Synthesis of Serine-Linked Phosphatidylinositol Mannosides (PIMs)

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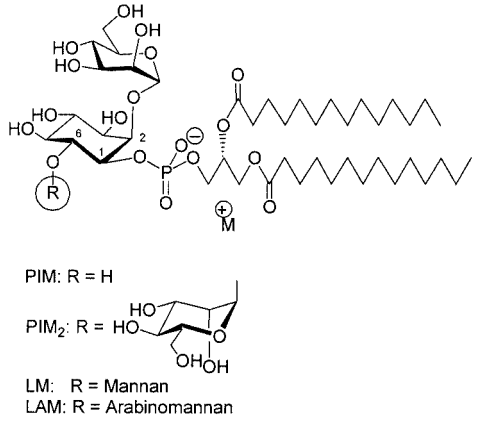
The 6-*O*-allyl group of inositol mannoside (D)-**6** was used for the generation of *O*-linked serine residues via a sequence of dihydroxylation, selective 3′′-*O*-protection, introduction of the 2′′-amino group, deprotection, and oxidation of the 3′′-position. Attachment of the phosphatidyl residue to 1-*O* of the inositol moiety and complete deprotection furnished target molecules (D)-**1** and (D)-**2**. Alternatively, instead of introduction of a 6-*O*-allyl group, 2′′,3′′-dihydroxy propanylation of the 6-*O*-position of the inositol moiety using a silyl-protected cyclic sulfate of glycerol was possible. Thus, target molecule (L)-**3** was obtained.

Introduction

Arabinogalactan-peptidoglycan (AGP) and lipidoarabinomannan (LAM) complexes are important constituents of mycobacterial cell walls. The LAM complexes are composed of phosphatidylinositol dimannosides (PIM_2) carrying further mannans (→ lipomannan, LM) or arabinomannan moieties (→ lipidoarabinomannan, LAM) (Scheme 1).[1−4] Phophatidylinositols that are α-mannopyranosylated at *O*-2 (→ PIM), or at *O*-2 and *O*-6 (→ PIM_2), are the precursors for the biosynthesis of LAMs.[5,6] The extension of the α-(1→2)-linked mannopyranosyl residue with further α-(1→2)- and α-(1→6)-linked mannopyranosyl residues leads to LMs, and by the further addition of arabinofuranosyl residues, LAMs are obtained.



Scheme 1. Structure of PIMs, LM, LAM

In mycobacterial infections, the lipoglycans localize to caveolae/lipid rafts of host membranes, which serve as signal transduction platforms, thus eliciting a biological response. Such responses involve induced expression and secretion of TNF-α and IL-6, and inhibition of T-cell proliferative responses.[7] LAMs have also been shown to inhibit expression of IL-2, IL-5 and GM-CSF genes in human T-cells, as well as inhibiting the IFN-γ-mediated activation of macrophages.

As the PIM substructure of LAMs is able to inhibit LAM-insertion into caveolae, the PIM substructure may contain the necessary structural characteristics to target caveolae. As the chain-extension at the 6-*O*-position of the PIM, giving LMs, does not seem to be necessary for targeting of the caveolae, it should be possible to synthesize conjugates of PIM that would deliver the coupled partner to the caveolae, and subsequently into the cell. Therefore, a serine residue attached to the 6-*O*-position of the inositol was chosen as a docking moiety for the coupling of partner molecules. This serine attachment was selected in accordance with the structure of naturally occurring GPI-anchors, which carry a glucosamine-residue at the 6-*O*-position of the inositol. Hence, we initiated a programme of investigation into the synthesis of PIMs and their structural variants. Methods to allow the required regioselective access to the 1-*O*-, 2-*O*- and 6-*O*-positions of (D)- and (L)-*myo*-inositol have been developed and reported.[8−10]

In this paper, the introduction of serine residues onto the 6-*O*-position of the inositol moiety of phosphatidyl-(D)-inositol-mannoside and its pseudo-enantiomer, phosphatidyl-(L)-inositol-mannoside, is reported. Several approaches to introduce optically active residues at the 6-*O*-position were investigated; these included nucleophilic opening of β-lactones and aziridines, nucleophilic substitution at activated glycerol species, and dihydroxylation of 6-*O*-allyl compounds. In the case of the (D)-inositol compounds, the in-

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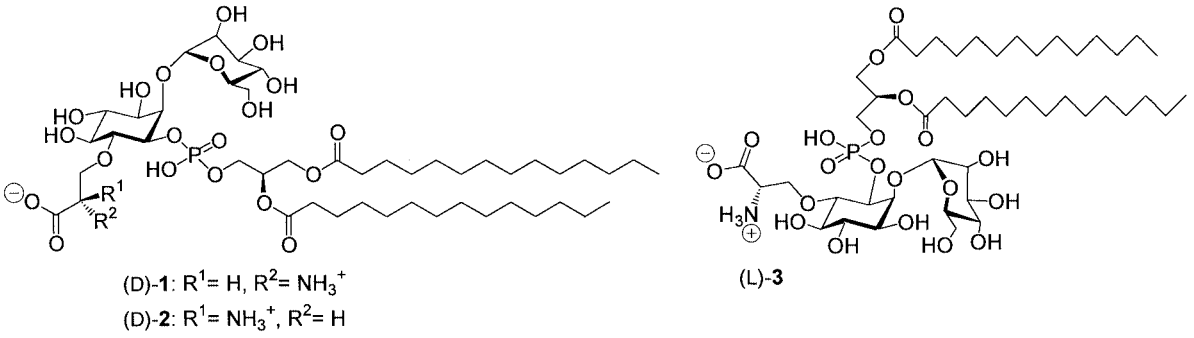
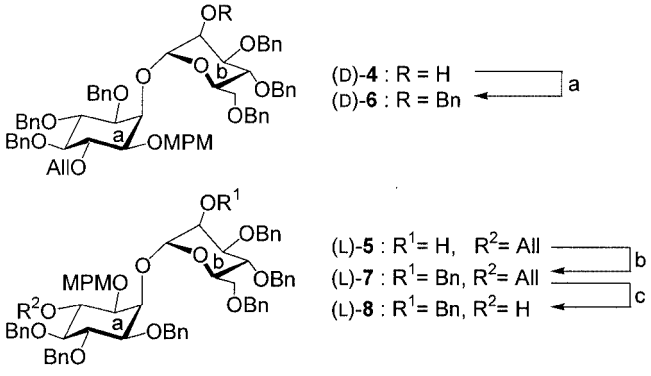


Scheme 2. Structure of target compounds (D)-**1**, (D)-**2** and (L)-**3**

troduction of the naturally and unnaturally configured serine residues was accomplished. Dihydroxylation of a 6-*O*-allyl functionality, and subsequent refunctionalization to give the amino acid, gave the target compounds (D)-**1** and (D)-**2**. The corresponding introduction of a serine residue into the pseudo-enantiomeric (L)-inositol compound was accomplished enantioselectively by coupling to an enantiomerically pure glycerol derivative and subsequent refunctionalization. These reactions yielded target compound (L)-**3**. In our synthesis, the efficient resolution of diastereomeric precursors of (D)-**1** and (D)-**2**, and the enantioselective preparation of (L)-**3** (Scheme 2), allowed access to PIM-like structures, which may be conjugated via standard peptide bond formation methods.

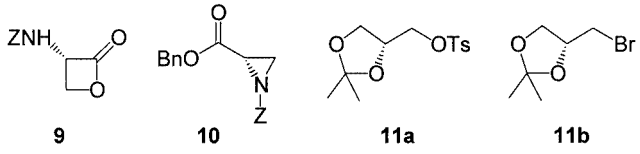
Results and Discussion

In the synthesis of (D)-**1**, (D)-**2** and (L)-**3**, the diastereoisomeric pseudodisaccharides (D)-**4** and (L)-**5** were used as known precursors.[9,10] Benzylation of (D)-**4** and (L)-**5** with benzyl bromide in DMF, using sodium hydride as a base, afforded the fully protected compounds (D)-**6** and (L)-**7** in high yields (Scheme 3). Removal of the *O*-allyl group in compound (L)-**7** with Wilkinson's catalyst and DBU in ethanol gave the free alcohol (L)-**8**. We had then planned to introduce a serine residue at the free hydroxyl group at the 6-*O*-position of the inositol moiety.



Scheme 3. Reagents and conditions: (a) BnBr, NaH, DMF, room temp., 86%; (b) BnBr, NaH, DMF, room temp., 98%; (c) 1. $(PPh_3)_3RhCl$, DBU, EtOH, 90 °C, 2. 1 M HCl/acetone, 1:9, 90%

Several possibilities for the introduction of serine to free hydroxyl groups have been reported.[11] In this case, the ring-opening addition of (L)-**8** to β-lactone **9**, as described by Vederas,[12–15] and the ring-opening of aziridine **10** by nucleophilic attack of alcohols[16] were investigated. In neither case could the desired serine-containing compound be isolated. Next, the formation of an ether bond via nucleophilic attack of the deprotonated alcohol (L)-**8** at activated *O*-isopropylidene-glycerol derivatives, as described by Hajdu,[17] were tested. The reaction of (L)-**8** with compound **11a** or **11b** in DMF in the presence of sodium hydride did not yield the desired derivatives (Scheme 4).

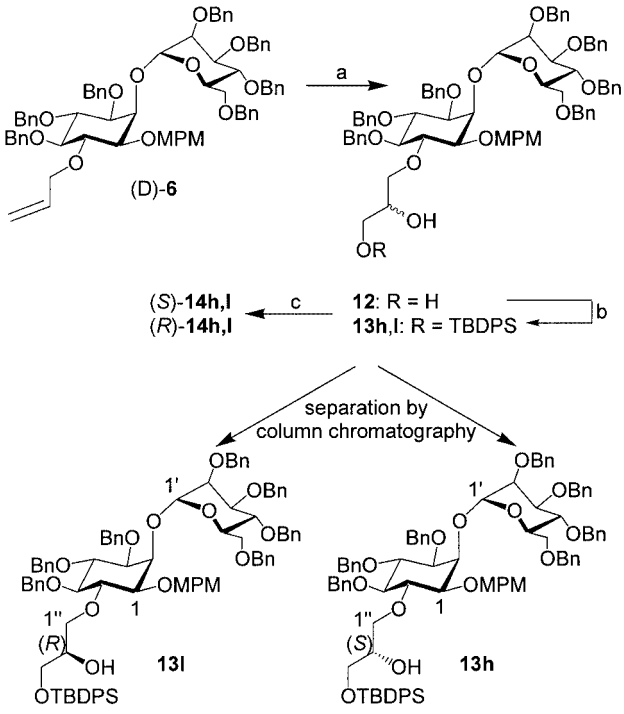


Scheme 4. Investigated serine precursors

As an alternative to the introduction of C_3-synthons to the partially deprotected (L)-**8**, functionalization of the 6-*O*-allyl group in compounds (D)-**6** and (L)-**7** by dihydroxylation would also lead to the type of compounds that are accessible by direct addition of glycerol derivatives. However, the creation of the secondary alcohol at the *C*-2′′-centre would presumably give a 1:1 mixture of diastereoisomers, and their subsequent separation would be required. To avoid this problem, reaction conditions must be chosen that would give diastereoselective dihydroxylation of the allyl group. But in both cases, the configuration of the newly formed stereogenic centre must be determined and assigned.

The dihydroxylation of allyl compound (D)-**6** with *N*-methylmorpholine *N*-oxide and catalytic amounts of osmium tetroxide[18–20] afforded the expected 1:1 mixture of the diastereoisomeric diols **12** in 97% yield. Selective protection of the primary hydroxyl group at the *C*-3′′-atom with the *tert*-butyldiphenylsilyl group under standard conditions gave a mixture of the diastereoisomeric alcohols **13h**,**l** in

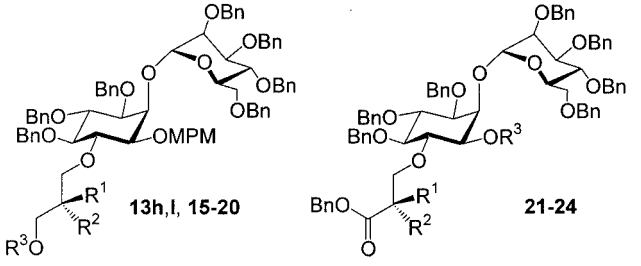
excellent yield. At this stage, the diastereoisomers, **13h** and **13l**, could be separated by column chromatography on silica gel (Scheme 5).



