JOC The Journal of Organic Chemistry

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Resolution of Orthogonally Protected *myo*-Inositols with Novozym 435 Providing an Enantioconvergent Pathway to Ac_2PIM_1

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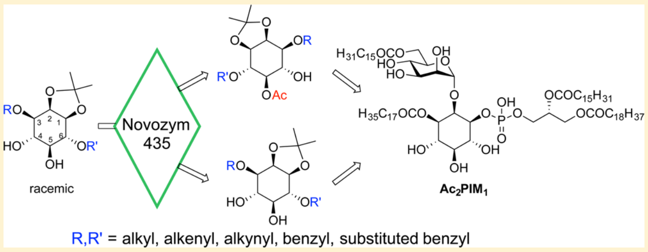
Supporting Information

ABSTRACT: Orthogonally protected chiral *myo*-inositol derivatives are important intermediates for higher order *myo*-inositol-containing compounds. Here, the use of the immobilized enzyme Novozym 435 to efficiently catalyze the acetylation of the 5*R* configured enantiomer of racemic 1,2-*O*-isopropylidene-*myo*-inositols possessing chemically and sterically diverse protecting groups at O-3 and O-6 is described. The resolutions were successful with allyl, benzyl, 4-bromo-, 4-methoxy-, 4-nitro-, and 4-(3,4-dimethoxyphenyl)benzyl, propyl, and propargyl protection at O-6 in combination with either allyl or benzyl groups at O-3. Bulky protecting groups slow the rate of acetylation. No reaction was observed for 3,6-di-*O*-triisopropylsilyl-1,2-*O*-isopropylidene-*myo*-inositol. The utility of this methodology was demonstrated by the first reported synthesis of an Ac_2PIM_1 (**9**), which used both enantiomers of the resolved 3-*O*-allyl-6-*O*-benzyl-1,2-*O*-isopropylidene-*myo*-inositol in a convergent synthesis.

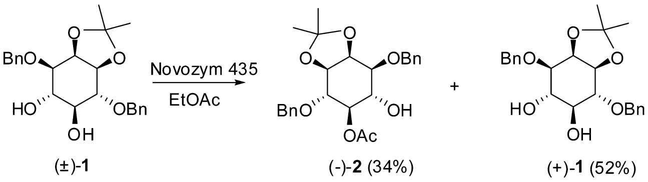


R,R' = alkyl, alkenyl, alkynyl, benzyl, substituted benzyl

■ INTRODUCTION

Phosphatidylinositol phosphates (PIPs),[1] glycophosphatidylinositols (GPIs),[2] phosphatidylinositol mannosides (PIMs), and lipomannans (LMs)[3] are examples of synthetically accessible classes of cell membrane anchors and signaling molecules that have significant roles in various biological processes. The structural complexity and diversity of these inositol-containing (glyco-)phospholipids makes the isolation of discrete compounds from cell wall extracts for biological evaluation difficult. Chemical synthesis[4] has provided a solution, but there are still synthetic challenges that need to be overcome to access these molecules. Many of the syntheses that have been reported to date use various strategies that start with the achiral cyclitol *myo*-inositol and involve a desymmetrization step to access an enantiomerically enriched or pure intermediate. An enantiodivergent approach reported by Miller et al.[5] utilizes a peptide-catalyzed phosphorylation of *meso*-configured inositols for the syntheses of 1D- and 3D-*myo*-inositol phosphates. However, approaches that have proven to be the most used are where the reactions of *myo*-inositol or protected *myo*-inositols with chiral auxilaries such as L-camphor,[6] (*R*)- and (*S*)-mandelic acid,[7] or L-menthyl derivatives[8] lead to diastereoisomers that can be separated by either chromatography or crystallization. Subsequent removal of the chiral auxiliary provides the homochiral inositol fit for derivatization. For targets containing carbohydrate groups glycosylation results in the formation of diastereoisomeric mixtures that are generally separated by chromatography.[9] The latter has the advantage that the chiral derivatizing agent is also a component of the target. Both approaches suffer from the fact that only one stereoisomer is useful and half of a valuable intermediate is generally wasted. More recently, the use of immobilized lipases that effect a kinetic resolution of racemic *myo*-inositol derivatives have been reported. Simas et al.[10,11] demonstrated the kinetic resolution of (±)-1,2-*O*-isopropylidene-3,6-di-*O*-benzyl-*myo*-inositol (**1**) with ethyl acetate using the immobilized enzyme *Candida antarctica* lipase B (Novozym 435), which gave acetate (−)-**2** in 34% yield with an ee of 99% (Scheme 1). The starting material was recovered enriched in enantiomer (+)-**1**. The use of vinyl acetate as the acetylating reagent increased the conversion to 49%.

Scheme 1. Kinetic Resolution by Simas et al.[10,11]

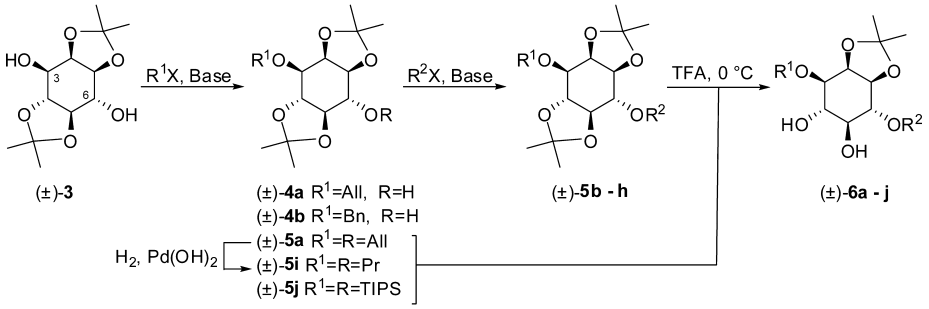


Further to this work Simas et al.[12] reported the kinetic resolution of (±)-1,3,4-tri-*O*-benzyl-*myo*-inositol using Novozym 435 and vinyl acetate. The conversion into (−)-5-*O*-acetyl-1,3,6-tri-*O*-benzyl-L-*myo*-inositol was in 43% yield with an ee of 98%. In a similar fashion (±)-4,6-di-*O*-benzyl-*myo*-inositol was successfully resolved using Lipozyme TL-IM.[13]

Received: August 18, 2014
Published: October 22, 2014

dx.doi.org/10.1021/jo5019188 | *J. Org. Chem.* 2014, 79, 10916−10931

Scheme 2. General Synthesis of Enzyme Substrates[a]



[a]Protecting groups R^1 and R^2 are given in Table 1.

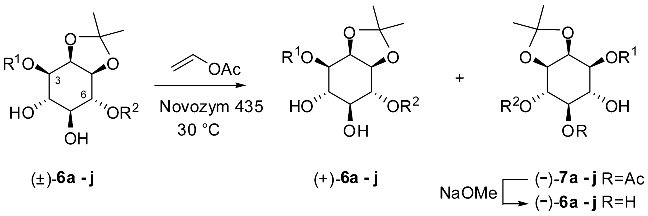
Despite the success of such lipase-catalyzed resolutions, there are relatively few examples where this methodology has been used for the syntheses of lipidated inositols. The advantages of a chemoenzymatic approach over a chemical resolution are that the desymmetrization reaction is catalytic and applicable to scale-up and the immobilized enzyme provides easily separable single enantiomers of *myo*-inositol precursors efficiently and economically. However, the immobilized lipase-catalyzed kinetic resolution of racemic *myo*-inositol derivatives that have a high degree of orthogonal protection, suitable for the synthesis of complex molecules such as GPIs and PIMs, has yet to be explored. Herein, we report our investigation into the Novozym 435 catalyzed kinetic resolution of racemic 1,2-*O*-isopropylidene-*myo*-inositols possessing different protecting groups at the O-3 and O-6 positions to determine the scope and limitations of this methodology. Furthermore, we then demonstrate their use by the first total synthesis of mycobacterial cell wall component Ac$_2$PIM$_1$.

■ RESULTS AND DISCUSSION

A range of O-3 and O-6 protected 1,2-*O*-isopropylidene-*myo*-inositols were synthesized from (±)-1,2:4,5-di-*O*-isopropylidene-*myo*-inositol ((±)-**3**), as shown in Scheme 2, to evaluate whether steric or electronic factors influence the reactivity of these molecules with the enzyme. The only examples utilizing Novozym 435 for the kinetic resolution of *myo*-inositol derivatives contain benzyl protection at O-4/O-6, adjacent to the acylation site. We proposed to explore alternative groups that include substituted aromatic, aliphatic, and sterically demanding silyl groups which are orthogonal to those at O-1/O-3 as well as the acetal protecting group. Also reported are a propargyl and *p*-bromobenzyl (PBB) group which can be further modified for the attachment of fluorescent probes or biologically active cargo.

The synthesis started with selective alkylation at the less hindered C-3 hydroxyl group of (±)-**3**,[14] with sodium hydride (NaH) and either allyl or benzyl bromide providing the allyl and benzyl ethers (±)-**4a** and (±)-**4b**, respectively. A small amount (10%) of the bis-allyl ether (±)-**5a** was recovered from the former reaction. The reaction of (±)-**4b** with NaH and allyl bromide gave (±)-**5b** in good yield. Protection of the C-6 hydroxyl group of 3-*O*-allyl-1,2:4,5-di-*O*-isopropylidene-*myo*-inositol ((±)-**4a**) gave the further six intermediates (±)-**5c**–**h**. The aromatic protecting groups of benzyl (±)-**5c**, *p*-methoxybenzyl (PMB) (±)-**5e**, *p*-(3,4-dimethoxyphenyl)benzyl (DMPB) (±)-**5f**, and PBB (±)-**5g** were installed using NaH and the requisite alkyl bromide. Installation of the propargyl moiety was achieved with NaH and propargyl chloride in the presence of tetrabutylammonium iodide (TBAI) to give (±)-**5d**, while the *p*-nitrobenzyl (PNB) protecting group in (±)-**5h** was incorporated using a Ag$_2$O-promoted alkylation with 4-nitrobenzyl bromide in CH$_2$Cl$_2$. The 3,6-di-*O*-propyl intermediate (±)-**5i** was prepared by catalytic hydrogenation of (±)-**5a**, and 3,6-di-*O*-triisopropylsilyl-1,2-*O*-isopropylidene-*myo*-inositol ((±)-**5j**) was synthesized by reaction of (±)-**3** with triisopropylsilyl trifluoromethanesulfonate (TIPSOTf) and triethylamine. The more labile 4,5-trans-fused isopropylidene group in intermediates (±)-**5a**–**j** was selectively hydrolyzed with TFA in CH$_2$Cl$_2$ at 0 °C, affording substrates (±)-**6a**–**j** fit for enzymatic resolution.

Table 1. Desymmetrization of Substituted *myo*-Inositols with Novozym 435



				ee (%)		
entry	reactant	R^1	R^2	(−)-**6**	(+)-**6**	conversn (%)[a]
1	(±)-**6a**	All	All	>98	>98	49
2	(±)-**6b**	Bn	All	>98	>98	50
3	(±)-**6c**	All	Bn	>98	>98	50
4	(±)-**6d**	All	propargyl	>98	>98	50
5	(±)-**6e**	All	PMB	>98	98	49
6	(±)-**6f**	All	DMPB	>98	42	24
7	(±)-**6g**	All	PBB	98	86	44
8	(±)-**6h**	All	PNB	>98	86	44
9	(±)-**6i**	Pr	Pr	>98	>98	50
10	(±)-**6j**	TIPS	TIPS	N/A	N/A	0

[a]Based on the ^{1}H NMR spectra (500 MHz, CDCl$_3$).

The kinetic resolutions of (±)-**6a**–**j** were carried out with vinyl acetate, as both reactant and solvent, and Novozym 435 at 30 °C for 24 h. The results are shown in Table 1. The conversions were determined by integration of relevant proton signals in the ^{1}H NMR spectra of the aforementioned reaction. To assess the enantiomeric excess of each product, isolated inositol acetates (−)-**7** were converted into inositols (−)-**6** and analyzed by chiral HPLC using a charged aerosol detector (CAD) (see Figure 1 for a representative example). Pleasingly, Novozym 435 converted the di-*O*-allyl-protected substrate (±)-**6a** into the monoacetate (−)-**7a** in a 46% isolated yield

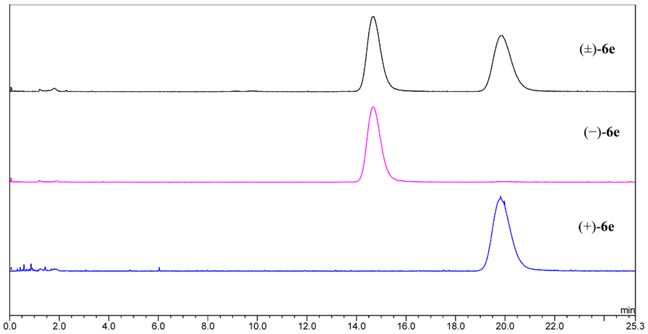
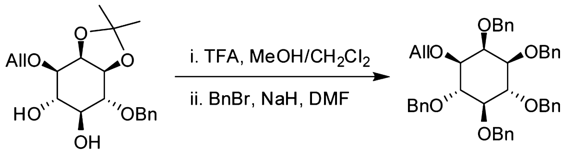


Figure 1. Chiral HPLC analysis of the resolution of **6e** using a (*R*,*R*)-Whelk-O 1 column (5 μm; 100 Å, 4.6 × 250 mm) with a 94/6 hexane/2-propanol mixture (1.5 mL/min) as the mobile phase at 40 °C.

with an ee of >98% (entry 1). Unreacted (+)-**6a** was recovered in 41% yield with >98% ee. The orthogonally protected benzyl allyl ethers (±)-**6b,c** resulted in efficient kinetic resolutions, with the corresponding acetates being isolated in high yields and ee values (entries 2 and 3). Both electron-withdrawing and -donating substituents on the 4-*O*-benzyl protecting group were well tolerated (entries 5 and 8), with acetate (−)-**7e** being isolated in 45% yield with 98% ee and recovered **6e** isolated in 48% yield (ee > 98%). The resolution of inositols **6d,g**, containing groups that could be modified by either copper-catalyzed azide−alkyne cycloaddition (CuAAC) or cross-coupling reactions, gave high conversions to the monoacetates **7d,g** with high ee's (entries 4 and 7). Unfortunately, the ee of **6d** was unable to be determined directly by chiral HPLC using either a Regis (*R,R*)-Whelk-O 1 or Chiracel OD-H column. Instead, both (−)-**6d** and (+)-**6d** were subjected to hydrogenation conditions and analyzed as the corresponding propyl ether derivatives. Unsaturation in the protecting group at O-6 was not essential, as resolution of di-*O*-propyl ether (±)-**6i** gave (−)-**7i** and recovered (+)-**6i** in both high yield and high ee (entry 9). The reaction of the bulkier DMPB-protected[15] inositol (±)-**6f** was slow, culminating in the acetate **7f** being isolated in 18% yield (ee >98%). To further probe the extent of steric constraint tolerated by the enzyme, inositol (±)-**6j** with the bulky TIPS protecting groups at O-4 and O-6 was subjected to the reaction conditions and unsurprisingly remained unreactive with no evidence of acylation by ^{1}H NMR spectroscopy.

To unequivocally prove that we had correctly identified the absolute stereochemistry of inositols (−)-**7a−i**, we embarked on a synthesis that converted (+)-**6c** into the known inositol **8** (Scheme 3). Removal of the isopropylidene group of (+)-**6c** followed by global benzylation gave inositol (−)-**8**. The ^{1}H and ^{13}C NMR spectra of the key intermediate **8** matched those reported by Aneja et al.[16] and Elie et al.,[17] as did the specific rotation, $[\alpha]_D^{20}$ = −1.5° (*c* 1.1, $CHCl_3$) (lit.[16] $[\alpha]_D^{20}$ = −2.3° (*c* 1, $CHCl_3$)).

Scheme 3. Synthesis of Known Intermediate 8



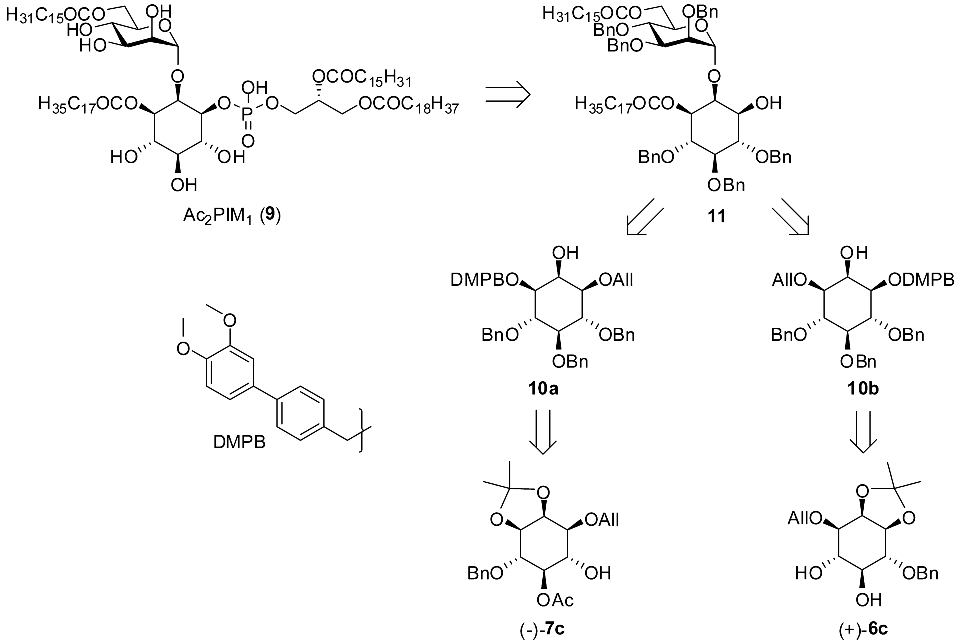
(+)-**6c** (-)-**8**

The relative ease of this methodology in successfully resolving *myo*-inositols prompted us to utilize it in the first synthesis of the complex mycobacterial cell wall phospholipid, Ac_2PIM_1 (**9**). McConville et al. and Besra et al.[18] have found that Ac_1PIM_1, which is acylated at O-6′ of the mannosyl residue, is a biosynthetic precursor of the more abundant Ac_1PIM_2s. Access to highly lipidated Ac_2PIM_1, which is further acylated at O-3 of the inositol, might be useful to determine if these molecules are part of the biosynthetic pathway to higher order Ac_2PIMs. A retrosynthetic analysis of Ac_2PIM_1 (**9**) showed that it could be accessed via an enantioconvergent synthesis from both components of the resolution of (±)-**6c**, i.e. (−)-**7c** and (+)-**6c**, both of which were available in gram quantities (Scheme 4). Routine manipulation of the protecting groups of each would provide the enantiomeric inositols **10a,b**, which would serve as precursors to the key intermediate **11**. The choice of DMPB as a protecting group was made on the basis that it is orthogonal to both benzyl and allyl groups and is stable to reaction conditions required for mannosylation and phosphatidylation.[4b,15]

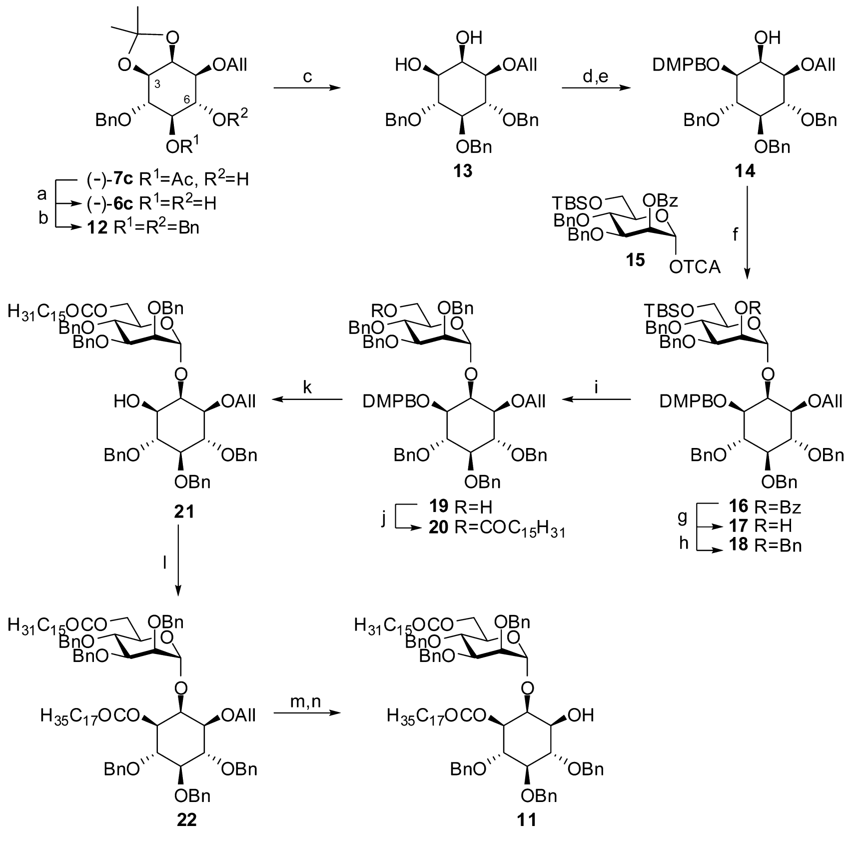
The forward synthesis of intermediate **11** from (−)-**7c** started with removal of the acetate to give (−)-**6c** and then benzylation to afford tri-*O*-benzyl ether **12** (Scheme 5). Acidic hydrolysis of the isopropylidene group gave diol **13**, which was selectively protected at O-3 via a stannylene acetal to give the protected inositol **14**. Mannosylation with the orthogonally protected mannosyl trichloroacetimidate donor **15** gave pseudodisaccharide **16** in an excellent yield of 92%. Zemplén deprotection of the O-2′ benzoate via **17** followed by benzylation afforded **18** in 93% yield for the two steps. Acidic methanolysis of the O-6′ silyl protecting group and acylation with palmitic acid gave the O-6′ palmitate **20** in 71% yield over the two steps. Deprotection of the DMPB ether was achieved by treatment with TFA and cation scavenger 3,4-(methylenedioxy)toluene[15] to give alcohol **21** in good yield. Esterification of the C-3 hydroxyl group with stearic acid gave allyl-inositol **22**, which upon treatment with a catalytic amount of hydrogen-activated (1,5-cyclooctadiene)bis(methyldiphenylphosphine)iridium(I) hexafluorophosphate followed by an oxymercuration protocol provided key intermediate **11** in 18% overall yield for the 12 steps from (−)-**7c**.

