# Synthesis of the Fully Phosphorylated GPI Anchor Pseudohexasaccharide of *Toxoplasma gondii*

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Retrosynthesis of the fully phosphorylated glycosylphosphatidyl inositol (GPI) anchor pseudohexasaccharide **1a** led to building blocks **2**−**6**, of which **5** and **6** are known. The formation of pseudodisaccharide building block **2** is based on readily available building block **7**, which gave, via derivative **11** and its glycosylation with known donor **12**, the desired compound **2**. Building block **3**, with the required access to all hydroxy groups being permitted, was prepared from mannose in five steps. From a readily available precursor, building block **4** was obtained, which on reaction with **3** gave disaccharide **23**. The synthesis of the decisive pseudohexasaccharide intermediate **32** was based on the reaction of **23** with **5**, then with **6**, and finally with **2**. To obtain high stereoselectivity and good yields in the glycosylation reactions, anchimeric assistance was employed. To enable regioselective attachment of the two different phosphorus esters, the 6f-*O*-silyl group of **32** was first removed and the aminoethyl phosphate residue was attached. Then the MPM group was oxidatively removed, and the second phosphate residue was introduced. Unprotected **1a** was then liberated in two steps: treatment with sodium methanolate removed the acetyl protecting groups, and finally, catalytic hydrogenation afforded the desired target molecule, which could be fully structurally assigned.

## Introduction

Glycosylphosphatidyl inositol (GPI) anchors constitute a class of glycolipids that link proteins and glycoproteins via their C-terminus to eucaryotic cell membranes. The first structure of a GPI anchor, that of *Trypanosoma brucei*, was published by Ferguson et al.[1] Since then quite a few examples of GPI anchors were described, allowing the definition of the core structure depicted in Figure 1.[2−5]

The diversity within GPI anchors is mainly reflected in the location and nature of the branching groups of the glycan residue ($R^2$, $R^3$, $R^4$). Additional ethanolamine phosphates ($R^1$) (i.e., Thy-1 GPI anchor in rat brain)[3] seem to be specific for higher eukaryotes. Concerning the lipid residue, many of the structures of GPI anchors contain a diacylglycerol moiety (i.e., *sn*-1,2-dimyristoylglycerol in *Trypanosoma brucei* VSG),[1] but alkylacylglycerol residues are not uncommon (i.e., *sn*-1-alkyl-2-acylgylcerol in human AChE or rat brain Thy-1), and ceramide structures have also been identified (i.e., in *Saccharomyces cerevisiae*).[2] These modifications of the evolutionary conserved structure give rise to species-, stage-, and tissue-specific GPI structures.

Various functions have been described for GPI anchors.[6,7] Some basic functions are common to higher and lower eukaryotes; the most fundamental function is to afford a stable association of proteins with the lipid bilayer in contrast to the "classical" transmembrane domains. The GPI anchor is an efficient and stable anchor and is comparable with a hydrophobic polypeptide domain. GPI anchoring seems to be a more general principle among protozoans; higher eukaryotes use this principle predominantly for certain proteins with specialized functions.[8]

Besides this obvious function of GPI anchors, it became clear that GPIs play an important role in other cellular mechanisms. GPI anchoring seems to provide a signal for transport to the cell membrane. In some polarized epithelial cells, GPI-anchored proteins are exclusively transported to the apical surface, which causes this anchor to function as a sorting and targeting signal.[8]

One of the most interesting and controversial aspects of GPI function is their ability to mediate signaling mechanisms or to function as second messengers in the plasma membrane. Since GPIs are structurally related to the more common second messengers as inositol phosphates, diacyl glycerol, phosphatidic acid, and ceramide, GPIs and/or their cleavage products are expected to participate in cellular signaling and hormone action.[9] Therefore, and as expected, free and protein-released GPIs are

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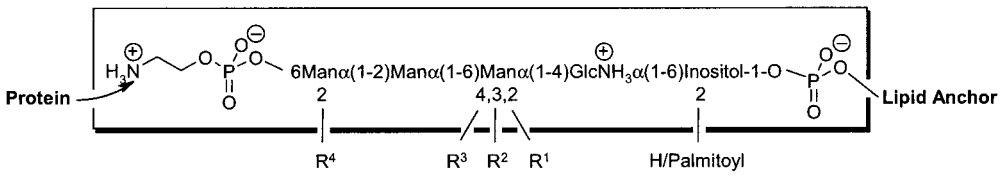
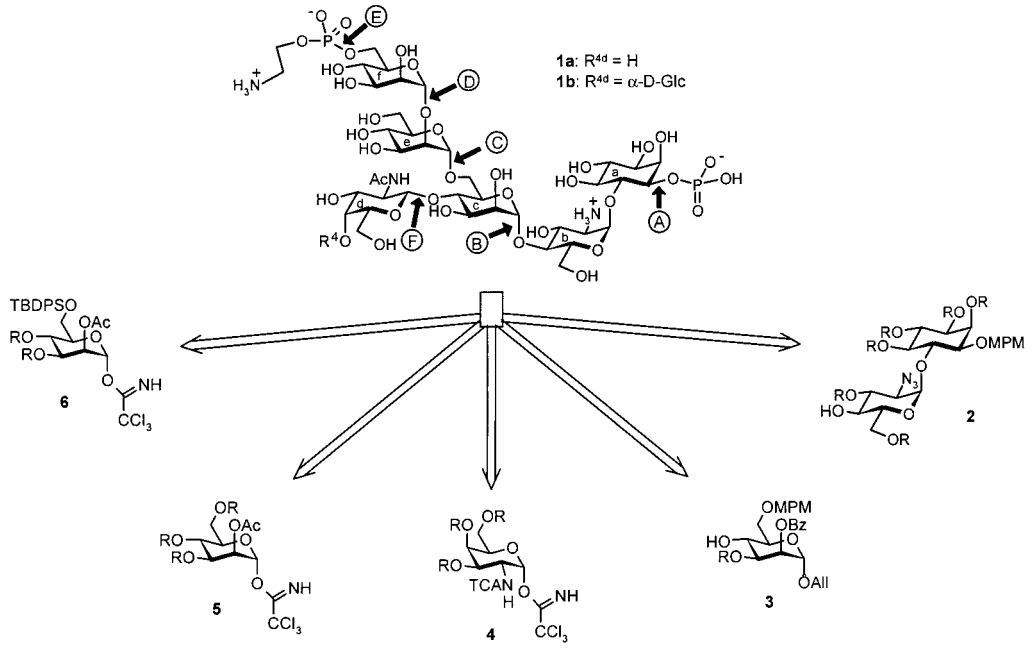



| Natural Source | $R^4$ | $R^3$ | $R^2$ | $R^1$ | Lipid | Ref. |
|---|---|---|---|---|---|---|
| *S. cerevisiae* | Manα(1-2) | H | H | H | Ceramide/DAG | 2 |
| *T. brucei* VSG | H | H | $Gal_{2\text{-}4}$α(1-3) | H | DAG | 1 |
| *T. gondii A* | H | GalNAcβ(1-4) | H | H | DAG | 4 |
| *B* | H | Glcα(1-4)GalNAcβ(1-4) | H | H | DAG | 4 |
| *Rat Brain* Thy-1 | Manα(1-2) | GalNAcβ(1-4) | H | EA-P | Acylalkylglycerol | 3 |

**Figure 1.** Structure of GPI anchors (EA, ethanolamine; P, phosphate; DAG, diacylglycerol).

**Scheme 1. Retrosynthesis (R = Bn)**




reported to mimic the effects of hormone-like peptides: interleukin-2, nerve-growth factor, and insulin.[10]

Another highly interesting aspect of this involvement of GPI anchors in signal transduction is their involvement in the pathogenicity of protozoan parasites. *Toxoplasma gondii* (*T. gondii*) is an ubiquitous parasitic protozoan causing congenital infection and severe and often lethal encephalitis in the course of the acquired immunodeficiency syndrome (AIDS). A carbohydrate-containing low molecular mass antigen has been described to exhibit immunological characteristics suitable for serological diagnosis of acute toxoplasmosis.[4] This antigen was identified to be a family of protein-free GPI glycolipids, and recently the structure of these GPIs was elucidated.[11] Two types of core glycans were identified: glycan A modified by GalNAc-linked $\beta$(1−4) to the core mannose adjacent to the nonacetylated glucosamine and glycan B containing a novel Glcα(1−4)GalNAc side branch. Subsequent immunological analysis revealed that only glucosylated GPIs containing glycan B were recognized by sera from infected humans, suggesting that the unique glucose modification is required for immunogenicity.

For a better understanding of this phenomenon, we synthesized the type A GPI glycan of *T. gondii* [4] in a water soluble form (**1a** in Scheme 1) without the lipid moiety in order to employ it in biological studies.

The first synthesis of a naturally occurring GPI anchor (*S. cerevisiae*) was published by us in 1994.[12] Approaches to the *T. brucei* GPI anchor (in 1992[13] and in 1998[14]) and to the rat brain Thy-1 GPI anchor (in 1995[15] and in 1999[16]) have also been reported. We now present a synthetic approach to the *T. gondii* GPI anchor involving

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(11) Striepen, B.; Dubremetz, J.-F.; Schwarz, R. T. *Biochemistry* **1999**, *38*, 14798−1487.
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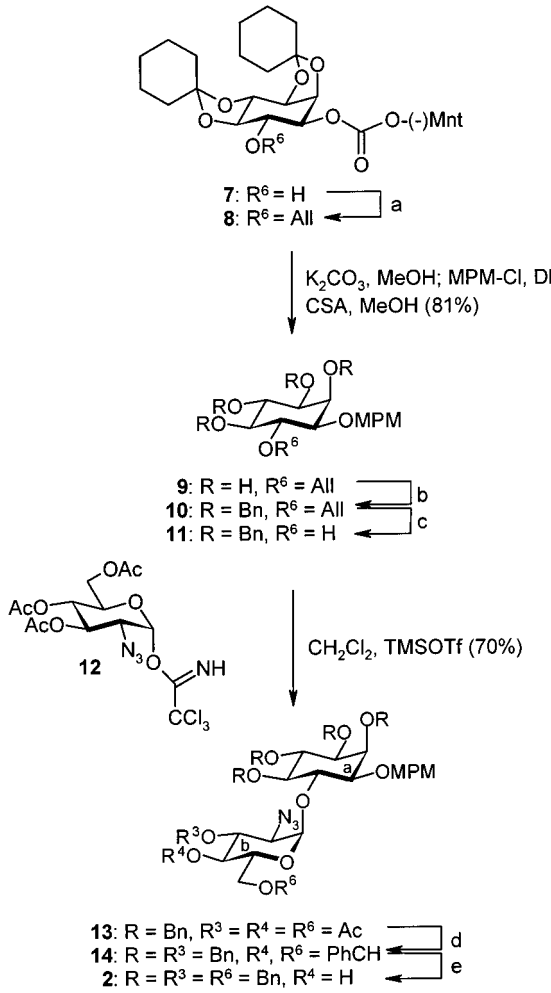
**Scheme 2. Synthesis of 2 (R = Bn)**[a]




[a] Key: a = All-Br, $Ag_2O$ (78%); b = BnBr, NaH (92%); c = Rh-cat, HCl (aq.) (qu.); d = NaOMe, $PhCH(OMe)_2$ (CSA), and BnBr (NaH) (86%); e = $NaBH_3CN$, HCl (87%).

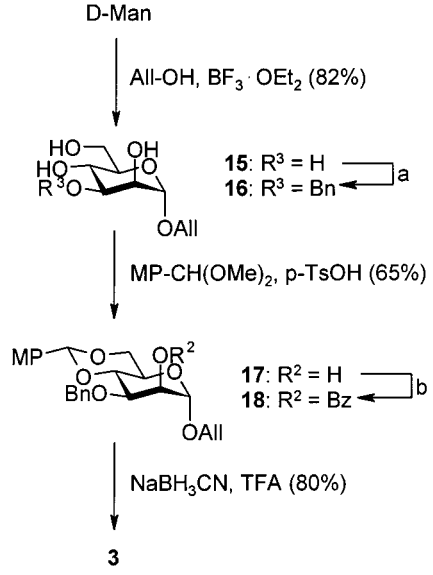
the coupling of building blocks which were newly designed in part. Particularly important is the protective group pattern of mannose residue c, because it plays a key role in the synthetic strategy that requires selective access to the 1-, 4-, and 6-position and provides anchimeric assistance for α-glycoside bond formation. Thus, the variations in the overall strategy presented in this paper should ease the construction of various GPI anchor types.

## Results and Discussion

The strategy which we have developed to synthesize **1a** is convergent and highly versatile. The target molecule **1a** is first disconnected at positions A−E (see arrows in Scheme 1) affording carbohydrate building blocks **2**, **5**, and **6** and a Gal$\beta$(1−4)Man unit which, via disconnection at position F, leads to monosaccharide building blocks **3** and **4**; **3** represents the building block for the sugar residue c in **1a**. Due to proper protection, **2**−**6** should be widely applicable in GPI anchor synthesis.[17] This has already been demonstrated for building blocks **5** and **6**, which have been previously employed.[16,17]

(17) Mayer, T. G.; Schmidt, R. R. *Eur. J. Org. Chem.* **1999**, *1153*, 3−1165.

