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Syntheses of arabinogalactans consisting of β-(1 → 6)-linked D-galactopyranosyl backbone and α-(1 → 3)-linked L-arabinofuranosyl side chains

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Abstract—Two arabinogalactosyl nonasaccharides, β-D-Gal*p*-(1 → 6)-[α-L-Ara*f*-(1 → 3)]-β-D-Gal*p*-(1 → 6)-β-D-Gal*p*-(1 → 6)-β-D-Gal*p*-(1 → 6)-[α-L-Ara*f*-(1 → 5)-α-L-Ara*f*-(1 → 3)]-β-D-Gal*p*-(1 → 6)-β-D-Gal*p* and β-D-Gal*p*-(1 → 6)-[α-L-Ara*f*-(1 → 5)-α-L-Ara*f*-(1 → 3)]-β-D-Gal*p*-(1 → 6)-β-D-Gal*p*-(1 → 6)-β-D-Gal*p*-(1 → 6)-[α-L-Ara*f*-(1 → 3)]-β-D-Gal*p*-(1 → 6)-β-D-Gal*p*, were synthesized as their 4-methoxyphenyl glycosides with 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**1**), 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**14**), 4-methoxyphenyl 3-*O*-allyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (**2**), 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (**5**), 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate (**8**), and 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate (**11**), as the key synthons. The tetra- (**10**) and pentasaccharide donor (**13**), and the tetra- (**20**) and pentasaccharide acceptor (**22**) were synthesized based on these synthons through simple transformations. Coupling of **22** with **10**, and coupling of **20** with **13** and subsequent deacylation gave nonasaccharides **24** and **26**, respectively, consisting of β-(1 → 6)-linked glactopyranosyl backbone and α-(1 → 3)-linked arabinofuranosyl side chains of different size.

Keywords: Galactose; Arabinose; Arabinogalactan

1. Introduction

Arabinogalactans with immunomodulating activity have been found from certain sources.[1] One of the first arabinogalactans for which an activity on the complement system was shown was an arabinogalactan from a hot water extract of the roots of the Chinese herb *Angelica acutiloba*.[2] Such activity was not found in the arabinogalactan from larch wood.[3] An arabinogalactan isolated from the roots of *Saposhnikova divaricata* or *Panex* notoginseng had reticuloendothelial system activating properties.[4] The arabinogalactans with β-(1 → 6)-linked galactopyranose backbone and α-(1 → 2)-linked arabinofuranose side chains may exist in *Echinacea purpurea*, which have immunomodulating activity,[1a] while a β-(1 → 6)-linked galactose trisaccharide backbone functionalized at 3-OH with at least one α-linked L-arabinofuranose unit was supposed to be the minimum epitope recognized by the CCRC-M7 antibody.[5] Although the presence of 2,6- and 3,6-branched residues in arabinogalactan is well known, the exact structure of these saccharides and the function of the arabinofuranose side chains remain to be established.

Some examples on the chemical synthesis of the arabinogalactans consisting of β-(1 → 6)-linked galactopyranose backbones and α-(1 → 2)-linked arabinofuranose side chains have been reported.[6] However, there have been very few papers dealing with the synthesis of the arabinogalactans consisting of β-(1 → 6)-linked galactopyranose backbones and α-(1 → 3)-linked arabinofuranose side chains.[7] We present herein convergent syntheses of the two nonasaccharides

