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Convergent synthesis of a galactofuranosylated mannan, the repeating unit of *Trichophyton mentagrophytes* IFO 5466 and *Trichophyton rubrum* IFO 5467

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Abstract—An undecasaccharide repeating unit of the polysaccharide of *Trichophyton mentagrophytes* IFO 5466 and *Trichophyton rubrum* IFO 5467, α-D-Man*p*-(1→2)-α-D-Man*p*-(1→6)-[β-D-Gal*f*-(1→3)]-α-D-Man*p*-(1→2)-[β-D-Gal*f*-(1→3)]-α-D-Man*p*-(1→2)-α-D-Man*p*-(1→2)-α-D-Man*p*-(1→6)-α-D-Man*p*-(1→2)-[β-D-Gal*f*-(1→3)]-Man*p* was synthesized as its allyl glycoside by coupling of a octasaccharide trichloroacetimidate donor **19** with a trisaccharide acceptor **28**. The donor **19** and **28** were obtained with allyl 3-*O*-acetyl-2-*O*-benzoyl-α-D-mannopyranoside **2**, allyl 3-*O*-acetyl-4,6-di-*O*-benzoyl-α-D-mannopyranoside **9**, allyl 3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside **13**, 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate **26** and 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl trichloroacetimidate **16** as the key synthons by appropriate combination through simple transformation.

1. Introduction

The anthropophilic dermatophytes *Trichophyton mentagrophytes* and *Trichophyton rubrum* cause chronic, relatively uninflamed, skin infections of the feet, groin and body. Around 90% of chronic dermatophyte infections are caused by the fungi *T. mentagrophytes* and *T. rubrum*.[1] One of the causes of the chronic infection resides in the immunosuppressive effects of the cell wall components of these organisms.[2] The cell wall polysaccharides of these fungi are known to be the major immunologically active substances.[3] The structures of the cell wall polysaccharides of *T. mentagrophytes* and *T. rubrum* have been studied and characterized, with two kinds of polysaccharides being found.[4] One is mannan consisting of an α-(1→6)-linked backbone with α-(1→2)-linked monosaccharide side chains, while the second one is galactomannan consisting of an α-(1→2)- and α-(1→6)-linked mannose backbone with galactofuranose side chains. A possible structure of the galactomannan is shown in Figure 1.

The synthesis of the above galactomannan may be useful for understanding the role galactofuranose plays

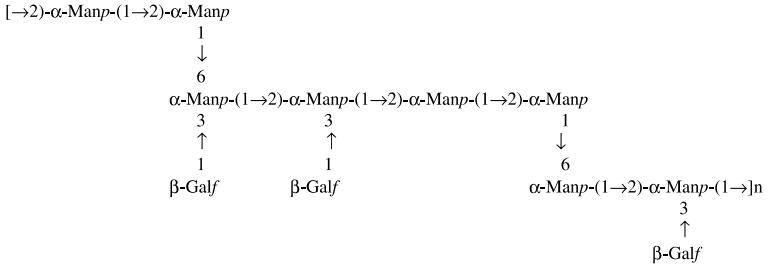

Figure 1. Possible structure of galactomannan of *T. mentagrophytes* IFO 5466 and *T. rubrum* IFO 5467.

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in microorganisms and for studying the biosynthesis of furanosyl-containing glycoconjugates. The galactomannan could also be used an inhibitor to probe the development of infections or to develop diagnostic methods, or to be used as a vaccine. The synthesis of the above galactomannan is also of interest for synthetic chemists because of its large size and complex structure, which contains different mannose linkages and rare galactofuranose residues. So far there have been very few reports dealing with the synthesis of galactofuranosylated mannan.[5] We report herein a convergent synthesis of an undecasaccharide, the repeating unit of the polysaccharide of *T. mentagrophytes* IFO 5466 and *T. rubrum* IFO 5467.

2. Results and discussion

We previously reported a method[6] for mannose oligosaccharide syntheses using unprotected or lightly protected sugars as the glycosyl acceptors, resulting in a variety of complex oligosaccharides being synthesized efficiently.[7] In the present research, a concise syntheses of the undecasaccharide repeating unit of the polysaccharide of *T. mentagrophytes* IFO 5466 and *T. rubrum* IFO 5467 was achieved. Scheme 1 shows the syntheses of octasaccharides donor **19**. Allyl 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside **1**[8] was chosen as the starting material. Benzoylation of **1** followed by debenzylidenation afforded the monosaccharide acceptor **2**. Subsequent coupling with perbenzoylated α-(1→2)-linked mannosyl disaccharide trichloroacetimidate **3**[9] selectively produced the (1→6)-linked trisaccharide **4** (79%). The regioselective coupling was confirmed by benzoylation of **4** to give **5**, which showed in its ^{1}H NMR spectrum a new signal at δ 5.88 ppm with $J_{3,4} = J_{4,5} = 10.1$ Hz for H-4 compared to **4**. Deallylation with $PdCl_2$[10] followed by trichloroacetimidate formation[11] yielded trisaccharide donor **7**. The other mannose component containing a potential hydroxyl group at C-3 was prepared from allyl 3-*O*-acetyl-2-*O*-chloroacetyl-α-D-mannopyranoside **8**. Benzoylation of **8** followed by dechloroacetylation with thiourea afforded monosaccharide acceptor **9**. Condensation of **9** with donor **7** gave tetrasaccharide **10** (80%), and subsequent deallylation followed by trichloroacetimidate formation produced tetrasaccharide donor **12** (73%), which contained two potential hydroxyl groups at C-3 and C-3′. Coupling of donor **12** with disaccharide acceptor **13**[9] afforded hexasaccharide **14** (68%), whose selective deacetylation[12] with MeCOCl/MeOH–CH_2Cl_2 gave hexasaccharide acceptor **15** (73%) with C-3″ and C-3‴ free hydroxyl groups. Coupling of **15** with 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl trichloroacetimidate **16**[13] gave octasaccharide **17** (73%); subsequent deallylation and trichloroacetimidate formation afforded octasaccharide donor **19** (71%).

Trisaccharide acceptor **28** was similarly prepared as shown in Scheme 2. Thus, allyl 4,6-*O*-benzylidene-α-D-mannopyranoside **20** was selectively coupled with **16** to give β-(1→3)-linked disaccharide **21** in good yield (71%). The regio- and stereoselectivity were confirmed by acetylation of **21**. The obtained product **22** showed in its NMR spectrum a sharp singlet at δ 5.46 for H-1′ indicating β-linkage, and a doublet of doublets at 5.42 with $J_{1,2}$ 1.4 Hz and $J_{2,3}$ 3.5 Hz for H-2 indicating the 3-glycosylation. Hydrolysis of **22** to cleave benzylidene group followed by benzoylation and selective deacetylation produced disaccharide acceptor **25**. Condensation of **25** with the donor 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate **26** gave trisaccharide **27**, and subsequent deacetylation gave the trisaccharide acceptor **28**. Finally, coupling of acceptor **28** with octasaccharide donor **19** afforded the undecasaccharide **29** (79%); debenzoylation in a saturated solution of NH_3 in methanol yielded target compound **30** (85%). The ^{1}H and ^{13}C NMR spectra of **30** showed all of the characteristic signals such as at δ 5.20, 5.16, 5.15, 5.11, 5.07, 5.02, 4.99 (7s, 11H) for H-1; δ 104.88, 104.85, 104.35 for Gal*f* C-1; 102.28, 101.71, 101.61, 100.76, 100.69, 98.26, 98.10, 97.59 for Man*p* C-1. A bioassay of sample **30** is currently in progress, with the results to be reported in due course.

