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Synthesis of monodeoxy and mono-*O*-methyl congeners of methyl β-D-mannopyranosyl-(1→2)-β-D-mannopyranoside for epitope mapping of anti-*Candida albicans* antibodies

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Dedicated to Professor Dr. Hans Kamerling on the occasion of his 65th birthday

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ABSTRACT

A panel of six complementary monodeoxy and mono-*O*-methyl congeners of methyl β-D-mannopyranosyl-(1→2)-β-D-mannopyranoside (**1**) were synthesized by stereoselective glycosylation of monodeoxy and mono-*O*-methyl monosaccharide acceptors with a 2-*O*-acetyl-glucosyl trichloroacetimidate donor, followed by a two-step oxidation–reduction sequence at C-2′. The β-*manno* configuration of the final deprotected congeners **2**–**7** was confirmed by measurement of $^{1}J_{C1,H1}$ heteronuclear and $^{3}J_{1',2'}$ homonuclear coupling constants. These disaccharide derivatives will be used to map the epitope recognized by a protective anti-*Candida albicans* monoclonal antibody C3.1 (IgG3) and to determine its key polar contacts with the binding site.

1. Introduction

Candida albicans, the causative agent of candidiasis, is a commensal fungus that commonly inhabits the gastrointestinal tract, oropharyngeal cavity and vulvovaginal tract of healthy humans.[1,2] However, risk of serious infection and occurrence of disease caused by this opportunistic pathogen is increased in immunocompromised patients and individuals undergoing long-term antibiotic treatment or major invasive surgery. Therapeutics to combat infection have been limited to triazole derivatives and amphotericin B.[3] However, the toxicity, emergence of resistance and costs of these antifungal agents are potential problems and highlight the need for alternative treatment strategies. The development of a vaccine against *Candida* is attracting attention and appears to be a potential soluion.[4,5] Whereas the α-mannan component of the *Candida* cell wall phosphomannan complex does not afford protective antibodies, the relatively short β-(1→2) mannan oligosaccharides that are attached to the α-mannan side chains are immunogenic and capable of raising protective antibodies. Consequently, antigens composed of this epitope have become an attractive component of a conjugate vaccine.[6,7]

Two monoclonal antibodies, an IgM (B6.1) and IgG (C3.1), raised against the PMC in mice, were both found to protect against subsequent infection.[8–10] Interestingly, though the β-(1→2)-linked mannan polymers vary in length from 1 to 7 residues, inhibition assays revealed that both mAbs were specific for a di- or trisaccharide. Furthermore, a novel pattern of antibody inhibition was observed using synthetic di- to hexasaccharides of (1→2)-β-D-mannopyranans, where maximum activity was reached with di- and trisaccharides and diminished significantly for larger structures.[11] This is in marked contrast to the paradigm elaborated by Kabat, wherein larger dextran homo-oligomers up to a hexa- or heptasaccharide exhibit increasing inhibitory activity with polyclonal antibodies.[12] Beyond the unique size dependence of the two *C. albicans* monoclonal antibodies described by Cutler and the conformational analysis of the homo-oligosaccharides,[9] no additional structural data are available for either the antibody or the antigenic determinant. Knowledge of the recognition elements of the protective epitope could provide important insights into the minimum-sized hapten that might be employed in a synthetic conjugate vaccine.

A strategy of chemical mapping, devised by Lemieux, is used to define the key polar contacts required for binding of the sugar to the antibody.[13,14] The relative activity of complementary monodeoxy and mono-*O*-methyl analogues in combination with conformational analysis helps to provide a three-dimensional model of

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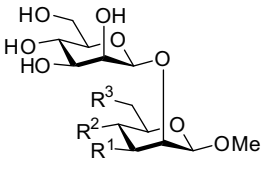


1, $R^1 = R^2 = R^3 = OH$
2, $R^1 = H$, $R^2 = R^3 = OH$
3, $R^1 = OCH_3$, $R^2 = R^3 = OH$
4, $R^2 = H$, $R^1 = R^3 = OH$
5, $R^2 = OCH_3$, $R^1 = R^3 = OH$
6, $R^3 = H$, $R^1 = R^2 = OH$
7, $R^3 = OCH_3$, $R^1 = R^2 = OH$

Figure 1. Native disaccharide **1** and the corresponding target deoxy and *O*-methyl congeners **2**–**7**.

the topography of the oligosaccharide epitope. To investigate in further detail the size and topology of the mAb IgG3 (C3.1) antibody binding site, a panel of six monodeoxy and mono-*O*-methyl congeners **2–7** of the disaccharide methyl β-D-mannopyranosyl-(1→2)-β-D-mannopyranoside (**1**) have been synthesized. For each congener, a single hydroxyl group on the reducing end residue of the parent disaccharide **1** has been modified by either deoxygenation or methylation (Fig. 1).

2. Results and discussion

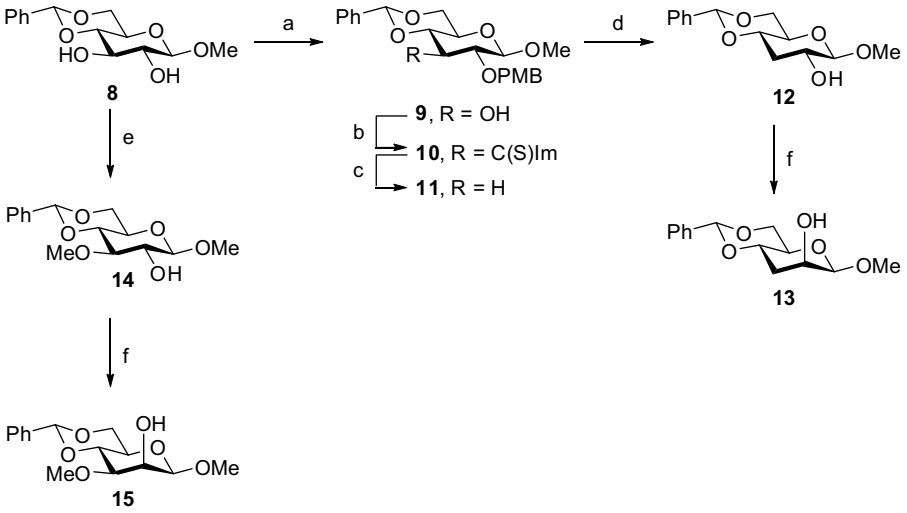
2.1. Synthesis of 3-deoxy and 3-*O*-methyl disaccharides 2 and 3

As illustrated in Scheme 1, the 3-deoxy and 3-*O*-methyl acceptors **13** and **15** were readily available from methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**8**).[15] Initial reaction of **8** under phase-transfer conditions[16] with *p*-methoxybenzyl chloride gave a mixture of 2-*O*- and 3-*O*-monobenzylated regioisomers. Although the desired 2-*O*-*p*-methoxybenzyl intermediate **9** was obtained in lower yield (30% yield), reaction scale-up provided sufficient quantities to proceed. Temporary protection of the 2-hydroxyl as the *p*-methoxybenzyl ether allowed for straightforward manipulation of the 3-hydroxyl group. The regiochemistry of **9** was confirmed by subsequent reaction with thiocarbonyl diimidazole in toluene at 80 °C to give **10** in 64% yield, in which the chemical shift of H-3 moved downfield from δ 3.82 to 6.11 ppm. The Barton–McCombie substrate **10** was then treated with tributyltin hydride in the presence of AIBN to afford the 3-deoxy intermediate **11** in 78% yield. Removal of the *p*-methoxybenzyl ether with DDQ in wet CH_2Cl_2 gave **12** in 86% yield and exposed the 2-hydroxyl group, which was then inverted from the *gluco* to the *manno* configuration via a standard two-step oxidation–reduction sequence.

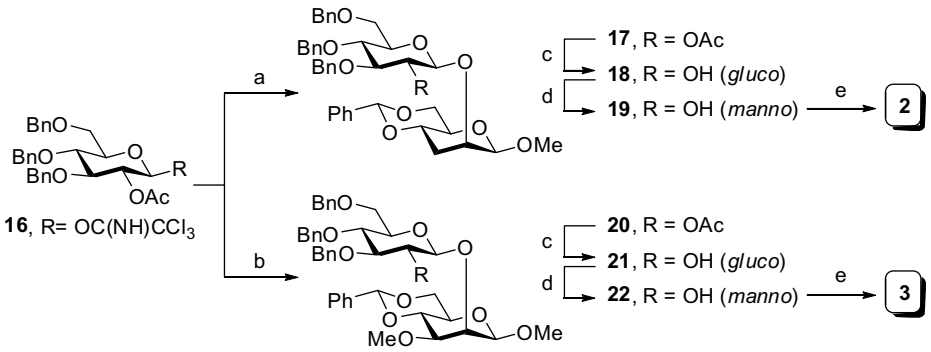
Oxidation of **12** by Me_2SO/Ac_2O[17] was followed by reduction with L-Selectride® in THF at −78 °C to give **13**. Lichtenthaler et al.[18] investigated the reduction of 2-keto groups with various hydride reagents and found L-Selectride® to reduce the carbonyl of several substrates with high *manno*-selectivity. Conversely, $NaBH_4$ was found to be selective with only fully benzylated substrates and gave poor *manno*- versus *gluco*-selectivity (7:1) with benzylidene-containing substrates.[15] In our case, oxidation then reduction of the benzylidene substrate **12** with L-Selectride® gave the desired 3-deoxy mannose acceptor **13** in 83% yield (exclusively *manno*); the observed $^3J_{1,2}$ 1.3 Hz for the product when compared to that of compound **12** indicated β-*manno* stereochemistry. A small amount of side product (usually 5–10%) was obtained and identified as methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-methylthiomethyl-β-D-glucopyranoside. It has previously been noted that the methylthiomethyl ether substituted by-product is formed under Me_2SO/Ac_2O oxidation conditions.[17]

The 3-*O*-methyl mannose acceptor **15** was prepared by direct methylation of methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**8**) using stannylidene chemistry (Scheme 1). Reaction with dibutyltin oxide in toluene at reflux, followed by treatment with methyl iodide in DMF, gave **14** in 71% yield. The *gluco*-intermediate **14** was then reacted following the standard oxidation–reduction sequence to afford the 3-*O*-methyl mannose acceptor **15** in 80% yield. The measured $^3J_{1,2}$ coupling constant (1.0 Hz) indicated inversion to the β-*manno*-configuration.

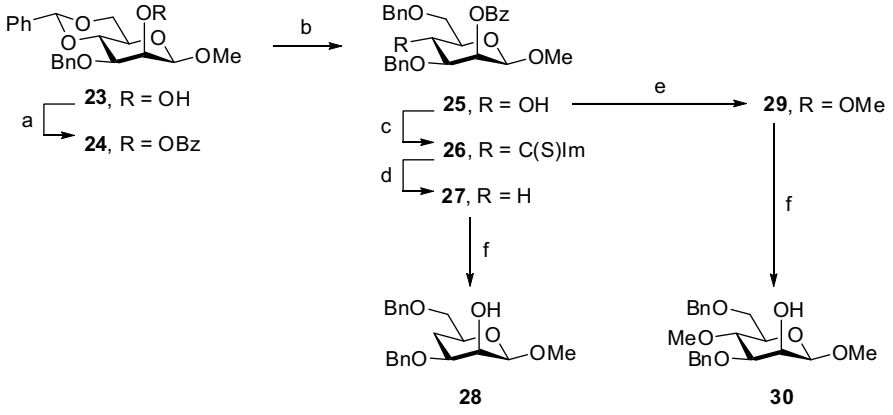
Glycosylation of the prepared 3-deoxy and 3-*O*-methyl acceptors **13** and **15**, with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate[19] donor **16,** gave intermediate disaccharides **17** (59% yield) and **20** (97% yield), respectively (Scheme 2). The synthesis of **17** was not optimized. Transesterification followed by the standard two-step oxidation–reduction sequence converted disaccharides **17** and **20** to intermediates **19** and **22**. For all oxidation–reduction sequences performed at C-2′ described in this paper, the inversion of stereochemistry was monitored by comparison of the $^3J_{1',2'}$ coupling constants preceding and following the two-step sequence. Typically, $^3J_{1,2}$ coupling for β-*gluco* structures is between 8 and 10 Hz and for β-*manno* <1 Hz. For compounds **18** and **21**, the $^3J_{1',2'}$ coupling constants measured 8.0 Hz, while the $^3J_{1',2'}$ proton coupling constants measured 0.8 Hz for both **19** and **22**, indicating inversion from β-*gluco* to β-*manno* stereochemistry. Global debenzylation by hydrogenolysis afforded the desired 3-deoxy **2** and 3-*O*-methyl **3** target analogues in 75% and 74% yields, respectively. The β-*manno* configurations of the final deprotected analogues



Scheme 1. Reagents and conditions: (a) PMBCl, CH_2Cl_2, *n*-Bu_4NHSO_4, 5% aq NaOH, 30%; (b) 1,1′-thiocarbonyldiimidazole, toluene, 64%; (c) *n*-Bu_3SnH, AIBN, toluene, 78%; (d) DDQ, CH_2Cl_2, H_2O, 86%; (e) *n*-Bu_2SnO, toluene, then MeI, DMF, 71%; (f) Me_2SO, Ac_2O, then L-Selectride, THF, −78 °C, 83% over two steps.



Scheme 2. Reagents and conditions: (a) **13**, TMSOTf, CH_2Cl_2, 0 °C, 59%; (b) **15**, TMSOTf, CH_2Cl_2, 0 °C, 97%; (c) $NaOCH_3$, CH_3OH, quant. (for **18**), 88% (for **21**); (d) Me_2SO, Ac_2O, then L-Selectride, THF, −78 °C, 65% (for **19** over two steps), 72% (for **22** over two steps); (e) H_2, Pd/C, CH_3OH, CH_2Cl_2, 75% (for **2**), 74% (for **3**).



Scheme 3. Reagents and conditions: (a) BzCl, pyridine, quant.; (b) $NaCNBH_3$, HCl, Et_2O, 81%; (c) 1,1′-thiocarbonyldiimidazole, toluene, 60%; (d) *n*-Bu_3SnH, AIBN, toluene, 68%; (e) MeI, NaH, DMF, 0 °C then AcOH, 97%; (f) $NaOCH_3$, CH_3OH, 89% (for **28**), 95% (for **30**).

described in this paper were confirmed by $^1J_{C1,H1}$ heteronuclear[20] and $^3J_{1',2'}$ homonuclear coupling constants. In all cases, the $^1J_{C1,H1}$ values were between 160 and 164 Hz, and the $^3J_{1',2'}$ values were <1 Hz.

2.2. Synthesis of 4-deoxy and 4-*O*-methyl disaccharides 4 and 5

The fully protected intermediate **24** obtained from benzoylation of methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (**23**)[15] provided a convenient strategy for accessing and modifying the C-4 hydroxyl group, while allowing temporary protection of the C-2 hydroxyl (Scheme 3). Regioselective reductive opening of the benzylidene acetal with sodium cyanoborohydride and HCl in ether[21] gave **25** in 81% yield and allowed for straightforward modification at C-4. The regioselectivity was confirmed by subsequent reaction of the hydroxyl with thiocarbonyl diimidazole in toluene at reflux to give **26** (60% yield), in which the chemical shift of H-4 moved downfield from δ 4.04 to 6.24. Treatment of the Barton–McCombie substrate with tributyltin hydride in the presence of AIBN gave the 4-deoxy substrate **27**. The temporary benzoyl group was removed by transesterification using sodium methoxide in methanol to give the 4-deoxy acceptor **28**.

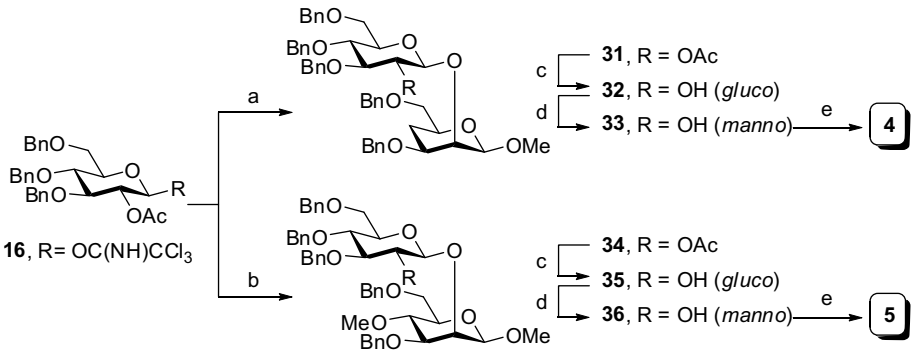
Methylation of intermediate **25** using methyl iodide and sodium hydride, followed by quenching with acetic acid, gave intermediate **29** (Scheme 3). Transesterification of the benzoyl group afforded the desired 4-*O*-methyl acceptor **30** in 95% yield.

Glycosylation of **28** and **30** with benzylated trichloroacetimidate[19] donor **16** under TMSOTf activation gave disaccharides **31** (83% yield) and **34** (97% yield), respectively (Scheme 4). The disaccharides were then treated with $NaOCH_3$–CH_3OH, followed by the standard oxidation–reduction sequence to provide intermediates **33** and **36**. Subsequent hydrogenolysis then afforded the 4-deoxy **4** (52% yield) and 4-*O*-methyl **5** (88% yield) disaccharide analogues, respectively. The $^1J_{C1,H1}$ and $^3J_{1',2'}$ coupling constants confirmed the β-*manno* configurations of both **4** and **5**.

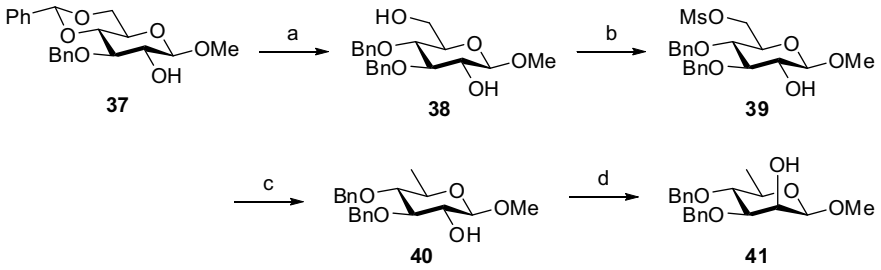
2.3. Synthesis of 6-deoxy and 6-*O*-methyl disaccharides 6 and 7

Reductive benzylidene acetal opening of methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**37**)[15] under anhydrous conditions with BH_3·THF and dibutylboron triflate[22] gave diol **38** in 83% yield (Scheme 5). Controlled reaction of the C-6 primary hydroxyl with methanesulfonyl chloride in pyridine gave intermediate **39** (66% yield). The downfield shift of the C-6 proton resonances (from δ 3.89 and 3.75 to δ 4.47 and 4.37) confirmed the regioselectivity of both the benzylidene acetal opening and selective sulfonylation. The 6-deoxy intermediate **40** was obtained in 80% yield by reductive displacement of the sulfonate using $NaBH_4$. The standard two-step oxidation–reduction sequence was then used to invert the *gluco*-configuration to yield the desired 6-deoxy mannose acceptor **41** (88% yield). The change in the $^3J_{1,2}$ coupling constant (from 7.6 to 1.1 Hz) indicated inversion to the β-*manno* configuration.

