ELSEVIER

www.elsevier.nl/locate/carres

Carbohydrate Research 332 (2001) 1–21

CARBOHYDRATE RESEARCH

A facile and effective synthesis of α-(1→6)-linked mannose di-, tri-, tetra-, hexa-, octa-, and dodecasaccharides, and β-(1→6)-linked glucose di-, tri-, tetra-, hexa-, and octasaccharides using sugar trichloroacetimidates as the donors and unprotected or partially protected glycosides as the acceptors

Yuliang Zhu, Fanzuo Kong*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Academia Sinica, PO Box 2871, Beijing 100085, People's Republic of China

Received 15 December 2000; accepted 28 February 2001

Abstract

Reaction of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl trichloroimidate with allyl α-D-mannopyranoside in the presence of TMSOTf selectively gave allyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside through an orthoester intermediate. Benzoylation of **3**, followed by deallylation, and then trichloroimidation afforded the disaccharide donor 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroimidate, while benzoylation of **3** followed by selective removal of acetyl groups yielded the disaccharide acceptor allyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside. Coupling of **5** with **6** gave the tetrasaccharide allyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside, which were converted into the tetrasaccharide donor 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroimdate and the tetrasaccharide acceptor allyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside, respectively, by the same strategies as used for conversion of **3** into **5** and **6**. Condensation of **5** with **13** gave the hexasaccharide **14**, while condensation of **12** with **13** gave the octasaccharide **17**. Dodecasaccharide **21** was obtained by the coupling of **12** with the octasaccharide acceptor **20**. Similar strategies were used for the syntheses of β-(1→6)-linked glucose di-, tri-, tetra-, hexa-, and octamers. Deprotection of the oligosaccharides in ammonia-saturated methanol yielded the free α-(1→6)-linked mannosyl and β-(1→6)-linked glucosyl oligomers.

Keywords: Oligosaccharides; Trichloroimidates; Regio- and stereoselective synthesis

1. Introduction

Great effort has been contributed to the development of new strategies for glycosidic coupling owing to the growing importance of

* Corresponding author. Tel.: +86-10-62936613; fax: 86-10-62923563.

E-mail address: fzkong@mail.rcees.ac.cn (F. Kong).

0008-6215/01/$ - see front matter
PII: S0008-6215(01)00070-2

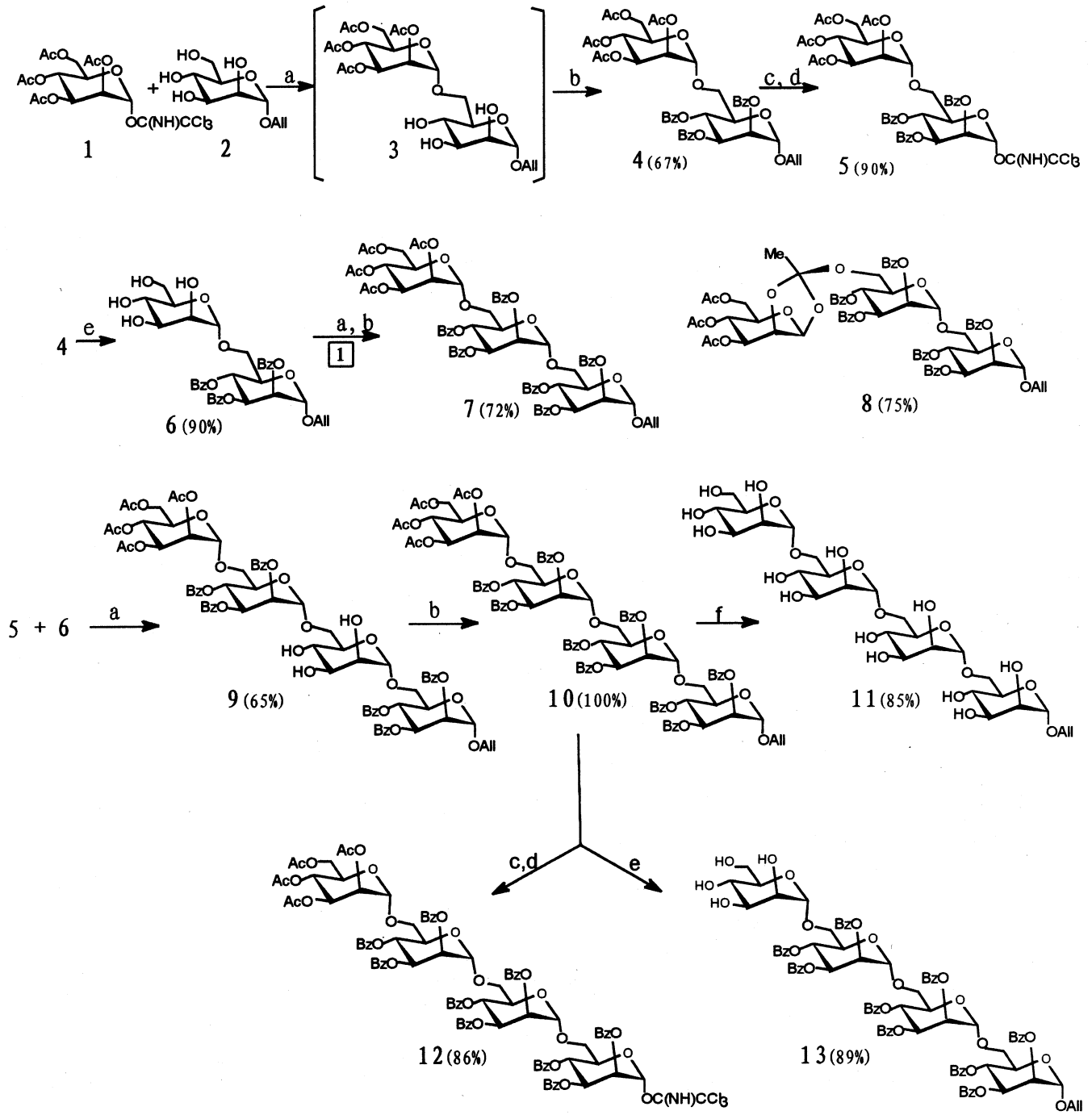
synthetic oligosaccharides in glycobiology.[1] In the past decades, there has been considerable progress[2] in the methods for construction of glycosidic linkages. However, compared to the synthesis of oligopeptides and oligonucleotides, the synthesis of oligosaccharides is still laborious work. The use of unprotected or partially protected sugars in glycosidic coupling is of particular interest since synthetic routes can be substantially simplified[3] to readily afford biologically important compounds. Our previous papers have described[3a–d] a new method for regio- and stereoselective synthesis of oligosaccharides via orthoester[4a–i] formation–rearrangement using unprotected or partially protected glycopyranosides as the glycosyl acceptors and acetylated glycosyl bromides as the donors. This method gave (1→6)-linked oligosaccharides in satisfactory yields. It was found, however, that careful separation and purification of the orthoesters was needed for the further rearrangement. To simplify the process we tried the glycosylation in a new way[5] by which the orthoesters that initially formed rearranged to the required glycosides in situ. This one-pot, two-step reaction ensured the high regioseletivity of glycosylation as it comes from the high regioselectivity of orthoester formation. No separation and purification of the orthoesters was needed, which simplified the glycosylation substantially and made the preparation of biologically important molecules possible in large scale. Herein we present this one-pot reaction in detail for the synthesis of α-(1→6)-linked mannooligosaccharides and β-(1→6)-linked glucooligosaccharides using unprotected or partially protected glycopyranosides as the glycosyl acceptors and sugar trichloroacetimidates as the glycosyl donors.

2. Results and discussion

α-(1→6)-Linked mannooligosaccharides occur in the cell-wall polysaccharides of yeast,[6] while β-(1→6)-linked glucooligosaccharides, known as gentiooligosaccharides, are found in lichens[7] and can be used as a bifidus factor to promote animal growth. Stepwise synthesis of β-(1→6)-linked galactooligosacchrides has been reported using 2,3,4-tri-*O*-benzoyl-6-*O*-bromoacetyl-α-D-galactopyranosyl chloride[8] or 6-*O*-acetyl-2-*O*-benzoyl-3,4-di-*O*-benzyl-α-D-galactopyranosyl tosylate[9] as the glycosyl donor and protected galactose derivatives with only six-free OH as the acceptors. In contrast to the synthesis of galactooligosaccharides, little attention[10] has been paid to the synthesis of α-(1→6)-linked mannooligosaccharides and β-(1→6)-linked glucooligosaccharides. The glycosyl imidate donors, initially proposed by Sinaÿ[11] and developed a few years later by Schmidt,[12] are by far one of the most convenient intermediates in oligosaccharide synthesis. It was found that orthoesters were the intermediates in the glycosylation with imidates as the donors. Conversion of the orthoesters to the corresponding glycosides can be achieved by simply extending the glycosylation time.[13a] Our experiment using a partially protected glycoside as the acceptor and a trichloroacetimidate as the donor also gave an orthoester as the intermediate, which was transformed to the corresponding glycoside by addition of extra catalyst or extension of the reaction time.[13b] Thus we assumed that glycosyl imidates will be good donors for the one-pot, two-step glycosylation. A concise and efficient synthesis of α-(1→6)-linked mannose di-, tri-, tetra-, hexa-, octa-, and dodecasaccharides and β-(1→6)-linked glucose di-, tri-, tetra-, hexa-, and octasaccharides indicated that this is indeed an excellent method for construction of (1→6)-linked manno- and glucooligosaccharides.

Scheme 1 outlines the synthesis of α-(1→6)-linked mannosyl tetrasaccharide. Allyl α-D-mannopyranoside[14] was chosen as the starting acceptor since its coupling product can be converted easily to either a new donor **5** or a new acceptor **6** by simple chemical transformation. Thus condensation of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl trichloroacetimidate[2d] (**1**) with allyl α-D-mannopyranoside (**2**) in DMF promoted by TMSOTf afforded allyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (**3**), and the crude **3** was benzoylated in situ with benzoyl chloride in pyridine to give allyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (**4**) in a satisfactory yield (67% for two steps). It

was noted that the reaction temperature at addition of TMSOTf was maintained below −40 °C to ensure orthoester formation with good regioselectivity; then it was gradually raised to ambient temperature. The (1→6) linkage in **4** was unambiguously verified from its ^{1}H NMR spectrum in which the resonance for H-2, -4, and -3 and H-2′, -3′, and -4′, were moved to a downfield position by either a benzoate or an acetate group, to give resonance at δ 5.92, 5.91, 5.41, 5.72, 5.33, and 5.27, respectively. Deallylation of **4** with $PdCl_2$ in CH_3COOH–CH_3CONa, followed by reaction with CCl_3CN in the presence of DBU, fur-



Scheme 1. Conditions and reagents: (a) TMSOTf, CH_2Cl_2 (DMF), 4 Å MS, −42 °C to rt, 3 h; (b) BzCl–pyridine (dry); (c) $PdCl_2$, CH_3COOH–CH_3CONa, rt, 12 h; (d) CCl_3CN, CH_2Cl_2, DBU, rt, 2 h; (e) CH_3COCl–CH_3OH, rt; (f) MeOH, NH_3, rt, 2–5 days or MeOH–MeONa rt.