Replacing inositol (−)-**6c** with its enantiomer (+)-**6c**, which was isolated in 49% yield (ee > 98%) from (±)-**6c**, in the synthesis would produce a series of intermediates where the O-1 and O-3 protecting groups are interchanged. Reversing the order of removal of the DMPB and allyl protecting groups should converge to give key intermediate **11**, as shown in Scheme 6. Inositol (+)-**6c** was benzylated, and the acetal protecting group was hydrolyzed to give the diol *ent*-**13**. Stannylene acetal mediated alkylation of O-1 with DMPBBr provided *ent*-**14** in moderate yield (71%) which, upon glycosylation with either mannosyl donor **15** or **23**,[4b] gave pseudodisaccharide **24**, both in good yield. Protecting group manipulation followed by acylation afforded palmitate **27**. Deallylation, acylation, and hydrolysis of the DMPB ether, all under the same conditions used in Scheme 5, gave pseudodisaccharide **11**. Spectroscopic and optical data of **11** were consistent with those from those for the preparation from (−)-**7c**. The overall yield for the 11-step sequence from (+)-**6c** was 24%.

Scheme 4. Retrosynthetic Analysis of Ac_2PIM_1 (9)



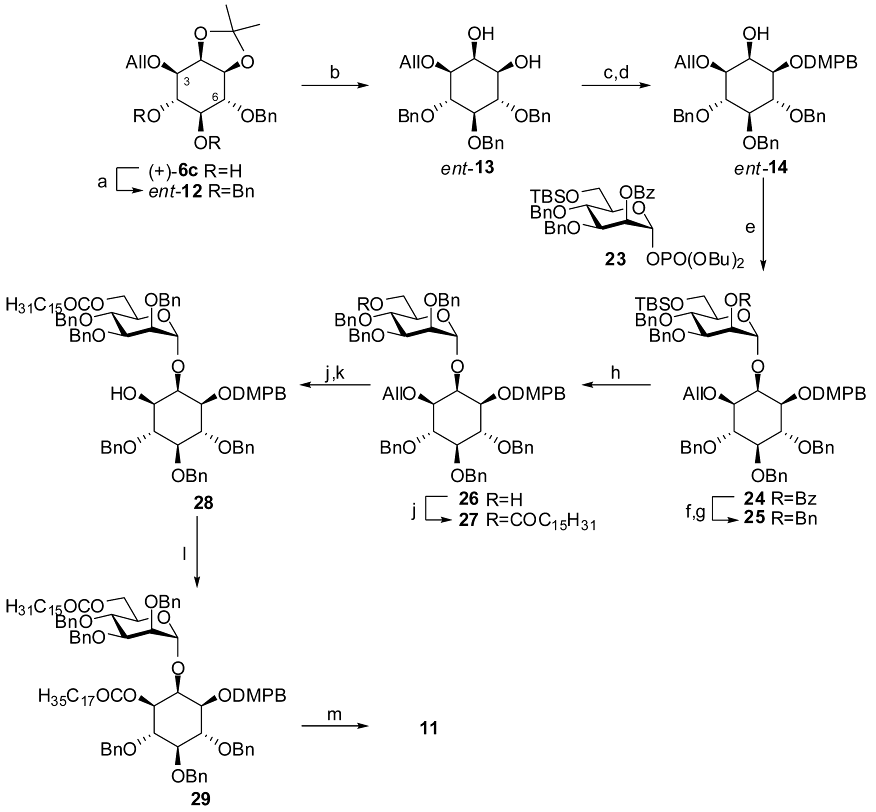
Scheme 5. Synthesis of Common Intermediate 11 from Acetylated Inositol (−)-7c[a]



[a]Reagents and conditions: (a) IRA-400 (OH^-), MeOH, room temperature, 94%; (b) NaH, BnBr, DMF, room temperature, 97%; (c) TFA, MeOH, CH_2Cl_2, room temperature. 93%; (d) $^n Bu_2SnO$, toluene, reflux; (e) CsF, 4-(3,4-dimethoxyphenyl)benzyl bromide (DMPBBr), DMF, 50 °C, 69%; (f) TMSOTf, **15**, toluene, −78 °C, 92%; (g) NaOMe, MeOH, room temperature, 98%; (h) NaH, BnBr, DMF, room temperature, 94%; (i) AcCl, CH_2Cl_2, MeOH, room temperature, 89%; (j) $C_{15}H_{31}COOH$, DMAP, DCC, CH_2Cl_2, room temperature, 80%; (k) TFA, 3,4-(methylenedioxy)-toluene, CH_2Cl_2, room temperature, 83%; (l) $C_{17}H_{35}COOH$, DMAP, DCC, CH_2Cl_2, room temperature. 83%; (m) (COD)($MePPh_2$)$IrPF_6$, H_2, THF, room temperature; (n) HgO, $HgCl_2$, acetone, H_2O, 100 °C, 71%.

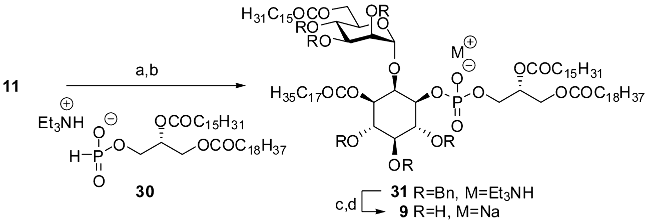
Phosphatidylation of **11** was achieved using *H*-phosphonate **30**[4b,c] and gave, after oxidation with iodine in pyridine, the protected PIM **31** in 87% yield (Scheme 7). After the triethylammoniun cation was exchanged for sodium, global

Scheme 6. Synthesis of Common Intermediate 11 from Inositol (+)-6c[a]



[a]Reagents and conditions: (a) NaH, BnBr, DMF, room temperature, 99%; (b) TFA, MeOH, CH_2Cl_2, room temperature, 81%; (c) ^{n}Bu$_2$SnO, toluene, relux, (d) CsF, DMPBBr, DMF; 50 °C, 71%; (e) either TMSOTf, **15**, toluene, 0 °C, 72%, or TBSOTf, **23**, toluene, −78 °C, 88%; (f) NaOMe, MeOH, room temperature, 81%; (g) NaH, BnBr, DMF, room temperature, 96%; (h) AcCl, CH_2Cl_2, MeOH, room temperature, 99%; (i) $C_{15}H_{31}COOH$ DMAP, DCC, CH_2Cl_2, room temperature, 99%; (j) (COD)($MePPh_2$)$IrPF_6$, H_2, THF, room temperature; (k) HgO, $HgCl_2$, acetone, H_2O, 100 °C, 92%; (l) $C_{17}H_{35}COOH$, DMAP, DCC, CH_2Cl_2, room temperature; 93%; (m) TFA, 3,4-(methylenedioxy)toluene, CH_2Cl_2, room temperature, 76%.

Scheme 7. Synthesis of Ac_2PIM_1 (9) from Common Intermediate 11[a]



[a]Reagents and conditions: (a) **30**, py, PivCl, room temperature; (b) I_2, py, H_2O, TEAB; room temperature. 87%; (c) DOWEX 50WX8-200 (Na^+), $CHCl_3$, MeOH, room temperature; (d) Pd/C, H_2, CH_2Cl_2, MeOH, room temperature. 98%.

hydrogenolysis of the benzyl protecting groups gave the target compound (16:0,18:0)(19:0,16:0)PIM_1 as its sodium salt **9** in 98% yield.

In conclusion, we have shown that the Novozym 435 efficiently catalyzes the acetylation of racemic 1,2-*O*-isopropylidene-*myo*-inositols bearing a range of protecting groups at O-3 and O-6, resulting in the formation of readily separable compounds. In general, the conversions are high, as are the ee values of the resolved products. Alkyl, alkenyl, alkynyl, and aromatic groups with either electron-withdrawing or -donating groups at O-3 are tolerated as substrates by the enzyme. However, bulky protecting groups slow the rate of acetylation. No reaction was observed for substrate (±)-**6j**, possessing triisopropylsilyl ethers at O-3 and O-6. The utility of this methodology was demonstrated by the first reported synthesis of an Ac_2PIM_1, which used both components of the resolution in a synthesis which converged at pseudodisaccharide **11**. Manipulation of the protecting groups of (−)-**7c** and (+)-**6c**, from the resolution of (±)-**6c**, gave orthogonally protected inositol **14** and *ent*-**14**, both of which were transformed into the key intermediate, pseudodisaccharide **11**. Phosphatidylation and global hydrogenolysis of the benzyl groups afforded Ac_2PIM_1 (**9**).

■ EXPERIMENTAL SECTION

General Experimental Considerations. Anhydrous solvents were sourced commercially and used without further treatment unless stated otherwise. Flash column chromatography was performed on silica cartridges (40 μm) or silica gel (40−63 μm). All flash chromatography solvents were AR grade. Petroleum ether used was either bp 40−60 or 60−80 °C range. All compounds were isolated after silica gel column chromatography, and fractions collected were one spot by thin-layer chromatography (TLC). TLC was performed on aluminum sheets coated with 60 F_{254} silica and were visualized under an UV lamp and/or with Hanessian's stain with subsequent charring. Specific optical rotations were measured at ambient temperature, unless otherwise stated, using a polarimeter with a cell of path length 1.0 dm at the wavelength and concentration (g/100 mL) and in the solvent indicated. ^{1}H NMR spectra were obtained at

500 MHz and were referenced to tetramethylsilane at 0 ppm (internal standard) or to the residual solvent peak (CHCl$_3$ 7.26 ppm, CHD$_2$OD 3.31 ppm). ^{13}C NMR spectra were recorded at 126 MHz and referenced to tetramethylsilane at 0 ppm (internal standard) or to the deuterated solvent peak (CDCl$_3$ 77.0 ppm, CD$_3$OD 49.0 ppm). CDCl$_3$−CD$_3$OD solvent mixtures were always referenced to the methanol peak. ^{31}P NMR spectra were recorded at 202 MHz with H$_3$PO$_4$ (δ 0.0 ppm) as the external reference. High-resolution electrospray ionization (ESI) mass spectra were recorded on Q-TOF mass spectrometers. Analytical chiral HPLC data were obtained with a charged aerosol detector (CAD) using a (*R*,*R*)-Whelk-O 1 column (5 μm; 100 Å, 4.6 × 250 mm) eluted with a 94/6 hexane/2-propanol mixture (1.5 mL/min) at 40 °C, except for compound (±)-**6f**, which was eluted with a 70/30 hexane/2-propanol mixture. Melting points were determined using a automatic melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded on FT-IR spectrometers (with a diamond attenuated total reflectance (ATR) top plate). The error on the quoted values for microanalyses is ±0.3%.

(±)-1-*O*-Allyl-2,3:5,6-di-*O*-isopropylidene-*myo*-inositol ((±)-4a). Allyl bromide (1.0 mL, 12 mmol) and then sodium hydride (60% in oil, 0.7 g, 29 mmol) were added to a solution of diol **3** (2.486 g, 8.40 mmol) in dry THF (150 mL) at 0 °C under nitrogen. The reaction mixture was heated for 6 h under reflux. The reaction mixture was quenched with water, extracted into EtOAc, and washed with water and then brine, and the organic phase was dried and evaporated. The crude product was purified using column chromatography (EtOAc/PE, 1/2 to 2/1) to give the title compound (±)-**4a**[19] (1.721 g, 68%) and (±)-1,4-di-*O*-allyl-2,3:5,6-di-*O*-isopropylidene-*myo*-inositol (±)-**5a**[19] (0.277 g, 10%), both as white solids.

Data for (±)-**4a**: ν_{max} (cm^{-1}) 3509, 2982, 1644, 1213, 1003, 867; ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.96 (1H, dddd, *J* = 17.1, 10.4, 6.6, 5.5 Hz), 5.30 (1H, ddd, *J* = 17.2, 3.1, 1.5 Hz), 5.22 (1H, ddd, *J* = 10.3, 3.0, 1.2 Hz), 4.46 (1H, t, *J* = 4.6 Hz), 4.31 (1H, ddt, *J* = 12.9, 5.5, 1.4 Hz), 4.22 (1H, ddt, *J* = 12.9, 6.6, 1.2 Hz), 4.00 (1H, dd, *J* = 6.5, 4.8 Hz), 3.96 (1H, dd, *J* = 9.5 Hz), 3.88 (1H, ddd, *J* = 10.6, 6.7, 2.8 Hz), 3.82 (1H, dd, *J* = 10.1, 4.2 Hz), 3.29 (1H, dd, *J* = 10.7, 9.3 Hz), 2.42 (1H, d, *J* = 2.9 Hz), 1.53 (3H, s), 1.45 (3H, s), 1.43 (3H, s), 1.37 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 134.81, 118.45, 112.70, 110.51, 81.92, 78.51, 77.32, 76.54, 75.02, 74.78, 71.41, 28.45, 27.18, 27.12, 26.14 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for C$_{15}$H$_{24}$O$_6$Na 323.1471, found 323.1465. Anal. Calcd for C$_{15}$H$_{24}$O$_6$: C, 59.98; H, 8.05. Found: C, 60.11; H, 8.17.

Data for (±)-**5a**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.04−5.88 (2H, m), 5.34 (1H, dq, *J* = 3.4, 1.6 Hz), 5.30 (1H, dq, *J* = 3.5, 1.7 Hz), 5.24−5.17 (2H, m), 4.48−4.45 (1H, m), 4.35−4.21 (4H, m), 4.09 (1H, dd, *J* = 6.5, 5.2 Hz), 4.00−3.95 (1H, m), 3.79 (1H, dd, *J* = 10.2, 4.3 Hz), 3.66 (1H, dd, *J* = 10.6, 6.5 Hz), 3.33 (1H, dd, *J* = 10.4, 9.5 Hz), 1.54 (3H, s), 1.45 (3H, s), 1.43 (3H, s), 1.38 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 134.80, 134.71, 118.06, 117.28, 112.09, 109.97, 81.42, 80.18, 78.60, 76.86, 76.47, 74.82, 71.27, 71.16, 28.07, 27.02, 26.96, 25.92 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for C$_{18}$H$_{28}$O$_6$Na 363.1778, found 363.1779.

(±)-1-*O*-Benzyl-2,3:5,6-di-*O*-isopropylidene-*myo*-inositol ((±)-4b). Using the procedure for the synthesis of (±)-**4a**, the reaction of benzyl bromide (0.460 mL, 3.88 mmol), sodium hydride (60% in oil, 0.184 g, 7.68 mmol), and (±)-**3** (1.000 g, 3.84 mmol) in dry THF (50 mL) gave after purification by column chromatography (EtOAc/PE, 1/2 to 2/1) the title compound (±)-**4b**[19] (0.915 g, 68%) as a white solid: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46−7.27 (5H, m), 4.90 (1H, d, *J* = 12.6 Hz), 4.79 (1H, d, *J* = 12.6 Hz), 4.32 (1H, t, *J* = 4.4 Hz), 4.11−3.99 (1H, m), 3.97−3.84 (2H, m), 3.79 (1H, dd, *J* = 10.2, 4.2 Hz), 3.26 (1H, dd, *J* = 10.4, 9.4 Hz), 2.38 (1H, d, *J* = 2.8 Hz), 1.55 (3H, s), 1.49 (3H, s), 1.46 (3H, s), 1.34 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.87, 128.42, 128.34, 127.90, 112.50, 110.23, 81.68, 78.36, 77.31, 76.68, 74.58, 74.47, 71.90, 28.23, 26.98, 26.95, 25.89 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for C$_{19}$H$_{26}$O$_6$Na 373.1627, found 373.1617.

Typical Procedure for the Alkylation of (±)-4a and (±)-4b: (±)-4-*O*-Allyl-1-*O*-benzyl-2,3;5,6-di-*O*-isopropylidene-*myo*-inositol ((±)-5b). Allyl bromide (48 μL, 0.56 mmol) and then sodium hydride (60% in oil, 33 mg, 1.4 mmol mmol) were added with stirring to a solution of benzyl ether (±)-**4b** (195 mg, 0.56 mmol) in dry DMF (5 mL) at 0 °C under nitrogen. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with water, diluted with EtOAc, and washed with water and then brine. The organic phase was dried and evaporated. The residue was purified by column chromatography (PE to EtOAc/PE 1/4) to give the title compound (±)-**5b** (135 mg, 62%) as a white solid: ν_{max} (cm^{-1}) 2984, 2933, 745, 697; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46−7.27 (5H, m), 5.93 (1H, ddt, *J* = 17.1, 10.4, 5.8 Hz), 5.31 (1H, dq, *J* = 17.2, 1.7 Hz), 5.20−5.14 (1H, m), 4.92−4.76 (2H, m), 4.33−4.29 (1H, m), 4.26 (2H, dt, *J* = 5.7, 1.4 Hz), 4.07−3.98 (2H, m), 3.74 (1H, dd, *J* = 10.2, 4.3 Hz), 3.65 (1H, dd, *J* = 10.7, 6.3 Hz), 3.29 (1H, dd, *J* = 10.7, 9.5 Hz), 1.54 (3H, s), 1.48 (3H, s), 1.44 (3H, s), 1.33 ppm (1H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ137.97, 134.81, 128.39, 128.32, 127.84, 117.25, 112.11, 109.92, 81.36, 80.15, 78.62, 77.07, 76.80, 74.47, 71.89, 71.23, 28.07, 27.04, 27.02, 25.90 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for C$_{22}$H$_{30}$O$_6$Na 413.1940, found 413.1940.

(±)-1-*O*-Allyl-4-*O*-benzyl-2,3:5,6-di-*O*-isopropylidene-*myo*-inositol ((±)-5c). Using the procedure for the preparation of (±)-**5b**, the reaction of allyl ether (±)-**4a** (1.858 g, 6.18 mmol), sodium hydride (60% in oil, 0.37 g, 15.5 mmol), and benzyl bromide (1.1 mL, 9.28 mmol) gave after purification by column chromatography (EtOAc/PE, 1/2) the title compound (±)-**5c** (2.366 g, 98%) as a white solid: mp 121−122 °C (lit.[20] mp 122−123 °C); ν_{max} (cm^{-1}) 2986, 1216, 868, 738, 695; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39−7.37 (2H, m), 7.34−7.29 (2H, m), 7.26−7.22 (1H, m), 5.96 (1H, dddd, *J* = 22.7, 10.3, 6.5, 5.5 Hz), 5.29 (1H, ddd, *J* = 17.2, 3.0, 1.6 Hz), 5.20 (1H, ddd, *J* = 10.3, 3.0, 1.3 Hz), 4.81 (2H, m), 4.47−4.41 (1H, m), 4.33−4.28 (1H, m), 4.24−4.19 (1H, m), 4.12 (1H, dd, *J* = 6.5, 5.0 Hz), 3.98−3.90 (1H, m), 3.78 (1H, dd, *J* = 10.2, 4.2 Hz), 3.66 (1H, dd, *J* = 10.6, 6.6 Hz), 3.37 (1H, dd, *J* = 10.6, 9.4 Hz), 1.44 (3H, s), 1.43 (3H, s), 1.37 (3H, s), 1.34 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 138.46, 134.91, 128.41, 128.19, 127.69, 118.34, 112.34, 110.22, 81.39, 80.18, 79.07, 77.15, 76.60, 74.96, 72.26, 71.37, 28.14, 27.27, 27.21, 26.18 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for C$_{22}$H$_{30}$O$_6$ 413.1921, found *m/z* 413.1914. Anal. Calcd for C$_{22}$H$_{30}$O$_6$: C, 67.67; H, 7.74. Found: C, 67.85: H 7.81.

