Attempted Synthesis of Type-A Inositolphosphoglycan Mediators – Synthesis of a Pseudohexasaccharide Precursor

Manuel Martín-Lomas,*[a] María Flores-Mosquera,[a] and José Luis Chiara[b]

Keywords: Inositolphosphoglycans / Oligosaccharide synthesis / Insulin mediators

A block synthesis approach to the inositol-containing pseudohexasaccharide **1** is presented. The *myo*-inositol building block **6** has been prepared using a key regioselective acylation through a boron–tin exchange reaction and the 2-azido-2-deoxy glycosyl donors **15** and **17** have been synthesized from D-glucosamine using a diazo transfer reaction. The anomeric position of the mono- and disaccharide building blocks has been temporarily protected as phenyl thioglycoside and this function was then converted into the different leaving groups to perform the glycosylation reactions. Both trichloroacetimidates and fluorides have been used as glycosyl donors for the construction of the different glycosidic linkages. The protected pseudohexasaccharides **44**, **48–50**, which are precursors of pseudohexasaccharide **1**, have been efficiently prepared and fully characterized. Pseudohexasaccharide **1** contains the fundamental structural features which have been proposed for type A inositolphosphoglycans, which may be involved in the insulin-signaling process.

Introduction

The mechanism of signal transduction associated with insulin action remains poorly understood, two main hypotheses having been advanced that may account for the existing experimental data: the phosphorylation cascade hypothesis and the second messenger hypothesis. The second messenger hypothesis[1–5] proposes the generation of partially characterized mediators, which have been called inositolphosphoglycans (IPGs), after receptor-mediated enzymatic cleavage of some uncharacterized membrane glycolipids, which may most likely be structurally related to glycosyl phosphatidylinositols (GPIs). The precise chemical structures of either the IPG mediators or the GPI precursors are presently unknown, but there is evidence for the existence of at least two families of compounds, with different chemical composition and biological activity, which have been called type A and type P.[6,7] IPGs of type A seem to be composed of *myo*-inositol, non-acetylated D-glucosamine, D-galactose, and phosphate[6] and IPGs of type P have been proposed to contain *chiro*-inositol, non-acetylated D-galactosamine, D-mannose, and phosphate.[7] Type A IPGs inhibit c-AMP-dependent protein kinase and mimic the lipogenic activity of insulin in adipocytes, while IPGs of type P activate pyruvate dehydrogenase phosphatase and mimic the glycogenic activity of insulin in muscle.[6–9]

The determination of the structures of these compounds is seriously hampered by the scarcity of biologically active material that can be isolated from mammalian tissues. From a large amount of bovine liver, we obtained[10] a partially purified glycolipid fraction which, after treatment with bacterial phosphatidylinositol-specific phospholipase C, gave a water-soluble fraction that inhibited c-AMP dependent protein kinase. This type A IPG active material could be partially sequenced and the results indicated that this family of substances contained *myo*-inositol, nonacetylated D-glucosamine, an undetermined hexose, either D-mannose or D-galactose, and a terminal *N*-acetyl-D-glucosamine residue. In addition, up to four α-D-galactopyranosyl units and up to four phosphate groups seemed to be present in this biologically active material.[10]

These incomplete data leave a considerable uncertainty regarding the precise chemical structure of the family of type A IPGs. Taking into account the immunological evidence that antibody probes, generated against the glycan chain of GPI anchors (**2**), cross react with IPGs from rat liver and block some of the effects of insulin,[11,12] structures such as **1**, having the above-mentioned structural motifs and showing a reasonable structural overlap with the conserved linear glycan chain of the GPI anchors (**2**), could be proposed as a working hypothesis for this family of compounds.

Aiming to contribute to disclose the molecular basis of this new IPG-based receptor-mediated pathway of intracellular signal transduction we are involved in a variety of synthetic, structural and biological studies.[13–17] A number of simple substructures have been synthesized, their shapes and spectroscopic properties have been studied and some aspects of their potential biological activity have been investigated. To follow up on these studies, we now report a synthetic strategy for the preparation of structures related to **1**. This strategy has permitted the effective synthesis of the protected pseudohexasaccharides **44**, **48–50** to be carried out. In spite of the fully compatible substitution pattern of compound **50**, the key final phosphorylation step failed and this synthetic route was abandoned, as a more

[a] Grupo de Carbohidratos, Instituto de Investigaciones Químicas, C.S.I.C.,
Américo Vespucio s/n, E-41092 Sevilla, Spain
Fax: (internat.) +34–954/46 05 65E-mail: mamartin@cica.es
[b] Instituto de Química Orgánica, C.S.I.C.
Juan de la Cierva 3, E-28006 Madrid, Spain

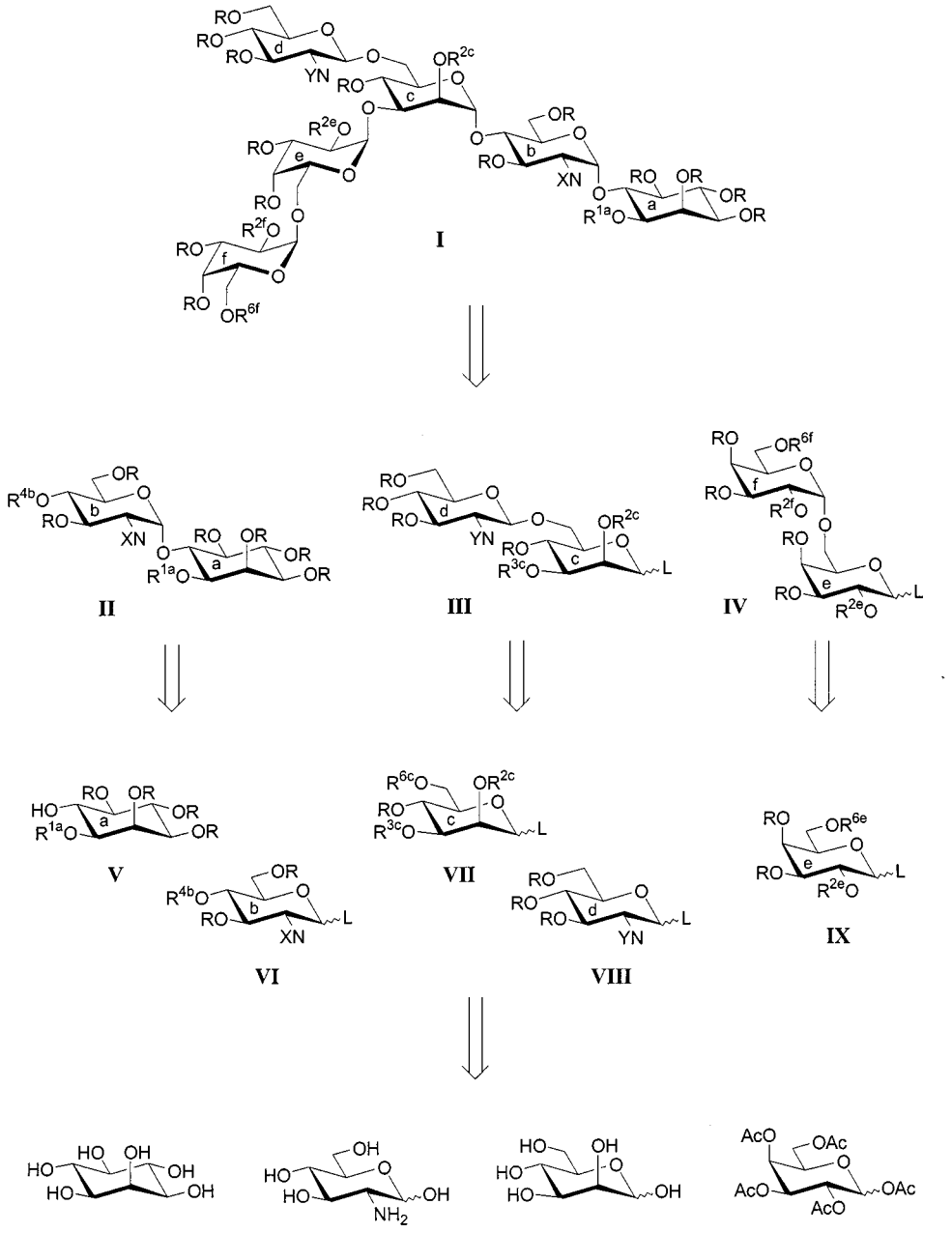
 © WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2000 1434−193X/00/0408−1547 $ 17.50+.50/0

efficient general strategy for the synthesis of these compounds was being developed in the laboratory.

Results and Discussion

The synthesis of compound **1** was envisaged according to the retrosynthetic analysis depicted in Scheme 1 from *myo*-inositol (unit a), D-glucosamine (units b and d), D-mannose (unit c), and D-galactose (units e and f). The anomeric position of the disaccharide and monosaccharide building blocks **III** and **IV**, and **VI**, **VII**, **VIII**, and **IX** has been temporarily protected as a phenyl thioglycoside throughout the synthetic route, owing to the stability and the additional versatility of this functional group, which can be easily converted into different leaving groups, to perform the successive glycosylation reactions.[18–23] The desired stereochemistry of the glycosidic linkages causes the protecting groups at positions 2c, 2e, and 2f to be permanently nonparticipating, the NX in unit b also to be nonparticipating and the NY in unit d to be participating. The temporary protecting groups at 1a and 6f were chosen so as to permit orthogonal deprotection with respect to all permanent protecting groups in **I**, while those at 3c and 6c in block **VII** were mutually orthogonal and allowed deprotection without affecting the remaining groups at positions 1 and 4. According to these general lines, the preparation of building blocks **II**, **III** and **IV** have been carried out as follows.

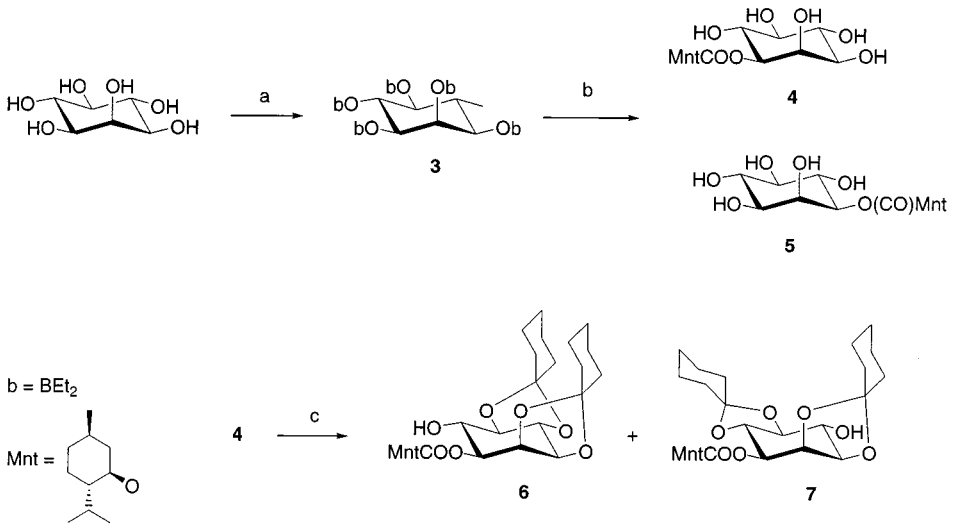
Building block II has been prepared from *myo*-inositol and D-glucosamine. *myo*-Inositol chemistry has received a



Scheme 1

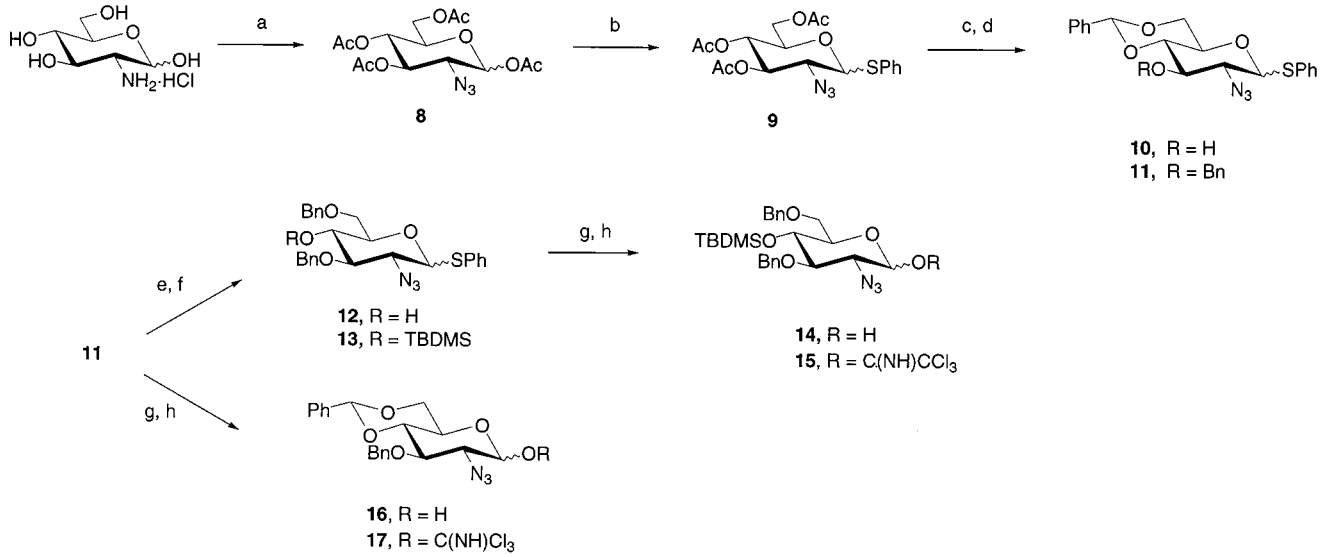
great deal of attention in recent years, particularly with regard to the preparation of regioselectively substituted and enantiomerically pure derivatives.[24] We have prepared the *myo*-inositol building block **6** as indicated in Scheme 2 following a procedure previously reported by us[25,26] that is based on the well-established regioselective enhancement of the nucleophilicity of hydroxyl groups as tributyltin ethers or as dibutyltin acetals,[27] but overcoming the insolubility problem of *myo*-inositol in most organic solvents by using a boron–tin exchange reaction.[28–30] Compound **6** was most conveniently prepared when the cyclohexylidenation[31,32] reaction was performed using 1-ethoxycyclohexene in cyclohexanone under thermodynamic control conditions. These conditions provided **7** as a minor product.

The 1,2-*cis* glycosylation of **6** was most conveniently carried out using a 2-azido-2-deoxy-D-glucopyranosyl trichloroacetimidate as glycosyl donor. 2-Azido-2-deoxy-glycosyl donors are currently employed in oligosaccharide synthesis but most of the methods used for the preparation of the 2-azido-2-deoxy building blocks involve low diasteroselectiv-



a) $Et_3B/^tBuCO_2BEt_2$, hexane, r.t.; b) i. $Bu_2Sn(acac)_2$, toluene, r.t. ii. (-)-MntCOCl, NMI, -30 °C to r.t. iii. MeOH; c) 1-ethoxycyclohexene, *p*-TsOH, r.t., cyclohexanone

Scheme 2

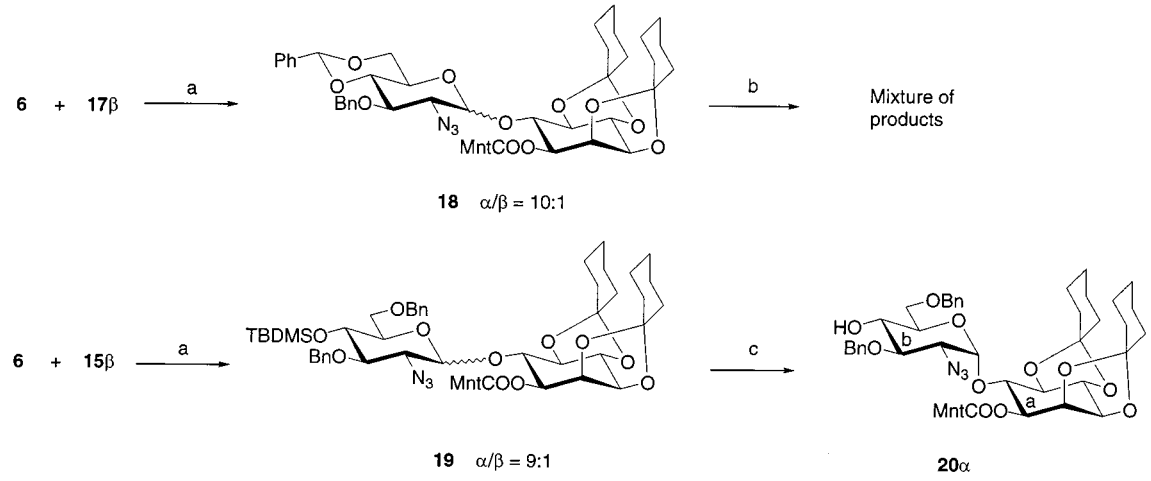


a) i. NaOMe, MeOH. ii. $CF_3SO_2N_3$, DMAP, CH_2Cl_2, r.t. iii. Ac_2O, py; b) $BF_3{\cdot}Et_2O$, PhSH, CH_2Cl_2, r.t.; c) i. NaOMe, MeOH; ii. benzaldehyde dimethyl acetal, *p*TsOH, CH_3CN, r.t.; d) BnBr, NaH, DMF, r.t.; e) i, $NaCNBH_3$,THF,r.t.; ii, HCl/Et_2O; f) TBDMSOTf, collidine, CH_2Cl_2, 0 °C, g) NBS, -15 °C, acetone/H_2O; g) CCl_3CN, K_2CO_3, CH_2Cl_2, r.t.

Scheme 3

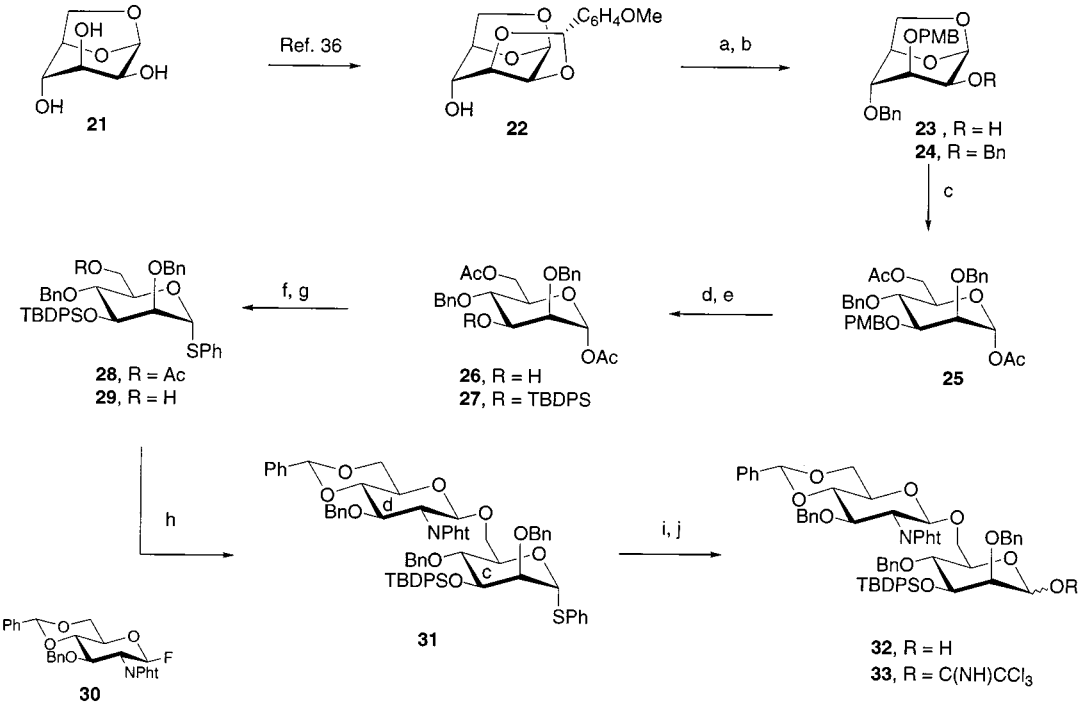
ity and a large number of steps.[33–36] We have reported the one-pot synthesis of peracetylated 2-azido-2-deoxy sugars from commercially available 2-amino-2-deoxy sugar hydrochlorides through a diazo transfer reaction from trifluoromethanesulfonyl azide,[37] and this method has now been used for the preparation of the glycosyl donors **15** and **17** as shown in Scheme 3. Thus, D-glucosamine hydrochloride was converted[37] into the tetra-*O*-acetylated 2-azido-2-deoxy derivative **8** and further into thioglycoside **9**,[38] which was then transformed using well-established chemistry[18,23,39–43] into the trichloroacetimidates **15** and **17** via the intermediates **10–14**, and **10**, **11** and **16**, respectively (Scheme 3).

