Glycosyl Phosphatidylinositol (GPI) Anchor Synthesis Based on Versatile Building Blocks – Total Synthesis of a GPI Anchor of Yeast[1]

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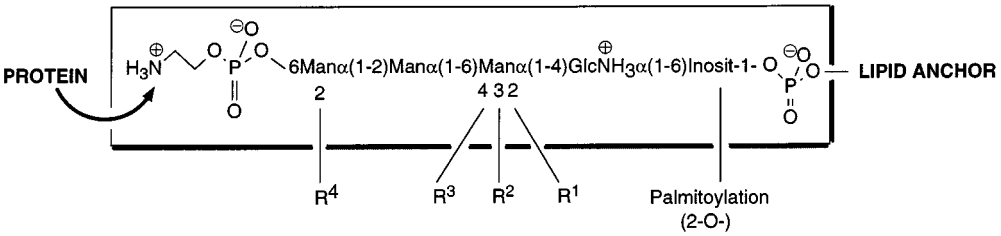
For the design of a synthesis of target molecule **1** the retrosynthetic analysis yielded building blocks **2–5**, of which ceramide 2-phosphite derivative **2** and aminoethyl phosphite derivative **5** are known. The generation of α-glucosaminyl (1→6)inositol building block **3** was based on pseudodisaccharide **6** which was selectively benzoylated at 6b-O and then selectively benzylated at 3b-O to give **3**. The synthesis of tetramannosyl building block **4** started from known ortho ester derivative **8** which was transformed into versatile mannosyl donors **13** and **18** and into acceptor **22**. Reaction of **13** with **22** gave α-disaccharide **23**, deacetylation and then mannosylation with **18** gave trisaccharide **25**; ensuing deacetylation and mannosylation with **13** gave tetrasaccharide **27**; deallylation, acetylation, regioselective removal of the anomeric *O*-acetyl group and treatment with CCl_3CN/DBU afforded **4**. Glycosylation of **3** with donor **4** led to pseudohexasaccharide **31** in high yield. Replacement of the *O*-acyl groups by *O*-benzyl groups and then exchange of the menthyloxycarbonyl group by an *O*-acetyl group gave **36** which enabled regioselective attachment of **2** and **5**. To this end, the 6e-*O*-silyl group was removed and then the aminoethyl phosphate residue was attached with reagent **5** to give **38** in high yield. 1a-*O*-Deacetylation and then reaction with **2** afforded **40** as fully protected **1** which was liberated in two steps; treatment with acid removed all acid labile protective groups and finally catalytic hydrogenation afforded the desired GPI anchor **1** which could be fully structurally assigned.

Glycosylphosphatidylinositols (GPIs) are a class of naturally occurring glycophospholipids that anchor the C termini of proteins and glycoproteins to the membrane of eukaryotic cells.[2,3] The first structure of a member of this family, the *Typanosoma brucei* variant surface glycoprotein (VSG) was reported by Ferguson et al. in 1988.[4,5] Since then various GPI anchors have been characterized, thus leading to a general structure as shown in Scheme 1 (frame) which was conserved during evolution of the various species. The occurrence of additional carbohydrate (R^2, R^3, and/or R^4) or ethanolamine phosphate (R^1) side chains is species-specific.[2,3] Their is also a variation in the membrane-anchoring lipid structures which depend on species and on cell type. For instance, in the case of glycerolipids (variation of the lipid anchor) the lipids are made up of sn-1,2-dimyristoylglycerol in *T. brucei* VSGs,[6] sn-1-stearyl-2-lysoglycerol in *T. brucei* procyclic acidic repetitive protein,[7] sn-1-alkyl-2-acylglycerol in bovine and human erythrocyte acetylcholinesterase[8] and human folate-binding protein,[9] and sn-1,2-diacylglycerol in torpedo acetylcholinesterase.[10] In addition, the inositol residue can be palmitoylated. In GPI anchors of yeast (*Saccharomyces cerevisiae*), ceramide-containing phytosphingosine was found as membrane anchor instead of glycerolipids.[11,12] The typical structure of a yeast GPI anchor is shown in Scheme 2 (**1**).

The role of GPI-anchored proteins as enzymes, in interactions with bioactive factors, and in cell-cell recognition has been extensively discussed.[2,3,13] Moreover, there is evidence that metabolites derived from GPI anchors or structurally related compounds are mediators of regulatory processes.[13] For instance, GPI-derived fragments are thought to participate in signal transduction which is triggered by insulin.[14] Therefore, the GPI anchors themselves and partial structures thereof are gaining in significance. Thus, the challenging chemical synthesis of structurally homogeneous GPI anchors and their derivatives is an important objective



Scheme 1

in order to perform biological studies. We report here details on the previously communicated first total synthesis of a GPI anchor,[1,15] namely the ceramide-containing GPI anchor **1** of yeast (Scheme 2). The required combination of

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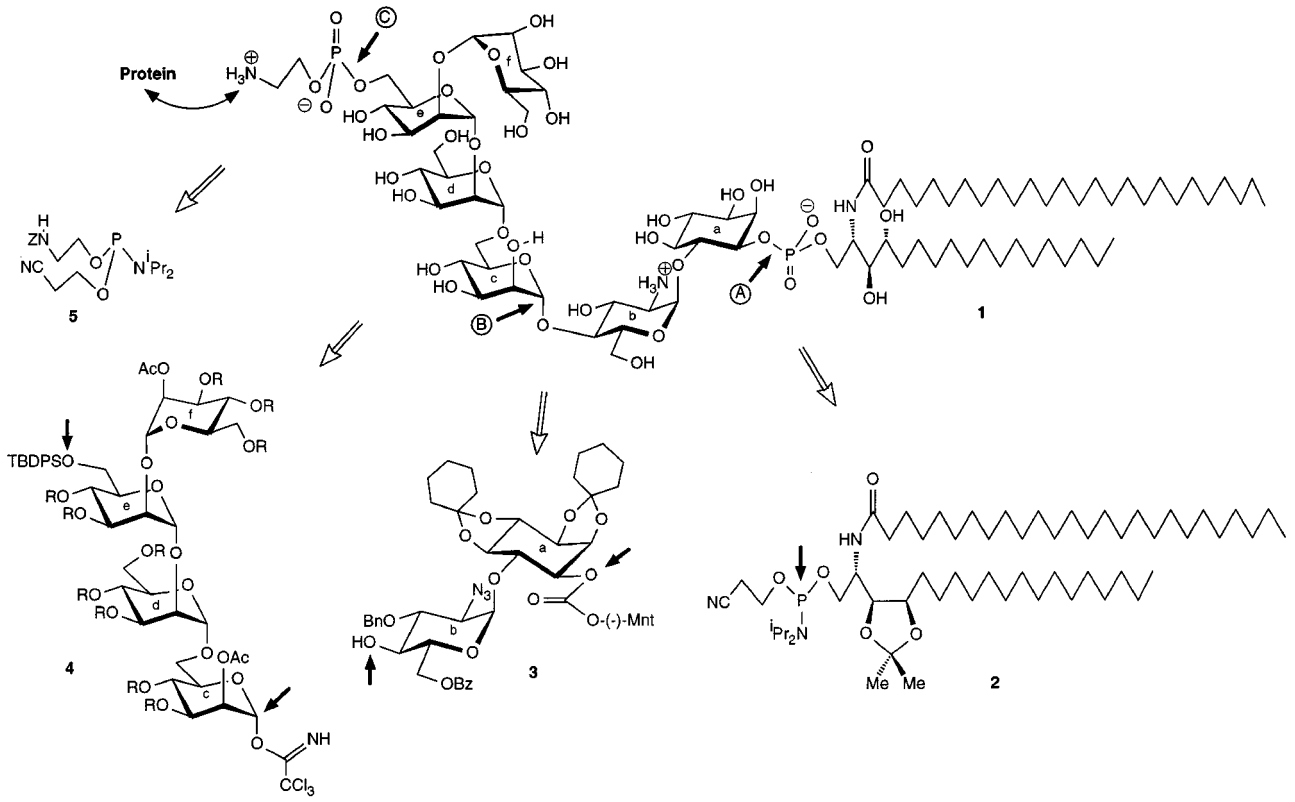


Scheme 2. R = Bn; Z = BnOCO

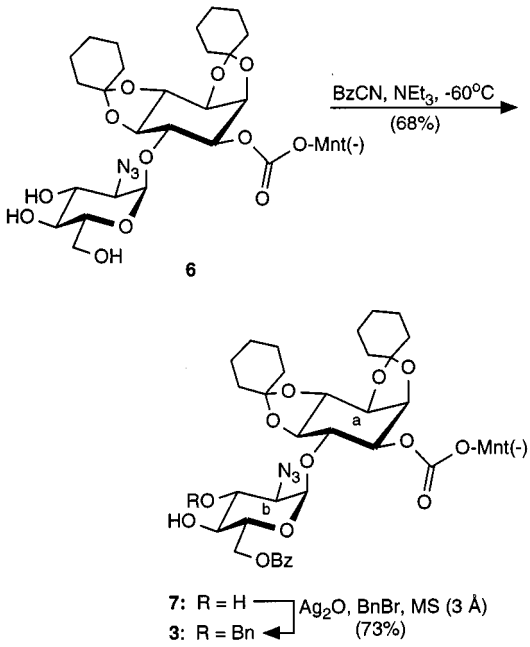
lipid, phosphate, and oligosaccharide chemistry has been meanwhile successfully employed to the synthesis of partial structures[16−26] and to the total synthesis of diacylglycerol-based GPI anchors of *Trypanosoma brucei* and rat brain Thy-1.[15,26−29]

The strategy, which we developed in order to synthesize **1**, is convergent and highly versatile. The target molecule **1** was disconnected at positions A−C , thus affording building blocks **2**−**5**, which due to proper protection are widely useful in GPI-anchor synthesis.[28] Slight protective-group modifications, especially at O-3 and/or O-4 of mannose residue c, will yield a great variety of structurally different GPI anchors. Our aim is to demonstrate the efficiency of this strategy with respect to the synthesis of the individual building blocks and their coupling in order to provide target molecule **1**.

Synthesis of Building Blocks 2−5

The ceramide-containing building block **2**, which contains phytosphingosine as nitrogen base, was prepared starting from the readily available azido derivative of phytosphingosine;[30] this was recently already reported in detail.[21]

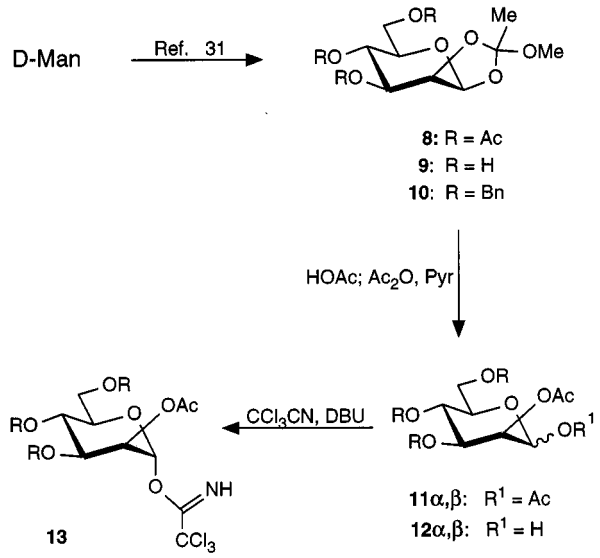
The synthesis of the α-glucosaminyl(1→6)inositol building block **3** was based on readily available derivative **6**[21] (Scheme 3) which on benzoylation with benzoyl cyanide in the presence of triethylamine afforded at −60°C regioselectively 6b-*O*-benzoyl derivative **7**. Ensuing regioselective 3b-*O*-benzylation with benzyl bromide in the presence of silver oxide gave the desired building block **3** in good overall yield. The structure of **3** was confirmed by the ^{1}H-NMR data.



Scheme 3

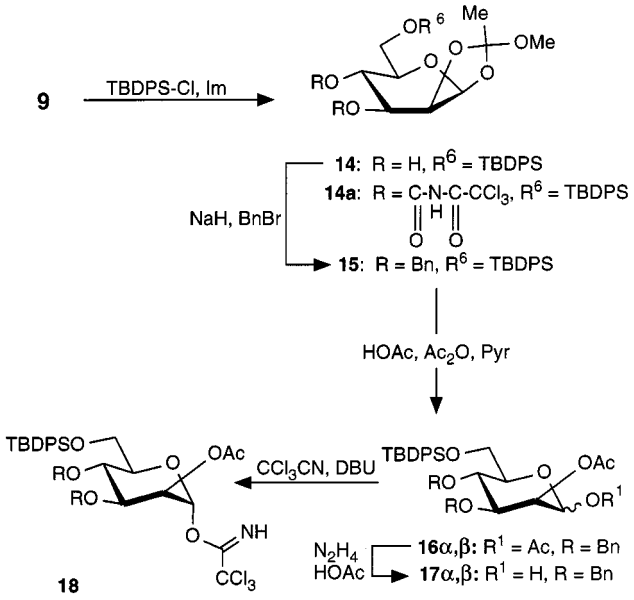
The synthesis of tetramannosyl building block **4** started from known ortho ester **8** (Scheme 4a) which is readily

available from D-mannose;[31] also *O*-deacetylation (→ **9**), benzylation (→ **10**), subsequent acid-catalyzed ortho ester opening and then *O*-acetylation (→ **11α,β**) followed essentially published procedures.[32,33] Selective 1-*O*-deacetylation with ammonium carbonate in DMF afforded **12α,β** in high yield. Ensuing treatment with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded almost exclusively α-trichloroacetimidate **13** (α/β ≈ 17:1) in 93% yield; **13** provides mannosyl residues d and f in the construction of tetramannosyl building block **4**. The 2-*O*-acetyl group in **13** promotes the desired α-selective *O*-glycosylations.