(±)-1-*O*-Allyl-2,3;5,6-di-*O*-isopropylidene-4-*O*-propargyl-*myo*-inositol ((±)-5d). Using the procedure for the preparation of (±)-**5b**, the reaction of allyl ether (±)-**4a** (155 mg, 0.52 mmol), sodium hydride (60% in oil, 40 mg, 1.7 mmol), propargyl chloride (70% in toluene, 115 μL, 104 mmol), and tetra-*n*-butylammonium iodide (10 mg, 0.03 mmol) in DMF (5 mL) gave after purification of the crude product by column chromatography (PE to EtOAc/PE, 1/4) the title compound (±)-**5d** (163 mg, 93%) as a white solid: ν_{max} (cm^{-1}) 3245, 2984, 2935; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.01−5.93 (1H, m), 5.32 (1H, dq, *J* = 17.3, 1.7 Hz), 5.24−5.21 (1H, m), 4.48−4.45 (1H, m), 4.45−4.43 (2H, m), 4.36−4.21 (2H, m), 4.08 (1H, ddd, *J* = 6.5, 5.0, 1.7 Hz), 4.00 (1H, td, *J* = 9.8, 1.9 Hz), 3.85 (1H, ddd, *J* = 10.7, 6.6, 1.9 Hz), 3.80 (1H, ddd, *J* = 10.2, 4.2, 1.7 Hz), 3.35−3.30 (1H, m), 2.43 (1H, td, *J* = 2.4, 1.1 Hz), 1.58 (3H, s), 1.46 (11H, s), 1.43 (11H, s), 1.38 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 134.67, 118.11, 112.35, 110.14, 80.79, 79.74, 79.39, 78.20, 77.02, 76.52, 74.73, 74.62, 71.19, 57.64, 28.03, 26.98, 26.92, 25.93 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for C$_{18}$H$_{26}$O$_6$Na 361.1627, found 361.1618.

(±)-1-*O*-Allyl-2,3:5,6-di-*O*-isopropylidene-4-*O*-*p*-methoxybenzyl-*myo*-inositol ((±)-5e). Using the procedure for the preparation of (±)-**5b**, the reaction of allyl ether (±)-**4a** (145 mg, 0.48 mmol), sodium hydride (60% in oil, 29 mg, 1.2 mmol), and *p*-methoxybenzyl bromide (80 μL, 0.59 mmol) in DMF (5 mL) gave after purification of the crude product by column chromatography (EtOAc/CH$_2$Cl$_2$, 1/1) the title compound (±)-**5e** (199 mg, 98%) as a white solid: ν_{max} (cm^{-1}) 2986, 2934, 1614, 1513, 868; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33−7.28 (2H, m), 6.87−6.82 (2H, m), 5.95 (1H, dddd, *J* = 17.0, 10.3, 6.5, 5.5 Hz), 5.29 (1H. dq, *J* = 17.2, 1.6 Hz), 5.22−5.17 (1H, m), 4.73 (2H, s), 4.43 (1H, dd, *J* = 5.0, 4.2 Hz), 4.30 (1H, ddt, *J*= 13.0, 5.5, 1.4 Hz), 4.21 (1H, ddt, *J* = 13.0, 6.5, 1.3 Hz), 4.10 (1H, dd, *J* = 6.5, 5.0 Hz), 3.93 (1H, dd, *J* = 10.2, 9.4 Hz), 3.79−

3.75 (4H, m), 3.64 (1H, dd, *J* = 10.6, 6.5 Hz), 3.35 (1H, dd, *J* = 10.6, 9.4 Hz), 1.44 (3H, s), 1.42 (3H, s), 1.38 (3H, s), 1.34 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 159.36, 134.91, 130.57, 129.85, 118.32, 113.84, 112.30, 110.15, 81.43, 79.84, 79.07, 77.14, 76.58, 74.97, 71.95, 71.36, 55.51, 28.16, 27.27, 27.22, 26.18 ppm; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{32}O_7Na$ 443.2040, found 443.2021.

(±)-1-*O*-Allyl-4-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-2,3:5,6-di-*O*-isopropylidene-*myo*-inositol ((±)-5f). Using the procedure for the preparation of (±)-**5b**, the reaction of allyl ether (±)-**4a** (200 mg, 0.67 mmol), sodium hydride (60% in oil, 40 mg, 1.7 mmol), and 4-(3,4-dimethoxyphenyl)benzyl bromide (281 mg, 0.92 mmol) in DMF (5 mL) gave after purification of the crude product by column chromatography (PE to EtOAc/PE 1/4) the title compound (±)-**5f** (290 mg, 87%) as a white solid: ν_{max} (cm^{-1}) 2928, 1505, 1217, 862; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.54−7.50 (2H, m), 7.47−7.43 (2H, m), 7.13 (1H, dd, *J* = 8.2, 1.9 Hz), 7.10 (1H, d, *J* = 1.9 Hz), 6.94 (1H, d, *J* = 8.2 Hz), 5.98 (1H, dddd, *J* = 17.1, 10.4, 6.5, 5.4 Hz), 5.32 (1H, dq, *J* = 17.3, 1.6 Hz), 5.22 (1H, dq, *J* = 10.4, 1.4 Hz), 4.86 (2H, s), 4.49−4.43 (1H, m), 4.33 (1H, ddt, *J* = 13.0, 5.4, 1.4 Hz), 4.24 (1H, ddt, *J* = 12.9, 6.6, 1.3 Hz), 4.15 (1H, dd, *J* = 6.6, 5.0 Hz), 4.00−3.94 (4H, m), 3.93−3.91 (3H, m), 3.81 (1H, dd, *J* = 10.2, 4.3 Hz), 3.71 (1H, dd, *J* = 10.4, 6.6 Hz), 3.40 (1H, dd, *J* = 10.4, 9.5 Hz), 1.48 (3H, s), 1.46 (3H, s), 1.42 (3H, s), 1.37 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 149.23, 148.68, 140.31, 136.94, 134.72, 134.15, 128.45, 126.69, 119.38, 118.06, 112.13, 111.61, 110.55, 109.98, 81.23, 80.11, 78.89, 76.97, 76.43, 74.82, 71.84, 71.16, 56.03, 55.99, 27.97, 27.06, 27.01, 25.96 ppm; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{38}O_8Na$ 549.2464, found 549.2464.

(±)-1-*O*-Allyl-4-*O*-*p*-bromobenzyl-2,3:5,6-di-*O*-isopropylidene-*myo*-inositol ((±)-5g). Using the procedure for the preparation of (±)-**5b**, the reaction of allyl ether (±)-**4a** (200 mg, 0.67 mmol), sodium hydride (60% in oil, 40 mg, 1.7 mmol), and *p*-bromobenzyl bromide (200 mg, 0.80 mmol) in DMF (5 mL) gave after purification of the crude product by column chromatography (EtOAc/CH$_2$Cl$_2$, 1:1) the title compound (±)-**5g** (310 mg, 99%): ν_{max} (cm^{-1}) 2990, 2934, 867; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49−7.44 (2H, m), 7.31−7.27 (2H, m), 5.98 (1H, dddd, *J* = 17.0, 10.3, 6.5, 5.5 Hz), 5.33 (1H, dq, *J* = 17.2, 1.6 Hz), 5.26−5.22 (1H, m), 4.78 (2H, s), 4.49−4.45 (1H, m), 4.34 (1H, ddt, *J* = 12.9, 5.5, 1.4 Hz), 4.25 (1H, ddt, *J* = 13.0, 6.5, 1.2 Hz), 4.13 (1H, dd, *J* = 6.5, 5.0 Hz), 3.96 (1H, dd, *J* = 10.1, 9.4 Hz), 3.81 (1H, dd, *J* = 10.2, 4.2 Hz), 3.65 (1H, dd, *J* = 10.6, 6.5 Hz), 3.38 (1H, dd, *J* = 10.6, 9.3 Hz), 1.47 (3H, s), 1.45 (3H, s), 1.43 (3H, s), 1.38 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.56, 134.87, 131.51, 129.72, 121.53, 118.39, 112.41, 110.25, 81.33, 80.50, 78.93, 77.12, 76.62, 74.89, 71.47, 71.40, 28.21, 27.27, 27.20, 26.14 ppm; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{29}BrO_6Na$ 491.1040, found 491.1052. Anal. Calcd for $C_{22}H_{29}BrO_6$: C, 56.30; H, 6.23; Br, 17.02. Found: C, 56.39; H, 6.23; Br, 16.87.

(±)-1-*O*-Allyl-2,3:5,6-di-*O*-isopropylidene-4-*O*-*p*-nitrobenzyl-*myo*-inositol ((±)-5h). A mixture of *p*-nitrobenzyl bromide (140 mg, 0.65 mmol), silver oxide (140 mg, 0.60 mmol), and allyl ether (±)-**4a** (116 mg, 0.37 mmol) in dry CH$_2$Cl$_2$ (5 mL) was stirred in the dark at room temperature overnight. The reaction mixture was cooled, quenched with MeOH, and filtered through Celite, which was then washed with CH$_2$Cl$_2$. The solvents were evaporated, and the residue was purified by column chromatography (PE to EtOAc/PE, 1/5) to give the title compound (±)-**5h** (132 mg, 79%) as a white solid: ν_{max} (cm^{-1}) 2990, 2885, 1606, 1515, 1350, 849; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.19 (2H, d, *J* = 8.7 Hz), 7.57 (2H, dt, *J* = 8.8, 0.8 Hz), 5.98 (1H, dddd, *J* = 17.0, 10.3, 6.5, 5.5 Hz), 5.32 (1H, dq, *J* = 17.2, 1.6 Hz), 5.23 (1H, dq, *J* = 10.3, 1.2 Hz), 4.95−4.91 (2H, m), 4.48 (1H, dd, *J* = 5.0, 4.2 Hz), 4.33 (1H, ddt, *J* = 12.9, 5.5, 1.4 Hz), 4.24 (1H, ddt, *J* = 12.9, 6.5, 1.2 Hz), 4.15 (1H, dd, *J* = 6.5, 5.0 Hz), 3.97 (1H, dd, *J* = 10.2, 9.3 Hz), 3.82 (1H, dd, *J* = 10.1, 4.1 Hz), 3.66 (1H, dd, *J* = 10.6, 6.5 Hz), 3.40 (1H, dd, *J* = 10.6, 9.3 Hz), 1.46 (3H, s), 1.45 (6H, s), 1.38 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 147.34, 146.12, 134.62, 127.82, 123.45, 118.17, 112.34, 110.14, 81.21, 81.04, 78.63, 76.94, 76.48, 74.66, 71.23, 70.86, 28.08, 27.06, 26.97, 25.88 ppm; HRMS (ESI-TOF) *m*/*z* [M +Na]$^+$ calcd for $C_{22}H_{29}NO_8Na$ 458.1791, found 458.1783.

(±)-2,3;5,6-Di-*O*-isopropylidene-1,4-di-*O*-propyl-*myo*-inositol ((±)-5i). A mixture of diallyl ether (±)-**5a** (281 mg, 0.83 mmol) and Pearlman's catalyst (6 mg) was dissolved in CH$_2$Cl$_2$ (5 mL) and stirred under an atmosphere of hydrogen at room temperature overnight. The reaction mixture was then filtered through Celite, and the solvents were evaporated. The crude product was purified by column chromatography (PE to EtOAa/PE, 1/1) to give the title compound (±)-**5i** (183 mg, 64%) as a white solid: ν_{max} (cm^{-1}) 2956, 2906, 1460, 1372; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.48 (1H, dd, *J* = 5.0, 4.2 Hz), 4.05 (1H, dd, *J* = 6.4, 5.0 Hz,), 3.95 (1H, dd, *J* = 10.1, 9.4 Hz), 3.76−3.64 (4H, m), 3.63−3.52 (2H, m), 3.30 (1H, dd, *J* = 10.6, 9.4 Hz), 1.66 (4 H, dq, *J* = 22.3, 7.2 Hz), 1.55 (3 H, s), 1.45 (3H, s), 1.43 (3H, s), 1.37 (3 H, s), 0.92 ppm (6H, td, *J* = 7.4, 3.0 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 112.10, 110.00, 81.78, 81.52, 78.97, 76.92, 76.50, 76.49, 72.78, 72.33, 28.38, 27.30, 27.22, 26.13, 23.36, 23.17, 10.62, 10.57 ppm; HRMS (ESI-TOF) *m*/*z* [M +Na]$^+$ calcd for $C_{18}H_{32}O_6Na$ 367.2097, found 367.2091.

(±)-2,3;5,6-Di-*O*-isopropylidene-1,4-di-*O*-triisopropylsilyl-*myo*-inositol ((±)-5j). Triisopropylsilyl triflate was added to a solution of diol (±)-**3** (201 mg, 0.77 mmol) and Et$_3$N (0.65 mL, 4.7 mmol) in CH$_2$Cl$_2$ (5 mL) at 0 °C under Ar over powdered 4 Å molecular sieves. The reaction mixture was stirred overnight at room temperature and then quenched with solid sodium bicarbonate. The reaction mixture was filtered through Celite and the filtrate washed with sodium bicarbonate, extracted into CH$_2$Cl$_2$, and washed with brine. The organic layer was dried and evaporated and the residue purified by column chromatography (PE to EtOAc/PE, 1/99) to give the title compound (±)-**5j** (220 mg, 50%) as a white solid: ν_{max} (cm^{-1}) 2986, 2939, 2867, 1463, 1377; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.30 (1H, t, *J* = 4.4 Hz), 4.09 (1H, dd, *J* = 10.0, 4.3 Hz), 3.99−3.91 (2H, m), 3.87 (1H, t, *J* = 9.7 Hz), 3.24−3.16 (1H, t, *J* = 9.7 Hz), 1.50 (3H,), 1.37 (3H, s), 1.35 (3H, s), 1.32 (3H, s), 1.18−1.02 ppm (42, m); ^{13}C NMR (126 MHz, CDCl$_3$) δ 110.85, 109.14, 83.21, 79.47, 79.01, 77.08, 75.82, 70.68, 28.26, 26.85, 26.83, 25.77, 17.96,17.85, 17.83, 12.44, 12.38 ppm; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{60}O_6Si_2Na$ 595.3826, found 595.3820.

Typical Procedure for the Selective Hydrolysis of (±)-5: (±)-1,4-Di-*O*-allyl-2,3-*O*-isopropylidene-*myo*-inositol ((±)-6a). Water (0.015 mL, 0.83 mmol) and trifluoroacetic acid (TFA) (0.10 mL, 1.3 mmol) were added with stirring to a solution of (±)-**5a** (0.216 g, 0.635 mmol) in dry CH$_2$Cl$_2$ (10 mL) at 0 °C under Ar. After 90 min, the reaction mixture was diluted with EtOAc, washed with sodium bicarbonate then brine. The organic layer was dried, the solvents evaporated, and the residue was purified by column chromatography (EtOAc/PE, 1:1) to give the title compound (±)-**6a**[19] (0.149 g, 78%) as a white solid: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.03−5.89 (2H, m), 5.35−5.28 (2H, m), 5.25−5.17 (2H, m), 4.48−4.36 (2H, m), 4.32−4.16 (3H, m), 4.08 (1H, dd, *J* = 6.9, 5.3 Hz), 3.90 (1H, td, *J* = 9.4, 1.9 Hz), 3.54−3.44 (2H, m), 3.40−3.33 (1H, m), 2.86−2.81 (2H, m), 1.54 (3H, s), 1.38 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 134.81, 134.67, 118.11, 117.42, 110.03, 81.76, 79.31, 76.97, 73.94, 73.03, 72.38, 71.71, 71.49, 28.06, 25.98 ppm; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{24}O_6Na$ 323.1465, found 323.1455.

(±)-4-*O*-Allyl-1-*O*-benzyl-2,3-*O*-isopropylidene-*myo*-inositol ((±)-6b). Using the procedure described for the preparation of (±)-**6a**, treatment of (±)-**5b** (126 mg, 0.32 mmol) in dry CH$_2$Cl$_2$ (5 mL) with water (45 μL, 2.5 mmol) and TFA (45 μL, 0.58 mmol) gave after column chromatography (EtOAc/PE, 1:1) the title compound (±)-**6b** (93 mg, 82%) as a white solid: ν_{max} (cm^{-1}) 3411, 2986, 2926, 1646, 1117, 741, 696; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44−7.27 (5H, m), 5.99−5.85 (1H, m), 5.33−5.23 (1H, m), 5.23−5.13 (1H, m), 4.81−4.73 (2H, m), 4.43−4.34 (1H, m), 4.30 (1H, dd, *J* = 5.0, 3.8 Hz), 4.22−4.16 (1H, m), 4.02 (1H, dd, *J* = 6.9, 5.0 Hz), 3.94 (1H, td, *J* = 9.5, 1.6 Hz), 3.52 (1H, dd, *J* = 9.6, 3.9 Hz), 3.46 (1H, dd, *J* = 9.5, 6.9 Hz), 3.33 (1H, td, *J* = 9.5, 2.0 Hz), 2.64 (1H, d, *J* = 1.9 Hz), 2.61 (1H, d, *J* = 1.9 Hz), 1.54 (3H, s), 1.33 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.85, 134.79, 128.56, 128.14, 128.08, 117.40, 109.96, 81.75, 79.30, 77.11, 74.01, 72.96, 72.66, 72.34, 71.60, 28.08, 25.93 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{19}H_{26}O_6Na$ 373.1627, found 373.1631.

(±)-1-*O*-Allyl-4-*O*-benzyl-2,3-*O*-isopropylidene-*myo*-inositol ((±)-6c). Using the procedure described for the preparation of (±)-**6a**, treatment of (±)-**5c** (2.204 g, 5.64 mmol) in dry CH_2Cl_2 (30 mL) with water (0.100 mL, 5.6 mmol) and TFA (0.870 mL, 11.29 mmol) gave after column chromatography (EtOAc/PE, 1/2 to 2/1) the title compound (±)-**6c** (1.879 g, 95%) as a white solid: ν_{max} (cm^{-1}) 3405, 2996, 1063, 735, 695; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.22 (5H, m), 5.96 (1H, dddd, *J* = 17.2, 10.3, 6.0 Hz), 5.31 (1H, dq, *J* = 17.2, 1.5 Hz), 5.22 (1H, dq, *J* = 2.8, 1.2 Hz), 4.93 (1H, d, *J* = 11.5 Hz), 4.67 (1H, d, *J* = 11.5 Hz), 4.44 (1H, dd, *J* = 5.1, 4.0 Hz), 4.31−4.17 (2H, m), 4.15 (1H, dd, *J* = 6.9, 3.6 Hz), 3.89 (1H, td, *J* = 9.5, 1.7 Hz), 3.56−3.48 (2H, m), 3.40 (1H, td, *J* = 9.5, 2.0 Hz), 2.63 (2H, dd, *J* = 8.2, 1.9 Hz), 1.49 (3H, s), 1.37 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.35, 134.85, 128.67, 128.27, 128.07, 118.42, 110.33, 82.27, 79.55, 77.15, 74.16, 73.62, 73.29, 71.95, 71.66, 28.27, 26.24 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{19}H_{26}O_6Na$ 373.1627, found 373.1609. Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.30; H, 7.63.

