Studies Related to Synthesis of Glycophosphatidylinositol Membrane-Bound Protein Anchors.[1] 6.[2] Convergent Assembly of Subunits

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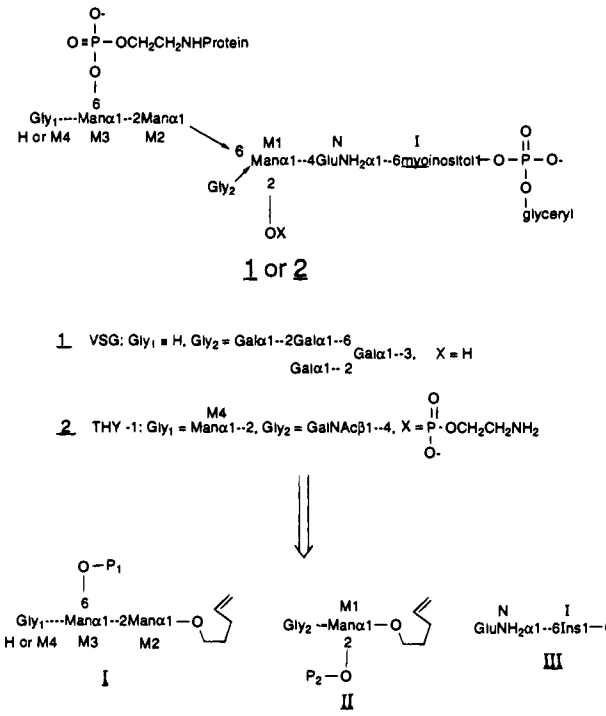
Abstract: Glycophosphatidylinositol anchors of membrane-bound proteins are thought to comprise a common pentasaccharide core containing mannan, glucosamine, and inositol residues. A synthetic route to this core is described. In addition, the complete heptasaccharide moiety of the rat brain Thy-1 membrane anchor, the first mammalian membrane anchor to be characterized, has been synthesized. In the case of the Thy-1 anchor, the synthetic plan is based on three building blocks comprising glucosamine−inositol, galactosamine−mannose, and trimannan residues. Although glycosyl donors other than *n*-pentenyl glycosides (NPGs) have been used in preparing each of these building blocks, the final assembly of the heptasaccharide utilizes NPGs as the only glycosyl donors. The mildness of the conditions for these coupling reactions has allowed us to make provisions for subsequent installation of the three phosphodiester units.

In the accompanying manuscript, we focused attention on developments in *n*-pentenyl glycoside (NPG) chemistry in the context of preparing versatile, stable synthons for rapid assembly of multigram amounts of mannan residues.[2] A retrosynthetic plan for a general approach to this structurally conserved group of glycophosphoinositol membrane anchors, as depicted in Scheme 1, generates the retrons **I**, **II**, and **III**. In addition to the biological importance of these membrane anchors, our interest was further stimulated by the desire to examine the use of NPG derivatives for the assembly of structures of such diverse complexity. Experience with older, established reactants has taught[5] that a given glycosyl donor may fare better than others for a specific task (*vide infra*). In this context, the versatility of NPGs needed to be tested, and in this manuscript, we give full accounts of our efforts to realize this plan for the core pentasaccharide of the VSG anchor **1**[6] and the full heptasaccharide moiety of the Thy-1 anchor **2**[7] (Scheme 1).

Glucosamine−Inositol Moieties[8] **(III).** The results summarized in Scheme 2 for this segment reflect two different

Scheme 1



strategies for the approach to the inositol component.[9] Garegg's excellent procedure for cyclohexylidenation of *myo*-inositol provides the bis derivative **3** as the major product (38%),[10] and hence it was chosen for use. The procedure of Vacca *et al.* for resolution *via* camphanate esters[11] was applied to the benzyl ether **4a**, the major product of regioselective benzylation,[10] and column chromatography afforded the optically active campha-

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(2) Part 5: Roberts, C.; Madsen, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1995**, *117*, 1546−1553.

(3) (a) R.M. thanks the Danish Technical Research Council for a P.D. Fellowship. (b) C.R. is the recipient of a NIH Award for Underrepresented Minorities.

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(5) Wulff, G.; Röhle, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 157. Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155. Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503.

(6) For preliminary account for **1**, see: Mootoo, D. R.; Konradsson, P.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1989**, *111*, 8540.

(7) For preliminary account for **2**, see: Udodong, U. E.; Madsen, R.; Roberts, C.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1993**, *115*, 7886.

(8) For other approaches to the glucosamine−inositol moiety, see: Verduyn, R.; Elie, C. J. J.; Dreef, C. E.; van der Marel, G. A.; van Boom, J. H. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 591. Plourde, R.; d'Alarco, M.; Saltiel, A. R. *J. Org. Chem.* **1992**, *57*, 2606. Ley, S. V.; Yeung, L. L. *Synlett* **1992**, 997. Cottaz, S.; Brimacombe, J. S.; Ferguson, M. A. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2945. Jaramillo, C.; Chiara, J.-L; Martin-Lomas, M. *J. Org. Chem.* **1994**, *59*, 3135.

(9) Billington, D. C. *Chem. Soc. Rev.* **1989**, *18*, 83.

(10) Garegg, P. J.; Iversen, T.; Johansson, R.; Lindberg, B. *Carbohydr. Res.* **1984**, *130*, 332.

(11) Vacca, J. P.; de Solms, S. J.; Huff, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3478. Vacca, J. P.; de Solms, S. J.; Huff, J. R.; Billington, D. C.; Baker, R.; Kulagowski, J. J.; Mawer, I. M. *Tetrahedron* **1989**, *45*, 5679.

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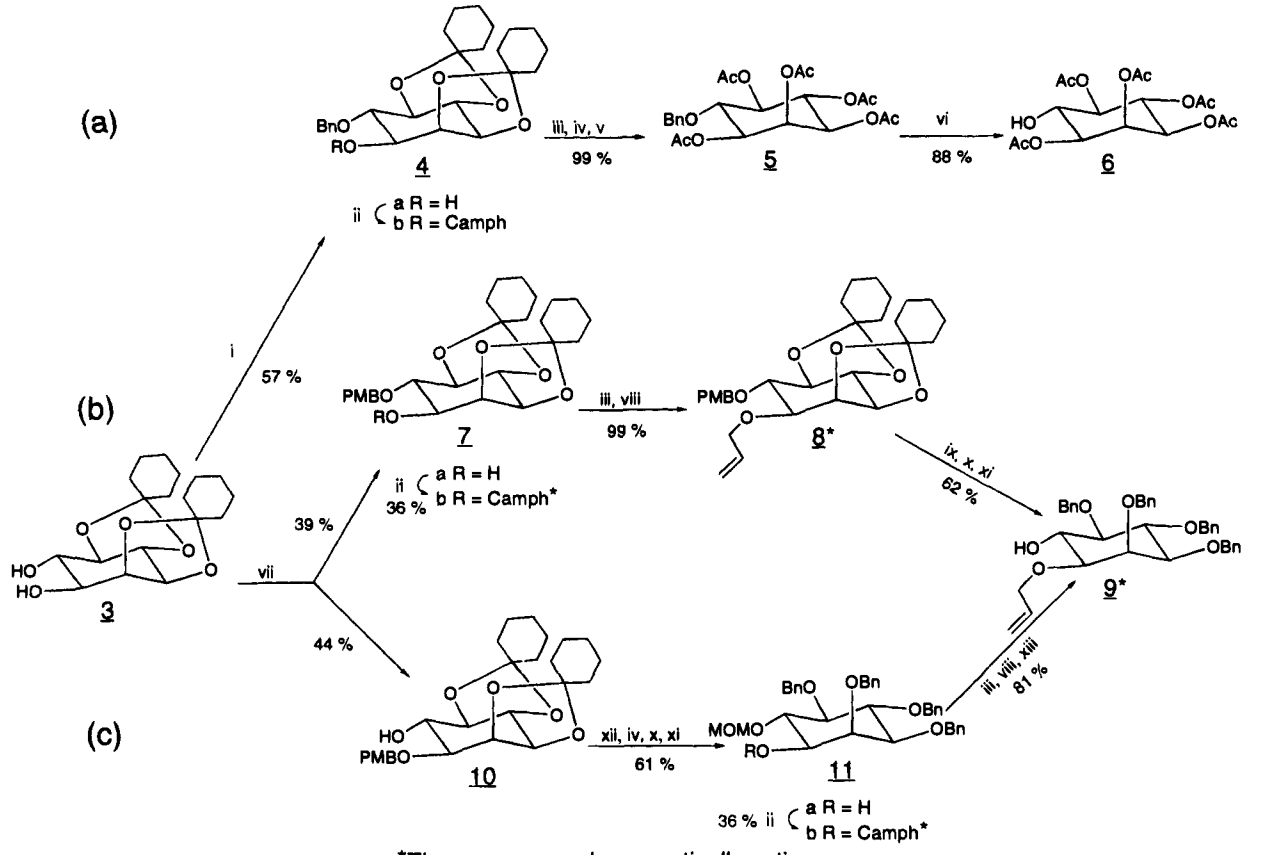
Scheme 2[a]



[a] (i) BnBr, aqueous NaOH, Bu_4NHSO_4, CH_2Cl_2; (ii) CamphCl, Et_3N, DMAP, CH_2Cl_2, then resolve; (iii) LiOH, DME, H_2O; (iv) AcOH, H_2O; (v) Ac_2O, pyridine, DMAP; (vi) H_2, Pd–C, HCOOH, EtOH, THF; (vii) Bu_2SnO, MeOH, then PMBCl, CsF, KI, DMF; (viii) allyl bromide, NaH, Bu_4NI, DMF; (ix) pTsOH, MeOH, CH_2Cl_2; (x) BnBr, NaH, Bu_4NI, DMF; (xi) CAN, CH_2Cl_2, MeCN, H_2O; (xii) MOMCl, NaH, DMF; (xiii) aqueous HCl, THF.

nate ester **4b**. Three high-yielding operations, saponification, mild acid hydrolysis, and acetylation gave the benzyl pentaacetate **5**, which upon hydrogenolysis afforded the desired material **6**.

However, compound **3** is not efficiently utilized in Scheme 2a since no use is made of the 1-*O*-benzyl regioisomer, which is produced in 25% yield along with **4a** upon benzylation. This loss could not be tolerated for our proposed large-scale preparations of **2**, and so an alternative plan was devised (Scheme 2b) which would make use of both regioisomers.

Accordingly, regioisomers **7a** and **10**, obtained by stannylene-mediated *p*-methoxybenzylation of **3**, were separated chromatographically, and the former was resolved as camphanate **7b** (Scheme 2b), in which the ester group now protects the site for future phosphorylation. The ester was replaced with allyl in **8**, this protecting group[12] being considered to be more amenable to the upcoming chemical manipulations. Selective processing of the various protecting groups of **8** then afforded the differentiated derivative **9**, which is ready for coupling.

The regioisomer **10** (Scheme 2c) carries the *p*-methoxybenzyl group at the future phosphorylation site. A series of routine functional group changes were required to free this site, **10** → **11a**, which was then camphanylated, processed, and resolved. Replacing the camphanate ester with an allyl group led to **9** identical to the material prepared in Scheme 2b as well as that reported by van Boom *via* another route.[13] Although the route in Scheme 2c is longer, the steps are efficient and thus add substantially to the stock of key intermediate **9**.

Different approaches were also taken to the glucosamine precursors. In the case of the VSG target, **1**, the aim was to see whether NPG methodology could be applied for coupling to the inositol. Accordingly, the well-known phthalimido tetraacetate **12**[14] was *n*-pentenylated under the agency of stannic chloride (Scheme 3), and benzylidene and benzyl group were installed as shown in **13**.

The chemistry of Campos-Valdes and co-workers was then applied to replace phthalimido with an anisylidene in **14**.[14,15] This change in protecting groups was necessary since phthalimido would have induced formation of the β-coupled product. In the event, the anisylidenated material **14** was coupled with the inositol **6** to give the α-linked product **15a** as the only disaccharide. The anisylidene group was then replaced with Cbz in **15b**, the overall yield, based on **6**, being 67%. Garegg reductive cleavage of the benzylidene ring[16] then afforded the glycosyl acceptor **16** (Scheme 3).

In the case of the Thy-1 target **2**, where the overall plan is tailored toward future installation of the three phosphodiester groups, the use of an azido group as a latent amino function was deemed to be the best of several options for "protecting" the C-2 amine moiety. With this objective in mind, the excellent procedure of Hori and co-workers for converting the 1,6-anhydro-β-D-mannopyranose derivative **17** into the 2-azido

(12) Gigg, R. *Am. Chem. Soc. Symp. Ser.* **1977**, *39*, 253. Gigg, R. *Am. Chem. Soc. Symp. Ser.* **1978**, *77*, 44. Gigg, R.; Conant, R. *Carbohydr. Res.* **1982**, *100*, C5.

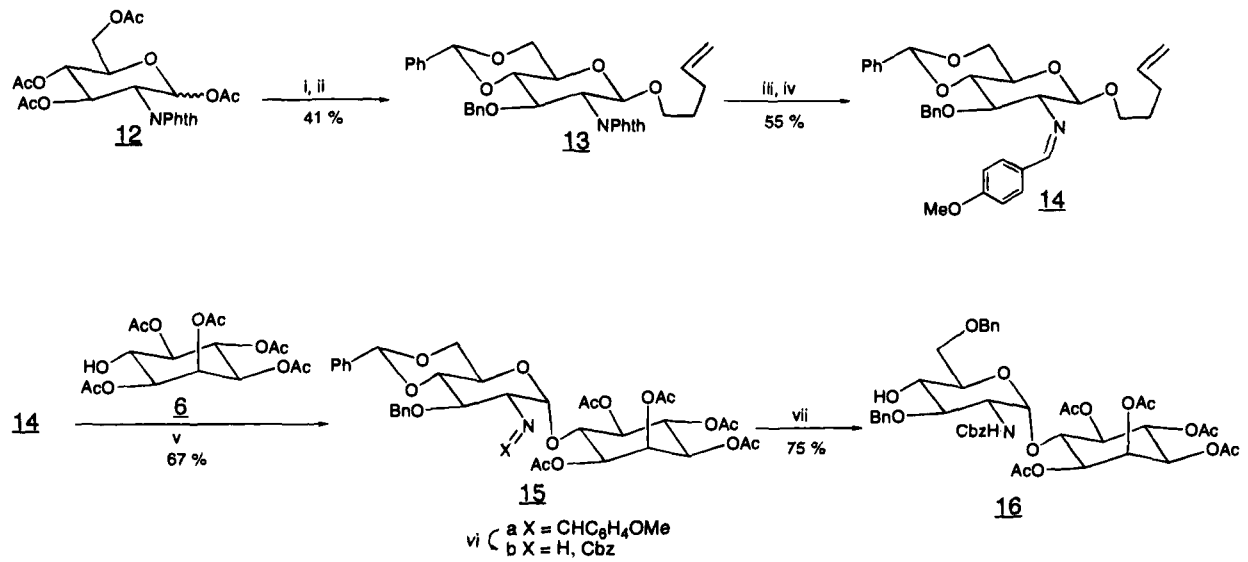
(13) Elie, C. J. J.; Verduyn, R.; Dreef, C. E.; Brounts, D. M.; van der Marel, G. A.; van Boom, J. H. *Tetrahedron* **1990**, *46*, 8243.