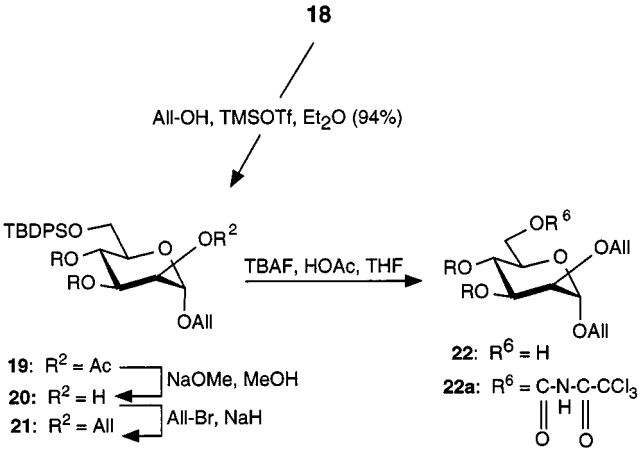


Scheme 4a. R = Bn

The c and e mannosyl residues were prepared starting from intermediate **9**. Regioselective 6-*O*-silylation with *tert*-butyldiphenylsilyl chloride (TBDPS-Cl) in the presence of imidazole afforded compound **14** (Scheme 4b); the structure of **14** was confirmed with the help of the ^{1}H-NMR data of the trichloroacetyl isocyanate addition product **14a** which exhibited the expected downfield shifts for the 3-H and 4-H signals (δ = 5.29, 5.60). Treatment of **14** with benzyl bromide in the presence of sodium hydride gave 3,4-di-*O*-benzyl derivative **15**. Acid-catalyzed ortho ester cleavage and then treatment with acetic anhydride and pyridine afforded 1,2-di-*O*-acetyl derivative **16α,β**. Selective 1-*O*-deacetylation with hydrazinium acetate in DMF afforded **17α,β** which on treatment with trichloroacetonitrile in the presence of DBU furnished in very high overall yield trichloroacetimidate **18** (α,β ≈ 12:1), which served as e mannosyl residue. The c mannosyl residue, required for tetrasaccharide **4**, was prepared from **18** in a straightforward reaction sequence. Reaction of **18** with allyl alcohol in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as catalyst afforded allyl α-mannoside **19** in practically quantitative yield (Scheme 4c). 2-*O*-Deacetylation under Zemplén conditions[34] gave **20**; ensuing treatment with allyl bromide in the presence of sodium hydride gave 1,2-di-*O*-allyl-mannoside **21**. Removal of the 6-*O*-TBDPS group with tetrabutylammonium fluoride (TBAF) in acetic acid/THF gave 6-O-unprotected mannoside **22** which served as mannosyl residue c. Its structure was confirmed with the help of the ^{1}H-NMR data of derivative **22a**.



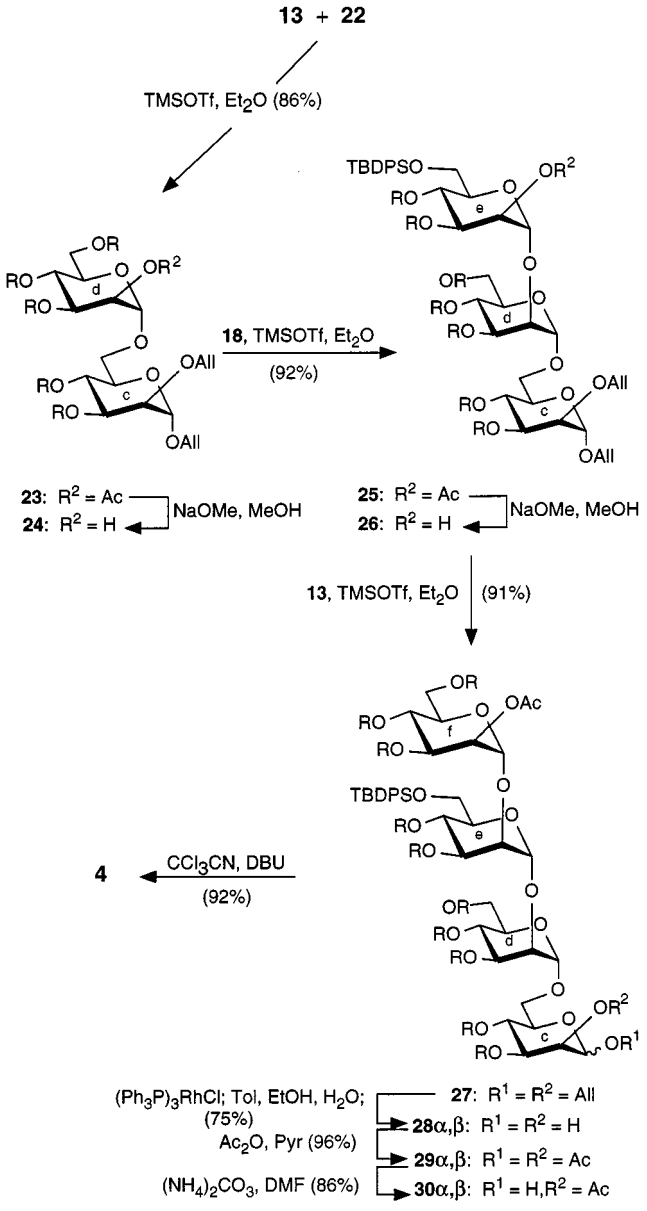
Scheme 4b



Scheme 4c. R = Bn

Reaction of mannosyl donor **13** with acceptor **22** in the presence of TMSOTf as the catalyst and ether as solvent gave at room temperature α(1→6)-linked disaccharide **23** in high yield (Scheme 4d). Cleavage of the 2d-*O*-acetyl group under Zemplén conditions[34] afforded glycosyl acceptor **24**; its reaction with mannosyl donor **18** under standard conditions afforded trisaccharide **25** in 92% yield. Cleavage of the 2e-*O*-acetyl group under Zemplén conditions led to **26** as acceptor which on treatment with **13** as mannosyl donor furnished again under standard conditions α(1→2)-α(1→2)-α(1→6)-linked tetramannosyl derivative **27** in 91% yield. Thus, a very high overall yield in the α-selective linkage of the four mannosyl residues c–f could be verified in only

five steps. The 1c- and 2c-*O*-allyl groups were then removed by treatment with the Wilkinson catalyst and ensuing hydrolysis (→ **28α,β**). Treatment with acetic anhydride in pyridine afforded *O*-acetyl derivative **29α,β (α/β** = 6:1). Regioselective removal of the 1-*O*-acetyl group with ammonium carbonate in DMF furnished **30α,β** which gave on treatment with trichloroacetonitrile in the presence of DBU the desired tetramannosyl donor **4** in very high overall yield; the structure of **4** was assigned on the basis of the ^{1}H-NMR data ($J_{1c,2c}$ = 1.4, $J_{1d,2d} \approx J_{1f,2f}$ < 1 Hz).

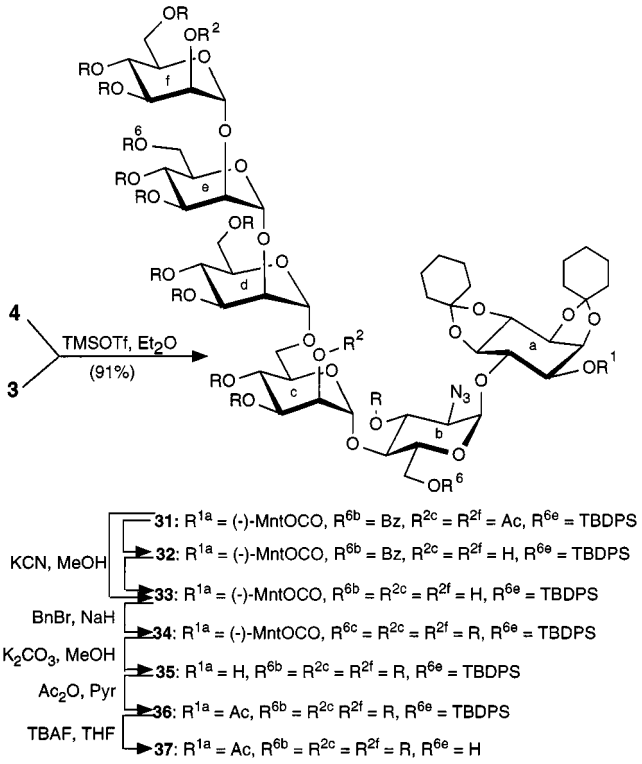


Scheme 4d. R = Bn

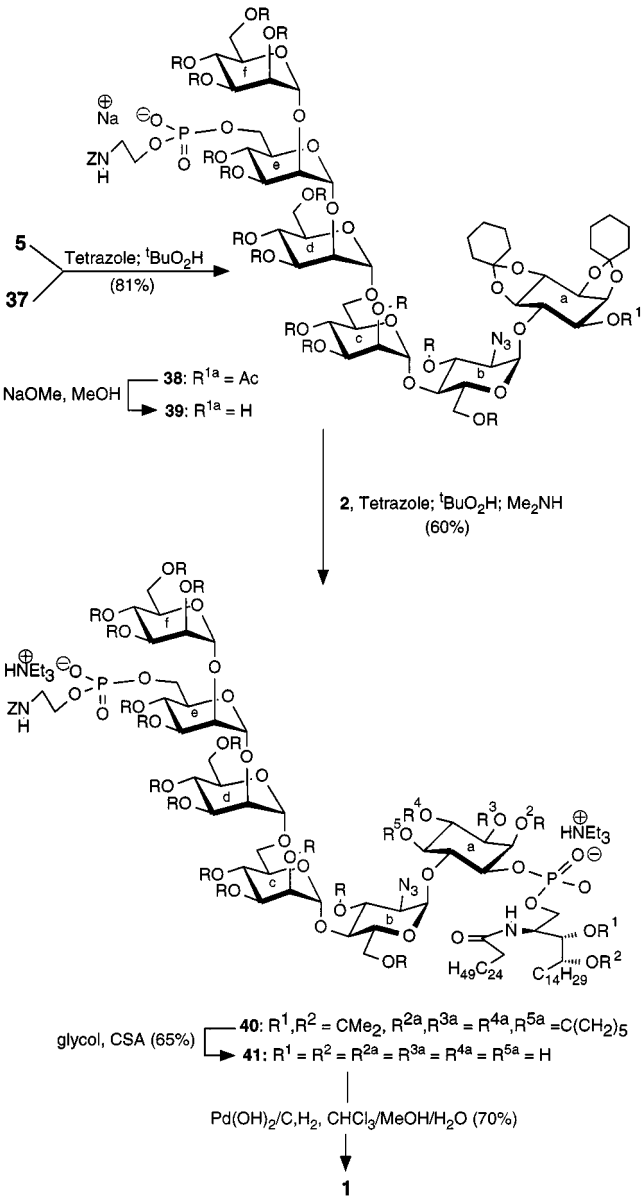
The *N*-benzyloxycarbonyl (Z)-protected aminoethyl phosphite compound **5** was prepared according to published procedures[15]. Thus, the synthesis of all building blocks required for the construction of target molecule **1** could be very successfully performed.

Construction of Target Molecule 1

In order to arrive at the final goal, glycosyl donor **4** was first treated with acceptor **3**; under standard glycosylation conditions, i.e. with TMSOTf as catalyst in ether as solvent at room temperature, the desired (pseudo) hexasaccharide **31** was obtained in almost quantitative yield (Scheme 5a). It was structurally assigned with the help of DQF-COSY, HMQC and HMBC experiments (see Experimental Section); formation of the α linkage was confirmed by the C,H-coupling constants (INEPT): 169.51 > $J_{C,H}$ > 177.30 Hz. The three different types of *O*-acyl groups in **31** (*O*-acetyl, *O*-benzoyl, and *O*-menthyloxycarbonyl) can be readily distinguished: Methanolysis in the presence of potassium cyanide as catalyst led to removal of the two *O*-acetyl groups yielding **32** accompanied by some **33**, where also the benzoyl group was removed; extension of the reaction time gave essentially only desired **33**. Treatment of **33** with benzyl bromide in the presence of sodium hydride led to introduction of three additional *O*-benzyl groups furnishing **34** in 86% yield. Methanolysis of the menthyloxycarbonyl group was accomplished with potassium carbonate in methanol, affording 1a-*O*-unprotected compound **35**, which on treatment with acetic anhydride in pyridine led to 1a-*O*-acetyl derivative **36**. This measure was undertaken to ease removal of the 1a-O protective group after introduction of the 6e-*O*-aminoethyl phosphate moiety. To this end, **36** was treated with TBAF in the presence of acetic acid in THF as the solvent leading to the 6e-*O*-unprotected compound **37**. Reaction with phosphite derivative **5** in the presence of tetra-



Scheme 5a. R = Bn



Scheme 5b. R = Bn

zole as activating agent and then oxidation with *tert*-butyl hydroperoxide gave Z-protected aminoethyl phosphate derivative **38** in 81% yield (Scheme 5b). Now, the 1a-*O*-acetyl group was removed under Zemplén conditions (→ **39**), thus permitting attachment of the ceramide 1-phosphate moiety. To this end, reaction of **39** with phosphite amide derivative **2** in the presence of tetrazole followed by oxidation with *tert*-butyl hydroperoxide was carried out, leading to the corresponding phosphotriester, which gave with dimethylamine in ethanol diester **40** in 60% overall yield. Simultaneous cleavage of the *O*-isopropylidene and *O*-cyclohexylidene groups with glycol in the presence of camphersulfonic acid (CSA) as the catalyst (→ **41**) followed by hydrogenolysis of the *O*-benzyl groups and the azido group with Pearlman's catalyst[35] afforded target molecule **1** which was characterized with the help of NMR and MS data (Experimental).