(±)-1-*O*-Allyl-2,3-*O*-isopropylidene-4-*O*-propargyl-*myo*-inositol ((±)-6d). Using the procedure described for the preparation of (±)-**6a**, treatment of (±)-**5d** (134 mg, 0.40 mmol) in dry CH_2Cl_2 (5 mL) with water (65 μL, 3.6 mmol) and TFA (65 μL, 0.84 mmol) gave after column chromatography (EtOAc/PE, 1/1) the title compound (±)-**6i** (96 mg, 81%) as a white solid: ν_{max} (cm^{-1}) 3476, 3309, 2980, 2906, 1098; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.02−5.93 (1H, m), 5.33 (1H, dq, *J* = 17.2, 1.5 Hz), 5.24 (1H, dq, *J* = 10.4, 1.3 Hz), 4.55−4.44 (2H, m), 4.45−4.42 (1H, m), 4.31−4.19 (2H, m), 4.07 (1H, dd, *J* = 7.3, 5.0 Hz), 3.93 (1H, td, *J* = 9.5, 1.9 Hz), 3.67 (1H, dd, *J* = 9.8, 7.3 Hz), 3.50 (1H, dd, *J* = 9.8, 4.1 Hz), 3.37 (1H, td, *J* = 9.6, 1.9 Hz), 2.68 (1H, d, *J* = 1.6 Hz), 2.64 (1H, d, *J* = 1.9 Hz), 2.47 (1H, t, *J* = 2.4 Hz), 1.58 (3H, s), 1.38 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.64, 118.16, 110.21, 81.01, 79.84, 78.99, 76.85, 74.88, 73.97, 72.66, 71.75, 71.55, 58.52, 28.09, 26.04 ppm; HRMS(ESI-TOF) *m/z* [M + Na]$^+$ calcd for$C_{15}H_{22}O_6Na$ 321.1314, found 321.1308.

(±)-1-*O*-Allyl-2,3-*O*-isopropylidene-4-*O*-*p*-methoxybenzyl-*myo*-inositol ((±)-6e). Using the procedure described for the preparation of (±)-**6a**, treatment of (±)-**5e** (237 mg, 0.56 mmol) in dry CH_2Cl_2 (5 mL) with water (85 μL, 4.7 mmol) and TFA (85 μL, 1.1 mmol) gave after column chromatography (EtOAc/PE, 1/1) the title compound (±)-**6d** (203 mg, 95%) as a white solid: ν_{max} (cm^{-1}) 3397, 2980, 2923, 1612, 1513, 1100, 867; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.25 (2H, m), 6.89−6.83 (2H, m), 5.96 (1H, ddt, *J* = 17.3, 10.3, 6.0 Hz), 5.30 (1H, dq, *J* = 17.2, 1.5 Hz), 5.21 (1H, dq, *J* = 10.3, 1.3 Hz), 4.86 (1H, d, *J* = 11.1 Hz), 4.59 (1H, d, *J* = 11.1 Hz), 4.42 (1H, dd, *J* = 5.1, 4.0 Hz), 4.26 (1H, ddt, *J* = 12.8, 6.1, 1.3 Hz), 4.19 (1H, ddt, *J* = 12.8, 6.0, 1.4 Hz), 4.12 (1H, dd, *J* = 7.0, 5.1 Hz), 3.91−3.83 (1H, m), 3.78 (3H, s), 3.55−3.44 (2H, m), 3.41−3.32 (1H, m), 2.70 (1H, d, *J* = 1.5 Hz), 2.67−2.63 (1H, m), 1.49 (3H, s), 1.37 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.57, 134.85, 130.47, 129.91, 118.37, 114.08, 110.28, 81.97, 79.60, 77.15, 74.16, 73.29, 73.23, 71.95, 71.66, 55.50, 28.29, 26.23 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{20}H_{28}O_7Na$ 403.1727, found 403.1723.

(±)-1-*O*-Allyl-4-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-2,3-*O*-isopropylidene-*myo*-inositol ((±)-6f). Using the procedure described for the preparation of (±)-**6a**, treatment of (±)-**5f** (271 mg, 0.51 mmol) in dry CH_2Cl_2 (5 mL) with water (60 μL, 3.3 mmol) and TFA (60 μL, 0.77 mmol) gave after column chromatography (EtOAc/PE, 1:1) the title compound (±)-**6f** (250 mg, 80%) as a white solid: ν_{max} (cm^{-1}) 3379, 2918, 1506, 1247, 1064, 866; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.50 (2H, m), 7.46−7.38 (2H, d, *J* = 8.5 Hz), 7.14 (1H, dd, *J* = 8.4, 2.0 Hz), 7.10 (1H, d, *J* = 2.2 Hz), 6.94 (1H, d, *J* = 8.5 Hz), 5.98 (1H, ddt, *J* = 17.2, 10.3, 6.0 Hz), 5.33 (1H, dq, *J* = 17.3, 1.5 Hz), 5.25−5.22 (1H, m), 4.98 (1H, d, *J* = 11.3 Hz), 4.73 (1H, d, *J* = 11.7 Hz), 4.47 (1H, dd, *J* = 5.0, 4.1 Hz), 4.33−4.25 (1H, m), 4.25−4.19 (1H, m), 4.18 (1H, dd *J* = 6.9, 5.0 Hz) 3.95−3.89 (7H, m), 3.58 (1H, dd, *J* = 9.5, 6.9 Hz), 3.52 (1H, dd, *J* = 9.6, 3.9 Hz), 3.43 (1H, td, *J* = 9.5, 1.9 Hz), 2.66 (2H, 2 × d, *J* = 1.9 Hz), 1.52 (3H, s), 1.40 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.26, 148.77, 140.69, 136.77, 134.67, 133.98, 128.56, 126.93, 119.43, 118.15, 111.62, 110.57, 110.15, 82.12, 79.40, 77.02, 73.98, 73.17, 71.74, 71.50, 56.04, 56.01, 28.09, 26.03 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{27}H_{34}O_8Na$ 509.2151, found 509.2145.

(±)-1-*O*-Allyl-4-*O*-*p*-bromobenzyl-5,6-*O*-isopropylidene-*myo*-inositol ((±)-6g). Using the procedure described for the preparation of (±)-**6a**, treatment of (±)-**5g** (311 mg, 0.66 mmol) in dry CH_2Cl_2 (5 mL) with water (100 μL, 5.6 mmol) and TFA (100 μL, 1.3 mmol) gave after column chromatography (EtOAc/PE, 1/1) the title compound (±)-**6g** (270 mg, 95%) as a white solid: ν_{max} (cm^{-1}) 3386, 2976, 2922, 1102, 802; ^{1}H NMR (500 MHz, $CDCl_3$) δ7.47−7.42 (2H, m), 7.26−7.21 (2H, m), 5.95 (1H, ddt, *J* = 17.3, 10.3, 6.0 Hz), 5.30 (1H, dq, *J* = 17.2, 1.5 Hz), 5.22 (1H, dq, *J* = 10.3, 1.3 Hz), 4.86 (1H, d, *J* = 11.8 Hz), 4.65 (1H, d, *J* = 11.9 Hz), 4.43 (1H, dd, *J* = 5.1, 3.9 Hz), 4.26 (1H, ddt, *J* = 12.8, 6.0, 1.3 Hz), 4.18 (1H, ddt, *J* = 12.8, 6.0, 1.3 Hz), 4.11 (1H, dd, *J* = 6.9, 5.1 Hz), 3.87 (1H, td, *J* = 9.5, 1.9 Hz), 3.53−3.46 (2H, m), 3.39 (1H, td, *J* = 9.5, 2.0 Hz), 2.72 (1H, d, *J* = 1.9 Hz), 2.69 (1H, d, *J* = 2.0 Hz), 1.46 (3H, s), 1.36 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.42, 134.77, 131.70, 129.86, 121.85, 118.46, 110.35, 82.38, 79.46, 77.11, 74.06, 73.33, 72.77, 71.90, 71.61, 28.27, 26.22 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{19}H_{25}{}^{79}BrO_6Na$ 451.0727, found 451.0729. Anal. Calcd for $C_{19}H_{25}BrO_6$: C, 53.16; H, 5.87; Br, 18.61. Found: C, 53.27; H, 5.88; Br, 18.74.

(±)-1-*O*-Allyl-2,3-*O*-isopropylidene-4-*O*-*p*-nitrobenzyl-*myo*-inositol ((±)-6h). Using the procedure described for the preparation of (±)-**6a**, treatment of (±)-**5h** (124 mg, 0.28 mmol) in dry CH_2Cl_2 (5 mL) with water (44 μL, 3.1 mmol) and TFA (55 μL, 0.57 mmol) gave after column chromatography (EtOAc/PE, 1/1) the title compound (±)-**6h** (113 mg, 85%) as a white solid: ν_{max} (cm^{-1}) 3408, 2993, 2925, 1603, 1519, 1343, 1091, 842; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24−8.15 (2H, m), 7.59−7.52 (2H, m), 5.98 (1H, ddt, *J* = 17.2, 10.3, 6.0 Hz), 5.33 (1H, dq, *J* = 17.2, 1.5 Hz), 5.25 (1H, dq, *J* = 10.3, 1.3 Hz), 5.02 (1H, d, *J* = 13.2 Hz), 4.88 (1H, d, *J* = 13.2 Hz), 4.47 (1H, dd, *J* = 5.1, 3.9 Hz), 4.29 (1H, ddt, *J* = 12.8, 6.0, 1.3 Hz), 4.20 (1H, ddt, *J* = 12.7, 6.0, 1.3 Hz), 4.15 (1H, dd, *J* = 6.9, 5.1 Hz), 3.89 (1H, td, *J* = 9.5, 1.9 Hz), 3.58−3.49 (2H, m), 3.47 (1H, td, *J* = 9.6, 1.9 Hz), 2.73 (1H, d, *J* = 1.9 Hz), 2.71 (1H, d, *J* = 2.0 Hz), 1.48 (3H, s), 1.39 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.42, 145.97, 134.50, 128.01, 123.56, 118.31, 110.26, 82.85, 79.16, 76.92, 73.76, 73.26, 72.12, 71.64, 71.42, 28.12, 26.02 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{19}H_{25}NO_8Na$ 418.1478, found 418.1477.

(±)-2,3-*O*-Isopropylidene-1,4-di-*O*-propyl-*myo*-inositol ((±)-6i). Using the procedure described for the preparation of (±)-**6a**, treatment of (±)-**5i** (120 mg, 0.35 mmol) in dry CH_2Cl_2 (5 mL) with water (50 μL, 2.8 mmol) and TFA (50 μL, 0.67 mmol) gave after column chromatography (EtOAc/PE, 1/1) the title compound (±)-**6i** (82 mg, 77%) as a white solid: ν_{max} (cm^{-1}) 3413, 2959, 2924, 1462, 1366, 1104; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.43 (1H, dd, *J* = 5.1, 3.9 Hz), 4.04 (1H, dd, *J* = 6.6, 5.2 Hz), 3.86 (1H, td, *J* = 9.2, 1.7 Hz), 3.81 (1H, dt, *J* = 9.3, 6.8 Hz), 3.69 (1H, ddd, *J* = 9.3, 7.1, 6.3 Hz), 3.58−3.53 (1H, m), 3.50 (1H, dt, *J* = 9.3, 7.0 Hz), 3.41−3.36 (2H, m), 3.34 (1H, td, *J* = 9.1, 1.9 Hz), 2.68 (1H, 2d, *J* = 1.9 Hz), 2.67 (1H, d, *J* = 1.7 Hz), 1.70−1.56 (4H, m), 1.53 (3H, s), 1.35 (3H, s), 0.92 ppm (6H, 2 × t, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 110.14, 82.82, 79.57, 78.34, 73.85, 73.77, 73.38, 72.59, 71.60, 28.30, 26.19, 23.53, 23.28, 10.72, 10.62 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{15}H_{28}O_6Na$ 327.1784, found 327.1781.

(±)-2,3-*O*-Isopropylidene-1,4-di-*O*-triisopropylsilyl-*myo*-inositol ((±)-6j). Using the procedure described for the preparation of (±)-**6a**, treatment of (±)-**5j** (224 mg, 0.39 mmol) in dry CH_2Cl_2 (5 mL) with water (45 μL, 2.5 mmol) and TFA (45 μL, 0.58 mmol) gave after column chromatography (EtOAc/PE, 1/4) the title compound (±)-**6j** (208 mg, 83%) as a white solid: ν_{max} (cm^{-1}) 2986, 2941, 2867, 1464, 1372, 1113; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (1H, dd, *J* = 5.9, 3.7 Hz), 4.10 (1H, t, *J* = 5.7 Hz), 4.00 (1H, dd, *J* = 9.4, 3.8 Hz), 3.93 (1H, dd, *J* = 6.9, 5.6 Hz), 3.85 (1H, ddd, *J* = 9.5, 7.9, 1.8 Hz), 3.45 (1H, ddd, *J* = 7.8, 6.9, 4.4 Hz), 2.48−2.46 (2H, m), 1.49 (3H, s), 1.32

(3H, s), 1.22−1.03 ppm (42H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 109.52, 79.60, 76.32, 76.25, 76.07, 73.27, 71.53, 27.38, 24.99, 18.10, 18.08, 18.06, 17.99, 12.59, 12.42 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{27}H_{56}O_6Si_2Na$ 555.3513, found 555.3513.

Typical Procedure for the Novozym 435 Catalyzed Resolution of (±)-5: (−)-5-*O*-Acetyl-1,4-di-*O*-allyl-2,3-*O*-isopropylidene-1D-*myo*-inositol ((−)-7a) and (+)-3,6-di-*O*-allyl-1,2-*O*-isopropylidene-1D-*myo*-inositol ((+)-6a). A mixture of (±)-**6a** (80 mg, 0.27 mmol) and Novozym 435 beads (40 mg) in freshly distilled vinyl acetate (5 mL) under Ar in a sealed flask at 30 °C was gently stirred for 24 h. The mixture was filtered and the beads washed with EtOAc. The solvents were removed from the combined filtrate and the residue purified by column chromatography (EtOAc/PE, 1/2 to 2/1) to give the *title compounds* (−)-**7a** (42 mg, 46%) and (+)-**6a** (33 mg, 41%) both as white solids.

Data for (−)-**7a**: $[\alpha]_D^{18}$ = −5.1° (*c* 0.94, $CHCl_3$); ν_{max} (cm^{-1}) 3526, 2991, 2929, 1722, 1648, 1107; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.00−5.91 (1H, m), 5.90−5.82 (1H, m), 5.34−5.29 (1H, m), 5.28−5.21 (2H, m), 5.16 (1H, dq, *J* = 10.4, 1.5 Hz), 4.82 (1H, t, *J* = 8.0 Hz), 4.49 (1H, dd, *J* = 6.0, 3.8 Hz), 4.30−4.14 (5H, m), 3.99 (1H, ddd, *J* = 9.1, 8.2, 2.2 Hz), 3.65 (1H, dd, *J* = 7.9, 6.0 Hz), 3.61 (1H, dd, *J* = 9.1, 3.5 Hz), 2.64 (1H, d, *J* = 2.2 Hz), 2.12 (3H, s), 1.54 (3H, s), 1.37 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.91, 134.63, 134.51, 118.08, 116.93, 110.02, 78.77, 78.30, 76.78, 75.54, 73.38, 72.05, 71.87, 70.36, 27.27, 25.27, 21.06 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{17}H_{26}O_7Na$ 365.1576, found 365.1568.

Data for (+)-**6a**: $[\alpha]_D^{19}$ = +16.0° (*c* 1.04, $CHCl_3$); HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{15}H_{24}O_6Na$ 323.1465, found 323.1472. All other spectroscopic data were consistent with those for (±)-**6a**.

(−)-5-*O*-Acetyl-4-*O*-allyl-1-*O*-benzyl-2,3-*O*-isopropylidene-1D-*myo*-inositol ((−)-7b) and (+)-4-*O*-Allyl-1-*O*-benzyl-2,3-*O*-isopropylidene-1D-*myo*-inositol ((+)-6b). Using the procedure for the resolution of (±)-**6a**, treatment of (±)-**6b** (93 mg, 0.27 mmol) with Novozym 435 beads (40 mg) in freshly distilled vinyl acetate (5 mL) gave after purification by column chromatography (EtOAc/PE, 1/2 to 2/1) the title compounds (−)-**7b** (41 mg, 40%) and (+)-**6b** (35 mg, 38%), both as white solids.

Data for (−)-**7b**: $[\alpha]_D^{19}$ = −4.9° (*c* 1.21, $CHCl_3$); ν_{max} (cm^{-1}) 3524, 2982, 2931, 1725, 1646, 1118, 740, 696; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40−7.27 (5H, m), 5.89−5.80 (1H, m), 5.26−5.20 (1H, m), 5.18−5.12 (1H, m), 4.82−4.77 (2H, m), 4.74−4.69 (1H, m), 4.38 (1H, dd, *J* = 6.0, 3.8 Hz), 4.28−4.22 (1H, m), 4.18−4.12 (2H, m), 4.05−3.99 (1H, m), 3.68−3.62 (2H, m), 2.63 (1H, d, *J* = 2.5 Hz), 2.11 (3H, s), 1.53 (3H, s), 1.34 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.91, 137.78, 134.66, 128.55, 128.05, 128.03, 116.88, 109.97, 78.84, 78.36, 77.03, 75.44, 73.44, 72.78, 72.06, 70.51, 27.36, 25.30, 21.06 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{21}H_{28}O_7Na$ 415.1733, found 415.1725.

Data for (+)-**6b**: $[\alpha]_D^{20}$ = +9.9° (*c* 1.13, $CHCl_3$); HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{19}H_{26}O_6Na$ 373.1627, found 373.1623. All other spectroscopic data were consistent with those for racemic (±)-**6b**.

(−)-5-*O*-Acetyl-1-*O*-allyl-4-*O*-benzyl-2,3-*O*-isopropylidene-1D-*myo*-inositol ((−)-7c) and (+)-3-*O*-Allyl-6-*O*-benzyl-1,2-*O*-isopropylidene-1D-*myo*-inositol ((+)-6c). Using the procedure for the resolution of (±)-**6a**, treatment of (±)-**6c** (1.937 g, 5.53 mmol) with Novozym 435 beads (0.999 g) in freshly distilled vinyl acetate (25 mL) gave after purification by column chromatography (EtOAc/PE, 1/2 to 2/1) the title compounds (−)-**7c** (1.063 g, 49%) and (+)-**6c** (0.949 g, 49%), both as white solids.

Data for (−)-**7c**: $[\alpha]_D^{20}$ = −9.4° (*c* 1.09, $CHCl_3$); ν_{max} (cm^{-1}) 3522, 2983, 1718, 1023, 729, 696; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.22 (5H, m), 5.99−5.87 (1H, m), 5.29 (1H, ddd, *J* = 17.2, 2.5, 1.5 Hz), 5.21 (1H, ddd, *J* = 10.3, 2.5, 1.2 Hz), 4.88 (1H, t, *J* = 8.1 Hz), 4.78 (1H, d, *J* = 12.0 Hz), 4.69 (1H, d, *J* = 12.0 Hz), 4.48 (1H, dd, *J* = 6.0, 3.6 Hz), 4.30−4.21 (2H, m), 4.16 (1H, ddt, *J* = 12.8, 5.9, 1.2 Hz), 3.97 (1H, t, *J* = 8.7 Hz), 3.69 (1H, dd, *J* = 8.0, 5.9 Hz), 3.61 (1H, dd, *J* = 9.2, 3.6 Hz), 2.58 (1H, s), 2.07 (1H, s), 1.48 (3H, s), 1.35 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.17, 138.30, 134.67, 128.50, 127.92, 127.86, 118.41, 110.32, 79.14, 78.68, 75.62, 75.62, 73.59, 73.06, 72.10, 70.48, 27.49, 25.53, 21.29 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{21}H_{28}O_7Na$ 415.1733, found 415.1729. Anal. Calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 64.48; H, 7.27.

Data for (+)-**6c**: $[\alpha]_D^{28}$ = +16.4° (*c* 1.06, $CHCl_3$); HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{19}H_{26}O_6Na$ 373.1627, found 373.1621. All other spectroscopic data were consistent with those for (±)-**6c**.

(−)-5-*O*-Acetyl-1-*O*-allyl-2,3-*O*-isopropylidene-4-*O*-propargyl-1D-*myo*-inositol ((−)-7d) and (+)-3-*O*-Allyl-1,2-*O*-isopropylidene-6-*O*-propargyl-1D-*myo*-inositol ((+)-6d). Using the procedure for the resolution of (±)-**6a**, treatment of (±)-**6d** (80 mg, 0.27 mmol) with Novozym 435 beads (40 mg) in freshly distilled vinyl acetate (5 mL) gave after purification by column chromatography (EtOAc/PE, 1/2 to 2/1) the title compounds (−)-**7d** (44 mg, 48%) and (+)-**6d** (39 mg, 48%) as white solids.

