

Synthesis of a hexasaccharide acceptor corresponding to the reducing terminus of mycobacterial 3-*O*-methylmannose polysaccharide (MMP)¹

Wensheng Liao^{*}, Depei Lu^{*}

*Research Center for Eco-Environmental Sciences, Academia Sinica, P.O. Box 2871, Beijing 100085,
PR China*

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Abstract

The title compound methyl *O*-(2,6-di-*O*-benzyl-3-*O*-methyl- α -D-mannopyranosyl)-[(1 \rightarrow 4)-*O*-(2,6-di-*O*-benzyl-3-*O*-methyl- α -D-mannopyranosyl)]₄-(1 \rightarrow 4)-2,6-di-*O*-benzyl-3-*O*-methyl- α -D-mannopyranoside (**2**) was synthesized in a blockwise manner, employing trichloroacetimidate (**11**) and (**20**) as glycosyl donors. The strategy relies on the single-step preparation of the 3-*O*-methyl ethers (**4**) and (**12**) as starting materials. Since all intermediates contain one or more OCH₃ groups, they are easily identified by NMR spectroscopy using the methyl proton signals. Compound **2** corresponds to the reducing terminal hexasaccharide of mycobacterial 3-*O*-methylmannose polysaccharide (MMP). MMP has the unusual property of stimulating the fatty acid synthetase multienzyme complex. Compound **2** can serve as a suitable glycosyl acceptor for the synthesis of extended fragments of MMP. © 1996 Elsevier Science Ltd.

Keywords: Synthesis; Glycosylation; 3-*O*-Methylmannose polysaccharide (MMP); Mycobacterium

1. Introduction

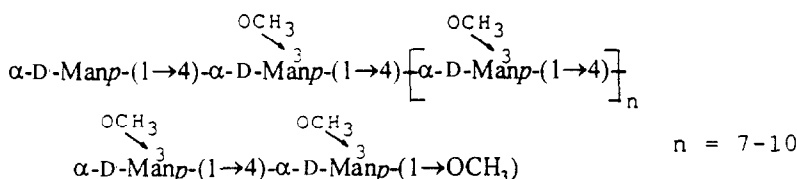
In recent decades, mycobacteria have been demonstrated to be one of the few higher organisms that have adapted the helical-forming, lipid-binding property of amylose-like

^{*} Corresponding authors.

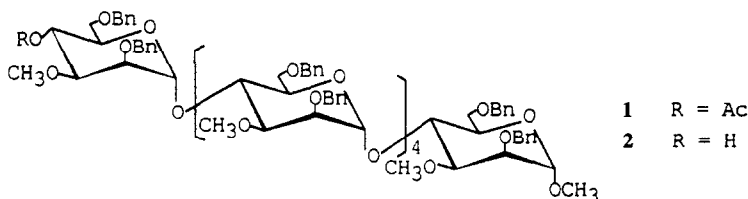
¹ Project supported by the National Natural Science Foundation of China.

oligosaccharides to regulate metabolic process [1,2]. Several polymethylpolysaccharides (PMPS) are found in *Mycobacterium smegmatis* [3,4], including a neutral polysaccharide (MMP) that contains 3-*O*-methyl-D-mannose. MMP can form a stable 1:1 complex with long-chain fatty acids and acyl coenzyme A derivatives in which the lipid is included in the interior of the helically coiled polysaccharide in a specific orientation [5,6]. The role of 3-*O*-methylation may be to stabilize the helical conformation of MMP as well as to enhance the direct interaction with lipids due to the hydrophobic nature of the methyl groups. It is postulated that MMP, along with other PMPs, serve as lipid carriers in the cell. They activate the fatty acid synthetase complex and alter the fatty acid product distribution [7].

The structure of MMP has been well defined [2,6]. It is composed of 10–13 3-*O*-methylmannoses joined by α -(1 \rightarrow 4) linkages, each molecule is terminated by an unmethylated mannose, and the reducing end of the linear chain is blocked by an α -methyl aglycon.



As part of a project on the total synthesis of MMP, we describe here a regio- and stereo-controlled synthesis of the hexasaccharide glycosyl acceptor **2**, which corresponds to the reducing terminal fragment of MMP. Compound **2** is suitably functionalized to serve as a precursor of higher-order structures.

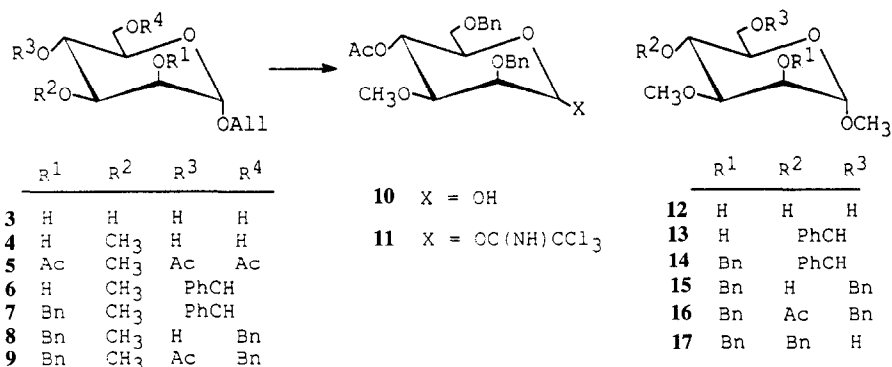


2. Results and discussion

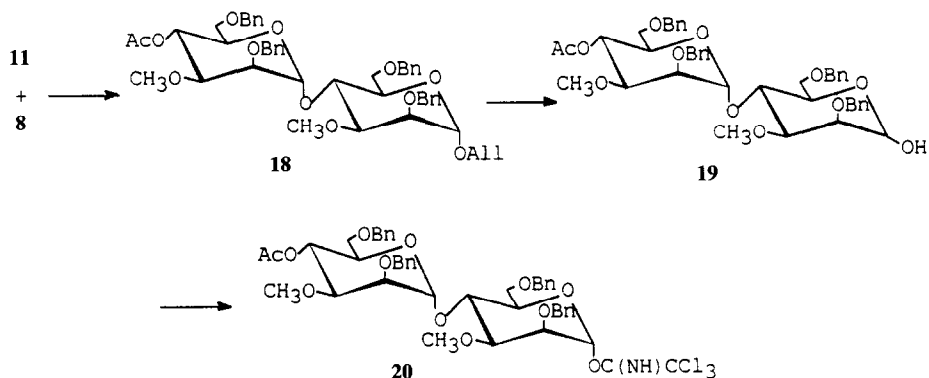
Based on retrosynthetic considerations, three monosaccharide synthons **8**, **11**, and **15** were designed; **11** can be obtained from **8** in a three-step sequence.