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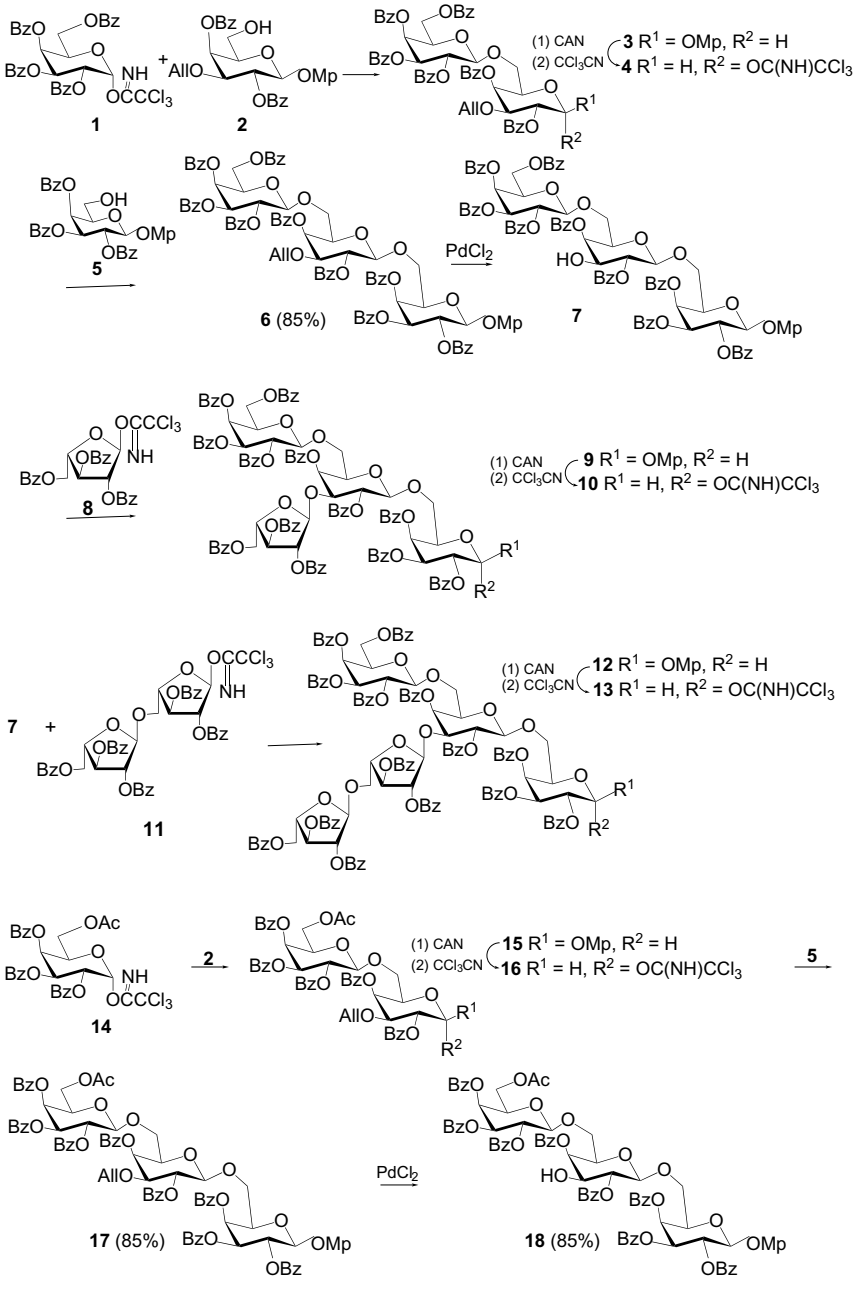
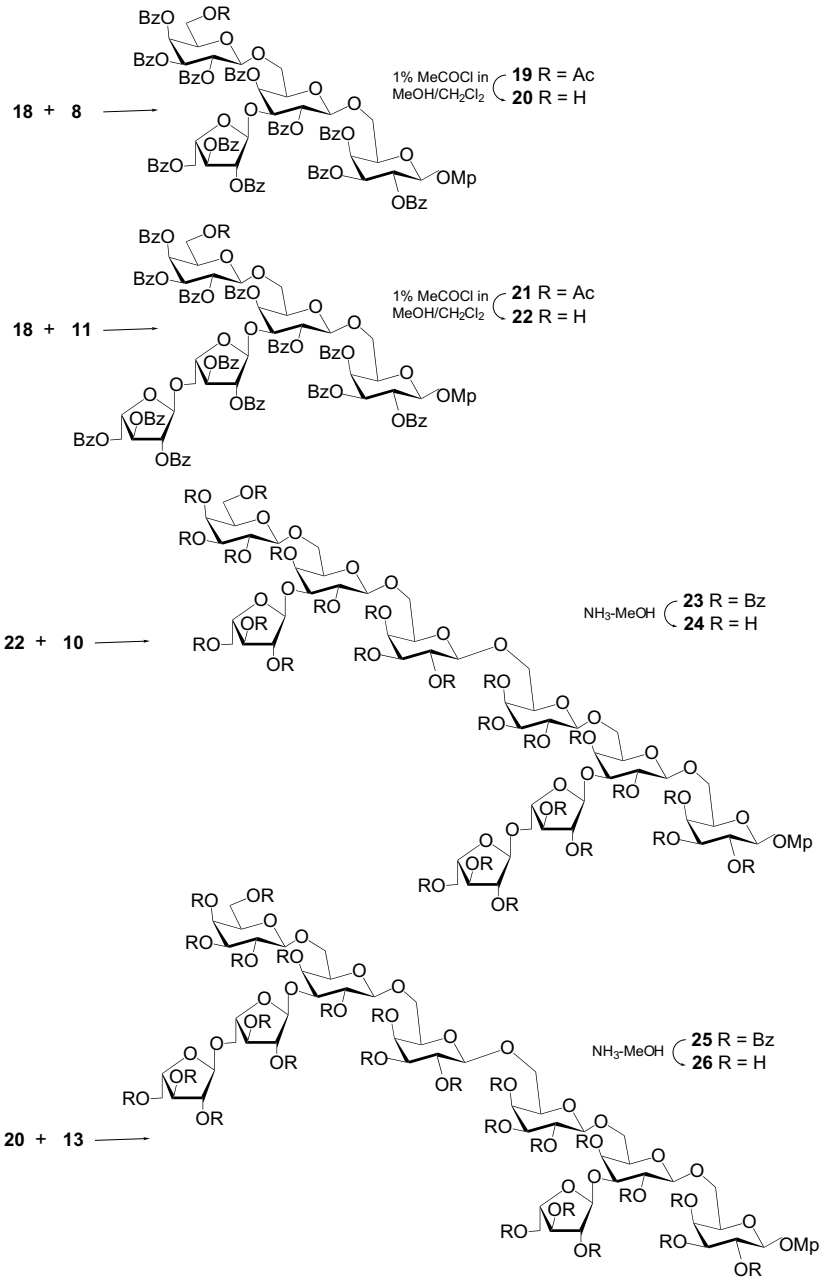
24 and **26** consisting of β-(1→6)-linked galactose hexasaccharide backbone with mono-arabinose side chain at C-3^{V}, α-(1→5)-linked arabinobiose at C-3^{II}, and mono-arabinose side chain at C-3^{II}, α-(1→5)-linked arabinobiose at C-3^{V}, respectively.

2. Results and discussion

As shown in Scheme 1, the syntheses of the tetrasaccharide donor **10** and the pentasaccharide donor **13** were readily achieved based on some monosaccharide derivatives. The key synthon, 4-methoxyphenyl 3-*O*-allyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (**2**), was prepared from 4-methoxyphenyl tetra-*O*-acetyl-β-D-galactopyranoside by deacetylation, selective 3-*O*-allylation via dibutyltin complex,[8] 6-*O*-tritylation and benzoylation, and detritylation. Condensation of **2** with perbenzoylated galactopyranosyl trichloroacetimidate[9] **1** afforded the disaccharide **3**, and subsequent oxidative cleavage of 4-methoxyphenyl group and tricholoroacetimidate formation gave the disaccharide donor **4**. Coupling of 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (**5**)[6i,j] with **4** gave the trisaccharide **6**, and subsequent deallylation yielded the trisaccharide acceptor **7**. Condensation of **7** with 2,3,5-tri-*O*-benzoyl-α-L-arabinofur-



Scheme 1.