Data for (−)-**7d**: $[\alpha]_D^{18}$ = −6.7° (*c* 1.02, $CHCl_3$); ν_{max} (cm^{-1}) 3464, 3266, 2990, 2914, 1749, 1102; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.95 (1H, ddt, *J* = 17.2, 10.3, 6.0 Hz), 5.35−5.29 (1H, m), 5.25−5.21(1H, m), 4.79 (1H, t, *J* = 8.4 Hz), 4.48 (1H, dd, *J* = 5.8, 3.6 Hz), 4.39 (2H, d, *J* = 2.2 Hz), 4.24−4.31 (1H, m), 4.23−4.15 (2H, m), 4.04−3.98 (1H, m), 3.86 (1H, dd, *J* = 8.5, 6.3 Hz), 3.59 (1H, dd, *J* = 9.1, 3.8 Hz), 2.60 (1H, d, *J* = 2.2 Hz), 2.43−2.40 (1H, m), 2.14 (3H, s), 1.57 (3H, s), 1.37 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.99, 134.46, 118.12, 110.21, 79.67, 78.33, 78.28, 76.77, 74.97, 74.42, 73.44, 71.91, 70.36, 58.29, 27.35, 25.39, 21.11 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{17}H_{24}O_7Na$ 363.1420, found 363.1418.

Data for (+)-**6d**: $[\alpha]_D^{20}$ = +38.2° (*c* 1.14, $CHCl_3$); HRMS(ESI-TOF) *m/z* [M + Na]$^+$ Calcd for$C_{15}H_{22}O_6Na$ 321.1314, found 321.1308. All other spectroscopic data were consistent with those for (±)-**6d**.

(−)-5-*O*-Acetyl-1-*O*-Allyl-2,3-*O*-isopropylidene-4-*O*-*p*-methoxybenzyl-1D-*myo*-inositol ((−)-7e) and (+)-3-*O*-Allyl-1,2-*O*-isopropylidene-6-*O*-*p*-methoxybenzyl-1D-*myo*-inositol ((+)-6e). Using the procedure for the resolution of (±)-**6a**, treatment of (±)-**6e** (99 mg, 0.26 mmol) with Novozym 435 beads (50 mg) in freshly distilled vinyl acetate (5 mL) gave after purification by column chromatography (EtOAc/PE, 1/2 to 2/1) the title compounds (−)-**7e** (50 mg, 45%) and (+)-**6e** (48 mg, 48%) as white solids.

Data for (−)-**7e**: $[\alpha]_D^{17}$ = −7.7° (*c* 0.99, $CHCl_3$); ν_{max} (cm^{-1}) 3521, 2891, 1723, 1615, 1110, 862; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25−7.20 (2H, m), 6.90−6.81 (2H, m), 5.95 (1H, ddt, *J* = 17.2, 10.3, 5.9 Hz), 5.31 (1H, dq, *J* = 17.2, 1.5 Hz), 5.22 (1H, dq, *J* = 10.4, 1.3 Hz), 4.88 (1H, t, *J* = 7.9 Hz), 4.72 (1H, d, *J* = 11.6 Hz), 4.64 (1H, d, *J* = 11.6 Hz), 4.49 (1H, dd, *J* = 6.1, 3.6 Hz), 4.33−4.21 (2H, m), 4.21−4.12 (1H, m), 3.99 (1H, t, *J* = 8.6 Hz), 3.80 (3H, s), 3.69 (1H, dd, *J* = 7.8, 5.8 Hz), 3.63 (1H, dd, *J* = 9.2, 3.6 Hz), 2.59 (1H, d, *J* = 2.4 Hz), 2.09 (3H, s), 1.50 (3H, s), 1.37 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.92, 159.27, 134.51, 130.21, 129.38, 118.10, 113.74, 110.07, 78.47, 78.45, 76.77, 75.61, 73.38, 72.47, 71.87, 70.32, 55.29, 27.25, 25.27, 21.10 ppm; HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{30}O_8Na$ 445.1838, found 445.1835.

Data for (+)-**6e**: $[\alpha]_D^{20}$ = +16.1° (*c* 1.27, $CHCl_3$); HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{20}H_{28}O_7Na$ 403.1727, found 403.1730. All other spectroscopic data were consistent with those for (±)-**6e**.

(−)-5-*O*-Acetyl-1-*O*-Allyl-4-*O*-(4-(3,4-dimethoxyphenyl)-benzyl)-2,3-*O*-isopropylidene-1D-*myo*-inositol ((−)-7f) and (+)-3-*O*-allyl-6-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1,2-*O*-isopropylidene-1D-*myo*-inositol ((+)-6f). Using the procedure for the resolution of (±)-**6a**, treatment of (±)-**6f** (116 mg, 0.24 mmol) with Novozym 435 beads (60 mg) in freshly distilled vinyl acetate (3 mL) and EtOAc (2 mL) gave after purification by column chromatography (EtOAc/PE, 1/2 to 2/1) the title compounds (−)-**7f** (23 mg, 18%) and (+)-**6f** (72 mg, 62%) as white solids.

Data for (−)-**7f**: $[\alpha]_D^{19}$ = −4.5° (*c* 0.99, $CHCl_3$); ν_{max} (cm^{-1}) 2499, 2987, 2936, 1739, 1504, 1247, 1247, 1143, 867; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55−7.49 (2H, m), 7.41−7.33 (2H, d, *J* = 8.2 Hz), 7.17−7.07 (2H, m), 6.94 (1H, d, *J* = 8.2 Hz), 6.01−5.88 (1H, m), 5.31 (1H, dq, *J* = 17.1, 1.6 Hz), 5.23 (1H, dq, *J* = 10.4, 1.3 Hz), 4.91 (1H, t, *J* =

8.0 Hz), 4.83 (1H, d, J = 12.0 Hz), 4.75 (1H, d, J = 12.0 Hz), 4.51 (1H, dd, J = 6.0, 3.5 Hz), 4.33−4.25 (2H, m), 4.18 (1H, ddt, J = 12.8, 6.0, 1.3 Hz), 4.01 (1H, t, J = 8.5 Hz), 3.95 (3H, s), 3.92 (3H, s), 3.75 (1H, dd, J = 7.9, 6.0 Hz), 3.65 (1H, dd, J = 9.1, 3.8 Hz), 2.62 (1H, s), 2.11 (3H, s), 1.52 (3H, s), 1.38 (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 170.95, 149.24, 148.73, 140.47, 136.72, 134.49, 133.96, 128.17, 126.76, 119.38, 118.13, 111.60, 110.52, 110.12, 78.97, 78.47, 76.77, 75.53, 73.41, 72.60, 71.87, 70.33, 56.01, 55.99, 27.28, 25.30, 21.09 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{29}H_{36}O_9Na$ 551.2257, found 551.2261.

Data for (+)-**6f**: $[\alpha]_D^{20}$ = +4.7° (c 1.33, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{27}H_{34}O_8Na$ 509.2151, found 509.2160. All other spectroscopic data were consistent with those for (±)-**6f**.

(±)-5-*O*-Acetyl-1-*O*-allyl-4-*O*-*p*-bromobenzyl-2,3-*O*-isopropylidene-1D-*myo*-inositol ((−)-7g) and (+)-3-*O*-Allyl-6-*O*-*p*-bromobenzyl-1,2-*O*-isopropylidene-1D-*myo*-inositol ((+)-6g). Using the procedure for the resolution of (±)-**6a**, treatment of (±)-**6g** (111 mg, 0.26 mmol) with Novozym 435 beads (55 mg) in freshly distilled vinyl acetate (5 mL) gave after purification by column chromatography (EtOAc/PE, 1/2 to 2/1) the title compounds (−)-**7g** (50 mg, 41%) and (+)-**6g** (55 mg, 49%) as white solids.

Data for (−)-**7g**: $[\alpha]_D^{19}$ = −5.8° (c 1.04, CHCl$_3$); ν_{max} (cm^{-1}) 3528, 2980, 2893, 1723, 1110, 801; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48−7.43 (2H, m), 7.22−7.16 (2H, m), 5.95 (1H, ddt, J = 17.2, 10.4, 5.9 Hz), 5.30 (1H, dq, J = 17.2, 1.5 Hz), 5.23 (1H, dq, J = 10.4, 1.3 Hz), 4.87 (1H, t, J = 8.1 Hz), 4.75 (1H, d, J = 12.3 Hz), 4.66 (1H, d, J = 12.3 Hz), 4.49 (1H, dd, J = 6.1, 3.6 Hz), 4.32−4.21 (2H, m), 4.17 (1H, ddt, J = 12.8, 6.0, 1.3 Hz), 3.99 (1H, ddd, J = 9.0, 8.1, 2.4 Hz), 3.69 (1H, dd, J = 8.2, 6.0 Hz), 3.62 (1H, dd, J = 9.0, 3.6 Hz), 2.57 (1H, d, J = 2.4 Hz), 2.09 (3H, s), 1.50 (3H, s), 1.37 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 170.93, 137.19, 134.45, 131.42, 129.29, 121.51, 118.16, 110.18, 79.14, 78.46, 76.76, 75.44, 73.41, 72.05, 71.90, 70.36, 27.30, 25.32, 21.06 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{21}H_{27}{}^{79}BrO_7Na$ 493.0838, found 493.0829.

Data for (+)-**6g**: $[\alpha]_D^{20}$ = +6.7° (c 1.40, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{19}H_{25}{}^{79}BrO_6Na$ 451.0727, found 451.0728. All other spectroscopic data were consistent with those for (±)-**6g**.

(−)-5-*O*-Acetyl-1-*O*-Allyl-2,3-*O*-isopropylidene-4-*O*-*p*-nitrobenzyl-1D-*myo*-inositol ((−)-7h) and (+)-3-*O*-Allyl-1,2-*O*-isopropylidene-6-*O*-*p*-nitrobenzyl-1D-*myo*-inositol ((+)-6h). Using the procedure for the resolution of (±)-**6a**, treatment of (±)-**6h** (95 mg, 0.24 mmol) with Novozym 435 beads (45 mg) in freshly distilled vinyl acetate (5 mL) gave after purification by column chromatography (EtOAc/PE, 1/2 to 2/1) the title compounds (−)-**7h** (38 mg, 36%) and (+)-**6h** (38 mg, 40%) as white solids.

Data for (−)-**7h**: $[\alpha]_D^{18}$ = −8.2° (c 1.32, CHCl$_3$); ν_{max} (cm^{-1}) 3510, 2913, 1720, 1603, 1512, 1348, 1108, 840; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.19 (2H, d, J = 8.7 Hz), 7.48 (2H, dd, J = 8.1, 0.8 Hz), 5.95 (1H, ddt, J = 17.2, 10.3, 5.9 Hz), 5.31 (1H, dq, J = 17.3, 1.6 Hz), 5.23 (1H, dq, J = 10.3, 1.3 Hz), 4.94 (1H, d, J = 13.4 Hz), 4.89 (1H, t, J = 8.4 Hz), 4.80 (1H, d, J = 13.4 Hz), 4.51 (1H, dd, J = 6.0, 3.6 Hz), 4.31−4.24 (2H, m), 4.18 (1H, ddt, J = 12.8, 6.0, 1.3 Hz), 4.00 (1H, td, J = 8.5, 2.3 Hz), 3.74 (1H, dd, J = 8.6, 6.2 Hz), 3.63 (1H, dd, J = 8.8, 3.6 Hz), 2.61 (1H, d, J = 2.4 Hz), 2.11 (3H, s), 1.51 (3H, s), 1.38 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 170.92, 147.41, 145.80, 134.41, 127.63, 123.54, 118.18, 110.30, 80.03, 78.44, 76.78, 75.29, 73.49, 71.94, 71.65, 70.45, 27.41, 25.39, 21.05 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{21}H_{27}NO_9Na$ 460.1584, found 460.1577.

Data for (+)-**6h**: $[\alpha]_D^{20}$ = +0.8° (c 1.26, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{19}H_{25}NO_8Na$ 418.1478, found 418.1477. All other spectroscopic data were consistent with those for (±)-**6h**.

(−)-5-*O*-Acetyl-2,3-*O*-isopropylidene-1,4-di-*O*-propyl-1D-*myo*-inositol ((−)-7i) and (+)-1,2-*O*-isopropylidene-3,6-di-*O*-propyl-1D-*myo*-inositol ((+)-6i). Using the procedure for the resolution of (±)-**6a**, treatment of (±)-**6i** (81 mg, 0.27 mmol) with Novozym 435 beads (40 mg) in freshly distilled vinyl acetate (5 mL) gave after purification by column chromatography (EtOAc/PE, 1/2 to 2/1) the title compounds (−)-**7i** (41 mg, 44%) and (+)-**6i** (38 mg, 37%) as white solids.

Data for (−)-**7i**: $[\alpha]_D^{19}$ = −3.9° (c 1.07, CHCl$_3$); ν_{max} (cm^{-1}) 3481, 2962, 2937, 1739, 1458, 1374, 1075; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.81 (1H, t, J = 8.1 Hz), 4.48 (1H, dd, J = 5.9, 3.6 Hz), 4.17 (1H, t, J = 6.0 Hz), 3.96 (1H, ddd, J = 9.3, 8.2, 2.0 Hz), 3.76−3.64 (2H, m), 3.59−3.41 (4H, m), 2.55 (1H, d, J = 2.1 Hz), 2.10 (3H, s), 1.71−1.58 (2H, m), 1.58−1.47 (5H, m), 1.35 (3H, s), 0.90 ppm (6H, 2xt, J = 7.4 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 171.01, 110.19, 80.11, 78.65, 78.05, 75.65, 73.68, 73.28, 72.72, 70.34, 27.61, 25.56, 23.42, 23.27, 21.29, 10.73, 10.64 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{17}H_{30}O_7Na$ 369.1889, found 369.1881.

Data for (+)-**6i**: $[\alpha]_D^{20}$ = +14.7° (c 0.95, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{28}O_6Na$ 327.1784, found 327.1777. All other spectroscopic data were consistent with those for (±)-**6i**.

Typical Procedure for the Deacetylation of (−)-7: (−)-1,4-Di-*O*-allyl-2,3-*O*-isopropylidene-1D-*myo*-inositol ((−)-6a). Method A. A solution of sodium methoxide in MeOH (5.4 M, 20 μL, 0.11 mmol) was added to a stirred solution of (−)-**7a** (42 mg, 0.13 mmol) in a 1:4 mixture of CH$_2$Cl$_2$ and methanol (5 mL) and the reaction was stirred overnight at room temperature. The reaction mixture was quenched with water and diluted with in EtOAc. The organic layer was washed with water then brine, dried and the solvent removed to give title compound (−)-**6a** (29 mg, 79%) as a white solid: $[\alpha]_D^{21}$ = −12.7° (c 0.75, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{24}O_6Na$ 323.1465, found 323.1470. All other spectroscopic data were consistent with those for (±)-**6a**.

(−)-4-*O*-Allyl-1-*O*-benzyl-2,3-*O*-isopropylidene-1D-*myo*-inositol ((−)-6b). Using method A, (−)-**7b** (41 mg, 0.11 mmol) gave the title compound (−)-**6b** (32 mg, 87%) as a white solid: $[\alpha]_D^{22}$ = −10.3° (c 0.79, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{19}H_{26}O_6Na$ 373.1627, found 373.1621. All other spectroscopic data were consistent with those for (±)-**6d**.

(−)-1-*O*-Allyl-4-*O*-benzyl-2,3-*O*-isopropylidene-1D-*myo*-inositol ((−)-6c). Method B. IRA-400 (OH$^-$) ion-exchange resin (~300 mg) was added to a stirred solution of (−)-**7c** (1.117 g, 2.85 mmol) in methanol (20 mL). The solution was stirred overnight then filtered and the solvent removed to give the title compound (−)-**6c** (0.935 g, 94%) as a white solid: $[\alpha]_D^{20}$ = −13.3° (c 1.01, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{19}H_{26}O_6Na$ 373.1627, found 373.1621. All other spectroscopic data were consistent with those for (±)-**6c**.

(−)-1-*O*-Allyl-2,3-*O*-isopropylidene-4-*O*-propargyl-1D-*myo*-inositol ((−)-6d). Using method A, (−)-**7i** (42 mg, 0.13 mmol) gave the title compound (−)-**6d** (35 mg, 95%) as a white solid: $[\alpha]_D^{22}$ = −39.0° (c 0.41, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{22}O_6Na$ 321.1314, found 321.1306. All other spectroscopic data were consistent with those for (±)-**6d**.

(−)-1-*O*-Allyl-2,3-*O*-isopropylidene-4-*O*-*p*-methoxybenzyl-1D-*myo*-inositol ((−)-6e). Using method A, (−)-**7e** (42 mg, 0.10 mmol) gave the title compound (−)-**6e** (36 mg, 87%) as a white solid: $[\alpha]_D^{22}$ = −18.9° (c 1.01, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{20}H_{28}O_7Na$ 403.1727, found 403.1737. All other spectroscopic data were consistent with those for (±)-**6e**.

(−)-1-*O*-Allyl-4-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-2,3-*O*-isopropylidene-1D-*myo*-inositol ((−)-6f). Using method A, (−)-**7f** (23 mg, 0.044 mmol) gave the title compound (−)-**6f** (14 mg, 66%) as a white solid: $[\alpha]_D^{20}$ = −5.7° (c 1.48, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{27}H_{34}O_8Na$ 509.2151, found 509.2154. All other spectroscopic data were consistent with those for (±)-**6f**.

(−)-1-*O*-Allyl-4-*O*-*p*-bromobenzyl-5,6-*O*-isopropylidene-1D-*myo*-inositol ((−)-6g). Using method A, (−)-**7g** (50 mg, 0.11 mmol) gave the title compound (−)-**6g** (45 mg, 98%) as a white solid: $[\alpha]_D^{20}$ = −7.6° (c 0.84, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{19}H_{25}{}^{79}BrO_6Na$ 451.0727, found 451.0736. All other spectroscopic data were consistent with those for (±)-**6g**.

(−)-1-*O*-Allyl-2,3-*O*-isopropylidene-4-*O*-*p*-nitrobenzyl-1D-*myo*-inositol ((−)-6h). Using method A, (−)-**7h** (38 mg, 0.11 mmol) gave the title compound (−)-**6h** (32 mg, 93%) as a white solid: $[\alpha]_D^{22}$ = −0.7° (c 0.94, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for

$C_{19}H_{25}NO_8Na$ 418.1478, found 418.1479. All other spectroscopic data were consistent with those for (±)-**6h**.

(−)-2,3-*O*-Isopropylidene-1,4-di-*O*-propyl-1D-*myo*-inositol ((−)-6i). Using method A, (−)-**7b** (44 mg, 0.13 mmol) gave the title compound (−)-**6i** (28 mg, 72%) as a white solid: $[\alpha]_D^{21} = -14.3°$ (*c* 0.71, $CHCl_3$). HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{28}O_6Na$ 327.1784, found 327.1780. All other spectroscopic data were consistent with those for (±)-**6i**.

(+)-1-*O*-Allyl-4,5,6-tri-*O*-benzyl-2,3-*O*-isopropylidene-1D-*myo*-inositol (12). Benzyl bromide (1.30 mL, 10.96 mmol) and then sodium hydride (60% in oil, 0.38 g, 9.4 mmol) were added with stirring to a solution of diol (−)-**6c** (1.097 g, 3.13 mmol) in dry DMF (50 mL) at 0 °C under Ar. The reaction mixture was stirred overnight at room temperature and then carefully quenched with water. The mixture was diluted with EtOAc, washed with water and then brine, and dried. After removal of the solvent the residue was purified by column chromatography (EtOAc/PE, 1/6 to 1/5) to give the title compound (+)-**12** (1.607 g, 97%) as a colorless oil: $[\alpha]_D^{20} = +33.1°$ (*c* 0.87, $CHCl_3$); ν_{max} (cm^{-1}) 2987, 2889, 736, 697; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40−7.22 (15H, m), 5.96 (1H, ddt, *J* = 17.2, 10.4, 5.8 Hz), 5.29 (1H, dq, *J* = 17.3, 1.6 Hz), 5.19 (1H, dq, *J* = 10.3, 1.3 Hz), 4.90−4.71 (6H, m), 4.41 (1H, d, *J* = 5.6, 3.8 Hz), 4.30−4.20 (2H, m), 4.17 (1H, dd, *J* = 6.8, 5.6 Hz), 3.90 (1H, t, *J* = 8.6 Hz), 3.79 (1H, dd, *J* = 9.3, 6.8 Hz), 3.65 (1H, dd, *J* = 8.7, 3.8 Hz), 3.44 (1H, dd, *J* = 9.3, 8.4 Hz), 1.51 (3H, s), 1.39 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.58, 138.56, 138.52, 134.92, 128.30, 128.26, 128.21, 127.97, 127.92, 127.58, 127.52, 127.49, 117.51, 109.85, 82.47, 82.19, 80.78, 79.09, 77.03, 75.20, 75.19, 74.59, 73.84, 72.49, 27.65, 25.80 ppm; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{33}H_{38}O_6Na$ 553.2566, found 553.2565.

