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Carbohydrate Research 340 (2005) 1949–1962
Carbohydrate RESEARCH

Syntheses of β-(1→6)-branched β-(1→3)-linked D-galactans that exist in the rhizomes of *Atractylodes lancea* DC

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Received 18 March 2005; accepted 28 May 2005
Available online 14 July 2005

Abstract—Effective syntheses of galactose hepta-, octa-, nona-, and decasaccharides that exist in the rhizomes of *Atractylodes lancea* DC were achieved with 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**1**), 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (**2**), 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**5**), 4-methoxyphenyl 6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (**22**), and 4-methoxyphenyl 2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (**26**) as the key synthons. Coupling of **2** with **1**, followed by oxidative cleavage of 1-OMP and subsequent trichloroacetimidate formation gave the β-(1→6)-linked disaccharide donor **4**. Condensation of **2** with **5** and subsequent selective deacetylation by methanolysis produced the β-(1→6)-linked disaccharide acceptor **7**. Reaction of **7** with **4**, oxidative cleavage of 1-OMP, and trichloroacetimidate formation produced the tetrasaccharide donor **9**. The penta- (**15**), the hexa- (**17**), and the heptasaccharide donor **19** were synthesized similarly. Meanwhile, treatment of **1** with **22** yielded β-(1→3)-linked disaccharide **23** and α-(1→3)-linked disaccharide **25**. Oxidative cleavage of 1-OMp of **23** followed by trichloroacetimidate formation produced the disaccharide donor **24**. Coupling of **26** with **24**, again, gave β-linked **27** and α-linked **29**. Selective 6-O-deacetylation of **27** afforded the trisaccharide acceptor **28**. TMSOTf-promoted condensation **28** of with the tetra- (**9**), penta- (**15**), hexa-(**17**), and heptasaccharide donor **19**, followed by deprotection, gave the target compounds.

Keywords: Galactose; Arabinogalactan

1. Introduction

An arabino-3,6-galactan, ALR-5IIa-1-1, which shows intestinal immune system modulating activity, has been found in the rhizomes of *Atractylodes lancea* DC.[1] The analysis of the structure–activity relationships of ALR-5IIa-1-1 by glycosidase digestions has suggested that the arabino-3,6-galactan moiety in the nonreducing terminal side of ALR-5IIa-1-1 mainly contributes to expression of the activity.[1] The study also suggested that Ara*f* side chain-trimmed ALR-5IIa-1-1 (AF-ALR-5IIa-1-1) still shows the intestinal immune system modulating activity, and the side-chain oligosaccharides released by exo-β-D-(1→3)-galactanase digestion are important for expression of the activity of AF-ALR-5IIa-1-1.[2] The following structure has been suggested for the galactan side chains of AF-ALR-5IIa-1-1.

As an ongoing project for study on structure–activity relationships of arabinogalactans, we have synthesized 2- and 3-α-L-arabinofuranose branched β-(1→6)-linked galactans.[3,4] The synthetic arabinogalactans have been tested, and a definite structure with strong immunoregulating activity has been established.[5a] Earlier, syntheses of structurally diverse arabinogalactans were reported.[5b–j] We present herein convergent syntheses of the galactan fragments that exist in AF-ALR-5IIa-1-1.

2. Results and discussion

Retrosynthetic analysis indicated that synthesis of the galactans as shown in Figure 1 can be achieved through

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doi:10.1016/j.carres.2005.05.017

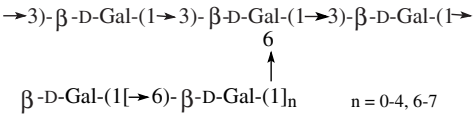


Figure 1. Galactan side chains of AF-ALR-5IIa-1-1.