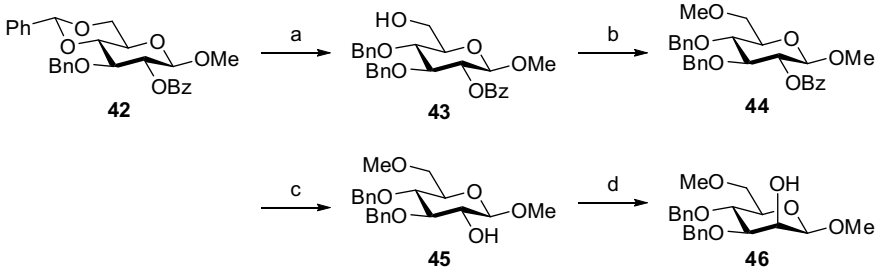
Reductive benzylidene acetal opening of methyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**42**)[23] under anhydrous conditions with BH_3·THF and dibutylboron triflate[22] gave **43** in 80% yield (Scheme 6). Methylation of the free C-6 hydroxyl group afforded **44**, which was subsequently reacted under Zemplén conditions to provide intermediate **45** (86% yield two steps). Again,



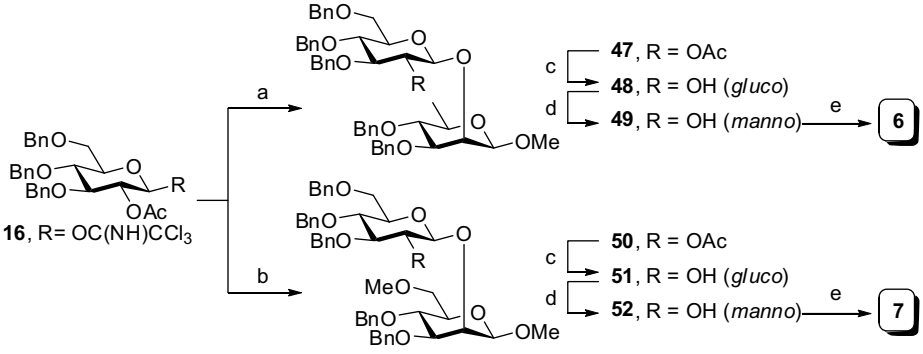
Scheme 4. Reagents and conditions: (a) **28**, TMSOTf, CH_2Cl_2, 0 °C, 83%; (b) **30**, TMSOTf, CH_2Cl_2, 0 °C, 97%; (c) $NaOCH_3$, CH_3OH, 78% (for **32**), 97% (for **35**); (d) Me_2SO, Ac_2O, then L-Selectride, THF, −78 °C, 65% (for **33** over two steps), 61% (for **36** over two steps); (e) H_2, Pd/C, CH_3OH, CH_2Cl_2, 52% (for **4**), 88% (for **5**).



Scheme 5. Reagents and conditions: (a) BH_3·THF, *n*-Bu_2BOTf, CH_2Cl_2, 0 °C, 83%; (b) MsCl, pyridine, 0 °C, 66%; (c) $NaBH_4$, DMF, 80 °C, 80%; (d) Me_2SO, Ac_2O, then L-Selectride, THF, −78 °C °C, 88%.



Scheme 6. Reagents and conditions: (a) BH_3·THF, *n*-Bu_2BOTf, CH_2Cl_2, 0 °C, 80%; (b) MeI, NaH, DMF, 0 °C, then AcOH, 96%; (c) $NaOCH_3$, CH_3OH, 90%; (d) Me_2SO, Ac_2O, then L-Selectride, THF, −78 °C, 85%.



Scheme 7. Reagents and conditions: (a) **41**, TMSOTf, CH_2Cl_2, 0 °C, 96%; (b) **46**, TMSOTf, CH_2Cl_2, 0 °C, 68%; (c) $NaOCH_3$, CH_3OH, quant. (for **48**), 96% (for **51**); (d) Me_2SO, Ac_2O, then L-Selectride, THF, −78 °C, 82% (for **49** over two steps), 78% (for **52** over two steps); (e) H_2, Pd/C, CH_3OH, CH_2Cl_2, 86% (for **6**), 69% (for **7**).

the standard two-step oxidation–reduction sequence was used to give the desired 6-*O*-methyl mannose acceptor **46** (85% yield). The change in the $^3J_{1,2}$ coupling constant (from 7.6 to 1.0 Hz) indicated inversion to the β-*manno* configuration.

Reaction of the 6-deoxy **41** and 6-*O*-methyl **46** acceptors with benzylated trichloroacetimidate[19] donor **16** under TMSOTf activation gave disaccharides **47** (96% yield) and **50** (68% yield), respectively (Scheme 7). The disaccharides were then treated with

$NaOCH_3$–CH_3OH followed by the oxidation–reduction sequence to provide intermediates **49** and **52**. Subsequent hydrogenolysis of **49** and **52** gave the desired 6-deoxy **6** (86% yield) and 6-*O*-methyl **7** (69% yield) disaccharide analogues, respectively. The $^1J_{C1,H1}$ and $^3J_{1',2'}$ coupling constants confirmed the β-*manno* configuration for both **6** and **7**.

2.4. Conclusion

In conclusion, a panel of six complementary deoxy and *O*-methyl analogues (**2**–**7**) modified on the reducing-end residue (C-3, C-4 and C-6) of methyl β-D-mannopyranosyl-(1→2)-β-D-mannopyranoside (**1**) have been synthesized. All deoxygenations and O-methylations were performed at the monosaccharide level producing six modified acceptors. The synthesis of the challenging (1→2)-β-D-*manno* linkage was approached by initial highly β-stereoselective glucosylation employing a common trichloroacetimidate donor capable of neighbouring group participation, followed by a two-step oxidation–reduction sequence at C-2′. The β-*manno* configurations of the final deprotected analogues were confirmed by measurement of $^1J_{C1,H1}$ heteronuclear and $^3J_{1',2'}$ homonuclear coupling constants. These final structures will serve as valuable tools to probe the key polar contacts involved in the binding of the protective anti-*C. albicans* mAb C3.1 (IgG3).[8–11]

3. Experimental

3.1. General methods

All chemical reagents were of analytical grade and used as obtained from commercial sources unless otherwise indicated. Solvents used in water-sensitive reactions were purified by successive passage through columns of alumina and copper under nitrogen, except for DMSO, which was distilled under vacuum and collected over 4 Å molecular sieves. Unless otherwise noted, reactions were carried out at room temperature, and water-sensitive reactions were performed under an atmosphere of argon. Molecular sieves were flame dried and then allowed to cool to room temperature under argon before use. Reactions were monitored by analytical thin-layer chromatography (TLC) performed on Silica Gel 60-F_{254} (E. Merck). Plates were visualized under UV light, and/or by treatment with 5% sulfuric acid in ethanol followed by heating. Organic solvents were removed under vacuum at <40 °C. Medium-pressure chromatography was conducted using silica gel (230–400 mesh, Silicycle, Montreal) at flow rates between 5 and 10 mL min^{-1}. Following deprotection, final compounds were passed through an Alltech Carbograph filter and then lyophilized. ^1H NMR spectra were recorded at 500 or 600 MHz, and chemical shifts, reported in δ (ppm), were referenced to internal residual protonated solvent signals or to external acetone (0.1% ext. acetone @ δ 2.225 ppm) in the case of D_2O. ^{13}C NMR spectra were recorded at 125 MHz, and chemical shifts are referenced to internal $CDCl_3$ (δ 77.23) or external acetone (δ 31.07).

3.2. Methyl β-D-mannopyranosyl-(1→2)-3-deoxy-β-D-*arabino*-hexopyranoside (2)

Compound **19** (49.0 mg, 0.070 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (10 mL) and stirred with 10% Pd/C (50 mg) under an H_2 atmosphere. The catalyst was separated by filtration through a Whatman membrane (0.45 μm, PVDF), and the filtrate was concentrated under reduced pressure. The residue was redissolved in H_2O, passed through an Alltech Carbograph filter and then lyophilized to yield **2** (17.8 mg, 75%) as a clear glass: R_f 0.25 (6:3.5:0.5, CH_2Cl_2–CH_3OH–H_2O); $[\alpha]_D$ −33 (*c* 0.27, H_2O); ^1H NMR (500 MHz, D_2O) δ 4.78 (d, 1H, $J_{1',2'}$ 0.8 Hz, H-1′), 4.63 (d, 1H, $J_{1,2}$ 1.2 Hz, H-1), 4.14 (m, 1H, H-2), 4.05 (dd, 1H, $J_{1',2'}$ 0.8, $J_{2',3'}$ 3.3 Hz, H-2′), 3.92 (dd, 1H, $J_{5',6'}$ 2.3, J_{gem} 12.3 Hz, H-6a′), 3.91 (dd, 1H, $J_{5,6}$ 2.7, J_{gem} 12.2 Hz, H-6a), 3.83 (ddd, 1H, $J_{3,4}$ 4.7, 11.0, $J_{4,5}$ 9.6 Hz, H-4), 3.73 (dd, 1H, $J_{5',6'}$ 6.5, J_{gem} 12.3 Hz, H-6b′), 3.72 (dd, 1H, $J_{5,6}$ 6.8, J_{gem} 12.2 Hz, H-6b), 3.63 (dd, 1H, $J_{2',3'}$ 3.3, $J_{3',4'}$ 9.6 Hz, H-3′), 3.56 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.6 Hz, H-4′), 3.53 (s, 3H, CH_3O), 3.50 (ddd, 1H, $J_{4,5}$ 9.3, $J_{5,6}$ 2.7, 6.8 Hz, H-5), 3.35 (ddd, 1H, $J_{4',5'}$ 9.6, $J_{5',6'}$ 2.3, 6.5 Hz, H-5′), 2.41 (ddd, 1H, $J_{2,3} \approx J_{3,4}$ 4.3, J_{gem} 13.6 Hz, H-3eq), 1.72 (ddd, 1H, $J_{2,3}$ 2.9, J_{gem} 13.6, $J_{3,4}$ 11.1 Hz, H-3ax); ^{13}C NMR (125 MHz, D_2O) δ 102.9 (C-1, $^1J_{C1,H1}$ 160.3 Hz, β), 101.8 (C-1′, $^1J_{C1',H1'}$ 160.6 Hz, β), 80.9 (C-5), 77.1 (C-5′), 75.7 (C-2), 73.7 (C-3′), 71.3 (C-2′), 67.7 (C-4′), 63.1 (C-4), 62.2, 62.0 (C-6′, C-6), 57.6 (CH_3O), 36.9 (C-3); HRESIMS: Calcd for $C_{13}H_{24}O_{10}Na$ 363.1262. Found 363.1264.

3.3. Methyl β-D-mannopyranosyl-(1→2)-3-O-methyl-β-D-mannopyranoside (3)

Compound **22** (50.7 mg, 0.070 mmol) was dissolved in 1:1 CH_2Cl_2–CH_3OH (10 mL) and stirred with 10% Pd/C (50 mg) under an H_2 atmosphere, then processed as described for **2**. Filtration, then lyophilization, gave **3** (19.1 mg, 74%) as a clear glass: R_f 0.23 (6.0:3.5:0.5, CH_2Cl_2–MeOH–H_2O); $[\alpha]_D$ −86 (*c* 0.37, H_2O); ^1H NMR (500 MHz, D_2O) δ 4.83 (s, 1H, H-1′), 4.60 (s, 1H, H-1), 4.52 (d, 1H, $J_{2,3}$ 3.1 Hz, H-2), 4.09 (d, 1H, $J_{2',3'}$ 1.8 Hz, H-2′), 3.93 (dd, 1H, $J_{5,6}$ 2.0, J_{gem} 12.3 Hz, H-6a), 3.93 (dd, 1H, $J_{5',6'}$ 1.8, J_{gem} 12.2 Hz, H-6a′), 3.77 (dd, 1H, $J_{5',6'}$ 5.8, J_{gem} 12.2 Hz, H-6b′), 3.74 (dd, 1H, $J_{5,6}$ 6.5, J_{gem} 12.3 Hz, H-6b), 3.64 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.9 Hz, H-4), 3.58-3.64 (m, 2H, H-3′, H-4′), 3.54 (s, 3H, CH_3O), 3.49 (s, 3H, CH_3O), 3.41 (ddd, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 2.2, 6.5 Hz, H-5), 3.38 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.8 Hz, H-3), 3.34 (ddd, 1H, $J_{4',5'}$ 9.5, $J_{5',6'}$ 2.2, 5.8 Hz, H-5′); ^{13}C NMR (125 MHz, D_2O) δ 102.6 (C-1, $^1J_{C1,H1}$ 158.5 Hz, β), 101.4 (C-1′, $^1J_{C1',H1'}$ 164.1 Hz, β), 82.2 (C-3), 77.3, 77.0 (C-5, C-5′), 73.9, 73.6 (C-2, C-4′), 71.3 (C-2′), 67.5, 66.7 (C-4, C-3′), 62.0, 61.9 (C-6, C-6′), 58.0 (CH_3O-C1), 57.2 (CH_3O-C3); HRESIMS: Calcd for $C_{14}H_{26}O_{11}Na$ 393.1367. Found 393.1366.

3.4. Methyl β-D-mannopyranosyl-(1→2)-4-deoxy-β-D-*lyxo*-hexopyranoside (4)

Compound **33** (49.1 mg, 0.062 mmol) was dissolved in 1:1 CH_2Cl_2–CH_3OH (10 mL) and stirred with 10% Pd/C (50 mg) under an H_2 atmosphere, then processed as described for **2**. Filtration, then lyophilization, gave **4** (11.0 mg, 52%) as a clear glass: R_f 0.27 (6:3.5:0.5, CH_2Cl_2–CH_3OH–H_2O); $[\alpha]_D$ −60 (*c* 0.58, H_2O); ^1H NMR (500 MHz, D_2O) δ 4.83 (s, 1H, H-1′), 4.51 (s, 1H, H-1), 4.12–4.13 (m, 2H, H-2′, H-2), 3.92 (dd, 1H, $J_{5',6'}$ 2.3, J_{gem} 12.3 Hz, H-6a′), 3.88 (ddd, 1H, $J_{2,3}$ 3.0, $J_{3,4eq}$ 5.0, $J_{3,4ax}$ 12.1 Hz, H-3) 3.63–3.73 (m, 5H, H-3′, H-6b′, H-5, H-6a, H-6b) 3.55 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.8, H-4′), 3.54 (s, 3H, CH_3O), 3.36 (ddd, 1H, $J_{5',6b'}$ 6.8 Hz, H-5′), 1.71 (ddd, 1H, J_{gem} 12.6, $J_{4,5}$ 0.8 Hz, H-4eq), 1.55 (ddd, 1H, $J_{4ax,5}$ 12.2 Hz, H-4ax); ^{13}C NMR (125 MHz, D_2O) δ 102.7 (C-1, $^1J_{C1,H1}$ 159.4 Hz, β), 101.3 (C-1′, $^1J_{C1',H1'}$ 162.4 Hz, β), 77.4 (C-2), 77.2 (C-5′), 74.0, 73.7 (C-3′, C-5), 71.3 (C-2′), 68.3 (C-3), 67.7 (C-4′), 64.6 (C-6), 62.0 (C-6′), 57.8 (CH_3O), 30.7 (C-4); HRESIMS: Calcd for $C_{13}H_{24}O_{10}Na$ 363.1262. Found 363.1261.

3.5. Methyl β-D-mannopyranosyl-(1→2)-4-O-methyl-β-D-mannopyranoside (5)

Compound **36** (51.8 mg, 0.063 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (10 mL) and stirred with 10% Pd/C (50 mg) under an H_2 atmosphere, then processed as described for **2**. Filtration, then lyophilization, gave **5** (20.4 mg, 88%) as a clear glass: R_f 0.48 (6:3.5:0.5, CH_2Cl_2–MeOH–H_2O); $[\alpha]_D$ −56 (*c* 0.50, H_2O); ^1H NMR

(500 MHz, D_2O) δ 4.82 (s, 1H, H-1′), 4.61 (s, 1H, H-1), 4.23 (d, 1H, $J_{2,3}$ 3.2Hz, H-2), 4.12 (d, 1H, $J_{2',3'}$ 3.3 Hz, H-2′), 3.91–3.93 (m, 2H, H-6a′, H-6a), 3.71–3.77 (m, 3H, H-6b′, H-3, H-6b), 3.63 (ddd, 1H, $J_{2',3'}$ 0.9, $J_{3',4'}$ 9.7 Hz, H-3′), 3.56 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.7 Hz, H-4′), 3.53 (s, 6H, CH_3OC-1, CH_3OC-4), 3.34–3.39 (m, 3H, H-5′, H-4, H-5); ^{13}C NMR (125 MHz, D_2O) δ 102.2 (C-1, $^1J_{C1,H1}$ 159.7Hz, β), 101.3 (C-1′, $^1J_{C1',H1'}$ 162.7 Hz, β), 78.7 (C-2), 78.0 (C-4), 77.2 (C-5′), 76.3 (C-5), 73.7 (C-3′), 73.0 (C-3), 71.2 (C-2′), 67.7 (C-4′), 62.0, 61.5 (C-6′, C-6), 61.1 (CH_3OC-4), 58.0 (CH_3OC-1); HRESIMS: Calcd for $C_{14}H_{26}O_{11}Na$ 393.1367. Found 393.1366.

3.6. Methyl β-D-mannopyranosyl-(1→2)-6-deoxy-β-D-mannopyranoside (6)

Compound **49** (55.0 mg, 0.070 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (10 mL) then stirred with 10% Pd/C (50 mg) under an H_2 atmosphere, then processed as described for **2**. Filtration, then lyophilization, gave **6** (20.4 mg, 86%) as a clear glass: R_f 0.49 (6:3.5:0.5, CH_2Cl_2–MeOH–H_2O); $[\alpha]_D$ −45 (*c* 1.1, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 4.82 (s, 1H, H-1′), 4.61 (s, 1H, H-1), 4.24 (d, 1H, $J_{2,3}$ 3.3 Hz, H-2), 4.10 (d, 1H, $J_{2',3'}$ 3.3 Hz, H-2′), 3.92 (dd, 1H, $J_{5',6'}$ 2.3, J_{gem} 12.3 Hz, H-6a′), 3.73 (dd, 1H, $J_{5',6'}$ 6.8, J_{gem} 12.3 Hz, H-6b′), 3.63 (dd, 1H, $J_{2',3'}$ 3.3, $J_{3',4'}$ 9.3Hz, H-3′), 3.58 (dd, 1H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.3 Hz, H-3) 3.55 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.7 Hz, H-4′), 3.51 (s, 3H, CH_3O), 3.34–3.42 (m, 3H, H-5′, H-4, H-5), 1.32 (d, 3H, $J_{5,6}$ 5.6 Hz, CH_3); ^{13}C NMR (125 MHz, D_2O) δ 102.1 (C-1, $^1J_{C1,H1}$ 152.3 Hz, β), 101.3 (C-1′, $^1J_{C1',H1'}$ 162.7 Hz, β), 78.6 (C-2), 77.2 (C-5′), 73.7, 73.4, 73.2, 72.9 (C-3′, C-3, C-4, C-5), 71.2 (C-2′), 67.7 (C-4′), 62.0 (C-6′), 57.9 (CH_3O), 17.5 (C-6); HRESIMS: Calcd for $C_{13}H_{24}O_{10}Na$ 363.1262. Found 363.1261.

