RT}$ + 11.4 (*c* 1, $CHCl_3$). Lit. + 6.4 (c 1.29, $CHCl_3$).[38] mp 82.5−83.5 °C. Lit. 83−84 °C.[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.66−7.59 (m, 2H, Ar*H*), 7.44−7.18 (m, 20H, Ar*H*), 6.88 (d, *J* 7.9 Hz, 1H, Ar*H*), 4.95 (d, *J* 10.8 Hz, 1H, C*H*HAr), 4.92−4.81 (m, 2H), 4.74−4.66 (m, 2H), 4.66−4.54 (m, 3H), 3.83 (s, 3H, OCH_3), 3.79−3.63 (m, 3H), 3.54 (t, *J* 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 159.5, 138.6, 138.5, 138.2, 134.1, 132.0, 130.4, 130.0, 129.0, 128.6, 128.6, 128.5, 128.1, 127.9, 127.9, 127.8, 127.7, 127.5, 114.0, 87.7, 86.9, 80.7, 79.2, 78.0, 75.9, 75.2, 73.6, 69.2, 55.4. HRMS (ES): calcd. for $C_{41}H_{42}O_6SNH_4^+$ 680.3040; found 680.3053. Spectral values were in accordance with those reported in ref 38 and 39.

Phenyl 3,4,6-tri-benzyl-2-*O*-(*p*-chlorobenzyl)-1-thio-β-D-glucopyranoside (10). Phenyl 3,4,6-tri-benzyl-1-thio-β-D-glucopyranoside[18] (0.50 g, 0.92 mmol) was dissolved in 10 mL of dry DMF. The solution were added NaH in mineral oil (60%, 0.060 g, 1.4 mmol), TBAI (0.50 g, 1.4 mmol) and *p*-chlorobenzyl chloride (0.19 mL, 1.4 mmol). The mixture was heated to 100 °C for 30 min, cooled to rt and quenched by addition of a saturated aqueous solution of ammonium chloride. The mixture was diluted with EtOAc and washed five times with water, once with aqueous 10% $Na_2S_2O_3$ solution then brine. The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The crude compound was purified by flash column chromatography with pentane as eluent with a gradient of EtOAc giving the product as a white solid. Yield: 368 mg, 60%. R_f: 0.48 (pentane/EtOAc 9:1). $[\alpha]_D^{RT}$ + 10 (*c* 1, $CHCl_3$). mp 102−103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.68−7.57 (m, 2H, Ar*H*), 7.44−7.19 (m, 22H, Ar*H*), 4.93−4.83 (m, 4H, CH_2Ar), 4.76−4.54 (m, 5H, CH_2Ar, H1), 3.87−3.64 (m, 4H, H6), 3.60−3.48 (m, 2H, H2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 138.5, 138.4, 138.1, 136.7, 133.9, 133.7, 132.0, 129.6, 129.1, 128.7, 128.6, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6 (Ar), 87.5 (C1), 86.9, 80.9, 79.3, 78.0, 75.9 (OCH_2Ar), 75.2 (OCH_2Ar), 74.6(OCH_2Ar), 73.6(OCH_2Ar), 69.1 (C6). HRMS (ES): calcd. for $C_{40}H_{39}ClO_5SNH_4^+$ 684.2545; found 684.2552.

Phenyl 3,4,6-tri-benzyl-2-*O*-(*p*-cyanobenzyl)-1-thio-β-D-glucopyranoside (11). Phenyl 3,4,6-tri-benzyl-1-thio-β-D-glucopyranoside[18] (0.50 g, 0.92 mmol) was dissolved in 10 mL of dry CH_3CN. The solution were added NaH in mineral oil (60%, 0.060 g, 1.4 mmol) and *p*-cyanobenzyl chloride (0.15 g, 1.0 mmol). The mixture was stirred overnight and quenched by methanol. The mixture was diluted with EtOAc and washed four times with water then brine. The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The crude compound was purified by flash column chromatography with pentane as eluent with a gradient of EtOAc giving the product as a white plastic solid. Yield: 0.40 g, 66%. R_f: 0.48 (pentane/EtOAc 5:1). $[\alpha]_D^{RT}$ + 20 (*c* 1, $CHCl_3$). mp 101−103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.68−7.63 (m, 4H, Ar*H*), 7.51 (d, *J* 8.0 Hz, 2H, Ar*H*), 7.48−7.35 (m, 11H, Ar*H*), 7.35−7.27 (m, 7H, Ar*H*), 4.99 (d, *J* 11.1 Hz, 1H, C*H*HAr), 4.97 (d, *J* 11.9 Hz, 1H C*H*HAr), 4.92 (d, *J* 10.8 Hz, 1H, C*H*HAr), 4.87 (d, *J* 11.1 Hz, 1H, CH*H*Ar), 4.85 (d, *J* 11.9 Hz, 1H, CH*H*Ar), 4.77 (d, *J* 9.7 Hz, 1H, H1), 4.74−4.69 (m, 2H, CH_2Ar), 4.64 (d, *J* 12.0 Hz, 1H, CH*H*Ar), 3.90 (dd, *J* 10.9, 2.0 Hz, 1H, H6a), 3.84 (dd, *J* 10.7, 4.3 Hz, 1H, H6b), 3.82−3.75 (m, 2H), 3.65−3.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 143.5, 138.2, 138.2, 137.9, 133.5, 132.1, 131.8, 129.0, 128.5, 128.4, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.6 (Ar), 118.9 (*C*N), 111.3 (Ar), 87.2 (C1), 86.6, 80.9, 79.1, 77.8, 75.8 (CH_2Ar), 75.0 (CH_2Ar), 74.1(CH_2Ar), 73.4(CH_2Ar), 68.9 (C6). HRMS (ES): calcd. for $C_{41}H_{39}NO_5SNH_4^+$ 675.2887; found 675.2895.

Phenyl 2,3,4,6-tetra-*O*-(*p*-cyanobenzyl)-1-thio-β-D-glucopyranoside (12). To a 20 mL screw-top vial equipped with a magnetic stir bar was added *t*BuXPhos Pd G3(15.5 mg, 5 mol %), *t*BuXPhos(8.3 mg, 5 mol %), $K_4[Fe(CN)_6]\cdot 3H_2O$ (329 mg, 0.78 mmol), and phenyl 2,3,4,6-tetra-*O*-(*p*-chlorobenzyl)-1-thio-β-D-glucopyranoside (300 mg, 0.39 mmol). After sealing with a Teflon-lined screw-cap septum, the vessel was evacuated and backfilled with nitrogen (this process was repeated for a total of three cycles). Dioxane (3.9 mL) and 0.05 M KOAc in degassed water (3.9 mL) were then added to the reaction tube via syringe. The test tube was placed in an oil bath preheated to 100 °C and stirred for 1 h with maximum stirring (1500 rpm). After 1 h the reaction mixture was then cooled to room temperature and the contents of the test tube were transferred to a separatory funnel using EtOAc and brine. The aqueous layer was further extracted with EtOAc (total 2 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (pentane as eluent with a gradient of EtOAc) giving the product as a plastic solid. Yield: 204 mg, 71%. R_f: 0.38 (pentane/EtOAc 3:2). mp: 188−190 °C $[\alpha]_D^{RT}$ + 31 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57−7.41 (m, 10H, Ar*H*), 7.35 (d, *J* 8.3 Hz, 2H, Ar*H*), 7.31 (d, *J* 8.2 Hz, 2H, Ar*H*), 7.23−7.15 (m, 7H, Ar*H*), 4.89 (d, *J* 11.8 Hz, 1H, C*H*HAr), 4.77 (d, *J* 12.7 Hz, 1H), 4.71 (d, *J* 11.8 Hz, 2H, CH_2Ar), 4.63−4.55 (m, 4H, CH_2Ar, H1), 4.50 (d, *J* 13.1 Hz, 1H, CH*H*Ar), 3.75−3.66 (m, 2H, H6), 3.64−3.56 (m, 2H, H3, H4), 3.49−3.39 (m, 2H, H2, H5). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 143.6, 143.4, 143.2, 143.1, 133.3, 132.3, 132.3, 131.8, 129.2, 128.0, 127.7, 127.5, 127.4, 127.4, 118.8 (*C*N), 118.7 (*C*N), 118.6 (*C*N), 118.6 (*C*N), 111.7, 111.7, 111.7, 111.5 (Ar), 87.4 (C1), 86.7, 81.2 (C2), 78.9 (C5), 78.0, 74.5 (CH_2Ar), 74.3(CH_2Ar), 73.9-(CH_2Ar), 72.6(CH_2Ar), 69.3 (C6). HRMS (ES): Calcd for $C_{44}H_{36}N_4O_5SNH_4^+$ 750.2745; found 750.2750.

Phenyl 4,6-*O*-(*p*-chlorobenzylidene)-1-thio-β-D-glucopyranoside. Phenyl 1-thio-β-D-glucopyranoside (2.92 g, 10.7 mmol) was dissolved in 10 mL of dry DMF. The solution was added 4-chlorobenzaldehyde (4.52 g, 32.2 mmol) and *p*-TsOH (20 mg, 0.1 mmol). The solution was stirred on a rotary evaporator (60 °C, 30 mbar) for 3 h. The reaction mixture was then neutralized with trimethylamine and concentrated and coevaporated with toluene. The crude product was crystallized from CH_2Cl_2/pentane giving white crystals. Yield: 3.70 g, 87%. R_f: 0.50 (pentane/EtOAc 1:1). $[\alpha]_D^{RT}$ −38.8 (*c* 1, $CHCl_3$). mp 174−175 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52 (s, 2H, Ar*H*), 7.41 (d, *J* 7.9 Hz, 2H, Ar*H*), 7.33 (s, 5H, Ar*H*), 5.48 (s, 1H, C*H*Ar), 4.62 (d, *J* 9.7 Hz, 1H, H1), 4.40−4.31 (m, 1H, H6a), 3.82 (t, *J* 8.2 Hz, 1H), 3.75 (t, *J* 9.5 Hz, 1H, H6b), 3.56−3.37 (m, 3H, H2, H5), 3.03 (s, 2H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 135.5, 135.3, 133.1, 131.4, 129.3, 128.7, 128.6, 127.9 (Ar), 101.2 (CHAr), 88.7 (C1), 80.2, 74.6, 72.8, 70.5, 68.6 (C6). HRMS (ES): calcd. for $C_{19}H_{19}ClO_5SNH_4^+$ 412.0980; found 412.0984.

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Phenyl 2,3-di-*O*-(*p*-chlorobenzyl)-4,6-*O*-(*p*-chlorobenzylidene)-1-thio-β-D-glucopyranoside. Phenyl 4,6-*O*-(*p*-chlorobenzylidene)-1-thio-β-D-glucopyranoside (3.70g, 9.4 mmol) was dissolved in 20 mL of dry DMF. The solution were added TBAI (3.5 g, 9.4 mmol) and NaH in minearal oil (60%, 1.5 g, 37 mmol). The solution was stirred for 5 min before 4-chlorobenzyl chloride (6.0 g, 37 mmol) was added. The mixture was stirred overnight and quenched by addition of a saturated aqueous solution of ammonium chloride. The mixture was diluted with EtOAc and washed five times with water, once with aqueous 10% $Na_2S_2O_3$ solution then brine. The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was crystallized from CH_2Cl_2/pentane giving white crystals. Yield: 4.40 g, 73%. R_f: 0.38 (pentane/EtOAc 10:1). $[\alpha]_D^{RT}$ −1.8 (*c* 1, $CHCl_3$). mp 164−165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.55−7.48 (m, 2H, Ar*H*), 7.40−7.18 (m, 15H, Ar*H*), 5.53 (s, 1H, C*H*Ar), 4.84 (d, *J* 11.4 Hz, 2H, CH_2Ar), 4.78−4.65 (m, 1H, 3H, CH_2Ar, H1), 4.37 (dd, *J* 10.0, 4.5 Hz, 1H, H6a), 3.83−3.72 (m, 2H, H6b), 3.67 (t, *J* 9.3 Hz, 1H), 3.53−3.38 (m, 2H, H2, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 136.8, 136.5, 135.7, 135.1, 133.8, 133.7, 133.0, 132.4, 129.4, 129.4, 129.2, 128.7, 128.7, 128.6, 128.1, 127.6 (Ar), 100.6 (*C*HAr), 88.4 (C1), 83.0, 81.4, 80.6, 75.1 (CH_2Ar), 74.5(CH_2Ar), 70.2, 68.7 (C6). HRMS (ES): calcd. for $C_{33}H_{29}{}^{35}Cl_2{}^{37}ClO_5SH^+$ 645.0845; found 645.0870.

Phenyl 2,3,4-tri-*O*-(*p*-chlorobenzyl)-1-thio-β-D-glucopyranoside (13). Phenyl 2,3,-di-*O*-(*p*-chlorobenzyl)-4,6-*O*-(*p*-chlorobenzylidene)-1-thio-β-D-glucopyranoside (310 mg, 0.48 mmol) was dissolved in BH_3·THF (1 M, 5.0 mL) at 0 °C. The mixture was stirred for 5 min and then added Bu_2BOTf (0.5 mL 1 M in DCM). The reactions was stirred for 90 min and then added Et_3N (0.5 mL) followed by addition of methanol. The reaction mixture was codistilled with methanol 3 times and then purified by flash column chromatography with pentane as eluent with a gradient of EtOAc giving the product as a white solid. Yield: 261 mg, 89%. R_f: 0.49 (pentane/EtOAc 3:1). $[\alpha]_D^{RT}$ + 18.2 (*c* 1, $CHCl_3$). mp 146−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.56−7.51 (m, 2H, Ar*H*), 7.37−7.27 (m, 11H, Ar*H*), 7.22−7.13 (m, 4H, Ar*H*), 4.89 (d, *J* 10.7 Hz, 1H, C*H*HAr), 4.82 (d, *J* 11.4 Hz, 1H, C*H*HAr), 4.78 (d, *J* 11.4 Hz, 1H, CH*H*Ar), 4.76 (d, *J* 11.1 Hz, 1H, C*H*HAr), 4.73 (d, *J* 9.6 Hz, 1H, H1), 4.67 (d, *J* 10.7 Hz, 1H, CH*H*Ar), 4.65 (d, *J* 11.1 Hz, 1H, CH*H*Ar), 3.92 (dd, *J* 12.2, 2.4 Hz, 1H, H6a), 3.73 (dd, *J* 12.2, 4.5 Hz, 1H, H6b), 3.68 (t, *J* 8.9 Hz, 1H, H3), 3.60 (t, *J* 9.3 Hz, 1H, H4), 3.46 (dd, *J* 9.6, 8.9 Hz, 1H, H2), 3.40 (ddd, *J* 9.5, 4.5, 2.4 Hz, 1H, H5), 2.23 (s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 136.8, 136.4, 133.7, 133.7, 133.5, 133.5, 131.7, 129.4, 129.2, 129.1, 128.8, 128.7, 128.7, 128.6, 127.8 (Ar), 87.6 (C1), 86.3 (C3), 81.1 (C2), 79.4 (C5), 77.5 (C4), 74.8 (CH_2Ar), 74.7(CH_2Ar), 74.2-(CH_2Ar), 61.9 (C6). HRMS (ES): calcd. for $C_{33}H_{31}{}^{35}Cl_2{}^{37}ClO_5SNH_4^+$ 664.1267; found 664.1286.

