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Synthesis of deoxy and methoxy analogs of octyl α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside as probes for mycobacterial lipoarabinomannan biosynthesis

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Abstract—A panel of analogs of the disaccharide α-D-Man*p*-(1→6)-α-D-Man*p*-OOctyl, a known acceptor substrate for a polyprenol monophosphomannose-dependent α-(1→6)-mannosyltransferase involved in the assembly of the α-(1→6)-linked mannan core of mycobacterial lipoarabinomannan, has been synthesized. Described are synthetic routes to the target deoxy and methoxy analogs in which one of the hydroxyl groups of the parent disaccharide has been modified. All glycosylation reactions involved the use of octyl glycoside acceptors and thioglycoside donors using iodonium-ion activation, and the stereochemistry of the mannopyranoside bond formed was established by measurement of the $^{1}J_{C\text{-}1,H\text{-}1}$. Depending on the target, the key methylation or deoxygenation reactions were carried out on either mono- or disaccharide substrates. This series of analogs will be useful for probing the substrate specificity of the enzyme, in particular, its steric and hydrogen-bonding requirements.

Keywords: Cell-wall biosynthesis; Mycobacteria; Mannosyltransferase; Synthesis; Deoxy analogs; Methoxy analogs; Lipoarabinomannan

1. Introduction

Tuberculosis (TB) is a common and deadly infectious disease caused by the human pathogen *Mycobacterium tuberculosis*. The difficulty in treating TB arises from the unusual structure of the mycobacterial cell wall, which protects the pathogen from the host's immunity and serves as a formidable barrier to the passage of antibiotics. Lipoarabinomannan (LAM) as well as its related precursors lipomannan (LM) and phosphatidyl-*myo*-inositol mannosides (PIMs) are the major lipoglycans found in the cell wall of mycobacteria.[1,2] These molecules have important roles in the modulation of and interaction with the immune system, and allow these organisms to survive in the hostile environment within infected human host macrophages.[3] The recent resurgence of TB, due to the emergence of multidrug-resistant *M. tuberculosis* strains[4,5] and the advent of the HIV/AIDS pandemic,[6] has generated increasing interest in the development of new anti-TB drugs. The mycobacterial cell wall is an ideal target for the action of new classes of anti-TB agents because of its important role in the structural integrity of the organism and its immunomodulatory effects. In particular, the enzymes involved in the cell-wall polysaccharide biosynthesis represent a rich source of potential therapeutic drug targets.

The structure of mycobacterial LAM (**1**, Fig. 1) consists of a phosphatidyl-*myo*-inositol (PI) moiety, a mannan core and a highly branched arabinan domain at the nonreducing end. With its lipid portion noncovalently associated with the plasma membrane, the PI moiety serves as the attachment point for the mannan and arabinan domains. The mannan core consists of a polymer of α-(1→6)-linked D-mannopyranose residues and is further elaborated, on approximately half of these core

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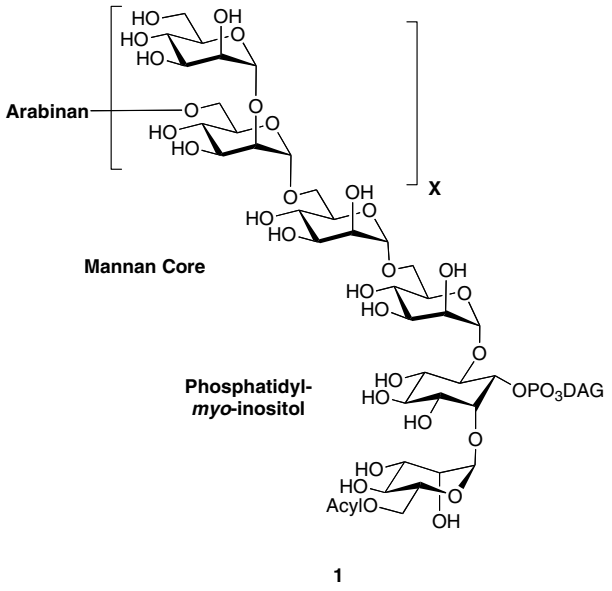


Figure 1. Structure of LAM, highlighting the mannan core region; DAG = diacylglycerol.

monosaccharides, by additional D-mannopyranose units on O-2 in species such as *M. tuberculosis*, *M. leprae*, *M. kansasii*, and *M. smegmatis*[1,2] or at O-3 in *M. chelonae*.[7] The arabinan domain is composed of α-(1→5)-, α-(1→3)-, β-(1→2)-linked D-arabinofuranose residues[8–10] and is substituted at its nonreducing terminus with a range of capping motifs including D-mannopyranose oligosaccharides, inositol phosphate groups, or 5-thiomethyl-D-xylofuranose residues.[11–16]

The biosynthesis of mycobacterial LAM has been proposed[16] to involve a number of glycosyltransferases, and over the past few years several of these enzymes have been identified.[3,17–21] Among these is a polyprenol monophosphomannose-dependent α-(1→6)-mannosyltransferase (ManT) that is involved in the synthesis of the linear α-(1→6)-linked mannan core.[22,23] This ManT catalyzes the transfer of mannopyranose residues from polyprenol monophosphomannose derivatives (PPM, **2a**, **2b**, Fig. 2) to an α-(1→6)-linked oligomannopyranoside acceptor. In turn PPM **2a** and **2b** are synthesized from GDP-mannose (GDP-Man, **3**) by the enzyme polyprenol monophosphomannose synthase.[24] To date, the gene encoding for this ManT has not been identified, nor has the protein been isolated; its activity has only been demonstrated using a cell-free assay.[23,25–28]

Earlier work by Brown et al. showed that the octyl glycosides containing two or three α-(1→6)-linked mannopyranose residues can act as acceptor substrates for this ManT.[23] The hydrophobic nature of the octyl agylcone allows convenient product isolation and characterization in cell-free enzymatic assays using reversed-phase chromatography. Analogs of these simplified acceptors can be used for probing the substrate specificity of the enzyme. For example, in very recent studies,[27,28] derivatives of octyl disaccharide **4** (Fig. 3) were synthesized and screened as potential substrates and inhibitors of this ManT. These analogs were those in which the hydroxyl groups at the C-2 and C-6 positions of the terminal mannose residue were singly or doubly modified by replacement with hydrogen or fluoro, amino, and methoxy functionalities.

Understanding of the complete substrate specificity of the ManT enzyme is essential and would provide guidelines for the further design of potent and specific inhibitors. Such compounds would be useful biochemical tools and may also have potential as lead compounds

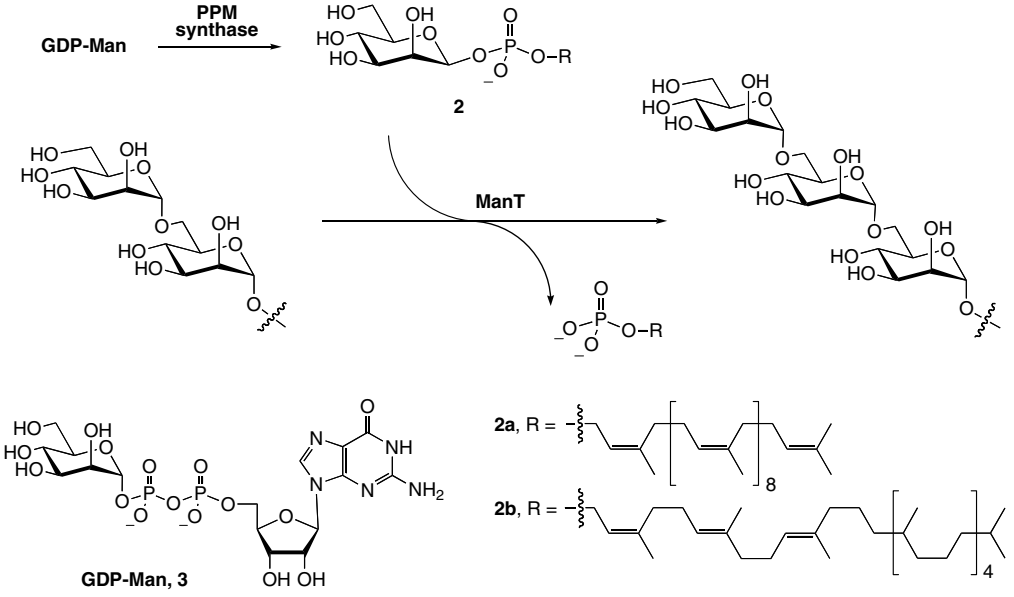


Figure 2. Reaction catalyzed by the polyprenol monophosphomannose-dependent α-(1→6)-mannosyltransferase (ManT) and structure of polyprenol monophosphomannose derivatives used as donor species.

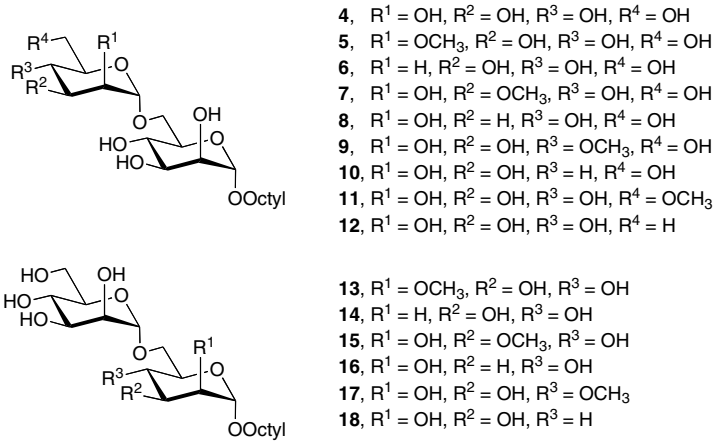


Figure 3. Deoxy and methoxy analogs of **4** targeted for synthesis (**5**–**18**).

for the development of new classes of anti-mycobacterial drugs as none of the anti-TB drugs currently in use are known to target this ManT. However, the polar interactions and steric requirements of the enzyme were only partially revealed in the previous studies.[27,28] To further characterize the substrate specificity of the enzyme, a panel of methoxy and deoxy disaccharide analogs of the known substrate, α-D-Man*p*-(1→6)-α-D-Man*p*-OOctyl (**4**), was synthesized. As shown in Figure 3, in each of these analogs a single hydroxyl group of the parent disaccharide was modified by methylation or deoxygenation yielding a total of 14 analogs (**5**–**18**). In this paper, we describe the synthesis of these modified oligosaccharide analogs.

2. Results and discussion

2.1. Synthesis of 2′- and 3′-deoxy and methoxy disaccharides 5–8

For the preparation of the 2′-methoxy (**5**),[27] 2′-deoxy (**6**),[27] 3′-methoxy (**7**), and 3′-deoxy (**8**) analogs, a divergent approach was chosen (Fig. 4) that involved as intermediates the protected disaccharides **19** and **20**. These oligosaccharides could, in turn, be obtained from thioglycosides **21** and **22** and glycosyl acceptor **23**.[27]

As illustrated in Scheme 1, the donors required for the synthesis of **5**–**8**, thioglycosides **21** and **22**, were obtained from the known thioglycoside **24**,[29] which was first protected as the di-benzylidene acetal using benzaldehyde dimethyl acetal in the presence of *p*-toluenesulfonic acid.[30] This reaction afforded a 1:3 mixture of the *exo*-isomer **25** and *endo*-isomer **26** in 72% combined yield. The diastereomers were discriminated by 2D NOESY experiments in which the dioxolane acetal hydrogen showed an NOE to H-2 for compound **26** and to H-4 for compound **25**. The more reactive dioxolane ring of diastereoisomer **25** was regio- and chemoselectively opened with lithium aluminum hydride and aluminum trichloride at room temperature to give alcohol **27** in 87% yield.[30] The regioselectivity was confirmed by the subsequent acetylation (vide infra) in which the chemical shift of H-2 moved from 4.28 to 5.63 ppm. Alternatively, under the same reaction conditions, the dioxolane ring of the *endo*-isomer **26** was opened to give, in addition

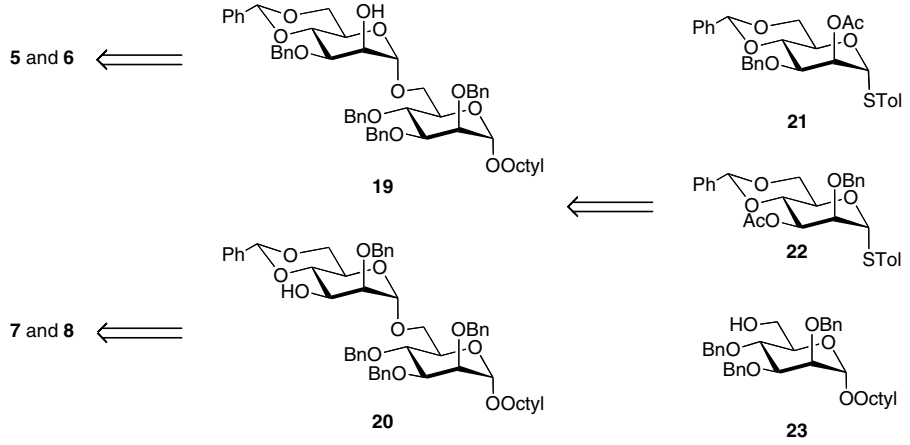
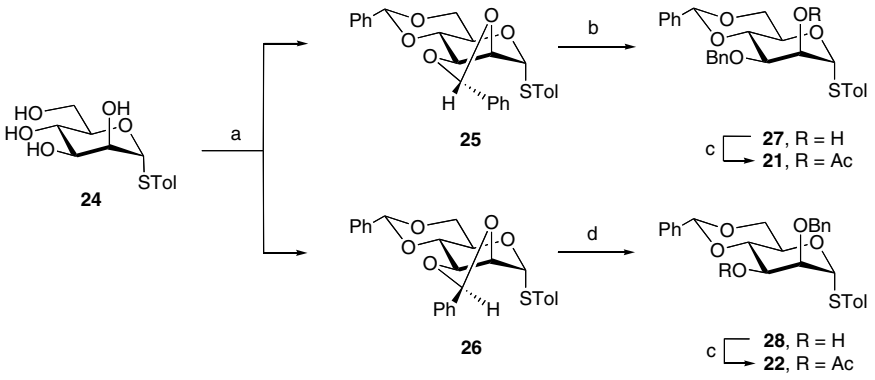


Figure 4. Retrosynthetic analysis of **5**–**8**.



Scheme 1. Reagents and conditions: (a) $PhCH(OCH_3)_2$, *p*-TsOH, DMF, 60 °C, 72% (1:3 *exo*:*endo* ratio); (b) $AlCl_3$, $LiAlH_4$, CH_2Cl_2, Et_2O, rt, 87%; (c) Ac_2O, pyridine, CH_2Cl_2, rt, 79% for **21**, 94% for **22**; (d) $AlCl_3$, $LiAlH_4$, CH_2Cl_2, Et_2O, rt, 0 °C, 66%.

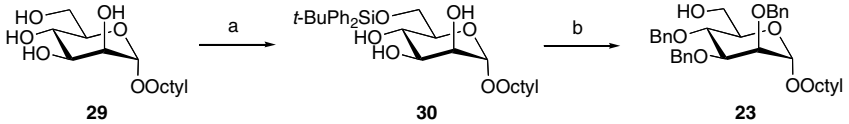
to the expected alcohol **28**, three major byproducts as indicated by TLC. Although the structures of these byproducts were not unequivocally established, they are presumably produced as the result of nonspecific opening or hydrolysis of the dioxolane and dioxane rings. The formation of these side products could be minimized by carrying out the reaction at lower temperature (0 °C), which provided alcohol **28** as the major product in 66% yield. The regioselectivity was established by the downfield shift of the H-3 hydrogen (5.34 ppm) after acetylation. This and the previously mentioned acetylation reactions were carried out by treatment of both **27** and **28** with acetic anhydride and pyridine to give glycosyl donors **21** and **22** in 79% and 94% yields, respectively.

The glycosyl acceptor needed for the synthesis of **5**–**8**, octyl glycoside **23**,[27] was synthesized from a known alcohol **29**[27] as illustrated in Scheme 2. Reaction of **29** with *tert*-butylchlorodiphenylsilane and imidazole provided silyl ether **30** in 94% yield. The remaining hydroxyl groups were protected as benzyl ethers by reaction with sodium hydride and benzyl bromide, and the silyl group was removed upon treatment with tetra-*n*-butylammonium fluoride, which furnished glycosyl acceptor **23** in 91% yield over the two steps.

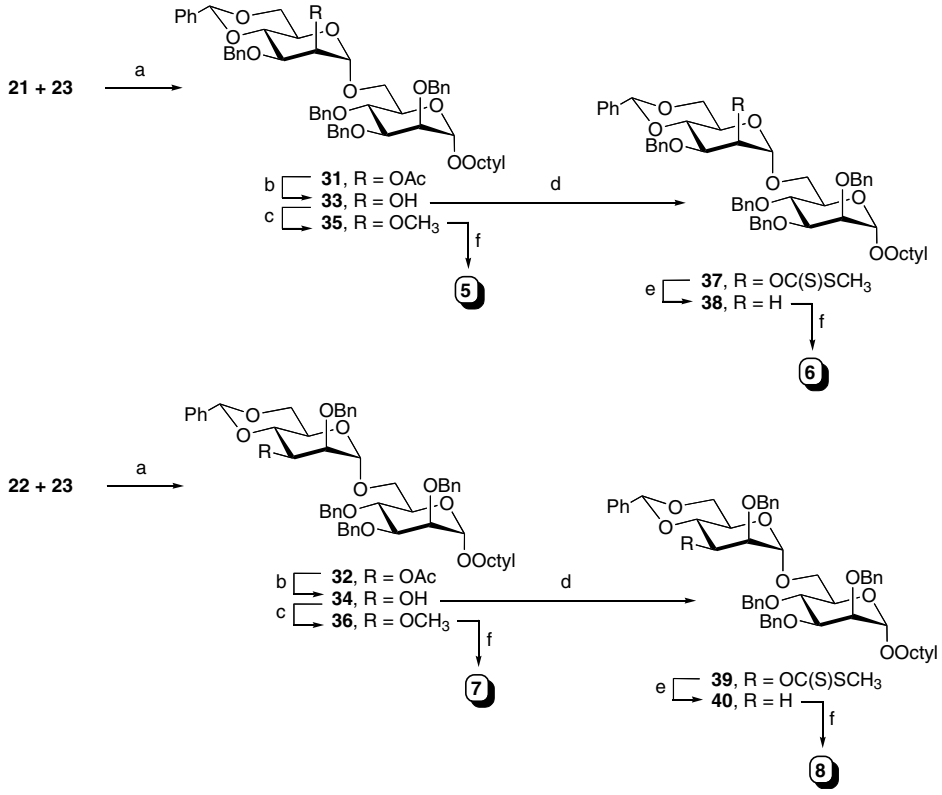
With these three monosaccharides in hand, coupling of thioglycosides **21** or **22** with alcohol **23** using NIS/AgOTf activation[31] afforded the corresponding disaccharides **31** or **32** in 89% and 83% yields, respectively (Scheme 3). Consistent with earlier work from the Crich group,[32] thioglycoside **22** was found to be a highly α-selective donor, and we could isolate none of the β-mannopyranoside. For all the glycosylation reactions described in this paper, the α-stereochemistry of the glycosidic linkages was confirmed by the one-bond $^1J_{C\text{-}1,H\text{-}1}$ heteronuclear coupling constants for the anomeric carbon atoms.[33] In all cases, this value was between 168 and 176 Hz, clearly indicating the α-stereochemistry.

Subsequent removal of the acetyl groups from these fully protected disaccharides using sodium methoxide gave **33** (94% yield) or **34** (89% yield). The target disaccharides **5**[27] and **7** were prepared by methylation of **33** and **34** with iodomethane and sodium hydride to give **35** and **36** (91% and 76%, respectively), followed by full deprotection by hydrogenolysis. This two-step sequence provided **5** in 90% yield from **35** and **7** in 94% yield from **36**.

To access the deoxy analog **6**,[27] disaccharide **33** was converted to the corresponding xanthate **37** and then reduced[34] with tri-*n*-butylstannane in the presence of AIBN yielding **38** in 41% yield. A number of other byproducts were observed on TLC, but these were not isolated and characterized. That the deoxygenation had occurred was clearly evident from the ^1H and ^{13}C NMR spectra for **38**. In the ^1H NMR spectrum, resonances for H-$2'_{ax}$ and H-$2'_{eq}$ of the expected multiplicity (ddd) were present at 1.78 and 2.35 ppm, respectively. In addition, in the ^{13}C NMR spectrum a resonance at 36.4 ppm could be assigned to C-2′. The target compound **6**[27] was obtained in 96% yield after deprotection with hydrogen and palladium hydroxide. As described for the preparation of **6**, a similar series of reactions starting with **34** gave first xanthate **39** and then deoxy analog **40** in 37% overall yield. As was the case for **37**, this reaction was accompanied by the formation of a



Scheme 2. Reagents and conditions: (a) *t*-$BuPh_2SiCl$, imidazole, DMF, 45 °C, 94%; (b) (i) NaH, BnBr, DMF; (ii) *n*-Bu_4NF, THF, rt, 91% over two steps.



Scheme 3. Reagents and conditions: (a) NIS, AgOTf, 4 Å MS, CH_2Cl_2, 0 °C, 89% for **31**, 83% for **32**; (b) $NaOCH_3$, CH_3OH, rt, 94% for **33**, 89% for **34**; (c) NaH, CH_3I, DMF, rt, 91% for **35**, 76% for **36**; (d) NaH, CS_2, THF, then CH_3I, rt, 96% for **37**, 94% for **39**; (e) *n*-Bu_3SnH, AIBN, toluene, 41% for **38**, 37% for **40**; (f) H_2, $Pd(OH)_2$, CH_3OH, 90% for **5**, 96% for **6**, 94% for **7**, 91% for **8**.

number of byproducts as detected by TLC but which were not structurally characterized. Presumably these byproducts result, at least in part, from radical abstraction of the benzylidene hydrogen in **37** and **39**. Removal of the protecting groups in **40** by hydrogenolysis provided a 91% yield of **8**.

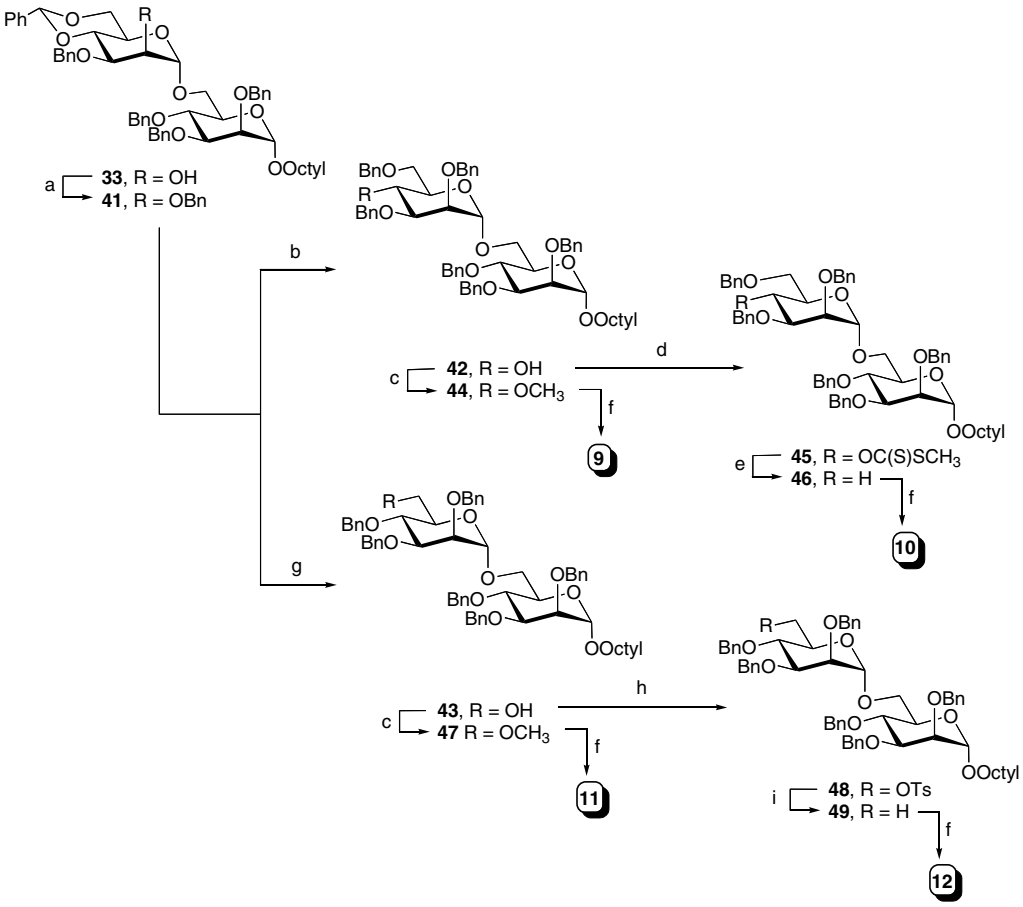
2.2. Synthesis of 4′- and 6′-deoxy and methoxy disaccharides 9–12

An intermediate used in the assembly of **5**–**8**, disaccharide **33**, was used in the synthesis of the 4′- and 6′-deoxy and methoxy disaccharides **9**–**12**, as illustrated in Scheme 4. The hydroxyl group of **33** was first protected as the benzyl ether affording **41** in good (94%) yield. Treatment of **41** with excess triethylsilane and trifluoromethanesulfonic acid[35] at −78 °C afforded alcohol **42** in 61% yield. Alternatively, reaction of **41** with lithium aluminum hydride and aluminum trichloride gave the expected alcohol **43** in 85% yield. The regioselectivities of both 4,6-*O*-benzylidene openings were excellent with less than 4% of the undesired regioisomers. The regioselectivities of both reactions were based on the ^{13}C NMR spectra of the products, in which the chemical shift of C-6′ of **42** (70.4 ppm) is more downfield than that of **43** (62.3 ppm).

With **42** in hand, disaccharides **9** and **10** were prepared via routes similar to those used for **5**–**8**. Methylation of **42** yielded disaccharide **44**, which was deprotected to furnish the 4′-methoxy analog **9** in 84% yield. Alternatively, **42** was converted to the corresponding xanthate **45** (96% yield), followed by reduction with tri-*n*-butylstannane in the presence of AIBN, to give a 64% yield of **46**. The target compound **10** was then obtained in 87% yield after hydrogenation. To synthesize **11**, alcohol **43** was methylated affording a 96% yield of **47**, which was then deprotected by hydrogenolysis providing the target in quantitative yield. Target **12** was also obtained from **43**. This disaccharide alcohol was first reacted with *p*-toluenesulfonyl chloride and pyridine to afford the tosylate **48** (90% yield), which was subsequently converted to **49** in 62% yield upon reaction with lithium aluminum hydride. In addition to the expected product **49**, alcohol **43**, the product of O–S bond cleavage by the reducing agent, was isolated in 33% yield. Final deprotection of **49** furnished the desired deoxy analog **12** (96% yield).

2.3. Synthesis of 2- and 3-deoxy disaccharides 14 and 16

As illustrated in Scheme 5, a divergent approach was used for the preparation of the 2- and 3-deoxy

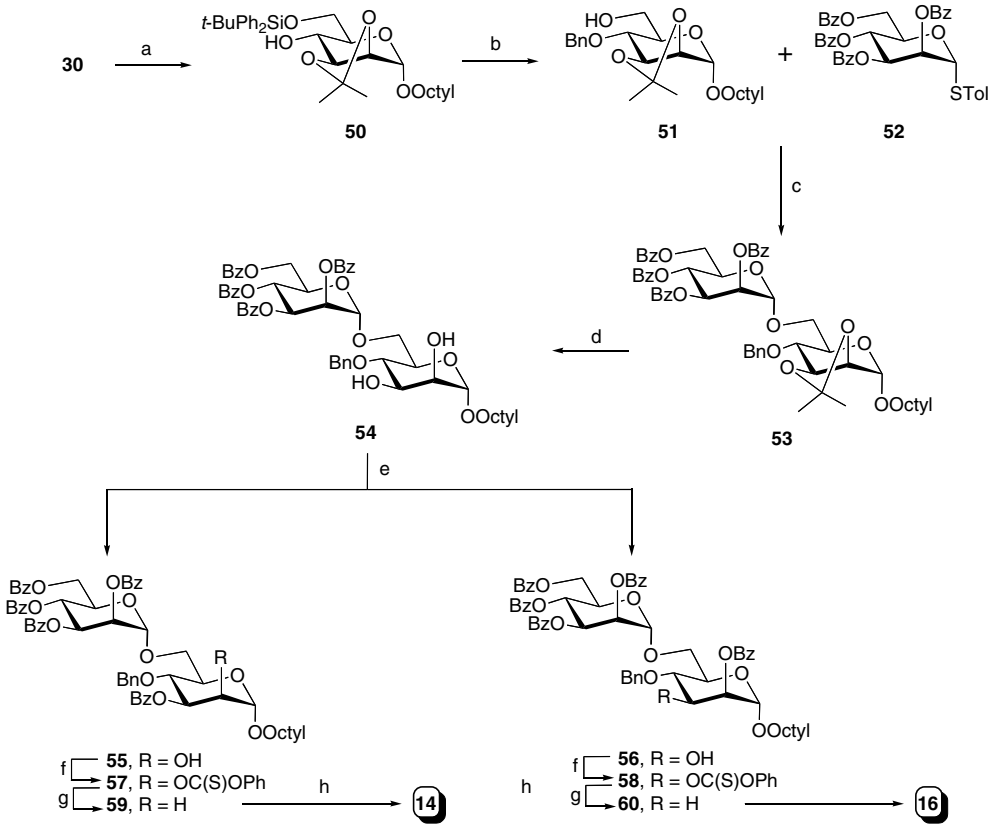


Scheme 4. Reagents and conditions: (a) NaH, BnBr, DMF, rt, 94%; (b) Et_3SiH, TfOH, CH_2Cl_2, rt, 61%; (c) NaH, CH_3I, DMF, rt, 77% for **44**, 96% for **47**; (d) NaH, CS_2, THF, then CH_3I, rt, 96%; (e) *n*-Bu_3SnH, AIBN, toluene, 64%; (f) H_2, $Pd(OH)_2$, CH_3OH, 84% for **9**, 87% for **10**, 98% for **11**, 96% for **12**; (g) $AlCl_3$, $LiAlH_4$, CH_2Cl_2, Et_2O, rt, 85%; (h) TsCl, pyridine, rt, 90%; (i) $LiAlH_4$, ether, rt, 62%.

disaccharide analogs **14** and **16**. Reaction of silyl ether **30** (prepared as described in Section 2.1) with 2,2-dimethoxypropane in the presence of a catalytic amount of *p*-TsOH gave a 96% yield of alcohol **50**. Benzylation of the hydroxyl group at C-4 and subsequent removal of the silyl protecting group provided the expected acceptor **51** in 76% yield over the two steps. The donor required for the synthesis of disaccharide **53**, thioglycoside **52**, was synthesized in 64% yield over two steps from D-mannose, by first benzoylation and, without purification, reaction with *p*-thiocresol and boron trifluoride etherate (see Section 3.44).