Scheme 1 (*continued*)

anosyl trichloroacetimidate (**8**),[10] followed by oxidative cleavage of the 1-OMp group and trichloroacetimidate formation, yielded the tetrasaccharide donor **10**, while coupling of **7** with 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate (**11**),[10] followed by oxidative cleavage of the 1-OMp group and trichloroacetimidate formation gave the pentasaccharide donor **13**. The precursor **19** of the tetrasaccharide acceptor, and the precursor **21** of the pentasaccharide acceptor, were prepared in the same way as described for the preparations of **9** and **12**, except that 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**14**) was used as the upstream unit instead of **1**. Thus, coupling of **14** with **2**, oxidative cleavage of 1-OMp, trichloroacetimidate formation, and condensation with **5**, subsequent deallylation gave **18**. Reaction of **18** with **8**, then selective deacetylation[11] gave the tetrasaccharide acceptor **20**, while reaction of **18** with **11**, then selective deacetylation[11] gave the pentasaccharide acceptor **22**.

With the tetra- and pentasaccharide building blocks in hand, the target nonamers were readily obtained. Thus, coupling of **22** with **10**, followed by deacylation with ammonia in methanol, yielded the nonasaccharide **24**, while coupling of **20** with **13**, followed by deacylation, gave the nonasaccharide **26**.

In summary, efficient syntheses of arabinogalactans consisting of a β-(1 → 6)-linked galactopyranosyl backbone and an α-L-arabinofuranosyl monomer or (1 → 5)-linked dimer side chains attached at C-3 was achieved. The method can be used for the preparation of a variety of different arabinogalactans with the similar structures.

3. Experimental

3.1. General methods

Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined at 25 °C with a digital polarimeter. The NMR spectra were recorded in $CDCl_3$ with Me_4Si as the internal standard or D_2O with EtOH as standard on a Bruker ARX 400 MHz. Mass spectral data were acquired in the positive-ion mode using a Bruker Biflex III matrix-assisted laser desorption/ionization time-of-flight (MALDITOF) mass spectrometer equipped with a 337 nm nitrogen laser using DHB as matrix and an acceleration voltage of 19 kV. Elemental analyses were carried out on an elemental analyzer model 1108 EA. 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 lamp. Column chromatography was conducted by elution of a column (10 × 240 mm, 18 × 300 mm, 35 × 400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Solutions were concentrated at <60 °C under diminished pressure. Dry solvents were distilled over CaH_2 and stored over molecular sieves.

3.2. 4-Methoxyphenyl 3-*O*-allyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (2)

To a solution of 4-methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (9.08 g, 20.0 mmol) in CH_3OH (100 mL) was added 4.0 M CH_3ONa–CH_3OH solution dropwise to pH 10. After stirring the mixture at rt for 5 h, TLC (5:1 EtOAc–CH_3OH) indicated that the reaction was complete. The reaction mixture was neutralized with 1:10 HOAc–CH_3OH, then the mixture was concentrated, and the residue was purified by column chromatography (5:1 EtOAc–CH_3OH) to give a solid (5.10 g, 18.0 mmol). To a solution of the solid in CH_3OH (100 mL) was added Bu_2SnO (5.22 g, 20.1 mol), and the mixture was heated under reflux for 2 h, then concentrated to dryness. The residue was diluted with toluene (200 mL), and then allyl bromide (17.1 mL, 200 mol) and Bu_4NI (7.38 g, 20.0 mol) were added to the mixture. The reaction mixture was stirred out at 60 °C for 24 h, TLC (EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated, and the residue was diluted with CH_2Cl_2 (20 mL). To the mixture was added pyridine (100 mL) and trityl chloride (6.5 g, 23.0 mmol). The mixture was stirred at 50 °C for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was cooled to 0 °C, then benzoyl chloride (5.6 mL, 40 mmol) was added dropwise within 30 min to keep the reaction temperature at 50 °C, and then the mixture was stirred at 50 °C overnight. Water (150 mL) was added to the reaction mixture, and stirring was continued for 30 min. The mixture was extracted with CH_2Cl_2 (3 × 100 mL), and the combined extracts were washed with 1 N HCl and satd aq $NaHCO_3$, dried (Na_2SO_4), and concentrated to a syrup that was subjected to column chromatography (5:1 petroleum ether–EtOAc as the eluent) to give 4-methoxyphenyl 3-*O*-allyl-2,4-di-*O*-benzoyl-6-*O*-trityl-β-D-galactopyranoside (10 g, 88%) as a solid. To a solution of 4-methoxyphenyl 3-*O*-allyl-2,4-di-*O*-benzoyl-6-*O*-trityl-β-D-galactopyranoside (10 g, 12.4 mmol) in CH_3OH (50 mL)–CH_2Cl_2 (50 mL) was added CH_3COCl (0.1 mL), and the mixture was stirred at rt for 3 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was neutralized with Et_3N, then concentrated, and the residue was passed through a silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give **2** (5.76 g, 87%) as a foamy solid: $[\alpha]_D$ +65.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.13–7.25 (m, 10H, 2 Ph*H*), 6.92 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.87 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.76 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.67 (m, 1H, CH_2=CH–CH_2O), 5.17–5.05 (m, 2H, CH_2=CH–CH_2O), 5.03 (d, 1H, $J_{1,2}$ 8 Hz, H-1), 4.25 (m, 1 H, H-5). 4.08–3.95 (m, 2H, CH_2=CH–CH_2), 3.90 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 3.78 (dd, 1H, H-6), 3.67 (s, 3H, CH_3O), 3.60 (dd, 1H, $J_{5,6}$ 6.4 Hz, $J_{6,6}$ 12.0 Hz, H-6). Anal. Calcd for $C_{30}H_{30}O_9$: C, 67.41; H, 5.66. Found: C, 67.62; H, 5.59.