3. Conclusion

In summary, a convergent synthesis of a complex galacto-mannosyl undecamer was achieved via a regio- and stereoselective manner with readily accessible materials. The described method is suitable for the preparation of other oligosaccharides consisting of mannan backbone linked by either an α-(1→2) or α-(1→6) with galactofuranose side chains.

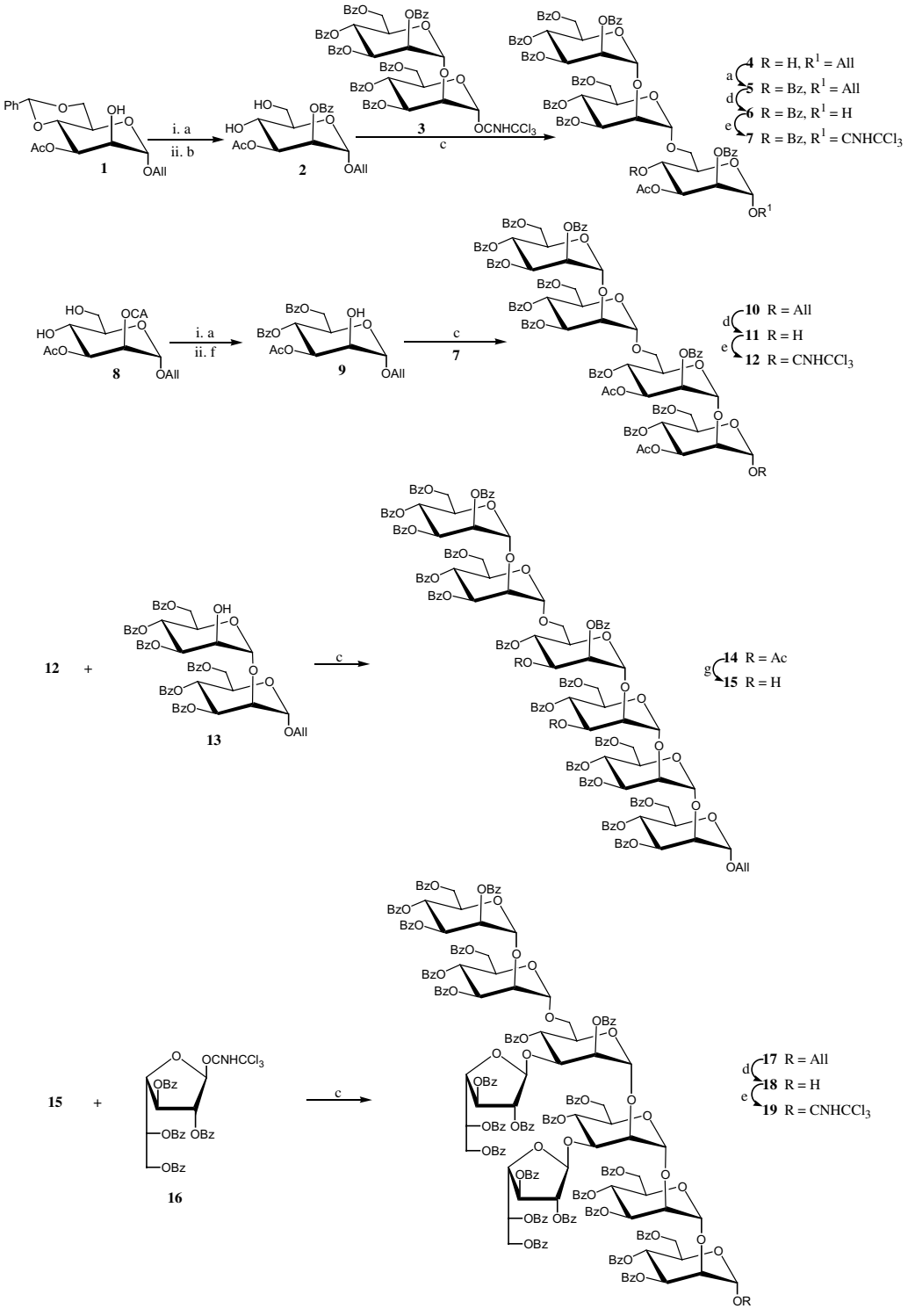
4. Experimental

4.1. General methods

Optical rotations were determined at 25 °C with a Perkin–Elmer Model 241-Mc automatic polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker ARX 400 spectrometers (400 MHz for ^{1}H, 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 or recorded with a VG PLATFORM mass spectrometer using the ESI mode. 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. General procedure for the glycosylations

A mixture of the donor and acceptor was dried together under high vacuum for 2 h, then dissolved in anhydrous CH_2Cl_2. TMSOTf (0.05 equiv) was added dropwise at −20 °C with nitrogen protection. The reaction mixture