With these building blocks in place, coupling of acceptor **51** with the glycosyl donor **52** in a NIS/TMSOTf-promoted reaction gave disaccharide **53** in 92% yield. Subsequent hydrolysis of the isopropylidene acetal with 80% aqueous AcOH provided diol **54** (88%), which was converted into a 2:1 mixture of **55** and **56** (63% and 32% yield, respectively) in a two-step sequence. The significant amount of benzoylation on O-2 was somewhat surprising as the tin-mediated benzoylation was envisioned to nearly exclusively take place at the equatorial 3-hydroxyl group.[36] Nevertheless, these compounds could be separated by chromatography, and this approach provided rapid access to both regioisomers **55** and **56**, which led to the target compounds in a few more steps.

Treatment of both **55** and **56** with phenyl chlorothionoformate and DMAP gave the corresponding thiocarbonyl derivative **57** and **58** in good yields (74% and 70%, respectively). These thiocarbonyl derivatives[37] were employed, as opposed to the xanthates we used in earlier deoxygenations, due to concerns about acyl migration occurring upon treatment with sodium hydride, as required for xanthate generation. Reaction of both derivatives with tri-*n*-butylstannane and AIBN provided the deoxy intermediates **59** and **60**, in 84% and 32% yield, respectively. We are unsure as to the origin of the poor product yield from the deoxygenation of **58**, and similar results were observed from repeated experiments. Subsequent hydrogenolysis of **59** and **60** followed by debenzoylation afforded the corresponding target deoxy analogs **14** and **16** in 78% and 93% overall yield, respectively.



Scheme 5. Reagents and conditions: (a) *t*-$BuPh_2SiCl$, imidazole, DMF, 45 °C, 96%; (b) (i) NaH, BnBr, DMF; (ii) *n*-Bu_4NF, THF, rt, 76% over two steps; (c) **52**, NIS, TMSOTf, 4 Å MS, CH_2Cl_2, 0 °C, 92%; (d) 80% $AcOH/H_2O$, 50 °C, 88%; (e) (i) *n*-Bu_2SnO, toluene, 110 °C; (ii) BzCl, rt, 63% of **55** and 32% of **56**; (f) PhO(C═S)Cl, imidazole, CH_3CN, 74% for **57**, 70% for **58**; (g) *n*-Bu_3SnH, AIBN, toluene, 84% for **59**, 32% for **60**; (h) (i) H_2, $Pd(OH)_2$, CH_3OH, rt; (ii) $NaOCH_3$, CH_3OH, rt, 78% for **14** (over 2 steps), 93% for **16** (over two steps).

2.4. Synthesis of 2- and 3-methoxy disaccharides 13 and 15

We envisioned that the synthesis of disaccharides **13** and **15** could be achieved from the coupling of either octyl glycoside **61** or **62** with thioglycoside **52** (Fig. 5). The preparation of **52** was discussed in Section 2.3, and the synthesis of **61** and **62** is presented in Scheme 6.

The preparation of **61** and **62** started with tetrol **29**,[27] which was converted to the 2,3:4,6-di-*O*-benzylidene derivative **63** upon reaction with benzaldehyde dimethyl acetal and *p*-TsOH. The product was obtained as a ~1:1 mixture of *exo*- and *endo*-diastereomers in 86% combined yield. Without separation, this mixture was subjected to reductive ring opening with lithium aluminum hydride and aluminum trichloride at 0 °C to afford chromatographically separable alcohols **64** and **65** (32% and 36% yield). These compounds were each independently methylated to furnish compounds **66** and **67** in good yield. Benzylidene ring opening of **66** and **67** with lithium aluminum hydride and aluminum trichloride (allowing the reaction to proceed overnight at room temperature as opposed to 1 h at 0 °C as for the opening of the dioxolane ring in **63**) provided the expected glycosyl acceptors **61** and **62** in 66% and 57%, respectively, together with the corresponding 6-*O*-benzyl regioisomers (**68** and **69**). Compared with the dioxane ring opening of **66**, the reaction with **67** was less regioselective, and a significant amount (22%) of regioisomer **69** was also obtained in addition to the desired product **62**. These results are consistent with those previously

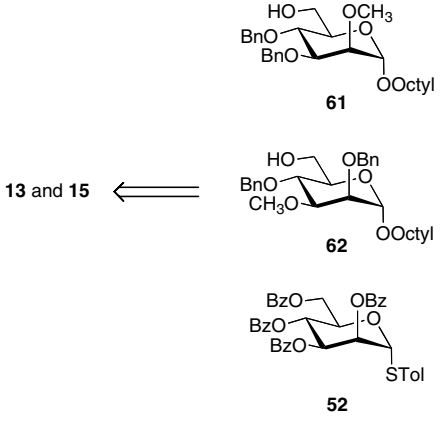
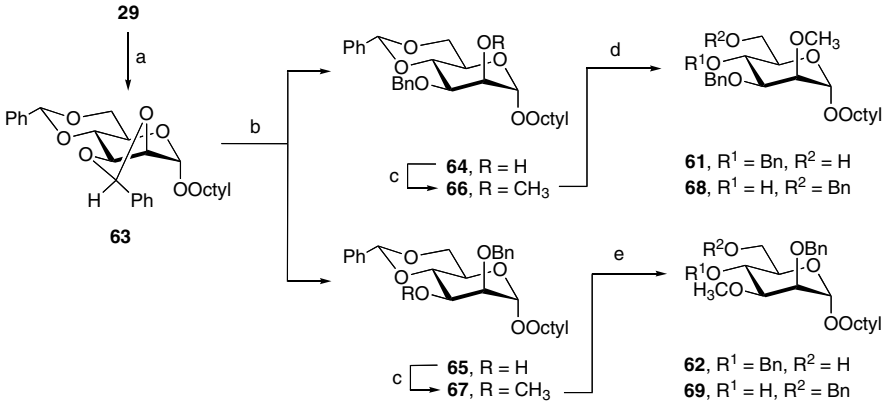
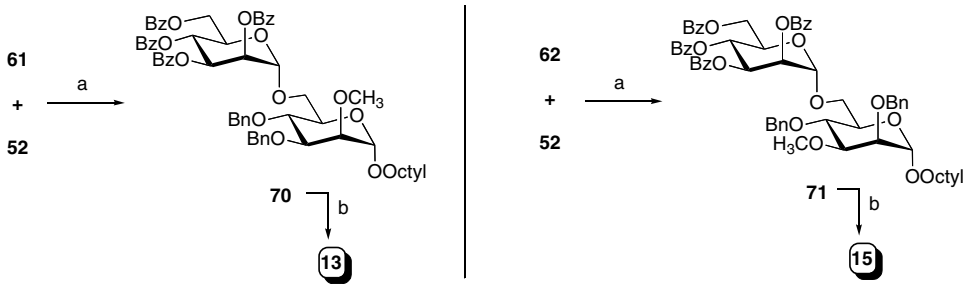


Figure 5. Retrosynthetic analysis of **13** and **15**.



Scheme 6. Reagents and conditions: (a) $PhCH(OCH_3)_2$, *p*-TsOH, acetone, rt, 86%; (b) $AlCl_3$, $LiAlH_4$, CH_2Cl_2, Et_2O, rt, 32% of **64** and 36% of **65**; (c) NaH, CH_3I, DMF, 94% for **66**, 92% for **67**; (d) $AlCl_3$, $LiAlH_4$, CH_2Cl_2, Et_2O, rt, 66% of **61** +6% of **68**; (e) $AlCl_3$, $LiAlH_4$, CH_2Cl_2, Et_2O, rt, 57% of **62** and 22% of **69**.



Scheme 7. Reagents and conditions: (a) NIS, TMSOTf, 4 Å MS, CH_2Cl_2, 0 °C, 89% for **70**, 96% for **71**; (b) (i) $NaOCH_3$, CH_3OH, rt; (ii) H_2, $Pd(OH)_2$, CH_3OH, rt, 91% and 98% for **13**, 87% and 93% for **15**.

reported in which the high regioselectivity of the 4,6-*O*-benzylidene ring openings under these conditions requires the presence of a bulky substituent at the C-3 position.[30]

Having in hand all of the monosaccharide building blocks, the assembly of disaccharides **13** and **15** was straightforward. Coupling of thioglycoside **52** with alcohols **61** and **62** under NIS/TMSOTf activation afforded the corresponding protected disaccharides **70** and **71** in 89% and 96% yields, respectively (Scheme 7). Subsequent removal of the benzoyl and benzyl protecting groups in **70** and **71** under standard conditions afforded the target methoxy analogs **13** and **15** in good yields over the two steps.

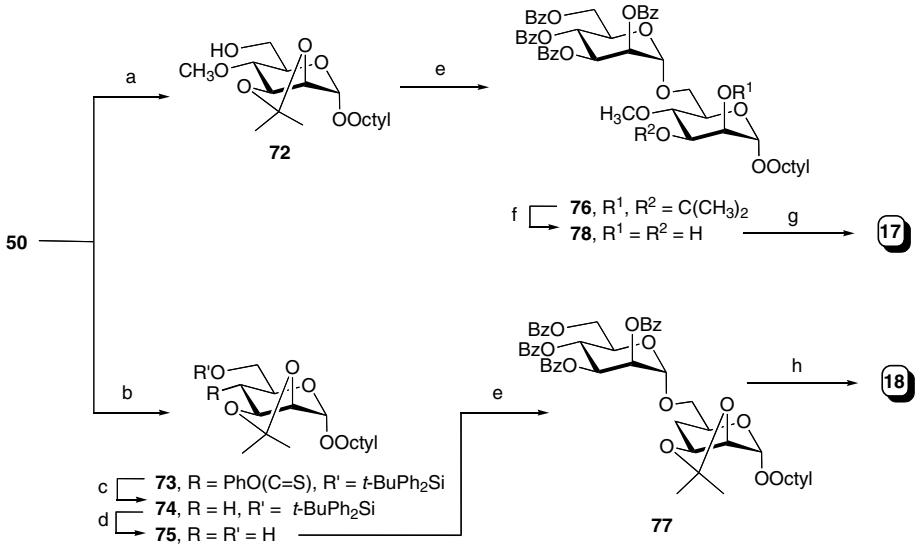
2.5. Synthesis of 4-deoxy and 4-methoxy disaccharides 17 and 18

To prepare the 4-deoxy and 4-methoxy analogs **17** and **18** we started with the protected octyl glycoside **50** (see Section 2.3). As illustrated in Scheme 8, methylation of the hydroxyl group at C-4 proceeded under standard conditions to provide an intermediate that was desilylated using tetra-*n*-butylammonium fluoride yielding **72** in 89% over two steps. To effect the deoxygenation at C-4, **50** was reacted with phenyl chlorothionoformate and DMAP to give the corresponding thiocarbonyl derivative **73** (84% yield), which was in turn reduced with tri-*n*-butylstannane and AIBN providing **74** in 88% yield. This deoxygenated intermediate was desilylated using tetra-*n*-butylammonium fluoride to give the desired monosaccharide **75** in 72% yield.

Glycosylation of alcohols **72** and **75** with thioglycoside **52** under the standard activation conditions (NIS/TMSOTf) afforded disaccharides **76** and **77** in 79% and 75% yields, respectively. Cleavage of the isopropylidene acetal in **76** yielded diol **78**, which was then treated with sodium methoxide in methanol giving **17** in 81% overall yield. Similar treatment of **77** provided disaccharide **18** in 94% yield over two steps.

2.6. Conclusion

In conclusion, 14 deoxy and methoxy analogs (**5**–**18**) of the α-D-Man*p*-(1→6)-α-D-Man*p*-OOctyl, disaccharide (**4**), were synthesized via routes in which the key methylation or deoxygenation reactions occurred at either the mono- or disaccharide level. All glycosylation reactions involved the use of octyl glycoside acceptors and thioglycoside donors, and the stereochemistry of the mannopyranoside bond formed was established by measurement of the $^1J_{C\text{-}1,H\text{-}1}$. This panel of compounds will



Scheme 8. Reagents and conditions: (a) (i) NaH, CH_3I, DMF; (ii) *n*-Bu_4NF, THF, two steps, 89%; (b) PhO(C=S)Cl, imidazole, CH_3CN, 84%; (c) *n*-Bu_3SnH, AIBN, toluene, 88%; (d) *n*-Bu_4NF, THF, 72%; (e) **52**, NIS, TMSOTf, 4 Å MS, CH_2Cl_2, 0 °C, 79% for **76**, 75% for **77**; (f) 80% $AcOH/H_2O$, 50 °C, 97%; (g) $NaOCH_3$, CH_3OH, rt, 86%; (h) (i) 80% $AcOH/H_2O$, 50 °C; (ii) $NaOCH_3$, CH_3OH, rt, 94%.

be tested as potential substrates and inhibitors for a polyprenol monophosphomannose-dependent α-(1→6)-mannosyltransferase involved in the biosynthesis of the α-(1→6)-linked mannan core of mycobacterial LAM. The use of these methoxy and deoxy derivatives will allow us to explore the steric requirements and hydrogen-bonding interactions in the active site of the enzyme. These studies are currently in progress and will be reported in a future paper.

3. Experimental

3.1. General methods

All reagents used were purchased from commercial sources and were used without further purification unless noted. Solvents used in reactions were purified by successive passage through columns of alumina and copper under nitrogen. Unless indicated otherwise, all reactions were performed under a positive pressure of argon. Reactions were monitored by analytical TLC on Silica Gel 60-F_{254} (0.25 mm, Silicycle), and spots were detected under UV light or by charring with acidified anisaldehyde solution in ethanol. Organic solvents were evaporated under reduced pressure at <40 °C. Column chromatography was performed on silica gel (40–60 μM) or Iatrobeads (Iatron Laboratories, Tokyo). Optical rotations were measured at 22 ± 2 °C and are in units of (deg mL)/(g dm). ^{1}H NMR spectra were recorded at 500 or 600 MHz, and chemical shifts are referenced to either TMS (0.0, $CDCl_3$) or HOD (4.78, D_2O and CD_3OD). ^{13}C NMR spectra were recorded at 100 or 125 MHz and chemical shifts are referenced to internal $CDCl_3$ (77.23, $CDCl_3$), or CD_3OD (48.9, CD_3OD). The stereochemistry at the following mannosylation reactions was proven by measuring $^1J_{C1-H1}$ values. Electrospray-ionization mass spectra (ESIMS) were recorded on samples suspended in mixtures of THF with MeOH and added NaCl.

3.2. Octyl 2-*O*-methyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (5)

Disaccharide **35** (105 mg, 0.11 mmol) was dissolved in CH_3OH (8 mL), and 20% $Pd(OH)_2$ (50 mg) was added. The mixture was stirred overnight under a H_2 atmosphere, and the catalyst was separated by filtration through a short pad of Celite. The filtrate was concentrated to give **5** (50 mg, 90%) as a foam: R_f 0.52 (4:1 CH_2Cl_2–CH_3OH); ^{1}H NMR (600 MHz, D_2O) δ_H 5.03 (br s, 1H, H-1′), 4.82 (br s, 1H, H-1), 3.99 (dd, 1H, $J = 11.1$, 4.5 Hz, H-6a), 3.92 (br s, 1H, H-2), 3.84–3.94 (m, 2H, H-3′, H-6a′), 3.64–3.80 (m, 7H, H-3, H-4, H-5, H-6b, H-5′, H-6b′, octyl OCH_2), 3.77–3.64 (m, 2H, H-2′, H-4′), 3.44–3.54 (m, 4H, OCH_3, octyl OCH_2), 1.55–1.66 (m, 2H, octyl OCH_2CH_2), 1.23–1.44 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, D_2O) δ_C 100.4 (C-1), 96.8 (C-1′), 80.4 (C-2′), 73.0 (C-5′), 71.4 (C-5), 71.3 (C-3), 70.8 (C-3′), 70.6 (C-2), 68.1 (octyl OCH_2), 67.4 (C-4′), 66.8 (C-4), 66.0 (C-6), 61.3 (C-6′), 59.3 (OCH_3), 31.9 (octyl CH_2), 29.3 (octyl CH_2), 29.3 (octyl CH_2), 29.2 (octyl CH_2), 26.2 (octyl CH_2), 22.7 (octyl CH_2), 14.0 (octyl CH_3). The ^{1}H and ^{13}C NMR spectral data were consistent with that reported.[27]

3.3. Octyl 2-*O*-deoxy-α-D-*arabino*-hexopyranosyl-(1→6)-α-D-mannopyranoside (6)

Prepared from disaccharide **38** (102 mg, 0.11 mmol) in CH_3OH (8 mL) and 20% $Pd(OH)_2$ (50 mg) as described for **5**, to give **6** (46 mg, 96%) as a foam: R_f 0.47 (4:1 CH_2Cl_2–CH_3OH); ^1H NMR (500 MHz, D_2O) δ_H 5.07 (d, 1H, $J = 2.5$ Hz, H-1′), 4.87 (br s, 1H, H-1), 3.93–4.04 (m, 3H, H-2, H-6a, H-3′), 3.90 (dd, 1H, $J = 12.5$, 2.3 Hz, H-6a′), 3.64–3.87 (m, 7H, H-3, H-4, H-5, H-6b, H-5′, H-6b′), 3.50–3.58 (m, 1H, octyl OCH_2), 3.43 (dd, 1H, $J = 9.5$, 9.5 Hz, H-4′), 2.22 (dd, 1H, $J = 12.8$, 5.3 Hz, H-2′$_{eq}$), 1.77 (ddd, 1H, $J = 12.8$, 12.8, 2.5 Hz, H-2′$_{ax}$), 1.60–1.72 (m, 2H, octyl OCH$_2$CH_2), 1.28–1.50 (m, 10H, octyl CH_2), 0.93 (t, 3H, $J = 6.5$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, D_2O) δ_C 100.9 (C-1), 97.9 (C-1′), 73.1 (C-5′), 72.0, 71.9, 71.8, 71.2, (C-2, C-3, C-5, C-4′), 69.2 (C-3′), 68.8 (octyl OCH_2), 67.4 (C-4), 66.1 (C-6), 61.6 (C-6′), 37.7 (C-2′), 32.5 (octyl CH_2), 29.9 (octyl CH_2), 29.8 (octyl CH_2), 29.8 (octyl CH_2), 26.7 (octyl CH_2), 23.2 (octyl CH_2), 14.6 (octyl CH_3). The ^1H and ^{13}C NMR spectral data were consistent with that reported.[27]

3.4. Octyl 3-*O*-methyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (7)

Prepared from disaccharide **36** (97 mg, 0.11 mmol) in CH_3OH (8 mL) and 20% $Pd(OH)_2$ (50 mg) as described for **5**, to give **7** (49 mg, 94%) as a foam: R_f 0.43 (4:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +65.4 (*c* 0.6, CH_3OH); ^1H NMR (600 MHz, D_2O) δ_H 4.93 (br s, 1H, H-1′), 4.82 (br s, 1H, H-1), 4.19 (br s, 1H, H-2′), 3.98 (dd, 1H, $J = 10.8$, 4.8 Hz, H-6a), 3.92 (br s, 1H, H-2), 3.87 (app d, 1H, $J = 11.4$ Hz, H-6a′), 3.66–3.80 (m, 8H, H-3, H-4, H-5, H-6b, H-4′, H-5′, H-6b′, octyl OCH_2), 3.46–3.54 (m, 2H, H-3′, octyl OCH_2), 3.48 (s, 3H, OCH_3), 1.56–1.66 (m, 2H, octyl OCH$_2$CH_2), 1.24–1.42 (m, 10H, octyl CH_2), 0.88 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, D_2O) δ_C 100.7 (C-1), 100.2 (C-1′), 80.9 (C-3′), 73.2 (C-5′), 71.8 (C-3/C-5), 71.8 (C-3/C-5), 70.9 (C-2), 68.4 (octyl OCH_2), 67.2 (C-2′), 66.6 (C-4), 66.4 (C-6), 66.2 (C-4′), 61.5 (C-6′), 57.0 (OCH_3), 32.2 (octyl CH_2), 29.7 (octyl CH_2), 29.7 (octyl CH_2), 29.6 (octyl CH_2), 26.5 (octyl CH_2), 23.0 (octyl CH_2), 14.4 (octyl CH_3). ESIMS: *m*/*z* calcd for $[C_{21}H_{40}O_{11}]Na^+$: 491.2463. Found: 491.2465.

3.5. Octyl 3-*O*-deoxy-α-D-*arabino*-hexopyranosyl-(1→6)-α-D-mannopyranoside (8)

Prepared from disaccharide **40** (71 mg, 0.080 mmol) in CH_3OH (7 mL) and 20% $Pd(OH)_2$ (35 mg) as described for **5**, after chromatographic purification on Iatrobeads (4:1 CH_2Cl_2–CH_3OH) to give **8** (32 mg, 91%) as a foam: R_f 0.47 (4:1, CH_2Cl_2–CH_3OH); $[\alpha]_D$ +86.6 (*c* 0.7, CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ_H 4.70 (d, 1H, $J = 1.2$ Hz, H-1), 4.65 (br s, 1H, H-1′), 3.89–3.93 (m, 1H, H-6a), 3.62–3.82 (m, 11H, H-2, H-3, H-4, H-5, H-6b, H-2′, H-4′, H-5′, H-6a′, H-6b′, octyl OCH_2), 3.40 (dt, 1H, $J = 9.6$, 6.3 Hz, octyl OCH_2), 1.97 (ddd, 1H, $J = 13.2$, 3.9, 3.9 Hz, H-3′$_{eq}$), 1.85 (ddd, 1H, $J = 13.2$, 11.4, 3.0 Hz, H-3′$_{ax}$), 1.53–1.63 (m, 2H, octyl OCH$_2$CH_2), 1.24–1.42 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 101.6 (C-1), 100.1 (C-1′), 75.3 (C-5′), 73.2 (C-5), 72.9, 72.2, 69.1, 69.1 (C-2, C-3, C-4, C-2′), 68.6 (octyl OCH_2), 67.3 (C-6), 63.1 (C-6′), 62.9 (C-4′), 35.9 (C-3′), 33.0 (octyl CH_2), 30.6 (octyl CH_2), 30.5 (octyl CH_2), 30.4 (octyl CH_2), 27.4 (octyl CH_2), 23.7 (octyl CH_2), 14.4 (octyl CH_3). ESIMS: *m*/*z* calcd for $[C_{20}H_{38}O_{10}]Na^+$: 461.2357. Found: 461.2360.

3.6. Octyl 4-*O*-methyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (9)

Prepared from disaccharide **44** (83 mg, 0.082 mmol) in CH_3OH (7 mL) and 20% $Pd(OH)_2$ (40 mg) as described for **5**, after chromatographic purification on Iatrobeads (4:1 CH_2Cl_2–CH_3OH) to give **9** (32 mg, 84%) as a foam: R_f 0.42 (4:1, CH_2Cl_2–CH_3OH); $[\alpha]_D$ +78.5 (*c* 0.9, CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ_H 4.79 (d, 1H, $J = 1.2$ Hz, H-1′), 4.69 (d, 1H, $J = 1.2$ Hz, H-1), 3.89 (dd, 1H, $J = 10.8$, 5.4 Hz, H-6a), 3.75–3.82 (m, 4H, H-2, H-2′, H-3′, H-6a′), 3.60–3.75 (m, 7H, H-3, H-4, H-5, H-6b, H-5′, H-6b′, octyl OCH_2), 3.53 (s, 3H, OCH_3), 3.35–3.44 (m, 2H, H-4′, octyl OCH_2), 1.51–1.63 (m, 2H, octyl OCH$_2$CH_2), 1.24–1.44 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 101.6 (C-1), 101.3 (C-1′), 78.4 (C-4′), 73.4, 73.4, 73.1, 72.9, 72.7, 72.5, 72.2, 68.6 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′), 68.6 (octyl OCH_2), 68.5, 67.5 (C-6), 62.5 (C-6′), 60.9 (OCH_3), 33.0 (octyl CH_2), 30.6 (octyl CH_2), 30.5 (octyl CH_2), 30.4 (octyl CH_2), 27.4 (octyl CH_2), 23.7 (octyl CH_2), 14.5 (octyl CH_3). ESIMS: *m*/*z* calcd for $[C_{21}H_{40}O_{11}]Na^+$: 491.2463. Found: 491.2463.

3.7. Octyl 4-deoxy-α-D-*lyxo*-hexopyranosyl-(1→6)-α-D-mannopyranoside (10)

Prepared from disaccharide **46** (68 mg, 0.069 mmol) in CH_3OH (6 mL) and 20% $Pd(OH)_2$ (30 mg) as described for **5**, after chromatographic purification on Iatrobeads (4:1 CH_2Cl_2–CH_3OH) to give **10** (27 mg, 87%) as a foam: R_f 0.40 (4:1, CH_2Cl_2–CH_3OH); $[\alpha]_D$ +71.9 (*c* 0.7, CH_3OH); ^1H NMR (500 MHz, CD_3OD) δ_H 4.85 (d, 1H, $J = 1.0$ Hz, H-1′), 4.70 (d, 1H, $J = 1.5$ Hz, H-1), 3.97 (ddd, 1H, $J = 12.0$, 5.0, 3.0 Hz, H-3′), 3.85–3.94 (m, 2H, H-6a, H-5′), 3.78 (dd, 1H, $J = 3.0$, 1.5 Hz, H-2), 3.61–3.72 (m, 6H, H-3, H-4, H-5, H-6b, H-2′, octyl OCH_2), 3.55 (d, 2H, $J = 5.0$ Hz, H-6a′, H-6b′), 3.40

(dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 1.68 (ddd, 1H, $J = 12.0$, 12.0, 12.0 Hz, H-4′$_{ax}$), 1.53–1.62 (m, 3H, H-4′$_{eq}$, octyl OCH$_2$CH_2), 1.24–1.42 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 102.0 (C-1′), 101.6 (C-1), 73.2 (C-3/C-4), 72.9 (C-3/C-4), 72.2, (C-2), 70.4 (C-5′), 70.2 (C-2′), 68.6 (C-5), 68.6 (octyl OCH$_2$), 67.3 (C-6), 66.8 (C-3′), 66.0 (C-6′), 33.0 (octyl CH$_2$), 31.3 (C-4′), 30.6 (octyl CH$_2$), 30.5 (octyl CH$_2$), 30.4 (octyl CH$_2$), 27.4 (octyl CH$_2$), 23.7 (octyl CH$_2$), 14.5 (octyl CH$_3$). ESIMS: m/z calcd for $[C_{20}H_{38}O_{10}]Na^+$: 461.2357. Found: 461.2359.