**Scheme 3. Synthesis of 3**[a]

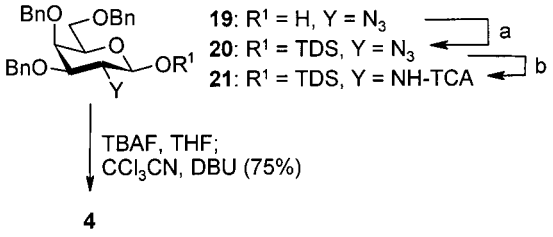



[a] Key: a = $Bu_2SnO$, TBAI, BnBr (75%); b = BzCN, $NEt_3$ (95%).

**Synthesis of Building Blocks 2−4.** The synthesis of building block **2** (Scheme 2) was based on the previously reported transformation of *myo*-inositol into the D-*myo*-inositol derivative **7**.[12] 6-*O*-Allylation (→**8**) and replacement of the menthyloxycarbonyl group by the 4-methoxyphenylmethyl (MPM) group, acid-catalyzed removal of the cyclohexylidene groups (→**9**), and introduction of the *O*-benzyl groups afforded the fully protected inositol derivative **10**. Selective 6-de-*O*-allylation with Wilkinson's catalyst followed by acid-catalyzed cleavage of the intermediary propenyl ether furnished 6-*O*-unprotected acceptor **11**. Glycosylation with known 2-azido-2-deoxy-glucopyranosyl trichloroacetimidate **12**,[12,17] as glycosyl donor, in dichloromethane, as solvent, and trimethylsilyl trifluoromethanesulfonate (TMSOTf), as catalyst, afforded the desired α(1−4)-linked pseudodisaccharide **13** in 70% yield. The structural assignment was based on the $^1$H NMR data (see below). The required 4b-*O*-unprotected acceptor **2** was readily obtained from **13** via de-*O*-acetylation, 4b,6b-*O*-benzylidenation, and finally 3b-*O*-benzylation affording intermediate **14** in high overall yield. Reductive opening of the benzylidene group with sodium cyanoborohydride in the presence of HCl furnished **2** in 87% yield.

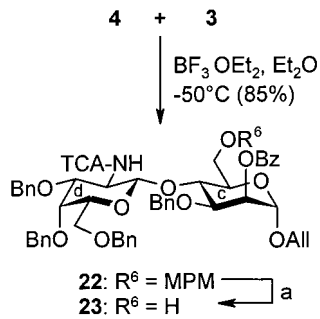
The synthesis of the strategically important building block **3** (Scheme 3) could be performed by starting from the known allyl mannopyranoside **15**.[18] Benzylation with benzyl bromide in the presence of dibutyltin oxide and tetrabutylammonium iodide (TBAI) afforded the desired 3-*O*-benzyl derivative **16** in 75% yield. Reaction with 4-methoxybenzaldehyde dimethylacetal [MP−$CH(OMe)_2$] in the presence of *p*-toluenesulfonic acid (*p*-TsOH) as catalyst afforded 4,6-*O*-arylidene derivative **17**. The 2-*O*-benzoylation of **17** with benzoyl cyanide/triethylamine (→**18**) and then the reductive opening of the *p*-methoxybenzylidene group containing ring afforded 4-*O*-unprotected 6-*O*-MPM-protected acceptor **3**. This compound offers the desired regio- and stereoselective reactions: (i) after 4-*O*-glycosylation, (ii) glycosylation at the 6-*O*-position, and (iii) transformation into a glycosyl donor permitting, via anchimeric assistance, α-selective glycosylation of acceptor **2**.

**Scheme 4. Synthesis of 4**[a]




[a] Key: a = TDS−Cl, Im. (96%); b = $NaBH_4$ (EtOH), TCA-Cl ($NEt_3$) (74%).

**Scheme 5. Synthesis of 23**[a]



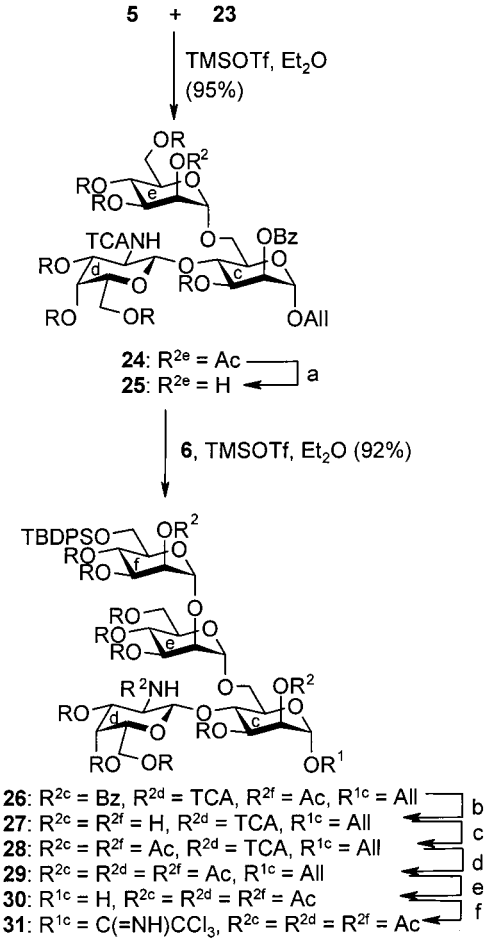

[a] Key: a = CAN, MeCN, Tol, $H_2O$ (85%).

The required galactosamine donor **4** was generated from known 2-azido-3,4,6-tri-*O*-benzyl-2-deoxygalactose **19**[19] (Scheme 4). For the introduction of an *N*-trichloroacetyl (TCA) group, to ensure high glycosyl donor properties and anchimeric assistance for $\beta$-glycoside bond formation, the anomeric hydroxy group was silylated with thexyldimethylsilyl (TDS) chloride in the presence of imidazole affording **20** in high yield. Reduction of the azido group with sodium borohydride in ethanol gave the amine, which upon treatment with trichloroacetyl chloride in the presence of triethylamine furnished *N*-TCA-protected **21**. The removal of the TDS group with tetrabutylammonium fluoride (TBAF) in THF and then treatment with trichloroacetonitrile in the presence of DBU as base afforded the desired trichloroacetimidate **4** as glycosyl donor.

Glycosylation of acceptor **3** with glycosyl donor **4** (Scheme 5) required mild reaction conditions; with catalytic amounts of $BF_3 \cdot Et_2$ in dichloromethane at −50 °C, the desired $\beta$(1−4)-linked disaccharide **22** was obtained in 85% yield ($^1$H NMR: $J_{1d,2d}$ = 8.2 Hz). Removal of the MPM group at 6d-*O* could be readily performed, upon treatment with ceric(IV) ammonium nitrate (CAN), affording acceptor **23**. Thus, the syntheses of all the building blocks required for the construction of target molecule **1a** could be very successfully carried out.

**Construction of Target Molecule 1a.** To arrive at the final goal, glycosyl acceptor **23** was treated with glycosyl donor **5** (Scheme 6). Anchimeric assistance by the 2-*O*-acetyl group with ether as solvent in the presence of TMSOTf as catalyst led to α(1−6)-linkage, furnishing the desired trisaccharide **24** in practically quantitative yield. Selective removal of the 2c-*O*-acetyl group could be performed with methylamine in ethanol, furnishing

**Scheme 6. Synthesis of 31 (R = Bn)**[a]




[a] Key: a = $MeNH_2$, EtOH (65%); b = NaOMe, MeOH, 50 °C (97%); c = $Ac_2O$, Pyr (qu.); d = $Bu_3SNH$, AIBN, Tol, 100 °C (84%); e = $Rh(PPh_3)_3$, Tol, EtOH, $H_2O$; THF/$H_2O$, $I_2$ (87%); f = $CCl_3CN$, DBU (82%).

2c-*O*-unprotected acceptor **25**, which on treatment with **6** as glycosyl donor with TMSOTf as catalyst led to α-(1−2)-linkage affording tetrasaccharide **26** (for structural assignment see below). Removal of the *O*-acyl groups with sodium methanolate in methanol at 50 °C (→**27**) followed by *O*-acetylation furnished di-*O*-acetyl derivative **28**. Transformation of the *N*-TCA group into the *N*-acetyl group was readily gained by treatment with tributylstannane/azoisobutyronitrile (AIBN) affording compound **29**. For the generation of the required donor, the 1-*O*-allyl group was removed by treatment with Wilkinson's catalyst and with iodine in aqueous THF (→**30**); the following reaction with trichloroacetonitrile/DBU afforded the desired trichloroacetimidate **31** as glycosyl donor.

Reaction of glycosyl donor **31** with pseudodisaccharide **2** as acceptor (see Scheme 7) under standard reaction conditions led to pseudohexasaccharide **32** in 74% yield. The newly generated α(1−4)-linkage could be assigned with the help of the NMR data ($^1J_{C,H}$ = 177.4 Hz) obtained from the heteronuclear multiple quantum coherence (HMQC) spectrum that is not decoupled. According to Bock and Petersen, $^1J_{C,H}$ coupling constants that are greater than 170 Hz are found for α-linkages and those smaller than 170 Hz are found for $\beta$-linkages.[20] Next, the phosphate residues were introduced. To this end, first, the 6f-*O*-TBDPS group was removed with TBAF in the presence of acetic acid at 40 °C affording

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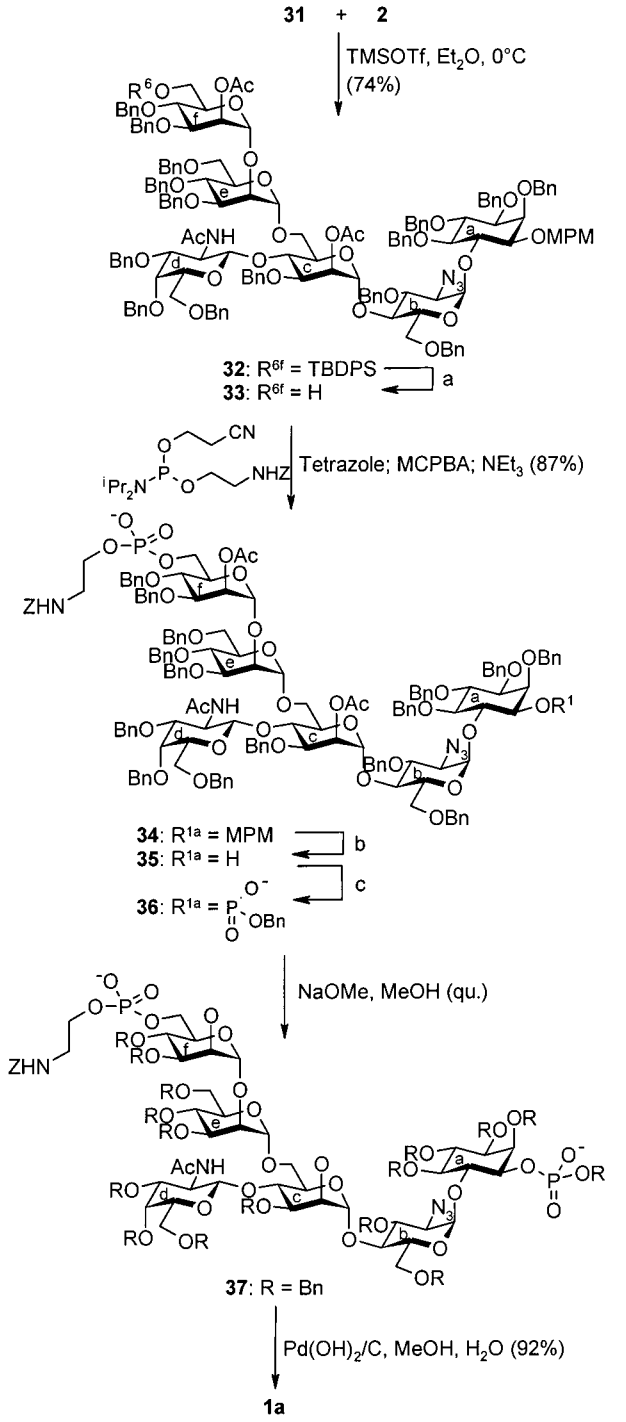
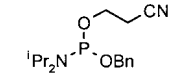
**Scheme 7. Synthesis of 1a (R = Bn)**[a]




[a] Key: a = TBAF, AcOH, THF, 40 °C (78%); b = CAN, MeCN, Tol, $H_2O$ (92%); c =



(Tetrazole), MCPBA ($HNMe_2$) (48%).

