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# Phospholipase Cleavage of D- and L-*chiro*-Glycosylphosphoinositides Asymmetrically Incorporated into Liposomal Membranes

**Julia B. Bonilla,[a] M. Belén Cid,[b] F.-Xabier Contreras,[c] Félix M. Goñi,[c] and Manuel Martín-Lomas*[a]**

**Abstract:** The nature of *chiro*-inositol-containing inositolphosphoglycans (IPGs), reported to be putative insulin mediators, was studied by examination of the substrate specificities of the phosphatidylinositol-specific phospholipase C (PI-PLC) and the glycosylphosphatidylinositol-specific phospholipase D (GPI-PLD) by using a series of synthetic D- and L-*chiro*-glycosylphosphoinositides. 3-*O*-α-D-Glucosaminyl- (**3**) and -galactosaminyl-2-phosphatidyl-L-*chiro*-inositol (**4**), which show the maximum stereochemical similarity to the 6-*O*-α-D-glucosaminylphosphatidylinositol pseudodisaccharide motifs of GPI anchors, were synthesized and asymmetrically incorporated into phospholipid bilayers in the form of large unilamellar vesicles (LUVs). Similarly, 2-*O*-α-D-glucosaminyl- (**5**) and -galactosaminyl-1-phosphatidyl-D-*chiro*-inositol (**6**), which differ from the corresponding pseudodisaccharide motif of the GPI anchors only in the axial orientation of the phosphatidyl moiety, were also synthesized and asymmetrically inserted into LUVs. The cleavage of these synthetic molecules in the liposomal constructs by PI-PLC from *Bacillus cereus* and by GPI-PLD from bovine serum was studied with the use of 6-*O*-α-D-glucosaminylphosphatidylinositol (**7**) and the conserved GPI anchor structure (**8**) as positive controls. Although PI-PLC cleaved **3** and **4** with about the same efficiency as **7** and **8**, this enzyme did not accept **5** or **6**. GPI-PLD accepted both the L-*chiro*- (**3** and **4**) and the D-*chiro*- (**5** and **6**) glycosylinositolphosphoinositides. Therefore, IPGs containing L-*chiro*-inositol only are expected to be released from *chiro*-inositol-containing GPIs if the cleavage is effected by a PI-PLC, whereas GPI-PLD cleavage could result in both L-*chiro*- and D-*chiro*-inositol-containing IPGs.

**Keywords:** glycolipids · glycophosphoinositides · inositols · liposomes · phospholipases

## Introduction

The biology and chemistry of glycosylphosphatidylinositols (GPIs) have received a great deal of attention.[1] Some GPIs serve to attach proteins to the outer faces of cellular membranes through covalent linkages. These protein GPI anchors present the conserved core structure $NH_2EtOPO_3$-6Manα(1→2)Manα(1→6)Manα(1→4)Glc$NH_2$α(1→6)-*myo*-Ins1-$OPO_3$–lipid, which may appear in forms modified by the presence of branching groups at specific positions.[2] Other GPIs serve to attach extracellular non-protein glycoconjugates to cell membranes, particularly in the case of protozoa. These non-protein GPI anchors share the common core structure Manα(1→4)Glc$NH_2$α(1→6)-*myo*-Ins1-$OPO_3$–lipid.[3] In addition, the existence of free GPIs (GPI-like molecules without anchoring functions, which do not seem to be derived from hydrolysis of GPI-anchored proteins or glycoconjugates) has also been described.[4] The structures of free GPIs are much less defined than those of the GPI anchors. It has been postulated that they may be involved in an intracellular signaling system that may operate for insulin and for several growth factors and cytokines. According to this proposal, free GPIs at the cell surface would be cleaved by specific phospholipases (PLs) to give water-soluble second messengers that have been termed inositolphosphoglycans (IPGs).[5] Two different families of IPGs have been proposed on the basis of chemical composition and biological activity data: type A, which inhibit cAMP-de-

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pendent protein kinase (PKA) and contain *myo*-inositol or 1D-*chiro*-inositol and glucosamine,[6] and type P, which activate pyruvate dehydrogenase phosphatase (PDHPase) and contain 1D-*chiro*-inositol and galactosamine.[7] Neither the IPG mediators nor the free GPI precursors have been fully characterized, with the sole exception of a biologically active IPG isolated from beef liver, the structure of which has recently been elucidated to be $GalNH_2\beta(1\rightarrow4)$-D-*chiro*-Ins-3Me.[8] According to these results, the GPI precursors of these IPG mediators would not share the minimum consensus structure of GPI anchors ($Man\alpha(1\rightarrow4)GlcNH_2\alpha(1\rightarrow6)$-*myo*-Ins), although they may at least contain a $GlcNH_2$ (or $GalNH_2$) 1→*x*-*myo*- (or *chiro*-)Ins pseudodisaccharide structural motif.

Although the presence of *chiro*-inositol in GPIs was first reported in 1985,[9] no PLs specifically involved in the cleavage of *chiro*-inositol-containing GPIs are currently known. Phosphatidylinositol-specific (PI-specific) PLs (PI-PLs) constitute a broad family of proteins of various sizes and sequences. Some of them have been used as tools for the structural study of GPIs; these include PI-PLC from *Bacillus cereus*,[10a,b] GPI-PLC from *Trypanosoma brucei*,[10b,c] and mammalian bovine GPI-PLD.[11] PI-PLCs play a central role in signal transduction, cleaving specialized PIs to form second messengers.[12] Bacterial PI-PLCs cleave GPIs if no acyl group is present at the 2-position in the *myo*-inositol unit, but show no hydrolytic activity towards phosphorylated forms of PI, phosphatidylcholine (PtdCho), or phosphatidylethanolamine (PtdEth).[13] GPI-PLC from *Tripanosoma* cleaves GPIs that do not bear an acyl group at the 2-position in the *myo*-inositol ring.[10b,14] It could also cleave PI, but only if presented in detergent-based micelles.[15] Mammalian GPI-PLD does not exhibit activity against PI or its phosphorylated forms and seems to be specific for GPIs with or without acyl groups at the 2-position in the *myo*-inositol moiety.[16] Importantly, in the only case in which the enzymatic hydrolysis of pure synthetic *chiro*-inositol-containing lipids was investigated, it was shown that bacterial PI-PLC from *Bacillus thuringiensis* cleaves 1L-*chiro*-PI at a rate $10^{-3}$ times that attained with the natural substrate (PI), and in addition, that synthetic 1D-*chiro*-PI is resistant to PI-PLC.[17] This result suggests that the natural *chiro*-inositol-containing GPIs should have the 1L configuration rather than the 1D configuration if the *chiro*-inositol-containing IPGs are produced after PI-PLC cleavage of a *chiro*-inositol-containing free GPI. In addition, it has also been shown that isomerization of *myo*-inositol to D-*chiro*-inositol may occur during acidic hydrolysis of GPIs.[18] Taken together, these results seem to suggest that the detection of D-*chiro*-inositol in GPI structures could be due either to incorrect assignment or to isomerization.

Under physiological conditions, PLs recognize their substrates in the form of bilayers; therefore, studies with these enzymes must be carried out on detergent-based micelles or artificial lipidic vesicles (liposomes) rather than on lipid monomers. In natural systems, the enzymatic cleavage of GPIs takes place during attachment to biological membranes. In biomembranes, glycolipids and cholesterol (Ch) assemble in microdomains ("rafts") that sometimes cluster and self-stabilize in flask-shaped invaginations of the cell plasma membrane, known as caveolae.[19] These microdomains have an asymmetric disposition in which the glycolipids and GPI-linked proteins are located on the outer leaflet.[19a,c,20,21]

Some of us have described the preparation of large unilamellar vesicles (LUVs) of approximately 100 nm in diameter, incorporating natural GPIs preferentially located in the outer monolayer. It was shown that these GPIs could be cleaved by specific PLs.[22] Because of the structural and functional importance of rafts and caveolae, these synthetic vesicles with asymmetric distributions of glycophosphoinositides constitute a highly attractive and relatively simple artificial system with which to study PL-mediated enzymatic cleavage of GPI-like structures. By using this system, we have investigated the enzymatic hydrolysis of some synthetic D- and L-*chiro*-inositol phosphoinositides as part of a program on the synthesis, structures, and biological activities of IPG-like molecules as putative insulin mediators.[23] In the context of this program, we have previously synthesized a variety of IPG-like structures and have explored their biological activities as potential insulin mimetics. The main aim of the current work was to investigate whether PI-PLC or GPI-PLD could accept unusual *chiro*-glycophosphoinositides in membrane-like environments to produce IPG-like structures capable of displaying insulin mimetic activity.

## Results and Discussion

As indicated above, the only available data on the enzymatic hydrolysis of *chiro*-inositol-containing lipids were reported more than ten years ago and involved bacterial PI-PLC.[17] On stereochemical grounds (Figure 1), it was predicted that PI-PLC would be more likely to accept the 1L-*chiro*-PI (**1**) than the 1D-*chiro*-PI diastereomer (**2**), and it was found experimentally that **1** was accepted at a reduced rate and **2** was not a substrate.[17] In the absence of structural information on *chiro*-inositol-containing phospholipids, these structures (2-phosphatidyl-*chiro*-inositols) were selected on the basis of the greatest stereochemical similarity to *myo*-inositol-containing phospholipids.

Also as a result of the absence of structural information, we have previously synthesized different types of IPG-like molecules containing a variety of $GlcNH_2$ and $GalNH_2$ α- and $\beta(1\rightarrow x)$-*myo*-, -D-*chiro*-, and -L-*chiro*-inositol structural motifs.[23] These include $GlcNH_2$- and $GalNH_2\alpha(1\rightarrow3)$-L-*chiro*-inositol (**I** and **II**) and $GlcNH_2$- and $GalNH_2\alpha(1\rightarrow2)$-D-*chiro*-inositol (**III** and **IV**).[23i] The former pair would permit access to 3-*O*-glycosaminyl-2-phosphatidyl-L-*chiro*-inositols (such as **3** and **4**), showing the maximum stereochemical similarity to the $GlcNH_2\alpha(1\rightarrow6)$-*myo*-Ins structural motif of the GPI anchors, and the latter pair would allow 2-*O*-glycosaminyl-1-phosphatidyl-D-*chiro*-inositols (such as **5** and **6**)—differing from the GPI anchor motif only in the ori-

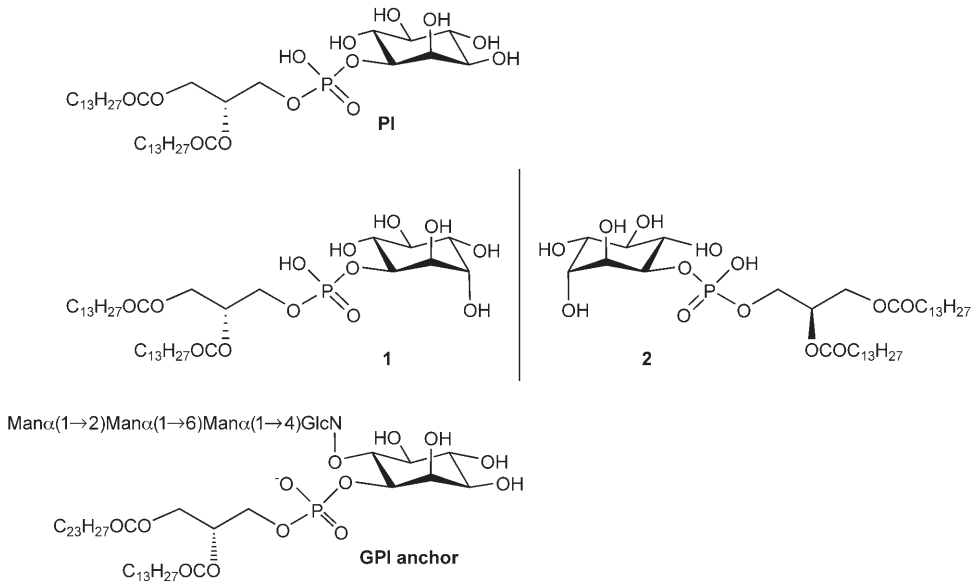
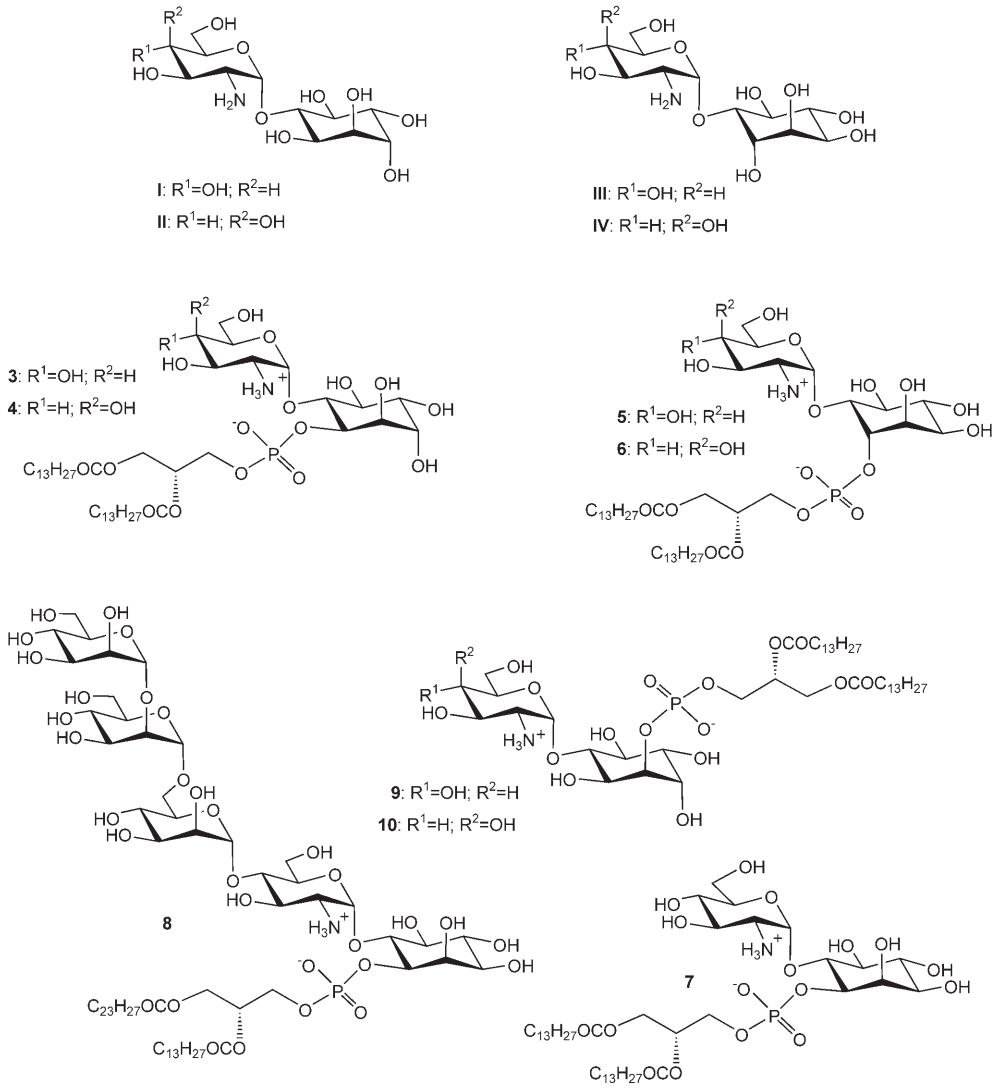



Figure 1. Structural relationship of 2-phosphatidyl-L-*chiro*-inositol (**1**), 2-phosphatidyl-D-*chiro*-inositol (**2**), PI, and GPI anchors.

entation of the phosphatidyl moiety—to be obtained. We synthesized these glycolipids and studied their behavior when asymmetrically incorporated in a liposomal membrane, versus PI-PLC from *Bacillus cereus* and GPI-PLD from bovine serum. For comparison, we similarly studied the behavior of the naturally occurring *myo*-inositol glycophosphoinositide structures **7** and **8** under the same conditions, as positive controls, together with that of the rearranged L-*chiro*-inositol glycophosphoinositides **9** and **10**, obtained from secondary intermediates in the synthesis of **3** and **4**, as predictable negative substrates.



We had already developed a short synthesis of L-*chiro*-inositol-containing pseudodisaccharides **11** and **12** (Scheme 1) as key intermediates for the preparation of IPG-like molecules with the structural motifs $GlcNH_2(1\rightarrow3)$-L-*chiro*-Ins and $GalNH_2(1\rightarrow3)$-L-*chiro*-Ins, respectively.[23i] Although protecting group manipulation was required to obtain the suitably protected derivatives **19** and **20**, these intermediates were chosen as starting materials for the synthesis of **3** and **4**. Attempted *p*-methoxybenzylation or allylation of **11** and **12** under mild acidic conditions[24] and *p*-methoxybenzylation with *p*-methoxybenzyl trichloroacetimidate[25] did not give satisfactory results. Allylation of **11** and **12** with methyl allylcarbonate/Pd[26] afforded the rearranged 1-*O*-allyl derivatives **13** and **14**, respectively. However, methoxymethylation in the presence of $iPr_2EtN$[17] afforded the 2-*O*-methoxymethyl derivatives **15** and **16** in good yields. Debenzoylation of **15** and **16** followed by conventional benzylation gave **17** and **18**, from which the methoxymethyl groups were removed to yield **19** and **20**, respectively. Treatment of **19** and **20** with benzyl-1,2-di-*O*-miristoyl-*sn*-glycero-*N*,*N*-diisopropyl phosphoramidite[27] followed by *m*-chloroperoxybenzoic acid (*m*-CPBA) under the usual conditions gave the fully protected glycolipids **21** and **22**, which were subjected to hydrogenation in an AcOEt/THF/EtOH/$H_2O$ solvent mixture and in the presence of 10% Pd/C catalyst to yield the L-*chiro*-inositol glycophosphoinositides **3** and **4**.

The 1-*O*-allyl derivatives **13** and **14** were debenzoylated to yield **23** and **24**, which were benzylated to give **25** and **26**, and these were in turn deallylated[28] to afford the key intermediates **27** and **28**, respectively. These compounds were treated in the same way as **19** and **20** to give **29** and **30**. The free glycolipids **9** and **10** were obtained after hydrogenation of **29** and **30**, as described for **21** and **22**.

We had also already reported the synthesis of the D-*chiro*-inositol-containing pseudodisaccharides **31** and **32**.[23i] These were transformed into glycophosphoinositides **5** and **6**, respectively (Scheme 2), via the intermediates **33** and **34**, by using the same chemistry described above for the preparation of **3** and **4** from **21** and **22**.

The synthesis of the *myo*-inositol glycophosphoinositide **7** through regioselective phosphorylation of diol **35** by phosphite–phosphonium salt methodology[29] was reported previously by us.[23b] As an alternative, **7** was also prepared from **35** (Scheme 3) by dibutyltin-mediated allylation[30] to afford **36** (68%) and **37** (20%), benzylation of **36** (→**38**), deallylation[28] (→**39**), phosphorylation with benzyl 1,2-dimyristoyl-*sn*-glycero-*N*,*N*-diisopropyl phosphoramidite[27] (→**40**), and final hydrogenation, as above. Finally, the conserved GPI structure **8** was synthesized as reported recently by us.[23m]

Each of the synthetic glycoinositol phospholipids **3**–**8** was asymmetrically incorporated (0.03 mM final concentration) into LUVs consisting of phosphatidylcholine(PtdCho)/egg phosphatidylethanolamine(PtdEth)/cholesterol(Ch) (molar ratio 2:1:1) at 0.3 mM total lipid concentration[22] and treated with PI-PLC and GPI-PLD. Assays of enzymatic hydrolysis were conducted at 39°C in 10 mM HEPES, 50 mM NaCl pH 7.5, in the presence of 0.1% bovine serum albumin (BSA) with continuous stirring. The final concentrations of PI-PLC from *Bacillus cereus* and bovine serum GPI-PLD were 0.16 and 0.5 $U\,mL^{-1}$, respectively. Aliquots were removed from the reaction mixture at regular intervals and extracted with chloroform/methanol/hydrochloric acid (66:33:1).[22a] The course of the enzymatic cleavage was followed by evaluation of aminosugar free-amino groups in the aqueous phase by fluorescamine assay,[30] which has previously been utilized for the quantitative evaluation of lysophosphatidylethanolamine in trace amounts and has proven to be a very sensitive and reliable method for the nanomolar-range quantification of amine-containing lipids.[31] In our hands, this was a more reliable and sensitive assay than phosphorus determination.[32] The time-courses of PI-PLC and GPI-PLD hydrolysis for selected synthetic glycophosphoinositides are shown in Figures 2 and 3, and more comprehensive data are collected in Table 1. The plots in Figure 2 show that PI-PLC accepts a "natural" lipid (**8**) as a substrate, whereas the "rearranged" molecule **9** is inactive in this respect. The synthetic L-*chiro*-glycoinositol phospholipid **3** permits an intermediate enzyme activity. The data in Table 1 demonstrate that the "natural" substrates **7** and **8**, together with the L-*chiro*-compound **4**, produce the highest rates and greatest extents of hydrolysis. The D-*chiro* **5** and **6** and the "rearranged" lipids **9** and **10** are totally inactive as PI-PLC substrates. The quantitative data in Table 1 also confirm that compound **3** is a PI-PLC substrate, but, under our conditions, not as good a one as **7** or **8**.