The monosaccharide units.—A method for the single-step 3-*O*-methylation of methyl glycopyranoside, which made large-scale preparation of the starting material **12** easy,

has been reported [8]. The method can also be applied to allyl glycopyranosides. Thus, allyl 3-*O*-methyl ether **4** was obtained in this fashion in 73% yield. The ^{13}C NMR spectrum of **5** contains a deshielded signal for C-3 at 76.8, in agreement with the 3-*O*-methyl structure. With O-3 protected by a methyl group, benzylidenation of **4** in the presence of ZnCl_2 and α, α -diethoxytoluene (instead of benzaldehyde) at room temperature gave a high yield of **6** (86%) [9,10]. Compound **6** was then benzylated (BnBr/THF) to give the benzylidene acetal **7**, followed by reductive ring-opening with sodium cyanoborohydride–hydrogen chloride ($\text{NaCNBH}_3/\text{HCl}$) [11–13]. This procedure produced highly regioselective 6-*O*-benzyl ether **8** (89%) containing a free OH group at HO-4.



Bn = benzyl
 Ph = phenyl

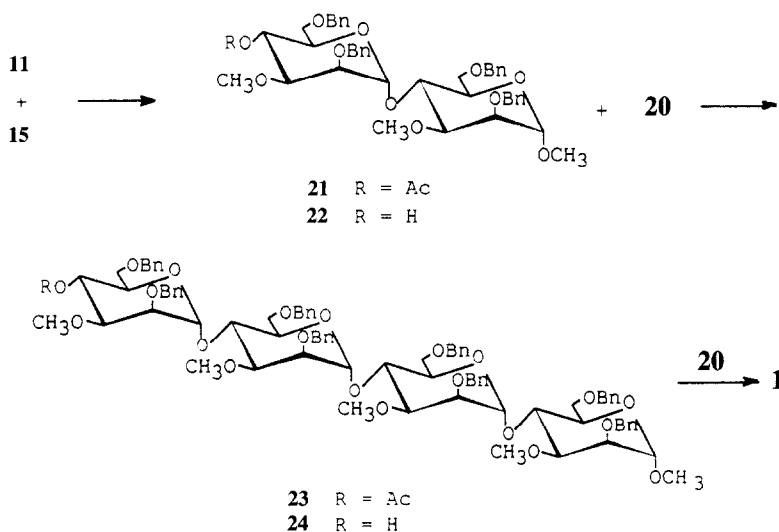


With the monosaccharide glycosyl acceptor **8** in hand, we prepared the monosaccharide glycosyl donor **11** from **8** by successive treatment with (1) acetic anhydride in pyridine by standard methods, (2) deallylation of **9** in methanol with PdCl_2 as the

catalyst [14,15] to generate hemiacetal **10** (87%), and (3) trichloroacetimidation of **10** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and CCl_3CN [16,17] in anhyd. CH_2Cl_2 (92%).

Another monosaccharide glycosyl acceptor **15** was prepared in an analogous fashion to the synthesis of **8**. Benzylidenation of **12** afforded benzylidene acetal **13** in 83% yield, followed by benzylation to give **14**. After regioselective ring-opening reduction as described for **7**, the acetal **14** was converted to **15** in 89% yield; using $\text{LiAlH}_4/\text{AlCl}_3$ as reductant [18], the alcohol **17** was obtained with a free OH group at O-6.

Glycosidation reactions.—Coupling of the imidate **11** with the alcohol **8** in the presence of triethylsilyl trifluoromethanesulfonate (TESTfI) and powdered 4 Å molecular sieves at -78°C afforded the protected allyl mannobioside **18**. The stereochemistry of the glycosidation reaction was assigned as α -D from the ^{13}C NMR data, which included two signals for C-1_A and C-1_B at δ 96.7 ($^1J_{\text{C,H}}$ 168.6 Hz) and 99.9 ($^1J_{\text{C,H}}$ 169.9 Hz), respectively. It is worth noting that deallylation of the disaccharide **18** failed with PdCl_2 in MeOH as described for monosaccharide **9**, but proceeded well in a mixed solvent of 1:1 MeOH– CH_2Cl_2 to give hemiacetal **19** (87%). The desired disaccharide glycosyl imidate (**20**) was then obtained from **19** in 85% yield by treatment with trichloroacetonitrile in the presence of DBU.



Glycosidation of the imidate **11** with the methyl glycopyranoside **15** was executed as described for **18** to provide the protected methyl mannobioside (**21**). Again, the reaction was performed in a highly α -stereoselective manner. Compound **21** was deacetylated to give disaccharide glycosyl acceptor **22**. We performed blockwise chain elongation of **22** with the imidate **20** to afford the protected tetrasaccharide (**23**) (61%). The structure of **23** was confirmed by ^{13}C NMR spectroscopy, in which four signals for C-1 in the α -D configuration appeared at δ 99.9 ($^1J_{\text{C,H}}$ 171.6 Hz), 99.8 ($^1J_{\text{C,H}}$ 170.1 Hz), 99.7 ($^1J_{\text{C,H}}$

169.1 Hz), and 98.6 ($^1J_{C,H}$ 168.2 Hz). Subsequent deacetylation of **23** provided mannotetraosyl glycosyl acceptor **24**. Compound **24** gave five methyl singlets at δ 3.37, 3.31, 3.23, 3.20, and 3.19 in its 1H NMR spectrum, of which δ 3.37 was assigned to the methyl aglycon (determined by NOE-DIFF technique), and the others to the 3-*O*-methyl groups.

The final condensation of the disaccharide donor **20** with the tetrasaccharide acceptor **24** proceeded at $-78^\circ C$ without incident. The reaction was complete in 15 min, and produced hexasaccharide **1** (52%). The 1H NMR spectrum of **1** showed clearly seven methyl singlets at 3.37, 3.24, 3.19, 3.18, 3.16, 3.15, and 3.10. After deacetylation, the target glycosyl mannohexaosyl acceptor **2** was obtained.