(14) Lemieux, R. U.; Takeda, T.; Chung, B. Y. *ACS Symp. Ser.* **1978**, *39*, 90. Mootoo, D. R.; Fraser-Reid, B. *Tetrahedron Lett.* **1989**, *30*, 2363.

(15) Compos-Valdez, M. T.; Marino-Albernas, J. R.; Verez-Bencomo, V. *J. Carbohydr. Chem.* **1987**, *6*, 509.

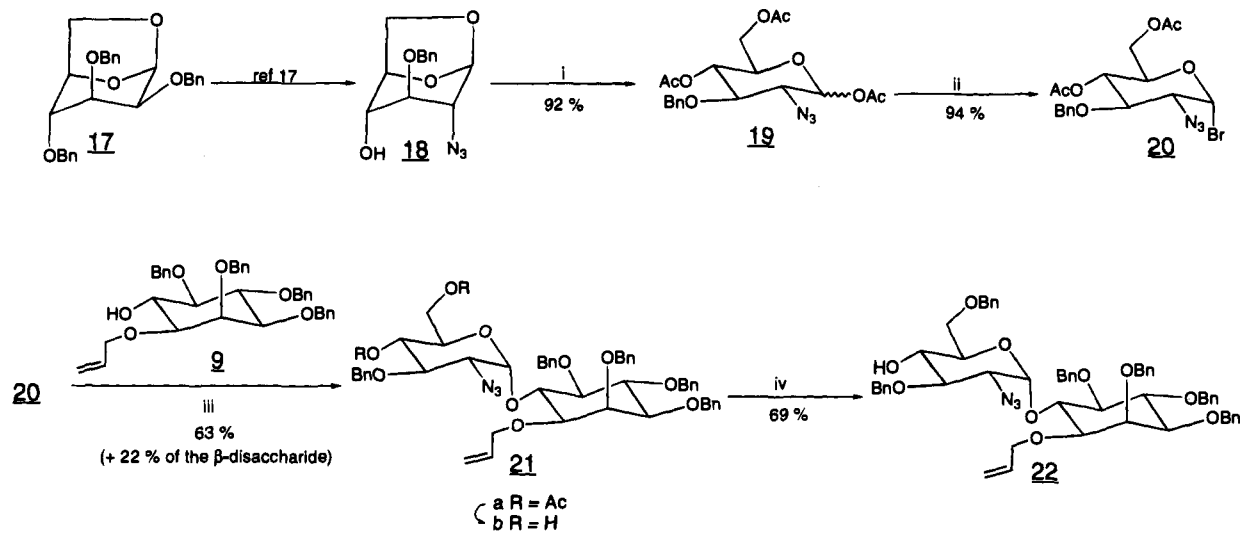
(16) Garegg, P. J.; Hultberg, H. *Carbohydr. Res.* **1981**, *93*, C10.

Scheme 3[a]



[a] (i) 4-Penten-1-ol, $SnCl_4$, CH_2Cl_2, then aqueous HCl, acetone, then $PhCH(OMe)_2$, CSA, MeCN; (ii) $BnOC(NH)CCl_3$, TfOH, CH_2Cl_2, cyclohexane; (iii) $H_2NOH{\cdot}HCl$, NaOMe, MeOH; (iv) *p*-anisaldehyde, pyridine, benzene; (v) IDCP, 4 Å MS, CH_2Cl_2, room temperature, 1 h; (vi) aqueous AcOH, MeOH, then BnOCOCl, Et_3N; (vii) $NaBH_3CN$, HCl, 3 Å MS, THF.

Scheme 4[a]



[a] (i) Ac_2O, Et_3N, DMAP, CH_2Cl_2 then Ac_2O, TFA; (ii) $TiBr_4$, CH_2Cl_2, EtOAc; (iii) $AgClO_4$, Et_2O, −35 °C → room temperature, 30 min, then NaOMe; (iv) Ac_2O, Et_3N, CH_2Cl_2, then DHP, PPTS, CH_2Cl_2, then NaOMe, then BnBr, NaH, Bu_4NI, DMF, then MeOH, PPTS.

anhydro glucose **18** was applied.[17] The latter was then treated with trifluoroacetic acid and acetic anhydride to give the glucosyl acetate **19** (Scheme 4).[18]

With respect to the choice of glycosyl donor, the NPG derivable from **19** was considered. However, the fact that the glycosyl bromide **20** had been reported by Paulsen and co-workers[18] made its use expedient. With silver triflate[19] or Helferich-type promoters,[20] coupling of **9** and **20** produced rich α/β mixtures. However, in keeping with the precedent of Kovac and Edgar,[21] silver perchlorate in ether was found to give the α-coupled disaccharide **21a** as the major product, along with some β-anomer (22%). These anomers were not resolved on TLC; however, upon deacetylation, chromatographic separation was readily achieved, affording the diol **21b**.

Selective installation of a benzyl group at the primary hydroxyl of **21b** proved to be more challenging than anticipated. Stannylene-mediated *O*-benzylation was an obvious choice;[22] but in this instance, the reaction was very sluggish and was attended by substantial decomposition. Eventually a sequence was developed which began with selective acetylation of the primary hydroxyl,[23] followed by tetrahydropyranylation of the C-4 OH. Deacetylation, benzylation, and mild acid hydrolysis then afforded the glycosyl acceptor **22**.

Assembly of the VSG Core 30

The M1 residue of the VSG anchor **1** carries two glycosyl groups at C-6 and C-3, and thus, provisions should have been

(17) Hori, H.; Nishida, Y.; Ohrui, H.; Meguro, H. *J. Org. Chem.* **1989**, *54*, 1346.

(18) Paulsen, H.; Richter, A.; Sinnwell, V.; Stenzel, W. *Carbohydr. Res.* **1978**, *64*, 339.

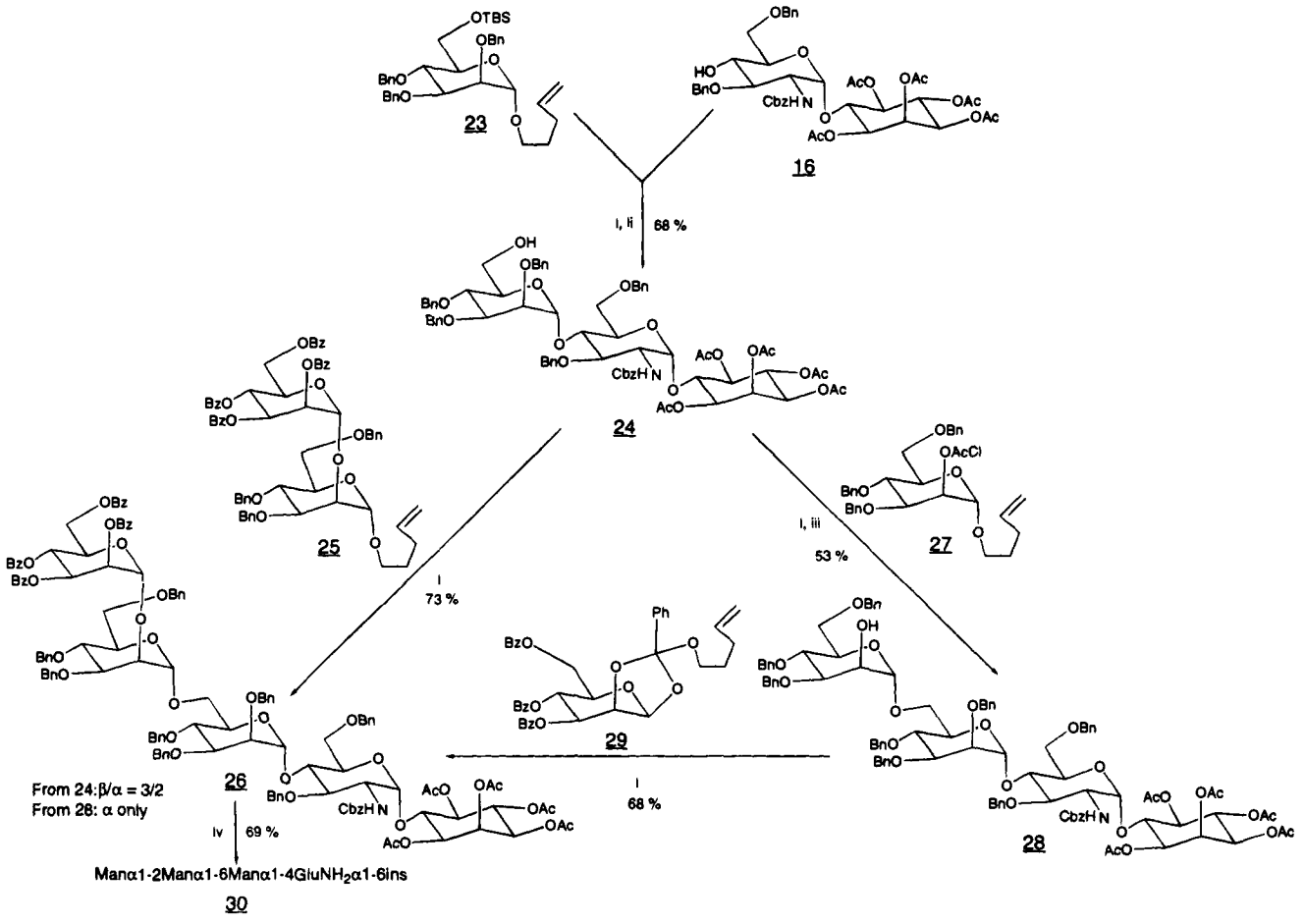
(19) Hanessian, S.; Banoub, J. *Carbohydr. Res.* **1877**, *53*, C13. Arcamone, F.; Penco, S.; Redaelli, S.; Hanessian, S. *J. Med. Chem.* **1976**, *19*, 1424.

(20) Helferich, B.; Gootz, R. *Ber. Dtsch. Chem. Ges. A* **1929**, *62*, 2505. Sharp, V. E.; Stacey, M. *J. Chem. Soc.* **1951**, 285. Micheel, F.; Klemer, A.; Nolte, M.; Nordiek, H.; Tork, L.; Westermann, H. *Chem. Ber.* **1957**, *90*, 1612.

(21) Kovac, P.; Edgar, K. J. *J. Org. Chem.* **1992**, *57*, 2455.

(22) Nagashima, N.; Ohno, M. *Chem. Pharm. Bull.* **1991**, *39*, 1972. Nagashima, N.; Ohno, M. *Chem. Lett.* **1987**, 141.

Scheme 5[a]



[a] (i) NIS, TfOH, 3 Å MS, CH_2Cl_2; (ii) HF-pyridine, THF; (iii) thiourea, EtOH; (iv) NaOMe, then HCOOH, Pd−C, MeOH.

made for both future glycosidations. However, in our early exploratory synthesis of **1**,[6] this requirement was ignored for the C-3 OH, and the silylated *n*-pentenyl mannoside **23** was utilized as the donor for the disaccharide **16** to give a trisaccharide. Cleavage of the silyl ether gave the acceptor **24** in 68% overall yield. This material was now ready for coupling to disaccharide **25**, whose preparation has been described in the accompanying manuscript.[2]

Under the agency of NIS/TfOH,[24] coupling of building blocks **24** and **25** was rapid and high yielding; however, the product turned out to be an anomeric mixture of **26**, the β:α ratio being 3:2.

On the assumption that this unfavorable result was correlated with the high reactivity of the primary hydroxyl of **24**, an alternative approach involving another glycosyl donor was attempted. In this stepwise plan, coupling of trisaccharide **24** with the differentially protected mannoside **27** under the agency of NIS/TfOH[24] afforded a tetrasaccharide and treatment with thiourea then gave the glycosyl acceptor **28** in 53% overall yield. The glycosyl donor was the *n*-pentenyl ortho ester **29**, and under the agency of NIS/TfOH, the desired α anomer, **26**, was obtained as the only coupling product in 68% yield.

Deesterification followed by debenzylation *via* hydrogen transfer from formic acid in the presence of 10% palladium on carbon[25] then afforded the VSG core material **30** in 69% yield from **26**.

(23) Selective acetylation of the primary OH was achieved by slowing down the reaction by using Ac_2O and Et_3N and omission of DMAP (see the Experimental Section).

(24) Konradsson, P.; Mootoo, D. R.; McDevitt, R. E.; Fraser-Reid, B. *J. Chem. Soc., Chem. Comm.* **1990**, 270.

The Thy-1 Anchor

The need to make provisions for the three phosphodiester groups of **2** has been met by installing three different protecting groups that can be selectively removed. All of the other hydroxyl groups are protected as benzyl ethers in order to simplify the final deprotection step(s).

