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Synthesis of a hexasaccharide fragment of the O-deacetylated GXM of *C. neoformans* serotype B

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Abstract—β-D-Xyl*p*-(1→4)-α-D-Man*p*-(1→3)-[β-D-Xyl*p*-(1→2)]-α-D-Man*p*-(1→3)-[β-D-Xyl*p*-(1→2)]-α-D-Man*p*, the fragment of the exopolysaccharide from *Cryptococcus neoformans* serovar B, was synthesized as its methyl glycoside. Thus, acetylation of allyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**1**) followed by debenzylidenation and selective 6-O-benzoylation afforded allyl 2-*O*-acetyl-3,6-di-*O*-benzoyl-α-D-mannopyranoside (**4**). Glycosylation of **4** with 2,3,4-tri-*O*-benzoyl-D-xylopyranosyl trichloroacetimidate (**5**) furnished the β-(1→4)-linked disaccharide **6**. Deallylation followed by trichloroacetimidate formation gave the disaccharide donor **8**, and subsequent coupling with allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzoyl-α-D-mannopyranoside (**9**), produced the tetrasaccharide **10**. Reiteration of deallylation and trichloroacetimidate formation from **10** yielded the tetrasaccharide donor **12**. The downstream disaccharide acceptor **18** was obtained by condensation of **5** with methyl 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside, followed by debenzylidenation, benzoylation, and selective 3-O-deacetylation. Coupling of **18** with **12** afforded the hexasaccharide **19**, and subsequent deprotection gave the hexasaccharide glycoside **20**. Selective 2″-O-deacetylation of **19** gave the hexasaccharide acceptor **21**. Condensation of **21** with glucopyranosyluronate imidate **22** did not produce the expected heptasaccharide glycoside; instead, a transacetylation product **19** was obtained. Meanwhile, there was no reaction between **21** and the bromide donor **23**.

Keywords: Mannose; Xylose; Glucuronic acid

1. Introduction

Glucuronoxylomannan (GXM) as the major capsule component is produced from *Cryptococcus neoformans*, a primary cause of opportunistic infections associated with AIDS.[1,2] Of the four major serotypes[3] A–D for GXM, D has the simplest pentaose structure while C has the most complex octasaccharide structure. All the four serotypes are composed of a linear α-(1→3)-linked mannosyl backbone with β-glucopyranosyluronic acid, β-xylopyranosyl, and 6-*O*-acetyl substituents[4] (Fig. 1).

The synthesis of trisaccharide and tetrasaccharide fragments[5] corresponding to structures in capsular polysaccharides of *C. neoformans* and the synthesis of a pentasaccharide[6]—the repeating unit of the polysaccharide in *C. neoformans* serovar D—have appeared. In our previous work,[7] the successful syntheses of the hexasaccharide repeating unit of O-deacetylated GXM of *C. neoformans* serotype A and its frame-shifted hexasaccharide glycoside were reported. We now report a convergent synthesis of the hexasaccharide fragment of O-deacetylated GXM of *C. neoformans* serotype B, and a trial for the synthesis of the repeating unit of the serotype B.

2. Results and discussion

As outlined in Scheme 1, acetylation of allyl 3-*O*-benzoyl-4,6-*O*-isopropylidene-α-D-mannopyranoside,[8] (**1**) followed by debenzylidenation (80%) and selective 6-O-benzoylation (90%), gave the glycosyl acceptor **4**.

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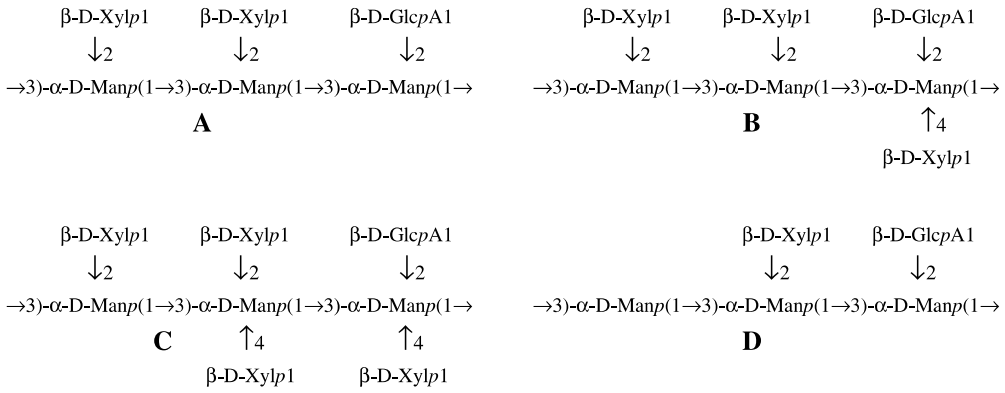


Figure 1. Model structures of deacetylated GXM of *C. neoformans* serotypes A–D.

Condensation of **4** with 2,3,4-tri-*O*-benzoyl-D-xylopyranosyl trichloroacetimidate[9] (**5**) afforded β-(1→4)-linked disaccharide **6** (90%), and subsequent deallylation (85%) with $PdCl_2$ in methanol, and trichloroacetimidate formation[10] produced the upstream disaccharide donor **8** (90%). Coupling of **8** with allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzoyl-α-D-mannopyranoside (**9**)[7] afforded the tetrasaccharide **10** (75%), subsequent deallylation (85%) and trichloroacetimidate formation (90%) produced the tetrasaccharide donor **12**.

The downstream disaccharide acceptor **18** was similarly prepared. Thus, selective 3-O-acetylation of methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**13**) gave methyl 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**14**) in satisfactory yield (80%). Coupling of **14** with **5** (80%) followed by debenzylidenation (80%), benzoylation (85%), and selective removal of the 3-*O*-acetyl group (85%) by methanolysis[11] with a mixture of MeCOCl (2.0 mL) in CH_2Cl_2 (10 mL) and MeOH (40 mL) produced the disaccharide acceptor **18**.

Condensation of **18** with **12** successfully yielded the hexasaccharide glycoside **19** (60%), and its deprotection in ammonia-saturated-methanol gave the free hexasaccharide fragment of *C. neoformans* serotype B.