Phenyl 2,3,6-tri-*O*-(*p*-chlorobenzyl)-1-thio-β-D-glucopyranoside (14). Phenyl 2,3,-di-*O*-(*p*-chlorobenzyl)-4,6-*O*-(*p*-chlorobenzylidene)-1-thio-β-D-glucopyranoside (322 mg, 0.5 mmol) was dissolved in 5 mL CH_2Cl_2 and the solution was cooled to −78 °C. The mixture were added triethylsilane (0.24 mL, 1.5 mmol) and triflic acid (0.24 mL 1.5 mmol). The reaction was stirred for 5 h at −78 °C, and then quenched with Et_3N (0.21 mL, 1.5 mmol). The volatiles were removed by evaporation and the remaining crude material purified by flash column chromatography with pentane as eluent with a gradient of EtOAc giving the product as a white solid. Yield: 289 mg, 89%. R_f: 0.28 (pentane/EtOAc 3:1). $[\alpha]_D^{RT}$ −1.2 (*c* 1, $CHCl_3$). mp 93−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57 (s, 2H, Ar*H*), 7.40−7.21 (m, 15H, Ar*H*), 4.91 (d, *J* 10.7 Hz, 1H, C*H*HAr), 4.85 (d, *J* 11.7 Hz, 1H, C*H*HAr), 4.80 (d, *J* 11.7 Hz, 1H, CH*H*Ar), 4.72 (d, *J* 10 Hz, 1H, H1), 4.67 (d, *J* 10.7 Hz, 1H, CH*H*Ar), 4.58 (t, *J* 14.8 Hz, 2H, CH_2Ph), 3.80 (s, 2H, H6), 3.71 (t, *J* 8.9 Hz, 1H), 3.58−3.43 (m, 3H), 2.71 (s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 136.9, 136.5, 136.4, 133.7, 133.7, 133.7, 133.6, 131.8, 129.4, 129.1, 129.1, 129.0, 128.8, 128.7, 128.6, 127.7 (Ar), 87.7 (C1), 86.2, 80.5, 78.1, 74.6 (CH_2Ar), 74.5 (CH_2Ar), 72.9 (CH_2Ar), 71.8, 70.4 (C6). HRMS (ES): calcd. for $C_{33}H_{31}{}^{35}Cl_2{}^{37}ClO_5SNH_4^+$ 664.1267; found 664.1279.

Phenyl 2,3,4-tri-*O*-(*p*-cyanobenzyl)-1-thio-β-D-glucopyranoside (15). To a 8 mL screw-top vial equipped with a magnetic stir bar was added *t*BuXPhos Pd G3 (18 mg, 5 mol %), *t*BuXPhos (9.6 mg, 5 mol %), $K_4[Fe(CN)_6]\cdot 3H_2O$ (288 mg, 0.7 mmol) and phenyl 2,3,4,-tri-*O*-(*p*-chlorobenzyl)-1-thio-β-D-glucopyranoside (300 mg, 0.47 mmol). After sealing with a Teflon-lined screw-cap septum, the vessel was evacuated and backfilled with nitrogen (this process was repeated for a total of three cycles). Dioxane (3 mL), and 0.05 M KOAc in degassed water (3 mL) were then added to the reaction tube via syringe. The test tube was placed in an oil bath preheated to 100 °C and stirred for 1 h with maximum stirring (1500 rpm). After 1 h of stirring at 100 °C, the reaction mixture was then cooled to room temperature. The contents of the test tube were transferred to a separatory funnel using EtOAc and brine, and the organic layer was separated from the aqueous layer. The aqueous layer was further extracted with EtOAc (2 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (pentane as eluent with a gradient of EtOAc) giving the product as a plastic solid. Yield: 243 mg, 84%. R_f: 0.25 (pentane/EtOAc 3:2). $[\alpha]_D^{RT}$ + 26.8 (*c* 1, $CHCl_3$). mp 126−128 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63−7.54 (m, 6H, Ar*H*), 7.53−7.47 (m, 2H, Ar*H*), 7.40 (d, *J* 8.2 Hz, 2H, Ar*H*), 7.36−7.26 (m, 7H, Ar*H*), 4.98 (d, *J* 11.9 Hz, 1H, C*H*HAr), 4.86 (d, *J* 12.8 Hz, 1H, C*H*HAr), 4.84−4.77 (m, 3H), 4.74 (d, *J* 9.8 Hz, 1H, H1), 4.71 (d, *J* 12.1 Hz, 1H, CH*H*Ar), 3.95 (dd, 1H, H6a), 3.81−3.65 (m, 3H), 3.53−3.41 (m, 2H), 2.20 (t, *J* 6.8 Hz, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 143.5, 143.2, 143.1, 133.1, 132.3, 132.3, 132.2, 131.7, 129.3, 128.9, 128.0, 127.9, 127.6, 127.3 (Ar), 118.7 (*C*N), 118.6 (*C*N), 118.6 (*C*N), 111.6, 111.6, 111.6 (Ar), 87.5 (C1), 86.5, 81.3, 79.3, 77.6, 74.4 (CH_2Ar), 74.3 (CH_2Ar), 73.8(CH_2Ar), 61.6 (C6). HRMS (ES): calcd. for $C_{36}H_{31}N_3O_5SNH_4^+$ 635.2323; found 635.2321.

Phenyl 2,3,6-tri-*O*-(*p*-cyanobenzyl)-1-thio-β-D-glucopyranoside (16). To a 8 mL screw-top vial equipped with a magnetic stir bar was added *t*BuXPhos Pd G3 (8 mg, 5 mol %), *t*BuXPhos (4.5 mg, 5 mol %), $K_4[Fe(CN)_6]\cdot 3H_2O$ (130 mg, 0.31 mmol), and phenyl 2,3,6,-tri-*O*-(*p*-chlorobenzyl)-1-thio-β-D-glucopyranoside (133 mg, 0.21 mmol). After sealing with a Teflon-lined screw-cap septum, the vessel was evacuated and backfilled with nitrogen (this process was repeated for a total of three cycles). Dioxane (1.3 mL), and 0.05 M KOAc in degassed water (1.3 mL) were then added to the reaction tube via syringe. The test tube was placed in an oil bath preheated to 100 °C and stirred for 1 h with maximum stirring (1500 rpm). After 1 h of stirring at 100 °C, the reaction mixture was then cooled to room temperature. The contents of the test tube were transferred to a separatory funnel using EtOAc and brine, and the organic layer was separated from the aqueous layer. The aqueous layer was further extracted with EtOAc (2 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (pentane as eluent with a gradient of EtOAc) giving the product as a white solid. Yield: 109 mg, 85%. R_f: 0.2 (pentane/EtOAc 2:1). $[\alpha]_D^{RT}$ + 30 (*c* 1, $CHCl_3$). mp 135−136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.58−7.45 (m, 6H, Ar*H*), 7.44−7.39 (m, 2H, Ar*H*), 7.37−7.28 (m, 6H, Ar*H*), 7.23−7.12 (m, 3H, Ar*H*), 4.88 (d, *J* 11.9 Hz, 1H, C*H*HAr), 4.85 (d, *J* 12.4 Hz, 1H, C*H*HAr), 4.79 (d, *J* 12.7 Hz, 1H, CH*H*Ar), 4.64 (d, *J* 12.0 Hz, 1H, CH*H*Ar), 4.63 (d, *J* 9.6 Hz, 1H, H1), 4.59 (d, *J* 13.1 Hz, 1H, C*H*HAr), 4.54 (d, *J* 13.1 Hz, 1H, CH*H*Ar), 3.78 (dd, *J* 10.6, 3.6 Hz, 1H, H6a), 3.73 (dd, *J* 10.6, 5.0 Hz, 1H, H6b), 3.66 (dt, *J* 9.3, 1.4 Hz, 1H, H4), 3.52−3.43 (m, 2H, H3, H5), 3.39 (t, *J* 9.2 Hz, 1H, H2), 2.83 (d, *J* 2.8 Hz, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 143.9, 143.6, 143.3, 133.4, 132.3, 132.2, 131.6, 129.1, 128.0, 127.8, 127.7, 127.7 (Ar), 118.8 (*C*N), 118.7 (*C*N), 118.7 (*C*N), 111.5, 111.4, 111.4 (Ar), 87.5 (C1), 86.5, 80.8 (C2), 78.3, 74.4 (CH_2Ar), 74.2(CH_2Ar), 72.6 (CH_2Ar), 71.5 (C4), 70.6 (C6). HRMS (ES): calcd. for $C_{36}H_{31}N_3O_5SNH_4^+$ 635.2323; found 635.2324.

General Procedure for Glycosylations (Table 1, 3 and 4). A mixture of glycosyl donor (0.10 mmol), glycosyl acceptor (0.15 mmol), and freshly activated molecular sieves (3 Å, 100 mg) in CH_2Cl_2 (2 mL) was stirred under argon for 1 h. The solution was cooled to −78 °C using a dry ice/acetone bath. NIS (0.11 or 0.2 mmol) and TfOH (0.1 mL of a 0.1 M solution of TfOH in CH_2Cl_2) were added. Lumps of dry ice were removed from the acetone bath

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and the reaction was slowly allowed to reach 0 °C (approximately 3 h). Upon completion, the solids were filtered off and the filtrate was washed with aqueous 10% $Na_2S_2O_3$ solution. The organic layer was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the corresponding glycoside. Anomeric ratios were measured by comparison of integral intensities of the anomeric protons and anomeric carbons from ^{1}H NMR and ^{13}C NMR spectra of crude reaction mixtures.

Competition Experiments (Table 2). The two glycosyl donors (0.10 mmol each) were dissolved in $CDCl_3$ (1 mL) and the ratios of donors were checked to be 1:1 by ^{1}H NMR and ^{13}C NMR. The solvent was evaporated and dry CH_2Cl_2 (2 mL), L-menthol (0.5 mmol) and freshly activated molecular sieves (3 Å, 100 mg) were added. The mixture was stirred under argon for 1 h. The solution was cooled to −78 °C and NIS (0.10 mmol) and TfOH (0.1 mL of a 0.1 M solution of TfOH in CH_2Cl_2) were added. Lumps of dry ice were removed from the acetone bath and the reaction was slowly allowed to reach 0 °C (approximately 3 h). Upon completion, the solids were filtered off and the filtrate was washed with aqueous 10% $Na_2S_2O_3$ solution. The organic layer was separated, dried over $MgSO_4$, and concentrated in vacuo. The crude mixture was dissolved in $CDCl_3$ (1 mL) and ^{1}H NMR and ^{13}C NMR was measured. Anomeric ratios were measured by comparison of integral intensities of the anomeric protons and anomeric carbons from ^{1}H NMR and ^{13}C NMR spectra of crude reaction mixtures.

Experimental Description for Table 4, Entry 1. A mixture of phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-*β*-D-glucopyranoside (**2**), (63 mg, 0.10 mmol), 1,2;3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (**24**), (39 mg, 0.15 mmol), L-menthyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranoside (**28**), (68 mg, 0.10 mmol) and freshly activated molecular sieves (3 Å, 100 mg) in CH_2Cl_2 (2 mL) were stirred under argon for 1 h. The solution was cooled to −78 °C using a dry ice/acetone bath. NIS (25 mg, 0.11 mmol) and TfOH (0.1 mL of a 0.1 M solution of TfOH in CH_2Cl_2) were added. Lumps of dry ice were removed from the acetone bath and the reaction was slowly allowed to reach 0 °C (approximately 3 h). Upon completion, the solids were filtered off and the filtrate was washed with aqueous 10% $Na_2S_2O_3$ solution. The organic layer was separated, dried over $MgSO_4$, and concentrated in vacuo. L-Menthyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranoside (**28**) was reisolated from the product mixture by flash column chromatography as the pure *β*-anomer (65 mg, 97%).

Chemoselective Activation of Thioglycosides (Armed/Disarmed Glycosylations, Table 5). A mixture of glycosyl donor (0.10 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 100 mg) in CH_2Cl_2 (2 mL) was stirred under argon for 1 h. The solution was cooled to −78 °C using a dry ice/acetone bath. NIS (0.10 mmol) and TfOH (0.1 mL of a 0.1 M solution of TfOH in CH_2Cl_2) were added. Lumps of dry ice were removed from the acetone bath and the reaction was slowly allowed to reach 0 °C (approximately 3 h). Upon completion, the solids were filtered off and the filtrate was washed with aqueous 10% $Na_2S_2O_3$ solution. The organic layer was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the corresponding glycoside. Anomeric ratios were measured by comparison of integral intensities of the anomeric protons and anomeric carbons from ^{1}H NMR and ^{13}C NMR spectra of crude reaction mixtures.

L-Menthyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranoside (28). White crystals. R_f 0.47 (pentane/EtOAc, 5:1). $[\alpha]_D^{RT}$ −16 (*c* 1.0, $CHCl_3$), lit. −17.2 (*c* 1.05, $CHCl_3$).[40] mp: 76.5−78.8 °C. Lit. 82−83 °C.[40] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.33−7.20 (m, 18H, Ar*H*) 7.17- 7.3 (m, 2H, Ar*H*), 4.90 (t, *J* 10.7 Hz, 2H, CH_2Ph), 4.80−4.72 (t, 2H, CH_2Ph), 4.65 (d, *J* 10.9 Hz, 1H, C*H*HPh), 4.60−4.48 (m, 3H, CH_2Ph), 4.44 (d, *J* 7.7 Hz, 1H, H1), 3.65 (d, *J* 3.1 Hz, 2H, H6a), 3.65−3.51 (m, 2H), 3.46 (td, *J* 10.7, 4.2 Hz, 1H, OC*H*), 3.40−3.34 (m, 2H, H2, H5), 2.38−2.25 (m, 1H), 2.10 (d, *J* 12.6 Hz, 1H), 1.62 (d, *J* 9.5 Hz, 2H), 1.38−1.15 (m, 4H), 1.03−0.83 (m, 10H), 0.78 (d, *J* 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.9, 138.7, 138.5, 138.3, 133.8, 130.3, 128.6, 128.5, 128.4, 128.2, 127.9, 127.9, 127.8, 127.8, 127.6, 127.6 (Ar), 100.9 (C1), 85.1, 82.3 (C2), 78.1, 77.9, 77.4, 75.7 (CH_2Ph), 75.1 (CH_2Ph), 75.0 (CH_2Ph), 74.9 (C5), 73.8 (CH_2Ph), 69.4 (C6), 48.2, 41.1 (CH_2), 34.6 (CH_2), 31.6, 25.4, 23.3 (CH_2), 22.4, 21.2 (CH_3), 16.1 (CH_3). HRMS (ES): Calcd for $C_{44}H_{54}O_6NH_4^+$ 696.4259; found 696.4266. Spectral values were in accordance with those reported in ref 41.

L-Menthyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranoside. Colorless syrup. R_f 0.38 (pentane/EtOAc 5:1). $[\alpha]_D^{RT}$ + 31 (*c* 1.0, $CHCl_3$), lit. + 31.3 (*c* 1.1, $CHCl_3$).[41] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.35−7.26 (m, 18H, Ar*H*), 7.16−7.11 (m, 2H, Ar*H*), 5.06−4.94 (m, 2H, H1, C*H*HPh), 4.88−4.76 (m, 2H, CH_2Ph), 4.76−4.61 (m, 3H, CH_2Ph), 4.52−4.41 (m, 2H, CH_2Ph), 4.11−3.92 (m, 2H, H6a), 3.80−3.72 (m, 1H), 3.70−3.60 (m, 2H), 3.59−3.51 (m, 1H, H2), 3.41−3.30 (m, 1H), 2.48−2.36 (m, 1H), 2.13 (d, *J* 12.0 Hz, 1H), 1.62 (d, *J* 13.2 Hz, 2H), 1.41−1.19 (m, 4H), 1.10−0.77 (m, 10H), 0.71 (d, *J* 6.9 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.9, 138.4, 138.3, 138.0, 128.4, 128.4, 128.3, 128.3, 127.9, 127.9, 127.7, 127.7, 127.5, 127.5 (Ar), 98.6 (C1), 82.0, 81.0, 80.5, 78.1, 77.2, 75.5 (CH_2Ph), 75.1 (CH_2Ph), 73.5 (CH_2Ph), 73.2 (CH_2Ph), 70.3, 68.6(C6), 48.8, 43.1, 34.3, 31.7, 24.6, 22.9, 22.3, 21.1 (CH_3), 16.1 (CH_3). HRMS (ES): Calcd for $C_{44}H_{54}O_6NH_4^+$ 696.4259; found 696.4273.Spectral values were in accordance with those reported in ref 41.

