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An effective synthesis of an arabinogalactan with a β-(1 → 6)-linked galactopyranose backbone and α-(1 → 2) arabinofuranose side chains

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Abstract—An octasaccharide, β-D-Gal*p*-(1 → 6)-[α-L-Ara*f*-(1 → 2)]-β-D-Gal*p*-(1 → 6)-β-D-Gal*p*-(1 → 6)-[α-L-Ara*f*-(1 → 5)-α-L-Ara*f*-(1 → 2)]-β-D-Gal*p*-(1 → 6)-β-D-Gal*p*-1 → OMP was synthesized. 4-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (**5**), 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**9**), and 4-methoxyphenyl 2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranoside (**11**), 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**12**), and 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate (**17**) were used as the synthons. A concise route was used to gain the tetrasaccharide donor **19** by the use of **11**, **12**, **5**, and **17**. Meanwhile, treatment of **5** with **9** yielded β-(1 → 6)-linked disaccharide **20**, and subsequent selective 6-O-deacetylation produced the disaccharide acceptor **21**. Reaction of **21** with **19** gave **22**, and subsequent selective 2-O-deacetylation afforded the hexasaccharide acceptor **23**. Condensation of **23** with α-L-(1 → 5)-linked arabinofuranose disaccharide **24**, followed by deprotection, yielded the target octasaccharide.

Keywords: Arabinogalactan; Trichloroacetimidates; Synthesis

1. Introduction

Arabinogalactans from certain sources have immunomodulating activity. Antibodies raised against arabinogalactan proteins from *Baptisia tinctoria* or *Echinacea purpurea* reacted selectively with their corresponding antigens.[1] An arabinogalactan isolated from the Chinese herb, *Angelica acutiloba*, was found to have potent anticomplement activity;[2] such activity was not found in an arabinogalactan from larch wood.[3] An arabinogalactan isolated from the roots of *Saposhnikova divaricata* or *Panex notoginseng* had reticuloendothelial system activating properties.[4] An arabinogalactan from ragweed enhanced vascular permeability in mice, when injected intravenously, by interacting with the natural antibody.[5] Arabinogalactans with a β-(1 → 6)-linked galactopyranose backbone and α-(1 → 2)-linked arabinofuranose side chains may exist in *E. purpurea*; these have immunomodulating activity.[1] Although the presence of 2,6-branched residues in arabinogalactans is well known, the exact structure of these saccharides remains to be established. Especially, for elucidation of the molecular structure responsible for their biological activity, it would be necessary to synthesize 2,6-branched arabinogalactans.

Until now, some examples exist of the chemical synthesis of arabinogalactans.[6,7] Our previous communication[8] reported a facile synthesis of an octasaccharide comprised of a β-(1 → 6)-linked galactose backbone with the same α-(1 → 2)-linked arabinose side chains. We present herein an effective synthesis of an octasaccharide consisting of a β-(1 → 6)-linked galactose backbone with arabinose side chains of a different size.

2. Results and discussion

Retrosynthetic analysis indicates that the best way to obtain the arabinogalactan octasaccharide **26** is to first prepare the tetrasaccharide donor **19**, which is composed of a β-(1 → 6)-linked galactose backbone with a

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2′-branched arabinofuranose. Then, condensation of **19** with the disaccharide acceptor **21**, and subsequent 2-O-deacetylation, followed by coupling with an arabinofuranose disaccharide donor, and deprotection would give the desired compound.

In our synthesis, we applied the benzoyl group as a relatively 'permanent' protecting group, and the acetyl group as a temporary protecting group. The benzoyl and acetyl protecting groups are well differentiated by treating the protected sugars with a ~2% solution of MeCOCl in CH_2Cl_2–MeOH[9] that produces dry HCl in situ that completely removes the acetyl group. It was found in our research that under much milder conditions, that is, 1:500:500 MeCOCl–CH_3OH–CH_2Cl_2, the acetate group on the primary hydroxyl group of galactose can be removed without affecting the secondary one. This finding greatly simplified our synthesis, since the use of orthogonal protective groups was conveniently avoided.

For construction of the target oligosaccharide with the method described above, several basic monosaccharide synthons were prepared as shown in Scheme 1. Compound **3** was obtained by 6-O-tritylation of galactose, benzoylation, acetolysis, 1-O-deacetylation, and trichloroacetimidate[10] formation. Monosaccharide acceptor **5** was gained by treating **3** with 4-methoxyphenol in the presence of a catalytic amount of TMSOTf, followed by selective 6-O-deacetylation with 1:500:500 MeCOCl–CH_3OH–CH_2Cl_2 in 88% yield. Another key donor **9** was prepared from 1,2-*O*-ethylidene-α-D-galactopyranose[11] (**6**) by tritylation, benzoylation, acetolysis, 1-O-deacetylation, and trichloroacetimidate formation. Meanwhile coupling of **9** with 4-methoxyphenol, followed by 6-O-deacetylation with 1:500:500 MeCOCl–CH_3OH–CH_2Cl_2, afforded the key acceptor **11**.

