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Simultaneous Regio- and Enantiodifferentiation in Carbohydrate Coupling

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Dedicated to Professor J. L. García Ruano

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The glycosylation of 1,2-*trans*-diequatorial diols derived from tetrabenzoylated and tetrabenzylated D- and L-*chiro*-inositol with several glycosyl donors has been investigated. An unprecedented dependence of the regioselectivity on the absolute configuration of the acceptor has been found. However this trend is also modulated by the nature of the protecting groups on both the donor and acceptor, with benzoylated acceptors affording higher levels of regioselectivity. Most of the results have been rationalized by DFT calculations which indicate that stereoelectronic factors and hydrogen bonding between the donor and acceptor govern their relative orientation and determine the regiochemical outcome of the process. These studies also highlight the role of the acyl group adjacent to the OH to be glycosylated in facilitating the glycosylation reaction.

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Introduction

A great deal of attention has been devoted to glycosylation reactions and a wide array of glycosylation methods, strategies and procedures have been reported in the literature.[1,2] Established mechanistic thinking[3] and extended experimental experience[4] emphasize the importance of protecting groups for the effective donor-acceptor match[4b] which determines the feasibility and the selectivity of the glycosylation. From the first observation[5] that stereoselective 1,2-*trans* glycosylation can be achieved through neighboring group participation,[6] careful design of protecting groups has been used to control the reactivity of the partners and the selectivity of the process.[1,7] These observations, which recently led to the reciprocal donor-acceptor selectivity concept (RDAS),[8] constitute outstanding experimental evidence of the key role of the donor-acceptor match[4b] in governing the glycosylation outcome.

Although glycosylations crucially depend on both the donor and acceptor,[4b] most glycosylation studies have focused on the role of glycosyl donors in controlling the stereoselectivity of the process. A remarkable exception is the glycosylation with glycosylidene diazirines where the key factor is the kinetic acidity of the acceptor OH group. In this case, the emphasis is shifted to the role of polyol glycosyl acceptors in controlling the regioselectivity of glycosylation.[9]

As part of our work on the synthesis of inositolphosphoglycans (IPGs) as potential mediators in the insulin signaling process, we have extensively studied the glycosylation reactions of *myo* and D- and L-*chiro* inositol derivatives with different glycosyl donors, in particular 2-azido-2-deoxy-glycopyranosyl trichloroacetimidates.[10] In an attempt to extend the applicability of the double stereodifferentiation principle[11a] in glycosylation reactions[11b] we have also studied the stereoselectivity of the glycosylation of D- and L-*chiro* inositol derivatives with several glycosyl donors.[12] We have now observed that when differently protected 1,2-diols, derived from both *chiro*-inositol enantiomers, are used as acceptors, both the absolute configuration of the acceptor as well as the nature of the donor's and acceptor's protecting groups play a key role in the regiochemistry of the coupling. A few examples of regioselective glycosylations of 1,2-*cis*-axial/equatorial[9,13] and 1,2-*trans*-diequatorial diols[9,10b,14] have been described and the influence of the donor's protecting groups on the regiochemistry of polyol glycosylation has been recently investigated.[8] A notable example of regioselective glycosylation of a 1,2-*trans*-

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diequatorial diol is the virtually complete regioselective galactosylation of the OH-4 group of *p*-methoxyphenyl-2-deoxy-2-tetrachlorophthalimido-β-D-glucopyranoside **I** (see Figure 1) using a 2,3,4-tri-*O*-acetyl thiophenyl galactopyranoside as glycosyl donor.[14] In this case it was also reported that OH-3 and OH-4 in **I** show different preferences for fucosylation depending on the nature of the protecting groups in the fucosyl donor. This was later observed in the mannosylation of the diequatorial diols of methyl 4,6-*O*-benzylidene-α- and -β-D-glucopyranoside (**II** and **III**) in the course of RDAS studies.[8a] The glycosylation of the OH-6 group of the *myo*-inositol derivative **IV** with 2-azido-2-deoxy-D-glucopyranosyl trichloroacetimidates is another case of regioselective glycosylation of a 1,2-*trans*-diequatorial diol system **IV** which is frequently performed in our laboratories for the preparation of building blocks for IPG synthesis.[10b] There may be some other examples of successful regioselective glycosylations of 1,2-*trans*-diequatorial diols in the course of complex glycoside and oligosaccharide synthesis. Nevertheless, to the best of our knowledge the results presented here constitute the first reported observations and rationalization of the effect of the absolute configuration and protecting groups of diol glycosyl acceptors[15] on the regiochemistry of glycosylations.

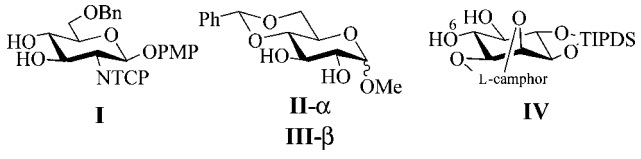
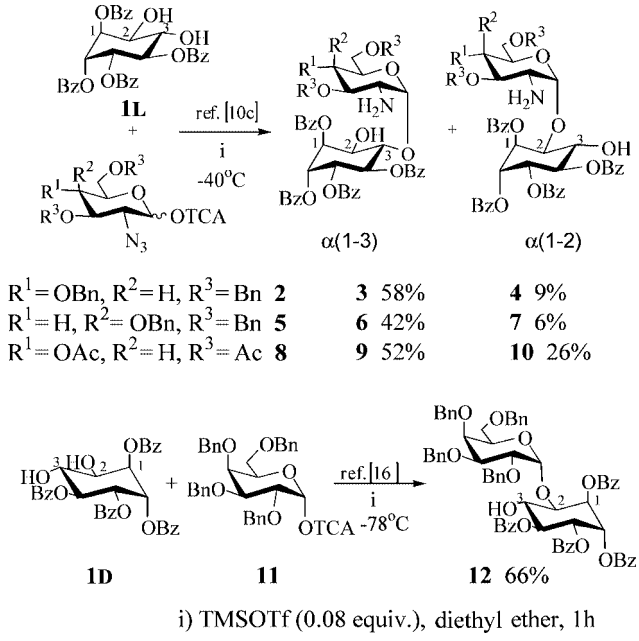


Figure 1. Acceptors that have shown good regioselectivities in glycosilation reactions.

We have previously shown that the coupling of L-*chiro*-inositol terabenzoate **1L** with trichloroacetimidate **2** gave a 6.4:1 mixture of the α(1→3) (**3**) and the α(1→2) (**4**) pseudodisaccharides in 67% combined yield (Scheme 1). Similarly, the glycosylation of **1L** with **5** gave a 7:1 mixture of the α(1→3) (**6**) and the α(1→2) (**7**) compounds in 48% overall yield.[10c] The regioselectivity was poorer but followed the same trend in the glycosylation with the less reactive trichloroacetimidate **8** which afforded a 2:1 mixture of the α(1→3) (**9**) and the α(1→2) (**10**) pseudodisaccharides in 78% overall yield. Interestingly, the glycosylation of the corresponding D-*chiro*-inositol diol **1D** with trichloroacetimidate **11** under the same conditions gave a α/β mixture. Here the 2-*O*-glycosylated products predominated and afforded the α(1→2) pseudodisaccharide **12** as the only product in 66% yield when the reaction temperature was decreased from –40 to –78 °C.[16] In neither case were transbenzoylation processes detected.



Scheme 1. Reaction of **1L** with **2**, **5** and **8** and **1D** with **11**.

These results allowed for the straightforward syntheses of IPG building blocks **V** and **VI** and fagopyritol B (**VII**) as indicated in Figure 2 which emphasizes the different behavior of both enantiomers regarding the regioselectivity of these specific glycosylations.

Results and Discussion

In order to confirm the influence of the absolute configuration of the acceptor on the regioselectivity of these glycosylations we have examined the reactions of **1D** with **2** and **5** and **1L** with **11**. The results are given in Table 1 (for structures see Figure 3). In the glycosylations of **1D** the α(1→2) compounds (**13** and **14**) slightly predominated over the α(1→3) pseudodisaccharides (**15** and **16**), thus confirming that the absolute configuration of the acceptor plays a role

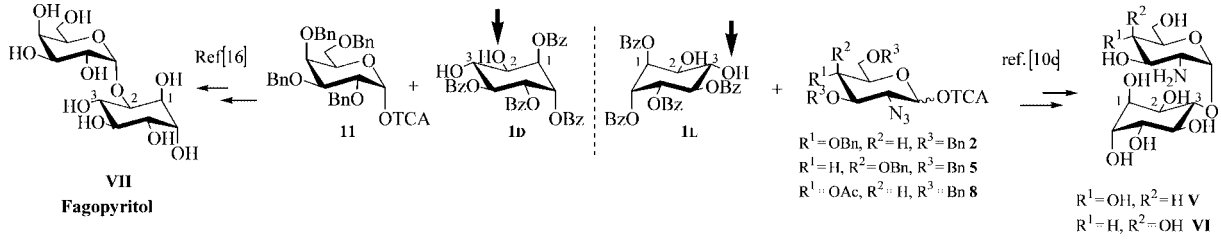


Figure 2. Regioselective reactions of D- and L-*chiro* inositol acceptors.

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in the regiochemistry of the process. Although, in these cases the regioselectivity was poorer than for **1L**. In the glycosylation of **1L** with **11** a mixture of the α(1→2) (**17**), β(1→2) (**18**) and α(1→3) (**19**) pseudodisaccharides was observed even when the reaction was performed at –78 °C. Thus, the tendency for the D enantiomer (**1D**) to form the α(1→2) pseudodisaccharide, as observed in the glycosylation with **11**, was also observed in the glycosylation with **2** and **5**. However, the tendency for the L enantiomer (**1L**) to form the α(1→3) glycosidic linkage, as observed in the glycosylation with **2** and **5**, was not observed in the glycosylation with **11**. As deduced, other factors, most likely the nature of the protecting group at C-2 in the glycosyl donor, also seem to be playing a role in the regiochemistry of the process (Table 1).

Table 1. Glycosylation reactions of acceptors **1L** and **1D** with donors **2**, **5**, **11** and **20**. Reaction conditions: TMSOTf (0.08 equiv.), –40 °C, diethyl ether, 1 h, –40 °C; TCA = trichloroacetimidate.

	1L	**1D**
2	α(1-3) **3** 58 % α(1-2) **4** 9 % 67 % C3/C2 = 6.4:1	α(1-3) **15** 27 % α(1-2) **13** 40 % 67 % C3/C2 = 1:1.5
5	α(1-3) **6** 42 % α(1-2) **7** 6 % 48 % C3/C2 = 7:1	α(1-3) **16** 28 % α(1-2) **14** 35 % 63 % C3/C2 = 1:1.25
11	α(1-2) **17** 24% β(1-2) **18** 6 % α(1-3) **19** 21% 51%[a] C3/C2 = 1:1.4	α(1-2) **12** 66 % 66%[a] C3/C2 = 0:1
20	β(1-3) **23** 30% 30%[b] C3/C2 = 100:0	β(1-2) **21** β(1-3) **22** 95%[c] C3/C2 = 1:5[d]

[a] T = –78 °C. [b] Reaction time: 3 h at –40 °C, 1 h at –10 °C. [c] Reaction time: 3 h at –40 °C. [d] Determined by ^{1}H NMR spectroscopy.

At this point, the glycosylation of **1D** and **1L** with trichloroacetimidate **20**, bearing a trifluoroacetamide participating group at C-2, was investigated. The results are also shown in Table 1 and Figure 3. In this case, the regiochemistry of the glycosylation followed the same trend as already observed for donors **2** and **5**: the reaction with **1D** afforded a 5:1 mixture of the β(1→2) (**21**) and the β(1→3) (**22**) compounds with excellent yield while the reaction with **1L** yielded the β(1→3) derivative **23** as the only product, albeit in lower yield.

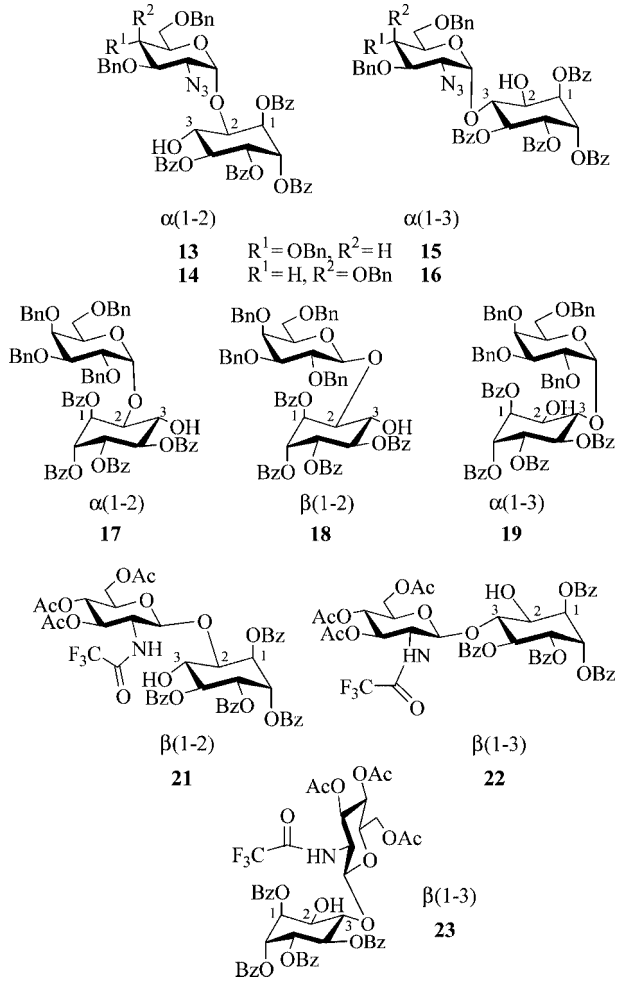

Figure 3. Structures of Table 1.