Conclusion

The ready accessibility of all starting materials, the high regio- and diastereoselectivities, and the high yields obtained in all reaction steps, including the glycosylation reactions which were carried out with trichloroacetimidates,[36] provide an excellent basis for further successful syntheses in this field. The versatility of the building blocks described in this paper has been meanwhile demonstrated in their successful utilization to the synthesis of *T. brucei* P_3 and *Thy-1* GPI anchors.[28]

Experimental Section

General: Solvents were purified in the usual way; boiling range of petroleum ether: 35−60°C. − Melting points are uncorrected. − Optical rotations: Perkin−Elmer polarimeter 241 MC; 1-dm cell, temperature 20°C. − Thin-layer chromatography (TLC): Plastic sheets, silica gel 60 F_{254} (Merck; layer thickness 0.2 mm). − Column chromatography: Kieselgel 60 (Merck; 0.063−0.200 mm). − Flash chromatography: Silica gel (J. T. Baker, particle size 40 mm). − ^{1}H NMR: Bruker AC 250 (250 MHz) Cryospec, Bruker DRX 600 (600 MHz), internal standard tetramethylsilane (TMS). − ^{31}P NMR: Jeol JNM-GX 400; external standard 85% phosphoric acid. − FAB MS: Finnigan MAT 312/AMD 5000; matrix NBOH (= 3-nitrobenzyl alcohol). − Elemental analyses: Heraeus CHN-O-Rapid.

***O*-(2-Azido-6-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-(1*R*)-menthyloxycarbonyl-D-*myo*-inositol (7):** A solution of benzoyl cyanide (0.79 g, 5.78 mmol) in dry acetonitrile (10 mL) was added dropwise within 1 h to a solution of crude **6**[21] (4.1 g, 5.78 mmol) in dry acetonitrile/diethyl ether/triethylamine (10:7:3, 200 mL) at −60°C under nitrogen. The mixture was stirred for 2 h at −60°C. Within 2 h, the mixture was warmed up to room temp. and concentrated in vacuo. The residue was purified by flash chromatography with toluene/ethyl acetate (5:1) to yield **7** (3.2 g,, 68%) as a colorless foam which was lyophilized from dioxane.− TLC (petroleum ether/ethyl acetate, 6:4): R_f = 0.45; (toluene/ethyl acetate, 3:1): R_f = 0.26. − $[\alpha]_D$ = +14 (*c* = 1, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 0.72−0.75 (d, ^3J = 6.9 Hz, 3 H, CH_3), 0.80−1.10 (2 d, m, 9 H, 2 CH_3, H_{Mnt}), 1.40−1.76 (m, 24 H, 20 $H_{cycloh.}$, 4 H_{Mnt}), 1.86−2.12 (m, 2 H, 2 H_{Mnt}), 2.84 (d, $^3J_{3b,OH}$ = 2.6 Hz, 1 H, OH), 3.20 (dd, $^3J_{1b,2b}$ = 3.6, $^3J_{2b,3b}$ = 10.3 Hz, 1 H, 2b-H), 3.38 (ddd, $^3J_{4b,OH}$ = 4.0, $^3J_{3b,4b}$ = $^3J_{4b,5b}$ = 9.5 Hz, 1 H, 4b-H), 3.53 (dd, $^3J_{4a,5a}$ = 10.8, $^3J_{5a,6a}$ = 8.5 Hz, 1 H, 5a-H), 3.60(d, $^3J_{4b,OH}$ = 3.9 Hz, 1 H, OH), 3.93−4.11 (m, 4 H, 4a-, 6a-, 3b-, 5b-H), 4.33−4.41 (m, 2 H, 6b-, 3a-H), 4.45−4.58 (m, 2 H, H_{Mnt}, 2a-H), 4.89−4.95 (m, 2 H, 6b′-, 1a-H), 5.29 (d, $^3J_{1b,2b}$ = 3.6 Hz, 1 H, 1b-H), 7.41−7.61 (m, 3 H, m, p-COPh), 8.02−8.06 (m, 2 H, OCOPh). − $C_{42}H_{59}N_3O_{13}$ (813.94): calcd. C 61.98, H 7.31, N 5.16; found C 61.49, H 7.44, N 5.72.

***O*-(2-Azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-(1*R*)-menthyloxycarbonyl-D-*myo*-inositol (3):** To a solution of **7** (10 g, 12.3 mmol) in dry dichloromethane (35 mL) freshly prepared Ag_2O (10 g), powdered molecular sieves (3 Å, 7 g), and benzyl bromide (1.68 mL, 14.1 mmol) were added. After stirring for 18 h at room temp., the mixture was filtered through Celite, concentrated in vacuo, and chromatographed on silica gel (toluene/ethyl acetate, 10:1). MPLC (toluene/ethyl acetate, 15:1) of the residue in order to remove the 4-*O*-benzyl isomer gave pure **3** (8.1 g, 73%) as a colorless foam. −

TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.51; (toluene/ethyl acetate, 10:1): R_f = 0.38. − $[\alpha]_D$ = +35 (*c* = 0.5, chloroform). − ^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.68−0.70 (d, ^3J = 7.3 Hz, 3 H, CH_3), 0.78−1.02 (2 d, m, 9 H, 2 CH_3, H_{Mnt}), 1.28−1.68 (m, 24 H, 20 $H_{cycloh.}$, 4 H_{Mnt}), 1.85−1.89 (m, 1 H, H_{Mnt}), 1.98−2.03 (m, 1 H, H_{Mnt}), 3.04 (d, $^3J_{4b,OH}$ = 4.4 Hz, 1 H, OH), 3.27 (dd, $^3J_{1b,2b}$ = 3.7, $^3J_{2b,3b}$ = 10.3 Hz, 1 H, 2b-H), 3.49−3.56 (m, 2 H, 5a-, 4b-H), 3.82 (dd, $^3J_{2b,3b}$ = $^3J_{3b,4b}$ = 9.5 Hz, 1 H, 3b-H), 3.94 (dd, $^3J_{3a,4a}$ = 7.3, $^3J_{4a,5a}$ = 10.3 Hz, 1 H, 4a-H), 4.32−4.36 (m, 2 H, 3a-, 6b-H), 4.45 (dd, ^3J = 4.4, ^3J = ^3J = 11.0 Hz, 1 H, H_{Mnt}), 4.51 (dd, $^3J_{1a,2a}$ = 4.4, $^3J_{2a,3a}$ = 6.6 Hz, 1 H, 2a-H), 4.79 (dd, $^3J_{5b,6b}$ = 2.9, $^3J_{gem}$ = 12.5 Hz, 1 H, 6b′-H), 4.84 (s, 2 H, CH_2Ph), 4.91 (dd, $^3J_{6a,1a}$ = $^3J_{1a,2a}$ = 4.9 Hz, 1 H, 1a-H), 5.24 (d, $^3J_{1b,2b}$ = 3.7 Hz, 1 H, 1b-H), 7.17−7.39 (m, 7 H, Ph, *m*-COPh), 7.49−7.53 (m, 1 H, *p*-COPh), 7.96−7.98 (m, 2 H, *o*-COPh). − $C_{49}H_{65}N_3O_{13}$ (904.06): calcd. C 65.09, H 7.25, N 4.65; found C 64.77, H 7.26, N 4.73.

3,4,6-Tri-*O*-acetyl-1,2-*O*-[1-(*R*)-methoxyethylidene]-β-D-mannopyranose (8): Compound **8** was prepared as described in ref.[31] − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.59. − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.72 (s, 3 H, CMe), 2.03 (s, 3 H, $COCH_3$), 2.05 (s, 3 H, $COCH_3$), 2.10 (s, 3 H, $COCH_3$), 3.25 (s, 3 H, OMe), 3.62−3.69 (m, 1 H, 5-H), 4.12 (dd, 1 H, $^3J_{5,6}$ = 2.7, $^3J_{6,6'}$ = 12.1 Hz, 6-H), 4.22 (dd, 1 H, $^3J_{5,6'}$ = 4.9, $^3J_{6,6'}$ = 12.2 Hz, 6′-H), 4.59 (dd, 1 H, $^3J_{1,2}$ = 2.6, $^3J_{2,3}$ = 3.9 Hz, 2-H), 5.12 (dd, 1 H, $^3J_{2,3}$ = 4.0, $^3J_{3,4}$ = 9.9 Hz, 3-H), 5.28 (dd, 1 H, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.7 Hz, 4-H), 5.47 (d, 1 H, $^3J_{1,2}$ = 2.6 Hz, 1-H). − $C_{15}H_{22}O_{10}$ (362.33): calcd. C 49.72, H 6.12; found C 49.73, H 6.03.

1,2-*O*-[1-(*R*)-Methoxyethylidene]-β-D-mannopyranose (9): Compound **9** was prepared as described previously.[32] Crude **9** was directly used for further preparations.

3,4,6-Tri-*O*-benzyl-1,2-*O*-[1-(*R*)-methoxyethylidene]-β-D-mannopyranose (10): Compound **10** was prepared according to the procedure described by Ponpipom.[32] − TLC (petroleum ether/ethyl acetate, 7:3): R_f = 0.42. − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.74 (s, 3 H, CMe), 3.28 (s, 3 H, OMe), 3.38−3.44 (m, 1 H, 5-H), 3.67−3.73 (m, 3 H, 6-, 6′-, 3-H), 3.92 (dd, 1 H, $^3J_{4,5}$ = $^3J_{5,6}$ = 9.3 Hz, 4-H), 4.39 (dd, 1 H, $^3J_{1,2}$ = 2.6, $^3J_{2,3}$ = 3.9 Hz, 2-H), 4.51−4.92 (m, 6 H, 3 CH_2Ph), 5.34 (d, 1 H, $^3J_{1,2}$ = 2.5 Hz, 1-H), 7.21−7.41 (m, 15 H, Ph). − $C_{30}H_{34}O_7$ (506.59): calcd. C 71.13, H 6.76; found C 71.16, H 6.72.

1,2-Di-*O*-acetyl-3,4,6-tri-*O*-benzyl-α/β-D-mannopyranose (11): Compound **10** was prepared as described previously.[32] A small amount of the anomeric mixture was separated for the determination of the physical data. − **11α:** colorless oil. − TLC (petroleum ether/ethyl acetate, 7:3): R_f = 0.45. − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 2.07 (s, 3 H, $COCH_3$), 2.16 (s, 3 H, $COCH_3$), 3.67−3.99 (m, 5 H, 3-, 4-, 5-, 6-, 6′-H), 4.48−4.88 (m, 6 H, 3 CH_2Ph), 5.36 (dd, 1 H, $^3J_{1,2}$ = $^3J_{2,3}$ = 2.5 Hz, 2-H), 6.12 (d, 1 H, $^3J_{1,2}$ = 2 Hz, 1-H), 7.15−7.37 (m, 15 H, Ph). − **11β:** colorless oil. − TLC (petroleum ether/ethyl acetate, 7:3): R_f = 0.36. − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 2.09 (s, 3 H, $COCH_3$), 2.22 (s, 3 H, $COCH_3$), 3.54−3.98 (m, 5 H, 3-, 4-, 5-, 6-, 6′-H), 4.48−4.99 (m, 6 H, 3 CH_2Ph), 5.61 (dd, 1 H, $^3J_{1,2}$ = 0.99, $^3J_{2,3}$ = 2.2 Hz, 2-H), 5.74 (d, 1 H, $^3J_{1,2}$ = 0.99 Hz, 1-H), 7.11−7.38 (m, 15 H, Ph). $C_{31}H_{34}O_8$ (534.60): calcd. C 69.65, H 6.41; found C 68.76, H 6.28.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α/β-D-mannopyranose (12): A solution of compound **11** (1.96 g, 3.67 mmol) and hydrazinium acetate (0.41 g, 4.42 mmol) in dry *N*,*N*-dimethylformamide (40 mL) was heated for 2 h at 50°C under nitrogen. After cooling to room temp., water (250 mL) was added and the mixture was extracted twice with ethyl acetate. The combined organic extracts were washed with water, dried (Na_2SO_4), and concentrated in vacuo. Purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 7:3) gave oily **12** (1.15 g, 84%) as an anomeric mixture (α/β = 6.5:1). − TLC (petroleum ether/ethyl acetate, 7:3): R_f = 0.25 (**12α**); R_f = 0.17 (**12β**). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 2.14 (s, $COCH_3$), 2.19 (s, $COCH_3$), 3.42−3.78 (m), 3.99−4.09 (m), 4.45−4.86 (m, CH_2Ph, 1-H), 5.19 (br. s, 1-H), 5.35 (dd, $^3J_{1,2}$ = 1.9, $^3J_{2,3}$ = 3.2 Hz, 2-H), 5.44 (dd, $^3J_{1,2}$ = 1, $^3J_{2,3}$ = 2 Hz, 2-H). − $C_{29}H_{32}O_7$ (492.57): calcd. C 70.71, H 6.55; found C 70.03, H 6.27.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α/β-D-mannopyranosyl) Trichloroacetimidate (13):** A cooled solution of **12** (1.4 g, 2.84 mmol) in dry dichloromethane (35 mL) and trichloroacetonitrile (1.4 mL) was treated with 140 μL of DBU and stirred for 1 h at 0°C under nitrogen. The reaction mixture was diluted with dichloromethane and extracted subsequently with satd. aqueous NH_4Cl solution and water. The organic solution was dried (Na_2SO_4) and concentrated to dryness. Flash chromatography (petroleum ether/ethyl acetate, 8:2 with 1% triethylamine) gave **13** (1.69 g, 93%) as a colorless foam in a α/β ratio of 17:1. − TLC (petroleum ether/ethyl acetate, 8:2 with 1% Et_3N): R_f = 0.26. − **13α:** ^{1}H NMR (250 MHz; $CDCl_3$): δ = 2.18 (s, 3 H, $COCH_3$), 3.68−4.09 (m, 5 H), 4.47−4.89 (m, 6 H, 3 CH_2Ph), 5.50 (dd, 1 H, $^3J_{1,2}$ = $^3J_{2,3}$ = 2.3 Hz, 2-H), 6.31 (d, 1 H, $^3J_{1,2}$ = 1.9 Hz, 1-H), 7.16−7.35 (m, 15 H, Ph), 8.68 (s, 1 H, NH). − **13β:** ^{1}H NMR (250 MHz; $CDCl_3$): δ = 5.38 (dd, 1 H, $^3J_{1,2}$ = $^3J_{2,3}$ = 2.0 Hz, 2-H), 5.67 (d, 1 H, $^3J_{1,2}$ = 2.0 Hz, 1-H), 8.54 (s, 1 H, NH). − $C_{31}H_{32}Cl_3NO_7$ (636.95): calcd. C 58.46, H 5.06, N 2.20; found C 58.30, H 5.30, N 2.00.