Condensation of 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**12**) with **11** in the presence of TMSOTf as catalyst gave exclusively the β-(1→6)-linked disaccharide building block **13** (81%). Oxidative cleavage of 1-OMP of **13** with CAN (4.5 equiv) in 4:1 CH_3CN–H_2O, followed by trichloroacetimidate formation with trichloroacetonitrile and DBU in dry dichloromethane, gave the disaccharide donor **14** (79%). Treatment of **14** with **5** under the same coupling conditions as described above produced the trisaccharide **15** (80%). Selective 2′-O-deacetyaltion of **15** with 1:50:50 MeCOCl–CH_3OH–CH_2Cl_2 for 48 h at room temperature gave the trisaccharide acceptor **16** (79%). Condensation of **16** with perbenzoylated α-L-arabinofuranosyl trichloroacetimidate[9] (**17**) yielded the tetrasaccharide **18** (78%), and subsequent oxidative cleavage of 1-OMP and trichloroacetimidate formation gave the required tetrasaccharide donor **19** (81%).

The disaccharide acceptor **21** was readily obtained by coupling of **5** with **9** (81%), followed by selective 6-O-deacetylation with 1:500:500 MeCOCl–CH_3OH–CH_2Cl_2 (82%) (Scheme 2). Condensation of **21** with the tetrasaccharide donor **19** smoothly gave the hexasaccharide **22** (75%), and subsequent 2′-O-deacetylation with 1:50:50 MeCOCl–CH_3OH–CH_2Cl_2 afforded the hexasaccharide acceptor **23** (72%). Coupling of **23** with the donor, 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate[9] (**24**), was successfully carried out yielding the protected octasaccharide **25** (75%). Finally, **25** was deprotected with a saturated solution of ammonia in MeOH (40 mL) for a week to give the target **26** (84%).

In these syntheses, which involved relatively uncomplicated reactions, all compounds described herein were obtained in satisfactory yields with easily accessible materials and inexpensive reagents. These compounds were isolated and identified by their ^1H and ^{13}C NMR spectra. Elemental analyses completed their full characterization.

In summary, a special strategy that is particularly suitable for the preparation of 2,6-branched arabino-galacto-oligosaccharides has been developed based on trichloroacetimidate donors and selective deacetylation reactions.

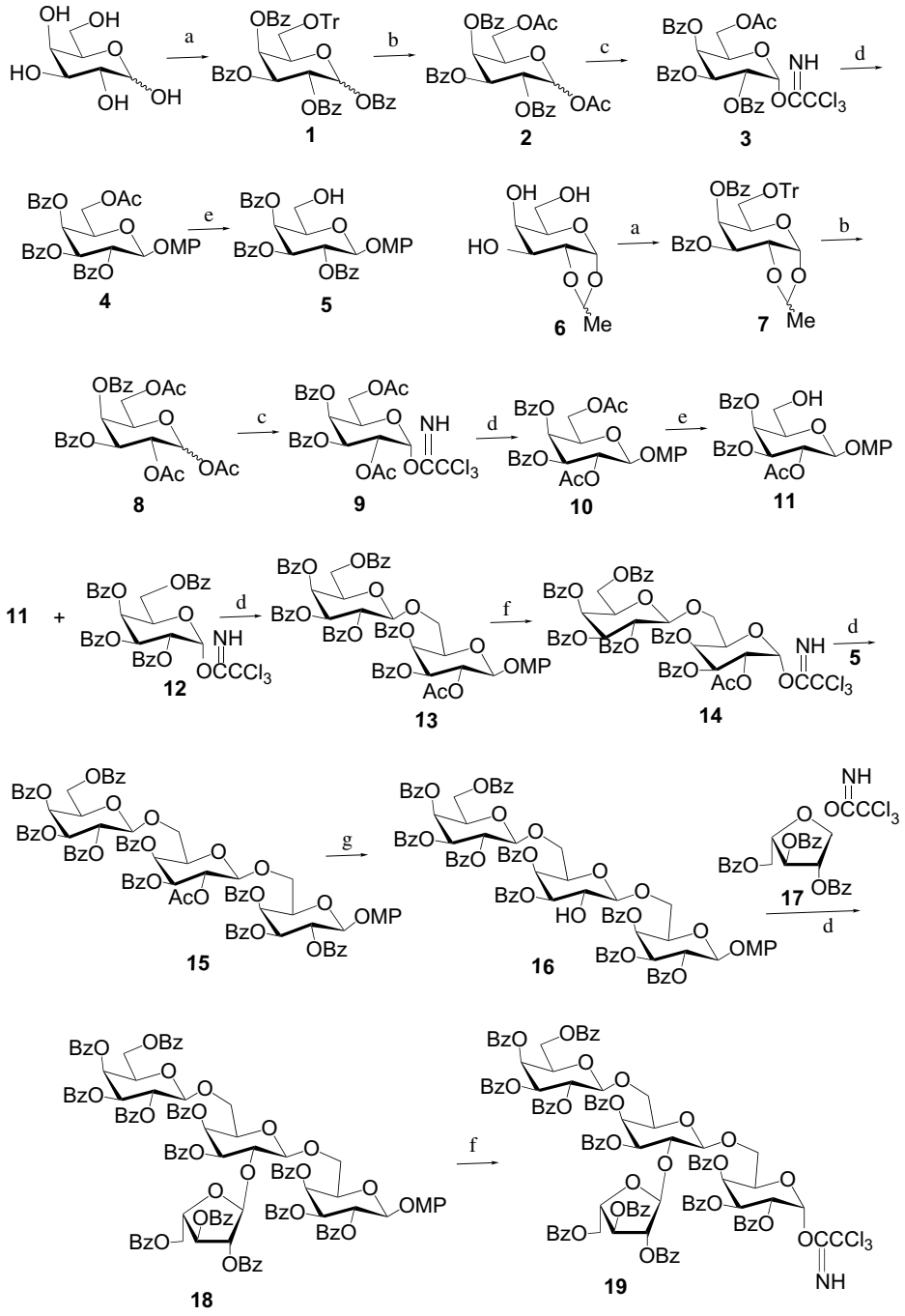
3. Experimental

3.1. General methods

Optical rotations were determined at 25 °C with a Perkin–Elmer Model 241-Mc automatic polarimeter. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker ARX 400 spectrometers (400 MHz for ^1H, 100 MHz for ^{13}C) at 25 °C for solutions in $CDCl_3$ or D_2O as indicated. Individual resonances could not be identified with the specific sugar residues. 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 (8×240 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 reduced pressure.