6f-*O*-unprotected derivative **33**. Reaction with benzyloxy-carbonylaminoethoxy-cyanoethoxy-diisopropylamino-phosphane[13] in the presence of tetrazole, oxidation with *m*-chloroperbenzoic acid (MCPBA), and ensuing treatment with triethylamine, to remove the cyanoethyl group, afforded the *Z*-protected aminoethyl phosphate derivative **34** in 87% yield. Removal of the **1a**-*O*-MPM group by treatment with CAN afforded **1a**-*O*-unprotected intermediate **35**, which on treatment with benzyloxy-cyanoethoxy-diisopropylaminophosphane[21] in the presence of tetrazole, oxidation with MCPBA, and cyanoethyl cleavage with methylamine afforded diphosphorylated compound **36**. De-*O*-acetylation with sodium methanolate in methanol (→**37**) followed by hydrogenolytic debenzylation (removal of 17 benzyl groups!!) afforded the desired target molecule **1a**, which could be fully assigned by the NMR data (see below).

**Table 1. Correlation Table of Compound 13**

| position | C: $\delta$ (ppm) 150.9 MHz | H: $\delta$ (ppm) 600 MHz | $^3J_{H,H}$ (Hz) | |
|---|---|---|---|---|
| 1a | 81.9 | 3.40 | $^3J_{1,2} = 2.1$ | OMe: 55.27/3.73 |
| 2a | 73.3 | 3.95 | $^3J_{2,3} = 2.3$ | |
| 3a | 80.8 | 3.32 | $^3J_{3,4} = 9.8$ | |
| 4a | 81.8 | 4.04 | $^3J_{4,5} = \sim 9.5$ | |
| 5a | 81.5 | 3.37 | $^3J_{5,6} = \sim 9.4$ | |
| 6a | 74.7 | 4.18 | $^3J_{6,1} = 9.8$ | |
| 1b | 97.3 | 5.66 | | |
| 2b | 62.5 | 3.10 | $^3J_{1,2} = 3.7$ | |
| 3b | 79.2 | 3.72 | $^3J_{2,3} = 10.3$ | |
| 4b | 72.1 | 3.62 | $^3J_{3,4} = 8.7$ | OH: 1.90, $^3J_{4,OH} = 3.7$ |
| 5b | 69.2 | 3.90 | $^3J_{4,5} = 9.8$ | |
| 6,6′b | 68.8 | 3.21/3.13 | $^3J_{5,6/6,6'} =$ 4.1/3.6 | |

**Structural Assignment.** Full structural assignment of synthetically important intermediates was done by detailed NMR studies using one- and two-dimensional NMR techniques.

Compound **13** could be fully assigned (see Table 1) by $^1H$ and $^{13}C$ NMR and HMQC spectra experiments. As is characteristic for 2-azido-2-deoxy-compounds, the C−N carbon signal is shifted downfield (2b: 62.5 ppm). The α-glycosidic linkage could be proved by the small $^3J_{1b,2b}$ coupling constant (3.7 Hz).

The determination of the anomeric configuration of mannopyranoses as in compound **26** was done according to Bock and Petersen.[20] $^1J_{C,H}$ coupling constants that are greater than 170 Hz refer to α-linkages ($^1J_{C,H-1c}$, $^1J_{C,H-1e}$, $^1J_{C,H-1f}$), and $^1J_{C,H}$ coupling constants that are smaller than 170 Hz refer to *β*-linkages ($^1J_{C,H-1d}$). Full structural assignment of all ring protons could be obtained by a combination of HMQC, DQF-COSY, and ROESY spectroscopy (see Table 2).

Full structural assignment of the final compound **1a** could be reached (see Table 3). The anomeric configurations were proven by $^1J_{C,H}$ coupling constants ($^1J_{C,H-1c}$ = 173.3 Hz, $^1J_{C,H-1e}$ = 174.5 Hz, $^1J_{C,H-1f}$ = 173.3 Hz, and $^1J_{C,H-1b}$ = 177.9 Hz, all of them being α-linked; $^1J_{C,H-1d}$ = 162.9 Hz, *β*-linked). The phosphorus signals, corresponding to the two phosphorus esters, were obtained at $\delta = -0.66$ and $-1.37$ ppm.

## Conclusion

In summary, a highly efficient synthesis of the fully phosphorylated GPI anchor pseudohexasaccharide **1a** could be carried out. It is based on versatile building blocks, high regio- and stereoselectivities, and high yields in all reaction steps including the glycosylation reactions. The versatility of the building blocks employed here has

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(21) Watanabe, Y.; Sofue, S.; Ozaki, S.; Hirata, M. *J. Chem. Soc., Chem. Commun.* **1996**, *15*, 1815−1816.

**Table 2. Correlation Table of Compound 26 ($^{13}$C and $^{1}$H Chemical Shifts at 150.9 and 600 MHz, Respectively)**

| position | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| c | 96.1/4.69 | 68.5/5.28 | 76.0/3.91 | 73.0/3.91 | 69.8/3.77 | 66.1/3.76 + 3.65 |
| d | 98.4/5.09 | 56.2/3.84 | 77.1/4.06 | 72.1/3.78 | 73.4/3.49 | 68.3/3.53 + 3.32 |
| e | 98.1/4.81 | 73.0/4.06 | 80.4/3.89 | 74.8/3.75 | 72.0/3.80 | 69.5/3.62 |
| f | 98.8/5.19 | 68.9/5.49 | 78.0/4.02 | 73.8/4.17 | 73.1/3.74 | 62.6/4.08 + 3.85 |

**Table 3. Correlation Table of Final Compound 1a ($^{13}$C and $^{1}$H Chemical Shifts at 150.9 and 600 MHz, Respectively)**

| position | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| a | 75.7/4.11 | 70.9/4.12 | 70.0/3.48 | 72.8/3.60 | 72.2/3.35 | 76.8/3.83 |
| b | 94.7/5.49 | 53.4/3.31 | 69.4/3.99 | 76.1/3.65 | 70.4/4.10 | 59.7/3.76 |
| c | 100.9/5.13 | 69.0/4.03 | 68.5/3.85 | 76.3/3.72 | 70.8/3.78 | 65.9/3.78 + 3.67 |
| d | 101.3/4.41 | 52.0/3.85 | 69.9/3.71 | 67.3/3.86 | 75.0/3.67 | 60.6/3.70 |
| e | 98.1/5.09 | 78.5/3.94 | 69.6/3.89 | 66.5/3.61 | 72.6/3.61 | 60.7/3.82 + 3.78 |
| f | 101.9/4.93 | 69.5/3.99 | 69.7/3.78 | 65.8/3.66 | 71.5/3.80 | 64.3/4.05 |

been meanwhile demonstrated in their successful utilization in other GPI anchor syntheses.

## Experimental Section

**General.** Solvents were purified in the usual way. Boiling range of petroleum ether: 35−65 °C. Melting points are uncorrected. Optical rotations were measured at 20 °C. $^{1}$H NMR were measured on a 250 and a 600 MHz spectrometer with the internal standard being tetramethylsilane (TMS).

**6-*O*-Allyl-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-(1*R*)-menthyloxycabonyl-D-*myo*-inositol (8).** To a mixture of compound **7**[12] (6.96 g, 13.3 mmol), allyl bromide (5.8 mL, 66.5 mmol), and silver(I) oxide (12.3 g, 53.2 mmol) in 100 mL of dry DMF was added KI (5.5 g, 33.3 mmol) at 0 °C. After being stirred at 0 °C for 1.5 h, the mixture was filtered through a pad of Celite, diluted with ethyl acetate, washed with brine and water, dried over $MgSO_4$, and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 15:1) of the residue afforded compound **8** (5.85 g, 10.4 mmol, 78%) as a colorless oil: TLC (petroleum ether/ethyl acetate, 5:1): $R_f = 0.65$; $[\alpha]_D = -32$ ($c = 0.9$, $CHCl_3$); $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta = 0.74-1.13$ (m, 12H, 3 Me, 3 $H_{Mnt}$), 1.38−1.70 (m, 24H), 1.92−2.17 (m, 2H, $2_{Mnt}$-H), 3.54 (dd, $J_{4,5} = 10.8$ Hz, $J_{3,4} = 7.8$ Hz, 1H, 4-H), 3.78 (dd, $J_{2,3} = 1.8$ Hz, $J_{3,4} = 7.8$ Hz, 1H, 3-H), 4.03 (dd, $J_{5,6} = 7.2$ Hz, $J_{4,5} = 10.8$ Hz, 1H, 5-H), 4.22 (m, 2H, allyl), 4.30 (dd, $J_{1,6} = J_{5,6} = 7.2$ Hz, 1H, 6-H), 4.46−4.57 (m, 2H, H-1, $1_{Mnt}$-H), 5.05 (m, 1H, 2-H), 5.18−5.36 (m, 2H, allyl), 5.85−6.00 (m, 1H, allyl). Anal. Calcd for $C_{32}H_{50}O_8$ (580.76): C, 66.18; H, 9.02 (+$H_2O$). Found: C, 66.37; H, 8.61.

**6-*O*-Allyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (9).** A mixture of compound **8** (6.15 g, 10.92 mmol), potassium carbonate (7.55 g, 5.46 mmol), and 110 mL of methanol was stirred at 60 °C for 20 h and then concentrated. The residue was dissolved in ethyl acetate, washed with water, dried over $MgSO_4$, and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 8:1) of the residue gave the 1-O-unprotected alcohol. To a solution of this alcohol (3.86 g, 10.14 mmol) and 4-methoxybenzyl chloride (3 mL, 22.32 mmol) in 100 mL of dry DMF was added by portions sodium hydride (730 mg, 30.42 mmol) at 0 °C. The mixture was stirred at 0 °C for 3 h, and the excess of 4-methoxybenzyl chloride was destroyed by dropwise addition of methanol. The solution was diluted with ethyl acetate, washed with brine and water, dried over $MgSO_4$, and concentrated. A solution of the residue and CSA (117 mg, 0.5 mmol) in methanol was stirred at room temperature for 8 h, then neutralized with $NEt_3$, and concentrated. Flash chromatography (toluene/methanol, 3:1) afforded compound **9** (3.0 g, 8.85 mmol, 81%) as a white solid. TLC (toluene/MeOH, 3:1): $R_f = 0.22$; $[\alpha]_D = -3$ ($c = 1.2$, $CHCl_3$); $^{1}$H NMR (250 MHz, $CD_3OD$): $\delta = 3.18-3.34$ (m, 3H), 3.59 (m, 2H), 3.7 (s, 3H, OMe), 4.07 (m, 1H), 4.29−4.34 (m, 2H, allyl), 4.51−4.66 (m, 2H, $CH_2$Ph), 5.07−5.29 (m, 2H, allyl), 5.94−6.04 (m, 1H, allyl), 6.84−6.90 (m, 2H, Ph), 7.29−7.33 (m, 2H, Ph). Anal. Calcd for $C_{17}H_{24}O_7$ (349.38): C, 58.44; H, 7.21. Found: C, 58.69; H, 7.16.

**6-*O*-Allyl-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (10).** To a solution of compound **9** (2.5 g, 7.34 mmol) and benzyl bromide (5.2 mL, 44.1 mmol) in 80 mL of dry DMF was added by portions sodium hydride (1.4 g, 58.8 mmol) at 0 °C. After the mixture was stirred at room temperature for 2 h, excess of benzyl bromide was destroyed by addition of methanol. The solution was diluted with ethyl acetate, washed with brine and water, dried over $MgSO_4$, and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 7:1) afforded compound **10** (4.73 g, 6.75 mmol, 92%) as a crystalline product. TLC (toluene/ethyl acetate, 3:1): $R_f = 0.56$; $[\alpha]_D = -2$ ($c = 1.0$, $CHCl_3$); mp 78−80 °C (ethanol 90 °C); $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta = 3.24$ (dd, $J = 2.2/9.8$, 1H, 1-H or 3-H), 3.30 (dd, $J = 2.2/9.8$, 1H, 1-H or 3-H), 3.39 (dd, $J_{4,5} = J_{5,6} = 9.2$ Hz, 1H, 5-H), 3.80 (s, 3H, OMe), 3.90 (m, 1H, 4-H or 6-H), 4.23−4.42 (m, 2H, allyl), 4.52−4.65 (m, 4H, $CH_2$Ph), 4.77−4.90 (m, 6H, C$H_2$Ph), 5.10−5.29 (m, 2H, allyl), 5.84−6.05 (m, 1H, allyl), 6.83−6.87 (m, 2H, Ph), 7.21−7.39 (m, 22H, Ph). Anal. Calcd for $C_{45}H_{48}O_7$ (700.87): C, 77.12; H, 6.90. Found: C, 77.14; H, 6.87.