6-*O*-*tert*-Butyldiphenylsilyl-1,2-*O*-[-1-(*R*)-methoxyethylidene]-β-D-mannopyranose (14): *tert*-Butylchlorodiphenylsilane (4 mL, 15.28 mmol) and imidazole (1.5 g, 22.62 mmol) were added to a cooled solution of crude **9** (3 g, 12.71 mmol) in dry *N*,*N*-dimethylformamide (50 mL) under nitrogen. After stirring for 24 h at 4°C, the solution was diluted with water and extracted several times with dichloromethane. The combined organic extracts were subsequently washed with satd. aqueous NH_4Cl solution, and satd. aqueous NaCl solution, dried with Na_2SO_4, and concentrated in vacuo until a white precipitate appeared. On cooling, **14** crystallized as a colorless powder which was filtered off. The mother liquor was concentrated to dryness and purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **14** as a syrup which was crystallized from diethyl ether/petroleum ether (10:1). Total yield was 3.8 g (64%); m.p. 161°C. − TLC (petroleum ether/ethyl acetate, 1:3): R_f = 0.35 − $[\alpha]_D$ = +12 (*c* = 1, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.06 (s, 9 H, *t*Bu), 1.68 (s, 3 H, CMe), 2.50 (d, 1 H, ^3J = 7.4 Hz, OH), 2.81 (d, 1 H, ^3J = 2.3 Hz, OH), 3.24−3.30 (m, 1 H), 3.31 (s, 3 H, OMe), 3.71−3.79 (m, 1 H, 5-H), 3.87−3.97 (m, 3 H), 4.50 (dd, 1 H, $^3J_{1,2}$ = 2.6, $^3J_{2,3}$ = 4.1 Hz, 2-H), 5.43 (d, 1 H, $^3J_{1,2}$ = 2.5 Hz, 1-H), 7.35−7.72 (m, 10 H, Ph). − $C_{25}H_{34}O_7Si$ (474.62): calcd. C 63.27, H 7.22; found C 63.17, H 7.20.

6-*O*-*tert*-Butyldiphenylsilyl-1,2-*O*-[1-(*R*)-methoxyethylidene]-3,4-di-*O*-trichloroacetylcarbamoyl-β-D-mannopyranose (14a): To a solution of diol **14** (10 mg) in chloroform (1 mL) trichloroacetyl isocyanate (1 drop) was added and the mixture was characterized by ^{1}H-NMR studies. − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.04 (s, 9 H, *t*Bu), 1.75 (s, 3 H, CMe), 3.31 (s, 3 H, OCH_3), 3.61−3.66 (m, 1 H, 5-H), 3.78 (dd, 1 H, $^3J_{5,6}$ = 3.3, $^3J_{6,6'}$ = 11.5 Hz, 6-H), 3.88 (dd, 1 H, $^3J_{5,6'}$ = 2.7, $^3J_{6,6'}$ = 11.5 Hz, 6′-H), 4.71 (dd, 1 H, $^3J_{1,2}$ = 2.5, $^3J_{2,3}$ = 4.0 Hz, 2-H), 5.29 (dd, 1 H, $^3J_{2,3}$ = 4.0, $^3J_{3,4}$ = 9.9 Hz, 3-H), 5.54 (d, 1 H, $^3J_{1,2}$ = 2.5 Hz, 1-H), 5.60 (dd, 1 H, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.7 Hz, 4-H), 7.29−7.71 (m, 10 H, Ph), 8.25 (s, 1 H, NH), 8.59 (s, 1 H, NH).

3,4-Di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-[1-(*R*)-methoxyethylidene]-β-D-mannopyranose (15): Sodium hydride (170 mg,

7.09 mmol) was cautiously added to a cooled solution of **14** (1.4 g, 2.95 mmol) in dry *N*,*N*-dimethylformamide (15 mL) under nitrogen. After 30 min, benzyl bromide (0.85 mL, 7.09 mmol) was added dropwise within 10 min. The solution was warmed up to room temp. and stirred overnight. The reaction mixture was diluted with methanol (1 mL) and water (150 mL) and extracted twice with ethyl acetate. The combined organic extracts were dried with Na_2SO_4, concentrated in vacuo, and flash-chromatographed (petroleum ether/ethyl acetate, 6:1) to yield **15** (1.53 g, 79%) as a colorless syrup. − TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.5. − $[\alpha]_D$ = +28 (*c* = 1, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.07 (s, 9 H, *t*Bu), 1.80 (s, 3 H, CMe), 3.24−3.30(m, 1 H, 5-H), 3.32 (s, 3 H, OCH_3), 3.75 (dd, 1 H, $^3J_{2,3}$ = 4.0, $^3J_{3,4}$ = 9.3 Hz, 3-H), 3.89 (dd, 1 H, $^3J_{5,6}$ = 1.9, $^3J_{6,6'}$ = 11.1 Hz, 6-H), 3.99 (dd, 1 H, $^3J_{5,6'}$ = 3.0, $^3J_{6,6'}$ = 11.2 Hz, 6′-H), 4.17 (dd, 1 H, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.4 Hz, 4-H), 4.40 (dd, 1 H, $^3J_{1,2}$ = 2.4, $^3J_{2,3}$ = 4.0 Hz, 2-H), 4.76−5.04 (m, 4 H, 2 CH_2Ph), 5.35 (d, 1 H, $^3J_{1,2}$ = 2.3 Hz, 1-H), 7.22−7.79 (m, 20 H, Ph). − $C_{39}H_{46}O_7Si$ (654.87): calcd. C 71.53, H 7.08; found C 71.23, H 7.13.

1,2-Di-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α/β-D-mannopyranose (16): To a mixture of acetic acid (30 mL), water (30 mL), and acetone (60 mL) **15** (1.4 g, 2.14 mmol) was added and stirred for 1 h at room temp. The clear solution was concentrated in vacuo. The residue was codistilled with toluene. The residue was dissolved in dry pyridine/acetic anhydride (1:1, 10 mL) and stirred for 7 h at room temp. Evaporation of the solvents, codistillation with toluene and flash chromatography with petroleum ether/ethyl acetate (8:2) gave **16** (1.41 g, 96%) as an anomeric mixture (α/β = 5:1). − TLC (petroleum ether/ethyl acetate, 9:1): R_f = 0.18 (**16α**), R_f = 0.10 (**16β**). − The anomeric mixture was separated by flash chromatography (petroleum ether/ethyl acetate, 9:1). − **16α:** $[\alpha]_D$ = +28 (*c* = 1, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.08 (s, 9 H, *t*Bu), 2.04 (s, 3 H, $COCH_3$), 2.16 (s, 3 H, $COCH_3$), 3.71−3.76 (m, 1 H, 5-H), 3.85−3.90 (dd, 1 H, $^3J_{5,6}$ = 1.5, $^3J_{6,6'}$ = 11.4 Hz, 6-H), 3.98−4.08 (m, 2 H, 6′-, 3-H), 4.23 (dd, 1 H, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.7 Hz, 4-H), 4.56−4.98 (m, 4 H, 2 CH_2Ph), 5.37 (dd, 1 H, $^3J_{1,2}$ = 2.2, $^3J_{2,3}$ = 3.1 Hz, 2-H), 6.15 (d, 1 H, $^3J_{1,2}$ = 2.0 Hz, 1-H), 7.18−7.77 (m, 20 H, Ph). − $C_{40}H_{46}O_8Si$ (682.88): calcd. C 70.35, H 6.79; found C 69.57, H 6.63.

2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α/β-D-mannopyranose (17): A solution of compound **16** (1.39 g, 2.09 mmol) and hydrazinium acetate (0.23 g, 1.50 mmol) in dry *N*,*N*-dimethylformamide (30 mL) was heated for 4 h at 50°C under nitrogen. After cooling to room temp., water (200 mL) was added and the mixture was extracted twice with ethyl acetate. The combined organic extracts were washed with water, dried (Na_2SO_4), and concentrated in vacuo. Purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 8:2) gave **17** (1.01 g, 77%, colorless foam) as an anomeric mixture (α/β = 12:1). − TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.25 (**17α**); R_f = 0.15 (**17β**). − **17α:** ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.08 (s, 9 H, *t*Bu), 2.14 (s, 3 H, $COCH_3$), 2.68 (d, 1 H, ^3J = 3.6 Hz, OH), 3.83−4.16 (m, 5 H), 4.55−4.96 (m, 4 H, 2 CH_2Ph), 5.22 (dd, 1 H, $^3J_{1,2}$ = 1.9, $^3J_{1,OH}$ = 3.5 Hz, 1-H), 5.37 (dd, 1 H, $^3J_{1,2}$ = 2.1, $^3J_{2,3}$ = 2.5 Hz, 2-H), 7.18−7.75 (m, 20 H, Ph). − $C_{38}H_{44}O_7Si$ (640.85): calcd. C 71.22, H 6.92; found C 71.01, H 6.86.

***O*-(2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α/β-D-mannopyranosyl) Trichloroacetimidate (18):** A cooled solution of **17** (0.25 g, 0.382 mmol) in dry dichloromethane (5 mL) and trichloroacetonitrile (0.15 mL) was treated with 10 μL of DBU and stirred for 1 h at 0°C under nitrogen. The reaction mixture was diluted with dichloromethane and extracted subsequently with satd. aqueous NH_4Cl solution and water. The organic solution was dried (Na_2SO_4) and concentrated in vacuo. Flash chromatography (petroleum ether/ethyl acetate, 9:1 with 1% triethylamine) gave **18** (0.27 g, 89%) as a colorless foam in a α/β ratio of 12:1. − TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.54. − **18α:** ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.08 (s, 9 H, *t*Bu), 2.19 (s, 3 H, $COCH_3$), 3.88−4.10 (m, 4 H), 4.24 (dd, 1 H, $^3J_{3,4}$ = $^3J_{4,5}$ = 9.7 Hz, 4-H), 4.58−4.97 (m, 4 H, 2 CH_2Ph), 5.50 (dd, 1 H, $^3J_{1,2}$ = $^3J_{2,3}$ = 3.1 Hz, 2-H), 6.33 (d, 1 H, $^3J_{1,2}$ = 1.9 Hz, 1-H), 7.18−7.75 (m, 20 H, Ph), 8.65 (s, 1 H, NH). − **18β:** ^{1}H NMR (250 MHz; $CDCl_3$): δ = 5.37 (dd, 1 H, 2-H), 5.57 (d, 1 H, 1-H), 8.28 (s, 1 H, NH). − $C_{40}H_{44}C_{13}NO_7Si$ (785.23): calcd. C 61.18, H 5.65, N 1.78; found C 61.03, H 5.71, N 1.77.

Allyl 2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (19): To a mixture of trichloroacetimidate **18** (16.0 g, 20.4 mmol), powdered molecular sieves (3 Å), and dry allyl alcohol (4 mL, 58.7 mmol) in dry diethyl ether (200 mL) was added TMSOTf (0.5 mL, 2.7 mmol) under nitrogen. After stirring for 15 min at room temp., triethylamine was added and the solvent was evaporated in vacuo. Flash chromatography (petroleum ether/ethyl acetate, 8:2) of the residue gave **19** (13.0 g, 94%) as a colorless syrup. − TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.65, $[\alpha]_D$ = +31 (*c* = 1, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.08 [s, 9 H, $C(CH_3)_3$], 2.14 (s, 3 H, $COCH_3$), 3.69−3.79 (m, 1 H, 5-H), 3.87−4.18 (m, 6 H), 4.54−4.76 (m, 3 H, 1.5 CH_2Ph), 4.89 (d, $^3J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.92 (d, J_{gem} = 10.8 Hz, 1 H, 0.5 CH_2Ph), 5.14−5.28 (m, 2 H, $CH_2CH{=}CH_2$), 5.40 (dd, $^3J_{1,2}$ = 1.8, $^3J_{2,3}$ = 2.6 Hz, 1 H, 2-H), 5.78−5.92 (m, 1 H, $CH_2CH{=}CH_2$), 7.16−7.44 (m, 16 H, 2 Ph, m, *p*-Ph_2Si), 7.69−7.77 (m, 4 H, *o*-Ph_2Si). − $C_{41}H_{48}O_7Si$ (680.91): calcd. C 72.32, H 7.11; found C 71.91, H 7.15.

