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Carbohydrate Research 337 (2002) 383–390

CARBOHYDRATE RESEARCH

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Synthesis of α-Man*p*-(1→2)-α-Man*p*-(1→3)-α-Man*p*-(1→3)-Man*p*, the tetrasaccharide repeating unit of *Escherichia coli* O9a, and α-Man*p*-(1→2)-α-Man*p*-(1→2)-α-Man*p*-(1→3)-α-Man*p*-(1→3)-Man*p*, the pentasaccharide repeating unit of *E. coli* O9 and *Klebsiella* O3

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Received 2 November 2001; accepted 28 December 2001

Abstract

The tetrasaccharide repeating unit of *Escherichia coli* O9a, α-D-Man*p*-(1→2)-α-D-Man*p*-(1→3)-α-D-Man*p*-(1→3)-D-Man*p*, and the pentasaccharide repeating unit of *E. coli* O9 and *Klebsiella* O3, α-D-Man*p*-(1→2)-α-D-Man*p*-(1→2)-α-D-Man*p*-(1→3)-α-D-Man*p*-(1→3)-D-Man*p*, were synthesized as their methyl glycosides. Thus, selective 3-O-allylation of *p*-methoxyphenyl α-D-mannopyranoside via a dibutyltin intermediate gave *p*-methoxyphenyl 3-*O*-allyl-α-D-mannopyranoside (**2**) in good yield. Benzoylation (→**3**), then removal of 1-*O*-methoxyphenyl (→**4**), and subsequent trichloroacetimidation afforded the 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**5**). Condensation of **5** with methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**6**) selectively afforded the (1→3)-linked disaccharide **7**. Benzoylation of **7**, debenzylidenation, benzoylation, and deallylation gave methyl 2,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-α-D-mannopyranoside (**11**) as the disaccharide acceptor. Coupling of **11** with (1→2)-linked mannose disaccharide donor **17** or trisaccharide donor **21**, followed by deacylation, furnished the target tetrasaccharide and pentasaccharide, respectively.

Keywords: Oligosaccharide; Mannose; Regioselective synthesis

O-Specific polysaccharides (O-PS) are a part of lipopolysaccharides (LPSs) and covalently bind to lipid A through the core oligosaccharide portion. The O-PS of gram-negative bacteria are structurally polymorphic, and they are utilized as the O antigen for serological typing. Each O-polysaccharide consists of many repeating units composed of several sugars with various linkages. The *Escherichia coli* O9a polysaccharide has a tetrasaccharide repeating unit, α-D-Man*p*-(1→2)-α-D-Man*p*-(1→3)-α-D-Man*p*-(1→3)-D-Man*p*, and the *E. coli* O9, and *Klebsiella* O3 polysaccharides have a pentasaccharide repeating unit, α-D-Man*p*-(1→2)-α-D-Man*p*-(1→2)-α-D-Man*p*-(1→3)-α-D-Man*p*-(1→3)-D-Man*p*.[1] Synthesis of these repeating units is important for investigation of structure–bioactivity relationships among oligosaccharides, and this communication will describe their facile preparation.

As outlined in Scheme 1, *p*-methoxyphenyl α-D-mannopyranoside (**1**), readily obtainable from reaction of mannose peracetate with *p*-methoxyphenol in the presence of $BF_3{\cdot}Et_2O$,[2] followed by Zemplén deacetylation,[3] was chosen as the starting material. Selective 3-O-allylation of **1** was achieved giving **2** in good yield (65%) using the reported method through a dibutyltin complex.[4] Benzoylation of **2** with benzoyl chloride in pyridine quantitatively gave **3**, and oxidative cleavage of the *p*-methoxyphenyl group with CAN went smoothly to give 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-α-D-mannopyranose (**4**) in satisfactory yield (80%). Trichloroacetimidation of **4** with trichloroacetonitrile in the presence of potassium carbonate or DBU[5] was

