Synthesis of Di- to Hexasaccharide 1,2-Linked β-Mannopyranan Oligomers, a Terminal S-Linked Tetrasaccharide Congener and the Corresponding BSA Glycoconjugates

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Homo oligomers of (1→2)-β-D-mannopyranosyl residues have been synthesized in order to study the unique immunological properties of the cell wall mannan of *C. albicans*. *p*-Chlorobenzyl-protected ulosyl bromide (**2**) in combination with the sterically hindered, participating solvent, pivaloyl nitrile, facilitated a new approach for the synthesis of these unique homooligomers ranging from disaccharide up to hexasaccharide. The glycosyl donor **2** demonstrates high diastereoselectivity over both the glycosylation and subsequent reduction step and minimizes the number of protecting group manipulations necessary for the synthesis. Congeners of the (1→2)-β-D-mannotetraose were synthesized containing a terminal S-linked (1→2)-β-D-mannopyranosyl residue. Deprotection of these compounds afforded the propyl glycosides as well as oligomers with amino terminated aglyconic tethers. The tethers were generated from the oligosaccharide allyl glycosides by photoaddition with 2-aminoethanethiol. The functionalized haptens were coupled to BSA via squarate conjugation, and the degree of incorporation was established by TOF mass spectrometry.

Introduction

The rational synthesis of β-mannopyranosides is a longstanding problem that lacks a general solution, despite several novel approaches.[1] The synthesis of a homopolymer containing contiguous β-D-mannopyranosides presents an especially formidable synthetic challenge.[2] Here, we show that an approach based upon a ulosyl bromide glycosyl donor developed by Lichtenthaler et al. is a versatile method for the generation of 1,2-linked β-mannopyranose oligomers.[3,4] Oligomers of this type are important antigens of the pathogenic yeast *Candida albicans*.

Although *C. albicans* is ubiquitous in the natural flora of humans, it is also the most common etiologic agent in candidiasis.[5] This potentially life-threatening infection commonly occurs in immunocompromised patients and those undergoing long-term antibiotic treatment.[6] The increasing resistance of *C. albicans* to available antifungal drugs necessitates the discovery of new treatments for this pathogen.[7] Understanding the relationship between the pathogen and its host is crucial to the development of new treatments for candidiasis.

Compelling data has focused attention on the mannan portion of the *C. albicans* cell wall as an important factor in pathogenicity. It has been shown to be associated with adhesion of yeast to different tissue types[8,9] and activation of macrophages[10] and is the receptor whereby yeast bind to macrophage membranes.[11,12] Monoclonal antibodies raised against *C. albicans* cell wall extracts, in mice, provided protection against disseminated candidiasis and vaginal candidiasis.[13] Further studies on these monoclonal antibodies indicated the active epitope to be a portion of the (1→2)-β-mannan oligomer found in the phosphomannan.[14]

In an effort to comprehend the conformation and biological properties of the (1→2)-β-mannopyranan, a series of oligomers were required. In elaboration of a 1,2-linked polymer, a ulosyl bromide provides first the corresponding ulopyranoside, which can be reduced to afford directly the selectively protected glycosyl acceptor of the next glycosylation step. Using this approach,

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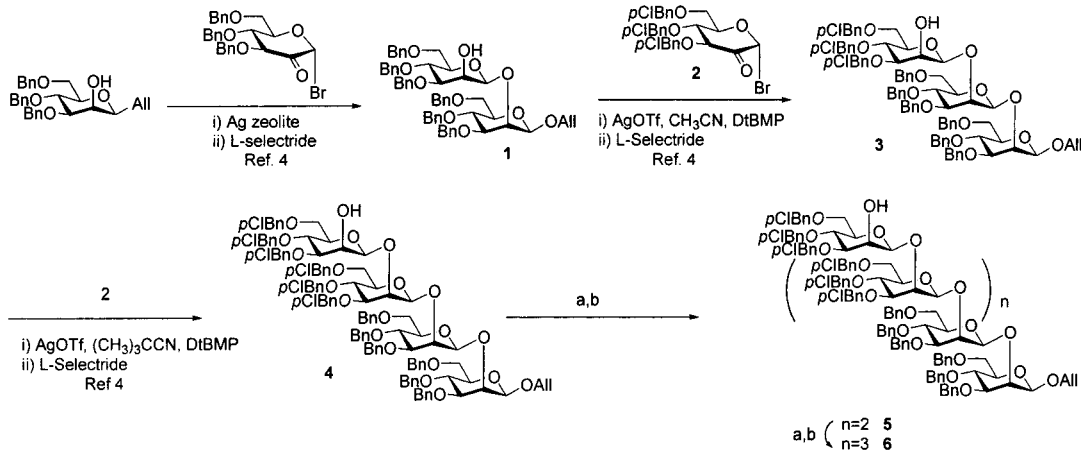

Figure 1. Synthesis of pentasaccharide and hexasaccharide (1→2)-β-D-mannopyranan Oligomers: (a) **2**, AgOTf, DtBMP, $(CH_3)_3$-CCN/CH_2Cl_2; (b) L-Selectride, THF.

structures as large as a hexasaccharide as well as a metabolically more stable tetrasaccharide, containing a terminal thioglycosidic linkage, were synthesized as their propyl glycosides. Amino terminated aglyconic tethers of the oligosaccharides were also generated and coupled to bovine serum albumin to form neoglycoconjugates. The S-linked tetrasaccharide congener containing a nonreducing terminal thioglycoside linkage was envisaged as a potentially better immunogen for anti-*C. albicans* vaccine development since the teriminal glycosidic linkage would be stable to *exo*-mannosidases.

The synthesis of an amino functionalized tetrasaccharide was communicated previously.[4] The work reported here demonstrates the versatility of the method for synthesis of higher oligomers up to and including a hexasaccharide. The orthogonal protection strategy was tailored to facilitate the conjugation of oligosaccharides to protein carriers, and the syntheses of neoglycoconjugates containing the di-, tri-, tetra-, and hexasaccharides are also reported.

Results and Discussion

Elaboration of (1→2)-β-Mannopyranotetraose to the Penta- and Hexasaccharide Oligomers. The synthesis of tetrasaccharide (**4**) was accomplished as outlined in Figure 1.[4] The use of nitriles as participating solvents to promote formation of the equatorial glycosides has been well documented in the carbohydrate literature.[15] These conditions have been modified for use with ulosyl bromide glycosyl donors. Previously, it was determined that a participating solvent and a soluble promotor were superior to the heterogeneous conditions initially employed for the glycosylation of the complex alcohols **1**, **3**, and **4**.[4] Furthermore, pivaloyl nitrile was chosen as the participating solvent for the glycosylation of **3** as the steric bulk of the *tert*-butyl group decreases side reactions at the nitrile carbon. Pentasaccharide (**5**) and hexasaccharide (**6**) were synthesized employing these conditions in 51% and 48% yield, respectively (combined yield of glycosylation and reduction). *p*-Chlorobenzyl-protected ulosyl bromide **2** was found to give higher glycosylation yields than its benzyl-protected counterpart,[4] likely due to the increased stability of the protecting groups. Formation of the ulosides was accomplished with good selectivity giving an approximate 4:1 β/α mixture in favor of the desired linkage. Separation of the α-anomer was readily accomplished by silica gel chromatography of the protected oligomer after direct reduction of the product obtained from the glycosylation. Excellent diastereoselectivity was observed upon reduction of the β ulopyranoside to the desired β-mannoside with L-Selectride, as no β-gluco epimer could be detected by ^{1}H NMR in this reaction. Heteronuclear one-bond coupling constants were used to unambiguously establish the anomeric configuration of the mannopyransyl residues.[16]

The yields and selectivities achieved in this synthesis compare well with those recently published for the synthesis of an analogous structure using 4,6-*O*-benzylidene-protected mannopyranosyl sulfoxide donors.[2] Crich et al. synthesized β-(1→2)-mannopyranosyl pentasaccharides and hexasaccharides in 68% and 69%, respectively, but given an extra deprotection step (achieved in 80−85% yield) prior to further glycosylation steps, no large gain in efficiency is evident over the approach reported here.

The protected oligosaccharides **1** and **3**−**6** were elaborated via photoaddition of 2-aminoethanethiol[17] to the allyl glycosides to give the amine-functionalized glycosides **7**−**10**. It was necessary to use long-wavelength (365 nm) UV irradiation to avoid complications with the aromatic protecting groups (Figure 2). Purification of these compounds was difficult, and they were carried through the subsequent deprotection step with minor impurities.

Compounds **7**−**10** were deprotected under dissolving metal conditions to yield the amino-functionalized glycosides **11**−**14** after purification. The allyl disaccharide **1** could be readily deprotected under standard hydrogenation conditions, but the allyl glycosides containing *p*-chlorobenzyl protecting groups **3**−**6** were resistant to

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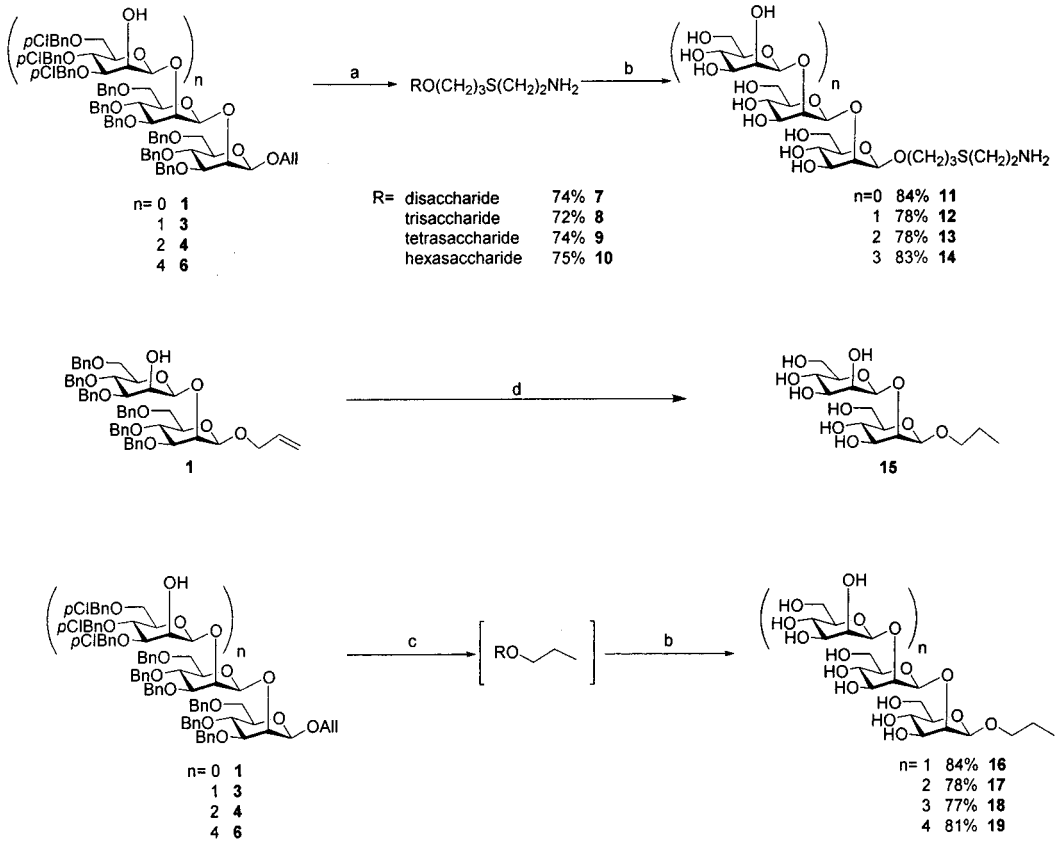

Figure 2. Deprotection of (1→2)-β-D-mannopyranan oligomers: (a) 2-aminoethanethiol hyrochloride, MeOH/CH_2Cl_2, *hν* 365 nm; (b) Na/NH_3, *t*-BuOH, THF; (c) $NH_2NH_2 \cdot H_2O$, EtOH/THF; (d) Pd/C, H_2, EtOH.

hydrogenation. Deprotection of these compounds (**3**−**6**) to their respective propyl glycosides (**15**−**19**) was most efficently achieved using a two-step procedure. The allyl glycoside was first reduced to the propyl glycoside via diimide reduction and then the protecting groups were removed under dissolving metal conditions (Figure 2).

The ^{1}H NMR spectra of these compounds (**11**−**19**) had exceptional signal dispersion when compared with other homooligomers such as kojitetraose ((1→2)-α-glucopyranotetrose)[18] or (1→2)-α-4,6-dideoxy-4-formamidomannopyranose).[19] This is indicative of an ordered structure that allows the internal mannopyranose rings in the homo polymer to occupy different chemical environments. Complete NMR and modeling investigations of these compounds is the subject of a subsequent publication.

Synthesis of Thioglycoside Mimetic. Retrosynthetic Analysis. Initial studies on the feasibility of forming the terminal thioglycosidic linkage indicated that direct displacement with a β-anomeric thiolate on allyl 3,4,6-*O*-benzyl-2-*O*-trifluoromethanesulfonyl-β-D-glucopyranoside was not feasible since only the α-thioglycoside was obtained. This was surprising given the recent success in forming 1-thio-β-mannopyranosides by this method.[20] Thus, the reciprocal approach was undertaken by installing a thiol on the trisaccharide to act as the nucleophile in the displacement of an anomeric leaving group on the glycosyl donor. The previously synthesized ulosyl bromide **2** was chosen as the glycosyl donor in this reaction. The nucleophilic displacement of a 2-chlorosialic acid derivative with sulfur nucleophiles,[21] which has shown success, is analogous to displacement of the bromide of uloside **2**, in that both anomeric halide leaving groups are α to a carbonyl group. Furthermore, ulosyl bromides had previously been shown to react with simple thiols to give 1-thio-β-D-ulosides in high yield.[3] Thus, the trisaccharide **28** was envisaged as the thiol acceptor for this thioglycosylation. It could be synthesized via the glycosylation of disaccharide **1**, with the glucosyl donor **23**, to give a trisaccharide functionalized as a 4,6-*O*-benzylidene acetal. This protecting group is necessary to lock the $^4C_1$ ring and thereby facilitate displacement at C-2 with a sulfur nucleophile to give access to trisaccharide **28**. Furthermore, these compounds would contain the reducing terminal allyl glycoside for elaboration to the amine functionalized tetrasaccharide or propyl glycoside late in the synthesis (Scheme 1).

Synthesis of the Thioglycoside Mimetic. The synthesis of the glucosyl donor (**23**) began by treating a DMF solution of 3-*O*-benzylglucose, available from a one-pot procedure,[22] with benzaldehyde dimethyl acetal and a catalytic amount of acid. This solution was slowly concentrated under vacuum to remove methanol and give the benzylidene acetal derivative **20** in 94% yield. More vigorous conditions, including the use of acetonitrile as a solvent, resulted in considerable accumulation of the other possible benzylidene acetals. The synthesis of

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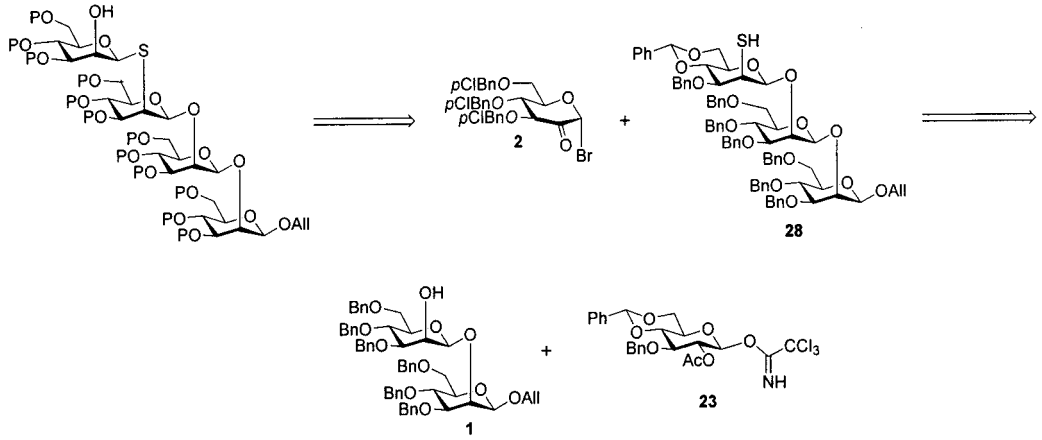
Scheme 1. Retrosynthetic Analysis of the Thioglyoside Mimetic of (1→2)-β-D-Mannopyranotetraose



compound **20** was recently reported using benzaldehyde and zinc chloride in 54% yield.[23] The diol **20** was acetylated to give **21**, and the anomeric acetate could be selectively removed with benzylamine in THF to give hemiacetal **22**.[24] Generation of the trichloracetimidate under standard conditions gave the glycosyl donor **23** (Figure 3).[25]

The formation of the trisaccharide (**24**) was accomplished in high yield from imidate donor **23** and disaccharide acceptor **1** by employing a catalytic amount of TMSOTf in dichloromethane at room temperature. The 2-*O*-acetate of the trisaccharide could then be removed using sodium methoxide in a solution of methanol and THF to give alcohol **25**. Introduction of the 2-*O*-trifluoromethanesulfonate under standard conditions gave trisaccharide **26**. Nucleophilic displacement of the triflate with thioacetate (→ **27**) was somewhat troublesome as it required elevated temperatures and short reaction times. Unfortunately, the yields of **27** could not be improved by the introduction of crown ether. Removal of the acetate proceeded smoothly to give the thiol **28**, which was stable to atmospheric oxidation and required no special handling. The thiol was condensed with the ulosyl bromide **2** under basic conditions to give, after reduction, the desired tetrasaccharide, **29**, in 49% unoptimized yield. The corresponding 1-thio-α-gluco epimer was also isolated from the reaction (~12%). This is likely formed from β-ulosyl bromide present in the reaction although base catalyzed isomerization of the ulosyl thioglycoside or an SN1 reaction with the ulosyl bromide may also be possible. The starting ulosyl bromide contained no detectable β-ulosyl bromide, as judged by ^{1}H NMR spectroscopy, but this anomer may be formed during the reaction via halide exchange. Previous studies have shown no isomerization of O-linked ulosyl glycosides under basic conditions and it seems unlikely that this would be occurring with the S-linked uloside (Figure 4).