Scheme 5. Reagents and conditions: (a) OsO_4, acetone/H_2O, NMO, room temp., 97%; (b) TBDPSCl, imidazole, CH_2Cl_2, 0 °C, 3 h, quant.; (c) MTPA-Cl, pyridine, room temp., 24 h, ≈ 90%

For the full structural assignment of **13l** and **13h**, assignment of the configuration of the newly created stereogenic centre at the *C*-2′′ was necessary. In this case, the nuclear magnetic resonance (NMR) method employing (α-methoxy-α-trifluoromethyl-phenyl acetate) esters (MTPA-esters) according to Dale and Mosher was employed.[21,22] After enriching the mixture of compounds **13h** +**13l** to a ratio of 4:1, the (*S*)-(−)-MTPA- and (*R*)-(+)-MTPA-esters were formed by reaction with the corresponding MTPA-chloride in pyridine. From these reactions, the mixtures of diastereoisomers (*S*)-**14h,l** and (*R*)-**14h,l**, respectively, were obtained. In the HMQC spectra, (*R*)-**14h** showed a low-field shift of the 1′′-protons, and (*S*)-**14h** had a low-field shift of the 3′′-protons, thus leading to an assignment of the (*S*)-configuration at *C*-2′′ of **13h**. As expected, (*R*)-**14l** exhibited a low-field shift for the 3′′-protons, whereas (*S*)-**14l** showed a low-field shift for the 1′′-protons, thus supporting an assignment of the (*R*)-configuration at *C*-2′′ in **13l**.

To convert the fully characterized pseudo-enantiomeric compounds **13l** and **13h** into the target compounds **1** and **2**, the functionalized propanyl residues have to be transformed into serine residues, and finally, phosphatidylglycerolipid moieties have to be introduced at *C*-1 of the inositol moieties. The conversion of the propanyl residue begins by converting the free secondary alcohol into an azido group, which will ultimately be transformed into the serine's amino group. This conversion can be achieved in a stereospecific fashion in two steps. The first is the introduction of a mesyl group at *C*-2′′ with mesyl chloride in dichloromethane/pyridine. From **13l** and **13h**, the corresponding mesylates **15** and **16** were formed in yields of 98% and 93%, respectively. In a second step, the mesyl groups are replaced by azides with inversion of configuration in an S_N2 reaction. Azides **17** and **18** were obtained from the mesylates in yields of 93% and 84% by treatment with sodium azide in DMF at elevated temperatures. The next step in the construction of the amino acid is the oxidation of the *C*-3′′-carbon from an alcohol to a carboxylic acid. To accomplish this conversion, the primary alcohol was deprotected by treating the silyl-protected compounds with TBAF in tetrahydrofuran,[23] affording alcohols **19** and **20** in excellent yields. Conversion of the primary alcohols into the benzyl esters **21** and **22** was achieved by oxidation with sodium hypochlorite in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in acetone, and immediate protection of the newly formed carboxylic acid with a benzyl group under standard conditions,[24] in yields of 77% and 81%, respectively, over two steps. Under these reaction conditions, the MPM protecting group at the 1-*O*-position is stable, and no racemization at *C*-2′′ was observed. Mild oxidative cleavage of the MPM group with ceric(IV)ammonium nitrate (CAN) furnished the 1-*O* unprotected compounds **23** and **24** in good yields (Scheme 6).

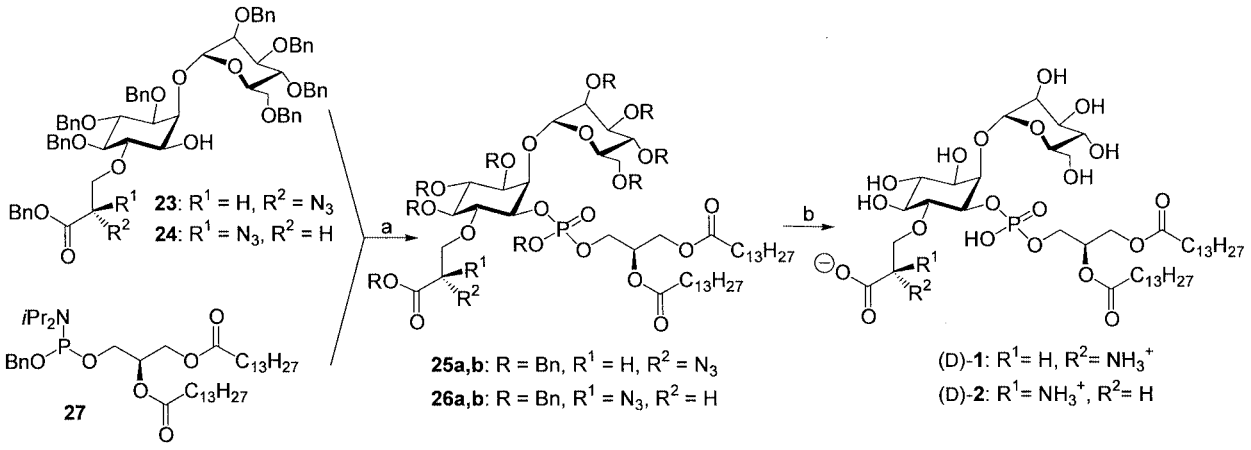


13l 13h
a ↓ ↓ a
15 16
b ↓ ↓ b
17 18
c ↓ ↓ c
19 20
d ↓ ↓ d
21 22
e ↓ ↓ e
23 24

	R^1	R^2	R^3
13l	OH	H	TBDPS
13h	H	OH	TBDPS
15	OMs	H	TBDPS
16	H	OMs	TBDPS
17	H	N_3	TBDPS
18	N_3	H	TBDPS
19	H	N_3	H
20	N_3	H	H
21	H	N_3	MPM
22	N_3	H	MPM
23	H	N_3	H
24	N_3	H	H

Scheme 6. Reagents and conditions: (a) MsCl, pyr/CH_2Cl_2, room temp., 3.5 h, ≈95%; (b) NaN_3, DMF, 90 °C, 24 h, ≈ 90%; (c) TBAF, THF, 3.5 h, ≈95%; (d) 1. NaOCl, TEMPO, KBr, acetone, 0 °C, 2. BnBr, CsF, DMF, room temp., 2 h, ≈ 80%; (e) CAN, CH_3CN/toluene/H_2O, 2 h, ≈ 80%

Diacylglycerol-containing phosphitamide **27** could be successfully linked to **23** and **24** in the presence of catalytic amounts of tetrazole. Subsequent oxidation of the phosphite to the phosphate with *tert*-butyl hydroperoxide led, due to generation of a stereogenic centre at the phosphorus atom, to mixtures of the fully benzyl-protected diastereoisomeric target compounds **25a**,**b** and **26a**,**b** in yields of 68%

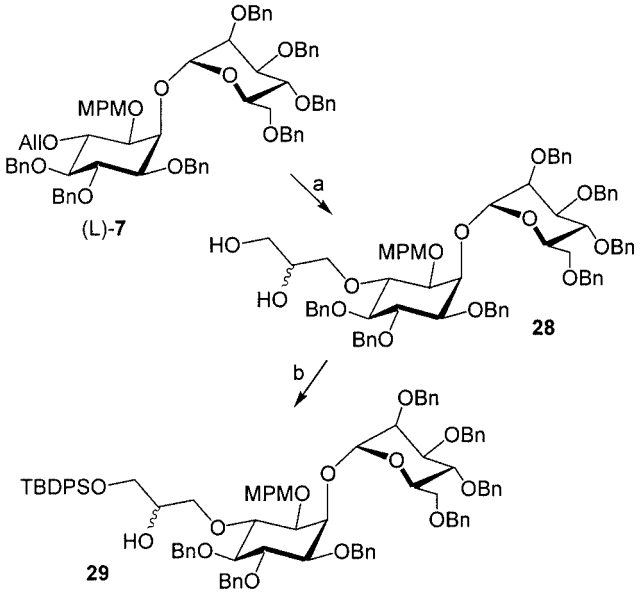


Scheme 7. Reagents and conditions: (a) 1. tetrazole, CH_2Cl_2, room temp., 2. *t*BuOOH, about 75%; (b) $Pd(OH)_2/C$, H_2, CH_2Cl_2/MeOH/H_2O, room temp., about 70%

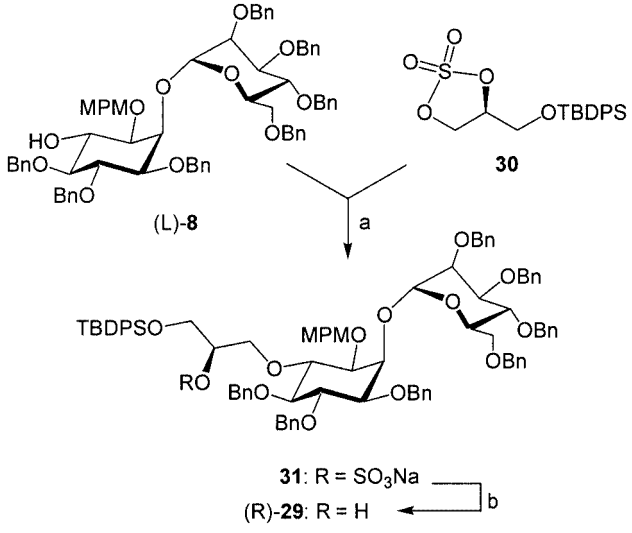
and 73%, respectively. The hydrogenolytic removal of the nine *O*-benzyl groups was successfully carried out using the more reactive Pearlman's catalyst [$Pd(OH)_2$ on carbon] in a 7.5:7.5:1 mixture of dichloromethane/ methanol/ water. The use of Pearlman's catalyst[25] ensured the reduction of the azido group at *C*-2′′ into an amino group, thus liberating the final compounds **1** and **2** from their protected precursors in one step (Scheme 7). The structures of (D)-**1** and (D)-**2** are fully supported by NMR and MS data.

Starting from fully protected (L)-**7**, the route described to gain access to compounds (D)-**1** and (D)-**2** should also lead to the corresponding compounds of the (L)-*myo*-inositol series. Use of the osmium-catalysed Sharpless asymmetric dihydroxylation reaction[26] means that the lengthy separation of diastereoisomers would be avoided. Upon treating 6-*O*-allyl compound (L)-**7** with AD-mix β in a mixture of acetone and water, a mixture of diastereoisomers (L)-**28h,l** was obtained in 71% yield, and was inseparable at this stage. Selectively protecting the primary hydroxyl groups in the mixture of diols (L)-**28h,l** with *tert*-butyldiphenylsilyl chloride and imidazole in dichloromethane gave a mixture of the alcohols **29h,l**. The ratio of **29h,l**, as determined by NMR spectroscopy, was only 1.8:1. Unfortunately, it was not possible to separate the compounds by column chromatography, so this route was abandoned at this stage and alternatives were considered (Scheme 8).

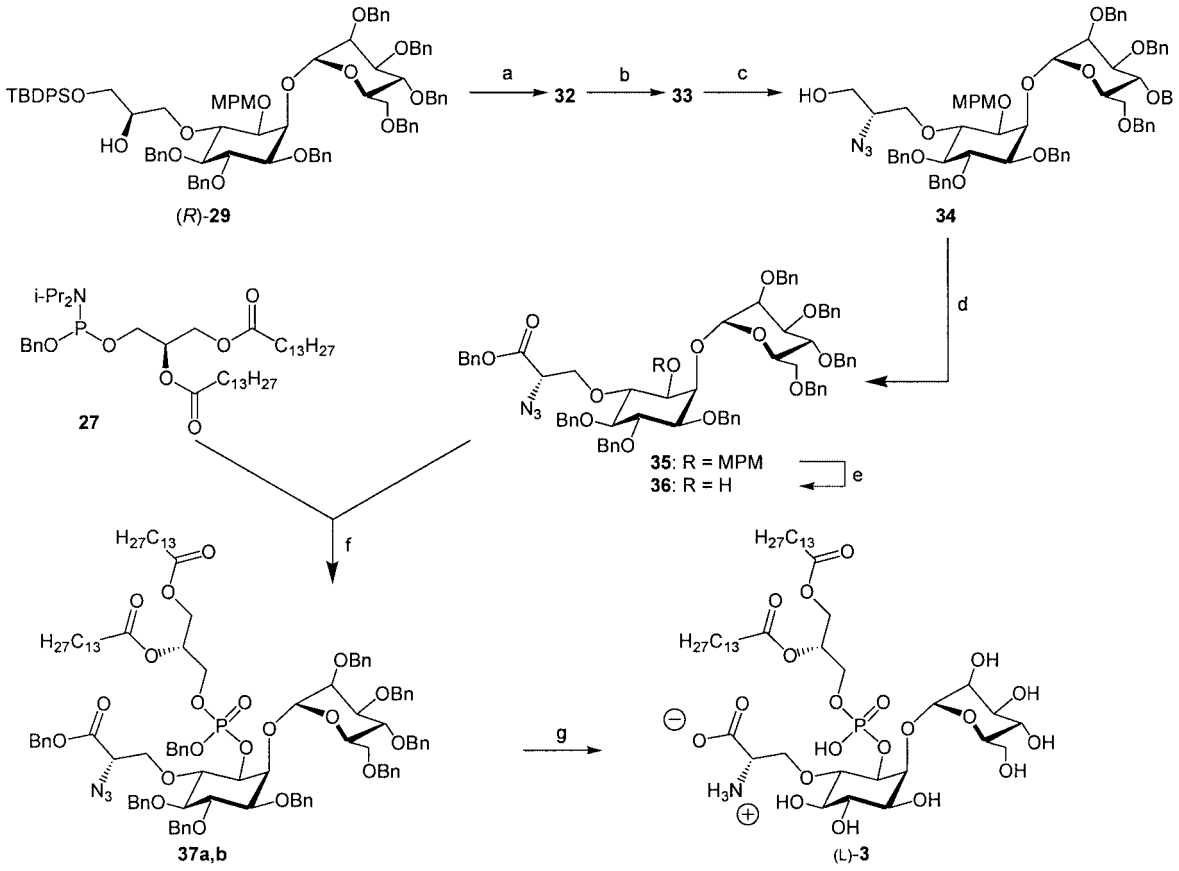
The addition of (L)-**8** to glycerol derivatives with defined stereochemistry was selected for further investigation, this time not using *O*-isopropylidene derivatives, but cyclic sulfates. Ring-opening reactions of cyclic 1,2-sulfates go via an S_N2 mechanism under basic conditions, and have been reported to be quite regioselective; the attack usually occurs at the sterically least hindered position.[27,28] The deprotonated alcohol (L)-**8** should attack the cyclic 1,2-sulfate **30** at the primary position, thus preserving the configuration at the central carbon atom. The sodium hydride mediated coupling of inositol derivative (L)-**8** with the cyclic sulfate **30** in DMF gave the sodium salt **31**, from which the desired