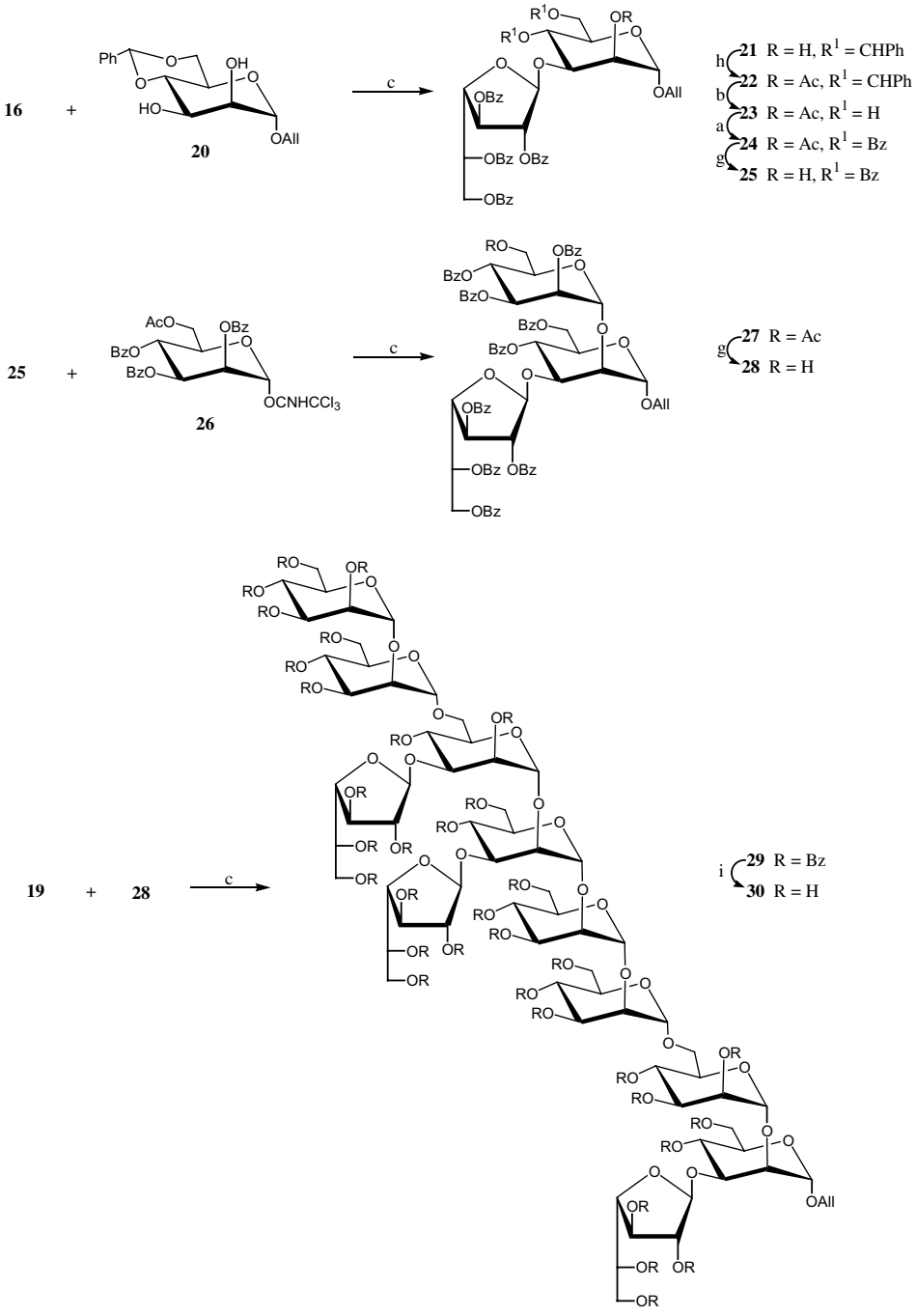


Scheme 1. Reagents and conditions: (a) BzCl–pyridine, 85% for **5**, 88% for **24**; (b) 90% TFA, rt, 2 h, 87% for **2**, 82% for **23**; (c) TMSOTf (0.01–0.05 equiv), CH_2Cl_2, −20 to 0 °C, 2–4 h, 79% for **4**, 80% for **10**, 68% for **14**, 73% for **17**, 71% for **21**, 77% for **27** and 79% for **29**, respectively; (d) $PdCl_2$, CH_3OH, rt, 4 h, 81% for **6**, 81% for **11**, 80% for **18**; (e) CCl_3CN, DBU, CH_2Cl_2, 2 h, 88% for **7**, 90% for **12**, 89% for **19**; (f) $(NH_2)_2CS$, CH_2Cl_2–CH_3OH, reflux, 16 h, 84%; (g) methanol/2–6% CH_3COCl, rt, 12 h, 73% for **15**, 75% for **25**, 81% for **28**; (h) Ac_2O–pyridine, 96%; (i) satd NH_3–MeOH, rt, 72 h, 85%.

was stirred for 3 h, during which time the temperature was gradually increased to ambient temperature. The mixture was then neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica-gel column, gave the desired products.

4.3. Allyl 3-*O*-acetyl-2-*O*-benzoyl-α-D-mannopyranoside 2

Compound **2** was obtained from **1**[8] by benzoylation followed by debenzylidenation. To a solution of **1**



Scheme 2. Reagents and conditions: (a) BzCl–pyridine, 85% for **5**, 88% for **24**; (b) 90% TFA, rt, 2 h, 87% for **2**, 82% for **23**; (c) TMSOTf (0.01–0.05 equiv), CH_2Cl_2, −20 to 0 °C, 2–4 h, 79% for **4**, 80% for **10**, 68% for **14**, 73% for **17**, 71% for **21**, 77% for **27** and 79% for **29**, respectively; (d) $PdCl_2$, CH_3OH, rt, 4 h, 81% for **6**, 81% for **11**, 80% for **18**; (e) CCl_3CN, DBU, CH_2Cl_2, 2 h, 88% for **7**, 90% for **12**, 89% for **19**; (f) $(NH_2)_2CS$, CH_2Cl_2–CH_3OH, reflux, 16 h, 84%; (g) methanol/2–6% CH_3COCl, rt, 12 h, 73% for **15**, 75% for **25**, 81% for **28**; (h) Ac_2O–pyridine, 96%; (i) satd NH_3–MeOH, rt, 72 h, 85%.

(0.70 g, 2.0 mmol) in pyridine (5 mL) was added benzoyl chloride (0.28 mL, 2.4 mmol). After stirring the mixture overnight at rt, TLC (2:3 petroleum ether–EtOAc) indicated that the reaction was complete. Methanol (2 drops) was added to the reaction mixture and stirring continued for 10 min. Water (10 mL) was added, the mixture extracted with CH_2Cl_2 (3×10 mL), the extracts were washed with 1 M HCl and satd aq $NaHCO_3$, dried over Na_2SO_4 and concentrated. The residue was dissolved in 90% TFA (10 mL) and stirred for 2 h at rt, after which TLC (2:1 petroleum ether–EtOAc) indicated that the reaction had gone to completion. The mixture was diluted with toluene (40 mL) and concentrated in vacuo directly. The residue was passed through a short silica-gel column with 2.5:1 petroleum ether–EtOAc as the eluent to give **2** (0.55 g, 75% for two steps) as a syrup. $[\alpha]_D^{25} = -3.5$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06–7.45 (m, 5H, *Ph*), 5.97–5.97 (m, 1H,

–CH_2–C*H*=CH_2), 5.49 (dd, 1H, $J_{1,2} = 1.7$ Hz, $J_{2,3} = 3.3$ Hz, H-2), 5.33 (dd, 1H, $J_{2,3} = 3.3$ Hz, $J_{3,4} = 10.0$ Hz, H-3), 5.35–5.23 (m, 2H, –CH_2–CH=CH_2), 4.98 (d, 1H, $J_{1,2} = 1.7$ Hz, H-1), 4.26–4.03 (m, 3H, H-4, –CH_2–CH=CH_2), 3.95–3.94 (m, 2H, H-6), 3.84–3.81 (m, 1H, H-5), 2.05 (s, 3H, CH_3CO). Anal. Calcd for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05. Found: C, 59.22; H, 6.10.

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

As described in the general procedure, **2** (0.40 g, 1.1 mmol) and **3**[9] (1.1 g, 0.92 mmol) were coupled, and the product purified by silica-gel column chromatography with 2.5:1 petroleum ether–EtOAc as the eluent to give **4** (1.0 g, 79%) as a foamy solid. $[\alpha]_D^{25} = -78.6$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.23 (m, 40H, 8*Ph*), 6.10 (dd, 1H, $J_{3'',4''} = J_{4'',5''} = 10.0$ Hz, H-4″), 6.03 (dd, 1H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz, H-4′), 6.06–5.90 (m, 3H, H-3′, H-3″, –CH_2–C*H*=CH_2), 5.85 (dd, 1H, $J_{1'',2''} = 1.8$ Hz, $J_{2'',3''} = 3.0$ Hz, H-2″), 5.50 (dd, 1H, $J_{1,2} = 1.6$ Hz, $J_{2,3} = 3.2$ Hz, H-2), 5.37–5.20 (m, 4H, H-1″, H-3, –CH_2–CH=CH_2), 5.07 (d, 1H, $J_{1',2'} = 1.5$ Hz, H-1′), 4.95 (d, 1H, $J_{1,2} = 1.6$ Hz, H-1), 4.68–3.85 (m, 13H, H-2′, H-4, H-5, H-6, –CH_2–CH=CH_2), 2.07 (s, 3H, CH_3CO) Anal. Calcd for $C_{79}H_{70}O_{25}$: C, 66.85; H, 4.97. Found: C, 67.09; H, 5.03.

4.5. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-3-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-mannopyranoside 5

To a solution of **4** (0.98 g, 0.69 mmol) in pyridine (10 mL) was added benzoyl chloride (97 μL, 0.83 mmol). After stirring the mixture overnight at rt, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Methanol (2 drops) was added to the reaction mixture, and stirring was continued for 10 min. Water (20 mL) was added, the mixture extracted with CH_2Cl_2 (3×20 mL), the extract washed with 1 M HCl and satd aq $NaHCO_3$, dried over Na_2SO_4 and concentrated. Purification by flash chromatography (2.5:1 petroleum ether–EtOAc) gave **5** as a foamy solid (0.90 g, 85%). $[\alpha]_D^{25} = -70.2$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.26 (m, 45H, 9*Ph*), 6.10 (dd, 1H, $J_{3'',4''} = J_{4'',5''} = 10.1$ Hz, H-4″), 6.06–5.96 (m, 4H, H-3′, H-3″, H-4′, –CH_2–C*H*=CH_2), 5.88 (dd, 1H, $J_{3,4} = J_{4,5} = 10.1$ Hz, H-4), 5.84 (dd, 1H, $J_{1'',2''} = 1.1$ Hz, $J_{2'',3''} = 3.0$ Hz, H-2″), 5.74 (dd, 1H, $J_{2,3} = 3.3$ Hz, $J_{3,4} = 10.1$ Hz, H-3), 5.60 (dd, 1H, $J_{1,2} = 1.4$ Hz, $J_{2,3} = 3.3$ Hz, H-2), 5.46–5.29 (m, 2H, –CH_2–CH=CH_2), 5.23 (d, 1H, $J_{1'',2''} = 1.1$ Hz, H-1″), 5.10 (d, 1H, $J_{1',2'} = 1.3$ Hz, H-1′), 5.08 (d, 1H, $J_{1,2} = 1.4$ Hz, H-1), 4.65–3.66 (m, 12H, H-2′, H-5, H-6, –CH_2–CH=CH_2), 1.89 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.01, 166.10, 165.91, 165.60, 165.46, 165.40, 165.38, 165.22, 164.95, 164.78, 118.38, 99.79, 98.46, 96.73, 70.54, 70.39, 70.06, 69.74, 69.62, 69.55, 69.33, 68.86, 68.77, 67.22, 67.13, 66.62, 66.33, 63.46, 62.62, 20.60. Anal. Calcd for $C_{86}H_{74}O_{26}$: C, 67.80; H, 4.90. Found: C, 67.66; H, 4.97.

4.6. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-3-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate 7

To a solution of **5** (0.89 g, 0.58 mmol) in anhydrous MeOH (10 mL) was added $PdCl_2$ (30 mg). After stirring the mixture at rt for 2 h, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the solution concentrated to dryness and the resultant residue purified by flash chromatography (2.5:1 petroleum ether–EtOAc) to give **6** (0.70 g, 81%) as a white foam. A mixture of **6** (0.70 g, 0.47 mmol), trichloroacetonitrile (94 μL, 0.94 mmol) and 1,8-diazabicyclo[5.4.0]-undecene (DBU) (30 μL) in dry CH_2Cl_2 (10 mL) was stirred under nitrogen for 3 h and then concentrated. The residue was purified by flash chromatography (3:1 petroleum ether–EtOAc) to give **7** (0.67 g, 88%) as a foamy solid: $[\alpha]_D^{25} = -68.4$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (s, 1H, CN*H*CCl_3), 8.15–7.26 (m, 45H, 9*Ph*), 6.51 (s, 1H, H-1), 6.10 (dd, 1H, $J_{3'',4''} = J_{4'',5''} = 10.1$ Hz, H-4″), 6.05–5.80 (m, 7H, H-2, H-2″, H-3, H-3′, H-3″, H-4, H-4′), 5.22 (s, 1H, H-1″), 5.12 (s, 1H, H-1′), 4.66–3.69 (m, 10H, H-2′, H-5, H-6), 1.92 (s, 3H, CH_3CO). Anal. Calcd for $C_{85}H_{70}Cl_3NO_{26}$: C, 62.72; H, 4.33. Found: C, 62.82; H, 4.41.

4.7. Allyl 3-*O*-acetyl-4,6-di-*O*-benzoyl-α-D-mannopyranoside 9

Compound **8** (0.34 g, 1.0 mmol) was benzoylated under the same conditions as those used in the preparation of **5** from **4**, to give a residue. To a solution of the residue in MeOH (15 mL)–CH_2Cl_2 (20 mL) was added thiourea (0.15 g), and the mixture was refluxed for 16 h, after which TLC (1:1 petroleum ether–EtOAc) indicated that the reaction had gone to completion. The mixture was then concentrated and the residue passed through a silica-gel column with 3:1 petroleum ether–EtOAc as the eluent to give **9** (0.33 g, 71% for two steps) as a foamy solid. $[\alpha]_D^{25} = +43.6$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.37 (m, 10H, 2*Ph*), 5.98–5.89 (m, 1H, –CH_2–C*H*=CH_2), 5.73 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.56 (dd, 1H, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 10.0$ Hz, H-3), 5.34–5.22 (m, 2H, –CH_2–CH=CH_2), 5.00 (d, 1H, $J_{1,2} = 1.6$ Hz, H-1), 4.55 (dd, 1H, $J_{5,6a} = 5.1$ Hz, $J_{6a,6b} = 12.0$ Hz, H-6a), 4.44 (dd, 1H, $J_{5,6b} = 5.5$ Hz, $J_{6a,6b} = 12.0$ Hz, H-6b), 4.32–4.06 (m, 4H, H-2, H-5, –CH_2–CH=CH_2), 2.00 (s, 3H, CH_3CO). Anal. Calcd for $C_{25}H_{26}O_9$: C, 63.82; H, 5.57. Found: C, 63.96; H, 5.62.