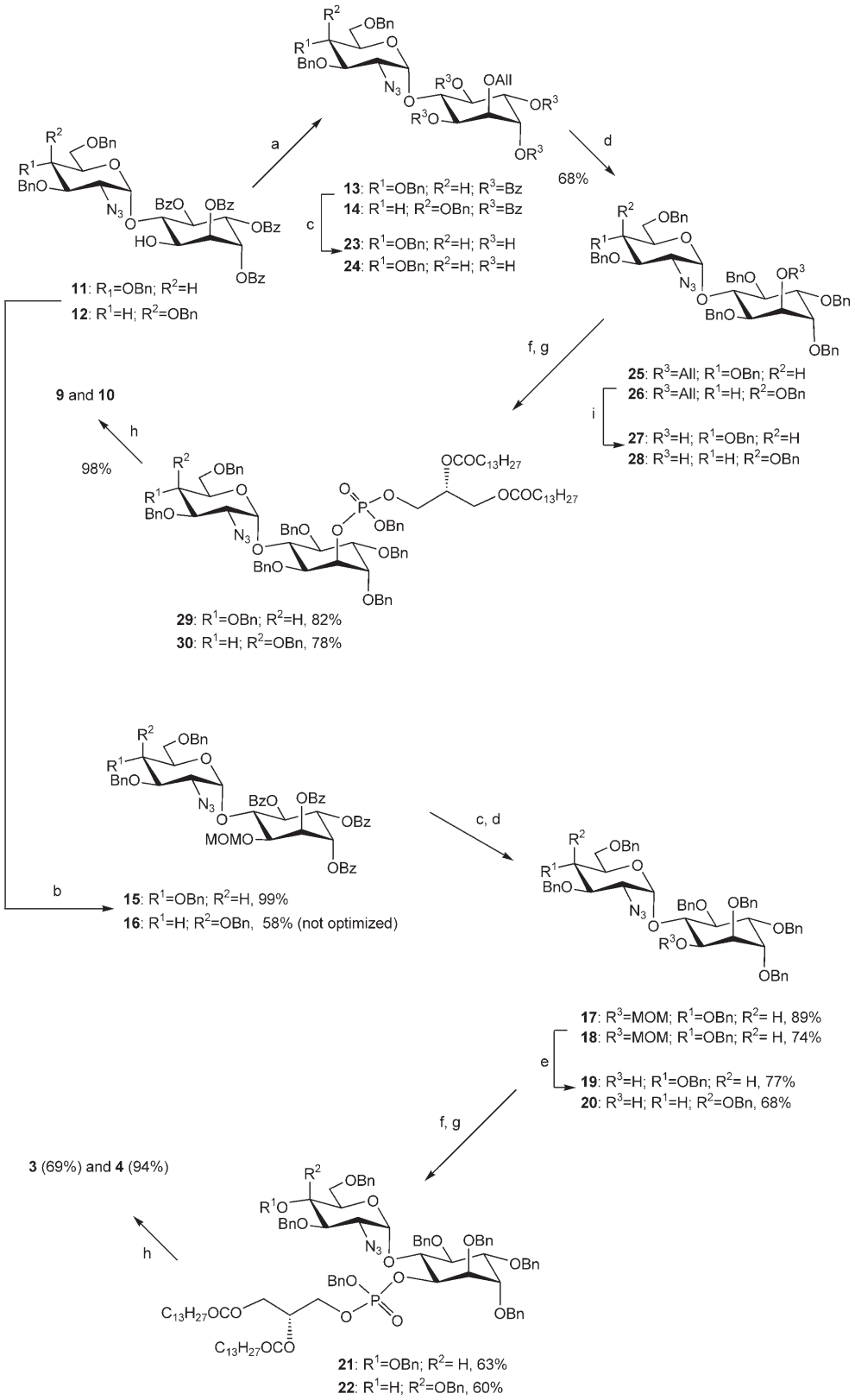
Table 1. Initial rates and maximum extent of hydrolysis of compounds **3**–**10** by PI-PLC and GPI-PLD. LUVs composition: PtdCho/PtEth/Ch (2:1:1 mole ratio). Substrate conc.: 0.03 mM. Enzyme units: PI-PLC (0.16 $U\,mL^{-1}$), GPI-PLD (0.5 $U\,mL^{-1}$).

| Compound | PI-PLC | | GPI-PLD | |
|---|---|---|---|---|
| | Rate [$mol\times10^{-10}\,s^{-1}$] | Extent[a] [nmol] | Rate [$mol\times10^{-10}\,s^{-1}$] | Extent[a] [nmol] |
| **3** | 4.5±0.3 | 15±0.0 | 4.2±0.5 | 27±0.03 |
| **4** | 8.2 | 23 | 2.0 | 16 |
| **5** | <0.1 | <1 | 1.9 | 24±0.9 |
| **6** | <0.1 | <1 | 2.1 | 22±3.2 |
| **7** | 8.9±0.3 | 29 | 4.7±0.3 | 25±0.6 |
| **8** | 8.2 | 29±0.0 | 9.6±0.1 | 28±0.0 |
| **9** | <0.1 | <1 | 0.93 | 4.2±1.0 |
| **10** | <0.1 | <1 | 0.48 | 3.9±0.9 |

[a] Nanomoles of substrate processed after apparent equilibrium was reached (15 min).

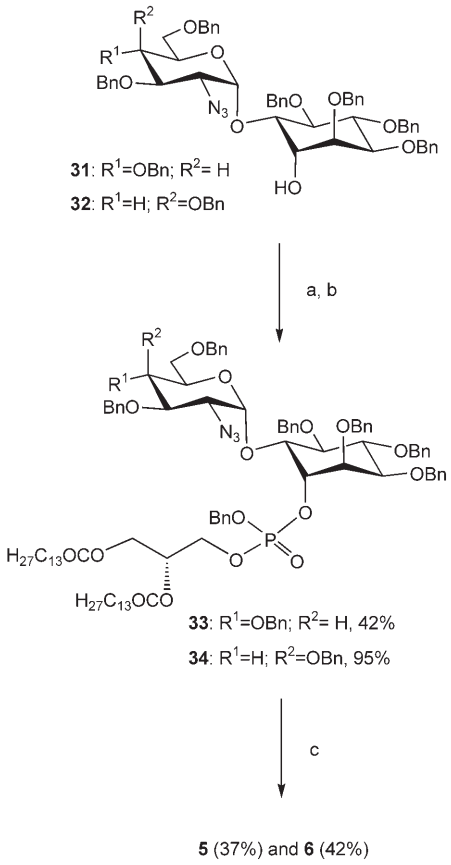
Data for GPI-PLD are given in Figure 3, and also in Table 1. All eight lipids tested are accepted as substrates by GPI-PLD, but the hydrolysis rates and extents differ vastly. Figure 3 shows representative time-courses for the hydrolyses of a good (**7**) and a poor (**10**) substrate. The highest initial rates under our conditions are found for the "natural" lipid **8**. This is followed by a group of molecules that are hydrolyzed at lower rates, such as the "natural" lipid **7**, the L-*chiro*-compounds **3** and **4**, and the D-*chiro* **5** and **6**. The "rearranged" molecules **9** and **10** are distinctly poorer GPI-




Scheme 1. Abbreviations: $[Pd_2(dba)_3]$: tris(dibenzylideneacetone)dipalladium; dppb: 1,4-bis(diphenylphosphino)butane; MOM: $CH_3OCH_2$. Reagents and conditions: a) $AllCO_2Me$ (×2.0), $[Pd_2(dba)_3]$ (×0.05), dppb (×0.2), THF, 80 °C, 2 h, 80%; b) MOMCl (×52), $iPr_2EtN$, DMF, 52 h; c) MeONa (×1.0), MeOH, 16 h, 100%; d) BnBr (×8.0), NaH (×6.0), DMF, overnight; e) PhSH (×1.2), $BF_3{\cdot}Et_2O$ (×1.0), $CH_2Cl_2$, 2 h; f) 1,2-di-*O*-myristoyl-*sn*-glycero-3-yl benzyl *N*,*N*-diisopropyl phosphoramidite (×2.0), 1*H*-tetrazole (×2.2), $CH_2Cl_2$, RT, 2 h; g) *m*-CPBA (×1.0), $CH_2Cl_2$, 20 min; h) $H_2$, Pd/C (×3.0), AcOEt/THF/EtOH/$H_2O$ 2:1:1:0.1, RT, 6 h, Sephadex LH-20; i) $[\{Ir(cod)Ph_2PMe\}_2]PF_6$, THF and then NBS (×1.5), $H_2O$, 72%.




Scheme 2. Reagents and conditions: a) 1,2-di-*O*-myristoyl-*sn*-glycero-3-yl benzyl *N*,*N*-diisopropyl phosphoramidite (×2.0), 1*H*-tetrazole (×2.2), $CH_2Cl_2$, RT, 2 h; b) *m*-CPBA (×1.0), $CH_2Cl_2$, 20 min; c) $H_2$, Pd/C (×3.0), AcOEt/THF/EtOH/$H_2O$ 2:1:1:0.1, RT, 6 h, Sephadex LH-20.

PLD substrates. Overall, both PI-PLC and GPI-PLD show a preference for the "natural" glycophosphoinositides, followed by the L-*chiro* molecules. The "rearranged" lipids **9** and **10** are poor or very poor substrates for both enzymes. The D-*chiro*-glycophosphoinositides **5** and **6** are hydrolyzed, albeit at a low rate, by GPI-PLD, but cannot be processed by PI-PLC.

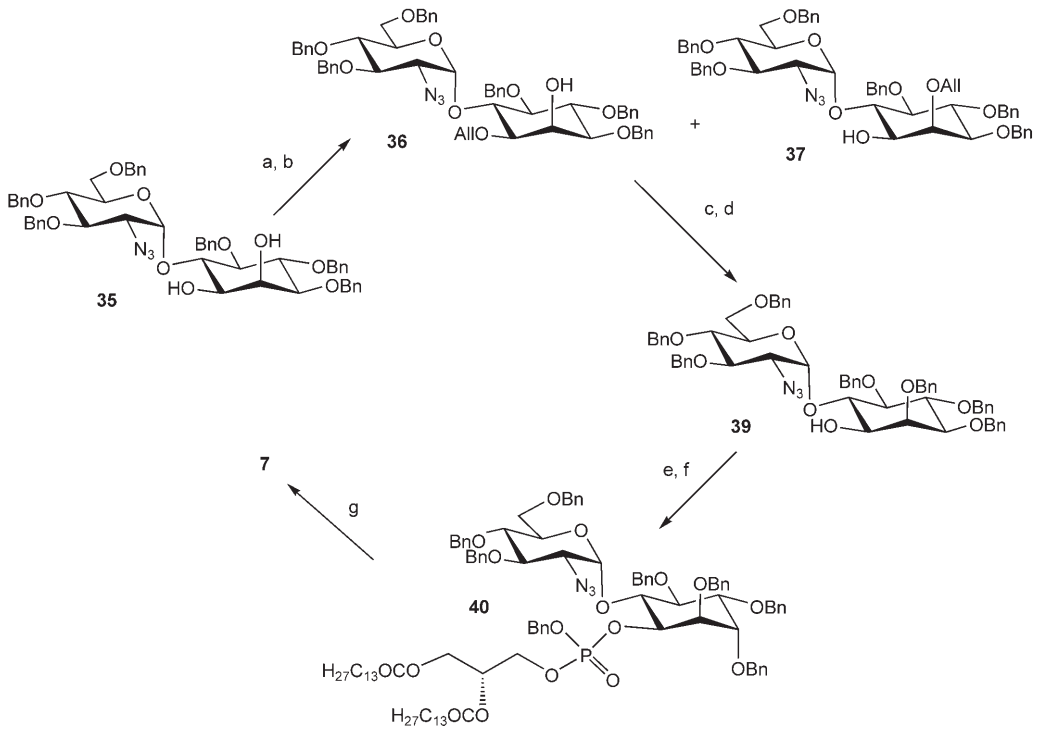
The observation that bacterial PI-PLC hydrolyzes both 3-*O*-glucosaminyl- (**3**) and 3-*O*-galactosaminyl-2-phosphatidyl-L-*chiro*-inositol (**4**) is in agreement with previous results on the hydrolysis of 2-*O*-phosphatidyl-L-*chiro*-inositol (**1**).[17] This enzyme cleaves neither the 2-*O*-glycosaminyl-1-phosphatidyl-D-*chiro*-inositols **5** and **6** (Table 1) nor the rearranged glycolipids **9** and **10** (Figures 2 and 3), in which the phosphatidyl moiety is axially oriented. However, in contrast to previous findings[17] that bacterial PLC cleaved **1** at a rate $10^{-3}$ times that attained with the natural substrate PI, this enzyme hydrolyzes **3** and **4** with efficiency similar to that for the *myo*-inositol lipid **7** and the GPI-anchor structure **8** (Figure 2 and Table 1), in which the glycophosphoinositides presented are incorporated asymmetrically in a liposomal membrane.

Both bacterial PI-PLC and mammalian GPI-PLD accept both **7** and **8**, but this is not the case for GPI-PLC from *Trypanosoma*.[37] GPI-PLD is also active against **5** and **6** in spite of the axial orientations of the phosphatidyl moieties in these glycophosphoinositides (Table 1).

## Conclusion

After almost twenty years of intensive chemical and biological research, the structures of *chiro*-inositol-containing IPGs proposed as putative insulin mediators remain controversial. It has been postulated that these IPGs are generated after PL cleavage of free GPIs at the cell surface, but neither the structures of these GPIs nor the nature of the specific PL involved in GPI hydrolysis is presently known. These issues have now been addressed through the synthesis of several D- and L-*chiro*-glycophosphoinositides and investigation of their enzymatic hydrolysis by PLs in membrane-like environments. Here we demonstrate for the first time that 3-*O*-α-D-glucosaminyl- (**3**) and -galactosaminyl-2-phosphatidyl-L-*chiro*-inositol (**4**)—showing the maximum stereochemical similarity to the 6-*O*-α-D-glucosaminylphosphatidylinositol structural motif of the GPI anchors—and 2-*O*-α-D-glucosaminyl- (**5**) and galactosaminyl-1-phosphatidyl-D-*chiro*-inositol (**6**)—which differ from the corresponding structural motif of the GPI anchors only in the orientation of the PI moiety—can be synthesized in a straightforward manner. To the best of our knowledge, these compounds constitute the first synthetic D- and L-*chiro*-glycosylphosphoinositides ever reported in the literature. These compounds, as well as the *myo*-glycophosphoinositide (**7**) and the conserved GPI structure (**8**), can be asymmetrically incorporated into LUVs to mimic the natural membrane environment. These liposomal constructs constitute a convenient system for studying the cleavage of synthetic phosphoinositide molecules by PLs, which is necessary to provide insight into the structure–activity relationship of these important enzymes. Investigation of the cleavage of compounds **2**–**8**, asymmetrically incorporated into these LUVs, by a bacterial PI-PLC and a mammalian GPI-PLD has provided interesting results. The configuration of the *chiro*-inositol unit in a *chiro*-inositol-containing naturally occurring IPG could be either D or L, depending on the nature of the PL responsible for IPG generation. Whereas a 3-*O*-glycosyl-2-*O*-phosphatidyl-L-*chiro*-inositol structural motif seems to be required for PI-PLC cleavage, mammalian GPI-PLD accepts 2-*O*-glycosyl-1-phosphatidyl-D-*chiro*-inositols, despite the axial orientations of the phosphatidyl moieties in these compounds. Therefore, until new PI-PLs or GPI-PLs specific for *chiro*-inositol-containing PIs or GPIs are discovered, the uncertainty as to whether GPI precursors of IPG mediators may be composed of either D- or L-*chiro*-inositol will remain. On the other hand, neither of the enzymes utilized in this study accepts exotic GPI structures such as **9** and **10**, and for none of them does the nature of the glycan chain beyond the glucosamine unit linked to the inositol ring seem to play a major role in enzymatic cleavage.




Scheme 3. Reagents and conditions: a) $Bn_2SnO$ (×1.2), toluene, reflux, 24 h; b) AllBr, TBAI (×1.1), reflux, 2 h, **36** (68%), **37** (20%); c) BnBr (×8.0), NaH (×6.0), DMF, overnight, 68%; d) $[\{Ir(cod)Ph_2PMe\}_2]PF_6$, THF and then NBS (×1.5), $H_2O$, 1 h 30 min, 72%; e) 1,2-di-*O*-myristoyl-*sn*-glycero-3-yl benzyl *N*,*N*-diisopropyl phosphoramidite (×2.0), 1*H*-tetrazole (×2.2), $CH_2Cl_2$, RT, 2 h; f) *m*-CPBA, $CH_2Cl_2$, 20 min, 82%; g) $H_2$, Pd/C (×3.0), AcOEt/THF/EtOH/$H_2O$, 2:1:1:0.1, RT, 16 h, Sephadex LH-20, 98%.

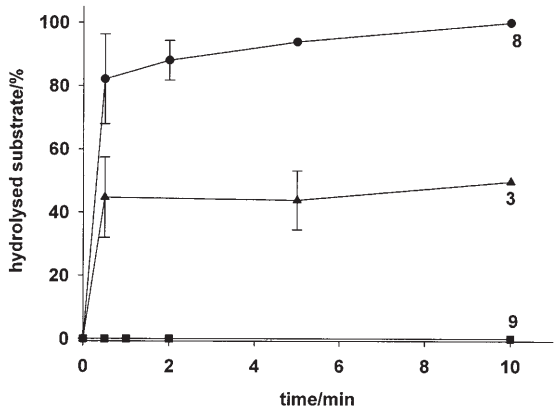



Figure 2. Time-courses of the enzymatic hydrolysis of compounds **3**, **8**, and **9**, asymmetrically incorporated into LUVs, by PI-PLC from *Bacillus cereus* under the experimental conditions indicated in Table 1.

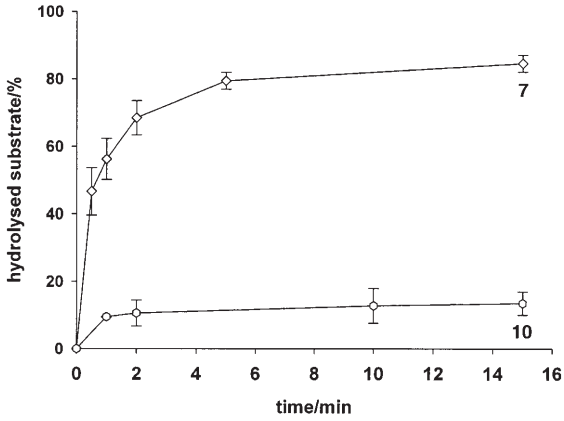



Figure 3. Time-courses of the enzymatic hydrolysis of compounds **7** and **10**, asymmetrically incorporated into LUVs, by GPI-PLD from bovine serum under the experimental conditions indicated in Table 1.

## Experimental Section

**General methods**: All organic solvents used were dried by established procedures.[33] Dichloromethane was distilled from calcium hydride, whilst hexane, diethyl ether, and THF were distilled from sodium/benzophenone. *i*$Pr_2EtN$ was distilled from ninhydrin and KOH, whilst DMF and MeOH were dried from molecular sieves (4 Å) unless otherwise stated (for the preparation of **15** and **16**, DMF was distilled from TsCl and BaO). Molecular sieves (4 Å, powdered) were predried in an oven and then activated for 10 min under vacuum at 500 °C. All aqueous (aq) solutions were saturated unless otherwise stated. All reactions were conducted under dry argon in oven-dried glassware and in freshly distilled and dried solvents unless otherwise stated. Purification by flash chromatography was performed by using Merck 60 silica gel (15–200 and 230–400 mesh) and eluents are given as volume ratios (v/v). Preparative thin-layer chromatography (PLC) was performed by using Merck silica gel (60 $F_{254}$). Preparative gel chromatography was performed by using Amersham Bioscience Sephadex LH-20. Analytical thin-layer chromatography (TLC) was performed by using Merck silica gel (60 $F_{254}$) with detection by UV light ($\lambda = 254$ nm) and heating with phosphomolybdic acid/EtOH or $Ce(SO_4)_2$/phosphomolybdic acid/$H_2SO_4$/$H_2O$, and with Mo/$MoO_4$/