3.8. Octyl 6-*O*-methyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (11)

Prepared from disaccharide **47** (93 mg, 0.092 mmol) in CH_3OH (8 mL) and 20% $Pd(OH)_2$ (45 mg) as described for **5**, to give **11** (42 mg, 98%) as a foam: R_f 0.38 (4:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +67.0 (c 2.1, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ_H 4.79 (d, 1H, $J = 1.5$ Hz, H-1′), 4.69 (d, 1H, $J = 1.2$ Hz, H-1), 3.86–3.91 (m, 1H, H-6a), 3.83 (dd, 1H, $J = 3.3$, 1.5 Hz, H-2′), 3.78 (dd, 1H, $J = 3.0$, 1.2 Hz, H-2), 3.75 (ddd, 1H, $J = 9.6$, 6.0, 2.1 Hz, H-5′), 3.56–3.75 (m, 9H, H-3, H-4, H-5, H-6b, H-3′, H-4′, H-6a′, H-6b′, octyl OCH_2), 3.37–3.42 (m, 4H, OCH_3, octyl OCH_2), 1.51–1.63 (m, 2H, octyl OCH$_2$CH_2), 1.24–1.44 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 101.6 (C-1′), 101.5 (C-1), 73.4 (C-6′), 73.1, 73.0 (C-3, C-3′), 72.9 (C-5), 72.7 (C-5′), 72.2 (C-2), 72.0 (C-2′), 68.8 (C-4/C-4′), 68.6 (octyl OCH$_2$), 68.5 (C-4/C-4′), 67.5 (C-6), 59.5 (OCH$_3$), 33.0 (octyl CH$_2$), 30.6 (octyl CH$_2$), 30.5 (octyl CH$_2$), 30.4 (octyl CH$_2$), 27.4 (octyl CH$_2$), 23.7 (octyl CH$_2$), 14.5 (octyl CH$_3$). ESIMS: m/z calcd for $[C_{21}H_{40}O_{11}]Na^+$: 491.2463. Found: 491.2458.

3.9. Octyl 6-deoxy-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (12)

Prepared from disaccharide **49** (77 mg, 0.079 mmol) in CH_3OH (7 mL) and 20% $Pd(OH)_2$ (35 mg) as described for **5**, to give **12** (33 mg, 96%) as a foam: R_f 0.48 (4:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +66.9 (c 1.2, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ_H 4.73 (d, 1H, $J = 2.0$ Hz, H-1′), 4.70 (d, 1H, $J = 1.5$ Hz, H-1), 3.82–3.87 (m, 2H, H-6a, H-2′), 3.78 (dd, 1H, $J = 3.0$, 1.5 Hz, H-2), 3.60–3.73 (m, 7H, H-3, H-4, H-5, H-6b, H-3′, H-5′, octyl OCH_2), 3.40 (dt, 1H, $J = 9.6$, 6.3, 6.3 Hz, octyl OCH_2), 3.36 (dd, 1H, $J = 9.5$, 9.5 Hz, H-4′), 1.51–1.63 (m, 2H, octyl OCH$_2$CH_2), 1.24–1.42 (m, 10H, octyl CH_2), 1.25 (d, 3H, $J = 6.5$ Hz, H-6′), 0.89 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 101.6 (C-1), 101.4 (C-1′), 74.1 (C-4′), 73.1 (C-3), 72.9 (C-3′), 72.5 (C-4), 72.2 (C-2, C-2′), 69.6 (C-5′), 68.6 (C-5), 68.6 (octyl OCH$_2$), 67.4 (C-6), 33.0 (octyl CH$_2$), 30.6 (octyl CH$_2$), 30.5 (octyl CH$_2$), 30.4 (octyl CH$_2$), 27.4 (octyl CH$_2$), 23.7 (octyl CH$_2$), 18.0 (C-6′), 14.4 (octyl CH$_3$). ESIMS: m/z calcd for $[C_{20}H_{38}O_{10}]Na^+$: 461.2357. Found: 461.2355.

3.10. Octyl α-D-mannopyranosyl-(1→6)-2-*O*-methyl-α-D-mannopyranoside (13)

Disaccharide **70** (251 mg, 0.24 mmol) was dissolved in CH_3OH (20 mL) and $NaOCH_3$ (108 mg) was added. After 2 h the solution was neutralized with AcOH, and following concentration, the crude product was purified by chromatography (10:1, CH_2Cl_2–CH_3OH) to give an intermediate as a pale-yellow oil (140 mg, 91%). Debenzylation of this intermediate was achieved using CH_3OH (10 mL) and 20% $Pd(OH)_2$ (30 mg) as described for **5** to give **13** (88 mg, 98%) as a foam: R_f 0.49 (4:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +57.6 (c 2.1, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ_H ^{1}H NMR (600 MHz, CD_3OD) δ_H 4.84 (d, 1H, $J = 1.8$ Hz, H-1), 4.81 (d, 1H, $J = 1.8$ Hz, H-1′), 3.86–3.90 (m, 1H, H-6a), 3.84 (dd, 1H, $J = 3.0$, 1.8 Hz, H-2′), 3.81 (dd, 1H, $J = 11.7$, 2.1 Hz, H-6a′), 3.58–3.74 (m, 9H, H-3, H-4, H-5, H-6b, H-3′, H-4′, H-5′, H-6b′, octyl OCH_2), 3.44 (s, 3H, OCH_3), 3.43 (dt, 1H, $J = 9.6$, 6.0 Hz, octyl OCH_2), 3.39 (dd, 1H, $J = 3.6$, 1.8 Hz, H-2), 1.53–1.63 (m, 2H, octyl OCH$_2$CH_2), 1.25–1.43 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 101.5 (C-1), 98.3 (C-1′), 82.2 (C-2), 74.4 (C-5′), 73.2 (C-5), 72.7 (C-3′), 72.7 (C-3), 72.1 (C-2′), 68.8 (C-4/C-4′), 68.7 (octyl OCH$_2$), 68.6 (C-4/C-4′), 67.4 (C-6), 62.9 (C-6′), 59.3 (OCH$_3$), 33.0 (octyl CH$_2$), 30.7 (octyl CH$_2$), 30.5 (octyl CH$_2$), 30.4 (octyl CH$_2$), 27.4 (octyl CH$_2$), 23.7 (octyl CH$_2$), 14.4 (octyl CH$_3$). ESIMS: m/z calcd for $[C_{21}H_{40}O_{11}]Na^+$: 491.2463. Found: 491.2462.

3.11. Octyl α-D-mannopyranosyl-(1→6)-2-deoxy-α-D-*arabino*-hexopyranoside (14)

Debenzylation of disaccharide **59** (107 mg, 0.10 mmol) was achieved using 20% $Pd(OH)_2$ (30 mg) in CH_3OH (8 mL) as described for **5** to obtain a white solid intermediate, which was dissolved in CH_3OH (10 mL) before $NaOCH_3$ (54 mg) was added. After stirring for 2 h, the solution was neutralized with AcOH and concentrated, and the crude product was purified by chromatography on Iatrobeads (4:1 CH_2Cl_2–CH_3OH) to give **14** (35 mg, 78%) as a foam: R_f 0.43 (4:1, CH_2Cl_2–CH_3OH); $[\alpha]_D$ +90.4 (c 2.0, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ_H 4.84 (d, 1H, $J = 1.2$ Hz, H-1), 4.80 (d, 1H, $J = 1.8$ Hz, H-1′), 3.91 (dd, 1H, $J = 11.1$, 5.1 Hz, H-6a), 3.78–3.84 (m, 3H, H-3, H-2′, H-6a′), 3.60–3.73 (m, 7H, H-5, H-6b, H-3′, H-4′, H-5′, H-6b′, octyl OCH_2), 3.35 (dt, 1H, $J = 9.6$, 6.3 Hz, octyl OCH_2), 3.28 (dd, 1H, $J = 9.6$, 9.6 Hz, H-4), 2.04 (ddd, 1H, $J = 13.2$, 5.4, 1.2 Hz, H-2$_{eq}$), 1.51–1.62 (m, 3H, H-2$_{ax}$,

octyl OCH_2CH_2), 1.24–1.42 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 6.9$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 101.5 (C-1′), 98.7 (C-1), 74.4 (C-3′), 73.2 (C-4), 72.7 (C-4′/C-5), 72.7 (C-4′/C-5), 72.1 (C-2′), 70.2 (C-3), 68.6 (C-5′), 68.4 (octyl OCH_2), 67.3 (C-6), 62.9 (C-6′), 39.0 (C-2), 33.0 (octyl CH_2), 30.7 (octyl CH_2), 30.6 (octyl CH_2), 30.4 (octyl CH_2), 27.5 (octyl CH_2), 23.7 (octyl CH_2), 14.4 (octyl CH_3). ESIMS: m/z calcd for $[C_{20}H_{38}O_{10}]Na^+$: 461.2357. Found: 461.2359.

3.12. Octyl α-D-mannopyranosyl-(1→6)-3-*O*-methyl-α-D-mannopyranoside (15)

Debenzoylation of disaccharide **71** (252 mg, 0.28 mmol) using $NaOCH_3$ (108 mg) in CH_3OH (25 mL) as described for **13** gave a pale-yellow oil intermediate (133 mg, 87%). A portion of this intermediate (60 mg, 0.092 mmol) was debenzylated in CH_3OH (5 mL) and 20% $Pd(OH)_2$ (15 mg) to give **15** (41 mg, 93%) as a foam: R_f 0.31 (4:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +70.4 (*c* 1.2, CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ_H 4.81 (d, 1H, $J = 1.8$ Hz, H-1′), 4.74 (d, 1H, $J = 1.8$ Hz, H-1), 3.99 (dd, 1H, $J = 3.2$, 1.8 Hz, H-2), 3.89 (dd, 1H, $J = 11.1$, 5.8 Hz, H-6a), 3.83 (dd, 1H, $J = 3.3$, 1.8 Hz, H-2′), 3.81 (dd, 1H, $J = 12.0$, 1.8 Hz, H-6a′), 3.61–3.74 (m, 8H, H-4, H-5, H-6b, H-3′, H-4′, H-5′, H-6b′, octyl OCH_2), 3.44 (s, 3H, OCH_3), 3.41 (dt, 1H, $J = 10.2$, 6.3 Hz, octyl OCH_2), 3.33 (dd, 1H, $J = 9.3$, 3.2 Hz, H-3), 1.54–1.64 (m, 2H, octyl OCH_2CH_2), 1.25–1.43 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 101.6 (C-1), 101.4 (C-1′), 82.6 (C-3), 74.3 (C-5′), 73.1 (C-5), 72.7 (C-4), 72.1 (C-2′), 68.7 (octyl OCH_2), 68.6 (C-3′), 68.1 (C-2), 67.4 (C-4′), 67.3 (C-6), 62.9 (C-6′), 57.4 (OCH_3), 33.0 (octyl CH_2), 30.6 (octyl CH_2), 30.5 (octyl CH_2), 30.4 (octyl CH_2), 27.4 (octyl CH_2), 23.7 (octyl CH_2), 14.4 (octyl CH_3). ESIMS: m/z calcd for $[C_{21}H_{40}O_{11}]Na^+$: 491.2463. Found: 491.2464.

3.13. Octyl α-D-mannopyranosyl-(1→6)-3-deoxy-α-D-*arabino*-hexopyranoside (16)

As described for **14**, disaccharide **60** (32 mg, 0.030 mmol) was debenzylated in CH_3OH (3 mL) and 20% $Pd(OH)_2$ (10 mg) to give a white solid intermediate, which was reacted with $NaOCH_3$ (22 mg) in CH_3OH (4 mL) to give **16** (12 mg, 93%) as a foam: R_f 0.45 (4:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +65.2 (*c* 0.6, CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ_H 4.81 (d, 1H, $J = 1.8$ Hz, H-1′), 4.54 (br s, 1H, H-1), 3.86 (dd, 1H, $J = 10.8$, 6.0 Hz, H-6a), 3.84 (dd, 1H, $J = 3.6$, 1.8 Hz, H-2′), 3.77–3.83 (m, 2H, H-4, H-6a′), 3.74–3.76 (m, 1H, H-2), 3.69–3.74 (m, 4H, H-6b, H-3′, H-6b′, octyl OCH_2), 3.62–3.67 (m, 3H, H-5, H-4′, H-5′), 3.41 (dt, 1H, $J = 9.6$, 6.3 Hz, octyl OCH_2), 1.99 (ddd, 1H, $J = 13.2$, 3.0, 3.0 Hz, H-3_{eq}), 1.80 (ddd, 1H, $J = 13.2$, 11.4, 3.0 Hz, H-3_{ax}), 1.53–1.64 (m, 2H, octyl OCH_2CH_2), 1.25–1.44 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 101.4 (C-1′), 100.3 (C-1), 74.3 (C-4′/C-5), 74.1 (C-4′/C-5), 72.7 (C-3′), 72.2 (C-2′), 69.2 (C-2), 68.6 (C-5′), 68.4 (octyl OCH_2), 67.6 (C-6), 62.9 (C-4), 62.8 (C-6′), 36.3 (C-3), 33.0 (octyl CH_2), 30.7 (octyl CH_2), 30.6 (octyl CH_2), 30.4 (octyl CH_2), 27.5 (octyl CH_2), 23.7 (octyl CH_2), 14.4 (octyl CH_3). ESIMS: m/z calcd for $[C_{20}H_{38}O_{10}]Na^+$: 461.2357. Found: 461.2360.

3.14. Octyl α-D-mannopyranosyl-(1→6)-4-*O*-methyl-α-D-mannopyranoside (17)

Prepared from diol **78** (69 mg, 0.078 mmol) in CH_3OH (7 mL) and $NaOCH_3$ (38 mg) as described for **13** to give **17** (32 mg, 86%) as a foam: R_f 0.44 (4:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +84.3 (*c* 0.6, CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ_H 4.85 (d, 1H, $J = 1.8$ Hz, H-1′), 4.67 (br s, 1H, H-1), 3.86–3.90 (m, 2H, H-6a, H-2′), 3.82 (dd, 1H, $J = 11.7$, 2.1 Hz, H-6a′), 3.60–3.76 (m, 8H, H-2, H-3, H-6b, H-3′, H-4′, H-5′, H-6b′, octyl OCH_2), 3.58 (ddd, 1H, $J = 10.2$, 5.4, 1.8 Hz, H-5), 3.54 (s, 3H, OCH_3), 3.34–3.41 (m, 2H, H-4, octyl OCH_2), 1.51–1.61 (m, 2H, octyl OCH_2CH_2), 1.24–1.41 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ_C 101.8 (C-1′), 101.5 (C-1), 78.7 (C-4), 74.6 (C-3′/C-5′), 72.9, 72.7, 72.5 (C-2, C-3, C-4′), 72.3 (C-5), 72.1 (C-2′), 68.6 (C-3′/C-5′), 68.6 (octyl OCH_2), 67.5 (C-6), 62.9 (C-6′), 61.1 (OCH_3), 33.0 (octyl CH_2), 30.6 (octyl CH_2), 30.5 (octyl CH_2), 30.4 (octyl CH_2), 27.4 (octyl CH_2), 23.7 (octyl CH_2), 14.5 (octyl CH_3). ESIMS: m/z calcd for $[C_{21}H_{40}O_{11}]Na^+$: 491.2463. Found: 491.2466.

3.15. Octyl α-D-mannopyranosyl-(1→6)-4-deoxy-α-D-*lyxo*-hexopyranoside (18)

Disaccharide **77** (99 mg, 0.11 mmol) was dissolved in 80% AcOH–H_2O (2 mL) and heated at 50 °C overnight. The solution was then diluted with EtOAc (20 mL), washed with satd aq $NaHCO_3$ (2 × 5 mL), dried ($MgSO_4$), and concentrated to a colorless residue that was reacted with $NaOCH_3$ (54 mg) in CH_3OH (10 mL) as described for **13** to give **18** (46 mg, 94% over two steps) as a foam: R_f 0.38 (4:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +64.7 (*c* 2.3, CH_3OH); ^1H NMR (500 MHz, CD_3OD) δ_H 4.78 (d, 1H, $J = 2.0$ Hz, H-1′), 4.75 (d, 1H, $J = 1.5$ Hz, H-1), 3.87–3.94 (m, 2H, H-3, H-5), 3.80–3.84 (m, 2H, H-2′, H-6a′), 3.76 (dd, 1H, $J = 10.6$, 6.5 Hz, H-6a), 3.56–3.73 (m, 6H, H-2, H-3′, H-4′, H-5′, H-6b′, octyl OCH_2), 3.46 (dd, 1H, $J = 10.6$, 3.8 Hz, H-6b), 3.38 (dt, 1H, $J = 9.6$, 6.8 Hz, octyl OCH_2), 1.73 (ddd, 1H, $J = 12.0$ Hz, H-4_{ax}), 1.52–1.62 (m, 3H, H-4_{eq}, octyl OCH_2CH_2), 1.24–1.41 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR

(125 MHz, CD_3OD) δ_C 102.2 (C-1), 101.4 (C-1′), 74.5 (C-3′), 72.7 (C-4′), 72.1 (C-2′), 70.7 (C-6), 70.3 (C-2), 68.7 (C-5/C-5′), 68.6 (C-5/C-5′), 68.5 (octyl O*C*H$_2$), 66.9 (C-3), 33.0 (octyl *C*H$_2$), 31.6 (C-4), 30.6 (octyl *C*H$_2$), 30.5 (octyl *C*H$_2$), 30.4 (octyl *C*H$_2$), 27.4 (octyl *C*H$_2$), 23.7 (octyl *C*H$_2$), 14.5 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{20}H_{38}O_{10}]Na^+$: 461.2357. Found: 461.2357.

3.16. *p*-Tolyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (21)

Monosaccharide **27** (2.2 g, 4.7 mmol) was dissolved in CH_2Cl_2 (50 mL), and pyridine (7.2 mL) and acetic anhydride (3.6 mL) were added. The reaction mixture was stirred overnight and then diluted with CH_2Cl_2 (150 mL), before being washed with 1 M HCl (3 × 50 mL), satd aq $NaHCO_3$ (50 mL), water (50 mL), dried ($MgSO_4$), and concentrated. The crude product was purified by chromatography (6:1 hexane–EtOAc) to give **21** (1.89 g, 79%) as a foam: R_f 0.42 (6:1 hexane–EtOAc); $[\alpha]_D$ +119.5 (*c* 7.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.52–7.55 (m, 2H, ArH), 7.29–7.43 (m, 10H, ArH), 7.13 (d, 2H, J = 8.4 Hz, ArH), 5.64 (s, 1H, benzylidene H), 5.63 (dd, 1H, J = 3.2, 1.2 Hz, H-2), 5.40 (d, 1H, J = 1.2 Hz, H-1), 4.75 (d, 1H, J = 12.0 Hz, PhC*H*$_2$), 4.70 (d, 1H, J = 12.0 Hz, PhC*H*$_2$), 4.37 (ddd, 1H, J = 10.0, 9.6, 4.8 Hz, H-5), 4.25 (dd, 1H, J = 10.4, 4.8 Hz, H-6a), 4.15 (dd, 1H, J = 9.6, 9.6 Hz, H-4), 4.03 (dd, 1H, J = 9.6, 3.2 Hz, H-3), 3.87 (dd, 1H, J = 10.4, 10.0 Hz, H-6b), 2.34 (s, 3H, SPhC*H*$_3$), 2.16 (s, 3H, C(O)C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 169.9 (C=O), 138.3 (Ar), 137.6 (Ar), 137.3 (Ar), 132.6 (2 × Ar), 129.9 (2 × Ar), 129.1 (Ar), 128.8 (Ar), 128.3 (2 × Ar), 128.1 (2 × Ar), 127.7 (3 × Ar), 126.0 (2 × Ar), 101.5 (benzylidene *C*H), 87.4 (C-1), 78.4 (C-4), 74.0 (C-3), 72.2 (Ph*C*H$_2$), 71.2 (C-2), 68.3 (C-6), 65.0 (C-5), 21.1 (Ph*C*H$_3$), 20.9 (C(O)*C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{29}H_{30}O_6S]Na^+$: 529.1655. Found: 529.1652.

3.17. *p*-Tolyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (22)

Prepared from monosaccharide **28** (1.8 g, 3.9 mmol), pyridine (7.0 mL) and acetic anhydride (3.5 mL) in CH_2Cl_2 (40 mL) as described for **21**, to give **22** (1.83 g, 94%) as a foam: R_f 0.45 (4:1 hexane–EtOAc); $[\alpha]_D$ +76.3 (*c* 5.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.50–7.53 (m, 2H, ArH), 7.33–7.42 (m, 10H, ArH), 7.16 (d, 2H, J = 8.0 Hz, ArH), 5.61 (s, 1H, benzylidene H), 5.51 (d, 1H, J = 1.2 Hz, H-1), 5.34 (dd, 1H, J = 10.4, 3.2 Hz, H-3), 4.70 (d, 1H, J = 12.0Hz, PhC*H*$_2$), 4.63 (d, 1H, J = 12.0 Hz, PhC*H*$_2$), 4.44 (ddd, 1H, J = 10.0, 10.0, 4.8 Hz, H-5), 4.25–4.30 (m, 3H, H-2, H-4, H-6a), 3.90 (dd, 1H, J = 10.0, 10.0 Hz, H-6b), 2.37 (s, 3H, SPhC*H*$_3$), 2.06 (s, 3H, C(O)C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 170.2 (C=O), 138.1 (Ar), 137.3 (Ar), 137.3 (Ar), 132.5 (2 × Ar), 130.0 (2 × Ar), 129.7 (Ar), 129.1 (Ar), 128.6 (2 × Ar) 128.3 (2 × Ar), 128.2 (Ar), 128.1 (2 × Ar), 126.3 (2 × Ar), 101.8 (benzylidene *C*H), 86.7 (C-1), 77.5 (C-2/C-4), 76.3 (C-2/C-4), 73.0 (Ph*C*H$_2$), 70.5 (C-3), 68.5 (C-6), 65.3 (C-5), 21.2 (SPh*C*H$_3$), 21.0 (C(O)*C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{29}H_{30}O_6S]Na^+$: 529.1655. Found: 529.1652.

3.18. Octyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (23)

Triol **30** (4.18 g, 7.87 mmol) was dissolved in DMF (25 mL), and BnBr (6.0 mL, 48.0 mmol) was added. The solution was cooled in an ice bath, and 60% NaH in mineral oil (2.05 g, 51.3 mmol) was added portionwise, and the mixture was warmed to room temperature. After 3 h, the reaction was quenched by the addition of CH_3OH (15 mL), diluted with EtOAc (90 mL), washed with water (3 × 40 mL), brine (40 mL) and dried ($MgSO_4$), filtered, and concentrated to a pale-yellow oil. The crude product was dissolved in THF (50 mL), 1.0 M tetra-*n*-butylammonium fluoride in THF (16.0 mL, 16.0 mmol) was added, and the solution was stirred at room temperature overnight. The solvent was evaporated, and the residue was purified by chromatography (4:1, hexane–EtOAc) to give **23** (4.03 g, 91% over two steps) as a colorless oil: R_f 0.24 (4:1, hexane–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.27–7.44 (m, 15H, ArH), 4.96 (d, 1H, J = 11.0 Hz, PhC*H*$_2$), 4.81 (d, 1H, J = 11.0 Hz, PhC*H*$_2$), 4.81 (d, 1H, J = 1.5 Hz, H-1), 4.64–4.74 (m, 4H, PhC*H*$_2$), 4.00 (dd, 1H, J = 9.5, 9.5 Hz, H-4), 3.95 (dd, 1H, J = 9.5, 3.0 Hz, H-3), 3.86 (ddd, 1H, J = 11.5, 3.0 Hz, H-6a), 3.76–3.83 (m, 2H, H-2, H-6b), 3.64–3.70 (m, 1H, H-5), 3.63 (dt, 1H, J = 9.5, 6.5 Hz, octyl OC*H*$_2$), 3.34 (dt, 1H, J = 9.5, 6.5 Hz, octyl OC*H*$_2$), 2.09 (dd, 1H, J = 7.5, 5.5 Hz, O*H*), 1.46–1.78 (m, 2H, octyl OCH$_2$C*H*$_2$), 1.24–1.38 (m, 10H, octyl C*H*$_2$), 0.91 (t, 3H, J = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.6 (Ar), 138.4 (Ar), 138.4 (Ar), 128.4 (3 × Ar), 128.4 (2 × Ar), 127.8 (2 × Ar), 127.7 (2 × Ar), 127.7 (2 × Ar), 127.6 (2 × Ar), 127.6 (2 × Ar), 98.2 (C-1), 80.3 (C-3), 75.3 (Ph*C*H$_2$), 75.1 (C-2, C-4), 72.9 (Ph*C*H$_2$), 72.1 (C-5), 67.7 (octyl O*C*H$_2$), 62.5 (C-6), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ^{1}H and ^{13}C NMR spectral data were consistent with that reported.[27]

3.19. *p*-Tolyl *exo*(phenyl)-2,3:4,6-di-*O*-benzylidene-1-thio-α-D-mannopyranoside (25) and 4-methylphenyl *endo*(phenyl)-2,3:4,6-di-*O*-benzylidene-1-thio-α-D-mannopyranoside (26)

Tetraol **24**[29] (2.0 g, 7.0 mmol) was dissolved in DMF (5.0 mL) and benzaldehyde dimethyl acetal (1.5 mL,

10.0 mmol) and *p*-TsOH (21 mg, 0.11 mmol) were added. The reaction mixture was rotated under reduced pressure at 60 °C on a rotary evaporator. After 2 h additional DMF (50 mL), benzaldehyde dimethyl acetal (1.5 mL, 10.0 mmol), and *p*-TsOH (21 mg, 0.11 mmol) were added, and stirring was continued for 3 h. The reaction mixture was neutralized with satd aq $NaHCO_3$, diluted with CH_2Cl_2 (100 mL), washed with water (3×50 mL), dried ($MgSO_4$), and concentrated. Recrystalization of the crude product from 1:1, acetone–EtOH (300 mL) gave a mixture of **25** and **26**. A second recrystalization of this material afforded a mixture of **25** and **26** in 23:1 ratio (584 mg, 18%). The mother liquor was concentrated, and the resulting solid was recrystalized from 1:1, acetone–EtOH (75 mL) to give crystalline of **26** and **25** in 20:1 ratio (964 mg, 30%). The mother liquor was concentrated and purified by chromatography (9:1, hexane–EtOAc) to give **26** and **25** in 12:1 ratio (773 mg, 24%).

3.19.1. Data for 25. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.53–7.58 (m, 2H, ArH), 7.44–7.59 (m, 2H, ArH), 7.36–7.41 (m, 8H, ArH), 7.15 (d, 2H, $J = 8.0$ Hz, ArH), 6.31 (s, 1H, dioxolane H), 5.80 (s, 1H, H-1), 5.65 (s, 1H, dioxane H), 4.68 (dd, 1H, $J = 9.0$, 5.5 Hz, H-3), 4.38 (d, 1H, $J = 5.5$ Hz, H-2), 4.34 (ddd, 1H, $J = 10.5$, 9.0, 5.0 Hz, H-5), 4.25 (dd, 1H, $J = 10.5$, 5.0 Hz, H-6a), 3.98 (dd, 1H, $J = 9.0$, 9.0 Hz, H-4), 3.79 (dd, 1H, $J = 10.5$, 10.5 Hz, H-6b), 2.35 (s, 3H, PhCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.5 (Ar), 138.5 (Ar), 137.1 (Ar), 133.1 (2 × Ar), 130.0 (2 × Ar), 129.2 (Ar), 129.2 (Ar), 128.7 (Ar), 128.4 (2 × Ar), 128.3 (2 × Ar), 126.3 (2 × Ar), 126.0 (2 × Ar), 103.1 (dioxolane *C*H), 102.0 (dioxane *C*H), 85.0 (C-1), 77.8 (C-4), 75.9 (C-2), 75.3 (C-3), 68.6 (C-6), 61.6 (C-5), 21.2 (Ph*C*H$_3$). Anal. Calcd for $C_{27}H_{26}O_5S$ (462.56): C, 70.11; H, 5.61; S, 6.93. Found: C, 69.93; H, 5.70; S, 7.01. ESIMS: *m*/*z* calcd for $[C_{27}H_{26}O_5S]Na^+$: 485.1393. Found: 485.1391.

3.19.2. Data for 26. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.50–7.55 (m, 4H, ArH), 7.34–7.43 (m, 8H, ArH), 7.15 (d, 2H, $J = 7.5$ Hz, ArH), 5.99 (s, 1H, dioxolane H), 5.86 (s, 1H, H-1), 5.51 (s, 1H, dioxane H), 4.54 (dd, 1H, $J = 8.0$, 8.0 Hz, H-3), 4.49 (d, 1H, $J = 8.0$ Hz, H-2), 4.27 (ddd, 1H, $J = 10.5$, 10.0, 5.0 Hz, H-5), 4.19 (dd, 1H, $J = 10.5$, 5.0 Hz, H-6a), 3.81 (dd, 1H, $J = 10.0$, 8.0 Hz, H-4), 3.69 (dd, 1H, $J = 10.5$, 10.5 Hz, H-6b), 2.35 (s, 3H, PhCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.5 (Ar), 137.2 (Ar), 137.0 (Ar), 133.2 (2 × Ar), 130.0 (2 × Ar), 130.0 (Ar), 129.5 (Ar), 129.1 (Ar), 128.5 (2 × Ar), 128.2 (2 × Ar), 126.5 (2 × Ar), 126.2 (2 × Ar), 104.1 (dioxolane *C*H), 101.8 (dioxane *C*H), 84.5 (C-1), 80.8 (C-4), 78.6 (C-2), 74.0 (C-3), 68.6 (C-6), 61.7 (C-5), 21.2 (Ph*C*H$_3$). Anal. Calcd for $C_{27}H_{26}O_5S$ (462.56): C, 70.11; H, 5.61; S, 6.93. Found: C, 69.92; H, 5.72; S, 7.02. ESIMS: *m*/*z* calcd for $[C_{27}H_{26}O_5S]Na^+$: 485.1393. Found: 485.1395.

