Pergamon

SCIENCE DIRECT®

Tetrahedron: *Asymmetry* 14 (2003) 1275–1283

TETRAHEDRON: *ASYMMETRY*

First syntheses of D-mannose penta- and decasaccharides, the repeating unit and its dimer of the cell-wall mannan of *Candida kefyr* IFO 0586

Ying Xing and Jun Ning*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, Beijing 100085, PR China

Received 11 January 2003; revised 18 February 2003; accepted 26 February 2003

Abstract—α-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)]-α-D-mannopyranose and α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)]-α-D-mannopyranosyl-(1→2)]-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)]-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)]-α-D-mannopyranose, the repeating unit and its dimer of the cell wall mannan of the pathogenic yeast Candida kefyr IFO 0586, have been efficiently synthesized via their allyl glycosides by using allyl 3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside, allyl 6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranoside, and allyl 3,4-di-*O*-benzoyl-α-D-mannopyranoside as synthons. The blocked pentasaccharide was regio- and stereoselectively prepared by coupling of allyl 3,4-di-*O*-benzoyl-α-D-mannopyranoside with 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate, and then with 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate in a one-pot manner.

1. Introduction

Candida species are opportunistic pathogens of humans that frequently cause severe systemic infections in patients with AIDS,[1] cancer,[2] and burns[3] as well as in those under immunosuppressive or radiation therapy.[4] An impressive feature of these fungi is that they synthesize cell wall polysaccharides containing predominantly mannose residues.[5–7] It has been reported that the mannose oligosaccharides present in the fungal D-mannans deeply influence many fundamental biological processes in the organisms. The α-linked oligo-D-mannosyl side chains of cell-wall mannan of the pathogenic yeast *Candida* species play important roles in the binding of yeast cells to the marginal zone of mouse spleen[8] and in the processes of several types of yeast flocculation.[9] The alkali-released α-linked D-manno-oligosaccharides obtained from a *Candida albicans* cell-wall mannan were potent inhibitors of lymphoproliferation induced by the parent D-mannan.[10,11] Furthermore, many of them (if not all) are antigenically relevant. Hence, there is a great need for usable quantities of the natural oligosaccharides with a well-defined structure and composition for biological studies aiming at a better understanding of these phenomena at the molecular level. Given the intrinsic difficulty in obtaining complex natural oligosaccharides and glycoconjugates in a pure and homogeneous form from natural sources because of the presence of mixtures of glycosylated species (glycoforms). A major opportunity is provided by chemical synthesis.

As part of our continuing efforts dedicated to developing efficient strategies for the construction of sugars, we have prepared a lot of oligosaccharides with various structures present in natural sources including fungi.[12–16] In 1994, Kobayashi et al.[17] conducted a structural analysis of an antigenic cell wall mannan isolated from the pathogenic yeast *Candida kefyr* IFO 0586 and found that this sugar has a long α-(1→6)-linked D-mannopyranosyl backbone and many short α-(1→2)-linked D-mannopyranosyl side-chains in a comb-like structure as shown in Figure 1. The reasons mentioned above, together with the fact that there have been no reports dealing with the synthesis of these highly branched oligosaccharides, prompted us to develop an efficient method for the synthesis of this kind of complex carbohydrate. The preparation of allyl-α-D-penta-

* Corresponding author. Tel.: 8610-62849157; fax: 8610-62923563; e-mail: jning@mail.rcees.ac.cn

0957-4166/03/$ - see front matter
doi:10.1016/S0957-4166(03)00216-7

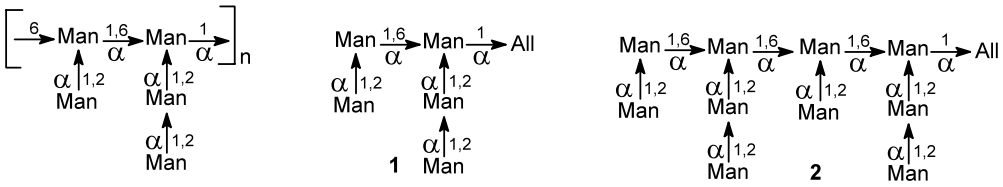


Figure 1. The structures of the cell-wall mannan of *Candida kefyr* IFO 0586 and the synthesized oligosaccharides **1** and **2**.

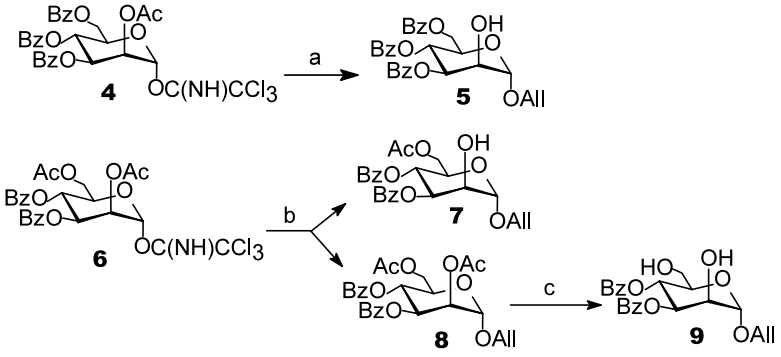
mannoside **1** and allyl-α-D-decamannoside **2** (Fig. 1), the repeating unit and its dimer of the cell wall mannan of the pathogenic yeast *Candida kefyr* IFO 0586 are presented as typical examples using the strategy developed here.