$H_2SO_4$ for glycophospholipids **3–7**, **9**, and **10**. Chemical shifts are given in ppm and coupling constants are reported in Hz. Resonance signals were assigned with the aid of 2D spectra (COSY, COSY-dqf, HMQC, HSQC, TOCSY, NOESY, and ROESY). $^1$H NMR and $^{13}$C NMR were recorded at 298 K by using Bruker Avance DRX 500, DRX 400, and DPX 300 spectrometers with TMS as internal reference signal. Microanalyses were determined by using a Leco CHNS-932 instrument, high-resolution mass spectra were recorded by using a Micromass Autospec apparatus, optical rotations were measured by using a Perkin–Elmer 341 polarimeter, and pH was measured by using a Cole Parmer apparatus.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-1-*O*-allyl-2,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (13)**: A solution of $[Pd_2(dba)_3]$ (dba = tris(dibenzylideneacetone)dipalladium) (8 mg, 0.009 mmol, 0.05 equiv) and 1,4-bis(diphenylphosphino)butane (dppb) (16 mg, 0.04 mmol, 0.2 equiv) in dry THF (1 mL) was added under argon to a solution of **11** (196 mg, 0.19 mmol, 1 equiv) and $AllCO_2Me$ (42 μL, 0.1 mmol, 2 equiv) in dry THF (9 mL). After the solution had been stirred at 80 °C for 2 h, the solvent was evaporated and the crude product was purified by column chromatography (*n*-hexane/AcOEt 8:1) to give **13** as a white foam (161 mg, 0.15 mmol, 80 %). $[\alpha]_D^{20} = +32$ ($c = 0.4$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 3:1): 0.31; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.11$ (d, $^3J(H,H) = 6.5$ Hz, 4 $H_{ortho}$; Bz), 7.92 (d, $^3J(H,H) = 8.0$ Hz, 2 $H_{ortho}$; Bz), 7.82 (d, $^3J(H,H) = 7.5$ Hz, 2 $H_{ortho}$; Bz), 7.62 (t, $^3J(H,H) = 7.5$ Hz, 1 $H_{para}$; Bz), 7.58 (t, $^3J(H,H) = 7.5$ Hz, 1 $H_{para}$; Bz), 7.52 (t, $^3J(H,H) = 7.5$ Hz, 2 $H_{meta}$; Bz), 7.45 (t, $^3J(H,H) = 6.5$ Hz, 2 $H_{meta}$; Bz), 7.41 (t, $^3J(H,H) = 6.5$ Hz, 2 $H_{para}$; Bz), 7.29–7.18 (m, 4H; Bz, 11H; Bn), 7.12 (m, 2H; Bn), 6.97 (m, 2H; Bn), 6.08 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_4$), 5.98–5.85 (m, 2H; $H_5$, C*H*=CH$_2$), 5.91 (app. s, 1H; $H_6$), 5.80 (app. d, $^3J(H,H) = 10.0$ Hz, 1H; $H_2$), 5.34 (app. d, $^3J(H,H) = 17.0$ Hz, 1H; CH=C$H_2$), 5.29 (d, $^3J(H,H) = 2.8$ Hz, 1H; $H_{1'}$), 5.20 (app. d, $^3J(H,H) = 10.5$ Hz, 1H; CH=C$H_2$), 4.74–4.58 (m, 5H; 4 × CH−Ph, $H_3$), 4.34–4.18 (m, 3H; CH−Ph, C$H_2$−CH=CH$_2$), 4.20 (s, 1H; $H_1$), 4.05 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 3.81 (br t, $^3J(H,H) = 10.0$ Hz, 1H; $H_{3'}$), 3.57 (m, 2H; $H_{4'}$, $H_{5'}$), 3.19 (dd, $^3J(H_{2'},H_{3'}) = 10.0$ Hz, $^3J(H_{2'},H_{1'}) = 2.8$ Hz, 1H; $H_{2'}$), 2.99 ppm (m, 2H; $H_{6a'}$, $H_{6b'}$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 165.7$, 165.6, 165.5, 165.4 (4 × *C*OPh), 138.3, 138.0, 137.6 (3C; Bn), 133.7, 133.4, 133.23, 133.16 (4 $CH_{para}$; Bz, *C*H=CH$_2$), 130.0, 129.8, 129.6 (8 × $CH_{ortho}$; Bz), 129.0–127.3 (23 × CH; Bz, Bn), 118.7 (CH=*C*H$_2$), 99.2 ($C_{1'}$), 80.1 ($C_{3'}$), 77.6 ($C_{4'}$), 76.5 ($C_3$), 75.4 (*C*H$_2$Ph), 74.7 ($C_1$), 74.4 (*C*H$_2$Ph), 74.4 ($C_2$, *C*H$_2$Ph), 73.2 (*C*H$_2$−CH=CH$_2$), 71.4 ($C_{5'}$), 71.2 ($C_4$), 70.6 ($C_5$), 68.8 ($C_6$), 67.1 ($C_{6'}$), 63.6 ppm ($C_{2'}$); FAB HRMS: *m*/*z* calcd for $[C_{64}H_{59}N_3O_{14}+Na]^+$: 1116.3895; found: 1116.3992.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-1-*O*-allyl-2,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (14)**: Compound **14** (161 mg, 0.15 mmol, 80 %) was obtained as a white foam from **12** (196 mg, 0.19 mmol) by the same experimental procedure as that used for the preparation of compound **13**. The product was purified by flash chromatography (*n*-hexane/AcOEt 10:1); $R_f$ (*n*-hexane/AcOEt 3:1): 0.23; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.11$ (d, $^3J(H,H) = 8.0$ Hz, 2 $H_{ortho}$; Bz), 8.08 (d, $^3J(H,H) = 8.5$ Hz, 2 $H_{ortho}$; Bz), 7.99 (d, $^3J(H,H) = 7.5$ Hz, 2 $H_{ortho}$; Bz), 7.79 (d, 2H; $^3J(H,H) = 7.5$ Hz, 2 $H_{ortho}$; Bz), 7.63 (t, $^3J(H,H) = 7.5$ Hz, 1 $H_{para}$; Bz), 7.58 (t, $^3J(H,H) = 7.5$ Hz, 1 $H_{para}$; Bz), 7.52 (t, $^3J(H,H) = 8.0$ Hz, 2 $H_{meta}$; Bz), 7.47 (t, $^3J(H,H) = 7.5$ Hz, 2 $H_{meta}$; Bz), 7.32–7.21 (m, 7H; Bz, 8H; Bn), 7.15 (m, 3H; Bn), 7.07 (m, 4H; Bn), 6.08 (t, $^3J(H,H) = 10.0$ Hz, 1H; $H_4$), 5.96–5.89 (m, 2H; $H_6$, C*H*=CH$_2$), 5.86 (dd, $^3J(H_5,H_4) = 10.0$ Hz, $^3J(H_5,H_6) = 3.5$ Hz, 1H; $H_5$), 5.80 (dd, $^3J(H_2,H_3) = 9.5$ Hz, $^3J(H_2,H_1) = 3.0$ Hz, 1H; $H_2$), 5.32 (dd, $^3J(H,H) = 17.0$ Hz, $^3J(H,H) = 1.5$ Hz, 1H; CH=C$H_2$), 5.30 (d, $^3J(H,H) = 4.0$ Hz, 1H; $H_{1'}$), 5.18 (dd, $^3J(H,H) = 10.5$ Hz, $^3J(H,H) = 1.5$ Hz, 1H; CH=C$H_2$), 4.68 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_3$), 4.64 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.54 (AB, 2H; $CH_2$Ph), 4.29 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.25–4.20 (m, 3H; $H_1$, C$H_2$−CH=CH$_2$), 3.95 (AB, 2H; $CH_2$Ph), 3.88–3.80 (m, 3H; $H_{3'}$, $H_{4'}$, $H_{5'}$), 3.68 (dd, $^3J(H_{2'},H_{3'}) = 10.5$ Hz, $^3J(H_{2'},H_{1'}) = 4.0$ Hz; $H_{2'}$), 3.36 (t, $^3J(H,H) = 8.5$ Hz, 1H; $H_{6a'}$), 3.00 ppm (m, 1H; $H_{6b'}$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 165.8$, 165.7, 165.6, 165.5 (4 × *C*OPh), 138.4, 138.0, 137.9 (3C; Bn), 133.9–133.3 (*C*H=CH$_2$, 4 × $CH_{para}$; Bz,), 130.2–128.6 (31 × CH, Bz, Bn), 118.8 (CH=*C*H$_2$), 99.4 ($C_{1'}$), 77.5–76.7 ($C_{3'}$), 75.1 (*C*H$_2$Ph), 74.8 ($C_3$), 74.6 ($C_1$), 74.0 ($C_2$), 73.3, 73.22, 73.17 (*C*H$_2$Ph, *C*H$_2$−CH=CH$_2$, $C_{4'}$), 72.3 (*C*H$_2$Ph), 71.5 ($C_4$), 70.9 ($C_5$), 69.7 ($C_{5'}$), 68.9 ($C_6$), 67.5 ($C_{6'}$), 60.0 ppm ($C_{2'}$); FAB HRMS: *m*/*z* calcd for $[C_{64}H_{59}N_3O_{14}+Na]^+$: 1116.3895; found: 1116.3965.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-2-methoxymethyl-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (15)**: MOMCl (MOM = $CH_3OCH_2$) (866 μL, 11.48 mmol, 52 equiv) was added dropwise under Ar to a solution of compound **11** (242 mg, 0.23 mmol, 1 equiv) and *i*$Pr_2$EtN (4 mL) in dry DMF (0.3 mL). After the reaction mixture had been stirred at RT for 52 h, $NH_4OH$ (1 mL) was added and the mixture was washed successively with a solution of saturated $NH_4Cl$, $H_2O$, and brine. The organic layer was dried ($MgSO_4$) and concentrated, and the crude product was purified by flash chromatography (*n*-hexane/AcOEt 2:1) to give **15** as a syrup (250 mg, 0.23 mmol, 99 %). $[\alpha]_D^{20} = +46$ ($c = 0.51$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 2:1): 0.43; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.16$ (d, $^3J(H,H) = 7.5$ Hz, 2 $H_{ortho}$; Bz), 8.08 (d, $^3J(H,H) = 7.5$ Hz, 2 $H_{ortho}$; Bz), 7.93 (d, $^3J(H,H) = 7.5$ Hz, 2 $H_{ortho}$; Bz), 7.76 (d, $^3J(H,H) = 7.8$ Hz, 2 $H_{ortho}$; Bz), 7.66 (t, $^3J(H,H) = 7.2$ Hz, 1 $H_{para}$; Bz), 7.63 (t, $^3J(H,H) = 6.9$ Hz, 1 $H_{para}$; Bz), 7.53 (t, $^3J(H,H) = 7.5$ Hz, 2 $H_{meta}$; Bz), 7.51 (t, $^3J(H,H) = 7.5$ Hz, 2 $H_{meta}$; Bz), 7.42 (t, $^3J(H,H) = 6.9$ Hz, 1 $H_{para}$; Bz), 7.40 (t, $J = 7.5$ Hz, 1 $H_{para}$; Bz), 7.36–7.18 (m, 4H; Bz, 13H; Bn), 6.92 (m, 2H; Bn), 6.05 (t, $^3J(H,H) = 9.3$ Hz, 1H; $H_4$), 5.99 (t, $^3J(H,H) = 3.8$ Hz, 1H; $H_6$), 5.89 (t, $^3J(H,H) = 3.8$ Hz, 1H; $H_1$), 5.81 (dd, $^3J(H_5,H_4) = 9.3$ Hz, $^3J(H_5,H_6) = 3.8$ Hz, 1H; $H_5$), 5.52 (d, $^3J(H,H) = 3.6$ Hz, 1H; $H_{1'}$), 4.96 (d, $^3J(H,H) = 7.0$ Hz, 1H; $CH_3OCH_2$), 4.79 (app. s, 2H; $CH_2$Ph), 4.78 (d, $^3J(H,H) = 7.0$ Hz, 1H; $CH_3OCH_2$), 4.62 (d, $^3J(H,H) = 11.1$ Hz, 1H; CH−Ph), 4.52 (t, $^3J(H,H) = 9.3$ Hz, 1H; $H_3$), 4.46 (d, $^3J(H,H) = 11.7$ Hz, 1H; CH−Ph), 4.43 (dd, $^3J(H_2,H_3) = 9.3$ Hz, $^3J(H_2,H_1) = 3.3$ Hz, 1H; $H_2$), 4.27 (d, $^3J(H,H) = 11.1$ Hz, 1H; CH−Ph), 4.20 (d, $^3J(H,H) = 11.7$ Hz, 1H; CH−Ph) 3.83 (m, 1H; $H_{3'}$), 3.62 (m, 2H; $H_{4'}$, $H_{5'}$), 3.39 (dd, $^3J(H_{2'},H_{3'}) = 10.5$ Hz, $^3J(H_{2'},H_{1'}) = 3.6$ Hz, 1H; $H_{2'}$), 3.31 (s, 3H; C$H_3$OCH$_2$), 3.18 (m, 1H; $H_{6a'}$), 3.02 ppm (m, 1H; $H_{6b'}$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 165.8$, 165.6, 165.2, 165.0 (4 × *C*OPh), 138.4, 138.1, 137.8 (3C; Bn), 133.8, 133.4, 133.3 (4 $CH_{para}$; Bz), 130.2, 130.1, 129.94, 129.87 (8 $CH_{ortho}$; Bz), 129.5–127.5 (23 × CH, 4 × C; Bz, Bn), 98.5 (*C*H$_2$OCH$_3$, $C_{1'}$), 80.0 ($C_{3'}$), 77.9 ($C_2$), 76.5 ($C_{4'}$), 74.5 (*C*H$_2$Ph), 73.6 ($C_3$), 71.3, 70.7 (2 × *C*H$_2$Ph), 70.6 ($C_4$, $C_{5'}$), 70.3 ($C_5$, $C_1$), 68.3 ($C_6$), 67.6 ($C_{6'}$), 63.7 ($C_{2'}$), 56.5 ppm ($CH_2OCH_3$); FAB HRMS: *m*/*z* calcd for $[C_{63}H_{59}N_3O_{15}+Na]^+$: 1120.3844; found: 1120.3969.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-2-methoxymethyl-1,4,5,6-tetra-*O*-benzoyl-L-*chiro*-inositol (16)**: Compound **16** was obtained as a colorless syrup (50 mg, 0.045 mmol, 58 %, no optimized yield) from **12** (83 mg, 0.079 mmol, 1 equiv) by the same experimental procedure as that used in the preparation of **15**. Compound **16** was purified by flash chromatography (*n*-hexane/AcOEt 2:1). $[\alpha]_D^{20} = +47$ ($c = 0.32$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 2:1): 0.40; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.12$ (d, $^3J(H,H) = 7.5$ Hz, 2 $H_{ortho}$; Bz), 8.06 (d, $^3J(H,H) = 7.5$ Hz, 2 $H_{ortho}$; Bz), 8.00 (d, $^3J(H,H) = 7.5$ Hz, 2 $H_{ortho}$; Bz), 7.78 (d, $^3J(H,H) = 7.0$ Hz, 2 $H_{ortho}$; Bz), 7.63 (t, $^3J(H,H) = 7.5$ Hz, 1 $H_{para}$; Bz), 7.60 (t, $^3J(H,H) = 7.5$ Hz, 1 $H_{para}$; Bz), 7.50 (t, $^3J(H,H) = 7.5$ Hz, 2 $H_{meta}$; Bz), 7.44 (t, $^3J(H,H) = 7.5$ Hz, 2 $H_{meta}$; Bz), 7.42–7.18 (m, 6H; Bz, 13H; Bn), 7.14 (m, 2H; Bn), 6.05 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_4$), 6.00 (app. s, 1H; $H_6$), 5.91 (app. s, 1H; $H_1$), 5.83 (dd, $^3J(H_5,H_4) = 9.5$ Hz, $^3J(H_5,H_6) = 3.5$ Hz, 1H; $H_5$), 5.53 (app. s, 1H; $H_{1'}$), 4.89 (d, $^3J(H,H) = 7.0$ Hz, 2H; $CH_3OCH_2$), 4.77 (d, $^3J(H,H) = 7.0$ Hz, 1H; $CH_3OCH_2$), 4.72 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.57 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_3$), 4.53 (app. s, 2H; $CH_2$Ph), 4.45 (dd, $^3J(H_2,H_3) = 9.5$ Hz, $^3J(H_2,H_1) = 3.5$ Hz, $H_2$), 4.32 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.24 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.14 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 3.95 (app. t, $^3J(H,H) = 7.0$ Hz, 1H; $H_{5'}$), 3.90 (dd, $^3J(H_{2'},H_{3'}) = 10.5$ Hz, $^3J(H_{2'},H_{1'}) = 3.5$ Hz, 1H; $H_{2'}$), 3.83 (dd, $^3J(H_{3'},H_{4'}) = 10.5$ Hz, $^3J(H_{3'},H_{4'}) = 2.5$ Hz, 1H; $H_{3'}$), 3.62 (app. s, 1H; $H_{4'}$), 3.18 (t, $^3J(H,H) = 8.5$ Hz, 1H; $H_{6a'}$), 3.31 ppm (m, 3H; C$H_3$OCH$_2$, 1H; $H_{6b'}$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 165.7$, 165.5, 165.2, 165.0 (4 × *C*OPh), 138.4, 138.0, 137.7 (3C; Bn), 133.8, 133.7, 133.5, 133.4 (4 $CH_{para}$; Bz), 130.1, 130.0, 129.8, (8$CH_{ortho}$; Bz), 129.2–127.8 (23 × CH, 4C; Bz, Bn), 98.3 ($C_{1'}$), 98.0 (*C*H$_2$OCH$_3$), 77.4 ($C_2$), 76.7 ($C_{3'}$), 74.8 (*C*H$_2$Ph), 74.1 ($C_3$), 73.3, 73.2 (*C*H$_2$Ph, $C_{4'}$), 72.2 (*C*H$_2$Ph), 70.9 ($C_4$), 70.6 ($C_5$), 70.0, 69.8 ($C_1$, $C_{5'}$), 68.2 ($C_6$, $C_{6'}$), 59.9 ($C_{2'}$), 56.5 ppm ($CH_2OCH_3$); FAB HRMS: *m*/*z* calcd for $[C_{63}H_{59}N_3O_{15}+Na]^+$: 1120.3844; found: 1120.3807.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-2-methoxymethyl-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (17)**: MeONa/MeOH (1.0 M, 0.23 mL, 0.23 mmol, 1 equiv) was added under Ar to a solution of compound **15** (242 mg, 0.23 mmol, 1 equiv) in dried MeOH (6 mL). The solution was stirred for 20 h and was then concentrated to dryness and treated directly with NaH (74 mg, 1.84 mmol, 8 equiv) in dried DMF (1.5 mL). After the mixture had been cooled to −15 °C in an ice/salt bath, BnBr (218 μL, 1.84 mmol, 8 equiv) was added dropwise. The reaction mixture was stirred overnight, $NH_4OH$ was then added, and the mixture was washed successively with a solution of saturated $NH_4Cl$, $H_2O$, and brine. The organic layer was dried ($MgSO_4$) and evaporated, and the crude product was purified by flash chromatography (*n*-hexane/AcOEt 10:1) to provide **17** as a syrup (181 mg, 0.17 mmol, 89 %). $[\alpha]_D^{20} = +54$ ($c = 0.38$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 3:1): 0.28; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.38$–$7.00$ (m, 35H; Ph), 5.52 (d, $^3J(H,H) = 4.0$ Hz, 1H; $H_{1'}$), 4.99 (d, $^3J(H,H) = 10.5$ Hz, 1H; CH−Ph), 4.87 (s, 2H; $CH_2Ph$), 4.82, 4.714 (2×d, $^3J(H,H) = 6.5$ Hz, 2H; $CH_3OCH_2$), 4.711 (d, $^3J(H,H) = 10.5$ Hz, 1H; CH−Ph), 4.67 (d, $^3J(H,H) = 12.5$ Hz, 1H; CH−Ph), 4.62 (d, $^3J(H,H) = 10.5$ Hz, 1H; CH−Ph), 4.58 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.57 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.50, 4.48, 4.40 (3×d, $^3J(H,H) = 12.0$ Hz, 3H; 3×CH−Ph), 4.39 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.30, 4.20 (2×d, $^3J(H,H) = 12.0$ Hz, 2H; 2×CH−Ph), 4.08 (app. d, $^3J(H,H) = 9.5$ Hz, 1H; $H_{5'}$), 4.06 (t, $^3J(H,H) = 10.0$ Hz, 1H; $H_3$), 3.99 (dd, $^3J(H_2,H_3) = 10.0$ Hz, $^3J(H_2,H_1) = 2.5$ Hz, 1H; $H_2$), 3.94 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_{3'}$), 3.80 (m, 2H; $H_1$, $H_5$), 3.78 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_4$), 3.70 (t, $^3J(H,H) = 3.0$ Hz, 1H; $H_{4'}$), 3.64 (t, $^3J(H,H) = 2.5$ Hz, 1H; $H_6$), 3.35 (m, 4H; $CH_3OCH_2$, $H_{2'}$), 3.20 (app. d, $^3J(H,H) = 10.5$ Hz, 1H; $H_{6a'}$), 3.14 ppm (app. d, $^3J(H,H) = 9.0$ Hz, 1H; $H_{6b'}$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 138.7$, 138.6, 138.3, 138.2 (7C; Ph), 128.6–127.4 (35×CH; Ph), 98.5 ($CH_2OCH_3$), 97.6 ($C_{1'}$), 81.1 ($C_2$), 80.6, 80.5 ($C_{3'}$, $C_5$), 79.6 ($C_4$), 78.5 ($C_{4'}$), 77.2 ($C_1$), 75.8, 75.7, 75.5, 74.9 (3×$CH_2$Ph, $C_3$), 73.9, 73.45, 73.38, 73.2, 73.1 (4×$CH_2$Ph, $C_6$), 70.3 ($C_{5'}$), 67.9 ($C_{6'}$), 63.9 ($C_{2'}$), 56.0 ppm ($CH_2OCH_3$); FAB HRMS: *m/z* calcd for $[C_{63}H_{67}N_3O_{11}+Na]^+$: 1064.4673; found: 1064.4720.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-2-methoxymethyl-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (18)**: Compound **18** (29 mg, 0.028 mmol, 74 %) was obtained from **16** (42 mg, 0.04 mmol) by the same experimental procedure as that used for the preparation of **17** and was purified by flash chromatography (*n*-hexane/AcOEt 6:1). $[\alpha]_D^{20} = +97$ ($c = 0.9$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 3:1): 0.22; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.40$–$7.12$ (m, 35H; Ph), 5.52 (d, $^3J(H,H) = 3.0$ Hz, 1H; $H_{1'}$), 5.99 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.794 (d, $^3J(H,H) = 6.5$ Hz, 1H; $CH_3OCH_2$), 4.788 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.681 (d, $^3J(H,H) = 12.5$ Hz, 1H; CH−Ph), 4.677 (d, $^3J(H,H) = 6.5$ Hz, 1H; $CH_3OCH_2$), 4.673 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.602 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.598 (app. s, 2H; $CH_2Ph$), 4.50 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.49 (d, $^3J(H,H) = 12.5$ Hz, 1H; CH−Ph), 4.44 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.34 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.33 (m, 1H; $H_{5'}$), 4.31 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.26, 4.21 (AB, $^3J(H,H) = 11.5$ Hz, 2H; 2×CH−Ph), 4.11 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_3$), 4.01 (dd, $^3J(H_2,H_3) = 9.5$ Hz, $^3J(H_2,H_1) = 2.5$ Hz, 1H; $H_2$), 3.87–3.82 (m, 2H; $H_4$, $H_{2'}$), 3.81–3.77 (m, 3H; $H_1$, $H_5$, $H_{3'}$), 3.72 (app. s, 1H; $H_{4'}$), 3.65 (t, $^3J(H,H) = 3.0$ Hz, 1H; $H_6$), 3.46 (t, 1H; $J = 9.0$ Hz, $J = 6.0$ Hz, $H_{6a'}$), 3.39 (m, 1H; $H_{6b'}$), 3.36 ppm (m, 3H; $CH_3OCH_2$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 139.2$, 138.8, 138.6, 138.5, 138.4, 138.0 (7C; Ph), 128.8–127.0 (35×CH; Ph), 98.0 ($CH_2OCH_3$), 97.4 ($C_{1'}$), 80.6, 80.5, 80.1, 79.7 ($C_2$, $C_{3'}$, $C_4$, $C_5$), 77.2 ($C_1$), 75.7, 74.9 (2×$CH_2$Ph), 74.3 ($C_3$), 74.1 ($C_6$), 73.8 ($C_{4'}$), 73.38, 73.26, 73.1, 72.1 (5×$CH_2$Ph), 69.0 ($C_{5'}$), 68.7 ($C_{6'}$), 60.3 ($C_{2'}$), 56.1 ppm ($CH_2OCH_3$); FAB HRMS: *m/z* calcd for $[C_{63}H_{67}N_3O_{11}+Na]^+$: 1064.4673; found: 1064.4656.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (19)**: PhSH (2.2 μL, 0.0218 mmol, 1.2 equiv) and $BF_3{\cdot}Et_2O$ (2.3 μL, 0.0218 mmol, 1.0 equiv) were added under Ar to a solution of **17** (19 mg, 0.0182 mmol) in $CH_2Cl_2$. After 2 h, the mixture was washed with solutions of saturated $NaHCO_3$ and NaCl, the organic layer was dried ($MgSO_4$), the solvent was evaporated, and the crude residue was purified by preparative chromatography (*n*-hexane/AcOEt 6:1) to give **19** as a syrup (14 mg, 0.01402 mmol, 77 %). $[\alpha]_D^{20} = +44$ ($c = 0.65$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 3:1): 0.19; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.38$–$7.07$ (m, 35H; Ph), 5.43 (d, $^3J(H,H) = 3.5$ Hz, 1H; $H_{1'}$), 5.04 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.90, 4.86 (AB, $^3J(H,H) = 11.0$ Hz, 2H; 2×CH−Ph), 4.73 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.70 (d, $^3J(H,H) = 12.5$ Hz, 1H; CH−Ph), 4.63 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.584 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.578 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.52 (d, $^3J(H,H) = 12.5$ Hz, 1H; CH−Ph), 4.46 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.44 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.41 (d, $^3J(H,H)$ $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.36 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.14 (d, $^3J(H,H) = 12.0$ Hz, CH−Ph), 4.08 (m, 1H; $H_2$), 3.99 (t, $^3J(H,H) = 10.0$ Hz, 1H; $H_{3'}$), 3.96 (app. d, $^3J(H,H) = 8.5$ Hz, 1H; $H_{5'}$), 3.84–3.77 (m, 3H; $H_1$, $H_4$, $H_5$), 3.76–3.71 (m, 2H; $H_3$, $H_{4'}$), 3.69 (m, 1H; $H_6$), 3.53 (dd, $^3J(H_2,H_3) = 10.5$ Hz, $^3J(H_2,H_1) = 3.5$ Hz, 1H; $H_2$), 3.29 (d, $^3J(H,H) = 6.0$ Hz, 1H; $C_2OH$), 3.26 (dd, $^3J(H_{6a'},H_{6b'}) = 10.5$ Hz, $^3J(H_{6a'},H_{5'}) = 2.0$ Hz; $H_{6a'}$), 3.06 ppm (dd, $^3J(H_{6b'},H_{6a'}) = 11.0$ Hz, $^3J(H_{6b'},H_{5'}) = 1.5$ Hz; $H_{6b'}$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 138.8$, 138.4, 138.2, 138.1, 137.99, 137.96 (7C; Ph), 128.5–127.3 (35×CH; Ph), 98.5 ($C_{1'}$), 81.2, 80.4, 79.1 ($C_1$, $C_4$, $C_5$), 81.0 ($C_{3'}$), 78.2, 77.5 ($C_{4'}$, $C_3$), 75.5, 75.2, 74.8, 73.9, 73.6, 73.4, 73.2, 73.0 (7×$CH_2$Ph, $C_6$), 72.7 ($C_2$), 70.8 ($C_{5'}$), 67.6 ($C_{6'}$), 64.4 ppm ($C_{2'}$); FAB HRMS: *m/z* calcd for $[C_{61}H_{63}N_3O_{10}+Na]^+$: 1020.4411; found: 1020.4455.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (20)**: Compound **20** (15 mg, 0.01503 mmol, 68 %) was obtained as a syrup from **18** (23 mg, 0.0221 mmol) by the same experimental procedure as that described for the preparation of **19**. Compound **20** was purified by PLC (*n*-hexane/AcOEt 3:1); $R_f$ (*n*-hexane/AcOEt 3:1): 0.17; $[\alpha]_D^{20} = +91$ ($c = 0.20$ in $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.38$–$7.16$ (m, 35H; Ph), 5.38 (d, $^3J(H,H) = 3.5$ Hz, 1H; $H_{1'}$), 4.98 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.80 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.73 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.66 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.65 (AB, 2H; $CH_2Ph$), 4.62 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.513 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.508 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.46 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.39 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.36 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.36 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.19 (t, $^3J(H,H) = 6.0$ Hz, 1H; $H_{5'}$), 4.16, 4.11 (AB, $^3J(H,H) = 11.5$ Hz, 2H; 2×CH−Ph), 4.06 (m, 1H; $H_2$), 4.03 (dd, $^3J(H,H) = 11.0$ Hz, $^3J(H,H) = 3.5$ Hz, 1H; $H_{2'}$), 3.94–3.90 (m, 2H; $H_3$, $H_{4'}$), 3.79–3.84 (m, 3H; $H_4$, $H_5$, $H_{3'}$), 3.75 (t, $^3J(H,H) = 4.0$ Hz, 1H; $H_1$), 3.68 (m, 1H; $H_6$), 3.61 (d, $^3J(H,H) = 5.5$ Hz, 1H; $C_2OH$), 3.44 (dd, $^3J(H_{6a'},H_{6b'}) = 8.8$ Hz, $^3J(H_{6a'},H_{5'}) = 6.0$ Hz, 1H; $H_{6a'}$), 3.26 ppm (dd, $^3J(H_{6b'},H_{6a'}) = 8.8$ Hz, $^3J(H_{6b'},H_{5'}) = 6.0$ Hz; $H_{6b'}$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 138.6$, 138.5, 138.4, 138.3, 138.2, 137.8 (7C; Ph), 128.6–127.2 (35×CH; Ph), 98.9 ($C_{1'}$), 81.6, 80.4, 79.4 ($C_{3'}$, $C_4$, $C_5$), 78.2 ($C_3$), 77.5 ($C_1$), 75.0, 74.7 (2×$CH_2$Ph), 74.2 ($C_6$), 73.8 ($CH_2$Ph), 73.4 ($C_{4'}$), 73.3, 73.2, 73.1 (3×$CH_2$Ph), 72.6 ($C_2$), 72.1 ($CH_2$Ph), 69.6 ($C_{5'}$), 68.3 ($C_{6'}$), 61.3 ppm ($C_{2'}$); FAB HRMS: *m/z* calcd for $[C_{61}H_{63}N_3O_{10}+Na]^+$: 1020.4411; found: 1020.4438.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-2-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-((*R*,*S*))-benzyl-phosphatidyl)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (21)**: Compound **19** (73 mg, 0.073 mmol) and 1*H*-tetrazole (11 mg, 0.161 mmol, 2.2 equiv) were coevaporated three times with toluene and dried under vacuum overnight in the presence of $P_2O_5$. The mixture was dissolved in $CH_2Cl_2$ (4 mL) and a solution of 1,2-di-*O*-myristoyl-*sn*-glycero-3-yl benzyl *N*,*N*-diisopropyl phosphoramidite (0.5 M, 292 μL, 2 equiv, 0.146 mmol) in $CH_2Cl_2$ was added under Ar. After 1 h 30 min, the mixture was cooled to −40 °C and a solution of *m*-CPBA (18 mg, 0.073 mmol, 1 equiv) in $CH_2Cl_2$ (3.2 mL) was added. The reaction mixture was neutralized with $Et_3N$ (1 mM in $CH_2Cl_2$) and purified on PLC plates (*n*-hexane/AcOEt 4:1) previously treated with $Et_3N$, to give a colorless syrup **21** as a 1:1 mixture of diastereomers (77 mg, 0.046 mmol, 63 %). $[\alpha]_D^{20} = +25$ ($c = 1.5$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 3:1): 0.37; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.44$–$7.01$ (m, 80H; Ph), 5.44 (d, $^3J(H,H) = 3.5$ Hz, 1H; $H_{1'}$), 5.42 (d, $^3J(H,H) = 4.0$ Hz, 1H; $H_{1'}$), 5.24–5.19 (m, 2H; CH−Ph, $C_{2a}H_{glycerol}$), 5.16 (d, $^3J(H,H) = 10.5$ Hz, 1H; CH−Ph), 5.11–5.07 (m, 3H; 2×CH−Ph, $C_{2b}H_{glycerol}$), 4.98 (app. d, $^3J(H,H) = 10.0$ Hz, 2H; 2×CH−Ph), 4.87 (m, 4H; 4×CH−Ph), 4.83 (m, 2H; 2×$H_2$), 4.74 (d, $^3J(H,H) = 11.0$ Hz; CH−Ph), 4.73 (d, $^3J$-

