Available online at www.sciencedirect.com
SCIENCE DIRECT®
Bioorganic & Medicinal Chemistry 13 (2005) 839–853
Bioorganic & Medicinal Chemistry

Concise syntheses of arabinogalactans with β-(1→6)-linked galactopyranose backbones and α-(1→3)- and α-(1→2)-linked arabinofuranose side chains

Aixiao Li and Fanzuo Kong*

Research Center for Eco-Environmental Sciences, Academia Sinica, PO Box 2871, Beijing 100085, PR China

Received 9 September 2004; revised 14 October 2004; accepted 16 October 2004

Abstract—4-Methoxyphenyl glycosides of 2,3″-bis-α-L-arabinofuranosyl branched β-D-(1→6)-linked galactopyranosyl tetraose (**16**), 3′,2‴-bis-α-L-arabinofuranosyl branched β-D-(1→6)-linked galactopyranosyl hexaose (**27**), and a twentyose (**42**) consisting of β-(1→6)-linked D-galactopyranosyl pentadecaoligosaccharide backbone with α-L-arabinofuranosyl side chains alternately attached at C-2 and C-3 of the middle galactose residue of each consecutive β-(1→6)-linked galactotriose unit of the backbone, were synthesized with isopropyl 3-*O*-allyl-2,4-di-*O*-benzoyl-1-thio-β-D-galactopyranoside (**6**), 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**7**), 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate (**12**), 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**17**), 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (**19**), and 2,6-di-*O*-acetyl-3,4-di-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**28**) as the key synthons. Condensation of **6** with **7** gave the disaccharide donor **8**, and subsequent condensation of **8** with 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranoside (**9**) followed by selective deacetylation afforded the tetrasaccharide acceptor **11**. Coupling of **11** with **12** gave the pentasaccharide **13**, its deallylation followed by coupling with **12**, and debenzoylation gave the hexasaccharide **16** with β-(1→6)-linked galactopyranose backbone and 2- and 3″-linked α-L-arabinofuranose side chains. The octasaccharide **27** was similarly synthesized, while the twentyoside **42** was synthesized with tetrasaccharides **33** or **24** as the donors and **23**, **36**, **38**, and **40** as the acceptors by consecutive couplings followed by deacylation.

1. Introduction

Arabinogalactans from certain sources have immunomodulating activity,[1] and they are often classified in three groups: arabino-4-galactans (Type I), arabino-3,6-galactans (Type II), and polysaccharides with arabinogalactan side chains.[2] The latter type is also called the real pectins. 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*,[3] such activity was not found in arabinogalactan from larch wood.[4] An arabinogalactan isolated from the roots of *Saposhnikova divaricata* or *Panex* notoginseng had reticuloendothelial system activating properties.[5] 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 β-(1→6)-linked galactan containing at least three galactopyranosyl residues functionalized at 3-OH with an α-linked L-arabinofuranose unit was supposed to be the epitope recognized by the CCRC-M7 antibody.[6] Although the presence of 2,6- and 3,6-branched residues in arabinogalactan is well known, the exact structure of these saccharides remains to be established. Thus far, there has been no definite conclusion regarding the core structure or fragment of arabinogalactans with immunomodulating activity. Is the arabinogalactan with β-(16)-linked galactopyranose backbone and α-(1→2)-linked arabinofuranose side chains active, or the arabinogalactan with the same backbone but with α-(1→3)-linked arabinofuranose branches active, or the arabinogalactan with the same backbone but with mixed α-(1→2)- and α-(1→3)-linked arabinofuranose branches active? To

Keywords: Arabinofuranose; Galactopyranose; Regio- and stereoselective synthesis.
* Corresponding author. Tel.: +86 1062936613; fax: +86 1062923563; e-mail: fzkong@mail.rcees.ac.cn

0968-0896/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.bmc.2004.10.035

answer this question, the synthesis of a series model structures of arabinogalactans, and consequent study on the biological activity of the synthetic samples is necessary.

Some examples on the chemical syntheses of the 2-arabinofuranosyl branched galactans[7,8] and 3-arabinofuranosyl branched galactans[9] have been reported. Since most of the synthetic samples were obtained very recently, there has been no report regarding their bioactivity so far. We believe that after the successful syntheses of samples with definite and different structures of arabinogalactans and their bioactivity study, the puzzle regarding the active core structure of arabinogalactans will be solved soon. As a part of this effort, we present herein convergent syntheses of a hexasaccharide consisting of β-(1→6)-linked galactose tetrasaccharide backbone with 2- and 3″-arabinose side chains, an octasaccharide consisting of β-(1→6)-linked galactose hexasaccharide backbone with 3′- and 2‴′-arabinose side chains and a twentysaccharide consisting of β-(1→6)-linked galactose pentadecasaccharide backbone with arabinofuranose side chains alternately attached at C-2 and C-3 of the middle galactose residue of each consecutive β-(1→6)-linked galactotriose unit of the backbone.

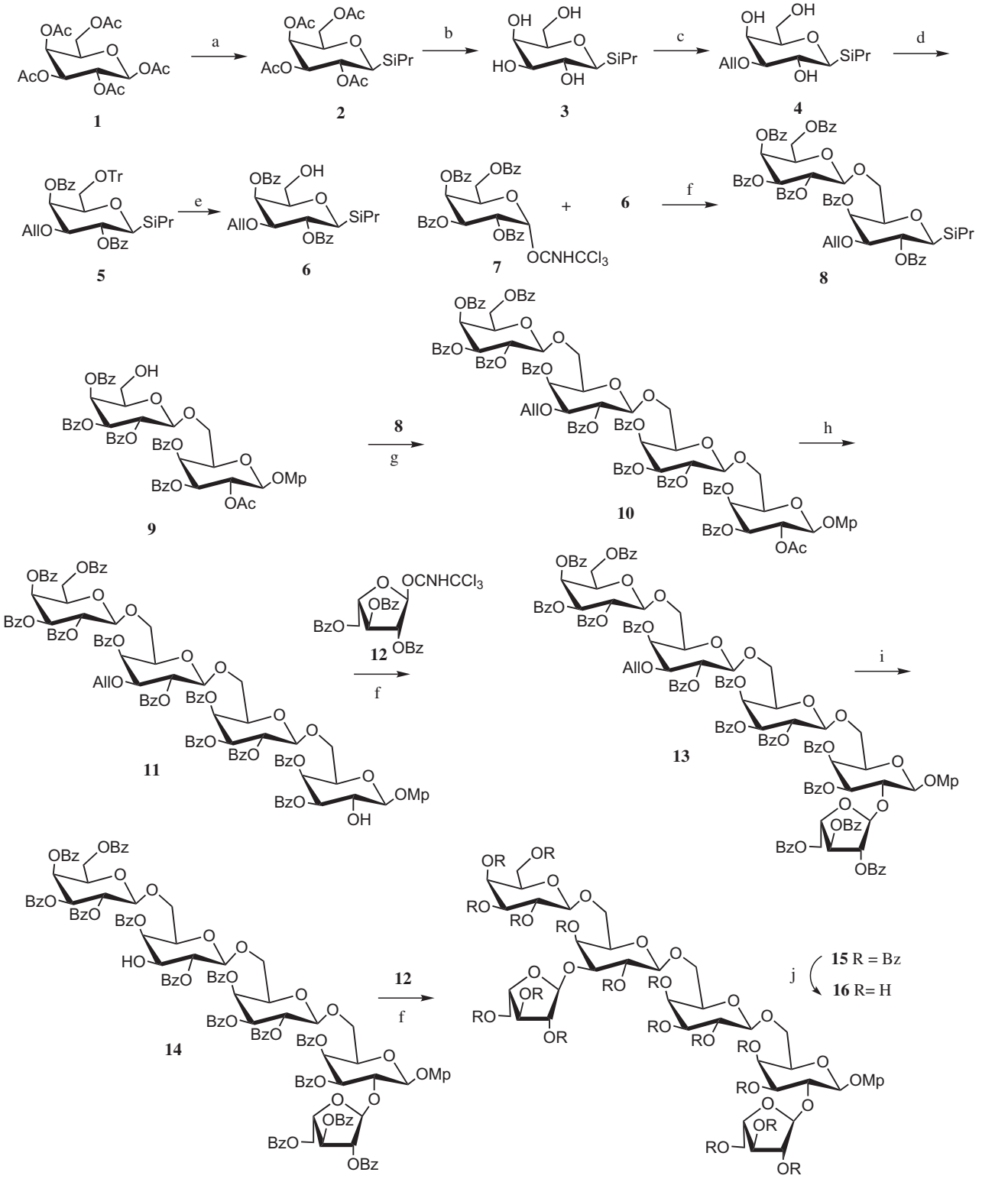
2. Results and discussion

In the past few years, most of the synthetic work was focused on tetrasaccharide or trisaccharide of the arabinogalactans[7,8] and our group contributed, very recently, the facile syntheses of higher arabinogalactans including octaoses and nonaoses with β-(1→6)-linked galactose backbone and α-(1→3)-,[9] and α-(1→2)-linked arabinose side chains.[10] However, with the reported methods, only the arabinogalactans with either sole α-(1→3)-linked arabinose branches or sole α-(1→2)-linked arabinose branches could be synthesized, the arabinogalactans with mixed α-(1→3)- and α-(1→2)-linked side chains could not be achieved by the reported methods. We present herewith concise syntheses of the arabinogalactans with both α-(1→3)- and α-(1→2)-linked arabinose branches. Scheme 1 shows the synthesis of hexasaccharides **16**. Isopropyl 1-thio-β-D-galactopyranoside (**3**), prepared readily from penta-*O*-acetyl-β-D-galactopyranose **1** by coupling with isopropyl thiol and subsequent deacetylation, was chosen as the starting material. Selective 3-*O*-allylation of **3** via dibutyltin complex[11] gave compound **4** in satisfactory yield (79%), and subsequent selective 6-*O*-tritylation followed by benzoylation and detritylation produced the glycosyl acceptor **6**. Condensation of **6** with perbenzoylated galactopyranosyl trichloroacetimidate[12] **7** afforded the disaccharide **8**. Then, condensation of 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranoside (**9**)[10] with **8** gave the tetrasaccharide **10** (92%) with two potential hydroxyl groups at C-2 and C-3″, respectively. Thus, selective deacetylation[13] of **10** with MeCOCl/CH_2Cl_2/MeOH (3 mL/50 mL/50 mL) afforded the tetrasaccharide acceptor **11** (78%), and subsequent condensation with 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate (**12**)[14] gave the pentasaccharide **13** (87%). Deallylation of **13** with $PdCl_2$ followed by coupling with **12**, and finally deacylation with saturated NH_3–MeOH gave the target hexasaccharide **16** consisting of β-(1→6)-linked galactopyranosyl tetrasaccharide backbone and α-L-arabinofuranose side chains at C-2 and C-3″, respectively.

