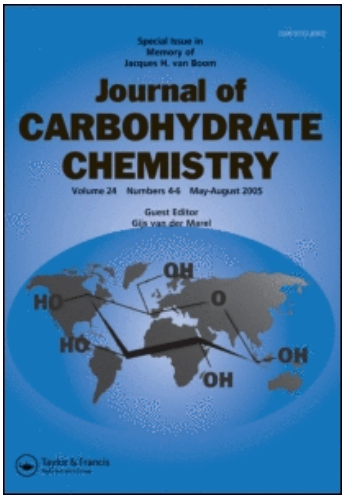

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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

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To cite this Article López-Prados, Javier and Martín-Lomas, Manuel(2005) 'Inositolphosphoglycan Mediators: An Effective Synthesis of the Conserved Linear GPI Anchor Structure', Journal of Carbohydrate Chemistry, 24: 4, 393 — 414
To link to this Article: DOI: 10.1081/CAR-200066956
URL: http://dx.doi.org/10.1081/CAR-200066956

Journal of Carbohydrate Chemistry, 24:393–414, 2005

ISSN: 0732-8303 print 1532-2327 online
DOI: 10.1081/CAR-200066956

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

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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 $\alpha(1\rightarrow 4)$ $GlcN_3$ $\alpha(1\rightarrow 6)$ *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 Insositolphosphoglycan 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.
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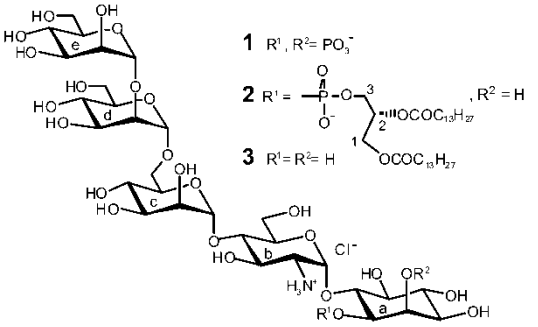
containing pseudooligosaccharides bearing some of the structural motifs that have been postulated for natural IPGs.[3–6]

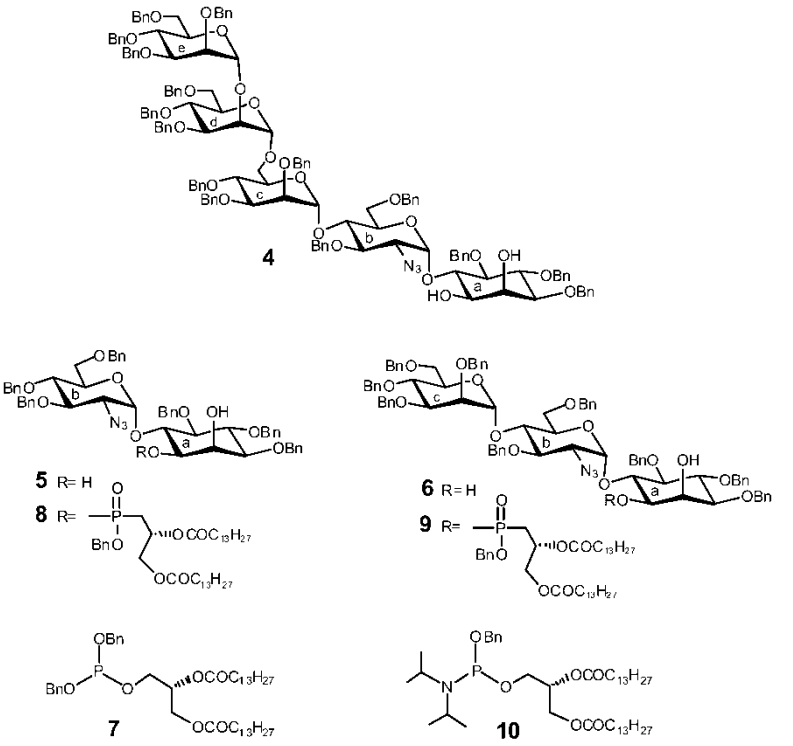


These studies have included the synthesis of pseudopentasaccharide **1** as the product to be expected from a GPI-specific phospholipase C (GPI-PLC)-mediated cleavage of a GPI anchor (**2**).[4] A further step in this investigation required the synthesis of pseudopentasaccharide **3**—the structure to 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

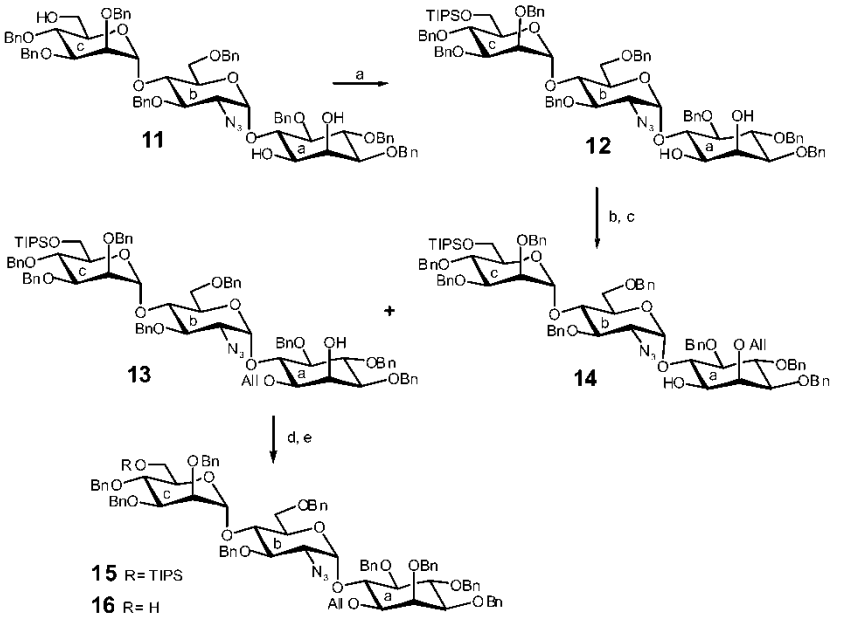
The synthesis of **2** was first envisaged from **4**, an advanced intermediate in the synthesis of **1**,[4] by regioselective phosphorylation using the phosphite-phosphonium salt methodology.[8] We have previously shown[3] that the equatorially oriented OH-1 in diols **5** and **6** regioselectively 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