(H,H) = 10.5 Hz, 1H; CH−Ph), 4.65 (m, 2H; 2×CH−Ph), 4.58–4.49 (m, 3H; 3×CH−Ph), 4.42–3.95 (m, 14H; 14×CH−Ph), 4.367, 4.32–4.26 (m, 3H; $H_1$, $C_{1a}H$, $C_{3b}H_{glycerol}$), 4.26 (m, 1H; $H_1$), 4.22–4.14 (m, 4H; 2×$H_3$, $C_{1a}H$, $C_{3b}H_{glycerol}$), 4.11–4.04 (m, 5H; 2×$H_{5'}$, $C_{3a}H_2$, $C_{1b}H_{glycerol}$), 4.00 (t, $^3J$-(H,H) = 9.0 Hz, 1H; $H_{3'}$), 3.98 (t, $^3J$(H,H) = 9.0 Hz, 1H; $H_{3'}$), 3.97 (m, 1H; $C_{1b}H_{glycerol}$), 3.88 (m, 4H; 2×$H_5$, 2×$H_4$), 3.71 (t, $^3J$(H,H) = 9.5 Hz, 1H; $H_{4'}$), 3.70 (t, $^3J$(H,H) = 10.0 Hz, 1H; $H_{4'}$), 3.60 (m, 2H; 2×$H_6$), 3.29 (dd, $^3J(H_{2'},H_{3'}) = 10.5$ Hz, $^3J(H_{2'},H_{1'}) = 4.0$ Hz, 2H; 2×$H_{2'}$), 3.24 (app. d, $^3J$-(H,H) = 11.0 Hz, 2H; 2×$H_{6a'}$), 3.18 (dd, $^3J(H_{6b'},H_{6a'}) = 11.0$ Hz, $^3J$-$(H_{6b'},H_{5'}) = 2.5$ Hz; 2×$H_{6b'}$), 2.35 (m, 4H; 2×$CH_2$CO), 2.23 (m, 4H; 2×$CH_2$CO), 1.65–1.50 (m, 8H; 4×C$H_2$$CH_2$CO), 1.34–1.20 (m, 80H; 40×$CH_2$), 0.89 ppm (t, $^3J$(H,H) = 7.0 Hz, 4H; 4×$CH_3$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 173.3, 173.2, 173.0, 172.8 (4×CO), 138.6, 138.3, 138.25, 138.20, 138.13, 138.10, 137.9 (16C; Ph), 129.2–127.4 (80×CH; Ph), 97.8, 97.6 (2×$C_{1'}$), 80.2, 80.1, 80.0, 79.2 (2×$C_{3'}$, 2×$C_2$, 2×$C_4$, 2×$C_5$), 78.4 (2×$C_{4'}$), 76.4, 76.3 (2×$C_1$), 75.9, 75.4 (4×$CH_2$Ph), 74.9 (2×$C_3$), 74.0, 73.8, 73.4 (6×$CH_2$Ph), 73.2, 72.9 (2×$C_6$), 72.9, 72.7 (4×$CH_2$Ph), 70.4 (2×$C_{5'}$), 70.0, 69.7 (2×d, $^3J$(H,H) = 5.4 Hz; 2×$C_2H_{glycerol}$), 69.6, 69.5 (2×d, J = 7.9 Hz; 2×PO$CH_2$Ph), 67.9 (2×$C_{6'}$), 66.1, 65.7 (2×d, $^3J$(H,H) = 5.1 Hz; 2×$C_3H_{2\,glycerol}$), 63.52, 63.47 (2×$C_{2'}$), 62.2, 61.7 (2×$C_1H_{2\,glycerol}$), 34.4, 34.3, 34.2, 34.1 (4×$CH_2$CO), 32.0 (4×$CH_2CH_2CH_3$), 29.8–29.2 (32×$CH_2$), 25.08, 25.02, 24.94, 24.91 (4×$CH_2CH_2$CO), 22.8 (4×$CH_2CH_2CH_3$), 12.2 ppm (4$CH_3$); $^{31}$P NMR (202 MHz, $CDCl_3$, 25 °C, TMS): δ = −2.87, −2.98 ppm; FAB HRMS: *m/z* calcd for $[C_{99}H_{129}N_3O_{17}P+Na]^+$: 1685.8957; found: 1684.8963.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-2-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-benzyl-phosphatidyl)-1,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (22)**: Compound **22** was obtained as a colorless syrup and as a 1:1 mixture of two diastereomers (15 mg, 0.009 mmol, 60%) from **20** (15 mg, 0.015 mmol) by the procedure described for the preparation of **21**. The crude product was fractionated on PLC plates (Hex/AcOEt 4:1) previously treated with $Et_3N$ to give **22** as a colorless syrup. $[\alpha]_D^{20} = +34$ ($c = 0.8$ in $CHCl_3$ diastereomers 1/1); $R_f$ (*n*-hexane/AcOEt 3:1): 0.27; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.40–7.07 (m, 80H; Ph), 5.44 (m, $^3J$(H,H) = 3.5 Hz, 2H; 2×$H_{1'}$), 5.21–5.12 (m, 1H; $C_{2a}H_{glycerol}$), 5.13–5.04 (m, 3H; 2×CH−Ph, $C_{2b}H_{glycerol}$), 4.81 (m, 1H; $H_2$), 4.78, 4.77 (2×d, $^3J$(H,H) = 11.0 Hz, 2H; 2×CH−Ph), 4.69–4.63 (m, 3H; 3×CH−Ph), 4.60–4.14 (m, 35H; 25×CH−Ph, 2×$H_{5'}$, 2×$H_1$, 2×$H_3$, $C_{1a}H$, $C_{1a}H$, $C_{3b}H$, $C_{3a}H_{glycerol}$), 4.13–3.95 (m, 4H; $C_{3a}H$, $C_{3b}H$, $C_{1b}H_{2\,glycerol}$), 3.89–3.84 (m, 2H; 2×$H_5$), 3.84–3.75 (m, 6H; 2×$H_4$, 2×$H_{2'}$, 2×$H_{3'}$), 3.67, 3.65 (2 brs, 2H; 2×$H_{4'}$), 3.60 (m, 2H; 2×$H_6$), 3.48 (dd, $^3J(H_{6b'},H_{6a'}) = 9.5$ Hz, $^3J(H_{6b'},H_{5'}) = 9.0$ Hz, 2H; 2×$H_{6a'}$), 3.36 (t, $^3J$(H,H) = 8.0 Hz, 2H; 2×$H_{6b'}$), 2.35 (m, 4H; 2×$CH_2$CO), 2.23 (m, 4H; 2×$CH_2$CO), 1.65–1.50 (m, 8H; 4×C$H_2$$CH_2$CO), 1.34–1.20 (m, 80H; 40×$CH_2$), 0.89 ppm (t, $^3J$(H,H) = 7.0 Hz, 12H; 4×$CH_3$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 173.7–172.9 (4×CO), 139.0, 138.6, 138.4, 137.9 (16C; Ph), 128.8–127.5 (80×CH; Ph), 97.6 (2×$C_{1'}$), 80.1 (2×$C_2$), 79.7, 79.8 (2×$C_4$, 2×$C_5$), 77.0 (2×$C_{3'}$), 76.3 (2×$C_1$), 74.6 (2×$CH_2$Ph), 74.1–72.4 (10×$CH_2$Ph), 73.6 ($C_{4'}$), 73.8 (2×$CH_2$Ph), 73.5 (2×$C_6$), 73.4 (2×$C_3$), 73.0 (2×$CH_2$Ph), 69.3 ($C_{5'}$), 69.7, 69.5 (2×$C_2H_{2\,glycerol}$), 68.9 (2×$C_{6'}$), 65.6, 65.3 (2×$C_3H_{2\,glycerol}$), 61.62 (2×$C_1H_{2\,glycerol}$), 60.0 (2×$C_{2'}$), 34.2, 34.1 (4×$CH_2$CO), 32.1 (4×$CH_2CH_2CH_3$), 29.8–29.3 (32×$CH_2$), 24.9 (4×$CH_2CH_2$CO), 22.8 (4×$CH_2CH_2CH_3$), 14.3 ppm (4×$CH_3$); $^{31}$P NMR (202 MHz, $CDCl_3$, 25 °C, TMS): δ = −2.74, −2.91 ppm; FAB HRMS: *m/z* calcd for $[C_{99}H_{128}N_3O_{17}P+Na]^+$: 1684.8879; found: 1684.8948.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-1-allyl-L-*chiro*-inositol (23)**: Compound **13** (432 mg, 0.40 mmol) was dissolved under Ar in dried MeOH (7 mL), treated with MeONa/MeOH (1.0 M, 3.2 mL, 3.2 mmol, 8 equiv), and stirred for 16 h. The solvent and BzOMe obtained as byproduct were evaporated by heating (50 °C) under vacuum to give **23** quantitatively as a syrup (270 mg, 0.40 mmol). $[\alpha]_D^{20} = -11$ ($c$ = 0.1 in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 1:3): 0.49; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.59–7.19 (m, 15H; Ph), 5.88 (m, 1H; C$H$=$CH_2$), 5.26 (app. d, $^3J$(H,H) = 17.0 Hz, 1H; CH=C$H_2$), 5.17 (app. d, $^3J$(H,H) = 10.0 Hz, 1H; CH=C$H_2$), 5.09 (d, $^3J$(H,H) = 3.6 Hz, 1H; $H_{1'}$), 4.88 (s, 2H; $CH_2$Ph), 4.82 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.63–4.53 (m, 3H; $CH_2$−Ph, CH−Ph), 4.24 (dd, $^3J$(H,H) = 12.5 Hz, $^3J$(H,H) = 5.0 Hz, 1H; C$H_2$−CH=$CH_2$), 4.17–4.07 (m, 3H; $H_{5'}$, $H_6$, C$H_2$−CH=$CH_2$), 3.98 (m, 1H; $H_2$), 3.94 (t, $^3J$(H,H) = 9.7 Hz, 1H; $H_{3'}$), 3.90 (t, $^3J$(H,H) = 3.5 Hz, 1H; $H_1$), 3.72 (app. d, $^3J$(H,H) = 6.5 Hz, 1H; $H_5$), 3.71–3.66 (m, 1H; $H_{6a'}$), 3.62 (dd, $^3J(H_{2'},H_{3'}) = 9.7$ Hz, $^3J(H_{2'},H_{1'}) = 3.6$ Hz, 1H; $H_{2'}$), 3.55 (m, 2H; $H_3$, $H_4$), 3.49 (m, 1H; $H_{6b'}$), 3.44 ppm (t, $^3J$(H,H) = 9.7 Hz, 1H; $H_{4'}$); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 137.5, 137.3 (3C; Ph), 134.8 (C$H$=$CH_2$), 128.7–127.3 (15×CH; Ph), 117.3 (CH=C$H_2$), 99.1 ($C_{1'}$), 87.5 ($C_3$), 81.6 ($C_{3'}$), 78.8 ($C_{4'}$), 77.4 ($C_1$), 76.0, 75.2, 73.8 (3×C$H_2$Ph), 72.8 (C$H_2$−CH=$CH_2$), 72.4 ($C_4$), 72.0, 69.2 ($C_{5'}$, $C_6$), 71.5 ($C_5$), 70.5 ($C_2$), 68.9 ($C_{6'}$), 65.0 ppm ($C_{2'}$); FAB HRMS: *m/z* calcd for $[C_{36}H_{43}N_3O_{10}+Na]^+$: 700.2846; found: 700.2892.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-1-allyl-L-*chiro*-inositol (24)**: Compound **24** (53 mg, 0.08 mmol) was obtained as a white foam from **14** (83 mg, 0.08 mmol) by the same experimental procedure as that used to obtain **23**. $[\alpha]_D^{20} = +2$ ($c = 0.2$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 1:3): 0.33; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.44–7.20 (m, 15H; Ph), 5.88 (m, 1H; C$H$=$CH_2$), 5.26 (dd, $^3J$(H,H) = 17.2 Hz, $^3J$(H,H) = 1.8 Hz, 1H; CH=C$H_2$), 5.16 (dd, $^3J$(H,H) = 17.2 Hz, $^3J$-(H,H) = 1.2 Hz, 1H; CH=C$H_2$), 5.05 (d, $^3J$(H,H) = 3.9 Hz, 1H; $H_{1'}$), 4.86 (d, $^3J$(H,H) = 11.7 Hz, 1H; CH−Ph), 4.74 (s, 2H; $CH_2$Ph), 4.50 (d, $^3J$-(H,H) = 11.7 Hz, 1H; CH−Ph), 4.48 (d, $^3J$(H,H) = 11.7 Hz, 1H; CH−Ph), 4.40 (d, $^3J$(H,H) = 11.7 Hz, 1H; CH−Ph), 4.24 (dd, $^3J$(H,H) = 13.2 Hz, $^3J$-(H,H) = 5.4 Hz; C$H_2$−CH=$CH_2$), 4.16–4.05 (m, 4H; $H_{2'}$, $H_{5'}$, $H_6$, C$H_2$−CH=$CH_2$), 3.94 (m, 1H; $H_2$), 3.91–3.85 (m, 2H; $H_{3'}$, $H_{4'}$), 3.84 (app. s, 1H; $H_1$), 3.72 (dd, $^3J(H_5,H_4) = 9.4$ Hz, $^3J(H_5,H_6) = 3.0$ Hz, 1H; $H_5$), 3.62 (t, $^3J$-(H,H) = 9.4 Hz, 1H; $H_{6a'}$), 3.53 (m, 1H; $H_3$), 3.50 (m, 1H; $H_4$), 3.27 ppm (dd, $^3J(H_{6b'},H_{6a'}) = 9.4$ Hz, $^3J(H_{6b'},H_{5'}) = 3.3$ Hz, 1H; $H_{6b'}$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 137.9, 137.3 (3C; Ph), 134.9 (CH$_2$−C$H$=$CH_2$), 128.8–128.0 (15×CH; Ph), 117.2 (CH=C$H_2$), 99.4 ($C_{1'}$), 87.2 ($C_3$), 79.0 ($C_{3'}$), 77.0 ($C_{4'}$), 74.5, 73.9 (2×C$H_2$Ph), 73.1 ($C_1$), 72.8 (C$H_2$Ph), 72.6 (C$H_2$−CH=$CH_2$), 72.3 ($C_4$), 71.7 ($C_5$), 71.1 ($C_{5'}$), 70.5 ($C_2$), 70.2 ($C_{6'}$), 69.3 ($C_6$), 61.4 ppm ($C_{2'}$); FAB HRMS: *m/z* calcd for $[C_{36}H_{43}N_3O_{10}+Na]^+$: 700.2846; found: 700.2861.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-1-allyl-2,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (25)**: A mixture of compound **23** (141 mg, 0.21 mmol) and NaH (50 mg, 1.26 mmol, 6 equiv) in dried DMF (8 mL) was stirred under Ar for 10 min. After the mixture had been cooled to −15 °C in an ice/salt bath, BnBr (200 μL, 1.68 mmol, 8 equiv) was added dropwise. The reaction mixture was stirred overnight, $NH_4OH$ was added, and the mixture was then successively washed with a solution of saturated $NH_4Cl$, $H_2O$, and brine. The organic layer was dried ($MgSO_4$) and evaporated, and the crude product was purified by flash chromatography (Hex/AcOEt 20:1, AcOEt) to provide **25** as a syrup (145 mg, 0.14 mmol, 68%). $[\alpha]_D^{20} = +32$ ($c = 0.4$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 3:1): 0.33; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.37–7.01 (m, 35H; Ph), 5.73–5.64 (m, 2H; $H_{1'}$, C$H$=$CH_2$), 5.07–5.01 (m, 2H; CH=C$H_2$), 4.99 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.88 (s, 2H; $CH_2$Ph), 4.75 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH−Ph), 4.70 (d, $^3J$(H,H) = 11.5 Hz, 2H; 2×CH−Ph) 4.64 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.62 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH−Ph), 4.58 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH−Ph), 4.50 (d, $^3J$(H,H) = 12.0 Hz, 1H; CH−Ph), 4.44 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH−Ph), 4.42 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH−Ph), 4.38 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.20 (d, $^3J$(H,H) = 12.0 Hz, 1H; CH−Ph), 4.08 (m, 1H; $H_{5'}$), 4.03 (t, $^3J$(H,H) = 9.5 Hz, 1H; $H_3$), 4.00–3.93 (m, 2H; $H_{3'}$, C$H_2$−CH=$CH_2$), 3.91 (dd, $^3J(H_2,H_3) = 9.5$ Hz, $^3J(H_2,H_1) = 3.0$ Hz, 1H; $H_2$), 3.85–3.77 (m, 2H; $H_4$, $H_5$), 3.78 (app. d, $^3J$(H,H) = 6.0 Hz, 1H; C$H_2$−CH=$CH_2$), 3.68 (t, 1H, $^3J$(H,H) = 9.5 Hz, 1H; $H_{4'}$), 3.67 (app. s, 1H; $H_6$), 3.56 (t, $^3J$-(H,H) = 3.0 Hz, 1H; $H_1$), 3.26 (dd, $^3J(H_{2'},H_{3'}) = 10.5$ Hz, $^3J(H_{2'},H_{1'}) = 4.0$ Hz, 1H; $H_{2'}$), 3.21 (app. d, $^3J$(H,H) = 10.0 Hz, 1H; $H_{6a'}$), 3.15 ppm (app. d, $^3J$(H,H) = 10.0 Hz, 1H; $H_{6b'}$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 138.7–138.2 (7C; Ph), 135.0 (C$H$=$CH_2$), 128.6–127.3 (35×CH; Ph), 117.1 (CH=C$H_2$), 97.6 ($C_{1'}$), 81.4 ($C_2$), 80.8 ($C_{3'}$), 80.6 ($C_5$), 79.7 ($C_4$), 78.6 ($C_{4'}$), 75.8 ($CH_2$Ph), 75.6 ($C_3$), 75.4 ($CH_2$Ph), 74.8 ($C_6$, $CH_2$Ph), 73.8 ($C_1$), 73.5 (2×C$H_2$Ph), 73.4, 72.5 (2×C$H_2$Ph), 72.4 (C$H_2$−CH=$CH_2$), 70.1 ($C_{5'}$), 67.9 ($C_{6'}$), 63.7 ppm ($C_{2'}$); FAB HRMS: *m/z* calcd for $[C_{64}H_{67}N_3O_{10}+Na]^+$: 1060.4724; found: 1060.4765.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-1-allyl-2,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (26)**: Compound **26** (151 mg, 0.15 mmol, 68%) was obtained as a syrup from **24** (147 mg, 0.22 mmol) by the experimental procedure described above for the preparation of