A trial for the synthesis the heptasaccharide repeating unit of the serotype B was carried out. Thus, selective 2″-O-deacetylation of **19** with a mixture of MeCOCl (3.5 mL) in CH_2Cl_2 (10 mL) and MeOH (40 mL) for 3 days afforded the hexasaccharide acceptor **21** in a fair yield (60%). This indicated that there was a serious steric hindrance at C-2″ position as the concentration of MeCOCl used was relatively higher, the reaction time was longer, but the yield was lower compared to selective deacetylation of **17**.

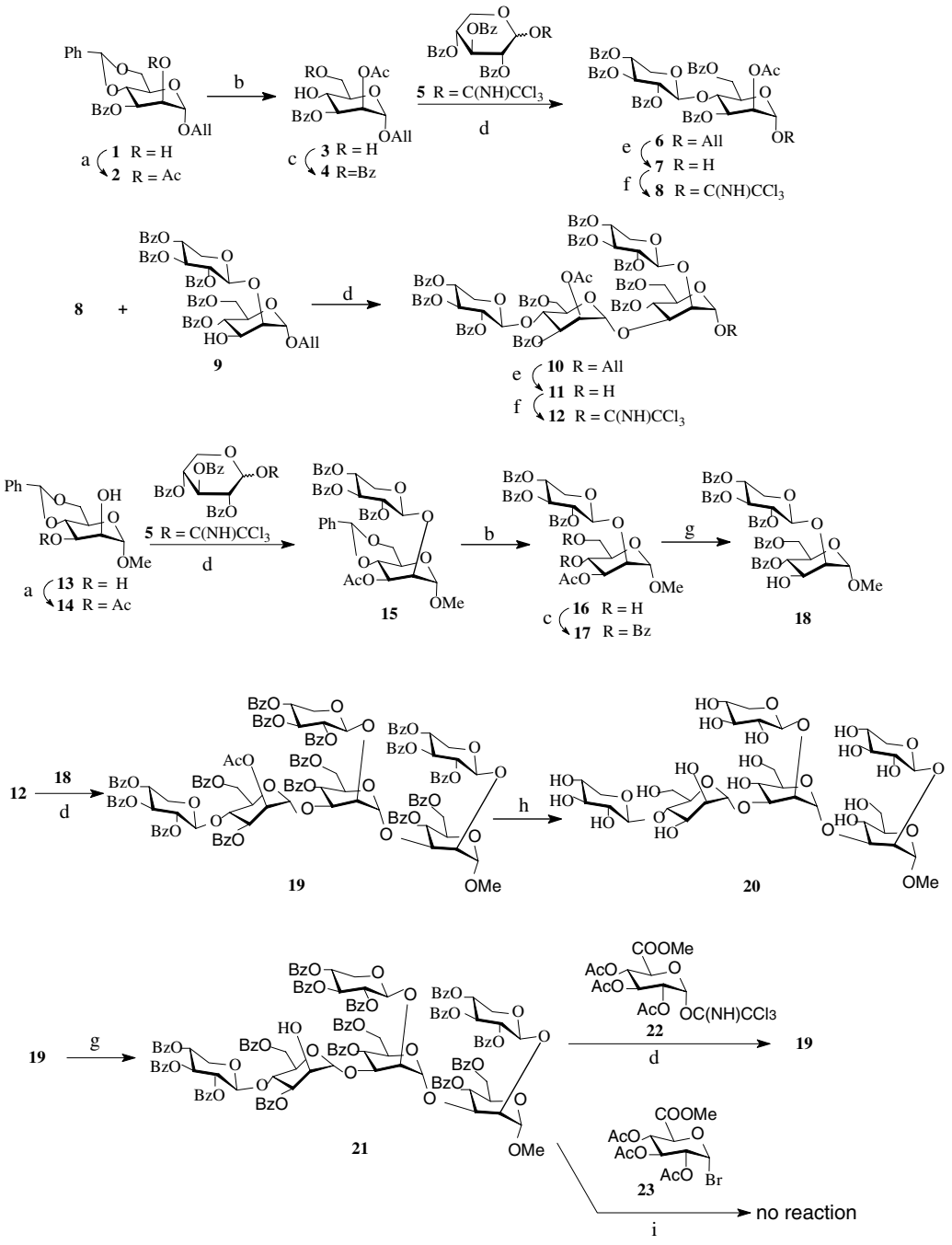
Reaction of **21** with methyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosyluronate trichloroacetimidate (**22**) under the coupling conditions did not give the expected heptasaccharide glycoside. Instead, acetyl transferring occurred giving **19** as the product. Meanwhile, reaction between **21** and methyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosyluronate bromide (**23**) did not occur at all. Thus, the synthesis of the repeating unit of *C. neoformans* serotype B should be tried in other different ways.

In summary, a convergent synthesis of the hexasaccharide fragment of *C. neoformans* serotype B was achieved, but the strategy presented here could not be used for the synthesis of the repeating unit of GXM of *C. neoformans* serotype B.

3. Experimental

3.1. General methods

Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined with a Perkin–Elmer model 241-MC automatic polarimeter for solutions in a 1-dm jacketed cell. ^1H NMR and ^{13}C NMR spectra were recorded with Varian XL-400 and Varian XL-200 spectrometers, for solutions in $CDCl_3$ or in D_2O as indicated. Chemical shifts are expressed in ppm downfield from the Me_4Si resonance. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the ESI mode. Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 30% (v/v) sulfuric acid in MeOH or by UV detection. Column chromatography was conducted by elution of a column (8×100 mm, 16×240 mm, 18×300 mm, 35×400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Analytical LC was performed with a Gilson HPLC consisting of a pump (model 306), stainless-steel column packed with silica gel (Spherisorb SiO_2, 10×300 mm or 4.6×250 mm), differential refractometer (132-RI detector), UV–vis detector (model 118). EtOAc–petroleum ether (bp 60–90 °C) was used as the eluent at a flow rate of 1–4 mL/min. Solutions were concentrated at a temperature <60 °C under diminished pressure.



Scheme 1. Reagents and conditions: (a) Ac_2O, Pyridine (CH_2Cl_2); (b) 90% HOAc–H_2O; (c) BzCl–Pyridine; (d) TMSOTf, CH_2Cl_2, −10 °C to rt; (e) $PdCl_2$, CH_2Cl_2–MeOH, rt, 4 h; (f) CCl_3CN, K_2CO_3, CH_2Cl_2, 10 h; (g) 4% (7%) CH_3COCl in CH_2Cl_2–MeOH, 0 °C–rt; (h) satd NH_3–MeOH, rt, 72 h; (i) silver triflate, CH_2Cl_2, 2,4-lutidine.

