CHEMISTRY
A EUROPEAN JOURNAL

A Study on the Influence of the Structure of the Glycosyl Acceptors on the Stereochemistry of the Glycosylation Reactions with 2-Azido-2-Deoxy-Hexopyranosyl Trichloroacetimidates

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Abstract: The stereochemical outcome of glycosylations with 2-azido-2-deoxy-D-gluco- and D-galactopyranosyl trichloroacetimidates as glycosyl donors has been investigated by using a series of *chiro*-inositol derivatives as glycosyl acceptors. The influence of the absolute configuration, the conformation and the conformational flexibility of the glycosyl acceptor has been studied by using different glycosyl donors under similar pre-established experimental conditions. Although the structure of the acceptor may play a role in governing the stereochemistry of these glycosylations, the results show that, in general terms, the relative influence of these factors is difficult to evaluate. For a given set of experimental conditions, the stereochemical course of these glycosylations depends on structural features of both glycosyl donor and glycosyl acceptor. It is a balance of these factors, where the structure of the glycosyl donor always plays a major role, which determines the stereochemistry of the coupling reaction. Therefore, the examples reported in the literature in which the structure of the glycosyl acceptor appears to be crucial in determining the stereochemistry of the reaction constitute particularly favorable cases which do not presently allow any further generalization.

Keywords: carbohydrates · glycosides · glycosylation · oligosaccharides

Introduction

A considerable number of oligosaccharides of biological significance contain α-linked D-glucosaminyl or D-galactosaminyl units.[1] Therefore, the stereoselective construction of these 1,2-*cis* glycosidic linkages is a matter of current interest in areas of glycobiology where the synthesis of these complex oligosaccharides is needed.[2] The major requirement for the stereoselective synthesis of 1,2-*cis* glycosidic bonds is the presence of a non-participating group at C-2 of the glycosyl donor, and the most commonly used non-participating group to install the α-D-glucosaminyl and the α-D-galactosaminyl linkages is the azido group.[3] The 2-azido moiety, serving both as a latent function and as a non-participating protecting group in glycosylation reactions, was first introduced by Paulsen[4] and has been extensively used in complex oligosaccharide synthesis ever since.[5] The stereochemical outcome of glycosylations by using 2-azido-2-deoxy sugars as glycosyl donors, however, is not always predictable and seems to depend on the nature of the anomeric leaving groups and on that of the promoters used in the glycosylations.[5] Furthermore, by using imidates as glycosyl donors, the stereochemistry has been reported to be also strongly dependent on the experimental conditions, the orientation of the leaving group and the nature of the acceptor.[5,6] Consequently, the stereoselectivity of these glycosylation reactions is difficult to forecast[6a] particularly when the trichloroacetimidate method, which is most frequently employed in the synthesis of complex oligosaccharide molecules, is used.[6b–d]

A remarkable example has been reported by Seeberger et al.[7] In developing a modular synthesis of heparin-like oligosaccharides, these authors have shown that, locking the conformation of a glucuronic acid acceptor in the $^1C_4$ form **1**, the glycosylation reaction with a conveniently protected 2-azido-2-deoxy-D-glucopyranosyl trichloroacetimidate led to the completely selective formation of the desired 1,2-*cis* disaccharide; the reaction of the same donor with the unlocked acceptor in the $^4C_1$ conformation **2** gave mixtures of

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DOI: 10.1002/chem.200400746

1,2-*cis* and 1,2-*trans* isomers.[7] These results, which have also been shown to occur when using fluorides as donors, seem to indicate that the stereochemical outcome of these glycosylations is, in this case, also related to the flexibility and the conformation of the acceptor. We have found, also in the field of synthetic heparin fragments, that the glycosylation of a tightly locked L-iduronic acid lactone **3** gives the corresponding α-glycoside with a good although poorer selectivity than the glycosylation of the corresponding unlocked L-iduronic acid derivative **4** (Figure 1).[8]

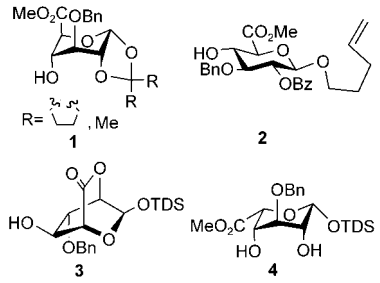


Figure 1. Glucuronic and iduronic acid glycosyl acceptors.

There are many cases in the literature showing the stereoselective formation of both 1,2-*cis* and 1,2-*trans* glycosidic bonds from donors bearing the 2-azido function, but the possible influence of the structure of the acceptor on the stereoselectivity has not been systematically investigated.[5,6] The intrinsic reactivity of the hydroxyl groups, primarily in terms of axial or equatorial orientation affecting the reactivity–selectivity balance[9] and steric factors resulting in matched/mismatched donor–acceptor pairs[10a] could be major players. However, our present understanding of the possible role of the acceptor in the stereochemistry of these complex reactions is still far from satisfactory.

As a consequence of our continued interest in the synthesis of inositolphosphoglycan (IPG)-type compounds as potential mediators in the insulin signaling process[11] we have worked extensively with 2-azido-2-deoxy-D-gluco- and D-galactopyranosyl trichloroacetimidates, as glycosyl donors, and with a variety of *myo*- and *chiro*-inositol derivatives as glycosyl acceptors. The stereoselectivity of these glycosylations also seemed to be somehow dependent on the structure of the acceptor. In the case of the D-*chiro*-inositol derivatives, where a series of pseudodisaccharides were required having the α1→1 glycosidic linkage, the reaction of acceptors **5**, **6** and **7** with 2-azido-2-deoxy-D-glucopyranosyl trichloroacetimidates, afforded anomeric mixtures containing a considerable amount of the β-anomers.[11c,g,h] By contrast, the α1→2 glycosidic linkage in the same D-*chiro* series and the α1→3 glycosidic linkage in the L-*chiro* series[11i] as well as the α1→6 glycosidic linkage in the D-*myo* series[11b,e] were formed with fair to good stereoselectivity under similar experimental conditions. These results apparently point to the conclusion that the orientation of the OH acceptor influences the steric course of the reaction as HO-1 has, in the *chiro* series, an axial-like orientation, whereas HO-2 and HO-3 in this series and also OH-6 in the D-*myo* series (see for instance compound **8** frequently used in our laboratory as glycosyl acceptor) can be described as equatorial-like according to NMR data. On the other hand, since no significant differences in the stereoselectivity were observed in the glycosylation of **5**–**7**, conformational constrain did not appear to play an important role in this case (Figure 2).

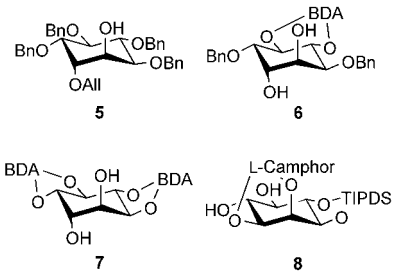


Figure 2. D-*myo*- and D-*chiro*-inositol glycosyl acceptors.

Because of our interest in obtaining building blocks for the synthesis of L-*chiro*-inositol containing IPGs[11i] we now have also investigated the stereochemistry of the formation of the 1→1 glycosidic linkage in the L-*chiro*-inositol series. Considering the difficulties found for the construction of this structural motif in the D series, we thought that a parallel study using the enantiomeric L-*chiro*-inositol acceptors would offer a good opportunity to get some additional insight into the influence of steric and conformational features of the acceptor on the stereoselectivity by comparing the data from both the D- and the L-*chiro* series. The results of this study are presented and discussed below.

Results and Discussion

It was expected[10a] that, according to the principle of double stereodifferentiation,[10b] the comparative study on the glycosylation of enantiomeric cyclitols with glycosyl donors carrying the 2-azido function should give additional information on the role of the glycosyl acceptor, particularly on the influence of steric factors in the selectivity of the process. Compound **9**, the enantiomer of **5**, was synthesized from D-*myo*-inositol[12] and compounds **10** and **11**, the enantiomers of **6** and **7**, respectively, from L-quebrachitol following the protocol described for the preparation of **6** and **7** from D-*chiro*-inositol (Figure 3).[11g]

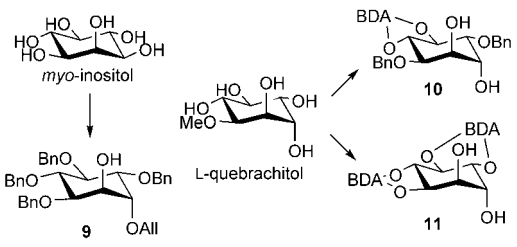


Figure 3. L-*chiro*-inositol glycosyl acceptors.

The stereochemical course of the glycosylation of these L-*chiro*-inositol derivatives was investigated under the same experimental conditions previously established for the glycosylation of the corresponding D-enantiomers. A general view of the reactions discussed is given in Scheme 1.

The glycosylation of **9** with glycosyl donors **12**–**14** (Figure 4) was studied under the same experimental conditions as used before for the glycosylation of the D-enantiomer **5**.[11c] These experimental conditions had been previously established, from a preparative point of view, to obtain the α pseudodisaccharides **15**α, **17**α and **19**α as the main products from each of the glycosyl donors investigated.

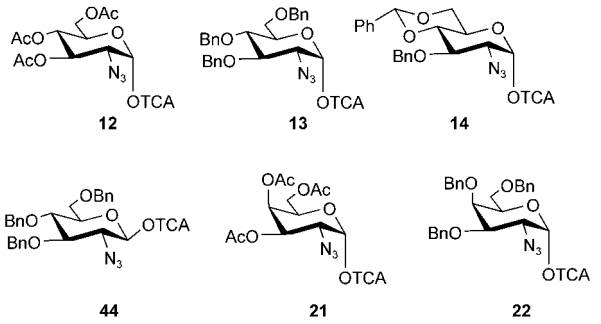


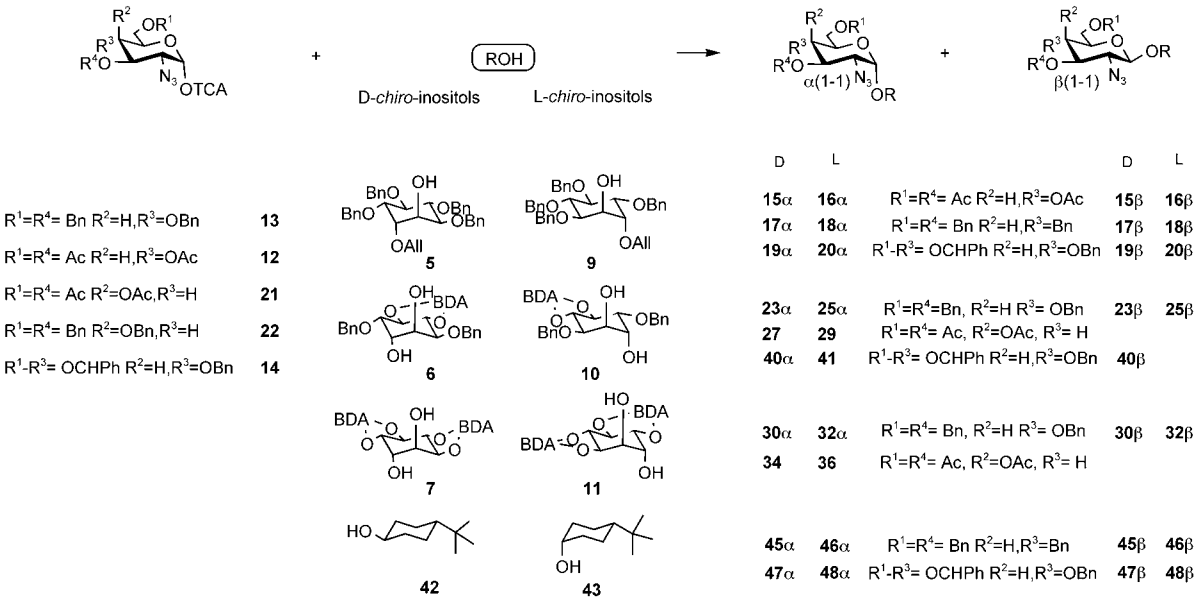
Figure 4. Glycosyl donors.