Allyl 3,4-Di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (20): To a solution of **19** (10 g, 14.7 mmol) in dry methanol (150 mL) satd. sodium methoxide solution in methanol (0.5 mL) was added. After stirring for 6 h at room temp., the solution was neutralized with Amberlite IR 120 (H^+). Evaporation of the solvent in vacuo and flash chromatography with petroleum ether/ethyl acetate (6:1) gave **20** (9 g, 95%) as a colorless foam.− TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.40, $[\alpha]_D$ = +28 (*c* = 2, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.06 [s, 9 H, $C(CH_3)_3$], 2.44 (d, $^3J_{2,OH}$ = 2.2 Hz, 1 H, OH), 3.72−4.22 (m, 8 H), 4.56 (d, J_{gem} = 10.7 Hz, 1 H, 0.5 CH_2Ph), 4.71 (s, 2 H, CH_2Ph), 4.85 (d, J_{gem} = 10.7 Hz, 1 H, 0.5 CH_2Ph), 4.96 (s, 1 H, 1-H), 5.16−5.29 (m, 2 H, $CH_2CH{=}CH_2$), 5.80−5.93 (m, 1 H, $CH_2CH{=}CH_2$), 7.14−7.42 (m, 16 H, 2 Ph, m, *p*-Ph_2Si), 7.69−7.75 (m, 4 H, *o*-Ph_2Si). − $C_{39}H_{46}O_6Si$ (638.87): calcd. C 73.32, H 7.26; found C 73.28, H 7.29.

Allyl 2-*O*-Allyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (21): Sodium hydride (0.4 g, 16.6 mmol) was cautiously added to a cooled solution of **20** (8.5 g, 13.3 mmol) in dry *N*,*N*-dimethylformamide (75 mL) under nitrogen. After 30 min, allyl bromide (3.52 mL, 26.6 mmol) was added dropwise within 15 min. The solution was warmed up to room temp. and then stirred for 2 h. After concentration in vacuo (0.1 bar), water was added, and the mixture was extracted twice with ethyl acetate. The combined organic extracts were dried with Na_2SO_4, concentrated in vacuo, and flash-chromatographed (petroleum ether/ethyl acetate, 9:1) to give **21** (8.1 g, 90%) as a colorless syrup. − TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.67. − $[\alpha]_D$ = +31 (*c* = 4, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.06 [s, 9 H, $C(CH_3)_3$] 3.68−3.74 (m, 1 H, 5-H), 3.44 (br. s, 1 H), 3.91−3.99 (m, 5 H), 4.11−4.28 (m, 3 H), 4.54 (d, J_{gem} = 10.7 Hz, 1 H, 0.5 CH_2Ph),

4.71 (s, 2 H, CH_2Ph), 4.90 (d, J_{gem} = 10.7 Hz, 1 H, 0.5 CH_2Ph), 4.92 (br. s, 1 H, 1-H), 5.13−5.35 (m, 4 H, 2 $CH_2CH{=}CH_2$), 5.80−6.03 (m, 2 H, 2 $CH_2CH{=}CH_2$), 7.12−7.43 (m, 16 H, 2 Ph, m, *p*-Ph_2Si), 7.69−7.76 (m, 4 H, *o*-Ph_2Si). − $C_{42}H_{50}O_6Si$ (678.94): calcd. C 74.30, H 7.42; found C 74.22, H 7.57.

Allyl 2-*O*-Allyl-3,4-di-*O*-benzyl-α-D-mannopyranoside (22): A solution of **21** (13 g, 19.1 mmol) in dry tetrahydrofuran was treated with tetrabutylammonium fluoride (1.1 M solution in THF, 40 mL, 44 mmol) and dry acetic acid (2.5 mL) at 0°C under nitrogen. Stirring was continued for 4 d at room temp. After addition of satd. aqueous $NaHC_3$ solution and water, the mixture was extracted twice with dichloromethane. The combined organic extracts were dried ($MGSO_4$) and concentrated in vacuo. Purification of the crude product by flash chromatography with petroleum ether/ethyl acetate (7:3) gave 7.74 g (92%) of **22** as a colorless oil. − TLC (petroleum ether/ethyl acetate, 7:3): R_f = 0.16. − $[\alpha]_D$ = +47 (*c* = 1, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 2.39 (br. s, 1 H, OH), 3.62−3.97 (m, 7 H), 4.09−4.26 (m, 3 H), 4.63 (d, J_{gem} = 10.8 Hz, 1 H, 0.5 CH_2Ph), 4.70 (s, 2 H, CH_2Ph), 4.86 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1-H), 4.92 (d, J_{gem} = 10.8 Hz, 1 H, 0.5 CH_2Ph), 5.14−5.32 (m, 4 H, 2 $CH_2CH{=}CH_2$), 5.77−5.99 (m, 2 H, 2 $CH_2CH{=}CH_2$), 7.21−7.39 (m, 10 H, 2 Ph). − $C_{26}H_{32}O_6$ (440.54): calcd. C 70.89, H 7.32; found C 70.78, H 7.38.

Allyl 2-*O*-Allyl-3,4-di-*O*-benzyl-6-*O*-trichloroacetylcarbamoyl-α-D-mannopyranoside (22a): To a solution of **22** (10 mg) in [D]chloroform (1 mL) trichloroacetyl isocyanide (1 drop) was added and the reaction mixture was characterized by ^{1}H-NMR studies. − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 3.77−4.01 (m, 5 H), 4.12−4.20 (m, 3 H), 4.47 (m, 2 H, 6-, 6′-H), 4.61 (d, J_{gem} = 11.0 Hz, 1 H, 0.5 CH_2Ph), 4.67 (d, J_{gem} = 11.6 Hz, 1 H, 0.5 CH_2Ph), 4.73 (d, J_{gem} = 11.6 Hz, 1 H, 0.5 CH_2Ph), 4.88 (d, $^3J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.94 (d, J_{gem} = 11.0 Hz, 1 H, 0.5 CH_2Ph), 5.17−5.33 (m, 4 H, 2 $CH_2CH{=}CH_2$), 5.79−6.00 (m, 2 H, 2 $CH_2CH{=}CH_2$), 7.27−7.41 (m, 10 H, 2 Ph), 8.38 (s, 11 H, NH).

Allyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranoside (23): To a mixture of **13** (14.3 g, 22.5 mmol), **22** (7.9 g, 17.9 mmol) and powdered molecular sieves (3 Å) in dry diethyl ether (200 mL) TMSOTf (0.4 mL, 2.21 mmol) was added under nitrogen. After stirring for 20 min at room temp., triethylamine was added and the solvent was evaporated in vacuo. The residue was redissolved in toluene/petroleum ether (1:1) and on cooling trichloroacetamide crystallized as a white powder which was filtered off. Concentration in vacuo and flash chromatography (petroleum ether/ethyl acetate, 9:1 → 8:2) gave **23** (14.2 g, 86%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.28. − $[\alpha]_D$ = +50 (*c* = 1, methanol). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 2.13 (s, 3 H, $COCH_3$), 3.56−4.00 (m, 12 H), 4.07−4.18 (m, 3 H), 4.40−4.74 (m, 8 H, 4 CH_2Ph), 4.83−4.94 (m, 2 H, CH_2Ph), 4.86 (d, $^3J_{1a,2a}$ = 1.8 Hz, 1 H, 1a-H), 4.95 (d, $^3J_{1b,2b}$ = 1.7 Hz, 1 H, 1b-H), 5.13−5.34 (m, 4 H, 2 $CH_2CH{=}CH_2$), 5.47(dd, $^3J_{1b,2b}$ = 1.9, $^3J_{2b,3b}$ = 2.9 Hz, 1 H, 2b-H), 5.77−6.00 (m, 2 H, 2 $CH_2CH{=}CH_2$), 7.09−7.40 (m, 25 H, 5 Ph). − $C_{55}H_{62}O_{12}$ (915.09): calcd. C 72.41, H 6.63; found C 71.84, H 6.73.

Allyl 2-*O*-Allyl-3,4-di-*O*-benzyl-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-α-D-mannopyranoside (24): To a solution of **23** (12.5 g, 13.7 mmol) in dry methanol (150 mL) satd. sodium methoxide solution in methanol (0.5 mL) was added. After stirring overnight at room temp., the solution was neutralized with Amberlite IR 120 (H^+). Evaporation of the solvent in vacuo and flash chromatography with petroleum ether/ethyl acetate (7:3) gave **24** (11.3 g, 94%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 7:3): R_f = 0.14. − $[\alpha]_D$ = +59 (*c* = 0.5, methanol). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 2.39 (d, $^3J_{2d,OH}$ = 2.6 Hz, 1 H, OH), 3.55−3.95 (m, 13 H), 4.07−4.19 (m, 3 H), 4.45−4.84 (m, 9 H, 4.5 CH_2Ph), 4.85 (d, $^3J_{1c,2c}$ = 1.6 Hz, 1 H, 1c-H), 4.92 (d, J_{gem} = 11.1 Hz, 1 H, 0.5 CH_2Ph), 5.04 (d, $^3J_{1d,2d}$ = 1.5 Hz, 1 H, 1d-H), 5.13−5.33 (m, 4 H, 2 $CH_2CH{=}CH_2$), 5.77−6.00 (m, 2 H, 2 $CH_2CH{=}CH_2$), 7.12−7.39 (m, 25 H, 5 Ph). − $C_{53}H_{60}O_{11}$ (873.05): calcd. C 72.91, H 6.93; found C 72.71, H 6.99.

Allyl *O*-(2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranoside (25): To a mixture of **24** (10.9 g, 12.2 mmol), **18** (12.6 g, 16.0 mmol), and powdered molecular sieves (3 Å) in dry diethyl ether (200 mL) TMSOTf (0.4 mL, 2.2 mmol) was added under nitrogen. After stirring for 20 min at room temp., solid $NaHCO_3$ was added and stirring was continued for 15 min. The solvent was evaporated in vacuo and the residue was purified by MPLC (toluene/ethyl acetate, 20:1) to yield **25** (17.2 g, 92%) as a colorless foam. − TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.51. − $[\alpha]_D$ = +34 (*c* = 2, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.07 [s, 9 H, $C(CH_3)_3$], 2.12 (s, 3 H, $COCH_3$), 3.49−3.94 (m, 14 H), 4.03−4.19 (m, 7 H), 4.36−4.74 (m, 11 H, 5.5 CH_2Ph), 4.78 (d, $^3J_{1c,2c}$ = 1.2 Hz, 1 H, 1c-H), 4.82−4.95 (m, 3 H, 1.5 CH_2Ph), 4.86 (br. s, 1 H, 1d-H), 5.07−5.29 (m, 4 H, 2 $CH_2CH{=}CH_2$), 5.22 (br. s, 1 H, 1e-H), 5.53 (br. t, 1 H, 2e-H), 5.71−5.92 (m, 2 H, 2 $CH_2CH{=}CH_2$), 7.10−7.42 (m, 41 H, 7 Ph, *m*,*p*-Ph_2Si), 7.66−7.75 (m, 4 H, *o*-Ph_2Si). − $C_{91}H_{102}O_{17}Si$ (1495.88): calcd. C 73.07, H 6.87; found C 72.36, H 6.96.

Allyl 2-*O*-Allyl-3,4-di-*O*-benzyl-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-α-D-mannopyranoside (26): To a solution of **25** (17.0 g, 11.5 mmol) in dry methanol/diethyl ether (300 mL, 5:1) satd. sodium methoxide solution in methanol (0.5 mL) was added. After stirring for 5 h at room temp., the solution was neutralized with Amberlite IR 120 (H^+). Evaporation of the solvents in vacuo and flash chromatography with petroleum ether/ethyl acetate (8:2) gave **26** (15.6 g, 94%) as a colorless foam. − TLC (petroleum ether/ethyl acetate, 8:2): R_f = 0.33. − $[\alpha]_D$ = +41 (*c* = 0.5, methanol). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.05 [s, 9 H, $C(CH_3)_3$], 2.34 (d, $^3J_{2e,OH}$ = 3.0 Hz, 1 H, OH), 3.48−4.20 (m, 22 H), 4.36−4.74 (m, 11 H, 5.5 CH_2Ph), 4.78−4.89 (m, 5 H, 1.5 CH_2Ph, 1c-, 1d-H), 5.07−5.30 (m, 5 H, 4 $CH_2CH{=}CH_2$, 1e-H), 5.70−5.97 (m, 2 H, 2 $CH_2CH{=}CH_2$), 7.13−7.39 (m, 41 H, 7 Ph, *m*,*p*-Ph_2Si), 7.67−7.75 (m, 4 H, *o*-Ph_2Si). − $C_{89}H_{100}O_{16}Si$ (1453.84): calcd. C 73.53, H 6.93; found C 73.51, H 6.93.