Therefore, with the only exception of the reaction of **1L** with **11** (with a benzyloxy group in position 2), in all the cases studied with tetrabenzoylated acceptors the regiochemistry of the glycosylations seems to be dictated by the absolute configuration of the glycosyl acceptor. These results constitute the first experimental evidence of simultaneous regio- and enantiodifferentiation in carbohydrate coupling.

The clear influence of the absolute configuration of the acceptor could not be observed when a similar study was carried out with the tetrabenzylated glycosyl acceptors **24D** and **24L** which were prepared from **1D**[10c] and **1L**,[16] respectively, as indicated in Scheme 2 for the D enantiomer. These syntheses required long protecting group manipulations due to the difficulties found when direct benzylation of the silylated tetraol D-*chiro*-inositol derivative was tried instead of the benzoylation that affords **1D** and **1L**.[10c,16] The results of the glycosylation reactions with acceptors **24D** and **24L** are presented in Table 2 and Figure 4.

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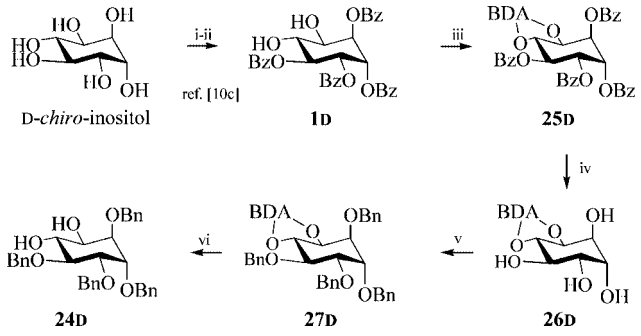

Scheme 2. Synthesis of benzylated acceptor **24D**. Reaction conditions: i) a) TIPDSCl2, DMAP, DMF, imidazole, r.t., 16 h; b) BzCl, DMAP, Py, room temp., 16 h, 36% (two steps); iii) (HF)*n*Py, THF, 90%; iii) 2,3-butanedione, trimethyl orthoformate, CSA, MeOH 70 °C, 5 h. 92%; iv) MeONa/MeOH 1 M, MeOH/THF room temp., 2 h, 100%; v) BnBr, NaH, *t*BuNH$_4$I, DMF, 20 °C to room temp., 12 h. 91%; vi) TFA/H$_2$O = 9:1, room temp., 4 h, 86%.

Substituting benzoyl for benzyl groups resulted in an increase of the proportions of the β anomers and small amounts of uncharacterized pseudotrisaccharides, probably due to the higher reactivity of the benzylated acceptors.[10e] Compared to the results described above for **1D**, the yield and the regioselectivity for the glycosylation of **24D** were similar when using donor **2** affording the α(1→2) **28** and β(1→2) **29** pseudodisaccharides in a slightly higher proportion than the α(1→3) **30** and β(1→3) **31** compounds (C3/C2 = 1:1.5). No selectivity at all was observed with donor **5** where the 1→2 (**32** and **33**) and the 1→3 (**34** and **35**) compounds were formed in similar proportions (C3/C2 = 1.1:1). For **24L**, the regioselectivity observed in the reactions with both **2** and **5**, was reversed compared to **1L**. The mixture of 1→2 pseudodisaccharides (α**36** and β**37** in the glycosylation with **2** and α**40** and β**41** in the glycosylation with **5**) predominated (C3/C2 = 1:2.5) over the 1→3 compounds (α**38** and β**39** in the glycosylation with **2** and β**42** in the glycosylation with **5**) and the yields were considerably decreased (Table 2 and Figure 4).

Table 2. Glycosylation reactions of acceptors **24L** and **24D** with donors **2** and **5**. Reaction conditions: TMSOTf (0.08 equiv.), –40 °C, diethyl ether, 1 h, –40 °C; TCA = trichloroacetimidate.

	24L	**24D**
2	α(1-2) **36** 21 %	α(1-2) **28** 23 %
	β(1-2) **37** 13 %	β(1-2) **29** 16 %
	α(1-3) **38** 8 %	α(1-3) **30** 13 %
	β(1-3) **39** 2 %	β(1-3) **31** 13 %
	αβ-Trisaccaride 4%	---
	48 %	65 %
	C3/C2 = 1:3.4	C3/C2 = 1:1.5
5	α(1-2) **40** 5 %	α(1-2) **32** 12 %
	β(1-2) **41** 20 %	β(1-2) **33** 14 %
	β(1-3) **42** 10 %	α(1-3) **34** 6 %
	---	β(1-3) **35** 22 %
	αβ-Trisaccaride 4%	αβ-Trisaccaride 17%
	39 %	71 %
	C3/C2 = 1:2.5	C3/C2 = 1.1:1

Therefore, the nature of the protecting group in the glycosyl acceptor also seems to exert an important influence on the regiochemical outcome of these glycosylations. While a comparison of the results obtained for **1L** and **1D**

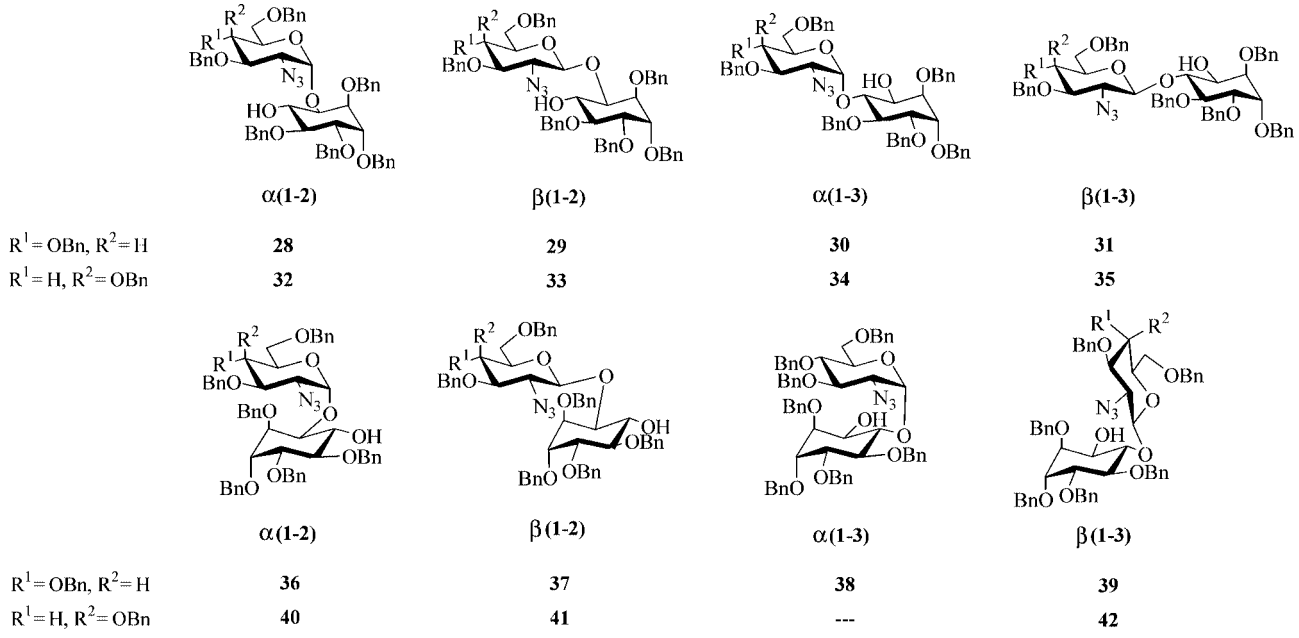

Figure 4. Structures of Table 2.

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under identical experimental conditions evidences the importance of stereoelectronic factors on the regiochemistry of the process, a comparison of the behavior of **1L** and **24L** also provides experimental evidence for the importance of protecting groups on the donor-acceptor match[4b] affecting the yield and the stereoselectivity but also the regioselectivity of the coupling.

In an attempt to rationalize the above experimental results, the interactions taking place in the process of glycosidic bond formation were analyzed by means of DFT calculations.[17] Glycosyl oxocarbenium ions with 2-azide and 2-methoxy groups without substituents at positions 3 and 4 (far from the reaction center) and methyl instead of benzyl ether at position 6 were used as glycosyl donor models. The benzoylated glycosyl acceptors were modeled by removing the substituents at positions 5 and 6 of the cyclitol ring and changing the benzoyl to acetyl groups. Methoxylated glycosyl acceptors were used as models for benzylated derivatives. Several nucleophile-carbonium ion complexes differing in the nucleophile orientation, acceptor configuration (D or L) and attacking OH group (OH-2 or OH-3 of the *chiro*-inositol ring) were optimized. Most of the complexes showed a C1′–O2(O3) bond length around 2 Å. However, some slightly more stable complexes with shorter distances for the incipient glycosidic bond were found. Complexes obtained with 2-azide (denoted as **A**) and 2-methoxy (denoted as **M**) substituted donors and L and D acetylated acceptors are named as **AL** and **ML** and **AD** and **MD** and are shown in Figure 5 and Figure 6, respectively. In each case the approximation through position 2 or 3 is indicated by the corresponding number. Complexes obtained from L methoxylated acceptor (denoted as **L′**) with 2-azide donor are also shown in Figure 5. The equivalence between models and real systems is also indicated.

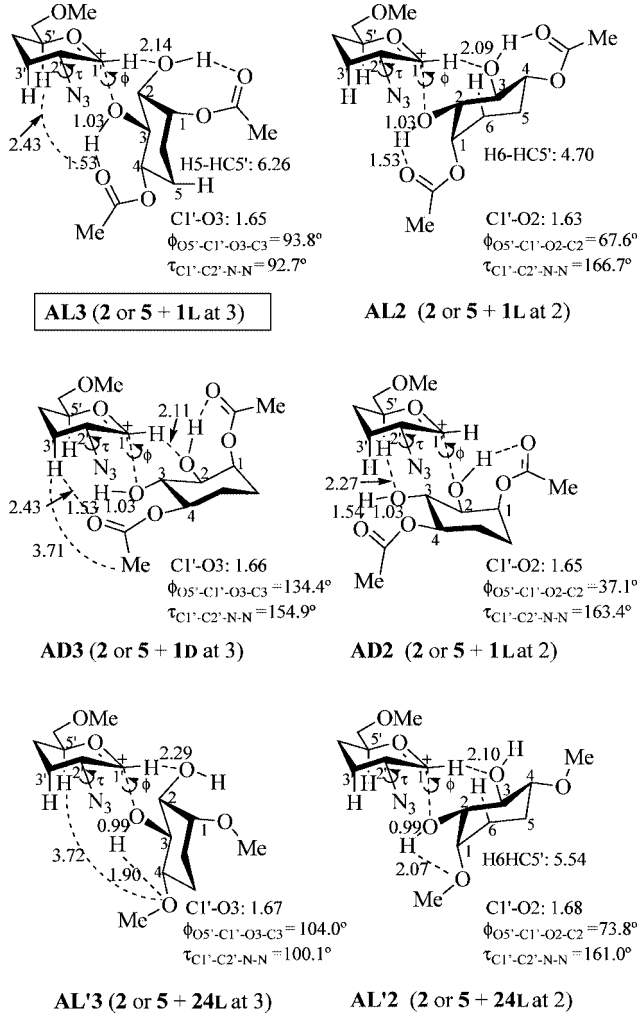

Figure 5. Significant interactions between groups at short and long distances [Å] determined on model complexes **AL3**, **AL2**, **AD3**, **AD2**, **AL′3** and **AL′2**.

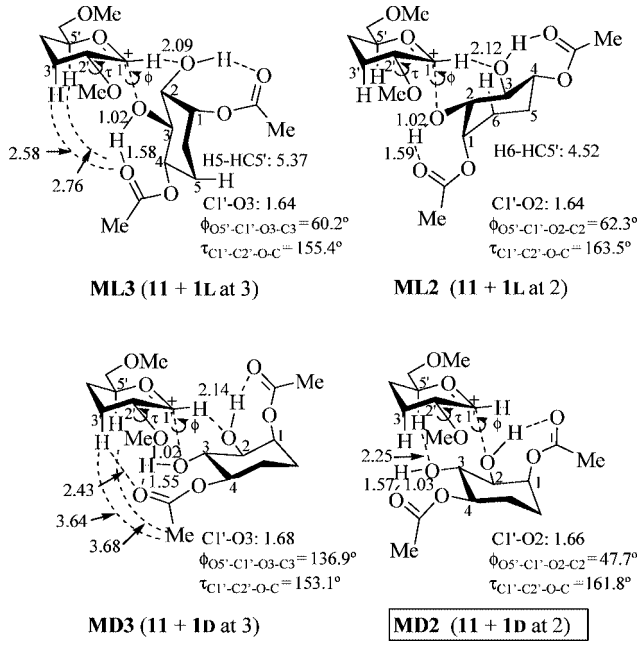

Figure 6. Significant interactions between groups at short and long distances [Å] determined on model complexes **ML3**, **ML2**, **MD3** and **MD2**.

Two main interactions seem to control all these approximations. First, a very strong hydrogen bond, according to the usual criteria,[18] which is present in all the complexes with acetylated acceptors between the O–H group to be glycosylated and the adjacent acyl group. In complexes **AL′3** and **AL′2** an equivalent but weaker interaction is also present with the adjacent methoxy group. Second, an important hydrogen bond between C1′ and the closest O2(O3) –H group, the directionality of which determines the conformation (especially Φ angle) of the pseudodisaccharide being formed. This interaction is present in all the complexes except in **AD2** and **MD2** where there is an equivalent interaction between C5′–H and O3.