3.7. Methyl β-D-mannopyranosyl-(1→2)-6-O-methyl-β-D-mannopyranoside (7)

Compound **52** (50.0 mg, 0.061 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (10 mL) and stirred with 10% Pd/C (50 mg) under an H_2 atmosphere, then processed as described for **2**. Filtration, then lyophilization, gave **7** (15.6 mg, 69%) as a clear glass: R_f 0.33 (6:3.5:0.5, CH_2Cl_2–CH_3OH–H_2O); $[\alpha]_D$ −73 (*c* 0.25, H_2O); ^{1}H NMR (500 MHz, D_2O) δ 4.82 (d, 1H, $J_{1',2'}$ 0.8 Hz, H-1′), 4.63 (s, 1H, H-1), 4.25 (d, 1H, $J_{2,3}$ 2.9 Hz, H-2), 4.11 (dd, 1H, $J_{1',2'}$ 0.7, $J_{2',3'}$ 3.3 Hz, H-2′), 3.92 (dd, 1H, $J_{5',6'}$ 2.3, J_{gem} 12.3 Hz, H-6a′), 3.80 (dd, 1H, $J_{5,6}$ 2.1, J_{gem} 11.2 Hz, H-6a), 3.73 (dd, 1H, $J_{5',6'}$ 6.7, J_{gem} 12.3 Hz, H-6b′), 3.67 (dd, 1H, $J_{5,6}$ 6.3, J_{gem} 11.3 Hz, H-6b), 3.62–3.64 (m, 2H, H-3′, H-3), 3.59 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.3Hz, H-4), 3.56 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.7 Hz, H-4′), 3.53 (s, 3H, CH_3O–C1), 3.49 (ddd, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 2.2, 6.3 Hz, H-5), 3.42 (s, 3H, CH_3O–C6), 3.36 (ddd, 1H, $J_{4',5'}$ 9.7, $J_{5',6'}$ 2.2, 6.6 Hz, H-5′); ^{13}C NMR (125 MHz, D_2O) δ 102.3 (C-1, $^1J_{C1,H1}$ 160.1 Hz, β), 101.3 (C-1′, $^1J_{C1,H1}$ 162.4 Hz, β), 78.5 (C-2), 77.2 (C-5′), 75.8 (C-5), 73.6, 73.1 (C-3′, C-3), 72.1 (C-6), 71.2 (C-2′), 68.1 (C-4), 67.7 (C-4′), 62.0 (C-6′), 59.4 (CH_3OC-6), 58.1 (CH_3OC-1); HRESIMS: Calcd for $C_{14}H_{26}O_{11}Na$ 393.1367. Found 393.1365.

3.8. Methyl 4,6-*O*-benzylidene-2-*O*-(4-methoxybenzyl)-β-D-glucopyranoside (9)

Methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**8**)[15] (3.0 g, 10.63 mmol), tetrabutylammonium hydrogensulfate (902 mg, 2.66 mmol) and 4-methoxybenzyl chloride (1.8 mL, 13.28 mmol) were dissolved in CH_2Cl_2 (80 mL). Aq NaOH (20 mL of a 5% solution) was added, and the mixture was stirred under reflux overnight. The reaction mixture was cooled, and the organic layer was separated, washed with water, dried (Na_2SO_4) and then concentrated under reduced pressure. Purification by chromatography on silica gel (4:1 hexanes–EtOAc) gave the 2-*O*-(4-methoxybenzyl) derivative **9** (1.28 g, 30%) and the 3-*O*-(4-methoxybenzyl) derivative (1.93 g, 45%) both as white solids; **9**: R_f 0.48 (1:1 hexanes–EtOAc); $[\alpha]_D$ −18 (*c* 0.73, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48–7.50 (m, 2H, ArH), 7.30–7.38 (m, 5H, ArH), 6.89–6.91 (m, 2H, ArH), 5.53 (s, 1H, PhCHO$_2$), 4.86 (d, 1H, J_{gem} 11.1Hz, PhCH_2O), 4.66 (d, 1H, PhCH_2O), 4.43 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 4.35 (dd, 1H, $J_{5,6}$ 4.9, J_{gem} 10.4 Hz, H-6a), 3.82 (dd, 1H, $J_{2,3} \approx J_{3,4}$ 9.1 Hz, H-3), 3.81 (s, 3H, CH_3O), 3.78 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.3 Hz, H-6b), 3.60 (s, 3H, CH_3O), 3.53 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.3 Hz, H-4), 3.42 (ddd, 1H, $J_{4,5}$ 9.7, $J_{5,6}$ 5.1, 9.7 Hz, H-5), 3.32 (dd, 1H, $J_{1,2}$ 7.8, $J_{2,3}$ 8.9 Hz, H-2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4 (Ar), 137.0 (Ar), 130.3 (Ar), 129.8 (Ar), 129.2 (Ar), 128.3 (Ar), 126.3 (Ar), 114.0 (Ar), 105.0 (C-1), 101.8 (PhCHO$_2$), 81.4 (C-2), 80.5 (C-4), 74.3 (PhCH_2O), 73.1 (C-3), 68.7 (C-6), 66.1 (C-5), 57.4 (CH_3O), 55.3 (CH_3O); HRESIMS: Calcd for $C_{22}H_{26}O_7Na$ 425.1571. Found 425.1570.

3.9. Methyl 4,6-*O*-benzylidene-2-*O*-(4-methoxybenzyl)-3-*O*-thiocarbonylimidazole-β-D-glucopyranoside (10)

The 2-*O*-(4-methoxybenzyl) derivative **9** (1.20 g, 2.98 mmol) was dissolved in dry toluene (20 mL). 1,1′-Thiocarbonyldiimidazole (1.06 g, 5.96 mmol) was added, and the reaction was stirred at reflux under argon overnight. The reaction mixture was cooled, then concentrated under reduced pressure. The black oily residue was subjected to chromatography on silica gel (7:3 hexanes–EtOAc) to give the Barton–McCombie substrate **10** (978 mg, 64%) as a white solid: R_f 0.24 (1:1 hexanes–EtOAc); $[\alpha]_D$ +10 (*c* 0.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (br s, 1H, imidazole), 7.44 (br s, 1H, imidazole), 7.36–7.38 (m, 2H, ArH), 7.31–7.32 (m, 3H, ArH), 7.08–7.10 (m, 2H, ArH), 6.99 (br s, 1H, imidazole), 6.66–6.67 (m, 2H, ArH), 6.11 (dd, 1H, $J_{2,3} \approx J_{3,4}$ 9.3 Hz, H-3), 5.46 (s, 1H, PhCHO$_2$), 4.74 (d, 1H, J_{gem} 11.8 Hz, PhCH_2O), 4.59 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.54 (d, 1H, J_{gem} 11.8 Hz, PhCH_2O), 4.41 (dd, 1H, $J_{5,6}$ 5.0, J_{gem} 10.5 Hz, H-6a), 3.80 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.3 Hz, H-6b), 3.76 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.5 Hz, H-4), 3.74 (s, 3H, CH_3O), 3.64 (s, 3H, CH_3O), 3.56–3.61 (m, 2H, H-2, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.7 (C=S), 159.5 (Ar), 136.7 (Ar), 136.5 (Ar), 130.5 (Ar), 130.0 (Ar), 129.2 (Ar), 129.1 (Ar), 128.2 (Ar), 126.1 (Ar), 118.2 (Ar), 113.6 (Ar), 105.3 (C-1), 101.4 (PhCHO$_2$), 81.0 (C-3), 78.7 (C-4), 78.0 (C-2/C-5), 73.6 (PhCH_2O), 68.7 (C-6), 65.7 (C-2/C-5), 57.7 (CH_3O), 55.1 (CH_3O); HRESIMS: Calcd for $C_{26}H_{28}N_2O_7SNa$ 535.1509. Found 535.1511. Anal. Calcd for $C_{26}H_{28}N_2O_7S$: C, 60.92; H, 5.51; N, 5.47; S, 6.26. Found: C, 61.03; H, 5.58; N, 5.46; S, 5.96.

3.10. Methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-(4-methoxybenzyl)-β-D-*ribo*-hexopyranoside (11)

To a solution of compound **10** (880 mg, 1.72 mmol) in dry toluene (20 mL) were added tributyltin hydride (1.50 mL, 5.16 mmol) and AIBN (71 mg, 0.43 mmol). The reaction was stirred at reflux under argon for 16 h, cooled then concentrated under reduced pressure. The residue was redissolved in a small volume of CH_2Cl_2 and passed through a plug of silica gel containing 10% (w/w) KF. The filtrate was concentrated, and the residue was subjected to chromatography on silica gel (4:1 hexane–EtOAc) to give the deoxygenated product **11** (515 mg, 78%) as a white solid: R_f 0.55 (1:1 hexanes–EtOAc); $[\alpha]_D$ −40 (*c* 0.76, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.48 (m, 2H, ArH), 7.34–7.47 (m, 3H, ArH), 7.26–7.29 (m, 2H, ArH), 6.87–6.89 (m, 2H, ArH), 5.49 (s, 1H, PhCHO$_2$), 4.72 (d, 1H, J_{gem} 11.5 Hz, PhCH_2O), 4.59 (d, 1H, J_{gem} 11.5 Hz, PhCH_2O), 4.39 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.32 (dd, 1H, $J_{5,6}$ 5.0, J_{gem} 10.6 Hz, H-6a), 3.81 (s, 3H, CH_3O), 3.74 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.3 Hz, H-6b), 3.59 (s, 3H, CH_3O), 3.51 (ddd, 1H, $J_{3eq,4}$ 4.4, $J_{3ax,4}$ 11.9, $J_{4,5}$ 9.1 Hz, H-4), 3.37–3.43 (m, 2H, H-2, H-5), 2.39 (ddd, 1H, $J_{2,3} \approx J_{3,4}$ 4.7, J_{gem} 12.1 Hz, H-3eq), 1.74 (ddd, 1H, $J_{2,3} \approx J_{3,4} \approx J_{gem}$ 11.8 Hz, H-3ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3 (Ar), 137.3

(Ar), 130.4 (Ar), 129.4 (Ar), 129.1 (Ar), 128.3 (Ar), 126.1 (Ar), 113.8 (Ar), 106.4 (C-1), 101.6 (PhCHO$_2$), 76.1 (C-4), 75.1 (C-2), 72.3 (PhCH$_2$O), 70.0 (C-5), 69.2 (C-6), 57.2 (CH$_3$O), 55.3 (CH$_3$O), 34.7 (C-3); HRESIMS: Calcd for $C_{22}H_{26}O_6Na$ 409.1622. Found 409.1618. Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 68.22; H, 6.77.

3.11. Methyl 4,6-*O*-benzylidene-3-deoxy-β-D-*ribo*-hexopyranoside (12)

To a solution of **11** (499 mg, 1.29 mmol mmol) in CH_2Cl_2 (22 mL) and H_2O (3 mL) at 0 °C (ice-water bath) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (879 mg, 3.87 mmol). The reaction was allowed to slowly warm to room temperature, and after 5 h it was diluted with CH_2Cl_2. The organic phase was washed with 10% aq $NaHCO_3$, distilled H_2O and brine, then dried (Na_2SO_4). Concentration under reduced pressure, followed by purification by column chromatography over silica gel (3:2 hexanes–EtOAc), gave **12** (294 mg, 86%) as a white solid: R_f 0.27 (1:1 hexanes–EtOAc); $[\alpha]_D$ −52 (*c* 0.47, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.50 (m, 2H, ArH), 7.34–7.40 (m, 3H, ArH), 5.54 (s, 1H, PhC*H*O$_2$), 4.34 (dd, 1H, $J_{5,6}$ 4.9, J_{gem} 10.5 Hz, H-6a), 4.26 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 3.78 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.4 Hz, H-6b), 3.57–3.63 (m, 2H, H-2, H-4), 3.58 (s, 3H, C*H*$_3$O), 3.46 (ddd, 1H, $J_{4,5}$ 9.1, $J_{5,6}$ 4.9, 10.1 Hz, H-5), 2.47 (ddd, 1H, $J_{2,3} \approx J_{3,4}$ 4.7, J_{gem} 11.9 Hz, H-3eq), 2.32 (br s, 1H, OH), 1.76 (ddd, 1H, $J_{2,3} \approx J_{gem} \approx J_{3,4}$ 11.7Hz, H-3ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3 (Ar), 129.1 (Ar), 128.3 (Ar), 126.2 (Ar), 106.4 (C-1), 101.8 (PhCHO$_2$), 76.2 (C-4), 70.6 (C-5), 69.2, 69.1 (C-2, C-6), 57.3 (CH$_3$O), 35.0 (C-3); HRESIMS: Calcd for $C_{14}H_{18}O_5Na$ 289.1047. Found 289.1046. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.11; H, 6.80.

3.12. Methyl 4,6-*O*-benzylidene-3-deoxy-β-D-*arabino*-hexopyranoside (13)

Compound **12** (294 mg, 1.10 mmol) was dissolved in a mixture of freshly distilled Me_2SO (6 mL) and Ac_2O (3 mL). After stirring for 8 h at room temperature, the reaction was concentrated under reduced pressure. The residue was redissolved in dry THF (10 mL) and cooled to −78 °C °C. A 1.0 M solution of L-Selectride® in THF (4.4 mL, 4.41 mmol) was added dropwise, and stirring was continued for 2 h at −78 °C. The reaction was quenched with MeOH then diluted with CH_2Cl_2. The mixture was washed with 10% aq H_2O_2, 1 M aq NaOH, distilled H_2O, then brine. The organic phase was dried (Na_2SO_4), then concentrated under reduced pressure. Purification by chromatography over silica gel (3:2 hexanes–EtOAc) gave **13** (243 mg, 83%) as a white solid: R_f 0.28 (1:1 hexanes–EtOAc); $[\alpha]_D$ −64 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.50 (m, 2H, ArH), 7.32–7.39 (m, 3H, ArH), 5.57 (s, 1H, PhC*H*O$_2$), 4.50 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.31 (dd, 1H, $J_{5,6}$ 5.0, J_{gem} 10.4 Hz, H-6eq), 3.98–4.03 (m, 2H, H-2, H-4), 3.84 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.3, H-6ax), 3.58 (s, 3H, C*H*$_3$O), 3.45 (dd, 1H, $J_{4,5}$ 9.3, $J_{5,6}$ 5.0, 10.1 Hz, H-5), 2.44 (dd, 1H, $J_{2,OH} \approx J_{3ax,OH}$ 1.7 Hz, C2-OH), 2.39 (ddd, 1H, *J* 3.2, 4.5, J_{gem} 13.4 Hz, H-3eq), 1.79 (dddd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 11.8, J_{gem} 13.5, $J_{3,OH}$ 1.9 Hz, H-3ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5 (Ar), 129.0 (Ar), 128.3 (Ar), 126.1 (Ar), 102.0, 101.8 (C-1, PhCHO$_2$), 73.5 (C-4), 70.6 (C-5), 69.0 (C-6), 67.9 (C-2), 56.8 (CH$_3$O), 33.9 (C-3); HRESIMS: Calcd for $C_{14}H_{18}O_5Na$ 289.1046. Found 289.1043. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.05; H, 6.88.

3.13. Methyl 4,6-*O*-benzylidene-3-*O*-methyl-β-D-glucopyranoside (14)

Methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**8**)[15] (1.5 g, 5.31 mmol) and dibutyltin oxide (1.46 g, 5.88 mmol) were refluxed overnight in toluene (40 mL) with azeotropic removal of water using a Dean–Stark trap. The reaction mixture was cooled to room temperature, then concentrated under reduced pressure. The solid residue was redissolved in DMF (15 mL), methyl iodide (3.3 mL, 53.4 mmol) added, and the reaction was stirred at 40 °C. After 15 h, the reaction was cooled, then concentrated under reduced pressure. Purification by chromatography over silica gel (1:1 toluene–EtOAc) gave **14** (1.11 g, 71%) as a white solid: R_f 0.22 (1:1 hexanes–EtOAc); $[\alpha]_D$ −50 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.50 (m, 2H, ArH), 7.34–7.40 (m, 3H, ArH), 5.56 (s, 1H, PhC*H*O$_2$), 4.36 (dd, 1H, $J_{5,6}$ 5.0, J_{gem} 10.4 Hz, H-6eq), 4.35 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 3.80 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.3 Hz, H-6ax), 3.68 (s, 3H, C*H*$_3$O), 3.63 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.2 Hz, H-4), 3.59 (s, 3H, C*H*$_3$O), 3.42–3.49 (m, 3H, H-2, H-3, H-5), 2.53 (d, 1H, $J_{2,OH}$ 1.9 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2 (Ar), 129.0 (Ar), 128.3 (Ar), 126.0 (Ar), 104.2 (C-1), 101.3 (PhCHO$_2$), 82.2 (C-3), 81.6 (C-4), 74.1 (C-2), 68.7 (C-6), 66.4 (C-5), 60.9 (CH$_3$O), 57.4 (CH$_3$O); HRESIMS: Calcd for $C_{15}H_{20}O_6Na$ 319.1152. Found 319.1152. Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.92; H, 6.75.

3.14. Methyl 4,6-*O*-benzylidene-3-O-methyl-β-D-mannopyranoside (15)

Compound **14** (446 mg, 1.51 mmol) was dissolved in a mixture of Me_2SO (6 mL) and Ac_2O (3 mL). After stirring overnight, the mixture was concentrated under reduced pressure. The remaining solid was redissolved in 1:1 CH_2Cl_2–MeOH (10 mL) and cooled to 0 °C (ice-water bath). $NaBH_4$ (286 mg, 7.53 mmol) was added, and the reaction was stirred until starting material was consumed according to TLC. The reaction was diluted with CH_2Cl_2, then washed successively with 2% aq citric acid, brine and dried (Na_2SO_4), then concentrated under reduced pressure. Chromatography over silica gel (7:3 hexanes–EtOAc) gave **15** (356 mg, 80%) as a white solid: R_f 0.07 (1:1 hexanes–EtOAc); $[\alpha]_D$ −74 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48–7.50 (m, 2H, ArH), 7.33–7.38 (m, 3H, ArH), 5.59 (s, 1H, PhC*H*O$_2$), 4.48 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.35 (dd, 1H, $J_{5,6}$ 5.0, J_{gem} 10.3 Hz, H-6eq), 4.21 (d, 1H, $J_{2,3}$ 3.2 Hz, H-2), 4.06 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.5 Hz, H-4), 3.89 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.3Hz, H-6ax), 3.59 (s, 3H, C*H*$_3$O), 3.58 (s, 3H, C*H*$_3$O), 3.47 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.6 Hz, H-3), 3.39 (ddd, 1H, $J_{4,5}$ 9.8, $J_{5,6}$ 4.9, 9.8 Hz, H-5), 2.49 (br s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4 (Ar), 129.0 (Ar), 128.2 (Ar), 126.1 (Ar), 101.7, 101.4 (C-1, PhCHO$_2$), 79.3 (C-3), 78.4 (C-4), 69.0 (C-2), 68.6 (C-6), 66.8 (C-5), 58.6 (CH$_3$O), 57.3 (CH$_3$O); HRESIMS: Calcd for $C_{15}H_{20}O_6Na$ 319.1152. Found 319.1154. Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 61.20; H, 6.73.