Glycosylation of **6** with **17** in the presence of trimethylsilyl triflate in diethyl ether[23] afforded **18** as a 10:1 α/β mixture in 95% yield (Scheme 4). The reductive opening of the benzylidene acetal[41] in this mixture, however, resulted in partial hydrolysis of the cyclohexylidene acetals and trichloro-



a) TMSOTf, r.t., Et_2O, 4 Å molecular sieves; b) i. $NaCNBH_3$, THF, r.t.; ii. HCl/Et_2O; c) TBAF, THF, r.t.

Scheme 4

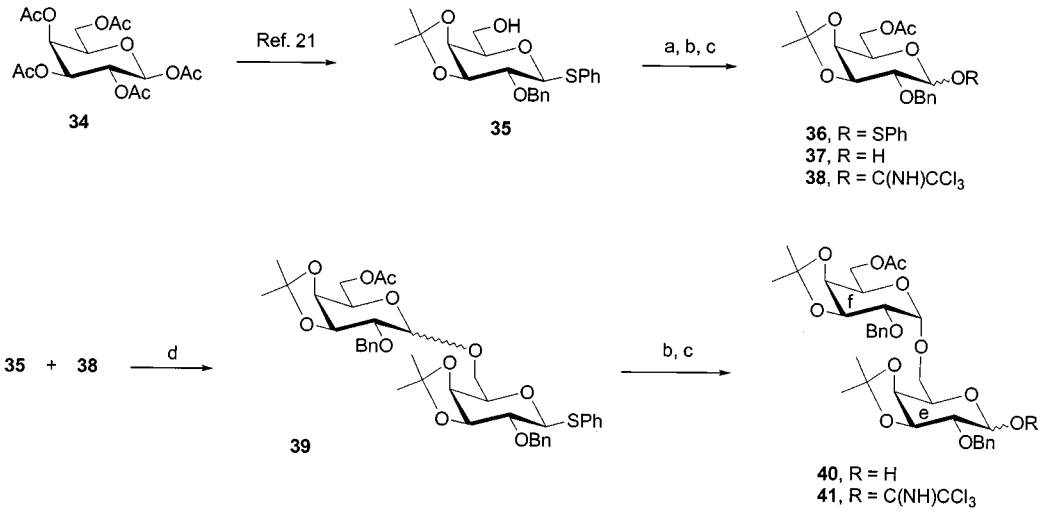


a) DIBALH, CH_2Cl_2, 0 °C to r.t.; b) NaH, BnBr, DMF, r.t.; c) TMSOTf, Ac_2O, 0 °C to rt; d) 4% TFA in CH_2Cl_2, r.t.; e) TBDPSCl, DMF, DMAP, imidazole, r.t.; f) $BF_3{\cdot}Et_2O$, PhSH, CH_2Cl_2 , r.t.; g) NaOMe/MeOH; h) i. AgOTf, Cp_2ZrCl_2, CH_2Cl_2, 4 Å molecular sieves, -40 °C. ii. **29**; i) NBS, acetone/H_2O, -15 °C; j) CCl_3CN, K_2CO_3, CH_2Cl_2, r.t.

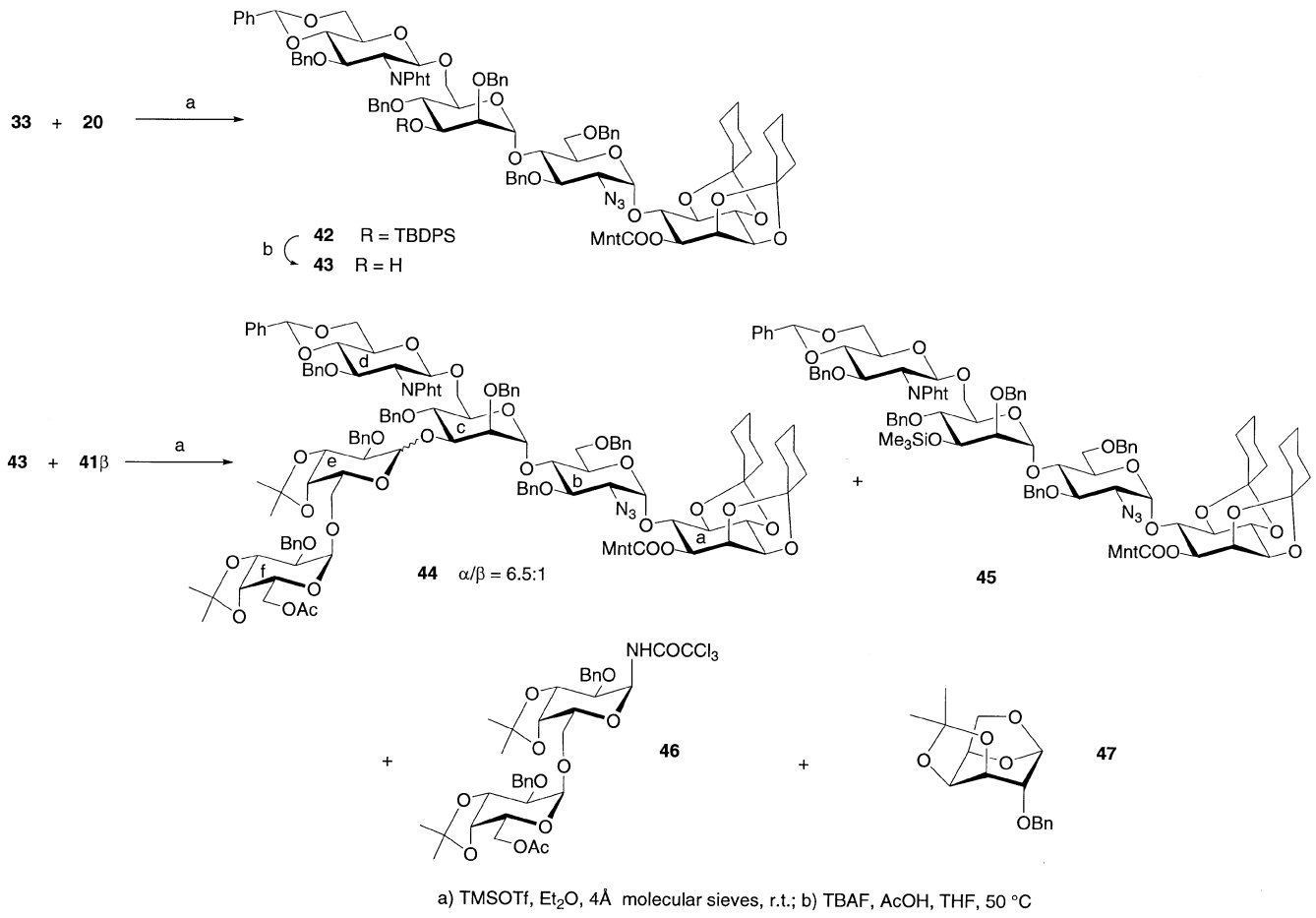
Scheme 5

acetimidate **15** was therefore preferred for the preparation of building block II. Thus, condensation of **15** with **6** under the above conditions gave **19** as a 9:1 α/βmixture in 73% yield. Treatment of **19** with tetrabutylammonium fluoride[44] finally afforded **20** in 83% yield.

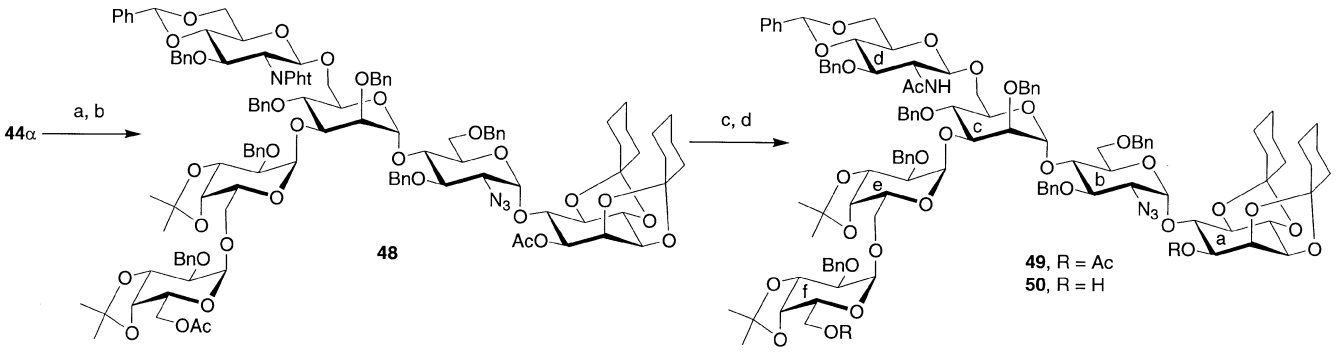
For the synthesis of building block **III** (Scheme 1), compound **29** (Scheme 5) was synthesized to provide the mannose unit (unit c). Thioglycoside **29** was prepared from the readily available 1,6-anhydro-β-D-mannopyranose (**21**)[36] as indicated in Scheme 5. After several attempts under differ-



Scheme 6



Scheme 7



a) LiOH, THF-MeOH; b) Et_3N, Ac_2O; c) ethylenediamine, 90 °C; d) Et_3N, Ac_2O

Scheme 8

ent experimental conditions, the glycosylation of **29** was most conveniently performed with fluoride **30** according to the methodology reported by Suzuki[45,46] to give, with excellent yield and selectivity, the disaccharide **31**, which was further transformed[18,19,23] into trichloroacetimidate **33** via **32**.

Block **IV** was prepared from β-D-galactopyranose pentaacetate (**34**) (Scheme 6) that gave both glycosyl acceptor **35**[38,45] and glycosyl donor **38** via **36** and **37**. The glycosylation reaction of **35** and **38** afforded disaccharide **39** as a 6:1 α/β mixture in 86% yield, which was transformed[18,19,23] into trichloroacetimidate **41** via **40**.

Condensation of **33** with **20** gave tetrasaccharide **42** in 81% yield (Scheme 7). Careful experimental control of the desilylation reaction of **42** resulted in the glycosyl acceptor **43** in good yield. The glycosylation of **43** with excess trichloroacetimidate **41**, in order to assure the completion of the glycosylation reaction, gave the hexasaccharide **44** as a 6.5:1 α/β mixture in 83% yield. From the reaction mixture, tetrasaccharide **45**, disaccharide **46** and 1,6-anhydro derivative **47** were also isolated. Compound **45** was most likely formed by reaction of **43** with the promoter and compound **46** by reaction of the glycosyloxocarbonium ion generated from **41** with trichloroacetimidate.[23] The 1,6-anhydro-β-D-galactopyranose derivative **47** may be formed by intramolecular nucleophilic attack of the interglycosidic oxygen of **41** on the glycosylcarbonium ion intermediate.[50] Having thus prepared the desired, fully protected pseudohexasaccharide backbone (**44**), the subsequent deprotection and final phosphorylation steps were undertaken. In order to avoid the possibility of carbamate formation when removing the phthalimido group in **44** using alkyl amines at high temperature, which may complicate the deprotection sequence, removal of the carbonate group at position 1 of the *myo*-inositol unit was first performed by treatment with excess lithium hydroxide. This caused simultaneous removal of the acetyl group at position 6 of the terminal galactopyranosyl unit and partial opening of the phthalimido group. The reaction mixture was therefore subsequently treated with acetic anhydride–triethylamine to give the fully protected derivative **48** in 78% yield (Scheme 8). Removal of the phthalimido group was then attempted under different reaction conditions and finally achieved with excess ethylenediamine in *n*-butyl alcohol at high temperature,[48,49] resulting in **49**, after *N*-acetylation, in 93% yield. *O*-Deacetylation of **49** gave diol **50** in 91% yield. After a careful study of experimental conditions using model compounds, the phosphorylation of **50** was attempted by treatment with dibenzyl *N*,*N*-diisopropyl phosphoramidate–tetrazole in acetonitrile, followed by oxidation with *tert*-butyl hydroperoxide.[51] Unfortunately, the purification and characterization of the final product proved not to be feasible in our hands. Other approaches to these kinds of substances were in progress in our laboratory and this synthetic route was finally abandoned.

Conclusion

A block synthesis approach to pseudohexasaccharide **44** containing the fundamental units suggested by previous structural work for type A IPGs from bovine liver[10] has been developed from building blocks **20**, **33**, and **41**. Building block **20** has been prepared using an efficient approach involving known methodologies[25,26,37] which allow for the preparation of multigram amounts of optically active *myo*-inositol derivative **6** and of 2-azido-2-deoxy trichloroacetimidate **15** in few steps. Building block **33** has been synthesized by glycosylation of **29**, prepared from 1,6-anhydro-β-D-mannopyranose, with fluoride **30.**[45,46] Finally, block **41** has been prepared from β-D-galactopyranose pentaacetate **34** through trichloroacetimidate glycosyl donor **38** and thioglycoside glycosyl acceptor **35**. Condensation of **33** with **20** to give **42**, and of **41** with **43** to give the pseudohexasaccaride **44** took place with good yield and selectivity using the trichloroacetimidate glycosylation method.[23] In spite of the compatibility of protecting groups in compound **44**, the final isolation of pseudohexasaccharide **1** failed after attempted phosphorylation of diol **50** using the phosphoramidite procedure. This failure illustrates an important but rarely discussed aspect of complex oligosaccharide synthesis: the need to develop methods for the effective manipulation, purification and isolation of small amounts of

highly elaborated synthetic oligosaccharide structures that may be utilized routinely in the synthetic laboratory.

Experimental Section

General Remarks: TLC was performed on precoated plates (Merck aluminium sheets silica 60 F_{254}, Art. no. 5554); detection was effected by observation under UV light (254 nm), then visualised using sulfuric acid or phosphomolybdic acid in EtOH followed by heating. – Column chromatography was conducted with Silica Gel 60 (0.023–0.040 mm, E. Merck), using a flash procedure. – Melting points were determined using a Reicher Jung Thermovar apparatus and are uncorrected. – Specific rotations were measured on a Perkin–Elmer model 241 polarimeter. – NMR spectra were recorded on Bruker AMX-200, Avance DRX-500, Varian Gemini-200, XL-300 or Unity 500 spectrometers. Chemical shifts are reported in ppm relative to the residual signal of the solvent used. – Microanalysis was carried out by the Analysis Department of the Instituto de Química Orgánica General (CSIC) on a Heraus CHNO-Rapid apparatus.

2,3:4,5-Di-*O*-cyclohexylidene-1-*O*-(–)-menthoxycarbonyl-1-D-*myo*-inositol (6) and 2,3:5,6-Di-*O*-cyclohexylidene-1-*O*-(–)-menthoxycarbonyl-1-D-*myo*-inositol (7): To a solution of 1-*O*-(–) menthoxycarbonyl-*myo*-inositol[26] (**4**) (100 mg, 0.276 mmol) and dried *p*TsOH (5.7 mg, 0.03 mmol) in cyclohexanone (2 mL) at room temperature was added 1-ethoxycyclohexene (350 mL, 2.76 mmol). The reaction mixture was stirred for 3 h 30 min, quenched with Et_3N and evaporated. Silica gel column chromatography (hexane/EtOAc, 5:1) afforded **6** (73 mg, 50%) and **7** (41 mg, 28%). Compound **6**: White solid. *Rf* (hexane/EtOAc, 4:1) = 0.26. Mp: 83–85 °C. $[\alpha]_D$ = –50.4 (c = 1.0, $CHCl_3$). – ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.76 (d, 3 H, CH_3 Mnt), 0.88 (d, 3 H, CH_3 Mnt), 0.92 (d, 3 H, CH_3 Mnt), 1.00–1.13 (m, 1 H, Mnt), 1.37–1.76 (m, 22 H, 16 H cyclohex, 6 H Mnt), 1.92–2.00 (m, 1 H, Mnt), 2.07–2.11 (m, 1 H, Mnt), 2.70 (d, 1 H, $J_{OH,6}$ = 3.5 Hz, 1 H, OH), 3.44 (dd, $J_{5,4}$ = 10.5 Hz, $J_{5,6}$ = 9.0 Hz, 1 H, H_5), 3.85 (dd, $J_{4,5}$ = 10.5 Hz, $J_{4,3}$ = 7.9 Hz, 1 H, H_4), 4.10–4.14 (m, 1 H, H_6), 4.33 (dd, $J_{3,2}$ = 6.2 Hz, $J_{3,4}$ = 7.9 Hz, 1 H, H_3), 4.54 (dt, 1 H, Ment), 4.60 (dd, $J_{2,1}$ = 4.5 Hz, $J_{2,3}$ = 6.1 Hz, 1 H, H_2), 4.79 (t, $J_{1,2}$ = $J_{1,6}$ = 4.6 Hz, 1 H, H_1). – ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 16.6, 21.2, 22.4, 23.7, 24.0, 24.1, 24.3, 25.4, 25.5, 26.5, 31.9, 32.1, 34.5, 35.0, 36.9, 37.0, 37.2, 41.1, 47.4, 72.5, 73.7, 76.6, 78.3, 79.1, 79.6, 111.6, 113.3, 154.3. – Compound **7**: Colorless oil. – *Rf*: 0.14 (hexane/EtOAc, 4:1). – ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.77 (d, 3 H, CH_3 Mnt), 0.88 (d, 3 H, CH_3 Ment), 0.91 (d, 3 H, CH_3 Mnt), 1.00–1.15 (m, 1 H, Mnt), 1.37–1.69 (m, 26 H, 20 H cyclohexylidene, 6 H Mnt), 1.93–2.09 (m, 2 H, Mnt), 2.95 (br. s, 1 H, OH), 3.40 (t, $J_{5,4}$ = $J_{5,6}$ = 10.1 Hz, 1 H, H_5), 3.88 (dd broad, $J_{4,5}$ = 10.6 Hz, $J_{4,3}$ = 6.5 Hz, 1 H, H_4), 4.01–4.13 (m, 2 H, H_6, H_3), 4.58 (dt, 1 H, Mnt), 4.70 (t, $J_{2,1}$ = $J_{2,3}$ = 4.7 Hz, 1 H, H_2), 4.89 (dd, $J_{1,2}$ = 4.4 Hz, $J_{1,6}$ = 10.5 Hz, 1 H, H_1). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ 16.8 (–), 21.1 (–), 22.4 (–), 23.9 (+), 24.0 (+), 24.4 (+), 25.4 (+), 26.7 (–), 31.9 (–), 34.5 (+), 35.2 (+), 36.8 (+), 36.9 (+), 38.2 (+), 41.2 (+), 47.6 (–), 74.5 (–), 74.6 (–), 74.7 (–), 75.3 (–), 78.4 (–), 79.3 (–), 81.8 (–), 111.4 (o), 114.0 (o), 154.5 (o).

Phenyl 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-1-thio-D-glucopyranoside (9): To a solution of 1,3,4,6-tetra-*O*-acetyl-2-azido-2-deoxy-D-glucopyranose[37] (2.10 g, 5.63 mmol) in CH_2Cl_2 (45 mL) at room temperature was added thiophenol (1.15 mL, 11.25 mmol) and boron trifluoride–diethyl ether (3.12 mL, 25.31 mmol). The reaction mixture was stirred for 8 days, diluted with CH_2Cl_2, washed with NaCl, and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **9** (1.58 g, 66%), as a 3:1 α/β mixture, and recovered **8** (0.53 g, 25%). – *Rf* (hexane/EtOAc, 3:1) = 0.27. – ^{1}H NMR for **9α**, taken from the spectra of the α/β mixture, (200 MHz, $CDCl_3$) δ: 1.96 (s, 3 H, CH_3CO), 1.99 (s, 3 H, CH_3CO), 2.04 (s, 3 H, CH_3CO), 3.96 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{6a,5}$ = 2.2 Hz, 1 H, H_{6a}), 4.02 (dd, $J_{2,3}$ = 10.6 Hz, $J_{2,1}$ = 5.7 Hz, 1 H, H_2), 4.23 (dd, $J_{6b,6a}$ = 12.4 Hz, $J_{6b,5}$ = 5.1 Hz, 1 H, H_{6b}), 4.53 (ddd, $J_{5,4}$ = 10.2 Hz, $J_{5,6b}$ = 5.1 Hz, $J_{5,6a}$ = 2.2 Hz, 1 H, H_5), 4.96 (t, $J_{4,3}$ = $J_{4,5}$ = 10.1 Hz, 1 H, H_4), 5.27 (dd, $J_{3,2}$ = 10.4 Hz, $J_{3,4}$ = 9.8 Hz, 1 H, H_3), 5.58 (d, $J_{1,2}$ = 5.7 Hz, 1 H, H_1), 7.20–7.45 (m, 5 H, ArH). – ^{1}H NMR for **9β**, taken from the spectra of the α/β mixture, (200 MHz, $CDCl_3$) δ: 1.94 (s, 3 H, CH_3CO), 1.97 (s, 3 H, CH_3CO), 2.02 (s, 3 H, CH_3CO), 3.34 (t, $J_{2,3}$ = $J_{2,1}$ = 10.1 Hz, 1 H, H_2), 3.63 (ddd, $J_{5,4}$ = 9.8 Hz, $J_{5,6b}$ = 4.9 Hz, $J_{5,6a}$ = 2.6 Hz, 1 H, H_5), 3.92–4.21 (m, 2 H, H_{6a}, H_{6b}), 4.42 (d, $J_{1,2}$ = 10.1 Hz, 1 H, H_1), 4.86 (t, $J_{4,3}$ = $J_{4,5}$ = 9.7 Hz, 1 H, H_4), 5.01 (t, $J_{3,2}$ = $J_{3,4}$ = 9.7 Hz, 1 H, H_3), 7.20–7.45 (m, 5 H, ArH).