three steps: (1) preparation of β-(1→6)-linked side chains, (2) construction of the β-(1→3)-linked backbone, and finally, (3) condensation of the above two moieties. Schemes 1 and 2 show the syntheses of the side chains, that is the tetrasaccharide donor **9**, the pentasaccharide donor **15**, the hexasaccharide donor **17** and the heptasaccharide donor **19**, and the trisaccharide backbone **28**. Condensation of the 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside **2**[3b] with perbenzoylated galactopyranosyl trichloroacetimidate[6] **1** afforded the disaccharide **3**. Subsequent oxidative cleavage of the 4-methoxyphenyl group and subsequent tricholoroacetimidate formation gave the β-(1→6)-linked disaccharide donor **4**. Coupling of **2** with **5** gave the disaccharide **6**, and subsequent deacetylation[7] yielded the β-(1→6)-linked disaccharide acceptor **7**. Condensation of **7** with **4**, followed by oxidative cleavage of 1-OMp and trichloroacetimidate formation, yielded the β-(1→6)-linked tetrasaccharide donor **9**. Meanwhile, coupling of **7** with 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**5**)[3b] followed by deacetylation gave trisaccharide acceptor **11**, and condensation of **2** with **4**, followed by oxidative cleavage of 1-OMP and trichloroacetimidate formation, yielded the trisaccharide donor **13**. Then coupling **11** with **4**, **13**, and **9**, followed by oxidative cleavage of 1-OMP and trichloroacetimidate formation, produced the pentasaccharide donor **15**, the hexasaccharide donor **17**, and the heptasaccharide donor **19**, respectively.

The β-(1→3)-linked galactose trisaccharide acceptor **28** was obtained with some difficulty mainly caused by poor stereoselectivity in the coupling reactions. First, the key synthon, 4-methoxyphenyl 6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (**22**), was prepared readily from 4-methoxyphenyl tetra-*O*-acetyl-β-D-galactopyranoside by deacetylation, selective 3-*O*-allylation via a dibutyltin complex,[8] 6-*O*-tritylation, benzoylation, detritylation, acetylation, and deallylation. However, coupling of **22** with **1** produced a mixture consisting of β-(1→3)-linked disaccharide **23** and α-(1→3)-linked disaccharide **25**, in spite of the existence of a C-2 ester group in the donor capable of neighboring group participation. Similar abnormal coupling with the galactose donor with a C-2 ester group was reported earlier by our group.[9] Oxidative cleavage of the 1-OMp group of **23**, followed by trichloroacetimidate formation, gave disaccharide donor **24**. Condensation of 4-methoxyphenyl 2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (**26**)[10] with **24** again gave an anomeric mixture composed of β-linked trisaccharide **27** and α-linked trisaccharide **29**. Fortunately, the mixture was well separated giving pure β-linked isomer. Selective deacetylation[7] of **27** by methanolysis gave the trisaccharide acceptor **28**.

With the tetra-, penta-, hexa-, and heptasaccharide donors and the trisaccharide acceptor building blocks at hand, the target hepta-, octa-, nona-, and decasaccharides were readily obtained as shown in Schemes 2 and 3. Thus, coupling **28** with **9**, **15**, **17**, and **19**, followed by deacylation with ammonia in methanol, yielded the heptasaccharide **31**, the octasaccharide **33**, the nonasaccharide **35**, and the decasaccharide **37**, respectively.

In summary, efficient syntheses of galactans consisting of a β-(1→3)-linked galactopyranosyl backbone and β-(1→6)-linked side chains of different size attached at the C-6 were achieved. The described method can be used in preparation of a variety of different 3,6-branched galactans.