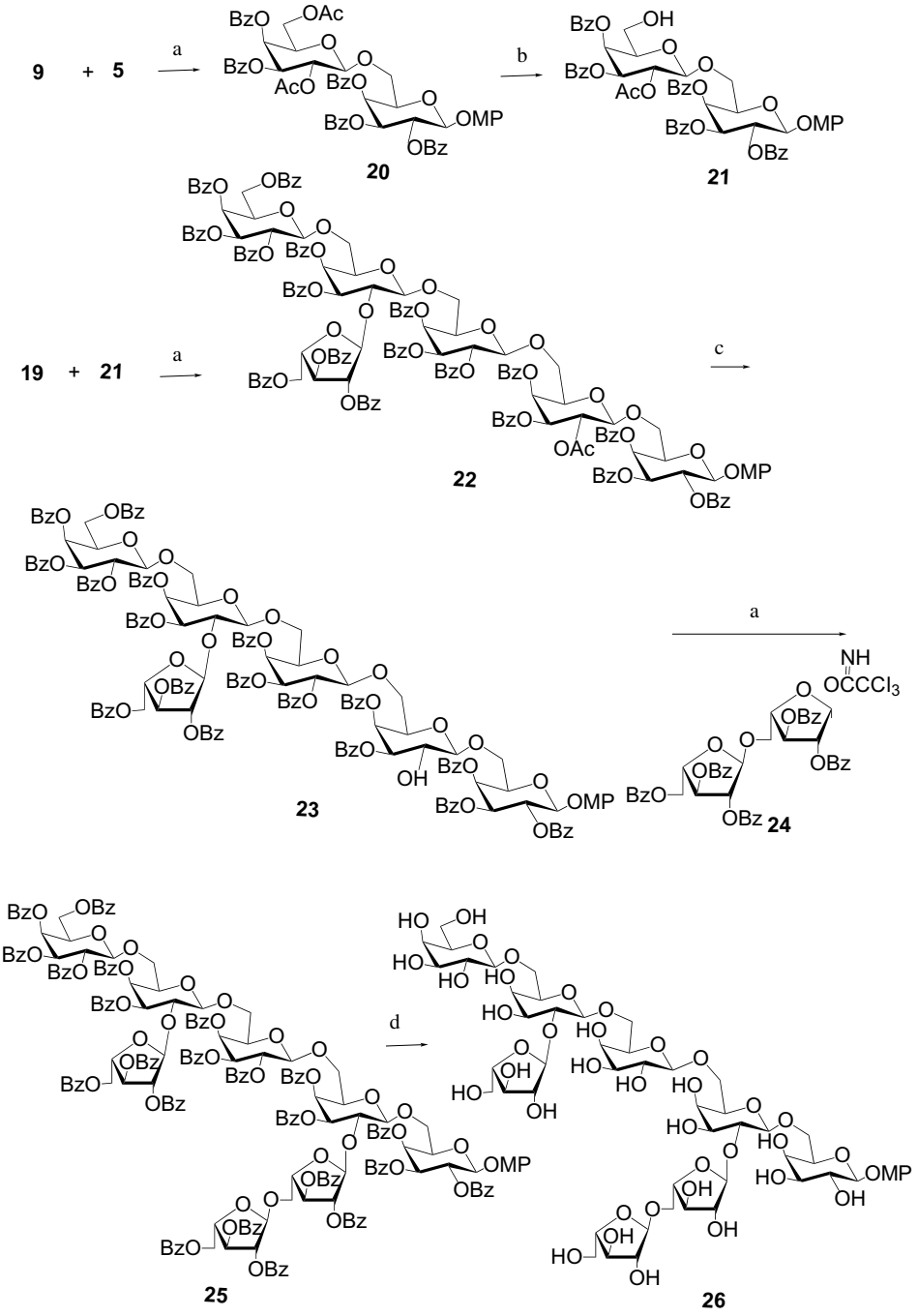
3.2. 6-*O*-Acetyl-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (3)

To a solution of D-galactose (10.0 g, 55.5 mmol) in pyridine was added chlorotriphenylmethane (trityl chloride, 17.0 g, 61.1 mmol). The mixture was stirred at 50 °C for 6 h, at the end of which time TLC (EtOAc) indicated that the reaction was complete. The reaction mixture was cooled to 0 °C, then benzoyl chloride



Scheme 1. Reagents and conditions: (a) (i) trityl chloride, pyridine, 50 °C, 6 h; (ii) PhCOCl, 50 °C, 24 h; (b) 1:1:0.6:0.18 CH_2Cl_2–HOAc–Ac_2O–H_2SO_4, rt, 20 h; (c) (i) benzylamine, THF, rt, 24 h ; (ii) CCl_3CN, K_2CO_3, CH_2Cl_2, rt, 10 h; (d) 4-methoxylphenol, TMSOTf, CH_2Cl_2, −20 °C to rt, 2 h; (e) 1:500:500 MeCOCl–CH_3OH–CH_2Cl_2, rt, 48 h; (f) (i) CAN, 4:1 H_2O–CH_3CN, rt, 0.5 h, (ii) CCl_3CN, K_2CO_3, CH_2Cl_2, rt, 10 h; (g) 1:50:50 MeCOCl–CH_3OH–CH_2Cl_2, rt, 48 h.