3.3. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-3-*O*-allyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (3)

A solution of **2** (2.4 g, 4.49 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**1**, 3.99 g, 5.39 mmol) in dry CH_2Cl_2 (100 mL) was stirred. TMSOTf (30 μL) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirred for 2 h, during which time the temperature gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 3:1 petroleum ether–EtOAc as the eluent, gave **3** (4.3 g, 87%) as a syrup: $[\alpha]_D$ +67.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.13–7.25 (m, 30H, 6Ph*H*), 6.92 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.75 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.98 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.84 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.76 (m, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.70 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz,

H-2), 5.63–5.58 (m, 1H, CH_2=CH–CH_2O), 5.54 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.17–5.05 (m, 2H, CH_2=CH–CH_2O), 5.02 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.94 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.43 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.4 Hz, H-6), 4.26 (m, 2H, H-6), 4.21 (m, 1H, H-5). 4.12–3.97 (m, 3H, CH_2=CH–CH_2O, H-5), 3.89 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.4 Hz, H-6), 3.78 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 3.67 (s, 3H, CH_3O). Anal. Calcd for $C_{64}H_{56}O_{18}$: C, 69.05; H, 5.07. Found: C, 69.19; H, 5.06.

3.4. 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-3-*O*-allyl-2,4-di-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (4)

To a solution of **3** (3.6 g, 3.24 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added ammonium cerium(IV) nitrate, (CAN), (7.8 g, 14.2 mmol), and the mixture was stirred at rt for 30 min, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was extracted with EtOAc (5 × 50 mL) and washed with water. The organic layer was concentrated, and the crude hemiacetal was purified by column chromatography (2:1 petroleum ether–EtOAc) to afford a solid (2.5 g, 2.4 mmol). To a solution of the solid in CH_2Cl_2 (80 mL) were added trichloroacetonitrile (0.48 mL, 4.8 mmol) and anhyd K_2CO_3 (2.2 g, 16 mmol). The reaction mixture was stirred overnight at rt and then filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (2:1 petroleum ether–EtOAc) to give **4** (2.54 g, 89%) as a syrup: $[\alpha]_D$ +57.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.70 (s, 1H, $CNHCCl_3$), 8.12–7.17 (m, 30H, 6Ph*H*), 6.34 (d, 1H, $J_{1,2}$ 3.2 Hz, α H-1), 5.97 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.81 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.80 (dd, 1H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.4 Hz, H-2′), 5.67 (dd, 1H, $J_{1,2}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.63–5.56 (m, 1H, CH_2=CH–CH_2O), 5.52 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.17–5.02 (m, 2H, CH_2=CH–CH_2O), 4.73 (d, 1H, $J_{1,2}$ 8.0 Hz, β H-1), 4.46 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 3.98 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 3.90 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3). Anal. Calcd for $C_{59}H_{50}Cl_3NO_{17}$: C, 61.54; H, 4.38. Found: C, 61.69; H, 4.25.

3.5. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-3-*O*-allyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (6)

Compounds **4** (2.81 g, 2.44 mmol) and 4-methoxyphenyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (**5**, 1.32 g, 2.21 mmol) in dry CH_2Cl_2 (80 mL) were coupled by the same procedure as described in the preparation of **3** to give trisaccharides **6** as a syrup (2.9 g, 85%): $[\alpha]_D$ +39.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.13–7.26 (m, 45H, 9Ph*H*), 6.90 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95–5.89 (m, 3H, H-2″, H-4″, H-4′), 5.74 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.71 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.61–5.56 (m, 1H, CH_2=CH–CH_2O), 5.42 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.14 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 5.13–5.09 (m, 2H, CH_2=CH–CH_2O), 4.65 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.61 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.02 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 3.69 (s, 3H, C*H*$_3$O), 3.69 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 165.6, 165.5, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1 (9C, 9*C*OPh), 101.0, 100.9, 100.8 (3C, C-1). Anal. Calcd for $C_{91}H_{78}O_{26}$: C, 68.84; H, 4.95. Found: C, 68.69; H, 4.91.

3.6. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (7)

To a solution of **6** (2.9 g, 1.87 mmol) in anhyd CH_3OH (50 mL) was added $PdCl_2$ (120 mg), and the mixture was stirred at rt for 5 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated. The residue was passed through a silica gel column with 1.5:1 petroleum ether–EtOAc as the eluent to give **7** as a syrup (2.57 g, 90%): $[\alpha]_D$ +56.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.19–7.23 (m, 45H, 9Ph*H*), 6.92 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.81 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.97–5.92 (m, 2H, H-2″, H-4″), 5.90 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.73 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.70 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.57 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3″), 5.51 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.46 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.15 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.64 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.53 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.24 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 10.4 Hz, H-6), 3.70 (s, 3H, CH_3O), 3.63 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 3.56 (m, 1H, H-5); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.1, 165.0 (9C, 9*C*OPh), 101.1, 100.7, 100.6 (3C, C-1). Anal. Calcd for $C_{88}H_{74}O_{26}$: C, 68.29; H, 4.82. Found: C, 68.20; H, 4.91.

3.7. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (9)

Compounds **7** (2.57 g, 1.66 mmol) and **8** (1.21 g, 1.99 mmol) in dry CH_2Cl_2 (80 mL) were coupled by the same procedure as described in the preparation of **3** to give tetrasaccharides **9** as a syrup (2.94 g, 89%): $[\alpha]_D$ +41.2 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09–7.20 (m, 60H, 12Ph*H*), 6.91 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.76 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95–5.91 (m, 2H, H-2″, H-4″), 5.85 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.83 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.68 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.64 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$

10.4 Hz, H-2), 5.58 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3″), 5.54 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.28 (s, 1H, Ara*f*-H-1), 5.26 (d, 1H, $J_{2,3}$ 1.2 Hz, Ara*f*-H-2), 5.13 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.63 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.62 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.21 (dd, 1H, $J_{5,6}$ 3.4 Hz, $J_{6,6}$ 10.8 Hz, H-6), 4.01 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 10.8 Hz, H-6), 3.68 (s, 3H, OCH_3), 3.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 166.0, 165.7, 165.8, 165.7, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (12C, 12*C*OPh), 106.9, 101.5, 101.4, 101.0 (4C, C-1). Anal. Calcd for $C_{114}H_{94}O_{33}$: C, 68.73; H, 4.76. Found: C, 68.87; H, 4.80.