The octasaccharide **27** was prepared in a similar way as outlined in Scheme 2. Coupling of the donor **17**[10] with the acceptor **6** produced the disaccharide **18** that was coupled with the acceptor **19**[10] to give the trisaccharide **20**. Subsequent deallylation followed by coupling with **12** gave **22**,[9b] then oxidative cleavage of 4-methoxyphenyl group and tricholoroacetimidate formation gave the tetrasaccharide donor **24**. Meanwhile, selective deacetylation of **22** gave **23**.[9b] Condensation of the donor **25**[10] with the acceptor **23** followed by deacylation gave the target octasaccharide **27** consisting of two tetrasaccharide fragments, one of which had β-(1→6)-linked galactopyranosyl trisaccharide backbone with α-L-arabinofuranose side chain at C-3′, and another one had the same backbone but with α-L-arabinofuranose side chain at C-2′.

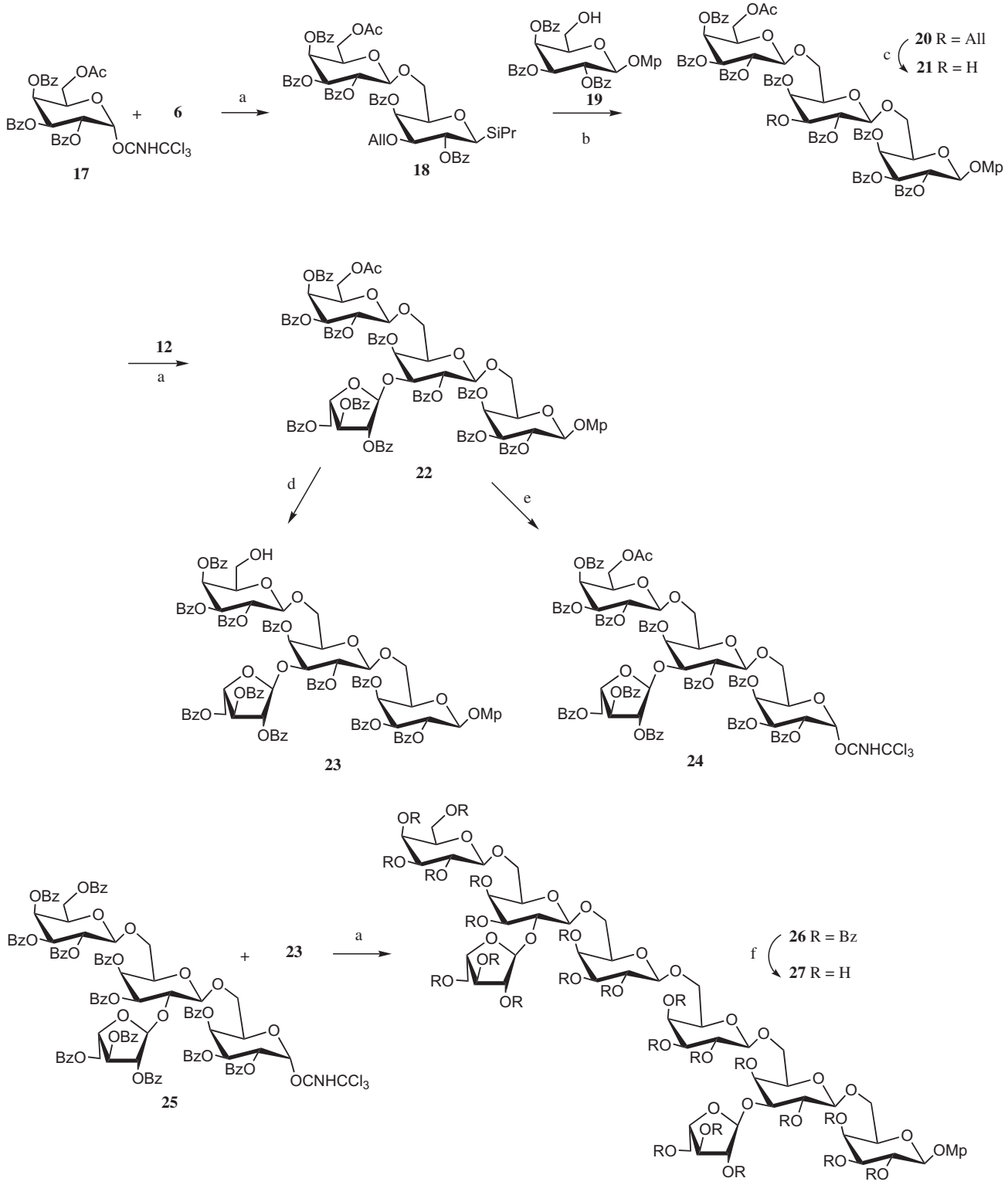
The twentysaccharide **42** was synthesized according to Scheme 3. Coupling of the donor **28**[10] with the acceptor **19** produced the disaccharide **29**, and subsequent selective 2′,6′-*O*-deacetylation with MeCOCl/CH_2Cl_2/MeOH (3 mL/50 mL/50 mL) yielded the disaccharide acceptor **30**. Condensation of **17** with the acceptor **30** regio- and sterospecifically afforded the trisaccharide **31** in 81% yield. No (1→2)-linked trisaccharide was detected from ^{1}H NMR and TLC. Coupling of the acceptor **31** with **12** afforded the tetrasaccharide **32**, subsequent oxidative cleavage of 4-methoxyphenyl group and trichloroacetimidate formation gave the tetrasaccharide donor **33**, while selective removal of 6″-*O*-acetyl group of **32** afforded the tetrasaccharide acceptor **34**. The octasaccharide acceptor **36** was obtained from condensation of **23** with **33** followed by 6-*O*-deacetylation with MeCOCl/CH_2Cl_2/MeOH. Condensation of **24** with the acceptor **36** afforded **37**, subsequent 6-*O*-deacetylation yielded the dodecasaccharide acceptor **38**. Coupling of **38** with **33** followed by deacetylation produced the hexadecasaccharide acceptor **40**. Then condensation of the donor **24** with the acceptor **40** followed by deacylation gave the target twentysaccharide **42**.

In the above syntheses, selective deacetylations of **22** to give **23**, **32** to give **34**, **35** to give **36**, **37** to give **38**, and **39** to give **40**, went out smoothly with no benzoyl group migration as indicated by TLC that showed a neat spot for the product. Also the couplings of **25** with **23**, **33** with **23**, **24** with **36**, **38** with **33**, and **40** with **24**, were carried out easily with high yields indicating the high activity of the primary OH of the acceptors. The β-(1→6)-linkages of galactopyranose and α-(1→2)- or α-(1→3)-linkages of arabinofuranose were also confirmed by the ^{1}H and ^{13}C NMR spectra of the compounds[9,10] from the chemical shifts and coupling constants of specific signals.



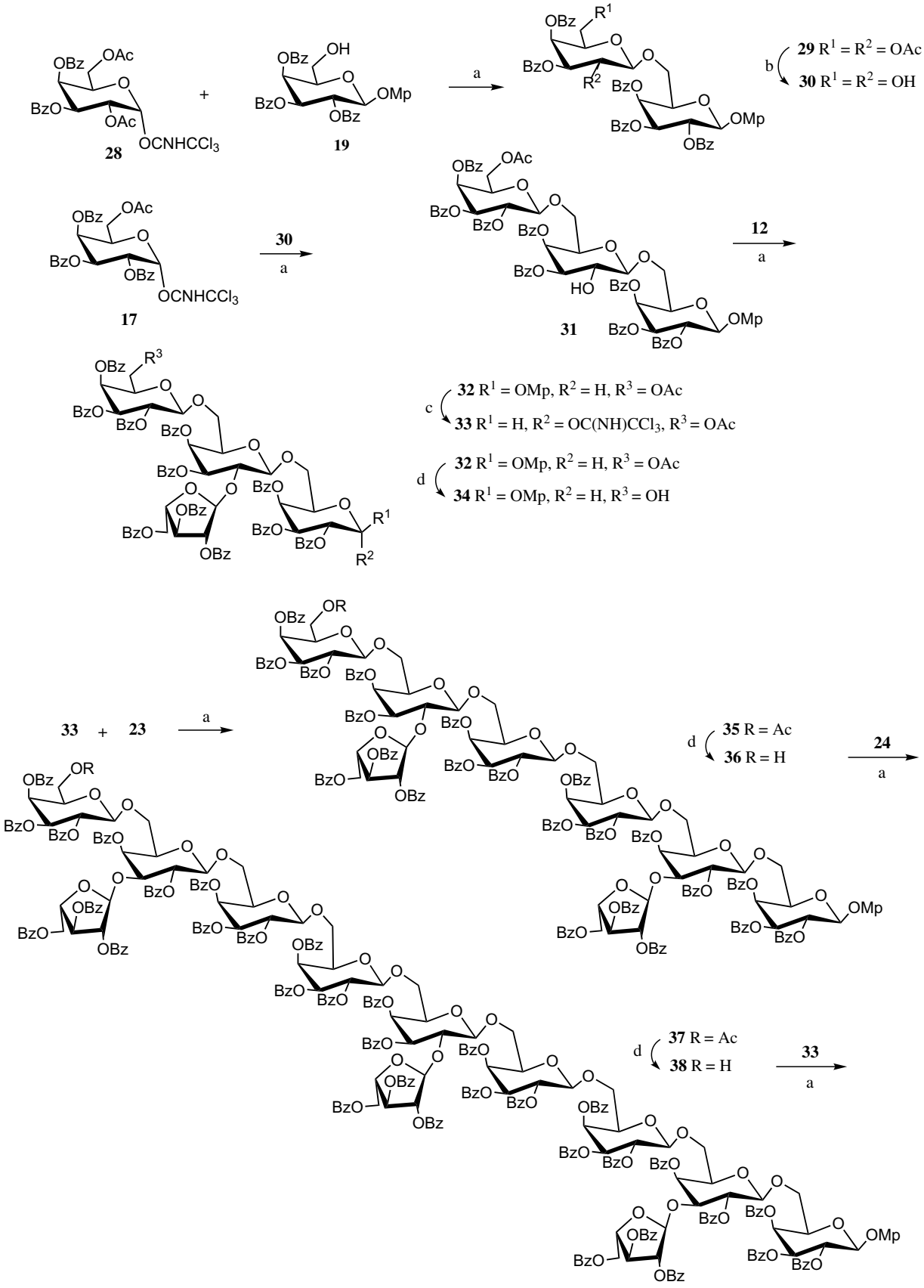
Schcme 1. Reagents and conditions: (a) CH_2Cl_2, *i*PrSH, $Et_2O{\cdot}BF_3$, rt, 1.5 h, 75%. (b) CH_3OH/CH_3ONa, pH 10, rt, 5 h, 81%. (c) CH_3OH, Bu_2SnO, reflux 2 h, then AllBr, Bu_4NI, toluene, 60 °C, 24 h, 79%. (d) Trityl chloride, (1.1 equiv), pyridine, 50 °C, 24 h, then PhCOCl, (2.4 equiv), 50 °C, overnight, 71%. (e) 1:500:500 $MeCOCl/CH_3OH/CH_2Cl_2$, rt, 3 h, 80%. (f) TMSOTf, CH_2Cl_2, −20 °C to rt, 2–4 h; 85% for **8**, 87% for **13**, 89% for **15**. (g) TMSOTf (0.1–0.5 equiv), CH_2Cl_2, NIS (1.5 equiv), −20 °C to rt, 2–4 h; 92%. (h) 3:50:50 $MeCOCl/CH_3OH/CH_2Cl_2$, rt, 48 h, 78%. (i) $PdCl_2$, CH_3OH, 40 °C, 5 h, 90% (j) satd NH_3/MeOH, rt, 7 d, 90%.

