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# Synthesis of inositol glycan cyclic phosphates

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**Abstract**

An efficient synthesis of tri-, tetra-, and pentasaccharide cyclic phosphates **1**–**5**, structurally related to natural inositol phosphate glycans, is reported. The title compounds were assembled by PhSeOTf-promoted glycosylation of the known glucosamine precursor, *t*-butyldimethylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**8**) with protected 1-methylthio mono-, di-, and trimannosides **7a**–**c**, and, after conversion into glycosyl fluorides, $Cp_2ZrCl_2$–AgOTf-promoted glycosylation of differentially protected optically pure 1D-myo-inositol **11**. The syntheses were completed by installing the cyclic phosphate moieties with methylpyridinium dichlorophosphate and finally, removal of all protecting groups by dissolving-metal reduction. 

*Keywords:* Inositol phosphate glycans; Cyclic phosphates; 1D-myo-inositol derivatives

## 1. Introduction

In the US, approximately 16 million people suffer from diabetes mellitus. Ninety to ninety-five percent of these are afflicted by non-insulin dependent diabetes mellitus (NIDDM), a condition characterized by insulin resistance. Diminished binding of insulin to its receptor usually does not adequately account for the decreased responsiveness on the cellular level. Therefore, NIDDM may be considered a disease of insulin signal transduction.[1]

During the past 15 years, small inositol-containing oligosaccharides have been implicated as signaling molecules in the insulin signal transduction pathway.[2] These oligosaccharides are believed to be structurally similar to the glycosylphosphatidyl-inositol (GPI) membrane anchors. This idea is supported by the observation that the compound obtained by PI-PLC and Pronase release of the variant surface glycoprotein (VSG) GPI anchor from variant clone 118 of *Trypanosoma bruceii* strain 427, presumed to have structure **6**, is insulin mimetic.[3,14]

However, due to the miniscule amounts of biological material available and the heterogeneity of many isolates, the precise chemical structures of these putative insulin mediators are not known. At least two general classes of compounds have been identified. One class, referred to by Larner's group[4] as the pH 1.3 mediator because of the pH of an eluting solvent during purification, inhibits cAMP-dependent protein kinase and contains myo-inositol and glucosamine.[5] The other, so-called pH 2 mediator, stimulates pyruvate dehydrogenase phosphatase and contains chiro-inositol and galactosamine.[6]

The lack of complete structural characterization has led to intense synthetic efforts by several groups[7–11] in the hope of determining the structural features necessary for mimicking insulin action. Herein, we report the syn-

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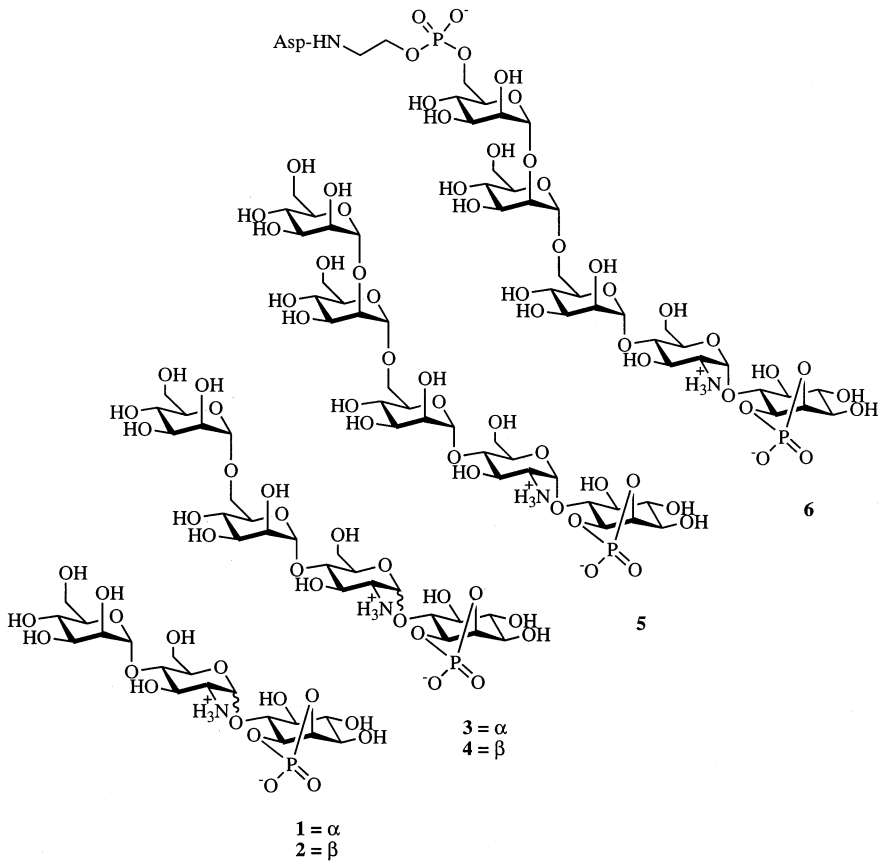



Fig. 1. Synthetic compounds **1**–**5**, and natural VSG membrane anchor fragment **6**.

thesis of oligosaccharides **1**–**5**.[12,13†‡] Compounds **1**, **3**, and **5** constitute the terminal tri-, tetra-, and pentasaccharide portion of **6**, the presumed structure of the VSG anchor fragment from *T. bruceii* variant 118. Compounds **2** and **4** differ from the truncated VSG anchor in that there is a β linkage between the inositol and the glucosamine residues (Fig. 1).

## 2. Results and discussion

*Synthetic strategy.*—The syntheses of compounds **1**–**5** were designed to be modular so that assembly of a variety of oligosaccharides could be achieved rapidly (Scheme 1). The two terminal portions of each target compound, an oligomannose unit and an inositol unit, would be attached to a suitably protected linking glucosamine unit. To minimize the number of manipulations, all protecting groups remaining after final assembly of the oligosaccharides were chosen to be removable in a single deprotection step.

The known glucosamine precursor *t*-butyldimethylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**8**)[15] satisfied these criteria. We envisioned glycosylating the 4-position of **8** with mono-, di-, and trimannoses **7a**,[16] **7b**, or **7c** to provide the corresponding di-, tri-, and tetrasaccharides **9a**–**c**. The methyl 1-thio-α-glycosides **7a**–**c** were selected to utilize Ogawa's α-selective phenylselenyl triflate-promoted glycosylation procedure.[22] After desilylation and conversion into the glycosyl fluorides **10a**–**c**, zirconocene dichloride-promoted coupling[17] to myo-inositol **11** would produce fully protected tri-, tetra-, and pentasaccharides **12a**–**c**, respectively. This glycosylation method was chosen since both the α and β anomers of the oligosaccharides were desired. Recent work by Müller's group[8] has

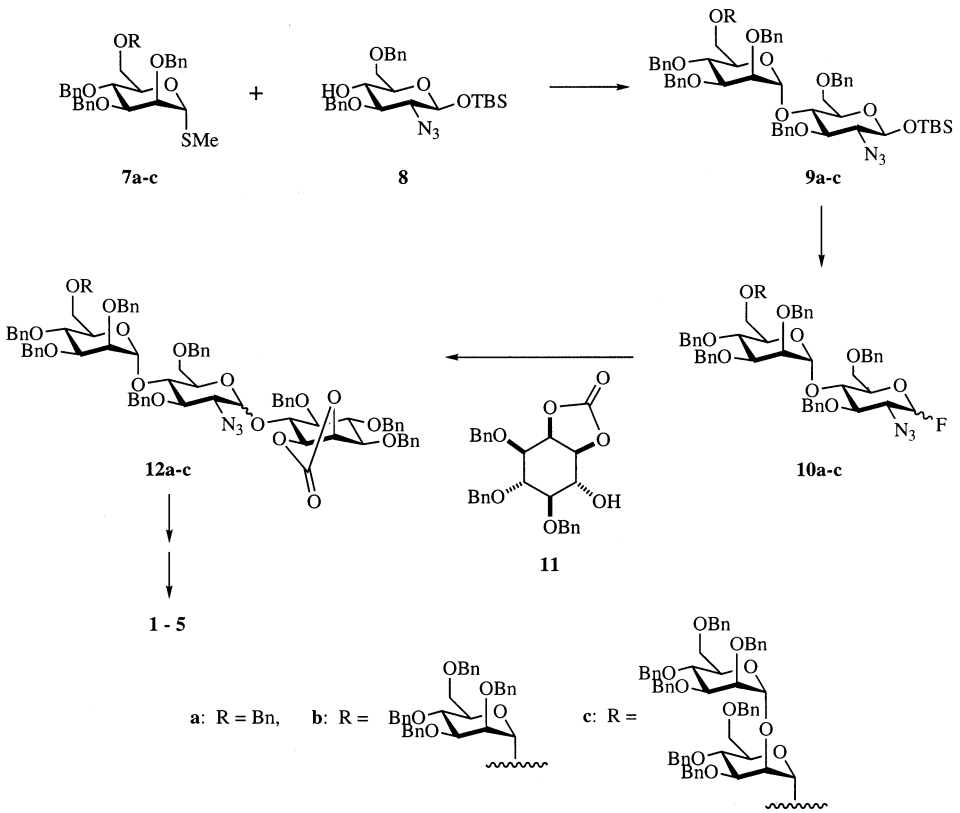
† Our synthesis of **1** has been communicated previously, without experimental details (Ref. 11) and has been synthesized independently (Ref. 10).

‡ A report on the synthesis of **5** by a different procedure appeared at the time of submission of this manuscript.[13]

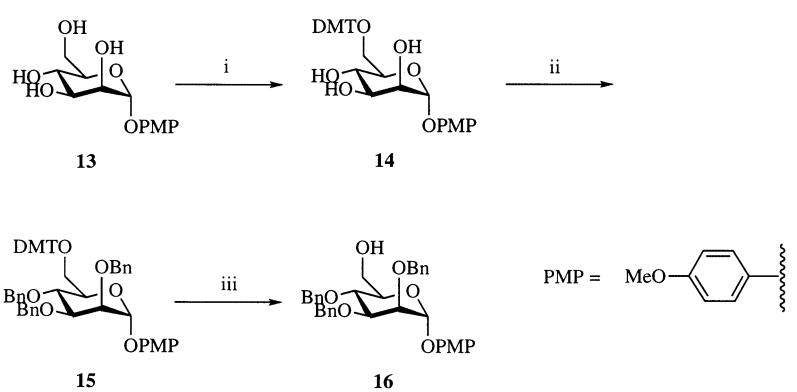
demonstrated that some IPGs with β-D inositol linkages are insulin mimetic.

Inositol **11** was chosen to allow selective removal of the carbonate moiety of **12a–c**, thereby freeing the hydroxyl groups to be esterified in the cyclic phosphate moiety of the targets. Cyclic phosphorylation could then be accomplished in one step by addition of methylpyridinium dichlorophosphate (**31**).[18] Finally, removal of the benzyl protecting groups and reduction of the azido functionality in a single reductive deprotection step would produce targets **1–5**.