Scheme 8. Reagents and conditions: (a) AD-mix β, acetone/H_2O, room temp., 71%; (b) TBDPSCl, imidazole, CH_2Cl_2, 0 °C, 1 h, 97%



Scheme 9. Reagents and conditions: (a) NaH, DMF, room temp., 24 h; (b) H^+, dioxane, room temp., 25−51% in 2 steps



Scheme 10. Reagents and conditions: (a) MsCl, pyr/CH_2Cl_2, room temp., 3.5 h, quant.; (b) NaN_3, DMF, 90 °C, 24 h, 88%; (c) TBAF, THF, 92%; (d) 1. NaOCl, TEMPO, KBr, acetone, 0 °C, 2. BnBr, CsF, DMF, room temp., 2 h, 92%; (e) CAN, CH_3CN/toluene/H_2O, 2 h, 83%; (f) 1. tetrazole, CH_2Cl_2, room temp., 2. *t*BuOOH, 71%; (g) $Pd(OH)_2$/C, H_2, CH_2Cl_2/MeOH/H_2O, room temp., 85%

coupling product (*R*)-**29** was liberated by treatment with acid.[29] Thus, in two steps, (*R*)-**29** was obtained in yields of 25−51%, and this compound may be used as a precursor for the preparation of (L)-**3** (Scheme 9). The NMR spectra of isolated (*R*)-**29** are identical to those of one compound in the mixture of **29**, and this also allows assignment of the configuration at *C*-2′′ in these compounds.

The synthesis of the (L)-*myo*-inositol derivative **3** from compound (*R*)-**29** follows the route described above for compounds of the (D)-*myo*-inositol series. Activation (→ **32**), azide introduction (→ **33**), removal of the *O*-silyl protecting group (→ **34**), oxidation with subsequent ester formation (→ **35**) and oxidative cleavage of the *p*-methoxybenzyl ether gave alcohol **36**, which was coupled with the benzyl protected phosphitamide **27**. Oxidation to the phosphate gave a diastereomeric mixture of the fully protected compounds **37a,b**. Using Pearlman's catalyst, the target molecule (L)-**3** was liberated. The structure of compound (L)-**3** is supported by NMR and MS data (Scheme 10).

Conclusion

This work describes synthetic routes to the serine-containing PIM compounds (D)-**1**, (D)-**2** and (L)-**3**. The possible conjugation of markers and biologically active compounds offers new ways of probing the lateral composition of lipid membranes and membrane transfer processes.[30]

Experimental Section

General Methods: Solvents were purified by distillation and dried by normal procedures, except for distilled CH_2Cl_2, which was passed through a column of commercially available neutral alumina (ICN Alumina N, activity grade super I) as an alternative drying procedure. Boiling range of the petroleum ether: 35−70 °C. Thin layer chromatography (TLC) was performed on E. Merck Silica Gel 60 F_{254} plates (0.2 mm). The plates were visualized by immersion in mostain [200 mL 10% H_2SO_4, 10 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 200 mg $Ce(SO_4)_2$] or ninhydrin solution (1% in EtOH) or 10% H_2SO_4 or $KMnO_4$ solution (1% in water, 1% $NaHCO_3$), followed by heating (165 °C). High performance thin layer chromatography (HPTLC) was performed on E. Merck HPTLC-glass plates, Silica Gel 60. Preparative flash chromatography was carried out on Baker Silica Gel 60 (30−60 mm) at a pressure of 0.02−0.04 MPa. FABMS was recorded on a modified Finnigan MAT 312/AMD 5000. ^1H NMR, ^{13}C NMR and ^{31}P spectra were recorded on a Bruker AC 250 Cryospec and a Bruker DRX 600 instrument. Proton chemical shifts are reported in ppm relative to Me_4Si as internal standard. Assignments of protons and carbons were carried out with the aid of 600 MHz spectra: COSY, HMQC, ROESY, TOCSY. Measurements of optical rotations were performed on a

Perkin−Elmer polarimeter 241 MC (1 dm cell) at 20 °C. Melting points: Gallenkamp metal block; not corrected. MALDI-MS were obtained on a Kratos Analytical Kompact Maldi 2 instrument with 2,5-dihydroxybenzoic acid (DHB) as matrix (positive mode) or 2′,4′,6′-trihydroxyacetophenone (THAP) and 6-aza-2-thiothymine (ATT) (negative mode).

6-*O*-[(2*S*)-2-Amino-2-hydroxycarbonylethyl]-2-*O*-α-D-mannopyranosyl-D-*myo*-inosit-1-yl-[(2*R*)-2,3-bis(myristoyloxy)propyl]phosphate [(D)-1]: Compound (D)-**1** was synthesized following the procedure described for compound (D)-**2**. Compound **25a,b** (250 mg, 0.14 mmol) gave (D)-**1** (96 mg, 68%) as a colourless powder. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.76−0.90 (t, 6 H, Me), 1.07−1.35 (s, 40 H, CH$_2$-chain), 1.42−1.55 (m, 4 H, COCH$_2$C*H*$_2$R), 2.18−2.35 (m, 4 H, COC*H*$_2$CH$_2$R), 3.11 (m, 1 H, 5a-H), 3.19 (m, 1 H, 3a-H), 3.34 (m, 2 H, 6a-H, 4a-H), 3.48 (m, 2 H, 6b-H, 4b-H), 3.49 (m, 1 H, 3b-H), 3.56 (m, 1 H, 6b-H), 3.66 (m, 1 H, 2b-H), 3.86 (m, 3 H, 1′-H, 5b-H), 3.92 (m, 1 H, 1′′-H), 3.93 (m, 1 H, 2′′-H), 3.94 (m, 1 H, 2a-H), 3.98 (m, 1 H, 1a-H), 4.09 (m, 1 H, 3′-H), 4.19 (m, 1 H, 1′′-H), 4.28 (m, 1 H, 3′-H), 4.97 (d, 1 H, J < 1 Hz, 1b-H), 5.11 (m, 1 H, 2′-H), 8.67 (br. s, 2 H, NH$_2$) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]DMSO): δ = 13.88 (2 C, Me), 22.04/28.43−29.04/31.25 (20 C, *C*H$_2$-chain) 24.36/24.43 (2 C, COCH$_2$*C*H$_2$R), 33.36/33.51 (2 C, CO*C*H$_2$CH$_2$R), 52.45 (1 C, C-2′′), 60.71 (1 C, C-6b), 62.07 (1 C, C-3′), 63.10 (1 C, C-1′), 66.44 (1 C, C-4b), 69.51 (1 C, C-1′′), 69.83 (1 C, C-3a), 69.86 (1 C, C-2′), 70.28 (1 C, C-2b), 70.64 (1 C,C-3b), 72.36 (1 C, C-4a), 72.49 (1 C, C-5b), 74.62 (1 C, C-1a), 74.71 (1 C, C-5a), 76.92 (1 C, C-2a), 81.66 (1 C, C-6a), 100.14 (1 C, C-1b), 168.97 (1 C, *C*OOH), 172.35/172.54 (2 C, *C*OR) ppm. ^{31}P NMR (242.9 MHz, [D$_6$]DMSO): δ = 0.847 (s, 1 P) ppm. MALDI-MS (negative mode, matrix THAP, acetonitrile/water, 3:2) [M − H$^+$]$^-$: calcd. m/z = 1003.2; found m/z = 1002.7. C$_{46}$H$_{86}$NO$_{20}$P·3.5H$_2$O (1067.2): calcd. C 51.77, H 8.78, N 1.31; found C 51.74, H 9.00, N 0.98.

6-*O*-[(2*R*)-2-Amino-2-hydroxycarbonylethyl]-2-*O*-α-D-mannopyranosyl-D-*myo*-inosit-1-yl-[(2*R*)-2,3-bis(myristoyloxy)propyl]phosphate [(D)-2]: A mixture of the diastereomeric compounds **26a,b** (250 mg, 0.14 mmol) and Pearlman's catalyst (4 mg, 0.2 equiv.) in CH$_2$Cl$_2$/methanol/water (7.5:7.5:1, 3 mL) was degassed under reduced pressure, and saturated with H$_2$ several times. The suspension was stirred at room temp. overnight, filtered through Celite and washed with CH$_2$Cl$_2$/methanol/water (7.5:7.5:1, 2 mL), and the filtrate was diluted with water. After lyophilization, the title compound (D)-**2** (102 mg, 73%) was obtained as a white powder. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.78−0.90 (t, 6 H, Me), 1.05−1.35 (s, 40 H, CH$_2$-chain), 1.40−1.56 (m, 4 H, COCH$_2$C*H*$_2$R), 2.18−2.33 (m, 4 H, COC*H*$_2$CH$_2$R), 3.14 (m, 1 H, 5a-H), 3.19 (m, 1 H, 3a-H), 3.34 (m, 1 H, 4a-H), 3.35 (m, 1 H, 6a-H), 3.47 (m, 2 H, 6b-H, 4b-H), 3.49 (m, 1 H, 3b-H), 3.57 (m, 1 H, 6b-H), 3.66 (m, 1 H, 2b-H), 3.74 (m, 1 H, 1′′-H), 3.83 (m, 2 H, 1′-H), 3.86 (m, 1 H, 5b-H), 3.95 (m, 1 H, 2a-H), 3.97 (m, 1 H, 2′′-H), 4.02 (m, 1 H, 1a-H), 4.09 (m, 1 H, 3′-H), 4.27 (m, 2 H, 1′-H, 3′-H), 4.98 (d, 1 H, J < 1 Hz, 1b-H), 5.10 (m, 1 H, 2′-H), 8.65−8.9 (br. s, 2 H, NH$_2$) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]DMSO): δ = 13.88 (2 C, Me), 22.05/28.42−29.04/31.26 (20C, *C*H$_2$-chain) 24.36/24.44 (2 C, COCH$_2$*C*H$_2$R), 33.37/33.53 (2 C, CO*C*H$_2$CH$_2$R), 52.72 (1 C, C-2′′), 60.74 (1 C, C-6b), 61.99 (1 C, C-3′), 62.85 (1 C, C-1′), 66.55 (1 C, C-4b), 69.48 (1 C, C-1′′), 69.87 (2 C, C-2′, C-3a), 70.25 (1 C, C-2b), 70.59 (1 C, C-3b), 72.27 (1 C, C-4a), 72.61 (1 C, C-5b), 74.53 (1 C, C-1a), 74.67 (1 C, C-5a), 76.93 (1 C, C-2a), 81.93 (1 C, C-6a), 100.0 (1 C, C-1b), 168.78 (1 C, *C*OOH), 172.25/172.51 (2 C, *C*OR) ppm. ^{31}P NMR (242.9 MHz, [D$_6$]DMSO): δ = 0.909 (s, 1 P) ppm. MALDI-MS (negative mode, matrix THAP, acetonitrile-water, 3:2) [M − H$^+$]$^-$: calcd. m/z = 1003.2; found m/z = 1002.3. C$_{46}$H$_{86}$NO$_{20}$P·2.5H$_2$O (1049.2): calcd. C 52.66, H 8.74, N 1.33; found C 52.79, H 8.94, N 1.03.