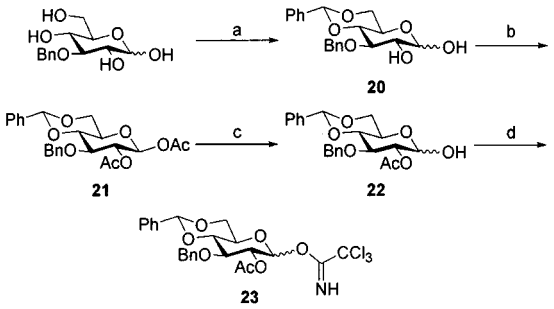


Figure 3. Synthesis of glucosyl donor **23**: (a) $PhCH(OMe)_2$, *p*-TSA, DMF, 94%; (b) Ac_2O, AcOH, NaOAc, 88%; (c) $BnNH_2$, THF, 78%; (d) Cl_3CCN, DBU, CH_2Cl_2, 86%.

Table 1. BSA Mannopyranan Conjugates

	molar excess of oligosaccharide employed	obsed hapten incorporation	efficiency (%)
39	20	16 ± 1	80
40	20	15 ± 1	75
41	20	13 ± 1	65
42	20	10 ± 1	50
43	20	15 ± 1	75

Tetrasaccharide **29** was subjected to the same conditions as were previously used to form 3-(2-aminoethylthio)propyl glycosides. The presence of a thioglycoside did not appear to complicate the photoaddition of the thiol giving functionalized glycoside **30** in reasonable yield. Allyl glycoside **29** was reduced with a solution of hydrazine hydrate,[26] which reduced the double bond to afford propyl glycoside **31**. Dissolving metal conditions then efficiently removed the benzyl and *p*-chlorobenzyl protecting groups to give the desired tetrasaccharides **32** and **33** (Figure 5).

Formation of Glycoside Conjugates. Reaction of the functionalized mannopyranosyl glycosides **11**−**14** and **32** with diethyl squarate in a solution of ethanol and water provided, in high yield, the activated oligosaccharides **34**−**38** for facile coupling to protein. ^{1}H NMR of these compounds showed doubling of some signals due to the vinylogous amide character of the squarate adducts, as has been previously observed (Figure 6).[27]

Coupling to BSA was achieved using the homobifunctional coupling reagent diethyl squarate as reported by Hindsgaul et al.[28] Conjugation efficiencies of between 65 and 70% were achieved, similar to those published for the coupling of oligosaccharides to BSA.[28] This corresponds to the incorporation of 13−15 ligands with a 20-fold molar excess of activated oligosaccharide. Targeted and observed incorporations are tabulated below (Table

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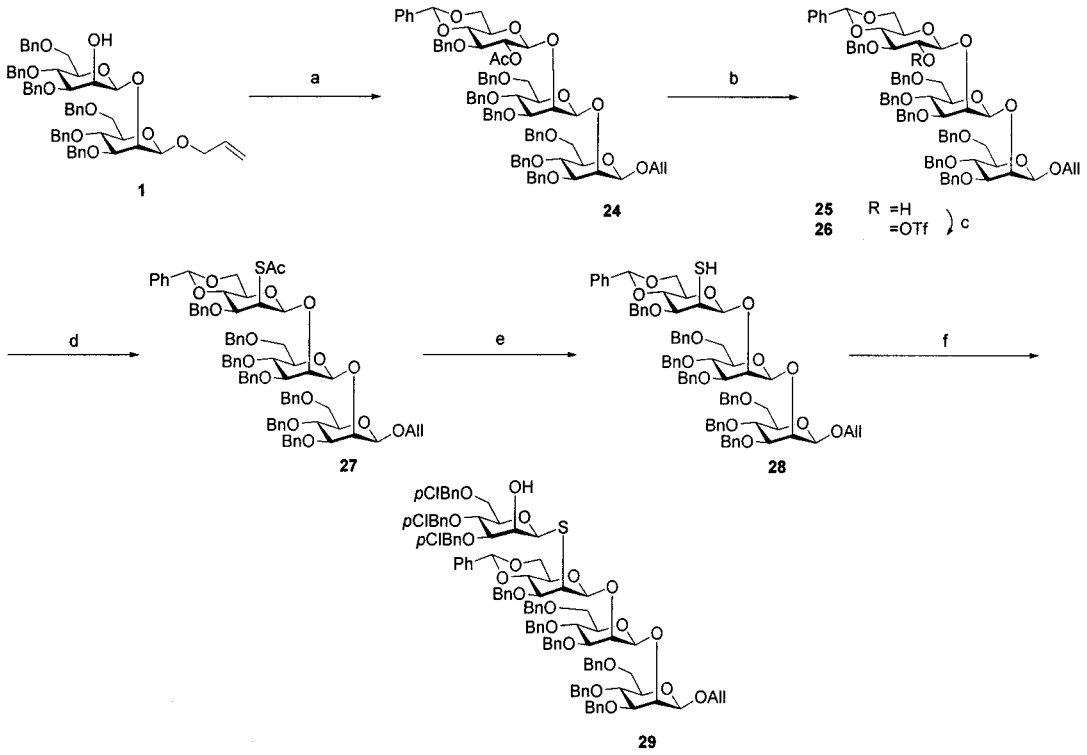

Figure 4. Synthesis of the thioglyoside mimetic of (1→2)-β-D-mannopyranotetraose: (a) **23**, TMSOTf, CH_2Cl_2, 76%; (b) MeONa, MeOH/THF, 94%; (c) Tf_2O, pyridine, 89%; (d) KSAc, DMF, 63%; (e) hydrazine hydrate, cyclohexene, EtOH/THF, 89%; (f) (i) **2**, lutidine, CH_2Cl_2, (ii) L-Selectride, THF, 49%.

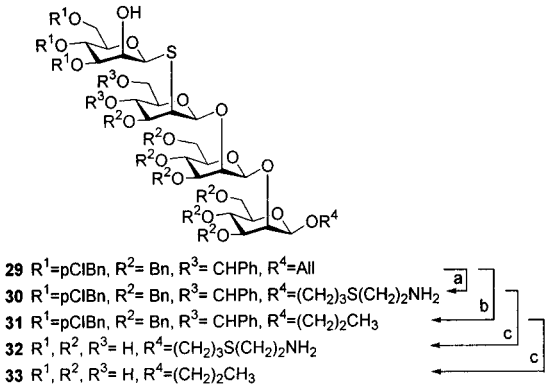

Figure 5. Deprotection of the thioglyoside mimetic of (1→2)-β-D-mannopyranotetraose: (a) 2-aminoethanethiol hyrochloride, MeOH/CH_2Cl_2, *hν* 365 nm; (b) $NH_2NH_2 \cdot H_2O$, EtOH/THF; (c) Na/NH_3, *t*-BuOH, THF.

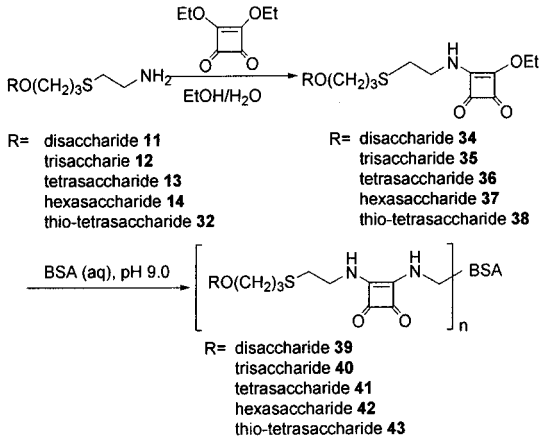

Figure 6. Synthesis of oligomannoside squarate conjugates.

1). The molecular weights of the protein conjugates were determined by MALDI-TOF spectroscopy, which indicated that all the conjugates produced had limited polydispersity in that the degree of hapten incorporation fell within a narrow range of ±1 haptens, Table 1.

Conclusion

Compounds that are derivatives of the unique (1→2)-β-D-mannopyranan found in the cell wall of *C. albicans* have been synthesized and deprotected to provide deprotected oligosaccharide glycosides **15**−**19** and **33**. These compounds have been used for conformational analysis, and characterization of the epitope recognized by monoclonal antibodies.[29] Glycoconjugates **39**−**43** derived from tethered ligands **34**−**38** are being evaluated for their efficiency as anti-*C. albicans* vaccines. The unique and interesting data from these studies are the subject of separate papers.[30]

Experimental Section

Analytical thin-layer chromatography (TLC) was performed on silica gel 60-F_{254} (Merck). TLC detection was achieved by charring with 5% sulfuric acid in ethanol. All commercial reagents were used as supplied. Column chromatography used silica gel (SiliCycle, 230−400 mesh, 60 Å), and solvents were distilled. High-performance liquid chromatography (HPLC) was performed using a Waters HPLC system that consisted of a Waters 600S controller, 626 pump, and 486 tunable absorbance detector. HPLC separations were performed on a

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(30) Nitz, M.; Bundle, D. R. In *NMR of Glyco-Conjugates*; J. Jimenez-Barbero, T. Peters, Eds.; Wiley-VCH Verlag: Weinheim, Germany, in press.

Beckmann C_{18} semipreparative reversed-phase column with a combination of methanol and water as eluents. Photoadditions were carried out using a spectroline model ENF-260C UV lamp and cylindrical quartz vessels. ^{1}H NMR spectra were recorded at either 500, 600, or 800 MHz, and are referenced to internal standards of the residual protonated solvent peaks; δ_H 7.24 ppm for solutions in $CDCl_3$, and 0.1% external acetone (δ_H 2.225 ppm) for solutions in D_2O. Assignments were made with the aid of GCOSY, TOCSY, and TROESY experiments. ^{13}C NMR spectra were recorded at 150 MHz and are referenced to internal $CDCl_3$ (δ_C 77.0 ppm) or to external acetone (δ_C 31.07 ppm). Optical rotations were measured with a Perkin-Elmer 241 polarimeter at 22 °C. Mass spectrometric analysis was performed by positive-mode electrospray ionization on a Micromass ZabSpec Hybrid Sector-TOF mass spectrometer. For exact measurements, the spectra were obtained by voltage scan over a narrow mass range at 10,000 resolution. MALDI mass spectrometric analysis of protein glycoconjugates was performed on a Voyager-Elite system from Applied Biosystems.

3,4,6-Tri-*O*-(4-chlorobenzyl)-α-D-*arabino*-hexopyranos-2-ulosyl Bromide (2). 2-*O*-Acetyl-1,5-anhydro-3,4,6-tri-*O*-(*p*-chlorobenzyl)-D-*arabino*-hex-1-enitol (2-acetoxy-3,4,6 tri-*O*-(*p*-chlorobenzyl)-D-glucal)[4] (500 mg, 0.868 mmol) was dissolved in dichloromethane (6.5 mL), and freshly dried 3A molecular sieves were added. The solution was stirred under argon for 20 min, and then the reaction was cooled to 0 °C. Anhydrous ethanol (60 μL, 1.02) was added followed by *N*-bromosuccinimide (183 mg, 0.102 mmol), and the stirring was continued at 0 °C. Approximately 1−2 min after *N*-bromosuccinimide addition, the solution turned pale yellow and the reaction was diluted with dichoromethane and filtered into an ice cold solution of thiosulfate. The organic layer was separated and diluted with EtOAc to a 1:1 mixture. This solution was filtered through a plug of silica gel (3 cm) and concentrated to give **2** as a pale yellow syrup (493 mg, 92%), sufficiently pure for glycosylations: ^{1}H NMR (600 MHz, $CHCl_3$) δ 7.30−7.04 (15 H, Ar), 6.34 (s, 1 H, H-1), 4.94 (d, 1 H, J = 11.4 Hz, OCH_2Ph), 4.84 (d, 1 H, J_{2-3} = 9.7 Hz, H-3), 4.76 (d, 1 H, J = 11.2 Hz, OCH_2Ph), 4.55 (d, 1 H, J = 11.4 Hz, OCH_2Ph), 4.51 (d, 1 H, J = 12.5 Hz, OCH_2Ph), 4.49 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.41 (d, 1 H, J = 12.1 Hz, OCH_2Ph), 4.20 (ddd, 1 H, J_{4-5} = 9.9 Hz, J_{5-6a} = 3.3 Hz, J_{5-6b} = 1.6 Hz, H-5), 3.95 (dd, 1 H, H-4), 3.80 (dd, J_{gem} = 11.0 Hz, H-6a), 3.67 (dd, 1 H, H-6b); ^{13}C NMR (125 MHz, $CDCl_3$) 195.0, 136.6, 136.2, 134.8, 134.6, 134.5, 131.6, 130.3−129.2, 86.2 (J^1_{C1-H1} = 189 Hz), 82.1, 77.6, 76.2, 75.2, 74.0, 73.5, 73.4, 67.9; ES HRMS calcd for $C_{27}H_{24}BrCl_3O_5Na$ 634.9770, found 634.9778.

Allyl (3,4,6-Tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)-(1→2)(3,4,6-tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)-(1→2)(3,4,6-tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)-(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (5). Glycosyl donor **2** (240 mg, 0.39 mmol), tetrasaccharide acceptor **4**,[4] (190 mg, 0.095 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (120 mg, 0.59 mmol) were dried together under vacuum for 1 h in a pear-shaped flask (25 mL). The contents of the flask were then dissolved in a pivaloylnitrile (800 μL)−dichloromethane (400 μL) solution, and activated 4A molecular sieves (200 mg) and a stir bar were then added. The suspension was stirred for 30 min at room temperature under argon, and then the temperature was reduced with a −40 °C bath. Silver triflate was added, and the reaction was stirred in the dark. The flask was slowly warmed over 4 h to room temperature. The reaction was then diluted with dichloromethane and filtered through Celite. Combined filtrates were washed with a solution of sodium bicarbonate, dried over anhydrous sodium sulfate, and concentrated. The syrup was then taken up in THF (10 mL) and cooled to −78 °C under argon. L-Selectride (2 mL, 1 M in THF) was added dropwise, and the cooling bath was removed. The reaction was allowed to warm to ambient temperature, and then methanol (1 mL) was added. The reaction was diluted with dichloromethane and washed with 5% hydrogen peroxide/1 M NaOH followed by 5% thiosulfate/brine to give a clear solution. After drying over sodium sulfate, concentration gave a colorless oil. Column chromatography in toluene/EtOAc (9:1) gave the pentasaccharide (123 mg, 51%): [α]$_D$ −48° (*c* 0.94, $CHCl_3$); ^{1}H NMR (600 Hz $CDCl_3$) δ 7.45−6.65 (66 H, Ar), 5.83 (m, 1 H, OCH_2CHCH_2), 5.53 (s, 1 H, H-1″), 5.53 (s, 1 H, H-1‴), 5.18 (m, 1 H, OCH_2CHCH_2), 5.12 (m, 1 H, OCH_2CHCH_2), 5.13 (s, 1 H, H-1⁗), 5.11 (s, 1 H, H-1′), 4.90 (d, 1 H, J_{gem} = 11.3 Hz, OCH_2Ph), 4.88 (d, 1 H, J_{gem} = 10.8 Hz, OCH_2Ph), 4.87 (d, 1 H, J_{gem} = 9.7 Hz, OCH_2Ph), 4.85 (d, 1 H, J_{gem} = 9.7 Hz, OCH_2-Ph), 4.80 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2′), 4.72 (d, 1 H, J_{gem} = 11.1 Hz, OCH_2Ph), 4.70 (d, 1 H, J_{gem} = 11.2 Hz, OCH_2Ph), 4.63 (d, $J_{2,3}$ = 3.1 Hz, H-2″), 4.56 (d, 2 H, J = 11.7 Hz, 2(OCH_2Ph)), 4.54 (d, 1 H, J_{gem} = 12.3 Hz, OCH_2Ph), 4.52 (d, 1 H, $J_{2,3}$ = 3.7 Hz, H-2), 4.52 (d, 1 H, J_{gem} = 9.3 Hz, OCH_2Ph), 4.50 (d, 1 H, J_{gem} = 9.7 Hz, OCH_2Ph), 4.48 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2‴), 4.45−4.34 (m, 13 H, 11(OCH_2Ph), H-1, OCH_2CHCH_2), 4.31 (d, 1 H, J_{gem} = 9.7 Hz, OCH_2Ph), 4.31 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2⁗), 4.25 (d, 1 H, J_{gem} = 12.3 Hz, OCH_2Ph), 4.23 (d, 1 H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.15 (d, 1 H, J_{gem} = 11.1 Hz, OCH_2Ph), 4.12 (d, 1 H, J_{gem} = 11.7 Hz, OCH_2Ph), 3.96 (m, 1 H, OCH_2CHCH_2), 3.93 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.5 Hz, H-4‴), 3.89 (d, 1 H, J_{gem} = 11.9 Hz, OCH_2Ph), 3.84 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.3 Hz, H-4), 3.79 (d, 2 H, J_{gem} = 12.3 Hz, OCH_2Ph), 4.79 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.5 Hz, H-4″), 3.78−3.54 (m, 17 H, H-5″, H-6a″, H-6b″, H-5‴, H-6a‴,H-6b‴, H-4⁗, H-5⁗, H-6a⁗, H-6b⁗, H-4′, H-6a′, H-6b′, H-3′, H-3, H-4, H-6, H-6, OCH_2Ph), 3.50−3.44 (m, 3 H, H-3″, H-3‴, H-5′), 3.42 (dd, 1 H, $J_{3,4}$ = 9.2 Hz, H-3⁗), 3.33 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6}$ = 2.0 Hz, $J_{5,6}$ = 4.2 Hz, H-5); ^{13}C NMR (125 Hz, $CDCl_3$), 138.2−135.2, 133.5−133.0, 129.8−127.5, 117.3, 101.1 (J^1_{C-H} = 162.8 Hz, C1″),100.7 (J^1_{C-H} 163.3 Hz, C1⁗), 100.4 (J^1_{C-H} = 162.8 Hz, C1‴), 100.3 (J^1_{C-H} = 154.2 Hz, C1), 99.9 (J^1_{C-H} = 160. Hz, C1′), 82.9, 81.6, 81.6, 80.4, 80.3, 75.6, 75.6, 75.5, 75.3, 75.2, 75.1, 75.1, 74.7, 74.3, 74.3, 74.0, 73.5, 73.4, 72.8, 72.7, 72.7, 72.7, 70.5, 70.3, 70.1, 70.0, 69.7, 69.7, 69.4, 69.4, 69.4, 69.3, 68.9, 68.9, 68.7, 68.7, 67.4, 67.4; EMS calcd (M + Na) 2553.6, found 2553.7 correct isotope intensities for Cl_9.