Comparing the hydrogen bond between the O3(O2)–H bond and the adjacent acyl group in complexes with acetylated acceptors, with respect to the situation in the acceptor model, the hydrogen atom seems to be partially transferred to the carbonyl group.[19] NBO analyses[20] show an important charge donation from a lone pair of the carboxylic oxygen to the O–H antibonding orbital that weakens this bond

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(Wiberg bond indexes of O–H bonds involved in glycosidic bond formation are in the range 0.50–0.52 whereas the values for the other O–H group are in the range 0.65–0.66).[21] The second-order perturbational energy associated with these stabilizing donations are in the range 43–46 kcal/mol, a big value compared with the interactions found for the other O–H groups (7–12 kcal/mol) that participate in a normal hydrogen bond. This suggests that glycosylation may be assisted by the basic character of the adjacent acyl group. In agreement with this, when the acyl groups in complexes **AL3** and **AL2** were substituted by methyl groups (see complexes **AL′3** and **AL′2** in Figure 5) the complexation process was less favorable and a slight elongation of the distances C1′–O3(O2) (1.67 and 1.68 Å) and C1′H–O2(O3) (2.29 and 2.10 Å) was observed. Although there also exists an interaction between the O–H group to be glycosylated and the adjacent methoxy group, this must be weaker according to the values of the distances and angles.[18]

Complexes shown in each Figure are quite similar in energy (see supporting information) and do not seem to have important differences in electronic interactions. However, a careful analysis of these structures may help to understand most of the experimental results presented in Tables 1 and 2. First, the high regioselectivity to position 3 shown by acceptor **1L** in reaction with 2-azide substituted donors **2** and **5**, which is inverted to position 2 with benzylated acceptor **24L** and the same donors. Second, the low regioselectivity observed for acceptor **1D** with 2-azide substituted donors **2** and **5**. Third, the role of the group at C-2 of the glycosyl donor: azide group induces high 3-regioselectivity with acceptor L whereas the benzyloxy group induces high 2-regioselectivity with acceptor D.

The interactions that take place during the approach of the acceptor to the lower face of the donor can be related to the value of the dihedral angle Φ as well as to the distances between certain groups indicated in Figures 5 and 6.

In order to analyze the results from the **AL3** and **AL2** approximations (see Figure 5), it must be mentioned that in complex **AL2**, the axial substituent at C-6 of the acceptor (that has been eliminated in the model) should be closer to the lower face of the donor (distance H6–HC5′ 4.70 Å) than in complex **AL3** where the closest substituent, at C-5 in this case, shows a longer distance (H5–HC5′ 6.26 Å). Additionally, complex **AL3** shows a stabilizing interaction between the 4-acyl group and C5′–H (distance C=O–HC5′ 2.43 Å). These factors would afford a high C3/C2 ratio which is in agreement with experimental results (see highly regioselective reactions of **1L** with **2** and **5**, Table 1).

When methoxylated glycosyl acceptors were used an increase in the dihedral angle Φ was observed. Thus, the dihedral angle $\Phi_{O5'–C1'–O3–C3}$ increased from 93.8 (in **AL3**) to 104.0° (in **AL′3**) (see Figure 5). In the case of approximation through position 2 the dihedral angle $\Phi_{O5'–C1'–O2–C2}$ varied from 67.6° (in **AL2**) to 73.8° (in **AL′2**). These variations provide fewer interactions between groups on the acceptor and the lower face of the donor in both **AL′** complexes. The absence of the carbonyl group in **AL′3** produces the loss of the stabilizing interaction that was present in **AL3** (the equivalent distance O–HC5′ with the OMe group in **AL′3** is 3.72 Å). The possible steric hindrance in **AL′2** would decrease (distance between axial H6 and C5′ = 5.54 Å) with respect to the situation in **AL2** (4.70 Å). These facts agree with the reverse regioselectivity experimentally observed for benzylated acceptors (see the results of the reaction of **24L** with **2** and **5** in Table 2).

On the other hand, in the case of the acceptor with D configuration, complex **AD3** also shows a stabilizing interaction (analogous to the one found in **AL3**) between the 4-acyl group and in this case C3′–H (distance C=O–HC3′ 2.43 Å). However due to the orientation of this acyl group steric effects should become important when the size of the acyl group increases (distance COCH3–HC3′ 3.71 Å). The approximation shown for complex **AD2** is almost totally free of steric interactions but does not present any additional favourable electronic interactions. The experimental result in this case is poor regioselectivity (see reaction of **1D** with **2** and **5** in Table 1).

In order to study the role of the group at C-2 of the glycosyl donor, complexes shown in Figure 5 and Figure 6 must be compared. Both types of complexes are quite similar. However, there exists a remarkable difference between complex **AL3** and **ML3** regarding the orientation of the C-2 substituent [torsion angles: C1′–C2′–N–N = 92.7°; C1′–C2′–O–CH_3 = 155.4°].[22] Probably with this orientation the nitrogen atom on the azide group can avoid electronic repulsion with O2, whereas the methoxy group cannot reach this conformation due to steric reasons. The different conformation of the C-2 substituent causes a dramatic decrease in the value of $\Phi_{O5'–C1'–O3–C3}$ from 93.8° in complex **AL3** to 60.2°[23] in complex **ML3**. Thus, complex **ML3** shows an orientation similar to **ML2** (and also to **AL2**, compare Φ angle values in Figure 5 and Figure 6) and therefore they should present similar interactions between the axial substituent at C-5 in **ML3** and C-6 in **ML2** and **AL2** of the acceptor and the lower face of the donor. Additionally, **ML3** shows the 4-acyl group inside the lower face of the donor (distances C=O–HC5′ 2.76 and C=O–HC3′ 2.58 Å) and thus the stabilizing interaction should be smaller than in complex **AL3**. Therefore, with these 2-methoxy **ML** complexes no regioselectivity should be expected as can be experimentally observed in the reaction of **1L** with **11** (Table 1). For the D enantiomer the approximation through OH-2 seems to be slightly favored according to the distance of the incipient bond (1.66 Å in complex **MD2** vs. 1.68 Å in complex **MD3**). The relatively unfavorable situation in **MD3** may also be ascribed to steric factors. The distance between methyl groups of the C2′-methoxy substituent and 4-acetyl is only 3.68 Å. In comparison with **AD3**, the COCH3–HC3′ distance in **MD3** is 3.64 Å. Most likely the influence of these effects on the regioselectivity of the glycosylation will increase as the size of the substituent at the 2-position of the glycosyl donor increases.

These calculations have highlighted the importance of hydrogen bonds on the acceptor residue in the regiochemical outcome of the glycosylation of diol acceptors. Particularly interesting is the assistance of an acyl group close to

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the hydroxy group to be glycosylated. This effect can help to explain the results presented herein as well as some others already described in the bibliography. For example, the regioselectivity in the glycosylation of a 3,4-diol of a glucuronic derivative in a $^1C_4$ conformation.[24] In this case, glycosylation at the 3-position is facilitated by the methoxycarbonyl group at the 6-position. The higher ratio of glycosylation at C2 of the 2,4-mannosyl diol acceptors, when a benzoyl group is at C3 compared with a benzyl group, is also in agreement with these observations.[15]

As can be seen in complexes **AL′3** and **AL′2** the hydrogen bond assistance can also be found, although to a lesser extent, with alkoxy substituents. This effect could explain the lower degree of glycosylation of hydroxy groups with either no possible or favorable hydrogen bond assistance described in the literature. That could be the case of the higher ratio of glycosylation of hydroxy groups at C3-positions, even being the most hindered one, compared to OH-2 in α-altrose diol acceptor derivatives described by Fraser-Reid and collaborators.[8b] This fact could also explain the low glycolysation tendency of the axial hydroxy group at C1 vs. C2 in D-*chiro*-inositol 1,2-*syn* diol acceptors.[10c]

Conclusions

In summary, we have presented experimental evidence for the simultaneous regio- and enantiodifferentiation in the glycosylation of 1,2-*trans*-diequatorial diol systems and for the influence of protecting groups, of both donor and acceptor partners on the regioselectivity of these processes. DFT calculations indicate that this regioselectivity is governed by stereoelectronic factors and predicts that an acyl group adjacent to the OH to be glycosylated facilitates the glycosylation itself. According to these studies, the trend of glycosylation of a determined hydroxy group could be modulated by the nature of the protecting groups close to the reaction centre, both those located on the donor and on the acceptor partners.

Experimental Section

General Remarks: Diethyl ether and dichloromethane were distilled from sodium benzophenone and calcium hydride, respectively. Molecular sieves (4 Å, powdered) were dried in the oven at 100 °C and activated for 5 min under vacuum at 500 °C. All reactions were run in an atmosphere of dry argon using oven-dried glassware and freshly distilled and dried solvents unless otherwise stated. TLC was performed using silica gel GF_{254}. Silica gel (230–400 mesh) was used for flash chromatography and eluents are given as volume to volume ratios (v/v). All aqueous solutions were saturated unless otherwise stated. ^{1}H NMR (300, 400 and 500 MHz) and ^{13}C NMR (125 and 75 MHz) spectra were recorded at 25 °C in $CDCl_3$ unless otherwise noted, chemical shifts are given in ppm relative to $CDCl_3$ (δ = 7.27 ppm) and coupling constants are reported in Hz. Resonances were assigned by means of 2D spectra (COSY, HMQC and HSQC).

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α(1→2)-1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (13), 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α(1→3)-1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (15): A mixture of 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl trichloroacetimidate (**2**) (296.0 mg, 0.477 mmol) and 1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (**1D**) (237.5 mg, 0.398 mmol) was co-evaporated 3 times with toluene, 4-Å molecular sieves were added and the residue was dried under vacuum overnight. The mixture was dissolved in dry ether (15 mL) in an argon atmosphere and stirred at room temperature for 30 min, then 0.08 equiv. (318 μL of a 0.1 M solution) of TMSOTf was added at –40 °C and the reaction mixture stirred for 1 h at –40 °C. Then it was quenched with Et_3N, concentrated and purified by flash chromatography (toluene/acetone, 40:1) to yield 167 mg (40%) of pseudodisaccharide **13** and 113 mg (27%) of pseudodisaccharide **15**.

Data of the α(1→2) Pseudodisaccharide 13: $[\alpha]_D^{20}$ = +86.4 (*c* = 0.7, $CHCl_3$).^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17–7.76 (m, 8 H, H*ortho*), 7.64–7.05 (m, 15 H, Bn and 12 H, Bz), 6.00–5.95 (m, 2 H, H^4 and H^6), 5.93 (br. t, *J* = 3.5 Hz, 1 H, H^1), 5.87 (dd, *J* = 10.4 and 3.1 Hz, 1 H, H^5), 5.22 (d, *J* = 3.6 Hz, 1 H, $H^{1'}$), 4.71–4.39 (3 AB systems, 6 H, $3CH_2Ph$), 4.44 (m, 1 H, H^3), 4.34 (dd, *J* = 9.5 and 3.4 Hz, 1 H, H^2), 4.10 (m, 1 H, $H^{5'}$), 3.80 (t, *J* = 9.9 Hz, 1 H, $H^{3'}$), 3.62 (d, *J* = 3.2 Hz, 2 H, $H^{6'}$), 3.57 (t, *J* = 9.8 Hz, 1 H, $H^{4'}$) and 3.37 (d, *J* = 10.0 and 3.6 Hz, 1 H, $H^{2'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 165.8, 165.3 and 165.0 (4CO), 138.2, 138.0 and 137.8 (3C, Bn), 134.1, 133.9, 133.6 and 133.5 (4CH*para*), 130.3–127.9 (15CH, Bn and 16CH, Bz), 129.6, 129.5, 129.2 and 129.1 (4C, Bz), 96.6 ($C^{1'}$), 80.4 (CH), 78.3 (CH), 76.9 (CH), 75.6 (CH_2Ph), 75.1 (CH_2Ph), 73.8 (CH_2Ph), 72.6 (CH), 71.7 (CH), 71.6 (CH), 70.2 (CH), 68.9 (CH), 68.6 (CH_2), 67.8 (CH) and 63.8 (CH) ppm. $C_{61}H_{55}O_{14}N_3$ (1054.12): calcd. C 69.50 %, H 5.25 %, N 3.98 %; found: C 69.00 %, H 5.43 %, N 3.73 %. FAB HRMS calcd. for $[C_{61}H_{55}O_{14}N_3+Na]^+$: 1076.3581, found: 1076.3545.

Data of the α(1→3) Pseudodisaccharide 15: $[\alpha]_D^{20}$ = +56.4 (*c* = 0.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15–7.76 (m, 8 H, H*ortho*), 7.65–7.10 (m, 15 H, 3Bn and 12 H, 4Bz), 6.08 (t, *J* = 10.3 Hz, 1 H, H^4), 5.91 (t, *J* = 3.6 Hz, 1 H, H^6), 5.82 (dd, *J* = 10.3 and 3.3 Hz, 1 H, H^5), 5.79 (t, *J* = 3.6 Hz, 1 H, H^1), 5.04 (d, *J* = 3.6 Hz, 1 H, $H^{1'}$), 4.80–4.38 (3 AB systems, 6 H, $3CH_2Ph$), 4.30 (m, 1 H, H^2), 4.23 (m, 1 H, $H^{5'}$), 4.18 (t, *J* = 9.3 Hz, 1 H, H^3), 3.95 (t, *J* = 9.7 Hz, 1 H, $H^{3'}$), 3.81 (d, *J* = 4.4 Hz, 1 H, C^2OH), 3.60 (dd, *J* = 10.4 and 2.0 Hz, 1 H, $H^{6a'}$), 3.53 (dd, *J* = 10.4 and 5.7 Hz, 1 H, $H^{6b'}$), 3.47 (t, *J* = 9.7 Hz, 1 H, $H^{4'}$), 3.37 (dd, *J* = 9.8 and 3.7 Hz, 1 H, $H^{2'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.0, 165.8, 165.4 and 165.1 (4CO), 137.9, 137.8 and 137.6 (3C, Bn), 134.0, 133.9, 133.6 and 133.2 (4CH*para*), 130.4–128.1 (15CH, Bn and 16CH, Bz), 129.6, 129.4, 129.2 and 129.2 (4C, Bz), 99.9 ($C^{1'}$), 83.5 (C^3), 80.9 (CH), 78.5 (CH), 76.0 (CH_2Ph), 75.5 (CH_2Ph), 73.9 (CH_2Ph), 72.1 (CH), 70.9 (CH), 70.7 (CH), 70.4 (CH), 70.1 (CH), 68.8 (CH), 68.6 (CH_2) and 64.2 (CH) ppm. FAB HRMS calcd. for $[C_{61}H_{55}O_{14}N_3+Na]^+$: 1076.3581, found: 1076.3612.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-α(1→2)-1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (14), 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-α(1→3)-1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (16): These pseudodisaccharides were prepared from 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl trichloroacetimidate (**5**) (74 mg, 0.12 mmol) and 1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (**1D**) (60 mg, 0.10 mmol) as described for the preparation of **13** and **15**, by addition of 0.08 equiv. (80 μL of 0.1 M solution) of TMSOTf at –40 °C in dry ether (3.5 mL) and by stirring the reaction mixture for 1 h at –40 °C; yield after flash chromatography (toluene/acetone, 40:1) 35 mg (33%) of pseudodisaccharide **14** and 31 mg (29%) of pseudodisaccharide **16**.