(+)-1-*O*-Allyl-4,5,6-tri-*O*-benzyl-1D-*myo*-inositol (13). TFA (1.38 mL, 17.9 mmol) and then methanol (0.73 mL, 17.9 mmol) were added to (+)-**12** (1.580 g, 2.98 mmol) in CH_2Cl_2 (15 mL), and the mixture was stirred overnight at room temperature. The reaction mixture was diluted with EtOAc, washed with sodium bicarbonate and then brine, and dried and the solvent removed. The residue was purified by column chromatography (EtOAc/PE, 1/1) to give the title compound (+)-**13** (1.325 g, 93%) as a white solid: $[\alpha]_D^{20} = +26.4°$ (*c* 0.96, $CHCl_3$); ν_{max} (cm^{-1}) 3435, 3031, 2886, 1130, 732, 697; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37−7.21 (15H, m), 5.93 (1H, ddt, *J* = 17.3, 10.4, 5.7 Hz), 5.30 (1H, dq, *J* = 17.2, 1.6 Hz), 5.19 (1H, dq, *J* = 10.4, 1.3 Hz), 4.98−4.72 (6H, m), 4.22−4.14 (3H, m), 3.92 (1H, t, *J* = 9.4 Hz), 3.82 (1H, t, *J* = 9.5 Hz), 3.53−3.43 (2H, m), 3.36 (1H, dd, *J* = 9.5, 2.8 Hz), 2.58−2.57 (1H, m), 2.49 ppm (1H, d, 4.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.67, 138.58, 138.54, 134.56, 128.56, 128.37, 128.03, 127.96, 127.85, 127.79, 127.61, 127.59, 117.59, 83.20, 81.62, 81.35, 79.85, 75.93, 75.68, 75.61, 71.79, 69.34 ppm; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{30}H_{34}O_6Na$ 513.2253, found 513.2253.

(−)-1-*O*-Allyl-4,5,6-*O*-benzyl-3-*O*-(4-(3,4-dimethoxyphenyl)-benzyl)-1D-*myo*-inositol (14). Diol (+)-**13** (1.300 g, 2.65 mmol) and dibutyltin oxide (0.788 g, 3.17 mmol) were coevaporated from toluene, dried under high vacuum, and then redissolved in toluene (25 mL). The reaction mixture was heated at reflux in a Dean−Stark apparatus for 1 h until a clear, yellow solution formed. Once the solution was cooled, the solvent was removed under reduced pressure. Cesium fluoride (0.650 g, 4.28 mmol) and 4-(3,4-dimethoxyphenyl)-benzyl bromide (0.895 g, 2.91 mmol) were added to the residue, which was coevaporated from toluene and dried under high vacuum. Dry DMF (20 mL) was added, and the reaction mixture was heated overnight at 55 °C. The reaction mixture was cooled to room temperature and diluted with ether. The mixture was washed with water, and the organic layers were washed with brine, dried, and evaporated. The residue was purified by column chromatography (EtOAc/PE, 1/6 to 1/4) to give the title compound (−)-**14** (1.312 g, 69%) as a white solid: $[\alpha]_D^{23} = -1.5°$ (*c* 1.10, $CHCl_3$); ν_{max} (cm^{-1}) 3437, 3029, 2904, 1131, 730, 694; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (dt, *J* = 8.2, 1.8 Hz), 7.43−7.37 (2H, m), 7.35−7.22 (15H, m), 7.13 (1H, dt, *J* = 8.3, 1.9 Hz), 7.08 (1H, t, *J* = 1.9 Hz), 6.94 (1H, dd, *J* = 8.4, 1.5 Hz), 5.93 (1H, ddtd, *J* = 17.7, 10.3, 5.7, 1.6 Hz), 5.28 (1H, dt, *J* = 17.2, 1.7 Hz), 5.17 (1H, dt, *J* = 10.5, 1.5 Hz), 4.94−4.77 (6H, m), 4.78−4.74 (2H, m), 4.25 (1H, q, *J* = 2.3 Hz), 4.18 (2H, dq, *J* = 5.7, 1.4 Hz), 4.03−3.89 (8H, m), 3.49−3.40 (2H, m), 3.30 (1H, ddd, *J* = 9.6, 2.7, 1.5 Hz), 2.47 ppm (1H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.20, 148.73, 140.67, 138.76, 138.73, 138.70, 136.54, 134.69, 133.80, 128.37, 128.36, 128.09, 128.04, 127.83, 127.61, 127.59, 127.55, 126.92, 119.37, 117.46, 111.53, 110.41, 83.13, 81.23, 81.19, 79.89, 79.63, 76.00, 75.97, 75.95, 72.50, 71.94, 67.73, 56.01, 55.98 ppm; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{45}H_{48}O_8Na$ 739.3247, found 739.3249.

2-*O*-Benzoyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-*α*-D-mannopyranosyl Trichloroacetimidate (15). A solution of 3,4-di-*O*-benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-D-mannopyranose (0.160 g, 0.276 mmol) in dry CH_2Cl_2 (2 mL) was cooled to 0 °C under nitrogen. Trichloroacetonitrile (0.270 mL, 2.76 mmol) and a catalytic amount of sodium hydride were added. After the mixture was stirred for 30 min, the solvent was removed under reduced pressure to give **15**[4b] in quantitative yield as a yellow oil: ^1H NMR (500 MHz, $CDCl_3$) δ 8.66 (1H, s), 8.15−8.12 (2H), 7.62−7.58 (1H), 7.49−7.45 (2H), 7.36−7.23 (10H, m), 6.39 (1H, d, *J* = 2.0 Hz), 5.73 (1H, dd, *J* = 2.1, 3.2 Hz), 4.92 (1H, d, *J* = 10.6 Hz), 4.81 (1H, d, *J* = 11.4 Hz), 4.69 (1H, d, *J* = 10.6 Hz), 4.62 (1H, d, *J* = 11.4 Hz), 4.23 (1H, t, *J* = 9.6 Hz), 4.14 (1H, dd, *J* = 3.3, 9.7 Hz), 4.03 (1H, dd, J = 2.9, 11.3 Hz), 3.92−3.86 (2H, m), 0.95 (s, 9H), 0.11 (s, 3H), 0.10 ppm (s, 3H).

1-*O*-Allyl-2-*O*-(2′-*O*-benzoyl-3′,4′-di-*O*-benzyl-6′-*O*-*tert*-butyldimethylsilyl-*α*-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-3-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (16). Trimethylsilyl triflate (TMSOTf; 4 *μ*L, 0.02 mmol) was added to a mixture of alcohol (−)-**14** (162 mg, 0.226 mmol), TCA donor **15** (200 mg, 0.277 mmol), and powdered 4 Å molecular sieves in dry toluene (5 mL) at 0 °C. After it was stirred for 40 min at that temperature, the reaction mixture was quenched with Et_3N, filtered through Celite, and evaporated to dryness. The residue was purified by column chromatography (EtOAc/toluene 1/9, then EtOAc/PE 1/4 to 1/3) to give the title compound **16** (265 mg, 92%) as a colorless oil: $[\alpha]_D^{20} = +18.1°$ (*c* 2.08, $CHCl_3$); ν_{max} (cm^{-1}) 2929, 2856, 1725, 737, 698; ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (2H, dd, *J* = 8.4, 1.4 Hz), 7.60−7.04 (34H, m), 6.94 (1H, d, *J* = 8.3 Hz), 5.86 (1H, ddt, *J* = 17.3, 10.5, 5.3 Hz), 5.74 (1H, dd, *J* = 2.7, 1.9 Hz), 5.32 (1H, d, *J* = 1.9 Hz), 5.25 (1H, dq, *J* = 17.3, 1.7 Hz), 5.07 (1H, dq, *J* = 10.5, 1.4 Hz), 4.94−4.74 (9H, m), 4.68−4.57 (3H, m), 4.37 (1H, t, *J* = 2.4 Hz), 4.19−4.04 (5H, m), 3.99−3.83 (8H, m), 3.71 (1H, dd, *J* = 11.4, 2.3 Hz), 3.54−3.41 (2H, m), 3.35 (1H, dd, *J* = 9.9, 2.6 Hz), 3.30 (1H, dd, *J* = 9.7, 2.2 Hz), 0.91 (9H, s), 0.03 (3H, s), −0.01 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.66, 149.41, 148.91, 140.40, 139.28, 138.98, 138.93, 138.33, 137.03, 134.70, 134.14, 133.14, 130.48, 130.22, 128.57, 128.53, 128.50, 128.43, 128.32, 128.17, 127.99, 127.80, 127.74, 127.61, 126.94, 119.61, 116.98, 111.77, 110.69, 99.26 ($^1J_{CH}$ = 172.4 Hz), 83.62, 81.61, 81.40, 80.73, 79.39, 78.02, 76.31, 76.10, 76.02, 75.15, 74.18, 72.77, 72.50, 72.33, 71.91, 71.86, 69.45, 62.00, 56.25, 56.17, 26.22, 18.55, −4.96, −5.19 ppm; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{78}H_{88}O_{14}SiNa$ 1299.5841, found 1299.5831.

1-*O*-Allyl-4,5,6-tri-*O*-benzyl-2-*O*-(3′,4′-di-*O*-benzyl-6′-*O*-*tert*-butyldimethylsilyl-*α*-D-mannopyranosyl)-3-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (17). A solution of sodium methoxide in methanol, formed from the reaction of sodium (10 mg, 0.4 mmol) and MeOH (2 mL), was added to a suspension of **16** (50 mg, 0.039 mmol) in CH_2Cl_2/MeOH (1/9, 5 mL). The reaction mixture was stirred for 36 h at room temperature, quenched with water, diluted with EtOAc, washed with water and then brine and the organic phase dried. The solvent was removed and the residue purified by column chromatography (EtOAc/PE 1/5) to give the title compound **17** (39 mg, 98%) as a colorless oil: $[\alpha]_D^{20} = +54.5°$ (*c* 0.91, $CHCl_3$); ν_{max} (cm^{-1}) 3476, 2927, 2855, 1129, 737, 398; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55−7.17 (30H, m), 7.11−7.03 (1H, m), 6.94 (1H, *J* = 8.3 Hz), 5.90 (1H, ddt, *J* = 17.3, 10.7, 5.5 Hz), 5.31 (1H, d, *J* = 1.7 Hz), 5.27 (1H, dq, *J* = 17.2, 1.6 Hz), 5.16 (1H, dq, *J* = 10.4, 1.4 Hz), 4.92 (1H, d, *J* = 10.8 Hz), 4.88−4.68 (9H, m), 4.63 (dd, *J* = 11.4, 2.2 Hz), 4.38 (t, *J* = 2.4 Hz), 4.20−4.10 (2H, m), 4.07 (2H, m), 3.95−3.78 (10H, m), 3.64 (1H, dd, *J* = 11.5, 3.4 Hz), 3.52 (1H, dd, *J* = 11.4, 1.6 Hz), 3.44 (1H, t, *J* = 9.3 Hz), 3.33 (1H, dd, *J* = 9.9, 2.5 Hz), 3.27 (1H, dd, *J* = 9.8, 2.1 Hz), 2.31 (1H, s), 0.85 (9H, s), 0.01 (3H, s), −0.02 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.20, 148.68, 140.18, 138.95, 138.75, 138.69, 138.08, 136.79, 134.59, 133.96, 128.54, 128.40, 128.34, 128.29, 128.22, 128.11, 128.04, 127.87, 127.83, 127.66, 127.60, 127.50, 126.71, 119.39, 117.12, 111.56, 110.48, 99.91, 83.46, 81.53, 81.20, 80.82, 79.56, 79.26, 76.16, 75.86, 75.72, 74.91, 74.05, 72.17, 72.12, 71.92, 71.84, 71.49, 68.76, 62.17, 56.03, 55.96, 25.99, 18.35, −5.09, −5.36 ppm; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{71}H_{84}O_{13}SiNa$ 1195.5579, found 1195.5562.

1-*O*-Allyl-4,5,6-tri-*O*-benzyl-2-*O*-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl)-3-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (18). Benzyl bromide (0.014 mL, 0.114 mmol) and then sodium hydride (60% in oil, 6 mg, 0.2 mmol) were added to a solution of **17** (76 mg, 0.076 mmol) in dry DMF (5 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature and then quenched with water and diluted with EtOAc. The mixture was washed with water and then brine, and the organic phase was dried. The solvent was removed, and the residue was purified by column chromatography (EtOAc/PE, 1/4) to give the title compound **18** (71 mg, 94%) as an oil: $[\alpha]_D^{20}$ = +36.5° (*c* 1.24, $CHCl_3$); ν_{max} (cm^{-1}) 2927, 2856, 737, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.13 (34H, m), 7.09 (1H, dd, *J* = 8.3, 2.1 Hz), 7.05 (1H, d, *J* = 2.1 Hz), 6.93 (1H, d, *J* = 8.3 Hz), 5.88 (1H, ddt, *J* = 17.2, 10.3, 5.6 Hz), 5.36 (1H, d, *J* = 1.7 Hz), 5.26 (1H, dq, *J* = 17.2, 1.6 Hz), 5.14 (1H, dq, *J* = 10.4, 1.4 Hz), 4.95−4.71 (8H, m), 4.67−4.56 (6H, m), 4.37 (1H, t, *J* = 2.4 Hz), 4.12 (2H, dt, *J* = 5.7, 1.4 Hz), 4.07 (1H, t, *J* = 9.7 Hz), 4.00 (1H, ddd, *J* = 9.9, 3.5, 1.6 Hz), 3.93 (3H, s), 3.92 (3H, s), 3.88 (1H, dd, *J* = 9.6, 3.2 Hz), 3.78 (1H, t, *J* = 9.5 Hz), 3.73 (1H, dd, *J* = 3.3, 1.7 Hz), 3.72−3.67 (2H, m), 3.54 (1H, dd, *J* = 11.5, 1.6 Hz), 3.40 (1H, t, *J* = 9.3 Hz), 3.31 (1H, dd, *J* = 9.9, 2.6 Hz), 3.23 (1H, dd, *J* = 9.8, 2.1 Hz), 0.86 (9H, s), 0.02 (3H, s), −0.01 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.35, 148.82, 140.33, 139.40, 138.95, 138.93, 138.91, 138.80, 138.70, 137.04, 134.81, 134.17, 128.60, 128.58, 128.55, 128.46, 128.46, 128.38, 128.31, 128.27, 128.21, 128.12, 128.10, 127.88, 127.84, 127.72, 127.71, 127.60, 126.91, 119.57, 117.57, 111.69, 110.61, 98.19, 83.58, 81.60, 81.33, 81.28, 79.37, 79.29, 77.43, 76.35, 76.07, 75.95, 75.16, 74.98, 74.71, 72.90, 72.35, 72.21, 72.02, 71.33, 62.53, 56.23, 56.15, 26.21, 18.59, −5.06, −5.30 ppm; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{78}H_{90}O_{13}SiNa$ 1285.6048, found 1285.6030.

1-*O*-Allyl-4,5,6-tri-*O*-benzyl-2-*O*-(2′,3′,4′-tri-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (19). Acetyl chloride (96 μL, 1.3 mmol) was added to a solution of **18** (85 mg, 0.067 mmol) in CH_2Cl_2/MeOH (3/7, 10 mL) and stirred at room temperature for 45 min. The reaction mixture was diluted with CH_2Cl_2 and washed with water and then brine. The organic phase was dried and evaporated, and the residue was purified by column chromatography (EtOAc/PE, 1/2 to 1/1) to give title compound **19** (69 mg, 89%) as a colorless oil: $[\alpha]_D^{20}$ = +43.2° (*c* 1.05, $CHCl_3$); ν_{max} (cm^{-1}) 3489, 3030, 2924, 739, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.20 (34H, m), 7.15 (1H, dd, *J* = 8.2, 2.1 Hz), 7.11 (1H, d, *J* = 2.1 Hz), 6.98 (1H, d, *J* = 8.3 Hz), 5.95 (1H, ddt, *J* = 17.3, 10.4, 5.6 Hz), 5.40 (1H, d, *J* = 1.7 Hz), 5.33 (1H, dq, *J* = 17.2, 1.6 Hz), 5.22 (1H, dq, *J* = 10.4, 1.4 Hz), 5.04−4.59 (14H, m), 4.35 (1H, t, *J* = 2.4 Hz), 4.22−4.10 (3H, m), 4.06 (1H, t, *J* = 9.6 Hz), 3.97 (3H, s), 3.96 (3H, s), 3.94 (1H, dd, *J* = 9.4, 3.1 Hz), 3.87−3.80 (2H, m), 3.73 (1H, t, *J* = 9.5 Hz), 3.66 (2H, t, *J* = 2.9 Hz), 3.46 (1H, t, *J* = 9.3 Hz), 3.37 (1H, dd, *J* = 9.9, 2.6 Hz), 3.29 (1H, dd, *J* = 9.8, 2.1 Hz), 1.88 ppm (1H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.34, 148.82, 140.44, 138.84, 138.81, 138.56, 138.37, 136.77, 134.72, 134.04, 128.62, 128.59, 128.58, 128.54, 128.53, 128.49, 128.30, 128.25, 128.19, 128.11, 127.96, 127.95, 127.87, 127.85, 127.83, 127.80, 127.71, 126.93, 119.54, 117.62, 111.68, 110.58, 98.78, 83.51, 81.54, 81.27, 81.06, 79.28, 79.00, 76.35, 76.02, 75.90, 75.32, 74.86, 74.60, 72.42, 72.40, 72.32, 72.26, 72.24, 62.31, 56.19, 56.14 ppm; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{72}H_{76}O_{13}Na$ 1171.5184, found 1171.5177.

1-*O*-Allyl-4,5,6-tri-*O*-benzyl-2-*O*-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-palmitoyl-α-D-mannopyranosyl)-3-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (20). Palmitic acid (78 mg, 0.30 mmol), dimethylaminopyridine (DMAP; 4 mg, 0.03 mmol), and dicyclohexylcarbodiimide (DCC; 0.052 g, 0.25 mmol) were added to a solution of the above compound (67 mg, 0.058 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred overnight at room temperature and the solvent evaporated. The residue was purified by column chromatography (EtOAc/PE, 1/9 to 1/2) to give the title compound **20** (65 mg, 80%) as a colorless oil: $[\alpha]_D^{30}$ = +28.0° (*c* 0.97, $CHCl_3$); ν_{max} (cm^{-1}) 2922, 2852, 1731, 736, 697; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57−6.86 (37H, m), 5.87 (1H, ddt, *J* = 17.3, 10.4, 5.7 Hz), 5.39 (1H, d, *J* = 1.7 Hz), 5.25 (1H, dq, *J* = 17.2, 1.6 Hz), 5.14 (1H, dq, *J* = 10.4, 1.3 Hz), 4.95−4.48 (14H, m), 4.32 (1H, t, *J* = 2.4 Hz), 4.25−4.08 (4H, m), 4.06 (1H, d, *J* = 11.1, 2.0 Hz), 3.98 (1H, t, *J* = 9.7 Hz), 3.94 (3H, s), 3.92 (3H, s), 3.86 (1H, dd, *J* = 9.6, 3.2 Hz), 3.78−3.73 (2H, m), 3.67 (1H, t, *J* = 9.5 Hz), 3.39 (1H, t, *J* = 9.3 Hz), 3.31 (1H, dd, *J* = 9.9, 2.6 Hz), 3.23 (1H, dd, *J* = 9.8, 2.2 Hz), 2.25 (2H, t, *J* = 7.6 Hz), 1.73−1.38 (2H, m), 1.38−1.09 (24H, m), 0.86 ppm (3H, t, *J* = 6.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.85, 149.37, 148.81, 140.65, 138.86, 138.84, 138.82, 138.65, 138.46, 138.37, 136.65, 134.72, 134.22, 128.66, 128.64, 128.63, 128.61, 128.60, 128.57, 128.55, 128.45, 128.35, 128.33, 128.28, 128.22, 128.20, 128.03, 127.91, 127.88, 127.86, 127.83, 127.75, 127.14, 119.61, 117.73, 111.66, 110.76, 98.40, 83.54, 81.56, 81.32, 81.05, 79.22, 78.81, 76.38, 76.05, 75.93, 75.48, 74.59, 74.21, 72.62, 72.50, 72.33, 72.21, 72.03, 70.21, 63.33, 56.22, 56.17, 34.44, 32.14, 29.92, 29.90, 29.88, 29.85, 29.72, 29.58, 29.51, 29.43, 25.11, 22.91, 14.34 ppm; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{88}H_{106}O_{14}Na$ 1409.7480, found 1409.7484.