Building Blocks for 2

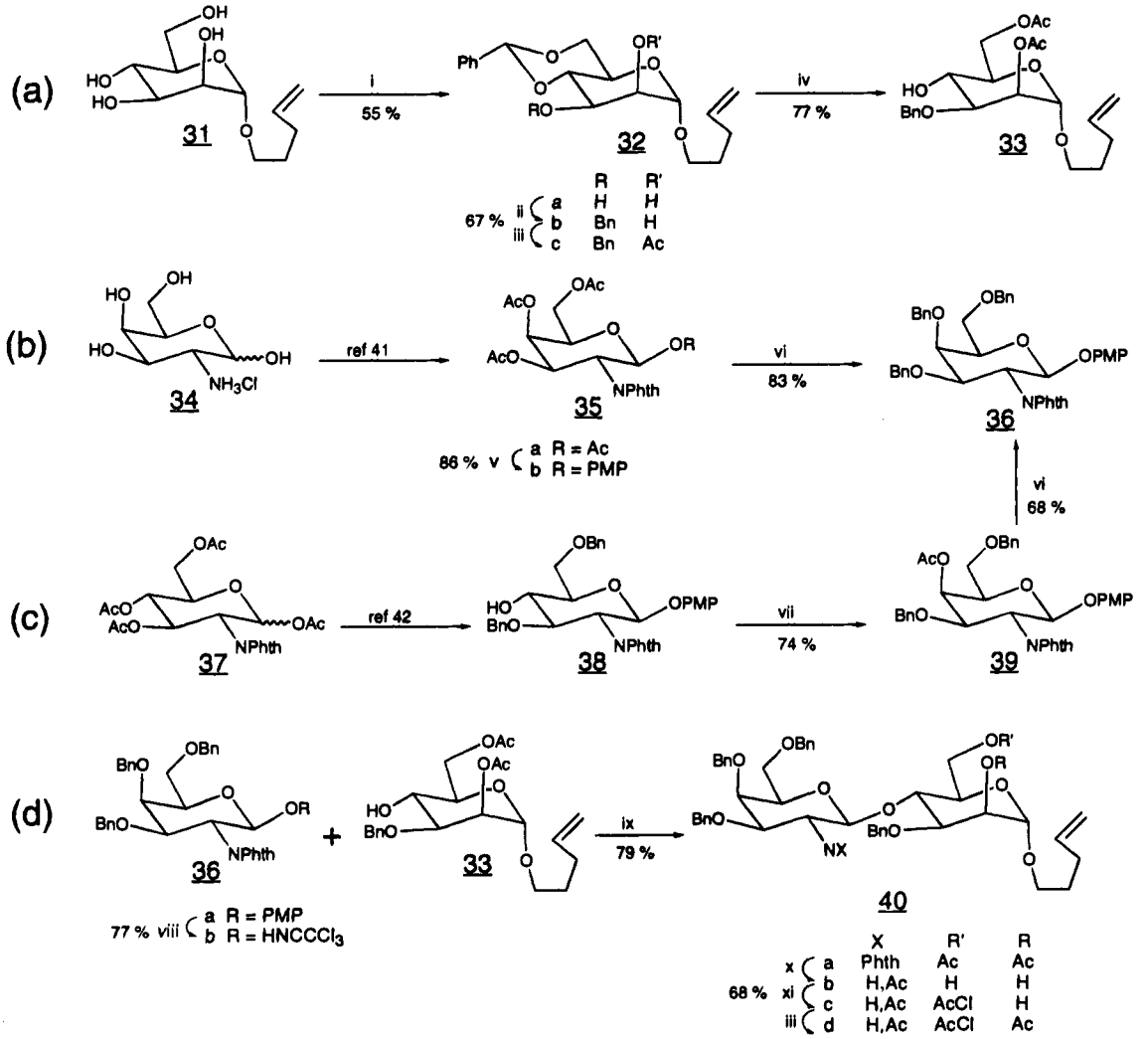
With regard to the M1 component of the Thy-1 target, **2**, selective access to the C-6 and C-4 hydroxy groups has been met with the differentially protected mannoside **33** prepared as outlined in Scheme 6a. Thus *n*-pentenyl α-D-mannopyranoside **31** was benzylidenated to compound **32a** and regioselectively benzylated and esterified to provide compounds **32b** and **32c**, respectively, in acceptable overall yields. Debenzylidenation and chemoselective acetylation[23] then afforded the glycosyl acceptor **33**.

The glycosyl donor that is to be attached at the C-4 site of **33** is a galactosaminide residue, and two routes were developed for its preparation as outlined in Scheme 6b,c. The first, which involves four steps, begins with expensive galactosamine hydrochloride, and standard operations led to the phthalimido derivatives **35a**,**b** and then to the tribenzylated counterpart **36**.

The second route begins with much cheaper glucosamine hydrochloride and utilizes the C-4 inversion protocol,[26] as developed by Chaplin *et al.*[27] (Scheme 6c). Although involving twice as many steps as the route in Scheme 6b, the latter

(25) ElAmin, B.; Anantharamaiah, G. M.; Royer, G. P.; Means, G. E. *J. Org. Chem.* **1979**, *44*, 3442.

Scheme 6[a]



[a] (i) $PhCH(OMe)_2$, PPTS, DMF; (ii) Bu_2SnO, MeOH, then BnBr, DMF; (iii) Ac_2O, Et_3N, DMAP, CH_2Cl_2; (iv) AcOH, H_2O, then Ac_2O, Et_3N, CH_2Cl_2; (v) *p*-methoxyphenol, TMSOTf, 4 Å MS, CH_2Cl_2; (vi) NaOMe, then BnBr, NaH, Bu_4NI, DMF; (vii) Tf_2O, pyridine, CH_2Cl_2, then CsOAc, DMSO; (viii) CAN, toluene, MeCN, H_2O, then CCl_3CN, DBU, toluene; (ix) TMSOTf, 4 Å MS, toluene, −20 °C, 2 h; (x) $MeNH_2$, EtOH, then Ac_2O; (xi) $(ClAc)_2O$, Et_3N, CH_2Cl_2.

sequence is more attractive for large-scale work because several of the early intermediates are crystalline and hence purification is facilitated.

The use of 2-deoxy-2-phthalimido trichloroacetimidates as glycosyl donors is well precedented,[28] since Schmidt has shown that their use educes high yields and high β selectivity.[29] Accordingly, compound **36b** was prepared as a crystalline material which seemed ideal for our purposes, since three benzyl ethers are already in place. In this coupling, the *n*-pentenyl mannoside **33** would therefore be utilized as a glycosyl acceptor. Trimethylsilyl triflate-mediated coupling afforded **40a** in 79% yield.

We now needed to differentiate between the two acetylated sites of **40a**, so as to provide for glycosidation at C-6 and phosphorylation at C-2. In addition, the phthalimido group had to be replaced. The latter task is classically carried out with hydrazine according to the Ing−Manske reaction;[30] however, with NPGs, we have found that this reagent sometimes causes saturation of the double bond,[31] and hence an alternative course was pursued.

It was convenient to modify all three acylated sites of **40a** simultaneously. This was achieved by complete deacylation using methylamine, and N-acetylation was effected directly to give **40b**. The primary hydroxyl group could then be chemoselectively chloroacetylated to **40c**, and then the latter subsequently acetylated to give the disaccharide donor **40d**.

Assembly of Heptasaccharide 43

The first stage involved coupling of the donor and acceptor disaccharides **40d** and **22**, respectively. It turned out that **22** was exceedingly prone to silylation when *N*-iodosuccinimide and triethylsilyl triflate (NIS/TESOTf) was used as the promoter. On previous occasions where this problem had been encoun-

(26) See, for example: Nashed, M. A.; Anderson, L. *Carbohydr. Res.* **1983**, *114*, 53. Vandana; Hindsgaul, O.; Baenziger, J. *Can. J. Chem.* **1987**, *65*, 1645. El-Sokkary, R. I.; Silwanis, B. A.; Nashed, M. A.; Paulsen, H. *Carbohydr. Res.* **1990**, *203*, 319. Lubineau, A.; Bienaymé, M. *Carbohydr. Res.* **1991**, *212*, 267.

(27) Chaplin, D.; Crout, D. H. G.; Bornemann, S.; Hutchinson, D. W.; Khan, R. *J. Chem. Soc., Perkin Trans 1* **1992**, 235.

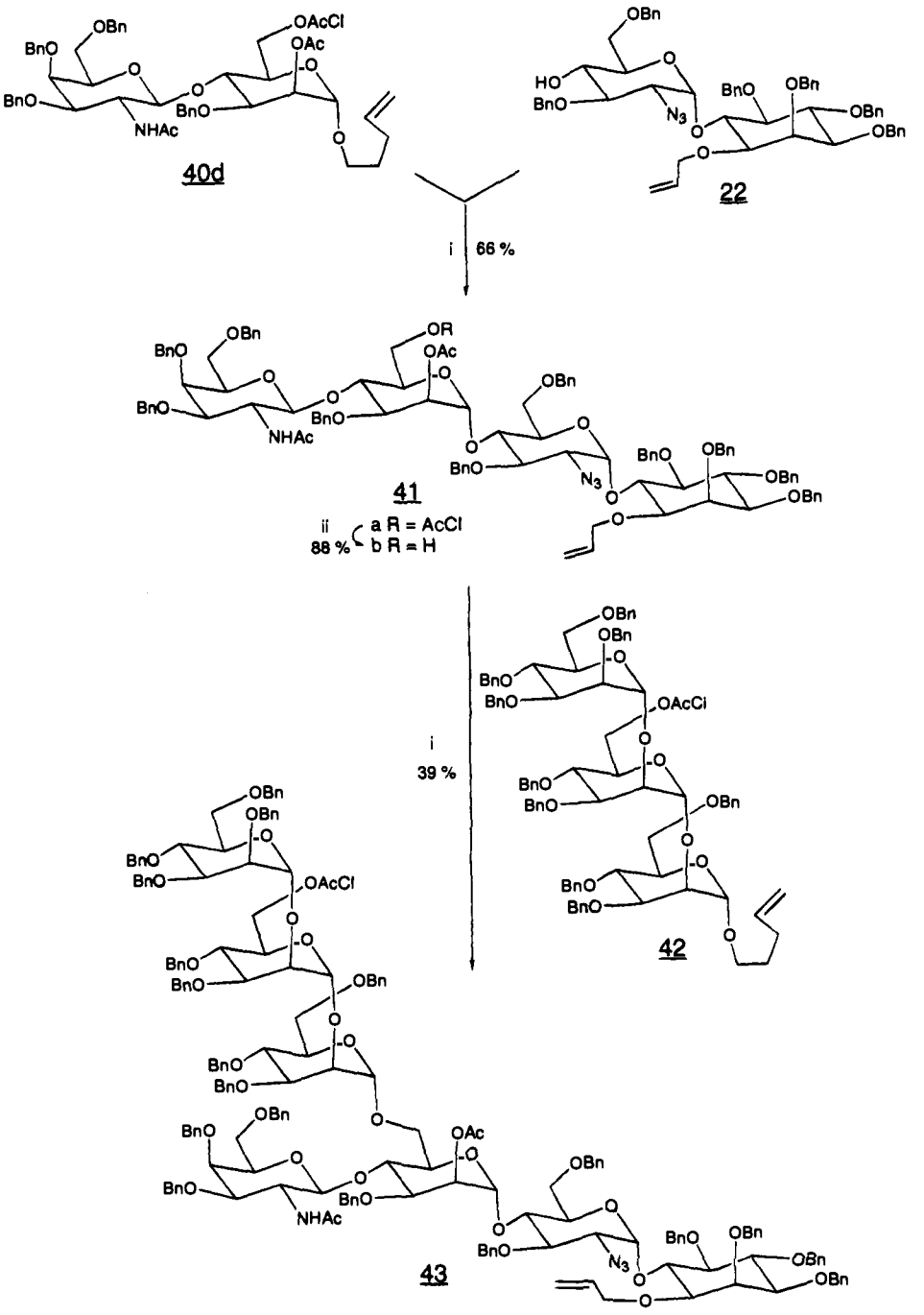
(28) See, for example: Ito, Y.; Nunomura, S.; Shibayama, S.; Ogawa, T. *J. Org. Chem.* **1992**, *57*, 1821. Kobayashi, M.; Yamazaki, F.; Ito, Y.; Ogawa, T. *Carbohydr. Res.* **1990**, *201*, 51.

(29) Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212. Schmidt, R. R. *Pure. Appl. Chem.* **1989**, *61*, 1257.

(30) Ing, H. R.; Manske, R. H. F. *J. Chem. Soc.* **1926**, 2348.

(31) Although the reaction was done under argon, it would appear that enough air was present to oxidize hydrazine to diimide, which then served as the reducing agent.

Scheme 7[a]



[a] (i) NIS, Et_3SiOTf, CH_2Cl_2, room temperature, 15 min; (ii) thiourea, MeOH, $CHCl_3$, 60 °C, 2.5 h.

tered, the solution was simply to change the Lewis acid. However with BF_3·OEt_2, the yield of coupled material **41a** was even lower than with NIS/TESOTf. Use of triflic acid (TfOH) was not availing because attendant acid-catalyzed decomposition was evident. Iodonium dicollidinylium perchlorate (IDCP) was not potent enough for coupling to proceed at a reasonable rate.

Our solution was to reverse the relative amounts of the partners. Thus use of a 1.2 M excess of acceptor **22** led to 66% yield of **41a** based on the donor **40d**. Upon column chromatography, the silylated acceptor was easily recovered and desilylated with the tetrabutylammonium fluoride (TBAF).

Dechloroacetylation then provided acceptor **41b**. The donor was the trimannan **42**, whose preparation is described in the accompanying manuscript. The latter was based in 1.5 M excess for coupling, with NIS/TESOTf as the promoter, which gave heptasaccharide **43** in 39% yield based on recovered acceptor **41b**.

The anomeric configurations in the heptasaccharide **43** were established by comparing C−H coupling constants[32] with those of the trisaccharide, **42**, and tetrasaccharide, **41a**, precursors. For the former, these values are 175, 169, and 171 Hz, which indicate three α manno orientations. For tetrasaccharide **41a**, there are three anomeric carbons with coupling constants of 163, 177, and 184 Hz, indicating β, α, and α, configurations, respectively. The heptasaccharide **43** showed the following: 162 Hz for a β anomer and 178, 177, 173, 183, and 177 Hz for

(32) Bock, K.; Pedersen, C. *J. Chem. Soc., Perkin Trans. 2* **1974**, 293.

five α anomers. This indicated that the product resulting from reaction of **41b** and **42** was indeed α-coupled.

Conclusion

Using the strategy described above, gram amounts of heptasaccharide **43** have been prepared in a matter of weeks, and the procedures should be readily adapted for larger scale production. Indeed our scale-up efforts have been generally attended by improvements in yields for the coupling reactions.

Although other glycosyl donors have been used for specific tasks, assembly of the advanced intermediates in both anchors takes place *via n*-pentenyl glycoside coupling only. In the case of **30**, the process is stepwise, whereas assembly of **43** employs a convergent (block) synthesis strategy.

The *n*-pentenyl group is exploited both as a protecting group for and as an activator of the anomeric center. Thus a wide variety of manipulations on the building blocks is permissible. However, coupling can be effected within minutes depending the promoter that is used. All *n*-pentenylated intermediates can be stored indefinitely.

In view of retrons **I**, **II**, and **III** generated by the retrosynthetic plan in Scheme 1, it is clear that the building blocks **16**, **22**, **25**, **40**, and **42** can be tailored for producing all of the known anchors.[33]

With respect to the feasibility of the planned selective deprotections/phosphorylations of **43** so as to install the three phosphodiester units, support studies in our laboratory have been carried out on model systems.[34] The results have been most encouraging, and application to **43** is therefore being vigorously pursued.