6-*O*-[(2*S*)-2-Amino-2-hydroxycarbonylethyl]-2-*O*-α-D-mannopyranosyl-L-*myo*-inosit-1-yl-[(2*R*)-2,3-bis(myristoyloxy)propyl]phosphate [(L)-3]: A mixture of the diastereomeric compounds **37a,b** (180 mg, 0.09 mmol) and Pearlman's catalyst (3 mg, 0.2 equiv.) in CH$_2$Cl$_2$/methanol/water (7.5:7.5:1, 3 mL) was degassed under reduced pressure and saturated, with H$_2$ several times. The suspension was stirred at room temp. overnight, filtered through Celite and washed with CH$_2$Cl$_2$/methanol/water (7.5:7.5:1, 2 mL), and the filtrate was diluted with water. After lyophilization, the title compound (L)-**3** (83 mg, 85%) was obtained as a white powder. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.78−0.90 (t, 6 H, Me), 1.08−1.35 (s, 40 H, CH$_2$-chain), 1.40−1.56 (m, 4 H, COCH$_2$C*H*$_2$R), 2.18−2.33 (m, 4 H, COC*H*$_2$CH$_2$R), 3.12 (m, 1 H, 5a-H), 3.23 (m, 1 H, 3a-H), 3.24 (m, 1 H, 6b-H), 3.27 (m, 1 H, 4b-H), 3.30 (m, 1 H, 6a-H), 3.38 (m, 1 H, 4a-H), 3.47 (m, 1 H, 3b-H), 3.65 (m, 1 H, 2b-H), 3.66 (m, 1 H, 1′′-H), 3.69 (m, 1 H, 6b-H), 3.78 (m, 1 H, 2′′-H), 3.8 (m, 1 H, 1′-H), 3.81 (m, 1 H, 5b-H), 3.93 (m, 1 H, 1′-H), 3.94 (m, 1 H, 2a-H), 3.99 (m, 1 H, 1a-H), 4.06 (m, 1 H, 3′-H), 4.26 (m, 1 H, 1′′-H), 4.29 (m, 1 H, 3′-H), 5.02 (m, 1 H, 1b-H), 5.10 (m, 1 H, 2′-H), 8.65−8.9 (br. s, 2 H, NH$_2$) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]DMSO, selection): δ = 52.8 (1 C, C-2′′), 61.6 (1 C, C-3′), 62.0 (1 C, C-6b), 62.3 (1 C, C-1′), 68.0 (1 C, C-4b), 68.9 (1 C, C-1′′), 69.9 (1 C, C-2b), 70.0 (1 C, C-2′), 70.3 (1 C, C-3b), 71.3 (1 C, C-3a), 72.2 (2 C, C-1a, C-5b), 72.5 (1 C, C-4a), 74.2 (1 C, C-5a), 76.3 (1 C, C-2a), 81.2 (1 C, C-6a), 100.2 (1 C, C-1b) ppm. ^{31}P NMR (242.9 MHz, [D$_6$]DMSO): δ = 0.023 (s, 1 P) ppm. MALDI-MS (negative mode, matrix ATT, H$_2$O) [M − H$^+$]$^-$: calcd. m/z = 1003.1; found. m/z = 1001.8. MALDI-MS (positive mode, matrix DHB, H$_2$O) [M + Na]$^+$: calcd. m/z = 1027.2; found m/z = 1027.5; [(M$^-$Na$^+$)+Na]$^+$: calcd. m/z = 1050.16; found m/z = 1049.4; [(M$^-$Na$^+$)+K]$^+$: calcd. m/z = 1066.16; found m/z = 1065.3. C$_{46}$H$_{86}$NO$_{20}$P·1.5H$_2$O (1031.2): calcd. C 53.58, H 8.70, N 1.36; found C 53.61, H 8.71, N 0.80.

6-*O*-Allyl-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-D-*myo*-inositol [(D)-4]: Compound (D)-**4** was prepared as previously reported.[10]

6-*O*-Allyl-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-L-*myo*-inositol [(L)-5]: Compound (L)-**5** was prepared as previously reported.[10]

6-*O*-Allyl-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-D-*myo*-inositol [(D)-6]: A solution of compound (D)-**4** (14 g, 13.42 mmol) in dry DMF (150 mL), was treated with benzyl bromide (2.87 mL, 24.16 mmol), then NaH (580 mg, 24.16 mmol) was added. The reaction mixture was stirred at room temp. for 3 h, then concentrated under reduced pressure. The residue was diluted with EtOAc and washed with water and brine. The organic phase was dried (MgSO$_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/EtOAc, 5:1) to yield compound (D)-**6** (13.1 g, 86%) as a colourless syrup. TLC (petroleum ether/EtOAc, 2:1): R_f = 0.74. [α]$_D$ = +12.8 (c = 1, CHCl$_3$). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.22−3.41 (m, 4 H), 3.48−3.65 (m, 2 H), 3.71 (s, 3 H, OMe), 3.65−3.87 (m, 2 H), 3.99−4.17 (m, 2 H), 4.2−4.69, 4.7−4.92 (m, 20 H, C*H*$_2$CH=CH$_2$, C*H*$_2$−Ph, a-H, b-H), 5.12−5.36 (m, 2 H, CH$_2$CH=C*H*$_2$), 5.42 (s, 1 H, 1b-H), 5.91−6.10 (m, 1 H, CH$_2$C*H*=CH$_2$), 6.76−6.86 (m, 2 H, H$_{PMB}$), 7.07−7.40 (m, 37 H, ArH) ppm. C$_{72}$H$_{76}$O$_{12}$ (1133.4): calcd. C 76.30, H 6.76; found C 76.09, H 6.77.

6-*O*-Allyl-3,4,5,-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-L-*myo*-inositol [(L)-7]: Compound (L)-**7** was synthesized following the procedure described for compound (D)-**6**. Compound (L)-**5** (15.9 g, 15.24 mmol) gave (L)-**7** (17 g, 98%) as a colourless syrup. $[\alpha]_D$ = +20.1 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.21 (dd, *J* = 9.8, *J* = 2.5 Hz, 1 H, a-H), 3.29−3.45 (m, 3 H), 3.51−3.87 (m, 5 H), 3.77 (s, 3 H, OMe), 4.0−4.19 (m, 2 H), 4.20−4.91 (m, 19 H, C*H*$_2$−Ph, C*H*$_2$CH=CH$_2$, 2a-H), 5.12 (dd, $J_{gem.}$ = 10.4, $J_{vic.}$ = 1.7 Hz, 1 H, CH$_2$CH=C*H*$_2$), 5.25 (dd, $J_{gem.}$ = 17.2, $J_{vic.}$ = 1.7 Hz, 1 H, CH$_2$CH=C*H*$_2$), 5.42 (d, *J* = 1.2 Hz, 1 H, 1b-H), 5.88−6.04 (m, 1 H, CH$_2$C*H*=CH$_2$), 6.75−6.84 (m, 2 H, H_{PMB}), 7.07−7.40 (m, 37 H, ArH) ppm. $C_{72}H_{76}O_{12}$ (1133.4): calcd. C 76.30, H 6.76; found C 76.10, H 6.57.

3,4,5-Tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-L-*myo*-inositol [(L)-8]: DBU (0.12 mL, 0.80 mmol) and $(Ph_3P)_3RhCl$ (0.91 g, 1.02 mmol) were added to a solution of (L)-**7** (7.74 g, 6.83 mmol) in dry EtOH (150 mL), and the mixture was refluxed at 90 °C. After 1.5 h for isomerization, the reaction mixture was concentrated under reduced pressure, and the residue was redissolved in 1 M HCl/acetone (1:9) and refluxed at 70 °C for 20 min. The solution was neutralized with NEt_3, diluted with EtOAc and washed with water. After drying ($MgSO_4$), the organic phase was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc, 4:1), to afford (L)-**8** (6.7 g, 90%). TLC (petroleum ether/EtOAc, 2:1): R_f = 0.61. $[\alpha]_D$ = +28.3 (*c* = 1, $CHCl_3$), ^1H NMR (250 MHz, $CDCl_3$): δ = 2.40 (d, *J* = 1.8 Hz, 1 H, OH), 3.01 (dd, *J* = 2.4, *J* = 10.0 Hz, 1 H, a-H), 3.32 (dd, 1 H, *J* = 9.2 Hz, a-H), 3.34−3.40 (m, 1 H, a-H), 3.45−3.52 (m, 1 H, 6b-H), 3.57−3.76 (m, 3 H), 3.80 (s, 3 H, OMe), 3.81−3.93 (m, 2 H) 4.02 (dd, 1 H, *J* = 9.4 Hz), 4.10−4.19 (m, 1 H, 5b-H), 4.38−4.91 (m, 17 H, C*H*$_2$−Ph, 2a-H), 5.40 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1b-H), 6.79−6.86 (m, 2 H, H_{PMB}), 7.10−7.40 (m, 37 H, ArH) ppm. $C_{69}H_{72}O_{12}$ (1093.3): calcd. C 75.80, H 6.64; found C 75.51, H 6.56.

3,4,5-Tri-*O*-benzyl-6-*O*-[(2*R*/2*S*)-2,3-dihydroxypropyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (12): Osmium tetroxide (100 mg, 0.39 mmol) and *N*-methylmorpholine *N*-oxide (3.3 g, 24.42 mmol) were added to a solution of alkene (D)-**6** (14 g, 12.35 mmol) in acetone/water (8:1). The solution was stirred at room temp. for 14 h, then saturated sodium hydrogen sulfite solution (170 mL) was added, and stirring was continued for a further 30 min. The solution was separated from the resultant precipitate, the filtrate was diluted with EtOAc (400 mL) and the phases were separated. The organic phase was dried ($MgSO_4$) and concentrated. Flash chromatography (petroleum ether/EtOAc, 1:1→1:2) of the residue gave a 1:1 mixture of diastereomeric diols **12** (14 g, 97%) as a colourless syrup. TLC (petroleum ether/EtOAc, 2:1): R_f = 0.11. $[\alpha]_D$ = +11.8 (*c* = 1, $CDCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.53 (s, 2 H, OH), 1.89−1.99 (m, 2 H, OH), 3.18−3.89 (m, 34 H, OMe, OMe), 3.99−4.16 (m, 4 H), 4.3−4.63, 4.68−4.80, 4.81−4.95 (m, 34 H, C*H*$_2$−Ph), 5.34 (d, 1 H, *J* < 1 Hz, 1b-H), 5.36 (d, *J* = 1.5 Hz, 1 H, 1b-H), 6.72−6.83 (m, 4 H, H_{PMB}), 7.09−7.39 (m, 74 H, ArH) ppm. $C_{72}H_{78}O_{16}$ (1167.4): calcd. C 74.08, H 6.74; found C 74.01, H 6.88.

3,4,5-Tri-*O*-benzyl-6-*O*-[(2*R*/2*S*)-2-hydroxy-3-(*tert*-butyldiphenylsilyloxy)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (13h,l): A mixture of diastereomeric diols **12** (12.87 g, 11.02 mmol) was dissolved in dry CH_2Cl_2 (300 mL). Imidazole (2.25 g, 33.05 mmol) and *tert*-butyldiphenylsilyl chloride (7.1 mL, 27.74 mmol) were added, and the reaction mixture was stirred at 0 °C for 3 h. NH_4Cl solution was added and the two layers were separated. The organic phase was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/EtOAc, 4:1). The mixture of diastereomeric alcohols **13h,l** was obtained quantitatively.