(30.9 mL, 267 mmol) was added dropwise within 30 min to keep the reaction temperature at 50 °C, and the mixture was stirred for 24 h. Water (300 mL) was added to the reaction mixture, and stirring was continued for 30 min. The mixture was extracted with CH_2Cl_2 (3 × 200 mL), and the combined extracts were washed with N HCl and satd aq $NaHCO_3$, dried (Na_2SO_4), and concentrated to a syrup that was subjected to column chromatography (4:1 petroleum ether–EtOAc) as the eluent to give compound **1** (34.9 g, 72%) as a syrup. Compound **1** (20 g, 22.8 mmol) was dissolved in a mixture of CH_2Cl_2 (50 mL), Ac_2O (50 mL), and AcOH (30 mL), the solution was cooled to 0 °C in an ice bath, and H_2SO_4 (8.8 mL) was added dropwise over 20 min. After the addition was complete, the ice bath was removed, and the reaction was allowed to continue for



Scheme 2. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt, 2 h; (b) 1:500:500 MeCOCl–CH_3OH–CH_2Cl_2, rt, 48 h; (c) 1:50:50 MeCOCl–CH_3OH–CH_2Cl_2, rt, 48 h; (d) satd NH_3–MeOH, rt, 7 d.

20 h at ambient temperature. The reaction solution was poured into ice water (400 mL), stirring was continued for 30 min, and the mixture was extracted with CH_2Cl_2 (3×200 mL). The combined extracts were washed with satd aq $NaHCO_3$, dried (Na_2SO_4), and concentrated to a syrup that was subjected to column chromatography (4:1 petroleum ether–EtOAc) as the eluent to give **2** (10.9 g, 83%) as a syrup. A solution of compound **2** (5 g, 8.7 mmol) and benzylamine (3 mL, 27.4 mmol) in anhyd THF (30 mL) was stirred at rt for 24 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was then concentrated under reduced pressure. Purification by flash column chromatography on silica gel (4:1 petroleum ether–EtOAc) gave 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-D-galactose (4.08 g, 88%). To a solution of the hemi-

acetal (5.2 g, 9.7 mmol) in dry CH_2Cl_2 (80 mL) were added trichloroacetonitrile (2.5 mL, 24 mmol) and anhyd K_2CO_3 (10.0 g). 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 (5:1 petroleum ether–EtOAc) to give **3** (4.6 g, 90%): $[\alpha]_D$ +35.3° (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.67 (s, 1H, N*H*), 8.09–7.25 (m, 15H, 3Ph*H*), 6.87 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 6.07 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 6.05 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.96 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2), 4.74 (m, 1H, H-5), 4.27–4.25 (m, 2H, H-6), 1.99 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{31}H_{26}Cl_3NO_{10}$: C, 54.87; H, 3.86. Found: C, 54.79; H, 3.83.

3.3. 4-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (5)

A solution of **3** (5.0 g, 7.4 mmol) and 4-methoxyphenol (1.01 g, 8.14 mmol) in dry CH_2Cl_2 (80 mL) was stirred, and TMSOTf (20 μL) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirring for 1 h, during which time the temperature was gradually raised to ambient temperature. The mixture was then neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 4:1 petroleum ether–EtOAc as the eluent, gave **4** (4.8 g, 84%). To a solution of **4** (4 g, 6.3 mmol) in 1:1 CH_3OH–CH_2Cl_2 (100 mL) was added CH_3COCl (0.1 mL), and the mixture was stirred at rt for 48 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was then neutralized with Et_3N. The reaction mixture was concentrated, then the reside was passed through a silica gel column with 3:1 petroleum ether–EtOAc as the eluent to give **5** (3.25 g, 87%): $[\alpha]_D$ +65.4° (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.13–7.25 (m, 15H, 3Ph*H*), 6.92 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.90 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.84 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.59 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 4.87 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.05–4.03 (m, 1H, H-5), 3.97–3.78 (m, 2H, H-6), 3.65 (s, 3H, CH_3O) Anal. Calcd for $C_{34}H_{30}O_{10}$: C, 68.26; H, 5.01. Found: C, 68.59; H, 5.26.