The results—which should be taken only as a qualitative indication of stereochemical outcome of these reactions as all experiments have been performed on a preparative basis and the yields calculated based on weight of isolated products—are summarized in Table 1 which also shows the results previously obtained for **5**.[11c] Although in general terms, the poor selectivity of the process in the D series was also observed in the L series, the results were indicative of a higher α selectivity in the case of the L-enantiomers. However, in this case, under the same experimental conditions, the steric course of the reaction leading to the L-*chiro* compounds **16**α and **16**β, **18**α and **18**β, **20**α and **20**β, seemed to essentially depend on the structure of the glycosyl donor, the most reactive tri-*O*-benzyl trichloroacetimidate **13** leading to the less stereoselective reaction (Figure 5).

Table 1. Glycosylation of enantiomers **5** and **9**. Reaction conditions, reaction products and yields (%).

Donors	Reaction conditions	Acceptors **5** (D series)	**9** (L series)
12	1 equiv acceptor, 1.3 equiv donor 0.1 equiv TMSOTf, CH_2Cl_2, rt, 1 h	**15**α (44) **15**β (31)	**16**α (65) **16**β (15)
13	1.6 equiv acceptor, 1 equiv donor 0.06 equiv TMSOTf, CH_2Cl_2, −25 °C (30 min) to rt (10 min)	**17**α (35) **17**β (25)	**18**α (42) **18**β (42)
14	1 equiv acceptor, 1.5 equiv donor 0.03 equiv TMSOTf, CH_2Cl_2, rt, 4.5 h	**19**α (49) **19**β (21)	**20**α (47) **20**β (5)

The glycosylation of the conformationally constrained L-*chiro*-inositols **10** and **11** was next investigated in the conditions previously used by us to obtain pseudodisaccharides **23**α, **30**α, **27** and **34** as the main products by coupling the D-enantiomers **6** and **7** with trichloroacetimidates **13** and **21**. Also, the course of the glycosylation of the enantiomeric pair **6** and **10** with trichloroacetimidate **14** under similar experimental conditions was examined (Figure 6). The structures of glycosyl acceptors **6**–**10** contain two equivalent axially oriented hydroxyl groups and therefore diglycosylated pseudotrisaccharides could be formed as minor products under the reaction conditions.



Scheme 1.

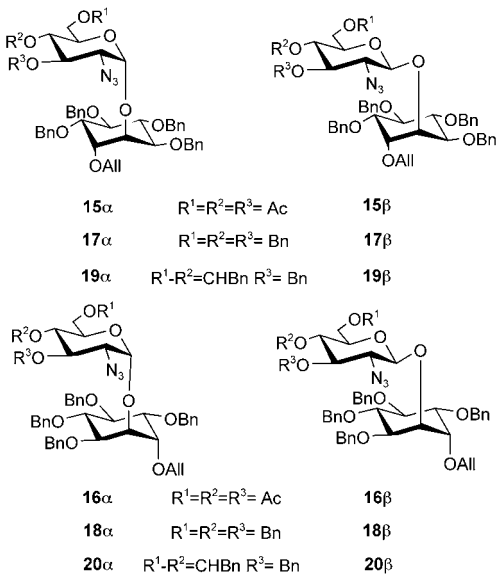


Figure 5. Pseudodisaccharides resulting from reaction of donors **12**, **13** and **14** with acceptors **5** and **9**.

Table 2 summarizes the results in comparison with those previously reported by us for the D-*chiro* series.[11g] Glycosylations with the per-O-benzylated D-glucotrichloroacetimidate **13**, which had shown poor stereoselectivity in the D-*chiro* series, showed no stereoselectivity in the L-*chiro* series and compounds **25**α and **25**β and **32**α and **32**β were isolated in similar proportions. However, as for the D-*chiro* compounds, excellent stereoselectivity was observed with the per-O-acetylated donor with D-*galacto* configuration **21**, compounds **29** and **36** being isolated as the only reaction products. These results parallel those already obtained for the conformationally restricted 3-*O*-methyl-D-*chiro*-inositol (D-pinitol) derivative **37** which gave a 2:1 **38**α, **38**β mixture when reacting with **13**, and **39** as the sole pseudodisaccharide when reacting with the perbenzylated trichloroacetimidate **22** (Figure 7).[11h]

As in the glycosylation of **5** and **9** with donor **14** (Table 1), the stereoselectivity of the reaction of **6** and **10** with donor **14** was higher than that observed in the glycosylation of these diols with donor **13**. Also, in this case, the glycosylation of the L-*chiro* compound **10**, which afforded **41** as the sole product, was more stereoselective than that of the D-*chiro* derivative **6** which gave a mixture of **40**α and **40**β (Figure 7). Noteworthy, the α,α-pseudotrisaccharides **24** and **31**, respectively, could be isolated in the glycosylation of **6** and **7** with trichloroacetimidate **13** while the coupling of their enantiomers **10** and **11** with the same donor afforded the β,β-pseudotrisaccharides **26** and **33** in similar yields. Also, in the reaction mixtures of the coupling of D-*galacto*

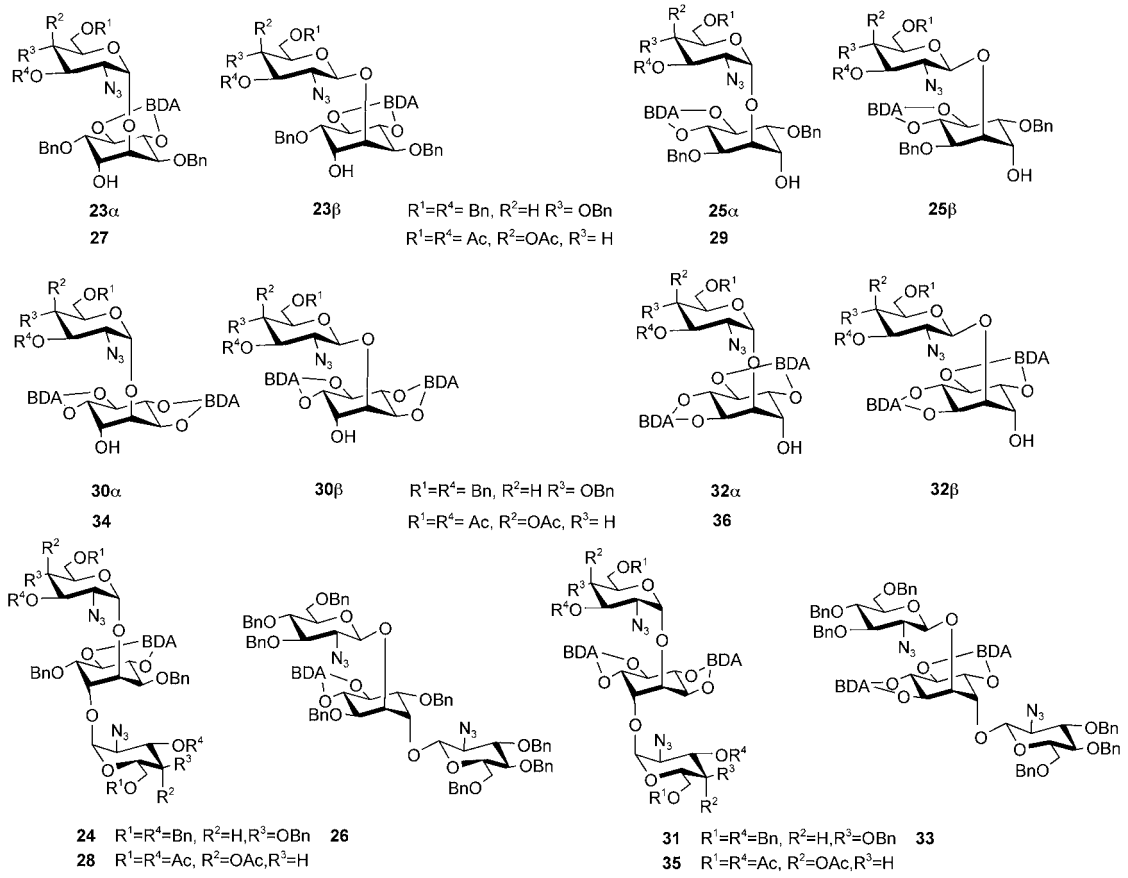


Figure 6. Pseudodisaccharides resulting from reaction of donors **13** and **21** with acceptors **6**,**7**,**10** and **11**.

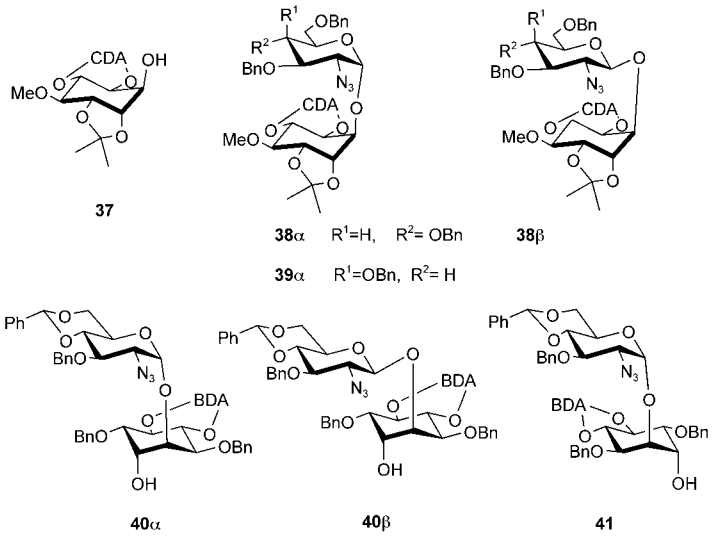


Figure 7. Pseudodisaccharides resulting from reaction of donors **13** and **21** with acceptors **6**, **7**, **10** and **11**.

Table 2. Glycosylation of enantiomers **6** and **10** and **7** and **11**. Reaction products and yields (%).

Donor	Acceptor				
	6 (D series)	**10** (L series)	**7** (D series)	**11** (L series)	**37** (D-pinitol)
	A	A	A	A	B
	23α (42)	**25**α (26)	**30**α (43)	**32**α (18)	**38**α (36)
13	**23**β (18)	**25**β (26)	**30**β (20)	**32**β (23)	**38**β (18)
	24 (7)	**26** (5)	**31** (5)	**33** (9)	
	C	C	C	C	
21	**27**α (51)	**29** (37)	**34**α (52)	**36** (69)	
	28 (14)		**35** (11)		
22					D
					39 (46)
	E	E			
14	**40**α (22)	**41** (56)			
	40β (6)				

[a] A: 1 equiv acceptor, 1.6 equiv donor, 0.1 equiv TMSOTf, CH_2Cl_2, −25 °C, 1 h. B: 1 equiv acceptor, 1.5 equiv donors, 0.08 equiv TMSOTf, CH_2Cl_2, rt. C: 1 equiv acceptor, 2 equiv donor, 0.1 equiv TMSOTf, CH_2Cl_2, rt, 1 h. D: 1 equiv acceptor, 1.3 equiv donor, 0.15 equiv TMSOTf, CH_2Cl_2/Hex, −40 °C. E: 1 equiv acceptor, 1.5 equiv donor, 0.03 equiv TMSOTf, CH_2Cl_2, rt, 4.5 h.

configurated trichloroacetimidate **21** the α,α-pseudotrisaccharides **28** and **35** were found whereas no formation of pseudotrisaccharide was observed in the glycosylation of their enantiomers (**10** and **11**) with the same donor.

It can be concluded that the stereoselectivity of these glycosylations of axially oriented hydroxyl groups of *chiro*-inositol derivatives, either of the D or the L series, with various protection patterns and different conformational flexibility and under similar experimental conditions, strongly depends on the structure of the 2-azido-2-deoxy trichloroacetimidate donor and on the orientation and, to some extent, the absolute configuration of the OH acceptor but not, to an important extent, on the conformational constrain of the inositol ring. While glycosylation of equatorially oriented OH groups of compounds belonging to either series occurs with good selectivity in most of the cases studied,[11i] the stereochemical outcome of the glycosylation of their axially oriented counterparts much more strongly depends on the structure and the reactivity of the donor.

But even the role of the orientation of the acceptor OH group is difficult to assess as was demonstrated by the following model study. In this study the stereochemistry of the glycosylation of *trans*- (**42**) and *cis*- (**43**) 4-*tert*-butyl cyclohexanol with trichloroacetimidates **13**, **14** and **44** was investigated by using experimental conditions similar to those in the experiments summarized in Tables 1 and 2. The results are shown in Figure 8 and Table 3.