3,4,5-Tri-*O*-benzyl-6-*O*-[(2*R*)-2-hydroxy-3-(*tert*-butyldiphenylsilyloxy)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (13l) and 3,4,5-Tri-*O*-benzyl-6-*O*-[(2*S*)-2-hydroxy-3-(*tert*-butyldiphenylsilyloxy)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (13h): Separation of the mixture of diastereomers **13h,l** into the pure alcohols **13l** and **13h** was possible by repetitive chromatography (6:1 petroleum ether/EtOAc) on silica gel columns. **13l**: HPTLC (toluene/EtOAc, 10:1): R_f = 0.40. $[\alpha]_D$ = +8.1 (*c* = 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.05 (s, 9 H, *t*Bu), 3.2−3.29 (m, 2 H, 1a-H, 3a-H), 3.3−3.45 (m, 2 H, 5a-H, 6b-H), 3.51−3.77 (m, 9 H, OMe, 3′′-H, 6b-H, 6a-H, 4a-H, 2b-H), 3.79−3.86 (m, 2 H, 1′′-H, 3b-H), 3.9 (m, 1 H, 2′′-H), 3.96 (dd, $J_{vic.}$ = 2.9, $J_{gem.}$ = 10.8 Hz, 1 H, 1′′-H), 4.0−4.12 (m, 2 H, 4b-H, 5b-H), 4.3−4.5, 4.51−4.61, 4.69−4.78, 4.8−4.91 (m, 17 H, C*H*$_2$−Ph, 2a-H), 5.35 (d, 1 H, 1b-H), 6.72−6.74 (m, 2 H, H_{PMB}), 7.06−7.43, 7.60−7.70 (m, 47 H, ArH) ppm. $C_{88}H_{96}O_{14}Si$ (1405.8): calcd. C 75.20, H 6.90; found C 74.95, H 6.90. **13h**: HPTLC (toluene/EtOAc, 10:1): R_f = 0.45. $[\alpha]_D$ = +10.8 (*c* = 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.05 (s, 9 H, *t*Bu), 3.21 (dd, $J_{1,2}$ = 1.2, $J_{1,6}$ = 9.8 Hz, 1 H, 1a-H), 3.25 (dd, $J_{3,4}$ = 9.9, $J_{3,2}$ = 2.0 Hz, 1 H, 3a-H), 3.32 (dd, $J_{5,6}$ = $J_{5,4}$ = 9.3 Hz, 1 H, 5a-H), 3.35−3.39 (m, 1 H, 6b-H), 3.54 (dd, $J_{vic.}$ = 3.7, $J_{gem.}$ = 12.1 Hz, 1 H, 6b-H), 3.75−3.68 (m, 6 H, OMe, 3′′-H, 6a-H), 3.69−3.75 (m, 2 H, 2b-H, 4a-H), 3.78−3.82 (m, 2 H, 3b-H, 2′′-H), 3.87−3.94 (m, 2 H, 1′′-H), 4.04 (dd, $J_{4,5}$ = $J_{4,3}$ = 9.7 Hz, 1 H, 4b-H), 4.07−4.13 (m, 1 H, 5b-H), 4.33−4.61, 4.70−4.80, 4.81−4.85 (m, 17 H, C*H*$_2$−Ph, 2a-H), 5.35 (d, 1 H, 1b-H), 6.65−6.67 (m, 2 H, H_{PMB}), 7.03−7.43, 7.59−7.69 (m, 47 H, ArH) ppm. $C_{88}H_{96}O_{14}Si$ (1405.8): calcd. C 75.20, H 6.90; found C 75.32, H 6.89.

3,4,5-Tri-*O*-benzyl-6-*O*-[3-(*tert*-butyldiphenylsilyloxy-2-(*R*)-α-methoxy-α-trifluoromethyl-phenylacetoxy)-(*R*,*S*)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-D-*myo*-inositol [(*R*)-14h,l]: (*S*)-(+)-α-Methoxy-α-trifluoromethylphenylacetyl chloride (40 μL, 0.21 mmol) was added to a solution of compounds **13h,l** (4:1) (194 mg, 0.14 mmol) in dry pyridine (2 mL). After stirring at room temp. for 24 h, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in diethyl ether, and washed with water and brine. The organic layer was dried ($MgSO_4$) and concentrated. Purification by flash chromatography (petroleum ether/EtOAc, 6:1) afforded a mixture of compounds (*R*)-**14h,l** (205 mg, 91%) as a colourless syrup. TLC (petroleum ether/EtOAc, 7:2): R_f = 0.54. $[\alpha]_D$ = +17 (*c* = 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.98 (s, 9 H, *t*Bu$_h$), 1.02 (s, 2.25 H, *t*Bu$_l$), 2.77 (dd, 0.25 H, $J_{1,6}$ = 9.6 Hz, 1a-H$_l$), 3.09 (dd, 1 H, $J_{1,6}$ = 9.7 Hz, 1a-H$_h$), 3.12−3.19 (m, 0.5 H, 3a-H$_l$, 5a-H$_l$), 3.20−3.26 (m, 2 H, 3a-H$_h$, 5a-H$_h$), 3.33−3.41 (m, 1.5 H, 6a-H$_l$, 6b-H$_l$, 6b-H$_h$), 3.48 (dd, $J_{6,1}$ = $J_{6,5}$ = 9.4 Hz, 1 H, 6a-H$_h$), 3.51−3.60 (m, 6 H, 6b-H$_h$, 6b-H$_l$, 1′′-H$_l$, OMe$_h$, OMe$_l$, OMe$_l$), 3.61−3.84 (m, 10.25 H, OMe$_h$, 3′′-H$_h$, 3′′-H$_l$, 1′′-H$_h$, 2b-H$_h$, 2b-H$_l$, 3b-H$_h$, 3b-H$_l$, 4a-H$_h$, 4a-H$_l$), 3.90 (m, 0.25 H, 1′′-H$_l$), 4.0−4.19 (m, 3.5 H, 1′′-H$_h$, 4b-H$_h$, 5b-H$_h$,), 4.28 (m, 0.25 H, 2a-H$_l$), 4.31 (m, 1 H, 2a-H$_h$), 4.32−4.92 (m, 20 H, C*H*$_2$-Ph), 5.31 (m, 0.25 H, 1b-H$_l$), 5.35 (m, 1 H, 1b-H$_h$), 5.47−5.55 (m, 1.25 H, 2′′-H$_l$, 2′′-H$_h$), 6.6−6.7 (m, 2.5 H, $H_{PMB\ h}$, $H_{PMB\ l}$), 7.01−7.41, 7.51−7.66 (m, 65 H, ArH) ppm. MALDI-MS (positive mode, matrix DHB, THF)

$[M + Na]^+$: calcd. *m*/*z* = 1645.0; found *m*/*z* = 1641.9; $[M + K]^+$: calcd. *m*/*z* = 1661.1; found *m*/*z* = 1657.9. $C_{98}H_{103}F_3O_{16}Si$ (1622.0): calcd. C 72.57, H 6.40; found C 72.51, H 6.56.

3,4,5-Tri-*O*-benzyl-6-*O*-[3-(*tert*-butyldiphenylsilyloxy)-(*S*)-α-methoxy-α-trifluoromethylphenylacetoxy)-(*R*,*S*)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-D-*myo*-inositol [(*S*)-14h,l]: (*R*)-(−)-α-Methoxy-α-trifluoromethylphenylacetyl chloride (50 μL, 0.27 mmol) was added to a solution of compounds **13h,l** (4:1) (248 mg, 0.18 mmol) in dry pyridine (2.5 mL). After stirring at room temp. for 24 h, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in diethyl ether, and washed with water and brine. The organic layer was dried ($MgSO_4$) and concentrated. Purification by flash chromatography (petroleum ether/EtOAc, 6:1) afforded a mixture of compounds (*S*)-**14h,l** (254 mg, 88%) as a colourless syrup. TLC (petroleum ether/EtOAc, 7:2): R_f = 0.54. $[\alpha]_D$ = −33 (*c* = 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.98 (s, 2.25 H, tBu_l), 1.0 (s, 9 H, tBu_h), 2.92 (dd, $J_{5,6} = J_{5,4}$ = 9.2 Hz, 1 H, 5a-H_h), 3.21−3.28 (m, 0.5 H, 5a-H_l, 3a-H_l), 2.99 (dd, $J_{1,2}$ = 1.4, $J_{1,6}$ = 9.7 Hz, 1 H 1a-H_h), 3.14 (dd, 1.25 H, $J_{3,4}$ = 9.8, $J_{3,2}$ = 2.2 Hz, 3a-H_h,1a-H_l), 3.34 (dd, 2.25 H, $J_{6,1} = J_{6,5}$ = 11.3 Hz, 6a-H_h, 6b-H_l,6b-H_h), 3.49−3.90 (m, 17.5 H, 4a-H_h, 4a-H_l, 6a-H_l, 6b-H_l, 6b-H_h, 2b-H_l, 2b-H_h, OMe_h, OMe_h, OMe_l, OMe_l, 3′′-H_l, 1′′-H_l, 3b-H_l, 3b-H_h, 3′′-H_h, 1′′-H_h), 4.0−4.12 (m, 2.75 H, $J_{4,5\ h} = J_{4,3\ h}$ = 9.7 Hz, 1′-H_l, 4b-H_h, 5b-H_h, 4b-H_l, 5b-H_l), 4.22−4.48, 4.49−4.62, 4.63−4.89 (m, 21.25 H, CH_2−Ph, 2a-H_l, 2a-H_h), 5.32 (d, 1 H, *J*<1 Hz, 1b-H_h), 5.36 (m, 1 H, 1b-H_l), 5.45−5.5 (m, 0.25 H, 2′′-H_l), 5.54 (m, 1 H, 2′′-H_h), 6.58−6.63 (m, 0.5 H, $H_{PMB\ l}$), 6.65−6.71 (m, 2 H, $H_{PMB\ h}$), 7.0−7.42, 7.5−7.69 (m, 65 H, ArH) ppm. $C_{98}H_{103}F_3O_{16}Si$ (1622.0): calcd. C 72.57, H 6.40; found C 72.63, H 6.56.

3,4,5-Tri-*O*-benzyl-6-*O*-[(2*R*)-3-(*tert*-butyldiphenylsilyloxy)-2-(methylsulfonyloxy)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (15): Compound **15** was synthesized following the procedure described for compound **16**. Compound **13l** (3.99 g, 2.84 mmol) gave **15** (4.15 g, 98%) as a colourless foam. $[\alpha]_D$ = +11.5 (*c* = 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.04 (s, 9 H, *t*Bu), 2.87 (s, 3 H, OMs), 3.13 (dd, $J_{1,2}$ = 1.5, $J_{1,6}$ = 8.9 Hz, 1 H, 1a-H), 3.19−3.26 (m, 2 H, 5a-H, 3a-H), 3.37 (m, 1 H, 6b-H), 3.46 (dd, $J_{6,5} = J_{6,1}$ = 9.4 Hz, 1 H, 6a-H), 3.55 (m, 1 H, 6b-H), 3.63−3.74 (m, 5 H, OMe, 2b-H, 4a-H), 3.77−3.85 (m, 4 H, 3′′-H, 1′′-H, 3b-H), 4.02−4.13 (m, 3 H, 1′′-H, 4b-H, 5b-H), 4.3−4.9, 4.52−4.66, 4.7−4.83, 4.83−4.90 (m, 18 H, 2′′, CH_2−Ph, 2a-H), 5.34 (d, 1 H, 1b-H), 6.68−6.75 (m, 2 H, H_{PMB}), 7.05−7.45, 7.60−7.69 (m, 47 H, ArH). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 19.17 [1 C, $C(CH_3)_3$], 26.78 [3 C, $C(CH_3)_3$], 38.40 (1 C, SO_2-CH_3), 55.14 (1 C, OMe), 63.79 (1 C, C-3′′), 68.95 (1 C, C-6b), 71.18 (1 C, C-2a), 71.85−75.83 (12 C, CH_2Ph, C-1′′, C-4b, C-5b, C-2b), 78.46 (1 C, C-3a), 79.04 (1 C, C-3b), 80.11 (1 C, C-1a), 80.95 (1 C, C-4a), 82.05 (1 C, C-6a), 82.12 (1 C, C-2′′), 82.88 (1 C, C-5a), 98.38 (1 C, C-1b), 113.92 (2 C, C_{PMB}), 127.3−138.37 (57 C, Ph), 159.38 (1 C, C_{OMe}) ppm. $C_{89}H_{98}O_{14}SSi$ (1483.9): calcd. C 72.00, H 6.66; found C 71.81, H 6.70.

3,4,5-Tri-*O*-benzyl-6-*O*-[(2*S*)-3-(*tert*-butyldiphenylsilyloxy)-2-(methylsulfonyloxy)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (16): Compound **13h** (5.25 g, 3.74 mmol) was dissolved in pyridine/CH_2Cl_2 (1:1, 80 mL) and treated with methanesulfonyl chloride (0.87 mL, 11.20 mmol) at room temp. The reaction mixture was stirred for 3.5 h, diluted with CH_2Cl_2 and washed with sat. $NaHCO_3$ solution and water. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether/EtOAc, 3:1) gave mesylate **18** (5.06 g, 93%) as a colourless foam. TLC (petroleum ether/EtOAc, 3:1): R_f = 0.33. $[\alpha]_D$ = +15.5 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.02 (s, 9 H, *t*Bu), 2.92 (s, 3 H, OMs), 3.09−3.18 (m, 1 H, 1a-H), 3.19−3.30 (m, 2 H, 5a-H, 3a-H), 3.36 (m, 1 H, 6b-H), 3.46 (m, 1 H, 6a-H), 3.56 (m, 1 H, 6b-H), 3.66−3.94 (m, 9 H, OMe, 2b-H, 4a-H, 3′′-H, 3b-H, 1′′-H), 3.96−4.18 (m, 3 H, 1′′-H, 4b-H, 5b-H), 4.29−4.93 (m, 18 H, 2′′-H, CH_2−Ph, 2a-H), 5.35 (d, 1 H, *J* < 1 Hz, 1b-H), 6.68−6.76 (m, 2 H, H_{PMB}), 7.10−7.47, 7.61−7.71 (m, 47 H, ArH) ppm. $C_{89}H_{98}O_{14}SSi$ (1483.9): calcd. C 72.00, H 6.66; found C 72.04, H 6.50.