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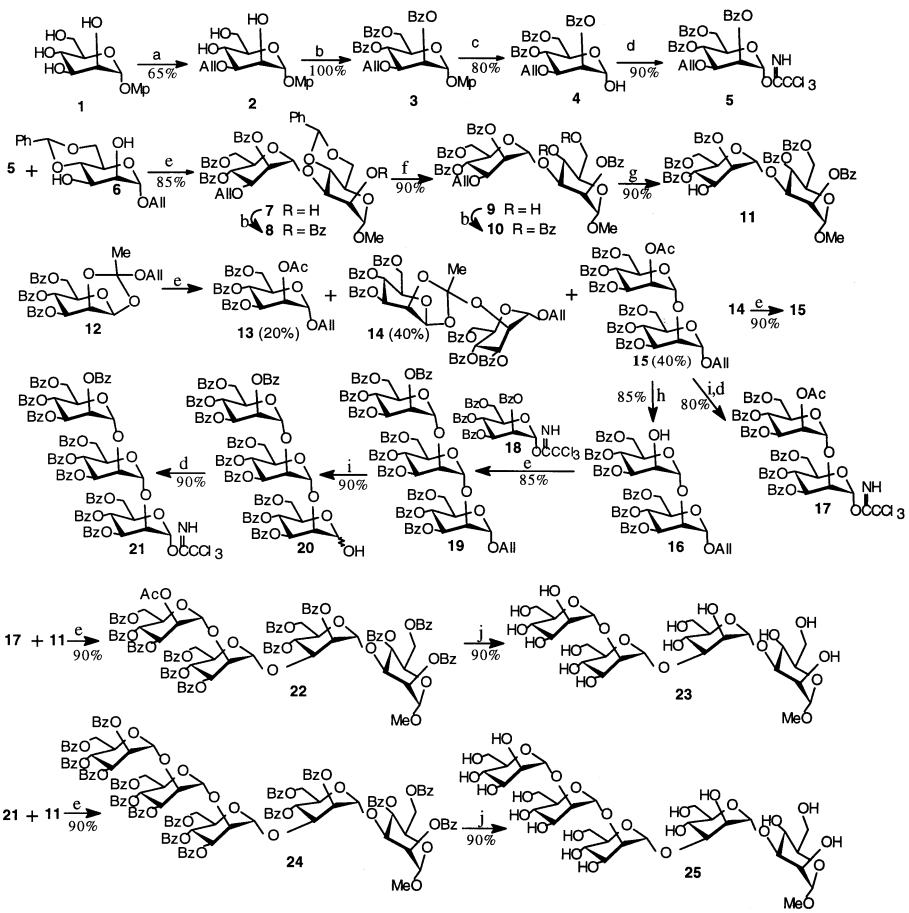
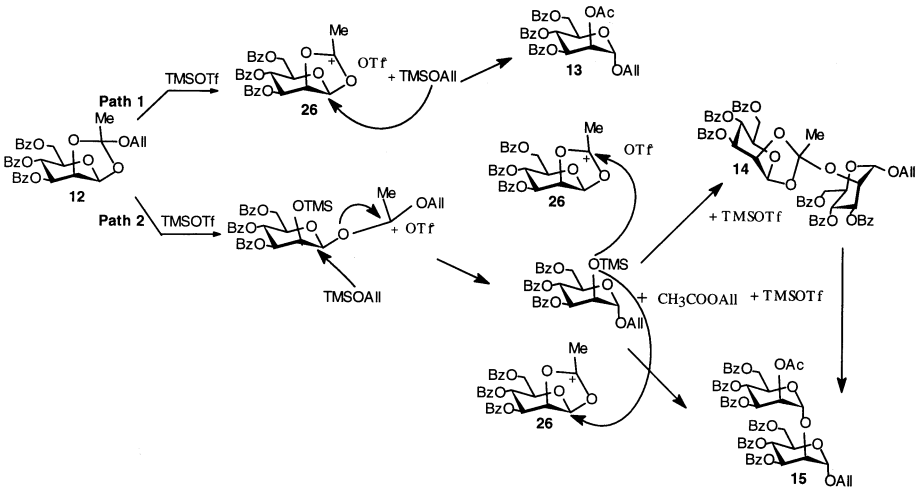
0008-6215/02/$ - see front matter
PII: S0008-6215(02)00011-3

carried out readily affording the mannose donor **5** in high yield (90%). Coupling of **5** with methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**6**) selectively gave (1→3)-linked disaccharide **7** (85%). The 3-selectivity was confirmed by benzoylation of **7** to give **8** showing a newly emerged doublet of doublets in its ^{1}H NMR spectrum at δ 5.55 ppm with $J_{1,2}$ 1.8 Hz and $J_{2,3}$ 3.2 Hz, which are the salient features for H-2. Hydrolysis to remove the benzylidene group, followed by benzoylation, gave the disaccharide **10** in good yield (90% for two steps). Deallylation of **10** with $PdCl_2$ in CH_3OH[6] gave the disaccharide acceptor **11** (90%).

The disaccharide donor **17** was prepared from allyl 2-*O*-acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside (**15**), which was obtained by the reported method through self-condensation of 3,4,6-tri-*O*-benzoyl-1,2-*O*-allyloxyethylidene-α-D-mannopyranose (**12**).[7] It was found that when the amount of Me_3SiOTf was less than 5% equiv of **12**, and the reaction time was relatively short (2 h), the product was a mixture consisting of monosaccharide **13** (20%), disaccharide **15** (40%), and disaccharide orthoester **14** (40%). The latter was isolated and identified by its ^{1}H NMR spectrum giving H-1 at δ 5.50–5.47 ppm and CH_3 at δ 1.78 ppm. Rearrangement of **14** with Me_3SiOTf gave the required disaccharide **15** in high yield. Scheme 2 shows the proposed mechanism for the disaccharide orthoester formation. Deallylation of **15**, followed by trichloroacetimidation, afforded the disaccharide donor **17**,[7] while selective deacetylation with CH_3COCl–MeOH gave the disaccharide acceptor **16**.[8] The trisaccharide donor **21** was prepared by condensation of **16** with perbenzoylated mannosyl trichloroacetimidate (**18**) (85%), followed by deallylation and trichloroacetimidation. Finally, coupling of the disaccharide acceptor **11** with the disaccharide donor **17**, followed by deacylation in ammonia-saturated methanol, gave the tetrasaccharide **23**, while condensation of **11** with the trisaccharide donor **21**, followed by deacylation, furnished the pentasaccharide **25**. The deacylation was carried out in the ammonia-saturated solution rather than by Zemplén deacylation because of the mildness and completion of debenzoylation.



Scheme 1. Reagents and conditions: (a) Bu_2SnO, CH_3OH, reflux, 2 h; then AllBr, Bu_4NI, C_6H_6, 60 °C, 24 h. (b) PhCOCl/Pyr, rt. (c) CAN, CH_3CN–H_2O, rt, 10 min. (d) CCl_3CN, CH_2Cl_2, K_2CO_3, rt. (e) Me_3SiOTf, CH_2Cl_2, −42 °C to rt. (f) 80% HOAc–H_2O, rt, 24 h. (g) $PdCl_2$, CH_3OH, 40 °C, 4 h. (h) 5% CH_3COCl–CH_3OH, 40 °C. (i) $PdCl_2$, CH_3OH, 40 °C. (j) NH_3–CH_3OH, rt.



Scheme 2.

In summary, a very concise and convergent synthesis of the target mannose tetrasaccharide and pentasaccharide was achieved in a regio- and stereoselective way. Because of its simplicity and efficiency, this method could be used for construction of higher mannose oligosaccharides with both α-(1→3) and α-(1→2) linkages.