Allyl (3,4,6-Tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)-(1→2)(3,4,6-tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)-(1→2)(3,4,6-tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)-(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (6). The procedure used was analogous to the preparation of **5**, using glycosyl donor **2** (143 mg, 0.23 mmol), pentasaccharide acceptor **5** (153 mg, 0.060 mmol), 2,6-di-*tert*-butyl-4-methylpyridine (106 mg, 0.52 mmol), pivaloylnitrile (500 μL), dichloromethane (250 μL), and activated 4A molecular sieves (148 mg). Column chromatography in toluene/EtOAc (9:1) gave the hexasaccharide **6** (89 mg, 48%): [α]$_D$ −61° (*c* 0.4, $CHCl_3$); ^{1}H NMR (600 Hz $CDCl_3$) δ 7.42−6.59 (66 H, Ar), 5.80 (m, 1 H, OCH_2CHCH_2), 5.56 (s, 1 H, H-1‴), 5.53 (s, 1 H, H-1″), 5.43 (s, 1 H, H-1⁗), 5.17 (m, 1 H, OCH_2CHCH_2), 5.11 (s, 1 H, H-1⁗′), 5.10 (m, 1 H, OCH_2-$CHCH_2$), 5.08 (s, 1 H, H-1′), 4.89 (d, 1 H, J_{gem} = 10.1 Hz, OCH_2-Ph), 4.87 (d, 1 H, J_{gem} = 10.6 Hz, OCH_2Ph), 4.85 (d, 1 H, J_{gem} = 11.2 Hz, OCH_2Ph), 4.80 (d, 1 H, J_{gem} = 10.4 Hz, OCH_2Ph), 4.79 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2′), 4.69 (d, 2 H, J_{gem} = 11.1 Hz, OCH_2Ph), 4.63 (d, 1 H, J_{gem} = 11.0 Hz, OCH_2Ph), 4.61 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2″), 4.60 (d, 1 H, $J_{2,3}$ = 3.8 Hz, H-2‴), 4.54 (d, 1 H, J = 12.4 Hz, OCH_2Ph), 4.54 (d, 1 H, J_{gem} = 11.1 Hz, OCH_2-Ph), 4.50 (d, 1 H, J_{gem} = 12.3 Hz, OCH_2Ph), 4.50 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2), 4.49−4.20 (m, 22 H, H-2⁗′, H-1, H-2⁗″, 18-(OCH_2Ph)), 4.22 (d, 1 H, J_{gem} = 10.6 Hz, OCH_2Ph), 4.18 (d, 1 H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.18 (d, 1 H, J_{gem} = 12.5 Hz, OCH_2Ph), 4.09 (d, 1 H, J_{gem} = 11.9 Hz, OCH_2Ph), 4.08 (d, 1 H, J_{gem} = 11.0 Hz, OCH_2Ph), 3.93 (m, 1 H, OCH_2CHCH_2), 3.91 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.7 Hz, H-4⁗′), 3.87 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.3 Hz, H-4⁗″), 3.84 (d, 1 H, J_{gem} = 11.7 Hz, OCH_2Ph), 3.83−3.53 (m, 23 H, H-3, H-4, H-6a, H-6b, H-3′, H-4′, H-5′, H-6a′, H-6b′, H-4″, H-5″, H-6a″, H-6b″, H-4‴, H-6a‴, H-6b‴, H-6a⁗, H-6b⁗, H-6a⁗′, H-6b⁗′, 3(OCH_2Ph)), 3.50 (ddd, 1 H, $J_{4,5}$ = 8.1 Hz, $J_{5,6}$ = 4.1 Hz, $J_{5,6}$ = 1.8 Hz, H-5⁗″), 3.45−3.37 (m, 4 H, H-3⁗″, H-3″, H-3‴, H-3⁗, H-3⁗″, H-5⁗), 3.31 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6}$ = 2.0 Hz, $J_{5,6}$ = 4.2 Hz, H-5); ^{13}C NMR (125 Hz, $CDCl_3$), 138.1−135.9, 133.6−133.0, 129.8−127.5, 117.3, 101.2 (J^1_{C-H} = 163.0 Hz, C1⁗″), 100.7 ($J^1_{C,H}$ = 163.6 Hz, C1⁗″), 100.5 ($J^1_{C,H}$ = 163.4 Hz, C1″), 100.4 ($J^1_{C,H}$ = 163.5 Hz, C1‴), 100.2

($J^1_{C,H}$ = 155.1 Hz, C1), 100.0 ($J^1_{C,H}$ = 159.5 Hz, C1′), 83.1, 83.0, 81.8, 81.8, 81.7, 80.6, 80.4, 75.8, 75.7, 75.6, 75.5, 75.4, 75.3, 75.3, 75.2, 75.2, 75.0, 74.8, 74.4, 74.4, 74.3, 74.3, 73.6, 72.9, 72.9, 72.8, 72.7, 70.7, 70.5, 70.4, 70.3, 70.1, 69.8, 69.7, 69.5, 69.4, 69.4, 69.3, 69.3, 69.2, 69.1, 68.9, 68.8, 67.5; EMS calcd for $C_{165}H_{162}Cl_{12}O_{31}Na$ 3081.7, found 3081.7 correct isotope pattern for Cl_{12}.

General Procedure for the Photoaddition of Thiol to the Allyl Glycosides. Allyl glycoside was added to a quartz vessel and dissolved in a minimum amount of dichloromethane (500 μL). Methanol (5 mL) was then added followed by 2-aminoethanethiol hydrochloride (1.0 g). The reaction was stirred until dissolution was complete. Irradiation (365 nm) was then carried out for 12−16 h. The solution was then diluted with dichloromethane and washed with 1 M sodium hydroxide. The combined organic layer was dried, concentrated, and subjected to column chromatography in dichloromethane containing 2% methanol to give the desired amine functionalized glycoside. These compounds contained minor impurities that could not be easily removed at this stage of the synthesis and thus were carried through and removed during the final purification.

3-(2-Aminoethylthio)propyl (3,4,6-Tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (7). Allyl disaccharide (100 mg) **1**,[4] using the above protocol, gave **7** (74 mg, 74%): $[\alpha]_D$ −33° (*c* 1.6, $CHCl_3$); ^{1}H NMR (600 Hz $CDCl_3$) δ 7.39−7.12 (30 H, m, Ar), 4.92 (d, 1 H, J_{gem} = 10.8 Hz, OCH_2Ph), 4.89 (s, 1 H, H-1′), 4.84 (d, 1 H, J_{gem} = 12.3 Hz, OCH_2Ph), 4.84 (d, 1 H, J_{gem} = 10.4 Hz, OCH_2Ph), 4.81 (d, 1 H, J_{gem} = 11.9 Hz, OCH_2Ph), 4.63 (d, 1 H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.60 (d, 1 H, J_{gem} = 12.0 Hz, OCH_2Ph), 4.52 (d, 1 H, J_{gem} = 10.8 Hz, OCH_2Ph), 4.52 (d, 1 H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.48 (d, 1 H, J_{gem} = 11.6 Hz, OCH_2Ph), 4.46 (d, 1 H, J_{gem} = 11.8 Hz, OCH_2Ph), 4.45 (d, 1 H, J_{gem} = 10.8 Hz, OCH_2Ph), 4.40 (d, 1 H, J_{gem} = 11.8 Hz, OCH_2Ph), 4.37 (s, 1 H, H-1), 4.36 (d, 1 H, d, $J_{2,3}$ = 3.3 Hz, H-2), 4.27 (d, 1 H, $J_{2,3}$ = 3.0 Hz, H-2′), 3.98 (dt, 1 H, J_{gem} = 9.6, J_{vic} = 6.2 Hz, OCH_2-CH_2), 3.91 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.3 Hz, H-4), 3.80 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.4 Hz, H-4′), 3.76 (1 H, dd, J_{gem} = 10.6, J_{vic} = 2.1 Hz, H-6a′), 3.74 (dd, 1 H, J_{gem} = 10.2, J_{vic} = 1.9 Hz, H-6a), 3.70 (dd, 1 H, J_{vic} = 5.1 Hz, H-6b′), 3.66 (dd, 1 H, J_{vic} = 5.5 Hz, H6b), 3.56−3.51 (m, 3 H, H-3, H-3′, OC$H_2$$CH_2$), 3.44 (ddd, 1 H, H-5′), 3.39 (ddd, 1 H, H-5), 2.84−2.74 (m, 2 H, C$H_2$$NH_2$), 2.59−2.50 (m, 2 H, SC$H_2$$CH_2$$NH_2$), 2.52 (t, 2 H, J 7.1 Hz, OCH_2-CH_2CH_2S), 1.82 (2 H, p, J 6.6 Hz, OCH_2C$H_2$$CH_2$S); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 138.2, 138.0, 137.9, 137.9, 137.9, 128.3−127.6, 100.8 ($^1J_{C-H}$ = 156 Hz), 99.7 ($^1J_{C-H}$ = 163 Hz), 81.4, 80.6, 75.6, 75.2, 75.2, 75.1, 74.2, 74.2, 73.5, 73.4, 71.4, 71.0, 70.7, 69.7, 69.2, 68.2, 40.6, 29.6, 29.2, 28.2; ES HRMS calcd for $C_{59}H_{70}NO_{11}S$ 1000.4669, found 1000.4660.

3-(2-Aminoethylthio)propyl (3,4,6-Tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (8). Allyl trisaccharide (65 mg) **3**[4] was treated as outlined above to give **8** (47 mg, 72%): $[\alpha]_D$ −48.7° (*c* 1.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46−6.89 (42 H, m, Ar), 5.15 (s, 1 H, H-1″), 5.08 (s, 1 H, H-1′), 4.92 (d, 3 H, *J* = 10.5 Hz, OCH_2Ph), 4.70 (d, 1 H, *J* = 11.3 Hz, OCH_2Ph), 4.66 (d, 1 H, $J_{2,3}$ = 3.2 Hz, H-2′), 4.63 (d, 1 H, *J* = 10.7 Hz, OCH_2Ph), 4.62 (d, 1 H, $J_{2,3}$ = 2.9 Hz, H-2), 4.54 (d, 1 H, *J* = 11.0 Hz, OCH_2Ph), 4.49 (d, 1 H, *J* = 11.9 Hz, OCH_2Ph), 4.45 (d, 1 H, *J* = 11.2 Hz, OCH_2Ph), 4.43−4.40 (m, 5 H, 4(OCH_2Ph), H-1), 4.37 (d, 1 H, *J* = 12.0 Hz, OCH_2Ph), 4.30 (m, 2 H, *J* = 11.9 Hz, 2(OCH_2-Ph)), 4.26 (d, 1 H, $J_{2,3}$ = 3.0 Hz, H-2″), 4.17 (d, 1 H, *J* = 10.1 Hz, OCH_2Ph), 4.01−3.95 (m, 3 H, OCH_2Ph, OC$H_2$$CH_2$, H-4′), 3.82−3.58 (m, 10 H, H-4″, H-6a″, H-6b″, H-3′, H-6a′, H-6b′, H-3, H-4, H-6a, H-6b), 3.51 (dt, 1 H, J_{vic} = 6.9, J_{gem} = 9.4 Hz, OC$H_2$$CH_2$), 3.47 (1 H, ddd, $J_{4,5}$ = 9.9 Hz, $J_{5,6}$ = 1.8 Hz, $J_{5,6}$ = 5.5 Hz, H-5′), 3.44 (dddd, 1 H, $J_{4,5}$ = 9.5, $H_{5,6}$ 2.9, $J_{5,6}$ = 6.8 Hz, H-5), 3.40−3.37 (2 H, m, H-5″, H-3″), 2.75 (2 H, t, *J* = 6.8, C$H_2$$NH_2$), 2.54 (t, 2 H, *J* = 6.8 Hz, SC$H_2$$CH_2$$NH_2$), 2.50 (t, 2 H, *J* = 6.8 Hz, OC$H_2$$CH_2CH_2$S), 1.88−177 (2 H, m, OC$H_2CH_2$-$CH_2$S); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.2, 138.1, 137.9, 137.6, 137.2, 136.9, 136.4, 133.2, 133.0, 132.9, 129.0−127.5, 101.5 ($^1J_{C-H}$ = 153 Hz), 99.3 ($^1J_{C-H}$ = 163 Hz), 99.2 ($^1J_{C-H}$ = 163 Hz), 83.7, 83.0, 80.4, 77.1, 75.4, 75.3, 75.1, 75.0, 74.8, 74.6, 74.1, 73.4, 73.3, 73.0, 72.6, 70.7, 70.4, 70.0, 69.8, 69.7, 68.7, 68.4, 40.7, 29.6, 28.6, 29.7; ES calcd 1536.5, found 1536.5 isotope pattern correct for Cl_3.

3-(2-Aminoethylthio)-propyl (3,4,6-Tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)(1→2)(3,4,6-tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)(1→2)(3,4,6-tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)-(1→2)(3,4,6-tri-*O*-*p*-chlorobenzyl-β-D-mannopyranosyl)(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (10). Allyl hexasaccharide (64 mg) **6** was treated as outlined above to give **10** (49 mg, 75%): $[\alpha]_D$ −67° (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 Hz $CDCl_3$) δ 7.43−6.59 (66 H, Ar), 5.57 (s, 1 H, H-1‴), 5.53 (s, 1 H, H-1″), 5.43 (s, 1 H, H-1⁗), 5.10 (s, 1 H, H-1⁗′), 5.06 (s, 1 H, H-1′), 4.89 (d, 1 H, J_{gem} = 10.3 Hz, OCH_2-Ph), 4.88 (d, 1 H, J_{gem} = 11.4 Hz, OCH_2Ph), 4.86 (d, 1 H, J_{gem} = 11.2 Hz, OCH_2Ph), 4.80 (d, 1 H, J_{gem} = 10.3 Hz, OCH_2Ph), 4.79 (d, 1 H, $J_{2,3}$ = 3.4 Hz, H-2′), 4.69 (d, 1 H, J_{gem} = 11.1 Hz, OCH_2Ph), 4.69 (d, 1 H, J_{gem} = 11.1 Hz, OCH_2Ph), 4.62 (d, 1 H, J_{gem} = 11.2 Hz, OCH_2Ph), 4.59 (d,1 H, $J_{2,3}$ 2.5 Hz, H-2‴), 4.59 (d, 1 H, $J_{2,3}$ = 2.4 Hz, H-2″), 4.55 (d, 1 H, *J* = 12.3 Hz, OCH_2-Ph), 4.54 (d, 1 H, J_{gem} = 10.0 Hz, OCH_2Ph), 4.52 (d, 1 H, $J_{2,3}$ = 3.5 Hz, H-2), 4.50 (d, 1 H, J_{gem} = 12.3 Hz, OCH_2Ph), 4.49−4.29 (m, 23 H, H-2⁗′, H-1, 21(OCH_2Ph), 4.27 (d, 1 H, J_{2-3} = 3.1 Hz, H-2⁗), 4.24 (d, 1 H, J_{gem} = 12.3 Hz, OCH_2Ph), 4.22 (d, 1 H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.18 (d, 1 H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.08 (d, 1 H, J_{gem} = 10.8 Hz, OCH_2Ph), 4.08 (d, 1 H, J_{gem} = 12.5 Hz, OCH_2Ph), 3.95 (dt, 1 H, J_{gem} = 9.5 Hz, J_{vic} = 6.0 Hz, OC$H_2$$CH_2$$CH_2$), 3.92 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.3 Hz, H-4⁗′), 3.87 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.3 Hz, H-4⁗′), 3.84 (d, 1 H, J_{gem} = 11.9 Hz, OCH_2Ph), 3.79 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 10.0 Hz, H-4′), 3.77 (d, 1 H, J_{gem} = 11.2 Hz, OCH_2Ph), 3.75−3.54 (m, 19 H, H-3, H-4, H-6a, H-6b, H-3′, H-6a′, H-6b′, H-4″, H-5″, H-6a″, H-6b″, H-4‴ H-5‴, H-6a‴, H-6b‴, H-6a⁗′, H-6b⁗′, H-6a⁗′, H-6b⁗′, 2(OCH_2Ph)), 3.51 (ddd, 1 H, J_{4-5} = 9.3 Hz, J_{5-6} = 3.6 Hz, J_{5-6} = 1.8 Hz, H-5⁗′), 3.47 (dt, 1 H, OC$H_2$$CH_2$-$CH_2$), 3.43−3.39 (m, 5-H, H-3″, H-3‴, H-3⁗′, H-5′, H-5⁗′), 3.36 (dd, 1 H, H-3‴), 3.31 (ddd, 2 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6}$ = 2.0 Hz, $J_{5,6}$ = 4.2 Hz, H-5), 2.74 (t, 2 H, *J* = 6.6 Hz, SCH_2CH_2-NH_2), 2.50 (t, 2 H, J_{vic} = 7.0 Hz, OC$H_2$$CH_2CH_2$S), 1.81−1.75 (m, 2 H, OCH_2C$H_2$$CH_2$S); ^{13}C NMR (125 Hz, $CDCl_3$), 101.6 (J^1_{C-H} = 154.0 Hz, C-1), 100.8 (J^1_{C-H} = 162.3 Hz, C-1′), 100.2 (J^1_{C-H} = 164.4 Hz, C-1‴), 100.1 (J^1_{C-H} = 163.7 Hz, C-1⁗′), 100.1 (J^1_{C-H} = 162.8 Hz, C-1), 99.7 (J^1_{C-H} = 163.9 Hz, C-1⁗′); EMS calcd for $C_{165}H_{163}Cl_{12}O_{31}$ 3144.8, found 3144.9.