3.4. 2,6-Di-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (9)

A solution of 1,2-*O*-ethylidene-α-D-galactopyranose (**6**, 6.4 g, 31.1 mmol) and chlorotriphenylmethane (trityl chloride, 9.8 g, 35.0 mmol) in pyridine (100 mL) was stirred at 50 °C for 6 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was cooled to 0 °C, and then benzoyl chloride (7.9 mL, 68 mmol) was added dropwise within 30 min to keep the reaction temperature at 50 °C. The mixture was stirred at rt overnight. Water (300 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 N HCl and satd aq $NaHCO_3$, dried (Na_2SO_4), and concentrated to a syrup that was subjected to column chromatography (4:1 petroleum ether–EtOAc) as the eluent to give **7** (14.5 g, 71%) as a syrup. Compound **7** (11 g, 16.77 mmol) was dissolved in a mixture of CH_2Cl_2 (50 mL), Ac_2O (50 mL), and AcOH (30 mL), the solution was cooled to 0 °C in an ice bath, and H_2SO_4 (8.8 mL) was added dropwise over 20 min. After the addition was complete, the ice bath was removed, and the reaction was allowed to continue for 20 h at ambient temperature. The reaction solution was poured into ice water (400 mL), stirring was continued for 30 min, and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were washed with satd aq $NaHCO_3$, dried (Na_2SO_4), and concentrated to a syrup that was subjected to column chromatography (4:1 petroleum ether–EtOAc) as the eluent to give **8** (7.2 g, 83%) as a syrup. A solution of compound **8** (5 g, 9.73 mmol) and benzylamine (3 mL, 27.4 mmol) in anhyd THF (30 mL) was stirred at rt for 24 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution then was concentrated under reduced pressure. Purification by flash column chromatography on silica gel (3:1 petroleum ether–EtOAc) gave 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-D-galactose (3.96 g, 88%). To a solution of 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-D-galactose (4 g, 8.47 mmol) in dry CH_2Cl_2 (30 mL) were added trichloroacetonitrile (2.5 mL, 24 mmol) and anhyd K_2CO_3 (5.8 g, 42 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 (5:1 petroleum ether–EtOAc) to give **9**: $[\alpha]_D$ +51 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.71 (s, 1H, N*H*), 8.04–7.35 (m, 10H, 2Ph*H*), 6.77 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 6.01 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.85 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.76 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2), 4.65–4.63 (m, 1H, H-5), 4.28–4.26 (m, 2H, H-6), 1.99, 1.98 (s, s, 6H, C*H*$_3$CO). Anal. Calcd for $C_{26}H_{24}Cl_3NO_{10}$: C, 50.65; H, 3.89. Found: C, 50.79; H, 3.83.

3.5. 4-Methoxyphenyl 2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranoside (11)

A solution of **9** (5.0 g, 8.1 mmol) and 4-methoxyphenol (1.11 g, 8.92 mmol) in dry CH_2Cl_2 (80 mL) was stirred, and TMSOTf (30 μL) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirred for 1 h, during which time the temperature was 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 4:1 petroleum ether–EtOAc as the eluent, gave **10** (3.9 g, 84%). To a solution of **10** (3.5 g, 6.1 mmol) in 1:1 CH_3OH–CH_2Cl_2 (100 mL) was added CH_3COCl (0.1 mL), and the mixture was stirred at rt for 48 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was then neutralized with Et_3N and concentrated, and the residue was passed through a silica gel column with 3:1 petroleum ether–EtOAc as the eluent to give **11** (2.82 g, 87%): $[\alpha]_D$ +65.4° (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.03–7.22 (m, 10H, 2Ph*H*), 6.90 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.81 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.74 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.59 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 4.89 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2), 4.67 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.06 (m, 1H, H-5), 3.97 (m, 2H, H-6), 3.67 (s, 3H, C*H*$_3$O), 1.99 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{29}H_{28}O_{10}$: C, 64.47; H, 5.18. Found: C, 64.69; H, 5.29.

3.6. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside-(1 → 6)-2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranoside (13)

A solution of **12** (7.0 g, 9.4 mmol) and 4-methoxyphenyl 2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranoside (**11**, 4.6 g, 8.6 mmol) in dry CH_2Cl_2 (80 mL) were coupled to give disaccharides **13** (7.74 g, 81%) by the same procedure as described in the preparation of **4** from **3** and 4-methoxyphenol: $[\alpha]_D$ +80.3° (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.10–7.24 (m, 30H, 6Ph*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′), 5.89 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.78 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.70 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.53 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.38 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.03 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.94 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.39 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 4.27–4.18 (m, 3H, 2 H-5, H-6), 4.13–4.10 (dd, 1H, $J_{5,6}$ 4.0 Hz, $J_{6,6}$ 10.4 Hz, H-6), 4.01–3.98 (dd, 1H, $J_{5,6}$ 4.0 Hz, $J_{6,6}$ 10.4 Hz, H-6), 3.73 (s, 3H, C*H*$_3$O), 1.99 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{63}H_{54}O_{19}$: C, 67.89; H, 4.84. Found: C, 67.99; H, 4.80.

3.7. 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (14)

To a solution of **13** (7.0 g, 6.3 mmol) in 4:1 CH_3CN–H_2O (60 mL) was added ceric ammonium nitrate (CAN, 15.54 g, 28.4 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 × 200 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. To a solution of the solid in CH_2Cl_2 (80 mL) were added trichloroacetonitrile (2.5 mL, 24 mmol) and anhyd K_2CO_3 (10.0 g, 72.4 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 **14** (5.7 g, 79%): $[\alpha]_D$ +85.2° (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.70 (s, 1H, N*H*), 8.12–7.17 (m, 30H, 6Ph*H*), 6.34 (d, 1H, $J_{1,2}$ 3.2 Hz, αH-1), 5.87 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.85 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.74 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.55 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.41 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.15 (dd, 1H, $J_{1,2}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.04 (d, 1H, $J_{1,2}$ 8.0 Hz, βH-1), 4.46 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 4.27–4.10 (m, 4H, 2H-5, 2H-6), 3.98 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 1.96 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{58}H_{48}Cl_3NO_{18}$: C, 60.42; H, 4.16. Found: C, 60.69; H, 4.12.