In conclusion, the linear methyl α -(1 \rightarrow 4)-D-mannohexasaccharide **2** was achieved by a blockwise strategy employing disaccharide donor **20** and disaccharide acceptor **22** as building blocks. Stereochemistry of all synthetic intermediates was deduced from the synthetic sequences, and intermediates and products were characterized by their ^{13}C and 1H NMR spectra. Compounds **1** and **2** were further characterized by microanalysis. Owing to their hydrophobic nature, field desorption mass spectra (FDMS) were obtained to confirm composition. In the case of **1**, signals appearing at m/z 2212 and m/z 2235 were assigned to the $[M]^+$ and $[M + Na]^+$ ions, respectively.

3. Experimental

General methods.—Preparative chromatography was performed on columns (16 \times 240, 18 \times 300 and 35 \times 400 mm) of silica gel (120–200 mesh). Thin-layer chromatography (TLC) was performed on silica gels G and HF, and products were detected either by charring with 30% (v/v) H_2SO_4 in MeOH or by UV light. Analytical LC was carried out in stainless-steel columns packed with silica gel (10 \times 150 mm, or 4.6 \times 250 mm), with peak detection by a differential refractometer (Perkin–Elmer LC-25 RI Detector), using petroleum ether–ethyl acetate as the eluent at a flow rate of 1–4 mL/min. Optical rotations were determined with a Perkin–Elmer model 241 MC automatic polarimeter for solutions in a 1-dm, jacketed cell. Solvents were distilled before use and were dried, as necessary, by literature procedures. 1H and ^{13}C NMR spectra were recorded on Varian XL-400 and Varian XL-200 spectrometers; chemical shifts (δ) are given in ppm, downfield from Me_4Si , for solutions in $CDCl_3$, unless noted otherwise. Subscripts A–F refer to the individual sugar residues, with A standing for the reducing-end unit. Field desorption mass spectra (FDMS) were recorded on a Finnigan MAT 90 mass spectrometer.

Allyl 3-*O*-methyl- α -D-mannopyranoside (4).—A mixture of allyl α -D-mannopyranoside **3** [19] (10.0 g, 45.5 mmol) and dibutyltin oxide (13.5 g, 54.0 mmol) in dry MeOH (250 mL) was boiled under reflux. After the solution became transparent, heating was continued for 1.5 h, and the solvent was concentrated in vacuo. The resulting white foamy residue was dissolved in *N,N*-dimethylformamide (225 mL), and methyl iodide (7.0 mL, 2.5 molar equiv) was added. The flask was capped and heated at $80^\circ C$ for 10 h. TLC (6:1 CH_2Cl_2 –MeOH) showed the presence of major product (R_f 0.52) together with a small amount of starting material (R_f 0.31). After cooling, the mixture was

filtered. The filtrate was evaporated to a syrup, which was applied to a column of silica gel in EtOAc to give **4** (7.8 g, 73%); $[\alpha]_D + 58.5^\circ$ (*c* 0.5, MeOH); ^1H NMR: δ 6.12–5.86 (m, 1 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.48–5.20 (m, 2 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 4.91 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 3.57 (s, 3 H, OCH_3). Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_6$: C, 51.27; H, 7.74. Found: C, 51.07; H, 7.69.

The triacetate **5** was obtained by standard methods as a syrup; $[\alpha]_D + 33.9^\circ$ (*c* 0.8, CHCl_3); ^{13}C NMR: δ 170.7, 170.3, 169.8 (3 CH_3CO), 133.0 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 118.3 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 96.8 (C-1), 76.8 (C-3), 68.5 (C-5), 67.7 (C-2), 67.4 (C-4), 62.7 (C-6), 57.7 (OCH_3), 21.0, 20.8, 20.7 (3 CH_3CO). Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_9$: C, 53.33; H, 6.71. Found: C, 53.25; H, 6.66.

Allyl 4,6-O-benzylidene-3-O-methyl- α -D-mannopyranoside (6).—Compound **4** (46.0 g, 0.20 mol) was dissolved in α,α -diethoxytoluene (69.0 g, 0.38 mol). Freshly dried ZnCl_2 (20.0 g) was added. The mixture was stirred vigorously at room temperature for 4 h. No starting material **4** remained after this time (TLC, 3:1 petroleum ether–EtOAc). CH_2Cl_2 (200 mL) was added to dilute the mixture. The precipitate was filtered off and washed with CH_2Cl_2 . The filtrate and washings were combined, washed with aqueous sodium hydrogen carbonate, then water, dried (Na_2SO_4), and concentrated to a syrup. Purification of the syrup by column chromatography (3:1 petroleum ether–EtOAc) yielded **6** (54.5 g, 86%); $[\alpha]_D + 72^\circ$ (*c* 1.4, CHCl_3); ^1H NMR: δ 7.54–7.30 (m, 5 H, aromatic H), 6.03–5.82 (m, 1 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.39–5.20 (m, 2 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.59 (s, 1 H, PhCH), 4.94 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 4.30–3.92 (m, 3 H, H-2,4,5), 3.90–3.82 (m, 2 H, H-6), 3.71 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 9.3 Hz, H-3), 3.56 (s, 3 H, OCH_3), 2.04 (br s, 1 H, OH); ^{13}C NMR: δ 137.3 (aromatic C-1), 133.3 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 128.8, 128.0, 126.0 (aromatic C), 117.7 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 101.5 (PhCH), 99.1 (C-1), 78.5 (C-3), 77.2 (C-4), 68.9 (C-2), 68.6 (C-6), 68.0 ($\text{CH}_2-\text{CH}=\text{CH}_2$), 63.2 (C-5), 58.5 (CH_3O). Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_6$: C, 63.34; H, 6.88. Found: C, 63.46; H, 6.84.