Phenyl 2-Azido-4,6-*O*-benzylidene-2-deoxy-1-thio-D-glucopyranoside (10): To a solution of **9** (3.00 g, 7.09 mmol) in MeOH (110 mL) at room temperature was added sodium methoxide in MeOH (0.3M, 5 mL). After 20 min, the solution was neutralized with Amberlite IR-120, filtered and evaporated. The crude mixture of phenyl 2-azido-2-deoxy-1-thio-D-glucopyranosides obtained was dissolved in CH_3CN (30 mL). Benzaldehyde dimethyl acetal (5.32 mL, 35.45 mmol) and p-toluensulfonic acid (67.4 mg, 0.35 mmol) were added and the reaction mixture was stirred for 2 h at room temp., quenched with Et_3N and evaporated. Silica gel column chromatography (hexane/EtOAc, 6:1) afforded **10α** (1.85 g) and **10β** (0.80 g, 7:3 ratio, 97% total yield). – Data for **10α**: white solid. – *Rf* (hexane/EtOAc, 3:1) = 0.34. Mp: 127–128 °C. $[\alpha]_D$ = +226.9 (c = 1.09, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.90 (d, $J_{OH,3}$ = 2.0 Hz, 1 H, OH), 3.58 (t, $J_{4,3}$ = $J_{4,5}$ = 9.3 Hz, 1 H, H_4), 3.76 (t, $J_{6a,5}$ = $J_{6a,6b}$ = 10.2 Hz, 1 H, H_{6a}), 3.92 (dd, $J_{2,3}$ = 9.8 Hz, $J_{2,1}$ = 5.4 Hz, 1 H, H_2), 4.07 (dt, $J_{3,4}$ = $J_{3,2}$ = 9.6 Hz, $J_{3,OH}$= 2.0 Hz, 1 H, H_3), 4.24 (dd, $J_{6b,6a}$ = 10.2 Hz, $J_{6b,5}$ = 4.9 Hz, 1 H, H_{6b}), 4.41 (dt, $J_{5,4}$ = $J_{5,6a}$ = 10.2 Hz, $J_{5,6b}$ = 4.9 Hz, 1 H, H_5), 5.57 (s, 1 H, H_7), 5.58 (d, $J_{1,2}$ = 5.4 Hz, 1 H, H_1), 7.30–7.56 (m, 10 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 63.46, 63.91, 68.51, 70.72, 81.68, 87.81, 102.18, 126.19, 126.29, 128.01, 128.40, 129.18, 129.42, 132.47, 133.05, 136.80. – $C_{19}H_{19}N_3O_4S$: calcd. C 59.21, H 4.97, N 10.90, S 8.32; found C 59.13, H 5.08, N 10.71, S 8.13. – Data for **10β**: white solid. – *Rf* (hexane/EtOAc, 3:1) = 0.36. – Mp: 152–154 °C. – $[\alpha]_D$ = –65.8 (c = 0.96, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.88 (d, $J_{OH,3}$ = 2.1 Hz, 1 H, OH), 3.35 (dd, $J_{2,1}$ = 10.2, $J_{2,3}$ = 9.0 Hz, 1 H, H_2), 3.41–3.52 (m, 2 H, H_4, H_5), 3.73 (dt, $J_{3,2}$ = $J_{3,4}$ = 8.9 Hz, $J_{3,OH}$= 2.1 Hz, 1 H, H_3), 3.77 (t, $J_{6a,6b}$ = $J_{6a,5}$ = 10.2 Hz, 1 H, H_{6a}), 4.38 (dd, $J_{6b,6a}$ = 10.2 Hz, $J_{6b,5}$ = 4.4 Hz, 1 H, H_{6b}), 4.52 (d, $J_{1,2}$ = 10.2 Hz, 1 H, H_1), 5.53 (s, 1 H, H_7), 7.35–7.61 (m, 10 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 65.20, 68.41, 70.27, 74.11, 80.22, 86.83, 101.94, 126.24, 128.38, 128.67, 129.12, 129.41, 130.88, 133.67, 136.74. – $C_{19}H_{19}N_3O_4S$: calcd. C 59.21, H 4.97, N 10.90, S 8.32; found C 59.09, H 4.65, N 10.81.

Phenyl 2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-D-glucopyranoside (11): To a solution of **10β** (546 mg, 1.42 mmol) in DMF (9 mL) at room temperature was added sodium hydride (43 mg, 1.70 mmol) and then benzyl bromide (0.21 mL, 2.84 mmol). The reaction mixture was stirred for 40 min, quenched with a saturated aqueous solution of $NaHCO_3$, and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc) afforded **11β** in 98% yield. Following the same procedure, **11α** was synthesized using **10α** as starting material in 95% yield. Data for **11β**: white solid. – *Rf* (hexane/EtOAc, 3:1) = 0.58. – Mp: 106–108 °C. $[\alpha]_D$ = –121.0 (c = 0.93, $CHCl_3$). – ^{1}H NMR (200 MHz,

$CDCl_3$) δ: 3.38 (dd, $J_{2,1}$ = 10.2, $J_{2,3}$ = 9.1 Hz, 1 H, H_2), 3.45 (m, 1 H, H_5), 3.60–3.69 (m, 2 H, H_3, H_4), 3.81 (t, $J_{6a,6b}$ = $J_{6a,5}$ = 10.2 Hz, 1 H, H_{6a}), 4.41 (dd, $J_{6b,6a}$ = 10.2 Hz, $J_{6b,5}$ = 4.9 Hz, 1 H, H_{6b}), 4.51 (d, $J_{1,2}$ = 10.2 Hz, 1 H, H_1), 4.87 (dd, 2 H, CH_2Ph), 5.59 (s, 1 H, H_7), 7.31–7.61 (m, 15 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 64.75, 68.50, 70.50, 75.19, 80.97, 81.31, 86.67, 101.29, 125.97, 128.00, 128.30, 128.42, 128.72, 129.11, 133.92, 137.09, 137.58. – $C_{26}H_{25}N_3O_4S$: calcd. C 65.67, H 5.30, N 8.84, S 6.74; found C 65.91 H, 5.21, N 8.52, S 6.58. Data for **11α**: white solid. – *Rf* (hexane/EtOAc, 3:1) = 0.54. – Mp: 145–147 °C. $[\alpha]_D$ = +125.6 (*c* = 0.74, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$) δ: 3.73–3.83 (m, 1 H, H_4), 3.78 (t, $J_{6a,6b}$ = $J_{6a,5}$ = 10.3 Hz, 1 H, H_{6a}), 3.92–4.04 (m, 2 H, H_2, H_3), 4.24 (dd, $J_{6b,6a}$ = 10.3 Hz, $J_{6b,5}$ = 5.0 Hz, 1 H, H_{6b}), 4.44 (dt, $J_{5,4}$ = $J_{5,6a}$ = 10.3 Hz, $J_{5,6b}$ = 5.0 Hz, 1 H, H_5), 4.92 (dd, 2 H, CH_2Ph), 5.58 (m, 1 H, H_1), 5.62 (s, 1 H, H_7), 7.30–7.53 (m, 15 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 63.61, 63.84, 68.60, 75.18, 77.82, 82.74, 87.90, 101.51, 126.01, 127.95, 128.23, 128.30, 128.42, 129.09, 129.17, 132.47, 133.01, 137.12, 137.67. – $C_{26}H_{25}N_3O_4S$: calcd. C 65.67, H 5.30, N 8.84, S 6.74; found C 65.50, H 5.12, N 8.68, S 6.42.

Phenyl 2-Azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-D-glucopyranoside (12): A solution of **11β** (447 mg, 0.94 mmol) in THF (9.4 mL) containing 3Å molecular sieves was stirred for 30 min at room temperature. After this, sodium cyanoborohydride (1.201 g, 18.16 mmol) was added. A saturated solution of hydrogen chloride in diethyl ether was then added dropwise until the evolution of gas had ceased (pH < 7) and TLC analysis showed conversion of all the starting material. The mixture was neutralized with a saturated aqueous solution of $NaHCO_3$, diluted with CH_2Cl_2, filtered through celite, washed with water, and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **12β** (430 mg, 96%) as a colorless oil. Following the same procedure, **12α** was synthesized using **11α** as starting material in 87% yield. Data for **12β**: *Rf* (hexane/EtOAc, 3:1) = 0.28. – $[\alpha]_D$ = –64.2 (*c* = 1.10, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$) δ: 2.70 (d, $J_{OH,4}$ = 2.4 Hz, 1 H, OH), 3.27–3.41 [m (*AB*X), 2 H, H_2, H_3], 3.47 (m, 1 H, H_5), 3.65 (dt, $J_{4,3}$ = $J_{4,5}$ = 8.5 Hz, $J_{4,OH}$ = 2.4 Hz, 1 H, H_4), 3.75 (dd, $J_{6a,6b}$ = 10.4 Hz, $J_{6a,5}$ = 4.3 Hz, 1 H, H_{6a}), 3.81 (dd, $J_{6b,6a}$ = 10.4 Hz, $J_{6b,5}$ = 4.9 Hz, 1 H, H_{6b}), 4.45 [m (AB*X*), $J_{1,2}$ = 9.9 Hz, 1 H, H_1], 4.59 (dd, 2 H, CH_2Ph), 4.87 (dd, 2 H, CH_2Ph), 7.28–7.61 (m, 15 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 64.55, 70.27, 71.88, 73.72, 75.42, 78.05, 84.60, 86.23, 127.66, 127.82, 128.08, 128.17, 128.33, 128.45, 128.59, 128.96, 131.29, 133.48, 137.71, 137.86. – $C_{26}H_{27}N_3O_4S$: calcd. C 65.39, H 5.70, N 8.80, S 6.71; found C 65.61, H 5.35, N 8.58, S 6.35. – Data for **12α**: *Rf* (hexane/EtOAc, 3:1) = 0.31. – $[\alpha]_D$ = +124.9 (*c* = 1.34, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$) δ: 2.51 (d, $J_{OH,4}$ = 2.7 Hz, 1 H, OH), 3.62–3.75 (m, 3 H, H_3, H_{6a}, H_{6b}), 3.77 (dt, $J_{4,3}$ = $J_{4,5}$ = 8.0 Hz, $J_{4,OH}$ = 2.7 Hz, 1 H, H_4), 3.92 (dd, $J_{2,3}$ = 10.0 Hz, $J_{2,1}$ = 5.4 Hz, 1 H, H_2), 4.35 (m, 1 H, H_5), 4.56 (dd, 2 H, CH_2Ph), 4.91 (dd, 2 H, CH_2Ph), 5.58 (d, $J_{2,1}$ = 5.4 Hz, 1 H, H_1), 7.25–7.54 (m, 15 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 63.59, 69.72, 71.05, 72.36, 73.63, 75.39, 81.32, 87.28, 127.68, 127.80, 128.11, 128.17, 128.43, 128.65, 129.05, 132.16, 133.43, 137.71, 137.95. – $C_{26}H_{27}N_3O_4S$: calcd. C 65.39, H 5.70, N 8.80, S 6.71; found C 65.74, H 6.05, N 8.81, S 6.60.

Phenyl 2-Azido-3,6-di-*O*-benzyl-4-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-1-thio-D-glucopyranoside (13): A solution of **12β** (345 mg, 0.72 mmol) and collidine (287 μL, 2.17 mmol) in CH_2Cl_2 (1 mL) was cooled at 0 °C. *tert*-Butyldimethylsilyl triflate (249 μL, 1.08 mmol) was added dropwise during 2 h. The mixture was stirred for 10 min and quenched with water/ice, diluted and extracted with CH_2Cl_2, washed with brine, and dried with Na_2SO_4. Silica gel column chromatography afforded **13β** (405 mg, 95%) as a colorless oil. **13α** was synthesized similarly using **12α** as starting material in 98% yield. Data for **13β**: *Rf* (hexane/EtOAc, 5:1) = 0.69. – $[\alpha]_D$ = –0.2 (*c* = 0.65, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$) δ: 0.01 (s, 3 H, CH_3), 0.03 (s, 3 H, CH_3), 0.88 (s, 9 H, *t*Bu), 3.24–3.40 [m (*AB*X), 2 H, H_2, H_3], 3.45 (m, 1 H, H_5), 3.57–3.68 (m, 1 H, H_4), 3.64 (dd, $J_{6a,6b}$ = 10.7 Hz, $J_{6a,5}$ = 5.4 Hz, 1 H, H_{6a}), 3.78 (dd, $J_{6b,6a}$ = 10.7 Hz, $J_{6b,5}$ = 2.1 Hz, 1 H, H_{6b}), 4.50 [m (AB*X*), $J_{1,2}$ = 9.7 Hz, 1 H, H_1], 4.59 (dd, 2 H, CH_2Ph), 4.84 (dd, 2 H, CH_2Ph), 7.20–7.66 (m, 15 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: –4.74, –3.78, 17.98, 25.91, 65.74, 69.12, 70.55, 73.37, 75.57, 80.70, 85.48, 86.49, 127.51, 127.59, 128.11, 128.33, 128.97, 131.71, 133.71, 137.98, 138.37. – $C_{32}H_{41}N_3O_4SSi$: calcd. C 64.94, H 6.98, N 7.10, S 5.42; found C 65.45, H 7.00, N 6.96, S 5.32. – Data for **13α**: *Rf* (hexane/EtOAc, 5:1) = 0.62. $[\alpha]_D$ = +160.0 (*c* = 1.38, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$) δ: 0.02 (s, 3 H, CH_3), 0.05 (s, 3 H, CH_3), 0.90 (s, 9 H, *t*Bu), 3.58 (dd, $J_{3,2}$ = 10.1 Hz, $J_{3,4}$ = 8.4 Hz, 1 H, H_3), 3.71 (bd, *J* = 3.8 Hz, 2 H, H_{6a}, H_{6b}), 3.74 (Ψt, $J_{4,3}$ = 8.4 Hz, $J_{4,5}$ = 9.4 Hz, 1 H, H_4), 3.95 (dd, $J_{2,3}$ = 10.1 Hz, $J_{2,1}$ = 5.4 Hz, 1 H, H_2), 4.37 (dt, $J_{5,4}$ = 9.4 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 3.8 Hz, 1 H, H_5), 4.55 (dd, 2 H, CH_2Ph), 4.87 (dd, 2 H, CH_2Ph), 5.63 (d, $J_{1,2}$ = 5.4 Hz, 1 H, H_1), 7.21–7.61 (m, 15 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: –4.75, –3.71, 18.03, 25.94, 64.78, 68.91, 71.29, 73.13, 73.17, 75.20, 81.84, 87.41, 127.30, 127.47, 127.70, 128.27, 129.01, 132.44, 133.62, 138.06, 138.15. – $C_{32}H_{41}N_3O_4SSi$: calcd. C 64.94, H 6.98, N 7.10, S 5.42; found C 65.26, H 6.77, N 7.20, S 5.50.

2-Azido-3,6-di-*O*-benzyl-4-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-glucopyranose (14): A solution of **13β** (331 mg, 0.56 mmol) in acetone (12 mL) was cooled to –15 °C in darkness and NBS (129 mg, 0.73 mmol) was added. After 45 min, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$, diluted and extracted with EtOAc, washed with brine, and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 7:1) afforded **14** (279 mg), as a 11:1 α/β mixture of anomers (quantitative yield). The same procedure was used for **13α** to afford **14** in 91% yield. – *Rf* (hexane/EtOAc, 6:1) = 0.15. – M.p.: 76–78 °C. – ^1H NMR for **14α** (200 MHz, $CDCl_3$) δ: –0.04 (s, 3 H, CH_3), –0.03 (s, 3 H, CH_3), 0.84 (s, 9 H, *t*Bu), 3.35 (dd, $J_{2,3}$ = 10.1 Hz, $J_{2,1}$ = 3.5 Hz, 1 H, H_2), 3.49 (dd, $J_{6a,6b}$ = 10.1 Hz, $J_{6a,5}$ = 6.9 Hz, 1 H, H_{6a}), 3.54 (dd, $J_{4,3}$ = 8.5 Hz, $J_{4,5}$ = 9.7 Hz, 1 H, H_4), 3.69 (dd, $J_{6b,6a}$ = 10.1 Hz, $J_{6b,5}$ = 2.1 Hz, 1 H, H_{6b}), 3.81 (dd, $J_{3,2}$ = 10.1 Hz, $J_{3,4}$ = 8.5 Hz, 1 H, H_3), 4.04–4.14 (m, 1 H, H_5), 4.59 (dd, 2 H, CH_2Ph), 4.84 (dd, 2 H, CH_2Ph), 5.37 (bd, *J* = 3.2 Hz, 1 H, H_1), 7.28–7.41 (m, 10 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: –4.81, –4.74, –3.75, 17.93, 25.85, 64.45, 67.78, 69.25, 71.16, 71.65, 71.83, 73.34, 73.47, 74.99, 76.07, 77.18, 80.11, 83.10, 92.05, 96.30, 127.38, 127.44, 127.66, 127.77, 127.91, 128.22, 128.42, 137.71, 138.15. – $C_{26}H_{37}N_3O_5Si$: calcd. C 62.50, H 7.46, N 8.41; found C 62.80, H 7.08, N 8.15.

2-Azido-3,6-di-*O*-benzyl-4-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-glucopyranosyl Trichloracetimidate (15): To a solution of **14** (241 mg, 0.48 mmol) in CH_2Cl_2 (2.5 mL) at room temperature, were added trichloroacetonitrile (484 μL, 4.83 mmol) and flame-dried potassium carbonate (67 mg, 0.48 mmol). After 1 h 45 min, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and evaporated at reduced pressure. Silica gel column chromatography (hexane/EtOAc, 10:1) afforded **15α** (198 mg) and **15β** (85 mg, 7:3 ratio, 91% total yield). Data for **15β**: *Rf* (hexane/EtOAc, 6:1) = 0.43. – $[\alpha]_D$ = +28.5 (*c* = 2.10, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$) δ: 0.07 (s, 3 H, CH_3), 0.09 (s, 3 H, CH_3), 0.87 (s, 9 H, *t*Bu), 3.35 (dd, *J* = 9.6 Hz, *J* = 8.4 Hz, 1 H, H_4), 3.54–3.83 (m, 4 H, H_3, H_5, H_{6a}, H_{6b}), 3.69 (dd, $J_{2,3}$ = 10.6 Hz, $J_{2,1}$ =

8.3 Hz, 1 H, H_2), 4.59 (dd, 2 H, CH_2Ph), 4.86 (dd, 2 H, CH_2Ph), 5.71 (d, $J_{1,2}$ = 8.3 Hz, 1 H, H_1), 7.28–7.40 (m, 10 H, ArH), 8.80 (s, 1 H, NH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: –4.82, –3.83, 18.00, 25.92, 66.13, 68.27, 70.28, 73.23, 75.07, 77.64, 83.42, 96.95, 127.36, 127.47, 127.54, 128.30, 138.15, 138.34, 161.01. Data for **15α**: *Rf* (hexane/EtOAc, 6:1) = 0.38. – $[\alpha]_D$ = +94.7 (*c* = 1.38, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$) δ: 0.06 (s, 3 H, CH_3), 0.08 (s, 3 H, CH_3), 0.90 (s, 9 H, *t*Bu), 3.65–3.95 (m, 6 H, H_2, H_3, H_4, H_5, H_{6a}, H_{6b}), 4.57 (dd, 2 H, CH_2Ph), 4.89 (dd, 2 H, CH_2Ph), 6.50 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H_1), 7.32–7.41 (m, 10 H, ArH), 8.75 (s, 1 H, NH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: –4.83, –3.76, 18.00, 25.94, 63.68, 68.24, 70.48, 73.26, 74.90, 75.07, 80.38, 94.98, 127.34, 127.48, 128.22, 128.26, 137.90, 138.12, 160.81. – $C_{28}H_{37}Cl_3N_4O_5Si$: calcd. C 52.22, H 5.79, N 8.70; found C 52.51, H 5.45, N 8.48.