Experimental Section

General Procedures. See the accompanying paper.[2]

1,2,3,4,5-Penta-*O*-acetyl-D-*myo*-inositol (6). The 6-*O*-benzyl-2,3,4,5-di-*O*-cyclohexylidene camphanate ester **4b**[11] (775 mg, 1.27 mmol) was dissolved in a mixture of dimethoxyethane (5 mL) and water (5 mL). $LiOH·H_2O$ (500 mg, 11.9 mmol) was added to the solution and the reaction mixture stirred at room temperature for 1 h. Most of the volatiles were removed *in vacuo*, and the slurry was diluted with water (10 mL) and extracted with EtOAc. The combined organics were evaporated *in vacuo* and dissolved in 80% aqueous AcOH. The temperature of the solution was raised to reflux for 1 h, at which time the volatiles were removed *in vacuo*. The crude residue was dried under high vacuum, dissolved in pyridine (2 mL) and EtOAc (10 mL), and treated with DMAP (50 mg) and Ac_2O (1 mL). The reaction mixture was stirred at room temperature for 1 h, at which time excess Ac_2O was decomposed by the addition of MeOH (0.5 mL). The volatiles were removed *in vacuo*, and the crude was residue purified by flash chromatography (7:3 petroleum ether/EtOAc) to give **5** (605 mg, 99%) as a white solid, $R_f = 0.40$. To a solution of **5** (520 mg, 1.05 mmol) in EtOH (5 mL) and THF (5 mL) were added formic acid (0.2 mL) and 10% palladium on carbon (200 mg). The suspension was shaken under hydrogen at 60 psi for 36 h. The catalyst was removed by filtration and the filtrate evaporated *in vacuo*. Flash chromatography (1:1 petroleum ether/EtOAc) of the resultant syrup afforded pentaacetate **6** (373 mg, 88%): mp 160−161 °C; $R_f = 0.51$; $[\alpha]^{20}_D$ +14.5° (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 5.58 (t, *J* = 3 Hz, H-2), 5.44 (t, *J* = 10 Hz, H-6), 5.16 (t, *J* = 10 Hz, H-5), 5.12 (dd, *J* = 3, 10 Hz, H-1), 5.06 (dd, *J* = 3, 10 Hz, H-3), 4.04 (m, H-4), 2.80 (bd, *J* = 8 Hz, O*H*), 2.17, 2.11, 2.07, 2.04, 1.98 (s, 5Ac); ^{13}C NMR δ 170.8, 170.1, 170.0, 170.0, 169.5, (5Ac), 73.2, 70.6, 69.9, 69.5, 68.9, 68.6 (C-1−C-6), 20.8, 20.7, 20.7, 20.6, 20.5 (5Ac). Anal. Calcd for $C_{16}H_{22}O_{11}$: C, 49.23; H, 5.68. Found: C, 49.17; H, 5.71.

2,3:4,5-Di-*O*-cyclohexylidene-6-*O*-(*p*-methoxybenzyl)-*myo*-inositol (7a) and 2,3:4,5-Di-*O*-cyclohexylidene-1-*O*-(*p*-methoxybenzyl)-*myo*-inositol (10). The diol **3**[10] (31.4 g, 92.2 mmol) in MeOH (150 mL) was treated with Bu_2SnO (23 g, 92.3 mmol). The mixture was refluxed for 2 h to obtain a homogeneous solution. MeOH was then removed at reduced pressure. Toulene was evaporated from the residual glue. To this were added CsF (19.1 g, 126 mmol) and KI (20.7 g, 125 mmol). The mixture was dried under high vacuum in the dark for 2 h. The mixture was then taken up in DMF (100 mL) and treated with *p*-methoxybenzyl chloride (25 mL, 184 mmol). The mixture was stirred for 18 h at room temperature before diluting with brine (400 mL) and Et_2O (400 mL). After filtration through Celite, the aqueous layer was extracted twice with Et_2O (400 mL). Flash chromatography (85:15 → 70:30 petroleum ether/EtOAc) of the dried and concentrated Et_2O extract gave 16.4 g (39%) of **7a** ($R_f = 0.45$, 4:1 petroleum ether/EtOAc) and 18.5 g (44%) of **10** ($R_f = 0.20$, 4:1 petroleum ether/EtOAc). Spectral data were as reported.[35] Structures **10** and **7a** were further confirmed by conversion to **4a**[11] ($R_f = 0.60$, 4:1 petroleum ether/EtOAc) and its 1-benzyl isomer[11] ($R_f = 0.23$, 4:1 petroleum ether/EtOAc), respectively, through the sequence of benzylation (NaH/DMF/Bu_4NI/BnBr) and de-*p*-methoxybenzylation (DDQ, 18:1 CH_2Cl_2/H_2O).

1-*O*-[(1*S*)-(−)-Camphanoyl]-2,3:4,5-di-*O*-cyclohexylidene-6-*O*-(*p*-methoxybenzyl)-D-*myo*-inositol (7b). The alcohol **7a** (4.0 g, 8.68 mmol) and (1*S*)-(−)-camphanic chloride (2.3 g, 10.6 mmol, 1.2 equiv) in CH_2Cl_2 (80 mL) was treated with Et_3N (2.41 mL, 17.2 mmol, 2 equiv), followed by catalytic amount of DMAP. After the mixture was stirred for 1 h at room temperature, TLC (4:1 petroleum ether/EtOAc) showed complete consumption of the starting material. The reaction mixture was then washed with brine and concentrated at reduced pressure. The crude product was flash chromatographed (98:2 → 97:3 CH_2Cl_2/Et_2O) to separate a pair of diastereomers D-**7b** (2.03 g, 36%) and L-**7b** (1.74 g, 31%) along with 1 g (18%) of DL mixture.

For compound D-**7b**: $R_f = 0.34$ (98:2 CH_2Cl_2/Et_2O); $[\alpha]^{20}_D$ −36.5° (*c* 1.4, $CHCl_3$); ^{1}H NMR δ 7.28 (m, 2H), 6.87 (m, 2H), 5.22 (t, *J* = 5.0 Hz, 1H), 4.75 (d, *J* = 11.4 Hz, 1H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.59 (dd, *J* = 4.7, 6.2 Hz, 1H), 4.31 (dd, *J* = 6.3, 8.3 Hz, 1H), 3.88−3.83 (m, 2H), 3.80 (s, OMe), 3.49 (dd, *J* = 8.8, 10.5 Hz, 1H), 2.37 (m, 1H), 2.04−1.86 (m, 2H), 1.80−1.30 (m, 21H), 1.10 (s, Me), 1.01 (s, Me), 0.90 (s, Me); ^{13}C NMR δ 178.0, 166.6 (2C=O), 159.3, 129.8, 129.6, 113.8 (PMB), 113.2, 110.1 (2O−C−O), 90.8 (C−O), 55.3 (OMe), 54.8, 54.5 (2C), 16.7, 16.6, 9.8 (3Me). Anal. Calcd for $C_{36}H_{48}O_{10}$: C, 67.48; H, 7.55. Found: C, 67.60; H, 7.59.

For compound L-**7b**: $R_f = 0.45$ (98:2, CH_2Cl_2/Et_2O); $[\alpha]^{20}_D$ +21.8° (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 7.31 (m, 2H), 6.87 (m, 2H), 5.24 (t, *J* = 4.7 Hz, 1H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.70 (d, *J* = 11.5 Hz, 1H), 4.58 (dd, *J* = 4.7, 6.3 Hz, 1H), 4.31 (dd, *J* = 6.4, 8.1 Hz, 1H), 3.89−3.82 (m, 2H), 3.80 (s, OMe), 3.51 (dd, *J* = 8.5, 10.5 Hz, 1H), 2.45 (m, 1H), 2.08−1.84 (m, 2H), 1.80−1.30 (m, 21H), 1.10 (s, Me), 1.00 (s, Me), 0.91 (s, Me); ^{13}C NMR δ 177.9, 166.5 (2C=O), 159.3, 129.7, 129.5, 113.8 (PMB), 113.1, 111.5 (2O−C−O), 90.9 (C−O), 55.3 (OMe), 54.9, 54.4 (2C), 17.0, 16.7, 9.8 (3Me). Anal. Calcd for $C_{36}H_{48}O_{10}$: C, 67.48; H, 7.55. Found: C, 67.64; H, 7.59.

1-*O*-Allyl-2,3:4,5-di-*O*-cyclohexylidene-6-*O*-(*p*-methoxybenzyl)-D-*myo*-inositol (8). The camphanate D-**7b** (0.3 g, 0.4 mmol) in 1,2-dimethoxyethane (1.8 mL) and H_2O (1.8 mL) was treated with $LiOH·H_2O$ (0.18 g, 4.29 mmol) and stirred for 1 h at room temperature. TLC (4:1 petroleum ether/EtOAc) indicated complete consumption of the starting material ($R_f = 0.43$) and the appearance of a higher ($R_f = 0.51$) product. The reaction mixture was then concentrated at reduced pressure to remove most of the DME. The residual matter was taken up in CH_2Cl_2/H_2O. The organic layer was decanted and the aqueous layer extracted three times with CH_2Cl_2. The combined organic solution was dried and concentrated, and the crude product was dried under high vacuum to obtain 232 mg. This in DMF (3 mL) was treated at 0 °C with NaH (37 mg, 0.93 mmol, 60% oil dispersion). After 5 min of stirring at room temperature, Bu_4NI (17 mg, 0.47 mmol) was added, followed at 0 °C by allyl bromide (0.081 mL, 0.93 mmol). The reaction mixture was stirred for 45 min at room temperature before quenching at 0 °C with MeOH. The mixture was then diluted with H_2O and extracted three times with Et_2O. Flash chromatography of the crude product (9:1 petroleum ether/EtOAc) gave 234 mg (99%) of **8**: $R_f = 0.41$; ^{1}H NMR δ 7.30 (m, 2H), 6.87 (m, 2H), 5.86 (m, −CH=), 5.28−5.15 (m, =CH_2), 4.68 (d, *J* = 11.3 Hz, 1H), 4.59 (d, *J* = 11.3 Hz,

(33) See Scheme 1 of ref 2.
(34) Campbell, A. S.; Fraser-Reid, B. *BioMed. Chem.*, in press.
(35) Murakata, C.; Ogawa, T. *Carbohydr. Res.* **1992**, *234*, 75.

1H), 4.38 (dd, J = 3.8, 6.8 Hz, 1H), 4.30 (t, J = 7.2 Hz, 1H), 4.12–4.06 (m, 3H), 3.81 (m, 1H), 3.80 (s, OMe), 3.67 (t, J = 3.2 Hz, 1H), 3.49 (dd, J = 7.8, 10.5 Hz, 1H), 1.90–1.30 (m, 20H).

1-*O*-Allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (9). The diketal **8** (234 mg, 0.46 mmol) in 1:1 MeOH/CH_2Cl_2 (6 mL) was stirred for 24 h with *p*-TsOH·H_2O (13 mg, 0.068 mmol). The reaction mixture was then quenched with Et_3N and concentrated at reduced pressure. The residual oil was dried under high vacuum to obtain 172 mg (R_f = 0.17, 9:1 CH_2Cl_2/MeOH). This in 4 mL of DMF was treated at 0 °C with NaH (92.7 mg of 60% oil dispersion, 2.32 mmol). The mixture was stirred for 5 min at room temperature before recooling to 0 °C and treating with Bu_4NI (17 mg, 0.046 mmol), followed by BnBr (0.28 mL, 2.31 mmol). After 1 h at room temperature, the reaction mixture was quenched with MeOH. Solvent was then removed at reduced pressure. The residual matter was diluted with H_2O and extracted three times with CH_2Cl_2. Flash chromatography (85:15 petroleum ether/EtOAc) of the dried and concentrated CH_2Cl_2 extract gave 243 mg, R_f = 0.39. To this in 7 mL of CH_2Cl_2/2 mL of MeCN/0.2 mL of H_2O at 0 °C was added $(NH_4)_2Ce(NO_3)_6$ (CAN, 0.373 g, 0.68 mmol). The mixture was stirred for 0.5 h at 0 °C before diluting with CH_2Cl_2 and washing with saturated aqueous $NaHCO_3$. The dried CH_2Cl_2 extract was concentrated at reduced pressure. The residual matter was flash chromatographed (4:1 → 3:1 petroleum ether/EtOAc) to collect 166.6 mg (62%) of **9**: R_f = 0.41 (4:1 petroleum ether/EtOAc); $[\alpha]^{20}_D$ −8.7° (c 1.2, $CHCl_3$) (lit.[13] $[\alpha]^{20}_D$ −6.5° (c 1, $CHCl_3$)); NMR data were as reported.[13] Anal. Calcd for $C_{37}H_{40}O_6$: C, 76.53; H, 6.94. Found: C, 76.33; H, 6.75.

2,3,4,5-Tetra-*O*-benzyl-6-*O*-(methoxymethyl)-*myo*-inositol (11a). The alcohol **10** (3.73 g, 8.10 mmol) in 20 mL of DMF was stirred for 0.5 h at 0 °C with NaH (0.53 g, 13.2 mmol, 60% oil dispersion). Methoxymethyl chloride (MOMCl, 1 mL, 13.2 mmol) was then added dropwise at 0 °C. After stirring for 3 h at room temperature, the mixture was recooled to 0 °C and quenched with saturated aqueous $NaHCO_3$. The mixture was diluted with water and extracted three times with Et_2O. Flash chromatography (85:15 petroleum ether/EtOAc) of the concentrated crude product gave 3.85 g, R_f = 0.43. This material (3.66 g, 7.25 mmol) was dissolved in 4:1 HOAc/H_2O (30 mL) and stirred at room temperature for 24 h. Solvent was then removed at reduced pressure. The crude product was chromatographed (9:1 CH_2Cl_2/EtOAc → 9:1 CH_2Cl_2/MeOH) on a short column to obtain 1.98 g (R_f = 0.29, 9:1 CH_2Cl_2/MeOH). This in DMF (50 mL) was treated at 0 °C with NaH (1.9 g, 47.5 mmol, 60% oil dispersion) portionwise. The mixture was stirred at room temperature for 25 min before being treated with Bu_4NI (0.2 g, 0.54 mmol) and BnBr (5.8 mL, 48.8 mmol) at 0 °C. After being stirred for 8 h at room temperature, the reaction mixture was quenched at 0 °C with MeOH, diluted with water, and extracted three times with Et_2O. The extract was shaken with brine, dried, and concentrated. Flash chromatography (85:15 → 80:20 petroleum ether/EtOAc) of the residual matter gave 3.8 g (R_f = 0.32, 85:15 petroleum ether/EtOAc). This in 23 mL of CH_2Cl_2/46 mL of MeCN/4.6 mL of H_2O was treated at 0 °C with CAN (7.1 g, 13.0 mmol). The reaction mixture was stirred at room temperature for 30 min before being quenched at 0 °C with saturated aqueous $NaHCO_3$ (100 mL). The mixture was then diluted with CH_2Cl_2 and filtered through Celite. The organic layer of the filtrate was separated and the aqueous layer extracted three times with CH_2Cl_2. The combined CH_2Cl_2 solution was shaken with brine and dried. Flash chromatography (85:15 → 70:30 petroleum ether/EtOAc) gave 2.73 g (61%) of **11a**: R_f = 0.38 (7:3 petroleum ether/EtOAc); ^{1}H NMR δ 7.44–7.26 (m, 20H, Ph), 4.96 (d, J = 11.7 Hz, 1H), 4.94 (d, J = 10.7 Hz, 1H), 4.88 (d, J = 10.7 Hz, 1H), 4.84 (d, J = 11.7 Hz, 1H), 4.82 (d, J = 10.7 Hz, 1H), 4.77 (s, 2H), 4.76 (d, J = 10.7 Hz, 1H), 4.68 (s, 2H), 4.09–4.03 (m, 2H), 3.83 (t, J = 9.3 Hz, 1H), 3.50–3.40 (m, 6H).

