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Design and synthesis of inositolphosphoglycan putative insulin mediators†

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The binding modes of a series of molecules, containing the glucosamine (1→6) *myo*-inositol structural motif, into the ATP binding site of the catalytic subunit of cAMP-dependent protein kinase (PKA) have been analysed using molecular docking. These calculations predict that the presence of a phosphate group at the non-reducing end in pseudodisaccharide and pseudotrisaccharide structures properly orientate the molecule into the binding site and that pseudotrisaccharide structures present the best shape complementarity. Therefore, pseudodisaccharides and pseudotrisaccharides have been synthesised from common intermediates using effective synthetic strategies. On the basis of this synthetic chemistry, the feasibility of constructing small pseudotrisaccharide libraries on solid-phase using the same intermediates has been explored. The results from the biological evaluation of these molecules provide additional support to an insulin-mediated signalling system which involves the intermediacy of inositolphosphoglycans as putative insulin mediators.

Introduction

An intracellular signalling mechanism which involves inositolphosphoglycans (IPGs) as intracellular mediators has been postulated for insulin as well as for several growth factors, classical hormones and cytokines.[1] IPGs are incompletely characterised molecules which are generated after the binding of these agonists to their receptors and act as second messengers which modulate the activity of a number of enzymes and mediate a variety of cellular events. The precise structures of IPGs have not been determined but two main groups have been proposed on the basis of chemical composition and biological activity data. Type-A IPGs inhibit cAMP-dependent protein kinase (PKA) and contain *myo*-inositol and D-glucosamine,[2] while type-P IPGs activate pyruvate dehydrogenase phosphatase (PDHPase) and contain *chiro*-inositol and D-galactosamine.[3] Both groups may additionally contain different sugars and phosphate groups. For type-P IPGs a structure of 4-*O*-(2-amino-2-deoxy-β-D-galactopyranosyl)-3-*O*-methyl-D-*chiro*-inositol **1** (Fig. 1) has been proposed in a recent study.[4]

This molecule, which could be a member of a family of closely related *chiro*-inositol containing oligosaccharides, activated PDHPase *in vitro* when chelated to Mn^{2+} and decreased *in vivo* blood glucose in diabetic rats in a dose dependent manner.[4] For type-A IPGs a close structural similarity with the glycosylphosphatidyl inositols (GPIs), which anchor proteins to the outer face of cellular membranes (GPI anchors), has been proposed.[5] However, we have previously synthesised compound **2**,[6] which contains the conserved pseudopentasaccharide structure of the GPI anchors,[7] and found that this molecule does not show significant activity with regards to either inhibiting PKA or activating PDHPase. Nevertheless, insulin-like activity has been found for synthetic molecules containing the basic structural motif D-glucosaminyl (1→6) *myo*-inositol. Thus, compound **3** stimulated both lipogenesis in rat adipocites[8] and proliferative growth in the otic vesicle of chicken embryos.[9,10] In contrast, an extensive study with synthetic molecules containing the conserved GPI anchor structure and a series of variations thereof, such as **4**, has shown different insulin mimetic activities which included stimulation of lipogenesis, activation of glycogen

† Electronic supplementary information (ESI) available: Synthesis and full characterisation of compounds **43–53**, **58**, **67**, **68**, **71–73**. See http://www.rsc.org/suppdata/dt/b4/b418041k/

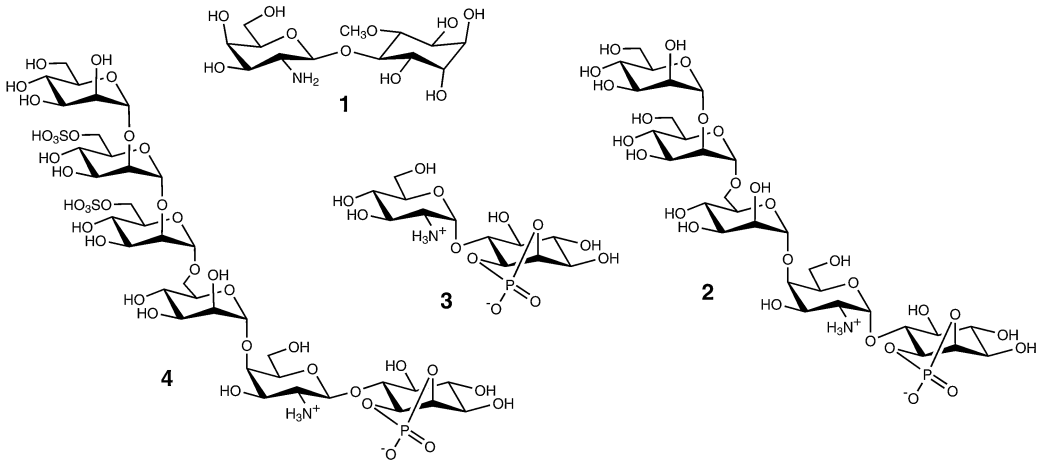

Fig. 1 Compounds **1–4**.

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synthase and glycerol-3-phosphate acyltransferase, activation of glucose transport, inhibition of lipolysis and induction of tyrosine phosphorylation of insulin receptor substrate-1.[11] All these results support the existence of an intracellular insulin-mediated signalling system, operating together with the tyrosine kinase cascade mechanism, which involves the intermediacy of putative insulin mediators.[12] They also indicate that these mediators must contain some of the structural features present in molecules **1–4**, although their precise chemical structures remain to be elucidated.

Further studies directed towards establishing the molecular basis of this postulated alternative mechanism of intracellular signal transduction have been seriously hampered by the limited amount of precise structural information. Taking into consideration that type-A IPGs are inhibitors of PKA, we reasoned that computational docking methods could be used as an additional tool to gain some insight into the structural requirements for molecules containing the structural motif D-glucosaminyl (1→6) *myo*-inositol to inhibit PKA. This information could be used to design and synthesise compounds that may show some of the biological activities which have been reported for type A-IPGs. Thus, we have performed molecular docking studies of a series of such compounds in the ATP binding site of the catalytic subunit of PKA and, according to the docking predictions, we have developed effective synthetic strategies to prepare a series of IPG-like molecules whose insulin mimetic activity has been tested. The results of this study are reported in this paper.

Results and discussion

Computational docking

Protein kinases are actually considered as major drug targets and there is a growing interest in developing protein kinase inhibitors.[13] PKA is a well characterised protein kinase.[14] Inactive PKA holoenzyme consists of two regulatory and two catalytic subunits that dissociate in response to elevated levels of intracellular cAMP. The catalytic subunit shares with other kinases a conserved catalytic core of approximately 260 amino acids and 11 invariant residues[15]. Owing to this, PKA has been used as a surrogate kinase to analyse inhibitor–kinase binding properties.[16] Therefore, the analysis of the binding modes of a set of IPG-like molecules to the catalytic subunit of PKA may provide information on the structural requirements for IPGs to display biological activity through interacting with protein kinases.

On the basis of this working hypothesis we decided to undertake studies of molecular docking, expecting that the structure of the PKA catalytic subunit will act as a template to provide structural information on IPGs. This is a similar approach to that employed in lead discovery using molecular docking.[17]

A considerable number of crystal structures of complexes involving different inhibitors and the PKA catalytic subunit have been published.[18–32] Most of these inhibitors bind to the catalytic domain and compete with ATP for binding.[33,34] ATP binds to the catalytic subunit of PKA within the active site cleft, which is formed by a large, predominantly α-helical lobe, connected by a short linker segment (residues 121–127). For the docking studies in this catalytic site, a small library of 29 IPG-like structures, some of which have been previously synthesised, was used. (Fig. 2). These pseudooligosaccharides are relatively flexible ligands[6,10,34] and require a thorough search of their conformational space. In contrast, all the reported crystalline structures of the catalytic subunit of PKA are consistently similar. Therefore, the semi-flexible Autodock programme[35] was used. To test the docking strategy, the docking of the natural inhibitor balanol **33** (Fig. 3), whose three dimensional structure complexed to the catalytic subunit of PKA has been previously reported,[36] was first studied. A series of modifications were made to achieve a good agreement between the calculated balanol conformation and that reported for balanol in the complex. With these modifications, calculations with a series of balanol derivatives whose inhibition data have been reported were subsequently carried out. The structures of these derivatives were built with Sybyl[37] and a good agreement between experimental and calculated K_i values was found (data not shown). Following this, the IPG-like pseudooligosaccharide structures **3,5–32** were examined. For the pseudooligosaccharide docking runs, the starting geometries were obtained from scratch building the structures using Sybyl.[37] References for good geometries were obtained by comparing Sybyl calculated geometries with those determined by NMR and molecular dynamics simulations for the previously synthesised compounds **3,5,14**.[10,34] Docked energies and RMS deviations are given as supporting information†.

IPG-like molecules showing the structural motif $GlcNH_2$-α-(1→6) *myo*-inositol lacking phosphate groups (compounds **5,10,12,13,28,29**) docked in the ATP binding site of the catalytic subunit of PKA. The docked geometry of these molecules showed interesting similarities with that of **33**. The cyclitol and the D-glucosamine rings superimpose respectively with the 4-hydroxybenzamide and the azepane ring of **33** and both the phenolic OH group in **33** and the 3-OH group of the *myo*-inositol unit bind to residues Glu121 and Val123 of the protein; an interaction which also takes place with the adenine unit of ATP (Fig. 4, bottom). Pseudotrisaccharides **10,12,13** seem to have the optimum molecular size for effective docking and an α-D-galactopyranosyl unit (*i.e.* **13**) seems to provide effective shape complementarity.

The presence of phosphate groups in these structures strongly determines the orientation into the binding site. When the phosphate group is sitting on the *myo*-inositol unit (compounds **3,14,24,30**) a strong interaction with Lys72 or Lys168 changes the orientation of the molecule in the binding site. This is in agreement with results obtained by calculating energy maps using a phosphate anion probe by means of GRID program[38] (see supporting information†). For effective docking, the negative charge should be located either on the glucosamine moiety (effective interaction with Lys72), on a pyranoid ring directly linked to it (effective interaction with Lys168) or on both of them (compounds **15–19,25,26,31**). In a molecule like **26**, the 3-OH and 1-OH groups of the *myo*-inositol unit interact through hydrogen bonding with Val123, Glu121 and Thr183 respectively; the phosphate groups interact with Lys72 and Lys168; and OH-2 of the terminal hexopyranose unit interacts with Phe154. These structural details are shown in Fig. 4 in comparison with the experimental X-ray diffraction data for ATP and **33**.

Molecules containing the $GlcNH_2$-β-(1→6) *myo*-inositol structural motif (**6,7,11,21,23,26**, and **27**) docked effectively in the binding site when lacking phosphate groups (compounds **6** and **11**). However, the presence of phosphate groups prevented effective docking. Steric congestion appeared to hinder effective docking of the phosphate group in these cases. In summary, a *myo*-inositol unit carrying no phosphate group linked to a α-configurated D-glucosaminyl moiety seems to be the minimum structural requirement for a type-A IPG-like molecule docking in the ATP binding site of the catalytic subunit of PKA. This α-configurated linkage could attach the D-glucosaminyl unit to any equatorially oriented OH group of the cyclitol ring. The presence of a phosphate group on this D-glucosaminyl unit seems to be important to orientate the molecule into the binding site and this effect is most pronounced when an additional hexopyranosyl unit carrying also a phosphate group is attached to the D-glucosaminyl moiety. Such a pseudotrisaccharide arrangement seems to provide the best shape complementarity.

Synthesis

On the basis of the above results we set up to synthesise compounds **8–10,13,17**, and **34–36** (Fig. 5) in an effective manner.

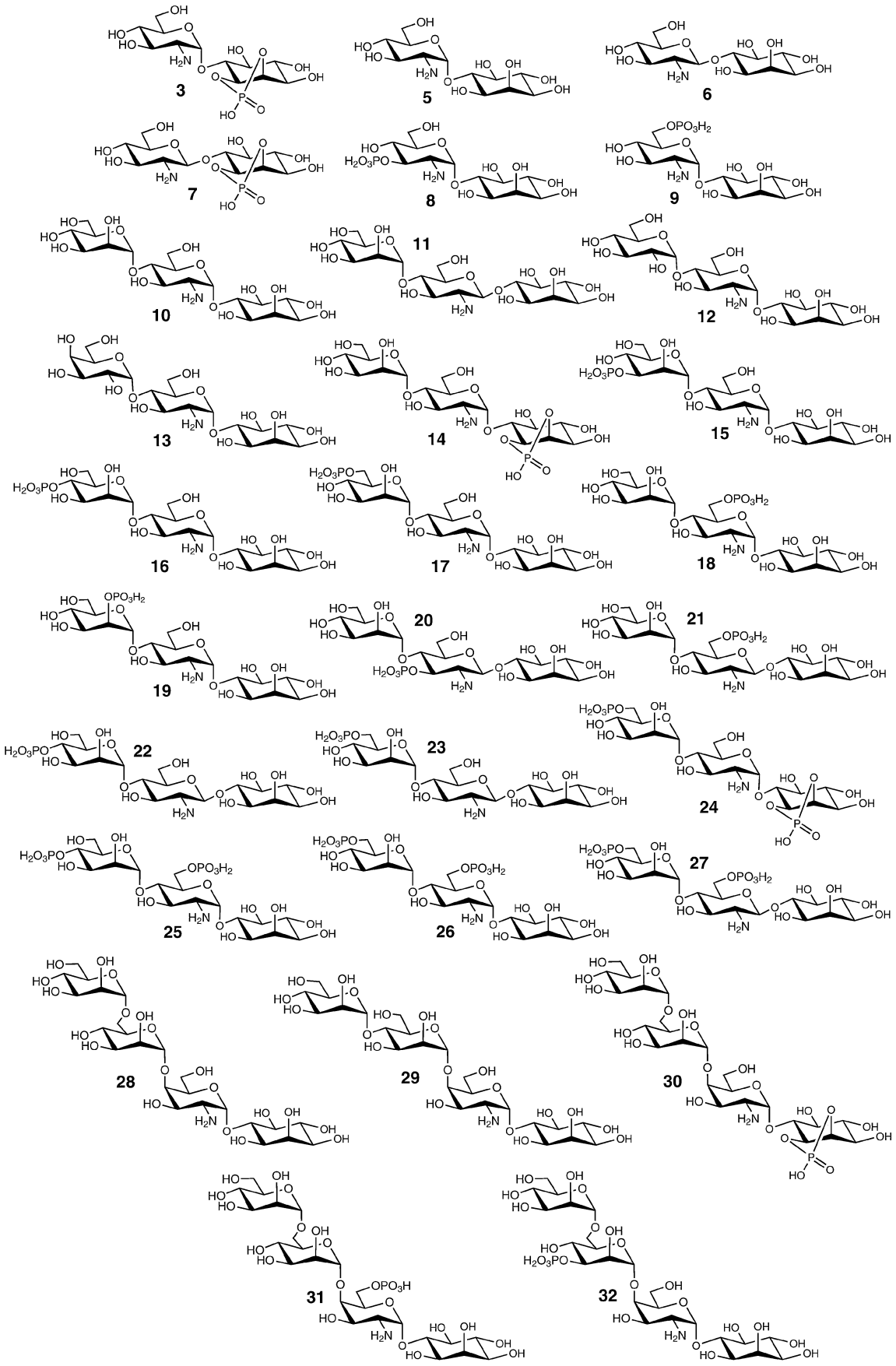


Fig. 2 Docked structures **3,5–32**.

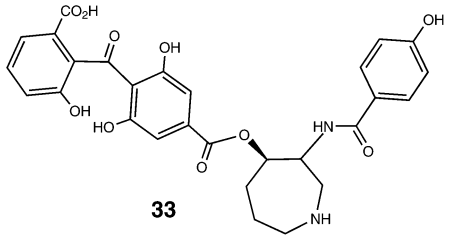


Fig. 3 Structure of balanol **33**.

With the exception of **8**, all these molecules have been synthesised from the common precursor **52** (Fig. 6). In our previous synthesis of type-A IPG-like compounds[6,10,34] we constructed the $GlcNH_2$-α-(1→6)-D-*myo*-inositol moiety by regio- and stereoselective glycosylation of diol **37**[10] with a conveniently protected 2-azido-2-deoxy-D-glucopyranosyl trichloroacetimidate. Following the same approach, we now have optimised this glycosylation reaction using trichloroacetimidates **42**[40,44] and **45**. Both compounds have been prepared as shown in Scheme 1 from the common intermediate **39**,[41,42] which has in turn been synthesised from **38**[43] readily prepared from D-glucosamine.[44] Conventional benzylation of **39** gave **40**,[41,44] which was desilylated to yield **41**[44] and this in turn transformed in trichloroacetimidate **42**.[40,44] Treatment of **39** with *p*-methoxybenzyl trichloroacetimidate afforded **43** which was desilylated to yield **44** and this converted into **45**.

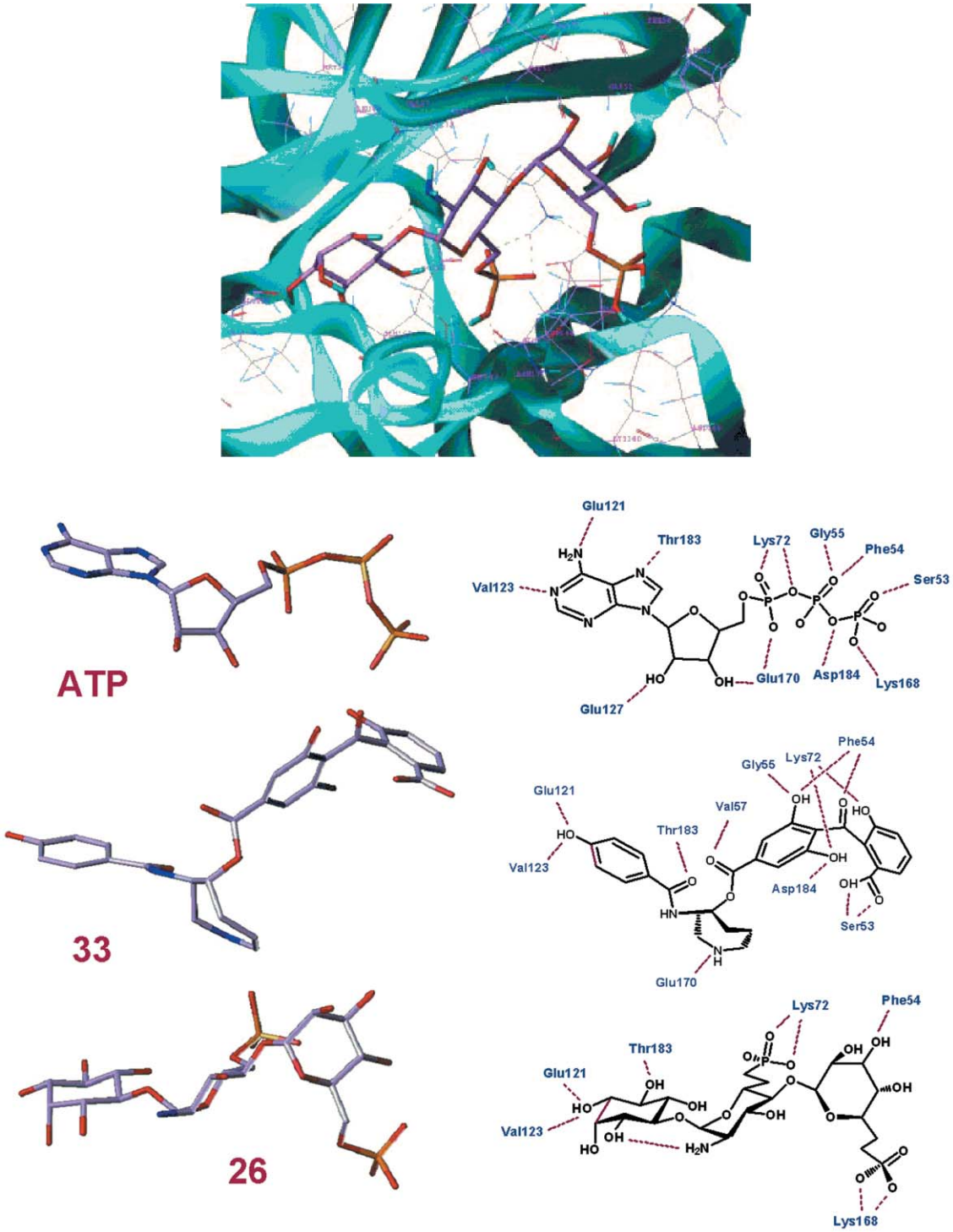


Fig. 4 Predicted binding modes of **26** into the ATP binding site of the catalytic subunit of PKA (top). Comparison of binding details in the X-ray structures of PKA–ATP and PKA–**33** complexes with the predicted binding of **26** (bottom).

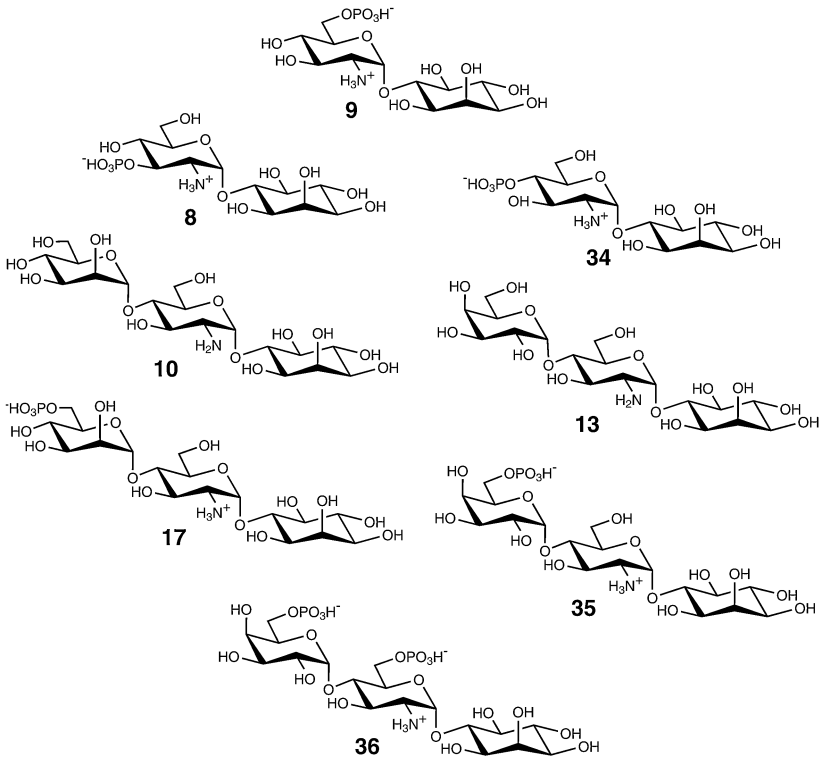


Fig. 5 Compounds **8–10,13,17** and **34–36**.

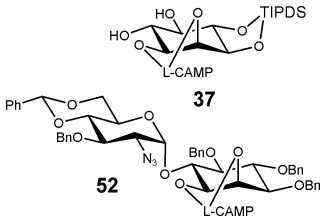
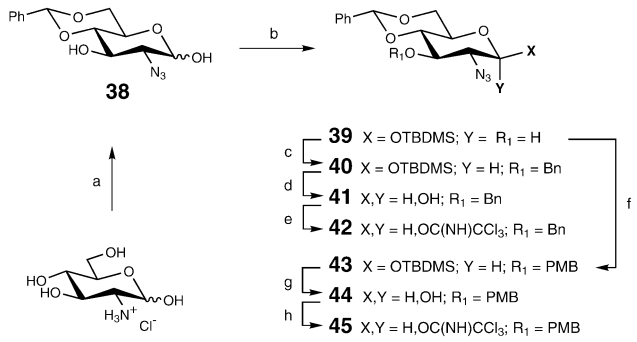


Fig. 6 Compounds **37** and **52**.

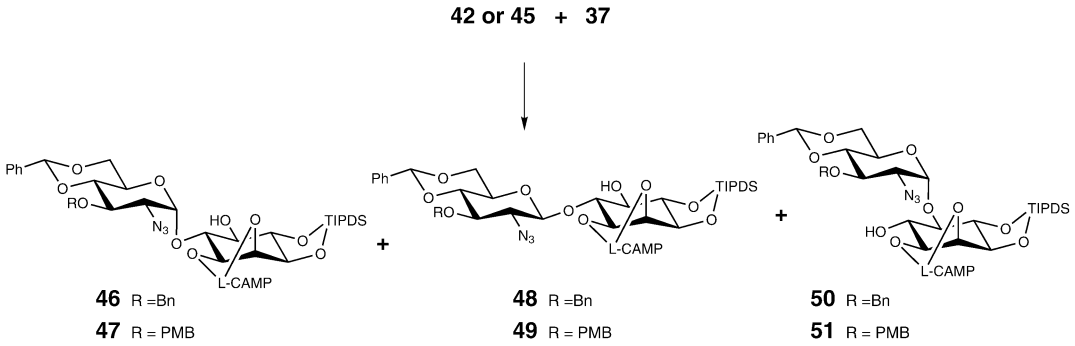


Scheme 1 *Reagents and conditions*: a) MeONa, MeOH, 10 min; TfN_3, DMAP, 48 h; $PhCH(OMe)_2$, pTsOH, DMF, 40 °C, 48 h, 71%. b) TBDMSCl, imidazol, CH_2Cl_2, −10 °C, 2 h, 70%. c) NaH, BnBr, TBAI, CH_2Cl_2, 24 h, 85%. d) AcOH, TBAF, THF, −40 °C, 100%. e) $CNCCl_3$, DBU, CH_2Cl_2, 2 h, 95%. f) $PMBOC(NH)CCl_3$, $BF_3{\cdot}OEt_2$, MS 4 Å, from 0 °C to rt, 18 h, 70%. g) AcOH, TBAF, −40 °C, 2 h, 98%. h) $CNCCl_3$, DBU, CH_2Cl_2, 2 h, 95%.

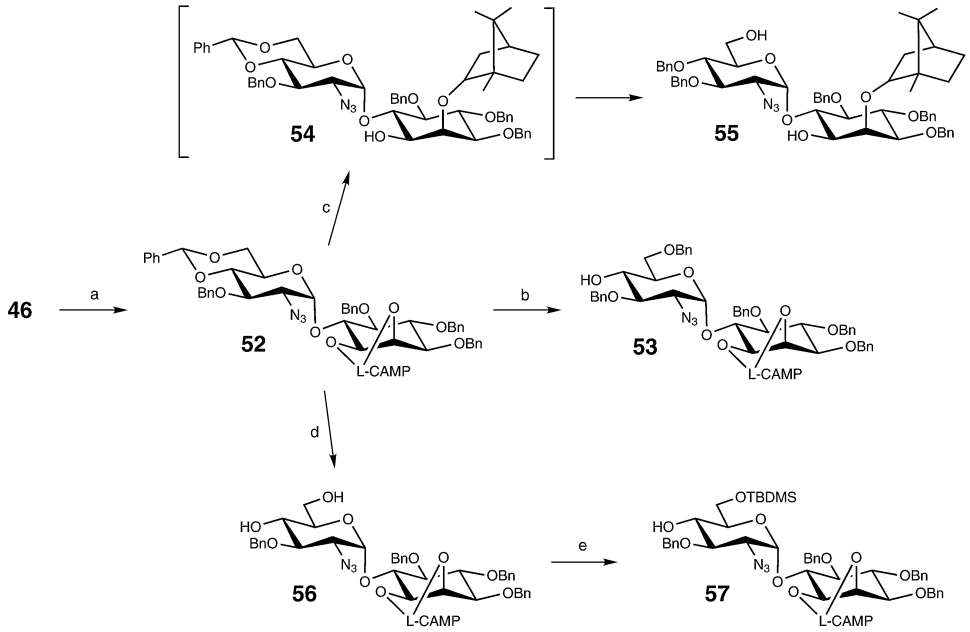
The glycosylation[6] of **42** with **37** was optimised affording, as indicated in Scheme 2, a major pseudodisaccharide **46**,[6] in 72% yield, accompanied by the β-(1→6) **48** (5%) and the α-(1→5) **50** (6%) isomers. Similarly, the condensation of **45** with **37** yielded **47** (66%), **49** (4%) and **51** (14%). From **46**, building blocks **53**[45] and **57** were prepared as depicted in Scheme 3. First, **46** was converted in **52** which was transformed into **53**[45] by regioselective reductive opening of the benzylidene ring with $NaCNBH_3$–HCl.[46,47] Attempts to direct the reductive opening of the benzylidene ring in **52** to the formation of the alternative 6-OH 4-OBn derivative using $BH_3{\cdot}Me_2NH$ and $BF_3{\cdot}OEt_2$[48] led to **54** and then **55** as a result of reductive cleavage of the dioxolane ring as a first step in the reaction.[49,50] Under carefully controlled experimental conditions however, the selective hydrolysis of the six membered acetal ring in **52** could be achieved, giving rise to **56** which was regioselectively silylated to yield building block **57**.