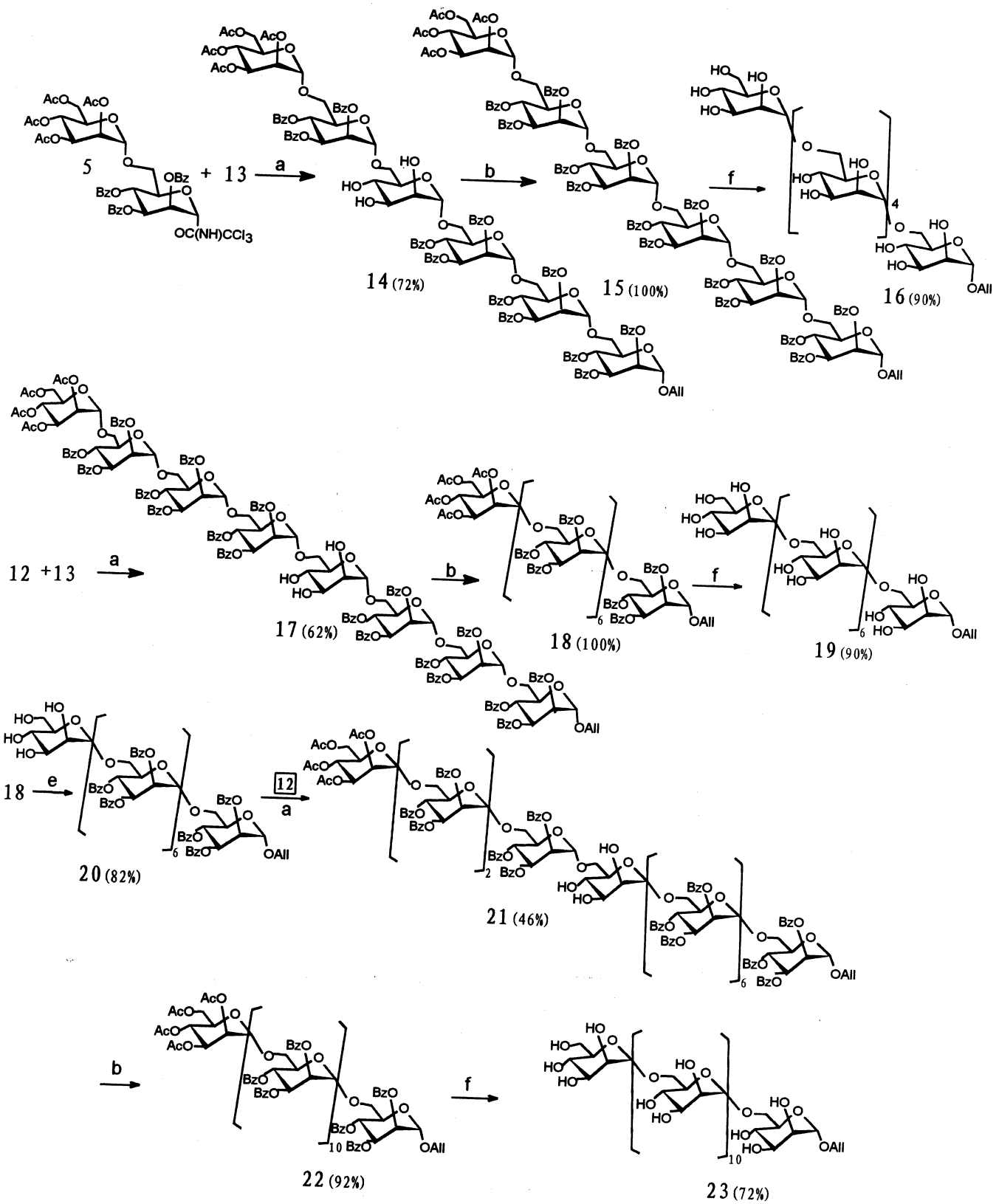
nished the disaccharide donor 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**5**) in a good yield (90%), while selective deacetylation of **4** with acetyl chloride in methanol[15] furnished the disaccharide acceptor α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (**6**) smoothly (93%). As **6** was more soluble in organic solvents than **2**, coupling of **1** with **6** was carried out in dichloromethane instead of DMF. Otherwise the conditions were the same as described for the condensation of **1** with **2**. Benzoylation of the product gave the trisaccharide 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (**7**) in a satisfactory yield (72% for two steps). It was found that the orthoester formed at the initial stage (within 30 min) of the coupling reaction could be benzoylated and isolated to give the orthoester **8**. The ^{1}H NMR spectrum of **8** gave a characteristic peak at δ 1.60 for the orthoester, and **8** was transformed easily to the corresponding trisaccharide **7** in the presence of a catalytic amount of TMSOTf. Similarly, condensation of **5** and **6** furnished the tetrasaccharide **9** in a good yield (65%). Benzoylation of **9** gave **10** in quantitative yield, and the 2D ^{1}H NMR spectrum of **10** gave a clear indication of (1→6) linkages as the 12 signals for H-2, -3, and -4 of the four mannose residues were found at δ 6.19–5.20. The ^{13}C NMR spectrum of **10** also indicated (1→6) linkages as all of the C-2, -3, -4, and -5 signals were at <73 ppm. Deprotection of tetrasaccharide **10** in methanol saturated with ammonia gave allyl α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (**11**). Tetrasaccharide **10** was transformed readily to the tetrasaccharide donor **12** by deallylation with palladium chloride in CH_3COOH–CH_3COONa, followed by reaction with trichloroacetonitrile (86% for two steps). Meanwhile the tetrasaccharide acceptor **13** was smoothly prepared (89%) by selective deacetylation of **10** with acetyl chloride–methanol.

Scheme 2 shows the synthesis of higher oligosaccharides. Coupling of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**5**) with the tetrasaccharide acceptor **13** furnished hexasaccharide **14** (72%), and benzoylation of **14** with benzoyl chloride in pyridine gave **15** in quantitative yield. Deprotection of **15** with ammonia-saturated methanol afforded unmasked hexasaccharide **16**. Condensation of the tetrasaccharide donor **12** with the tetrasaccharide acceptor **13** yielded the octasaccharide **17** (62%), and further benzoylation quantitatively gave the fully protected octasaccharide **18**. Serious overlapping resonances in the ^{1}H NMR spectrum of **18** made the assignment difficult, while the ^{13}C NMR of **18** still showed no signals at the region >71 ppm that would indicate (1→6) linkages. We were gratified to find that neither the coupling reaction nor the selective deacetylation presents any difficulties when the donor or acceptor oligosaccharide chain became longer. Unprotected octasaccharide **19** was readily obtained by deacylation of **18** in ammonia-saturated methanol. The octasaccharide acceptor **20** was prepared in a satisfactory yield (82%) by selective deacetylation of **18** under the same conditions as used for the preparation of tetrasaccharide acceptor **13** from **10**. Coupling of the acceptor **20** with the tetrasaccharide donor **12** gave the dodecasaccharide **21**. Subsequent benzoylation (→**22**) and then deprotection gave the unmasked dodecasaccharide **23**.

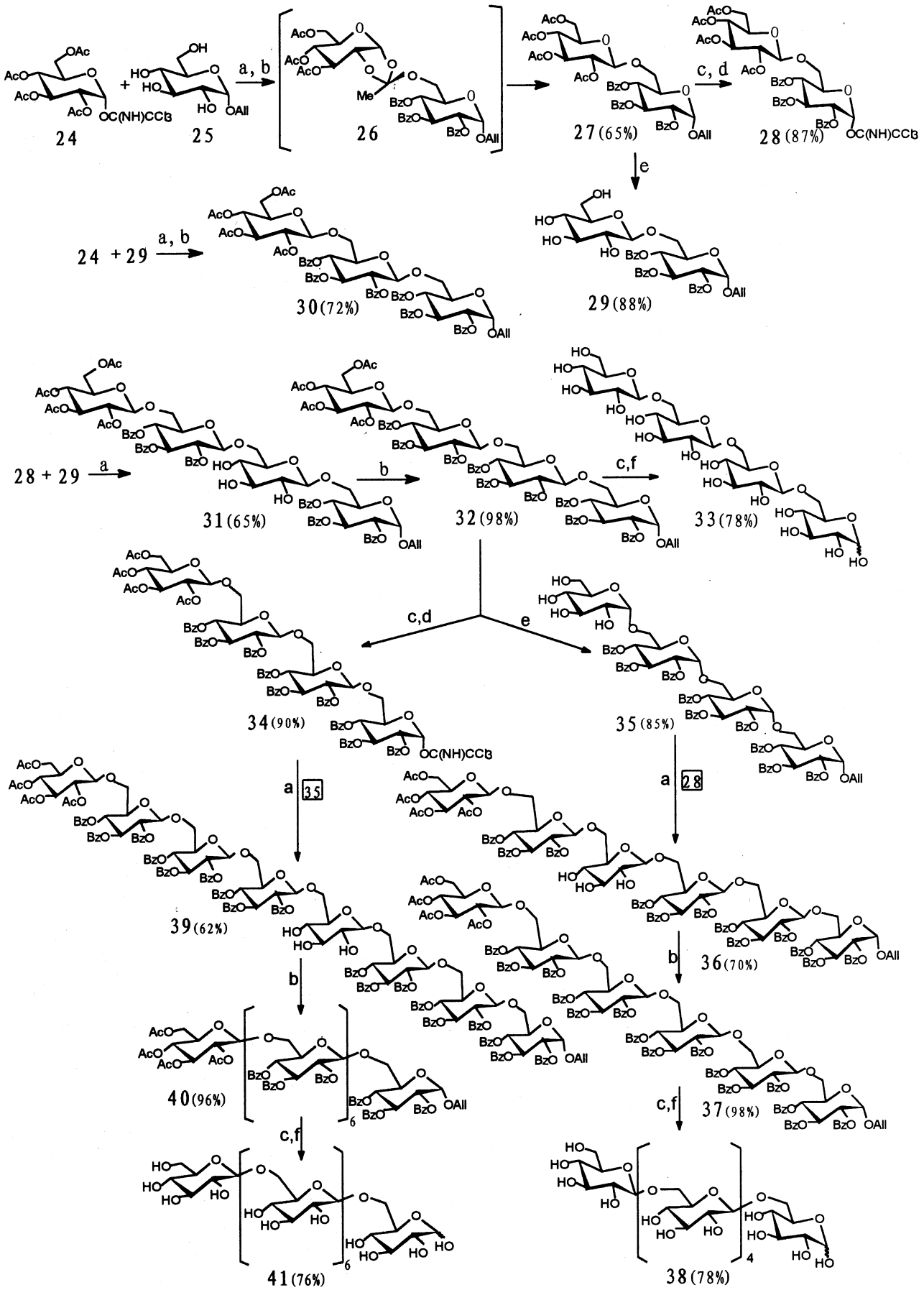
β-(1→6)-Linked glucose di-, tri-, tetra-, hexa- and octasaccharides were also successfully synthesized using the same strategy as described above. Orthoester **26**, obtained as the intermediate in the preparation of disaccharide **27**, was also isolated and characterized. Scheme 3 shows the syntheses of glucose oligosaccharides with the yields for each step.

It is noteworthy that almost all of the oligosacchairides described above were obtained as crystals or solids.

In summary, here we present a very effective method for the synthesis of α-(1→6)-linked mannose oligosaccharides and β-(1→6)-linked glucose oligosaccharides using sugar imidates as the glycosyl donors and unprotected or partially protected glycosides as the glycosyl acceptors.



Scheme 2. Conditions and reagents: (a) TMSOTf, CH_2Cl_2 (DMF), 4 Å MS, −42 °C to rt, 3 h; (b) BzCl–pyridine (dry); (c) $PdCl_2$, CH_3COOH–CH_3CONa, rt, 12 h; (d) CCl_3CN, CH_2Cl_2, DBU, rt, 2 h; (e) CH_3COCl–CH_3OH, rt; (f) MeOH, NH_3, rt, 2–5 days.



Scheme 3. Conditions and reagents: (a) TMSOTf, CH_2Cl_2 (DMF), 4 Å MS, −42 °C to rt, 3 h; (b) BzCl–pyridine (dry); (c) $PdCl_2$, CH_3COOH–CH_3CONa, rt, 12 h; (d) CCl_3CN, CH_2Cl_2, DBU, rt, 2 h; (e) CH_3COCl–CH_3OH, rt; (f) MeOH, NH_3, rt, 2–5 days.

