Synthesis of Tethered Trisaccharides To Probe Inter-Saccharide Flexibility in Carbohydrate−Protein Interactions

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Two crystal structures of the trisaccharide epitope α-D-Gal*p*(1→2)[α-D-Abe*p*(1→3)α-D-Man*p*1→OCH_3 **1** bound to antibody Fab and single-chain Fv fragments have been used to guide the design of an intramolecular tether that constrains the trisaccharide ligand to conformations close to those of the bound state. Preorganization of the ligand should overcome entropic penalties to binding and provide enhanced affinity. Three tethers [$O(CH_2)_nO$, n = 6, 7, and 8] were used to anchor the solvent-exposed C6 atoms of the mannose and galactose residues. Two synthetic schemes were employed. The first utilized an ethyl 1-thiogalactoside bearing the tether protected as a trityl ether **6**−**8**. Glycosylation of the mannopyranoside **5** that contains a methanesulfonate at C6 by any of the donors **6**−**8** afforded disaccharides **37**−**39**. Subsequent removal of the trityl group allowed an alkoxide to be generated on the ω-hydroxyl group of the tether for displacement of the sulfonate in 38% yield. By comparison when a ω-methanesulfonyloxy tether was incorporated as the mannoside **9**, the disaccharide product **52** after reaction with the galactosyl donor **10** was converted to the macrocycle **4** in 61% yield. The 3,6-dideoxy-*xylo*-hexopyranose residue was introduced by thioglycoside chemistry to yield the protected, tethered trisaccharide target molecules **49**−**51**, which were deprotected in a single hydrogenation step. Solid-phase enzyme immunoassays showed the tethered trisaccharides **2**−**4** to be weaker inhibitors than trisaccharide **1** (+0.2−0.3 kcal mol^{-1}). This suggests that preorganization of oligosaccharides provides negligible gains in binding affinity.

Introduction

To assess the effect of interresidue flexibility on the free energy of association between oligosaccharides and their protein receptors, a series of tethered trisaccharides has been designed and synthesized. The model system selected is based upon a monoclonal antibody−trisaccharide complex for which several protein crystal structures are available.[1−3] This structural detail simplifies the selection of solvent-exposed portions of the saccharide that avoid contact with the protein surface and hence are suitable sites for tethering.

Carbohydrate−protein interactions are notable for the weak affinity that characterizes association between oligosaccharides and lectins,[4−7] antibodies,[8,9] and enzymes.[10,11] Other small ligands such as steroids[12] and peptides[13] exhibit K_A values for their respective antibodies that are several orders of magnitude higher than those observed for sugars. There is evidence to suggest that when oligosaccharides are part of larger macromolecules, interactions between protein receptors and oligosaccharide exhibit higher intrinsic affinity.[4] The increase in univalent association could arise through preorganization of the oligosaccharide via steric factors and protein−oligosaccharide interactions inherent to each glycoprotein.[14] Since low molecular weight oligosaccharides or molecules derived from them are potential candidates for therapeutic intervention in cell−cell interactions,[15−17] it is of considerable interest to probe the effect of restricted oligosaccharide flexibility on the association between ligand−protein complexes of known structure. For example, is it possible to significantly increase affinity by reducing interresidue flexibility so that the oligosaccharide ligand is preorganized in its bound state, thereby avoiding entropic losses that arise from freezing-out a small set of bound conformers from

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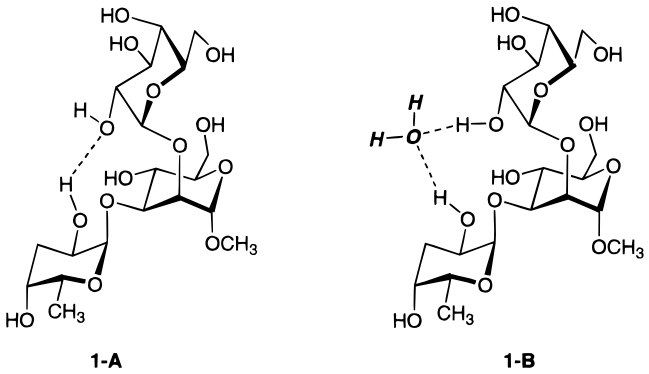


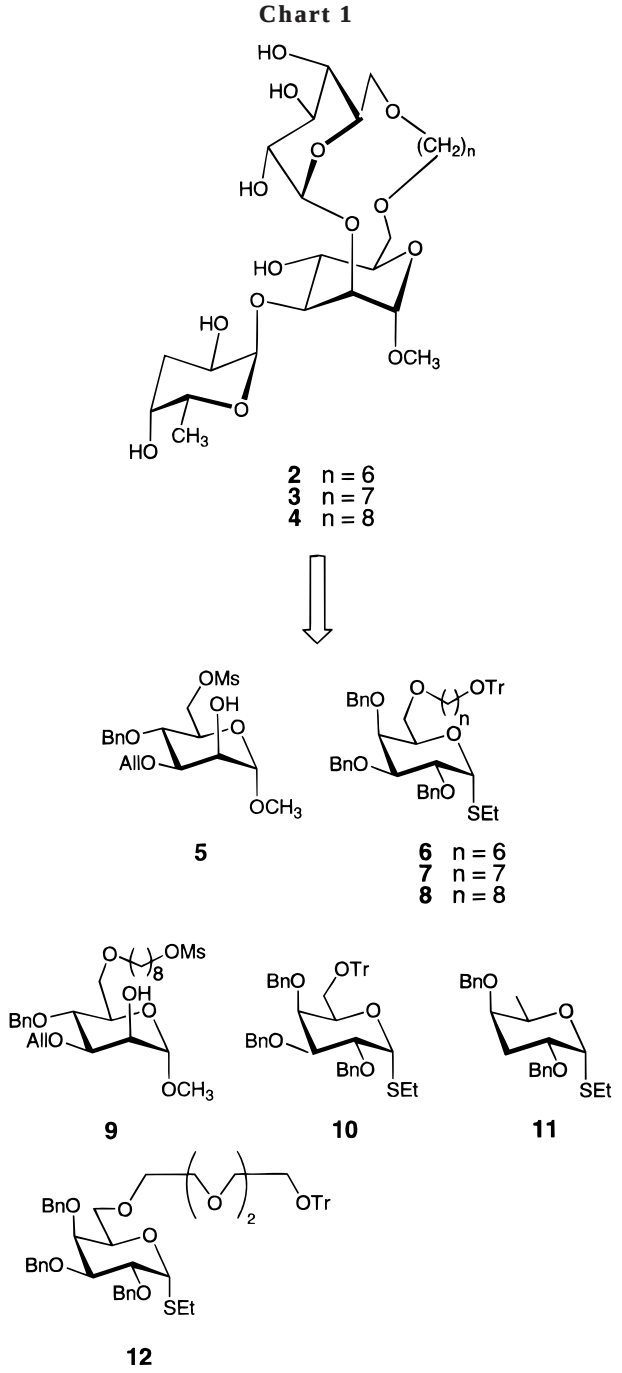
Figure 1. (A) A direct Abe O-2 to Gal O-2 hydrogen bond was observed in the crystal structure of Se155.4 antibody complex with trisaccharide **1**[2]. (B) When trisaccharide **1** was crystallized with a single chain antibody, the oligosaccharide forms a Abe O-2 to Gal O-2 hydrogen bond bridged by a water molecule.

the large number of conformational families that are sampled by typical oligosaccharides?

A large, favorable enthalpy of association compensated by unfavorable entropy observed for lectin−oligosaccharide complex formation is cited as supporting evidence for the dominant role of inter-saccharide flexibility as a determinant of weak sugar−protein binding constants.[4,18] The entropic barrier associated with the loss of degrees of freedom when an oligosaccharide binds to a protein receptor has been estimated to be as large as 1−2 kcal mol^{-1} for each glycosidic torsional angle immobilized.[18] Estimates from other work suggest values in the range ~0.6 kcal mol^{-1} per torsion angle.[19,20] On the basis of the results of extensive molecular recognition studies for a large number of lectins and antibodies, Lemieux has suggested that enthalpy−entropy compensation has its origins in solvation effects at polyamphiphilic surfaces.[5,6] Support for this interpretation has come from thermodynamic solvent isotope effects determined by titration microcalorimetry.[21]

To probe the entropic barrier resulting from flexibility about glycosidic bonds and to place an empirical estimate on its cost to overall free energy of association, it is necessary to synthesize a relatively rigid oligosaccharide. Ideally such a derivative would preserve the enthalpic stabilization while reducing the entropic barrier. This could be accomplished by reducing interresidue flexibility with a tether that avoids contact with the protein surface and maintains the distribution of three-dimensional structures to sets that populate the conformation of the bound state. We realized that the structure of the complex between monoclonal antibody Se-155.4 and its trisaccharide ligand **1** were ideally suited to this purpose since the conformation in the bound state places the primary hydroxyl groups of the partially solvent-exposed galactose and mannose residues in positions that are both solvent exposed and well removed from the protein surface (Figure 1). Trisaccharide **1** has been observed in one of two bound conformations, **1-A** and **1-B**, which correspond to the interatomic distances Man O-6 to Gal O-6 of 7.5 and 5.7 Å, respectively. To satisfy these distance constraints as well as preserve the interresidue distances between the abequose and galactose residues, three tethered trisaccharide **2**−**4** were selected as targets for synthesis. The synthesis and characterization of these molecules is reported here, together with binding data from a solid-phase assay.

Chart 1



Results

Strategy. Retrosynthetic analysis suggested the use of the multifunctionalized monosaccharide **5** and the galactose synthons **6**−**8** to construct tethered disaccharides enroute to the target trisaccharides **2**−**4** (Chart 1). The mannose acceptor **5** contains a good leaving group at the exocyclic C-6 atom for attack by the alkoxide of the tether, that is preassembled as part of the galactosyl

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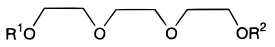
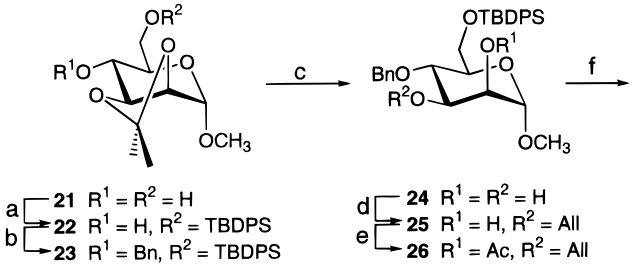
Chart 2

13 R^1 = Tr, R^2 = H, n = 6
14 R^1 = Tr, R^2 = H, n = 7
15 R^1 = Tr, R^2 = H, n = 8
16 R^1 = Tr, R^2 = Ms, n = 6
17 R^1 = Tr, R^2 = Ms, n = 7
18 R^1 = Tr, R^2 = Ms, n = 8



19 R^1 = Tr, R^2 = H
20 R^1 = Tr, R^2 = Ms



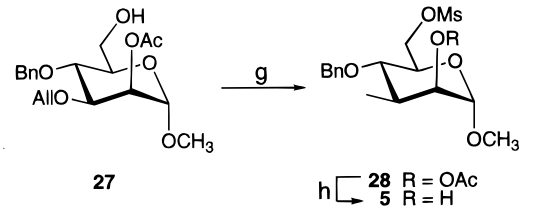


Figure 2. Conditions: (a) *t*-$BuPh_2SiCl$, DMAP, CH_2Cl_2, 93%; (b) BnBr, NaH, DMF, 84%; (c) aq, 80%, HOAc, 84%; (d) Bu_2SnO, Et_4NI, AllBr, 92%; (e) Ac_2O, pyridine, 84%; (f) TBAF, THF, 85%; (g) MsCl, pyridine, CH_2Cl_2, 88%; (h) NaOMe, MeOH, 95%.

donors **6**−**8**. An alternative approach reverses the positions of the leaving group and nucleophile so that the leaving group is placed on the tether as part of the mannose glycoside **9**. The corresponding galactose synthon **10** would then provide an alkoxide nucleophile after glycosylation of **9** and selective deprotection steps of the intermediate disaccharide. In both instances the six, seven, and eight carbon tethers could be accessed from the corresponding diols protected as their *ω*-trityl methanesulfonates **16**−**18** (Chart 2). The final steps of either approach involve selective deprotection of the allyl ether of a tethered disaccharide and reaction with 3,6-dideoxyhexose donor **11**.[22] A less hydrophobic tether based on triethylene glycol was envisaged, and for this purpose the galactosyl donor **12** could be synthesized following an approach similar to that used to synthesize compounds **6**−**8**.

Preparation of Monosaccharide Building Blocks. The selectively protected acetonide **23** was a common starting point for the high-yield syntheses of the mannose synthons **5** and **9** (Figures 2 and 3). The readily prepared

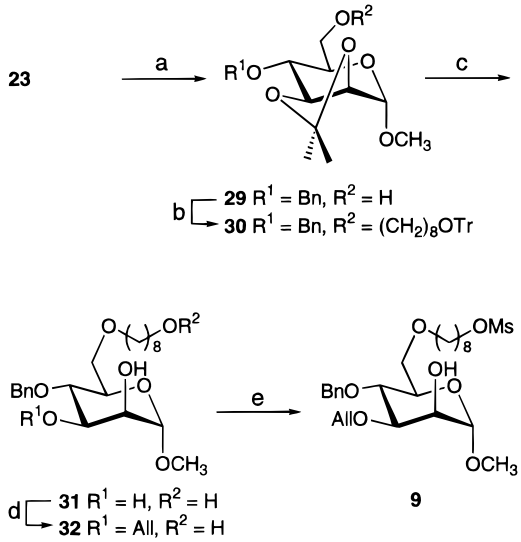


Figure 3. Conditions: (a) TBAF, THF, 86%; (b) **18**, NaH, THF, 65 °C, 84%; (c) TSA, MeOH:EtOAc (9:1), 48 h, 80%; (d) Bu_2SnO, Bu_4NI, AllBr, 70%; (e) MsCl, pyridine, CH_2Cl_2, 73%.

acetonide[23] **21** was first protected as its *tert*-butyldiphenylsilyl ether **22** and then benzylated under standard conditions to give **23**.[24] Treatment with aqueous acetic acid followed by regioselective allylation employing dibutyltin oxide[25] afforded the selectively protected alcohol **25** via the diol **24**. Temporary protection at O-2 was achieved by acetylation (**26**), followed by cleavage of the silyl ether (**27**), and then methanesulfonylation provided the fully protected monosaccharide **28**. Transesterification gave the selectively protected glycoside **5**, which functions as an acceptor to the glycosyl donors **6**−**8**.

By converting **23** to the primary alcohol derivative **29**, the alternate glycosyl acceptor **9** may be accessed in five steps (Figure 3). Alkylation of the primary alcohol with **18** introduced the tether protected as its trityl ether **30**. The isopropylidene and trityl groups were cleaved by treatment of **30** with *p*-toluenesulfonic acid at room temperature. The resulting triol **31** was reacted with dibutyltin oxide in methanol, and the intermediate stannane was regioselectively alkylated by allyl bromide in the presence of tetrabutylammonium iodide[25] to afford the diol **32**. The primary alcohol moiety of **32** was selectively esterified to give the glycosyl acceptor **9**.

The three galactosyl donors **6**−**8** each with a different sized tether attached at O-6 were prepared starting from the ethyl 1-thiogalactopyranoside **33**[26] (Figure 4). Protection of the primary hydroxyl group as its *tert*-butyldiphenylsilyl ether **34** followed by per-O-benzylation and hydrolysis of the silyl ether **35** gave the tri-O-benzylated thioglycoside **36**. Hexane, heptane, and octane diols were first converted to the monotrityl ethers **13**,[27] **14**, **15**.[28] These were then derivatized as the corresponding *ω*-trityl methanesulfonates **16**−**18**. Alkylation of **36** by the

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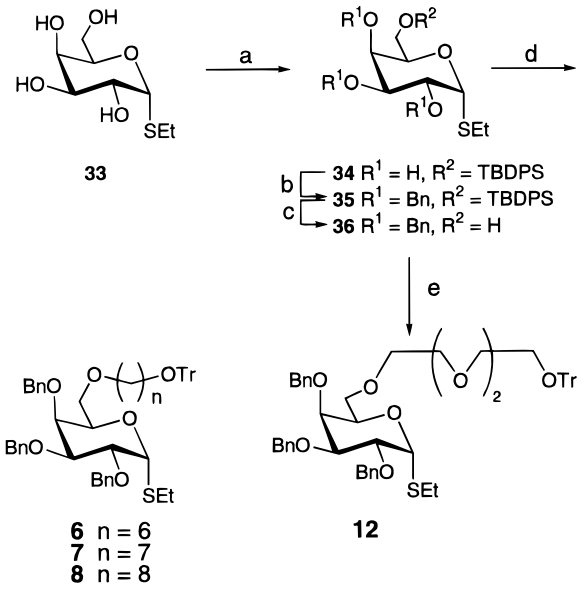

Figure 4. Conditions: (a) *t*-BuPh$_2$SiCl, imidazole, DMF, 88%; (b) NaH, BnBr, DMF, 74%; (c) TBAF, THF, 95%; (d) NaH, THF, **16** (**17** or **18**), 85−91%; (e) NaH, THF, **20**, 89%.

protected alkanediols yielded the respective six, seven, and eight carbon ether derivatives **6**−**8**. Triethylene glycol was derivatized in fashion similar to give **20**[29] and then the galactosyl donor **12** by reaction with the thiogalactoside **36**. The 3,6-dideoxyhexose donor **11** was synthesized from glucose according to a previously published method.[22]

Assembly of the Tethered Trisaccharide. The thiogalactoside **6** was activated in situ by *N*-iodosuccinimide/triflic acid in the presence of the selectively protected mannopyranoside **5** to give disaccharide **37** in 77% yield (Figure 5). Cleavage of the trityl ether gave the alcohol **40**. Slow addition of the alcohol **40** to a boiling mixture of sodium hydride and Cs_2CO_3 in THF resulted in a 38% yield of the fully protected and tethered disaccharide **43**. An identical sequence of reactions was employed to synthesize the disaccharides **44** and **45**, tethered by the C_7 and C_8 linkers. The yields of each step were comparable to those obtained in the synthesis of the C_6-tethered disaccharide **43**.

A more efficient synthesis of the tethered disaccharide **45** was accomplished by placing the leaving group on the tether attached to the mannose residue and displacing it with the alkoxide generated at C-6 of the galactose residue (Figure 6). The 6-*O*-trityl galactosyl donor **10** reacted with the mannose alcohol **9** under NIS/triflic acid activation to give the disaccharide **52**. Removal of the trityl ether gave the alcohol **53**, and under reaction conditions similar to those described to tether the disaccharides **40**−**42**, this route resulted in a 61% yield of the macrocycle **45**. The approach was not applied to the synthesis of **43** and **44** since there was insufficient material available to complete the syntheses.