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

Donor **7** (0.65 g, 0.40 mmol) was coupled with acceptor **9** (0.22 g, 0.48 mmol) as described in the general procedure, and the product purified by chromatography with 2:1 petroleum ether–EtOAc as the eluent to give **10**

(0.62 g, 80%) as a foamy solid. $[\alpha]_D^{25} = -71.2$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06–7.26 (m, 55H, 11*Ph*), 6.11 (dd, 1H, $J_{3''',4'''} = J_{4''',5'''} = 10.0$ Hz, H-4'''), 6.10 (dd, 1H, $J_{3'',4''} = J_{4'',5''} = 10.0$ Hz, H-4''), 6.04–5.75 (m, 7H, H-2''',H-3', H-3'', H-3''', H-4, H-4', $-CH_2-CH{=}CH_2$), 5.70 (dd, 1H, $J_{1',2'} = 1.7$ Hz, $J_{2',3'} = 3.1$ Hz, H-2'), 5.67 (dd, 1H, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 9.8$ Hz, H-3), 5.28 (d, 1H, $J_{1''',2'''} = 1.6$ Hz, H-1'''), 5.26–5.12 (m, 2H, $-CH_2-CH{=}CH_2$), 5.24 (d, 1H, $J_{1'',2''} = 1.5$ Hz, H-1''), 5.10 (d, 1H, $J_{1',2'} = 1.7$ Hz, H-1'), 4.98 (d, 1H, $J_{1,2} = 1.9$ Hz, H-1), 4.63–3.64 (m, 16H, H-2', H-2'', H-5, H-6, $-CH_2-CH{=}CH_2$), 2.06 (s, 3H, CH_3CO), 1.94 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.45, 169.84, 166.29, 166.17, 165.95, 165.50, 165.47, 165.43, 165.38, 164.81, 163.38, 99.89, 99.83, 98.93, 97.95, 70.73, 70.43, 70.28, 70.08, 69.87, 69.60, 69.05, 68.96, 68.93, 68.73, 67.91, 67.14, 66.64, 66.56, 65.91, 63.77, 63.38, 62.50, 60.38, 21.02, 20.72. Anal. Calcd for $C_{108}H_{94}O_{34}$: C, 67.01; H, 4.89. Found: C, 66.88; H, 4.79.

4.9. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 6)-3-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3-*O*-acetyl-4,6-di-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate 12

Deallylation of tetrasaccharide **10** (0.60 g, 0.31 mmol) followed by trichloroacetimidation under the same conditions as those used in the preparation of **7** from **5** gave a residue, which was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **12** (0.46 g, 73% for two steps) as a foamy solid. $[\alpha]_D^{25} = -69.5$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H, $CNHCCl_3$), 8.05–7.26 (m, 55H, 11*Ph*), 6.56 (s, 1H, H-1), 6.12 (dd, 1H, $J_{3''',4'''} = J_{4''',5'''} = 10.0$ Hz, H-4'''), 6.09 (dd, 1H, $J_{3'',4''} = J_{4'',5''} = 10.0$ Hz, H-4''), 6.04–5.68 (m, 8H, H-2', H-2''', H-3, H-3', H-3'', H-3''', H-4, H-4'), 5.36 (s, 1H, H-1'''), 5.25 (s, 1H, H-1''), 5.00 (d, 1H, $J_{1',2'} = 1.7$ Hz, H-1'), 4.67–3.72 (m, 14H, H-2', H-2'', H-5, H-6), 2.09 (s, 3H, CH_3CO), 1.95 (s, 3H, CH_3CO). Anal. Calcd for $C_{107}H_{90}Cl_3NO_{34}$: C, 62.99; H, 4.45. Found: C, 63.22; H, 4.53.

4.10. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 6)-3-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3-*O*-acetyl-4,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside 14

Compound **12** (0.46 g, 0.22 mmol) and **13** (0.27 g, 0.27 mmol) were coupled under the same conditions as those used in the preparation of **10** from **7** and **9**, giving **17** (0.44 g, 68%) as a foamy solid. $[\alpha]_D^{25} = -16.5$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.13–7.26 (m, 85H, 17*Ph*), 6.26 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 6.14–5.65 (m, 14H, 2H-2, 6H-3, 5H-4, $-CH_2-CH{=}CH_2$), 5.42 (d, 1H, $J_{1,2} = 1.6$ Hz, H-1), 5.30–5.18 (m, 2H, $-CH_2-CH{=}CH_2$), 5.27 (d, 1H, $J_{1,2} = 1.2$ Hz, H-1), 5.22 (d, 1H, $J_{1,2} = 1.1$ Hz, H-1), 5.11 (d, 1H, $J_{1,2} = 1.4$ Hz, H-1), 5.08 (d, 1H, $J_{1,2} = 1.1$ Hz, H-1), 4.94 (d, 1H, $J_{1,2} = 1.3$ Hz, H-1), 4.67–3.72 (m, 24H, 4H-2, 6H-5, 12H-6, $-CH_2-CH{=}CH_2$), 2.04 (s, 3H, CH_3CO), 1.97 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.05, 169.89, 166.14, 166.04, 165.99, 165.66, 165.61, 165.58, 165.57, 165.50, 165.43, 165.38, 165.32, 165.30, 164.81, 163.38, 100.26, 100.13, 99.76, 99.64, 98.84, 97.99, 71.09, 70.38, 70.26, 70.11, 69.96, 69.86, 69.70, 69.58, 68.99, 68.85, 68.75, 67.89, 67.45, 67.12, 67.04, 66.33, 66.10, 65.19, 63.68, 63.57, 63.23, 61.98, 60.34, 20.76, 20.65. Anal. Calcd for $C_{162}H_{138}O_{50}$: C, 67.45; H, 4.82. Found: C, 67.68; H, 4.73.

4.11. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 6)-2,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-4,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside 15

To a solution of **14** (0.42 g, 0.15 mmol) in anhydrous CH_2Cl_2 (5 mL) was added anhydrous MeOH (25 mL), then acetyl chloride (1 mL) added to the reaction mixture at 0 °C. The solution was stoppered in a flask and stirred at rt until TLC (1:1 petroleum ether–EtOAc) showed that the reaction was complete. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was passed through a short silica-gel column to give **15** (0.30 g, 73%) as a foamy solid. $[\alpha]_D^{25} = +12.7$ (*c* 1.0, $CHCl_3$); δ 8.04–7.15 (m, 85H, 17*Ph*), 6.12 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 6.08–5.51 (m, 12H, 2H-2, 4H-3, 5H-4, $-CH_2-CH{=}CH_2$), 5.36 (s, 1H, H-1), 5.31 (s, 1H, H-1), 5.30–5.20 (m, 2H, $-CH_2-CH{=}CH_2$), 5.30 (s, 1H, H-1), 5.18 (s, 1H, H-1), 5.12 (s, 1H, H-1), 5.11 (s, 1H, H-1), 4.66–3.92 (m, 26H, 4H-2, 2H-3, 6H-5, 12H-6, $-CH_2-CH{=}CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.14, 166.75, 166.63, 166.16, 166.14, 166.10, 166.02, 165.97, 165.77, 165.73, 165.63, 165.56, 165.52, 165.37, 165.29, 165.09, 164.78, 100.28, 100.26, 99.92, 99.74, 98.81, 98.04, 72.96, 71.33, 71.20, 70.14, 70.04, 69.73, 69.67, 69.57, 69.20, 69.08, 68.78, 68.02, 66.94, 66.37, 65.29, 63.78, 63.66, 63.48, 63.33, 62.99, 62.16, 60.43. Anal. Calcd for $C_{158}H_{134}O_{48}$: C, 67.76; H, 4.82. Found: C, 67.93; H, 4.91.

4.12. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 6)-[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)]-4,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside 17

Acceptor **15** (0.29 g, 0.10 mmol) was coupled with donor **16** (0.18 g, 0.24 mmol) as described in the general procedure, and the product purified by chromatography with 1.5:1 petroleum ether–EtOAc as the eluent to give **17** (0.30 g, 73%) as a foamy solid. $[\alpha]_D^{25} = -18.6$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.14–6.89 (m, 125H, 25*Ph*), 6.32 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4),

6.14–5.75 (m, 14H, Gal*f* 2H-5, Man*p* 2H-2, 4H-3, 5H-4, –CH_2–C*H*=CH_2), 5.57 (d, 1H, $J_{3,4}$ = 4.5 Hz, Gal*f* H-3), 5.49 (d, 1H, $J_{3,4}$ = 5.1 Hz, Gal*f* H-3), 5.48 (s, 2H, Gal*f* 2H-1), 5.44 (s, 1H, Man*p* H-1), 5.41 (s, 2H, Gal*f* 2H-2), 5.33 (s, 1H, Man*p* H-1), 5.29 (s, 2H, Man*p* 2H-1), 5.27–5.13 (m, 2H, –CH_2–CH=C*H*$_2$), 4.95 (s, 1H, Man*p* H-1), 4.75–3.86 (m, 32H, Gal*f* 2H-4, 4H-6, Man*p* 4H-2, 2H-3, 6H-5, 12H-6, –C*H*$_2$–CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.07, 166.09, 165.95, 165.82, 165.69, 165.65, 165.57, 165.55, 165.52, 165.41, 165.33, 165.28, 165.26, 165.01, 164.99, 164.84, 164.77, 104.27, 102.24, 100.65, 100.56, 100.17, 99.74, 98.96, 97.98, 83.06, 82.83, 82.22, 81.62, 75.10, 73.91, 71.91, 71.59, 70.92, 70.20, 70.07, 69.94, 69.77, 69.66, 69.54, 68.99, 68.86, 68.73, 68.64, 67.88, 67.52, 67.25, 66.94, 66.63, 66.30, 65.74, 63.93, 63.71, 63.35, 62.08, 60.34. Anal. Calcd for $C_{226}H_{186}O_{66}$: C, 68.58; H, 4.74. Found: C, 68.75; H, 4.78.

4.13. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 6)-[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)]-4,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate 19

Deallylation of tetrasaccharide **17** (0.28 g, 71 μmol) followed by trichloroacetimidation under the same conditions as those used for the preparation of **7** from **5** gave a residue, which was purified by flash chromatography (3:2 petroleum ether–EtOAc) to give **19** (0.20 g, 71% for two steps) as a foamy solid. $[\alpha]_D^{25} = -13.5$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H, CN*H*CCl_3), 8.14–6.92 (m, 125H, 25*Ph*), 6.62 (s, 1H, Man*p* H-1), 6.31 (dd, 1H, $J_{3,4} = J_{4,5}$ = 10.4 Hz, H-4), 6.15–5.74 (m, 13H, Gal*f* 2H-5, Man*p* 2H-2, 4H-3, 5H-4), 5.60 (s, 1H, Man*p* H-1), 5.57 (d, 1H, $J_{3,4}$ = 4.5 Hz, Gal*f* H-3), 5.50 (d, 1H, $J_{3,4}$ = 5.1 Hz, Gal*f* H-3), 5.47 (s, 2H, Gal*f* 2H-1), 5.42 (s, 2H, Gal*f* 2H-2), 5.33 (s, 2H, Man*p* 2H-1), 5.30 (s, 1H, Man*p* H-1), 4.92 (s, 1H, Man*p* H-1), 4.78–3.92 (m, 30H, Gal*f* 2H-4, 4H-6, Man*p* 4H-2, 2H-3, 6H-5, 12H-6). Anal. Calcd for $C_{225}H_{182}Cl_3NO_{66}$: C, 66.53; H, 4.52. Found: C, 66.25; H, 4.44.

4.14. Allyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)-4,6-di-*O*-benzylidene-α-D-mannopyranoside 21

As described in the general procedure, **16** (0.36 g, 0.49 mmol) and **20** (0.18 g, 0.59 mmol) were coupled, and the product purified by silica-gel column chromatography with 2.5:1 petroleum ether–EtOAc as the eluent to give **7** (0.43 g, 71%) as a foamy solid. $[\alpha]_D^{25} = +10.2$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.19 (m, 25H, 5*Ph*), 5.96–5.86 (m, 2H, Gal*f* H-5, –CH_2–C*H*=CH_2), 5.55 (dd, 1H, $J_{2,3}$ = 1.2 Hz, $J_{3,4}$ = 5.5 Hz, Gal*f* H-3), 5.50 (s, 1H, PhC*H*), 5.44 (s, 1H, Gal*f* H-1), 5.43 (d, 1H, $J_{2,3}$ = 1.2 Hz, Gal*f* H-2), 5.34–5.22 (m, 2H, –CH_2–CH=CH_2), 4.99 (d, 1H, $J_{1,2}$ = 1.2 Hz, Man*p* H-1), 4.74 (dd, 1H, $J_{3,4}$ = 5.5 Hz, $J_{2,3}$ = 3.1 Hz, Gal*f* H-4), 4.60–3.82 (m, 10H, Gal*f* H-6, Man*p* H-2, H-3, H-4, H-5, H-6, –CH_2–CH=CH_2). Anal. Calcd for $C_{50}H_{46}O_{15}$: C, 67.71; H, 5.23. Found: C, 67.97; H, 5.30.