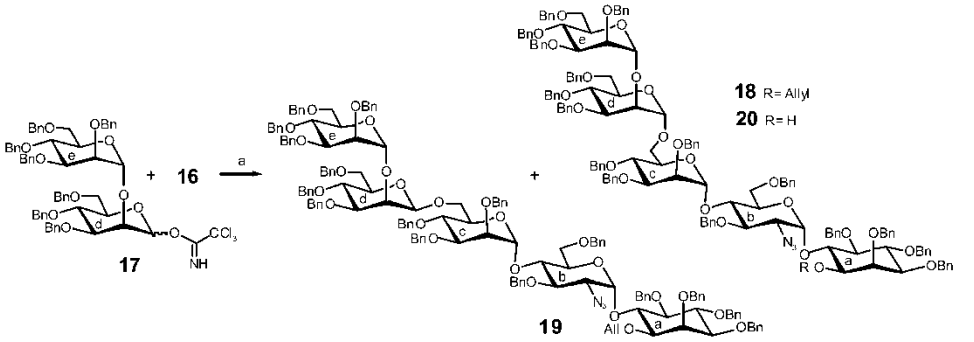


Scheme 1: Reagents and conditions: a) TIPSCl, imidazol, DMAP, DMF nt 10 hr, 95%; b) Bn_2SnO, toluene, 140°C, 12 hr; c) All Br, TBAI, 90°C, 2 hr; d) NaH, BnBr, DMF rt 2 hr, 96%; e) TBAF, THF, rt, 2 hr, 92%.

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 ß-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 intermediately 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 : H_2O



Scheme 2: a) TMSOTf, Et_2O, −15°C, 1 hr; b) Ir.H_2, THF, rt, 30 min; c) NBS, H_2O, rt, 10 min, 98%.

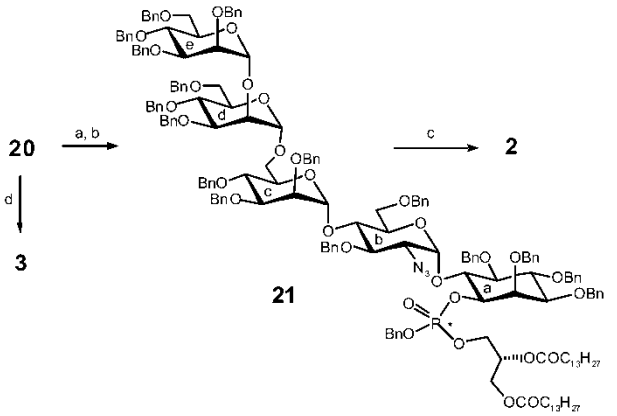
mixture[3] rather than in the usual 3 : 3 : 1 $CHCl_3$: MeOH : H_2O mixture, which has been used so far in the synthesis of GPI anchors.[7]

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 F_{254} 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) H_2 Pd/c, AcOEt/THF/EtOH/H_2O, rt 3 hr, 92%; d) H_2, Pd/c, MeOH/H_2O, 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 H_2SO_4/MoO_3 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 H_2O/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 ^{13}C NMR spectra were acquired on a Brucker DRX-500 spectrometer and chemical shifts are given in ppm (δ) relative to tetramethylsilane as an internal reference or relative to D_2O. 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 $NaHCO_3$ 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 $MgSO_4$, 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. $[\alpha]_D$ 32.7 ($c = 1.0$, $CHCl_3$). ^1H-RMN ($CDCl_3$,): δ 7.36–7.19 (m, 37H, Ar*H*), 7.18–7.13 (m, 3H, Ar*H*), 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, C$H_{benzyl.}$), 4.89 (d, $J = 10.5$ Hz, 1H, C$H_{benzyl.}$), 4.88 (d, $J = 10.5$ Hz, 1H, C$H_{benzyl.}$), 4.84 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.737 (d, $J = 10.5$ Hz, 2H, 2 × C$H_{benzyl.}$), 4.735 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.71 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.673 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.668 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.53 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.45 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.38 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.32 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.25 (d, $J = 12.5$ Hz, 1H, C$H_{benzyl.}$), 4.24 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 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, $3 \times (CH_3)_2CH$ *TIPS* $+ 3 \times (CH_3)_2CH$ *TIPS*). ^{13}C-RMN ($CDCl_3$): δ 139.05, 138.63, 138.57 (Ar*C*), 138.43 ($2 \times$ Ar*C*), 138.29, 137.69, 137.54 (Ar*C*), 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 (Ar*C*H), 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 ($CH_{2\,benzyl.}$), 74.15 ($C_{4c} + C_{5c}$), 73.04, 72.71 ($CH_{2\,benzyl.}$), 72.66 (C_{1a}), 72.08, 72.02 ($CH_{2\,benzyl.}$), 71.14 (C_{5b}), 69.46 (C_{2a}), 68.56 (C_{6b}), 64.43 (C_{2b}), 62.54 (C_{6c}), 17.99, 17.93 (($CH_3)_2$CH *TIPS*), 11.97 ((C$H_3)_2$CH *TIPS*). FAB$^+$ calcd. for $C_{83}H_{99}O_{15}N_3Si$: $M^+ = 1405.69$, $[M + Na]^+ = 1428.68$. Found: m/z 1428 $[M + Na]^+$. Anal. calcd. for $C_{83}H_{99}O_{15}N_3Si$: 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 → 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1 → 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→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→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**: $[\alpha]_D + 41.5$ ($c = 0.7$, $CHCl_3$). ^{1}H-RMN ($CDCl_3$): δ 7.38–7.16 (m, 37H, Ar*H*), 7.13 (m, 2H, Ar*H*), 7.07 (m, 1H, Ar*H*), 5.96 (ddt, $J_1 = 6.0$ Hz, $J_2 = 10.5$ Hz, $J_3 = 17.0$ Hz, 1H, H_2), 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, H_3), 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, C$H_{benzyl.}$), 4.896 (d, $J = 12.5$ Hz, 1H, C$H_{benzyl.}$), 4.895 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.89 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.76 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.75 (d, $J = 12.5$ Hz, 1H, C$H_{benzyl.}$), 4.73 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.72 (d, $J = 12.5$ Hz, 1H, C$H_{benzyl.}$), 4.69 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.61 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.55 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.45 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.40 (d, $J = 12.0$ Hz, 1H,