1. Experimental

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. ^{1}H NMR spectra were recorded with Varian XL-400 and Varian XL-200 spectrometers, for solutions in $CDCl_3$ with tetramethylsilane (Me_4Si) as the internal standard. Chemical shifts are expressed in ppm downfield from the internal Me_4Si absorption. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the electrospray-ionization mode. Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 30% (v/v) H_2SO_4 in MeOH or by UV detection. Column chromatography was conducted by elution of a column (8 × 100 mm, 16 × 240 mm, 18 × 300 mm, and 35 × 400 mm) of silica gel (100–200 mesh) and 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) and 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.

p-*Methoxyphenyl 3-O-allyl-α-*D*-mannopyranoside* (**2**).—*p*-Methoxyphenyl α-D-mannopyranoside (**1**) (5.00 g, 17.5 mmol) and Bu_2SnO (4.80 g,19.3 mmol) were added to CH_3OH (200 mL), and the mixture was heated under reflux for 2 h, then concentrated to dryness. The residue was diluted with benzene (200 mL), and allyl bromide (18.0 mL, 211 mmol), and Bu_4NI (6.46 g, 17.5 mmol) were added to the mixture. The reaction was carried out at 60 °C for 24 h at which time TLC (3:1 EtOAc–CH_3OH) indicated that the reaction was complete. Concentration of the reaction mixture and purification by column chromatography (EtOAc) gave **2** as a syrup (3.70 g, 65%): $[\alpha]_D^{20}$ +95.4° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 6.98 (d, 2 H, *J* 9.1 Hz, *p*-CH_3OPhH), 6.82 (d, 2 H, *J* 9.1 Hz, *p*-CH_3OPhH), 6.00 (m, 1 H, CH_2=C*H*–CH_2–), 5.51 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 5.40–5.25 (m, 2 H, CH_2=CH–CH_2–), 4.30–4.16 (m, 2 H, CH_2=CH–CH_2–), 4.21 (m, 1 H), 4.11 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 3.91–3.87 (dd, 1 H, $J_{5,6}$ 3.2, $J_{6,6'}$ 12.3 Hz, H-6), 3.86–3.83 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.5 Hz, H-3), 3.78–3.73 (m, 2 H), 3.77 (s, 3 H, CH_3), 2.98 (br, 3 H, OH). Anal. Calcd for $C_{16}H_{22}O_7$: C, 58.90; H, 6.75. Found: C, 58.61; H, 6.77.

p-*Methoxyphenyl 3*-O-*allyl-2,4,6-tri*-O-*benzoyl-α-*D*-mannopyranoside* (**3**).—To a solution of **2** (3.26 g, 10.0 mmol) in pyridine (8 mL), BzCl (4.17 mL, 36.0 mmol) was added dropwise, and the mixture was stirred overnight at rt, at which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2, and washed with 1 N HCl, water, and satd aq $NaHCO_3$. The organic layers were combined, dried, and concentrated. Purification by column chromatography (3:1 petroleum ether–EtOAc) gave **3** quantitatively as a syrup (6.38 g, 100%): $[\alpha]_D^{20}$ +19.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.12–7.38 (m, 15 H, PhH), 7.08 (d, 2 H, *J* 9.1 Hz, *p*-CH_3OPhH), 6.76 (d, 2 H, *J* 9.1 Hz, *p*-CH_3OPhH),

5.86 (t, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.79–5.69 (m, 2 H, H-2, CH_2=CH–CH_2–), 5.61 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 5.23–5.06 (m, 2 H, CH_2=CH–CH_2–), 4.63–4.61 (m, 1 H), 4.45–4.42 (m, 2 H), 4.38–4.34 (dd, 1 H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.8 Hz, H-3), 4.22–4.04 (m, 2 H, CH_2=CH–CH_2–), 3.73 (s, 3 H, CH_3). Anal. Calcd for $C_{37}H_{34}O_{10}$: C, 69.59; H, 5.33. Found: C, 69.92; H, 5.31.

3-O-Allyl-2,4,6-tri-O-benzoyl-α-D-mannopyranose (**4**).—To a solution of **3** (6.38 g, 10.0 mmol) in 4:1 CH_3CN–water (600 mL) was added CAN ($(NH_4)_2Ce(NO_3)_6$, 21.93 g, 40.0 mmol), and the mixture was stirred for 10 min at rt, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was extracted with EtOAc and washed with satd aq $NaHCO_3$. The organic layer was concentrated under reduced pressure and purified by column chromatography (3:1 petroleum ether–EtOAc) to afford **4** as a syrup (4.26 g, 80%): $[\alpha]_D^{20}$ −31.6° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.11–7.34 (m, 15 H, PhH), 5.88 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.73–5.66 (m, 1 H, CH_2=C*H*–CH_2–), 5.61 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.2 Hz, H-2), 5.44 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 5.19–5.03 (m, 2 H, CH_2=CH–CH_2–), 4.74–4.70 (dd, 1 H, *J* 2.6, *J* 12.1 Hz), 4.52–4.48 (m, 1 H, H-5), 4.39–4.35 (dd, 1 H, *J* 4.1, *J* 12.1 Hz), 4.25–4.21 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.8 Hz, H-3), 4.15–3.97 (m, 2 H, CH_2=CH–CH_2–), 3.50 (br, 1 H, OH). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.67; H, 5.26. Found: C, 67.34; H, 5.27.

3-O-Allyl-2,4,6-tri-O-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**5**).—Compound **4** (9.00 g, 16.9 mmol) was dissolved in CH_2Cl_2 (80 mL), then trichloroacetonitrile (5 mL) and anhyd K_2CO_3 (9.00 g) were added. The reaction mixture was stirred overnight at rt, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Concentration of the reaction mixture, followed by purification on a silica-gel column with 3:1 petroleum ether–EtOAc as the eluent, gave the monosaccharide donor **5** as foamy solid (10.30 g, 90%): ^{1}H NMR ($CDCl_3$): δ 8.81 (s, N*H*=), 8.11–7.27 (m, 15 H, PhH), 6.49 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 5.95 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.79 (dd, 1 H, $J_{1,2}$ 1.6, $J_{2,3}$ 3.3 Hz, H-2), 5.70 (m, 1 H, CH_2=C*H*–CH_2–), 5.26–5.08 (m, 2 H, CH_2=CH–CH_2–), 4.70–4.67 (dd, 1 H, *J* 1.6, *J* 11.7 Hz, H-6), 4.47–4.40 (m, 2 H, H-5, H-6), 4.27–4.24 (dd, 1 H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.8 Hz, H-3), 4.18–4.01 (m, 2 H, CH_2=CH–CH_2–). Anal. Calcd for $C_{32}H_{28}Cl_3NO_9$: C, 56.76; H, 4.14. Found: C, 56.60; H, 4.15.