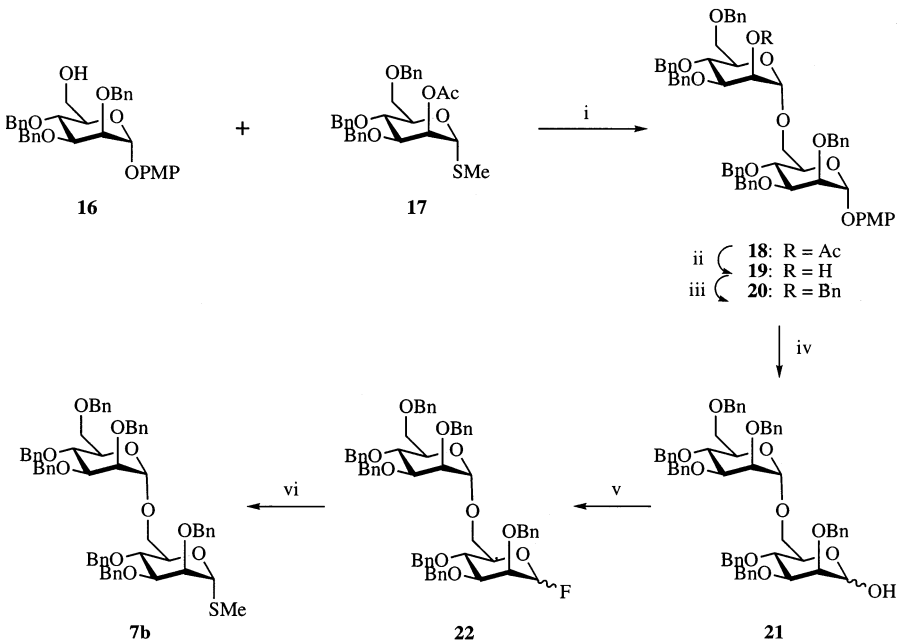
*Synthesis of mannose methyl 1-thioglycosides* **7a–c**.—Selective dimethoxytritylation of the C-6 hydroxyl of the known mannose glycoside **13**[19,20] (Scheme 2) with 4,4′-dimethoxytrityl tetrafluoroborate[21] yielded triol **14**. Exhaustive benzylation under standard conditions ((i) NaH, DMF, 0 °C; (ii) BnBr) yielded fully protected **15**. Removal of the DMT protecting group with 50% HOAc provided alcohol **16** in 64% overall yield from **13**.




Scheme 1. Overview of the syntheses of compounds **1–5**.




Scheme 2. (i) DMTBF, DBMP, $CH_3CN$, reflux (92%); (ii) (a) NaH, DMF; (b) BnBr; (iii) $CHCl_3$, 50% $CH_3CO_2H$, 80 °C (70%, from **14**).




Scheme 3. (i) PhSeCl, AgOTf, toluene, 4 Å molecular sieves, −40 °C (56–71%); (ii) $NH_3$, MeOH, 20 °C (78%); (iii) (a) NaH, DMF; (b) BnBr (85%); (iv) $CH_3CN–H_2O$, +1.55 V, 0.1 M $Bu_4NPF_6$, 20 °C (74%); (v) DAST, THF (86%); (vi) $Bu_3SnSMe$, $SnCl_4$, $ClCH_2CH_2Cl$ (85%).

Coupling of **16** to the known methyl 1-thiomannoside **17**[16] (Scheme 3) using Ogawa's protocol[22] yielded the differentially protected mannose disaccharide **18**. The α configuration of the glycosidic linkage in the product was confirmed by the $^{13}C–^{1}H$ coupling constant (171 Hz) at the anomeric position according to the observation of Bock and Pedersen[23] that α-mannosides exhibit anomeric $J_{C,H} \sim 170$ Hz while β-mannosides exhibit anomeric $J_{C,H} \sim 160$ Hz. In every case in our work where a glycosidic bond was formed from mannose, the anomeric configuration of the product(s) was confirmed by this method.

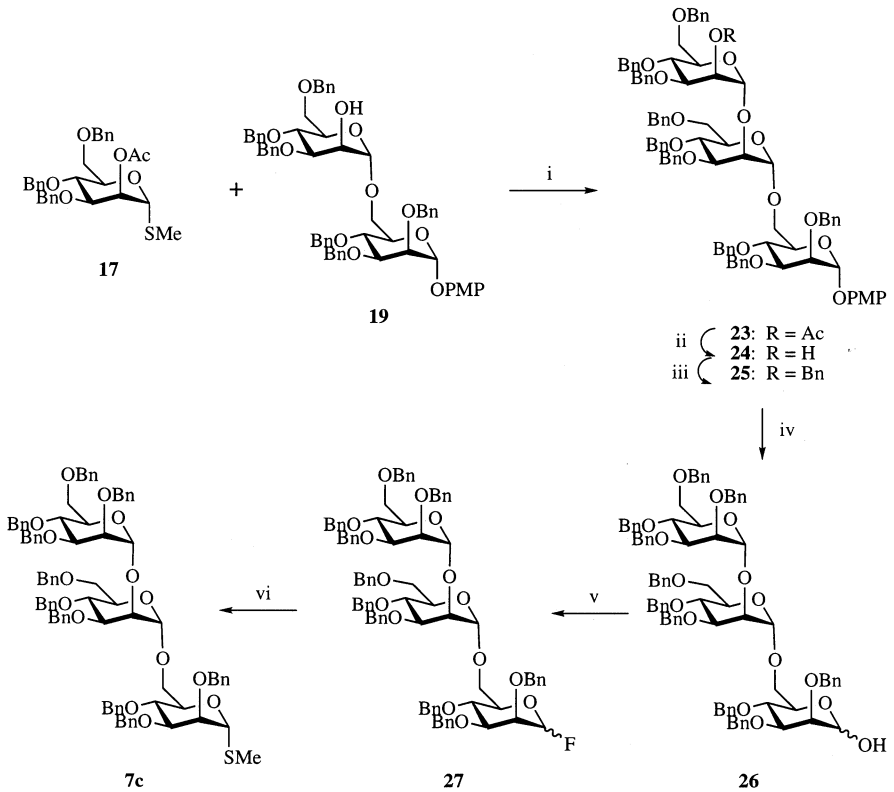
Deacetylation of **18** with methanolic ammonia produced alcohol **19**, which was a common intermediate in the synthesis of methyl 1-thioglycoside donors **7b** and **7c** (Schemes 3 and 4).

The synthesis of **7b** was easily realized as shown in Scheme 3. Compound **19** was benzylated to produce **20** and this was subjected to electrochemical oxidation in aqueous acetonitrile[24] to remove the *p*-methoxyphenyl (PMP) protecting group providing an anomeric mixture of alcohols **21**. This mixture was readily converted into a mixture of anomeric fluorides **22** by treatment with DAST.[25] Finally, $SnCl_4$-promoted thiomethylation with $Bu_3SnSMe$[16,26] produced the glycosyl donor **7b**, ready to couple with acceptor **8**.

For the synthesis of trisaccharide **7c** (Scheme 4), the common intermediate **19** was glycosylated with methyl 1-thiomannoside **17** to produce trisaccharide **23**. Elaboration of **23** to **7c** proceeded in direct analogy to the synthesis of **7b**, producing **7c** in 24% overall yield from the common intermediate **19**.

*Synthesis of myo-inositol* **11**.—The differentially protected inositol **11** (Scheme 5), ready for coupling, was prepared from known, optically pure diol **28**[27] by protection of the two free hydroxyl groups as the cyclic carbonate (*N*,*N*′-carbonyldiimidazole, benzene) followed by removal of the triisopropylsilyl (TIPS) protecting group. Use of acetyl groups to protect the 1- and 2-positions of the inositol ring proved unsuitable because of acetyl group migrations upon fluoride-induced removal of the TIPS group at position 6. The cyclic carbonate did not suffer migration, presumably because the more rigid structure prevents intramolecular attack of the intermediate C-6 alkoxide on the carbonyl group.

*Synthesis of oligosaccharides* **1**–**5**.—With the necessary precursors in hand, each final oligosaccharide could be synthesized in seven steps (Scheme 6). The mannose mono-, di-,

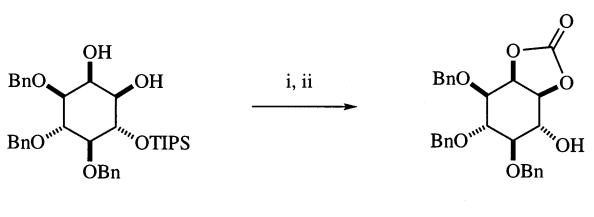



Scheme 4. (i) PhSeCl, AgOTf, toluene, 4 Å molecular sieves, −40 °C (88%); (ii) $NH_3$, MeOH, 20 °C (85%); (iii) (a) NaH, DMF; (b) BnBr (81%); (iv) $CH_3CN–H_2O$, +1.55 V, 0.1 M $Bu_4NPF_6$, 20 °C (78%); (v) DAST, THF (90%); (vi) $Bu_3SnSMe$, $SnCl_4$, $ClCH_2CH_2Cl$ (52%).

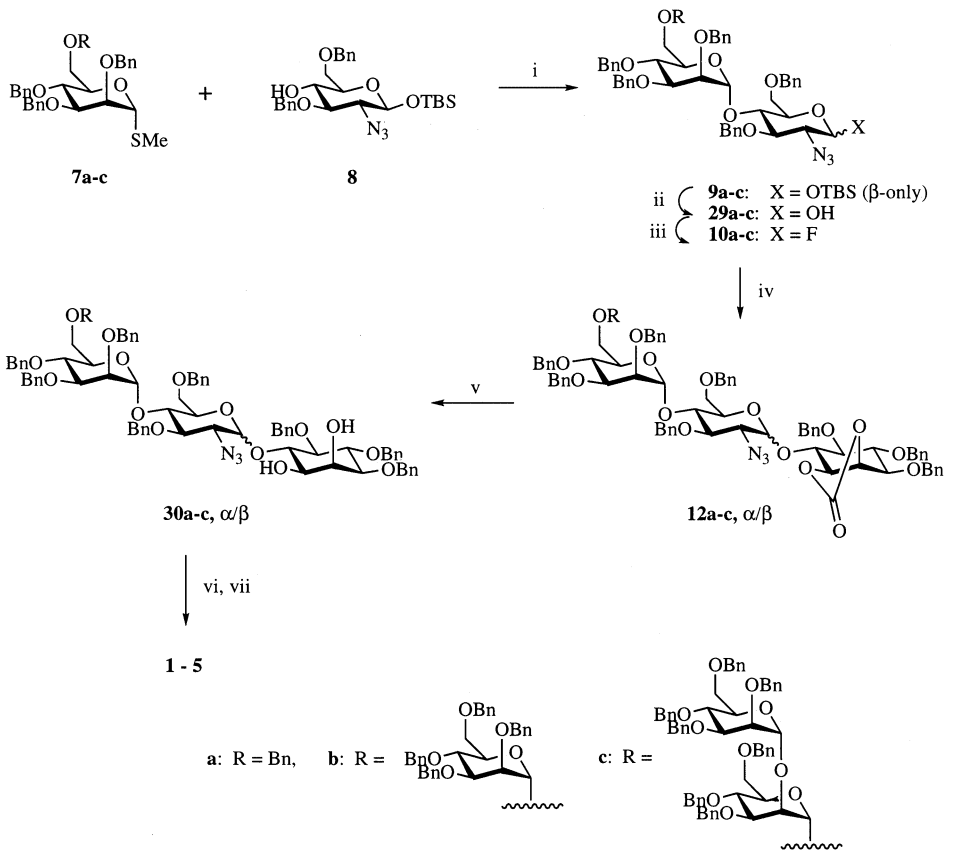
and trisaccharides **7a–c** were coupled with glucosamine derivative **8** utilizing Ogawa's method[16] resulting in α-linked disaccharide **9a**, trisaccharide **9b**, and tetrasaccharide **9c** in 56, 36, and 37% yield, respectively. Fluoride-promoted desilylation of each, followed by conversion into the anomeric fluorides with DAST yielded glycosyl donors suitable for coupling with the inositol. Silver triflate and $Cp_2ZrCl_2$-promoted coupling of **11** with **10a–c** yielded the corresponding trisaccharide **12a**, tetrasaccharide **12b**, and pentasaccharide **12c**. In each case, a mixture of α and β anomers was obtained. These were separated chromatographically and each was carried forward independently.