Allyl 2-O-benzyl-4,6-O-benzylidene-3-O-methyl- α -D-mannopyranoside (7).—To a solution of **6** (37.0 g, 0.115 mol) in dry THF (350 mL) cooled in an ice bath was added sodium hydride (80% in oil; 11.0 g, 0.37 mol) with stirring. Benzyl bromide (15.9 mL, 0.131 mol) was added dropwise and the mixture was heated under reflux with vigorous agitation for 5 h. TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. After cooling, the remaining sodium hydride was filtered off and the filtrate was concentrated. The residue was partitioned between water and dichloromethane. The organic layer was washed with saturated saline, dried (Na_2SO_4), and concentrated to a syrup, which was chromatographed on a column of silica gel (4:1 petroleum ether–EtOAc) to give **7** (43.6 g, 92%); $[\alpha]_D + 47.1^\circ$ (*c* 0.5, CHCl_3); ^1H NMR: δ 7.54–7.30 (m, 10 H, aromatic H), 5.97–5.76 (m, 1 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.63 (s, 1 H, PhCH), 5.33–5.15 (m, 2 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 4.86 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.82 and 4.70 (ABq, 2 H, J 12.4 Hz, PhCH_2), 4.29–4.11 (m, 1 H, H-5), 4.01–3.80 (m, 4 H, H-2,4,6 and 6'), 3.75 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.2 Hz, H-3), 3.51 (s, 3 H, OCH_3); ^{13}C NMR: δ 137.9 and 137.5 (aromatic C-1), 133.4 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 128.9–126.1 (aromatic C), 117.7 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 101.5 (PhCH), 98.2 (C-1), 78.9 (C-3), 77.9 (C-4), 75.4 (C-2), 73.4 (PhCH_2), 68.7 (C-6), 67.9 ($\text{CH}_2-\text{CH}=\text{CH}_2$), 64.1 (C-5), 58.6 (OCH_3). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_6$: C, 69.89; H, 6.84. Found: C, 70.01; H, 6.83.

Allyl 2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranoside (8).—Hydrogen chloride in diethyl ether was added dropwise at 0 °C to compound **7** (18.0 g, 43.7 mmol) and sodium cyanoborohydride (33.0 g, 0.53 mol) in tetrahydrofuran (distilled from lithium aluminum hydride, 300 mL) containing 3 Å molecular sieves until the evolution of gas ceased (pH 5). TLC (3:1 petroleum ether–EtOAc) after 15 min indicated complete reaction. The mixture was neutralized with solid sodium carbonate and filtered. The filtrate was concentrated, and the residue was partitioned between water and dichloromethane. The organic layer was dried (Na_2SO_4) and concentrated. The resulting syrup was applied to a column of silica gel which was eluted with 2:1 petroleum ether–EtOAc to give **8** (16.1 g, 89%); $[\alpha]_{\text{D}} + 7^\circ$ (*c* 1.3, CHCl_3); ^1H NMR: δ 7.43–7.27 (m, 10 H, aromatic H), 5.99–5.78 (m, 1 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.33–5.13 (m, 2 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 4.95 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.74 and 4.67 (ABq, 2 H, J 11.9 Hz, PhCH_2), 4.63 and 4.57 (ABq, 2 H, J 11.2 Hz, PhCH_2), 4.26–3.91 (m, 3 H, $\text{CH}_2=\text{CH}-\text{CH}_2$, H-5), 3.85–3.73 (m, 4 H, H-2,4,6 and 6'), 3.49 (dd, 1 H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.3 Hz, H-3), 3.35 (s, 3 H, OCH_3); ^{13}C NMR: δ 138.1, 138.0 (aromatic C-1), 133.6 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 128.2–127.4 (aromatic C), 117.5 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 96.9 (C-1), 81.0 (C-3), 73.4, 72.5 (2 PhCH_2), 72.6 (C-2), 71.3 (C-5), 70.2 (C-6), 67.8 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 67.6 (C-4), 57.0 (OCH_3). Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{O}_6$: C, 69.55; H, 7.29. Found: C, 69.61; H, 7.37.

Allyl 4-O-acetyl-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranoside (9).—Compound **8** (8.0 g, 19.3 mmol) was acetylated by standard methods and compound **9** was obtained in a quantitative yield as a syrup; $[\alpha]_{\text{D}} + 15.5^\circ$ (*c* 1.1, CHCl_3); ^1H NMR: δ 7.69–7.27 (m, 10 H, aromatic H), 6.00–5.78 (m, 1 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.38–5.13 (m, 3 H, $\text{CH}_2=\text{CH}-\text{CH}_2$, H-4), 4.92 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1), 4.79 and 4.68 (ABq, 2 H, J 11.2 Hz, PhCH_2), 4.55 (s, 2 H, PhCH_2), 4.37–3.76 (m, 3 H, $\text{CH}_2=\text{CH}-\text{CH}_2$, H-5), 3.69–3.42 (m, 3 H, H-2,6 and 6'), 3.35 (s, 3 H, OCH_3), 1.98 (s, 3 H, CH_3CO); ^{13}C NMR: δ 169.9 (CH_3CO), 138.0 (2 aromatic C-1), 133.3 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 128.2–127.4 (aromatic C), 117.5 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 97.1 (C-1), 79.0 (C-3), 73.3 (C-2), 73.4, 72.7 (2 PhCH_2), 70.3 (C-5), 69.8 (C-6), 68.9 (C-4), 67.9 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 57.5 (OCH_3), 20.9 (CH_3CO). Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{O}_6$: C, 68.40; H, 7.06. Found: C, 68.32; H, 7.11.

4-O-Acetyl-2,6-di-O-benzyl-3-O-methyl-D-mannopyranoside (10).—A mixture of compound **9** (7.8 g, 17.2 mmol) and PdCl_2 (0.62 g, 3.5 mmol) in dry methanol (90 mL) was stirred vigorously for 4 h at room temperature, then filtered through Celite. The filtrate was evaporated and the residue was chromatographed on a column of silica gel in 2:1 petroleum ether–EtOAc to afford **10** (mainly α -anomer, 6.2 g, 87%). The data are given for the anomer only: $[\alpha]_{\text{D}} + 3.2^\circ$ (*c* 1.2, CHCl_3); ^1H NMR: δ 7.50–7.26 (m, 10 H, aromatic H), 5.23 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.19 (t, 1 H, $J_{3,4}$ 9.8 Hz, H-4), 5.38–5.13 (m, 2 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 4.77 and 4.66 (ABq, 2 H, J 12.2 Hz, PhCH_2), 4.52 (s, 2 H, PhCH_2), 4.15–4.05 (m, 1 H, H-5), 3.85–3.51 (m, 3 H, H-2,6 and 6'), 3.46 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 10.2 Hz, H-3), 3.34 (s, 3 H, OCH_3), 1.99 (s, 3 H, CH_3CO); ^{13}C NMR: δ 169.9 (CH_3CO), 137.9–137.3 (aromatic C-1), 128.0–127.3 (aromatic C), 92.2 (C-1), 78.3 (C-3), 73.5 (C-2), 73.0, 72.3 (2 PhCH_2), 69.8 (C-6), 69.3 (C-5), 68.8 (C-4), 57.4 (OCH_3), 20.7 (CH_3CO). Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_7$: C, 66.33; H, 6.78. Found: C, 66.25; H, 6.79.