Allyl *O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2-*O*-allyl-3,4-di-*O*-benzyl-α-D-mannopyranoside (27): To a mixture of **13** (7.7 g, 12.09 mmol), **26** (14.5 g, 9.97 mmol), and powdered molecular sieves (3 Å) in dry diethyl ether (175 mL) was added TMSOTf (40 mL, 0.22 mmol) under nitrogen. After stirring for 15 min at room temp., triethylamine was added in order to neutralize the reaction mixture. The solvent was evaporated in vacuo and the residue was filtered through silica gel (petroleum ether/ethyl acetate, 6:1). Purification of the crude product by MPLC with toluene/ethyl acetate (25:1) gave **27** (17.5 g, 91% as a colorless foam. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.49. − $[\alpha]_D$ = +31 (*c* = 0.5, methanol). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.03 [s, 9 H, $C(CH_3)_3$], 2.12 (s, 3 H, $COCH_3$), 3.47−3.68 (m, 7 H), 3.72 (dd, $^3J_{1c,2c}$ = $^3J_{2c,3c}$ = 2.0 Hz, 1 H, 2c-H), 3.74−4.10 (m, 17 H), 4.13 (br. t, 1 H, 2e-H), 4.16 (br. t, 1 H, 2d-H), 4.27−4.70 (m, 16 H, 8

CH_2Ph), 4.76 (d, $^3J_{1c,2c}$ = 1.5 Hz, 1 H, 1c-H), 4.79−4.93 (m, 4 H, 2 CH_2Ph), 4.84 (br. s, 1 H, 1d-H), 5.05−5.27 (m, 4 H, 2 CH_2CH=CH_2), 5.10 (br. s, 1 H, 1f-H), 5.36 (br. s, 1 H, 1e-H), 5.58 (dd, $^3J_{1f,2f}$ = $^3J_{2f,3f}$ = 1.8 Hz, 1 H, 2f-H), 5.71−5.92 (m, 2 H, 2 CH_2CH=CH_2), 7.03−7.36 (m, 56 H, 10 Ph, *m*,*p*-Ph_2Si), 7.66−7.77(m, 4 H, *o*-Ph_2Si). − FAB MS (positive ion mode, matrix: NBOH with NaI): *m*/*z* = 1951 [M + Na^+]. − $C_{118}H_{130}O_{22}Si$ (1928.40): calcd. C 73.50, H 6.79; found C 73.52, H 6.80.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-3,4-di-*O*-benzyl-α/β-D-mannopyranose (28):** A solution of **27** (6.0 g, 3.11 mmol) in a mixture of toluene (25 mL), ethanol (13 mL) and water (1.2 mL) was heated to 95°C. Then Wilkinson′s catalyst (0.5 g, 0.54 mmol) was added and the red solution was stirred under reflux for 5 h. The reaction was monitored by TLC and color. After cooling, the yellow reaction mixture was concentrated in vacuo. The residue was redissolved in toluene/ethanol (5:1) and again concentrated in vacuo. Flash chromatography of the syrup (toluene/ethyl acetate, 9:1 → 5:1) gave **28** (4.3 g, 75%) as an anomeric mixture (α:β = 4:1). − TLC (toluene/ethyl acetate, 10:1): R_f = 0.08. − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.09 [s, 9 H, $C(CH_3)_3$], 2.12 (s, 3 H, $COCH_3$), 2.26 (d, ^3J = 1.3 Hz, 1 H, OH), 2.65 (d, ^3J = 2.5 Hz, 0.5 H, OH), 3.46−4.17 (m, 28 H), 4.26−4.68 (m, 16 H, 8 CH_2Ph), 4.74−4.98 (m, 6 H, 2 CH_2Ph, 1c-, 1d-H), 5.11 (s, 1 H, 1f-H), 5.32 (s, 0.8 H, 1e-H), 5.38 (s, 0.2 H, 1e-H), 5.58 (br. t, 1 H, 2f-H), 7.08−7.34 (m, 56 H, 10 Ph, *m*,*p*-Ph_2Si), 7.67−7.77 (m, 4 H, *o*-Ph_2Si). − $C_{112}H_{122}O_{22}Si$ (1848.7): calcd. C 72.78, H 6.65; found C 72.68, H 6.66.

Acetyl-2-*O*-acetyl-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-3,4-di-*O*-benzyl-α,β-D-mannopyranose (29): A solution of **28** (3.8 g, 2.06 mmol) in dry pyridine/acetic anhydride (1:1, 30 mL) was stirred overnight at room temp. When the reaction was completed, the solution was concentrated in vacuo, codistilled with toluene, and flash-chromatographed on silica gel (toluene/ethyl acetate, 15:1) to gave **29** (3.8 g, 96%, α:β = 3.5:1) as a colorless foam. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.38. − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.03 [s, 9 H, $C(CH_3)_3$], 1.93−2.12 (several s, 9 H, 3 $COCH_3$), 3.43−4.16 (m, 22 H), 4.28−4.73 (m, 16 H, 8 CH_2Ph), 4.77−4.92 (m, 5 H, 2 CH_2Ph, 1d-H), 5.09 (d, $^3J_{1f,2f}$ = 1.5 Hz, 1 H, 1f-H), 5.33−5.35 (m, 2 H, 2c-, 1e-H), 5.57 (br. t, 1 H, 2f-H), 5.70 (s, 0.2 H, β-1c-H), 6.01 (d, $^3J_{1c,2c}$ = 2.0 Hz, 0.8 H, α-1c-H), 7.00−7.38 (m, 56 H, 10 Ph, *m*,*p*-Ph_2Si), 7.66−7.76 (m, 4 H, *o*-Ph_2Si). − $C_{116}H_{126}O_{24}Si$ (1932.34): calcd. C 72.10, H 6.57; found C 71.93, H 6.59.

2-*O*-Acetyl-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-3,4-di-*O*-benzyl-α/β-D-mannopyranose (30): A solution of **29** (0.8 g, 0.41 mmol) in *N*,*N*-dimethylformamide (8 mL) was treated with ammonium carbonate (1 g) at 40°C. The reaction was monitored by TLC. After 4 d the mixture was concentrated in vacuo (0.1 bar), and flash-chromatographed on silica gel (toluene/ethyl acetate, 13:1) to yield **30** (0.67 g, 86%) as an anomeric mixture (α/β = 6:1). − TLC (petroleum ether/ethyl acetate, 7:3): R_f = 0.45 (**30α**) and R_f = 0.28 (**30β**). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.09 [s, 9 H, $C(CH_3)_3$], 2.03−2.12 (several s, 6 H, 2 $COCH_3$), 3.36−4.02 (m, 21 H), 4.10−4.12 (m, 2 H, 2e-, 2d-H), 4.25−4.74 (m, 17 H, 8.5 CH_2Ph), 4.80−4.91 (m, 5 H, 1.5 CH_2Ph, 1c-, 1d-H), 5.09 (d, $^3J_{1f,2f}$ = 1.5 Hz, 1 H, 1f-H), 5.25 (dd, $^3J_{1c,2c}$ < 1, $^3J_{2c,3c}$ = 2.8 Hz, 1 H, 2c-H), 5.30 (d, $^3J_{1e,2e}$ < 1 Hz, 1 H, 1e-H), 5.56 (dd, $^3J_{1f,2f}$ = 1.8, $^3J_{2f,3f}$ = 2.9 Hz, 1 H, 2f-H), 7.08−7.37 (m, 56 H, 10 Ph, *m*,*p*-Ph_2Si), 7.67−7.76 (m, 4 H, *o*-Ph_2Si). − $C_{114}H_{124}O_{23}Si$ (1890.31): calcd. C 72.44, H 6.61; found C 72.11, H 6.57.

***O*-[2-*O*-Acetyl-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-3,4-di-*O*-benzyl-α-D-mannopyranosyl] Trichloroacetimidate (4):** A solution of **30** (4.0 g, 2.12 mmol) in dry dichloromethane (30 mL) and trichloroacetonitrile (4 mL) was treated with DBU (1−2 drops) and stirred for 1.5 h at room temp. The solvents were evaporated in vacuo, and the residue was purified by flash chromatography (toluene/ethyl acetate, 20:1 with 1% triethylamine) to yield **4** (3.97 g, 92%) as a colorless foam. − TLC (petroleum ether/ethyl acetate, 5:1, with 1% triethylamine): R_f = 0.19. − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.03 [s, 9 H, $C(CH_3)_3$], 2.03 (s, 3 H, $COCH_3$), 2.12 (s, 3 H, $COCH_3$), 3.55−4.12 (m, 22 H), 4.27−4.93 (m, 20 H, 10 CH_2Ph), 4.85 (br. s, 1 H, 1d-H), 5.09 (d, $^3J_{1f,2f}$ < 1 Hz, 1 H, 1f-H), 5.37 (d, $^3J_{1e,2e}$ < 1 Hz, 1 H, 1e-H), 5.48 (dd, $^3J_{1c,2c}$ = 1.9, $^3J_{2c,3c}$ = 2.9 Hz, 1 H, 2c-H), 5.58 (br. t, 1 H, 2f-H), 6.14 (d, $^3J_{1c,2c}$ = 1.4 Hz, 1 H, 1c-H), 7.08−7.35 (m, 56 H, 10 Ph, *m*,*p*-Ph_2Si), 7.67−7.77 (m, 4 H, *o*-Ph_2Si), 8.63 (s, 1 H, NH). − $C_{116}H_{124}Cl_3NO_{23}Si$ (2034.69): calcd. C 68.48, H 6.14, N 0.69; found C 68.80, H 6.09, N 0.77.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-(1*R*)-menthyloxycarbonyl-D-*myo*-inositol (31):** To a mixture of **3** (444 mg, 0.491 mmol), **4** (1.19 g, 0.585 mmol), and powdered molecular sieves (3 Å) in dry diethyl ether (15 mL) a solution of TMSOTf in dry diethyl ether (17 μL, 0.094 mmol TMSOTf in 0.1 mL dry diethyl ether) was added under nitrogen. After stirring for 30 min at room temp., solid $NaHCO_3$ was added and stirring was continued for 15 min. The solvent was evaporated in vacuo and the residue was filtered through silica gel with the mixed solvent toluene/ethyl acetate (20:1). MPLC (toluene/ethyl acetate, 25:1) of the crude mixture yielded **31** (1.24 g, 91%) as a colorless oil which was lyophilized from dioxane. − TLC (toluene/ethyl acetate, 20:1): R_f = 0.48. − $[\alpha]_D$ = +41 (*c* = 1, chloroform). − ^{1}H NMR (600 MHz; $CDCl_3$): δ = 0.75−0.77 (d, ^3J = 6.9 Hz, 3 H, CH_3), 0.83−0.88 (2 d, m, 7 H, 2 CH_3, H_{Mnt}), 0.96−1.07 [s, m, 11 H, $C(CH_3)_3$, 2 H_{Mnt}], 1.25−1.75 (m, 24 H, 20 $H_{cycloh.}$, 4 H_{Mnt}), 1.85 (s, 3 H, $COCH_3$), 1.90−2.05 (m, 2 H, 2 H_{Mnt}), 2.11 (s, 3 H, $COCH_3$), 6.92−7.37 (m, 64 H, 11 Ph, *m*,*p*-Ph_2Si, *m*,*p*-COPh), 7.67−7.75 (m, 4 H, *o*-Ph_2Si), 7.91−7.93 (m, 2 H, *o*-COPh). Signal assignment based on DQF-COSY and HMQC, connection of the sugar moieties based on HMBC experiments: ^{1}H NMR (600 MHz): δ = 3.28 (6c-H), 3.30 (6d-H), 3.31 (2b-H), 3.40 (dd, 6d′-H), 3.50 (5d-H), 3.51 (6f-H), 3.60 (dd, $^3J_{4a,5a}$ = 10.8, $^3J_{5a,\ 6a}$ = 9.0 Hz, 5a-H), 3.66 (6f′-H), 3.69 (5e-H), 3.73 (dd, $^3J_{3c,4c}$ = $^3J_{4c,5c}$ = 9.3 Hz, 4c-H), 3.78 (4d-H), 3.79 (5c-H), 3.84 (3d-H), 3.84 (6e-H), 3.85 (6c′-H), 3.86 (4b-H), 3.88 (5f-H), 3.91 (3c-H), 3.94 (3e-H), 3.94 (4f-H), 3.98 (4a-H), 4.00 (3f-H), 4.00 (6e′-H), 4.01 (3b-H), 4.11 (dd, $^3J_{1a,6a}$ = 3.2, $^3J_{5a,6a}$ = 9.0 Hz, 6a-H), 4.12 (2e-H), 4.15 (4e-H), 4.17 (2d-H), 4.19 (5b-H), 4.33 (6b-H), 4.40 (3a-H), 4.58 (dd, $^3J_{1a,2a}$ = 3.2, $^3J_{2a,3a}$ = 7.5 Hz, 2a-H), 4.61 (1d-H), 4.64 (6b′-H), 4.97 (dd, $^3J_{1a,2a}$ = $^3J_{1a,6a}$ = 3.2 Hz, 1a-H), 5.09 (s, 1f-H), 5.30 (d, $^3J_{1b,2b}$ = 3.5 Hz, 1b-H), 5.36 (s, 1e-H), 5.42 (s, 1c-H), 5.53 (2c-H), 5.58 (2f-H). − ^{13}C NMR (150.9 MHz): δ = 62.94 (C-6e), 63.13 (C-2b), 63.33 (C-6b), 65.68 (C-6c),

68.44 (C-6f), 68.58 (C-2c), 68.71 (C-2f), 68.71 (C-5b), 68.71 (C-6d), 71.75 (C-5c), 71.89 (C-5f), 72.00 (C-5d), 72.40 (C-2d), 73.14 (C-4c), 73.14 (C-5e), 74.04 (C-4f), 74.14 (C-4e), 74.32 (C-4d), 74.97 (C-2e), 75.54 (C-4b),76.14 (C-3a), 76.36 (C-1a), 76.36 (C-5a), 76.55 (C-6a), 77.11 (C-4a), 78.64 (C-3f), 78.68 (C-3c), 79.51 (C-3d), 79.64 (C-3e), 80.32 (C-3b), 96.25 (C-1b), 98.69 (C-1d), 99.30 (C-1c), 99.82 (C-1f), 99.90 (C-1e), 154.15 (OCOO), 165.84 (OCOPh), 169.72 (OCOMe), 170.06 (OCOMe). − PD MS (positive-ion mode; matrix: nitrocellulose with NaI): *m*/*z* = 2801 [M + Na^+]. − $C_{163}H_{187}N_3O_{35}Si$ (2776.35): calcd. C 70.52, H 6.79, N 1.51; found C 70.40, H 6.78, N 1.90.