Methyl 3-O-allyl-2,4,6-tri-O-benzoyl-α-D-mannopyranosyl-(1→3)-4,6-O-benzylidene-α-D-mannopyranoside (**7**).—Trichloroacetimidate **5** (3.38 g, 5.0 mmol) and methyl 4, 6-*O*-benzylidene-α-D-mannopyranoside (**6**) (1.41 g, 5.0 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (70 mL), Me_3SiOTf (40 μL, 0.21 mmol) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, at the end of which time TLC indicated that the reaction was complete. Then the mixture was neutralized with triethylamine and concentrated under reduced pressure to dryness. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **7** as a syrup (3.89 g, 85%): $[\alpha]_D^{20}$ −0.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08–7.27 (m, 20 H, PhH), 5.80–5.63 (m, 4 H, H-4^{II}, CH_2=C*H*–CH_2–, H-2^{II}, PhC*H*=), 5.47 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{II}), 5.15–5.00 (m, 2 H, CH_2=CH–CH_2–), 4.69 (s, 1 H, H-1^{I}), 4.66–4.63 (m, 2 H), 4.47–4.40 (m, 1 H), 4.31–4.23 (m, 2 H), 4.17–4.09 (m, 3 H), 4.00–3.96 (m, 2 H), 3.89–3.80 (m, 1 H), 3.29 (s, 3 H, CH_3), 2.07 (br, 1 H, OH). Anal. Calcd for $C_{44}H_{44}O_{14}$: C, 66.33; H, 5.53. Found: C, 66.60; H, 5.51.

Methyl 3-O-allyl-2,4,6-tri-O-benzoyl-α-D-mannopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-α-D-mannopyranoside (**8**).—To a solution of **7** (3.98 g, 5.0 mmol) in pyridine (3 mL), BzCl (0.7 mL, 6.0 mmol) was added dropwise, and the mixture was stirred overnight at rt, at which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2, washed with 1 N HCl, water, and satd aq $NaHCO_3$. The organic layer was combined, dried, and concentrated. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **8** quantitatively as a syrup (4.50 g, 100%): $[\alpha]_D^{20}$ −57.7° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.19–7.26 (m, 25 H, Ph), 5.76 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4$^{II'}$), 5.73 (s, 1 H, PhC*H*=), 5.66 (dd, 1 H, $J_{1,2}$ 1.3, $J_{2,3}$ 3.8 Hz, H-2^{I}), 5.55 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.2 Hz, H-2^{II}), 5.49 (m, 1 H, CH_2=C*H*–CH_2–), 5.44 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.84 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1^{I}), 4.82–4.67 (m, 2 H, CH_2=CH–CH_2–), 4.68 (m, 1 H), 4.51 (dd, 1 H, $J_{2,3}$ 3.8, $J_{3,4}$ 9.5 Hz, H-3^{I}), 4.48–4.35 (m, 3 H), 4.21 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H-4^{I}), 3.94–3.90 (m, 3 H), 3.89–3.71 (m, 2 H, CH_2=CH–C*H*$_2$–), 3.37 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 166.23, 165.68, 165.45, 165.28 (4 Ph*C*O), 136.95, 133.92, 133.57, 133.54, 133.13, 132.77 (5 Ph, CH_2=*C*H–CH_2–), 130.09, 129.85, 129.68, 129.62, 129.56, 128.75, 128.63, 128.35, 128.26, 128.11, 125.87 (5 Ph), 117.22 (*C*H$_2$=CH–CH_2–), 101.32 (Ph*C*H=), 99.80, 98.50 (C-1), 79.30 (C-3), 73.91, 71.82, 71.15, 70.61, 69.47, 68.88, 68.70, 68.15, 63.35, 63.26 (C-2,3,4,5,6, CH_2=CH–*C*H$_2$–), 55.11 (CH_3). Anal. Calcd for $C_{51}H_{48}O_{15}$: C, 68.00; H, 5.33. Found: C, 68.25; H, 5.30.

Methyl 3-O-allyl-2,4,6-tri-O-benzoyl-α-D-mannopyranosyl-(1→3)-2-O-benzoyl-α-D-mannopyranoside (**9**).—Compound **8** (2.25 g, 2.5 mmol) was dissolved in 80% AcOH (50 mL), and the mixture was stirred at 50 °C for 24 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated under reduced pressure, and the residue was passed through a silica gel column with 2:1 petroleum ether–EtOAc as

the eluent to give **9** as foamy solid (1.83 g, 90%): $[\alpha]_D^{20}$ −31.2° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.16–7.32 (m, 20 H, PhH), 5.77 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4^{II}), 5.56–5.45 (m, 4 H, H-2^{II}, H-2^{I}, CH_2=C*H*–CH_2–, H-1^{II}), 4.90–4.75 (m, 2 H, CH_2=CH–CH_2–), 4.83 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1^{I}), 4.65–4.62 (m, 1 H), 4.40–4.33 (m, 2 H), 4.28–4.26 (m, 2 H), 3.97–3.94 (m, 3 H), 3.93–3.71 (m, 2 H, CH_2=CH–CH_2–), 3.72 (m, 1 H, H-5^{II}), 3.35 (s, 3 H, CH_3), 2.46 (br, 2 H, OH). Anal. Calcd for $C_{44}H_{44}O_{15}$: C, 65.02; H, 5.42. Found: C, 65.31; H, 5.40.