3.15. Methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-4,6-*O*-benzylidene-3-deoxy-β-D-*arabino*-hexopyranoside (17)

Monosaccharide acceptor **13** (120 mg, 0.45 mmol) was reacted with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (**16**) (344 mg, 0.54 mmol) in CH_2Cl_2 (5 mL) using TMSOTf (5 μL, 0.03 mmol) under argon at 0 °C. The reaction was neutralized with Et_3N, filtered through Celite then concentrated under reduced pressure. The product was purified by chromatography over silica gel (7:3 hexanes–EtOAc) to give **17** (196 mg, 59%) as a white solid: R_f 0.52 (1:1 hexanes–EtOAc); $[\alpha]_D$ −24 (*c* 0.24, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.48 (m, 2H, ArH), 7.25–7.38 (m, 16H, ArH), 7.18–7.20 (m, 2H, ArH), 5.57 (s, 1H, PhC*H*O$_2$), 5.00 (dd, 1H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 9.3 Hz, H-2′), 4.81 (d, 1H, J_{gem} 10.8 Hz, PhC*H*$_2$O), 4.78 (d, 1H, J_{gem} 11.5 Hz, PhC*H*$_2$O), 4.73 (d, 1H, J_{gem} 11.2 Hz, PhC*H*$_2$O), 4.73 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.62 (d, 1H, J_{gem} 12.4 Hz, PhC*H*$_2$O), 4.57 (d, 1H, J_{gem} 10.9 Hz, PhC*H*$_2$O), 4.55 (d, 1H, J_{gem} 12.3 Hz, PhC*H*$_2$O), 4.39 (d, 1H, $J_{1,2}$ 0.8 Hz, H-1), 4.26 (dd,

1H, $J_{5,6}$ 4.9, J_{gem} 10.3 Hz, H-6eq), 4.03 (ddd, 1H, $J_{1,2}$ 0.9, $J_{2,3}$ 3.1 Hz, H-2), 3.93 (ddd, 1H, $J_{3,4}$ 4.6, 12.6 Hz, $J_{4,5}$ 9.5 Hz, H-4), 3.80 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.2 Hz, H-6ax), 3.63–3.74 (m, 4H, H-3′, H-4′, H-6a′, H-6b′), 3.48 (ddd, 1H, $J_{4',5'}$ 9.6, $J_{5',6'}$ 2.6, 4.7Hz, H-5′), 3.47 (s, 3H, CH_3O), 3.40 (ddd, 1H, $J_{4,5}$ 9.4, $J_{5,6}$ 4.9, 10.1 Hz, H-5), 2.39 (ddd, 1H, $J_{2,3}$ 4.0, J_{gem} 12.7, $J_{3,4}$ 4.0 Hz, H-3eq), 2.00 (s, 3H, $CH_3C(O)O$), 1.76 (ddd, 1H, $J_{2,3}$ 2.7, J_{gem} 12,4, $J_{3,4}$ 12.4Hz, H-3ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9 (C═O), 138.4 (Ar), 138.2 (Ar), 138.0 (Ar), 137.7 (Ar), 128.9 (Ar), 128.3(8) (Ar), 128.3(6) (Ar), 128.3 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7(4) (Ar), 127.6(7) (Ar), 127.6(2) (Ar), 127.5(7) (Ar), 126.1 (Ar), 103.2 (C-1), 101.8 ($PhCHO_2$), 101.5 (C-1′), 82.8 (C-3′), 77.9 (C-4′), 75.0(4), 75.0(0), 74.8 (C-5′, $PhCH_2O \times 2$), 73.7, 73.6 (C-2′, C-2, C-4), 73.4 ($PhCH_2O$), 71.1 (C-5), 69.0, 68.9 (C-6′, C-6), 56.8 (CH_3O), 34.7 (C-3), 21.1 ($CH_3C(O)O$); HRESIMS: Calcd for $C_{43}H_{48}O_{11}Na$ 763.3089. Found 763.3084. Anal. Calcd for $C_{43}H_{48}O_{11}$: C, 69.71; H, 6.53. Found: C, 69.68; H, 6.64.

3.16. Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-4,6-*O*-benzylidene-3-deoxy-β-D-arabino-hexopyranoside (18)

Disaccharide **17** (176 mg, 0.24 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (2 mL) and treated with 0.5 M $NaOCH_3$–CH_3OH (2 mL). After 2 h, the reaction was neutralized with Amberlite IR-120 (H^+) resin and filtered. Purification of the product by chromatography over silica gel (7:3 hexanes–EtOAc) gave **18** (166 mg, quant.) as a white solid: R_f 0.33 (1:1 hexanes–EtOAc); $[\alpha]_D$ −5 (*c* 0.82, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.47–7.50 (m, 2H, ArH), 7.23–7.42 (m, 16H, ArH), 7.18–7.20 (m, 2H, Ar), 5.59 (s, 1H, $PhCHO_2$), 5.05 (d, 1H, J_{gem} 11.2 Hz, $PhCH_2O$), 4.87 (d, 1H, J_{gem} 10.9 Hz, $PhCH_2O$), 4.80 (d, 1H, J_{gem} 11.2 Hz, $PhCH_2O$), 4.60 (d, 1H, J_{gem} 12.2 Hz, $PhCH_2O$), 4.55 (d, 1H, J_{gem} 12.4 Hz, $PhCH_2O$), 4.54 (d, 1H, J_{gem} 10.8 Hz, $PhCH_2O$), 4.50 (s, 1H, H-1), 4.41 (d, 1H, $J_{1',2'}$ 7.3 Hz, H-1′), 4.32 (dd, 1H, $J_{5,6}$ 4.9, J_{gem} 10.4 Hz, H-6eq), 4.01–4.06 (m, 2H, H-2, H-4), 3.87 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.4 Hz, H-6ax), 3.63–3.74 (m, 4H, H-2′, H-3′, H-6a′, H-6b′), 3.56–3.60 (m, 4H, H-4′, CH_3O), 3.44–3.52 (m, 2H, H-5′, H-5), 2.55 (ddd, 1H, $J_{2,3} \approx J_{3,4}$ 3.8, J_{gem} 13.1 Hz, H-3eq), 1.84 (ddd, 1H, $J_{2,3}$ 1.8, $J_{3,4} \approx J_{gem}$ 12.9 Hz, H-3ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9 (Ar), 138.2 (Ar), 138.1 (Ar), 137.5 (Ar), 129.0 (Ar), 128.3(8) (Ar), 128.3(5) (Ar), 128.3(2) (Ar), 128.3(1) (Ar), 128.0(0) (Ar), 127.9(8) (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 126.1 (Ar), 106.0 (C-1′), 102.5 (C-1), 101.9 ($PhCHO_2$), 84.8 (C-2′), 77.6 (C-2), 77 (C-4′), 75.6, 75.3 (C-5′, C-3), 75.1 ($PhCH_2O$), 74.9 ($PhCH_2O$), 73.7, 73.5 (C-4, $PhCH_2O$), 70.9 (C-5), 69.0(2), 68.9(7) (C-6′, C-6), 57.2 (CH_3O), 35.0 (C-3); HRESIMS: Calcd for $C_{41}H_{46}O_{10}Na$ 721.2983. Found 721.2986. Anal. Calcd for $C_{41}H_{46}O_{10}$: C, 70.47; H, 6.63. Found: C, 70.47; H, 6.68.

3.17. Methyl 3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1→2)-4,6-*O*-benzylidene-3-deoxy-β-D-arabino-hexopyranoside (19)

Disaccharide **18** (140 mg, 0.200 mmol) was dissolved in freshly distilled Me_2SO (5 mL) and Ac_2O (5 mL). The mixture was concentrated under reduced pressure, then the residue was redissolved in dry THF and cooled to −78 °C under argon. The reaction mixture was then treated with 1.0 M L-Selectride® in THF (1 mL, 1 mmol) in dry THF (10 mL). Purification by column chromatography over silica gel (7:3 hexanes–EtOAc) gave **19** (90.8 mg, 65%) as a white solid: R_f 0.26 (1:1 hexanes–EtOAc); $[\alpha]_D$ −15 (*c* 0.60, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.47–7.49 (m, 2H, ArH), 7.21–7.39 (m, 18H, ArH), 5.56 (s, 1H, $PhCHO_2$), 4.91 (d, 1H, J_{gem} 10.9 Hz, $PhCH_2O$), 4.80 (d, 1H, J_{gem} 11.9 Hz, $PhCH_2O$), 4.71 (d, 1H, $J_{1',2'}$ 0.8 Hz, H-1′), 4.65 (d, 1H, J_{gem} 12.0 Hz, $PhCH_2O$), 4.60 (d, 1H, J_{gem} 12.2 Hz, $PhCH_2O$), 4.56 (d, 1H, J_{gem} 10.9Hz, $PhCH_2O$), 4.55 (d, 1H, J_{gem} 12.3 Hz, $PhCH_2O$), 4.46 (d, 1H, $J_{1,2}$ 1.1 Hz, H-1), 4.31 (dd, 1H, $J_{5,6}$ 4.9, J_{gem} 10.4 Hz, H-6eq), 4.29 (dd, 1H, $J_{1',2'}$ 0.9, $J_{2',3'}$ 3.0 Hz, H-2′), 4.14 (ddd, 1H, H-2), 4.01 (ddd, 1H, $J_{3,4}$ 3.3, 12.0, $J_{4,5}$ 9.2 Hz, H-4), 3.87 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.3 Hz, H-6ax), 3.85 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.3 Hz, H-4′), 3.76 (dd, 1H, $J_{5',6'}$ 2.0, J_{gem} 10.8 Hz, H-6a′), 3.68 (dd, 1H, $J_{5',6'}$ 5.7, J_{gem} 10.8 Hz, H-6b′), 3.57 (dd, 1H, $J_{2',3'}$ 3.0, $J_{3',4'}$ 9.1 Hz, H-3′), 3.52 (s, 3H, CH_3O), 3.42–3.48 (m, 2H, H-5′, H-5), 2.51 (ddd, 1H, $J_{2,3} \approx J_{3,4}$ 4.0, J_{gem} 13.1 Hz, H-3eq), 1.83 (ddd, 1H, $J_{2,3}$ 2.9, J_{gem} 13.0, $J_{3,4}$ 12.0 Hz, H-3ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2(8), 138.2(6), 137.9, 137.5, 129.0, 128.4, 128.3(4), 128.2(8), 128.1, 127.9, 127.8, 127.7(1), 127.6(9), 127.5, 126.1, 103.2, 101.8, 100.9, 81.4, 75.4, 75.1, 74.3, 74.1, 73.8, 73.5, 71.1(3), 71.0(9), 69.5, 68.9, 67.8, 57.3, 34.7; HRESIMS: Calcd for $C_{41}H_{46}O_{10}Na$ 721.2983. Found 721.2985.

3.18. Methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-methyl-β-D-mannopyranoside (20)

Monosaccharide acceptor **15** (205 mg, 0.69 mmol) was reacted with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (**16**) (484 mg, 0.76 mmol) in CH_2Cl_2 (5 mL) using TMSOTf (6 μL, 0.03 mmol) under argon at 0 °C, then processed as described for **17**. The product was purified by chromatography over silica gel (7:3 hexanes–EtOAc) to give **20** (513 mg, 97%) as a white solid: R_f 0.49 (1:1 hexanes–EtOAc); $[\alpha]_D$ −40 (*c* 0.67, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.46–8.48 (m, 2H, ArH), 7.27–7.36 (m, 16H, ArH), 7.21–7.22 (m, 2H, ArH), 5.57 (s, 1H, $PhCHO_2$), 5.10 (dd, 1H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 9.6 Hz, H-2′), 4.82 (d, 1H, J_{gem} 11.0 Hz, $PhCH_2O$), 4.79 (d, 1H, J_{gem} 11.5 Hz, $PhCH_2O$), 4.77 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.75 (d, 1H, J_{gem} 11.5 Hz, $PhCH_2O$), 4.58 (d, 1H, J_{gem} 12.1 Hz, $PhCH_2O$), 4.57 (d, 1H, J_{gem} 11.0 Hz, $PhCH_2O$), 4.54 (d, 1H, J_{gem} 12.0 Hz, $PhCH_2O$), 4.35 (s, 1H, H-1), 4.28 (dd, 1H, $J_{5,6}$ 4.7, J_{gem} 10.1 Hz, H-6eq), 4.26 (d, 1H, $J_{2,3}$ 3.0 Hz, H-2), 3.99 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.6 Hz, H-4), 3.82 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.2 Hz, H-6b), 3.75 (dd, 1H, $J_{2',3'}$ 9.5, $J_{3',4'}$ 8.5 Hz, H-3′), 3.74 (dd, 1H, $J_{5',6'}$ 1.8, J_{gem} 10.9 Hz, H-6a′), 3.63 (dd, 1H, $J_{5',6'}$ 6.2, J_{gem} 10.9 Hz, H-6b′), 3.57 (dd, 1H, $J_{3',4'}$ 8.6, $J_{4',5'}$ 9.8 Hz, H-4′), 3.53 (ddd, 1H, $J_{4',5'}$ 9.8, $J_{5',6'}$ 1.7, 6.0Hz, H-5′), 3.49 (s, 3H, CH_3O), 3.46 (s, 3H, CH_3O), 3.37 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 10.0 Hz H-3), 3.33 (ddd, 1H, $J_{4,5}$ 9.9, $J_{5,6}$ 5.0, 9.9 Hz, H-5), 1.99 (s, 3H, $CH_3C(O)O$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7 (C═O), 138.5 (Ar), 138.2 (Ar), 138.0 (Ar), 137.5 (Ar), 128.9 (Ar), 128.4 (Ar), 128.3(4) (Ar), 128.3(3) (Ar), 128.2 (Ar), 128.1 (Ar), 127.8 (Ar), 127.7(2) (Ar), 127.6(9) (Ar), 127.5(9) (Ar), 127.5(7) (Ar), 126.2 (Ar), 102.7 (C-1), 101.9 ($PhCHO_2$), 101.1 (C-1′), 83.0 (C-3′), 78.6 (C-3), 78.1 (C-4′), 77.7 (C-4), 75.1, 75.0, 74.8 (C-5′, $PhCH_2O \times 2$), 73.6(1), 73.5(8), 73.2 (C-2′, C-2, $PhCH_2O$), 69.7 (C-6′), 68.6 (C-6), 67.7 (C-5), 57.0 (CH_3O), 56.8 (CH_3O), 21.1 ($CH_3C(O)O$); HRESIMS: Calcd for $C_{44}H_{50}O_{12}Na$ 793.3195. Found 793.3195.

3.19. Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-methyl-β-D-mannopyranoside (21)

Disaccharide **20** (513 mg, 0.67 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (4 mL) and treated with 0.5 M CH_3ONa–CH_3OH (1 mL) then processed as described for **18**. Purification of the product by chromatography over silica gel (7:3 hexanes–EtOAc) gave **21** (428 mg, 88%) as a white solid: R_f 0.27 (1:1 hexanes–EtOAc); $[\alpha]_D$ −38 (*c* 0.37, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.47–7.49 (m, 2H, ArH), 7.42–7.46 (m, 16H, ArH), 7.19–7.21 (m, 2H, ArH), 5.55 (s, 1H, $PhCHO_2$), 5.06 (d, 1H, J_{gem} 11.2 Hz, $PhCH_2O$), 4.87 (d, 1H, J_{gem} 11.0 Hz, $PhCH_2O$), 4.81 (d, 1H, J_{gem} 11.2 Hz, $PhCH_2O$), 4.54 (s, 2H, $PhCH_2O$), 4.54 (d, 1H, J_{gem} 10.9 Hz, $PhCH_2O$), 4.50 (d, 1H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.46 (d, 1H, $J_{1,2}$ 0.6 Hz, H-1), 4.34 (dd, 1H, $J_{5,6}$ 4.9, J_{gem} 10.4 Hz, H-6eq), 4.26 (d, 1H, $J_{2,3}$ 3.2, H-2), 4.02 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.7 Hz, H-4), 3.87 (dd, 1H, $J_{5,6} \approx J_{gem}$ 10.3 Hz, H-6ax), 3.76 (dd, 1H, $J_{5',6'}$ 1.7, J_{gem} 10.5 Hz, H-6a′), 3.74 (dd, 1H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 8.9Hz, H-2′), 3.67 (dd, 1H, $J_{2',3'} \approx J_{3',4'}$ 8.8 Hz, H-3′), 3.63 (dd, 1H, $J_{5',6'}$ 6.4, J_{gem} 10.5 Hz, H-6b′), 3.58 (s, 3H, CH_3O), 3.56 (ddd, 1H, $J_{4',5'}$ 10.0, $J_{5',6'}$ 1.7, 6.5 Hz, H-5′), 3.47 (dd, 1H, $J_{3',4'}$ 8.5, $J_{4',5'}$

9.7 Hz, H-4′), 3.48 (s, 3H, CH_3O), 3.42 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 10.0 Hz, H-3), 3.38 (ddd, 1H, $J_{4,5}$ 9.9, $J_{5,6}$ 4.9, 9.9 Hz, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0 (Ar), 138.3 (Ar), 138.2 (Ar), 137.4 (Ar), 128.9 (Ar), 128.4 (Ar), 128.3(1) (Ar), 128.2(9) (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5(4) (Ar), 127.4(8) (Ar), 126.2 (Ar), 105.1 (C-1′), 102.1 (C-1), 101.8 (PhCHO_2), 85.2 (C-3′), 78.8 (C-3), 77.8 (C-4), 77.3 (C-4′), 76.4 (C-2), 75.4(9), 75.4(6) (C-2′, C-5′), 75.0 (PhCH_2O), 74.8 (PhCH_2O), 73.5 (PhCH_2O), 69.8 (C-6′), 68.6 (C-6), 67.5 (C-5), 57.5 (CH_3O), 57.4 (CH_3O); HRESIMS: Calcd for $C_{42}H_{48}O_{11}Na$ 751.3089. Found 751.3089. Anal. Calcd for $C_{42}H_{48}O_{11}$: C, 69.21; H, 6.64. Found: C, 68.95; H, 6.82.

3.20. Methyl 3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-methyl-β-D-mannopyranoside (22)

Disaccharide **21** (428 mg, 0.59 mmol) was dissolved in freshly distilled Me_2SO (10 mL) and Ac_2O (5 mL) then processed as described for compound **19**. The concentrated reaction mixture was then treated with 1.0 M L-Selectride® in THF (2.4 mL, 2.35 mmol) in dry THF (10 mL) at −78 °C under argon. Purification by column chromatography over silica gel (7:3 hexanes–EtOAc) gave **22** (308 mg, 72%) as a white solid: R_f 0.19 (1:1 hexanes–EtOAc); $[\alpha]_D$ −60 (*c* 0.47, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49–7.50 (m, 2H, ArH), 7.24–7.40 (m, 18H, ArH), 5.58 (s, 1H, PhC*H*O_2), 4.94 (d, 1H, J_{gem} 11.0Hz, PhCH_2O), 4.85 (d, 1H, $J_{1',2'}$ 0.8 Hz, H-1′), 4.82 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.65 (d, 1H, J_{gem} 12.0 Hz, PhCH_2O), 4.58 (d, 1H, J_{gem} 12.0 Hz, PhCH_2O), 4.57 (d, 1H, J_{gem} 11.0Hz, PhCH_2O), 4.52 (m, 1H, H-2), 4.51 (d, 1H, J_{gem} 12.0 Hz, PhCH_2O), 4.42 (d, 1H, $J_{1,2}$ 0.9 Hz, H-1), 4.33 (dd, 1H, $J_{5,6}$ 5.0, J_{gem} 10.4 Hz, H-6eq), 4.28 (dd, 1H, $J_{1',2'}$ 0.7, $J_{2',3'}$ 3.0 Hz, H-2′), 4.01 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.6 Hz, H-4), 3.89 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.4 Hz, H-4′), 3.88 (dd, 1H, $J_{5,6}$ 10.3 Hz, H-6ax), 3.77 (dd, 1H, $J_{5',6'}$ 2.0, J_{gem} 10.8 Hz, H-6a′), 3.71 (dd, 1H, $J_{5',6'}$ 5.8 J_{gem} 10.8 Hz, H-6b′), 3.55 (dd, 1H, $J_{2',3'}$ 3.0, $J_{3',4'}$ 9.1 Hz, H-3′), 3.52 (s, 3H, CH_3O), 3.47 (ddd, 1H, $J_{4',5'}$ 9.7, $J_{5',6'}$ 1.9, 5.7Hz, H-5′), 3.45 (s, 3H, CH_3O), 3.43 (dd, 1H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.9 Hz, H-3), 3.38 (ddd, 1H, $J_{4,5}$ 9.9, $J_{5,6}$ 4.9, 9.9 Hz, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4 (Ar), 138.3 (Ar), 138.1 (Ar), 137.3 (Ar), 129.0 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.7 (Ar), 127.6(4) (Ar), 127.5(7) (Ar), 126.2 (Ar), 102.9 (C-1), 101.8 (PhCHO_2), 98.1 (C-1′), 81.4 (C-3′), 78.8 (C-3), 77.7 (C-4), 75.3, 75.1, 74.3 (C-4′, C-5′, PhCH_2O), 73.4 (PhCH_2O), 70.8, 70.7 (C-2, PhCH_2O), 69.8 (C-6′), 68.6 (C-6), 67.8, 67.5 (C-2′, C-5), 57.5 (CH_3O), 57.1 (CH_3O); HRESIMS: Calcd for $C_{42}H_{48}O_{11}Na$ 751.3089. Found 751.3087. Anal. Calcd for $C_{42}H_{48}O_{11}$: C, 69.21; H, 6.64. Found: C, 68.85; H, 6.70.