3. 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 at 20 °C. ^{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 measured using MALTI-TOF–MS with CCA as matrix or recorded with a VG PLATFORM mass spectrometer using the ESI technique to introduce the sample. Thin-layer chromatography (TLC) was performed on silica gel HF, detection being effected by charring with 30% (v/v) H_2SO_4 in MeOH or sometimes 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) 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 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), and 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. Ethyl acetate–petroleum ether were used for crystallization and recrystallization.

Allyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**4**).—2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl trichloroacetimidate (**1**) (1970 mg, 4 mmol) and allyl α-D-mannopyranoside (**2**) (880 mg, 4 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd DMF (60 mL). TMSOTf (60 μL, 0.08 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N, and concentrated to dryness under reduced pressure to afford the crude allyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (**3**). To the solution of crude **3** in Py (20 mL) BzCl (1.4 mL, 12 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Ice water was added, and 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 (3:1 petroleum ether–EtOAc) gave **4** (2310 mg, 67% for two steps) as colorless crystals: mp 152–154 °C; $[\alpha]_D$ −14.2° (*c* 1.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.13–7.22 (m, 15 H, Bz–H), 6.02 (m, 1 H, CH_2=C*H*–CH_2–), 5.92–5.90 (m, 2 H, H-2, H-4), 5.72 (dd, 1 H, $J_{1,2}$ 1.6, $J_{2,3}$ 2.9 Hz, H-2^I), 5.47–5.40 (m, 2 H, CH_2=CH–CH_2, H-3), 5.33–5.29 (m, 2 H, CH_2=CH–CH_2, H-3^I), 5.27 (t, 1 H, $J_{3,4}$, $J_{4,5}$ 10.0 Hz, H-4^I), 5.13 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.86 (d, 1 H, H-1^I), 4.36–4.33 (m, 2 H), 4.20–4.10 (m, 2 H), 4.00–3.94 (m, 3 H), 3.68–3.65 (dd, 1 H), 2.12 (s, 3 H, CH_3CO), 2.05 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO), 1.94 (s, 3 H, CH_3CO). Anal. Calcd for $C_{44}H_{46}O_{18}$: C, 61.25; H, 5.34. Found: C, 61.38; H, 5.29.

2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**5**).—To a solution of allyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (**4**) (862 mg, 1 mmol) in 90% AcOH (10 mL) containing AcONa (293 mg, 3 mmol) was added $PdCl_2$ (89 mg, 0.5 mmol), and the mixture was stirred for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (30 mL), washed with water and satd aq $NaHCO_3$. The organic layer was concentrated under reduced pressure, and the residue thus obtained was passed through a short silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to give crude 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-D-mannopyranose (782 mg). The product was dissolved in CH_2Cl_2 (20 mL), and then CCl_3CN (0.2 mL, 2 mmol) and

DBU (27 μL, 0.18 mmol) were added. The reaction mixture was stirred for 2 h, 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 2:1 petroleum ether–EtOAc as the eluent furnished the disaccharide donor **5** as crystals in a good yield (869.9 mg, 90%): mp 150–153 °C; $[\alpha]_D$ −11.3° (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.62 (s, 1 H, C=N*H*), 8.14–7.26 (m, 15 H, Bz–H), 6.59 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1), 6.16–6.12 (m, 2 H), 5.86 (dd, 1 H, $J_{2,3}$ 2.8 Hz, H-2), 5.44 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.1 Hz, H-3^I), 5.36 (dd, 1 H, $J_{1,2}$ 1.7 Hz, H-2^I), 5.27 (t, 1 H, H-3^I), 4.85 (d, 1 H, H-1^I), 4.59–4.56 (m, 1 H), 4.15–4.06 (m, 2 H), 3.99–3.95 (m, 1 H), 3.90–3.84 (m, 1 H), 3.73–3.70 (m, 1 H), 2.13 (s, 3 H, CH_3CO), 2.08 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO), 1.91 (s, 3 H, CH_3CO). Anal. Calcd for $C_{43}H_{42}Cl_3NO_{18}$: C, 53.39; H, 4.35. Found: C, 53.14; H, 4.42.

Allyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**6**).—To a solution of allyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (**4**) (862 mg, 1 mmol) in anhyd MeOH (50 mL) was added AcCl (1.5 mL) at 0 °C. The solution was sealed in a flask and stirred for 10 h at rt, and then another portion of AcCl (1 mL) was added. The reaction was monitored by TLC (1:2 petroleum ether–EtOAc) until the starting material disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica-gel column to give crystalline **6** (625 mg, 90%), which was directly used for the next reaction: mp 159–162 °C; $[\alpha]_D$ −13.8° (*c* 2.3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.04–7.21 (m, 15 H, Bz–H), 6.00 (m, 1 H, CH_2=C*H*CH_2–), 5.95 (t, 1 H, $J_{3,4}$ 9.8 Hz, H-4), 5.88 (dd, 1 H, $J_{2,3}$ 3.1 Hz, H-3), 5.68 (s, 1 H, H-2), 5.42 (dd, 1 H, C*H*$_2$=CH–CH_2), 5.23 (dd, 1 H, C*H*$_2$=CH–CH_2), 5.08 (s, 1 H, H-1), 4.80 (s, 1 H, H-1^I), 4.30–4.28 (m, 2 H), 4.25–4.23 (m, 1 H), 3.92–3.45 (m, 8 H). Anal. Calcd for $C_{36}H_{38}O_{14}$: C, 62.25; H, 5.48. Found: C, 62.16; H, 5.53.

Allyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**7**).—2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl trichloroacetimidate (**1**, 493 mg, 1 mmol) and allyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (**6**, 694 mg, 1 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (60 mL). TMSOTf (15 μL, 0.08 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to give a syrupy residue. To the solution of the residue in Py (20 mL), BzCl (0.35 mL, 3 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2, washed sequentially 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 **7** (962 mg, 72% for two steps) as a colorless solid: mp 144–147 °C; $[\alpha]_D$ −10.3° (*c* 1.5, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.19–7.26 (m, 30 H, Bz-H), 6.18 (t, 1 H, $J_{3,4}$ 10.1 Hz, H-4), 6.10–5.95 (m, 3 H, CH_2=C*H*–CH_2, H-3, H-3^I), 5.94 (t, 1 H, $J_{3,4}$ 10.1 Hz, H-4^I), 5.84 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 3.2 Hz, H-2), 5.77 (dd, 1 H, $J_{1,2}$ 1.6, $J_{2,3}$ 3.2 Hz, H-2^I), 5.50 (d, 1 H, C*H*$_2$=CH–CH_2), 5.34–5.31 (m, 2 H, CH_2=CH–CH_2, H-3^{II}), 5.22–5.18 (m, 2 H, H-4^{II}, H-2^{II}), 5.12 (s, 2 H, H-1, H-1^I), 4.57 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1^{II}), 4.50–4.39 (m, 2 H, H-6$_B$, H-6^I_B), 4.25–4.15 (m, 2 H, H-5, H-5^I), 4.15–4.03 (m, 2 H, H-6$_A$, H-6^I_A), 3.91–3.87 (m, 2 H, H-6$^{II}_B$, H-5^{II}), 3.76–3.73 (m, 2 H, H-6$^{II}_A$, CH_2=CH–C*H*$_2$), 3.31 (d, 1 H, CH_2=CH–C*H*$_2$), 2.10 (s, 3 H, CH_3CO), 2.05 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO), 1.92 (s, 3 H, CH_3CO). Anal. Calcd for $C_{71}H_{68}O_{26}$: C, 63.77; H, 5.09. Found: C, 63.63; H, 5.12.

Orthoester **8**.—2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl trichloroacetimidate (**1**) (493 mg, 1 mmol) and allyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (**6**) (694 mg, 1 mmol) were dried to-

gether under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (60 mL). TMSOTf (7.5 μL, 0.04 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 0.5 h. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure. The residue was dissolved in Py (20 mL), BzCl (0.35 mL, 3 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated under reduced pressure to dryness. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **8** (1002 mg, 75% for two steps) as a colorless solid: mp 139–142 °C; $[\alpha]_D$ −23.8° (*c* 2.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.17–7.25 (m, 30 H, Bz–H), 6.01 (m, 1 H, CH_2=C*H*–CH_2–), 6.00–5.91 (m, 4 H, H-4, H-4^{I}, H-3, H-1^{II}), 5.76 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.0 Hz, H-2), 5.70 (dd, 1 H, $J_{1,2}$ 1.8 Hz, H-2^{I}), 5.50 (d, 1 H, C*H*$_2$=CH–CH_2–), 5.32 (d, 1 H, C*H*$_2$=CH–CH_2–), 5.23–5.19 (m, 2 H, H-3^{I}, H-4^{II}), 5.17 (d, 1 H, H-1) 5.13 (d, 1 H, H-1^{I}), 5.10 (dd, 1 H, $J_{2,3}$ 2.9, $J_{3,4}$ 10.0 Hz, H-3^{II}), 4.51 (dd, 1 H, $J_{1,2}$ 1.6 Hz, H-2^{II}), 4.43–4.41 (m, 2 H, H-6$_B$, H-6$^{I}_B$), 4.24–4.06 (m, 5 H, H-5, H-5^{I}, H-6$_A$, H-6$^{I}_A$, H-6$^{II}_B$), 3.75 (dd, 1 H, CH_2=CH–C*H*$_2$), 3.60–3.57 (m, 3 H, H-5^{II}, H-6$^{II}_A$, CH_2=CH–C*H*$_2$), 2.04 (s, 3 H, CH_3CO), 2.02 (s, 3 H, CH_3CO), 1.92 (s, 3 H, CH_3CO), 1.60 (s, 3 H, orthester C*H*$_3$). Anal. Calcd for $C_{71}H_{68}O_{26}$: C, 63.77; H, 5.09. Found: C, 63.60; H, 5.11.

Preparation of **7** *by rearrangement of* **8**.—A solution of **8** (668 mg, 0.5 mmol) in anhyd CH_2Cl_2 (20 mL) was cooled to −5 to −10 °C, then TMSOTf (5 μL) was added under N_2 flow. The mixture was stirred at this temperature for about 90 min, then neutralized with Et_3N. After concentration under diminished pressure, the residue was subjected to column chromatography to give a product (601 mg, 90%) that was identical to **7**.

*Allyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-manno-pyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-manno-pyranoside* (**9**).—2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**5**) (483 mg, 0.5 mmol) and allyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (**6**) (347 mg, 0.5 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (60 mL). TMSOTf (10 μL, 0.10 equiv) was added dropwise at −42 °C with N_2 protection. The temperature was gradually raised to ambient temperature, and the reaction mixture was stirred totally for 3 h, at the end of which time TLC (1:1.5 petroleum ether–EtOAc) indicated that the reaction was complete. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to dryness. Purification by column chromatography (1:1.5 petroleum ether–EtOAc) gave **9** (487 mg, 65%) as a colorless solid: $[\alpha]_D$ −26.7° (*c* 1.3, $CHCl_3$). ^{13}C NMR ($CDCl_3$). δ 170.53, 170.35, 170.10, 169.74, (4 CH_3*C*O), 166.01, 165.56, 165.48, 165.44, 165.36, 165.31, (6C_6H_5*C*O), 99.75, 97.08, 96.92, 96.71, (C-1$^{I–IV}$), 72.22, 71.02, 70.73, 70.55, 70.45, 69.88, 69.57, 69.49, 69.30, 69.21, 68.82, 68.63, 68.38, 67.14, 66.64, 66.46, 66.31, 65.87, 65.22, 62.26, (C-2,3,4,5,6$^{I–IV}$): ^1H NMR δ 8.12–7.23 (m, 30 H, Bz–H), 6.26 (t, 1 H, $J_{3,4}$ 10.1 Hz, H-4^{II} or H-4), 5.99 (m, 1 H, CH_2=C*H*–CH_2–), 5.92 (dd, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 10.1 Hz, H-3^{II}, or H-3), 5.78–5.76 (m, 2 H), 5.73 (dd, 1 H, $J_{2,3}$ 2.8, $J_{1,2}$ 1.6 Hz, H-2^{II}, or H-2), 5.41–5.36 (m, 2 H), 5.31 (dd, 1 H, *J* 2.7, *J* 1.3 Hz), 5.27–5.24 (m, 3 H), 5.18 (d, 1 H, *J* 1.6 Hz), 5.06 (s, 1 H), 4.83 (d, 1 H, *J* 1.3 Hz), 4.74 (d, 1 H, *J* 1.3 Hz), (H-1, H-1^{I}, H-1^{II}, H-1^{III}), 4.48 (d, 1 H), 4.39–4.32 (m, 2 H), 4.16–4.10 (m, 5 H), 4.00–3.97(m, 2 H), 3.91–3.85 (m, 2 H), 3.79–3.60 (m, 5 H), 2.11 (s, 3 H, CH_3CO), 2.03 (s, 3 H, CH_3CO), 1.99 (s, 3 H, CH_3CO), 1.95 (s, 3 H, CH_3CO). Anal. Calcd for $C_{77}H_{78}O_{31}$: C, 61.68; H, 5.21. Found: C, 61.53; H, 5.26.

*Allyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-manno-pyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside* (**10**).—To a solution of **9** (300 mg, 0.2 mmol) in Py (10 mL), BzCl (0.1 mL, 0.86 mmol) was added dropwise, and the mixture was stirred overnight at rt. 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 **10** quantitatively as a colorless solid: mp 143–146 °C; $[\alpha]_D$ −16.9° (*c* 1.3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.17–7.25 (m, 45 H, Bz–H), 6.18 (t, 1 H, *J* 9.7 Hz), 6.10 (t, 1 H, *J* 9.6 Hz), 6.09–6.05 (m, 2 H), 6.04–5.96 (m, 2 H), 5.94 (dd, 1 H, *J* 9.6, *J* 3.0 Hz), 5.88 (dd, 1 H, *J* 1.5, *J* 3.0 Hz), 5.79 (dd, 1 H, *J* 1.7, *J* 3.2 Hz), 5.63 (dd, 1 H, *J* 1.6, *J* 2.8 Hz), 5.46 (d, 1 H, C*H*$_2$=CH–CH$_2$), 5.36 (dd, 1 H, *J* 3.2, *J* 10.2 Hz), 5.28 (d, 1 H, C*H*$_2$=CH–CH$_2$), 5.25–5.21 (m, 2 H), 5.20 (s, 1 H) 4.84 (s, 1 H), 4.65 (d, 1 H, *J* 1.4 Hz, H-1^{III}), 4.58–4.52 (m, 1 H), 4.49–4.42 (m, 1 H), 4.37–4.32 (m, 1 H), 4.28–4.22 (m, 2 H), 4.18–4.14 (m, 1 H), 4.06–4.01 (m, 1 H), 3.97–3.92 (m, 1 H), 3.86–3.75 (m, 4 H), 3.74–3.71 (m, 1 H),3.45 (d, 1 H), 3.34 (d, 1 H), 2.10 (s, 3 H, CH_3CO), 2.04 (s, 3 H, CH_3CO), 1.98 (s, 3 H, CH_3CO), 1.90 (s, 3 H, CH_3CO). Anal. Calcd for $C_{98}H_{90}O_{34}$: C, 64.97; H, 4.97. Found: C, 64.93; H, 5.01.

Allyl α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (**11**).—To the solution of **10** (181 mg, 0.1 mmol) in CH_3OH (10 mL) was added dropwise CH_3ONa (0.1 mL, 0.1 mmol), and the mixture was stirred at rt for 12 h, at the end of which time the reaction was complete as indicated by TLC (2:1 MeOH–EtOAc). The solution was neutralized with Amberlite-120 (H^+), and concentrated to give **11** (63.5 mg, 90%) as a colorless solid: $[\alpha]_D$ −46.9° (*c* 1.1, water). ^{13}C NMR (D_2O): δ 100.85, 100.60, 100.38, 97.27 (C-1$^{I–IV}$), 73.76, 73.51, 73.33, 72.71, 71.22, 71.06, 70.87, 70.51, 69.04, 68.46, 67.48, 67.17, 66.63, 66.39, 66.17, 58.61 (C-2,3,4,5,6$^{I–IV}$, some signals overlapped): ^1H NMR (D_2O): δ 6.03–5.98 (m, 1 H, CH$_2$=C*H*–CH$_2$), 5.39–5.28 (m, 2 H, C*H*$_2$=CH–CH$_2$), 4.91–4.89 (4 H, H-1, H-1^{I}, H-1^{II}, H-1^{III}), 4.21–3.66 (m, 26 H). Anal. Calcd for $C_{27}H_{46}O_{21}$: C, 45.89; H, 6.52. Found: C, 45.92; H, 6.51.

2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**12**).—To a solution of allyl **10** (905 mg, 0.5 mmol) in 90% AcOH (10 mL) containing AcONa (293 mg, 3 mmol) was added $PdCl_2$ (89 mg, 0.5 mmol), and the mixture was stirred for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (30 mL), washed with water and satd aq $NaHCO_3$. The organic layer was concentrated under reduced pressure, and the residue thus obtained was passed a short silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give crude 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-D-mannopyranose (883 mg), which was dissolved in CH_2Cl_2 (20 mL), then CCl_3CN (0.1 mL, 2 mmol) and DBU (14 μL, 0.18 mmol) were added. The reaction mixture was stirred for 2 h, 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 2:1 petroleum ether–EtOAc as the eluent furnished the tetrasaccharide donor **12** as crystals in a good yield (823 mg, 86%): mp 136–139 °C; $[\alpha]_D$ −26.2° (*c* 1.4, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 9.00 (s, 1 H, C=N–H), 8.14–7.25 (m, 45 H, Bz–H), 6.62 (s, 1 H, H-1), 6.34 (t, 1 H, *J* 9.8 Hz, H-4), 6.05–5.89 (m, 5 H), 5.87–5.85 (m, 2 H), 5.49 (dd, 1 H, *J* 1.7, *J* 3.1 Hz), 5.37 (dd, 1 H, *J* 10.1, *J* 3.4 Hz), 5.27 (dd, 1 H, *J* 1.6, *J* 3.4 Hz), 5.23 (t, 1 H, *J* 10.0 Hz), 5.18 (d, 1 H, *J* 1.3 Hz), 4.80 (d, 1 H, *J* 1.3 Hz), 4.73–4.70 (m, 1 H), 4.67 (d, 1 H, *J* 1.4 Hz, H-1^{III}), 4.35–4.28 (m, 2 H), 4.15–4.11 (m, 1 H), 4.02–4.00 (m, 1 H), 3.92–3.90 (m, 2 H), 3.86–3.74 (m, 3 H), 3.39–3.35 (m, 2 H), 2.10 (s, 3 H, CH_3CO), 2.04 (s, 3 H, CH_3CO), 1.98 (s, 3 H, CH_3CO), 1.88 (s, 3 H, CH_3CO). Anal. Calcd for $C_{97}H_{86}Cl_3NO_{34}$: C, 60.80; H, 4.49. Found: C, 60.75; H, 4.52.

Allyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**13**).—To a solution of **10** (905

mg, 0.5 mmol) in anhyd MeOH (50 mL) was added AcCl (1.5 mL) at 0 °C. The solution was sealed in a flask and stirred for 10 h at rt, and then another portion of AcCl (1 mL) was added. The reaction was monitored by TLC (1:2 petroleum ether–EtOAc) until the starting material disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica-gel column to give crystalline **13** (731 mg, 89%) which was directly used for the next reaction: mp 145–148 °C; $[\alpha]_D$ −16.9° (*c* 1.4, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.14–7.25 (m, 45 H, Bz–H), 6.26 (t, 1 H, *J* 10.0 Hz), 6.06–6.94 (m, 5 H), 5.90 (dd, 1 H, *J* 1.4, *J* 3.3 Hz), 5.85 (dd, 1 H, *J* 2.8, *J* 10.1 Hz), 5.79 (dd, 1 H, *J* 1.6, *J* 3.3 Hz), 5.51 (dd, 1 H, *J* 1.7, *J* 2.9 Hz), 5.42 (d, 1 H, C*H*$_2$=CH–CH$_2$), 5.24 (d, 1 H, C*H*$_2$=CH–CH$_2$), 5.22 (d, 1 H, *J* 1.4 Hz), 5.20 (d, 1 H, *J* 1.6 Hz), 4.76 (d, 1 H, *J* 1.7 Hz), (H-1, H-1^I, H-1^{II}), 4.74 (d, 1 H, *J* 1.5 Hz, H-1^{III}), 4.53–4.57 (m, 1 H), 4.40–4.47 (dd, 1 H), 4.29–4.15 (m, 5 H), 3.92–3.83 (m, 5 H), 3.69–3.63 (m, 2 H), 3.47–3.34 (m, 3 H). Anal. Calcd for $C_{90}H_{82}O_{30}$: C, 65.77; H, 4.99. Found: C, 65.90; H, 5.04.

*Allyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**14**).—2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**5**) (97 mg, 0.1 mmol) and the tetrasaccharide acceptor **13** (164 mg, 0.1 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL). TMSOTf (2 μL, 0.10 equiv) was added dropwise at −42 °C with N_2 protection. The temperature of the reaction was gradually raised to ambient temperature, and the mixture was stirred for a total of 3 h, at the end of which time TLC (1:1.5 petroleum ether–EtOAc) indicated that the reaction was complete. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to dryness. Purification by column chromatography (1:1.5 petroleum ether–EtOAc) gave **14** (176 mg, 72%) as a colorless solid: $[\alpha]_D$ −4.6° (*c* 0.8, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.07–7.20 (m, 60 H, Bz–H), 6.30 (t, 1 H, *J* 9.7 Hz), 6.09–6.06 (m, 2 H), 6.00–5.95 (m, 2 H), 5.92–5.88 (m, 2 H), 5.81–5.78 (m, 4 H), 5.53 (dd, 1 H, *J* 1.4, *J* 2.8 Hz), 5.45 (dd, 1 H, *J* 1.5, *J* 2.9 Hz), 5.40–5.38 (m, 2 H), 5.27–5.22 (m, 3 H), 5.21 (s, 1 H), 5.19 (s, 1 H), 4.89 (s, 1 H), 4.84 (s, 1 H), 4.82 (s, 1 H), 4.77 (s, 1 H), (H-1, H-1^I, H-1^{II}, H-1^{III}, H-1^{IV}, H-1^V), 4.59–4.53 (m, 1 H), 4.42–4.33 (m, 3 H), 4.30–4.17 (m, 4 H), 4.13–4.08 (m, 2 H), 4.05–3.86 (m, 7 H), 3.62–3.55 (m, 5 H), 3.50 (d, 1 H), 2.11 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO), 1.96 (s, 3 H, CH_3CO), 1.94 (s, 3 H, CH_3CO). Anal. Calcd for $C_{131}H_{122}O_{47}$: C, 64.27; H, 4.99. Found: C, 64.03; H, 5.01.

*Allyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-*D*-mannopyranoside* (**15**).—To a solution of **14** (122 mg, 0.05 mmol) in Py (5 mL), BzCl (0.1 mL, 18 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (1.5:1 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 layers were combined, dried, and concentrated. Purification by column chromatography (1.5:1 petroleum ether–EtOAc) gave **15** quantitatively as a colorless solid: $[\alpha]_D$ −6.3° (*c* 1.3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.16–7.20 (m, 75 H, Bz–H), 6.28 (t, 1 H, *J* 9.8 Hz), 6.14–6.07 (m, 4 H), 6.01–5.92 (m, 6 H), 5.79–5.68 (m, 4 H), 5.44–5.39 (m, 2 H), 5.29–5.21 (m, 4 H), 4.97 (s, 1 H), 4.95 (s, 1 H), 4.90 (s, 1 H), 4.89 (s, 1 H), 4.83 (s, 1 H), (H-1, H-1^I, H-1^{II}, H-1^{III}, H-1^{IV}), 4.63 (s, 1 H, H-1^V), 4.56–4.52 (m, 1 H), 4.41–4.21 (m, 6 H), 4.06–3.90 (m, 7 H), 3.87–3.76 (m, 2 H), 3.63–3.51 (m, 2 H), 3.38–3.36 (m, 1 H), 3.20–3.17 (m, 1 H), 2.11 (s, 3 H, CH_3CO), 2.09 (s, 3 H, CH_3CO), 1.92 (s, 3 H, CH_3CO), 1.89 (s, 3 H, CH_3CO). Anal. Calcd for $C_{152}H_{134}O_{50}$: C, 66.13; H, 4.86. Found: C, 66.37; H, 4.82.

Allyl α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyran-

osyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (**16**).—A satd solution of NH_3 in MeOH (5 mL) was added to a solution of **15** (83 mg, 30 μmol) in MeOH (4 mL). After 48 h at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **16** (28 mg, 90%) as a syrup: ^{1}H NMR (D_2O): δ 6.01–5.93 (m, 1 H, C*H*$_2$=CH–CH$_2$–), 5.37 (d, 1 H, C*H*$_2$=CH–CH$_2$), 5.33 (d, 1 H, C*H*$_2$=CHCH$_2$), 4.93–4.89 (6 H, H-1), 4.25–4.21 (dd, 1 H), 4.19–4.15 (dd, 1 H), 4.09–3.90 (m, 12 H), 3.85–3.69 (m, 24 H). Anal. Calcd for $C_{39}H_{66}O_{31}$: C, 45.44; H, 6.41. Found: C, 45.58; H, 6.37.

Allyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**17**).—The tetrasaccharide donor **12** (191 mg, 0.1 mmol) and the tetrasaccharide acceptor **13** (164 mg, 0.1 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL). TMSOTf (1.5 μL, 0.08 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the reaction temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to an oily residue. Purification by column chromatography (1:1.5 petroleum ether–EtOAc) gave **17** (210 mg, 62%) as a colorless solid: mp 138–140 °C; $[\alpha]_D$ −32.0° (*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.20–7.20 (m, 90 H, Bz–H), 6.33 (t, 1 H, *J* 10.1 Hz), 6.15–5.80 (m, 15 H), 5.62 (dd, 1 H, *J* 1.4, *J* 2.7 Hz), 5.56 (dd, 1 H, *J* 1.4, *J* 2.8 Hz), 5.53 (dd, 1 H, *J* 1.5, *J* 2.8 Hz), 5.42 (d, 1 H, C*H*$_2$=CH–CH$_2$–), 5.37 (dd, 1 H, *J* 10.1, *J* 3.0 Hz), 5.26–5.18 (m, 6 H), 5.17 (s, 1 H), 4.96 (s, 1 H), 4.84 (s, 1 H), 4.79 (s, 1 H), 4.62 (s, 1 H), 4.60–4.56 (m, 2 H), 4.38–3.72 (m, 24 H), 3.50 (m, 1 H), 3.42 (m, 1 H), 3.30 (m, 1 H), 2.10 (s, 3 H, CH_3CO), 2.04 (s, 3 H, CH_3CO), 1.98 (s, 3 H, CH_3CO), 1.89 (s, 3 H, CH_3CO). Anal. Calcd for $C_{185}H_{166}O_{63}$: C, 65.41; H, 4.89. Found: C, 65.24; H, 4.85.

Allyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**18**).—To a solution of **17** (119 mg, 0.035 mmol) in Py (5 mL), BzCl (0.1 mL, 24 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (1.5:1 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 (1.5:1 petroleum ether–EtOAc) gave **18** quantitatively as a colorless solid: $[\alpha]_D$ −14.1° (*c* 0.8, $CHCl_3$). ^{13}C NMR ($CDCl_3$): δ 170.40, 169.70, 169.69, 169.33, (4 CH_3CO), 165.76, 165.56, 165.51, 165.55, 165.43, 165.40, 165.35, 165.35, 165.31, 165.25, 165.22, 165.10, (21C_6H_5CO, some signals overlapped), 98.2, 98.1, 97.8, 97.7, 96.9, (C-1$^{I–VIII}$ some signals overlapped), 70.63, 70.47, 70.33, 70.17, 69.30, 69.14, 66.42, 65.64, 61.96, (C-2,3,4,5,6$^{I–VIII}$ some signals overlapped). ^{1}H NMR ($CDCl_3$): δ 8.08–7.25 (m, 105 H, Bz–H), 6.28–5.92 (m, 16 H), 5.85–5.65 (m, 7 H), 5.46–5.35 (m, 2 H), 5.28–5.19 (m, 6 H), 5.02 (s, 1 H), 4.97 (s, 1 H), 4.89 (s, 1 H), 4.65 (s, 1 H, H-1^{VII}), 4.57–3.16 (m, 26 H), 2.09 (s, 3 H, CH_3CO), 2.04 (s, 3 H, CH_3CO), 1.97 (s, 3 H, CH_3CO), 1.89 (s, 3 H, CH_3CO). Anal. Calcd for $C_{206}H_{178}O_{66}$: C, 66.70; H, 4.80. Found: C, 66.53; H, 4.83.

Allyl α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (**19**).—A satd solution of NH_3 in MeOH (5 mL) was added to a solution of **18** (74 mg, 20 μmol) in MeOH (4 mL). After 48 h at rt, the reaction mixture

was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **19** as a colorless solid (24.4 mg, 90%): ^{1}H NMR (D_2O): δ 6.05–5.97 (m, 1 H, CH_2=C*H*–CH_2–), 5.40 (d, 1 H, C*H*$_2$=CH–CH_2), 5.33 (d, 1 H, C*H*$_2$=CH–CH_2), 4.93–4.87 (8 H, H-1), 4.28–4.24 (dd, 1 H), 4.25–4.19 (dd, 2 H), 4.05–3.92 (m, 16 H), 3.90–3.67 (m, 31 H). Anal. Calcd for $C_{51}H_{86}O_{41}$: C, 45.20; H, 6.35. Found: C, 45.16; H, 6.40.

Allyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**20**).—To a solution of **18** (371 mg, 0.1 mmol) in anhyd MeOH (10 mL) was added AcCl (0.3 mL) at 0 °C. The solution was sealed in a flask and stirred for 10 h at rt, and then another portion of AcCl (0.2 mL) was added. The reaction was monitored by TLC (1:2 petroleum ether–EtOAc) until the starting material disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica-gel column to give crystalline **20** (290 mg, 82%) that was directly used for the next reaction: mp 143–146 °C; $[\alpha]_D$ −12.9° (*c* 1.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.06–7.24 (m, 105 H, Bz–H), 6.25–5.94 (m, 14 H), 5.82–5.64 (m, 7 H), 5.42–5.33 (m, 2 H), 5.30–5.21 (m, 5 H), 5.05 (s, 1 H), 5.00 (s, 1 H), 4.93 (s, 1 H), 4.69 (s, 1 H, H-1^{VII}), 4.60–3.12 (m, 29 H). Anal. Calcd for $C_{198}H_{170}O_{62}$: C, 66.16; H, 4.80. Found: C, 66.33; H, 4.83.

Allyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**21**).—The tetrasaccharide donor **12** (96 mg, 0.05 mmol) and the octasaccharide acceptor **20** (177 mg, 0.05 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (1.5 µL, 0.16 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the reaction temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to an oily residue. Purification by column chromatography (1:2 petroleum ether–EtOAc) gave **21** (122 mg, 46%) as a colorless solid: mp 122–125 °C; $[\alpha]_D$ −4.1° (*c* 0.9, $CHCl_3$). MALDI-TOF–MS Anal. Calcd for $C_{293}H_{254}O_{95}$: 5291.5 [M]. Found: 5314 [M + Na], 5330 [M + K]: ^{1}H NMR ($CDCl_3$): δ 8.16–7.22 (m, 150 H, Bz–H), 6.26–5.70 (m, 30 H), 5.40–5.21 (m, 8 H), 4.96–3.20 (m, 51 H), 2.15 (s, 3 H, CH_3CO), 2.10 (s, 3 H, CH_3CO), 1.98 (s, 3 H, CH_3CO), 1.89 (s, 3 H, CH_3CO). Anal. Calcd for $C_{293}H_{254}O_{95}$: C, 66.47; H, 4.80. Found: C, 66.64; H, 4.82.

Allyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (**22**).—To a solution of **21** (106 mg, 0.02 mmol) in Py (5 mL) BzCl (0.1 mL, 24 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (1.5:1 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 (1:1 petroleum

ether–EtOAc) gave **22** (103 mg, 92%) as a colorless solid: $[\alpha]_D$ −6.5° (*c* 0.6, $CHCl_3$). ^{13}C NMR ($CDCl_3$): δ 170.33, 169.80, 169.80, 169.47, (4 CH_3CO), 166.74, 166.34, 165.98, 165.86, 165.80, 165.79, 165.78, 165.76, 165.70, 165.68, 165.65, 165.63, 165.60, 165.59, 165.55, 165.52, 165.48, 165.45, 165.43, 165.40, 165.37, 165.35, 165.32, 165.31, 165.22, 165.10, (33C_6H_5CO, some signals overlapped), 98.37, 98.34, 98.29, 98.10, 98.03, 97.88, 97.46, 97.40, 97.33, (C-1^{I-XII} some signals overlapped), 70.64, 70.62, 70.61, 70.59, 70.55, 70.52, 70.44, 70.38, 70.33, 70.30, 70.24, 70.19, 69.97, 69.90, 69.84, 69.80, 69.70, 69.62, 69.59, 69.20, 69.11, 67.86, 67.80, 67.73, 67.65, 67.37, 67.19, 66.89, 66.73, 66.58, 66.50, 66.42, 66.29, 66.07, 65.78, 63.98, 63.80, 63.57, 63.29, 62.77, 62.37, 62.07, 61.73, 61.50, 61.40, (C-2,3,4,5,6^{I-XII} some signals overlapped); MALDI-TOF–MS Anal. Calcd for $C_{314}H_{266}O_{98}$: 5603.6 [M]. Found: 5601.8 [M]. ^1H NMR ($CDCl_3$): δ 8.16–7.22 (m, 165 H, Bz–H), 6.30–5.70 (m, 35 H), 5.42–5.22 (m, 6 H), 5.00–4.85 (m, 4 H), 4.70–3.30 (m, 44 H), 2.11 (s, 3 H, CH_3CO), 2.05 (s, 3 H, CH_3CO), 1.98 (s, 3 H, CH_3CO), 1.90 (s, 3 H, CH_3CO). Anal. Calcd for $C_{314}H_{266}O_{98}$: C, 66.26; H, 4.75. Found: C, 66.19; H, 4.82.