*Methyl 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**10**).—To a solution of **9** (3.17 g, 3.9 mmol) in pyridine (4 mL), BzCl (1.1 mL, 9.5 mmol) was added dropwise, and the mixture was stirred overnight at rt, at which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 and washed with 1 N HCl, water and satd aq $NaHCO_3$. The organic layer was combined, dried, and concentrated. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **10** quantitatively as a syrup (3.98 g, 100%): $[\alpha]_D^{20}$ −32.9° (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.11–7.25 (m, 30 H, PhH), 5.97 (dd, 1 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4^{II}), 5.72 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4^{I}), 5.67 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.1 Hz, H-2^{II}), 5.41 (m, 1 H, CH_2=C*H*–CH_2–), 5.21–5.18 (m, 2 H, H-1^{II}, H-2), 4.95 (d, 1 H, H-1^{I}, $J_{1,2}$ 1.4 Hz), 4.87–4.72 (m, 2 H, CH_2=CH–CH_2–), 4.70–4.66 (dd, 1 H, *J* 2.6, *J* 12.1 Hz), 4.61–4.57 (m, 2 H), 4.52–4.48 (dd, 1 H), 4.35–4.26 (m, 3 H), 3.89–3.86 (dd, 1 H), 3.76–3.59 (m, 2 H, CH_2=CH–CH_2–), 3.42 (s, 3 H, CH_3). Anal. Calcd for $C_{58}H_{52}O_{17}$: C, 68.24; H, 5.10. Found: C, 68.30; H, 5.07.

*Methyl 2,4,6-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**11**).—To a solution of **10** (2.04 g, 2.0 mmol) in anhyd CH_3OH (70 mL) was added $PdCl_2$ (0.2 g), and the mixture was stirred for 4 h at 40 °C, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtrated, the filtrate was concentrated, and the residue was passed over a silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to give **11** as a syrup (1.76 g, 90%): $[\alpha]_D^{20}$ −27.4° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.18–7.28 (m, 30 H, PhH), 5.97 (dd, 1 H, $J_{3,4} = J_{4,5} =$ 10.0 Hz, H-4^{II}), 5.65 (dd, 1 H, $J_{1,2}$ 1.2, $J_{2,3}$ 3.1 Hz, H-2^{II}), 5.59 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4^{I}), 5.27 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1^{II}), 5.07 (dd, 1 H, $J_{1,2}$ 1.4, $J_{2,3}$ 3.1 Hz, H-2^{I}), 4.94 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1^{I}), 4.71–4.67 (dd, 1 H, *J* 2.5, *J* 12.1 Hz), 4.61–4.57 (m, 2 H), 4.48–4.44 (dd, 1 H, *J* 4.5, *J* 12.2 Hz), 4.40–4.34 (m, 2 H), 4.27–4.24 (m, 1 H), 4.19–4.16 (dd, 1 H, *J* 3.2, *J* 9.8 Hz), 3.42 (s, 3 H, CH_3), 2.40 (br, 1 H, OH); ^{13}C NMR ($CDCl_3$): δ 166.39, 166.14, 166.06, 165.73, 165.60, 165.07 (6 Ph*C*O), 133.60, 133.41, 133.25, 132.98, 132.87, 129.91, 129.89, 129.83, 129.76, 129.69, 129.62, 129.27, 129.08, 128.97, 128.73, 128.46, 128.37, 128.32, 128.28 (6 Ph), 99.41, 98.52 (C-1), 75.79 (C-3), 72.33, 71.71, 69.78, 69.24, 68.72, 68.55, 68.40, 62.99, 62.75 (C-2,3,4,5,6), 55.39 (CH_3). Anal. Calcd for $C_{55}H_{48}O_{17}$: C, 67.35; H, 4.90, Found: C, 67.30; H, 4.91.

*Allyl 2-*O*-acetyl-3,4,6-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**15**).—3,4,6-Tri-*O*-benzoyl-α-D-mannopyranose 1,2-(allyl orthoacetate)[7] (**12**, 1.25 g, 2.2 mmol) was dried under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL), Me_3SiOTf (6.0 μL, 0.031 mmol) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, at the end of which time TLC indicated that the reaction was complete. Then the mixture was neutralized with triethylamine and concentrated to a syrup. Purification by column chromatography (3:1 petroleum ether–EtOAc) gave **15** (0.36 g) and 3,4,6-tri-*O*-benzoyl-α-D-mannopyranose 1,2-(allyl 3,4,6-tri-*O*-benzoyl-α-D-mannopyranosid-2-yl orthoacetate) (**14**, 0.36 g), and allyl 2-*O*-acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside (**13**, 0.18 g). Compound **14** (0.60 g, 0.57 mmol) was easily converted to **15** (0.54 g, 90%) with Me_3SiOTf (0.1 equiv) by the same procedure as described in the preparation of **14** from **12**. For **14**: $[\alpha]_D^{20}$ −20.8° (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.01–7.26 (m, 30 H, PhH), 5.88 (dd, 1 H, $J_{3,4} = J_{4,5} = 10.1$ Hz, H-4^{II}), 5.83 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4^{I}), 5.78 (m, 1 H, CH_2=C*H*–CH_2–), 5.55–5.52 (dd, 1 H, $J_{2,3}$ 3.7, $J_{3,4}$ 10.1 Hz, H-3^{II}), 5.50–5.47 (m, 2 H, H-3^{I}, H-1^{II}), 5.16–4.91 (m, 2 H, CH_2=CH–CH_2–), 4.94 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1^{I}), 4.83 (dd, 1 H, $J_{1,2}$ 2.8, $J_{2,3}$ 3.7 Hz, H-2^{II}), 4.57–4.51 (m, 2 H), 4.44–4.36 (m, 3 H), 4.29–4.24 (m, 1 H), 4.13–3.88 (m, 2 H, CH_2=CH–CH_2–), 3.97 (m, 1 H, H-5), 1.78 (s, 3 H, CH_3). Anal. Calcd for $C_{59}H_{52}O_{18}$: C, 67.56; H, 4.96. Found: C, 67.67; H, 4.89. For **15**: $[\alpha]_D^{20}$ +3.0° (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.01–7.33 (m, 30 H, PhH), 5.97 (dd, 1 H, $J_{3,4} = J_{4,5} =$ 9.9 Hz, H-4^{II}), 5.91–5.82 (m, 4 H, CH_2=C*H*–CH_2–, H-4^{I}, H-3^{II}, H-3^{I}), 5.69 (dd, 1 H, H-2^{II}), 5.28–5.17 (m, 2 H, CH_2=CH–CH_2–), 5.15 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{II}), 5.09 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1^{I}), 4.63–4.44 (m, 5 H, 4 H-6, H-5^{II}), 4.39–4.35 (m, 2 H, H-2^{I}, H-5^{I}), 4.20–3.89 (m, 2 H, CH_2=CH–CH_2–). Anal. Calcd for $C_{59}H_{52}O_{18}$: C, 67.56; H, 4.96. Found: C, 67.63; H, 4.90.