L-Menthyl 2,3,4,6-tetra-*O*-(*p*-methoxybenzyl)-*β*-D-glucopyranoside. White solid. R_f 0.47 (pentane/EtOAc 5:1). $[\alpha]_D^{RT}$ −18 (*c* 1.0, $CHCl_3$). mp: 116.5−117.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.33−7.22 (m, 6H, Ar*H*), 7.11 (d, *J* 8.2 Hz, 2H, Ar*H*), 6.90−6.80 (m, 8H, Ar*H*), 4.92−4.83 (m, 2H, C*H*HAr), 4.73 (dd, *J* 10.7, 2.4 Hz, 2H, C*H*HAr), 4.64 (d, *J* 10.6 Hz, 1H, CH*H*Ar), 4.55 (d, *J* 11.8 Hz, 1H, CH*H*Ar), 4.51−4.47 (m, 2H, C*H*HAr), 4.45 (d, *J* 7.3 Hz, 1H, H1), 3.83−3.79 (m, 12H, OCH_3), 3.68−3.61 (m, 2H, H6a), 3.58 (d, *J* 8.9 Hz, 1H, H6b), 3.62−3.47 (m, 2H, OC*H*), 3.41−3.35 (m, 1H, H5) 3.38 (t, *J* 8.2 Hz, 1H, H2), 2.37 (dsep, *J* 7.0, 2.4 Hz, 1H, C*H*(CH_3)$_2$), 2.16 (d, *J* 12.7 Hz, 1H), 1.68 (d, *J* 13.2 Hz, 1H), 1.43−1.33 (m, 1H), 1.34−1.22 (m, 1H), 1.09−0.96 (m, 2H), 0.94 (dd, *J* 6.8, 2.6 Hz, 6H, CH(CH_3)$_2$), 0.84 (d, *J* 6.8 Hz, 3H, CHCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.4, 159.3, 159.3, 159.2, 131.3, 131.0, 130.6, 130.6, 130.1, 129.8, 129.5, 129.4, 113.9, 113.9, 113.8 (Ar), 101.0 (C1), 84.9, 82.1 (C2), 77.9, 75.4 (CH_2Ar), 74.9 (C5), 74.7 (CH_2Ar), 74.6 (CH_2Ar), 73.4 (CH_2Ar), 69.2 (C6), 55.4 (OCH_3), 48.3, 41.2 (CH_2), 34.6 (CH_2), 31.6, 25.4 (CH(CH_3)$_2$), 23.3(CH_2), 22.4 (CH_3CHCH_3), 21.2 (CH_3CHCH_3), 16.1 (CH_3). HRMS (ES) Calcd for $C_{48}H_{62}O_{10}NH_4^+$ 816.4681; found 816.4697.

L-Menthyl 2,3,4,6-tetra-*O*-(*p*-methoxybenzyl)-*α*/*β*-D-glucopyranoside. Colorless oil. R_f(*α*) 0.53 (pentane/EtOAc 5:1). R_f(*β*) 0.47 (pentane/EtOAc 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.31−7.20 (m, 12H, Ar*H*), 7.09 (d, *J* 8.1 Hz, 2H, Ar*H*, *β*), 7.02 (d, *J* 8.1 Hz, 2H, Ar*H*, *α*), 6.89−6.75 (m, 16H, Ar*H*), 4.96 (d, *J* 3.6 Hz, 1H, H1*α*), 4.88 (d, *J* 10.6 Hz, 1H, C*H*HAr, *α*), 4.85 (t, *J* 11.2 Hz, 2H, C*H*HAr, *β*), 4.74 (d, *J* 10.6 Hz, 4H, C*H*HAr), 4.71−4.68 (m, 1H, C*H*HAr, *β*), 4.65−4.60 (m, 4H, C*H*HAr), 4.58 (s, 2H, C*H*HAr), 4.54 (d, *J* 11.9 Hz, 1H, C*H*HAr, *β*), 4.47 (t, *J* 5.2 Hz, 1H, C*H*HAr, *β*), 4.43 (d, *J* 7.7 Hz, 1H, H1*β*), 4.39 (d, *J* 11.9 Hz, 1H, C*H*HAr, *α*), 4.33 (d, *J* 10.3 Hz, 1H, C*H*HAr, *α*), 3.99−3.83 (m, 2H, H3*α*, H5*α*), 3.82−3.75 (m, 24H, OCH_3), 3.70 (dd, *J* 10.5, 3.6 Hz, 1H, H6a*α*), 3.65−3.61 (m, 1H, H6a*β*) 3.64−3.52 (m, 4H, H4*α*, H6b*α*, H3*β*, H4*β* H6b*β*), 3.49 (dd, *J* 9.8, 4.0 Hz, 2H, H2*α*, OC*H*β), 3.39−3.29 (m, 3H, OC*H*α, H2*β*, H5*β*), 2.46−2.29 (m, 3H), 2.18−2.05 (m, 4H), 1.70−1.55 (m, 10H), 1.41−1.20 (m, 9H), 0.92 (d, *J* 5.1 Hz, 6H, CH(CH_3)$_2$), *β*), 1.08−0.76 (m, 4H), 0.86 (t, *J* 6.4 Hz, 6H, CH(CH_3)$_2$), *α*), 0.82 (d, *J* 6.9 Hz, 3H, CHCH_3, *β*), 0.72 (d, *J* 6.8 Hz, 3H, CHCH_3, *α*). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.2, 159.2, 159.2, 159.2, 159.1, 159.1, 159.1, 159.1, 131.3, 131.3, 130.7, 130.6, 130.2, 130.0, 129.7, 129.6, 129.6, 129.5, 129.5, 129.4, 129.3, 129.3, 113.8, 113.7, 113.7 (Ar), 100.8 (C1*β*), 98.6 (C1*α*), 84.8, 82.0, 81.7 (C3*α*), 80.7 (C2*β*), 80.7 (OCH, *α*), 80.3 (C2*α*), 77.8, 77.7, 77.2, 75.2 (CH_2Ar, *β*), 75.1 (CH_2Ar, *α*), 74.8 (C5*β*), 74.6 (CH_2Ar, *α*), 74.6 (CH_2Ar, *β*), 74.5 (CH_2Ar, *β*), 73.3 (CH_2Ar, *β*), 73.0 (CH_2Ar, *α*), 72.9 (CH_2Ar, *α*), 70.3 (C5*α*), 69.1 (C6*β*), 68.1 (C6*α*), 55.3 (OCH_3, *α*), 55.2 (OCH_3, *β*), 48.8, 48.2, 43.0 (CH_2, *α*), 41.1 (CH_2, *β*), 34.5 (CH_2, *β*), 34.3 (CH_2, *α*), 31.74, 31.5, 25.3, 23.2(CH_2, *β*), 23.0 (CH_2, *α*), 22.3 (CH_3CHCH_3, *α*), 22.3 (CH_3CHCH_3, *β*), 21.2

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(CH_3CHCH_3, α), 21.1 (CH_3CHCH_3, β), 16.1 (CH_3, α), 15.9 (CH_3, β). HRMS (ES): Calcd for $C_{48}H_{62}O_{10}NH_4^+$ 816.4681; found 816.4694.

L-Menthyl 2,3,4,6-tetra-*O*-(*p*-chlorobenzyl)-β-D-glucopyranoside (35). White solid, R_f: 0.60 (pentane/EtOAc 9:1), $[\alpha]_D^{RT}$ −18.6 (*c* 1, $CHCl_3$). mp 155−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.35−7.23 (m, 12H, Ar*H*), 7.16 (d, *J* 8.0 Hz, 2H, Ar*H*), 7.09 (d, *J* 8.0 Hz, 2H, Ar*H*), 4.91 (d, *J* 11.3 Hz, 1H, C*H*HAr), 4.83 (d, *J* 11.5 Hz, 1H, C*H*HAr), 4.74−4.68 (m, 2H, CH_2Ar), 4.63 (d, *J* 11.4 Hz, 1H, CH*H*Ar), 4.62−4.50 (m, 3H, CH_2Ar, CH*H*Ph), 4.47 (d, *J* 8.4 Hz, 1H, H1), 3.74−3.63 (m, 2H, H6), 3.61−3.55 (m, 2H, H3, H4), 3.50 (td, *J* 10.7, 3.3 Hz, 1H), 3.44−3.34 (m, 2H, H2, H5), 2.38−2.29 (m, 1H), 2.13 (d, *J* 12.0 Hz, 1H), 1.69 (d, *J* 11.4 Hz, 2H), 1.49−1.22 (m, 3H), 1.09−0.76 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 137.2, 137.1, 136.9, 136.7, 133.7, 133.6, 133.5, 133.4, 129.6, 129.2, 129.1, 128.9, 128.7, 128.7, 128.6, 128.6 (Ar), 100.7 (C1), 84.8, 82.1, 77.9, 77.9, 74.8, 74.7 (CH_2Ar), 74.2 (CH_2Ar), 73.9 (CH_2Ar), 73.1 (CH_2Ar), 69.3 (C6), 48.2, 41.0, 34.5, 31.6, 25.4, 23.3, 22.4, 21.2, 16.1. HRMS (ES): calcd. for $C_{44}H_{50}{}^{35}Cl_3{}^{37}ClO_6NH_4^+$ 834.2670; found 834.2690.

L-Menthyl 2,3,4,6-tetra-*O*-(*p*-chlorobenzyl)-α-D-glucopyranoside. Clear Syrup, R_f: 0.23 (pentane/EtOAc 9:1), $[\alpha]_D^{RT}$ + 30 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.28−7.11 (m, 12H, Ar*H*), 7.08 (d, *J* 8.0 Hz, 2H, Ar*H*), 6.93 (d, *J* 8.0 Hz, 1H, Ar*H*), 4.95 (d, *J* 2.2 Hz, 1H, H1), 4.79 (d, *J* 11.4 Hz, 1H, C*H*HAr), 4.63 (d, *J* 11.2 Hz, 2H, CH_2Ar), 4.58−4.48 (m, 3H, CH_2Ph), 4.35−4.28 (m, 2H, CH_2Ph), 3.92−3.81 (m, 2H, H3, H5), 3.63 (d, *J* 9.0 Hz, 1H, H6a), 3.52 (d, *J* 9.0 Hz, 1H, H6b), 3.47 (d, *J* 9.5 Hz, 1H, H4), 3.41 (dd, *J* 9.6, 2.2 Hz, 1H, H2), 3.26 (td, *J* 10.5, 3.7 Hz, 1H) 2.29 (p, *J* 6.5 Hz, 1H), 2.04 (d, *J* 11.9 Hz, 1H), 1.62−1.51 (m, 2H), 1.29 (br s, 1H), 1.26−1.16 (m, 1H), 1.02−0.84 (m, 2H), 0.83−0.71 (m, 7H), 0.62 (d, *J* 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 137.3, 136.8, 136.7, 136.5, 133.7, 133.6, 133.5, 133.4, 129.3, 129.1, 128.9, 128.9, 128.7, 128.7, 128.6, 128.6 (Ar), 98.6 (C1), 81.8 (C3), 81.6, 80.7 (C2), 78.1 (C4), 74.6 (CH_2Ar), 74.2 (CH_2Ar), 72.8 (CH_2Ar), 72.3 (CH_2Ar), 70.3 (C5), 68.7 (C6), 48.8, 43.2, 34.3, 31.8, 24.8, 23.1, 22.4, 21.2, 16.2. HRMS (ES): calcd. for $C_{44}H_{50}{}^{35}Cl_3{}^{37}ClO_6NH_4^+$ 834.2670; found 834.2685.

L-Menthyl 2,3,4,6-tetra-*O*-(*p*-cyanobenzyl)-β-D-glucopyranoside (36). Clear syrup, R_f: 0.75 (pentane/EtOAc 3:2), $[\alpha]_D^{RT}$ −7.2 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.56 (d, *J* 8.2 Hz, 2H, Ar*H*), 7.53−7.45 (m, 6H, Ar*H*), 7.34 (d, *J* 8.1 Hz, 2H, Ar*H*), 7.30 (d, *J* 8.0 Hz, 2H, Ar*H*), 7.24−7.18 (m, 4H, Ar*H*), 4.93 (d, *J* 12.5 Hz, 1H, C*H*HAr), 4.82 (d, *J* 12.8 Hz, 1H, C*H*HAr), 4.73 (d, *J* 12.5 Hz, 1H, C*H*HAr), 4.68 (d, *J* 12.8 Hz, 1H, CH*H*Ar), 4.64−4.57 (m, 3H, CH_2Ar), 4.52 (d, *J* 13.2 Hz, 1H, CH*H*Ar), 4.43 (d, *J* 7.7 Hz, 1H, H1), 3.73 (dd, *J* 11.2, 3.7 Hz, 1H, H6a), 3.64 (d, *J* 11.2 Hz, 1H, H6b), 3.62−3.51 (m, 2H, H3, H4), 3.43 (dd, *J* 10.8, 3.7 Hz, 1H, H5), 3.40−3.34 (m, 1H), 3.32 (t, *J* 8.2 Hz, 1H, H2), 2.25−2.15 (m, 1H), 1.99 (d, *J* 12.0 Hz, 1H), 1.59 (d, *J* 13.1 Hz, 3H), 1.26 (m, 1H), 1.21−1.09 (m, 1H), 0.84 (d, *J* 7.1 Hz, 3H), 0.81 (d, *J* 6.5 Hz, 3H), 0.71 (d, *J* 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 143.9, 143.8, 143.5, 132.3, 132.3, 132.2, 128.0, 127.6, 127.6, 127.4 (Ar), 118.8 (CN), 118.8 (CN), 118.7 (CN), 111.7, 111.5, 111.5 (Ar), 100.5 (C1), 84.9, 82.2 (C2), 78.1, 77.9 (C5), 74.7, 74.4 (CH_2Ar), 73.9 (CH_2Ar), 73.5 (CH_2Ar), 73.0(CH_2Ar), 69.6 (C6), 48.1, 40.9, 34.4, 31.5, 25.5, 23.3, 22.3, 21.1, 16.2. HRMS (ES): calcd. for $C_{48}H_{50}N_4O_6NH_4^+$ 796.4069 found 796.4074.

L-Menthyl 2,3,4,6-tetra-*O*-(*p*-cyanobenzyl)-α-D-glucopyranoside. Clear syrup, R_f: 0.27 (pentane/EtOAc 3:2), $[\alpha]_D^{RT}$ + 52 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.64−7.57 (m, 6H, Ar*H*), 7.55 (d, *J* 8.3 Hz, 2H, Ar*H*), 7.43 (d, *J* 8.3 Hz, 2H, Ar*H*), 7.38 (d, *J* 8.3 Hz, 2H, Ar*H*), 7.34−7.25 (m, 4H, Ar*H*), 5.10 (d, *J* 3.5 Hz, 1H, H1), 4.96 (d, *J* 12.6 Hz, 1H, C*H*HPh), 4.84 (d, *J* 12.6 Hz, 1H, C*H*HPh), 4.79 (d, *J* 12.7 Hz, 1H, CH*H*Ph), 4.74 (d, *J* 12.8 Hz, 1H, C*H*HPh), 4.67 (d, *J* 13.1 Hz, 1H, C*H*HPh), 4.66 (d, *J* 12.8 Hz, 1H, CH*H*Ph), 4.61 (d, *J* 12.6 Hz, 1H, CH*H*Ph), 4.54 (d, *J* 13.1 Hz, 1H, CH*H*Ph), 4.03 (t, *J* 9.4 Hz, 2H, H3, H5), 3.79 (dd, *J* 10.6, 3.7 Hz, 1H, H6a), 3.69 (dd, *J* 10.6, 1.4 Hz, 1H, H6b), 3.64 (t, *J* 9.5 Hz, 1H, H4), 3.54 (dd, *J* 9.7, 3.5 Hz, 1H, H2), 3.36 (td, *J* 10.6, 4.3 Hz, 1H), 2.32 (ddd, *J* 13.8, 7.9, 4.4 Hz, 1H), 2.15 (d, *J* 12.0 Hz, 1H), 1.73−1.58 (m, 3H), 1.46−1.23 (m, 3H), 1.08 (q, *J* 11.9 Hz, 1H), 1.02−0.91 (m, 2H), 0.87 (d, *J* 6.5 Hz, 3H), 0.82 (d, *J* 7.0 Hz, 3H), 0.66 (d, *J* 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 144.0, 143.5, 143.5, 143.4, 132.3, 132.3, 132.3, 132.3, 127.8, 127.5, 127.4, 127.4 (Ar), 118.8 (CN), 118.7 (CN), 118.7 (CN), 118.6 (CN), 111.7, 111.6, 111.6, 111.5 (Ar), 98.3 (C1), 82.2, 82.0, 81.0 (C2), 78.4 (C4), 74.3 (CH_2Ar), 73.9(CH_2Ar), 72.7-(CH_2Ar), 71.9(CH_2Ar), 70.2, 69.4 (C6), 48.8, 43.1, 34.2, 31.8, 24.8, 23.0, 22.4, 21.1, 16.1. HRMS (ES): calcd. for $C_{48}H_{50}N_4O_6NH_4^+$ 796.4069 found 796.4080.