Allyl α-D-*mannopyranosyl-(1→6)-*α-D-*mannopyranosyl - (1→6) - α - D - mannopyranosyl - (1→6) - α - D - mannopyranosyl - (1→6)-α - D - mannopyranosyl - (1→6) - α - D - mannopyranosyl - (1→6) - α - D - mannopyranosyl - (1→6) - α - D - mannopyranosyl - (1→6) - α - D - mannopyranosyl - (1→6) - α - D - mannopyranosyl - (1→6) - α - D - mannopyranosyl - (1→6)-α-D-mannopyranoside* (**23**).—A satd solution of NH_3 in MeOH (5 mL) was added to a solution of **22** (112 mg, 20 μmol) in MeOH (4 mL). After 48 h at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **23** (29 mg, 72%) as a syrup: ^1H NMR (D_2O): δ 6.00–5.92 (m, 1 H, CH_2=C*H*–CH_2–), 5.38 (d, 1 H, CH_2=CH–CH_2), 5.32 (d, 1 H, CH_2=CH–CH_2), 4.88–4.82 (12 H, H-1), 4.30–4.26 (m, 2 H), 4.22–4.17 (m, 3 H), 3.98–3.80 (m, 25 H), 3.78–3.60 (m, 44 H). Anal. Calcd for $C_{75}H_{126}O_{61}$: C, 44.96; H, 6.29. Found: C, 44.92; H, 6.33.

Orthoester **26**.—2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl trichloroacetimidate (**24**) (1972 mg, 4 mmol) and allyl α-D-glucopyranoside (**25**) (880 mg, 4 mmol) were dried together under high vacuum for 0.5 h, then dissolved in anhyd DMF (60 mL). TMSOTf (30 μL, 0.04 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 0.5 h. Then the mixture was neutralized with Et_3N and concentrated under reduced pressure to dryness. To the solution of the residue in Py (20 mL), BzCl (1.4 mL, 12 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Then the mixture was concentrated under reduced pressure to dryness. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **26** (2414 mg, 70% for two steps) as a colorless solid: $[\alpha]_D$ +3.6° (*c* 1.4, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.98–7.26 (m, 15 H, Bz–H), 6.14 (t, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 10.0 Hz, H-3), 5.95–5.89 (m, 1 H, CH_2=C*H*–CH_2–), 5.74 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1^I), 5.55 (t, 1 H, H-4), 5.37–5.27 (m, 3 H, H-4^I, H-1, CH_2=CHCH_2–), 5.18 (dd, 1 H, CH_2=CH–CH_2–), 5.15 (dd, 1 H, $J_{1,2}$ 3.1 Hz, H-2), 4.89 (dd, 1 H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.5 Hz, H-3^I), 4.33 (dd, 1 H, H-2^I), 4.30–4.17 (m, 4 H), 4.10–4.06 (m, 1 H), 3.97–3.94 (m, 1 H), 3.69–3.67 (m, 2 H), 2.10 (s, 3 H, CH_3CO), 2.08 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO), 1.69 (s, 3 H, orthester CH_3). Anal. Calcd for $C_{44}H_{46}O_{18}$: C, 61.25; H, 5.34. Found: C, 61.52; H, 5.27.

*Allyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside* (**27**).—2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**24**) (1972 mg, 4 mmol) and allyl α-D-glucopyranoside (**25**) (880 mg, 4 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd DMF (60 mL). TMSOTf (60 μL, 0.08 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to afford crude allyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-α-D-glucopyranoside. To the solution of the crude product in Py (20 mL), BzCl (1.4 mL, 12 mmol) was

added dropwise, and the mixture was stirred overnight at rt. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (30 mL), washed with water and satd aq $NaHCO_3$. The organic layer was combined, dried, and concentrated. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **27** (2241 mg, 65% for two steps) as a colorless solid: mp 156–158 °C; $[\alpha]_D$ +24.1° (*c* 1.3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.98–7.26 (m, 15 H, Bz–H), 6.16 (t, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 9.8 Hz,, H-3), 5.85 (m, 1 H, CH_2=C*H*–CH_2–), 5.43 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 5.37–5.28 (m, 2 H, H-1, H-2), 5.26–5.17 (m, 3 H, C*H*$_2$=CH–CH_2, H-2^I, H-3^I), 5.08–5.05 (m, 2 H, C*H*$_2$=CH–CH_2, H-4^I), 4.57 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^I), 4.30–4.20 (m, 3 H), 4.08–4.03 (m, 3 H), 3.71–3.67 (m, 2 H), 2.10 (s, 3 H, CH_3CO), 2.04 (s, 9 H, 3CH_3CO). Anal. Calcd for $C_{44}H_{46}O_{18}$: C, 61.25; H, 5.34. Found: C, 61.20; H, 5.39.

Preparation of **27** *by rearrangement of* **26**.—A solution of **26** (862 mg, 1 mmol) in anhyd CH_2Cl_2 (20 mL) was cooled to −5 to −10 °C, then TMSOTf (5 μL) was added under N_2 flow. The mixture was stirred at this temperature for about 90 min, then neutralized with Et_3N. After concentration under diminished pressure, the residue was subjected to column chromatography to give a product (776 mg, 90%) that was identical to **27**.

2,3,4,6-Tetra-O-*acetyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-α*-D-*glucopyranosyl trichloroacetimidate* (**28**).—To a solution of allyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**27**) (862 mg, 1 mmol) in 90% AcOH (10 mL) containing AcONa (293 mg, 3 mmol) was added $PdCl_2$ (89 mg, 0.5 mmol), and the mixture was stirred for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (30 mL), washed with water and satd aq $NaHCO_3$. The organic layer was concentrated under reduced pressure, and the residue was passed through a short silica-gel column with 2:1 petroleum ether–EtOAc as the eluent. The obtained crude 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-D-glucopyranose (741 mg) was dissolved in CH_2Cl_2 (20 mL), then CCl_3CN (0.2 mL, 2 mmol) and DBU (27 μL, 0.18 mmol) were added. The reaction mixture was stirred for 2 h and the disaccharide donor **28** was obtained as crystals in a good yield (841 mg, 87% for two steps): mp 147–150 °C; $[\alpha]_D$ +1.5° (*c* 1.3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.60 (s, 1 H, C=N*H*), 8.14–7.26 (m, 15 H, Bz–H), 6.65 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 6.24 (t, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 9.8 Hz, H-3), 5.60 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 5.53 (dd, 1 H, H-2), 5.19 (t, $J_{2,3}$ 9.7, $J_{3,4}$ 9.7 Hz, H-3^I), 5.08–4.95 (m, 2 H, H-4^I, H-2^I), 4.60 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^I), 4.49–4.44 (m, 1 H), 4.25–4.20 (m, 2 H), 4.11–4.05 (m, 2 H), 3.67–3.64 (m, 1 H), 2.08 (s, 3 H, CH_3CO), 2.05 (s, 3 H, CH_3CO), 2.02 (s, 3 H, CH_3CO), 1.97 (s, 3 H, CH_3CO). Anal. Calcd for $C_{43}H_{42}Cl_3NO_{18}$ C, 53.39; H, 4.35. Found: C, 53.55; H, 4.39.

Allyl β-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-α*-D-*glucopyranoside* (**29**).—To a solution of allyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**27**) (862 mg, 1 mmol) in anhyd MeOH (50 mL) was added AcCl (1.5 mL) at 0 °C. The solution was sealed in a flask and stirred for 10 h at rt, and then another portion of AcCl (1 mL) was added. The reaction was monitored by TLC until the starting material disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica-gel column to give **29** (611 mg, 88%) that was directly used for the next reaction: mp 161–164 °C; $[\alpha]_D$ −18.0° (*c* 1.4, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.98–7.26 (m, 15 H, Bz–H), 6.20 (t, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 9.8 Hz, H-3), 5.90–5.80 (m, 2 H, H-4, CH_2=C*H*CH_2–), 5.41 (dd, 1 H, C*H*$_2$=CH–CH_2–), 5.36–5.30 (m, 2 H, H-2, H-1), 5.17–5.15 (dd, 1 H, C*H*$_2$=CH–CH_2–), 4.50 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^I), 4.49–4.18 (m, 3 H), 4.10–4.04 (m, 2 H), 3.92–3.78 (m, 2 H), 3.70–3.48 (m, 4 H). Anal. Calcd for $C_{36}H_{38}O_{14}$: C, 62.25; H, 5.48. Found: C, 62.36; H, 5.50.

Allyl 2,3,4,6-tetra-O-*acetyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-α*-D-*glucopyranoside* (**30**).—2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**24**)

(493 mg, 1 mmol) and allyl β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**29**) (694 mg, 1 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (60 mL). TMSOTf (15 μL, 0.08 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to an oily residue. To the solution of the residue in Py (20 mL) was added dropwise BzCl (0.35 mL, 3 mmol), and the mixture was stirred overnight at rt. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (30 mL), washed with water and satd aq $NaHCO_3$. The organic layer was combined, dried, and concentrated. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **30** (962 mg, 72% for two steps) as a colorless solid: $[\alpha]_D$ +1.9° (*c* 1.4, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.94–7.26 (m, 30 H, Bz–H), 6.07–5.86 (m, 3 H), 5.44–5.23 (m, 5 H), 5.14–4.89 (m, 5 H), 4.88 (d, 1 H, *J* 7.7 Hz), 4.67 (d, 1 H, *J* 7.9 Hz), 4.22–4.16 (m, 3 H), 4.11–3.99 (m, 3 H), 3.79–3.69 (m, 5 H), 2.05 (s, 3 H, CH_3CO), 2.04 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO), 1.97(s, 3 H, CH_3CO). Anal. Calcd for $C_{71}H_{68}O_{26}$: C, 63.77; H, 5.09. Found: C, 63.67; H, 5.12.

Allyl 2,3,4,6-tetra-O-*acetyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-α*-D-*glucopuranoside* (**31**).—2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (**28**) (483 mg, 0.5 mmol) and allyl β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**29**) (347 mg, 0.5 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (60 mL). TMSOTf (10 μL, 0.10 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (1:1.5 petroleum ether–EtOAc) gave **31** (487 mg, 65%) as a colorless solid: mp 151–152 °C; $[\alpha]_D$ +12.0° (*c* 1.3, $CHCl_3$). ^{13}C HMR ($CDCl_3$): δ 170.61, 170.55, 169.41, 169.41 (4 CH_3CO), 166.07, 165.77, 165.68, 165.68, 165.40, 165.38 (6 C_6H_5CO), 103.29, 101.75, 100.20, 97.30 (C-1^{I-IV}), 75.36, 75.33, 73.60, 73.11, 72.71, 71.89, 71.83, 71.69, 71.51, 70.49, 69.68, 69.53, 68.65, 68.51, 68.51, 67.89, 67.60, 67.30, 62.81, 61.93 (C-2,3,4,5,6^{I-IV}). ^1H NMR ($CDCl_3$): δ 7.99–7.26 (m, 30 H, Bz–H), 6.17 (t, 1 H, *J* 9.9 Hz), 5.92 (t, 1 H, *J* 9.7 Hz), 5.83 (m, 1 H, CH_2=C*H*–CH_2–), 5.78 (t, 1 H, *J* 9.9 Hz), 5.53 (dd, 1 H, *J* 8.1, *J* 9.8 Hz), 5.38–5.32 (m, 3 H), 5.28–5.23 (m, 3 H), 5.17–5.14 (dd, 1 H, CH_2=CH–CH_2), 5.07 (t, 1 H, *J* 8.1 Hz), 5.04 (d, 1 H, *J* 8.0 Hz), 5.02–4.95 (m, 2 H), 4.26–4.17 (m, 4 H), 4.09–4.01 (m, 3 H), 3.97–3.87 (m, 2 H), 3.86–3.72 (m, 2 H), 3.71–3.66 (m, 1 H), 3.60–3.55 (m, 2 H), 3.53–3.45 (m, 1 H), 3.43 (t, 1 H, *J* 8.5 Hz), 3.39–3.37 (m, 1 H), 2.03 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO), 1.99 (s, 3 H, CH_3CO), 1.95 (s, 3 H, CH_3CO). Anal. Calcd for $C_{77}H_{78}O_{31}$: C, 61.68; H, 5.21. Found: C, 61.43; H, 5.26.