2. Results and discussion

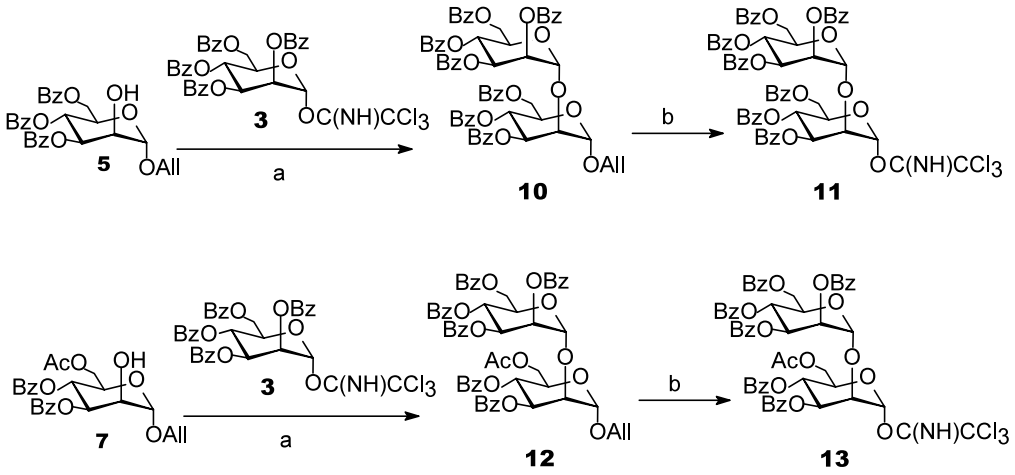
For the synthesis of the complex decasaccharide **2**, we needed 2,3,4,6-tetra-*O*-benzoyl-D-mannopyranosyl trichloroacetimidate **3**, allyl 3,4,6-tri-*O*-benzoyl-D-mannopyranoside **5**, allyl 6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranoside **7**, and allyl 3,4-di-*O*-benzoyl-D-mannopyranoside **9** as building materials. Compound **3** was prepared according to the reported procedure.[18] The glycosyl acceptor **5** was obtained from coupling of 2-*O*-acetyl-3,4,6-tri-*O*-benzoyl-D-mannopyranosyl trichloroacetimidate **4**[18] with allyl alcohol followed by 2-*O*-deacetylation in 87% yield (Scheme 1). The glycosyl acceptors **7** and **9** were derived from 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-D-mannopyranosyl trichloroacetimidate **6** which was made according to the method developed in our laboratory.[16] We were lucky to find that coupling of **6** with allyl alcohol in the presence of TMSOTf (0.3 equiv.) gave two compounds; one was the required glycosyl acceptor **7** in 31%, and another was allyl 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-D-mannopyranoside **8** in 63% yield. During the glycosylation process of **6** with allyl alcohol, some of the 2-*O*-acetyl groups of **6** were removed, and it was observed that with the increase of the amount of TMSOTf added to the reaction system, the 2-*O*-acetyl group removed product **7** was increased. Selective removal of the acetyl groups of **8** in MeOH containing 0.5% HCl gave the glycosyl acceptor **9** in 93% yield.

Condensation of **3** and **5** with TMSOTf as catalyst and 4 Å molecular sieves in CH_2Cl_2 at rt afforded the disaccharides **10** in 88% yield. Deallylation of **10** with $PdCl_2$ followed by activation with CCl_3CN in the presence of DBU, afforded the disaccharide donor **11** in 80% yield (for two steps) (Scheme 2). Similar procedures gave another disaccharide donor **13**.

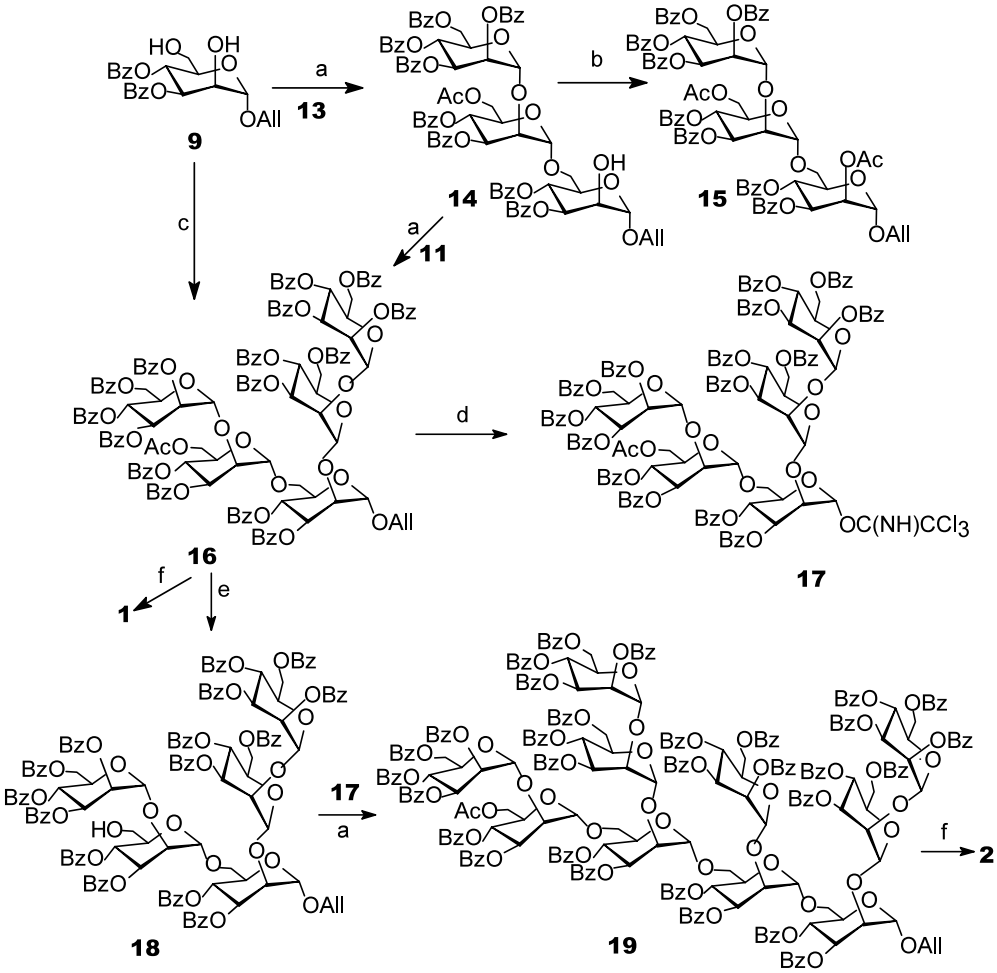
Coupling of **9** and **13** with TMSOTf as catalyst and 4 Å molecular sieves in CH_2Cl_2 at −45°C regio- and stereoselectively afforded the trisaccharides **14** in 91% yield (Scheme 3). No (1→2)-linked trisaccharide was detected both from ^{1}H NMR and TLC. Acetylation of **14** confirmed 6-*O*-glycosylation as the ^{1}H NMR spectrum of acetylated trisaccharide **15** showed a newly emerged doublet of doublets at δ 5.54 ppm for H-2. Condensation of **14** with **11** afforded the blocked pentasaccharide **16** in 90% yield. The ^{1}H NMR data of **16** contained structurally characteristic information, i.e. one acetyl signal (δ 1.95), one allyl signal (δ 5.43–5.27) and five H-1 signals (δ 5.60, 5.58, 5.39, 5.27, and 5.12). The ^{13}C NMR spectrum of **16** gave five signals for C-1 (100.04, 99.65, 99.42, 98.36, 98.04) with $^2J_{C1-H1}$ from 170 to 176.8 Hz indicating complete α-linkages. Encouraged by the smooth coupling reaction results, a one-pot procedure for the synthesis of the pentasaccharide **16** was carried out. Thus, treatment of **9** and **13** with TMSOTf as catalyst and 4 Å molecular sieves in CH_2Cl_2 at −45°C, followed by addition of **11** at rt afforded compound **16** in 83% yield. Selective removal of the 6-*O*-acetyl group of the pentasaccharide **16** gave the glycosyl accepter **18**. Deallylation of **16** with $PdCl_2$ followed by activation with CCl_3CN in the presence of DBU gave the pentasaccharide donor **17**. The fully protected decasaccharide **19** was obtained by coupling **17** with **18** in 50% yield. The ^{1}H NMR data of **19**