L-Menthyl 3,4,6-tri-benzyl-2-*O*-(*p*-methoxybenzyl)-β-D-glucopyranoside. White solid, R_f: 0.7 (pentane/EtOAc 9:1), $[\alpha]_D^{RT}$ −14.8 (*c* 1, $CHCl_3$). mp 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37−7.15 (m, 17H, Ar*H*), 6.82 (d, *J* 8.1 Hz, 2H), 4.92 (d, *J* 11.1 Hz, 1H, C*H*Ph), 4.87 (d, *J* 10.5 Hz, 1H, C*H*HAr), 4.79 (t, *J* 11.5 Hz, 2H, CH_2Ar), 4.66−4.51 (m, 4H, CH_2Ar), 4.46 (d, *J* 7.6 Hz, 1H, H1), 3.78 (s, 3H, OCH_3), 3.69 (s, 2H, H6), 3.60 (p, *J* 8.9 Hz, 2H), 3.55−3.46 (m, 1H), 3.41 (d, *J* 7.2 Hz, 2H), 2.43−2.29 (m, 1H), 2.15 (d, *J* 11.8 Hz, 1H), 1.67 (d, *J* 11.3 Hz, 2H), 1.36 (s, 1H), 1.32−1.22 (m, 2H), 1.06−0.80 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 159.3, 139.1, 138.6, 138.4, 130.9, 130.1, 128.5, 128.4, 128.4, 128.2, 127.8, 127.8, 127.6, 127.6, 113.9 (Ar), 100.9 (C1), 85.1, 82.1, 78.1, 77.9, 75.7 (CH_2Ar), 75.1 (CH_2Ar), 74.9, 74.6 (CH_2Ar), 73.8 (CH_2Ar), 69.5 (C6), 55.4 (OCH_3), 48.3, 41.2, 34.6, 31.6, 25.4, 23.4, 22.4, 21.2, 16.1. HRMS (ES): calcd. for $C_{45}H_{56}O_7NH_4^+$ 726.4364; found 726.4373.

L-Menthyl 3,4,6-tri-benzyl-2-*O*-(*p*-methoxybenzyl)-α-D-glucopyranoside. Clear syrup, R_f: 0.53 (pentane/EtOAc 9:1), $[\alpha]_D^{RT}$ + 35.6 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37−7.21 (m, 15H, Ar*H*), 7.14 (s, 2H, Ar*H*), 6.84 (d, *J* 7.8 Hz, 2H, Ar*H*), 4.98 (d, *J* 10.9 Hz, 2H, H1, C*H*Ph), 4.82 (t, *J* 10.3 Hz, 2H, CH_2Ar), 4.64 (d, *J* 12.7 Hz, 3H, CH_2Ar), 4.53−4.41 (m, 2H, CH_2Ar), 4.05−3.91 (m, 2H, H2, H5), 3.80 (s, 3H, OCH_3), 3.76 (d, *J* 10.4 Hz, 1H, H6), 3.69−3.58 (m, 2H, H6, H4), 3.53 (dd, *J* 7.9, 1.6 Hz, 1H, H1), 3.41−3.29 (m, 1H), 2.51−2.36 (m, 1H), 2.13 (d, *J* 11.5 Hz, 1H), 1.62 (d, *J* 11.4 Hz, 2H), 1.47−1.24 (m, 4H), 1.13−0.78 (m, 10H), 0.74 (d, *J* 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 159.3, 139.1, 138.5, 138.2, 130.7, 129.4, 128.5, 128.5, 128.0, 128.0, 127.8, 127.8, 127.6, 113.8 (Ar), 98.8 (C1), 82.1, 81.0, 80.4 (C2), 78.3 (C4), 75.6 (CH_2Ar), 75.2 (CH_2Ar), 73.6 (CH_2Ar), 73.0 (CH_2Ar), 70.4, 68.9 (C6), 55.4 (OCH_3), 48.9, 43.2, 34.4, 31.9, 24.8, 23.1, 22.4, 21.3, 16.3. HRMS (ES): calcd. for $C_{45}H_{56}O_7NH_4^+$ 726.4364; found 726.4374.

L-Menthyl 3,4,6-tri-benzyl-2-*O*-(*p*-chlorobenzyl)-β-D-glucopyranoside. White solid, R_f: 0.78 (pentane/EtOAc 9:1), $[\alpha]_D^{RT}$ −18.6 (*c* 1, $CHCl_3$). mp 142−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.54−7.28 (m, 19H, Ar*H*), 5.04−4.95 (m, 2H, Ar*H*), 4.91 (d, *J* 8.6 Hz, 2H, Ar*H*), 4.78−4.61 (m, 4H, Ar*H*), 4.56 (d, *J* 7.7 Hz, 1H, H1), 3.80 (s, 2H, H6), 3.76−3.66 (m, 2H), 3.64−3.56 (m, 1H), 3.56−3.45 (m, 1H), 2.50−2.37 (m, 1H), 2.29−2.16 (m, 1H), 1.77 (d, *J* 12.1 Hz, 2H), 1.46 (s, 1H), 1.42−1.30 (m, 1H), 1.17−0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 138.9, 138.5, 138.3, 137.2, 133.4, 129.7, 128.5, 128.5, 128.2, 127.9, 127.8, 127.7, 127.6 (Ar), 100.8 (C1), 85.0, 82.2, 78.1, 77.8, 75.7 (CH_2Ar), 75.1, 74.9 (CH_2Ar), 74.0 (CH_2Ar), 73.8 (CH_2Ar), 69.4 (C6), 48.3, 41.1, 34.6, 31.6, 25.4, 23.3, 22.4, 21.2, 16.1. HRMS (ES): calcd. for $C_{44}H_{53}{}^{35}ClO_6NH_4^+$ 730.3869; found 730.3874.

L-Menthyl 3,4,6-tri-benzyl-2-*O*-(*p*-chlorobenzyl)-α-D-glucopyranoside. Clear syrup, R_f: 0.54 (pentane/EtOAc 9:1), $[\alpha]_D^{RT}$ −46.8 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.30−7.12 (m, 17H, Ar*H*), 7.09−7.03 (m, 2H, Ar*H*), 4.94 (d, *J* 3.5 Hz, 1H, H1), 4.84 (d, *J* 11.0 Hz, 1H, C*H*HPh), 4.75 (d, *J* 10.7 Hz, 2H, CH_2Ph), 4.60−4.52 (m, 3H, CH_2Ph), 4.44−4.35 (m, 2H, CH_2Ph), 3.98−3.86 (m, 2H, H3, H5), 3.68 (dd, *J* 10.5, 3.7 Hz, 1H, H6a), 3.60−3.51 (m, 2H, H6b, H4), 3.43 (dd, *J* 9.7, 3.5 Hz, 1H, H1), 3.27 (td, *J* 10.6, 6.0 Hz, 1H), 2.36−2.25 (m, 1H), 2.06 (d, *J* 12.0 Hz, 1H), 1.33−1.16 (m, 4H), 1.03−0.67 (m, 10H), 0.62 (d, *J* 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 138.9, 138.4, 138.1, 137.0, 133.3, 128.9, 128.5, 128.5, 128.5, 128.0, 127.9, 127.8, 127.8, 127.7 (Ar), 98.7 (C1), 82.0 (C3), 81.3, 80.7 (C2), 78.2 (C4), 75.6 (CH_2Ar), 75.2 (CH_2Ar), 73.6 (CH_2Ar), 72.4 (CH_2Ar), 70.4 (C5), 68.7 (C6), 48.9, 43.2, 34.4, 31.9, 24.7, 23.1, 22.4, 21.3, 16.2. HRMS (ES): calcd. for $C_{44}H_{53}{}^{35}ClO_6NH_4^+$ 730.3869; found 730.3879.

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L-Menthyl 3,4,6-tri-benzyl-2-*O*-(*p*-cyanobenzyl)-*β*-D-glucopyranoside. White solid, R_f: 0.25 (pentane/EtOAc 20:1), $[\alpha]_D^{RT}$ −15.4 (*c* 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.45 (d, *J* 8.1 Hz, 2H, Ar*H*), 7.32 (d, *J* 8.1 Hz, 2H, Ar*H*), 7.27−7.15 (m, 13H, Ar*H*), 7.14−7.10 (m, 2H, Ar*H*), 4.88 (d, *J* 12.7 Hz, 1H, C*H*HAr), 4.80−4.71 (m, 3H, CH_2Ar), 4.66 (d, *J* 12.7 Hz, 1H, CH*H*Ar), 4.53 (d, *J* 12.2 Hz, 1H, C*H*HAr), 4.52 (d, *J* 10.7 Hz, 1H, CH*H*Ar), 4.46 (d, *J* 12.2 Hz, 1H, CH*H*Ar), 4.38 (d, *J* 7.8 Hz, 1H, H1), 3.64−3.60 (m, 2H, H6), 3.57−3.51 (m, 2H), 3.42 (td, *J* 10.7, 4.1 Hz, 1H), 3.36−3.31 (m, 1H), 3.28 (td, *J* 7.7, 2.3 Hz, 1H, H2), 2.23 (dsept, *J* 6.8, 2.3 Hz, 1H), 1.99 (d, *J* 12.1 Hz, 1H), 1.58 (d, *J* 10.7 Hz, 2H), 1.36−1.08 (m, 3H), 0.98−0.68 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 144.3, 138.7, 138.4, 138.2, 132.1, 128.5, 128.5, 128.5, 128.2, 128.2, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6 (Ar), 119.1 (*C*N), 111.2 (Ar), 100.6 (C1), 84.9, 82.3 (C2), 78.1, 77.8, 75.7, 75.1, 74.9, 73.8, 73.5, 69.2, 48.2, 41.0, 34.5, 31.5, 25.4, 23.3, 22.4, 21.2, 16.0. HRMS (ES): calcd. for $C_{45}H_{53}NO_6NH_4^+$ 721.4211; found 721.4226.

L-Menthyl 3,4,6-tri-benzyl-2-*O*-(*p*-cyanobenzyl)-*α*-D-glucopyranoside. Clear syrup, R_f: 0.23 (pentane/EtOAc 9:1), $[\alpha]_D^{RT}$ + 65.2 (*c* 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ_H ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.49 (d, *J* 8.1 Hz, 2H, Ar*H*), 7.33 (d, *J* 8.0 Hz, 2H, Ar*H*), 7.28−7.16 (m, 13H, Ar*H*), 7.08−7.01 (m, 2H, Ar*H*), 4.98 (d, *J* 3.3 Hz, 1H, H1), 4.80 (s, 2H, CH_2Ar), 4.75 (d, *J* 10.7 Hz, 1H, C*H*HAr), 4.65 (s, 2H, CH_2Ar), 4.58 (d, *J* 12.1 Hz, 1H, C*H*HAr), 4.40 (d, *J* 12.4 Hz, 1H, CH*H*Ar), 4.39 (d, *J* 10.3 Hz, 1H, CH*H*Ar), 3.95 (t, *J* 9.3 Hz, 1H, H3), 3.90 (bd, *J* 9.8 Hz, 1H, H5), 3.69 (dd, *J* 10.5, 3.3 Hz, 1H, H6a), 3.58 (t, *J* 9.8 Hz, 2H, H4, H6b), 3.44 (dd, *J* 9.7, 3.4 Hz, 1H, H2), 3.26 (td, *J* 10.6, 4.2 Hz, 1H), 2.27 (dt, *J* 12.9, 6.0 Hz, 1H), 2.07 (d, *J* 11.8 Hz, 1H), 1.61−1.48 (m, 2H), 1.35−1.13 (m, 3H), 1.01−0.83 (m, 2H), 0.78 (d, *J* 6.4 Hz, 3H), 0.74 (d, *J* 7.1 Hz, 3H), 0.58 (d, *J* 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 144.0, 138.8, 138.3, 138.1, 132.2, 128.5, 128.5, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6 (Ar), 119.0 (*C*N), 111.3 (Ar), 98.6 (C1), 82.0 (C3), 81.6, 80.9 (C2), 78.3 (C4), 75.6 (*C*H$_2$Ar), 75.2 (*C*H$_2$Ar), 73.6 (*C*H$_2$Ar), 72.0 (*C*H$_2$Ar), 70.5 (C5), 68.6 (C6), 48.8, 43.2, 34.3, 31.8, 24.8, 23.1, 22.4, 21.2, 16.2. HRMS (ES): calcd. for $C_{45}H_{53}NO_6NH_4^+$ 721.4211; found 721.4216.

L-Menthyl 2,3,4,6-tetra-*O*-benzyl-*α*/*β*-D-galactopyranoside. Yield: 63 mg, 93%, *α*/*β* 1:7, syrup, R_f: 0.50 (pentane/EtOAc 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.46−7.27 (m, 25H), 5.07 (d, *J* 3.6 Hz, 0.2H, H1*α*), 5.03−4.95 (m, 2.3H), 4.88−4.70 (m, 4H), 4.67 (d, *J* 11.8 Hz, 1H), 4.63 (d, *J* 11.5 Hz, 0.2H), 4.54−4.38 (m, 3.6H), 4.16 (t, *J* 6.4 Hz, 0.2H), 4.10−3.99 (m, 0.5H), 3.90 (d, *J* 2.7 Hz, 1H), 3.81 (dd, *J* 9.6, 7.8 Hz, 1H, H2*β*), 3.65−3.53 (m, 4.5H), 3.48 (td, *J* 10.7, 4.2 Hz, 1H), 3.38 (td, *J* 10.5, 4.3 Hz, 0.2H), 2.51−2.37 (m, 1.2H), 2.17 (d, *J* 12.4 Hz, 1.2H), 1.69 (d, *J* 11.4 Hz, 2.9H), 1.45−1.22 (m, 2.9H), 1.12−0.84 (m, 11H), 0.81 (d, *J* 6.8 Hz, 3.3H), 0.74 (d, *J* 6.9 Hz, 0.6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 139.0, 138.9, 138.8, 138.2, 138.1, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.5, 127.4, 101.8 (C1*β*), 99.4 (C1*α*), 82.8, 80.3, 79.6 (C2*β*), 79.4, 78.5, 77.0, 75.3, 75.2, 74.8, 74.5, 74.1, 73.7, 73.7, 73.5, 73.4, 73.3, 72.8, 69.4, 69.4, 69.3, 49.0, 48.2, 43.0, 41.3, 34.6, 34.4, 31.9, 31.6, 25.0, 24.6, 23.2, 23.0, 22.4, 21.3, 16.1, 15.8. HRMS (ES): calcd. for $C_{44}H_{54}O_6NH_4^+$ 696.4259; found 696.4272 Spectral values were in accordance with those reported in ref 42.