**25**. The crude product was purified by flash chromatography (*n*-hexane/AcOEt 20:1, AcOEt) and preparative chromatography (*n*-hexane/AcOEt 18:1). $[\alpha]_D^{20}=+53$ ($c=1.3$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 6:1): 0.21; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C. TMS): $\delta=7.40$–$7.17$ (m, 35H; Ph), 5.73–5.63 (m, 1H; C*H*=CH$_2$), 5.66 (d, $^3J$(H,H) = 3.0 Hz, 1H; H$_{1'}$), 5.07–5.01 (m, 2H; *CH*$_2$–CH=CH$_2$), 4.99 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH–Ph), 4.77 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH–Ph), 4.73 (d, $^3J$(H,H) = 12.5 Hz, 1H; CH–Ph), 4.68 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH–Ph), 4.61 (m, 4H; 4×CH–Ph), 4.52 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH–Ph), 4.44 (m, 3H; 3×CH–Ph), 4.32 (app. t, $^3J$(H,H) = 7.0 Hz, 1H; H$_{5'}$), 4.30, 4.24 (AB, $^3J$(H,H) = 11.5 Hz, 2H; 2×CH–Ph), 4.08 (t, $^3J$(H,H) = 9.0 Hz, 1H; H$_3$), 3.98 (dd, $^3J$(H,H) = 12.5 Hz, $^3J$(H,H) = 5.0 Hz, 1H; CH=C*H*$_2$), 3.90 (m, 1H; CH=C*H*$_2$), 3.87–3.79 (m, 4H; H$_4$, H$_{3'}$, H$_5$, H$_{2'}$), 3.76 (dd, $^3J$(H,H) = 10.5 Hz, 1H; H$_2$), 3.72 (s, 1H; H$_{4'}$), 3.69 (app. s, 1H; H$_6$), 3.58 (app. s, 1H; H$_1$), 3.46 (app. t, $^3J$-(H,H) = 9.0 Hz, 1H; H$_{6a'}$), 3.38 ppm (app. t, $^3J$(H,H) = 9.0 Hz, 1H; H$_{6b'}$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta=139.2$–$138.0$ (7C; Ph), 134.8 (CH=CH$_2$), 128.6–127.3 (35×CH; Ph), 116.9 (CH=CH$_2$), 97.4 (C$_{1'}$), 81.2, 80.6, 80.1 (C$_2$, C$_4$, C$_5$), 77.4 (C$_{3'}$), 75.6 (*C*H$_2$Ph), 75.1 (C$_6$), 74.8 (2×*C*H$_2$Ph), 74.2 (C$_3$), 73.8 (C$_1$, C$_{4'}$), 73.5, 73.6, 73.1 (3×*C*H$_2$Ph), 72.4 (*C*H$_2$–CH=CH$_2$), 72.0 (*C*H$_2$Ph), 71.1 (C$_{5'}$), 68.8 (C$_{6'}$), 60.2 ppm (C$_{2'}$); FAB HRMS: *m*/*z* calcd for $[C_{64}H_{67}N_3O_{10}+Na]^+$: 1060.4724; found: 1060.4793.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-2,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (27)**: A solution (6 mM) of [{Ir(cod)Ph$_2$PMe}$_2$]PF$_6$ (cod = cyclooctadiene) (84 μL, 2.3 μmol, 0.03 equiv) in THF was added to a solution of **25** (80 mg, 0.077 mmol, 1 equiv) in freshly distilled THF (2.2 mL). After 1 h, the solvent was evaporated with a stream of Ar and a freshly prepared solution (6 mM) of [{Ir(cod)Ph$_2$PMe}$_2$]PF$_6$ in THF (384 μL) was added. After 30 min, *N*-bromosuccinimide (NBS) (21 mg, 0.116 mmol, 1.5 equiv) and H$_2$O (232 μL, 12.94 mmol, 168 equiv) were added and the mixture was stirred for 10 min. AcOEt was added, and the organic layer was separated and washed with a solution of cold saturated NaHCO$_3$ (2×5 mL) and NaCl (3×5 mL), and dried with MgSO$_4$. The crude product was purified by flash chromatography (*n*-hexane/AcOEt 3:1) to provide **27** as a colorless syrup (55 mg, 0.055 mmol, 72 %). $[\alpha]_D^{20}=+10$ ($c=0.15$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 4:1): 0.20; $^1$H NMR (500 MHz, $CDCl_3$,): $\delta=7.37$–$7.01$ (m, 35H; Ph), 5.62 (d, $^3J$(H,H) = 3.5 Hz, 1H; H$_{1'}$), 4.99 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH–Ph), 4.88 (AB, 2H; CH$_2$Ph), 4.79 (d, $^3J$(H,H) = 12.0 Hz, 1H; CH–Ph), 4.70 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH–Ph), 4.68 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH–Ph), 4.67, 4.62 (AB, $^3J$(H,H) = 10.5 Hz, 2H; 2×CH–Ph), 4.61 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH–Ph), 4.52 (d, $^3J$(H,H) = 12.0 Hz, 1H; CH–Ph), 4.48 (d, $^3J$(H,H) = 12.0 Hz, 1H; CH–Ph), 4.46 (d, $^3J$-(H,H) = 11.0 Hz; CH–Ph), 4.36 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH–Ph), 4.19 (d, $^3J$(H,H) = 12.0 Hz, 1H; CH–Ph), 4.08 (app. d, $^3J$(H$_{5'}$,H$_{4'}$) = 9.5 Hz, 1H; H$_{5'}$), 3.99–3.84 (m, 7H; H$_1$, H$_2$, H$_3$, H$_4$, H$_5$, H$_6$, H$_{3'}$), 3.68 (t, $^3J$(H,H) = 9.5 Hz, 1H; H$_{4'}$), 3.32 (dd, $^3J$(H$_{2'}$,H$_{3'}$) = 10.0 Hz, $^3J$(H$_{2'}$,H$_{1'}$) = 3.5 Hz, 1H; H$_{2'}$), 3.19–3.10 (m, 2H; H$_{6a'}$, H$_{6b'}$), 2.29 ppm (s, 1H; C$_1$OH); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta=138.8$–$137.6$ (7C; Ph), 128.8–127.4 (35×CH; Ph), 97.6 (C$_{1'}$), 81.9 (C$_{inositol}$), 80.7 (C$_{3'}$), 80.5, 79.0 (2×C$_{inositol}$), 78.5 (C$_{4'}$), 75.7 (2×C$_{inositol}$, 2×*C*H$_2$Ph), 74.8, 73.8, 73.5, 73.2, 72.5 (5×*C*H$_2$Ph), 70.2 (C$_{5'}$), 67.8 (C$_{6'}$), 67.3 (C$_1$), 63.6 ppm (C$_{2'}$); elemental analysis calcd (%) for $C_{61}H_{63}N_3O_{10}\cdot H_2O$: C 72.10, H 6.45, N 4.14; found: C 72.40, H 6.85, N 4.06; FAB HRMS: *m*/*z* calcd for $[C_{61}H_{63}N_3O_{10}+Na]^+$: 1020.4411; found: 1020.4386.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-2,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (28)**: Compound **28** (22 mg, 0.021 mmol, 72 %) was prepared from **26** (30 mg, 0.029 mmol) by the same procedure as that described for the preparation of **27**. Syrup **28** was purified by flash chromatography (*n*-hexane/AcOEt 4:1). $[\alpha]_D^{20}=+31$ ($c=0.2$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 4:1): 0.21; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.41$–$7.16$ (m, 35H; Ph), 5.62 (d, $^3J$(H,H) = 2.4 Hz, 1H; H$_{1'}$), 5.01 (d, $^3J$(H,H) = 11.7 Hz, 1H; CH–Ph), 4.80 (d, $^3J$(H,H) = 12.1 Hz, 1H; CH–Ph), 4.78 (d, $^3J$(H,H) = 11.2 Hz, 1H; CH–Ph), 4.67 (d, $^3J$-(H,H) = 11.7 Hz, 1H; CH–Ph), 4.65 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH–Ph), 4.63–4.59 (m, 4H; 2×CH$_2$Ph), 4.55 (d, $^3J$(H,H) = 12.1 Hz, 1H; CH–Ph), 4.51 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH–Ph), 4.44 (d, $^3J$(H,H) = 11.2 Hz, 1H; CH–Ph), 4.32 (m, 1H; H$_{5'}$), 4.25 (AB, 2H; CH$_2$Ph), 4.06–3.88 (m, 6H; H$_1$, H$_2$, H$_3$, H$_4$, H$_5$, H$_6$), 3.82 (s, 2H; H$_{2'}$, H$_{3'}$), 3.68 (s, 1H; H$_{4'}$), 3.44 (dd, $^3J$(H$_{6a'}$,H$_{6b'}$) = 9.3 Hz, $^3J$(H$_{6a'}$,H$_{5'}$) = 9.0 Hz, 1H; H$_{6a'}$), 3.32 ppm (t, $^3J$-(H,H) = 9.3 Hz, 1H; H$_{6b'}$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta=139.1$–$137.5$ (7C; Ph), 128.8–127.4 (35×CH; Ph), 97.3 (C$_{1'}$), 81.9, 80.5, 79.5 (3C$_{inositol}$), 77.0 (C$_{3'}$), 75.6, 75.5 (2C$_{inositol}$), 74.9, 74.2, 73.8, (3×*C*H$_2$Ph), 73.7 (C$_{4'}$), 73.2, 73.1, 72.5, 72.1 (4×*C*H$_2$Ph), 68.9 (C$_{5'}$), 68.8 (C$_{6'}$), 67.4 (C$_1$), 60.1 ppm (C$_{2'}$); elemental analysis calcd (%) for $C_{61}H_{63}N_3O_{10}\cdot 3H_2O$: C 69.63, H 6.61, N 3.99; found: C 70.00, H 6.99, N 3.68; FAB HRMS: *m*/*z* calcd for $[C_{61}H_{63}N_3O_{10}+Na]^+$: 1020.4411; found: 1020.4352.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→3)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-benzylphosphatidyl)-2,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (29)**: Compound **29** was obtained as a colorless syrup from **27** (39 mg, 0.039 mmol) by the procedure described for the preparation of **21**. The crude product was fractionated on PLC plates (*n*-hexane/AcOEt 3:1) previously treated with Et$_3$N to give **29** as a mixture of two diastereomers (1:1, 53 mg, 0.032 mmol, 82 %). $[\alpha]_D^{20}=+15$ ($c=0.47$ in $CHCl_3$, diastereomers 3/1); $R_f$ (*n*-hexane/AcOEt 3:1): 0.29; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.43$–$7.02$ (m, 80H; Ph), 5.66 (d, $^3J$-(H,H) = 3.5 Hz, 1H; H$_{1'}$), 5.64 (d, $^3J$(H,H) = 4.0 Hz, 1H; H$_{1'}$), 5.13 (m, 1H; C$_{2a}$H$_{glycerol}$), 5.01 (m, 3H; 2×CH–Ph, C$_{2b}$H$_{glycerol}$), 4.94–4.81 (m, 12H; 10×CH–Ph, 2×H$_1$), 4.77–4.42 (m, 16H; 16×CH–Ph), 4.38 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH–Ph), 4.37 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH–Ph), 4.24 (dd, $^3J$(H,H) = 12.0 Hz, $^3J$(H,H) = 4.0 Hz, 1H; C$_{1a}$H$_{glycerol}$), 4.20 (d, $^3J$(H,H) = 12.0 Hz, 2H; 2×CH–Ph), 4.09–3.82 (m, 21H; 2×H$_2$, 2×H$_3$, 2×H$_4$, 2×H$_5$, 2×H$_6$, 2×H$_{3'}$, 2×H$_{5'}$, C$_{1a}$H, C$_{3a}$H, C$_{1b}$H, C$_{3a}$H, C$_{1b}$H, C$_{3b}$H$_{2\,glycerol}$), 3.71 (t, $^3J$(H,H) = 9.5 Hz, 2H; 2×H$_{4'}$), 3.30 (dd, $^3J$(H$_{2'}$,H$_{3'}$) = 10.5 Hz, $^3J$(H$_{2'}$,H$_{1'}$) = 3.7 Hz, 2H; 2×H$_{2'}$), 3.21–3.12 (m, 4H; 2×H$_{6a'}$, 2×H$_{6b'}$), 2.26, 2.20 (2×m, 8H; 4×CH$_2$CO), 1.60–1.50 (m, 8H; 4×*CH*$_2$CH$_2$CO), 1.33–1.20 (m, 80H; 40×CH$_2$), 0.89 ppm (t, $^3J$(H,H) = 7.0 Hz, 12H; 4×CH$_3$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta=173.6$, 173.2 (4×CO), 138.8, 138.6, 138.5, 138.43, 138.35, 138.2, 137.6, 135.9 (16C; Ph), 129.1–127.8 (80×CH; Ph), 99.4, 98.0 (2×C$_{1'}$), 80.8, 80.4, 79.5, 78.6 (2×C$_3$, 2×C$_4$, 2×C$_6$, 2×C$_{3'}$), 78.4 (2×C$_{4'}$), 77.6 (2×*C*H$_2$Ph), 76.2, 75.8, 75.4, 75.1, 74.4, 73.8, 73.3, 72.7 (12×*C*H$_2$Ph, 2×C$_2$, 2×C$_5$), 73.2 (m; PO*C*H$_2$Ph), 73.1 (m; PO*C*H$_2$Ph), 70.5 (2×C$_{5'}$), 70.2 (d, $^3J$(H,H) = 5.4 Hz; 2×C$_2$H$_{glycerol}$), 69.65, 69.55 (2×C$_1$), 68.0 (2×C$_{6'}$), 66.1 (m; C$_3$H$_{2\,glycerol}$), 65.6 (d, $^3J$(H,H) = 5.4 Hz, C$_3$H$_{2\,glycerol}$), 63.7 (2×C$_{2'}$), 62.0 (2×C$_1$H$_{2\,glycerol}$), 34.5, 34.4 (4×CH$_2$CO), 32.4 (4×*C*H$_2$CH$_2$CH$_3$), 30.1–29.6 (32×CH$_2$), 25.2 (4×*C*H$_2$CH$_2$CO), 23.1 (4×*C*H$_2$CH$_2$CH$_3$), 14.6 ppm (4×CH$_3$); $^{31}$P NMR (202 MHz, $CDCl_3$, 25 °C; TMS): $\delta=-1.96$, $-2.1$ ppm; elemental analysis calcd (%) for $C_{99}H_{128}N_3O_{17}P\cdot 2H_2O$: C 69.98, H 7.83, N, 2.47; found: C 70.13, H 8.09, N 2.26; FAB HRMS: *m*/*z* calcd for $[C_{99}H_{128}N_3O_{17}P+Na]^+$: 1684.8879; found: 1684.9006.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→3)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-benzylphosphatidyl)-2,4,5,6-tetra-*O*-benzyl-L-*chiro*-inositol (30)**: Compound **30** was obtained as a mixture of two diastereomers (1:1, 29 mg, 0.017 mmol, 78 %) from **28** (22 mg, 0.022 mmol) by the procedure described for the preparation of **29**. The crude product was fractionated on PLC plates (*n*-hexane/AcOEt 3:1) previously treated with Et$_3$N to give **30** as a colorless syrup. $[\alpha]_D^{20}=+22$ ($c=0.7$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 2:1): 0.44; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=7.44$–$7.12$ (m, 80H; Ph), 5.66 (d, $^3J$-(H,H) = 3.5 Hz, 1H; H$_{1'}$), 5.63 (d, $^3J$(H,H) = 3.0 Hz, 1H; H$_{1'}$), 5.11 (m, 1H; C$_{2a}$H$_{glycerol}$), 5.03 (m, 1H; C$_{2b}$H$_{glycerol}$), 4.99 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH–Ph), 4.98 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH–Ph), 4.90–4.73 (m, 10H; 2×H$_1$, 8×CH–Ph), 4.68 (d, $^3J$(H,H) = 11.5 Hz, 1H; CH–Ph), 4.66 (d, $^3J$-(H,H) = 11.5 Hz, 1H; CH–Ph), 4.63–4.38 (m, 16H; 16×CH–Ph), 4.30 (m, 2H; 2×H$_{5'}$), 4.28–4.18 (m, 3H; C$_{1a}$H$_{glycerol}$, 2×CH–Ph), 4.07–3.94 (m, 8H; 2×H$_2$, C$_{1a}$H, C$_{3a}$H$_2$, C$_{1b}$H$_{glycerol}$, 2×CH–Ph), 3.93–3.75 (m, 13H; 2×H$_3$, 2×H$_4$, 2×H$_6$, 2×H$_{3'}$, 2×H$_{2'}$, C$_{1b}$H, C$_{3b}$H$_2$), 3.72 (app. s, 2H; 2×H$_{4'}$), 3.68 (m, 2H; 2×H$_{5'}$), 3.46–3.40 (m, 2H; 2×H$_{6a'}$), 3.34 (m, 2H; 2×H$_{6b'}$), 2.25 (m, 4H; 2×CH$_2$CO), 2.18 (m, 4H; 2×CH$_2$CO), 1.57–1.40 (m, 8H; 4×*CH*$_2$CH$_2$CO), 1.33–1.20 (m, 80H; 40×CH$_2$), 0.90 ppm (t, $^3J$(H,H) = 7.0 Hz, 12H; 4×CH$_3$); $^{13}$C NMR and HSQC (125 and 500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=138.0$–$137.2$ (16C; Ph), 129.1–127.5 (80×CH; Ph), 97.4 (2×C$_{1'}$), 80.2 (2×C$_6$), 79.8 (2×C$_4$), 77.2 (2×C$_3$), 75.8–72.1 (14×*C*H$_2$Ph, 2×C$_2$, 2×C$_5$, 2×C$_{3'}$, 2×C$_{4'}$), 70.0–68.7 (2×C$_{5'}$, 2×C$_1$, 2×C$_{6'}$, 2×PO*C*H$_2$Ph, 2×C$_2$H$_{glycerol}$), 65.3, 66.0 (2×C$_3$H$_{2\,glycerol}$), 61.8 (2×C$_1$H$_{2\,glycerol}$), 60.0 (2×C$_{2'}$), 34.3, 34.1 (4×*C*H$_2$CO), 32.1 (4×*C*H$_2$CH$_2$CH$_3$), 29.8–29.3 (32×CH$_2$), 25.0 (4×*C*H$_2$CH$_2$CO), 22.8 (4×CH$_2$*C*H$_2$CH$_3$), 14.3 ppm (4×CH$_3$);