4.15. Allyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)-2-*O*-acetyl-4,6-di-*O*-benzylidene-α-D-mannopyranoside 22

To a solution of compound **21**(0.42 g, 0.47 mmol) in pyridine (10 mL) was added Ac_2O (5 mL, 5 mmol). The reaction mixture was stirred at rt for 12 h and concentrated to give the crude product, which was purified by flash chromatography (2.5:1 petroleum ether–EtOAc) to give **22** (0.42 g, 96%) as a foamy solid. $[\alpha]_D^{25} = -14.5$ (*c* 1.3, H_2O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–7.16 (m, 25H, 5*Ph*), 5.95–5.85 (m, 2H, Gal*f* H-5, –CH_2–C*H*=CH_2), 5.53 (s, 1H, PhC*H*), 5.47 (d, 1H, $J_{3,4}$ = 5.4 Hz, Gal*f* H-3), 5.43 (s, 1H, Gal*f* H-1), 5.42 (dd, 1H, $J_{1,2}$ = 1.4 Hz, $J_{2,3}$ = 3.5 Hz, Man*p* H-2), 5.41 (s, 1H, Gal*f* H-2), 5.33–5.22 (m, 2H, –CH_2–CH=CH_2), 4.86 (d, 1H, $J_{1,2}$ = 1.3 Hz, Man*p* H-1), 4.70 (dd, 1H, $J_{3,4}$ = 5.3 Hz, $J_{2,3}$ = 3.0 Hz, Gal*f* H-4), 4.64–3.81 (m, 9H, Gal*f* H-6, Man*p* H-3, H-4, H-5, H-6, –CH_2–CH=CH_2). Anal. Calcd for $C_{52}H_{48}O_{16}$: C, 67.23; H, 5.21. Found: C, 67.01; H, 5.15.

4.16. Allyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)-2-*O*-acetyl-4,6-di-*O*-benzoyl-α-D-mannopyranoside 24

Compound **22** (0.40 g, 0.43 mmol) was dissolved in 90% TFA (10 mL), and the mixture stirred for 2 h at rt, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with toluene (40 mL) and concentrated in vacuo directly to give crude product **23**. Benzoylation of compound **23** under the same conditions used in the preparation of **5** from **4** gave a residue, which was purified by flash chromatography (3:1 petroleum ether–EtOAc) to give **24** (0.31 g, 72% for two steps) as a foamy solid. $[\alpha]_D^{25} = +8.7$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.15 (m, 30H, 6*Ph*), 5.98–5.86 (m, 2H, Gal*f* H-5, –CH_2–C*H*=CH_2), 5.72 (dd, 1H, $J_{3,4} = J_{4,5}$ = 10.0 Hz, Man*p* H-4), 5.49 (s, 1H, Gal*f* H-1), 5.47 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.4 Hz, Man*p* H-2), 5.43 (d, 1H, $J_{3,4}$ = 5.1 Hz, Gal*f* H-3), 5.35 (s, 1H, Gal*f* H-2), 5.33–5.22 (m, 2H, –CH_2–CH=CH_2), 4.98 (d, 1H, $J_{1,2}$ = 1.7 Hz, Man*p* H-1), 4.70 (dd, 1H, $J_{3,4}$ = 5.3 Hz, $J_{2,3}$ = 3.0 Hz, Gal*f* H-4), 4.62–4.05 (m, 9H, Gal*f* H-4, H-6, Man*p* H-3, H-5, H-6, –CH_2–CH=CH_2). Anal. Calcd for $C_{59}H_{52}O_{18}$: C, 67.55; H, 5.00. Found: C, 67.63; H, 4.95.

4.17. Allyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)-4,6-di-*O*-benzoyl-α-D-mannopyranoside 25

Deacetylation of **24** (0.29 g, 0.27 mmol) under the same conditions as those used in the preparation of **15** from **14** gave the crude product, which was purified by flash

chromatography (2.5:1 petroleum ether–EtOAc) to furnish **25** (0.21 g, 75%) as a foamy solid. $[\alpha]_D = +17.2$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.00–7.23 (m, 30H, 6*Ph*), 5.99–5.89 (m, 1H, $-CH_2-CH{=}CH_2$), 5.82–5.77 (m, 2H, Gal*f* H-5, Man*p* H-4), 5.58 (dd, 1H, $J_{2,3} = 1.5$ Hz, $J_{3,4} = 5.1$ Hz, Gal*f* H-3), 5.47 (s, 1H, Gal*f* H-1), 5.36 (d, 1H, $J_{2,3} = 1.5$ Hz, Gal*f* H-2), 5.33–5.22 (m, 2H, $-CH_2-CH{=}CH_2$), 5.10 (d, 1H, $J_{1,2} = 1.4$ Hz, Man*p* H-1), 5.47 (dd, 1H, $J_{1,2} = 1.7$ Hz, $J_{2,3} = 3.4$ Hz, Man*p* H-2), 4.70 (dd, 1H, $J_{3,4} = 5.3$ Hz, $J_{2,3} = 3.0$ Hz, Gal*f* H-4), 4.57–4.12 (m, 10H, Gal*f* H-4, H-6, Man*p* H-2, H-3, H-5, H-6, $-CH_2-CH{=}CH_2$). Anal. Calcd for $C_{57}H_{50}O_{17}$: C, 67.99; H, 5.00. Found: C, 68.12; H, 5.09.

4.18. Allyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)]-4,6-di-*O*-benzoyl-α-D-mannopyranoside 27

Donor **26** (0.15 g, 0.22 mmol) was coupled with acceptor **25** (0.18 g, 0.18 mmol) as described in the general procedure, and the product purified by chromatography with 2:1 petroleum ether–EtOAc as the eluent to give **27** (0.22 g, 78%) as a foamy solid. $[\alpha]_D^{25} = -20.2$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.09–6.98 (m, 45H, 9*Ph*), 6.07–5.88 (m, 6H, Gal*f* H-5, Man*p* H-2′, H-3′, H-4, H-4′, $-CH_2-CH{=}CH_2$), 5.62 (d, 1H, $J_{1',2'} = 1.0$ Hz, Man*p* H-1′), 5.52 (d, 1H, $J_{3,4} = 4.4$ Hz, Gal*f* H-3), 5.51 (s, 1H, Gal*f* H-1), 5.43 (s, 1H, Gal*f* H-2), 5.36–5.24 (m, 2H, $-CH_2-CH{=}CH_2$), 5.18 (d, 1H, $J_{1,2} = 1.2$ Hz, Man*p* H-1), 4.65–4.10 (m, 13H, Gal*f* H-4, H-6, Man*p* H-2, H-3, H-5, H-5′, H-6, H-6′, $-CH_2-CH{=}CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.49, 166.32, 166.12, 165.62, 165.55, 165.11, 164.98, 164.63, 102.83, 100.70, 98.19, 82.82, 75.75, 72.73, 70.06, 69.74, 69.26, 69.05, 68.69, 67.64, 67.30, 64.06, 63.82, 63.07, 20.67. Anal. Calcd for $C_{86}H_{74}O_{26}$: C, 67.80; H, 4.90. Found: C, 68.03; H, 5.01.