The synthesis of pseudodisaccharides **8** and **9** was carried out from **47** as shown in Scheme 4. From **47**, compound **58** was prepared in two steps. Removal of the *p*-methoxybenzyl group in **58**[51] gave **59** which was treated with *N*,*N*-diisopropyl dibenzyl phosphoramidite[52] and then with *m*-chloroperbenzoic acid to afford **60**. The acetals groups in **60** were removed to give **61** which was submitted to catalytic hydrogenation. This reaction gave **8** quantitatively when performed in a mixture of methanol–water. In the presence of acetic acid, a rearrangement of the phosphate group took place and compound **9** was isolated also in quantitative yield. Similarly, pseudodisaccharide **34** was prepared from **53** through **62** and **63** as shown in Scheme 5. Also in this case, the catalytic hydrogenation of **63** in the presence of acetic acid afforded **9** in quantitative yield.

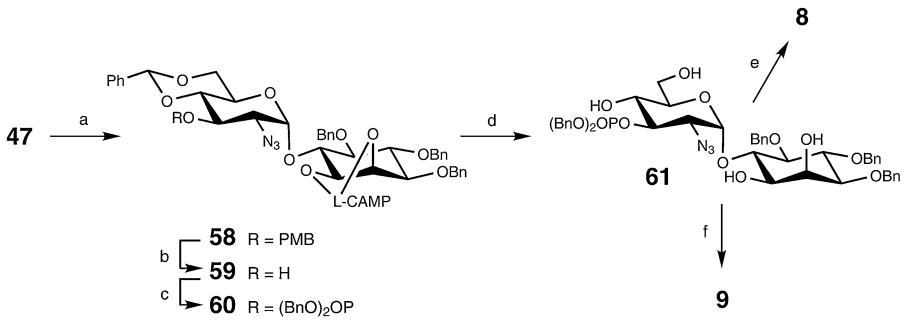
The synthesis of the pseudotrisaccharides **10,13,17** and **35** was performed from the common precursor **53** as shown in Scheme 7 and 8. Trichloroacetimidates **68** and **73** were synthesised following the same synthetic procedure, starting from the corresponding pentacetate derivatives **64** and **69** respectively (Scheme 6). For the synthesis of **10** and **17** (Scheme 7), trichloroacetimidate **68** was reacted with **53** in ether using TMSOTf as promoter to give **74** in 93% yield. Acid hydrolysis transformed **74** into **75** from which pseudotrisaccharide **10** was obtained after catalytic hydrogenation. According to previous experience,[6,39,53] removal of the silyl group in **74** required treatment with ten eq. of TBAF for twenty four hours to afford **76**. Phosphorylation of **76** gave **77**. Removal of the ketal function as before gave **78** which was quantitatively transformed into **17**. A similar sequence from **53**



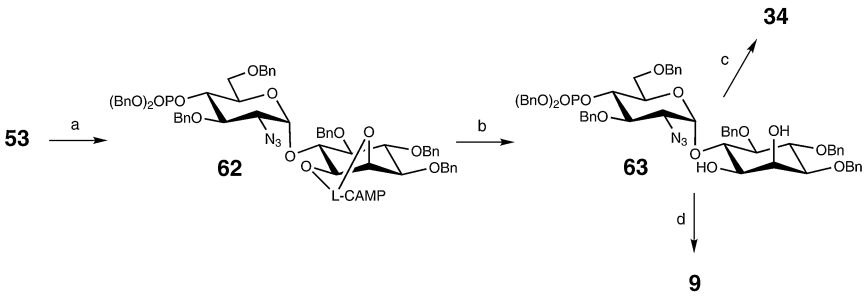
Scheme 2 *Reagents and conditions*: TMSOTf, Et_2O, MS 4 Å, −40 °C, 2 h; yielding **46** (72%), **48** (5%) and **50** (6%) from **42**, and **47** (66%), **49** (4%) and **51** (14%) from **45**.



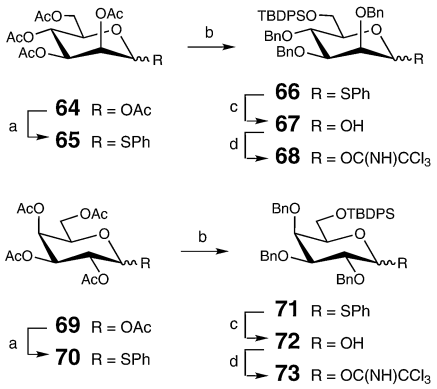
Scheme 3 *Reagents and conditions*: a) TBAF, THF, 1 h; BnBr, NaH, DMF, 10 h, 95%. b) $NaCNBH_3$, HCl, THF, MS 3 Å, 5 min, 90%. c) $BH_3{\cdot}NHMe_2$, $BF_3{\cdot}OEt_2$, 10 min, 79% of **55**. d) EtSH, $BF_3{\cdot}OEt_2$, 0 °C, 45 min, 98%. e) TBDMSCl, imidazol, DMF, −15 °C, 2 h, 96%.



Scheme 4 *Reagents and conditions*: a) TBAF, THF, 1 h; BnBr, NaH, DMF, 10 h, 95%. b) DDQ, CH_2Cl_2–H_2O 9 : 1, 1 h, 90%. c) 1H-tetrazol, $(^iPr_2N)_2P(OBn)_2$, CH_2Cl_2, 30 min; MCPBA, 0 °C, 10 min, 96%. d) TFA, H_2O, CH_2Cl_2, 2 h, 82%. e) H_2, Pd/C, MeOH–H_2O 9 : 1, 5 h, 100%. f) H_2, Pd/C, MeOH–H_2O–AcOH 9 : 1 : 0.1, 48 h, 100%.



Scheme 5 *Reagents and conditions*: a) 1H-tetrazol, $(^iPr_2N)_2P(OBn)_2$, CH_2Cl_2, 30 min; MCPBA, 0 °C, 10 min, 95%. b) TFA, H_2O, CH_2Cl_2, 2 h, 83%. c) H_2, Pd/C, MeOH–H_2O 9 : 1, 5 h, 100%. d) H_2, Pd/C, MeOH–H_2O–AcOH 9 : 1 : 0.1, 24 h, 100%.



Scheme 6 *Reagents and conditions*: a) PhSH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 20 h, 83–100%. b) MeONa, MeOH, 10 min; TBDPSCl, imidazol, THF, 0 °C, 20 h; NaH, BnBr, TBAI, THF, 24 h, 75%. c) H_2O, NBS, acetone, 0 °C, 30 min, 95%. Pd/C, MeOH–H_2O 9 : 1, 5 h, 100%. d) $CNCCl_3$, DBU, CH_2Cl_2, 2 h, 96%.

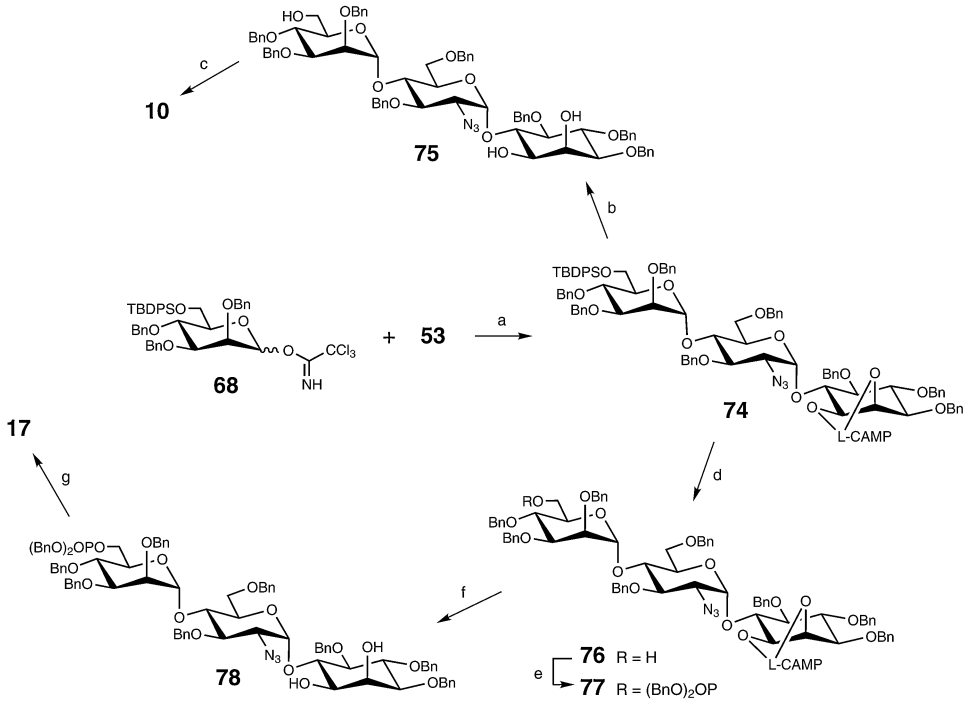
using **73** as a glycosyl donor led to **79** in 71% yield. Compound **79** was converted into **13** through **80** and into **35** through the sequence **81,82** and **83**. (Scheme 8).

For the synthesis of **36**, compound **57** was glycosylated with trichloroacetimidate **73** to afford **84** which without further purification was directly submitted to desilylation to obtain **85** in 45% overall yield from **57** (Scheme 9). Compound **85** was then transformed into **36** through the sequence **86,87**.

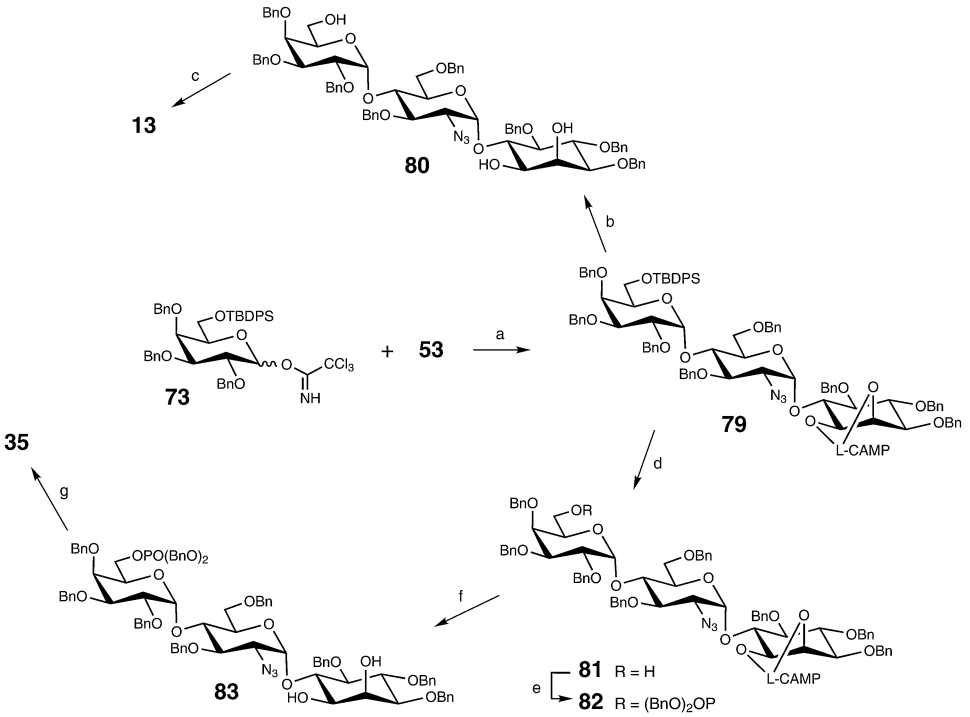
According to the docking predictions, these pseudotrisaccharide structures present the best shape complementarity with the ATP binding site of the catalytic subunit of PKA. In order to facilitate the synthetic process for searching for biologically active synthetic IPG-like molecules, we also explored the feasibility of constructing small pseudotrisaccharide libraries on solid-phase using the same intermediates. We have already developed a step by step solid-phase synthesis of GPI anchor precursors which may allow for the synthesis of a variety of pseudotrisaccharide structures.[39]

In this synthetic approach, the common precursor **52** was transformed in three steps into diol **88** which was attached to a functionalised resin through OH-1 of the *myo*-inositol unit. We also explored a different approach however, starting from alcohol **57** and attaching the pseudodisaccharide building block to the solid-support through 6-OH of the 2-azido-2-deoxy-α-D-glucopyranosyl moiety. As a first attempt, an amino Merrifield-type resin was functionalised with the benzylamino-type linker **90** prepared from **89** which was in turn obtained from 1-nitro-4-triphenylmethyloxymethylbenzene (Scheme 10). Benzylamino type linkers have been previously used in oligosaccharide synthesis[54] and can be easily cleaved under oxidative conditions with DDQ.[54] The trityl group in the functionalised resin **91** was removed[55] and the benzylic function in **92** was activated as trichloroacetimidate **93**.[56] Pseudodisaccharide **95**, that was prepared from **57** after levulination[57] and removal of the silyl group in the levulinated derivative **94**, was immobilized[56] on the solid-support. The loading, determined by cleaving a preparative sample of the functionalised resin **96**, was 0.71 mmol g^{-1}. Delevulination[58] of **96** gave the resin-bound glycosyl acceptor **97**.

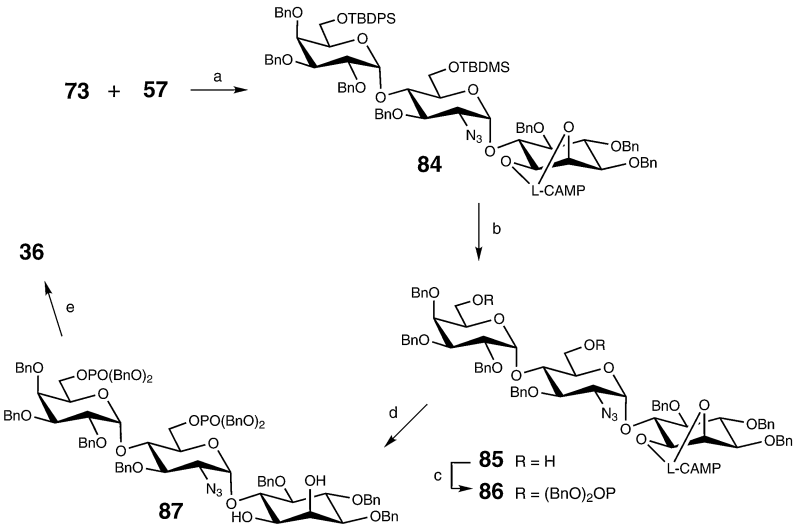
Unfortunately, the attempted glycosylation with glycosyl donor **68** did not afford the desired pseudotrisaccharide, most likely as a result of steric hindrance due to the high resin loading.[59] The approach was therefore redesigned using Merrifield resins of decreased loading[59] functionalised as in **93**, with a linker distribution of 0.2 mmol g^{-1}, on one hand, and changing the solid-support to a Wang-chloride functionalised PEG-grafted polystyrene resin on the other. Also, the attachment of the glycosyl acceptor to the solid-support was simplified by directly reacting diol **56** with the functionalised resin. In the case of the low loading Merrifield-type resin, **56** was reacted with the trichloroacetimidate functionalised support at −15 °C and the selectivity of the benzylation was determined by benzoylating on solid-phase, cleaving and analysing the reaction mixture. Under these conditions the selectivity was around 2 : 1 for the 4-*O*-Bz *versus* the 6-*O*-Bz regioisomers. In the case of the Wang-chloride functionalised PEG-grafted polystyrene resin, a similar regioselectivity was observed in the attachment of diol **56** under basic conditions. Nevertheless, several glycosylation



Scheme 7 *Reagents and conditions*: a) TMSOTf, Et_2O, MS 4 Å, 0 °C, 30 min, 93%. b) TFA–H_2O 9 : 1, 30 min; MeONa, MeOH, 10 min, 90%. c) H_2, Pd/C, MeOH–H_2O 9 : 1, 12 h, 100%. d) TBAF, THF, 48 h, 94%. e) 1H-tetrazol, $(^iPr_2N)_2P(OBn)_2$, CH_2Cl_2, 30 min; MCPBA, 0 °C, 10 min, 95%. f) TFA, H_2O, CH_2Cl_2, 2 h, 92%. g) H_2, Pd/C, MeOH–H_2O 9 : 1, 12 h, 100%.



Scheme 8 *Reagents and conditions*: a) TMSOTf, Et_2O, MS 4 Å, 0 °C, 1 h, 71%. b) TFA, H_2O, CH_2Cl_2, 2 h, 92%. c) H_2, Pd/C, MeOH–H_2O 9 : 1, 24 h, 100%. d) TBAF, THF, 4 h, 96%. e) 1H-tetrazol, $(^iPr_2N)_2P(OBn)_2$, CH_2Cl_2, 30 min; MCPBA, 0 °C, 10 min, 96%. f) TFA, H_2O, CH_2Cl_2, 2 h, 90%. g) H_2, Pd/C, MeOH–H_2O 9 : 1, 12 h, 100%.



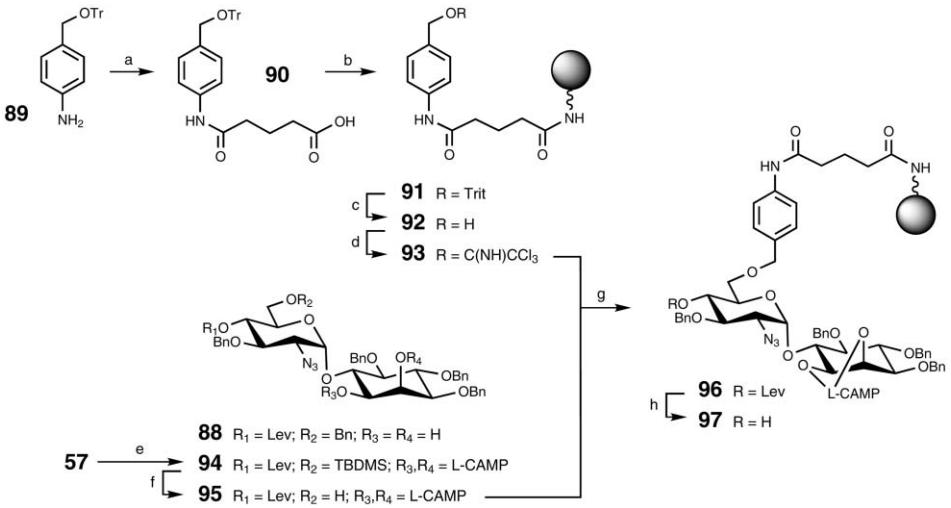
Scheme 9 *Reagents and conditions*: a) TMSOTf, Et_2O, MS 4 Å, rt, 30 min. b) TBAF, THF, 6 h, 45% (two steps). c) 1H-tetrazol, $(^iPr_2N)_2P(OBn)_2$, CH_2Cl_2, 30 min; MCPBA, 0 °C, 10 min, 94%. d) TFA, H_2O, CH_2Cl_2, 2 h, 82%. e) H_2, Pd/C, MeOH–H_2O 9 : 1, 12 h, 100%.

reactions were studied using these regioisomeric mixtures of functionalised Merrifield resin with decreased loading and of PEG-grafted functionalised resins with a loading around 0.15 mmol g^{-1}.

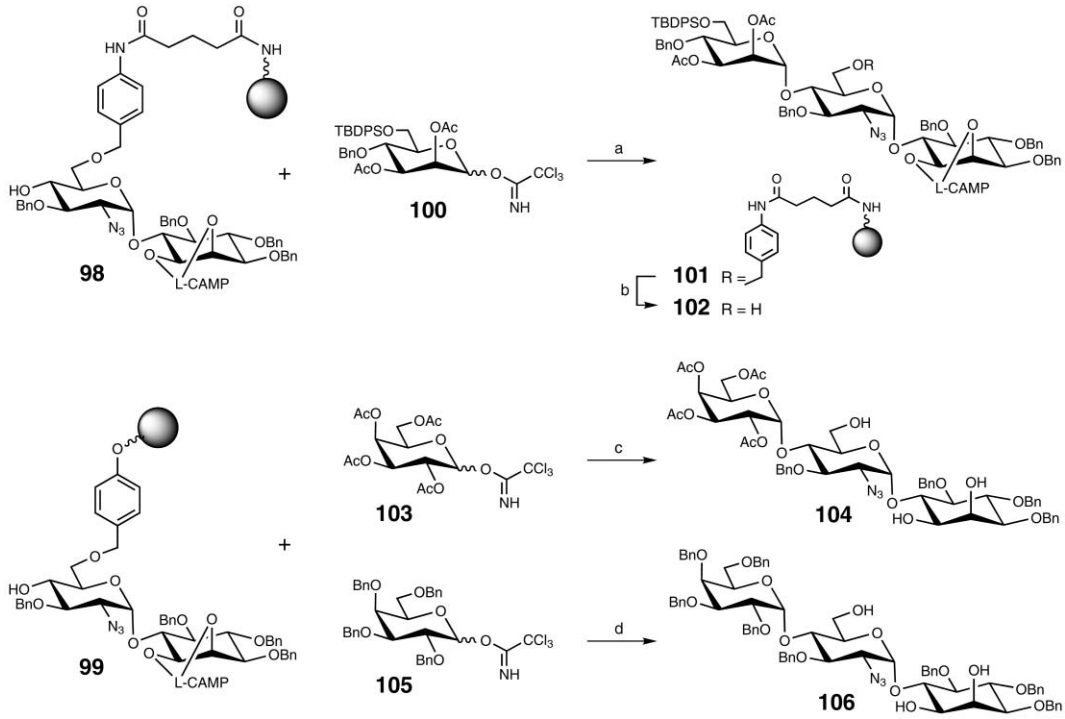
The results are summarised in Scheme 11, where only the major regioisomers (**98** and **99**) are shown. In all cases the glycosylations were monitored by MALDI-TOF MS and the corresponding pseudotrisaccharides, which were released from the resin either by treatment with DDQ (compound **102**) or after treatment with TFA[60] (compounds **104** and **106**), could be isolated and the yields ranged from 71% (compound **104**) and 40% (compound **106**). It was concluded that solid-phase generation of small libraries of IPG-like structures is most conveniently performed using our previously reported approach, by regioselectively attaching diol **88** to the solid-support through OH-1 of the *myo*-inositol moiety.

Biological activity

The insulin-like activity of the synthesised IPG-like molecules was tested *in vitro* and some of the molecules were submitted to *in vivo* assays using animal models of diabetes. A full account of this work will be reported elsewhere. It is interesting to note that only **8** inhibited PKA at μM concentrations and that this molecule also activated PDHPase at μM concentrations. Compounds **9,17** and **34** also activated PDHPase. Thus, contrary to expectations, these results have not greatly contributed to elucidate the molecular basis of this mechanism of intracellular



Scheme 10 *Reagents and conditions*: a) Glutaric anhydride, Py, 45 °C, 2 h, 95%. b) PS-NH_2 resin, DIC, DMF, 1-OH benzotriazol; Ac_2O, Py, DMAP, 98%. c) TFA, *sec*-butanol, 97%. d) Cl_3CCN, DBU, 0 °C, 90%. e) LevOH, DCC, DMAP, CH_2Cl_2, 96%. f) HF·Py, AcOH, THF, −20 °C to rt, 99%. g) $BF_3{\cdot}Et_2O$, C_6H_{12}, CH_2Cl_2. h) $N_2H_4{\cdot}AcOH$, CH_2Cl_2, 18 h.



Scheme 11 *Reagents and conditions*: a) TMSOTf, CH_2Cl_2, 5 cycles, 60%. b) DDQ, CH_2Cl_2–H_2O 20 : 1. c) TMSOTf, CH_2Cl_2, 2 cycles, −20 °C; TFA, CH_2Cl_2, H_2O, 6 h, 71%. d) TMSOTf, CH_2Cl_2, 2 cycles, −20 °C; TFA, CH_2Cl_2, H_2O, 6 h, 40%.

signal transduction. However, they provide additional proof that cAMP-dependent and cAMP-independent protein kinases and phosphoprotein phosphatases are intracellular targets for IPGs. They also confirm the capacity of these types of structures to induce the phosphorylation and the dephosphorylation of cellular proteins which are modified in response to insulin.

Experimental

General

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) sulfate (13 g), phosphomolybdic acid (10 g), sulfuric acid (60 mL) solution in water (1 L); with phosphomolybdic acid (40 g) solution in water (1 L); with sulfuric acid–ethanol solution (1 : 9); or with anisaldehyde (25 mL) solution in sulfuric acid (25 mL), ethanol (450 mL) and acetic acid (1 mL), followed by heating to over 200 °C. Column chromatography was carried out on silica gel 60 (0.2 – 0.063 mm or 0.040 – 0.015 mm; Merck). Optical rotations were determined with a Perkin-Elmer 341 polarimeter. ^{1}H- and ^{13}C-NMR spectra were acquired on Bruker DPX-300, DRX-400 and DRX-500 spectrometers 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 a vacuum over phosphorous pentoxide for 24 h. High (HRMS) and low resolution (FAB-MS) fast atom bombardment mass spectra were carried out by the Mass Spectrometry Service, Facultad Química, Seville, with a Kratos MS-80 RFA spectrometer. Maldi-tof mass spectra were recorded with a MALDITOF GSG System spectrometer. Gel filtration chromatography (Sephadex G-10 and Sephadex G-25;

Pharmacia) and ion-exchange chromatography (Amberlite IRA-402 Cl^-, Merck) were used in order to achieve purification of the final products.

Docking calculations. All docking calculations were made using the PKA structure obtained from 1BX6.pdb (Brookhaven Data Bank) after removal of all substructures except the catalytic subunit and adding all H atoms possible. Kollman type charges for the PKA structure were obtained from Sybyl. A grid of 22.5 Å was used with a spacing of 0.375 Å. The center of the grid was the same as the calculated centroid for **33** before removal. Obtention of the ligands was made as described in the main text.[33] All of non-cyclic bonds were marked as rotatables. The root ring was in all cases the D-glucosamine ring. The docking process was carried out mainly following the guidelines given in Autodock User Guide 3.0.5. Affinity maps were created for each of the atoms present in each molecule (C, H, O, N, P). For each compound, several conformational geometries were used as a starting point for the docking calculations, obtaining equivalent results. For each of these studies, 10 runs were calculated using a population of 50 individuals with a limit of 250 000 energy evaluations.

Compounds 43–53,58,67,68,71–73. The synthesis and the full characterisation of these compounds are included as supporting information†.