3.21. Methyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (24)

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**23**)[15] (1.54 g, 4.14 mmol) was dissolved in pyridine (40 mL). Benzoyl chloride (1.5 mL, 12.41 mmol) was added, and the reaction mixture was stirred at room temperature overnight, then concentrated under reduced pressure. The residue was dissolved in EtOAc then washed with 1 M aq HCl, satd aq $NaHCO_3$, distilled H_2O and brine. The organic phase was dried (Na_2SO_4), then concentrated under reduced pressure. Column chromatography (4:1 hexanes–EtOAc) on silica gel gave **24** (1.97 g, quant.) as a white solid: R_f 0.51 (1:1 hexanes–EtOAc); $[\alpha]_D$ −115 (*c* 0.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.16 (m, 2H, ArH), 7.23–7.59 (m, 13H, ArH), 5.88 (dd, 1H, $J_{1,2}$ 1.1, $J_{2,3}$ 3.4 Hz, H-2), 5.68 (s, 1H, PhC*H*O_2), 4.79 (d, 1H, J_{gem} 12.6 Hz, PhCH_2O), 4.69 (d, 1H, PhCH_2O), 4.60 (d, 1H, $J_{1,2}$ 1.2Hz, H-1), 4.41 (dd, 1H, $J_{5,6eq}$ 4.9, J_{gem} 10.5 Hz, H-6eq), 4.14 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.6 Hz, H-4), 3.98 (dd, 1H, $J_{5,6ax}$ 9.7, J_{gem} 10.4 Hz, H-6ax) 3.84 (dd, 1H, $J_{2,3}$ 3.4, $J_{3,4}$ 9.8 Hz, H-3), 3.53 (s, 3H, CH_3O), 3.47 (ddd, 1H, $J_{4,5}$ 9.7, $J_{5,6}$ 4.8, 9.7 Hz, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1 (*C*═O), 137.7 (Ar), 137.4 (Ar), 133.1 (Ar), 130.1 (Ar), 129.9 (Ar), 129.0 (Ar), 128.3(3) (Ar), 128.3(0) (Ar), 128.2 (Ar), 127.7 (Ar), 126.1 (Ar), 101.6 (PhCHO_2), 101.1 (C-1), 78.4 (C-4), 75.6 (C-3), 71.6 (PhCH_2O), 69.3 (C-2), 68.7 (C-6), 67.4 (C-5), 57.5 (CH_3O); HRESIMS: Calcd for $C_{28}H_{28}O_7Na$ 499.1727. Found 499.1729. Anal. Calcd for $C_{28}H_{28}O_7$: C, 70.57; H, 5.92. Found: C, 70.81; H, 5.73.

3.22. Methyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-mannopyranoside (25)

Compound **24** (3.43 g, 6.77 mmol) was dissolved in dry THF, and the solution was cooled to 0 °C (ice-water bath) under argon. Activated 4 Å molecular sieves and $NaCNBH_3$ (2.13 g, 33.86 mmol) were added. A satd solution of HCl in Et_2O was added dropwise until the solution was acidic (pH paper, gas evolution). After 3 h, the reaction was diluted with EtOAc and filtered through Celite. The organic phase was washed with satd aq $NaHCO_3$, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by column chromatography (4:1 hexanes–EtOAc) to give **25** (2.80 g, 81%) as a white solid: R_f 0.40 (1:1 hexanes–EtOAc); $[\alpha]_D$ −113 (*c* 0.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–8.09 (m, 2H, ArH), 7.54 (m, 1H, ArH), 7.26–7.41 (m, 12H, ArH), 5.84 (dd, 1H, $J_{1,2}$ 0.9, $J_{2,3}$ 3.1 Hz, H-2) 4.85 (d, 1H, J_{gem} 11.4 Hz, PhCH_2O) 4.72 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O) 4.64 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O) 4.55 (d, 1H, $J_{1,2}$ 0.9 Hz, H-1) 4.50 (d, 1H, J_{gem} 11.4 Hz, PhCH_2O), 4.04 (ddd, 1H, $J_{4,OH}$ 2.0, $J_{3,4} \approx J_{4,5}$ 9.4 Hz, H-4), 3.92 (ABX, 1H, $J_{5,6}$ 3.2, J_{gem} 10.7 Hz, H-6a), 3.88 (ABX, 1H, $J_{5,6}$ 5.3, J_{gem} 10.7 Hz, H-6b), 3.54–3.58 (m, 2H, H-3, H-5), 3.53 (s, 3H, CH_3O), 2.57 (d, 1H, $J_{4,OH}$ 2.1 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1 (*C*═O), 138.2 (Ar), 137.3 (Ar), 133.0 (Ar), 130.1 (Ar), 129.9 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.6 (Ar), 100.3 (C-1), 79.6 (C-3), 75.3 (C-5), 73.7 (PhCH_2O), 71.2 (PhCH_2O), 70.2 (C-6), 67.8(4), 67.8(0) (C-2, C-4), 57.2 (CH_3O); HRESIMS: Calcd for $C_{28}H_{30}O_7Na$ 501.1884. Found 501.1884.

3.23. Methyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-thiocarbonyl imidazole-β-D-mannopyranoside (26)

To a solution of **25** (1.43 g, 2.98 mmol) in dry toluene (20 mL) under argon was added 1,1′-thiocarbonyldiimidazole (1.60 g, 8.95 mmol). The reaction was stirred at 90 °C. After 20 h, the reaction was cooled to room temperature, then concentrated under reduced pressure to give a brown oily residue. Purification of the product by chromatography (1:1 hexanes–EtOAc) yielded **26** (1.05 g, 60%) as a white solid: R_f 0.28 (1:1 hexanes–EtOAc); $[\alpha]_D$ −166 (*c* 0.29, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.15 (m, 2H, ArH), 8.10 (m, 1H, ArH), 7.59 (m, 1H, ArH), 7.43–7.46 (m, 3H, ArH), 7.12–7.28 (m, 10H, ArH), 7.02 (m, 1H, ArH), 6.24 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.3 Hz, H-4), 5.90 (dd, 1H, $J_{1,2}$ 0.9, $J_{2,3}$ 3.2 Hz, H-2), 4.69 (d, 1H, J_{gem} 12.8 Hz, PhCH_2O), 4.61 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.54 (AB, 1H, J_{gem} 11.7 Hz, PhCH_2O), 4.52 (AB, 1H, J_{gem} 11.7 Hz, PhCH_2O), 4.45 (d, 1H, J_{gem} 12.8 Hz, PhCH_2O), 3.83 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.4 Hz, H-3), 3.72–3.82 (m, 3H, H-5, H-6a, H-6b), 3.45 (s, 3H, CH_3O); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.4 (*C*═S), 166.0 (*C*═O), 137.6 (Ar), 136.8 (Ar), 136.6 (Ar), 133.2 (Ar), 130.8 (Ar), 130.2 (Ar), 129.7 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.7 (Ar), 127.6 (Ar), 118.2 (Ar), 100.2 (C-1), 77.2 (C-4), 75.8 (C-3), 73.9 (PhCH_2O), 73.6 (C-5), 70.6 (PhCH_2O), 69.7 (C-6), 67.8 (C-2), 57.4 (CH_3O); HRESIMS: Calcd for $C_{32}H_{32}N_2O_7SNa$ 611.1822. Found 611.1820. Anal. Calcd for $C_{32}H_{32}N_2O_7S$: C, 65.29; H, 5.48; N, 4.76; S, 5.45. Found: C, 65.55; H, 5.53; N, 4.76; S, 5.27.

3.24. Methyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-deoxy-β-D-*lyxo*-hexopyranoside (27)

To a solution of the Barton–McCombie substrate **26** (1.05 g, 1.78 mmol) in dry toluene (15 mL) was added tributyltin hydride

(2 mL), and the mixture was then (1.43 mL, 5.33 mmol) and AIBN (73 mg, 0.25 mmol). The reaction was refluxed under argon overnight, then cooled to room temperature. The reaction mixture was filtered through a plug of silica gel containing 10% (w/w) KF. The filtrate was concentrated, then subjected to chromatography (4:1 hexanes–EtOAc) to give **27** (562.2 mg, 68%) as a white solid: R_f 0.55 (1:1 hexanes–EtOAc); $[\alpha]_D$ −101 (*c* 0.59, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11–8.12 (m, 2H, ArH), 7.53–7.56 (m, 1H, ArH), 7.25–7.43 (m, 12H, ArH), 5.78 (dd, 1H, $J_{1,2}$ 0.8, $J_{2,3}$ 2.8 Hz, H-2), 4.74 (d, 1H, J_{gem} 12.0Hz, PhCH_2O), 4.65 (s, 2H, PhCH_2O), 4.52 (d, 1H, J_{gem} 12.0 Hz, PhCH_2O), 4.42 (d, 1H, $J_{1,2}$ 1.1 Hz, H-1), 3.76 (dd, 1H, $J_{5,6}$ 5.5, J_{gem} 9.4Hz, H-6a), 3.68–3.74 (m, 2H, H-3, H-5), 3.65 (dd, 1H, $J_{5,6}$ 4.2, J_{gem} 9.4 Hz, H-6b) 3.51 (s, 3H, CH_3O), 1.91–1.94 (m, 2H, H-4a, H-4b); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2 (*C*═O), 138.3 (Ar), 137.8 (Ar), 132.9 (Ar), 130.2 (Ar), 130.1 (Ar), 128.4 (Ar), 128.2 (Ar), 127.7(1) (Ar), 127.6(8) (Ar), 100.7 (C-1), 74.0 (C-3), 73.6 (PhCH_2O), 72.7 (C-6), 72.0 (C-5), 70.0 (PhCH_2O), 67.2 (C-2), 57.1 (CH_3O), 30.0 (C-4); HRESIMS: Calcd for $C_{28}H_{30}O_6Na$ 485.1935. Found 485.1936.

3.25. Methyl 3,6-di-*O*-benzyl-4-deoxy-β-D-*lyxo*-hexopyranoside (28)

Compound **27** (534.3 mg, 1.16 mmol) was dissolved in MeOH (10 mL). A solution of 0.5 M CH_3ONa–CH_3OH (6 mL) was added, then the reaction was stirred at room temperature until TLC (1:1 hexanes–EtOAc) indicated the consumption of starting material. The reaction was neutralized with Amberlite IR-120 (H^+) resin. The resin was filtered and the filtrate was concentrated under reduced pressure. Purification by chromatography (1:1 hexanes–EtOAc) gave **28** (369.5 mg, 89%) as a white solid: R_f 0.30 (1:1 hexanes–EtOAc); $[\alpha]_D$ −45 (*c* 1.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.36 (m, 10H, ArH), 4.56–4.66 (m, 4H, PhCH_2O × 4), 4.25 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.04 (br s, 1H, H-2), 3.67 (m, 1H, H-6a), 3.51–3.60 (m, 3H, H-3, H-5, H-6b), 3.56 (s, 3H, CH_3O), 2.28 (d, 1H, $J_{2,OH}$ 2.4Hz, OH), 1.84 (m, 1H, H-4a), 1.76 (m, 1H, H-4b); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2 (Ar), 137.9 (Ar), 128.5 (Ar), 128.4 (Ar), 127.8 (Ar), 127.7(2) (Ar), 127.6(9) (Ar), 127.6(7) (Ar), 101.3 (C-1), 75.0 (C-3), 73.6 (PhCH_2O), 72.7 (C-6), 71.7 (C-5), 69.9 (PhCH_2O), 67.3 (C-2), 56.9 (CH_3O), 28.3 (C-4); HRESIMS: Calcd for $C_{21}H_{26}O_5Na$ 381.1672. Found 381.1671.

3.26. Methyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-methyl-β-D-mannopyranoside (29)

Compound **25** (643.3 mg, 1.34 mmol) was dissolved in dry DMF (10 mL) under argon. Methyl iodide (167 μL, 2.69 mmol) was added, and the reaction was cooled to 0 °C (ice-water bath). NaH (107.5 mg, 2.69 mmol; 60% in oil) was added in one portion, and the reaction was stirred at 0 °C for 3 h. The reaction was quenched with HOAc, then concentrated under reduced pressure. Purification of the product by chromatography (4:1 hexanes–EtOAc) yielded **29** (643.8 mg, 97%) as a white solid: R_f 0.54 (1:1 hexanes–EtOAc); $[\alpha]_D$ −96 (*c* 0.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09–8.11 (m, 2H, ArH), 7.53 (m, 1H, ArH), 7.42–7.44 (m, 2H, ArH), 7.26–7.38 (m, 10H, ArH), 5.81 (dd, 1H, $J_{1,2}$ 0.8, $J_{2,3}$ 3.0 Hz, H-2), 4.83 (d, 1H, J_{gem} 11.6 Hz, PhCH_2O), 4.81 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.65 (d, 1H, J_{gem} 12.0Hz, PhCH_2O), 4.58 (d, 1H, J_{gem} 11.6 Hz, PhCH_2O), 4.49 (d, 1H, $J_{1,2}$ 0.9 Hz, H-1), 3.90 (dd, 1H, $J_{5,6}$ 4.3, J_{gem} 11.0Hz, H-6a), 3.87 (dd, 1H, $J_{5,6}$ 2.1, J_{gem} 11.0 Hz, H-6b), 3.71 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.3 Hz, H-4), 3.66 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.2Hz, H-3), 3.55 (s, 3H, CH_3O), 3.52 (s, 3H, CH_3O), 3.46 (ddd, 1H, $J_{4,5}$ 9.3, $J_{5,6}$ 2.1, 4.3Hz, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0 (*C*═O), 138.6 (Ar), 137.8 (Ar), 132.9 (Ar), 130.1 (Ar), 128.3(4) (Ar), 128.3(3) (Ar), 128.2(6) (Ar), 128.0 (Ar), 127.7 (Ar), 127.5(0) (Ar), 127.4(6) (Ar), 100.2 (C-1), 80.1 (C-3), 76.2 (C-4), 75.8 (C-5), 73.5 (PhCH_2O), 71.2 (PhCH_2O), 69.3 (C-6), 68.4 (C-2), 61.0 (CH_3O), 57.2 (CH_3O); HRESIMS: Calcd for $C_{29}H_{32}O_7Na$ 515.2040. Found 515.2042. Anal. Calcd for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55. Found: C, 70.58; H, 6.54.

3.27. Methyl 3,6-di-*O*-benzyl-4-*O*-methyl-β-D-mannopyranoside (30)

To a solution of mannopyranoside **29** (793.3 mg, 1.61 mmol) in CH_2Cl_2 (10 mL) and MeOH (10 mL) was added 0.5 M CH_3ONa–CH_3OH (6 mL), and the reaction was stirred overnight. The reaction was neutralized with Amberlite IR-120 (H^+) resin, the resin was filtered and the filtrate was concentrated under reduced pressure. Purification of the product by chromatography (1:1 hexanes–EtOAc) gave **30** (592.5 mg, 95%) as a white solid: R_f 0.28 (1:1 hexanes–EtOAc); $[\alpha]_D$ −34 (*c* 0.44, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.41 (m, 10H, ArH), 4.76 (d, 1H, J_{gem} 11.9 Hz, PhCH_2O), 4.69 (d, 1H, J_{gem} 11.8 Hz, PhCH_2O), 4.67 (d, 1H, J_{gem} 12.0 Hz, PhCH_2O), 4.60 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.31 (d, 1H, H-1), 4.06 (m, 1H, H-2), 3.80 (dd, 1H, $J_{5,6}$ 2.2, J_{gem} 10.8Hz, H-6a), 3.75 (dd, 1H, $J_{5,6}$ 5.3, J_{gem} 10.9 Hz, H-6b), 3.57 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.3 Hz, H-4), 3.55 (s, 3H, CH_3O), 3.53 (s, 3H, CH_3O), 3.46 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.0 Hz, H-3), 3.36 (ddd, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 2.1, 5.3Hz, H-5), 2.39 (d, 1H, $J_{2,OH}$ 2.4 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4 (Ar), 138.0 (Ar), 128.5 (Ar), 128.3 (Ar), 127.8(2) (Ar), 127.8(0) (Ar), 127.7 (Ar), 127.5 (Ar), 100.7 (C-1), 81.3 (C-3), 76.2 (C-4), 75.4 (C-5), 73.6 (PhCH_2O), 71.5 (PhCH_2O), 69.4 (C-6), 68.3 (C-2), 60.8 (CH_3O), 56.9 (CH_3O); HRESIMS: Calcd for $C_{22}H_{28}O_6Na$ 411.1778. Found 411.1778.