Removal of the cyclic carbonate moiety by alkaline hydrolysis yielded diols ready for installation of the cyclic phosphate moiety. Addition of methylpyridinium dichlorophosphate (**31**), prepared according to the literature procedure[18] from methyl phosphorodichloridate and pyridine, to diols **30a**α, **30a**β, **30b**α, **30b**β, and **30c**α resulted in the formation of the protected oligosaccharide cyclic phosphates. Finally, dissolving-metal reduction (Na (s), $NH_3$ (l), −78 °C, 15 min) followed by careful quenching at −78 °C with $NH_4Cl$ (s), then MeOH, resulted in removal of all benzyl protecting groups and reduction of the azido group to provide compounds **1–5** contaminated with NaCl. Pure products were obtained by desalting with Sephadex G-10 (56–85% yield).

The biological activity of these compounds is currently being evaluated and will be reported elsewhere.




Scheme 5. (i) *N*,*N*′-Carbonyldiimidazole, benzene, 20 °C; (ii) TBAF, THF, 0 °C, 3 min (84%, from **28**).




Scheme 6. (i) PhSeCl, AgOTf, toluene, 4 Å molecular sieves, −42 °C; (ii) TBAF, HOAc, THF, 20 °C; (iii) DAST, THF, −42 to 20 °C; (iv) $Cp_2ZrCl_2$, AgOTf, **11**, toluene, 4 Å molecular sieves, −42 to 20 °C; (v) LiOH, THF, 12 h, 20 °C; (vi) **31**, pyridine; (vii) (a) Na, $NH_3$ (l), THF, −78 °C, 15 min; (b) $NH_4Cl$ (s), −78 °C; (c) MeOH, −78 °C.

## 3. Experimental

*General methods.*—All nonaqueous reactions were performed under an Ar atmosphere. Organic extracts were dried with anhyd $MgSO_4$ unless otherwise noted. Solvents were removed in vacuo on a Büchi rotary evaporator. Solvents and reagents obtained from commercial sources were used without further purification with the following exceptions. Tetrahydrofuran (THF) and benzene were distilled from Na and benzophenone. Acetonitrile, $CH_2Cl_2$, pyridine, and toluene were distilled from $CaH_2$. Benzyl bromide was fractionally distilled. *N*,*N*′-Dimethylformamide (DMF) was dried with $MgSO_4$, filtered, and then distilled. 1,2-Dichloroethane was dried with $MgSO_4$, filtered, and distilled from $P_2O_5$. Silver triflate was dried in vacuo (0.1 mmHg) for 24 h. Reactions were monitored by thin-layer chromatography (TLC) on Baker glass-backed silica gel plates (0.25 μm thickness) with a 254 nm fluorescent indicator. Chromatograms were visualized by one or more of the following techniques: (a) ultraviolet illumination; (b) dipping in an ethanolic solution of 2.5% *p*-anisaldehyde, 3.5% $H_2SO_4$ and 1% AcOH followed by heating; (c) dipping in an ethanolic solution of Hanes–Isherwood stain (ammonium molybdate–HCl–perchloric acid–acetone);[28] (d) dipping in a 2-propanol solution of ninhydrin–AcOH–pyridine.[28] Purifications were performed by flash chromatography on Baker silica gel (40 μm), by preparative TLC, or by gel-filtration utilizing Sephadex G-10. Nuclear magnetic resonance (NMR) data were obtained on a Bruker AM-300 FT NMR spectrometer operating at 300 MHz for $^1H$. Tetramethylsilane ($Me_4Si$, 0.03%) was used as the internal standard for most $^1H$ and $^{13}C$ NMR spectra. $CFCl_3$ and $H_3PO_4$ (85% in $D_2O$) were used as the external standards for the $^{19}F$ and $^{31}P$ NMR spectra, respectively. High-resolution and low-resolution mass spectrometry data were obtained on a JEOL AX-

505 or JEOL SX-102 mass spectrometer using FAB or electrospray as the ionization method at the Harvard University Department of Chemistry and Chemical Biology Mass Spectrometry Facility. An EG&G model 174A polarographic analyzer was used as the potentiostat for the electrochemical oxidations and the Pt (98 $cm^2$) electrodes were rinsed with concd $HNO_3$ followed by water prior to use.

p-*Methoxyphenyl 6-O-(4,4′-dimethoxytrityl)-α-*D*-mannopyranoside* (**14**).—To a flame-dried flask was added 4,4′-dimethoxytrityl tetrafluoroborate ($DMTBF_4$, 3.4 g, 8.8 mmol) and 2,6-di-*t*-butyl-4-methylpyridine (DBMP, 1.8 g, 8.8 mmol, both were dried by coevaporation with toluene). Acetonitrile (5 mL) was added followed by glycoside **13**,[19,20] (1.6 g, 5.9 mmol, previously dried by coevaporation with toluene). The reaction mixture was warmed at reflux. After 12 h and several additions of more reagent ($DMTBF_4$ and DBMP, $3\times\sim200$ mg), though the reaction had not gone to completion, the reaction was stopped by addition of $NaHCO_3$ (1 M, 10 mL), the mixture extracted with ether ($3\times30$ mL), and the ethereal extracts were dried, filtered, and concentrated. Purification of the resulting oil via flash-column chromatography utilizing step gradient elution, $CHCl_3$ to remove excess $DMTBF_4$ followed by 9:1 $CHCl_3$–MeOH, produced 3.2 g of **14** (92% yield); $R_f$ **14** 0.37 (ether); $^1$H NMR ($CDCl_3$): $\delta$ 2.61 (d, $J$ 4.0 Hz, OH-2), 2.83 (d, $J$ 5.0 Hz, OH-3), 2.89 (d, $J\sim3.0$ Hz, OH-4), 3.37 (pseudo-t, 1 H, $J$ 4.0 Hz), 3.69 (m, 1 H), 3.77 (s, 9 H, $OCH_3$), 3.83 (m, 1 H), 4.00 (m, 1 H, H-3), 4.11 (m, 1 H, H-2), 5.42 (s, 1 H, H-1), 6.70–6.85 (pseudo-t, 6 H, $J$ 7.0 Hz), 7.01 (d, 2 H, $J$ 7.0 Hz), 7.15–7.35 (m, 7 H), 7.39 (d, 2 H, $J$ 8.0 Hz).

p-*Methoxyphenyl 2,3,4-tri-*O*-benzyl-6-*O*-(4,4-dimethoxytrityl)-α-*D*-mannopyranoside* (**15**).—To a solution of **14** (3.0 g, 5.0 mmol) in DMF (18.3 mL) at 0 °C was added NaH (0.9 g, 50% dispersion in mineral oil). The mixture was allowed to warm to 20 °C and stirred at that temperature for 25 min. The suspension was again cooled to 0 °C and BnBr (3.0 mL, 0.025 mol) was added and the mixture was stirred in the dark for 2 h. After the reaction was complete, $NaHCO_3$ (1 M, 1 mL) was added and the mixture was extracted with ether ($4\times1$ mL). The ether layer was washed with $NaHCO_3$ (1 M, $4\times1$ mL), dried, and concentrated. The crude sample was used directly in the next step. A small portion of the crude product was purified for analysis using flash silica gel chromatography with step gradient elution. To prevent hydrolysis, the column was first treated with 1% triethylamine in hexane. Compound **15** was purified via flash-column chromatography utilizing step gradient elution: hexane to remove excess BnBr followed by 2:1 hexane–ether to obtain a pure sample of **15**; $R_f$ **15** 0.40 (2:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 3.24 (dd, 1 H, $J$ 5.0 Hz), 3.45 (d, 1 H, $J$ 10.0 Hz), 3.76 (s, 9 H, $OCH_3$), 3.8–4.1 (m, 4 H), 4.3 (d, 1 H, $J$ 11.0 Hz), 4.68–4.73 (m, 4 H), 4.88 (d, 1 H, $J$ 11.0 Hz), 5.5 (s, 1 H, H-1), 6.74–6.82 (m, 5 H), 6.9 (d, 2 H, $J$ 9.0 Hz), 7.02 (d, 2 H, $J$ 9.0 Hz), 7.17–7.48 (m, aryl H's, 21 H).

p-*Methoxyphenyl 2,3,4-tri-*O*-benzyl-α-*D*-mannopyranoside* (**16**).—To a solution of **15** (1.0 g, 1.0 mmol) in $CHCl_3$ (8 mL) was added a solution of 4 mL of 1:1 AcOH–water and the mixture was stirred for 2 h at 80 °C. When the reaction was complete, ether (25 mL) was added and the solution was neutralized with $NaHCO_3$ (1 M, 20 mL). The layers were separated and the aqueous layer was extracted with ether ($3\times50$ mL). The combined organic extracts were dried, filtered, and concentrated. Compound **16** was purified via flash-column chromatography utilizing step gradient elution: 2:1 hexane–ether was first used to remove nonpolar side-products followed by 1:1 hexane–ether to obtain pure **16** (454 mg, 70% yield); $R_f$ **16** 0.20 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 1.9 (bs, 1 H, OH), 3.75 (s, 3 H, $OCH_3$), 3.77 (m, 2 H), 3.92 (m, 1 H), 4.05–4.15 (m, 2 H), 4.69–4.77 (m, 5 H, H-2, 4 H, C$H_2$Ph), 4.82 (d, 1 H, $J$ 10.0 Hz, C$H_2$Ph), 4.93 (d, 1 H, $J$ 10.0 Hz, C$H_2$Ph), 5.40 (s, 1 H, H-1), 6.78 (d, 2 H, $J$ 9.0 Hz, PMP), 6.88 (d, 2 H, $J$ 9.0 Hz, PMP), 7.35–7.45 (m, 15 H, phenyl H's); HRMS: Calcd for $C_{34}H_{36}O_7Na^+$: 579.2359; Found: 579.2352.

p-*Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-*D*-mannopyranoside* (**18**).—To a flame-dried flask was added 4 Å molecular sieves ($\sim100$ mg), phenylselenium chloride