$CH_{benzyl.}$), 4.35 (d, $J = 12.0$ Hz, 1H, $CH_{benzyl.}$), 4.31 (d, $J = 12.0$ Hz, 1H, $CH_{benzyl.}$), 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, $CH_{benzyl.}$), 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, $OH_{ax.}$), 1.03–0.95 (m, 21H, $3 \times (CH_3)_2CH$ *TIPS* + $3 \times (CH_3)_2$-CH *TIPS*). ^{13}C-RMN ($CDCl_3$,): δ 139.34, 138.78, 138.74 (Ar*C*), 138.47 ($2 \times$ Ar*C*), 138.17 (Ar*C*), 137.82 ($2 \times$ Ar*C*), 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 (Ar*C*H), 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 ($CH_{2\,benzyl.}$), 74.66 (C_{6a}), 74.08 (C_{4c}), 73.90 (C_{5c}), 73.58, 73.03, 72.77, 72.14, 71.94 ($CH_{2\,benzyl.}$), 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)$_2$CH *TIPS*), 11.98 ((CH_3)$_2$*C*H *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**: $[\alpha]_D + 34.1$ ($c = 0.6$ $CHCl_3$). ^{1}H-RMN ($CDCl_3$): δ 7.35–7.18 (m, 37H, Ar*H*), 7.16–7.10 (m, 3H, Ar*H*), 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, $CH_{benzyl.}$), 4.90 (d, $J = 10.5$ Hz, 2H, $2 \times CH_{benzyl.}$), 4.86 (d, $J = 11.0$ Hz, 1H, $CH_{benzyl.}$), 4.78 (d, $J = 10.5$ Hz, 2H, $2 \times CH_{benzyl.}$), 4.70 (s, 2H, CH_2 benzyl.), 4.68 (d, $J = 11.0$ Hz, 1H, $CH_{benzyl.}$), 4.65 (d, $J = 11.5$ Hz, 1H, $CH_{benzyl.}$), 4.54 (d, $J = 12.0$ Hz, 1H, $CH_{benzyl.}$), 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, $CH_{benzyl.}$), 4.35 (d, $J = 12.5$ Hz, 1H, $CH_{benzyl.}$), 4.34 (d, $J = 11.5$ Hz, 1H, $CH_{benzyl.}$), 4.28 (d, $J = 11.5$ Hz, 1H, $CH_{benzyl.}$), 4.222 (d, $J = 12.5$ Hz, 1H, $CH_{benzyl.}$), 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 (Ar*C*), 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 (Ar*C*H), 117.15 (C_3), 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 ($CH_{2\,benzyl.}$), 74.12 (C_{5c}), 74.10 (C_{4c}), 73.86 (C_1), 73.25 (C_{1a}), 73.01, 72.96, 72.06, 72.05 ($CH_{2\,benzyl.}$), 70.71 (C_{5b}), 68.56 (C_{6b}), 64.07 (C_{2b}), 62.50 (C_{6c}), 18.00, 17.94 (($CH_3)_2$CH *TIPS*), 11.98 (($CH_3)_2$CH *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 → 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 (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 μL, 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 × 25) and the combined organic phases were washed with saturated NaCl solution (3 × 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. $[\alpha]_D + 46.5$ ($c = 0.8$, $CHCl_3$). ^{1}H-RMN ($CDCl_3$): δ 7.41 (m, 2H, Ar*H*), 7.36–7.11 (m, 42H, Ar*H*), 7.07 (m, 1H, Ar*H*), 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 × $CH_{benzyl.}$), 4.83 (s, 2H, $CH_{2\,benzyl.}$), 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, $3 \times (CH_3)_2CH$ *TIPS* + $3 \times (CH_3)_2CH$ *TIPS*). ^{13}C-RMN ($CDCl_3$): δ 139.37 (Ar*C*), 138.76 ($2 \times$ Ar*C*), 138.54, 138.43, 138.33, 138.23, 137.86 (Ar*C*), 134.20 (C_2), 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 (Ar*C*H), 117.01 (C_3), 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 ($CH_{2\,\text{benzyl.}}$), 75.36 (C_{6a}), 75.24, 74.74 ($CH_{2\,\text{benzyl.}}$), 74.03 ($CH_{2\,\text{benzyl.}}$ - C_{4c}), 73.88 (C_{5c}), 73.63, 73.02, 72.80 ($CH_{2\,\text{benzyl.}}$), 72.72 (C_{2a}), 72.13, 71.92 ($CH_{2\,\text{benzyl.}}$), 70.76 (C_1), 69.86 (C_{5b}), 68.47 (C_{6b}), 63.17 (C_{2b}), 62.37 (C_{6c}), 17.99, 17.93 ($(CH_3)_2CH$ *TIPS*), 11.96 ($(CH_3)_2CH$ *TIPS*). FAB^+ calcd. for $C_{93}H_{109}O_{15}N_3Si$: $M^+ = 1535.77$; $[M + Na]^+ = 1558.76$. Found: m/z 1559 $[M + Na]^+$. Anal. calcd. for $C_{93}H_{109}O_{15}N_3Si$: 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 → 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 (16). TBAF (1.0 M in THF, 468 μL) 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 $NaHCO_3$ 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 $MgSO_4$, 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. $[\alpha]_D + 54.2$ ($c = 1.0$, $CHCl_3$). ^{1}H-RMN ($CDCl_3$): δ 7.42 (m, 2H, Ar*H*), 7.38–7.16 (m, 40H, Ar*H*), 7.13–7.05 (m, 3H, Ar*H*), 5.94 (ddt, $J_1 = 5.5$ Hz, $J_2 = 10.5$ Hz, $J_3 = 17.5$ Hz, 1H, H_2), 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, H_3), 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, $CH_{\text{benzyl.}}$), 4.94 (broad d, $J = 10.5$ Hz, 2H, $2 \times CH_{\text{benzyl.}}$), 4.88 (d, $J = 11.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.85 (s, 2H, $CH_{2\,\text{benzyl.}}$), 4.75 (d, $J = 10.5$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.69 (d, $J = 11.5$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.68 (d, $J = 12.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.63 (broad d, $J = 12.0$ Hz, 2H, $2 \times$ C *H*benzyl.), 4.60 (d, $J = 11.5$ Hz, 2H, $2 \times CH_{\text{benzyl.}}$), 4.51 (d, $J = 12.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.48 (d, $J = 12.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.39 (d, $J = 12.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 4.32 (d, $J = 12.0$ Hz, 1H, $CH_{\text{benzyl.}}$), 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, $CH_{\text{benzyl.}}$), 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, H_1), 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 (Ar*C*), 138.45 (2 × Ar*C*), 138.31, 138.20, 138.16, 138.88 (Ar*C*), 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 (Ar*C*H), 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 ($CH_{2\,benzyl.}$), 75.52 (C_{6a}), 75.23 ($CH_{2\,benzyl.}$), 74.86 (C_{4c}), 74.71, 74.06, 73.94, 73.56 ($CH_{2\,benzyl.}$), 73.23 (C_{5c}), 72.81 ($CH_{2\,benzyl.}$), 72.73 (C_{2a}), 72.37, 72.18 ($CH_{2\,benzyl.}$), 70.77 (C_1), 70.05 (C_{5b}), 67.94 (C_{6b}), 63.36 (C_{2b}), 62.24 (C_{6c}). FAB$^+$ calcd. for $C_{84}H_{89}O_{15}N_3$: $M^+ = 1379.63$; $[M + Na]^+ = 1402.62$. Found: m/z 1402 $[M + Na]^+$. Anal. calcd. for $C_{84}H_{89}O_{15}N_3 \cdot H_2O$: 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 → 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 redisolved 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 ß anomers. *Data for the α anomer*: ^{1}H-RMN ($CDCl_3$): δ 8.52 (s, 1H, OCN*H*CCl_3), 7.36–7.14 (m, 35H, Ar*H*), 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 × C$H_{benzyl.}$), 4.70 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.69 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.66 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.64 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.60 (broad d, $J = 12.5$ Hz, 2H, 2 × C$H_{benzyl.}$), 4.56 (d, $J = 12.5$ Hz, 1H, C$H_{benzyl.}$), 4.51 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.504 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.497 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.49 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.46 (d, $J = 12.0$ Hz, 1H, CH_{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 (O*C*NHCCl_3), 138.57, 138.52 (Ar*C*), 138.41 (2 × Ar*C*), 138.33, 138.15, 137.82 (Ar*C*), 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 (Ar*C*H), 99.59 (C_{1e}), 96.83 (C_{1d}), 90.94 (OCNH*C*Cl_3), 79.74 (C_{3e}), 78.97 (C_{3d}), 75.31, 74.92 (*C*$H_{2\,benzyl.}$), 74.88 (C_{2e}), 74.84 (C_{4e}), 74.78 (C_{4d}), 74.12 (C_{5d}), 73.34, 73.23, 72.72 (*C*$H_{2\,benzyl.}$), 72.69 (C_{2d}), 72.29 (C_{5e}), 72.26, 72.24 (*C*$H_{2\,benzyl.}$), 69.02 (C_{6e}), 68.75 (C_{6d}). Coupled ^{13}C-RMN ($CDCl_3$): δ 99.59 (d, $J_{C\text{-}H} = 172.3$ Hz, C_{1e}), 96.83 (d, $J_{C\text{-}H} = 178.1$ 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 Et_2O, 66 μL) was added and the reaction mixture stirred for 1 hr. Then the mixture was neutralized with Et_3N 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**: $[\alpha]_D + 49.4$ ($c = 1.1$, $CHCl_3$). ^{1}H-RMN (C_6D_6): δ 7.49–7.42 (m, 8H, Ar*H*), 7.40–7.26 (m, 25H, Ar*H*), 7.24–6.97 (m, 47H, Ar*H*), 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, H_2), 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, H_3), 5.18 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzyl.}$), 5.13 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzyl.}$), 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, C*H*$_{benzyl.}$), 4.98 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzyl.}$), 4.95 (broad d, $J = 12.0$ Hz, 3H, 3 × C*H*$_{benzyl.}$), 4.89 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.84 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.77 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.72 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzyl.}$), 4.71 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzyl.}$), 4.68 (d, $J = 12.5$ Hz, 1H, C*H*$_{benzyl.}$), 4.664 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.656 (t, $J = 9.5$ Hz, 1H, H_{6a}), 4.62 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.60 (broad s, 2H, C$H_{2\,benzyl.}$), 4.59 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.55 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.54 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.49 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.46 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzyl.}$), 4.45 (broad s, 2H, C$H_{2\,benzyl.}$), 4.44 (m, 1H, H_{5b}), 4.43 (d, $J = 12.5$ Hz, 1H, C*H*$_{benzyl.}$), 4.42 (d, $J = 11.5$ Hz, 2H, 2 × C*H*$_{benzyl.}$), 4.41 (d, $J = 12.5$ Hz, 1H, C*H*$_{benzyl.}$), 4.38 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzyl.}$), 4.37 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzyl.}$), 4.36 (t, $J = 9.5$ Hz, 1H, H_{4c}), 4.33 (m, 3H, $H_{2d} + 2 \times$ C*H*$_{benzyl.}$), 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, H_1), 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}). ^{13}C-RMN (C_6D_6): δ 140.25 (2 × Ar*C*), 140.22 (Ar*C*), 140.15 (3 × Ar*C*), 140.07 (2 × Ar*C*), 139.95 (Ar*C*), 139.88 (2 × Ar*C*), 139.82, 139.55, 139.52, 139.47, 139.07 (Ar*C*), 135.46 (C_2), 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 (Ar*C*H), 117.62 (C_3), 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 (*C*H$_{2\,\text{benzyl.}}$), 76.33 (C_{6a}), 76.26 (C_{2d}), 75.97, 75.95, 75.91 (*C*H$_{2\,\text{benzyl.}}$), 75.84 (C_{4e}), 75.80 (C_{4d}), 75.75 (C_{4c}), 75.07, 74.36, 74.21, 74.04 (*C*H$_{2\,\text{benzyl.}}$), 73.84 (C_{5e}), 73.80 (*C*H$_{2\,\text{benzyl.}}$), 73.77 (C_{2a}), 73.61 (C_{5c}), 73.52 (*C*H$_{2\,\text{benzyl.}}$), 73.44 (C_{5d} + *C*H$_{2\,\text{benzyl.}}$), 73.11, 72.90, 72.73, 72.31 (*C*H$_{2\,\text{benzyl.}}$), 71.61 (C_1), 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 ^{13}C-RMN (C_6D_6): δ 101.43 (d, $J_{C\text{-}H} = 168.8$ Hz, C_{1c}), 101.21 (d, $J_{C\text{-}H} = 168.4$ Hz, C_{1e}), 100.85 (d, $J_{C\text{-}H} = 170.5$ Hz, C_{1d}), 98.80 (d, $J_{C\text{-}H} = 175.5$ Hz, C_{1b}). FAB$^+$ calcd. for $C_{145}H_{151}O_{25}N_3$ $M^+ = 2333.89$; $[M + Na]^+ = 2356.88$. Found: m/z 2357 $[M + Na]^+$. Anal: calcd. for $C_{141}H_{151}O_{25}N_3$: C, 74.56: H, 5.62; N, 1.80. Found: C, 74.17; H, 6.85; N, 1.52.