3.20. *p*-Tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (27)

$AlCl_3$ (0.16 g, 1.2 mmol) was dissolved in prechilled Et_2O (4 mL) and stirred for 10 min before $LiAlH_4$ (1.2 mL of 1.0 M solution in ether) was added. This mixture was stirred for an additional 10 min before addition to **25** (480 mg, 1.0 mmol) in 1:1, CH_2Cl_2–Et_2O (15 mL). The reaction mixture was stirred for 1 h and then quenched by the addition of EtOAc followed by water. The reaction mixture was diluted with EtOAc (60 mL), washed with water (3×20 mL), dried ($MgSO_4$), and concentrated to a light-yellow oil that was purified by chromatography (4:1, hexane–EtOAc) to give **27** (419 mg, 87%) as a light yellow oil: R_f 0.21 (4:1 hexane–EtOAc); $[\alpha]_D$ +222.2 (*c* 2.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.50–7.55 (m, 2H, ArH), 7.31–7.42 (m, 10H, ArH), 7.13 (d, 2H, $J = 8.5$ Hz, ArH), 5.63 (s, 1H, benzylidene H), 5.53 (d, 1H, $J = 1.3$ Hz, H-1), 4.90 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.75 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.36 (ddd, 1H, $J = 10.4$, 9.5, 5.0 Hz, H-5), 4.28 (dd, 1H, $J = 3.4$, 1.3 Hz, H-2), 4.22 (dd, 1H, $J = 10.4$, 5.0 Hz, H-6a), 4.19 (dd, 1H, $J = 9.5$, 9.5 Hz, H-4), 3.98 (dd, 1H, $J = 9.5$, 3.4 Hz, H-3), 3.86 (dd, 1H, $J = 10.4$, 10.4 Hz, H-6b), 2.85 (br s, 1H, O*H*), 2.34 (s, 3H, PhCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.0 (Ar), 137.8 (Ar), 137.5 (Ar), 132.4 (2 × Ar), 129.9 (2 × Ar), 129.4 (Ar), 129.0 (Ar), 128.5 (2 × Ar), 128.2 (2 × Ar), 128.0 (Ar), 127.9 (2 × Ar), 126.1 (2 × Ar), 101.6 (benzylidene *C*H), 88.2 (C-1), 79.1 (C-4), 75.7 (C-3), 73.2 (Ph*C*H$_2$), 71.4 (C-2), 68.6 (C-6), 64.5 (C-5), 21.1 (Ph*C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{27}H_{28}O_5S]Na^+$: 487.1550. Found: 487.1552.

3.21. *p*-Tolyl 2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (28)

Prepared from a solution of $AlCl_3$ (0.24 g, 1.8 mmol) and $LiAlH_4$ (1.8 mmol) in ether (7.8 mL) and **26** (655 mg, 1.4 mmol) in 1:1, CH_2Cl_2–ether (15 mL) at 0 °C as described for **27** to give **28** (430 mg, 66%) as a light-yellow oil: R_f 0.36 (4:1 hexane–EtOAc); $[\alpha]_D$ +145.4 (*c* 3.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.54–7.56 (m, 2H, ArH), 7.33–7.42 (m, 10H, ArH), 7.16 (d, 2H, $J = 8.0$ Hz, ArH), 5.60 (s, 1H, benzylidene H), 5.54 (d, 1H, $J = 1.0$ Hz, H-1), 4.75 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.66 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.35 (ddd, 1H, $J = 10.0$, 10.0, 5.0 Hz, H-5), 4.25 (dd, 1H, $J = 10.0$, 5.0 Hz, H-6a), 4.16 (dd, 1H, $J = 10.0$, 3.5 Hz, H-3), 4.12 (dd, 1H, $J = 3.5$, 1.0 Hz, H-2), 4.02 (dd, 1H, $J = 10.0$, 10.0 Hz, H-4), 3.86 (dd, 1H, $J = 10.0$, 10.0 Hz, H-6b), 2.54 (br s, 1H, O*H*), 2.39 (s, 3H, SPhCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.1

(Ar), 137.4 (Ar), 137.3 (Ar), 132.5 (2 × Ar), 130.0 (2 × Ar), 129.8 (Ar), 129.2 (Ar), 128.7 (2 × Ar), 128.3 (2 × Ar), 128.2 (Ar), 128.1 (2 × Ar), 126.4 (2 × Ar), 102.2 (benzylidene *C*H), 86.7 (C-1), 80.1 (C-2), 79.7 (C-4), 73.2 (Ph*C*H$_2$), 69.1 (C-3), 68.5 (C-6), 64.7 (C-5), 21.2 (SPh*C*H$_3$). Anal. Calcd for $C_{27}H_{28}O_5S$ (464.57): C, 69.80; H, 6.07; S, 6.90. Found: C, 69.60; H, 6.15; S, 6.62. ESIMS: *m*/*z* calcd for $[C_{27}H_{28}O_5S]Na^+$: 487.1550. Found: 487.1555.

3.22. Octyl 6-*O*-(*tert*-butyldiphenylsilyl)-α-D-manno-pyranoside (30)

Tetraol **29**[27] (3.93 g, 13.4 mmol) and imidazole (2.29 g, 33.6 mmol) were dissolved in DMF (15 mL), and *tert*-butylchlorodiphenylsilane (4.2 mL, 16.1 mmol) was added. The reaction mixture was heated at 45 °C for 3 h and was quenched with water (2 mL). The mixture was then diluted with EtOAc (60 mL), washed with water (3 × 20 mL), 1 M HCl (20 mL), satd aq $NaHCO_3$ (20 mL), dried ($MgSO_4$), and concentrated to colorless oil. The crude product was purified by chromatography (1:1 hexane–EtOAc) to give **30** (6.69 g, 94%) as a colorless oil: R_f 0.35 (1:1 hexane–EtOAc); $[\alpha]_D$ +21.1 (*c* 7.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.68–7.71 (m, 4H, ArH), 7.37–7.45 (m, 6H, ArH), 4.77 (d, 1H, $J = 1.6$ Hz, H-1), 3.78–3.96 (m, 5H, H-2, H-3, H-4, H-6a, H-6b), 3.58–3.68 (m, 2H, H-5, octyl OCH_2), 3.35 (dt, 1H, $J = 9.6$, 6.8 Hz, octyl OCH_2), 2.06–3.00 (br s, O*H*), 1.51–1.56 (m, 2H, octyl OCH$_2$CH_2), 1.20–1.37 (m, 10H, octyl CH_2), 1.07 (s, 9H, *tert*-butyl CH_3), 0.89 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 135.6 (4 × Ar), 132.9 (Ar), 132.8 (Ar), 129.9 (2 × Ar), 127.8 (4 × Ar), 99.4 (C-1), 71.8 (C-2), 70.7 (C-3/C-4/C-5), 70.6 (C-3/C-4/C-5), 70.5 (C-3/C-4/C-5), 67.7 (octyl O*C*H$_2$), 65.3 (C-6), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (*tert*-butyl *C*), 29.2 (octyl *C*H$_2$), 26.8 (*tert*-butyl *C*H$_3$), 26.1 (octyl *C*H$_2$), 22.6 (octyl *C*H$_2$), 19.2 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{30}H_{46}O_6Si]Na^+$: 553.2956. Found: 553.2956.

3.23. Octyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-manno-pyranoside (31)

Thioglycoside **21** (460 mg, 0.91 mmol), alcohol **23** (378 mg, 0.67 mmol), and powdered 4 Å molecular sieves (350 mg) were dried overnight under vacuum with P_2O_5. Dry CH_2Cl_2 (20 mL) was added, and the reaction mixture was cooled to 0 °C before the addition of *N*-iodosuccinimide (240 mg, 1.1 mmol) and AgOTf (52 mg, 0.20 mmol). The mixture was stirred for 1 h at 0 °C and neutralized with Et_3N, before being filtered through Celite and concentrated. The crude residue was purified by chromatography (4:1 hexane–EtOAc) to give **31** (272 mg, 89%) as a yellow oil: R_f 0.34 (4:1 hexane–EtOAc); $[\alpha]_D$ +33.4 (*c* 2.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.48–7.50 (m, 2H, ArH), 7.19–7.41 (m, 23H, Ar), 5.63 (s, 1H, benzylidene H), 5.52 (dd, 1H, $J = 3.2$, 1.5 Hz, H-2′), 4.93 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.91 (d, 1H, $J = 1.5$ Hz, H-1′), 4.82 (d, 1H, $J = 2.0$ Hz, H-1), 4.75 (s, 2H, PhCH_2), 4.66 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.63 (s, 2H, PhCH_2), 4.59 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.53 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.23 (dd, 1H, $J = 10.0$, 4.5 Hz, H-6a′), 4.06 (dd, 1H, $J = 9.5$, 9.5 Hz, H-4′), 3.99 (dd, 1H, $J = 9.5$, 3.2 Hz, H-3′), 3.90–3.97 (m, 2H, H-3, H-5′), 3.80–3.90 (m, 3H, H-4, H-6a, H-6b′), 3.79 (dd, 1H, $J = 2.5$, 2.0 Hz, H-2), 3.69–3.70 (m, 2H, H-5, H-6b), 3.60 (dt, 1H, $J = 10.0$, 6.5 Hz, octyl OCH_2), 3.34 (dt, 1H, $J = 10.0$, 6.5 Hz, octyl OCH_2), 2.16 (s, 3H, (CO)CH_3), 1.45–1.55 (m, 2H, octyl OCH$_2$CH_2), 1.20–1.35 (m, 10H, octyl CH_2), 0.89, (t, 3H, $J = 7.5$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.0 (*C*═O), 138.7 (Ar), 138.6 (Ar), 138.5 (Ar), 138.1 (Ar), 137.8 (Ar), 128.9 (Ar), 128.5 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 126.3 (Ar), 101.7 (benzylidene *C*H), 99.1 (C-1′, $^1J_{C,H} = 173.5$ Hz), 97.8 (C-1, $^1J_{C,H} = 167.5$ Hz), 80.5 (C-3), 78.5 (C-4′), 75.2 (Ph*C*H$_2$), 75.0 (C-2), 74.8 (C-4), 73.9 (C-3′), 72.8 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 72.0 (Ph*C*H$_2$), 71.3 (C-5), 69.7 (C-2′), 68.9 (C-6′), 67.8 (octyl O*C*H$_2$), 67.3 (C-6), 64.1 (C-5′), 32.0 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 22.8 (octyl *C*H$_2$), 21.1 ((CO)*C*H$_3$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{57}H_{68}O_{12}$ (945.14): C, 72.43; H, 7.25. Found: C, 72.72; H, 7.31. ESIMS: *m*/*z* calcd for $[C_{57}H_{68}O_{12}]Na^+$: 967.4603. Found: 967.4606.

3.24. Octyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-manno-pyranoside (32)

Prepared from thioglycoside **22** (353 mg, 0.70 mmol), alcohol **23** (299 mg, 0.53 mmol), powdered 4 Å molecular sieves (500 mg), *N*-iodosuccinimide (190 mg, 0.85 mmol), and AgOTf (41 mg, 0.16 mmol) in CH_2Cl_2 (20 mL) as described for **31** to give **32** (417 mg, 83%) as a colorless oil: R_f 0.42 (6:1 hexane–EtOAc); $[\alpha]_D$ +23.8 (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.42–7.48 (m, 2H, ArH), 7.22–7.39 (m, 23H, ArH), 5.56 (s, 1H, benzylidene H), 5.33 (dd, 1H, $J = 10.0$, 3.3 Hz, H-3′), 5.14 (d, 1H, $J = 1.5$ Hz, H-1′), 4.98 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.77 (br s, 1H, H-1), 4.76 (s, 1H, $J = 13.0$ Hz, PhCH_2), 4.63–4.70 (m, 4H, PhCH_2), 4.57 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.44 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.26 (dd, 1H, $J = 10.0$, 5.0 Hz, H-6a′), 4.15 (dd, 1H, $J = 10.0$, 10.0 Hz, H-4′), 3.76–4.45 (m, 8H, H-2, H-3, H-4, H-6a, H-6b, H-2′, H-5′, H-6b′), 3.73 (m, 1H, H-5), 3.63 (dt, 1H, $J = 10.0$, 6.8 Hz, octyl OCH_2), 3.35 (dt, 1H, $J = 10.0$, 6.8 Hz,

octyl OCH_2), 2.00 (s, 3H, (CO)CH_3), 1.47–1.56 (m, 2H, octyl OCH$_2$CH_2), 1.21–1.35 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 170.0 (*C*=O), 138.5 (Ar), 138.5 (Ar), 138.4 (Ar), 138.0 (Ar), 137.5 (Ar), 128.9 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 127.8 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.5 (Ar), 126.2 (Ar), 101.7 (benzylidene *C*H), 98.7 (C-1′, $^1J_{C,H} = 175.8$ Hz), 97.9 (C-1, $^1J_{C,H} = 175.8$ Hz), 80.5 (C-3), 76.8 (C-2′), 76.4 (C-4′), 75.2 (Ph*C*H$_2$), 75.1 (C-2), 74.8 (C-4), 73.4 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 72.0 (C-5), 70.4 (C-3′), 68.9 (C-6′), 67.7 (octyl O*C*H$_2$), 66.2 (C-6), 64.0 (C-5′), 31.9 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 21.0 ((CO)*C*H$_3$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{57}H_{68}O_{12}$ (945.14): C, 72.43; H, 7.25. Found: C, 71.96; H, 7.17. ESIMS: *m*/*z* calcd for [$C_{57}H_{68}O_{12}$]Na$^+$: 967.4603. Found: 967.4605.

3.25. Octyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (33)

Disaccharide **31** (502 mg, 0.53 mmol) was dissolved in CH_3OH (25 mL) and $NaOCH_3$ (140 mg) was added. After 1 h the solution was neutralized with AcOH, and the crude product was purified by chromatography (3:1 hexane–EtOAc) to give **33** (450 mg, 94%) as a colorless oil: R_f 0.23 (3:1 hexane–EtOAc); $[\alpha]_D$ +49.7 (*c* 2.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.46–7.52 (m, 2H, ArH), 7.22–7.42 (m, 23H, ArH), 5.61 (s, 1H, benzylidene H), 5.06 (d, 1H, $J = 1.5$ Hz, H-1′), 4.93 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.83 (d, 1H, $J = 2.0$ Hz, H-1), 4.78 (d, 2H, $J = 12.0$ Hz, PhCH_2), 4.70 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.67 (s, 2H, PhCH_2), 4.66 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.56 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.25 (dd, 1H, $J = 10.0$, 4.5 Hz, H-6a′), 4.16 (dd, 1H, $J = 3.5$, 1.5 Hz, H-2′), 4.11 (dd, 1H, $J = 9.5$, 9.5 Hz, H-4′), 3.82–3.97 (m, 6H, H-3, H-4, H-6a, H-3′, H-5′, H-6b′), 3.80 (dd, 1H, $J = 2.0$ Hz, H-2), 3.76 (dd, 2H, $J = 11.5$, 2.3 Hz, H-6b), 3.68–3.73 (m, 1H, H-5), 3.61 (dt, 1H, $J = 10.0$, 6.5 Hz, octyl OCH_2), 3.35 (dt, 1H, $J = 10.0$, 6.5 Hz, octyl OCH_2), 2.54 (br s, 1H, O*H*), 1.47–1.56 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.36 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.7 (Ar), 138.6 (Ar), 138.6 (Ar), 138.2 (Ar), 137.9 (Ar), 129.0 (Ar), 128.6 (Ar), 128.5 (Ar), 128.5 (Ar), 128.5 (Ar), 128.3 (Ar), 128.1 (Ar), 127.9 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 126.3 (Ar), 101.7 (benzylidene *C*H), 100.4 (C-1′), 97.8 (C-1), 80.3 (C-3), 78.9 (C-4′), 75.3 (C-3′), 75.2 (Ph*C*H$_2$), 75.1 (C-2), 74.6 (C-4), 72.7 (Ph*C*H$_2$), 72.7 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 71.6 (C-5), 69.8 (C-2′), 68.9 (C-6′), 67.8 (octyl O*C*H$_2$), 66.6 (C-6), 63.4 (C-5′), 32.0 (octyl *C*H$_2$), 29.6 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 22.8 (octyl *C*H$_2$), 14.2 (octyl *C*H$_3$). Anal. Calcd for $C_{55}H_{66}O_{11}$ (903.11): C, 73.15; H, 7.37. Found: C, 72.89; H, 7.40. ESIMS: *m*/*z* calcd for [$C_{55}H_{66}O_{11}$]Na$^+$: 925.4497. Found: 925.4498.

3.26. Octyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (34)

Prepared from disaccharide **32** (232 mg, 0.25 mmol) in CH_3OH (15 mL) and $NaOCH_3$ (81 mg) as described for **33** to give **34** (197 mg, 89%) as a pale-yellow oil: R_f 0.31 (4:1 hexane–EtOAc); $[\alpha]_D$ +33.8 (*c* 3.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.46–7.54 (m, 2H, ArH), 7.24–7.44 (m, 23H, ArH), 5.58 (s, 1H, benzylidene H), 5.17 (d, 1H, $J = 1.0$ Hz, H-1′), 4.99 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.79 (d, 1H, $J = 2.0$ Hz, H-1), 4.78 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.63–4.71 (m, 5H, PhCH_2), 4.51 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.25 (dd, 1H, $J = 10.3$, 4.3 Hz, H-6a′), 4.10 (dd, 1H, $J = 9.4$, 3.8 Hz, H-3′), 4.00 (dd, 1H, $J = 9.4$, 9.4 Hz, H-4′), 3.86–4.38 (m, 5H, H-3, H-4, H-6a, H-2′, H-5′), 3.74–3.86 (m, 3H, H-2, H-6b, H-6b′), 3.72 (m, 1H, H-5), 3.62 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 3.35 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 2.28 (br s, 1H, O*H*), 1.48–1.58 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.36 (m, 10H, octyl CH_2), 0.91 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.5 (Ar), 138.4 (Ar), 138.3 (Ar), 137.9 (Ar), 137.5 (Ar), 129.0 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.4 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 126.4 (Ar), 102.1 (benzylidene *C*H), 98.4 (C-1′), 98.0 (C-1), 80.4 (C-3), 79.6 (C-4′), 78.9 (C-2′), 75.2 (Ph*C*H$_2$), 75.0 (C-2), 74.6 (C-4), 73.3 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.9 (C-5), 68.9 (C-6′), 68.6 (C-3′), 67.7 (octyl O*C*H$_2$), 66.4 (C-6), 63.5 (C-5′), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for [$C_{55}H_{66}O_{11}$]Na$^+$: 925.4497. Found: 925.4499.

3.27. Octyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-methyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (35)

Disaccharide **33** (270 mg, 0.30 mmol) was dissolved in DMF (5 mL), and the solution was cooled in an ice bath. Then 60% NaH in mineral oil (18 mg, 0.45 mmol) was added, and the mixture was stirred for 10 min before the addition of CH_3I (60 μL, 0.90 mmol). The reaction mixture was stirred for 1 h and quenched by the addition of CH_3OH (5 mL). The mixture was diluted with EtOAc (50 mL), washed with water (3 × 15 mL), and dried ($MgSO_4$), filtered, and concentrated to a colorless oil. The crude product was purified by chromatography (4:1 hexane–EtOAc) to give **35** (251 mg, 91%) as a color-

less oil: R_f 0.32 (4:1 hexane–EtOAc); $[\alpha]_D$ +58.5 (*c* 1.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.46–7.51 (m, 2H, ArH), 7.24–7.42 (m, 22H, ArH), 7.16–7.20 (m, 1H, ArH), 5.61 (s, 1H, benzylidene H), 5.07 (d, 1H, $J = 1.8$ Hz, H-1′), 4.89 (d, 1H, $J = 10.5$ Hz, PhCH_2), 4.76–4.82 (m, 3H, H-1, PhCH_2), 4.71 (d, 2H, $J = 13.0$ Hz, PhCH_2), 4.67 (s, 2H, PhCH_2), 4.49 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.37–4.25 (m, 1H, H-6a′), 4.14 (dd, 1H, $J = 9.3$, 9.3 Hz, H-4′), 3.80–3.95 (m, 6H, H-3, H-4, H-6a, H-3′, H-5′, H-6b′), 3.80 (br s, 1H, H-2), 3.74 (dd, 1H, $J = 12.0$, 1.5 Hz, H-6b), 3.70 (dd, 1H, $J = 3.0$, 1.8 Hz, H-2′), 3.65–3.72 (m, 1H, H-5), 3.59 (dt, 1H, $J = 9.5$, 6.8 Hz, octyl OCH_2), 3.47 (s, 3H, OCH_3), 3.33 (dt, 1H, $J = 9.5$, 6.8 Hz, octyl OCH_2), 1.45–1.55 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.36 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.7 (Ar), 138.7 (Ar), 138.6 (Ar), 138.5 (Ar), 138.0 (Ar), 128.9 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.3 (Ar), 101.6 (benzylidene *C*H), 99.2 (C-1′), 98.1 (C-1), 80.5 (C-3), 79.4 (C-2′), 79.3 (C-4′), 75.5 (C-2/C-3′), 75.3 (C-2/C-3′), 75.3 (Ph*C*H$_2$), 74.7 (C-4), 73.1 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.4 (Ph*C*H$_2$), 71.9 (C-5), 69.0 (C-6′), 67.9 (octyl O*C*H$_2$), 66.5 (C-6), 64.3 (C-5′), 59.9 (O*C*H$_3$), 32.0 (octyl *C*H$_2$), 29.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 22.8 (octyl *C*H$_2$), 14.2 (octyl *C*H$_3$). Anal. Calcd for $C_{56}H_{68}O_{11}$ (917.13): C, 73.34; H, 7.47. Found: C, 73.04; H, 7.44. ESIMS: *m*/*z* calcd for $C_{56}H_{68}O_{11}$: 939.4654. Found: 939.4656.

3.28. Octyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-methyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (36)

Prepared from disaccharide **34** (197 mg, 0.22 mmol), 60% NaH in mineral oil (13 mg, 0.33 mmol), and CH_3I (42 μL, 0.66 mmol) in DMF (5 mL) as described for **35** to give **36** (154 mg, 76%) as a colorless oil: R_f 0.38 (6:1 hexane–EtOAc); $[\alpha]_D$ +35.6 (*c* 4.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.46–7.52 (m, 2H, $J = 7.8$, 1.8 Hz, ArH), 7.24–7.42 (m, 23H, ArH), 5.62 (s, 1H, benzylidene H), 5.07 (d, 1H, $J = 2.0$ Hz, H-1′), 5.00 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.81 (d, 1H, $J = 1.5$ Hz, H-1), 4.75 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.72 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.63–4.71 (m, 5H, PhCH_2), 4.24 (dd, 1H, $J = 10.0$, 4.5 Hz, H-6a′), 4.16 (dd, 1H, $J = 9.5$, 9.5 Hz, H-4′), 3.90–4.00 (m, 5H, H-3, H-4, H-6a, H-2′, H-5′), 3.85 (dd, 1H, $J = 10.0$, 10.0 Hz, H-6b′), 3.80 (dd, 1H, $J = 2.0$, 1.8 Hz, H-2), 3.70–3.78 (m, 3H, H-5, H-6b, H-3′), 3.63 (dt, 1H, $J = 10.0$, 6.8 Hz, octyl OCH_2), 3.44 (s, 3H, OCH_3), 3.37 (dt, 1H, $J = 10.0$, 6.8 Hz, octyl OCH_2), 1.49–1.58 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.36 (m, 10H, octyl CH_2), 0.91 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.5 (Ar), 138.4 (Ar), 138.3 (Ar), 137.8 (Ar), 128.8 (Ar), 128.4 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 126.3 (Ar), 101.7 (benzylidene *C*H), 99.3 (C-1′), 97.9 (C-1), 80.4 (C-3), 79.0 (C-4′), 77.9 (C-3′), 76.1 (C-4), 75.1 (Ph*C*H$_2$), 75.0 (C-2′), 74.7 (C-2), 73.3 (Ph*C*H$_2$), 72.8 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.6 (C-5), 68.9 (C-6′), 67.8 (octyl O*C*H$_2$), 66.5 (C-6), 64.2 (C-5′), 58.5 (O*C*H$_3$), 31.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{56}H_{68}O_{11}]Na^+$: 939.4654. Found: 939.4657.

3.29. Octyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(methylthio)thiocarbonyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (37)

Disaccharide **33** (293 mg, 0.32 mmol) was dissolved in THF (20 mL), and then 60% NaH in mineral oil (38 mg, 0.96 mmol) and imidazole (10 mg) were added. The mixture was stirred for 1 h before the addition of carbon disulfide (0.19 mL, 3.2 mmol), and stirring was continued for 1 h. CH_3I (0.10 mL, 1.6 mmol) was added, and the mixture was stirred overnight. The solvent was evaporated, and the crude product was dissolved in CH_2Cl_2 (25 mL), washed with water (10 mL), dried ($MgSO_4$), and concentrated to a yellow oil. The crude product was then purified by chromatography (6:1 hexane–EtOAc) to give **37** (310 mg, 96%) as a yellow oil: R_f 0.41 (6:1 hexane–EtOAc); $[\alpha]_D$ +24.6 (*c* 2.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.47–7.52 (m, 2H, ArH), 7.18–7.42 (m, 23H, ArH), 6.26 (dd, 1H, $J = 2.8$, 1.5 Hz, H-2′), 5.65 (s, 1H, benzylidene H), 5.07 (d, 1H, $J = 1.5$ Hz, H-1′), 4.93 (d, 1H, $J = 11.3$ Hz, PhCH_2), 4.81 (d, 1H, $J = 2.0$ Hz, H-1), 4.74 (s, 2H, PhCH_2), 4.67 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.63 (s, 2H, PhCH_2), 4.62 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.55 (d, 1H, $J = 11.3$ Hz, PhCH_2), 4.26 (dd, 1H, $J = 9.8$, 4.8 Hz, H-6a′), 4.08–4.14 (m, 2H, H-3′, H-4′), 3.94–4.00 (m, 1H, H-5′), 3.91 (dd, 1H, $J = 9.0$, 3.0 Hz, H-3), 3.82–3.88 (m, 3H, H-4, H-6a, H-6b′), 3.76–3.81 (m, 2H, H-2, H-6b), 3.72 (ddd, 1H, $J = 9.5$, 6.0, 1.5 Hz, H-5), 3.60 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 3.34 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 2.61 (s, 3H, SCH_3), 1.45–1.55 (m, 2H, octyl OCH$_2$CH_2), 1.21–1.35 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 215.7 (*C*=S), 138.5 (Ar), 138.4 (Ar), 138.3 (Ar), 137.9 (Ar), 137.6 (Ar), 128.9 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.7 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.6 (Ar), 126.2 (Ar), 101.7 (benzylidene *C*H), 97.6 (C-1), 97.6 (C-1′), 80.3 (C-3), 78.8 (C-4′), 77.9 (C-2′), 75.1 (Ph*C*H$_2$), 74.7 (C-2/C-4), 74.8 (C-2/C-4), 73.9 (C-3′), 72.7 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 72.0 (Ph*C*H$_2$), 71.0 (C-5), 68.8 (C-6′),

67.7 (octyl O*C*H$_2$), 66.9 (C-6), 63.9 (C-5′), 31.9 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 19.2 (S*C*H$_3$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for [$C_{57}H_{68}O_{11}S_2$]-Na$^+$: 1015.4095. Found: 1015.4096.

3.30. Octyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-*arabino*-hexopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (38)

Xanthate **37** (310 mg, 0.31 mmol) was dissolved in toluene (15 mL), and tri-*n*-butylstannane (1.3 mL, 0.47 mmol) and AIBN (51 mg, 0.31 mmol) were added. The mixture was heated at reflux for 3 h, and the solvent was evaporated. The crude product was purified by chromatography (4:1 hexane–EtOAc) to give **38** (113 mg, 41%) as a colorless oil: R_f 0.42 (4:1 hexane–EtOAc); $[\alpha]_D$ +50.8 (*c* 3.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.46–7.54 (m, 2H, ArH), 7.20–7.42 (m, 23H, ArH), 5.62 (s, 1H, benzylidene H), 5.08 (br d, 1H, $J = 3.5$ Hz, H-1′), 4.95 (d, 1H, $J = 11.0$ Hz, PhC*H*$_2$), 4.83 (d, 1H, $J = 1.5$ Hz, H-1), 4.80 (d, 1H, $J = 12.0$ Hz, PhC*H*$_2$), 4.78 (d, 1H, $J = 12.5$ Hz, PhC*H*$_2$), 4.70 (d, 1H, $J = 12.5$ Hz, PhC*H*$_2$), 4.63–4.68 (m, 3H, PhC*H*$_2$), 4.60 (d, 1H, $J = 11.0$ Hz, PhC*H*$_2$), 4.23 (dd, 1H, $J = 10.0$, 5.0 Hz, H-6a′), 4.03 (ddd, 1H, $J = 11.0$, 11.0, 5.0 Hz, H-3′), 3.84–3.98 (m, 4H, H-3, H-4, H-6a, H-5′), 3.66–3.82 (m, 5H, H-2, H-5, H-6b, H-4′, H-6b′), 3.63 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OC*H*$_2$), 3.36 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OC*H*$_2$), 2.35 (dd, 1H, $J = 13.3$, 5.0 Hz, H-2′$_{eq}$), 1.78 (ddd, 1H, $J = 13.3$, 11.0, 3.5 Hz, H-2′$_{ax}$), 1.47–1.56 (m, 2H, octyl OCH$_2$C*H*$_2$), 1.22–1.35 (m, 10H, octyl C*H*$_2$), 0.90 (t, 3H, $J = 7.3$ Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.7 (Ar), 138.5 (Ar), 138.5 (Ar), 138.4 (Ar), 137.8 (Ar), 128.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.7 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.5 (Ar), 127.5 (Ar), 126.1 (Ar), 101.4 (benzylidene *C*H), 98.1 (C-1′), 97.7 (C-1), 84.0 (C-4′), 80.4 (C-3), 75.2 (Ph*C*H$_2$), 75.0 (C-2), 74.9 (C-4), 72.8 (C-3′), 72.8 (Ph*C*H$_2$), 72.7 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 71.5 (C-5), 69.2 (C-6′), 67.7 (octyl O*C*H$_2$), 66.1 (C-6), 63.1 (C-5′), 36.4 (C-2′), 31.9 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{55}H_{66}O_{10}$ (887.11): C, 74.47; H, 7.50. Found: C, 74.10; H, 7.89. ESIMS: *m*/*z* calcd for [$C_{55}H_{66}O_{10}$]Na$^+$: 909.4548. Found: 909.4551.