2-Azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicycloheptyl)-D-*myo*-inositol 55. To a solution of **52** (350 mg, 0.368 mmol) and $BH_3{\cdot}HNMe_2$ (87 mg, 1.477 mmol) in dry CH_2Cl_2 (7.4 mL) under an argon atmosphere, $Et_2O{\cdot}BF_3$ (192 µl, 1.484 mmol) was added dropwise. The solution was stirred for 10 min, diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solutions. The organic layer was washed over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane–AcOEt 9 : 1, 4 : 1) to yield 277 mg (79%) of **55** as a white foam. TLC (hexane–AcOEt 4 : 1) $R_f = 0.10$. $[\alpha]_D^{20} = +50.6$ ($c = 1.3$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.35 − 7.25 (m, 18H, Ar*H*), 7.24 − 7.18 (m, 7H, Ar*H*), 5.38 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 5.00 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.91 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.88 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.86 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.82 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.731 (d, $J = 12.0$ Hz, 1H, $CH_{benzylic}$), 4.728 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.64 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 4.63 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.62 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 3.99 (t, $J_{3,2} = J_{3,4} = 10.0$ Hz, 1H, H_{3b}), 3.892 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4a}), 3.887 (t, $J_{2,1} = J_{2,3} = 2.5$ Hz, 1H, H_{2a}), 3.87 (t, $J_{6,1} = J_{6,5} = 9.5$ Hz, 1H, H_{6a}), 3.85 (dt, $J_{5,6} = J_{5,6'} = 2.5$ Hz, $J_{5,4} = 10.0$ Hz, 1H, H_{5b}), 3.66 (dd, $J_A = 3.5$ Hz, $J_B = 8.0$ Hz, 1H, CH_α L-*camphor*), 3.61 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 3.59 (ddd, $J_{1,2} = 2.5$ Hz, $J_{1,OHeq} = 6.0$ Hz, $J_{1,6} = 9.0$ Hz, 1H, H_{1a}), 3.46 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, 1H, H_{2b}), 3.34 (t, $J_{5,4} = J_{5,6} = 9.5$ Hz, 1H, H_{5a}), 3.33 (dd, $J_{3,2} = 2.0$ Hz, $J_{3,4} = 10.0$ Hz, 1H, H_{3a}), 3.31 (d, $J_{OHeq,1} = 6.0$ Hz, 1H, $OH_{eq.}$), 3.30 (m, 2H, $H_{6b} + H_{6b'}$), 2.02 (m, 1H, L-*camphor*), 1.63 (m, 3H, L-*camphor*), 1.49 (m, 1H, L-*camphor*), 1.31 (br t, $J_{OH,6} = J_{OH,6'}$ 4.5 Hz, 1H, OH_{6b}), 1.06 (s, 3H, CH_3 L-*camphor*), 1.00 (m, 1H, L-*camphor*), 0.98 (s, 3H, CH_3 L-*camphor*), 0.94 (m, 1H, L-*camphor*), 0.81 (s, 3H, CH_3 L-*camphor*). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.47, 138.38, 138.12, 138.09, 137.76 (Ar*C*), 128.45, 128.41, 128.32, 128.27, 128.08, 128.04, 127.88, 127.80, 127.76, 127.65, 127.59, 127.50, 127.45 (Ar*C*H), 98.40 (C_{1b}), 89.64 (CH_α L-*camphor*), 81.78 (C_{4a}), 81.27 (C_{5a}), 80.89 (C_{6a}), 80.62 (C_{3b}), 80.37 (C_{3a}), 77.80 (C_{4b}), 77.16 (C_{2a}), 75.60, 75.52, 75.22, 74.91 ($CH_{2benzylic}$), 74.11 (C_{1a}), 72.73 ($CH_{2benzylic}$), 71.51 (C_{5b}), 64.39 (C_{2b}), 60.77 (C_{6b}), 49.64, 46.60 (C L-*camphor*), 45.15 (*C*H L-*camphor*), 39.70, 34.41, 27.28 (CH_2 L-*camphor*), 20.45, 20.19, 12.71 (CH_3 L-*camphor*). FAB-MS: m/z 976 $(M + Na)^+$. Anal. calcd. for $C_{57}H_{67}O_{10}N_3{\cdot}H_2O$: C 70.42%; H 7.15%; N 4.32%; found C 70.61%; H 7.14%; N 3.92%.

*Data for intermediate **54**.* TLC (hexane–AcOEt, 4 : 1) $R_f = 0.36$. $[\alpha]_D^{20} = +43.1$ ($c = 0.7$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.44 (m, 2H, Ar*H*), 7.41 − 7.19 (m, 23H, Ar*H*), 5.51 (s, 1H, $CH_{benzylic}$ *benzylidene*), 5.35 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 4.97 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 4.95 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 4.88 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.77 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.74 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 4.72 (d, $J = 10.5$ Hz, 1H, $CH_{benzylic}$), 4.71 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 4.64 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 4.05 (t, $J_{3,2} = J_{3,4} = 9.5$ Hz, 1H, H_{3b}), 4.05 (td, $J_{5,6} = 4.5$ Hz, $J_{5,4} = J_{5,6'} = 10.5$ Hz, 1H, H_{5b}), 3.91 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4a}), 3.90 (t, $J_{6,1} = J_{6,5} = 9.5$ Hz, 1H, H_{6a}), 3.89 (br s, 1H, H_{2a}), 3.84 (dd, $J_{6,5} = 5.0$ Hz, $J_{6,6'} = 10.5$ Hz, 1H, H_{6b}), 3.67 (dd, $J_A = 3.0$ Hz, $J_B = 7.5$ Hz, 1H, CH_α L-*camphor*), 3.66 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 3.59 (br ddd, $J_{1,2} = 2.0$ Hz, $J_{1,OHeq} = 5.0$ Hz, $J_{1,6} = 9.0$ Hz, 1H, H_{1a}), 3.57 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, 1H, H_{2b}), 3.54 (d, $J_{OH,1} = 5.0$ Hz, 1H, $OH_{eq.}$), 3.53 (t, $J_{6',5} = J_{6',6} = 10.5$ Hz, 1H, $H_{6b'}$), 3.38 (t, $J_{5,4} = J_{5,6} = 9.5$ Hz, 1H, H_{5a}), 3.34 (dd, $J_{3,2} = 2.5$ Hz, $J_{3,4} = 10.0$ Hz, 1H, H_{3a}), 2.02 (m, 1H, L-*camphor*), 1.63 (m, 3H, L-*camphor*), 1.49 (m, 1H, L-*camphor*), 1.06 (s, 3H, CH_3 L-*camphor*), 1.03 (m, 1H, L-*camphor*), 0.98 (s, 3H, CH_3 L-*camphor*), 0.95 (m, 1H, L-*camphor*), 0.81 (s, 3H, CH_3 L-*camphor*). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.52, 138.32, 138.15, 137.75, 137.39 (Ar*C*), 128.90, 128.40, 128.31, 128.25, 128.21, 128.17, 128.01, 127.88, 127.65, 127.57, 127.47, 127.41, 126.05 (Ar*C*H), 101.24 ($CH_{benzylic}$ *benzylidene*), 99.08 (C_{1b}), 89.49 (CH_α L-*camphor*), 82.80 (C_{4b}), 81.91 (C_{4a}), 81.83 (C_{6a}), 81.03 (C_{5a}), 80.30 (C_{3a}), 77.00 (C_{3b}), 76.75 (C_{2a}), 75.57 ($CH_{2benzylic}$), 75.03 (2 × $CH_{2benzylic}$), 74.01 (C_{1a}), 72.66 ($CH_{2benzylic}$), 68.62 (C_{6b}), 64.10 (C_{2b}), 63.11 (C_{5b}), 49.61, 46.60 (C L-*camphor*), 45.17 (*C*H L-*camphor*), 39.56, 34.39, 27.30 (CH_2 L-*camphor*), 20.46, 20.20, 12.68 (CH_3 L-*camphor*). FAB-MS: m/z 974 $(M + Na)^+$.

2-Azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclohept-2-ylidene)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 56. To a solution of **52** (450 mg, 0.474 mmol) in dry CH_2Cl_2 (9.5 mL) under an argon atmosphere, ethanethiol (526 µl, 7.102 mmol) and $Et_2O{\cdot}BF_3$ (3 µl, 0.024 mmol) were added at 0 °C. The solution was stirred for 45 min, diluted with AcOEt (100 mL) and washed with sat. $NaHCO_3$ (125 mL) and sat. NaCl (3 × 125 mL) solutions. The organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane–AcOEt 9 : 1, 4 : 1, 2 : 1) to yield 400 mg (98%) of **56** as a white foam. $[\alpha]_D^{20} = +41.3$ ($c = 1.3$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.41 − 7.26 (m, 20H, Ar*H*), 5.55 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 4.89 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 4.82 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.81 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.76 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 4.75 (d, $J = 11.5$ Hz, 1H, $CH_{benzylic}$), 4.70 (d, $J = 10.5$ Hz, 1H, $CH_{benzylic}$), 4.69 (d, $J = 12.0$ Hz, 1H, $CH_{benzylic}$), 4.62 (d, $J = 11.0$ Hz, 1H, $CH_{benzylic}$), 4.29 (dd, $J_{2,3} = 4.0$ Hz, $J_{2,1} = 6.0$ Hz, 1H, H_{2a}), 4.03 (dd, $J_{1,2} = 6.0$ Hz, $J_{1,6} = 7.0$ Hz, 1H, H_{1a}), 3.99 (dd, $J_{6,1} = 7.5$ Hz, $J_{6,5} = 10.0$ Hz, 1H, H_{6a}), 3.86 (dt, $J_{5,6} = J_{5,6'} = 3.5$ Hz, $J_{5,4} = 10.0$ Hz, 1H, H_{5b}), 3.83 (t, $J_{4,3} = J_{4,5} = 8.0$ Hz, 1H, H_{4a}), 3.80 (dd, $J_{3,2} = 4.0$ Hz, $J_{3,4} = 8.0$ Hz, 1H, H_{3a}), 3.73 (dd, $J_{3,4} = 9.0$ Hz, $J_{3,2} = 10.5$ Hz, 1H, H_{3b}), 3.60 (br t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 3.57 (m, 2H, $H_{6b} + H_{6b'}$), 3.44 (dd, $J_{5,4} = 7.5$ Hz, $J_{5,6} = 10.0$ Hz, 1H, H_{5a}), 3.26 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, 1H, H_{2b}), 1.92 (m, 1H, L-*camphor*), 1.86 (m, 2H, L-*camphor* + OH_{4b}), 1.76 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.56 (br s, 1H, OH_{6b}), 1.47 (d, $J = 13.0$ Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.87 (s, 6H, 2 × CH_3 L-*camphor*). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.37 (Ar*C*), 138.30 (2 × Ar*C*), 138.05 (Ar*C*), 128.62, 128.42, 128.38, 128.35, 128.10, 128.03, 128.00, 127.87, 127.81, 127.76, 127.73, 127.65 (Ar*C*H), 118.11 ($C_{acetalic}$ L-*camphor*), 95.59 (C_{1b}), 80.75 (C_{5a}), 80.65 (C_{4a}),

79.45 (C_{3b}), 77.94 (C_{6a}), 76.91 (C_{3a}), 76.04 (C_{1a}), 75.00, 74.80, 74.73 ($CH_{2benzylic}$), 73.90 (C_{2a}), 72.61 ($CH_{2benzylic}$), 71.61 (C_{4b}), 70.55 (C_{5b}), 62.88 (C_{2b}), 62.29 (C_{6b}), 51.58, 47.97 (C L-*camphor*), 45.14 (*C*H L-*camphor*), 44.79, 29.89, 26.96 (CH_2 L-*camphor*), 20.60, 20.34, 9.77 (CH_3 L-*camphor*). FAB-MS: *m/z* 884 $(M + Na)^+$. Anal. calcd. for $C_{50}H_{59}O_{10}N_3 \cdot H_2O$: C 68.31%; H 6.99%; N 4.77%; found C 68.31%; H 6.99%; N 4.47%.

2-Azido-3-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclohept-2-ylidene)-D-*myo*-inositol 57. To a solution of **56** (350 mg, 0.406 mmol) and imidazol (88 mg, 1.293 mmol) in dry DMF (5 mL) under an argon atmosphere, a solution of TBDMSCl (73 mg, 0.484 mmol) in dry DMF (3 mL) was added at −15 °C. The solution was stirred for 2 h, diluted with AcOEt (50 mL) and washed with 10% HCl solution (50 mL). The aqueous layer was extracted with AcOEt (2 × 25 mL) and the combined organic layers were washed with sat. NaCl solution (3 × 100 mL), dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane–AcOEt 19 : 1) to yield 380 mg (96%) of **57** as a white foam. $[\alpha]_D^{20} = +37.5$ ($c = 1.7$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.44 − 7.26 (m, 20H, Ar*H*), 5.55 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 4.88 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzylic}$), 4.86 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.81 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzylic}$), 4.76 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzylic}$), 4.72 (d, $J = 11.0$ Hz, 2H, 2 × C*H*$_{benzylic}$), 4.70 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.69 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.28 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 6.0$ Hz, 1H, H_{2a}), 4.01 (t, $J_{1,2} = J_{1,6} = 7.0$ Hz, 1H, H_{1a}), 3.96 (dd, $J_{6,1} = 7.0$ Hz, $J_{6,5} = 10.0$ Hz, 1H, H_{6a}), 3.88 (br dt, $J_{5,6} = J_{5,6'} = 4.0$ Hz, $J_{5,4} = 9.5$ Hz, 1H, H_{5b}), 3.82 (t, $J_{3,2} = J_{3,4} = 9.5$ Hz, 1H, H_{3b}), 3.81 (t, $J_{4,3} = J_{4,5} = 8.5$ Hz, 1H, H_{4a}), 3.78 (dd, $J_{3,2} = 4.0$ Hz, $J_{3,4} = 8.0$ Hz, 1H, H_{3a}), 3.74 (td, $J_{4,OH} = 3.0$ Hz, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 3.71 (dd, $J_{6,5} = 3.5$ Hz, $J_{6,6'} = 11.0$ Hz, 1H, H_{6b}), 3.60 (dd, $J_{6',5} = 5.0$ Hz, $J_{6',6} = 11.0$ Hz, 1H, $H_{6b'}$), 3.42 (dd, $J_{5,4} = 7.5$ Hz, $J_{5,6} = 9.5$ Hz, 1H, H_{5a}), 3.25 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.5$ Hz, 1H, H_{2b}), 2.35 (d, $J_{OH,4} = 3.0$ Hz, 1H, OH), 1.88 (m, 2H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.46 (d, $J = 13.0$ Hz, 1H, L-*camphor*), 1.38 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.87 (s, 3H, CH_3 L-*camphor*), 0.86 (s, 12H, CH_3 L-*camphor* + (CH_3)C *TBDMS*), 0.02 (CH_3 *TBDMS*), 0.01 (CH_3 *TBDMS*). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.56, 138.34, 138.26, 138.20 (Ar*C*), 128.51, 128.36, 128.35, 128.31, 128.25, 128.23, 127.88, 127.834, 127.825, 127.71, 127.66, 127.56 (Ar*C*H), 118.04 ($C_{acetalic}$ L-*camphor*), 95.30 (C_{1b}), 80.80 (C_{5a}), 80.65 (C_{4a}), 79.10 (C_{3b}), 77.66 (C_{6a}), 77.20 (C_{3a}), 76.19 (C_{1a}), 75.38, 74.92, 74.86 ($CH_{2benzylic}$), 73.90 (C_{2a}), 72.84 (C_{4b}), 72.53 ($CH_{2benzylic}$), 70.47 (C_{5b}), 63.56 (C_{6b}), 62.73 (C_{2b}), 51.59, 47.94 (C L-*camphor*), 45.13 (*C*H L-*camphor*), 44.89, 29.82, 26.98 (CH_2 L-*camphor*), 25.94 ((CH_3)$_3$C *TBDMS*), 20.62, 20.37 (CH_3 L-*camphor*), 18.34 ((CH_3)$_3$*C TBDMS*), 9.78 (CH_3 L-*camphor*), −5.22 (2 × CH_3 *TBDMS*). FAB-MS: *m/z* 975 M^+, 998 $(M + Na)^+$. Anal. calcd. for $C_{56}H_{73}O_{10}SiN_3$: C 68.89%; H 7.54%; N 4.30%; found C 68.62%; H 7.56%; N 4.07%.

2-Azido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclohept-2-ylidene)-D-*myo*-inositol 59. To a solution of **58** (445 mg, 0.454 mmol) in a mixture CH_2Cl_2–H_2O 9 : 1 (9 mL), DDQ (155 mg, 0.683 mmol) was added. The mixture was stirred for 1 h, diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solutions. The organic layer was dried over $MgSO_4$, concentrated in *vacuo* and the residue was purified by flash chromatography (hexane–AcOEt 9 : 1, 4 : 1) to yield 352 mg (90%) of **59** as a white foam. $[\alpha]_D^{20} = +56.3$ ($c = 1.2$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.38 − 7.23 (m, 17H, Ar*H*), 7.18 (m, 3H, Ar*H*), 5.63 (d, $J_{1,2} = 4.0$ Hz, 1H, H_{1b}), 5.94 (s, 1H, C*H*$_{benzylic}$ *benzylidene*), 4.78 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzylic}$), 4.77 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzylic}$), 4.75 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzylic}$), 4.72 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.70 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzylic}$), 4.67 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.29 (br t, $J_{2,1} = J_{2,3} = 4.5$ Hz, 1H, H_{2a}), 4.19 (dd, $J_{6,5} = 5.0$ Hz, $J_{6,6'} = 10.0$ Hz, 1H, H_{6b}), 4.16 (m, 1H, H_{5b}), 4.14 (td, $J_{OH,3} = 2.5$ Hz, $J_{3,2} = J_{3,4} = 10.0$ Hz, 1H, H_{3b}), 4.03 (m, 2H, $H_{1a} + H_{6a}$), 3.83 (t, $J_{4,3} = J_{4,5} = 8.5$ Hz, 1H, H_{4a}), 3.81 (dd, $J_{3,2} = 4.0$ Hz, $J_{3,4} = 8.0$ Hz, 1H, H_{3a}), 3.66 (t, $J_{6',5} = J_{6',6} = 10.0$ Hz, 1H, $H_{6b'}$), 3.50 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 3.45 (m, 1H, H_{5a}), 3.28 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, 1H, H_{2b}), 2.56 (d, $J_{OH,3} = 2.5$ Hz, 1H, OH), 1.92 (m, 1H, L-*camphor*), 1.86 (m, 1H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.46 (d, $J = 13.0$ Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.873 (s, 3H, CH_3 L-*camphor*), 0.868 (s, 3H, CH_3 L-*camphor*). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.42, 138.33, 138.00, 137.11 (Ar*C*), 129.20, 128.44, 128.36, 128.30, 128.19, 128.08, 127.85, 127.82, 127.71, 127.59, 127.52, 126.46 (Ar*C*H), 118.10 ($C_{acetalic}$ L-*camphor*), 102.03 ($CH_{benzylic}$ *benzylidene*), 95.97 (C_{1b}), 81.95 (C_{4b}), 80.65 (C_{4a}), 80.59 (C_{5a}), 78.12 (C_{6a}), 76.85 (C_{3a}), 75.99 (C_{1a}), 75.20, 74.71 ($CH_{2benzylic}$), 73.94 (C_{2a}), 72.61 ($CH_{2benzylic}$), 68.76 (C_{6b}), 68.58 (C_{3b}), 63.09 (C_{2b}), 62.18 (C_{5b}), 51.60, 47.96 (C L-*camphor*), 45.15 (*C*H L-*camphor*), 44.81, 29.87, 26.97 (CH_2 L-*camphor*), 20.60, 20.36, 9.71 (CH_3 L-*camphor*). FAB-MS: *m/z* 860 M^+, 882 $(M + Na)^+$. Anal. calcd. for $C_{50}H_{57}O_{10}N_3$: C 69.83%; H 6.68%; N 4.89%; found C 69.59%; H 6.90%; N 5.03%.

2-Azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-dibenzylphosphate-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclohept-2-ylidene)-D-*myo*-inositol 60. To a solution of **59** (300 mg, 0.349 mmol) and 1H-tetrazol (61 mg, 0.871 mmol) in dry CH_2Cl_2 (7 mL) under an argon atmosphere, *N*,*N*-diisopropyl dibenzyl phosphoramidite (230 µl, 0.699 mmol) was added. The solution was stirred for 30 min and 70% MCPBA (172 mg, 0.698 mmol) was added at 0 °C. After 10 min the mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solutions. The organic layer was dried over $MgSO_4$, concentrated in *vacuo* and the residue was purified by double flash chromatography (hexane–AcOEt 2 : 1 and hexane–AcOEt 9 : 1, 8 : 1, 7 : 1, 6 : 1, 5 : 1, 4 : 1, 3 : 1, 2 : 1) to yield 375 mg (96%) of **60** as a white foam. $[\alpha]_D^{20} = +55.6$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.38 − 7.18 (m, 25H, Ar*H*), 7.14 (m, 3H, Ar*H*), 7.04 (m, 2H, Ar*H*), 5.70 (d, $J = 4.0$ Hz, 1H, H_{1b}), 5.45 (s, 1H, C*H*$_{benzylic}$ *benzylidene*), 5.08 (dd, $J_1 = 7.0$ Hz, $J_2 = 11.5$ Hz, 1H, C*H*$_{benzylic}$), 4.99 (dd, $J_1 = 8.0$ Hz, $J_2 = 11.5$ Hz, 1H, C*H*$_{benzylic}$), 4.97 (q, $J = 9.5$ Hz, 1H, H_{3b}), 4.95 (dd, $J_1 = 7.0$ Hz, $J_2 = 12.0$ Hz, 1H, C*H*$_{benzylic}$), 4.85 (dd, $J_1 = 8.0$ Hz, $J_2 = 12.0$ Hz, 1H, C*H*$_{benzylic}$), 4.76 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzylic}$), 4.751 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.749 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzylic}$), 4.71 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.68 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzylic}$), 4.67 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzylic}$), 4.30 (dd broad, $J_1 = 3.5$ Hz, $J_2 = 5.5$ Hz, 1H, H_{2a}), 4.21 (td, $J_1 = 5.0$ Hz, $J_2 = 10.0$ Hz, 1H, H_{5b}), 4.14 (dd, $J_1 = 5.0$ Hz, $J_2 = 10.5$ Hz, 1H, H_{6b}), 4.06 (m, 2H, $H_{6a} + H_{1a}$), 3.83 (m, 2H, $H_{4a} + H_{3a}$), 3.68 (t, $J = 9.5$ Hz, 1H, H_{4b}), 3.63 (t, $J = 10.5$ Hz, 1H, $H_{6b'}$), 3.47 (m, 1H, H_{5a}), 3.32 (dd, $J_1 = 4.0$ Hz, $J_2 = 10.5$ Hz, 1H, H_{2b}), 1.92 (m, 1H, L-*camphor*), 1.86 (m, 1H, L-*camphor*), 1.76 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.46 (d, $J = 13.0$ Hz, 1H, L-*camphor*), 1.40 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.88 (s, 3H, CH_3 L-*camphor*), 0.86 (s, 3H, CH_3 L-*camphor*). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ −2.52. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.35, 138.31, 137.86, 136.96 (Ar*C*), 135.93 (d, $J_{C,P} = 7.5$ Hz, Ar*C phosphate*), 135.93 (d, $J_{C,P} = 7.8$ Hz, Ar*C phosphate*), 129.07, 128.41, 128.38, 128.35, 128.34, 128.27, 128.21, 128.16, 128.09, 128.04, 127.82, 127.80, 127.69, 127.63, 127.54, 127.48, 126.56 (Ar*C*H), 118.08 (C_{acetal} L-*camphor*), 102.05 ($CH_{benzylic}$ *benzylidene*), 96.76 (C_{1b}), 80.55 (C_{4a}), 80.38 (C_{5a}), 80.29 (d, $J_{C,P} = 2.9$ Hz, C_{4b}), 78.74 (C_{6a}), 76.55 (C_{3a}), 75.81 (C_{1a}), 75.07 ($CH_{2benzylic}$), 74.82 (d, $J_{C,P} = 6.4$ Hz, C_{3b}), 74.41 ($CH_{2benzylic}$),

73.91 (C_{2a}), 72.72 ($CH_{2benzylic}$), 69.23 (d, $J_{C,P}$ = 5.4 Hz, $CH_{2benzylic}$ *phosphate*), 69.20 (d, $J_{C,P}$ = 5.4 Hz, $CH_{2benzylic}$ *phosphate*), 68.64 (C_{6b}), 62.49 (d, $J_{C,P}$ = 3.1 Hz, C_{2b}), 62.45 (C_{5b}), 51.57, 47.95 (C L-*camphor*), 45.16 (*CH* L-*camphor*), 44.69, 29.92, 26.97 (CH_2 L-*camphor*), 20.59, 20.34, 9.76 (CH_3 L-*camphor*). FAB-MS: *m/z* 1119 M^+, 1142 $(M + Na)^+$. Anal. calcd. for $C_{64}H_{70}O_{13}N_3P$: C 68.62%; H 6.30%; N 3.75%; found C 68.40%; H 6.10%; N 3.56%.

2-Azido-2-deoxy-3-*O*-dibenzylphosphate-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 61. To a solution of **60** (300 mg, 0.268 mmol) in CH_2Cl_2 (13.4 mL), H_2O (483 µl, 26.811 mmol) and TFA (2.06 mL, 26.83 mmol) were added and the resulting mixture was stirred for 2 h. The mixture was diluted with AcOEt (100 mL) and washed with sat. $NaHCO_3$ (2 × 100 mL) and sat. NaCl (3 × 100 mL) solutions. The organic layer was dried over $MgSO_4$, concentrated in *vacuo* and the residue was purified by flash chromatography (hexane–AcOEt 1 : 1, 1 : 4, AcOEt 100%) to yield 197 mg (82%) of **61** as a colorless syrup. $[\alpha]_D^{20}$ = +49.8 (*c* = 1.3, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.38 – 7.22 (m, 25H, Ar*H*), 5.47 (d, *J* = 3.5 Hz, 1H, H_{1b}), 5.16 – 5.03 (m, 4H, 4 × $CH_{benzylic}$ *phosphate*), 5.01 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.92 (d, *J* = 10.5 Hz, 1H, $CH_{benzylic}$), 4.80 (d, *J* = 10.5 Hz, 1H, $CH_{benzylic}$), 4.73 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.70 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.62 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.60 (ddd, $J_{3,P}$ = 6.5 Hz, $J_{3,4}$ = 8.5 Hz, $J_{3,2}$ = 10.0 Hz, 1H, H_{3b}), 4.32 (d, $J_{OH,4}$ = 3.0 Hz, 1H, OH_{4b}), 4.15 (br t, $J_{2,1}$ = $J_{2,3}$ = 2.5 Hz, 1H, H_{2a}), 3.98 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4a}), 3.95 (t, $J_{6,5}$ = $J_{6,1}$ = 9.5 Hz, 1H, H_{6a}), 3.80 (dt, $J_{5,6}$ = $J_{5,6'}$ = 3.0 Hz, $J_{5,4}$ = 10.0 Hz, 1H, H_{5b}), 3.69 (td, $J_{4,OH}$ = 3.0 Hz, $J_{4,3}$ = $J_{4,5}$ = 9.0 Hz, H_{4b}), 3.61 (ddd, $J_{1,2}$ = 2.5 Hz, $J_{1,OH}$ = 5.5 Hz, $J_{1,6}$ = 8.5 Hz, 1H, H_{1a}), 3.48 (dd, $J_{3,2}$ = 2.5 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_{3a}), 3.44 (d, $J_{OH,1}$ = 5.5 Hz, 1H, OH_{1a}), 3.41 (dt, $J_{6,OH}$ = $J_{6,5}$ = 3.5 Hz, $J_{6,6'}$ = 12.0 Hz, 1H, H_{6b}), 3.38 (dd, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, H_{2b}), 3.36 (t, $J_{5,4}$ = $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.34 (dt, $J_{6',OH}$ = $J_{6',5}$ = 4.0 Hz, $J_{6',6}$ = 12.0 Hz, 1H, $H_{6b'}$), 2.62 (s, 1H, OH_{2a}), 1.51 (br t, $J_{OH,6}$ = $J_{OH,6'}$ = 4.0 Hz, 1H, OH_{6b}). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ −0.41. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.34, 138.12, 137.60 (Ar*C*), 135.32 (d, $J_{C,P}$ = 6.8 Hz, Ar*C* *phosphate*), 135.24 (d, $J_{C,P}$ = 7.1 Hz, Ar*C* *phosphate*), 128.67, 128.60, 128.58, 128.54, 128.39, 128.35, 128.03, 128.00, 127.96, 127.93, 127.83, 127.64, 127.61, 127.48 (Ar*C*H), 98.00 (C_{1b}), 81.59 (C_{4a}), 80.67 (C_{5a}), 80.61 (d, $J_{3,P}$ = 5.5 Hz, C_{3b}), 79.84 (C_{6a}), 79.57 (C_{3a}), 75.81, 75.39, 72.87 ($CH_{2benzylic}$), 72.72 (C_{1a}), 71.42 (C_{5b}), 70.12 (d, $J_{C,P}$ = 5.8 Hz, $CH_{2benzylic}$ *phosphate*), 70.05 (d, $J_{C,P}$ = 5.8 Hz, $CH_{2benzylic}$ *phosphate*), 69.70 (C_{4b}), 69.56 (C_{2a}), 62.59 (d, $J_{2,P}$ = 6.8 Hz, C_{2b}), 61.19 (C_{6b}). FAB-MS: *m/z* 920 $(M + Na)^+$. Anal. calcd. for $C_{47}H_{52}O_{13}N_3P{\cdot}H_2O$: C 61.63%; H 5.94%; N 4.59%; found C 61.81%; H 6.11%; N 4.40%.