In the cases of glycosyl donors **13** and **44** both glycosides **45**α and **45**β and **46**α and **46**β were formed but the stereochemistry was always predominantly β. As expected according to the reaction conditions, the configuration of the leaving group did not seem to have any effect on the selectivity. In the case of glycosyl donor **14**, glycosides **47**α and **47**β and **48**α and **48**β were formed as well but the stereochemistry was predominantly α. Therefore, all other things being equal, it seems to be the glycosyl donor that mainly dictates the stereochemical course of the glycosylations in these specific cases.

The configuration of the acceptor also seems to play a role as evidenced in some of the results shown in Tables 1 and 2, particularly the glycosylation of **5** and **9** (Table 1) and that of **6** and **10** (Table 2) with trichloroacetimidate **14**. Both in the case of the less sterically constrained **5** and **9** and in that of the conformationally restricted **6** and **11**, the glycosylations occurred with higher α stereoselectivity in the L-*chiro* series.

Table 3. Glycosylation of **42** and **43**. Reaction products and yields (%).[a]

Acceptor	Donors		
	13	**44**	**14**
42	**45**α (12)	**45**α (17)	**47**α (48)
	45β (52)	**45**β (51)	**47**β (17)
43	**46**α (12)	**46**α (13)	**48**α (48)
	46β (37)	**46**β (42)	**48**β (22)

[a] Reaction conditions: 1 equiv acceptor, 1.2 equiv donor, CH_2Cl_2, 0.1 equiv TMSOTf, −25 °C, 1 h.

This glycosyl donor gave a good stereoselectivity in all cases, most likely as a result of the flattening and the restriction of the conformational flexibility of the pyranoid ring,

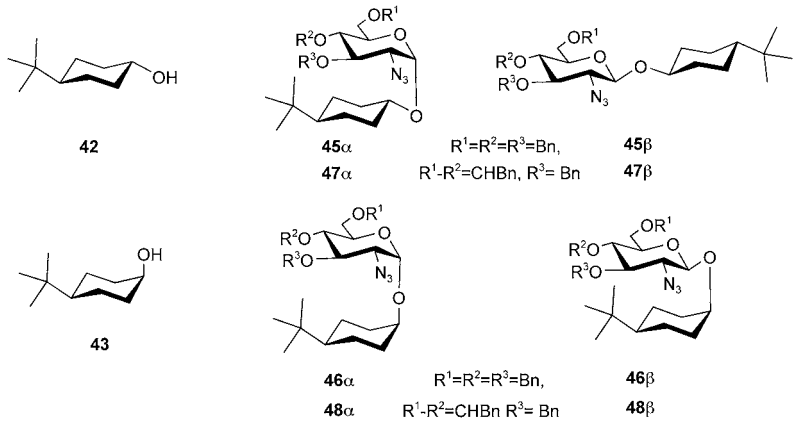


Figure 8. Pseudodisaccharides resulting from reaction of donors **13, 44** and **14** with cyclohexenol acceptors **42** and **43**.

caused by the benzylidene ring, which may also favor the axial nucleophilic attack.[14]

The glycosylations with the per-O-acetylated trichloroacetimidate with the D-*galacto* configuration **21** occurred with excellent stereoselectivity and those with the per-O-benzylated trichloroacetimidate with the D-*gluco* configuration **13** gave very poor results. It is known that the long range participation of the 4-OH group of glycosyl donors with the *galacto* configuration may stabilize the $^4C_1$ conformation of the pyranoid ring thus favoring axial nucleophilic attack on the intermediate glycosyl oxocarbenium ion.[13] But the system is too complex to draw precise conclusions on the relative influence of the factors governing the stereochemistry of these glycosylations, particularly when using reactive donors with the D-*gluco* configuration.

Conclusion

In summary, we have examined the steric course of the glycosylation of the relatively unreactive axially oriented hydroxyl groups of D- and L-*chiro* inositol derivatives with 2-azido-2-deoxy-D-gluco- and D-galactopyranosyl trichloroacetimidates. The influence of the absolute configuration of the acceptor and the conformational flexibility and substitution pattern of both donor and acceptor on the stereoselectivity of the reaction has been investigated. The effect of the orientation of the acceptor hydroxyl group and the orientation of the leaving group of the donor have been further studied by using *cis*- and *trans*-4-hydroxy-*tert*-butyl cyclohexanol and α- and β-trichloroacetimidates. The results indicate that the influence of the absolute configuration, the orientation of the acceptor OH group and the conformational constrain of the acceptor on the stereochemical outcome of the reaction are difficult to asses and the existing data in the literature difficult to rationalize. According to our data, it is the structure of the glycosyl donor that always plays the major role. The control of the stereochemical course of these glycosylations with 2-azido-2-deoxy-trichloroacetimidates still requires considerable experimentation. Only a careful investigation of the effect of reaction conditions, solvent, temperature and promoter, and the choice of a glycosyl donor that, fitting the synthesis needs, matches its reactivity–selectivity requirements with those of the given acceptor may permit to achieve the desired stereochemistry. Two very recent cases in the field of glycosaminoglycan synthesis have clearly shown that undesired stereochemical surprises may arise when a glycosylation step with a 2-azido-2-deoxy glycosyl donor is involved at the late stage of a complex synthetic process.[15] The interesting results by Seeberger et al.[7] on the conformational locking of the acceptor for stereocontrol of glycosylations with these glycosyl donors and the impressive demonstration by Spijker and van Boeckel of the double stereodifferentiation in carbohydrate coupling reactions[10a] constitute brilliant demonstrations of principles whose practical consequences can be clearly observed only in particularly favorable cases.

Experimental Section

General remarks: Diethyl ether and dichloromethane were distilled from sodium/benzophenone and calcium hydride, respectively. 4-*tert*-Butylcyclohexanol was purchased from Aldrich as a mixture of isomers that was separated by flash chromatography (hexane/ethyl acetate 4:1) to give pure *cis*-*tert*-butylcyclohexanol and *trans*-4-*tert*-butylcyclohexanol. Molecular sieves (4 Å, powered) was dried in the oven at 100 °C and activated for 5 min under vacuum at 500 °C. All reactions were run under an atmosphere of dry argon using oven-dried glassware and freshly distilled and dried solvents unless otherwise stated. TLC was performed on 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 (300, 400 and 500 MHz) and ^{13}C (125 and 75 MHz) NMR spectra were recorded at 25 °C in $CDCl_3$ unless otherwise noted, chemical shifts are given in ppm relative to $CDCl_3$ (7.27 ppm) and coupling constants are reported in Hz. Resonances were assigned by means of 2D spectra (COSY, HMQC).

2-Azido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl-α-(1→1)-6-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-L-*chiro*-inositol (16α) and 2-azido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl-β-(1→1)-6-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-L-*chiro*-inositol (16β): A mixture of 2-azido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl trichloroacetimidate (**12**) (86 mg, 0.181 mmol) and **9** (35 mg, 0.06 mmol) was co-evaporated with toluene (3×), 4 Å molecular sieves was added and the residue dried under vacuum overnight. The mixture was dissolved in CH_2Cl_2 (2 mL) under argon and stirred at room temperature for 30 min, then TMSOTf (0.1 equiv, 28.5 μL of a solution 0.2 M in CH_2Cl_2) was added at rt. After 1 h the reaction mixture was quenched with Et_3N, concentrated and purified by flash chromatography (cyclohexane/ethyl acetate 3:1) to yield **16**α (36 mg, 65 %) and **16**β (8 mg, 15 %). **16**α: $[\alpha]_D = +78.5$ ($c = 1.6$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.40$–7.20 (m, 20H, 4Bn), 5.78–5.71 (m, 1H, CH vinylic), 5.43 (d, 1H, $J = 3.8$ Hz, $H_{1'}$), 5.22 (t, 1H, $J = 9.9$ Hz, $H_{3'}$), 5.11 (m, 2H, CH_2 vi-

nylic), 4.96 (t, 1H, $J=9.9$ Hz, $H_{4'}$), 4.98–4.58 (4AB, 8H), 4.17 (dd, 1H, $J=12.3$, 4.6 Hz, $H_{6'a}$), 4.08 (dd, 1H, $J=10.3$, 6.0 Hz, CH allylic), 3.96 (t, 1H, $J=9.5$ Hz, H_3 or H_4), 3.92 (brt, 1H, $J=2.9$ Hz, H_1 or H_6), 3.90–3.83 (m, 2H, CH allylic, $H_{6'b}$), 3.82 (t, 1H, $J=9.5$ Hz, H_4 or H_3), 3.77 (dd, 1H, $J=9.5$, 2.9 Hz, H_2 or H_5), 3.72 (dd, 1H, $J=9.5$, 3.1 Hz, H_5 or H_2), 3.50 (m, 1H, $H_{5'}$), 3.34 (dd, 1H, $J=9.9$, 3.8 Hz, $H_{2'}$), 3.23 (t, 1H, $J=3.1$ Hz, H_6 or H_1), 2.10 (3s, 9H, $3OCOCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=170.8$ ($OCOCH_3$), 170.1 ($OCOCH_3$), 169.8 ($OCOCH_3$), 139.3 (C), 139.2 (C), 138.9 (C), 138.7 (C), 135.0 (*C*H vinylic), 128.9–127.7 (20CH, Bn), 117.6 (CH_2 vinylic), 98.4 ($C_{1'}$), 82.3 (CH), 81.8 (CH), 79.8 (CH), 79.4 (CH), 76.7 (CH), 76.2 ($2CH_2$), 74.5 (CH_2), 74.2 (CH_2), 74.0 (CH), 72.5 (CH_2), 70.3 (CH), 68.8 (CH), 68.0 (CH), 62.1 (CH_2), 61.4 (CH), 21.1 ($OCOCH_3$), 21.0 ($OCOCH_3$), 20.9 ($OCOCH_3$); FAB HRMS: *m/z*: calcd for $C_{49}H_{55}O_{13}N_3Na$: 916.3632; found: 916.3645 $[M+Na]^+$.

Compound **16**β: $[\alpha]_D = -4.0$ ($c=0.4$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.40$–7.20 (m, 20H, 4Bn), 5.77 (m, 1H, CH vinylic), 5.14 (m, 2H, CH_2 vinylic), 4.98 (m, 2H, $H_{1'}$ and $H_{6'a}$), 4.89–4.62 (4 AB syst, 8H), 4.23 (m, 3H, CH allylic, $H_{3'}$ and $H_{6'b}$), 4.12 (brs, 1H, H_1 or H_6), 4.09 (t, 1H, $J=10.3$ Hz, $H_{4'}$), 3.95 (dd, 1H, $J=13.0$, 6.2 Hz, CH allylic), 3.86–3.80 (m, 4H, H_2, H_3, H_4, H_5), 3.76 (brs, 1H, H_6 or H_1), 3.57 (brt, 1H, $J=9.3$ Hz, $H_{2'}$), 3.53 (m, 1H, $H_{5'}$), 2.10 (s, 3H, $OCOCH_3$), 2.00 (s, 6H, $2OCOCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=170.9$ ($OCOCH_3$), 170.4 ($OCOCH_3$), 169.8 ($OCOCH_3$), 139.3 (2C), 138.8 (C), 138.6 (C), 135.2 (*C*H vinylic), 128.7–127.7 (20CH, Bn), 117.5 (CH_2 vinylic), 100.7 ($C_{1'}$), 82.0 (CH), 81.9 (CH), 80.2 (CH), 78.5 (CH), 77.7 (CH), 76.2 ($2CH_2$), 75.2 (CH), 74.2 (CH), 73.8 (CH_2), 73.3 (CH_2), 73.0 (CH), 72.5 (CH_2), 68.6 (CH), 63.9 (CH), 62.4 (CH_2), 30.0 ($OCOCH_3$), 21.0 ($OCOCH_3$), 20.9 ($OCOCH_3$); FAB HRMS: *m/z*: calcd for $C_{49}H_{55}O_{13}N_3Na$: 916.3632; found: 916.3637.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α-(1→1)-6-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-L-*chiro*-inositol (18α) and 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-β-(1→1)-6-allyl-2,3,4,5-tetra-*O*-benzyl-L-*chiro*-inositol (18β): The pseudodisacharides were prepared from **13** (50 mg, 0.08 mmol) and **9** (74 mg, 0.129 mmol) in dry CH_2Cl_2 (1 mL), as described for the preparation of **16**α and **16**β adding TMSOTf (0.06 equiv, 50 μL of a solution 0.1 M) at −25 °C and stirring the reaction mixture for 30 min at −25 °C, and 10 min at rt, yielding after flash chromatography (hexane/diethyl ether 4:1) **18**α (35 mg, 42%) and **18**β (35 mg, 42%). **18**α: $[\alpha]_D = +48.2$ ($c=1.7$, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): $\delta=7.50$–7.10 (m, 35H, 7Bn), 5.96–5.86 (m, 1H, CH vinylic), 5.50 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 5.29 (dd, 1H, $J=17.2$, 1.6 Hz, CH vinylic), 5.23–4.41 (7AB syst, 14H), 5.11 (dd, 1H, $J=17.2$, 1.6 Hz, CH vinylic), 4.43 (t, 1H, $J=9.5$ Hz, H_4), 4.34–4.30 (m, 2H, CH allylic, H_6), 4.28 (t, 1H, $J=9.5$ Hz, H_3), 4.14 (m, 1H, H_5), 4.12 (m, 1H, H_2), 4.07–4.02 (m, 1H, CH allylic), 4.00 (t, 1H, $J=9.3$ Hz, $H_{3'}$), 3.95 (brt, 1H, $J=3.1$ Hz, H_1), 3.94–3.89 (m, 1H, $H_{5'}$), 3.76–3.67 (m, 2H, $H_{6'a}$, $H_{6'b}$), 3.57 (t, 1H, $J=9.3$ Hz, $H_{4'}$), 3.13 (dd, 1H, $J=9.3$, 3.8 Hz, $H_{2'}$); ^{13}C NMR (125 MHz, C_6D_6): $\delta=140.5$ (C), 139.8 (2C), 139.4 (C), 139.3 (C), 139.2 (C), 138.6 (C), 136.2 (*C*H vinylic), 129.3–128.0 (35CH, Bn), 117.1 (CH_2 vinylic), 99.7 ($C_{1'}$), 83.1 (CH), 83.0 (CH), 80.8 (CH), 80.5 (2CH), 79.5 (CH), 77.5 (C_1), 76.5 (CH_2), 75.9 (CH_2), 75.8 (CH_2), 74.8 (CH), 74.3 ($2CH_2$), 74.1 (CH_2), 73.5 (CH_2), 72.7 (CH), 70.1 (CH_2), 69.0 (CH_2), 64.5 (CH); FAB HRMS: *m/z*: calcd for $C_{64}H_{67}O_{10}N_3Na$: 1060.4724; found: 1060.4668 $[M+Na]^+$.