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Data of the α(1→2) Pseudodisaccharide 14: $[\alpha]_D^{20}$ = +80.9 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.16–7.76 (m, 8 H, H*ortho*), 7.65–7.15 (m, 15 H, 3Bn and 12 H, 4Bz), 5.98–5.94 (m, 2 H, H^4, H^6), 5.92 (br. t, *J* = 3.5 Hz, 1 H, H^1), 5.85 (dd, *J* = 10.4 and 3.3 Hz, 1 H, H^5), 5.20 (d, *J* = 3.6 Hz, 1 H, $H^{1\prime}$), 4.80–4.34 (3 AB systems, 6 H, $3CH_2Ph$), 4.41 (m, 1 H, H^3), 4.32 (dd, *J* = 9.5 and 3.4 Hz, 1 H, H^2), 4.15 (m, 1 H, $H^{5\prime}$), 3.89 (dd, *J* = 10.4 and 3.6 Hz, 1 H, $H^{2\prime}$), 3.75 (m, 2 H, $H^{3\prime}$ and $H^{4\prime}$), 3.59 (d, *J* = 4.4 Hz, 1 H, C^3OH), 3.51 (dd, *J* = 9.5 and 7.1 Hz, 1 H, $H^{6a\prime}$) and 3.32 (dd, *J* = 9.5 and 5.3 Hz, 1 H, $H^{6b\prime}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 165.8, 165.1 and 165.0 (4CO), 138.3, 137.8 and 137.7 (3C, Bn), 134.1, 133.9, 133.6 and 133.5 (4CH*para*), 130.3–128.1 (15CH, Bn and 16CH, Bz), 129.7, 129.6, 129.2 and 129.0 (4C, Bz), 97.8 ($C^{1\prime}$), 77.9 (CH), 77.7 (CH), 74.9 (CH_2Ph), 73.8 (CH_2Ph), 73.7 (CH), 72.8 (CH_2Ph), 72.6 (CH), 71.7 (CH), 71.0 (CH), 70.3 (CH), 69.4 (CH_2), 68.8 (CH), 68.5 (CH) and 60.1 (CH) ppm. FAB HRMS calcd. for $C_{61}H_{55}O_{14}N_3$+Na^+: 1076.3581, found: 1076.3621.

Data of the α(1→3) Pseudodisaccharide 16: $[\alpha]_D^{20}$ = +59.8 (*c* = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.11–7.76 (m, 8 H, H*ortho*), 7.65–7.10 (m, 15 H, Bn and 12 H, Bz), 6.09 (t, *J* = 9.7 Hz, 1 H, H^4), 5.90 (t, *J* = 3.6 Hz, 1 H, H^6), 5.78 (dd, *J* = 9.6 and 3.5 Hz, 1 H, H^5), 5.74 (t, *J* = 3.6 Hz, 1 H, H^1), 5.11 (d, *J* = 3.8 Hz, 1 H, $H^{1\prime}$), 4.80–4.20 (3 AB systems, 6 H, $3CH_2Ph$), 4.32 (m, 1 H, $H^{5\prime}$), 4.28 (m, 1 H, H^2), 4.25 (t, *J* = 9.7 Hz, 1 H, H^3), 3.90 (dd, *J* = 10.6 and 2.7 Hz, 1 H, $H^{3\prime}$), 3.85 (dd, *J* = 10.6 and 3.8 Hz, 1 H, $H^{2\prime}$), 3.80 (s, 1 H, $H^{4\prime}$), 3.76 (d, *J* = 6.05 Hz, 1 H, C^2), 3.48 (dd, *J* = 9.5 and 8.1 Hz, 1 H, $H^{6a\prime}$), 3.22 (dd, *J* = 9.5 and 4.0 Hz, 1 H, $H^{6b\prime}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 165.8, 165.3 and 165.1 (4CO), 138.2, 137.9 and 137.5 (3C, Bn), 134.0, 133.9, 133.6 and 133.3 (4CH*para*), 130.4–127.9 (15CH, Bn and 16CH, Bz), 129.4, 129.3, 129.2 and 129.1 (4C, Bz), 99.9 ($C^{1\prime}$), 81.6 (CH), 78.5 (CH), 74.8 (CH_2Ph), 73.8 (CH_2Ph), 73.7 (CH), 73.0 (CH_2Ph), 71.3 (CH), 71.1 (CH), 71.1 (CH), 70.4 (CH), 69.9 (CH), 69.8 (CH_2), 68.8 (CH) and 60.4 (CH) ppm. FAB HRMS calcd. for $[C_{61}H_{55}O_{14}N_3$+Na$]^+$: 1076.3581, found: 1076.3598.

2,3,4,6-Tetra-*O*-benzyl-D-galactopyranosyl-α(1→2)-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (17), 2,3,4,6-Tetra-*O*-benzyl-D-galactopyranosyl-β(1→2)-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (18) and 2,3,4,6-Tetra-*O*-benzyl-D-galactopyranosyl-α(1→3)-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (19): These pseudodisaccharides were prepared from 2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl trichloroacetimidate (**11**) (100 mg, 0.146 mmol) and 1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (**1L**) (87 mg, 0.146 mmol) as described for the preparation of **13** and **15** by addition of 0.08 equiv. (117 μL of 0.1 M solution) of TMSOTf at –40 °C in dry ether (3.7 mL) and stirring the reaction mixture for 1 h at –40 °C. The crude product was purified by preparative TLC (hexane/AcOEt = 3:1) to separate the resulting trichloroacetamide (26 mg, R_f = 0.79 in hexane/AcOEt = 2:1) and the remaining acceptor **1L** (22 mg, 25%, R_f = 0.05 in hexane/AcOEt = 2:1). Products with intermediate R_f values were repurified by preparative TLC (toluene/AcOEt, 95:5) to yield pseudodisaccharides α(1–2) **17** (40 mg, 24%), β(1–2) **18** (11 mg, 7%) and α(1–3) **19** (33 mg, 20%) as colourless syrups. When the reaction was carried out at –78 °C for 2 h, trichloroacetamide (14 mg), the remaining acceptor **1L** (16 mg, 10%) and disaccharides α(1–2) **17** (40 mg, 24%), β(1–2) **18** (10 mg, 6%) and α(1–3) **19** (35 mg, 21%) were obtained.

Data for the α(1–2) Pseudodisaccharide 17: TLC, toluene/AcOEt = 9:1, R_f = 0.42. $[\alpha]_D^{20}$ = –20.7 (*c* = 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.14 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 8.03 (d, *J* = 7.0 Hz, 2 H, H*ortho*), 8.02 (d, *J* = 8.0 Hz, 2 H, H*ortho*), 7.78 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 7.67–7.15 (m, 20 H, Bn and 12 H, Bz), 6.01 (t, *J* = 10.5 Hz, 1 H, H^4), 5.93 (t, *J* = 3.5 Hz, 1 H, H^6), 5.84 (t, *J* = 3.5 Hz, 1 H, H^1), 5.79 (dd, *J* = 10.5 and 3.5 Hz, 1 H, H^5), 5.13 (d, *J* = 4.0 Hz, 1 H, $H^{1\prime}$), 4.83 (d, *J* = 11.5 Hz, 1 H, CH_2Ph), 4.81 (d, *J* = 11.5 Hz, 1 H, CH_2Ph), 4.70 (d, *J* = 11.5 Hz, 1 H, CH_2Ph), 4.56 (AB system, 2 H, CH_2Ph), 4.50 (d, *J* = 11.5 Hz, 1 H, CH_2Ph), 4.45 (br. t, *J* = 10.0 Hz, 1 H, H^3), 4.40 (AB system, 2 H, CH_2Ph), 4.16 (dd, *J* = 9.5 and 3.0 Hz, 1 H, H^2), 4.06 (dd, *J* = 4.0 and 10.0 Hz, 1 H, $H^{2\prime}$), 4.05 (s, 1 H, OH), 4.03 (br. t, *J* = 7.0 Hz, 1 H, $H^{5\prime}$), 3.90 (br. s, 1 H, $H^{4\prime}$), 3.79 (dd, *J* = 10.0 and 2.5 Hz, 1 H, $H^{3\prime}$), 3.54 (t, *J* = 8.5 Hz, 1 H, $H^{6a\prime}$), 3.50 (dd, *J* = 6.0 and 9.0 Hz, 1 H, $H^{6b\prime}$) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.0, 1656, 164.8, 164.7 (CO, Bz), 138.6, 138.3, 138.1, 137.5 (C, Bn), 133.69, 133.65, 133.2, 133.1 (CH*para*, Bz), 130.0, 129.9, 129.8, 129.7 (CH*ortho*, Bz), 129.6, 129.3, 128.93, 128.88 (C, Bz), 128.73, 128.67, 128.5, 128.4, 128.33, 128.27, 128.2, 127.9, 127.7, 127.52, 127.48, 127.4 (CH, Bn and Bz), 102.1 ($C^{1\prime}$), 80.5 (C^2), 79.4 ($C^{3\prime}$), 75.8 ($C^{2\prime}$), 74.7 (CH_2), 74.4 (CH_2, $C^{4\prime}$), 73.2 (CH_2), 72.4 (CH_2), 71.6 (C^3 and C^4), 70.1 (C^1, C^5), 69.9 ($C^{5\prime}$), 68.8 (C^6), 68.0 ($C^{6\prime}$) ppm. FAB HRMS calcd. for $[C_{68}H_{62}O_{15}$+Na$]^+$: 1141.3981, found: 1141.3953, calcd. for $C_{68}H_{62}O_{15}$+K: 1157.3720, found: 1157.3705.

Data for Pseudodisaccharide β(1→2) 18: TLC, toluene/AcOEt = 9:1, R_f = 0.38. $[\alpha]_D^{20}$ = –57.6 (*c* = 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.12 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 8.04 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 8.03 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 7.77 (d, *J* = 8.0 Hz, 2 H, H*ortho*), 7.64–7.15 (m, 20 H, Bn and 12 H, Bz), 6.04 (t, *J* = 10.0 Hz, 1 H, H^4), 5.93 (m, 2 H, H^1, H^6), 5.82 (br. d, *J* = 10.5 Hz, 1 H, H^5), 4.85 (d, *J* = 11.5 Hz, 1 H, CH_2Ph), 4.78 (d, *J* = 11.5 Hz, 1 H, CH_2Ph), 4.72 (s, 1 H, OH), 4.68 (AB system, 2 H, CH_2Ph), 4.59 (d, *J* = 11.0 Hz, 1 H, CH_2Ph), 4.55 (d, *J* = 8.0 Hz, 1 H, $H^{1\prime}$), 4.53 (d, *J* = 12.0 Hz, 1 H, CH_2Ph), 4.48 (br. t, *J* = 9.5 Hz, 1 H, H^3), 4.32 (AB system, 2 H, CH_2Ph), 4.25 (br. d, *J* = 9.5 Hz, 1 H, H^2), 3.79 (br. s, 1 H, $H^{4\prime}$), 3.78 (t, *J* = 9.0 Hz, 1 H, $H^{2\prime}$), 3.63 (t, *J* = 6.0 Hz, 1 H, $H^{5\prime}$), 3.58 (dd, *J* = 9.0 and 6.5 Hz, 1 H, $H^{6a\prime}$), 3.50 (dd, *J* = 10.0 and 3.0 Hz, 1 H, $H^{3\prime}$), 3.36 (dd, *J* = 9.5 and 5.5 Hz, 1 H, $H^{6b\prime}$) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.0, 165.6, 164.8, 164.6 (CO, Bz), 138.1 (3C, Bn), 137.3 (C, Bn), 133.7, 133.6, 133.1, 133.0 (CH*para*, Bz), 130.1, 130.0, 129.84 (CH*ortho*, Bz), 129.83 (C, Bz), 129.7 (CH*ortho*, Bz), 129.1, 128.93, 128.86 (C, Bz), 128.7, 128.64, 128.41, 128.38, 128.36, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5 (CH Bn and Bz), 105.2 ($C^{1\prime}$), 82.5 (C^3), 82.1 ($C^{3\prime}$), 78.9 ($C^{2\prime}$), 75.4 (CH_2), 74.6 (CH_2), 74.0 ($C^{5\prime}$), 73.7 (CH_2), 73.3 (CH_2), 73.0 ($C^{4\prime}$), 71.8 (C^4), 70.96 (C^2), 70.05 (C^5), 70.00 (C^1), 68.7 ($C^{6\prime}$), 68.6 (C^6) ppm. FAB HRMS calcd. for $[C_{68}H_{62}O_{15}$+H$]^+$: 1119.4167, found: 1119.4156.