Scheme 1. *Reagents and conditions*: (a) i. allyl alcohol (2 equiv.), TMSOTf (0.1 equiv.), CH_2Cl_2, rt, 1 h; ii. methanol/0.5% HCl, rt, 12 h, 87% (over the two steps); (b) allyl alcohol (2 equiv.), TMSOTf (0.3 equiv), CH_2Cl_2, rt, 1 h, 31% for **7** and 63% for **8**; (c) methanol/0.5% HCl, rt, 12 h, 93%.



Scheme 2. *Reagents and conditions*: (a) CH_2Cl_2, TMSOTf (cat.), rt, 1 h, 88% for **10** and 92% for **12**; (b) i. $PdCl_2$, CH_3OH, rt, 4 h; ii. CCl_3CN, DBU, CH_2Cl_2, rt, 2 h, 80% for **11** and 81% for **13** (over the two steps).



Scheme 3. *Reagents and conditions*: (a) CH_2Cl_2, TMSOTf (cat.), rt, 1 h, 91% for **14**, 90% for **16**, 50% for **19**; (b) Ac_2O, pyridine, rt, 3 h, 100%; (c) i. **13** (1.0 equiv.), TMSOTf (cat.), CH_2Cl_2, MS 4 Å Powder, −45°C–rt, 1.5 h; ii. **11** (1.2 equiv.), rt, 1 h, 83% (over the two steps); (d) i. $PdCl_2$, CH_3OH–CH_2Cl_2, 4 h; ii: CCl_3CN, DBU, CH_2Cl_2 2 h, 85% (over the two steps); (e) methanol/0.5% HCl, rt, 12 h, 92%; (f) CH_3OH–CH_2Cl_2 (9:1) satd with dry NH_3, 40°C, 24 h, 91% for **1**, 95% for **2**.

contained structurally characteristic information, i.e. one acetyl signal (δ 1.87), one allyl signal (δ 5.36–5.20) and ten H-1 signals (δ 5.70, 5.62, 5.62, 5.48, 5.39, 5.32, 5.28, 5.24, 5.20, and 4.98). The ^{13}C NMR spectrum of **19** gave ten signals for C-1 (100.07, 99.99, 99.72, 99.55, 99.43, 99.34, 98.89, 98.26, 98.19, 98.17). Deprotection

of **16** and **19** using NH_3 in CH_3OH–CH_2Cl_2 gave compounds **1** and **2**. The NMR spectra of the **1** and **2** are shown in Figures 2–5.

3. Conclusion

In summary, a highly efficient and concise synthesis of the mannose pentasaccharide and decasaccharide of the cell-wall mannan of the pathogenic yeast *Candida kefyr* IFO 0586 was achieved by regio- and stereoselective glycosylation using glycosyl trichloroimidates as the donors and partially protected sugars as the acceptors. The sole use of acyl groups in the synthesis substantially simplified the procedure. This method should be useful for the synthesis of other complex mannose oligosaccharides in the future.

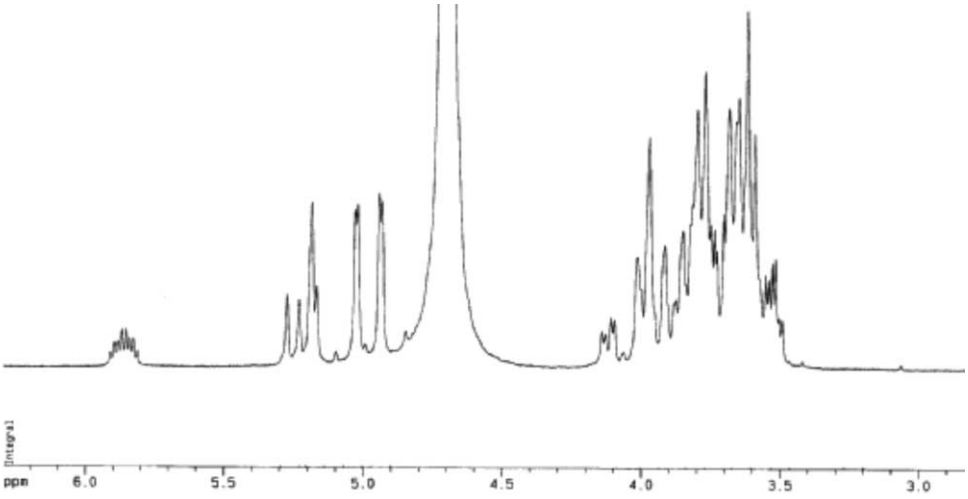


Figure 2. ^1H NMR spectrum of compound **1** (solvent D_2O at 25°C, 400 MHz Bruker ARX 400 spectrometer).

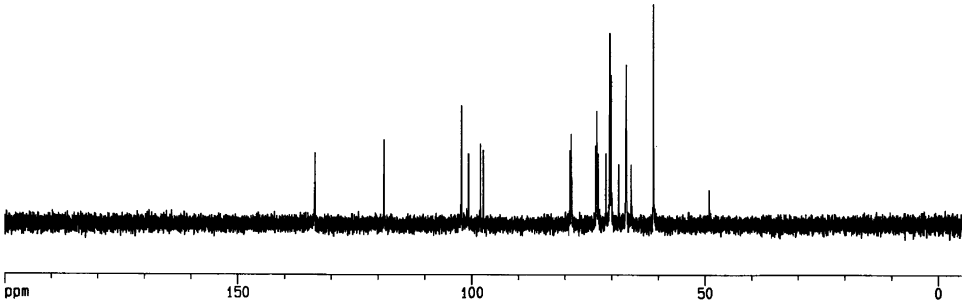


Figure 3. ^{13}C NMR spectrum of compound **1** (solvent D_2O at 25°C, 100 MHz Bruker ARX 400 spectrometer).