An alternative strategy of 8+12 for the preparation of **42** was also carried out. Thus, coupling of the tetrasaccharide acceptor **34** with the donor **24** followed by C-1-activation gave the octasaccharide trichloroacetimidate

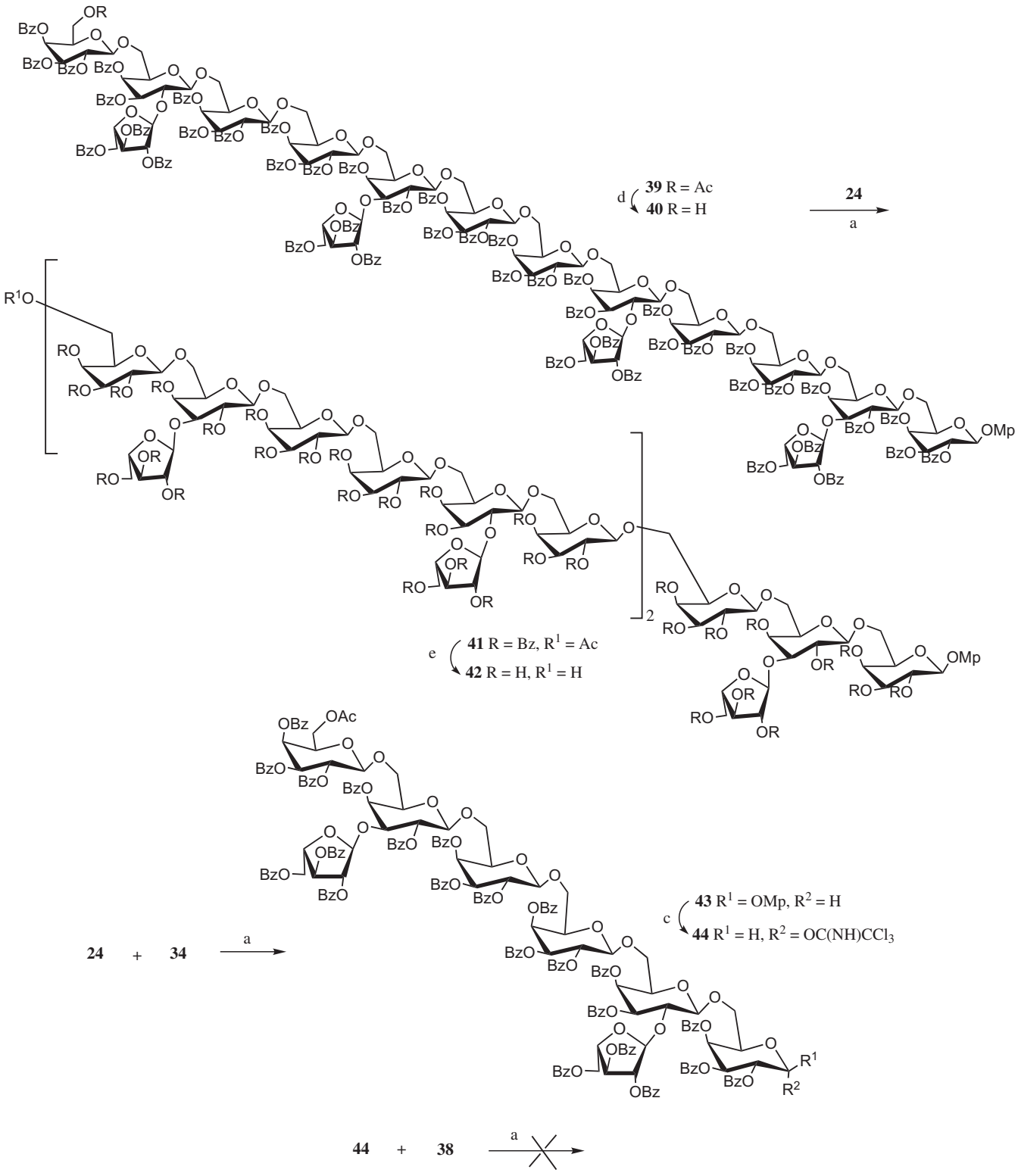


Scheme 2. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt, 2–4 h; 83% for **18**, 81% for **26**. (b) TMSOTf (0.1–0.5 equiv), CH_2Cl_2, NIS (1.5 equiv), −20 °C to rt, 2–4 h; 90%. (c) $PdCl_2$, CH_3OH, 40 °C, 5 h, 94%. (d) 1:50:50 MeCOCl/CH_3OH/CH_2Cl_2, rt, 48 h, 87%. (e) (i) CAN in MeCN–H_2O, rt, 0.5 h; (ii) CH_2Cl_2, CCl_3CN, K_2CO_3, rt, 10 h. (f) satd NH_3/MeOH, rt, 7 d, 85%.

44. However, when the donor **44** was reacted with the dodecasaccharide acceptor **38**, very complex and hardly separated product was obtained. This indicated that the octasaccharide donor did not match the dodecasaccharide acceptor, and tetrasaccharides were suitable building blocks for preparation of high arabinogalactans.



Scheme 3. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt, 2–4 h; 89% for **29**, 81% for **31**, 89% for **32**, 81% for **35**, 75% for **37**, 71% for **39**, 65% for **41**, 81% for **43**. (b) 3:50:50 $MeCOCl/CH_3OH/CH_2Cl_2$, rt, 48 h, 71%. (c) (i) CAN in $MeCN–H_2O$, rt, 0.5 h; (ii) CH_2Cl_2, CCl_3CN, K_2CO_3, rt, 10 h. (d) 1:50:50 $MeCOCl/CH_3OH/CH_2Cl_2$, rt, 48 h; 83% for **34**, 81% for **36**, 71% for **38**, 71% for **40**. (e) satd NH_3/MeOH, rt, 7 d, 85%.



Scheme 3 (*continued*)

3. Conclusion

In summary, here we described a method by which we can efficiently synthesize 4-methoxyphenyl glycosides of hexaose, octaose, and twentyose consisting of β-D-galactopyranosyl (1→6)-linked backbone and α-L-arabinofuranosyl side chains linked at C-2 or C-3 of the galactose residue. This method is simple, highly regio-

and chemoselective, and can be used in preparation of structurally different arabinogalactans.

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. Isopropyl 3-*O*-allyl-2,4-di-*O*-benzoyl-1-thio-β-D-galactopyranoside (6)

To a solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (50.0 g, 128 mmol) in CH_2Cl_2 was added $Et_2O{\cdot}BF_3$ (33.0 mL) and *i*PrSH (17.0 mL). The mixture was stirred at rt for 1.5 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was neutralized with dry Na_2CO_3, and then extracted with CH_2Cl_2 (3 × 200 mL). The combined extracts were concentrated to a syrup that was subjected to column chromatography with 3:1 petroleum ether–EtOAc as the eluent to give compound **2** (40.5 g, 75%) as a syrup. To a solution of compound **2** (40.5 g, 97.3 mmol) in CH_3OH (200 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 **3** (18.7 g, 81%) as a syrup. To a solution of **3** (18.7 g, 78.5 mmol) in dry CH_3OH (300 mL) was added Bu_2SnO (22.9 g, 91.9 mmol), and the mixture was heated under reflux for 2 h, then concentrated to dryness. The residue was diluted with toluene (300 mL), and then allyl bromide (87 mL, 1.0 mol), Bu_4NI (28.9 g, 78.5 mol) were added to the mixture. The reaction was carried out at 60 °C for 24 h, at the end of which time TLC (EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated, and the residue was purified by column chromatography (1:1 petroleum ether–EtOAc) to give **4** (17.1 g, 79%) as a solid. A solution of **4** (17.1 g, 58.1 mmol) and trityl chloride (17.8 g, 63.9 mmol) in pyridine (150 mL) was stirred at 50 °C for 24 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 (17.2 mL, 123 mmol) was added dropwise within 30 min to keep the reaction temperature at 0 °C. The mixture was stirred at 50 °C for 12 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 × 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 with 5:1 petroleum ether–EtOAc as the eluent to give **5** (30.0 g, 71%) as a solid. To a solution of **5** (30.0 g, 41.2 mmol) in CH_3OH (100 mL)–CH_2Cl_2 (100 mL) was added CH_3COCl (0.2 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 triethylamine, then concentrated, and the residue was passed through a silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give **6** (15.6 g, 80%) as a syrup. $[\alpha]_D$ +5.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.11–7.23 (m, 10H, 2*Ph*), 5.69 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.67 (m, 1H, $CH_2{=}CH{-}CH_2O$), 5.58 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.17–5.03 (m, 2H, $CH_2{=}CH{-}CH_2O$), 4.75 (d, 1H, $J_{1,2}$ = 8 Hz, H-1), 4.08–3.95 (m, 2H, $CH_2{=}CH{-}CH_2O$), 3.87 (dd, 1H, $J_{3,4}$ = 3.2, $J_{2,3}$ = 10.4 Hz, H-3), 3.79 (dd, 1H, $J_{5,6}$ = 6.4, $J_{6,6}$ = 12.0 Hz, H-6), 3.58 (dd, 1H, $J_{5,6}$ = 6.4, $J_{6,6}$ = 12.0 Hz, H-6), 3.23 (m, 1H, H-5). Anal. Calcd for $C_{26}H_{30}O_7S$: C, 64.17; H, 6.21. Found: C, 64.32; H, 6.19.