2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranose (16): To a solution of **11α** (80 mg, 0.168 mmol) in acetone (1.7 mL), cooled at –15 °C in the dark was added NBS (51.5 mg, 0.289 mmol). After stirring for 1 h 15 min, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$, diluted and extracted with EtOAc, washed with brine, and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 2:1), afforded **16** (62 mg, 96%) as a white solid, mixture of α/β (1:1) isomers. *Rf* (hexane/EtOAc, 2:1) = 0.41. – M.p.: 115–117 °C. – ^1H NMR ($CDCl_3$, 200 MHz) δ: 3.08 (bd, $J_{OH,1}$ = 3.0 Hz, 1 H, OH), 3.31 (dd, $J_{2,1}$ = 7.7 Hz, $J_{2,3}$ = 8.8 Hz, 1 H, $H_{2\alpha}$), 3.30–3.37 (m, 1 H, $H_{5\alpha}$), 3.39 (dd, $J_{2,1}$ = 3.7 Hz, $J_{2,3}$ = 10.0 Hz, 1 H, $H_{2\alpha}$), 3.51 (t, $J_{4,3}$ = $J_{4,5}$ = 9.2 Hz, 1 H, $H_{4\alpha}$), 3.60–3.73 (m, 4 H, $H_{3\beta}$, $H_{6\beta}$, 2× $H_{6\alpha}$), 3.98–4.07 (m, 2 H, $H_{6\alpha}$), 4.20 (dd, $J_{6,5}$ = 4.9 Hz, $J_{6,6'}$ = 10.3 Hz, 1 H, H_6), 4.24 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.5 Hz, 1 H, H_6), 4.50 (bdd, $J_{1,OH}$ = 3.1 Hz, $J_{1,2}$ = 7.8 Hz, 1 H, H_{1b}), 4.78 (dd, 2 H, CH_2Ph_β), 4.80 (dd, 2 H, CH_2Ph_α), 5.16 (bt, $J_{1,2}$ = $J_{1,OH}$ = 3.1 Hz, 1 H, $H_{1\alpha}$), 5.49 (s, 1 H, $H_{7\beta}$), 5.51 (s, 1 H, $H_{7\alpha}$), 7.16–7.44 (m, 10 H, ArH). – ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 62.7, 63.5, 66.3, 67.2, 68.4, 68.9, 74.9, 75.1, 76.2, 79.0, 81.4, 82.7, 92.7 (C-1α), 96.4 (C-1β), 101.3 (C-7), 101.4 (C-7), 125.9, 126.0, 127.9, 128.2, 128.3, 128.4, 129.1, 137.0, 137.1, 137.7.

2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosyl Trichloracetimidate (17): To a solution of **16** (177 mg, 0.46 mmol) in CH_2Cl_2 (2.5 mL) at room temperature, were added trichloroacetonitrile (463 μL, 4.62 mmol) and activated potassium carbonate (64 mg, 0.46 mmol). After 1 h 30 min, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and evaporated. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **17β** (99 mg) and **17α** and **17β** (125 mg, 1:5 mixture, respectively), (92% total yield, 1:10 α/β mixture). Data for **17β**: *Rf* (hexane/EtOAc, 4:1) = 0.45. – $[\alpha]_D$ = –59.9 (*c* = 0.99, $CHCl_3$). – ^1H NMR (200 MHz, $CDCl_3$) δ: 3.56–3.89 (m, 5 H, H_2, H_3, H_4, H_5, $H_{6'}$), 4.41 (dd, $J_{6,5}$ = 4.8 Hz, $J_{6,6}$ = 10.5 Hz, 1 H, H_6), 4.90 (dd, 2 H, CH_2Ph), 5.60 (s, 1 H, H_7), 5.70–5.74 (m, 1 H, H_1), 7.30–7.52 (m, 10 H, ArH), 8.77 (s, 1 H, NH). – ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 65.5, 66.9, 68.3, 74.9, 79.0, 81.1, 96.7 (C-1), 101.4 (C-7), 125.9, 127.9, 128.1, 128.2, 128.3, 129.1, 136.9, 137.6, 160.8. Data for **17α**: *Rf* (hexane/EtOAc, 4:1) = 0.36. – ^1H NMR (200 MHz, $CDCl_3$) δ: 3.60–3.88 (m, 3 H), 4.00–4.12 (m, 1 H, H_5), 4.19 (t, *J* = 9.5 Hz, 1 H), 4.35 (dd, $J_{6,5}$ = 4.7 Hz, $J_{6,6'}$ = 10.2 Hz, 1 H, H_6), 4.94 (dd, 2 H, CH_2Ph), 5.63 (s, 1 H, H_7), 6.38 (d, *J1,2* = 3.7 Hz, 1 H, H_1), 7.31–7.51 (m, 10 H, ArH), 8.75 (s, 1 H, NH).

6-*O*-[2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl]-2,3:4,5-di-*O*-cyclohexyliden-1-*O*-menthoxycarbonyl-1-D-*myo*-inositol (18α): A mixture of **17β** (56 mg, 0.11 mmol), **6** (23 mg, 0.04 mmol), and powdered 4Å molecular sieves in diethyl ether (1.1 mL) was stirred for 45 min at room temperature. At this time, a solution of trimethylsilyl triflate in diethyl ether (0.108 M, 76 μL, 0.008 mmol)) was added dropwise. The reaction mixture was stirred for 15 min, quenched with triethylamine, diluted with CH_2Cl_2, filtered through celite, and evaporated in vacuo. Silica gel column chromatography (hexane/EtOAc, 12:1) afforded **18** (37 mg, 95%) as a 10:1 α/β mixture of anomers. Data for **18α**: *Rf* (hexane/EtOAc, 6:1) = 0.38. – ^1H NMR (500 MHz, $CDCl_3$) δ: 0.77 (d, 3 H, CH_3Mnt), 0.88 (d, 3 H, CH_3Mnt), 0.92 (d, 3 H, CH_3Mnt), 1.04–1.12 (m, 2 H, Mnt), 1.27–1.74 (m, 25 H, cyclohex, Mnt), 1.90–2.02 (m, 1 H, Mnt), 2.10–2.18 (m, 1 H, Mnt), 3.41 (dd, $J_{2b,3b}$ = 9.8 Hz, $J_{2b,1b}$ = 3.9 Hz, 1 H, H_{2b}), 3.57 (dd, $J_{5a,4a}$ = 10.7 Hz, $J_{5a,6a}$ = 8.8 Hz, 1 H, H_{5a}), 3.72 (Ψt, $J_{4b,3b}$ = 9.3 Hz, $J_{4b,5b}$ = 9.8 Hz, 1 H, H_{4b}), 3.74 (t, $J_{6b,6b'}$ = $J_{6b,5b}$ = 10.0 Hz, 1 H, H_{6b}), 3.99 (dd, $J_{4a,5a}$ = 10.7 Hz, $J_{4a,3a}$ = 7.8 Hz, 1 H, H_{4a}), 4.05 (dd, $J_{6a,5a}$ = 8.8 Hz, $J_{6a,1a}$ = 2.9 Hz, 1 H, H_{6a}), 4.07 (Ψt, $J_{3b,4b}$ = 9.3 Hz, $J_{3b,2b}$ = 9.8 Hz, 1 H, H_{3b}), 4.14 (dt, $J_{5b,6b'}$ = 4.9 Hz, $J_{5b,6b}$ = 10.2 Hz, $J_{5b,4b}$ = 9.8 Hz, 1 H, H_{5b}), 4.31 (dd, $J_{6b',6b}$ = 10.0 Hz, $J_{6b',5b}$ = 5.1 Hz, 1 H, $H_{6b'}$), 4.39 (t, $J_{3a,2a}$ = $J_{3a,4a}$ = 7.3 Hz, 1 H, H_{3a}), 4.50–4.55 (m, 1 H, Mnt), 4.56 (dd, $J_{2a,3a}$ = 6.9 Hz, $J_{2a,1a}$ = 4.1 Hz, 1 H, H_{2a}), 4.86 (dd, 2 H, CH_2Ph), 4.95 (Ψt, $J_{1a,2a}$ = 3.9 Hz, $J_{1a,6a}$ = 2.9 Hz, 1 H, H_{1a}), 5.27 (d, $J_{1b,2b}$ = 3.9 Hz, 1 H, H_{1b}), 5.57 (s, 1 H, H_{7b}), 7.25–7.35 (m, 10 H, ArH). – ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 16.1, 20.7, 21.9, 23.2, 23.5, 23.7, 23.8, 24.9, 25.0, 26.0, 31.4, 34.0, 34.6, 36.2, 36.4, 36.6, 40.6, 47.0, 62.7, 62.8, 68.8, 73.1, 74.9, 76.2, 76.3, 76.4, 76.7, 79.0, 82.6, 97.5 (C-1b), 101.4 (C-7b), 112.1 (C_{ipso} cyclohex), 113.3 (C_{ipso} cyclohex), 125.9, 126.0, 127.8, 128.0, 128.2, 128.3, 128.4, 137.3, 137.9, 154.2.

6-*O*-[2-Azido-3,6-di-*O*-benzyl-4-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-α-D-glucopyranosyl]-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-menthoxycarbonyl-1-D-*myo*-inositol (19α): A mixture of **15β** (180 mg, 0.28 mmol), **6** (73 mg, 0.14 mmol), and powdered 4Å molecular sieves in diethyl ether (3 mL) was stirred for 45 min at room temperature. At this time, a solution of trimethylsilyl triflate in diethyl ether (0.108 M, 194 μL, 0.02 mmol) was added dropwise over 45 min. The reaction mixture was stirred for 15 min, quenched with triethylamine, diluted with CH_2Cl_2, filtered through celite, and evaporated in vacuo. Silica gel column chromatography (hexane/EtOAc) afforded **19** (102 mg, 73%) as a 9:1 α/β mixture of anomers. Data for **19α**. *Rf* (hexane/EtOAc, 3:1) = 0.76. – M.p.: 72–74 °C. $[\alpha]_D$ = +47.2 (*c* = 1.36, $CHCl_3$). – ^1H NMR (500 MHz, $CDCl_3$) δ: –0.03 (s, 3 H, CH_3Si), 0.02 (s, 3 H, CH_3Si), 0.76 (d, 3 H, Mnt), 0.86 (s, 9 H, *t*Bu), 0.87 (d, 3 H, CH_3Mnt), 0.92 (d, 3 H, CH_3Mnt), 1.00–1.10 (m, 2 H, Mnt), 1.20–1.70 (m, 25 H, cyclohex., Mnt), 1.90–1.97 (m, 1 H, Mnt), 2.07–2.13 (m, 1 H, Mnt), 3.32 (dd, $J_{2b,3b}$ = 9.8 Hz, $J_{2b,1b}$ = 3.4 Hz, 1 H, H_{2b}), 3.59 (dd, $J_{5a,4a}$ = 10.7 Hz, $J_{5a,6a}$ = 8.8 Hz, 1 H, H_{5a}), 3.64 (dd, $J_{6b,6b'}$ = 10.9 Hz, $J_{6b,5b}$ = 1.9 Hz, 1 H, H_{6b}), 3.72 (dd, $J_{6b',6b}$ = 10.9 Hz, $J_{6b',5b}$ = 3.7 Hz, 1 H, $H_{6b'}$), 3.76 (Ψt, $J_{3b,4b}$ = $J_{3b,2b}$ = 9.8 Hz, 1 H, H_{3b}), 3.81 (Ψt, $J_{4b,3b}$ = $J_{4b,5b}$ = 9.8 Hz, 1 H, H_{4b}), 3.98 (dd, $J_{4a,5a}$ = 10.7 Hz, $J_{4a,3a}$ = 7.3 Hz, 1 H, H_{4a}), 3.98–4.02 (m, 1 H, H_{5b}), 4.14 (dd, $J_{6a,5a}$ = 8.8 Hz, $J_{6a,1a}$ = 3.4 Hz, 1 H, H_{6a}), 4.37 (t, $J_{3a,2a}$ = $J_{3a,4a}$ = 7.3 Hz, 1 H, H_{3a}), 4.52 (dt, 1 H, Mnt), 4.55 (dd, 2 H, CH_2Ph), 4.58 (dd, $J_{2a,3a}$ = 7.3 Hz, $J_{2a,1a}$ = 3.4 Hz, 1 H, H_{2a}), 4.82 (dd, 2 H, CH_2Ph), 5.00 (t, $J_{1a,2a}$ = $J_{1a,6a}$ = 3.4 Hz, 1 H, H_{1a}), 5.31 (d, $J_{1b,2b}$ = 3.4 Hz, 1 H, H_{1b}), 7.25–7.35 (m, 10 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: –4.95, –3.65, 16.13, 18.04, 20.76, 21.92, 23.22, 23.52, 23.63, 23.83, 23.90, 24.90, 25.06, 25.92, 31.43, 34.09, 34.53, 36.33, 36.65, 40.62, 47.01, 63.46, 68.40, 70.66, 72.14, 73.26, 74.51, 76.21, 76.55, 76.71, 77.18, 79.21, 80.39, 96.80, 112.06, 113.23, 127.30, 127.42, 128.24, 138.26, 154.14. – $C_{55}H_{81}N_3O_{12}Si$: calcd. C 65.77, H 8.13, N 4.28; found C 65.72, H 8.40, N 4.28.

6-*O*-(2-Azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-menthoxycarbonyl-1-D-*myo*-inositol (20α): To a solution of **19α** (82 mg, 0.08 mmol) in THF (0.8 mL)

was added a solution of tetrabutylammonium fluoride in THF (1 M, 204 μL, 0.24 mmol). The reaction mixture was stirred for 45 min, quenched with water, diluted and extracted with CH_2Cl_2, and washed with brine. Silica gel column chromatography (hexane/EtOAc, 6:1) afforded **20α** (61 mg, 84%). *Rf* (hexane/EtOAc, 3:1) = 0.46. – M.p.: 74–76 °C. $[\alpha]_D$ = +25.9 (*c* = 0.99, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.77 (d, 3 H, Mnt), 0.89 (d, 3 H, CH_3Mnt), 0.93 (d, 3 H, CH_3Mnt), 0.99–1.17 (m, 2 H, Mnt), 1.23–1.75 (m, 25 H, cyclohex., Mnt), 1.87–2.05 (m, 1 H, Mnt), 2.07–2.20 (m, 1 H, Mnt), 2.75 (d, $J_{OH,4b}$ = 2.2 Hz, 1 H, OH), 3.35 (dd, $J_{2b,3b}$ = 9.9 Hz, $J_{2b,1b}$ = 3.6 Hz, 1 H, H_{2b}), 3.57 (dd, $J_{5a,4a}$ = 10.8 Hz, $J_{5a,6a}$ = 8.5 Hz, 1 H, H_{5a}), 3.67 (dd, $J_{6b,b'}$ = 10.1 Hz, $J_{6b,5b}$ = 4.9 Hz, 1 H, H_{6b}), 3.77–3.86 (m, 3 H), 4.00 (dd, $J_{4a,5a}$ = 10.8 Hz, $J_{4a,3a}$ = 7.4 Hz, 1 H, H_{4a}), 4.01–4.09 (m, 1 H), 4.06 (dd, $J_{6a,5a}$ = 8.5 Hz, $J_{6a,1a}$ = 2.6 Hz, 1 H, H_{6a}), 4.40 (t, $J_{3a,4a}$ = $J_{3a,2a}$ = 7.2 Hz, 1 H, H_{3a}), 4.46–4.60 (m, 2 H, H_{2a}, Mnt), 4.58 (dd, 2 H, CH_2Ph), 4.89 (dd, 2 H, CH_2Ph), 4.99 (dd, $J_{1a,2a}$ = 3.9 Hz, $J_{1a,6a}$ = 2.6 Hz, 1 H, H_{1a}), 5.26 (d, $J_{1b,2b}$ = 3.6 Hz, 1 H, H_{1b}), 7.29–7.45 (m, 10 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 16.12, 20.73, 21.92, 23.22, 23.50, 23.65, 23.81, 23.88, 24.94, 25.04, 25.98, 31.42, 34.07, 34.55, 36.23, 36.49, 36.57, 40.61, 46.98, 62.50, 69.67, 70.50, 72.85, 73.16, 73.74, 76.19, 76.55, 76.70, 79.23, 79.72, 97.15, 112.12, 113.24, 127.66, 127.83, 127.90, 128.00, 128.44, 128.53, 137.69, 138.21, 154.16. – $C_{49}H_{67}N_3O_{12}$: calcd. C 66.12, H 7.59, N 4.72; found C 65.91, H 7.67, N 4.52.

1,6-Anhydro-3-*O*-(4-methoxybenzyl)-β-D-mannopyranose (23): To a solution of 1,6-anhydro-2,3-*O*-*endo*-(4-methoxybenzylidene)-β-D-mannopyranose[36] (3.5 g, 12.5 mmol) in CH_2Cl_2 (125 mL) at 0 °C was added slowly a solution of DIBALH in toluene (1 M, 40 mL, 40 mmol). After 5 h, Et_3N and MeOH were added. The crude reaction mixture was diluted with EtOAc, washed with a solution of HCl (10%), and extracted with EtOAc. The organic layers were evaporated and the crude was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20:1) affording **23** (2.8 g, 79%). – *Rf* (CH_2Cl_2/MeOH, 20:1) = 0.16. – M.p. 108–110 °C. – $[\alpha]_D$ = –66.8 (*c* = 0.72, $CHCl_3$). – ^{1}H NMR (acetone, 200 MHz) δ: 2.88 (s, 1 H, OH), 3.33 (d, 1 H, OH), 3,56 (bt, 1 H, H-6), 3.62–3.68 (m, 1 H, H_2), 3.78 (s, 3 H, CH_3O), 3.92 (d, 1 H, H_3), 4.08 (d, 1 H, $H_{6'}$), 4.27 (d, 1 H, H_4), 4.40 (d, 1 H, H_5), 4.56 (dd, 2 H, CH_2Ph), 5.12 (br. s, 1 H, H_1), 6.91 (d, 2 H, ArH), 7.31 (d, 2 H, ArH). – ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 55.1, 64.5, 65.8, 69.0, 73.4, 75.7, 78.0, 101.8 (C-1), 129.2, 129.3, 129.5, 158.4.

1,6-Anhydro-2,4-di-*O*-benzyl-3-*O*-(4-methoxybenzyl)-β-D-mannopyranose (24): To a solution of **23** (2.4 g, 8.5 mmol) in DMF (20 mL) at room temperature were added NaH (472 mg, 18.7 mmol) and BnBr (1.9 mL, 25.5 mmol). After 2 h, MeOH was added and the reaction mixture was diluted with EtOAc, washed with H_2O, dried with Na_2SO_4, and evaporated. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **24** (3.9 g, quantitative yield). *Rf* (hexane/EtOAc, 2:1) = 0.31. – M.p. 68–70 °C. $[\alpha]_D$ = –20.3 (*c* = 0.84, $CHCl_3$). – ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 3.48 (bt, 1 H, H_4), 3.60 (dd, $J_{2,1}$ = 1.7 Hz, $J_{2,3}$ = 5.3 Hz, 1 H, H_2), 3.66 (dd, $J_{6,6'}$ = 7.0 Hz, $J_{6,5}$ = 6.0 Hz, 1 H, H_6), 3.74 (s, 3 H, CH_3O), 3.74–3.80 (m, 1 H, H_3), 4.18 (dd, $J_{6',5}$ = 0.9 Hz, $J_{6',6}$ = 7.1 Hz, 1 H, $H_{6'}$), 4.35–4.56 (m, 7 H, H_5, 3 CH_2Ph), 5.41 (bt, 1 H, H_1), 6.89 (d, 2 H, ArH), 7.26–7.40 (m, 12 H, ArH). – ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 55.1, 64.8, 71.1, 71.2, 72.7, 73.9, 74.4, 76.4, 100.0 (C-1), 127.5, 127.6, 127.8, 128.2, 128.3, 129.7, 137.6, 137.9, 159.2.