***O*-(3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(3,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-(1*R*)-menthyloxycarbonyl-D-*myo*-inositol (33) and *O*-(3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-manno-pyranosyl)-(1→6)-*O*-(3,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-(1*R*)-menthyloxycarbonyl-D-*myo*-inositol (32):** A suspension of **31** (2.4 g, 0.864 mmol) and KCN (0.9 g) in dry diethyl ether/methanol (30 mL, 1:1) was vigorously stirred at 35°C. The progress of the reaction was monitored by TLC (toluene/ethyl acetate, 3:1). After 36 h, the reaction mixture, containing about 50% triol **32** (R_f = 0.56) and about 50% diol **33** (R_f = 0.63), was concentrated in vacuo, and the residue was chromatographed on silica gel (toluene/ethyl acetate, 10:1). The crude mixture was purified by MPLC (toluene/ethyl acetate, 7:1) in order to remove diol **33** (0.97 g, 45%) to yield triol **32** (1.05 g, 47%) as a colorless oil which was lyophilized from dioxane. − **33**: $[\alpha]_D$ = +43 (*c* = 1, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 0.67−0.70 (d, ^3J = 6.9 Hz, 3 H, CH_3), 0.76−1.02 [m, 18 H, 2 CH_3, $C(CH_3)_3$, 3 H_{Mnt}], 1.19−1.71 (m, 24 H, 20 $H_{cycloh.}$, 4 H_{Mnt}), 1.81−2.03 (m, 3 H, 2 H_{Mnt}, OH), 2.37 (m, 1 H, OH), 3.20−3.29 (m, 3 H), 3.35−4.91 (m), 5.15 (s, 1 H, 1-H), 5.21−5.23 (m, 2 H, 1-, 1b-H), 5.34 (m, 1 H, 1-H), 6.87−7.32 (m, 64 H, 11 Ph, *m*,*p*-Ph_2Si, *m*,*p*-COPh), 7.59−7.69 (m, 4 H, *o*-Ph_2Si) 7.83−7.87 (m, 2 H, *o*-COPh). − **32**: $[\alpha]_D$ = +36 (*c* = 1, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 0.76−0.79 (d, ^3J = 6.9 Hz, 3 H, CH_3), 0.81−1.14 [m, 18 H, 2 CH_3, $C(CH_3)_3$, 3 H_{Mnt}], 1.28−1.78 (m, 24 H, 20 $H_{cycloh.}$, 4 H_{Mnt}), 1.88−2.16 (m, 3 H, 2 H_{Mnt}, OH), 2.39−2.44 (m, 2 H, 2 OH), 3.23 (dd, $^3J_{1b,2b}$ = 3.6 Hz, $^3J_{2b,3b}$ = 9.7 Hz, 1 H, 2b-H), 3.42−4.21 (m, 32 H), 4.27−4.92 (m, 26 H, 11 CH_2Ph, 3a-, 2a-, 1d-H, H_{Mnt}), 4.97 (dd, $^3J_{1a,2a}$ = $^3J_{6a,1a}$ = 3.2 Hz, 1 H, 1a-H), 5.14 (d, $^3J_{1b,2b}$ = 3.6 Hz, 1 H, 1b-H), 5.20−5.22 (m, 2 H, 2 1-H), 5.39 (br. s, 1 H, 1-H), 7.01−7.39 (m, 61 H, 11 Ph, *m*,*p*-Ph_2Si), 7.67−7.77 (m, 4 H, *o*-Ph_2Si). − **33**: $C_{159}H_{183}N_3O_{33}Si$ (2692.28): calcd. C 70.93, H 6.85, N 1.56; found C 70.38, H 6.86, N 1.50. − **32**: $C_{152}H_{179}N_3O_{32}Si$ (2588.17): calcd. C 70.54, H 6.97, N 1.62; found C 70.38, H 6.94, N 2.01.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-(1*R*)-menthyloxycarbonyl-D-*myo*-inositol (34):** Sodium hydride (90 mg, 3.75 mmol) was cautiously added to a cooled solution of **32** (1.13 g, 0.437 mmol) in dry *N*,*N*-dimethylformamide (7.5 mL) under nitrogen. After 30 min, benzyl bromide (1.2 mL, 10.11 mmol) was added dropwise within 10 min. The solution was warmed up to room temp. and stirred until TLC (toluene/ethyl acetate, 20:1) showed complete turnover. After about 24 h, ethyl acetate was added in order to destroy excess of NaH. The solvents were evaporated in vacuo (0.1 bar) and the residue was purified by MPLC (petroleum ether/ethyl acetate, 5:1) to give **34** (1.07 g, 86%) as a colorless foam, which was lyophilized from dioxane. − TLC (toluene/ethyl acetate, 20:1): R_f = 0.48. − $[\alpha]_D$ = +28 (*c* = 1, chloroform). − ^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.76−0.78 (d, ^3J = 6.6 Hz, 3 H, CH_3), 0.84−1.12 [m, 18 H, 2 CH_3, $C(CH_3)_3$, 3 H_{Mnt}], 1.20−1.80 (m, 24 H, 20 $H_{cycloh.}$, 4 H_{Mnt}), 1.91−2.13 (m, 2 H, 2 H_{Mnt}), 3.27 (dd, $^3J_{1b,2b}$ = 3.6 Hz, $^3J_{2b,3b}$ = 10.2 Hz, 1 H, 2b-H), 3.31−3.39 (m, 2 H, 2 6-H), 3.45−4.01 (m, 25 H), 4.04−4.13 (m, 4 H, 6a-, 2d-H), 4.18−4.67 (m, 26 H, 11 CH_2Ph, 3a-, 2a-, 2-H, H_{Mnt}), 4.77 (s, 1 H, 1d-H), 4.77−4.92 (m, 6 H, 3 CH_2Ph), 4.99 (dd, $^3J_{1a,2a}$ = $^3J_{6a,1a}$ = 3.3 Hz, 1 H, 1a-H), 5.26−5.28 (m, 3 H, 1b-H, 2 1-H), 5.34 (s, 1 H, 1-H), 6.96−7.34 (m, 76 H, 14 Ph, m, *p*-Ph_2Si), 7.65−7.74 (m, 4 H, *o*-Ph_2Si). − FAB MS (positive-ion mode; matrix: NBOH with NaI): *m*/*z* = 2882 [M + Na^+]. − $C_{173}H_{197}N_3O_{32}Si$ (2858.55): calcd. C 72.69, H 6.95, N 1.47; found C 72.69, H 6.98, N 2.11.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-D-*myo*-inositol (35) and 1-*O*-Acetyl-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-D-*myo*-inositol (36):** A mixture of **34** (0.41 g, 0.143 mmol) and K_2CO_3 (0.5 g) in dry methanol/diethyl ether (1:1, 30 mL) was vigorously stirred for about 24 h at 40°C. The reaction was monitored by TLC [toluene/ethyl acetate, 20:1; R_f(**35**) = 0.22]. After concentration in vacuo, water was added, and the mixture was extracted twice with ethyl acetate. The combined organic solutions were dried (Na_2SO_4) and concentrated in vacuo to give crude **35** as a colorless oil which was of sufficient purity for the preparation of **36**. Crude **35** was dissolved in dry pyridine/acetic anhydride (1:1, 5 mL). After stirring overnight at room temp., the solution was concentrated in vacuo (0.1 bar). Flash chromatography (toluene/ethyl acetate, 25:1) of the residue yielded **36** (319 mg, 82%) as a colorless foam which was lyophilized from dioxane. − **35**: $[\alpha]_D$ = +35 (*c* = 2, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 0.99 [s, 9 H, $C(CH_3)_3$], 2.75 (d, $^3J_{1a,OH}$ = 2.5 Hz, 1 H, OH), 3.28 (dd, $^3J_{1b,2b}$ = 3.5, $^3J_{2b,3b}$ = 9.7 Hz, 1 H, 2b-H), 3.31−3.39 (m, 2 H), 3.46−3.54 (m, 3 H), 3.60−4.13 (m, 27 H), 4.18−4.67 (m, 26 H, 11.5 CH_2Ph, 3a-, 2a-H, 2-H), 4.74−4.94 (m, 6 H, 2.5 CH_2Ph, 1d-H), 5.10 (d, $^3J_{1b,2b}$ = 3.5 Hz, 1 H, 1b-H), 5.29−5.31 (m, 2 H, 2 1-H), 5.35 (br. s, 1 H, 1-H), 6.96−7.37 (m, 76 H, 14 Ph, *m*,*p*-Ph_2Si), 7.64−7.75 (m, 4 H, *o*-Ph_2Si). − **36**: TLC (toluene/ethyl acetate, 15:1): R_f = 0.45. − $[\alpha]_D$ = +23 (*c* = 0.5, chloroform). − ^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.99 [s, 9 H, $C(CH_3)_3$], 1.24−1.67 (m, 20 H, 20 $H_{cycloh.}$), 2.10 (s, 3 H, $COCH_3$), 3.25 (dd, $^3J_{1b,2b}$ = 3.5, $^3J_{2b,3b}$ = 9.6 Hz, 1 H, 2b-H), 3.31−3.39 (m, 2 H, 2 6-H), 3.46−4.12 (m, 29 H), 4.18−4.66 (m, 26 H, 11.5 CH_2Ph, 3a-, 2a-, 2-H), 4.76−4.91 (m, 6 H, 2.5 CH_2Ph, 1d-H), 5.13 (dd, $^3J_{1a,2a}$ = $^3J_{6a,1a}$ = 3.7 Hz, 1 H, 1a-H), 5.23 (d, $^3J_{1b,2b}$ = 3.6 Hz, 1 H, 1b-H), 5.27−5.28 (m, 2 H, 2 1-H), 5.34 (br. s, 1 H, 1-H), 6.96−7.31 (m, 76 H, 14 Ph, *m*,*p*-Ph_2Si), 7.65−7.74 (m, 4 H, *o*-Ph_2Si). − **35**: $C_{162}H_{179}N_3O_{30}Si$ (2676.28): calcd. C 72.70, H 6.74, N 1.57; found C 72.90, H 6.61, N 1.65. − **36**: $C_{164}H_{181}N_3O_{31}Si$ (2718.32): calcd. C 72.46, H 6.71, N 1.55; found C 72.12, H 6.73, N 2.01.

1-*O*-Acetyl-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-D-*myo*-inositol (37): A solution of **36** (160 mg, 58.9 μmol) in dry tetrahydrofuran (2 mL) was treated with TBAF (1.1 M solution in THF, 0.4 mL, 440 mmol) and dry acetic acid (26 μL, 440 μmol) at 0°C under nitrogen. Stirring was continued for about 2 d at 40°C until TLC showed complete disapperance of the substrate. After addition of satd. aqueous $NaHC_3$ solution and ice, the mixture was extracted twice with dichloromethane. The combined organic extracts were dried (Na_2SO_4), concentrated in vacuo, and filtered through silica gel (toluene/ethyl acetate, 10:1). MPLC (toluene/ethyl acetate, 10:1) of the crude product yielded **37** (129 mg, 89%) as a colorless foam which was lyophilized from dioxane. − TLC (toluene/ethyl acetate, 12:1): R_f = 0.38. − $[\alpha]_D$ = +47 (c = 1, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.31−1.79 (m, 20 H, 20 $H_{cycloh.}$), 2.11 (s, 3 H, $COCH_3$), 3.31 (dd, $^3J_{1b,2b}$ = 3.5, $^3J_{2b,3b}$ = 9.5 Hz, 1 H, 2b-H), 3.44−3.49 (m, 2 H, 2 6-H), 3.52−4.07 (m, 29 H), 4.16 (br. t, 1 H, 2-H), 4.22−4.66 (m, 25 H, 11.5 CH_2Ph, 3a-, 2a-H), 4.78−4.91 (m, 5 H, 2.5 CH_2Ph), 4.92 (br. s, 1 H, 1d-H), 5.10 (s, 1 H, 1-H), 5.14 (dd, $^3J_{1a,2a}$ = $^3J_{6a,1a}$ = 3.6 Hz, 1 H, 1a-H), 5.21 (br. s, 1 H, 1-H), 5.26 (d, $^3J_{1b,2b}$ = 3.5 Hz, 1 H, 1b-H), 5.29 (br. s, 1 H, 1-H), 7.02−7.35 (m, 70 H, 14 Ph). − $C_{148}H_{163}N_3O_{31}$ (2479.92): calcd. C 71.68, H 6.62, N 1.69; found C 71.49, H 6.51, N 1.96.

2-[*N*-(Benzyloxycarbonyl)amino]ethanol: This compound was prepared according to the procedure described by Rose.[37] Flash chromatography (petroleum ether/ethyl acetate, 6:4 → 1:1, R_f = 0.15) of the crude product gave pure product.