4.3. Isopropyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-3-*O*-allyl-2,4-di-*O*-benzoyl-1-thio-β-D-galactopyranoside (8)

A solution of **6** (2.4 g, 4.9 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate **7** (4 g, 5.4 mmol) in dry CH_2Cl_2 (100 mL) was stirred. TMSOTf (40 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 an ambient temperature. Then the mixture was neutralized with triethylamine. Concentration of the reaction mixture followed by purification on a silica gel column with 3:1 petroleum ether–EtOAc as the eluent gave **8** (4.8 g, 85%) as a syrup. $[\alpha]_D$ +13.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.11–7.23 (m, 30H, 6*Ph*), 5.94 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.80–5.68 (m, 2H, H-2, H-4), 5.68–5.58 (m, 1H, $CH_2{=}CH{-}CH_2O$), 5.56 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.2 Hz, H-3), 5.43 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.17–5.00 (m, 2H, $CH_2{=}CH{-}CH_2O$), 4.87 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.67 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.43 (dd, 1H, $J_{5,6}$ = 6.0, $J_{6,6}$ = 10.4 Hz, H-6), 4.12–3.97 (m, 3H, $CH_2{=}CH{-}CH_2O$, H-5), 3.87 (dd, 1H, $J_{5,6}$ = 6.0, $J_{6,6}$ = 10.4 Hz, H-6), 3.77 (dd, 1H, $J_{3,4}$ = 3.2, $J_{2,3}$ = 10.4 Hz, H-3), 3.05 (m, 1H, H-5). Anal. Calcd for $C_{60}H_{56}O_{16}S$: C, 67.65; H, 5.30. Found: C, 67.59; H, 5.26.

4.4. 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-galactopyranosyl-(1→6)-2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranoside (10)

To a solution of 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-galactopyranoside (**9**, 1.9 g, 1.88 mmol) and **8** (2.0 g, 1.88 mmol) in dry CH_2Cl_2 (80 mL) were added NIS (635 mg, 2.84 mmol) and TMSOTf (169 μL, 0.94 mmol) at −20 °C, the reaction mixture was stirred for 4 h, during which time the reaction temperature gradually raised to ambient temperature. Then the reaction mixture was worked up by conventional procedure, and the product was purified on a silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give **10** (3.45 g, 92%) as a foamy solid. $[\alpha]_D$ +42.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.13–7.26 (m, 55H, 11P*h*), 6.96 (d, 2H, *J* = 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* = 9.1 Hz, $CH_3OC_6H_4O$–), 5.88–5.86 (m, 2H, 2H-4), 5.83 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.70 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.68 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ 10.4 Hz, H-2), 5.65–5.62 (m, 2H, H-2), 5.60–5.56 (m, 1H, CH_2=C*H*–CH_2O), 5.53 (dd, 1H, $J_{3,4}$ = 3.2, $J_{2,3}$ = 10.4 Hz, H-3), 5.46 (dd, 1H, $J_{3,4}$ = 3.4, $J_{2,3}$ = 10.4 Hz, H-3), 5.35 (dd, 1H, $J_{3,4}$ = 3.2, $J_{2,3}$ 10.4 Hz, H-3), 5.30 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.13–5.00 (m, 2H, C*H*$_2$=CH–CH_2O), 4.98 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.77 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.57 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.37 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.20 (dd, 1H, $J_{5,6}$ = 5.4, $J_{6,6}$ = 11.2 Hz, H-6), 4.11–3.95 (m, 7H, CH_2=CH–C*H*$_2$O, 1H-5, 4H-6), 3.92 (s, 3H, C*H*$_3$O), 3.60 (dd, 1H, $J_{3,4}$ = 3.2, $J_{2,3}$ = 10.4 Hz, H-3), 1.99 (s, 3H, C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0 (1C, 1CH_3*C*O), 165.8, 165.7, 165.6, 165.5, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0 (11C, 11*C*OPh), 100.9, 100.9, 100.8, 100.6 (4C, 4C-1). Anal. Calcd for $C_{113}H_{98}O_{34}$: C, 67.86; H, 4.84. Found: C, 67.99; H, 4.80.

4.5. 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-galactopyranosyl-(1→6)-3,4-di-*O*-benzoyl-β-D-galactopyranoside (11)

To a solution of **10** (3.45 g, 1.72 mmol) in CH_3OH (50 mL)–CH_2Cl_2 (50 mL) was added CH_3COCl (3 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 neutralized with triethylamine, and then concentrated, and the residue was passed through a silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give **11** (3.25 g, 78%) as a foamy solid. $[\alpha]_D$ +39.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.14–7.23 (m, 55H, 11P*h*), 6.96 (d, 2H, *J* = 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* = 9.1 Hz, $CH_3OC_6H_4O$–), 5.88–5.86 (m, 2H, 2H-4), 5.81 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.70 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.68 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.65–5.62 (m, 2H, 2H-2), 5.60–5.56 (m, 1H, CH_2=C*H*–CH_2O), 5.53 (dd, 1H, $J_{3,4}$ = 3.2, $J_{2,3}$ = 10.4 Hz, H-3), 5.46 (dd, 1H, $J_{3,4}$ = 3.4, $J_{2,3}$ = 10.4 Hz, H-3), 5.35 (dd, 1H, $J_{3,4}$ = 3.2, $J_{2,3}$ 10.4 Hz, H-3), 5.13–5.00 (m, 2H, C*H*$_2$=CH–CH_2O), 4.98 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.77 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.57 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.37 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.20 (dd, 1H, $J_{5,6}$ = 5.4, $J_{6,6}$ = 11.2 Hz, H-6), 4.10–3.93 (m, 8H, CH_2=CH–C*H*$_2$O, H-2, H-5, 4H-6), 3.82 (s, 3H, C*H*$_3$O), 3.60 (dd, 1H, $J_{3,4}$ = 3.2, $J_{2,3}$ = 10.4 Hz, H-3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 165.6, 165.5, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0 (11C, 11*C*OPh), 100.9, 100.9, 100.8, 100.6 (4C, 4C-1). Anal. Calcd for $C_{111}H_{96}O_{33}$: C, 68.09; H, 4.94. Found: C, 68.29; H, 4.72.

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

Coupling of **11** (2.63 g, 1.34 mmol) and **12** (978 mg, 1.61 mmol) in anhyd CH_2Cl_2 (80 mL) was carried out by the same procedure as described in the coupling of **6** and **7**. Purification by chromatography with 1.5:1 petroleum ether–EtOAc as the eluent gave **13** as a foamy solid (2.8 g, 87%). $[\alpha]_D$ +53.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.13–7.23 (m, 70H, 14P*h*), 6.92 (d, 2H, *J* = 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* = 9.1 Hz, $CH_3OC_6H_4O$–), 5.87–5.86 (m, 2H, 2H-4), 5.82 (d, 1H, $J_{3,4}$ = 3.4 Hz, H-4), 5.69 (d, 1H, $J_{3,4}$ = 3.4 Hz, H-4), 5.64 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.63–5.57 (m, 2H, 1H-2, CH_2=C*H*–CH_2O), 5.51 (s, 1H, Ara*f*-H-1), 5.50–5.41 (m, 3H), 5.38 (d, 1H, $J_{2,3}$ = 1.2 Hz, Ara*f*-H-2), 5.26 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.13–5.00 (m, 2H, C*H*$_2$=CH–CH_2O), 4.97 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.77 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.53 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.51 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 4.37 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.17 (dd, 1H, $J_{5,6}$ = 5.4, $J_{6,6}$ = 11.2 Hz, H-6), 4.10–3.70 (m, 11H, CH_2=CH–C*H*$_2$O, 2H-5, 7H-6), 3.68 (s, 3H, C*H*$_3$O), 3.60 (dd, 1H, $J_{3,4}$ = 3.4, $J_{2,3}$ = 10.4 Hz, H-3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.8, 165.7, 165.6, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0, 165.0, 165.0, 164.9 (14C, 14*C*OPh), 106.3 (Ara*f*-C-1), 101.9, 101.8, 100.7, 100.6 (4Gal*p*-C-1). Anal. Calcd for $C_{137}H_{116}O_{40}$: C, 68.49; H, 4.87. Found: C, 68.22; H, 4.73.

4.7. 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-galactopyranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→2)]-3,4-di-*O*-benzoyl-β-D-galactopyranoside (14)

To a solution of **13** (2.8 g, 1.16 mmol) in anhyd CH_3OH (50 mL) was added $PdCl_2$ (100 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 **14** as a foamy solid (2.47 g, 90%). $[\alpha]_D$ +69.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.13–7.23 (m, 70H, 14P*h*), 6.92 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 5.86–5.83 (m, 3H, 3H-4), 5.66 (d, 1H, $J_{3,4} = 3.4$ Hz, H-4), 5.64–5.60 (m, 2H, H-2), 5.53 (s, 1H, Ara*f*-H-1), 5.52–5.48 (m, 2H, 2H-3), 5.44 (dd, 1H, $J_{3,4} = 3.4$, $J_{2,3} = 10.4$ Hz, H-3), 5.38 (d, 1H, $J_{2,3} = 1.2$ Hz, Ara*f*-H-2), 5.14 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 4.97 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.78 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.53 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 4.51 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.45 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.17 (dd, 1H, $J_{5,6} = 5.4$, $J_{6,6} = 11.2$ Hz, H-6), 3.73 (s, 3H, CH_3O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.8, 165.7, 165.6, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0, 165.0, 165.0, 164.9 (14C, 14*C*OPh), 107.1 (Ara*f*-C-1), 102.0, 101.9, 100.9, 100.7 (4Gal*p*-C-1). Anal. Calcd for $C_{134}H_{112}O_{40}$: C, 68.13; H, 4.78. Found: C, 68.29; H, 4.70.