L-Menthyl 2,3,4,6-tetra-*O*-(*p*-methoxybenzyl)-*α*/*β*-D-galactopyranoside. Yield: 47 mg, 59%, *α*/*β* 1:6, syrup, R_f: 0.35 (pentane/EtOAc 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.25−7.07 (m, 10H, Ar*H*), 6.81−6.71 (m, 10H, Ar*H*), 4.88 (d, *J* 3.7 Hz, 0.2H, H1*α*), 4.79−4.74 (m, 2.2H), 4.67−4.50 (m, 4H), 4.47 (d, *J* 11.5 Hz, 1H, CH*H*Ar), 4.42 (d, *J* 11.2 Hz, 0.2H, CH*H*Ar), 4.34 (d, *J* 11.5 Hz, 0.2H, C*H*HAr), 4.32−4.24 (m, 2.2H), 4.22 (d, *J* 11.3 Hz, 1H, CH*H*Ar), 3.97 (t, *J* 6.5 Hz, 0.2H), 3.90−3.78 (m, 0.8H), 3.75−3.68 (m, 16H, OCH_3), 3.61 (dd, *J* 9.7, 7.8 Hz, 1H, H2*β*), 3.53 (t, *J* 5.0 Hz, 0.2H), 3.43−3.29 (m, 5.6H), 3.27−3.16 (m, 4H), 2.36−2.25 (m, 1.2H), 2.05 (d, *J* 12.2 Hz, 1H), 1.97 (d, *J* 12.1 Hz, 0.2H), 1.56 (d, *J* 12.4 Hz, 3H), 1.32−1.10 (m, 3.4H), 0.97−0.72 (m, 12H), 0.67 (d, *J* 6.8 Hz, 3H), 0.62 (d, *J* 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 159.4, 159.2, 131.3, 131.2, 131.1, 131.0, 130.4, 130.2, 130.0, 130.0, 129.9, 129.6, 129.4, 129.2, 129.1, 113.9, 113.9, 113.8, 113.8, 113.7, 113.6, 101.9 (C1*β*), 99.4 (C1*α*), 82.6, 79.3 (C2*β*), 79.2, 78.5, 76.6, 75.9, 74.7, 74.3, 74.0, 73.6, 73.5, 73.4, 73.3, 73.2, 73.0, 72.4, 69.3, 69.3 (C6*β*), 68.9, 55.4 (OCH$_3$), 49.0, 48.2, 43.0, 41.4, 34.6, 34.4, 31.9, 31.7, 24.9, 24.6, 23.1, 23.0, 22.4, 21.3, 16.2, 15.8. HRMS (ES): calcd. for $C_{48}H_{62}O_{10}NH_4^+$ 816.4681; found 816.4699.

6-*O*-(2,3,4,6-Tetra-*O*-benzyl-*α*/*β*-D-glucopyranosyl)-1,2;3,4-di-*O*-isopropylidene-*α*-D-galactopyranose. Yield: 60 mg, 74%, *α*/*β* 1:4, syrup, R_f: 0.66 (pentane/EtOAc 3:1). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.45 (d, *J* 2.0 Hz, 2H, Ar*H*), 7.39−7.25 (m, 23H, Ar*H*), 7.15 (dd, *J* 7.1, 2.4 Hz, 3H), 5.59 (d, *J* 5.0 Hz, 1H, H1), 5.54 (d, *J* 5.0 Hz, 0.3H, H1), 5.08 (d, *J* 11.1 Hz, 1H, C*H*HAr), 5.04−4.95 (m, 1.6H), 4.87−4.69 (m, 4.6H), 4.67−4.59 (m, 3H), 4.58−4.46 (m, 4H), 4.38 (dd, *J* 8.0, 1.9 Hz, 0.3H), 4.33 (dt, *J* 4.6, 2.3 Hz, 1.6H), 4.27 (dd, *J* 7.9, 1.9 Hz, 1H), 4.19 (dd, *J* 10.6, 3.6 Hz, 1H), 4.11 (ddd, *J* 7.4, 3.5, 1.8 Hz, 1H), 4.06 (td, *J* 6.9, 6.2, 1.8 Hz, 0.3H), 4.01 (t, *J* 9.3 Hz, 0.3H), 3.87−3.58 (m, 8.3H), 3.52−3.42 (m, 2.3H), 1.55 (s, 1.3H), 1.52 (s, 3H), 1.47 (s, 4H), 1.34 (s, 4H), 1.33 (s, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 139.0, 138.8, 138.4, 138.3, 138.2, 138.1, 128.8, 128.5, 128.5, 128.5, 128.3, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 109.5, 109.3, 108.7, 108.7, 104.5 (C1′*β*), 97.2 (C1′*α*), 96.5 (C1*β*), 96.4 (C1*α*), 84.7, 82.1, 81.7, 79.9, 77.8, 77.7, 75.8, 75.8, 75.1, 74.9, 74.5, 73.6, 73.6, 72.5, 71.6, 70.9, 70.7, 70.6, 70.3, 69.8, 68.9, 67.5, 66.3, 65.8, 26.3, 26.2, 26.2, 26.1, 25.2, 25.1, 24.8, 24.6. HRMS (ES): calcd. for $C_{46}H_{54}O_{11}NH_4^+$ 800.4004; found 800.4020. Spectral values were in accordance with those reported in ref 43.

6-*O*-(2,3,4,6-Tetra-*O*-(*p*-methoxybenzyl)-*α*/*β*-D-glucopyranosyl)-1,2;3,4-di-*O*-isopropylidene-*α*-D-galactopyranose. Yield: 81 mg, 90%, *α*/*β* 1:4, syrup, R_f: 0.38 (pentane/EtOAc 2:1). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.40 (d, *J* 8.3 Hz, 2H, Ar*H*), 7.29 (t, *J* 8.4 Hz, 6H, Ar*H*), 7.07 (d, *J* 8.3 Hz, 2H, Ar*H*), 6.93−6.80 (m, 10H, Ar*H*), 5.61 (d, *J* 5.0 Hz, 1H, H1′*β*), 5.56 (d, *J* 5.0 Hz, 0.2 H*α*), 5.01 (d, *J* 10.7 Hz, 1H), 4.98 (d, *J* 3.8 Hz, 0.2H, H1′*α*) H 4.93−4.89 (m, 1.2H), 4.77−4.68 (m, 4H), 4.65−4.61 (m, 1.4H), 4.59 (d, *J* 11.7 Hz, 1.3H), 4.49 (d, *J* 12.0 Hz, 1H), 4.47−4.41 (m, 2.6H), 4.40−4.34 (m, 1.6H), 4.29 (d, *J* 8.0 Hz, 1H), 4.20 (dd, *J* 10.6, 3.4 Hz, 1H), 4.14−4.12 (m, 1H), 4.07 (t, *J* 6.8 Hz, 0.3H), 3.95 (t, *J* 9.2 Hz, 0.3H), 3.83−3.81 (m, 16 H), 3.78−3.74 (m, 1.6H), 3.71−3.66 (m, 1.6H), 3.63−3.54 (m, 3H), 3.48−3.42 (m, 2H), 1.56 (s, 0.6H), 1.54 (s, 3H), 1.49 (s, 4H), 1.36−1.35(m, 2H), 1.30 (s, 1.6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 159.3, 159.3, 159.3, 159.2, 131.4, 131.1, 131.1, 130.7, 130.6, 130.5, 130.4, 130.3, 130.1, 129.7, 129.6, 129.6, 129.6, 129.5, 113.8, 113.7, 109.4, 109.3, 108.7, 104.5 (C1′*β*), 97.2 (C1′*α*), 96.5 (C1*β*), 96.4(C1*α*), 84.4, 81.8, 81.4, 79.6, 77.6, 75.4, 74.9, 74.7, 74.0, 73.2, 73.2, 72.1, 71.6, 70.8, 70.8, 70.7, 70.6, 70.3, 69.8, 68.4, 67.9, 67.5, 66.2, 65.7, 55.3, 55.3, 55.3, 55.3, 29.8, 26.3, 26.2, 26.1, 26.1, 25.1, 25.0, 24.8, 24.6. HRMS (ES): calcd. for $C_{50}H_{62}O_{15}NH_4^+$ 920.4427; found 920.4446.

6-*O*-(2,3,4,6-Tetra-*O*-(*p*-chlorobenzyl)-*α*/*β*-D-glucopyranosyl)-1,2;3,4-di-*O*-isopropylidene-*α*-D-galactopyranose. Yield: 81 mg, 88%, *α*/*β* 1:2, syrup, R_f: 0.59 (pentane/EtOAc 3:1). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.38−7.27 (m, 15H), 7.23−7.16 (m, 3H), 7.05 (d, *J* 8.0 Hz, 3H), 5.60 (d, *J* 4.4 Hz, 1H, H1*β*), 5.57 (d, *J* 4.4 Hz, 1H, H1*α*), 5.07−5.01 (m, 1.5H), 4.94−4.86 (m, 1.5H), 4.77−4.67 (m, 4.5H), 4.67−4.58 (m, 4H), 4.53−4.40 (m, 4H), 4.40−4.31 (m, 2H), 4.26 (d, *J* 7.9 Hz, 1H), 4.19 (d, *J* 10.8 Hz, 1H), 4.14−4.04 (m, 1.5H), 3.96 (t, *J* 9.1 Hz, 0.5H), 3.88−3.81 (m, 1H), 3.79−3.67 (m, 4H), 3.67−3.62 (m, 1H), 3.61−3.54 (m, 3H), 3.48−3.36 (m, 2H), 1.57 (s, 1.5H), 1.52 (s, 3H), 1.50 (s, 4.5H), 1.37 (s, 4.5H), 1.35 (s, 4.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 137.4, 137.1, 137.1, 136.8, 136.6, 136.6, 136.4, 133.6, 133.6, 133.5, 133.4, 133.4, 130.1, 129.3, 129.3, 129.2, 129.1, 129.0, 129.0, 128.9, 128.6, 128.6, 128.6, 128.4, 109.6, 109.4, 108.7, 108.7, 104.5 (C1′*β*), 96.6 (C1′*α*), 96.5 (C1*β*), 96.4 (C1*α*), 84.4, 81.8, 81.3, 79.9, 77.7, 77.6, 74.8, 74.6, 74.1, 74.1, 73.3, 72.8, 72.8, 71.6, 71.5, 71.0, 70.9, 70.8, 70.7, 70.5, 70.2, 70.1, 68.7, 68.4, 67.6, 66.3, 65.7, 26.3, 26.2, 26.1, 26.1, 25.1, 25.0, 24.8, 24.5. HRMS (ES): calcd. for $C_{46}H_{50}{}^{35}Cl_3{}^{37}ClO_{11}NH_4^+$ 938.2416; found 938.2416.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-*α*/*β*-D-glucopyranosyl)-*α*-D-glucopyranoside. Yield: 85 mg, 86%, *α*/*β* 1:4, syrup, R_f: 0.57 (pentane/EtOAc 3:1). ^1H NMR (400 MHz,