The three disaccharides **43**−**45** were selectively deprotected at O-3 of the mannose residue by a base-catalyzed isomerization of the allyl ethers.[30] The isopropenyl ether intermediates were not isolated but hydrolyzed by an aqueous solution of mercuric chloride. Each of the disaccharide alcohols **46**−**48** was isolated in ∼85% yield. The abequose thioglycoside donor **11** was activated by NIS/silver triflate, and the trisaccharides **49**−**51** were isolated in 54−62% yields (Figure 5). Deprotection of the tethered trisaccharides was accomplished in a single hydrogenation step to yield **2**−**4** (Figure 7).

Attempts to tether the disaccharide by a triethylene glycol spacer were unsuccessful. The galactosyl donor **12** was used to successfully glycosylate the mannopyranoside alcohol **5** under conditions similar to those employed for the synthesis of **39**. The trityl ether of the resulting disaccharide **54** was selectively cleaved to give the alcohol **55**. However, reaction of **55** under the basic conditions employed to yield the macrocycles **43**−**45** failed to yield the tethered disaccharide target molecule (Figure 8). The failure of this reaction is attributed to the strong preference of the triethylene glycol tether for *syn clinal* conformers about the C−C bonds linking oxygen heteroatoms. Several torsional angles in the tether have to adopt near eclipsed conformations in order to close the macrocycle, and this presumably provides a sufficiently elevated energy barrier to the formation of the tethered product from **55**.

The stereochemistry of the newly formed glycosidic bonds was conveniently established by proton homonuclear ^3J coupling constants. As both glycosyl donors possessed the *galacto* configuration, the chemical shift and ^3J coupling constants unambiguously established the α configuration of the Abe-Man and Gal-Man anomeric linkages[31] in the protected oligosaccharides. This was confirmed for the tethered molecules **2**−**4** by the heteronuclear ^1J coupling constants at each anomeric center.[32] A thorough NMR study of **2**−**4** by multidimensional NMR methods established the assignment of all proton and carbon-13 resonances prior to conformational analysis employing NOE measurements and molecular dynamics calculations.[33] These studies showed that the tethers succeeded in constraining the range of motions in compounds **2**−**4** close to torsional angles found in the bound conformer **1B** (Figure 1).

Biological Activity. Affinity-purified Se-155.4 antibody absorbed to enzyme immunoassay microtiter plates was allowed to compete for biotin-labeled polysaccharide antigen[34,35] in the presence and absence of inhibitors **1**−**4**. The inhibition data show that the inhibitory powers of tethered trisaccharides **2**−**4** are comparable to but slightly less than that of the native trisaccharide **1** (Figure 9). Estimates of IC_{50} values for **2**−**4** suggest an approximate free energy difference, $\Delta\Delta G \approx 0.2-0.3$ kcal mol^{-1} relative to the reference trisaccharide **1.** More precise calorimetry data showed that the free energy difference $\Delta\Delta G \approx 0.1$ kcal mol^{-1} is even smaller.[33]

Discussion

The most serious obstacles to be overcome in the generation of constrained epitopes is the avoidance of

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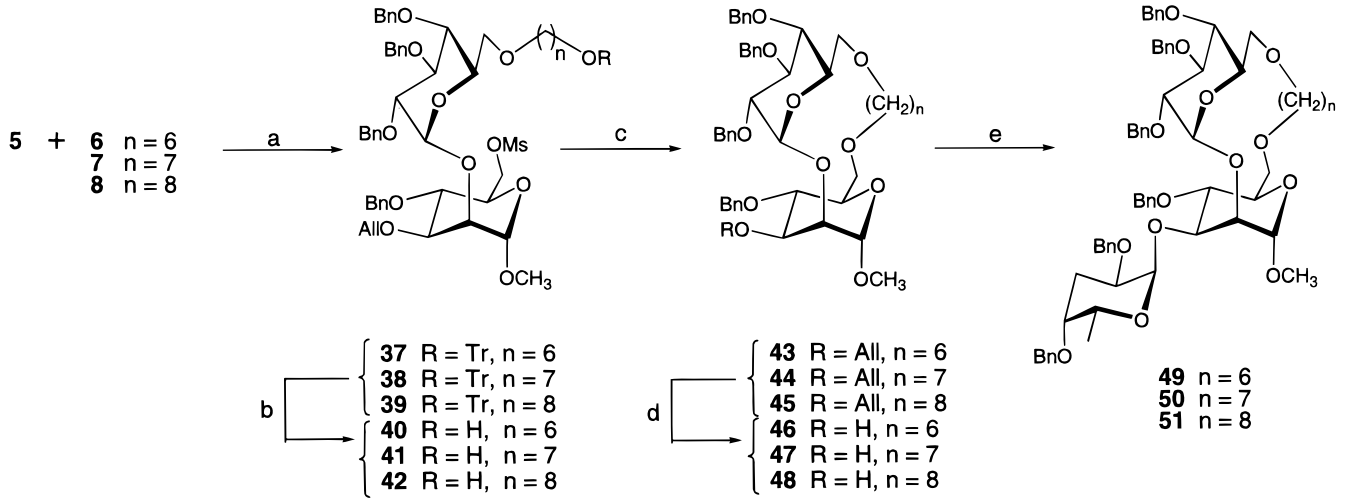

Figure 5. Conditions: (a) NIS, TfOH, CH_2Cl_2, 77%; (b) TSA, MeOH/EtOAc, 85−87%; (c) NaH, Cs_2CO_3, THF, 85 °C, 34−38%; (d) (i)KO^{t}Bu, DMSO, (ii) HgO, $HgCl_2$, H_2O, 85%; (e) **11**, NIS, AgOTf, 4AMS, CH_2Cl_2, PhMe, 54−62%.

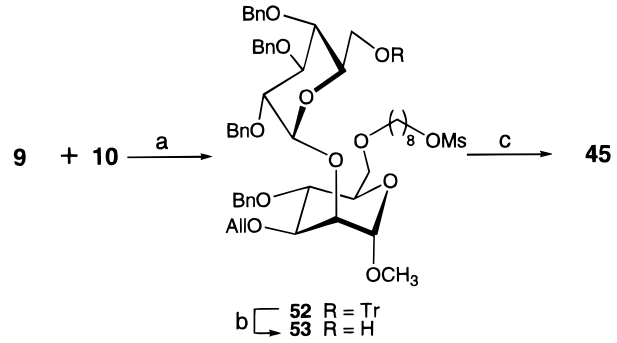

Figure 6. Conditions: (a) NIS, TfOH, CH_2Cl_2, 82%; (b) TSA, MeOH/EtOAc, 81%; (c) NaH, Cs_2CO_3 THF, 85 °C, 61%.

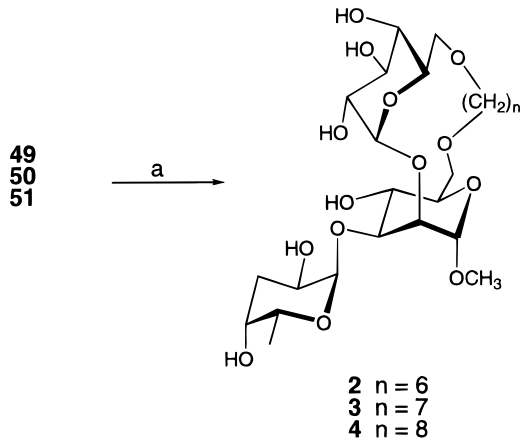

Figure 7. Conditions: (a) H_2, Pd/C, HOAc, 83−90%.

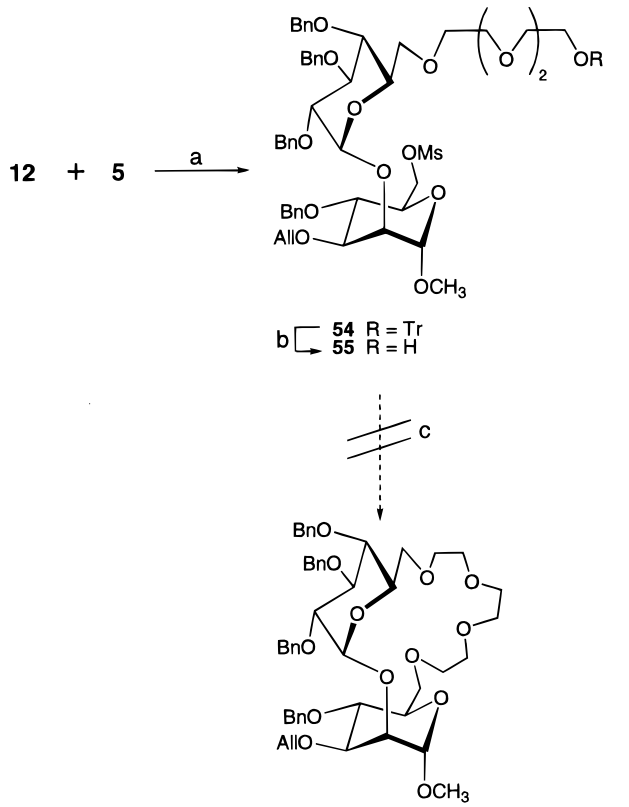

Figure 8. Conditions: (a) NIS, TfOH, CH_2Cl_2, 74%; (b) TSA, MeOH/EtOAc, 80%; (c) NaH, Cs_2CO_3, THF, 85 °C.

steric clashes between the tether and protein binding site and the fidelity with which the bound conformation is reproduced. However, in the example reported here two solved crystal structures of ligand−antibody complexes ensured that the former was not an issue, while NMR studies confirmed that the linkages adopted constrained torsional angles that spanned those of the bound state.[33] Several investigators have synthesized constrained oligosaccharides to probe binding strength with antibodies,[36] enzymes,[11] bacterial adhesins/toxins,[37] and lectins.[38,39] Where binding has been measured, the improvement in ΔG has been modest.[11,36−38] The data for trisaccharides **2**−**4** are consistent with these observations and suggest that the preordering of glycosidic bond conformation is an approach in the search for tight binding sugar-based inhibitors, which by itself seems unlikely to facilitate the design of carbohydrate-based therapeutics.

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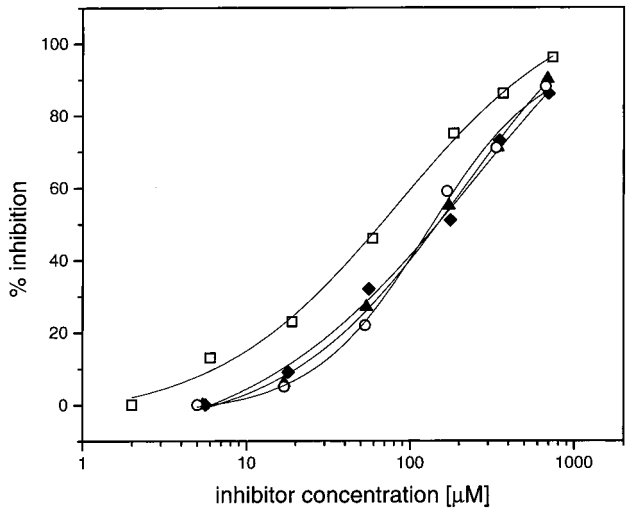

Figure 9. Affinity-purified Se155.4 antibody was coated on microtiter plates. Biotin-labeled *O*-polysaccharide antigen was allowed to bind to antibody coated plates in the presence and absence of inhibitors **1**−**4**. Percentage inhibition is plotted against molar concentration: trisaccharide **1**, □; trisaccharide **2**, ♦; trisaccharide **3**, ○; trisaccharide **4**, ▲.

Experimental Section

Optical rotations were measured with a polarimeter at 22 ± 2 °C. TLC was performed on silica gel 60-F_{254} (E. Merck, Darmstadt) with detection by quenching of fluorescence and/or by charring with 5% sulfuric acid in ethanol. Iatrobeads refers to a beaded silica gel 6RS-8060 manufactured by Iatron Laboratories (Tokyo). All commercial reagents were used as supplied, and chromatography solvents were distilled prior to use. Column chromatography was performed on silica gel 60 (E. Merck 40−60 μM, Darmstadt) or Iatrobeads. ^{1}H NMR spectra were recorded either at 360 or at 500 MHz and are referenced to either internal $CHCl_3$ (δ 7.24, $CDCl_3$) or internal acetone (δ 2.225, D_2O). ^{13}C NMR spectra were recorded either at 75.5 or at 125 MHz and are referenced to either internal $CHCl_3$ (δ 77.0, $CDCl_3$) or internal acetone (δ 37.01, D_2O). The assignments of resonances for the target compounds **2**−**4** were made by two-dimensional homonuclear and heteronuclear shift correlation experiments. Organic solutions were dried prior to concentration under vacuum at < 40 °C (bath). Microanalyses were carried out by the analytical service at this department, and all samples submitted for elemental analyses were dried overnight under vacuum with phosphorus pentoxide at 56 °C (refluxing acetone). Fast atom bombardment mass spectra were recorded on samples suspended in Cleland's matrix with xenon as the bombarding gas. Electrospray high-resolution mass spectra (ES HRMS) were recorded on a ZabSpecTOF mass spectrometer for aqueous solution of deprotected oligosaccharides.

Solid-phase immunoassay (EIA) was performed as previously described.[34,35] The data were plotted with Origin software (Microcal Software, Northampton, MA).

Methyl 3-*O*-Allyl-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (5). Compound **28** (4.21 g, 9.48 mmol) was dissolved in dry methanol (30 mL), a small piece of sodium was added, and the reaction was stirred overnight. The solution was neutralized and concentrated, and the residue was purified by chromatography (1:1 EtOAc−pentane) to afford **5** (4.21 g, 95%) as an oil: $[\alpha]_D$ +84.5° (*c* 1.6, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.32 (m, 5H), 5.91 (ddd, 1H, *J* = 17.2, 10.4, 5.7 Hz), 5.31 (ddd, 1H, *J* = 17.2, 3.1, 1.6 Hz), 5.21 (ddd, 1H, *J* = 10.4, 3.1, 1.3 Hz), 4.87 (d, 1H, *J* = 10.8 Hz), 4.74 (d, 1H, *J* = 1.7 Hz), 4.61 (d, 1H, *J* = 10.8 Hz), 4.47 (dd, 1H, *J* = 11.2, 1.7 Hz), 4.39 (dd, 1H, *J* = 11.2, 3.7 Hz), 4.18 (dddd, 1H, *J* = 12.6, 5.6, 1.6, 1.3 Hz), 4.12 (dddd, 1H, *J* = 12.6, 5.6, 1.6, 1.3 Hz), 3.99 (dd, 1H, *J* = 2.5, 1.7 Hz), 3.75 (m, 3H), 3.35 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 134.2, 128.3, 127.9, 127.8, 117.5, 100.2, 79.4, 74.9, 73.2, 70.8, 69.4, 69.0, 67.9, 54.9, 37.6; FABMS calcd for $[C_{18}H_{26}O_8SNa]$ 425.1, found 425.1. Anal. Calcd for $C_{18}H_{26}O_8S$ (402.46): C, 53.72; H, 6.51. Found: C, 53.34; H, 6.43.

Ethyl 2,3,4-Tri-O-benzyl-6-O-(6′-trityloxyhexyl)-1-thio-α-D-galactopyranoside (6), Ethyl 2,3,4-Tri-O-benzyl-6-O-(7′-trityloxyheptyl)-1-thio-α-D-galactopyranoside (7), Ethyl 2,3,4-Tri-O-benzyl-6-O-(8′-trityloxyoctyl)-1-thio-α-D-galactopyranoside (8), or Ethyl 2,3,4-Tri-O-benzyl-6-O-(1″,1″,1″-triphenyloxy-3,6-dioxaoctanyl)-1-thio-α-D-galactopyranoside (12). To a solution of alcohol **36** (3.24 mmol) in dry THF (50 mL) was added NaH (10.4 mmol) under an Ar atmosphere. After being stirred for 1 h at 50 °C, a solution of **16**, **17**, **18**, or **20** (5.62 mmol) in dry THF (8 mL) was added dropwise. The reaction mixture was stirred at 65 °C for 18 h and cooled to room temperature, and excess NaH was decomposed with MeOH. The solvent was evaporated under reduced pressure, and the resulting residue was taken up in CH_2Cl_2, washed with a saturated NaCl solution, and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by chromatography.

6: eluent 98:2 pentane−EtOAc; yield 89%; $[\alpha]_D$ +77.7° (*c* 2.2, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.30−7.15 (m, 30H), 5.49 (d, 1H, *J* = 5.5 Hz), 4.94 (d, 1H, *J* = 11.5 Hz), 4.83 (d, 1H, *J* = 11.8 Hz), 4.74 (d, 1H, *J* = 11.7 Hz), 4.68 (d, 1H, *J* = 11.8 Hz), 4.67 (d, 1H, *J* = 11.7 Hz), 4.59 (d, 1H, *J* = 11.5 Hz), 4.26 (dd, 1H, *J* = 9.9, 5.5 Hz), 4.22 (t, 1H, *J* = 6.4 Hz), 3.88 (d, 1H, *J* = 2.9 Hz), 3.79 (dd, 1H, *J* = 9.9, 2.9 Hz), 3.44 (d, 2H, *J* = 6.4 Hz), 3.35 (dt, 1H, *J* = 9.3, 6.7 Hz), 3.27 (dt, 1H, *J* = 9.3, 6.7 Hz), 3.02 (t, 2H, *J* = 6.6 Hz), 2.55 (dq, *J* = 7.4 Hz), 2.47 (dq, *J* = 7.4 Hz), 1.59 (dt, 2H, *J* = 6.9, 6.6 Hz), 1.48 (dt, 2H, *J* = 7.2, 6.8 Hz), 1.40−1.25 (m, 4H), 1.24 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.42, 138.75, 138.64, 138.24, 128.60, 128.24, 128.19, 128.11, 127.83, 127.61, 127.50, 127.44, 127.39, 126.74, 86.22, 83.18, 79.53, 76.18, 75.16, 74.72, 73.27, 72.36, 71.41, 69.53, 69.33, 63.48, 29.96, 29.62, 26.10, 25.97, 23.35, 14.62. Anal. Calcd for $C_{54}H_{60}O_6S$ (837.12): C, 77.48; H, 7.22; S, 3.83. Found: C, 77.44; H, 7.11; S, 3.92.