Allyl 2,3,4,6-tetra-O-*acetyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-α*-D-*glucopyranoside* (**32**).—To the solution of **31** (300 mg, 0.2 mmol) in Py (10 mL), BzCl (0.1 mL, 0.86 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (30 mL), washed with water and satd aq $NaHCO_3$. The organic layer was combined, dried, and concentrated. Column chromatography (2:1 petroleum ether–EtOAc) gave **32** quantitatively as a colorless solid: $[\alpha]_D$ +4.8° (*c* 1.4, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.10–7.46 (m, 45 H, Bz–H), 6.20 (t, 1 H, *J* 9.8 Hz), 5.99 (t, 1 H, *J* 9.6 Hz), 5.87–5.80 (m, 2 H), 5.76 (t, 1 H, *J* 9.6 Hz), 5.45 (t, 1 H, *J* 8.6 Hz), 5.38–4.96 (m, 10 H), 4.80 (d, 1 H, *J* 7.9 Hz), 4.72 (d, 1 H, *J* 7.8 Hz), 4.57 (dd, 1 H, *J* 9.7, *J* 7.9 Hz), 4.23–4.05 (m, 8 H), 3.80–3.62 (m, 6 H). 2.03 (s, 3 H, CH_3CO), 2.01 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO), 1.99 (s, 3 H, CH_3CO). Anal. Calcd for $C_{98}H_{90}O_{34}$: C, 64.97; H, 4.97. Found: C, 64.89; H, 5.04.

β-D-*Glucopyranosyl-(1→6)-β*-D-*glucopyranosyl-(1→6)-β*-D-*glucopyranosyl-(1→6)*-D-

glucopyranose (**33**).—To a solution of **32** (72 mg, 40 μmol) in 90% AcOH (1 mL) containing AcONa (29.3 mg, 0.3 mmol) was added $PdCl_2$ (8.9 mg, 0.5 mmol), and the mixture was stirred for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (30 mL), washed with water and satd aq $NaHCO_3$. The organic layer was concentrated under reduced pressure, and the residue was passed through a short silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to give crude 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-D-glucopyranose (65 mg), which was dissolved in a satd solution of NH_3 in MeOH (5 mL). After 48 h at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **33** (20.8 mg, 78%) as a syrup: ^{1}H NMR (D_2O): δ 4.74 (s,1 H, H-1), 4.48 (d, 1 H, *J* 8.1 Hz), 4.46 (d, 1 H, *J* 8.0 Hz), 4.43 (d, 1 H, *J* 8.1 Hz), 3.98–3.75 (m, 8 H), 3.62–3.52 (m, 12 H), 3.36–3.30 (m, 4 H). Anal. Calcd for $C_{24}H_{42}O_{21}$: C, 43.24; H, 6.31. Found: C, 43.17; H, 6.35.

Allyl 2,3,4,6-tetra-O-*acetyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-α*-D-*glucopyranosyl trichloroacetimidate* (**34**).—To a solution of **32** (905 mg, 0.5 mmol) in 90% AcOH (10 mL) containing AcONa (293 mg, 3 mmol) was added $PdCl_2$ (89 mg, 0.5 mmol), and the mixture was stirred for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (30 mL), washed with water and satd aq $NaHCO_3$. The organic layer was concentrated under reduced pressure, and the residue was passed a short silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give crude 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-D-glucopyranose (860 mg). The product was dissolved in CH_2Cl_2 (20 mL), then CCl_3CN (0.1 mL, 2 mmol) and DBU (14 μL, 0.18 mmol) were added. The reaction mixture was stirred for 2 h, 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 2:1 petroleum ether–EtOAc as the eluent gave the tetrasaccharide donor **34** as crystals in a good yield (862 mg, 90%): mp 129–131 °C; $[\alpha]_D$ +4.8° (*c* 1.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 9.02 (s, 1 H, C=N–*H*), 8.13–7.26 (m, 45 H, Bz–H), 6.62 (s, 1 H, H-1), 6.21 (t, 1 H, *J* 9.8 Hz), 5.95 (t, 1 H, *J* 9.6 Hz), 5.92–5.85 (m, 2 H), 5.60 (t, 1 H, *J* 9.6 Hz), 5.57 (t, 1 H, *J* 8.0 Hz), 5.52 (dd, 1 H, *J* 9.7, *J* 7.9 Hz), 5.40–5.10 (m, 5 H), 5.05 (d, 1 H, *J* 7.9 Hz), 5.01 (d, 1 H, *J* 7.8 Hz), 4.95 (d, 1 H, *J* 7.9 Hz), 4.25–4.15 (m, 3 H), 4.07–3.90 (m, 3 H), 3.80–3.70 (m, 2 H), 3.65–3.54 (m, 2 H), 3.50–3.46 (m, 2 H), 2.05 (s, 3 H, CH_3CO), 2.03 (s, 3 H, CH_3CO), 2.01 (s, 3 H, CH_3CO), 1.99 (s, 3 H, CH_3CO). Anal. Calcd for $C_{97}H_{86}Cl_3NO_{34}$ C, 60.80; H, 4.49. Found: C, 60.63; H, 4.53.

Allyl β-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-2,3,4-tri*-O-*benzoyl-α*-D-*glucopyranoside* (**35**).—To a solution of **32** (905 mg, 0.5 mmol) in anhyd MeOH (50 mL) was added AcCl (1.5 mL) at 0 °C. The solution was sealed in a flask and stirred for 10 h at rt, and then another portion of AcCl (1 mL) was added. The reaction was monitored by TLC (1:2 petroleum ether–EtOAc) until the starting material disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica-gel column to give **35** as a colorless solid (698 mg, 85%) that was directly used for the next reaction: $[\alpha]_D$ +7.6° (*c* 1.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.15–7.25 (m, 45 H, Bz–H), 6.18 (t, 1 H, *J* 9.9 Hz), 5.98 (t, 1 H, *J* 9.7 Hz), 5.95–5.87 (m, 2 H), 5.80 (t, 1 H, *J* 9.8 Hz), 5.59 (t, 1 H, *J* 8.1 Hz), 5.48 (dd, 1 H, *J* 9.8, *J* 7.9 Hz), 5.35–5.25 (m, 3 H), 5.18–5.09 (m, 3 H), 5.04 (d, 1 H, *J* 7.8 Hz), 4.99 (d, 1 H, *J* 7.7 Hz), 4.96 (d, 1 H, *J* 7.9 Hz), 4.60–4.50 (m, 3 H), 4.41–4.16 (m, 9 H), 3.98–3.87 (m, 3 H),

3.60–3.51 (m, 2 H). Anal. Calcd for $C_{90}H_{82}O_{30}$: C, 65.77; H, 4.99. Found: C, 65.62; H, 5.03.

Allyl 2,3,4,6-tetra-O-*acetyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-α-D-*glucopyranoside* (**36**).—2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (**28**) (97 mg, 0.1 mmol) and allyl β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**35**) (164 mg, 0.1 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL). TMSOTf (2 μL, 0.10 equiv) 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 (1:1.5 petroleum ether–EtOAc) indicated that the reaction was complete. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to dryness. Further purification by column chromatography (1:1.5 petroleum ether–EtOAc) gave **36** (171 mg, 70%) as a colorless solid: mp 126–129 °C; $[\alpha]_D$ +5.4° (*c* 1.3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.10–7.25 (m, 60 H, Bz–H), 6.20 (t, 1 H, *J* 9.7 Hz), 6.15 (t, 1 H, *J* 9.8 Hz), 6.06 (t, 1 H, *J* 9.9 Hz), 5.90–5.70 (m, 6 H), 5.46–5.09 (m, 10 H), 5.07 (d, 1 H, *J* 7.9 Hz), 5.00 (d, 1 H, *J* 8.0 Hz), 4.90 (d, 1 H, *J* 7.9 Hz), 4.85 (d, 1 H, *J* 7.8 Hz), 4.78 (d, 1 H, *J* 7.8 Hz), 4.65–4.53 (m, 3 H), 4.40–3.92 (m, 12 H), 3.84–3.56 (m, 5 H), 3.44–3.40 (m, 2 H), 3.26–3.17 (m, 1 H), 2.05 (s, 3 H, CH_3CO), 2.03 (s, 3 H, CH_3CO), 2.01 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO). Anal. Calcd for $C_{131}H_{122}O_{47}$: C, 64.27; H, 4.99. Found: C, 64.40; H, 4.93.

Allyl 2,3,4,6-tetra-O-*acetyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-α-D-*glucopyranoside* (**37**).—To the solution of **36** (122 mg, 0.05 mmol) in Py (5 mL), BzCl (0.1 mL, 18 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (1.5:1 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 (1.5:1 petroleum ether–EtOAc) gave **37** (135 mg, 98%) as a colorless solid: mp 125–128 °C; $[\alpha]_D$ +11.2° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.10–7.46 (m, 75 H, Bz–H), 6.22 (t, 1 H, *J* 9.7 Hz), 6.19 (t, 1 H, *J* 9.8 Hz), 6.14 (t, 1 H, *J* 9.9 Hz), 6.07 (t, 1 H, *J* 9.7 Hz), 6.01 (t, 1 H, *J* 9.7 Hz), 5.88–5.73 (m, 6 H), 5.65–5.50 (m, 5 H), 5.40–5.08 (m, 7 H), 5.06 (d, 1 H, *J* 7.9 Hz), 5.02 (d, 1 H, *J* 7.8 Hz), 4.89 (d, 1 H, *J* 7.9 Hz), 4.82 (d, 1 H, *J* 7.8 Hz), 4.65–4.60 (m, 3 H), 4.52–4.38 (m, 5 H), 4.22–4.05 (m, 6 H), 3.85–3.42 (m, 6 H), 2.04 (s, 3 H, CH_3CO), 2.01 (s, 3 H, CH_3CO), 2.00 (s, 3 H, CH_3CO), 1.98 (s, 3 H, CH_3CO). Anal. Calcd for $C_{152}H_{134}O_{50}$: C, 66.13; H, 4.86. Found: C, 66.19; H, 4.81.

β-D-*Glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-α-D-*glucopyranoside* (**38**).—To a solution of **37** (83 mg, 30 μmol) in 90% AcOH (1 mL) containing AcONa (29.3 mg, 0.3 mmol) was added $PdCl_2$ (8.9 mg, 0.5 mmol), and the mixture was stirred for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (20 mL), washed with water and satd aq $NaHCO_3$. The organic layer was concentrated under reduced pressure, and the residue was passed through a short silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to give crude 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-D-glucopyranose, which was dissolved in a satd solution of NH_3 in MeOH (5 mL). After 48 h at rt, the reaction mixture was concentrated and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **38** (23 mg, 78%) as a syrup: ^1H

NMR (D_2O): δ 4.76 (s, 1 H, H-1), 4.50–4.43 (m, 5 H), 3.97–3.70 (m, 12 H), 3.68–3.51 (m, 18 H), 3.36–3.30 (m, 6 H). Anal. Calcd for $C_{152}H_{134}O_{50}$: C, 66.13; H, 4.86. Found: C, 66.17; H, 4.82.