3.28. Methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-deoxy-β-D-lyxo-hexopyranoside (31)

Monosaccharide acceptor **28** (347 mg, 0.97 mmol) was reacted with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (**16**) (758 mg, 1.19 mmol) in CH_2Cl_2 (5 mL) using TMSOTf (5 μL, 0.03 mmol) under argon at 0 °C (ice-water bath), then processed as described for **17**. The product was purified by chromatography over silica gel (4:1 hexanes–EtOAc) to give **31** (669 mg, 83%) as a clear syrup: R_f 0.59 (1:1 hexanes–EtOAc); $[\alpha]_D$ −55 (*c* 0.43, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18–7.34 (m, 25H, ArH), 5.09 (dd, 1H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 9.5 Hz, H-2′), 4.84 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1′) 4.81 (d, 1H, J_{gem} 10.9 Hz, PhCH_2O), 4.80 (d, 1H, J_{gem} 12.2Hz, PhCH_2O), 4.78 (d, 1H, J_{gem} 11.5 Hz, PhCH_2O), 4.74 (d, 1H, J_{gem} 11.4 Hz, PhCH_2O), 4.54–4.59 (m, 2H, PhCH_2O), 4.54 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.47 (d, 1H, J_{gem} 12.2Hz, PhCH_2O), 4.42–4.47 (m, 2H, PhCH_2O), 4.17 (d, 1H, $J_{2,3}$ 2.5 Hz, H-2), 4.11 (s, 1H, H-1), 3.72–3.77 (m, 2H, H-3′, H-6a′), 3.54–3.63 (m, 5H, H-4′, H-5′, H-6b′ H-5, H-6a), 3.48 (dd, 1H, $J_{5,6}$ 4.0, J_{gem} 9.7 Hz, H-6b), 3.46 (s, 3H, CH_3O), 3.40 (ddd, 1H, $J_{2,3}$ 2.7, $J_{3,4eq}$ 4.7, $J_{3,4ax}$ 11.7Hz, H-3), 1.96 (s, 3H, CH_3C(O)O), 1.75 (ddd, 1H, $J_{3,4} \approx J_{gem} \approx J_{4,5}$ 12.0 Hz, H-4ax), 1.65 (ddd, 1H, $J_{3,4}$ 4.5, J_{gem} 12.6, $J_{4,5}$ 2.2 Hz, H-4eq); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7 (*C*═O), 138.5 (Ar), 138.4 (Ar), 138.3 (Ar), 138.2 (Ar), 138.0 (Ar), 128.4 (Ar), 128.3(2) (Ar), 128.2(9) (Ar), 128.2(6) (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7(2) (Ar), 127.6(7) (Ar), 127.6(1) (Ar), 127.5(8) (Ar), 127.5(5) (Ar), 127.4(9) (Ar), 127.4 (Ar), 102.4 (C-1), 100.9 (C-1′), 83.1 (C-3′), 78.2 (C-4′/C-5′/C-5), 75.0, 74.9, 74.7 (C-4′/C-5′/C-5, PhCH_2O × 2), 73.9 (PhCH_2O), 73.7 (C-3), 73.5, 73.4, 73.2 (C-2′, C-6, PhCH_2O), 72.0 (C-4′/C-5′/C-5), 71.4 (C-2), 69.9 (C-6′), 68.7 (PhCH_2O), 56.5 (CH_3O), 29.2 (C-4), 21.1 (CH_3C(O)O); HRESIMS: Calcd for $C_{50}H_{56}O_{11}Na$ 855.3715. Found 855.3710. Anal. Calcd for $C_{50}H_{56}O_{11}$: C, 72.10; H, 6.78. Found: C, 72.10; H, 6.79.

3.29. Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-deoxy-β-D-lyxo-hexopyranoside (32)

Disaccharide **31** (448 mg, 0.54 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (10 mL) and treated with 0.5 M CH_3ONa–CH_3OH

(2 mL), then processed as described for **18**. Purification of the product by chromatography over silica gel (7:3 hexanes–EtOAc) gave **32** (334 mg, 78%) as a colourless syrup: R_f 0.42 (1:1 hexanes–EtOAc); $[\alpha]_D$ −60 (*c* 0.88, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.42 (m, 2H, ArH), 7.22–7.37 (m, 21H, ArH), 7.17–7.18 (m, 2H, ArH), 5.06 (d, 1H, J_{gem} 11.3 Hz, PhC*H*$_2$O), 4.86 (d, 1H, J_{gem} 10.9Hz, PhC*H*$_2$O), 4.79 (d, 1H, J_{gem} 11.3 Hz, PhC*H*$_2$O), 4.78 (d, 1H, J_{gem} 12.5 Hz, PhC*H*$_2$O), 4.61 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O) 4.59 (d, 1H, $J_{1',2'}$ 8.8Hz, H-1′), 4.56 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O), 4.52 (d, 1H, J_{gem} 11.0 Hz, PhC*H*$_2$O), 4.51 (d, 1H, J_{gem} 12.5Hz, PhC*H*$_2$O), 4.46 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O), 4.42 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O), 4.22 (s, 1H, H-1), 4.15 (d, 1H, $J_{2,3}$ 2.5 Hz, H-2) 3.44–3.74 (m, 11H, H-2′, H-3′, H-4′, H-5′, H-6a′, H-6b′, OH, H-3, H-5, H-6a, H-6b), 3.54 (s, 3H, C*H*$_3$O), 1.85 (ddd, 1H, $J_{3,4} \approx J_{gem} \approx J_{4,5}$ 12.5 Hz, H-4ax), 1.78 (ddd, 1H, *J* 2.0, 4.6, J_{gem} 12.4Hz, H-4eq); ^{13}C^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1 (Ar), 138.3 (Ar), 138.2(3) (Ar), 138.1(8) (Ar), 128.4 (Ar), 128.3(1) (Ar), 128.2(5) (Ar), 128.0 (Ar), 127.9 (Ar), 127.7(3) (Ar), 127.6(9) (Ar), 127.6(8) (Ar), 127.6(5) (Ar), 127.5 (Ar), 127.4(4) (Ar), 127.3(9) (Ar), 104.5 (C-1′), 101.9 (C-1), 85.2, 77.4, 75.5, 75.4, 75.0, 74.7, 74.3, 74.1, 73.6, 73.4, 72.7, 72.1, 69.7, 69.3 (C-2′, C-3′, C-4′, C-5′, C-6′, C-2, C-3, C-5, C-6, PhC*H*$_2$O × 5), 56.9 (*C*H$_3$O), 29.4 (C-4); HRESIMS: Calcd for $C_{48}H_{54}O_{10}Na$ 813.3609. Found 813.3608.

3.30. Methyl 3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-deoxy-β-D-*lyxo*-hexopyranoside (33)

Disaccharide **32** (312 mg, 0.39 mmol) was dissolved in Me_2SO (5 mL), Ac_2O (2.5 mL) was added, and the reaction mixture was stirred overnight, then concentrated under reduced pressure. The residue was redissolved in dry THF (5 mL), and the solution was cooled to −78 °C. L-Selectride® (1.7 mL, 1.0 M in THF) was added dropwise, and the reaction was allowed to slowly warm to room temperature. The reaction was quenched with MeOH and concentrated under reduced pressure. Purification by column chromatography over silica gel (7:3 hexanes–EtOAc) gave **33** (200 mg, 65%) as a white solid: R_f 0.28 (1:1 hexanes–EtOAc); $[\alpha]_D$ −66 (*c* 0.73, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21–7.41 (m, 25H, ArH), 4.95 (d, 1H, J_{gem} 11.1 Hz, PhC*H*$_2$O), 4.93 (d, 1H, $J_{1',2'}$ 0.7 Hz, H-1′), 4.87 (d, 1H, J_{gem} 11.4 Hz, PhC*H*$_2$O), 4.83 (d, 1H, J_{gem} 12.2 Hz, PhC*H*$_2$O), 4.64 (d, 1H, J_{gem} 12.1Hz, PhC*H*$_2$O), 4.60 (d, 1H, J_{gem} 11.9 Hz, PhC*H*$_2$O), 4.55 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O), 4.54 (d, 1H, J_{gem} 11.0Hz, PhC*H*$_2$O), 4.45 (d, 1H, $J_{2,3}$ 2.7 Hz, H-2), 4.41 (d, 1H, J_{gem} 11.5 Hz, PhC*H*$_2$O), 4.38–4.43 (m, 2H, PhC*H*$_2$O), 4.33 (d, 1H, $J_{2',3'}$ 2.8 Hz, H-2′), 4.21 (d, 1H, $J_{1,2}$ 0.7Hz, H-1), 3.88 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.3 Hz, H-4′), 3.75 (dd, 1H, $J_{5',6'}$ 1.8, J_{gem} 10.5 Hz, H-6a′), 3.66 (dd, 1H, $J_{5,6}$ 5.9, J_{gem} 9.6Hz, H-6a), 3.47–3.62 (m, 6H, H-3′, H-5′, H-6b′, H-3, H-5, H-6b), 3.50 (s, 3H, C*H*$_3$O), 2.74 (br s, 1H, OH), 1.74–1.85 (m, 2H, H-4ax, H-4eq); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5 (Ar), 138.2(2) (Ar), 138.2(1) (Ar), 138.1(7) (Ar), 138.1(5) (Ar), 128.3(9) (Ar), 128.3(6) (Ar), 128.3(5) (Ar), 128.3(0) (Ar), 128.2(7) (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.7(0) (Ar), 127.6(8) (Ar), 127.6(4) (Ar), 127.5(9) (Ar), 127.5(8) (Ar), 127.5(3) (Ar), 127.4(7) (Ar), 102.7 (C-1), 98.8 (C-1′), 81.4 (C-3′), 75.0(9), 75.0(5), 74.5, 74.0, 73.6, 73.3, 72.8 (C-3, C-6, C-4′, C-5′, PhC*H*$_2$O × 3), 72.0 (C-5), 70.7 (PhC*H*$_2$O), 70.0 (C-6′), 69.2 (PhC*H*$_2$O), 68.7 (C-2), 67.7 (C-2′), 57.1 (*C*H$_3$O), 29.7 (C-4); HRESIMS: Calcd for $C_{48}H_{54}O_{10}Na$ 813.3609. Found 813.3609.

3.31. Methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-methyl-β-D-mannopyranoside (34)

Monosaccharide acceptor **30** (238 mg, 0.44 mmol) was reacted with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (**16**) (469 mg, 0.74 mmol) in CH_2Cl_2 (5 mL) using TMSOTf (7 μL, 0.04 mmol) under argon at 0 °C, then processed as described for **17**. The product was purified by chromatography over silica gel (4:1 hexanes–EtOAc) to give **34** (511 mg, 97%) as a colourless syrup: R_f 0.54 (1:1 hexanes–EtOAc); $[\alpha]_D$ −53 (*c* 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17–7.39 (m, 25H, ArH), 5.09 (dd, 1H, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.6 Hz, H-2′), 4.86 (d, 1H, J_{gem} 12.1Hz, PhC*H*$_2$O), 4.80 (d, 1H, J_{gem} *11.9 Hz,* PhC*H*$_2$O), 4.79 (d, 1H, H-1′), 4.78 (d, 1H, J_{gem} 11.5 Hz, PhC*H*$_2$O), 4.74 (d, 1H, J_{gem} 11.5 Hz, PhC*H*$_2$O), 4.61 (d, 1H, J_{gem} 12.3Hz, PhC*H*$_2$O), 4.57 (d, 1H, J_{gem} 12.2 Hz, PhC*H*$_2$O), 4.54 (d, 1H, J_{gem} 11.0 Hz, PhC*H*$_2$O), 4.52 (d, 1H, J_{gem} 12.1 Hz, PhC*H*$_2$O), 4.43–4.48 (m, 2H, PhC*H*$_2$O), 4.18–4.19 (m, 2H, H-1, H-2), 3.71–3.79 (m, 3H, H-3′, H-6a′, H-6a), 3.56–3.66 (m, 4H, H-4′, H-5′, H-6b′, H-6b), 3.51 (s, 3H, C*H*$_3$O), 3.47 (s, 3H, C*H*$_3$O), 3.36 (dd, 1H, $J_{2,3}$ 2.9, $J_{3,4}$ 8.9 Hz, H-3), 3.34 (ddd, 1H, $J_{4,5}$ 9.5 Hz, $J_{5,6}$ 1.6, 6.8 Hz, H-5), 3.28 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.2 Hz, H-4), 1.95 (s, 3H, C*H*$_3$C(O)O)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8 (*C*=O), 138.6 (Ar), 138.5 (Ar), 138.3 (Ar), 138.1 (Ar), 138.0 (Ar), 128.4 (Ar), 128.3(2) (Ar), 128.3(0) (Ar), 128.2 (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5(7) (Ar), 127.5(6) (Ar), 127.4(5) (Ar), 127.4 (Ar), 101.6, 101.1 (C-1, C-1′), 83.1 (C-3′), 79.9 (C-3), 78.0, 76.4, 75.7, 74.9, 74.8, 74.7, 73.5(4), 73.4(8), 73.3, 72.4, 70.7, 69.9, 69.7 (C-2′, C-4′, C-5′, C-6′, C-2, C-4, C-5, C-6, PhC*H*$_2$O × 5), 61.0 (C*H*$_3$O), 56.6 (C*H*$_3$O), 21.0 (C*H*$_3$C(O)O); HRESIMS: Calcd for $C_{51}H_{58}O_{12}Na$ 885.3821. Found 885.3828.

3.32. Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-methyl-β-D-mannopyranoside (35)

Disaccharide **34** (511 mg, 0.59 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (10 mL) and treated with 0.5 M CH_3ONa–CH_3OH (5 mL), then processed as described for **18**. Purification of the product by chromatography over silica gel (7:3 hexanes–EtOAc) gave **35** (470 mg, 97%) as a clear syrup*:* R_f 0.38 (1:1 hexanes–EtOAc); $[\alpha]_D$ −52 (*c* 0.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.41 (m, 23H, ArH), 7.16–7.18 (m, 2H, ArH), 5.06 (d, 1H, J_{gem} *11.3 Hz,* PhC*H*$_2$O), 4.84–4.87 (m, 2H, PhC*H*$_2$O), 4.78 (d, 1H, J_{gem} 11.2 Hz, PhC*H*$_2$O), 4.67 (d, 1H, J_{gem} *12.1 Hz,* PhC*H*$_2$O), 4.61 (d, 1H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.59 (d, 1H, J_{gem} 11.1 Hz, PhC*H*$_2$O), 4.56 (d, 1H, J_{gem} *11.9 Hz,* PhC*H*$_2$O), 4.52 (d, 1H, J_{gem} 11.0 Hz, PhC*H*$_2$O), 4.47 (d, 1H, J_{gem} 12.1 Hz, PhC*H*$_2$O), 4.44 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O), 4.27 (s, 1H, H-1), 4.19 (d, 1H, $J_{2,3}$ 3.1 Hz, H-2), 3.78 (dd, 1H, $J_{5,6}$ 2.1, J_{gem} 10.9Hz, H-6a), 3.73 (dd, 1H, $J_{5,6}$ 5.1, J_{gem} 11.0 Hz, H-6b), 3.49–3.72 (m, 7H, H-2′, H-3′, H-4′, H-5′, H-6a′, H-6b′, H-4), 3.52 (s, 6H, C*H*$_3$O × 2), 3.41 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.3 Hz, H-3), 3.32 (ddd, 1H, $J_{4,5}$ 9.5, $J_{5,6}$ 2.0,4.9Hz, H-5), 3.31 (br s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1 (Ar), 138.4 (Ar), 138.2(5) (Ar), 138.1(8) (Ar), 138.1(7) (Ar), 128.3(1) (Ar), 128.2(8) (Ar), 128.2 (Ar), 128.0 (Ar), 127.9(4) (Ar), 127.9(0) (Ar), 127.7 (Ar), 127.6(4) (Ar), 127.6(3) (Ar), 127.5 (Ar), 127.4 (Ar), 104.2 (C-1′), 101.5 (C-1), 85.2 (C-3′), 80.1 (C-3), 77.1 (C-5′), 76.0, 75.8 (C-4, C-5), 75.4, 75.3, 75.0, 74.8, 74.7 (C-2, C-2′, C-4′, PhC*H*$_2$O × 2), 73.5 (PhC*H*$_2$O), 73.4 (PhC*H*$_2$O), 70.4 (PhC*H*$_2$O), 69.7 (C-6′), 69.4 (C-6), 61.0 (C*H*$_3$O), 57.1 (C*H*$_3$O); HRESIMS: Calcd for $C_{49}H_{56}O_{11}Na$ 843.3715. Found 843.3719. Anal. Calcd for $C_{49}H_{56}O_{11}$: C, 71.69; H, 6.88. Found: C, 71.48; H, 7.09.

3.33. Methyl 3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-methyl-β-D-mannopyranoside (36)

As described for compound **19**, disaccharide **35** (446 mg, 0.54 mmol) was dissolved in freshly distilled Me_2SO (10 mL) and Ac_2O (5 mL). The concentrated reaction mixture was then treated with 1.0 M L-Selectride® in THF (2.2 mL, 2.17 mmol) in dry THF (10 mL) at −78 °C under argon. Purification by column chromatography over silica gel (7:3 hexanes–EtOAc) gave **36** (273 mg, 61%) as a white solid: R_f 0.29 (1:1 hexanes–EtOAc); $[\alpha]_D$ −60 (*c* 0.47, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21–740 (m, 25H, ArH),

4.94 (d, 1H, J_{gem} 10.9 Hz, PhCH_2O), 4.89–4.90 (m, 2H, H-1′, PhCH_2O), 4.82 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.66 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.63 (d, 1H, J_{gem} 12.0Hz, PhCH_2O), 4.57 (d, 1H, J_{gem} 12.0 Hz, PhCH_2O), 4.54 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.41–4.48 (m, 4H, H-2, 3(PhCH_2O)), 4.31 (dd, 1H, $J_{1',2'}$ 0.7, $J_{2',3'}$ 3.0 Hz, H-2′), 4.26 (d, 1H, $J_{1,2}$ 0.6Hz, H-1), 3.88 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.5 Hz, H-4′), 3.78 (dd, 1H, $J_{5,6}$ 2.1, J_{gem} 10.9 Hz, H-6a), 3.75 (dd, 1H, $J_{5',6'}$ 2.0, J_{gem} 10.4 Hz, H-6a′), 3.73 (dd, 1H, $J_{5,6}$ 5.4, J_{gem} 10.8Hz, H-6b), 3.62 (dd, 1H, $J_{5',6'}$ 6.2, J_{gem} 10.6 Hz, H-6b′), 3.56 (dd, 1H, $J_{2',3'}$ 3.0, $J_{3',4'}$ 9.1 Hz, H-3′), 3.47–3.52 (m, 2H, H-5′, H-4), 3.49 (s, 3H, CH_3O), 3.48 (s, 3H, CH_3O), 3.43 (dd, 1H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.2Hz, H-3), 3.33 (ddd, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 1.9, 5.4 Hz, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4(4) (Ar), 138.3(6) (Ar), 138.3 (Ar), 138.2 (Ar), 138.1 (Ar), 128.4 (Ar), 128.3(1) (Ar), 128.2(6) (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5(4) (Ar), 127.5(3) (Ar), 127.4 (Ar), 102.1 (C-1), 99.1 (C-1′), 81.5 (C-3′), 80.1 (C-3), 75.9, 75.7, 75.1, 75.0, 74.4 (C-4, C-5, C-4′, C-5′, PhCH_2O), 73.5 (PhCH_2O), 73.4 (PhCH_2O), 70.7 (PhCH_2O), 70.3 (C-2), 69.9(7), 69.9(6), 69.6 (C-6, C-6′, PhCH_2O), 67.7 (C-2′), 60.9 (CH_3O), 57.2 (CH_3O); HRESIMS: Calcd for $C_{49}H_{56}O_{11}Na$ 843.3715. Found 843.3716.