3.8. 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (10)

To a solution of **9** (2.94 g, 1.48 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added CAN (3.9 g, 7.5 mmol), and the mixture was treated by the same procedure as described in the preparation of **4** to give **10** as a syrup (1.87 g, 63%): $[\alpha]_D$ +57.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.09 (s, 1H, N*H*), 8.02–7.21 (m, 60H, 12Ph*H*), 6.73 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1″), 6.04 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4″), 5.85–5.77 (m, 3H, H-2″, H-4′, H-4), 5.65 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.59 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.52 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3″), 5.48 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.26 (s, 1H, Ara*f*-H-1), 5.23 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 4.59 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 166.0, 165.7, 165.8, 165.7, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (12C, 12*C*OPh), 106.9 (Ara*f*-C-1), 101.5, 101.4, 101.0 (3Gal*p*-C-1). Anal. Calcd for $C_{109}H_{88}Cl_3NO_{32}$: C, 64.48; H, 4.37. Found: C, 64.22; H, 4.28.

3.9. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (12)

Compounds **7** (2.0 g, 1.29 mmol) and **11** (1.47 g, 1.55 mmol) in dry CH_2Cl_2 (60 mL) were coupled by the same procedure as described in the preparation of **3** to give pentasaccharide **12** as a syrup (2.68 g, 89%): $[\alpha]_D$ +38.2 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.09–7.18 (m, 70H, 14Ph*H*), 6.90 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.73 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4″), 5.94 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2″), 5.88 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.79 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.68 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.66–5.60 (m, 2H), 5.63 (d, 1H, $J_{2,3}$ 1.2 Hz, Ara*f*-H-2), 5.60 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.56 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3″), 5.52 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.48 (s, 1H, Ara*f*-H-1), 5.27 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.25 (s, 1H, Ara*f*-H-1), 5.13 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.63 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.61 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.65 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 166.1, 165.7, 165.7, 165.7, 165.6, 165.5, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0 (14C, 14*C*OPh), 107.7, 105.9 (2Ara*f*-C-1), 101.4, 101.0, 100.9 (3Gal*p*-C-1). Anal. Calcd for $C_{133}H_{110}O_{39}$: C, 68.49; H, 4.75. Found: C, 68.26; H, 4.87.

3.10. 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (13)

To a solution of **12** (2.68 g, 1.15 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added CAN (3.0 g, 5.75 mmol), and the mixture was treated by the same procedure as described in the preparation of **4** to give **13** as a syrup (1.60 g, 59%): $[\alpha]_D$ +43.2 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H, N*H*), 8.03–7.16 (m, 70H, 14Ph*H*), 6.73 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 6.05 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4″), 6.02 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2″), 5.98 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.87 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.81 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.64 (d, 1H, $J_{2,3}$ 1.2 Hz, Ara*f*-H-2), 5.60 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.57 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3″), 5.52 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.46 (s, 1H, Ara*f*-H-1), 5.27 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.26 (s, 1H, Ara*f*-H-1), 5.14 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.61 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.59 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 166.1, 165.8, 165.7, 165.7, 165.6, 165.5, 165.4, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (14C, 14*C*OPh), 107.8, 105.8 (2Ara*f*-C-1), 101.3, 101.0, 100.9 (3Gal*p*-C-1). Anal. Calcd for $C_{128}H_{104}Cl_3NO_{38}$: C, 64.85; H, 4.42. Found: C, 64.61; H, 4.32.

3.11. 4-Methoxyphenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-3-*O*-allyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (15)

A solution of **2** (3.0 g, 5.61 mmol) and 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**14**, 4.2 g, 6.18 mmol) in dry CH_2Cl_2 (100 mL) was stirred. TMSOTf (50 μL) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirred for 2 h, during which time the temperature gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 3:1 petroleum ether–EtOAc as the eluent, gave **15** as a syrup (4.78 g, 81%): $[\alpha]_D$ +68.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.13–7.24 (m, 25H, 5Ph*H*), 6.91 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.73 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.83 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.80 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.76 (m, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.68 (dd, 1H, $J_{1,2}$ 8.0 Hz,

$J_{2,3}$ 10.4 Hz, H-2), 5.70–5.65 (m, 1H, CH_2=CH–CH_2O), 5.50 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.18–5.03 (m, 2H, CH_2=CH–CH_2O), 5.01 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.90 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.81 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.4 Hz, H-6), 3.67 (s, 3H, CH_3O), 1.94 (s, 3H, CH_3CO). Anal. Calcd for $C_{59}H_{54}O_{18}$: C, 67.42; H, 5.18. Found: C, 67.49; H, 5.22.