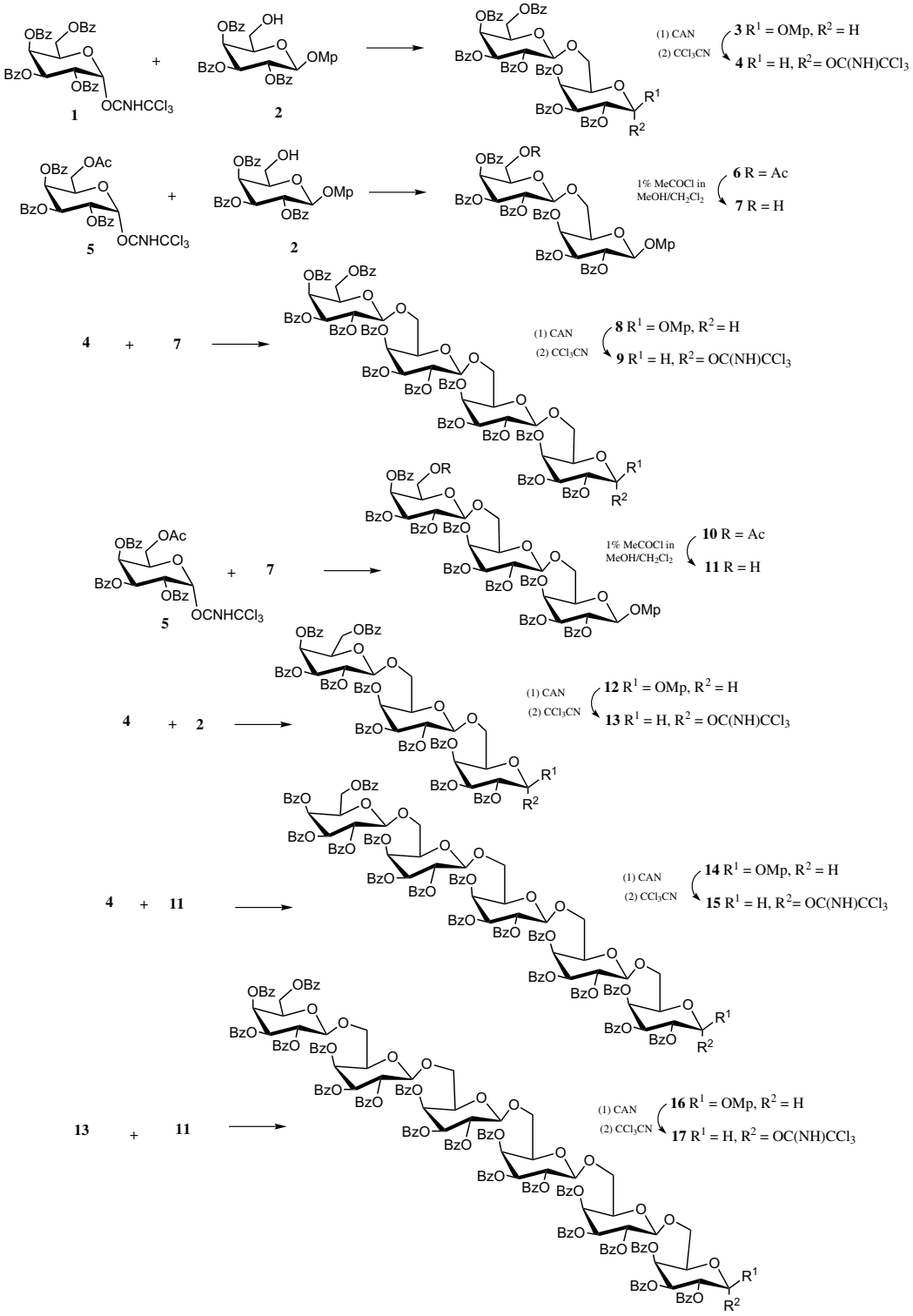
3. Experimental

3.1. General methods

Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined at 25 °C with a digital polarimeter. The NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard or D_2O with ethanol as the standard on an ARX at 400 MHz. Mass spectra were recorded on an autospec mass spectrometer using the ESI mode. Elemental analyses were done on elemental analyzer model 1108 EA. Thin-layer chromatography (TLC) was performed on silica gel HF_{254} with detection by charring with 30% (v/v) H_2SO_4 in MeOH or in some cases by a UV detector. Column chromatography was conducted by elution of a column (10 × 240 mm, 18 × 300 mm, 35 × 400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (60–90 °C) as the eluent. Solutions were concentrated at <60 °C under diminished pressure. Dry solvents were distilled over CaH_2 and stored over molecular sieves.