Data for Pseudodisaccharide α(1→3) 19: TLC, toluene/AcOEt = 9:1, R_f = 0.54. $[\alpha]_D^{20}$ = –28.6 (*c* = 0.8, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.19 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 8.07 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 7.92 (d, *J* = 8.0 Hz, 2 H, H*ortho*), 7.73 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 7.70–7.04 (m, 20 H, Bn and 12 H, Bz), 6.00 (t, *J* = 10.0 Hz, 1 H, H^4), 5.92 (t, *J* = 3.5 Hz, 1 H, H^6), 5.87 (t, *J* = 3.5 Hz, 1 H, H^1), 5.77 (dd, *J* = 10.5 and 3.0 Hz, 1 H, H^5), 5.23 (s, 1 H, OH), 4.86 (d, *J* = 12.0 Hz, 1 H, CH_2Ph), 4.85 (br. s, 1 H, $H^{1\prime}$), 4.80 (d, *J* = 11.0 Hz, 1 H, CH_2Ph), 4.72 (AB system, 2 H, CH_2Ph), 4.67 (d, *J* = 12.0 Hz, 1 H, CH_2Ph), 4.44 (br. dd, *J* = 9.5 and 3.5 Hz, 1 H, H^2), 4.42 (d, *J* = 11.0 Hz, 1 H, CH_2Ph), 4.13 (t, *J* = 9.5 Hz, 1 H, H^3), 4.03 (m, 3 H, $H^{2\prime}$, $H^{3\prime}$, $H^{4\prime}$), 4.02 (AB system, 2 H, CH_2Ph), 3.94 (dd, *J* = 9.5 and 4.5 Hz, 1 H, $H^{5\prime}$), 3.22 (t, *J* = 9.0 Hz, 1 H, $H^{6a\prime}$), 2.60 (dd, *J* = 9.0 and 4.5 Hz, 1 H, $H^{6b\prime}$) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 165.6, 165.4, 165.0, 164.7 (CO, Bz), 138.7, 138.3, 138.0, 137.0 (C, Bn), 133.6, 133.5, 133.13, 133.08 (CH*para*, Bz), 130.02, 129.95, 129.86, 129.6 (CH*ortho*, Bz), 129.6, 129.4, 129.0, 128.9 (C, Bz), 128.8, 128.7, 128.4, 128.3, 128.2, 128.14, 128.10, 127.8, 127.62, 127.58, 127.4, 127.3 (CH, Bn and

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Bz), 102.9 ($C^{1'}$), 84.0 (C^3), 79.2 ($C^{3'}$), 75.9 ($C^{2'}$), 74.9, 74.6 (CH_2Ph), 74.1 ($C^{4'}$), 73.0, 72.3 ($2CH_2Ph$), 71.0 (C^4), 70.7 (C^5), 70.6 (C^2), 69.9 ($C^{5'}$), 69.7 (C^1), 68.6 (C^6), 67.0 ($C^{6'}$) ppm. FAB HRMS calcd. for $[C_{68}H_{62}O_{15}+Na]^+$: 1141.3981, found: 1141.3983, calcd. for $[C_{68}H_{62}O_{15}+K]^+$: 1157.3720, found: 1157.3718.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-D-glucopyranosyl-β(1→2)-1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (21) and 3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-D-glucopyranosyl-β(1→3)-1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (22): These pseudodisaccharides were prepared from 3,4,6-tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-D-glucopyranosyl trichloroacetimidate (**20**) (160 mg, 0.269 mmol) and 1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (**1D**) (134 mg, 0.225 mmol) as described for the preparation of **13** and **15** by addition of 180 μL (0.08 equiv.) of a 0.1 M solution of TMSOTf at –40 °C in dry ether (5.6 mL) and stirring the reaction mixture for 3 h at –40 °C. The reaction was quenched with Et_3N, the solvent was evaporated and the crude residue was purified by flash chromatography (toluene/AcOEt = 8:2) to yield a mixture of pseudodisaccharides **21** β(1–2) and **22** β(1–3) (5:1, 220 mg, 95%) as a white solid.

Data for the Mixture of Pseudodisaccharides 21/22: 21 β(1–2)/**22** β(1–3) = I/II = 5:1, TLC, toluene/AcOEt = 7:3, R_f = 0.28. ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.17 (d, *J* = 7.5 Hz, 0.4 H, H*ortho*, II), 8.14 (d, *J* = 7.5 Hz, 2 H, H*ortho*, I), 8.10 (d, *J* = 7.5 Hz, 2 H, H*ortho*, I), 8.03 (d, *J* = 7.5 Hz, 0.4 H, H*ortho*, II), 8.02 (d, *J* = 8.0 Hz, 0.4 H, H*ortho*, II), 7.98 (d, *J* = 7.5 Hz, 2 H, H*ortho*, I), 7.83 (d, *J* = 7.0 Hz, 0.4 H, H*ortho*, II), 7.75 (d, *J* = 7.5 Hz, 2 H, H*ortho*, I), 7.66–7.20 (m, 14.4 H, 12 H, I and 2.4 H, II, Bz), 7.18 (d, *J* = 8.5 Hz, 0.2 H, $NHCOCCl_3$, II), 7.03 (d, *J* = 8.5 Hz, 1 H, $NHCOCCl_3$, II), 6.004 (t, *J* = 3.5 Hz, 1 H, H^6, I), 5.997 (t, *J* = 9.5 Hz, 0.2 H, H^4, II), 5.93 (t, *J* = 10.0 Hz, 1 H, H^4, I), 5.92 (m, 0.2 H, H^6, II), 5.87 (dd, *J* = 10.5 and 3.0 Hz, 0.2 H, H^5, II), 5.79 (t, *J* = 3.5 Hz, 1 H, H^1, I), 5.76 (dd, *J* = 10.5 and 3.5 Hz, 1 H, H^5, I), 5.75 (m, 0.2 H, H^1, II), 5.23 (t, *J* = 9.5 Hz, 1 H, $H^{3'}$, I), 5.17 (t, *J* = 10.0 Hz, 0.2 H, $H^{3'}$, II), 5.09 (d, *J* = 8.0 Hz, 1 H, $H^{1'}$, I), 5.03 (t, *J* = 9.5 Hz, 1 H, $H^{4'}$, I), 5.00 (d, *J* = 8.5 Hz, 0.2 H, $H^{1'}$, II), 4.97 (t, *J* = 9.5 Hz, 0.2 H, $H^{4'}$, II), 4.49 (td, *J* = 9.5 and 3.5 Hz, 1 H, H^3, I), 4.47 (dt, *J* = 9.5 and 3.5 Hz, 0.2 H, H^2, II), 4.35 (dd, *J* = 9.5 and 3.5 Hz, 1 H, H^2, I), 4.24 (t, *J* = 9.5 Hz, 0.2 H, H^3, II), 4.11 (dd, *J* = 12.0 and 4.5 Hz, 1 H, $H^{6a'}$, I), 4.01 (dd, *J* = 12.0 and 2.0 Hz, 1 H, $H^{6b'}$, I), 4.00 (m, 0.2 H, $H^{2'}$, II), 3.99 (dt, *J* = 10.5 and 8.5 Hz, 1 H, $H^{2'}$, I), 3.91 (dd, *J* = 12.5 and 4.5 Hz, 0.2 H, $H^{6a'}$, II), 3.70 (ddd, *J* = 9.5, 4.5 and 2.0 Hz, 1 H, $H^{5'}$, I), 3.65 (dd, *J* = 12.5 and 2.0 Hz, 0.2 H, $H^{6b'}$, II), 3.53 (m, 0.2 H, $H^{5'}$, II), 3.21 (d, *J* = 3.5 Hz, 0.2 H, OH, II), 3.13 (d, *J* = 3.5 Hz, 1 H, OH, II), 1.98 (s, 6.6 H, $2CH_3CO$, II + CH_3CO, II), 1.94 (s, 0.6 H, CH_3CO, II), 1.89 (s, 0.6 H, CH_3CO, II), 1.89 (s, 3 H, CH_3CO, II) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.0, 170.6, 169.1 (CH_3CO, II), 166.6, 165.3, 164.9, 164.5 (CO, II, Bz), 162.3 ($NHCOCCl_3$, II), 133.8, 133.5, 133.4, 133.2 (CH*para* Bz), 130.1, 129.9, 129.8 (CH*ortho*, II, Bz), 129.7 (C, II, Bz), 129.6 (CH*ortho*, II, Bz), 129.3, 129.0, 128.9 (C, II, Bz), 128.8, 128.6, 128.4, 128.3 (CH*meta*, II, Bz), 101.3 ($C^{1'}$, II), 101.2 ($C^{1'}$, I), 92.2 ($NHCOCCl_3$, II), 80.4 (C^3, II), 78.5 (C^2, I), 72.43 (C^4, I), 73.38 ($C^{3'}$, II), 70.07 ($C^{5'}$, I), 71.97 (C^3, I + $C^{5'}$, II), 71.69 ($C^{3'}$, I), 71.61 (C^2, II), 71.34 (C^1, II), 70.03 (C^5, II), 69.96 (C^4, II), 69.8 (C^1, I), 69.6 (C^5, I), 68.7 (C^6, I, II), 68.6 (C^6, I), 67.9 ($C^{4'}$, II), 67.74 ($C^{4'}$, I), 61.72 ($C^{6'}$, II), 61.6 ($C^{6'}$, I), 56.3 ($C^{2'}$, I), 56.1 ($C^{2'}$, II), 20.5, 20.4, 20.3 (CH_3CO, II) ppm. FAB HRMS calcd. for $[C_{48}H_{44}NO_{18}Cl_3+H]^+$: 1028.1702, found: 1028.1652.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-D-glucopyranosyl-β(1→3)-1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (23): This pseudodisaccharide (29 mg, 0.028 mmol, 30%) was prepared from **20** (60 mg, 0.106 mmol, 1.2 equiv.) and **1L** (55 mg, 0.092 mmol, 1 equiv.) as described for the preparation of **13** and **15** by addition of 41 μL (0.08 equiv.) of a solution 0.2 M of TMSOTf at –40 °C in dry ether (3 mL) and stirring the reaction mixture for 30 h at –40 °C, then additionally for 1 h at –10 °C. The suspension was filtered through a short pad of celite, the solvent evaporated under vacuum to provide a residue which was separated by flash chromatography (hexane/AcOEt = 3:1, then 2:1, 1:1, AcOEt). $[\alpha]_D^{20}$ = –68.2 (*c* = 0.67, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.09 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 8.03 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 8.01 (d, *J* = 8.5 Hz, 2 H, H*ortho*), 7.78 (d, *J* = 7.5 Hz, 2 H, H*ortho*), 7.64, 7.63 (2t, *J* = 7.5 Hz, 2 H, H*para*), 7.53 (t, *J* = 7.5 Hz, 2 H, H*meta*), 7.51 (t, *J* = 7.5 Hz, 1 H, H*para*), 7.50 (t, *J* = 7.5 Hz, 2 H, H*meta*), 7.39 (t, *J* = 7.5 Hz, 1 H, H*meta*), 7.37 (m, 2 H, H*meta*, H*para*), 7.24 (t, *J* = 7.5 Hz, 2 H, H*meta*), 6.97 (d, *J* = 8.0 Hz, 1 H, $NHCOCCl_3$), 6.02 (m, 1 H, H^4), 5.87 (m, 1 H, H^6), 5.85(m, 1 H, H^5), 5.82 (m, 1 H, H^1), 5.51 (t, *J* = 9.5 Hz, 1 H, $H^{3'}$), 5.17 (d, *J* = 8.5 Hz, 1 H, $H^{1'}$), 5.00 (t, *J* = 9.5, 1 H, $H^{4'}$), 4.38 (m, 1 H, H^2), 4.34 (m, 1 H, H^3), 4.12 (dd, *J* = 12.2 and 6.0 Hz, 1 H, $H^{6a'}$), 4.07 (dd, *J* = 12.2 and 3.0 Hz, 1 H, $H^{6b'}$), 3.83 (ddd, 1 H, *J* = 9.5, 6.0 and 3.0 Hz, 1 H, $H^{5'}$), 3.73 (m, 1 H, OH), 3.71 (c, *J* = 8.5 Hz, 1 H, $H^{2'}$), 2.02, 1.99, 1.88 (3s, 9 H, $3CH_3CO$) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.7, 170.4, 169.5 (3CO, Ac), 166.2, 165.7, 165.3, 164.9 (4CO, Bz), 162.6 ($NHCOCCl_3$), 134.14, 134.07, 133.5, 133.4 (4C, Bz), 130.3–128.5 (4CH*para*, Bz), 99.5 ($C^{1'}$), 80.0 (C^3), 72.5 ($C^{5'}$), 71.5 (C^4), 70.88, 70.84 (C^2, $C^{3'}$), 69.9 (C^6), 69.0 (C^5), 68.54, 68.50 (C^1, $C^{4'}$), 62.0 ($C^{6'}$), 57.1 ($C^{2'}$), 20.7, 20.6, 20.5 (CH_3CO) ppm. FAB HRMS calculated for $[C_{48}H_{44}NO_{18}Cl_3+Na]^+$: 1050.1516, found: 1050.1499; calculated for $[C_{48}H_{44}NO_{18}Cl_3+K]^+$: 1066.1256, found: 1066.1246.

1,4,5,6-Tetra-*O*-benzoyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (25D): A suspension of 1,4,5,6-tetra-*O*-benzoyl-D-*chiro*-inositol (**1D**) (0.7 g, 1.17 mmol), 2,3-butanedione (0.154 mL, 1.76 mmol) and trimethyl orthoformate (0.512 mL, 4.68 mmol) in dry MeOH (13 mL) was treated with CSA (0.032 g, 0.138 mmol). The resulting mixture was refluxed in an argon atmosphere for 5 h, whereupon it was cooled, neutralised with Et_3N and concentrated under vacuum. The crude product was purified by flash chromatography (hexane/EtOAc = 8:1) to give 0.76 g of **3** (92%).