$^{31}$P NMR (202 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.16$, $-2.36$ ppm; FAB HRMS: $m/z$ calcd for $[C_{99}H_{128}N_3O_{17}P+Na]^+$: 1684.8879; found: 1684.9006.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→2)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-benzylphosphatidyl)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (33)**: Compound **33** was obtained as a colorless syrup and as a mixture of two diastereomers (1:1, 43 mg, 0.026 mmol, 42 % with 24 % of starting material **31**) from **31** (82 mg, 0.015 mmol), by the procedure described for the preparation of **29**. The crude product was fractionated on PLC plates (*n*-hexane/AcOEt 4:1) previously treated with $Et_3N$ to provide **33**. $[\alpha]_D^{20} = +42$ ($c = 1.0$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 3:1): 0.28; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.38$–$7.01$ (m, 80H; Ph), 5.200 (m, 1H; $C_{2a}H_{glycerol}$), 5.198, 5.15 (2×d, $^3J$(H,H) = 3.5 Hz, 2H; 2×$H_{1'}$), 5.12 (m, 2H; 2×CH−Ph), 5.09 (m, 1H; $C_{2b}H_{glycerol}$), 4.97 (m, 2H; 2×CH−Ph), 4.91–4.81 (m, 4H; 2×CH−Ph, 2×$H_1$), 4.81–4.62 (m, 16H; 16×CH−Ph), 4.60–4.43 (m, 8H; 8×CH−Ph), 4.34–4.28 (m, 3H; 2×CH−Ph, $C_{1a}H_{glycerol}$), 4.28–4.21 (m, 2H; $C_{1b}H$, $C_{3a}H_{glycerol}$), 4.19 (t, $^3J$(H,H) = 3.6 Hz, 1H; $H_6$), 4.18–4.06 (m, 5H; $C_{1a}H$, $C_{3a}H$, $H_6$, 2×$H_2$), 4.04–3.94 (m, 7H; 2×$H_{3'}$, 2×$H_{5'}$, $C_{1b}H$, $C_{3b}H_{2\,glycerol}$), 3.92 (t, $^3J$(H,H) = 9.3 Hz, 1H; $H_4$), 3.88 (t, $^3J$(H,H) = 9.3 Hz, 1H; $H_3$), 3.83 (dd, $^3J(H_5,H_4)$ = 9.6 Hz, $^3J(H_5,H_6)$ = 3.1 Hz, 1H; $H_5$), 3.79–3.70 (m, 5H; $H_5$, $H_3$, $H_4$, 2×$H_{4'}$), 3.59 (dd, $^3J(H_{6a'},H_{6b'})$ = 11.0 Hz, $^3J(H_{6a'},H_{5'})$ = 2.9 Hz, $H_{6a'}$), 3.56 (dd, $^3J(H_{6a'},H_{6b'})$ = 10.6 Hz, $^3J(H_{6a'},H_{5'})$ = 2.9 Hz, 1H; $H_{6a'}$), 3.45 (app. d, $^3J(H_{6b'},H_{6a'})$ = 11.0 Hz, 1H; $H_{6b'}$), 3.42 (app. d, $^3J(H_{6b'},H_{6a'})$ = 10.6 Hz, 1H; $H_{6b'}$), 3.37 (dd, $^3J(H_{2'},H_{3'})$ = 10.1 Hz, $^3J(H_{2'},H_{1'})$ = 3.5 Hz, 1H; $H_{2'}$), 3.34 (dd, $^3J(H_{2'},H_{3'})$ = 10.3 Hz, $^3J(H_{2'},H_{1'})$ = 3.5 Hz, 1H; $H_{2'}$), 2.30–2.13 (m, 8H; 4×$CH_2$CO), 1.61–1.48 (m, 8H; 4×C$H_2$CH$_2$CO), 1.32–1.18 (m, 80H; 40×$CH_2$), 0.86 ppm (t, $^3J$(H,H) = 7.1 Hz, 12H; 4×$CH_3$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 173.3$, 173.2, 173.0, 172.8 (4×CO), 138.97, 138.93, 138.49, 138.44, 138.29, 138.0, 135.7 (16C; Ph), 128.9–127.6 (80×CH; Ph), 94.4, 94.1 (2×$C_{1'}$), 82.0 ($C_3$, $C_4$), 80.1 (2×$C_{3'}$), 79.6 ($C_5$), 80.4 ($C_3$, 2×$C_{4'}$), 78.2 ($C_4$, $C_5$), 76.5, 76.2, (6×C$H_2$Ph), 74.4 ($C_6$), 74.2 (2×$C_2$), 73.9, 73.6, 73.1, 72.8 (8×C$H_2$Ph), 72.8 ($C_6$), 71.13 (2×$C_1$), 71.1 (2×$C_{5'}$), 70.0, 69.8 (2×d, $^3J$(H,H) = 5.8 Hz, 2×$C_2H_{glycerol}$), 69.5, 69,4 (d, $^3J$(H,H) = 7.7 Hz, 2×POC$H_2$Ph), 68.2 (2×$C_{6'}$), 66.0, 65.8 (2×d, $^3J$(H,H) = 4.8 Hz, 2×$C_3H_{2\,glycerol}$), 63.53, 63.31 (2×$C_{2'}$), 61.95, 61.92 (2×$C_1H_{2\,glycerol}$), 34.3, 34.2 34.13, 34.10 (4×C$H_2$CO), 32.1 (4×C$H_2$CH$_2$CH$_3$), 29.8–29.2 (32×$CH_2$), 25.0 (4×C$H_2$CH$_2$CO), 22.8 (4×CH$_2$C$H_2$CH$_3$), 14.3 ppm (4×$CH_3$); $^{31}$P NMR (202 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -1.56$, $-1.98$ ppm; FAB HRMS: $m/z$ calcd for $[C_{99}H_{128}N_3O_{17}P+Na]^+$: 1684.8879; found: 1684.9002.

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl-α-(1→2)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-benzylphosphatidyl)-3,4,5,6-tetra-*O*-benzyl-D-*chiro*-inositol (34)**: Compound **34** was obtained as a colorless syrup and as a mixture of two diastereomers (1:1, 86 mg, 0.052 mmol, 91 % with 8 % of starting material **32**) from **32** (70 mg, 0.070 mmol) by the procedure described for the preparation of **29**. The crude product was fractionated on PLC plates (*n*-hexane/AcOEt 4:1) previously treated with $Et_3N$ to give **34**. $[\alpha]_D^{20} = +42$ ($c = 0.9$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 3:1): 0.23; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.38$–$7.20$ (m, 80H; Ph), 5.22 (m, 1H; $C_{2a}H_{glycerol}$), 5.20, 5.15 (2×s, 2H; 2×$H_{1'}$), 5.14–5.05 (m, 3H; 2×CH−Ph, $C_{2b}H_{glycerol}$), 4.98 (m, 2H; 2×CH−Ph), 4.58 (d, $^3J$(H,H) = 11.7 Hz, 1H; CH−Ph), 4.55 (d, $^3J$(H,H) = 11.7 Hz, 1H; CH−Ph), 4.53 (d, $^3J$(H,H) = 11.4 Hz, 1H; CH−Ph), 4.96–4.73 (m, 12H; 10×CH−Ph, 2×$H_1$), 4.73–4.65 (m, 3H; 3×CH−Ph), 4.49–4.37 (m, 9H; 9×CH−Ph), 4.38–4.28 (m, 3H; 2×CH−Ph $C_{1a}H_{glycerol}$), 4.28–4.06 (m, 10H; CH−Ph, 2×$H_6$, $H_2$, 2×$H_{5'}$, $C_{1a}H$, $C_{1b}H$, $C_{3a}H_{2\,glycerol}$), 4.07–3.91 (m, 6H; $C_{1b}H$, $C_{3b}H_2$, $H_2$, 2×$H_4$), 3.87–3.68 (m, 10H; 2×$H_{2'}$, 2×$H_{3'}$, 2×$H_{4'}$, 2×$H_{5'}$, 2×$H_3$), 3.53–3.42 (m, 4H; 2×$H_{6a'}$, 2×$H_{6b'}$), 2.30–2.18 (m, 8H; 4×$CH_2$CO), 1.61–1.50 (m, 8H; 4×C$H_2$CH$_2$CO), 1.38–1.20 (m, 80H; 40×$CH_2$), 0.89 ppm (t, $^3J$(H,H) = 6.6 Hz, 12H; 4×$CH_3$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 173.30$, 173.25, 172.89, 172.83 (4×CO), 139.17, 139.12, 138.9, 138.6, 138.5, 138.35, 138.33, 138.02, 137.96, 137.8, 135.75, 135.70 (16C; Ph), 128.8–127.1 (80×CH; Ph), 94.6, 94.9 (2×$C_{1'}$), 82.3 (2×$C_4$), 80.9 (2×$C_5$), 79.9 (2×$C_3$), 77.7 (2×$C_{3'}$), 76.5, 76.08, 75.3 (9×C$H_2$Ph), 75.2, 74.8 (2×$C_2$), 73.7, 73.2 (4×C$H_2$Ph), 73.69 (2×$C_{4'}$), 72.67 (2×$C_6$), 72.4 (C$H_2$Ph), 72.02, 71.96 (2×$C_1$), 69.45, 69.39 (2×d, $^3J$(H,H) = 7.6 Hz; 2×POC$H_2$Ph), 69.6 (2×$C_{5'}$), 69.93, 69.75 (2×d, $^3J$(H,H) = 5.4 Hz; 2×$C_2H_{glycerol}$), 69.1 (2×$C_{6'}$), 65.9, 65.8 (2×d, $^3J$(H,H) = 4.6 Hz; 2×$C_3H_{2\,glycerol}$), 62.3, 62.1 (2×$C_1H_{2\,glycerol}$), 59.92, 59.76 (2×$C_{2'}$), 34.2, 34.1 (4×C$H_2$CO), 32.1 (4×C$H_2$CH$_2$CH$_3$), 29.8–29.2 (32×$CH_2$), 24.9 (4×C$H_2$CH$_2$CO), 23.4 (4×CH$_2$C$H_2$CH$_3$), 14.2 ppm (4×$CH_3$); $^{31}$P NMR (202 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -1.78$, $-2.21$ ppm; FAB HRMS: $m/z$ calcd for $[C_{99}H_{128}N_3O_{17}P+Na]^+$: 1684.8879; found: 1684.8856.

***O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-1-*O*-allyl-3,4,5-tri-*O*-benzyl-D-*myo*-inositol (36) and *O*-(2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2-*O*-allyl-3,4,5-tri-*O*-benzyl-D-*myo*-inositol (37)**: Dibutyltin oxide (30 mg, 0.121 1.2 equiv) was added to a solution of **35** (90 mg, 0.099 mmol, 1 equiv) in dry toluene (10 mL) and the mixture was heated at reflux overnight under a Dean–Stark apparatus. The reaction mixture was then evaporated to dryness and the residue was dissolved in AllBr (3 mL). Tetra-*n*-butylammonium iodide (TBAI) (41 mg, 0.109 mmol, 1.1 equiv) was added and the mixture was heated at reflux for 2 h. The mixture was treated with $NH_4OH$ (3.7 mL) in an ice/water bath, diluted with AcOEt, washed with brine (3×20 mL), and dried over $MgSO_4$. The crude product was purified by flash chromatography (*n*-hexane/AcOEt 6:1, 4:1, 2:1) to give **36** (54 mg, 0.057 mmol, 68 %) and **37** as syrups (19 mg, 0.020 mmol, 20 %).

*Data for **36***: $[\alpha]_D^{20} = +43$ ($c = 0.50$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 2:1): 0.27; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.40$–$7.05$ (m, 30H; Ph), 5.98 (ddd, $^3J$(H,H) = 16.5 Hz, $^3J$(H,H) = 10.5 Hz, $^3J$(H,H) = 6.0 Hz, 1H; C$H$=CH$_2$), 5.67 (d, $^3J$(H,H) = 3.5 Hz, 1H; $H_{1'}$), 5.30 (app. d, $^3J$(H,H) = 16.5 Hz, 1H; CH=C$H_2$), 5.22 (app. d, $^3J$(H,H) = 10.5 Hz, 1H; CH=C$H_2$), 4.99 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.97 (d, $^3J$(H,H) = 10.5 Hz, 1H; CH−Ph), 4.88 (s, 2H; $CH_2$Ph), 4.83 (d, $^3J$(H,H) = 10.5 Hz, 1H; CH−Ph), 4.75 (s, 2H; $CH_2$Ph), 4.72 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.67 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.53 (d, $^3J$(H,H) = 12.0 Hz, 1H; CH−Ph), 4.41 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.26 (d, $^3J$(H,H) = 12.0 Hz, 1H; CH−Ph), 4.23 (app. s, 1H; $H_2$), 4.21–4.01 (m, 5H; $H_4$, $H_{5'}$, $H_6$, C$H_2$−CH=CH$_2$), 3.94 (t, $^3J$(H,H) = 9.2 Hz, 1H; $H_{3'}$), 3.72 (t, $^3J$(H,H) = 9.2 Hz, 1H; $H_{4'}$), 3.48–3.38 (m, 3H; $H_1$, $H_3$, $H_5$), 3.32 (dd, $^3J(H_{2'},H_{3'})$ = 10.5 Hz, $^3J(H_{2'},H_{1'})$ = 3.5 Hz, 1H; $H_{2'}$), 3.24 (app. d, $^3J$(H,H) = 11.0 Hz, 1H; $H_{6a'}$), 3.16 (app. d, $^3J$(H,H) = 11.0 Hz, 1H; $H_{6b'}$), 2.41 ppm (s, 1H; $C_2$OH); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 138.7$, 138.6, 138.21, 138.18, 138.1, 138.0 (6C; Ph), 134.2 (C$H$=CH$_2$), 128.6–127.4 (30CH, Ph), 117.9 (CH=C$H_2$), 97.7 ($C_{1'}$), 81.6 ($C_4$), 81.3, 81.0, 80.3, 79.8 ($C_1$, $C_3$, $C_5$, $C_{3'}$), 78.4 ($C_{4'}$), 76.0, 75.9, 75.4, 75.0, 74.8, 73.5, 72.9 (6×C$H_2$Ph, $C_6$), 71.2 (C$H_2$−CH=CH$_2$), 67.8 ($C_{5'}$, $C_2$), 66.6 ($C_{6'}$), 63.6 ppm ($C_{2'}$); FAB HRMS: $m/z$ calcd for $[C_{57}H_{61}N_3O_{10}+Na]^+$: 970.4255; found: 970.4313.

*Data for **37***: $[\alpha]_D^{20} = +4.3$ ($c = 1.1$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 2:1): 0.38; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.37$–$7.04$ (m, 30H; Ph), 5.96 (ddd, $^3J$(H,H) = 17.0 Hz, $^3J$(H,H) = 11.0 Hz, $^3J$(H,H) = 6.0 Hz, 1H; C$H$=CH$_2$), 5.46 (d, $^3J$(H,H) = 3.5 Hz, 1H; $H_{1'}$), 5.30 (dd, $^3J$(H,H) = 17.0 Hz, $^3J$(H,H) = 1.5 Hz, CH=C$H_2$), 5.19 (app. d, $^3J$(H,H) = 11.0 Hz, 1H; CH=C$H_2$), 5.02 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.93 (d, $^3J$(H,H) = 10.5 Hz, 1H; CH−Ph), 4.88, 4.84 (AB, $^3J$(H,H) = 11.0 Hz, 2H; 2×CH−Ph), 4.78 (d, $^3J$(H,H) = 10.5 Hz, 1H; CH−Ph), 4.71 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.70 (s, 2H; $CH_2$Ph), 4.64 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.47 (d, $^3J$(H,H) = 11.8 Hz, 1H; CH−Ph), 4.47–4.40 (m, 1H; C$H_2$−CH=CH$_2$), 4.40 (d, $^3J$(H,H) = 11.0 Hz, 1H; CH−Ph), 4.24 (dd, $^3J$(H,H) = 12.5 Hz, $^3J$(H,H) = 6.0 Hz, C$H_2$−CH=CH$_2$), 4.15 (d, $^3J$(H,H) = 11.8 Hz, 1H; CH−Ph), 4.04 (t, $^3J$(H,H) = 9.5 Hz, 1H; $H_4$), 3.98–3.89 (m, 4H; $H_2$, $H_{3'}$, $H_{5'}$, $H_6$), 3.72 (t, $^3J$(H,H) = 9.5 Hz, 1H; $H_{4'}$), 3.60 (m, 1H; $H_1$), 3.50 (dd, $^3J(H_{2'},H_{3'})$ = 10.5 Hz, $^3J(H_{2'},H_{1'})$ = 3.5 Hz, 1H; $H_{2'}$), 3.44 (dd, $^3J(H_3,H_4)$ = 9.5 Hz, $^3J(H_3,H_2)$ = 2.0 Hz, 1H; $H_3$), 3.36 (t, $^3J$(H,H) = 9.5 Hz, 1H; $H_5$), 3.28 (d, $^3J$(H,H) = 6.0 Hz, 1H; $C_1$OH), 3.24 (dd, $^3J(H_{6a'},H_{6b'})$ = 11.0 Hz, $^3J(H_{6a'},H_{5'})$ = 2.5 Hz, 1H; $H_{6a'}$), 3.07 ppm (app. d, $^3J$(H,H) = 11.0 Hz, 1H; $H_{6b'}$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 138.7$, 138.6, 138.4, 138.2, 138.03, 137.99 (6C; Ph), 135.3 (C$H$=CH$_2$), 128.6–127.4 (30×CH; Ph), 117.2 (CH=C$H_2$), 98.5 ($C_{1'}$), 82.1 ($C_4$), 81.3 ($C_5$), 81.0 ($C_3$), 80.8, 80.5 ($C_6$, $C_{3'}$), 78.3 ($C_{4'}$), 76.8 ($C_2$), 75.9, 75.5, 75.3, 74.9 (4×C$H_2$Ph), 74.0 (C$H_2$−CH=CH$_2$), 73.6 ($C_1$), 73.5, 73.0 (2×C$H_2$Ph), 71.0 ($C_{5'}$), 67.7 ($C_{6'}$), 64.3 ppm ($C_{2'}$); FAB HRMS: $m/z$ calcd for $[C_{57}H_{61}N_3O_{10}+Na]^+$: 970.4255; found: 970.4276.