(0.258 g, 1.349 mmol) and toluene (2 mL). The mixture was cooled to −30 °C [$CH_3CN$–$CO_2$(s)] and silver trifluoromethanesulfonate (462 mg, 1.798 mmol) was added. Slowly a solution of **16** (500 mg, 0.899 mmol) and **17**[16] (704 mg, 1.349 mmol) in toluene (2 mL) was added to the vigorously stirred mixture. After ~30 min, $NaHCO_3$ (1 M, ~5 mL) and bleach (~5 mL) were added to the reaction mixture. The mixture was stirred until the solution was no longer orange (pale yellow) and extractions were done with ether (3 × 5 mL). The combined organic layers were dried, filtered and concentrated. Compound **18** was purified via flash-column chromatography utilizing step gradient elution: hexane was first used to remove nonpolar side-products followed by 3:2 hexane–ether to obtain pure **18** (56–71% yield); $R_f$ **17** 0.63, $R_f$ **18** 0.49, $R_f$ **16** 0.14 (1:1 hexane–ether); $^1$H NMR ($CDCl_3$): $\delta$ 2.14 (s, 3 H, $CH_3CO$), 3.58 (s, 3 H, $CH_3O$), 3.62 (2pseudo-t, 2 H, H-4 mannose-1, H-4 mannose-2), 3.73 (dd, 1 H, *J* 3.7, *J* 10 Hz, H-3 mannose-1), 3.82–3.89 (m, 6 H), 3.96 (dd, 1 H, H-2 mannose-1), 4.12 (dd, 1 H, *J* 8.9, *J* 3 Hz, H-3 mannose-2), 4.37 (d, 1 H, *J* 11 Hz, C$H_2$Ph), 4.42 (d, 1 H, *J* 11 Hz, C$H_2$Ph), 4.45 (d, 1 H, *J* 11 Hz, C$H_2$Ph), 4.51 (d, 1 H, *J* 11 Hz, C$H_2$Ph), 4.59 (d, 1 H, *J* 11 Hz, C$H_2$Ph), 4.66 (d, 1 H, *J* 11 Hz, C$H_2$Ph), 4.68 (s, 2 H, C$H_2$Ph), 4.77 (s, 2 H, C$H_2$Ph), 4.86 (d, 1 H, *J* 11 Hz, C$H_2$Ph), 4.90 (d, 1 H, *J* 1.8 Hz, H-2 mannose-2), 4.93 (d, 1 H, *J* 11 Hz, C$H_2$Ph), 5.40 (s, 1 H, H-1 mannose-1), 5.42 (d, *J* 1.8 Hz, H-1 mannose-2), 6.78 (d, 2 H, *J* 9 Hz, PMP), 6.98 (d, 2 H, *J* 9 Hz, PMP), 7.15–7.42 (m, 30 H, phenyl H); $^{13}$C NMR ($CDCl_3$): $\delta$ 21 ($H_3CCO$), 55 ($CH_3O$), 66.4 ($CH_2$), 68.4 (CH), 68.6 (CH), 71.2 (CH), 71.4 ($CH_2$), 71.6 (CH), 72.2 ($CH_2$), 72.7 ($CH_2$), 73.2 ($CH_2$), 74.1 (CH), 74.5 (CH), 75.0 ($CH_2$), 77.0 (t, $CDCl_3$), 77.8 (CH), 80.0 (CH), 96.6 (d, *J* 171 Hz, C-1), 97.8 (d, *J* 171 Hz, C-1), 114.5 (CH, PMP), 117.4 (CH, PMP, 127.6–128.3 (phenyl Cs), 137.9–138.6 (phenyl Cs), 150.1 (C–O, PMP), 154.8 (C–O, PMP), 170.1 (C=O).

p-*Methoxyphenyl 3,4,6-Tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranoside* (**19**).—Compound **18** (550 mg, 0.534 mmol) was dissolved in $CH_2Cl_2$ (5 mL) and transferred to a pressure vessel. Methanol (5 mL) was added and the mixture was cooled to 0 °C. Ammonia (g) was bubbled through the solution for 5 min then the flask was tightly stoppered. The solution was stirred for 12 h at 20 °C, cooled again to 0 °C and additional $NH_3$ (g) was added. The reaction was then stirred for 24 h at 20 °C. The solution was then transferred to a round-bottom flask and concentrated. Purification via silica gel-flash chromatography (1:1 hexane–ether) produced **19** (412 mg, 78% yield). Crude **19** was not usually purified and was used directly in the production of **20**; $R_f$ **18** 0.76, $R_f$ **19** 0.40 (1:2 hexane–ether); $^1$H NMR ($CDCl_3$): $\delta$ 2.28 (s, 1 H, OH), 3.48 (s, 3 H, $CH_3O$), 3.50 (s, 1 H), 3.54–3.57 (m, 2 H), 3.63–3.76 (m, 5 H), 3.81–3.82 (m, 2 H), 3.85–3.86 (m, 1 H), 3.95 (dd, 1 H, *J* 3, *J* 11 Hz), 4.30 (d, 2 H, *J* 11 Hz), 4.36 (d, 2 H, *J* 11 Hz), 4.37 (s, 1 H), 4.46 (d, 1 H, *J* 11 Hz), 4.54 (s, 2 H), 4.58 (d, 2 H), 4.64 (d, 1 H, *J* 11 Hz), 4.75 (d, 1 H, *J* 11 Hz), 4.81 (s, 1 H, H-1), 5.22 (s, 1 H, H-1), 6.53 (d, 2 H, *J* 9 Hz, PMP), 6.68 (d, 2 H, *J* 9 Hz, PMP), 6.91–7.15 (m, 30 H, phenyl H's).

p-*Methoxyphenyl 2,3,4,6-tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranoside* (**20**).—Compound **19** (400 mg, 0.405 mmol) was dried by coevaporation with toluene, then dissolved in DMF (0.4 mL). The solution was cooled to 0 °C and NaH (40 mg of a 50% dispersion in mineral oil, 0.81 mmol) was added. The mixture was stirred for 30 min, and then BnBr (136 mg, 0.096 mL, 0.81 mmol) was added. The mixture was stirred in the dark at 20 °C and monitored by TLC. When the reaction was complete (~1 h), 5.0 mL of ether was added and the mixture was washed with $NaHCO_3$ to remove the DMF. The ether layer was dried with $MgSO_4$, filtered, and concentrated. Compound **20** was purified via flash-column chromatography. The crude evaporate was applied to a hexane-equilibrated column as a solution in hexane with a few drops of $CH_2Cl_2$ added to enhance solubility. The column was eluted with a step gradient: hexane was first used to remove excess BnBr followed by 1.5:1 hexane–ether to obtain pure **20** (370 mg, 85% yield); $R_f$ **20** 0.80, $R_f$ **19** 0.30 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 3.60 (s, 3 H, $CH_3O$), 3.65–4.15 (m, 12 H, mannose), 4.45–4.55 (m, 4 H), 4.65–4.82 (m, 8 H), 4.88–4.95

(m, 2 H), 5.15 (d, 1 H, *J* 1 Hz, H-1 mannose-2), 5.45 (d, 1 H, *J* 1 Hz, H-1 mannose-1), 6.78 (d, 2 H, *J* 9 Hz, PMP), 6.92 (d, 2 H, *J* 9 Hz, PMP), 7.15–7.40 (m, 35 H, phenyl H's).

*2,3,4,6-Tetra-*O*-benzyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α,β-*D*-mannopyranose* (**21**).—The reaction vessel used was simply a beaker equipped with an Ag | AgCl reference electrode and two Pt (98 $cm^2$) electrodes separated by a porous glass plate. Compound **20** (150 mg, 0.139 mmol) was dissolved in 6:1 MeCN–water (140 mL) with tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$, 0.1 M, 2.32 g) as the electrolyte. The solution was stirred for 72 h at 25 °C as a voltage of +1.55 V was applied. When the reaction was complete, the solution was transferred to a round-bottom flask and concentrated; water (30 mL) was added, and the mixture was extracted with ether (3 × 30 mL). The white precipitate, $Bu_4NPF_6$, was collected by filtration for future reuse. The combined ether layers were dried, filtered, and concentrated. Compounds **21** were purified via flash-column chromatography utilizing step gradient elution: 2.5:1 hexane–ether was first used to remove nonpolar side-products followed by 1:2.5 hexane–ether to obtain **21** (100 mg, 74% yield); $R_f$ **21** 0.20 (1:1 hexane–ether); $^1$H NMR ($CDCl_3$): $\delta$ 1.65 (bs, 1 H, OH), 3.28–3.40, 3.55–4.0 (2m, 12 H, mannose), 4.20–4.75, 4.82–4.90 (2m, 14 H, C$H_2$Ph), 5.05 (s, 1 H, H-1 mannose), 5.15 (s, 1 H, H-1 mannose), 7.10–7.40 (m, 35 H, phenyl H's).

*2,3,4,6-Tetra-*O*-benzyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α,β-*D*-mannopyranosyl fluoride* (**22**).—Compounds **21** (87 mg, 0.089 mmol) were azeotropically dried with toluene then dissolved in THF (0.25 mL) and cooled to −30 °C. Diethylaminosulfur trifluoride (DAST, 18 μL, 0.135 mmol) was added and the reaction mixture was slowly brought to 20 °C over 30 min. When the reaction was complete, the mixture was cooled to −30 °C and MeOH was added to quench any unreacted DAST. After warming the mixture to 20 °C, $NaHCO_3$ (1 M, ~1 mL) was added and the mixture was extracted with ether (3 × 5 mL). The combined ether layers were dried, filtered, and concentrated. Flash silica gel-column chromatography (3:1 hexane–ether) was used to obtain **22** (75 mg, 86% yield), $R_f$ **22** 0.63 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 3.60–3.78, 3.80–4.00 (2m, 12 H, mannose), 4.45–4.75, 4.80–5.20 (2m, 14 H, $CH_2$Ph), 5.52 (d, 1 H, *J* 50 Hz, H-1), 7.10–7.40 (m, 35 H, phenyl H's).

*Methyl 2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-1-thio-α-*D*-mannopyranoside* (**7b**).—To pre-dried **22** (140 mg, 0.144 mmol) cooled to 0 °C was added $Bu_3SnSMe$ in $CH_2ClCH_2Cl$ (97 mg, 0.288 mmol, 1.3 mL of a 74 mg/mL stock solution). After stirring for 5 min, $SnCl_4$ in $CH_2ClCH_2Cl$ (75 mg, 0.29 mmol, 1.3 mL of a 57 mg/mL stock solution) was added. The yellowish solution was stirred at 0 °C for 15 min. When the reaction was complete, NaF (1 M, 15 mL) and EtOAc were added and the reaction was stirred for 1 h. The resulting white precipitate was removed by filtration through Celite. The organic layer was separated, washed with $NaHCO_3$ (1 M, 3 × 15 mL), dried, filtered and concentrated. To obtain pure product, two flash chromatography separations were required. After the first separation (8:1 toluene–EtOAc, $R_f$ α,β RSMe ~ 0.80), the mixture of anomers was collected and applied to a second column (1:1 hexanes–ether) to produce pure **7b** (122 mg, 85% yield). For **7b**: $R_f$ 0.56 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 2.05 (s, 3 H, $CH_3S$), 3.62–4.05 (m, 12 H, mannose), 4.55–4.70 (m, 13 H, C$H_2$Ph), 4.88 (d, *J* 12 Hz, C$H_2$Ph), 5.10 (s, 1 H, H-1), 5.20 (s, 1 H, H-1), 7.10–7.38 (m, 35 H, phenyl H's).