Data for **19**: $[\alpha]_D + 26.8$ ($c = 0.6$, $CHCl_3$. ^{1}H-RMN (C_6D_6): δ 7.46 (m, 6H, Ar*H*), 7.41–7.23 (m, 26H, Ar*H*), 7.20–6.96 (m, 48H, Ar*H*), 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, H_2), 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, H_3), 5.13 (d, $J = 11.0$ Hz, 1H, C*H*$_{\text{benzyl.}}$), 5.11 (broad d, $J = 10.5$ Hz, 1H, $H_{3'}$), 4.99 (broad d, $J = 11.0$ Hz, 4H, 4 × C*H*$_{\text{benzyl.}}$), 4.98 (d, $J = 11.0$ Hz, 1H, C*H*$_{\text{benzyl.}}$), 4.96 (d, $J = 11.0$ Hz, 1H, C*H*$_{\text{benzyl.}}$), 4.87 (d, $J = 12.0$ Hz, 1H, C*H*$_{\text{benzyl.}}$), 4.81 (d, $J = 12.0$ Hz, 1H, C*H*$_{\text{benzyl.}}$), 4.78 (d, $J = 12.0$ Hz, 1H, C*H*$_{\text{benzyl.}}$), 4.74 (d, $J = 11.5$ Hz, 1H, C*H*$_{\text{benzyl.}}$), 4.71 (m, 1H, H_{5e}), 4.70 (d, $J = 11.0$ Hz, 2H, 2 × C*H*$_{\text{benzyl.}}$), 4.69 (d, $J = 11.0$ Hz, 1H, C*H*$_{\text{benzyl.}}$), 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 × C*H*$_{\text{benzyl.}}$), 4.57 (broad d, $J = 11.5$ Hz, 2H, 2 × C*H*$_{\text{benzyl.}}$), 4.56 (t, $J = 9.5$ Hz, 1H, H_{4e}), 4.53 (broad s, 2H, C*H*$_{2\,\text{benzyl.}}$), 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, $CH_{2\,benzyl.}$), 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, H_1), 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}). ^{13}C-RMN (C_6D_6): δ 140.62, 140.50, 140.46, 140.25, 140.21, 140.20, 140.16, 140.13, 139.98 (Ar*C*), 139.86 (3 × Ar*C*), 139.53, 139.45, 139.19, 139.12 (Ar*C*), 135.40 (C_2), 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 (Ar*C*H), 117.70 (C_3), 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 ($CH_{2\,benzyl.}$), 76.47 (C_{4c}), 76.33 ($CH_{2\,benzyl.}$), 76.17 (C_{4e}), 76.06 (C_{6a}), 75.81 (C_{4d} - 2 × $CH_{2\,benzyl.}$), 75.62, 75.03 ($CH_{2\,benzyl.}$), 74.51 (C_{5c}), 74.33, 74.30, 74.21, 74.05 ($CH_{2\,benzyl.}$), 73.81 (C_{2a}), 73.76 (C_{5e}), 73.51 ($CH_{2\,benzyl.}$), 73.46 (C_{2d}), 73.41 ($CH_{2\,benzyl.}$), 73.12 ($CH_{2\,benzyl.}$), 73.09 (2 × $CH_{2\,benzyl.}$), 72.77 ($CH_{2\,benzyl.}$), 71.62 (C_1), 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 ^{13}C-RMN (C_6D_6): δ 101.56 (d, $J_{C\text{-}H} = 156.0$ Hz, C_{1d}), 101.00 (d, $J_{C\text{-}H} = 167.8$ Hz, C_{1c}), 99.79 (d, $J_{C\text{-}H} = 168.9$ Hz, C_{1e}), 98.67 (d, $J_{C\text{-}H} = 174.8$ Hz, C_{1b}). FAB$^+$ calcd. for $C_{145}H_{151}O_{25}N_3$; $M^+ = 2333.89$; $[M + Na]^+ = 2356.88$. Found: m/z 2359 $[M + Na + 2]^+$.