***O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (38)**: A mixture of compound

**23** (187 mg, 0.02 mmol) and NaH (66 mg, 1.67 mmol, 6 equiv) in dried DMF (11 mL) was stirred for 10 min under Ar. After the mixture had been cooled to −15 °C in an ice/salt bath, BnBr (265 μL, 2.23 mmol, 8 equiv) was added dropwise. The reaction mixture was stirred overnight, $NH_4OH$ was added, and the mixture was then washed successively with a saturated solution of $NH_4Cl$, $H_2O$, and brine. The organic layer was dried ($MgSO_4$) and concentrated, and the crude product was purified by flash chromatography (*n*-hexane/AcOEt 10:1, AcOEt) to provide **38** as a white foam (145 mg, 0.14 mmol, 68 %). $[\alpha]_D^{20} = +51$ ($c = 0.45$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 3:1): 0.49; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.48$–$7.05$ (m, 35H; Ph), 5.96 (ddd, $^3J(H,H) = 17.2$ Hz, $^3J(H,H) = 10.5$ Hz, $^3J(H,H) = 5.1$ Hz, 1H; C*H*=CH$_2$), 5.75 (d, $^3J(H,H) = 3.6$ Hz, 1H; $H_{1'}$), 5.30 (dd, $^3J(H,H) = 17.2$, $^3J(H,H) = 1.2$ Hz, 1H; CH=C*H*$_2$), 5.22 (app. d, $^3J(H,H) = 10.5$ Hz, CH=C*H*$_2$), 5.05 (d, $^3J(H,H) = 10.8$ Hz, 1H; CH−Ph), 5.00 (d, $^3J(H,H) = 10.5$ Hz, 1H; CH−Ph), 4.88 (2 AB, 4H; 2× $CH_2$Ph), 4.87 (m, 1H; CH−Ph), 4.84 (d, $^3J(H,H) = 10.5$ Hz, 1H; CH−Ph), 4.74 (d, $^3J(H,H) = 11.1$ Hz, 1H; CH−Ph), 4.71–4.62 (m, 4H; CH−Ph), 4.56 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.40 (d, $^3J(H,H) = 10.8$ Hz, 1H; CH−Ph), 4.26 (t, $^3J(H,H) = 9.6$ Hz, 1H; $H_6$), 4.24 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.16 (t, $^3J(H,H) = 9.6$ Hz, 1H; $H_4$), 4.10–4.00 (m, 4H; C$H_2$−CH=C$H_2$, $H_2$, $H_{5'}$) 3.97 (t, $^3J(H,H) = 9.8$ Hz, 1H; $H_{3'}$), 3.74 (t, $^3J(H,H) = 9.8$ Hz, 1H; $H_{4'}$), 3.48–3.30 (m, 3H; $H_1$, $H_3$, $H_5$), 3.33 (dd, $^3J(H_{2'},H_{3'}) = 9.8$ Hz, $^3J(H_{2'},H_{1'}) = 3.6$ Hz, 1H; $H_{2'}$), 3.24 (app. d, $^3J(H,H) = 9.8$ Hz, 1H; $H_{6a'}$), 3.12 ppm (dd, $^3J(H_{6b'},H_{6a'}) = 9.8$ Hz, $^3J(H_{6b'},H_{5'}) = 1.8$ Hz, 1H; $H_{6b'}$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 139.2$, 139.0, 138.6 (7C; Ph), 134.7 (*C*H=CH$_2$), 128.8–127.6 (35C; Ph), 117.3 (CH=*C*H$_2$), 98.1 ($C_{1'}$), 82.4 ($C_4$), 82.3, 81.7, 81.2 ($C_1$, $C_3$, $C_5$), 80.6 ($C_{3'}$), 78.6 ($C_{4'}$), 76.2, 76.0 (2× *C*H$_2$Ph), 75.8 ($C_6$), 75.7, 75.1, 74.5, 73.8, 73.3 (5× *C*H$_2$Ph), 73.2, 71.3, 70.4 ($C_2$, $C_{5'}$, *C*H$_2$−CH=CH$_2$), 68.0 ($C_{6'}$), 63.9 ppm ($C_{2'}$); FAB HRMS: *m*/*z* calcd for $[C_{64}H_{67}N_3O_{10}+Na]^+$: 1060.4724; found: 1060.4791.

***O*-(2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (39)**:[34] Compound **39** (41 mg, 0.041 mmol, 72 %) was obtained as a colorless syrup from **38** (59 mg, 0.057 mmol) by the same experimental procedure as that used for the preparation of **27**. $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.45$–$7.05$ (m, 35H; Ph), 5.45 (d, $^3J(H,H) = 3.0$ Hz, 1H; $H_{1'}$), 5.03 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.99 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.96 (d, $^3J(H,H) = 10.5$ Hz, 1H; CH−Ph), 4.87 (AB, 2H; $CH_2$Ph), 4.80 (d, $^3J(H,H) = 10.5$ Hz, 1H; CH−Ph), 4.77 (d, $^3J(H,H) = 11.5$ Hz, 1H; CH−Ph), 4.74 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.70 (s, 2H; $CH_2$Ph), 4.64 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.46 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.41 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.14 (d, $^3J(H,H) = 12.0$ Hz, 1H; CH−Ph), 4.10 (t, $^3J(H,H) = 9.1$ Hz, 1H; $H_4$), 4.01 (s, 1H; $H_2$), 4.03–3.91 (m, 3H; $H_6$, $H_{3'}$, $H_{5'}$), 3.73 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_{4'}$), 3.66 (m, 1H; $H_1$), 3.50 (m, 2H; $H_{2'}$, $H_3$), 3.38 (t, 1H; $^3J(H,H) = 9.1$ Hz, 1H; $H_5$), 3.22 (m, 2H; $C_1$OH, $H_{6a'}$), 3.06 ppm (app. d, $^3J(H,H) = 11.0$ Hz, 1H; $H_{6b'}$).

**2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl-α-(1→6)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-benzylphosphatidyl)-1,4,5,6-tetra-*O*-benzyl-D-*myo*-inositol (40)**: Compound **40** was obtained as a colorless syrup and as a mixture of two diastereomers (1:1, 31 mg, 0.0188 mmol, 82 %) from **39** (23 mg, 0.023 mmol) by the procedure described for the preparation of **29**. The crude product was fractionated on PLC plates (*n*-hexane/AcOEt 3:1) previously treated with $Et_3N$ to give **40**. $[\alpha]_D^{20} = +37$ ($c = 0.31$ in $CHCl_3$); $R_f$ (*n*-hexane/AcOEt 2:1): 0.54; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.43$–$7.01$ (m, 80H; Ph), 5.45 (d, $^3J(H,H) = 3.5$ Hz, 1H; $H_{1'}$), 5.42 (d, $^3J(H,H) = 3.5$ Hz, 1H; $H_{1'}$), 5.24 (m, 1H; $C_{2a}H_{glycerol}$), 5.22–5.15 (m, 2H; 2×CH−Ph), 5.11–4.97 (m, 6H; $C_{2b}H_{glycerol}$, 5× CH−Ph), 4.94 (d, $^3J(H,H) = 10.5$ Hz, 1H; CH−Ph), 4.93 (d, $^3J(H,H) = 10.5$ Hz, 2H; 2×CH−Ph), 4.87 (AB, 2H; $CH_2$Ph), 4.86 (AB, 2H; $CH_2$Ph), 4.77 (app. d, $^3J(H,H) = 10.5$ Hz, 3H; 3×CH−Ph), 4.74–4.59 (m, 7H; 7×CH−Ph), 4.51 (app. d, $^3J(H,H) = 12.0$ Hz, 2H; 2×CH−Ph), 4.47 (br t, $^3J(H,H) = 2.0$ Hz, 1H; $H_2$), 4.48 (br t, $^3J(H,H) = 2.0$ Hz, 1H; $H_2$), 4.45–4.41 (m, 1H; $H_1$), 4.370 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.367 (d, $^3J(H,H) = 11.0$ Hz, 1H; CH−Ph), 4.34–4.27 (m, 4H; $H_1$, 2×$H_6$, $C_{1a}H_{glycerol}$), 4.21 (app. d, $^3J(H,H) = 12.0$ Hz, 2H; 2×CH−Ph), 4.23–4.12 (m, 4H; $C_{3a}H_2$, $C_{1a}H$, $C_{1b}H_{glycerol}$), 4.10 (t, $^3J(H,H) = 10.0$ Hz, 2H; 2×$H_4$), 4.06–4.00 (m, 5H; $C_{3b}H_{2\,glycerol}$, POCH−Ph, 2×$H_{5'}$), 3.98–3.92 (m, 4H; 2×$H_{3'}$, POCH−Ph, $C_{1b}H_{glycerol}$), 3.70 (m, 2H; 2×$H_{4'}$), 3.52 (dd, $^3J(H_3,H_4) = 10.0$ Hz, $^3J(H_3,H_2) = 2.0$ Hz, 1H; $H_3$), 3.47 (dd, $^3J(H_3,H_4) = 10.0$ Hz, $^3J(H_3,H_2) = 2.0$ Hz, 1H; $H_3$), 3.42, 3.40 (2× t, $^3J(H,H) = 10.0$ Hz, 2H; 2× $H_5$), 3.26–3.18 (m, 4H; 2×$H_{2'}$, 2×$H_{6a'}$), 3.11 (dt, $^3J(H_{6b'},H_{6a'}) = 11.0$ Hz, $^3J(H_{6b'},H_{5'}) = 2.5$ Hz, 2H; 2×$H_{6b'}$), 2.30–2.21 (m, 8H; 4×$CH_2$CO), 1.65–1.50 (m, 8H; 4×$CH_2CH_2$CO), 1.34–1.20 (m, 80H; 40×$CH_2$), 0.89 ppm (t, $^3J(H,H) = 7.0$ Hz, 12H; 4×$CH_3$); $^{13}$C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 173.3$, 173.2, 173.0, 172.8 (4×CO), 139.0, 138.6, 138.2, 138.0 (16C; Ph), 129.0–127.5 (80×CH; Ph), 98.0, 97.9 (2×$C_{1'}$), 81.7 (2×$C_4$), 80.8 (2× $C_3$, 2×$C_5$), 80.7, 80.2 (2×$C_1$, 2×$C_6$), 79.9, 79.8 (2×$C_{3'}$), 78.3 (2×$C_{4'}$), 75.6 (2×$C_2$), 76.0–72.9 (14×*C*H$_2$Ph), 70.5 (2×$C_{5'}$), 70.2, 69.8 (2× d, $^3J(H,H) = 5.4$ Hz, 2×$C_2H_{glycerol}$,), 69.6, 69.4 (2× d, $^3J(H,H) = 7.8$ Hz, 2×PO*C*H$_2$Ph), 67.7 (2×$C_{6'}$), 66.1, 65.7 (2× d, $^3J(H,H) = 5.0$ Hz; 2×$C_3H_{2\,glycerol}$), 63.2 (2× $C_{2'}$), 61.7, 61.6 (2×$C_1H_{2\,glycerol}$), 34.3, 34.2, 34.14, 34.09 (4×*C*H$_2$CO), 32.1 (4×*C*H$_2$CH$_2$CH$_3$), 29.8–29.2 (32×$CH_2$), 25.0 (4×*C*H$_2$CH$_2$CO), 22.8 (4× $CH_2$*C*H$_2$CH$_3$), 14.3 ppm (4×$CH_3$); $^{31}$P NMR (202 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.59$, $-2.77$ ppm; elemental analysis calcd (%) for $C_{99}H_{128}N_3O_{17}P \cdot H_2O$: C 70.73, H 7.80, N 2.50; found: C 71.00, H 7.90, N 2.87; FAB HRMS: *m*/*z* calcd for $[C_{99}H_{128}N_3O_{17}P+Na]^+$: 1684.8879; found: 1684.8352.

**2-Amino-2-deoxy-D-glucopyranosyl-α-(1→6)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-phosphatidyl)-D-*myo*-inositol (7)**:[23b] A suspension of **21** (12 mg, 0.007 mmol) in an AcOEt/THF/EtOH/$H_2O$ mixture (2:1:1:0.1, 3.5 mL) was stirred for 16 h under $H_2$ in the presence of Pd on charcoal (10 %, 22 mg, 0.021 mmol) as catalyst. The reaction mixture was filtered over celite, washed with MeOH (10 mL), and carefully neutralized with a solution of NaOH in MeOH (0.1 %). The slurry was evaporated to dryness and the residue was purified on Sephadex LH-20 in MeOH to give **7** (6 mg, 0.007 mmol, 98 %) as a white dust. $R_f$ (*t*BuOH/EtOH/aqueous $NH_3$ 30 %/$H_2O$ 4:2:0.5:1): 0.19. NMR experiments were performed at pH 7.6; $^1$H NMR (500 MHz, [D$_4$]MeOH, 25 °C, TMS): $\delta = 5.50$ (d, $^3J(H,H) = 4.0$ Hz, 1H; $H_{1'}$), 5.25 (m, 1H; $C_2H_{glycerol}$), 4.45 (dd, $^3J(H,H) = 12.0$ Hz, $^3J(H,H) = 3.0$ Hz, 1H; $C_1H_{glycerol}$), 4.20 (dd, $^3J(H,H) = 12.0$ Hz, $^3J(H,H) = 6.5$ Hz, 1H; $C_1H_{glycerol}$), 4.17–4.11 (m, 2H; $H_1$, $H_{5'}$), 4.09 (t, $^3J(H,H) = 2.5$ Hz, 1H; $H_2$), 4.04 (m, 2H; $C_3H_{2\,glycerol}$), 3.97 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_6$), 3.82 (dd, $^3J(H_{6a'},H_{6b'}) = 11.5$ Hz, $^3J(H_{6a'},H_{5'}) = 2.5$ Hz, 1H; $H_{6a'}$), 3.80 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_{3'}$), 3.71 (dd, $^3J(H_{6b'},H_{6a'}) = 11.5$ Hz, $^3J(H_{6b'},H_{5'}) = 4.5$ Hz, 1H; $H_{6b'}$), 3.67 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_4$), 3.40 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_{4'}$), 3.37 (dd, $^3J(H_3,H_4) = 9.5$ Hz, $^3J(H_3,H_2) = 2.5$ Hz, 1H; $H_3$), 3.28 (t, $^3J(H,H) = 9.5$ Hz, 1H; $H_5$), 3.08 (dd, $^3J(H_{2'},H_{3'}) = 9.5$ Hz, $^3J(H_{2'},H_{1'}) = 4.0$ Hz, 1H; $H_{2'}$), 2.34 (m, 4H; 2×$CH_2$CO), 1.60 (m, 4H; 2×*C*H$_2$CH$_2$CO), 1.30 (app. s, 40H; 20×$CH_2$), 0.90 ppm (t, $^3J(H,H) = 7.0$ Hz, 6H; 2×$CH_3$); $^{13}$C NMR and HMQC (125 and 500 MHz, [D$_4$]MeOH, 25 °C, TMS): $\delta = 97.2$ ($C_{1'}$), 79.4 ($C_6$), 78.4 ($C_1$), 74.9 ($C_5$), 74.2 ($C_4$), 73.5 ($C_{5'}$), 73.4 ($C_2$), 72.5 ($C_3$), 72.0 ($C_{3'}$), 71.9 ($C_2H_{glycerol}$), 71.5 ($C_{4'}$), 65.0 ($C_3H_{2\,glycerol}$), 62.5 ($C_1H_{2\,glycerol}$), 62.1 ($C_{6'}$), 56.2 ($C_{2'}$), 35.1, 35.0 (2×*C*H$_2$CO), 33.1 (2×*C*H$_2$CH$_2$CH$_3$), 30.8–30.2 (16×$CH_2$), 26.0 (2× *C*H$_2$CH$_2$CO), 23.8 (2×*C*H$_2$CH$_2$CH$_3$), 14.4 ppm (2×$CH_3$); $^{31}$P NMR (202 MHz, [D$_4$]MeOD, 25 °C, TMS): $\delta = -0.58$ ppm.

**2-Amino-2-deoxy-D-glucopyranosyl-α-(1→3)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-phosphatidyl)-L-*chiro*-inositol (9)**: Compound **9** (12 mg, 0.0131 mmol, 98 %) was obtained as a white dust from **29** (23 mg, 0.0138 mmol) by the procedure described for the preparation of **7**. Purification was on Sephadex LH-20 in MeOH/$CH_2Cl_2$ (9:1). $[\alpha]_D^{20} = +13$ ($c = 0.19$ in MeOH); $R_f$ (*t*BuOH/EtOH/aqueous $NH_3$ 30 %/$H_2O$ 4:2:0.5:1): 0.30. NMR experiments were performed at pH 7.6; $^1$H NMR (500 MHz, [D$_4$]MeOH, 25 °C, TMS): $\delta = 5.32$ (d, $^3J(H,H) = 3.5$ Hz, 1H; $H_{1'}$), 5.24 (ddd, $^3J(H,H) = 6.5$ Hz, $^3J(H,H) = 5.5$ Hz, $^3J(H,H) = 3.5$ Hz, 1H; $C_2H_{glycerol}$), 4.46 (dd, $^3J(H,H) = 12.0$ Hz, $^3J(H,H) = 3.5$ Hz, 1H; $C_1H_{glycerol}$), 4.42 (ddd, $^3J(H_1,HP) = 8.5$ Hz, $^3J(H_1,H_2) = 3.5$ Hz, $^3J(H_1,H_6) = 2.5$ Hz, 1H; $H_1$), 4.20 (dd, $^3J(H,H) = 12.0$ Hz, $^3J(H,H) = 6.5$ Hz, 1H; $C_1H_{glycerol}$), 4.06 (ddd, $^3J(H,H) = 11.0$ Hz, $^3J(H,H) = 5.5$ Hz, $^3J(H,H) = 5.5$ Hz, 1H; $C_3H_{glycerol}$), 4.03 (ddd, $^3J(H_{5'},H_4) = 9.5$ Hz, $^3J(H_{5'},H_{6b'}) = 5.0$ Hz, $^3J(H_{5'},H_{6a'}) = 2.5$ Hz, 1H; $H_{5'}$), 4.05 (m, 1H; $H_6$), 4.00 (ddd, $^3J(H,H) = 11.0$ Hz, $^3J(H,H) = 5.5$ Hz, $^3J(H,H) = 5.5$ Hz, 1H; $C_3H_{glycerol}$), 3.96 (dd, $^3J(H_2,H_3) = 9.0$ Hz, $^3J(H_2,H_1) = 3.5$ Hz, 1H; $H_2$), 3.82 (dd, $^3J(H_{6a'},H_{6b'}) = 12.0$ Hz, $^3J(H_{6a'},H_{5'}) = 2.5$ Hz, 1H; $H_{6a'}$), 3.78 (dd, $^3J(H_{3'},H_{2'}) = 10.5$ Hz, $^3J(H_{3'},H_{4'}) = 9.5$ Hz, 1H; $H_{3'}$), 3.73 (dd, $^3J(H_{6b'},H_{6a'}) = 12.0$ Hz, $^3J(H_{6b'},H_{5'}) = 5.0$ Hz, 1H; $H_{6b'}$), 3.72 (dd, $^3J(H_5,H_4) = 9.0$ Hz, $^3J(H_5,H6) = 4.0$ Hz, 1H; $H_5$), 3.67 (t, $^3J(H,H) = 9.0$ Hz, 1H; $H_3$), 3.59 (t, $^3J(H,H) = 9.0$ Hz, 1H; $H_4$), 3.41 (t, $^3J(H,H) = 9.5$ Hz,

1H; $H_{4'}$), 3.07 (dd, $^3J(H_{2'},H_{3'})=10.5$ Hz, $^3J(H_{2'},H_{1'})=3.5$ Hz, 1H; $H_{2'}$), 2.36 (t, $^3J(H,H)=7.5$ Hz, 4H; $CH_2CO$), 2.33 (t, $^3J(H,H)=7.5$ Hz, 4H; 2× $CH_2CO$), 1.58 (m, 4H; 2×$CH_2CH_2CO$), 1.29 (app.s, 40H; 20×$CH_2$), 0.90 ppm (t, $^3J(H,H)=6.5$ Hz, 6H; 2×$CH_3$); $^{13}C$ NMR and HMQC (125 and 500 MHz, [D$_4$]MeOH, 25°C, TMS): $\delta=98.2$ ($C_{1'}$), 83.5 ($C_3$), 76.8 ($C_1$), 73.0 ($C_{5'}$), 72.1 ($C_4$), 71.7 ($C_5$), 71.3 ($C_2$, $C_6$), 71.0 ($C_{3'}$), 70.8 ($C_2H_{glycerol}$), 70.4 ($C_{4'}$), 63.7 ($C_3H_{2\,glycerol}$), 62.4 ($C_1H_{2\,glycerol}$), 60.6 ($C_{6'}$), 55.5 ($C_{2'}$), 36.0, 35.8 (2×$C$H$_2$CO), 34.0 (2×$C$H$_2$CH$_2$CH$_3$), 31.7–31.1 (16×$CH_2$), 26.9 (2×$C$H$_2$CH$_2$CO), 24.6 (2×CH$_2$$C$H$_2$CH$_3$), 15.4 ppm (2×$CH_3$); $^{31}P$ NMR (121 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=-0.09$ ppm; FAB HRMS: $m/z$ calcd for $[C_{43}H_{82}NO_{17}P+Na]^+$: 938.5218; found: 938.5239.