For the β anomer: $R_f$ 0.33; $^1$H NMR ($CDCl_3$): $\delta$ 2.18 (s, 3 H, $CH_3S$), 3.35, 3.58–4.05 (2m, mannose), 4.39–4.98 (m, C$H_2$Ph and mannose), 5.15 (d, 1 H, *J* 1.5 Hz, H-1 mannose-2), 7.15–7.48 (m, phenyl H's).

p-*Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-*D*-mannopyranosidee* (**23**).—Compound **23** was synthesized in a manner analogous to the synthesis of compound **18** except that **19** was used as the glycosyl acceptor in place of **16**. The trisaccharide product **23** was purified via flash chromatography utilizing step gradient elution: hexane was first used to remove nonpolar

side-products followed by 3:1 hexane–ether to obtain pure **23** (88% yield); $R_f$ **23** 0.47 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 2.12 (s, 3 H, C$H_3$CO), 3.58 (s, 3 H, C$H_3$O), 3.50–4.20 (m, 17 H, mannose), 4.10 (dd, 1 H, *J* 3, *J* 11 Hz), 4.34 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.43 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.48 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.52 (s, 2 H, C$H_2$Ph), 4.56 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.62 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.63 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.67 (s, 2 H, C$H_2$Ph), 4.75 (s, 2 H, C$H_2$Ph), 4.82 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.86 (d, *J* 12 Hz, C$H_2$Ph), 4.91 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.93 (pseudo-t, 1 H, *J* 1 Hz, H-1 mannose-2), 5.03 (d, 1 H, *J* 1 Hz, H-1 mannose-3), 5.41 (d, 1 H, *J* 1 Hz, H-1 mannose-1), 5.52 (pseudo-t, 1 H, *J* 1 Hz, H-2 mannose-3), 6.70 (d, 2 H, *J* 9 Hz, PMP), 6.93 (d, 2 H, *J* 9 Hz, PMP), 7.10–7.42 (m, 45 H, phenyl H's); $^{13}$C NMR ($CDCl_3$): $\delta$ 21 (*C*$H_3$CO), 53.45, 55.44 ($CH_3O$), 66.49, 68.83, 71.88, 72.30, 72.34, 73.30, 74.62, 75.02, 77.04 (t, $CDCl_3$) 78.18, 79.32, 80.15, 96.94 (d, *J* 170 Hz, C–H, C-1), 98.81 (d, *J* 171 Hz, C–H, C-1), 99.57 (d, *J* 173 Hz, C–H, C-1), 114.64 (CH, PMP), 117.52 (CH, PMP), 127.55–133.58 (phenyl Cs), 137.9–140.0 (aromatic), 151 (C–O, PMP), 156 (C–O, PMP), 171 (C=O); HRMS: Calcd for $C_{90}H_{94}O_{18}$ + Na: 1485.6337; Found: 1485.4656.

p-*Methoxyphenyl 3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→2)-*3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranoside* (**24**).—Compound **24** was synthesized in a manner analogous to compound **19** except that compound **23** was deacetylated instead of compound **18**. After work-up, silica gel-flash chromatography (1:1 hexane–ether) was used to obtain pure product **24** (554 mg, 85% yield); $R_f$ **24** 0.20 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 2.45 (s, 1 H, OH), 3.58 (s, 3 H, C$H_3$O), 3.52–3.98 (m, 24 H, mannose), 4.05 (m, 1 H, H-2 mannose-3), 4.09 (d, 1 H, *J* 2 Hz), 4.11 (d, 1 H, *J* 1 Hz), 4.34 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.45 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.47 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.50 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.52 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.54 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.56 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.58 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.63 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.68 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.70 (s, 2 H, C$H_2$Ph), 4.77 (s, 2 H, C$H_2$Ph), 4.82 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 4.88 (d, *J* 12 Hz, C$H_2$Ph), 4.92 (d, 1 H, *J* 12 Hz, C$H_2$Ph), 5.1 (pseudo-s, 1 H, H-1 mannose), 5.2 (pseudo-s, 1 H, H-1 mannose), 5.5 (pseudo-s, 1 H, H-1 mannose), 6.78 (d, 2 H, *J* 9 Hz, PMP), 7.00 (d, 2 H, *J* 9 Hz, PMP), 7.15–7.45 (m, 45 H, phenyl H's).

p-*Methoxyphenyl 2,3,4,6-tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→2)-*3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranoside* (**25**).—Compound **25** was synthesized in a manner analogous to synthesis of compound **20** except that alcohol **24** was benzylated instead of alcohol **19**. After work-up, product **25** was purified via flash-column chromatography utilizing step gradient elution: hexane was used first to remove nonpolar side-products followed by 2:1 hexane–ether to obtain pure **25** (81% yield); $R_f$ **25** 0.49 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 3.55 (s, 3 H, C$H_3$O), 3.60–4.12 (m, 18 H, mannose), 4.42–4.90 (m, 20 H, C$H_2$Ph), 4.93 (m, 1 H, H-1), 5.13 (d, 1 H, *J* 1 Hz, H-1), 5.42 (d, 1 H, *J* 2 Hz, H-1), 6.75 (d, 2 H, *J* 9 Hz, PMP), 6.95 (d, 2 H, *J* 9 Hz, PMP), 7.15–7.45 (m, 50 H, aromatic).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→2)-*3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α,β-D-*mannopyranose* (**26**).—Compound **26** were synthesized by a procedure analogous to that utilized for the synthesis of compounds **21** except that trisaccharide **25** was oxidized instead of disaccharide **20**. After work-up, product **26** was purified via flash-column chromatography utilizing step gradient elution: 2:1 hexane–ether was used first to remove nonpolar side-products followed by 1:2 hexane–ether to obtain **26** (78% yield); $R_f$ **26** 0.18 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 3.60–4.00 (m, 17 H, mannose), 4.18 (m, 1 H), 4.45–4.90 (m, 20 H, C$H_2$Ph), 4.92 (m, 1 H, H-1), 4.96 (d, 1 H, *J* 2 Hz, H-1), 5.16 (d, 1 H, *J* 1 Hz, H-1), 7.15–7.40 (m, 50 H, aromatic).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→2)-*3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α,β-D-*mannopyranosyl fluoride* (**27**).—Compound **27** were synthesized in a manner analogous to the synthesis of compound **22** except that trisaccharide **26** were fluorinated instead of di-

saccharide **21**. After work-up, flash silica gel-column chromatography (2:1 hexanes–ether) was used to obtain pure **27** (as an anomeric mixture), 90% yield; $R_f$ **27** 0.62 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 3.55–4.03 (m, 17 H, mannose), 4.15 (pseudo-t, 1 H, *J* 2 Hz), 4.40–4.89 (m, 20 H, C$H_2$Ph), 4.96 (d, 1 H, *J* 1 Hz, H-1), 5.15 (d, 1 H, *J* 1 Hz, H-1), 5.56 (d, 1 H, *J* 51 Hz, H-1 mannose-1), 7.10–7.36 (m, 50 H, phenyl H's); $^{19}$F NMR ($CDCl_3$) $\delta$ −138.5 (d, $J_{FH}$ 51 Hz).

*Methyl 2,3,4,6-tetra-*O*-benzyl-α-*D*-manno-pyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-1-thio-α,β-*D*-mannopyranoside* (**7c**).—Compound **7c** was synthesized in a manner analogous to the synthesis of compound **7b** except that trisaccharides **27** were thiomethylated instead of disaccharides **22**. To obtain the pure α anomer, two flash chromatography column separations were required. After the first column (8:1 toluene–EtOAc, $R_f$ α,β RSMe ~ 0.80), the mixture of anomers were collected and applied to a second column (3:2 hexanes–ether) providing 80 mg (52% yield) of **7c** (α anomer) and 7 mg (5% yield) of the corresponding β anomer; $R_f$ **7c** 0.50 (1:1 hexanes–ether); $^1$H NMR **7c** ($CDCl_3$): $\delta$ 2.05 (s, 3 H, $CH_3S$), 3.55–3.95, 4.05–4.10 (2m, mannose), 4.15 (pseudo-t, 1 H, *J* 2 Hz), 4.45–4.95 (m, 20 H, C$H_2$Ph), 4.95 (d, 1 H, *J* 1.5 Hz, H-1), 5.18 (d, 1 H, *J* 1.5 Hz, H-1), 7.15–7.42 (m, 50 H, phenyl H's); $R_f$ (β anomer) 0.25 (1:1 hexanes–ether); $^1$H NMR (β anomer, $CDCl_3$): $\delta$ 3.40, 3.55–4.05 (2m, mannose), 4.10 (pseudo-t, 1 H, *J* 1 Hz), 4.40–4.95 (m, C$H_2$Ph and mannose), 5.20 (d, 1 H, *J* 1 Hz, H-1), 5.30 (d, 1 H, *J* 1 Hz, H-1), 5.30 ($CH_2Cl_2$), 7.10–7.40 (m, 50 H, phenyl H's).

*3,4,5-Tri-*O*-benzyl-1D-*myo*-inositol 1,2-cyclic carbonate* (**11**).—To 335 mg of diol **28**[27] (0.55 mmol) in 27.5 mL of benzene was added 275 mg of 1,1′-carbonyldiimidazole (1.7 mmol). The reaction was stirred at 20 °C for 17 h and quenched by the addition of water (20 mL). The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (4 × 20 mL). The combined organic extracts were washed with satd NaCl (20 mL), dried, concentrated by co-evaporation with toluene, and dissolved in 24 mL of dry THF. The reaction was cooled to 0 °C and 5.5 mL of 1 M *t*-butylammonium fluoride (TBAF) in THF was added. The reaction was stirred at 0 °C for 3 min and quenched by addition of 12 mL of water at 0 °C. The mixture was extracted with $CH_2Cl_2$ (4 × 12 mL). The combined organic extracts were washed with water (2 × 10 mL) and then satd NaCl (10 mL), dried, and concentrated. Purification via flash silica-column chromatography yielded 262 mg of **11** (84%). $[\alpha]_D$ +22.7° (*c* 0.0075, $CH_2Cl_2$); $R_f$ **11** 0.29 (7:3 hexanes–EtOAc); $^1$H NMR ($CDCl_3$): $\delta$ 2.7 (bs, 1 H, OH), 3.38 (dd, 1 H, *J* 4.5, 10.7 Hz), 3.79 (dd, 1 H, *J* 2.5, 4.5 Hz), 3.90 (pseudo-t, 1 H, *J* 2.8 Hz), 4.31 (d, 1 H, *J* 11.5 Hz, *H*CHPh), 4.38 (d, 1 H, *J* 11.5 Hz, *H*CHPh), 4.45 (dd, 1 H, *J* 7.0, 10.7 Hz), 4.56 (d, 1 H, *J* 11.4 Hz, *H*CHPh), 4.58 (d, 1 H, *J* 11.9 Hz, *H*CHPh), 4.62–2.67 (m, 2 H), 4.71 (d, 1 H, *J* 11.9 Hz, *H*CHPh), 4.86 (dd, 1 H, *J* 3.3, 8.7 Hz), 7–7.5 (m, 15 H, phenyl H's); $^{13}$C NMR ($CDCl_3$): $\delta$ 70.57 (C–O), 72.02 (C–O), 73.34 (C–O), 73.43 (C–O), 73.72 (C–O), 74.34 (C–O), 79.26 (C–O), 80.07 (C–O), 80.92 (C–O), 127.89 (phenyl C), 128.15 (phenyl C), 128.52 (phenyl C), 136.76 (phenyl C), 137.46 (phenyl C), 154.46 (C=O). HRMS-FAB$^+$: Calcd for $C_{28}H_{28}O_7$ + Na 499.1733; Found 499.1744.