1-*O*-Allyl-4,5,6-tri-*O*-benzyl-2-*O*-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-palmitoyl-α-D-mannopyranosyl)-1D-*myo*-inositol (21). TFA (0.80 mL, 10.4 mmol) was added to a solution of **20** (0.065 g, 0.047 mmol) and 3,4-(methylenedioxy)toluene (0.064 g, 0.47 mmol) in dry CH_2Cl_2 (3.5 mL), and the reaction mixture was stirred at room temperature for 3 h. Water was added to the mixture, which was then extracted into CH_2Cl_2. The organic phase was washed with sodium bicarbonate and brine, dried, and evaporated. The residue was purified by column chromatography (EtOAc/PE, 1/4) to give the title compound **21** (45 mg, 83%) as a colorless oil: $[\alpha]_D^{30}$ = +0.4° (*c* 0.60, $CHCl_3$); ν_{max} (cm^{-1}) 2922, 2952, 1734, 734, 697; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44−7.15 (30H, m), 5.88 (1H, ddt, *J* = 17.3, 10.5, 5.7 Hz), 5.31−5.25 (1H, m), 5.23 (1H, d, *J* = 1.8 Hz), 5.17 (1H, dq, *J* = 10.4, 1.4 Hz), 4.97−4.64 (9H, m), 4.62−4.53 (3H, m), 4.33 (1H, dd, *J* = 11.9, 4.7 Hz), 4.25 (1H, dd, *J* = 11.9, 2.1 Hz), 4.16 (1H, t, *J* = 2.5 Hz), 4.11 (2H, dt, *J* = 5.6, 1.4 Hz), 4.06 (1H, ddd, *J* = 9.9, 4.7, 2.0 Hz), 3.93 (1H, t, *J* = 9.5 Hz), 3.84−3.75 (2H, m), 3.70 (1H, t, *J* = 9.5 Hz), 3.55 (1H, t, *J* = 9.5 Hz), 3.46−3.36 (2H, m), 3.31 (1H, dd, *J* = 9.7, 2.3 Hz), 2.35−2.29 (2H, m), 2.08 (1H, d, *J* = 4.1 Hz), 1.66−1.53 (2H, m), 1.34−1.19 (24H, m), 0.88 ppm (3H, t, *J* = 6.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.99, 138.79, 138.69, 138.55, 138.41, 138.33, 134.72, 128.94, 128.68, 128.66, 128.65, 128.62, 128.50, 128.35, 128.33, 128.23, 128.21, 128.18, 128.01, 127.96, 127.95, 127.92, 127.90, 117.70, 99.04, 83.62, 82.02, 81.25, 80.62, 79.27, 76.18, 76.11, 75.77, 75.57, 75.48, 74.73, 74.36, 72.30, 72.19, 72.15, 70.91, 70.54, 63.53, 34.45, 32.15, 29.92, 29.91, 29.89, 29.88, 29.85, 29.73, 29.59, 29.53, 29.43, 25.12, 22.92, 14.35 ppm; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{73}H_{92}O_{12}Na$ 1183.6481, found 1183.6479.

1-*O*-Allyl-4,5,6-tri-*O*-benzyl-2-*O*-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-palmitoyl-α-D-mannopyranosyl)-3-*O*-stearoyl-1D-*myo*-inositol (22). Stearic acid (19 mg, 0.067 mmol), DMAP (3 mg, 0.02 mmol), and DCC (5 mg, 0.02 mmol) were added to a solution of **21** (12 mg, 0.010 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred overnight at room temperature. The reaction mixture was filtered through a plug of basic alumina and eluted with CH_2Cl_2. The crude residue was purified by column chromatography (PE to EtOAc/PE 1/9) to give the title compound **22** (13 mg, 83%) as a colorless oil: $[\alpha]_D^{31}$ = +19.8° (*c* 0.62, $CHCl_3$); ν_{max} (cm^{-1}) 2921, 2852, 1737, 733, 697; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.12 (30 H, m), 5.88 (1H, ddt, *J* = 17.3, 10.4, 5.7 Hz), 5.35 (1H, d, *J* = 1.7 Hz), 5.28 (1H, dq, *J* = 17.2, 1.6 Hz), 5.17 (1H, dq, *J* = 10.4, 1.3 Hz), 4.97 (1H, d, *J* = 10.7 Hz), 4.88−4.54 (13H, m), 4.41 (1H, dd, *J* = 11.7, 3.8 Hz), 4.23 (1H, t, *J* = 2.4 Hz), 4.16 (1H, dd, *J* = 11.8, 1.6 Hz), 4.14−4.09 (2H, m), 4.01−

3.92 (2H, m), 3.84 (1H, dd, J = 8.9, 3.0 Hz), 3.79 (1H, dd, J = 3.1, 1.8 Hz), 3.75 (1H, dd, J = 10.4, 9.2 Hz), 3.68 (1H, t, J = 9.5 Hz), 3.48 (1H, t, J = 9.3 Hz), 3.40 (1H, dd, J = 9.7, 2.1 Hz), 2.35−2.28 (2H, m), 2.20−2.01 (2H, m), 1.68−1.44 (4H, m), 1.39−1.12 (52H, m), 0.88 ppm (6H, t, J = 6.8 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 173.88, 173.19, 138.73, 138.59, 138.53, 138.50, 138.31, 138.26, 134.45, 128.71, 128.66, 128.64, 128.62, 128.58, 128.51, 128.38, 128.32, 128.29, 128.22, 128.18, 128.01, 127.98, 127.96, 127.92, 127.78, 118.04, 98.12, 83.51, 81.46, 80.75, 79.28, 79.11, 76.43, 76.14, 75.60, 75.58, 74.58, 73.95, 72.94, 72.39, 72.17, 72.05, 71.74, 70.51, 63.33, 34.39, 34.33, 32.15, 29.96, 29.95, 29.93, 29.91, 29.89, 29.87, 29.75, 29.69, 29.59, 29.58, 29.56, 29.45, 29.39, 25.13, 24.93, 22.92, 14.35 ppm; HRMS (ESI-TOF) m/z calcd for $C_{91}H_{126}O_{13}Na$ [M + Na]$^+$ 1449.9091, found 1449.9089.

4,5,6-Tri-*O*-benzyl-2-*O*-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-palmitoyl-*α*-D-mannopyranosyl)-3-*O*-stearoyl-1D-*myo*-inositol (11). (1,5-Cyclooctadiene)bis(methyldiphenylphosphine)iridium(I) hexafluorophosphate (4 mg, 0.005 mmol) was added to a stirred solution of **22** (16 mg, 0.011 mmol), in dry THF (2 mL) at room temperature under an atmosphere of Ar. The atmosphere was replaced with hydrogen for ca. 1 min and then replaced by Ar, the red solution changing to yellow. The reaction mixture was stirred for 2 h, the solvent removed, and the residue dissolved in acetone/water (9/1, 10 mL). To the solution were added mercuric oxide (50 mg, 0.023 mmol) and mercuric chloride (60 mg, 0.022 mmol), and this mixture was then heated to 100 °C for 3 h. Once it was cooled to room temperature, the reaction mixture was filtered through Celite and washed with CH$_2$Cl$_2$ and the solvent from the filtrate evaporated. The residue was dissolved in CH$_2$Cl$_2$, the solution washed with aqueous potassium iodide (5%) and dried, and the solvent evaporated. The residue was purified by column chromatography (PE to EtOAc/PE 1/4) to give the title compound **11** (11 mg, 71%) as a colorless oil: $[\alpha]_D^{20}$ = +10.1° (c 1.07, CHCl$_3$); ν_{max} (cm^{-1}) 3506, 2921, 2853, 1739, 735, 697; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43−7.14 (30H, m), 5.29 (1H, d, J = 1.8 Hz), 4.99−4.73 (5H, m), 4.69−4.53 (8H, m), 4.43−4.36 (1H, m), 4.21−4.13 (2H, m), 3.95 (2H, m), 3.85 (1H, dt, J = 6.9, 3.0 Hz), 3.77 (1H, ddd, J = 10.4, 6.6, 2.6 Hz), 3.68 (1H, dd, J = 3.1, 1.8 Hz), 3.57 (1H, dt, J = 6.7, 2.3 Hz), 3.54−3.49 (2H, m), 2.32−2.25 (2H, m), 2.22−2.03 (3H, m), 1.65−1.45 (6H, m), 1.30−1.13 (52H, m), 0.88 ppm (6H, t, J = 6.8 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 173.66, 172.85, 138.33, 138.28, 138.24, 138.22, 138.18, 128.76, 128.52, 128.49, 128.42, 128.39, 128.21, 128.14, 128.07, 128.00, 127.89, 127.87, 127.80, 127.61, 127.58, 127.48, 98.37, 83.59, 80.97, 79.83, 78.88, 75.92, 75.44, 75.36, 74.64, 74.51, 74.37, 72.17, 71.98, 71.95, 71.68, 70.34, 63.08, 34.18, 34.15, 31.94, 29.71, 29.69, 29.68, 29.65, 29.63, 29.51, 29.44, 29.35, 29.33, 29.30, 29.22, 29.16, 24.91, 24.72, 22.70, 14.11 ppm; HRMS (ESI-TOF): calcd for $C_{88}H_{122}O_{13}Na$ [M + Na]$^+$ m/z 1409.8783, Found m/z 1409.8773.

(−)-3-*O*-Allyl-4,5,6-tri-*O*-benzyl-1,2-*O*-isopropylidene-1D-*myo*-inositol (*ent*-12). Benzyl bromide (0.58 mL, 4.8 mmol) and then sodium hydride (60% in oil, 0.16 g, 6.5 mmol) were added with stirring to a solution of diol (+)-**6c** (0.565 g, 1.612 mmol) in dry DMF (20 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with water, diluted with EtOAc, and washed with water and then brine. The organic phase was dried, the solvent removed, and the residue purified by column chromatography (EtOAc/PE, 1/4) to give the title compound *ent*-**12** (0.847 g, 99%) as a colorless oil: $[\alpha]_D^{20}$ = −36.3° (c 1.11, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{33}H_{38}O_6Na$ 553.2566, found m/z 553.2563. All other spectroscopic data were consistent with those for **12**.

(−)-3-*O*-Allyl-4,5,6-tri-*O*-benzyl-1D-*myo*-inositol (*ent*-13). TFA (120 μL, 1.6 mmol) and then methanol (80 μL, 1.9 mmol) were added to *ent*-**12** (133 mg, 0.251 mmol) in CH$_2$Cl$_2$ (15 mL), and the mixture was stirred overnight at room temperature. The mixture was diluted with EtOAc, washed with sodium bicarbonate and then brine, and dried. The solvents were removed, and the residue was purified by column chromatography (EtOAc/PE, 1/1) to give the title compound *ent*-**13** (99 mg, 81%) as a white solid: $[\alpha]_D^{20}$ = −26.3° (c 1.29, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{30}H_{34}O_6Na$ 513.2253, found 513.2230. All other spectroscopic data were consistent with those for **13**.

(+)-3-*O*-Allyl-4,5,6-*O*-benzyl-1-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (*ent*-14). Diol *ent*-**13** (0.680 g, 1.39 mmol) and dibutyltin oxide (0.416 g, 1.67 mmol) were coevaporated from toluene, dried under high vacuum, and then redissolved in toluene (25 mL). The reaction mixture was refluxed in a Dean−Stark apparatus for 1 h until a clear, yellow solution formed. Once the solution was cooled, the solvent was removed under reduced pressure. Cesium fluoride (0.316 g, 2.08 mmol) and 4-(3,4-dimethoxyphenyl)benzyl bromide (0.468 g, 1.525 mmol) were added to the residue which was coevaporated from toluene and dried under high vacuum. The mixture was dissolved in dry DMF (20 mL) and heated overnight at 50 °C. The reaction mixture was cooled to room temperature and then diluted with ether and washed with water. The combined organic layers were washed with brine, dried, and evaporated. The residue was purified by column chromatography (EtOAc/PE, 1/6 to 1/4) to give the title compound *ent*-**14** (702 mg, 71%) as a white solid: $[\alpha]_D^{27}$ = +1.3° (c 1.06, CHCl$_3$); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{45}H_{48}O_8Na$ 739.3247, found m/z 739.3265. All other spectroscopic data were consistent with those for **14**.

3-*O*-Allyl-2-*O*-(2′-*O*-benzoyl-3′,4′-di-*O*-benzyl-6′-*O*-*tert*-butyldimethylsilyl-*α*-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-1-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (24). (a) TMSOTf (4 μL, 0.02 mmol) was added to a mixture of the alcohol *ent*-**14** (61 mg, 0.085 mmol), TCA donor **15** (0.08 g, 0.111 mmol), and powdered 4 Å molecular sieves in dry toluene (3 mL) at 0 °C. After it was stirred for 40 min at that temperature, the reaction mixture was quenched with Et$_3$N, filtered through Celite, and evaporated to dryness. The residue was purified by column chromatography (EtOAc/toluene 1/9, then EtOAc/PE 1/4) to give the title compound **24** (61 mg, 72%) as a colorless oil: $[\alpha]_D^{28}$ = +4.4° (c 2.15, CHCl$_3$); ν_{max} (cm^{-1}) 2928, 2855, 1723, 738, 697; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.08 (2H, dt, J = 8.3, 1.2 Hz), 7.56−7.47 (1H, m), 7.42−7.10 (30H, m), 6.97−6.92 (2H, m), 6.88 (1H, d, J = 7.9 Hz), 5.84 (1H, ddtd, J = 16.9, 10.6, 5.3, 1.0 Hz), 5.76−5.71 (1H, m), 5.41−5.36 (1H, m), 5.25 (1H, dt, J = 17.2, 1.4 Hz), 5.11 (1H, dt, J = 10.6, 1.4 Hz), 4.95−4.56 (14H, m), 4.35 (1H, t, J = 2.5 Hz), 4.20−3.86 (13H, m), 3.82−3.74 (2H, m), 3.44 (1H, td, J = 9.3, 1.1 Hz), 3.40 (1H, ddd, J = 9.9, 2.3, 1.1 Hz), 3.22 (1H, ddd, J = 10.0, 2.8, 1.1 Hz), 0.95 (9H, s), 0.10 (3H, s), 0.08 ppm (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.58, 149.28, 148.78, 140.36, 139.18, 138.91, 138.84, 138.27, 136.71, 134.91, 134.05, 133.02, 130.37, 130.14, 128.53, 128.49, 128.45, 128.39, 128.32, 128.26, 128.12, 128.02, 127.98, 127.75, 127.70, 127.60, 126.90, 119.49, 116.78, 111.66, 110.62, 99.08 ($^1J_{CH}$ = 171.9 Hz), 83.53, 81.57, 81.27, 81.08, 79.11, 78.02, 76.26, 76.06, 75.92, 75.21, 74.20, 72.66, 72.47, 72.27, 71.87, 71.69, 69.47, 62.30, 56.16, 56.09, 26.19, 18.57, −4.94, −5.15 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{78}H_{88}O_{14}SiNa$ 1299.5836, found 1299.5811.

(b) A solution of (+)-**14** (476 mg, 0.664 mmol), phosphate donor **23**[4b] (669 mg, 0.868 mmol), and 4 Å molecular sieves, dried from toluene, under Ar were dissolved in dry toluene (15 mL), and this mixture was cooled to −78 °C before the dropwise addition of TBSOTf (0.20 mL, 0.87 mmol). After 1 h Et$_3$N (0.20 mL) was added. The solution was then warmed to room temperature and filtered through Celite, and the solvents were removed to give a yellow oil. The residue was purified by column chromatography (PE to EtOAc/PE, 1/5) to give the title compound **24** (747 mg, 88%) as a colorless oil.

3-*O*-Allyl-2-*O*-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-*tert*-butyldimethylsilyl-*α*-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-1-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (25). A solution of sodium methoxide, prepared from the reaction of sodium (31 mg, 1.6 mmol) and MeOH (2 mL), was added to **24** (173 mg, 0.135 mmol) suspended in CH$_2$Cl$_2$/MeOH (1/9, 5 mL) and the mixture was stirred overnight at room temperature. The reaction mixture was quenched with water, diluted with EtOAc, and washed with water and then brine, and the organic phase was dried and evaporated. The crude product was purified by column chromatography (EtOAc/PE, 1/3) to give the intermediate 3-*O*-allyl-2-*O*-(3′,4′-di-*O*-benzyl-6′-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-1-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (110 mg, 81%) as a colorless oil: $[\alpha]_D^{33}$ = +14.6° (*c* 1.84, $CHCl_3$); ν_{max} (cm^{-1}) 3489, 2927, 2855, 738, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.48 (2H, m), 7.40−7.20 (27H, m), 7.13 (1H, dd, *J* = 8.3, 2.1 Hz), 7.09 (1H, d, *J* = 2.1 Hz), 6.94 (1H, d, *J* = 8.3 Hz), 5.86 (1H, ddt, *J* = 17.4, 10.6, 5.4 Hz), 5.41 (1H, d, *J* = 1.6 Hz), 5.25 (1H, dq, *J* = 17.3, 1.7 Hz), 5.11 (1H, dq, *J* = 10.5, 1.5 Hz), 4.90−4.64 (14H, m), 4.38 (1H, t, *J* = 2.4 Hz), 4.18 (ddt, *J* = 12.9, 5.4, 1.5 Hz), 4.12−4.05 (2H, m), 4.02 (1H, ddt, *J* = 12.8, 5.4, 1.6 Hz), 3.95−3.76 (13H, m), 3.44 (1H, t, *J* = 9.3 Hz), 3.39 (1H, dd, *J* = 9.8, 2.1 Hz), 3.21 (1H, dd, *J* = 9.9, 2.6 Hz), 2.33 (1H, s), 0.91 (9H, s), 0.10 (3H, s), 0.08 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.37, 148.86, 140.71, 139.11, 138.96, 138.94, 138.86, 138.26, 136.70, 134.93, 134.08, 128.73, 128.62, 128.55, 128.54, 128.53, 128.50, 128.35, 128.28, 128.27, 128.22, 128.09, 128.07, 127.88, 127.78, 127.76, 127.09, 119.55, 116.91, 111.71, 110.60, 99.78, 83.63, 81.72, 81.36, 81.30, 79.83, 79.19, 76.40, 76.10, 75.92, 75.15, 74.34, 72.79, 72.42, 72.11, 71.72, 70.86, 69.02, 62.76, 56.21, 56.16, 26.23, 18.64, −4.81, −5.08 ppm.

Benzyl bromide (105 μL, 0.884 mmol), and sodium hydride (60 mg, 1.5 mmol) were added to a solution of the above intemediate (0.689 g, 0.587 mmol) in dry DMF (10 mL) at 0 °C. The reaction mixture was stirred over 72 h at room temperature and then quenched with water, diluted with EtOAc, and washed with water then brine, and the organic phase was dried and evaporated. The crude product was purified using column chromatography (EtOAc/PE, 1/4) to give the title compound **25** (709 mg, 96%) as an oil: $[\alpha]_D^{28}$ = +0.9° (*c* 1.21, $CHCl_3$); ν_{max} (cm^{-1}) 2926, 2855, 735, 697; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.41 (2H, m), 7.39−7.11 (27H, m, 7.06 (1H, dd, *J* = 8.3, 2.1 Hz), 7.01 (1H, d, *J* = 2.1 Hz), 6.92 (1H, d, *J* = 8.3 Hz), 5.87 (1H, ddt, *J* = 17.2, 10.6, 5.4 Hz), 5.43 (1H, d, *J* = 1.6 Hz), 5.26 (1H, dq, *J* = 17.3, 1.6 Hz), 5.12 (1H, dq, *J* = 10.5, 1.4 Hz), 4.96−4.54 (12H, m), 4.49−4.37 (3H, m), 4.19 (1H, ddt, *J* = 12.9, 5.3, 1.5 Hz), 4.10−3.97 (3H, m), 3.97−3.83 (8H, m), 3.82−3.69 (3H, m), 3.67 (1H, dd, *J* = 3.2, 1.7 Hz), 3.42 (1H, t, *J* = 9.3 Hz), 3.38 (1H, dd, *J* = 9.8, 2.1 Hz), 3.22 (1H, dd, *J* = 9.9, 2.6 Hz), 0.92 (9H, s), 0.11 (3H, s), 0.09 ppm (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.36, 148.93, 140.91, 139.38, 139.00, 138.96, 138.90, 138.82, 138.58, 136.58, 135.01, 133.88, 128.85, 128.62, 128.55, 128.48, 128.40, 128.27, 128.24, 128.19, 128.17, 127.97, 127.85, 127.75, 127.69, 127.64, 127.46, 127.08, 119.58, 116.90, 111.69, 110.57, 97.91, 83.56, 81.60, 81.58, 81.29, 79.41, 79.09, 76.36, 76.07, 75.94, 75.21, 74.98, 74.84, 73.09, 72.87, 72.39, 71.85, 71.49, 70.59, 62.91, 56.22, 56.15, 26.24, 18.67, −4.98, −5.22 ppm; HRMS (ESI-TOF) *m*/*z* [M +Na]$^+$ calcd for $C_{78}H_{90}O_{13}SiNa$ 1285.6048, found 1285.6041.