4.8. 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)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→2)]-3,4-di-*O*-benzoyl-β-D-galactopyranoside (15)

Coupling of **12** (308 mg, 0.51 mmol) with **14** (1 g, 0.42 mmol) in anhyd CH_2Cl_2 (50 mL) was carried out using the same procedure as described in the coupling of **6** and **7**, and **15** was obtained as a foamy solid (purified with 1.5:1 petroleum ether–EtOAc, 1.05 g, 89%). $[\alpha]_D$ +63.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.09–7.21 (m, 85H, 17P*h*), 6.92 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 5.88 (d, 1H, $J_{3,4} = 3.4$ Hz, H-4), 5.83 (d, 1H, $J_{3,4} = 3.4$ Hz, H-4), 5.79–5.75 (m, 2H, 2H-4), 5.68–5.59 (m, 3H, 3H-2), 5.53–5.42 (m, 4H, Ara*f*-H-1, 3H-3), 5.38 (s, 1H, Ara*f*-H-1), 5.27 (d, 1H, $J_{2,3} = 1.2$ Hz, Ara*f*-H-2), 5.23 (d, 1H, $J_{2,3} = 1.2$ Hz, Ara*f*-H-2), 4.97 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.78 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.52 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 4.51 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.33 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 3.65 (s, 3H, CH_3O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.6, 165.9, 165.8, 165.7, 165.6, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.1, 165.0, 164.9, 164.6, 163.2 (17C, 17*C*OPh), 107.6, 106.3 (2Ara*f*-C-1), 101.9, 101.1, 100.9, 100.6 (4Gal*p*-C-1). Anal. Calcd for $C_{160}H_{132}O_{47}$: C, 68.46; H, 4.63. Found: C, 68.67; H, 4.70.

4.9. 4-Methoxyphenyl β-D-galactopyranosyl-(1→6)-[α-L-arabinofuranosyl-(1→3)]-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-[α-L-arabinofuranosyl-(1→2)]-β-D-galactopyranoside (16)

Compound **15** (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 **16** (99 mg, 90%) as an amorphous solid. $[\alpha]_D$ +38.9 (*c* 1.0, H_2O); ^1H NMR (400 MHz, D_2O) δ 7.09 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.91 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 5.25 (s, 1H, Ara*f*-H-1), 5.13 (s, 1H, Ara*f*-H-1), 5.00 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.70 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1), 4.37 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1), 4.34 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1); ^{13}C NMR (100 MHz, D_2O) δ 109.3, 108.5 (2Ara*f*-C-1), 103.4, 103.2, 103.1, 102.1 (4Gal*p*-C-1). Anal. Calcd for $C_{41}H_{64}O_{30}$: C, 47.48; H, 6.22. Found: C, 47.63; H, 6.32.

4.10. Isopropyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-3-*O*-allyl-2,4-di-*O*-benzoyl-1-thio-β-D-galactopyranoside (18)

Coupling of **6** (3.0 g, 6.17 mmol) with **17** (4.6 g, 6.79 mmol) under the same conditions as described in the coupling of **6** with **7** gave **18** as a foamy solid (purified with 3:1 petroleum ether–EtOAc, 5.1 g, 83%). $[\alpha]_D$ +35.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.11–7.23 (m, 25H, 5P*h*), 5.83 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.78 (m, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.74 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.68–5.60 (m, 1H, CH_2═C*H*–CH_2O), 5.47 (dd, 1H, $J_{3,4} = 3.2$, $J_{2,3} = 10.4$ Hz, H-3), 5.43 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.17–5.02 (m, 2H, CH_2═CH–CH_2O), 4.83 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.65 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.14–4.05 (m, 4H, CH_2═CH–CH_2O, 2H-6), 3.82 (dd, 1H, $J_{5,6} = 6.0$, $J_{6,6} = 10.4$ Hz, H-6), 3.77 (dd, 1H, $J_{3,4} = 3.2$, $J_{2,3} = 10.4$ Hz, H-3). Anal. Calcd for $C_{55}H_{54}O_{16}S$: C, 65.85; H, 5.43. Found: C, 65.79; H, 5.36.

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

Coupling of **18** (8.0 g, 8.0 mmol) with **19** (4.0 g, 6.7 mmol) in anhyd CH_2Cl_2 (80 mL) was carried out by the same procedure as described in the coupling of **8** with **9**. Purification by chromatography with 2:1 petroleum ether–EtOAc as the eluent gave **20**[9b] as a syrup (8.8 g, 87%). Deallylation of **20** followed by coupling with **12** gave **22**.[9b]

4.12. 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-α-D-galactopyranosyl trichloroacetimidate (24)

To a solution of **22** (7.0 g, 3.6 mmol) in 4:1 CH_3CN–H_2O (100 mL) was added CAN (8.0 g, 14.4 mmol), and the mixture was stirred at rt for 30 min, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was extracted with CH_2Cl_2 (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 (5.7 g, 3.1 mmol). To a solution of the solid in CH_2Cl_2 (80 mL) were added trichloroacetonitrile (1.0 mL, 10 mmol) and anhyd potassium carbonate (1.7 g, 12 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 **24** as a syrup (5.0 g, 69% for two steps). $[\alpha]_D$ +61.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.67 (s, 1H, N*H*), 8.07–7.21 (m, 55H, 11P*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), 6.01–5.95 (m, 2H), 5.81 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.78 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.71 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.65 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.61 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.58 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.48–5.42 (m, 2H), 5.27 (s, 1H, Ara*f*-H-1), 5.23 (d, 1H, $J_{2,3}$ = 1.2 Hz, Ara*f*-H-2), 4.96 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.56 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.52 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.6 (1C, CH_3CO), 166.1, 165.8, 165.7, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 164.9, 164.5 (11C, 11*C*OPh), 107.6 (Ara*f*-C-1), 101.5, 100.8, 100.5 (3Gal*p*-C-1). Anal. Calcd for $C_{104}H_{86}Cl_3NO_{32}$: C, 63.46; H, 4.40. Found: C, 64.22; H, 4.28.

4.13. 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)-2,3,4-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 (26)

Coupling of **23** (1.0 g, 0.53 mmol) with **25** (1.29 g, 0.64 mmol) under the same conditions as described for the coupling of **6** with **7** gave octasaccharide **26** (1.65 g, 81%) as a foamy solid. $[\alpha]_D$ +43.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03–7.19 (m, 115H, 23P*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, 3H, 1H-2, 2H-4), 5.84–5.79 (m, 3H, 3H-4), 5.73 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.62–5.47 (m, 10H), 5.42 (s, 1H, Ara*f*-H-1), 5.36 (d, 1H, $J_{2,3}$ = 1.2 Hz, Ara*f*-H-2), 5.26 (s, 1H, Ara*f*-H-1), 5.24 (d, 1H, $J_{2,3}$ = 1.2 Hz, Ara*f*-H-2), 5.10 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.74–4.68 (m, 3H), 4.54 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.15 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 3.64 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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, 165.1, 165.0, 165.0, 164.9, 164.9, 164.8, 164.7, 164.7, 164.6, 164.6 (23C, 23*C*OPh), 107.6, 106.5 (2Ara*f*-C-1), 101.6, 101.5, 101.1, 100.9, 100.6, 100.5 (6Gal*p*-C-1). Anal. Calcd for $C_{214}H_{176}O_{63}$: C, 68.43; H, 4.72. Found: C, 68.37; H, 4.81.

4.14. 4-Methoxyphenyl β-D-galactopyranosyl-(1→6)-[α-L-arabinofuranosyl-(1→2)]-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 (27)

Compound **26** (500 mg, 0.13 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 **27** (154 mg, 85%) as an amorphous solid. $[\alpha]_D$ +24.9 (*c* 1.0, H_2O); ^1H NMR (400 MHz, D_2O) δ 7.08 (d, 2H, *J* = 9.1 Hz, CH_3O-C_6H_4O–), 6.72 (d, 2H, *J* = 9.1 Hz, $CH_3OC_6H_4O$–), 5.17 (s, 1H, H-1, Ara*f*-H-1), 5.09 (s, 1H, H-1, Ara*f*-H-1), 4.87 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.70 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.64 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.47 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.34 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.26 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1); ^{13}C NMR (100 MHz, D_2O) δ 109.3, 108.3 (2Ara*f*-C-1), 103.4, 103.2, 103.2, 102.9, 102.1, 101.6 (6Gal*p*-C-1). Anal. Calcd for $C_{53}H_{84}O_{40}$: C, 46.76; H, 6.22. Found: C, 46.51; H, 6.39.

4.15. 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 (29)

Coupling of **19** (6.0 g, 10 mmol) with **28** (7.4 g, 12 mmol) under the same conditions as described for the coupling of **6** with **7** gave disaccharide **29** (9.4 g, 89%) as a foamy solid. $[\alpha]_D$ +57.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.12–7.26 (m, 25H, 5P*h*), 7.02 (d, 2H, *J* = 9.2 Hz, $CH_3OC_6H_4O$–), 6.84 (d, 2H, *J* = 9.2 Hz, $CH_3OC_6H_4O$–), 6.03 (dd, 1H, $J_{2,1}$ = 8.0, $J_{2,3}$ = 10.4 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), 5.62 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.52 (dd, 1H, $J_{2,1}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.33 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.27 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.73 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 3.97 (dd, 1H, $J_{5,6}$ = 6.6, $J_{6,6}$ = 10.8 Hz, H-6), 3.72 (s, 3H, OCH_3), 2.00 (s, 3H, CH_3CO), 1.86 (s, 3H, CH_3CO). Anal. Calcd for $C_{58}H_{52}O_{19}$: C, 66.15; H, 4.98. Found: C, 66.27; H, 4.89.