7: eluent 98:2 pentane−EtOAc; yield 91%; $[\alpha]_D$ +66.7° (*c* 0.7, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.30−7.15 (m, 30H), 5.49 (d, 1H, *J* = 5.5 Hz), 4.94 (d, 1H, *J* = 11.5 Hz), 4.82 (d, 1H, *J* = 11.8 Hz), 4.74 (d, 1H, *J* = 11.7 Hz), 4.68 (d, 1H, *J* = 11.8 Hz), 4.66 (d, 1H, *J* = 11.7 Hz), 4.60 (d, 1H, *J* = 11.5 Hz), 4.28 (dd, 1H, *J* = 9.9, 5.5 Hz), 4.22 (t, 1H, *J* = 6.4 Hz), 3.89 (d, 1H, *J* = 2.9 Hz), 3.79 (dd, 1H, *J* = 9.9, 2.9 Hz), 3.43 (d, 2H, *J* = 6.4 Hz), 3.35 (dt, 1H, *J* = 9.3, 6.8 Hz), 3.27 (dt, 1H, *J* = 9.3, 6.7 Hz), 3.02 (t, 2H, *J* = 6.6 Hz), 2.60 (dq, 1H, *J* = 7.4 Hz), 2.48 (dq, 1H, *J* = 7.4 Hz), 1.59 (dt, 2H, *J* = 6.9 Hz), 1.46 (dt, 2H, *J* = 6.7 Hz), 1.38−1.22 (m, 6H), 1.24 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.40, 138.71, 138.61, 138.20, 128.57, 128.04, 128.16, 128.08, 127.80, 127.57, 127.47, 127.41, 127.36, 126.69, 86.17, 83.11, 79.46, 76.14, 75.10, 74.67, 73.22, 72.29, 71.41, 69.48, 69.30, 63.45, 29.89, 29.59, 29.24, 26.14, 25.98, 23.30, 14.59. Anal. Calcd for $C_{55}H_{62}O_6S$ (851.15): C, 77.61; H, 7.34; S, 3.77. Found: C, 77.61; H, 7.34; S, 3.95.

8: eluent 98:2 pentane−EtOAc; yield 85%; $[\alpha]_D$ +77.6° (*c* 0.8, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.30−7.15 (m, 30H), 5.47 (d, 1H, *J* = 5.5 Hz), 4.93 (d, 1H, *J* = 11.5 Hz), 4.81 (d, 1H, *J* = 11.9 Hz), 4.73 (d, 1H, *J* = 11.7 Hz), 4.68 (d, 1H, *J* = 11.8 Hz), 4.66 (d, 1H, *J* = 11.7 Hz), 4.58 (d, 1H, *J* = 11.5 Hz), 4.27 (dd, 1H, *J* = 9.9, 5.5 Hz), 4.23 (t, 1H, *J* = 6.5 Hz), 3.89 (d, 1H, *J* = 2.9 Hz), 3.78 (dd, 1H, *J* = 9.9, 2.9 Hz), 3.44 (d, 2H, *J* = 6.5 Hz), 3.35 (dt, 1H, *J* = 9.2, 6.6 Hz), 3.27 (dt, 1H, *J* = 9.2, 6.7 Hz), 3.02 (t, 2H, *J* = 6.6 Hz), 2.60 (dq, 1H, *J* = 4 Hz), 2.48 (dq, 1H, *J* = 7.4 Hz), 1.59 (dt, 2H, *J* = 6.9 Hz), 1.46 (dt, 2H, *J* = 6.7 Hz), 1.38−1.22 (m, 8H), 1.24 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.40, 138.71, 138.61, 138.20, 128.57, 128.18, 128.13, 128.06, 127.80, 127.45, 127.39, 127.33, 126.67, 86.17, 83.11, 79.46, 76.14, 75.10, 74.66, 73.20, 72.29, 71.41, 69.48, 69.30, 63.49, 29.91, 29.59, 29.33, 29.28, 26.10, 25.96, 23.29, 14.56. Anal. Calcd for $C_{56}H_{64}O_6S$ (865.18): C,-77.74; H, 7.46; S, 3.71. Found: C, 77.53; H, 7.46; S, 3.87.

12: eluent 1:1 pentane−EtOAc; yield 89%; $[\alpha]_D$ +66.3° (*c* 0.8, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.30−7.20 (m, 30H), 5.48 (d, 1H, *J* = 5.5 Hz), 4.95 (d, 1H, *J* = 11.5 Hz), 4.86 (d,

1H, J = 12.1 Hz), 4.78 (d, 1H, J = 10.5 Hz), 4.72 (d, 1H, J = 12.1 Hz), 4.68 (d, 1H, J = 10.5 Hz), 4.60 (d, 1H, J = 11.5 Hz), 4.28 (dd, 1H, J = 9.9, 5.5 Hz), 4.27 (t, 1H, J = 6.4 Hz), 3.91 (d, 1H, J = 2.8 Hz), 3.79 (dd, 1H, J = 9.9, 2.8 Hz), 3.70−3.55 (m, 9H), 3.51 (d, 2H, J = 6.4 Hz), 3.48 (m, 1H), 3.22 (t, 2H, J = 5.3 Hz), 2.52 (dq, 1H, J = 7.4 Hz), 2.48 (dq, 1H, J = 7.4 Hz), 1.24 (t, 1H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 138.75, 138.6, 138.2, 128.6, 128.2, 128.2, 128.1, 127.8, 127.7, 127.5, 127.5, 127.4, 126.8, 86.5, 83.2, 79.5, 76.1, 74.9, 74.7, 73.2, 72.3, 70.7, 70.6, 70.62, 70.5, 69.8, 69.4, 63.2, 23.4, 14.6. Anal. Calcd for $C_{54}H_{60}O_8S$ (869.12): C, 74.63; H, 6.96; S, 3.69. Found: C, 74.64; H, 7.08; S, 3.87.

Methyl 3-*O*-Allyl-4-*O*-benzyl-6-*O*-(8′-methanesulfoxyoctyl)-α-D-mannopyranoside (9). To an ice-cooled solution of **32** (595 mg, 1.31 mmol) and dry pyridine (1 mL) in dry CH_2Cl_2 (14 mL) was added methanesulfonyl chloride (122 μL, 1.57 mmol) dropwise. The mixture was stirred overnight as it came to room temperature. The mixture was diluted with CH_2Cl_2, washed successively with 1 M HCl and a saturated NaCl solution, and dried (Na_2SO_4). Evaporation of solvent and chromatography (1:1 EtOAc−pentane) gave **9** (513 mg, 73%) as an oil: $[\alpha]_D$ +53.5° (*c* 2.1, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.35−7.25 (m, 5H), 5.92 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.30 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.17 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.83 (d, 1H, J = 11.0 Hz), 4.75 (d, 1H, J = 1.6 Hz), 4.57 (d, 1H, J = 11.0 Hz), 4.18 (t, 2H, J = 6.6 Hz), 4.17 (m, 1H), 4.11 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 3.96 (m, 1H), 3.75 (dd, 1H, J = 8.7, 8.7 Hz), 3.71 (dd, 1H, J = 8.7, 3.0 Hz), 3.68−3.59 (m, 3H), 3.50 (dt, 1H, J = 9.3, 6.5 Hz), 3.39 (dt, 1H, J = 9.2, 6.7 Hz), 3.33 (s, 3H), 2.45 (s, 1H, J = 2.6 Hz), 1.65−1.55 (m, 4H), 1.25 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 134.4, 128.1, 127.6, 127.4, 117.0, 100.1, 79.5, 74.7, 74.1, 71.3, 70.6, 70.5, 69.8, 69.5, 68.2, 54.5, 37.0, 29.2, 28.9, 28.8, 28.6, 25.7, 25.1. Anal. Calcd for $C_{26}H_{42}O_9S$ (530.67): C, 58.85; H, 7.98; S, 6.04. Found: C, 58.86; H, 8.01; S, 6.17.

Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-trityl-1-thio-α-D-galactopyranoside (10). Trityl chloride (4.22 g, 15.16 mmol) was added to a solution of alcohol **36** (6.25 g, 12.63 mmol) in dry pyridine (150 mL). The reaction mixture was stirred at 40 °C for 8 h. The solvent was evaporated, and the resulting solid was taken up in $CHCl_3$, washed with a saturated NaCl solution, dried (Na_2SO_4), and evaporated. Chromatography (96:4 pentane−EtOAc) gave **10** (8.27 g, 89%): ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.40−7.00 (m, 30H), 5.45 (d, 1H, J = 5.5 Hz), 4.76 (d, 1H, J = 12.0 Hz), 4.72 (d, 1H, J = 12.0 Hz), 4.66 (d, 1H, J = 11.5 Hz), 4.61 (d, 1H, J = 11.5 Hz), 4.57 (d, 1H, J = 11.5 Hz), 4.36 (d, 1H, J = 11.5 Hz), 4.18 (t, 1H, J = 6.5 Hz), 4.15 (dd, 1H, J = 9.9, 5.5 Hz), 3.80 (d, 1H, J = 2.5 Hz), 3.72 (dd, 1H, J = 9.9, 2.5 Hz), 3.34 (dd, 1H, J = 10.9, 6.5 Hz), 3.04 (dd, 1H, J = 10.9, 6.5 Hz), 2.51 (dq, 1H, J = 7.4 Hz), 2.40 (dq, 1H, J = 7.4 Hz), 1.25 (t, 3H, J = 7.4 Hz). Anal. Calcd for $C_{48}H_{48}O_5S$ (736.97): C, 78.23; H, 6.57;10; S, 4.34. Found: C, 77.98; H, 6.43; S, 4.25.

8,8,8-Triphenyl-7-oxactanol (13), 9,9,9-Triphenyl-8-oxanonanol (14), 10,10,10-Triphenyl-9-oxadecanol (15), or 10,10,10-Triphenyl-3,6,9-trioxadecanol (19). To an ice-cooled solution of 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, or triethylene glycol (30.34 mmol) in dry pyridine (30 mL) and dry CH_2Cl_2 (307 mL) was added trityl chloride (36.40 mmol). The mixture was stirred overnight as it came to room temperature. The solution was washed successively with 1 M HCl and brine and dried (Na_2SO_4). The solvent was evaporated, and the resulting residue was purified by chromatography.

13:[27] eluent 4:1 pentane−EtOAc; yield 52%; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.55−7.15 (m, 15H), 3.60 (t, 2H, J = 6.0 Hz), 3.00 (t, 2H, J = 6.5 Hz), 1.68−1.44 (m, 5H), 1.25−1.45 (m, 4H). Anal. Calcd for $C_{25}H_{28}O_2$ (360.50): C, 83.29; H, 7.83. Found: C, 83.32; H, 7.83.

14: eluent 4:1 pentane−EtOAc; yield 57%; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.55−7.15 (m, 15H), 3.52 (t, 2H, J = 6.4 Hz), 3.05 (t, 2H, J = 6.2 Hz), 1.63 (dt, 2H, J = 6.3 Hz), 1.55 (dt, 2H, J = 6.4 Hz) 1.45−1.20 (m, 7H). Anal. Calcd for $C_{26}H_{30}O_2$ (374.52): C, 83.38; H, 8.07. Found: C, 83.35; H, 8.17.

15:[28] eluent 4:1 pentane−EtOAc; yield 55%; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.55−7.15 (m, 15H), 3.52 (t, 2H, J = 6.4 Hz), 3.05 (t, 2H, J = 6.2 Hz), 1.63 (dt, 2H, J = 6.3 Hz), 1.55 (dt, 2H, J = 6.4 Hz) 1.45−1.20 (m, 9H). Anal. Calcd for $C_{27}H_{32}O_2$ (388.24): C, 83.45; H, 8.31. Found: C, 83.89; H, 8.16.

19: eluent 1:1 pentane−EtOAc; yield 49%; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.50−7.18 (m, 15H), 3.72 (m, 2H), 3.66 (m, 6H), 3.64 (t, 2H, J = 5.3 Hz), 3.21 (t, 2H, J = 5.9 Hz). Anal. Calcd for $C_{25}H_{28}O_4$ (392.49): C, 76.49; H, 7.20. Found: C, 76.41; H, 7.33.

8,8,8-Triphenyl-7-oxactanyl Methanesulfonate (16), 9,9,9-Triphenyl-8-oxanonanyl Methanesulfonate (17), 10,-10,10-Triphenyl-9-oxadecanyl Methanesulfonate (18), or 10,10,10-Triphenyl-3,6,9-trioxadecanyl Methanesulfonate (20). To an ice-cooled solution of MsCl (36.25 mmol) in dry pyridine (18 mL) was added a solution of **13**, **14**, **15**, or **19** (7.25 mmol) in dry CH_2Cl_2 (110 mL) dropwise under an Ar atmosphere. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with CH_2Cl_2, washed successively with 1 M HCl and brine, and dried (Na_2SO_4). The solvent was evaporated, and the residue was purified by chromatography.

16: eluent 9:1 pentane−EtOAc; yield 81%; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.55−7.15 (m, 15H), 4.18 (t, 2H, J = 6.5 Hz), 3.04 (t, 2H, J = 6.5 Hz), 2.95 (s, 3H), 1.72 (dt, 2H, J = 7.0 Hz), 1.61 (dt, 2H, J = 6.8 Hz), 1.45−1.25 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 128.6, 127.6, 126.8, 86.3, 69.9, 63.2, 37.2, 29.7, 29.0, 25.6, 25.2. Anal. Calcd for $C_{26}H_{30}O_4S$ (438.58): C, 71.20; H, 6.89; S, 7.31. Found: C, 71.43; H, 6.86; S, 7.44.

17: eluent 9:1 pentane−EtOAc; yield 78%; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.55−7.15 (m, 15H), 4.18 (t, 2H, J = 6.5 Hz), 3.03 (t, 2H, J = 6.5 Hz), 2.97 (s, 3H), 1.73 (dt, 2H, J = 7.0 Hz), 1.52 (dt, 2H, J = 6.5 Hz), 1.45−1.25 (m, 6H). Anal. Calcd for $C_{27}H_{32}O_4S$ (452.61): C, 71.65; H, 7.13; S, 7.08. Found: C, 71.59; H, 7.16; S, 7.05.

18: eluent 9:1 pentane−EtOAc; yield 82%; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.55−7.15 (m, 15H), 4.19 (t, 2H, J = 6.6 Hz), 3.04 (t, 2H, J = 6.5 Hz), 2.96 (s, 3H), 1.72 (dt, 2H, J = 7.0 Hz), 1.60 (dt, 2H, J = 6.5 Hz), 1.39−1.23 (m, 8H). Anal. Calcd for $C_{28}H_{34}O_4S$ (466.64): C, 72.07; H, 7.34; S, 6.87. Found: C, 72.21; H, 7.49; S, 6.94.

20:[29] eluent 2:1 pentane−EtOAc; yield 82%; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.50−7.18 (m, 15H), 4.34 (m, 2H), 3.78 (m, 2H), 3.66 (m, 4H), 3.64 (t, 2H, J = 5.3 Hz), 3.21 (t, 2H, J = 5.9 Hz), 2.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 128.6, 127.7, 126.9, 86.5, 70.6, 70.6, 70.6, 69.2, 68.9, 63.2, 37.4. Anal. Calcd for $C_{26}H_{30}O_6S$ (470.58): C, 66.36; H, 6.43; S, 6.81. Found: C, 66.26; H, 6.46; S, 6.99.

Methyl 2,3-*O*-Isopropylidene-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (22). To an ice-cooled solution of methyl 2,3-*O*-isopropylidene-α-D-mannopyranoside[23] **21** (2.41 g, 10.33 mmol) and imidazole (3.80 g, 31.10 mmol) in dry DMF (70 mL) was added *tert*-butyldiphenylsilyl chloride (4.02 mL, 15.49 mmol) under an Ar atmosphere. The mixture was stirred for 5 h at room temperature. The reaction mixture was washed successively with 5% HCl and a saturated NaCl solution and dried (Na_2SO_4). The solvent was evaporated, and the resulting residue was purified by chromatography (3:1 pentane−EtOAc) to afford **22** (4.87 g, 93%) as an oil: $[\alpha]_D$ +2.5° (*c* 0.9, $CHCl_3$, lit.[24]); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.70 (m, 4H), 7.40 (m, 6H), 4.86 (s, 1H), 4.12 (dd, 1H, J = 6.4, 5.9 Hz), 4.09 (d, 1H, J = 5.9 Hz), 3.91 (dd, 1H, J = 10.7, 5.0 Hz), 3.84 (dd, 1H, J = 10.7, 4.9 Hz), 3.78 (dd, 1H, J = 9.3, 6.4 Hz), 3.61 (ddd, 1H, J = 9.3, 5.0, 4.9 Hz), 3.34 (s, 3H), 2.70 (bs, 1H), 1.48 (s, 3H), 1.32 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 135.5, 133.1, 132.9, 129.7, 127.7, 127.6, 109.4, 98.1, 78.4, 75.3, 70.2, 69.6, 64.3, 54.7, 27.8, 26.73, 26.03, 19.2. Anal. Calcd for $C_{26}H_{36}O_6Si$ (472.65): C, 66.07; H, 7.68. Found: C, 66.02; H, 7.34.

Methyl 4-*O*-Benzyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-isopropylidene-α-D-mannopyranoside (23). The alcohol **22** (2.41 g, 5.12 mmol) was dissolved in dry DMF (30 mL) and cooled to 0 °C. Then NaH (307 mg, 10.20 mmol) was added, and the solution was stirred for 30 min, at which point benzyl bromide (1.21 mL, 10.24 mmol) was added dropwise. The

reaction was stirred overnight as it warmed to room temperature. Excess sodium hydride was quenched with methanol, and the solution was concentrated under reduced pressure. The resulting solid was taken up in CH_2Cl_2, washed with a saturated NaCl solution, dried (Na_2SO_4), and evaporated. Chromatography (95:5 pentane−EtOAc) gave **23** (2.42 g, 84%) as a solid: $[\alpha]_D$ +12.3° (*c* 1.1, $CHCl_3$, lit.[24]); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.72 (m, 4H), 7.36 (m, 6H), 7.25 (m, 5H), 4.93 (s, 1H), 4.85 (d, 1H, J = 11.5 Hz), 4.55 (d, 1H, J = 11.5 Hz), 4.31 (dd, 1H, J = 6.3, 5.9 Hz), 4.13 (d, 1H, J = 5.9 Hz), 3.94 (dd, 1H, J = 10.9, 1.3 Hz), 3.85 (dd, 1H, J = 10.9, 4.3 Hz), 3.62 (m, 2H), 3.36 (s, 3H), 1.51 (s, 3H), 1.40 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 135.8, 135.6, 133.7, 133.3, 129.5, 128.2, 127.8, 127.60, 127.53, 127.45, 109.2, 98.1, 78.9, 75.9, 75.6, 72.8, 69.5, 63.3, 54.5, 27.9, 26.7, 26.3, 19.3. Anal. Calcd for $C_{33}H_{42}O_6Si$ (562.78): C, 70.43; H, 7.52. Found: C, 70.49; H, 7.64.