Allyl 2,3,4,6-tetra-O-*acetyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-α-D-*glucopyranoside* (**39**).—Compound **34** (191 mg, 0.1 mmol) and **35** (164 mg, 0.1 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL). TMSOTf (1.5 μL, 0.08 equiv) was added dropwise at −42 °C with N_2 protection. The reaction mixture was stirred for 3 h. Then the mixture was neutralized with Et_3N, and concentrated under reduced pressure to an oily residue. Purification by column chromatography (1:1.5 petroleum ether–EtOAc) gave **39** (210 mg, 62%) as a colorless solid: mp 123–126 °C; $[\alpha]_D$ +9.6° (*c* 1.2, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.16–7.26 (m, 90 H, Bz–H), 6.30 (t, 1 H, *J* 9.8 Hz), 6.24 (t, 1 H, *J* 9.8 Hz), 6.18 (t, 1 H, *J* 9.9 Hz), 6.15–5.75 (m, 11 H), 5.60–5.26 (m, 8 H), 5.22–5.06 (m, 6 H), 5.02 (d, 1 H, *J* 7.8 Hz), 4.96 (d, 1 H, *J* 7.7 Hz), 4.85 (d, 1 H, *J* 7.8 Hz), 4.75 (d, 1 H, *J* 7.9 Hz), 4.60–4.42 (m, 8 H), 4.36–4.04 (m, 11 H), 4.00–3.70 (m, 5 H), 3.67–3.50 (m, 5 H), 2.08 (s, 3 H, CH_3CO), 2.04 (s, 3 H, CH_3CO), 1.96 (s, 3 H, CH_3CO), 1.89 (s, 3 H, CH_3CO). Anal. Calcd for $C_{185}H_{166}O_{63}$: C, 65.41; H, 4.89. Found: C, 65.47; H, 4.83.

Allyl 2,3,4,6-tetra-O-*acetyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)-2,3,4-*tri*-O-*benzoyl*-α-D-*glucopyranoside* (**40**).—To a solution of **39** (119 mg, 0.035 mmol) in Py (5 mL), BzCl (0.1 mL, 24 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (1.5:1 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 (1.5:1 petroleum ether–EtOAc) gave **40** (125 mg, 96%) as a colorless solid: $[\alpha]_D$ +12.6° (*c* 1.3, $CHCl_3$). ^{13}C HMR ($CDCl_3$): δ 170.58, 170.22, 169.34, 169.30, (4 CH_3CO), 166.09, 166.05, 166.01, 165.90, 165.87, 165,84, 165.81, 165.68, 165.47, 165.22, 165.14, 165.03, 164.93, 164.90, 164.82, 164.77, (21 C_6H_5CO, some signals overlapped), 104.11, 103.76, 102.75, 102.34, 101.85, 101.29, (C-$1^{I–VIII}$ some signals overlapped), 75.42, 75.40, 75.36, 75.22, 75.12, 74.89, 74.68, 74.52, 74.48, 74.29, 73.87, 73.65, 73.44, 73.38, 73.11, 72.98, 72.90, 72.85, 72.62, 72.34, 72.29, 72.19, 72.12, 72.04, 71.77, 71.34, 69.37, 68.76, (C-2,3,4,5,$6^{I–VIII}$ some signals overlapped); MALDI-TOF–MS Anal. Calcd for $C_{206}H_{178}O_{66}$: 3707.1 [M]. Found: 3730.1 [M + Na], 3746.0 [M + K]: ^1H NMR ($CDCl_3$): δ 8.08–7.25 (m, 105 H, Bz–H), 6.30–5.60 (m, 19 H), 5.38–5.23 (m, 9 H), 4.90–3.30 (m, 33 H), 2.10 (s, 3 H, CH_3CO), 2.05 (s, 3 H, CH_3CO), 1.98 (s, 3 H, CH_3CO), 1.88 (s, 3 H, CH_3CO). Anal. Calcd for $C_{206}H_{178}O_{66}$: C, 66.70; H, 4.80. Found: C, 66.63; H, 4.83.

β-D-*Glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl*-(1→6)-α-D-*glucopyranoside* (**41**).—To a solution of **40** (148 mg, 40 μmol) in 90% AcOH (1 mL) containing AcONa (29.3 mg, 0.3 mmol) was added $PdCl_2$ (8.9 mg, 0.5 mmol), and the mixture was stirred for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2 (30 mL), washed with water and satd aq $NaHCO_3$. The organic layer was concentrated under reduced pressure, and the residue was passed a short silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to give crude 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-

tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranose (122 mg), which was dissolved in a satd solution of NH_3 in MeOH (5 mL). After 48 h at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **41** as a syrup (40 mg, 76%): ^{1}H NMR (D_2O): δ 4.78 (s, 1 H, H-1), 4.52–4.41 (m, 7 H), 3.98–3.71 (m, 16 H), 3.69–3.50 (m, 24 H), 3.39–3.28 (m, 8 H). Anal. Calcd for $C_{48}H_{82}O_{41}$: C, 43.84; H, 6.24. Found: C, 43.80; H, 6.27.

Acknowledgements

This work was supported by The Chinese Academy of Sciences (Projects KJ952J$_1$510 and RCEES9904) and by The National Natural Science Foundation of China (Projects 29802009, 30070185 and 39970864).

References

1. (a) Dwek, R. A. *Chem. Rev.* **1996**, *96*, 683–718;
(b) *Synthetic Oligosaccharides. Indispensable Probes for the Life Sciences*; Kovac, P., Ed.; ACS Symposium Series 560; American Chemical Society: Washington, DC, 1994.
2. (a) General reviews: Davis, B. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2137–2160;
(b) Hanessian, S. *Preparative Carbohydrate Chemistry;* Marcel Dekker: New York, 1997, Chapters 12–22;
(c) Khan, S. H.; O'Neill, R. A. *Modern Methods in Carbohydrate Synthesis*; Harwood Academic: United States, 1996, p. 125;
(d) Barresi, F.; Hindsgaul, O. *J. Carbohydr. Chem.* **1995**, *14*, 1043–1064;
(e) Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–123;
(f) Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503–1531;
(g) Glycosyl sulfoxide donors: Yan, L.; Kahne, D. *J. Am. Chem. Soc.* **1996**, *118*, 9239–9246; (h) 1-Hydroxy glycosyl donors: Garcia, B. A.; Poole, J. A.; Gin, D. Y. *J. Am. Chem. Soc.* **1997**, *119*, 7597–7598;
(i) Glycal donors: Danishefsky, S. J.; Bilodeau, M. T. *Angew. Chem.* **1996**, *108*, 1482–1486; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1380–1384;
(j) 1,2-Anhyrdo glycosyl donors: Du, Y.; Kong, F. *Tetrahedron Lett.* **1995**, 427–430.
3. (a) Wang, W.; Kong, F. *J. Org. Chem.* **1999**, *64*, 5091–5095;
(b) Wang, W.; Kong, F. *J. Org. Chem.* **1998**, *63*, 5744–5745;
(c) Kong, F.; Wang, W. Chinese Pat. Appl. 971257788.4; 98103242.7;
(d) Wang, W.; Kong, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1247–1250; *Angew. Chem.* **1999**, *111*, 1330–1334;
(e) Becker, B.; Furneaux, R. H.; Reck, F.; Zubkov, O. A. *Carbohydr. Res.* **1999**, *315*, 148–157;
(f) Kaur, K. J.; Hindsgaul, O. *Glycoconjugate J.* **1991**, *8*, 90–96;
(g) Roy, R.; Page, D.; Figueroa-Perez, S.; Verez-Bencomo, V. *Glycoconjugate J.* **1998**, *15*, 251–258;
(h) Gan, Z.; Cao, S.; Wu, Q.; Roy, R. *J. Carbohydr. Chem.* **1999**, *18*, 755–765;
(i) Numomura, S.; Iida, M.; Numata, M.; Sugimoto, M.; Ogawa, T. *Carbohydr. Res.* **1994**, *263*, 148–157;
(j) Zhang, Y.-M.; Brodzky, A.; Sinaÿ, P.; Saint-Marcoux, G.; Perly, B. *Tetrahedron: Asymmetry* **1995**, *6*, 1195–1202;
(k) Jain, R. K.; Huang, B. -G.; Chandrasekaran, E. V.; Matta, K. L. *Chem. Commun. (Cambridge)* **1997**, 23–26;
(l) Figueroa-Perez, S.; Verez-Bencomo, V. *Tetrahedron Lett.* **1998**, 9143–9146.
4. (a) Ernst, B.; De Mesmaeker, A.; Wagner, B.; Winkler, T. *Tetrahedron Lett.* **1990**, 6167–6170;
(b) Banoub, J.; Boullanger, P.; Potier, M.; Descotes, G. *Tetrahedron Lett.* **1986**, 4145–4148;
(c) Dahlin, B. M.; Garegg, P. J.; Johansson, R.; Samuelsson, B.; Orn, U. *Acta Chem. Scand. Ser. B* **1981**, *35*, 669–672;
(d) Banoub, J.; Bundle, D. R. *Can J. Chem.* **1979**, *57*, 2091–2096;
(e) Ogawa, T.; Matsui, M. *Carbohydr. Res.* **1976**, *51*, C13;
(f) Zurabyan, S. E.; Tikhomirov, M. M.; Nesmeyanov, V. A.; Khorlin, A. Y. *Carbohydr. Res.* **1973**, *26*, 117–126;
(g) Wulff, G.; Kruger, W. *Carbohydr. Res.* **1971**, *19*, 139–146;
(h) Kochetkov, N. K.; Bochkov, A. F.; Sokolovskaya, T. A.; Snyatkova, V. J. *Carbohydr. Res.* **1971**, *16*, 17–25;
(i) Kochetkov, N. K.; Khorlin, A. J.; Bochkov, A. F. *Tetrahedron* **1967**, *23*, 693–702.
5. Zhu, Y.; Kong, F. *Synlett* **2000**, 663–667.
6. (a) Stratford, M. *Yeast* **1992**, *8*, 635–643;
(b) Kanbe, T.; Culter, J. E. *Infect. Immunol.* **1994**, *62*, 1662–1669;
(c) Nelson, R. D.; Shibata, N.; Podzorski, R. P.; Herron, M. J. *Clin. Microbiol. Rev.* **1991**, *4*, 1–11;
(d) Podzorski, R. P.; Gray, G. R.; Nelson, R. D. *J. Immunol.* **1990**, *144*, 707–714.
7. Corradi da Silva, M. L.; Iacomini, M.; Jablonski, E.; Gorin, P. A. J. *Phytochemistry* **1993**, *33*, 547–552.
8. Kovac, P. *Carbohydr. Res.* **1986**, *153*, 237–248.
9. Srivastava, V. K.; Sondheimer, S. J.; Schuerch, C. *Carbohydr. Res.* **1994**, *86*, 203–212.
10. Examples for *manno*triose synthesis: (a) Khan, S. H.; Jain, R. K.; Matta, K. L. *Carbohydr. Res.* **1990**, *207*, 57–65. For glucotriose synthesis: (b) Hashimoto, S.; Sakamoto, H.; Honda, T.; Ikegami, S. *Tetrahedron Lett.* **1997**, *38*, 5184–5187.
11. Pougny, J. R.; Jacquinet, J. C.; Nassr, M.; Duchet, D.; Milat, M.-L.; Sinaÿ, P. *J. Am. Chem. Soc.* **1977**, *99*, 6762–6763.
12. Schmidt, R. R.; Grundler, G. *Angew. Chem.* **1982**, *94*, 790–794.
13. (a) Han, X. -B.; Jiang, Z. -H.; Schmidt, R. R. *Liebigs. Ann. Chem.* **1993**, 853–861;
(b) Wang, W.; Kong, F. unpublished results.

14. Xiong, S.; Kong, F.; Yang, C. *Youji Huaxue* **1994**, *14*, 280–284; *Chem. Abstr.* **1994**, *121*, 205804d.
15. (a) Petrakova, E.; Schraml, J. *Collect. Czech. Chem. Commun.* **1983**, *48*, 877–882;
(b) Auzanneau, F.-I.; Forooghian, F.; Pinto, B. M. *Carbohydr. Res.* **1996**, *291*, 21–30;
(c) Wang, W.; Kong, F. *Carbohydr. Res.* **1999**, *315*, 128–135.