4.16. 4-Methoxyphenyl 3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (30)

To a solution of **29** (9.4 g, 8.9 mmol) in CH_3OH (50 mL)–CH_2Cl_2 (50 mL) was added CH_3COCl (3 mL), and the mixture was stirred at rt for 48 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was neutralized with triethylamine, then concentrated, and the residue was passed through a silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give **30** (6.3 g, 71%) as a foamy solid. $[\alpha]_D$ +40.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.06–7.25 (m, 25H, 5P*h*), 7.01 (d, 2H, *J* = 9.2 Hz, $CH_3OC_6H_4O$–), 6.80 (d, 2H, *J* = 9.2 Hz, $CH_3OC_6H_4O$–), 6.07 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 6.01 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.67 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.64 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.31 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.28 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.56 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.16 (dd, 1H, $J_{5,6}$ = 6.4, $J_{6,6}$ = 10.8 Hz, H-6), 4.08 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 3.71 (s, 3H, OCH_3), 3.52 (dd, 1H, $J_{5,6}$ = 6.8, $J_{6,6}$ = 12 Hz, H-6), 3.35 (dd, 1H, $J_{5,6}$ = 6.8, $J_{6,6}$ = 12 Hz, H-6). Anal. Calcd for $C_{54}H_{48}O_{17}$: C, 68.12; H, 4.81. Found: C, 68.27; H, 4.89.

4.17. 4-Methoxyphenyl 6-*O*-acetyl-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 (31)

Coupling of **30** (6.0 g, 6.0 mmol) with **17** (4.4 g, 6.4 mmol) under the same conditions as described in the coupling of **6** with **7** gave **31** as a syrup (purified with 2:1 petroleum ether–EtOAc, 7.1 g, 81%). $[\alpha]_D$ +67.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.11–7.25 (m, 40H, 8P*h*), 7.00 (d, 2H, $J = 9.2$ Hz, $CH_3OC_6H_4O$–), 6.79 (d, 2H, $J = 9.2$ Hz, $CH_3OC_6H_4O$–), 6.05 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 6.01 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.90 (m, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.78 (m, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.68 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.65 (dd, 1H, $J_{3,4} = 3.2$, $J_{2,3} = 10.4$ Hz, H-3), 5.52 (dd, 1H, $J_{3,4} = 3.2$, $J_{2,3} = 10.4$ Hz, H-3), 5.28 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 5.21 (dd, 1H, $J_{3,4} = 3.2$, $J_{2,3} = 10.4$ Hz, H-3), 4.63 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.47 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 3.65 (s, 3H, OCH_3), 1.98 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6 (1C, CH_3CO), 166.1, 165.7, 165.6, 165.4, 165.3, 165.2, 165.1, 165.0 (8C, 8*C*OPh), 100.9, 100.8, 100.3 (3C, 3C-1). Anal. Calcd for $C_{83}H_{72}O_{26}$: C, 67.11; H, 4.89. Found: C, 67.29; H, 4.76.

4.18. 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→2)]-3,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (32)

Coupling of **31** (6.4 g, 4.3 mmol) with **12** (3.14 g, 5.2 mmol) under the same conditions as described for the coupling of **6** with **7** gave tetrasaccharide **32** (7.4 g, 89%) as a syrup. $[\alpha]_D$ +33.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04–7.22 (m, 55H, 11P*h*), 7.01 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.80 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.04 (d, 1H, $J_{3,4} = 3.6$ Hz, H-4), 5.98 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.79 (d, 1H, $J_{3,4} = 3.6$ Hz, H-4), 5.75 (d, 1H, $J_{3,4} = 3.6$ Hz, H-4), 5.66 (dd, 1H, $J_{2,3} = 10.4$, $J_{3,4} = 3.6$ Hz, H-3), 5.59 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.50 (s, 1H, Ara*f*-H-1), 5.44–5.40 (m, 2H, 2H-3), 5.39 (d, 1H, $J_{2,3} = 1.6$ Hz, Ara*f*-H-2), 5.26 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.76 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.51 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.27 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 3.82 (dd, 1H, $J_{5,6} = 6.4$, $J_{6,6} = 10.8$ Hz, H-6), 3.69 (s, 3H, OCH_3), 2.02 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 (1C, CH_3CO), 166.2, 166.1, 165.7, 165.7, 165.5, 165.4, 165.3, 165.2, 165.2, 165.0, 165.0 (11C, 11*C*OPh), 107.1 (1Ara*f*-C-1), 101.5, 101.3, 101.0 (3Gal*p*-C-1). Anal. Calcd for $C_{109}H_{92}O_{33}$: C, 67.83; H, 4.81. Found: C, 68.57; H, 4.89.

4.19. 6-*O*-Acetyl-2,3,4-tri-*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 (33)

To a solution of **32** (7.0 g, 3.6 mmol) in 4:1 CH_3CN–H_2O (100 mL) was added CAN (8.0 g, 14.4 mmol), and the mixture was treated by the same procedure as described in the preparation of **24** to give **33** (5.0 g, 70% for two steps) as a syrup. $[\alpha]_D$ +46.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H, N*H*), 8.26–7.17 (m, 55H, 11P*h*), 6.71 (d, 1H, $J_{1,2} = 3.6$ Hz, H-1), 6.04 (d, 1H, $J_{3,4} = 3.6$ Hz, H-4), 5.87 (dd, 1H, $J_{1,2} = 3.6$, $J_{2,3} = 10.4$ Hz, H-2), 5.80 (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, $J_{2,3} = 10.4$, $J_{3,4} = 3.6$ Hz, H-3), 5.56 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.48 (s, 1H, Ara*f*-H-1), 5.43–5.41 (m, 2H), 5.38 (d, 1H, $J_{2,3} = 1.6$ Hz, Ara*f*-H-2), 4.79 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.61 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.31 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 2.00 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9 (1C, CH_3CO), 166.1, 166.0, 165.7, 165.7, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (11C, 11*C*OPh), 106.9 (Ara *f*-*C*-1), 101.5, 101.4, 101.0 (3Gal*p* *C*-1). Anal. Calcd for $C_{104}H_{86}Cl_3NO_{32}$: C, 63.46; H, 4.40. Found: C, 63.22; H, 4.28.

4.20. 4-Methoxyphenyl 2,3,4-tri-*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 (34)

To a solution of **32** (4.0 g, 2.1 mmol) in CH_3OH (50 mL)–CH_2Cl_2 (50 mL) was added CH_3COCl (1 mL), and the mixture was treated by the same procedure as described in the preparation of **11** to give **34** (3.3 g, 83%) as a syrup. $[\alpha]_D$ +54.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07–7.21 (m, 55H, 11P*h*), 7.00 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.80 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.03 (d, 1H, $J_{3,4} = 3.6$ Hz, H-4), 5.95 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.83 (d, 1H, $J_{3,4} = 3.6$ Hz, H-4), 5.68–5.63 (m, 3H, H-4, H-2, H-3), 5.48 (s, 1H, Ara*f*-H-1), 5.38 (d, 1H, $J_{2,3} = 1.6$ Hz, Ara*f*-H-2), 5.24 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.74 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.49 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.25 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 3.82 (dd, 1H, $J_{5,6} = 6.4$, $J_{6,6} = 10.8$ Hz, H-6), 3.69 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.0, 165.9, 165.7, 165.6, 165.4, 165.4, 165.2, 165.2, 165.1, 165.0 (11C, 11*C*OPh), 107.3 (1Ara*f*-C-1), 101.4, 101.3, 101.0 (3Gal*p*-C-1). Anal. Calcd for $C_{107}H_{90}O_{32}$: C, 68.07; H, 4.80. Found: C, 68.27; H, 4.89.

4.21. 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→2)]-3,4-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 (35)

Compounds **33** (1.87 g, 0.94 mmol) and **23** (1.5 g, 0.79 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **8** to give **35** as a foamy solid (2.3 g, 81%). $[\alpha]_D$ +59.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.15–7.20 (m, 110H, 22Ph*H*), 6.99 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–),

6.81 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.02 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.94 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.84 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.79 (d, 1H, $J_{3,4} = 3.6$ Hz, H-4), 5.76–5.74 (m, 2H), 5.67 (d, 1H, $J_{3,4} = 4.0$ Hz, H-4), 5.64 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.60 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3}$ 10.4 = Hz, H-2), 5.58–5.52 (m, 3H), 5.48 (s, 1H, Ara*f*-H-1), 5.46–5.42 (m, 6H), 5.40 (d, 1H, $J_{2,3} = 1.6$ Hz, Ara*f*-H-2), 5.26 (s, 1H, Ara*f*-H-1), 5.24 (d, 1H, $J_{2,3} = 1.2$ Hz, Ara*f*-H-2), 5.11 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.72 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.36 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.34 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.32 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.22 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3}$ 10.4 Hz, H-2), 4.14 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.04 (dd, 1H, $J_{2,3} = 10.4$, $J_{3,4} = 3.6$ Hz, H-3), 3.69 (s, 3H, C*H*$_3$O), 1.80 (s, 3H, C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7 (1C, CH_3CO), 166.3, 166.2, 165.9, 165.6, 165.5, 165.5, 165.4, 165.4, 165.4, 165.3, 165.3, 165.1, 165.1, 165.0, 165.0, 165.0, 164.9, 164.9, 164.9, 164.8, 164.8, 164.5 (22C, 22*C*OPh), 107.6, 106.8 (2Ara*f*-C-1), 101.5, 100.8, 100.7, 100.6, 100.6, 100.4 (6Gal*p*-C-1). Anal. Calcd for $C_{209}H_{174}O_{63}$: C, 67.96; H, 4.75. Found: C, 67.58; H, 4.87.

4.22. 4-Methoxyphenyl 2,3,4-tri-*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)-2,3,4-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 (36)

To a solution of **35** (2.0 g, 0.54 mmol) in CH_3OH (25 mL)–CH_2Cl_2 (25 mL) was added CH_3COCl (0.5 mL), and the mixture was treated by the same procedure as described in the preparation of **11** to give **36** as a foamy solid (1.6 g, 81%). $[\alpha]_D$ +31.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.23–7.19 (m, 110H, 22Ph*H*), 6.98 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.80 (d, 2H, $J = 9.1$ Hz, $CH_3OC_6H_4O$–), 6.01 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.94 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.84 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.80–5.74 (m, 3H), 5.66 (d, 1H, $J_{3,4} = 4.0$ Hz, H-4), 5.62–5.60 (m, 2H), 5.58–5.54 (m, 2H), 5.52 (dd, 1H, $J_{2,3} = 10.4$, $J_{3,4} = 3.6$ Hz, H-3), 5.47 (s, 1H, Ara*f*-H-1), 5.46–5.42 (m, 6H), 5.39 (d, 1H, $J_{2,3} = 1.6$ Hz, Ara*f*-H-2), 5.26 (s, 1H, Ara*f*-H-1), 5.24 (d, 1H, $J_{2,3} = 1.2$ Hz, Ara*f*-H-2), 5.12 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.71 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.30 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.23 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 4.14 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 3.69 (s, 3H, C*H*$_3$O); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 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, 165.1, 165.0, 164.9, 164.7, 164.7 (22C, 22*C*OPh), 107.5, 106.7 (2Ara*f*-C-1), 101.5, 101.2, 101.0, 100.7, 100.6, 100.4 (6Gal*p*-C-1). Anal. Calcd for $C_{207}H_{172}O_{62}$: C, 68.08; H, 4.75. Found: C, 68.40; H, 4.89.