3-*O*-Allyl-2-*O*-(2′,3′,4′-tri-*O*-benzyl-α-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-1-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (26). Acetyl chloride (0.80 mL, 11 mmol) was added to a solution of **25** (701 mg, 0.555 mmol) in CH_2Cl_2/MeOH (3/7, 10 mL), and the mixture was stirred at room temperature for 40 min. The reaction mixture was diluted with CH_2Cl_2 and washed with water and then brine, and the organic phase was dried and evaporated. The residue was purified using column chromatography (EtOAc/PE, 2/3) to give the title compound **26** (709 mg, 99%) as an oil: $[\alpha]_D^{29}$ = +2.8° (*c* 1.26, $CHCl_3$); ν_{max} (cm^{-1}) 3504, 2922, 2871, 737, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45−7.39 (2H, m), 7.36−7.05 (32H, m), 7.02 (1H, dd, *J* = 8.3, 2.1 Hz), 6.96 (1H, d, *J* = 2.1 Hz), 6.87 (1H, d, *J* = 8.3 Hz), 5.81 (1H, ddt, *J* = 17.3, 10.7, 5.4 Hz), 5.31 (1H, d, *J* = 1.7 Hz), 5.20 (1H, dq, *J* = 17.3, 1.7 Hz), 5.08 (1H, dq, *J* = 10.5, 1.4 Hz), 4.92−4.39 (14H, m), 4.24 (1H, t, *J* = 2.4 Hz), 4.12 (1H, ddt, *J* = 12.9, 5.5, 1.5 Hz), 4.04 (1H, dt, *J* = 9.9, 3.3 Hz), 4.01−3.91 (2H, m), 3.89 (3H, s), 3.88 (3H, s), 3.81 (1H, dd, *J* = 9.5, 3.1 Hz), 3.74 (2H, d, *J* = 3.3 Hz), 3.71−3.63 (3H, m), 3.41−3.31 (2H, m), 3.17 (1H, dd, *J* = 9.9, 2.6 Hz), 1.60 ppm (1H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.37, 148.95, 140.99, 138.90, 138.83, 138.80, 138.58, 138.32, 136.52, 134.90, 133.79, 128.72, 128.64, 128.62, 128.61, 128.60, 128.56, 128.39, 128.35, 128.23, 128.11, 127.91, 127.88, 127.87, 127.80, 127.79, 127.70, 127.11, 119.56, 117.17, 111.70, 110.55, 98.78, 83.53, 81.59, 81.27, 81.23, 79.34, 78.93, 76.38, 76.03, 75.93, 75.38, 75.01, 74.87, 73.41, 72.41, 72.40, 72.33, 72.17, 71.75, 62.63, 56.21, 56.15 ppm; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{72}H_{76}O_{13}Na$ 1171.5184, found 1171.5186.

3-*O*-Allyl-2-*O*-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-palmitoyl-α-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-1-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (27). Palmitic acid (300 mg, 1.2 mmol), DMAP (12 mg, 0.10 mmol), and DCC (190 mg, 0.90 mmol) were added to a solution of **26** (551 mg, 0.479 mmol) in CH_2Cl_2. The reaction mixture was stirred overnight at room temperature and then filtered through a plug of basic alumina and eluted with five column volumes of CH_2Cl_2. The residue was purified using column chromatography (PE to EtOAc/PE, 1/4) to give the title compound **27** (660 mg, 99%) as an oil: $[\alpha]_D^{20}$ = +1.7° (*c* 1.79, $CHCl_3$); ν_{max} (cm^{-1}) 2925, 2854, 1735, 740, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45−7.38 (2H, m), 7.38−7.10 (32H, m), 7.03 (1H, dd, *J* = 8.3, 2.1 Hz), 6.98 (1H, d, *J* = 2.1 Hz), 6.90 (1H, d, *J* = 8.3 Hz), 5.86 (1H, ddt, *J* = 17.4, 10.6, 5.4 Hz), 5.38 (1H, d, *J* = 1.7 Hz), 5.26 (1H, dq, *J* = 17.3, 1.7 Hz), 5.14 (1H, dq, *J* = 10.5, 1.5 Hz), 4.95−4.47 (13H, m), 4.45−4.38 (2H, m), 4.33 (1H, t, *J* = 2.4 Hz), 4.29−4.21 (2H, m), 4.17 (1H, ddt, *J* = 12.9, 5.4, 1.5 Hz), 4.03 (1H, ddt, *J* = 12.9, 5.4, 1.6 Hz), 3.98 (1H, t, *J* = 9.8 Hz), 3.91 (3H, s), 3.89 (3H, s), 3.84 (1H, dd, *J* = 9.6, 3.1 Hz), 3.76−3.65 (3H, m), 3.41 (1H, t, *J* = 9.3 Hz), 3.38 (1H, dd, *J* = 9.8, 2.2 Hz), 3.23 (1H, dd, *J* = 9.9, 2.6 Hz), 2.31 (2H, td, *J* = 7.4, 2.1 Hz), 1.67−1.55 (2H,m), 1.32−1.16 (24H,m), 0.90−0.83 ppm (3H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.82, 149.14, 148.71, 140.70, 138.67, 138.63, 138.60, 138.45, 138.26, 138.18, 136.27, 134.62, 128.46, 128.42, 128.39, 128.37, 128.35, 128.20, 128.16, 128.10, 128.01, 127.96, 127.89, 127.80, 127.70, 127.66, 127.65, 127.63, 127.59, 127.38, 126.84, 119.34, 117.03, 111.45, 110.33, 98.29, 83.31, 81.35, 80.98, 80.96, 79.07, 78.66, 76.16, 75.79, 75.73, 75.26, 74.42, 74.38, 73.17, 72.26, 72.02, 71.76, 71.43, 69.89, 63.38, 55.99, 55.93, 34.28, 31.92, 29.69, 29.68, 29.66, 29.65, 29.62, 29.50, 29.35, 29.30, 29.24, 24.93, 22.69, 14.12 ppm; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{88}H_{106}O_{14}Na$ 1409.7480, found 1409.7466;

2-*O*-(2′,3′,4′-Tri-*O*-benzyl-6′-*O*-palmitoyl-α-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-1-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-1D-*myo*-inositol (28). (1,5-Cyclooctadiene)bis(methyldiphenylphosphine)iridium(I) hexafluorophosphate (36 mg, 0.04 mmol) was added to a stirred solution of **27** (610 mg, 0.440 mmol), in dry THF (20 mL) at room temperature under an atmosphere of Ar. The atmosphere was replaced with H_2 for ca. 1 min, followed by a gentle stream of Ar. The reaction mixture was stirred for 3 h, the solvent was removed, and the residue was dissolved in acetone/water (9/1, 20 mL). To the solution were added mercuric oxide (220 mg, 1.0 mmol) and mercuric chloride (250 mg, 0.9 mmol), and this mixture was then heated to 100 °C for 4 h. Once it was cooled to room temperature, the reaction mixture was filtered through Celite, the pad was washed with CH_2Cl_2, and the solvent from the filtrate was evaporated. The residue was dissolved in CH_2Cl_2, this solution was washed with aqueous potassium iodide (5%) and dried, and the solvent was evaporated. The residue was purified by column chromatography (PE to EtOAc/PE, 1/2) to give the title compound **28** (557 mg, 92%) as a pale yellow oil: $[\alpha]_D^{20}$ = +4.3° (*c* 1.09, $CHCl_3$); ν_{max} (cm^{-1}) 3560, 2924, 2854, 1734, 736, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46−7.40 (2H, m), 7.38−7.15 (32H, m), 7.05 (1H, dd, *J* = 8.3, 2.1 Hz), 7.01 (1H, d, *J* = 2.1 Hz), 6.92 (1H, d, *J* = 8.3 Hz), 5.25 (1H, d, *J* = 1.6 Hz), 4.96−4.80 (6H, m), 4.73−4.44 (8H, m), 4.35−4.24 (2H, m), 4.23 (1H, t, *J* = 2.5 Hz), 4.05 (1H, ddd, *J* = 9.9, 4.7, 2.3 Hz), 3.92 (3H, s), 3.90 (3H, m), 3.89 (1H, d, *J* = 1.4 Hz), 3.81−3.74 (3H, m), 3.57 (1H, t, *J* = 9.5 Hz), 3.49−3.40 (3H, m), 2.30 (2H, dd, *J* = 8.4, 6.9 Hz), 2.09 (1H, d, *J* = 4.4 Hz), 1.63−1.54 (2H, m), 1.32−1.18 (24H, m), 0.88 ppm (3H, t, *J* = 6.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.73, 149.22, 148.78, 140.74, 138.66, 138.49, 138.36, 138.26, 138.20, 136.29, 133.66, 128.72, 128.44, 128.39, 128.27, 128.17, 128.11, 128.01, 127.95, 127.85, 127.83, 127.78, 127.74, 127.70, 127.67, 127.48, 126.90, 119.39, 111.55, 110.45, 99.05, 83.52, 81.91, 81.16, 80.56, 79.09, 75.98, 75.82, 75.36, 75.21, 74.66, 74.59, 72.911, 72.121, 71.961, 70.82, 70.49, 63.34, 56.02, 55.96, 34.25, 31.93, 29.70, 29.64, 29.51, 29.36, 29.32, 29.22, 24.92, 22.69, 14.11 ppm; HRMS (ESI-TOF) [M + Na]$^+$ *m*/*z* calcd for $C_{85}H_{102}O_{14}Na$ 1369.7167, found 1369.7177.

2-*O*-(2′,3′,4′-Tri-*O*-benzyl-6′-*O*-palmitoyl-α-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-1-*O*-(4-(3,4-dimethoxyphenyl)benzyl)-3-*O*-stearoyl-1D-*myo*-inositol (29). Stearic acid (220 mg, 0.77 mmol), DCC (160 mg, 0.78 mmol), and DMAP (13 mg, 0.11 mmol) were added to a solution of **28** (524 mg, 0.389 mmol) in anhydrous CH_2Cl_2. The reaction mixture was stirred at room temperature for 60 h. The reaction mixture was filtered through a plug of basic alumina which was eluted with five column volumes of CH_2Cl_2. The solvent was removed from the combined filtrate, and the residue was purified by column chromatography (PE to EtOAc/PE, 1/4) to give the title compound **29** (582 mg, 93%) as a colorless oil: $[\alpha]_D{}^{20} = +8.2°$ (*c* 2.12, $CHCl_3$); ν_{max} (cm^{-1}) 2923, 2853, 1738, 736, 697; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (2H, d, *J* = 8.2 Hz), 7.38–7.15 (32H, m), 7.05 (1H, dd, *J* = 8.3, 2.1 Hz), 7.01 (1H, d, *J* = 2.1 Hz), 6.92 (1H, d, *J* = 8.3 Hz), 5.39 (1H, d, *J* = 1.8 Hz), 4.96 (1H, d, *J* = 10.7 Hz), 4.92–4.74 (6H, m), 4.71–4.53 (6H, m), 4.51–4.37 (3H, m), 4.35 (1H, t, *J* = 2.4 Hz), 4.20 (1H, dd, *J* = 11.8, 1.4 Hz), 3.98–3.88 (8H, m), 3.87–3.84 (1H, m), 3.79 (1H, dd, *J* = 10.4, 9.2 Hz), 3.77–3.72 (m), 3.57–3.50 (2H, m), 2.35–2.26 (2H, m), 2.22–2.02 (2H, m), 1.65–1.55 (2H, m), 1.54–1.44 (2H, m), 1.34–1.11 (52H, m), 0.88 ppm (6H, td, *J* = 6.9, 2.3 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.62, 173.01, 149.21, 148.78, 140.82, 138.59, 138.37, 138.32, 138.15, 138.09, 136.01, 133.67, 128.60, 128.48, 128.45, 128.42, 128.38, 128.16, 128.13, 128.11, 127.95, 127.85, 127.77, 127.73, 127.70, 127.57, 127.48, 126.91, 119.40, 111.54, 110.47, 97.97, 83.41, 81.33, 80.84, 79.16, 78.93, 76.22, 75.86, 75.38, 75.34, 74.43, 74.13, 73.08, 72.51, 71.90, 71.81, 71.65, 70.44, 63.15, 56.01, 55.96, 34.20, 34.14, 31.94, 29.74, 29.72, 29.54, 29.48, 29.37, 29.25, 29.20, 24.94, 24.72, 22.69, 14.11 ppm; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{103}H_{136}O_{15}Na$ 1635.9777, found 1635.9768.

2-*O*-(2′,3′,4′-Tri-*O*-benzyl-6′-*O*-palmitoyl-α-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-3-*O*-stearoyl-1D-*myo*-inositol (11). TFA (0.80 mL, 10 mmol) was added to a solution of **29** (582 mg, 0.361 mmol) and the scavenger 3,4-(methylenedioxy)toluene (250 mg, 1.8 mmol) in CH_2Cl_2 (3.2 mL), and the reaction mixture was stirred overnight at room temperature. The reaction mixture was washed with sodium bicarbonate and then brine, and the organic phase was dried and evaporated. The residue was purified by column chromatography (EtOAc/toluene, toluene to 1/19) to give the title compound **11** (381 mg, 76%) as a colorless oil. All spectroscopic data were consistent with those for **11** synthesized from (−)-**7c**.

Triethylammonium 2-*O*-(2′,3′,4′-Tri-*O*-benzyl-6′-*O*-palmitoyl-α-D-mannopyranosyl)-4,5,6-tri-*O*-benzyl-3-*O*-stearoyl-1-*O*-(1-*O*-(*R*)-tuberculostearoyl-2-*O*-palmitoyl-*sn*-glycero-3-phosphoryl)-1D-*myo*-inositol (31). *H*-Phosphonate **30**[4b,c] (26 mg, 0.034 mmol) and **29** (25 mg, 0.018 mmol) were coevaporated from pyridine and then dried under high vacuum. The residue was dissolved in dry, distilled pyridine (4 mL) at room temperature under Ar. Freshly distilled pivaloyl chloride (25 μL, 0.20 mmol) was added in one portion, and the reaction mixture was stirred overnight at room temperature. A freshly prepared solution of iodine (42 mg, 0.17 mmol) in pyridine/water (9/1, 10 mL) was added, and the mixture was stirred for a further 1 h. The solution was diluted with chloroform, stirred for 15 min, and then washed with sodium thiosulfate solution (10%). The organic phase was washed with a triethylammonium bicarbonate (TEAB) buffer (1 M, pH 7.5) and then dried and evaporated. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH/Et_3N 96/3/1) to give the title compound **31** (34 mg, 87%) as a pale yellow oil: $[\alpha]_D{}^{20} = +15.4°$ (*c* 0.59, $CHCl_3$); ν_{max} (cm^{-1}) 2923, 2854, 1740, 736, 698; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (2H, d, *J* = 7.4 Hz), 7.39 (2H, d, *J* = 7.4 Hz), 7.34–7.13 (26H, m), 5.49 (1H, s), 5.09 (1H, dq, *J* = 8.9, 5.1 Hz), 4.97 (1H, d, *J* = 10.7 Hz), 4.90 (1H, d, *J* = 11.1 Hz), 4.85–4.72 (8H, m), 4.65–4.53 (3H, m), 4.51–4.45 (2H, m), 4.34 (1H, dd, *J* = 11.9, 3.5 Hz), 4.27–4.20 (1H, m), 4.17 (2H, m), 4.04–3.90 (5H, m), 3.88–3.84 (1H, m), 3.81 (1H, dd, *J* = 9.5, 3.1 Hz), 3.75–3.65 (2H, m), 3.51 (1H, t, *J* = 9.2 Hz), 2.91 (6H, d, *J* = 7.3 Hz), 2.29–1.96 (8H, m), 1.52 (8H, m), 1.40–1.01 (43H, m), 0.91–0.81 ppm (15H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.63, 173.15, 172.87, 172.63, 138.47, 138.41, 138.36, 138.10, 128.45, 128.37, 128.34, 128.31, 128.21, 128.18, 128.06, 128.02, 127.84, 127.74, 127.67, 127.58, 127.54, 127.48, 98.27, 82.96, 80.18, 78.94, 78.48, 77.02, 76.14, 75.48, 75.35, 75.24, 74.23, 73.43, 71.45, 71.32, 70.46, 70.03, 64.48, 62.95, 62.27, 45.51, 37.16, 34.17, 34.09, 34.01, 32.81, 31.94, 30.06, 29.73, 29.58, 29.50, 29.37, 29.29, 29.20, 27.13, 24.93, 24.85, 24.78, 22.70, 19.71, 14.12, 8.43 ppm; ^{31}P NMR (202 MHz, $CDCl_3$) δ −1.54 ppm; HRMS (ESI-TOF) *m/z* $[M - Et_3N]^-$ calcd for $C_{126}H_{194}O_{20}P$ 2058.3901, found 2058.3894.

Sodium 2-*O*-(6′-*O*-Palmitoyl-α-D-mannopyranosyl)-3-*O*-stearoyl-1-*O*-(1-*O*-(*R*)-tuberculostearoyl-2-*O*-palmitoyl-*sn*-glycero-3-phosphoryl)-1D-*myo*-inositol (9; Ac_2PIM_1). A solution of triethylammonium salt **31** (22 mg, 0.010 mmol) in $CHCl_3$/MeOH (1/1, 10 mL) was stirred in the presence of DOWEX 50WX8-200 (Na^+) resin for 3 h. The resin was filtered off and the solvent evaporated. The residue was dissolved in CH_2Cl_2/MeOH (2/3, 5 mL), $Pd(OH)_2/C$ (10% *w/w*, 10 mg) was added, and the reaction mixture was stirred under an atmosphere of hydrogen for 2 h at room temperature. The reaction mixture was filtered through Celite and washed with $CHCl_3$/MeOH/water (70/40/6), and the solvents were evaporated. The residue was purified on C-18 reversed-phase silica (MeOH to MeOH/$CHCl_3$) to give the title compound **9** (15 mg, 98%) as a white solid: $[\alpha]_D{}^{20} = +22.7°$ (*c* 0.41, $CHCl_3$/MeOH 70/40); ^1H NMR (500 MHz, $CDCl_3/CD_3OD/D_2O$ 70/40/6) δ 5.22–5.27 (1H, m), 5.11 (1H, d, *J* = 1.6 Hz), 4.77 (1H, dd, *J* = 10.6, 2.7 Hz), 4.45 (1H, dd, *J* = 12.0, 3.0 Hz), 4.40 (1H, dd, *J* = 12.3, 4.8 Hz), 4.27 (1H, t, *J* = 2.4 Hz), 4.24 (1H, dd, *J* = 12.4, 2.4 Hz), 4.18 (1H, dd, *J* = 12.0, 7.2 Hz), 3.94–4.10 (5H, m), 3.73–3.83 (3H), 3.63–3.71 (1H, m), 3.34 (1H, m), 2.28–2.47 (8H, m), 1.55–1.68 (8H, m), 1.18–1.41 (43H, m), 0.82–0.94 ppm (15H, m): ^{13}C NMR (126 MHz, $CDCl_3/CD_3OD/D_2O$ 70/40/6) δ 175.05, 174.52, 174.15, 174.13, 102.20, 77.14, 76.89, 74.94, 72.77, 72.27, 71.12, 71.00, 70.93, 70.79, 70.73, 70.37, 67.62, 64.19, 63.11, 37.47, 37.44, 34.51, 34.44, 34.41, 34.28, 33.11, 32.25, 30.37, 30.35, 30.06, 30.04, 29.99, 29.97, 29.94, 29.91, 29.86, 29.77, 29.72, 29.67, 29.60, 29.54, 29.49, 27.44, 27.40, 25.27, 25.21, 25.15, 22.14, 22.97, 19.90, 14.21 ppm; ^{31}P NMR (202 MHz, $CDCl_3/MeOD/D_2O$ 70/40/6) δ 0.04 ppm; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{84}H_{159}O_{20}PNa$ 1542.1060, found 1542.1049; HRMS (ESI-TOF) *m/z* $[M - Na]^-$ calcd for $C_{84}H_{158}O_{20}P$ 1518.1084, found 1518.1071.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^1H and ^{13}C NMR spectra for all novel compounds and chromatograms from the chiral HPLC analyses of compounds **6a–i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the IRL Charitable Trust and the University of Otago for financial assistance for A.M.M.L.

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