2,3,4,5-Tetra-*O*-benzyl-1-*O*-[(1*S*)-(−)-camphanoyl]-6-*O*-(methoxymethyl)-D-*myo*-inositol (11b). The alcohol **11a** (2.73 g, 4.67 mmol) and (1*S*)-(−)-camphanic chloride (1.25 g, 5.77 mmol) in CH_2Cl_2 (45 mL) was cooled to 0 °C and treated with Et_3N (1.3 mL, 9.33 mmol), followed by a catalytic amount of DMAP. After being stirred for 1 h at room temperature, the reaction was diluted with CH_2Cl_2 and washed with brine. The solvent was removed at diminished pressure and the residue purified by flash chromatography (97:3 CH_2Cl_2/Et_2O) to separate the diastereomers D-**11b** (1.3 g, 36%) and L-**11b** (1.58 g, 44%) together with 0.3 g (8%) of a DL mixture.

For D-**11b**: R_f = 0.38; $[\alpha]^{20}_D$ −15.7° (c 1.2, $CHCl_3$); ^{1}H NMR δ 7.35–7.25 (m, 20H, Ph), 4.97 (d, J = 11.5 Hz, 1H), 4.91 (d, J = 9.8 Hz), 4.88–4.75 (m, 6H), 4.71 (s, 2H), 4.62 (d, J = 11.5 Hz, 1H), 4.20–4.16 (m, 2H), 4.09 (t, J = 9.7 Hz, 1H), 3.58 (dd, J = 2.0, 9.8 Hz, 1H), 3.49 (t, J = 9.3 Hz, 1H), 3.33 (s, OMe), 2.39 (m, 1H), 2.04–1.85 (m, 2H), 1.69 (m, 1H), 1.10, 1.01, 0.97 (3Me); ^{13}C NMR δ 178.4, 166.8 (2C=O), 98.6 (O–CH_2–O), 90.9 (C–O), 56.6 (OMe), 54.8, 54.3 (2C), 30.9, 29.0 ($2CH_2$), 16.8, 16.7, 9.7 (3 Me). Anal. Calcd for $C_{46}H_{52}O_{10}$: C, 72.23; H, 6.85. Found: C, 72.06; H, 6.91.

For L-**11b**: R_f = 0.44; $[\alpha]^{20}_D$ +7.5° (c 1.2, $CHCl_3$); ^{1}H NMR δ 7.38–7.25 (m, 20H, Ph), 4.99–4.77 (m, 8H) 4.70 (s, 1H), 4.69 (s, 1H), 4.66 (d, J = 11.5 Hz, 1H), 4.19 (t, J = 9.7 Hz, 1H), 4.09–4.07 (m, 2H), 3.57 (dd, J = 2.1, 9.8 Hz, 1H), 3.50 (t, J = 9.3 Hz, 1H), 3.33 (s, OMe), 2.43 (m, 1H), 2.07–1.87 (m, 2H), 1.69 (m, 1H), 1.11, 1.08, 0.94 (3Me); ^{13}C NMR δ 178.0, 167.4 (2C=O), 98.6 (O–CH_2–O), 90.8 (C–O), 56.6 (OMe), 54.8, 54.4 (2C), 30.9, 28.9 ($2CH_2$), 16.9, 16.7, 9.7 (3Me). Anal. Calcd for $C_{46}H_{52}O_{10}$: C, 72.23; H, 6.85. Found: C, 71.99; H, 6.94.

1-*O*-Allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (9). To the camphanate D-**11b** (4.56 g, 5.96 mmol) in 1,2-dimethoxyethane (25 mL) and water (25 mL)) was added LiOH·H_2O (2.4 g, 57.2 mmol). The reaction mixture was stirred at room temperature for 3 h and then concentrated to remove DME. The residue was taken up in CH_2Cl_2 (40 mL) and washed successively with water (30 mL) and brine (40 mL). The organic solution was dried, concentrated, and flash chromatographed (7:3 petroleum ether/EtOAc) to yield 3.24 g, R_f = 0.49. To an ice-cooled solution of this material in DMF (40 mL) was added NaH (500 mg of a 60% oil dispersion, 12.5 mmol). The mixture was stirred at room temperature for 15 min before recooling to 0 °C. Bu_4NI (200 mg) and allyl bromide (1.1 mL, 12.7 mmol) were added, and the reaction mixture was stirred at room temperature for 1 h. The mixture was quenched with MeOH, diluted with water (150 mL), and extracted with Et_2O (3 × 150 mL). The combined extracts were dried, concentrated, and chromatographed (85:15 petroleum ether/EtOAc) to give 3.53g, R_f = 0.50. To this material in THF (35 mL) was added 4 M HCl (7 mL) and the mixture was heated at 60 °C for 5 h. The solution was concentrated, and CH_2Cl_2 (90 mL) was added to the residue. The mixture was washed with saturated aqueous $NaHCO_3$ (90 mL) and brine (90 mL), respectively. The dried solution was concentrated and purified by flash chromatography (3:1 petroleum ether/EtOAc) to afford 2.80 g (81%) of **9** $[\alpha]^{20}_D$ −9.6° (c 1.8, $CHCl_3$), identical to the material prepared above.

Pent-4-enyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (13). Tin(IV) chloride (15.8 mL, 0.14 mmol) was added at 0 °C to a solution of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-D-glucopyranose (**12**)[14] (28.5 g, 0.061 mol) and 4-penten-1-ol (14.0 mL, 0.14 mol) in CH_2Cl_2 (500 mL). The reaction mixture was stirred at room temperature for 2 h, then diluted with CH_2Cl_2 and washed with water (3 × 200 mL). The organic phase was dried, filtered, and evaporated *in vacuo* to give a brown oil which was dissolved in a solution of acetone (300 mL), water (150 mL), and concentrated HCl (60 mL). The resultant solution was heated at reflux for 4 h, at which time most of the volatiles were removed *in vacuo*. The slurry was diluted with EtOAc (500 mL) and washed with water (200 mL) and saturated aqueous $NaHCO_3$ (200 mL). The organic phase was dried, filtered, and evaporated to give a buff solid (16 g), which was dried and then dissolved in MeCN (100 mL). Benzaldehyde dimethyl acetal (20 mL, 0.13 mol) and camphorsulfonic acid were added to the solution, and the reaction mixture was stirred at room temperature for 2 h, at which time Et_3N was added and the volatiles removed *in vacuo*. The residual oil was purified by flash chromatography (7:3 petroleum ether/EtOAc) to give 13.4 g (R_f = 0.50; $[\alpha]^{20}_D$ −35.9° (c 1.1, $CHCl_3$)). To a solution of this material (11.2 g, 24 mmol) and benzyl 2,2,2-trichloroacetimidate (8.9 mL, 0.048 mol) in CH_2Cl_2 (20 mL) and cyclohexane (80 mL) was added TfOH (0.05 mL). The reaction mixture was stirred for 2 h, neutralized by the addition of pyridine (0.5 mL), and filtered. The filtrate was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, dried, and evaporated *in vacuo*. Flash chromatography (4:1 petroleum ether/EtOAc) of the crude residue afforded **13** (11.4 g, 41%): R_f = 0.59; $[\alpha]^{20}_D$ +42.1° (c 1.3,

$CHCl_3$); ^1H NMR δ 7.80–6.90 (m, 12H, Ph), 5.65 (s, PhCH), 5.58 (m, =CH–), 5.22 (d, J = 10.5 Hz, H-1), 4.74 (m, $=CH_2$), 4.78 (d, J = 13.0 Hz, 1H), 4.56 (d, J = 13.0 Hz, 1H), 4.41 (m, H-3, H-6b), 4.24 (t, J = 10.5 Hz, H-2), 3.83 (m, H-1'b, H-4, H-6a), 3.65 (dt, J = 5.0, 10.2 Hz, H-5), 3.41 (m, H-1'a), 1.85 (CH_2), 1.50 (m, CH_2); ^{13}C NMR δ 167.8 (Phth), 114.8 ($=CH_2$), 101.3 (PhCH), 98.9 (C-1), 55.9 (C-2), 29.8, 28.5, ($2CH_2$). Anal. Calcd for $C_{33}H_{33}NO_7$: C, 71.34; H, 5.99; N, 2.52. Found: C, 71.47; H, 5.98; N, 2.45.

Pent-4-enyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-[(*p*-methoxybenzylidene)imino]-β-D-glucopyranoside (14). A 3.2 M solution of NaOMe in MeOH (20 mL) was added to a solution of $H_2NOH{\cdot}HCl$ (2.2 g, 32 mmol) in MeOH (20 mL), and the mixture was stirred for 20 min. The supernatant solution was decanted into a solution of **13** (2.0 g, 3.6 mmol) in MeOH (10 mL) and the reaction mixture stirred at room temperature for 24 h. The mixture was diluted with CH_2Cl_2 and filtered, and the filtrate concentrated *in vacuo*. Flash chromatography (3:2 petroleum ether/EtOAc) of the residue afforded a white solid (940 mg), R_f = 0.50. A mixture of this material, *p*-anisaldehyde (0.38 mL, 3.1 mmol), and pyridine 91 mL) in benzene was heated at reflux for 2 h using a Dean Stark trap. Afterward, the solvent was removed *in vacuo* and the residual oil purified by flash chromatography (85:15 petroleum ether/EtOAc) to give **14** (1.07 g, 55%): mp 97–98 °C; R_f = 0.40; $[\alpha]^{20}_D$ +18.8° (*c* 1.5, $CHCl_3$); ^1H NMR δ 8.38 (s, C*H*=N), 7.85–6.95 (m, 16H, Ph), 5.70 (m, =CH–), 5.65 (s, PhCH), 4.88 (m, $=CH_2$), 4.79 (d, J = 12.5 Hz, 1H), 4.75 (d, J = 8.8 Hz, H-1), 4.64 (d, J = 12.5 Hz, 1H), 4.41 (dd, J = 5.6, 12.5 Hz, H-6b), 3.96 (t, J = 9.0 Hz, H-3), 3.92–3.80 (m, H-4, H-6a, H-1'b, OMe), 3.63–3.48 (m, H-1'a, H-5), 3.29 (t, J = 9.0 Hz, H-2), 2.03 (m, CH_2), 1.61 (m, CH_2); ^{13}C NMR δ 164.1 (CH=N), 114.0 ($=CH_2$), 102.7, 101.3 (C-1, PhCH), 55.4 (C-2), 30.0, 28.7 ($2CH_2$). Anal. Calcd for $C_{33}H_{37}NO_6$: C, 72.91; H, 6.86. Found: C, 73.14; H, 6.81.

1,2,3,4,5-Penta-*O*-acetyl-6-*O*-(3-*O*-benzyl-4,6-benzylidene-2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-glucopyranosyl)-D-*myo*-inositol (15b). A mixture of **14** (530 mg, 0.98 mmol), **6** (373 mg, 0.96 mmol), iodonium dicollidinylium perchlorate (897 mg, 1.91 mmol), and activated, powdered 4 Å molecular sieves (1.0 g) in CH_2Cl_2 (20 mL) was stirred for 1 h at room temperature. At this time, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and filtered and the filtrate washed with 10% aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and brine. The organic extract was dried, filtered, and concentrated *in vacuo* to give crude **15a**. This was dissolved in MeOH (20 mL), and 10% aqueous AcOH (2 mL) was added. The mixture was stirred at room temperature for 20 min, at which time *p*-toluenesulfonhydrazide (186 mg, 1.0 mmol) was added, and stirring continued for an additional 20 min. The reaction mixture was then cooled to 0 °C, Et_3N added to pH 8, and benzyl chloroformate (0.5 mL) added to the solution. After 20 min, the volatiles were evaporated *in vacuo*, the residue was diluted with CH_2Cl_2 (50 mL), and the resultant solution was washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried, filtered, and evaporated *in vacuo*. Flash chromatography (3:2 petroleum ether/EtOAc) of the crude product gave **15b** (543 mg, 67%): R_f = 0.38; $[\alpha]^{20}_D$ +57.7° (*c* 2.2, $CHCl_3$); ^1H NMR δ 7.45–7.15 (m, 18H, Ph), 5.55 (s, PhCH), 5.53 (t, J = 2.7 Hz, H-2e), 5.40 (t, J = 10.2 Hz, H-6e), 5.15 (d, J = 3.6 Hz, H-1d), 5.14 (t, J = 10.2 Hz, H-5e), 5.13 (d, J = 12.3 Hz, 1H), 5.06 (dd, J = 2.7, 10.2 Hz, H-1e), 5.03 (d, J = 12.3 Hz, 1H), 5.02 (dd, J = 2.7, 10.2 Hz, H-3e), 4.81 (d, J = 12 Hz, 1H), 4.72 (d, J = 9.6 Hz, N*H*), 4.59 (d, J = 12 Hz, 1H), 4.29 (bd, J = 6.0 Hz, H-6d''), 4.20 (t, J = 10.2 Hz, H-4e), 3.94 (dt, J = 3.6, 9.6 Hz, H-2d), 3.74 (m, H-4d, H-5d, H-6d'), 3.52 (t, J = 9.6 Hz, H-3d), 2.16, 2.09, 2.01, 1.98, 1.86 (s, 5Ac); ^{13}C NMR δ 170.0, 169.9, 169.8, 169.4, 169.3 (5Ac), 156.1 (HNCOO), 101.5, 98.9, (C-1d, PhCH), 54.6 (C-2d), 20.8, 20.7, 20.6, 20.5, 20.4 (5Ac). Anal. Calcd for $C_{44}H_{49}NO_{17}$: C, 61.18; H, 5.72; N, 1.62. Found: C, 61.16; H, 5.86; N, 1.80.

1,2,3,4,5-Penta-*O*-acetyl-6-*O*-(3,6-di-*O*-benzyl-2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-glucopyranosyl)-D-*myo*-inositol (16). To **15b** (430 mg, 0.5 mmol), $NaBH_3CN$ (500 mg, 7.9 mmol), and activated, powdered 3 Å molecular sieves (500 mg) in THF (10 mL) was added a saturated solution of HCl in Et_2O until the evolution of gas had ceased (~pH 3). The reaction mixture was diluted with CH_2Cl_2 and filtered, and the filtrate was washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried and concentrated *in vacuo*. Flash chromatography (1:1 petroleum ether/EtOAc) of the crude product afforded **16** (322 mg, 75%): R_f = 0.40; $[\alpha]^{20}_D$ +74.5° (*c* 1.4, $CHCl_3$); ^1H NMR δ 7.40–7.20 (m, 18H, Ph), 5.53 (t, J = 2.7 Hz, H-2e), 5.44 (t, J = 9.9 Hz, H-6e), 5.21 (t, J = 9.6 Hz, H-5e), 5.21 (d, J = 3.9 Hz, H-1d), 5.01–4.97 (m, PhCH_2, H-1e, H-3e), 4.67 (d, J = 11.4 Hz, 1H), 4.60 (d, J = 11.4 Hz, 1H), 4.56 (d, J = 12 Hz, 1H), 4.50 (d, J = 12 Hz, 1H), 4.25 (t, J = 9.9 Hz, H-4e), 3.92 (dt, J = 3.9, 10.4 Hz, H-2d), 3.76–3.60 (m, H-4d, H-5d, H-6d', H-6d'', N*H*), 3.36 (dd, J = 8.7, 10.5 Hz, H-3d), 2.76 (bs, OH), 2.13, 2.10, 1.97, 1.91, 1.89 (s, 5Ac); ^{13}C NMR δ 170.3, 170.1, 169.9, 169.6, 169.3 (5Ac), 156.1 (HNCOO), 98.1 (C-1d), 53.8 (C-2d), 20.8, 20.7, 20.6, 20.5, 20.5 (5Ac). Anal. Calcd for $C_{44}H_{51}NO_{17}$: C, 61.03; H, 5.94. Found: C, 60.89; H, 6.05.