2-Ammonio-2-deoxy-3-*O*-phosphate-α-D-glucopyranosyl-(1→6)-D-*myo*-inositol 8. A suspension of **61** (120 mg, 0.134 mmol) and 10% Pd on charcoal (285 mg, 0.268 mmol) in a mixture of MeOH–H_2O 9 : 1 (13 mL) under a hydrogen atmosphere was stirred for 5 h. The mixture was filtered through a pad of celite and the filter cake washed with H_2O. The solution was concentrated in *vacuo* and lyophilised to yield 56 mg (100%) of **8** as a white solid. $[\alpha]_D^{20}$ = +55.0 (*c* = 0.5, H_2O). *NMR data at pH = 5.6*: ^{1}H-NMR (D_2O, 500 MHz): δ 5.38 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 4.34 (q, $J_{3,2}$ = $J_{3,4}$ = 9.0 Hz, 1H, H_{3b}), 4.07 (dt, $J_{5,6}$ = $J_{5,6'}$ = 3.0 Hz, $J_{5,4}$ = 10.0 Hz, 1H, H_{5b}), 3.99 (t, $J_{2,1}$ = $J_{2,3}$ = 3.0 Hz, 1H, H_{2a}), 3.82 (dd, $J_{6,5}$ = 3.5 Hz, $J_{6,6'}$ = 12.5 Hz, 1H, H_{6b}), 3.77 (dd, $J_{6',5}$ = 2.5 Hz, $J_{6',6}$ = 12.5 Hz, 1H, $H_{6b'}$), 3.74 (dd, $J_{1,2}$ = 3.0 Hz, $J_{1,6}$ = 10.0 Hz, 1H, H_{1a}), 3.69 (t, $J_{6,1}$ = $J_{6,5}$ = 10.0 Hz, 1H, H_{6a}), 3.65 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4b}), 3.60 (t, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, 1H, H_{4a}), 3.50 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 10.0 Hz, 1H, H_{3a}), 3.40 (t, $J_{5,4}$ = $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.40 (dd, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2b}). ^{31}P-NMR (D_2O, 202 MHz): δ 2.54. ^{13}C-NMR (D_2O, 125 MHz): δ 96.61 (C_{1b}), 80.52 (C_{6a}), 73.08 (br s, C_{3b}), 72.53 (C_{4a} + C_{5a}), 72.41 (C_{2a}), 71.66 (C_{5b}), 71.56 (C_{1a}), 70.89 (C_{3a}), 68.95 (C_{4b}), 59.90 (C_{6b}), 54.27 (C_{2b}). HRMS *m/z* calcd. for $C_{12}H_{24}O_{13}NPNa^+$: 444.0876; found 444.0885 $(M + Na)^+$.

2-Azido-2-deoxy-3,6-di-*O*-benzyl-4-*O*-dibenzylphosphate-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicycloheptan-2-yliden)-D-*myo*-inositol 62. To a solution of **53** (200 mg, 0.210 mmol) and 1H-tetrazol (37 mg, 0.528 mmol) in dry CH_2Cl_2 (4.2 mL) under an argon atmosphere, *N*,*N*-diisopropyl dibenzyl phosphoramidite (138 µl, 0.420 mmol) was added. The solution was stirred for 30 min and 70% MCPBA (129 mg, 0.525 mmol) was added at 0 °C. After 10 min the mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solutions. The organic layer was dried over $MgSO_4$, concentrated in *vacuo* and the residue was purified by double flash chromatography (hexane–AcOEt 2 : 1 and hexane–AcOEt 9 : 1, 8 : 1, 7 : 1, 6 : 1, 5 : 1, 4 : 1, 3 : 1, 2 : 1) to yield 242 mg (95%) of **62** as a white foam. $[\alpha]_D^{20}$ = +48.4 (*c* = 1.9, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.44 (m, 2H, Ar*H*), 7.37 – 7.19 (m, 28H, Ar*H*), 7.14 (m, 5H, Ar*H*), 5.60 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 4.89 (d, *J* = 10.5 Hz, 1H, $CH_{benzylic}$), 4.89 – 4.79 (m, 5H, 4 × $CH_{benzylic}$ *phosphate* + $CH_{benzylic}$), 4.77 (br d, *J* = 11.0 Hz, 2H, 2 × $CH_{benzylic}$), 4.74 (d, *J* = 12.0 Hz, 1H, $CH_{benzylic}$), 4.676 (q, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4b}), 4.674 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.65 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.62 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.43 (d, *J* = 12.0 Hz, 1H, $CH_{benzylic}$), 4.34 (d, *J* = 12.0 Hz, 1H, $CH_{benzylic}$), 4.28 (br dd, $J_{2,3}$ = 3.0 Hz, $J_{2,1}$ = 6.0 Hz, 2H, H_{2a}), 4.16 (br dt, $J_{5,6}$ = $J_{5,6'}$ = 2.0 Hz, $J_{5,4}$ = 10.5 Hz, 1H, H_{5b}), 4.02 (m, 2H, H_{6a} + H_{1a}), 3.97 (t, $J_{3,2}$ = $J_{3,4}$ = 9.5 Hz, 1H, H_{3b}), 3.80 (m, 2H, H_{4a} + H_{3a}), 3.49 (dd, $J_{6,5}$ = 2.5 Hz, $J_{6,6'}$ = 11.0 Hz, 1H, H_{6b}), 3.44 (dd, $J_{6',5}$ = 1.5 Hz, $J_{6',6}$ = 11.0 Hz, 1H, $H_{6b'}$), 3.43 (br dd, $J_{5,4}$ = 4.0 Hz, $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.39 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H_{2b}), 1.89 (m, 2H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.71 (m, 1H, L-*camphor*), 1.46 (d, *J* = 13.0 Hz, 1H, L-*camphor*), 1.37 (m, 1H, L-*camphor*), 1.21 (m, 1H, L-*camphor*), 1.06 (s, 3H, CH_3 L-*camphor*), 0.87 (s, 3H, CH_3 L-*camphor*), 0.82 (s, 3H, CH_3 L-*camphor*). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ − 2.96. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.31 (Ar*C*), 138.28 (2 × Ar*C*), 137.94, 137.73 (Ar*C*), 135.88 (d, $J_{C,P}$ = 7.6 Hz, Ar*C* *phosphate*), 135.85 (d, $J_{C,P}$ = 7.1 Hz, Ar*C* *phosphate*), 128.41, 128.37, 128.32, 128.27, 128.25, 128.21, 128.17, 128.12, 127.95, 127.82, 127.77, 127.73, 127.67, 127.60, 127.57, 127.26 (Ar*C*H), 118.09 ($C_{acetalic}$ L-*camphor*), 95.42 (C_{1b}), 80.67 (C_{4a}), 80.51 (C_{5a}), 78.04 (C_{6a}), 78.00 (d, $J_{3,P}$ = 2.5 Hz, C_{3b}), 76.75 (C_{3a}), 76.03 (C_{1a}), 75.47 (d, $J_{4,P}$ = 7.3 Hz, C_{4b}), 74.90, 74.56, 74.00 ($CH_{2benzylic}$), 73.80 (C_{2a}), 73.04, 72.57 ($CH_{2benzylic}$), 69.45 (d, $J_{5,P}$ = 4.9 Hz, C_{5b}), 69.26 (d, $J_{C,P}$ = 4.9 Hz, $CH_{2benzylic}$ *phosphate*), 69.24 (d, $J_{C,P}$ = 4.8 Hz, $CH_{2benzylic}$ *phosphate*), 67.50 (C_{6b}), 62.59 (C_{2b}), 51.54, 47.92 (C L-*camphor*), 45.09 (*CH* L-*camphor*), 44.69, 29.83, 26.94 (CH_2 L-*camphor*), 20.57, 20.34, 9.68 (CH_3 L-*camphor*). FAB-MS: *m/z* 1234 $(M + Na)^+$. Anal. calcd. for $C_{71}H_{78}O_{13}N_3P$: C 70.34%; H 6.49%; N 3.47%; found C 70.49%; H 6.81%; N 3.27%.

2-Azido-3,6-di-*O*-benzyl-4-*O*-dibenzylphosphate-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 63. To a solution of **62** (180 mg, 0.149 mmol) in CH_2Cl_2 (7.4 mL), H_2O (268 µl, 14.876 mmol) and TFA (1.15 mL, 14.977 mmol) were added and the resulting mixture was stirred for 2 h. The mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solutions. The organic layer was dried over $MgSO_4$, concentrated in *vacuo* and the residue was purified by flash chromatography (hexane–AcOEt 2 : 1, 1 : 1, 1 : 4) to yield 133 mg (83%) of **63** as a white syrup. $[\alpha]_D^{20}$ = +40.9 (*c* = 1.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.43 (m, 2H, Ar*H*), 7.35 – 7.10 (m, 33H, Ar*H*), 5.44 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1b}), 5.00 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.94 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.91 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.88 – 4.75 (m, 6H, 4 × $CH_{benzylic}$ *phosphate* + 2 × $CH_{benzylic}$), 4.73 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$),

4.70 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.67 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.61 (q, $J_{4,P} = J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 4.27 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.23 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.17 (br t, $J = 3.0$ Hz, 1H, H_{2a}), 4.04 (br dt, $J_{5,6} = J_{5,6'} = 2.0$ Hz, $J_{5,4} = 9.5$ Hz, 1H, H_{5b}), 3.99 (t, $J_{4,3} = J_{4,5} = 9.0$ Hz, 1H, H_{4a}), 3.98 (t, $J_{6,5} = J_{6,6'} = 9.5$ Hz, 1H, H_{6a}), 3.97 (t, $J_{3,2} = J_{3,4} = 9.5$ Hz, 1H, H_{3b}), 3.63 (ddd, $J_{1,2} = 3.0$ Hz, $J_{1,OH} = 5.0$ Hz, $J_{1,6} = 9.0$ Hz, 1H, H_{1a}), 3.52 (d, $J_{OH,1} = 5.0$ Hz, 1H, $OH_{eq.}$), 3.50 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, 1H, H_{2b}), 3.48 (dd, $J_{3,2} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, 1H, H_{3a}), 3.39 (t, $J_{5,4} = J_{5,6} = 9.5$ Hz, 1H, H_{5a}), 3.34 (dd, $J_{6,5} = 3.0$ Hz, $J_{6,6'} = 11.0$ Hz, 1H, H_{6b}), 3.21 (dd, $J_{6',5} = 1.5$ Hz, $J_{6',6} = 11.0$ Hz, 1H, $H_{6b'}$), 2.52 (s, 1H, $OH_{ax.}$). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ − 2.94. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.17, 138.08, 137.96, 137.53, 137.33 (Ar*C*), 135.61 (d, $J_{C,P} = 6.9$ Hz, Ar*C phosphate*), 135.55 (d, $J_{C,P} = 6.6$ Hz, Ar*C phosphate*), 128.41, 128.35, 128.32, 128.27, 128.22, 128.16, 128.13, 128.01, 127.87, 127.83, 127.80, 127.75, 127.66, 127.55, 127.48, 127.31, 127.21, 127.17 (Ar*C*H), 97.96 (C_{1b}), 81.50 (C_{4a}), 80.55 (C_{5a}), 79.65 (C_{6a}), 79.56 (C_{3a}), 78.65 (d, $J_{3,P} = 2.9$ Hz, C_{3b}), 75.77 (*C*$H_{2benzylic}$), 75.34 (d, $J_{4,P} = 7.0$ Hz, C_{4b}), 75.12, 74.55, 72.89 (*C*$H_{2benzylic}$), 72.73 (C_{1a}), 72.47 (*C*$H_{2benzylic}$), 69.85 (d, $J_{5,P} = 4.3$ Hz, C_{5b}), 69.36 (C_{2a}), 69.25 (d, $J_{C,P} = 5.1$ Hz, 2 × *C*$H_{2benzylic}$ *phosphate*), 67.17 (C_{6b}), 63.36 (C_{2b}). FAB-MS: m/z 1100 $(M + Na)^+$. Anal. calcd. for $C_{61}H_{64}O_{13}N_3P$: C 67.96%; H 5.98%; N 3.90%; found C 67.86%; H 6.27%; N 3.64%.

2-Ammonio-2-deoxy-4-*O*-phosphate-α-D-glucopyranosyl-(1→6)-D-*myo*-inositol 34. A suspension of **63** (80 mg, 0.074 mmol) and 10% Pd on charcoal (157 mg, 0.148 mmol) in a mixture of MeOH–H_2O 9 : 1 (7.4 mL) under a hydrogen atmosphere was stirred for 5 h. The mixture was filtered through a pad of celite and the filter cake washed with H_2O. The solution was concentrated in *vacuo* and lyophilised to yield 31 mg (100%) of **34** as a white solid. $[\alpha]_D^{20} = +59.4$ ($c = 0.2$, H_2O). *NMR data at pH = 5.5*: ^{1}H-NMR (D_2O, 500 MHz): δ 5.40 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 4.10 (br dt, $J_{5,6} = J_{5,6'} = 3.0$ Hz, $J_{5,4} = 10.0$ Hz, 1H, H_{5b}), 4.07 (dd, $J_{3,4} = 9.0$ Hz, $J_{3,2} = 10.5$ Hz, 1H, H_{3b}), 3.99 (br t, $J_{2,1} = J_{2,3} = 2.5$ Hz, 1H, H_{2a}), 3.98 (q, $J_{4,P} = J_{4,3} = J_{4,5} = 9.0$ Hz, 1H, H_{4b}), 3.88 (dd, $J_{6,5} = 3.5$ Hz, $J_{6,6'} = 13.0$ Hz, 1H, H_{6b}), 3.73 (dd, $J_{6',5} = 1.5$ Hz, $J_{6',6} = 13.0$ Hz, 1H, $H_{6b'}$), 3.71 (dd, $J_{1,2} = 3.0$ Hz, $J_{1,6} = 9.5$ Hz, 1H, H_{1a}), 3.69 (t, $J_{6,1} = J_{6,5} = 10.0$ Hz, 1H, H_{6a}), 3.61 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4a}), 3.49 (dd, $J_{3,2} = 3.0$ Hz, $J_{3,4} = 10.5$ Hz, 1H, H_{3a}), 3.37 (dd, $J_{2,1} = 4.0$ Hz, $J_{2,3} = 10.0$ Hz, 1H, H_{2b}), 3.36 (t, $J_{5,4} = J_{5,6} = 9.0$ Hz, 1H, H_{5a}). ^{31}P-NMR (D_2O, 202 MHz): δ 0.71. ^{13}C-NMR (D_2O, 125 MHz): δ 96.20 (C_{1b}), 80.44 (C_{6a}), 72.68 (br s, C_{4b}), 72.57 (C_{5a}), 72.52 (C_{4a}), 72.38 (C_{2a}), 71.61 (C_{1a}), 71.33 (br d, $J_{5,P} = 3.9$ Hz, C_{5b}), 70.89 (C_{3a}), 69.15 (C_{3b}), 59.79 (C_{6b}), 54.34 (C_{2b}). HRMS m/z calcd. for $C_{12}H_{24}O_{13}NPNa^+$: 444.0876; found 444.0843 $(M + Na)^+$.

2-Ammonio-2-deoxy-6-*O*-phosphate-α-D-glucopyranosyl-(1→6)-D-*myo*-inositol 9. *From* **63**: A suspension of **63** (30 mg, 0.033 mmol) and 10% Pd on charcoal (70 mg, 0.066 mmol) in a mixture MeOH–H_2O–$AcOH_{glacial}$ 9 : 1 : 0.1 (3.3 mL) under a hydrogen atmosphere was stirred for 24 h. The mixture was filtered through a pad of celite and the filter cake washed with H_2O. The solution was concentrated in *vacuo* and lyophilised to yield 14 mg (100%) of **9** as white solid. *From* **61**: The suspension was stirred for 48 h in this case, using the same procedure. $[\alpha]_D^{20} = +55.0$ ($c = 0.2$, H_2O). *NMR data at pH = 6.3*: ^{1}H-NMR (D_2O, 500 MHz): δ 5.39 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 4.14 (br d, $J_{5,4} = 10.0$ Hz, 1H, H_{5b}), 4.11 (m, 1H, H_{6b}), 3.99 (br t, $J_{2,1} = J_{2,3} = 2.5$ Hz, 1H, H_{2a}), 3.98 (m, 1H, $H_{6b'}$), 3.90 (dd, $J_{3,4} = 9.5$ Hz, $J_{3,2} = 10.5$ Hz, 1H, H_{3b}), 3.70 (m, 2H, $H_{1a} + H_{6a}$), 3.63 (t, $J_{4,3} = J_{4,5} = 9.0$ Hz, 1H, H_{4b}), 3.62 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4a}), 3.49 (dd, $J_{3,2} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, 1H, H_{3a}), 3.36 (dd, $J_{2,1} = 4.0$ Hz, $J_{2,3} = 10.5$ Hz, 1H, H_{2b}), 3.35 (t, $J_{5,4} = J_{5,6} = 9.5$ Hz, 1H, H_{5a}). ^{31}P-NMR (D_2O, 202 MHz): δ 0.86. ^{13}C-NMR (D_2O, 125 MHz): δ 96.47 (C_{1b}), 80.62 (C_{6a}), 72.62 (C_{5a}), 72.57 (C_{4a}), 72.36 (C_{2a}), 71.59 (C_{1a}), 71.40 (d, $J_{5,P} = 7.6$ Hz, C_{5b}), 70.89 (C_{3a}), 69.39 (C_{3b}), 68.82 (C_{4b}), 63.08 (d, $J_{6,P} = 4.9$ Hz, C_{6b}), 54.44 (C_{2b}). HRMS m/z calcd. for $C_{12}H_{25}O_{13}NP^+$: 422.1056; found 422.1063 $(M + H)^+$.

6-*O*-*tert*-Butyldiphenylsilyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl-(1→4)-2-azido-2-deoxy-3,6-di-*O*-benzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicycle-hept-2-yliden)-D-*myo*-inositol 74. To a solution of **68** (567 mg, 0.680 mmol) and **53** (540 mg, 0.567 mmol) in dry Et_2O (11.3 mL) with 4 Å molecular sieves under an argon atmosphere, TMSOTf (5 µl, 0.028 mmol) at −40 °C was added. The solution was stirred for 30 min, neutralised with Et_3N and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane–AcOEt 19 : 1, 14 : 1, 9 : 1) to yield 856 mg (93%) of **74** as a white foam. $[\alpha]_D^{20} = +41.4$ ($c = 1.8$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.71 (dd, $J_A = 1.5$ Hz, $J_B = 8.0$ Hz, 2H, Ar*H TBDPS*), 7.64 (dd, $J_A = 1.0$ Hz, $J_B = 8.0$ Hz, 2H, Ar*H TBDPS*), 7.40 − 7.15 (m, 41H, Ar*H*), 7.13 − 7.06 (m, 4H, Ar*H*), 6.96 (br t, $J = 7.5$ Hz, 1H, Ar*H TBDPS*), 5.60 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 5.28 (d, $J_{1,2} = 1.5$ Hz, 1H, H_{1c}), 4.97 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.89 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.724 (br d, $J = 12.5$ Hz, 2H, 2 × C$H_{benzylic}$), 4.717 (d, $J = 10.5$ Hz, 1H, C$H_{benzylic}$), 4.69 (s, 2H, C$H_{2benzylic}$), 4.67 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.60 (d, $J = 10.5$ Hz, 1H, C$H_{benzylic}$), 4.57 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.54 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.44 (d, $J = 12.5$ Hz, 1H, C$H_{benzylic}$), 4.43 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.35 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.32 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4c}), 4.28 (t, $J_{2,1} = J_{2,3} = 3.5$ Hz, 1H, H_{2a}), 4.27 (d, $J = 12.5$ Hz, 1H, C$H_{benzylic}$), 4.17 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.02 (m, 2H, $H_{6a} + H_{1a}$), 4.01 (m, 1H, H_{5b}), 3.92 (dd, $J_{6,5} = 3.0$ Hz, $J_{6,6'} = 11.0$ Hz, 1H, H_{6c}), 3.86 (t, $J_{4,3} = J_{4,5} = 9.0$ Hz, 1H, H_{4b}), 3.831 (t, $J_{3,2} = J_{3,4} = 9.5$ Hz, 1H, H_{3b}), 3.827 (dd, $J_{3,2} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, 1H, H_{3c}), 3.77 (m, 2H, $H_{4a} + H_{3a}$), 3.74 (t, $J_{2,1} = J_{2,3} = 2.5$ Hz, 1H, H_{2c}), 3.70 (dd, $J_{6',5} = 1.0$ Hz, $J_{6',6} = 11.0$ Hz, 1H, $H_{6c'}$), 3.59 (br d, $J_{5,4} = 9.5$ Hz, 1H, H_{5c}), 3.48 (dd, $J_{6,5} = 3.0$ Hz, $J_{6,6'} = 11.0$ Hz, 1H, H_{6b}), 3.44 (dd, $J_{6',5} = 1.5$ Hz, $J_{6',6} = 11.0$ Hz, 1H, $H_{6b'}$), 3.43 (m, 1H, H_{5a}), 3.34 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 9.5$ Hz, 1H, H_{2b}), 1.89 (m, 2H, L-*camphor*), 1.74 (m, 1H, L-*camphor*), 1.71 (m, 1H, L-*camphor*), 1.46 (d, $J = 12.5$ Hz, 1H, L-*camphor*), 1.38 (m, 1H, L-*camphor*), 1.21 (m, 1H, L-*camphor*), 1.06 (s, 3H, CH_3 L-*camphor*), 1.01 (s, 9H, (CH_3)$_3$C *TBDPS*), 0.87 (s, 3H, CH_3 L-*camphor*), 0.82 (s, 3H, CH_3 L-*camphor*). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 139.12, 138.72, 138.61, 138.40, 138.33, 138.21, 138.13, 137.86 (Ar*C*), 135.92, 135.62 (Ar*C*H *TBDPS*), 133.92, 133.17 (Ar*C TBDPS*), 129.45 (Ar*C*H *TBDPS*), 128.46, 128.34, 128.27, 128.25, 128.20, 128.10, 128.04, 127.87, 127.81, 127.68, 127.61, 127.56, 127.48, 127.45, 127.31, 127.21, 127.11, 127.07, 127.05 (Ar*C*H), 118.09 (*C*$_{acetal}$ L-*camphor*), 100.78 (C_{1c}), 95.41 (C_{1b}), 80.85 (C_{5a}), 80.58 (C_{4a}), 79.89 (C_{3c}), 79.67 (C_{3b}), 77.94 (C_{6a}), 77.18 (C_{4b}), 76.91 (C_{3a}), 76.41 (C_{2c}), 76.08 (C_{1a}), 75.01, 74.90, 74.72 (*C*$H_{2benzylic}$), 74.23 (C_{4c}), 73.87 (C_{2a}), 73.69 (C_{5c} + *C*$H_{2benzylic}$), 72.99, 72.56, 72.27, 72.18 (*C*$H_{2benzylic}$), 70.10 (C_{5b}), 68.37 (C_{6b}), 62.98 (C_{2b}), 62.72 (C_{6c}), 51.60, 47.96 (C L-*camphor*), 45.12 (*C*H L-*camphor*), 44.77, 29.83, 26.97 (*C*H_2 L-*camphor*), 26.78 ((*C*H_3)$_3$C *TBDPS*), 20.59, 20.38 (*C*H_3 L-*camphor*), 19.31 ((CH$_3$)$_3$*C TBDPS*), 9.67 (*C*H_3 L-*camphor*). ^{13}C-NMR-*undecoupled* ($CDCl_3$, 125 MHz): δ 100.78 (d, $J_{C,H} = 170.0$ Hz, C_{1c}), 95.41 (d, $J_{C,H} = 173.5$ Hz, C_{1b}). FAB-MS: m/z 1645 $(M + Na)^+$. Anal. calcd. for $C_{100}H_{111}O_{15}N_3Si$: C 74.00%; H 6.89%; N 2.59%; found C 73.75%; H 6.55%; N 2.68%.

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)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 75. A solution of **74** (690 mg, 0.425 mmol) in a mixture TFA–H_2O 9 : 1 (8.5 mL) was stirred for 30 min, concentrated in *vacuo* and coevaporated with AcOEt (2 × 10 mL) and Et_3N (5 mL). To a solution of the above residue in dry MeOH (8.5 mL), MeONa (1.0 M solution in MeOH, 43 µl) was added. The solution was stirred for 10 min, neutralized with Amberlite IR-120, filtered and concentrated in *vacuo*. The

residue was purified by flash chromatography (hexane–AcOEt 4 : 1, 2 : 1, 1 : 1) to yield 478 mg (90%) of **75** as a colourless syrup. $[\alpha]_D^{20} = +48.8$ ($c = 1.8$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.37 – 7.12 (m, 40H, Ar*H*), 5.44 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 5.22 (d, $J_{1,2} = 2.0$ Hz, 1H, H_{1c}), 4.98 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.90 (d, $J = 10.5$ Hz, 1H, C$H_{benzylic}$), 4.88 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.87 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.76 (d, $J = 10.5$ Hz, 1H, C$H_{benzylic}$), 4.74 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.71 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.70 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.67 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.59 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.57 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.50 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.39 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.37 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.29 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.183 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.176 (t, $J_{2,1} = J_{2,3} = 3.0$ Hz, 1H, H_{2a}), 4.00 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4a}), 3.99 (t, $J_{6,1} = J_{6,5} = 9.5$ Hz, 1H, H_{6a}), 3.88 (m, 2H, H_{5b} + H_{4b}), 3.85 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4c}), 3.83 (m, 1H, H_{3b}), 3.79 (dd, $J_{3,2} = 2.5$ Hz, $J_{3,4} = 9.0$ Hz, 1H, H_{3c}), 3.69 (t, $J_{2,1} = J_{2,3} = 2.5$ Hz, 1H, H_{2c}), 3.64 (br dt, $J_{1,2} = J_{1,OH} = 3.0$ Hz, $J_{1,6} = 9.5$ Hz, 1H, H_{1a}), 3.58 (br d, $J_{6,5} = J_{6',5} = 3.0$ Hz, 2H, H_{6c} + $H_{6c'}$), 3.512 (br dt, $J_{5,6} = J_{5,6'} = 3.5$ Hz, $J_{5,4} = 10.0$ Hz, 1H, H_{5c}), 3.506 (br d, $J_{OH,1} = 3.0$ Hz, 1H, $OH_{eq.}$), 3.49 (dd, $J_{3,2} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, 1H, H_{3a}), 3.46 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 9.5$ Hz, 1H, H_{2b}), 3.41 (br d, $J_{6,6'} = 11.5$ Hz, 1H, H_{6b}), 3.40 (t, $J_{5,4} = J_{5,6} = 9.5$ Hz, 1H, H_{5a}), 3.19 (br d, $J_{6',6} = 11.5$ Hz, 1H, $H_{6b'}$), 2.54 (br s, 1H, $OH_{ax.}$), 2.11 (br s, 1H, OH_{6c}). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.47, 138.42 (Ar*C*), 138.35 (3 × Ar*C*), 138.17, 137.66, 137.58 (Ar*C*), 128.57, 128.50, 128.44, 128.34, 128.23, 128.15, 128.04, 128.01, 127.95, 127.93, 127.89, 127.78, 127.67, 127.65, 127.59, 127.53, 127.48, 127.44, 127.37, 127.25, 126.94, 126.89 (Ar*C*H), 100.53 (C_{1c}), 98.48 (C_{1b}), 81.59 (C_{4a}), 80.92 (C_{5a}), 80.73 (C_{3b}), 80.40 (C_{6a}), 79.79 (C_{3a}), 79.25 (C_{3c}), 76.66 (C_{4b}), 76.35 (C_{2c}), 75.91, 75.03 (*C*$H_{2benzylic}$), 74.84 (*C*$H_{2benzylic}$ + C_{4c}), 74.58, 73.58 (*C*$H_{2benzylic}$), 73.34 (C_{5c}), 72.79 (C_{1a}), 72.76, 72.54, 72.15 (*C*$H_{2benzylic}$), 71.17 (C_{5b}), 69.54 (C_{2a}), 68.03 (C_{6b}), 64.50 (C_{2b}), 62.29 (C_{6c}). FAB-MS: m/z 1272 $(M + Na)^+$. Anal. calcd. for $C_{74}H_{79}O_{15}N_3 \cdot H_2O$: C 70.07%; H 6.44%; N 3.31%; found C 70.25%; H 6.41%; N 3.34%.