3.34. Methyl 3,4-di-*O*-benzyl-β-D-glucopyranoside (38)

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**37**)[15] (1.56 g, 4.19 mmol) in a flame-dried flask was dissolved in dry CH_2Cl_2 (20 mL) and cooled to 0 °C (ice-water bath) under argon. A 1.0 M solution of BH_3·THF complex in THF (21 mL, 20.95 mmol) was added, followed by the dropwise addition of a 1.0 M solution of dibutylboron triflate (2.1 mL, 2.10 mmol). After 3 h, the reaction was quenched with MeOH, neutralized with Et_3N, then concentrated under reduced pressure. Chromatography over silica gel (1:1 hexanes–EtOAc) yielded **38** (1.30 g, 83%) as a white solid: R_f 0.12 (1:1 hexanes–EtOAc); $[\alpha]_D$ −10 (*c* 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.40 (m, 10H, ArH), 4.93 (d, 1H, J_{gem} 11.3 Hz, PhCH_2O), 4.89 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.88 (d, 1H, J_{gem} 11.3 Hz, PhCH_2O), 4.67 (d, 1H, J_{gem} 10.9 Hz, PhCH_2O), 4.24 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 3.89 (ddd, 1H, $J_{5,6}$ 2.7, J_{gem} 12.0, $J_{6,OH}$ 5.5 Hz, H-6a), 3.75 (ddd, 1H, $J_{5,6}$ 4.4, J_{gem} 12.0, $J_{6,OH}$ 8.0 Hz, H-6b), 3.60–3.62 (m, 2H, H-3, H-4), 3.56 (s, 3H, CH_3O), 3.50 (m, 1H, H-2), 3.40 (ddd, 1H, $J_{4,5}$ 9.2, $J_{5,6}$ 2.8, 4.4 Hz, H-5), 2.45 (d, 1H, $J_{2,OH}$ 2.3 Hz, C2-OH), 1.97 (dd, 1H, $J_{6,OH}$ 5.7, 8.0 Hz, C6-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5 (Ar), 137.9 (Ar), 128.5 (Ar), 128.1 (Ar), 127.9(4) (Ar), 127.9(3) (Ar), 127.8(Ar), 103.8 (C-1), 84.3, 77.3 (C-3, C-4), 75.4, 75.2, 75.1 (C-5, PhCH_2O × 2), 74.6 (C-2), 61.9 (C-6), 57.3 (CH_3O); HRESIMS: Calcd for $C_{21}H_{26}O_6Na$ 397.1622. Found 397.1619. Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.10; H, 7.02.

3.35. Methyl 3,4-di-*O*-benzyl-6-*O*-methanesulfonyl-β-D-glucopyranoside (39)

Compound **38** (489 mg, 1.31 mmol) was dissolved in dry CH_2Cl_2 (5 mL) and dry pyridine (5 mL), and the mixture was cooled to 0 °C (ice-water bath) under argon. Methanesulfonyl chloride (152 μL, 1.96 mmol) was added dropwise, and the reaction was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 and washed with 1 M aq HCl, satd aq $NaHCO_3$, distilled water and brine, then dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography over silica gel (1:1, toluene–EtOAc) yielded **39** (389 mg, 66%) as a white solid: R_f 0.23 (1:1 hexanes–EtOAc); $[\alpha]_D$ −17 (*c* 0.34 $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.40 (m, 10H, ArH), 4.96 (d, 1H, J_{gem} 11.3 Hz, PhCH_2O), 4.92 (d, 1H, J_{gem} *10.8 Hz,* PhCH_2O), 4.87 (d, 1H, J_{gem} 11.3 Hz, PhCH_2O), 4.65 (d, 1H, J_{gem} 10.8 Hz, PhCH_2O), 4.47 (dd, 1H, $J_{5,6}$ 1.7, J_{gem} 11.1Hz, H-6a), 4.37 (dd, 1H, $J_{5,6}$ 4.2, J_{gem} *11.2 Hz,* H-6b), 4.21 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.63 (dd, 1H, $J_{2,3} \approx J_{3,4}$ 8.8 Hz, H-3), 3.49–3.58 (m, 3H, H-2, H-4, H-5), 3.55 (s, 3H, CH_3O), 3.03 (s, 3H, CH_3S(O)$_2$O), 2.37 (d, 1H, $J_{1,2}$ 2.2 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3 (Ar), 137.5 (Ar), 128.5(8) (Ar), 128.5(4) (Ar), 128.2 (Ar), 128.1 (Ar), 127.9(4) (Ar), 127.8(9) (Ar), 103.7 (C-1), 84.1 (C-3), 76.7 (C-4), 75.2(2) (PhCH_2O), 75.1(7) (PhCH_2O), 74.6 (C-2), 73.1 (C-5), 68.3 (C-6), 57.3 (CH_3O), 37.7 (CH_3S(O)$_2$O); HRESIMS: Calcd for $C_{22}H_{28}O_8SNa$ 475.1397. Found 475.1395.

3.36. Methyl 3,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (40)

To a solution of **39** (370 mg, 0.82 mmol) in DMF (8 mL) was added $NaBH_4$ (309 mg, 8.2 mmol). The mixture was heated at 80 °C for 3 h. The reaction was diluted with CH_2Cl_2 and washed with 2% aq citric acid, distilled water and brine, then dried (Na_2SO_4) and concentrated under reduced pressure. Purification by chromatography over silica gel (1:1 hexanes–EtOAc) gave **40** (235 mg, 80%) as a white solid: R_f 0.48 (1:1 hexanes–EtOAc); $[\alpha]_D$ −16 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.40 (m, 10H, ArH), 4.93 (d, 1H, J_{gem} 11.3 Hz, PhCH_2O), 4.90 (d, 1H, J_{gem} 10.9 Hz, PhCH_2O), 4.87 (d, 1H, J_{gem} 11.3Hz, PhCH_2O), 4.66 (d, 1H, J_{gem} 10.9 Hz, PhCH_2O), 4.17 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 3.56 (dd, 1H, $J_{2,3} \approx J_{3,4}$ 9.2Hz, H-3), 3.55 (s, 3H, CH_3O), 3.52 (ddd, 1H, $J_{1,2}$ 7.6, $J_{2,3}$ 9.6, $J_{2,OH}$ 2.0 Hz, H-2), 3.44 (dq, 1H, $J_{4,5}$ 9.5, $J_{5,6}$ 6.3 Hz, H-5), 3.22 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 8.8 Hz, H-4), 2.35 (d, 1H, $J_{2,OH}$ 2.1 Hz, OH), 1.34 (d, 3H, $J_{5,6}$ 6.2 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6 (Ar), 138.1 (Ar), 128.5 (Ar), 128.4 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 103.5 (C-1), 84.3 (C-3), 82.3 (C-4), 75.3, 75.1, 74.9 (C-2, PhCH_2O × 2), 71.5 (C-5), 57.1 (CH_3O), 17.9 (C-6); HRESIMS: Calcd for $C_{21}H_{26}O_5Na$ 381.1672. Found 381.1670. Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.68; H, 7.19.

3.37. Methyl 3,4-di-*O*-benzyl-6-deoxy-β-D-mannopyranoside (41)

Compound **40** (362 mg, 1.01 mmol) was dissolved in a mixture of Me_2SO (6 mL) and Ac_2O (3 mL). After stirring overnight at room temperature, the reaction was concentrated under reduced pressure. The remaining residue was dissolved in a mixture of 1:1 CH_2Cl_2–MeOH (10 mL) and cooled to 0 °C (ice-water bath). $NaBH_4$ (192 mg, 5.05 mmol) was added, and the reaction mixture was allowed to slowly warm to room temperature. After 3 h, the reaction was diluted with CH_2Cl_2 and washed with 2% aq citric acid, distilled water and brine. The organic phase was dried (Na_2SO_4), then concentrated under reduced pressure. Chromatography over silica gel (7:3 hexanes–EtOAc) yielded **41** (320 mg, 88%) as a white solid: R_f 0.27 (1:1 hexanes–EtOAc); $[\alpha]_D$ −36 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.39 (m, 10H, ArH), 4.95 (d, 1H, J_{gem} *10.9 Hz,* PhCH_2O), 4.77 (d, 1H, J_{gem} *11.9 Hz,* PhCH_2O), 4.69 (d, 1H, J_{gem} 11.9 Hz, PhCH_2O), 4.66 (d, 1H, J_{gem} 10.9 Hz, PhCH_2O), 4.30 (d, 1H, $J_{1,2}$ 1.1 Hz, H-1), 4.10 (m, 1H, H-2), 3.51–3.55 (m, 5H, H-3, H-4, CH_3O), 3.33 (dq, 1H, $J_{4,5}$ 9.8, $J_{5,6}$ 6.0 Hz, H-5), 2.37 (br s, 1H, OH), 1.36 (d, 3H, $J_{5,6}$ 6.2 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4 (Ar), 137.9 (Ar), 128.5 (Ar), 128.4 (Ar), 128.1 (Ar), 127.9(1) (Ar), 127.8(8) (Ar), 127.7 (Ar), 100.6 (C-1), 81.4, 79.7 (C-3, C-4), 75.5 (PhCH_2O), 71.4(7), 71.4(6) (C-5, PhCH_2O), 68.4 (C-2), 56.9 (CH_3O), 17.9 (C-6); HRESIMS: Calcd for $C_{21}H_{26}O_5Na$ 381.1672. Found 381.1672. Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.59; H, 7.38.

3.38. Methyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-glucopyranoside (43)

Methyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**42**)[23] (1.28 g, 2.68 mmol) in a flame-dried flask was dissolved in dry CH_2Cl_2 (20 mL) and cooled to 0 °C (ice-water bath)

under argon. A 1.0 M solution of BH_3·THF complex in THF (13.4 mL, 13.43 mmol) was added, followed by the dropwise addition of a 1.0 M solution of dibutylboron triflate (1.3 mL, 1.34 mmol). After 2 h, the reaction was quenched with MeOH, neutralized with Et_3N and then concentrated under reduced pressure. Chromatography over silica gel (7:3 hexanes–EtOAc) yielded **43** (1.03 g, 80%) as a white solid: R_f 0.29 (1:1 hexanes–EtOAc); $[\alpha]_D$ +39 (*c* 0.65. $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02–8.04 (m, 2H, ArH), 7.57 (m, 1H, ArH) 7.43–7.46 (m, 2H, ArH), 7.29–7.37 (m, 5H, ArH), 7.14 (br s, 5H, ArH), 5.25 (dd, 1H, $J_{1,2}$ 8.0, $J_{2,3}$ 9.3 Hz, H-2), 4.88 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.76 (d, 1H, J_{gem} 11.1 Hz, PhCH_2O), 4.69 (m, 2H, PhCH_2O), 4.50 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.93 (ddd, 1H, $J_{6,OH}$ 5.6, $J_{5,6}$ 2.8, J_{gem} *12.0 Hz,* H-6a), 3.86 (dd, 1H, $J_{2,3} \approx J_{3,4}$ 9.1 Hz, H-3), 3.78 (ddd, 1H, $J_{6,OH}$ 8.0, $J_{5,6}$ 4.5, J_{gem} 12.3 Hz, H-6b), 3.73 (dd, 1H, $J_{3,4}$ 9.0, $J_{4,5}$ 9.5 Hz, H-4), 3.48 (ddd, 1H, $J_{4,5}$ 9.4, $J_{5,6}$ 2.7, 4.4 Hz, H-5), 3.48 (s, 3H, CH_3O), 1.93 (dd, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2 (*C*═O), 137.8 (Ar), 137.7 (Ar), 133.1 (Ar), 129.9 (Ar), 129.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0(0) (Ar), 127.9(7) (Ar), 127.7 (Ar), 102.1 (C-1), 82.6 (C-3), 77.7 (C-4), 75.4, 75.1(2), 75.0(8) (C-5, PhCH_2O × 2), 73.7 (C-2), 61.9 (C-6), 57.0 (*C*H_3O); HRESIMS: Calcd for $C_{28}H_{30}O_7Na$ 501.1884. Found 501.1886; Anal. Calcd for $C_{28}H_{30}O_7$: C, 70.28; H, 6.32. Found: C, 70.30; H, 6.45.

3.39. Methyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-6-*O*-methyl-β-D-glucopyranoside (44)

To a solution of compound **43** (953 mg, 1.99 mmol) in dry DMF (20 mL) was added methyl iodide (248 μL, 3.98 mmol). The reaction was cooled to 0 °C (ice-water bath) under argon before the addition of NaH (159 mg, 3.98 mmol). After 3 h stirring at 0 °C, the reaction was quenched with HOAc, then concentrated under reduced pressure. Purification by chromatography over silica gel (4:1 hexanes–EtOAc) gave **44** (937 mg, 96%) as a white solid: R_f 0.51 (1:1 hexanes–EtOAc); $[\alpha]_D$ +34 (*c* 0.27, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02–8.04 (m, 2H, ArH), 7.57 (m, 1H, ArH), 7.42–7.45 (m, 2H, ArH), 7.29–7.37 (m, 5H, ArH), 7.13 (br s, 5H, ArH), 5.27 (dd, 1H, $J_{1,2}$ 8.0, $J_{2,3}$ 9.2 Hz, H-2), 4.86 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.75 (d, 1H, J_{gem} 11.1 Hz, PhCH_2O), 4.64–4.69 (m, 2H, PhCH_2O), 4.45 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 3.84 (dd, 1H, $J_{2,3} \approx J_{3,4}$ 9.1 Hz, H-3), 3.76 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.4 Hz, H-4), 3.70 (ABX, 1H, $J_{5,6}$ 4.6, J_{gem} 10.8 Hz, H-6a), 3.66 (ABX, 1H, $J_{5,6}$ 1.9, J_{gem} 10.8Hz, H-6b), 3.53 (ABX, 1H, $J_{4,5}$ 9.7, $J_{5,6}$ 1.9, 4.6 Hz, H-5), 3.47 (s, 3H, CH_3O), 3.42 (s, 3H, CH_3O); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2 (*C*═O), 138.1 (Ar), 137.8 (Ar), 133.0 (Ar), 130.0 (Ar), 129.8 (Ar), 128.5 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9(9) (Ar), 127.9(5) (Ar), 127.6 (Ar), 102.0 (C-1), 82.8 (C-3), 77.9 (C-4), 75.1, 75.0(4), 74.9(8) (C-5, PhCH_2O × 2), 73.7 (C-2), 71.2 (C-6), 59.5 (*C*H_3O), 56.7 (*C*H_3O); HRESIMS: Calcd for $C_{29}H_{32}O_7Na$ 515.2040. Found 515.2042. Anal. Calcd for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55. Found: C, 70.82; H, 6.64.

3.40. Methyl 3,4-di-*O*-benzyl-6-*O*-methyl-β-D-glucopyranoside (45)

Compound **44** (937 mg, 1.90 mmol) was dissolved in a mixture of 1:1 CH_2Cl_2–MeOH (20 mL). A 0.5 M solution of NaOMe in MeOH (5 mL) was added, and the reaction was stirred at room temperature overnight. The reaction mixture was neutralized with Amberlite IR-120 (H^+) resin, and filtered, and the filtrate was concentrated under reduced pressure. Chromatography over silica gel (1:1 hexanes–EtOAc) gave **45** (663 mg, 90%) as a white powdery solid: R_f 0.31 (1:1 hexanes–EtOAc); $[\alpha]_D$ −15 (*c* 0.59, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.39 (m, 10H, ArH), 4.92 (d, 1H, J_{gem} 11.4 Hz, PhCH_2O), 4.88 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.87 (d, 1H, J_{gem} *11.4 Hz,* PhCH_2O), 4.63 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.18 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 3.66 (dd, 1H, $J_{5,6}$ 2.2, J_{gem} 10.8, H-6a), 3.57–3.63 (m, 3H, H-3, H-4, H-6b), 3.56 (s, 3H, CH_3O), 3.53 (ddd, 1H, $J_{2,OH}$ 2.0, $J_{1,2} \approx J_{2,3}$ 7.9 Hz, H-2), 3.45 (ddd, 1H, $J_{4,5}$ 9.3, $J_{5,6}$ 2.1, 4.1 Hz, H-5), 3.39 (s, 3H, CH_3O), 2.35 (d, 1H, $J_{2,OH}$ 2.1 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6 (Ar), 138.2 (Ar), 128.5 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 103.7 (C-1), 84.4 (C-3), 77.5 (C-4), 75.1, 75.0(2), 75.0(0) (C-5, PhCH_2O × 2), 74.6 (C-2), 71.2 (C-6), 59.4 (*C*H_3O), 57.2 (*C*H_3O); HRESIMS: Calcd for $C_{22}H_{28}O_6Na$ 411.1778. Found 411.1775; Anal. Calcd for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27. Found: C, 68.11; H, 7.39.

3.41. Methyl 3,4-di-*O*-benzyl-6-*O*-methyl-β-D-mannopyranoside (46)

Compound **45** (600 mg, 1.54 mmol) was dissolved in a mixture of Me_2SO (5 mL) and Ac_2O (5 mL). After stirring overnight at room temperature, the reaction was concentrated under reduced pressure. The remaining residue was dissolved in a mixture of 1:1 CH_2Cl_2–MeOH (10 mL) and cooled to 0 °C (ice-water bath). $NaBH_4$ (294 mg, 7.72 mmol) was added, and the reaction mixture was allowed to slowly warm to room temperature. After 3 h, the reaction mixture was diluted with CH_2Cl_2 and washed with 2% aq citric acid, distilled water and brine. The organic phase was dried (Na_2SO_4), and then concentrated under reduced pressure. Chromatography over silica gel (7:3 hexanes–EtOAc) yielded **46** (508 mg, 85%) as a white solid: R_f 0.14 (1:1 hexanes–EtOAc); $[\alpha]_D$ −27 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.39 (m, 10H, ArH), 4.93 (d, 1H, J_{gem} 10.9 Hz, PhCH_2O), 4.78 (d, 1H, J_{gem} 11.9 Hz, PhCH_2O), 4.69 (d, 1H, J_{gem} 11.9 Hz, PhCH_2O), 4.62 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.32 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.09 (m, 1H, $J_{1,2}$ 0.9, $J_{2,3}$ 3.0 Hz, H-2), 3.88 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.4 Hz, H-4), 3.68 (dd, 1H, $J_{5,6}$ 2.2, J_{gem} *10.7 Hz,* H-6a), 3.63 (dd, 1H, $J_{5,6}$ 5.0, J_{gem} 10.6 Hz, H-6b), 3.57 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.1 Hz, H-3), 3.54 (s, 3H, CH_3O), 3.39 (s, 3H, CH_3O), 3.38 (ddd, 1H, $J_{4,5}$ 9.6, $J_{5,6}$ 2.1, 4.9 Hz, H-5), 2.38 (d, 1H, $J_{2,OH}$ 2.3 Hz, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4 (Ar), 137.9 (Ar), 128.5 (Ar), 128.4 (Ar), 128.1 (Ar), 127.8(8) (Ar), 127.8(4) (Ar), 127.7(6) (Ar), 100.8 (C-1), 81.4 (C-3), 75.2(1) (PhCH_2O), 75.1(5) (C-5), 74.2 (C-4), 71.5(4), 71.4(7) (C-6, PhCH_2O), 68.3 (C-2), 59.4 (*C*H_3O), 56.9 (*C*H_3O); HRESIMS: Calcd for $C_{22}H_{28}O_6Na$ 411.1778. Found 411.1782.