3.8. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (15)

Coupling of **14** (4.6 g, 4.0 mmol) and **5** (2.17 g, 3.6 mmol) in anhyd CH_2Cl_2 (80 mL) was carried out by the same procedure as described in the preparation of **4** to give **15** as a syrup (purified with 2.5:1 petroleum ether–EtOAc, 4.6 g, 80%): $[\alpha]_D$ +83.4° (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.07–7.23 (m, 45H, 9Ph*H*), 6.92 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.99 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.92 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.88 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.84 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.65 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.60 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.54 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.44 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.27 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.22 (d, 1H, $J_{1,2}$ 8.0 Hz, βH-1), 4.69 (d, 1H, $J_{1,2}$ 8.0 Hz, βH-1), 4.62 (d, 1H, $J_{1,2}$ 8.0 Hz, βH-1), 4.30 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 4.27–4.10 (m, 3H, 1H-5, 2H-6), 4.09–3.98 (m, 5H, 2H-5, 3H-6), 3.73 (s, 3H, C*H*$_3$O), 1.84 (s, 3H, C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8, 165.7, 165.6, 165.5, 165.4, 165.3, 165.2, 165.1, 165.0 (9C, 9*C*OPh), 101.7, 101.0, 100.9 (3C, C-1), 80.7, 78.0, 73.6, 73.4, 72.2, 71.9, 71.6, 71.3, 69.8, 68.3, 68.1, 67.9, 67.8, 67.1, 66.7 (C-2,-3,-4,-5,-6). Anal. Calcd for $C_{90}H_{76}O_{27}$: C, 68.04; H, 4.78. Found: C, 68.07; H, 4.73.

3.9. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (16)

To a solution of **15** (3.35 g, 2.1 mmol) in 1:1 CH_3OH–CH_2Cl_2 (100 mL) was added CH_3COCl (1 mL), and the reaction was carried out to give **16** (2.57 g, 79%) using the same procedure as described in the preparation of **5**: $[\alpha]_D$ +79.6° (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.11–7.26 (m, 45H, Ph*H*), 6.92 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), δ 5.90–5.88 (m, 2H, 2H-4), 5.82 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.81 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.71 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.64 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.57 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.27 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.17 (d, 1H, $J_{1,2}$ 8.0 Hz, βH-1), 4.75 (d, 1H, $J_{1,2}$ 8.0 Hz, βH-1), 4.59 (d, 1H, $J_{1,2}$ 8.0 Hz, βH-1), 4.30 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 4.27–4.10 (m, 3H,1 H-5, 2H-6), 4.09–3.98 (m, 6H, 1H-2, 2H-5, 3H-6), 3.73 (s, 3H, C*H*$_3$O); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8, 165.7, 165.6, 165.5, 165.4, 165.3, 165.2, 165.1, 165.0 (9C, 9*C*OPh), 101.7, 101.0, 100.9 (3C, C-1), 80.7, 78.0, 73.7, 73.4, 72.2, 71.9, 71.6, 71.3, 69.8, 68.3, 68.2, 67.9, 67.8, 67.3, 66.7 (C-2,-3,-4,-5,-6). Anal. Calcd for $C_{88}H_{74}O_{26}$: C, 68.33; H, 4.78. Found: C, 68.29; H, 4.70.

3.10. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 2)]-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (18)

Coupling of **17** (1.12 g, 1.84 mmol) and **16** (2.34 g, 1.51 mmol) in anhyd CH_2Cl_2 (50 mL) using the same procedure as described in the preparation **4** gave **18** as a syrup (purified with 1.5:1 petroleum ether–EtOAc, 2.34 g, 78%): $[\alpha]_D$ +65.1° (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.03–7.21 (m, 60H, 12Ph*H*), 6.92 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.05 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.85 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.77 (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), 5.63 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.56–5.49 (m, 3H, H-3), 5.48 (s, 1H, Ara*f*-H-1), 5.38 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.37 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-3), 4.75 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.70 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.54 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.43–4.30 (m, 2H), 4.26 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 4.12–4.08 (m, 3H), 4.01–3.95 (m, 2H), 3.92–3.68 (m, 3H), 3.65 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 165.8, 165.7, 165.6, 165.5, 165.4, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (12C, 12*C*OPh), 106.7, 101.7, 101.0, 100.9 (4C, C-1), 82.5, 80.7, 78.0, 73.6, 73.5, 73.4, 72.2, 71.9, 71.6, 71.3, 69.8, 68.3, 68.2, 68.1, 67.9, 67.8, 67.1, 66.7, 63.8 (C-2,-3,-4,-5,-6). Anal. Calcd for $C_{114}H_{94}O_{33}$: C, 68.77; H, 4.72. Found: C, 68.97; H, 4.70.