t-*Butyldimethylsilyl 2,3,4,6-tetra-*O*-benzyl-α-*D*-mannopyranosyl-(1→4)-2-azido-2-deoxy-3,6-di-*O*-benzyl-β-*D*-glucopyranoside* (**9a**).—To a flame-dried flask containing a stir bar was added PhSeCl (60 mg, 0.313 mmol), 4 Å molecular sieves, and 2.4 mL of toluene. The reaction mixture was cooled to 0 °C and AgOTf (80 mg, 0.311 mmol) was added. After stirring at 0 °C for 10 min, the mixture was cooled to −42 °C and a solution containing **7a** (120 mg, 0.206 mmol) and **8**[15] (86 mg, 0.171 mmol), pre-dried by coevaporation with toluene, in 7.5 mL of toluene was added. The reaction was stirred at −42 °C for 30 min, then quenched by addition of 1 M $NaHCO_3$ (5 mL) followed by filtration through Celite. The layers were separated, the filtrate was diluted with $CHCl_3$ (5 mL) and the organic layer was washed with water (3 × 5 mL), dried, and concentrated. Purification via silica gel chromatography with 4:1 hexane–ether provided 99 mg of **9a** as an oil (56% yield); $R_f$ **9a** 0.26 (4:1 hexane–ether); $^1$H NMR

($CDCl_3$): $\delta$ 0.19 (s, 3 H, $CH_3$), 0.20 (s, 3 H, $CH_3$), 0.94 (s, 9 H, *t*-butyl), 3.25 (dd, 1 H, *J* 8.6, 9.9 Hz, H-3 glucosamine), 3.36–3.42 (m, 2 H, H-5 and H-2 of glucosamine), 3.58 (dd, 1 H, *J* 1.5, 9.1 Hz, H-3 mannose), 3.64–3.83 (m, 7 H), 3.98 (pseudo-t, 1 H, *J* 9.3 Hz, H-4 mannose), 4.25 (d, 1 H, *J* 12.2 Hz, *H*CHPh), 4.35 (d, 1 H, *J* 12.2 Hz, *H*CHPh), 4.43–4.63 (m, 9 H), 4.82 (d, 1 H, *J* 10.8 Hz, *H*CHPh), 4.94 (d, 1 H, *J* 11.4 Hz, *H*CHPh), 5.30 (d, 1 H, *J* 2.0 Hz, H-1 mannose), 7.14–7.40 (m, phenyl H's); $^{13}C$ NMR ($CDCl_3$): $\delta$ 100.15 (d, *J* 169 Hz, C-1 mannose), 97.15 (d, *J* 160 Hz, C-1 glucosamine).

t-*Butyldimethyl 2,3,4,6-tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido*-*2-deoxy*-*3,6-di*-O-*benzyl*-*silyl*-β-D-*glucopyranoside* (**9b**).—Compound **9b** was synthesized according to the procedure outlined for compound **9a** except that disaccharide **7b** was used as the glycosyl donor instead of monosaccharide **7a**. After work-up, purification via silica gel chromatography with 2.5:1 hexane–ether provided **9b** as an oil (36% yield); $R_f$ **9b** 0.43 (2.5:1 hexane–ether); $^1H$ NMR ($CDCl_3$): $\delta$ 0.18 (s, 3 H, $CH_3$), 0.19 (s, 3 H, $CH_3$), 0.96 (s, 9 H, *t*-butyl), 3.26 (dd, 1 H, *J* 8.6, 9.9 Hz, H-3 glucosamine), 3.32–3.40 (m, 2 H), 3.54–3.75 (m), 3.78–3.90 (m, 4 H), 3.92–4.01 (m, 2 H), 4.20 (d, 1 H, *J* 12.1 Hz, *H*CHPh), 4.33 (d, 1 H, *J* 12.2 Hz, *H*CHPh), 4.39–4.55 (m, 14 H), 4.61 (d, 1 H, *J* 12.1 Hz, *H*CHPh), 4.83 (d, 1 H, *J* 11.0 Hz, *H*CHPh), 4.86 (d, 1 H, *J* 10.8 Hz, *H*CHPh), 4.95 (d, 1 H, *J* 11.5 Hz, *H*CHPh), 5.07 (d, 1 H, *J* 1.03 Hz, H-1 mannose), 5.26 (d, 1 H, *J* 1.8 Hz, H-1 mannose), 7.09–7.38 (m, phenyl H's); $^{13}C$ NMR ($CDCl_3$): $\delta$ 99.86 (d, *J* 171.5 Hz, C-1 mannose), 98.20 (d, *J* 171.3 Hz, C-1 mannose), 97.15 (d, *J* 155.6 Hz, C-1 glucosamine). LRMS (electrospray): Calcd for $C_{87}H_{99}N_3O_{15}Si$: 1453.7; Found: 1454.

t-*Butyldimethylsilyl 2,3,4,6-tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→2)-*3,4,5-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido*-*2-deoxy*-*3,6-di*-O-*benzyl*-β-D-*glucopyranoside* (**9c**).—Compound **9c** was synthesized according to the procedure outlined for compound **9a** except that trisaccharide **7c** was used as the glycosyl donor instead of monosaccharide **7a**. After work-up, purification via column chromatography 4:1 hexanes–ether yielded **9c** (37% yield); $R_f$ **9c** 0.65 (1:1 hexanes–ether); $^1H$ NMR ($CDCl_3$): $\delta$ 0.15 (s, 6 H, 2 $CH_3$), 0.96 (s, 9 H, *t*-butyl), 3.21–3.33 (m, 2 H), 3.37–3.60 (m), 3.64–3.92 (m), 4.02 (t, 1 H, *J* 9.5 Hz), 4.11 (t, 1 H, *J* 2.1 Hz), 4.25 (d, 1 H, *J* 12.3 Hz, *H*CHPh), 4.30 (d, 1 H, *J* 12.3 Hz, *H*CHPh), 4.37–4.57 (m), 4.58 (d, 1 H, *J* 12.3 Hz, *H*CHPh), 4.65 (d, *J* 12.3 Hz, *H*CHPh), 4.79 (d, 1 H, *J* 11.1 Hz, *H*CHPh), 4.84 (d, 1 H, *J* 10.9 Hz, *H*CHPh), 4.85 (d, 1 H, *J* 11.3 Hz, *H*CHPh), 4.91 (d, 1 H, *J* 11.4 Hz, *H*CHPh), 4.92 (d, 1 H, *J* 1.6 Hz, H-1 mannose), 5.14 (d, 1 H, *J* 1.6 Hz, H-1 mannose), 5.28 (d, 1 H, *J* 1.9 Hz, H-1 mannose), 7.12–7.36 (m, phenyl H's); $^{13}C$ NMR ($CDCl_3$): $\delta$ 97.12 (d, *J* 155 Hz, C-1 glucosamine), 99.27 (d, *J* 168.3 Hz, 2 × C-1 mannose), 99.83 (d, *J* 169.7 Hz, C-1 mannose).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido*-*2-deoxy*-*3,6-di*-O-*benzyl*-α,β-D-*glucopyranose* (**29a**).—To 360 mg (0.348 mmol) of **9a** in 11 mL of THF was added 700 μL of glacial AcOH followed by 5.3 mL of *t*-butylammonium fluoride (TBAF, 5.32 mmol in THF). The reaction was stirred at 20 °C for 14 h. The mixture was quenched with 1 mL of 1 M $NaHCO_3$ and extracted with $CHCl_3$ (2 × 1 mL). The organic phase was washed sequentially with water (2 × 5 mL), satd NaCl (5 mL), dried, and concentrated. Purification via silica gel chromatography yielded 270 mg of **29a** (84% yield); $R_f$ **29a** 0.29 (1:1 hexanes–ether); $^1H$ NMR ($CDCl_3$): $\delta$ 2.36–3.40 (m, 4 H), 3.48–4.05 (m, 22 H), 4.21 (d, 1 H, *J* 12.1 Hz), 4.24 (d, 1 H, *J* 12.1 Hz), 4.35 (d, 2 H, *J* 12.0 Hz), 4.41–4.46 (m, 17 H), 4.80 (d, 1 H, *J* 10.8 Hz), 4.82 (d, 1 H, *J* 10.8 Hz), 4.90 (d, 1 H, *J* 10.8 Hz), 4.93 (d, 1 H, *J* 10.8 Hz), 5.25 (d, 1 H, *J* 2.4 Hz, H-1 mannose of β anomer), 5.27 (d, 1 H, *J* 1.8 Hz, H-1 mannose of α anomer), 5.33 (d, 1 H, *J* 3.4 Hz, H-1 glucosamine of α anomer), 7.16–7.39 (m, phenyl H's).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido*-*2-deoxy*-*3,6-di*-O-*benzyl*-α,β-D-*glucopyranoside* (**29b**).—Compounds **29b** were synthesized according to the