Data of 25D: $[\alpha]_D^{20}$ = –6.2 (*c* = 0.8, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.0 Hz, 2 H, H*ortho*), 8.05 (m, *J* = 8.0 Hz, 2 H, H*ortho*), 7.99 (d, *J* = 8.0 Hz, 2 H, H*ortho*), 7.77 (d, *J* = 8.0 Hz, 2 H, H*ortho*), 7.65–7.20 (m, 12 H, 4Bz), 6.06 (t, *J* = 10.1 Hz, 1 H, H^4), 5.92 (t, *J* = 3.6 Hz, 1 H, H^6), 5.75 (dd, *J* = 10.1 and 3.5 Hz, 1 H, H^5), 5.68 (t, *J* = 3.6 Hz, 1 H, H^1), 4.52 (t, *J* = 10.2 Hz, 1 H, H^3), 4.36 (dd, *J* = 10.1 and 3.6 Hz, 1 H, H^2), 3.28–3.25 (2s, 6 H, $2OCH_3$), 1.27 (s, 3 H, CH_3) and 1.22 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8, 165.7, 165.5, 165.1 (4CO), 134.0, 133.7, 133.5, 133.4 (4CH*para*), 130.4–128.6 (16CH, Bz), 130.0, 129.9, 129.3, 129.2 (4C, Bz), 100.4, 99.7 (2C, BDA), 71.3 (C^5), 70.2 (C^4), 69.5 (C^1), 69.2 (C^6), 67.3 (C^3), 67.0 (C^2), 48.5, 48.1 ($2OCH_3$) and 17.9, 17.7 ($2CH_3$) ppm. FAB HRMS calcd. for $[C_{40}H_{38}O_{12}+Na]^+$: 733.2256, found: 733.2260.

2,3-*O*-(2′,3′-Dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (26D): A solution of 1,4,5,6-tetra-*O*-benzoyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (**25D**) (0.76 g, 1.07 mmol) in 9 mL of MeOH/THF (8:1) was treated in an argon atmosphere with 2 mL of a 1.0 M solution of MeONa/MeOH. After stirring the reaction mixture for 2 h at room temperature, the reaction was stopped with IR-120 and acidified to pH = 7, filtered and concentrated to give 0.31 g of **26D** (quantitative).

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Data of 26D: $[\alpha]_D^{20}$ = –51.0 (*c* = 0.2, $CHCl_3$), ^{1}H NMR (500 MHz, MeOD): δ = 3.88 (t, *J* = 3.2 Hz, 1 H, H^1), 3.86 (t, *J* = 3.2 Hz, 1 H, H^6), 3.83 (dd, *J* = 10.0 and 3.0 Hz, 1 H, H^5), 3.77 (t, *J* = 8.9 Hz, 1 H, H^4), 3.66 (dd, *J* = 9.0 and 3.1 Hz, 1 H, H^2), 3.63 (t, *J* = 8.9 Hz, 1 H, H^3), 3.25 (s, 3 H, OCH_3), 3.20 (s, 3 H, OCH_3) and 1.27 (2s, 6 H, $2CH_3$) ppm. ^{13}C NMR (125 MHz, MeOD): δ = 101.8, 101.2 (2C, BDA), 74.5 (CH), 73.7 (CH), 73.1 (CH), 72.9 (CH), 71.1 (CH), 69.9 (CH), 49.0, 48.9 ($2OCH_3$) and 18.8 ($2CH_3$) ppm. FAB HRMS calcd. for $[C_{12}H_{22}O_8+Na]^+$: 317.1212, found: 317.1212.

1,4,5,6-Tetra-*O*-benzyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (27D): 2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (**26D**) (0.31 g, 1.06 mmol) and tetrabutylammonium iodide (39 mg, 0.106 mmol) in DMF (30 mL) at –20 °C were added to a suspension of sodium hydride (60% in mineral oil, 0.34 g, 8.51 mmol). The resulting mixture was stirred at 0 °C for 30 min and BnBr (1.01 mL, 8.51 mmol) was added dropwise. After stirring the mixture for 12 h at room temperature, the reaction was complete and methanol was added to the mixture. The solvent was evaporated, the residue diluted with CH_2Cl_2 and washed with a saturated solution of ammonium chloride and brine. The organic layer was dried with Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (hexane/Et_2O = 4:1) to give 630 mg of **5** (91%). $[\alpha]_D^{20}$ = –82.5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.20 (m, 20 H, 4Ph), 4.95–4.36 (4 AB systems, 8 H, $4CH_2Ph$), 4.11 (t, *J* = 9.8 Hz, 1 H, H^3), 4.02 (dd, *J* = 10.1 and 2.6 Hz, 1 H, H^2), 3.93 (t, *J* = 9.7 Hz, 1 H, H^4), 3.77 (dd, *J* = 9.5 and 3.4 Hz, 1 H, H^5), 3.69 (t, *J* = 3.5 Hz, 1 H, H^6), 3.67 (t, *J* = 2.6 Hz, 1 H, H^1), 3.3 (s, 3 H, OCH_3), 3.24 (s, 3 H, OCH_3), 1.36 (s, 3 H, CH_3) and 1.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.8 (C), 139.3 (C), 139.3 (C), 138.9 (C), 128.8–127.6 (20CH, Bn), 99.9 (C, BDA), 99.2 (C, BDA), 80.5 (C^5), 80.2 (C^4), 76.8 (C^6), 76.1 (C^1), 76.0 (CH_2Ph), 73.9 (CH_2Ph), 73.8 (CH_2Ph), 73.7 (CH_2Ph), 70.5 (C^3), 68.9 (C^2), 48.1 (OCH_3), 48.0 (OCH_3), 18.3 (CH_3) and 18.1 (CH_3) ppm. FAB HRMS calcd. for $[C_{40}H_{46}O_8+Na]^+$: 677.3102, found: 677.3090.

1,4,5,6-Tetra-*O*-benzyl-D-*chiro*-inositol (24D): A mixture of TFA/H_2O = 9:1 (20 mL) was added to 1,4,5,6-tetra-*O*-benzyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (**27D**) (0.63 g, 0.97 mmol) and the reaction mixture was stirred at room temperature for 4 h. The solvent was evaporated and co-evaporated four times with toluene until dry. The residue was purified by flash chromatography (hexane/AcOEt = 4:1) to obtain 0.45 g of **27D** (86%). $[\alpha]_D^{20}$ = –20.0 (*c* = 2.0, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.40–7.20 (m, 20 H, 4Ph), 5.09–4.35 (4 AB systems, 8 H, $4CH_2Ph$), 4.19 (dd, *J* = 9.5 and 3.5 Hz, 1 H, H^2), 4.09 (t, *J* = 9.3 Hz, 1 H, H^4), 4.02 (t, *J* = 9.3 Hz, 1 H, H^3), 3.99 (dd, *J* = 9.4 and 2.9 Hz, 1 H, H^5), 3.89 (t, *J* = 3.6 Hz, 1 H, H^1), 3.83 (t, *J* = 3.2 Hz, 1 H, H^6), 2.58 (s, 1 H, OH) and 2.42 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 140.5 (C), 139.8 (C), 139.6 (C), 139.5 (C), 129.2–128.1 (20CH, Ph), 82.4 (C^4), 80.9 (C^5), 78.4 (C^1), 76.1 (C^6), 76.0 (CH_2Ph), 75.5 (C^3), 74.4 (CH_2Ph), 74.1 (CH_2Ph), 73.8 (CH_2Ph) and 73.0 (C^2) ppm. FAB HRMS calcd. for $[C_{34}H_{36}O_6+Na]^+$: 563.2407, found: 563.2409.

1,4,5,6-Tetra-*O*-benzyl-L-*chiro*-inositol (24L): This compound was prepared from L-quebrachitol, following the same experimental procedure described for 1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (**24D**). $[\alpha]_D^{20}$ = +20.0 (*c* = 2.0, $CHCl_3$).

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α(1→2)-1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (28), 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α(1→3)-1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (30), 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-β(1→2)-1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (29) and 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-β(1→3)-1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (31): These pseudodisaccharides were prepared from 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl trichloroacetimidate (**2**) (68 mg, 0.11 mmol) and 1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (**24D**) (60 mg, 0.11 mmol) as described for the preparation of **13** and **15** by addition of 0.08 equiv. (88 μL of a 0.1 M solution) of TMSOTf at –40 °C in dry ether (2.5 mL) and stirring the reaction mixture for 1 h at –40 °C; yield, after flash chromatography (toluene/acetone = 30:1), 40 mg of a mixture (2:1) of pseudodisaccharides **28** and **30** (36%), 18 mg of pseudodisaccharide **29** (16%) and 14 mg of pseudodisaccharide **31** (13%). In order to confirm the regiochemistry of these pseudodisaccharides some of them were treated with Ac_2O/Py.

Data of the α(1→2) Pseudodisaccharide 28: ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50–7.10 (m, 35 H, 7Ph), 5.11–4.17 (7 AB systems, 14 H, $7CH_2Ph$), 4.85 (d, *J* = 3.7 Hz, 1 H, $H^{1\prime}$), 4.55 (m, 1 H, $H^{5\prime}$), 4.40 (m, 1 H, H^3), 4.27 (dd, *J* = 8.4 and 3.7 Hz, 1 H, H^2), 4.20 (m, 2 H, $H^{3\prime}$ and H^4), 4.18 (dd, *J* = 9.7 and 2.6 Hz, 1 H, H^5), 4.01 (t, *J* = 3.8 Hz, 1 H, H^1), 3.89 (m, 1 H, H^6), 3.77 (m, 1 H, $H^{4\prime}$), 3.73 (dd, *J* = 10.8 and 4.4 Hz, 1 H, $H^{6a\prime}$), 3.67 (dd, *J* = 10.4 and 1.6 Hz, 1 H, $H^{6b\prime}$), 3.33 (d, *J* = 8.4 Hz, 1 H, OH) and 3.25 (dd, *J* = 10.2 and 3.7 Hz, 1 H, $H^{2\prime}$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 140.7, 139.9, 139.7, 139.6, 139.5, 139.4, 139.3 (7C), 129.2–127.9 (35CH, Ph), 98.3 ($C^{1\prime}$), 81.5 (CH), 81.2 (CH), 80.5 (CH), 79.7 (CH), 77.2 (CH), 76.5 (CH), 75.9 (CH_2Ph), 75.8 (CH_2Ph), 75.5 (CH_2Ph), 75.1 (CH), 74.7 (CH_2Ph), 74.4 (CH_2Ph), 74.2 (CH), 74.1 (CH_2Ph), 74.0 (CH_2Ph), 72.3 (CH), 69.6 (CH_2) and 64.9 (CH) ppm.

Data of the Acetylated α(1→2) Pseudodisaccharide 28: ^{1}H NMR (500 MHz, C_6D_6): δ = 6.12 (t, 1 H, *J* = 9.8 Hz, H^3) ppm.

Data of the α(1→3) Pseudodisaccharide 30: ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50–7.10 (m, 35 H, 7Ph), 5.55 (d, 1 H, *J* = 3.8 Hz, $H^{1\prime}$), 5.11–4.17 (7 AB systems, 14 H, $7CH_2Ph$), 4.93 (m, 1 H, $H^{5\prime}$), 4.40 (m, 1 H, H^4), 4.20 (m, 2 H, $H^{3\prime}$ and H^3), 4.18 (dd, *J* = 9.7 and 2.6 Hz, 1 H, H^2), 4.04 (dd, *J* = 9.8 and 2.6 Hz, 1 H, H^5), 3.89 (m, 1 H, H^1), 3.77 (m, 2 H, $H^{6a\prime}$ and H^6), 3.63 (dd, *J* = 10.4 and 4.1 Hz, 1 H, $H^{6b\prime}$), 3.47 (dd, *J* = 10.0 and 9.0 Hz, 1 H, $H^{4\prime}$) and 3.10 (dd, *J* = 10.3 and 3.8 Hz, 1 H, $H^{2\prime}$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 140.7, 140.6, 139.7, 139.5, 139.5, 139.4, 139.3 (7C, Ph), 129.2–127.9 (35CH, Ph), 99.7 ($C^{1\prime}$), 83.1 (CH), 82.9 (CH), 82.3 (CH), 81.5 (CH), 81.2 (CH), 79.9 (CH), 79.5 (CH), 76.3 (CH_2Ph), 76.1 (CH_2Ph), 75.9 (CH_2Ph), 75.4 (CH_2Ph), 74.5 (CH_2Ph), 73.9 (CH_2Ph), 73.8 (CH_2Ph), 71.9 (CH), 71.8 (CH), 70.3 (CH_2) and 64.9 (CH) ppm.

Data of the Acetylated α(1→3) Pseudodisaccharide 30: ^{1}H NMR (500 MHz, C_6D_6): δ = 5.79 (dd, *J* = 9.3 and 2.6 Hz, 1 H, H^2) ppm.