3.2. Allyl 2-*O*-acetyl-3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (2)

Compound **1** (4.14 g, 10 mmol) was dissolved in pyridine (30 mL), and Ac_2O (3.00 mL, 25 mmol) was added. The mixture was stirred at rt for 12 h, then was concentrated to give a residue. Purification of the residue by silica gel column chromatography (3:1 petroleum ether–EtOAc) gave **2** (4.96 g, 90.0%) as a syrup: $[\alpha]_D$+42.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.99–7.29 (m, 10 H, 2Ph*H*), 5.88 (m, 1H, CH_2=C*H*CH_2O), 5.72 (dd, 1H, $J_{2,3}$ 3.6 Hz, $J_{3,4}$ 10.3 Hz, H-3), 5.63 (s, 1H, PhC*H*O_2), 5.50 (dd, 1H, $J_{1,2}$ 1.3 Hz, H-2), 5.30 (m, 1H, CH_2=CHCH_2O), 5.20 (m, 1H, CH_2=CHCH_2O), 4.88 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.23 (dd, 1H, *J* 4.8, 10.6 Hz, H-6a), 4.18 (m, 1H, CH_2=CHCH_2O), 4.08 (dd, 1H, *J* 10.0, 10.6 Hz, H-6b), 4.02 (m, 1H, CH_2=CHCH_2O), 3.98 (ddd, 1H, *J* 4.8, 10.0, 10.6 Hz, H-5), 3.83 (dd, 1H,

$J_{3,4} = J_{4,5}$ 10.0 Hz, H-4), 2.14 (s, 3H, CH_3CO). Anal. Calcd for $C_{25}H_{26}O_8$: C, 66.08; H, 5.73. Found: C, 65.94; H, 5.77.

3.3. Allyl 2-*O*-acetyl-3-*O*-benzoyl-α-D-mannopyranoside (3)

A mixture of **2** (4.1 g, 9.1 mmol) and 90% HOAc–H_2O (80 mL) was stirred for 2 h at 70 °C, then concentrated to dryness. Purification of the residue by silica gel column chromatography (1:1 petroleum ether–EtOAc) gave **3** (2.66 g, 80%) as a syrup: $[\alpha]_D$+42.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.41 (m, 5H, Ph*H*), 5.89 (m, 1H, CH_2=C*H*CH_2O), 5.47 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.9 Hz, H-3), 5.37 (dd, 1H, $J_{1,2}$ 1.6 Hz, H-2), 5.30 (m, 1H, CH_2=CHCH_2O), 5.20 (m, 1H, CH_2=CHCH_2O), 4.88 (d, 1H, H-1), 4.20 (m, 1H, CH_2=CHCH_2O), 4.15 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 4.12 (m, 1H, CH_2=CHCH_2O), 3.93–3.91 (m, 2H, H-6a, H-6b), 3.81 (m, 1H, H-5), 2.10 (s, 3H, H_3CO). Anal. Calcd for $C_{18}H_{22}O_8$: C, 59.02; H, 6.01. Found: C, 59.32; H, 5.98.

3.4. Allyl 2-*O*-acetyl-3,6-di-*O*-benzoyl-α-D-mannopyranoside (4)

Compound **3** (2.52 g, 7.0 mmol) was dissolved in anhyd CH_2Cl_2 (30 mL) containing pyridine (4.1 mL, 50 mmol), then under N_2 protection and stirring, a solution of benzoyl chloride (0.5 mL, 7.0 mmol) in anhyd CH_2Cl_2 (6 mL) was added dropwise within 30 min at 0 °C. The reaction temperature slowly raised to rt. After stirring the mixture for 8 h, TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated to give a residue. Purification of the residue by silica gel column chromatography (3:1 petroleum ether–EtOAc) gave **4** (2.95 g, 90%) as a syrup: $[\alpha]_D$+46.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.39 (m, 10H, 2Ph*H*), 5.90 (m, 1H, CH_2=C*H*CH_2O), 5.54 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.6 Hz, H-3), 5.38 (dd, 1H, $J_{1,2}$ 1.6 Hz, H-2), 5.30 (m, 1H, CH_2=CHCH_2O), 5.20 (m, 1H, CH_2=CHCH_2O), 4.92 (d, 1H, H-1), 4.73–4.64 (m, 2H, H-6a, H-6b), 4.16 (m, 1H, CH_2=CHCH_2O), 4.12 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 4.12 (m, 1H, CH_2=CHCH_2O), 4.08 (m, 1H, H-5), 2.10 (s, 3H, H_3CO). Anal. Calcd for $C_{25}H_{26}O_9$: C, 63.83; H, 5.53. Found: C, 63.99; H, 5.51.

3.5. Allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)-2-*O*-acetyl-3,6-di-*O*-benzoyl-α-D-mannopyranoside (6)

Compound **4** (2.64 g, 5.60 mmol) and 2,3,4-tri-*O*-benzoyl-α-D-xylopyranosyl trichloroacetimidate **5** (3.62 g, 6.0 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (50 mL). TMSOTf (10 μL, 0.09 mmol) was added dropwise at −10 °C with nitrogen protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually warmed to ambient temperature. Then the mixture was neutralized with Et_3N and concentrated to dryness. Purification of the residue by silica gel column chromatography (3:1 petroleum ether–EtOAc) gave **6** (4.80 g, 90%) as a foamy solid: $[\alpha]_D$ −25.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.17 (m, 25H, 5Ph*H*), 5.89 (m, 1H, CH_2=C*H*CH_2O), 5.76 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.6 Hz, H-3 of Man*p*), 5.66 (dd, 1H, $J_{2,3} = J_{3,4} = 7.1$ Hz, H-3 of Xyl*p*), 5.37 (dd, 1H, $J_{1,2}$ 1.7 Hz, H-2 of Man*p*), 5.32 (dd, 1H, $J_{1,2}$ 5.2 Hz, H-2 of Xyl*p*), 5.30–5.10 (m, 3H, H-4 of Man*p*, CH_2=CHCH_2O), 4.97 (d, 1H, $J_{1,2}$ 5.2 Hz, H-1 of Xyl*p*), 4.87 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1 of Man*p*), 4.63 (dd, 1H, $J_{5,6a}$ 1.8, $J_{6a,6b}$ 12.2 Hz, H-6a of Man*p*), 4.48 (dd, 1H, $J_{5,6b}$ 4.2, $J_{6a,6b}$ 12.2 Hz, H-6b of Man*p*), 4.35 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4 of Man*p*), 4.10 (dd, 1H, $J_{4,5a}$ 3.0 Hz, $J_{5a,5b}$ 11.8 Hz, H-5a of Xyl*p*), 4.17–3.26 (m, 4H), 2.07 (s, 3H, H_3CO). Anal. Calcd for $C_{51}H_{46}O_{16}$: C, 66.96; H, 5.03. Found: C, 67.07; H, 5.22.