procedure outlined for compound **29a** except that trisaccharide **9b** was desilylated instead of disaccharide **9a**. After work-up, purification via preparative TLC (1:1 hexanes–ether) yielded 1:1 anomeric mixture of alcohols (85% yield); $R_f$ **29b** 0.34 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 2.43 (bs, 1 H, OH), 3.28–3.56 (m, 4 H), 3.61–4.02 (m, 14 H), 4.16 (d, 1 H, *J* 12.1 Hz, *H*CHPh), 4.31 (d, 1 H, *J* 12 Hz, *H*CHPh), 4.32 (d, 1 H, *J* 12 Hz, *H*CHPh), 4.39–4.63 (m, 13.5 H), 4.80–4.91 (m, 3 H), 5.04 (pseudo-s, 1 H, H-1 mannose 2), 5.21 (d, 0.5 H, *J* 1.92 Hz, H-1 mannose 1), 5.23 (d, 0.5 H, *J* 2.01 Hz, H-1 mannose 1), 5.26 (d, 0.5 H, *J* 3.32 Hz, H-1 glucosamine of α anomer), 7.2–7.5 (m, phenyl H's).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-*(1→4)*-*2-azido*-*2-deoxy*-*3,6-di*-O-*benzyl*-α,β-D-*glucopyranosyl fluoride* (**10a**).—Compounds **10a** were synthesized according to the procedure outlined for compound **22** except that **29a** was fluorinated instead of **21**. After work-up, the crude products were chromatographed on silica gel with 3:1 hexane–ether yielding a 1:2 α,β mixture of anomeric fluorides (84% yield); $R_f$ **10a** 0.18 (3:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 3.31–3.41(m), 3.42–3.88 (m), 3.8–4.03 (m), 4.27 (d, 1 H, *J* 10.2 Hz), 4.31 (d, 1 H, *J* 10.1 Hz), 4.39–4.66 (m), 4.81 (d, 1 H, *J* 10.8 Hz), 4.83 (d, 1 H, *J* 10.9 Hz), 4.87 (d, 1 H, *J* 11.2 Hz), 4.88 (d, 1 H, *J* 11.1 Hz), 5.09 (dd, 1 H, *J* 7.1, *J* 52.7 Hz, H-1 glucosamine of β anomer), 5.26 (d, 1 H, *J* 2.2 Hz, H-1 mannose), 5.30 (d, 1 H, *J* 2.3 Hz, H-1 mannose), 5.66 (dd, 1 H, *J* 2.6, *J* 52.9 Hz, H-1 glucosamine of α anomer), 7.14–7.39 (m, phenyl H's).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-*(1→6)*-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl*-*(1→4)*-*2-azido*-*2-deoxy*-*3,6-di*-O-*benzyl*-α,β-D-*glucopyranosyl fluoride* (**10b**).—Compounds **10b** were synthesized according to the procedure outlined for compound **22** except that **29b** was fluorinated instead of **21**. After work-up, purification via preparative TLC (1:1 hexanes–ether) yielded a 1:1 (α,β) mixture of fluorides (86% yield); $R_f$ **10b** 0.42 (1:1 hexanes–ether); $^1$H NMR ($CDCl_3$): $\delta$ 3.31–4.02 (m, 18 H), 4.24 (d, 1 H, *J* 12.4 Hz, *H*CHPh), 4.25 (d, 1 H, 12.1 Hz, *H*CHPh), 4.35–4.67 (m, 13 H, C*H*$_2$Ph), 4.81–4.89 (m, 3 H, C*H*$_2$Ph), 5.03 (pseudo-s, 1 H, H-1 mannose 2), 5.07 (dd, 0.5 H, *J* 7.1, *J* 52.7 Hz, H-1 glucosamine of β anomer), 5.22 (d, 0.5 H, *J* 1.92 Hz, H-1 mannose 1), 5.27 (d, 0.5 H, *J* 2.1 Hz, H-1 mannose 1), 5.60 (dd, 0.5 H, *J* 2.4, *J* 53 Hz, H-1 glucosamine of α anomer), 7.1–7.5 (m, 45 H, phenyl H's).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-*(1→4)*-*2-azido*-*2-deoxy*-*3,6-di*-O-*benzyl*-α,β-D-*glucopyranosyl*-*(1→6)*-*3,4,5-tri*-O-*benzyl*-*1*-D-myo-*inositol 1,2-cyclic carbonate* (**12a**,α,β).—To a pre-dried mixture of donors **10a** (45 mg, 0.049 mmol) and acceptor **11** (47 mg, 0.099 mmol) was added 4 Å molecular sieves, toluene (3.7 mL), and $ZrCp_2Cl_2$ (72 mg, 0.25 mmol). The mixture was cooled to −42 °C and AgOTf (127 mg, 0.49 mmol) was added. The reaction was stirred briefly at −42 °C (~5 min) and then allowed to warm to 20 °C. The reaction was stirred for 5 h, and then quenched by addition of 1 M $NaHCO_3$ (6 mL), diluted with 6 mL of $CH_2Cl_2$, and filtered through Celite. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (4 × 4 mL). The combined organic extracts were washed with satd NaCl (4 mL), dried, and concentrated. Purification via preparative TLC (7:3 hexanes–EtOAc) yielded 18.6 mg of α product and 17.8 mg of β product (54% combined yield); $R_f$ **12a**,α 0.37, $R_f$ **12a**,β 0.45 (7:3 hexanes–EtOAc); $^1$H NMR ($CDCl_3$) **12a**,α: $\delta$ 3.39 (dd, 1 H, *J* 3.6, 9.7 Hz, H-2 glucosamine), 3.51–3.90 (m, 12 H), 4.02 (pseudo-t, 2 H, 9.3 Hz), 4.20–4.66 (m, 17 H), 4.79–5.02 (m, 4 H), 5.27 (d, 1 H, *J* 1.9 Hz, H-1 mannose), 5.34 (d, 1 H, *J* 3.6 Hz, H-1 glucosamine), 7–7.5 (m, 45 H, phenyl H's); $^1$H NMR ($CDCl_3$) **12a**,β: $\delta$ 3.23 (pseudo-t, 1 H, *J* 9.3 Hz, H-2 glucosamine), 3.37 (m, 1 H), 3.44 (dd, 1 H, *J* 8.1, 9.8 Hz), 3.57–3.83 (m, 10 H), 3.88 (pseudo-s, 1 H), 4.00 (pseudo-t, 1 H, *J* 9.2 Hz), 4.30 (m, 2 H), 4.37–4.63 (m, 14 H), 4.70 (d, 1 H, *J* 10.6 Hz, *H*CHPh), 4.82 (d, 1 H, *J* 10 Hz, *H*CHPh), 4.82 (pseudo-s, 2 H, C*H*$_2$Ph), 4.88 (d, 1 H, *J* 11.3 Hz, *H*CHPh), 5.31 (d, 1 H, *J* 2.0 Hz, H-1 mannose), 7–7.5 (m, 45 H, phenyl H's). LRMS **12a**,α: Calcd for $C_{82}H_{83}N_3O_{16}$ + Na: 1388.57; Found: 1388.

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-*(1→6)*-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl*-*(1→4)*-*2-azido*-*2-deoxy*-*3,6-di*-O-*benzyl*-α,β-D-*glucopyranosyl*-*(1→6)*-*3,4,5-tri*-

O-*benzyl-1*-D-myo-*inositol 1,2 cyclic carbonate* (**12b**,α,β).—Compounds **12b**,α,β were synthesized in a manner analogous to that for compounds **12a**,α,β except that trisaccharides **10b** were used as glycosyl donor instead of disaccharides **10a**. After work-up, purification via preparative TLC (7:3 hexanes–EtOAc) yielded 17.5 mg of **12b**,α and 6.6 mg of slightly impure **12b**,β (57% combined yield); $R_f$ **12b**,α 0.38, $R_f$ **12b**,β 0.46 (7:3 hexanes–EtOAc); $^1$H NMR ($CDCl_3$) **12b**,α: δ 3.37 (dd, 1 H, *J* 3.6, 9.6 Hz, H-2 glucosamine), 3.49–3.7 (m, 11 H), 3.75–3.88 (m, 8 H), 3.94–4.0 (m, 3 H), 4.16 (d, 1 H, *J* 12.0 Hz, *H*CHPh), 4.27–4.65 (m, 19 H), 4.80–4.91 (m, 5 H), 5.04 (pseudo-s, 1 H, H-1 mannose), 5.23 (pseudo-s, 1 H, H-1 mannose), 5.32 (d, 1 H, *J* 3.6 Hz, H-1 glucosamine), 7.0–7.5 (m, 60 H, phenyl H's); $^{13}$C NMR ($CDCl_3$) **12b**,α: δ 96.21 (anomeric C), 98.10 (anomeric C), 100.40 (anomeric C), 153.97 (carbonate carbon); LRMS: Calcd for $C_{109}H_{111}N_3O_{21} + NH_4^+$ 1815.8; Found: 1816.

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→2)-*3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido-2-deoxy-3,6-di*-O-*benzyl*-α,β-D-*glucopyranosyl*-(1→6)-*3,4,5-tri*-O-*benzyl-1*-D-myo-*inositol 1,2-cyclic carbonate* (**12c**,α,β).—Compounds **12c**,α,β were synthesized in a manner analogous to that for compounds **12a**,α,β except that tetrasaccharides **10c** were used as the glycosyl donor instead of disaccharides **10a**. After work-up, purification via preparative TLC (7:3 hexanes–EtOAc) yielded 5.2 mg of **12c**,α and 2.0 mg of **12c**,β (53% combined yield); $R_f$ **12c**,α 0.44, $R_f$ **12c**,β 0.52 (7:3 hexanes–EtOAc); $^1$H NMR ($CDCl_3$) **12c**,α: δ 3.28 (dd, 1 H, *J* 3.5, *J* 9.7 Hz, H-2 glucosamine), 3.38–3.94 (m, 24 H), 3.98–4.09 (m, 3 H), 4.23–4.67 (m, 27 H), 4.76–4.89 (m, 6 H), 5.13 (s, 1 H, H-1 mannose), 5.27 (m, 2 H, H-1 mannose, H-1 glucosamine), 7.2–7.4 (m, 75 H, phenyl H's).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido-2-deoxy-3,6-di*-O-*benzyl*-α-D-*glucopyranosyl*-(1→6)-*3,4,5-tri*-O-*benzyl-1*-D-myo-*inositol* (**30a**,α).—To 17.5 mg of **12a**,α (0.0128 mmol) in 1.4 mL of THF was added 192 μL of 1 M LiOH. The reaction was stirred at 20 °C for 17 h and quenched by addition of 1 M $NH_4Cl$ (3 mL). The mixture was extracted with $CH_2Cl_2$ (4 × 3 mL). The combined organic extracts were washed with satd NaCl (3 mL), dried, and concentrated. Purification via preparative TLC (1:1 $CHCl_3$–ether) yielded 13.8 mg of diol **30a**,α (80% yield); $R_f$ **30a**,α 0.57 (1:1 $CHCl_3$–ether); $^1$H NMR ($CDCl_3$): δ 2.51 (bs, OH), 3.29–3.56 (m), 3.58–3.63 (m), 3.65–4.06 (m), 4.16 (pseudo-t, 1 H, *J* 2.7 Hz, H-2 inositol), 4.23 (d, 1 H, *J* 12.2 Hz, *H*CHPh), 4.26–4.38 (m), 4.44–4.68 (m), 4.72–4.94 (m), 5.23 (d, 1 H, *J* 2.1 Hz, H-1 mannose), 5.45 (d, 1 H, *J* 3.6 Hz, H-1 glucosamine), 7.10–7.39 (m, phenyl H's).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido-2-deoxy-3,6-di*-O-*benzyl*-β-D-*glucopyranosyl*-(1→6)-*3,4,5-tri*-O-*benzyl-1*-D-myo-*inositol* (**30a**,β).—Compound **30a**,β was synthesized in a manner analogous to that for compound **30a**,α except that **12a**,β was hydrolyzed instead of **12a**,α. After work-up, purification via preparative TLC (1:1 $CHCl_3$–ether) yielded 12.3 mg of diol **30a**,β (75% yield); $R_f$ **30a**,β 0.80 (1:1 $CHCl_3$–ether); $^1$H NMR ($CDCl_3$): δ 3.26 (pseudo-t, 1 H, *J* 10 Hz, H-2 glucosamine), 3.4–4.1 (m, 15 H), 4.2 (pseudo-t, 1 H, *J* 2.7, H-2 inositol), 4.25–5.1 (m, 20 H), 5.26 (pseudo-s, 1 H, H-1 mannose), 7.0–7.5 (m, 45 H, phenyl H's).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido-2-deoxy-3,6-di*-O-*benzyl*-α-D-*glucopyranosyl*-(1→6)-*3,4,5-tri*-O-*benzyl-1*-D-myo-*inositol* (**30b**,α).—Compound **30b**,α was synthesized in a manner analogous to that for compound **30a**,α except that **12b**,α was hydrolyzed instead of **12a**,α. After work-up, purification via preparative TLC (1:1 $CHCl_3$–ether) yielded 14 mg of diol (86% yield); $R_f$ **30b**,α 0.61 (1:1 $CHCl_3$–ether); $^1$H NMR ($CDCl_3$) δ 2.6 (s, 1 H, OH), 3.25–3.66 (m, 11 H), 3.71 (pseudo-t, 1 H, *J* 2.3 Hz), 3.79–3.85 (m, 6 H), 3.87–4.02 (m, 5 H), 4.14–4.18 (m, 2 H), 4.21–4.50 (m, 12 H), 4.54 (d, 1 H, *J* 11.9 Hz, *H*CHPh), 4.58 (d, 1 H, *J* 12.0 Hz, *H*CHPh), 4.64 (d, 1 H, *J* 11.3 Hz, *H*CHPh), 4.70–4.76 (m, 4 H), 4.82–4.90 (m, 4 H), 4.94 (d, 1 H, *J* 11.0 Hz, *H*CHPh), 5.03 (pseudo-s, 1 H, H-1 mannose), 5.22 (d, 1 H, *J* 1.7 Hz, H-1 mannose), 5.44 (d, 1 H, *J* 3.6 Hz,