2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl-(1 → 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)-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 μL) of a solution of [(1,5-cyclooctadiene)-bis-(methyl-diphenylphosphine)-iridium], hexafluorophosphate (4 mg, 4.7×10^{-3} mmol) in THF (390 μL), previously treated with H_2, 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 μL, 10.214 mmol) and stirred for 10 min at rt. The mixture was then diluted with AcOEt (25 mL), washed with saturated $NaHCO_3$ solution (2 × 25 mL) and NaCl (3 × 25 mL), dried over $MgSO_4$, 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 $CHCl_3$). ^{1}H-RMN (C_6D_6): δ 7.49–6.97 (m, 80H, Ar*H*), 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, C$H_{benzyl.}$), 5.09 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 5.05 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.99 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.97 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.95 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.94 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.84 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.82 (d, $J = 12.0$ Hz, 1H, C$H_{benzyl.}$), 4.78 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.71 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.68 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.67 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.65 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.60 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.59 (broad s, 2H, C$H_{2\,benzyl.}$), 4.56 (d, $J = 11.0$ Hz, 1H, C$H_{benzyl.}$), 4.54 (d, $J = 10.5$ Hz, 1H, C$H_{benzyl.}$), 4.51 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.48 (d, $J = 11.5$ Hz, 1H, C$H_{benzyl.}$), 4.45–4.30 (m, 11H, 11 × C$H_{benzyl.}$), 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, $H_{6e'}$), 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}). ^{13}C-RMN (C_6D_6, 125 MHz): δ 139.54 (2 × Ar*C*), 139.49 (3 × Ar*C*), 139.47, 139.40 (Ar*C*), 139.27 (2 × Ar*C*), 139.23, 139.20, 139.09, 139.04, 138.90, 138.82, 138.25 (Ar*C*), 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 (Ar*C*H), 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 (C3d), 77.41 (C_{2a}), 76.86 (C_{2c}), 76.80 (C_{4b}), 76.01 (C_{2e}), 75.73 (2 × *C*$H_{2\,benzyl.}$), 75.64 (C_{4e}), 75.40, 75.34 (*C*$H_{2\,benzyl.}$), 75.20 (C_{2d}), 75.17 ($C_{4c} + 2 \times$ *C*$H_{2\,benzyl.}$), 75.15 (C_{4d}), 74.13, 73.76 (*C*$H_{2\,benzyl.}$), 73.70 (C_{1a}), 73.59, 73.40 (*C*$H_{2\,benzyl.}$), 73.17 (C_{5c}), 73.15 (C_{5e}), 72.82 (2 × *C*$H_{2\,benzyl.}$), 72.77 (C_{5d}), 72.68, 72.29, 72.11, 71.79 (*C*$H_{2\,benzyl.}$), 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 $C_{142}H_{147}O_{25}N_3$: $M^+ = 2294.03$, $[M + Na]^+ = 2317.02$. Found: m/z 2317 $[M + Na]^+$.