1,6-Di-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-(4-methoxybenzyl)-α-D-mannopyranose (25): A solution of **24** (94.88 g, 10.55 mmol) and trimethylsilyltrifluoromethanesulfonate (240 μL, 1.24 mmol) in acetic anhydride (33 mL) was stirred for 1 h at 0 °C and for 2 h at room temperature. The reaction mixture was diluted with EtOAc, carefully washed with a saturated aqueous solution of $NaHCO_3$, extracted with EtOAc, and dried with Na_2SO_4. Silica gel column chromatography afforded **25α** (4.72 g, 79%) and **25β (**169 mg, 3%). – Data for **25α**: *Rf* (hexane/EtOAc, 2:1) = 0.36. – $[\alpha]_D$ = +28.1 (*c* = 0.78, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.04 (s, 3 H, CH_3CO), 2.05 (s, 3 H, CH_3CO), 3.72 (Ψt, $J_{2,1}$ = $J_{2,3}$ = 2.4 Hz, 1 H, H_2), 3.81 (s, 3 H, CH_3O), 3.82–4.03 (m, 3 H, H_3, H_4, H_5), 4.30–4.33 (m 2 H, H_{6a}, H_{6b}), 4.54 (s, 2 H, CH_2Ph), 4.75 (dd, 2 H, CH_2Ph), 4.77 (dd, 2 H, CH_2Ph), 6.18 (d, $J_{1,2}$ = 2.1 Hz, 1 H, H_1), 6.83–7.40 (m, 14 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 20.79, 20.91, 55.24, 63.17, 71.71, 72.39, 73.38, 73.80, 75.25, 78.77, 91.65, 113.80, 113.95, 127.78, 127.86, 128.11, 128.35, 128.42, 129.37, 130.04, 137.78, 138.00. – $C_{32}H_{36}O_9$: calcd. C 68.08, H 6.43; found C 68.29, H 6.12. – Data for **25β**: *Rf* (hexane/EtOAc, 2:1) = 0.31. – $[\alpha]_D$ = +0.7 (*c* = 4.22, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.05 (s, 3 H, CH_3CO), 2.09 (s, 3 H, CH_3CO), 3.55–3.66 (m, 1 H, H_5), 3.63 (dd, $J_{3,2}$ = 2.8 Hz, $J_{3,4}$ = 9.1 Hz, 1 H, H_3), 3.82 (s, 3 H, CH_3O), 3.87–3.96 (m, 2 H, H_2, H_4), 4.30–4.35 (m 2 H, H_{6a}, H_{6b}), 4.57 (dd, 2 H, CH_2Ph), 4.76 (dd, 2 H, CH_2Ph), 4.87 (s, 2 H, CH_2Ph), 5.60 (d, $J_{1,2}$ = 0.9 Hz, 1 H, H_1), 6.84–7.48 (m, 14 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 14.10, 20.80, 20.93, 55.16, 60.27, 63.25, 71.78, 73.37, 73.81, 74.07, 74.36, 75.03, 81.75, 92.92, 113.81, 127.61, 127.79, 128.00, 128.10, 128.14, 128.35, 129.24, 129.76, 137.83, 138.16, 159.28, 168.8, 170.74. – $C_{32}H_{36}O_9$: calcd. C 68.08, H 6.43; found C 67.84, H 6.71.

1,6-Di-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranose (26): To a solution of **25** (100 mg, 0.18 mmol) in CH_2Cl_2 (1.5 mL) was added trifluoroacetic acid (50 μL) in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 3 h at room temperature, neutralized with a saturated aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2, and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **26** (77 mg, 98%). *Rf* (hexane/EtOAc, 2:1) = 0.24. – $[\alpha]_D$ = +29.7 (*c* = 1.52, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.08 (s, 3 H, CH_3CO), 2.09 (s, 3 H, CH_3CO), 2.43 (d, $J_{OH,3}$ = 9.7 Hz, 1 H, OH), 3.68 (t, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, 1 H, H_4), 3.74 (dd, $J_{2,3}$ = 3.8 Hz, $J_{2,1}$ = 1.8 Hz, 1 H, H_2), 3.88 (dd., $J_{5,4}$ = 9.8 Hz, $J_{5,6a}$ = 4.6 Hz, $J_{5,6b}$ = 2.3 Hz, 1 H, H_5), 4.01 (dt, $J_{3,4}$ = $J_{3,OH}$ = 9.6 Hz, $J_{3,2}$ = 3.8 Hz, 1 H, H_3), 4.30 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{6a,5}$ = 4.6 Hz, 1 H, H_{6a}), 4.38 (dd, $J_{6b,6a}$ = 12.0 Hz, $J_{6b,5}$ = 2.3 Hz, 1 H, H_{6b}), 4.71 (dd, 2 H, CH_2Ph), 4.78 (dd, 2 H, CH_2Ph), 6.27 (d, $J_{1,2}$ = 1.8 Hz, 1 H, H_1), 7.30–7.41 (m, 10 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 20.80, 20.91, 63.14, 71.47, 71.62, 72.67, 75.05, 75.63, 76.78, 90.73, 127.98, 128.11, 128.25, 128.48, 128.64, 128.64, 137.15, 137.91, 168.91, 170.74. – $C_{24}H_{28}O_8$: calcd. C 64.86, H 6.35; found C 64.44, H 6.38.

1,6-Di-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranose (27): To a solution of **26** (1.40 g, 3.15 mmol), 4-dimethylaminopyridine (170 mg, 1.39 mmol) and imidazole (857 mg, 12.60 mmol) in DMF (5 mL), was added *tert*-butyldiphenylsilyl chloride (1.64 mL, 6.30 mmol). The reaction mixture was stirred for 17 h at room temperature, diluted with diethyl ether, washed with water and brine and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 10:1, 4:1) afforded **27** (1.91 g, 89%). *Rf* (hexane/EtOAc, 2:1) = 0.55. – M.p. 107–109 °C. – $[\alpha]_D$ = +44.8 (*c* = 1.13, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.14 (s, 9 H, *t*Bu), 1.89 (s, 3 H, CH_3CO), 2.04 (s, 3 H, CH_3CO), 3.03 (br. s, 1 H, H_2), 3.85 (ddd, $J_{5,4}$ = 9.6 Hz, $J_{5,6a}$ = 4.3 Hz, $J_{5,6b}$ = 2.2 Hz, 1 H, H_5), 4.07 (bt, $J_{4,3}$ = $J_{4,5}$ = 9.2 Hz, 1 H, H_4), 4.22–4.37 (m, 2 H, H_{6a}, H_{6b}), 4.32 (dd, $J_{3,4}$ = 8.9 Hz, $J_{3,2}$ = 3.1 Hz, 1 H, H_3), 4.42 (dd, 2 H, CH_2Ph), 4.58–4.72 (bm, 1 H, CH_2Ph), 4.99–5.12 (bm, 1 H, CH_2Ph), 5.95 (d, $J_{1,2}$ = 2.1 Hz, 1 H, H_1), 7.24–7.77 (m, 20 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 19.32, 20.81,

27.06, 63.22, 72.05, 72.69, 72.99, 75.23, 76.36, 77.05, 91.30, 127.21, 127.31, 127.46, 127.66, 127.72, 127.77, 128.00, 128.18, 128.38, 129.83, 130.03, 133.12, 134.13, 135.92, 136.08, 137.86, 138.16. – $C_{40}H_{46}O_8Si$: calcd. C 70.36, H 6.79; found C 70.61, H 6.77.

Phenyl 6-*O*-Acetyl-2,4-di-*O*-benzyl-3-*O*-(*tert*-butyldiphenylsilyl)-1-thio-α-D-mannopyranoside (28α): To a solution of **27** (1.80 g, 2.64 mmol) in CH_2Cl_2 (26 mL) at room temperature were added thiophenol (592 μL, 4.80 mmol) and boron trifluoride–diethyl ether (1.32 mL, 10.5 mmol). The reaction mixture was stirred for 30 min, quenched with a saturated aqueous solution of $NaHCO_3$ and the organic layer dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 10:1) afforded **28α** (1.735 g) and **28β** (115 mg) in a total yield of 97% (15:1 α/β ratio). Data for **28α**. *Rf* (hexane/EtOAc, 5:1) = 0.40. – $[\alpha]_D$ = +126.1 (*c* = 1.21, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.17 (s, 9 H, *t*Bu), 2.02 (s, 3 H, CH_3CO), 3.29 (m, 1 H, H_2), 3.97–4.07 (m, 1 H, H_4), 4.21–4.37 (m, 5 H, H_5, H_{6a}, H_{6b}, CH_2Ph), 4.37 (dd, $J_{3,4}$ = 8.8 Hz, $J_{3,2}$ = 2.8 Hz, 1 H, H3), 4.59–4.68 (bm, 1 H, CH_2Ph), 4.97–5.18 (bm, 1 H, CH_2Ph), 5.26 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H_1), 7.21–7.84 (m, 25 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 19.32, 20.79, 27.17, 29.67, 63.57, 71.03, 71.83, 74.04, 74.08, 75.25, 76.13, 77.19, 79.59, 85.23, 127.28, 127.36, 127.42, 127.27, 127.76, 127.89, 127.97, 128.17, 128.26, 128.36, 128.81, 129.82, 129.96, 131.62, 133.11, 134.31, 136.08, 138.00, 138.26, 170.72. – $C_{44}H_{48}O_6SSi$: calcd. C 72.10, H 6.60, S 4.37; found C 72.31, H 6.35, S 4.12.

Phenyl 2,4-Di-*O*-benzyl-3-*O*-(*tert*-butyldiphenylsilyl)-1-thio-α-D-mannopyranoside (29): To a solution of **28α** (100-mg, 0.14 mmol) in methanol (2 mL), was added sodium methoxide in methanol (1 M, 0.4 mL). The reaction mixture was stirred for 1 h at room temperature, neutralized with Amberlite IR-120 H^+, filtered, and evaporated. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **29** (95 mg, quantitative yield). *Rf* (hexane/EtOAc, 3:1) = 0.46. – M.p. 46–48 °C. – $[\alpha]_D$ = +131.1 (*c* = 1.17, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.16 (s, 9 H, *t*Bu), 3.32 (m, 1 H, H_2), 3.77–3.81 (m, 2 H), 4.05–4.08 (m, 2 H, H_4), 4.32 (dd, 2 H, CH_2Ph), 4.38 (dd, $J_{3,4}$ = 8.8 Hz, $J_{3,2}$ = 3.1 Hz, 1 H, H_3), 4.62–4.77 (bm, 1 H, CH_2Ph), 4.97–5.10 (bm, 1 H, CH_2Ph), 5.20 (d, $J_{1,2}$ = 1.7 Hz, 1 H, H_1), 7.21–7.84 (m, 25 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 19.31, 27.16, 62.21, 72.24, 73.34, 73.89, 75.16, 76.02, 127.39, 127.41, 127.63, 127.71, 127.88, 128.23, 128.33, 128.90, 129.77, 129.92, 131.66, 133.21, 134.46, 136.07, 138.27. – $C_{42}H_{46}O_5SSi$: calcd. C 73.10, H 6.71, S 4.64; found C 73.12, H 6.43, S 4.37.

3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranosyl Fluoride (30): To a solution of phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[46] (100 mg, 0.17 mmol) in CH_2Cl_2 (1.7 mL) at –15 °C, diethylaminosulfur trifluoride (68 μL, 0.52 mmol) was added dropwise, followed by NBS (46 mg, 0.26 mmol). The reaction mixture was stirred for 4 h 30 min, quenched with a saturated solution of $NaHCO_3$ in water/ice, extracted with CH_2Cl_2, and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 4:1) afforded **30** in quantitative yield. *Rf* (toluene-EtOAc, 10:1) = 0.56. – M.p.: 173–175 °C. – $[\alpha]_D$ = +62.0 (*c* = 0.99, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.60–3.78 (m, 1 H), 3.84–3.96 (m, 2 H), 4.24–4.52 (m, 3 H), 4.65 (dd, 2 H, CH_2Ph), 5.64 (s, 1 H, H_7), 5.90 (dd, 1 H, $J_{F,1}$ = 53.4 Hz, $J_{1,2}$ = 7.6 Hz, H_1), 6.84–7.80 (m, 14 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 41.98, 55.57, 55.98, 65.72, 65.82, 68.36, 73.74, 73.93, 74.15, 82.36, 101.48, 102.93, 107.22, 123.49, 126.04, 127.52, 128.07, 128.30, 129.12, 131.51, 134.04, 137.04, 137.62. – $C_{28}H_{24}FNO_6$: calcd. C 68.70, H 4.94, N 2.86; found C 68.48, H 5.10, N 2.85.

Phenyl *O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-α-D-glucopyranosyl)-(1→6)-2,4-di-*O*-benzyl-3-*O*-(*tert*-butyldiphenylsilyl)-1-thio-α-D-mannopyranoside (31): A mixture of **29** (475 mg, 0.688 mmol), zirconocene dichloride (800 mg, 2.68 mmol), silver triflate (1.39 g, 5.37 mmol), and powdered 4Å molecular sieves in CH_2Cl_2 (14 mL) was stirred in the dark and at room temperature for 30 min. At this time, the reaction mixture was cooled to –40 °C and **30** (437 mg, 1.3 mmol) in CH_2Cl_2 (6 mL) was added dropwise over 30 min. After stirring for 1 h 30 min, the mixture was quenched with a saturated aqueous solution of $NaHCO_3$, diluted with CH_2Cl_2, washed with brine, dried with Na_2SO_4, concentrated, and purified by chromatography (diethyl ether/cyclohexane, 1:2) to yield **31** (654 mg, 82%). *Rf* (hexane/EtOAc, 3:1) = 0.36. – M.p. 82–85 °C. – $[\alpha]_D$ = +89.6 (*c* = 0.95, $CHCl_3$). – ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.99 (s, 9 H, *t*Bu), 3.15 (br. s, 1 H, H_{2d}), 3.61 (dt, $J_{5d,4d}$ = $J_{5d,6d}$ = 9.8 Hz, $J_{5d,6d'}$ = 4.9 Hz, 1 H, H_{5d}), 3.70–3.79 (m, 4 H), 3.99–4.08 (m, 3 H), 4.17–4.25 (m, 3 H), 4.30–4.36 (m, 2 H), 4.41–4.54 (m, 2 H), 4.63 (dd, 2 H, CH_2Ph), 5.13 (br. s, 1 H, H_c), 5.29 (d, $J_{1d,2d}$ = 8.3 Hz, 1 H, H_{1d}), 5.56 (s, 1 H, H_{7d}), 7.18–7.66 (m, 39 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 19.21, 27.09, 55.57, 66.12, 68.48, 68.70, 71.57, 72.17, 73.72, 74.03, 74.63, 75.91, 76.66, 76.81, 77.20, 77.42, 78.00, 78.15, 79.58, 82.97, 85.27, 99.00, 101.30, 123.21, 126.07, 126.94, 127.18, 127.31, 127.51, 127.60, 127.99, 128.19, 128.27, 128.80, 128.97, 129.63, 129.84, 131.13, 131.65, 133.17, 133.59, 134.35, 134.89, 136.03, 137.42, 138.00, 138.31. – $C_{70}H_{69}NO_{11}SSi$: calcd. C 72.45, H 5.99, N 1.21, S 2.76; found C 72.21, H 6.10, N 1.29, S 2.57.

***O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-2,4-di-*O*-benzyl-3-*O*-(*tert*-butyl-diphenylsilyl)-α-D-mannopyranose (32):** To a solution of **31** (105 mg, 0.09 mmol) in acetone (1.8 mL) in the dark at –15 °C, NBS (24 mg, 0.14 mmol) was added. Ten minutes later, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$, diluted and extracted with EtOAc, washed with brine, and dried. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **31** (91 mg, 94%). *Rf* (hexane/EtOAc, 3:1) = 0.15. – M.p. 74–76 C. – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.04 (s, 9 H, *t*Bu), 2.60 (d, $J_{OH,1c}$ = 2.5 Hz, 1 H, OH), 3.03 (Ψt, $J_{2c,1c}$ = $J_{2c,3c}$ = 2.8 Hz, 1 H, H_{2c}), 3.41–3.90 (m, 7 H), 4.11–4.80 (m, 12 H), 5.55 (d, $J_{1d,2d}$ = 8.3 Hz, 1 H, H_{1d}), 5.60 (s, 1 H, H_{7d}), 7.10–7.71 (m, 34 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 19.22, 27.18, 55.88, 66.13, 68.19, 68.85, 72.51, 72.79, 73.21, 74.01, 74.36, 74.57, 74.65, 75.79, 76.67, 77.20, 77.40, 78.19, 78.32, 83.26, 92.32, 98.86, 101.38, 123.24, 126.09, 127.34, 127.48, 127.62, 127.68, 127.80, 128.19, 128.01, 128.15, 128.26, 128.97, 129.56, 129.69, 129.83, 131.56, 131.63, 133.53, 133.76, 133.91, 134.37, 136.12, 137.44, 137.80, 137.98, 138.59. – $C_{64}H_{65}NO_{12}Si$: calcd. C 71.96, H 6.13, N 1.31; found C 71.71, H 5.85, N 1.37.

***O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-2,4-di-*O*-benzyl-3-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl Trichloracetimidate (33):** To a solution of **32** (53 mg, 0.05 mmol) in CH_2Cl_2 (0.25 mL) at room temperature, were added trichloroacetonitrile (50 μL, 0.50 mmol) and flame-dried potassium carbonate (7 mg, 0.05 mmol). After 4 h, the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and evaporated. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **33** (53 mg, 88%) as a 13:1 α/β mixture. – Data for **33α**: *Rf* (hexane/EtOAc, 3:1) = 0.36. – M.p. 76–78 °C. – $[\alpha]_D$ = +34.2 (*c* = 0.61, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.02 (s, 9 H, *t*Bu), 3.21 (m, 1 H, H_2), 3.56–3.87 (m, 6 H), 4.04–4.62 (m, 9 H), 4.64 (dd, 2 H, CH_2Ph), 5.28 (d, $J_{1d,2d}$ = 8.2 Hz, 1 H, H_{1d}), 5.60 (s, 1 H, H_{7d}), 5.74 (m, 1 H, H_{1c}), 7.10–7.65 (m, 34 H, ArH), 8.09 (s, 1 H, NH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 19.23, 27.13, 55.69, 66.09, 68.84, 72.19, 72.96, 73.87, 74.02, 74.76, 75.54, 76.23, 83.04, 95.81, 99.22, 101.32, 123.19, 126.08, 127.23, 127.29, 127.52, 127.67, 127.97, 128.19, 128.25, 128.96, 129.59, 129.80, 131.72,

133.08, 133.51, 134.27, 136.02, 137.44, 137.85, 138.04, 138.33, 159.80, 167.54. – $C_{66}H_{65}Cl_3N_2O_{12}Si$: calcd. C 65.37, H 5.40, N 2.31; found C 65.10, H 5.10, N 2.07.

Phenyl 6-*O*-Acetyl-2-*O*-benzyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside (36): To a solution of phenyl 2-*O*-benzyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside (**35**)[45] (193 mg, 0.48 mmol) in pyridine (0.77 mL) and DMAP (cat.) at 0 °C, was added dropwise acetic anhydride (0.11 mL, 1.20 mmol). After stirring for 5 min at 0 °C, and for 90 min at room temperature, the reaction mixture was evaporated. Silica gel column chromatography (hexane/EtOAc, 4:1) of the crude afforded **36** (213 mg, quantitative yield). *Rf* (hexane/EtOAc, 3:1) = 0.35. – $[\alpha]_D$ = +9.2 (c = 1.10, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.35 (s, 3 H, *i*Pr), 1.41 (s, 3 H, *i*Pr), 2.06 (s, 3 H, Ac), 3.54 (dd, $J_{2,3}$ = 6.2 Hz, $J_{2,1}$ = 9.4 Hz, 1 H, H_2), 3.94 (dt, $J_{5,4}$ = 2.1 Hz, $J_{5,6}$ = 6.0 Hz, 1 H, H_5), 4.19 (dd, $J_{4,5}$ = 2.0 Hz, $J_{4,3}$ = 5.8 Hz, 1 H, H_4), 4.28 (t, $J_{3,4}$ = $J_{3,2}$ = 6.0 Hz, 1 H, H_3), 4.34 (d, $J_{6,5}$ = 6.1 Hz, 2 H, H_{6a}, H_{6b}), 4.63 (d, $J_{1,2}$ = 9.4 Hz, 1 H, H_1), 4.76 (dd, 2 H, CH_2Ph), 7.25–7.57 (m, 10 H, ArH). – ^{13}C NMR (50 MHz, C_6D_6) δ: 20.33, 26.29, 27.73, 63.92, 73.52, 73.89, 74.42, 78.81, 79.89, 86.38, 110.27, 127.52, 127.83, 128.28, 128.92, 129.62, 130.02, 130.24, 132.58, 134.82, 138.73, 169.87. – $C_{24}H_{28}O_6S$: calcd. C 64.85, H 6.35, S 7.21; found C 65.17, H 6.08, S 7.25.