4.23. 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-galactopyranosyl-(1→6)-2,3,4-tri-*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)-2,3,4-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 (37)

Compounds **24** (1.13 g, 0.57 mmol) and **36** (1.5 g, 0.41 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **8** to give **37** as a foamy solid (1.68 g, 75%). $[\alpha]_D$ +101.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.23–7.18 (m, 165H, 33Ph*H*), 6.84 (dd, 4H, $CH_3OC_6H_4O$–), 6.04–5.98 (m, 4H), 5.96 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.91 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.84 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.77 (d, 1H, $J_{3,4} = 3.6$ Hz, H-4), 5.74–5.70 (m, 2H), 5.58 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.56 (dd, 1H, $J_{2,3} = 10.4$, $J_{3,4} = 3.6$ Hz, H-3), 5.55–5.53 (m, 8H), 5.52 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4), 5.50 (dd, 1H, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, H-2), 5.49–5.44 (m, 7H), 5.43 (s, 1H, Ara*f*-H-1), 5.41 (d, 1H, $J_{2,3} = 1.6$ Hz, Ara*f*-H-2), 5.25 (s, 2H, 2Ara*f*-H-1), 5.21 (d, 2H, $J_{2,3} = 1.2$ Hz, 2Ara*f*-H-2), 5.10 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.61 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.49 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.33 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.31 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.03 (dd, 1H, $J_{2,3} = 10.4$ Hz, $J_{3,4} = 3.6$ Hz, H-3), 3.71 (s, 3H, C*H*$_3$O), 1.98 (s, 3H, C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9 (1C, CH_3CO), 166.5, 166.3, 166.3, 166.1, 166.1, 165.9, 165.9, 165.6, 165.6, 165.5, 165.5, 165.4, 165.4, 165.4, 165.3, 165.3, 165.2, 165.1, 165.1, 165.1, 165.0, 165.0, 165.0, 164.9, 164.9, 164.8, 164.8, 164.7, 164.7, 164.6, 164.6, 164.5, 164.5 (33C, 33*C*OPh), 107.7, 107.7, 106.7 (3Ara*f*-C-1), 101.7, 101.7, 101.1, 100.9, 100.7, 100.6, 100.5, 100.5, 100.2 (9Gal*p*-C-1). Anal. Calcd for $C_{309}H_{256}O_{93}$: C, 68.00; H, 4.73. Found: C, 67.78; H, 4.94.

4.24. 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-galactopyranosyl-(1→6)-2,3,4-tri-*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)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-L-arabino- furanosyl-(1→3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (38)

To a solution of **37** (1.5 g, 0.27 mmol) in CH_3OH (25 mL)–CH_2Cl_2 (25 mL) was added CH_3COCl (0.5 mL), and the mixture was treated by the same pro-

cedure as described in the preparation of **11** to give **38** as a foamy solid (1.05 g, 71%). $[\alpha]_D$ +89.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.21–7.15 (m, 165H, 33Ph*H*), 6.82 (dd, 4H, $CH_3OC_6H_4O$–), 6.02 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 6.00–5.96 (m, 3H), 5.93 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.91 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.84 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.82 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.78–5.71 (m, 3H), 5.63 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.59 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.57–5.53 (m, 8H), 5.50 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.48–5.46 (m, 6H), 5.45 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.41 (s, 1H, Ara*f*-H-1), 5.39 (d, 1H, $J_{2,3}$ = 1.6 Hz, Ara*f*-H-2), 5.23 (s, 2H, 2Ara*f*-H-1), 5.21 (d, 2H, $J_{2,3}$ = 1.2 Hz, 2Ara*f*-H-2), 5.13 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.81 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.61 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.33 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.31 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 3.67 (s, 3H, C*H*$_3$O); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 166.5, 166.3, 166.3, 166.1, 166.0, 165.9, 165.9, 165.6, 165.6, 165.5, 165.5, 165.4, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.1, 165.0, 165.0, 165.0, 164.9, 164.9, 164.8, 164.8, 164.8, 164.7, 164.6, 164.6, 164.5, 164.3 (33C, 33*C*OPh), 107.8, 107.7, 106.9 (3Ara*f*-C-1), 101.7, 101.1, 101.0, 100.9, 100.6, 100.5, 100.5, 100.4, 100.2 (9Gal*p*-C-1). Anal. Calcd for $C_{307}H_{254}O_{92}$: C, 68.09; H, 4.73. Found: C, 68.45; H, 4.59.

4.25. 4-Methoxyphenyl hexadecaoside 39

Coupling of **38** (1.0 g, 0.18 mmol) with **33** (508 mg, 2.6 mmol) under the same conditions as described for the coupling of **6** with **7** gave compound **39** (946 mg, 71%) as a foamy solid. $[\alpha]_D$ +61.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.13–7.18 (m, 220H, 44Ph*H*), 6.89 (dd, 4H, $CH_3OC_6H_4O$–), 5.98 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.94 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.91–5.87 (7H), 5.84 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.79 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.73 (d, 1H, $J_{3,4}$ = 4.0 Hz, H-4), 5.69–5.59 (m, 10H), 5.56 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.53 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.50–5.43 (m, 8H), 5.42 (s, 1H, Ara*f*-H-1), 5.40 (d, 1H, $J_{2,3}$ = 1.6 Hz, Ara*f*-H-2), 5.36 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.30 (s, 1H, Ara*f*-H-1), 5.28 (s, 2H, 2Ara*f*-H-1), 5.24 (d, 1H, $J_{2,3}$ = 1.2 Hz, Ara*f*-H-2), 5.23–5.20 (m, 2H), 5.12 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.81 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.61 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.39 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.14 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 3.68 (s, 3H, C*H*$_3$O), 1.92 (s, 3H, C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0 (1C, CH_3CO), 167.0, 166.9, 166.3, 166.2, 166.1, 166.1, 166.1, 166.0, 166.0, 166.0, 165.9, 165.9, 165.9, 165.9, 165.8, 165.7, 165.6, 165.6, 165.6, 165.5, 165.5, 165.4, 165.4, 165.4, 165.3, 165.3, 165.3, 165.3, 165.2, 165.2, 165.2, 165.1, 165.1, 165.0, 165.0, 165.0, 164.9, 164.9, 164.9, 164.8, 164.8, 164.8, 164.7, 164.6, 164.5 (44C, 44*C*OPh), 107.6, 107.6, 107.3, 106.8 (4Ara*f*-C-1), 101.7, 101.6, 100.9, 100.9, 100.8, 100.7, 100.7, 100.6, 100.5, 100.5, 100.4, 100.4 (12Gal*p*-C-1). Anal. Calcd for $C_{409}H_{338}O_{123}$: C, 68.03; H, 4.72. Found: C, 68.32; H, 4.90.

4.26. Hexadecaoside acceptor 40

To a solution of **39** (946 mg, 0.13 mmol) in CH_3OH (20 mL)–CH_2Cl_2 (20 mL) was added CH_3COCl (0.4 mL), and the mixture was treated by the same procedure as described in the preparation of **11** to give **40** as a foamy solid (667 mg, 71%). $[\alpha]_D$ +75.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.11–7.09 (m, 220H, 44Ph*H*), 6.91 (dd, 4H, $CH_3OC_6H_4O$–), 6.00 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.96–5.90 (7H), 5.89 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.84 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.77 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.73 (d, 1H, $J_{3,4}$ = 4.0 Hz, H-4), 5.70 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.68–5.60 (m, 8H), 5.58 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.56 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.54 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.53–5.50 (m, 3H), 5.51 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.49–5.43 (m, 4H), 5.41 (s, 1H, Ara*f*-H-1), 5.39 (d, 1H, $J_{2,3}$ = 1.6 Hz, Ara*f*-H-2), 5.35 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ 10.4 Hz, H-2), 5.30 (s, 1H, Ara*f*-H-1), 5.28 (s, 2H, 2Ara*f*-H-1), 5.24 (d, 1H, $J_{2,3}$ = 1.2 Hz, Ara*f*-H-2), 5.23–5.20 (m, 2H), 5.10 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.81 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.60 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.44 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.39 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.33 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.12 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 3.65 (s, 3H, C*H*$_3$O); ^3C NMR ($CDCl_3$, 100 MHz): δ 167.1, 167.0, 166.5, 166.4, 166.3, 166.2, 166.2, 166.1, 166.1, 166.0, 165.0, 165.9, 165.9, 165.9, 165.8, 165.7, 165.7, 165.6, 165.6, 165.5, 165.5, 165.4, 165.4, 165.4, 165.4, 165.3, 165.3, 165.3, 165.2, 165.2, 165.1, 165.1, 165.0, 165.0, 165.0, 164.9, 164.9, 164.9, 164.8, 164.8, 164.8, 164.7, 164.6, 164.4 (44C, 44*C*OPh), 107.7, 107.6, 107.4, 106.9 (4Ara*f*-C-1), 101.7, 101.6, 101.1, 100.9, 100.8, 100.8, 100.7, 100.6, 100.5, 100.4, 100.4, 100.2 (12Gal*p*-C-1). Anal. Calcd for $C_{407}H_{336}O_{122}$: C, 68.09; H, 4.72. Found: C, 68.37; H, 4.58.