α-D-Mannopyranosyl-(1→4)-2-ammonio-2-deoxy-α-D-glucopyranosyl-(1→6)-D-*myo*-inositol 10. A suspension of **75** (115 mg, 0.092 mmol) and 10% Pd on charcoal (196 mg, 0.184 mmol) in a mixture MeOH–H_2O 9 : 1 (9.2 mL) under a hydrogen atmosphere was stirred for 12 h. The mixture was filtered through a pad of celite and the filter cake washed with H_2O. The solution was concentrated in *vacuo*, loaded on a small column of Amberlite IRA-408 (Cl^-), eluted with H_2O and lyophilised to yield 50 mg (100%) of **10** as a white solid. $[\alpha]_D^{20} = +75.0$ ($c = 0.1$, H_2O). *NMR data at pH = 6.8:* ^{1}H-NMR (D_2O, 500 MHz): δ 5.37 (d, $J_{1,2} = 3.0$ Hz, 1H, H_{1b}), 5.25 (d, $J_{1,2} = 1.5$ Hz, 1H, H_{1c}), 4.12 (dt, $J_{5,6} = J_{5,6'} = 2.5$ Hz, $J_{5,4} = 10.0$ Hz, 1H, H_{5b}), 4.04 (t, $J_{3,2} = J_{3,4} = 10.0$ Hz, 1H, H_{3b}), 4.03 (dd, $J_{2,1} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, 1H, H_{2c}), 3.99 (t, $J_{2,1} = J_{2,3} = 2.5$ Hz, 1H, H_{2a}), 3.86 (dd, $J_{6,5} = 1.0$ Hz, $J_{6,6'} = 12.0$ Hz, 1H, H_{6c}), 3.84 (dd, $J_{6,5} = 3.5$ Hz, $J_{6,6'} = 12.5$ Hz, 1H, H_{6b}), 3.81 (dd, $J_{6',5} = 2.5$ Hz, $J_{6',6} = 12.5$ Hz, 1H, $H_{6b'}$), 3.78 (dd, $J_{3,2} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, 1H, H_{3c}), 3.75 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 3.73 (dd, $J_{6',5} = 5.5$ Hz, $J_{6',6} = 12.0$ Hz, 1H, $H_{6c'}$), 3.71 (m, 2H, H_{6a} + H_{1a}), 3.672 (dd, $J_{4,3} = 8.0$ Hz, $J_{4,5} = 11.5$ Hz, 1H, H_{4c}), 3.670 (m, 1H, H_{5c}), 3.61 (t, $J_{4,3} = J_{4,5} = 10.0$ Hz, 1H, H_{4a}), 3.49 (dd, $J_{3,2} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, 1H, H_{3a}), 3.35 (m, 1H, H_{5a}), 3.29 (br d, $J_{2,3} = 9.5$ Hz, 1H, H_{2b}). ^{13}C-NMR (D_2O, 125 MHz): δ 100.10 (C_{1c}), 96.11 (C_{1b}), 79.90 (C_{6a}), 75.37 (C_{4b}), 73.34 (C_{5c}), 72.24 (C_{5a}), 72.13 (C_{4a}), 71.98 (C_{2a}), 71.19 (C_{1a}), 70.47 (C_{3a} + C_{5b}), 69.90 (C_{3c}), 69.80 (C_{2c} + C_{3b}), 66.07 (C_{4c}), 60.44 (C_{6c}), 59.51 (C_{6b}), 54.13 (C_{2b}). HRMS m/z calcd. for $C_{18}H_{33}O_{15}NNa^+$: 526.1738; found 526.1748 $(M + Na)^+$.

2,3,4-Tri-*O*-benzyl-α-D-mannopyranosyl-(1→4)-2-azido-2-deoxy-3,6-di-*O*-benzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclehept-2-yliden)-D-*myo*-inositol 76. To a solution of **74** (290 mg, 0.179 mmol) in dry THF (3.6 mL) under an argon atmosphere, TBAF (1.0 M solution in THF, 1.8 mL) was added. The solution was stirred for 48 h, diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ solution (50 mL). The aqueous layer was extracted with AcOEt (2 × 25 mL) and the combined organic layers were washed with sat. NaCl solution (3 × 100 mL), dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane–AcOEt 9 : 1, 6 : 1, 4 : 1) to yield 233 mg (94%) of **76** as a white foam. $[\alpha]_D^{20} = +46.6$ ($c = 1.7$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.38 – 7.19 (m, 37H, Ar*H*), 7.14 – 7.06 (m, 3H, Ar*H*), 5.61 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 5.25 (d, $J_{1,2} = 2.0$ Hz, 1H, H_{1c}), 4.90 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.87 (d, $J = 10.5$ Hz, 1H, C$H_{benzylic}$), 4.76 (d, $J = 10.5$ Hz, 1H, C$H_{benzylic}$), 4.74 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.72 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.70 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.69 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.63 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.60 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.58 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.54 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.51 (s, 2H, C$H_{2benzylic}$), 4.44 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.34 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.29 (br dd, $J_{2,1} = 3.0$ Hz, $J_{2,3} = 6.0$ Hz, 1H, H_{2a}), 4.14 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.05 (br dt, $J_{5,6} = J_{5,6'} = 2.5$ Hz, $J_{5,4} = 10.0$ Hz, 1H, H_{5b}), 4.03 (m, 2H, H_{6a} + H_{1a}), 3.92 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 3.87 (t, $J_{4,3} = J_{4,5} = 9.0$ Hz, 1H, H_{4c}), 3.84 (dd, $J_{3,4} = 9.0$ Hz, $J_{3,2} = 10.0$ Hz, 1H, H_{3b}), 3.80 (m, 2H, H_{4a} + H_{3a}), 3.77 (dd, $J_{3,2} = 2.5$ Hz, $J_{3,4} = 9.0$ Hz, 1H, H_{3c}), 3.66 (t, $J_{2,1} = J_{2,3} = 2.5$ Hz, 1H, H_{2c}), 3.64 (m, 2H, H_{6c} + $H_{6c'}$), 3.61 (dd, $J_{6,5} = 2.5$ Hz, $J_{6,6'} = 11.5$ Hz, 1H, H_{6b}), 3.60 (m, 1H, H_{5c}), 3.47 (dd, $J_{6',5} = 1.5$ Hz, $J_{6',6} = 11.5$ Hz, 1H, $H_{6b'}$), 3.44 (m, 1H, H_{5a}), 3.34 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, 1H, H_{2b}), 2.23 (br s, 1H, OH), 1.91 (m, 2H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.47 (d, $J = 13.0$ Hz, 1H, L-*camphor*), 1.40 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.88 (s, 3H, CH_3 L-*camphor*), 0.87 (s, 3H, CH_3 L-*camphor*). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.59, 138.47, 138.44, 138.38, 138.33, 138.29, 138.12, 137.85 (Ar*C*), 128.52, 128.46, 128.36, 128.32, 128.30, 128.27, 128.12, 127.89, 127.84, 127.80, 127.73, 127.71, 127.67, 127.61, 127.57, 127.54, 127.45, 127.31, 127.22, 127.00 (Ar*C*H), 118.13 (*C*$_{acetal}$ L-*camphor*), 100.73 (C_{1c}), 95.44 (C_{1b}), 80.76 (C_{5a}), 80.56 (C_{4a}), 80.05 (C_{3b}), 79.30 (C_{3c}), 78.18 (C_{6a}), 76.88 (C_{3a}), 76.84 (C_{4b}), 76.59 (C_{2c}), 76.09 (C_{1a}), 74.95 (*C*$H_{2benzylic}$), 74.91 (C_{4c}), 74.76, 74.73 (*C*$H_{2benzylic}$), 74.04 (*C*$H_{2benzylic}$), 73.90 (C_{2a}), 73.59 (*C*$H_{2benzylic}$), 73.37 (C_{5c}), 72.59, 72.51, 72.24 (*C*$H_{2benzylic}$), 70.36 (C_{5b}), 68.03 (C_{6b}), 63.27 (C_{2b}), 62.41 (C_{6c}), 51.62, 47.98 (C L-*camphor*), 45.14 (*C*H L-*camphor*), 44.78, 29.88, 26.98 (*C*H_2 L-*camphor*), 20.60, 20.38, 9.78 (*C*H_3 L-*camphor*). FAB-MS: m/z 1406 $(M + Na)^+$. Anal. calcd. for $C_{84}H_{93}O_{15}N_3$: C 72.86%; H 6.77%; N 3.04%; found C 72.65%; H 6.67%; N 2.92%.

6-*O*-Dibenzylphosphate-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl-(1→4)-2-azido-2-deoxy-3,6-*O*-dibenzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclehept-2-yliden)-D-*myo*-inositol 77. To a solution of **76** (190 mg, 0.137 mmol) and 1H-tetrazol (24 mg, 0.343 mmol) in dry CH_2Cl_2 (2.7 mL) under an argon atmosphere, *N*,*N*-diisopropyl dibenzyl phosphoramidite (90 µl, 0.274 mmol) was added. The solution was stirred for 30 min and 70% MCPBA (68 mg, 0.276 mmol) was added at 0 °C. After 10 min the mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solution. The organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by double flash chromatography (hexane–AcOEt 2 : 1 and hexane–AcOEt 9 : 1, 8 : 1, 7 : 1, 6 : 1, 5 : 1, 4 : 1, 3 : 1, 2 : 1) to yield 214 mg (95%) of **77** as a white foam. $[\alpha]_D^{20} = +36.8$ ($c = 0.5$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.37 – 7.12 (m, 47H, Ar*H*), 7.10 (m, 2H, Ar*H*), 7.03 (m, 1H, Ar*H*), 5.61 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 5.23 (d, $J_{1,2} = 2.0$ Hz, 1H, H_{1c}), 4.98 – 4.85 (m, 4H, 4 × C$H_{benzylic}$ *phosphate*), 4.88

(d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.87 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.74 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.73 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.71 (s, 2H, C$H_{2benzylic}$), 4.68 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.61 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.60 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.54 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.51 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.49 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.40 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.38 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.292 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.286 (m, 1H, H_{2a}), 4.21 (ddd, $J_{6,5}$ = 3.5 Hz, $J_{6,P}$ = 5.5 Hz, $J_{6,6'}$ = 11.0 Hz, 1H, H_{6c}), 4.17 (ddd, $J_{6',5}$ = 1.5 Hz, $J_{6',P}$ = 5.0 Hz, $J_{6',6}$ = 11.0 Hz, 1H, $H_{6c'}$), 4.13 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.03 (m, 3H, H_{6a} + H_{1a} + H_{5b}), 4.00 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4c}), 3.86 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4b}), 3.82 (t, $J_{3,2}$ = $J_{3,4}$ = 10.0 Hz, 1H, H_{3b}), 3.79 (m, 2H, H_{4a} + H_{3a}), 3.77 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_{3c}), 3.67 (t, $J_{2,1}$ = $J_{2,3}$ = 2.5 Hz, 1H, H_{2c}), 3.66 (br d, J = 9.5 Hz, 1H, H_{5c}), 3.50 (m, 2H, H_{6b} + $H_{6b'}$), 3.43 (m, 1H, H_{5a}), 3.31 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, 1H, H_{2b}), 1.90 (m, 2H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.46 (d, J = 13.0 Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.88 (s, 3H, CH_3 L-*camphor*), 0.85 (s, 3H, CH_3 L-*camphor*). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ − 1.80. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.60 (Ar*C*), 138.38 (3 × Ar*C*), 138.34, 138.33, 138.18, 137.79 (Ar*C*), 135.96 (d, $J_{C,P}$ = 7.8 Hz, Ar*C phosphate*), 135.93 (d, $J_{C,P}$ = 7.4 Hz, Ar*C phosphate*), 128.49, 128.45, 128.43, 128.40, 128.36, 128.30, 128.28, 128.25, 128.23, 128.09, 127.89, 127.87, 127.82, 127.80, 127.71, 127.68, 127.65, 127.62, 127.60, 127.54, 127.52, 127.32, 127.25, 127.15, 126.91 (Ar*C*H), 118.13 (C_{acetal} L-*camphor*), 100.60 (C_{1c}), 95.42 (C_{1b}), 80.83 (C_{5a}), 80.61 (C_{4a}), 79.80 (C_{3b}), 79.66 (C_{3c}), 77.98 (C_{6a}), 77.16 (C_{4b}), 76.88 (C_{3a}), 76.09 (C_{1a}), 76.04 (C_{2c}), 74.97, 74.92, 74.74 (*C*H$_{2benzylic}$), 73.91 (C_{4c}), 73.88 (C_{2a}), 73.75, 73.14, 72.58, 72.35, 72.07 (*C*H$_{2benzylic}$), 71.74 (d, $J_{5,P}$ = 7.9 Hz, C_{5c}), 70.07 (C_{5b}), 69.17 (d, $J_{C,P}$ = 5.8 Hz, *C*H$_{2benzylic}$ *phosphate*), 69.07 (d, $J_{C,P}$ = 5.5 Hz, *C*H$_{2benzylic}$ *phosphate*), 68.37 (C_{6b}), 66.37 (d, $J_{6,P}$ = 5.3 Hz, C_{6c}), 63.08 (C_{2b}), 51.62, 47.98 (C L-*camphor*), 45.14 (*C*H L-*camphor*), 44.78, 29.86, 26.99 (*C*H$_2$ L-*camphor*), 20.60, 20.39, 9.72 (*C*H$_3$ L-*camphor*). FAB-MS: m/z 1667 $(M + Na)^+$.

6-Dibenzylphosphate-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl-(1→4)-2-azido-2-deoxy-3,6-*O*-dibenzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 78. To a solution of **77** (170 mg, 0.103 mmol) in CH_2Cl_2 (5.2 mL), H_2O (186 µl, 10.325 mmol) and TFA (791 µl, 10.302 mmol) were added and the resulting mixture was stirred for 2 h. The mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL). The organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane–AcOEt 4 : 1, 2 : 1, 1 : 1) to yield 143 mg (92%) of **78** as a colourless syrup. $[a]_D^{20}$ = +34.3 (c = 1.3, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.36 − 7.07 (m, 50H, Ar*H*), 5.46 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 5.20 (d, $J_{1,2}$ = 2.0 Hz, 1H, H_{1c}), 4.96 − 4.84 (m, 4H, 4 × C$H_{benzylic}$ *phosphate*), 4.88 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.87 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.86 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.74 (br d, J = 12.0 Hz, 2H, 2 × C$H_{benzylic}$), 4.73 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.70 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.61 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.58 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.53 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.45 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.33 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.30 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.25 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.17 (ddd, $J_{6,5}$ = 3.5 Hz, $J_{6,P}$ = 6.0 Hz, $J_{6,6'}$ = 11.5 Hz, 1H, H_{6c}), 4.16 (t, $J_{2,1}$ = $J_{2,3}$ = 2.5 Hz, 1H, H_{2a}), 4.14 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.10 (ddd, $J_{6',5}$ = 2.0 Hz, $J_{6',P}$ = 6.0 Hz, $J_{6',6}$ = 11.5 Hz, 1H, $H_{6c'}$), 4.00 (t, $J_{6,1}$ = $J_{6,5}$ = 9.5 Hz, 1H, H_{6a}), 3.99 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4c}), 3.97 (t, $J_{4,3}$ = $J_{4,5}$ = 9.0 Hz, 1H, H_{4a}), 3.90 (m, 1H, H_{5b}), 3.82 (m, 2H, H_{4b} + H_{3b}), 3.78 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_{3c}), 3.69 (t, $J_{2,1}$ = $J_{2,3}$ = 2.5 Hz, 1H, H_{2c}), 3.63 (m, 1H, H_{1a}), 3.59 (br d, $J_{5,4}$ = 9.5 Hz, 1H, H_{5c}), 3.479 (br s, 1H, $OH_{eq.}$), 3.477 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_{3a}), 3.42 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, 1H, H_{2b}), 3.39 (t, $J_{5,4}$ = $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.38 (dd, $J_{6,5}$ = 3.0 Hz, $J_{6,6'}$ = 11.0 Hz, 1H, H_{6b}), 3.28 (dd, $J_{6',5}$ = 1.5 Hz, $J_{6',6}$ = 11.0 Hz, 1H, $H_{6b'}$), 2.53 (br s, 1H, $OH_{ax.}$). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ − 1.80. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.48, (Ar*C*), 138.39 (2 × Ar*C*), 138.34, 138.28, 138.18, 137.68, 137.54 (Ar*C*), 135.93 (d, $J_{C,P}$ = 7.5 Hz, Ar*C phosphate*), 135.91 (d, $J_{C,P}$ = 7.4 Hz, Ar*C phosphate*), 128.56, 128.48, 128.44, 128.41, 128.34, 128.33, 128.30, 128.27, 128.24, 128.20, 128.10, 128.03, 127.92, 127.85, 127.78, 127.75, 127.62, 127.59, 127.50, 127.47, 127.36, 127.28, 127.15, 127.00, 126.79 (Ar*C*H), 100.42 (C_{1c}), 98.25 (C_{1b}), 81.55 (C_{4a}), 80.98 (C_{5a}), 80.53 (C_{3b}), 80.08 (C_{6a}), 79.75 (C_{3a}), 79.58 (C_{3c}), 77.20 (C_{4b}), 75.88 (*C*H$_{2benzylic}$ + C_{2c}), 75.04, 75.00, 74.36 (*C*H$_{2benzylic}$), 73.85 (C_{4c}), 73.22 (*C*H$_{2benzylic}$), 72.76 (*C*H$_{2benzylic}$ + C_{1a}), 72.39, 72.01 (*C*H$_{2benzylic}$), 71.75 (d, $J_{5,P}$ = 7.9 Hz, C_{5c}), 70.89 (C_{5b}), 69.59 (C_{2a}), 69.15 (d, $J_{C,P}$ = 5.6 Hz, *C*H$_{2benzylic}$ *phosphate*), 69.07 (d, $J_{C,P}$ = 5.4 Hz, *C*H$_{2benzylic}$ *phosphate*), 68.43 (C_{6b}), 66.29 (d, $J_{6,P}$ = 5.5 Hz, C_{6c}), 64.38 (C_{2b}). FAB-MS: m/z 1533 $(M + Na)^+$.

6-*O*-Phosphate-α-D-mannopyranosyl-(1→4)-2-ammonio-2-deoxy-α-D-glucopyranosyl-(1→6)-D-*myo*-inositol 17. A suspension of **78** (90 mg, 0.060 mmol) and 10% Pd on charcoal (128 mg, 0.120 mmol) in a mixture of MeOH–H_2O 9 : 1 (6 mL) under hydrogen atmosphere was stirred for 6 h. The mixture was filtered through a pad of celite and the filter cake washed with H_2O. The solution was concentrated in *vacuo* and lyophilised to yield 35 mg (100%) of **17** as a white solid. $[a]_D^{20}$ = +107.9 (c = 0.2, H_2O). *NMR data at pH = 6.5*: ^{1}H-NMR (D_2O, 500 MHz): δ 5.40 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1b}), 5.25 (d, $J_{1,2}$ = 1.5 Hz, 1H, H_{1c}), 4.17 (dt, $J_{5,6}$ = $J_{5,6'}$ = 2.5 Hz, $J_{5,4}$ = 10.0 Hz, 1H, H_{5b}), 4.11 (dd, $J_{3,4}$ = 9.5 Hz, $J_{3,2}$ = 10.5 Hz, 1H, H_{3b}), 4.08 (br dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.0 Hz, 1H, H_{6c}), 4.02 (m, 1H, $H_{6c'}$), 4.01 (dd, $J_{2,1}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, 1H, H_{2c}), 3.99 (br s, 1H, H_{2a}), 3.84 (dd, $J_{6,5}$ = 3.5 Hz, $J_{6,6'}$ = 12.0 Hz, 1H, H_{6b}), 3.82 (m, 1H, $H_{6b'}$), 3.80 (m, 1H, H_{5c}), 3.79 (m, 1H, H_{3c}), 3.78 (m, 1H, H_{4b}), 3.75 (dd, J_A = 9.5 Hz, J_B = 12.0 Hz, 1H, H_{4c}), 3.70 (m, 2H, H_{6a} + H_{1a}), 3.61 (t, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, 1H, H_{4a}), 3.49 (dd, $J_{3,2}$ = 2.5 Hz, $J_{3,4}$ = 10.0 Hz, 1H, H_{3a}), 3.351 (t, $J_{5,4}$ = $J_{5,6}$ = 9.0 Hz, 1H, H_{5a}), 3.345 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H_{2b}). ^{31}P-NMR (D_2O, 202 MHz): δ 0.80. ^{13}C-NMR (D_2O, 125 MHz): δ 100.58 (C_{1c}), 95.79 (C_{1b}), 79.89 (C_{6a}), 75.33 (C_{4b}), 72.38 (d, $J_{5,P}$ = 7.6 Hz, C_{5c}), 72.20 (C_{5a}), 72.14 (C_{4a}), 71.97 (C_{2a}), 71.19 (C_{1a}), 70.47 (C_{3a}), 70.20 (C_{5b}), 69.84 (C_{2c}), 69.73 (C_{3c}), 69.21 (C_{3b}), 65.79 (C_{4c}), 63.54 (C_{6c}), 59.48 (C_{6b}), 54.11 (C_{2b}). HRMS m/z calcd. for $C_{18}H_{34}O_{18}NPNa^+$: 606.1401; found 606.1411 $(M + Na)^+$.

6-*O*-*tert*-Butyldiphenylsilyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-2-deoxy-3,6-di-*O*-benzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclehept-2-yliden)-D-*myo*-inositol 79. To a solution of **53** (540 mg, 0.567 mmol) with 4 Å molecular sieves in dry Et_2O (5.6 mL) under an argon atmosphere, TMSOTf (10 µl, 0.055 mmol) was added at 0 °C. A solution of **73** (945 mg, 1.134 mmol) in dry Et_2O (5.6 mL) was slowly added (1 drop per sec) and the mixture was stirred for 1 h after the addition was completed. The mixture was neutralised, concentrated in *vacuo* and purified by flash chromatography (hexane–AcOEt 24 : 1, 19 : 1, 9 : 1) to yield 653 mg (71%) of **79** as a white foam. $[a]_D^{20}$ = +59.0 (c = 0.4, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.59 − 7.55 (m, 5H, Ar*H*), 7.38 − 7.12 (m, 42H, Ar*H*), 7.11 − 7.06 (m, 3H, Ar*H*), 5.59 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 5.44 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1c}), 4.96 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.93 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.84 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.74 (d, J = 11.5 Hz, 2H, 2 × C$H_{benzylic}$), 4.71 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.69 (d, J = 11.0 Hz, 2H, 2 × C$H_{benzylic}$), 4.66 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.64 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.613 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.610 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.56 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.49 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.33 (d, J = 12.5 Hz, 1H, C$H_{benzylic}$),

4.28 (br dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 6.0 Hz, 1H, H_{2a}), 4.24 (d, J = 12.5 Hz, 1H, C$H_{benzylic}$), 4.11 (br dt, $J_{5,6}$ = $J_{5,6'}$ = 2.5 Hz, $J_{5,4}$ = 9.5 Hz, 1H, H_{5b}), 4.04 (t, $J_{6,1}$ = $J_{6,5}$ = 8.0 Hz, 1H, H_{6a}), 4.03 (t, $J_{3,2}$ = $J_{3,4}$ = 9.5 Hz, 1H, H_{3b}), 4.014 (dd, $J_{1,2}$ = 3.0 Hz, $J_{1,6}$ = 7.0 Hz, 1H, H_{1a}), 4.006 (br s, 1H, H_{4c}), 3.98 (dd, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H_{2c}), 3.97 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4b}), 3.86 (br t, $J_{5,6}$ = $J_{5,6'}$ = 7.0 Hz, 1H, H_{5c}), 3.82 (dd, $J_{3,4}$ = 2.5 Hz, $J_{3,2}$ = 10.5 Hz, 1H, H_{3c}), 3.80 (m, 2H, H_{3a} + H_{4a}), 3.72 (dd, $J_{6,5}$ = 8.0 Hz, $J_{6,6'}$ = 10.0 Hz, 1H, H_{6c}), 3.67 (dd, $J_{6',5}$ = 6.0 Hz, $J_{6',6}$ = 10.0 Hz, 1H, $H_{6c'}$), 3.59 (dd, $J_{6,5}$ = 4.0 Hz, $J_{6,6'}$ = 11.5 Hz, 1H, H_{6b}), 3.46 (br t, $J_{5,4}$ = $J_{5,6}$ = 9.0 Hz, 1H, H_{5a}), 3.45 (dd, $J_{6',5}$ = 2.0 Hz, $J_{6',6}$ = 11.5 Hz, 1H, $H_{6b'}$), 3.30 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2b}), 1.91 (m, 2H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.46 (d, J = 13.0 Hz, 1H, L-*camphor*), 1.37 (m, 1H, L-*camphor*), 1.21 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 1.05 (s, 9H, (CH_3)$_3$C *TBDPS*), 0.88 (s, 3H, CH_3 L-*camphor*), 0.84 (s, 3H, CH_3 L-*camphor*). ^{13}C-NMR (CDCl$_3$, 125 MHz): δ 138.78, 138.73, 138.60 (Ar*C*), 138.47 (2 × Ar*C*), 138.43 (Ar*C*), 138.36 (2 × Ar*C*), 135.59, 135.55 (Ar*C*H *TBDPS*), 133.21, 133.06 (Ar*C TBDPS*), 129.69, 129.67, 128.35, 128.31, 128.27, 128.20, 128.12, 128.06, 127.97, 127.84, 127.74, 127.70, 127.63, 127.53, 127.44, 127.42, 127.38, 127.21, 127.16 (Ar*C*H), 118.04 (C_{acetal} L-*camphor*), 99.12 (C_{1c}), 95.21 (C_{1b}), 80.76 (C_{4a}), 80.69 (C_{5a}), 79.67 (C_{3b}), 78.97 (C_{3c}), 77.87 (C_{6a}), 77.20 (C_{3a}), 76.39 (C_{4b}), 76.06 (C_{2c}), 76.02 (C_{1a}), 75.09 (*C*H$_{2benzylic}$), 75.00 (C_{4c}), 74.80, 74.70 (*C*H$_{2benzylic}$), 73.89 (C_{2a}), 73.70, 73.21, 72.80, 72.75, 72.61 (*C*H$_{2benzylic}$), 71.37 (C_{5c}), 70.25 (C_{5b}), 68.99 (C_{6b}), 63.08 (C_{2b}), 62.43 (C_{6c}), 51.60, 47.96 (C L-*camphor*), 45.13 (*C*H L-*camphor*), 44.77, 29.79 (*C*H$_2$ L-*camphor*), 26.98 ((*C*H$_3$)$_3$C *TBDPS*), 26.90 (*C*H$_2$ L-*camphor*), 20.62, 20.39 (*C*H$_3$ L-*camphor*), 19.16 ((CH$_3$)$_3$*C TBDPS*), 9.74 (*C*H$_3$ L-*camphor*). FAB-MS: m/z 1645 (M + Na)$^+$.