Data of the β(1→2) Pseudodisaccharide 29: $[\alpha]_D^{20}$ = –11.7 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50–7.10 (m, 35 H, 7Ph), 5.15–4.38 (7 AB systems, 14 H, $7CH_2Ph$), 4.64 (d, *J* = 8.2 Hz, 1 H, $H^{1\prime}$), 4.55 (t, *J* = 9.7 Hz, 1 H, H^3), 4.37 (dd, *J* = 9.8 and 3.4 Hz, 1 H, H^2), 4.31 (t, *J* = 3.4 Hz, 1 H, H^1), 4.24 (t, *J* = 9.7 Hz, 1 H, H^4), 4.14 (dd, *J* = 9.7 and 3.7 Hz, 1 H, H^5), 3.90 (t, *J* = 3.5 Hz, 1 H, H^6), 3.68 (t, *J* = 9.2 Hz, 1 H, $H^{4\prime}$), 3.64 (dd, *J* = 10.8 and 4.2 Hz, 1 H, $H^{6a\prime}$), 3.57 (dd, *J* = 11.0 and 1.6 Hz, 1 H, $H^{6b\prime}$), 3.51 (dd, *J* = 9.4 and 8.2 Hz, 1 H, $H^{2\prime}$), 3.37 (t, *J* = 9.3 Hz, 1 H, $H^{3\prime}$), 3.11 (m, 1 H, $H^{5\prime}$) and 2.95 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 140.6, 140.0, 139.9, 139.7, 139.6, 139.4, 139.3 (7C), 129.2–128.1 (35CH, Ph), 104.1 ($C^{1\prime}$), 83.9 (CH), 82.7 (CH), 81.9 (CH), 80.7 (CH), 78.8 (CH), 78.7 (CH), 77.0 (CH), 76.1 (CH_2Ph), 75.9 (CH_2Ph), 75.6 (CH), 75.4 (CH_2Ph), 74.9 (CH_2Ph), 74.6 (CH), 74.2 (CH_2Ph), 74.0 (CH_2Ph), 73.9 (CH_2Ph), 69.7 (CH_2) and 67.7

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(CH) ppm. FAB HRMS calcd. for $[C_{61}H_{63}O_{10}N_3+Na]^+$: 1020.4411, found: 1020.4398.

Data of the β(1→3) Pseudodisaccharide 31: $[\alpha]_D^{20}$ = –18.7 (*c* = 0.7, $CHCl_3$), ^{1}H NMR (500 MHz, C_6D_6): δ = 7.65–7.10 (m, 35 H, 7Ph), 5.45–4.25 (7 AB systems, 14 H, 7CH_2Ph), 4.82 (d, *J* = 8.2 Hz, 1 H, H$^{1\prime}$), 4.54 (m, 1 H, H^2), 4.40 (t, *J* = 9.3 Hz, 1 H, H^3), 4.29 (t, *J* = 9.3 Hz, 1 H, H^4), 4.09 (dd, *J* = 9.4 and 3.7 Hz, 1 H, H^5), 3.98 (t, *J* = 3.7 Hz, 1 H, H^1), 3.87 (t, *J* = 3.7 Hz, 1 H, H^6), 3.74 (t, *J* = 9.2 Hz, 1 H, H$^{4\prime}$), 3.59 (dd, *J* = 11.0 and 3.8 Hz, 1 H, H$^{6a\prime}$), 3.53 (dd, *J* = 11.0 and 1.6 Hz, 1 H, H$^{6b\prime}$), 3.51 (dd, *J* = 9.5 and 8.2 Hz, 1 H, H$^{2\prime}$), 3.37 (t, *J* = 9.5 Hz, 1 H, H$^{3\prime}$) and 3.13 (m, 1 H, H$^{5\prime}$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 141.3, 140.0, 139.6, 139.6, 139.6, 139.5, 139.3 (7C), 129.2–127.7 (35CH, Ph), 103.2 (C$^{1\prime}$), 85.5 (CH), 84.5 (CH), 81.2 (CH), 80.5 (CH), 78.9 (CH), 78.8 (CH), 76.2 (CH_2Ph), 76.1 (CH), 76.0 (CH), 75.9 (CH_2Ph), 75.2 (CH_2Ph), 74.5 (CH_2Ph), 74.3 (CH_2Ph), 74.2 (CH_2Ph), 74.1 (CH_2Ph), 73.6 (CH), 69.5 (CH_2) and 67.7 (CH) ppm. FAB HRMS calcd. for $[C_{61}H_{63}O_{10}N_3+Na]^+$: 1020.4411, found: 1020.4378.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-α(1→2)-1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (32), 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-α(1→3)-1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (34), 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-β(1→2)-1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (33) and 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-β(1→3)-1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (35): These pseudodisaccharides were prepared from 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl trichloroacetimidate (**5**) (68 mg, 0.11 mmol) and 1,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (**24D**) (60 mg, 0.11 mmol) as described for the preparation of **13** and **15** by addition of 0.08 equiv. (88 μL of 0.1 M solution) of TMSOTf at –40 °C in dry ether (2.5 mL) and stirring the reaction mixture for 1 h at –40 °C to yield, after flash chromatography (hexane/AcOEt = 4:1), 13 mg of the pseudodisaccharide **32** (12%), 7 mg of the pseudodisaccharide **34** (6%), 16 mg of the pseudodisaccharide **33** (14%) and 24 mg of the pseudodisaccharide **35** (22%).

Data of the α(1→2) Pseudodisaccharide 32: ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50–7.10 (m, 35 H, 7Ph), 5.24–4.32 (7 AB systems, 14 H, 7CH_2Ph), 4.93 (d, *J* = 3.5 Hz, 1 H, H$^{1\prime}$), 4.60 (m, 1 H, H$^{5\prime}$), 4.31 (m, 1 H, H^4), 4.26 (dd, *J* = 9.5 and 3.8 Hz, 1 H, H^5), 4.20–4.12 (m, 3 H, H$^{2\prime}$, H^2 and H^3), 4.07 (dd, *J* = 11.6 and 2.5 Hz, 1 H, H$^{3\prime}$), 4.00 (br. t, *J* = 3.8 Hz, 1 H, H^6), 3.92 (s, 1 H, H$^{4\prime}$), 3.87 (br. t, *J* = 3.8 Hz, 1 H, H^1), 3.79 (dd, *J* = 8.2 and 6.4 Hz, 1 H, H$^{6\prime a}$) and 3.68 (dd, *J* = 8.2 and 6.4 Hz, 1 H, H$^{6\prime b}$) ppm. ^{13}C NMR (dep135) (125 MHz, C_6D_6): δ = 128.4–127.1 (35CH, Ph), 98.1 (C$^{1\prime}$), 82.4 (CH), 80.9 (CH), 79.7 (CH), 77.7 (CH), 76.2 (CH), 75.9 (CH), 75.7 (CH_2Ph), 74.8 (CH_2Ph), 73.8 (CH_2Ph), 73.7 (CH), 73.6 (CH_2Ph), 73.5 (CH), 73.4 (CH_2Ph), 73.3 (CH_2Ph), 71.8 (CH_2Ph), 70.3 (CH), 69.2 (CH_2) and 60.7 (CH) ppm. FAB HRMS calcd. for $[C_{61}H_{63}O_{10}N_3+Na]^+$: 1020.4411, found: 1020.4420.

Data of the Acetylated α(1→2) Pseudodisaccharide 32: ^{1}H NMR (500 MHz, C_6D_6): δ = 6.11 (t, *J* = 10.1 Hz, 1 H, H^3) ppm.

Data of the α(1→3) Pseudodisaccharide 34: $[\alpha]_D^{20}$ = +21.4 (*c* = 0.3, $CHCl_3$).^{1}H NMR (500 MHz, C_6D_6): δ = 7.60–7.10 (m, 35 H, 7Ph), 5.78 (dd, *J* = 3.5 Hz, 1 H, H$^{1\prime}$), 5.34–4.20 (7 AB systems, 14 H, 7CH_2Ph), 5.02 (m, 1 H, H$^{5\prime}$), 4.44–4.38 (m, 3 H, H^2, H^3, and H^4), 4.12 (dd, *J* = 10.7 and 2.6 Hz, 1 H, H$^{3\prime}$), 4.08 (dd, *J* = 10.8 and 3.5 Hz, 1 H, H$^{2\prime}$), 3.99 (dd, *J* = 9.5 and 3.6 Hz, 1 H, H^5), 3.92 (t, *J* = 3.8 Hz, 1 H, H^1), 3.81 (dd, *J* = 9.5 and 7.9 Hz, 1 H, H$^{6a\prime}$), 3.76 (t, *J* = 3.7 Hz, 1 H, H^6), 3.70 (s, 1 H, H$^{4\prime}$), 3.54 (dd, *J* = 9.5 and 4.2 Hz, 1 H, H$^{6b\prime}$) and 3.39 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 140.6, 139.8, 139.7, 139.6, 139.3, 139.1, 138.4 (7C), 129.0–128.0 (35CH, Ph), 99.9 (C$^{1\prime}$), 82.6, 81.6, 80.3, 79.8, 79.1, 76.2, 75.2, 75.1, 75.0, 74.3, 74.2, 74.1, 73.9, 72.7, 72.0, 71.9, 71.5 and 71.0 (10CH and 8CH_2) ppm. $C_{61}H_{63}O_{10}N_3$ (998.1872): calcd. C 73.40 %, H 6.36 %, N 4.20 %; found: C 73.57 %, H 6.44 %, N 4.05 %.

Data of the Acetylated α(1→3) Pseudodisaccharide 34: ^{1}H NMR (500 MHz, C_6D_6): δ = 5.80 (dd, *J* = 9.8 and 3.1 Hz, 1 H, H^2) ppm.

Data of the β(1→2) Pseudodisaccharide 33: $[\alpha]_D^{20}$ = –16.2 (*c* = 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50–7.10 (m, 35 H, 7Ph), 5.12–4.30 (7 AB systems, 14 H, CH_2Ph), 4.63 (d, *J* = 8.2 Hz, 1 H, H$^{1\prime}$), 4.56 (m, 1 H, H^3), 4.38 (dd, *J* = 9.9 and 2.9 Hz, 1 H, H^2), 4.27–4.23 (m, 2 H, H^1 and H^4), 4.16 (dd, *J* = 10.3 and 8.2 Hz, 1 H, H$^{2\prime}$), 4.13 (dd, *J* = 9.7 and 2.7 Hz, 1 H, H^5), 3.86 (t, *J* = 3.5 Hz, 1 H, H^6), 3.76 (s, 1 H, H$^{4\prime}$), 3.75 (dd, *J* = 8.9 and 7.9 Hz, 1 H, H$^{6a\prime}$), 3.57 (dd, *J* = 8.8 and 5.7 Hz, 1 H, H$^{6b\prime}$), 3.23 (m, 1 H, H$^{5\prime}$), 3.16 (dd, *J* = 10.3 and 2.9 Hz, 1 H, H$^{3\prime}$) and 3.03 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.7, 140.1, 139.9, 139.7, 139.7, 139.1, 138.9 (7C), 129.3–128.1 (35CH, Ph), 104.3 (C$^{1\prime}$), 82.7(CH), 81.8 (CH), 81.8 (CH), 80.7 (CH), 78.2 (CH), 77.1 (CH), 76.1 (CH_2Ph), 75.7 (CH_2Ph), 74.8 (CH), 74.6 (CH_2Ph), 74.2 (CH_2Ph), 74.1 (CH), 74.0 (CH_2Ph), 73.9 (CH_2Ph), 73.6 (CH), 73.0 (CH_2Ph), 69.3 (CH_2) and 64.7 (CH) ppm. FAB HRMS calcd. for $[C_{61}H_{63}O_{10}N_3+Na]^+$: 1020.4411, found: 1020.4409.

Data of the β(1→3) Pseudodisaccharide 35: $[\alpha]_D^{20}$ = –21.1 (*c* = 1.2, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.63–7.10 (m, 35 H, 7Ph), 5.28–4.17 (7 AB systems, 14 H), 4.73 (d, *J* = 8.2 Hz, 1 H, H$^{1\prime}$), 4.52 (m, 1 H, H^2), 4.37 (t, *J* = 9.6 Hz, 1 H, H^3), 4.23 (t, *J* = 9.7 Hz, 1 H, H^4), 4.17 (dd, *J* = 10.2 and 8.2 Hz, 1 H, H$^{2\prime}$), 4.09 (dd, *J* = 9.7 and 3.5 Hz, 1 H, H^5), 3.99 (t, *J* = 3.7 Hz, 1 H, H^1), 3.87 (t, *J* = 3.6 Hz, 1 H, H^6), 3.83(d, *J* = 2.6 Hz, 1 H, H$^{4\prime}$), 3.72 (t, *J* = 8.8 Hz, 1 H, H$^{6a\prime}$), 3.67 (s, 1 H, OH), 3.37 (dd, *J* = 8.9 and 5.3 Hz, 1 H, H$^{6b\prime}$), 3.24 (m, 1 H, H$^{5\prime}$) and 3.21 (dd, *J* = 10.3 and 2.6 Hz, 1 H, H$^{3\prime}$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 141.1, 140.1, 139.8, 139.6, 139.6, 139.3, 138.7 (7C), 129.3–127.7 (35CH, Bn), 103.7 (C$^{1\prime}$), 85.6 (CH), 82.8 (CH), 80.9 (CH), 80.6 (CH), 78.7 (CH), 76.3 (CH), 76.2 (CH_2Ph), 75.6 (CH_2Ph), 74.5 (CH_2Ph), 74.4 (CH_2Ph), 74.2 (CH_2Ph), 74.1 (CH_2Ph), 74.0 (CH), 73.7 (CH), 73.1 (CH), 72.6 (CH_2Ph), 68.9 (CH_2) and 64.9 (CH) ppm. FAB HRMS calcd. for $[C_{61}H_{63}O_{10}N_3+Na]^+$: 1020.4411, found: 1020.4395.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α(1→2)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (36), 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α(1→3)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (38), 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-β(1→2)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (37) and 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-β(1→3)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (39): These pseudodisaccharides were prepared from 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl trichloroacetimidate (**2**) (63 mg, 0.101 mmol) and 1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (**24L**) (55 mg, 0.101 mmol) as described for the preparation of **13** and **15** by addition of 0.08 equiv. (80 μL of 0.1 M solution) of TMSOTf at –40 °C in dry ether (2.0 mL) and stirring the reaction mixture for 1 h at –40 °C to yield, after flash chromatography (hexane/EtOAc = 4:1), 23 mg of a mixture (9:1) of the pseudodisaccharides **36** and **39** (23%), 8 mg of the pseudodisaccharide **38** (8%) and 13 mg of the pseudodisaccharide **37** (13%). In order to confirm the regiochemistry of these pseudodisaccharides, some of them were treated with Ac_2O/Py.