6-*O*-[(2*S*)-2-Azido-3-(*tert*-butyldiphenylsilyloxy)propyl]-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (17): Compound **17** was synthesized following the procedure described for compound **18**. Compound **15** (4.12 g, 2.78 mmol) gave **17** (3.60 g, 93%) as a colourless syrup. $[\alpha]_D$ = +5.3 (*c* = 0.54, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.02−1.12 (s, 9 H, *t*Bu), 3.14−3.58 (m, 6 H), 3.6−3.85 (m, 8 H), 3.69 (s, 3 H, OMe), 4.0−4.14 (m, 2 H), 4.3−4.63, 4.69−4.92 (m, 17 H, CH_2−Ph, 2a-H), 5.34 (d, 1 H, 1b-H), 6.68−6.73 (m, 2 H, H_{PMB}), 7.07−7.46, 7.62−7.72 (m, 47 H, ArH) ppm. MALDI-MS (positive mode, matrix DHB, THF) $[M + Na]^+$: calcd. *m*/*z* = 1453.82; found *m*/*z* = 1453.3. $C_{88}H_{95}N_3O_{13}Si$ (1430.8): calcd. C 73.87, H 6.69, N 2.90; found C 73.96, H 6.97, N 2.60.

6-*O*-[(2*R*)-2-Azido-3-(*tert*-butyldiphenylsilyloxy)propyl]-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (18): Sodium azide (3.33 g, 3.41 mmol) was added to a solution of mesylate **16** (5.06 g, 3.41 mmol) in dry DMF (150 mL). This suspension was stirred at 90 °C for 24 h. After letting the reaction mixture cool to room temp., it was diluted with diethyl ether and washed with water. The aqueous phase was extracted with diethyl ether (3 × 200 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (petroleum ether/EtOAc, 5:1) to yield **18** (4.1 g, 84%) as a colourless syrup. TLC (petroleum ether/EtOAc, 5:1): R_f = 0.24. $[\alpha]_D$ = +18 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.02−1.12 (s, 9 H, *t*Bu), 3.14−3.58 (m, 6 H), 3.6−3.85 (m, 8 H), 3.69 (s, 3 H, OMe), 4.0−4.14 (m, 2 H), 4.3−4.63, 4.69−4.92 (m, 17 H, CH_2−Ph, 2a-H), 5.34 (d, 1 H, 1b-H), 6.69−6.74 (m, 2 H, H_{PMB}), 7.07−7.46, 7.62−7.72 (m, 47 H, ArH) ppm. $C_{88}H_{95}N_3O_{13}Si$ (1430.8): calcd. C 73.87, H 6.69, N 2.90; found C 73.63, H 6.78, N 2.48.

6-*O*-[(2*R*)-2-Azido-3-hydroxypropyl]-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (19): Compound **19** was synthesized following the procedure described for compound **20**. Compound **17** (3.59 g, 2.51 mmol) gave **19** (2.80 g, 93%) as a colourless oil. $[\alpha]_D$ = +19.2 (*c* = 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.9 (s, 1 H, OH), 3.23 (dd, $J_{1,2}$ = 1.4, $J_{1,6}$ = 9.7 Hz, 1 H, 1a-H), 3.26 (dd, $J_{3,4}$ = 9.9, $J_{3,2}$ = 2.2 Hz, 1 H, 3a-H), 3.33 (dd, $J_{5,6} = J_{5,4}$ = 9.2 Hz, 1 H, 5a-H), 3.36−3.41 (m, 1 H, 6b-H), 3.45 (dd, $J_{6,1} = J_{6,5}$ = 9.5 Hz, 1 H, 6a-H), 3.52−3.58 (m, 2 H, 2′′-H, 6b-H), 3.59−3.77 (m, 7 H, OMe, 2b-H, 3′′-H, 4a-H), 3.80−3.88 (m, 3 H, 1′′-H, 3b-H), 4.05 (dd, $J_{4,5} = J_{4,3}$ = 9.8 Hz, 1 H, 4b-H), 4.13 (m, 1 H, 5b-H), 4.34−4.41, 4.41−4.46, 4.71−4.78, 4.84−4.94 (m, 17 H, CH_2−Ph, 2a-H), 5.37 (d, 1 H, 1b-H), 6.78−6.83 (m, 2 H, H_{PMB}), 7.10−7.38 (m, 37 H, ArH) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 55.21 (1 C, OMe), 62.58 (1 C, C-2′′), 62.77 (1 C, C-3′′), 68.94 (1 C, C-6b), 71.11 (1 C, C-2a), 71.82−75.93 (12 C, CH_2Ph, C-1′′, C-4b, C-5b, C-2b), 78.63 (1 C, C-3a), 79.16 (1 C, C-3b), 80.27 (1 C, C-1a), 81.08 (1 C, C-4a), 81.96 (1 C, C-6a), 83.08 (1 C, C-5a),

98.35 (1 C, C-1b), 113.96 (2 C, C_{PMB}), 127.3−138.79 (45 C, Ph), 159.52 (1 C, C_{OMe}) ppm. $C_{72}H_{77}N_3O_{13}$ (1192.4): calcd. C 72.50, H 6.50, N 3.52; found C 72.42, H 6.26, N 3.28.

6-*O*-[(2*S*)-2-Azido-3-hydroxypropyl]-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (20): A solution of compound **18** (3.7 g, 2.59 mmol) in THF (100 mL) at 0 °C was treated with tetrabutylammonium fluoride solution (1 M in THF, 0.9 mL). After removing the cooling bath, the solution was stirred at room temp. for 3.5 h. The reaction mixture was diluted with EtOAc, washed with NH_4Cl solution and water. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatographic purification of the residue with silica gel (petroleum ether/EtOAc, 3:1) gave **20** (2.93 g, 95%) as a colourless oil. TLC (petroleum ether/EtOAc, 3:1): R_f = 0.14. $[\alpha]_D$ = +13.8 (c = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.99 (dd, 1 H, J = 7.1 Hz, OH), 3.20−3.90 (m, 17 H, OMe, 1a-H, 3a-H, 5a-H, 6b-H, 6a-H, 2′′-H, 3′′-H, 4a-H, 2b-H), 4.0−4.18 (m, 2 H, 4b-H, 5b-H), 4.32−4.66, 4.7−4.95 (m, 17 H, CH_2−Ph, 2a-H), 5.38 (d, J = 1.3 Hz, 1 H, 1b-H), 6.76−6.84 (m, 2 H, H_{PMB}), 7.10−7.40 (m, 37 H, ArH) ppm. MALDI-MS (positive mode, matrix DHB, THF) [M + Na]$^+$: calcd. m/z = 1215.4; found m/z = 1214.0; [M + K]$^+$: calcd. m/z = 1231.5; found m/z = 1230.0. $C_{72}H_{77}N_3O_{13}$ (1192.4): calcd. C 72.52, H 6.51, N 3.52; found C 72.38, H 6.30, N 2.99.

6-*O*-[(2*S*)-2-Azido-2-(benzyloxycarbonyl)ethyl]-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (21): Compound **21** was synthesized following the procedure described for compound **22**. Compound **19** (2.75 g, 2.31 mmol) gave **21** (2.30 g, 77%) as a colourless syrup. $[\alpha]_D$ = +20.5 (c = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.20−3.39 (m, 4 H, 1a-H, 3a-H, 6b-H), 3.42−3.58 (m, 2 H, 6a-H, 6b-H), 3.61−3.67 (m, 1 H, 2b-H), 3.69 (s, 3 H, OMe), 3.70−3.84 (m, 2 H, 4a-H, 3b-H), 3.93−4.23 (m, 5 H, 2′′-H, 4b-H, 1′′-H, 5b-H), 4.30−4.63, 4.69−4.92 (m, 17 H, CH_2−Ph, 2a-H), 5.02 (d, 1 H, $J_{gem.}$ = 12.2 Hz, COOCH_2−Ph), 5.23 (d, 1 H, $J_{gem.}$ = 12.2 Hz, COOCH_2−Ph), 5.34 (d, 1 H, J < 1 Hz, 1b-H), 6.73−6.81 (m, 2 H, H_{PMB}), 7.09−7.40 (m, 42 H, ArH) ppm. $C_{79}H_{81}N_3O_{14}$ (1296.5): calcd. C 73.19, H 6.30, N 3.25; found C 73.12, H 6.42, N 2.80.

6-*O*-[(2*R*)-2-Azido-2-(benzyloxycarbonyl)ethyl]-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (22): $NaHCO_3$ solution (5% w/v, 10 mL), KBr (295 mg, 2.45 mmol) and TEMPO (427 mg, 1.67 mmol) were added to a solution of compound **20** (2.9 g, 2.43 mmol) in acetone (20 mL), and the reaction mixture was cooled to 0 °C. NaOCl solution (13% w/v, 5 mL) was added to this suspension over 5 min, and stirring was continued for 10 min at 0 °C. The reaction mixture was diluted with water and extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with sat. NaCl solution, dried ($MgSO_4$), concentrated under reduced pressure and dried for 1 h under reduced pressure; R_f (toluene/acetone, 1:1) = 0.26. The crude carboxylic acid was converted into the ester without further purification. A solution of the crude acid in dry DMF (50 mL) was treated with benzyl bromide (0.59 mL, 4.97 mmol) and CsF (754 mg, 4.97 mmol) and stirred at room temp. for 3 h. The reaction mixture was diluted with EtOAc, washed with NH_4Cl solution and brine, dried ($MgSO_4$) and concentrated. Purification of the residue by silica gel chromatography (petroleum ether/EtOAc, 4:1) gave ester **22** (2.55 g, 81%) as a colourless syrup. TLC (petroleum ether/EtOAc, 3:1): R_f = 0.41. $[\alpha]_D$ = +18.8 (c = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.18 (dd, $J_{1,2}$ = 1.3, $J_{1,6}$ = 9.6 Hz, 1 H, 1a-H), 3.23 (dd, $J_{3,4}$ = 9.9, $J_{3,2}$ = 2.1 Hz, 1 H, 3a-H), 3.32 (dd, $J_{5,6}$ = $J_{5,4}$ = 9.2 Hz, 1 H, 5a-H), 3.34−3.38 (m, 1 H, 6b-H), 3.47 (dd, $J_{6,1}$ = $J_{6,5}$ = 9.4 Hz, 1 H, 6a-H), 3.54 (dd, $J_{gem.}$ = 10.7, $J_{vic.}$ = 3.5 Hz, 1 H, 6b-H), 3.64 (m, 1 H, 2b-H), 3.69 (s, 3 H, OMe), 3.72 (dd, $J_{4,5}$ = $J_{4,3}$ = 9.5 Hz, 1 H, 4a-H), 3.81 (dd, $J_{3,4}$ = 9.4, $J_{3,2}$ = 3.0 Hz, 1 H, 3b-H), 4.01 (dd, 1 H, $J_{vic.}$ = 5.4 Hz, 2′′-H), 4.05 (dd, $J_{4,5}$ = $J_{4,3}$ = 9.6 Hz, 1 H, 4b-H), 4.07−4.13 (m, 3 H, 1′′-H, 5b-H), 4.29−4.39, 4.41−4.48, 4.51−4.62, 4.7−4.79, 4.82−4.92 (m, 17 H, CH_2−Ph, 2a-H), 5.12 (d, 1 H, $J_{gem.}$ = 12.2 Hz, COOCH_2−Ph), 5.23 (d, 1 H, $J_{gem.}$ = 12.2 Hz, COOCH_2−Ph), 5.34 (d, 1 H, 1b-H), 6.72−6.8 (m, 2 H, H_{PMB}), 7.10−7.40 (m, 42 H, ArH) ppm. MALDI-MS (positive mode, matrix DHB, THF) [M + Na]$^+$: calcd. m/z = 1319.5; found m/z = 1318.3; [M + K]$^+$: calcd. m/z = 1335.6; found m/z = 1333.7. $C_{79}H_{81}N_3O_{14}$ (1296.5): calcd. C 73.19, H 6.30, N 3.24; found C 73.03, H 6.28, N 2.73.

6-*O*-[(2*S*)-2-Azido-2-(benzyloxycarbonyl)ethyl]-3,4,5-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (23): Compound **23** was synthesized following the procedure described for compound **24**. Compound **21** (1.03 g, 0.79 mmol) gave **23** (757 mg, 81%) as a colourless syrup. $[\alpha]_D$ = +15.8 (c = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.10 (d, J = 1.5 Hz, 1 H, OH), 3.18−3.41 (m, 5 H), 3.58 (dd, 1 H, $J_{gem.}$ = 12.0 Hz, 6b-H), 3.65−3.77 (m, 3 H), 3.78−3.89 (m, 1 H), 4.02−4.13 (m, 3 H), 4.19−4.28 (m, 1 H), 4.29−4.95 (m, 15 H), 5.20 (d, J = 9.2 Hz, 1 H, COOCH_2−Ph), 5.30 (d, J = 10.4 Hz, 1 H, COOCH_2−Ph), 5.46 (d, J = 1.6 Hz, 1 H, 1b-H), 7.12−7.43 (m, 40 H, ArH) ppm. $C_{71}H_{73}N_3O_{13}$ (1176.4): calcd. C 72.49, H 6.26, N 3.57; found C 72.33, H 6.36, N 2.95.