3.31. Octyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(methylthio)thiocarbonyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (39)

Prepared from disaccharide **34** (219 mg, 0.24 mmol), 60% NaH in mineral oil (29 mg, 0.72 mmol), imidazole (10 mg), carbon disulfide (0.15 mL, 2.4 mmol), and CH_3I (0.15 mL, 2.4 mmol) in THF (13 mL) as described for **37** to give **39** (227 mg, 94%) as a colorless oil: R_f 0.31 (6:1 hexane–EtOAc); $[\alpha]_D$ +5.2 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.44–7.50 (m, 2H, ArH), 7.21–7.40 (m, 23H, ArH), 6.15 (dd, 1H, $J = 10.0$, 3.5 Hz, H-3′), 5.61 (s, 1H, benzylidene H), 5.14 (d, 1H, $J = 1.5$ Hz, H-1′), 4.99 (d, 1H, $J = 11.0$ Hz, PhC*H*$_2$), 4.77 (d, 1H, $J = 1.5$ Hz, H-1), 4.76 (d, 1H, $J = 12.0$ Hz, PhC*H*$_2$), 4.64–4.70 (m, 4H, PhC*H*$_2$), 4.51 (d, 1H, $J = 11.5$ Hz, PhC*H*$_2$), 4.48 (d, 1H, $J = 12.0$ Hz, PhC*H*$_2$), 4.40 (dd, 1H, $J = 10.0$, 10.0 Hz, H-4′), 4.36 (dd, 1H, $J = 3.5$, 1.5 Hz, H-2′), 4.29 (dd, 1H, $J = 10.5$, 5.0 Hz, H-6a′), 4.09 (ddd, 1H, $J = 10.0$, 10.0, 5.0 Hz, H-5′), 3.99 (dd, 1H, $J = 9.5$, 9.5 Hz, H-6a), 3.85–4.02 (m, 3H, H-3, H-4, H-6b′), 3.72–3.81 (m, 3H, H-2, H-5, H-6b), 3.65 (dt, 1H, $J = 9.8$, 6.5 Hz, octyl OC*H*$_2$), 3.35 (dt, 1H, $J = 9.8$, 6.5 Hz, octyl OC*H*$_2$), 2.55 (s, 3H, SC*H*$_3$), 1.46–1.58 (m, 2H, octyl OCH$_2$C*H*$_2$), 1.22–1.36 (m, 10H, octyl C*H*$_2$), 0.90 (t, 3H, $J = 7.0$ Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 215.0 (*C*=S), 138.6 (Ar), 138.5 (Ar), 138.4 (Ar), 137.9 (Ar), 137.4 (Ar), 128.9 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 127.9 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 126.2 (Ar), 101.6 (benzylidene *C*H), 99.2 (C-1′), 97.9 (C-1), 80.5 (C-3), 79.1 (C-3′), 76.3 (C-4′), 75.8 (C-2′), 75.3 (Ph*C*H$_2$), 75.1 (C-2), 74.9 (C-4), 73.6 (Ph*C*H$_2$), 73.0 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 72.0 (C-5), 68.9 (C-6′), 67.6 (octyl O*C*H$_2$), 66.4 (C-6), 64.1 (C-5′), 31.9 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 19.1 (S*C*H$_3$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{57}H_{68}O_{11}S_2$ (993.27): C, 68.92; H, 6.90; S, 6.46. Found: C, 68.41; H, 6.86; S, 6.18. ESIMS: *m*/*z* calcd for [$C_{57}H_{68}O_{11}S_2$]Na$^+$: 1015.4095. Found: 1015.4094.

3.32. Octyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-*arabino*-hexopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (40)

Xanthate **39** (206 mg, 0.21 mmol) was dissolved in toluene (10 mL) and added dropwise to a solution of tri-*n*-butylstannane (85 μL, 0.32 mmol) and AIBN (10 mg, 0.063 mmol) in toluene (15 mL) at reflux, over a period of 1 h. The mixture was heated under reflux for 1 h, tri-*n*-butylstannane (85 μL, 0.32 mmol) and AIBN (10 mg, 0.063 mmol) in toluene (5 mL) were added, and the reaction mixture was continually heated under reflux for 1 h. The solvent was evaporated, and the crude product was purified by chromatography (6:1 hexane–EtOAc) to give **40** (69 mg, 37%) as a colorless oil: R_f 0.41 (6:1 hexane–EtOAc); $[\alpha]_D$ +52.1 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.45–7.50 (m, 2H, ArH), 7.23–7.39 (m, 23H, AHr), 5.57 (s, 1H, benzylidene H), 4.99 (br s, 1H, H-1′), 4.98 (d, 1H, $J = 11.0$ Hz, PhC*H*$_2$), 4.79 (d, 1H, $J = 1.5$ Hz, H-1), 4.76 (d, 1H, $J = 12.0$ Hz, PhC*H*$_2$), 4.64–4.69 (m, 4H, PhC*H*$_2$), 4.52 (s, 2H,

PhCH_2), 4.21 (dd, 1H, $J = 5.3$, 4.8 Hz, H-6a′), 3.92–4.04 (m, 5H, H-3, H-4, H-6a, H-4′, H-5′), 3.76–3.83 (m, 4H, H-2, H-6b, H-2′, H-6b′), 3.70–3.75 (m, 1H, H-5), 3.62 (dt, 1H, $J = 9.5$, 6.8 Hz, octyl OCH_2), 3.35 (dt, 1H, $J = 9.5$, 6.8 Hz, octyl OCH_2), 2.19 (ddd, 1H, $J = 12.5$, 3.5, 3.5 Hz, H-3′$_{eq}$), 2.01 (ddd, 1H, $J = 12.5$, 12.5, 3.0 Hz, H-3′$_{ax}$), 1.47–1.56 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.35 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.5 (Ar), 138.5 (Ar), 138.4 (Ar), 138.2 (Ar), 137.8 (Ar), 128.9 (Ar), 128.4 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.6 (Ar), 126.2 (Ar), 102.0 (benzylidene *C*H), 97.9 (C-1′), 97.9 (C-1), 80.4 (C-3), 75.5 (C-2/C-2′), 75.2 (Ph*C*H$_2$), 75.0 (C-2/C-2′), 74.7 (C-4/C-4′), 74.3 (C-4/C-4′), 72.8 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.8 (C-5), 71.3 (Ph*C*H$_2$), 69.4 (C-6′), 67.7 (octyl O*C*H$_2$), 66.4 (C-6), 65.2 (C-5′), 31.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (C-3′), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{55}H_{66}O_{10}$ (887.11): C, 74.47; H, 7.50. Found: C, 74.39; H, 7.55. ESIMS: *m*/*z* calcd for $[C_{55}H_{66}O_{10}]Na^+$: 909.4548. Found: 909.4551.

3.33. Octyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (41)

Prepared from disaccharide **33** (1.57 g, 1.6 mmol), 60% NaH in mineral oil (0.10 g, 2.6 mmol), and BnBr (0.32 mL, 2.6 mmol) in DMF (15 mL) as described for **23** to give **41** (1.62 g, 94%) as a colorless oil: R_f 0.28 (9:1 hexane–EtOAc); $[\alpha]_D$ +35.6 (*c* 2.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.48–7.52 (m, 2H, ArH), 7.18–7.40 (m, 28H, ArH), 5.64 (s, 1H, benzylidene H), 5.09 (br s, 1H, H-1′), 4.90 (d, 1H, $J = 11.4$ Hz, PhCH_2), 4.80 (d, 1H, $J = 1.8$ Hz, H-1), 4.75 (d, 1H, $J = 12.6$ Hz, PhCH_2), 4.74 (d, 1H, $J = 12.6$ Hz, PhCH_2), 4.63–4.72 (m, 5H, PhCH_2), 4.63 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.52 (d, 1H, $J = 10.8$ Hz, PhCH_2), 4.20–4.27 (m, 2H, H-4′, H-6a′), 3.90–3.98 (m, 2H, H-2′, H-3′), 3.84–3.95 (m, 5H, H-3, H-4, H-6a, H-5′, H-6b′), 3.79 (dd, 1H, $J = 1.8$, 1.8 Hz, H-2), 3.73 (dd, 1H, $J = 11.7$, 1.5 Hz, H-6b), 3.66–3.71 (m, 1H, H-5), 3.59 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 3.34 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 1.46–1.54 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.34 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.6 (Ar), 138.5 (Ar), 138.5 (Ar), 138.4 (Ar), 138.3 (Ar), 137.9 (Ar), 128.7 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 101.5 (benzylidene *C*H), 99.5 (C-1′), 97.8 (C-1), 80.4 (C-3), 79.1 (C-4′), 76.9 (C-3′), 75.8 (C-2′), 75.2 (Ph*C*H$_2$), 75.0 (C-2), 74.6 (C-4), 73.4 (Ph*C*H$_2$), 72.8 (Ph*C*H$_2$), 72.6 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.7 (C-5), 68.9 (C-6′), 67.7 (octyl O*C*H$_2$), 66.4 (C-6), 64.3 (C-5′), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{62}H_{72}O_{11}$ (993.23): C, 74.97; H, 7.31. Found: C, 74.63; H, 7.54. ESIMS: *m*/*z* calcd for $[C_{62}H_{72}O_{11}]Na^+$: 1015.4967. Found: 1015.4963.

3.34. Octyl 2,3,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (42)

A solution of disaccharide **41** (450 mg, 0.45 mmol) and powdered 4 Å molecular sieves (1.8 g) in CH_2Cl_2 (6 mL) was stirred at room temperature for 1 h. The solution was cooled to −78 °C, followed by the addition of Et_3SiH (0.22 mL, 1.4 mmol) and TfOH (0.14 mL, 1.5 mmol). After 1 h the reaction was quenched with Et_3N and CH_3OH, diluted with CH_2Cl_2, washed with satd aq $NaHCO_3$, dried ($MgSO_4$), and concentrated. The crude product was purified by chromatography (4:1 hexane–EtOAc) to give **42** (276 mg, 61%) and **43** (17 mg, 4%) as colorless oils: R_f 0.33 (4:1 hexane–EtOAc); $[\alpha]_D$ +7.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.18–7.42 (m, 30H, ArH), 5.16 (d, 1H, $J = 1.5$ Hz, H-1′), 4.91 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.81 (d, 1H, $J = 1.8$ Hz, H-1), 4.75 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.64–4.71 (m, 4H, PhCH_2), 4.61 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.60 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.55 (d, 2H, $J = 11.5$ Hz, PhCH_2), 4.51 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.40 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.07 (ddd, 1H, $J = 10.0$, 10.0, 1.3 Hz, H-4′), 3.91–4.00 (m, 4H, H-3, H-4, H-6a, H-2′), 3.81 (dd, 1H, $J = 3.0$, 1.8 Hz, H-2), 3.67–3.81 (m, 6H, H-5, H-6b, H-3′, H-5′, H-6a′, H-6b′), 3.60 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 3.34 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 2.43 (d, 1H, $J = 1.3$ Hz, O*H*), 1.47–1.56 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.36 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.5 (Ar), 138.5 (Ar), 138.4 (Ar), 138.3 (Ar), 138.1 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.4 (Ar), 127.4 (Ar), 98.4 (C-1′), 97.9 (C-1), 80.4 (C-3), 78.7 (C-3′), 75.2 (C-2), 75.1 (Ph*C*H$_2$), 75.1 (C-2′), 74.2 (C-4), 73.5 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.4 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.7 (C-5), 71.5 (C-5′), 71.1 (Ph*C*H$_2$), 70.4 (C-6′), 67.7 (C-4′), 67.7 (octyl O*C*H$_2$), 66.2 (C-6), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{62}H_{74}O_{11}]Na^+$: 1017.5123. Found: 1017.5128.

3.35. Octyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (43)

Prepared from a solution of $AlCl_3$ (62 mg, 0.46 mmol) and $LiAlH_4$ (0.46 mmol) in ether (3.5 mL) and disaccharide

41 (382 mg, 0.39 mmol) in 1:1 CH_2Cl_2–ether (15 mL) as described for **27** (except that the reaction mixture was stirred overnight), to give **43** (324 mg, 85%) and **42** (11 mg, 3%) as colorless oils: R_f 0.24 (3:1 hexane–EtOAc); $[\alpha]_D$ +33.5 (*c* 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.18–7.40 (m, 30H, ArH), 5.09 (br s, 1H, H-1′), 4.94 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.91 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.80 (d, 1H, $J = 1.5$ Hz, H-1), 4.47–4.77 (m, 10H, PhCH_2), 3.87–4.00 (m, 6H, H-3, H-4, H-6a, H-2′, H-3′, H-4′), 3.64–3.81 (m, 6H, H-2, H-5, H-6b, H-5′, H-6a′, H-6b′), 3.59 (dt, 1H, $J = 9.7$, 6.4 Hz, octyl OCH_2), 3.33 (dt, 1H, $J = 9.7$, 6.4 Hz, octyl OCH_2), 1.78 (br s, 1H, O*H*), 1.45–1.55 (m, 2H, octyl OCH$_2$CH_2), 1.21–1.35 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.6 (Ar), 138.6 (Ar), 138.5 (Ar), 138.5 (Ar), 138.3 (Ar), 128.8 (Ar), 128.8 (Ar), 128.6 (Ar), 128.6 (Ar), 128.5 (Ar), 128.5 (Ar), 128.5 (Ar), 128.3 (Ar), 128.3 (Ar), 128.3 (Ar), 127.9 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.5 (Ar), 127.5 (Ar), 127.5 (Ar), 127.5 (Ar), 98.3 (C-1′), 97.8 (C-1), 80.4 (C-3), 79.4 (C-3′), 79.4 (C-4′), 75.1 (C-2), 75.1 (Ph*C*H$_2$), 74.7 (C-2′), 74.6 (C-4), 72.8 (Ph*C*H$_2$), 72.7 (Ph*C*H$_2$), 72.7 (Ph*C*H$_2$), 72.2 (C-5′), 72.1 (Ph*C*H$_2$), 71.6 (Ph*C*H$_2$), 71.6 (C-5), 67.7 (octyl O*C*H$_2$), 66.1 (C-6), 62.3 (C-6′), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.6 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{62}H_{74}O_{11}]Na^+$: 1017.5123. Found: 1017.5136.

3.36. Octyl 2,3,6-tri-*O*-benzyl-4-*O*-methyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (44)

Prepared from disaccharide **42** (134 mg, 0.14 mmol), 60% NaH in mineral oil (8.1 mg, 0.20 mmol), and CH_3I (13 μL, 0.20 mmol) in DMF (3 mL) as described for **35** to give **44** (105 mg, 77%) as a colorless oil: R_f 0.22 (4:1 hexane–EtOAc); $[\alpha]_D$ +30.3 (*c* 1.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ_H 7.19–7.40 (m, 30H, ArH), 5.12 (d, 1H, $J = 2.1$ Hz, H-1′), 4.89 (d, 1H, $J = 10.8$ Hz, PhCH_2), 4.78 (d, 1H, $J = 2.1$ Hz, H-1), 4.73 (d, 1H, $J = 12.6$ Hz, PhCH_2), 4.69 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.67 (d, 1H, $J = 12.6$ Hz, PhCH_2), 4.65 (s, 2H, PhCH_2), 4.65 (s, 2H, PhCH_2), 4.57 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.54 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.52 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.51 (d, 1H, $J = 10.8$ Hz, PhCH_2), 3.90–3.96 (m, 3H, H-3, H-4, H-6a), 3.90 (dd, 1H, $J = 3.6$, 2.1 Hz, H-2′), 3.81 (dd, 1H, $J = 7.8$, 3.6 Hz, H-3′), 3.78 (dd, 1H, $J = 2.1$, 2.1 Hz, H-2), 3.64–3.76 (m, 6H, H-5, H-6b, H-4′, H-5′, H-6a′, H-6b′), 3.58 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 3.49 (s, 3H, OCH_3), 3.32 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 1.46–1.54 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.34 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.8 (Ar), 138.6 (Ar), 138.6 (Ar), 138.5 (Ar), 138.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.3 (Ar), 128.2 (Ar), 128.2 (Ar), 127.9 (Ar), 127.8 (Ar), 127.6 (Ar), 127.6 (Ar), 127.6 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 127.3 (Ar), 98.1 (C-1′), 97.8 (C-1), 80.4 (C-3), 79.4 (C-3′), 76.5 (C-4′), 75.1 (C-2), 75.1 (C-2′), 75.1 (Ph*C*H$_2$), 74.7 (C-4), 73.3 (Ph*C*H$_2$), 72.8 (Ph*C*H$_2$), 72.4 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.9 (C-5′), 71.7 (C-5), 71.6 (Ph*C*H$_2$), 69.4 (C-6′), 67.6 (octyl O*C*H$_2$), 66.1 (C-6), 60.6 (O*C*H$_3$), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{63}H_{76}O_{11}]Na^+$: 1031.5280. Found: 1031.5280.

3.37. Octyl 2,3,6-tri-*O*-benzyl-4-*O*-(methylthio)thiocarbonyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (45)

Prepared from disaccharide **42** (148 mg, 0.15 mmol), 60% NaH in mineral oil (18 mg, 0.45 mmol), carbon disulfide (0.092 mL, 1.5 mmol), and CH_3I (0.094 mL, 1.5 mmol) in THF (9 mL) as described for **37** to give **45** (154 mg, 96%) as a light-yellow oil: R_f 0.37 (6:1 hexane–EtOAc); $[\alpha]_D$ +34.1 (*c* 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.16–7.42 (m, 30H, ArH), 6.36 (dd, 1H, $J = 9.5$, 9.5 Hz, H-4′), 5.14 (br s, 1H, H-1′), 4.88 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.81 (d, 1H, $J = 1.9$ Hz, H-1), 4.63–4.77 (m, 6H, PhCH_2), 4.53 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.49 (s, 2H, PhCH_2), 4.45 (d, 1H, $J = 11.5$ Hz, PhCH_2), 4.42 (d, 1H, $J = 12.0$ Hz, PhCH_2), 3.91–4.01 (m, 6H, H-3, H-4, H-6a, H-2′, H-3′, H-5′), 3.81 (dd, 1H, $J = 1.9$, 1.9 Hz, H-2), 3.72 (dd, 1H, $J = 11.8$, 1.3 Hz, H-6b), 3.66–3.71 (m, 1H, H-5), 3.54–3.63 (m, 3H, H-6a′, H-6b′, octyl OCH_2), 3.34 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 2.48 (s, 3H, SCH_3), 1.48–1.56 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.36 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 215.4 (*C*═S), 138.6 (Ar), 138.6 (Ar), 138.5 (Ar), 138.3 (Ar), 138.3 (Ar), 138.0 (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.6 (Ar), 127.5 (Ar), 127.5 (Ar), 127.3 (Ar), 127.3 (Ar), 98.7 (C-1′), 97.8 (C-1), 80.4 (C-3), 77.7 (C-4′), 76.4 (C-3′), 75.2 (C-2), 75.1 (Ph*C*H$_2$), 75.0 (C-2′), 74.5 (C-4), 73.4 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.8 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.6 (C-5), 71.3 (Ph*C*H$_2$), 70.5 (C-5′), 69.7 (C-6′), 67.7 (octyl O*C*H$_2$), 66.5 (C-6), 31.9 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 19.2 (S*C*H$_3$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{64}H_{76}O_{11}S_2$ (1084.48): C, 70.82; H, 7.06; S, 5.91. Found: C, 71.04; H, 6.91; S, 5.93. ESIMS: *m*/*z* calcd for $[C_{64}H_{76}O_{11}S_2]Na^+$: 1107.4721. Found: 1107.4725.

3.38. Octyl 2,3,6-tri-*O*-benzyl-4-deoxy-α-D-*lyxo*-hexopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (46)

Prepared from xanthate **45** (129 mg, 0.12 mmol) in toluene (2 mL) and tri-*n*-butylstannane (50 μL, 0.18 mmol) and AIBN (6 mg, 0.037 mmol) as described for **40** to give **46** (76 mg, 64%) as a colorless oil: R_f 0.31 (6:1 hexane–EtOAc); $[\alpha]_D$ +20.8 (*c* 0.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.18–7.41 (m, 30H, ArH), 5.15 (d, 1H, $J = 1.2$ Hz, H-1′), 4.89 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.81 (d, 1H, $J = 1.8$ Hz, H-1), 4.75 (d, 1H, $J = 12.6$ Hz, PhCH_2), 4.74 (d, 1H, $J = 12.6$ Hz, PhCH_2), 4.70 (d, 1H, $J = 12.6$ Hz, PhCH_2), 4.70 (d, 1H, $J = 12.6$ Hz, PhCH_2), 4.69 (s, 2H, PhCH_2), 4.54 (s, 2H, PhCH_2), 4.49 (d, 2H, $J = 12.0$ Hz, PhCH_2), 4.45 (d, 1H, $J = 12.0$ Hz, PhCH_2), 3.91 (m, 4H, H-3, H-4, H-6a, H-5′), 3.84–3.91 (m, 2H, H-2′, H-3′), 3.80 (dd, 1H, $J = 2.4$, 1.8 Hz, H-2), 3.72 (dd, 1H, $J = 12.0$, 1.8 Hz, H-6b), 3.68–3.72 (m, 1H, H-5), 3.59 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 3.56 (dd, 1H, $J = 10.2$, 6.0 Hz, H-6a′), 3.45 (dd, 1H, $J = 10.2$, 4.2 Hz, H-6b′), 3.33 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 1.98 (ddd, 1H, $J = 12.0$, 12.0, 12.0 Hz, H-4′$_{ax}$), 1.73–1.78 (m, 1H, H-4′$_{eq}$), 1.47–1.55 (m, 2H, octyl OCH$_2$CH_2), 1.21–1.35 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 139.0 (Ar), 138.6 (Ar), 138.6 (Ar), 138.5 (Ar), 138.4 (Ar), 138.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.3 (Ar), 128.2 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.6 (Ar), 127.6 (Ar), 127.4 (Ar), 127.3 (Ar), 99.3 (C-1′), 97.8 (C-1), 80.4 (C-3), 75.1 (C-2), 75.0 (Ph*C*H$_2$), 74.8 (C-4), 73.6 (C-2′), 73.3 (Ph*C*H$_2$), 73.2 (C-3′), 73.0 (C-6′), 72.7 (Ph*C*H$_2$), 72.5 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.6 (C-5), 70.0 (Ph*C*H$_2$), 68.2 (C-5′), 67.6 (octyl O*C*H$_2$), 66.2 (C-6), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 29.2 (C-4′), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{62}H_{74}O_{10}]Na^+$: 1001.5174. Found: 1001.5174.

3.39. Octyl 2,3,4-tri-*O*-benzyl-6-*O*-methyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (47)

Prepared from disaccharide **43** (109 mg, 0.11 mmol) in DMF (3 mL) and 60% NaH in mineral oil (7.2 mg, 0.18 mmol) and CH_3I (12 μL, 0.18 mmol) as described for **35** to give **47** (107 mg, 96%) as a colorless oil: R_f 0.41 (4:1 hexane–EtOAc); $[\alpha]_D$ +31.1 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.18–7.40 (m, 30H, ArH), 5.15 (d, 1H, $J = 1.5$ Hz, H-1′), 4.94 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.90 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.79 (d, 1H, $J = 1.5$ Hz, H-1), 4.64–4.76 (m, 6H, PhCH_2), 4.59 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.57 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.90 (d, 2H, $J = 12.0$ Hz, PhCH_2), 3.89–3.99 (m, 6H, H-3, H-4, H-6a, H-2′, H-3′, H-4′), 3.66–3.81 (m, 4H, H-2, H-5, H-6b, H-5′), 3.51–3.62 (m, 3H, H-6a′, H-6b′, octyl OCH_2), 3.30–3.37 (m, 4H, OCH_3, octyl OCH_2), 1.46–1.55 (m, 2H, octyl OCH$_2$CH_2), 1.21–1.35 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.9 (Ar), 138.7 (Ar), 138.6 (Ar), 138.5 (Ar), 138.5 (Ar), 138.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.3 (Ar), 128.3 (Ar), 128.2 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 127.3 (Ar), 98.3 (C-1′), 97.8 (C-1), 80.5 (C-3), 79.5 (C-3′), 75.1 (C-2), 75.1 (Ph*C*H$_2$), 75.0 (Ph*C*H$_2$), 75.0 (C-2′), 74.9 (C-4), 74.6 (C-4′), 72.8 (Ph*C*H$_2$), 72.4 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 71.7 (C-6′), 71.6 (C-5), 71.5 (C-5′), 71.5 (Ph*C*H$_2$), 67.6 (octyl O*C*H$_2$), 66.1 (C-6), 59.1 (O*C*H$_3$), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{63}H_{76}O_{11}$ (1008.54): C, 74.97; H, 7.59. Found: C, 74.30; H, 7.71. ESIMS: *m*/*z* calcd for $[C_{63}H_{76}O_{11}]Na^+$: 1031.5280. Found: 1031.5282.

3.40. Octyl 2,3,4-tri-*O*-benzyl-6-*O*-*p*-tolylsulfonyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (48)

Disaccharide **43** (241 mg, 0.24 mmol) was dissolved in pyridine (1 mL) and the solution was cooled in an ice bath followed by the addition of *p*-toluenesulfonyl chloride (137 mg, 0.72 mmol). The reaction mixture was stirred overnight. The mixture was diluted with CH_2Cl_2 (25 mL), washed with 1 M HCl (3 × 10 mL), satd aq $NaHCO_3$ (10 mL), water (10 mL), dried ($MgSO_4$), and concentrated to a colorless oil. The crude product was then purified by chromatography (4:1 hexane–EtOAc) to give **48** (251 mg, 90%) as a colorless oil: R_f 0.37 (4:1 hexane–EtOAc); $[\alpha]_D$ +27.9 (*c* 0.9, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.74–7.78 (m, 2H, ArH), 7.14–7.39 (m, 32H, ArH), 5.04 (d, 1H, $J = 1.8$ Hz, H-1′), 4.88 (d, 1H, $J = 10.8$ Hz, PhCH_2), 4.87 (d, 1H, $J = 10.8$ Hz, PhCH_2), 4.78 (d, 1H, $J = 1.8$ Hz, H-1), 4.73 (d, 1H, $J = 12.6$ Hz, PhCH_2), 4.67 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.59–4.66 (m, 4H, PhCH_2), 4.54 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.46 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.45 (d, 1H, $J = 11.4$ Hz, PhCH_2), 4.42 (d, 1H, $J = 10.8$ Hz, PhCH_2), 4.15–4.21 (m, 2H, H-6a′, H-6b′), 3.81–3.93 (m, 6H, H-3, H-4, H-6a, H-2′, H-3′, H-4′), 3.78 (dd, 1H, $J = 2.4$, 1.8 Hz, H-2), 3.72–3.80 (m, 1H, H-5), 3.61–3.67 (m, 2H, H-5′, H-6b), 3.57 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 3.31 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 2.37 (s, 3H, SPhCH_3), 1.45–1.53 (m, 2H, octyl OCH$_2$CH_2), 1.21–1.34 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 6.9$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 144.4 (Ar), 138.6 (Ar), 138.5 (Ar), 138.5 (Ar), 138.3 (Ar), 138.1 (Ar), 129.6 (Ar),

128.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.5 (Ar), 127.4 (Ar), 98.0 (C-1′), 97.8 (C-1), 80.4 (C-3), 79.2 (C-3′), 75.1 (C-2), 75.0 (PhCH$_2$), 74.9 (PhCH$_2$), 74.7 (C-4/C-2′/C-4′), 74.6 (C-4/C-2′/C-4′), 73.9 (C-4/C-2′/C-4′), 72.9 (PhCH$_2$), 72.4 (PhCH$_2$), 72.2 (PhCH$_2$), 71.6 (C-5), 71.3 (PhCH$_2$), 70.0 (C-5′), 68.9 (C-6′), 67.7 (octyl OCH$_2$), 66.2 (C-6), 59.1 (OCH$_3$), 31.8 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.2 (octyl CH$_2$), 26.2 (octyl CH$_2$), 22.7 (octyl CH$_2$), 21.6 (SPhCH$_3$), 14.1 (octyl CH$_3$). Anal. Calcd for $C_{69}H_{80}O_{13}S$ (1149.43): C, 72.10; H, 7.02; S, 2.79. Found: C, 71.96; H, 6.93; S, 2.66. ESIMS: *m*/*z* calcd for $[C_{69}H_{80}O_{13}S]Na^+$: 1171.5212. Found: 1171.5211.