3.11. 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 2)]-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (19)

To a solution of **18** (2 g, 1.0 mmol) in 4:1 CH_3CN–H_2O (20 mL) was added ceric ammonium nitrate (CAN, 2.46 g, 4.5 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 × 100 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. To a solution of the solid in CH_2Cl_2 (20 mL) were added trichloroacetonitrile (1 mL, 9.6 mmol) and anhyd K_2CO_3 (2 g, 14.5 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 **19** (1.65 g, 81%) as a syrup: $[\alpha]_D$ +56.7° (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.67 (s, 1H, N*H*), 8.03–7.21 (m, 60H, 12Ph*H*), 6.04 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.81 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.75 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.67 (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), 5.54–5.47 (m, 3H, H-3), 5.48 (s, 1H, Ara*f*-H-1), 5.38 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.35 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-3), 4.75 (d, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 4.63 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.58 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.43–4.26 (m, 2H), 4.24 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 4.15–4.08 (m, 3H), 4.01–3.95 (m, 2H), 3.92–3.68 (m, 4H), 3.65 (s, 3H, OCH_3);^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 165.8, 165.7, 165.6, 165.5, 165.4, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (12C, 12*C*OPh), 106.7, 101.7, 101.0, 100.9 (4C, C-1), 82.5, 80.7, 78.0, 73.6, 73.5, 73.4, 72.2, 71.9, 71.6, 71.3, 69.8, 68.3, 68.2, 68.1, 67.8, 67.1, 66.7, 63.8, 61.6 (C-2,-3,-4,-5,-6). Anal. Calcd for $C_{109}H_{88}Cl_3NO_{32}$: C, 64.50; H, 4.33. Found: C, 64.77; H, 4.20.

3.12. 4-Methoxyphenyl 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (20)

Compound **20** (2.85 g, 81%) was obtained as a syrup by coupling of **9** (2.4 g, 3.9 mmol) with **5** (2.0 g, 3.3 mmol) under the same conditions as described for the preparation of **4**: $[\alpha]_D$ +75.5° (*c* 1.0, $CHCl_3$); ^1H NMR

(400 Hz, $CDCl_3$): δ 7.95–7.25 (m, 25H, 5Ph*H*), 7.02 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.04 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, H-2), 5.97 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.79 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.63 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.52 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, H-2), 5.32 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.28 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.75 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.40 (dd, 1H, $J_{5,6}$ 3.6 Hz, $J_{6,6}$ 10.4 Hz, H-6), 4.17–4.06 (m, 4H), 3.98 (dd, 1H, $J_{5,6}$ 3.6 Hz, $J_{6,6}$ 10.8 Hz), 3.72(s, 3H, CH_3O), 1.97, 1.96 (s, s, 6H, C*H*$_3$CO). Anal. Calcd for $C_{58}H_{52}O_{19}$: C, 66.19; H, 4.94. Found: C, 66.10; H, 4.89.

3.13. 4-Methoxyphenyl 2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (21)

To a solution of **20** (2.5 g, 2.4 mmol) in 1:1 CH_3OH–CH_2Cl_2 (100 mL) was added CH_3COCl (0.1 mL), and the reaction was carried out to give **21** (1.9 g, 79%) using the same procedure as described in the preparation of **5**: $[\alpha]_D$ +38.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–7.26 (m, 25H, 5Ph*H*), 7.05 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.85 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.01 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, H-2), 5.97 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.77 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.62 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.52 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, H-2), 5.33 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.28 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.75 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.40 (dd, 1H, $J_{5,6}$ 3.6 Hz, $J_{6,6}$ 10.4 Hz, H-6), 4.17–4.06 (m, 4H), 3.72 (s, 3H, CH_3O), 1.97 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{56}H_{50}O_{18}$: C, 66.56; H, 4.95. Found: C, 66.87; H, 4.90.

3.14. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 2)]-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (22)

Compound **22** was obtained as a syrup (1.45 mg, 75%) by coupling of **19** (1.5 g, 0.74 mmol) and **21** (678 mg, 0.67 mmol) under the same conditions as described for the preparation of **4**: $[\alpha]_D$ +36.7° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.24 (m, 85H, 17Ph*H*), 6.95 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.86 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.88 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.87 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.76–5.75 (m, 2H, 2H-4), 5.66 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.62 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.61–5.58 (m, 3H), 5.54 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, H-2), 5.52 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, H-2), 5.50–5.44 (m, 5H), 5.38 (s, 1H, Ara*f*-H-1), 5.33 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.31 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-3), 4.97 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.93 (dd, 1H, $J_{5,6}$ 3.4 Hz, $J_{6,6}$ 10.8 Hz, H-6), 4.83–4.57 (m, 5H), 4.42 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.26 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.16–3.98 (m, 7H), 3.93–3.83 (m, 5H), 3.75 (s, 3H, OCH_3), 1.82 (s, 3H, CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5 (1C, *C*OCH_3), 166.3, 166.2, 165.8, 165.7, 165.7, 165.6, 165.5, 165.5, 165.4, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0, 165.0 (17C, 17*C*OPh), 106.2, 101.4, 101.3, 101.0, 100.8, 100.4 (6C, C-1), 82.0, 81.1, 77.8, 73.6, 72.8, 72.7, 72.2, 71.9, 71.8, 71.6, 71.5, 71.3, 69.9, 69.8, 69.6, 69.4, 69.2, 69.2, 68.1, 68.0, 67.9, 67.9, 67.8, 67.7, 67.4, 66.9, 66.8, 65.5, 65.4 (C-2,-3,-4,-5, -6). Anal. Calcd for $C_{163}H_{136}O_{49}$: C, 68.04; H, 4.73. Found: C, 68.39; H, 4.70.