*Allyl 3,4,6-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**16**).—To a solution of **15** (1.00 g, 0.95 mmol) in anhyd CH_3OH (30 mL) was added CH_3COCl (1.5 mL), and the mixture was stirred for 3–4 h at 40 °C, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated under reduced pressure, then passed through a silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to gave **16** as a syrup (0.82 g, 85%): $[\alpha]_D^{20}$ +0.1° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.08–7.33

(m, 30 H, PhH), 5.98 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4^{II}), 5.92 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4^{I}), 5.88 (m, 1 H, CH_2=C*H*–CH_2–), 5.82 (dd, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.9 Hz, H-3^{II}), 5.78 (dd, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.8 Hz, H-3^{I}), 5.29–5.15 (m, 2 H, C*H*$_2$=CH–CH_2–), 5.18 (d, 1 H, $J_{1,2}$ 1.1 Hz, H-1^{II}), 5.15 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.63–4.59 (m, 1 H), 4.57–4.35 (m, 5 H), 4.50 (m, 1 H, H-2), 4.41 (m, 1 H, H-2), 4.21–3.91 (m, 2 H, CH_2=CH–C*H*$_2$–), 2.40 (br, 1 H, OH); ^{13}C NMR ($CDCl_3$): δ 166.23, 166.06, 165.58, 165.52, 165.28, 165.09 (Ph*C*O), 133.33, 133.25, 133.14, 132.95, 129.81, 129.72, 129.64, 129.59, 129.16, 128.96, 128.91, 128.84, 128.48, 128.36, 128.28, 117.94 (C*H*$_2$=CH–CH_2–), 101.48, 97.89 (C-1), 72.15, 71.27, 69.58, 69.29, 68.79, 68.65, 67.34, 66.83, 63.61, 63.41. Anal. Calcd for $C_{57}H_{50}O_{17}$: C, 67.99; H, 4.97. Found: C, 68.29; H, 4.95.

Allyl 2,3,4,6-tetra-O-*benzoyl*-α-D-*mannopyranosyl-(1→2)-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl-(1→2)-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranoside* (**19**).—2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**18**, 0.67 g, 0.9 mmol) and **16** (0.60 g, 0.6 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (40 mL). Me_3SiOTf (10 μL, 0.053 mmol) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, at the end of which time TLC indicated that the reaction was complete. Then the mixture was neutralized with triethylamine and concentrated under reduced pressure to dryness. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **19** as a syrup (0.80 g, 85%): $[\alpha]_D^{20}$ +7.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08–7.11 (m, 50 H, PhH), 6.00–5.88 (m, 5 H), 5.95 (m,1 H, CH_2=C*H*–CH_2–), 5.74–5.70 (m, 2 H, H-2^{III}, H-3^{I}), 5.41 (d,1 H, H-1^{III}), 5.32–5.20 (m, 2 H, C*H*$_2$=CH–CH_2–), 5.12 (d, 1 H, H-1^{II}), 4.92 (d, 1 H, H-1^{I}), 4.62–4.52 (m, 5 H), 4.49–4.43 (m, 2 H, H-2^{I}, H-5^{I}), 4.23–3.96 (m, 1 H, CH_2=CH–C*H*$_2$–), 4.18 (m, 1 H, H-6^{I}); ^{13}C NMR ($CDCl_3$): δ 166.21, 166.12, 165.77, 165.51, 165.48, 165.28, 165.28, 165.14, 164.86, 164.63 (Ph*C*O), 133.36, 133.25, 133.18, 133.15, 133.09, 132.95, 132.88, 129.97, 129.91, 129.81, 129.73, 129.60, 129.56, 129.18, 129.09, 128.98, 128.92, 128.88, 128.84, 128.73, 128.59, 128.45, 128.37, 128.32, 128.27, 128.24, 128.20, 117.90 (C*H*$_2$=CH–CH_2–), 99.95, 99.56, 97.98 (C-1), 71.16, 70.07, 69.94, 69.65, 69.55, 68.73, 68.63, 67.39, 66.44, 63.75, 63.56, 62.88. Anal. Calcd for $C_{91}H_{76}O_{26}$: C, 68.94; H, 4.80. Found: C, 68.65; H, 4.82.

2,3,4,6-Tetra-O-*benzoyl*-α-D-*mannopyranosyl-(1→2)-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl-(1→2)-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranose* (**20**).—To a solution of **19** (0.57 g, 0.36 mmol) in anhyd CH_3OH (30 mL) was added $PdCl_2$ (0.30 g), and the mixture was stirred for 4 h at 40 °C, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the filtrate was concentrated, and the residue was passed over a silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to gave **20** as a syrup (0.50 g, 90%): $[\alpha]_D^{20}$ −28.2° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08–7.11 (m, 50 H, PhH), 6.00–5.90 (m, 5 H, H-4^{III}, H-4^{II}, H-4^{I}, H-3^{III}, H-3^{II}), 5.79–5.74 (m, 2 H, H-3^{I}, H-2^{III}), 5.51 (d, 1 H, H-1^{III}), 5.42 (d, 1 H, H-1^{II}), 4.96 (s, 1 H, H-1^{I}), 4.64–4.45 (m, 8 H), 4.39 (m, 1 H, H-2^{I}), 4.33 (m, 1 H), 4.20–4.16 (dd, 1 H, $J_{5,6}$ 4.25, $J_{6,6'}$ 12.2 Hz, H-6^{I}), 2.85 (br,1 H, OH). Anal. Calcd for $C_{88}H_{72}O_{26}$: C, 68.39; H, 4.66. Found: C, 68.66; H, 4.64.