3.41. Octyl 2,3,4-tri-*O*-benzyl-6-deoxy-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (49)

Disaccharide **48** (130 mg, 0.11 mmol) was dissolved in ether (5 mL), and 1 M $LiAlH_4$ (0.22 mL, 0.22 mmol) was added. The mixture was stirred overnight and quenched with EtOAc, followed by water. The mixture was diluted with EtOAc (25 mL), washed with water (3 × 10 mL), and dried ($MgSO_4$), filtered, and concentrated to a colorless oil. The crude product was purified by chromatography (9:1 hexane–EtOAc) to give **49** (69 mg, 62%) and **43** (37 mg, 33%) both as colorless oils. Compound **49**: R_f 0.44 (6:1 hexane–EtOAc); $[\alpha]_D$ +25.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 7.18–7.40 (m, 30H, ArH), 5.03 (d, 1H, $J = 1.8$ Hz, H-1′), 4.94 (d, 1H, $J = 11.8$ Hz, PhCH$_2$), 4.90 (d, 1H, $J = 10.8$ Hz, PhCH$_2$), 4.79 (d, 1H, $J = 1.8$ Hz, H-1), 4.73 (d, 1H, $J = 11.7$ Hz, PhCH$_2$), 4.68 (s, 2H, PhCH$_2$), 4.68 (d, 1H, $J = 12.0$ Hz, PhCH$_2$), 4.65 (s, 2H, PhCH$_2$), 4.61 (d, 1H, $J = 11.7$ Hz, PhCH$_2$), 4.57 (d, 1H, $J = 12.0$ Hz, PhCH$_2$), 4.51 (d, 1H, $J = 11.8$ Hz, PhCH$_2$), 4.51 (d, 1H, $J = 10.8$ Hz, PhCH$_2$), 3.89–3.97 (m, 4H, H-3, H-4, H-6a, H-2′), 3.87 (dd, 1H, $J = 9.0$, 3.0 Hz, H-3′), 3.78 (dd, 1H, $J = 2.7$, 1.8 Hz, H-2), 3.70–3.76 (m, 1H, H-5′), 3.66–3.70 (m, 2H, H-5, H-6b), 3.55–3.62 (m, 2H, H-4′, octyl OCH$_2$), 3.32 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH$_2$), 1.46–1.53 (m, 2H, octyl OCH$_2$CH$_2$), 1.21–1.33 (m, 13H, H-6′, octyl CH$_2$), 0.88 (t, 3H, $J = 6.9$ Hz, octyl CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.8 (Ar), 138.7 (Ar), 138.5 (Ar), 138.5 (Ar), 138.5 (Ar), 138.4 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 98.1 (C-1′), 97.8 (C-1), 80.5 (C-3), 80.5 (C-4′), 79.5 (C-3′), 75.3 (C-2′), 75.2 (PhCH$_2$), 75.1 (C-2), 75.1 (PhCH$_2$), 74.7 (C-4), 72.8 (PhCH$_2$), 72.6 (PhCH$_2$), 72.2 (PhCH$_2$), 71.6 (C-5), 71.5 (PhCH$_2$), 68.1 (C-5′), 67.6 (octyl OCH$_2$), 66.0 (C-6), 31.8 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.2 (octyl CH$_2$), 26.2 (octyl CH$_2$), 22.7 (octyl CH$_2$), 18.0 (C-6′), 14.1 (octyl CH$_3$). Anal. Calcd for $C_{62}H_{74}O_{10}$ (979.24): C, 76.04; H, 7.62. Found: C, 75.97; H, 7.72. ESIMS: *m*/*z* calcd for $[C_{62}H_{74}O_{10}]Na^+$: 1001.5174. Found: 1001.5177.

3.42. Octyl 2,3-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside (50)

Triol **30** (595 mg, 1.12 mmol), 2,2-dimethoxypropane (1.2 mL, 9.0 mmol), and *p*-TsOH (4.3 mg) were dissolved in acetone (15 mL), and the mixture was stirred for 2 h. The reaction mixture was neutralized with Et_3N, concentrated, and purified by chromatography (6:1 hexane–EtOAc) to give **50** (615 mg, 96%) as a colorless oil: R_f 0.29 (6:1 hexane–EtOAc); $[\alpha]_D$ +1.0 (c 2.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.68–7.73 (m, 4H, ArH), 7.36–7.46 (m, 6H, ArH), 4.97 (s, 1H, H-1), 4.17 (dd, 1H, $J = 6.5$, 6.5 Hz, H-3), 4.13 (d, 1H, $J = 6.0$ Hz, H-2), 3.85–3.94 (m, 2H, H-6a, H-6b), 3.80 (dd, 1H, $J = 9.3$, 6.5 Hz, H-4), 3.63–3.70 (m, 2H, H-5, octyl OCH$_2$), 3.38 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH$_2$), 2.81 (br s, 1H, OH), 1.51–1.60 (m, 2H, octyl OCH$_2$CH$_2$), 1.50 (s, 3H, isopropylidene CH$_3$), 1.36 (s, 3H, isopropylidene CH$_3$), 1.20–1.38 (m, 10H, octyl CH$_2$), 1.07 (s, 9H, *tert*-butyl CH$_3$), 0.89 (t, 3H, $J = 6.5$ Hz, octyl CH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 135.8 (4 × Ar), 133.3 (Ar), 133.2 (Ar), 129.9 (2 × Ar), 127.9 (4 × Ar), 109.6 (isopropylidene *C*), 97.2 (C-1), 78.3 (C-3), 75.6 (C-2), 70.7 (C-4), 69.8 (C-5), 67.9 (octyl OCH$_2$), 64.9 (C-6), 32.0 (octyl CH$_2$), 29.5 (octyl CH$_2$), 29.5 (octyl CH$_2$), 29.4 (octyl CH$_2$), 28.0 (isopropylidene CH$_3$), 27.0 (*tert*-butyl CH$_3$), 26.3 (*tert*-butyl *C*), 26.2 (isopropylidene CH$_3$), 22.8 (octyl CH$_2$), 19.3 (octyl CH$_2$), 14.2 (octyl CH$_3$). Anal. Calcd for $C_{33}H_{50}O_6Si$ (570.83): C, 69.43; H, 8.83. Found: C, 68.98; H, 8.75. ESIMS: *m*/*z* calcd for $[C_{33}H_{50}O_6Si]Na^+$: 593.3269. Found: 593.3270.

3.43. Octyl 2,3-*O*-isopropylidene-4-*O*-benzyl-α-D-mannopyranoside (51)

Benzylation of monosaccharide **50** (2.3 g, 4.0 mmol) using BnBr (0.73 mL, 6.0 mmol) and 60% NaH in mineral oil (0.24 g, 6.0 mmol) in DMF (10 mL) was performed as described for **23** to obtain a residue as a yellow oil. Desilylation of the crude product was performed in THF (50 mL) and TBAF (8.0 mL, 8.0 mmol) as described for **23** to give **51** (1.29 g, 76% over two steps) as a crystalline solid. R_f 0.38 (4:1 hexane–EtOAc); $[\alpha]_D$ +45.8 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.26–7.48 (m, 5H, ArH), 5.02 (s, 1H, H-1), 4.77 (d, 1H, $J = 11.4$ Hz, PhCH$_2$), 4.64 (d, 1H, $J = 11.4$ Hz, PhCH$_2$), 4.34 (dd, 1H, $J = 6.4$, 6.4 Hz, H-3), 4.15 (d, 1H, $J = 6.4$ Hz, H-2), 3.85 (dd, 1H, $J = 11.6$, 3.2 Hz, H-6a), 3.75 (dd, 1H, $J = 11.6$, 4.8 Hz, H-6b), 3.62–3.72

(m, 2H, H-5, octyl OCH_2), 3.54 (dd, 1H, $J = 10.0$, 6.4 Hz, H-4), 3.40 (dt, 1H, $J = 9.6$, 6.4 Hz, octyl OCH_2), 1.94 (br s, 1H, OH), 1.48–1.62 (m, 5H, isopropylidene CH_3, octyl OCH$_2$CH_2), 1.20–1.49 (m, 13H, isopropylidene CH_3, octyl CH_2), 0.89 (t, 3H, $J = 6.8$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.3 (Ar), 128.5 (2 × Ar), 128.2 (2 × Ar), 127.9 (Ar), 109.4 (isopropylidene *C*), 97.3 (C-1), 78.9 (C-3), 76.4 (C-2/H-4), 76.2 (C-2/H-4), 73.0 (PhCH_2), 68.5 (C-5), 68.0 (octyl OCH_2), 62.8 (C-6), 31.9 (octyl CH_2), 29.5 (octyl CH_2), 29.5 (octyl CH_2), 29.3 (octyl CH_2), 28.1 (isopropylidene CH_3), 26.5 (isopropylidene CH_3), 26.3 (octyl CH_2), 22.8 (octyl CH_2), 14.1 (octyl CH_3). Anal. Calcd for $C_{24}H_{38}O_6$ (422.27): C, 68.22; H, 9.06. Found: C, 68.28; H, 9.06. ESIMS: *m*/*z* calcd for $[C_{24}H_{38}O_6]Na^+$: 445.2561. Found: 445.2559.

3.44. *p*-Tolyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside (52)

D-Mannose (2.74 g, 15.0 mmol) was dissolved in pyridine (19 mL) and cooled at 0 °C. Benzoyl chloride (19.0 mL, 140 mmol) was added dropwise, and the reaction mixture was stirred overnight. The reaction mixture was then diluted with CH_2Cl_2 (100 mL), washed with water (2 × 50 mL), 1 M HCl (3 × 50 mL), satd aq $NaHCO_3$ (50 mL), dried ($MgSO_4$), and concentrated to yellow syrup. The crude product (6.29 g, 8.9 mol) and *p*-thiocresol (1.3 g, 11.0 mol) were dissolved in CH_2Cl_2 (50 mL). After the addition of $BF_3{\cdot}Et_2O$ (3.4 mL, 0.061 mol), the reaction mixture was stirred for 24 h. The solution was diluted with CH_2Cl_2 (100 mL), washed with satd aq $NaHCO_3$ (50 mL), water (2 × 50 mL), dried ($MgSO_4$), and concentrated. The crude product was purified by chromatography (4:1 hexane–EtOAc) to give **52** (3.95 g, 64%) as a white foam: R_f 0.38 (4:1 hexane–EtOAc); $[\alpha]_D$ +33.0 (*c* 2.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.04–8.10 (m, 4H, ArH), 8.01 (m, 2H, ArH), 7.87 (m, 2H, ArH), 7.59 (m, 3H, ArH), 7.36–7.48 (m, 9H, ArH), 7.25–7.32 (m, 2H, ArH), 7.01 (d, 2H, $J = 8.0$ Hz, ArH), 6.15 (dd, 1H, $J = 10.0$, 10.0 Hz, H-4), 5.98 (dd, 1H, $J = 3.3$, 1.5 Hz, H-2), 5.90 (dd, 1H, $J = 10.0$, 3.3 Hz, H-3), 5.72 (d, 1H, $J = 1.5$ Hz, H-1), 5.03 (ddd, 1H, $J = 10.0$, 5.0, 2.5 Hz, H-5), 4.67 (dd, 1H, $J = 12.5$, 2.5 Hz, H-6a), 4.57 (dd, 1H, $J = 12.5$, 5.0 Hz, H-6b), 2.30 (s, 3H, SPhCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.1 (C═O), 165.5 (C═O), 165.4 (C═O), 165.3 (C═O), 138.4 (Ar), 133.5 (2 × Ar), 133.3 (Ar), 133.0 (Ar), 132.7 (2 × Ar), 130.0 (2 × Ar), 129.9 (2 × Ar), 129.9 (2 × Ar), 129.8 (2 × Ar), 129.8 (2 × Ar), 129.5 (Ar), 129.3 (Ar), 128.9 (Ar), 128.9 (Ar), 128.8 (Ar), 128.6 (2 × Ar), 128.5 (2 × Ar), 128.4 (2 × Ar), 128.3 (2 × Ar), 86.3 (C-1), 71.9 (C-2), 70.4 (C-3), 69.8 (C-5), 67.2 (C-4), 63.1 (C-6), 21.1 (SPh*C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{41}H_{34}O_9S]Na^+$: 725.1816. Found: 725.1813.

3.45. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-4-*O*-benzyl-2,3-*O*-isopropylidene-α-D-mannopyranoside (53)

Prepared from thioglycoside **52** (498 mg, 0.71 mmol), alcohol **51** (250 mg, 0.59 mmol), powdered 4 Å molecular sieves (0.5 g), *N*-iodosuccinimide (210 mg, 0.89 mmol), and TMSOTf (32 μL, 0.18 mmol) as described for **31** to give **53** (547 mg, 92%) as a yellow oil: R_f 0.36 (4:1 hexane–EtOAc); $[\alpha]_D$ −1.1 (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.10–8.14 (m, 2H, ArH), 8.03–8.07 (m, 2H, ArH), 7.88–7.92 (m, 2H, ArH), 7.81–7.85 (m, 2H, ArH), 7.55–7.61 (m, 2H, ArH), 7.49–7.54 (m, 1H, ArH), 7.23–7.45 (m, 14H, ArH), 6.13 (dd, 1H, $J = 10.3$, 10.3 Hz, H-4′), 5.92 (dd, 1H, $J = 10.3$, 3.3 Hz, H-3′), 5.72 (dd, 1H, $J = 3.3$, 1.5 Hz, H-2′), 5.17 (d, 1H, $J = 1.5$ Hz, H-1′), 5.09 (br s, 1H, H-1), 4.99 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.66 (dd, 1H, $J = 12.3$, 2.5 Hz, H-6a′), 4.65 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.50 (ddd, 1H, $J = 10.3$, 2.5 Hz, H-5′), 4.35–4.42 (m, 2H, H-3, H-6b′), 4.21 (d, 1H, $J = 6.0$ Hz, H-2), 3.87–3.98 (m, 4H, H-5, H-6a, H-6b, octyl OCH_2), 3.50–3.58 (m, 2H, H-4, octyl OCH_2), 1.64–1.72 (m, 2H, octyl OCH$_2$CH_2), 1.58 (s, 3H, isopropylidene CH_3), 1.41 (s, 3H, isopropylidene CH_3), 1.16–1.42 (m, 10H, octyl CH_2), 0.83 (t, 3H, $J = 6.8$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.1 (C═O), 165.4 (C═O), 165.2 (C═O), 165.2 (C═O), 138.1 (Ar), 133.3 (Ar), 133.0 (Ar), 132.9 (Ar), 130.0 (Ar), 129.8 (Ar), 129.8 (Ar), 129.8 (Ar), 129.7 (Ar), 129.4 (Ar), 129.2 (Ar), 129.1 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 127.7 (Ar), 127.7 (Ar), 109.4 (isopropylidene *C*), 97.4 (C-1′, $^1J_{C,H} = 172.9$ Hz), 96.9 (C-1, $^1J_{C,H} = 169.9$ Hz), 78.8 (C-3), 76.1 (C-2), 76.1 (C-4), 72.6 (PhCH_2), 70.4 (C-2′), 70.0 (C-3′), 68.8 (C-5′), 67.8 (octyl OCH_2), 67.6 (C-4′), 67.1 (C-6), 66.9 (C-5), 62.7 (C-6′), 31.8 (octyl CH_2), 29.5 (octyl CH_2), 29.4 (octyl CH_2), 29.3 (octyl CH_2), 28.1 (isopropylidene CH_3), 26.4 (isopropylidene CH_3), 26.3 (octyl CH_2), 22.6 (octyl CH_2), 14.0 (octyl CH_3). ESIMS: *m*/*z* calcd for $[C_{58}H_{64}O_{15}]Na^+$: 1023.4137. Found: 1023.4133.

3.46. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-4-*O*-benzyl-α-D-mannopyranoside (54)

Disaccharide **53** (496 mg, 0.50 mmol) was dissolved in 80% AcOH–H_2O (10 mL) and heated at 50 °C overnight. The reaction mixture was then diluted with EtOAc (50 mL), washed with satd aq $NaHCO_3$ (2 × 25 mL), dried ($MgSO_4$), and concentrated. The crude residue was purified by chromatography (1:1 hexane–EtOAc) to give **54** (421 mg, 88%) as a colorless oil: R_f 0.28 (1:1 hexane–EtOAc); $[\alpha]_D$ +4.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.09–8.12 (m, 2H, ArH), 8.05–8.08 (m, 2H, ArH), 7.93–7.96 (m, 2H, ArH), 7.84–7.88 (m, 2H, ArH), 7.55–7.62 (m,

2H, ArH), 7.49–7.54 (m, 1H, ArH), 7.35–7.46 (m, 12H, ArH), 7.26–7.33 (m, 2H, ArH), 6.14 (dd, 1H, $J = 10.2$, 10.2 Hz, H-4′), 5.93 (dd, 1H, $J = 10.2$, 3.6 Hz, H-3′), 5.75 (dd, 1H, $J = 3.6$, 1.8 Hz, H-2′), 5.38 (d, 1H, $J = 1.8$ Hz, H-1′), 4.98 (d, 1H, $J = 11.4$ Hz, PhCH_2), 4.85 (d, 1H, $J = 1.2$ Hz, H-1), 4.82 (d, 1H, $J = 11.4$ Hz, PhCH_2), 4.69 (dd, 1H, $J = 12.2$, 2.4 Hz, H-6a′), 4.51 (ddd, 1H, $J = 10.2$, 3.9, 2.4 Hz, H-5′), 4.44 (dd, 1H, $J = 12.2$, 3.9 Hz, H-6b′), 4.08 (dd, 1H, $J = 12.0$, 4.2 Hz, H-6a), 4.02 (dd, 1H, $J = 8.4$, 3.6 Hz, H-3), 3.90–3.96 (m, 2H, H-2, H-6b), 3.77–3.85 (m, 2H, H-4, H-5), 3.72 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 3.44 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 2.65 (br s, 1H, O*H*), 2.48 (br s, 1H, O*H*), 1.56–1.63 (m, 2H, octyl OCH$_2$CH_2), 1.20–1.40 (m, 10H, octyl CH_2), 0.86 (t, 3H, $J = 6.9$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.2 (C═O), 165.6 (C═O), 165.5 (C═O), 165.5 (C═O), 138.4 (Ar), 133.5 (Ar), 133.4 (Ar), 133.2 (Ar), 133.0 (Ar), 130.0 (Ar), 129.9 (Ar), 129.7 (Ar), 129.3 (Ar), 129.1 (Ar), 129.1 (Ar), 128.6 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 127.9 (Ar), 99.4 (C-1), 97.8 (C-1′), 75.9 (C-4), 74.9 (Ph*C*H$_2$), 72.2 (C-3), 71.3 (C-2), 71.0 (C-5), 70.8 (C-2′), 69.9 (C-3′), 69.0 (C-5′), 68.0 (octyl O*C*H$_2$), 66.9 (C-4′), 66.8 (C-6), 62.8 (C-6′), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.6 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{50}H_{60}O_{15}$ (961.06): C, 68.74; H, 6.29. Found: C, 68.23; H, 6.23. ESIMS: *m*/*z* calcd for $[C_{55}H_{60}O_{15}]Na^+$: 983.3824. Found: 983.3823.

3.47. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-3-*O*-benzoyl-4-*O*-benzyl-α-D-mannopyranoside (55) and octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2-*O*-benzoyl-4-*O*-benzyl-α-D-mannopyranoside (56)

Disaccharide **54** (637 mg, 0.66 mmol) and Bu_2SnO (168 mg, 0.66 mmol) in toluene (15 mL) was heated under reflux for 3 h. The reaction mixture was cooled to room temperature, and BzCl (0.10 mL, 0.83 mmol) was added and stirring was continued overnight. The solvent was then evaporated and the crude residue was purified by chromatography (3:1 hexane–EtOAc) to give **55** (442 mg, 63%) and **56** (227 mg, 32%), both as white foams.

3.47.1. Data for 56. R_f 0.28 (3:1 hexane–EtOAc); $[\alpha]_D$ −2.3 (*c* 1.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.08–8.13 (m, 4H, ArH), 7.99–8.04 (m, 2H, ArH), 7.88–7.92 (m, 2H, ArH), 7.83–7.87 (m, 2H, ArH), 7.53–7.61 (m, 2H, ArH), 7.25–7.53 (m, 18H, ArH), 6.14 (dd, 1H, $J = 10.3$, 10.3 Hz, H-4′), 5.96 (dd, 1H, $J = 10.3$, 3.3 Hz, H-3′), 5.81 (dd, 1H, $J = 3.3$, 2.0 Hz, H-2′), 5.41 (dd, 1H, $J = 3.5$, 1.5 Hz, H-2), 5.29 (d, 1H, $J = 2.0$ Hz, H-1′), 5.05 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.96 (d, 1H, $J = 1.5$ Hz, H-1), 4.85 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.66 (dd, 1H, $J = 12.0$, 2.5 Hz, H-6a′), 4.44 (ddd, 1H, $J = 10.0$, 3.1, 2.5 Hz, H-5′), 4.37–4.40 (m, 2H, H-6b′, H-3), 4.15 (dd, 1H, $J = 11.3$, 4.3 Hz, H-6a), 3.92–4.02 (m, 3H, H-4, H-5, H-6b), 3.77 (dt, 1H, $J = 9.5$, 6.8 Hz, octyl OCH_2), 3.49 (dt, 1H, $J = 9.5$, 6.8 Hz, octyl OCH_2), 1.59–1.68 (m, 2H, octyl OCH$_2$CH_2), 1.20–1.43 (m, 10H, octyl CH_2), 0.87 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.5 (C═O), 166.1 (C═O), 165.4 (C═O), 165.3 (C═O), 165.1 (C═O), 138.2 (Ar), 133.4 (Ar), 133.3 (Ar), 133.3 (Ar), 133.1 (Ar), 133.0 (Ar), 129.9 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.4 (Ar), 129.2 (Ar), 129.0 (Ar), 128.6 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 127.8 (Ar), 97.9 (C-1′), 97.5 (C-1), 75.9 (C-4), 75.0 (Ph*C*H$_2$), 73.3 (C-2), 71.1 (C-3), 70.7 (C-5), 70.3 (C-2′), 70.2 (C-3′), 69.0 (C-5′), 68.2 (octyl O*C*H$_2$), 66.8 (C-4′), 66.5 (C-6), 62.7 (C-6′), 31.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{62}H_{64}O_{16}]Na^+$: 1087.4087. Found: 1087.4086.

3.47.2. Data for 55. R_f 0.16 (3:1 hexane–EtOAc); $[\alpha]_D$ +11.1 (*c* 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.15–8.19 (m, 2H, ArH), 8.06–8.14 (m, 4H, ArH), 7.95–7.99 (m, 2H, ArH), 7.86–7.90 (m, 2H, ArH), 7.56–7.62 (m, 3H, ArH), 7.35–7.55 (m, 10H, ArH), 7.19–7.32 (m, 7H, ArH), 6.16 (dd, 1H, $J = 10.0$, 10.0 Hz, H-4′), 5.99 (dd, 1H, $J = 10.0$, 3.5 Hz, H-3′), 5.82 (dd, 1H, $J = 3.5$, 1.5 Hz, H-2′), 5.62 (dd, 1H, $J = 9.8$, 3.0 Hz, H-3), 5.45 (d, 1H, $J = 1.5$ Hz, H-1′), 4.88 (d, 1H, $J = 1.8$ Hz, H-1), 4.85 (d, 1H, $J = 11.0$ Hz, PhCH_2), 4.75 (d, 1H, $J = 11.5$ Hz, PhCH_2), 4.70 (dd, 1H, $J = 11.5$, 2.0 Hz, H-6a′), 4.44–4.52 (m, 2H, H-5′, H-6b′), 4.31 (dd, 1H, $J = 9.8$, 9.8 Hz, H-4), 4.23 (dd, 1H, $J = 3.0$, 1.8 Hz, H-2), 4.10 (dd, 1H, $J = 12.0$, 4.0 Hz, H-6a), 3.94–4.00 (m, 2H, H-5, H-6b), 3.74 (dt, 1H, $J = 9.5$, 6.8 Hz, octyl OCH_2), 3.48 (dt, 1H, $J = 9.5$, 6.8 Hz, octyl OCH_2), 1.59–1.67 (m, 2H, octyl OCH$_2$CH_2), 1.20–1.42 (m, 10H, octyl CH_2), 0.87 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.2 (C═O), 165.6 (C═O), 165.6 (C═O), 165.6 (C═O), 165.5 (C═O), 137.8 (Ar), 133.5 (Ar), 133.4 (Ar), 133.2 (Ar), 133.0 (Ar), 130.0 (Ar), 129.9 (Ar), 129.9 (Ar), 129.8 (Ar), 129.4 (Ar), 129.2 (Ar), 129.1 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 99.7 (C-1), 98.0 (C-1′), 75.2 (C-3), 75.0 (Ph*C*H$_2$), 72.9 (C-4), 71.7 (C-5), 70.9 (C-2′), 69.9 (C-2/C-3′), 69.8 (C-2/C-3′), 69.0 (C-5′), 68.3 (octyl O*C*H$_2$), 67.0 (C-4′), 66.5 (C-6), 62.8 (C-6′), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{62}H_{64}O_{16}]Na^+$: 1087.4087. Found: 1087.4083.

3.48. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-phenoxythiocarbonyl-α-D-mannopyranoside (57)

Disaccharide **55** (224 mg, 0.21 mmol) was dissolved in CH_3CN (2.2 mL), and DMAP (64 mg, 0.52 mmol), and phenyl chlorothionoformate (37 μL, 0.27 mmol) were added. The reaction mixture was stirred overnight and concentrated. The crude product was dissolved in CH_2Cl_2 (50 mL), washed with water (15 mL), brine (15 mL), dried ($MgSO_4$), and concentrated as a yellow crude. The crude product was purified by chromatography (3:1 hexane–EtOAc) to give **57** (186 mg, 74%) as a foam: R_f 0.40 (3:1 hexane–EtOAc); $[\alpha]_D$ +11.2 (*c* 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.11–8.18 (m, 4H, ArH), 8.03–8.07 (m, 2H, ArH), 7.92–7.96 (m, 2H, ArH), 7.75–7.80 (m, 2H, ArH), 7.55–7.65 (m, 3H, ArH), 7.48–7.54 (m, 3H, ArH), 7.34–7.45 (m, 7H, ArH), 7.14–7.31 (m, 10H, ArH), 6.89–6.92 (m, 2H, ArH), 6.15 (dd, 1H, $J = 10.0$, 10.0 Hz, H-4′), 6.03 (dd, 1H, $J = 10.0$, 3.5 Hz, H-3′), 5.89 (dd, 1H, $J = 3.5$, 1.5 Hz, H-2), 5.88 (dd, 1H, $J = 3.5$, 1.5 Hz, H-2′), 5.84 (dd, 1H, $J = 10.0$, 3.5 Hz, H-3), 5.34 (d, 1H, $J = 1.5$ Hz, H-1′), 5.16 (d, 1H, $J = 1.5$ Hz, H-1), 4.86 (d, 1H, $J = 11.5$ Hz, PhCH_2), 4.69–4.77 (m, 2H, PhCH_2, H-6a′), 4.46–4.52 (m, 2H, H-5′, H-6b′), 4.25 (dd, 1H, $J = 10.0$, 10.0 Hz, H-4), 4.05–4.11 (m, 2H, H-5, H-6a), 3.95–4.01 (m, 1H, H-6b), 3.82 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 3.57 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 1.64–1.72 (m, 2H, octyl OCH$_2$CH_2), 1.20–1.46 (m, 10H, octyl CH_2), 0.86 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 194.6 (C═S), 166.2 (C═O), 165.5 (C═O), 165.4 (C═O), 165.3 (C═O), 165.1 (C═O), 153.3 (Ar), 137.7 (Ar), 133.4 (Ar), 133.3 (Ar), 133.3 (Ar), 133.0 (Ar), 133.0 (Ar), 130.0 (Ar), 129.9 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 129.3 (Ar), 129.2 (Ar), 129.1 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 126.4 (Ar), 121.7 (Ar), 98.2 (C-1′), 96.4 (C-1), 79.6 (C-2), 75.2 (Ph*C*H$_2$), 73.5 (C-4), 72.4 (C-3), 71.4 (C-5), 70.6 (C-2′), 69.8 (C-3′), 69.0 (C-5′), 68.6 (octyl O*C*H$_2$), 67.1 (C-4′), 66.6 (C-6), 62.8 (C-6′), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{69}H_{68}O_{17}]Na^+$: 1223.4070. Found: 1223.4070.