**2,3,4,5-Tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (11).** To a solution of compound **10** (4.3 g, 6.13 mmol), dissolved in 64 mL of EtOH by heating, was added DBU (92 $\mu$L, 0.61 mmol) and Wilkinson's catalyst ($(Ph_3P)_3RhCl$; 57 mg, 61.3 $\mu$mol). The mixture was refluxed for 1 h and concentrated ($R_f = 0.6$, petrolether/ethyl acetate). The residue was dissolved in 1 N HCl/acetone (1:9) and heated to reflux for 10 min. After neutralization with $NEt_3$, the solution was diluted with ethyl acetate, washed with water, dried over $MgSO_4$, and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 4:1) afforded compound **11** (3.8 g, 5.8 mmol, 95%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 4:1): $R_f = 0.27$. $[\alpha]_D = -7$ ($c = 1.0$, $CHCl_3$). mp 65−66 °C. $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta = 2.46$ (bs, 1H, OH), 3.14 (dd, $J_{2,3} = 1.8$ Hz, $J_{3,4} = 9.8$ Hz, 1H, 3-H), 3.36 (dd, $J_{4,5} = J_{5,6} = 9.8$ Hz, 1H, 5-H), 3.37 (dd, $J_{1,2} = 2.1$ Hz, $J_{1,6} = 9.6$ Hz, 1H, 1-H), 3.80 (s, 3H, OMe), 4.00 (bs, 1H, 2-H or 6-H), 4.08 (dd, $J_{3,4} = J_{4,5} = 9.8$ Hz, 1H, 4-H), 4.13 (m, 1H, 6-H), 4.41−4.92 (m, 10H, $CH_2$Ph), 6.84−6.87 (m, 2H, Ph), 7.19−7.39 (m, 22H, Ph). Anal. Calcd for $C_{42}H_{44}O_7$ (660.81): C, 76.34; H, 6.71. Found: C, 76.23, H 6.72.

**(3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (13).** A mixture of trichloroacetimidate **12**[12,17] (100 mg, 151.3 mmol), acceptor **11** (86 mg, 181.5 mmol), and 4 Å molecular sieve in 2 mL of dry $CH_2Cl_2$ was stirred under argon at room temperature for 30 min and then cooled to 0 °C. A 0.2 N TMSOTf solution in $CH_2Cl_2$ (76 $\mu$L, 15.1 mmol) was added; the solution was stirred at 0 °C for 20 min, neutralized with $NEt_3$, filtered, and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 3:1) gave compound **13** (103 mg, 105.9 mg, 70%) as a colorless solid. TLC (petroleum ether/ethyl acetate, 7:4): $R_f = 0.45$. $[\alpha]_D = +76$ ($c = 1.0$, $CHCl_3$). mp 101−102 °C. $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta = 1.83$ (s, 3H, OAc), 1.96 (s, 3H, OAc), 2.07 (s, 3H, OAc), 3.12 (dd, $J_{1b,2b} = 3.6$ Hz, $J_{2b,3b} = 10.6$ Hz, 1H, 2b-H), 3.40 (dd, $J = 1.8/9.5$ Hz, 1H, 1a-H or 3a-H), 3.45 (dd, $J_{4a,5\ a} = J_{5a,6\ a} = 9.5$ Hz, 1H, 5a-H), 3.49 (dd, $J = 1.8/9.5$ Hz, 1H, 1a-H or 3a-H), 3.62 (m, 2H, 6/6′b-H), 3.81 (s, 3H, OMe), 4.05 (bs, 1H, 2a-H), 4.13(dd, $J = 9.5$ Hz, 1H, 4a-H or 6a-H), 4.21−4.30 (m, 2H, 5b-H, 4a-H or 6a-H), 4.40−5.15 (m, 10H, $CH_2$Ph), 4.92 (dd, $J_{3b,4b} = J_{4b,5b} = 9.5$ Hz,

1H, 4b-H), 5.42 (dd, $J_{2b,3b} = J_{3b,4b} = 10.5$ Hz, 1H, 3b-H), 5.79 (d, $J_{1b,2b} = 3.6$ Hz, 1H, 1b-H), 6.84−6.87 (m, 2H, Ph), 7.21−7.41 (m, 22H, Ph). Anal. Calcd for $C_{54}H_{59}O_{14}N_3$ (974.16): C, 66.59; H, 6.10; N, 4.31. Found: C, 66.40; H, 6.19; N, 4.59.

**(2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (14).** To a solution of disaccharide **13** (2.82 g, 2.89 mmol) in 60 mL of dry methanol/diethyl ether (5:1) was added sodium (10 mg, 0.43 mmol). The reaction mixture was stirred at room temperature for 2 h, neutralized with Amberlite IR 120($H^+$), filtered, and concentrated. A mixture of the residue, α,α-dimethoxytoluene (1.3 mL, 8.6 mmol), and CSA (20 mg, 86 μmol) in 30 mL of dry acetonitrile was stirred at room temperature for 2.5 h, neutralized with $NEt_3$, and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 4:1 → 2:1) gave the acetal as a syrup. (TLC (petroleum ether/ethyl acetate, 4:1): $R_f = 0.33$. To a mixture of this material and benzyl bromide (464 μL, 3.9 mmol) in 25 mL of dry DMF was added sodium hydride (125 mg, 5.2 mmol) at 0 °C. The reaction was allowed to warm to room temperature and was quenched after 2 h with methanol. The solution was diluted with ethyl acetate, washed with brine and water, dried over $MgSO_4$, and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 5:1) afforded compound **14** (2.56 g, 2.51 mmol, 87%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 4:1): $R_f = 0.55$. $[\alpha]_D = +50$ ($c = 1.0$, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta = 3.24$ (dd, $J_{1b,2b} = 3.8$ Hz, $J_{2b,3b} = 10.0$ Hz, 1H, 2b-H), 3.38 (dd, $J = 2.2/9.8$, 1H, 1a-H or 3a-H), 3.45 (dd, $J = 2.2/9.8$, 1H, 1a-H or 3a-H), 3.46 (dd, $J = 9.3$ Hz, 1H), 3.52 (m, 2H), 3.80 (s, 3H, OMe), 3.96−4.04 (m, 2H, 2a-H, 3a-H), 4.06−4.29 (m, 4H), 4.48 (s, 2H, C$H_2$Ph), 4.57−4.96 (m, 10H, $CH_2$Ph), 5.47 (s, 1H), 5.72 (d, $J_{1b,2b} = 3.8$ Hz, 1H, 1b-H), 6.83−6.89 (m, 2H, Ph), 7.08−7.13 (m, 2H, Ph), 7.17−7.45 (m, 30H, Ph). Anal. Calcd for $C_{62}H_{63}O_{11}N_3$ (1026.19): C, 72.57; H, 6.19; N, 4.09. Found: C, 72.47; H, 6.17; N, 4.23.

**(2-Azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (2).** To a solution of compound **14** (8.9 g, 8.7 mmol) and sodium cyanoborohydride (4.5 g, 72 mmol) in 270 mL of dry THF was added HCl·$OEt_2$ in a dropwise manner under argon until pH = 1 was reached. After being stirred at room temperature for 3 h, the solution was neutralized by addition of solid $NaHCO_3$. The solution was diluted with diethyl ether and extracted with water. Flash chromatography (petroleum ether/ethyl acetate, 5:1) afforded compound **2** (7.76 g, 7.54 mmol, 87%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 5:2): $R_f = 0.45$. $[\alpha]_D = +34$ ($c = 1.4$, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta = 1.92$ (d, $J_{OH} = 3.7$, 1H, OH), 3.17 (dd, $J_{1b,2b} = 3.8$ Hz, $J_{2b,3b} = 9.9$ Hz, 1H, 2b-H), 3.22 (m, 1H, 6b-H), 3.28 (dd, $J_{5b,6b} = 3.8$ Hz, $J_{6b,6'b} = 10.5$ Hz, 1H, 6′b-H), 3.38 (dd, $J_{2a,3a} = 2.2$ Hz, $J_{3a,4a} = 9.8$ Hz, 1H, 3a-H), 3.44 (m, 1H, 5a-H), 3.47 (dd, $J_{1a,2a} = 2.2$ Hz, $J_{1a,6a} = 9.8$ Hz, 1H, 1a-H), 3.68 (m, 1H, 4b-H), 3.76 (m, 1H, 3b-H), 3.80 (s, 3H, OMe), 3.95 (m, 1H, 5b−H), 4.01 (dd, $J_{1a,2a} = J_{2a,3a} = 2.2$ Hz, 1H, 2a-H), 4.11 (dd, $J_{3,4} = J_{4,5} = 9.4$ Hz, 1H, 4a-H), 4.25 (m, 1H, 6a-H), 4.23−5.04 (m, 14H, $CH_2$Ph), 5.72 (d, $J_{1b,2b} = 3.7$ Hz, 1H, 1b-H), 6.82−6.88 (m, 2H, Ph), 7.17−7.45 (m, 32H, Ph); HMQC data ($^{13}$C (150.9 MHz)/$^1$H (600 MHz)): 81.9/3.40 (1a), 73.3/3.95 (2a), 80.8/3.32 (3a), 81.8/4.04 (4a), 81.5/3.37 (5a), 74.7/4.18 (6a), 97.3/5.66 (1b), 62.5/3.10 (2b), 79.2/3.72 (3b), 72.1/3.62 (4b), 69.2/3.90 (5b), 68.8/3.21 + 3.13 (6b). Anal. Calcd for $C_{62}H_{65}O_{11}N_3$ (1028.21): C, 72.43; H, 6.37; N, 4.09. Found: C, 72.29; H, 6.62; N, 4.42.

**Allyl α-D-Mannopyranoside (15).** D-Mannose (60 g, 333 mmol) was refluxed for 4 h in the presence of $BF_3$·$Et_2O$ (2.9 mL, 23.3 mmol) in allyl alcohol (700 mL, stored over MS 4 Å). After neutralization with $NEt_3$, the allyl alcohol was removed by evaporation, and flash chromatography ($CH_2Cl_2$/MeOH, 9:1 → 8:2) afforded an α/β-mixture of **15** (α/β, ca. 20:1) (59.5 g, 273 mmol, 82%) as a slightly yellow syrup. TLC ($CH_2Cl_2$/MeOH): $R_f = 0.5$. $^1$H NMR (250 MHz, $D_2O$): $\delta = 3.16$ (s, 3H, OMe), 3.41−4.11 (m, 11H), 4.72 (d, $J_{1,2} = 2.0$ Hz, 1H, 1-H), 5.06−5.21 (m, 2H, all), 5.68−5.83 (m, 1H, all). HMQC data ($^{13}$C (150.9 MHz)/$^1$H (600 MHz)): 98.5/4.83 (1c), 69.7/3.85 (2c), 70.2/3.71 (3c), 72.5/3.56 (4c), 66.5/3.56 (5c), 60.6/3.79 + 3.66 (6c). $C_9H_{16}O_6$ (220.25).

**Allyl 3-*O*-Benzyl-α-D-mannopyranoside (16).** Allyl mannoside **15** (6 g, 27.3 mmol), dibutyltin oxide (7.5 g, 30 mmol), and tetrabutylammonium iodide (TBAI, 15.1 g, 41 mmol) in 400 mL of toluene were refluxed in a Dean−Stark apparatus for 3 h. After it was cooled to 0 °C and benzyl bromide was added (4.1 mL, 34.1 mmol), the solution was refluxed for 20 h. The solution was then cooled, diluted with ethyl acetate, washed with $Na_2S_2O_3$ (5% in water), saturated NaCl solution, and water, and dried ($MgSO_4$). Flash chromatography ($CH_2Cl_2$/MeOH, 15:1) gave compound **16** (6.4 g, 20.5 mmol, 75%) as a colorless syrup. TLC ($CH_2Cl_2$/MeOH, 9:1): $R_f = 0.5$. $^1$H NMR (250 MHz, $CDCl_3$): $\delta = 3.13$ (dd, $J_{OH,6} = J_{OH,6'} = 6.6$ Hz, 1H, OH), 3.32 (d, $J_{OH,4} = 3.5$ Hz, 1H, OH), 3.48 (d, $J_{OH,2} = 2.6$ Hz, 1H, OH), 3.57 (ddd, $J_{2,3} = J_{3,4} = 9.8$ Hz, $J_{OH,3} = 3.1$ Hz, 1H, 3-H), 3.68−3.80 (m, 3H, 5-H, 6/6′-H), 3.93 (m, 1H, C$H_2$−CH=$CH_2$), 3.93−4.00 (m, 1H, 2-H), 4.02 (ddd, $J_{3,4} = J_{4,5} = 9.6$ Hz, $J_{OH,4} = 3.8$ Hz, 1H, 4-H), 4.13 (m, 1H, C$H_2$−CH=$CH_2$), 4.63 (m, 2H, C$H_2$Ph), 4.89 (d, $J_{1,2} = 1.6$ Hz, 1H, 1-H), 5.18 (dd, $J_{cis} = 10$ Hz, $J_{gem} = 1$ Hz, 1H, CH=C$H_{cis}H_{trans}$), 5.25 (dd, $J_{trans} = 17$ Hz, $J_{gem} = 1$ Hz, 1H, CH=C$H_{cis}H_{trans}$), 5.86 (ddt, $J_{cis} = 10$ Hz, $J_{trans} = 17$ Hz, $J_{vic} = 5$ Hz, 1H, C$H$=$CH_2$), 7.40−7.26 (m, 5H, Ph). Anal. Calcd for $C_{16}H_{22}O_6$ (310.38): C, 61.91; H, 7.16. Found: C, 61.91; H, 7.46.