{2-[*N*-(Benzyloxycarbonyl)amino]ethoxy}(2-cyanoethoxy)-(diisopropylamino)phosphane (5): To a solution of 2-[*N*-(benzyloxycarbonyl)amino]ethanol (690 mg, 3.54 mmol) and 2-cyanoethyl-*N*,*N*,*N*′,*N*′-tetraisopropylphosphorodiamidite (1.6 g, 5.31 mmol) in dry acetonitrile (15 mL) 1*H*-tetrazole (75 mg, 1.06 mmol) was added. After stirring overnight at room temp., the mixture was diluted with satd. aqueous $NaHCO_3$ solution and extracted twice with dichloromethane. The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. Flash chromatography (toluene/ethyl acetate, 10:1 with 1% triethylamine) of the residue yielded **5** (1.23 g, 88%) as a wax. Physical data were in agreement with those reported by Ogawa et al.[15] − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.13−1.20 [2 d, 2 ^3J = 6.8 Hz, 12 H, 2 $CH(CH_3)_2$], 2.61 (t, ^3J = 6.3 Hz, 2 H, OCH_2CH_2CN), 3.39−3.46 (q, ^3J = ^3J = 6.2 Hz, 2 H, OCH_2CH_2NHCOO), 3.52−3.89 [m, 6 H, 2 $CH(CH_3)_2$, OCH_2CH_2NHCOO, OCH_2CH_2CN], 5.12 (s, 2 H, CH_2Ph), 5.23 (br. t, 1 H, NHCOO), 7.31−7.38 (m, 5 H, Ph).

1-*O*-Acetyl-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-[3,4-di-*O*-benzyl-6-{2-[*N*-(benzyloxycarbonyl)amino]ethyl 2-cyanoethyl phosphate}-α-D-mannopyranosyl]-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-D-*myo*-inositol (38): To a mixture of alcohol **37** (200 mg, 80.65 μmol), phosphoroamidite **5** (200 mg, 505.8 μmol), and powdered molecular sieves (3 Å) in dry acetonitrile (4 mL) 1*H*-tetrazole (11 mg, 157.1 μmol) was added under nitrogen. After stirring for 1.5 h at room temp., *tert*-butyl hydroperoxide (3 M solution in toluene, 0.3 mL) was added. The progress of the coupling reaction and of the oxidation was monitored by TLC [petroleum ether/ethyl acetate, 6:4; R_f(**37**) = 0.74; R_f(phosphite) = 0.68; R_f(**38**) = 0.38]. After 2 h, the reaction mixture was poured onto a satd. aqueous $NaHCO_3$ solution and extracted several times with dichloromethane. The combined extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (7:3 → 6:4) to yield **38** (182 mg, 81%) as a colorless foam. − TLC (petroleum ether/ethyl acetate, 6:4): R_f = 0.38, − $[\alpha]_D$ = +30 (c = 0.33, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$): δ = 1.27−1.69 (m, 20 H, 20 $H_{cycloh.}$), 2.08−2.18 (m, 2 H, CH_2CN), 2.11 (s, 3 H, $COCH_3$), 3.20−4.08 (m, 39 H), 4.18−4.63 (m, 25 H, 11.5 CH_2Ph, 3a-, 2a-H), 4.75−4.90 (m, 6 H, 2.5 CH_2Ph, 1d-H), 5.00−5.04 (m, 3 H, 1.5 CH_2Ph), 5.14 (dd, $^3J_{1a,2a}$ = $^3J_{6a,1a}$ = 3.4 Hz, 1 H, 1a-H), 5.19−5.30 (m, 4 H, 1b-H, 2 1-H, NHCOO), 7.06−7.34 (m, 75 H, 15 Ph). − ^{31}P NMR (161.7 MHz; $CDCl_3$): δ = −0.31, −0.60. − FAB MS (positive-ion mode; matrix: NBOH with NaI): m/z = 2814 [M + Na^+].

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-[3,4-di-*O*-benzyl-6-{2-[*N*-(benzyloxycarbonyl)amino]ethyl triethylammonium phosphate}-α-D-mannopyranosyl]-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-D-*myo*-inositol (39):** To a solution of **38** (130 mg, 46.59 μmol) in dry methanol/diethyl ether (1:1, 3 mL), satd. sodium methoxide solution in methanol (5 drops) was added. After stirring for 3 h under TLC control, the solution was neutralized with Amberlite IR 120 (H^+). Evaporation of the solvents in vacuo and chromatography (chloroform/methanol 100:0 → 100:7 with 1% triethylamine) yielded **39** (125 mg, 96%) as triethylammonium salt. − TLC (chloroform/methanol, 9:1): R_f = 0.48. − $[\alpha]_D$ = +25 (c = 0.33, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3/CD_3OD$, 3:1): δ = 1.04 [t, ^3J = 7.4 Hz, 9 H, $(CH_3CH_2)_3NH^+$], 1.27−1.80 (m, 20 H, 20 $H_{cycloh.}$), 2.73 [q, ^3J = 7.3 Hz, 6 H, $(CH_3CH_2)_3NH^+$], 3.18−4.68 (m, 61 H), 4.72−5.03 (m, 10 H, 4.5 CH_2Ph, 1d-H), 5.20−5.23 (m, 3 H, 1b-H, 2 1-H), 5.36 (br. s, 1 H, 1-H), 7.04−7.38 (m, 75 H, 15 Ph). − ^{31}P NMR (161.7 MHz; $CDCl_3/CD_3OD$, 3:1): δ = 4.9. − FAB MS (negative-ion mode; matrix: NBOH): m/z = 2694 [M^-].

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-[3,4-di-*O*-benzyl-6-{2-[*N*-(benzyloxycarbonyl)amino]ethyl sodium phosphate}-α-D-mannopyranosyl}-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3:4,5-di-*O*-cyclohexylidene-1-[(2*S*,3*S*,4*R*)-2-*N*-(hexacosanoyl)amino-3,4-*O*-isopropylideneoctadecan-3,4-diol-1-yl sodium phosphate]-D-*myo*-inositol (40):** To a solution of **39** (135 mg, 48.28 μmol), phosphitamide **2** (200 mg, 213.9 μmol), and powdered molecular sieves (3 Å) in dry dichloromethane/acetonitrile (1:1, 6 mL) was added 1*H*-tetrazole (15 mg, 213.9 μmol) under nitrogen. The reaction was monitored by TLC chloroform/methanol, 9:1; R_f(**39**) = 0.39; R_f(phosphite) = 0.43]. After stirring for 6 h at room temp., *tert*-butyl hydroperoxide (3 M solution in toluene, 1 mL) was added in order to oxidize the phosphorus(III) species. The mixture was stirred for 2 h at room temp. After addition of brine and satd. aqueous $NaHCO_3$ solution, the mixture was extracted three times with dichloromethane. The combined organic extracts were dried (Na_2SO_4), concentrated in vacuo, and redissolved in a mixture of dichloromethane (3 mL) and ethanolic dimethylamine solution (33% in ethanol, 3 mL). After stirring for 1 h at room temp., the mixture was concentrated in vacuo. The residue was chromatographed on silica gel (chloroform/methanol, 100:0 → 100:2 → 100:3) to yield diphosphate **40**. The disodium salt of **40** (101 mg, 60%) was obtained by treating a solution of **40** in chloroform/methanol (1:1.4 mL) with ion-exchange resin (Amberlite IR 120, Na^+

form). − TLC (chloroform/methanol, 9:1): R_f = 0.32, − $[\alpha]_D$ = +43 (c = 2.5, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$/CD_3OD, 1:1): δ = 0.76−0.82 (t, ^3J = 6.5 Hz, 6 H, 2 CH_3), 1.12−1.82 (m, 98 H, CMe_2, 20 $H_{cyclohex.}$, 36 CH_2), 2.07 (t, ^3J = 7.2 Hz, 2 H, $COCH_2$), 3.25−4.87 (m), 4.71 (1d-H), 4.92 (br. s, 1 H, 1-H), 5.02 (br. s, 1 H, 1-H), 5.14 (s, 1 H, 1-H), 5.48 (d, $^3J_{1b,2b}$ = 3.3 Hz, 1 H, 1b-H), 7.01−7.30 (m, 75 H, 15 Ph). − ^{31}P NMR (161.7 MHz; $CDCl_3$/CD_3OD, 1:1): δ = −0.36, −3.90. − FAB MS (negative-ion mode, matrix: NBOH with NaI): m/z = 3514 [M^{2-} + Na^+] and 3664 [M^{2-} + NaI + Na^+].

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-[3,4-di-*O*-benzyl-6-{2-[*N*-(benzyloxycarbonyl)amino]ethyl triethylammonium phosphate}-α-D-mannopyranosyl]-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-1-[(2*S*,3*S*,4*R*)-2-*N*-(hexacosanoyl)amino-3,4-dihydroxy-1-yl triethylammonium phosphate]-D-*myo*-inositol (41):** To a solution of **40** (50 mg, 14.14 μmol) and ethylene glycol (0.1 mL) in dry acetonitrile/dichloromethane (1:1, 3 mL) (1*S*)-camphor-10-sulphonic acid (20 mg) was added to adjust the pH to 1. After stirring at room temp. for 4 h, the reaction was completed. The solution was neutralized by addition of triethylamine and then concentrated in vacuo (0.1 mbar). Brine and water were added and the mixture was extracted three times with chloroform. The combined organic solutions were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (chloroform/methanol, 100:0 → 100:8 → 9:1 with 1% triethylamine) of the residue gave oily **41** (31 mg, 63%) as bis(triethylammonium) salt. − TLC (chloroform/methanol, 8:2): R_f = 0.48. − $[\alpha]_D$ = +39 (c = 2, chloroform). − ^{1}H NMR (250 MHz; $CDCl_3$/CD_3OD, 3:1): δ = 0.86−0.92 (t, ^3J = 6.9 Hz, 6 H, 2 CH_3), 1.17 [t, ^3J = 7.2 Hz, 18 H, $(CH_3CH_2)_3NH^+$], 1.21−1.63 (m, 72 H, 36 CH_2), 2.17 (t, ^3J = 7.5 Hz, 2 H, $COCH_2$), 2.91 [q, ^3J = 7.3 Hz, 12 H, $(CH_3CH_2)_3NH^+$], 3.14−4.61 (m, 65 H), 4.69−4.99 (m, 11 H, 5 CH_2Ph, 1d-H), 5.21 (s, 1 H, 1-H), 5.23 (br. s, 1 H, 1-H), 5.31 (s, 1 H, 1-H), 5.48 (d, $^3J_{1b,2b}$ = 3.0 Hz, 1 H, 1b-H), 7.03−7.35 (m, 75 H, 15 Ph). − ^{31}P NMR (161.7 MHz; $CDCl_3$/CD_3OD, 3:1): δ = 4.19, 4.92.

***O*-(α-D-Mannopyranosyl)-(1→2)-*O*-[6-(2-aminoethyl hydrogen phosphate)-α-D-mannopyranosyl]-(1→2)-*O*-(α-D-mannopyranosyl)-(1→6)-*O*-(α-D-mannopyranosyl)-(1→4)-(2-amino-2-deoxy-α-D-glucopyranosyl)-(1→6)-1-[(2*S*,3*S*,4*R*)-2-*N*-(hexacosanoyl)amino-3,4-dihydroxyoctadecan-1-yl hydrogen phosphate]-D-*myo*-inositol (1):** To a solution of **42** (25 mg, 7.15 μmol) in chloroform/methanol/water (1:1:9.25, 3 mL) Pearlman′s catalyst (8 mg) was added and the mixture was stirred at room temp. for 2 h under hydrogen (1 bar). Then methanol (0.25 mL) and water (0.25 mL) were added and hydration was continued overnight. After evaporation of the solvents in vacuo (0.1 mbar), the residue was chromatographed on silica gel (ethanol/*n*-butanol/30% aqueous NH_3/water, 2:2:1.05 → 2:2:1:1.5) to give GPI anchor **1** (9 mg, 70%). − TLC (EtOH/*n*BuOH/conc. NH_3/H_2O, 2:2:1.5:1): R_f = 0.60. − ^{1}H NMR (250 MHz; [D_6]DMSO/D_2O, 40:1, T = 60°C): δ = 4.86, 4.91, 5.02, 5.16 (d, J < 1 Hz, s, s, d J < 1 Hz, 1c, d, e, f-H), 5.42 d (J ≈ 3 Hz, 1b-H). − Data based on DQF-COSY and NOESY experiments in SDS micelles: δ = 4.18 (1a-H), 4.07 (2a-H), 3.56 (3a-H), 3.59 (4a-H), 3.42 (5a-H), 3.84 (6a-H); 5.44 (d, $J_{1b,2b}$ ≈ 3 Hz, 1b-H), 3.24 (2b-H), 4.00 (3b-H), 3.64 (4b-H), 4.11 (5b-H), 3.70, 3.79 (6b- and 6b′-H), 5.15 (s, 1c-H), 4.02 (2c-H), 3.76 (3c-H), 3.70, 3.79 (6c-, 6c′-H), 5.00 (s, 1d-H), 3.94 (2d-H); 5.22 (s, 1e-H), 4.05 (2e-H), 3.90 (3e-H), 3.73 (4e-H), 4.97 (s, 1f-H), 3.99 (2f-H), 3.77 (3f-H). − ^{31}P NMR (161.7 MHz; [D_6]DMSO, 60°C): δ = 0.79, 1.41. − FAB MS (negative-ion mode, matrix: NBOH/glycerine, 1:1): m/z = 1868 [M^{2-} + H^+]. − FAB MS (positive-ion mode, matrix: NBOH/glycerine, 1:1): m/z = 1872 [M + H^+]. − PD MS (positive-ion mode, matrix: nitrocellulose with NaI): m/z = 1939 [M^{2-} + 3 Na^+].

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