4.19. Allyl 2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)]-4,6-di-*O*-benzoyl-α-D-mannopyranoside 28

Deacetylation of compound **27** (0.20 g, 0.13 mmol) was carried out under the same conditions as those used in the preparation of **15** from **14**, giving the crude product, which was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **28** (0.16 g, 81%) as a foamy solid. $[\alpha]_D^{25} = -52.5$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.98–6.99 (m, 45H, 9*Ph*), 6.12 (dd, 1H, $J_{2',3'} = 3.4$ Hz, $J_{3',4'} = 10.0$ Hz, Man*p* H-3′) 6.05 (dd, 1H, $J_{1',2'} = 1.5$ Hz, $J_{2',3'} = 3.4$ Hz, Man*p* H-2′), 5.98–5.87 (m, 3H, Gal*f* H-5, Man*p* H-4′, $-CH_2-CH{=}CH_2$), 5.84 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, Man*p* H-4), 5.67 (d, 1H, $J_{1',2'} = 1.5$ Hz, Man*p* H-1′), 5.52 (d, 1H, $J_{3,4} = 4.9$ Hz, Gal*f* H-3), 5.51 (s, 1H, Gal*f* H-1), 5.42 (s, 1H, Gal*f* H-2), 5.34–5.23 (m, 2H, $-CH_2-CH{=}CH_2$), 5.16 (d, 1H, $J_{1,2} = 1.6$ Hz, Man*p* H-1), 4.64–3.80 (m, 13H, Gal*f* H-4, H-6, Man*p* H-2, H-3, H-5, H-5′, H-6, H-6′, $-CH_2-CH{=}CH_2$). Anal. Calcd for $C_{84}H_{72}O_{25}$: C, 68.10; H, 4.90. Found: C, 68.21; H, 4.95.

4.20. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 6)-[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)]-4,6-di-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1 → 2)-[2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1 → 3)]-4,6-di-*O*-benzoyl-α-D-mannopyranoside 29

Donor **19** (0.19 g, 46 μmol) was coupled with acceptor **28** (82 mg, 55 μmol) as described in the general procedure to give the crude product, which was purified by flash chromatography (1.2:1 petroleum ether–EtOAc) to give target compound **29** (0.20 g, 79%) as a foamy solid. $[\alpha]_D^{25} = -41.7$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04–6.91 (m, 170H, 34*Ph*), 6.33 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 6.21 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 6.15–5.63 (m, 18H, Gal*f* 3H-5, Man*p* 3H-2, 5H-3, 6H-4, $-CH_2-CH{=}CH_2$), 5.59 (d, 1H, $J_{3,4} = 4.4$ Hz, Gal*f* H-3), 5.50–5.46 (m, 5H, Gal*f* 3H-1, 2H-3), 5.43 (s, 2H, Gal*f* 2H-2), 5.34 (s, 1H, Man*p* H-1), 5.32 (s, 1H, Gal*f* H-2), 5.28 (s, 1H, Man*p* H-1), 5.26 (s, 2H, Man*p* 2H-1), 5.24–5.07 (m, 2H, $-CH_2-CH{=}CH_2$), 5.23 (s, 2H, Man*p* 2H-1), 5.21 (s, 1H, Man*p* H-1), 4.92 (s, 1H, Man*p* H-1), 4.68–3.68 (m, 43H, Gal*f* 3H-4, 6H-6, Man*p* 5H-2, 3H-3, 8H-5, 16H-6, $-CH_2-CH{=}CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.88, 166.23, 166.00, 165.94, 165.80, 165.75, 165.72, 165.55, 165.48, 165.43, 165.36, 165.29, 165.19, 165.16, 165.07, 164.76, 164.73, 164.64, 164.58, 163.17, 104.12, 102.73, 102.21, 101.12, 100.61, 100.19, 99.62, 98.83, 98.44, 98.32, 95.92, 82.85, 82.76, 82.62, 82.10, 81.50, 75.24, 74.78, 73.78, 72.87, 71.99, 71.72, 71.46, 70.33, 70.15, 69.98, 69.86, 69.79, 69.51, 69.36, 68.93, 68.74, 67.56, 67.20, 67.02, 66.85, 66.65, 66.51, 66.24, 66.05, 63.97, 63.75, 63.49, 63.21, 63.05, 61.83. Anal. Calcd for $C_{307}H_{252}O_{90}$: C, 68.52; H, 4.72. Found: C, 68.78; H, 4.64.

4.21. Allyl α-D-mannopyranosyl-(1 → 2)-α-D-mannopyranosyl-(1 → 6)-[β-D-galactofuranosyl-(1 → 3)]-α-D-mannopyranosyl-(1 → 2)-[β-D-galactofuranosyl-(1 → 3)]-α-D-mannopyranosyl-(1 → 2)-α-D-mannopyranosyl-(1 → 2)-α-D-mannopyranosyl-(1 → 6)-α-D-mannopyranosyl-(1 → 2)-[β-D-galactofuranosyl-(1 → 3)]-α-D-mannopyranoside 30

Undecasaccharide **29** (0.19 g, 34 μmol) was dissolved in satd NH_3–MeOH (30 mL). After 96 h at rt, the reaction mixture was concentrated, and the residue purified by chromatography on Sephadex LH-20 (MeOH) to afford **30** (54 mg, 85%) as a foamy solid. $[\alpha]_D^{25} = +8.5$ (*c* 1.0, H_2O); ^1H NMR (400 MHz, D_2O): δ 5.88–5.98 (m, 1H, $-CH_2-CH{=}CH_2$), 5.35–5.31 (dd, 1H, $J = 17.1$ Hz, $-CH_2-CH{=}CH_{trans}$), 5.26–5.24 (dd, 1H, $J = 10.4$ Hz, $-CH_2-CH{=}CH_{cis}$), 5.20, 5.16, 5.15, 5.11, 5.07, 5.02, 4.99 (7s, 11H, 11H-1); ^{13}C NMR (100 MHz, D_2O): δ 104.88, 104.85, 104.35, 102.28, 101.71, 101.61, 100.76, 100.69, 98.26, 98.10, 97.59, 78.79, 78.68, 78.47, 77.05, 76.84, 75.78, 75.55, 75.23, 74.24, 73.99, 73.34, 73.26, 73.21,

72.95, 72.68, 71.80, 71.58, 70.72, 70.69, 70.64, 70.46, 70.32, 70.26, 70.03, 69.97, 69.91, 68.15, 67.09, 67.03, 66.89, 66.50, 65.97, 65.40, 65.29, 65.23, 64.51, 62.84, 62.78, 61.17, 60.94, 60.88, 60.82. Anal. Calcd for $C_{69}H_{116}O_{56}$: C, 45.00; H, 6.35. Found: C, 45.11; H, 6.38.

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