3.12. 6-*O*-Acetyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-3-*O*-allyl-2,4-di-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (16)

To a solution of **15** (4.78 g, 4.55 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added CAN (12.1 g, 22.8 mmol), and the mixture was stirred at rt for 30 min, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was extracted with EtOAc (5 × 50 mL) and washed with water. The organic layer was concentrated under reduced pressure, and the crude hemiacetal was purified by column chromatography (2:1 petroleum ether–EtOAc) to afford a solid (3.2 g, 3.38 mmol). To a solution of the solid in CH_2Cl_2 (80 mL) were added trichloroacetonitrile (0.58 mL, 0.52 mmol) and anhyd K_2CO_3 (2.0 g, 13.5 mmol). The reaction mixture was stirred overnight at rt and then filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (2:1 petroleum ether–EtOAc) to give **16** as a syrup (3.2 g, 89%): $[\alpha]_D$ +49.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.24 (s, 1H, N*H*), 8.12–7.22 (m, 25H, 5Ph*H*), 6.64 (d, 1H, $J_{1,2}$ 3.6 Hz, α H-1), 5.90 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.81 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.80–5.69 (m, 1H, CH_2=CH–CH_2O), 5.70 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.67 (dd, 1H, $J_{1,2}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.57 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.23–5.06 (m, 2H, CH_2=CH–CH_2O), 4.80 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.46 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 3.79 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 1.94 (s, 3H, CH_3CO). Anal. Calcd for $C_{54}H_{48}Cl_3NO_{17}$: C, 59.54; H, 4.44. Found: C, 59.71; H, 4.32.

3.13. 4-Methoxyphenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-3-*O*-allyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (17)

Compounds **16** (3.0 g, 2.7 mmol) and 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (**5**, 1.37 g, 2.25 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give trisaccharide **17** (3.14 g, 85%) as a syrup: $[\alpha]_D$ +22.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.09–7.23 (m, 40H, 8Ph*H*), 6.96 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95–5.90 (m, 2H, H-2″, H-4″), 5.78 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.73 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.66 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.61–5.58 (m, 1H, CH_2=CH–CH_2O), 5.56 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3″), 5.47 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.39 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.15 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 5.13–4.98 (m, 2H, CH_2=CH–CH_2O), 4.61 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.58 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.24 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 4.12–4.02 (2H, CH_2=CH–CH_2O), 3.70 (s, 3H, CH_3O), 3.65 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 1.99 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.1, 165.0 (8C, 8*C*OPh), 101.2, 100.7, 100.6 (3C, C-1). Anal. Calcd for $C_{86}H_{76}O_{26}$: C, 67.71; H, 5.02. Found: C, 67.99; H, 4.93.

3.14. 4-Methoxyphenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (18)

To a solution of **17** (3.14 g, 2.06 mmol) in anhyd CH_3OH (50 mL) was added $PdCl_2$ (100 mg), and the mixture was stirred at rt for 5 h. Purification of the product by column chromatography with 1.5:1 petroleum ether–EtOAc as the eluent gave **18** (2.59 g, 85%) as a syrup: $[\alpha]_D$ +69.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.09–7.23 (m, 40H, 8Ph*H*), 6.96 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.97–5.92 (m, 2H, H-2″, H-4″), 5.78 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.67 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.65 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.57 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3″), 5.47 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.26 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.15 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.64 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.53 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.24 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 3.70 (s, 3H, CH_3O), 1.99 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.1, 165.0 (8C, 8*C*OPh), 101.2, 100.7, 100.6 (3C, C-1). Anal. Calcd for $C_{83}H_{72}O_{26}$: C, 67.11; H, 4.88. Found: C, 67.27; H, 4.80.

3.15. 4-Methoxyphenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (19)

Coupling of **18** (2.87 g, 1.93 mmol) with **8** (1.52 g, 2.5 mmol) under the same conditions as described for the coupling of **1** with **2** gave tetrasaccharide **19** (3.3 g, 89%) as a syrup: $[\alpha]_D$ +41.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.20 (m, 55H, 11Ph*H*), 6.96 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.86 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95–5.90 (m, 2H, H-2″, H-4″), 5.83 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4′), 5.73 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.66–5.60 (m, 2H, H-2′, H-2), 5.58 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3″), 5.49 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.28 (s, 1H, Ara*f*-H-1), 5.26 (d, 1H, $J_{2,3}$ 1.2 Hz, Ara*f*-H-2), 5.13 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.68 (d, 1H,

$J_{1,2}$ 8.0 Hz, H-1′), 4.58 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.21 (dd, 1H, $J_{5,6}$ 3.4 Hz, $J_{6,6}$ 10.8 Hz, H-6), 4.13 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 4.03 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.8 Hz, H-6), 3.68 (s, 3H, OCH_3), 3.47 (m, 1H, H-5), 1.99 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 166.0, 165.8, 165.7, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (11C, 11*C*OPh), 107.2 (Ara*f*-C-1), 101.5, 101.4, 101.0 (3Gal*p*-C-1). Anal. Calcd for $C_{109}H_{92}O_{33}$: C, 67.83; H, 4.81. Found: C, 68.01; H, 4.89.

3.16. 4-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (20)

To a solution of **19** (2 g, 1.03 mmol) in 1:1 CH_3OH–CH_2Cl_2 (100 mL) was added CH_3COCl (1 mL), and the reaction was carried out at rt for 24 h. Tetrasaccharide **20** (1.7 g, 87%) was obtained as a syrup after purifying the product by column chromatography with 1.5:1 petroleum ether–EtOAc as the eluent: $[\alpha]_D$ +31.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.03–7.19 (m, 55H, 11Ph*H*), 6.96 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.86 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95–5.90 (m, 2H, H-2″, H-4″), 5.89 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.71 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.68 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.62 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.58 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3″), 5.46 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.28 (s, 1H, Ara*f*-H-1), 5.23 (d, 1H, $J_{2,3}$ 1.2 Hz, Ara*f*-H-2), 5.13 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 5.04 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 12 Hz, H-6), 4.75 (dd, 1H, $J_{5,6}$ 3.4 Hz, $J_{6,6}$ 12 Hz, H-6), 4.64 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.57 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.21 (dd, 1H, $J_{5,6}$ 3.4 Hz, $J_{6,6}$ 10.8 Hz, H-6), 4.13 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3′), 3.64 (s, 3H, OCH_3), 3.51 (m, 1H, H-5), 3.36 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.8 Hz, H-6), 3.24 (dd, 1H, $J_{5,6}$ 5.6 Hz, $J_{6,6}$ 10.8 Hz, H-6); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 166.0, 165.8, 165.7, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (11C, 11*C*OPh), 107.2 (Ara*f*-C-1), 101.5, 101.4, 101.0 (3Gal*p*-C-1). Anal. Calcd for $C_{107}H_{90}O_{32}$: C, 68.07; H, 4.81. Found: C, 68.37; H, 4.69.