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*-(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 CH_2Cl_2 (200 μL), phosphoramidite **10**[11] (0.2 M in CH_2Cl_2, 200 μL) 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 Et_3N (10% solution in CH_2Cl_2) and fractionated using three preparative TLC plates previously treated with Et_3N (hexane/AcOEt 3/1) to obtain **21** (51 mg, 86%) as a mixture of two diastereomers I and II 1:0.2. ^{1}H-RMN (C_6D_6): δ 7.60–7.01 (m, 153H, 85 × ArH_{I} + 85 × 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, C$H_{\mathrm{benzyl.I}}$ *phosphate*), 5.24–4.92 (m, 18.8H, 10 × $H_{\mathrm{benzyl.I}}$ + 10 × C$H_{\mathrm{benzyl.II}}$ + C$H_{\mathrm{benzyl.\ II}}$ *phosphate*), 4.88 (broad s, 0.8H, H_{2aII}), 4.81–4.62 (m, 10.8H, 6 × C$H_{\mathrm{benzyl.\ I}}$ + 6 × C$H_{\mathrm{benzyl.\ II}}$), 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 × C$H_{\mathrm{benzyl.\ I}}$ + 6 × C$H_{\mathrm{benzyl.\ II}}$), 4.47 (m, 1H, H_{5bI}), 4.46 (m, 0.8H, H_{5bII}), 4.46–4.30 (m, 18.8H, 10 × C$H_{\mathrm{benzyl.\ I}}$ + 11 × C$H_{\mathrm{benzyl.\ II}}$), 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, $H_{3I} + H_{3'I}$), 4.10 (dd, $J_1 = 4.5$ Hz, $J_2 = 11.0$ Hz, 1H, $H_{1'I}$), 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, $H_{6c'I} + H_{6c'II} + H_{6e'I} + H_{6e'II}$), 3.65 (broad s, 3.6H, $H_{6bI} + H_{6bII} + H_{6b'I} + H_{6b'II}$), 3.64 (broad d, $J = 11.0$ Hz, 1.8H, $H_{6d'I} + H_{6d'II}$), 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 × OCOC$H_{2\ \alpha II}$), 2.17 (m, 4H, 2 × OCOC$H_{2\ \alpha I}$), 1.58 (m, 7.2H, 2 × C$H_{2\ \beta I}$ + 2 × C$H_{2\ \beta II}$), 1.37–1.16

(m, 72H, 2 × 10 × C$H_{2\ I}$ + 2 × 10 × C$H_{2\ II}$), 0.91 (t, J = 7.0 Hz, 10.8H, 2 × C$H_{3\ I}$ + 2 × C$H_{3\ II}$). ^{13}C-RMN (C_6D_6): δ 173.45, 173.42, 173.34, 173.33 (O*C*O$C_{13}H_{27}$), 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 (Ar*C*), 137.06 (d, $J_{C\text{-}P}$ = 5.5 Hz, ArC_I *phosphate*), 136.89 (d, $J_{C\text{-}P}$ = 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 (Ar*C*H), 101.81 (C_{1cII}), 101.73 (C_{1cI}), 101.21 (C_{1eI} + C_{1eII}), 100.88 (C_{1dI} + C_{1dII}), 98.80 (C_{1bI}), 98.73 (C_{1bII}), 82.62 (C_{4aII}), 82.57 (C_{4aI}), 82.33 (C_{5aII}), 82.24 (C_{5aI}), 81.72 (C_{3aII}), 81.53 (C_{3aI}), 81.40 (C_{3eI} + C_{3eII}), 81.14 (m, C_{1aII} + C_{3cI} + C_{3cII}), 81.00 (m, C_{1aI}), 80.59 (C_{3bII}), 80.56 (C_{3bI}), 80.38 (C_{3dI} + C_{3dII}), 78.11 (C_{4bII}), 78.01 (C_{4bI}), 77.94 (C_{2aI}), 77.76 (C_{2aII}), 77.58 (C_{2cI} + C_{2cII}), 76.98, 76.90 (*C*H$_{2\ benc}$), 76.63 (C_{2eI} + C_{2eII} + *C*H$_{2\,benzyl.}$), 76.48, 76.42, 76.35 (*C*H$_{2\,benzyl.}$), 76.32 (C_{2dI} + C_{2dII} + 2 × *C*H$_{2\,benzyl.}$), 75.94 (3 × *C*H$_{2\,benzyl.}$), 75.89 (*C*H$_{2\,benzyl.}$), 75.83 (C_{6aI} + C_{6aII} + 2 × *C*H$_{2\,benzyl.}$), 75.77 (C_{4dI} + C_{4dII} + C_{4eI} + C_{4eII}), 75.70 (C_{4cI} + C_{4cII}), 74.29, 74.27 (*C*H$_{2\,benzyl.}$), 74.20 (2 × *C*H$_{2\,benzyl.}$), 74.04 (2 × *C*H$_{2\,benzyl.}$), 73.97 (*C*H$_{2\,benzyl.}$), 73.79 (C_{5eI} + C_{5eII}), 73.62 (C_{5cI} + C_{5cII}), 73.53, 73.46 (*C*H$_{2\,benzyl.}$), 73.43 (C_{5dI} + C_{5dII} + 2 × *C*H$_{2\,benzyl.}$), 73.17, 73.15 (*C*H$_{2\,benzyl.}$), 72.85 (2 × *C*H$_{2\ benc}$), 72.72 (2 × *C*H$_{2\,benzyl.}$), 72.29 (2 × *C*H$_{2\,benzyl.}$), 71.59 (C_{5bI}), 71.57 (C_{5bII}), 70.90 (d, $J_{C\text{-}P}$ = 6.0 Hz, C_{2II}), 70.86 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*H$_{2\,benzyl.I}$ *phosphate*), 70.71 (C_{6eI} + C_{6eII}), 70.62 (d, $J_{C\text{-}P}$ = 7.1 Hz, C_{2I}), 70.55 (d, $J_{C\text{-}P}$ = 5.6 Hz, *C*H$_{2benzyl.II}$ *phosphate*), 70.32 (C_{6dI} + C_{6dII}), 70.07 (C_{6bII}), 70.04 (C_{6bI}), 68.05 (C_{6cI} + C_{6cII}), 66.65 (d, $J_{C\text{-}P}$ = 6.3 Hz, C_{3II}), 66.56 (d, $J_{C\text{-}P}$ = 5.4 Hz, C_{3I}), 63.81 (C_{2bII}), 63.69 (C_{2bI}), 62.50 (C_{1II}), 62.45 (C_{1I}), 35.02, 34.96, 34.76, 34.71 (OCO*C*H$_{2\,\alpha}$), 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 (*C*H$_2$), 25.85, 25.82 (*C*H$_{2\,\beta}$), 25.80 (2 × *C*H$_{2\,\beta}$), 23.70 (4 × *C*H$_2$), 14.96 (4 × *C*H$_3$). ^{31}P-RMN (C_6D_6, 202 MHz): δ –1.15 (P^*_I),–1.50 (P^*_{II}). FAB$^+$ calcd. for $C_{180}H_{212}O_{32}N_3P$: M^+ = 2958.47; $[M + Na]^+$ = 2981.46. Found: m/z 2982 $[M + Na]^+$.