Compound **18**β: $[\alpha]_D = -6.1$ ($c=1.7$, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): $\delta=7.50$–7.10 (m, 35H, 7Bn), 5.96–5.87 (m, 1H, CH vinylic), 5.31 (dd, 1H, $J=17.2$, 1.6 Hz, CH vinylic), 5.20–4.55 (7AB syst, 14H), 5.13 (dd, 1H, $J=17.2$, 1.6 Hz, CH vinylic), 4.56 (brt, 1H, $J=3.4$ Hz, H_1 or H_6), 4.45 (m, 2H, CH allylic and H_2 or H_5), 4.40–4.30 (m, 2H, H_3, H_4), 4.28 (d, 1H, $J=7.7$ Hz, $H_{1'}$), 4.22 (dd, 1H, $J=9.3$, 3.4 Hz, H_5 or H_2), 4.10 (m, 2H, CH allylic and H_6 or H_1), 3.66 (m, 3H, $H_{4'}$, $H_{6'a}$, $H_{6'b}$), 3.43 (m, 2H, $H_{2'}$ and $H_{3'}$), 3.30 (m, 1H, $H_{5'}$); ^{13}C NMR (125 MHz, C_6D_6): $\delta=140.7$ (C), 140.6 (C), 140.1 (C), 140.0 (C), 139.4 (C), 139.3 (C), 139.2 (C), 136.1 (*C*H vinylic), 129.1–128.0 (35CH, Bn), 117.1 (CH_2 vinylic), 101.5 ($C_{1'}$), 84.0 (CH), 83.0 (2CH), 81.3 (CH), 79.5 (CH), 78.7 (CH), 76.5 (CH_2), 76.4 (CH), 76.2 (CH_2), 76.1 (CH_2), 75.8 (CH), 75.5 (CH), 75.1 (CH_2), 74.5 (CH_2), 74.3 (CH_2), 73.7 (CH_2), 73.1 (CH_2), 69.8 (CH_2), 67.3 (CH); FAB HRMS: *m/z*: calcd for $C_{64}H_{67}O_{10}N_3Na$: 1060.4724; found: 1060.4695.

2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-α-(1→1)-6-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*chiro*-inositol (19α) and 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-β-(1→1)-6-allyl-2,3,4,5-tetra-*O*-benzyl-D-*chiro*-inositol (19β): The pseudodisaccharides were prepared from **14** (520 mg, 0.985 mmol) and **5** (382 mg, 0.657 mmol) as described for the preparation of **16**α and **16**β, adding at rt TMSOTf (0.1 equiv, 350 μL of a solution 0.2 M) and stirring the reaction mixture for 4.5 h at rt, yielding after flash chromatography (hexane/ethyl acetate 8:1) **19**α (302 mg, 49%) and **19**β (130.5 mg, 21%). **19**α: $[\alpha]_D = +5.6$ ($c=1.2$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.47$–7.21 (m, 30H, 6Bn), 5.79 (m, 1H, CH vinylic), 5.51 (s, 1H, CHPh), 5.17 (m, 1H, CH vinylic), 5.13 (m, 1H, CH_2 vinylic), 4.97–4.76 (5 AB, 10H), 4.70 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 4.25–4.17 (m, 2H, $H_{5'}$, CH allylic), 3.99 (t, 1H, $J=9.4$ Hz, $H_{3'}$), 3.97 (m, 1H, CH allylic), 3.95 (m, 1H, $H_{6'a}$), 3.97–3.74 (m, 6H, H_1, H_2, H_3, H_4, H_5, H_6), 3.64 (t, 1H, $J=9.4$ Hz, $H_{4'}$), 3.56 (t, 1H, $J=10.3$ Hz, $H_{6'b}$), 3.49 (dd, 1H, $J=9.4$, 3.8 Hz, $H_{2'}$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=139.3$ (C), 139.2 (C), 139.1 (C), 138.7 (C), 138.2 (C), 137.7 (C), 135.2 (*C*H vinylic), 129.3–126.3 (30CH, Bn), 117.5 (CH_2 vinylic), 101.6 (CHPh), 98.0 ($C_{1'}$), 83.2 (CH), 82.6 (CH), 82.1 (CH), 80.3 (CH), 78.5 (CH), 77.6 (CH), 76.4 (CH_2), 76.1 (CH_2), 75.5 (CH_2), 75.5 (CH), 74.1 (CH), 73.7 (CH_2), 73.7 (CH_2), 72.8 (CH_2), 69.1 (CH_2), 63.7 (CH), 63.2 (CH); FAB HRMS: *m/z*: calcd for $C_{57}H_{59}O_{10}N_3Na$: 968.4098; found: 968.4091 $[M+Na]^+$.

Compound **19**β: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.50$–7.20 (m, 30H, 6Bn), 5.74 (m, 1H, CH vinylic), 5.54 (s, 1H, CHPh), 5.15 (m, 1H, CH vinylic), 5.11 (m, 1H, CH vinylic), 4.90–4.60 (5 AB syst, 10H), 4.54 (d, 1H, $J=8.1$ Hz, $H_{1'}$), 4.21 (dd, 1H, $J=10.4$, 5.1 Hz, $H_{6'a}$), 4.13 (m, 1H, CH allylic), 3.92–3.74 (m, 6H, H_1, H_2, H_3, H_4, H_5, H_6), 3.70 (t, 1H, $J=9.3$ Hz, $H_{6'a}$), 3.61 (t, 1H, $J=9.3$ Hz, $H_{4'}$), 3.46 (t, 1H, $J=9.4$ Hz, $H_{3'}$), 3.28 (t, 1H, $J=8.1$ Hz, $H_{2'}$), 3.23 (dd, 1H, $J=9.3$, 5.1 Hz, $H_{5'}$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=139.4$ (C), 139.3 (C), 138.9 (C), 138.8 (C), 137.9 (C), 137.5 (C), 135.3 (*C*H vinylic), 129.9–127.2 (30CH, Bn), 117.2 (CH_2 vinylic), 103.2 ($C_{1'}$), 101.7 (CHPh), 82.1, 81.8, 81.6, 79.9, 79.7, 78.8, 76.1, 76.1, 76.0, 75.9, 75.7, 75.2, 73.8, 73.4, 72.5, 68.8, 66.2 (CH); FAB HRMS: *m/z*: calcd for $C_{57}H_{59}O_{10}N_3Na$: 968.4098; found: 968.4089.

2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-α-(1→1)-6-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-L-*chiro*-inositol (20α) and 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-β-(1→1)-6-allyl-2,3,4,5-tetra-*O*-benzyl-L-*chiro*-inositol (20β): The pseudodisaccharides were prepared from **14** (71 mg, 0.134 mmol) and **9** (52 mg, 0.09 mmol) in dry CH_2Cl_2 (1 mL) as described for the preparation of **16**α and **16**β adding at rt TMSOTf (0.1 equiv, 13.95 μL of a solution 0.2 M) and stirring the reaction mixture for 4.5 h, yielding after flash chromatography (hexane/ethyl acetate 8:1) **20**α (40 mg, 47%) and **20**β (4 mg, 5%). **20**α: $[\alpha]_D = +39.6$ ($c=2.0$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.50$–7.10 (m, 30H, 6Bn), 5.81–5.72 (m, 1H, CH vinylic), 5.57 (s, 1H, CHPh), 5.37 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 5.18–5.12 (m, 2H, CH_2 vinylic), 4.98–4.60 (5 AB syst, 10H), 4.15 (dd, 1H, $J=10.4$, 4.9 Hz, $H_{6'a}$), 4.09 (m, 1H, CH allylic), 4.01 (t, 1H, $J=9.5$ Hz, H_4), 3.96 (brs, 1H, H_6), 3.92 (m, 1H, CH allylic), 3.85 (t, 1H, $J=9.5$ Hz, H_3), 3.82–3.69 (m, 4H, $H_{3'}$, H_5, H_2, $H_{6'b}$), 3.65 (t, 1H, $J=9.3$ Hz, $H_{4'}$), 3.58–3.52 (m, 1H, $H_{5'}$), 3.47 (brs, 1H, H_1), 3.36 (dd, 1H, $J=9.9$, 3.8 Hz, $H_{2'}$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=139.4$ (C), 139.3 (C), 138.8 (C), 138.6 (C), 138.2 (C), 137.5 (C), 135.1 (*C*H vinylic), 129.4–126.2 (30CH, Bn), 117.8 (CH_2 vinylic), 101.6 (CHPh), 99.1 ($C_{1'}$), 82.8 (CH), 82.3 (CH), 81.9 (CH), 80.1 (CH), 79.4 (CH), 76.3 (CH_2), 76.2 (CH_2), 76.1 (CH), 75.8 (C_1), 75.5 (CH_2), 73.9 ($2CH_2$), 73.3 (CH), 72.4 (CH_2), 69.0 (CH_2), 63.5 (CH), 63.4 (CH); FAB HRMS: *m/z*: calcd for $C_{57}H_{59}O_{10}N_3Na$: 968.4098; found: 968.4108 $[M+Na]^+$.

Compound **20**β: $[\alpha]_D = -23.0$ ($c=0.2$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.50$–7.20 (m, 30H, 6Bn), 5.80–5.70 (m, 1H, CH vinylic), 5.60 (s, 1H, CHPh), 5.15–5.08 (m, 2H, CH_2 vinylic), 4.94–4.63 (5 AB syst, 10H), 4.33 (dd, 1H, $J=10.4$, 4.9 Hz, $H_{6'a}$), 4.17 (m, 1H, CH allylic), 4.15 (d, 1H, $J=8.2$ Hz, $H_{1'}$), 3.98 (brt, 1H, $J=3.1$ Hz, H_6), 3.92 (m, 1H, CH allylic), 3.88–3.77 (m, 6H, $H_{6'b}$, H_2, H_3, H_4, H_5, H_1), 3.76 (t, 1H, $J=9.3$ Hz, $H_{4'}$), 3.60 (t, 1H, $J=9.2$ Hz, $H_{3'}$), 3.50 (dd, 1H, $J=9.2$, 8.2 Hz, $H_{2'}$), 3.36–3.30 (m, 1H, $H_{5'}$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=139.4$ (C), 139.3 (C), 139.0 (C), 138.8 (C), 137.9 (C), 137.4 (C), 135.2 (*C*H vinylic), 129.5–126.3 (30CH, Bn), 117.3 (CH_2 vinylic), 101.7 (CHPh), 101.6 ($C_{1'}$), 82.1 (CH), 81.6 (CH), 80.3 (CH), 79.9 (C_1H), 78.5 (CH), 77.1 (CH_2), 77.0

(CH), 76.3 (CH_2), 76.2 (CH), 75.1 (CH_2), 74.4 (CH), 73.7 ($2CH_2$), 72.9 (CH_2), 68.8 (CH_2), 66.8 (CH), 65.9 (CH); FAB HRMS: m/z: calcd for $C_{57}H_{59}O_{10}N_3Na$: 968.409; found: 968.4100.

2,5-Di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-L-*chiro*-inositol (10): The compound has been prepared following the same experimental procedure described for its D-enantiomer **6** in ref. [11g]. $[\alpha]_D = -79.6$ ($c = 1$, $CHCl_3$).

2,3:4,5-Di-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-L-*chiro*-inositol (11): The compound has been prepared following the same experimental procedure described for its D-enantiomer **7** in ref. [11g]. $[\alpha]_D = +135.3$ ($c = 1$, $CHCl_3$).

Di(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-α,α-1→1:1→6)-2,5-di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (24): Prepared by reaction of acceptor **6** with donor **13**. $[\alpha]_D^{20} = +48.4$ ($c = 0.7$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.34$–7.03 (m, 40H, 8Ph), 4.86–4.81 (m, 4H, 4CHPh), 4.76 (d, 2H, $J_{H1',H2'} = 3.6$ Hz, $2H_1'$), 4.67–4.10 (m, 12H, 12CHPh), 4.02–3.98 (m, 4H, H_1, H_3, H_4, H_6), 3.93–3.90 (m, 2H, H_2, H_5), 3.80 (dd, 2H, $J_{H3',H2'} = 10.1$, $J_{H3',H4'} = 9.6$ Hz, $2H_3'$), 3.68 (dd, 2H, $J_{H4',H3'} = 10.1$, $J_{H4',H5'} = 9.5$ Hz, $2H_4'$), 3.47 (dd, 2H, $J_{H2',H3'} = 10.1$, $J_{H2',H1'} = 3.6$ Hz, $2H_2'$), 3.33 (s, 6H, $2OCH_3$), 3.23 (dd, 2H, $J_{H6'a,H6'b} = 11.1$, $J_{H6'a,H5'} = 2.0$ Hz, $2H_{6'a}$), 3.03 (dd, 2H, $J_{H6'b,H6'a} = 11.1$, $J_{H6'b,H5'} = 1.5$ Hz, $2H_{6'b}$), 1.36 (s, 6H, $2CH_3$).

Di(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl)-α,α(1→1:1→6)-2,5-di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (28): Prepared by reaction of acceptor **6** with donor **21**. $[\alpha]_D^{20} = +47.0$ ($c = 0.4$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.33$–7.19 (m, 10H, 2Ph), 5.32 (br d, 2H, $J_{H4',H3'} = 3.2$ Hz, $2H_4'$), 5.20 (dd, 2H, $J_{H3',H2'} = 11$, $J_{H3',H4'} = 3.2$ Hz, $2H_3'$), 4.93 (AB, 2H, 2CHPh), 4.85 (d, 2H, $J_{H1',H2'} = 3.5$ Hz, $2H_1'$), 4.64 (AB, 2H, 2CHPh), 4.60 (dd, 2H, $J_{H5',H6'} = 7.1$, $J_{H5',H6'} = 6.9$ Hz, $2H_5'$), 4.05–3.90 (m, 6H, H_1, H_2, H_3, H_4, H_5, H_6), 3.87–3.80 (m, 4H, $2H_2'$, $2H_{6'a}$), 3.57 (dd, 1H, $J_{H6'b,H6'a} = 10.9$, $J_{H6'b,H5'} = 6.9$ Hz, $2H_{6'b}$), 3.34 (s, 6H, $2OCH_3$), 2.08, 2.03, 1.85 (3s, 18H, $6CH_3CO$), 1.35 (s, 6H, $2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.7$, 170.4, 170.0 ($6CH_3CO$), 139.7 (2C, Bn), 127.8 (4CH, Bn), 127.6 (4CH, Bn), 127.4 (2CH, Bn), 99.7 (2C, BDA), 96.9 ($2C_1'$), 76.5, 74.5, 74.2 (C_1, C_2, C_5, C_6, $2CH_2Ph$), 71.1 (C_3, C_4), 70.0 ($2C_3'$), 67.7 ($2C_4'$), 66.8 ($2C_5'$), 61.3 ($2C_6'$), 58.1 ($2C_2'$), 46.5 ($2OCH_3$), 21.1, 21.0 ($6CH_3CO$), 18.3($2CH_3$).

Di(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-α,α-(1→1:1→6)-2,3:4,5-di-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (31): Prepared by reaction of acceptor **7** with donor **13**. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.31$–7.17 (m, 30H, 6Ph), 4.87–4.80 (m, 6H, 4CHPh, $2H_1'$), 4.77–4.41 (m, 8H, 8CHPh), 4.35 (br d, 2H, $J_{H5',H4'} = 9.2$ Hz, $2H_5'$), 3.99–3.85 (m, 8H, H_1, H_2, H_3, H_4 H_5, H_6, $2H_3'$), 3.76 (dd, 2H, $J_{H4',H3'} = 9.9$, $J_{H4',H5'} = 9.2$ Hz, $2H_4'$), 3.73 (dd, 2H, $J_{H6'a,H6'b} = 10.9$, $J_{H6'a,H5'} = 2.5$ Hz, $2H_{6'a}$), 3.63 (dd, 2H, $J_{H6'b',H6'a} = 10.9$, $J_{H6'b,H5'} = 1.7$ Hz, $2H_{6'b}$), 3.52 (dd, 2H, $J_{H2',H3'} = 10.0$, $J_{H2',H1'} = 3.5$ Hz, $2H_2'$), 3.25, 3.20 (2s, 12H, $4OCH_3$), 1.28, 1.18 (2s, 12H, $4CH_3$).

Di(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl)-α,α-(1→1:1→6)-2,3:4,5-di-*O*-(2′,3′-dimethoxy-butane-2′,3′-diyl)-D-*chiro*-inositol (35): Prepared by reaction of acceptor **7** with donor **21**. $[\alpha]_D^{20} = -33.6$ ($c = 0.3$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.32$ (dd, 2H, $J_{H4',H3'} = 3.2$, $J_{H4',H5'} = 1.2$ Hz, $2H_4'$), 5.23 (dd, 2H, $J_{H3',H2'} = 10.9$, $J_{H3',H4'} = 3.2$ Hz, $2H_3'$), 4.86 (d, 2H, $J_{H1',H2'} = 3.5$ Hz, $2H_1'$), 4.81 (ddd, 2H, $J_{H5',H6'a} = 7.6$, $J_{H5',H6'b} = 6.1$, $J_{H5',H4'} = 1.2$ Hz, $2H_5'$), 4.09 (dd, 2H, $J_{H6'a,H6'b} = 11$, $J_{H6'a,H5'} = 7.6$ Hz, $2H_{6'a}$), 4.01 (dd, 2H, $J_{H6'b,H6'a} = 11$, $J_{H6'b,H5'} = 6.1$ Hz, $2H_{6'b}$), 3.98–3.89 (m, 4H, H_1, H_3, H_4, H_6), 3.87 (dd, 2H, $J_{H2',H3'} = 10.9$, $J_{H2',H1'} = 6.5$ Hz, $2H_2'$), 3.82 (br d, 2H, $J = 2.0$ Hz, H_2, H_5), 3.27, 3.20 (2s, 12H, $4OCH_3$), 2.14, 2.04, 2.00 (3s, 9H, $3CH_3CO$), 1.28, 1.19 (2s, 12H, $4CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 170.3$, 170.1, 169.5 ($6CH_3CO$); 99.9, 98.6 (4C, BDA), 96.4 ($2C_1'$), 73.4, 69.5, 67.5, 67.1, 66.5, 66.1 (C_1, C_2, C_3, C_4, C_5, C_6, $2C_3'$, $2C_4'$, $2C_5'$), 61.1 ($2C_6'$), 57.9 ($2C_2'$), 48.2, 47.4 ($4OCH_3$), 20.7 ($6CH_3CO$), 17.6, 17.4 ($4CH_3$); MALDI-TOF: m/z: calcd for $C_{42}H_{62}N_6O_{24}Na$: 1058.0; found: 1057.5 $[M+Na]^+$; calcd for $C_{42}H_{62}N_6O_{24}K$: 1074.1; found: 1073.8 $[M+K]^+$.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α-(1→1)-2,5-di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-L-*chiro*-inositol (25α), 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-β-(1→1)-2,5-di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxy-butane-2′,3′-diyl)-L-*chiro*-inositol (25β) and di(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-β,β-(1→1:1→6)-2,5-di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxy-butane-2′,3′-diyl)-L-*chiro*-inositol (26): The pseudosaccharides were prepared from **13** (64 mg, 0.104 mmol) and **10** (31 mg, 0.065 mmol) as described for the preparation of **16**α and **16**β, adding TMSOTf (0.1 equiv, 0.65 mL of a solution 0.01 M) at −25 °C, in CH_2Cl_2 (2 mL) and stirring the reaction mixture for 1 h, yielding after flash chromatography (hexane/ethyl acetate 4:1) **25**α (16 mg, 25%), **25**β (15 mg, 25%), and β,β-pseudotrisaccharide **26** (5 mg, 5%). **25**α: $[\alpha]_D = -1.5$ ($c = 1.4$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.40$–7.10 (m, 25H, 5Bn), 5.44 (d, 1H, $J = 3.8$ Hz, $H_{1'}$), 4.96–4.45 (5 AB syst, 10H), 4.28 (t, 1H, $J = 10.3$ Hz, H_3), 4.22 (br t, 1H, $J = 3.5$ Hz, H_1), 4.02 (t, 1H, $J = 9.9$ Hz, H_4), 3.89 (dd, 1H, $J = 10.3$, 3.5 Hz, H_2), 3.87 (br t, 1H, $J = 3.5$ Hz, H_6), 3.75 (dd, 1H, $J = 8.2$, 3.5 Hz, H_5), 3.74–3.55 (m, 5H, $H_{3'}$, $2H_{6'}$, $H_{4'}$, $H_{5'}$), 3.38 (dd, 1H, $J = 10.1$, 3.8 Hz, $H_{2'}$), 3.31, 3.30 (2s, 6H, $2OCH_3$), 2.50 (s, 1H, $C_6O\mathit{H}$), 1.39, 1.34 (2s, 6H, $2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 139.5$, 138.7, 138.4, 138.2, 138.1 (5C, Bn), 128.8–127.4 (25CH, Bn), 99.7, 99.5 (2C BDA), 98.8 ($C_{1'}$), 80.3, 78.4, 77.1, 76.6, 75.7, 75.6, 75.2, 74.3, 74.2, 74.0, 71.4, 71.2, 70.5, 69.8, 68.5, 64.2 (10CH, $6CH_2$), 48.1 ($2OCH_3$), 18.3, 18.2 ($2CH_3$); elemental analysis calcd (%) for $C_{53}H_{61}O_{12}N_3 + {}^1/_2H_2O$: C 67.64, H 6.64, N 4.46; found: C 67.60, H 7.07, N 4.10.

Compound **25**β: $[\alpha]_D = -45.0$ ($c = 0.66$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.38$–7.12 (m, 25H, 5Bn), 4.91–4.35 (5 AB syst, 10H), 4.26 (br t, 1H, $J = 3.6$ Hz, H_1), 4.19 (d, 1H, $J = 7.7$ Hz, $H_{1'}$), 4.11 (br t, 1H, $J = 3.5$ Hz, H_6), 4.07 (t, 1H, $J = 9.9$ Hz, H_3), 4.00 (t, 1H, $J = 9.9$ Hz, H_4), 3.86 (dd, 1H, $J = 9.9$, 3.4 Hz, H_5), 3.83 (dd, 1H, $J = 10.0$, 3.6 Hz, H_2), 3.61–3.55 (m, 3H, $H_{6'b}$, $H_{4'}$, $H_{3'}$), 3.45–3.40 (m, 2H, $H_{2'}$, $H_{6'a}$), 3.35–3.30 (m, 1H, $H_{5'}$), 3.26 (s, 6H, $2OCH_3$), 2.48 (s, 1H, $C_6O\mathit{H}$), 1.34 (2s, 6H, $2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 139.3$, 138.5, 137.9, 137.8, 137.7 (5C, Bn), 128.8–127.4 (25CH, Bn), 101.1 ($C_{1'}$), 99.4, 99.2 (2C BDA), 83.7 (CH), 77.7 (CH), 76.3 (2CH), 75.4 (CH_2), 75.2 (CH), 75.0 (CH_2), 74.8 (CH), 73.6 (CH_2), 73.5 (CH_2), 72.4 (CH_2), 69.8 (CH), 69.2 (CH), 68.9 (CH), 68.2 (CH_2), 65.8 (CH), 48.1, 47.7 ($2OCH_3$), 17.8 ($2CH_3$); elemental analysis calcd (%) for $C_{53}H_{61}O_{12}N_3 + H_2O$: C 67.00, H 6.68, N 4.42; found: C 67.31, H 6.71, N 4.20.

Compound **26**: $[\alpha]_D = -52.4$ ($c = 0.25$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.40$–7.10 (m, 40H, 8Bn), 4.80–4.35 (8AB syst, 16H), 4.24 (d, 2H, H_1, H_6), 4.16 (d, 2H, $J = 7.9$ Hz, $2H_{1'}$), 4.07 (m, 2H, H_2, H_5), 3.84 (m, 2H, H_3, H_4), 3.60–3.52 (m, 6H, $4H_{6'}$, $2H_{4'}$), 3.40–3.27 (m, 6H, $2H_{2'}$, $2H_{3'}$, $2H_{5'}$), 3.33 (s, 12H, $2OCH_3$), 1.36 (s, 12H, $2CH_3$); FAB HRMS: m/z: calcd for $C_{80}H_{88}O_{16}N_6Na$: 1410.6156; found: 1410.6099 $[M+Na]^+$.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α-(1→1)-2,3:4,5-di-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-L-*chiro*-inositol (32α), 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-β-(1→1)-2,3:4,5-di-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-L-*chiro*-inositol (32β) and di(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-β,β-(1→1:1→6)-2,3:4,5-di-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-L-*chiro*-inositol (33): The pseudodisaccharides were prepared from **13** (64 mg, 0.104 mmol) and **11** (27 mg, 0.066 mmol) as described for the preparation of **16**α and **16**β, adding TMSOTf (0.1 equiv, 0.26 mL of a solution 0.025 M) at −25 °C in CH_2Cl_2 (2 mL) and stirring the reaction mixture for 1 h, yielding after flash chromatography (hexane/ethyl acetate 4:1) **32**α (10 mg, 18%), **32**β (13 mg, 23%) and β,β-pseudotrisaccharide **33** (8 mg, 9%). **32**α: $[\alpha]_D = +98.0$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.40$–7.10 (m, 15H, 3Bn), 5.57 (d, 1H, $J = 3.8$ Hz, $H_{1'}$), 4.87–4.42 (3AB syst, 6H), 4.16 (t, 1H, $J = 10.2$ Hz, H_3), 4.13 (br t, 1H, $J = 2.9$ Hz, H_1), 3.95 (dd, 1H, $J = 9.9$, 3.0 Hz, H_2), 3.94 (t, 1H, $J = 10.1$ Hz, H_4), 3.88 (br t, 1H, $J = 3.1$ Hz, H_6), 3.85 (dd, 1H, $J = 9.9$, 2.9 Hz, H_5), 3.76–3.63 (m, 5H, $H_{3'}$, $H_{4'}$, $H_{5'}$, $2H_{6'}$), 3.37 (dd, 1H, $J = 9.9$, 3.8 Hz, $H_{2'}$), 3.25, 3.23, 3.16, 3.18 (4s, 12H, $4OCH_3$), 2.50 (s, 1H, $C_6O\mathit{H}$), 1.30, 1.29, 1.25, 1.18 (4s, 12H, $4CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 138.4$, 138.3, 138.1 (3C, Bn), 128.8–128.1 (15CH, Bn), 100.6, 100.2, 99.3, 99.0 (4C, BDA), 98.3 ($C_{1'}H$), 80.1 (CH), 78.4 (CH), 75.7 (CH_2), 75.5 (CH_2), 73.9 (C_1H), 73.6 (CH_2), 71.5 (CH), 70.9 (CH), 69.4 (CH), 69.0 (CH), 68.6 (CH_2), 66.6 (CH), 66.4 (CH), 60.7 (CH), 48.4, 48.3, 48.2, 48.2 (4C, $2OCH_3$) and 18.2, 18.1, 18.0, 18.0 ($4CH_3$); elemental analysis calcd (%) for $C_{45}H_{59}O_{14}N_3 + {}^3/_2H_2O$: C 60.52, H 6.99, N 4.70; found: C 60.40, H 6.95, N 4.38.

Compound **32**β: $[\alpha]_D = +64.3$ ($c=0.6$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.40$–7.10 (m, 15H, 3Bn), 4.85–4.52 (3AB syst, 6H), 4.29 (d, 1H, $J=7.5$ Hz, $H_{1'}$), 4.08 (br t, 1H, H_1), 4.06–4.02 (m, 2H, H_6, H_5), 3.96–3.92 (m, 3H, H_2, H_3, H_4), 3.77 (dd, 1H, $J=11.1$, 2.2 Hz, $H_{6'a}$), 3.72 (dd, 1H, $J=11.0$, 3.7 Hz, $H_{6'b}$), 3.68 (t, 1H, $J=9.0$ Hz, $H_{3'}$), 3.46–3.39 (m, 2H, $H_{2'}$, $H_{4'}$), 3.36 (m, 1H, $H_{5'}$), 3.25–3.21 (3s, 9H, $3OCH_3$), 3.17 (s, 3H, $3OCH_3$), 2.50 (s, 1H, O*H*), 1.30, 1.29, 1.25, 1.18 (4s, 12H, $4CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=138.6$, 138.3, 138.3 (3C, Bn), 128.7–127.9 (15CH, Bn), 101.4, 100.5, 100.2, 99.3 (4C, BDA), 98.9 ($C_{1'}H$), 83.9 (CH), 78.0 (CH_2), 77.5 (C_1H), 77.1 (CH_2), 75.9 (CH), 75.6 (CH), 75.2 (CH), 74.2 (CH_2), 69.7 (CH), 68.6 (CH_2), 68.5 (CH), 67.7 (CH), 66.9 (CH), 66.5 (CH), 48.4, 48.2, 48.1, 47.9 (4C, $2OCH_3$), 18.2, 18.1, 18.1, 18.0 ($4CH_3$); elemental analysis calcd (%) for $C_{45}H_{59}O_{14}N_3+3H_2O$: C 58.74, H 7.12, N 4.56; found: C 58.60, H 7.24, N 4.85.

Compound **33**: ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.40$–7.10 (m, 30H, 6Bn), 4.80–4.12 (6AB syst, 12H), 4.35 (d, 2H, $J=7.8$ Hz, $2H_{1'}$), 4.03 (dd, 2H, $J=7.8$, 3.2 Hz), 3.97 (m, 2H), 3.80–3.69 (m, 6H), 3.47–3.12 (m, 8H), 3.22 (s, 6H, $2OCH_3$), 3.18 (s, 6H, $2OCH_3$), 1.25 (s, 6H, $2CH_3$), 1.20 (s, 6H, $2CH_3$); elemental analysis calcd (%) for $C_{72}H_{86}O_{18}N_6$: C 65.34, H 6.55, N 6.35; found: C 65.31, H 6.57, N 6.25.

3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl-α(1→1)-2,5-di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-L-*chiro*-inositol (29): This pseudodisaccharide was prepared from **21** (46 mg, 0.096 mmol) and **10** (23 mg, 0.048 mmol) as described for the preparation of **16**α and **16**β, adding TMSOTf (0.1 equiv, 0.96 mL of a solution 0.05 M) at −25 °C in CH_2Cl_2 (1 mL) and stirring the reaction mixture for 1 h, yielding after flash chromatography (hexane/ethyl acetate 4:1) **28**α (14 mg, 37%) and the unreacted acceptor **10** (14 mg, 61%). **29**: $[\alpha]_D = +24.3$ ($c=0.7$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.40$–7.20 (m, 10H, 2Bn), 5.48 (d, 1H, $J=3.8$ Hz, $H_{1'}$), 5.34 (br d, 1H, $J=3.0$ Hz, $H_{4'}$), 5.00 (dd, 1H, $J=11.2$, 3.1 Hz, $H_{3'}$), 4.95–4.64 (2 AB syst, 4H), 4.23 (t, 1H, $J=10.1$ Hz, H_3), 4.16 (br t, 1H, $J=3.1$ Hz, H_1), 4.02–3.96 (m, 3H, $2H_{6'}$, H_4), 3.88 (dd, 1H, $J=10.1$, 3.0 Hz, H_2), 3.79 (m, 1H, $H_{5'}$), 3.74–3.68 (m, 3H, $H_{2'}$, H_5 and H_6), 3.28, 3.25 (2s, 6H, $2OCH_3$), 2.48 (s, 1H, $C_6O\mathit{H}$), 2.10, 2.08, 2.06 (3s, 9H, $3CH_3CO$), 1.37, 1.35 (2s, 6H, $2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=170.7$, 170.4, 170.1 ($3CH_3\mathit{C}O$), 139.4, 138.7 (2C, Bn), 128.8–127.4 (10CH, Bn), 99.8, 99.6 (2C, BDA), 98.5 ($C_{1'}$), 77.0 (CH), 76.3 (CH), 75.3 (C_1), 74.5, 74.4 ($2CH_2$), 71.3 (CH), 70.2 (CH), 69.9 (CH), 68.7 (CH), 67.7 (CH), 67.0 (CH), 62.1 (CH_2), 58.0 (CH), 48.1, 47.9 ($2OCH_3$), 21.0, 21.0, 20.9 ($3\mathit{C}H_3CO$), 18.2 ($2CH_3$); MALDI-TOF: *m*/*z*: calcd for $C_{38}H_{49}N_3O_{15}$+Na: 810.8; found: 811.0 $[M+Na]^+$; calcd for $C_{38}H_{49}N_3O_{15}+K^+$: 826.9; found: 828.0 $[M+K]^+$; elemental analysis calcd (%) for $C_{38}H_{49}O_{15}N_3+2H_2O$: C 55.40, H 6.40, N 5.10; found: C 55.54, H 6.10, N 5.43.

3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl-α-(1→1)-2,3:4,5-di-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-L-*chiro*-inositol (36): The pseudodisaccharide was prepared from **21** (40 mg, 0.084 mmol) and **11** (18 mg, 0.042 mmol) as described for the preparation of **16**α and **16**β, adding TMSOTf (0.1 equiv, 0.84 mL of a solution 0.05 M) at −25 °C in CH_2Cl_2 (1 mL) and stirring the reaction mixture for 1 h, yielding after flash chromatography (hexane/ethyl acetate 2:1) **36** (21 mg, 69%) and the unreacted acceptor **11** (5 mg, 30%). **36**: $[\alpha]_D = +78.3$ ($c=1.0$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=5.63$ (d, 1H, $J=3.7$ Hz, $H_{1'}$), 5.40 (d, 1H, $J=3.0$ Hz, $H_{4'}$), 5.07 (dd, 1H, $J=11.3$, 3.1 Hz, $H_{3'}$), 4.15–4.09 (m, 4H, $H_{5'}$, $H_{6'a}$, H_3, H_1), 4.03 (m, 1H, $H_{6'b}$), 3.97 (dd, 1H, $J=9.9$, 2.7 Hz, H_2), 3.92 (t, 1H, $J=9.9$ Hz, H_4), 3.87 (br t, 1H, $J=3.1$ Hz, H_6), 3.82 (dd, 1H, $J=10.1$, 3.1 Hz, H_5), 3.72 (dd, 1H, $J=11.2$, 3.7 Hz, $H_{2'}$), 3.25, 3.24, 3.22, 3.22 (4s, 12H, $4OCH_3$), 2.12, 2.04, 2.00 (3s, 9H, $3CH_3CO$), 1.29, 1.27, 1.24, 1.21 (4s, 12H, $4CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=170.1$, 170.4, 170.2 ($3CH_3\mathit{C}O$), 100.6, 100.2, 99.3, 98.9 (4C, BDA), 98.0 ($C_{1'}H$), 73.5 (C_1H), 70.9 (CH), 69.5 (CH), 68.9 (CH), 68.1 (CH), 67.8 (CH), 67.2 (CH), 66.5 (CH), 66.4 (CH), 62.1 (CH_2), 58.3 (CH), 48.4, 48.3, 48.2, 48.1 ($4OCH_3$), 21.0, 21.0, 20.9 ($3\mathit{C}H_3CO$), 18.1, 18.0, 17.9, 17.8 ($4CH_3$); MALDI-TOF: *m*/*z*: calcd for $C_{30}H_{47}N_3O_{17}Na$: 744.7; found: 745.6 $[M+Na]^+$; calcd for $C_{30}H_{47}N_3O_{17}K$: 760.8; found: 762.6 $[M+K]^+$; elemental analysis calcd (%) for $C_{30}H_{47}O_{17}N_3$: C 49.92, H 6.56, N 5.82; found: C 50.05, H 6.84, N 5.60.

2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-α-(1→1)-2,5-di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (40α), 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-β-(1→1)-2,5-di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-D-*chiro*-inositol (40β): The pseudodisaccharides were prepared from **14** (50 mg, 0.094 mmol) and **6** (30 mg, 0.063 mmol) as described for the preparation of **16**α and **16**β, adding TMSOTf (0.03 equiv, 18.9 μL of a solution 0.1 M) at −25 °C in CH_2Cl_2 (2 mL) and stirring the reaction mixture for 1 h at −25 °C, yielding after flash chromatography (hexane/ethyl acetate 4:1), **40**α (12 mg, 22%) and **40**β (3 mg, 6%). **40**α: $[\alpha]_D = +58.5$ ($c=0.6$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.40$–7.20 (m, 20H, 4Bn), 5.45 (s, 1H, C*H*Ph), 4.94–4.65 (4 AB syst, 8H), 4.78 (d, 1H, $J=3.7$ Hz, $H_{1'}$), 4.17 (m, 1H, $H_{5'}$), 4.06 (t, 1H, $J=3.1$ Hz, H_6), 4.06–4.02 (m, 3H, H_1, H_3, H_4), 3.95 (t, 1H, $J=9.4$ Hz, $H_{3'}$), 3.92 (dd, 1H, $J=9.3$, 2.6 Hz, H_5), 3.87 (dd, 1H, $J=9.5$, 2.7 Hz, H_2), 3.70 (dd, 1H, $J=10.0$, 5.0 Hz, $H_{6'a}$), 3.60 (t, 1H, $J=9.4$ Hz, $H_{4'}$), 3.45 (m, 2H, $H_{2'}$, $H_{6'b}$), 3.32 (2s, 6H, $2OCH_3$), 2.52 (s, 1H, $C_6O\mathit{H}$), 1.38, 1.33 (2s, 6H, $2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=139.3$ (C), 138.8 (C), 138.2 (C), 137.8 (C), 129.2–126.3 (20CH, Bn), 101.6 (CHPh), 99.7, 99.6 (2C, BDA), 99.0 ($C_{1'}$), 83.1 (C_1), 78.4 (CH), 76.6 (CH), 75.2 (CH_2), 75.1 (CH), 74.4 (CH_2), 74.3 ($2CH_2$), 70.6 (CH), 70.3 (CH), 69.9 (2CH), 69.4 (CH), 63.7 (CH), 48.2 (OCH_3), 48.1 (OCH_3), 18.2 ($2CH_3$); elemental analysis calcd (%) for $C_{46}H_{53}O_{12}N_3$: C 65.80, H 6.35, N 5.00; found: C 65.53, H 6.29, N 4.53.

Compound **40**β: $[\alpha]_D = +10.0$ ($c=0.1$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.40$–7.20 (m, 20H, 4Bn), 5.52 (s, 1H, C*H*Ph), 5.01–4.61 (4AB syst, 8H), 4.59 (d, 1H, $J=8.0$ Hz, $H_{1'}$), 4.26 (dd, 1H, $J=10.4$, 4.9 Hz, $H_{6'a}$), 4.18 (t, 1H, $J=10.1$ Hz, H_3), 4.12 (br s, 1H, H_1), 4.10 (br s, 1H, H_6), 4.02 (t, 1H, $J=10.1$ Hz, H_4), 3.90 (dd, 1H, $J=10.1$, 3.1 Hz, H_2), 3.80 (dd, 1H, $J=10.0$, 3.2 Hz, H_5), 3.71 (t, 1H, $J=10.4$ Hz, $H_{6'b}$), 3.61 (t, 1H, $J=9.3$ Hz, $H_{4'}$), 3.45 (t, 1H, $J=9.3$ Hz, $H_{3'}$), 3.31–3.24 (m, 8H, $H_{2'}$, $H_{5'}$, $2OCH_3$), 2.52 (s, 1H, $C_6O\mathit{H}$), 1.38, 1.33 (2s, 6H, $2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=139.8$ (C), 138.9 (C), 138.2 (C), 137.4 (C), 129.4–126.3 (20CH, Bn), 103.7 ($C_{1'}$), 101.6 (CHPh), 99.8, 99.6 (2C, BDA), 81.8, 79.3, 78.2, 76.9, 76.3, 75.4, 75.3, 74.1, 74.0, 70.1, 70.4, 68.9, 66.8, 66.3 (10CH, $4CH_2$), 48.2, 48.1 ($2OCH_3$), 18.2 ($2CH_3$); elemental analysis calcd (%) for $C_{46}H_{53}O_{12}N_3$: C 65.80, H 6.35, N 5.00; found: C 65.71, H 6.43, N 4.77.

2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-α-(1→1)-2,5-di-*O*-benzyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-L-*chiro*-inositol (41): The pseudodisaccharide was prepared from **14** (30 mg, 0.056 mmol) and **10** (18 mg, 0.038 mmol) as described for the preparation of **16**α and **16**β, adding TMSOTf (0.03 equiv, 5.2 μL of a solution 0.22 M) at −25 °C in CH_2Cl_2 (1 mL) and stirring the reaction mixture for 1 h at −25 °C, yielding after flash chromatography (hexane/ethyl acetate 4:1) **41** (18 mg, 56%) and unreacted acceptor **14** (8 mg, 42%). **41**: $[\alpha]_D = -30.7$ ($c=0.6$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.50$–7.20 (m, 20H, 4Bn), 5.56 (s, 1H, C*H*Ph), 5.43 (d, 1H, $J=4.0$ Hz, $H_{1'}$), 4.97–4.62 (4AB syst, 8H), 4.31 (t, 1H, $J=10.1$ Hz, H_3), 4.22 (m, 1H, $H_{6'a}$), 4.20 (t, 1H, $J=3.0$ Hz, H_1), 4.02 (t, 1H, $J=9.9$ Hz, H_4), 3.91 (dd, 1H, $J=10.2$, 2.9 Hz, H_2), 3.89 (t, 1H, $J=3.4$ Hz, H_6), 3.85 (t, 1H, $J=9.4$ Hz, $H_{3'}$), 3.78 (dd, 1H, $J=9.9$, 3.4 Hz, H_5), 3.73–3.64 (m, 3H, $H_{5'}$, $H_{6'b}$, $H_{4'}$), 3.41 (dd, 1H, $J=9.4$, 4.0 Hz, $H_{2'}$), 3.33, 3.32 (2s, 6H, $2OCH_3$), 2.52 (s, 1H, $C_6O\mathit{H}$), 1.38, 1.33 (2s, 6H, $2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=139.5$ (C), 138.6 (C), 138.3 (C), 137.5 (C), 129.3–126.2 (20CH, Bn), 101.5 (CHPh), 99.8, 99.6 (2C, BDA), 99.0 ($C_{1'}$), 82.9 (CH), 77.5 (CH), 76.6 (2CH), 75.5 (CH_2), 75.1 (C_1H), 74.4 (CH_2), 74.3 (CH_2), 71.2 (CH), 70.4 (CH), 69.8 (CH), 69.1 (CH_2), 63.7 (CH), 63.4 (CH), 48.0 ($2OCH_3$), 18.2 ($2CH_3$); elemental analysis calcd (%) for $C_{46}H_{53}O_{12}N_3$: C 65.80, H 6.35, N 5.00; found: C 65.40, H 6.44, N 4.54.

***trans*-4-*tert*-Butylcyclohexyl-2-azido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (45α) and *trans*-4-*tert*-butylcyclohexyl-2-azido-2-deoxy-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (45β)**: A) From trichloroacetimidate **13** prepared as the pure α isomer (95 mg, 0.153 mmol) and *trans*-4-*tert*-butylcyclohexanol (**42**) (20 mg, 0.13 mmol) as described for the preparation of **16**α and **16**β, adding TMSOTf (0.1 equiv, 130 μL of a solution 0.1 M) at −25 °C in CH_2Cl_2 (2 mL) and stirring the reaction mixture for 1 h at −25 °C, yielding after flash chromatography (hexane/ethyl acetate 4:1) **45**α (10 mg, 12%) and **45**β (42 mg, 52%).

B) From trichloroacetimidate **44**, prepared as the pure β isomer, using the experimental procedure described above **45**α (14 mg, 17%) and **45**β (41 mg, 51%) were obtained.

Compound **45**α: $[\alpha]_D$ = +77.1 (c=0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.40–7.20 (m, 15H, 3Bn), 5.06 (d, 1H, J=3.6 Hz, $H_{1'}$), 4.89–4.46 (3AB syst, 6H), 4.00 (t, 1H, J=9.3 Hz, $H_{3'}$), 3.91 (m, 1H, $H_{5'}$), 3.76 (dd, 1H, J=11.0, 3.8 Hz, $H_{6'a}$), 3.68 (t, 1H, J=9.3 Hz, $H_{4'}$), 3.64 (dd, 1H, J=11.0, 2.0 Hz, $H_{6'b}$), 3.48 (m, 1H, H_1), 3.26 (dd, 1H, J=9.3, 3.6 Hz, $H_{2'}$), 2.10 (m, 1H), 2.00 (m,1H), 1.80 (m, 2H), 1.40–1.20 (m, 2H), 1.00 (m, 3H), 0.80 (s, 9H, $3CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ=138.4 (C), 138.3 (C), 138.2 (C), 129.8–128.0 (15CH, Bn), 96.6 (CH), 80.4 (CH), 78.8 (CH), 77.9 (CH), 75.6 (CH_2), 75.4 (CH_2), 73.8 (CH_2), 70.9 (CH), 68.7 (CH_2), 63.5 (CH), 47.5 (CH), 34.1 (CH_2), 32.6 (C), 32.3 (CH_2), 27.9 ($3CH_3$), 26.0 (CH_2), 25.8 (CH_2); elemental analysis calcd (%) for $C_{37}H_{47}O_5N_3$: C 72.40, H 7.71, N 6.84; found: C 72.13, H 7.70, N 6.62.

Compound **45**β: $[\alpha]_D$ = −3.0 (c=1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.40–7.20 (m, 15H, 3Bn), 4.89–4.52 (3AB syst, 6H), 4.38 (d, 1H, J=7.5 Hz, $H_{1'}$), 3.72 (dd, 1H, J=11.0, 1.8 Hz, $H_{6'a}$), 3.65 (dd, 1H, J=11.0, 5.1 Hz, $H_{6'b}$), 3.61–3.52 (m, 3H, $H_{4'}$, $H_{3'}$, H_1), 3.42–3.36 (m, 2H, $H_{5'}$, $H_{2'}$), 2.10 (brs, 2H), 1.80 (m, 2H), 1.30 (m, 2H), 1.00 (m, 3H), 0.80 (s, 9H, $3CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ=138.5 (C), 138.4 (C), 138.3 (C), 128.8–127.9 (15CH, Bn), 101.0 (CH), 83.55 (CH), 79.7 (CH), 78.2 (CH), 75.8 (CH_2), 75.4 (CH_2), 75.3 (CH), 73.8 (CH_2), 69.2 (CH_2), 66.6 (CH), 47.5 (CH), 34.3 (CH_2), 32.7 (CH_2), 32.6 (C), 27.9 ($3CH_3$), 26.0 (CH_2), 25.8 (CH_2); elemental analysis calcd (%) for $C_{37}H_{47}O_5N_3$: C 72.40, H 7.71, N 6.84; found: C 72.58, H 7.83, N 6.50.

***cis*-4-*tert*-Butylcyclohexyl-2-azido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (46α), *cis*-4-*tert*-butylcyclohexyl-2-azido-2-deoxy-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (46β)**: A) From trichloroacetimidate **13** prepared as the pure α isomer (95 mg, 0.153 mmol) and *cis*-4-*tert*-butylcyclohexanol (**43**) (20 mg, 0.13 mmol) as described for the preparation of **16**α and **16**β, adding TMSOTf (0.1 equiv, 130 μL of a solution 0.1 M) at −25°C in CH_2Cl_2 (2 mL) and stirring the reaction mixture for 1 h at −25°C, yielding after flash chromatography (hexane/ethyl acetate 4:1) **46**α (10 mg, 12%) and **46**β (30 mg, 37%).

B) From trichloroacetimidate **44**, prepared as the pure β isomer, following the same experimental procedure described above to yield **46**α (11 mg, 13%) and **46**β (34 mg, 42%).

Compound **46**α: $[\alpha]_D$ = +85.0 (c=0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.40–7.20 (m, 15H, 3Bn), 5.00 (d, 1H, J=3.6 Hz, $H_{1'}$), 4.89–4.46 (3 AB syst, 6H), 4.05 (dd, 1H, J=10.3, 9.0 Hz, $H_{3'}$), 3.91–3.85 (m, 2H, $H_{5'}$ and H_1), 3.76 (dd, 1H, J=11.0, 3.6 Hz, $H_{6'a}$), 3.71 (t, 1H, J=9.0 Hz, $H_{4'}$), 3.63 (dd, 1H, J=10.6, 2.0 Hz, $H_{6'b}$), 3.22 (dd, 1H, J=10.2, 3.6 Hz, $H_{2'}$), 2.00 (m, 1H), 1.90 (m, 1H), 1.60–1.30 (m, 6H), 1.00 (m, 1H), 0.80 (s, 9H, $3CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ=138.4 (C), 138.3 (C), 138.2 (C), 128.8–128.1 (15CH, Bn), 96.3 (CH), 79.9 (CH), 78.9 (CH), 75.5 (CH_2), 75.4 (CH_2), 73.9 (CH_2), 71.8 (CH), 71.1 (CH), 68.7 (CH_2), 63.6 (CH), 48.3 (CH), 32.9 (CH_2), 32.4 (CH_2), 30.0 (C), 27.8 ($3CH_3$), 22.1 (CH_2), 21.7 (CH_2); elemental analysis calcd (%) for $C_{37}H_{47}O_5N_3$: C 72.40, H 7.71, N 6.84; found: C 72.48, H 7.73, N 6.70.

Compound **46**β: $[\alpha]_D$ = −13.8 (c=1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.40–7.20 (m, 15H, 3Bn), 4.89–4.52 (3 AB syst, 6H), 4.31 (d, 1H, J=7.7 Hz, $H_{1'}$), 4.02 (brs, 1H, H_1), 3.69 (dd, 1H, J=11.0, 2.0 Hz, $H_{6'b}$), 3.64 (dd, 1H, J=11.0, 4.7 Hz, $H_{6'a}$), 3.58 (t, 1H, J=9.2 Hz, $H_{4'}$), 3.43–3.35 (m, 3H, $H_{2'}$, $H_{3'}$, $H_{5'}$), 2.02 (brs, 2H), 1.58–1.32 (m, 6H), 1.00 (m, 1H), 0.85 (s, 9H, $3CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ=138.5 (2C), 138.3 (C), 128.8–127.9 (15CH, Bn), 100.2 (CH), 83.5 (CH), 78.2 (CH), 75.8 (CH_2), 75.4 (CH_2), 75.3 (CH), 73.8 (CH_2), 73.2 (CH), 69.1 (CH_2), 67.3 (CH), 48.3 (CH), 32.9 (CH_2), 32.6 (C), 30.0 (CH_2), 27.8 ($3CH_3$), 21.8 (CH_2), 21.6 (CH_2); elemental analysis calcd (%) for $C_{37}H_{47}O_5N_3$: C 72.40, H 7.71, N 6.84; found: C 72.38, H 7.61, N 6.72.

***trans*-4-*tert*-Butylcyclohexyl-2-azido-2-deoxy-3-*O*-benzyl-4,6-benzylidene-α-D-glucopyranoside (47α) and *trans*-4-*tert*-butylcyclohexyl-2-azido-2-deoxy-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (47β)**: The compounds were prepared from **14** (81 mg, 0.153 mmol) and *trans*-4-*tert*-butylcyclohexanol (20 mg, 0.13 mmol) **42** as described for the preparation of **16**α and **16**β, adding (0.1 equiv, 130 μL of a solution 0.1 M) of TMSOTf at −25°C in CH_2Cl_2 (2 mL) and stirring the reaction mixture for 1 h at −25°C, yielding after flash chromatography (hexane/ethyl acetate 4:1) **47**α (33 mg, 48%) and **47**β (12 mg, 17%). **47**α: $[\alpha]_D$ = +52.6 (c=0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.50–7.20 (m, 10H, 2Bn), 5.56 (s, 1H, CHPh), 5.01 (d, 1H, J=3.5 Hz, $H_{1'}$), 4.90 (AB syst, 2H), 4.25 (dd, 1H, J=10.3, 4.9 Hz, $H_{6'b}$), 4.10 (t, 1H, J=9.3 Hz, $H_{3'}$), 4.00 (m, 1H, $H_{5'}$), 3.73 (t, 1H, J=10.4 Hz, $H_{6'a}$), 3.68 (t, 1H, J=9.3 Hz, $H_{4'}$), 3.50 (m, 1H, H_1), 3.26 (dd, 1H, J=9.3 and 3.5 Hz, $H_{2'}$), 2.10 (m, 2H), 1.80 (brs, 2H), 1.40–1.20 (m, 3H), 1.00 (m, 2H), 0.80 (s, 9H, $3CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ=138.3 (C), 137.6 (C), 129.3–126.3 (10CH, Bn), 101.7 (CH), 97.4 (CH), 83.3 (CH), 78.4 (CH), 76.3 (CH), 75.3 (CH_2), 69.3 (CH_2), 63.2 (CH), 63.1 (CH), 47.5 (CH), 34.2 (CH_2), 32.6 (CH_2), 30.0 (C), 27.9 ($3CH_3$), 25.9 (CH_2), 25.8 (CH_2); elemental analysis calcd (%) for $C_{30}H_{39}O_5N_3$: C 69.07, H 7.53, N 8.05; found: C 68.88, H 7.58, N 8.34.

Compound **47**β: $[\alpha]_D$ = −62.5 (c=0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.50–7.20 (m, 10H, 2Bn), 5.50 (s, 1H, CHPh), 4.80 (AB syst, 2H), 4.50 (d, 1H, J=7.9 Hz, $H_{1'}$), 4.32 (dd, 1H, J=10.8, 5.3 Hz, $H_{6'b}$), 3.78 (t, 1H, J=10.3 Hz, $H_{6'a}$), 3.67 (t, 1H, J=9.3 Hz, $H_{4'}$), 3.60–3.53 (m, 1H, H_1), 3.49 (t, 1H, J=9.2 Hz, $H_{3'}$), 3.42 (t, 1H, J=9.1 Hz, $H_{2'}$), 3.36 (m, 1H, $H_{5'}$), 2.10 (m, 2H), 1.80 (m, 2H), 1.40–1.20 (m, 3H), 1.00 (m, 2H), 0.80 (s, 9H, $3CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ=138.3 (C), 137.5 (C), 129.3–126.3 (10CH, Bn), 101.6 (CH), 101.4 (CH), 81.8 (CH), 79.9 (CH), 79.3 (CH), 75.2 (CH_2), 69.0 (CH_2), 66.6 (CH), 66.5 (CH), 47.4 (CH), 34.2 (CH_2), 32.6 (CH_2), 30.0 (C), 27.9 ($3CH_3$), 25.9 (CH_2), 25.8 (CH_2); elemental analysis calcd (%) for $C_{30}H_{39}O_5N_3$: C 69.07, H 7.53, N 8.05; found: C 68.73, H 7.28, N 7.95.

***cis*-4-*tert*-Butylcyclohexyl 2-azido-2-deoxy-3-*O*-benzyl-4,6-benzylidene-α-D-glucopyranoside (48α) *cis*-4-*tert*-butylcyclohexyl 2-azido-2-deoxy-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (48β)**: The compounds were prepared from **14** (81 mg, 0.153 mmol) and *cis*-4-*tert*-butylcyclohexanol (**43**) (20 mg, 0.13 mmol) as described for the preparation of **16**α and **16**β, adding (0.1 equiv, 130 μL of a solution 0.1 M) of TMSOTf at −25°C in CH_2Cl_2 (2 mL) and stirring the reaction mixture for 1 h at −25°C, yielding after flash chromatography (hexane/ethyl acetate 4:1) **48**α (33 mg, 48%) and **48**β (15 mg, 22%). **48**α: $[\alpha]_D$ = +68.8 (c=0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.50–7.20 (m, 10H, 2Bn), 5.60 (s, 1H, CHPh), 4.97 (d, 1H, J=3.8 Hz, $H_{1'}$), 4.90 (AB syst, 2H), 4.27 (dd, 1H, J=10.1, 4.7 Hz, $H_{6'b}$), 4.15 (t, 1H, J=9.5 Hz, $H_{3'}$), 3.95 (m, 1H, $H_{5'}$), 3.90 (m, 1H, H_1), 3.77–3.70 (m, 2H, $H_{6'a}$, $H_{4'}$), 3.25 (dd, 1H, J=9.6, 3.8 Hz, $H_{2'}$), 2.00–1.90 (m, 2H), 1.60–1.30 (m, 6H), 1.00 (m, 1H), 0.80 (s, 9H, $3CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ=138.3 (C), 137.5 (C), 129.3–126.3 (10CH, Bn), 101.7 (CH), 97.0 (CH), 83.5 (CH), 75.7 (CH), 75.3 (CH_2), 72.2 (CH), 69.3 (CH_2), 63.2 (2CH), 48.2 (CH), 33.0 (CH_2), 32.5 (C), 29.6 (CH_2), 27.9 ($3CH_3$), 22.0 (CH_2), 21.6 (CH_2); elemental analysis calcd (%) for $C_{30}H_{39}O_5N_3$: C 69.07, H 7.53, N 8.05; found: C 68.84, H 7.39, N 7.84.

Compound **48**β: $[\alpha]_D$ = −80.6 (c=0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.50–7.20 (m, 10H, 2Bn), 5.50 (s, 1H, CHPh), 4.85 (AB syst, 2H), 4.40 (d, 1H, J=7.9 Hz, $H_{1'}$), 4.32 (dd, 1H, J=10.3, 4.9 Hz, $H_{6'b}$), 4.00 (brs, 1H, H_1), 3.78 (t, 1H, J=10.3 Hz, $H_{6'a}$), 3.69 (t, 1H, J=8.7 Hz, $H_{4'}$), 3.48 (t, 1H, J=8.7 Hz, $H_{3'}$), 3.42 (dd, 1H, J=8.7, 7.9 Hz, $H_{2'}$), 3.45 (m, 1H, $H_{5'}$), 2.00 (m, 2H), 1.50 (m, 2H), 1.47–1.33 (m, 4H), 1.00 (m, 1H) and 0.80 (s, 9H, $3CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ=138.4 (C), 137.5 (C), 129.3–126.3 (6CH), 101.6 (CH), 100.7 (CH), 81.9 (CH), 79.3 (CH), 75.2 (CH_2), 73.6 (CH), 69.0 (CH_2), 67.3 (CH), 66.5 (CH), 48.2 (CH), 32.6 (CH_2), 30.0 (C), 29.9 (CH_2), 27.8 ($3CH_3$), 21.8 (CH_2), 21.5 (CH_2); elemental analysis calcd (%) for $C_{30}H_{39}O_5N_3$: C 69.07, H 7.53, N 8.05; found: C 69.17, H 7.67, N 8.13.

Acknowledgement

We thank the Dirección General de Investigación for financial support (Grant BQU 2002-03734) and the Ministry of Science and Technology for a Ramón y Cajal contract (to M.B.C.).

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Received: July 20, 2004
Published online: December 9, 2004