3-(2-Aminoethylthio)propyl (β-D-Mannopyranosyl)-(1→2)-β-D-mannopyranoside (11). The protected disaccharide (**7**) (55 mg) was dissolved in THF (2 mL) and *tert*-butyl alcohol (2 mL). The solution was added in one portion to a solution of ammonia (∼50 mL) and sodium metal (50 mg) stirred with a glass-coated stir bar at −78 °C. The flask previously containing **7** was rinsed with THF (2 mL) and *tert*-butyl alcohol (2 mL), and this solution was added to the ammonia solution. After 30 min, the reaction was quenched with methanol, and the ammonia was allowed to evaporate at room temperature. The remaining THF was removed under vacuum, and the resulting white solid was taken up in water (5 mL). The suspension was neutralized with a 5 M acetic acid solution against pH paper and filtered through a 0.2 μM filter. The solution was then passed through a C18 Sep-pak cartridge and eluted with methanol. This step removed any compounds that would be irreversibly absorbed to the reverse phase silica. After concentration of the eluents final purification by HPLC on C18 silica was carried out to give a colorless glass **11** (21 mg, 85%): $[\alpha]_D$ −51° (*c* 0.3, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 4.84 (s, 1 H, H-1′), 4.75 (s, 1 H, H-1), 4.27 (d, 1 H, $J_{2,3}$ = 3.4 Hz, H-2), 4.13 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2′), 3.99 (dt, 1 H, J_{gem} = 10.1, J_{vic} = 6.0 Hz, OC$H_2$$CH_2$), 3.94 (dd, 1 H, J_{gem} = 12.3, $J_{5,6}$ = 2.3 Hz, H-6a), 3.93 (d, 1 H, J_{gem} = 12.5, $J_{5,6}$ = 2.3 Hz, H-6a′), 3.77−3.72 (m, 3H, H-6b, H-6b′, OC$H_2$$CH_2$), 3.65 (dd, 1 H, $J_{3,4}$ = 9.8 Hz, H-3), 3.62 (dd, 1 H, $J_{3,4}$ = 9.7 Hz, H-3′), 3.59 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ 9.2 Hz, H-4), 3.57 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.5 Hz, H-4′), 3.40 (ddd, 1 H, $H_{5,6}$, *J* = 6.6 Hz, H-5), 3.36 (ddd, 1 H, $J_{5,6}$ = 6.8 Hz, H-5′) 3.24 (t, 2 H, J_{vic} = 6.6 Hz, $CH_2NH_3^+$), 2.88 (t, 2 H, *J* = 6.7, $SCH_2CH_2NH_3^+$), 2.88 (t, 2 H, OCH$_2$-

CH_2CH_2S), 2.69 (t, 1 H, J = 7.4 Hz, $CH_2CH_2CH_2S$), 1.39 (p, 2 H, J 7.3 Hz, $OCH_2CH_2CH_2S$); ^{13}C NMR (125 MHz, D_2O) δ 101.5 ($^1J_{C-H}$ = 163 Hz, C-1′), 101.0 ($^1J_{C-H}$ = 156.3 Hz, C-1″), 78.9, 77.3, 73.7, 73.1, 71.2, 69.3, 68.1, 67.6, 61.9, 61.8, 39.2, 29.2, 29.6, 28.5; ES HRMS calcd for $C_{17}H_{34}N_1O_{11}S$ 460.1852, found 460.1852.

3-(2-Aminoethylthio)propyl (β-D-Mannopyranosyl)-(1→2)(β-D-mannopyranosyl)(1→2)-β-D-mannopyranoside (12). Employing the same procedure used for compound **11**, compound **8** (40 mg) gave a colorless glass **12** (16 mg 78%). This compound contained a small amount of disaccharide impurity that could not be easily removed by standard purification methods: $[\alpha]_D$ −52° (*c* 0.2, H_2O); ^1H NMR (600 MHz, D_2O) δ 4.96 (s, 1 H, H-1″), 4.91 (s, 1 H, H-1′), 4.73 (s, 1 H, H-1), 4.36 (d, 1 H, $J_{2,3}$ = 2.7 Hz, H-2′), 4.24 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2), 4.15 (d, 1 H, $J_{2,3}$ = 3.2 Hz, H-2″), 3.99 (dt, 1 H, J_{gem} = 10.1 Hz, J_{vic} = 6.1 Hz, OCH_2CH_2), 3.94 (dd, 1 H, J_{gem} = 12.2 Hz, H-6a), 3.93 (d, 1 H, J_{gem} = 12.0 Hz, H-6a″), 3.92 (d, 1 H, J_{gem} = 11.8 Hz, H-6a′), 3.76 (dd, 1 H, $J_{5,6}$ = 7.1 Hz, H-6b′), 3.74 (dd, 1 H, $J_{5,6}$ = 6.5 Hz, H-6b″), 3.72 (d, 1 H, $J_{5,6}$ = 6.5 Hz, H-6b), 3.74 (dt, 1 H, J_{vic} = 6.0 Hz, OCH_2CH_2), 3.68 (dd, 1 H, $J_{3,4}$ = 9.7 Hz, H-3), 3.63 (dd, 1 H, $J_{3,4}$ = 9.2 Hz, H-3′), 3.62 (dd, 1 H, $J_{3,4}$ = 10.7 Hz, H-3″), 3.60 (dd, 1 H, $J_{4,5}$ = 9.0 Hz, H-4′), 3.57 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.6 Hz, H-4″), 3.49 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 10.2 Hz, H-4), 3.38 (ddd, 1 H, H-5″), 3.38 (ddd, 1 H, H-5), 3.37 (ddd, 1 H, H-5′), 3.24 (t, 2 H, J_{vic} = 6.9 Hz, $CH_2NH_3^+$), 2.88 (t, 2 H, $SCH_2CH_2NH_3^+$), 2.73−2.65 (m, 2 H, $OCH_2CH_2CH_2S$), 1.97−1.91 (m, 2H, $OCH_2CH_2CH_2S$); ^{13}C NMR (125 MHz, D_2O) δ 101.9 ($^1J_{C-H}$ = 161.1 Hz, C-1″), 101.6 ($^1J_{C-H}$ = 162 Hz, C-1′), 101.0 ($^1J_{C-H}$ = 159.1 Hz, C-1), 79.7, 78.3, 77.3, 77.2, 77.1, 73.8, 73.1, 72.9, 71.2, 69.3, 68.3, 67.8, 67.6, 62.0, 61.7, 61.7, 39.2, 29.6, 29.2, 28.6 ES HRMS calcd for $C_{23}H_{44}N_1O_{16}S$ 622.2381, found 622.2384.

3-(2-Aminoethylthio)propyl (β-D-Mannopyranosyl)-(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)-(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)-(1→2)-β-D-mannopyranoside (14). Employing the same procedure used for compound **11**, compound **10** (25 mg) gave a colorless glass **14** (7 mg 83%): ^1H NMR (600 MHz D_2O) δ 5.06 (s, 1 H, H-1‴″), 5.02 (s, 2 H, H-1″, H-1‴), 4.97 (s, 1 H, H-1⁗), 4.90 (s, 1 H, H-1′), 4.74 (s, 1 H, H-1), 4.41 (d, 1 H, $J_{2,3}$ = 4.4 Hz, H-2″), 4.40 (d, 1 H, $J_{2,3}$ = 3.8 Hz, H-2⁗), 4.37 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2‴), 4.34 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2′), 4.25 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2), 4.16 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2⁗), 4.00 (dt, 1 H, J_{vic} = 6.0 Hz, J_{gem} = 10.1 Hz, OCH_2CH_2), 3.95 (dd, 1 H, J_{vic} < 2.5 Hz, J_{gem} = 11.6 Hz, H-6a‴), 3.94 (dd, 1 H, J_{vic} < 2.5 Hz, J_{gem} = 11.5 Hz, H-6a), 3.94 (dd, 1 H, J_{vic} < 2.5 Hz, J_{gem} = 11.9 Hz, H-6a′), 3.94 (dd, 1 H, J_{vic} < 2.5 Hz, J_{gem} = 12.0 Hz, H-6a⁗), 3.93 (dd, 1 H, J_{vic} < 2.5 Hz, J_{gem} = 11.6 Hz, H-6a″), 3.93 (dd, 1 H, J_{vic} < 2.5 Hz, J_{gem} = 11.6 Hz, H-6a‴), 3.76 (dd, 1 H, J_{vic} = 6.4 Hz, H-6b‴), 3.75 (dd, 1 H, $J_{5,6}$ = 6.4 Hz, H-6b″), 3.74 (dd, 1 H, $J_{5,6}$ = 8.1 Hz, H-6b⁗), 3.75 (dd, 1 H, $J_{5,6}$ = 6.2 Hz, H-6b), 3.74 (dd, 1 H, $J_{5,6}$ = 6.2 Hz, H-6b′), 3.72 (dd, 1 H, $J_{5,6}$ = 6.7 Hz, H-6b‴), 3.69 (dd, 1 H, $J_{3,4}$ = 10.3 Hz, H-3), 3.67 (dd, 1 H, $J_{3,4}$ = 10.4 Hz, H-3′), 3.67 (dd, 1 H, $J_{3,4}$ = 9.3 Hz, H-3″), 3.67 (dd, 1 H, $J_{3,4}$ = 9.3 Hz, H-3‴), 3.65 (dd, 1 H, $J_{3,4}$ = 11.0 Hz, H-3⁗), 3.63 (dd, 1 H, $J_{3,4}$ = 10.0 Hz, H-3⁗), 3.60 (dd, 1 H, $J_{4,5}$ = 10.0 Hz, H-4″), 3.58 (dd, 1 H, $J_{4,5}$ = 10.0 Hz, H-4‴), 3.51 (dd, 1 H, $J_{4,5}$ = 10.0 Hz, H-4⁗), 3.51 (dd, 1 H, $J_{4,5}$ = 10.0 Hz, H-4‴), 3.51 (dd, 1 H, $J_{4,5}$ = 10.0 Hz, H-4′), 3.48 (dd, 1 H, $J_{4,5}$ = 10.0 Hz, H-4), 3.43−3.35 (m, 6H, H-5⁗, H-5⁗, H-5‴, H-5′, H-5, H-5″), 3.23 (t, 1 H, J_{vic} = 6.6, $SCH_2CH_2NH_3^+$), 2.84 (t, 1 H, $SCH_2CH_2NH_3^+$), 2.71−2.68 (m, 2H, $CH_2CH_2CH_2S$), 1.96−1.92 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) 102.1 (C-1′, C-1″,C-1‴), 101.9 (C-1⁗), 101.7 (C-1⁗), 101,0 (C-1), 80.0, 80.0, 79.3(C-2, C-2″, C-2′, C-2‴), 79.3 (C-2⁗), 77.1−76.8 (C-5, C-5′, C-5″, C-5‴, C-5⁗, C-5⁗), 73.8 (C-3⁗), 73.1−72.7 (C-3, C-3′,C-3″, C-3‴, C-3⁗), 71.3 (C-2⁗), 69.3 (OCH_2CH_2), 68.5, 68.1, 68.0, 68.1, 68.0, 67.9, 67.7 (C-4, C-4′, C-4″, C-4‴, C-4⁗, C-4⁗), 62.1−61.2 (C-6, C-6′, C-6″, C-6‴, C-6⁗, C-6⁗), 39.3 ($SCH_2CH_2NH_3^+$), 29.6 ($SCH_2CH_2NH_3^+$), 29.4 ($CH_2CH_2CH_2S$), 28.6($CH_2CH_2CH_2$); ES HRMS calcd for $C_{41}H_{74}NO_{31}S$ 1108.3966, found 1108.3956.

Propyl β-D-Mannopyranosyl)(1→2)-β-D-mannopyranoside (15). Protected disaccharide **1**[4] (106 mg) was dissolved in an EtOH/toluene (10:1) solution, and palladium on carbon (10%)(5 mg) was added. The flask was sealed and a hydrogen balloon attached. The solution was stirred for 48 h and then filtered through Celite. After concentration, final purification by HPLC on C18 silica was carried out to give a colorless glass **76** (36 mg, 82%): ^1H NMR (500 MHz D_2O) δ 4.82 (s, 1 H, H-1′), 4.71 (s, 1 H, H-1), 4.23 (1 H, d, $J_{2,3}$ = 3.1 Hz, H-2), 4.12 (d, 1 H, $J_{2,3}$ = 3.2 Hz, H-2′), 3.91 (d, 1 H, J_{vic} = 2.1 Hz, J_{gem} = 12.2 Hz, H-6), 3.91 (d, 1 H, J_{vic} = 2.1 Hz, J_{gem} = 12.2 Hz, H-6a′), 3.83 (dt, 1 H, J_{vic} = 6.6 Hz, J_{gem} = 9.6 Hz, OCH_2CH_2), 3.76 (dd, 1 H, $J_{5,6}$ 6.7 Hz, J_{gem} = 12.3 Hz, H-6b′), 3.76 (dd, 1 H, $J_{5,6}$ 6.7, J_{gem} = 12.3 Hz, H-6b), 3.64−3.60 (m, 3 H, H-3, H-3′, OCH_2CH_2), 3.56 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ 9.5 Hz, H-4), 3.54 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ 9.7 Hz, H-4′), 3.39−3.32 (m, 2 H, H-5, H-5′), 1.60 (p, 2 H, J 7.0 Hz, $OCH_2CH_2CH_3$), 0.90 (t, 3 H, $CH_2CH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$), 101.5 (J^1_{C-H} 162.0 Hz, C-1′), 100.9 (J^1_{C-H} 158.5 Hz, C-1), 79.0 (C-2), 77.2, 77.2 (C-5, C-5′), 73.6, 73.1 (C-3, C3′), 72.7 (OCH_2CH_2), 71.2 (C-2′), 68.1, 67.6 (C-4′,C-4), 61.9−61.8 (C-6, C-6′, C-6″), 23.2 ($CH_2CH_2CH_3$), 10.8 (CH_2CH_3); ES HRMS calcd for $C_{21}H_{38}O_{16}Na$ 384.2058.

Propyl (β-D-Mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)-β-D-mannopyranoside (16). Protected allyl trisaccharide **3**[4](40 mg) was dissolved in THF/ethanol (1:1, 4 mL) solution, and hydrazine hydrate (400 μL) was added. The reaction mixture was stirred vigorously, in an open flask, for 3 h. The reaction was then diluted with toluene and washed repeatedly with water. Concentration gave a colorless syrup that showed no allyl resonances in the ^1H NMR. This syrup was dissolved in THF (2 mL) and *tert*-butyl alcohol (2 mL). The solution was added in one portion to a solution of ammonia (∼50 mL) and sodium metal (50 mg) stirred with a glass-coated stir bar at −78 °C. The flask previously containing **3** was rinsed with THF (2 mL) and *tert*-butyl alcohol (2 mL), and this solution was added to the ammonia solution. After 30 min, the reaction was quenched with methanol, and the ammonia was allowed to evaporate at room temperature. The remaining THF was removed under vacuum, and the resulting white solid was taken up in water (5 mL). The suspension was neutralized with a 5 M aqueous acetic acid solution against pH paper and filtered through a 0.2 μM filter. The solution was then passed through a C18 Sep-Pak cartridge and eluted with methanol. This step was carried out to remove any compounds that would be irreversibly absorbed to the reversed-phase silica. After concentration, final purification by HPLC on C18 silica was carried out to give a colorless glass **15** (11 mg, 84%). This compound contained a small amount of disaccharide impurity that could not be easily removed by standard purification methods: $[\alpha]_D$ −69° (*c* 0.4, H_2O); ^1H NMR (600 MHz D_2O) δ 4.95 (s, 1 H, H-1″), 4.91 (s, 1 H, H-1′), 4.72 (s, 1 H, H-1), 4.37 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2′), 4.23 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2), 4.15 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2″), 3.93 (dd, 1 H, J_{vic} < 2.5 Hz, H-6a), 3.92 (dd, 1 H, J_{vic}< 2.5 Hz, H6a″), 3.93 (dd, 1 H, J_{vic} < 2.5 Hz, H-6a′), 3.86 (dt, 1 H, J_{vic} = 6.6 Hz, J_{gem} = 9.7 Hz, OCH_2CH_2), 3.76 (dd, 1 H, $J_{5,6}$ = 6.2 Hz, J_{gem} = 13.6 Hz, H-6b′), 3.73 (dd, 1 H, $J_{5,6}$ = 6.8 Hz, J_{gem} = 12.4 Hz, H-6b″), 3.71 (dd, 1 H, $J_{5,6}$ = 5.9 Hz, J_{gem} = 11.9 Hz, H-6b), 3.67 (dd, 1 H, $J_{3,4}$ = 9.9 Hz, H-3), 3.64 (dd, 1 H, $J_{3,4}$ = 9.7 Hz, H-3′), 3.61 (dd, 1 H, $J_{3,4}$ = 9.0 Hz, H-3″), 3.59 (dt, 1 H, J_{vic} = 7.1 Hz, OCH_2CH_2), 3.59 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4′), 3.57 (dd, 1 H, $J_{4,5}$ = 9.7 Hz, H-4″), 3.48 (dd, 1 H, $J_{4,5}$ = .7 Hz, H-4), 3.38 (ddd, 1 H, H-5′), 3.37 (ddd, 1 H, H-5″), 3.37 (dd, 1 H, H-5), 1.62 (p, 2 H, J = 7.1 Hz, $OCH_2CH_2CH_3$), 0.91 (t, 3 H, $CH_2CH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$), 101.9 (J^1_{C-H} = 162.0 Hz, C-1′), 101.6 (J^1_{C-H} = 162.2 Hz, C-1″), 100.9 (J^1_{C-H} = 158.8 Hz, C-1), 79.7 (C-2), 79.0 (C-2′), 77.2, 77.2, 77.1 (C-5, C-5′, C-5″), 73.8 (C-4′), 73.1 (C-3′), 73.0 (C-3″), 72.6 (OCH_2CH_2), 71.3 (C-2″), 68.3 (C-4), 67.8 (C-4′), 67.6 (C-4″), 62.0−61.6 (C-6, C-6′, C-6″), 23.3 ($CH_2CH_2CH_3$), 10.8 (CH_2CH_3); ES HRMS calcd for $C_{21}H_{38}O_{16}Na$ 569.2058, found 569.2053.