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$CDCl_3$): δ_H 7.50−7.31 (m, 37H, Ar*H*), 7.32−7.25 (m, 8H, Ar*H*), 5.10−5.06 (m, 2.5H), 5.03 (bs, 1H), 5.00 (bs, 1H), 4.96−4.76 (m, 9H), 4.76−4.60 (m, 9H), 4.56 (d, *J* 11.1 Hz, 0.3H), 4.52 (d, *J* 12.2 Hz, 0.3H), 4.46 (d, *J* 7.7 Hz, 1H, H1′*β*), 4.29 (d, *J* 10.4 Hz, 1H), 4.15−4.05 (m, 1.5H), 3.97−3.87 (m, 1.5H), 3.86−3.58 (m, 10H), 3.56−3.52 (m, 2H), 3.46 (s, 0.9H), 3.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 138.9, 138.6, 138.5, 138.5, 138.5, 138.4, 138.4, 138.3, 138.2, 138.2, 138.2, 138.0, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 103.9 (C1′*β*), 98.1 (C1*β*), 98.0 (C1*α*), 97.3 (C1′*α*), 84.9, 82.2, 82.1, 82.0, 81.7, 80.2, 80.1, 79.8, 78.1, 78.0, 77.8, 77.7, 75.8, 75.7, 75.5, 75.1, 75.0, 74.9, 74.9, 73.5, 73.4, 72.4, 70.4, 70.3, 69.9, 69.1, 68.6, 68.6, 66.1, 55.3, 55.2. HRMS (ES): calcd. for $C_{62}H_{66}O_{11}NH_4^+$ 1004.4943; found 1004.4954. Spectral values were in accordance with those reported in ref 44 and 45.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-(*p*-methoxybenzyl)-*α*/*β*-D-glucopyranosyl)-*α*-D-glucopyranoside. Yield: 75 mg, 68%, *α*/*β* 1:4, syrup, R_f: 0.41 (pentane/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39−7.26 (m, 22H), 7.12 (d, *J* 8.3 Hz, 1H), 7.06 (d, *J* 8.3 Hz, 0.5H), 6.90−6.85 (m, 7H), 6.80 (d, *J* 8.4 Hz, 2H), 5.04 (d, *J* 10.9 Hz, 1H), 4.96 (d, *J* 10.6 Hz, 1H), 4.92−4.80 (m, 4H), 4.80−4.71 (m, 4H), 4.71−4.63 (m, 2H), 4.62−4.53 (m, 3H), 4.52−4.45 (m, 1H), 4.38 (d, *J* 7.6 Hz, 1H, H1), 4.25 (d, *J* 10.4 Hz, 1H), 4.07 (t, *J* 9.3 Hz, 1H), 3.88 (m, 1H), 3.84 (s, 6H), 3.82 (s, 3H), 3.78 (s, 3H), 3.75−3.50 (m, 12H), 3.45(m, 1H), 3.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.4, 159.3, 159.3, 159.2, 159.2, 138.9, 138.5, 138.4, 138.2, 131.2, 130.9, 130.8, 130.7, 130.6, 130.3, 130.1, 129.7, 129.6, 129.6, 129.5, 129.4, 129.4, 129.3, 128.5, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 113.8, 113.8, 113.7, 103.9 (C1′*β*), 98.1 (C1*β*), 98.0 (C1*α*), 97.3 (C1′*α*), 84.6, 82.2, 82.1, 81.9, 81.4, 80.2, 79.9, 79.7, 78.1, 77.9, 75.8, 75.4, 75.1, 75.0, 74.7, 74.6, 73.5, 73.1, 73.1, 70.5, 70.3, 69.9, 68.6, 55.3, 55.2. HRMS (ES): calcd. for $C_{66}H_{74}O_{15}NH_4^+$ 1124.5366; found 1124.5395.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-(*p*-chlorobenzyl)-*α*/*β*-D-glucopyranosyl)-*α*-D-glucopyranoside. Yield: 97 mg, 68%, *α*/*β* 1:3, syrup, R_f: 0.45 (pentane/EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42−7.13 (m, 40H, Ar*H*), 7.08 (d, *J* 7.7 Hz, 1H, Ar*H*), 7.03 (d, *J* 7.8 Hz, 1H, Ar*H*), 5.08−4.99 (m, 2H), 4.99−4.93 (m, 1H), 4.91−4.75 (m, 6H), 4.75−4.66 (m, 5H), 4.66−4.60 (m, 2H), 4.60−4.55 (m, 3H), 4.55−4.47 (m, 3H), 4.42 (d, *J* 9.1 Hz, 1H), 4.36 (d, *J* 8.0 Hz, 1H, H1$_{\beta}$′), 4.21 (d, *J* 10.7 Hz, 1H), 4.05 (t, *J* 9.1 Hz, 1H), 3.95−3.84 (m, 2H), 3.83−3.68 (m, 5H), 3.65−3.49 (m, 6H), 3.49−3.43 (m, 1H), 3.40 (s, 1H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.8, 138.5, 138.3, 138.2, 138.1, 137.2, 136.9, 136.8, 136.8, 136.7, 136.7, 136.5, 136.4, 133.7, 133.6, 133.5, 133.5, 129.3, 129.2, 129.1, 129.0, 129.0, 129.0, 128.9, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.2, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.7, 103.8 (C1′*β*), 98.2 (C1*β*), 98.1 (C1*α*), 97.1 (C1′*α*), 84.6, 82.2, 82.0, 81.9, 81.5, 80.2, 80.0, 79.9, 78.1, 77.8, 77.7, 77.6, 75.9, 75.9, 75.0, 75.0, 74.9, 74.8, 74.6, 74.1, 74.0, 74.0, 73.5, 72.7, 71.5, 70.4, 70.2, 69.9, 68.8, 68.8, 68.4, 66.0, 55.4, 55.3. HRMS (ES): calcd. for $C_{62}H_{62}{}^{35}Cl_3{}^{37}ClO_{11}NH_4^+$ 1142.3355; found 1142.3390.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-*α*/*β*-D-glucopyranosyl)-*α*-D-glucopyranoside. Yield: 88 mg, 89%, *α*/*β* 1:1.2, syrup, R_f: 0.25 (pentane/EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52−7.46 (m, 2.6H), 7.41−7.27 (m, 68H), 7.19−7.14 (m, 2.5H), 5.78 (d, *J* 3.2 Hz, 1H, H1′*α*), 5.17 (d, *J* 11.3 Hz, 1H), 5.11 (d, *J* 11.6 Hz, 1H), 4.99−4.91 (m, 2.4H), 4.91−4.74 (m, 11H), 4.72−4.59 (m, 10H), 4.59−4.54 (m, 2H.6), 4.54−4.41 (m, 6H), 4.34 (d, *J* = 12.1 Hz, 1H), 4.21−4.09 (m, 2H), 4.08−3.87 (m, 6H), 3.81−3.69 (m, 4H), 3.69−3.62 (m, 4H), 3.61−3.51 (m, 6H), 3.44 (s, 3H), 3.43 (s, 3H), 3.37 (dd, *J* 9.6, 3.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 139.7, 139.0, 138.8, 138.7, 138.7, 138.6, 138.5, 138.4, 138.2, 138.1, 138.0, 137.9, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.8, 102.6 (C1′*β*), 98.5 (C1*β*), 97.9 (C1*α*), 96.7 (C1*α*), 85.0, 82.9, 82.1, 80.5, 80.3, 79.5, 78.9, 78.1, 77.7, 76.7, 75.7, 75.7, 75.5, 75.3, 75.0, 75.0, 74.9, 74.5, 73.7, 73.5, 73.5, 73.4, 73.4, 73.3, 73.2, 72.3, 71.0, 70.0, 69.6, 69.1, 68.2, 67.9, 55.4, 55.3. HRMS (ES): calcd. for $C_{62}H_{66}O_{11}NH_4^+$ 1004.4943; found 1004.4962. Spectral values were in accordance with those reported in ref 44 and 45.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-(*p*-methoxybenzyl)-*α*/*β*-D-glucopyranosyl)-*α*-D-glucopyranoside. Yield: 75 mg, 68%, *α*/*β* 1:1.3, syrup, R_f: 0.25 (pentane/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.35 (d, *J* 6.9 Hz, 3H), 7.27−6.93 (m, 55H), 6.89 (d, *J* 8.0 Hz, 2H), 6.77−6.1 (m, 18H), 6.64 (d, *J* 8.0 Hz, 2H), 5.59 (d, *J* 2.6 Hz, 1H, H1′*α*), 5.03 (d, *J* 11.3 Hz, 1H), 4.95 (d, *J* 11.5 Hz, 1H), 4.74−4.59 (m, 15H), 4.56−4.22 (m, 20H), 4.19 (d, *J* 10.5 Hz, 1H), 4.09 (d, *J* 11.8 Hz, 1H), 4.05−3.94 (m, 3H), 3.89 (t, *J* 9.3 Hz, 2H), 3.83−3.62 (m, 37H), 3.62−3.15 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.3, 159.2, 159.2, 159.2, 159.1, 139.8, 139.1, 138.5, 138.4, 138.1, 138.0, 132.1, 131.2, 131.0, 130.9, 130.8, 130.6, 130.3, 130.1, 129.9, 129.6, 129.5, 129.5, 129.4, 128.5, 128.5, 128.5, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.5, 127.3, 127.2, 127.0, 113.9, 113.9, 113.8, 113.8, 113.8, 113.7, 102.8 (C1′*β*), 98.6 (C1*β*), 97.9 (C1*α*), 96.9 (C1′*α*), 84.8, 82.7, 82.2, 82.0, 80.6, 80.3, 79.2, 78.9, 77.9, 76.9, 75.5, 75.4, 75.3, 74.7, 74.7, 74.6, 73.8, 73.5, 73.4, 73.2, 73.1, 73.1, 73.0, 72.3, 71.1, 70.2, 69.6, 69.1, 68.8, 68.1, 67.7, 55.4, 55.4, 55.4, 55.3, 55.3. HRMS (ES): calcd. for $C_{66}H_{74}O_{15}NH_4^+$ 1124.5366; found 1124.5395.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-(*p*-chlorobenzyl)-*α*/*β*-D-glucopyranosyl)-*α*-D-glucopyranoside. Yield: 112 mg, 100%, *α*/*β* 2:1, syrup, R_f: 0.38 (pentane/EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48−7.43 (m, 1H), 7.36−7.24 (m, 36H), 7.22−7.06 (m, 11H), 7.00 (d, *J* 7.9 Hz, 2H), 5.76 (d, *J* 2.0 Hz, 1H, H1′*α*), 5.12 (t, *J* 11.4 Hz, 1H), 4.87−4.75 (m, 5H), 4.75−4.58 (m, 9H), 4.58−4.44 (m, 6H), 4.44−4.32 (m, 3H), 4.24 (d, *J* 12.3 Hz, 1H), 4.17−4.08 (m, 2H), 4.01 (t, *J* 9.4 Hz, 1H), 3.96−3.80 (m, 4H), 3.77−3.49 (m, 8H), 3.44 (s, 3H), 3.42 (s, 2H), 3.40−3.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 139.6, 138.9, 138.3, 138.2, 137.9, 137.8, 137.2, 137.0, 136.9, 136.8, 136.7, 136.4, 136.3, 133.6, 133.6, 133.5, 133.5, 133.4, 133.4, 133.2, 129.4, 129.0, 128.9, 128.9, 128.9, 128.8, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.5, 127.3, 127.2, 126.6, 102.4 (C1′*β*), 98.5 (C1*β*), 97.8 (C1*α*), 96.5(C1′*α*), 84.7, 82.7, 82.1, 81.9, 80.4, 80.3, 79.5, 78.9, 78.0, 77.6, 76.5, 75.5, 75.1, 74.7, 74.6, 74.4, 74.1, 74.0, 73.9, 73.7, 73.5, 73.4, 73.3, 72.7, 72.6, 72.3, 70.8, 70.0, 69.6, 69.1, 68.9, 68.1, 67.9, 55.5, 55.3. HRMS (ES): calcd. for $C_{62}H_{62}{}^{35}Cl_3{}^{37}ClO_{11}NH_4^+$ 1142.3355; found 1142.3403.

4-*O*-(2,3,4,6-Tetra-*O*-benzyl-*α*/*β*-D-glucopyranosyl)-1,2-*O*-isopropylidene-5-*O*-pivaloyl-*α*-D-xylofuranose. Yield: 70 mg, 88%, *α*/*β* 7:1, white solid, R_f: 0.60 (pentane/EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43−7.28 (m, 20H), 7.22−7.15 (m, 2H), 5.96 (d, 1H, H1$_{\alpha}$), 5.85 (d, *J* 2.7 Hz, 0.1H, H1$_{\beta}$), 5.05−4.95 (m, 2H), 4.92−4.69 (m, 6H), 4.69−4.38 (m, 8H), 4.38−4.31 (m, 0.2H), 4.17 (s, 1H), 3.98 (t, *J* 9.3 Hz, 1H), 3.87 (d, *J* 9.9 Hz, 1H), 3.73 (s, 1H), 3.70−3.66 (m, 0.4H), 3.65−3.57 (m, 2H), 3.51−3.44 (m, 0.3H), 1.55 (s, 0.6H), 1.53 (s, 3H), 1.31 (s, 0.9H), 1.27 (s, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.4, 178.2, 138.6, 138.5, 138.2, 138.1, 138.0, 138.0, 137.8, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 111.9, 105.2 (C1*β*), 105.1 (C1*α*), 101.3 (C1′*β*), 98.9 (C1′*α*), 84.6, 83.1, 82.5, 81.8, 81.6, 80.2, 79.8, 78.5, 78.1, 77.7, 75.7, 75.3, 75.2, 75.0, 73.6, 73.5, 73.5, 71.3, 68.9, 68.7, 62.8, 61.8, 38.8, 27.3, 27.2, 26.8, 26.8, 26.2. HRMS (ES): calcd. for $C_{47}H_{56}O_{11}NH_4^+$ 814.4161; found 814.4153.

4-*O*-(2,3,4,6-Tetra-*O*-(*p*-methoxybenzyl)-*α*/*β*-D-glucopyranosyl)-1,2-*O*-isopropylidene-5-*O*-pivaloyl-*α*-D-xylofuranosen. Yield: 53 mg, 58%, *α*/*β* 7:1, syrup, R_f: 0.48 (pentane/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.24 (s, 2H), 7.03 (d, *J* 8.1 Hz, 2H), 6.91−6.77 (m, 9H), 5.88 (d, *J* 2.9 Hz, 1H, H1*α*), 4.89−4.81 (m, 2H, H1′*α*), 4.77−4.70 (m, 3H), 4.65 (d, *J* 11.3 Hz, 1H), 4.59 (d, *J* 11.5 Hz, 1H), 4.54 (d, *J* 11.8 Hz, 1H), 4.50−4.46 (m, 1H), 4.42−4.39 (m, 2H), 4.37−4.29 (m, 2H), 4.10 (s, 1H), 3.92−3.83 (m, 1H), 3.84−3.72 (m, 12H), 3.65−3.58 (m, 2H), 3.49 (t, *J* 8.8 Hz, 1H), 1.50 (s, 0.3H), 1.48 (s, 3H), 1.22 (s, 12H).). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.4, 178.3, 159.4, 159.3, 131.0, 130.9, 130.3, 129.9, 129.8, 129.7, 129.7, 129.7, 129.6, 129.5, 129.5, 129.5, 114.0, 113.9, 112.0, 111.9, 105.3 (C1*β*), 105.1 (C1*α*), 101.3 (C1′*β*), 99.0 (C1*α*), 84.5, 83.2, 82.6, 82.4, 81.6, 81.4, 80.1, 79.6, 78.6, 78.2, 77.4, 75.4, 75.2, 74.9, 74.8, 73.2, 73.1,

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71.4, 68.5, 68.2, 62.9, 61.9, 55.4, 55.4, 55.4, 55.3, 38.8, 27.3, 26.9, 26.2. HRMS (ES): calcd. for $C_{51}H_{64}O_{15}NH_4^+$ 934.4583; found 934.4595.

4-*O*-(2,3,4,6-Tetra-*O*-(*p*-chlorobenzyl)-α/β-D-glucopyranosyl)-1,2-*O*-isopropylidene-5-*O*-pivaloyl-α-D-xylofuranose. Yield: 81 mg, 87%, α/β 9:1, white solid, R_f: 0.30 (pentane/EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.34−7.23 (m, 15H, ArH), 7.18 (d, J 8.2 Hz, 2H, ArH), 7.04 (d, J 7.9 Hz, 2H, ArH), 5.94 (d, J 2.6 Hz, 1H, H1α), 5.82 (d, J 3.0 Hz, 0.1H, H1β), 4.98 (d, J 2.0 Hz 1H, H1′α), 4.85 (d, J 11.4 Hz, 1H, CHHAr), 4.79−4.69 (m, 3H), 4.69−4.60 (m, 2H), 4.60−4.50 (m, 1H), 4.51−4.42 (m, 3H), 4.42−4.33 (m, 3H), 4.15 (s, 1H), 3.88 (t, J 9.3 Hz, 1H), 3.81 (d, J 10.0 Hz, 1H), 3.65 (s, 2H), 3.57 (d, J 7.6 Hz, 0.3H), 3.54−3.45 (m, 2H), 1.51 (s, 3H), 1.28 (s, 1.5H), 1.23 (s, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.4, 178.2 (C═O), 136.9, 136.8, 136.5, 136.5, 136.3, 136.3, 136.2, 136.2, 133.7, 133.7, 133.7, 133.4, 129.2, 129.1, 129.0, 129.0, 128.9, 128.9, 128.8, 128.7, 128.6, 128.6, 128.6, 112.0 ($C(CH_3)_2$), 112.0 ($C(CH_3)_2$), 105.1(C1β), 105.0 (C1α), 101.1 (C1′β), 98.6 (C1′α), 84.3, 83.1, 82.8, 82.4, 81.5, 81.3, 80.1, 79.8, 78.5, 78.0, 77.6, 77.5, 75.0, 74.7, 74.6, 74.2, 74.1, 73.9, 72.8, 72.7, 72.5, 71.2, 68.7, 62.8, 61.9, 38.7 ($C(CH_3)_3$), 29.7 (CH_3), 27.2 (CH_3), 27.1 (CH_3), 26.8 (CH_3), 26.7 (CH_3), 26.2 (CH_3). HRMS (ES): calcd. for $C_{62}H_{62}{}^{35}Cl_3{}^{37}ClO_{11}NH_4^+$ 952.2572; found 952.2599.

Phenyl 2,3,4-tri-*O*-(*p*-chlorobenzyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (17). Yield: 76 mg, 65%, α/β 1:4, syrup, R_f: 0.30 (pentane/EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.60 (d, J 6.5 Hz, 3H, ArH), 7.48 (d, J 6.9 Hz, 1H, ArH), 7.46−7.21 (m, 42H, ArH), 7.21−7.09 (m, 6H, ArH), 5.18 (d, J 2.6 Hz, 1H, H1′α), 5.07 (d, J 10.9 Hz, 0.5H), 5.01 (d, J 11.0 Hz, 2H), 4.97−4.85 (m, 4H), 4.85−4.71 (m, 6H), 4.71−4.51 (m, 8H), 4.47 (d, J 7.7 Hz, 1H, H1′β), 4.25 (d, J 10.8 Hz, 1H), 4.06 (t, J 9.2 Hz, 0.4H), 3.90 (s, 1H), 3.86−3.62 (m, 9H), 3.61−3.44 (m, 4H), 3.25 (t, J 9.3 Hz, 0.3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.9, 138.6, 138.6, 138.6, 138.5, 138.2, 138.2, 138.1, 137.0, 136.9, 136.7, 136.6, 136.5, 133.9, 133.8, 133.7, 133.7, 133.6, 133.6, 133.5, 133.4, 132.1, 131.6, 129.4, 129.2, 129.1, 128.9, 128.8, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 103.9 (C1′β), 97.5 (C1′α), 88.2, 87.4, 86.6, 86.5, 84.8, 82.3, 81.8, 81.2, 80.9, 80.3, 79.0, 78.8, 78.1, 78.0, 77.7, 75.8, 75.7, 75.1, 75.1, 75.0, 74.9, 74.8, 74.7, 74.6, 74.1, 74.0, 73.6, 73.5, 72.5, 70.4, 69.1, 68.7, 68.6, 66.0. HRMS (ES): calcd. for $C_{67}H_{65}Cl_3O_{10}SNH_4^+$ 1184.3702; found 1184.3724.

Phenyl 2,3,4-tri-*O*-(*p*-chlorobenzyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (18). Yield: 93 mg, 80%, α/β 1:1, syrup, R_f: 0.5 (pentane/EtOAc 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.59 (t, J 7.8 Hz, 4H, ArH), 7.52−7.23 (m, 67H, ArH), 7.18 (s, 8H, ArH), 7.11 (d, J 8.3 Hz, 2H, ArH), 5.20 (d, J 3.4 Hz, 1H, H1′α), 5.04 (d, J 11.5 Hz, 1H, CHHAr), 5.04 (d, J 11.4 Hz, 1H, CHHAr), 4.97 (d, J 11.0 Hz, 1H, CHHAr), 4.94 (d, J 2.8 Hz, 1H), 4.89 (d, J 12.2 Hz, 3H), 4.86−4.75 (m, 10H), 4.75−4.58 (m, 10H), 4.57−4.44 (m, 6H), 4.41 (d, J 7.7 Hz, 1H), 4.22 (d, J 10.0 Hz, 1H), 4.16 (dd, J 10.0, 3.5 Hz, 1H, H2′α), 4.04 (t, J 6.4 Hz, 1H), 4.01−3.98 (m, 2H), 3.97−3.90 (m, 2H), 3.87 (d, J 2.5 Hz, 2H), 3.79 (dd, J 11.0, 5.5 Hz, 1H), 3.75−3.44 (m, 15H), 3.24 (t, J 9.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.9, 138.9, 138.8, 138.7, 138.7, 138.5, 138.2, 137.9, 137.0, 136.9, 136.7, 136.6, 136.5, 136.5, 133.8, 133.7, 133.6, 133.5, 133.4, 131.9, 131.4, 129.4, 129.4, 129.1, 129.1, 129.1, 128.9, 128.8, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7, 127.5, 127.5, 127.5, 127.4, 127.4, 104.2 (C1′β), 97.9 (C1′α), 87.8, 87.1, 86.6, 86.5, 82.3, 81.2, 80.7, 79.4, 79.0, 78.7, 78.3, 78.1, 77.7, 75.3, 75.1, 74.9, 74.8, 74.6, 74.6, 74.5, 74.1, 74.0, 73.6, 73.5, 73.4, 73.1, 73.0, 72.6, 69.4, 69.1, 68.8, 68.7, 65.9. HRMS (ES): calcd. for $C_{67}H_{65}Cl_3O_{10}SNH_4^+$ 1184.3702; found 1184.3665.