1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-mannopyranose (17). Using a modified procedure of Lafont *et al.*,[36] *p*-TsCl (23 g, 120.64 mmol) in dry pyridine (45 mL) was added dropwise over 20 min to a solution of D-mannose (20 g, 111.01 mmol) in pyridine (80 mL). The solution was stirred for 4 h at room temperature. The reaction mixture was then quenched with MeOH (5 mL), diluted with 300 mL of $CHCl_3$, and washed twice with ice-cold water (200 mL). The $CHCl_3$ solution was dried, and $CHCl_3$ was removed at reduced pressure. After coevaporation with toluene to remove pyridine, the residual oil was dried at high vacuum to obtain 29 g, R_f = 0.30 (9:1 CH_2Cl_2/MeOH). This (22 g) in absolute MeCN (600 mL, distilled from CaH_2) was treated with DBU (20 mL, added all at once). The reaction, which went from yellow to light orange, was stirred for 30 min at room temperature until the starting material vanished (TLC). The mixture was then concentrated at diminished pressure and dried briefly at high vacuum. To this crude brown product was added pyridine (200 mL), followed dropwise at 0 °C by Ac_2O (28 mL) and a catalytic amount of DMAP. The mixture was then stirred overnight at room temperature before diluting with ice-cold water and extracting three times with CH_2Cl_2. The extract was shaken with brine. The crude product was flash chromatographed (3:2 petroleum ether/EtOAc) to collect 13 g (41%) of 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-mannopyranose (R_f = 0.45), which was saponified with NaOMe and converted into **17** (R_f = 0.47, 7:3 petroleum ether/EtOAc) by the standard procedure (NaH/BnBr/Bu_4NI/DMF). Spectral data of **17** were as reported.[37]

1,4,6-Tri-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-D-glucopyranose (19). Compound **18** was prepared from **17** by the procedure of Hori et al.[17] A solution of the material (4.84 g, 17.5 mmol) in CH_2Cl_2 (50 mL) was treated with Ac_2O (2 mL), Et_3N (5 mL), and a catalytic amount of DMAP overnight and then concentrated. Using the method of Paulsen *et al.*,[37] an ice-cooled solution of this 4-acetate in Ac_2O (120 mL) was then treated dropwise with trifluoroacetic acid (12 mL). After being stirred for 4 days at room temperature, the reaction was concentrated and co-concentrated with toluene. Flash chromatography (75:25 → 70:30 petroleum ether/EtOAc) gave 6.09 g (92%) of triacetate **19** as a white solid, R_f = 0.40 (75:25 petroleum ether/EtOAc). Spectral data for the α anomer were as reported.[18]

4,6-Di-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl bromide (20). The triacetate **19** (4.2 g, 11.07 mmol) was dissolved in a minimum amount of CH_2Cl_2 (~5 mL) and treated with $TiBr_4$ (78 mL of 0.3 M stock solution obtained by treating 10.0 g of $TiBr_4$ in 82.2 mL of dry CH_2Cl_2 with 8.10 mL of dry EtOAc, 23.4 mmol) according to the modified Paulsen's procedure.[18] The reaction was stirred for 22 h before diluting with $CHCl_3$ and washing with ice-cold water, saturated aqueous $NaHCO_3$, and brine. Flash chromatography (petroleum ether/EtOAc) of the dried and concentrated crude extract gave 4.6 g (94% yield) of the bromide **20** (R_f = 0.53; $[\alpha]^{20}_D$ +99.4° (*c* 1.4, $CHCl_3$)). Spectral data were as reported.[18]

1-*O*-Allyl-6-*O*-(2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (21b). To a solution of **20** (2.4 g, 5.43 mmol) and **9** (2.10 g, 3.62 mmol) in Et_2O (30 mL) was added at −35 °C a solution of $AgClO_4$ (1.5 g, 7.24 mmol) in Et_2O (80 mL) during 10 min. The cooling bath was removed and the mixture stirred at room temperature for 30 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and filtered through Celite. The filtrate was washed with saturated aqueous $NaHCO_3$ (70 mL) and brine (70 mL), dried, and concentrated. The residue was chromatographed through a short column (1:1 petroleum ether/EtOAc) to give 3.40 g of

(36) Lafont, D.; Boullanger, P.; Cadas, O.; Descotes, G. *Synthesis* **1989**, 191.

(37) Paulsen, H.; Lockhoff, C. *Chem. Ber.* **1981**, *114*, 3102.

crude **21a**, $R_f = 0.49$ (4:1 petroleum ether/EtOAc). To a solution of this material in CH_2Cl_2 (5 mL) was added 0.07 M methanolic NaOMe (30 mL), and the mixture was stirred for 1 h before being quenched with AcOH. Evaporation of the solvent and flash chromatography (4:1 CH_2Cl_2/EtOAc) gave 1.95 g (63%) of **21b** ($R_f = 0.66$) and 0.69 g (22%) of the corresponding β-disaccharide ($R_f = 0.36$). For **21b**: ^{1}H NMR δ 7.48−7.22 (m, 25H, Ph), 5.96 (m, =CH−), 5.66 (d, $J = 3.7$ Hz, H-1), 5.26 (m, $=CH_2$), 5.13 (d, $J = 11.0$ Hz, 1H), 5.00 (d, $J = 10.7$ Hz, 1H), 4.92 (d, $J = 11.0$ Hz, 1H), 4.88−4.82 (m, 4H), 4.71−4.63 (m, 3H), 4.19 (m, 2H), 4.07−4.00 (m, 3H), 3.87−3.74 (m, 2H), 3.58 (dd, $J = 9.0$, 9.6 Hz, 1H), 3.49−3.29 (m, 5H), 3.20 (dd, $J = 3.8$, 10.2 Hz, 1H); ^{13}C NMR δ 117.2, ($=CH_2$), 97.5 (C-1). Anal. Calcd for $C_{50}H_{55}N_3O_{10}$: C, 69.99; H, 6.46; N, 4.90. Found: C, 70.05; H, 6.34; N, 4.69.

1-*O*-Allyl-6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (22). To a solution of **21b** (2.29 g, 3.69 mmol) in CH_2Cl_2 (30 mL) were added Ac_2O (0.3 mL, 3.18 mmol) and Et_3N (0.6 mL, 4.30 mmol). The mixture was stirred for 4 h before being quenched with MeOH. Evaporation of the solvent and flash chromatography (3:1 petroleum ether/EtOAc) gave 2.21 g of a foam, $R_f = 0.47$. To this material in CH_2Cl_2 (15 mL) were added 3,4-dihydro-2*H*-pyran (1.1 mL, 12.1 mmol) and pyridinium *p*-toluenesulfonate (60 mg), and the mixture was refluxed for 15 h. It was then diluted with CH_2Cl_2 (15 mL) and washed with brine. The dried solution was concentrated and the residue flash chromatographed (3:1 petroleum ether/EtOAc) to afford 2.26 g of a syrup ($R_f = 0.64$) which was dissolved in CH_2Cl_2 (4 mL) and treated with 0.07 M methanolic NaOMe (20 mL) for 8 h. The solution was then quenched with AcOH, concentrated, and co-concentrated with toluene. The residue was taken up in DMF (20 mL) and cooled to 0 °C while NaH (200 mg of a 60% oil dispersion, 5.0 mmol), Bu_4NI (50 mg), and BnBr (0.55 mL, 4.62 mmol) were added. The mixture was stirred at room temperature for 1 h before being quenched with MeOH. It was then diluted with water (80 mL) and washed with Et_2O (3 × 60 mL). The combined extracts were dried, concentrated, and chromatographed (85:15 petroleum ether/EtOAc) to give 2.11 g of a syrup, $R_f = 0.57$. To a solution of this material in CH_2Cl_2 (6 mL) and MeOH (24 mL) was added pyridinium *p*-toluenesulfonate (50 mg), and the mixture was heated at 50 °C for 7 h. The solution was diluted with CH_2Cl_2 (50 mL), washed with brine (50 mL), dried, concentrated, and chromatographed (4:1 petroleum ether/EtOAc) to yield 1.75 g (69%) of **22**: $R_f = 0.42$; $[\alpha]^{20}_D$ +40.9° (*c* 1.5, $CHCl_3$); ^{1}H NMR δ 7.46−7.15 (m, 30H, Ph), 5.93 (m, =CH−), 5.71 (d, $J = 3.7$ Hz, H-1), 5.23 (m, $=CH_2$), 5.04 (d, $J = 11.0$ Hz, 1H), 4.97 (d, $J = 10.6$ Hz, 1H), 4.94−4.79 (m, 4H), 4.70−4.60 (m, 3H), 4.41 (d, $J = 12.2$ Hz, 1H), 4.26 (d, $J = 12.2$ Hz, 1H), 4.24 (dd, $J = 9.5$, 9.7 Hz, 1H), 4.13 (dd, $J = 9.5$, 9.6 Hz, 1H), 4.04−3.95 (m, 4H), 3.82−3.67 (m, 3H), 3.45−3.17 (m, 6H); ^{13}C NMR 117.2 ($=CH_2$), 97.6 (C-1), 62.9 (C-2). Anal. Calcd for $C_{57}H_{61}N_3O_{10}$: C, 72.21; H, 6.48; N, 4.43. Found: C, 71.99; H, 6.49; N, 4.37.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-glucopyranosyl)-(1→6)-1,2,3,4,5-penta-*O*-acetyl-D-*myo*-inositol (24).** The pentenyl mannoside **23** was prepared under standard conditions. A portion of this material (350 mg, 0.46 mmol), **16** (200 mg, 0.23 mmol), NIS (258 mg, 1.15 mmol), and activated, powdered 3 Å molecular sieves (1 g) in CH_2Cl_2 (10 mL) was stirred under argon for 20 min. A saturated solution of TfOH (0.33 mL of a ca. 0.14 N solution) in CH_2Cl_2 was then slowly added over a period of 20 min. The reaction mixture was then diluted with CH_2Cl_2 (25 mL) and filtered, and the filtrate was washed with 10% aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$. The organic extract was dried and evaporated *in vacuo*. The residue was dissolved in THF (2 mL) and treated with HF-pyridine (2 mL of a solution containing 1 mL of HF-py in 7 mL of THF) for 2 h at room temperature. The reaction mixture was diluted with saturated aqueous $NaHCO_3$ (10 mL) and extracted with Et_2O. The organic extract was washed with brine, dried, and concentrated *in vacuo*. Flash chromatography (1:2 petroleum ether/EtOAc) of the residue afforded **24** (202 mg, 68%): $R_f = 0.40$; $[\alpha]^{20}_D$ +61.1° (*c* 1.7, $CHCl_3$); ^{1}H NMR δ 7.38−7.10 (m, 30H, Ph), 5.54 (bt, $J = 2.3$ Hz, H-2e), 5.40 (t, $J = 9.6$ Hz, H-6e), 5.26 (bs, H-1e), 5.17−4.95 (m, H-1d, H-1e, H-3e, H-5e, $PhCH_2$), 4.88 (d, $J = 11$ Hz, 1H), 4.81 (d, $J = 9$ Hz, NH), 4.70−4.46 (m, 9H), 4.38 (d, $J = 12$ Hz, H-6d″), 4.22 (m, H-6d′, H-4e), 3.98 (dt, $J = 3$, 9 Hz, H-2d), 3.95−3.54 (m, 10H), 3.45 (t, $J = 10$ Hz, H-3d), 2.12, 2.03, 2.00, 1.98, 1.96 (s, 5Ac); ^{13}C NMR δ 169.9, 169.8, 169.7, 169.5, 169.4 (5Ac), 155.8 (HNCOO), 100.2 ($J = 176.6$ Hz), 98.4 ($J = 168.2$ Hz) (C-1d, C-1c), 54.5 (C-2d), 20.9, 20.8, 20.6, 20.5, 20.5 (5Ac). Anal. Calcd for $C_{71}H_{79}NO_{22}$: C, 65.68; H, 6.13; N, 1.08. Found: C, 65.51; H, 6.25; N, 1.05. FAB: $m/z = 1320.9$ $(M + Na)^+$.

***O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-[(benzyloxycarboxyl)-amino]-2-deoxy-α-D-glucopyranosyl)-(1→6)-1,2,3,4,5-penta-*O*-acetyl-D-*myo*-inositol (26).** A mixture of **25** (170 mg, 0.16 mmol), **24** (150 mg, 0.12 mmol), NIS (88 mg, 0.39 mmol), and activated, powdered 4 Å molecular sieves (300 mg) in CH_2Cl_2 was stirred for 20 min. A saturated solution of TfOH (0.10 mL of a ca. 0.14 N solution) in CH_2Cl_2 was then slowly added over a period of 20 min, at which time the reaction mixture was processed as described for the preparation of **24**. Flash chromatography (95:5 → 80:20 $CHCl_3$/acetone) of the crude product afforded **26** (201 mg, 73%) as a 2:3 mixture of α:β anomers.

For **26**β: $R_f = 0.15$ (95:5 $CHCl_3$/acetone); partial ^{1}H NMR δ 6.21 (t, $J = 10$ Hz, H-4a), 6.00 (m, H-2a, H-3a), 5.55 (bt, $J = 2$ Hz, H-2e), 5.42 (t, $J = 10$ Hz, H-6c), 5.31 (bs, 1H), 5.28 (bs, 1H), 2.04, 2.01, 1.99, 1.86, 1.85 (s, 5Ac); ^{13}C NMR δ 100.3 ($J = 157.6$ Hz, C-1b), 99.1 ($J = 173.4$ Hz), 99.8 ($J = 175.7$ Hz), 98.3 ($J = 168.9$ Hz) (C-1d, C-1c, C-1a).