Propyl (β-D-Mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)-β-D-mannopyranoside (17). Employing the same procedure used for compound **15**, compound **4**[4](52 mg) gave a colorless glass **16** (14 mg 78%): $[\alpha]_D$ −70° (*c* 0.4, H_2O); ^1H NMR (600 MHz D_2O) δ 5.04 (s, 1 H,

H-1″), 4.94 (s, 1 H, H-1‴), 4.89 (s, 1 H, H-1′), 4.73 (s, 1 H, H-1), 4.40 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2″), 4.35 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2′), 4.24 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2), 4.16 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2‴), 3.94 (dd, 1 H, J_{gem} = 12.2 Hz, J_{vic} < 2.5 Hz, H-6a′), 3.94 (dd, 1 H, J_{gem} = 12.2 Hz, J_{vic} < 2.5 Hz, H-6a″), 3.92 (dd, 1 H, J_{gem} = 11.8 Hz, J_{vic} < 2.5 Hz, H-6a), 3.92 (dd, 1 H, J_{gem} = 11.9 Hz, J_{vic} < 2.5 Hz, H-6a‴), 3.87 (dt, 1 H, J_{vic} = 6.8 Hz, J_{gem} = 9.7 Hz, OCH_2CH$_2$), 3.76 (dd, 1 H, $J_{5,6}$ = 8.0 Hz, H-6b″), 3.74 (dd, 1 H, $J_{5,6}$ = 8.0 Hz, H-6b‴), 3.74 (dd, 1 H, $J_{5,6}$ = 6.5 Hz, H-6b), 3.72 (dd, 1 H, $J_{5,6}$ = 7.1 Hz, H-6b′), 3.67 (dd, 1 H, $J_{3,4}$ = 9.6 Hz, H-3), 3.68 (dd, 1 H, $J_{3,4}$ = 9.5 Hz, H-3′), 3.64 (dd, 1 H, $J_{3,4}$ = 10.8 Hz, H-3″), 3.62 (dd, 1 H, $J_{3,4}$ = 10.8 Hz, H-3‴), 3.61 (dt, 1 H, J_{vic} = 6.8 Hz, OCH_2CH$_2$), 3.60 (dd, 1 H, $J_{4,5}$ = 10.1 Hz, H-4″), 3.57 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4‴), 3.50 (dd, 1 H, $J_{4,5}$ = 9.9 Hz, H-4′), 3.48 (dd, 1 H, $J_{4,5}$ = 9.9 Hz, H-4), 3.39 (ddd, 1 H, H-5‴), 3.39 (ddd, 1 H, H-5′), 3.38 (ddd, 1 H, H-5″), 3.38 (ddd,1 H, H-5), 1.63 (p, 2 H, J = 7.0 Hz, OCH$_2$CH_2CH$_3$), 0.93 (t, 3 H, CH$_2$CH$_2$CH_3); ^{13}C NMR (125 MHz, CDCl$_3$), 102.0 (J^1_{C-H} = 161.9 Hz, C-1′), 102.0 (J^1_{C-H} = 162.3 Hz, C-1″), 101.8 (J^1_{C-H} = 163.9 Hz, C-1‴), 101.8 (J^1_{C-H} = 158.9 Hz, C-1), 80.1 (C-2), 79.9 (C-2′), 79.2 (C-2″), 77.1, 77.1, 77.0, 77.0 (C-5, C-5′, C-5″, C-5‴), 73.8 (C-3‴), 73.2 (C-3″), 72.8, 72.8 (C-3, C-3′), 72.6 (OCH$_2$CH$_2$), 71.3 (C-2‴), 68.5 (C-4), 68.0 (C-4′), 67.8 (C-4″), 67.6 (C-4‴), 62.1−61.5 (C-6, C-6′, C-6″, C-6‴), 23.3 (CH$_2$CH$_2$CH$_3$), 10.8 (CH$_2$CH$_3$); ES HRMS calcd for $C_{27}H_{48}O_{21}Na$ 731.2586, found 731.2588.

Propyl (β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)-β-D-mannopyranoside (18). Employing the same procedure used for compound **15**, compound **5** (32 mg) gave a colorless glass **17** (8 mg 77%): [α]$_D$ −22° (*c* 0.2, H$_2$O); ^{1}H NMR (800 MHz D$_2$O) δ 5.03 (s, 1 H, H-1‴), 5.00 (s, 1 H, H-1″), 4.95 (s, 1 H, H-1⁗), 4.89 (s, 1 H, H-1′), 4.72 (s, 1 H, H-1), 4.38 (d, 1 H, $J_{2,3}$ = 3.7 Hz, H-2″), 4.38 (d, 1 H, $J_{2,3}$ = 3.7 Hz, H-2‴), 4.34 (d, 1 H, $J_{2,3}$ = 3.4 Hz, H-2′), 4.23 (d, 1 H, $J_{2,3}$ = 3.4 Hz, H-2), 4.15 (d, 1 H, $J_{2,3}$ = 3.4 Hz, H-2⁗), 3.92 (dd, 1 H, J_{gem} = 10.1 Hz, J_{vic} = 2.0 Hz, H-6a⁗), 3.92 (dd, 1 H, J_{gem} = 10.7 = , J_{vic} = 2.0 Hz, H-6a′), 3.92 (dd, 1 H, J_{gem} = 10.7 Hz, J_{vic} = 2.0 Hz, H-6a″), 3.92 (dd, 1 H, J_{gem} = 10.9 Hz, J_{vic} = 2.2 Hz, H-6a), 3.92 (dd, 1 H, J_{gem} = 10.9 Hz, J_{vic} = 2.2 Hz, H-6a‴), 3.85 (dt, 1 H, J_{vic} = 6.6 Hz, J_{gem} = 9.8 Hz, OCH_2CH$_2$), 3.74 (dd, 1 H, $J_{5,6}$ = 6.5 Hz, H-6b‴), 3.73 (dd, 1 H, $J_{5,6}$ = 5.6 Hz, H-6b), 3.73 (dd, 1 H, $J_{5,6}$ = 6.2 Hz, H-6b⁗), 3.72 (1dd, H, $J_{5,6}$ = 5.9 Hz, H-6b′), 3.72 (dd, 1 H, $J_{5,6}$ = 5.6 Hz, H-6b″), 3.68 (dd, 1 H, $J_{3,4}$ = 9.5 Hz, H-3), 3.67 (dd, 1 H, $J_{3,4}$ = 9.8 Hz, H-3′), 3.66 (dd, 1 H, $J_{3,4}$ = 9.7 Hz, H-3″), 3.63 (dd, 1 H, $J_{3,4}$ = 9.7 Hz, H-3‴), 3.62 (dd, 1 H, $J_{3,4}$ = 9.3 Hz, H-3⁗), 3.60 (dt, 1 H, J_{vic} = 7.5 Hz, OCH_2CH$_2$), 3.58 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4‴), 3.56 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4⁗), 3.51 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4″), 3.49 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4′), 3.48 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4), 3.39 (ddd, 1 H, H-5⁗), 3.39 (ddd, 1 H, H-5‴), 3.37 (ddd, 1 H, H-5′), 3.36 (ddd, 1 H, H-5″), 3.36 (ddd, 1 H, H-5), 1.62 (p, 2 H, J = 7.0 Hz, OCH$_2$CH_2CH$_3$), 0.93 (t, 3 H, CH$_2$CH$_2$CH_3); ^{13}C NMR (125 MHz, CDCl$_3$), 102.2 (J^1_{C-H} = 161.9 Hz, C-1″), 102.1 (J^1_{C-H} = 162.3 Hz, C-1′), 101.9 (J^1_{C-H} = 162.9 Hz, C-1‴), 101.8 (J^1_{C-H} = 162.3 Hz, C-1⁗), 100.8 (J^1_{C-H} = 159.3 Hz, C-1), 80.1 (C-2, C-2′), 79.8 (C-2″), 79.3 (C-2‴), 77.1, 77.1, 77.0, 77.0 (C-5, C-5′, C-5″, C-5‴. C-5⁗), 73.8 (C-3⁗), 73.2, 72.9, 72.9, 72.7 (C-3, C-3′, C-3″, C-3‴), 71.3 (C-2⁗), 71.2 (OCH$_2$CH$_2$), 68.5, 68.1, 67.9, 67.6 (C-4, C-4′, C-4″, C-4‴, C-4⁗), 62.0, 61.7, 61.7, 61.5, 61.5 (C-6, C-6′, C-6″, C-6‴, C-6⁗), 23.3 (CH$_2$CH$_2$CH$_3$), 10.8 (CH$_2$CH$_3$); ES HRMS calcd for $C_{33}H_{58}O_{26}Na$ 893.3114, found 893.3110.

Propyl (β-D-Mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)-β-D-mannopyranoside (19). Employing the same procedure used for compound **15**, compound **6** (45 mg) gave a colorless glass **18** (11 mg 81%): [α]$_D$ −75° (*c* 0.15, H$_2$O); ^{1}H NMR (600 MHz D$_2$O) δ 5.06 (s, 1 H, H-1⁗), 5.02 (s, 2 H, H-1″, H-1‴), 4.96 (s, 1 H, H-1⁗⁗), 4.90 (s, 1 H, H-1′), 4.77 (s, 1 H, H-1), 4.40 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2″), 4.40 (d, 1 H, $J_{2,3}$ = 3.5 Hz, H-2⁗), 4.37 (d, 1 H, $J_{2,3}$ = 3.5 Hz, H-2‴), 4.34 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2′), 4.24 (d, 1 H, $J_{2,3}$= 3.1 Hz, H-2), 4.16 (d, 1 H, $J_{2,3}$ = 3.3 Hz, H-2⁗⁗), 3.94 (dd, 1 H, H-6a‴), 3.93 (dd, 1 H, H-6a⁗⁗), 3.93 (dd, 1 H, H-6a), 3.93 (dd, 1 H, H-6a′), 3.92 (dd, 1 H, H-6a⁗⁗), 3.92 (dd, 1 H, H-6a″), 3.86 (dt, 1 H, J_{vic} = 6.6 Hz, J_{gem} = 9.7 Hz, OCH_2CH$_2$), 3.75 (dd, 1 H, $J_{5,6}$ = 7.2 Hz, J_{gem} = 13.3 Hz, H-6b⁗⁗), 3.73 (dd, 1 H, $J_{5,6}$ = 6.5 Hz, J_{gem} = 10.8 Hz, H-6b⁗⁗), 3.73 (dd, 1 H, $J_{5,6}$ = 6.8 Hz, J_{gem} = 13.0 Hz, H-6b), 3.73 (dd, 1 H, $J_{5,6}$ = 6.5 Hz, J_{gem} = 13.4 Hz, H-6b′), 3.73 (dd, 1 H, $J_{5,6}$ = 6.1 Hz, J_{gem} = 12.0 Hz, H-6b″), 3.72 (dd, 1 H, $J_{5,6}$ = 6.1 Hz, J_{gem} = 12.0 Hz, H-6b‴), 3.68 (dd, 1 H, $J_{3,4}$ = 10.8 Hz, H-3), 3.68 (dd, 1 H, $J_{3,4}$ = 9.0 Hz, H-3′), 3.67 (dd, 1 H, $J_{3,4}$ = 10.5 Hz, H-3″), 3.67 (dd, 1 H, $J_{3,4}$ = 9.0 Hz, H-3‴), 3.65 (dd, 1 H, $J_{3,4}$ = 10.6 Hz, H-3⁗⁗), 3.63 (dd, 1 H, $J_{3,4}$ = 10.1 Hz, H-3⁗⁗), 3.61 (dt, 1 H, J_{vic} = 7.3 Hz, OCH$_2$-CH$_2$), 3.59 (dd, 1 H, $J_{4,5}$ = 9.9 Hz, H-4⁗⁗), 3.57 (dd, 1 H, $J_{4,5}$ = 10.1 Hz, H-4⁗⁗), 3.51 (dd, 1 H, $J_{4,5}$ = 10.1 Hz, H-4″), 3.50 (dd, 1 H, $J_{4,5}$ = 9.8 Hz, H-4‴), 3.50 (dd, 1 H, $J_{4,5}$ = 9.4 Hz, H-4′), 3.48 (dd, 1 H, $J_{4,5}$ = 10.5 Hz, H-4), 3.41 (ddd, 1 H, H-5⁗⁗), 3.39 (ddd, 1 H, H-5⁗⁗), 3.40 (ddd, 1 H, H-5‴), 3.38 (ddd, 1 H, H-5′), 3.37 (ddd, 1 H, H-5), 3.37 (ddd, 1 H, H-5″), 1.63 (p, 2 H, J = 7.0 Hz, OCH$_2$CH_2CH$_3$), 0.92 (t, 3 H, CH$_2$CH$_2$CH_3); ^{13}C NMR (125 MHz, CDCl$_3$), 102.1 (J^1_{C-H} = 161.0 Hz, C-1′), 102.1 (J^1_{C-H} = 162.3 Hz, C-1″,C-1‴), 101.9 (J^1_{C-H} = 162.1 Hz, C-1⁗⁗), 101.8 (J^1_{C-H} = 162.0 Hz, C-1⁗⁗), 100.8 (J^1_{C-H} = 158.4 Hz, C-1), 80.0 (C-2, C-2″), 80.0 (C-2′), 79.9 (C-2‴), 79.3 (C-2⁗⁗), 77.1−76.8 (C-5, C-5′, C-5″, C-5‴, C-5⁗⁗, C-5⁗⁗), 73.8 (C-3⁗⁗), 73.1−72.7 (C-3, C-3′,C-3″, C-3‴, C-3⁗⁗), 72.6 (OCH$_2$CH$_2$), 71.3 (C-2⁗⁗), 68.5, 68.1, 68.0, 67.9, 67.6 (C-4, C-4′, C-4″, C-4‴, C-4⁗⁗, C-4⁗⁗), 62.0−61.4 (C-6, C-6′, C-6″, C-6‴, C-6⁗⁗, C-6⁗⁗), 23.3 (CH$_2$CH$_2$-CH$_3$), 10.8 (CH$_2$CH$_3$); ES HRMS calcd for $C_{39}H_{68}O_{31}Na$ 1055.3642, found 1055.3648.

3-*O*-Benzyl-4,6-*O*-benzylidene-D-*glucopyranose* (20). To a solution of 3-*O*-benzyl-D-glucopyranose[22] (3.0 g, 110 mmol) dissolved in DMF (20 mL) was added benzaldehyde dimethyl acetal (2.0 mL, 130 mmol) followed by *p*-toluenesulfonic acid (110 mg). The solution was subjected to rotary evaporation for 2 h at 25 °C with a standard water aspirator. The solution was quenched with pyridine (200 μL) and concentrated to a yellow oil under vacuum. The oil was chromatographed on silica gel in toluene/EtOAc (1:1) to yield a white solid (3.9 g, 94%) after concentration. This solid could be recrystallized from EtOAc/hexane mixtures: mp 148−149 °C; [α]$_D$ −20.5° (*c* 1.1, CHCl$_3$); ^{1}H NMR (500 MHz, CH$_3$OD) δ 7.45−7.20 (m, 10 H, Ar), 5.59 (s, 1 H, O$_2$C*H*Ph, β anomer), 5.58 (s, 1 H, O$_2$C*H*Ph, α anomer), 5.13 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1, α anomer), 4.87−4.80 (m, 4 H, 4(OCH_2Ph)), 4.61 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H-1, β anomer), 4.25 (dd, 1 H, $J_{5,6}$ = 5.1 Hz, J_{gem} = 10.4 Hz, H-6eq, β anomer) 4.18 (dd, 1 H, $J_{5,6}$ = 5.0 Hz, J_{gem} = 10.3 Hz, H-6eq, α anomer), 3.99 (ddd, 1 H, $J_{4,5} \approx J_{5,6ax}$ = 10.1 Hz, H-5, α anomer), 3.84 (dd, 1 H, $J_{2,3} \approx J_{3,4}$ = 9.2 Hz, H-3, α anomer), 3.77 (dd, 1 H, H-6ax, β anomer), 3.73 (dd, 1 H, H-6ax, α anomer), 3.66−3.58 (m, 4 H, H-2, H-4, α anomer, H-3, H-4, β anomer), 3.46 (ddd, 1 H, $J_{4,5} \approx J_{5,6}$ = 9.5 Hz, H-5 β anomer), 3.37 (ddd, 1 H, $J_{2,3} \approx J_{3,4}$ = 8.1 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 129.8−128.4, 127.2, 102.6, 102.5, 99.0, 94.9, 83.5, 82.8, 82.5, 80.1, 76.8, 75.8, 75.6, 74.1, 70.4, 69.8, 67.6, 63.6. Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.03; H, 6.28; O, 26.79. Found: C, 66.82; H, 6.28.

1,2-Di-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranose (21). 4,6-*O*-Benzylidene-3-*O*-benzyl-D-glucopyranose (**20**) (3.84 g, 10.6 mmol) was dissolved in a solution of acetic anhydride (50 mL) containing acetic acid (10 mL), and sodium acetate (3.0 g) was added. The mixture was warmed to reflux over 20 min and allowed to cool to room temperature. The solvent was removed under vacuum, and the colorless oil was taken up in dichloromethane (200 mL). The solution was washed repeatedly with water, dried over anhydrous sodium sulfate and concentrated to yield a 6:1 β:α anomeric mixture (4.13 g, 88%) from which the β anomer could be crystallized with EtOAc/hexane mixtures: mp 162−164 °C [α]$_D$ +16° (*c* 1.3, CHCl$_3$); ^{1}H NMR (500 MHz, CHCl$_3$) δ 7.48−7.24 (m, 10 H, Ar), 5.68 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1), 5.56 (s, 1 H, O$_2$C*H*Ph), 5.13−5.10 (m, 2 H, H-2, H-3), 4.87 (d, 1 H, J = 12.1 Hz, OCH_2-Ph), 4.66 (d, 1 H, OCH_2Ph), 4.36 (dd, 1 H, $J_{4,5}$ = 4.9, $J_{5,6}$ = 10.4 Hz, H-6ax), 3.80 (m, 2 H, H-4, H-6eq), 3.57 (ddd, 1 H, $J_{4,5} \approx J_{5,6ax}$ = 9.7 Hz, $J_{5,6eq}$ = 4.9 Hz, H-5), 2.07 (s, 3 H, COCH$_3$), 1.96 (s, 1 H, COCH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 169.1, 169.0, 137.9, 136.9, 129.0, 128.3, 128.2, 127.8, 127.7, 126.0,

125.9, 101.3, 92.5, 81.2, 78.4, 74.3, 71.8, 68.4, 66.9, 20.9, 20.8. Anal. Calcd for $C_{20}H_{22}O_6$: C, 65.15; H, 5.92; O, 28.93. Found: C, 64.97; H, 6.03.