Data of the α(1→2) Pseudodisaccharide 36: ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50–7.10 (m, 35 H, 7Ph), 5.24–4.40 (7 AB systems, 14 H, 7CH_2Ph), 5.17 (d, *J* = 3.4 Hz, 1 H, H$^{1\prime}$), 4.30–4.12 (m, 6 H, H$^{3\prime}$, H$^{5\prime}$, H^3, H^4, H^6 or H^1 and H^2 or H^5), 4.07 (dd, *J* = 9.7 and 2.6 Hz, 1 H, H^2 or H^5), 3.91 (br. t, *J* = 3.5 Hz, 1 H, H^1 or H^6), 3.70–3.63 (m, 2 H, H$^{6a\prime}$, H$^{6b\prime}$), 3.57 (t, *J* = 9.5 Hz, 1 H, H$^{4\prime}$) and

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3.12 (dd, J = 10.2 and 3.4 Hz, 1 H, H$^{2'}$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 140.7, 140.1, 139.6, 139.5, 139.4, 139.3, 139.3 (7C), 129.4–128.1 (35CH, Ph), 100.7 (C$^{1'}$), 82.7, 81.7, 81.5, 80.3, 79.6, 78.7, 76.2, 76.1, 75.9, 75.5, 75.0, 74.4, 74.3, 74.2, 73.6, 72.8, 70.2 and 65.2 (10CH and 8CH_2) ppm.

Data of the Acetylated α(1→2) Pseudodisaccharide 36: ^{1}H NMR (500 MHz, C_6D_6): δ = 6.17 (t, J = 9.8 Hz, 1 H, H^3) ppm.

Data of the α(1→3) Pseudodisaccharide 38: $[\alpha]_D^{20}$ = +25.7 (c = 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50–7.10 (m, 35 H, 7Ph), 5.23–4.20 (7 AB systems, 14 H, 7CH_2Ph), 5.47 (d, J = 3.5 Hz, 1 H, H$^{1'}$), 4.30–4.17 (m, 5 H, H$^{3'}$, H$^{5'}$,H^2, H^3, and H^4), 4.10 (dd, J = 9.4 and 3.6 Hz, 1 H, H^5), 3.96 (br. t, J = 3.5 Hz, 1 H, H^1), 3.92 (t, J = 9.6 Hz, 1 H, H$^{4'}$), 3.83 (t, J = 3.5 Hz, 1 H, H^6), 3.53 (dd, J = 11.3 and 2.6 Hz, 1 H, H$^{6'a}$), 3.33 (d, J = 11.0 Hz, 1 H, H$^{6'b}$) and 3.20 (dd, J = 10.1 and 3.5 Hz, 1 H, H$^{2'}$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 140.4, 139.9, 139.7, 139.7, 139.6, 139.5, 139.5 (7C), 129.5–128.0 (35CH, Bn), 99.8 (C$^{1'}$), 83.1, 81.9, 81.7, 80.6, 79.5, 78.5, 76.0, 75.9, 75.8, 75.5, 74.8, 74.2, 74.1, 74.0, 73.8, 72.5, 69.3 and 65.6 (10CH and 8CH_2) ppm. $C_{61}H_{63}O_{10}N_3$ (998.1872): calcd. C 73.40 %, H 6.36 %, N 4.20 %; found: C 73.53 %, H 6.39 %, N 4.46 %.

Data of the Acetylated α(1→3) Pseudodisaccharide 38: ^{1}H NMR (500 MHz, C_6D_6): δ = 6.17 (dd, J = 10.2 and 3.4 Hz, 1 H, H^2).

Data of the β(1→2) Pseudodisaccharide 37: $[\alpha]_D^{20}$ = +9.7 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.56–7.10 (m, 35 H, 7Ph), 5.56–4.35 (7 AB systems, 14 H, 7CH_2Ph), 4.37 (m, 2 H, H^3 and H^4), 4.24 (dd, J = 9.7 and 3.7 Hz, 1 H, H^2), 4.21 (dd, J = 9.6 and 2.7 Hz, 1 H, H^5), 4.13 (br. t, J = 3.7 Hz, 1 H, H^1), 4.07 (d, J = 7.5 Hz, 1 H, H$^{1'}$), 3.96 (br. t, J = 3.6 Hz, 1 H, H^6), 3.62–3.49 (m, 3 H, H$^{6a'}$, H$^{6b'}$ and H$^{4'}$), 3.32–3.25 (m, 2 H, H$^{2'}$ and H$^{3'}$) and 3.21 (m, 1 H, H$^{5'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.8, 139.1, 138.8, 138.7, 138.1, 138.0, 139.9 (7C), 128.8–127.6 (35CH, Ph), 103.1 (C$^{1'}$), 84.8, 83.5, 82.2, 79.3, 78.0, 77.8, 75.9, 75.9, 75.7, 75.4, 75.3, 75.2, 74.1, 73.9, 73.9, 73.8, 68.8 and 66.9 (10CH and 8CH_2) ppm. $C_{61}H_{63}O_{10}N_3$ (998.1872): calcd. C 73.40 %, H 6.36 %, N 4.20 %; found: C 73.28 %, H 6.23 %, N 4.33 %.

Data of the Acetylated β(1→2) Pseudodisaccharide 37: ^{1}H NMR (500 MHz, C_6D_6): δ = 6.15 (t, J = 9.9 Hz, 1 H, H^3) ppm.

Data of the β(1→3) Pseudodisaccharide 39: ^{1}H NMR (500 MHz, C_6D_6): δ = 7.70–7.10 (m, 35 H, 7Ph), 5.27–4.40 (7 AB systems, 14 H, 7CH_2Ph), 4.64 (d, J = 8.1 Hz, 1 H, H$^{1'}$), 4.35 (t, J = 9.2 Hz, 1 H, H^3 or H^4), 4.30–3.90 (m, 5 H, H^1, H^2, H^3 or H^4, H^5 and H^6), 3.68 (m, 2 H, H$^{6a'}$, H$^{6b'}$), 3.59 (t, J = 9.1 Hz, 1 H, H$^{4'}$), 3.35 (dd, J = 8.1 and 2.2 Hz, 1 H, H$^{2'}$), 3.27 (t, J = 8.1 Hz, 1 H, H$^{3'}$) and 3.02 (m, 1 H, H$^{5'}$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 140.8, 140.2, 139.6, 139.5, 139.5, 139.3, 139.2 (7C), 129.4–128.1 (35CH, Ph), 103.2 (C$^{1'}$), 84.4, 83.7, 83.1, 82.7, 81.9, 81.6, 81.2, 78.3, 77.8, 75.5, 75.3, 74.3, 74.2, 73.8, 73.5, 71.8, 69.2 and 67.5 (10CH and 8CH_2) ppm.

Data of the Acetylated β(1→3) Pseudodisaccharide 39: ^{1}H NMR (500 MHz, C_6D_6): δ = 5.93 (dd, J = 7.1 and 1.8 Hz, 1 H, H^2) ppm.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-α(1→2)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (40), 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-β(1→2)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (41) and 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-β(1→3)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (42): These pseudodisaccharides were prepared from 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl trichloroacetimidate (**5**) (50 mg, 0.08 mmol) and 1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (**6L**) (43 mg, 0.08 mmol) as described for the preparation of **13** and **15** by addition of 0.08 equiv. (64 μL of 0.1 M solution) of TMSOTf at –40 °C in dry ether (2 mL) and stirring the reaction mixture for 1 h at –40 °C to yield, after flash chromatography (hexane/AcOEt = 4:1), 20 mg of the pseudodisaccharides **41** (20%), 5 mg of the pseudodisaccharide **40** (5%) and 10 mg of the pseudodisaccharide **42** (10%).

Data of the α(1→2) Pseudodisaccharide 40: $[\alpha]_D^{20}$ = +30.8 (c = 0.2, $CHCl_3$). $_1$H NMR (500 MHz, C_6D_6): δ = 7.60–7.10 (m, 35 H, 7Ph), 5.32–4.30 (7 AB systems, 14 H, 7CH_2Ph), 5.12 (d, J = 2.5 Hz, 1 H, H$^{1'}$), 4.28 (m, 2 H, H$^{5'}$ and H^4), 4.22 (dd, J = 9.7 and 3.0 Hz, 1 H, H^2), 4.20–4.13 (m, 2 H, H^3 and H^1), 4.08–4.02 (m, 2 H, H$^{3'}$ and H^5), 3.99 (dd, J = 10.5 and 2.5 Hz, 1 H, H$^{2'}$), 3.92 (t, J = 3.3 Hz, 1 H, H^6), 3.81 (s, 1 H, H$^{4'}$), 3.72 (dd, J = 9.2 and 6.4 Hz, 1 H, H$^{6a'}$) and 3.67 (dd, J = 9.2 and 6.1 Hz, 1 H, H$^{6b'}$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 140.9, 140.2, 139.8, 139.7, 139.4, 139.2 and 138.9 (7C), 129.8–128.2 (35CH, Ph), 101.5 (C$^{1'}$), 82.8, 82.7, 80.3, 79.5, 79.3, 76.3, 76.3, 75.6, 75.1, 74.8, 74.4, 74.3, 73.8, 72.8, 72.4, 71.6, 70.7 and 62.0 (10CH and 8CH_2) ppm. $C_{61}H_{63}O_{10}N_3$ (998.1872): calcd. C 73.40 %, H 6.36 %, N 4.20 %; found: C 73.78 %, H 6.72 %, N 4.17 %.

Data of the Acetylated α(1→2) Pseudodisaccharide 40: ^{1}H NMR (500 MHz, C_6D_6): δ = 6.16 (t, J = 9.8 Hz, 1 H, H^3) ppm.

Data of the β(1→2) Pseudodisaccharide 41: $[\alpha]_D^{20}$ = +14.3 (c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.65–7.10 (m, 35 H, 7Ph), 5.50–4.21 (7 AB systems, 14 H, 7CH_2Ph), 4.30 (m, 1 H, H^4), 4.26 (dd, J = 9.3 and 3.8 Hz, 1 H, H^2), 4.20 (m, 1 H, H^5), 4.16 (br. t, J = 3.8 Hz, 1 H, H^6), 4.11 (t, J = 9.3 Hz, 1 H, H^3), 4.09 (m, 2 H, H$^{1'}$ and H$^{2'}$), 3.95 (br. t, J = 3.7 Hz, 1 H, H^1), 3.66 (br. s, 1 H, H$^{4'}$), 3.61–3.55 (m, 2 H, H$^{5'}$ and H$^{6'a}$), 3.26 (br. t, J = 6.4 Hz, 1 H, H$^{6'b}$), 3.07 (dd, J = 9.5 and 2.5 Hz, 1 H, H$^{3'}$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 141.1, 140.3, 139.8, 139.8, 139.4, 139.1 and 138.8 (7C), 129.6–127.9 (35CH, Ph), 104.1 (C$^{1'}$), 86.3, 83.3, 81.8, 80.3, 78.9, 77.4, 76.5, 75.7, 74.9, 74.9, 74.8, 74.7, 74.6, 74.3, 73.1, 72.9, 69.5 and 64.7 (10CH and 8CH_2) ppm. $C_{61}H_{63}O_{10}N_3$ (998.1872): calcd. C 73.40 %, H 6.36 %, N 4.20 %; found: C 73.45 %, H 6.21 %, N 4.36 %.

Data of the Acetylated β(1→2) Pseudodisaccharide 41: ^{1}H NMR (500 MHz, C_6D_6): δ = 6.12 (t, J = 10.7 Hz, 1 H, H^3) ppm.

Data of the β(1→3) Pseudodisaccharide 42: $[\alpha]_D^{20}$ = +5.0 (c = 0.5, $CHCl_3$).^{1}H NMR (500 MHz, C_6D_6): δ = 7.68–7.10 (m, 35 H, 7Ph), 5.22–4.25 (7 AB systems, 14 H, 7CH_2Ph), 4.63 (d, J = 8.1 Hz, 1 H, H$^{1'}$), 4.49 (m, 1 H, H^4), 4.37 (m, 1 H, H^3), 4.21 (dd, J = 9.1 and 2.8 Hz, 1 H, H^2), 4.15 (dd, J = 10.2 and 8.1 Hz, 1 H, H$^{2'}$), 4.14–4.11 (m, 2 H, H^5 and H^6), 3.88 (t, J = 2.9 Hz, 1 H, H^1), 3.65 (d, J = 2.6 Hz, 1 H, H$^{4'}$), 3.63–3.57 (m, 2 H, H$^{5'}$ and H$^{6a'}$), 3.17 (t, J = 6.5 Hz, 1 H, H$^{6b'}$) and 3.07 (dd, J = 10.3 and 2.7 Hz, 1 H, H$^{3'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.3, 139.1, 138.8, 138.6, 138.5, 138.0 and 137.8 (7C), 128.8–127.4 (35 CH, Ph), 102.7 (C$^{1'}$), 83.1, 81.1, 81.0, 80.5, 78.2, 75.8, 75.0, 74.8, 74.3, 73.9, 73.8, 73.8, 73.2, 72.8, 72.5, 70.6, 68.5 and 63.6 (10CH and 8CH_2) ppm. $C_{61}H_{63}O_{10}N_3$ (998.1872): calcd. C 73.40 %, H 6.36 %, N 4.20 %; found: C 73.62 %, H 6.39 %, N 4.45 %.

Data of the Acetilated β(1→3) Pseudodisaccharide 42: ^{1}H NMR (500 MHz, C_6D_6): δ = 5.91 (dd, J = 10.2 and 1.4 Hz, 1 H, H^2) ppm.

Supporting Information (see also the footnote on the first page of this article): Cartesian coordinates (Å) and Absolute Energies (a.u.) for carbonium ions (2-N_3) and (2-OMe), acceptors (1,4-diOAc) and (1,4-diOMe) models and complexes **AL3**, **AL2**, **AD3**, **AD2**, **ML3**, **ML2**, **MD3**, **MD2**, **AL′3** and **AL′2** and the spatial arrangement of all the optimized complexes.

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