4.27. 4-Methoxyphenyl twentyoside 41

Coupling of **40** (500 mg, 0.069 mmol) with **24** (205 mg, 0.10 mmol) under the same conditions as described for the coupling of **6** with **7** gave compound **41** (404 mg, 65%) as a foamy solid. $[\alpha]_D$ +89.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$) δ 8.04–7.16 (m, 275H, 55Ph*H*), 6.75 (dd, 4H, $CH_3OC_6H_4O$–), 6.09 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.91 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.90 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.89–5.80 (13H), 5.78 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.76 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.75–5.72 (m, 7H), 5.70 (d, 1H, $J_{3,4}$ = 4.0 Hz, H-4), 5.60 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.53 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 5.51–5.43 (m, 15H), 5.41 (s, 2H, Ara*f*-H-1), 5.38 (d, 2H, Ara*f*-H-2), 5.36–5.33 (m, 7H), 5.25 (s, 3H, 3Ara*f*-H-1), 5.23 (d, 3H, 3Ara*f*-H-2), 5.10

(d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.78 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.61 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.46 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.26 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.15 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 3.69 (s, 3H, CH_3O), 2.00 (s, 3H, CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.2 (1C, CH_3CO), 166.4, 166.4, 166.3, 166.3, 166.2, 166.2, 166.1, 166.1, 166.1, 166.0, 166.0, 166.0, 165.9, 165.9, 165.9, 165.9, 165.8, 165.8, 165.7, 165.7, 165.6, 165.6, 165.6, 165.5, 165.5, 165.5, 165.5, 165.4, 165.4, 165.4, 165.4, 165.3, 165.3, 165.3, 165.2, 165.2, 165.2, 165.1, 165.1, 165.0, 165.0, 165.0, 165.0, 164.9, 164.9, 164.9, 164.9, 164.8, 164.8, 164.8, 164.7, 164.7, 164.7, 164.6, 164.5 (55C, 55*C*OPh), 107.7, 107.7, 107.6, 106.8, 106.3 (5Ara*f*-C-1), 101.7, 101.0, 100.9, 100.9, 100.8, 100.7, 100.7, 100.6, 100.5, 100.5, 100.4, 100.4, 100.3, 100.2, 100.1 (15Gal*p*-C-1). MALDI-TOF MS Calcd for $C_{509}H_{420}O_{153}$: 8984.5 [M]. Found: 9007 [M+Na$^+$].

4.28. 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→2)]-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-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-[α-L-arabinofuranosyl-(1→2)]-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 (42)

Compound **41** (400 mg, 0.044 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 **42** as an amorphous solid (120 mg, 85%). $[\alpha]_D$ +121.4 (*c* 1.0, H_2O); ^{1}H NMR (D_2O, 400 MHz) δ 7.07 (dd, 4H, $CH_3OC_6H_4O$–), 5.30 (s, 2H, 2Ara*f*-H-1), 5.23 (s, 2H, 2Ara*f*-H-1), 5.21 (s, 1H, Ara*f*-H-1), 5.10 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal-*p*-H-1), 4.98 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal-*p*-H-1), 4.80 (d, 1H, $J_{1,2}$ = 7.6 Hz, Gal*p*-H-1), 4.61 (d, 3H, 3Gal*p*-H-1), 4.51 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal-*p*-H-1), 4.48 (d, 3H, 3Gal*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), 4.25 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal-*p*-H-1), 4.21 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal-*p*-H-1); ^{13}C NMR (100 MHz, D_2O) δ 109.3, 109.3, 109.1, 108.3, 108.3 (5 Ara*f*-C-1), 103.4, 103.4, 103.4, 103.3, 103.3, 103.1, 102.9, 102.9, 102.8, 102.5, 102.4, 102.4, 102.1, 102.1, 101.7 (15Gal*p*-C-1). MALDI-TOF MS Calcd for $C_{122}H_{198}O_{97}$: 3216.8 [M]. Found: 3237 [M+Na$^+$].

4.29. 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-galactopyranosyl-(1→6)-2,3,4-tri-*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 (43)

Compounds **24** (1.87 g, 0.94 mmol) and **34** (1.5 g, 0.79 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **8** to give **43** as a foamy solid (2.5 g, 81%). $[\alpha]_D$ +61.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.11–7.15 (m, 110H, 22Ph*H*), 6.97 (d, 2H, *J* = 9.1 Hz, $CH_3OC_6H_4O$–), 6.83 (d, 2H, *J* = 9.1 Hz, $CH_3OC_6H_4O$–), 6.00–5.92 (m, 3H, H-2, 2H-4), 5.83 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.79 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.76 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.74 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.66 (d, 1H, $J_{3,4}$ = 4.0 Hz, H-4), 5.64 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.60–5.52 (m, 4H), 5.47 (s, 1H, Ara*f*-H-1), 5.42–5.39 (m, 5H), 5.41 (d, 1H, $J_{2,3}$ = 1.6 Hz, Ara*f*-H-2), 5.26 (s, 1H, Ara*f*-H-1), 5.24 (d, 1H, $J_{2,3}$ = 1.2 Hz, Ara*f*-H-2), 5.20 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.73 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.38 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.34 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.31 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.24 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ 10.4 Hz, H-2), 4.16 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.06 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 3.72 (s, 3H, CH_3O), 1.96 (s, 3H, CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0 (1C, CH_3CO), 166.7, 166.4, 166.1, 166.0, 165.8, 165.7, 165.7, 165.6, 165.6, 165.6, 165.2, 165.1, 165.1, 165.0, 165.0, 165.0, 164.9, 164.9, 164.9, 164.8, 164.8, 164.6 (22C, 22*C*OPh), 107.6, 106.9 (2Ara*f*-C-1), 101.5, 100.9, 100.7, 100.7, 100.6, 100.5 (6Gal*p*-C-1). Anal. Calcd for $C_{209}H_{174}O_{63}$: C, 67.96; H, 4.75. Found: C, 67.68; H, 4.87.

4.30. 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-galactopyranosyl-(1→6)-2,3,4-tri-*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 (44)

To a solution of **43** (2.0 g, 0.54 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added CAN (1.5 g, 14.4 mmol), and the mixture was treated by the same procedure as described in the preparation of **24** to give **44** (1.31 g, 65% for two steps) as a syrup. $[\alpha]_D$ +70.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.66 (s, 1H, N*H*), 8.06–7.18 (m, 110H, 22Ph*H*), 6.78 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 6.04 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.94 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4 Hz, H-2), 5.85 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4), 5.77 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 5.76–5.74 (m, 2H, 2H-4), 5.68 (d, 1H, $J_{3,4}$ = 4.0 Hz, H-4), 5.58–5.52 (m, 5H), 5.48 (s, 1H, Ara*f*-H-1), 5.46 (d, 1H, $J_{2,3}$ = 1.6 Hz, Ara*f*-H-2), 5.28 (s, 1H, Ara*f*-H-1), 5.25 (d, 1H, $J_{2,3}$ = 1.2 Hz, Ara*f*-H-2), 4.73 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.37 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.35 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.30 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.22 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 4.19 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.03 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6 Hz, H-3), 3.68 (s, 3H, CH_3O), 1.92 (s, 3H, CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7 (1C, CH_3CO), 166.7, 166.3, 166.1, 166.0, 165.8, 165.8, 165.7, 165.7, 165.6, 165.6, 165.4, 165.3, 165.2, 165.1, 165.0, 165.0, 164.9, 164.9, 164.8, 164.8, 164.7, 164.5 (22C, 22*C*OPh), 107.8, 106.6 (2Ara*f*-C-1), 101.7, 101.3, 101.0, 100.9, 100.8, 100.6 (6Gal*p*-C-1). Anal.

Calcd for $C_{204}H_{168}Cl_3NO_{62}$: C, 65.65; H, 4.54. Found: C, 65.28; H, 4.77.

Acknowledgements

This work was supported by The Chinese Academy of Sciences (KZCX3-J-08) and by The National Natural Science Foundation of China (Projects 30070185 and 39970864).

References and notes

1. (a) Egert, D.; Beuscher, N. *Planta Med.* **1992**, *58*, 163–165; (b) Paulsen, B. S. *Curr. Org. Chem.* **2001**, *5*, 939–950.
2. Clarke, A. E.; Anderson, R. L.; Stone, B. A. *Phytochemistry* **1979**, *18*, 521–528.
3. Yamada, H.; Kiyohara, H.; Cyong, J. C.; Otsuka, Y. *Mol. Immunol.* **1985**, *22*, 295–304.
4. Kiyohara, H.; Yamada, H.; Cyong, J. C.; Otsuka, Y. *J. Pharmacobio-Dyn.* **1986**, *9*, 339–346.
5. Shimizu, N.; Tomoda, M.; Gonda, R. *Chem. Pharm. Bull. (Tokyo)* **1989**, *37*, 1329–1332.
6. Steffan, W.; Kovac, P.; Albersheim, P.; Darvill, A. G.; Hahn, M. G. *Carbohydr. Res.* **1995**, *275*, 295–307.
7. (a) Du, Y.; Pan, Q.; Kong, F. *Carbohydr. Res.* **2000**, *323*, 28–35; (b) Lipták, A.; Nánás, P. *Tetrahedron Lett.* **1977**, *18*, 921–924; (c) Koeners, H. J.; Verhoeven, J.; van Boom, J. H. *Tetrahedron Lett.* **1980**, *21*, 381–382; (d) Csávás, M.; Borbás, A.; Jánossy, L.; Lipták, A. *Tetrahedron Lett.* **2003**, *44*, 631–635.
8. (a) Csávás, M.; Borbás, A.; Szilagyi, L.; Lipták, A. *Synlett* **2002**, 887–890; (b) Koeners, H. J.; Verdegaal, C. H. M.; van Boom, J. H. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 118–122; (c) 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; (d) Borbás, A.; Jánossy, L.; Lipták, A. *Carbohydr. Res.* **1999**, *318*, 98–109; (e) Csávás, M.; Borbás, A.; Jánossy, L.; Batta, G.; Lipták, A. *Carbohydr. Res.* **2001**, *336*, 107–115; (f) Lowary, T. L. Mycobacterial cell wall components. In *Glycoscience III Chemistry and Chemical Biology*; Fraser-Reid, B., Tatsuta, K., Thiem, J., Eds.; Springer: Berlin, 2001; pp 2005–2080.
9. (a) Du, Y.; Pan, Q.; Kong, F. *J. Carbohydr. Chem.* **2001**, *20*, 297–306; (b) Li, A.; Kong, F. *Carbohydr. Res.* **2004**, *339*, 1847–1856.
10. (a) Zeng, Y.; Li, A.; Kong, F. *Tetrahedron Lett.* **2003**, *44*, 8325–8329; (b) Li, A.; Zeng, Y.; Kong, F. *Carbohydr. Res.* **2004**, *339*, 673–681.
11. Kong, F.; Lu, D.; Zhou, S. *Carbohydr. Res.* **1990**, *198*, 141–148.
12. Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–125.
13. Byramova, N. E.; Ovchinnikov, M. V.; Backinowsky, L. V.; Kochetkov, N. K. *Carbohydr. Res.* **1983**, *124*, c8.
14. Du, Y.; Pan, Q.; Kong, F. *Synlett* **1999**, 1648–1652.