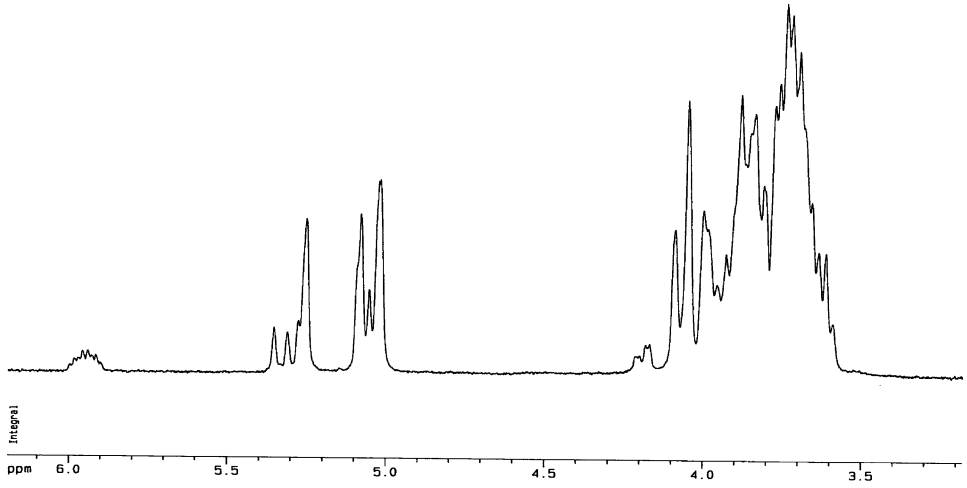


Figure 4. ^1H NMR spectrum of compound **2** (solvent D_2O at 25°C, 400 MHz Bruker ARX 400 spectrometer).

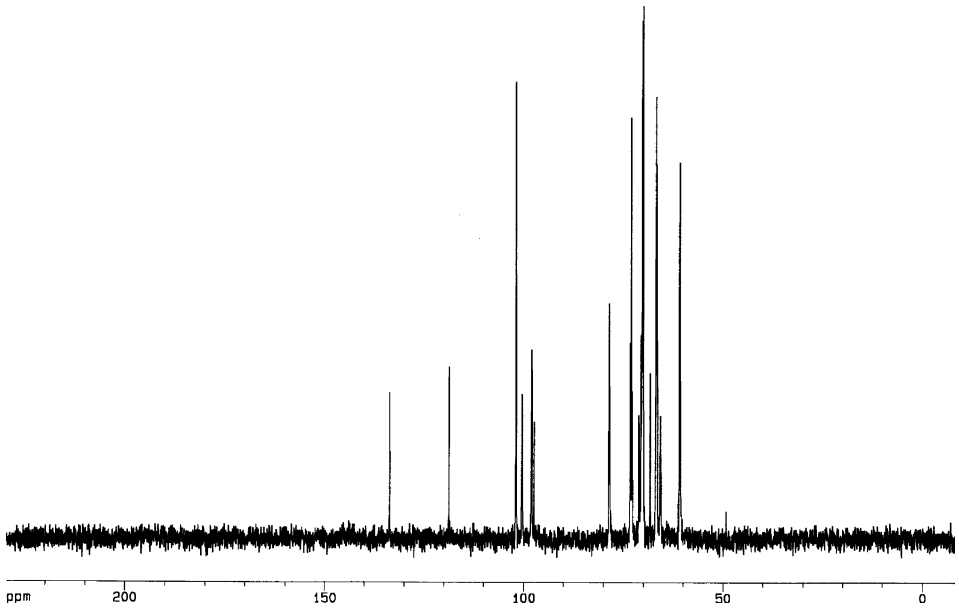


Figure 5. ^{13}C NMR spectrum of compound **2** (solvent D_2O at 25°C, 100 MHz Bruker ARX 400 spectrometer).

4. Experimental

4.1. General methods

Optical rotations were determined at 25°C with a Perkin-Elmer Model 241-Mc automatic polarimeter. Melting points were determined with a 'Mel-Temp' apparatus. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker ARX 400 spectrometers (400 MHz for ^1H, 100 MHz for ^{13}C) for solutions in $CDCl_3$ or D_2O as indicated. Chemical shifts are given in ppm downfield from internal Me_4Si. Mass spectra were measured using MALTI-TOF-MS with CCA as matrix. Thin-layer chromatography (TLC) was performed on silica gel HF_{254} with detection by charring with 30% (v/v) H_2SO_4 in MeOH or in some cases by a UV detector. Column chromatography was conducted by elution of a column (16×240 mm, 18×300 mm, 35×400 mm) of silica gel (100–200 mesh) with EtOAc-petroleum ether (60–90°C) as the eluent. Solutions were concentrated at <60°C under reduced pressure.

4.2. Allyl 3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside 5

A solution of 2-*O*-acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate **4** (4.3 g, 6.4 mmol) and allyl alcohol (0.7 ml, 10 mmol) in dry CH_2Cl_2 (50 mL) was stirred with dried molecular sieves (4 Å, 1 g) under N_2 for 15 min, and then TMSOTf (135 μL, 0.7 mmol) was added. After 1 h, the reaction mixture was neutralized with Et_3N, filtered and the filtrate was concentrated. The resulting residue without purification was directly dissolved in MeOH (150 mL) containing 0.5% HCl. The solution was stirred at rt for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the starting material had disappeared. The mixture was neutralized with Et_3N and then concentrated to dryness. The residue was partitioned between water and CH_2Cl_2, the organic layer was dried over Na_2SO_4 and concentrated to a syrup. Purification of the residue by flash chromatography (2:1 petroleum ether–EtOAc) gave **5** as a syrup (2.9 g, 87% for the two steps): $[\alpha]_D$ −15.1 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400MHz): δ 8.03–7.33 (m, 15 H, 3 Ph*H*), 5.95 (m, 1 H, C*H*=CH_2), 5.94 (dd, 1 H, $J_{3,4}=J_{4,5}=9.8$ Hz, H-4), 5.70 (dd, 1 H, $J_{2,3}=3.1$ Hz, $J_{4,5}=9.8$ Hz, H-3), 5.33 (dd, 1H, $^2J=1.5$ Hz, $^3J_{trans}=17.2$ Hz, CH=CH_2), 5.24 (dd, 1 H, $^2J=1.5$ Hz, $^3J_{cis}=10.4$ Hz, CH=CH_2), 5.03 (d, 1 H, $J_{1,2}=1.6$ Hz, H-1), 4.58 (dd, 1 H, H-6), 4.48 (dd, 1 H, H-6′), 4.40–4.08 (m, 4 H, CH_2CH=CH_2, H-2, 5). Anal. calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.93; H, 5.27.