**Allyl 3-*O*-Benzyl-4,6-*O*-(4-methoxybenzylidene)-α-D-mannopyranoside (17).** Compound **16** (5.6 g, 18 mmol) was stirred for 6 h with *p*-methoxy benzylidene acetate (3.7 mL, 21.6 mmol) and some PTSA·$H_2O$ in 100 mL of DMF. After neutralization with $NEt_3$ and removal of the solvent, flash chromatography afforded compound **17** (4.9 g, 11.7 mmol, 65%) as a colorless syrup. TLC (petroleum ether/ethyl acetate, 1:1): $R_f = 0.55$. $[\alpha]_D = +43.4$ ($c = 1.5$, $CDCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta = 2.67$ (d, $J_{2,OH} = 1.3$ Hz, 1H, OH), 3.82 (s, 3H, OMe), 3.78−3.90 (m, 2H, 5-H, 6′-H), 3.98 (m, 1H, 3-H), 3.99 (m, 1H, C$H_2$−CH=$CH_2$), 4.05−4.14 (m, 2H, 2-H, 6-H), 4.19 (m, 1H, C$H_2$−CH=$CH_2$), 4.24−4.28 (m, 1H, 4-H), 4.78 (m, 2H, C$H_2$Ph), 4.92 (d, 1H, $J_{1,2} = 1.3$ Hz, 1-H), 5.19−5.33 (m, 2H, CH=C$H_2$), 5.58 (s, 1H, C$H$(4-MeOPh)), 5.90 (ddt, $J_{cis} = 10$ Hz, $J_{trans} = 17$ Hz, $J_{vic} = 5$ Hz, 1H, C$H$=$CH_2$), 6.87−6.93 (m, 2H, PMB), 7.27−7.45 (m, 7H, Ph + PMB). Anal. Calcd for $C_{24}H_{28}O_7$ (428.52): C, 67.26; H, 6.60. Found: C, 67.30; H, 6.81.

**Allyl 2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-α-D-mannopyranoside (18).** Compound **17** (13.3 g, 31 mmol), benzoyl cyanide (4.48 g, 34.1 mmol), and 7 mL of dry $NEt_3$ were stirred in 20 mL of dry acetonitrile for 3 h. After addition of some methanol and dilution with ethyl acetate, the solution was washed with saturated $NaHCO_3$ solution and water and dried over $Na_2SO_4$. Flash chromatography (petroleum ether/ethyl acetate, 4:1) gave compound **18** (15.7 g, 29.5 mmol, 95%) as a colorless syrup. TLC (petroleum ether/ethyl acetate, 2:1): $R_f = 0.70$. $[\alpha]_D = -34.4$ ($c = 1.3$, $CDCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta = 3.82$ (3H, s, OMe), 3.78−4.32 (m, 7H, 3,4,5,6,6′-H+Allyl), 4.69 (d, $J_{H,H'} = 12.3$ Hz, 1H, C$H_2$Ph), 4.75 (d, $J_{H,H'} = 12.3$ Hz, 1H, C$H_2$Ph), 4.98 (d, $J_{1,2} = 1.5$ Hz, 1H, 1-H), 5.23 (dd, $J_{cis} = 10$ Hz, $J_{gem} = 1$ Hz, 1H, CH=C$H_{cis}H_{trans}$), 5.30 (dd, $J_{trans} = 17$ Hz, $J_{gem} = 1$ Hz, 1H, CH=C$H_{cis}H_{trans}$), 5.62 (dd, $J_{1,2} = 1.9$ Hz, $J_{2,3} = 3.0$ Hz, 1H, 2-H), 5.65 (s, 1H, *p*-methoxybenzylidene), 5.86 (ddt, $J_{cis} = 10$ Hz, $J_{trans} = 17$ Hz, $J_{vic} = 5$ Hz, 1H, C$H$=$CH_2$), 6.86−6.92 (m, 2H, PMB), 7.17−7.52 (m, 9H, Ph), 7.54−7.62 (m, 1H, Bz), 8.00−8.12 (m, 2H, Bz). Anal. Calcd for $C_{31}H_{32}O_8$ (532.63): C, 69.90; H, 6.07. Found: C, 69.96; H, 6.48.

**Allyl 2-*O*-Benzoyl-3-*O*-benzyl-6-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (3).** Compound **18** (6 g, 11.3 mmol) and sodium cyanoborohydride (6.34 g, 100 mmol) were dissolved in 60 mL of dry DMF. After addition of MS 4 Å and cooling to −15 °C, 10 mL of TFA in 30 mL of DMF was slowly added and the solution was stirred at −15 °C for 3 days. Neutralization with $NEt_3$, filtration through a pad of Celite, removal of the solvent, and flash chromatography (petroleum ether/ethyl acetate, 3:1) afforded compound **18** (4.26 g, 8.0 mmol, 70%) besides allyl-*O*-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (0.9 g, 1.7 mmol, 15%) (both of them as colorless syrups) and unreacted compound

**18** (0.9 g, 1.3 mmol, 12%). TLC (petroleum ether/ethyl acetate, 2:1): $R_f = 0.60$; $[\alpha]_D = -22$ ($c = 2.5$, $CDCl_3$); $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 2.52$ (d, $J_{OH,4} = 2.1$ Hz, 1H, OH), 3.81 (s, 3H, OMe), 3.78−3.95 (m, 4H, 3,5,6,6′-H), 4.03 (m, 1H, C$H_2$−CH=$CH_2$), 4.13 (ddd, $J_{OH,4} = 2.1$ Hz, $J_{3,4} = J_{4,5} = 9.3$ Hz, 1H, 4b−H), 4.24 (m, 1H, C$H_2$−CH=$CH_2$), 4.48−4.82 (m, 4H, C$H_2$-Ph), 5.03 (d, $J_{1,2} = 1.8$ Hz, 1H, 1b−H), 5.22 (dd, $J_{cis} = 10$ Hz, $J_{gem} = 1$ Hz, 1H, CH=C$H_{cis}H_{trans}$), 5.30 (dd, $J_{trans} = 17$ Hz, $J_{gem} = 1$ Hz, 1H, CH=C$H_{cis}H_{trans}$), 5.61 (dd, $J_{1,2} = 1.9$ Hz, $J_{2,3} = 3.1$ Hz, 1H, 2-H), 5.87 (ddt, $J_{cis} = 10$ Hz, $J_{trans} = 17$ Hz, $J_{vic} = 5$ Hz, 1H, C$H$=$CH_2$), 6.84−6.90 (m, 2H, PMB), 7.16−7.44 (m, 9H, Ph), 7.52−7.59 (m, 1H, Bz), 7.97−8.07 (m, 2H, Bz); HMQC data ($^{13}C$ (150.9 MHz)/$^1H$ (600 MHz) ($^1J_{CH}$ in Hz)): 97.0/5.02 (173.5) (1), 68.3/5.6 (2), 77.7/3.93 (3), 67.3/4.12 (4), 71.4/3.86 (5), 69.5/3.8 (6). Anal. Calcd for $C_{31}H_{34}O_8$ (534.65): C, 69.64; H, 6.42. Found: C, 69.55; H, 6.38.

**Thexyldimethylsilyl 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranoside (20).** 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-glucose (59.4 g, 125 mmol) and texyldimethylsilyl chloride (TDS−Cl; 26.8 g, 150 mmol) were dissolved in 500 mL of dry $CH_2Cl_2$, and imidazole (10.6 g, 150 mmol) was added. After the mixture was stirred for 1 h, the solvent was removed and the remaining residue was subjected to flash chromatography (petroleum ether/ethyl acetate, 6:1). Compound **20** (74.1 g, 120 mmol, 96%) was obtained as a colorless foam. TLC (petroleum ether/ethyl acetate, 3:1): $R_f = 0.65$; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 0.16$ (s, 6H, 2 Me), 0.84−0.91 (12H, 4 Me), 1.66 (m, 1H, $(H_3C)_2CH$), 3.26 (dd, $J_{3,4} = 3.0$ Hz, $J_{2,3} = 10.0$ Hz, 1H, 3-H), 3.48 (m, 1H, 5-H), 3.52−3.63 (m, 2H, 6/6′-H), 3.71 (dd, $J_{1,2} = J_{2,3} = 8.0$ Hz, 1H, 2-H), 3.84 (m, 1H, 4-H), 4.40 (d, $J_{1,2} = 8.0$ Hz, 1H, 1-H), 4.43−4.93 (m, 6H, $CH_2$Ph), 7.26−7.48 (m, 15H, Ph). $C_{35}H_{47}O_5N_3Si$ (617.94).

**Thexyldimethylsilyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-galactopyranoside (21).** To a solution of azido compound **20** (1.36 g, 2.2 mmol) in ethanol was added sodium borohydride (416 mg, 11 mmol) followed by the addition of a 0.17 N solution of $NiCl_2 \cdot 6H_2O$ in ethanol (1 mL, 0.17 mmol). The mixture was stirred at room temperature for 1 h, then neutralized with acetic acid, and concentrated to dryness. The residue was titured in $CH_2Cl_2$, and the mixture was filtered on a pad of Celite and concentrated. To a solution of the crude amine in 20 mL of $CH_2Cl_2$ and $NEt_3$ (1.85 mL, 13.2 mmol), trichloroacetyl chloride (490 $\mu$L, 4.4 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature for 15 min, then diluted with $CH_2Cl_2$, washed with water, saturated aqueous $NaHCO_3$ solution, and water, dried ($MgSO_4$), and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 12:1) of the residue afforded compound **20** (1.2 g, 1.63 mmol, 74%) as a white solid. TLC (petroleum ether/ethyl acetate, 3:1): $R_f = 0.70$; $[\alpha]_D = +5$ ($c = 1.0$, $CHCl_3$); mp 107−108 °C; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 0.12$ (s, 3H, 2 Me), 0.15 (s, 3H, Me), 0.82−0.85 (12H, 4 Me), 1.61 (m, 1H, $(H_3C)_2CH$), 3.56−3.64 (m, 3H, 5-H, 6/6′-H), 3.76 (ddd, $J_{NH,2} = 7.3$ Hz, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 11.0$ Hz, 1H, 2-H), 3.98 (m, 1H, 4-H), 4.22 (dd, $J_{3,4} = 2.8$ Hz, $J_{2,3} = 11.0$ Hz, 1H, 3-H), 4.40−4.93 (m, 6H, $CH_2$Ph), 5.10 (d, $J_{1,2} = 7.8$ Hz, 1H, 1-H), 6.89 (d, $J_{NH,2} = 7.3$ Hz, 1H, NH), 7.29−7.39 (m, 15H, Ph). Anal. Calcd for $C_{37}H_{48}O_6Cl_3NSi$ (737.30): C, 60.26; H, 6.56; N, 1.90. Found: C, 60.10; H, 6.55; N, 2.10.

**3,4,6-Tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl Trichloroacetimidate (4).** To a solution of compound **20** (3.24 g, 4.4 mmol) in 43 mL of dry THF was added a 1 N solution of tetrabutylammonium fluoride in THF (4.8 mL, 4.8 mmol) at −20 °C. The mixture was stirred at 0 °C for 2 h, diluted with ethyl acetate, washed with brine and water, dried over $Na_2SO_4$, and concentrated. A mixture of the crude oil, trichloroacetonitrile (4.4 mL, 44 mmol), and some drops of DBU was stirred in 32 mL of $CH_2Cl_2$ at room temperature for 90 min and then concentrated. Flash chromatography (petroleum ether/ethyl acetate, 5:1, 0.1% $NEt_3$) gave trichloroacetimidate **21** (2.45 g, 3.3 mmol, 75%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 7:2): $R_f = 0.55$. $[\alpha]_D = +42$ ($c = 1.1$, $CHCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 3.59$ (dd, $J_{5,6} = 5.3$ Hz, $J_{6,6'} = 9.0$ Hz, 1H, 6-H), 3.71 (dd, $J_{5,6} > 1$ Hz, $J_{6,6'} = 8.3$ Hz, 1H, 6′-H), 3.88 (dd, $J_{3,4} = 2.4$ Hz, $J_{2,3} = 11.0$ Hz, 1H, 3-H), 4.11 (m, 1H, 5-H), 4.20 (bs, 1H, 4-H), 4.77 (m, 1H, 2-H), 6.43 (d, $J_{NH} = 8.2$ Hz, 1H, NH), 6.47 (d, $J_{1,2} = 3.4$ Hz, 1H, 1-H), 7.19−7.39 (m, 15H, Ph) 8.62 (s, 1H, NH). Anal. Calcd for $C_{31}H_{30}O_6Cl_6N_2$ (739.33): C, 49.16; H, 4.27; N, 3.70 (+$H_2O$). Found: C, 49.44; H, 4.48; N, 3.69.