2,3,4,6-Tetra-O-*benzoyl*-α-D-*mannopyranosyl-(1→2)-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl-(1→2)-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl trichloroacetimidate* (**21**).—Compound **20** (0.95 g, 0.62 mmol) was dissolved in CH_2Cl_2 (40 mL), then trichloroacetonitrile (3 mL) and anhyd K_2CO_3 (0.95 g) were added. The reaction mixture was stirred overnight at rt, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Concentration of the reaction mixture, followed by purification on a silica-gel column with 3:1 petroleum ether–EtOAc as the eluent, gave the trisaccharide donor **21** as foamy solid (0.94 g, 90%): ^{1}H NMR ($CDCl_3$): δ 8.75 (s, 1 H, HN=), 8.08–7.11 (m, 50 H, PhH), 6.61 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1^{I}), 6.09–5.92 (m, 5 H, H-4^{III}, H-4^{II}, H-4^{I}, H-3^{III}, H-3^{II}), 5.85–5.80 (m, 2 H, H-3^{I}, H-2^{III}), 5.57 (s, 1 H, H-1^{III}), 5.05 (s, 1 H, H-1^{II}), 4.75 (m, 1 H, H-2^{II}), 4.70 (dd, 1 H, $J_{5,6}$ 2.3, $J_{6,6'}$ 11.7 Hz, H-6^{III}), 4.67–4.47 (m, 7 H), 4.39 (m, 1 H, H-5^{I}), 4.17 (m, 1 H, H-6^{I}). Anal. Calcd for $C_{90}H_{72}Cl_3NO_{26}$: C, 63.96; H, 4.26. Found: C, 63.74; H, 4.28.

Methyl 2-O-*acetyl-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl-(1→2)-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl-(1→3)-2,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl-(1→3)-2,4,6-tri*-O-*benzoyl*-α-D-*mannopyranoside* (**22**).—2-*O*-Acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate[9] (**17**, 0.23 g, 0.2 mmol) and **11** (0.20 g, 0.2 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). Me_3SiOTf (6.0 μL, 0.031 mmol) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, at the end of which time TLC indicated that the reaction was complete. The mixture was then neutralized with triethylamine and concentrated under reduced pressure to a syrup. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **22** as foamy solid (0.39 g, 90%): $[\alpha]_D^{20}$ −6.2° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08–7.24 (m, 60 H, PhH), 6.01 (dd, 1 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4^{IV}), 5.91–5.82 (m, 3 H, H-4^{III}, H-4^{II}, H-4^{I}), 5.79–5.75 (m, 1 H, H-3^{IV}), 5.68 (m, 1 H, H-2^{IV}), 5.56–5.52 (dd, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 10.0 Hz, H-3^{III}), 5.49 (m, 1 H, H-2^{III}), 5.34 (s, 1 H, H-1^{IV}), 5.31 (m, 1 H, H-2^{II}), 5.15 (s, 1 H, H-1^{III}), 4.95 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1^{II}), 4.69–4.66 (m, 1 H), 4.65 (s, 1 H, H-1^{I}), 4.63–4.60 (dd, 1 H, *J* 3.3, *J* 9.8 Hz),

4.59–4.55 (dd, 1 H, *J* 2.2, *J* 12.3 Hz), 4.49–4.46 (m, 2 H), 4.35 (m, 1 H), 4.32–4.18 (m, 3 H), 4.13–4.08 (m, 3 H), 4.00–3.95 (m, 3 H), 3.44 (s, 3 H, CH_3O), 1.96 (s, 3 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 168.87 (CH_3CO), 166.08, 166.03, 165.97, 165.83, 165.68, 165.63, 165.34, 165.15, 164.85, 164.81, 164.81, 164.58 (12 Ph*C*O), 133.65, 133.59, 133.59, 133.30. 133.25, 133.07, 132.99, 132.93, 132.83, 132.79, 132.61, 129.90, 129.80, 129.78, 129.71, 129.66, 129.62, 129.56, 129.28, 129.15, 129.00, 128.92, 128.87, 128.85, 128.75, 128.60, 128.54, 128.39, 128.35, 128.32, 128.27, 128.01 (Ph), 100.38, 99.49, 99.08, 98.49 (C-1), 77.18, 76.75 (C-3), 76.17, 75.45, 71.74, 71.44, 70.42, 69.63, 69.60, 69.41, 69.38, 69.12, 68.67, 68.30, 68.00, 66.51, 66.44, 62.95, 62.68, 62.49, 62.00 (C-2,3,4,5,6), 55.43 (CH_3O), 20.42 (CH_3CO). Anal. Calcd for $C_{111}H_{94}O_{34}$: C, 67.61; H, 4.77. Found: C, 67.29; H, 4.78.