3.6. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)-2-*O*-acetyl-3,6-di-*O*-benzoyl-D-mannopyranose (7)

To a solution of **6** (4.21 g, 4.6 mmol) in anhyd CH_2Cl_2 (10 mL) and anhyd MeOH (40 mL), $PdCl_2$ (450 mg, 2.55 mmol) was added with N_2 protection. After stirring the reaction mixture for 4 h at rt, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Then the mixture was filtered, and the solution was concentrated to dryness. Purification of the residue by column chromatography (2:1 petroleum ether–EtOAc) gave **7** (3.62 g, 85%) as a syrup, and the α-anomer was isolated and characterized: $[\alpha]_D$ −45.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.17 (m, 25H, 5 Ph*H*), 5.80 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 9.6 Hz, H-3 of Man*p*), 5.66 (dd, 1H, $J_{2,3} = J_{3,4} = 7.1$ Hz, H-3 of Xyl*p*), 5.38 (dd, 1H, $J_{1,2} = 1.6$ Hz, H-2 of Man*p*), 5.33 (dd, 1H, $J_{1,2}$ 5.2 Hz, H-2 of Xyl*p*), 5.23 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1 of Man*p*), 5.08 (m, 1H, H-4 of Xyl*p*), 5.00 (d, 1H, $J_{1,2}$ 5.2 Hz, H-1 of Xyl*p*), 4.66 (dd, 1H, $J_{5,6a}$ 1.6 Hz, $J_{6a,6b}$ 12.2 Hz, H-6a of Man*p*), 4.46 (dd, 1H, $J_{5,6b}$ 3.4 Hz, H-6b of Man*p*), 4.38 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4 of Man*p*), 4.24 (m, 1H, H-5 of Man*p*), 4.03 (dd, 1H, $J_{4,5a}$ 4.0 Hz, $J_{5a,5b}$ 12.3 Hz, H-5a of Xyl*p*), 3.30 (dd, 1H, $J_{4,5b}$ 6.6 Hz, $J_{5a,5b}$ 12.3 Hz, H-5b of Xyl*p*), 2.03 (s, 3H, CH_3CO). Anal. Calcd for $C_{48}H_{42}O_{16}$: C, 65.90; H, 4.80. Found: C, 66.01; H, 4.71.

3.7. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)-2-*O*-acetyl-3,6-di-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (8)

Compound **7** (3.20 g, 3.7 mmol) was dissolved in CH_2Cl_2 (40 mL), and CCl_3CN (0.5 mL, 5 mmol) and K_2CO_3 (1.5 g) were added. The reaction mixture was stirred for

10 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Then the mixture was filtered, and the solution was concentrated to dryness. Purification of the residue on a silica gel column with 3:1 petroleum ether–EtOAc furnished the disaccharide donor **8** (3.50 g, 90%) as a foamy solid: $[\alpha]_D$ −18.1 (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H, CN*H*CCl_3), 8.08–7.16 (m, 25H, 5Ph*H*), 6.28 (s, 1H, $J_{1,2}$ 2.0 Hz, H-1 of Man*p*), 5.80 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.6 Hz, H-3 of Man*p*), 5.65 (dd, 1H, $J_{2,3} = J_{3,4} = 6.6$ Hz, H-3 of Xyl*p*), 5.60 (dd, 1H, H-2 of Man*p*), 5.31 (dd, 1H, $J_{1,2}$ 4.7 Hz, H-2 of Xyl*p*), 5.09 (m, 1H, H-4 of Xyl*p*), 5.03 (d, 1H, $J_{1,2}$ 4.7 Hz, H-1 of Xyl*p*), 4.72 (dd, 1H, $J_{5,6a}$ 1.9 Hz, $J_{6a,6b}$ 12.4 Hz, H-6a of Man*p*), 4.53 (dd, 1H, $J_{5,6b}$ 3.8 Hz, H-6b of Man*p*), 4.49 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4 of Man*p*), 4.22 (m, 1H, H-5 of Man*p*), 4.10 (dd, 1H, $J_{4,5a}$ 4.5 Hz, $J_{5a,5b}$ 12.4 Hz, H-5a of Xyl*p*), 3.33 (dd, 1H, $J_{4,5b}$ 6.0 Hz, $J_{5a,5b}$ 12.4 Hz, H-5b of Xyl*p*), 2.10 (s, 3H, CH_3CO). Anal. Calcd for $C_{50}H_{42}Cl_3NO_{16}$: C, 58.88; H, 4.12. Found: C, 58.62; H, 4.21.

3.8. Allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)-2-*O*-acetyl-3,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 3)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)]-4,6-di-*O*-benzoyl-α-D-mannopyranoside (10)