2,3,4-Tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-2-deoxy-3,6-di-*O*-benzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 80. To a solution of **79** (270 mg, 0.166 mmol) in CH_2Cl_2 (8.3 mL), H_2O (0.3 mL, 16.7 mmol) and TFA (1.3 mL, 16.9 mmol) were added and the resulting mixture was stirred for 2 h. The mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solutions. The organic layer was dried over $MgSO_4$, concentrated in *vacuo* and the residue was purified by flash chromatography (hexane–AcOEt 4 : 1, 2 : 1, 1 : 1) to yield 191 mg (92%) of **80** as a colourless syrup. $[\alpha]_D^{20}$ = +44.0 (c = 1.1, $CHCl_3$). ^{1}H-NMR (CDCl$_3$, 500 MHz): δ 7.38 − 7.14 (m, 40H, Ar*H*), 5.58 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1c}), 5.32 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 4.97 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.94 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.89 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.88 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.80 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.730 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.734 (s, 2H, C$H_{2benzylic}$), 4.72 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.70 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.66 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.63 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.58 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.56 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.32 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.20 (br s, 1H, H_{2a}), 4.18 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.05 (br t, $J_{4,3}$ = $J_{4,5}$ = 9.0 Hz, 1H, H_{4b}), 4.02 (m, 1H, H_{4a}), 4.01 (m, 1H, H_{2c}), 4.00 (m, 1H, H_{3b}), 3.99 (m, 1H, H_{5b}), 3.96 (d, $J_{OH,1}$ = 3.5 Hz, 1H, $OH_{eq.}$), 3.95 (t, $J_{6,5}$ = $J_{6,1}$ = 9.5 Hz, 1H, H_{6a}), 3.77 (br s, 1H, H_{4c}), 3.76 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 10.0 Hz, 1H, H_{3c}), 3.60 (dt, $J_{1,2}$ = 3.0 Hz, $J_{1,6}$ = 9.5 Hz, 1H, H_{1a}), 3.57 (br t, $J_{5,6}$ = $J_{5,6'}$ = 6.0 Hz, 1H, H_{5c}), 3.56 (dd, $J_{6,5}$ = 2.5 Hz, $J_{6,6'}$ = 12.0 Hz, 1H, H_{6b}), 3.52 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2b}), 3.50 (m, 1H, H_{6c}), 3.49 (dd, $J_{3,2}$ = 2.5 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H_{3a}), 3.41 (t, $J_{5,4}$ = $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.33 (ddd, $J_{6',OH}$ = 5.0 Hz, $J_{6',5}$ = 7.5 Hz, $J_{6',6}$ = 12.5 Hz, 1H, $H_{6c'}$), 3.23 (br dd, $J_{6',5}$ = 1.5 Hz, $J_{6',6}$ = 12.0 Hz, 1H, $H_{6b'}$), 2.53 (s, 1H, $OH_{ax.}$), 1.71 (br t, $J_{OH,6}$ = $J_{OH,6'}$ = 4.5 Hz, 1H, OH_{6c}). ^{13}C-NMR (CDCl$_3$, 125 MHz): δ 138.81 (Ar*C*), 138.38 (2 × Ar*C*), 138.16 (2 × Ar*C*), 138.09, 137.74, 137.71 (Ar*C*), 128.54, 128.45, 128.43, 128.32, 128.26, 128.24, 127.99, 127.93, 127.89, 127.74, 127.61, 127.55, 127.50, 127.36, 127.22, 127.15, 126.88 (Ar*C*H), 99.16 (C_{1b}), 97.81 (C_{1c}), 82.17 (C_{6a}), 81.70 (C_{4a}), 81.07 (C_{3b}), 81.05 (C_{5a}), 79.75 (C_{3a}), 79.20 (C_{3c}), 75.90 (*C*H$_{2benzylic}$), 75.71 (C_{2c}), 74.49 (C_{4c}), 74.43, 74.34, 74.14, 74.01, 73.74 (*C*H$_{2benzylic}$), 73.17 (C_{4b}), 72.86, 72.67 (*C*H$_{2benzylic}$), 72.37 (C_{1a}), 71.68 (C_{5b}), 71.49 (C_{5c}), 69.26 (C_{2a}), 68.66 (C_{6b}), 64.98 (C_{2b}), 62.26 (C_{6c}). FAB-MS: m/z 1249 M$^+$, 1275 (M + Na)$^+$. Anal. calcd. for $C_{74}H_{79}O_{15}N_3$: C 71.08%; H 6.37%; N 3.36%; found C 71.06%; H 6.30%; N 2.96%.

α-D-Galactopyranosyl-(1→4)-2-ammonio-2-deoxy-α-D-glucopyranosyl-(1→6)-D-*myo*-inositol 13. A suspension of **80** (100 mg, 0.080 mmol) and 10% Pd on charcoal (170 mg, 0.160 mmol) in a mixture MeOH–H_2O 9 : 1 (8 mL) under a hydrogen atmosphere was stirred for 24 h. The mixture was filtered through a pad of celite and the filter cake washed with H_2O. The solution was concentrated in *vacuo*, loaded on a small column of Amberlite IRA-408 (Cl^-), eluted with H_2O and lyophilised to yield 43 mg (100%) of **13** as a white solid. $[\alpha]_D^{20}$ = +88.7 (c = 0.4, H_2O). *NMR data at pH = 5.8*: ^{1}H-NMR (D_2O, 500 MHz): δ 5.42 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1c}), 5.41 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 4.18 (dd, $J_{3,4}$ = 9.0 Hz, $J_{3,2}$ = 10.5 Hz, 1H, H_{3b}), 4.16 (br dt, $J_{5,6}$ = $J_{5,6'}$ = 3.0 Hz, $J_{5,4}$ = 10.0 Hz, 1H, H_{5b}), 3.99 (m, 2H, H_{2a} + H_{5c}), 3.97 (br d, $J_{4,3}$ = 3.0 Hz, 1H, H_{4c}), 3.88 (dd, $J_{6,5}$ = 3.5 Hz, $J_{6,6'}$ = 12.0 Hz, 1H, H_{6b}), 3.86 (dd, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2c}), 3.82 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 10.5 Hz, 1H, H_{3c}), 3.80 (dd, $J_{6,5}$ = 2.5 Hz, $J_{6,6'}$ = 12.0 Hz, 1H, $H_{6b'}$), 3.77 (t, $J_{4,3}$ = $J_{4,5'}$ = 9.5 Hz, 1H, H_{4b}), 3.71 (m, 4H, H_{1a} + H_{6a} + H_{6c} + $H_{6c'}$), 3.62 (t, $J_{4,3}$ = $J_{4,5'}$ = 10.0 Hz, 1H, H_{4a}), 3.49 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 10.0 Hz, 1H, H_{3a}), 3.36 (m, 1H, H_{5a}), 3.34 (dd, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H_{2b}). ^{13}C-NMR (D_2O, 125 MHz): δ 99.26 (C_{1c}), 95.86 (C_{1b}), 79.86 (C_{6a}), 75.58 (C_{4b}), 72.23 (C_{5a}), 72.12 (C_{4a}), 71.99 (C_{2a}), 71.35 (C_{5c}), 71.23 (C_{1a}), 70.51 (C_{3a}), 70.25 (C_{5b}), 69.77 (C_{3b}), 68.84 (C_{3c}), 68.74 (C_{4c}), 68.09 (C_{2c}), 60.75 (C_{6c}), 59.46 (C_{6b}), 53.89 (C_{2b}). HRMS: m/z calcd. for $C_{18}H_{33}O_{15}NNa^+$: 526.1738; found 526.1748 (M + Na)$^+$.

2,3,4-Tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-2-deoxy-3,6-di-*O*-benzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclehept-2-yliden)-D-*myo*-inositol 81. To a solution of **79** (256 mg, 0.158 mmol) in dry THF (3.2 mL) under an argon atmosphere, TBAF (1.0 M solution in THF, 468 µl) was added. The solution was stirred for 4 h, diluted with AcOEt (50 mL) and washed with sat. NaCl solution (50 mL). The aqueous layer was extracted with AcOEt (2 × 25 mL) and the combined organic layers were washed with sat. NaCl solution (3 × 100 mL), dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane–AcOEt 9 : 1, 6 : 1, 4 : 1) to yield 210 mg (96%) of **81** as colourless syrup. $[\alpha]_D^{20}$ = +68.7 (c = 1.4, $CHCl_3$). ^{1}H-NMR (CDCl$_3$, 500 MHz): δ 7.37 − 7.08 (m, 40H, Ar*H*), 5.61 (d, 2 × $J_{1,2}$ = 4.0 Hz, 2H, H_{1b} + H_{1c}), 4.88 (d, J = 11.5 Hz, 2H, 2 × C$H_{benzylic}$), 4.81 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.75 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.73 (d, J = 11.5 Hz, 2H, 2 × C$H_{benzylic}$), 4.71 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.684 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.676 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.63 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.62 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.61 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.58 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.54 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.50 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.49 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.29 (br dd, $J_{2,3}$ = 3.5 Hz, $J_{2,1}$ = 5.5 Hz, 1H, H_{2a}), 4.09 (m, 1H, H_{5b}), 4.08 (m, 1H, H_{4b}), 4.04 (m, 2H, H_{1a} + H_{6a}), 4.03 (m, 1H, H_{3b}), 3.98 (dd, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2c}), 3.80 (m, 2H, H_{3a} + H_{4a}), 3.77 (br d, $J_{4,3}$ = 2.5 Hz, 1H, H_{4c}), 3.74 (dd, $J_{3,4}$ = 2.5 Hz, $J_{3,2}$ = 10.5 Hz, 1H, H_{3c}), 3.71 (dd, $J_{6,5}$ = 2.5 Hz, $J_{6,6'}$ = 12.0 Hz, 1H, H_{6b}), 3.56 (m, 1H, H_{6c}), 3.55 (m, 1H, H_{5c}), 3.52 (br d, $J_{6,6'}$ = 12.0 Hz, 1H, $H_{6b'}$), 3.47 (m, 1H, H_{5a}), 3.36 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, 1H, H_{2b}), 3.35 (dt, $J_{6,5}$ = $J_{6,OH}$ = 7.5 Hz, $J_{6,6'}$ = 13.5 Hz, 1H, $H_{6c'}$), 1.92 (m, 2H, L-*camphor*), 1.91 (br dd, $J_{OH,6}$ = 4.0 Hz, $J_{OH,6'}$ = 7.5 Hz, 1H, OH_{6c}), 1.75 (m, 1H,

L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.47 (d, $J = 13.0$ Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.87 (s, 6H, 2 × CH_3 L-*camphor*). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.53 (Ar*C*), 138.50 (2 × Ar*C*), 138.40, 138.34, 138.25, 138.21, 138.17 (Ar*C*), 128.45, 128.41, 128.39, 128.35, 128.31, 128.28, 128.26, 128.08, 127.88, 127.85, 127.80, 127.69, 127.59, 127.56, 127.51, 127.36, 127.33, 127.28, 127.26, 127.09 (Ar*C*H), 118.06 (C_{acetal} L-*camphor*), 98.10 (C_{1c}), 95.42 (C_{1b}), 80.79 (C_{5a}), 80.53 (C_{4a}), 80.16 (C_{3b}), 79.16 (C_{3c}), 78.33 (C_{6a}), 76.89 (C_{3a}), 76.03 (C_{1a}), 75.87 (C_{2c}), 74.72 (C_{4c} + $CH_{2benzylic}$), 74.62, 74.31 ($CH_{2benzylic}$), 73.96 (C_{4b}), 73.87 (C_{2a}), 73.69, 73.44, 73.40, 72.86, 72.60 ($CH_{2benzylic}$), 71.47 (C_{5c}), 70.73 (C_{5b}), 68.57 (C_{6b}), 63.14 (C_{2b}), 62.53 (C_{6c}), 51.61, 47.96 (C L-*camphor*), 45.14 (*C*H L-*camphor*), 44.73, 29.89, 26.99 (CH_2 L-*camphor*), 20.60, 20.38, 9.83 (CH_3 L-*camphor*). FAB-MS: *m/z* 1406 $(M + Na)^+$. Anal. calcd. for $C_{84}H_{93}O_{15}N_3$: C 72.86%; H 6.77%; N 3.04%; found C 72.46%; H 7.00%; N 3.16%.

6-*O*-Dibenzylphosphate-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-2-deoxy-3,6-*O*-di-benzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclehept-2-yliden)-D-*myo*-inositol 82. To a solution of **81** (105 mg, 0.076 mmol) and 1H-tetrazol (13 mg, 0.186 mmol) in dry CH_2Cl_2 (1.5 mL) under an argon atmosphere, *N*,*N*-diisopropyl dibenzyl phosphoramidite (50 µl, 0.152 mmol) was added. The solution was stirred for 30 min and 70% MCPBA (18 mg, 0.150 mmol) was added at 0 °C. After 10 min the mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solutions. The organic layer was dried over $MgSO_4$, concentrated in *vacuo* and the residue was purified by double flash chromatography (hexane–AcOEt 2 : 1 and hexane–AcOEt 9 : 1, 8 : 1, 7 : 1, 6 : 1, 5 : 1, 4 : 1, 3 : 1, 2 : 1) to yield 120 mg (96%) of **82** as a white foam. $[\alpha]_D^{20} = +68.3$ ($c = 1.2$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.37 − 7.08 (m, 50H, Ar*H*), 5.58 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 5.54 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1c}), 4.99 − 4.84 (m, 4H, 4 × C$H_{benzylic}$ *phosphate*), 4.87 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.86 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.81 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.73 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.702 (br d, $J = 11.5$ Hz, 2H, 2 × C$H_{benzylic}$), 4.700 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.67 (d, $J = 12.5$ Hz, 1H, C$H_{benzylic}$), 4.64 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.58 (d, $J = 10.5$ Hz, 1H, C$H_{benzylic}$), 4.57 (s, 2H, C$H_{2benzylic}$), 4.51 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.49 (d, $J = 12.5$ Hz, 1H, C$H_{benzylic}$), 4.48 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 3.39 (d, $J = 12.5$ Hz, 1H, C$H_{benzylic}$), 4.28 (br dd, $J_{2,3} = 2.5$ Hz, $J_{2,1} = 5.5$ Hz, 1H, H_{2a}), 4.12 (br dt, $J_{5,6} = J_{5,6'} = 3.0$ Hz, $J_{5,4} = 9.5$ Hz, 1H, H_{5b}), 4.03 (m, 2H, H_{6a} + H_{6c}), 4.02 (m, 1H, H_{1a}), 4.01 (m, 1H, H_{3b}), 4.00 (m, 1H, H_{4b}), 3.99 (m, 1H, $H_{6c'}$), 3.95 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, 1H, H_{2c}), 3.82 (br t, $J_{5,6} = J_{5,6'} = 6.5$ Hz, 1H, H_{5c}), 3.78 (m, 2H, H_{4a} + H_{3a}), 3.77 (m, 1H, H_{4c}), 3.72 (dd, $J_{3,4} = 2.5$ Hz, $J_{3,2} = 10.0$ Hz, 1H, H_{3c}), 3.64 (dd, $J_{6,5} = 3.5$ Hz, $J_{6,6'} = 11.0$ Hz, 1H, H_{6b}), 3.51 (br dd, $J_{6',5} = 2.5$ Hz, $J_{6',6} = 11.0$ Hz, 1H, $H_{6b'}$), 3.46 (m, 1H, H_{5a}), 3.27 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 9.5$ Hz, 1H, H_{2b}), 1.91 (m, 2H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.46 (d, $J = 13.0$ Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.88 (s, 3H, CH_3 L-*camphor*), 0.85 (s, 3H, CH_3 L-*camphor*). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ − 1.79. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.50 (Ar*C*), 138.46 (2 × Ar*C*), 138.42 (2 × Ar*C*), 138.37 (2 × Ar*C*), 138.21 (Ar*C*), 135.76 (d, $J_{C,P} = 6.8$ Hz, 2 × Ar*C* *phosphate*), 128.56, 128.48, 128.40, 128.34, 128.25, 128.20, 128.12, 128.07, 128.02, 127.89, 127.86, 127.82, 127.80, 127.69, 127.66, 127.61, 127.59, 127.53, 127.49, 127.42, 127.38, 127.32, 127.28, 127.21, 127.17 (Ar*C*H), 118.02 (C_{acetal} L-*camphor*), 98.20 (C_{1c}), 95.42 (C_{1b}), 80.70 (C_{5a}), 80.62 (C_{4a}), 79.96 (C_{3b}), 78.69 (C_{3c}), 78.16 (C_{6a}), 76.83 (C_{3a}), 76.05 (C_{1a}), 75.66 (C_{2c}), 74.75, 74.64 ($CH_{2benzylic}$), 74.60 (C_{4b}), 74.57 ($CH_{2benzylic}$), 74.17 (C_{4c}), 73.85 (C_{2a}), 73.37, 73.28, 72.94, 72.74, 72.57 ($CH_{2benzylic}$), 70.10 (C_{5b}), 69.49 (d, $J_{5,P} = 10.0$ Hz, C_{5c}), 69.26 (d, $J_{C,P} = 5.4$ Hz, 2 × $CH_{2benzylic}$ *phosphate*), 68.91 (C_{6b}), 65.79 (d, $J_{6,P} = 5.1$ Hz, C_{6c}), 63.00 (C_{2b}), 51.59, 47.95 (C L-*camphor*), 45.14 (*C*H L-*camphor*), 44.71, 29.87, 26.99 (CH_2 L-*camphor*), 20.60, 20.39, 9.73 (CH_3 L-*camphor*). FAB-MS: *m/z* 1667 $(M + Na)^+$. Anal. calcd. for $C_{98}H_{106}O_{18}N_3P{\cdot}H_2O$: C 70.78%; H 6.55%; N 2.53%; found C 70.85%; H 6.80%; N 2.55%.

6-*O*-Dibenzylphosphate-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-2-deoxy-3,6-di-*O*-benzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 83. To a solution of **82** (100 mg, 0.061 mmol) in CH_2Cl_2 (3 mL), TFA (468 µl, 6.095 mmol) and H_2O (110 µl, 6.106 mmol) were added and the resulting mixture was stirred for 2 h. The mixture was diluted with AcOEt (25 mL) and washed with sat. $NaHCO_3$ (2 × 25 mL) and sat. NaCl (3 × 25 mL) solutions. The organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane–AcOEt 4 : 1, 2 : 1, 1 : 1) to yield 83 mg (90%) of **83** as white foam. $[\alpha]_D^{20} = +45.9$ ($c = 2.3$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.37 − 7.10 (m, 50H, Ar*H*), 5.45 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1c}), 5.27 (d, $J_{1,2} = 4.0$ Hz, 1H, H_{1b}), 4.96 − 4.91 (m, 5H, 4 × C$H_{benzylic}$ *phosphate* + C$H_{benzylic}$), 4.91 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.89 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.85 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.81 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.72 (s, 2H, C$H_{2benzylic}$), 4.70 (d, $J = 10.5$ Hz, 1H, C$H_{benzylic}$), 4.67 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.66 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.58 (d, $J = 11.5$ Hz, 1H, C$H_{benzylic}$), 4.55 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.53 (d, $J = 12.0$ Hz, 1H, C$H_{benzylic}$), 4.50 (d, $J = 11.0$ Hz, 1H, C$H_{benzylic}$), 4.20 (s, 2H, C$H_{2benzylic}$), 4.19 (br t, $J_{2,1} = J_{2,3} = 3.0$ Hz, 1H, H_{2a}), 4.02 (br dd, $J_{6,5} = 6.5$ Hz, $J_{6,6'} = 10.0$ Hz, 1H, H_{6c}), 4.00 (m, 2H, H_{4a} + H_{5b}), 3.97 (m, 1H, $OH_{ax.}$), 3.96 (m, 3H, H_{3b} + H_{4b} + H_{2c}), 3.94 (t, $J_{6,1} = J_{6,5} = 10.0$ Hz, 1H, H_{6a}), 3.93 (br dd, $J_{6',5} = 5.5$ Hz, $J_{6',6} = 10.0$ Hz, 1H, $H_{6c'}$), 3.81 (br t, $J_{5,6} = J_{5,6'} = 6.5$ Hz, 1H, H_{5c}), 3.72 (br s, 1H, H_{4c}), 3.71 (dd, $J_{3,4} = 2.5$ Hz, $J_{3,2} = 10.5$ Hz, 1H, H_{3c}), 3.57 (dt, $J_{1,2} = 3.5$ Hz, $J_{1,6} = 9.5$ Hz, 1H, H_{1a}), 3.56 (dd, $J_{6,5} = 3.0$ Hz, $J_{6,6'} = 10.5$ Hz, 1H, H_{6b}), 3.47 (dd, $J_{3,2} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, 1H, H_{3a}), 3.40 (t, $J_{5,4} = J_{5,6} = 9.5$ Hz, 1H, H_{5a}), 3.39 (dd, $J_{2,1} = 3.0$ Hz, $J_{2,3} = 9.5$ Hz, 1H, H_{2b}), 3.28 (dd, $J_{6',5} = 2.0$ Hz, $J_{6',6} = 10.5$ Hz, 1H, $H_{6b'}$), 2.51 (s, 1H, $OH_{eq.}$). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ − 1.72. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.77, 138.49, 138.37, 138.29, 138.20, 138.13, 137.81, 137.77 (Ar*C*), 135.73 (d, $J_{C,P} = 6.6$ Hz, 2 × Ar*C* *phosphate*), 128.57, 128.52, 128.36, 128.29, 128.26, 128.23, 128.21, 128.16, 128.13, 127.94, 127.91, 127.87, 127.83, 127.69, 127.65, 127.55, 127.53, 127.48, 127.35, 127.31, 127.28, 127.25, 127.20 (Ar*C*H), 99.00 (C_{1b}), 97.98 (C_{1c}), 82.17 (C_{6a}), 81.69 (C_{4a}), 81.14 (C_{5a}), 80.73 (C_{3b}), 79.67 (C_{3a}), 78.69 (C_{3c}), 75.82 ($CH_{2benzylic}$), 75.54 (C_{2c}), 74.58 (2 × $CH_{2benzylic}$ + C_{4b}), 74.16 ($CH_{2benzylic}$), 74.08 (C_{4c}), 73.77, 73.08, 72.80, 72.60 ($CH_{2benzylic}$), 72.20 (C_{1a}), 71.32 (C_{5b}), 69.69 (d, $J_{5,P} = 9.8$ Hz, C_{5c}), 69.27 (d, $J_{C,P} = 5.4$ Hz, 2 × $CH_{2benzylic}$ *phosphate*), 69.20 (C_{2a}), 69.02 (C_{6b}), 65.91 (d, $J_{6,P} = 5.3$ Hz, C_{6c}), 64.82 (C_{2b}). FAB-MS: *m/z* 1533 $(M + Na)^+$. Anal. calcd. for $C_{88}H_{92}O_{18}N_3P{\cdot}2H_2O$: C 68.34%; H 6.26%; N 2.72%; found C 68.47%; H 6.14%; N 2.66%.

6-*O*-Phosphate-α-D-galactopyranosyl-(1→4)-2-ammonio-2-deoxy-α-D-glucopyranosyl-(1→6)-D-*myo*-inositol 35. A suspension of **83** (60 mg, 0.040 mmol) and 10% Pd on charcoal (85 mg, 0.080 mmol) in a mixture of MeOH–H_2O 9 : 1 (4 mL) under a hydrogen atmosphere was stirred for 6 h. The mixture was filtered through a pad of celite and the filter cake washed with H_2O. The solution was concentrated in *vacuo* and lyophilised to yield 23 mg (100%) of **35** as a white solid. $[\alpha]_D^{20} = +65.0$ ($c = 0.2$, H_2O). *NMR data at pH = 5.8:* ^{1}H-NMR (D_2O, 500 MHz): δ 5.42 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 5.40 (br d, $J_{1,2} = 2.0$ Hz, 1H, H_{1c}), 4.25 (dd, $J_{3,4} = 9.5$ Hz, $J_{3,2} = 10.5$ Hz, 1H, H_{3b}), 4.23 (dt, $J_{5,6} = J_{5,6'} = 3.0$ Hz, $J_{5,4} = 10.0$ Hz, 1H, H_{5b}), 4.15 (br dd, $J_{5,6} = 5.5$ Hz, $J_{5,6'} = 7.0$ Hz, H_{5c}), 4.04 (br s, 1H, H_{4c}), 4.00 (br t, $J_{2,1} = J_{2,3} = 2.5$ Hz, 1H, H_{2a}), 3.95 (m, 2H, H_{6c} + $H_{6c'}$), 3.90 (dd, $J_{6,5} = 3.5$ Hz, $J_{6,6'} = 12.5$ Hz, 1H, H_{6b}),

3.85 (m, 2H, H_{2c} + H_{3c}), 3.84 (dd, $J_{6',5}$ = 2.5 Hz, $J_{6',6}$ = 12.5 Hz, 1H, $H_{6b'}$), 3.78 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4b}), 3.72 (m, 2H, H_{1a} + H_{6a}), 3.62 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4a}), 3.50 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 10.0 Hz, 1H, H_{3a}), 3.37 (t, $J_{5,4}$ = $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.36 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H_{2b}). ^{31}P-NMR (D_2O, 202 MHz): δ 3.19. ^{13}C-NMR (D_2O, 125 MHz): δ 98.57 (C_{1c}), 95.76 (C_{1b}), 79.90 (C_{6a}), 75.64 (C_{4b}), 72.22 (C_{5a}), 72.13 (C_{4a}), 71.99 (C_{2a}), 71.22 (C_{1a}), 70.49 (C_{3a}), 70.11 (d, $J_{5,P}$ = 7.6 Hz, C_{5c}), 69.91 (C_{5b}), 69.14 (C_{3b}), 68.64 (C_{3c}), 68.41 (C_{4c}), 68.02 (C_{2c}), 63.64 (br s, C_{6c}), 59.48 (C_{6b}), 53.98 (C_{2b}). HRMS *m/z* calcd. for $C_{18}H_{34}O_{18}NPNa^+$: 606.1411 $(M + Na)^+$.