6-*O*-Acetyl-2-*O*-benzyl-3,4-*O*-isopropylidene-D-galactopyranose (37): To a solution of **36** (115 mg, 0.259 mmol) in acetone (5 mL) at –15 °C were added NBS (60 mg, 0.336 mmol) and water (5 μL, 0.284 mmol). After stirring for 10 min, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$, diluted and extracted with EtOAc, washed with brine, and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **37** (86 mg, 94%). *Rf* (hexane/EtOAc, 2:1) = 0.17. – M.p. 122–124 °C. – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.34 (s, 3 H, $i\mathrm{Pr}_{\alpha+\beta}$), 1.43 (s, 3 H, $i\mathrm{Pr}_{\alpha}$), 1.46 (s, 3 H, $i\mathrm{Pr}_{\beta}$), 2.09 (s, 3 H, Ac_{α}), 2.10 (s, 3 H, Acβ), 3.32 (d, $J_{OH,1}$= 6.4 Hz, 1 H, OH), 3.52 (t, $J_{2,1}$ = $J_{2,3}$ = 5.5 Hz, 1 H, $H_{2\alpha}$), 3.67 (dd, $J_{2,1}$ = 3.8 Hz, $J_{2,3}$ = 5.7 Hz, 1 H, $H_{2\alpha}$), 4.08 (ddd, J = 2.1 Hz, J = 4.8 Hz, J = 7.0 Hz, 1 H, $H_{5\alpha}$), (dt, J = 4.3 Hz, J = 1.6 Hz, 1 H, $H_{5\alpha}$), 4.21–4.39 (m, 4 H, $H_{3\alpha}$, H_4, H_{6a}, H_{6b}), 4.45 (t, J = 6.0 Hz, 1 H, $H_{3\alpha}$), 4.75 (dd, 2 H, CH_2Ph), 4.85 (dd, $J_{1,OH}$ = 5.4 Hz, $J_{1,2}$ = 7.9 Hz, 1 H, $H_{1\alpha}$), 5.22 (dd, $J_{1,2}$ = 3.8 Hz, $J_{3,OH}$ = 6.3 Hz, 1 H, $H_{1\alpha}$), 7.29–7.39 (m, 5 H, ArH). – ^{13}C NMR (50 MHz, C_6D_6) δ: 13.38, 20.90, 25.58, 25.75, 27.15, 27.24, 63.74, 63.89, 66.85, 70.14, 72.96, 73.17, 73.41, 74.07, 75.36, 78.46, 90.57, 95.66, 109.95, 110.33, 127.92, 128.03, 128.18, 128.46, 128.58, 137.41, 137.70, 170.84. – $C_{18}H_{24}O_7$: calcd. C 61.36, H 6.86; found C 61.14, H 6.66.

6-*O*-Acetyl-2-*O*-benzyl-3,4-*O*-isopropylidene-D-galactopyranosyl Trichloracetimidate (38): To a solution of **37** (81 mg, 0.230 mmol) in CH_2Cl_2 (1.2 mL) at room temperature, were added trichloroacetonitrile (230.5 μL, 2.30 mmol) and flame-dried potassium carbonate (76 mg, 0.552 mmol). After 5 h 45 min, the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and evaporated. Silica gel column chromatography (hexane/EtOAc, 6:1) afforded **38α** (29 mg) and **38β** (76 mg) (92% total yield). – Data for **38β**: *Rf* (hexane/AcOEt, 3:1) = 0.17. – ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.35 (s, 3 H, *i*Pr), 1.42 (s, 3 H, *i*Pr), 2.08 (s, 3 H, Ac), 3.70 (dd, $J_{2,3}$ = 6.3 Hz, $J_{2,1}$ = 7.3 Hz, 1 H, H-2), 4.12–4.17 (m, 1 H, H-5), 4.23 (dd, $J_{4,5}$ = 2.2 Hz, $J_{4,3}$ = 5.9 Hz, 1 H, H-4), 4.30–4.38 (m, 3 H, H-3, H-6a, H-6b), 4.34 (dd, 2 H, CH_2Ph), 5.76 (d, $J_{1,2}$ = 7.6 Hz, 1 H, H-1), 7.28–7.40 (m, 5 H, ArH), 8.66 (s, 1 H, NH). – Data for **38α**: *Rf* (hexane/AcOEt, 3:1) = 0.37. – ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.35 (s, 3 H, *i*Pr), 1.41 (s, 3 H, *i*Pr), 2.05 (s, 3 H, Ac), 3.81 (dd., $J_{2,3}$ = 6.8 Hz, $J_{2,1}$ = 3.5 Hz, 1 H, H_2), 4.23–4.49 (m, 5 H, H_3, H_4, H_5, H_{6a}, H_{6b}), 4.76 (dd., 2 H, CH_2Ph), 6.43 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H_1), 7.28–7.37 (m, 5 H, ArH), 8.64 (s, 1 H, NH).

Phenyl *O*-(6-*O*-Acetyl-2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)-(1→6)-2-*O*-benzyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside (39): A mixture of **38α** (64 mg, 0.129 mmol), **35** (45 mg, 0.112 mmol), and activated powdered 4Å molecular sieves in diethyl ether (2.1 mL) was stirred for 90 min at room temperature. At this time, a solution of trimethylsilyl triflate in diethyl ether (0.108 M, 155 μL, 0.017 mmol) was added. The reaction mixture was stirred for 45 min, quenched with triethylamine, diluted with CH_2Cl_2, filtered through celite, and evaporated in vacuo. Silica gel column chromatography (hexane/EtOAc) afforded **39α** (62 mg) and **39β** (10 mg) in a total yield of 86%. – Data for **39α**: *Rf* (hexane/EtOAc, 2:1) = 0.42. – M.p.: 45–47 °C. – $[\alpha]_D$ = +48.3 (c = 0.88, $CHCl_3$). – ^{1}H NMR (300 MHz, C_6D_6, 30 °C) δ: 1.24 (s, 3 H, *i*Pr), 1.26 (s, 3 H, *i*Pr), 1.35 (s, 3 H, *i*Pr), 1.41 (s, 3 H, *i*Pr), 1.77 (s, 3 H, Ac), 3.50–3.59 (m, 2 H, H_{5e}, H_{6e}), 3.69 (dd, $J_{2e,3e}$ = 6.3 Hz, $J_{2e,1e}$ = 9.5 Hz, 1 H, H_{2e}), 3.71 (dd, $J_{2f,3f}$ = 7.7 Hz, $J_{2f,1f}$ = 3.5 Hz, 1 H, H_{2f}), 3.76 (dd, $J_{4e,5e}$ = 1.9 Hz, $J_{4e,3e}$ = 5.7 Hz, 1 H, H_{4e}), 3.85 (dd, $J_{4f,5f}$ = 2.6 Hz, $J_{4f,3f}$ = 5.5 Hz, 1 H, H_{4f}), 4.05 (t, $J_{3e,4e}$ = $J_{3e,2e}$ = 6.0 Hz, 1 H, H_{3e}), 4.19 (dd, $J_{6e',6e}$ = 9.5 Hz, $J_{6e',5e}$ = 7.0 Hz, 1 H, $H_{6e'}$), 4.44 (ddd, $J_{5f,4f}$ = 2.6 Hz, $J_{5f,6f}$ = 8.0 Hz, $J_{5f,6f}$ = 4.1 Hz, 1 H, H_{5f}), 4.46–4.63 (m, 2 H, H_{6f}, $H_{6f'}$), 4.56 (dd, $J_{3f,4f}$ = 5.5 Hz, $J_{3f,2f}$ = 7.7 Hz, 1 H, H_{3f}), 4.68 (d, $J_{1e,2e}$ = 9.5 Hz, 1 H, H_{1e}), 4.75 (dd, 2 H, CH_2Ph), 4.84 (dd, 2 H, CH_2Ph), 4.96 (d, $J_{1f,2f}$ = 3.5 Hz, 1 H, H_{1f}), 7.01–7.64 (m, 15 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 20.82, 26.29, 27.72, 27.96, 63.35, 65.56, 66.90, 72.43, 73.37, 73.73, 74.90, 75.85, 76.18, 78.00, 79.59, 84.74, 96.68, 109.15, 110.14, 126.58, 127.76, 127.89, 128.19, 128.25, 128.32, 128.76, 129.76, 134.57, 137.65, 138.06, 170.59. – $C_{40}H_{48}O_{11}S$: calcd. C 65.20, H 6.57, S 4.35; found C 65.05, H 6.54, N 4.14. – Data for **39β**: *Rf* (hexane-AcOEt, 2:1) = 0.33. – ^{1}H NMR (300 MHz, C_6D_6, 30 °C) δ: 1.33 (s, 3 H, *i*Pr), 1.35 (s, 3 H, *i*Pr), 1.37 (s, 3 H, *i*Pr), 1.42 (s, 3 H, *i*Pr), 2.09 (s, 3 H, Ac), 3.39 (dd, $J_{2f,3f}$ = 6.4 Hz, $J_{2f,1f}$ = 7.8 Hz, 1 H, H_{2f}), 3.55 (dd, $J_{2e,3e}$ = 6.1 Hz, $J_{2e,1e}$ = 9.2 Hz, 1 H, H_{2e}), 3.88 (dt, $J_{5f,6f}$ = $J_{5f,6f'}$ = 6.1 Hz, $J_{5f,4f}$ = 2.0 Hz, 1 H, H_{5f}), 3.94–4.21 (m, 4 H), 4.10 (dd, $J_{4f,5f}$ = 2.0 Hz, $J_{4f,3f}$ = 5.7 Hz, 1 H, H_{4f}), 4.14 (t, $J_{3f,4f}$ = $J_{3f,2f}$ = 6.0 Hz, 1 H, H_{3f}), 4.28 (t, $J_{3e,4e}$ = $J_{3e,2e}$ = 5.9 Hz, 1 H, H_{3e}), 4.33 (d, $J_{6e,5e}$ = $J_{6e',5e}$ = 6.1 Hz, 2 H, H_{6e}, $H_{6e'}$), 4.42 (d, $J_{1f,2f}$ = 7.8 Hz, 1 H, H_{1f}), 4.72 (d, $J_{1e,2e}$ = 9.2 Hz, 1 H, H_{1e}), 4.66–4.84 (m, 4 H, 2 CH_2Ph), 7.16–7.53 (m, 15 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 20.85, 26.30, 27.66, 63.47, 69.09, 70.70, 73.39, 73.44, 73.87, 75.81, 77.96, 78.72, 79.16, 79.42, 86.00, 103.10, 110.12, 110.21, 127.01, 127.46, 127.73, 128.19, 128.28, 128.84, 131.12, 137.83, 138.22, 170.70.

***O*-(6-*O*-Acetyl-2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)-(1→6)-2-*O*-benzyl-3,4-*O*-isopropylidene-D-galactopyranose (40):** To a solution of **39α** (233 mg, 0.316 mmol) in acetone (6.5 mL) at –15 °C, were added NBS (73 mg, 0.411 mmol) and water (6.3 μL, 0.348 mmol). After stirring for 5 min, the reaction was quenched with a saturated aqueous solution of sodium bicarbonate. The mixture was diluted and extracted with EtOAc and washed with brine. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **40** (203 mg, quantitative yield). *Rf* (hexane-EtOAc, 2:1) = 0.12. – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.30 (s, 3 H, *i*Pr), 1.33 (s, 3 H, *i*Pr), 1.38 (s, 3 H, *i*Pr), 1.40 (s, 3 H, *i*Pr), 2.05 (s, 3 H, Ac_{α}), 2.06 (s, 3 H, Ac_{β}), 2.74 (s, 1 H, OH), 3.37 (t, $J_{2e,3e}$ = $J_{2e,1e}$ = 6.3 Hz, 1 H, $H_{2e\beta}$), 3.52 (dd, $J_{2f,3f}$ = 7.7 Hz, $J_{2f,1f}$ = 3.6 Hz, 1 H, H_{2f}), 3.63 (dd, $J_{2e,3e}$ = 5.7 Hz, $J_{2e,1e}$ = 3.7 Hz, 1 H, $H_{2e\alpha}$), 3.68–3.92 (m, 2 H), 4.00–4.46 (m, 8 H), 4.66–4.84 (m, 6 H), 4.82 (m, 1 H, $H_{1e\alpha}$), 7.26–7.38 (m, 10 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 20.85, 21.03, 25.78, 25.89, 26.34, 27.31, 27.41, 28.02, 63.71, 63.87, 65.38, 65.56, 67.34, 67.60, 67.88, 71.40, 72.26, 72.35,

72.97, 73.07, 73.50, 73.68, 74.20, 75.41, 75.88, 75.97, 78.31, 78.58, 79.22, 79.31, 79.54, 90.54, 96.20, 97.08, 97.28, 109.37, 109.41, 109.57, 109.93, 127.72, 127.81, 127.86, 127.97, 128.01, 128.14, 128.33, 128.50, 137.59, 137.99, 138.16, 138.23, 170.01. 171.75.

***O*-(6-*O*-Acetyl-2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)-(1→6)-2-*O*-benzyl-3,4-*O*-isopropylidene-D-galactopyranosyl trichloracetimidate (41):** To a solution of **40** (185 mg, 0.287 mmol) in CH_2Cl_2 (1.5 mL), were added trichloroacetonitrile (288 μL, 2.870 mmol) and flame-dried potassium carbonate (80 mg, 0.574 mmol). The reaction mixture was stirred for 2 hours, diluted with CH_2Cl_2, and filtered through celite. The solvent was evaporated at reduced pressure and the crude was purified by silica gel column chromatography (hexane/EtOAc, 4:1), affording **41α** (69 mg) and **41β** (111 mg) (80% total yield). – Data for **41α**: *Rf* (hexane/EtOAc, 2:1) = 0.49. – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.31 (s, 3 H, *i*Pr), 1.32 (s, 3 H, *i*Pr), 1.37 (s, 3 H, *i*Pr), 1.39 (s, 3 H, *i*Pr), 2.04 (s, 3 H, Ac), 3.51 (dd, $J_{2f,3f}$ = 7.7 Hz, $J_{2f,1f}$ = 3.4 Hz, 1 H, H_{2f}), 3.72 (dd, $J_{6e,6e'}$ = 10.5 Hz, $J_{6e,5e}$ = 5.2 Hz, 1 H, H_{6e}), 3.80 (dd, $J_{2e,3e}$ = 6.6 Hz, $J_{2e,1e}$ = 3.6 Hz, 1 H, H_{2e}), 3.88 (dd, $J_{6e',6e}$ = 10.5 Hz, $J_{6e',5e}$ = 7.1 Hz, 1 H, $H_{6e'}$), 4.14 (dd, J = 2.5 Hz, J = 5.6 Hz, 1 H), 4.17–4.50 (m, 5 H, H_{3e}, H_{3f}, H_{5e}, H_{5f}), 4.30 (d, $J_{5f,6f}$ = 8.4 Hz, 2 H, H_{6f}, $H_{6f'}$), 4.65–4.85 (m, 4 H, 2 CH_2Ph), 4.72 (d, $J_{1f,2f}$ = 3.5 Hz, 1 H, H_{1f}), 6.38 (d, $J_{1e,2e}$ = 3.6 Hz, 1 H, H_{1e}), 7.25–7.38 (m, 10 H, ArH), 8.57 (s, 1 H, NH). – Data for **41β**. *Rf* (hexane-AcOEt, 2:1) = 0.27. – $[\alpha]_D$ = +66.8 (*c* = 0.92, $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.32 (s, 6 H, *i*Pr), 1.38 (s, 3 H, *i*Pr), 1.39 (s, 3 H, *i*Pr), 2.05 (s, 3 H, Ac), 3.53 (dd, $J_{2',3'}$ = 7.5 Hz, $J_{2',1'}$ = 3.4 Hz, 1 H, $H_{2'}$), 3.67 (dd, $J_{2,3}$ = 6.1 Hz, $J_{2,1}$ = 7.7 Hz, 1 H, H_2), 3.71 (dd, $J_{6a,6b}$ = 10.0 Hz, $J_{6a,5}$ = 5.6 Hz, 1 H, H_{6a}), 3.94 (dd, $J_{6b,6a}$ = 10.3 Hz, $J_{6b,5}$ = 6.8 Hz, 1 H, H_{6b}), 4.08–4.38 (m, 8 H, H_3, $H_{3'}$, H_4, $H_{4'}$, H_5, $H_{5'}$, $H_{6'a}$, $H_{6'b}$), 4.74 (dd, 2 H, CH_2Ph), 4.83 (dd, 2 H, CH_2Ph), 4.85 (d, $J_{1',2'}$ = 3.4 Hz, 1 H, $H_{1'}$), 5.72 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H_1), 7.26–7.41 (m, 10 H, ArH), 8.63 (s, 1 H, NH). – $C_{36}H_{44}Cl_3NO_{12}$: calcd. C 54.80, H 5.62, N 1.77; found C 55.00, H 5.76, N 1.81.

***O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-*O*-[2,4-di-*O*-benzyl-3-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranosyl]-(1→4)-*O*-[6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)]-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-menthoxycarbonyl—1-D-*myo*-inositol (42):** A mixture of **33** (281 mg, 0.232 mmol), **20** (147 mg, 0.165 mmol) and powdered 4Å molecular sieves in diethyl ether (3.3 mL) was stirred for 45 min at room temperature. At this time, a solution of trimethylsilyl triflate in diethyl ether (0.108 M, 275 μL, 0.030 mmol) was added dropwise. The reaction mixture was stirred for 15 min, quenched with triethylamine, diluted with CH_2Cl_2, filtered through celite, evaporated in vacuo, and purified by chromatography (toluene/EtOAc 20:1) to yield **42** (261 mg, 81%), **33** (44 mg, 18% referred to starting **33**), and unchanged **20** (22 mg, 15%). *Rf* (hexane/EtOAc, 3:1) = 0.46. – M.p. 104–107 °C. – $[\alpha]_D$ = +40.6 (*c* = 1.31, $CHCl_3$). – ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.69 (d, 3 H, Mnt), 0.81 (d, 3 H, CH_3Mnt), 0.83 (d, 3 H, CH_3Mnt), 0.90 (s, 9 H, *t*Bu), 0.91–1.01 (m, 2 H, Mnt), 1.08–1.15 (m, 1 H, Mnt), 1.16–1.23 (m, 1 H, Mnt), 1.30–1.70 (m, 23 H, cyclohex., 3 Mnt), 1.85–1.92 (m, 1 H, Mnt), 2.01–2.06 (m, 1 H, Mnt), 2.75 (br. s, 1 H, H_{2e}), 3.13 (dd, $J_{2b,3b}$ = 9.6 Hz, $J_{2b,1b}$ = 3.4 Hz, 1 H, H_{2b}), 3.42–3.55 (m, 8 H), 3.57 (dd, $J_{5a,4a}$ = 10.9 Hz, $J_{5a,6a}$ = 8.4 Hz, 1 H, H_{5a}), 3.60–3.69 (m, 4 H), 3.65 (t, $J_{4d,3d}$ = $J_{4d,5d}$ = 8.9 Hz, 1 H, H_{4d}), 3.79–3.87 (m, 3 H), 3.95 (dd, $J_{4a,5a}$ = 10.9 Hz, $J_{4a,3a}$ = 7.3 Hz, 1 H, H_{4a}), 4.08 (dd, $J_{6a,5a}$ = 8.4 Hz, $J_{6a,1a}$ = 2.4 Hz, 1 H, H_{6a}), 4.12–4.18 (m, 2 H), 4.21 (dd, $J_{2d,3d}$ = 10.3 Hz, $J_{2d,1d}$ = 8.3 Hz, 1 H, H_{2d}), 4.32 (dd, $J_{3d,2d}$ = 10.3 Hz, $J_{3d,4d}$ = 8.9 Hz, 1 H, H_{3d}), 4.36 (t, $J_{3a,4a}$ = $J_{3a,2a}$ = 7.3 Hz, 1 H, H_{3a}), 4.39–4.52 (m, 6 H), 4.53 (dd, $J_{2a,3a}$ = 6.9 Hz, $J_{2a,1a}$ = 4.0 Hz, 1 H, H_{2a}), 4.67 (dd, 1 H, CH_2Ph), 4.87 (br. s, 1 H), 4.96 (dd, $J_{1a,2a}$ = 4.0 Hz, $J_{1a,6a}$ = 2.4 Hz, 1 H, H_{1a}), 5.13 (d, $J_{1d,2d}$ = 8.3 Hz, 1 H, H_{1d}), 5.25 (d, $J_{1b,2b}$ = 3.4 Hz, 1 H, H_{1b}), 5.44 (s, 1 H, H_{7d}), 6.76–7.61 (m, 44 H, ArH). – ^{13}C NMR (50 MHz, $CDCl_3$) δ: 16.08, 19.31, 20.78, 21.92, 23.17, 23.60, 23.73, 23.90, 24.77, 25.06, 25.93, 26.97, 31.43, 34.08, 34.52, 36.16, 36.30, 36.68, 40.60, 47.00, 55.57, 62.68, 66.10, 68.73, 69.43, 70.44, 71.23, 72.09, 73.10, 73.25, 73.95, 74.66, 76.50, 76.70, 78.84, 79.28, 80.00, 82.91, 96.22, 98.07, 98.90, 101.24, 112.19, 113.49, 123.12, 126.08, 126.61, 126.77, 127.29, 127.51, 127.72, 127.91, 127.97, 128.10, 128.20, 128.26, 128.95, 129.69, 129.81, 131.54, 133.46, 133.62, 134.48, 136.07, 137.46, 137.75, 138.05, 138.59, 154.16. – $C_{113}H_{130}N_4O_{23}Si$: calcd. C 69.95, H 6.75, N 2.89; found C 69.78, H 6.85, N 2.72.