Methyl 4-*O*-Benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (24). Compound **23** (1.46 g, 2.59 mmol) was dissolved in 80% acetic acid (60 mL), and the mixture was heated in an oil bath at 80 °C for 4 h. The solution was cooled, the solvent was evaporated, and the residue was coevaporated twice with toluene. Chromatography (2:1 pentane−EtOAc) gave **24** (1.14 g, 84%) as a solid: $[\alpha]_D$ +41.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.75 (m, 4H), 7.35 (m, 6H), 7.22 (m, 5H), 4.74 (d, 1H, J = 11.3 Hz), 4.72 (d, 1H, J = 1.6 Hz), 4.63 (d, 1H, J = 11.3 Hz), 3.94 (dd, 1H, J = 8.3, 3.5 Hz), 3.93 (d, 1H, J = 3.1 Hz), 3.89 (dd, 1H, J = 3.5, 1.6 Hz), 3.72 (dd, 1H, J = 9.6, 8.3 Hz), 3.65 (dt, 1H, J = 9.6, 3.1 Hz), 3.35 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 135.7, 135.6, 133.6, 133.3, 129.6, 128.5, 127.8, 127.76, 127.6, 127.5, 100.3, 75.9, 74.7, 71.9, 71.8, 71.0, 63.1, 54.6, 26.8, 19.3. Anal. Calcd for $C_{30}H_{38}O_6Si$ (522.71): C, 68.93; H, 7.33. Found: C, 69.01; H, 7.21.

Methyl 3-*O*-Allyl-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (25). A solution of **24** (3.25 g, 6.22 mmol) and dibutyltin oxide (1.54 g, 6.21 mmol) in freshly distilled methanol (40 mL) was boiled for 2.50 h. The solvent was evaporated to dryness to give a residue, which was dissolved in freshly distilled toluene (40 mL); then tetrabutylammonium iodide (2.29 g, 6.22 mmol) and allyl bromide (30 mL) were added. The mixture was stirred for 15 h at 60 °C, cooled to room temperature, and washed successively with 10% $Na_2S_2O_3$ and a saturated NaCl solution. The organic layer was dried over Na_2SO_4 and evaporated. Chromatography of the resulting residue (8:1 pentane−EtOAc) gave **25** (3.20 g, 92%) as an oil: $[\alpha]_D$ +44.8° (*c* 1.2, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.72 (m, 4H), 7.36 (m, 6H), 7.25 (m, 5H), 5.92 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.33 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.18 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.80 (d, 1H, J = 10.8 Hz), 4.76 (d, 1H, J = 1.6 Hz), 4.58 (d, 1H, J = 10.8 Hz), 4.20 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 4.15 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 4.05 (dd, 1H, J = 2.7, 1.6 Hz), 3.88 (m, 2H), 3.78 (dd, 1H, J = 9.0, 8.1 Hz), 3.74 (dd, 1H, J = 8.1, 2.8 Hz), 3.65 (m, 1H), 3.37 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 135.8, 135.6, 134.6, 133.7, 133.4, 129.5, 128.3, 127.8, 127.5, 117.4, 100.1, 79.9, 75.1, 74.2, 72.3, 70.9, 68.5, 63.2, 54.5, 26.7, 19.3. Anal. Calcd for $C_{33}H_{42}O_6Si$ (562.78): C, 70.43; H, 7.52. Found: C, 70.45; H, 7.71.

Methyl 2-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (26). To an ice-cooled solution of **25** (3.39 g, 6.03 mmol) in dry pyridine (30 mL) was added acetic anhydride (2 mL, 21 mmol) dropwise. The mixture was stirred overnight at room temperature. Evaporation of the solvent and chromatography of the residue (95:5 pentane−EtOAc) gave **26** (3.06 g, 84%) as an oil: $[\alpha]_D$ +33.0° (*c* 0.8, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.72 (m, 4H), 7.36 (m, 6H), 7.25 (m, 5H), 5.90 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.29 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.25 (dd, 1H, J = 3.3, 1.7 Hz), 5.16 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz, 1H), 4.90 (d, 1H, J = 10.8 Hz), 4.69 (d, 1H, J = 1.7 Hz), 4.58 (d, 1H, J = 10.8 Hz), 4.16 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 4.05 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 3.97 (dd, 1H, J = 11.1, 4.1 Hz), 3.94 (dd, 1H, J = 11.1, 9.3 Hz), 3.90 (dd, 1H, J = 11.1, 2.1 Hz), 3.86 (dd, 1H, J = 9.3, 3.3 Hz), 3.64 (ddd, 1H, J = 11.1, 4.1, 2.1 Hz), 3.35 (s, 3H), 2.15 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 138.6, 135.9, 135.6, 134.7, 133.9, 133.3, 129.6, 128.3, 127.8, 127.7, 127.5, 117.3, 98.6, 77.8, 75.3, 74.3, 72.5, 70.9, 69.3, 62.9, 54.7, 26.8, 21.1, 19.4. Anal. Calcd for $C_{35}H_{44}O_7Si$ (604.81): C, 69.51; H, 7.33. Found: C, 69.41; H, 7.59.

Methyl 2-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-α-D-mannopyranoside (27). A 1 M solution of tetrabutylammonium fluoride in THF (27 mL, 27 mmol) was added dropwise to compound **26** (8.18 g, 13.5 mmol) under an Ar atmosphere. The mixture was stirred for 6 h at room temperature. Evaporation of the solvent and chromatography of the residue (2:1 pentane−EtOAc) gave the alcohol **27** (4.15 g, 84%) as an oil: $[\alpha]_D$ +53.3° (*c* 1.5, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.30 (m, 5H), 5.88 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.27 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.24 (dd, 1H, J = 3.4, 1.7 Hz), 5.16 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.90 (d, 1H, J = 10.9 Hz), 4.64 (d, 1H, J = 1.7 H), 4.61 (d, 1H, J = 10.9 Hz), 4.14 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 4.02 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 3.84 (dd, 1H, J = 9.3, 3.4 Hz, 1H), 3.80 (m, 2H), 3.72 (dd, 1H, J = 9.7, 9.3 Hz), 3.62 (ddd, 1H, J = 9.7, 3.8, 3.1 Hz), 3.32 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 138.3, 134.5, 128.3, 127.9, 127.7, 117.1, 98.7, 77.5, 75.1, 74.1, 71.5, 70.6, 68.8, 62.0, 54.8, 20.9. Anal. Calcd for $C_{19}H_{26}O_7$ (366.41): C, 62.28; H, 7.15. Found: C, 62.08; H, 7.10.

Methyl 2-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (28). To an ice-cooled solution of methanesulfonyl chloride (5.43 g, 70.42 mmol) in dry pyridine (30 mL) was added a solution of **27** (5.15 g, 14.08 mmol) dropwise under an Ar atmosphere. The solution was stirred overnight as it came to room temperature. The reaction mixture was diluted with CH_2Cl_2 and then washed with 1 M HCl and a saturated NaCl solution, dried over Na_2SO_4, and evaporated. Chromatography (3:1 pentane−EtOAc) afforded **28** (5.50 g, 88%) as an oil: $[\alpha]_D$ +59.2° (*c* 0.6, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.30 (m, 5H), 5.87 (ddd, 1H, J = 17.2, 10.4, 5.7 H), 5.28 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.24 (dd, 1H, J = 3.3, 1.7 Hz), 5.16 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.93 (d, 1H, J = 10.8 Hz), 4.65 (d, 1H, J = 1.7 Hz), 4.61 (d, 1H, J = 10.8 Hz), 4.45 (d, 2H, J = 3.3 Hz), 4.14 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 4.01 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 3.85 (dd, 1H, J = 9.1, 3.3 Hz), 3.81 (ddd, 1H, J = 9.9, 3.3 Hz), 3.70 (dd, 1H, J = 9.9, 9.1 Hz), 3.35 (s, 3H), 3.05 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 137.8, 134.2, 128.3, 127.9, 127.7, 117.2, 98.7, 77.4, 75.1, 73.3, 70.5, 69.6, 68.9, 68.4, 55.1, 37.5, 20.8. Anal. Calcd for $C_{20}H_{28}O_9S$ (444.50): C, 54.04; H, 6.35, S, 7.21. Found: C, 53.89; H, 6.39; S, 7.46.

Methyl 4-*O*-Benzyl-2,3-isopropylidene-α-D-mannopyranoside (29). A 1 M solution of tetrabutylammonium fluoride in THF (48.7 mL, 48.70 mmol) was added dropwise to compound **23** (18.25 g, 32.47 mmol) under an Ar atmosphere. The mixture was stirred for 9 h at room temperature. The solvent was evaporated, and the resulting residue was purified by chromatography (4:1 pentane−EtOAc) to provide **29** (9.03 g, 86%) as an oil: $[\alpha]_D$ +63.6° (*c* 1.2, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.35−7.25 (m, 5H), 4.89 (s, 1H), 4.87 (d, 1H, J = 11.6 Hz), 4.61 (d, 1H, J = 11.6 Hz), 4.29 (dd, 1H, J = 6.7, 5.9 Hz), 4.11 (d, 1H, J = 5.9 Hz), 3.83 (ddd, 1H, J = 11.7, 5.7, 3.2 Hz), 3.71 (ddd, 1H, J = 11.7, 7.6, 4.3 Hz), 3.60 (ddd, 1H, J = 10.0, 4.3, 3.2 Hz), 3.51 (dd, 1H, J = 10.0, 6.7 Hz), 3.35 (s, 3H), 2.05 (dd, 1H, J = 7.6, 5.7 Hz), 1.49 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 128.2, 127.9, 127.6, 109.2, 98.1, 78.5, 75.6, 68.4, 62.3, 54.7, 27.8, 26.2. Anal. Calcd for $C_{17}H_{24}O_6$ (324.37): C, 62.95; H, 7.46. Found: C, 62.66; H, 7.78.

Methyl 4-*O*-Benzyl-2,3-isopropylidene-6-*O*-(8′-trityloxyoctyl)-α-D-mannopyranoside (30). To a solution of alcohol **29** (1.21 g, 3.76 mmol) in dry THF (50 mL) was added NaH (338 mg, 11.28 mmol) under Ar. After being stirred for 1 h at 50 °C, a solution of **18** (2.36 g, 5.07 mmol) in dry THF (8 mL) was added dropwise. Then, the reaction mixture was stirred at 65 °C for 19 h and cooled to room temperature and the excess of NaH decomposed with MeOH. The solvent was evaporated, and the resulting residue dissolved in CH_2Cl_2, washed with a saturated NaCl solution, and dried (Na_2SO_4).

Evaporation of the solvent and chromatography (0 → 10% EtOAc in pentane) gave **30** (2.19 g, 84%) as an oil: $[\alpha]_D$ + 23.0° (*c* 1.4, $CHCl_3$); ^1H NMR (360 MHz, $CDCl_3$) δ 7.48−7.15 (m, 20H), 4.91 (s, 1H), 4.86 (d, 1H, *J* = 11.6 Hz), 4.57 (d, 1H, *J* = 11.6 Hz), 4.28 (dd, 1H, *J* = 6.4, 6.4 Hz), 4.09 (d, 1H, *J* = 6.4 Hz), 3.70−3.64 (m, 2H), 3.58 (ddd, 1H, *J* = 10.5, 5.2 Hz), 3.52 (dd, 1H, *J* = 10.3, 6.4 Hz), 3.48 (dt, 1H, *J* = 9.2, 6.6 Hz), 3.39 (dt, 1H, *J* = 9.2, 6.8 Hz), 3.35 (s, 3H), 3.01 (t, 2H, *J* = 6.6 Hz), 1.55 (m, 4H), 1.49 (s, 3H), 1.35 (s, 3H), 1.25 (m, 8H). Anal. Calcd for $C_{44}H_{54}O_7$ (694.91): C, 76.05; H, 7.83. Found: C, 75.90; H, 7.94.

Methyl 4-*O*-Benzyl-6-*O*-(8′-hydroxyoctyl)-α-D-mannopyranoside (31). Trityl compound **30** (1.69 g, 2.44 mmol) was dissolved in 9:1 MeOH:EtOAc (30 mL), and *p*-toluensulfonic acid was added until the pH was 4. The reaction mixture was stirred for 48 h, triethylamine (500 μL) was added, and the solvents were evaporated. The residue was purified by chromatography (EtOAc) to afford **31** (800 mg, 80%) as an oil: $[\alpha]_D$ +59.6° (*c* 1.7, $CHCl_3$); ^1H NMR (360 MHz, $CDCl_3$) δ 7.35−7.25 (m, 5H), 4.78 (d, 1H, *J* = 11.4 Hz), 4.71 (d, 1H, *J* = 1.4 Hz), 4.67 (d, 1H, *J* = 11.4 Hz), 3.88 (dd, 1H, *J* = 8.1, 3.5 Hz), 3.85 (d, 1H, *J* = 3.5, 1.4 Hz), 3.72−3.62 (m, 4H), 3.59 (t, 2H, *J* = 6.6 Hz), 3.53 (dt, 1H, *J* = 9.3, 6.5 Hz), 3.40 (dt, 1H, *J* = 9.3, 6.8 Hz), 3.33 (s, 3H), 2.55 (sb, 3H), 1.65−1.55 (m, 4H), 1.25 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 128.3, 127.7, 127.5, 100.7, 75.6, 74.5, 71.8, 71.6, 70.9, 70.3, 69.4, 62.5, 54.7, 32.3, 29.3, 29.2, 29.1, 25.8, 25.5. Anal. Calcd for $C_{22}H_{36}O_7$ (412.52): C, 64.05; H, 8.80. Found: C, 63.64; 8.92.

Methyl 3-*O*-Allyl-4-*O*-benzyl-6-*O*-(8′-hydroxyoctyl)-α-D-mannopyranoside (32). A solution of **31** (794 mg, 1.92 mmol) and dibutyltin oxide (526 mg, 2.11 mmol) in freshly distilled methanol (15 mL) was boiled for 2.30 h. The solvent was evaporated to dryness to give a residue, which was dissolved in freshly distilled toluene (15 mL); then tetrabutylammonium iodide (711 mg, 1.92 mmol) and allyl bromide (1.46 mL, 19.2 mmol) were added. The mixture was stirred for 15 h at 65 °C, cooled to room temperature, and washed successively with 10% $Na_2S_2O_3$ and a saturated NaCl solution. The organic layer was dried over Na_2SO_4 and evaporated. Chromatography of the resulting residue (1:1 EtOAc−pentane) gave **32** (610 mg, 70%) as an oil: $[\alpha]_D$ +62.5° (*c* 2.2, $CHCl_3$); ^1H NMR (360 MHz, $CDCl_3$) δ 7.35−7.25 (m, 5H), 5.92 (ddd, 1H, *J* = 17.2, 10.4, 5.7 Hz), 5.33 (ddd, 1H, *J* = 17.2, 3.1, 1.6 Hz), 5.18 (ddd, 1H, *J* = 10.4, 3.1, 1.3 Hz), 4.84 (d, 1H, *J* = 11.0 Hz), 4.75 (d, 1H, *J* = 1.7 Hz), 4.58 (d, 1H, *J* = 11.0 Hz), 4.17 (dddd, 1H, *J* = 12.6, 5.6, 1.6, 1.3 Hz), 4.11 (dddd, 1H, *J* = 12.6, 5.6, 1.6, 1.3 Hz), 3.96 (ddd, 1H, *J* = 3.2, 3.0, 1.7 Hz), 3.77 (dd, 1H, *J* = 8.9, 8.8 Hz), 3.71 (dd, 1H, *J* = 8.9, 3.2 Hz), 3.68−3.60 (m, 3H), 3.58 (t, 2H, *J* = 6.6 Hz), 3.51 (dt, 1H, *J* = 9.3, 6.5 Hz), 3.39 (dt, 1H, *J* = 9.3, 6.7), 3.33 (s, 3H), 2.51 (d, 1H, *J* = 3.0 Hz), 1.65−1.55 (m, 4H), 1.25 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 134.5, 128.2, 127.7, 127.5, 117.1, 100.3, 79.6, 74.9, 74.1, 71.6, 70.7, 69.5, 68.3, 62.6, 54.6, 32.5, 29.4, 29.2, 29.1, 25.9, 25.5; HR FABMS (M^+ + Na) 475.2672, found 475.2670.

Ethyl 6-*O*-*tert*-Butyldiphenylsilyl-1-thio-α-D-galactopyranoside (34). To an ice-cooled solution of **33**[26] (1.43 g, 6.40 mmol) and imidazole (871 mg, 12.08 mmol) in dry DMF (60 mL) was added *tert*-butyldiphenylsilyl chloride (1.8 mL, 7.04 mmol). The stirred mixture was allowed to reach room temperature overnight under an Ar atmosphere. The solvent was evaporated, and the resulting residue was purified by chromatography (EtOAc) to provide **34** (2.58 g, 88%) as a white foam: $[\alpha]_D$ +135.2° (*c* 0.8, $CHCl_3$); ^1H NMR (360 MHz, $CDCl_3$) δ 7.65 (m, 4H), 7.40 (m, 6H), 5.42 (d, 1H, *J* = 5.5 H), 4.17 (dd, 1H, *J* = 5.5, 5.5 Hz), 4.12 (dd, 1H, *J* = 9.9, 5.5 Hz), 4.11 (d, 1H, *J* = 3.3 Hz), 3.91 (dd, 1H, *J* = 10.7, 5.5 Hz), 3.70 (dd, 1H, *J* = 10.7, 5.2 Hz), 3.54 (dd, 1H, *J* = 9.9, 3.3 Hz), 2.62 (dq, 1H, *J* = 7.4 Hz), 2.55 (dq, 1H, *J* = 7.4 Hz), 1.26 (t, 3H, *J* = 7.4 Hz), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.62, 135.56, 133.2, 133.05, 129.8, 127.7, 85.8, 71.7, 70.9, 69.8, 68.7, 63.7, 26.8, 24.5, 19.1, 14.9. Anal. Calcd for $C_{24}H_{34}O_5SSi$ (462.67): C, 62.30; H, 7.41; S, 6.93. Found: C, 62.31; H, 7.55; S, 6.54.

Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-galactopyranoside (35). The alcohol **34** (2.47 g, 5.34 mmol) was dissolved in dry DMF (40 mL) and cooled to 0 °C. Then NaH (1.025 g, 34.19 mmol) was added and the solution stirred for 30 min, at which point benzyl bromide (4 mL, 34.19 mmol) was added dropwise. The reaction was stirred overnight as the solution warmed to room temperature. Excess sodium hydride was quenched with methanol, and the solution was concentrated under reduced pressure. The resulting solid was taken up in $CHCl_3$, washed with a saturated NaCl solution, dried (Na_2SO_4), and evaporated. Chromatography (96:4 pentane−EtOAc) gave **35** (2.84 g, 74%) as a solid: $[\alpha]_D$ +95.5° (*c* 1.7, $CHCl_3$); ^1H NMR (360 MHz, $CDCl_3$) δ 7.60 (m, 4H), 7.40−7.18 (m, 21H), 5.48 (d, 1H, *J* = 5.5 Hz), 4.94 (d, 1H, *J* = 11.4 Hz), 4.87 (d, 1H, *J* = 11.8 Hz), 4.75 (d, 1H, *J* = 12.5 Hz), 4.71 (d, 2H, *J* = 12.5 Hz), 4.67 (d, 1H, *J* = 11.8 Hz), 4.59 (d, 1H, *J* = 11.4 Hz), 4.26 (dd, 1H, *J* = 9.9, 5.5 Hz), 4.15 (t 1H, *J* = 6.5 Hz), 3.93 (d, 1H, *J* = 2.9 Hz), 3.80 (dd, 1H, *J* = 9.9, 2.9 Hz), 3.69 (d, 2H, *J* = 6.5 Hz), 2.51 (dq, 1H, *J* = 7.4 Hz), 2.40 (dq, 1H, *J* = 7.4 Hz), 1.19 (t, 3H, *J* = 7.4 Hz), 1.05 (s, 9H). Anal. Calcd for $C_{45}H_{52}O_5Si$ (733.05): C, 73.73; H, 7.15; S, 4.37. Found: C, 73.87; H, 7.27; S, 4.48.

Ethyl 2,3,4-Tri-*O*-benzyl-1-thio-α-D-galactopyranoside (36). A 1 M solution of tetrabutylammonium fluoride in THF (5.5 mL, 5.5 mmol) was added dropwise to compound **35** (2.03 g, 2.77 mmol) under an Ar atmosphere, and the mixture was stirred for 6 h at room temperature. Evaporation of the solvent and chromatography (2:1 pentane−EtOAc) of the residue afforded the alcohol **36** (1.30 g, 95%) as a white solid: $[\alpha]_D$ +110° (*c* 1.0, $CHCl_3$); ^1H NMR (360 MHz, $CDCl_3$) δ 7.30 (m, 15H), 5.49 (d, 1H, *J* = 5.5 Hz), 4.96 (d, 1H, *J* = 11.6 Hz), 4.86 (d, 1H, *J* = 11.6 Hz), 4.74 (d, 1H, *J* = 11.6 Hz), 4.70 (d, 1H, *J* = 11.6 Hz), 4.66 (d, 1H, *J* = 11.6 Hz), 4.62 (d, 1H, *J* = 11.6 Hz), 4.29 (dd, 1H, *J* = 9.8, 5.5 Hz), 4.10 (ddd, 1H, *J* = 6.4, 5.2, 1.2 Hz), 3.86 (dd, 1H, *J* = 2.8, 1.2 Hz), 3.78 (dd, 1H, *J* = 9.9, 2.9 Hz), 3.71 (dd, 1H, *J* = 11.5, 6.4 Hz), 3.50 (dd, 1H, *J* = 11.5, 5.2 Hz), 2.70 (dq, 1H, *J* = 7.4 Hz), 2.62 (dq, 1H, *J* = 7.4 Hz), 1.24 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) 138.6, 138.1, 128.4, 128.34, 128.28, 127.8, 127.5, 127.45, 83.2, 79.4, 76.1, 75.0, 74.4, 73.5, 72.4, 70.61, 62.2, 23.4, 14.5. Anal. Calcd for $C_{29}H_{34}O_5S$ (494.64): C, 70.42; H, 6.93; S, 6.48. Found: C, 70.24; H, 6.97; S, 6.68.

Methyl 3-*O*-Allyl-2-*O*-[2′,3′,4′-tri-*O*-benzyl-6′-*O*-(6″-trityloxyhexyl)-α-D-galactopyranosyl]-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (37). The alcohol **5** (387 mg, 0.96 mmol) and the thioglycoside **6** (1.16 g, 1.39 mmol) were dried in vacuo with powdered 4 Å molecular sieves over P_2O_5 overnight. The mixture was suspended in CH_2Cl_2 (15 mL) under an Ar atmosphere and stirred for 2 h at room temperature. *N*-Iodosuccinimide (476 mg, 2.11 mmol) was added, and the suspension was stirred for 10 min before rapid, dropwise addition of a saturated solution of triflic acid in ca. 0.15 M CH_2Cl_2 (770 μL, 0.11 mmol). The reaction was quenched with triethylamine, diluted with CH_2Cl_2, and filtered through Celite. The filtrate was washed successively with 10% $Na_2S_2O_3$ and a saturated NaCl solution. After evaporation of the solvent the residue was chromatographed (0 → 25% ethyl acetate in pentane) to provide **37** (1.26 g, 77%) as an oil: $[\alpha]_D$ +62.5° (*c* 1.3, $CHCl_3$); ^1H NMR (360 MHz, $CDCl_3$) δ 7.5−7.15 (m, 35H), 5.89 (ddd, 1H, *J* = 17.2, 10.4, 5.7 Hz), (d, 1H, *J* = 3.8 Hz), 5.28 (ddd, 1H, *J* = 17.2, 3.1, 1.6 Hz), 5.16 (ddd, 1H, *J* = 10.4, 3.1, 1.3 Hz), 4.97 (d, 2H, *J* = 11.9 Hz), 4.83 (d, 1H, *J* = 12.2 Hz), 4.76 (d, 1H, *J* = 12.2 Hz), 4.71 (d, 1H, *J* = 11.6 Hz), 4.67 (s, 1H), 4.66 (d, 1H, *J* = 11.4 Hz), 4.61 (d, 1H, *J* = 11.5 Hz), 4.51 (dd, 1H, *J* = 11.7, 0.5 Hz), 4.39 (dd, 1H, *J* = 11.7, 4.0 Hz), 4.31 (d, 1H, *J* = 10.9 Hz), 4.16 (dddd, 1H, *J* = 12.6, 5.6, 1.6, 1.3 Hz), 4.12 (m, 2H), 4.08 (dd, 1H, *J* = 9.9, 3.8 Hz), 3.94 (d, 1H, *J* = 2.5 Hz), 3.90 (dd, 1H, *J* = 9.8, 9.7 Hz), 3.85 (dd, 1H, *J* = 6.2, 5.5 Hz), 3.79 (dd, 2H, *J* = 9.9, 2.5 Hz and *J* = 9.8, 2.5 Hz), 3.69 (ddd, 1H, *J* = 9.7, 4.0, 0.5 Hz), 3.49 (dd, 1H, *J* = 9.7, 6.2 Hz), 3.41 (m, 2H), 3.30 (s, 3H), 3.28 (dt, 1H, *J* = 9.2, 2.7 Hz), 3.05 (t, 2H, *J* = 6.6 Hz), 2.95 (s, 3H), 1.70−1.20 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.40, 138.8, 138.7, 138.5, 138.2, 134.4, 128.6, 128.4, 128.3, 128.2, 127.7, 127.6, 127.6, 127.3, 127.1, 126.8, 117.1, 100.2, 97.3, 86.2, 80.0, 78.0, 76.3, 74.8, 74.8, 74.7, 73.8, 72.6, 71.6, 71.5, 71.3, 71.2, 70.5, 69.9, 69.8, 69.3, 63.5, 54.9, 37.9, 29.9, 29.6, 26.1, 25.9.

Anal. Calcd for $C_{70}H_{80}O_{14}S$ (1177.46): C, 71.41; H, 6.85; S, 2.72. Found: C, 71.47; H, 6.78; S, 2.78.

Methyl 3-*O*-Allyl-2-*O*-[2′,3′,4′-tri-*O*-benzyl-6′-*O*-(6″-hydroxyhexyl)-α-D-galactopyranosyl]-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (40). Disaccharide **37** (584 mg, 0.49 mmol) was dissolved in 9:1 MeOH:EtOAc (10 mL), and a catalytic amount of *p*-toluensulfonic acid was added. The reaction mixture was stirred for 6 h. Triethylamine (100 μL) was added, solvents were evaporated, and the residue was purified by chromatography (6:4 pentane−EtOAc) to provide **40** (404 mg, 87%) as an oil: $[\alpha]_D$ +78.8° (*c* 1.8, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.50−7.15 (m, 20H), 5.89 (ddd, 1H, *J* = 17.2, 10.4, 5.7 Hz), 5.50 (d, 1H, *J* = 3.5 Hz), 5.28 (ddd, 1H, *J* = 17.2, 3.1, 1.6 Hz), 5.16 (ddd, 1H, *J* = 10.4, 3.1, 1.3 Hz), 4.98 (d, 1H, *J* = 11.5 Hz), 4.97 (d, 1H, *J* = 11.6 Hz), 4.82 (d, 1H, *J* = 12.2 Hz), 4.76 (d, 1H, *J* = 12.2 Hz), 4.70 (d, 1H, *J* = 11.5 Hz), 4.68 (s, 1H), 4.66 (d, 1H, *J* = 11.4 Hz), 4.62 (d, 1H, *J* = 11.8 Hz), 4.50 (d, 1H, *J* = 11.7 Hz), 4.38 (dd, 1H, *J* = 11.7, 2.5 Hz), 4.30 (d, 1H, *J* = 10.9 Hz), 4.16 (m, 2H), 4.12 (m, 1H), 4.08 (dd, 1H, *J* = 9.9, 3.5 Hz), 3.92 (bs, 1H), 3.88 (dd, 1H, *J* = 9.9, 9.4), 3.85 (dd, 1H, *J* = 6.4, 5.7 Hz), 3.78 (m, 2H), 3.67 (dd, 1H, *J* = 9.4, 2.5 Hz), 3.61 (t, 2H, *J* = 6.5 Hz), 3.48 (dd, 1H, *J* = 9.5, 6.4 Hz), 3.41 (m, 2H), 3.32 (m, 1H), 3.31 (s, 3H), 2.92 (s, 3H), 1.70−1.20 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.6, 138.4, 138.1, 134.4, 128.3, 128.2, 128.1, 128.1, 127.6, 127.5, 127.5, 127.5, 127.2, 127.1, 117.1, 100.1, 97.3, 79.8, 77.9, 76.2, 74.8, 74.8, 74.6, 73.7, 72.6, 71.5, 71.3, 71.3, 71.2, 70.4, 69.8, 69.8, 69.3, 62.5, 54.8, 37.8, 32.5, 29.5, 25.8, 25.4. Anal. Calcd for $C_{51}H_{66}O_{14}S$ (935.14): C, 65.50, H, 7.11; S, 3.43. Found: C, 65.60; H, 7.17; S, 3.49.

Methyl 2-*O*-(3′-*O*-Allyl-4′-*O*-benzyl-α-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-6,6′-di-*O*-(hexane-1,6-diyl)-α-D-mannopyranoside (43). A solution of disaccharide **40** (350 mg, 0.37 mmol) in dry THF (20 mL) was slowly added to a boiling mixture of NaH (116 mg, 4.86 mmol) and Cs_2CO_3 (171 mg, 0.48 mmol) in dry THF (25 mL) over a 2 h period, and the reaction mixture was then refluxed for 24 h. After an excess of NaH has been decomposed with MeOH, the solvent was evaporated under reduced pressure and the resulting residue taken up in CH_2Cl_2 and washed with a saturated NaCl solution. Evaporation of the solvent and chromatography (85:15 pentane−EtOAc) gave **43** (120 mg, 38%) as an oil: $[\alpha]_D$ +42.3° (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.15 (m, 20H), 5.83 (ddd, 1H, *J* = 17.2, 10.4, 5.7 Hz), 5.21 (ddd, 1H, *J* = 17.2, 3.1, 1.6 Hz), 5.04 (ddd, 1H, *J* = 10.4, 3.1, 1.3 Hz), 4.98 (d, 1H, *J* = 2.0 Hz), 4.93 (d, 1H, *J* = 11.5 Hz), 4.91 (d, 1H, *J* = 11.0 Hz), 4.88 (d, 1H, *J* = 3.0 Hz), 4.81 (d, 1H, *J* = 11.5 Hz), 4.78 (d, 1H, *J* = 11.5 Hz), 4.76 (d, 1H, *J* = 11.5 Hz), 4.67 (d, 1H, *J* = 12.5 Hz), 4.64 (d, 1H, *J* = 12.0 Hz), 4.55 (d, 1H, *J* = 11.0 Hz), 4.20 (dd, 1H, *J* = 8.5, 5.3 Hz), 4.14 (dddd, 1H, *J* = 12.6, 5.6, 1.6, 1.3 Hz), 4.05−4.00 (m, 3H), 3.99 (dd, 1H, *J* = 10.1, 2.7 Hz), 3.84 (dd, 1H, *J* = 9.1, 3.2 Hz), 3.79 (dd, 1H, *J* = 3.2, 2.0 Hz), 3.72 (dd, 1H, *J* = 9.8, 9.1 Hz), 3.68 (dd, 1H, *J* = 9.9, 1.7 Hz), 3.64 (ddd, 1H, *J* = 9.8, 6.1, 1.7 Hz), 3.54 (dd, 1H, *J* = 9.3, 8.5 Hz), 3.49 (ddd, 1H, *J* = 10.2, 6.1, 4.1 Hz), 3.43 (m, 2H), 3.40 (m, 1H), 3.39 (dd, 1H, *J* = 9.9, 6.1 Hz), 3.29 (s, 3H), 3.05 (dd, 1H, *J* = 9.3, 5.3 Hz), 1.69−1.20 (m, 8H); FABMS calcd for $[C_{50}H_{62}O_{11}Na]$ 861.4, found 861.2. Anal. Calcd for $C_{50}H_{62}O_{11}$: C, 71.58; H, 7.45. Found: C,71.38; H, 7.34.

Methyl 2-*O*-(2′,3′,4′-Tri-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-benzyl-6,6′-di-*O*-(hexane-1,6-diyl)-α-D-mannopyranoside (46). A solution of disaccharide **43** (205 mg, 0.24 mmol) in dry DMSO (2 mL) was heated at 80 °C, and KO^{t}Bu (109 mg, 0.97 mmol) was added. After 2 h, the isomerization was complete. The mixture was cooled to room temperature, diluted with CH_2Cl_2, washed with water, and dried (Na_2SO_4). The solvent was evaporated and the residue redissolved in 9:1 acetone−water (15 mL). Mercuric oxide (25 mg, 0.11 mmol) and mercuric chloride (1.46 g, 5.38 mmol) were added, and the solution was stirred for 30 min. The solvent was evaporated, and the residue was purified by chromatography (80:20 pentane−EtOAc) to afford **46** (167 mg, 86%) as an oil: $[\alpha]_D$ +55.5° (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.15 (m, 20H), 4.93 (d, 1H, *J* = 11.5 Hz), 4.91 (d, 1H, *J* = 11.1 Hz), 4.84 (d, 1H, *J* = 11.9 Hz), 4.80 (d, 1H, *J* = 1.8 Hz), 4.73 (d, 1H, *J* = 3.7 Hz), 4.73 (bs, 2H), 4.65 (d, 1H, *J* = 11.8 Hz), 4.57 (d, 1H, *J* = 11.3 Hz), 4.11 (dd, 1H, *J* = 8.4, 5.3 Hz), 3.99 (bs, 1H), 3.98 (dd, 1H, *J* = 9.9, 3.7 Hz), 3.95 (dd, 1H, *J* = 9.0, 3.5 Hz), 3.83 (dd, 1H, *J* = 9.9, 2.9 Hz), 3.64 (dd, 1H, *J* = 10.1, 1.9 Hz), 3.62 (m, 1H), 3.60 (dd, 1H, *J* = 10.1, 8.4 Hz), 3.57 (ddd, 1H, *J* = 9.9, 5.2, 1.9 Hz), 3.50−3.36 (m, 6H), 3.29 (s, 3H), 3.23 (dd, 1H, *J* = 10.1, 5.3 Hz), 1.20−1.69 (m, 8H). Anal. Calcd for $C_{47}H_{58}O_{11}$: C, 70.66; H, 7.32. Found: C,70.47; H, 7.27.

Methyl 2-*O*-(2″,3″,4″-Tri-*O*-benzyl-α-D-galactopyranosyl)-3-*O*-(2′,4′-di-*O*-benzyl-3′,6′-dideoxy-α-D-*xylo*-hexopyranosyl)-4-*O*-benzyl-6,6′-di-*O*-(hexane-1,6-diyl)-α-D-mannopyranoside (49). The disaccharide alcohol **46** (135 mg, 0.17 mmol) and the 3,6-dideoxyhexose thioglycoside **11** (288 mg, 0.77 mmol) were dried in vacuo with powdered and freshly activated 4 Å molecular sieves over P_2O_5 overnight. The mixture was suspended in dry CH_2Cl_2 (5 mL), cooled to −45 °C, and stirred for 20 min. *N*-Iodosuccinimide (185 mg, 0.82 mmol) and a solution of silver triflate (21 mg, 0.08 mmol) in dry toluene (200 μL) was added rapidly, dropwise, and after 30 min the reaction was quenched with triethylamine. The reaction was then diluted with CH_2Cl_2 and filtered, and the filtrate was washed successively with $Na_2S_2O_3$ and a saturated NaCl solution and dried (Na_2SO_4). After evaporation of solvent, the residue was purified by chromatography (84:16 pentane−EtOAc) to afford **49** (112 mg, 60%) as an oil: $[\alpha]_D$ +77.7° (*c* 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.15 (m, 30H), 5.09 (d, 1H, *J* = 11.6 Hz), 5.04 (d, 1H, *J* = 3.3 Hz), 4.98 (d, 1H, *J* = 1.8 Hz), 4.94 (d, 1H, *J* = 2.7 Hz), 4.92 (d, 1H, *J* = 12.5 Hz), 4.89 (d, 1H, *J* = 11.6 Hz), 4.75 (bs, 2H), 4.64 (d, 1H, *J* = 10.8 Hz), 4.62 (d, 1H, *J* = 11.4 Hz), 4.58 (d, 1H, *J* = 11.8 Hz), 4.39 (d, 1H, *J* = 12.5 Hz), 4.32 (d, 1H, *J* = 12.5 Hz), 4.30 (dd, 1H, *J* = 9.3, 5.0 Hz), 4.22 (d, 1H, *J* = 12.0 Hz), 4.10 (dd, 1H, *J* = 9.5, 3.2 Hz), 4.09−4.05 (m, 4H), 4.04 (d, 1H, *J* = 12.06 Hz), 3.83 (dd, 1H, *J* = 3.2, 1.8 Hz), 3.76 (dd, 1H, *J* = 9.9, 9.5 Hz), 3.69 (ddd, 1H, *J* = 9.9, 6.1, 1.7 Hz), 3.67 (m, 1H), 3.63 (dd, 1H, *J* = 9.9, 1.7 Hz), 3.59 (dd, 1H, *J* = 9.3, 9.1 Hz), 3.50−3.35 (m, 4H), 3.32 (s, 3H), 3.31 (dd, 1H, *J* = 9.9, 6.1 Hz), 3.24 (dd, 1H, *J* = 9.1, 5.0 Hz), 2.36 (bs, 1H), 1.75 (ddd, 12.9, 11.9, 2.4 Hz), 1.70 (ddd, 1H, *J* = 12.9, 3.5, 3.5 Hz), 1.25−1.62 (m, 8H), 1.36 (d, 3H, *J* = 6.6 Hz). Anal. Calcd for $C_{67}H_{80}O_{14}$: C, 72.54; H, 7.27. Found: C,72.63; H, 7.24.