Compound **8** (2.64 g, 2.60 mmol) and **9** (2.27 g, 2.60 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (50 mL). TMSOTf (15 μL, 0.12 mmol) was added dropwise at −10 °C with nitrogen protection. The reaction mixture was stirred for 3 h, during which time it was allowed to warm to ambient temperature. The mixture was then neutralized with Et_3N and concentrated to dryness. Purification of the residue by silica gel column chromatography (2:1 petroleum ether–EtOAc) gave **10** (3.36 g, 75%) as a foamy solid: $[\alpha]_D$ −36.3 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.15–7.02 (m, 50H, 10Ph*H*), 5.85 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 8.9 Hz, H-3 of Man*p*), 5.75 (dd, 1H, $J_{2,3} = J_{3,4} = 5.9$ Hz, H-3 of Xyl*p*), 5.70 (m, 1H, $CH_2{=}CHCH_2O$), 5.65 (dd, 1H, $J_{2,3} = J_{3,4} = 7.2$ Hz, H-3 of Xyl*p*), 5.61 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4 of Man*p*), 5.40 (dd, 1H, $J_{1,2}$ 5.2 Hz, H-2 of Xyl*p*), 5.30 (dd, 1H, $J_{1,2}$ 5.1 Hz, H-2 of Xyl*p*), 5.20 (m, 1H, H-4 of Xyl*p*), 5.18 (m, 1H, H-4 of Xyl*p*), 5.15–5.05 (m, 4H), 4.96 (d, 1H, $J_{1,2}$ 5.1 Hz, H-1 of Xyl*p*), 4.95 (d, 1H, $J_{1,2}$ 5.2 Hz, H-1 of Xyl*p*), 4.87 (s, 1H, H-1 of Man*p*), 4.81–3.25 (m, 15H), 1.94 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): 168.6 (*C*OCH_3), 165.9, 165.7, 165.4, 165.4, 165.3, 165.1, 164.9, 164.9, 164.8, 164.6, (10C, 10 *C*OPh), 118.1 ($OCH_2CH{=}C_2$), 101.0, 99.4, 98.4, 96.3 (4C, C-$1^{I–IV}$), 75.62, 75.13, 70.55, 70.12, 70.10, 69.96, 69.60, 69.31, 69.27, 69.05, 68.85, 68.58, 68.40, 68.30, 63.83, 62.93, 61.44, 60.25 (C-2 to C-6), 20.3 ($COCH_3$). Anal. Calcd for $C_{99}H_{84}O_{30}$: C, 67.36; H, 4.86. Found: C, 67.49; H, 5.03.

3.9. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)-2-*O*-acetyl-3,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 3)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)]-4,6-di-*O*-benzoyl-α-D-mannopyranose (11)

To a solution of **10** (3.20 g, 1.86 mmol) in anhyd CH_2Cl_2 (10 mL) and anhyd MeOH (40 mL), $PdCl_2$ (220 mg, 1.22 mmol) was added with nitrogen protection. After stirring the reaction mixture for 4 h at rt, TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. Then the mixture was filtered, and the solution was concentrated to dryness. Purification of the residue by column chromatography (2:1 petroleum ether–EtOAc) gave **11** (2.66 g, 85%) as a foamy solid: $[\alpha]_D$ − 39.4 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.16–7.04 (m, 50H, 10Ph*H*), 5.86 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 8.7 Hz, H-3 of Man*p*), 5.77 (dd, 1H, $J_{2,3} = J_{3,4} = 5.1$ Hz, H-3 of Xyl*p*), 5.69 (dd, 1H, $J_{2,3} = J_{3,4} = 7.1$ Hz, H-3 of Xyl*p*), 5.67 (dd, 1H, $J_{3,4} = J_{4,5} =$ 10.1 Hz, H-4 of Man*p*), 5.42 (dd, 1H, $J_{1,2}$ 5.3 Hz, H-2 of Xyl*p*), 5.30–5.24 (m, 3H), 5.18 (m, 1H, H-4 of Xyl*p*), 5.14 (dd, 1H, H-2 of Man*p*), 5.07 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1 of Man*p*), 4.98 (d, 1H, $J_{1,2}$ 4.8 Hz, H-1 of Xyl*p*), 4.94 (d, 1H, $J_{1,2}$ 5.3 Hz, H-1 of Xyl*p*), 4.87–3.25 (m, 13H), 1.89 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): 168.6 (*C*OCH_3), 166.1, 165.7, 165.5, 165.2, 165.1, 165.0, 164.9, 164.9, 164.8, 164.6, (10C, 10 *C*OPh), 101.1, 99.3, 98.1, 92.0 (4C, C-$1^{I–IV}$), 75.18, 74.57, 70.63, 70.30, 70.13, 69.97, 69.64, 69.57, 69.27, 69.16, 68.81, 68.45, 68.30, 63.89, 63.02, 61.57, 60.19 (C-2 to C-6), 20.3 ($COCH_3$). Anal. Calcd for $C_{94}H_{80}O_{30}$: C, 66.82; H, 4.74. Found: C, 66.93; H, 4.64.

3.10. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)-2-*O*-acetyl-3,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 3)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)]-4,6-di-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (12)

Compound **11** (2.6 g, 1.54 mmol) was dissolved in CH_2Cl_2 (30 mL), and CCl_3CN (0.5 mL, 5 mmol) and K_2CO_3 (1.0 g) were added. The reaction mixture was stirred for 10 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Then the mixture was filtered, and the solution was concentrated to dryness. Purification of the residue on a silica gel column with 3:1 petroleum ether–EtOAc as the eluent furnished the tetrasaccharide donor **12** (2.54 g, 90.6%) as a foamy solid: $[\alpha]_D$ −46.9 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.71 (s, 1H, CN*H*CCl_3), 8.15–7.02 (m, 50H, 10Ph*H*), 6.38 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1 of Man*p*), 5.88 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 8.9 Hz, H-3 of Man*p*), 5.85 (dd, 1H, $J_{2,3} = J_{3,4} = 5.0$ Hz,

H-3 of Xyl*p*), 5.76 (dd, 1H, $J_{3,4} = J_{4,5} = 10.1$ Hz, H-4 of Man*p*), 5.66 (dd, 1H, $J_{2,3} = J_{3,4} = 7.1$ Hz, H-3 of Xyl*p*), 5.43–5.40 (m, 2H), 5.30 (m, 1H, H-4 of Xyl*p*), 5.21–5.14 (m, 2H), 5.14 (d, 1H, $J_{1,2}$ 5.0 Hz, H-1 of Xyl*p*), 5.11 (s, 1H, H-1 of Man*p*), 4.97 (d, 1H, $J_{1,2}$ 5.2 Hz, H-1 of Xyl*p*), 4.87–3.30 (m, 13H), 2.03 (s, 3H, COCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 168.6 (*C*OCH$_3$), 165.9, 165.6, 165.4, 165.3, 165.2, 165.1, 165.0, 164.9, 164.8, 164.6, (10C, 10*C*OPh), 101.1, 99.5, 98.5, 94.8 (4C, C-1$^{I–IV}$), 90.5 (–*C*Cl$_3$), 75.16, 74.99, 74.77, 71.65, 70.70, 70.31, 69.88, 69.60, 69.33, 69.15, 69.00, 68.43, 68.40, 63.30, 62.59, 61.60, 60.64, 60.31 (C-2 to C-6), 20.2 (CO*C*H$_3$). Anal. Calcd for $C_{96}H_{80}Cl_3NO_{30}$: C, 62.85; H, 4.36. Found: C, 63.08; H, 4.54.