**Allyl (3,4,6-Tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-galactopyranosyl)-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (22).** Acceptor **3** (1.3 g, 2.4 mmol) and trichloroacetimidate **4** (2 g, 2.7 mmol) were dissolved in 30 mL of dry toluene under argon and cooled to −40 °C. $BF_3 \cdot OEt_2$ (30 $\mu$L) was added five times every 30 min. After 1 h, the temperature was raised to −30 °C. Neutralization with $NEt_3$, removal of the solvent, and flash chromatography (petroleum ether/ethyl acetate, 6:1→5:1→2:1) gave compound **22** (2.3 g, 2.0 mmol, 85%) as a colorless syrup. TLC (petroleum ether/ethyl acetate, 3:1): $R_f = 0.42$. $[\alpha]_D = +4.2$ ($c = 1.2$, $CDCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 3.31-4.08$ (m, 13H; 3.75/3.74: 3H, s, OMe), 4.12−4.55 (m, 7H), 4.58−5.05 (m, 6H), 5.16−5.45 (m, 2H), 5.53−5.56 (m, 1H, 2c-H), 5.80−5.98 (m, 1H, Allyl), 6.71 (d, $J_{NH} = 7.4$, 1H, NH), 6.79−6.87 (m, 2H, PMB), 7.06−7.39 (m, 24H), 7.43−7.58 (m, 1H, Bz), 7.95−7.99 (m, 2H, Bz), (2 diastereomers at amide bond); HMQC data ($^{13}C$ (150.9 MHz)/$^1H$ (600 MHz) ($^1J_{CH}$ in Hz)): 96.8/5.02 (172.4) (1c), 69.3/5.59 (2c), 75.8/4.07 (3c), 74.9/4.38 (4c), 71.2/3.94 (5c), 68.6/3.98 + 3.83 (6c), 101.2/4.41 (165.3) (1d), 61.9/3.59 (2d), 71.8/4.69 (3d), 66.2/5.19 (4d), 70.4/3.41 (5d), 60.9/3.95 + 3.82 (6d). Anal. Calcd for $C_{60}H_{62}O_{13}Cl_3N$ (1111.58): C, 64.83; H, 5.63; N, 1.26. Found: C, 64.55; H, 5.88; N, 0.96.

**Allyl (3,4,6-Tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-galactopyranosyl)-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-α-D-mannopyranoside (23).** Disaccharide **22** (1.69 g, 1.5 mmol) and CAN (4.4 g, 7.5 mmol) were stirred in 85 mL of $CH_3CN$/toluene/$H_2O$ (91:5:4) at 0 °C for 30 min and at room temperature for 1.5 h. The reaction mixture was diluted with ethyl acetate, washed with a saturated $NaHCO_3$ solution, dried over $Na_2SO_4$, and evaporated. Flash chromatography (petroleum ether/ethyl acetate, 3:1 → 2:1) afforded compound **23** (1.26 g, 1.27 mmol, 85%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f = 0.34$. $[\alpha]_D = +1.3$ ($c = 1.7$, $CDCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 2.16$ (bs, 1H, OH), 3.32−3.51 (m, 3H), 3.68−4.15 (m, 9H), 4.19−4.29 (m, 3H), 4.35−4.53 (m, 4H, Bn), 4.70−4.78 (m, 2H, Bn), 4.90 (d, $J_{1,2} = 1.8$ Hz, 1H, 1c−H), 5.14 (dd, $J_{cis} = 10$ Hz, $J_{gem} = 1$ Hz, 1H, CH=C$H_{cis}H_{trans}$), 5.17 (d, $J_{1,2} = 8.1$ Hz, 1H, 1d-H), 5.21 (dd, $J_{trans} = 17$ Hz, $J_{gem} = 1$ Hz, 1H, CH=C$H_{cis}H_{trans}$), 5.50 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.1$ Hz, 1H, 2c-H), 5.82 (ddt, $J_{cis} = 10$ Hz, $J_{trans} = 17$ Hz, $J_{vic} = 5$ Hz, 1H, C$H$=$CH_2$), 6.79 (d, $J_{NH} = 7.2$ Hz, 1H, NH), 7.03−7.31 (m, 22H, Bn + Bz), 7.41−7.47 (m, 1H, Bz), 7.91−7.95 (m, 2H, Bz). HMQC data ($^{13}C$ (150.9 MHz)/$^1H$ (600 MHz)): 96.7/4.97 (1c), 68.9/5.57 (2c), 76.6/4.11 (3c), 72.3/4.32 (4c), 71.5/3.77 (5c), 61.7/3.87 + 3.83 (6c), 98.6/5.24 (1d), 56.2/3.97 (2d), 77.1/4.12 (3d), 71.6/3.94 (4d), 73.2/3.53 (5d), 68.2/3.55 + 3.40 (6d). Anal. Calcd for $C_{52}H_{54}O_{12}Cl_3N$ (991.43): C, 62.99; H, 5.50; N, 1.41. Found: C, 63.22; H, 5.71; N, 1.28.

**Allyl (2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(3,4,6-tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-galactopyranosyl)-(1→4)]-2-*O*-benzoyl-3-*O*-benzyl-α-D-mannopyranoside (24).** Acceptor **23** (2.2 g, 2.2 mmol) and donor **5** (1.7 g, 2.67 mmol) were dissolved in 25 mL of dry diethyl ether under argon. After addition of 2 mL of TMSOTf solution (0.1 N in dry diethyl ether), the solution was stirred at room temperature for 10 min, neutralized with $NEt_3$, and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 4:1) afforded compound **24** (3.09 g, 2.1 mmol, 95%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f = 0.70$. $[\alpha]_D = +15$ ($c = 1.5$, $CDCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 2.14$ (s, 3H, OAc), 3.32 (dd, $J_{5,6} = 3.1$ Hz, $J_{6,6'} = 6.5$ Hz, 1H, 6d-H), 3.45−3.58 (m, 2H, 5d−H, 6′d-H), 3.68−3.72 (m, 2H, 6/6′e-H), 3.76−3.80 (m, 1H, 4d-H), 3.80−4.02 (m, 8H, 2d-H, 3e-H, 4e-H, 5c-H, 5e-H, 6/6′c-H, 3c-H), 4.04−4.18 (m, 3H, allyl+4c-H, 3d-H), 4.20 (m, 2H, C$H_2$Ph), 4.26−4.54 (m, 6H, C$H_2$Ph), 4.59−4.85 (m, 6H, C$H_2$Ph), 4.91 (d, $J_{1,2} = 1.8$ Hz, 1H, 1c-H), 4.96 (d, $J_{1,2} = 1.7$ Hz, 1H, 1e-H), 5.25 (d, $J_{1,2} = 8.1$ Hz, 1H, 1d-H), 5.18 (dd, $J_{cis} = 10$ Hz, $J_{gem} = 1$ Hz, 1H, CH=C$H_{cis}H_{trans}$), 5.27 (dd, $J_{trans} = 17$ Hz, $J_{gem} = 1$

Hz, 1H, CH=CH$_{cis}H_{trans}$), 5.54 (bs, 1H, 2c-H), 5.78−5.94 (m, 2H, allyl, 1e-H), 6.58 (bs, 1H, NH), 7.06−7.50 (m, 38H, Bn + Bz), 7.96−7.99 (m, 2H, Bz). HMQC data ($^{13}$C (150.9 MHz)/$^{1}$H (600 MHz) ($^{1}J_{CH}$ in Hz)): 96.4/4.90 (173.1) (1c), 69.0/5.53 (2c), 76.7/4.05 (3c), 73.5/4.09 (4c), 69.7/3.89 (5c), 66.3/3.84 + 3.92 (6c), 98.6/5.23 (165.5) (1d), 56.6/3.84 (2d), 76.7/4.06 (3d), 72.0/3.76 (4d), 73.4/3.50 (5d), 68.2/3.52 + 3.32 (6d), 96.9/4.95 (173.1) (1e), 68.3/5.84 (2e), 78.5/3.98 (3e), 74.5/3.82 (4e), 71.5/3.88 (5e), 69.0/3.70 (6e). $C_{81}H_{84}O_{18}Cl_3N$ (1466.01): calcd. C 66.36, H 5.79, N 0.96; found C 66.24, H 5.87, N 0.79.

**Allyl (3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(3,4,6-tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-galactopyranosyl)-(1→4)]-2-*O*-benzoyl-3-*O*-benzyl-α-D-mannopyranoside (25).** Compound **24** (3 g, 2.05 mmol) was stirred in 24 mL of $MeNH_2$ solution (33% in dry ethanol) at room temperature for 4.5 h (TLC). After removal of the solvent at room temperature, flash chromatography (petroleum ether/ethyl acetate, 2:1) afforded deacetylated compound **25** (1.90 g, 1.33 mmol, 65%) besides 510 mg (17%) of unreacted compound **24**. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.33. $[\alpha]_D = +10$ ($c$ = 2.0, $CDCl_3$). $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta$ = 2.39 (1H, d, $J_{OH}$ = 2.5 Hz, OH), 3.28−5.31 (m, 38H), 5.54 (bs, 1H, 2c-H), 5.79−5.94 (m, 1H, allyl), 7.02−7.36 (m, 38H, Bz+Bn+NH), 7.44−7.50 (m, 1H, Bz), 7.96−7.99 (m, 2H, Bz). $C_{79}H_{82}O_{17}Cl_3N$ (1423.97): calcd. C 66.63, H 5.83, N 0.98; found C 66.97, H 5.81, N 0.86.

**Allyl (2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-[(3,4,6-tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-galactopyranosyl)-(1→4)]-2-*O*-benzoyl-3-*O*-benzyl-α-D-mannopyranoside (26).** Acceptor **25** (2.0 g, 2.14 mmol) and trichloroacetimidate **6** (1.32 g, 1.68 mmol) were dissolved in 25 mL of dry diethyl ether under argon. After addition of 25 $\mu$L of TMSOTf (0.14 mmol), the solution was stirred at room temperature for 10 min, neutralized with $NEt_3$, and concentrated. Flash chromatography (petroleum ether/ethyl acetate, 4:1) of the residue gave compound **56** (2.62 g, 1.28 mmol, 92%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.81. $[\alpha]_D = +15$ ($c$ = 2.0, $CDCl_3$). $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.06 (s, 9H, $^{t}$Bu), 2.10 (s, 3H, OAc), 3.25−3.32 (m, 1H), 3.43−4.29 (m, 21H), 4.40−5.22 (m, 16H), 5.51 (bs, 2H, 2e-H, 2c-H), 5.65−5.80 (m, 1H, allyl), 7.07−7.37 (m, 55H, Ph), 7.64−7.74 (m, 4H, TBDPS), 7.93−7.96 (m, 2H, Bz). $C_{117}H_{124}O_{23}Cl_3NSi$ (2046.86): calcd. C 68.65, H 6.12, N 0.68; found C 68.21, H 6.16, N 0.63.

**Allyl (3,4-di-*O*-Benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(3,4,6-tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-galactopyranosyl)-(1→4)]-3-*O*-benzyl-α-D-mannopyranoside (27).** Compound **26** (3.36 g, 1.64 mmol) was dissolved under argon in 8 mL of dry methanol, and sodium methanolate (410 $\mu$L, 1 N solution in methanol) was added. After 5 h at 50 °C, the solution was neutralized with Amberlite IR 120 ($H^+$) and the solvent was removed. Flash chromatography (petroleum ether/ethyl acetate, 3:1) afforded compound **27** (3.03 g, 1.59 mmol, 97%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.57. $[\alpha]_D = +28$ ($c$ = 3.1, $CDCl_3$). $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.06 (s, 9H, $^{t}$Bu), 2.29 (bs, 1H, OH), 2.33 (bs, 1H, OH), 3.38−4.13 (m, 26H), 4.16−4.92 (m, 20H), 4.59−5.23 (m, 4H, allyl + 2H), 5.65−5.80 (m, 1H, allyl), 6.86 (bs, 1H, NH), 7.10−7.40 (m, 51H, Ph), 7.68−7.76 (m, 4H, TBDPS). $C_{108}H_{118}O_{21}Cl_3NSi$ (1900.71): calcd. C 67.60, H 6.32, N 0.73; found C 67.72, H 6.21, N 0.71.