4.3. Allyl 6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranoside 7 and Allyl 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranoside 8

A solution of 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate **6** (11 g, 17.8 mmol) and allyl alcohol (2.4 mL, 35 mmol) in CH_2Cl_2 (200 mL) was stirred with dried molecular sieves (4 Å, 4 g) under N_2 for 15 min, and then TMSOTf (1.0 mL, 5.3 mmol) was added. After 1 h, the reaction mixture was neutralized with Et_3N, filtered and the filtrate was concentrated. Purification of the residue by chromatography (3:1 petroleum ether–EtOAc) gave allyl 6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranoside **7** (2.6 g, 31%) and allyl 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranoside **8** (5.7 g, 63%). For **7**: $[\alpha]_D$ −13.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.97–7.26 (m, 10 H, 2 Bz*H*), 5.98 (m, 1 H, C*H*=CH_2), 5.85 (dd, 1H, $J_{3,4}=J_{4,5}=10$ Hz, H-4), 5.65 (dd, 1 H, $J_{2,3}=3.0$ Hz, $J_{3,4}=10$ Hz, H-3), 5.37 (dd, 1H, $^2J=1.5$ Hz, $^3J_{trans}=17.2$ Hz, CH=CH_2), 5.27 (dd, 1 H, $^2J=1.5$ Hz, $^3J_{cis}=10.4$ Hz, CH=CH_2), 5.00 (d, 1 H, $J_{1,2}=1.5$ Hz, H-1), 4.34–4.19 (m, 5 H, CH_2CH=CH_2, H-2, H-5, H-6), 4.10 (dd, 1 H, $J_{5,6'}=6.1$ Hz, $J_{6,6'}=12.8$ Hz, H-6′), 2.05 (s, 3 H, COCH_3). Anal. calcd for $C_{25}H_{26}O_9$: C, 63.82; H,

5.57. Found: C, 63.61; H, 5.53. For **8**: $[\alpha]_D$ −17.5 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.96–7.33 (m, 10 H, 2 BzH), 5.96 (m, 1 H, CH=CH_2), 5.78–5.76 (m, 2 H, H-3, 4), 5.48 (dd, 1 H, H-2), 5.36 (dd, 1H, ^2J=1.3 Hz, $^3J_{trans}$=17.1 Hz, CH=CH_2), 5.28 (dd, 1 H, ^2J=1.3 Hz, $^3J_{cis}$=10.4 Hz, CH=CH_2), 4.99 (d, 1 H, $J_{1,2}$=1.7 Hz, H-1), 4.37-4.09 (m, 5 H, CH_2CH=CH_2, H-5, 6, 6′), 2.16, 2.07 (2s, 6 H, 2 COCH_3). Anal. calcd for $C_{27}H_{28}O_{10}$: C, 63.28; H, 5.51. Found: C, 63.03; H, 5.47.

4.4. Allyl 3,4-di-*O*-benzoyl-α-D-mannopyranoside 9

A solution of **8** (5.6 g, 10.9 mmol) in MeOH (160 mL) containing 0.5% HCl was stirred at rt for 12 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that the starting material had disappeared. The mixture was neutralized with Et_3N and then concentrated to dryness. The residue was partitioned between water and CH_2Cl_2, the organic layer was dried over Na_2SO_4 and concentrated to a syrup. Purification of the residue by flash chromatography (2:1 petroleum ether–EtOAc) gave **9** as a syrup (4.4 g, 93%): $[\alpha]_D$ −18.6 (*c* 2.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400MHz): δ 8.00–7.32 (m, 10 H, 2 PhH), 5.97 (m, 1 H, CH=CH_2), 5.82–5.75 (m, 2 H, H-3, 4), 5.39–5.27 (m, 2 H, CH=CH_2), 5.05 (d, 1 H, $J_{1,2}$=1.6 Hz, H-1), 4.31-3.70 (m, 6 H, CH_2CH=CH_2, H-2, 5, 6, 6′). Anal. calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.23; H, 5.68.

4.5. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside 10

A solution of allyl 3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside **5** (2.90 g, 5.45 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate **3** (4.44 g, 6.00 mmol) in dry CH_2Cl_2 (60 mL) was stirred with dried molecular sieves (4 Å, 2 g) under N_2 for 15 min, and then TMSOTf (105 μL, 0.55 mmol) was added. After 1 h, the reaction mixture was neutralized with Et_3N, filtered and the filtrate was concentrated. Purification of the residue by flash chromatography (3:1 petroleum ether-EtOAc) gave **10** as a syrup (5.33 g, 88%): $[\alpha]_D$ −37.9 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.10–7.20 (m, 35 H, 5 BzH), 6.14–5.86 (m, 6 H, CH=CH_2, 2 H-4, 2 H-3, H-2), 5.31 (dd, 1 H, ^2J=1.4 Hz, $^3J_{trans}$=18.5 Hz, CH=CH_2), 5.22 (dd, 1 H, ^2J=1.3 Hz, $^3J_{cis}$=10.4 Hz, CH=CH_2), 5.28 (d, 1 H, $J_{1,2}$=1.6 Hz, H-1), 5.22 (d, 1 H, $J_{1,2}$=1.6 Hz, H-1), 4.69–4.40 (m, 7 H, H-2, 2 H-5, 4 H-6), 4.27-3.99 (m, 2 H, CH_2CH=CH_2). Anal. calcd for $C_{64}H_{54}O_{18}$: C, 69.18; H, 4.90. Found: C, 68.98; H, 4.99.

4.6. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate 11

A mixture of compound **10** (3.82 g, 3.44 mmol) and $PdCl_2$ (100 mg) in MeOH (150 mL) was stirred vigorously for 4 h at rt, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was filtered through Celite and the filtrate was concentrated to dryness. The resulting compound was dissolved in CH_2Cl_2 (40 mL), then CCl_3CN (1.5 ml, 15 mmol) and DBU (100 μL, 0.71 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 **11** (3.34 g, 80% two steps): $[\alpha]_D$ −24.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1 H, NH), 8.09–7.26 (m, 35 H, 7 BzH), 6.64 (d, 1 H, $J_{2,1}$=1.9 Hz, H-1), 6.19-5.93 (m, 5 H, 2 H-4, 2 H-3, 1 H-2), 5.37 (d, 1 H, $J_{1',2'}$=1.5 Hz, H-1), 4.75–4.48 (m, 7 H, H-2, 2 H-5, 4 H-6). Anal. calcd for $C_{63}H_{50}Cl_3NO_{18}$: C, 62.26; H, 4.15. Found: C, 62.08; H, 4.19.