α-D-Mannopyranosyl-(1 → 2)-α-D-mannopyranosyl-(1 → 6)-α-D-mannopyranosyl-(1 → 4)-2-ammonio-2-deoxy-α-D-glucopyranosyl-(1 → 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/H_2O (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. $[\alpha]_D$ + 29.1 (c = 0.2, MeOH). ^{1}H-RMN (CD_3OD): δ 5.54 (d, J = 4.0 Hz, 1H, H_{1b}), 5.29 (m, 1H, H_2), 5.27 (d, J = 1.5 Hz, 1H, H_{1c}), 5.16 (d, J = 1.5 Hz, 1H, H_{1d}), 5.02 (d, J = 2.0 Hz, 1H, H_{1e}), 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, H_{5b}), 4.23 (dd, J_1 = 7.0 Hz, J_2 = 12.0 Hz, 1H, $H_{1'}$), 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, $H_3 + H_{3'}$), 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, OCOC$H_{2\ \alpha}$), 2.34 (t, $J = 7.5$ Hz, 2H, OCOC$H_{2\ \alpha}$), 1.64 (m, 4H, $2 \times$ C$H_{2\ \beta}$), 1.32 (m, 40H, $2 \times 10 \times$ CH_2), 0.93 (t, $J = 7.0$ Hz, 6H, $2 \times$ CH_3). ^{13}C-RMN (CD_3OD, 125 MHz): δ 175.00, 174.72 (O*C*O$C_{13}H_{27}$), 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, $J_{C\text{-}P} = 6.1$ 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 (C_2), 71.72 (C_{3b}), 69.05 (C_{4d}), 68.76 (C_{4e}), 68.56 (C_{4c}), 68.06 (C_{6c}), 65.02 (C_3), 63.70 (C_1), 63.02 ($C_{6d} + C_{6e}$), 62.06 (C_{6b}), 56.04 (C_{2b}), 35.12, 34.95 (OCO*C*H$_{2\ \alpha}$), 33.09, 30.83, 30.79, 30.69, 30.67, 30.50, 30.24, 30.21 (*C*H$_2$), 26.05, 26.02 (*C*H$_{2\ \beta}$), 23.74 ($2 \times$ *C*H$_2$), 14.44 ($2 \times$ *C*H$_3$). ^{31}P-RMN (CD_3OD, 202 MHz): δ −0.81. FAB$^+$ HRMS calcd. for $C_{61}H_{112}O_{32}NP$: $M^+ = 1401.6873$; $[M + H]^+ = 1402.7143$; $[M + Na]^+ = 1424.6961$. Found: m/z 1402.6983 $[M + H]^+$; 1424.6803 $[M + Na]^+$.

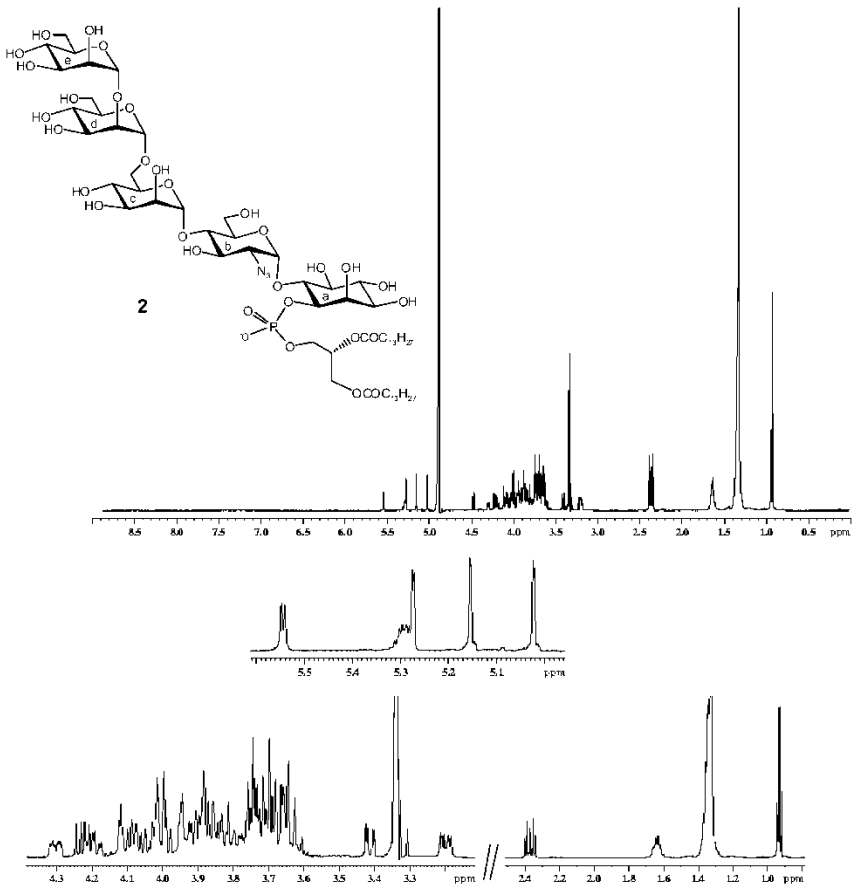
α-D-Mannopyranosyl-(1 → 2)-α-D-mannopyranosyl-(1 → 6)-α-D-mannopyranosyl-(1 → 4)-2-ammonio-2-deoxy-α-D-glucopyranosyl-(1 → 6)-D-*myo*-inositol (3). A suspension of **20** (30 mg, 0.013 mmol) in a 9/1 MeOH/H_2O mixture (6.5 mL) was hydrogenated with stirring for 12 hr in the presence of 10% Pd on charcoal (69 mg, 0.065 mmol). The mixture was filtered over Celite and evaporated to dryness. The residue was dissolved in H_2O 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, H_2O). ^{1}H-RMN (D_2O): 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