O-(4-O-Acetyl-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranosyl)-trichloroacetimide (11).—To a mixture of compound **10** (3.8 g, 9.1 mmol) and trichloroacetonitrile (1.05 mL, 10.4 mmol) in anhyd. CH_2Cl_2 (30 mL) at -10°C was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.3 mL, 2.02 mmol). The mixture was stirred at 0°C under argon for 2 h. The solvent was removed by evaporation and the residue was purified by column chromatography with 2:1 petroleum ether–EtOAc as the eluent to yield **11** as an amorphous solid (4.7 g, 92%); $[\alpha]_{\text{D}} + 26.2^\circ$ (c 1.0, CHCl_3); ^1H NMR: δ 8.70 (s, 1 H, $\text{OC}(\text{NH})\text{CCl}_3$), 7.65–7.18 (m, 10 H, aromatic H), 6.43 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 5.48 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-4), 4.82, 4.58 (2 s, 4 H, 2 PhCH_2), 3.37 (s, 3 H, OCH_3), 2.05 (s, 3 H, CH_3CO); ^{13}C NMR: δ 169.6 (CH_3CO), 160.0 ($\text{C}=\text{NH}$), 137.8, 137.5 (aromatic C-1), 129.1–127.4 (aromatic C), 95.7 (C-1), 78.6 (C-3), 73.2 (C-2), 73.1, 73.0 (2 PhCH_2), 71.9 (C-6), 69.3 (C-5), 68.4 (C-4), 57.8 (OCH_3), 20.8 (CH_3CO). The compound was used immediately in the coupling reaction.

Methyl 4,6-O-benzylidene-3-O-methyl- α -D-mannopyranoside (13).—Benzylidenation of compound **12** (20.0 g, 0.1 mol) as described for **6** afforded **13** as a syrup (24.4 g, 83%); $[\alpha]_{\text{D}} + 57.6^\circ$ (c 2.1, CHCl_3) (lit. [20] $[\alpha]_{\text{D}}^{25} + 73.6^\circ$); ^1H NMR: δ 7.54–7.29 (m, 5 H, aromatic H), 5.60 (s, 1 H, PhCH), 4.80 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 4.32–4.24 (m, 1 H, H-5), 4.11 (dd, 1 H, $J_{1,2}$ 1.4, $J_{2,3}$ 3.4 Hz, H-2), 4.01 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-4), 3.88–3.77 (m, 2 H, H-6), 3.67 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 9.7 Hz, H-3), 3.58, 3.42 (2 s, 6 H, 2 OCH_3), 2.06 (br s, 1 H, OH).

Methyl 2-O-benzyl-4,6-O-benzylidene-3-O-methyl- α -D-mannopyranoside (14).—Compound **13** (18.5 g, 62.5 mmol) was benzylated as described for **7** to afford **14** [21] as a syrup (22.5 g, 93%); $[\alpha]_{\text{D}} + 34^\circ$ (c 1.3, CHCl_3); ^1H NMR: δ 7.59–7.32 (m, 10 H, aromatic H), 5.64 (s, 1 H, PhCH), 4.84 and 4.74 (ABq, 2 H, J 12.2 Hz, PhCH_2), 4.32–4.25 (m, 1 H, H-5), 4.18 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-4), 3.94–3.79 (m, 3 H, H-2,6 and 6'), 3.74 (dd, 1 H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.7 Hz, H-3), 3.50, 3.38 (2 s, 6 H, 2 OCH_3).

Methyl 2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranoside (15).—Reductive ring-opening of the benzylidene group in **14** (15.5 g, 40.2 mmol) as described for **8** afforded **15** as a syrup (13.8 g, 89%); $[\alpha]_{\text{D}} - 5.3^\circ$ (c 2.6, CHCl_3); ^1H NMR: δ 7.46–7.31 (m, 10 H, aromatic H), 4.81 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.71 and 4.67 (ABq, 2 H, J 11.4 Hz, PhCH_2), 4.64 and 4.61 (ABq, 2 H, J 11.3 Hz, PhCH_2), 3.97 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-4), 3.37, 3.34 (2 s, 6 H, 2 OCH_3), 2.07 (br s, 1 H, OH); ^{13}C NMR: δ 138.3, 138.1 (aromatic C-1), 128.3–127.5 (aromatic C), 99.0 (C-1), 81.1 (C-3), 73.5, 72.5 (2 PhCH_2), 71.9, 71.2 (C-2,5), 70.3 (C-6), 67.6 (C-4), 57.0 (OCH_3 -3), 54.8 (OCH_3 -1). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_6$: C, 68.02; H, 7.26. Found: C, 67.96; H, 7.26.

Methyl 4-O-acetyl-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranoside (16).—Compound **15** (150 mg, 0.35 mmol) was acetylated by standard methods and **16** was obtained in a quantitative yield; $[\alpha]_{\text{D}} + 10.7^\circ$ (c 0.5, CHCl_3); ^1H NMR: δ 7.54–7.08 (m, 10 H, aromatic H), 5.25 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-4), 4.76 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.75 and 4.70 (ABq, 2 H, J 12.2 Hz, PhCH_2), 4.56 and 4.54 (ABq, 2 H, J 11.3 Hz, PhCH_2), 3.36, 3.32 (2 s, 6 H, 2 OCH_3), 1.96 (s, 3 H, CH_3CO); ^{13}C NMR: δ 169.9 (CH_3CO), 138.2, 138.0 (aromatic C-1), 128.2–127.5 (aromatic C), 99.1 (C-1), 79.1 (C-3), 73.4 (C-2), 73.3, 72.7 (2 PhCH_2), 70.1 (C-5), 69.9 (C-6), 68.9 (C-4), 57.7 (OCH_3 -3), 54.7 (OCH_3 -1), 20.9 (CH_3CO). Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{O}_7$: C, 66.96; H, 7.02. Found: C, 66.75; H, 6.99.