3.11. Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside (14)

Compound **13** (2.90 g, 10 mmol) was dissolved in anhyd CH_2Cl_2 (30 mL) containing pyridine (8.1 mL, 100 mmol), a solution of Ac_2O (1.20 mL, 10 mmol) in anhyd CH_2Cl_2 (10 mL) was added dropwise within 30 min at 0 °C. The reaction temperature was slowly raised to rt. After stirring the mixture for 12 h, TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated to give a residue, and purification of the residue by column chromatography on a silica gel column (3:1 petroleum ether–EtOAc) gave compound **14** (2.62 g, 80.6%) as a syrup: $[\alpha]_D$+62.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.26 (m, 5H, Ph*H*), 5.55 (s, 1H, PhC*H*O$_2$), 5.32 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 10.1 Hz, H-3), 4.75 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.30 (dd, 1H, *J* 4.2 Hz, 10.1 Hz, H-6a), 4.15 (dd, 1H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.3 Hz, H-2), 4.09 (dd, 1H, *J* 10.1 Hz, 10.1 Hz, H-6b), 3.93 (m, 1H, H-5), 3.84 (dd, 1H, $J_{3,4} = J_{4,5} = 10.1$ Hz, H-4), 3.40 (s, 3H, OCH_3), 2.13 (s, 3H, CH_3CO). Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.26; H, 6.17. Found: C, 59.42; H, 6.21.

3.12. Methyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)-3-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside (15)

Compound **14** (2.11 g, 6.50 mmol) and 2,3,4-tri-*O*-benzoyl-D-xylopyranosyl trichloroacetimidate (**5**) (4.00 g, 6.60 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (50 mL). TMSOTf (15 μL, 0.10 mmol) was added dropwise at −10 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time it was allowed to warm to ambient temperature. The mixture was then neutralized with Et_3N and concentrated to dryness. Purification of the residue by silica gel column chromatography (3:1 petroleum ether–EtOAc) gave **15** (4.05 g, 80%) as a foamy solid: $[\alpha]_D$ −38.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.33 (m, 20H, 4Ph*H*), 5.70 (dd, 1H, $J_{2,3} = J_{3,4} = 5.6$ Hz, H-3 of Xyl*p*), 5.40 (dd, 1H, $J_{1,2}$ 4.6 Hz, $J_{2,3}$ 5.6 Hz, H-2 of Xyl*p*), 5.31 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 10.5 Hz, H-3 of Man*p*), 5.29 (m, 1H, H-4 of Xyl*p*), 5.23 (s, 1H, PhC*H*O$_2$), 4.93 (d, 1H, $J_{1,2}$ 4.6 Hz, H-1 of Xyl*p*), 4.67 (d, 1H, $J_{1,2}$ 1.2 Hz, H-1 of Man*p*), 4.60 (dd, 1H, $J_{5,6a}$ 3.3 Hz, $J_{6a,6b}$ 12.4 Hz, H-6a of Man*p*), 4.28 (dd, 1H, $J_{1,2}$ 1.2 Hz, $J_{2,3}$ 3.4 Hz, H-2 of Man*p*), 4.08 (dd, 1H, $J_{4,5a}$ 4.6 Hz, $J_{5a,5b}$ 10.1 Hz, H-5a of Xyl*p*), 3.98 (dd, 1 H, $J_{4,5b} = J_{5a,5b}$ 10.1 Hz, H-5b of Xyl*p*), 3.82–3.76 (m, 2H, H-5 of Man*p*, H-6b of Man*p*), 3.48 (dd, 1H, $J_{3,4} = J_{4,5} = 10.1$ Hz, H-4 of Man*p*), 3.32 (s, 3H, CH_3O), 2.14 (s, 3H, CH_3CO). Anal. Calcd for $C_{42}H_{40}O_{14}$: C, 65.63; H, 5.21. Found: C, 65.30; H, 5.38.

3.13. Methyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)-3-*O*-acetyl-α-D-mannopyranoside (16)

A mixture of **15** (3.85 g, 5.0 mmol) and 90% HOAc–H_2O (60 mL) was stirred for 2 h at 70 °C. The solution was concentrated to dryness. Purification of the residue by silica gel column chromatography (1:1 petroleum ether–EtOAc) gave **16** (2.71 g, 80%) as a foamy solid: $[\alpha]_D$ −31.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.31 (m, 15H, 3 Ph*H*), 5.73 (dd, 1H, $J_{2,3} = J_{3,4} =$ 7.6 Hz, H-3 of Xyl*p*), 5.38 (dd, 1H, $J_{1,2}$ 5.6 Hz, $J_{2,3}$ 7.6 Hz, H-2 of Xyl*p*), 5.28 (m, 1H, H-4 of Xyl*p*), 4.96 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 10.0 Hz, H-3 of Man*p*), 4.72 (d, 1H, $J_{1,2}$ 5.6 Hz, H-1 of Xyl*p*), 4.47 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1 of Man*p*), 4.42 (dd, 1H, $J_{4,5a}$ 4.4 Hz, $J_{5a,5b}$ 12.0 Hz, H-5a of Xyl*p*), 4.10 (dd, 1H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.2 Hz, H-2 of Man*p*), 4.01 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4 of Man*p*), 3.62–3.44 (m, 4H, H-5b of Xyl*p*, H-6a of Man*p*, H-6b of Man*p*, H-5 of Man*p*), 3.16 (s, 3H, CH_3O), 2.10 (s, 3H, CH_3CO). Anal. Calcd for $C_{35}H_{36}O_{14}$: C, 61.76; H, 5.29. Found: C, 61.94; H, 5.38.