4.7. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranoside 12

A solution of **7** (1.5 g, 3.19 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**3**) (2.60 g, 3.51 mmol) in dry CH_2Cl_2 (40 mL) was stirred with dried molecular sieves (4 Å, 1 g) under N_2 for 15 min, and then TMSOTf (50 μL) was added. After 1 h, the reaction mixture was neutralized with Et_3N, filtered and the filtrate was concentrated. Purification of the residue by flash chromatography (3:1 petroleum ether–EtOAc) gave **12** as a syrup (3.35 g, 92%): $[\alpha]_D$ −45.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.01–7.26 (m, 30 H, 6 BzH), 6.10–5.86 (m, 6 H, CH=CH_2, 2 H-4, 2 H-3, H-2), 5.35-5.31 (dd, 1 H, ^2J=1.5 Hz, $^3J_{trans}$=17.2 Hz, CH=CH_2), 5.27–5.24 (dd, 1 H, ^2J=1.3 Hz, $^3J_{cis}$=10.4 Hz, CH=CH_2), 5.25 (d, 1 H, $J_{2,1}$=1.7 Hz, H-1), 5.21 (d, 1 H, $J_{2,1}$=1.7 Hz, H-1), 4.72-4.01 (m, 9 H, CH_2CH=CH_2, H-2, 2 H-5, 4 H-6), 2.17 (s, 3 H, COCH_3). Anal. calcd for $C_{59}H_{52}O_{18}$: C, 67.55; H, 5.00. Found: C, 67.75; H, 5.04.

4.8. ,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate 13

A mixture of compound **12** (2.30 g, 2.19 mmol) and $PdCl_2$ (70 mg) in MeOH (100 mL) was stirred vigorously for 4 h at rt, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was filtered through Celite, and the filtrate was concentrated to dryness. The resulting compound was dissolved in CH_2Cl_2 (30 mL), then CCl_3CN (1.0 mL, 10 mmol) and DBU (50 μL) 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 **13** (2.05 g, 81% two steps): $[\alpha]_D$ −43.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1 H, NH), 8.09–7.26 (m, 30 H, 6 BzH), 6.65 (d, 1 H, $J_{2',1}$=1.7 Hz, H-1), 6.19-5.89 (m, 5 H, 2 H-4, 2 H-3, H-2), 5.35 (d, 1 H, $J_{2',1'}$=1.3 Hz, H-1), 4.80–4.34 (m, 7 H, H-2, 2 H-5, 4 H-6), 2.17 (s, 3 H,

COCH_3). Anal. calcd for $C_{58}H_{48}Cl_3NO_{18}$: C, 60.40; H, 4.19. Found: C, 60.61; H, 4.16.

4.9. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-3,4-di-*O*-benzoyl-α-D-mannopyranoside 14

A solution of **13** (1.76 g, 1.53 mmol) and 3,4-di-*O*-benzoyl-α-D-mannopyranoside **9** (647 mg, 1.51 mmol) in dry CH_2Cl_2 (30 mL) was stirred with dried molecular sieves (4 Å, 1 g) under N_2 for 15 min, and then TMSOTf (30 μL) was added. After 1 h, the reaction mixture was neutralized with Et_3N, filtered and the filtrate was concentrated. Purification of the residue by column chromatography (2:1 petroleum ether-EtOAc) gave **14** as a syrup (1.96 g, 91%): $[\alpha]_D$ −33.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–7.32 (m, 40 H, 8 Bz*H*), 6.13–5.72 (m, 8 H, C*H*=CH_2, H-2, 3 H-3, 3 H-4), 5.44 (dd, 1 H, ^2J=1.5 Hz, $^3J_{trans}$=17.2 Hz, CH=CH_2), 5.28 (dd, 1 H, ^2J=1.3 Hz, $^3J_{cis}$=10.5 Hz, CH=CH_2), 5.29 (d, 1 H, $J_{1,2}$=1.5 Hz, H-1), 5.23 (d, 1 H, $J_{1,2}$=1.5 Hz, H-1), 5.05 (d, 1 H, $J_{1,2}$=1.5 Hz, H-1), 4.76 (dd, 1 H, H-6), 4.65 (dd, 1 H, H-6), 4.46–4.10 (m, 9 H, CH_2CH=CH_2, 3 H-5, 2 H-6, 2 H-2), 3.90 (dd, 1 H, H-6), 3.71 (dd, 1 H, H-6), 2.11 (s, 3 H, COCH_3). Anal. calcd for $C_{79}H_{70}O_{25}$: C, 66.85; H, 4.97; Found: C, 67.07; H, 4.92.

4.10. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranoside 15

To a solution of **14** (1.20 g, 0.84 mmol) in pyridine (20 mL) Ac_2O (2 mL) was added. After the mixture was stirred for 3 h at rt, it 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 (2:1 petroleum ether–EtOAc) quantitatively gave **15** as a syrup: $[\alpha]_D$ −29.3 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.27 (m, 40 H, 8 Bz*H*), 6.14–5.79 (m, 8 H, C*H*=CH_2, H-2, 3 H-3, 3 H-4), 5.53 (dd, 1 H, H-2), 5.46 (dd, 1 H, ^2J=1.5 Hz, $^3J_{trans}$=17.2 Hz, CH=CH_2), 5.31 (dd, 1 H, ^2J=1.3 Hz, $^3J_{cis}$=10.5 Hz, CH=CH_2), 5.23 (d, 1 H, $J_{1,2}$=1.5 Hz, H-1), 5.20 (d, 1 H, $J_{1,2}$=1.5 Hz, H-1), 5.02 (d, 1 H, $J_{1,2}$=1.5 Hz, H-1), 4.73 (dd, 1 H, H-6), 4.62 (dd, 1 H, H-6), 4.47–4.09 (m, 8 H, CH_2CH=CH_2, 3 H-5, 2 H-6, H-2), 3.92 (dd, 1 H, H-6), 3.65 (dd, 1 H, H-6), 2.19, 2.08 (2s, 6 H, 2 COCH_3). Anal. calcd for $C_{81}H_{72}O_{26}$: C, 66.57; H, 4.97; Found: C, 66.34; H, 5.01.