2,3,4-Tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclehept-2-yliden)-D-*myo*-inositol 85. To a solution of **57** (330 mg, 0.338 mmol) with 4 Å molecular sieves in dry Et_2O (3.4 mL) under an argon atmosphere, TMSOTf (6 µl, 0.033 mmol) was added at 0 °C. A solution of **73** (845 mg, 1.014 mmol) in dry Et_2O (5.1 mL) was slowly added (0.5 drop per sec) and the mixture was stirred for 30 min after the addition was completed. The mixture was neutralised with Et_3N, diluted with AcOEt (10 mL), filtered and concentrated in *vacuo*. To a solution of the above residue in dry THF (6.8 mL) under an argon atmosphere, TBAF (1.0 M solution in THF, 5.1 mL) was added and the resulting mixture was stirred for 6 h. The mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ solution (50 mL). The aqueous layer was extracted with AcOEt (2 × 25 mL) and the combined organic layers were washed with sat. NaCl solution (3 × 100 mL), dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by double flash chromatography (hexane–AcOEt 6 : 1, 4 : 1, 3 : 1, 2 : 1, 1 : 1 and toluene–AcOEt 2 : 1) to yield 143 mg (45%) of **85** as a white foam. TLC (toluene–AcOEt 2 : 1) R_f = 0.64; $[\alpha]_D^{20}$ = +66.1 (*c* = 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.38 − 7.21 (m, 27H, Ar*H*), 7.21 − 7.11 (m, 8H, Ar*H*), 5.74 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1c}), 5.56 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1b}), 4.88 (d, *J* = 12.0 Hz, 1H, $CH_{benzylic}$), 4.84 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.77 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.751 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.748 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.74 (br s, 2H, $CH_{2\ benzylic}$), 4.71 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.68 (s ancho, 2H, $CH_{2\ benzylic}$), 4.67 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.63 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.59 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.49 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.30 (br s, 1H, H_{2a}), 4.07 (t, $J_{4,3}$ = $J_{4,5}$ = 9.0 Hz, 1H, H_{4b}), 4.04 (m, 2H, H_{1a} + H_{6a}), 4.035 (m, 1H, H_{3b}), 4.02 (m, 1H, H_{2c}), 3.99 (br d, $J_{5,4}$ = 10.5 Hz, 1H, H_{5b}), 3.86 (br s, 1H, H_{4c}), 3.82 (m, 2H, H_{4a} + H_{3a}), 3.81 (m, 1H, H_{3c}), 3.79 (m, 1H, H_{6c}), 3.67 (br dd, $J_{5,6'}$ = 2.5 Hz, $J_{5,6}$ = 8.0 Hz, 1H, H_{5c}), 3.60 (br s, 2H, H_{6b} + $H_{6b'}$), 3.47 (m, 1H, H_{5a}), 3.45 (br dd, $J_{6',5}$ = 2.5 Hz, $J_{6',6}$ = 12.0 Hz, 1H, $H_{6c'}$), 3.36 (dd, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2b}), 2.53 (br s, 1H, OH_{6c}), 2.37 (br s, 1H, OH_{6b}), 1.89 (m, 2H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.71 (m, 1H, L-*camphor*), 1.46 (d, *J* = 12.5 Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.87 (s, 6H, 2 × CH_3 L-*camphor*). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.43, 138.35 (Ar*C*), 138.30 (3 × Ar*C*), 138.10, 138.06 (Ar*C*), 128.43, 128.40, 128.35, 128.33, 128.27, 128.09, 127.92, 127.86, 127.76, 127.69, 127.64, 127.46, 127.43, 127.32, 127.27, 126.81 (Ar*C*H), 118.05 (C_{acetal} L-*camphor*), 98.10 (C_{1c}), 95.89 (C_{1b}), 80.72 (C_{5a}), 80.53 (C_{4a}), 80.40 (C_{3b}), 79.26 (C_{3c}), 78.67 (C_{6a}), 76.59 (C_{3a}), 75.95 (C_{1a}), 75.63 (C_{2c}), 74.69 (C_{4c}), 74.45, 74.39, 74.25 ($CH_{2benzylic}$), 73.80 (C_{2a}), 73.63, 73.38, 72.87, 72.66 ($CH_{2benzylic}$), 72.40 (C_{5c}), 72.12 (C_{4b}), 70.46 (C_{5b}), 63.43 (C_{2b}), 63.00 (C_{6c}), 60.78 (C_{6b}), 51.56, 47.95 (C L-*camphor*), 45.14 (*C*H L-*camphor*), 44.55, 29.93, 26.96 (CH_2 L-*camphor*), 20.59, 20.33, 9.87 (CH_3 L-*camphor*). FAB-MS: *m/z* 1316 $(M + Na)^+$. Anal. calcd. for $C_{77}H_{87}O_{15}N_3 \cdot H_2O$: C 70.46%; H 6.84%; N 3.20%; found C 70.43%; H 6.85%; N 2.93%.

6-*O*-Dibenzylphosphate-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-dibenzylphosphate-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclehept-2-yliden)-D-*myo*-inositol 86. To a solution of **85** (140 mg, 0.108 mmol) and 1H-tetrazol (38 mg, 0.542 mmol) in dry CH_2Cl_2 (2.2 mL) under an argon atmosphere, *N*,*N*-diisopropyl dibenzyl phosphoramidite (142 µl, 0.432 mmol) was added. The solution was stirred for 30 min and 70% MCPBA (18 mg, 0.150 mmol) was added at 0 °C. After 10 min the mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solutions. The organic layer was dried over $MgSO_4$, concentrated in *vacuo* and the residue was purified by double flash chromatography (hexane–AcOEt 1 : 1 and hexane–AcOEt 9 : 1, 8 : 1, 7 : 1, 6 : 1, 5 : 1, 4 : 1, 3 : 1, 2 : 1, 1 : 1) to yield 184 mg (94%) of **86** as a white foam. $[\alpha]_D^{20}$ = +57.0 (*c* = 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.36 − 7.18 (m, 46H, Ar*H*), 7.16 − 7.07 (m, 9H, Ar*H*), 5.51 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 5.43 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1c}), 5.03 − 4.90 (m, 8H, 8 × $CH_{benzylic}$ *phosphate*), 4.84 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.83 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.76 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.72 (d, *J* = 12.0 Hz, 1H, $CH_{benzylic}$), 4.70 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.68 (d, *J* = 11.5 Hz, 1H, $CH_{benzylic}$), 4.65 (d, *J* = 12.5 Hz, 1H, $CH_{benzylic}$), 4.61 (d, *J* = 11.0 Hz, 1H, $CH_{benzylic}$), 4.60 (d, *J* = 12.0 Hz, 1H, $CH_{benzylic}$), 4.58 (s, 2H, $CH_{2benzylic}$), 4.49 (d, *J* = 10.5 Hz, 1H, $CH_{benzylic}$), 4.48 (d, *J* = 10.5 Hz, 1H, $CH_{benzylic}$), 4.44 (d, *J* = 12.0 Hz, 1H, $CH_{benzylic}$), 4.26 (br dd, $J_{2,3}$ = 3.5 Hz, $J_{2,1}$ = 6.5 Hz, 1H, H_{2a}), 4.23 (m, 1H, H_{6b}), 4.16 (m, 1H, $H_{6b'}$), 4.14 (m, 2H, H_{5b} + H_{6c}), 4.05 (dd, $J_{6,1}$ = 7.5 Hz, $J_{6,5}$ = 9.5 Hz, 1H, H_{6a}), 4.01 (m, 1H, $H_{6c'}$), 4.00 (m, 1H, H_{1a}), 3.98 (t, $J_{3,2}$ = $J_{3,4}$ = 10.0 Hz, 1H, H_{3b}), 3.94 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2c}), 3.88 (t, $J_{4,3}$ = $J_{4,5}$ = 9.0 Hz, 1H, H_{4b}), 3.80 (m, 2H, H_{4c} + H_{5c}), 3.77 (m, 1H, H_{3a}), 3.75 (m, 2H, H_{4a} + H_{3c}), 3.43 (dd, $J_{5,6}$ = 6.5 Hz, $J_{5,4}$ = 9.5 Hz, 1H, H_{5a}), 3.08 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2b}), 1.90 (m, 1H, L-*camphor*), 1.86 (m, 1H, L-*camphor*), 1.74 (m, 1H, L-*camphor*), 1.68 (m, 1H, L-*camphor*), 1.45 (d, *J* = 12.5 Hz, 1H, L-*camphor*), 1.33 (m, 1H, L-*camphor*), 1.20 (m, 1H, L-*camphor*), 1.05 (s, 3H, CH_3 L-*camphor*), 0.89 (s, 3H, CH_3 L-*camphor*), 0.82 (s, 3H, CH_3 L-*camphor*). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ − 1.45, −1.77. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.48 (Ar*C*), 138.44 (2 × Ar*C*), 138.39, 138.31, 138.29, 138.16 (Ar*C*), 136.04 (d, $J_{C,P}$ = 6.9 Hz, Ar*C phosphate*), 136.01 (d, $J_{C,P}$ = 6.9 Hz, Ar*C phosphate*), 135.95 (d, $J_{C,P}$ = 6.9 Hz, Ar*C phosphate*), 135.90 (d, $J_{C,P}$ = 6.9 Hz, Ar*C phosphate*), 128.55, 128.51, 128.50, 128.46, 128.45, 128.39, 128.37, 128.33, 128.25, 128.22, 128.09, 128.07, 127.99, 127.93, 127.89, 127.84, 127.82, 127.77, 127.71, 127.69, 127.62, 127.55, 127.54, 127.48, 127.44, 127.36, 127.32, 127.21, 127.19 (Ar*C*H), 118.07 (C_{acetal} L-*camphor*), 98.31 (C_{1c}), 95.54 (C_{1b}), 80.81 (C_{4a}), 80.46 (C_{5a}), 79.42 (C_{3b}), 78.53 (C_{3c}), 78.42 (C_{6a}), 76.54 (C_{3a}), 76.05 (C_{1a}), 75.62 (C_{2c}), 74.65 ($CH_{2benzylic}$), 74.42 (C_{4b} + $CH_{2benzylic}$), 74.21 (C_{4c}), 73.79 (C_{2a}), 73.36, 73.33, 72.70, 72.60 ($CH_{2benzylic}$), 69.81 (d, $J_{5,P}$ = 10.5 Hz, C_{5c}), 69.66 (d, $J_{5,P}$ = 7.0 Hz, C_{5b}), 69.27 (d, $J_{C,P}$ = 5.5 Hz, $CH_{2benzylic}$ *phosphate*), 69.21 (d, $J_{C,P}$ = 5.4 Hz, $CH_{2benzylic}$ *phosphate*), 69.06 (d, $J_{C,P}$ = 5.5 Hz, $CH_{2benzylic}$ *phosphate*), 68.94 (d, $J_{C,P}$ = 5.1 Hz, $CH_{2benzylic}$ *phosphate*), 66.68 (d, $J_{6,P}$ = 6.3 Hz, C_{6b}), 65.74 (d, $J_{6,P}$ = 6.4 Hz, C_{6c}), 62.79 (C_{2b}), 51.54, 47.95 (C L-*camphor*), 45.12 (*C*H L-*camphor*), 44.65, 29.92, 26.97 (CH_2 L-*camphor*), 20.57, 20.36, 9.84 (CH_3 L-*camphor*). FAB-MS: *m/z* 1837 $(M + Na)^+$. Anal. calcd. for $C_{105}H_{113}O_{21}N_3P_2$: C 69.48%; H 6.28%; N 2.32%; found C 69.74%; H 6.57%; N 2.08%.

6-*O*-Dibenzylphosphate-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-dibenzylphosphate-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 87. To a solution of **86** (140 mg, 0.077 mmol) in CH_2Cl_2 (3.8 mL), TFA (590 µl, 7.684 mmol) and H_2O (139 µl, 7.716 mmol) were added and the resulting mixture was stirred for 2 h. The mixture was diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ (2 × 50 mL) and sat. NaCl (3 × 50 mL) solutions. The organic layer was dried over $MgSO_4$, concentrated in

vacuo and the residue was purified by flash chromatography (hexane–AcOEt 2 : 1, 1 : 1, 1 : 2) to yield 106 mg (82%) of **87** as a colourless syrup. $[\alpha]_D^{20} = +29.0$ ($c = 0.5$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.35 – 7.15 (m, 54H, Ar*H*), 7.11 (m, 1H, Ar*H*), 5.38 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1c}), 5.32 (d, $J_{1,2} = 3.5$ Hz, 1H, H_{1b}), 4.99 – 4.87 (m, 8H, 8 × C*H*$_{benzylic}$ *phosphate*), 4.89 (br d, $J = 11.0$ Hz, 2H, 2 × C*H*$_{benzylic}$), 4.86 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.84 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.78 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzylic}$), 4.71 (s, 2H, C*H*$_{2benzylic}$), 4.69 (d, $J = 10.5$ Hz, 1H, C*H*$_{benzylic}$), 4.65 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzylic}$), 4.63 (d, $J = 11.5$ Hz, 1H, C*H*$_{benzylic}$), 4.62 (br s, 2H, C*H*$_{2benzylic}$), 4.50 (d, $J = 11.0$ Hz, 1H, C*H*$_{benzylic}$), 4.49 (d, $J = 12.0$ Hz, 1H, C*H*$_{benzylic}$), 4.16 (t, $J_{2,1} = J_{2,3} = 2.5$ Hz, 1H, H_{2a}), 4.12 (m, 1H, H_{6c}), 4.08 (m, 1H, H_{6b}), 4.04 (m, 1H, $H_{6b'}$), 4.01 (m, 2H, H_{5b} + $H_{6c'}$), 3.96 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 9.5$ Hz, 1H, H_{2c}), 3.95 (t, $J_{6,1} = J_{6,5} = J_{4,3} = J_{4,5} = 9.5$ Hz, 2H, H_{6a} + H_{4a}), 3.93 (dd, $J_{3,4} = 9.0$ Hz, $J_{3,2} = 10.0$ Hz, 1H, H_{3b}), 3.823 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 3.818 (br s, 1H, H_{4c}), 3.80 (m, 1H, H_{5c}), 3.77 (dd, $J_{3,2} = 2.5$ Hz, $J_{3,4} = 10.0$ Hz, 1H, H_{3c}), 3.67 (br s, 1H, $OH_{eq.}$), 3.56 (br dd, $J_{1,2} = 3.0$ Hz, $J_{1,6} = 9.5$ Hz, 1H, H_{1a}), 3.44 (dd, $J_{3,2} = 2.5$ Hz, $J_{3,4} = 9.5$ Hz, 1H, H_{3a}), 3.37 (t, $J_{5,4} = J_{5,6} = 9.5$ Hz, 1H, H_{5a}), 3.15 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, 1H, H_{2b}), 2.62 (br s, 1H, $OH_{ax.}$). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ –1.63, –1.67. ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 138.55, 138.47 (Ar*C*), 138.35 (2 × Ar*C*), 138.23, 137.85, 137.74 (Ar*C*), 135.96 (d, $J_{C,P} = 6.5$ Hz, Ar*C phosphate*), 135.91 (d, $J_{C,P} = 6.5$ Hz, Ar*C phosphate*), 135.83 (d, $J_{C,P} = 6.8$ Hz, Ar*C phosphate*), 135.79 (d, $J_{C,P} = 6.2$ Hz, Ar*C phosphate*), 128.51, 128.47, 128.44, 128.34, 128.31, 128.25, 128.22, 128.16, 128.06, 127.95, 127.93, 127.90, 127.87, 127.81, 127.77, 127.73, 127.57, 127.53, 127.50, 127.45, 127.32, 127.25, 127.22 (Ar*C*H), 98.20 (C_{1c}), 97.74 (C_{1b}), 81.54 (C_{4a}), 80.92 (C_{5a}), 79.99 (C_{6a}), 79.92 (C_{3b}), 79.63 (C_{3a}), 78.44 (C_{3c}), 75.72 (*C*H$_{2benzylic}$), 75.56 (C_{2c}), 74.85, 74.62 (*C*H$_{2benzylic}$), 74.54 (C_{4b}), 74.15 (C_{4c}), 73.96, 73.57, 72.72 (*C*H$_{2benzylic}$), 72.66 (C_{1a}), 72.57 (*C*H$_{2benzylic}$), 70.28 (d, $J_{5,P} = 6.5$ Hz, C_{5b}), 69.93 (d, $J_{5,P} = 9.8$ Hz, C_{5c}), 69.63 (C_{2a}), 69.30 (d, $J_{C,P} = 6.1$ Hz, *C*H$_{2benzylic}$ *phosphate*), 69.24 (d, $J_{C,P} = 5.6$ Hz, *C*H$_{2benzylic}$ *phosphate*), 69.08 (d, $J_{C,P} = 4.8$ Hz, *C*H$_{2benzylic}$ *phosphate*), 69.05 (d, $J_{C,P} = 4.5$ Hz, *C*H$_{2benzylic}$ *phosphate*), 66.72 (d, $J_{6,P} = 5.3$ Hz, C_{6b}), 65.75 (d, $J_{6,P} = 5.0$ Hz, C_{6c}), 63.87 (C_{2b}). FAB-MS: m/z 1703 $(M + Na)^+$.

6-*O*-Phosphate-α-D-galactopyranosyl-(1→4)-2-ammonio-2-deoxy-6-*O*-phosphate-α-D-glucopyranosyl-(1→6)-D-*myo*-inositol 36. A suspension of **87** (80 mg, 0.048 mmol) and 10% Pd on charcoal (102 mg, 0.096 mmol) in a mixture of MeOH–H_2O 9 : 1 (4 mL) under a hydrogen atmosphere was stirred for 12 h. The mixture was filtered through a pad of celite and the filter cake washed with H_2O. The solution was concentrated in *vacuo* and lyophilised to yield 32 mg (100%) of **36** as a white solid. $[\alpha]_D^{20} = +134.0$ ($c = 0.2$, H_2O). *NMR data at pH = 5.9:* ^{1}H-NMR (D_2O, 500 MHz): δ 5.45 (d, $J_{1,2} = 4.0$ Hz, 1H, H_{1c}), 5.40 (d, $J_{1,2} = 3.0$ Hz, 1H, H_{1b}), 4.40 (br d, $J_{5,4} = 10.0$ Hz, 1H, H_{5b}), 4.30 (t, $J_{3,2} = J_{3,4} = 10.0$ Hz, 1H, H_{3b}), 4.19 (br t, $J_{5,6} = J_{5,6'} = 6.5$ Hz, 1H, H_{5c}), 4.11 (br s, 2H, H_{6b} + $H_{6b'}$), 4.03 (br d, $J_{4,3} = 3.0$ Hz, 1H, H_{4c}), 4.00 (br s, 1H, H_{2a}), 3.96 (br t, $J_{6+6',5} = J_{6+6',P} = 6.0$ Hz, 2H, H_{6c} + $H_{6c'}$), 3.88 (dd, $J_{3,4} = 3.0$ Hz, $J_{3,2} = 10.5$ Hz, 1H, H_{3c}), 3.823 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.5$ Hz, 1H, H_{2c}), 3.816 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4b}), 3.72 (m, 2H, H_{1a} + H_{6a}), 3.63 (t, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H_{4a}), 3.50 (dd, $J_{3,2} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, 1H, H_{3a}), 3.39 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.5$ Hz, 1H, H_{2b}), 3.37 (m, 1H, H_{5a}). ^{31}P-NMR (D_2O, 202 MHz): δ 0.80, –0.06. ^{13}C-NMR (D_2O, 125 MHz): δ 97.25 (C_{1c}), 95.78 (C_{1b}), 80.34 (C_{6a}), 74.71 (C_{4b}), 72.26 (C_{5a}), 72.10 (C_{4a}), 71.96 (C_{2a}), 71.12 (C_{1a}), 70.46 (C_{3a}), 70.08 (d, $J_{5,P} = 7.4$ Hz, C_{5c}), 68.76 (d, $J_{5,P} = 7.5$ Hz, C_{5b}), 68.72 (C_{3b}), 68.55 (C_{3c}), 68.47 (C_{4c}), 67.94 (C_{2c}), 63.77 (C_{6c}), 63.26 (C_{6b}), 54.06 (C_{2b}).

1-Amino-4-triphenylmethyloxymethylbenzene 89. A solution of 1-nitro-4-triphenylmethyl oxymethylbenzene[61] (2.7 g, 6.8 mmol) in THF (250 mL) under an argon atmosphere was cooled to 0 °C and freshly prepared "Zn–Cu-couple"[62] (7.2 g) was added in small portions. 2,4-Pentadione (38 mL, 0.37 mol) was then added dropwise to the stirred suspension and after 2.5 h of stirring at 5 °C, no starting material was detected by TLC-analysis. The solids were removed by filtration through a pad of celite, the filtrate was concentrated in *vacuo* and the residue was purified by flash chromatography (hexane–AcOEt 8 : 1, 2 : 1,1 : 1) to obtain the amine **89** (2.04 g, 5.58 mmol, 82%) as a fair yellow solid next to a small amount of hydrazine as the autocoupling product (460 mg, 0.61 mmol). TLC (hexane–AcOEt 4 : 1) $R_f = 0.36$. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.50 (d, 6H, $J_{ortho/meta} = 7.7$Hz, *ortho* aromat. Trit), 7.29 (m, 6H, *meta* aromat. Trit), 7.22 (m, 3H, *para* aromat. Trit.), 7.15 (d, 2H, $J_{ortho/meta} = 8.3$Hz, *meta* aromat.), 6.66 (d, 2H, $J_{ortho/meta} = 8.3$Hz, *ortho* aromat.), 4.03 (s, 2H, CH_2OTr), 3.62 (br s, 2H, NH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 196.52, 144.39, 137.98, 136.98, 129.09, 128.30, 128.07, 127.49, 125.03, 97.95, 87.47, 65.63, 29.59, 20.32. FAB-MS: m/z 388 $(M + Na^+)$.

1-Glutarylamino-4-triphenylmethyloxymethylbenzene 90. To a solution of **89** (2.5 g, 6.8 mmol) in pyridine (90 mL), glutaric anhydride (931 mg, 8.16 mmol) was added and the reaction mixture was stirred at 45 °C for 2 h, when TLC-analysis indicated the complete consumption of the starting material. The reaction crude was extracted with water–ethyl acetate, dried over $MgSO_4$ and after concentration in *vacuo* the residue was purified by flash chromatography (CH_2Cl_2–MeOH 15 : 1) to obtain **90** (3.01 g, 6.46 mmol, 95%) as a white solid. TLC (CH_2Cl_2–MeOH 20 : 1) $R_f = 0.55$. ^{1}H-NMR (300 MHz, DMSO): δ 4.76 (s, 1H, N*H*), 7.59 – 7.24 (m, 19H, Ph*H*), 4.00 (s, 2H, OCH_2Ph), 3.37 (br s, 1H, COO*H*), 2.35 (t, 2H, $J = 7.2$Hz, CH_2), 2.27 (t, 2H, $J = 7.2$Hz, CH_2), 1.81 (q, 2H, $J = 7.1$Hz, CH_2). ^{13}C-NMR (75 MHz, DMSO): δ 171.60, 144.65, 139.30, 133.78, 129.07, 128.86, 128.21, 127.96, 119.92, 87.27, 65.82, 41.14, 36.28, 33.92, 21.39. FAB-MS: m/z 502 $(M + Na^+)$.

Attachment of linker 90 to PS-NH_2 resin (resin 91). Prior to use, the PS-NH_2 resin (substitution: 1.23 mmol g^{-1}, Calbiochem/Novabiochem AG, Läufelfingen, Switzerland; 423 mg, 1.23 mmol g^{-1} loading, 0.52 mmol) was washed 3 times with diisopropylamine (5% solution in CH_2Cl_2, 5 mL for each cycle) and with CH_2Cl_2 (3 × 5 mL) in a specially designed reactor equipped with a sintered glass filter. After drying the resin under a high vacuum for two hours, the resin was swollen in CH_2Cl_2 (3 mL) and the linker **90** (250 mg, 0.52 mmol) was added as a solution in DMF (3 mL). After addition of 1-hydroxybenzotriazol (703 mg, 5.2 mmol) and DIC (162 µL, 1.1 mmol) the resin was shaken on an IKA-vibramax-shaker for three days. The resin was washed subsequently with water (3 × 5 mL), MeOH (4 × 5 mL), CH_2Cl_2 (4 × 5 mL) and THF (3 × 5 mL) and dried *in vacuo* until weight remained constant. Weight gain of the resin (+245 mg after reaction, 98% transformation) and check for free amine groups by the test of Kaiser,[63] indicated quantitative completion of the reaction. Remaining free amine groups were capped by treatment with Ac_2O–pyr (2 : 1, 5 mL) for 2 h at rt, followed by washing of the resin **91** with water (3 × 5 mL), MeOH (3 × 5 mL), CH_2Cl_2 (3 × 5 mL) and THF (2 × 5 mL) and drying under a high vacuum until weight remained constant (weight of resin after linker attachment: 668 mg, 99% of attachment).

Detritylation of resin 91 (resin 92). Linker-equipped resin **91** (668 mg, 0.51 mmol) was treated with a TFA-solution in *sec*-butanol (1 mL TFA in 2 mL *sec*-butanol) and shaken for 30 min. After removal of the liquid phase by filtering through the incorporated sintered glass and washing of the resin with CH_2Cl_2 (4 × 5 mL), the detritylation procedure was repeated three times until TLC-analysis of the liquid phase indicated absence of any UV-active compound. Washing of the resin with CH_2Cl_2 (4 × 5 mL) and drying under a high vacuum afforded the resin **92** (548 mg, 0.49 mmol, 97%), as determined by weight loss (–120 mg).

Preparation of PS-benzylaminolinker-TCA resin (resin 93, 0.72 mmol g^{-1}). To resin **92** bearing free benzylaminotype-linker (548 mg, 0.89 mmol g^{-1} loading) swollen in CH_2Cl_2 (5 mL), trichloroacetonitrile (2.3 mL, 23 mmol) was added and the resin was shaken for 10 min at rt. After cooling to 0 °C, a solution of DBU (154 μL in 1 mL CH_2Cl_2) was added over a period of 5 min. The resin was shaken at 0 °C for 40 min, the liquid phase removed by pressure-assisted filtering through the sintered glass, and after subsequent washing of the resin with CH_2Cl_2 (4 × 5 mL) and THF (4 × 5 mL) the resin was dried under a high vacuum. Formation of the trichloroacetimidate was monitored by IR, following the disappearance of the hydroxy stretching band at ~3500 cm^{-1} of the original polymer with the appearance of a strong C=N stretching band at 1664 cm^{-1}. The yield was determined by weight gain (+64 mg, 0.44 mmol, 90% transformation) after drying under a high vacuum (weight of resin 612 mg, 0.44 mmol, 0.72 mmol g^{-1}).

2-Azido-3-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl[2.2.1]bicyclohept-6-ylidine)-D-*myo*-inositol 94. To a solution of **57** (635 mg, 0.65 mmol) and DCC (670 mg, 3.25 mmol) in CH_2Cl_2 (5 mL) levulinic acid (668 μL, 6.5 mmol) was added at rt. After a few seconds precipitation of the formed urea was observed. DMAP (8 mg, 0.07 mmol) dissolved in CH_2Cl_2 (100 μL) was added by syringe and the reaction stirred at rt for 1.5 h. The mixture was diluted with CH_2Cl_2 (20 mL) and filtered through a pad of celite to remove insoluble urea. The solvent was removed under reduced pressure and the obtained residue purified by column chromatography (hexane–AcOEt 8 : 1) to furnish **94** (670 mg, 0.62 mmol, 96%) as a colorless oil. TLC (hexane–AcOEt 3 : 1) $R_f = 0.48$; $[\alpha]_D^{20} = +39.7°$ ($c = 0.55$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.22 (m, 20H, Ph*H*), 5.66 (d, 1H, $J_{1,2} = 3.4$Hz, H_{1b}), 5.15 – 5.07 (m, 1H, H_{4b}), 4.86 – 4.68 (m, 6H, CH_2Ph), 4.59 – 4.55 (m, 2H, CH_2Ph), 4.15 – 4.13 (m, 1H, H_{2a}), 4.02 – 3.95 (m, 4H, H_{5b}, H_{1a}, H_{6a}, H_{4a}), 3.63 (dd, 1H, $J_{2,3} = 2.98$ Hz, $J_{3,4} = 8.0$ Hz, H_{3a}), 3.52 (m, 1H, H_{6b}), 3.43 – 3.39 (m, 1H, H_{5a}), 3.37 – 3.31 (m, 2H, $H_{6b'}$, H_{2b}), 2.64 – 2.52 (m, 2H, CH_2 *Lev*), 2.40 (m, 1H, L-*camphor*), 2.38 – 2.26 (m, 2H, CH_2 *Lev*), 2.11 (s, 3H, CH_3 *Lev*), 1.69 – 1.65 (m, 3H, L-*camphor*), 1.58 – 1.55 (m, 3H, L-*camphor*), 0.96 (s, 3H, CH_3, L-*camphor*), 0.84 (s, 9H, ^{t}Bu *TBDMS*), 0.81 (s, 3H, CH_3 L-*camphor*), 0.76 (s, 3H, CH_3 L-*camphor*), −0.03 (s, 3H, CH_3 *TBDMS*), −0.04 (s, 3H, CH_3 *TBDMS*). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 128.50, 128.40, 128.36, 128.33, 128.28, 128.27, 128.18, 128.14, 128.02, 127.97, 127.92, 127.90, 127.80, 127.71, 127.60, 119.39, 94.69, 80.61, 78.07, 76.22, 74.19, 73.08, 70.12, 62.86, 53.58, 48.83, 47.99, 45.16, 37.77. FAB-MS: m/z 1096 ($M + Na^+$).