Methyl 2,4-di-O-benzyl-3-O-methyl- α -D-mannopyranoside (17).—To a boiling mixture of **14** (200 mg, 0.52 mmol), anhyd. CH_2Cl_2 /ether (1.5 mL, 1/1, v/v) and LiAlH_4 (30 mg) was added a solution of AlCl_3 (105 mg) in ether, and boiling was continued for 2 h. After cooling, EtOAc and water were added, the organic layer was separated and the aqueous layer extracted with CH_2Cl_2 . The combined extracts were washed with water, dried, and evaporated. The residue was applied to a column of silica gel (petroleum ether–EtOAc) to yield **17** (176 mg, 87%); $[\alpha]_D + 18.4^\circ$ (c 0.5, CHCl_3); ^{13}C NMR: δ 138.4, 138.1 (aromatic C-1), 128.2–127.4 (aromatic C), 99.0 (C-1), 81.8 (C-3), 74.9, 74.6 (2 PhCH_2), 73.7 (C-4), 72.4, 71.7 (C-2,5), 62.3 (C-6), 57.5 (OCH_3 -3), 54.6 (OCH_3 -1). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_6$: C, 68.02; H, 7.26. Found: C, 67.90; H, 7.21.

Allyl O-(4-O-acetyl-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranosyl)-(1 \rightarrow 4)-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranoside (18).—A mixture of compound **11** (3.75 g, 6.69 mmol) and **8** (2.33 g, 5.63 mmol) in anhyd. CH_2Cl_2 (30 mL) under argon was stirred with finely powdered 4 Å molecular sieves, for 30 min at room temperature. The mixture was cooled to -78°C and triethylsilyl trifluoromethanesulfonate (TESTfl) (50 μL , 0.13 mmol) was added dropwise. The mixture was stirred for 15 min after which TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was neutralized with Et_3N (0.5 mL), filtered through Celite and the filtrate was evaporated in vacuo. The residue was purified by column chromatography with 2:1 petroleum ether–EtOAc as the eluent to yield **18** as an amorphous solid (3.48 g, 76%); $[\alpha]_D + 28.7^\circ$ (c 2.8, CHCl_3); ^1H NMR: δ 7.49–7.05 (m, 20 H, aromatic H), 6.02–5.78 (m, 1 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.37–5.12 (m, 2 H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 5.29 (t, 1 H, $J_{3,4}$ 9.6 Hz, H-4_B), 5.31 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1_B), 4.94 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1_A), 4.73–4.44 (m, 8 H, 4 PhCH_2), 3.34, 3.20 (2 s, 6 H, OCH_3 -3_A, 3_B), 1.97 (s, 3 H, CH_3CO); ^{13}C NMR: δ 170.1 (CH_3CO), 138.6–138.1 (aromatic C-1), 133.7 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 128.9–127.2 (aromatic C), 117.6 ($\text{CH}_2=\text{CH}-\text{CH}_2$), 99.9 ($^1J_{\text{C-1,H-1}}$ 169.9 Hz, C-1_B), 96.7 ($^1J_{\text{C-1,H-1}}$ 168.6 Hz, C-1_A), 81.7, 78.7 (C-3_B, 3_A), 57.6, 56.6 (OCH_3 -3_B, 3_A), 21.0 (CH_3CO). Anal. Calcd for $\text{C}_{47}\text{H}_{56}\text{O}_{12}$: C, 69.44; H, 6.94. Found: C, 69.78; H, 6.94.

O-(4-O-Acetyl-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranosyl)-(1 \rightarrow 4)-2,6-di-O-benzyl-3-O-methyl-D-mannopyranoside (19).—A mixture of **18** (1.3 g, 1.6 mmol) and PdCl_2 (100 mg, 0.57 mmol) in 1:1 MeOH– CH_2Cl_2 (22.5 mL) was stirred for 4 h at room temperature and filtered through Celite. The filtrate was evaporated and the residue was purified by column chromatography with 1:1 petroleum ether–EtOAc as the eluent to give **19** (mainly α -anomer, 1.08 g, 87%); The data are given for α -anomer only: $[\alpha]_D + 16.1^\circ$ (c 2.6, CHCl_3); ^1H NMR: δ 7.60–7.20 (m, 20 H, aromatic H), 5.33 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1_B), 5.32 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-4_B), 5.29 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1_A), 4.79–4.41 (m, 8 H, 4 PhCH_2), 4.01 (t, 1 H, $J_{3,4}$ 9.4 Hz, H-4_A), 3.35, 3.19 (2 s, 6 H, OCH_3 -3_A, 3_B), 2.02 (s, 3 H, CH_3CO); ^{13}C NMR: δ 169.8 (CH_3CO), 138.3–138.1 (aromatic C-1), 128.3–127.4 (aromatic C), 100.0 (C-1_B), 92.3 (C-1_A), 81.2, 78.7 (C-3_B, 3_A), 57.6, 56.6 (OCH_3 -3_B, 3_A), 20.5 (CH_3CO). Anal. Calcd for $\text{C}_{44}\text{H}_{52}\text{O}_{12}$: C, 67.38; H, 6.78. Found: C, 67.39; H, 6.80.

O-(4-O-Acetyl-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranosyl)-(1 \rightarrow 4)-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranosyl trichloroacetimidate (20).—To a mixture of compound **19** (0.8 g, 1.04 mmol) and Cl_3CCN (0.3 mL, 2.98 mmol) in anhyd. CH_2Cl_2

(15 mL) at -10°C was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (70 μL , 0.46 mmol). The mixture was stirred at 0°C under argon for 3 h. Processing and chromatography on silica gel in 2:1 petroleum ether–EtOAc as eluent yielded **20** (810 mg, 85%); $[\alpha]_{\text{D}} + 24.8^{\circ}$ (c 0.7, CHCl_3); ^1H NMR: δ 8.63 (s, 1 H, $\text{OC}(\text{NH})\text{CCl}_3$), 7.63–7.08 (m, 20 H, aromatic H), 6.44 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1_A), 5.35 (t, 1 H, $J_{3,4}$ 9.3 Hz, H-4_B), 5.22 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1_B), 3.34, 3.16 (2 s, 6 H, OCH_3 -3_A, 3_B), 1.96 (s, 3 H, CH_3CO); ^{13}C NMR: δ 169.7 (CH_3CO), 160.1 ($\text{C}=\text{NH}$), 138.2–137.4 (aromatic C-1), 128.6–127.1 (aromatic C), 99.6 (C-1_B), 95.5 (C-1_A), 81.1, 78.5 (C-3_B, 3_A), 57.5, 56.5 (OCH_3 -3_B, 3_A), 20.8 (CH_3CO). The compound was used immediately in the coupling reaction.