***O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-α-D-glucopyranosyl)-(1→6)-*O*-(2,4-di-*O*-benzyl-3-β-D-mannopyranosyl)-(1→4)-*O*-[6-*O*-(2-azido-3,6-di-*O*-benzyl-3-deoxy-α-D-glucopyranosyl)]-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-menthoxycarbonyl-1-D-*myo*-inositol (43):** A solution of tetrabutylammonium fluoride in THF (0.92 M, 6 mL) buffered with acetic acid, was added to **42** (71 mg, 0.036 mmol). The reaction mixture was stirred for 10 days at 50 °C, then cooled and quenched with water, diluted and extracted with CH_2Cl_2, and dried with Na_2SO_4. Silica gel column chromatography (hexane/EtOAc, 3:1) afforded **43** (55 mg, 88% yield). *Rf* (hexane/EtOAc, 3:1) = 0.23. – M.p. 103–105 °C. – $[\alpha]_D$ = +37.9 (*c* = 0.60, $CHCl_3$). – ^{1}H NMR (300 MHz, C_6D_6) δ: 0.69–0.71 (m, 1 H, Mnt), 0.81 (d, 3 H, CH_3Mnt), 0.95 (d, 6 H, CH_3Mnt), 0.87–1.80 (m, 24 H), 1.99–2.03 (m, 2 H, Mnt), 2.13 (d, $J_{3c,OH}$= 9.5 Hz, 1 H, OH), 2.15–2.27 (m, 2 H, Mnt), 3.17 (dd, $J_{2b,3b}$ = 10.4 Hz, $J_{2b,1b}$ = 3.5 Hz, 1 H, H_{2b}), 3.49–3.53 (m, 2 H), 3.62–3.65 (m, 1 H), 3.67 (dd, $J_{2c,3c}$ = 3.3 Hz, $J_{2c,1c}$ = 1.5 Hz, 1 H, H_{2c}), 3.72–3.89 (m, 4 H), 4.18 (dd, $J_{3b,2b}$ = 10.2 Hz, $J_{3b,4b}$ = 9.0 Hz, 1 H, H_{3b}), 3.96–4.48 (m, 13 H), 4.58 (dd, $J_{6a,1a}$ = 2.9 Hz, 1 H, H_{6a}), 4.68 (dd, $J_{2a,3a}$ = 6.7 Hz, $J_{2a,1a}$ = 4.1 Hz, 1 H, H_{2a}), 4.56–4.91 (m, 9 H), 5.33 (s, 1 H, H_{7d}), 5.40 (d, $J_{1c,2c}$ = 1.4 Hz, 1 H, H_{1c}), 5.44 (dd, $J_{1a,2a}$ = 3.9 Hz, $J_{1a,6a}$ = 3.1 Hz, 1 H, H_{1a}), 5.50 (d, $J_{1d,2d}$ = 8.1 Hz, 1 H, $H_{1'''}$), 5.69 (d, $J_{1b,2b}$ = 3.5 Hz, 1 H, H_{1b}), 6.78–6.83 (m, 2 H, ArH), 6.85–6.90 (m, 2 H, ArH), 7.04–7.40 (m, 26 H, ArH), 7.47–7.41 (m, 2 H, ArH), 7.66–7.69 (m, 2 H, ArH). – ^{13}C NMR (50 MHz, C_6D_6) δ: 16.53, 20.86, 22.01, 23.57, 23.94, 24.10, 24.35, 25.14, 25.42, 26.48, 31.46, 34.23, 35.06, 36.67, 36.88, 37.08, 40.89, 47.50, 56.35, 63.21, 66.42, 68.57, 68.83, 69.84, 71.65, 71.81, 71.98, 72.06, 73.57, 73.83, 74.15, 74.87, 75.30, 76.32, 76.72, 77.04, 77.25, 77.43, 77.96, 79.20, 79.29, 80.45, 83.35, 97.12, 98.79, 99.26, 101.43, 112.15, 113.48, 118.92, 123.26, 126.65, 127.70, 128.98, 129.48, 129.66, 129.92, 132.16, 133.46, 138.32, 138.43, 138.62, 138.75, 139.30, 139.37, 154.90, 167.91. – $C_{97}H_{112}N_4O_{23}$: calcd. C 68.46, H 6.63, N 3.29; found C 68.11, H 6.55, N 3.33.

***O*-(6-*O*-Acetyl-2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)-(1→6)-*O*-(2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)-(1→3)-*O*-[*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-]-*O*-(2,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-[6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)]-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-menthoxycarbonyl-*myo*-inositol (44):** A solution of **41β** (94 mg, 0.119 mmol), **43** (45 mg, 0.026 mmol), and activated powdered 4Å molecular sieves in diethyl ether (0.6 mL) was stirred for 90 min at room temperature. At this point, a solution of trimethylsilyl triflate in diethyl ether (0.108 M, 37 μL, 0.004 mmol) was added. The reaction mixture was stirred for 45 min, quenched with triethylamine, diluted with CH_2Cl_2, filtered through celite, and evaporated in vacuo. Silica gel column chromatography (2 × cyclohexane/Et_2O, 5:2) afforded **44α** (44 mg) and **44β** (7 mg) in 83% total yield, **45** (2.3 mg, 5% relative to starting **43**), **46** (35.5 mg, 38% rel-

ative to starting **41β**), and **47** (2.8 mg, 8% relative to starting **41β**). – **44α:** *Rf* (hexane/EtOAc, 3:1) = 0.26. M.p.: 93–96 °C. – $[\alpha]_D$ = +54.1 (*c* = 0.880, acetone). – ^{1}H NMR (500 MHz, C_6D_6, 70 °C) δ: 0.62–0.71 (m, 1 H, Mnt), 0.76 (d, 3 H, CH_3Mnt), 0.88 (d, 3 H, CH_3Mnt), 0.89 (d, 3 H, CH_3Mnt), 1.20 (s, 3 H, *i*Pr), 1.29 (s, 3 H, *i*Pr), 1.33 (s, 6 H, *i*Pr), 0.84–1.78 (m, 24 H), 1.74 (s, 3 H, Ac), 1.89–1.93 (m, 2 H, Mnt), 2.12–2.18 (m, 2 H, Mnt), 3.35 (dd, $J_{2b,3b}$ = 10.4 Hz, $J_{2b,1b}$ = 3.7 Hz, 1 H, H_{2b}), 3.44–3.46 (m, 1 H), 3.49 (t, *J* = 9.9 Hz, 1 H, H_d), 3.58–3.61 (m, 2 H, H_{2e}, H_d), 3.64 (dd, $J_{2f,1f}$ = 3.4 Hz, $J_{2f,3f}$ = 7.6 Hz, 1 H, H_{2f}), 3.67–3.74 (m, 2 H, H_a), 3.96 (t, *J* = 9.2 Hz, 1 H), 3.99–4.01 (m, 2 H, H_e), 4.06–4.20 (m, 9 H, H_f, H_d, H_{2c}, H_a), 4.23 (t, *J* = 9.6 Hz, 1 H, H_b), 4.30–4.69 (m, 24 H), 4.71 (dt, 1 H, Mnt), 4.78–5.00 (m, 4 H, CH_2Ph), 4.94 (d, $J_{1f,2f}$ = 3.1 Hz, 1 H, H_{1f}), 5.13 (d, *J* = 3.0 Hz, 1 H, H_e), 5.3 (s, 1 H, H_{7d}), 5.33 (t, $J_{1a,2a}$ = 3.5 Hz, 1 H, H_{1a}), 5.42 (m, 1 H, H_{1d}), 5.58 (d, $J_{1b,2b}$ = 3.7 Hz, 1 H, H_{1b}), 5.62 (d, $J_{1c,2c}$ = 1.8 Hz, 1 H, H_{1c}), 6.76–7.57 (m, 44 H, ArH). – ^{13}C NMR (75 MHz, C_6D_6, 50 °C) δ: 16.67, 20.52, 20.84, 21.99, 23.79, 24.14, 24.24, 24.38, 25.28, 25.50, 26.45, 26.65, 26.99, 28.19, 30.12, 31.56, 34.38, 35.14, 36.75, 37.03, 37.23, 41.01, 47.63, 56.47, 63.15, 64.06, 66.51, 66.56, 67.35, 67.64, 68.93, 70.14, 71.34, 71.79, 72.63, 72.79, 73.52, 73.66, 73.89, 74.01, 74.24, 74.74, 74.93, 75.61, 76.22, 76.91, 77.06, 77.23, 77.48, 78.02, 78.16, 78.81, 79.31, 80.97, 83.42, 97.56 (C1N3), 97.94 (C1Man, C1Gal'), 99.36 (C1NPht), 99.43 (C1Gal), 101.57 (Benzylidene), 108.94 (*i*Pr), 109.56 (*i*Pr), 112.16 (CHex), 113.42 (CHex), 123.36, 126.69, 127.03, 127.20, 129.28, 129.36, 132.33, 133.51, 138.75, 138.87, 138.94, 139.03, 139.50, 139.65, 154.88 (carbonate), 167,97 (NPht), 169.99 (Npht). – Data for **44β:** *Rf* (hexane/EtOAc 3:1) = 0.25. – $[\alpha]_D^{20}$ = +38.1 (*c* = 0.69, $CHCl_3$). – ^{1}H NMR (C_6D_6, 500 MHz, 50 °C): δ 0.71–1.76 (m, 25 H, cyclohex, 5 H Mnt), 0.72 (d, 3 H, CH_3Mnt), 0.84 (d, 3 H, CH_3Mnt), 0.86 (d, 3 H, CH_3Mnt), 1.23 (s, 3 H, *i*Pr), 1.27 (s, 3 H, *i*Pr), 1.37 (s, 3 H, *i*Pr), 1.48 (s, 3 H, *i*Pr), 1.74 (s, 3 H, CH_3CO), 1.93–1.98 (m, 2 H, Mnt), 2.16–2.20 (m, 2 H, Mnt), 3.08 (dd, $J_{2b,3}b$ = 10.2 Hz, $J_{2b,1b}$ = 3.7 Hz, 1 H, H_{2b}), 3.34–3.38 (m, 1 H), 3.42–3.65 (m, 5 H, 2× H_d), 3.68–3.75 (m, 2 H, H_f), 3.85–4.86 (m, 39 H, H_{1e}), 4.91–4.97 (m, 4 H, H_{1f}), 5.29 (s, 1 H, H_{7d}), 5.43–5.46 (m, 3 H, H_{1a}, H_{1c}, H_{1d}), 5.48 (d, $J_{2b,1b}$ = 3.8 Hz, 1 H, H_{1b}), 6.72–7.61 (m, 44 H, ArH). – ^{13}C NMR (C_6D_6, 75 MHz, 50 °C): δ 16.4, 20.6, 20.9, 22.0, 23.5, 24.2, 25.3, 25.5, 26.4, 26.6, 26.7, 27.2, 28.0, 28.3, 30.1, 31.4, 34.3, 35.0, 36.7, 37.0, 40.9, 47.5, 56.3, 63.7, 64.1, 66.4, 68.8, 70.0, 71.5, 71.9, 72.4, 72.9, 73.1, 73.3, 73.5, 73.8, 74.2, 74.8, 75.0, 75.3, 75.7, 76.9, 77.5, 77.7, 79.1, 80.0, 83.5, 97.4 (C-1b), 97.7 (C-1f), 99.0 (C-1c), 100.3 (C-1e), 101.0 (C-1d), 101.5 (C-7d), 109.5 (*i*Pr), 109.8 (*i*Pr), 112.2 (cyclohex), 113.4 (cyclohex), 123.3, 126.7, 127.5, 128.0, 128.4, 129.3, 132.2, 133.5, 138.4, 138.7, 139.1, 139.4, 154.8 (OCO_2), 168.9 (NCO), 170.0 (CH_3CO). – Data for **45:** *Rf*: 0.49 (hexane/EtOAc 2:1). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.00 (s, 9 H, $(CH_3)_3$Si), 0.78–2.09 (m, 29 H, cyclohex, Mnt), 0.75 (d, 3 H, CH_3Mnt), 0.81 (d, 3 H, CH_3Mnt), 0.85 (d, 3 H, CH_3Mnt), 3.39–3.41 (m, 2 H, H_{2b}, H_{2c}), 3.50–4.00 (m, 14 H), 4.10–4.85 (m, 18 H), 4.99 (dd, $J_{1a,2a}$ = 2.7 Hz, $J_{1a,6a}$ = 3.9 Hz, 1 H, H_{1a}), 5.16 (d, $J_{1c,2c}$ = 2.0 Hz, 1 H, H_{1c}), 5.20 (d, $J_{1d,2d}$ = 8.0 Hz, 1 H, H_{1d}), 5.30 (d, $J_{1b,2b}$ = 3.2 Hz, 1 H, H_{1b}), 5.53 (s, 1 H, H_{7d}), 6.82–7.52 (m, 34 H, ArH). – Data for **46**: *Rf*: 0.27 (hexane/EtOAc, 2:1). – ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.29 (s, 3 H, *i*Pr), 1.34 (s, 3 H, *i*Pr), 1.35 (s, 3 H, *i*Pr), 1.50 (s, 3 H, *i*Pr), 2.06 (s, 3 H, CH_3CO), 3.47 (dd, $J_{2f,3f}$ = 8.0 Hz, $J_{2f,1f}$ = 3.3 Hz, 1 H, H_{2f}), 3.56 (dd, $J_{6,6'}$ = 10.3 Hz, $J_{6,5}$= 4.3 Hz, 1 H, H_6), 3.81 (dd, $J_{6',6}$ = 10.2 Hz, $J_{6',5}$ = 7.7 Hz, 1 H, $H_{6'}$), 3.93 (dd, *J* = 4.6 Hz, *J* = 3.2 Hz, 1 H, H_4), 4.13–4.48 (m, 7 H), 4.52–4.58 (m, 1 H), 4.66 (m, 2 H, CH_2Ph), 4.74 (m, 2 H, CH_2Ph), 4.78 (d, $J_{1f,2f}$ = 3.5 Hz, 1 H, H_{1f}), 5.65 (dd, $J_{1e,2e}$ = 4.6 Hz, $J_{1e,NH}$ = 8.5 Hz, 1 H, H_{1e}), 7.29–7.41 (m, 10 H, ArH), 8.57 (s, $J_{NH,1e}$ = 8.5 Hz, 1 H, NH). – Data for **47**: *Rf*: 0.38 (hexane/EtOAc, 2:1). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.28 (s, 3 H, *i*Pr), 1.46 (s, 3 H, *i*Pr), 3.51 (dd, $J_{6,6}$ = 7.6 Hz, $J_{6,5}$= 5.4 Hz, 1 H, H_6), 3.52 (s, 1 H, H_2), 4.01 (d, $J_{6',6}$ = 7.6 Hz, 1 H, $H_{6'}$), 4.17 (d, $J_{3,4}$ = 7.0 Hz, 1 H, H_3), 4.39 (Ψt, $J_{4,3}$ = 6.8 Hz, $J_{4,5}$ = 6.0 Hz, 1 H, H_4), 4.44 (Ψt, $J_{5,4}$= 5.7 Hz, $J_{5,6}$= 5.4 Hz, 1 H, H_5), 4.59 (dd, 2 H, CH_2Ph), 5.36 (s, 1 H, H_1), 7.18–7.30 (m, 5 H, ArH).

***O*-(6-*O*-Acetyl-2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)-(1→6)-*O*-(2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)–(1→3)–*O*-[*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phtalimido-β-D-glucopyranosyl)–(1→6)]-*O*-(2,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-[6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)]-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-acetyl-1-D-*myo*-inositol (48):** A solution of **44**α (11.5 mg, 4.94 μmol) in 3:2 tetrahydrofuran/methanol (2.2 mL) was treated at room temperature with aqueous lithium hydroxide (2.1 M, 0.35 mL, 0.741 mmol). After 31 h, the reaction mixture was diluted with dichloromethane and washed with water, the water phase washed with dichloromethane, and the combined organic phases dried with sodium sulfate and twice co-evaporated with toluene. The residue was suspended in chloroform (0.25 mL) and triethylamine (0.7 mL, 4.94 mmol) added to the suspension. After cooling at 0° C, acetic anhydride (0.12 mL, 1.23 mmol), and dimethylaminopyridine were added. The reaction mixture was kept at room temperature for six days with further additions of triethylamine and acetic anhydride as above, every 24 h. The reaction mixture was diluted with dichloromethane, washed with water, the aqueous phase washed with dichloromethane and the combined organic phases washed with a saturated aqueous solution of sodium chloride and dried with sodium sulfate and evaporated. The residue was chromatographically purified. The NMR spectrum of the reaction mixture revealed a 5.5:1 mixture of **48** and an intermediate compound, and the mixture was therefore dissolved in chloroform (0.25 mL), treated with triethylamine (0.7 mL, 4.94 mmol), cooled at 0° C, treated with acetic anhydride (0.12 mL, 1.23 mmol) and dimethylaminopyridine and warmed at 40° C. The reaction mixture was kept at this temperature for four days, cooled at room temperature, and worked up as above to give 8.4 mg (78%) of **48**. – ^{1}H NMR (500 MH_z, C_6D_6, 50° C) δ: 1.27 (s, 3 H, *i*Pr), 1,35 (s, 3 H, *i*Pr), 1.41 (s, 3 H, *i*Pr), 1.44 (s, 3 H, *i*Pr), 1.78 (s, 3 H, CH_3CO), 1.79 (s, 3 H, CH_3CO), 1.30–1.86 (m, 20 H, cyclohex), 3.43 (dd, $J_{2b,3b}$ = 10.0 Hz, $J_{2b,1b}$ = 3.7 Hz, 1 H, H_{2b}), 3.48–3.58 (m, 2 H), 3.63–3.71 (m, 2 H, H_{5d}), 3.65 (dd, $J_{2e,1e}$ = 3.5 Hz, $J_{2e,3e}$ = 7.6 Hz, 1 H, H_{2e}), 3.72 (dd, $J_{2f,1f}$ = 3.6 Hz, $J_{2f,3f}$ = 7.7 Hz, 1 H, H_{2f}), 3.77 (dd, *J* = 8.7 Hz, *J* = 10.2 Hz, 1 H, H_{5a}), 3.79 (dd, *J* = 6.0 Hz, *J* = 10.1 Hz, 1 H), 4.04 (t, *J* = 8.9 Hz, 1 H), 4.07–4.12 (m, 3 H, H_{4e}, H_{4d}, H_{6d}), 4.15 (dd, *J* = 2.4 Hz, *J* = 5.5 Hz, 1 H, H_{4f}), 4.17–4.21 (m, 2 H), 4.22 (s, 1 H, H_{2c}), 4.25–4.36 (m, 7 H, H_{3a}, H_{4a}, H_{3b}), 4.38–4.49 (m, 6 H, H_{6a}, H_{3d}, H_{3e}), 4.52–4.78 (m, 15 H, H_{2a}, H_{3f}, H_{2d}, H_{6d}), 4.87 (d, 1 H, CH_2Ph), 4.98 (dd, 2 H, CH_2Ph), 5.00 (d, $J_{1f,2f}$ = 3.5 Hz, 1 H, H_{1f}), 5.13 (d, 1 H, CH_2Ph), 5.20 (d, $J_{1e,2e}$ = 3.4 Hz, 1 H, H_{1e}), 5.36 (s, 1 H, H_{7d}), 5.47–5.50 (m, 2 H, H_{1a}, H_{1d}), 5.60 (d, $J_{1b,2b}$ = 3.7 Hz, 1 H, H_{1b}), 5.76 (d, $J_{1c,2c}$ = 2.0 Hz, 1 H, H_{1c}), 6.80–7.66 (m, 44 H, ArH). – ^{13}C NMR (C_6D_6, 125 MHz, 50 °C) δ: 20.2, 20.3, 23.6, 23.9, 24.0, 25.0, 25.1, 26.2, 26.8, 27.9, 28.0, 34.7, 36.7, 36.9, 37.0, 56.2, 62.7, 63.8, 66.2, 67.0, 67.3, 68.6, 71.4, 72.3, 72.4, 72.5, 73.1, 73.4, 73.6, 73.7, 74.0, 74.6, 75.3, 76.0, 76.6, 76.7, 76.8, 76.9, 77.2, 77.4, 78.0, 78.5, 80.6, 83.1, 97.4 (C_1), 97.5 (C_1), 97.6 (C_1), 99.0 (C_1), 101.3 (C_{7d}), 108.7 (C*ipso*), 110.0 (C*ipso*), 111.5 (C*ipso*), 113.0 (C*ipso*), 123.1, 126.4, 127.0, 127.1, 127.1, 127.2, 127.3, 127.3, 127.4, 127.5, 127.6, 127.6, 127.7, 127.8, 127.8, 127.9, 128.0, 128.0, 128.1, 128.2, 128.2, 128.2, 128.3, 128.4, 128.4, 128.7, 132.0, 133.3, 138.2, 138.5, 138.6, 138.6, 138.7, 139.2, 139.4, 169.1, 169.7.