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (22). 1,2-Di-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-benzyl-β-D-glucopyranose (**21**) (4.13 g, 93.4 mmol) was dissolved in THF (40 mL), and benzylamine (1.1 mL, 101 mmol) was added. The mixture was stirred for 16 h at room temperature and concentrated to a yellow syrup under vacuum. Chromatography on silica gel using hexane/EtOAc (2:1) yielded a colorless syrup (2.9 g, 78%) that crystallized upon standing: mp 149−150 °C; $[\alpha]_D$ +21° (*c* 0.98, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.24 (m, 10 H, Ar), 5.58 (s, 1 H, O_2CHPh, α anomer), 5.57 (s, 1 H, O_2CHPh, β anomer), 5.42 (d, 1 H, $J_{1,2} = 3.9$ Hz, H-1, α anomer), 4.89−4.84 (m, 3 H, H-2 α anomer, 2(OCH_2-Ph)), 4.80 (dd, 1 H, $J_{1,2} \approx J_{2,3} = 8.9$ Hz, H-2, β anomer), 4.68 (d, 1 H, $J = 11.7$ Hz, OCH_2Ph), 4.66 (d, 1 H, $J = 11.9$ Hz, OCH_2Ph), 4.65 (d, 1 H, H-1, β anomer), 4.34 (dd, 1 H, $J_{5,6} = 5.0$ Hz, $J_{gem} = 10.5$ Hz, H-6eq, β anomer), 4.26 (dd, 1 H, $J_{5,6} = 5.0$ Hz, $J_{gem} = 10.2$ Hz, H-6eq, α anomer), 4.09 (ddd, 1 H, $J_{5,6ax} \approx J_{4,5} = 9.9$ Hz, H-5 α anomer), 4.05 (dd, 1 H, $J_{2,3} \approx J_{3,4} = 9.5$ Hz, H-3, α anomer), 3.80−3.68 (m, 4 H, H-6ax, α anomer, H-3, H-4, H-6ax, β anomer), 3.45 (ddd, 1 H, $J_{5,6ax} \approx J_{4,5} = 10.1$ Hz, H-5 β anomer), 2.06 (s, 3 H, $COCH_3$, α anomer), 2.05 (s, 3 H, $COCH_3$, α anomer), ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 137.1, 128.9−125.9, 101.3, 101.3, 96.4, 91.2, 82.1, 81.6, 78.0, 75.8, 75.7, 74.8, 74.5, 73.1, 68.9, 68.6, 66.6, 62.6, 21.0. Anal. Calcd for $C_{24}H_{24}O_7$: C, 65.99; H, 6.09; O, 27.97. Found: C, 65.79; H, 6.18.

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl Trichloroacetimidate (23). 2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-benzyl-D-glucopyranose (**22**) (1.6 g, 4.0 mmol) was dissolved in dichloromethane (20 mL), and the solution was cooled to 0 °C. Trichloroacetonitrile (600 μL, 6.0 mmol) was added followed by DBU (20 μL, 0.001 mmol). The ice bath was removed, the reaction was warmed to room temperature, and stirring was continued for 2 h. Concentration gave a dark brown syrup that was purified by silica gel chromatography to give two products (1.86 g, 86%) in a 4:1 ratio, identified as the β and α anomers, respectively. β anomer: $[\alpha]_D$ +28.7° (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (1 H, s, NH), 7.49−7.24 (m, 10 H, Ar), 5.85 (d, 1 H, $J_{1-2} = 7.9$ Hz, H-1), 5.58 (s, 1 H, O_2CHPh), 5.29 (dd, 1 H, $J_{1,2} \approx J_{2,3} = 8.5$ Hz, H-2), 4.86 (d, 1 H, $J = 12.3$ Hz, OCH_2Ph) 4.69 (d, 1 H, OCH_2Ph), 4.41 (dd, 1 H, $J_{5,6} = 5.0$ Hz, $J_{gem} = 10.4$ Hz, H-6eq), 3.89 (dd, 1 H, $J_{4,5} \approx J_{3,4}$ 9.3 Hz, H-4), 3.82 (dd, 1 H, $J_{5,6} = 10.8$ Hz, H-6ax), 3.80 (dd, 1 H, H-3), 3.64 (ddd, 1 H, H-5), 1.95 (s, 3H, $COCH_3$), ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 161.1, 129.0−125.9, 101.4, 96.2, 81.1, 81.5, 78.2, 74.0, 71.6, 68.6, 66.9, 20.8; ES HRMS calcd for $C_{24}H_{24}NO_7NaCl_3$ 566.0516, found 566.0521. α anomer: $[\alpha]_D$ +37.6° (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 1 H, NH), 7.49−7.23 (m, 10 H, Ar), 6.49 (d, 1 H, $J_{1,2} = 3.7$ Hz, H-1), 5.60 (s, 1 H, O_2CHPh), 5.07 (dd, 1 H, $J_{2,3} = 9.7$ Hz, H-2), 4.91 (d, 1 H, J 11.7 Hz, OCH_2Ph), 4.73 (d, 1 H, OCH_2Ph), 4.34 (dd, 1 H, $J_{5,6} = 4.9$ Hz, $J_{gem} = 10.4$ Hz, H-6eq), 4.12 (dd, 1 H, $J_{3,4} = 9.7$ Hz, H-3), 4.04 (ddd, 1 H, $J_{4,5} \approx J_{5,6ax} = 10.1$ Hz, H-5), 3.81 (dd, 1 H, H-6eq), 3.77 (dd, 1 H, H-4), 1.97 (s, 3 H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 160.9, 138.1, 136.9, 129.0−125.9, 101.4, 93.9, 81.4, 75.6, 74.8, 68.6, 65.2, 20.6; ES HRMS for $C_{24}H_{24}NO_7NaCl_3$ 566.0516, found 566.0520.

Allyl (2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (24). Disaccharide acceptor **1**[4] (1.1 g 1.2 mmol) and 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl trichloroacetimidate (**23**) (780 mg, 1.4 mmol) were dissolved in dichloromethane (10 mL) at room temperature. To the stirred solution was added TMSOTf (50 μL, 50 μM) and the reaction stirred for 15 min at room temperature. Triethylamine (20 μL) was then added, and the reaction was concentrated to give a yellow oil. Column chromatography in toluene/EtOAc (8:1) gave the title compound as a colorless syrup (1.2 g, 76%): $[\alpha]_D$ −54.2° (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.00 (40 H, Ar), 5.81 (m, 1 H, OCH_2CHCH_2), 5.50 (s, 1 H, O_2CHPh), 5.32 (d, 1 H, $J_{1,2} = 8.1$ Hz, H-1″), 5.20 (dd, 1 H, $J_{2,3} = 8.3$ Hz, H-2″), 5.17 (m, 1 H, OCH_2CHCH_2), 5.10 (m, 1 H, OCH_2-$CHCH_2$), 4.90 (d, 1 H, $J = 10.8$ Hz, OCH_2Ph), 4.86 (d, 1 H, $J = 10.6$ Hz, OCH_2Ph), 4.78 (d, 1 H, $J = 11.8$ Hz, OCH_2Ph), 4.76 (d, 1 H, J = 12.2 Hz, OCH_2Ph), 4.75 (d, 1 H, $J = 12.2$ Hz, OCH_2Ph), 4.67 (s, 1 H, H-1′) 4.67−4.61 (m, 3 H, 3(OCH_2Ph)), 4.54−4.43 (m, 5 H, 4(OCH_2Ph), H-2), 4.38−4.31 (m, 4 H, 2(OCH_2Ph), H-6ax″, H-1), 4.14 (d, 1 H, $J_{2,3} = 3.1$ Hz, H-2′), 3.97 (m, 1 H, OCH_2CHCH_2), 3.90−3.75 (m, 5 H, H-4, H-6a′, H-3″, H-4″, H-6eq″), 3.68−3.57 (m, 5 H, H-6a, H-6b, H4′, H-6a′ H-5″), 3.49−3.44 (m, 3 H, H-3, H-3′, H-5′), 3.30 (ddd, $J_{4,5} \approx J_{5,6} = 3.5$ Hz, $J_{5,6} = 9.9$ Hz, H-5), 1.96 (s, 3 H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 138.5, 138.4, 138.2, 138.2, 138.2, 138.0, 137.8, 137.3, 133.9, 129.0−127.5, 126.1, 117.0, 102.3, 101.4, 101.4, 100.3, 81.6, 80.8, 80.6, 79.0, 75.7, 75.6, 75.3, 75.2, 74.6, 74.4, 73.7, 73.3, 73.3, 73.0, 72.6, 70.8, 70.6, 70.1, 70.0, 69.0, 68.9, 66.1, 21.3; ES HRMS calcd for $C_{24}H_{24}O_7$ 1327.5601, found 1327.5601

Allyl (3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (25). Trisaccharide **24** (900 mg, 0.69 mmol) was dissolved in THF (5 mL), and methanol was added (15 mL) followed by a small piece of sodium metal (∼10 mg). The reaction was stirred for 16 h and concentrated to dryness. Column chromatography in toluene/EtOAc (8:1) gave a colorless syrup (823 mg, 94%) containing the title compound **25**: $[\alpha]_D$ −56.9° (*c* 1.5, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43−6.99 (40 H, Ar), 5.83 (m, 1 H, OCH_2CHCH_2), 5.50 (s, 1 H, O_2CHPh), 5.19 (m, 1 H, OCH_2-$CHCHaHb$), 5.14 (m, 1 H, $OCH_2CHCHaHb$), 4.98 (d, 1 H, $J = 11.8$ Hz, OCH_2Ph), 4.97 (d, 1 H, $J = 10.9$ Hz, OCH_2Ph), 4.93 (d, 1 H, $J = 10.9$ Hz, OCH_2Ph), 4.93 (s, 1 H, H-1′), 4.83 (d, 1 H, $J = 12.2$ Hz, OCH_2Ph), 4.81 (d, 1 H, $J = 6.9$ Hz, H-1″), 4.76 (d, 1 H, $J = 11.9$ Hz, OCH_2Ph), 4.72 (d, 1 H, $J = 11.9$ Hz, OCH_2Ph), 4.63 (d, 1 H, $J = 12.2$ Hz, OCH_2Ph), 4.53 (d, 1 H, $J = 12.8$ Hz, OCH_2Ph), 4.50 (d, 1 H, $J = 13.1$ Hz, OCH_2Ph), 4.48 (d, 1 H, $J = 11.2$ Hz, OCH_2Ph), 4.45−4.35 (m, 7 H, H-2′, H-1, 4(OCH_2Ph), OCH_2CHCH_2), 4.16 (m, 1 H, H-4″), 4.10 (dd, 1 H, $J_{3,4} \approx J_{4,5} = 9.5$ Hz, H-4′), 4.00 (m, 1 H, OCH_2CHCH_2), 3.81−3.60 (m, 10 H, H-3, H-5, H-6a, H-6b, H-6a′, H-6b′, H-2″, H-3″, H-6a″, H-6b″), 3.55 (dd, 1 H, $J_{1,2} = 2.9$ Hz, $J_{2,3} = 9.6$ Hz, H-2), 3.50−3.45 (m, 2 H, H-4, H-3′), 3.39 (ddd, 1 H, $J_{4,5} \approx J_{5,6ax} = 9.8$ Hz, $J_{4,5eq} = 5.0$ Hz, H-5″), 3.34 (ddd, 1 H, $J_{4,5} = 9.9$ Hz, $J_{5,6a} = 3.1$ Hz, $J_{5,6b} = 4.6$ Hz, H-5′); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 138.9, 138.5, 138.3, 138.0, 137.9, 137.9, 137.9, 137.5, 133.6, 129.0, 127.0, 125.2, 117.3, 105.9, 101.2, 100.1, 99.8, 82.1, 82.1, 80.9, 80.1, 80.4, 75.5, 75.4, 75.3, 74.8, 74.5, 73.8, 73.6, 73.4, 71.3, 70.8, 70.3, 70.1, 70.1, 70.1, 69.3, 69.3, 68.6, 66.4; ES HRMS $C_{77}H_{82}NaO_{16}$ 1285.5495, found 1285.5495.

Allyl (3-*O*-Benzyl-4,6-*O*-benzylidene-*2-O*-trifluoromethanesulfonyl-β-D-glucopyranosyl)(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (26). The alcohol **25** (800 mg, 0.633 mmol) was dissolved in dichloromethane (5 mL), and pyridine (300 μL) was added followed by *N*,*N*-dimethyl-4-aminopyridine (50 mg, 0.40 mmol). The solution was cooled to 0 °C, and trifluoromethanesulfonic anhydride (200 μL, 1.18 mmol) was added dropwise. The reaction was then warmed to room temperature and stirred for 16 h. The solution was diluted with dichloromethane, washed with a sodium bicarbonate solution, dried over sodium sulfate, and concentrated to a brown oil. Column chromatography in toluene/EtOAc (8:1) gave a colorless syrup (789 mg, 89%): $[\alpha]_D$ −72.9° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−6.96 (m, 40 H, Ar), 5.82 (m, 1 H, OCH_2CHCH_2), 5.75 (d, 1 H, $J_{1,2} = 8.0$ Hz, H-1″), 5.44 (s, 1 H, O_2CHPh), 5.20 (m, 1 H, OCH_2CHCH_2), 5.12 (m, 1 H, OCH_2CHCH_2), 4.97 (d, 1 H, $J = 10.7$ Hz, OCH_2Ph), 4.87 (d, 1 H, $J = 10.9$ Hz, OCH_2-Ph), 4.85 (d, 1 H, $J = 11.6$ Hz, OCH_2Ph), 4.75 (d, 1 H, $J = 11.9$ Hz, OCH_2Ph), 4.70 (d, 1 H, $J = 12.4$ Hz, OCH_2Ph), 4.68 (d, 1 H, $J_{2,3} = 2.9$ Hz, H-2′), 4.60−4.33 (m, 14 H, 9(OCH_2Ph), H-2″, H-6a″, H-1, H-2, OCH_2CHCH_2), 3.96 (m, 1 H, OCH_2-$CHCH_2$), 3.87−3.74 (m, 5 H, H-4, H-6a, H-4′, H6a′, H-6b′), 3.70−3.59 (m, 5 H, H-6a, H-5′, H-4″, H-5″, H-6b″), 3.57 (dd, 1 H, $J_{3,4} = 9.2$ Hz, H-3′), 3.52 (dd, 1 H, $J_{2,3} = 3.4$ Hz, $J_{3,4} = 9.3$ Hz, H-3), 3.42 (dd, 1 H, $J_{2,3} \approx J_{3,4} = 9.0$ Hz, H-3″), 3.31 (ddd,

1 H, $J_{4,5}$ = 8.1 Hz, $J_{5,6a}$ = 3.6 Hz, $J_{5,6b}$ = 1.6 Hz, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5−136.9, 133.6, 128.9−127.3, 125.2, 117.4, 101.4, 101.0, 100.5, 97.4, 85.4, 82.3, 81.1, 80.5, 77.9, 76.3, 75.5, 75.3, 75.2, 74.9, 74.7, 74.0, 73.7, 73.3, 70.7, 70.7, 70.4, 70.0, 69.6, 69.6, 68.5, 68.3, 66.2; EMS calcd for $C_{78}H_{81}F_3O_{18}S$ 1417.5, found 1417.5.

Allyl (2-*S*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-mannopyranosyl)(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (27). Triflate **26** (600 mg, 0.43 mmol) was dissolved in DMF (5 mL), and potassium thioacetate (3 g) was added. The flask was purged with argon and immersed in an oil bath preheated to 150 °C for 5 min. The bath was removed, and reaction was cooled to room temperature. The dark brown solution was diluted with toluene (50 mL) and repeatedly washed with water to give a yellow solution. After drying over anhydrous sodium sulfate and concentration, the yellow oil was subjected to column chromatography using toluene with a gradient to 10% EtOAc. Compound **27** was obtained as a colorless syrup (359 mg, 63%): $[\alpha]_D$ −65.2° (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−6.90 (m, 40 H, Ar), 5.84 (s, 1 H, H-1″), 5.83 (m, 1 H, OCH_2CHCH_2), 5.48 (s, 1 H, O_2CHPh), 5.19 (m, 1 H, OCH_2CHCH_2), 5.14 (s, 1 H, H-1′), 5.12 (m, 1 H, OCH_2CHCH_2), 4.92 (d, 1 H, *J* = 10.7 Hz, OCH_2Ph), 4.84 (d, 2 H, *J* = 10.5 Hz, 2 (OCH_2Ph)), 4.85 (d, 1 H, *J* = 11.3 Hz, OCH_2-Ph), 4.72 (d, 1 H, $J_{2,3}$ = 2.1 Hz, H-2′), 4.68 (d, 1 H, *J* = 11.3 Hz, OCH_2Ph), 4.63−4.62 (m, 2 H, H-2, H-2″), 4.54−4.36 (m, 10 H, 7(OCH_2Ph), OCH_2CHCH_2, H-6ax″, H-1), 4.31 (d, 1 H, *J* = 11.9 Hz, OCH_2Ph), 4.68 (d, 1 H, *J* = 12.1 Hz, OCH_2Ph), 3.96 (m, 1 H, OCH_2CHCH_2), 3.83−3.52 (m, 13 H, H-3, H-4, H-6a, H-6b, H-3′, H-4′, H-5′, H-6a′, H-6b′, H-3″, H-4″, H5″, H-6eq″), 3.31 (ddd, 1 H, $J_{4.5}$ = 3.7 Hz, $J_{5.6}$ = 1.7 Hz, $J_{5.6}$ = 11.5 Hz, H-5), 2.21 (s, 3H, $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6−135.4, 133.5, 128.9−127.1, 117.3, 101.5, 101.0, 100.3, 97.2, 81.0, 80.5, 80.3, 76.3, 75.8, 75.6, 75.3, 75.2, 75.2, 74.2, 73.8, 73.4, 71.4, 70.7, 70.5, 70.0, 69.5, 69.3, 68.6, 68.6, 68.4, 67.6, 30.7; ES HRMS calcd for $C_{79}H_{84}O_{16}SNa$ 1343.5372, found 1343.5370.