3.14. Methyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)-3-*O*-acetyl-4,6-di-*O*-benzoyl-α-D-mannopyranoside (17)

Compound **16** (2.5 g, 3.67 mmol) was dissolved in pyridine (30 mL), and benzoyl chloride (2.47 mL, 20 mmol) was added. The mixture was stirred at rt for 12 h, then quenched with MeOH (3 mL). The reaction mixture was concentrated to give a residue. Purification of the residue by silica gel column chromatography (3:1 petroleum ether–EtOAc) gave **17** (2.78 g, 85%) as a foamy solid: $[\alpha]_D$ −27.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–7.30 (m, 25H, 5Ph*H*), 5.70 (dd, 1H, $J_{2,3} =$ $J_{3,4} = 5.1$ Hz, H-3 of Xyl*p*), 5.67 (dd, 1H, $J_{3,4} = J_{4,5} =$ 10.0 Hz, H-4 of Man*p*), 5.48 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 10.0 Hz, H-3 of Man*p*), 5.37 (dd, 1H, $J_{1,2}$ 5.0 Hz, $J_{2,3}$ 5.1 Hz, H-2 of Xyl*p*), 5.27 (m, 1H, H-4 of Xyl*p*), 4.99 (d, 1H, $J_{1,2}$ 5.0 Hz, H-1 of Xyl*p*), 4.81 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1 of Man*p*), 4.64 (dd, 1H, $J_{4,5a}$ 3.0, $J_{5a,5b}$ 12.4 Hz, H-5a of Xyl*p*), 4.34 (dd, 1H, $J_{5,6a}$ 3.0 Hz, $J_{6a,6b}$ 11.8 Hz, H-6a

of Man*p*), 4.24 (dd, 1H, H-2 of Man*p*), 4.18 (m, 1H, H-5 of Man*p*), 4.03 (dd, 1H, $J_{5,6b}$ 6.5 Hz, $J_{6a,6b}$ 11.8 Hz, H-6b of Man*p*), 3.80 (dd, 1H, $J_{4,5b}$ 4.5 Hz, $J_{5a,5b}$ 12.4 Hz, H-5b of Xyl*p*), 3.39 (s, 3H, CH_3O), 1.98 (s, 3H, CH_3CO). Anal. Calcd for $C_{49}H_{44}O_{16}$: C, 66.22; H, 4.95. Found: C, 66.09; H, 5.01.

3.15. Methyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)-4,6-di-*O*-benzoyl-α-D-mannopyranoside (18)

To a solution of **17** (2.71 g, 3.1 mmol) in anhyd CH_2Cl_2 (10 mL) was added anhyd MeOH (40 mL), then AcCl (2.0 mL) was added to the reaction mixture at 0 °C. The solution was stoppered in a flask and stirred at rt overnight, TLC (2:1 petroleum ether–EtOAc) showed that the starting material disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. Purification of the residue by silica gel column chromatography (2:1 petroleum ether–EtOAc) gave **18** (2.20 g, 85%) as a foamy solid: $[\alpha]_D$ − 10.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.30 (m, 25H, 5Ph*H*), 5.77 (dd, 1H, $J_{2,3} = J_{3,4} = 6.8$ Hz, H-3 of Xyl*p*), 5.46 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4 of Man*p*), 5.41 (dd, 1H, $J_{1,2}$ 5.0 Hz, $J_{2,3}$ 6.7 Hz, H-2 of Xyl*p*), 5.30 (m, 1H, H-4 of Xyl*p*), 5.01 (d, 1H, $J_{1,2}$ 5.0 Hz, H-1 of Xyl*p*), 4.72 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1 of Man*p*), 4.62 (dd, 1H, $J_{4,5a}$ 4.0 Hz, $J_{5a,5b}$ 12.3 Hz, H-5a of Xyl*p*), 4.49 (dd, 1H, $J_{5,6a}$ 2.6, $J_{6a,6b}$ 11.9 Hz, H-6a of Man*p*), 4.24 (dd, 1H, $J_{5,6b}$ 5.8, $J_{6a,6b}$ 11.9 Hz, H-6b of Man*p*), 4.16–4.09 (m, 3H, H-3 of Man*p*, H-5 of Man*p*, H-2 of Man*p*), 3.87 (dd, 1H, $J_{4,5b}$ 6.5 Hz, $J_{5a,5b}$ 12.3 Hz, H-5b of Xyl*p*), 1.60 (br s, 1H, O*H*). Anal. Calcd for $C_{47}H_{42}O_{15}$: C, 66.67; H, 5.20. Found: C, 66.89; H, 5.11.

3.16. Methyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)-2-*O*-acetyl-3,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 3)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)]-4,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 3)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)]-4,6-di-*O*-benzoyl-α-D-mannopyranoside (19)

To a cooled solution (0 °C) of **12** (1.83 g, 1.0 mmol) and **18** (580 mg, 0.7 mmol) in anhyd CH_2Cl_2 (10 mL) was added TMSOTf (8 μL, 0.05 mmol). The mixture was stirred at this temperature for 2 h, and then quenched with Et_3N (one drop). The solution was concentrated to give a residue. Purification of the residue by silica gel column chromatography (1:1.5 petroleum ether–EtOAc) gave **19** (1.02 g, 60%) as a foamy solid: $[\alpha]_D$ −26.9 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09–7.23 (m, 75H, 15Ph*H*), 5.82 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 10.0 Hz, H-3 of Man*p*), 5.70 (dd, 1H, $J_{2,3} = J_{3,4} = 5.8$ Hz, H-3 of Xyl*p*), 5.66 (dd, 1H, $J_{2,3} = J_{4,5} = 7.0$ Hz, H-3 of Xyl*p*), 5.54 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4 of Man*p*), 5.50 (dd, 1H, $J_{2,3} = J_{3,4} = 10.0$ Hz, H-4 of Man*p*), 5.47 (m, 1H, H-4 of Xyl*p*), 5.47–5.36 (m, 3H), 5.21–5.15 (m, 2H), 5.10 (s, 1H, H-1 of Man*p*), 5.10 (d, 1H, $J_{1,2}$ 5.0 Hz, H-1 of Xyl*p*), 5.04 (d, 1H, $J_{1,2}$ 4.9 Hz, H-1 of Xyl*p*), 5.00 (m, 1H, H-4 of Xyl*p*), 4.84 (s, 1H, H-1 of Man*p*), 4.80 (d, 1H, $J_{1,2}$ 4.8 Hz, H-1 of Xyl*p*), 4.55 (s, 1H, H-1 of Man*p*), 4.75–3.10 (m, 21H), 3.21 (s, 3H, OCH_3), 1.81 (1s, 3H, COCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 168.9 (*C*OCH_3), 166.0, 166.0, 165.6, 165.5, 165.4, 165.3, 165.3, 165.2, 165.1, 165.1, 165.1, 164.9, 164.6, 164.6, 164.5 (15C, 15*C*OPh), 100.9, 100.1, 99.7, 99.6, 99.5, 98.8 (6C, C-1$^{I–IV}$), 78.88, 77.57, 77.26, 76.85, 75.17, 74.46, 70.55, 70.21, 70.18, 70.10, 69.93, 69.77, 69.62, 69.30, 69.23, 69.11, 68.97, 68.40, 68.32, 64.36, 64.00, 62.13, 61.40, 60.95, 60.40 (C-2 to C-6), 54.9 (O*C*H_3), 20.3 (CO*C*H_3). Anal. Calcd for $C_{141}H_{120}O_{44}$: C, 67.25; H, 4.77. Found: C, 67.48; H, 4.66.