Phenyl 2,3,6-tri-*O*-(*p*-chlorobenzyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (19). Yield: 54 mg, 46%, α/β 3:1, syrup, R_f: 0.29 (pentane/EtOAc 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49−7.40 (m, 3H, ArH), 7.28−7.10 (m, 44H, ArH), 7.10−6.99 (m, 10H, ArH), 6.94 (d, J 8.3 Hz, 1H, ArH), 6.89 (d, J 8.3 Hz, 2H, ArH), 5.49 (d, J 3.7 Hz, 1H, H1′α), 4.94 (d, J 10.7 Hz, 0.4H, CHHAr), 4.89 (d, J 11.2 Hz, 0.4H, CHHAr), 4.80 (d, J 11.4 Hz, 1H, CHHAr), 4.76−4.71 (m, 2H), 4.70−4.61 (m, 5H), 4.61−4.51 (m, 5H), 4.51−4.41 (m, 3H), 4.41−4.33 (m, 4H), 4.33−4.28 (m, 2H), 4.28−4.17 (m, 3H), 3.96−3.84 (m, 4H), 3.85−3.76 (m, 3H), 3.76 (dd, J 10.3, 2.3 Hz, 1H), 3.71−3.59 (m, 4H), 3.54−3.46 (m, 2H), 3.35 (m, 8H), 3.20 (dd, J 7.7, 4.2 Hz, 0.4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.9, 138.6, 138.5, 138.4, 138.4, 138.1, 137.9, 137.9, 137.3, 137.1, 137.0, 136.9, 136.7, 136.2, 133.7, 133.6, 133.6, 133.5, 133.2, 133.1, 132.9, 132.8, 131.9, 131.7, 131.7, 129.4, 129.3, 129.0, 129.0, 128.9, 128.8, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.9, 127.8, 127.6, 127.6, 127.5, 127.5, 127.4, 102.8 (C1′β), 98.1 (C1′α), 87.3, 87.2, 86.8, 84.8, 82.6, 81.0, 80.2, 80.0, 79.4, 79.2, 78.6, 76.3, 75.4, 74.9, 74.8, 74.7, 74.7, 74.5, 74.4, 74.2, 73.6, 73.6, 73.5, 73.2, 73.1, 72.7, 72.6, 72.4, 72.3, 70.1, 69.5, 68.8, 68.3, 67.9. HRMS (ES): calcd. for $C_{67}H_{65}Cl_3O_{10}SNH_4^+$ 1184.3702; found 1184.3699.

Phenyl 2,3,4-tri-*O*-(*p*-methoxybenzyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (20). An oven-dried 8 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with *t*BuBrettPhos (1.3 mg, 4 mol %), sodium *tert*-butoxide (35 mg, 0.36 mmol, 5.6 equiv), and phenyl 2,3,4-tri-*O*-(*p*-chlorobenzyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (76 mg, 0.065 mmol). The test tube was evacuated and backfilled with nitrogen (this sequence was repeated a total of three times), and methanol (0.053 mL, 1.3 mmol, 20 equiv) Simultaneously, an oven-dried 8 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with RockPhos Pd G3 (2.2 mg, 4 mol %). The test tube was then evacuated and backfilled with nitrogen (this sequence was repeated a total of three times), and 1,4-dioxane (0.33 mL) was added into tube via syringe. The mixture in the tube was stirred at room temperature for ∼1 min to form a homogeneous solution. The precatalyst solution was transferred into the other test tube via syringe. The resulting reaction mixture was stirred at 50 °C in a preheated oil bath for 20 h. After cooling to room temperature, the crude product was diluted with ethyl acetate and added Celite. The mixture was concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography (pentane as eluent with a gradient of EtOAc) giving the product as an oil. Yield: 67 mg, 89%, α/β 1:3, syrup, R_f: 0.66 (pentane/EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.40 (m, 2H), 7.32 (d, J 6.9 Hz, 1H), 7.26−7.00 (m, 40H), 6.84−6.76 (m, 6H), 6.73 (d, J 8.6 Hz, 3H), 4.95 (d, J 3.3 Hz, 1H, H1′α), 4.91 (d, J 10.9 Hz, 1H), 4.87−4.81 (m, 2H), 4.78−4.65 (m, 8H), 4.65−4.55 (m, 5H), 4.55−4.42 (m, 6H), 4.39 (d, J 13.1 Hz, 1H), 4.33 (d, J 7.9 Hz, 1H), 4.08 (d, J 10.7 Hz, 1H), 3.90 (t, J 9.2 Hz, 1H), 3.78 (d, J 12.8 Hz, 1H), 3.74−3.68 (m, 9H), 3.66 (d, J 7.1 Hz, 4H), 3.63−3.46 (m, 10H), 3.40−3.31 (m, 4H), 3.17 (d, J 9.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.4, 159.4, 159.3, 159.3, 159.2, 139.0, 138.7, 138.6, 138.5, 138.2, 138.2, 138.1, 134.2, 132.1, 131.3, 130.9, 130.8, 130.5, 130.4, 130.2, 130.0, 129.9, 129.7, 129.6, 129.5, 129.4, 129.1, 129.0, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.2, 113.9, 113.9, 103.9 (C1′β), 97.5 (C1′α), 88.2, 87.4, 86.5, 84.7, 82.3, 81.9, 81.0, 80.7, 80.1, 79.0, 78.9, 77.9, 77.8, 77.7, 75.8, 75.7, 75.5, 75.4, 75.2, 75.2, 75.1, 75.0, 74.9, 74.7, 74.7, 73.6, 73.5, 72.5, 70.3, 69.0, 68.8, 68.6, 66.4, 55.4, 55.4, 55.3. HRMS (ES): calcd. for $C_{70}H_{74}O_{13}SNH_4^+$ 1172.5188; found 1172.5165.

Phenyl 2,3,4-tri-*O*-(*p*-methoxybenzyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (21). An oven-dried 8 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with *t*BuBrettPhos (1.5 mg, 4 mol %), sodium *tert*-butoxide (43 mg, 0.54 mmol, 5.6 equiv), and phenyl 2,3,4-tri-*O*-(*p*-chlorobenzyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (93 mg, 0.080 mmol). The test tube was evacuated and backfilled with nitrogen (this sequence was repeated a total of three times), and methanol (0.06 mL, 1.6 mmol, 20 equiv) was added. Simultaneously, an oven-dried 8 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with RockPhos Pd G3 (3 mg, 4 mol %). The test tube was then evacuated and backfilled with nitrogen (this sequence was repeated a total of three times), and 1,4-dioxane

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(0.4 mL) was added into tube via syringe. The mixture in the tube was stirred at room temperature for ∼1 min to form a homogeneous solution. The precatalyst solution was transferred into the other test tube via syringe. The resulting reaction mixture was stirred at 50 °C in a preheated oil bath for 20 h. After cooling to room temperature, the crude product was diluted with ethyl acetate and added Celite. The mixture was concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography (pentane as eluent with a gradient of EtOAc) giving the product as an oil. Yield: 80 mg, 87%, α/β 3:1, syrup, R_f: 0.60 (pentane/EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (d, J 7.3 Hz, 5H, ArH), 7.39−6.99 (m, 61H, ArH), 6.93 (t, J 7.4 Hz, 1H, ArH), 6.83−6.64 (m, 13H, ArH), 4.94 (d, J 3.5 Hz, 1H, H1′α), 4.91−4.79 (m, 3H), 4.77−4.62 (m, 14H), 4.62−4.54 (m, 7H), 4.51 (d, J 4.2 Hz, 2H), 4.47 (d, J 4.6 Hz, 2H), 4.43 (d, J 5.5 Hz, 1H), 4.39 (d, J 2.9 Hz, 1H), 4.34 (d, J 11.5 Hz, 3H), 4.33−4.26 (m, 3H), 4.29 (d, J 7.7 Hz, 1H, H1′β), 4.03 (d, J 9.9 Hz, 1H), 3.97 (dd, J 10.3, 3.0 Hz, 1H, H2′α), 3.91 (t, J 6.5 Hz, 1H), 3.85−3.74 (m, 4H), 3.74−3.64 (m, 23H), 3.64−3.38 (m, 14H), 3.33 (td, J 9.6, 2.4 Hz, 3H), 3.17 (d, J 9.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.4, 159.3, 159.3, 159.2, 139.0, 138.9, 138.8, 138.8, 138.6, 138.2, 138.0, 134.3, 134.1, 131.8, 131.1, 130.9, 130.8, 130.5, 130.4, 130.3, 130.3, 130.0, 129.9, 129.6, 129.6, 129.5, 129.3, 129.0, 129.0, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.3, 127.0, 113.9, 113.9, 104.4 (C1′β), 97.9 (C1′α), 87.7, 87.1, 86.5, 82.3, 80.9, 80.6, 79.6, 79.0, 78.5, 77.9, 77.7, 75.5, 75.4, 75.3, 75.2, 75.1, 74.9, 74.8, 74.7, 74.6, 73.7, 73.6, 73.4, 73.3, 73.2, 73.1, 72.7, 69.2, 69.1, 69.0, 68.8, 66.4, 55.4, 55.3. HRMS (ES): calcd. for $C_{70}H_{74}O_{13}SNH_4^+$ 1172.5188; found 1172.5168.

Phenyl 2,3,6-tri-*O*-(*p*-methoxybenzyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (22). An oven-dried 8 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with *t*BuBrettPhos (2 mg, 4 mol %), sodium *tert*-butoxide (52 mg, 0.54 mmol, 5.6 equiv), and phenyl 2,3,6-tri-*O*-(*p*-chlorobenzyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α,β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (0.096 mmol). The test tube was evacuated and backfilled with nitrogen (this sequence was repeated a total of three times), and methanol (0.08 mL, 1.9 mmol, 20 equiv) Simultaneously, an oven-dried 8 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with RockPhos Pd G3 (3.3 mg, 4 mol %). The test tube was then evacuated and backfilled with nitrogen (this sequence was repeated a total of three times), and 1,4-dioxane (0.48 mL) was added into tube via syringe. The mixture in the tube was stirred at room temperature for ∼1 min to form a homogeneous solution. The precatalyst solution was transferred into the other test tube via syringe. The resulting reaction mixture was stirred at 50 °C in a preheated oil bath for 20 h. After cooling to room temperature, the crude product was diluted with ethyl acetate and added Celite. The mixture was concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography (pentane as eluent with a gradient of EtOAc) giving the product as an oil. Yield: 101 mg, 91%, α/β 3:1, syrup, R_f: 0.43 (pentane/EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52−7.43 (m, 3H, ArH), 7.26−7.04 (m, 47H, ArH), 7.00 (d, J 8.6 Hz, 2H, ArH), 6.81−6.75 (m, 1H, ArH), 6.74−6.69 (m, 9H, ArH), 6.57 (d, J 8.6 Hz, 1H, ArH), 5.63 (d, J 3.8 Hz, 1H, H1′α), 4.91 (dd, J 10.7, 3.3 Hz, 1H), 4.79 (d, J 11.4 Hz, 1H), 4.74−4.60 (m, 8H), 4.57 (d, J 9.8 Hz, 1H, H1α), 4.54 (s, 3H), 4.50−4.39 (m, 5H), 4.39−4.14 (m, 6H), 3.94 (dd, J 10.4, 3.6 Hz, 2H, H2′α), 3.91−3.87 (m, 2H), 3.87−3.81 (m, 2H), 3.78−3.72 (m, 2H), 3.72−3.58 (m, 18H), 3.51−3.26 (m, 9H), 7.30−7.08 (m, 33H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.4, 159.3, 159.1, 159.0, 158.8, 139.1, 138.8, 138.6, 138.6, 138.6, 138.2, 138.2, 138.0, 134.0, 133.9, 132.0, 131.8, 131.2, 130.8, 130.6, 130.2, 129.9, 129.8, 129.3, 129.2, 129.0, 128.9, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 127.4, 127.4, 113.8, 113.8, 113.7, 113.5, 102.8 (C1′β), 97.6 (C1′α), 87.5, 87.3 (C1α), 86.7, 84.8, 82.7, 80.8, 80.1, 79.9, 79.2, 78.6, 76.3, 75.5, 75.3, 74.9, 74.9, 74.6, 74.0, 73.9, 73.6, 73.5, 73.2, 72.9, 72.8, 72.7, 72.6, 69.9, 69.3, 68.7, 68.3, 68.1, 55.3(OCH_3), 55.3 (OCH_3), 55.3 (OCH_3). HRMS (ES): calcd. for $C_{70}H_{74}O_{13}SNH_4^+$ 1172.5188; found 1172.5172.

Phenyl 2,3,4-tri-*O*-(*p*-chlorobenzyl)-6-*O*-(2,3,4,6-tetra-*O*-(*p*-methoxybenzyl)-α/β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (29). Yield: 84 mg, 66%, α/β 1:3, syrup, R_f: 0.38 (toluene/acetone 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 (d, J 6.6 Hz, 2H, ArH), 7.27−7.08 (m, 20H, ArH), 7.08−6.95 (m, 6H, ArH), 6.93 (d, J 8.2 Hz, 1H, ArH), 6.81−6.63 (m, 9H, ArH), 4.97 (s, 1H, H1′α), 4.84−4.72 (m, 3H), 4.73−4.39 (m, 12H), 4.39−4.31 (m, 2H), 4.31−4.22 (m, 1H), 4.08 (d, J 10.8 Hz, 1H), 3.90−3.76 (m, 1H), 3.76−3.59 (m, 15H), 3.59−3.25 (m, 10H), 3.24 (s, 0.3H), 3.10 (t, J 9.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 159.4, 159.4, 159.3, 159.3, 159.3, 159.3, 159.2, 159.2, 137.0, 136.9, 136.7, 136.6, 136.6, 133.9, 133.8, 133.7, 133.6, 133.6, 133.6, 133.5, 132.1, 131.5, 131.2, 131.0, 130.8, 130.8, 130.7, 130.4, 130.3, 130.2, 129.7, 129.7, 129.6, 129.6, 129.5, 129.4, 129.4, 129.2, 129.2, 129.2, 129.1, 129.0, 128.8, 128.8, 128.7, 128.7, 128.7, 127.8, 127.5, 114.0, 113.9, 113.9, 113.9, 113.9, 113.8, 113.8, 104.0 (C1′β), 97.6 (C1′α), 88.2, 87.4 (C1β), 86.7, 86.5, 84.6, 82.1, 81.5, 81.2, 80.9, 80.1, 79.1, 78.8, 78.2, 77.9, 77.7, 77.0, 75.5, 75.3, 75.1, 74.8, 74.7, 74.7, 74.7, 74.6, 74.6, 74.5, 74.1, 74.1, 73.2, 73.1, 72.2, 71.7, 71.3, 70.7, 70.5, 68.8, 68.7, 68.1, 66.0, 65.8, 55.4, 55.4, 55.3, 55.3. HRMS (ES): calcd. for $C_{71}H_{73}Cl_3O_{14}SNH_4^+$ 1304.4125; found 1304.4163.