3.15. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 2)]-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (23)

To a solution of **22** (1.12 g, 0.39 mmol) in 1:1 CH_3OH–CH_2Cl_2 (60 mL) was added CH_3COCl (0.6 mL). The reaction mixture was worked up using the same procedure as described in the preparation of **5** to give **23** (795 mg, 72%) as a syrup: $[\alpha]_D$ +43.2° (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.22 (m, 85H, Ph*H*), 6.96 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.86 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.01 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.95 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.93 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.76–5.72 (m, 2H, 2H-4), 5.67 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.64 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.63–5.58 (m, 3H), 5.54 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, H-2), 5.52–5.47 (m, 5H), 5.47 (s, 1H, Ara*f*-H-1), 5.34 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.32 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-3), 5.19 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.92 (dd, 1H, $J_{5,6}$ 3.4 Hz, $J_{6,6}$ 10.8 Hz, H-6), 4.85–4.68 (m, 5H), 4.46 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.44 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.43–4.32 (m, 5H), 4.19 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, H-2), 3.93–3.90 (m, 6H), 3.75 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 166.2, 165.8, 165.7, 165.7, 165.6, 165.5, 165.5, 165.4, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0, 165.0 (17C, 17*C*OPh), 106.2, 101.4, 101.3, 101.0, 100.8, 100.4 (6C, C-1), 82.5, 82.0, 81.1, 77.8, 73.6, 72.8, 72.7, 72.2, 71.9, 71.8, 71.7, 71.5, 71.4, 71.3, 69.9, 69.6, 69.4, 69.2, 68.1, 68.0, 67.9, 67.8, 67.7, 67.4, 66.9, 66.8, 65.5, 65.4, 63.8 (C-2,-3,-4,-5,-6). Anal. Calcd for $C_{161}H_{134}O_{48}$: C, 68.20; H, 4.75. Found: C, 68.37; H, 4.80.

3.16. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 2)]-3,4-di-*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-arabinofuranoside-(1 → 5)-2,3-di-*O*-benzoyl-α-L-arabinofuranosyl-(1 → 2)]-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (25)

Compound **25** (382 mg, 75%) was obtained as a syrup by coupling of **23** (400 mg, 0.14 mmol) with **24** (160 mg, 0.17 mmol) under the same conditions as described for the preparation of **4**: $[\alpha]_D$ +39.6° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.08–7.21 (m, 110H, 22Ph*H*), 7.01 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.86 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.01 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.98 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.89 (m, 3H, 3 H-4), 5.76 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.71–5.60 (m, 3H), 5.59 (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, $J_{1,2}$ 8.0 Hz, H-2), 5.51 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, H-2), 5.50–5.44 (m, 5H), 5.40 (s, 1H, Ara*f*-H-1), 5.36 (d, 1H, $J_{2,3}$ 2.4 Hz, Ara*f*-H-2), 5.34 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.32–5.16 (m, 7H), 4.99 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.79–4.70 (m, 7H), 4.67 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.44 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.43–4.32 (m, 6H), 4.03–3.95 (m, 5H), 3.90–3.74 (m, 4H), 3.73 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 166.2, 166.2, 165.8, 165.8, 165.7, 165.7, 165.6, 165.6, 165.5, 165.5, 165.4, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0, 164.9, 164.9, 164.8 (22 C, 22 *C*OPh), 106.3, 105.9, 102.8, 101.7, 101.6, 101.2, 100.9, 100.6 (8C, C-1), 82.5, 82.0, 81.1, 77.8, 73.6, 72.8, 72.7, 72.2, 72.2, 71.9, 71.8, 71.7, 71.6 71.5, 71.4, 71.3, 69.9, 69.8, 69.6, 69.4, 69.2, 69.2, 68.1, 68.0, 67.9, 67.9, 67.8, 67.7, 67.4, 66.9, 66.8, 66.7, 66.6, 65.5, 65.4, 63.8, 61.6, (C-2,-3,-4,-5,-6). Anal. Calcd for $C_{206}H_{170}O_{61}$: C, 68.35; H, 4.69. Found: C, 68.37; H, 4.81.

3.17. 4-Methoxyphenyl β-D-galactopyranosyl-(1 → 6)-[α-L-arabinofuranosyl-(1 → 2)]-β-D-galactopyranosyl-(1 → 6)-β-D-galactopyranosyl-(1 → 6)-[α-L-arabinofuranosyl-(1 → 5)-α-L-arabinofuranosyl-(1 → 2)]-β-D-galactopyranosyl-(1 → 6)-β-D-galactopyranoside (26)

Compound **25** (300 mg, 0.083 mmol) was dissolved in a satd solution of NH_3 in MeOH (50 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** (92 mg, 84%): $[\alpha]_D$ +28.9° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, D_2O): δ 7.12 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 7.08 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.21 (s, 1H, H-1), 5.06 (s, 1H, H-1), 5.04 (s, 1H, H-1), 4.70 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.66 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.49 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.36 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.25 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1); ^{13}C NMR (D_2O, 100 MHz): 108.3, 107.3, 103.4, 103.2, 103.2, 102.1, 101.7, 101.6 (8C, C-1), 84.5, 84.0, 82.9, 80.9, 80.8, 77.1, 76.7, 76.0, 75.2, 74.3, 73.8, 73.7, 73.6 73.5, 72.8, 72.7, 72.6, 72.4, 72.3, 71.5, 70.7, 70.6, 69.3, 69.1, 69.0, 68.9, 68.8, 68.7, 68.4, 68.0, 67.8, 67.5, 67.4, 67.1, 66.8, 66.4, 66.2 (C-2,-3,-4,-5,-6). MALDI-TOF MS Calcd for $C_{52}H_{82}O_{39}$: 1331.17 [M]. Found: 1330.96 [M].

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