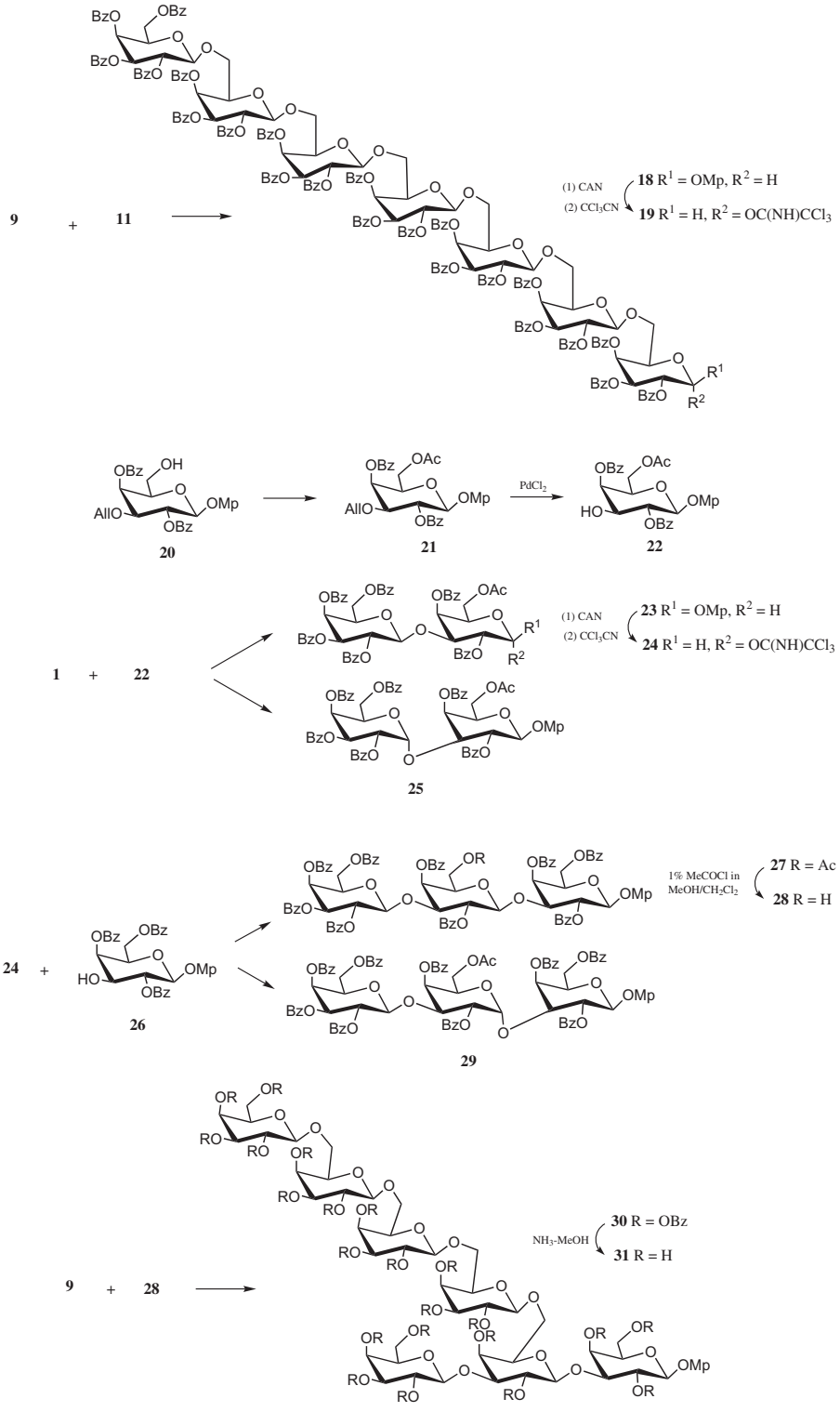
3.2. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (3)

A solution of **2** (2.0 g, 3.3 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**1**, 3.0 g, 4.0 mmol) in dry CH_2Cl_2 (80 mL) was stirred. TMSOTf (30 μL) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirred for 2 h, during which time the temperature was gradually raised to ambient. Then the mixture was neutralized with triethylamine. