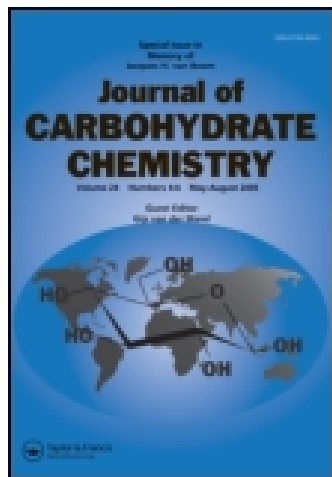




Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcar20>

Inositolphosphoglycan Mediators: An Effective Synthesis of the Conserved Linear GPI Anchor Structure

Javier López-Prados^a & Manuel Martín-Lomas^a

^a Grupo de Carbohidratos, Instituto de Investigaciones Químicas, CSIC, Américo Vespucio, s/n, Sevilla, Spain

Published online: 16 Aug 2006.

To cite this article: Javier López-Prados & Manuel Martín-Lomas (2005) Inositolphosphoglycan Mediators: An Effective Synthesis of the Conserved Linear GPI Anchor Structure, Journal of Carbohydrate Chemistry, 24:4-6, 393-414

To link to this article: <http://dx.doi.org/10.1081/CAR-200066956>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Inositolphosphoglycan Mediators: An Effective Synthesis of the Conserved Linear GPI Anchor Structure

Javier López-Prados and Manuel Martín-Lomas

Grupo de Carbohidratos, Instituto de Investigaciones Químicas, CSIC, Américo Vespucio, s/n, Sevilla, Spain

An effective new preparative synthesis of the conserved linear pseudopentasaccharide structure of the GPI anchors and of the full GPI structure has been carried out that has permitted obtaining both molecules in sufficient quantities as to perform further structural and biologic studies. The synthesis involves a 3 + 2 block synthesis strategy in which a conveniently protected Man $\alpha(1 \rightarrow 4)$ GlcN₃ $\alpha(1 \rightarrow 6)$ *myo*-Ins building block, previously used in the synthesis of inositolphosphoglycan (IPG) mediators, is glycosylated with a protected Man $\alpha(1 \rightarrow 2)$ Man trichloroacetimidate.

Keywords Inositolphosphoglycan mediators, Glycosylphosphatidyl inositol, Oligosaccharides synthesis

INTRODUCTION

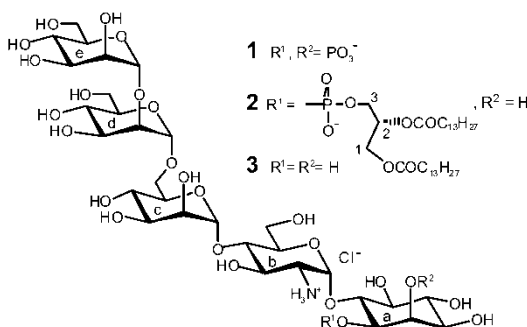
Inositolphosphoglycans (IPGs) are partially characterized intracellular mediators generated by enzymatic cleavage of glycosylphosphatidylinositols (GPIs).^[1,2] As a part of an ongoing program we have reported on the synthesis, the three-dimensional structure, and the biologic activity of *myo*-inositol

Received January 27, 2005; accepted March 4, 2005.

Dedicated to the memory of Professor Jacques H. van Boom.

Address correspondence to Manuel Martín-Lomas, Grupo de Carbohidratos, Instituto de Investigaciones Químicas, CSIC, Américo Vespucio, s/n, Isla de La Cartuja, 41092 Sevilla, Spain. E-mail: mauel.martin-lomas@iiq.csic.es

containing pseudooligosaccharides bearing some of the structural motifs that have been postulated for natural IPGs.^[3–6]

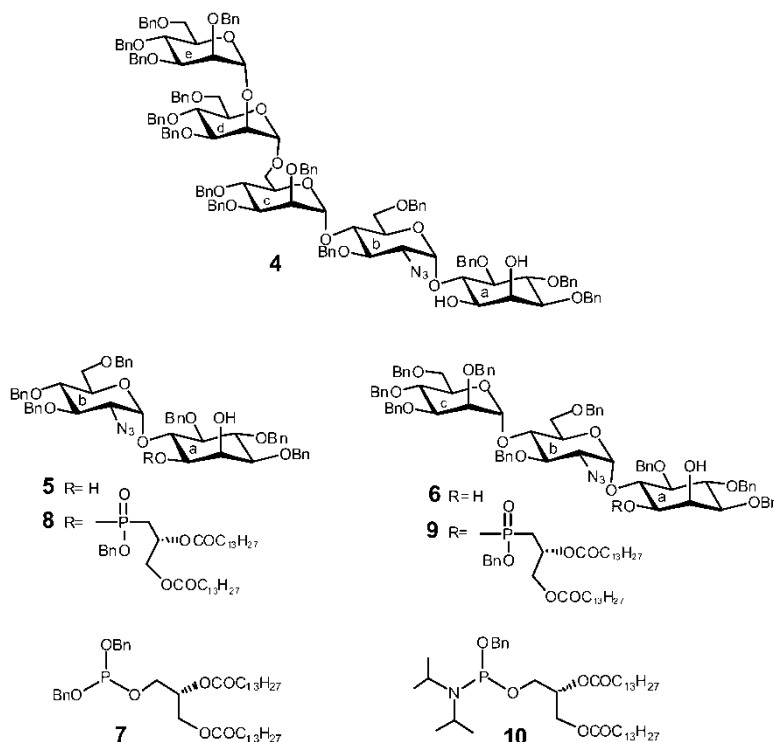


These studies have included the synthesis of pseudopentasaccharide **1** as the product to be expected from a GPI-specific phospholipase C (GPI-PLC)-mediated cleavage of a GPI anchor (**2**).^[4] A further step in this investigation required the synthesis of pseudopentasaccharide **3**—the structure to be expected from a GPI-specific phospholipase D (GPI-PLD)-mediated cleavage of **2**—and the synthesis of **2**—the basic GPI anchor structure—as a model substrate to investigate the structural requirements involved in the regulation of GPI enzymatic cleavage. Because of their biochemical importance and as a result of the challenges involved in their total synthesis, GPIs have received a great deal of attention and have been chosen as a target to test methods and strategies in complex oligosaccharide synthesis.^[7] As a further contribution, we describe herein an effective synthesis of **2** and **3** using the chemistry and the intermediates developed in our laboratory in the course of this program.

RESULTS AND DISCUSSION

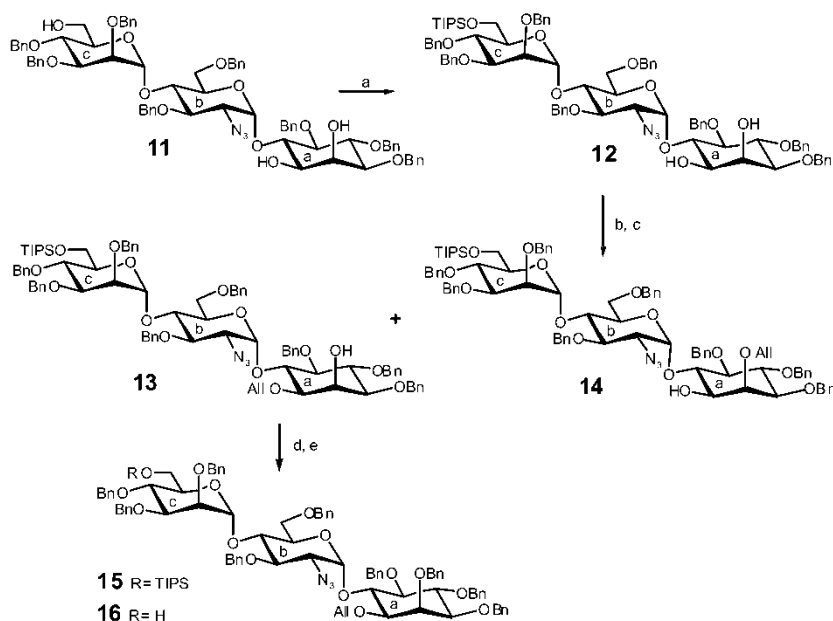
The synthesis of **2** was first envisaged from **4**, an advanced intermediate in the synthesis of **1**,^[4] by regioselective phosphorylation using the phosphite-phosphonium salt methodology.^[8] We have previously shown^[3] that the equatorially oriented OH-1 in diols **5** and **6** regioselectively reacts with 1,2-dimiristoyl-*sn*-glycero-3-yl dibenzyl phosphite (**7**)^[3,9] leading to the phospholipids **8** and **9** in 54% and 28% yield, respectively. The drastic effect of the additional α -D-mannopyranosyl unit in **6** on the yield of this regioselective reaction could be taken as an indication that the size of the glycan chain at C-6 of the *myo*-inositol unit may play a role in this regioselective phosphorylation. Indeed, pseudopentasaccharide **4** did not react with phosphite **7** even when using a large excess of **7** in a wide range of temperatures. It may be expected that the use of a more reactive phosphorylating agent would result

in a mixture of products since no regioselectivity had been observed^[10] in the reaction of phosphoramidite **10**^[11] with diol **5**. It was therefore decided to abandon this straightforward but rather costly route to **2** from **4** and to develop a new synthetic strategy using some less elaborated intermediates also prepared in our laboratory in the course of these studies.



Therefore, pseudotrisaccharide **16**, with a convenient protecting group pattern to construct the desired GPI structure, was chosen as its preparation from **11**, an intermediate in the synthesis of IPG- like molecules designed as inhibitors of c-AMP dependent protein kinase (PKA),^[6] seemed to be readily feasible (Sch. 1). But also in this case the key step involved a regioselective reaction on the *myo*-inositol 1,2 axial-equatorial diol system in which the more reactive equatorially oriented hydroxyl group at position 1 may be sterically hindered by the presence of the bulky disaccharide unit at position 6. The free primary hydroxyl group in **11** was regioselectively silylated to give **12** in almost quantitative yield. As could be expected, the dibutyltin mediated regioselective allylation of **12** gave the desired 1-*O*-allyl derivative **13** in 66% yield accompanied by the 2-*O*-allyl derivative **14** that could be isolated in 24% yield.

The ratio **13**:**14** could not be significantly improved by changing the reaction conditions. The influence of glycosylation at position 6 of *myo*-inositol

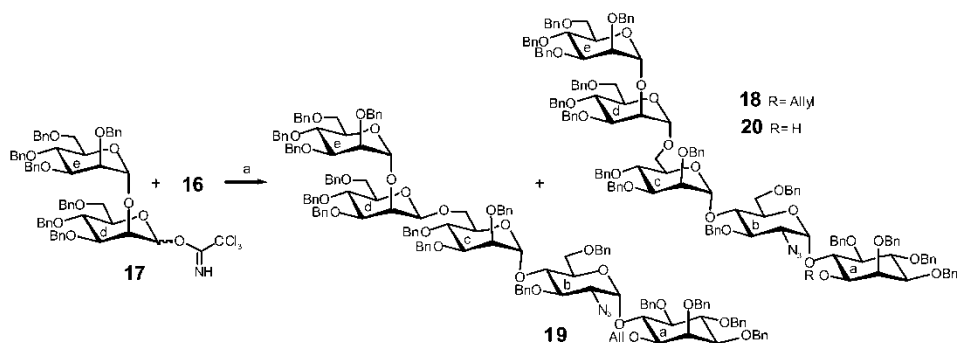


Scheme 1: Reagents and conditions: a) TIPSCl, imidazol, DMAP, DMF rt 10 hr, 95%; b) Bn_2SnO , toluene, 140°C , 12 hr; c) All Br, TBAI, 90°C , 2 hr; d) NaH, BnBr, DMF rt 2 hr, 96%; e) TBAF, THF, rt, 2 hr, 92%.

on the regioselectivity of this reaction is clearly evident when this result is compared with that obtained by van Boom et al.^[12] in the dibutyltin-mediated regioselective allylation of the 1,2-diol system of 3,4,5,6-tetra-*O*-benzyl-D-*myo*-inositol under similar experimental conditions. Conventional benzylation of **13** gave **15**, the silyl group of which was then removed to give the desired pseudotrisaccharide **16** in excellent yield.

The glycosylation of **16** to complete the pseudopentasaccharide skeleton in **2** was performed with trichloroacetimidate **17** to afford the desired compound **18** in 80% yield accompanied by a small amount (11%) of the β -anomer **19**. The allyl group in **18** was removed^[13] to give **20** (Sch. 2). From **20**, both the IPG-like structure **3** and the GPI **2** were prepared. Removal of the benzyl groups in **20** afforded **3** in quantitative yield (Sch. 3). Compound **3** has been previously synthesized by Fraser-Reid and coworkers following a different procedure.^[14] For the synthesis of **2**, compound **20** was phosphorylated using phosphoramidite **10**^[11] to give the fully protected phospholipid **21** as a pair of diastereomers in 86% yield (Sch. 3).

Since **21** is a considerably elaborated intermediate and a reasonable amount of **2** was needed for the enzymatic studies, the final hydrogenation step was carefully optimized. The best results were found using 10% Pd/C and performing the hydrogenation in a 2:1:1:1 AcOEt:THF:EtOH:H₂O



Scheme 2: a) TMSOTf, Et₂O, -15°C, 1 hr; b) Ir.H₂, THF, rt, 30 min; c) NBS, H₂O, rt, 10 min, 98%.

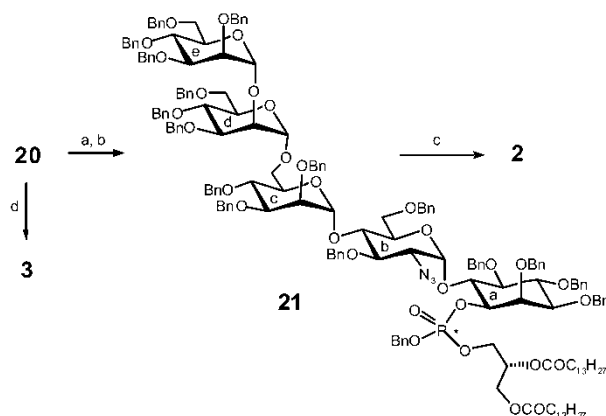
mixture^[3] rather than in the usual 3 : 3 : 1 CHCl₃ : MeOH : H₂O mixture, which has been used so far in the synthesis of GPI anchors.^[7]

In summary, an effective new preparative synthesis of the conserved linear pseudopentasaccharide structure of the GPI anchors (**3**) and of the full GPI structure (**2**) has been carried out that has permitted obtaining both molecules in sufficient quantities as to perform further structural and biological studies.

EXPERIMENTAL

General Procedures

Thin layer chromatography (TLC) analyses were performed on silica gel 60 F₂₅₄ precoated on aluminium plates (Merck), and the compounds were detected by staining with cerium (IV) sulphate (13 g), phosphomolybdic acid (10 g), and



Scheme 3: Reagents and conditions: a) 10, tetrazol, nt, 30 min; b) MCPBA, -40°C, 10 min, 86%; c) H₂ Pd/c, AcOEt/THF/EtOH/H₂O, rt 3 hr, 92%; d) H₂, Pd/c, MeOH/H₂O, rt, 12 hr, 100%.

sulphuric acid (60 mL) solution in water (1 L). Pseudopentasaccharide **3** was visualized with sulphuric acid/ethanol solution (1:9) followed by heating at over 100°C. Phospholipid **2** was visualized with H₂SO₄/MoO₃ Dittmer stainer^[15] at rt. Column liquid chromatography was carried out on silica gel 60 (0.2–0.063 mm or 0.040–0.015 mm; Merck). Gel filtration chromatography was performed on Sephadex G-25 Pharmacia H₂O/MeOH 9/1 for **2** and Sephadex LH-20 Pharmacia in MeOH 100% for **1**. Ion-exchange chromatography was performed on Amberlite IRA-402 Cl[−]. Optical rotations were determined with a Perkin-Elmer 341 polarimeter. ¹H and ¹³C NMR spectra were acquired on a Bruker DRX-500 spectrometer and chemical shifts are given in ppm (δ) relative to tetramethylsilane as an internal reference or relative to D₂O. Elemental analyses were performed with a Leco CHNS-932 apparatus after drying analytical samples under vacuum over phosphorous pentoxide for 24 hr. High-(HRMS) and low-resolution fast atom bombardment mass spectra (F AB-MS) were carried out by the Mass Spectrometry Service, University of Seville, with a Kratos MS-80 RFA spectrometer. MALDI-TOF mass spectra were recorded with a MALDI-TOF GSG System spectrometer.

2,3,4-Tri-*O*-benzyl-6-*O*-triisopropylsilyl-α-D-mannopyranosyl-(1→4)-2-azido-3,di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol (12**).** TIPSCl (245 μL, 1.145 mmol) was added under argon to a stirred solution of **11**^[6] (478 mg, 0.382 mmol), imidazol (156 mg, 2.92 mmol), and DMAP (5 mg, 0.041 mmol) in DMF (7.6 mL); stirring was continued at rt for 10 hr. The reaction mixture was then diluted with AcOEt (50 mL) and washed with a saturated NaHCO₃ solution (50 mL), and the aqueous phase was extracted with AcOEt (2 × 25 mL). The combined organic phases were washed with saturated NaCl solution (3 × 100 mL), dried over MgSO₄, and evaporated to dryness. The residue was purified by column chromatography (hexane/AcOEt 9/1, 4/1, 2/1) to yield **12** (510 mg, 95%) as a white foam. [α]_D 32.7 (*c* = 1.0, CHCl₃). ¹H-RMN (CDCl₃): δ 7.36–7.19 (m, 37H, *ArH*), 7.18–7.13 (m, 3H, *ArH*), 5.43 (d, *J* = 3.5 Hz, 1H, H_{1b}), 5.22 (d, *J* = 1.5 Hz, 1H, H_{1c}), 4.93 (d, *J* = 11.0 Hz, 1H, CH_{benzyl}), 4.89 (d, *J* = 10.5 Hz, 1H, CH_{benzyl}), 4.88 (d, *J* = 10.5 Hz, 1H, CH_{benzyl}), 4.84 (d, *J* = 11.0 Hz, 1H, CH_{benzyl}), 4.737 (d, *J* = 10.5 Hz, 2H, 2 × CH_{benzyl}), 4.735 (d, *J* = 11.5 Hz, 1H, CH_{benzyl}), 4.71 (d, *J* = 11.5 Hz, 1H, CH_{benzyl}), 4.673 (d, *J* = 11.0 Hz, 1H, CH_{benzyl}), 4.668 (d, *J* = 11.5 Hz, 1H, CH_{benzyl}), 4.53 (d, *J* = 11.5 Hz, 1H, CH_{benzyl}), 4.45 (d, *J* = 12.0 Hz, 1H, CH_{benzyl}), 4.38 (d, *J* = 12.0 Hz, 1H, CH_{benzyl}), 4.32 (d, *J* = 11.5 Hz, 1H, CH_{benzyl}), 4.25 (d, *J* = 12.5 Hz, 1H, CH_{benzyl}), 4.24 (d, *J* = 11.5 Hz, 1H, CH_{benzyl}), 4.17 (t, *J* = 2.5 Hz, 1H, H_{2a}), 4.13 (t, *J* = 9.5 Hz, 1H, H_{4c}), 3.980 (t, *J* = 9.5 Hz, 1H, H_{6a}), 3.975 (t, *J* = 9.5 Hz, 1H, H_{4a}), 3.91 (m, 1H, H_{5b}), 3.89 (dd, *J*₁ = 3.5 Hz, *J*₂ = 11.0 Hz, 1H, H_{6c}), 3.87 (t, *J* = 9.5 Hz, 1H, H_{4b}), 3.820 (dd, *J*₁ = 3.0 Hz, *J*₂ = 9.5 Hz, 1H, H_{3c}), 3.819 (t, *J* = 9.5 Hz, 1H, H_{3b}), 3.72 (t, *J* = 2.5 Hz, 1H, H_{2c}), 3.71 (dd, *J*₁ = 1.0 Hz, *J*₂ = 11.0 Hz, 1H, H_{6c}), 3.63

(m, 1H, H_{1a}), 3.62 (broad s, 1H, OH_{eq}), 3.53 (dd, $J_1 = 3.0$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6b}), 3.52 (m, 1H, H_{5c}), 3.50 (dd, $J_1 = 4.0$ Hz, $J_2 = 10.0$ Hz, 1H, H_{2b}), 3.48 (dd, $J_1 = 2.5$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3a}), 3.39 (t, $J = 9.5$ Hz, 1H, H_{5a}), 3.31 (dd, $J_1 = 1.0$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6b'}), 2.51 (broad s, 1H, OH_{ax}), 1.05–0.95 (m, 21H, $3 \times (\text{CH}_3)_2\text{CH TIPS} + 3 \times (\text{CH}_3)_2\text{CH TIPS}$). ¹³C-RMN (CDCl₃): δ 139.05, 138.63, 138.57 (ArC), 138.43 ($2 \times$ ArC), 138.29, 137.69, 137.54 (ArC), 128.54, 128.47, 128.35, 128.33, 128.24, 128.13, 127.97, 127.91, 127.83, 127.73, 127.60, 127.48, 127.42, 127.38, 127.28, 127.17, 127.12, 127.08, 126.95 (ArCH), 100.27 (C_{1c}), 98.52 (C_{1b}), 81.58 (C_{4a}), 81.02 (C_{5a}), 80.61 (C_{6a}), 80.57 (C_{3b}), 79.74 (C_{3a} + C_{3c}), 76.66 (C_{4b}), 75.99 (C_{2c}), 75.85, 75.00, 74.89, 74.39 (CH_{2benzyl}), 74.15 (C_{4c} + C_{5c}), 73.04, 72.71 (CH_{2benzyl}), 72.66 (C_{1a}), 72.08, 72.02 (CH_{2benzyl}), 71.14 (C_{5b}), 69.46 (C_{2a}), 68.56 (C_{6b}), 64.43 (C_{2b}), 62.54 (C_{6c}), 17.99, 17.93 ((CH₃)₂CH TIPS), 11.97 ((CH₃)₂CH TIPS). FAB⁺ calcd. for C₈₃H₉₉O₁₅N₃Si: M⁺ = 1405.69, [M + Na]⁺ = 1428.68. Found: m/z 1428 [M + Na]⁺. Anal. calcd. for C₈₃H₉₉O₁₅N₃Si: C, 70.86; H, 7.09; N, 2.77; found: C, 70.76; H, 7.28; N, 2.77.

2,3,4-tri-*O*-benzyl-6-*O*-triisopropylsilyl- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-3,4,6-tri-*O*-benzyl-D-*myo*-inositol (13) and 2,3,4-tri-*O*-benzyl-6-*O*-triisopropyl- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-2-*O*-allyl-3,4,6-tri-*O*-benzyl-D-*myo*-inositol (14). Dibutyltin oxide (100 mg, 0.402 mmol) was added to a solution of **12** (470 mg, 0.334 mmol) in dry toluene (16.7 mL), and the mixture was gently heated under reflux in a dean-stark apparatus for 12 hr. The reaction mixture was then evaporated to dryness and the residue was solved in allyl bromide (3.2 mL). TBAI (148 mg, 0.401 mmol) was added and the mixture was gently refluxed for 2 hr under argon. The mixture was then evaporated and the residue was coevaporated with AcOEt (2×5 mL). The residue was fractionated by column chromatography (hexane/AcOEt 9/1, 8/1, 7/1, 6/1, 5/1) to give **13** (319 mg, 66%) and **14** (116 mg, 24%) as white foams.

Data for 13: $[\alpha]_D + 41.5$ ($c = 0.7$, CHCl₃). ¹H-RMN (CDCl₃): δ 7.38–7.16 (m, 37H, ArH), 7.13 (m, 2H, ArH), 7.07 (m, 1H, ArH), 5.96 (ddt, $J_1 = 6.0$ Hz, $J_2 = 10.5$ Hz, $J_3 = 17.0$ Hz, 1H, H₂), 5.70 (d, $J = 3.5$ Hz, 1H, H_{1b}), 5.29 (broad dd, $J_1 = 1.5$ Hz, $J_2 = 17.0$ Hz, 1H, H₃), 5.21 (d, $J = 2.0$ Hz, 1H, H_{1c}), 5.20 (broad dd, $J_1 = 1.0$ Hz, $J_2 = 10.0$ Hz, 1H, H_{3'}), 4.92 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.896 (d, $J = 12.5$ Hz, 1H, CH_{benzyl}), 4.895 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.89 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.76 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.75 (d, $J = 12.5$ Hz, 1H, CH_{benzyl}), 4.73 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.72 (d, $J = 12.5$ Hz, 1H, CH_{benzyl}), 4.69 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.61 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.55 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.45 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.40 (d, $J = 12.0$ Hz, 1H,

$CH_{\text{benzyl.}}$), 4.35 (d, $J = 12.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.31 (d, $J = 12.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.22 (broad t, $J = 2.5$ Hz, 1H, H_{2a}), 4.18 (t, $J = 9.5$ Hz, 1H, H_{6a}), 4.17 (d, $J = 12.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.16 (t, $J = 9.5$ Hz, 1H, H_{4c}), 4.15 (m, 1H, H_1), 4.07 (broad dd, $J_1 = 6.0$ Hz, $J_2 = 12.5$ Hz, 1H, $H_{1'}$), 4.05 (broad d, $J = 9.5$ Hz, 1H, H_{5b}), 4.01 (t, $J = 9.5$ Hz, 1H, H_{4a}), 3.87 (dd, $J_1 = 3.0$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6c}), 3.84 (m, 2H, $H_{3b} + H_{4b}$), 3.76 (dd, $J_1 = 2.5$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3c}), 3.66 (t, $J = 2.5$ Hz, 1H, H_{2c}), 3.65 (broad dd, $J_1 = 1.0$ Hz, $J_2 = 11.5$ Hz, 1H, $H_{6c'}$), 3.43 (m, 3H, $H_{6b} + H_{1a} + H_{3a}$), 3.41 (t, $J = 9.5$ Hz, 1H, H_{5a}), 3.39 (broad d, $J = 10.0$ Hz, 1H, H_{5c}), 3.36 (dd, $J_1 = 3.5$ Hz, $J_2 = 11.5$ Hz, 1H, $H_{6b'}$), 3.28 (dd, $J_1 = 3.5$ Hz, $J_2 = 10.0$ Hz, 1H, H_{2b}), 2.39 (s, 1H, $OH_{\text{ax.}}$), 1.03–0.95 (m, 21H, $3 \times (CH_3)_2CH\ TIPS + 3 \times (CH_3)_2CH\ TIPS$). ^{13}C -RMN ($CDCl_3$): δ 139.34, 138.78, 138.74 (ArC), 138.47 ($2 \times$ ArC), 138.17 (ArC), 137.82 ($2 \times$ ArC), 133.98 (C_2), 128.50, 128.47, 128.45, 128.30, 128.23, 128.19, 128.12, 127.94, 127.89, 127.71, 127.67, 127.59, 127.56, 127.42, 127.37, 127.32, 127.20, 127.11, 127.02, 126.94 (ArCH), 117.87 (C_3), 100.36 (C_{1c}), 97.34 (C_{1b}), 81.35 (C_{4a}), 81.13 (C_{1a}), 80.88 (C_{5a}), 79.87 (C_{3b}), 79.65 (C_{3a}), 79.59 (C_{3c}), 76.40 (C_{2c}), 76.38 (C_{4b}), 75.90, 75.44, 74.74 ($CH_2\text{ benzyl.}$), 74.66 (C_{6a}), 74.08 (C_{4c}), 73.90 (C_{5c}), 73.58, 73.03, 72.77, 72.14, 71.94 ($CH_2\text{ benzyl.}$), 70.88 (C_1), 70.01 (C_{5b}), 68.53 (C_{6b}), 66.38 (C_{2a}), 63.10 (C_{2b}), 62.39 (C_{6c}), 18.00, 17.94 ($(CH_3)_2CH\ TIPS$), 11.98 ($(CH_3)_2CH\ TIPS$). FAB⁺ calcd. for $C_{86}H_{103}O_{15}N_3Si$: $M^+ = 1445.71$; Found: 1468, $[M + Na]$. Anal. calcd. for $C_{86}H_{103}O_{15}N_3Si \cdot H_2O$: C, 70.51; H, 7.23; N, 2.87. Found: C, 70.43; H, 7.18; N, 2.75.

Data for 14: $[\alpha]_D + 34.1$ ($c = 0.6$ $CHCl_3$). 1H -RMN ($CDCl_3$): δ 7.35–7.18 (m, 37H, ArH), 7.16–7.10 (m, 3H, ArH), 5.94 (ddt, $J_1 = 6.0$ Hz, $J_2 = 10.5$ Hz, $J_3 = 17.0$ Hz, 1H, H_2), 5.55 (d, $J = 4.0$ Hz, 1H, H_{1b}), 5.29 (dq, $J_1 = 1.5$ Hz, $J_2 = 17.5$ Hz, 1H, H_3), 5.22 (d, $J = 2.0$ Hz, 1H, H_{1c}), 5.18 (broad dd, $J_1 = 1.5$ Hz, $J_2 = 10.0$ Hz, 1H, $H_{3'}$), 4.95 (d, $J = 11.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.90 (d, $J = 10.5$ Hz, 2H, $2 \times CH_{\text{benzyl.}}$), 4.86 (d, $J = 11.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.78 (d, $J = 10.5$ Hz, 2H, $2 \times CH_{\text{benzyl.}}$), 4.70 (s, 2H, $CH_2\text{ benzyl.}$), 4.68 (d, $J = 11.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.65 (d, $J = 11.5$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.54 (d, $J = 12.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.46 (ddt, $J_1 = 1.5$ Hz, $J_2 = 5.5$ Hz, $J_3 = 13.0$ Hz, 1H, H_1), 4.44 (d, $J = 11.5$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.35 (d, $J = 12.5$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.34 (d, $J = 11.5$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.28 (d, $J = 11.5$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.222 (d, $J = 12.5$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.215 (ddt, $J_1 = 1.0$ Hz, $J_2 = 6.0$ Hz, $J_3 = 13.0$ Hz, 1H, $H_{1'}$), 4.15 (t, $J = 9.5$ Hz, 1H, H_{4c}), 4.01 (t, $J = 9.5$ Hz, 1H, H_{4a}), 3.96 (t, $J = 9.5$ Hz, 1H, H_{6a}), 3.94 (broad d, $J = 9.0$ Hz, 1H, H_{5b}), 3.91 (t, $J = 2.5$ Hz, 1H, H_{2a}), 3.89 (dd, $J_1 = 3.5$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6c}), 3.86 (t, $J = 9.0$ Hz, 1H, H_{4b}), 3.82 (t, $J = 10.0$ Hz, 1H, H_{3b}), 3.81 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3c}), 3.70 (t, $J = 3.0$ Hz, 1H, H_{2c}), 3.69 (dd, $J_1 = 1.0$ Hz, $J_2 = 11.0$ Hz, 1H, $H_{6c'}$), 3.61 (ddd, $J_1 = 3.0$ Hz, $J_2 = 7.0$ Hz, $J_3 = 10.0$ Hz, 1H, H_{1a}), 3.49 (m, 1H, H_{5c}), 3.48 (dd, $J_1 = 3.5$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6b}), 3.45 (dd, $J_1 = 4.0$ Hz, $J_2 = 10.0$ Hz, 1H, H_{2b}), 3.44 (dd, $J_1 = 2.0$ Hz,

$J_2 = 9.5$ Hz, 1H, H_{3a}), 3.39 (t, $J = 9.5$ Hz, 1H, H_{5a}), 3.33 (dd, $J_1 = 1.5$ Hz, $J_2 = 11.0$ Hz, 1H, $H_{6b'}$), 3.13 (d, $J = 7.0$ Hz, 1H, $OH_{eq.}$), 1.07–0.93 (m, 21H, $3 \times (CH_3)_2CH$ TIPS + $3 \times (CH_3)_2CH$ TIPS). ^{13}C -RMN ($CDCl_3$): δ 139.16, 138.67, 138.63, 138.52, 138.47, 138.33, 138.03, 137.67 (ArC), 135.11 (C2), 128.46, 128.41, 128.30, 128.24, 128.13, 127.95, 127.93, 127.79, 127.72, 127.69, 127.53, 127.43, 127.41, 127.40, 127.38, 127.26, 127.18, 127.08, 127.04, 127.93 (ArCH), 117.15 (C₃), 100.34 (C_{1c}), 97.85 (C_{1b}), 81.78 (C_{4a}), 81.26 (C_{5a}), 80.83 (C_{3a}), 80.41 (C_{3b}), 79.97 (C_{6a}), 79.73 (C_{3c}), 76.92 (C_{2a}), 76.68 (C_{4b}), 76.12 (C_{2c}), 75.77, 75.11, 74.85, 74.22 ($CH_{2benzyl.}$), 74.12 (C_{5c}), 74.10 (C_{4c}), 73.86 (C₁), 73.25 (C_{1a}), 73.01, 72.96, 72.06, 72.05 ($CH_{2benzyl.}$), 70.71 (C_{5b}), 68.56 (C_{6b}), 64.07 (C_{2b}), 62.50 (C_{6c}), 18.00, 17.94 ($((CH_3)_2CH$ TIPS), 11.98 ($((CH_3)_2CH$ TIPS). FAB⁺ calcd. for $C_{86}H_{103}O_{15}N_3Si$: $M^+ = 1445.71$, $[M + Na]^+ = 1468.70$. Found: m/z 1468 $[M + Na]^+$.

2,3,4-Tri-*O*-benzyl-6-*O*-triisopropylsilyl- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (15). A solution of **13** (280 mg, 0.194 mmol) in dry DMF (3.9 mL) cooled to 0°C was treated under argon with NaH (24 mg of a 60% suspension in mineral oil, 0.600 mmol). Benzyl bromide (70 μ L, 0.589 mmol) was added and the mixture was stirred for 2 hr at rt. After cooling in an ice bath, 30% NH_3 (0.1 mL) was added and the solution was stirred for 10 min. The reaction mixture was then diluted with AcOEt (50 mL) and washed with 10% HCl (25 mL). The aqueous phase was extracted with AcOEt (2 $\times$ 25) and the combined organic phases were washed with saturated NaCl solution (3 $\times$ 100 mL), dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography (hexane/AcOEt 19/1, 14/1, 9/1) to give **15** (286 mg, 96%) as a white foam. $[\alpha]_D + 46.5$ ($c = 0.8$, $CHCl_3$). 1H -RMN ($CDCl_3$): δ 7.41 (m, 2H, ArH), 7.36–7.11 (m, 42H, ArH), 7.07 (m, 1H, ArH), 5.92 (ddt, $J_1 = 5.5$ Hz, $J_2 = 10.5$ Hz, $J_3 = 17.5$ Hz, 1H, H_2), 5.76 (d, $J = 3.5$ Hz, 1H, H_{1b}), 5.27 (broad dd, $J_1 = 1.5$ Hz, $J_2 = 17.0$ Hz, 1H, H_3), 5.21 (d, $J = 2.0$ Hz, 1H, H_{1c}), 5.17 (broad dd, $J_1 = 1.0$ Hz, $J_2 = 10.5$ Hz, 1H, H_3), 4.97 (d, $J = 11.5$ Hz, 1H, $CH_{benzyl.}$), 4.92 (d, $J = 10.5$ Hz, 1H, $CH_{benzyl.}$), 4.90 (broad d, $J = 11.0$ Hz, 2H, $2 \times CH_{benzyl.}$), 4.83 (s, 2H, $CH_{2benzyl.}$), 4.73 (d, $J = 11.5$ Hz, 1H, $CH_{benzyl.}$), 4.72 (d, $J = 10.5$ Hz, 1H, $CH_{benzyl.}$), 4.70 (d, $J = 11.0$ Hz, 1H, $CH_{benzyl.}$), 4.66 (d, $J = 12.0$ Hz, 1H, $CH_{benzyl.}$), 4.614 (d, $J = 11.0$ Hz, 1H, $CH_{benzyl.}$), 4.612 (d, $J = 11.5$ Hz, 1H, $CH_{benzyl.}$), 4.57 (d, $J = 12.0$ Hz, 1H, $CH_{benzyl.}$), 4.47 (d, $J = 12.0$ Hz, 1H, $CH_{benzyl.}$), 4.37 (d, $J = 11.5$ Hz, 1H, $CH_{benzyl.}$), 4.34 (d, $J = 11.5$ Hz, 1H, $CH_{benzyl.}$), 4.31 (d, $J = 12.0$ Hz, 1H, $CH_{benzyl.}$), 4.27 (t, $J = 9.5$ Hz, 1H, H_{6a}), 4.18 (t, $J = 10.0$ Hz, 1H, H_{4c}), 4.16 (d, $J = 12.5$ Hz, 1H, $CH_{benzyl.}$), 4.11 (t, $J = 9.5$ Hz, 1H, H_{4a}), 4.024 (t broad, $J = 2.0$ Hz, 1H, H_{2a}), 4.018 (broad d, $J = 10.0$ Hz, 1H, H_{5b}), 4.01 (m, 1H, H_1), 3.97 (broad dd, $J_1 = 5.5$ Hz, $J_2 = 12.0$ Hz, 1H, $H_{1'}$), 3.87 (dd, $J_1 = 2.5$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6c}), 3.85

(t, $J = 9.0$ Hz, 1H, H_{4b}), 3.83 (t, $J = 9.0$ Hz, 1H, H_{3b}), 3.78 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3c}), 3.67 (t, $J = 2.5$ Hz, 1H, H_{2c}), 3.63 (broad dd, $J_1 = 1.0$ Hz, $J_2 = 11.5$ Hz, 1H, H_{6c'}), 3.43 (t, $J = 9.5$ Hz, 1H, H_{5a}), 3.39 (m, 2H, H_{3a} + H_{6b}), 3.37 (m, 2H, H_{5c} + H_{1a}), 3.31 (dd, $J_1 = 3.0$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6b'}), 3.26 (dd, $J_1 = 4.0$ Hz, $J_2 = 10.0$ Hz, 1H, H_{2b}), 1.02–0.93 (m, 21H, $3 \times (\text{CH}_3)_2\text{CH TIPS} + 3 \times (\text{CH}_3)_2\text{CH TIPS}$). ¹³C-RMN (CDCl₃): δ 139.37 (ArC), 138.76 ($2 \times$ ArC), 138.54, 138.43, 138.33, 138.23, 137.86 (ArC), 134.20 (C₂), 128.44, 128.40, 128.26, 128.23, 128.21, 128.18, 128.08, 128.00, 127.86, 127.69, 127.63, 127.50, 127.46, 127.42, 127.39, 127.31, 127.16, 127.02, 126.99, 126.97, 126.91 (ArCH), 117.01 (C₃), 100.38 (C_{1c}), 97.55 (C_{1b}), 81.90 (C_{1a}), 81.87 (C_{4a}), 81.38 (C_{5a}), 80.85 (C_{3a}), 79.93 (C_{3b}), 79.57 (C_{3c}), 76.52 (C_{4b}), 76.41 (C_{2c}), 75.78 (CH₂benzyl.), 75.36 (C_{6a}), 75.24, 74.74 (CH₂benzyl.), 74.03 (CH₂benzyl. - C_{4c}), 73.88 (C_{5c}), 73.63, 73.02, 72.80 (CH₂benzyl.), 72.72 (C_{2a}), 72.13, 71.92 (CH₂benzyl.), 70.76 (C₁), 69.86 (C_{5b}), 68.47 (C_{6b}), 63.17 (C_{2b}), 62.37 (C_{6c}), 17.99, 17.93 ((CH₃)₂CH TIPS), 11.96 ((CH₃)₂CH TIPS). FAB⁺ calcd. for C₉₃H₁₀₉O₁₅N₃Si: M⁺ = 1535.77; [M + Na]⁺ = 1558.76. Found: m/z 1559 [M + Na]⁺. Anal. calcd. for C₉₃H₁₀₉O₁₅N₃Si: C, 72.68; H, 7.15; N, 2.73. Found: C, 72.75; H, 7.48; N, 2.33.

2,3,4-Tri-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-myo-inositol (16). TBAF (1.0 M in THF, 468 μ L) was added to a solution of **15** (240 mg, 0.156 mmol) in dry THF (3.1 mL) under argon, and the mixture was stirred for 2 hr at rt. The reaction mixture was diluted with AcOEt (25 mL) and washed with saturated NaHCO₃ solution (25 mL). The aqueous phase was extracted with AcOEt (2×25 mL) and the combined organic phases were washed with saturated NaCl solution (3×100 mL), dried over MgSO₄, and evaporated to dryness. The residue was purified by column chromatography (hexane/AcOEt 9/1, 4/1, 2/1) to give **16** (198 mg, 92%) as a white foam. $[\alpha]_D + 54.2$ ($c = 1.0$, CHCl₃). ¹H-RMN (CDCl₃): δ 7.42 (m, 2H, ArH), 7.38–7.16 (m, 40H, ArH), 7.13–7.05 (m, 3H, ArH), 5.94 (ddt, $J_1 = 5.5$ Hz, $J_2 = 10.5$ Hz, $J_3 = 17.5$ Hz, 1H, H₂), 5.72 (d, $J = 3.5$ Hz, 1H, H_{1b}), 5.28 (broad dd, $J_1 = 1.5$ Hz, $J_2 = 17.0$ Hz, 1H, H₃), 5.21 (d, $J = 2.0$ Hz, 1H, H_{1c}), 5.19 (broad dd, $J_1 = 1.5$ Hz, $J_2 = 10.5$ Hz, 1H, H_{3'}), 5.02 (d, $J = 11.5$ Hz, 1H, CH_{benzyl.}), 4.94 (broad d, $J = 10.5$ Hz, 2H, $2 \times$ CH_{benzyl.}), 4.88 (d, $J = 11.0$ Hz, 1H, CH_{benzyl.}), 4.85 (s, 2H, CH₂benzyl.), 4.75 (d, $J = 10.5$ Hz, 1H, CH_{benzyl.}), 4.69 (d, $J = 11.5$ Hz, 1H, CH_{benzyl.}), 4.68 (d, $J = 12.0$ Hz, 1H, CH_{benzyl.}), 4.63 (broad d, $J = 12.0$ Hz, 2H, $2 \times$ CH_{benzyl.}), 4.60 (d, $J = 11.5$ Hz, 2H, $2 \times$ CH_{benzyl.}), 4.51 (d, $J = 12.0$ Hz, 1H, CH_{benzyl.}), 4.48 (d, $J = 12.0$ Hz, 1H, CH_{benzyl.}), 4.39 (d, $J = 12.0$ Hz, 1H, CH_{benzyl.}), 4.32 (d, $J = 12.0$ Hz, 1H, CH_{benzyl.}), 4.25 (t, $J = 10.0$ Hz, 1H, H_{6a}), 4.14 (t, $J = 9.5$ Hz, 1H, H_{4a}), 4.09 (d, $J = 12.0$ Hz, 1H, CH_{benzyl.}), 4.04 (t, $J = 2.5$ Hz, 1H, H_{2a}), 4.03 (broad dd, $J_1 = 5.5$ Hz, $J_2 = 12.0$ Hz, 1H, H₁), 3.99 (broad d, $J = 10.0$ Hz, 1H, H_{5b}), 3.98

(broad dd, $J_1 = 6.0$ Hz, $J_2 = 12.5$ Hz, 1H, $H_{1'}$), 3.88 (t, $J = 9.0$ Hz, 1H, H_{4b}), 3.85 (t, $J = 9.5$ Hz, 1H, H_{4c}), 3.83 (t, $J = 9.5$ Hz, 1H, H_{3b}), 3.75 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.0$ Hz, 1H, H_{3c}), 3.64 (t, $J = 2.5$ Hz, 1H, H_{2c}), 3.56 (m, 2H, $H_{6c} + H_{6c'}$), 3.43 (t, $J = 9.5$ Hz, 1H, H_{5a}), 3.40 (m, 1H, H_{3a}), 3.39 (m, 1H, H_{1a}), 3.38 (m, 1H, H_{5c}), 3.31 (dd, $J_1 = 1.5$ Hz, $J_2 = 12.0$ Hz, 1H, H_{6b}), 3.26 (dd, $J_1 = 2.0$ Hz, $J_2 = 12.5$ Hz, 1H, $H_{6b'}$), 3.23 (dd, $J_1 = 3.5$ Hz, $J_2 = 10.0$ Hz, 1H, H_{2b}), 2.17 (broad s, 1H, OH). ^{13}C -RMN (CDCl_3): δ 138.71, 138.65, 138.49 (ArC), 138.45 ($2 \times$ ArC), 138.31, 138.20, 138.16, 138.88 (ArC), 134.17 (C_2), 128.48, 128.44, 128.39, 128.31, 128.26, 128.20, 128.17, 128.06, 128.00, 127.84, 127.76, 127.69, 127.64, 127.62, 127.58, 127.54, 127.52, 127.48, 127.43, 127.32, 127.24, 127.15, 126.90, 126.80 (ArCH), 117.09 (C_3), 100.64 (C_{1c}), 97.57 (C_{1b}), 81.87 (C_{4a}), 81.77 (C_{1a}), 81.35 (C_{5a}), 80.83 (C_{3a}), 80.11 (C_{3b}), 79.00 (C_{3c}), 76.81 (C_{4b}), 76.67 (C_{2c}), 75.80 ($\text{CH}_2\text{benzyl.}$), 75.52 (C_{6a}), 75.23 ($\text{CH}_2\text{benzyl.}$), 74.86 (C_{4c}), 74.71, 74.06, 73.94, 73.56 ($\text{CH}_2\text{benzyl.}$), 73.23 (C_{5c}), 72.81 ($\text{CH}_2\text{benzyl.}$), 72.73 (C_{2a}), 72.37, 72.18 ($\text{CH}_2\text{benzyl.}$), 70.77 (C_1), 70.05 (C_{5b}), 67.94 (C_{6b}), 63.36 (C_{2b}), 62.24 (C_{6c}). FAB $^+$ calcd. for $\text{C}_{84}\text{H}_{89}\text{O}_{15}\text{N}_3$: $M^+ = 1379.63$; $[\text{M} + \text{Na}]^+ = 1402.62$. Found: m/z 1402 $[\text{M} + \text{Na}]^+$. Anal. calcd. for $\text{C}_{84}\text{H}_{89}\text{O}_{15}\text{N}_3 \cdot \text{H}_2\text{O}$: C, 72.14; H, 6.56; N, 3.00. Found: C, 71.92; H, 6.71; N, 2.81.

2,3,4,6-Tetra-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-*O*-benzyl- α , β -D-mannopyranosyl trichloroacetimidate (17). To a solution of the corresponding lactol^[16] (300 mg, 0.308 mmol) in anhydrous CH_2Cl_2 (3.1 mL), trichloroacetonitrile (463 μL , 4.618 mmol) and DBU (0.1 M in CH_2Cl_2 , 154 μL) were added and the solution was stirred at rt for 2 hr. The solution was evaporated to dryness and the residue was redissolved in AcOEt and coevaporated (2×5 mL). The crude product was purified on a short silica gel column (hexane/AcOEt/ Et_3N 4/0.9/0.1) to give **17** (324 mg, 94%) as a mixture of the α and β anomers. *Data for the α anomer*: ^1H -RMN (CDCl_3): δ 8.52 (s, 1H, OCNHCCl_3), 7.36–7.14 (m, 35H, ArH), 6.32 (d, $J = 1.5$ Hz, 1H, H_{1d}), 5.24 (d, $J = 1.5$ Hz, 1H, H_{1e}), 4.85 (d, $J = 10.5$ Hz, 2H, $2 \times \text{CH}_{\text{benzyl.}}$), 4.70 (d, $J = 11.5$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.69 (d, $J = 12.0$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.66 (d, $J = 12.0$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.64 (d, $J = 11.5$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.60 (broad d, $J = 12.5$ Hz, 2H, $2 \times \text{CH}_{\text{benzyl.}}$), 4.56 (d, $J = 12.5$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.51 (d, $J = 12.0$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.504 (d, $J = 12.0$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.497 (d, $J = 11.0$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.49 (d, $J = 11.5$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.46 (d, $J = 12.0$ Hz, 1H, $\text{CH}_{\text{benzyl.}}$), 4.17 (t, $J = 2.0$ Hz, 1H, H_{2d}), 4.01 (t, $J = 9.5$ Hz, 1H, H_{4e}), 3.95 (m, 2H, $H_{3d} + H_{5d}$), 3.945 (m, 1H, H_{5e}), 3.938 (m, 1H, H_{4d}), 3.89 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.0$ Hz, 1H, H_{3e}), 3.84 (t, $J = 3.0$ Hz, 1H, H_{2e}), 3.81 (m, 2H, $H_{6e} + H_{6d}$), 3.75 (dd, $J_1 = 1.5$ Hz, $J_2 = 11.0$ Hz, 1H, $H_{6e'}$), 3.70 (broad d, $J = 10.5$ Hz, 1H, $H_{6d'}$). ^{13}C -RMN (CDCl_3): δ 159.94 (OCNHCCl_3), 138.57, 138.52 (ArC), 138.41 ($2 \times$ ArC), 138.33, 138.15, 137.82 (ArC), 128.48, 128.40, 128.25, 128.22, 128.18, 128.09,

128.01, 127.94, 127.84, 127.80, 127.75, 127.67, 127.47, 127.43, 127.40, 127.37 (ArCH), 99.59 (C_{1e}), 96.83 (C_{1d}), 90.94 (OCNHCCl₃), 79.74 (C_{3e}), 78.97 (C_{3d}), 75.31, 74.92 (CH₂benzyl.), 74.88 (C_{2e}), 74.84 (C_{4e}), 74.78 (C_{4d}), 74.12 (C_{5d}), 73.34, 73.23, 72.72 (CH₂benzyl.), 72.69 (C_{2d}), 72.29 (C_{5e}), 72.26, 72.24 (CH₂benzyl.), 69.02 (C_{6e}), 68.75 (C_{6d}). Coupled ¹³C-RMN (CDCl₃): δ 99.59 (d, *J*_{C-H} = 172.3 Hz, C_{1e}), 96.83 (d, *J*_{C-H} = 178.1 Hz, C_{1d}).

2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl-(1 → 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1 → 6)-1-*O*-allyl-2,3,4, 5-tetra-*O*-benzyl-D-*myo*-inositol (18) and 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl-(1 → 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1 → 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (19). To a solution of **16** (100 mg, 0.072 mmol) and **17** (97 mg, 0.087 mmol) in anhydrous ether (1.5 mL), 4 Å molecular sieves were added and the mixture was cooled to -15°C under argon atmosphere. TMSOTf (0.055 M in Et₂O, 66 μL) was added and the reaction mixture stirred for 1 hr. Then the mixture was neutralized with Et₃N and evaporated to dryness. The residue was purified by column chromatography (hexane/EtOAc 9/1) to give **18** (166 mg, 80%) and **19** (18 mg, 11%) as white foams.

Data for 18: [α]_D + 49.4 (*c* = 1.1, CHCl₃). ¹H-RMN (C₆D₆): δ 7.49–7.42 (m, 8H, ArH), 7.40–7.26 (m, 25H, ArH), 7.24–6.97 (m, 47H, ArH), 5.974 (d, *J* = 3.5 Hz, 1H, H_{1b}), 5.968 (ddt, *J*₁ = 5.5 Hz, *J*₂ = 11.0 Hz, *J*₃ = 17.0 Hz, 1H, H₂), 5.59 (d, *J* = 2.0 Hz, 1H, H_{1c}), 5.45 (d, *J* = 2.0 Hz, 1H, H_{1d}), 5.31 (d, *J* = 2.0 Hz, 1H, H_{1e}), 5.28 (dq, *J*₁ = 2.0 Hz, *J*₂ = 17.5 Hz, 1H, H₃), 5.18 (d, *J* = 11.0 Hz, 1H, CH_{benzyl.}), 5.13 (d, *J* = 11.5 Hz, 1H, CH_{benzyl.}), 5.12 (broad dd, *J*₁ = 1.5 Hz, *J*₂ = 10.5 Hz, 1H, H_{3'}), 5.06 (d, *J* = 11.0 Hz, 1H, CH_{benzyl.}), 4.98 (d, *J* = 11.5 Hz, 1H, CH_{benzyl.}), 4.95 (broad d, *J* = 12.0 Hz, 3H, 3 × CH_{benzyl.}), 4.89 (d, *J* = 12.0 Hz, 1H, CH_{benzyl.}), 4.84 (d, *J* = 12.0 Hz, 1H, CH_{benzyl.}), 4.77 (d, *J* = 11.0 Hz, 1H, CH_{benzyl.}), 4.72 (d, *J* = 11.5 Hz, 1H, CH_{benzyl.}), 4.71 (d, *J* = 11.5 Hz, 1H, CH_{benzyl.}), 4.68 (d, *J* = 12.5 Hz, 1H, CH_{benzyl.}), 4.664 (d, *J* = 12.0 Hz, 1H, CH_{benzyl.}), 4.656 (t, *J* = 9.5 Hz, 1H, H_{6a}), 4.62 (d, *J* = 12.0 Hz, 1H, CH_{benzyl.}), 4.60 (broad s, 2H, CH₂benzyl.), 4.59 (d, *J* = 12.0 Hz, 1H, CH_{benzyl.}), 4.55 (d, *J* = 11.0 Hz, 1H, CH_{benzyl.}), 4.54 (d, *J* = 12.0 Hz, 1H, CH_{benzyl.}), 4.49 (d, *J* = 12.0 Hz, 1H, CH_{benzyl.}), 4.46 (d, *J* = 11.5 Hz, 1H, CH_{benzyl.}), 4.45 (broad s, 2H, CH₂benzyl.), 4.44 (m, 1H, H_{5b}), 4.43 (d, *J* = 12.5 Hz, 1H, CH_{benzyl.}), 4.42 (d, *J* = 11.5 Hz, 2H, 2 × CH_{benzyl.}), 4.41 (d, *J* = 12.5 Hz, 1H, CH_{benzyl.}), 4.38 (d, *J* = 11.5 Hz, 1H, CH_{benzyl.}), 4.37 (d, *J* = 12.0 Hz, 1H, CH_{benzyl.}), 4.36 (t, *J* = 9.5 Hz, 1H, H_{4c}), 4.33 (m, 3H, H_{2d} + 2 × CH_{benzyl.}), 4.32 (t, *J* = 9.5 Hz, 1H, H_{4a}), 4.31 (m, 2H, H_{5e} + H_{4e}), 4.27 (t, *J* = 9.5 Hz, 1H, H_{4d}), 4.22 (dd, *J*₁ = 3.0 Hz, *J*₂ = 9.0 Hz,

1H, H_{3d}), 4.21 (m, 1H, H_{6c}), 4.20 (t, $J = 10.0$ Hz, 1H, H_{3b}), 4.19 (dd, $J_1 = 3.0$ Hz, $J_2 = 8.5$ Hz, 1H, H_{3e}), 4.11 (t, $J = 9.5$ Hz, 1H, H_{4b}), 4.09 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.0$ Hz, 1H, H_{3c}), 4.08 (broad t, $J = 2.5$ Hz, 1H, H_{2e}), 4.06 (broad ddd, $J_1 = 1.0$ Hz, $J_2 = 4.0$ Hz, $J_3 = 9.5$ Hz, 1H, H_{5d}), 3.96 (broad dt, $J_1 = 2.5$ Hz, $J_2 = 9.5$ Hz, 1H, H_{5c}), 3.93 (t, $J = 2.5$ Hz, 1H, H_{2a}), 3.91 (t, $J = 2.5$ Hz, 1H, H_{2c}), 3.90 (m, 1H, H₁), 3.88 (m, 1H, H_{6e}), 3.85 (m, 1H, H_{6d}), 3.84 (m, 1H, H_{1'}), 3.78 (dd, $J_1 = 1.5$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6c'}), 3.76 (broad d, $J = 11.5$ Hz, 1H, H_{6e'}), 3.65 (dd, $J_1 = 1.5$ Hz, $J_2 = 11.5$ Hz, 1H, H_{6d'}), 3.62 (m, 2H, H_{6b} + H_{6b'}), 3.52 (t, $J = 9.5$ Hz, 1H, H_{5a}), 3.33 (dd, $J_1 = 2.0$ Hz, $J_2 = 10.0$ Hz, 1H, H_{1a}), 3.20 (dd, $J_1 = 2.5$ Hz, $J_2 = 10.0$ Hz, 1H, H_{3a}), 3.03 (dd, $J_1 = 3.5$ Hz, $J_2 = 10.0$ Hz, 1H, H_{2b}). ¹³C-RMN (C₆D₆): δ 140.25 (2 $\times$ ArC), 140.22 (ArC), 140.15 (3 $\times$ ArC), 140.07 (2 $\times$ ArC), 139.95 (ArC), 139.88 (2 $\times$ ArC), 139.82, 139.55, 139.52, 139.47, 139.07 (ArC), 135.46 (C₂), 129.56, 129.33, 129.29, 129.28, 129.26, 129.22, 129.15, 129.13, 129.10, 129.06, 129.04, 129.02, 128.96, 128.92, 128.86, 128.82, 128.76, 128.74, 128.72, 128.68, 128.62, 128.53, 128.48, 128.43, 128.20, 128.18, 128.13, 128.09, 128.05, 128.01, 127.98, 127.93 (ArCH), 117.62 (C₃), 101.43 (C_{1c}), 101.21 (C_{1e}), 100.85 (C_{1d}), 98.80 (C_{1b}), 83.10 (C_{1a}), 82.99 (C_{4a}), 82.68 (C_{5a}), 81.96 (C_{3a}), 81.43 (C_{3e}), 81.18 (C_{3c}), 80.84 (C_{3b}), 80.43 (C_{3d}), 77.61 (C_{2e}), 77.49 (C_{4b}), 76.68 (C_{2c}), 76.67, 76.39 (CH₂benzyl.), 76.33 (C_{6a}), 76.26 (C_{2d}), 75.97, 75.95, 75.91 (CH₂benzyl.), 75.84 (C_{4e}), 75.80 (C_{4d}), 75.75 (C_{4c}), 75.07, 74.36, 74.21, 74.04 (CH₂benzyl.), 73.84 (C_{5e}), 73.80 (CH₂benzyl.), 73.77 (C_{2a}), 73.61 (C_{5c}), 73.52 (CH₂benzyl.), 73.44 (C_{5d} + CH₂benzyl.), 73.11, 72.90, 72.73, 72.31 (CH₂benzyl.), 71.61 (C₁), 71.30 (C_{5b}), 70.68 (C_{6e}), 70.34 (C_{6d}), 70.03 (C_{6b}), 68.03 (C_{6c}), 63.61 (C_{2b}). Coupled ¹³C-RMN (C₆D₆): δ 101.43 (d, $J_{C-H} = 168.8$ Hz, C_{1c}), 101.21 (d, $J_{C-H} = 168.4$ Hz, C_{1e}), 100.85 (d, $J_{C-H} = 170.5$ Hz, C_{1d}), 98.80 (d, $J_{C-H} = 175.5$ Hz, C_{1b}). FAB⁺ calcd. for C₁₄₅H₁₅₁O₂₅N₃ M⁺ = 2333.89; [M + Na]⁺ = 2356.88. Found: m/z 2357 [M + Na]⁺. Anal: calcd. for C₁₄₁H₁₅₁O₂₅N₃: C, 74.56; H, 5.62; N, 1.80. Found: C, 74.17; H, 6.85; N, 1.52.

Data for 19: $[\alpha]_D + 26.8$ ($c = 0.6$, CHCl₃). ¹H-RMN (C₆D₆): δ 7.46 (m, 6H, ArH), 7.41–7.23 (m, 26H, ArH), 7.20–6.96 (m, 48H, ArH), 6.03 (d, $J = 4.0$ Hz, 1H, H_{1b}), 5.95 (ddt, $J_1 = 6.5$ Hz, $J_2 = 10.5$ Hz, $J_3 = 17.0$ Hz, 1H, H₂), 5.62 (broad s, 1H, H_{1e}), 5.58 (broad d, $J = 1.5$ Hz, 1H, H_{1c}), 5.27 (broad dd, $J_1 = 1.5$ Hz, $J_2 = 17.5$ Hz, 1H, H₃), 5.13 (d, $J = 11.0$ Hz, 1H, CH_{benzyl.}), 5.11 (broad d, $J = 10.5$ Hz, 1H, H_{3'}), 4.99 (broad d, $J = 11.0$ Hz, 4H, 4 $\times$ CH_{benzyl.}), 4.98 (d, $J = 11.0$ Hz, 1H, CH_{benzyl.}), 4.96 (d, $J = 11.0$ Hz, 1H, CH_{benzyl.}), 4.87 (d, $J = 12.0$ Hz, 1H, CH_{benzyl.}), 4.81 (d, $J = 12.0$ Hz, 1H, CH_{benzyl.}), 4.78 (d, $J = 12.0$ Hz, 1H, CH_{benzyl.}), 4.74 (d, $J = 11.5$ Hz, 1H, CH_{benzyl.}), 4.71 (m, 1H, H_{5e}), 4.70 (d, $J = 11.0$ Hz, 2H, 2 $\times$ CH_{benzyl.}), 4.69 (d, $J = 11.0$ Hz, 1H, CH_{benzyl.}), 4.67 (t, $J = 10.0$ Hz, 1H, H_{6a}), 4.65 (broad s, 1H, H_{1d}), 4.63 (d, $J = 12.0$ Hz, 2H, 2 $\times$ CH_{benzyl.}), 4.57 (broad d, $J = 11.5$ Hz, 2H, 2 $\times$ CH_{benzyl.}), 4.56 (t, $J = 9.5$ Hz, 1H, H_{4e}), 4.53 (broad s, 2H, CH₂benzyl.), 4.520

(m, 1H, H_{5b}), 4.518 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.51 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.49 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.48 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.47 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.444 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.443 (broad t, $J = 2.5$ Hz, 1H, H_{2d}), 4.41 (d, $J = 12.0$ Hz, 2H, 2 × CH_{benzyl}), 4.40 (broad s, 2H, CH_{2benzyl}), 4.398 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.35 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.31 (dd, $J_1 = 3.5$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3e}), 4.30 (t, $J = 10.0$ Hz, 1H, H_{4a}), 4.21 (broad t, $J = 10.0$ Hz, 2H, H_{3b} + H_{4c}), 4.15 (t, $J = 9.5$ Hz, 1H, H_{4b}), 4.13 (m, 4H, H_{6e} + H_{6e'} + H_{6c} + H_{2e}), 4.12 (m, 1H, H_{5c}), 4.10 (t, $J = 9.5$ Hz, 1H, H_{4d}), 4.05 (broad d, $J = 11.5$ Hz, 1H, H_{6c}), 4.03 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3c}), 3.92 (broad t, $J = 2.0$ Hz, 1H, H_{2a}), 3.89 (broad t, $J = 3.0$ Hz, 1H, H_{2c}), 3.88 (broad dd, $J_1 = 6.0$ Hz, $J_2 = 12.0$ Hz, 1H, H₁), 3.83 (broad dd, $J_1 = 5.5$ Hz, $J_2 = 12.0$ Hz, 1H, H_{1'}), 3.79 (dd, $J_1 = 5.0$ Hz, $J_2 = 11.5$ Hz, 1H, H_{6d}), 3.71 (broad d, $J = 12.0$ Hz, 1H, H_{6d'}), 3.70 (broad s, 2H, H_{6b} + H_{6b'}), 3.51 (t, $J = 9.5$ Hz, 1H, H_{5a}), 3.42 (dd, $J_1 = 2.5$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3d}), 3.38 (broad dd, $J_1 = 3.0$ Hz, $J_2 = 9.0$ Hz, 1H, H_{5d}), 3.32 (dd, $J_1 = 2.0$ Hz, $J_2 = 9.5$ Hz, 1H, H_{1a}), 3.19 (dd, $J_1 = 2.0$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3a}), 3.16 (dd, $J_1 = 4.0$ Hz, $J_2 = 10.0$ Hz, 1H, H_{2b}). ¹³C-RMN (C₆D₆): δ 140.62, 140.50, 140.46, 140.25, 140.21, 140.20, 140.16, 140.13, 139.98 (ArC), 139.86 (3 × ArC), 139.53, 139.45, 139.19, 139.12 (ArC), 135.40 (C₂), 129.49, 129.37, 129.34, 129.28, 129.22, 129.14, 129.09, 129.06, 129.04, 128.96, 128.91, 128.86, 128.81, 128.72, 128.68, 128.62, 128.54, 128.51, 128.43, 128.38, 128.26, 128.20, 128.16, 128.14, 128.09, 127.93, 127.88, 127.86, 127.82 (ArCH), 117.70 (C₃), 101.56 (C_{1d}), 101.00 (C_{1c}), 99.79 (C_{1e}), 98.67 (C_{1b}), 84.27 (C_{3d}), 83.10 (C_{1a}), 82.95 (C_{4a}), 82.69 (C_{5a}), 81.92 (C_{3a}), 81.56 (C_{3e}), 81.02 (C_{3b}), 80.72 (C_{3c}), 77.50 (C_{2c}), 77.15 (C_{5d}), 77.08 (C_{2e}), 77.04 (C_{4b}), 76.78 (CH_{2benzyl}), 76.47 (C_{4c}), 76.33 (CH_{2benzyl}), 76.17 (C_{4e}), 76.06 (C_{6a}), 75.81 (C_{4d} - 2 × CH_{2benzyl}), 75.62, 75.03 (CH_{2benzyl}), 74.51 (C_{5c}), 74.33, 74.30, 74.21, 74.05 (CH_{2benzyl}), 73.81 (C_{2a}), 73.76 (C_{5e}), 73.51 (CH_{2benzyl}), 73.46 (C_{2d}), 73.41 (CH_{2benzyl}), 73.12 (CH_{2benzyl}), 73.09 (2 × CH_{2benzyl}), 72.77 (CH_{2benzyl}), 71.62 (C₁), 71.18 (C_{5b}), 70.93 (C_{6c}), 70.43 (C_{6d}), 70.05 (C_{6b}), 69.63 (C_{6e}), 64.07 (C_{2b}). Coupled ¹³C-RMN (C₆D₆): δ 101.56 (d, $J_{C-H} = 156.0$ Hz, C_{1d}), 101.00 (d, $J_{C-H} = 167.8$ Hz, C_{1c}), 99.79 (d, $J_{C-H} = 168.9$ Hz, C_{1e}), 98.67 (d, $J_{C-H} = 174.8$ Hz, C_{1b}). FAB⁺ calcd. for C₁₄₅H₁₅₁O₂₅N₃; M⁺ = 2333.89; [M + Na]⁺ = 2356.88. Found: m/z 2359 [M + Na + 2]⁺.

2,3,4,6-Tetra-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (20). To a solution of **18** (120 mg, 0.051 mmol) in anhydrous THF (1 mL) under argon atmosphere (230 μ L) of a solution of [(1,5-cyclooctadiene)-bis-(methyl-diphenylphosphine)-iridium], hexafluorophosphate (4 mg, 4.7×10^{-3} mmol) in THF (390 μ L), previously treated with H₂, was added and the mixture was stirred for 30 min. Then, the reaction

mixture was treated in the dark with NBS (14 mg, 0.079 mmol) and water (184 μ L, 10.214 mmol) and stirred for 10 min at rt. The mixture was then diluted with AcOEt (25 mL), washed with saturated NaHCO₃ solution (2 $\times$ 25 mL) and NaCl (3 $\times$ 25 mL), dried over MgSO₄, and evaporated to dryness. The residue was purified by column chromatography to give pure **20** (115 mg, 98%) as a white foam. $[\alpha]_D + 41.9$ ($c = 1.1$ CHCl₃). ¹H-RMN (C₆D₆): δ 7.49–6.97 (m, 80H, ArH), 5.59 (d, $J = 2.0$ Hz, 1H, H_{1c}), 5.48 (d, $J = 3.5$ Hz, 1H, H_{1b}), 5.47 (d, $J = 1.5$ Hz, 1H, H_{1d}), 5.31 (d, $J = 1.5$ Hz, 1H, H_{1e}), 5.13 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 5.09 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 5.05 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.99 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.97 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.95 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.94 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.84 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.82 (d, $J = 12.0$ Hz, 1H, CH_{benzyl}), 4.78 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.71 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.68 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.67 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.65 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.60 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.59 (broad s, 2H, CH_{2benzyl}), 4.56 (d, $J = 11.0$ Hz, 1H, CH_{benzyl}), 4.54 (d, $J = 10.5$ Hz, 1H, CH_{benzyl}), 4.51 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.48 (d, $J = 11.5$ Hz, 1H, CH_{benzyl}), 4.45–4.30 (m, 11H, 11 $\times$ CH_{benzyl}), 4.33 (m, 1H, H_{2d}), 4.32 (m, 2H, H_{4c} + H_{5e}), 4.30 (m, 1H, H_{5b}), 4.293 (t, $J = 9.5$ Hz, 1H, H_{4e}), 4.285 (t, $J = 9.5$ Hz, 1H, H_{4d}), 4.27 (t, $J = 9.5$ Hz, 1H, H_{6a}), 4.25 (t, $J = 10.0$ Hz, 1H, H_{4a}), 4.22 (m, 2H, H_{3d} + H_{6c}), 4.19 (dd, $J_1 = 3.5$ Hz, $J_2 = 9.0$ Hz, 1H, H_{3e}), 4.09 (t, $J = 9.5$ Hz, 1H, H_{3b}), 4.08 (m, 3H, H_{3c} + H_{2e} + H_{5d}), 4.05 (m, 1H, H_{5c}), 4.04 (t, $J = 9.5$ Hz, 1H, H_{4b}), 3.90 (broad t, $J = 2.5$ Hz, 1H, H_{2c}), 3.88 (broad s, 1H, H_{2a}), 3.87 (dd, $J_1 = 5.5$ Hz, $J_2 = 10.5$ Hz, 1H, H_{6e}), 3.85 (dd, $J_1 = 3.5$ Hz, $J_2 = 11.5$ Hz, 1H, H_{6d}), 3.79 (broad d, $J = 10.5$ Hz, 1H, H_{6c}), 3.77 (broad d, $J = 11.0$ Hz, 1H, H_{6c'}), 3.71 (dd, $J_1 = 3.5$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6b}), 3.64 (broad d, $J = 11.5$ Hz, 1H, H_{6d'}), 3.62 (broad d, $J = 11.0$ Hz, 1H, H_{6b'}), 3.59 (ddd, $J_1 = 2.5$ Hz, $J_2 = 6.0$ Hz, $J_3 = 9.0$ Hz, 1H, H_{1a}), 3.43 (t, $J = 9.5$ Hz, 1H, H_{5a}), 3.23 (dd, $J_1 = 2.5$ Hz, $J_2 = 10.0$ Hz, 1H, H_{3a}), 3.15 (d, $J = 6.0$ Hz, 1H, OH_{eq}), 3.07 (dd, $J_1 = 4.0$ Hz, $J_2 = 10.5$ Hz, 1H, H_{2b}). ¹³C-RMN (C₆D₆, 125 MHz): δ 139.54 (2 $\times$ ArC), 139.49 (3 $\times$ ArC), 139.47, 139.40 (ArC), 139.27 (2 $\times$ ArC), 139.23, 139.20, 139.09, 139.04, 138.90, 138.82, 138.25 (ArC), 128.73, 128.68, 128.66, 128.64, 128.61, 128.55, 128.53, 128.51, 128.47, 128.45, 128.44, 128.40, 128.35, 128.24, 128.19, 128.12, 128.09, 128.05, 128.00, 127.92, 127.91, 127.88, 127.86, 127.84, 127.80, 127.61, 127.59, 127.57, 127.56, 127.54, 127.50, 127.45, 127.41, 127.38, 127.26 (ArCH), 100.59 (C_{1c} + C_{1e}), 100.15 (C_{1d}), 98.33 (C_{1b}), 82.31 (C_{4a}), 82.10 (C_{5a}), 81.29 (C_{3a}), 81.02 (C_{3b}), 80.78 (C_{3e}), 80.65 (C_{6a}), 80.58 (C_{3c}), 79.95 (C_{3d}), 77.41 (C_{2a}), 76.86 (C_{2c}), 76.80 (C_{4b}), 76.01 (C_{2e}), 75.73 (2 $\times$ CH_{2benzyl}), 75.64 (C_{4e}), 75.40, 75.34 (CH_{2benzyl}), 75.20 (C_{2d}), 75.17 (C_{4c} + 2 $\times$ CH_{2benzyl}), 75.15 (C_{4d}), 74.13, 73.76 (CH_{2benzyl}), 73.70 (C_{1a}), 73.59, 73.40 (CH_{2benzyl}), 73.17 (C_{5c}), 73.15 (C_{5e}), 72.82 (2 $\times$ CH_{2benzyl}), 72.77 (C_{5d}), 72.68, 72.29, 72.11, 71.79 (CH_{2benzyl}), 71.42 (C_{5b}), 70.14 (C_{6e}), 69.70 (C_{6d}), 69.47 (C_{6b}), 67.38 (C_{6c}), 64.24

(C_{2b}). FAB⁺ calcd. for C₁₄₂H₁₄₇O₂₅N₃: M⁺ = 2294.03, [M + Na]⁺ = 2317.02. Found: *m/z* 2317 [M + Na]⁺.

2,3,4,6-Tetra-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-(1',2'-di-*O*-miristoyl-*sn*-glycero-3'-*R*,*S*-benzyl-phosphatidyl)-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (21). To a solution of **20** (45 mg, 0.020 mmol) and 1H-tetrazol (3 mg, 0.043 mmol) in anhydrous CH₂Cl₂ (200 μ L), phosphoramidite **10**^[11] (0.2 M in CH₂Cl₂, 200 μ L) was added and the mixture was stirred under argon for 30 min. The reaction mixture was cooled to -40°C, MCPBA (70%, 5 mg, 0.020 mmol) was added, and the mixture was stirred for 10 min. The reaction mixture was neutralized with Et₃N (10% solution in CH₂Cl₂) and fractionated using three preparative TLC plates previously treated with Et₃N (hexane/AcOEt 3/1) to obtain **21** (51 mg, 86%) as a mixture of two diastereomers I and II 1:0.2. ¹H-RMN (C₆D₆): δ 7.60–7.01 (m, 153H, 85 $\times$ ArH_I + 85 $\times$ ArH_{II}), 5.80 (d, *J* = 3.5 Hz, 1H, H_{1bI}), 5.75 (d, *J* = 3.5 Hz, 0.8H, H_{1bII}), 5.57 (q, *J* = 5.0 Hz, 1H, H_{2II}), 5.54 (broad s, 0.8H, H_{1cII}), 5.53 (broad s, 1H, H_{1cI}), 5.45 (s, 1.8H, H_{1dI} + H_{1dII}), 5.35 (q, *J* = 5.0 Hz, 1H, H_{2I}), 5.30 (broad s, 1.8H, H_{1eI} + H_{1eII}), 5.29 (dd, *J*₁ = 9.0 Hz, *J*₂ = 11.5 Hz, 1H, CH_{benzyl.I} phosphate), 5.24–4.92 (m, 18.8H, 10 $\times$ H_{benzyl.I} + 10 $\times$ CH_{benzyl.II} + CH_{benzyl.II} phosphate), 4.88 (broad s, 0.8H, H_{2aII}), 4.81–4.62 (m, 10.8H, 6 $\times$ CH_{benzyl.I} + 6 $\times$ CH_{benzyl.II}), 4.79 (m, 1.6H, H_{1aII} + H_{6aII}), 4.77 (t, *J* = 10.0 Hz, 1H, H_{6aI}), 4.75 (broad s, 1H, H_{2aI}), 4.64 (m, 1H, H_{1aI}), 4.61–4.50 (m, 11.8H, 7 $\times$ CH_{benzyl.I} + 6 $\times$ CH_{benzyl.II}), 4.47 (m, 1H, H_{5bI}), 4.46 (m, 0.8H, H_{5bII}), 4.46–4.30 (m, 18.8H, 10 $\times$ CH_{benzyl.I} + 11 $\times$ CH_{benzyl.II}), 4.38 (m, 0.8H, H_{3II}), 4.35 (m, 1.8H, H_{4cI} + H_{4cII}), 4.33 (m, 2.6H, H_{4aII} + H_{2dI} + H_{2dII}), 4.31 (m, 4.6H, H_{1I} + H_{5eI} + H_{5eII} + H_{4eI} + H_{4eII}), 4.30 (m, 1.6H, H_{1II} + H_{1'II}), 4.29 (t, *J* = 10.0 Hz, 1H, H_{4aI}), 4.24 (t, *J* = 10.0 Hz, 1H, H_{3bI}), 4.23 (m, 2.6H, H_{3bII} + H_{4dI} + H_{4dII}), 4.21 (m, 2.6H, H_{3'II} + H_{3dI} + H_{3dII}), 4.20 (m, 1.8H, H_{6cI} + H_{6cII}), 4.18 (m, 1.8H, H_{3eI} + H_{3eII}), 4.16 (m, 2H, H_{3I} + H_{3'II}), 4.10 (dd, *J*₁ = 4.5 Hz, *J*₂ = 11.0 Hz, 1H, H_{1'II}), 4.08 (m, 1.8H, H_{3cI} + H_{3cII}), 4.07 (m, 2.8H, H_{4bI} + H_{2eI} + H_{2eII}), 4.06 (t, *J* = 10.0 Hz, 0.8H, H_{4bII}), 4.03 (broad dd, *J*₁ = 3.5 Hz, *J*₂ = 10.0 Hz, 1.8H, H_{5dI} + H_{5dII}), 3.95 (broad d, *J* = 9.5 Hz, 1.8H, H_{5cI} + H_{5cII}), 3.91 (broad t, *J* = 2.0 Hz, 0.8H, H_{2cII}), 3.90 (broad t, *J* = 2.0 Hz, 1H, H_{2cI}), 3.87 (broad dd, *J*₁ = 3.5 Hz, *J*₂ = 10.5 Hz, 1.8H, H_{6eI} + H_{6eII}), 3.83 (dd, *J*₁ = 4.0 Hz, *J*₂ = 11.5 Hz, 1.8H, H_{6dI} + H_{6dII}), 3.75 (broad d, *J* = 11.0 Hz, 3.6H, H_{6cI} + H_{6cII} + H_{6eI} + H_{6eII}), 3.65 (broad s, 3.6H, H_{6bI} + H_{6bII} + H_{6b'II} + H_{6b'II}), 3.64 (broad d, *J* = 11.0 Hz, 1.8H, H_{6dI} + H_{6dII}), 3.63 (t, *J* = 10.0 Hz, 0.8H, H_{5aII}), 3.56 (dd, *J*₁ = 2.0 Hz, *J*₂ = 10.0 Hz, 0.8H, H_{3aII}), 3.49 (t, *J* = 9.5 Hz, 1H, H_{5aI}), 3.36 (dd, *J*₁ = 1.5 Hz, *J*₂ = 10.0 Hz, 1H, H_{3aI}), 3.11 (dd, *J*₁ = 3.5 Hz, *J*₂ = 10.5 Hz, 0.8H, H_{2bII}), 3.07 (dd, *J*₁ = 3.5 Hz, *J*₂ = 10.5 Hz, 1H, H_{2bI}), 2.27 (m, 3.2H, 2 $\times$ OCOCH₂ α II), 2.17 (m, 4H, 2 $\times$ OCOCH₂ α I), 1.58 (m, 7.2H, 2 $\times$ CH₂ β I + 2 $\times$ CH₂ β II), 1.37–1.16

(m, 72H, $2 \times 10 \times \text{CH}_2\text{I} + 2 \times 10 \times \text{CH}_2\text{II}$), 0.91 (t, $J = 7.0$ Hz, 10.8H, $2 \times \text{CH}_3\text{I} + 2 \times \text{CH}_3\text{II}$). ^{13}C -RMN (C_6D_6): δ 173.45, 173.42, 173.34, 173.33 ($\text{OCOC}_{13}\text{H}_{27}$), 140.23, 140.20, 140.12, 140.07, 140.05, 140.03, 139.99, 139.92, 139.81, 139.78, 139.50, 139.39, 139.36, 139.05, 139.03 (ArC), 137.06 (d, $J_{\text{C-P}} = 5.5$ Hz, ArC_I phosphate), 136.89 (d, $J_{\text{C-P}} = 6.4$ Hz, ArC_II phosphate), 129.59, 129.56, 129.55, 129.51, 129.31, 129.29, 129.26, 129.23, 129.22, 129.20, 129.18, 129.16, 129.15, 129.12, 129.09, 129.07, 129.04, 129.02, 128.96, 128.91, 128.81, 128.74, 128.72, 128.67, 128.62, 128.58, 128.55, 128.53, 128.43, 128.38, 128.19, 128.11, 128.06, 128.01, 127.99, 127.89 (ArCH), 101.81 ($\text{C}_{1\text{cII}}$), 101.73 ($\text{C}_{1\text{cI}}$), 101.21 ($\text{C}_{1\text{eI}} + \text{C}_{1\text{eII}}$), 100.88 ($\text{C}_{1\text{dI}} + \text{C}_{1\text{dII}}$), 98.80 ($\text{C}_{1\text{bI}}$), 98.73 ($\text{C}_{1\text{bII}}$), 82.62 ($\text{C}_{4\text{aII}}$), 82.57 ($\text{C}_{4\text{aI}}$), 82.33 ($\text{C}_{5\text{aII}}$), 82.24 ($\text{C}_{5\text{aI}}$), 81.72 ($\text{C}_{3\text{aII}}$), 81.53 ($\text{C}_{3\text{aI}}$), 81.40 ($\text{C}_{3\text{eI}} + \text{C}_{3\text{eII}}$), 81.14 (m, $\text{C}_{1\text{aII}} + \text{C}_{3\text{cI}} + \text{C}_{3\text{cII}}$), 81.00 (m, $\text{C}_{1\text{aI}}$), 80.59 ($\text{C}_{3\text{bII}}$), 80.56 ($\text{C}_{3\text{bI}}$), 80.38 ($\text{C}_{3\text{dI}} + \text{C}_{3\text{dII}}$), 78.11 ($\text{C}_{4\text{bII}}$), 78.01 ($\text{C}_{4\text{bI}}$), 77.94 ($\text{C}_{2\text{aI}}$), 77.76 ($\text{C}_{2\text{aII}}$), 77.58 ($\text{C}_{2\text{cI}} + \text{C}_{2\text{cII}}$), 76.98, 76.90 (CH_2benc), 76.63 ($\text{C}_{2\text{eI}} + \text{C}_{2\text{eII}} + \text{CH}_2\text{benzyl.}$), 76.48, 76.42, 76.35 ($\text{CH}_2\text{benzyl.}$), 76.32 ($\text{C}_{2\text{dI}} + \text{C}_{2\text{dII}} + 2 \times \text{CH}_2\text{benzyl.}$), 75.94 ($3 \times \text{CH}_2\text{benzyl.}$), 75.89 ($\text{CH}_2\text{benzyl.}$), 75.83 ($\text{C}_{6\text{aI}} + \text{C}_{6\text{aII}} + 2 \times \text{CH}_2\text{benzyl.}$), 75.77 ($\text{C}_{4\text{dI}} + \text{C}_{4\text{dII}} + \text{C}_{4\text{eI}} + \text{C}_{4\text{eII}}$), 75.70 ($\text{C}_{4\text{cI}} + \text{C}_{4\text{cII}}$), 74.29, 74.27 ($\text{CH}_2\text{benzyl.}$), 74.20 ($2 \times \text{CH}_2\text{benzyl.}$), 74.04 ($2 \times \text{CH}_2\text{benzyl.}$), 73.97 ($\text{CH}_2\text{benzyl.}$), 73.79 ($\text{C}_{5\text{eI}} + \text{C}_{5\text{eII}}$), 73.62 ($\text{C}_{5\text{cI}} + \text{C}_{5\text{cII}}$), 73.53, 73.46 ($\text{CH}_2\text{benzyl.}$), 73.43 ($\text{C}_{5\text{dI}} + \text{C}_{5\text{dII}} + 2 \times \text{CH}_2\text{benzyl.}$), 73.17, 73.15 ($\text{CH}_2\text{benzyl.}$), 72.85 ($2 \times \text{CH}_2\text{benc}$), 72.72 ($2 \times \text{CH}_2\text{benzyl.}$), 72.29 ($2 \times \text{CH}_2\text{benzyl.}$), 71.59 ($\text{C}_{5\text{bI}}$), 71.57 ($\text{C}_{5\text{bII}}$), 70.90 (d, $J_{\text{C-P}} = 6.0$ Hz, $\text{C}_{2\text{II}}$), 70.86 (d, $J_{\text{C-P}} = 5.0$ Hz, $\text{CH}_2\text{benzyl.I}$ phosphate), 70.71 ($\text{C}_{6\text{eI}} + \text{C}_{6\text{eII}}$), 70.62 (d, $J_{\text{C-P}} = 7.1$ Hz, $\text{C}_{2\text{I}}$), 70.55 (d, $J_{\text{C-P}} = 5.6$ Hz, $\text{CH}_2\text{benzyl.II}$ phosphate), 70.32 ($\text{C}_{6\text{dI}} + \text{C}_{6\text{dII}}$), 70.07 ($\text{C}_{6\text{bII}}$), 70.04 ($\text{C}_{6\text{bI}}$), 68.05 ($\text{C}_{6\text{cI}} + \text{C}_{6\text{cII}}$), 66.65 (d, $J_{\text{C-P}} = 6.3$ Hz, $\text{C}_{3\text{II}}$), 66.56 (d, $J_{\text{C-P}} = 5.4$ Hz, $\text{C}_{3\text{I}}$), 63.81 ($\text{C}_{2\text{bII}}$), 63.69 ($\text{C}_{2\text{bI}}$), 62.50 ($\text{C}_{1\text{II}}$), 62.45 ($\text{C}_{1\text{I}}$), 35.02, 34.96, 34.76, 34.71 ($\text{OCOCH}_2\alpha$), 32.92, 30.77, 30.75, 30.74, 30.72, 30.70, 30.57, 30.55, 30.42, 30.39, 30.35, 30.33, 30.13, 30.08 (CH_2), 25.85, 25.82 ($\text{CH}_2\beta$), 25.80 ($2 \times \text{CH}_2\beta$), 23.70 ($4 \times \text{CH}_2$), 14.96 ($4 \times \text{CH}_3$). ^{31}P -RMN (C_6D_6 , 202 MHz): δ -1.15 (P_I^*), -1.50 (P_II^*). FAB^+ calcd. for $\text{C}_{180}\text{H}_{212}\text{O}_{32}\text{N}_3\text{P}$: $\text{M}^+ = 2958.47$; $[\text{M} + \text{Na}]^+ = 2981.46$. Found: m/z 2982 $[\text{M} + \text{Na}]^+$.

α -D-Mannopyranosyl-(1 $\rightarrow$ 2)- α -D-mannopyranosyl-(1 $\rightarrow$ 6)- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-2-ammonio-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-O-(1',2'-O-miristoyl-sn-glycero-3'-phosphatidyl)-D-myo-inositol (2). A suspension of **21** (25 mg, 8.4×10^{-3} mmol) in a 1/1/1/0.1 mixture of AcOEt/THF/EtOH/H₂O (4.3 mL) was hydrogenated for 3 hr with stirring using 10% Pd over charcoal (45 mg, 0.042 mol) as catalyst. The reaction mixture was filtered over Celite, washed with MeOH (10 mL), and evaporated to dryness to afford **2** as a white solid. $[\alpha]_\text{D} + 29.1$ ($c = 0.2$, MeOH). ^1H -RMN (CD_3OD): δ 5.54 (d, $J = 4.0$ Hz, 1H, $\text{H}_{1\text{b}}$), 5.29 (m, 1H, H_2), 5.27 (d, $J = 1.5$ Hz, 1H, $\text{H}_{1\text{c}}$), 5.16 (d, $J = 1.5$ Hz, 1H, $\text{H}_{1\text{d}}$), 5.02 (d, $J = 2.0$ Hz, 1H, $\text{H}_{1\text{e}}$), 4.48 (dd, $J_1 = 3.0$ Hz, $J_2 = 12.0$ Hz, 1H, H_1), 4.30 (broad ddd, $J_1 = 2.0$ Hz, $J_2 = 4.0$ Hz, $J_3 = 10.0$ Hz, 1H, $\text{H}_{5\text{b}}$), 4.23 (dd, $J_1 = 7.0$ Hz, $J_2 = 12.0$ Hz, 1H, $\text{H}_{1'}$), 4.20

(broad td, $J_1 = 2.5$ Hz, $J_2 = 9.5$ Hz, 1H, H_{1a}), 4.12 (broad t, $J = 2.5$ Hz, 1H, H_{2a}), 4.08 (m, 2H, H₃ + H_{3'}), 4.03 (dd, $J_1 = 9.5$ Hz, $J_2 = 10.0$ Hz, 1H, H_{3b}), 4.02 (dd, $J_1 = 2.0$ Hz, $J_2 = 3.0$ Hz, 1H, H_{2e}), 4.00 (t, $J = 9.5$ Hz, 1H, H_{6a}), 3.99 (dd, $J_1 = 2.0$ Hz, $J_2 = 3.0$ Hz, 1H, H_{2c}), 3.95 (dd, $J_1 = 1.5$ Hz, $J_2 = 3.5$ Hz, 1H, H_{2d}), 3.93 (m, 1H, H_{3d}), 3.90 (m, 1H, H_{6c}), 3.89 (m, 1H, H_{6b}), 3.88 (m, 1H, H_{6e}), 3.87 (m, 1H, H_{6d}), 3.83 (m, 2H, H_{6b'} + H_{6c'}), 3.80 (m, 1H, H_{5c}), 3.76 (m, 1H, H_{5e}), 3.74 (m, 2H, H_{3e} + H_{6e'}), 3.72 (m, 1H, H_{6d'}), 3.697 (broad t, $J = 9.5$ Hz, 2H, H_{4b} + H_{4a}), 3.696 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3c}), 3.66 (m, 2H, H_{4d} + H_{5d}), 3.65 (t, $J = 9.5$ Hz, 1H, H_{4c}), 3.62 (t, $J = 9.5$ Hz, 1H, H_{4e}), 3.41 (dd, $J_1 = 3.0$ Hz, $J_2 = 10.0$ Hz, 1H, H_{3a}), 3.33 (t, $J = 9.0$ Hz, 1H, H_{5a}), 3.20 (dd, $J_1 = 4.0$ Hz, $J_2 = 10.5$ Hz, 1H, H_{2b}), 2.39 (t, $J = 7.5$ Hz, 2H, OCOCH₂ α), 2.34 (t, $J = 7.5$ Hz, 2H, OCOCH₂ α), 1.64 (m, 4H, 2 $\times$ CH₂ β), 1.32 (m, 40H, 2 $\times$ 10 $\times$ CH₂), 0.93 (t, $J = 7.0$ Hz, 6H, 2 $\times$ CH₃). ¹³C-RMN (CD₃OD, 125 MHz): δ 175.00, 174.72 (OCOC₁₃H₂₇), 104.15 (C_{1e}), 102.81 (C_{1c}), 100.01 (C_{1d}), 96.98 (C_{1b}), 80.47 (C_{2d}), 79.33 (C_{6a}), 78.22 (d, $J_{C-P} = 6.1$ Hz, C_{1a}), 78.01 (C_{4b}), 74.92 (C_{5e}), 74.90 (C_{5a}), 74.49 (C_{5d}), 74.34 (C_{4a}), 74.30 (C_{5c}), 73.35 (C_{2a}), 72.63 (C_{3a}), 72.48 (C_{3c}), 72.44 (C_{3e} + C_{5b}), 72.09 (C_{2c}), 72.01 (C_{3d}), 71.92 (C_{2e}), 71.79 (C₂), 71.72 (C_{3b}), 69.05 (C_{4d}), 68.76 (C_{4e}), 68.56 (C_{4c}), 68.06 (C_{6c}), 65.02 (C₃), 63.70 (C₁), 63.02 (C_{6d} + C_{6e}), 62.06 (C_{6b}), 56.04 (C_{2b}), 35.12, 34.95 (OCOCH₂ α), 33.09, 30.83, 30.79, 30.69, 30.67, 30.50, 30.24, 30.21 (CH₂), 26.05, 26.02 (CH₂ β), 23.74 (2 $\times$ CH₂), 14.44 (2 $\times$ CH₃). ³¹P-RMN (CD₃OD, 202 MHz): δ -0.81. FAB⁺ HRMS calcd. for C₆₁H₁₁₂O₃₂NP: M⁺ = 1401.6873; [M + H]⁺ = 1402.7143; [M + Na]⁺ = 1424.6961. Found: m/z 1402.6983 [M + H]⁺; 1424.6803 [M + Na]⁺.

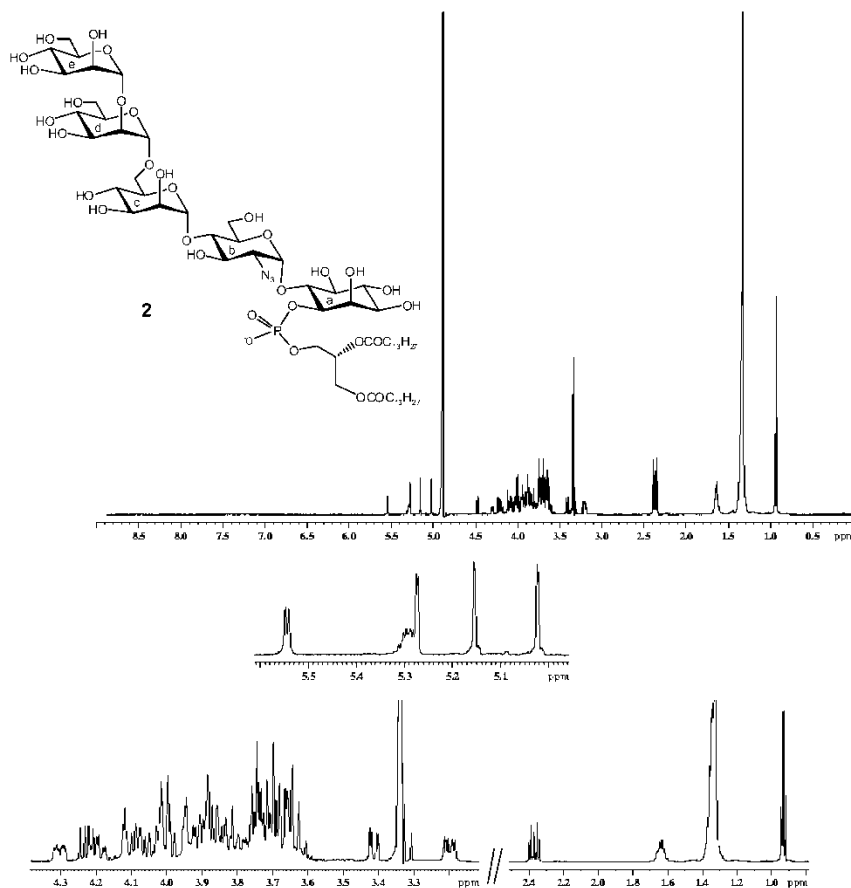
α -D-Mannopyranosyl-(1 $\rightarrow$ 2)- α -D-mannopyranosyl-(1 $\rightarrow$ 6)- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-2-ammonio-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-D-myoinositol (3). A suspension of **20** (30 mg, 0.013 mmol) in a 9/1 MeOH/H₂O mixture (6.5 mL) was hydrogenated with stirring for 12 hr in the presence of 10% Pd on charcoal (69 mg, 0.065 mmol). The mixture was filtered over Celite and evaporated to dryness. The residue was dissolved in H₂O and passed through an Amberlite IRA-408 (Cl⁻ form) column and lyophilized to give **3** (12 mg, 100%) as a white solid. $[\alpha]_D + 90.4$ (c = 0.3, H₂O). ¹H-RMN (D₂O): δ 5.39 (d, $J = 4.0$ Hz, 1H, H_{1b}), 5.21 (d, $J = 1.5$ Hz, 1H, H_{1c}), 5.12 (d, $J = 1.5$ Hz, 1H, H_{1d}), 5.00 (d, $J = 1.5$ Hz, 1H, H_{1e}), 4.13 (dt, $J_1 = 3.0$ Hz, $J_2 = 10.0$ Hz, 1H, H_{5b}), 4.05 (broad dd, $J_1 = 2.0$ Hz, $J_2 = 3.0$ Hz, 2H, H_{2c} + H_{2e}), 4.02 (t, $J = 9.0$ Hz, 1H, H_{3b}), 4.00 (m, 2H, H_{2a} + H_{2d}), 3.95 (dd, 1H, $J_1 = 3.5$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3d}), 3.93 (dd, $J_1 = 5.0$ Hz, $J_2 = 11.0$ Hz, 1H, H_{6c}), 3.87 (broad dd, 2H, $J_1 = 1.5$ Hz, $J_2 = 12.0$ Hz, 1H, H_{6d} + H_{6e}), 3.82 (m, 4H, H_{6b} + H_{6b'} + H_{3e} + H_{5c}), 3.78 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.5$ Hz, 1H, H_{3c}), 3.76 (m, 1H, H_{5e}), 3.74 (m, 1H, H_{6d'}), 3.72 (m, 2H, H_{4b} + H_{6c'}), 3.71 (m, 4H, H_{6e'} - H_{4c} + H_{1a} + H_{6a}), 3.67 (m, 2H, H_{4d} + H_{5d}), 3.62 (t, $J = 10.0$ Hz, 1H, H_{4a}), 3.60

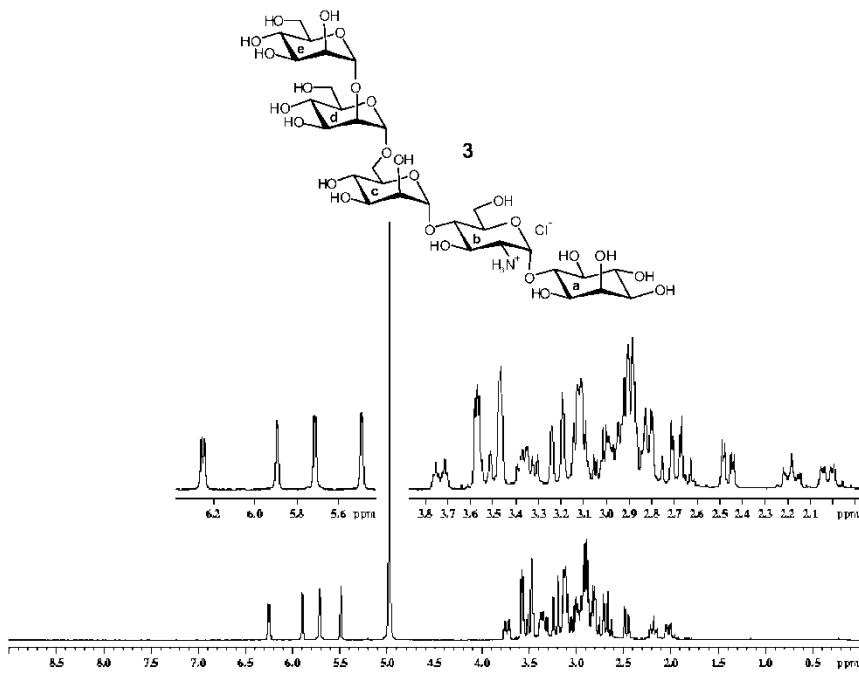
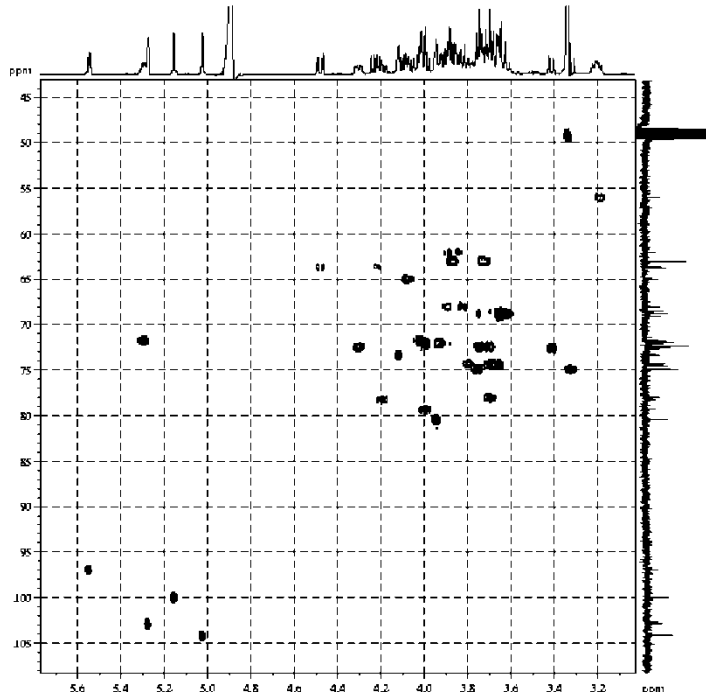
(t, $J = 9.5$ Hz, 1H, H_{4e}), 3.49 (dd, $J_1 = 2.5$ Hz, $J_2 = 10.0$ Hz, 1H, H_{3a}), 3.35 (m, 1H, H_{5a}), 3.27 (dd, $J_1 = 3.5$ Hz, $J_2 = 10.5$ Hz, 1H, H_{2b}). ¹³C-RMN (C₆D₆): δ 101.91 (C_{1e}), 101.50 (C_{1c}), 97.95 (C_{1d}), 96.59 (C_{1b}), 79.92 (C_{6a}), 78.24 (C_{2d}), 76.30 (C_{4b}), 72.83 (C_{5e}), 72.32 (C_{5d}), 72.31 (C_{5a}), 72.13 (C_{4a}), 72.01 (C_{2a}), 71.84 (C_{5c}), 71.18 (C_{1a}), 70.58 (C_{5b}), 70.49 (C_{3a}), 70.01 (C_{3c}), 69.90 (C_{3b} + C_{3e}), 69.79 (C_{3d} + C_{2c}), 69.56 (C_{2e}), 66.53 (C_{4d}), 66.47 (C_{4e}), 66.04 (C_{4c}), 65.88 (C_{6c}), 60.72 (C_{6e}), 60.53 (C_{6d}), 59.80 (C_{6b}), 54.21 (C_{2b}). FAB⁺ HRMS calcd. for C₃₀H₅₃O₂₅N: M⁺ = 827.2890; [M + Na]⁺ = 850.2788. Found: m/z 850.2796 [M + Na]⁺.

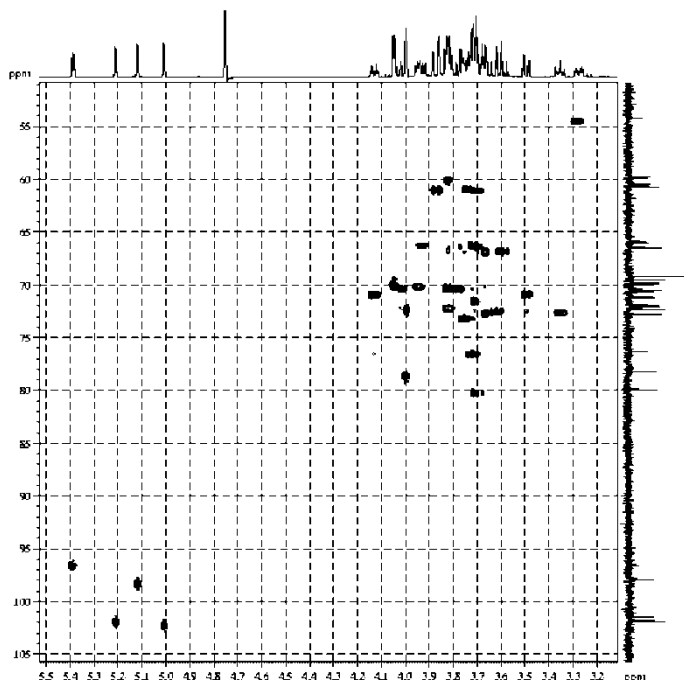
SUPPORTING INFORMATION

RMN Spectra

¹H-RMN and HSQC spectra of GPI **2** and pseudopentasaccharide **3** acquired on a Bruker DRX-500 spectrometer in CD₃OD at pH = 6.4 and deuterium oxide at pH = 6.9, respectively, are shown:







ACKNOWLEDGMENTS

We thank the Ministry of Science and Technology (Grant BQU 2002-03734) and Rodaris Pharmaceuticals for financial support.

REFERENCES

- [1] Jones, D.R.; Varela-Nieto, I. Diabetes and the role of inositol-containing lipids in insulin signalling. *Mol. Med.* **1999**, *5*, 505–514.
- [2] Field, M.C. Is there evidence for phospho-oligosaccharides as insulin mediators → *Glycobiology* **1997**, *7*, 161–168.
- [3] Dietrich, H.; Espinosa, J.F.; Chiara, J.L.; Jiménez-Barbero, J.; León, Y.; Varela-Nieto, I.; Mato, J.M.; Cano, F.H.; Foces-Foces, C.; Martín-Lomas, M. Glycosyl inositol derivatives related to inositolphosphoglycan mediators: synthesis, structure and biological activity. *Chem. Eur. J.* **1999**, *5*, 320–336.
- [4] Martín-Lomas, M.; Khair, N.; García, S.; Koessler, J.L.; Nieto, P.M.; Rademacher, T.W. Inositolphosphoglycan mediators related to glycosylphosphatidylinositol anchors: synthesis, structure and biological activity. *Chem. Eur. J.* **2000**, *6*, 3608–3621.
- [5] Reichardt, N-C.; Martín-Lomas, M. A practical solid phase synthesis of glycosyl-phosphatidylinositol precursors. *Angew. Chem. Int. Ed.* **2003**, *42*, 4674–4677.
- [6] López-Prados, J.; Cuevas, F.; Reichardt, N-C.; De Paz, J-L.; Morales, E.Q.; Martín-Lomas, M. Design and synthesis of inositolphosphoglycan putative insulin mediators. *Org. Biomol. Chem.* **2005**, in press.

- [7] For a recent review see: Guo, Z.; Bishop, L. Chemical synthesis of GPIs and GPI-anchored glycopeptides. *Eur. J. Org. Chem.* **2004**, 3585–3596.
- [8] Watanabe, Y.; Inada, E.; Jinno, M.; Ozaki, S. Phosphonium salt methodology for the synthesis of phosphoric monoesters and diesters and its application to selective phosphorylation. *Tetrahedron Lett.* **1993**, *34*, 497–500.
- [9] Yu, K.L.; Fraser-Reid, B. A novel reagent for the synthesis of myo-inositol phosphates: N, N-didisopropyl phosphoramidite. *Tetrahedron Lett.* **1988**, *29*, 979–982.
- [10] López-Prados, J.; Martín-Lomas, M. Unpublished results.
- [11] Baeschlin, D.K.; Chaperon, A.R.; Charboneau, V.; Green, L.G.; Ley, S.V.; Lüking, U.; Walther, E. Rapid assembly of oligosaccharides: total synthesis of a glycosylphosphatidylinositol anchor of *Trypanosoma brucei*. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 3423–3428.
- [12] Elie, C.J.J.; Dref, C.E.; Verduyn, R.; van der Marel, G.A.; van Boom, J. Synthesis of 1-O-(1,2-di-O-palmitoyl-sn-glycero-3-phosphoryl)-2-O- α -D-mannopyranosyl-D-myo-inositol: a fragment of mycobacterial phospholipids. *Tetrahedron* **1989**, *45*, 3477–3486.
- [13] Lamberth, C.; Bernarski, M.D. An efficient method for the deprotection of allyl glycosides with adjacent azides: the circumvention of unwanted dipolar cycloaddition products. *Tetrahedron Lett.* **1991**, *32*, 7369–7372.
- [14] Mootoo, D.; Konradsson, P.; Fraser-Reid, B. n-Pentenyl glycosides facilitate a stereoselective synthesis of the pentasaccharide core of the protein membrane anchor found in *Trypanosoma brucei*. *J. Am. Chem. Soc.* **1989**, *111*, 8540–8542.
- [15] Euns, K.R.; Malcom, M.C. Modification of the Dittmer–Lester reagent for the detection of phospholipid derivatives on thin-layer chromatograms. *J. Lipid Res.* **1979**, *20*, 561–563.
- [16] Ogawa, T.; Nabuda, T. Synthesis of a branched mannohexoside, a part structure of the high mannose-type glycan of a glycoprotein. *Carbohydr. Res.* **1985**, *136*, 135–152.