**2-Amino-2-deoxy-D-galactopyranosyl-α-(1→3)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-phosphatidyl)-L-*chiro*-inositol (10)**: Compound **10** (9 mg, 0.01 mmol, 98%) was obtained as a white dust from **30** (16 mg, 0.01 mmol) by the procedure described for compound **7**. Compound **10** was purified on Sephadex LH-20 in MeOH. $[\alpha]_D^{20}=-32$ ($c=0.03$ in MeOH); $R_f$ (*n*BuOH/EtOH/aqueous $NH_3$ (30%)/$H_2O$ 2:2:1:3): 0.62. NMR experiments were performed at pH 6.7; $^1H$ NMR (500 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=5.28$ (d, $^3J(H,H)=3.5$ Hz, 1H; $H_{1'}$), 5.24 (m, 1H; $C_2H_{glycerol}$), 4.46 (dd, $^3J(H,H)=12.0$ Hz, $^3J(H,H)=3.5$ Hz, 1H; $C_1H_{glycerol}$), 4.40 (ddd, $^3J(H_1,HP)=8.5$ Hz, $^3J(H_1,H_6)=^3J(H_1,H_2)=4.5$ Hz, 1H; $H_1$), 4.24 (t, $^3J(H,H)=6.0$ Hz, 1H; $H_{5'}$), 4.20 (dd, $^3J(H,H)=12.0$ Hz, $^3J(H,H)=6.0$ Hz, 1H; $C_1H_{glycerol}$), 4.07 (m, 1H; $C_3H_{glycerol}$), 4.06 (t, $^3J(H,H)=4.5$ Hz, 1H; $H_6$), 4.00 (dd, $^3J(H,H)=11.0$ Hz, $^3J(H,H)=5.5$ Hz, 1H; $C_3H_{glycerol}$), 3.96 (app.d, $^3J(H,H)=9.5$ Hz, 1H; $H_2$), 3.90 (d, $^3J(H,H)=3.5$ Hz, 1H; $H_{4'}$), 3.82 (app.dd, $^3J(H_{3'},H_{2'})=10.5$ Hz, $^3J(H_{3'},H_{4'})=3.5$ Hz, 1H; $H_{3'}$), 3.77–3.70 (m, 3H; $H_5$, $H_{6a'}$, $H_{6b'}$), 3.67 (t, $^3J(H,H)=9.5$ Hz, 1H; $H_3$), 3.59 (t, $^3J(H,H)=9.5$ Hz, 1H; $H_4$), 3.26 (m, 1H; $H_{2'}$), 2.35 (t, $^3J(H,H)=7.5$ Hz, 2H; $CH_2CO$), 2.32 (t, $^3J(H,H)=7.5$ Hz, 2H; $CH_2CO$), 1.60 (m, 4H; 2×$CH_2CH_2CO$), 1.29 (app.s, 40H; 20×$CH_2$), 0.90 ppm (t, $^3J(H,H)=6.5$ Hz, 6H; 2×$CH_3$); HMQC (500 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=100.8$ ($C_{1'}$), 84.0 ($C_3$), 77.7 ($C_1$), 74.2 ($C_6$), 73.2 ($C_4$), 72.5 ($C_{5'}$), 72.0 ($C_2$, $C_5$), 71.6 ($C_2H_{glycerol}$), 70.5 ($C_{3'}$), 70.0 ($C_{4'}$), 64.9 ($C_3H_{2\,glycerol}$), 63.5 ($C_1H_{2\,glycerol}$), 62.5 ($C_{6'}$), 49.0 ($C_{2'}$), 34.8 (2×$C$H$_2$CO), 31.5–29.6 (18×$CH_2$), 26.0 (2×$C$H$_2$CH$_2$CO), 23.2 (2×CH$_2$$C$H$_2$CH$_3$), 14.4 ppm (2×$CH_3$); $^{31}P$ NMR (202 MHz,[D$_4$]MeOD, 25°C, TMS): $\delta=-0.32$ ppm; FAB HRMS: $m/z$ calcd for $[C_{43}H_{82}NO_{17}P+Na]^+$: 938.5218; found: 938.5232.

**2-Amino-2-deoxy-D-glucopyranosyl-α-(1→3)-2-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-phosphatidyl)-L-*chiro*-inositol (3)**: Compound **10** (7 mg, 0.0079 mmol, 69%) was obtained as a white dust from **21** (19 mg, 0.0114 mmol) by the procedure described for compound **7**. Compound **3** was purified on Sephadex LH-20 in MeOH. $[\alpha]_D^{20}=-21$ ($c=1.15$ in MeOH); $R_f$ (*t*BuOH/EtOH/aqueous $NH_3$ (30%)/$H_2O$ 4:2:0.5:1): 0.44. NMR experiments were performed at pH 7.7; $^1H$ NMR (500 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=5.51$ (d, $^3J(H,H)=3.2$ Hz, 1H; $H_{1'}$), 5.26 (m, 1H; $C_2H_{glycerol}$), 4.55 (td, $^3J(H_2,HP)=^3J(H_2,H_3)=9.0$ Hz, $^3J(H_2,H_1)=2.5$ Hz, 1H; $H_2$), 4.47 (dd, $^3J(H,H)=12.5$ Hz, $^3J(H,H)=3.5$ Hz, 1H; $C_1H_{glycerol}$), 4.21 (dd, $^3J(H,H)=12.0$ Hz, $^3J(H,H)=6.5$ Hz, 1H; $C_1H_{glycerol}$), 4.15 (m, 1H; $H_{5'}$), 4.098 (t, $^3J(H,H)=3.0$ Hz, 1H; $H_1$), 4.08, 4.06 (2×m, 2H; $C_3H_{2\,glycerol}$), 3.94 (t, $^3J(H,H)=3.5$ Hz, 1H; $H_6$), 3.91 (t, $^3J(H,H)=9.0$ Hz, 1H; $H_3$), 3.85 (app.d, $^3J(H,H)=11.5$ Hz, 1H; $H_{6a'}$), 3.82 (t, $^3J(H,H)=10.5$ Hz, 1H; $H_{3'}$), 3.76 (dd, $^3J(H_5,H_4)=9.5$ Hz, $^3J(H,H)=3.5$ Hz, 1H; $H_5$), 3.72 (dd, $^3J(H_{6b'},H_{6a'})=11.5$ Hz, $^3J(H_{6b'},H_{5'})=4.5$ Hz, 1H; $H_{6b'}$), 3.67 (t, $^3J(H,H)=9.0$ Hz, 1H; $H_4$), 3.41 (t, $^3J(H,H)=9.5$ Hz, 1H; $H_{4'}$), 3.07 (dd, $^3J(H_{2'},H_{3'})=10.5$ Hz, $^3J(H_{2'},H_{1'})=3.2$ Hz, 1H; $H_{2'}$), 2.37 (t, $^3J(H,H)=7.5$ Hz, 2H; $CH_2CO$), 2.34 (t, $^3J(H,H)=7.5$ Hz, 2H; 2×$CH_2CO$), 1.62 (m, 4H; 2×$C$H$_2$CH$_2$CO), 1.29 (app.s, 40H; 20×$CH_2$), 0.92 ppm (t, $^3J(H,H)=6.5$ Hz, 6H; 2×$CH_3$); HMQC (500 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=99.0$ ($C_{1'}$), 80.9 ($C_3$), 78.0 ($C_2$), 74.1 ($C_1$), 73.7 ($C_5$), 73.0 ($C_6$), 72.9 ($C_{5'}$), 72.3 ($C_{3'}$), 71.84 ($C_2H_{glycerol}$), 71.80 ($C_{4'}$), 71.5 ($C_4$), 65.0 ($C_1H_{2\,glycerol}$), 63.7 ($C_3H_{2\,glycerol}$), 62.4 ($C_{6'}$), 56.5 ($C_{2'}$), 34.9 (2×$C$H$_2$CO), 33.0 (2×$C$H$_2$CH$_2$CH$_3$), 31.8–29.2 (16×$CH_2$), 26.0 (2×$C$H$_2$CH$_2$CO), 23.6 (2×CH$_2$$C$H$_2$CH$_3$), 14.4 ppm (2×$CH_3$); $^{31}P$ NMR (121 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=-0.74$ ppm; FAB HRMS: $m/z$ calcd for $[C_{43}H_{82}NO_{17}P+Na]^+$: 938.5218; found: 938.5155.

**2-Amino-2-deoxy-D-galactopyranosyl-α-(1→3)-2-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-phosphatidyl)-L-*chiro*-inositol (4)**: Compound **4** (5 mg, 0.0057 mmol, 94%) was obtained as a white dust from **22** (10 mg, 0.006 mmol) by the procedure described for compound **7**. Compound **4** was purified on Sephadex LH-20 in MeOH. $[\alpha]_D^{20}=+18$ ($c=0.12$ in $CHCl_3$); $R_f$ (*t*BuOH/EtOH/aqueous $NH_3$ (30%)/$H_2O$ 4:2:0.5:1): 0.25. NMR experiments were performed at pH 6.5; $^1H$ NMR ([D$_4$]methanol, 500 MHz): $\delta=5.47$ (d, $^3J(H,H)=4.0$ Hz, 1H; $H_{1'}$), 5.18 (m, 1H; $C_2H_{glycerol}$), 4.46 (td, $^3J(H_2,HP)=^3J(H_2,H_3)=9.5$ Hz, $^3J(H_2,H_1)=3.0$ Hz, 1H; $H_2$), 4.39 (dd, $^3J(H,H)=12.0$ Hz, $^3J(H,H)=3.0$ Hz, 1H; $C_1H_{glycerol}$), 4.29 (app.t, $^3J(H,H)=6.0$ Hz, 1H; $H_{5'}$), 4.13 (dd, $^3J(H,H)=12.0$ Hz, $^3J(H,H)=6.5$ Hz, 1H; $C_1H_{glycerol}$), 4.00 (t, $^3J(H,H)=4.0$ Hz, 1H; $H_1$), 3.99, 4.06 (2×t, $^3J(H,H)=5.5$ Hz, 2H; 2×$C_3H_{glycerol}$), 3.92 (dd, $^3J(H,H)=10.5$ Hz, $^3J(H,H)=3.0$ Hz, 1H; $H_{3'}$), 3.85 (m, 2H; $H_{4'}$, $H_6$), 3.84 (t, $^3J(H,H)=9.5$ Hz, 1H; $H_3$), 3.72–3.57 (m, 4H; $H_4$, $H_5$, $H_{6a'}$, $H_{6b'}$), 3.35 (dd, $^3J(H_{2'},H_{3'})=11.0$ Hz, $^3J(H_{2'},H_{1'})=4.0$ Hz, 1H; $H_{2'}$), 2.28 (t, $^3J(H,H)=7.0$ Hz, 2H; $CH_2CO$), 2.24 (t, $^3J(H,H)=7.5$ Hz, 2H; $CH_2CO$), 1.54 (m, 4H; 2×$CH_2CH_2CO$), 1.23 (app.s, 40H; 20×$CH_2$), 0.84 ppm (t, $^3J(H,H)=6.5$ Hz, 6H; 2×$CH_3$); HMQC (500 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=96.4$ ($C_{1'}$), 79.2 ($C_3$), 77.4 ($C_2$), 72.8 ($C_4$), 72.38 ($C_6$), 72.35 ($C_1$), 71.7 ($C_{5'}$), 71.6 ($C_5$), 71.2 ($C_2H_{glycerol}$), 69.3 ($C_{4'}$), 68.1 ($C_{3'}$), 64.3 ($C_1H_{2\,glycerol}$), 63.0 ($C_3H_{2\,glycerol}$), 61.7 ($C_{6'}$), 51.9 ($C_{2'}$), 34.3 (2×$C$H$_2$CO), 32.8 (2×$C$H$_2$CH$_2$CH$_3$), 29.1–31.4 (16×$CH_2$), 25.4 (2×$C$H$_2$CH$_2$CO), 23.2 (2×CH$_2$$C$H$_2$CH$_3$), 13.8 ppm (2×$CH_3$); $^{31}P$ NMR (121 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=-0.42$ ppm; FAB HRMS: $m/z$ calcd for $[C_{43}H_{82}NO_{17}P+Na]^+$: 938.5218; found: 938.5164.

**2-Amino-2-deoxy-D-glucopyranosyl-α-(1→2)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-phosphatidyl)-D-*chiro*-inositol (5)**: Compound **5** (7 mg, 0.0076 mmol, 42%) was obtained as a white dust from **33** (10 mg, 0.006 mmol) by the procedure described for compound **7**. Compound **5** was purified on Sephadex LH-20 in MeOH. $[\alpha]_D^{20}=-64$ ($c=0.02$ in MeOH); $R_f$ (*t*BuOH/EtOH/aqueous $NH_3$ (30%)/$H_2O$ 4:2:0.5:1): 0.13. NMR experiments were performed at pH 6.8; $^1H$ NMR (500 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=5.33$ (d, $^3J(H,H)=4.0$ Hz, 1H; $H_{1'}$), 5.24 (m, 1H; $C_2H_{glycerol}$), 4.57 (m, 1H; $H_1$), 4.43 (dd, $^3J(H,H)=11.9$ Hz, $^3J(H,H)=3.2$ Hz, 1H; $C_1H_{glycerol}$), 4.18 (dd, $^3J(H,H)=12.1$ Hz, $^3J(H,H)=6.9$ Hz, 1H; $C_1H_{glycerol}$), 4.05 (t, $^3J(H,H)=3.7$ Hz, 1H; $H_6$), 4.04–3.93 (m, 4H; $H_2$, $H_{5'}$, $C_3H_{2\,glycerol}$), 3.90 (t, $^3J(H,H)=9.8$ Hz, $H_3$), 3.82 (dd, $^3J(H_{6a'},H_{6b'})=12.1$ Hz, $^3J(H_{6a'},H_{5'})=2.3$ Hz, 1H; $H_{6a'}$), 3.75–3.69 (m, 2H; $H_5$, $H_{6b'}$), 3.67 (t, $^3J(H,H)=9.5$ Hz, 1H; $H_3$), 3.60 (t, $^3J(H,H)=9.5$ Hz, 1H; $H_4$), 3.40 (t, $^3J(H,H)=9.8$ Hz, 1H; $H_{4'}$), 3.12 (dd, $^3J(H_{2'},H_{3'})=9.8$ Hz, $^3J(H_{2'},H_{1'})=4.0$ Hz, 1H; $H_{2'}$), 2.36 (t, $^3J(H,H)=7.3$ Hz, 2H; $CH_2CO$), 2.33 (t, $^3J(H,H)=7.3$ Hz, 2H; $CH_2CO$), 1.61 (m, 4H; 2×$CH_2CH_2CO$), 1.29 (m, 40H; 20×$CH_2$), 0.90 ppm (t, $^3J(H,H)=7.0$ Hz, 6H; 2×$CH_3$); HSQC (500 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=93.3$ ($C_{1'}$), 75.3 ($C_2$), 74.4 ($C_4$), 73.5 ($C_{5'}$), 72.8 ($C_3$), 72.3 ($C_1$), 72.0 ($C_5$), 71.9 ($C_6$), 71.8 ($C_{3'}$), 71.6 ($C_2H_{glycerol}$), 71.3 ($C_{4'}$), 64.8 ($C_1H_{2\,glycerol}$), 63.3 ($C_3H_{2\,glycerol}$), 61.8 ($C_{6'}$), 55.1 ($C_{2'}$), 34.8 (2×$C$H$_2$CO), 32.9 (2×$C$H$_2$CH$_2$CH$_3$), 29.7–31.0 (16×$CH_2$), 25.8 (2×$C$H$_2$CH$_2$CO), 23.5 (2×CH$_2$$C$H$_2$CH$_3$), 14.3 ppm (2×$CH_3$); $^{31}P$ NMR (202 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=-0.09$ ppm; FAB HRMS: $m/z$ calcd for $[C_{43}H_{82}NO_{17}P+Na]^+$: 938.5218; found: 938.5159.

**2-Amino-2-deoxy-D-galactopyranosyl-α-(1→2)-1-*O*-(1′,2′-di-*O*-myristoyl-*sn*-glycero-3′-(*R*,*S*)-phosphatidyl)-D-*chiro*-inositol (6)**[23b]: Compound **6** (8 mg, 0.0082 mmol, 37%) was obtained as a white dust from **31** (37 mg, 0.022 mmol) by the procedure described for compound **7**. Compound **6** was purified on Sephadex LH-20 in MeOH. NMR experiments were performed at pH 6.3; $[\alpha]_D^{20}=+35$ ($c=0.24$ in MeOH); $R_f$ (*t*BuOH/EtOH/aqueous $NH_3$ (30%)/$H_2O$ 4:2:0.5:1): 0.07; $^1H$ NMR (500 MHz, [D4]MeOD, 25°C, TMS): $\delta=5.36$ (d, $^3J(H,H)=4.0$ Hz, 1H; $H_{1'}$), 5.25 (m, 1H; $C_2H_{glycerol}$), 4.59 (m, 1H; $H_1$), 4.45 (dd, $^3J(H,H)=12.0$ Hz, $^3J(H,H)=3.2$ Hz, 1H; $C_1H_{glycerol}$), 4.20 (m, 2H; $H_{5'}$, $C_1H_{glycerol}$), 4.08 (dd, $^3J(H,H)=10.6$ Hz, $^3J(H,H)=3.0$ Hz, 1H; $H_{3'}$), 4.05–3.95 (m, 4H; $H_6$, $H_2$, $C_3H_{2\,glycerol}$), 3.93 (app.s, 1H; $H_{4'}$), 3.80–3.70 (m, 3H; $H_{6a'}$, $H_{6b'}$, $H_5$), 3.68 (t, $^3J(H,H)=9.3$ Hz, 1H; $H_3$), 3.62 (t, $^3J(H,H)=9.3$ Hz, 1H; $H_4$), 3.44 (dd, $^3J(H_{2'},H_{3'})=10.6$ Hz, $^3J(H_{2'},H_{1'})=4.0$ Hz, 1H; $H_{2'}$), 2.37 (t, $^3J(H,H)=7.5$ Hz, 2H; $CH_2CO$), 2.34 (t, $^3J(H,H)=7.5$ Hz, 2H; $CH_2CO$), 1.62 (m, 4H; 2×$CH_2CH_2CO$), 1.31 (app.s, 40H; 20×$CH_2$), 0.92 ppm (t, $^3J(H,H)=7.2$ Hz, 6H; 2×$CH_3$); HSQC (500 MHz, [D$_4$]MeOD, 25°C, TMS): $\delta=93.7$ ($C_{1'}$), 75.5 ($C_5$), 74.5 ($C_3$), 73.0 ($C_4$), 72.5 ($C_6$), 72.3 ($C_{5'}$), 72.03 ($C_2$), 71.95 ($C_1$), 71.8 ($C_2H_{glycerol}$), 69.8 ($C_{4'}$), 68.7 ($C_{3'}$), 64.8 ($C_1H_{2\,glycerol}$), 63.4 ($C_3H_{2\,glycerol}$), 62.3 ($C_{6'}$), 52.0 ($C_{2'}$), 34.9 (2×$C$H$_2$CO), 33.1 (2×

$CH_2CH_2CH_3$), 29.3–31.7 ($16\times CH_2$), 25.8 ($2\times CH_2CH_2CO$), 24.2 ($2\times CH_2CH_2CH_3$), 14.3 ppm ($2\times CH_3$); $^{31}$P NMR (202 MHz, [D$_4$]MeOD, 25 °C, TMS): $\delta=-0.10$ ppm; FAB HRMS: *m/z* calcd for $[C_{43}H_{82}NO_{17}P+Na]^+$: 938.5218; found: 938.5210.

**PI-PLC and GPI-PLD hydrolysis of glycosylphosphoinositides**

*Materials and methods*: PI-PLC from *Bacillus cereus* was purchased from Molecular Probes (Eugene, OR, USA). GPI-PLD from bovine serum was a generous gift from Dr. Urs Brodbeck. Egg PtdCho, Egg PtdEth, and Ch were purchased from Avanti Polar Lipids (Alabaster, AL, USA), bovine serum albumin (BSA) and Triton X-100 were from Sigma. HEPES was purchased from Apollo. Salts, organics solvents, and other reagents were of analytical grade and were supplied by Merck (Darmstadt, Germany).

*Liposome preparation*: Glycophosphoinositides **3**–**10** were reconstituted asymmetrically into preformed liposomal membranes as described previously.[22b] Briefly, LUVs composed of PtdCho/PtdEth/Ch (2:1:1 mole ratio) were prepared by the extrusion method,[35] with the use of 100 nm pore diameter Nuclepore filters (Merck, Darmstadt, Germany) at RT, as detailed previously.[36] Total lipid concentration was adjusted to 0.3 mM after lipid phosphate analysis.[32] The appropriate amount of glycophosphoinositide was then dissolved in methanol and mixed with the liposomes in buffer (10 mM HEPES, 50 mM NaCl, 0.1 % BSA, pH 7.5) so that the glycophosphoinositide mole fraction in the lipid was 10 %, unless otherwise stated, and the volume of the methanolic solution was 5 % of the vesicle suspension. The resulting mixture was incubated for 15 min at RT. This causes the glycophosphoinositides to become asymmetrically inserted into the outer monolayer of the vesicle. The resulting suspension was then used in the PL assays with the enzymes mentioned previously.[22]

*Hydrolysis of GPI by phospholipases*: For optimal catalytic activity, all experiments were performed at 39 °C in the buffer described above. PI-PLC was used at a final concentration of 0.16 U mL$^{-1}$ and GPI-PLD at 0.5 U mL$^{-1}$. Enzyme activity was assayed as follows: Aliquots were removed from the reaction mixture at regular intervals and extracted with $CHCl_3$/MeOH/HCl (66:33:1). Amine determination in the aqueous phase was performed by using the fluorescamine-based method.[30] An AMINCO Bowman® Series 2 luminescence spectrofluorimeter was used at RT, and excitation and emission wavelengths were 390 and 475 nm, respectively. The method was validated by control experiments involving enzymatic hydrolysis with LUVs with and without incorporation of glycophosphoinositide **8**.

The linear dependence of fluorescence intensity on the concentration of phospholipase-released amino groups in the fluorescamine assay was checked by using control solutions of glucosamine, galactosamine, and phosphorylethanolamine.

*Data presentation*: Unless specified otherwise, data are presented as averaged results of at least two similar, independent measurements. Activity data ± SD were calculated from three measurements.

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