3.49. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-phenoxythiocarbonyl-α-D-mannopyranoside (58)

Prepared from disaccharide **56** (227 mg, 0.21 mmol), DMAP (64 mg, 0.52 mmol) and phenyl chlorothionoformate (37 μL, 0.27 mmol) in CH_3CN (1.6 mL) as described for **57**, to give **58** (180 mg, 70%) as a foam: R_f 0.39 (3:1 hexane–EtOAc); $[\alpha]_D$ −14.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.13–8.17 (m, 2H, ArH), 8.09–8.13 (m, 2H, ArH), 8.01–8.05 (m, 2H, ArH), 7.90–7.94 (m, 2H, ArH), 7.84–7.88 (m, 2H, ArH), 7.55–7.61 (m, 2H, ArH), 7.24–7.54 (m, 21H, ArH), 7.07–7.11 (m, 2H, ArH), 6.15 (dd, 1H, $J = 10.3$, 10.3 Hz, H-4′), 6.05 (dd, 1H, $J = 10.0$, 3.5 Hz, H-3), 5.96 (dd, 1H, $J = 10.3$, 3.0 Hz, H-3′), 5.86 (dd, 1H, $J = 3.5$, 1.8 Hz, H-2), 5.83 (dd, 1H, $J = 3.0$, 2.0 Hz, H-2′), 5.30 (d, 1H, $J = 2.0$ Hz, H-1′), 5.02 (d, 1H, $J = 1.8$ Hz, H-1), 4.98 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.79 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.63–4.68 (m, 1H, H-6a′), 4.33–4.43 (m, 3H, H-5′, H-6b′, H-4), 4.16 (dd, 1H, $J = 11.5$, 4.0 Hz, H-6a), 4.10 (m, 1H, H-5), 3.95 (dd, 1H, $J = 11.5$, 1.5 Hz, H-6b), 3.79 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 3.54 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 1.64–1.71 (m, 2H, octyl OCH$_2$CH_2), 1.21–1.44 (m, 10H, octyl CH_2), 0.86 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 193.7 (C═S), 166.1 (C═O), 165.7 (C═O), 165.4 (C═O), 165.3 (C═O), 165.1 (C═O), 153.4 (Ar), 137.8 (Ar), 133.4 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.0 (Ar), 129.9 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.5 (Ar), 129.4 (Ar), 129.2 (Ar), 129.0 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 127.9 (Ar), 127.7 (Ar), 126.5 (Ar), 121.9 (Ar), 98.1 (C-1′), 97.7 (C-1), 82.1 (C-3), 75.1 (Ph*C*H$_2$), 73.1 (C-4), 71.0 (C-5), 70.2 (C-2′/C-3′), 70.1 (C-2′/C-3′), 69.7 (C-2), 69.0 (C-5′), 68.5 (octyl O*C*H$_2$), 66.8 (C-4′), 66.2 (C-6), 62.6 (C-6′), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 22.6 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{69}H_{68}O_{17}$ (1200.42): C, 68.98; H, 5.71; S, 2.67. Found: C, 69.27; H, 5.71; S, 2.55. ESIMS: *m*/*z* calcd for $[C_{69}H_{68}O_{17}]Na^+$: 1223.4070. Found: 1223.4068.

3.50. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (59)

Prepared from phenoxythiocarbonyl derivative **57** (154 mg, 0.13 mmol) in toluene (2.2 mL), tri-*n*-butylstannane (55 μL, 0.20 mmol), and AIBN (8 mg, 0.049 mmol) in toluene (9 mL) as described for **40** to give **59** (113 mg, 84%) as a foam: R_f 0.30 (4:1 hexane–EtOAc); $[\alpha]_D$ 13.9 (*c* 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2) δ_H 8.08–8.12 (m, 4H, ArH), 8.05–8.09 (m, 2H, ArH), 7.93–7.96 (m, 2H, ArH), 7.84–7.87 (m, 2H, ArH), 7.58–7.65 (m, 3H, ArH), 7.36–7.56 (m, 10H, ArH), 7.19–7.33 (m, 7H, ArH), 6.09 (dd, 1H, $J = 10.5$, 10.5 Hz, H-4′), 5.92 (dd, 1H, $J = 10.5$, 3.5 Hz, H-3′), 5.82 (dd, 1H, $J = 3.5$, 2.0 Hz, H-2′), 5.58 (ddd, 1H, $J = 11.5$, 9.5, 5.5 Hz, H-3), 5.28 (d, 1H, $J = 2.0$ Hz, H-1′), 4.97 (br d, 1H, $J = 3.5$ Hz, H-1), 4.86 (d, 1H, $J = 11.5$ Hz, PhCH_2), 4.76 (d, 1H, $J = 11.5$ Hz, PhCH_2), 4.66 (dd, 1H, $J = 12.0$, 2.5 Hz, H-6a′), 4.52 (ddd, 1H, $J = 10.5$, 4.3, 2.5 Hz, H-5′), 4.43 (dd, 1H, $J = 12.0$,

4.3 Hz, H-6b′), 4.11 (dd, 1H, $J = 11.2$, 4.5 Hz, H-6a), 4.00 (ddd, 1H, $J = 9.5$, 4.5, 1.8 Hz, H-5), 3.96 (dd, 1H, $J = 11.2$, 1.8 Hz, H-6b), 3.84 (dd, 1H, $J = 9.5$, 9.5 Hz, H-4), 3.75 (ddd, 1H, $J = 9.5$, 6.5, 6.5 Hz, octyl OCH_2), 3.45 (ddd, 1H, $J = 9.5$, 6.5, 6.5 Hz, octyl OCH_2), 2.36 (dd, 1H, $J = 13.0$, 6.0, 1.0 Hz, H-2_{eq}), 1.87 (ddd, 1H, $J = 13.0$, 11.5, 3.5 Hz, H2_{ax}), 1.62–1.72 (m, 2H, octyl OCH$_2$CH_2), 1.20–1.46 (m, 10H, octyl CH_2), 0.86 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, CD_2Cl_2) δ_C 166.3 (C═O), 166.0 (C═O), 165.7 (C═O), 165.7 (C═O), 165.7 (C═O), 138.6 (Ar), 133.8 (Ar), 133.8 (Ar), 133.6 (Ar), 133.5 (Ar), 133.4 (Ar), 130.8 (Ar), 130.5 (Ar), 130.1 (Ar), 130.0 (Ar), 130.0 (Ar), 130.0 (Ar), 130.0 (Ar), 129.9 (Ar), 129.7 (Ar), 129.7 (Ar), 129.0 (Ar), 128.9 (Ar), 128.8 (Ar), 128.8 (Ar), 128.7 (Ar), 128.1 (Ar), 128.1 (Ar), 98.3 (C-1′), 97.3 (C-1), 77.3 (C-4), 75.1 (PhCH$_2$), 73.2 (C-3), 71.0 (C-5), 70.8 (C-2′/C-3′), 70.7 (C-2′/C-3′), 69.4 (C-5′), 68.2 (octyl OCH$_2$), 67.3 (C-4′), 67.1 (C-6), 63.2 (C-6′), 35.8 (C-2), 32.3 (octyl CH$_2$), 30.0 (octyl CH$_2$), 29.9 (octyl CH$_2$), 29.7 (octyl CH$_2$), 26.7 (octyl CH$_2$), 23.1 (octyl CH$_2$), 14.2 (octyl CH$_3$). Anal. Calcd for $C_{62}H_{64}O_{15}$ (1048.42): C, 70.98; H, 6.15. Found: C, 70.56; H, 6.27. ESIMS: m/z calcd for $[C_{62}H_{64}O_{15}]Na^+$: 1071.4137. Found: 1071.4138.

3.51. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2-*O*-benzoyl-4-*O*-benzyl-3-deoxy-α-D-*arabino*-hexopyranoside (60)

Prepared from phenoxythiocarbonyl derivative **58** (154 mg, 0.13 mmol) in toluene (2.2 mL) and tri-*n*-butylstannane (55 μL, 0.20 mmol) and AIBN (8 mg, 0.049 mmol) in toluene (9 mL) at reflux as described for **40** to give **60** (42 mg, 32%) as a colorless oil: R_f 0.32 (4:1 hexane–EtOAc); $[\alpha]_D$ +5.6 (*c* 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.08–8.14 (m, 4H, ArH), 8.03–8.06 (m, 2H, ArH), 7.87–7.91 (m, 2H, ArH), 7.83–7.86 (m, 2H, ArH), 7.54–7.61 (m, 2H, ArH), 7.23–7.52 (m, 18H, ArH), 6.14 (dd, 1H, $J = 10.2$, 10.2 Hz, H-4′), 5.98 (dd, 1H, $J = 10.2$, 3.6 Hz, H-3′), 5.81 (dd, 1H, $J = 3.6$, 1.5 Hz, H-2′), 5.27 (d, 1H, $J = 1.5$ Hz, H-1′), 5.24–5.27 (m, 1H, H-2), 4.87 (br s, 1H, H-1), 4.76 (d, 1H, $J = 11.4$ Hz, PhCH_2), 4.65 (dd, 1H, $J = 12.0$, 2.4 Hz, H-6a′), 4.58 (d, 1H, $J = 11.4$ Hz, PhCH_2), 4.49 (ddd, 1H, $J = 10.2$, 4.2, 2.4 Hz, H-5′), 4.36 (dd, 1H, $J = 12.0$, 4.2 Hz, H-6b′), 4.15 (dd, 1H, $J = 10.9$, 4.5 Hz, H-6a), 3.99–4.06 (m, 2H, H-4, H-5), 3.93 (dd, 1H, $J = 10.9$, 1.2 Hz, H-6b), 3.84 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 3.54 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 2.48 (ddd, 1H, $J = 13.4$, 3.6, 3.6 Hz, H-3_{eq}), 2.13 (ddd, 1H, $J = 13.4$, 13.4, 3.0 Hz, H3_{ax}), 1.58–1.72 (m, 2H, octyl OCH$_2$CH_2), 1.20–1.46 (m, 10H, octyl CH_2), 0.87 (t, 3H, $J = 6.9$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.1 (C═O), 165.8 (C═O), 165.4 (C═O), 165.3 (C═O), 165.1 (C═O), 137.9 (Ar), 133.4 (Ar), 133.3 (Ar), 133.1 (Ar), 133.1 (Ar), 133.0 (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.8 (Ar), 129.7 (Ar), 129.7 (Ar), 129.4 (Ar), 129.2 (Ar), 129.1 (Ar), 128.6 (Ar), 128.6 (Ar), 128.5 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 127.8 (Ar), 127.6 (Ar), 127.6 (Ar), 127.0 (Ar), 97.7 (C-1′), 96.4 (C-1), 71.2 (C-4), 70.9 (PhCH$_2$), 70.6 (C-2), 70.4 (C-2′), 70.2 (C-3′), 69.4 (C-5), 68.8 (C-5′), 67.9 (octyl OCH$_2$), 66.9 (C-4′), 66.7 (C-6), 62.7 (C-6′), 31.8 (octyl CH$_2$), 29.6 (octyl CH$_2$), 29.5 (octyl CH$_2$), 29.3 (octyl CH$_2$), 26.3 (octyl CH$_2$), 22.7 (octyl CH$_2$), 22.7 (C-3), 14.1 (octyl CH$_3$). ESIMS: m/z calcd for $[C_{62}H_{64}O_{15}]Na^+$: 1071.4137. Found: 1071.4140.

3.52. Octyl 3,4-di-*O*-benzyl-2-*O*-methyl-α-D-mannopyranoside (61) and octyl 3,6-di-*O*-benzyl-2-*O*-methyl-α-D-mannopyranoside (68)

Prepared from a solution of $AlCl_3$ (150 mg, 1.1 mmol) and $LiAlH_4$ (1.1 mmol) in ether (4.1 mL) and **66** (317 mg, 0.63 mmol) in 1:1 CH_2Cl_2–ether (8 mL) as described for **27** (except that the reaction mixture was stirred overnight) to give **61** (194 mg, 66%) and its regioisomer **68** (19 mg, 6%) as colorless oils.

3.52.1. Data for 61. R_f 0.27 (2:1 hexane–EtOAc); $[\alpha]_D$ +41.9 (*c* 2.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.26–7.42 (m, 10H, ArH), 4.93 (d, 1H, $J = 10.8$ Hz, PhCH_2), 4.85 (d, 1H, $J = 1.9$ Hz, H-1), 4.74 (s, 2H, PhCH_2), 4.64 (d, 1H, $J = 10.8$ Hz, PhCH_2), 3.93 (dd, 1H, $J = 9.8$, 3.2 Hz, H-3), 3.86 (dd, 1H, $J = 9.8$, 9.8 Hz, H4), 3.83 (dd, 1H, $J = 11.5$, 3.0 Hz, H-6a), 3.77 (dd, 1H, $J = 11.5$, 5.0 Hz, H-6b), 3.61–3.68 (m, 2H, H-5, octyl OCH_2), 3.54 (dd, 1H, $J = 3.2$, 1.9 Hz, H-2), 3.52 (s, 3H, OCH_3), 3.37 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 1.97 (br s, 1H, OH), 1.52–1.69 (m, 2H, octyl OCH$_2$CH_2), 1.24–1.36 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.4 (Ar), 138.4 (Ar), 128.4 (2 × Ar), 128.4 (2 × Ar), 128.1 (2 × Ar), 127.8 (2 × Ar), 127.7 (Ar), 127.6 (Ar), 97.5 (C-1), 80.1 (C-3), 78.1 (C-2), 75.3 (PhCH$_2$), 75.0 (C-4), 72.4 (PhCH$_2$), 72.0 (C-5), 67.8 (octyl OCH$_2$), 62.5 (C-6), 59.4 (OCH$_3$), 31.8 (octyl CH$_2$), 29.5 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.2 (octyl CH$_2$), 26.2 (octyl CH$_2$), 22.7 (octyl CH$_2$), 14.1 (octyl CH$_3$). Anal. Calcd for $C_{29}H_{42}O_6$ (486.64): C, 71.57; H, 8.70. Found: C, 71.44; H, 8.78. ESIMS: m/z calcd for $[C_{29}H_{42}O_6]Na^+$: 509.2874. Found: 509.2877.

3.52.2. Data for 68. R_f 0.44 (2:1 hexane–EtOAc); $[\alpha]_D$ +22.6 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.24–7.42 (m, 10H, ArH), 4.89 (d, 1H, $J = 2.0$ Hz, H-1), 4.74 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.65 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.57–4.62 (m, 2H, PhCH_2), 3.94 (dd, 1H, $J = 9.5$, 9.5 Hz, H4), 3.67–3.80 (m, 5H, H-3, H-5, H-6a, H-6b, octyl OCH_2), 3.53 (dd, 1H, $J = 3.0$,

2.0 Hz, H-2), 3.47 (s, 3H, OCH_3), 3.40 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 2.49 (br s, 1H, OH), 1.53–1.62 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.40 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.3 (2 × Ar), 128.5 (2 × Ar), 128.3 (2 × Ar), 127.9 (2 × Ar), 127.6 (2 × Ar), 127.5 (2 × Ar), 97.5 (C-1), 79.7 (C-3), 77.3 (C-2), 73.5 (PhCH$_2$), 72.0 (PhCH$_2$), 71.3 (C-5), 70.5 (C-6), 68.0 (C-4), 67.8 (octyl OCH$_2$), 59.1 (OCH$_3$), 31.8 (octyl CH$_2$), 29.5 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.3 (octyl CH$_2$), 26.2 (octyl CH$_2$), 22.7 (octyl CH$_2$), 14.1 (octyl CH$_3$). ESIMS: m/z calcd for $[C_{29}H_{42}O_6]Na^+$: 509.2874. Found: 509.2876.

3.53. Octyl 2,4-di-*O*-benzyl-3-*O*-methyl-α-D-mannopyranoside (62) and octyl 2,6-di-*O*-benzyl-3-*O*-methyl-α-D-mannopyranoside (69)

Prepared from a solution of $AlCl_3$ (150 mg, 1.1 mmol) and $LiAlH_4$ (1.1 mmol) in ether (4.1 mL) and disaccharide **67** (317 mg, 0.66 mmol) in 1:1 CH_2Cl_2–ether (8 mL) as described for **27** (except that the reaction mixture was stirred overnight) to give **62** (182 mg, 57%) and **69** (71 mg, 22%) as colorless oils.

3.53.1. Data for 62. R_f 0.33 (3:1 hexane–EtOAc); $[\alpha]_D$ +42.8 (*c* 3.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.26–7.42 (m, 10H, ArH), 4.93 (d, 1H, $J = 11.5$ Hz, PhCH_2), 4.81 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.80 (d, 1H, $J = 1.8$ Hz, H-1), 4.71 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.65 (d, 1H, $J = 11.5$ Hz, PhCH_2), 3.88 (dd, 1H, $J = 10.0$, 10.0 Hz, H-4), 3.84 (dd, 1H, $J = 11.5$, 3.0 Hz, H-6a), 3.81 (dd, 1H, $J = 3.3$, 1.8 Hz, H-2), 3.77 (dd, 1H, $J = 11.5$, 5.0 Hz, H-6b), 3.59–3.67 (m, 3H, H-3, H-5, octyl OCH_2), 3.47 (s, 3H, OCH_3), 3.34 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 2.00 (br s, 1H, OH), 1.48–1.56 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.34 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.6 (Ar), 138.4 (Ar), 128.4 (2 × Ar), 128.4 (2 × Ar), 128.0 (2 × Ar), 127.8 (2 × Ar), 127.7 (Ar), 127.7 (Ar), 98.1 (C-1), 82.1 (C-3), 75.1 (PhCH$_2$), 75.1 (C-4), 74.4 (C-2), 72.9 (PhCH$_2$), 71.9 (C-5), 67.8 (octyl OCH$_2$), 62.5 (C-6), 57.7 (OCH$_3$), 31.8 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.2 (octyl CH$_2$), 26.1 (octyl CH$_2$), 22.6 (octyl CH$_2$), 14.1 (octyl CH$_3$). Anal. Calcd for $C_{29}H_{42}O_6$ (486.64): C, 71.57; H, 8.70. Found: C, 71.40; H, 8.78. ESIMS: m/z calcd for $[C_{29}H_{42}O_6]Na^+$: 509.2874. Found: 509.2875.

3.53.2. Data for 69. R_f 0.26 (3:1 hexane–EtOAc); $[\alpha]_D$ +3.7 (*c* 2.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.24–7.40 (m, 10H, ArH), 4.89 (d, 1H, $J = 1.5$ Hz, H-1), 4.71 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.68 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.64 (d, 1H, $J = 12.5$ Hz, PhCH_2), 4.60 (d, 1H, $J = 12.5$ Hz, PhCH_2), 3.98 (dd, 1H, $J = 9.4$, 9.4 Hz, H-4), 3.73–3.83 (m, 4H, H-2, H-5, H-6a, H-6b), 3.68 (dt, 1H, $J = 9.5$, 7.0 Hz, octyl OCH_2), 3.66 (dd, 1H, $J = 9.4$, 3.0 Hz, H-3), 3.36–3.43 (m, 4H, octyl OCH_2, OCH_3), 2.57 (br s, 1H, OH), 1.51–1.60 (m, 2H, octyl OCH$_2$CH_2), 1.22–1.36 (m, 10H, octyl CH_2), 0.89 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 138.3 (Ar), 138.2 (Ar), 128.3 (2 × Ar), 128.3 (2 × Ar), 127.8 (2 × Ar), 127.7 (2 × Ar), 127.5 (Ar), 127.5 (Ar), 97.9 (C-1), 81.2 (C-3), 73.5 (PhCH$_2$), 73.0 (C-2), 72.6 (PhCH$_2$), 71.3 (C-5), 70.5 (C-6), 68.0 (C-4), 67.8 (octyl OCH$_2$), 57.2 (OCH$_3$), 31.8 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.4 (octyl CH$_2$), 29.2 (octyl CH$_2$), 26.2 (octyl CH$_2$), 22.7 (octyl CH$_2$), 14.1 (octyl CH$_3$). ESIMS: m/z calcd for $[C_{29}H_{42}O_6]Na^+$: 509.2874. Found: 509.2877.

3.54. Octyl 2,3:4,6-di-*O*-benzylidene-α-D-mannopyranoside (63)

Prepared from tetraol **29**[27] (3.68 g, 12.6 mmol), benzaldehyde dimethyl acetal (2.5 mL, 16.4 mmol), and *p*-TsOH (24 mg, 0.13 mmol) in DMF (5.0 mL) as described for **25** and **26** to give an ~1:1 mixture of diastereomers **63** (5.10 g, 86%) as a colorless oil: R_f 0.35 (12:1 hexane–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.23–7.67 (m, 20H, Ar), 6.30 (s, 1H), 5.98 (s, 1H), 5.66 (s, 1H), 5.54 (s, 1H), 5.12 (s, 1H), 5.19 (s, 1H), 4.67 (t, 1H, 6.5 Hz), 4.51 (t, 1H, 6.5 Hz), 4.24–4.38 (m, 4H), 4.16 (d, 1H, $J = 6.6$ Hz), 3.68–3.80 (m, 9H), 3.41–4.52 (m, 2H), 1.54–1.67 (m, 4H, octyl OCH$_2$CH_2), 1.23–1.46 (m, 20H, octyl CH_2), 0.86–0.96 (m, 6H, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.7, 137.3, 137.2, 137.1, 129.7, 129.4, 129.1, 129.0, 129.0, 128.5, 128.4, 128.3, 128.2, 128.2, 126.6, 126.3, 126.3, 126.1, 104.1, 103.0, 102.0, 101.7, 97.8, 97.6, 80.7, 78.6, 77.7, 77.3, 77.0, 76.8, 75.6, 75.5, 74.2, 69.0, 68.9, 68.2, 68.1, 60.4, 60.4, 31.8, 31.8, 29.4, 29.4, 29.4, 29.2, 29.2, 26.2, 26.1, 22.7, 22.7, 14.1.

3.55. Octyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (64) and octyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (65)

Prepared from a solution of $AlCl_3$ (1.63 g, 12.2 mmol) and $LiAlH_4$ (12.2 mmol) in ether (47.2 mL) and **63** (4.77 g, 10.2 mmol) in 1:1 CH_2Cl_2–ether (70 mL) at 0 °C as described for **27** to give **65** (1.72 g, 36%) and **64** (1.52 g, 32%) as a colorless oil.

3.55.1. Data for 65. R_f 0.40 (4:1 hexane–EtOAc); $[\alpha]_D$ +14.2 (*c* 4.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.49–7.52 (m, 2H, ArH), 7.26–7.41 (m, 8H, ArH), 5.59 (s, 1H, benzylidene H), 4.84 (d, 1H, $J = 1.2$ Hz, H-1), 4.77 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.72 (d, 1H, $J = 11.8$ Hz, PhCH_2), 4.26 (dd, 1H, $J = 9.0$, 3.8 Hz H-6a), 4.11 (dd, 1H, $J = 9.4$, 3.6 Hz, H-3), 3.92 (dd, 1H,

$J = 9.4$, 9.4 Hz, H-4), 3.76–3.87 (m, 3H, H-2, H-5, H-6b), 3.67 (dt, 1H, $J = 9.6$, 6.8 Hz, octyl OCH_2), 3.38 (dt, 1H, $J = 9.6$, 6.8 Hz, octyl OCH_2), 2.30 (br s, 1H, OH), 1.54–1.59 (m, 2H, octyl OCH$_2$CH_2), 1.24–1.40 (m, 10H, octyl CH_2), 0.91 (t, 3H, $J = 6.8$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 137.7 (Ar), 137.4 (Ar), 129.0 (Ar), 128.6 (Ar), 128.2 (2 × Ar), 128.0 (2 × Ar), 127.9 (2 × Ar), 126.3 (2 × Ar), 102.1 (benzylidene *C*H), 98.3 (C-1), 79.6 (C-4), 78.7 (C-2), 73.7 (Ph*C*H$_2$), 68.9 (C-6), 68.8 (C-3), 68.0 (octyl O*C*H$_2$), 63.4 (C-5), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{28}H_{38}O_6$ (470.60): C, 71.46; H, 8.14. Found: C, 71.75; H, 8.34. ESIMS: *m*/*z* calcd for $[C_{28}H_{38}O_6]H^+$: 471.2741. Found: 471.2742.

3.55.2. Data for 64. R_f 0.23 (4:1 hexane–EtOAc); $[\alpha]_D$ +40.8 (*c* 2.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.51–7.53 (m, 2H, ArH), 7.26–7.42 (m, 8H, ArH), 5.63 (s, 1H, benzylidene H), 4.88 (d, 1H, $J = 11.6$ Hz, PhCH_2), 4.87 (d, 1H, $J = 1.4$ Hz, H-1), 4.74 (d, 1H, $J = 11.6$ Hz, PhCH_2), 4.24–4.33 (m, 1H, H-6a), 4.11 (dd, 1H, $J = 9.4$, 9.4 Hz, H-4), 4.07 (dd, 1H, $J = 3.5$, 1.4 Hz, H-2), 3.94 (dd, 1H, $J = 9.4$, 3.5 Hz, H-3), 3.81–3.91 (m, 2H, H-5, H-6b), 3.69 (dt, 1H, $J = 9.6$, 6.8 Hz, octyl OCH_2), 3.42 (dt, 1H, $J = 9.6$, 6.8 Hz, octyl OCH_2), 2.68 (br s, 1H, OH), 1.54–1.62 (m, 2H, octyl OCH$_2$CH_2), 1.23–1.40 (m, 10H, octyl CH_2), 0.90 (t, 3H, $J = 6.8$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.1 (Ar), 137.6 (Ar), 129.4 (Ar), 128.4 (Ar), 128.9 (2 × Ar), 128.2 (2 × Ar), 127.8 (2 × Ar), 126.0 (2 × Ar), 101.5 (benzylidene *C*H), 99.9 (C-1), 79.0 (C-4), 75.8 (C-3), 73.1 (Ph*C*H$_2$), 70.1 (C-2), 68.9 (C-6), 68.0 (octyl O*C*H$_2$), 63.2 (C-5), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 22.6 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{28}H_{38}O_6$ (470.60): C, 71.46; H, 8.14. Found: C, 71.33; H, 8.55. ESIMS: *m*/*z* calcd for $[C_{28}H_{38}O_6]Na^+$: 493.2561. Found: 493.2561.

3.56. Octyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-methyl-α-D-mannopyranoside (66)

Prepared from monosaccharide **64** (461 mg, 0.98 mmol), 60% NaH in mineral oil (60 mg, 1.5 mmol), and CH_3I (0.20 mL, 3.0 mmol) in DMF (15 mL) as described for **35** to give **66** (445 mg, 94%) as a colorless oil: R_f 0.48 (4:1 hexane–EtOAc); $[\alpha]_D$ +56.15 (*c* 3.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.49–7.54 (m, 2H, ArH), 7.26–7.43 (m, 8H, ArH), 5.64 (s, 1H, benzylidene H), 4.91 (d, 1H, $J = 12.4$ Hz, PhCH_2), 4.85 (d, 1H, $J = 1.6$ Hz, H-1), 4.74 (d, 1H, $J = 12.4$ Hz, PhCH_2), 4.26 (dd, 1H, $J = 9.8$, 4.2 Hz, H-6a), 4.17 (dd, 1H, $J = 9.6$, 9.6 Hz, H-4), 3.98 (dd, 1H, $J = 9.8$, 3.3 Hz, H-3), 3.87 (dd, 1H, $J = 9.8$, 9.8 Hz, H-6b), 3.80 (ddd, 1H, $J = 9.8$, 9.6, 4.2 Hz, H-5), 3.68 (dt, 1H, $J = 9.6$, 7.0 Hz, octyl OCH_2), 3.61 (dd, 1H, $J = 3.3$, 1.6 Hz, H-2), 3.58 (s, 3H, OCH_3), 3.41 (dt, 1H, $J = 9.6$, 7.0 Hz, octyl OCH_2), 1.54–1.62 (m, 2H, octyl OCH$_2$CH_2), 1.24–1.39 (m, 10H, octyl CH_2), 0.91 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.7 (Ar), 137.7 (Ar), 129.2 (Ar), 128.8 (Ar), 128.3 (2 × Ar), 128.2 (2 × Ar), 127.5 (2 × Ar), 126.0 (2 × Ar), 101.4 (benzylidene *C*H), 98.9 (C-1), 79.8 (C-2), 79.3 (C-4), 76.4 (C-3), 73.2 (Ph*C*H$_2$), 68.9 (C-6), 67.9 (octyl O*C*H$_2$), 64.1 (C-5), 60.1 (O*C*H$_3$), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). Anal. Calcd for $C_{29}H_{40}O_6$ (484.62): C, 71.87; H, 8.32. Found: C, 71.57; H, 8.37. ESIMS: *m*/*z* calcd for $[C_{29}H_{40}O_6]Na^+$: 507.2717. Found: 507.2716.