H-1 glucosamine), 7.2–7.5 (m, 60 H, phenyl H's).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido-2-deoxy-3,6-di*-O-*benzyl*-β-D-*glucopyranosyl*-(1→6)-*3,4,5-tri*-O-*benzyl-1*-D-myo-*inositol* (**30b**,β).—Compound **30b**,β was synthesized in a manner analogous to that for compound **30a**,α except that **12b**,β was hydrolyzed instead of **12a**,α. After work-up, purification via preparative TLC (1:1 $CHCl_3$–ether) yielded 4.3 mg of diol (66% yield); $^1$H NMR ($CDCl_3$): $\delta$ 2.50 (bs, 1 H, OH), 3.28 (pseudo-t, 1 H, $J$ 9.3 Hz), 3.35–4.07 (m, 26 H), 4.17–4.22 (m, 2 H), 4.32–4.62 (m, 13 H), 4.68–5.03 (m, 9 H), 5.24 (pseudo-s, 1 H, H-1 mannose), 7.0–7.4 (m, 60 H, phenyl Hs).

*2,3,4,6-Tetra*-O-*benzyl*-α-D-*mannopyranosyl*-(1→2)-*3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→6)-*2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl*-(1→4)-*2-azido-2-deoxy-3,6-di*-O-*benzyl*-α-D-*glucopyranosyl*-(1→6)-*3,4,5-tri*-O-*benzyl-1*-D-myo-*inositol* (**30c**,α).—Compound **30c**,α was synthesized in a manner analogous to that for compound **30a**,α except that **12c**,α was hydrolyzed instead of **12a**,α. After work-up, purification via preparative TLC (1:1 $CHCl_3$–ether) yielded 5.1 mg of diol **30c**,α (97% yield); $^1$H NMR ($CDCl_3$): $\delta$ 2.50 (bs, 1 H, OH), 3.28–4.95 (m, 60 H), 5.02 (pseudo-s, 1 H, H-1 mannose), 5.14 (pseudo-s, 1 H, H-1 mannose), 5.25 (pseudo-s, 1 H, H-1 mannose), 5.40 (pseudo-s, 1 H, H-1 glucosamine) 7.0–7.4 (m, 75 H, phenyl H's).

*Preparation of phosphorylating reagent* **31**[18].—Methyl dichlorophosphoridate ($PCl_2O_2Me$, 500 μL) was added slowly to 5.0 mL of freshly-distilled pyridine. The reaction was stirred at 20 °C for 30 min prior to use.

α-D-*Mannopyranosyl*-(1→4)-*2-amino-2-deoxy*-α-D-*glucopyranosyl*-(1→6)-*1*-D-myo-*inositol 1:2-(cyclic) phosphate* (**1**).—To a solution of **30a**,α (13.0 mg, 9.70 μmol) in pyridine (230 μL) was added freshly prepared phosphorylating reagent **31** (518 μL). The reaction was stirred at 20 °C until judged complete (30 min) by TLC analysis (1:1:1, $CHCl_3$–ether–MeOH, $R_f$ diol 1.0, $R_f$ cyclic phosphate 0.73, $R_f$ acyclic 0; 1:1, $CHCl_3$–ether, $R_f$ diol 0.57, $R_f$ cyclic and acyclic phosphate 0). The reaction was quenched by addition of 1 mL of satd $NaHCO_3$ and concentrated by coevaporation with heptane. The solid was dissolved in 3 mL of water followed by dropwise acidification with 2 M HCl to pH 1 (~20 drops). The suspension was extracted with EtOAc (5 × 3 mL) and the combined organic extracts were dried ($Na_2SO_4$), concentrated, dried by co-evaporation with toluene, and dissolved in dry THF (2.5 mL). In a separate flask, $NH_3$ (5 mL) was condensed at −78 °C and Na (45 mg, 1.94 mmol) was added. Once the blue color persisted, the THF solution was added dropwise. The reaction mixture was stirred at −78 °C for 15 min (blue color persisted) and then carefully quenched by addition of 167 mg (3.12 mmol) of $NH_4Cl$ (s) at −78 °C. The suspension was stirred vigorously at −78 °C until the blue color had completely disappeared. Methanol (6.0 mL) was added at −78 °C, the cooling bath and the septum covering the flask were removed, and the reaction mixture was allowed to thaw and evaporate for 12 h at 20 °C. The resulting white powder was dissolved in water (4 mL) and filtered through Celite. The filtrate was evaporated to dryness, dissolved in water (1.0 mL), and desalted by passing over 12 g of Sephadex G-10, eluting with water (12 mL). Evaporation of the eluate yielded 3.1 mg of **1** (56% yield over two steps). $^1$H NMR ($D_2O$): $\delta$ 3–4 (m, 16 H), 4.35 (ddd, 1 H, H-1 inositol), 4.5 (pseudo-t, 1 H, H-2 inositol), 5.1 (pseudo-s, 1 H, H-1 mannose), 5.3 (pseudo-s, 1 H, H-1 glucosamine); $^{31}$P NMR ($D_2O$): $\delta$ 3.62 (trace of acyclic phosphate), 17.14 (cyclic phosphate); HRMS (FAB, negative ion mode): Calcd for $C_{18}H_{31}NO_{17}P$: 564.1329; Found: 564.1354.

α-D-*Mannopyranosyl*-(1→4)-*2-amino-2-deoxy*-β-D-*glucopyranosyl*-(1→6)-*1*-D-myo-*inositol 1:2-(cyclic) phosphate* (**2**).—Compound **2** was synthesized in a manner analogous to that for compound **1** except that β anomer **30a**,β was phosphorylated and deprotected instead of the α anomer **30a**,α. After work-up, desalting with Sephadex G-10 yielded 8.0 mg of **2** (84% yield over two steps); $^1$H NMR ($D_2O$): $\delta$ 2.9 (m, 1 H), 3.3–4 (m, 15 H), 4.4 (ddd, 1 H, H-1 inositol), 4.55 (pseudo-s, 1 H, H-2 inositol), 4.85 (pseudo-s, 1 H, H-1

glucosamine), 5.1 (pseudo-s, 1 H, H-1 mannose); $^{31}$P NMR ($D_2O$): $\delta$ 16.79.

*α-D-Mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→4)-2-amino-2-deoxy-α-D-glucopyranosyl-(1→6)-1-D-myo-inositol 1:2-(cyclic) phosphate* (**3**).—Compound **3** was synthesized in a manner analogous to that for compound **1** except that tetrasaccharide **30b**,α was phosphorylated and deprotected instead of trisaccharide **30a**,α. After work-up, desalting with Sephadex G-10 yielded 3.1 mg of **3** (75% yield over two steps). $^1$H NMR ($D_2O$): $\delta$ 3.1–4.0 (m, 22 H), 4.35 (ddd, 1 H, *J* 4, 12, 20 Hz, H-1 inositol), 4.5 (pseudo-t, 1 H, *J* 4 Hz, H-2 inositol), 4.7 (pseudo-s, 1 H, H-1-mannose), 5.05 (pseudo-s, 1 H, H-1 mannose), 5.33 (d, 1 H, H-1 glucosamine); $^{31}$P NMR ($D_2O$): $\delta$ 17.13; HRMS (electrospray): Calcd for $[C_{24}H_{42}NO_{22}P + H]^+$ 728.2014; Found: 728.1996.

*α-D-Mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→4)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-1-D-myo-inositol 1:2-(cyclic) phosphate* (**4**).—Compound **4** was synthesized in a manner analogous to that for compound **1** except that β-tetrasaccharide **30b**,β was phosphorylated and deprotected instead of α-trisaccharide **30a**,α. After work-up, desalting with Sephadex G-10 yielded 3.1 mg of **4** (83% yield over two steps). $^1$H NMR ($D_2O$): $\delta$ 2.97 (m, 1 H), 3.33 (pseudo-t, 1 H), 3.44–4.14 (m, 20 H), 4.29 (ddd, 1 H, *J* 4.7, 8.1, 20 Hz, H-1 inositol), 4.5 (pseudo-t, 1 H, H-2 inositol), 4.73 (pseudo-s, 1 H, H-1 mannose), 4.81 (d, 1 H, *J* 7.4 Hz, H-1 glucosamine), 5.03 (pseudo-s, 1 H, H-1 mannose); $^{31}$P NMR ($D_2O$): $\delta$ 16.89.

*α-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→4)-2-amino-2-deoxy-α-D-glucopyranosyl-(1→6)-1-D-myo-inositol 1:2-(cyclic) phosphate* (**5**).—Compound **5** was synthesized in a manner analogous to that for compound **1** except that α-pentasaccharide **30c**,α was phosphorylated and deprotected instead of α-trisaccharide **30a**,α. After work-up, desalting with Sephadex G-10 yielded 1.1 mg of **5** (75% yield over two steps); $^1$H NMR ($D_2O$): $\delta$ 2.62 (pseudo-d, 1 H, *J* 7.7 Hz, H-2 glucosamine), 3.20 (pseudo-t, 1 H, *J* 9.5 Hz), 3.39–3.88 (m, 26 H), 4.36 (ddd, 1 H, H-1 inositol), 4.5 (pseudo-t, 1 H, H-2 inositol), 4.84 (pseudo-s, 1 H, H-1 mannose), 4.95 (pseudo-s, 1 H, H-1 mannose), 5.04 (pseudo-s, 1 H, H-1 mannose), 5.13 (d, 1 H, *J* 3.1 Hz, H-1 glucosamine); $^{31}$P NMR ($D_2O$): $\delta$ 17.12; HRMS (FAB, negative ion mode): Calcd for $C_{30}H_{51}NO_{27}P$: 888.2385; Found: 888.2415.

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