Methyl O-(4-O-acetyl-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranosyl)-(1 \rightarrow 4)-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranoside (21).—Coupling of the imidate **11** (1.70 g, 4.38 mmol) with the alcohol **15** (2.82 g, 5.04 mmol) was performed as described for **18** to provide **21** as a syrup (2.6 g, 76%); $[\alpha]_{\text{D}} + 20.2^{\circ}$ (c 1.3, CHCl_3); ^1H NMR: δ 7.45–7.18 (m, 20 H, aromatic H), 5.31 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1_B), 5.29 (t, 1 H, $J_{3,4}$ 9.8 Hz, H-4_B), 4.78 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1_A), 4.74–4.42 (m, 8 H, 4 PhCH_2), 3.38, 3.33, 3.18 (3 s, 9 H, OCH_3 -1_A, 3_A, 3_B), 2.19 (s, 3 H, CH_3CO); ^{13}C NMR: δ 169.8 (CH_3CO), 138.4–137.9 (aromatic C-1), 128.2–127.1 (aromatic C), 99.7 ($^1J_{\text{C-1,H-1}}$ 170.3 Hz, C-1_B), 98.5 ($^1J_{\text{C-1,H-1}}$ 169.1 Hz, C-1_A), 81.6, 78.6 (C-3_B, 3_A), 57.4, 56.4 (OCH_3 -3_B, 3_A), 54.7 (OCH_3 -1_A), 20.8 (CH_3CO). Anal. Calcd for $\text{C}_{45}\text{H}_{54}\text{O}_{12}$: C, 68.69; H, 6.92. Found: C, 68.35; H, 6.89.

Methyl O-(2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranosyl)-(1 \rightarrow 4)-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranoside (22).—A solution of **21** (2.1 g, 2.67 mmol) in THF (15 mL) and 0.15 N NaOMe–MeOH (20 mL) was stirred for 4 h at room temperature. The reaction mixture was neutralized with Amberlite IR-120, filtered, and concentrated. Chromatography on silica gel in 1:1 petroleum ether–EtOAc afforded **22** (1.88 g, 95%); $[\alpha]_{\text{D}} + 7.4^{\circ}$ (c 1.7, CHCl_3); ^1H NMR: δ 7.64–7.13 (m, 20 H, aromatic H), 5.34 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1_B), 4.79 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1_A), 4.76–4.44 (m, 8 H, 4 PhCH_2), 3.98 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-4_B), 3.97 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-4_A), 3.47 (dd, 1 H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 9.7 Hz, H-3_B), 3.38 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.8 Hz, H-3_A), 3.36, 3.33, 3.23 (3 s, 9 H, OCH_3 -1_A, 3_A, 3_B); ^{13}C NMR: δ 138.4, 138.2, 138.0, 137.9 (aromatic C-1), 128.2–127.1 (aromatic C), 99.6 (C-1_B), 98.4 (C-1_A), 81.7, 80.5 (C-3_B, 3_A), 56.8, 56.5 (OCH_3 -3_B, 3_A), 54.8 (OCH_3 -1_A). Anal. Calcd for $\text{C}_{43}\text{H}_{52}\text{O}_{11}$: C, 69.34; H, 7.04. Found: C, 69.01; H, 6.95.

Methyl O-(4-O-acetyl-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranosyl)-[(1 \rightarrow 4)-O-(2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranosyl)]₂-(1 \rightarrow 4)-2,6-di-O-benzyl-3-O-methyl- α -D-mannopyranoside (23).—Coupling of the disaccharide donor **20** (0.96 g, 1.05 mmol) with the acceptor **22** (0.52 g, 0.70 mmol) was carried out using a catalytic amount of TESTfl (50 μL , 0.13 mmol) as described for **18**, to yield **23** as an amorphous solid (0.45 g, 61%); $[\alpha]_{\text{D}} + 20.9^{\circ}$ (c 1.5, CHCl_3); ^1H NMR: δ 7.70–6.99 (m, 40 H, aromatic H), 5.38–5.24 (m, 4 H, H-1_D, 1_C, 1_B, H-4_D), 4.80 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1_A), 4.75–4.37 (m, 16 H, 8 PhCH_2), 3.36 (s, 3 H, OCH_3 -1_A), 3.30, 3.20 (2 s, 6 H, OCH_3 -3_A, 3_D), 3.21 (s, 6 H, OCH_3 -3_B, 3_C), 2.00 (s, 3 H, CH_3CO); ^{13}C NMR: 169.9 (CH_3CO), 138.7–138.1 (aromatic C-1), 128.4–127.2 (aromatic C), 99.9 ($^1J_{\text{C,H}}$ 171.6 Hz, C-1_D), 99.8 ($^1J_{\text{C,H}}$ 170.1 Hz, C-1_C), 99.7 ($^1J_{\text{C,H}}$ 169.1 Hz, C-1_B), 98.6 ($^1J_{\text{C,H}}$ 168.2

Hz, C-1_A), 81.7, 81.4, 81.1 (C-3_D, 3_C, 3_B), 78.8 (C-3_A), 57.6, 56.6 (OCH₃-3_D, 3_C), 56.4 (OCH₃-3_B, 3_A), 54.9 (OCH₃-1_A), 21.0 (CH₃CO). Anal. Calcd for C₈₇H₁₀₂O₂₂: C, 69.68; H, 6.85. Found: C, 69.35; H, 6.80.