Methyl 2,3,4,6-tetra-O-*benzoyl*-α-D-*mannopyranosyl-(1→2)-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl-(1→2)-3,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl-(1→3)-2,4,6-tri*-O-*benzoyl*-α-D-*mannopyranosyl-(1→3)-2,4,6-tri*-O-*benzoyl*-α-D-*mannopyranoside* (**24**).—Donor **21** (0.34 g, 0.20 mmol) and acceptor **11** (0.20 g, 0.2 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (25 mL). Me_3SiOTf (6.0 μL, 0.031 mmol) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, at the end of which time TLC indicated that the reaction was complete. Then the mixture was neutralized with triethylamine and concentrated under reduced pressure to dryness. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **24** as a syrup (0.45 g, 90%): $[\alpha]_D^{20}$ −25.9° (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.07–7.02 (m, 80 H, PhH), 6.02–5.82 (m, 7 H, H-4^V, H-4^{IV}, H-4^{III}, H-4^{II}, H-4^I, H-3^V, H-3^{IV}), 5.75 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.0, H-2^V), 5.69 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.2 Hz, H-2^{IV}), 5.44–5.41 (m, 1 H, H-3^{III}), 5.33 (s, 2 H, H-1^V, H-2^{III}), 5.16 (s, 1 H, H-1^{IV}), 5.02 (s, 1 H, H-1^{III}), 4.95(d, 1 H, $J_{1,2}$ 1.5 Hz, H-1^{II}), 4.91 (s, 1 H, H-1^I), 4.71–4.66 (m, 1 H), 4.63–4.57 (m, 3 H), 4.54–4.51 (m, 1 H), 4.49–4.45 (m, 1 H), 4.40 (m, 1 H), 4.33–4.26 (m, 3 H), 4.19–4.00 (m, 8 H), 3.92 (m, 1 H), 3.44 (s, 3 H, CH_3O); ^{13}C NMR ($CDCl_3$): δ 166.13, 166.05, 166.05, 165.98, 165.91, 165.64, 165.62, 165.38, 165.19, 165.12, 165.01, 164.98, 164.94, 164.94, 164.72, 164.67 (16 Ph), 133.75, 133.57, 133.55, 133.38, 133.34, 133.22, 133.18, 133.09, 133.07, 132.98, 132.88, 132.84, 132.68, 129.99, 129.95, 129.86, 129.84, 129.80, 129.79, 129.76, 129.71, 129.65, 129.61, 129.57, 129.50, 129.30, 129.19, 129.14, 129.07, 129.05, 129.02, 128.98, 128.88, 128.83, 128.61, 128.57, 128.54, 128.51, 128.49, 128.39, 128.35, 128.32, 128.29, 128.27, 128.21, 128.18, 128.06 (16 Ph), 100.48, 100.10, 99.53, 99.35, 98.55 (C-1), 77.24, 76.65 (C-3), 76.11, 75.02, 71.77, 71.50, 71.12, 70.49, 70.02, 69.74, 69.67, 69.47, 69.42, 69.16, 68.70, 68.40, 68.19, 66.64, 66.42, 66.34, 62.96, 62.60, 62.41, 62.25 (C-2, 3, 4, 5, 6), 55.45 (CH_3O). Anal. Calcd for $C_{143}H_{118}O_{42}$: C, 68.48; H, 4.71. Found: C, 68.69; H, 4.69.

Methyl α-D-*mannopyranosyl-(1→2)*-α-D-*mannopyranosyl-(1→3)*-α-D-*mannopyranosyl-(1→3)*-α-D-*mannopyranoside* (**23**).—Compound **22** (0.23 g, 0.12 mmol) was dissolved in a satd solution of NH_3 in anhyd CH_3OH (10 mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **23** as a syrup (75 mg, 90%): $[\alpha]_D^{20}$ +6.0° (*c* 0.9, $CHCl_3$); ^1H NMR (D_2O): δ 5.25 (s, 1 H, H-1^{IV}), 4.96 (s, 1 H, H-1^{III}), 4.92 (s, 1 H, H-1^{II}), 4.61 (s, 1 H, H-1^I), 4.09 (m, 1 H), 3.97–3.94 (d, 3 H), 3.88–3.85 (m, 2 H), 3.80–3.70 (m, 7 H), 3.66–3.50 (m, 12 H), 3.28 (s, 3 H, CH_3); ^{13}C NMR (D_2O): δ 104.86, 104.81, 103.32, 103.27 (C-1), 80.99, 76.04, 75.79, 72.90, 72.54, 72.12, 68.64, 63.49, 63.40, 57.32 (CH_3). MALDI-TOFMS Calcd for $C_{25}H_{44}O_{21}$: [M] 680.2, Found: [M + Na] 703.6.

Methyl α-D-*mannopyranosyl-(1→2)*-α-D-*mannopyranosyl-(1→2)*-α-D-*mannopyranosyl-(1→3)*-α-D-*mannopyranosyl-(1→3)*-α-D-*mannopyranoside* (**25**).—Compound **24** (0.10 g, 0.04 mmol) was dissolved in a satd solution of NH_3 in anhyd CH_3OH (5 mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **25** as a syrup (31 mg, 90%): $[\alpha]_D^{20}$ +47.1° (*c* 0.8, $CHCl_3$); ^1H NMR (D_2O): δ 5.25 (s, 1 H, H-1^V), 5.18 (s, 1 H, H-1^{IV}), 4.96 (s, 1 H, H-1^{III}), 4.92 (s, 1 H, H-1^{II}), 4.62 (s, 1 H, H-1^I), 4.09 (m, 1 H), 3.98–3.95 (d, 4 H), 3.87–3.72 (m, 14 H), 3.66–3.48 (m, 18 H), 3.28 (s, 3 H, CH_3); ^{13}C NMR (D_2O): δ 104.82, 104.82, 103.36, 103.26, 103.26 (C-1), 81.22, 81.12, 80.97, 80.91, 76.06, 75.83, 75.29, 74.33, 72.94, 72.58, 72.25, 72.16, 69.66, 69.48, 69.41, 68.67, 63.64, 63.52, 63.44, 57.37 (CH_3). MALDI-TOFMS Calcd for $C_{31}H_{54}O_{26}$: [M] 842.3, Found: [M + Na] 865.6.

Acknowledgements

This work was supported by The Chinese Academy of Sciences (KIP-RCEES9904), by The National Natural Science Foundation of China (Projects 39970864 and 30070815), and by The Ministry of Science and Technology.

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