4.11. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[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-di-*O*-benzoyl-α-D-mannopyranoside 16

A solution of **14** (1.65 g, 1.16 mmol) and **11** (1.56 g, 1.28 mmol) in dry CH_2Cl_2 (30 mL) was stirred with dried molecular sieves (4 Å, 1.5 g) under N_2 for 15 min, and then TMSOTf (20 μL) was added. After 1 h, the reaction mixture was neutralized with Et_3N, filtered and the filtrate was concentrated. Purification of the residue by column chromatography (1.5:1 petroleum ether–EtOAc) gave **16** as a syrup (2.87 g, 90%): $[\alpha]_D$ −45.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–6.93 (m, 75 H, 15 Bz*H*), 6.20–5.75 (m, 13 H, C*H*=CH_2, 5 H-4, 5 H-3, 2 H-2), 5.60 (d, 1 H, $J_{1,2}$=1.6 Hz, H-1), 5.58 (d, 1 H, $J_{1,2}$=1.6 Hz, H-1), 5.41 (dd, 1 H, ^2J=1.5 Hz, $^3J_{trans}$=18.7 Hz, CH=CH_2), 5.39 (d, 1 H, $J_{1,2}$=1.6 Hz, H-1), 5.28 (dd, 1 H, ^2J=1.3 Hz, $^3J_{cis}$=11.8 Hz, CH=CH_2), 5.27 (d, 1 H, $J_{1,2}$=1.6 Hz, H-1), 5.12 (d, 1 H, $J_{1,2}$=1.6 Hz, H-1), 1.95 (s, 3 H, COCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.66 (1 C, *C*OCH$_3$), 166.17, 166.03, 165.70, 165.59, 165.59, 165.59, 165.44, 165.19, 165.19, 165.19, 165.13, 164.94, 164.94, 164.66, 164.65 (15 C, 15 *C*OPh), 133.4-128.0 (91 C, 15 Ph, CH_2CH=CH_2), 117.80 (CH_2CH=CH_2), 100.04, 99.65, 99.42, 98.36, 98.04 (5 C-1, $^2J_{C1\text{-}H1}$=170-176.8 Hz), 78.95, 77.66, 77.20 (3 C-2), 20.5 (1 C, CO*C*H$_3$). Anal. calcd for $C_{140}H_{118}O_{42}$: C, 68.01; H, 4.81. Found: C, 68.29; H, 4.77.

4.12. A one-pot procedure for the preparation of the pentasaccharide 16

A solution of **9** (0.9 g, 2.10 mmol) and **13** (2.45 g, 2.13 mmol) in dry CH_2Cl_2 (100 mL) was stirred with activated 4 Å molecular sieves (2 g) at rt under N_2 for 20 min. Then the reaction mixture was cooled to −45°C, and TMSOTf (10 μL) was added. After 30 min, temperature was allowed to rise to rt. After the reaction mixture was stirred for further 1 h, to the reaction mixture was added **11** (2.83 g, 2.33 mmol) under N_2 at rt. The reaction mixture was stirred for 1 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was neutralized with Et_3N, filtered and the filtrate was concentrated. Purification of the resultant residue by column chromatography with 2:1 petroleum ether–EtOAc as eluent gave **16** (4.7 g, 83%).

4.13. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[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-di-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate 17

A mixture of compound **16** (1.00 g, 0.36 mmol) and $PdCl_2$ (30 mg) in MeOH (50 mL) was stirred vigorously for 4 h at rt, TLC (1.5:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was filtered through Celite and the filtrate was concentrated to dryness. The resulting compound was dissolved in CH_2Cl_2 (15 mL), then CCl_3CN (0.5 ml, 5 mmol) and DBU (50 μL) 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 pentasaccharide donor **17** (798 mg, 85% two steps): $[\alpha]_D$ −35.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1 H, N*H*), 8.05–6.81 (m, 75 H, 15 Bz*H*), 6.55 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 6.16–5.87 (m, 12 H, 5 H-4, 5 H-3, 2 H-2), 5.70 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 5.63 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 5.38 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 5.36 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 4.99–3.60 (m, 18 H, 3 H-2, 5 H-5, 10 H-6), 1.93 (s, 3 H, COCH_3). Anal. calcd for $C_{139}H_{114}Cl_3NO_{42}$: C, 64.79; H, 4.46. Found: C, 64.56; H, 4.50.

4.14. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[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-di-*O*-benzoyl-α-D-mannopyranoside 18

A solution of **16** (1.2 g, 0.44 mmol) in MeOH (100 mL) containing 0.5% HCl was stirred at rt for 12 h, at the end of which time TLC (1.5:1 petroleum ether–EtOAc) indicated that the starting material had disappeared. The mixture was neutralized with Et_3N, and then concentrated to dryness. The residue was partitioned between water and CH_2Cl_2, the organic layer was dried over Na_2SO_4, and concentrated to a syrup. Purification of the residue by column chromatography (1.5:1 petroleum ether–EtOAc) gave **18** as a syrup (978 mg, 92%): $[\alpha]_D$ −62.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.03–6.96 (m, 75 H, 15 Bz*H*), 6.13–5.71 (m, 13 H, C*H*=CH_2, 5 H-4, 5 H-3, 2 H-2), 5.56 (d, 1 H, $J_{1,2}$ = 1.2 Hz, H-1), 5.51 (d, 1 H, $J_{1,2}$ = 1.2 Hz, H-1), 5.40 (dd, 1 H, ^2J = 1.5 Hz, $^3J_{trans}$ = 17.2 Hz, CH=CH_2), 5.31 (d, 1 H, $J_{1,2}$ = 1.2 Hz, H-1), 5.29 (dd, 1 H, ^2J = 1.3 Hz, $^3J_{cis}$ = 10.4 Hz), 5.25 (d, 1 H, $J_{1,2}$ = 1.2 Hz, H-1), 5.08 (d, 1 H, $J_{1,2}$ = 1.2 Hz, H-1), 4.86–3.41 (m, 20 H,CH_2CH=CH_2, 3 H-2, 5 H-5, 10 H-6). Anal. calcd for $C_{138}H_{116}O_{41}$: C, 68.20; H, 4.81. Found: C, 68.41; H, 4.71.