Methyl 2-*O*-(α-D-Galactopyranosyl)-3-*O*-(3′,6′-dideoxy-α-D-*xylo*-hexopyranosyl)-6,6″-di-*O*-(hexane-1,6-diyl)-α-D-mannopyranoside (2). A stirred solution of **49** (87 mg, 0.08 mmol) in acetic acid (9 mL) was hydrogenated over 10% Pd/C (101 mg) under a flow of H_2 overnight. The catalyst was removed by filtration, and the solvent was evaporated. Chromatography (85:15 CH_2Cl_2−MeOH) on Iatrobeads afforded **2** (40 mg, 90%) as a white solid: $[\alpha]_D$ +102.8° (*c* 1.5, H_2O);^{1}H NMR (500 MHz, D_2O) δ 5.10 (d, 1H, $J_{1,2}$ = 1.9 Hz, H1), 5.05 (d, 1H, $J_{1,2}$ = 3.8 Hz, H1′), 5.01 (d, 1H, $J_{1,2}$ = 4.0 Hz, H1″), 4.30 (m, 1H, H5″), 4.02 (m, 1H, $J_{2,3ax}$ = 8.6, $J_{2,3eq}$ = 8.6 Hz, H2′), 4.10 (m, H-5′), 4.00 (dd, 1H, $J_{4,5}$ = 0.9, Hz, H4″), 3.96 (dd 1H, $J_{3,4}$ = 9.7 Hz, H3), 3.92 (m, $J_{5,6a}$ = 1.7 Hz, H6a), 3.91 (ddd, 1H, $J_{3,4}$ = 3.4, Hz, H3″), 3.88 (dd, 1H, $J_{2,3}$ = 3.1 Hz, H2), 3.85 (m, $J_{4,5}$ = 1.2 Hz, H-4′), 3.82 (dd 1H, $J_{4,5}$ = 9.7 Hz, H4), 3.75 (dd, 1H, $J_{2,3}$ = 10.4, Hz, H2″), 3.71 (m, 1H, OCH_2), 3.70 (m, H5), 3.69 (dd, 1H, $J_{5,6a}$ = 6.6, Hz, H6a″), 3.64 (m, 1H, OCH_2), 3.59 (m, 1H, OCH_2), 3.59 (m, $J_{5,6b}$ = 7.5 Hz, H6b), 3.55 (m, 1H, OCH_2), 3.52 (dd, 1H, $J_{5,6a}$ = 6.6, Hz, H6b″), 1.97 (m, 2H, $J_{3eq,4} = J_{3ax,4}$ = 3.2 Hz, H-3′), 1.7−1.3 (m, 8H, $OCH_2(CH_2)_4$-CH_2O), 1.17 (d, 3H, $J_{5,6}$ = 6.7 Hz, H-6′). ^{13}C NMR (125 MHz, D_2O) δ 102.7 (1C, $^1J_{C,H}$ = 169.5 Hz, C1″), 101.5 (1C, $^1J_{C,H}$ = 170.6 Hz, C1′), 99.7 (1C, $^1J_{C,H}$ = 173.3 Hz, C1), 81.2 (1C, C2), 78.5 (1C, C3), 72.1 (1C, C5), 71.3 (1C, OCH_2), 71.2 (1C, OCH_2), 70.9 (1C, C6), 70.4 (1C, C3″), 69.8 (1C, C4″), 69.7 (1C, C5″), 69.5 (1C, C2″), 69.1 (1C, C4′), 68.8 (1C, C6″), 67.9 (1C, C4), 67.4 (1C, C5′), 64.2 (1C, C2′), 33.7 (1C, C3′), 28.5 (1C, -CH_2-), 28.2 (1C, -CH_2-), 24.7 (2C, -CH_2-), 16.2 (1C, C6′); ES HRMS calcd for $[C_{25}H_{44}O_{14}Na]$ 591.2629, found 591.2626.

Methyl 2-*O*-[2′,3′,4′-Tri-*O*-benzyl-6′-*O*-(7″-trityloxyheptyl)-α-D-galactopyranosyl]-3-*O*-allyl-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (38). The alcohol **5** (476 mg, 1.18 mmol) and the thioglycoside **7** (1.31 g, 1.55 mmol)

were dried in vacuo with powdered 4 Å molecular sieves over P_2O_5 overnight. The mixture was suspended in CH_2Cl_2 (20 mL) under an Ar atmosphere and stirred for 2 h at room temperature. *N*-Iodosuccinimide (586 mg, 2.60 mmol) was added, and the suspension was stirred for 10 min before rapid, dropwise addition of a saturated solution of triflic acid in ca. 0.15 M CH_2Cl_2 (933 μL, 0.14 mmol). The reaction was quenched with triethylamine, diluted with CH_2Cl_2, and filtered through Celite. The filtrate was washed successively with 10% $Na_2S_2O_3$ and a saturated NaCl solution. After evaporation of the solvent the residue was chromatographed (0 → 20% ethyl acetate in pentane) to provide **38** (1.07 g, 77%) as an oil: $[\alpha]_D$ +60.6° (*c* 0.8, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.50−7.15 (m, 35H), 5.85 (ddd, 1H, *J* = 17.2, 10.4, 5.7 Hz), 5.51 (d, 1H, *J* = 3.9 Hz), 5.26 (ddd, 1H, *J* = 17.2, 3.1, 1.6 Hz), 5.13 (ddd, 1H, *J* = 10.4, 3.1, 1.3 Hz), 4.95 (d, 2H, *J* = 11.6 Hz), 4.81 (d, 1H, *J* = 12.1 Hz), 4.74 (d, 1H, *J* = 12.1 Hz), 4.68 (d, 1H, *J* = 11.7 Hz), 4.64 (s, 1H), 4.63 (d, 1H, *J* = 11.0 Hz), 4.60 (d, 1H, *J* = 11.1 Hz), 4.48 (dd, 1H, *J* = 11.9, 1.7 Hz), 4.36 (dd, 1H, *J* = 11.9, 4.0 Hz), 4.28 (d, 1H, *J* = 11.0 Hz), 4.13 (m, 2H), 4.06 (dd, 1H, *J* = 9.5, 3.9 Hz), 4.05 (m,1H), 3.91 (d, 1H, *J* = 2.3 Hz), 3.86 (dd, 1H, *J* = 9.6, 9.5 Hz), 3.82 (dd, 1H, *J* = 6.4, 6.1 Hz), 3.76 (dd, 2H, *J* = 9.5, 2.6 Hz and *J* = 9.5, 2.6 Hz), 3.65 (ddd, 1H, *J* = 9.6, 4.0, 1.7 Hz), 3.46 (dd, 1H, *J* = 9.6, 6.1 Hz), 3.39 (dd, 1H, *J* = 9.6, 6.4 Hz), 3.36 (m, 1H), 3.27 (s, 3H), 3.26 (m, 1H), 3.01 (t, 2H, *J* = 6.6 Hz), 2.89 (s, 3H), 1.55−1.15 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 138.8, 138.7, 138.5, 138.2, 134.4, 128.6, 128.3, 128.3, 128.2, 128.2, 127.7, 127.6, 127.3, 127.1, 126.7, 117.1, 100.2, 97.3, 86.2, 80.0, 77.9, 76.3, 74.9, 74.9, 74.7, 73.8, 72.6, 71.6, 71.6, 71.3, 71.2, 70.5, 69.9, 69.8, 69.3, 63.5, 54.9, 37.9, 29.9, 29.6, 29.3, 26.2, 26.0. Anal. Calcd for $C_{71}H_{82}O_{14}S$ (1191.48): C,71.57; H, 6.94; S, 2.69. Found: C, 71.74; H, 6.92; S, 2.67.

Methyl 2-*O*-[2′,3′,4′-Tri-*O*-benzyl-6′-*O*-(7″-hydroxyheptyl)-α-D-galactopyranosyl]-3-*O*-allyl-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (41). Disaccharide **38** (855 mg, 0.71 mmol) was dissolved in 9:1 MeOH:EtOAc (10 mL), and a catalytic amount of *p*-toluensulfonic acid was added. The reaction mixture was stirred for 6 h at room temperature. Triethylamine (200 μL) was added, solvents were evaporated, and the residue was purified by chromatography (6:4 pentane−EtOAc) to provide **41** (579 mg, 85%) as an oil: $[\alpha]_D$ + 77.5° (*c* 2.0, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.48−7.27 (m, 20H), 5.87 (ddd, 1H, *J* = 17.2, 10.4, 5.7 Hz), 5.50 (d, 1H, *J* = 3.8 Hz), 5.26 (ddd, 1H, *J* = 17.2, 3.1, 1.6 Hz), 5.15 (ddd, 1H, *J* = 10.4, 3.1, 1.3 Hz), 4.96 (d, 1H, *J* = 11.5 Hz), 4.95 (d, 1H, *J* = 11.7 Hz), 4.81 (d, 1H, *J* = 12.2 Hz), 4.74 (d, 1H, *J* = 12.2 Hz), 4.68 (d, 1H, *J* = 11.7 Hz), 4.66 (s, 1H), 4.64 (d, 1H, *J* = 10.9 Hz), 4.60 (d, 1H, *J* = 11.5 Hz), 4.49 (dd, 1H, *J* = 11.8, 1.4 Hz), 4.36 (dd, 1H, *J* = 11.8 Hz, 4.1 Hz), 4.29 (d, 1H, *J* = 10.9 Hz), 4.15 (dddd, 1H, *J* = 12.6, 5.6, 1.6, 1.3 Hz), 4.08 (m, 2H), 4.06 (dd, 1H, *J* = 9.7, 3.8 Hz), 3.92 (d, 1H, *J* = 2.7 Hz), 3.87 (dd, 1H, *J* = 9, 9.7 Hz), 3.84 (dd, 1H, *J* = 6.4, 5.9 Hz), 3.77 (dd, 2H, *J* = 9.7, 2.7 Hz and *J* = 9.7, 2.7 Hz), 3.67 (ddd, 1H, *J* = 9.8, 4.0, 1.4 Hz), 3.61 (t, 2H, *J* = 6.6 Hz), 3.47 (dd, 1H, *J* = 9.5, 6.4 Hz), 3.41 (dd, 1H, *J* = 9.5, 5.9 Hz), 3.39 (dt, 1H, *J* = 9.5, 6.5 Hz), 3.30 (s, 3H), 3.29 (dt, 1H, *J* = 9.5, 6.7 Hz), 2.92 (s, 3H), 1.64−1.22 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.5, 138.3, 138.0, 134.3, 128.2, 128.1, 128.0, 128.0, 127.5, 127.4, 127.4, 127.3, 127.1, 127.1, 126.9, 116.9, 100.1, 97.2, 79.8, 77.7, 76.1, 74.7, 74.7, 74.5, 73.6, 72.4, 71.4, 71.3, 71.2, 71.1, 70.3, 69.7, 69.6, 69.2, 62.4, 54.7, 37.7, 32.7, 29.4, 29.0, 25.8, 25.4. Anal. Calcd for $C_{52}H_{68}O_{14}S$ (949.16): C, 65.80; H, 7.22; S, 3.38. Found: C, 65.41; H, 7.39; S, 3.56.

Methyl 2-*O*-(3′-*O*-Allyl-4′-*O*-benzyl-α-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-6,6′-di-*O*-(heptane-1,7-diyl)-α-D-mannopyranoside (44). A solution of disaccharide **41** (397 mg, 0.42 mmol) in dry THF (19 mL) was slowly added to a boiling mixture of NaH (130 mg, 5.45 mmol) and Cs_2CO_3 (192 mg, 0.54 mmol) in dry THF (22 mL) over a 2 h period, and the reaction mixture was then refluxed for 24 h. After an excess of NaH was decomposed with MeOH, the solvent was evaporated under reduced pressure and the resulting residue taken up in CH_2Cl_2 and washed with a saturated NaCl solution. Evaporation of the solvent and chromatography (85:15 pentane−EtOAc) gave **44** (120 mg, 34%) as an oil: $[\alpha]_D$ +49.8° (*c* 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.15 (m, 20H), 5.90 (ddd, 1H, *J* = 17.2, 10.4, 5.7 Hz), 5.20 (ddd, 1H, *J* = 17.2, 3.1, 1.6 Hz), 5.02 (ddd, 1H, *J* = 10.4, 3.1, 1.3 Hz, 1H), 4.95 (d, 1H, *J* = 3.6 Hz), 4.94 (d, 1H, *J* = 11.5 Hz), 4.91 (d, 1H, *J* = 1.8 Hz), 4.90 (d, 1H, *J* = 11.0 Hz), 4.83 (d, 1H, *J* = 12.0 Hz), 4.76 (d, 1H, *J* = 12.0 Hz), 4.74 (d, 1H, *J* = 12.5 Hz), 4.72 (d, 1H, *J* = 12.5 Hz), 4.63 (d, 1H, *J* = 11.5 Hz), 4.55 (d, 1H, *J* = 11.0 Hz), 4.14 (m, 1H), 4.13 (dd, 1H, *J* = 8.1, 5.8 Hz), 4.05 (dd, 1H, *J* = 9.9, 3.6 Hz), 4.02 (m, 1H), 3.97 (bs, 1H), 3.98 (dd, 1H, *J* = 9.9, 2.7 Hz), 3.82 (dd, 1H, *J* = 9.0, 3.2 Hz), 3.79 (dd, 1H, *J* = 3.2, 1.8 Hz), 3.73 (d, 1H, *J* = 10.1 Hz), 3.66 (m, 2H), 3.51 (ddd, 1H, *J* = 9.7, 6.5, 6.2 Hz), 3.49 (dd, 1H, *J* = 10.9, 8.1 Hz), 3.47 (ddd, 1H, *J* = 9.7, 6.3, 6.3 Hz), 3.42 (ddd, 1H, *J* = 9.7, 6.1, 6.1 Hz), 3.41 (dd, 1H, *J* = 10.1, 5.7 Hz), 3.38 (dd, 1H, *J* = 10.9, 5.8 Hz), 3.36 (ddd, 1H, *J* = 9.6, 6.7, 6.7 Hz), 3.31 (s, 3H), 1.60−1.26 (m, 10H); FABMS calcd for $[C_{51}H_{64}O_{11}Na]$ 875.4, found 875.2. Anal. Calcd for $C_{50}H_{62}O_{11}$: C, 71.81; H, 7.56. Found: C, 71.82; H, 7.61.

Methyl 2-*O*-(2′,3′,4′-Tri-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-benzyl-6,6′-di-*O*-(heptane-1,7-diyl)-α-D-mannopyranoside (47). A solution of disaccharide **44** (290 mg, 0.34 mmol) in dry DMSO (3 mL) was heated at 80 °C, and KO^{t}Bu (153 mg, 1.35 mmol) was added. After 2 h, the isomerization was complete. The mixture was cooled to room temperature, diluted with CH_2Cl_2, washed with water, and dried (Na_2SO_4). The solvent was evaporated, and the residue was redissolved in 9:1 acetone−water (23 mL). Mercuric oxide (36 mg, 0.16 mmol) and mercuric chloride (2.0 g, 7.36 mmol) were added, and the solution was stirred for 30 min. The solvent was evaporated, and the residue was purified by chromatography (80:20 pentane−EtOAc) to afford **47** (235 mg, 85%) as an oil: $[\alpha]_D$ +67.3° (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.15 (m, 20H), 4.92 (d, 1H, *J* = 11.4 Hz), 4.89 (d, 1H, *J* = 11.3 Hz), 4.86 (d, 1H, *J* = 11.8 Hz), 4.77 (d, 1H, *J* = 3.7 Hz), 4.75 (d, 1H, *J* = 1.7 Hz), 4.74 (bs, 2H), 4.68 (d, 1H, *J* = 11.8 Hz), 4.64 (d, 1H, *J* = 11.5 Hz), 4.57 (d, 1H, *J* = 11.3 Hz), 4.06 (dd, 1H, *J* = 6.7, 6.6 Hz), 4.00 (dd, 1H, *J* = 10.1, 3.7 Hz), 3.95(dd, 1H, *J* = 2.7, 0.9 Hz), 3.94 (dd, 1H, *J* = 9.2, 3.8 Hz), 3.85 (dd, 1H, *J* = 9.9, 2.7 Hz), 3.70 (dd, 1H, *J* = 10.1, 1.8 Hz), 3.64 (dd, 1H, *J* = 3.8, 1.7 Hz), 3.59 (ddd, 1H, *J* = 9.9, 6.1, 1.8 Hz), 3.52 (ddd, 1H, *J* = 9.7, 6.5, 6.2 Hz), 3.48−3.40 (m, 5H), 3.31 (dd, 1H, *J* = 9.9, 9.2 Hz), 3.31 (ddd, 1H, *J* = 9.5, 6.3, 6.3 Hz), 3.30 (s, 3H), 1.60−1.26 (m, 10H). Anal. Calcd for ($C_{48}H_{60}O_{11}$): C, 70.91; H, 7.44. Found: C, 70.92; H, 7.50.