Allyl (2-*S*-Acetyl-3-*O*-benzyl-4,6-*O*-benzyilidene-2-deoxy-β-D-mannopyranosyl)(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (28). Thioacetate **27** (300 mg, 0.23 mmol) was dissolved in THF (5 mL), and cyclohexene (1 mL), ethanol (1 mL), and hydrazine hydrate (100 μL, ∼1.7 mmol) were added. The solution was stirred at room temperature for 3 h and diluted with toluene. Concentration gave a colorless syrup that could be chromatographed in toluene/EtOAc (8:1) to yield the thiol **28** (262 mg, 89%): $[\alpha]_D$ −78.1° (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47−6.90 (40 H, Ar), 5.87 (m, 1 H, OCH_2CH-CH_2), 5.57 (s, 1 H, O_2CHPh), 5.51 (d, 1 H, $J_{1,2}$ = 1.8 Hz, H-1″), 5.22 (m, 1 H, OCH_2CHCH_2), 5.12 (m, 1 H, OCH_2CHCH_2), 5.14 (s, 1 H, H-1′), 4.95 (d, 1 H, *J* = 10.8 Hz, OCH_2Ph), 4.94 (d, 1 H, *J* = 10.2 Hz, OCH_2Ph), 4.90 (d, 1 H, *J* = 11.5 Hz, OCH_2-Ph), 4.76 (d, 1 H, *J* = 10.3 Hz, OCH_2Ph), 4.72 (d, 1 H, *J* = 11.7 Hz, OCH_2Ph), 4.71 (d, 1 H, $J_{2,3}$ = 2.4 Hz, H-2′), 4.61 (d, 1 H, $J_{2,3}$ = 3.5 Hz, H-2), 4.58 (d, 1 H, *J* = 10.8 Hz, OCH_2Ph), 4.53 (d, 1 H, *J* = 11.9 Hz, OCH_2Ph), 4.50−4.40 (m, 5 H, 3(OCH_2Ph), OCH_2CHCH_2, H-1), 4.33 (d, 1 H, *J* = 10.1 Hz, OCH_2Ph), 4.29 (dd, $J_{5,6}$ = 4.9 Hz, J_{gem} = 10.3 Hz, H-6eq″), 4.25 (dd, $J_{5,6} \approx J_{gem}$ = 9.4 Hz, H-6ax″), 4.24 (d, 1 H, *J* = 10.1 Hz, OCH_2Ph), 4.19 (d, 1 H, *J* = 11.9 Hz, OCH_2Ph), 4.11 (d, 1 H, *J* = 11.9 Hz, OCH_2Ph), 4.10 (ddd, $J_{2,3}$ = 4.5 Hz, $J_{2,SH}$ = 2.6 Hz, H-2″), 4.01 (m, 1 H, OCH_2CHCH_2), 3.93 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.3 Hz, H-4′), 3.85 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 10.3 Hz, H-4″), 3.81 (dd, 1 H, $J_{5,6}$ = 1.5 Hz, J_{gem} = 10.4 Hz, H-6a′), 3.76−3.67 (m, 5 H, H-4, H-6a, H-6b, H-6b′, H-3″), 3.62 (dd, 1 H, H-3′), 3.59 (dd, 1 H, $J_{3,4}$ = 9.3 Hz, H-3), 3.54 (ddd, 1H, $J_{5,6}$ = 6.0 Hz, H-5′), 3.50 (ddd, 1 H, H-5″), 3.38 (ddd, 1 H, $J_{5,6a}$ = 1.8 Hz, $J_{5,6b}$ = 4.2 Hz, $J_{4,5}$ 9.7 Hz, H-5), 2.27 (d, 1H, SH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 137.5, 133.5, 129.0−127.1, 117.4, 101.5, 100.7, 100.1, 99.1, 80.7, 80.6, 78.0, 76.8, 75.5, 75.4, 75.2, 75.2, 74.5, 74.4, 73.7, 73.4, 71.0, 70.6, 70.4, 70.2, 70.1, 69.8, 69.7, 68.7, 68.5, 67.7; ES HRMS calcd for $C_{77}H_{82}O_{15}SNa$ 1301.5267, found 1301.5293.

Allyl (3,4,6-Tri-*O*-*p*-chlorobenzyl-1-thio-β-D-mannopyranosyl)(1→2)(2-*S*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-mannopyranosyl)(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (29). Thiol **28** (250 mg, 0.200 mmol) and freshly prepared 3,4,6-tri-*O*-*p*-chlorobenzyl-α-D-*arabino*-hexopyrano-2-ulosyl bromide (240 mg, 0.390 mmol) (**2**) were dissolved in dichloromethane (2 mL) at room temperature. The flask was purged with argon, and lutidine (55 μL, 0.470 mmol) was added. The reaction was stirred at room temperature for 2 h and concentrated to dryness. The syrup was dissolved in THF (10 mL) and cooled to −78 °C. L-Selectride (1.0 M, 1.5 mL) was then added dropwise, and the cooling bath was removed. Once the reaction had reached room temperature, the solution was quenched with methanol (2 mL) and diluted with dichloromethane. Washing with water, bicarbonate solution, and finally a brine solution gave a pale yellow solution. Drying over anhydrous sodium sulfate, and concentration followed by silica gel chromatography gave **29** as a colorless oil (180 mg, 49%) and similarly the α anomer (45 mg): $[\alpha]_D$ −79.4° (*c* 0.81, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52−6.85 (m, 52 H, Ar), 5.91 (s, 1 H, H-1″), 5.82 (m, 1 H, OCH_2CHCH_2), 5.52 (s, 1 H, O_2CHPh), 5.52 (s, 1 H, H-1‴), 5.22 (s, 1 H, H-1′), 5.19 (m, 1 H, OCH_2CHCH_2), 5.13 (m, 1 H, OCH_2-$CHCH_2$), 4.94 (d, 1 H, *J* = 10.1 Hz, OCH_2Ph), 4.93 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2′), 4.90 (d, 1 H, *J* = 10.4 Hz, OCH_2Ph), 4.85 (d, 1 H, *J* = 11.0 Hz, OCH_2Ph), 4.77 (d, 1 H, *J* = 10.9 Hz, OCH_2-Ph), 4.71 (d, 1 H, *J* = 12.3 Hz, OCH_2Ph), 4.63 (d, 1 H, *J* = 10.9 Hz, OCH_2Ph), 4.62 (d, 1 H, *J* = 12.8 Hz, OCH_2Ph), 4.60 (d, 1 H, $J_{2,3}$ = 4.0 Hz, H-2), 4.55 (d, 1 H, *J* = 11.4 Hz, OCH_2-Ph), 4.51 (dd, 1 H, $J_{5,6}$ = 5.0 Hz, J_{gem} = 10.6 Hz, H-6ax″), 4.49−4.37 (m, 10 H, 8(OCH_2Ph), H-1, OCH_2CHCH_2), 4.32 (d, 1 H, *J* = 12.4 Hz, OCH_2Ph), 4.07 (d, 1 H, *J* = 11.5 Hz, OCH_2Ph), 4.04 (d, 1 H, *J* = 12.3 Hz, OCH_2Ph), 4.03 (d, 1 H, $J_{2,3}$ = 4.4 Hz, H-2‴), 3.96 (m, 1 H, OCH_2CHCH_2), 3.93 (d, 1 H, $J_{2,3}$ = 4.6 Hz, H-2″), 3.91−3.84 (m, 3 H, H-4, H6a″, H6a′), 3.82−3.79 (m, 4 H, H-6a, H-4‴, H-6b′, OCH_2Ph), 3.75−3.58 (m, 9 H, H-5‴, H-6a‴, H-6b‴, H-5″, H-4″, H-4′, H-6b), 3.65 (m, 2 H, H-3′, H-3″) 3.56 (dd, $J_{3,4}$ = 9.5 Hz, H-3), 3.51 (ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6}$ = 4.9 Hz, $J_{5,6}$ = 1.8 Hz, H-5′), 3.48 (dd, $J_{3,4}$ = 9.2 Hz, H-3‴), 3.32 (ddd, 1 H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 3.9 Hz, $J_{5,6}$ = 1.5 Hz, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2−136.3, 133.4, 129.0, 129.1−126.2, 117.4, 101.6 ($^1J_{C1-H1}$ = 154.0 Hz, C-1), 101.1, 101.1 ($^1J_{C-H}$ = 160.9, C-1′), 99.3 ($^1J_{C-H}$ = 165.6, C-1″), 83.9 ($^1J_{C-H}$ = 160.4, C-1‴), 81.3, 80.3, 79.6, 79.3, 76.3, 75.8, 75.7, 75.6, 75.4, 75.4, 74.2, 74.1, 73.5, 72.9, 70.5, 70.1, 70.0, 70.0, 69.8, 69.7, 69.6, 69.5, 69.4, 68.5, 68.4, 68.4, 68.3, 68.3, 68.1, 68.1, 68.0; EMS calcd for $C_{107}H_{113}Cl_3O_{17}S$ 1837.6, found 1837.6 correct isotopic intensity pattern.

3-(2-Aminoethylthio)propyl (3,4,6-Tri-*O*-*p*-chlorobenzyl-1-thio-β-D-mannopyranosyl)(1→2)(2-*S*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-mannopyranosyl)(1→2)-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (30). Allyl glycoside **29** (50 mg, 0.028 mmol) was subjected to the general procedure for the synthesis of compounds **11**−**14** to give **30** as a colorless syrup (38 mg, 73%): $[\alpha]_D$ −70.2° (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48−6.82 (52 H, Ar), 5.88 (s, 1 H, H-1″), 5.51 (s, 1 H, O_2CHPh), 5.50 (s, 1 H, H-1‴), 5.13 (s, 1 H, H-1′), 4.90 (d, 1 H, *J* = 10.3 Hz, OCH_2Ph), 4.85 (d, 1 H, *J* = 10.3 Hz, OCH_2Ph), 4.85 (d, 1 H, $J_{2,3}$ = 3.1 Hz, H-2′), 4.82 (d, 1 H, *J* = 10.8 Hz, OCH_2Ph), 4.85 (d, 1 H, *J* = 10.8 Hz, OCH_2Ph), 4.67 (d, 1 H, *J* = 12.5 Hz, OCH_2Ph), 4.58 (d, 1 H, *J* = 11.9 Hz, OCH_2Ph), 4.58 (d, 1 H, *J* = 12.6 Hz, OCH_2Ph), 4.57 (d, 1 H, $J_{2,3}$ = 3.8 Hz, H-2), 4.52 (d, 1 H, *J* = 11.7 Hz, OCH_2Ph), 4.48−4.38 (m, 9 H, 7(OCH_2Ph), H-1, H-6a″), 4.33 (d, 1 H, *J* = 11.4 Hz, OCH_2Ph), 4.30 (d, 1 H, *J* = 11.4 Hz, OCH_2Ph), 4.04 (d, 1 H, *J* = 11.4 Hz, OCH_2Ph), 4.02 (d, 1 H, *J* = 11.4 Hz, OCH_2-Ph), 4.02 (d, 1 H, *J* = 3.3 Hz, H-2‴), 3.95 (dt, 1 H, J_{gem} = 9.7 Hz, J_{vic} = 6.2 Hz, OCH_2CH_2), 3.89 (d, 1 H, *J* = 4.8 Hz, H-2″), 3.87−3.58 (m, 18 H, H-3, H-4, H-6a, H-6b, H-3′, H-4′, H-6a′, H-6b′, H-4″, H-5″, H-6b″, H-4‴, H-5‴, H-6a‴, H-6b‴, OCH_2-Ph), 3.55 (dd, $J_{3,4}$ = 9.0 Hz, H-3″), 3.48−3.43 (m, 3 H, H-5′, H-3‴, OCH_2CH_2), 3.32 (ddd, 1 H, $J_{4,5}$ = 9.3, $J_{5,6}$ = 1.8 Hz, $J_{5,6}$ = 4.0 Hz, H-5), 3.03 (t, 2 H, *J* = 7.0 Hz, $CH_2CH_2NH_2$), 2.70 (ABX_2, 2 H, SCH_2CH_2), 2.50 (t, 2 H, *J* = 6.7 Hz, OCH_2-

CH_2CH_2S), 1.79 (p, 2 H, $J = 6.7$ Hz, $OCH_2CH_2CH_2S$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 99.1($^1J_{C-H} = 167.3$ Hz, H-1″), 103.8 ($^1J_{C-H} = 158.3$ Hz, H-1‴), 100.9 ($^1J_{C-H} = 158.3$ Hz, H-1′), 101.9 ($^2J_{C-H} = 152.7$ Hz, H-1); EMS calcd for $C_{109}H_{120}Cl_3O_{17}S_2$ 1914.5, found 1914.6 correct isotope pattern.

Propyl (3,4,6-Tri-*O*-*p*-chlorobenzyl-1-thio-β-D-mannopyranosyl)(1→2)(2-*S*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-mannopyranosyl)(1→2)(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (31). Allyl glycoside (50 mg, 0.028 mmol) **29** was dissolved in THF (5 mL), ethanol (1 mL), and hydrazine hydrate (500 μL). The reaction was stirred open to the atmosphere for 3 h and then diluted with toluene. Concentration followed by column chromatography in toluene/EtOAc (8:1) gave the propyl glycoside as a colorless syrup (45 mg, 90%): $[\alpha]_D$ −68.5° (*c* 1.2, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.49−6.80 (52 H, Ar), 5.86 (d, H-1, $J_{1,2} = 0.9$ Hz, H-1″), 5.49 (s, 1 H, O_2CHPh), 5.48 (s, 1 H, H-1‴), 5.17 (s, 1 H, H-1′), 4.90 (d, 1 H, $J = 9.9$ Hz, OCH_2Ph), 4.90 (d, 1 H, $J_{2,3} = 3.5$ Hz, H-2′), 4.87 (d, 1 H, $J = 10.4$ Hz, OCH_2Ph), 4.83 (d, 1 H, $J = 10.8$ Hz, OCH_2Ph), 4.74 (d, 1 H, $J = 11.2$ Hz, OCH_2Ph), 4.67 (d, 1 H, $J = 2.4$ Hz, OCH_2Ph), 4.59 (d, 1 H, $J = 11.3$ Hz, OCH_2Ph), 4.59 (d, 1 H, $J = 12.5$ Hz, OCH_2Ph), 4.53 (d, 1 H, $J_{2,3} = 3.7$ Hz, H-2), 4.53 (d, 1 H, $J = 11.2$ Hz, OCH_2Ph), 4.48−4.39 (m, 8 H, 7(OCH_2Ph), H-6a″), 4.36 (d, 1 H, $J = 11$ Hz, OCH_2Ph), 4.33 (s, 1 H, H-1), 4.29 (d, 1 H, $J = 12.2$ Hz, OCH_2Ph), 4.04 (d, 1 H, $J = 11.6$ Hz, OCH_2Ph), 4.02 (d, 1 H, $J = 11.8$ Hz, OCH_2Ph), 4.00 (d, 1 H, $J = 2.9$ Hz, H-2‴), 3.91 (d, 1 H, $J = 4.8$ Hz, H-2″), 3.89−3.58 (m, 18 H, H-3, H-4, H-6a, H-6b, H-4′, H-6a′, H-6b′, H-4″, H-5″, H-6b″, H-4‴, H-5‴, H-6a‴, H-6b‴, OCH_2Ph, OCH_2CH_2), 3.56 (dd, 1 H, $J_{3,4} = 9.5$ Hz, H-3″), 3.53 (dd, 1 H, $J_{3,4} = 9.5$ Hz, H-3′), 3.46 (ddd, 1 H, $J_{4,5} = 9.3$ Hz, $J_{5,6} = 4.6$ Hz, $J_{5,6} = 1.7$ Hz, H-5′), 3.45 (dd, 1 H, $J_{3,4} = 7.5$ Hz, H-3‴), 3.30 (ddd, 1 H, $J_{4,5} = 9.9$ Hz, $J_{5,6} = 4.13$ Hz, $J_{5,6} = 1.8$ Hz, H-5), 3.27 (dt, 1 H, $J_{gem} = 9.3$ Hz, $J_{vic} = 6.9$ Hz, OCH_2CH_2), 1.53 (hextet, 2 H, $J = 7.0$ Hz, $OCH_2CH_2CH_3$), 0.85 (t, 2 H, $J = 7.0$ Hz, $OCH_2CH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2−136.3, 133.1, 133.0, 128.9−127.2, 102.0, 101.6, 101.2, 99.3, 83.9, 81.3, 80.3, 79.6, 79.3, 76.2, 75.9, 75.7, 75.6, 75.4, 75.4, 74.2, 74.2, 74.2, 73.8, 73.5, 72.8, 72.0, 70.2, 70.1, 70.0, 69.8, 69.7, 69.7, 69.6, 69.4, 68.6, 68.4, 68.4, 68.1, 68.0, 48.8, 22.9, 10.7; EMS calcd for $C_{107}H_{115}C_{l3}O_{17}S$ 1814.6, found 1814.6.