For **26**α: $R_f = 0.20$ (95:5 $CHCl_3$/acetone); partial ^{1}H NMR δ 6.17 (t, $J = 10$ Hz, H-4a), 5.94 (m, H-2a, H-3a), 5.53 (bt, $J = 2$ Hz, H-2e), 5.40 (t, $J = 10$ Hz, H-6e), 5.30 (bs, 1H), 2.06, 1.99, 1.98, 1.94, 1.88 (5Ac); ^{13}C NMR δ 100.2, 99.5, 99.3, 98.3 (5C-1).

***O*-(3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-[(benzyloxycarboxyl)amino]-2-deoxy-α-D-glucopyranosyl)-(1→6)-1,2,3,4,5-penta-*O*-acetyl-D-*myo*-inositol (28).** A mixture of **27** (36 mg, 0.061 mmol), **24** (53 mg, 0.041 mmol), NIS (34 mg, 0.15 mmol), and activated, powdered 4 Å molecular sieves in CH_2Cl_2 was stirred for 20 min. A saturated solution of TfOH (0.05 mL of a ca. 0.14 N solution) in CH_2Cl_2 was then slowly added over a period of 20 min, at which time the reaction mixture was processed as described for the preparation of **24**. The crude residue was dissolved in absolute EtOH (2 mL) and treated with thiourea (5 mg, 0.07 mmol) at reflux for 1 h. The solvent was removed *in vacuo* and the crude residue purified by flash chromatography (1:1 petroleum ether/EtOAc) to give **28** (38 mg, 53%): $R_f = 0.5$; partial ^{1}H NMR δ 5.57 (bt, $J = 2$ Hz, H-2e), 5.44 (t, $J = 10$ Hz, H-6e), 5.30 (bs, H-1e), 5.20−5.00 (m, 5H), 2.11, 2.04, 2.02, 1.98, 1.90 (s, 5Ac).

***O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-[(benzyloxycarboxyl)-amino]-2-deoxy-α-D-glucopyranosyl)-(1→6)-1,2,3,4,5-penta-*O*-acetyl-D-*myo*-inositol (26).** A mixture of **29** (26 mg, 0.039 mmol), **28** (45 mg, 0.026 mmol), NIS (22 mg, 0.1 mmol), and freshly activated, powdered 4 Å molecular sieves (100 mg) in CH_2Cl_2 (2 mL) was treated with a saturated solution of TfOH in CH_2Cl_2 (0.02 mL), according to the procedure outlined for the preparation of **24**. Flash chromatography of the crude product afforded **26**α (40 mg, 68%), which was identical (NMR, TLC) to the minor product previously outlined in the reaction of **24** and **25**.

***O*-(α-D-mannopyranosyl)-(1→2)-*O*-(α-D-mannopyranosyl)-(1→6)-*O*-(α-D-mannopyranosyl)-(1→4)-*O*-(2-amino-2-deoxy-α-D-glucopyranosyl)-(1→6)-D-*myo*-inositol (30).** A solution of the pentasaccharide **26**α (75 mg) in MeOH (2 mL) was treated with NaOMe (ca. 5 mg) at room temperature for 1 h. At this time, the solution was neutralized with 1% HCl in MeOH, concentrated *in vacuo*, diluted with CH_2Cl_2, and filtered. The filtrate was evaporated *in vacuo* and the residue purified by flash chromatography (9:1 $CHCl_3$/MeOH) to give a clear gum (42 mg) which was dissolved in MeOH (5 mL) and treated with formic acid (0.5 mL) and 10% palladium on carbon (200 mg) under an argon atmosphere for 2 h. The suspension was filtered and the filter cake washed with MeOH (50 mL) and H_2O (50 mL). Evaporation of the combined washings yielded **30** (17 mg, 69%): amorphous powder; partial ^{1}H NMR (D_2O) δ 5.45 (d, $J = 3.6$ Hz, H-1d), 5.24 (d, $J = 1.5$ Hz, H-1a), 5.15 (d, $J = 1.3$ Hz, H-1b), 5.04 (d, $J = 1.5$ Hz, H-1c); ^{13}C

NMR (D_2O) δ 105.0 (J = 169.6 Hz), 104.6 (J = 169.3 Hz), 101.0 (J = 172.8 Hz), 98.8 (J = 173.5 Hz) (4C-1). FAB: m/z = 828.3 (M + H)$^+$.

Pent-4-enyl 4,6-*O*-Benzylidene-α-D-mannopyranoside (32a). By following the method of Patroni *et al.*,[38] **31**[39] (5.0 g, 20.1 mmol) was stirred with benzaldehyde dimethyl acetal (3.8 mL, 25.3 mmol) and pyridinium *p*-toluenesulfonate (50 mg) in DMF (40 mL) for 2 h at 80 °C under a stream of argon to remove MeOH. The mixture was quenched with Et_3N, concentrated, and chromatographed (7:3 CH_2Cl_2/EtOAc) to afford 3.70 g (55%) of **32a**: R_f = 0.53; $[\alpha]^{20}_D$ +53.5° (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 7.44 (m, 5H, Ph), 5.81 (m, =CH−), 5.57 (s, PhCH), 5.03 (m, $=CH_2$), 4.84 (d, J = 1.1 Hz, H-1), 4.29−3.79 (m, H-2,3,4,5,6,6′), 3.72 (m, 1H, OCH_2), 3.43 (m, 1H, OCH_2), 2.14 (m, 2H, CH_2), 1.71 (m, 2H, CH_2); ^{13}C NMR δ 115.2 ($=CH_2$), 102.2 (PhCH), 100.4 (C-1), 30.3, 28.6 ($2CH_2$). Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.37; H, 7.01.

Pent-4-enyl 2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (32c). By following the method of Nashed,[40] **32a** (5.0 g, 14.9 mmol) and Bu_2SnO (3.8 g, 15.3 mmol) were suspended in MeOH (70 mL) and the mixture was heated under reflux for 1.5 h. The solvent was removed under diminished pressure, and the residue was coevaporated with toluene and dried *in vacuo* for 1 h. To this material in DMF (50 mL) was added BnBr (2.5 mL, 21.0 mmol), and the mixture was heated at 90 °C for 3 h before it was concentrated and chromatographed (95:5 CH_2Cl_2/EtOAc) to give 4.77 g (R_f = 0.48) of **32b**. This material was taken up in CH_2Cl_2 (40 mL) and treated with Ac_2O (1.5 mL, 15.9 mmol), Et_3N (3 mL, 21.5 mmol), and DMAP (50 mg) for 4 h. The solution was concentrated and chromatographed (CH_2Cl_2) to yield 4.68 g (67%) of **32c**: R_f = 0.54; $[\alpha]^{20}_D$ +17.0° (*c* 1, $CHCl_3$); ^{1}H NMR δ 7.55−7.25 (m, 10H, Ph), 5.79 (m, =CH−), 5.64 (s, PhCH), 5.39 (dd, J = 1.5, 3.0 Hz, H-2), 5.02 (m, $=CH_2$), 4.77 (d, J = 1.5 Hz, H-1), 4.71 (d, J = 12.1 Hz, 1H), 4.68 (d, J = 12.1 Hz, 1H), 4.28−3.82 (m, H-3,4,5,6,6′), 3.69 (m, 1H, OCH_2), 3.41 (m, 1H, OCH_2), 2.17 (s, Ac), 2.11 (m, 2H, CH_2), 1.69 (m, 2H, CH_2); ^{13}C NMR δ 170.3 (Ac), 115.2 ($=CH_2$), 101.6 (PhCH), 98.8 (C-1), 30.2, 28.5 ($2CH_2$), 21.1 (Ac). Anal. Calcd for $C_{27}H_{32}O_7$: C, 69.21; H, 6.88. Found: C, 69.28; H, 6.92.

Pent-4-enyl 2,6-Di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranoside (33). A solution of **32c** (4.68 g, 9.99 mmol) in 80% AcOH (50 mL) was stirred at room temperature for 40 h. Concentration and flash chromatography (1:1 CH_2Cl_2/EtOAc) gave 3.25 g (R_f = 0.5) which was subsequently treated with Ac_2O (0.9 mL, 9.54 mmol) and Et_3N (2.0 mL, 14.3 mmol) in CH_2Cl_2 (50 mL) for 3 h. Evaporation of the solvent and purification by flash chromatography (9:1 CH_2Cl_2/EtOAc) yielded 3.27 g (77%) of **33**: R_f = 0.45; $[\alpha]^{20}_D$ +1.2° (*c* 1.9, $CHCl_3$); ^{1}H NMR δ 7.34 (m, 5H, Ph), 5.81 (m, =CH−), 5.35 (d, J = 1.5 Hz, H-2), 5.02 (m, $=CH_2$), 4.81 (d, J = 1.5 Hz, H-1), 4.73 (d, J = 11.1 Hz, 1H), 4.47 (d, J = 11.1 Hz, 1H), 4.42 (dd, J = 4.6, J = 11.4 Hz, H-6), 4.33 (d, J = 0.7, 11.4 Hz, H-6′), 3.79 (m, H-3,4,5), 3.69 (m, 1H, OCH_2), 3.44 (m, 1H, OCH_2), 2.12 (s, Ac), 2.11 (m, 2H, CH_2), 2.10 (s, Ac), 1.70 (m, 2H, CH_2); ^{13}C NMR δ 171.2, 170.3 (2Ac), 115.1 ($=CH_2$), 98.0 (C-1), 30.2, 28.5 ($2CH_2$), 21.0, 20.9 (2Ac). Anal. Calcd for $C_{22}H_{30}O_8$: C, 62.55; H, 7.16. Found: C, 62.46; H, 7.11.

***p*-Methoxyphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (35b).** To a mixture of **35a**[41] (2.38 g, 4.99 mmol), *p*-methoxyphenol (1.2 g, 9.67 mmol) and powdered, activated 4 Å molcular sieves (1 g) in CH_2Cl_2 (20 mL) was added TMSOTf (1.3 mL, 6.73 mmol). The mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with Et_3N (1 mL) and filtered through Celite. The filtrate was concentrated and flash chromatographed (3:2 petroleum ether/EtOAc) to obtain 2.32 g (86% yield) of **35b**: R_f = 0.36; $[\alpha]^{20}_D$ +29.7° (*c* 0.9, $CHCl_3$); ^{1}H NMR δ 7.81 (m, 4H, Phth), 6.78 (m, 4H, PMP), 5.87 (dd, J = 3.4, 11.4 Hz, H-3), 5.80 (d, J = 8.4 Hz, H-1), 5.53 (d, J = 3.2 Hz, H-4), 4.80 (dd, J = 8.4, 11.4 Hz, H-2), 4.3−4.1 (m, H-5,6,6′), 3.72 (s, OMe), 2.23, 2.04, 1.89 (3 s, Ac); ^{13}C NMR δ 170.4, 170.4, 169.8 (3Ac), 168.3, 167.5 (Phth), 97.9 (C-1), 55.6 (OMe), 51.3 (C-2), 20.8, 20.7, 20.6 (3Ac). Anal. Calcd for $C_{27}H_{27}NO_{11}$: C, 59.89; H, 5.03; N, 2.59. Found: C, 59.74; H, 5.11; N, 2.52.

***p*-Methoxyphenyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (39).** To a solution of **38**[42] (19.0 g, 31.9 mmol) and pyridine (11.0 mL, 136 mmol) in CH_2Cl_2 (200 mL) was added at −20 °C Tf_2O (10.5 mL, 62.4 mmol). The reaction was stirred at −20 °C for 5 min and then allowed to warm to room temperature during 30 min. The solution was washed successively with ice-cooled 5% aqueous HCl (120 mL) and saturated aqueous $NaHCO_3$ (120 mL), dried, concentrated, and co-concentrated with toluene. The residue was taken up in DMSO (120 mL) and cooled to 0 °C while CsOAc (12.0 g, 62.5 mmol) was added. The mixture was stirred at room temperature for 1 h. It was then diluted with CH_2Cl_2 (400 mL) and washed with water (2 × 300 mL). The organic layer was dried, concentrated, and purified by flash chromatography (7:3 petroleum ether/EtOAc) to give 15.1 g (74%) of **39**: R_f = 0.5; $[\alpha]^{20}_D$ +75.9° (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 7.75 (m, 4H, Phth), 7.4−6.9 (m, 10H, Ph), 6.76 (m, 4H, PMP), 5.71 (d, J = 3.4 Hz, H-4), 5.66 (d, J = 8.6 Hz, H-1), 4.65 (dd, J = 8.6 Hz, 11.0 Hz, H-2), 4.62 (d, J = 12.5 Hz, 1H), 4.60 (d, J =11.4 Hz, 1H), 4.50 (d, J = 11.9 Hz, 1H), 4.37 (dd, J = 3.4, 11.0 Hz, H-3), 4.28 (d, J = 12.5 Hz, 1H), 4.04 (dd, J = 6.1, 6.6 Hz, H-5), 3.71−3.61 (m, H-6, H-6′), 3.70 (s, OMe), 2.18 (s, Ac); ^{13}C NMR δ 170.5 (Ac), 168.2, 167.7 (Phth), 97.8 (C-1), 55.6 (OMe), 52.8 (C-2), 21.0 (Ac). Anal. Calcd for $C_{37}H_{35}NO_9$: C, 69.69; H, 5.53; N, 2.20. Found: C, 69.59; H, 5.62; N, 2.12.

***p*-Methoxyphenyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (36).** From **35**: The triacetate **35** (1.24 g, 2.29 mmol) in CH_2Cl_2 (2.5 mL) and 0.043 M methanolic NaOMe was stirred at 0 °C for 15 min. The mixture was quenched with Amberlite IR-120 (H^+) ion-exchange resin and filtered through Celite. The filtrate was concentrated and azeotroped twice with toluene, and the residue was dried overnight at high vacuum. To the residue in DMF (15 mL) were added at 0 °C Bu_4NI (70 mg), BnBr (3.0 mL, 25.2 mmol), and NaH (500 mg of a 60% oil dispersion, 12.5 mmol). The mixture was stirred at room temperature for 1 h before being quenched with AcOH. The solution was partitioned between CH_2Cl_2 (60 mL) and water (60 mL). The organic layer was washed with water (80 mL), dried, concentrated, and flash chromatographed (7:3 petroleum ether/EtOAc) to yield 1.30 g (83%) of **36**. From **39**: To a solution of the acetate **39** (15.1 g, 23.7 mmol) in CH_2Cl_2 (10 mL) was added 0.13 M methanolic NaOMe (150 mL). The reaction was stirred at room temperature for 3 h before being quenched with Amberlite IR-120 (H^+) ion exchange resin. The resin was removed by filtration through Celite, and the filtrate was concentrated and co-concentrated with toluene. The residue was dried at high vacuum overnight and then benzylated with NaH (1.4 g of 60% oil dispersion, 35 mmol), BnBr (11 mL, 92.5 mmol), and Bu_4NI (750 mg) in DMF (100 mL) in the same way as described above to give after workup 11.0 g (68%) of **36**: R_f = 0.4; $[\alpha]^{20}_D$ +62.8° (*c* 1.4, $CHCl_3$); ^{1}H NMR δ 7.80 (m, 4H, Phth), 7.45−6.97 (m, 15H, Ph), 6.75 (m, 4H, PMP), 5.62 (d, J = 8.5 Hz, H-1), 5.01 (d, J = 11.5 Hz, 1H), 4.94 (dd, J = 8.5, 11.1 Hz, H-2), 4.66 (d, J = 11.7 Hz, 1H), 4.63 (d, J = 12.2 Hz, 1H), 4.48 (d, J = 11.8 Hz, 1H), 4.45 (d, J = 11.8 Hz, 1H), 4.39 (dd, J = 2.7, 11.2 Hz, H-3), 4.33 (d, J = 12.2 Hz, 1H), 4.09 (d, J = 2.5 Hz, H-4), 3.85 (dd, J = 6.3, 6.4 Hz, H-5), 3.74−3.65 (m, H-6, 6′), 3.70 (s, OMe); ^{13}C NMR δ 168.7, 167.8 (Phth), 97.9 (C-1), 55.6 (OMe), 52.9 (C-2). Anal. Calcd for $C_{42}H_{39}NO_8$: C, 73.56; H, 5.73; N, 2.04. Found: C, 73.29; H, 5.72; N, 1.98.