6-*O*-[(2*R*)-2-Azido-2-(benzyloxycarbonyl)ethyl]-3,4,5-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (24): A solution of compound **22** (1 g, 0.77 mmol) in acetonitrile/toluene/water (60:3:4, 40 mL) was cooled to 0 °C and treated with $Ce(NH_4)_2(NO_3)_6$ (2.1 g, 3.83 mmol). After stirring for 1 h, the cooling bath was removed and the solution was stirred for further 90 min at room temp. The reaction mixture was diluted with EtOAc, washed with sat. $NaHCO_3$ solution, dried ($MgSO_4$) and concentrated. Flash chromatography (petroleum ether/EtOAc, 4:1) of the residue afforded the free alcohol **24** (0.77 g, 85%) as a colourless syrup. TLC (petroleum ether/EtOAc, 2:1): R_f = 0.51. $[\alpha]_D$ = +43 (c = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.88 (d, 1 H, J < 1 Hz, OH), 3.18−3.40 (m, 5 H), 3.55 (dd, 1 H, $J_{gem.}$ = 11.4 Hz, 6b-H), 3.62−3.85 (m, 4 H), 3.93−4.01 (m, 1 H), 4.02−4.20 (m, 3 H), 4.27−4.96 (m, 15 H), 5.28 (s, 2 H, COOCH_2−Ph), 5.43 (d, 1 H, J < 1 Hz, 1b-H), 7.09−7.41 (m, 40 H, ArH)ppm. MALDI-MS (positive mode, matrix DHB, THF) [M + Na]$^+$: calcd. m/z = 1199.37; found m/z = 1198.9; [M + K]$^+$: calcd. m/z = 1215.5; found m/z = 1215.9. $C_{71}H_{73}N_3O_{13}$ (1176.4): calcd. C 72.49, H 6.26, N 3.57; found C 72.32, H 6.38, N 3.00.

6-*O*-[(2*S*)-2-Azido-2-(benzyloxycarbonyl)ethyl]-3,4,5-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inosit-1-yl-[benzyl]-[(2*R*)-2,3-bis(myristoyloxy)propyl]-phosphate (25a,b): Compound **25a,b** was synthesized following the procedure described for compound **26a,b**. Compound **23** (417 mg, 0.35 mmol) gave **25a,b** (490 mg, 75%) as a colourless syrup. $[\alpha]_D$ = +7 (c = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.8−0.95 (t, 6 H, Me), 1.14−1.39 (s, 40 H, CH_2-chain), 1.46−1.56 (m, 4 H, $COCH_2CH_2R$), 2.15−2.35 (m, 4 H, $COCH_2CH_2R$), 3.20−3.38 (m, 3 H), 3.45−3.59 (m, 2 H), 3.65−3.85 (m, 3 H), 3.93−4.32 (m, 10 H), 4.40−4.92 (m, 15 H), 5.04−5.25 (m, 5 H, 2′, COOCH_2−Ph, POCH_2Ph), 5.31 (d, 0.5 H, J < 1 Hz, 1b-H), 5.34 (d, 0.5 H, J < 1 Hz, 1b-H), 7.10−7.41 (m, 45 H, ArH) ppm.

6-*O*-[(2*R*)-2-Azido-2-(benzyloxycarbonyl)ethyl]-3,4,5-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inosit-1-yl-

benzyl-[(2*R*)-2,3-bis(myristoyloxy)propyl]phosphate (26a,b): A solution of alcohol **24** (600 mg, 0.51 mmol) in dry CH_2Cl_2 (20 mL) was treated with dry tetrazole (93 mg, 1.33 mmol) and stirred at room temp. in an inert atmosphere. The phosphoramidite **27** (765 mg, 1.02 mmol) was added to this solution, and after stirring for 2 h, *tert*-butyl hydroperoxide solution (4.7 M in isooctane, 1 mL) was added over 15 min. The reaction mixture was diluted with CH_2Cl_2, and sodium hydrogen sulfite solution (5% w/v in water) added. After phase-separation, the organic phase was washed with brine, dried ($MgSO_4$) and concentrated. Purification of the residue by flash chromatography (petroleum ether/EtOAc, 4:1 and toluene/EtOAc, 10:1) gave a mixture of the diastereomers **26a,b** (732 mg, 78%) as a colourless syrup. TLC (petroleum ether/EtOAc, 4:1): R_f = 0.27. $[\alpha]_D$ = +12.7 (*c* = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.8−0.92 (t, 6 H, Me), 1.08−1.40 (s, 40 H, CH_2-chain), 1.44−1.67 (m, 4 H, $COCH_2CH_2R$), 2.12−2.36 (m, 4 H, $COCH_2CH_2R$), 3.21−3.38 (m, 3 H, 3a-H, 5a-H, 6b-H), 3.45−3.56 (m, 2 H, 6a-H, 6b-H), 3.68−3.77 (m, 2 H, 4a-H, 2b-H), 3.82 (dd, $J_{3,4}$ = 9.4, $J_{3,2}$ = 2.5 Hz, 1 H, 3b-H), 3.88−4.35 (m, 10 H, 1′-H, 3′-H, 1′′-H, 2′′-H, 4b-H, 1a-H, 5b-H), 4.40−4.92, (m, 15 H, 2a-H, CH_2−Ph), 5.03−5.28 (m, 5 H, 2′-H, $COOCH_2$−Ph, $POCH_2Ph$), 5.32 (d, 0.5 H, *J* < 1 Hz, 1b-H), 5.34 (d, 0.5 H, *J* < 1 Hz, 1b-H), 7.03−7.42 (m, 45 H, ArH) ppm. ^{31}P NMR (242.9 MHz, $CDCl_3$): δ = 0.1 (s, 1 P), 0.402 (s, 1 P) ppm. MALDI-MS (positive mode, matrix *p*-nitroaniline + NaI, MeOH) $[M + Na]^+$: calcd. *m*/*z* = 1864.4; found *m*/*z* = 1865.

Diacylglycerophosphite (27): Compound **27** was prepared as reported by Baeschlin et al.[31]

3,4,5-Tri-*O*-benzyl-6-*O*-[(2*R*/2*S*)-2,3-dihydroxypropyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-L-*myo*-inositol (28): AD-mixβ[26] (866 mg) was added to a solution of *O*-allyl compound (L)-**7** (0.7 g, 0.62 mmol) in acetone/water (3:1, 8 mL), and the solution was stirred at room temp. for 100 h. Sodium sulfite (3 g) was added to the reaction mixture, and stirring was continued for 1 h. The reaction mixture was diluted with EtOAc and washed with water. After phase-separation, the aqueous phase was extracted one further time with EtOAc. The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel (petroleum ether/EtOAc, 2:1→1:2) gave the mixture of diastereomers **28** (516 mg, 71%) as a colourless oil. TLC (petroleum ether/EtOAc, 2:1): R_f = 0.06. $[\alpha]_D$ = +29.8 (*c* = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.87−1.97 (br. s, 1 H, OH), 1.97−2.09 (br. s, 1 H, OH), 3.12−3.21 (m, 1 H, 1a-H), 3.24−3.36 (m, 2 H, 5a-H, 3a-H), 3.38−3.93 (m, 14 H, 1′-H, 2′-H, 3′-H, 4a-H, 6a-H, 2b-H, 3b-H, 6b-H, OMe), 4.00−4.14−3.74 (m, 2 H, 4b-H, 5b-H), 4.34−4.96 (m, 17 H, CH_2−Ph, 2a-H), 5.42 (d, $J_{1,2}$ = 1.2 Hz, 1 H, 1b-H), 6.76−6.86 (m, 2 H, Ph_{PMB}), 7.11−7.43 (m, 37 H, Ph) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 55.23 (1 C, OMe), 63.57 (1 C, C-3′), 69.08 (1 C, C-6b), 71.0 (1 C, C-2a), 71.1−76.0 (8 C, CH_2Ph), 71.49 (1 C, C-2′), 71.79 (1 C, C-5b), 74.34 (1 C, C-2b), 74.6 (1.72 C, C-1′, C-4b), 75.4 (1.28 C, C-1′), 77.21 (1 C, C-1a), 78.95 (1 C, C-3b), 80.85 (1 C, C-3a), 81.12 (0.34 C, C-6a), 81.33 (1 C, C-4a), 81.73 (0.64 C, C-6a), 83.36 (1 C, C-5a), 98.44 (1 C, C-1b), 113.85 (2 C, C_{PMB}), 127.39−138.68 (45 C, Ph), 159.27 (1 C, C_{OMe}) ppm. $C_{72}H_{78}O_{16}$·0.5H_2O (1176.4): calcd. C 73.51, H 6.77; found C 73.56, H 6.74.

3,4,5-Tri-*O*-benzyl-6-*O*-[(2*R*/2*S*)-2-hydroxy-3-*O*-(*tert*-butyldiphenylsilyloxy)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-L-*myo*-inositol (29): Imidazole (65 mg, 0.96 mmol) and *tert*-butyldiphenylsilyl chloride (100 μL, 0.35 mmol) were added to a solution of the diastereomers **28** (370 mg, 0.32 mmol) in dry CH_2Cl_2 (10 mL). The reaction mixture was stirred at 0 °C for 1 h. NH_4Cl solution was added, and after subsequent washing with water, the organic phase was dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (petroleum ether/EtOAc, 4:1). This gave the mixture of diastereomeric compounds **29** (433 mg, 97%) as a colourless syrup. TLC (petroleum ether/EtOAc, 2:1): R_f = 0.72; HPTLC (petroleum ether/EtOAc, 10:1): R_f = 0.33. $[\alpha]_D$ = +23.5 (*c* = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.00, 1.01 (2s, 9 H, *t*Bu), 3.09−3.20 (m, 1 H, 1a-H), 3.20−3.36 (m, 2 H, 3a-H, 5a-H), 3.45 (dd, 1 H, $J_{gem.}$ = 10.7 Hz, 6b-H), 3.52−3.76 (m, 9 H, OMe, 3′′-H, 6b-H, 6a-H, 4a-H, 2b-H), 3.77−3.88 (m, 2.36 H, 2′′-H, 3b-H, 1′′-H), 3.88−3.92 (m, 1.28 H, 1′′-H), 3.95−4.09 (m, 2.36 H, 4b-H, 5b-H, 1′′-H), 4.32−4.65, 4.70−4.88 (m, 17 H, CH_2−Ph, 2a-H), 5.40 (d, 1 H, 1b-H), 6.66−6.73 (m, 0.72 H, Ph_{PMB}), 6.73−6.79 (m, 1.28 H, Ph_{PMB}), 7.03−7.45, 7.56−7.68 (m, 47 H, ArH) ppm. $C_{88}H_{96}O_{14}Si$·0.5H_2O (1414.8): calcd. C 74.71, H 6.91; found C 74.71, H 6.90.

***tert*-Butyl-(2,2-dioxo-2λ^6-[1,3,2]dioxathiolan-4-yl-methoxy)diphenylsilane (30):** The cyclic sulfate **30** was prepared from 1,2-*O*-isopropylidene-*sn*-glycerol as described.[32−34]

5-Tri-*O*-benzyl-6-*O*-[(2*R*)-2-hydroxy-3-*O*-(*tert*-butyldiphenylsilyloxy)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-L-*myo*-inositol [(*R*)-29]: Sodium hydride (4 mg, 0.17 mmol) was added to a solution of the alcohol (L)-**8** (40 mg, 0.037 mmol) and the sulfate **30** (143.6 mg, 0.37 mmol) in dry DMF (2.5 mL), and the mixture was stirred under argon. The reaction was monitored by TLC (EtOAc/MeOH, 18:1): R_f = 0.30; (petroleum ether/EtOAc, 2:1): R_f = 0. After stirring for 4 h at room temp., further sulfate **30** (70 mg, 0.18 mmol) and sodium hydride (10 mg, 0.42 mmol) were added. Stirring was continued for 20 h at room temp., after which time the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/MeOH, 18:1). The sodium salt **31** so-obtained was immediately dissolved in dioxane (2 mL) and acidified with sulfuric acid (0.1 M). After stirring for 1 h at room temp., the reaction mixture was diluted with EtOAc, washed with aqueous $NaHCO_3$ solution and dried ($MgSO_4$). After removal of the solvent, the residue was purified by flash chromatography on silica gel to afford the diol (*R*)-**29** (26 mg, 51%) as a colourless syrup. TLC (petroleum ether/EtOAc, 2:1): R_f = 0.72. $[\alpha]_D$ = +24.5 (*c* = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.00 (s, 9 H, *t*Bu), 3.14 (dd, $J_{1,2}$ = 2.2, $J_{1,6}$ = 7.8 Hz, 1 H, 1a-H), 3.23−3.29 (m, 1 H, 3a-H), 3.31 (dd, $J_{5,6}$ = $J_{5,4}$ = 7.9 Hz, 1 H, 5a-H), 3.44 (dd, 1 H, $J_{gem.}$ = 10.2 Hz, 6b-H), 3.54−3.74 (m, 9 H, OMe, 3′′-H, 6b-H, 6a-H, 4a-H, 2b-H), 3.76−3.84 (m, 2 H, 2′′-H, 3b-H), 3.86−3.93 (m, 2 H, 1′′-H), 4.0−4.09 (m, 2 H, 4b-H, 5b-H), 4.32−4.65, 4.70−4.88 (m, 17 H, CH_2−Ph, 2a-H), 5.40 (d, 1 H, 1b-H), 6.66−6.73 (m, 2 H, H_{PMB}), 7.03−7.45, 7.56−7.68 (m, 47 H, ArH) ppm. $C_{88}H_{96}O_{14}Si$·0.5H_2O (1414.8): calcd. C 74.71, H 6.91; found C 74.73, H 6.82.