3-(2-Aminoethylthio)propyl (1-Thio-β-D-mannopyranosyl)(1→2)(2-deoxy-2-thio-β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)(1→2)-β-D-mannopyranoside (32). Tetrasaccharide (**30**) (40 mg, 0.021 mmol) was treated in a fashion similar to that used to form compounds **16**-**19** to yield **32** as a colorless glass (12 mg 79%); ^1H NMR (600 MHz, $CDCl_3$) δ 5.18 (s, H-1, H-1″), 5.02 (s, 1 H, H-1‴), 4.89 (s, 1 H, H-1′), 4.75 (s, 1 H, H-1), 4.39 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2′), 4.26 (d, 1 H, $J_{1,2}$ 3.1 Hz, H-2), 4.11 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-2‴), 4.01 (dt, $J_{gem} = 10.1$, $J_{vic} = 6.1$ Hz, $OCH_2CH_2CH_3$), 3.97 (dd, 1 H, $J_{gem} = 12.1$, $J_{5,6}$ 2.2 Hz, H-6a′), 3.94 (dd, 1 H, $J_{gem} = 12.1$, $J_{5,6}$ 2.2 Hz, H-6a), 3.93 (dd, 1 H, $J_{gem} = 9.7$, $J_{5,6}$ 1.6 Hz, H-6a‴), 3.91 (dd, $J_{3,4}$ 9.5 Hz, H-3″), 3.89 (dd, 1 H, $J_{gem} = 12.1$ Hz, $J_{5,6}$ 2.0 Hz, H-6a″), 3.82 (d, 1 H, $J_{1,2}$ 4.4 Hz, H-2″), 3.77−3.67 (m, 6 H, H-6b, H-6b′, H-6b″, H-6b‴, H-3, OCH_2CH_2), 3.66 (dd, 1 H, $J_{3,4}$ 9.9 Hz, H-3′), 3.63 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3‴), 3.58 (dd, 1 H, $J_{4,5}$ 9.7 Hz, H-4‴), 3.48 (dd, 1 H, $J_{3,4} \approx J_{4,5} = 9.7$ Hz, H-4), 3.47 (dd, 1 H, $J_{3,4} \approx J_{4,5} = 9.7$ Hz, H-4′), 3.45 (ddd, 1 H, H-5‴), 3.40−3.36 (m, 3 H, H-5′, H-5″, H-5‴), 3.27 (dd, 1 H, $J_{3,4} \approx J_{4,5} = 9.7$ Hz, H-4″), 3.16 (t, 2 H, J 6.6 Hz, $CH_2NH_3^+$), 2.84 (t, 2 H, J 6.8 Hz, $SCH_2CH_2NH_3^+$), 2.70−2.68 (m, 2 H, $OCH_2CH_2CH_2S$), 1.95 (p, 2 H, J 6.6 Hz, $OCH_2CH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.2 ($^1J_{C1-H1}$ 163.9 Hz, C-1″), 102.0 ($^1J_{C1-H1}$ 157.5 Hz, C-1′), 100.9 ($^1J_{C1-H1}$ 159.6 Hz, C-1), 86.7 ($^1J_{C1-H1}$ 157.5 Hz, C-1‴), 80.9, 80.1, 79.4, 77.6, 77.1, 74.7, 73.0, 72.8, 72.8, 69.3, 68.7, 68.6, 68.4, 67.6, 62.2, 61.8, 54.3, 39.4, 29.9, 29.6, 28.6; ES HRMS calcd for $C_{29}H_{54}NO_{20}S_2$ 800.2680, found 800.2676.

Propyl (1-Thio-β-D-mannopyranosyl)(1→2)(2-deoxy-2-thio-β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)-(1→2)-β-D-mannopyranoside (33). A solution of the propyl glycoside (**31**) (30 mg, 0.016 mmol) in THF (3 mL) and *tert*-butyl alcohol (1 mL) was added to freshly distilled ammonia (75 mL) containing sodium metal (100 mg) at −78 °C. The reaction was stirred at −78 °C for 20 min and then quenched with methanol. Ammonia was allowed to evaporate under a stream of argon, and the remaining solvent was removed under vacuum. The resulting solid was taken up in water (20 mL) and filtered through a 0.2 μM membrane. It was then brought to neutral pH with the addition of 5 M acetic acid and concentrated to a solid under vacuum. Purification on reversed-phase silica (C18) was accomplished with a water/methanol gradient to yield a colorless glass (10 mg 84%): ^1H NMR (800 Hz D_2O) δ 5.17 (s, 1 H, H-1″), 5.00 (s, 1 H, H-1‴), 4.88 (s, 1 H, H-1′), 4.73 (s, 1 H, H-1), 4.39 (d, 1 H, $J_{2,3} = 3.4$ Hz, H-2′), 4.24 (d, 1 H, $J_{2,3} = 3.7$ Hz, H-2), 4.10 (d, 1 H, $J_{2,3} = 3.4$ Hz, H-2‴), 3.95 (dd, 1 H, $J_{gem} = 12.2$ Hz, $J_{vic} = = 2.2$ Hz, H-6a′), 3.93 (dd, 1 H, $J_{gem} = 11.0$ Hz, $J_{vic} = = 2.2$ Hz, H-6a), 3.92 (dd, 1 H, $J_{gem} = 9.2$ Hz, $J_{vic} = = 2.2$ Hz, H-6a‴), 3.91 (dd, 1H, $J_{3,4} = 9.8$ Hz, H-3″), 3.87 (dd, 1 H, $J_{gem} = 12.6$, $J_{vic} = 2.2$ Hz, H-6a″), 3.86 (dt, 1 H, $J_{vic} = 6.6$ Hz, $J_{gem} = 9.5$ Hz, OCH_2CH_2), 3.80 (d, 1 H, $J_{2,3} = 4.6$ Hz, H-2″), 3.72 (dd, 1 H, $J_{5,6} = 6.1$ Hz, H-6b), 3.71 (dd, 1 H, $J_{5,6} = 7.1$ Hz, H-6b‴), 3.70 (dd, 1 H, $J_{5,6} = 6.5$ Hz, H-6b″), 3.68 (dd, 1 H, $J_{5,6} = 6.4$ Hz, H-6b′), 3.67 (dd, 1 H, $J_{3,4} = 9.4$ Hz, H-3), 3.67 (dd, 1 H, $J_{3,4} = 9.4$ Hz, H-3′), 3.62 (dd, 1 H, $J_{3,4} = 9.5$ Hz, H-3‴), 3.61 (dt, 1 H, $J_{vic} = 7.1$ Hz, OCH_2CH_2), 3.56 (dd, 1 H, $J_{4,5} = 9.5$ Hz, H-4‴), 3.47 (dd, 1 H, $J_{4,5} = 9.8$ Hz, H-4), 3.45 (dd, 1 H, $J_{4,5} = 9.7$ Hz, H-4′), 3.44 (ddd, 1 H, H-5‴), 3.39 (ddd, 1 H, H-5′), 3.37 (ddd, 1 H, H-5″), 3.36 (ddd, 1 H, H-5), 3.25 (dd, 1 H, $J_{4,5} = 9.5$ Hz, H-4″), 1.62 (p, 2 H, $J = 7.0$ Hz, $OCH_2CH_2CH_3$), 0.93 (t, 3 H, $CH_2CH_2CH_3$); ^{13}C NMR (125 Hz, $CDCl_3$), 102.2 ($^1J_{C-H} = 162.4$ Hz, C-1′), 102.0 ($^1J_{C-H} = 163.4$ Hz, C-1″), 101.8 ($^1J_{C-H} = 159.5$ Hz, C-1), 86.7 ($^1J_{C-H} = 157.6$ Hz, C-1‴), 80.9 (C-5‴), 80.3 (C-2), 79.4 (C-2′), 77.6, 77.1, 77.1(C-5, C-5′, C-5″), 74.7 (C-3‴), 72.9−72.6 (C-3, C-3′,C-3″), 72.6 (OCH_2CH_2), 68.7, 68.6, 68.4 (C-4, C-4′, C-4″), 67.6 (C-4‴), 62.2−61.7 (C-6, C-6′, C-6″, C-6‴), 54.3 (C-2″), 23.3 ($CH_2CH_2CH_3$), 10.8 (CH_2CH_3); ES HRMS calcd for $C_{27}H_{48}NaO_{20}S$ 747.2357, found 747.2352.

1-[3-(2-Aminoethylthio)propyl (β-D-Mannopyranosyl)-(1→2)-β-D-mannopyranoside]-2-ethoxycyclobutene-3,4-dione (34). Amine **11** (7 mg) was dissolved in a 1:1 solution of ethanol/water (2 mL), and 3,4-diethoxy-3-cyclobutene-1,2-dione (8 μL, 5 equiv) was added. A saturated solution of sodium carbonate was then added in 2 μL aliquots, allowing the reaction to stir for 5 min between additions. The addition was continued until TLC analysis indicated the free amine had been completely converted into a faster moving product. The reaction mixture was then concentrated and purified by HPLC on C18 silica gel to give **34** (6 mg 74%): ^1H NMR (600 MHz, D_2O) δ 4.85, 4.83 (s, 1 H, H-1′), 4.77, 4.73 (q, 2 H, OCH_2CH_3), 4.72 (s, 1 H, H-1), 4.25 (br s, 1 H, H-2), 4.12 (br, s, 1 H, H-2′), 3.99 (dt, 1 H, $J_{gem} = 9.2$ Hz, $J_{vic} = 7.1$ Hz, OCH_2CH_2), 3.91−3.94 (m, 2 H, H-6a, H-6a′), 3.83 (t, $J_{vic} = 6.81$ Hz, SCH_2CH_2NH), 3.77−3.72 (m, 4 H, H6b, H6b′, OCH_2CH_2, SCH_2CH_2NH), 3.65−3.55 (m, 4 H, H-3, H-3′, H-4, H4′), 3.40−3.33 (2 H, m, H-5, H-5′), 2.82 (t, 2 H, $J_{vic} = 6.4$ Hz, SCH_2CH_2NH), 2.69 (t, 2 H, $J = 6.6$ Hz, $CH_2CH_2CH_2S$), 1.94−1.89 (m, 2 H, $OCH_2CH_2CH_2S$); 1.47, 1,44 (t, J 6.8 Hz, OCH_2CH_3); ES HRMS calcd for $C_{23}H_{37}NO_{14}SNa$ 606.1832, Found 606.1823.

1-[3-(2-Aminoethylthio)propyl (β-D-Mannopyranosyl)-(1→2)(β-D-mannopyranosyl)(1→2)-β-D-mannopyranoside]-2-ethoxycyclobutene-3,4-dione (35). Amine **12** (14 mg) was treated with diethyl squarate as described above to give **35** (13 mg, 78%): ^1H NMR (600 MHz, D_2O) δ 4.95 (s, 1 H, H-1″), 4.93, 4.90 (s, 1 H, H-1′), 4.77, 4.73 (q, 2 H, OCH_2CH_3), 4.71 (s, 1 H, H-1), 4.34 (br s, 1 H, H-2′), 4.22 (br s, 1 H, H-2), 4.15 (d, 1 H, $J_{2,3} = 3.1$ Hz, H-2″), 3.99 (dt, 1 H, $J_{gem} = 10.1$ Hz, $J_{vic} = 5.6$ Hz, OCH_2CH_2), 3.94−3.91 (m, 3 H, H-6a, H6a′, H6a″), 3.83 (t, $J_{vic} = 6.4$ Hz, SCH_2CH_2NH), 3.77−3.71 (m, 5 H, H-6b, H-6b′, H6b″, OCH_2CH_2, SCH_2CH_2NH), 3.67 (dd, 1 H, $J_{2,3} = 3.3$ Hz, $J_{3,4} = 9.9$ Hz, H-3), 3.64−3.56 (m, 4 H, H-3′, H-3″, H-4′, H4″), 3.49 (dd, 1 H, $J_{3,4} \approx J_{4,5} = 9.7$ Hz, H-4), 3.38−3.34 (m, 3 H, H-5, H-5″, H-5″), 2.83 (t, 2 H, $J_{vic} = 6.4$ Hz, SCH_2CH_2NH), 2.70 (m, 2 H, $CH_2CH_2CH_2S$), 1.94−1.90 (m, 2H, $OCH_2CH_2CH_2S$), 1.47, 1.45 (t, J 7.1 Hz, OCH_2CH_3); ES HRMS calcd for $C_{29}H_{47}NO_{19}NaS$ 768.2361, found 768.2370.

1-[3-(2-Aminoethylthio)propyl (β-D-Mannopyranosyl)-(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)-

(1→2)-β-D-mannopyranoside]-2-ethoxycyclobutene-3,4-dione (36). The amine **13**[4] (6 mg) was treated with diethyl squarate as described above to give **36** (5.2 mg, 74%): ^{1}H NMR (600 MHz, D_2O) δ 5.03 (s, 1 H, H-1″), 4.93 (s, 1 H, H-1‴), 4.90, 4.89 (s, 1 H, H-1′), 4.77, 4.73 (q, 2 H, OCH_2CH_3), 4.71 (s, 1 H, H-1), 4.40 (br s, 1 H, H-2″), 4.32 (br s, 1 H, H-2′), 4.23 (br s, 1 H, H-2), 4.16 (d, 1 H, $J_{2,3}$ = 2.6 Hz, H-2‴), 3.99 (dt, 1 H, J_{gem} = 10.1 Hz, J_{vic} = 5.9 Hz, OCH_2CH_2), 3.95−3.91 (m, 4 H, H-6a, H-6a′, H-6a″, H-6a‴), 3.83 (t, J_{vic} = 6.4 Hz, SCH_2CH_2NH), 3.78−3.55 (m, 8 H, H-3, H-3′, H-3″, H-3‴, H-4″, H-4‴,OCH_2CH_2, SCH_2CH_2NH),, 3.50 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.7 Hz, H-4′), 3.49 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.9 Hz, H-4), 3.40−3.34 (m, 4-H, H-5, H-5′, H-5″, H-5‴), 2.83 (t, 2 H, J_{vic} = 6.6 Hz, SCH_2CH_2NH), 2.70 (m, 2 H, $CH_2CH_2CH_2S$), 1.96−1.88 (m, 2H, $OCH_2CH_2CH_2S$), 1.47, 1.45 (t, J = 7.1 Hz, OCH_2CH_3); ES HRMS (M + Na) calcd 930.2888, found 930.2871.

1-[3-(2-Aminoethylthio)propyl (β-D-Mannopyranosyl)-(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)-(1→2)(β-D-mannopyranosyl)(1→2)(β-D-mannopyranosyl)-(1→2)-β-D-mannopyranoside]-2-ethoxycyclobutene-3,4-dione (37). The amine **14** (4.0 mg) was treated with diethyl squarate as described above to give **37** (3.1 mg, 71%): ^{1}H NMR (600 Hz D_2O) δ 5.06 (1 H, s, H-1⁗), 5.02 (1 H, s, H-1″), 5.01 (1 H, s, H-1‴), 4.96 (1 H, s, H-1⁗′), 4.91, 4.89 (1 H, s, H-1′), 4.78, 4.73 (q, 2 H, OCH_2CH_3), 4.71 (1 H, s, H-1), 4.39 (2 H, br s, H-2″, H-2⁗), 4.37 (1 H, d, $J_{2,3}$ = 3.3 Hz, H-2‴), 4.32 (1 H, br s, H-2′), 4.23 (1 H, br s, H-2), 4.08 (1 H, d, $J_{2,3}$ = 3.1 Hz, H-2⁗′), 3.99 (1 H, dt, J_{vic} = 6.0 Hz, J_{gem} = 9.9 Hz, OCH_2CH_2), 3.95−3.91 (m, 6 H, H-6, H-6′, H-6″, H-6‴, H-6⁗, H-6⁗′), 3.91 (t, J_{vic} = 6.4 Hz, SCH_2CH_2NH), 3.77−3.35 (m, 26 H), 2.83 (t, 2 H, J_{vic} = 6.4 Hz, SCH_2CH_2NH), 2.70 (m, 2 H, $CH_2CH_2CH_2S$), 1.96−1.88 (m, 2H, $OCH_2CH_2CH_2S$), 1.47, 1.44 (t, J 7.1 Hz, OCH_2CH_3); EMS (M + Na) calcd 1254.4, found 1254.3.

1-[3-(2-Aminoethylthio)propyl (1-Thio-β-D-mannopyranosyl)(1→2)(2-deoxy-2-thio-β-D-mannopyranosyl)(1→2)-(β-D-mannopyranosyl)(1→2)-β-D-mannopyranoside]-2-ethoxycyclobutene-3,4-dione (38). Amine **33** (9 mg) was treated with diethyl squarate as described above to give **38** (9 mg, 89%): ^{1}H NMR (600 MHz, CDCl3) δ 5.17 (s, 1 H, H-1″), 5.01 (s, 1 H, H-1‴), 4.90, 4.88 (s, 1 H, H-1′), 4.78, 4.73 (q, 2 H, OCH_2CH_3), 4.72 (s, 1 H, H-1), 4.38 (br s, 1 H, H-2′), 4.23 (br s, 1 H, H-2), 4.07 (d, 1 H, $J_{1,2}$ = 3.3 Hz, H-2‴), 4.00 (dt, J_{gem} = 10.1 Hz, J_{vic} = 5.2 Hz, $OCH_2CH_2CH_2$), 3.97−3.89 (m, 4 H, H-6, H-6′, H-6″,H-3″,H-6‴), 3.83 (t, J_{vic} = 6.3 Hz, SCH_2CH_2NH), 3.81 (d, 1 H, $J_{1,2}$ = 4.8 Hz, H-2″), 3.74−3.62 (m, 9 H, H-6, H-6′, H-6″, H-6‴, H-3, H-3′, H-3‴OCH_2CH_2, SCH_2CH_2NH), 3.58 (dd, $J_{4,5}$ = 9.6 Hz, H-4‴), 3.48 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.5 Hz, H-4), 3.47 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.6 Hz, H-4′), 3.45 (ddd, 4 H, H-5‴), 3.44−3.34 (m, 3 H, H-5′, H-5″, H-5‴), 3.27 (dd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.6 Hz, H-4″), 2.83 (t, 2 H, J_{vic} = 6.3 Hz, SCH_2CH_2NH), 2.70 (m, 2 H, $CH_2CH_2CH_2S$), 1.96−1.88 (m, 2H, $OCH_2CH_2CH_2S$), 1.47, 1.44 (t, J 7.1 Hz, OCH_2CH_3); EMS (M + Na) calcd 946.3, found 946.3.

Glycoconjugates. The general procedure for generating protein−carbohydrate conjugates was as follows: BSA (∼20 mg/mL) was dissolved in borate buffer (Na_2BO_4 0.07M, $KHCO_3$ 0.035 M, pH 9.0). The squarate coupled carbohydrate was then added, and the reaction was left for 72 h at room temperature. The reaction was then diluted with deionized water and dialyzed in a MICROSEP microconcentrator against changes changes of deionized water (3 mL) where the final volume after concentration was no greater than 500 μL. The solution from the final concentration was then lyphophilized to a white solid.

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Supporting Information Available: ^{1}H NMR spectra for compounds **5**, **6**, **11**, **12**, **14**−**19**, **24**−**29**, and **31**−**36**. This material is available free of charge via the Internet at http://pubs.acs.org.

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