3.17. 4-Methoxyphenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (21)

Compounds **18** (1.50 g, 1.01 mmol) and **11** (1.14 g, 1.21 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give pentasaccharides **21** as a syrup (1.90 g, 83%): $[\alpha]_D$ +67.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.03–7.18 (m, 65H, 13Ph*H*), 6.93 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.73 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2″), 5.93 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4″), 5.78 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.74 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.65 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.61 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.56 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3″), 5.49 (s, 1H, Ara*f*-H-1), 5.43 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.28 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.27 (s, 1H, Ara*f*-H-1), 5.13 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.61 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.55 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.67 (s, 3H, OCH_3), 1.92 (CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 166.1, 165.7, 165.7, 165.6, 165.5, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0 (13C, 13*C*OPh), 107.6, 105.9 (2Ara*f*-C-1), 101.4, 100.9, 100.6 (3Gal*p*-C-1). Anal. Calcd for $C_{128}H_{108}O_{39}$: C, 67.72; H, 4.79. Found: C, 67.87; H, 4.65.

3.18. 4-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (22)

To a solution of **21** (1.9 g, 0.84 mmol) in 1:1 CH_3OH–CH_2Cl_2 (100 mL) was added CH_3COCl (1 mL), and the reaction was carried out at rt for 24 h. After purifying the product by column chromatography with 1.5:1 petroleum ether–EtOAc as the eluent, **22** was obtained as a syrup (1.5 g, 81%): $[\alpha]_D$ +61.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.08–7.15 (m, 65H, 13Ph*H*), 6.91 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.73 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95 (dd, 1 H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2″), 5.93 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4″), 5.84 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.50 (s, 1H, Ara*f*-H-1), 5.46 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.28 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.27 (s, 1H, Ara*f*-H-1), 5.14 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.68 (dd, 1H, $J_{5,6}$ 4.4 Hz, $J_{6,6}$ 10.4 Hz, H-6), 4.61 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.55 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.67 (s, 3H, OCH_3), 3.49 (dd, 1H), 3.37 (dd, 1H, $J_{5,6}$ 6.8 Hz, $J_{6,6}$ 12 Hz, H-6), 3.28 (dd, 1H, $J_{5,6}$ 6.8 Hz, $J_{6,6}$ 12 Hz, H-6); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 166.1, 165.7, 165.7, 165.6, 165.5, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0 (13C, 13*C*OPh), 107.6, 105.9 (2Ara*f*-C-1), 101.4, 100.9, 100.6 (3Gal*p*-C-1). Anal. Calcd for $C_{126}H_{106}O_{38}$: C, 67.91; H, 4.79. Found: C, 67.73; H, 4.72.

3.19. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (23)

Compounds **10** (436 mg, 0.22 mmol) and **22** (400 mg, 0.18 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to

give **23** as a syrup (595 mg, 81%): $[\alpha]_D$ +73.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.03–7.16 (m, 125H, 25Ph*H*), 6.88 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.73 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.90 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.89 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.88 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.72 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.38 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3), 5.09 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.56 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.43 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.41 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.29 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.23 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.69 (s, 3H, CH_3O); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.3, 167.1, 167.0, 166.3, 166.3, 166.2, 166.1, 166.0, 165.8, 165.7, 165.6, 165.6, 165.5, 165.4, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0, 164.9, 164.7, 164.7, 164.5 (25C, 25*C*OPh), 107.9, 107.7, 105.7 (3Ara*f*-C-1), 101.5, 101.4, 101.1, 101.0, 100.9, 100.5 (6Gal*p*-C-1). Anal. Calcd for $C_{233}H_{192}O_{69}$: C, 68.32; H, 4.72. Found: C, 68.49; H, 4.61.

3.20. 4-Methoxyphenyl β-D-galactopyranosyl-(1 → 6)-[α-L-arabinofuranosyl-(1 → 3)]-β-D-galactopyranosyl-(1 → 6)-β-D-galactopyranosyl-(1 → 6)-β-D-galactopyranosyl-(1 → 6)-[α-L-arabinofuranosyl-(1 → 5)-α-L-arabinofuranosyl-(1 → 3)]-β-D-galactopyranosyl-(1 → 6)-β-D-galactopyranoside (24)

Compound **23** (595 mg, 0.14 mmol) was dissolved in a satd solution of NH_3 in MeOH (80 mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **24** as an amorphous solid(175 mg, 81%): $[\alpha]_D$ +56.7 (*c* 1.0, H_2O); ^1H NMR (D_2O, 400 MHz): δ 7.08 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.89 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.29 (s, 1H, Ara*f*-H-1), 5.13 (s, 1H, Ara*f*-H-1), 5.11 (s, 1H, Ara*f*-H-1), 4.97 (d, 1H, $J_{1,2}$ 8.0 Hz, Gal*p*-H-1), 4.86 (d, 1H, $J_{1,2}$ 7.6 Hz, Gal*p*-H-1), 4.70 (d, 1H, $J_{1,2}$ 8.0 Hz, Gal*p*-H-1), 4.40 (d, 1H, $J_{1,2}$ 7.2 Hz, Gal*p*-H-1), 4.38 (m, 2H, 2Gal*p*-H-1); ^{13}C NMR (100 MHz, D_2O): δ 109.4, 109.3, 107.4 (3Ara*f*-C-1), 103.4, 103.4, 100.3, 103.2, 102.9, 101.7 (6Gal*p*-C-1). MALDITOF-MS calcd for $C_{58}H_{92}O_{44}$: 1493.32 [M]. Found: 1493.2 [M].