**Allyl (2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(3,4,6-tri-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-galactopyranosyl)-(1→4)]-2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranoside (28).** Compound **27** (640 mg, 337 $\mu$mol) was stirred overnight in 30 mL of acetic acid anhydrate/pyridine (1:1). Coevaporation with toluene and subsequent flash chromatography (petroleum ether/ethyl acetate, 4:1) gave compound **28** (668 mg, 337 $\mu$mol, qu.) as a colorless foam. TLC (petroleum ether/ethyl acetate, 3:1): $R_f$ = 0.55. $[\alpha]_D = +22$ ($c$ = 1.2, $CDCl_3$). $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.07 (s, 9H, $^{t}$Bu), 1.86 (s, 3H, OAc), 2.11 (s, 3H, OAc), 3.32 (dd, $J_{5,6}$ = 4.6 Hz, $J_{6,6'}$ = 8.2 Hz, 1H, 6d-H), 3.45−3.97 (m, 18H), 3.98−4.12 (m, 4H, 2e-H, 3c-H, 3f-H, 6f-H), 4.13−4.26 (m, 2H, 4f-H), 4.27−4.36 (m, 2H), 4.42−4.52 (m, 5H), 4.53−4.96 (m, 12H), 4.98−5.24 (m, 4H, 1d-H, 1f-H, allyl), 5.29 (bs, 1H, 2c-H), 5.50 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 2.8 Hz, 1H, 2f-H), 5.63−5.79 (m, 1H, allyl), 7.02 (d, $J_{NH}$ = 7.2, 1H, NH), 7.10−7.43 (m, 51H, Ph), 7.67−7.76 (m, 4H, TBDPS). HMQC data ($^{13}$C (150.9 MHz)/$^{1}$H (600 MHz)): 96.1/4.69 (1c), 68.5/5.28 (2c), 76.0/3.91 (3c), 73.0/3.91 (4c), 69.8/3.77 (5c), 66.1/3.76 + 3.65 (6c), 98.4/5.09 (1d), 56.2/3.84 (2d), 77.1/4.06 (3d), 72.1/3.78 (4d), 73.4/3.49 (5d), 68.3/3.53 + 3.32 (6d), 98.1/4.81 (1e), 73.0/4.06 (2e), 80.4/3.89 (3e), 74.8/3.75 (4e), 72.0/3.80 (5e), 69.5/3.62 (6e), 98.8/5.19 (1f), 68.9/5.49 (2f), 78.0/4.02 (3f), 73.8/4.17 (4f), 73.1/3.74 (5f), 62.6/4.08 + 3.85 (6f). $C_{112}H_{122}O_{23}Cl_3NSi$ (1984.79): calcd. C 67.77, H 6.21, N 0.71; found C 67.52, H 6.21, N 0.53.

**Allyl (2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranoside (29).** Compound **28** (630 mg, 317 $\mu$mol), $Bu_3SnH$ (380 $\mu$L, 1.43 mmol), and two small spatulas of AIBN were dissolved in 21 mL of dry toluene, and the solution was vigorously stirred for 25 min under a stream of argon. After heating to 100 °C for 20 min and the addition of another 200 $\mu$L of $Bu_3SnH$ and one small spatula of AIBN, the solution was heated again for 15 min. After removal of the solvent, the remaining residue was immediately purified by flash chromatography (petroleum ether/ethyl acetate, 5:1 → 3:1 → 3:2). Compound **29** (500 mg, 266 $\mu$mol, 84%) was obtained as a colorless foam. TLC (petroleum ether/ethyl acetate, 3:1): $R_f$ = 0.11. $[\alpha]_D = 24$ ($c$ = 1.5, $CDCl_3$). $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.07 (s, 9H, $^{t}$Bu), 1.68 (s, 3H, NAc), 1.90 (s, 3H, OAc), 2.11 (s, 3H, OAc), 3.19 (dd, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = 8.2 Hz, 1H, 6-H), 3.40−3.89 (m, 15H), 3.90−4.29 (m, 11H), 4.35−4.53 (m, 6H), 4.59−4.86 (m, 10H), 4.92−5.21 (m, 5H), 5.25 (dd, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.1 Hz, 1H, 2c-H), 5.47 (dd, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 2.8 Hz, 1H, 2e-H), 5.58−5.69 (m, 1H, allyl), 6.23 (d, $J_{NH}$ = 7.5, 1H, NH), 7.09−7.43 (m, 51H, Ph), 7.66−7.76 (m, 4H, TBDPS). $C_{112}H_{125}O_{23}NSi$ (1881.47): calcd. C 71.49, H 6.71, N 0.74; found C 71.33, H 6.80, N 0.50.

**(2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-2-*O*-acetyl-3-*O*-benzyl-D-mannopyranose (30).** Compound **29** (241 mg, 128 $\mu$mol) and Wilkinson's catalyst ($Rh(PPh_3)_3$, 18 mg, 19 $\mu$mol) were dissolved in 1.5 mL of toluene/ethanol/water (20:10:1) and heated to reflux for 5.5 h. After cooling, the solution was filtered through a pad of Celite and the solvent was evaporated. The remaining residue was dissolved in 8 mL of THF/$H_2O$ (4:1). $I_2$ (65 mg, 500 $\mu$mol) was added, and after 30 min, the solution was diluted with $CH_2Cl_2$ and washed with $Na_2S_2O_3$ (5% in water). The aqueous fraction was reextracted at least four times (TLC!), then the combined organic fractions were dried over $MgSO_4$, and the solvent was removed. Flash chromatography (petroleum ether/ethyl acetate, 2:1) gave compound **30** (205 mg, 111 $\mu$mol, 87%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.15. $[\alpha]_D = +15$ ($c$ = 1.4, $CDCl_3$). $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.08 (s, 9H, $^{t}$Bu), 1.79 (s, 3H, NAc), 1.96 (s, 3H, OAc), 2.15 (s, 3H, OAc), 3.02 (dd, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = 8.1 Hz, 1H), 3.35−3.59 (m, 8H), 3.76−4.30 (m, 17H), 4.31−4.98 (m, 17H), 5.04 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 2.8 Hz, 1H, 2c-H), 5.22 (d, $J_{1,2}$ = 8.2 Hz, 1H, 1d-H), 5.39 (bs, 1H, 2f-H), 6.49 (d, $J_{NH}$ = 7.4, 1H, NH), 7.05−7.42 (m, 51H, Ph), 7.69−7.76 (m, 4H, TBDPS). $C_{169}H_{121}O_{23}NSi$ (1841.40): calcd. C 71.09, H 6.64, N 0.76; found C 71.24, H 6.71, N 0.58.

**(2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl Trichloroacetimidate (31).** Compound **30** (443 mg, 240 $\mu$mol) and $Cl_3CCN$ (170 $\mu$L, 1.7 mmol) were dissolved in 1.8 mL of $CH_2Cl_2$. After the addition of 2 drops of DBU and stirring at room temperature for 1.5 h, the solvent

was removed. Flash chromatography (petroleum ether/ethyl acetate, 2:1) gave trichloroacetimidate **31** (392 mg, 197 $\mu$mol, 82%) as a colorless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.50. $[\alpha]_D$ = +30 ($c$ = 1.4, $CDCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.08 (s, 9H, $^t$Bu), 1.65 (s, 3H, NAc), 1.94 (s, 3H, OAc), 1.94 (s, 3H, OAc), 2.11 (s, 3H, OAc), 3.21 (dd, $J_{5,6}$ = 3.5 Hz, $J_{6,6'}$ = 7.0 Hz, 1H), 3.45−4.07 (m, 20H), 4.08−4.29 (m, 4H), 4.33−4.92 (m, 16H), 5.09 (d, $J_{1,2}$ = 8.3 Hz, 1H, 1d-H), 5.19 (d, $J_{1,2}$ = 1.5 Hz, 1H, 1-H), 5.37 (bs, 1H, 2-H), 5.47 (dd, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 2.9 Hz, 1H, 2-H), 6.13 (d, $J_{1,2}$ = 1.9 Hz, 1H, 1c-H), 6.17 (d, $J_{NH}$ = 7.8, 1H, NH), 7.10−7.43 (m, 51H, Ph), 7.67−7.75 (m, 4H, TBDPS), 8.60 (s, 1H, $NHCCl_3$). $C_{111}H_{121}O_{23}Cl_3NSi$ (1985.78): calcd. C 67.13, H 6.15, N 1.41; found C 66.67, H 6.48, N 1.05.

**(2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-(2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (32).** Trichloroacetimidate **31** (360 mg, 181 $\mu$mol) and acceptor **2** (205 mg, 200 $\mu$mol) were dissolved in 5 mL of dry ethyl ether under argon and cooled to 0 °C, and 0.1 N TMSOTf solution (180 $\mu$L, 18 $\mu$mol) was added. After 30 min, the solution was neutralized with $NEt_3$, the solvent was evaporated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1). Compound **31** (382 mg, 134 $\mu$mol, 74%) was obtained as a colorless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.60. $[\alpha]_D$ = +24 ($c$ = 1.8, $CDCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.06 (s, 9H, $^t$Bu), 1.54 (s, 3H, NAc), 1.61 (s, 3H, OAc), 2.10 (s, 3H, OAc), 3.15−3.33 (m, 5H, 2b-H, 6/6′b-H, 6c-H, 6d-H), 3.78 (s, 3H, OMe), 3.36−3.82 (m, 15H), 3.83−5.07 (m, 46H), 5.35 (bs, 1H, 1c-H), 5.40 (bs, 1H, 2c-H), 5.45 (bs, 1H, 2f-H), 5.72 (d, $J_{1,2}$ = 3.7 Hz, 1H, 1b-H), 6.61 (d, $J_{NH}$ = 8.4 Hz, 1H, NH), 6.83−6.86 (m, 2H, PMB), 6.97−7.40 (m, 83H, Ph), 7.65−7.72 (m, 4H, TBDPS); HMQC data ($^{13}$C (150.9 MHz)/$^1$H (600 MHz) ($^1J_{CH}$ in Hz)): 82.2/3.48 (1a), 73.8/4.02 (2a), 81.2/3.39 (3a), 82.3/4.10 (4a), 81.6/3.44 (5a), 75.6/4.26 (6a), 97.7/5.72 (179.8) (1b), 63.8/3.18 (2b), 81.0/3.93 (3b), 73.7/3.90 (4b), 70.0/4.02 (5b), 68.6/3.21 (6b), 98.6/5.34 (177.4) (1c), 69.8/5.39 (2c), 75.8/3.69 (3c), 73.6/3.99 (4c), 71.3/3.57 (5c), 66.9/3.77 + 3.21 (6c), 101.1/4.71 (158.1) (1d), 53.3/4.15 (2d), 80.0/3.55 (3d), 72.5/3.46 (4d), 74.3/3.53 (5d), 69.4/3.44 + 3.29 (6d), 99.3/4.56 (172.6) (1e), 73.8/4.00 (2e), 80.7/3.87 (3e), 75.2/3.51 (4e), 72.8/3.74 (5e), 70.9/3.63 + 3.48 (6e), 99.4/5.05 (172.6) (1f), 69.2/5.45 (2f), 77.9/3.96 (3f), 74.2/4.21 (4f), 73.4/3.67 (5f), 62.8/4.04 + 3.78 (6f). $C_{171}H_{184}O_{33}N_4Si$ (2851.68): calcd. C 72.02, H 6.52, N 1.97; found C 71.63, H 6.67, N 1.51.

**(2-*O*-Acetyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-(2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (33).** Compound **32** (300 mg, 105 $\mu$mol) was dissolved under argon in 1.35 mL of THF. At 0 °C, TBAF (1 N solution in THF, 520 $\mu$L, 520 $\mu$mol) and acetic acid (30 $\mu$L, 525 $\mu$mol) were added and the solution was stirred at 0 °C for 15 min, at room temperature for 1 h, and at 40 °C for 24 h. After removal of the solvent and flash chromatography (petroleum ether/ethyl acetate, 2:1 → 3:2), compound **33** (214 mg, 82 $\mu$mol, 78%) was obtained as a colorless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.20. $[\alpha]_D$ = +43 ($c$ = 1.4, $CDCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.65 (s, 3H, NAc), 1.69 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.28 (dd, $J_{OH}$ = 3.8 Hz, $J_{OH}$ = 4.2 Hz, 1H, OH), 3.17−3.31 (m, 4H), 3.78 (s, 3H, OMe), 3.33−4.15 (m, 30H), 4.19−5.03 (m, 34H), 5.30 (bs, 1H, 1-H), 5.37 (bs, 1H, 2-H), 5.44 (bs, 1H, 2-H), 5.74 (d, $J_{1,2}$ = 3.6 Hz, 1H, 1-H), 5.99 (d, $J_{NH}$ = 8.5 Hz, 1H, NH), 6.82−6.85 (m, 2H, PMB), 7.06−7.38 (m, 78H, Ph). $C_{155}H_{166}O_{33}N_4$ (2613.25): calcd. C 71.24, H 6.42, N 2.14; found C 70.84, H 6.47, N 1.78.