2-Azido-3-*O*-benzyl-2-deoxy-4-*O*-levulinoyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl[2.2.1]bicyclohept-6-ylidine)-D-myo-inositol 95. Pseudodisaccharide **94** (670 mg, 0.686 mmol) was dissolved in THF (50 mL) under an argon atmosphere placed in a sealed PE-flask, cooled to −20 °C and treated with AcOH (14 mL) and HF–pyridine complex (8 mL). The solution was allowed to warm up to rt and left stirring for 4 h . After dilution with Et_2O the reaction mixture was neutralized with sat. $NaHCO_3$ solution and the organic layer washed with sat. $NaHCO_3$ solution and brine, dried over $MgSO_4$ and the solvent removed in *vacuo*. The residue was purified by flash chromatography (hexane–AcOEt 2 : 1) to furnish **95** as a colourless oil (598 mg, 0.68 mmol, 99%). TLC (hexane–AcOEt 3 : 1) $R_f = 0.17$. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.21 (m, 20H, Ph*H*), 5.59 (d, 1H, $J_{1,2} = 3.5$Hz, H_{1b}), 4.93 (t, 1H, $J_{3,4} = J_{4,5} = 10.1$ Hz, H_{4b}), 4.83 – 4.62 (m, 8H, CH_2Ph), 4.27 (dd, 1H, $J_{2,3} = 3.9$ Hz, $J_{2,1} = 5.6$ Hz, H_{2a}), 4.19 – 4.00 (m, 2H, H_{1a} + H_{6a}), 3.95 – 3.91 (m, 2H, H_{3b} + H_{5b}), 3.83 – 3.77 (m, 2H, H_{4a} + H_{3a}), 3.49 – 3.45 (m, 1H, H_{6b}), 3.41 (t, 1H, $J_{4,5} = J_{5,6} = 9.4$ Hz, H_{5a}), 3.37 (dd, 1H, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 10.2$Hz, H_{2b}), 3.35 – 3.21 (m, 1H, $H_{6b'}$), 2.68 – 2.63 (m, 1H, CH_2 *Lev*), 2.60 – 2.55 (m, 1H, CH_2 *Lev*), 2.37 – 2.30 (m, 1H, CH_2 *Lev*), 2.26 – 2.20 (m, 1H, CH_2 *Lev*), 2.13 (s, 3H, CH_3 *Lev*), 1.91 – 1.82 (m, 2H, L-*camphor*), 1.74 – 1.72 (m, 1H, L-*camphor*), 1.69 – 1.67 (m, 1H, L-*camphor*), 1.45 (d, $J = 12.9$ Hz, 1H, L-*camphor*), 1.41 – 1.35 (m, 1H, L-*camphor*), 1.22 – 1.17 (m, 1H, L-*camphor*), 1.05 (s, 3H, CH_3 L-*camphor*), 0.86 (s, 3H, CH_3 L-*camphor*), 0.85 (s, 3H, CH_3 L-*camphor*). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 205.98, 173.14, 138.35, 138.31, 138.29, 138.13, 137.83, 128.50, 128.46, 128.43, 128.40, 128.34, 128.17, 128.07, 127.96, 127.94, 127.91, 127.89, 127.86, 127.82, 127.76, 127.72, 127.68, 127.55, 127.53, 127.44, 127.42, 119.69, 95.33, 80.82, 80.69, 80.65, 80.42, 79.58, 77.09, 76.96, 76.91, 76.82, 76.70, 76.07, 74.98, 74.96, 74.78, 74.74, 74.67, 74.62, 73.89, 73.03, 72.63, 71.14, 71.12, 69.73, 69.61, 62.99, 62.95, 60.55, 53.69, 51.60, 48.78, 47.99, 45.16, 45.06, 37.68, 29.76, 29.71, 29.52, 27.71, 26.99, 26.92, 20.62, 20.57, 20.48, 20.38, 11.52, 9.79. FAB-MS: m/z 982 ($M + Na^+$).

Loading of high-loading resin 93 with acceptor 95 (resin 96, 0.71 mmol g^{-1}) and cleavage. Resin **93** (111 mg, 0.08 mmol) weighed into a 5 mL SP-reactor was suspended in cyclohexane (1.5 mL) and shaken for 10 min under an atmosphere of inert gas. The acceptor **95** (168 mg, 0.19 mmol, 2.4 eq.) as a solution in CH_2Cl_2 (1.5 mL) was added *via* syringe and the components mixed thoroughly by shaking for 5 min. $BF_3{\cdot}Et_2O$ (200 μL of a 0.2 M solution in CH_2Cl_2) was added at rt and shaking of the resin continued for 2 h, followed by capping with MeOH (1 mL) and further shaking for 15 min. After separation of the liquid components, the resin was washed with MeOH (3 × 4 mL) and CH_2Cl_2 (5 × 4 mL) and dried under a high vacuum overnight. Loading with **95** was determined by cleaving the alcohol from a resin aliquot (27 mg) with DDQ in CH_2Cl_2–H_2O 9 : 1 and weighing the returned alcohol **95** (17 mg, 0.019 mmol, 0.71 mmol g^{-1}). MALDI-TOF MS m/z 985 ($M + Na + 2H)^+$, calcd. for $C_{55}H_{65}N_3O_{12}$: 960.

Delevulination of resin 96 (resin 97). Resin **96** (90 mg, 0.71 mmol g^{-1}, 0.064 mmol) was swollen in CH_2Cl_2 (2 mL) and shaken for 10 min at rt. Hydrazine-acetate (18 mg, 0.2 mmol) as a solution in MeOH (400 μL) was added and the resin shaken at rt for 18 h. After washing with CH_2Cl_2–MeOH 9 : 1 (4 × 5 mL), CH_2Cl_2 (4 × 5 mL) and THF (4 × 5 mL) the resin was dried *in vacuo*. A resin sample (6 mg) was treated with DDQ (1.5 mg) in CH_2Cl_2–H_2O (20 : 1, 250 μL) for 1 h, and the liquid phase used as reference for TLC-analysis (hexane–AcOEt 2 : 1; $R_f = 0.39$) and MALDI-TOF-monitoring of the reaction. MALDI-TOF MS m/z 887 ($M + Na + 2H)^+$, calcd. for $C_{50}H_{59}N_3O_{10}$: 862.

Glycosylation of liberated acceptor 97 with glycosyl donor 68 and cleavage from resin. Resin-bound acceptor **97** (84 mg, 0.06 mmol) was washed with freshly distilled THF (3 × 3 mL) to remove traces of water and dried *in vacuo*. Donor **68** (123 mg, 0.147 mmol) was divided into three aliquots and each aliquot dissolved in CH_2Cl_2 (2 mL). The resin was swollen with donor-solution (0.049 mol in 2 mL CH_2Cl_2) by shaking for 10 min at rt. After cooling the reactor to 0 °C, 200 μL of a freshly prepared TMSOTf solution (0.05 M in CH_2Cl_2) was added, the mixture shaken for 1 h at rt and then quenched with triethylamine (100 μL). After removal of the liquid phase by filtration, the resin was washed with MeOH (3 × 3 mL), THF (3 × 3 mL) and CH_2Cl_2 (3 × 3 mL). After drying the resin *in vacuo*, the glycosylation was repeated twice with the remaining two donor-aliquots. After repeated washing and drying of the resin to weight constancy the crude yield of the transformation was calculated to be 13% as suggested by the weight gain (+5 mg) observed after performing the three glycosylation cycles. A sample of the resin (7 mg) was subjected to the oxidative cleavage conditions with DDQ (1 mg) in CH_2Cl_2–H_2O 20 : 1 (0.5 mL) for 4 h. TLC and MALDI-TOF analysis showed the presence of unreacted acceptor **56** besides a small portion of the attached donor employed in the glycosylation. The formation of the

desired trisaccharide was not observed. MALDI-TOF MS *m/z* 887 $(M + Na + 2H)^+$ calcd. for $C_{50}H_{59}N_3O_{10}$: 862.

Preparation of low-loading PS-benzylaminolinker-TCA resin (93, 0.20 mmol/g). Prior to use the PS-NH_2 resin (1 g, 1.23 mmol, substitution: 1.23 mmol g^{-1}, Calbiochem/Novabiochem AG, Läufelfingen, Switzerland) was washed 3 times with diisopropylamine (5% solution in CH_2Cl_2, 5 mL for each cycle) and CH_2Cl_2 (3 × 5 mL) in a specially designed reactor equipped with a sintered glass filter. After drying the resin under a high vacuum for 2 h, the resin was swollen in DCM (3 mL) and a substechiometric amount of linker **90** (96 mg, 0.2 mmol) was added as a solution in DMF (6 mL). After addition of 1-hydroxybenzotriazol (306 mg, 2 mmol) and DIC (66 µL, 0.2 mmol), the resin was shaken on an IKA-vibramax-shaker for three days. The resin was washed subsequently with water (3 × 6 mL), MeOH (4 × 6 mL), CH_2Cl_2 (4 × 6 mL) and THF (3 × 6 mL) and dried *in vacuo*. Free amine groups were capped by treatment with Ac_2O–pyr (2 : 1 5 mL) for 2 h at rt, followed by washing of the resin with water (3 × 5 mL), MeOH (3 × 5 mL), CH_2Cl_2 (3 × 5 mL) and THF (2 × 5 mL) and drying under a high vacuum until weight remained constant. Weight gain of the resin (+1.32 g after reaction) and check for free amine groups by the Kaiser-test,[63] indicated quantitative completion of the reaction. Acidic cleavage of the trityl ether and formation of the benzylic trichloroacetimidate **93** (loading 0.20 mmol g^{-1}) was performed following the procedure for the high-loading resin **93**.

Selective attachment of diol 56 to low-loading PS-benzylamino-linker-TCA resin 93 (resin 98, 0.14 mmol g^{-1}). PS-resin **93** (914 mg, 0.2 mmol g^{-1}, 0.182 mmol) was washed prior to use with freshly distilled THF (4 × 5 mL) and dried under a vacuum to remove traces of moisture. The resin was suspended in cyclohexane (6 mL) and the diol **56** (486 mg, 0.543 mmol) was added as a solution in CH_2Cl_2 (6 mL). Shaking was continued at rt for 10 min to achieve a thorough mixture of the components, the reaction then cooled to −15 °C and $BF_3{\cdot}OEt_2$ (45 µL) was added by syringe. After shaking at −15 °C for 1.5 h, MeOH was added to cap unreacted linker sites and shaking was continued for 10 min. The liquid phase was separated by filtration and the resin was washed subsequently with MeOH (3 × 10 mL) and CH_2Cl_2 (4 × 8 mL). Weight gain after drying indicated the yield of attachment (109 mg, 0.126 mmol, 70%) resulting in a loading of 0.14 mmol g^{-1} based on the diol attached. MALDI-TOF MS *m/z* 885 $(M + Na^+)$, 901 $(M + K^+)$, calcd. for $C_{50}H_{59}N_3O_{10}$: 862.

Determination of the selectivity of attachment of 56 to low-loading resin 93. The resin **93** was swollen in CH_2Cl_2 (5 mL) and pyridine (2.5 mL) and treated with benzoyl chloride (325 µL) for 20 h to determine the selectivity of the attachment reaction. Cleavage of the benzoylated compound mixture was performed by swelling an aliquot of the resin (383 mg, 0.054 mmol) in CH_2Cl_2–H_2O (20 : 1, 4 mL) and shaking vigorously after addition of DDQ (21 mg, 0.093 mmol) for 2 h. The cleavage was repeated once under the same conditions and the filtered liquid fractions combined, washed with sat. $NaHCO_3$ solution, dried over $MgSO_4$ and purified through a short plug of silica gel (hexane–AcOEt 3 : 1) to afford the benzoylated pseudodisaccharide (15.1 mg, 0.016 mmol, 30%) as a mixture of regioisomers. The selectivity was determined by ^{1}H-NMR spectroscopy to be 2 : 1 for the ratio of 4-OBz *versus* 6-OBz in the glucosamine-moiety. ^{1}H-NMR (500 MHz, $CDCl_3$) selected data: anomeric signals of major fraction δ 5.71 (d, 1H, $J_{1,2}$ = 3.6 Hz, H_{1b}, 4-Benzoyl), anomeric signals minor fraction 5.53 (d, 1H, $J_{1,2}$ = 3.4 Hz, H_{1b}, 6-benzoyl).

Glycosylation of resin-bound acceptor 98 with donor 100 (resin-bound trisaccharide 101). Resin **98** (265 mg, 0.053 mmol) was directly swollen in a CH_2Cl_2 solution (2 mL) of donor **100**[64] (216 mg, 0.29 mmol, 5.5 eq.), shaken for 10 min at rt and then cooled to 0 °C. TMSOTf solution (200 µL of a 0.46 M solution) was added by syringe and the resin shaken at rt. for 1 h. Reaction of donor was monitored by TLC-analysis of the liquid phase. The resin was washed extensively with CH_2Cl_2–MeOH 9 : 1 (5 × 4 mL) and CH_2Cl_2 (5 × 4 mL) and dried under a high vacuum until the weight remained constant. Weight gain of the resin suggested a transformation of 50% for the first coupling. Cleavage of the product from a resin sample by treatment with DDQ in CH_2Cl_2–H_2O (20 : 1) and subsequent analysis by TLC and MALDI-TOF demonstrated the appearance of a two new products with the consistant weight of the desired trisaccharide **102**, next to unreacted disaccharidic acceptor **56**. The appearance of two isomeric forms were attributed to the 4′-OH and 6′-OH-glycosylated products due to the 2 : 1 mixture obtained when attaching the diol **56** to the linker. The reaction was repeated 4 times with donor charges ranging from 3.5 to 5 eq., resulting in a final transformation of 60% as suggested by the observed weight gain and the acceptor:product ratio on TLC-sheet and in the mass-spectra. TLC (hexane–AcOEt 3 : 1) R_f = 0.52 of major product **102**; (hexane–AcOEt 3 : 1) R_f = 0.17 acceptor **56**. MALDI-TOF MS *m/z* 885 $(M + Na^+)$, 901 $(M + K^+)$ unreacted acceptor **56**; 1371 $(M + Na^+)$, 1385 $(M + K^+)$ trisaccharide **102**.

Resin-bound acceptor 99. ArgoGel-Wang-Cl (loading: 0.43 mmol g^{-1} from Argonaut Technologies, San Carlos, CA, USA; 274 mg, 118 µmol) and sodium hydride (8.5 mg, 0.35 mmol) were weighed into a flask and purged with argon. A solution of diol **56** (406 mg, 0.47 mmol) in dry THF (2.5–3 mL) was added and the reaction was stirred at rt. After 16 h., the resin was successively washed with MeOH (1 × 4 mL), THF (1 × 4 mL) and CH_2Cl_2 (3 × 4 mL). These organic layers were washed with sat. NH_4Cl solution (25 mL) and water (25 mL), dried over $MgSO_4$ and concentrated *in vacuo* to recover the excess of diol **56**. The resin was washed further with H_2O (1 × 4 mL), sat. NH_4Cl solution (1 × 4 mL), H_2O (5 × 4 mL), DMF (2 × 4 mL), THF (2 × 4 mL), CH_2Cl_2 (2 × 4 mL) and finally dried under a high vacuum overnight. According to the amount of product isolated from the resin, the new loading value was around 0.15 mmol g^{-1}. Gel-phase ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.30, 138.89, 138.73, 138.61, 138.34, 130.47, 130.27, 129.73, 129.33, 128.93, 128.80, 128.61, 128.25, 128.15, 128.05, 118.45, 115.21, 114.85, 95.96 (C_1), 81.15, 81.03, 80.16, 79.60, 78.53, 76.50, 75.70, 75.61, 75.41, 75.26, 75.19, 74.29, 73.44, 72.94, 71.76, 71.25, 70.15, 70.08, 69.97, 69.54, 68.41, 63.78, 63.11, 52.01, 48.37, 46.70, 45.52, 45.27, 43.28, 30.26, 27.42, 21.08, 20.86, 11.97, 10.27, 10.16.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 104. Resin-bound acceptor **99** (123 mg, 18 µmol) was swollen in a solution of donor **103**[61] (58 mg, 0.12 mmol) in dry CH_2Cl_2 (1.5 mL), shaken for 30 min and cooled at −20 °C. TMSOTf (100 µL of a 0.06 M solution in dry CH_2Cl_2, 6 µmol) was added and the reaction mixture was shaken at −20 °C. After 4 h., the resin was washed with CH_2Cl_2 (5 × 4 mL), H_2O (2 × 4 mL), DMF (2 × 4 mL), THF (2 × 4 mL) and CH_2Cl_2 (2 × 4 mL). The glycosylation (**103** (30 mg, 0.06 mmol), TMSOTf (75 µL of a 0.06 M solution in dry CH_2Cl_2, 4.5 µmol)) and washing were repeated and the resin was dried under a vacuum for 12 h. The reaction was monitored by removing several mg of resin and cleaving from resin using TFA–CH_2Cl_2–H_2O, followed by TLC analysis and MALDI-TOF mass spectrometry. Resin-bound trisaccharide (110 mg, 16 µmol) was swollen in CH_2Cl_2 (2 mL) and shaken for 5 min. TFA (146 µL, 1.89 mmol) and water (34 µL, 1.89 mmol) were added and the reaction mixture was shaken for 6 h. at rt. The solution and CH_2Cl_2 washings (4 × 4 mL) were collected by filtration. This organic layer was washed with sat. $NaHCO_3$ solution (15 mL) and H_2O (15 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The purification of the residue was carried out by flash column chromatography (toluene–acetone 2 : 1) to give **104** (12 mg, 71%). TLC: (toluene–acetone 2 : 1) R_f = 0.21. $[\alpha]_D^{20}$ = +18.3° (c = 0.42, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 − 7.15

(m, 20H, PhH), 5.30 (dd, 1H, $J_{3,4} = J_{4,5} = 3.0$ Hz, H_{4c}), 5.25 (d, 1H, $J_{1,2} = 3.9$ Hz, H_{1b}), 5.17 (dd, 1H, $J_{1,2} = 8.1$ Hz, $J_{2,3} = 10.5$ Hz, H_{2c}), 5.10 – 4.97 (2d, 2H, $J = 10.5$ Hz, CH_2Ph), 4.96 (dd, 1H, $J_{3,4} = 3.3$ Hz, $J_{2,3} = 10.5$ Hz, H_{3c}), 4.90 (1d, 1H, $J = 10.2$ Hz, CH_2Ph), 4.77 – 4.65 (m, 6H, H_{1c} + CH_2Ph), 4.22 (br s, 1H, H_{2a}), 4.14 (d, 1H, $J = 3.5$ Hz, OH), 4.01 (dd, 1H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H_{4a}), 3.97 – 3.88 (m, 4H), 3.85 – 3.74 (m, 3H), 3.61 (m, 1H, H_{1a}), 3.54 – 3.46 (m, 2H, H_{2b}, H_{3a}), 3.42 – 3.36 (m, 3H), 2.56 (br s, 1H, OH), 2.12, 1.96, 1.96, 1.89 (4s, 12H, $OCOCH_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.14, 170.02, 169.39, 157.47 (C=O), 138.60 – 126.54 (Ph), 100.72 and 99.21 (C_{1b} and C_{1c}), 82.35, 81.67, 80.75, 79.84, 78.65, 76.24, 75.86, 75.03, 74.22, 72.64, 72.37, 71.74, 71.07, 70.64, 69.72, 69.18, 66.84, 64.42, 60.42, 59.89, 20.61 and 20.53 ($OCOCH_3$). MALDI-TOF-MS: m/z 1080 (MNa^+). Anal. calcd. for $C_{54}H_{63}N_3O_{19}\cdot 1/2H_2O$: C, 60.78%; H, 6.05%; N, 3.94%; found: C, 60.75%; H, 6.47%; N, 3.72%.

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 106. Resin-bound acceptor **99** (157 mg, 24 μmol) was swollen in a solution of donor **105**[65] (113 mg, 0.16 mmol) in dry CH_2Cl_2 (1.5 mL), shaken for 30 min and cooled at −20 °C. TMSOTf (100 μL of a 0.08 M solution in dry CH_2Cl_2, 8 μmol) was added and the reaction mixture was shaken at −20 °C. After 4 h, the resin was washed with CH_2Cl_2 (5 × 4 mL), H_2O (2 × 4 mL), DMF (2 × 4 mL), THF (2 × 4 mL) and CH_2Cl_2 (2 × 4 mL). The glycosylation (**105** (70 mg, 0.10 mmol), TMSOTf (50 μL of a 0.10 M solution in dry CH_2Cl_2, 5 μmol)) and washing were repeated and the resin was dried under a vacuum for 12 h. The reaction was monitored by removing several mg of resin and cleaving from resin using TFA–CH_2Cl_2–H_2O, followed by TLC analysis and MALDI-TOF mass spectrometry.

Resin-bound trisaccharide (157 mg, 24 μmol) was swollen in CH_2Cl_2 (2 mL) and shaken for 5 min. TFA (229 μL, 2.97 mmol) and water (53 μL, 2.97 mmol) were added and the reaction mixture was shaken for 6 h. at room temperature. The solution and CH_2Cl_2 washings (4 × 4 mL) were collected by filtration. This organic layer was washed with sat. $NaHCO_3$ solution (15 mL) and H_2O (15 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The purification of the residue was carried out by flash chromatography (toluene–acetone 8 : 1 → 4 : 1 → 2 : 1) to give **106** (12 mg, 40%). TLC: (toluene–acetone 2 : 1) $R_f = 0.41$. $[\alpha]_D^{20} = +43.1°$ ($c = 0.58$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.11 (m, 40H, PhH), 5.61 (d, 1H, $J_{1,2} = 4.0$ Hz, H_{1c}), 5.34 (d, 1H, $J_{1,2} = 3.5$ Hz, H_{1b}), 4.99 – 4.47 (m, 15H, CH_2Ph), 4.38 (d, 1H, $J = 12.0$ Hz, CH_2Ph), 4.17 (br s, 1H, H_{2a}), 4.05 – 3.97 (m, 4H, H_{4a} + H_{3b} + H_{4b} + H_{2c}), 3.94 (dd, 1H, $J_{1,6} = J_{5,6} = 9.5$ Hz, H_{6a}), 3.86 (m, 2H, H_{4c} + H_{5b}), 3.81 – 3.75 (m, 3H, H_{3c} + H_{5c} + OH_{1a}), 3.58 (m, 1H, H_{1a}), 3.52 – 3.45 (m, 4H, H_{3a} + H_{2b} + H_{6b} + H_{6c}), 3.38 (dd, 1H, $J_{4,5} = J_{5,6} = 9.5$ Hz, H_{5a}), 3.33 (dd, 1H, $J_{6,6'} = 12.5$ Hz, $J_{5,6'} = 5.0$ Hz, $H_{6b'}$), 3.26 (dd, 1H, $J_{5,6'} = 4.5$ Hz, $J_{6,6'} = 9.5$ Hz, $H_{6c'}$), 2.76 (m, 1H, OH_{6b}), 2.54 (br s, 1H, OH_{2a}). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 138.64 – 126.96 (Ph), 99.14 (C_{1b}), 98.34 (C_{1c}), 81.66, 81.48, 81.03, 79.85, 79.22, 75.88, 75.40, 74.66, 74.56, 74.37, 74.09, 73.86, 73.54, 72.71, 71.73, 70.85, 69.38, 69.27, 64.87, 60.30. Anal. calcd. for $C_{74}H_{79}N_3O_{15}\cdot 1/2H_2O$: C, 70.57%; H, 6.40%; N, 3.34%; found: C, 70.46%; H, 6.60%; N, 3.09%.

Tetraol 2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 107 and 6-*O* regioisomers 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 108 and 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl-(1→6)-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-D-*myo*-inositol 109. These compounds were also isolated from the reaction mixture due to incompleted coupling and formation of 4-*O* resin-bound acceptors during the immobilization of diol **56**, respectively.

107: TLC (toluene–acetone 2 : 1) $R_f = 0.25$. $[\alpha]_D^{20} = +33.4°$ ($c = 1.25$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.21 (m, 20H, Ph), 5.37 (d, 1H, $J_{1,2} = 3.5$ Hz, H_{1b}), 5.05 – 4.63 (m, 8H, CH_2Ph), 4.15 (br s, 1H, H_{2a}), 3.98 (dd, 1H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H_{4a}), 3.94 (dd, 1H, $J_{5,6} = J_{1,6} = 9.5$ Hz, H_{6a}), 3.76 (dd, 1H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H_{3b}), 3.70 (m, 2H), 3.62 – 3.57 (m, 2H, H_{1a}, H_{4b}), 3.46 (dd, 1H, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, H_{3a}), 3.40 – 3.29 (m, 4H), 2.72 (s, 1H, OH), 2.32 (br s, 1H, OH). Anal. calcd. for $C_{40}H_{45}N_3O_{10}\cdot 1/4H_2O$: C, 65.60%; H, 6.26%; N, 5.74%; found: C, 65.70%; H, 6.62%; N, 5.45%.

108: TLC (toluene–acetone 6 : 1) $R_f = 0.30$. $[\alpha]_D^{20} = +32.8°$ ($c = 0.25$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.12 (m, 40H, Ph), 5.27 (d, 1H, $J_{1,2} = 3.6$ Hz, H_{1b}), 4.96 – 4.59 (m, 14H, CH_2Ph, H_{1c}), 4.49 (d, 1H, $J = 11.5$ Hz, CH_2Ph), 4.39 (2d, 2H, $J = 12.0$ Hz, CH_2Ph), 4.15 (br s, 1H, H_{2a}), 3.97 (dd, 1H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H_{4a}), 3.94 – 3.90 (m, 2H, H_{6a} + H_{2c}), 3.87 – 3.82 (m, 2H, H_{6b}, OH), 3.79 (dd, 1H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H_{3b}), 3.74 (dd, 1H, $J_{3,4} = 2.5$ Hz, $J_{2,3} = 10.0$ Hz, H_{3c}), 3.70 – 3.65 (m, 2H, H_{4b}, H_{5c}), 3.59 – 3.55 (m, 3H, H_{1a} + H_{5b} + OH), 3.45 (dd, 1H, $J_{2,3} = 2.5$ Hz, $J_{3,4} = 9.5$ Hz, H_{3a}), 3.39 – 3.34 (m, 3H, H_{6c} + H_{2b} + H_{5a}), 3.29 (dd, 1H, $J_{6,6'} = 9.5$ Hz, $J_{5,6'} = 6.0$ Hz, $H_{6c'}$), 3.14 (dd, 1H, $J_{5,6'} = 5.0$ Hz, $J_{6,6'} = 10.5$ Hz, $H_{6b'}$), 2.47 (s, 1H, OH_{2a}). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 138.47 – 127.19 (Ph), 98.67 and 98.48 (C_{1b} and C_{1c}), 81.74, 80.98, 80.07, 79.82, 79.04, 76.11, 75.87, 75.32, 74.93, 74.70, 74.59, 73.52, 73.37, 73.08, 72.74, 72.68, 70.70, 69.81, 69.44, 69.28, 68.33, 63.85. FAB-MS: m/z (MNa^+) calcd for $C_{74}H_{79}O_{15}N_3Na$ 1272.5409; found 1272.5386.

109: TLC (toluene–acetone 6 : 1) $R_f = 0.23$. $[\alpha]_D^{20} = +16.5°$ ($c = 0.17$, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.08 (m, 40H, Ph), 5.28 (d, 1H, $J_{1,2} = 4.0$ Hz, H_{1b}), 4.95 – 4.54 (m, 14H, CH_2Ph), 4.39 (2d, 2H, $J = 11.5$ Hz, CH_2Ph), 4.15 (m, 2H, H_{2a} + H_{1c}), 3.95 (dd, 1H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H_{4a}), 3.89 (dd, 1H, $J_{1,6} = J_{5,6} = 9.5$ Hz, H_{6a}), 3.84 – 3.77 (m, 2H), 3.76 – 3.69 (m, 4H), 3.58 – 3–31 (m, 9H), 2.58 (br s, 1H, OH), 2.54 (br s, 1H, OH_{2a}). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 138.22 – 127.34 (Ph), 103.56 (C_{1c}), 98.76 (C_{1b}), 82.26, 81.70, 80.91, 80.70, 80.10, 79.81, 78.80, 75.84, 75.06, 75.03, 74.68, 73.52, 73.41, 72.88, 72.76, 72.67, 71.84, 70.72, 69.39, 68.50, 67.69, 63.90. FAB-MS: m/z (MNa^+) calcd. for $C_{74}H_{79}O_{15}N_3Na$ 1272.5409, found 1272.5381.

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