Phenyl 2,3,6-tri-*O*-(*p*-cyanobenzyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl)-α/β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (30). Yield: 52 mg, 46%, α/β 3:1, syrup, R_f: 0.57 (pentane/EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.53−7.37 (m, 10H, ArH), 7.31−7.00 (m, 40H, ArH), 5.29 (d, J 3.4 Hz, 1H, H1$_{\alpha}$′), 5.13 (d, J 12.6 Hz, 1H, CHHAr), 4.88 (d, J 13.2 Hz, 1H, CHHAr), 4.86−4.67 (m, 6H), 4.65−4.57 (m, 3H), 4.57−4.51 (m, 2H), 4.49−4.39 (m, 5H), 4.37 (d, J 10.7 Hz, 1H, CHHAr), 4.31 (d, J 12.2 Hz, 2H, CHHAr), 4.28−4.20 (m, 1H), 3.94 (t, J 9.2 Hz, 2H), 3.89−3.77 (m, 2H), 3.76−3.69 (m, 2H), 3.66 (t, J 8.8 Hz, 1H), 3.60−3.27 (m, 9H), 3.24 (dd, J 8.3, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 144.4, 144.0, 143.9, 143.7, 143.4, 143.0, 138.4, 138.4, 138.2, 138.1, 138.0, 137.9, 137.9, 137.7, 133.4, 133.3, 132.5, 132.3, 132.2, 132.2, 132.1, 132.0, 131.9, 131.7, 129.5, 129.2, 129.1, 128.6, 128.6, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.6, 127.6, 127.4, 127.3, 126.5, 119.0 (CN), 118.9 (CN), 118.9 (CN), 118.8 (CN), 118.8 (CN), 118.7 (CN), 111.7, 111.6, 111.3, 111.2, 111.1, 111.1, 102.8 (C1′β), 98.1 (C1′α), 87.3 (C1α), 87.2 (C1β), 86.8, 85.4, 85.1, 82.8, 82.0, 81.3, 80.5, 79.6, 79.2, 78.8, 77.8, 77.8, 76.5, 75.9, 75.7, 75.3, 75.1, 75.0, 74.6, 74.5, 74.4, 74.3, 73.8, 73.7, 73.6, 73.2, 72.3, 72.2, 71.4, 69.6, 68.9, 68.6, 68.4. HRMS (ES): calcd. for $C_{70}H_{65}N_3O_{10}SNH_4^+$ 1157.4729; found 1157.4708.

Phenyl 2,3,4-tri-*O*-(*p*-cyanobenzyl)-6-*O*-(2,3,4,6-tetra-*O*-(*p*-chlorobenzyl)-α/β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (31). Yield: 63 mg, 60%, α/β 1:2, syrup, R_f: 0.41 (pentane/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52−7.41 (m, 20H, ArH), 7.41−7.34 (m, 7H, ArH), 7.29 (s, 5H, ArH), 7.26−7.01 (m, 75H, ArH), 6.95 (d, J 8.4 Hz, 5H, ArH), 6.90 (d, J 8.3 Hz, 2H, ArH), 5.10 (d, J 3.4 Hz, 1H, H1′α), 4.86 (d, J 11.8 Hz, 2H, CHHAr), 4.80 (d, J 11.3 Hz, 1H, CHHAr), 4.78−4.67 (m, 9H), 4.67−4.58 (m, 15H), 4.58−4.54 (m, 5H), 4.53−4.48 (m, 8H), 4.48−4.43 (m, 2H), 4.40 (d, J 4.4 Hz, 3H), 4.38−4.34 (m, 4H), 4.33−4.28 (m, 4H), 4.26 (d, J 7.7 Hz, 2H, H1′β), 4.08 (d, J 9.8 Hz, 2H), 3.79 (t, J 9.3 Hz, 1H), 3.75 (s, 2H), 3.68−3.60 (m, 5H), 3.56−3.43 (m, 19H), 3.43−3.35 (m, 3H), 3.34−3.24 (m, 9H), 2.74 (t, J 9.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 143.4, 143.3, 143.2, 143.1, 143.1, 137.1, 137.0, 136.9, 136.8, 136.5, 136.5, 136.4, 136.3, 133.7, 133.7, 133.6, 133.5, 133.5, 133.4, 133.2, 132.4, 132.3, 132.3, 132.3, 132.3, 131.8, 131.4, 129.3, 129.3, 129.2, 129.1, 129.1, 129.1, 129.0, 129.0, 128.8, 128.7, 128.7, 128.7, 128.6, 128.4, 128.0, 127.9, 127.7, 127.3, 118.7 (CN), 118.7 (CN), 118.6 (CN), 118.6 (CN), 118.6 (CN), 111.7, 111.7, 111.7, 111.6, 103.7(C1′β), 97.3 (C1′α), 88.2, 87.3, 86.8, 86.5, 84.5, 82.0, 81.4, 81.2, 80.3, 78.9, 78.5, 78.3, 77.7, 77.6, 74.8, 74.8, 74.7, 74.5, 74.5, 74.3, 74.1, 73.9, 73.8, 73.7, 72.7, 72.7, 71.2, 70.3, 68.8, 68.6, 68.4, 65.5. HRMS (ES): calcd. for $C_{70}H_{61}{}^{35}Cl_3{}^{37}ClN_3O_{10}SNH_4^+$ 1295.3141; found 1295.3151.

Phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-(*p*-cyanobenzyl)-β-D-glucopyranosyl)-1-thio-β-D-galactopyranoside (33-β). Clear syrup, R_f: 0.37 (pentane/EtOAc 4:3), $[\alpha]_D^{RT}$ + 64 (c 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93−7.86 (m, 2H, ArH),

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7.76−7.71 (m, 2H, ArH), 7.70−7.64 (m, 2H, ArH), 7.58−7.41 (m, 15H, ArH), 7.40−7.12 (m, 23H), 5.85 (d, J 2.7 Hz, 1H, H4), 5.63 (t, J 9.9 Hz, 1H, H2), 5.43 (dd, J 10.0, 3.1 Hz, 1H, H3), 4.99 (d, J 12.5 Hz, 1H, CHHAr), 4.93 (d, J 9.9 Hz, 1H, H1), 4.82 (d, J 12.7 Hz, 1H, CHHAr), 4.68 (t, J 12.5 Hz, 2H, CH_2Ar), 4.60 (d, J 12.6 Hz, 1H, CHHAr), 4.54 (d, J 12.6 Hz, 1H, CHHAr), 4.50 (d, J 13.1 Hz, 1H, CHHAr), 4.38 (d, J 11.2 Hz, 1H, CHHAr), 4.35 (d, J 7.6 Hz, 1H, H1′β), 4.19−4.12 (m, 1H), 3.97 (dd, J 10.5, 4.8 Hz, 1H), 3.36 (d, J 7.6 Hz, 2H), 4.66−4.61 (m, 1H), 4.61−4.54 (m, 2H), 3.80−3.69 (m, 2H), 3.61 (s, 2H), 3.54 (dd, J 7.6, 4.8 Hz, 2H), 4.54−4.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.7 (C═O), 165.5 (C═O), 165.2 (C═O), 143.6, 143.6, 143.5, 143.3, 133.9, 133.8, 133.5, 133.5, 132.4, 132.3, 132.3, 132.3, 130.9, 130.0, 129.9, 129.8, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.8, 127.5, 127.4, 118.8 (CN), 118.8 (CN), 118.6 (CN), 118.6 (CN), 111.7, 111.6, 111.5, 111.5, 103.6 (C1′β), 85.3, 84.6 (C1β), 82.2, 77.8, 76.7, 74.7, 74.5, 73.9, 73.6, 73.3 (C3), 72.7, 69.1, 68.6 (C4), 68.4, 67.6 (C2). HRMS (ES): calcd. for $C_{71}H_{58}N_4O_{13}SNH_4^+$ 1224.4059; found 1224.4050.

Phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-(*p*-cyanobenzyl)-α-D-glucopyranosyl)-1-thio-β-D-galactopyranoside (33-α). Clear syrup, R_f: 0.21 (pentane/EtOAc 4:3), $[\alpha]_D^{RT}$ + 53 (c 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.90 (d, J 7.3 Hz, 2H, ArH), 7.76 (d, J 7.3 Hz, 2H, ArH), 7.67 (d, J 7.3 Hz, 2H, ArH), 7.59−7.41 (m, 11H, ArH), 7.39−7.23 (m, 14H, ArH), 7.23−7.14 (m, 5H, ArH), 5.89 (d, J 2.7 Hz, 1H, H4), 5.66 (t, J 9.9 Hz, 1H, H2), 5.48 (dd, J 9.9, 3.1 Hz, 1H, H3), 4.93 (d, J 9.9 Hz, 1H, H1), 4.84 (d, J 12.7 Hz, 1H, CHHAr), 4.78 (d, J 3.3 Hz, 1H, H1′), 4.73 (d, J 12.8 Hz, 1H, CHHAr), 4.67 (d, J 12.4 Hz, 2H, CH_2Ar), 4.59−4.45 (m, 3H, CH_2Ar), 4.42 (d, J 13.2 Hz, 1H, CHHAr), 4.19 (t, J 6.0 Hz, 1H, H5), 3.93−3.81 (m, 3H), 3.70−3.52 (m, 5H), 3.45 (dd, J 9.6, 3.4 Hz, 1H, H2′). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.6 (C═O), 165.6 (C═O), 165.2 (C═O), 143.9, 143.5, 143.3, 143.1, 134.2, 133.9, 133.5, 132.3, 132.3, 132.3, 131.1, 130.0, 129.9, 129.8, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.2, 127.8, 127.5, 127.3, 118.8 (CN), 118.7 (CN), 118.7 (CN), 118.6 (CN), 111.7, 111.6, 111.6, 97.0 (C1′α), 85.9 (C1), 81.8, 80.3 (C2′), 77.8, 76.0 (C5), 74.4, 73.8, 73.2 (C3), 72.6, 72.0, 70.5, 69.0, 68.6 (C4), 67.7 (C2), 66.3. HRMS (ES): calcd. for $C_{71}H_{58}N_4O_{13}SNH_4^+$ 1224.4059; found 1224.4042.

Phenyl 2,3,6-tri-*O*-(*p*-cyanobenzyl)-6-*O*-((2,3,6-tri-*O*-(*p*-chlorobenzyl)-α/β-D-glucopyranosyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α,β-D-galactopyranosyl))-1-thio-β-D-glucopyranoside (34). Yield: 50 mg, 72%, syrup, R_f: 0.62 (pentane/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.69−7.05 (m, 150H, ArH), 7.02 (d, J 8.2 Hz, 2H, ArH), 5.68 (d, J 3.5 Hz, 1H, $H1_\alpha$), 5.63 (d, J 3.6 Hz, 1H, H1′α or H1″α), 5.22 (d, J 3.4 Hz, 1H, H1′α or H1″α), 5.16 (d, J 3.2 Hz, 1H, H1′α or H1″α), 5.07−4.28 (m, 67H), 4.19 (d, J 11.3 Hz, 2H), 4.11−3.31 (m, 52H), 3.16 (t, J 9.3 Hz, 1H), 2.94 (t, J 9.3 Hz, 1H), 2.84 (t, J 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 143.7, 143.6, 143.6, 143.5, 143.4, 143.3, 143.3, 139.1, 139.1, 138.9, 138.9, 138.6, 138.6, 138.6, 138.5, 138.3, 138.2, 138.1, 138.1, 138.1, 137.9, 137.8, 137.5, 137.5, 137.3, 137.3, 137.2, 137.0, 136.9, 136.8, 136.7, 136.7, 133.8, 133.6, 133.5, 133.3, 133.3, 133.1, 133.0, 132.5, 132.5, 132.4, 132.0, 131.6, 129.6, 129.5, 129.4, 129.2, 129.2, 129.1, 129.1, 128.9, 128.6, 128.5, 128.5, 128.4, 128.4, 128.1, 128.1, 128.0, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 118.9 (CN), 118.9 (CN), 118.8 (CN), 118.7 (CN), 118.7 (CN), 111.9, 111.8, 111.8, 103.8 (C1′β or C1″β), 103.6 (C1′β or C1″β), 103.3 (C1′β or C1″β), 103.1 (C1′β or C1″β), 98.3 (C1′α or C1″α), 98.1 (C1′α or C1″α), 97.6 (C1′α or C1″α), 97.1 (C1′α or C1″α), 91.5, 88.3, 87.5, 87.4, 86.9, 86.7, 85.0, 83.1, 82.9, 82.8, 82.3, 81.8, 81.6, 81.5, 81.3, 80.4, 80.1, 79.6, 79.5, 79.4, 79.3, 79.2, 78.6, 78.6, 78.5, 78.4, 75.8, 75.6, 75.6, 75.3, 75.1, 75.1, 75.0, 74.7, 74.6, 74.5, 74.4, 74.4, 74.3, 74.1, 74.0, 74.0, 74.0, 73.9, 73.8, 73.7, 73.6, 73.4, 72.9, 72.9, 72.8, 72.7, 72.0, 71.3, 70.7, 70.6, 70.4, 70.4, 70.0, 69.8, 69.6, 69.2, 69.1, 68.6, 68.3, 68.1, 65.9, 65.7, 65.3. HRMS (ES): calcd. for $C_{97}H_{90}Cl_3N_3O_{15}SNH_4^+$ 1691.5501; found 1691.5505.

L-Menthyl β-D-glucopyranoside (37). From L-Menthyl 2,3,4,6-tetra-*O*-(*p*-chlorobenzyl)-β-D-glucopyranoside: The protected glucoside (80 mg, 0.1 mmol) was dissolved in 4 mL 1:1 mixture of MeOH and EtOAc. The flask was flushed with nitrogen and Pd/C was added (10%, 100 mg). The flask was evacuated and backfilled with hydrogen gas. A drop of concentrated hydrochloric acid was added and the mixture was stirred overnight. The mixture was filtered and evaporated to dryness giving the product as a syrup, 28 mg, 90%. From L-Menthyl 2,3,4,6-tetra-*O*-(*p*-cyanobenzyl)-β-D-glucopyranoside: The protected glucoside (39 mg, 0.05 mmol) was dissolved in 4 mL 1:1 mixture of MeOH and EtOAc. The flask was flushed with nitrogen and Pd/C was added (10%, 50 mg). The flask was evacuated and backfilled with hydrogen gas. A drop of concentrated hydrochloric acid was added and the mixture was stirred overnight. The mixture was filtered and evaporated to dryness. The crude compound was purified by flash column chromatography with EtOAc as eluent with a gradient of MeOH giving the product as a syrup, 12 mg, 70%.R_f: 0.58 (EtOAc/MeOH 10:1), $[\alpha]_D^{RT}$ −42.4 (c 1, MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ_H 4.35 (d, J 7.7 Hz, 1H, H1), 3.89−3.81 (m, 1H, H6a), 3.67 (dd, J 11.7, 5.2 Hz, 1H, H6b), 3.57 (t, J 10.7 Hz, 1H), 3.38−3.26 (m, 2H, H3, H4), 3.26−3.21 (m, 1H, H5), 3.14 (t, J 8.4 Hz, 1H, H2), 2.31 (s, 1H), 2.11 (d, J 13.2 Hz, 1H), 1.66 (s, 1H), 1.36 (s, 1H), 1.32−1.26 (m, 1H), 1.28−1.18 (m, 1H), 1.14−0.96 (m, 1H), 0.93 (d, J 6.6 Hz, 3H), 0.88 (d, J 7.1 Hz, 3H), 0.80 (d, J 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ_C 101.3 (C1), 78.2, 77.7, 75.1, 71.9, 63.0, 49.3, 41.7, 35.7, 32.8, 26.2, 24.2, 22.7, 21.5, 16.3. HRMS (ES): calcd. for $C_{16}H_{30}O_6NH_4^+$ 336.2381; found 336.2384.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00528.

^{1}H and ^{13}C spectra of all compounds. (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hhj@chem.au.dk.

Notes

The authors declare no competing financial interest.

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