**Triethylammonium (2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-(2-(*N*-benzyloxycarbonyl)aminoethyl-phosphonato)-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-(2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (34).** Compound **33** (200 mg, 77 $\mu$mol), [2-[*N*-(benzyloxycarbonyl)amino]ethoxy](2-cyanoethoxy)(diisopropylamino) phosphin (121 mg, 306 $\mu$mol), and tetrazole (21 mg, 306 mmol) were dried in a vacuum for 2 h. After addition of 4 mL of dry $CH_2Cl_2$, the solution was stirred at room temperature under argon for 3 h. Then MCPBA (52 mg, 30,6 mmol) was added, the solution was stirred for another 2 h, and 10 drops of $NEt_3$ were added. After the mixture was stirred overnight, the solvent was removed and flash chromatography (toluene/acetone, 1:1; 1% $NEt_3$) of the residue afforded compound **34** (198 mg, 66 $\mu$mol, 87%) as a triethylammonium salt, which was lyophilized from dioxane. TLC ($CH_2Cl_2$ /MeOH, 9:1): $R_f$ = 0.44. $[\alpha]_D$ = +18 ($c$ = 1.4, $CDCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.64 (s, 3H, NAc), 1.88 (s, 3H, OAc), 2.04 (s, 3H, OAc), 3.15−5.05 (m, 78H; 3.70: s, 3H, OMe), 5.32 (bs, 1H, 2c-H), 5.48 (bs, 1H, 2f-H), 5.77 (d, $J_{1,2}$ = 3.5 Hz, 1H, 1b-H), 6.78−6.80 (m, 2H, PMB), 7.08−7.38 (m, 83H, Ph). HMQC data ($^{13}$C (150.9 MHz)/$^1$H (600 MHz) ($^1J_{CH}$ in Hz)): 86.0/3.52 (1a), 77.6/4.06 (2a), 85.0/3.42 (3a), 86.1/4.06 (4a), 85.6/3.46 (5a), 78.8/4.33 (6a), 101.4/5.77 (180.0) (1b), 67.2/3.26 (2b), 84.6/3.97 (3b), 77.2/3.88 (4b), 73.6/4.18 (5b), 73.1/3.42 + 3.39 (6b), 102.0/5.37 (176.2) (1c), 73.6/5.31 (2c), 80.6/3.71 (3c), 105.8/4.68 (161.2) (1d), 57.2/4.24 (2d), 84.2/3.58 (3d), 76.6/3.73 (4d), 77.7/3.49 (5d), 72.8/3.49 + 3.26 (6d), 102.3/4.86 (175.0) (1e), 80.1/3.84 (2e), 84.4/3.94 (3e), 78.6/3.63 (4e), 75.9/3.92 (5e), 74.1/3.58+3.53 (6e), 104.0/4.76 (172.5) (1f), 72.9/5.47 (2f), 81.9/3.91 (3f). $^{31}$P NMR (242.94 MHz, $CDCl_3$): $\delta$ = −1.88 ppm. $C_{165}H_{178}O_{38}N_5P$ (2870.45): calcd. C 68.09, H 6.25, N 2.41 (Na-Form + $H_2O$); found C 67.63, H 6.36, N 2.06.

**Triethylammonium (2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-(2-(*N*-benzyloxycarbonyl)aminoethyl-phosphonato)-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-(2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (35).** Compound **34** (190 mg, 64 mmol) was dissolved in 6 mL of $CH_3CN$/Toluene/Water (91:5:4). CAN (175 mg, 320 $\mu$mol) was added at 0 °C, and the solution was stirred at 0 °C for 30 min and at room temperature for 1.5 h. After $CH_2Cl_2$ was added, the solution was washed with saturated $NAHCO_3$ solution (the aqueous solution was washed three times with $CH_2Cl_2$) and the combined organic fractions were dried over $MgSO_4$. Flash chromatography (toluene/acetone, 1:1) afforded compound **35** (168 mg, 59 mmol, 92%), which was lyophilized as a colorless powder from dioxane. TLC ($CH_2Cl_2$/MeOH, 9:1): $R_f$ = 0.43. $^1$H NMR (250 MHz, MAS). $\delta$ = 1.67 (s, 3H, NAc), 1.89 (s, 3H, OAc), 2.04 (s, 3H, OAc), 3.22−5.00 (m, 73H), 5.31 (bs, 1H, 2c-H), 5.36 (bs, 1H, 1c-H), 5.47 (bs, 1H, 2f-H), 5.77 (d, $J_{1,2}$ = 3.6 Hz, 1H, 1b-H), 7.08−7.38 (m, 80H, Ph); HMQC data ($^{13}$C (150.9 MHz)/$^1$H (600 MHz) ($^1J_{CH}$ in Hz)): 72.8/3.62 (1a), 77.2/3.95 (2a), 80.4/3.45 (3a), 81.3/4.00 (4a), 80.9/3.37 (5a), 78.1/3.99 (6a), 96.7/5.46 (176.3) (1b), 63.3/3.27 (2b), 80.3/3.86 (3b), 74.3/3.80 (4b), 69.5/4.02 (5b), 68.5/3.38 (6b), 97.3/5.30 (176.3) (1c), 68.9/5.25 (2c), 75.7/3.70 (3c), 72.9/3.79 (4c), 71.2/3.70 (5c), 66.0/3.78 + 3.59 (6c), 101.2/4.65 (160.9) (1d), 52.4/4.15 (2d), 79.4/3.54 (3d), 71.9/3.68 (4d), 73.1/3.44 (5d), 68.1/3.44 + 3.23 (6d), 97.8/4.82 (172.4) (1e), 75.8/3.82 (2e), 79.7/3.88 (3e), 73.7/3.68 (4e), 71.2/3.86 (5e), 69.4/3.52 (6e), 99.3/4.74 (174.3) (1f), 68.3/5.41 (2f), 77.1/3.87 (3f), 74.2/3.61 (4f), 71.2/3.68 (5f), 64.3/4.09 + 4.05 (6f). $^{31}$P NMR (242.94 MHz, $CDCl_3$): $\delta$ = −2.25. $C_{157}H_{170}O_{37}N_5P$ (2750.29): calcd. C 67.55, H 6.22, N 2.51 (Na−Form + $H_2O$); found C 67.29, H 6.36, N 2.14.

**Bistriethylammonium (2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-(2-(*N*-benzyloxycarbonyl)aminoethyl-phosphonato)-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-(2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inosit-1-yl-(benzyl-)phosphate (36).** Compound **35** (145 mg,

53 $\mu$mol), (benzyloxy)(cyanoethoxy)(diisopropylamino)phosphin (50 mg, 157 $\mu$mol), and tetrazole (7.4 mg, 105 $\mu$mol) were dried in a vacuum for 1 h. After addition of 2 mL of dry $CH_2Cl_2$, the solution was stirred at room temperature under argon for 3 h and then MCPBA (10 mg, 58 $\mu$mol) was added. The solution was stirred for another 2 h and concentrated to half of its volume. A 2 mL portion of $Me_2NH$ solution (33% in dry ethanol) was added, the solution was stirred at room temperature for 2 h, and the solvent was removed. Flash chromatography (toluene/acetone/methanol, 1:1:0 → 7:3:0 → 1:1:0 → 45:45:10; 1% $NEt_3$) gave compound **36** (76 mg, 24.4 $\mu$mol, 48%) as a colorless bistriethylammonium salt. TLC ($CH_2Cl_2$/MeOH, 9:1): $R_f = 0.3$. $^1$H NMR (250 MHz, MAS). $\delta = 1.66$ (s, 3H, NAc), 1.84 (s, 3H, OAc), 2.08 (s, 3H, OAc), 3.18−5.10 (m, 76H), 5.31 (bs, 1H, 2-H), 5.49 (bs, 1H, 2-H), 5.90 (d, $J_{1,2} = 3.0$ Hz, 1H, 1-H), 7.05−7.54 (m, 81H, Ph), 7.90−8.01 (m, 4H). $^{31}$P NMR (242.94 MHz, $CDCl_3$): $\delta = 2.78, -2.44$. $C_{164}H_{177}O_{40}N_5P_2$ (2920.40): FAB-MS (positive mode; matrix: 3-nitrobenzyl alcohol/$CH_2Cl_2$, 1:1): $m/z = 2966$ $[M - H^+ + 2Na]^+$, 2989 $[M - 2H^+ + 3Na]^+$.

**Bistriethylammonium (3,4-Di-*O*-benzyl-6-*O*-(2-(*N*-benzyloxycarbonyl)aminoethyl-phosphonato)-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-3-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inosit-1-yl-(benzyl-)phosphate (37).** Compound **36** (56 mg, 18 $\mu$mol) was dissolved in 250 $\mu$L of dry methanol and 1 N NaOMe solution (90 $\mu$L, 90 $\mu$mol), and the solution was stirred at 40 °C for 24 h, then neutralized with Amberlite IR 120 ($H^+$), and filtered through a 0.45 $\mu$m filter. Evaporation gave compound **37** (50 mg, 18 $\mu$mol, 98%) as a colorless powder, which was lyophilized from dioxane. TLC ($CH_2Cl_2$/MeOH, 6:1): $R_f = 0.7$. $^1$H NMR (250 MHz, MAS): $\delta = 1.87$ (s, 3H, NAc), 3.18−5.09 (m, 76H), 5.21 (bs, 1H, 2-H), 5.78 (d, $J_{1,2} = 3.0$ Hz, 1H, 1-H), 7.05−7.55 (m, 81H), 7.88−8.02 (m, 4H). $C_{160}H_{173}O_{38}N_5P_2$ (2836.32): FAB-MS (positive mode; matrix: 3-nitrobenzyl alcohol/glycerol, 1:1 with NaI): $m/z = 2880$ $[M - H + 2Na]^+$, 2903 $[M - 2H + 3Na]^+$.

**(6-*O*-(2-Aminoethyl-phosphonato)-α-D-mannopyranosyl)-(1→2)-(α-D-mannopyranosyl)-(1→6)-[(2-acetamido-2-deoxy-*β*-D-galactopyranosyl)-(1→4)]-α-D-mannopyranosyl)-(1→4)-(2-ammonium-2-deoxy-α-D-glucopyranosyl)-(1→6)-D-*myo*-inosit-1-yl-(hydrogen phosphate) (1a).** Compound **74** (20 mg, 6.4 $\mu$mol) was dissolved in 1.4 mL of methanol and 300 $\mu$L of $H_2O$. After addition of 10 mg of $Pd(OH)_2$/C, the solution was stirred under $H_2$ for 4 h, diluted with 1.1 mL of water, filtered through a 0.45 $\mu$m filter (the filter was washed two times with 2.5 mL MeOH/$H_2O$, 1:1), washed three times with $CH_2Cl_2$, and lyophilized. Compound **1a** (6.9 mg, 5.9 $\mu$mol, 92%) was obtained as a colorless powder. TLC ($CHCl_3$/MeOH/$NH_{3,concd}$, 2:4:1): $R_f = 0.02$. $^1$H NMR (250 MHz, $D_2O$): $\delta = 1.92$ (s, 3H, NAc), 3.12−4.03 (m, 57H), 4.32 (d, $J_{1,2} = 8.2$ Hz, 1H, 1f-H), 4.84 (bs, 1H, 1e-H), 5.00 (bs, 1H, 1d-H), 5.04 (bs, 1H, 1c-H), 5.40 (d, $J_{1,2} = 3.8$ Hz, 1H, 1b-H). HMQC data $^{13}$C (150.9 MHz)/$^1$H (600 MHz): 75.7/4.11 (1a), 70.9/4.12 (2a), 70.0/3.48 (3a), 72.8/3.60 (4a), 72.2/3.35 (5a), 76.8/3.83 (6a), 94.7/5.49 (1b), 53.4/3.31 (2b), 69.4/3.99 (3b), 76.1/3.65 (4b), 70.4/4.10 (5b), 59.7/3.76 (6b), 100.9/5.13 (1c), 69.0/4.03 (2c), 68.5/3.85 (3c), 76.3/3.72 (4c), 70.8/3.78 (5c), 65.9/3.78 + 3.67 (6c), 101.3/4.41 (1d), 52.0/3.85 (2d), 69.9/3.71 (3d), 67.3/3.86 (4d), 75.0/3.67 (5d), 60.6/3.70 (6d), 98.1/5.09 (1e), 78.5/3.94 (2e), 69.6/3.89 (3e), 66.5/3.61 (4e), 72.6/3.61 (5e), 60.7/3.82 + 3.78 (6e), 101.9/4.93 (1f), 69.5/3.99 (2f), 69.7/3.78 (3f), 65.8/3.66 (4f), 71.5/3.80 (5f), 64.3/4.05 (6f). $^{31}$P NMR (242.94 MHz, $CDCl_3$): $\delta = -0.66, -1.37$. $C_{40}H_{73}O_{36}N_3P_2$ (1234.10). FAB-MS (positive mode; matrix: 1% TFA/glycerol, 1:1): $m/z = 1234$ $[M + H]^+$, 1256 $[M + Na]^+$.

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**Supporting Information Available:** $^1$H NMR spectra of all described compounds as well as selected HMQC and mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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