***O*-(6-*O*-Acetyl)-2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)-(1→6)-*O*-(2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-**

galactopyranosyl)-(1→3)-*O*-[*O*-(2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl-(1→6)]-*O*-(2,4-di-*O*-benzyl-α-D-manopyranosyl)-(1→4)-*O*-[6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)]-2,3:4,5-di-*O*-cyclohexylidene-1-*O*-acetyl-1-D-*myo*-inositol (49): To a solution of **48** (8.4 mg, 3.84 μmol) in *n*-butyl alcohol (0.77 mL), ethylenediamine (167 μL, 2.50 μmol) was added at room temperature. After 90 minutes, the temperature was raised to 90 °C and the reaction mixture was kept at this temperature for 18 h, then cooled, evaporated, and the residue coevaporated twice with toluene. The residue was dissolved in chloroform (0.25 mL), treated with triethylamine (0.8 mL, 5.76 mmol) and the solution cooled to 0° before adding acetic anhydride (0.25 mL, 2.69 mmol) and a catalytic amount of dimethylaminopyridine. The reaction mixture was allowed to warm and kept at room temperature for 20 h. The solvent was then evaporated, and the residue purified by column chromatography (2:1 hexane/ethyl acetate) to give pure **49** (7.5 mg, 93%). – ^{1}HNMR (C_6D_6, 500 MHz, 50° C): δ 1.29 (s, 3 H, *i*Pr), 1.38 (s, 3 H, *i*Pr), 1.42 (s, 6 H, 2 *i*Pr), 1.78 (s, 3 H, CH_3CO), 1.81 (s, 3 H, CH_3CO), 1.25–1.84 (m, 23 H, ciclohex, CH_3CO), 3.22–3.31 (m, 1 H, H_{2d}), 3.34–3.39 (m, 1 H, H_{2b}), 3.47–3.53 (m, 1 H, H_{5d}), 3.57 (t, $J_{6d,5d}$=$J_{6d,6d}$= 10.0 Hz, 1 H, H_{6d}), 3.61–3.66 (m, 1 H, H_{4d}), 3.73–3.77 (m, 3 H, H_{5a}, H_{2e}, H_{2f}), 3.79–3.84 (m, 1 H, H_{6e}), 3.86–3.90 (m, 1 H), 4.06 (d, $J_{6b,6b}$ = 10.2 Hz, 1 H, H_{6b}), 4.15–4.19 (m, 3 H, H_{4f}, H_{6d}, H_{6e}), 4.21–4.44 (m, 12 H, H_{4e}, H_{6b}, H_{3a}, H_{4a}, H_{3b}, H_{2c}, H_{6a}, H_{3c}, H_{4b}), 4.50–4.87 (m, 19 H, H_{5b}, H_{3e}, H_{3f}, H_{2a}, H_{3d}, H_{4f}, H_{5e}), 4.98 (d, 1 H, CH_2Ph), 5.03–5.07 (m, 4 H, CH_2Ph, H_{1d}, H_{1f}), 5.21 (d, $J_{NH,2d}$= 6.7 Hz, 1 H, NH), 5.38 (d, $J_{1e,2e}$ = 3.3 Hz, 1 H, H_{1e}), 5.40 (s, 1 H, H_{7d}), 5.44 (d, 1 H, CH_2Ph), 5.45 (t, $J_{1a,2a}$ = $J_{1a,6\alpha}$ = 3.8 Hz, 1 H, H_{1a}), 5.55 (d, $J_{1b,2b}$ = 3.2 Hz, 1 H, H_{1b}), 5.91 (s, 1 H, H_{1c}), 7.05–7.65 (m, 40 H, ArH). – ^{13}C NMR (C_6D_6, 125 MHz, 50 °C): δ 20.2, 20.3, 23.6, 23.9, 24.0, 25.0, 25.1, 26.2, 26.6, 27.9, 28.0, 34.7, 36.7, 36.9, 37.1, 59.1, 63.0, 63.8, 65.9, 66.3, 67.2, 67.4, 68.9, 69.4, 71.3, 71.4, 72.5, 72.6, 73.6, 73.6, 73.7, 73.8, 73.9, 74.4, 74.5, 74.7, 76.2, 76.6, 76.7, 76.8, 77.0, 77.4, 78.1, 80.7, 83.1, 97.4, (C_{1b}), 97.7 (C_{1d}, C_{1f}), 98.1 (C_{1c}), 100.3 (C_{1e}), 101.3 (C_{7d}), 108.8 (C*ipso*, *i*Pr), 109.3 (C*ipso*, *i*Pr), 111.5 (C*ipso*, cyclohex), 113.0 (C*ipso*, cyclohex), 126.4, 127.3, 127.4, 127.6, 127.8, 127.8, 127.9, 127.9, 128.0, 128.0, 128.1, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.6, 138.3, 138.5, 138.6, 138.7, 139.2, 139.2, 169.1, 169.8.

***O*-(2-*O*-Benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)-(1→6)-*O*-(2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl)-(1→3)-*O*-[*O*-(2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-(1→6)-]-*O*-(2,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-[6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)]-2,3:4,5-di-*O*-cyclohexylidene-1-D-*myo*-inositol (50):** To a solution of **49** (9.8 mg, 4.67 μmol) in 3:7 tetrahydrofuran/methanol (0.5 mL), a solution of sodium methoxide in methanol (0.2 M, 70 μL, 14.0 μmol) was added at room temperature. After 8 h, the reaction mixture was neutralized with Dowex 50WX resin, filtered, and evaporated. The residue was purified by column chromatography (3:2 hexane/ethyl acetate) to give **50** (8.6 mg, 91%). – ^{1}H NMR (C_6D_6, 500 MHz, 50 °C): δ 1.31 (s, 3 H, *i*Pr), 1.33 (s, 3 H, *i*Pr), 1.39 (s, 3 H, *i*Pr), 1.43 (s, 3 H, *i*Pr), 1.22–1.43 (m, 5 H, cyclohex), 1.45–1.75 (m, 18 H, cyclohex, CH_3CO), 1.05 (s, 1 H, OH), 2.69 (d, $J_{OH,1????}$ = 2.3 Hz, 1 H, OH), 3.24–3.28 (m, 1 H, H_{2d}), 3.30–3.34 (m, 1 H, H_{2b}), 3.48–3.53 (m, 1 H, H_{5d}), 3.57 (t, $J_{6d,5d}$ = $J_{6d,6d}$ = 10.0 Hz, 1 H, H_{6d}), 3.61–3.66 (m, 1 H, H_{4d}), 3.73 (dd, $J_{2f,1f}$ = 3.6 Hz, $J_{2f,3f}$ = 7.4 Hz, 1 H, H_{2f}), 3.75 (dd, J = 8.5 Hz, J = 10.1 Hz, 1 H, H_{5a}), 3.82 (dd, $J_{2e,1e}$= 3.4 Hz, $J_{2e,3e}$ = 7.4 Hz, 1 H, H_{2e}), 3.85–3.91 (m, 2 H, H_{4c}), 3.94–4.01 (m, 2 H, H_{6e}), 4.04 (d, $J_{6b,6b}$ = 11.3 Hz, 1 H, H_{6b}), 4.10–4.16 (m, 3 H, H_{4f}, H_{1a}, H_{6e}), 4.19–4.23 (m, 3 H, H_{6d}), 4.24 4.04 (dd, $J_{6b,5b}$ = 2.9 Hz, $J_{6b,6b}$ = 11.1 Hz, 1 H, H_{6b}), 4.29–4.56 (m, 14 H, H_{2a}, H_{3a}, H_{4a}, H_{6a}, H_{3c}, H_{2c}, H_{3b}, H_{4b}, H_{5b}, H_{3f}, H_{4e}), 4.65–4.86 (m, 9 H, H_{3e}, H_{3d}, H_{5e}), 4.99 (d, 2 H, CH_2Ph), 5.07 (d, $J_{1f,2f}$ = 3.5 Hz, 1 H, H_{1f}), 5.08 (d, 1 H, CH_2Ph), 5.17–5.19 (m, 2 H, H_{1d}, H_{1b}), 5.23 (d, $J_{NH,2d}$ = 7.1 Hz, 1 H, NH), 5.41 (d, 1 H, CH_2Ph), 5.41 (s, 1 H, H_{7d}), 5.42 (d, $J_{1e,2e}$ = 3.2 Hz, 1 H, H_{1e}), 5.83 (s, 1 H, H_{1c}), 7.14–7.65 (m, 40 H, ArH). – ^{13}C NMR (C_6D_6, 125 MHz, 33 °C): δ 20.7, 23.2, 23.5, 23.8, 23.9, 24.0, 24.1, 25.0, 25.1, 26.2, 26.4, 27.9, 28.0, 33.6, 36.6, 36.6, 36.9, 59.2, 62.5, 62.8, 65.8, 67.4, 67.9, 68.9, 69.2, 71.3, 71.4, 72.6, 72.8, 73.0, 73.6, 73.8, 74.1, 74.4, 75.7, 76.1, 76.4, 76.4, 76.7, 76.8, 77.2, 77.3, 77.4, 78.5, 80.6, 83.3, 96.8, (C_1), 98.2 (C_1), 98.5 (C_1), 100.0 (C_1), 101.3 (C_{7d}), 108.9 (C*ipso*, *i*Pr), 109.1, (C*ipso*, *i*Pr), 111.1 (C*ipso*, cyclohex), 126.5, 127.3, 127.4, 127.7, 128.1, 128.2, 128.3, 128.4, 128.6, 128.7, 138.3, 138.4, 138.7, 138.8, 139.3, 169.8.

Attempted Phosphorylation of 50: To a solution of **50** (6 mg, 2.98 μmol) in acetonitrile (0.25 mL), dibenzyl *N*,*N*-diisopropylphosphoramidite (16 μL, 47.6 μmol) and a solution of tetrazol (2,2 mg, 31.3 μmol) in acetonitrile (0.35 mL) were added at room temperature. After 1 h, an additional amount of dibenzyl *N*,*N*-dibenzylphosphoramidite (16 μL, 47.6 μmol) was added and 1 h later a further amount of tetrazol (2.2 mg, 31.3 μmol) was also added. Decomposition products were observed by tlc after 2.5 h, and the temperature was decreased to 0° before adding a solution of *tert*-butyl peroxide in isooctane (4.7 M, 35μL, 0.155 mmol). The temperature was then allowed to rise and the reaction mixture kept at room temperature for 45 min. The solvent was evaporated and the residue fractionated by column chromatography (5:1 toluene/acetone) and subjected twice to chromatography (2:3 cyclohexane/ethyl acetate). Two chromatographically pure fractions, whose structures could not be ascertained, were obtained.

Acknowledgments

We thank DGES (Grant PB 96 0820) and the Rademacher Group Ltd. for financial suport and Mr. Ignacio Moreno for technical assistence.

[1] G. Romero, J. Larner, *Adv. Pharmacol* **1993**, *24*, 21–50 and references therein.
[2] I. Varela-Nieto, Y. León, H. N. Caro, *Comp. Biochem. Physiol.* **1996**, *115B*, 223–241.
[3] P. Strälford, *Bioessays* **1997**, *19*, 327–335.
[4] M. C. Field, *Glycobiobly* **1997**, *7*, 161–168.
[5] D. R. Jones, I. Varela-Nieto, *Int. J. Biochem. Cell Biol.* **1998**, *30*, 313–326.
[6] J. M. Mato, K. Kelly, A. Abler, L. Jarrett, B. E. Corkey, B. E. Cashel, D. Zopf, *Biochem. Biophys. Res. Commun.* **1987**, *146*, 764–770.
[7] J. Larner, L. C. Huang, C. F. W. Schwartz, A. S. Oswald, T. Y. Shen, M. Kinter, G. Tang, K Zeller. *Biochem. Biophys. Res. Commun*. **1988**, *151*, 1416–1426.
[8] L. C. Huang, M. C. Fonteles, D. B. Houston, C. Zhang, J. Larner, *Endocrinology*, **1993**, *132*, 652–657.
[9] J. Larner, P. J. Roach, L. C. Huang, G. Brocker, F. Murad, R. Hazen, *Adv. Exp. Biol*, **1979**, *111*, 103–112.
[10] H. N. Caro, A. Guadaño, M. Bernabé, M. Martín-Lomas, J. M. Mato, R. A. Dwek, T. W. Rademacher, *Glycoconjugate J.* **1993**, *10*, 242.
[11] G. Romero, G. Gómez, L. Huang, K. Lilley, L. Lutrell, *Proc. Natl. Acad. Sci. USA*, **1990**, *87*, 1476–1480.
[12] J. Represa, M. A. Avila, C. Miner, F. Giráldez, G. Romero, R. Clemente, J. M. Mato, I. Varela-Nieto, *Proc. Natl. Acad. Sci. USA*, **1991**, *88*, 8016–8019.
[13] A. Zapata, M. Martín-Lomas, *Carbohydr. Res.* **1992**, *234*, 93–106.
[14] A. Zapata, Y. León, J. M. Mato, I. Varela-Nieto, S. Penadés, M. Martín-Lomas, *Carbohydr. Res.* **1994**, *264*, 21–31.

[15] C. Jaramillo, J. L. Chiara, M. Martín-Lomas, *J. Org. Chem.* **1994**, *59*, 3135–3141.
[16] N. Khiar, M. Martín-Lomas, *J. Org. Chem.* **1995**, *60*, 7017–7021.
[17] H. Dietrich, J. F. Espinosa, J. L. Chiara, J. Jiménez-Barbero, Y. León, I. Varela-Nieto, J. M. Mato, F. H. Cano, C. Foces-Foces, M. Martín-Lomas, *Chem. Eur. J.* **1999**, *5,* 320–336.
[18] R. D. Groneberg, T. Nuzayaki, N. A. Stylianides, T. J. Schulze, W. Stahl, E. P. Schreiner, T. Suzuki, Y. Iwabuchi, A. L. Smith, K. C. Nicolaou, *J. Am. Chem. Soc.* **1993**, *115*, 7593–7611.
[19] K. C. Nicolaou, R. E. Dolle, D. P. Papakatjis, J. L. Randall, *J. Am. Chem. Soc.* **1984**, *106*, 4189–4192.
[20] V. Pozsgay, H. J. Jennings, *J. Org. Chem.* **1988**, *53*, 4042–4052.
[21] D. S. Brocon, S. V. Ley, S. Vile, M. Thompson, *Tetrahedron.* **1991**, *47*, 1329–1342.
[22] D. Khane, S. Walker, Y. Cheng, van Engen, *J. Am. Chem. Soc.* **1989**, *111*, 6881–6882.
[23] R. R. Schmidt, W. Kinzy, *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–123.
[24] For a review see B. V. L. Potter, D. Lampe, *Angew. Chem. Int. Edn. Engl.* **1995**, *34*, 1933–1979.
[25] A. Zapata, R. Fernández de la Pradilla, M. Martín-Lomas, S. Penadés, *J. Org. Chem.* **1991**, *56*, 444–447.
[26] A. Aguiló, M. Martín-Lomas, S. Penadés, *Tetrahedron Lett.* **1992**, *33*, 401–404.
[27] S. David, S. Hanessian, *Tetrahedron.* **1985**, *41*, 643–663.
[28] R. C. Mechrotra, V. D. Gupta, *J. Organometal. Chem.* **1965**, *4*, 2370–2378.
[29] R. Köster, K. L. Amen, W. V. Dahlhoff, *Liebigs Ann. Chem.* **1975**, 752–788.
[30] K. M. Taba, R. Köster, W. W. Dahloff, *Synthesis.* **1984,** 39–401.
[31] P. J. Garegg, T. Iversen, R. Johansson, B. Lindberg, *Carbohydr. Res.* **1984**, *130*, 322–326.
[32] B. Kratzer, T. G. Meyer, R. R. Schmidt, *Tetrahedron Lett.* **1993**, *34*, 6881–6884.
[33] R. U. Lemieux, R. M. Ratcliffe, *Can. J. Chem.* **1979**, *57*, 1244–1251.
[34] N. V. Borin, S. E. Zurabyan, A. Y. Khorlin, *Carbohydr. Res.* **1981**, *98*, 25–35.
[35] H. Paulsen, W. Stenzel, *Chem. Ber.* **1978**, *111*, 2334–2347.
[36] M. Kloorterman, M. P. de Niijs, H. Van Boom, *J. Carbohydr. Chem.* **1986**, *5*, 215–233.
[37] A. Vasella, C. Witzig, J. L. Chiara, M. Martín-Lomas, *Helv. Chim. Acta***. 1991**, *74*, 2073–2077.
[38] R. J. Ferrier, R. H. Furneaus, *Carbohydr. Res.* **1976**, *52*, 63–68.
[39] J. Gelas, *Adv. Carbohydr. Chem. Biochem.* **1981**, *39*, 71–156.
[40] P. J. Garegg, H. Hultberg, S. Wallin, *Carbohydr. Res.* **1982**, *108*, 97–101.
[41] R. Johansson, B. Samuelsson, *J. Chem. Soc., Perkin Trans.* **1984**, *1*, 2371–2374.
[42] M. Naruto, K. Ohno, N. Narusa, H. Takeuchi, *Tetrahedron Lett.* **1979**, 251–254.
[43] E. J. Corey, H. Cho, C. Rücker, D. H. Hua, *Tetrahedron Lett.* **1981**, *22*, 3455–3458.
[44] E. J. Corey, A. Venkateswarlu, *J. Am. Chem. Soc*, **1972**, *94*, 6190–6191.
[45] K. Suzuki, H. Maeta, T. Suzuki, T. Matsumoto, *Tetrahedron Lett.* **1989**, *30*, 6879–6882.
[46] T. Matsumoto, K. Suzuki, H. Maeta, G. I. Tsudihashi, *Tetrahedron Lett.* **1988**, *29*, 3567–3570.
[47] A. Fernández-Mayorales, A. Marra, M. Trumptel, A. Veyrieres P. Sinay, *Carbohydr. Res.* **1989**, *188*, 81–95.
[48] P. L. Durette, E. P. Meitzner, T. Y. Shen, *Tetrahedron Lett.* **1979**, 4013–4016.
[49] O. Kanie, S. C. Crawley, M. M. Palcic, O. Hindsgaul, *Carbohydr. Res.* **1993**, *243*, 139–164.
[50] T. Ogawa, C. Murakata, *Carbohydr. Res.* **1992**, *235*, 95–114.
[51] K. L. Yu and B. Fraser-Reid, *Tetrahedron Lett*. **1988**, *29*, 979–982.

Received July 13, 1999
[O99422]