Methyl 2-*O*-(2″,3″,4″-Tri-*O*-benzyl-α-D-galactopyranosyl)-3-*O*-(2′,4′-di-*O*-benzyl-3′,6′-dideoxy-α-D-*xylo*-hexopyranosyl)-4-*O*-benzyl-6,6″-di-*O*-(heptane-1,7-diyl)-α-D-mannopyranoside (50). The disaccharide alcohol **47** (119 mg, 0.14 mmol) and the 3,6-dideoxyhexose thioglycoside **11** (250 mg, 0.67 mmol) were dried in vacuo with powdered and freshly activated 4 Å molecular sieves over P_2O_5 overnight. The mixture was suspended in dry CH_2Cl_2 (5 mL), cooled to −45 °C, and stirred for 20 min. *N*-Iodosuccinimide (168 mg, 0.71 mmol) and a solution of silver triflate (17 mg, 0.07 mmol) in dry toluene (200 μL) were added rapidly, dropwise, and after 30 min the reaction was quenched with triethylamine. The reaction was then diluted with CH_2Cl_2 and filtered, and the filtrate was washed successively with $Na_2S_2O_3$ and a saturated NaCl solution and dried (Na_2SO_4). After evaporation of solvent, the residue was purified by chromatography (85:15 pentane−EtOAc) to afford **50** (89 mg, 54%) as an oil: $[\alpha]_D$ +83.3° (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.15 (m, 30H), 5.09 (d, 1H, *J* = 11.8 Hz), 5.03 (d, 1H, *J* = 3.3 Hz), 4.97 (bs, 1H), 4.94 (d, 1H, *J* = 12.2 Hz), 4.91 (d, 1H, *J* = 2.0 Hz), 4.90 (d, 1H, *J* = 11.3 Hz), 4.75 (bs, 2H), 4.63 (d, 1H, *J* = 12.2 Hz), 4.62 (d, 1H, *J* = 11.5 Hz), 4.59 (d, 1H, *J* = 11.8 Hz), 4.38 (d, 1H, *J* = 12.4 Hz), 4.32 (d, 1H, *J* = 12.4 Hz), 4.25 (d, 1H, *J* = 12.2 Hz), 4.23 (dd, 1H, *J* = 8.2, 5.8 Hz), 4.09 (dd, 1H, *J* = 8.8, 2.9 Hz), 4.07 (m, 2H), 4.06 (d, 1H, *J* = 12.2 Hz), 4.05 (m, 1H), 4.02 (bs, 1H), 3.84 (dd, 1H, *J* = 2.9, 2.0 Hz), 3.72 (dd, 1H, *J* = 9.9, 8.8 Hz), 3.69 (m 1H), 3.66 (m, 1H), 3.55 (dd, 1H, *J* = 9.9, 5.8 Hz), 3.45−3.40 (m, 4H), 3.34 (dd, 1H, *J* = 9.9, 5.3 Hz), 3.32 (s, 3H), 3.31 (dd, 1H, *J* = 9.3, 5.6 Hz), 2.43 (bs, 1H),

1.70 (m, 2H), 1.55−1.30 (m, 10H), 0.98 (d, 3H, J = 6.5 Hz, 1H). Anal. Calcd for $C_{68}H_{82}O_{14}$: C, 72.70; H, 7.36. Found: C, 72.68; H, 7.42.

Methyl 2-*O*-(α-D-Galactopyranosyl)-3-*O*-(3′,6′-dideoxy-α-D-*xylo*-hexopyranosyl)-6,6″-di-*O*-(heptane-1,7-diyl)-α-D-mannopyranoside (3). A stirred solution of **50** (65 mg, 0.06 mmol) in acetic acid (7 mL) was hydrogenated over 10% Pd/C (73 mg) under a flow of H_2 overnight. The catalyst was removed by filtration and the solvent evaporated. Chromatography (85:15 CH_2Cl_2−MeOH) on Iatrobeads afforded **3** (28 mg, 83%) as a white solid: $[\alpha]_D$ +99.8° (*c* 0.5, H_2O); ^{1}H NMR (500 MHz, D_2O) δ 5.07 (d, 1H, $J_{1,2}$ = 3.7 Hz, H1′), 5.06 (d, 1H, $J_{1,2}$ = 1.8 Hz, H1), 5.02 (d, 1H, $J_{1,2}$ = 4.0 Hz, H1″), 4.28 (m, 1H, H5″), 4.09 (m, H-5′), 4.02 (m, 1H, $J_{2,3ax}$ = 9.3, $J_{2,3eq}$ = 8.4 Hz, H2′), 3.98 (dd, 1H, $J_{4,5}$ = 0.9, Hz, H4″), 3.94 (m 1H, $J_{3,4}$ = 9.7 Hz, H3), 3.94 (m, $J_{5,6a}$ = 1.4 Hz, H6a), 3.91 (ddd, 1H, $J_{3,4}$ = 3.4, Hz, H3″) 3.88 (dd, 1H, $J_{2,3}$ = 3.2 Hz, H2), 3.86 (m, $J_{4,5}$ = 1.3 Hz, H-4′), 3.78 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H4), 3.75 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H2″), 3.72 (m, H5), 3.70 (dd, 1H, $J_{5,6a}$ = 7.6, Hz, H6a″), 3.70 (m, 1H, OCH_2), 3.66 (m, 1H, OCH_2), 3.63 (dd, 1H, $J_{5,6a}$ = 4.1, Hz, H6b″), 3.62 (m, 1H, OCH_2), 3.59 (m, $J_{5,6b}$ = 8.1 Hz, H6b), 3.52 (m, 1H, OCH_2), 1.97 (m, 2H, $J_{3eq,4}$ = $J_{3ax,4}$ = 3.1 Hz, H-3′), 1.7−1.3 (m, 10H, $OCH_2(CH_2)_5CH_2O$), 1.18 (d, 3H, $J_{5,6}$ = 6.7 Hz, H-6′). ^{13}C NMR (125 MHz, D_2O) δ 103.3 (1C, $^1J_{C,H}$ = 169.2 Hz, C1″), 101.6 (1C, $^1J_{C,H}$ = 170.6 Hz, C1′), 100.0 (1C, $^1J_{C,H}$ = 173.2 Hz, C1), 82.4 (1C, C2), 78.4 (1C, C3), 73.0 (1C, C5), 72.1 (1C, OCH_2), 71.8 (1C, OCH_2), 70.8 (1C, C6″), 70.6 (1C, C6), 70.5 (1C, C4″), 70.2 (1C, C3″), 69.9 (1C, C5″), 69.5 (1C, C2″), 69.1 (1C, C4′), 67.9 (1C, C4), 67.5 (1C, C5′), 64.2 (1C, C2′), 33.7 (1C, C3′), 28.4 (1C, -CH_2-), 28.2 (1C, -CH_2-), 27.4 (1C, -CH_2-), 25.8 (1C, -CH_2-), 25.6 (1C, -CH_2-), 16.2 (1C, C6′); ES HRMS calcd for [$C_{26}H_{46}O_{14}$Na] 605.2785, found 605.2766.

Methyl 3-*O*-Allyl-2-*O*-[2′,3′,4′-tri-*O*-benzyl-6′-*O*-(8″-trityloxyoctyl)-α-D-galactopyranosyl]-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (39). The alcohol **5** (495 mg, 1.23 mmol) and the thioglycoside **8** (1.23 g, 1.42 mmol) were dried in vacuo with powdered 4 Å molecular sieves over P_2O_5 overnight. The mixture was suspended in CH_2Cl_2 (18 mL) under an Ar atmosphere and stirred for 2 h at room temperature. *N*-Iodosuccinimide (639 mg, 2.84 mmol) was added, and the suspension was stirred for 10 min before rapid, dropwise addition of a saturated solution of triflic acid in ca. 0.15 M CH_2Cl_2 (1.4 mL, 0.21 mmol). The reaction was quenched with triethylamine, diluted with CH_2Cl_2, and filtered through Celite. The filtrate was washed successively with 10% $Na_2S_2O_3$ and a saturated NaCl solution. After evaporation of the solvent the residue was chromatographed (0 → 20% ethyl acetate in pentane) to provide **39** (1.12 g, 76%) as an oil: $[\alpha]_D$ +50.5° (*c* 1.7, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.50−7.15 (m, 35H), 5.88 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.51 (d, 1H, J = 3.8 Hz), 5.25 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.14 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.95 (d, 2H, J = 11.6 Hz), 4.80 (d, 1H, J = 12.2 Hz), 4.74 (d, 1H, J = 12.2 Hz), 4.68 (d, 1H, J = 11.6 Hz), 4.65 (s, 1H), 4.63 (d, 1H, J = 11.3 Hz), 4.60 (d, 1H, J = 11.5 Hz), 4.49 (dd, 1H, J = 11.9, 1.7 Hz), 4.36 (dd, 1H, J = 11.9, 4.0 Hz), 4.28 (d, 1H, J = 10.9 Hz), 4.15 (m, 1H), 4.10 (m, 2H), 4.06 (dd, 1H, J = 9.9, 3.8 Hz), 3.92 (d, 1H, J = 2.6 Hz), 3.87 (dd, 1H, J = 9.6, 9.5 Hz), 3.83 (dd, 1H, J = 6.5, 6.3 Hz), 3.76 (dd, 2H, J = 9.9, 2.6 Hz and J = 9.5, 2.6 Hz), 3.66 (ddd, 1H, J = 9.7, 4.0, 1.7 Hz), 3.47 (dd, 1H, J = 9.6, 6.3 Hz), 3.39 (dd, 1H, J = 9.6, 6.5 Hz), 3.37 (m, 1H), 3.28 (s, 3H), 3.26 (m, 1H), 3.02 (t, 2H, J = 6.6 Hz), 2.90 (s, 3H), 1.15−1.55 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 138.8, 138.7, 138.5, 138.2, 134.4, 128.6, 128.3, 128.3, 128.2, 128.2, 128.0, 127.7, 127.6, 127.4, 127.3, 126.7, 117.1, 100.2, 97.3, 86.2, 80.0, 77.9, 76.3, 74.9, 74.9, 74.7, 73.8, 72.6, 71.6, 71.6, 71.3, 71.2, 70.5, 69.9, 69.8, 69.3, 63.5, 54.9, 37.8, 29.9, 29.7, 29.5, 29.3, 26.2, 26.0; FABMS calcd for [$C_{72}H_{84}O_{14}$SNa] 1227.5, found 1227.7.

Methyl 3-*O*-Allyl-2-*O*-[2′,3′,4′-tri-*O*-benzyl-6′-*O*-(8″-hydroxyoctyl)-α-D-galactopyranosyl]-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (42). Disaccharide **39** (1.34 g, 1.11 mmol) was dissolved in 9:1 MeOH:EtOAc (10 mL), and a catalytic amount of *p*-toluensulfonic acid was added. The reaction mixture was stirred for 6 h at room temperature. Triethylamine (200 μL) was added, solvents were evaporated, and the residue was purified by chromatography (6:4 pentane−EtOAc) to provide **42** (912 mg, 85%) as an oil: $[\alpha]_D$ + 75.6° (*c* 2.3, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.48−7.27 (m, 20H), 5.88 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.50 (d, 1H, J = 3.9 Hz), 5.26 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.14 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.96 (d, 1H, J = 11.4 Hz), 4.95 (d, 1H, J = 11.7 Hz), 4.81 (d, 1H, J = 12.2 Hz), 4.74 (d, 1H, J = 12.2 Hz), 4.68 (d, 1H, J = 11.5 Hz), 4.66 (s, 1H), 4.63 (d, 1H, J = 11.1 Hz), 4.60 (d, 1H, J = 11.5 Hz), 4.49 (dd, 1H, J = 11.8, 1.6 Hz), 4.36 (dd, 1H, J = 11.8, 4.1 Hz), 4.28 (d, 1H, J = 10.9 Hz), 4.15 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 4.08 (m, 2H), 4.06 (dd, 1H, J = 10.1, 3.9 Hz), 3.92 (d, 1H, J = 2.3 Hz), 3.87 (dd, 1H, J = 9.8, 9.6 Hz), 3.83 (dd, 1H, J = 6.4, 6.0 Hz), 3.77 (dd, 2H, J = 9.8, 2.7 Hz and J = 9.8, 2.7 Hz), 3.66 (ddd, 1H, J = 9.8, 4.1, 1.6 Hz), 3.61 (t, 2H, J = 6.4 Hz), 3.47 (dd, 1H, J = 9.7, 6.4 Hz), 3.40 (dd, 1H, J = 9.7, 6.0 Hz), 3.39 (dt, 1H, J = 9.5, 6.5 Hz), 3.30 (s, 3H), 3.29 (dt, 1H, J = 9.3, 6.8 Hz), 2.92 (s, 3H), 1.64−1.22 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.5, 138.4, 138.0, 134.3, 128.2, 128.2, 128.1, 127.6, 127.5, 127.4, 127.2, 127.1, 127.0, 116.9, 100.1, 97.2, 79.8, 77.8, 76.1, 74.8, 74.7, 74.5, 73.7, 72.5, 71.5, 71.4, 71.2, 71.1, 70.3, 69.8, 69.7, 69.2, 62.5, 54.7, 37.7, 32.5, 29.5, 29.2, 29.1, 25.8, 25.5. Anal. Calcd for $C_{53}H_{70}O_{14}S$ (963.19): C, 66.09; H, 7.33; S, 3.33. Found: C, 65.93; H, 7.55; S, 3.42.

Methyl 2-*O*-(3′-*O*-Allyl-4′-*O*-benzyl-α-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-6,6′-di-*O*-(octane-1,8-diyl)-α-D-mannopyranoside (45). Method A. A solution of disaccharide **42** (322 mg, 0.33 mmol) in dry THF (18 mL) was slowly added to a boiling mixture of NaH (104 mg, 4.35 mmol) and Cs_2CO_3 (153 mg, 0.44 mmol) in dry THF (15 mL) over a 2 h period, and the reaction mixture was then refluxed for 24 h. After an excess of NaH was decomposed with MeOH, the solvent was evaporated under reduced pressure and the resulting residue taken up in CH_2Cl_2 and washed with a saturated NaCl solution. Evaporation of the solvent and chromatography (85:15 pentane−EtOAc) gave **45** (101 mg, 35%) as an oil.

Method B. A solution of disaccharide **53** (377 mg, 0.39 mmol) in dry THF (19 mL) was slowly added to a boiling mixture of NaH (121 mg, 5.07 mmol) and Cs_2CO_3 (179 mg, 0.507 mmol) in dry THF (20 mL) over a 2 h period. The reaction mixture was refluxed for 24 h. After an excess of NaH was decomposed with MeOH, the solvent was evaporated under reduced pressure and the resulting residue taken up in CH_2Cl_2 and washed with a saturated NaCl solution. Evaporation of the solvent and chromatography gave **45** (208 mg, 61% yield) as an oil: $[\alpha]_D$ +52.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.15 (m, 20H), 5.82 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.20 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.03 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 5.01 (d, 1H, J = 3.8 Hz), 4.94 (d, 1H, J = 11.6 Hz), 4.88 (d, 1H, J = 11.1 Hz), 4.86 (d, 1H, J = 1.4 Hz), 4.83 (d, 1H, J = 11.9 Hz), 4.78 (d, 1H, J = 11.6 Hz), 4.75 (d, 1H, J = 12.1 Hz), 4.69 (d, 1H, J = 11.6 Hz), 4.62 (d, 1H, J = 11.6 Hz), 4.55 (d, 1H, J = 11.1 Hz), 4.12 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 4.08 (m, 2H), 4.03 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 3.98 (dd, 1H, J = 2.9, 0.9 Hz), 3.95 (dd, 1H, J = 9.9, 2.9 Hz), 3.81 (m, 1H), 3.79 (dd, 1H, J = 9.0, 3.1 Hz), 3.70 (d, 1H, J = 10.4 Hz), 3.65 (m, 2H), 3.52 (dt, 1H, J = 9.5, 5.8 Hz), 3.44−3.36 (m, 6H), 3.31 (s, 3H), 1.60−1.26 (m, 12H); FABMS calcd for [$C_{52}H_{66}O_{11}$Na] 889.4, found 889.3.

Methyl 2-*O*-(2′,3′,4′-Tri-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-benzyl-6,6′-di-*O*-(octane-1,8-diyl)-α-D-mannopyranoside (48). A solution of disaccharide **45** (219 mg, 0.25 mmol) in dry DMSO (2 mL) was heated at 80 °C, and KO^{t}Bu (113 mg, 1.01 mmol) was added. After 2 h, the isomerization was complete. The mixture was cooled to room temperature, diluted with CH_2Cl_2, washed with water, and dried (Na_2SO_4). The solvent was evaporated, and the residue was redissolved in 9:1 acetone−water (20 mL). Mercuric oxide (25 mg, 0.11 mmol) and mercuric chloride (1.5 g, 5.52 mmol) were added, and the solution was stirred for 30 min. The solvent was evaporated, and the residue was purified by chromatography (80:20 pentane−EtOAc) to afford **48** (179 mg, 85%) as an oil: $[\alpha]_D$ +68.0° (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.15 (m, 20H), 4.91 (d, 1H, J = 11.6 Hz), 4.87 (d, 1H, J = 11.5

Hz), 4.86 (d, 1H, J = 11.3 Hz), 4.81 (d, 1H, J = 3.8 Hz), 4.74 (b, 2H), 4.73 (m, 1H), 4.68 (d, 1H, J = 11.6 Hz), 4.62 (d, 1H, J = 11.6 Hz), 4.54 (d, 1H, J = 10.8 Hz), 4.02 (dd, 1H, J = 7.3, 5.5 Hz), 4.01 (dd, 1H, J = 9.9, 3.7 Hz), 3.96 (dd, 1H, J = 2.9, 0.9 Hz), 3.94 (m, 1H), 3.87 (dd, 1H, J = 9.9, 2.9 Hz), 3.70 (dd, 1H, J = 10.4, 1.8 Hz), 3.65 (dd, 1H, J = 3.8, 1.7 Hz), 3.60 (ddd, 1H, J = 9.9, 6.5, 1.8 Hz), 3.58 (b, 1H), 3.52 (ddd, 1H, J = 9.7, 6.5, 6.2 Hz), 3.48−3.40 (m, 6H), 3.30 (dd, 1H, J = 9.9, 9.2 Hz), 3.30 (s, 3H), 1.60−1.26 (m, 12H). Anal. Calcd for ($C_{49}H_{62}O_{11}$): C, 71.16; H, 7.56. Found: C, 71.08; H, 7.57.