3.57. Octyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-methyl-α-D-mannopyranoside (67)

Prepared from monosaccharide **65** (461 mg, 0.98 mmol), 60% NaH in mineral oil (60 mg, 1.5 mmol), and CH_3I (0.20 mL, 3.0 mmol) in DMF (15 mL) as described for **35** to give **67** (444 mg, 92%) as a colorless oil: R_f 0.41 (6:1 hexane–EtOAc); $[\alpha]_D$ +39.9 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.49–7.55 (m, 2H, ArH), 7.27–7.44 (m, 8H, ArH), 5.63 (s, 1H, benzylidene), 4.84 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.80 (d, 1H, $J = 1.6$ Hz, H-1), 4.72 (d, 1H, $J = 12.0$ Hz, PhCH_2), 4.26 (dd, 1H, $J = 9.8$, 4.2 Hz, H-6a), 4.18 (dd, 1H, $J = 9.8$, 9.8 Hz, H-4), 3.88 (dd, 1H, $J = 9.8$, 9.8 Hz, H-6b), 3.87 (dd, 1H, $J = 3.2$, 1.6 Hz, H-2), 3.82 (ddd, 1H, $J = 9.8$, 9.8, 4.2 Hz, H-5), 3.75 (dd, 1H, $J = 9.8$, 3.2 Hz, H-3), 3.66 (dt, 1H, $J = 9.6$, 6.8 Hz, octyl OCH_2), 3.52 (s, 3H, OCH_3), 3.37 (dt, 1H, $J = 9.6$, 6.8 Hz, octyl OCH_2), 1.52–1.62 (m, 2H, octyl OCH$_2$CH_2), 1.24–1.38 (m, 10H, octyl CH_2), 0.91 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 138.2 (Ar), 137.7 (Ar), 128.8 (Ar), 128.4 (2 × Ar), 128.2 (2 × Ar), 128.0 (2 × Ar), 127.7 (Ar), 126.1 (2 × Ar), 101.6 (benzylidene *C*H), 99.2 (C-1), 79.1 (C-4), 78.1 (C-3), 75.9 (C-2), 73.5 (Ph*C*H$_2$), 68.9 (C-6), 67.9 (octyl O*C*H$_2$), 64.1 (C-5), 58.8 (O*C*H$_3$), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{29}H_{40}O_6]Na^+$: 507.2717. Found: 507.2715.

3.58. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-methyl-α-D-mannopyranoside (70)

Prepared from thioglycoside **52** (252 mg, 0.36 mmol), alcohol **61** (145 mg, 0.29 mmol), powdered 4 Å molecular sieves (250 mg), *N*-iodosuccinimide (110 mg, 0.44 mmol), and TMSOTf (27 mg, 0.12 mmol) in

CH_2Cl_2 (10 mL) as described for **31** to give **70** (272 mg, 89%) as a yellow oil: R_f 0.37 (3:1 hexane–EtOAc); $[\alpha]_D$ +5.6 (*c* 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 8.11–8.14 (m, 2H, ArH), 8.04–8.08 (m, 2H, ArH), 7.90–7.94 (m, 2H, ArH), 7.81–7.85 (m, 2H, ArH), 7.55–7.61 (m, 2H, ArH), 7.48–7.53 (m, 1H, ArH), 7.23–7.46 (m, 19H, ArH), 6.11 (dd, 1H, $J = 10.0$, 10.0 Hz, H-4′), 5.94 (dd, 1H, $J = 10.0$, 3.3 Hz, H-3′), 5.75 (dd, 1H, $J = 3.3$, 1.5 Hz, H-2′), 5.19 (d, 1H, $J = 1.5$ Hz, H-1′), 5.03 (d, 1H, $J = 11.5$ Hz, PhCH_2), 4.90 (d, 1H, $J = 2.0$ Hz, H-1), 4.78 (d, 1H, $J = 11.5$ Hz, PhCH_2), 4.74 (d, 1H, $J = 11.5$ Hz, PhCH_2), 4.61–4.69 (m, 2H, H-6a′, PhCH_2), 4.51 (ddd, 1H, $J = 10.0$, 4.3, 4.3 Hz, H-5′), 4.44 (dd, 1H, $J = 12.3$, 4.3 Hz, H-6b′), 3.94–4.00 (m, 2H, H-3, H-6a), 3.83–3.90 (m, 3H, H-4, H-5, H-6b), 3.80 (dt, 1H, $J = 10.0$, 6.5 Hz, octyl OCH_2), 3.58 (dd, 1H, $J = 3.0$, 2.0 Hz, H-2), 3.52 (s, 3H, OCH_3), 3.46 (dt, 1H, $J = 10.0$, 6.5 Hz, octyl OCH_2), 1.58–1.70 (m, 2H, octyl OCH_2CH_2), 1.19–1.43 (m, 10H, octyl CH_2), 0.85 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.2 (C=O), 165.4 (C=O), 165.2 (C=O), 165.2 (C=O), 138.4 (Ar), 133.3 (Ar), 133.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.7 (Ar), 129.5 (Ar), 129.3 (Ar), 129.2 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.2 (Ar), 127.9 (Ar), 127.7 (Ar), 127.7 (Ar), 97.6 (C-1′, $^1J_{C,H} = 175.8$ Hz), 97.1 (C-1, $^1J_{C,H} = 169.9$ Hz), 80.4 (C-3), 77.9 (C-2), 75.2 (Ph*C*H_2), 74.8 (C-4), 72.3 (Ph*C*H_2), 71.3 (C-5), 70.5 (C-2′), 70.0 (C-3′), 68.7 (C-5′), 67.9 (octyl O*C*H_2), 67.1 (C-6), 67.1 (C-4′), 62.8 (C-6′), 59.2 (O*C*H_3), 31.8 (octyl *C*H_2), 29.6 (octyl *C*H_2), 29.5 (octyl *C*H_2), 29.3 (octyl *C*H_2), 26.3 (octyl *C*H_2), 22.7 (octyl *C*H_2), 14.1 (octyl *C*H_3). ESIMS: *m*/*z* calcd for $[C_{63}H_{68}O_{15}]Na^+$: 1087.4450. Found: 1087.4455.

3.59. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,4-di-*O*-benzyl-3-*O*-methyl-α-D-mannopyranoside (71)

Prepared from thioglycoside **52** (225 mg, 0.32 mmol), alcohol **62** (130 mg, 0.27 mmol), powdered 4 Å molecular sieves (225 mg), *N*-iodosuccinimide (96 mg, 0.41 mmol), and TMSOTf (24 mg, 0.11 mmol) in CH_2Cl_2 (9 mL) as described for **31** to give **71** (275 mg, 96%) as a yellow oil: R_f 0.26 (4:1 hexane–EtOAc); $[\alpha]_D$ +2.1 (*c* 1.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 8.10–8.14 (m, 2H, ArH), 8.04–8.08 (m, 2H, ArH), 7.90–7.94 (m, 2H, ArH), 7.80–7.84 (m, 2H, ArH), 7.48–7.62 (m, 3H, ArH), 7.20–7.44 (m, 19H, ArH), 6.11 (dd, 1H, $J = 10.3$, 10.3 Hz, H-4′), 5.94 (dd, 1H, $J = 10.3$, 3.3 Hz, H-3′), 5.75 (dd, 1H, $J = 3.3$, 2.0 Hz, H-2′), 5.20 (d, 1H, $J = 2.0$ Hz, H-1′), 5.02 (d, 1H, $J = 12.3$ Hz, PhCH_2), 4.84 (d, 1H, $J = 1.5$ Hz, H-1), 4.79 (d, 1H, $J = 13.0$ Hz, PhCH_2), 4.73 (d, 1H, $J = 13.0$ Hz, PhCH_2), 4.67 (d, 1H, $J = 12.3$ Hz, PhCH_2), 4.63 (dd, 1H, $J = 12.4$, 2.5 Hz, H-6a′), 4.51 (ddd, 1H, $J = 10.3$, 3.8, 2.5 Hz, H-5′), 4.43 (dd, 1H, $J = 12.4$, 3.8 Hz, H-6b′), 3.99 (dd, 1H, $J = 11.0$, 5.5 Hz, H-6a), 3.80–3.92 (m, 4H, H-2, H-4, H-5, H-6b), 3.76 (dt, 1H, $J = 9.5$, 7.0 Hz, octyl OCH_2), 3.69 (dd, 1H, $J = 9.0$, 3.0 Hz, H-3), 3.39–3.48 (m, 4H, OCH_3, octyl OCH_2), 1.54–1.64 (m, 2H, octyl OCH_2CH_2), 1.16–1.42 (m, 10H, octyl CH_2), 0.84 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.2 (C=O), 165.4 (C=O), 165.2 (C=O), 165.2 (C=O), 138.6 (Ar), 138.4 (Ar), 133.3 (Ar), 133.0 (Ar), 133.0 (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.8 (Ar), 129.7 (Ar), 129.5 (Ar), 129.3 (Ar), 129.2 (Ar), 128.5 (Ar), 128.4 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.8 (Ar), 127.6 (Ar), 127.6 (Ar), 97.7 (C-1′, $^1J_{C,H} = 175.8$ Hz), 96.9 (C-1, $^1J_{C,H} = 175.8$ Hz), 82.2 (C-3), 75.0 (Ph*C*H_2), 74.9 (C-4), 74.1 (C-2), 72.7 (Ph*C*H_2), 71.1 (C-5), 70.5 (C-2′), 70.0 (C-3′), 68.7 (C-5′), 67.8 (octyl O*C*H_2), 67.2 (C-6), 67.1 (C-4′), 62.7 (C-6′), 57.5 (O*C*H_3), 31.8 (octyl *C*H_2), 29.5 (octyl *C*H_2), 29.5 (octyl *C*H_2), 29.3 (octyl *C*H_2), 26.2 (octyl *C*H_2), 22.6 (octyl *C*H_2), 14.1 (octyl *C*H_3). ESIMS: *m*/*z* calcd for $[C_{63}H_{68}O_{15}]Na^+$: 1087.4450. Found: 1087.4451.

3.60. Octyl 2,3-*O*-isopropylidene-4-*O*-methyl-α-D-mannopyranoside (72)

Methylation of monosaccharide **50** (735 mg, 1.3 mmol) was carried out using CH_3I (0.25 mL, 3.9 mmol) and 60% NaH in mineral oil (77 mg, 1.9 mmol) in DMF (20 mL) as described for **35**. The crude product that was desilylated in THF (8 mL) and TBAF (2.6 mL, 2.6 mmol) as described for **23** to give **72** (395 mg, 89% over two steps) as a colorless oil: R_f 0.23 (4:1 hexane–EtOAc); $[\alpha]_D$ +47.4 (c 2.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 5.00 (s, 1H, H-1), 4.20 (dd, 1H, $J = 7.0$, 7.0 Hz, H-3), 4.11 (d, 1H, $J = 7.0$ Hz, H-2), 3.91 (dd, 1H, $J = 11.5$, 3.5 Hz, H-6a), 3.74 (dd, 1H, $J = 11.5$, 4.5 Hz, H-6b), 3.67 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 3.52–3.58 (m, 4H, H-5, OCH_3), 3.40 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 3.31 (dd, 1H, $J = 10.0$, 7.0 Hz, H-4), 2.00 (br s, 1H, O*H*), 1.50–1.60 (m, 5H, isopropylidene CH_3, octyl OCH_2CH_2), 1.20–1.38 (m, 13H, isopropylidene CH_3, octyl CH_2), 0.88 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 109.2 (isopropylidene *C*), 97.1 (C-1), 78.4 (C-3), 78.4 (C-4), 75.9 (C-2), 68.3 (C-5), 67.8 (octyl O*C*H_2), 62.6 (C-6), 59.2 (O*C*H_3), 31.8 (octyl *C*H_2), 29.4 (octyl *C*H_2), 29.4 (octyl *C*H_2), 29.2 (octyl *C*H_2), 28.0 (isopropylidene *C*H_3), 26.3 (isopropylidene *C*H_3), 26.1 (octyl *C*H_2), 22.6 (octyl *C*H_2), 14.1 (octyl *C*H_3). Anal. Calcd for $C_{18}H_{34}O_6$ (346.46): C, 62.40; H, 9.89. Found: C, 62.45; H, 10.01. ESIMS: *m*/*z* calcd for $[C_{18}H_{34}O_6]Na^+$: 369.2248. Found: 369.2248.

3.61. Octyl 2,3-*O*-isopropylidene-4-*O*-phenoxythiocarbonyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (73)

Prepared from monosaccharide **50** (404 mg, 0.71 mmol), DMAP (220 mg, 1.78 mmol), and phenyl chlorothionoformate (0.13 mL, 0.92 mmol) in CH_3CN (2 mL) as described for **57**, to give **73** (419 mg, 84%) as a colorless oil: R_f 0.58 (9:1 hexane–EtOAc); $[\alpha]_D$ −21.3 (c 1.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.69–7.75 (m, 4H, ArH), 7.33–7.46 (m, 8H, ArH), 7.25–7.29 (m, 1H, ArH), 6.88–6.92 (m, 2H, ArH), 5.60 (dd, 1H, $J = 10.3$, 7.0 Hz, H-4), 5.11 (br s, 1H, H-1), 4.46 (dd, 1H, $J = 7.0$, 5.5 Hz, H-3), 4.23 (d, 1H, $J = 5.5$ Hz, H-2), 3.94–4.00 (m, 1H, H-5), 3.78–3.89 (m, 3H, H-6a, H-6b, octyl OCH_2), 3.46 (dt, 1H, $J = 9.5$, 6.8 Hz, octyl OCH_2), 2.09 (br s, 1H, OH), 1.56–1.64 (m, 2H, octyl OCH_2CH_2), 1.59 (s, 3H, isopropylidene CH_3), 1.39 (s, 3H, isopropylidene CH_3), 1.22–1.39 (m, 10H, octyl CH_2), 1.07 (s, 9H, *tert*-butyl CH_3), 0.89 (t, 3H, $J =$ 7.0 Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 194.8 (C=S), 153.5 (Ar), 135.8 (2 × Ar), 135.6 (2 × Ar), 133.3 (Ar), 133.2 (Ar), 129.6 (Ar), 129.6 (Ar), 129.4 (2 × Ar), 127.7 (2 × Ar), 127.7 (2 × Ar), 126.5 (Ar), 121.9 (2 × Ar), 110.1 (isopropylidene *C*), 96.6 (C-1), 79.9 (C-4), 76.1 (C-2), 75.7 (C-3), 69.2 (C-5), 67.6 (octyl OCH_2), 63.1 (C-6), 31.8 (octyl CH_2), 29.5 (octyl CH_2), 29.4 (octyl CH_2), 29.3 (octyl CH_2), 27.6 (isopropylidene CH_3), 26.8 (*tert*-butyl CH_3), 26.5 (isopropylidene CH_3), 26.2 (*tert*-butyl *C*), 22.7 (octyl CH_2), 19.2 (octyl CH_2), 14.1 (octyl CH_3). Anal. Calcd for $C_{40}H_{54}O_7SSi$ (706.34): C, 67.95; H, 7.70; S, 4.54. Found: C, 67.86; H, 7.78; S, 4.37. ESIMS: *m*/*z* calcd for $[C_{40}H_{54}O_7SSi]Na^+$: 729.3250. Found: 729.3252.

3.62. Octyl 4-deoxy-2,3-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-*lyxo*-hexopyranoside (74)

Prepared from phenoxythiocarbonyl derivative **73** (398 mg, 0.56 mmol) in toluene (12 mL) and a solution of tri-*n*-butylstannane (290 μL, 1.1 mmol) and AIBN (35 mg, 0.21 mmol) in toluene (50 mL) at reflux as described for **40** to give **74** (274 mg, 88%) as a colorless oil: R_f 0.27 (15:1 hexane–EtOAc); $[\alpha]_D$ +12.5 (c 2.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.67–7.72 (m, 4H, ArH), 7.36–7.45 (m, 6H, ArH), 5.04 (s, 1H, H-1), 4.37 (ddd, 1H, $J = 9.5$, 6.6, 6.3 Hz, H-3), 3.97 (d, 1H, $J = 6.3$ Hz, H-2), 3.78–3.84 (m, 1H, H-5), 3.70–3.78 (m, 2H, H-6a, octyl OCH_2), 3.62 (dd, 1H, $J = 10.3$, 4.8 Hz, H-6b), 3.41 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 1.90 (ddd, 1H, $J = 13.5$, 6.6, 2.3 Hz, H-4_{eq}), 1.50–1.62 (m, 3H, H-4_{ax}, octyl OCH_2CH_2), 1.49 (s, 3H, isopropylidene CH_3), 1.35 (s, 3H, isopropylidene CH_3), 1.22–1.36 (m, 10H, octyl CH_2), 1.07 (s, 9H, *tert*-butyl CH_3), 0.89 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 135.6 (4 × Ar), 133.5 (2 × Ar), 129.6 (Ar), 129.6 (Ar), 127.6 (4 × Ar), 108.7 (isopropylidene *C*), 97.4 (C-1), 73.4 (C-3), 71.0 (C-2), 67.4 (C-6), 67.0 (C-5), 66.7 (octyl OCH_2), 31.8 (octyl CH_2), 30.7 (C-4), 29.4 (octyl CH_2), 29.4 (octyl CH_2), 29.2 (octyl CH_2), 28.1 (isopropylidene CH_3), 26.8 (*tert*-butyl CH_3), 26.3 84 (isopropylidene CH_3), 26.2 (*tert*-butyl, *C*), 22.6 (octyl CH_2), 19.2 (octyl CH_2), 14.1 (octyl CH_3). Anal. Calcd for $C_{33}H_{50}O_5Si$ (554.34): C, 71.44; H, 9.08. Found: C, 71.45; H, 9.19. ESIMS: *m*/*z* calcd for $[C_{33}H_{50}O_5Si]Na^+$: 577.3320. Found: 577.3321.

3.63. Octyl 4-deoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hexopyranoside (75)

Prepared from deoxy monosaccharide **74** (237 mg, 0.43 mmol) in THF (12 mL) and TBAF (2.2 mL, 2.2 mmol) as described for **23** to give **75** (97 mg, 72%) as a colorless oil: R_f 0.27 (3:1 hexane–EtOAc); $[\alpha]_D$ +52.1 (*c* 0.9, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ_H 5.00 (br s, 1H, H-1), 4.39 (ddd, 1H, $J = 8.5$, 6.0, 6.0 Hz, H-3), 3.97 (d, 1H, $J = 6.0$ Hz, H-2), 3.80–3.86 (m, 1H, H-5), 3.71 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 3.65 (dd, 1H, $J = 11.8$, 3.5 Hz, H-6a), 3.61 (dd, 1H, $J = 11.8$, 6.8 Hz, H-6b), 3.43 (dt, 1H, $J = 9.5$, 6.5 Hz, octyl OCH_2), 1.88 (ddd, 1H, $J = 13.5$, 6.0, 3.8 Hz, H-4_{eq}), 1.54–1.66 (m, 3H, H-4_{ax}, octyl OCH_2CH_2), 1.52 (s, 3H, isopropylidene CH_3), 1.34 (s, 3H, isopropylidene CH_3), 1.22–1.36 (m, 10H, octyl CH_2), 0.88 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 109.0 (isopropylidene *C*), 97.7 (C-1), 73.4 (C-2), 70.4 (C-3), 67.9 (octyl OCH_2), 66.8 (C-5), 65.7 (C-6), 31.8 (octyl CH_2), 29.5 (octyl CH_2), 29.4 (octyl CH_2), 29.2 (octyl CH_2), 29.0 (C-4), 27.9 (isopropylidene CH_3), 26.2 (octyl CH_2), 26.1 (isopropylidene CH_3), 22.6 (octyl CH_2), 14.1 (octyl CH_3). Anal. Calcd for $C_{17}H_{32}O_5$ (316.22): C, 64.53; H, 10.19. Found: C, 64.58; H, 10.12. ESIMS: *m*/*z* calcd for $[C_{17}H_{32}O_5]Na^+$: 339.2142. Found: 339.2142.

3.64. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3-*O*-isopropylidene-4-*O*-methyl-α-D-mannopyranoside (76)

Prepared from thioglycoside **52** (130 mg, 0.19 mmol), alcohol **72** (54 mg, 0.16 mmol), powdered 4 Å molecular sieves (125 mg), *N*-iodosuccinimide (54 mg, 0.24 mmol), and TMSOTf (14 mg, 0.064 mmol) in CH_2Cl_2 (5 mL) as described for **31** to give **76** (117 mg, 79%) as a yellow oil: R_f 0.34 (4:1 hexane–EtOAc); $[\alpha]_D$ −19.0 (c 2.7, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ_H 8.11–8.15 (m, 2H, ArH), 8.04–8.08 (m, 2H, ArH), 7.90–7.94 (m, 2H, ArH), 7.81–7.84 (m, 2H, ArH), 7.56–7.62 (m, 2H, ArH), 7.49–7.53 (m, 1H, ArH), 7.34–7.45 (m, 7H, ArH), 7.24–7.29 (m, 2H, ArH), 6.14 (dd, 1H, $J = 10.2$, 10.2 Hz, H-4′), 5.94 (dd, 1H, $J = 10.2$, 3.3 Hz, H-3′), 5.73 (dd, 1H, $J = 3.3$, 1.8 Hz, H-2′), 5.19 (d, 1H,

$J = 1.8$ Hz, H-1′), 5.08 (br s, 1H, H-1), 4.74 (dd, 1H, $J = 12.3$, 2.4 Hz, H-6a′), 4.56 (ddd, 1H, $J = 10.2$, 3.9, 2.4 Hz, H-5′), 4.49 (dd, 1H, $J = 12.3$, 3.9 Hz, H-6b′), 4.27 (dd, 1H, $J = 6.9$, 6.0 Hz, H-3), 4.18 (d, 1H, $J = 6.0$ Hz, H-2), 3.99 (dd, 1H, $J = 10.8$, 6.6 Hz, H-6a), 3.86–3.92 (m, 2H, H-6b, octyl OCH_2), 3.83 (ddd, 1H, $J = 10.2$, 6.6, 1.8 Hz, H-5), 3.56 (s, 3H, OCH_3), 3.53 (dt, 1H, $J = 9.0$, 6.6 Hz, octyl OCH_2), 3.32 (dd, 1H, $J = 10.2$, 6.9 Hz, H-4), 1.62–1.72 (m, 2H, octyl OCH$_2$CH_2), 1.60 (s, 3H, isopropylidene CH_3), 1.17–1.46 (m, 13H, octyl CH_2, isopropylidene CH_3), 0.83 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.2 (C═O), 165.4 (C═O), 165.2 (C═O), 165.2 (C═O), 133.4 (Ar), 133.0 (Ar), 133.0 (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.4 (Ar), 129.2 (Ar), 129.1 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 109.3 (isopropylidene *C*), 97.3 (C-1′, $^1J_{C,H} = 172.3$ Hz), 96.9 (C-1, $^1J_{C,H} = 168.8$ Hz), 78.6 (C-3), 78.2 (C-4), 76.0 (C-2), 70.4 (C-2′), 70.0 (C-3′), 68.8 (C-5′), 67.8 (octyl O*C*H$_2$), 67.6 (C-4′), 66.9 (C-5), 66.9 (C-6), 62.8 (C-6′), 59.0 (O*C*H$_3$), 31.8 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 28.1 (isopropylidene *C*H$_3$), 26.4 (isopropylidene *C*H$_3$), 26.2 (octyl *C*H$_2$), 22.6 (octyl *C*H$_2$), 14.0 (octyl *C*H$_3$). Anal. Calcd for $C_{52}H_{60}O_{15}$ (925.02): C, 67.52; H, 6.54. Found: C, 67.20; H, 6.57. ESIMS: *m*/*z* calcd for $[C_{52}H_{60}O_{15}]Na^+$: 947.3824. Found: 947.3822.

3.65. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-4-deoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hexopyranoside (77)

Prepared from thioglycoside **52** (95 mg, 0.14 mmol), alcohol **75** (36 mg, 0.11 mmol), powdered 4 Å molecular sieves (100 mg), *N*-iodosuccinimide (39 mg, 0.17 mmol), and TMSOTf (4 μL, 0.023 mmol) in CH_2Cl_2 (4 mL) as described for **31** to give **77** (76 mg, 75%) as a colorless oil: R_f 0.27 (4:1 hexane–EtOAc); $[\alpha]_D$ −16.7 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.10–8.14 (m, 2H, ArH), 8.04–8.08 (m, 2H, ArH), 7.91–7.95 (m, 2H, ArH), 7.81–7.85 (m, 2H, ArH), 7.55–7.62 (m, 2H, ArH), 7.49–7.54 (m, 1H, ArH), 7.34–7.45 (m, 7H, ArH), 7.24–7.30 (m, 2H, ArH), 6.14 (dd, 1H, $J = 10.3$, 10.3 Hz, H-4′), 5.92 (dd, 1H, $J = 10.3$, 3.0 Hz, H-3′), 5.71 (dd, 1H, $J = 3.0$, 1.8 Hz, H-2′), 5.14 (d, 1H, $J = 1.8$ Hz, H-1′), 5.09 (br s, 1H, H-1), 4.73 (dd, 1H, $J = 12.3$, 2.3 Hz, H-6a′), 4.56–4.61 (m, 1H, H-5′), 4.48 (dd, 1H, $J = 12.3$, 4.3 Hz, H-6b′), 4.43 (ddd, 1H, $J = 9.0$, 6.4 Hz, H-3), 4.01–4.07 (m, 1H, H-5), 4.02 (d, 1H, $J = 6.0$ Hz, H-2), 3.88–3.97 (m, 2H, H-6a, octyl OCH_2), 3.60 (dd, 1H, $J = 10.0$, 3.5 Hz, H-6b), 3.54 (dt, $J = 9.5$, 6.5 Hz, octyl OCH_2), 1.94 (ddd, 1H, $J = 13.0$, 6.4, 2.5 Hz, H-4$_{eq}$), 1.53–1.72 (m, 3H, H-4$_{ax}$, octyl OCH$_2$CH_2), 1.54 (s, 3H, isopropylidene CH_3), 1.16–1.44 (m, 10H, octyl CH_2), 1.37 (s, 3H, isopropylidene CH_3), 0.82 (t, 3H, $J = 7.0$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.2 (C═O), 165.4 (C═O), 165.4 (C═O), 165.3 (C═O), 133.4 (Ar), 133.4 (Ar), 133.1 (Ar), 133.0 (Ar), 130.0 (Ar), 129.8 (Ar), 129.8 (Ar), 129.7 (Ar), 129.7 (Ar), 129.4 (Ar), 129.2 (Ar), 129.1 (Ar), 128.6 (Ar), 128.4 (Ar), 128.4 (Ar), 128.3 (Ar), 109.0 (isopropylidene *C*), 97.5 (C-1, $^1J_{C,H} = 168.5$ Hz), 97.1 (C-1′, $^1J_{C,H} = 172.9$ Hz), 73.3 (C-2), 70.6 (C-3), 70.5 (C-2′), 70.4 (C-6), 70.0 (C-3′), 68.8 (C-5′), 67.8 (octyl O*C*H$_2$), 66.8 (C-4′), 65.0 (C-5), 62.8 (C-6′), 31.8 (octyl *C*H$_2$), 30.3 (C-4), 29.5 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 28.1 (isopropylidene *C*H$_3$), 26.3 (octyl *C*H$_2$), 26.2 (isopropylidene *C*H$_3$), 22.6 (octyl *C*H$_2$), 14.0 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{51}H_{58}O_{14}]Na^+$: 917.3719. Found: 917.3716.

3.66. Octyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-4-*O*-methyl-α-D-mannopyranoside (78)

Prepared from disaccharide **76** (85 mg, 0.092 mmol) in 80% AcOH–H_2O (2 mL) as described for **54** to give **78** (79 mg, 97%) as a yellow oil: R_f 0.26 (1:1 hexane–EtOAc); $[\alpha]_D$ −12.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.10–8.13 (m, 2H, ArH), 8.06–8.09 (m, 2H, ArH), 7.93–7.97 (m, 2H, ArH), 7.84–7.87 (m, 2H, ArH), 7.55–7.62 (m, 2H, Ar), 7.49–7.53 (m, 1H, ArH), 7.34–7.45 (m, 7H, ArH), 7.24–7.29 (m, 2H, ArH), 6.15 (dd, 1H, $J = 10.2$, 10.2 Hz, H-4′), 5.94 (dd, 1H, $J = 10.2$, 3.0 Hz, H-3′), 5.74 (dd, 1H, $J = 3.0$, 1.8 Hz, H-2′), 5.41 (d, 1H, $J = 1.8$ Hz, H-1′), 4.84 (br s, 1H, H-1), 4.73 (dd, 1H, $J = 12.0$, 2.7 Hz, H-6a′), 4.58 (ddd, 1H, $J = 10.2$, 4.2, 2.7 Hz, H-5′), 4.51 (dd, 1H, $J = 12.0$, 4.2 Hz, H-6b′), 4.08 (dd, 1H, $J = 12.0$, 4.8 Hz, H-6a), 3.92–3.96 (m, 3H, H-2, H-3, H-6b), 3.69–3.78 (m, 2H, H-5, octyl OCH_2), 3.67 (s, 3H, OCH_3), 3.49 (dd, 1H, $J = 10.2$, 10.2 Hz, H-4), 3.44 (dt, 1H, $J = 9.6$, 6.6 Hz, octyl OCH_2), 2.55 (br s, 2H, O*H*), 1.55–1.64 (m, 2H, octyl OCH$_2$CH_2), 1.19–1.41 (m, 10H, octyl CH_2), 0.85 (t, 3H, $J = 7.2$ Hz, octyl CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.2 (C═O), 165.7 (C═O), 165.5 (C═O), 165.5 (C═O), 133.5 (Ar), 133.4 (Ar), 133.2 (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.3 (Ar), 129.1 (Ar), 129.0 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3 (Ar), 99.4 (C-1), 97.6 (C-1′), 77.6 (C-4), 72.1 (C-3), 71.3 (C-2), 70.9 (C-2′), 70.9 (C-5), 69.9 (C-3′), 69.0 (C-5′), 68.0 (octyl O*C*H$_2$), 66.9 (C-4′), 66.7 (C-6), 62.9 (C-6′), 60.9 (O*C*H$_3$), 31.8 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 26.2 (octyl *C*H$_2$), 22.6 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{52}H_{60}O_{15}]Na^+$: 907.3511. Found: 907.3509.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2007.05.001.

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