3,4,5-Tri-*O*-benzyl-6-*O*-[(2*R*)-3-*O*-(*tert*-butyldiphenylsilyloxy-2-*O*-methylsulfonyloxy)propyl]-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-L-*myo*-inositol (32): Compound **32** was synthesized following the procedure described for compound **16**. Compound (*R*)-**29** (1.74 g, 1.24 mmol) gave **32** (1.77 g) quantitatively as a colourless syrup. $[\alpha]_D$ = +18 (*c* = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.99 (s, 9 H, *t*Bu), 2.78 (s, 3 H, OMs), 3.08 (dd, $J_{1,2}$ = 2.2, $J_{1,6}$ = 9.8 Hz, 1 H, 1a-H), 3.21−3.29 (m, 2 H, 5a-H, 3a-H), 3.46 (dd, 1 H, $J_{gem.}$ = 9.7, 6b-H), 3.51 (dd, $J_{6,5}$ = $J_{6,1}$ = 12.5 Hz, 1 H, 6a-H), 3.61 (m, 1 H, 6b-H), 3.66 (dd, $J_{4,5}$ = $J_{4,3}$ = 10.1 Hz, 1 H, 4a-H), 3.69 (m, 1 H, 2b-

H), 3.73 (s, 3 H, OMe), 3.75−3.84 (m, 3 H, 3′′-H, 3b-H), 3.89−3.95 (m, 1 H, 1′′-H), 4.0−4.13 (m, 3 H, 1′′-H, 4b-H, 5b-H), 4.29−4.89, (m, 18 H, 2′′-H, CH_2−Ph, 2a-H), 5.42 (d, 1 H, 1b-H), 6.69−6.77 (m, 2 H, H_{PMB}), 7.03−7.41, 7.53−7.66 (m, 47 H, ArH) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 19.13 [1 C, $C(CH_3)_3$], 27.74 [3 C, C(CH_3)$_3$], 38.42 (1 C, SO_2−CH_3), 55.20 (1 C, OMe), 63.68 (1 C, C-3′′), 69.08 (1 C, C-6b), 71.12 (1 C, C-2a), 71.72−77.3 (13 C, CH_2Ph, C-1′′, C-1a, C-4b, C-5b, C-2b), 79.15 (1 C, C-3b), 80.87 (1 C, C-3a), 81.26 (1 C, C-4a), 81.79 (1 C, C-6a), 82.44 (1 C, C-2′′), 83.09 (1 C, C-5a), 98.24 (1 C, C-1b), 113.76 (2 C, C_{PMB}), 127.41−138.74 (57 C, Ph), 159.12 (1 C, C_{OMe}) ppm. $C_{89}H_{98}O_{14}SSi$ (1483.9): calcd. C 72.00, H 6.66; found C 71.38, H 6.69.

6-*O*-[(2*S*)-2-Azido-3-*O*-(*tert*-butyldiphenylsilyloxy)propyl]-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-L-*myo*-inositol (33): Compound **33** was synthesized following the procedure described for compound **18**. Compound **32** (1.77 g, 1.19 mmol) gave **33** (1.50 g, 88%) as a colourless syrup. $[\alpha]_D$ = +12.7 (*c* = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.02 (s, 9 H, *t*Bu), 3.13 (dd, $J_{1,2}$ = 2.3, $J_{1,6}$ = 9.8 Hz, 1 H, 1a-H), 3.25−3.30 (m, 2 H, 5a-H, 3a-H), 3.36 (dd, 1 H, $J_{gem.}$ = 10.6 Hz, 6b-H), 3.46 (dd, $J_{6,5}$ = $J_{6,1}$ = 9.5 Hz, 1 H, 6a-H), 3.5−3.79 (m, 11 H, 6b-H, OMe, 1′′-H, 2′′-H, 3′′-H, 4a-H, 2b-H, 3b-H), 3.84 (m, 1 H, 1′′-H), 4.01−4.06 (m, 2 H, 4b-H, 5b-H), 4.29−4.66, 4.69−4.86 (m, 17 H, CH_2−Ph, 2a-H), 5.39 (d, 1 H, 1b-H), 6.68−6.76 (m, 2 H, H_{PMB}), 7.06−7.41, 7.56−7.65 (m, 47 H, ArH) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 19.09 [1 C, $C(CH_3)_3$], 26.69 [3 C, C(CH_3)$_3$], 55.19 (1 C, OMe), 63.65 (1 C, C-3′′), 64.57 (1 C, C-2′′), 68.86 (1 C, C-6b), 71.5−76.02 (13 C, CH_2Ph, C-1′′, C-2a, C-4b, C-5b, C-2b), 77.91 (1 C, C-1a), 79.19 (1 C, C-3b), 80.91 (1 C, C-3a), 81.24 (1 C, C-4a), 82.01 (1 C, C-6a), 83.18 (1 C, C-5a), 98.35 (1 C, C-1b), 113.69 (2 C, C_{PMB}), 127.37−138.81 (57 C, Ph), 159.0 (1 C, C_{OMe}) ppm. $C_{88}H_{95}N_3O_{13}Si$ (1430.8): calcd. C 73.87, H 6.69, N 2.90; found C 73.63, H 6.78, N 2.35.

6-*O*-[(2*R*)-2-Azido-3-hydroxypropyl]-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-L-*myo*-inositol (34): Compound **34** was synthesized following the procedure described for compound **20**. Compound **33** (1.47 g, 1.03 mmol) gave **34** (1.23 g, 92%) as a colourless syrup. $[\alpha]_D$ = +15.6 (*c* = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.15 (s, 1 H, OH), 3.17 (dd, $J_{1,2}$ = 1.9, $J_{1,6}$ = 9.9 Hz, 1 H, 1a-H), 3.26−3.36 (m, 2 H, 3a-H, 5a-H), 3.38−3.69 (m, 7 H, 3′′-H, 2′′-H, 6b-H, 4a-H, 6a-H), 3.71 (m, 1 H, 2b-H), 3.75−3.83 (m, 4 H, OMe, 3b-H), 3.85−3.95 (m, 2 H, 1′′-H), 4.01−4.09 (m, 2 H, 4b-H, 5b-H), 4.32−4.71, 4.72−4.88 (m, 17 H, CH_2−Ph, 2a-H), 5.42 (d, 1 H, 1b-H), 6.75−6.84 (m, 2 H, H_{PMB}), 7.04−7.35 (m, 37 H, ArH) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 55.25 (1 C, OMe), 62.06 (1 C, C-3′′), 62.65 (1 C, C-2′′), 68.95 (1 C, C-6b), 71.09−76.0 (13 C, CH_2Ph, C-1′′, C-2a, C-4b, C-5b, C-2b), 77.46 (1 C, C-1a), 79.1 (1 C, C-3b), 80.80 (1 C, C-3a), 81.34 (1 C, C-4a), 81.73 (1 C, C-6a), 82.29 (1 C, C-5a), 98.45 (1 C, C-1b), 113.83 (2 C, C_{PMB}), 127.4−138.61 (45 C, Ph), 159.21 (1 C, C_{OMe}) ppm. $C_{72}H_{77}O_{13}N_3$·0.5H_2O (1201.4): calcd. C 71.98, H 6.54, N 3.50; found C 71.96, H 6.38, N 2.97.

6-*O*-[(2*S*)-2-Azido-2-(benzyloxycarbonyl)ethyl]-3,4,5-tri-*O*-benzyl-1-*O*-(4-methoxybenzyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-L-*myo*-inositol (35): Compound **35** was synthesized following the procedure described for compound **22**. Compound **34** (1.15 g, 0.96 mmol) gave **35** (1.15 g, 92%) as a colourless syrup. $[\alpha]_D$ = +29.1 (*c* = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.15 (dd, $J_{1,2}$ = 1.8, $J_{1,6}$ = 9.7 Hz, 1 H, 1a-H), 3.25−3.40 (m, 3 H), 3.55 (m, 2 H), 3.63−3.85 (m, 3 H), 3.76 (s, 3 H, OMe), 3.93 (dd, *J* = 3.9, *J* = 6.1 Hz, 1 H), 4.40−4.24 (m, 4 H), 4.30−4.69, 4.70−4.90 (m, 17 H, CH_2−Ph, 2a-H), 4.99 (d, 1 H, $J_{gem.}$ = 12.2 Hz, COOCH_2−Ph), 5.20 (d, 1 H, $J_{gem.}$ = 12.2 Hz, COOCH_2−Ph), 5.41 (d, *J* = 1.4 Hz, 1 H, 1b-H), 6.76−6.83 (m, 2 H, H_{PMB}), 7.06−7.39 (m, 42 H, ArH) ppm. $C_{79}H_{81}N_3O_{14}$ (1296.5): calcd. C 73.19, H 6.30, N 3.24; found C 72.87, H 6.35, N 2.95.

6-*O*-[(2*S*)-2-Azido-2-(benzyloxycarbonyl)ethyl]-3,4,5-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-L-*myo*-inositol (36): Compound **36** was synthesized following the procedure described for compound **24**. Compound **35** (1.10 g, 0.85 mmol) gave **36** (828 mg, 83%) as a colourless syrup. $[\alpha]_D$ = +3.9 (*c* = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.83 (d, *J* = 4.2 Hz, 1 H, OH), 3.38−3.45 (m, 4 H), 3.65−3.85 (m, 5 H), 3.89−4.00 (m, 2 H), 4.05−4.27 (m, 4 H), 4.42−4.70, 4.71−4.92 (m, 14 H, CH_2−Ph), 5.13 (d, 1 H, $J_{gem.}$ = 12.1 Hz, COOCH_2−Ph), 5.22 (d, 1 H, $J_{gem.}$ = 12.1 Hz, COOCH_2−Ph), 5.27 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1b-H), 7.11−7.40 (m, 40 H, ArH) ppm. $C_{71}H_{73}N_3O_{13}$ (1176.4): calcd. C 72.49, H 6.26, N 3.57; found C 72.32, H 6.27, N 3.15.

6-*O*-[(2*S*)-2-Azido-2-(benzyloxycarbonyl)ethyl]-3,4,5-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-L-*myo*-inosit-1-yl-[benzyl]-[(2*R*)-2,3-bis(myristoyloxy)propyl]-phosphate (37a,b): Compound **37a,b** was synthesized following the procedure described for compound **26a,b**. Compound **36** (1.10 g, 0.85 mmol) gave the mixture of diastereomeric compounds **37a,b** (456 mg, 71%) as a colourless syrup. $[\alpha]_D$ = +7.6 (*c* = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.78−0.93 (t, 6 H, Me), 1.03−1.37 (s, 40 H, CH_2-chain), 1.44−1.65 (m, 4 H, COCH_2CH_2R), 2.16−2.35 (m, 4 H, COCH_2CH_2R), 3.30-.40 (m, 2 H, 3a-H, 5a-H), 3.53−3.87 (m, 6 H, 1′′-H, 6a-H, 4a-H, 3b-H, 2b-H), 3.90−4.00 (m, 3 H, 2′′-H, 5b-H, 6b-H,), 4.03−4.28 (m, 7 H, 1′-H, 3′-H, 6b-H, 1a-H, 4a-H), 4.34−4.90, (m, 15 H, 2a-H, CH_2-Ph), 5.02−5.14, 5.16−5.28 (m, 5 H, 2′-H, COOCH_2−Ph, POCH_2Ph), 5.30 (d, 0.5 H, $J_{1,2}$ = 1.5 Hz, 1b-H), 5.37 (d, 0.5 H, 1b-H), 7.02−7.44 (m, 45 H, ArH) ppm. ^{31}P NMR (242.9 MHz, $CDCl_3$): δ = −0.1407 (s, P), 0.0651 (s, P) ppm. MALDI-MS (positive mode, matrix DHB, THF) $[M + Na]^+$: calcd. *m*/*z* = 1864.4; found *m*/*z* = 1863.8.

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