3,4,6-Tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl Trichloroacetimidate (36b). A solution of **36** (1.60 g, 2.33 mmol) and ceric ammonium nitrate (6.0 g, 10.9 mmol) in toluene (25 mL), MeCN (40 mL), and water (25 mL) was stirred at room temperature for 1 h. The mixture was diluted with water (50 mL) and washed with CH_2Cl_2 (2 × 80 mL). The combined organic extracts were washed with water (80 mL), dried, and concentrated. Flash chromatography (3:2 petroleum ether/EtOAc) gave 1.20 g of a foam, R_f = 0.55. To an ice-cooled solution of this material (1.01 g) and CCl_3CN (1.65 mL, 16.5 mmol) in toluene (18 mL) was added DBU (0.6 mL of a 1 M solution in toluene, 0.6 mmol) during 15 min. The mixture was stirred at 0 °C for 2 h, after which time precipitated **36b** was filtered off. The

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filtrate was diluted with EtOAc (15 mL) and washed successively with ice-cooled saturated aqueous NH_4Cl (20 mL) and water (20 mL). The dried solution was evaporated and the residue crystallized from EtOAc, providing a second crop of **36b**: total yield 1.09 g (77%); $R_f = 0.58$ (7:3 petroleum ether/EtOAc); $[\alpha]^{20}_D$ +58.6° (*c* 0.8, $CHCl_3$); ^1H NMR δ 8.50 (s, NH), 7.75 (m, 4H, Phth), 7.42−6.98 (m, 15H, Ph), 6.41 (d, $J = 8.9$ Hz, H-1), 5.00 (d, $J = 11.6$ Hz, 1H), 4.98 (dd, $J = 8.9$ Hz, 11.1 Hz, H-2), 4.66 (d, $J = 11.6$ Hz, 1H), 4.64 (d, $J = 12.2$ Hz, 1H), 4.52 (d, $J = 11.9$ Hz, 1H), 4.47 (d, $J = 11.9$ Hz, 1H), 4.47 (dd, $J = 1.9$, 11.1 Hz, H-3), 4.35 (d, $J = 12.2$ Hz, 1H), 4.14 (d, $J = 1.9$ Hz, H-4), 4.00 (dd, $J = 5.4$, 7.6 Hz, H-5), 3.75 (dd, $J = 7.6$, 7.8 Hz, H-6), 3.70 (dd, $J = 5.4$, 7.8 Hz, H-6′); ^{13}C NMR δ 168.3, 167.8 (Phth), 161.1 ($OC(NH)CCl_3$), 94.7 (C-1), 90.5 (CCl_3), 51.9 (C-2).

Pent-4-enyl 2,6-Di-*O*-acetyl-3-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl)-α-D-mannopyranoside (40a). To a mixture of **36b** (5.94 g, 8.20 mmol), **33** (2.80 g, 6.63 mmol) and powdered, activated 4 Å molcular sieves (8 g) in toluene (230 mL) was added at −20 °C TMSOTf (3.2 mL of a 0.5 M solution in toluene, 1.6 mmol). The mixture was stirred at −20 °C for 2 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$, diluted with EtOAc (350 mL), and filtered through Celite. The filtrate was washed with water (350 mL), dried, and concentrated. Flash chromatography (3:2 petroleum ether/EtOAc) gave 5.13 g (79%) of **40a**: $R_f = 0.48$; $[\alpha]^{20}_D$ +77.6° (*c* 1.3, $CHCl_3$); ^1H NMR δ 7.76 (m, 4H, Phth), 7.37−6.92 (m, 20H, Ph), 5.77 (m, =CH−), 5.44 (d, $J = 8.5$ Hz, H-1′), 5.20 (dd, $J = 1.7$, 2.5 Hz, H-2), 4.97 (m, $=CH_2$), 4.91 (d, $J = 11.2$ Hz, 1H), 4.70−4.50 (m, 6H), 4.27−4.14 (m, 5H), 4.00−3.45 (m, 8H), 3.27 (m, 2H), 2.05 (m, 2H, CH_2), 1.99 (s, Ac), 1.60 (m, 5H, CH_2, Ac); ^{13}C NMR δ 170.2, 170.1 (2Ac), 168.7, 168.0 (Phth), 115.2 ($=CH_2$), 98.9, 97.5 (2 C-1), 53.7 (C-2′), 30.1, 28.4 ($2CH_2$), 20.9, 20.3 (2Ac). Anal. Calcd for $C_{57}H_{61}NO_{14}$: C, 69.57; H, 6.25; N, 1.42. Found: C, 69.55; H, 6.22; N, 1.47.

Pent-4-enyl 4-*O*-(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)-2-*O*-acetyl-3-*O*-benzyl-6-*O*-(chloroacetyl)-α-D-mannopyranoside (40d). A solution of **40a** (7.92 g, 8.05 mmol) and 40% aqueous $MeNH_2$ (30 mL) in EtOH (500 mL) was heated at 70 °C for 35 h. The solution was concentrated to one-half the volume, and Ac_2O (70 mL) was added. This mixture was stirred for 3 h before it was concentrated and chromatographed (85:15 EtOAc/acetone) to give 6.94 g of **40b**, $R_f = 0.4$. To this in CH_2Cl_2 (110 mL) were added chloroacetic anhydride (1.50 g, 8.81 mmol) and Et_3N (1.9 mL, 13.6 mmol), and the mixture was stirred for 3 h. The solution was then evaporated and the residue chromatographed (2:3 petroleum ether/EtOAc) to give 5.84 g of **40c**, $R_f = 0.54$. This material was taken up in CH_2Cl_2 (80 mL) and treated with Ac_2O (1 mL, 10.6 mmol), Et_3N (1.8 mL, 12.9 mmol), and DMAP (50 mg) for 2 h. The mixture was then concentrated and purified by flash chromatography (55:45 petroleum ether/EtOAc) to afford 5.12 g (68%) of **40d**: $R_f = 0.49$; $[\alpha]^{20}_D$ +37.5° (*c* 1.1, $CHCl_3$); ^1H NMR δ 7.40−7.15 (m, 20H, Ph), 5.79 (m, =CH−), 5.53 (d, $J = 7.6$ Hz, NH), 5.27 (brs, H-2), 5.17 (d, $J = 8.5$ Hz, H-1′), 5.01 (m, $=CH_2$), 4.85 (d, $J = 11.5$ Hz, 1H), 4.73−4.53 (m, 6H), 4.37 (d, $J = 11.5$ Hz, 1H), 4.31−4.11 (m, 4H), 4.07 (s, AcCl), 3.96−3.86 (m, 4H), 3.69−3.24 (m, 6H), 2.08 (m, 2H, CH_2), 1.97, 1.81 (2 s, Ac), 1.65 (m, 2H, CH_2); ^{13}C NMR δ 171.1, 170.3, 167.2 (2Ac, AcCl), 115.2 ($=CH_2$), 99.8, 97.5 (2 C-1), 55.2 (C-2′), 40.8 (AcCl), 30.2, 28.5 ($2CH_2$), 23.6, 20.9 (2Ac). Anal. Calcd for $C_{51}H_{60}ClNO_{13}$: C, 65.83; H, 6.50; N, 1.51; Cl, 3.81. Found: C, 65.73; H, 6.54; N, 1.52; Cl, 3.76.

***O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2-*O*-acetyl-3-*O*-benzyl-6-*O*-(chloroacetyl)-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (41a).** To a solution of **40d** (824 mg, 0.886 mmol) and **22** (1.03 g, 1.09 mmol) in CH_2Cl_2 (11 mL) were added powdered NIS (240 mg, 1.07 mmol) and Et_3SiOTf (280 μL, 1.24 mmol), and the mixture was stirred at room temperature for 15 min before being quenched with Et_3N. The solution was diluted with CH_2Cl_2 (50 mL) and washed successively with 10% aqueous $Na_2S_2O_3$ (50 mL) and saturated aqueous $NaHCO_3$ (50 mL). The dried crude product was concentrated and flash chromatographed (3:2 petroleum ether/EtOAc) to give 1.05 g (66% based on **40d**) of **41a** and 465 mg of triethylsilylated **22**, which by treatment with Bu_4NF in THF was converted into 380 mg of recovered **22**. For **41a**: $R_f = 0.53$; $[\alpha]^{20}_D$ +55.6° (*c* 1.1, $CHCl_3$); ^1H NMR δ 7.46−7.14 (m, 50H, Ph), 5.94 (m, =CH−), 5.73 (d, $J = 3.7$ Hz, H-1″), 5.44 (d, $J = 7.3$ Hz, NH), 5.35 (dd, $J = 1.5$, 2.5 Hz, H-2′), 5.28 (d, $J = 1.5$ Hz, H-1′), 5.24 (m, $=CH_2$), 5.09 (d, $J = 8.4$ Hz, H-1), 5.04 (d, $J = 11.5$ Hz, 1H), 4.95 (d, $J = 10.5$ Hz, 1H), 4.93−4.61 (m, 12H), 4.55 (d, $J = 11.3$ Hz, 1H), 4.46−3.18 (m, 32H), 1.81, 1.75 (2 s, Ac); ^{13}C NMR δ 170.9, 169.8, 167.2 (2Ac, AcCl), 117.2 ($=CH_2$), 100.0 ($J = 163$ Hz), 98.6 ($J = 177$ Hz), 97.7 ($J = 184$ Hz), 55.1 (C-2″), 40.9 (AcCl), 23.7, 20.7 (2Ac). Anal. Calcd for $C_{103}H_{111}ClN_4O_{22}$: C, 69.02; H, 6.24; N, 3.13; Cl, 1.98. Found: C, 68.87; H, 6.29; N, 3.11; Cl, 1.96.

***O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (41b).** A mixture of **41a** (1.647 g, 0.919 mmol) and thiourea (500 mg, 6.57 mmol) in $CHCl_3$ (17 mL) and MeOH (17 mL) was heated at 60 °C for 2.5 h. The solution was diluted with $CHCl_3$ (90 mL), washed with saturated aqueous $NaHCO_3$ (75 mL), dried, and concentrated. Flash chromatography (2:3 petroleum ether/EtOAc) on the residue gave 1.38 g (88%) of **41b**: $R_f = 0.54$; $[\alpha]^{20}_D$ +56.5° (*c* 1.1, $CHCl_3$); ^1H NMR δ 7.46−7.15 (m, 50H, Ph), 5.94 (m, =CH−), 5.71 (d, $J = 3.7$ Hz, H-1″), 5.48 (d, $J = 7.1$ Hz, NH), 5.38 (dd, $J = 1.8$, 2.7 Hz, H-2′), 5.33 (d, $J = 1.8$ Hz, H-1′), 5.24 (m, $=CH_2$), 5.21 (d, $J = 8.2$ Hz, H-1), 5.04 (d, $J = 11.3$ Hz, 1H), 4.95 (d, $J = 10.7$ Hz, 1H), 4.94−3.15 (m, 43H), 1.78, 1.69 (2 s, Ac); ^{13}C NMR δ 170.9, 169.9 (2Ac), 117.2 ($=CH_2$), 99.4, 98.8, 97.7 (3C-1), 55.0 (C-2″), 23.6, 20.7 (2Ac). Anal. Calcd for $C_{101}H_{110}N_4O_{21}$: C, 70.69; H, 6.46; N, 3.26. Found: C, 70.41; H, 6.50; N, 3.32.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-(3,4-di-*O*-benzyl-6-*O*-(chloroacetyl)-α-D-mannopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-[(2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)-(1→4)]-*O*-(2-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (43).** To a solution of **42** (250 mg, 0.171 mmol) and **41b** (200 mg, 0.117 mmol) in CH_2Cl_2 (3 mL) were added NIS (48 mg, 0.213 mmol) and Et_3SiOTf (45 μL, 0.199 mmol), and the mixture was stirred for 15 min before being quenched with Et_3N. The solution was diluted with $CHCl_3$ (10 mL) and washed successively with 10% aqueous $Na_2S_2O_3$ (10 mL) and saturated aqueous $NaHCO_3$ (10 mL). The dried solution was evaporated and the residue flash chromatographed (7:3 petroleum ether/EtOAc) to give 115 mg (39% based on recovered **41b**) of **43** and 48 mg of triethylsilylated **41b**, which by treatment with Bu_4NF in THF was converted into 38 mg of recovered **41b**. For **43**: $R_f = 0.46$; $[\alpha]^{20}_D$ +18.9° (*c* 1, $CHCl_3$); ^1H NMR δ 7.40−6.98 (m, 95H), 6.08 (d, $J = 9.0$ Hz, NH), 5.95 (m, =CH−), 5.70 (d, $J = 3.7$ Hz, H-1″), 5.44 (d, $J = 1.6$, 1.8 Hz, H-2), 5.35 (brs, H-1′), 5.24 (m, $=CH_2$), 5.06−3.09 (m, 87H), 1.68, 1.58 (2 s, Ac); ^{13}C NMR δ 170.2, 170.0, 167.3 (3Ac), 117.3 ($=CH_2$), 100.7 ($J = 162$ Hz), 100.4 ($J = 178$ Hz), 99.5 ($J = 172$ Hz), 99.2 ($J = 173$ Hz), 98.5 ($J = 183$ Hz), 97.7 ($J = 177$ Hz), 53.2 (C-2), 40.8 (AcCl), 23.1, 20.7 (2Ac). Anal. Calcd for $C_{184}H_{195}ClN_4O_{37}$: C, 71.52; H, 6.36; N, 1.81; Cl, 1.15. Found: C, 71.58; H, 6.33; N, 1.75; Cl, 1.00. FAB$^-$: The cluster observed for M^- ion is present. The most abundant ion containing two ^{13}C's is observed at $m/z = 3089.14$. The isotopic abundances at all ions in the cluster closely match the theoretical percentages predicted.

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