3.42. Methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-deoxy-β-D-mannopyranoside (47)

Monosaccharide acceptor **41** (250 mg, 0.70 mmol) was reacted with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (**16**) (533 mg, 0.84 mmol) in CH_2Cl_2 (5 mL) using TMSOTf (8 μL, 0.04 mmol) under argon at 0 °C, then processed as described for **17**. The product was purified by chromatography over silica gel (4:1 hexanes–EtOAc) to give **47** (560 mg, 96%) as a colourless syrup: R_f 0.65 (1:1 hexanes–EtOAc); $[\alpha]_D$ −43 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19–7.39, (m, 25H, ArH), 5.13 (dd, 1H, *J* 8.1, 9.5 Hz, H-2′), 4.99 (d, 1H, J_{gem} *10.8 Hz,* PhCH_2O), 4.88 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.82–4.84 (m, 2H, H-1′, PhCH_2O), 4.80 (d, 1H, J_{gem} 11.5 Hz, PhCH_2O), 4.76 (d, 1H, J_{gem} *11.4 Hz,* PhCH_2O), 4.59 (d, 1H, J_{gem} 10.8 Hz, PhCH_2O), 4.52–4.57 (m, 2H, PhCH_2O), 4.51 (d, 1H, J_{gem} 12.2 Hz, PhCH_2O), 4.48 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.23 (d, 1H, $J_{2,3}$ 2.8 Hz, H-2), 4.15 (s, 1H, H-1), 3.74–3.79 (m, 2H, H-3′, H-6a′), 3.55–3.67 (m, 3H, H-4′, H-5′, H-6b′), 3.48 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.1 Hz, H-4), 3.43 (s, 3H, CH_3O), 3.41 (dd, 1H, $J_{3,4}$ 9.3 Hz, H-3), 3.24 (dq, 1H, $J_{4,5}$ 9.1, $J_{5,6}$ 6.0 Hz, H-5), 2.03 (s, 3H, CH_3C(O)O), 1.32 (d, 3H, $J_{5,6}$ 6.0 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8 (*C*═O), 138.8 (Ar), 138.6 (Ar), 138.3 (Ar), 138.1 (Ar), 128.4 (Ar), 128.3(4) (Ar), 128.3(0) (Ar), 128.2 (Ar), 128.1(2) (Ar), 128.1(0) (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 101.7 (C-1), 101.1 (C-1′), 83.1 (C-3′),

79.9, 79.8 (C-3, C-4), 78.1 (C-4′), 75.5 (PhCH$_2$O), 75.0, 74.8, 74.7 (C-5′, PhCH$_2$O × 2), 73.6, 73.5 (C-2′, PhCH$_2$O), 72.5 (C-2), 71.7 (C-5), 69.9, 69.8 (C-6, PhCH$_2$O), 56.5 (CH$_3$O), 21.1 (CH$_3$C(O)O), 18.0 (C-6); HRESIMS: Calcd for $C_{50}H_{56}O_{11}Na$ 855.3715. Found 855.3715.

3.43. Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-deoxy-β-D-mannopyranoside (48)

Disaccharide **47** (529 mg, 0.63 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (20 mL) and treated with 0.5 M CH_3ONa–CH_3OH (5 mL), then processed as described for **18**. Purification of the product by chromatography over silica gel (7:3 hexanes–EtOAc) gave **48** (502 mg, quant.) as a colourless syrup: R_f 0.49 (1:1 hexanes–EtOAc); $[\alpha]_D$ −45 (*c* 0.57, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.44 (m, 23H, ArH), 7.17–7.19 (m, 2H, ArH), 5.09 (d, 1H, J_{gem} 11.3 Hz, PhC*H*$_2$O), 5.00 (d, 1H, J_{gem} 10.8 Hz, PhC*H*$_2$O), 4.90 (d, 1H, J_{gem} 12.1Hz, PhC*H*$_2$O), 4.87 (d, 1H, J_{gem} 10.9 Hz, PhC*H*$_2$O), 4.82 (d, 1H, J_{gem} 11.3 Hz, PhC*H*$_2$O), 4.61 (d, 1H, J_{gem} 10.8 Hz, PhC*H*$_2$O), 4.59 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.56 (d, 1H, J_{gem} 12.4 Hz, PhC*H*$_2$O), 4.54 (d, 1H, J_{gem} 11.1 Hz, PhC*H*$_2$O), 4.49 (d, 1H, J_{gem} 12.1 Hz, PhC*H*$_2$O), 4.45 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O), 4.27 (s, 1H, H-1), 4.22 (d, 1H, $J_{2,3}$ 3.0 Hz, H-2), 3.75 (dd, 1H, $J_{2',3'}$ 9.0 Hz, H-2′), 3.64–3.72 (m, 3H, H-3′, H-6a′, H-6b′), 3.52–3.59 (m, 3H, H-4′, H-5′, H-4), 3.52 (s, 3H, C*H*$_3$O), 3.49 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.3 Hz, H-3), 3.31 (dq, 1H, $J_{4,5}$ 9.0, $J_{5,6}$ 6.1 Hz, H-5), 1.37 (d, 3H, $J_{5,6}$ 6.1 Hz, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1 (Ar), 138.6 (Ar), 138.3 (Ar), 138.2 (Ar), 138.1 (Ar), 128.3(4) (Ar), 128.3(0) (Ar), 128.2(8) (Ar), 128.0(7) (Ar), 128.0(6) (Ar), 127.9(6) (Ar), 127.8 (Ar), 127.6(8) (Ar), 127.6(5) (Ar), 127.5(4) (Ar), 127.5(3) (Ar), 127.4 (Ar), 104.7 (C-1′), 101.3 (C-1), 85.3 (C-3′), 80.1, 79.9 (C-3, C-4), 77.3 (C-4′, C-5′), 75.5(3), 75.5(2), 75.5(0) (C-2, C-2′, PhCH$_2$O), 75.3 (PhCH$_2$O), 75.0 (PhCH$_2$O), 74.8 (C-4′, C-5′), 73.4 (PhCH$_2$O), 71.8 (C-5), 70.4 (PhCH$_2$O), 69.7 (C-6′), 57.0 (CH$_3$O), 18.0 (C-6); HRESIMS: Calcd for $C_{48}H_{54}O_{10}Na$ 813.3609. Found 813.3609.

3.44. Methyl 3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-deoxy-β-D-mannopyranoside (49)

As described for compound **19**, disaccharide **48** (475 mg, 0.60 mmol) was dissolved in freshly distilled Me_2SO (10 mL) and Ac_2O (5 mL). The concentrated reaction mixture was then treated with 1.0 M L-Selectride® in THF (2.4 mL, 2.40 mmol) in dry THF (10 mL) at −78 °C under argon. Purification by column chromatography over silica gel (1:1 hexanes–EtOAc) gave **49** (390 mg, 82%) as a white solid: R_f 0.41 (1:1 hexanes–EtOAc); $[\alpha]_D$ −52 (*c* 0.71, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22–7.24 (m, 25H, ArH), 4.96 (d, 1H, J_{gem} 11.3 Hz, PhC*H*$_2$O), 4.94 (d, 1H, J_{gem} 12.2 Hz, PhC*H*$_2$O), 4.93 (d, 1H, J_{gem} 10.9 Hz, PhC*H*$_2$O), 4.90 (d, 1H, $J_{1',2'}$ 0.7 Hz, H-1′), 4.85 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O), 4.65 (d, 1H, J_{gem} *12.1 Hz,* PhC*H*$_2$O), 4.60 (d, 1H, J_{gem} 10.8 Hz, PhC*H*$_2$O), 4.56 (d, 1H, J_{gem} *11.0 Hz,* PhC*H*$_2$O), 4.50 (d, 1H, $J_{2,3}$ 2.8 Hz, H-2), 4.46 (d, 1H, J_{gem} 11.4 Hz, PhC*H*$_2$O), 4.45 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O), 4.42 (d, 1H, J_{gem} *12.0 Hz,* PhC*H*$_2$O), 4.34 (d, 1H, $J_{2',3'}$ 2.8 Hz, H-2′), 4.26 (s, 1H, H-1), 3.91 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.3 Hz, H-4′), 3.76 (dd, 1H, $J_{5',6'}$ 2.0, J_{gem} *10.6 Hz,* H-6a′), 3.63 (dd, 1H, $J_{5',6'}$ 6.1, J_{gem} 10.5 Hz, H-6b′), 3.58 (dd, 1H, H-3′), 3.44–3.52 (m, 3H, H-5′, H-3, H-4), 3.48 (s, 3H, C*H*$_3$O), 3.31 (dq, 1H, $J_{4,5}$ 8.7, $J_{5,6}$ 6.0 Hz, H-5), 1.37 (d, 3H, $J_{5,6}$ 6.1 Hz, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4(9) (Ar), 138.4(5) (Ar), 138.2 (Ar), 138.1 (Ar), 128.4 (Ar), 128.3(1) (Ar), 128.2(8) (Ar), 128.2(1) (Ar), 128.2(0) (Ar), 128.1 (Ar), 127.9(Ar), 127.7 (Ar), 127.6(4) (Ar), 127.6(3) (Ar), 127.5(5) (Ar), 127.5(0) (Ar), 102.0 (C-1), 99.1 (C-1′), 81.4 (C-3′), 80.1 (C-3/C-5′), 79.4 (C-4), 75.4 (PhCH$_2$O), 75.1 (PhCH$_2$O), 75.0 (C-3/C-5′), 74.4 (C-4′), 73.4 (PhCH$_2$O), 71.8 (C-5), 70.7 (PhCH$_2$O), 70.4, 70.1, 70.0 (C-2, C-6′, PhCH$_2$O), 67.7 (C-2′), 57.1 (CH$_3$O), 18.0 (C-6); HRESIMS: Calcd for $C_{48}H_{54}O_{10}Na$ 813.3609. Found 813.3614. Anal. Calcd for $C_{48}H_{54}O_{10}$: C, 71.90; H, 6.21. Found: C, 71.95; H, 6.22.

3.45. Methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-methyl-β-D-mannopyranoside (50)

Monosaccharide acceptor **46** (198 mg, 0.51 mmol) was reacted with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate (**16**) (390 mg, 0.61 mmol) in CH_2Cl_2 (5 mL) using TMSOTf (6 μL, 0.03 mmol) under argon at 0 °C. The mixture was then processed as described for **17**. The product was purified by chromatography over silica gel (4:1 hexanes–EtOAc) to give **50** (298 mg, 68%) as a colourless syrup: R_f 0.43 (1:1 hexanes–EtOAc); $[\alpha]_D$ −43 (*c* 0.47, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18–7.37 (m, 25H, ArH), 5.12 (dd, 1H, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.5 Hz, H-2′), 4.96 (d, 1H, J_{gem} 11.1 Hz, PhC*H*$_2$O), 4.89 (d, 1H, J_{gem} 11.9 Hz, PhC*H*$_2$O), 4.82 (d, 1H, J_{gem} 11.5 Hz, PhC*H*$_2$O), 4.82 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.79 (d, 1H, J_{gem} 11.6 Hz, PhC*H*$_2$O), 4.75 (d, 1H, J_{gem} 11.5 Hz, PhC*H*$_2$O), 4.55 (d, 1H, J_{gem} 10.9 Hz, PhC*H*$_2$O), 4.53 (d, 1H, J_{gem} 10.9 Hz, PhC*H*$_2$O), 4.52 (d, 1H, J_{gem} 11.9Hz, PhC*H*$_2$O), 4.48 (d, 1H, J_{gem} 12.1 Hz, PhC*H*$_2$O), 4.46 (d, 1H, J_{gem} 11.9 Hz, PhC*H*$_2$O), 4.23 (d, 1H, $J_{2,3}$ 2.9 Hz, H-2), 4.19 (s, 1H, H-1), 3.76 (dd, 1H, $J_{2',3'}$ 8.2, $J_{3',4'}$ 9.4Hz, H-3′), 3.74 (dd, 1H, $J_{5',6'}$ 1.4, J_{gem} 8.9 Hz, H-6a′), 3.53–3.66 (m, 6H, H-4′, H-5′, H-6b′, H-4, H-6a, H-6b), 3.46–3.48 (m, 4H, H-3, C*H*$_3$O), 3.36–3.39 (m, 4H, H-5, C*H*$_3$O), 2.03 (s, 3H, C*H*$_3$C(O)O); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8 (*C*═O), 138.7 (Ar), 138.5 (Ar), 138.2 (Ar), 138.1 (Ar), 138.0 (Ar), 128.4 (Ar), 128.3(3) (Ar), 128.3(0) (Ar), 128.2(5) (Ar), 128.1(3) (Ar), 128.0(9) (Ar), 128.0 (Ar), 127.8 (Ar), 127.7(2) (Ar), 127.7(1) (Ar), 127.6 (Ar), 127.5(5) (Ar), 127.4(8) (Ar), 101.7 (C-1), 101.1 (C-1′), 83.2 (C-3′), 80.0 (C-3), 78.1 (C-4′/C-5′/C-4), 75.5, 75.2, 74.9, 74.8(2), 74.7(5) (C-4′/C-5′/C-4, C-5, PhCH$_2$O × 3), 73.6, 73.5, 72.8, 72.2 (C-2, C-6, C-2′, PhCH$_2$O), 69.8(4), 69.8(0) (C-6′, PhCH$_2$O), 59.3 (CH$_3$O), 56.7 (CH$_3$O), 21.1 (CH$_3$C(O)O); HRESIMS: Calcd for $C_{51}H_{58}O_{12}Na$ 885.3821. Found 885.3811.

3.46. Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-methyl-β-D-mannopyranoside (51)

Disaccharide **50** (281 mg, 0.33 mmol) was dissolved in 1:1 CH_2Cl_2–MeOH (10 mL) and treated with 0.5 M CH_3ONa–CH_3OH (3 mL), then processed as described for **18**. Purification of the product by chromatography over silica gel (7:3 hexanes–EtOAc) gave **51** (257 mg, 96%): R_f 0.31 (1:1 hexanes–EtOAc); $[\alpha]_D$ −42 (*c* 0.80, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.43 (m, 23H, ArH), 7.16–7.18 (m, 2H, ArH), 5.08 (d, 1H, J_{gem} 11.2 Hz, PhC*H*$_2$O), 4.97 (d, 1H, J_{gem} 10.9 Hz, PhC*H*$_2$O), 4.90 (d, 1H, J_{gem} *12.0 Hz,* PhC*H*$_2$O), 4.86 (d, 1H, J_{gem} 10.9 Hz, PhC*H*$_2$O), 4.80 (d, 1H, J_{gem} *11.4 Hz,* PhC*H*$_2$O), 4.61 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.57 (d, 1H, J_{gem} *10.9 Hz,* PhC*H*$_2$O), 4.55 (d, 1H, J_{gem} 12.2 Hz, PhC*H*$_2$O), 4.53 (d, 1H, J_{gem} 11.0 Hz, PhC*H*$_2$O), 4.48 (d, 1H, J_{gem} 12.1 Hz, PhC*H*$_2$O), 4.44 (d, 1H, J_{gem} 12.0 Hz, PhC*H*$_2$O), 4.28 (s, 1H, H-1), 4.23 (d, 1H, $J_{2,3}$ 3.2 Hz, H-2), 3.84 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.5 Hz, H-4), 3.73 (dd, 1H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 8.9 Hz, H-2′), 3.61–3.71 (m, 5H, H-3′, H-6a′, H-6b′, H-6a, H-6b), 3.51–3.55 (m, 3H, H-4′, H-3, H-4), 3.53 (s, 3H, C*H*$_3$O), 3.39 (s, 3H, C*H*$_3$O), 3.37 (ddd, 1H, $J_{4,5}$ 9.7, $J_{5,6}$ 2.0, 5.2 Hz, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1 (Ar), 138.5 (Ar), 138.2 (Ar), 138.1(3) (Ar), 138.1(1) (Ar), 128.3(5) (Ar), 128.3(2) (Ar), 128.3(0) (Ar), 128.2(5) (Ar), 128.1 (Ar), 128.0(4) (Ar), 128.0(3) (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 104.4 (C-1′), 101.6 (C-1), 85.2 (C-3′), 80.2 (C-3), 77.3 (C-4′/C-5′) 75.6, 75.5, 75.3, 75.0, 74.9, 74.8 (C-2′, C-4′/C-5′, C-2, C-5, PhCH$_2$O × 3), 74.4 (C-4), 73.4 (PhCH$_2$O), 71.7 (C-6), 70.4 (PhCH$_2$O), 69.7 (C-6′), 59.4 (CH$_3$O), 57.2 (CH$_3$O); HRESIMS: Calcd for $C_{49}H_{56}O_{11}Na$ 843.3715. Found 843.3718.

3.47. Methyl 3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1→2)-3,4-di-*O*-benzyl-6-*O*-methyl-β-D-mannopyranoside (52)

As described for compound **19**, disaccharide **51** (257 mg, 0.31 mmol) was dissolved in freshly distilled Me_2SO (8 mL) and Ac_2O (4 mL). The concentrated reaction mixture was then treated with 1.0 M L-Selectride® in THF (1.3 mL, 1.25 mmol) in dry THF (10 mL) at −78 °C under argon. Purification by column chromatography over silica gel (7:3 hexanes–EtOAc) gave **52** (200 mg, 78%) as a white solid: R_f 0.25 (1:1 hexanes–EtOAc); $[\alpha]_D$ −49 (*c* 0.62, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.37–7.41 (m, 4H, ArH), 7.21–7.34 (m, 21H, ArH), 4.96 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.93 (d, 1H, J_{gem} 10.7 Hz, PhCH_2O), 4.91 (d, 1H, $J_{1',2'}$ 0.8 Hz, H-1′), 4.91 (d, 1H, J_{gem} 10.0 Hz, PhCH_2O), 4.84 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.64 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.56 (d, 1H, J_{gem} 10.9 Hz, PhCH_2O), 4.55 (d, 1H, J_{gem} 11.0 Hz, PhCH_2O), 4.50 (d, 1H, $J_{2,3}$ 3.1 Hz, H-2), 4.46 (d, 1H, J_{gem} 11.5 Hz, PhCH_2O), 4.45 (d, 1H, J_{gem} 12.1 Hz, PhCH_2O), 4.42 (d, 1H, J_{gem} 11.9 Hz, PhCH_2O), 4.34 (d, 1H, $J_{2',3'}$ 2.9 Hz, H-2′), 4.27 (d, 1H, $J_{1,2}$ 0.7 Hz, H-1), 3.90 (dd, 1H, $J_{3',4'} \approx J_{4',5'}$ 9.3 Hz, H-4′), 3.80 (dd, 1H, $J_{3,4} \approx J_{4,5}$ 9.6 Hz, H-4), 3.76 (dd, 1H, $J_{5',6'}$ 2.0, J_{gem} 10.6 Hz, H-6a′), 3.67 (dd, 1H, $J_{5,6}$ 2.0, J_{gem} 10.6 Hz, H-6a), 3.62 (dd, 1H, $J_{5',6'}$ 6.0, J_{gem} 10.7 Hz, H-6b′), 3.61 (dd, 1H, $J_{5,6}$ 5.2, J_{gem} 10.7 Hz, H-6b), 3.56 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.1 Hz, H-3), 3.54 (dd, 1H, $J_{2',3'}$ 3.4, $J_{3',4'}$ 9.3Hz, H-3′), 3.49 (ddd, 1H, $J_{4',5'}$ 9.7, $J_{5',6'}$ 1.9, 6.1 Hz, H-5′), 3.48 (s, 3H, CH_3O), 3.38 (s, 3H, CH_3O), 3.36 (ddd, 1H, $J_{4,5}$ 9.8, $J_{5,6}$ 2.0, 5.2 Hz, H-5), 2.78 (br s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ38.4(8) (Ar), 138.4(6) (Ar), 138.2 (Ar), 138.1(4) (Ar), 138.1(1) (Ar), 128.4 (Ar), 128.3(2) (Ar), 128.3(0) (Ar), 128.2(9) (Ar), 128.2(7) (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.7 (Ar), 127.6(4) (Ar), 127.6(1) (Ar), 127.5(2) (Ar), 127.4(9) (Ar), 102.2 (C-1), 99.0 (C-1′), 81.4 (C-3), 80.2 (C-3′), 75.3, 75.2, 75.1, 75.0 (C-5, C-5′, PhCH_2O × 2), 74.4 (C-4′), 73.9 (C-4), 73.4 (PhCH_2O), 71.6 (C-6), 70.6 (PhCH_2O), 70.1, 70.0 (C-6′, PhCH_2O), 67.7 (C-2′), 59.2 (CH_3O), 57.2 (CH_3O); HRESIMS: Calcd for $C_{49}H_{56}O_{11}Na$ 843.3715. Found 843.3705.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.12.011.

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