Methyl O-(2,6-di-O-benzyl-3-O-methyl-α-D-mannopyranosyl)-[(1 → 4)-O-(2,6-di-O-benzyl-3-O-methyl-α-D-mannopyranosyl)]₂-(1 → 4)-2,6-di-O-benzyl-3-O-methyl-α-D-mannopyranoside (24).—A solution of **23** (0.3 g, 0.2 mmol) in THF (4 mL) and 0.10 N NaOMe–MeOH (6 mL) was stirred for 2 h at room temperature. Processing and chromatography on silica gel in 3:2 petroleum ether–EtOAc gave **24** (262 mg, 90%); $[\alpha]_D + 14.5^\circ$ (*c* 0.8, CHCl₃); ¹H NMR: δ 7.54–7.06 (m, 40 H, aromatic H), 5.38 (d, 1 H, *J*_{1,2} 1.9 Hz, H-1_D), 5.29 (d, 1 H, *J*_{1,2} 1.8 Hz, H-1_C), 5.27 (d, 1 H, *J*_{1,2} 1.8 Hz, H-1_B), 4.78 (d, 1 H, *J*_{1,2} 1.7 Hz, H-1_A), 4.77–4.37 (m, 16 H, 8 PhCH₂), 3.37 (s, 3 H, OCH₃-1_A), 3.31, 3.23, 3.20, 3.19 (4 s, 12 H, OCH₃-3_A, 3_B, 3_C, 3_D); ¹³C NMR: δ 138.7–138.4 (aromatic C-1), 128.4–127.2 (aromatic C), 99.8, 99.7, 99.6 (C-1_D, 1_C, 1_B), 98.6 (C-1_A), 81.7, 81.5, 81.4 (C-3_D, 3_C, 3_B), 80.6 (C-3_A), 57.0, 56.7 (OCH₃-3_D, 3_C), 56.4 (OCH₃-3_B, 3_A), 54.9 (OCH₃-1_A). Anal. Calcd for C₈₅H₁₀₀O₂₁: C, 75.24; H, 7.43. Found: C, 74.98; H, 7.35.

Methyl O-(4-O-acetyl-2,6-di-O-benzyl-3-O-methyl-α-D-mannopyranosyl)-[(1 → 4)-O-(2,6-di-O-benzyl-3-O-methyl-α-D-mannopyranosyl)]₄-(1 → 4)-2,6-di-O-benzyl-3-O-methyl-α-D-mannopyranoside (1).—Glycosylation of the imidate **20** (236 mg, 0.26 mmol) with the tetrasaccharide acceptor **24** (150 mg, 0.10 mmol) was carried out using a catalytic amount of TESTfl (15 μL, 39 μmol) as described for **18**, to yield **1** as an amorphous solid (117 mg, 52%); $[\alpha]_D + 26.6^\circ$ (*c* 0.9, CHCl₃); ¹H NMR: δ 7.80–7.63 (m, 60 H, aromatic H), 5.43–5.23 (m, 6 H, H-1_F, 1_E, 1_D, 1_C, 1_B, H-4_F), 4.78 (d, 1 H, *J*_{1,2} 1.8 Hz, H-1_A), 4.75–4.32 (m, 24 H, 12 PhCH₂), 3.36 (s, 3 H, OCH₃-1_A), 3.24, 3.19, 3.18, 3.17, 3.16, 3.10 (6 s, 18 H, OCH₃-3_A, 3_B, 3_C, 3_D, 3_E, 3_F), 1.98 (s, 3 H, CH₃CO); ¹³C NMR: δ 170.0 (CH₃CO), 138.7–138.2 (aromatic C-1), 128.4–127.4 (aromatic C), 99.87, 99.74, 99.73, 99.70, 99.66 (C-1_F, 1_E, 1_D, 1_C, 1_B), 98.65 (C-1_A), 81.71, 81.40, 81.35, 81.34, 81.32 (C-3_F, 3_E, 3_D, 3_C, 3_B), 78.76 (C-3_A), 57.58, 56.62 (OCH₃-3_F, 3_E), 56.39 (OCH₃-3_D, 3_C, 3_B), 56.36 (OCH₃-3_A), 54.94 (OCH₃-1_A), 21.04 (CH₃CO); FDMS: *m/z* 2212 [M]⁺, 2235 [M + Na]⁺. Anal. Calcd for C₁₂₉H₁₅₀O₃₂: C, 70.03; H, 6.83. Found: C, 69.85; H, 6.75.

Methyl O-(2,6-di-O-benzyl-3-O-methyl-α-D-mannopyranosyl)-[(1 → 4)-O-(2,6-di-O-benzyl-3-O-methyl-α-D-mannopyranosyl)]₄-(1 → 4)-2,6-di-O-benzyl-3-O-methyl-α-D-mannopyranoside (2).—A solution of **1** (55 mg, 24.9 μmol) in THF (1 mL) and 0.15 N NaOMe–MeOH (1:1, 1.5 mL) was stirred for 2 h at room temperature. Processing and chromatography on silica gel in 1:1 petroleum ether–EtOAc afforded **2** as an amorphous solid (46.5 mg, 86%); $[\alpha]_D + 19.5^\circ$ (*c* 0.8, CHCl₃); ¹H NMR: δ 7.64–7.16 (m, 60 H, aromatic H), 5.42–5.21 (m, 5 H, H-1_F, 1_E, 1_D, 1_C, 1_B), 4.79 (d, 1 H, *J*_{1,2} 1.7 Hz, H-1_A), 4.76–4.34 (m, 24 H, 12 PhCH₂), 3.37 (s, 3 H, OCH₃-1_A), 3.25, 3.20, 3.19, 3.18, 3.17, 3.10 (6 s, 18 H, OCH₃-3_A, 3_B, 3_C, 3_D, 3_E, 3_F); ¹³C NMR: δ 138.7–138.3 (aromatic C-1), 128.4–127.3 (aromatic C), 99.86, 99.75, 99.74, 99.70, 99.68 (C-1_F, 1_E, 1_D, 1_C, 1_B), 98.64 (C-1_A), 81.71, 81.39, 81.34, 81.33, 81.32 (C-3_F, 3_E, 3_D, 3_C, 3_B), 78.76 (C-3_A), 57.58, 56.62 (OCH₃-3_F, 3_E), 56.40 (OCH₃-3_D, 3_C, 3_B), 56.39 (OCH₃-3_A), 54.95 (OCH₃-1_A); FDMS: *m/z* 2170 [M]⁺. Anal. Calcd for C₁₂₇H₁₄₈O₃₁: C, 70.28; H, 6.87. Found: C, 70.01; H, 6.79.

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