Synthesis of New Hexosaminyl D- and L-*chiro*-Inositols Related to Putative Insulin Mediators

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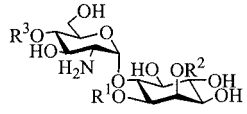
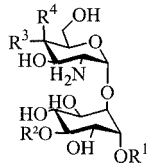
We have developed an efficient synthetic strategy to $HexNH_2$-α(1→3)-L-*chiro*-inositol (**XII**–**XIII**) and $HexNH_2$-α(1→2)-D-*chiro*-inositol (**XIV**–**XV**) based on the regio and stereoselective glycosylation of tetrabenzoyl-L-*chiro*-inositol **2** and tetrabenzyl-D-*chiro*-inositol **14**. Compounds **XII**–**XV** may constitute the central structural motifs of inositolphosphoglycans, which have been proposed as putative insulin mediators, and their syntheses have been designed on the basis of biosynthetic considerations. The syntheses of **XII**–**XIII** and **XIV**–**XV** involve the selective monoglycosylation of an L-*chiro* inositol diequatorial diol system (**2**) and a D-*chiro* inositol axial/equatorial diol system (**14**), respectively. To establish the experimental conditions to achieve the best reactivity–selectivity balance, the glycosylation reactions were studied using D-gluco- and D-galacto-configured 2-azido-2-deoxytrichloacetimidate glycosyl donors with different reactivities. The results obtained provide a practical synthetic route and new reactivity–selectivity data.

Introduction

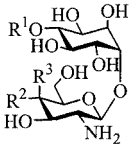
We have reported the synthesis and three-dimensional structure in solution of a variety of substances containing the structural motifs α-D-glucosaminyl-(1→6)-*myo*-inositol (**I**−**III**) and α- and β-D-gluco- and galactosaminyl-(1→1)-D-*chiro*-inositol (**IV**−**VIII**) (Figure 1).[1] This earlier study was based on the finding that some unidentified inositolphosphoglycans (IPGs), which may contain these structural motifs, are involved in insulin signalling.[2] These IPGs, which are thought to be generated from glycosylphosphatidylinositols (GPIs) by receptor-activated phospholipases (PLs), have been reported to be either inhibitors of c-AMP-dependent protein kinase (PKA) (A-type IPGs, containing *myo*-inositol) or activators of pyruvate dehydrogenase phosphatase (PDH) (P-type IPGs, containing *chiro*-inositol).[2] Although the precise chemical structure of the biologically active IPGs remains elusive, the existing structural data for A-type IPGs reveal close structural similarities with the GPI anchors (**IX**) (Figure 3).[3] This finding provided the basis for the design and synthesis of compounds carrying the structural motifs **I**−**III**.[1a,1b,1d,1e] There is no general consensus, however, regarding the structure of P-type *chiro*-inositol-containing IPGs.[4d] Previously, we synthesized a variety of compounds with the structural motifs **IV**−**VIII**[1c,1g,1h] because we found incidentally that some of them behaved as P-type IPGs in inducing cellular differentiation in cultures of chicken embryo,[4] but there is no solid experimental evidence for the presence of these structural motifs in the family of naturally occurring P-type IPGs. On the contrary, assuming that *chiro*-inositol-containing GPIs are biosynthesized by the same pathway as their *myo*-inositol counterparts, it has been reasoned that their *chiro*-inositol moieties would have the 1-L configuration.[5] Furthermore, it has been shown experimentally that both 1-phosphatidyl-D-*myo*-inositol and 2-phosphatidyl-L-*chiro*-inositol are substrates for phospholipase C (PI-PLC) (Figure 2).[6]



I $R^1 = R^2 = H$; R^3 = H or glycan
II $R^1 = PO_3H_2$, $R^2 = H$; R^3 = H or glycan
III $R^1 = R^2 = PO_2H$ R^3 = H or glycan



IV $R^1 = R^4 = H$; $R^3 = OH$; R^2 = H or Me
V $R^1 = H$, $R^3 = H$; $R^4 = OH$; R^2 = H or Me
VI $R^1 = PO_3H_2$, $R^2 = R^4 = H$; $R^3 = OH$



VII R^1 = H or Me; $R^2 = OH$, $R^3 = H$
VIII R^1 = Me; $R^2 = H$, $R^3 = OH$

Figure 1. Previously synthesized IPG-type structures

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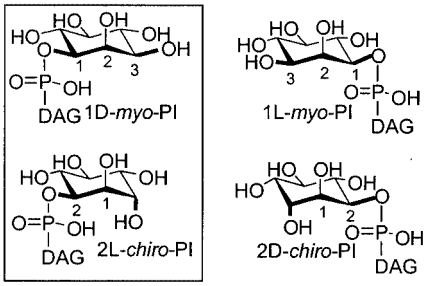
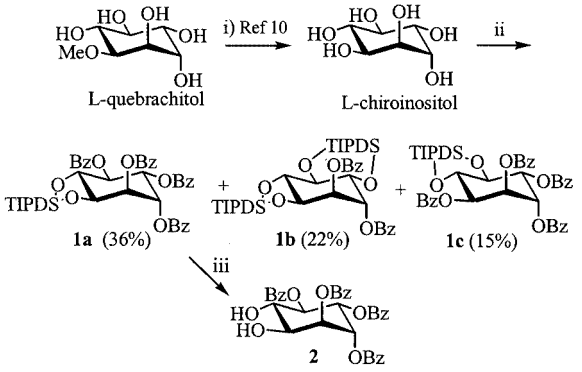


Figure 2. Stereochemical relationship between phosphatidylinositols of the D-*myo* and D-*chiro* series

This finding may have important consequences, particularly if the IPG mediators are generated following GPI-PLC cleavage. In this case, the *chiro*-inositol-containing GPIs would most likely contain an L-*chiro*-inositol unit carrying a phosphodiester linkage at position 2 and, seeking maximum similarity with the GPI anchor structure **IX** (Figure 3), the glycan chain would be attached at position 3 (**X**). On the other hand, it has also been postulated that *chiro*-inositol-containing GPIs could be generated from *myo*-inositol-containing GPIs after isomerisation.[7] Should this be the case, the *chiro*-inositol unit of natural P-type IPGs would rather belong to the D series and would present the phosphodiester linkage at position 1 and the glycan chain at position 2 (**XI**). Figure 3 summarises these two possible mechanisms proposed for the generation of *chiro*-inositol-containing IPGs and shows the stereochemical relationship between the *myo*- and *chiro*- series.

Within our programme investigating the structure, synthesis and biological activity of IPG mediators,[1] it became a key issue to have access to compounds bearing the structural motifs **X** and **XI** to investigate their behaviour as substrates of GPI-PLC and as activators of PDH. In this paper we report synthetic routes for the preparation of these types of molecules, the effectiveness of which is illustrated by the synthesis of the basic pseudodisaccharide structures present in **X** and **XI**, namely **XII**, **XIII**, **XIV**, and **XV**. These syntheses involve the preparation of two conveniently functionalized diols derived from L- (compound **2**, Scheme 1) and D- (compound **14**, see Scheme 4) *chiro*-inositol as building blocks for the construction of the structural motifs sought (**X** and **XI**) through regio- and stereoselective monoglycosylation. The reactivity−selectivity balance in glycosylation reactions is a matter of current interest that has particular importance when unprotected polyhydroxylated glycosyl acceptors are involved.[8] In addition to disclosing direct synthetic routes to structures like **X** and **XI**, the results reported herein provide further data to the wealth of experimental information available on selective glycosylation of diol systems.



Scheme 1. Reagents and conditions: ii) a) $TIPDSCl_2$, DMAP, DMF, imidazole, r.t, 16 h; b) BzCl, DMAP, Py, room temp., 16 h, 36% (two steps); iii) $(HF)_nPy$, THF, −15 °C, 90%

Results and Discussion

The L-*chiro*-inositol building block **2** was prepared in four steps from naturally occurring L-quebrachitol as shown in Scheme 1. The methyl ether group of L-quebrachitol was cleaved as previously reported[9] to give L-*chiro*-inositol. Treatment of L-*chiro*-inositol with the bifunctional protecting agent 1,3-dichoro-1,1,3,3-tetraisopropyldisiloxane ($TIPDSCl_2$) under carefully controlled experimental conditions[1c] gave a mixture of silylated derivatives that was directly submitted to conventional benzoylation to give compounds **1a** (36%), **1b** (22%), and **1c** (15%). Removal of the silyl protecting group in **1a** afforded diol **2** in 90% yield. This diequatorial diol was a potentially useful candidate for

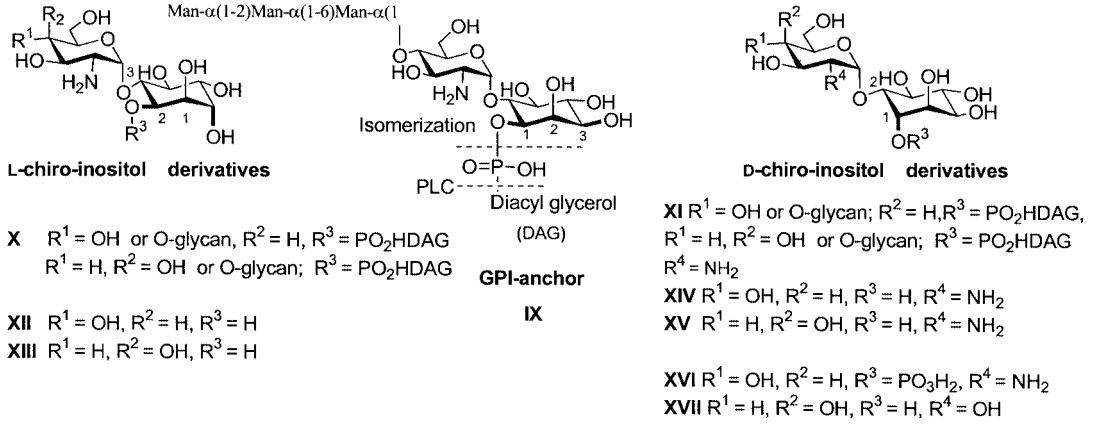
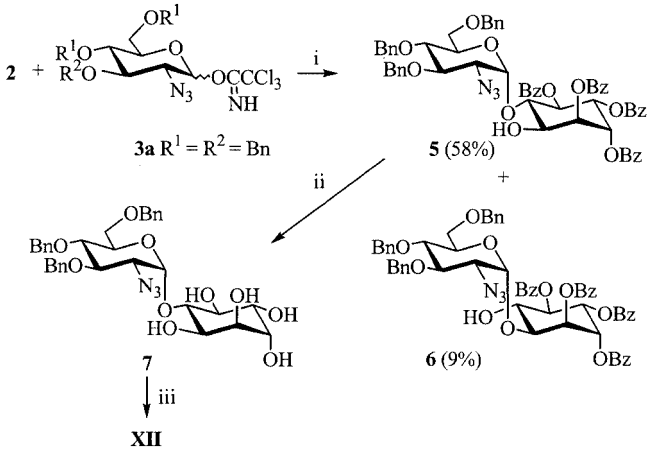


Figure 3. D- and L-*chiro*-inositol containing IPG-type structures which may be generated from GPI anchors

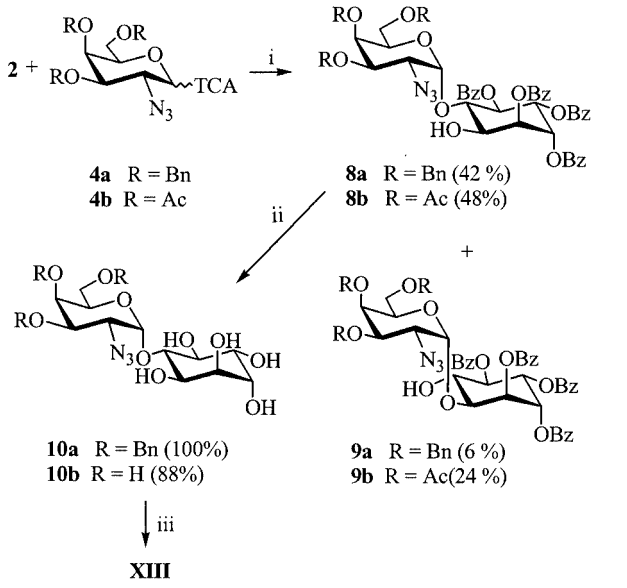
the construction of the structural motif **X** — if experimental conditions could be established that allowed regioselective glycosylation at position 3. Thus, we undertook an investigation of the glycosylation of **2** with glycosyl donors containing the needed 2-azido-2-deoxy function as a non-participating amine-precursor group. The reactivity of **2** as a glycosyl acceptor was expected to be relatively low and the use of activated glycosyl donors seemed, in principle, advisable to achieve a reasonable reactivity−selectivity balance to drive the reaction primarily to the desired α-monoglycosylation stage. Our wide experience[1] also led us to use trichloroacetimidates[10a] as glycosyl donors and to carefully adjust the reaction conditions, particularly the temperature and solvent.

Therefore, we first investigated the reaction of **2** with the activated 2-azido-2-deoxy-D-glucopyranosyl trichloroacetimidate[11] **3a**. Glycosylation of **2** with 1.2 equiv. of **3a** at low temperature (−40 → −5 °C) in diethyl ether gave a mixture of the α(1→3)- (**5**) and α(1→2)- (**6**) pseudodisaccharides in an 86:14 ratio and 67% combined yield (Scheme 2). The unpredicted higher reactivity of the 3-OH group of **2** permitted the desired compound **5** to be isolated in 58% yield.



Scheme 2. Reagents and conditions: i) TMSOTf (0.08 equiv.); **2** (1 equiv.), **3a** (1.2 equiv.), diethyl ether, −40 °C to −5 °C over 3 h and then r.t., 1 h, 67% (**5**/**6** = 86:14). ii) MeONa/ MeOH, r.t, overnight, quantitative. iii) H_2/Pd/C, EtOH/H_2O (4:1), overnight, 95%

This enhanced reactivity of the 3-OH group was similarly observed when the glycosylation reaction was carried out under the same experimental conditions with the activated donor[11] **4a** having the D-galacto configuration (Scheme 3). In this case, an 88:12 mixture of the α(1→3)- (**8a**) and α(1→2)- (**9a**) pseudodisaccharides was formed, although in lower yield (48% combined). Compound **8a** was isolated from this reaction mixture in 42% yield. The balance was not so favorable when using the deactivated 2-azido-2-deoxy-D-galactopyranosyl trichloroacetimidate **4b**.[12] Under these conditions, a 67:33 mixture of the α(1→3)- (**8b**, 48% by NMR spectroscopy) and α(1→2)- (**9b**, 24% by NMR spectroscopy) pseudodisaccharides was formed (Scheme 3).

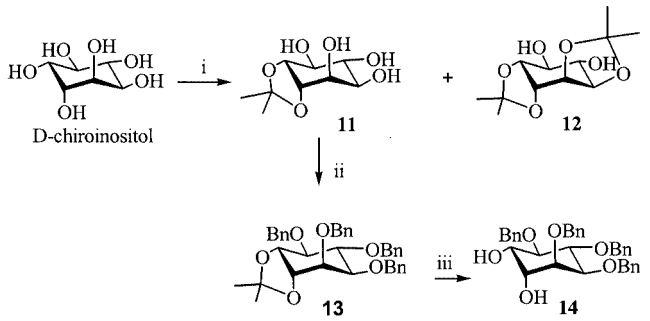


Scheme 3. Reagents and conditions: a) i) TMSOTf (0.08 equiv.); **2** (1 equiv.), **4a** (1.2 equiv.), diethyl ether, −40 °C for 1 h and then −40 °C to 5 °C over 2 h, 48%, α(1−3)-**8a** (42%)/α(1−2)-**9a** (6%) = 88:12. ii) MeONa/MeOH, r.t., overnight,100%. iii) H_2/Pd/C, EtOH/H_2O (4:1), overnight, 80%. b) i) TMSOTf (0.15 equiv.); **2** (1 equiv.), **4b** (1.2 equiv.), diethyl ether, −40 °C to −5 °C over 2 h and then r.t., 1 h, 72% as a mixture of pseudodisaccharides α(1−3)-**8b** (48%)/α(1−2)-**9b** (24%) = 67:33. ii) MeONa/ MeOH, r.t., overnight, 88%. iii) H_2/Pd/C, EtOH/H_2O (4:1), overnight, 98%

A thorough rationalization of the above results requires further investigation. The outcome of the reaction with the activated donors, however, was good enough for practical purposes, particularly regarding the simplicity of the overall process, and no additional experiments were carried out at this stage to improve the construction of the structural motif **X**. Furthermore, the isolation of the 2-*O*-glycosyl derivatives **6**, **9a**, and **9b** as by-products, confers additional value to this synthetic route providing an entry into the glycosaminyl-α(1→2)-L-*chiro*-inositol structural motif. Additionally, the protecting group pattern in compounds **5**, **8a**, and **8b** allows further installation of the phosphodiester linkage at position 2 after conventional manipulation. Deacylation of **5** gave **7**, which was submitted to hydrogenation to be transformed into **XII** in 55% yield from diol acceptor **2** (Scheme 2). Similarly, deacylation of **8a**−**b** gave **10a**−**b**, respectively, which afforded compound **XIII** after hydrogenation (Scheme 3).

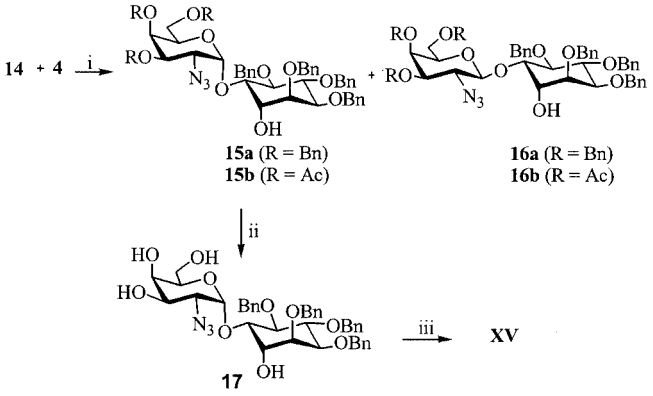
Building block **14** was chosen as a conveniently funtionalised D-*chiro*-inositol unit for the synthesis of the D-*chiro*-inositol-containing structural motif **XI**. Compound **14** was prepared from D-*chiro*-inositol as shown in Scheme 4. Treatment of D-*chiro*-inositol with 1 equiv. of 2,2-dimethoxypropane caused a rapid transformation into mono- (**11**, 30%)[13] and di- (**12**, 22%)[14] isopropylidene derivatives. Conventional benzylation of **11** gave the tetra-*O*-benzyl derivative **13**, which was converted into diol **14**.[15] As discussed above for compound **2**, diol **14** was considered as a useful candidate for obtaining the basic pseudodisaccharide

structural motif **XI**. In this case, the different orientation of the free hydroxyl functions of **2** predicted a far more favorable regioselective outcome of the glycosylation reaction to give the 2-*O*-glycosyl structure.



Scheme 4. Reagents and conditions: i) 2,2-Dimethoxypropane (1 equiv.), *p*TsOH, DMSO, 100 °C, 30 min, 52% (**11**, 30%; **12**, 22%). ii) BnBr (6 equiv.), NaH (6 equiv.), DMF, 12 h, room temp., 90%. iii) AcOH/THF (5:1), 80 °C, 8 h, 100%

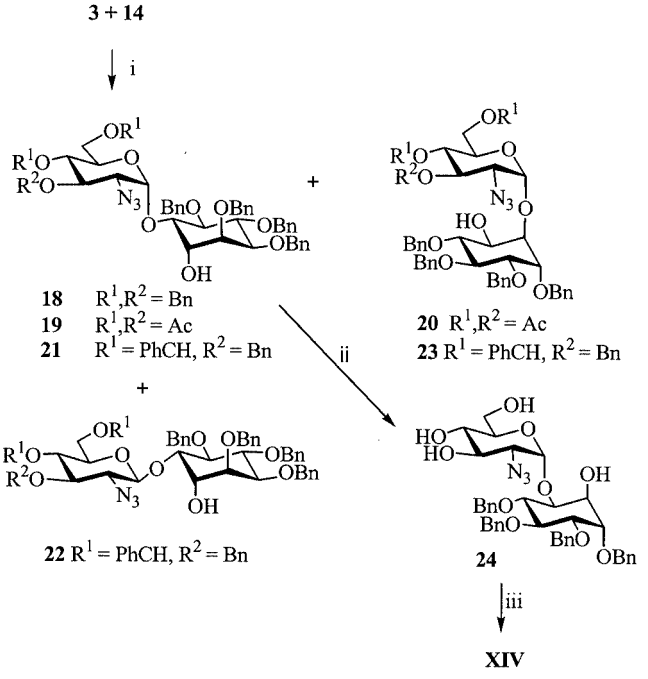
The regioselective monoglycosylation of **14** was first attempted with a deactivated donor with D-galacto configuration. Reaction of **4b** (1.2 equiv.) and **14** at −40 °C took place in diethyl ether with complete regioselectivity to afford a 94:6 mixture of the α(1→2)- (**15b**) and β(1→2)- (**16b**) pseudodisaccharides in 70% overall yield (Scheme 5). The regioselectivity was not affected when the reaction was carried out with the more-reactive glycosyl donor **4a**, although the stereoselectivity and yield decreased considerably to afford a 70:30 mixture of the α(1→2)- (**15a**) and β(1→2)-



Scheme 5. Reagents and conditions. **4a** (R = Bn): i) TMSOTf (0.06 equiv.), diethyl ether, −40 °C, 4 h, 58% (**15a**, 40%, **16a**, 18%). **4b** (R = Ac): i) TMSOTf (0.12 equiv.), diethyl ether, −40 °C, 4 h, 70% (**15b**, 66%, **16b**, 4%). ii) MeONa/MeOH, 30 min, 100%. iii) H_2/Pd/C, MeOH/H_2O, overnight, 100%

(**16a**) pseudodisaccharides in 58% overall yield (Scheme 5).

The results obtained in the D-gluco series are summarized in Scheme 6. Under the above experimental conditions, the glycosylation of **14** with **3b** gave a 97:3 mixture of the α(1→2)- (**19**) and α(1→1)- (**20**) regioisomers in 63% yield that only could be partially separated after deacetylation, affording pure **24** (Scheme 6). When the reaction was conducted using the more-reactive glycosyl donor **3a**, a glycosylation mixture containing all the possible isomers was formed in 52% yield. The α(1→2) pseudodisaccharide (**18**) was isolated in 33% yield from this mixture. Glycosylation of **14** with donor **3c**, which may permit elongation of the glycan chain of the basic structural motifs after manipulation of the 4,6-*O*-benzylidene group of the resulting pseudodisaccharides, gave an 8:1:1 mixture of the α(1→2)- (**21**), β(1→2)- (**22**), and α(1→1)- (**23**) compounds in 66% overall yield. Pseudodisaccharide **21** was isolated in 52% yield from this mixture.



Scheme 6. Reagents and conditions. R^1/R^2 = Bn, **3a**: i) TMSOTf (0.04 equiv.), diethyl ether, −40 °C to room temp., 6 h (**18**, 33%; mixture of 3 pseudodisaccharides, 19%). iii) **18**, H_2/Pd/C, MeOH/H_2O, overnight, 100%. R^1/R^2 = Ac, **3b**: i) TMSOTf (0.14 equiv.), diethyl ether, −40 °C, 4 h; 3 h at room temp. (**19**/**20** = 93:7, 63%); ii) Mix. of **19** and **20**, MeONa/MeOH, 30 min, 98%; iii) **24**, H_2/Pd/C, MeOH/H_2O, overnight, 93%. R^1 = PhCH, R^2 = Bn, **3c**: i) TMSOTf (0.12 equiv.), diethyl ether, −40 °C, 4 h (**21**, 52%, **22**, 7%, **23**, 7%)

The free α(1→2)-linked pseudodisaccharide **XV** was obtained in 58% overall yield from **4b** and **14** after conventional deacetylation of **15b** to give **17** and then subsequent hydrogenolysis (Scheme 5). Similarly, the free α(1→2)-linked disaccharide **XIV** was formed in quantitative yield by hydrogenolysis of **18** or from the mixture of **19** and **20** after deacetylation and hydrogenolysis of pure **24** (Scheme 6). The phosphorylated pseudodisaccharide **XVI** has been reported previously starting from (−)-quinic acid,[16] and compound **XVII** has been isolated previously from jojoba beans and also synthesized using a D-*chiro*-inositol unit prepared in twelve steps from L-xylose.[16b]

Conclusion

This paper describes a practical approach to the synthesis of D-glycosaminyl-(1→3)-L-*chiro*-inositols and D-glycosami-

nyl-(1→2)-D-*chiro*-inositols. On the basis of biosynthetic considerations, these pseudodisaccharide structures could be parts of inositolphosphoglycans that have been postulated to be involved in insulin signalling. The access to these inositolphosphoglycan substructures may permit the preparation of a diverse range of substances bearing these structural motifs for biological investigation. We conclude, therefore, that in providing new substances, the relatively simple and straightforward procedures here reported herein represents an important step in our ongoing studies on the role of receptor-activated phospholipases in the signalling process. Importantly, the construction of the pseudodisaccharide structures has been carried out by studying the regio- and stereoselectivity of the glycosylation reaction of a diequatorial and an axial−equatorial diol system using 2-azido-2-deoxy-D-glycopyranosyl trichloroacetimidates as glycosylating agents. The influence of the glycosyl acceptor in the outcome of glycosylation reactions is not completely understood. The selectivity of these reactions when the glycosyl donor contains a 2-azido-2-deoxy functionality as a non-participating amino-masking group is still far from predictable. While a thorough rationalisation of the results in this paper requires further experimentation and extensive elaboration, the data reported herein constitute a solid contribution to the understanding of the different factors governing the selectivity of these processes.

Experimental Section

General Remarks: Diethyl ether was distilled from sodium benzophenone. Dichloromethane was distilled from calcium hydride. Molecular sieves (4 Å, powdered) were pre-dried in an oven and activated for 5 min under vacuum at 300 °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. Chemical shifts are given in ppm and coupling constants are reported in Hz. Resonances were assigned by means of 2D spectra (COSY, HMQC).

1,4,5,6-Tetra-*O*-benzoyl-2,3-*O*-(tetraisopropyldisiloxane-1′,3′-diyl)-L-*chiro*-inositol (1a): $TIPDSCl_2$ (432 μL, 1.33 mmol, 1.2 equiv.) was added dropwise to a solution of L-*chiro*-inositol (200 mg, 1.11 mmol, 1 equiv.), imidazole (189 mg, 2.78 mmol, 2.5 equiv.), and dimethylaminopyridine (54 mg, 0.44 mmol, 0.4 equiv.) in DMF (15 mL). The reaction mixture was stirred overnight at room temperature, diluted with EtOAc, washed twice with a saturated solution of ammonium chloride and then with water and brine, dried with magnesium sulfate, and then the solvent was evaporated under vacuum. The residue was immediately dissolved in pyridine (20 mL) and then benzoyl chloride (1.4 mL, 8.90 mmol, 8.0 equiv.) and dimethylaminopyridine (8 mg, 0.06 mmol, 0.05 equiv.) were added and the mixture was stirred overnight. The pyridine was evaporated and the residue was diluted with CH_2Cl_2, quenched with ammonium hydroxide (0.2 mL), washed with a saturated solution of ammonium chloride and then with brine, dried with magnesium sulfate, and then the solvent was evaporated under vacuum. The crude product was purified by flash chromatography (Hex/EtOAc, 15:1) to give **1a** (212 mg, 0.25 mmol, 36%), **1b** (102 mg, 0.12 mmol, 22%) and **1c** (47 mg, 0.06 mmol, 15%). R_f (Hex/EtOAc, 10:1): 0.41. $[\alpha]_D^{20} = -40$ (c = 1.2, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.0 Hz, 2 H, H_{ortho}), 8.06 (d, J = 8.0 Hz, 2 H, H_{ortho}), 7.98 (d, J = 8.0 Hz, 2 H, H_{ortho}), 7.77 (d, J = 8.0 Hz, 2 H, H_{ortho}), 7.65−7.21 (m, 12 H, Bz), 6.00 (m, 1 H, H^4), 5.92 (br. t, J = 3.5 Hz, 1 H, H^6), 5.84−5.75 (m, 2 H, H^5, H^1), 4.44 (m, 2 H, H^2, H^3), 1.09−0.79 (m, 28 H, 4 CH and 8 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8 (2 CO), 165.0, 164.9 (2 CO), 133.9, 133.6, 133.4, 133.2 (4 CH_{para}, Bz), 130.0−128.4 (16 CH, 4 C, Bz), 75.1, 73.7 (C^2, C^3), 72.2 (C^4), 70.9 (C^1), 70.3 (C^5), 69.0 (C^6), 17.6−17.0 (4 CH), 13.0 (4 CH_3), 12.5, 12.0 (4 CH_3) ppm. $C_{46}H_{54}O_{11}Si_2$ (839.102): calcd. C 65.84, H 6.49; found C 65.82, H 6.14. HR-FABMS: calcd. for $C_{46}H_{54}O_{11}Si_2+Na^+$, 861.3102; found, 861.3070.

1,4,5,6-Tetra-*O*-benzoyl-L-*chiro*-inositol (2): A solution of **1a** (228 mg, 0.27 mmol, 1 equiv.) in THF (10 mL) was treated with $(HF)_nPy$ (0.73 mL) at −15 °C. The reaction mixture was stirred for 3 h at room temperature, whereupon it was diluted with EtOAc and quenched with a saturated solution of $NaHCO_3$ until pH = 7. The layers were separated and the aqueous phase was extracted extensively with EtOAc. The combined extracts were dried ($MgSO_4$) and concentrated under vacuum to provide a residue that was purified by flash chromatography (Hex/ EtOAc, 2:1) to give **2** (146 mg, 0.24 mmol, 90%) as a white solid. M.p: 148−150 °C; R_f (Hex/EtOAc, 1:2): 0.45. $[\alpha]_D^{20} = -37$ (c = 0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.0 Hz, 2 H, H_{ortho}), 8.05 (d, J = 8.0 Hz, 2 H, H_{ortho}), 8.00 (d, J = 8.0 Hz, 2 H, H_{ortho}), 7.78 (d, J = 8.0 Hz, 2 H, H_{ortho}), 7.65−7.22 (m, 12 H, Bz), 5.93 (br. t, J = 4.5 Hz, 1 H, H^6), 5.91−5.88 (m, 2 H, H^5, H^4), 5.80 (t, J = 4.5 Hz, 1 H, H^1), 4.37 (dt, J_{H2-H3} = 8.5, J_{H2-H1} = J_{H2-OH} = 4.5 Hz, 1 H, H^2), 4.28 (td, J_{H3-H2} = J_{H3-H4} = 8.5, J_{H3-OH} = 4.5 Hz, 1 H, H^3), 2.91 (d, J = 4.5 Hz, 1 H, C^3OH), 2.76 (d, J = 4.5 Hz, 1 H, C^2OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9, 165.8, 165.7, 164.9 (4 CO), 134.0 (2 CH_{para}), 134.6, 133.5 (2 CH_{para}), 130.3−128.5 (4 C, Ph), 130.3, 130.2, 130.1, 130.0, 128.9, 128.8, 128.6, 128.5 (16 CH, Bz), 72.9 (C^5), 72.7 (C^3), 71.4 (C^2), 70.5 (C^1), 70.1 (C^4), 69.1 (C^6) ppm. $C_{34}H_{28}O_{10}$ (596.591): calcd. C 68.45, H 4.73; found C 68.14, H 5.01; HR-CIMS: calcd. for $[C_{34}H_{28}O_{10}]^+$, 597.1761; found, 597.1759.

2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (5) and 2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→2)-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (6): Toluene was evaporated three times from a mixture of **3a** (197 mg, 0.32 mmol, 1.2 equiv.) and **2** (158 mg, 0.26 mmol, 1 equiv.) and then the residue was dried under vacuum overnight. Freshly activated 4 Å molecular sieves and diethyl ether (10 mL) were added under argon and the mixture was stirred for 1 h at room temperature. A solution of TMSOTf in diethyl ether (0.1 M, 225 μL, 0.08 equiv.) was added at −40 °C and the reaction mixture was stirred for 3 h between −40 °C and −5 °C and then additionally for 1 h at room temperature. The suspension was filtered through a short pad of celite and the solvent was evaporated under vacuum to provide a residue that was purified by flash chromatography (toluene/acetone, 35:1) to obtained **5** (158 mg, 0.15 mmol, 58%) and **6** (24 mg, 0.02 mmol, 9%) as white solids. Data for **5**: M.p. 125−128 °C; R_f (toluene/acetone, 3:1): 0.67. $[\alpha]_D^{20} = -14$ (c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, J = 10.0 Hz, 2 H, H_{ortho}), 8.08 (d, J = 10.0 Hz, 2 H, H_{ortho}), 8.00 (d, J = 10.0 Hz, 2 H, H_{ortho}), 7.76 (d, J = 10.0 Hz, 2 H, H_{ortho}), 7.64 (t, J = 10.0 Hz, 2 H, H_{para}), 7.61−7.04 (m, 25 H, Bz, Ph), 6.02 (t, J = 10.0 Hz, 1 H, H^{4e}), 5.92 (br. s, 1 H, H^6), 5.89 (br. s, 1 H, H^1), 5.82 (dd, J_{H5-H4} = 10.0, J_{H5-H6} = 2.0 Hz, 1 H, H^5), 5.19

(d, J = 3.5 Hz, 1 H, $H^{1'}$), 4.90 (AB, J = 11.0 Hz, 1 H, CH-Ph), 4.83 (AB, J = 1.0 Hz, 1 H, CH-Ph), 4.68 (AB, J = 11.0 Hz, 1 H, CH-Ph), 4.49 (m, 2 H, H^2, C^2OH), 4.48 (m, 1 H, H^2), 4.39 (AB, J = 11.0 Hz, 1 H, CH-Ph), 4.25−4.20 (m, 2 H, H^3, CH-Ph), 3.99 (t, J = 10.0 Hz, 1 H, $H^{3'}$), 3.88 (AB, J = 11.0 Hz, 1 H, CH-Ph), 3.73−3.66 (m, 2 H, $H^{4'}$, $H^{5'}$), 3.60 (dd, $J_{H2'\text{-}H3'}$ = 10.0, $J_{H2'\text{-}H1'}$ = 3.5 Hz, 1 H, $H^{2'}$), 3.22 (br. d, J = 11.2 Hz, 1 H, $H^{6a'}$), 2.69 (br. d, J = 11.2 Hz, 1 H, $H^{6b'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8, 165.5, 165.1, 164.7 (4 CO), 138.0 (C, Ph), 137.6 (2 C, Ph), 133.8−133.2 (4 CH_{para}, Bz), 130.1−127.9 (35 C, Bz, Ph), 100.4 ($C^{1'}$), 83.2 (C^3), 80.9 ($C^{3'}$), 77.7 ($C^{4'}$), 75.7, 74.7, 73.4 (3 CH_2Ph), 72.0 ($C^{5'}$), 70.9 (C^2), 70.7 (C^5), 70.6 (C^4), 69.7 (C^1), 68.6 (C^6), 67.0 ($C^{6'}$), 64.6 ($C^{2'}$) ppm. $C_{61}H_{55}N_3O_{14}$ (1054.121): calcd. C 69.50, H 5.26, N 3.99 found C 69.55, H 5.25, N 3.99. HR-FABMS: calcd. for $[C_{61}H_{55}N_3O_{14} + Na]^+$, 1076.3582; found, 1076.3616; Data for **6**: M.p. 122−126 °C; R_f (toluene/acetone, 3:1): 0.51. $[\alpha]_D^{20}$ = −39 (c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.0 Hz, 2 H, H_{ortho}), 8.02 (m, 4 H, H_{ortho}), 7.76 (d, J = 8.0 Hz, 2 H, H_{ortho}), 7.64 (t, J = 8.0 Hz, 2 H, H_{para}), 7.55−7.00 (m, 25 H, Bz, Ph), 6.01 (t, J = 9.8 Hz, 1 H, H^4), 5.93 (t, J = 4.0 Hz, 1 H, H^6), 5.82 (m, 2 H, H^1, H^5), 5.24 (d, J = 3.5 Hz, 1 H, $H^{1'}$), 4.68 (AB, J = 10.5 Hz, 1 H, CH-Ph), 4.65 (AB, J = 11.5 Hz, 1 H, CH-Ph), 4.61 (AB, J = 10.5 Hz, 1 H, CH-Ph), 4.57 (AB, J = 12.0 Hz, 1 H, CH-Ph), 4.49 (td, J_{H3-H2} = $J_{H3\text{-}H4}$ = 9.8, $J_{H3\text{-}OH}$ = 2.0 Hz, 1 H, H^3), 4.42 (AB, J = 11.2 Hz, 1 H, CH-Ph), 4.35 (AB, J = 12.0 Hz, 1 H, CH-Ph), 4.22 (dd, J_{H2-H3} = 9.8, J_{H2-H1} = 3.5 Hz, 1 H, H^2), 3.88 (d, J = 2.0 Hz, 1 H, C^3OH), 3.80 (br. d, 1 H, J = 9.5 Hz, $H^{6a'}$), 3.73−3.61 (m, 4 H, $H^{3'}$, $H^{4'}$, $H^{5'}$,$H^{6a'}$), 3.54 (dd, $J_{H2'\text{-}H3'}$ = 9.5, $J_{H2'\text{-}H1'}$ = 3.5 Hz, 1 H, $H^{2'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 165.6, 165.0, 164.7 (4 CO), 138.0, 137.7, 137.5 (3 C, Ph), 138.1, 137.7, 137.6, 137.5 (4 CH_{para}, Bz) 130.1−127.3 (35 C, Bz, Ph), 100.9 ($C^{1'}$), 80.7 (C^2, $C^{3'}$), 77.8 ($C^{4'}$), 75.5, 74.4, 73.5 (3 CH_2Ph), 71.9 (C^3), 71.8 ($C^{5'}$), 71.5 (C^4), 70.0, 69.8 (C^1, C^5), 68.7 (C^6), 67.6 ($C^{6'}$), 64.3 ($C^{2'}$) ppm. $C_{61}H_{55}N_3O_{14}$ (1054.121): calcd. C 69.50, H 5.26, N 3.99 found C 69.35, H 5.39, N 4.08. HR-FABMS: calcd. for $[C_{61}H_{55}N_3O_{14} + Na]^+$, 1076.3582; found, 1076.3602.

2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α(1→3)-L-*chiro*-inositol (7): MeONa in MeOH (2 M, 7 mL) was added at room temperature to a solution of **5** (101 mg, 0.10 mmol, 1.0 equiv.) in MeOH (10 mL). The solution was stirred overnight and then it was quenched with Amberlite IRA-120 resin. The solvent and BzOMe were evaporated by heating at 50 °C under vacuum to provide the solid **7** (61 mg, 0.1 mmol, quantitative). M.p. 148−152 °C; R_f (acetone): 0.61. $[\alpha]_D^{20}$ = +67 (c = 0.6, MeOH). ^{1}H NMR (400 MHz, [D_6]acetone): δ = 7.37−7.24 (m, 15 H, Ph), 5.44 (d, J = 3.6 Hz, 1 H, $H^{1'}$), 4.88 (AB, 2 H, 2 CH-Ph), 4.80 (AB, J = 10.8 Hz, 1 H, CH-Ph), 4.64 (AB, J = 10.8 Hz, 1 H, CH-Ph), 4.56 (AB, 2 H, 2 CH-Ph), 4.38 (m, 1 H, $H^{5'}$), 4.02−3.92 (m, 5 H, H^1, H^6, H^4, H^5, $H^{3'}$), 3.80−3.63 (m, 5 H, H^2, H^3, $H^{4'}$, $H^{6a'}$, $H^{6b'}$), 3.42 (dd, 1 H, $J_{H2'H3'}$ = 10.0, $J_{H2'\text{-}H1'}$ = 3.6 Hz, $H^{2'}$), 2.82 (s, 5 H, OH) ppm. ^{13}C NMR (100 MHz, [D_6]acetone): δ = 139.4 (3 C, Ph), 130.5−129.6 (15 CH, Ph), 98.0 ($C^{1'}$), 81.0, 79.5 (C^3, C^2), 75.4, 75.3, 73.7 (3 CH_2Ph), 73.1, 72.7, 72.6, 72.4, 72.3, 72.2 (C^1, C^4, C^5, C^6, $C^{3'}$, $C^{4'}$), 71.3, ($C^{5'}$), 69.6 ($C^{6'}$), 64.7 ($C^{2'}$) ppm. $C_{33}H_{39}N_3O_{10}$ (637.688): calcd. C 62.16, H 6.165, N, 6.589; found C 61.68, H 6.043, N 6.236. HR-FABMS: calcd. for $[C_{33}H_{39}N_3O_{10} + Na]^+$, 660.2533; found, 660.2543.

2-Amino-2-deoxy-D-glucopyranosyl-α(1→3)-L-*chiro*-inositol (XII): Compound **7** (12 mg, 0.02 mmol, 1.0 equiv.) and 10% Pd/C (5 mg, 0.04 mmol) were stirred overnight in ethanol/water (4:1) under a hydrogen atmosphere. The slurry was filtered through celite and washed with water and finally lyophilized to give the fully deprotected pseudodissacharide **XII** (6.1 mg, 0.02 mmol, 95%). R_f (EtOAc/MeOH/H_2O/AcOH, 2:2:1:1): 0.34. $[\alpha]_D^{20}$ = +38 (c = 0.2, H_2O). ^{1}H NMR (500 MHz, D_2O): δ = 5.36 (d, J = 3.8 Hz, 1 H, $H^{1'}$), 4.04 (dt, $J_{H5'\text{-}H4'}$ = 10.0, $J_{H5'\text{-}H6a'}$ = $J_{H5\text{-}H6b'}$ = 3.0 Hz, 1 H, $H^{5'}$), 3.99 (t, J = 3.5 Hz, 1 H, H^6), 3.96 (t, J = 3.5 Hz, 1 H, H^1), 3.92 (dd, J_{H2-H3} = 9.5, J_{H2-H1} = 3.5 Hz, 1 H, H^2), 3.82 (t, J = 10.0 Hz, 1 H, 1 H, $H^{3'}$), 3.80 (m, 2 H, $H^{6a'}$, $H^{6b'}$), 3.74 (dd, J_{H5-H4} = 9.5, J_{H5-H6} = 3.5 Hz, 1 H, H^5), 3.66 (t, J = 9.5 Hz, 1 H, H^3), 3.62 (t, J = 9.5 Hz, 1 H, H^4), 3.50 (t, J = 10.0 Hz, 1 H, $H^{4'}$), 3.16 (dd, $J_{H2'\text{-}H3'}$ = 10.5, $J_{H2'\text{-}H1'}$ = 3.8 Hz, 1 H, $H^{2'}$) ppm. ^{13}C NMR (D_2O, 125 MHz): δ = 97.1 ($C^{1'}$), 80.2 (C^3), 71.7 ($C^{5'}$), 71.4 (C^1), 70.9 (C^6), 70.7 (C^4), 70.6 ($C^{3'}$), 70.5 (C^5), 70.1 (C^2), 68.9 ($C^{4'}$), 59.6 ($C^{6'}$), 54.2 ($C^{2'}$) ppm. HR-FABMS: calcd. for $[C_{12}H_{23}NO_{10} + Na]^+$, 364.1220; found, 364.1225.

2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (8a) and 2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→2)-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (9a). These pseudodisaccharides were prepared from **4a** (62 mg, 0.10 mmol, 1.2 equiv.) and **2** (50 mg, 0.08 mmol, 1 equiv.) as described for the preparation of **5**, stirring the reaction mixture for 1 h at −40 °C, 2 h between −40 °C and −30 °C and then overnight at room temperature, yielding **8a** (37 mg, 0.04 mmol, 42%) and **9a** (5 mg, 0.005 mmol, 6%) after flash chromatography (toluene/acetone, 40:1). Data for **8a**: R_f (toluene/acetone, 15:1): 0.48. $[\alpha]_D^{20}$ = −5 (c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.0 Hz, 2 H, H_{ortho}), 8.06 (d, J = 7.5 Hz, 2 H, H_{ortho}), 7.99 (d, J = 7.2 Hz, 2 H, H_{ortho}), 7.72 (d, J = 8.0 Hz, 2 H, H_{ortho}), 7.63 (m, 2 H, H_{para}), 7.52 (m, 4 H, H_{meta}), 7.46 (t, J = 7.2 Hz, 1 H, H_{para}), 7.41−6.98 (m, 20 H, Bz, Ph), 6.02 (t, J = 10.0 Hz, 1 H, H^4), 5.88 (br. t, J = 3.5 Hz, 1 H, H^6), 5.83 (br. t, J = 3.5 Hz, 1 H, H^1), 5.79 (dd, J_{H5-H4} = 10.5, J_{H5-H6} = 3.5 Hz, 1 H, H^5), 5.16 (d, J = 3.5 Hz, 1 H, $H^{1'}$), 4.72−4.64 (m, 3 H, CH-Ph, CH_2-Ph), 4.45 (m, 1 H, H^2), 4.36 (AB, J = 11.5 Hz, 1 H, CH-Ph), 4.21 (t, J = 9.5 Hz, 1 H, H^3), 4.08 (dd, $J_{H2'\text{-}H3'}$ = 10.0, $J_{H2'\text{-}H1'}$ = 3.0 Hz, 1 H, $H^{2'}$), 4.02−3.89 (m, 3 H, $H^{3'}$, $H^{4'}$, $H^{5'}$) 3.28 (t, J = 8.5 Hz, 1 H, $H^{6a'}$), 2.72 (dd, $J_{H6b'\text{-}H6a'}$ = 8.5 Hz, $J_{H6b'\text{-}H6a'}$ = 8.0 Hz, 1 H, $H^{6b'}$) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.0, 165.6, 165.2, 164.9 (4 CO), 138.4, 137.8, 137.6 (3 C, Ph), 133.9−133.4 (4 CH_{para}, Bz), 130.2−127.8 (31 CH, Bz, Ph), 100.2 ($C^{1'}$), 82.7 (C^3), 78.4 ($C^{3'}$), 70.0 (CH_2Ph), 73.2 ($C^{4'}$), 72.8, 72.1 (2 CH_2Ph), 70.9 (C^2), 70.5 (C^5), 70.1, 70.0 (C^1, $C^{5'}$), 68.7 (C^6), 67.5 ($C^{6'}$), 61.2 ($C^{2'}$) ppm. $C_{61}H_{55}N_3O_{14}$ (1054.121): calcd. C 69.50, H 5.26, N 3.99 found C 69.51, H 5.12, N 4.13. HR-FABMS: calcd. for $[C_{61}H_{53}N_3O_{14} + Na]^+$, 1076.3592; found, 1076.3585. Some of the most significant data for **9a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.26 (d, J = 5.3 Hz, 1 H, $H^{1'}$), 3.91 (br. s, 1 H, $H^{4'}$), 3.75 (dd, $J_{H3'\text{-}H2'}$ = 9.5, $J_{H3'\text{-}H4'}$ = 2.5 Hz, 1 H, $H^{3'}$) ppm.

2-Azido-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α(1→3)-L-*chiro*-inositol (10a): This compound was prepared from the fully protected pseudodisaccharide **8a** (29 mg, 0.03 mmol, 1.0 equiv.), using the procedure described for the preparation of **7**, to yield **10a** (18 mg, 0.03 mmol, quantitative). R_f (acetone): 0.33. $[\alpha]_D^{20}$ = +9 (c = 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 7.40−7.17 (m, 15 H, 3Ph), 4.99 (d, J = 4.0 Hz, 1 H, $H^{1'}$), 4.83 (AB, J = 11.5 Hz, 1 H, CH-Ph), 4.71 (s, 2 H, CH_2Ph), 4.49 (AB, J = 11.5 Hz, 1 H, CH-Ph), 4.46 (AB, J = 11.5 Hz, 1 H, CH-Ph), 4.39 (AB, J = 11.5 Hz, 1 H, CH-Ph), 4.15−4.10 (m, 3 H, H^1, $H^{2'}$, H^6), 4.07 (dd, $J_{H5'\text{-}H6a'}$ = 9.2, $J_{H5'\text{-}H6b'}$ = 3.0 Hz, 1 H, $H^{5'}$), 3.90 (dd, $J_{H3'\text{-}H2'}$ = 9.5, $J_{H3'\text{-}H4'}$ = 2.5 Hz, 1 H, $H^{3'}$), 3.87 (dd, J_{H2-H3} = 10.0, J_{H2-H1} = 3.0 Hz, 1 H, H^2), 3.82 (d, $J_{H4'\text{-}H3'}$ = 2.5 Hz, 1 H, $H^{4'}$), 3.78 (dd, J_{H5-H4} = 9.2, J_{H5-H6} = 2.5 Hz, 1 H, H^5), 3.59 (m, 2 H, H^4, $H^{6a'}$), 3.51 (t, J =

10.0 Hz, 1 H, H^3), 3.24 (dd, $J_{H6b'-H6b'}$ = 9.2, $J_{H6b'-H5'}$ = 3.0 Hz, 1 H, $H^{6b'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.9, 137.7, 137.3 (3 C, Ph), 128.8−128.0 (15 CH, Ph), 99.2 ($C^{1'}$), 86.9 (C^3), 79.0 (C^2), 74.6, 73.9 (CH_2Ph), 73.1 ($C^{4'}$), 72.6 (CH_2Ph), 71.8 (C^5), 71.4 ($C^{5'}$), 71.2 ($C^{3'}$), 70.7, 70.63, 70.59 (C^1, C^4, C^6), 70.0 ($C^{6'}$), 61.5 ($C^{2'}$) ppm. HR-FABMS: calcd. for $[C_{33}H_{39}N_3O_{10} + Na]^+$, 660.2533; found, 660.2589.

2-Azido-2-deoxy-3,4,6-tri-*O*-acetyl-D-galactopyranosyl-α-(1→3)-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (8b): These pseudodisaccharides were prepared from **4b** (70 mg, 0.15 mmol, 1.2 equiv.) and **2** (72 mg, 0.12 mmol, 1 equiv.) using the procedure described for the preparation of **5**, adding of a solution of TMSOTf (0.1 M, 0.15 equiv.) and stirring the reaction mixture for 2 h between −40 °C and −5 °C, to yield, after flash chromatography (toluene/acetone, 30:1), a 2:1 mixture of **8b** and **9b** (81 mg, 72%). Data for **8b**: R_f (toluene/acetone, 4:1): 0.40. $[\alpha]_D^{20}$ = +18 (*c* = 0.9, $CHCl_3$, enriched mixture of pseudodisaccharides, α(1−3) **8b** /α(1−2) **9b** = 1:0.1). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 7.5 Hz, 2 H, H_{ortho}), 8.08 (d, *J* = 7.5 Hz, 2 H, H_{ortho}), 7.98 (d, *J* = 7.5 Hz, 2 H, H_{ortho}), 7.72 (d, *J* = 7.5 Hz, 2 H, H_{ortho}), 7.67−7.17 (m, 27 H, Bz, Ph), 6.01 (t, *J* = 10.5 Hz, 1 H, H^4), 5.91 (m, 1 H, H^6), 5.87 (m, 1 H, H^1), 5.82 (dd, J_{H5-H4} = 10.5, J_{H5-H6} = 3.0 Hz, 1 H, H^5), 5.38 (dd, $J_{H3'-H2'}$ = 11.0, $J_{H3'-H4'}$ = 3.0 Hz, 1 H, $H^{3'}$), 5.29 (br. s, 1 H, $H^{4'}$), 5.26 (d, *J* = 3.5 Hz, 1 H, $H^{1'}$), 4.50 (br. d, J_{H2-H3} = 9.5 Hz, 1 H, H^2), 4.26 (s, 1 H, C^2OH), 4.22 (t, *J* = 10.5 Hz, 1 H, H^3), 4.08 (m, 1 H, $H^{5'}$), 3.94 (dd, $J_{H2'-H3'}$ = 11.0, $J_{H2'-H1'}$ = 3.5 Hz, 1 H, $H^{2'}$), 3.74 (t, *J* = 10.2 Hz, 1 H, $H^{6a'}$), 3.06 (dd, $J_{H6b'-H6a'}$ = 10.2, $J_{H6b'-H5'}$ = 4.5 Hz, 1 H, $H^{6b'}$), 2.09, 1.96, 1.91 (3s, 9 H, CH_3CO) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 134.0−133.2 (4 CO), 130.1−128.3 (42 C, Bz, Ph), 100.0 ($C^{1'}$), 83.2 (C^3), 71.0 (C^2), 70.6, 70.5 (C^4, C^5), 69.8, 69.7 (C^1, $C^{3'}$), 68.4 (C^6), 67.1 ($C^{5'}$), 66.6 ($C^{4'}$), 59.8 ($C^{6'}$), 59.0 ($C^{2'}$), 20.7, 20.6, 20.5 (3 CH_3CO) ppm. HR-FABMS: calcd. for $[C_{46}H_{43}N_3O_{17} + Na]^+$, 932.2490; found, 932.2523. Some of the most significant data for **9b**: ^1H NMR (500 MHz, $CDCl_3$): δ = 6.15 (t, *J* = 10.2 Hz, 1 H, H^4), 5.19 (d, $J_{H4'-H5'}$ = 2.1 Hz, 1 H, $H^{4'}$), 5.17 (br. s, 1 H, $H^{1'}$) ppm.

2-Azido-D-galactopyranosyl-α(1→3)-L-*chiro*-inositol (10b): Compound **10b** was obtained from a 1:0.2 mixture of **8b** and **9b** (40 mg, 0.04 mmol, 1.0 equiv.) following the same experimental procedure as described for the preparation of **7** to yield a mixture of pseudodisaccharide α(1−3) (**10b**) and the partially deprotected α(1−2)-pseudodisaccharide of **9b** (1:0.2, 14 mg, 0.04 mmol, 88%) after precipitating with diethyl ether. $[\alpha]_D^{20}$ = +78 [*c* = 0.6, MeOH mixture of pseudodisaccharides α(1−3)/α(1−2) = 1:0.2]. ^1H NMR (500 MHz, [D$_4$]MeOH): 5.35 (d, *J* = 4.0 Hz, 1 H, $H^{1'}$), 4.26 (br. t, *J* = 5.5 Hz, 1 H, $H^{5'}$), 4.01 (dd, $J_{H3'-H2'}$ = 10.5, $J_{H3'-H4'}$ = 3.0 Hz, 1 H, $H^{3'}$), 3.94−3.85 (m, 4 H, $H^{4'}$, H^1, H^5, H^6), 3.77−3.55 (m, 5 H, H^2, H^3, H^4, $H^{6a'}$, $H^{6b'}$), 3.51 (dd, $J_{H2'-H3'}$ = 10.8, $J_{H2'-H1'}$ = 4.0 Hz, 1 H, $H^{2'}$) ppm. ^{13}C NMR (125 MHz, [D$_4$]MeOH): δ = 100.2 ($C^{1'}$), 81.3 (C^3), 72.3, 71.92, 71.88, 71.5 (C^1, C^4, C^5, C^6), 71.2 (C^2), 70.9 ($C^{5'}$), 69.6 ($C^{4'}$), 68.3 ($C^{3'}$), 61.4 ($C^{6'}$), 60.9 ($C^{2'}$) ppm. HR-FABMS: calcd. for $[C_{12}H_{21}N_3O_{10} + Na]^+$, 390.1125; found, 390.1125.

2-Amino-2-deoxy--galactopyranosyl-α(1→3)-L-*chiro*-inositol (XIII): The fully deprotected pseudodisaccharide **XIII** was obtained following the same experimental procedure as described for **XII** starting from **10a** (14 mg, 0.022 mmol, 1.0 equiv.) and after purification by reverse-phase flash chromatography (H_2O/MeOH, 95:5; yield = 6 mg, 80%) or by starting from a 1:0.2 mixture of α(1−3)-pseudodisaccharide **10b** and the partially deprotected α(1−2)-disaccharide of **9b** (6.0 mg, 0.016 mmol, 1.0 equiv.) to give a 1:0.2 mixture (5.1 mg, 0.015 mmol, 94%) of α(1−3)-pseudodisaccharide **XIII** and fully deprotected α(1−2)-pseudodisaccharide **9b**. R_f (EtOAc/MeOH/H_2O/AcOH, 2:2:1:1): 0.39. $[\alpha]_D^{20}$ = +29 (*c* = 0.1, H_2O). ^1H NMR (500 MHz, D_2O): δ = 5.44 (d, *J* = 3.8 Hz, 1 H, $H^{1'}$), 4.29 (m, 1 H, $H^{5'}$), 4.07 (dd, $J_{H3'-H2'}$ = 10.5, $J_{H3'-H4'}$ = 3.0 Hz, 1 H, $H^{3'}$), 4.02 (d, *J* = 3.0 Hz, 1 H, $H^{4'}$), 3.99 (br. t, *J* = 3.5 Hz, 1 H, H^6), 3.96 (br. t, *J* = 3.5 Hz, 1 H, H^1), 3.91 (dd, J_{H2-H3} = 9.5, J_{H2-H1} = 3.5 Hz, 1 H, H^2), 3.76 (dd, J_{H5-H4} = 9.5, J_{H5-H6} = 3.5 Hz, 1 H, H^5), 3.71 (m, 2 H, $H^{6a'}$, $H^{6b'}$), 3.69 (t, *J* = 9.5 Hz, 1 H, H^3), 3.63 (t, *J* = 9.5 Hz, 1 H, H^4), 3.47 (dd, $J_{H2'-H3'}$ = 10.5, $J_{H2'-H1'}$ = 3.8 Hz, 1 H, $H^{2'}$) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 95.8 ($C^{1'}$), 79.9 (C^3), 71.4 (C^1), 70.9 (C^6), 70.7 ($C^{5'}$), 79.59, 70.57 (C^2, C^4), 70.0 (C^5), 67.6 ($C^{4'}$), 66.0 ($C^{3'}$), 60.2 ($C^{6'}$), 50.9 ($C^{2'}$) ppm. HR-FABMS: calcd. for $[C_{12}H_{23}NO_{10} + Na]^+$, 364.1220; found, 364.1226.

1,2-*O*-Isopropylidene-D-*chiro*-inositol (11): A mixture of D-*chiro*-inositol (1 g, 5.55 mmol), 2,2-dimethoxypropane (0.68 mL, 5.55 mmol) and *p*-toluenesulfonic acid monohydrate (10 mg, 0.05 mmol) in dry DMSO (3 mL) was stirred at 100 °C for 30 min, at which time a clear solution was obtained. The reaction mixture was then cooled and triethylamine (0.1 mL) was added. The solution was concentrated and purified by flash chromatography (CH_2Cl_2/MeOH, 20:1 to 1:1) to give a mixture of bisacetal **12** (0.32 g, 22%) and monoacetal **11** (0.37 g, 30%). Data for **11**: M.p. 150−155 °C. $[\alpha]_D^{20}$ = +82 (*c* = 0.28, MeOH). ^1H NMR (500 MHz, DMSO): δ = 4.95 (d, *J* = 4.6 Hz, 1 H, OH), 4.83 (d, *J* = 5.1 Hz, 1 H, OH), 4.67 (d, *J* = 4.6 Hz, 1 H, OH), 4.64 (d, *J* = 4.6 Hz, 1 H, OH), 4.03 (dd, *J* = 6.1, 1.6 Hz, 1 H, H^1), 3.85 (dd, *J* = 7.9, 1.6 Hz, H^2), 3.78 (m, 1 H, H^6), 3.37 (m, 1 H, H^5), 3.28 (m, 1 H, H^4), 3.19 (m, 1 H, H^3), 1.33 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3) ppm.^{13}C NMR (125 MHz, DMSO): δ = 108.9 (C), 79.8 (CH), 78.6 (CH), 76.8 (CH), 74.1 (CH), 73.9 (CH), 70.2 (CH), 29.0 (CH_3), 28.7 (CH_3) ppm. $C_9H_{16}O_6$ (220.219): calcd. C 49.0, H 7.32; found C 49.12, H 7.30. MALDI-TOF-MS: calcd. for $[C_9H_{16}O_6 + Na]^+$, 243.2, found, 244.3.

1,2-*O*-Isopropylidene-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (13): 1,2-*O*-Isopropylidene-D-*chiro*-inositol (**11**; 1 g, 4.54 mmol) in DMF (30 mL) at −20 °C was added to a suspension of sodium hydride (60% in mineral oil; 1.09 g, 27.24 mmol). The resulting mixture was stirred at 0 °C for 30 min and then benzyl bromide (3.24 mL, 27.27 mmol) was added dropwise. After 12 h at room temperature the reaction was complete and the mixture was treated with MeOH. The solvent was evaporated and the residue diluted with CH_2Cl_2 and washed with a saturated solution of ammonium chloride and brine. The organic layer was dried with sodium sulfate, filtered, and concentrated. The residue was purified by column chromatography (Hex/EtOAc, 8:1) to give **13** as a white solid (2.35 g, 90%). M.p. 109−114 °C. $[\alpha]_D^{20}$ = +33 (*c* = 1.4, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.4−7.2 (m, 20 H, 4Ph), 4.9 (d, 1 H, AB), 4.78−4.53 (m, 7 H, AB), 4.46 (dd, *J* = 6.7, 5.6 Hz, 1 H), 4.40 (dd, *J* = 8.5, 6.7 Hz, 1 H), 3.92 (dd, *J* = 5.6, 1.7 Hz, 1 H), 3.81−3.74 (m, 2 H), 3.58 (dd, *J* = 8.5, 6.9 Hz, 1 H), 1.5 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.7 (C), 138.5 (C), 138.3 (C), 138.2 (C), 128.4 (2 CH), 128.35 (2 CH), 128.3 (2 CH), 128.2 (2 CH), 128.0 (2 CH), 127.9 (2 CH), 127.7 (CH), 127.6 (CH), 127.6 (2 CH), 127.55 (2 CH), 127.5(CH), 127.4 (CH), 109.5 (C), 83.2 (CH), 81.3 (CH), 78.4 (CH), 78.2 (CH), 77.5 (CH), 74.0 (CH), 27.6 (CH_3) 27.3 (CH_3) ppm. $C_{37}H_{40}O_6$ (580.717): calcd. C 76.52, H 6.94; found C 76.62, H 7.02. MALDI-TOF-MS: calcd. for $[C_{37}H_{40}O_6 + Na]^+$, 603.7, found, 603.9.

3,4,5,6-Tetra-*O*-benzyl-D-*chiro*-inositol (14): Acetic acid (80%, 50 mL) was added to a solution of **13** (2.35 g, 4.05 mmol) in THF

(10 mL). The reaction mixture was stirred under reflux at 80 °C for 8 h. The solvent was evaporated and the residue co-evaporated four times with toluene to dryness. The residue was purified by flash chromatography (Hex/EtOAc, 3:1) to yield **14** as a white solid (2.18 g, quantitative). M.p. 69−73 °C. $[\alpha]_D^{20}$ = +36 (*c* = 0.4, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.4−7.2 (m, 20 H, 4Ph), 5.05 and 4.60 (m, 8 H, AB), 4.07 (t, *J* = 3.3 Hz, 1 H, H^1), 3.98 (t, *J* = 9.0 Hz, 1 H, H^4), 3.92−3.86 (m, 3 H, H^6, H^5, and H^2), 3.65 (t, *J* = 9.1 Hz, 1 H, H^3), 2.33 (s, 1 H, OH), 2.29 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.7 (C), 138.6 (C), 138.5 (C), 138.3 (C), 128.6, 128.3, 128.25, 128.0 127.85, 127.6, 127.55, 127.45 (8 CH, 4 CH), 81.6 (CH), 81.5 (CH), 80.4 (CH), 75.7 (CH), 75.5 (CH_2), 75.3 (CH_2), 73.5 (CH_2), 73.1 (CH_2), 71.2 (CH), 69.4 (CH) ppm. $C_{34}H_{36}O_6$ (540.652).: calcd. C 75.52, H 6.71; found C 75.47, H 6.67. MALDI-TOF-MS: calcd. for $[C_{34}H_{36}O_6 + Na]^+$, 563.6, found, 564.1 Da.

3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl-α(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (15b) and 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl-β(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (16b): These pseudodisaccharides were prepared from **4b** (50 mg, 0.105 mmol) and **14** (56 mg, 0.105 mmol) using the procedure described for the preparation of **5**, by adding a solution (108 μL, 0.12 equiv.) of TMSOTf (100 μL in 5 mL of ether) in four portions (one per hour) at −40 °C. After 4 h the reaction mixture was quenched with Et_3N, concentrated and purified by flash chromatography (toluene/acetone, 30:1) to yield of **15b** (59 mg, 66%) and of **16b** (3 mg, 4%). Data for **15b:** $[\alpha]_D^{20}$ = +71 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.4−7.2 (m, 20 H, 4 Ph), 5.27 (dd, *J* = 10.8, 3.25 Hz, 1 H, $H^{3'}$), 5.11 (br. d, *J* = 2.25 Hz, 1 H, $H^{4'}$), 5.05−4.57 (m, 8 H, AB), 4.9 (d, *J* = 3.6 Hz, 1 H, $H^{1'}$), 4.15 (t, *J* = 6.5 Hz, 1 H, $H^{5'}$), 4.1−3.9 (m, 5 H), 3.85 (dd, *J* = 10.8, 7.2 Hz, 1 H, $H^{2'}$), 3.77 (dd, *J* = 11, 6.5 Hz, 1 H, $H^{6a'}$), 3.76 (m, 1 H), 3.68 (dd, *J* = 11, 6.5 Hz, 1 H, $H^{6b'}$), 2.15 (s, 3 H, CH_3), 2.1 (s, 3 H, CH_3), 1.85 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2 (CO), 169.9 (CO), 169.7 (CO), 138.7 (C), 138.65 (C), 138.6 (C), 138.4 (C), 128−127.6 (12 CH), 94.2 (CH), 81.7, 80.2, 80.1, 76.0, 75.7, 75.6, 73.9, 73.4, 69.6, 67.4, 66.7, 66.5, 66.4, 61.1, 58.4, 20.8 (CH_3), 20.65 (CH_3), 20.6 (CH_3) ppm. $C_{46}H_{51}O_{13}N_3$ (853.917): calcd. C 64.70, H 6.02, N 4.92; found C 64.73, H 6.07, N 5.05. MALDI-TOF-MS: calcd. for $[C_{46}H_{51}O_{13}N_3 + Na]^+$, 876.8; found, 875.9. Data for **16b**: ^1H NMR (500 MHz, C_6D_6): 7.70−7.01 (m, 20 H, 4 Ph), 5.39 (br. d, *J* = 3.3 Hz, 1 H, $H^{4'}$), 5.20 and 5.09 (m, 2 H, AB), 5.15 and 5.0 (m, 2 H, AB), 4.90 and 4.60 (m, 2 H, AB), 4.9 (dd, *J* = 10.7, 3.3 Hz, 1 H, $H^{3'}$), 4.67 and 4.54 (m, 2 H, AB), 4.56 (d, *J* = 8.1 Hz, 1 H, $H^{1'}$), 4.39−4.33 (m, 2 H, H^4 and H^2), 4.25 (m, 1 H, H^1), 4.21−4.16 (m, 2 H, H^3 and H^5), 4.11−4.01 (m, 3 H, $H^{6a'}$, $H^{6b'}$ and H^6), 3.98 (dd, *J* = 10.7, 8.1 Hz, 1 H, $H^{2'}$), 3.00 (br. t, *J* = 5.7 Hz, 1 H, $H^{5'}$), 2.03 (br. s, 1 H, C^1-OH), 1.77 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.78 (s, 3 H, CH_3) ppm. $C_{46}H_{51}O_{13}N_3$ (853.917): calcd. C 64.70, H 6.02, N 4.92; found C 64.58, H 5.93, N 4.82.

2-Amino-2-deoxy-D-galactopyranosyl-α(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (17): A solution of **15b** (27 mg, 0.031 mmol) in MeOH/THF (10:1, 2.2 mL) was treated under argon with solution of MeONa in MeOH (1 M, 0.4 mL). After 15 min at room temperature, the reaction was neutralized with acidic IR-120 resin to pH = 7, filtered, concentrated, and purified by flash chromatography (Hex/EtOAc, 1:2) to yield **17** (20 mg, 88%). $[\alpha]_D^{20}$ = +53 (*c* = 0.9, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40−7.20 (m, 20 H, 4 Ph), 5.03−4.45 (m, 8 H, AB), 4.80 (d, *J* = 2.3 Hz, 1 H, $H^{1'}$), 3.97 (m, 3 H, H^1, H^6 and H^3 or H^4), 3.86 (m, 2 H, H^2 and H^5), 3.79 (dd, *J* = 9.7, 2.1 Hz, 1 H, $H^{3'}$), 3.75−3.65 (m, 3 H, H^4 or H^3, $H^{4'}$, and $H^{2'}$), 3.57 (br. s, 1 H, $H^{5'}$), 3.48 (dd, *J* = 12 and 4 Hz, 1 H, $H^{6a'}$), 3.25 (br. d, 1 H, *J* = 12 Hz, $H^{6b'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.9 (C), 138.6 (C), 138.5 (C), 138.4 (C), 128.5−127.4 (12 CH), 94.6 (CH), 81.6 (CH), 80.5 (CH), 80.1 (CH), 76.8 (CH), 75.7 (CH), 75.7 (CH_2),73.9 (CH_2), 73.3 (CH_2), 70.8 (CH), 69.9 (CH), 68.7 (CH), 66.5 (CH),63.4 (CH_2) 63.3 (CH_2), 61.4 (CH) ppm. $C_{40}H_{45}O_{10}N_3$ (727.806): calcd. C 66.01, H 6.23, N 5.77; found C 65.95, H 6.13, N 5.73. MALDI-TOF-MS: calcd. for $[C_{40}H_{45}O_{10}N_3 + Na]^+$, 750.5, found, 750.7.

2-Amino-2-deoxy-D-galactopyranosyl-α(1→2)-D-*chiro*-inositol (XV): Compound **17** (13 mg, 0.018 mmol) and 10% Pd/C in a mixture of MeOH, EtOH, and H_2O (10:3:1, 3 mL) was saturated with a stream of H_2 for 30 min and then stirred under H_2 overnight. The slurry was filtered through celite and the solvent was evaporated to give **XV** (6 mg, quantitative). $[\alpha]_D^{20}$ = +95 (*c* = 0.2, MeOH). ^1H NMR (500 MHz, D_2O): δ = 5.15 (d, *J* = 3.6 Hz, 1 H, $H^{1'}$), 4.21 (t, *J* = 3.0 Hz, 1 H, H^1), 4.17 (t, *J* = 6.2 Hz, 1 H, $H^{5'}$), 4.03 (t, *J* = 3.4 Hz, 1 H, H^6), 3.96 (d, *J* = 2.6 Hz, 1 H, $H^{4'}$), 3.92 (dd, *J* = 10.7, 2.6 Hz, 1 H, $H^{3'}$), 3.82 (dd, *J* = 9.6, 3.0 Hz, 1 H, H^2), 3.76 (dd, *J* = 9.6, 3.4 Hz, 1 H, H^5), 3.72 (m, 2 H, $H^{6a'}$ and $H^{6b'}$), 3.67 (t, *J* = 9.6 Hz, 1 H, H^3), 3.61 (t, *J* = 9.6 Hz, 1 H, H^4), 3.21 (dd, *J* = 10.7, 3.6 Hz, 1 H, $H^{2'}$) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 94.2, 74.7, 72.2, 70.9, 70.8, 70.7, 69.9, 68.5, 67.9, 67.0, 60.5, and 50.2 ppm. $C_{12}H_{23}O_{10}N$ (341.310): calcd. C 42.22, H 6.79, N 4.10; found C 42.35, H 6.73, N 4.15. MALDI-TOF-MS: calcd. for $[C_{12}H_{23}O_{10}N + Na]^+$, 364.0; found, 365.0.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-α(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (15a) and 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranosyl-β(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (16a): These pseudodisaccharides were prepared from **4a** (57 mg, 0.09 mmol) and **14** (50 mg, 0.09 mmol) using the procedure described for the preparation of **5**, adding TMSOTf [0.06 equiv.; 48 μL of a solution of TMSOTf (100 μL) in ether (100 mL)] in three portions (one per half hour) at −40 °C. The reaction was quenched with Et_3N after 2 h from the initial addition to yield **15a** (36 mg, 40%) and **16a** (16 mg, 18%) after flash chromatography (toluene/acetone, 30:1). Data for **15a**: $[\alpha]_D^{20}$ = +57 (*c*= 0.7, $CHCl_3$).^1H NMR (500 MHz, $CDCl_3$): δ = 7.40−7.20 (m, 35 H, 7 Ph), 4.93−4.20 (m, 14 H, AB), 4.86 (d, *J* = 3.8 Hz, 1 H, $H^{1'}$), 4.11 (m, 1 H, $H^{5'}$), 4.03 (dd, *J* = 10.1, 3.8 Hz, 1 H, $H^{2'}$), 4.02 (br. s, 1 H, H^1), 4.0−3.96 (m, 3 H, H^3, H^5, H^6), 3.91 (dd, *J* = 9.7, 2.7 Hz, 1 H, H^2), 3.88 (br. d, 1 H, *J* = 2.6 Hz, $H^{4'}$), 3.81 (dd, *J* = 10.2, 2.6 Hz, 1 H, $H^{3'}$), 3.75 (t, *J* = 9.0 Hz, 1 H, H^4), 3.50 (t, *J* = 8.8 Hz, 1 H, $H^{6a'}$), 3.42 (dd,1 H, *J* = 8.8, 5.7 Hz, $H^{6b'}$), 3.07 (s, 1 H, C^1-*OH*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.2 (C), 138.9 (C), 138.7 (C), 138.7 (C), 138.3 (C), 137.7 (2 C), 128.8−127.6 (21 CH), 94.9 (CH), 81.8 (CH), 80.6 (CH), 80.3 (CH), 78.3 (CH), 77.5 (CH), 76.1 (CH), 76.0 (CH_2), 75.8 (CH_2), 75.1 (CH_2), 74.1 (CH_2), 73.6 (CH_2), 73.5 (CH_2), 73.3 (CH), 72.2 (CH_2), 69.9 (CH), 68.3 (CH_2), 66.6 (CH), 61.0 (CH) ppm. HR-FABMS: calcd. for $[C_{61}H_{63}O_{10}N_3 + Na]^+$, 1020.4411; found, 1020.4426. Data for **16a**: $[\alpha]_D^{20}$ = +0.8 ($CHCl_3$, *c*= 0.6). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.4−7.2 (m, 35 H, 7 Ph), 4.93−4.38 (m, 14 H, AB), 4.35 (d, *J* = 8.0 Hz, 1 H, $H^{1'}$), 4.08 (br. t, *J* = 3.3 Hz, 1 H, H^1), 4.01 (dd, *J* = 9.2, 3.3 Hz, 1 H, H^2), 3.94 (t, *J* = 9.2 Hz, 1 H, H^4), 3.89−3.87 (m, 2 H, H^5 and H^6), 3.86 (br. s, 1 H, $H^{4'}$), 3.84 (t, *J* = 9.2 Hz, 1 H, H^3), 3.81 (dd, *J* = 10.4, 8.0 Hz, 1 H, $H^{2'}$), 3.52 (dd, *J* = 9.0, 7.3 Hz, 1 H, $H^{6a'}$), 3.46 (dd, *J* = 9.0, 5.7 Hz, 1 H, $H^{6b'}$), 3.42 (m, 1 H, $H^{5'}$), 3.29 (dd, *J* = 10.4, 2.7 Hz, 1 H, $H^{3'}$), 2.55 (s, 1 H, C^1-*OH*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.3 (C), 139.2 (C), 139.1 (C), 138.9 (C), 138.4 (C), 138.0 (C), 137.7 (C), 128.9−127.7 (21 CH), 102.6 (C), 82.0 (CH), 81.7 (CH), 81.3 (CH), 81.0 (CH), 80.2 (CH), 76.5 (CH),

76.1 (CH_2), 75.1 (CH_2), 73.8 (2 CH_2), 73.7 (CH), 73.7 (CH_2), 73.5 (CH_2), 72.8 (CH_2), 72.2 (CH), 69.8 (CH), 68.6 (CH_2), 63.7 (CH) ppm. HR-FABMS: calcd. for $[C_{61}H_{63}O_{10}N_3 + Na]^+$, 1020.4411; found, 1020.4421.

2-Azido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl-α(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (19) and 2-Azido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl-α(1→1)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (20): These pseudodisaccharides were prepared from **3b** (40 mg, 0.84 mmol) and **14** (45 mg, 0.84 mmol) using the procedure described for the preparation of **5**, adding TMSOTf [0.14 equiv.; 108 μL of a solution of TMSOTf (100 μL) in ether (5 mL)] at −40 °C in four portions (one per hour). After an additional 3 h at room temperature, the reaction was quenched by adding Et_3N to yield, after flash chromatography (toluene/acetone, 30:1), mixture of pseudodisaccharides α-(1→2) **19** and α-(1→1) **20** that could not be separated (45 mg, 63%; 93:7). Data for **19**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40−7.20 (m, 20 H, 4 Ph), 5.40 (t, J = 9.8 Hz, 1 H, $H^{3'}$), 5.05−4.57 (m, 8 H, AB), 4.93 (t, J = 9.8 Hz, 1 H, $H^{4'}$), 4.86 (d, J = 3.7 Hz, 1 H, $H^{1'}$), 4.08 (m, 1 H, $H^{5'}$), 4.02−3.89 (m, 5 H, H^1, H^2, H^5, H^6, and H^3 or H^4), 3.76 (t, J = 9.4 Hz, 1 H, H^3 or H^4), 3.72 (dd, J = 12.8, 2.9 Hz, 1 H, $H^{6a'}$), 3.65 (dd, J = 12.8, 1.6 Hz, 1 H, $H^{6b'}$), 3.62 (dd, J = 10, 3.7 Hz, 1 H, $H^{2'}$), 2.10 (s, 3 H, CH_3), 2.00 (s, 3 H, CH_3), 1.90 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.4 (CO), 169.9 (CO), 169.6 (CO), 138.7 (C), 138.6 (C), 138.5 (C), 138.4 (C), 128.4−127.3 (12 CH), 93.9 (CH), 81.6 (CH), 80.1 (CH), 79.8 (CH), 77.5 (CH), 75.7 (CH_2), 75.6 (CH_2), 75.5 (CH), 73.9 (CH_2), 73.4 (CH_2), 71.9 (CH), 67.7 (CH), 67.6 (CH), 66.5 (CH), 61.7 (CH), 60.9 (CH_2), 20.7 (CH_3), 20.6 (CH_3), 20.5 (CH_3) ppm. $C_{46}H_{51}O_{13}N_3$ (853.917): calcd. C 64.70, H 6.02, N 4.92; found C 64.85, H 6.12, N 4.81. Some of the most representative signals of the α(1→1)-pseudodisaccharide **20**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.29 (t, J = 9.8 Hz, 1 H, $H^{3'}$), 4.27 (m, 1 H, $H^{5'}$), 3.46 (dd, J = 10.0, 3.5 Hz, 1 H, $H^{2'}$) ppm. Data for the 93:7 mixture of pseudodisaccharides α-(1→2) **19** and α-(1→1) **20**: $[\alpha]_D^{20}$ = +81 (c = 0.6, $CHCl_3$). MALDI-TOF-MS: calcd. for $[C_{46}H_{51}O_{13}N_3 + Na]^+$, 876.5; found, 877.8.

2-Azido-2-deoxy-D-glucopyranosyl-α(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (24): Compound **24** was obtained from a 93:7 mixture of **19** and **20** (34 mg, 0.039 mmol) following the same experimental procedure as that described for the preparation of **17** to yield, after flash chromatography (Hex/EtOAc, 1:2), pure **24** (18 mg, 63%) and a mixture of **15** and the deprotected α(1→1)-disaccharide of **20** (75:25; 7 mg, 25%). Data for **24**: $[\alpha]_D^{20}$ = +42 (c = 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40−7.20 (m, 20 H, 4 Ph), 5.0−4.56 (m, 8 H, AB), 4.75 (d, J = 3.7 Hz, 1 H, $H^{1'}$), 4.02−3.95 (m, 3 H, H^1, H^6, H^3 or H^4), 3.94−3.87 (m, 2 H, H^2, H^5), 3.84 (t, J = 9.4 Hz, 1 H, $H^{3'}$), 3.72 (t, J = 9.3 Hz, 1 H, H^3 or H^4), 3.62 (dt, J = 9.7, 3.1 Hz, 1 H, $H^{5'}$), 3.45 (t, J = 9.4 Hz, 1 H, $H^{4'}$), 3.37 (m, 3 H, $H^{2'}$, $H^{6a'}$, $H^{6b'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.8 (C), 138.6 (C), 138.5 (C), 138.4 (C), 128.5−127.5 (12 CH), 94.7 (CH), 81.6 (CH), 80.2 (CH), 80.1 (CH), 77.9 (CH), 75.9 (CH_2), 75.8 (CH), 75.5 (CH_2), 73.9 (CH_2), 73.3 (CH_2), 73.2 (CH), 71.0 (CH), 70.9 (CH), 66.7 (CH), 63.7 (CH), 61.6 (CH_2) ppm. $C_{40}H_{45}O_{10}N_3$ (727.806): calcd. C 66.01, H 6.23, N 5.77; found C 66.11, H 6.35, N 5.67. MALDI-TOF-MS: calcd. for $[C_{40}H_{45}O_{10}N_3 + Na]^+$, 750.5; found, 750.3. Some of the most representative signals of the deprotected α(1→1)-pseudodisaccharide of **20**: 4.62, (d, J = 3.6 Hz, 1 H, $H^{1'}$), 3.71 (dd, J = 10.2, 9.3 Hz, 1 H, $H^{3'}$), 3.23 (dd, J = 10.2, 3.6 Hz, 1 H, $H^{2'}$) ppm.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-α(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (18): This pseudodisaccharide was prepared from **3a** (74 mg, 0.120 mmol) and **14** (65 mg, 0.120 mmol) using the procedure described for the preparation of **5**, adding TMSOTf [0.04 equiv.; 42 μL of a solution of TMSOTf (100 μL) in ether (5 mL)] at −40 °C in two portions (one per hour). The reaction mixture was warmed to room temperature and then stirred for 4 h to yield of **18** (40 mg, 33%) and a mixture of three pseudodisaccharides (18 mg, 19%) after flash chromatography (toluene/acetone, 30:1). Data for pseudodisaccharide **18**: $[\alpha]_D^{20}$ = +43.0 (c = 0.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40−7.10 (m, 35 H, 7 Ph), 4.97−4.8 (m, 7 H, AB and $H^{1'}$), 4.75−4.56 (m, 5 H, AB), 4.51 (d, J = 13 Hz, 1 H, AB), 4.48 (d, J = 13 Hz, 1 H, AB), 4.43 (d, J = 11 Hz, 1 H, AB), 4.02−3.87 (m, 7 H, $H^{5'}$, $H^{3'}$, H^1, H^2, H^3 or H^4, H^5, H^6), 3.76−3.69 (m, 2 H, H^4 or H^3 and $H^{4'}$), 3.57−3.52 (dd, J = 10, 3.2 Hz, 1 H, $H^{2'}$), 3.30 (d, J = 11.0 Hz, 1 H, $H^{6a'}$), 3.22 (d, J = 11.0 Hz, 1 H, $H^{6b'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.85 (C), 138.65 (C), 138.45 (C), 138.4 (C), 138.25 (C), 137.8 (C), 137.7 (C), 128.5−127.4 (14 CH_2, 7 CH), 94.2 ($C^{1'}$), 81.6 (CH), 81.2 (CH), 80.15 (2 CH), 78.1 (CH), 77.9 (CH), 75.9 (CH_2), 75.8 (CH_2), 75.7 (CH), 75.6 (CH_2), 74.7 (CH_2), 73.8 (CH_2), 73.4 (CH_2), 73.3 (CH_2), 70.9 (CH), 67.5(CH_2), 66.45 (CH), 64.0 (CH) ppm. $C_{61}H_{63}O_{10}N_3$ (998.179): calcd. C 73.40, H 6.36, N 4.20; found C 73.33, H 6.26, N 4.33.

2-Amino-2-deoxy-D-glucopyranosyl-α(1→2)-D-*chiro*-inositol (XIV): The fully deprotected pseudodisaccharide **XIV** was obtained following the same experimental procedure as that describe for obtaining **XV** starting from **19** (14 mg, 0.019 mmol) to yield **XIV** (6.5 mg, quantitative) or starting from **18** (23 mg, 0.023 mmol) to give **XIV** (7.3 mg, 93%). $[\alpha]_D^{20}$ = +80 (c = 0.2, MeOH). ^{1}H NMR (500 MHz, D_2O): δ = 5.05 (d, J = 3.5 Hz, 1 H, $H^{1'}$), 4.19 (t, J = 3.5 Hz, 1 H, H^1), 4.02 (t, J = 3.5 Hz, 1 H, H^6), 3.98−3.93 (m, 1 H, $H^{5'}$), 3.80 (m, 1 H, H^2), 3.77 (m, 2 H, $H^{6a'}$ and $H^{6b'}$), 3.75 (m, 1 H, H^5), 3.67 (t, J = 9.6 Hz, 1 H, $H^{3'}$), 3.66 (t, J = 9.4 Hz, 1 H, H^3), 3.59 (t, J = 9.4 Hz, 1 H, H^4), 3.43 (t, J = 9.6 Hz, 1 H, $H^{4'}$), 2.84 (dd, J = 10.2, 3.5 Hz, 1 H, $H^{2'}$) ppm. ^{13}C NMR (125 MHz, D_2O): δ = 95.3, 75.0, 72.8, 72.3, 71.7, 70.9, 70.8, 69.9, 69.2, 67.3, 59.9, 54.3 ppm. $C_{12}H_{23}O_{10}N$ (341.310): calcd. C 42.22, H 6.79, N 4.10; found C 42.09, H 6.65, N 4.18. MALDI-TOF-MS: calcd. for $[C_{12}H_{23}O_{10}N + Na]^+$, 364.0; found, 364.9.

2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-α(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (21), 2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-β(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (22), and 2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl-α(1→1)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (23): These pseudodisaccharides were prepared from **3c** (31 mg, 0.06 mmol) and **14** (32 mg, 0.06 mmol) using the procedure described for the preparation of **15b**, adding TMSOTf (0.12 equiv.) in five portions (one per half hour) at −40 °C. After 3 h from the initial addition, the reaction was quenched with Et_3N to yield, after flash chromatography (toluene/acetone, 30:1), **21** (28 mg, 52%), of **22** (4 mg, 7%) and of 23 (4 mg, 7%).

Data for **21**: $[\alpha]_D^{20}$ = +11.0 (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.60−7.10 (m, 30 H, 6Ph), 5.31 (s, 1 H, CHPh), 5.13−4.57 (m, 10 H, AB), 4.6 (d, J = 3.3 Hz, 1 H, $H^{1'}$), 4.34 (m, 2 H, $H^{5'}$, H^3 or H^4), 4.25 (m, 2 H, H^2 and H^5), 4.19 (br. t, J = 6.5, 3.5 Hz, 1 H, H^6), 4.16 (br. t, J = 6.7, 3.5 Hz, 1 H, H^1), 4.14 (t, J = 9.5 Hz, 1 H, $H^{3'}$), 4.08 (t, J = 9.4 Hz, 1 H, H^3 or H^4), 4.0 (dd, J = 10.3, 5.0 Hz, 1 H, $H^{6a'}$), 3.46 (t, J = 9.5 Hz, 1 H, $H^{4'}$), 3.37 (t, J = 10.3 Hz, 1 H, $H^{6b'}$), 3.22 (dd, J = 9.5, 3.3 Hz, 1 H, $H^{2'}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.2 (C), 138.9 (C), 138.8 (C), 138.4 (C), 137.9 (C), 137.7 (C), 129.3−126.4 (18 CH), 101.7 (CH), 95.2 (CH), 83.0 (CH), 81.9 (CH), 80.4 (CH), 80.1 (CH), 78.5 (CH), 76.3 (CH_2), 76.2 (CH), 76.0 (CH_2), 75.4 (CH_2), 74.2 (CH_2), 73.6 (CH_2), 73.6 (CH), 68.9 (CH_2), 66.8 (CH), 64.0 (CH), 63.5 (CH)

ppm. $C_{54}H_{55}O_{10}N_3$ (906.039): calcd. C 71.58, H 6.11, N 4.63; found C 71.69, H 6.11, N 4.58. HR-FAB MS: calcd. for $[C_{54}H_{55}O_{10}N_3 + Na]^+$, 928.3785; found, 928.3830.

Data for **22**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60−7.20 (m, 30 H, 6 Ph), 5.53 (s, 1 H, CHPh), 4.96−4.52 (m, 10 H, AB), 4.6 (d, J = 8.1 Hz, 1 H, H$^{1'}$), 4.21 (dd, J = 10.5, 5.0 Hz, 1 H H$^{6a'}$), 4.06 (dd, J = 9.2, 3.4 Hz, 1 H, H^2), 4.01 (br. t, J = 3.4 Hz, 1 H, H^1), 3.96 (t, J = 9.2 Hz, 1 H, H^4), 3.9 (m, 2 H, H^5 and H^6), 3.84 (t, J = 9.2 Hz, 1 H, H^3), 3.71 (t, J = 10.5 Hz, 1 H, H$^{6b'}$), 3.66 (t, J = 9.2 Hz, 1 H, H$^{4'}$), 3.54 (t, J = 9.2 Hz, 1 H, H$^{3'}$), 3.42 (dd, J = 9.2, 8.1 Hz, 1 H, H$^{2'}$), 3.28 (dt, J = 9.2, 5.0 Hz, 1 H, H$^{5'}$) ppm.

Some of the most representative signals for **23**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60−7.20 (m, 30 H, 6Ph), 5.53 (s, 1 H, CHPh), 5.00−4.56 (m, 10 H, AB), 4.65 (d, J = 3.8 Hz, 1 H, H$^{1'}$), 4.17 (dd, J = 10.1, 4.9 Hz, 1 H H$^{6a'}$), 4.12 (m, 1 H, H$^{5'}$), 3.43 (dd, J = 9.9, 3.8 Hz, 1 H, H$^{2'}$) ppm.

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