3.21. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (25)

Compounds **13** (603 mg, 0.25 mmol) and **20** (400 mg, 0.21 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give **25** as a syrup (712 mg, 81%): $[\alpha]_D$ +71.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.11–7.17 (m, 125H, 25Ph*H*), 6.92 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.91 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.90 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.89 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.27 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.26 (s, 1H, Ara*f*-H-1), 5.10 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.59 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.69 (s, 3H, CH_3O); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 167.1, 167.0, 166.4, 166.3, 166.2, 166.1, 166.0, 165.8, 165.7, 165.7, 165.6, 165.5, 165.4, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0, 164.8, 164.7, 164.7, 164.5 (25C, 25*C*OPh), 107.8, 107.7, 105.8 (3Ara*f*-C-1), 101.5, 101.4, 101.3, 101.0, 100.9, 100.5 (6Gal*p*-C-1). Anal. Calcd for $C_{233}H_{192}O_{69}$: C, 68.32; H, 4.72. Found: C, 68.61; H, 4.89.

3.22. 4-Methoxyphenyl β-D-galactopyranosyl-(1 → 6)-[α-L-arabinofuranosyl-(1 → 5)-α-L-arabinofuranosyl-(1 → 3)]-β-D-galactopyranosyl-(1 → 6)-β-D-galactopyranosyl-(1 → 6)-β-D-galactopyranosyl-(1 → 6)-[α-L-arabinofuranosyl-(1 → 3)]-β-D-galactopyranosyl-(1 → 6)-β-D-galactopyranoside (26)

Compound **25** (712 mg, 0.17 mmol) was dissolved in a satd solution of NH_3 in MeOH (80 mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **26** as an amorphous solid (218 mg, 84%): $[\alpha]_D$ +49.1 (*c* 1.0, H_2O); ^1H NMR (D_2O, 400 MHz): δ 7.07 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.98 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.21 (s, 1H, Ara*f*-H-1), 5.11 (s, 1H, Ara*f*-H-1), 5.01 (s, 1H, Ara*f*-H-1), 4.95 (d, 1H, $J_{1,2}$ 8.0 Hz, Gal*p*-H-1), 4.85 (d, 1H, $J_{1,2}$ 7.6 Hz, Gal*p*-H-1), 4.66 (d, 1H, $J_{1,2}$ 8.0 Hz, Gal*p*-H-1), 4.38 (d, 1H, $J_{1,2}$ 7.2 Hz, Gal*p*-H-1), 4.32 (m, 2H, 2Gal*p*-H-1); ^{13}C NMR (100 MHz, D_2O): δ 109.3, 109.3, 107.2 (3 Ara*f*-C-1), 103.4, 103.3, 103.3, 103.1, 102.8, 101.6 (6Gal*p*-C-1). MALDITOF-MS calcd for $C_{58}H_{92}O_{44}$: 1493.32 [M]. Found: 1493.2 [M].

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References

1. (a) Egert, D.; Beuscher, N. *Planta Med.* **1992**, *58*, 163–172; (b) Paulsen, B. S. *Curr. Org. Chem.* **2001**, *5*, 939–950.
2. Yamada, H.; Kiyohara, H.; Cyong, J. C.; Otsuka, Y. *Mol. Immunol.* **1985**, *22*, 295–303.
3. Kiyohara, H.; Yamada, H.; Cyong, J. C.; Otsuka, Y. *J. Pharmacobio-Dyn.* **1986**, *9*, 339–346.

4. Shimizu, N.; Tomoda, M.; Gonda, R. *Chem. Pharm. Bull. (Tokyo)* **1989**, *37*, 1329–1335.
5. Steffan, W.; Kovac, P.; Albersheim, P.; Darvill, A. G.; Hahn, M. G. *Carbohydr. Res.* **1995**, *275*, 295–307.
6. (a) Lipták, A.; Nánás, P. *Tetrahedron Lett.* **1977**, 921–924; (b) Csávás, M.; Borbás, A.; Jánossy, L.; Lipták, A. *Tetrahedron Lett.* **2003**, *44*, 631–634; (c) Csávás, M.; Borbás, A.; Szilagyi, L.; Lipták, A. *Synlett* **2002**, 887–891; (d) Koeners, H. J.; Verdegaal, C. H. M.; van Boom, J. H. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 118–125; (e) Timmers, C. M.; Wigchert, S. C. M.; Leeuwenburgh, M. A.; van der Marel, G. A.; van Boom, J. H. *Eur. J. Org. Chem.* **1998**, *1*, 91–97; (f) Borbás, A.; Jánossy, L.; Lipták, A. *Carbohydr. Res.* **1999**, *318*, 98–109; (g) Gu, G.; Yang, F.; Du, Y.; Kong, F. *Carbohydr. Res.* **2001**, *336*, 99–106; (h) Csávás, M.; Borbás, A.; Jánossy, A.; Batta, G.; Lipták, A. *Carbohydr. Res.* **2001**, *336*, 107–115; (i) Zeng, Y.; Li, A.; Kong, F. *Tetrahedron Lett.* **2003**, *44*, 8325–8329; (j) Li, A.; Zeng, Y.; Kong, F. *Carbohydr. Res.* **2003**, *339*, 673–681; (k) Du, Y.; Pan, Q.; Kong, F. *Carbohydr. Res.* **2000**, *323*, 28–35.
7. Du, Y.; Pan, Q.; Kong, F. *J. Carbohydr. Chem.* **2001**, *20*, 297–301.
8. Kong, F.; Lu, D.; Zhou, S. *Carbohydr. Res.* **1990**, *198*, 141–147.
9. Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–125.
10. Du, Y.; Pan, Q.; Kong, F. *Synlett* **1999**, 1648–1652.
11. Byramova, N. E.; Ovchinnikov, M. V.; Backinowsky, L. V.; Kochetkov, N. K. *Carbohydr. Res.* **1983**, *124*, c8.