4.15. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[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-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)]-3,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-[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-di-*O*-benzoyl-α-D-mannopyranoside 19

A solution of **17** (550 mg, 0.21 mmol) and **18** (461 mg, 0.19 mmol) in dry CH_2Cl_2 (20 mL) was stirred with dried molecular sieves (4 Å, 0.5 g) under N_2 for 15 min, and then TMSOTf (5 μL) was added. After 1 h, the reaction mixture was neutralized with Et_3N, filtered and the filtrate was concentrated. Purification of the residue by a column chromatography (1.3:1 petroleum ether–EtOAc) gave **19** as a syrup (460 mg, 50%): $[\alpha]_D$ −33.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.02–6.60 (m, 150 H, 30 Bz*H*), 6.40–5.82 (m, 25 H, C*H*=CH_2 10 H-4, 10 H-3, 4 H-2), 5.70 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 5.62 (m, 2 H, 2 H-1), 5.48 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 5.39(d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 5.34 (dd, 1 H, ^2J = 1.3 Hz, $^3J_{trans}$ = 17.1 Hz, CH=CH_2), 5.32 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 5.28 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 5.24 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 5.22 (dd, 1 H, ^2J = 1.3 Hz, $^3J_{cis}$ = 10.4 Hz, CH=CH_2), 5.20 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 4.98 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 4.93–3.26 (m, 38 H, CH_2CH=CH_2, 10 H-5, 20 H-6·6 H-2), 1.87 (s, 3 H, COCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.69 (1 C, *C*OCH$_3$), 166.2-164.5 (30 C, 30 *C*OPh), 133.4–127.5 (181 C, 30 Ph, *C*H=CH_2), 117.7 (CH=*C*H_2), 100.07, 99.99, 99.72, 99.55, 99.43, 99.34, 98.89, 98.26, 98.19, 98.17 (10 C-1), 20.4 (1 C, CO*C*H$_3$). Anal. calcd for $C_{275}H_{228}O_{82}$: C, 68.18; H, 4.74. Found: C, 68.32; H, 4.80.

4.16. Allyl α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)]-α-D-mannopyranoside 1

Compound **16** (758 mg, 0.28 mmol) was dissolved in an ammonia-saturated solution of 1:9 CH_2Cl_2–CH_3OH (100 mL) at 40°C. After 24 h, the reaction mixture was concentrated to about 10 mL, and then CH_2Cl_2 (100 mL) was added. The resultant precipitate was filtered and washed four times with CH_2Cl_2 to afford **1** as white solid (219 mg, 91%): $[\alpha]_D$ +12.3 (*c* 1.0, H_2O); ^1H NMR (D_2O, 400 MHz): δ 5.85 (m, 1 H, C*H*=CH_2), 5.27–5.17 (m, 2 H, CH=CH_2), 5.19, 5.03, 5.02, 4.94, 4.93 (5s, 5 H, 5 H-1); ^{13}C NMR (100 MHz, D_2O): 133.52 (1 C, CH_2CH=CH_2), 118.71 (1 C, CH_2CH=*C*H_2), 102.23, 102.23, 100.7, 98.12, 97.50 (5 C-1). MALDI-TOF MS calcd for $C_{33}H_{56}O_{26}$: 868.79 [M]. found: 891.65 $(M+Na)^+$.

4.17. Allyl α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)]-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)]-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)]-α-D-mannopyranoside 2

Compound **19** (386 mg, 0.08 mmol) was dissolved in an ammonia-saturated solution of 1:9 CH_2Cl_2–CH_3OH (120 mL) at 40°C. After 24 h, the reaction mixture was concentrated to about 30 mL, and then CH_2Cl_2 (100 mL) was added. The resultant precipitate was filtered and washed four times with CH_2Cl_2 to afford **2** as white solid (127 mg, 95%): $[\alpha]_D$ +35.8 (*c* 1.0, H_2O); ^1H NMR (D_2O, 400 MHz): δ 5.94 (m, 1 H, C*H*=CH_2), 5.35–5.25 (2 H, CH=CH_2), 5.25–5.02 (10 H-1); ^{13}C NMR (100 MHz, D_2O): 133.6 (1 C, CH_2CH=CH_2), 118.7 (1 C, CH_2CH=*C*H_2), 101.97, 101.97, 101.97, 101.97, 100.46, 100.38, 98.11, 97.96, 97.96, 97.39 (10 C-1). MALDI-TOF MS calcd for $C_{63}H_{106}O_{51}$: 1679.50 [M]. found: 1702.61 $(M+Na)^+$.

Acknowledgements

This work was supported by the Beijing Natural Science Foundation (6021004).

References

1. Goodman, D. S.; Teplitz, E. D.; Wishner, A.; Klein, R. S.; Burk, P. G.; Hershenbaum, E. *J. Am. Acad. Dermatol.* **1987**, *17*, 210–218.
2. Bodey, G. P. *Am. J. Med.* **1984**, *77*, 13–22.
3. Spebar, M. J.; Pruitt, B. A. *J. Trauma* **1981**, *21*, 237–243.
4. Silverman, S. J.; Luangjarmekorn, L.; Greenspan, D. *J. Oral Med.* **1984**, *39*, 194–201.
5. Nakajima, T.; Ballou, C. E. *J. Biol. Chem.* **1974**, *249*, 7679–7684.
6. Suzuki, S.; Shibata, N.; Kobayashi, H. In *Fungal Cell Wall and Immune Response*, *NATA ASI Ser.*; Latgé, J. P.; Boucias, D., Eds.; Springer-Verlag: Berlin, 1991; Vol. H53, pp. 111–121.
7. Kobayashi, H.; Kojimahara, T.; Takahashi, K.; Takihawa, M.; Takahashi, S.; Shibata, N.; Okawa, Y.; Suzuki, S. *Carbohydr. Res.* **1991**, *214*, 131–145.
8. Kanbe, T.; Cutler, J. E. *Infect. Immun.* **1994**, *62*, 1662–1668.
9. Stratford, M. *Yeast* **1992**, *8*, 635–645.
10. Nelson, R. D.; Shibata, N.; Podzorski, R. P.; Herron, M. J. *Clin. Microbiol. Rev.* **1991**, *4*, 1–19.
11. Podzorski, R. P.; Gray, G. R.; Nelson, R. D. *J. Immunol.* **1990**, *144*, 707–716.
12. Ning, J.; Yi, Y.; Kong, F. *Tetrahedron Lett.* **2002**, *43*, 5545–5549.
13. Ning, J.; Wang, H.; Yi, Y. *Tetrahedron Lett.* **2002**, *43*, 7349–7352.
14. Wang, H.; Ning, J. *J. Org. Chem.* **2003**, *68*, 2521–2524.
15. Ning, J.; Heng, L.; Kong, F. *Tetrahedron Lett.* **2002**, *43*, 673–675.
16. Ning, J.; Heng, L.; Kong, F. *Carbohydr. Res.* **2002**, *337*, 1159–1164.
17. Kobayashi, H.; Komido, M.; Watanabe, M.; Matsuda, K.; Ikeda-Hasebe, T.; Suzuki, M.; Oyamada, H.; Shibata, N.; Suzuki, S. *Infect. Immun.* **1994**, *62*, 4425–4431.
18. Heng, L.; Ning, J.; Kong, F. *J. Carbohydr. Chem.* **2001**, *20*, 285–296.