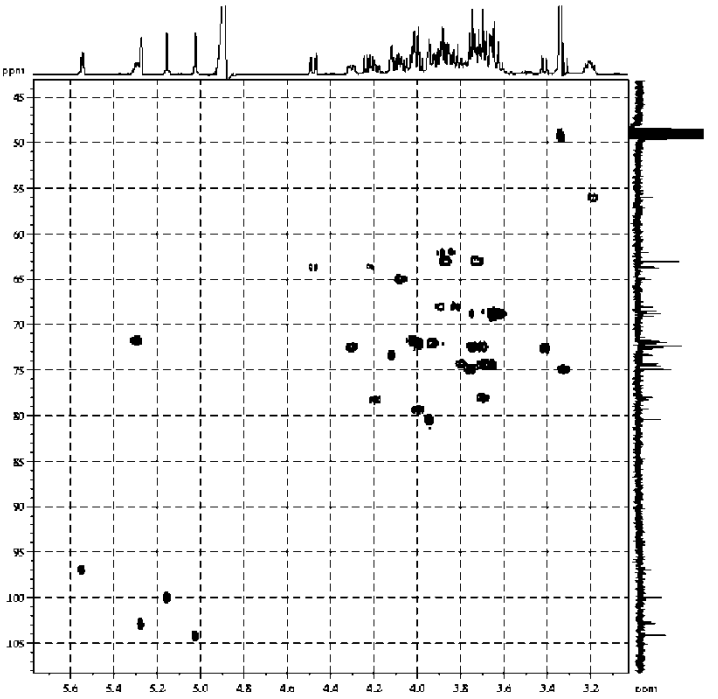
(t, $J = 9.5\,Hz$, 1H, H_{4e}), 3.49 (dd, $J_1 = 2.5\,Hz$, $J_2 = 10.0\,Hz$, 1H, H_{3a}), 3.35 (m, 1H, H_{5a}), 3.27 (dd, $J_1 = 3.5\,Hz$, $J_2 = 10.5\,Hz$, 1H, H_{2b}). ^{13}C-RMN (C_6D_6): δ 101.91 (C_{1e}), 101.50 (C_{1c}), 97.95 (C1d), 96.59 (C_{1b}), 79.92 (C_{6a}), 78.24 (C_{2d}), 76.30 (C_{4b}), 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 $C_{30}H_{53}O_{25}N$: $M^+ = 827.2890$; $[M + Na]^+ = 850.2788$. Found: m/z 850.2796 $[M + Na]^+$.

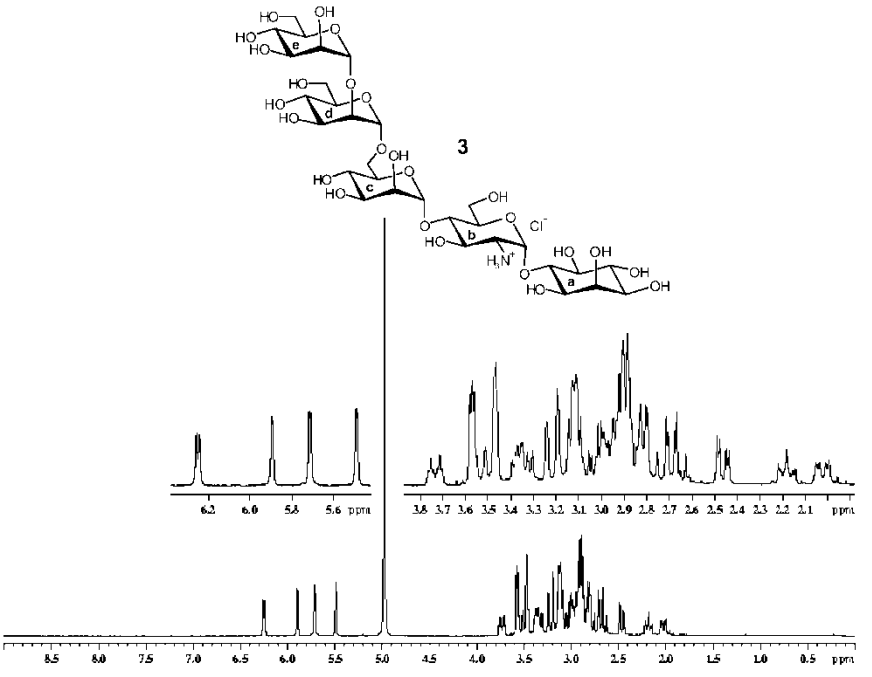
SUPPORTING INFORMATION

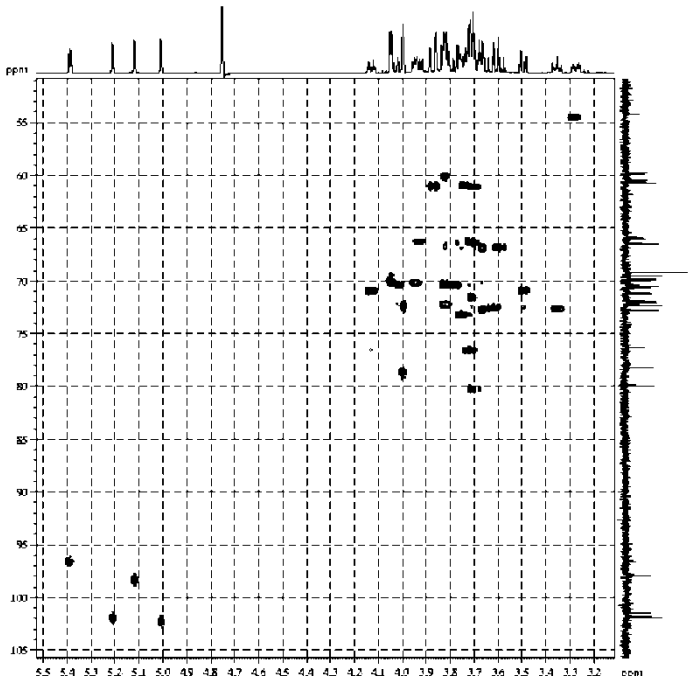
RMN Spectra

^{1}H-RMN and HSQC spectra of GPI **2** and pseudopentasaccharide **3** acquired on a Bruker DRX-500 spectrometer in CD_3OD 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.

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