3.17. Methyl β-D-xylopyranosyl-(1 → 4)-α-D-mannopyranosyl-(1 → 3)-[β-D-xylopyranosyl-(1 → 2)]-α-D-mannopyranosyl-(1 → 3)-[β-D-xylopyranosyl-(1 → 2)]-α-D-mannopyranoside (20)

Hexasaccharide **19** (100 mg, 0.04 mmol) was dissolved in a satd methanolic ammonia (10 mL). After stirring at rt for 72 h, the reaction mixture was concentrated and purified on a Bio-Gel P2 column (eluent: water), affording the target hexasaccharide **20** (30 mg, 80%) as a foamy solid: $[\alpha]_D$+70.1 (*c* 0.5, H_2O); ^{1}H NMR (D_2O, 400 MHz): δ 5.09 (s, 1H, H-1 of Man*p*), 5.00 (s, 1H, H-1 of Man*p*), 4.75 (s, 1H, H-1 of Man*p*), 4.32 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1 of Xyl*p*), 4.30 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1 of Xyl*p*), 4.28 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1 of Xyl*p*), 4.16–3.20 (m, 36H); ^{13}C NMR (100 MHz, D_2O): 103.6, 103.5, 103.4, 102.2, 100.5, 99.0 (6C, C-1$^{I–IV}$), 78.85, 78.00, 77.11, 76.28, 76.05, 75.84, 75.56, 73.40, 73.29, 72.69, 72.64, 71.98, 69.72, 69.50, 69.30, 69.26, 69.18, 69.11, 66.41, 66.09, 65.16, 64.99, 60.74, 60.23 (C-2 to C-6), 54.9 (O*C*H_3). Anal. Calcd for $C_{34}H_{58}O_{28}$: C, 44.64; H, 6.35. Found: C, 44.53; H, 6.42.

3.18. Methyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 4)-3,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 3)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)]-4,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 3)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1 → 2)]-4,6-di-*O*-benzoyl-α-D-mannopyranoside (21)

To a solution of **19** (470 mg, 0.17 mmol) in anhyd CH_2Cl_2 (10 mL) was added anhyd MeOH (40 mL), then AcCl (3.5 mL) was added to the reaction mixture at 0 °C. The mixture was stirred at rt for 3 days, TLC (1:1 petroleum ether–EtOAc) showed that the starting material disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. Purification of the residue by silica gel column chromatography (1:1.9 petroleum ether–EtOAc) gave **21** (244 mg, 60%) as a foamy solid: $[\alpha]_D$ −37.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$): δ 8.13–7.25 (m, 75H, 15 Ph*H*), 5.70 (dd, 1H, $J_{3,4} = J_{4,5} = 5.6$ Hz, H-3 of Xyl*p*), 5.68 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 10.1 Hz, H-3 of Man*p*), 5.62 (dd, 1H, $J_{2,3} = J_{3,4} = 7.2$ Hz, H-3 of Xyl*p*), 5.52 (dd, 1H, $J_{3,4} = J_{4,5} = 10.2$ Hz, H-4 of Man*p*), 5.49 (dd, 1H, $J_{3,4} = J_{4,5} = 10.1$ Hz, H-4 of Man*p*), 5.40–5.36 (m, 4H), 5.19–5.15 (m, 2H), 5.10 (s, 1H, H-1 of Man*p*), 5.03 (d, 1H, $J_{1,2}$ 4.8 Hz, H-1 of Xyl*p*), 5.00 (m, 1H, H-4 of Xyl*p*), 4.84 (d, 1H, $J_{1,2}$ 4.9 Hz, H-1 of Xyl*p*), 4.82 (s, 1H, H-1 of Man*p*), 4.51 (d, 1H, $J_{1,2}$ 4.9 Hz, H-1 of Xyl*p*), 4.41 (s, 1H, H-1 of Man*p*), 4.75–3.10 (m, 22H), 3.20 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 165.9, 165.9, 165.5, 165.5, 165.4, 165.3, 165.2, 165.1, 165.0, 165.0, 165.0, 164.8, 164.8, 164.4, 164.4 (15C, 15*C*OPh), 102.0, 100.9, 100.9, 99.7, 99.7, 98.7 (6C, C-$1^{I–IV}$), 78.73, 77.59, 77.20, 76.27, 74.87, 77.17, 72.20, 70.70, 70.47, 70.29, 70.10, 69.88, 69.81, 69.50, 69.35, 69.13, 69.08, 68.97, 68.90, 68.83, 68.21, 64.21, 63.80, 62.14, 61.40, 60.97, 60.83, 60.22 (C-2 to C-6), 54.7 (OCH_3). Anal. Calcd for $C_{139}H_{118}O_{43}$: C, 67.42; H, 4.77. Found: C, 67.20; H, 4.88.

3.19. Acetyl-transfer reaction and a trial with bromide 23 as the donor

To a cooled solution (0 °C) of **21** (120 mg, 0.05 mmol) and **22** (50 mg, 0.10 mmol) in anhyd CH_2Cl_2 (5 mL) was added TMSOTf (2 μL, 0.01 mmol). The mixture was stirred at this temperature for 2 h, and then quenched with Et_3N (one drop). The solution was concentrated to give a residue. Purification of the residue by silica gel column chromatography (1:1.5 petroleum ether–EtOAc) gave a product (40 mg) as a foamy solid, and its ^1H NMR data were identical with that of **19**.

To a cooled solution (0 °C) of **21** (120 mg, 0.05 mmol) and **23** (23 mg, 0.06 mmol) in anhyd CH_2Cl_2 (5 mL) and 2,4-lutidine (6 μL, 0.05 mmol), was added silver triflate (14 mg, 0.06 mmol). The mixture was stirred at this temperature for 6 h, and no reaction occurred.

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