Methyl 2-*O*-(2″,3″,4″-Tri-*O*-benzyl-α-D-galactopyranosyl)-3-*O*-(2′,4′-di-*O*-benzyl-3′,6′-dideoxy-α-D-*xylo*-hexopyranosyl)-4-*O*-benzyl-6,6″-di-*O*-(octane-1,8-diyl)-α-D-mannopyranoside (51). The disaccharide alcohol **48** (136 mg, 0.16 mmol) and the 3,6-dideoxyhexose thioglycoside **11** (281 mg, 0.75 mmol) were dried in vacuo with powdered and freshly activated 4 Å molecular sieves over P_2O_5 overnight. The mixture was suspended in dry CH_2Cl_2 (5.5 mL), cooled to −45 °C, and stirred for 20 min. *N*-Iodosuccinimide (178 mg, 0.79 mmol) and a solution of silver triflate (20 mg, 0.08 mmol) in dry toluene (200 μL) were added rapidly, dropwise, and after 30 min the reaction was quenched with triethylamine. The reaction was then diluted with CH_2Cl_2 and filtered, and the filtrate was washed successively with $Na_2S_2O_3$ and a saturated NaCl solution and dried (Na_2SO_4). After evaporation of solvent, the residue was purified by chromatography (84:16 pentane−EtOAc) to afford **51** (116 mg, 62%) as an oil: $[\alpha]_D$ +82.1° (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15−7.50 (m, 30H), 5.09 (d, 1H, J = 11.8 Hz), 5.04 (d, 1H, J = 3.3 Hz), 5.00 (d, 1H, J = 2.9 Hz), 4.94 (d, 1H, J = 12.0 Hz), 4.91 (d, 1H, J = 11.4 Hz), 4.89 (d, 1H, J = 1.8 Hz), 4.75 (b, 2H), 4.65 (d, 1H, J = 12.1 Hz), 4.61 (d, 1H, J = 11.4 Hz), 4.59 (d, 1H, J = 11.6 Hz), 4.38 (d, 1H, J = 12.4 Hz), 4.31 (d, 1H, J = 12.5 Hz), 4.27 (d, 1H, J = 12.2 Hz), 4.19 (dd, 1H, J = 7.0, 6.7 Hz), 4.10 (m, 2H), 4.08−4.05 (m, 3H), 4.02 (b, 1H), 3.85 (dd, 1H, J = 2.7, 2.0 Hz), 3.75 (dd, 1H, J = 9.9, 9.5 Hz), 3.70 (ddd, 1H, J = 9.9, 6.1, 1.2 Hz), 3.67 (m, 1H), 3.63 (dd, 1H, J = 10.0, 1.2 Hz), 3.50−3.35 (m, 6H), 3.32 (s, 3H), 3.31 (ddd, 1H, J = 9.5, 6.4, 6.4 Hz), 2.48 (b, 1H), 1.70 (m, 2H), 1.55−1.25 (m, 12H), 0.99 (d, 3H, J = 6.7 Hz). Anal. Calcd for $C_{69}H_{84}O_{14}$: C, 72.86; H, 7.44. Found: C,72.80; H, 7.43.

Methyl 2-*O*-(α-D-Galactopyranosyl)-3-*O*-(3′,6′-dideoxy-α-D-*xylo*-hexopyranosyl)-6,6″-di-*O*-(octane-1,8-diyl)-α-D-mannopyranoside (4). A stirred solution of **51** (81 mg, 0.07 mmol) in acetic acid (9 mL) was hydrogenated over 10% Pd/C (93 mg) under a flow of H_2 overnight. The catalyst was removed by filtration, and the solvent was evaporated. Chromatography (85:15 CH_2Cl_2−MeOH) on Iatrobeads afforded **4** (38 mg, 89%) as a white solid: $[\alpha]_D$ +105.2° (*c* 0.8, H_2O); ^{1}H NMR (500 MHz, D_2O) δ 5.10 (d, 1H, $J_{1,2}$ = 1.6 Hz, H1), 5.08 (d, 1H, $J_{1,2}$ = 3.8 Hz, H1′), 5.02 (d, 1H, $J_{1,2}$ = 4.0 Hz, H1″), 4.23 (m, 1H, H5″), 4.09 (m, H-5′), 4.01 (m, 1H, $J_{2,3ax}$ = 10.8, $J_{2,3eq}$ = 6.7 Hz, H2′), 3.97 (dd, 1H, $J_{4,5}$ = 0.9, Hz, H4″), 3.95 (m, H6a), 3.92 (m, H3), 3.90 (ddd, 1H, $J_{3,4}$ = 3.4, Hz, H3″), 3.89 (d, 1H, $J_{2,3}$ = 3.1 Hz, H2), 3.86 (m, $J_{4,5}$ = 1.2 Hz, H-4′), 3.76 (m, H4), 3.76 (m, H5), 3.75 (dd, 1H, $J_{2,3}$ = 10.4, Hz, H2″), 3.73 (m, 1H, OCH_2), 3.67 (dd, 1H, $J_{5,6a}$ = 8.3, Hz, H6a″), 3.62 (m, 1H, OCH_2), 3.59 (dd, 1H, $J_{5,6a}$ = 3.5, Hz, H6b″), 3.57 (m, H6b), 3.53 (m, 1H, OCH_2), 3.51 (m, 1H, OCH_2), 1.98 (m, 2H, $J_{3eq,4}$ = $J_{3ax,4}$ = 3.4 Hz, H-3′), 1.6−1.3 (m, 12H, $OCH_2(CH_2)_6$-CH_2O), 1.18 (d, 3H, $J_{5,6}$ = 6.7 Hz, H-6′); ^{13}C NMR (125 MHz, D_2O) δ 103.5 (1C, $^1J_{C,H}$ = 170.4 Hz, C1″), 101.5 (1C, $^1J_{C,H}$ = 170.4 Hz, C1′), 100.2 (1C, $^1J_{C,H}$ = 174.0 Hz, C1), 82.3 (1C, C2), 78.5 (1C, C3), 71.5 (OCH_2), 71.4 (OCH_2), 70.9 (1C, C5″), 70.8 (1C, C6), 70.5 (1C, C4″), 70.2 (1C, C3″), 70.2 (1C, C6″), 69.5 (1C, C2″), 69.2 (1C, C4′), 68.2 (1C, C4), 68.2 (1C, C5), 67.5 (1C, C5′), 64.2 (1C, C2′), 33.6 (1C, C3′), 28.8 (2C, -CH_2-), 28.7 (2C, -CH_2-), 25.4 (1C, -CH_2-), 25.3 (1C, -CH_2-), 16.2 (1C, C6′); ES HRMS calcd for [$C_{27}H_{48}O_{14}$Na] 619.2942, found 619.2947.

Methyl 3-*O*-Allyl-2-*O*-[2′,3′,4′-tri-*O*-benzyl-6′-*O*-trityl-α-D-galactopyranosyl]-4-*O*-benzyl-6-*O*-(8″-methanesulfonyloxyoctyl)-α-D-mannopyranoside (52). Alcohol **9** (428 mg, 0.90 mmol) and thioglycoside **10** (1.19 g, 1.61 mmol) were dried in vacuo with powdered 4 Å molecular sieves over P_2O_5 overnight. The mixture was suspended in CH_2Cl_2 (19 mL) under an Ar atmosphere and stirred for 2 h at room temperature. *N*-Iodosuccinimide (729 mg, 3.24 mmol) was added and the suspension stirred for 10 min before a solution of triflic acid in CH_2Cl_2 (0.15 M, 1.62 mL) was added rapidly, dropwise. After being stirred for 30 min, the reaction was quenched with triethylamine, diluted with CH_2Cl_2, and filtered. The filtrate was washed with 10% $Na_2S_2O_3$ and a saturated NaCl solution. Evaporation of the solvent and chromatography (75:25 EtOAc−pentane) afforded disaccharide **52** (902 mg, 82%) as an oil: $[\alpha]_D$ +51.1° (*c* 1.8, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.50−6.90 (m, 35H), 5.90 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.48 (d, 1H, J = 2.6 Hz), 5.24 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.11 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.97 (d, 2H, J = 11.9 Hz), 4.90 (d, 1H, J = 11.8 Hz), 4.82 (d, 1H, J = 1.8 Hz), 4.76 (d, 1H, J = 11.3 Hz), 4.71 (d, 1H, J = 11.7 Hz), 4.64 (d, 1H, J = 11.1 Hz), 4.63 (d, 1H, J = 11.8 Hz), 4.38 (d, 1H, J = 11.3 Hz), 4.31 (d, 1H, J = 11.2 Hz),4.20 (dd, 1H, J = 2.6, 1.2 Hz), 4.19−4.15 (m, 1H), 4.13 (t, 2H, J = 6.6 Hz), 4.12 (m, 1H), 4.02 (bm, 2H), 3.90 (d, 1H, J = 1.8 Hz), 3.89 (dd, 1H, J = 9.6, 9.3 Hz), 3.80 (dd, 1H, J = 9.3, 2.6 Hz), 3.73−3.63 (m, 3H), 3.53 (dt, 1H, J = 9.2, 6.6 Hz), 3.40 (dt, 1H, J = 9.2, 6.8 Hz), 3.39 (m, 1H), 3.29 (s, 3H), 3.03 (dd, 1H, J = 9.2, 5.7 Hz), 2.93 (s, 3H), 1.15−1.55 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.40, 138.82, 138.67, 138.50, 138.18, 134.42, 128.58, 128.34, 128.27, 128.21, 128.16, 128.02, 127.68, 127.59, 127.35, 127.27, 126.72, 117.05, 100.17, 97.5, 86.5, 78.4, 76.6, 76.4, 75.8, 75.1, 74.8, 74.5, 73.3, 72.1, 71.7, 71.4, 71.1, 70.0, 69.9, 63.4, 54.6, 37.0, 29.7, 29.1, 28.9, 28.8, 25.9, 25.2. Anal. Calcd for $C_{72}H_{84}O_{14}S$ (1205): C, 71.74; H, 7.02; S, 2.66. Found: C, 71.80; H, 6.84; S, 2.75.

Methyl 3-*O*-Allyl-2-*O*-[2′,3′,4′-tri-*O*-benzyl-α-D-galactopyranosyl]-4-*O*-benzyl-6-*O*-(methanesulfonyloxyoctyl)-α-D-mannopyranoside (53). Disaccharide **52** (787 mg, 0.65 mmol) was dissolved in 9:1 MeOH:EtOAc, and a catalytic amount of *p*-toluenesulfonic acid was added. The reaction mixture was stirred for 7 h. Triethylamine (100 μL) was added, the solvents were evaporated, and the residue was purified by chromatography (1:1 EtOAc−pentane) to afford **53** (505 mg, 81%) as an oil: $[\alpha]_D$ +53.3° (*c* 2.2, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.40−7.10 (m, 20H), 5.90 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.41 (d, 1H, J = 3.6 Hz), 5.24 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.11 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.95 (d, 1H, J = 11.6 Hz), 4.93 (d, 1H, J = 11.7 Hz), 4.90 (d, 1H, J = 11.7 Hz), 4.76 (d, 1H, J = 1.8 Hz), 4.72 (d, 1H, J = 11.7 Hz), 4.69 (d, 1H, J = 11.6 Hz), 4.68 (d, 1H, J = 11.2 Hz), 4.60 (d, 1H, J = 11.6 Hz), 4.33 (d, 1H, J = 11.2 Hz), 4.31 (d, 1H, J = 11.2 Hz), 4.13 (m, 1H), 4.12 (t, 2H, J = 6.6 Hz), 4.09 (m, 2H), 4.14 (dd, 1H, J = 2.7, 1.8 Hz), 3.99 (dd, 1H, J = 10.1, 3.6 Hz), 3.90 (m, 1H), 3.86 (b, 1H), 3.85 (dd, 1H, J = 9.5, 9.3 Hz), 3.77 (dd, 1H, J = 9.3, 2.7 Hz), 3.73 (dd, 1H, J = 11.4, 6.8 Hz), 3.68−3.59 (m, 3H), 3.45 (m, 2H), 3.36 (dt, 1H, J = 9.2, 6.8 Hz), 3.30 (s, 3H), 2.93 (s, 3H), 1.15−1.55 (m, 12H); FABMS calcd for [$C_{53}H_{70}O_{14}$SNa] 985.4, found 985.3.

Methyl 2-*O*-[2′,3′,4′-Tri-*O*-benzyl-6′-*O*-(1″,1″,1″-triphenyloxy-3,6-dioxaoctanyl)-α-D-galactopyranosyl]-3-*O*-allyl-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (54). The alcohol **5** (450 mg, 1.12 mmol) and the thioglycoside **12** (1.19 g, 1.37 mmol) were dried in vacuo with powdered 4 Å molecular sieves over P_2O_5 overnight. The mixture was suspended in CH_2Cl_2 (24 mL) under an Ar atmosphere and stirred for 2 h at room temperature. *N*-Iodosuccinimide (554 mg, 2.46 mmol) was added, and the suspension was stirred for 10 min before a saturated solution of triflic acid in ca. 0.15 M CH_2Cl_2 (900 μL, 0.13 mmol) was added rapidly, dropwise. The reaction was quenched with triethylamine and diluted with CH_2Cl_2, and the reaction was filtered through Celite. The filtrate was washed successively with 10% $Na_2S_2O_3$ and a saturated NaCl solution. After evaporation of the solvent the residue was chromatographed (2:1 pentane−EtOAc) to provide **54** (1.00 g, 74%) as an oil: $[\alpha]_D$ +65.04° (*c* 2.02, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.48−7.15 (m, 35H), 5.86 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.51 (d, 1H, J = 3.9 Hz), 5.25 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.13 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.94 (d, 1H, J = 11.7 Hz), 4.93 (d, 1H, J = 11.5 Hz), 4.78 (d, 1H, J = 12.2 Hz), 4.72 (d, 1H, J = 12.2 Hz), 4.68 (d, 1H, J = 11.9 Hz), 4.64 (d, 1H, J = 1.9 Hz), 4.62 (d, 1H, J = 10.9 Hz),

4.60 (d, 1H, J = 11.5 Hz), 4.48 (dd, 1H, J = 11.8, 1.7 Hz), 4.36 (dd, 1H, J = 11.8, 4.0 Hz), 4.26 (d, 1H, J = 10.9 Hz), 4.13 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 4.09 (dd, 1H, J = 2.5, 1.9 Hz), 4.06 (m, 1H), 4.05 (dd, 1H, J = 9.8, 3.9 Hz), 3.94 (d, 1H, J = 2.0 Hz), 3.86 (t, 1H, J = 5.5 Hz), 3.86 (dd, 1H, J = 9.7, 9.5 Hz), 3.75 (dd, 2H, J = 9.8, 2.0 Hz and J = 9.7, 2.5 Hz), 3.42−3.68 (m, 11H), 3.27 (s, 3H), 3.28 (m, 1H), 3.20 (t, 2H, J = 5.3 Hz), 2.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 138.8, 138.6, 138.5, 138.1, 134.4, 128.6, 128.3, 128.3, 128.2, 128.2, 127.7, 127.6, 127.5, 127.5, 127.3, 127.1, 126.8, 117.1, 100.2, 97.2, 86.2, 80.0, 77.8, 76.2, 74.9, 74.7, 73.8, 72.6, 71.6, 71.3, 71.2, 70.8, 70.7, 70.6, 70.5, 70.0, 69.7, 69.3, 63.2, 54.8, 37.9; FABMS calcd for [$C_{70}H_{80}O_{16}$SNa] 1231.5, found 1231.2.

Methyl 2-*O*-[2′,3′,4′-Tri-*O*-benzyl-6′-*O*-(1″-hydroxy-3,6-dioxaoctyl)-D-galactopyranosyl]-3-*O*-allyl-4-*O*-benzyl-6-*O*-methanesulfonyl-α-D-mannopyranoside (55). Disaccharide **54** (708 mg, 0.58 mmol) was dissolved in 9:1 MeOH:EtOAc (10 mL), and a catalytic amount of *p*-toluensulfonic acid was added. The reaction mixture was stirred for 5 h. Triethylamine (200 μL) was added, solvents were evaporated, and the residue was purified by chromatography (2:1 EtOAc−pentane) to provide **55** (453 mg, 80%) as an oil: $[\alpha]_D$ +71.4° (*c* 0.7, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.48−7.15 (m, 20H), 5.88 (ddd, 1H, J = 17.2, 10.4, 5.7 Hz), 5.50 (d, 1H, J = 3.9 Hz), 5.27 (ddd, 1H, J = 17.2, 3.1, 1.6 Hz), 5.14 (ddd, 1H, J = 10.4, 3.1, 1.3 Hz), 4.96 (d, 1H, J = 11.5 Hz), 4.95 (d, 1H, J = 11.7 Hz), 4.81 (d, 1H, J = 12.2 Hz), 4.75 (d, 1H, J = 12.2 Hz), 4.69 (d, 1H, J = 11.5 Hz), 4.68 (d, 1H, J = 1.9 Hz), 4.63 (d, 1H, J = 10.9 Hz), 4.61 (d, 1H, J = 11.5 Hz), 4.49 (dd, 1H, J = 11.8, 1.7 Hz), 4.37 (dd, 1H, J = 11.8, 4.0 Hz), 4.27 (d, 1H, J = 11.0 Hz), 4.15 (dddd, 1H, J = 12.6, 5.6, 1.6, 1.3 Hz), 4.10 (dd, 1H, J = 2.4, 1.8 Hz), 4.08 (m,1H), 4.07 (dd, 1H, J = 10.1, 3.8 Hz), 3.97 (d, 1H, J = 2.0 Hz), 3.88 (t, 1H, J = 5.5 Hz), 3.87 (dd, 1H, J = 9.7, 9.6 Hz), 3.78 (dd, 1H, J = 10.1, 2.0 Hz), 3.77 (dd, 1H, J = 9.7, 2.4 Hz), 3.43−3.72 (m, 15H), 3.27 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.5, 138.4, 138.0, 134.3, 128.2, 128.1, 128.1, 128.0, 127.5, 127.4, 127.4, 127.1, 126.9, 116.9, 100.0, 97.2, 79.8, 77.7, 76.1, 74.7, 73.6, 72.4, 74.2, 71.6, 71.5, 71.2, 71.1, 70.5, 70.3, 70.3, 70.2, 70.0, 69.9, 69.5, 69.2, 61.4, 54.7, 37.7. Anal. Calcd for $C_{51}H_{66}O_{16}S$ (967.14): C, 63.34; H, 6.88; S, 3.31. Found: C, 63.21; H, 6.84; S, 3.44.

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Supporting Information Available: ^{1}H NMR spectra of the target compounds **2**−**4** and a list of the ^{1}H and ^{13}C NMR chemical shift assignments and homonuclear ^3J coupling constants (40 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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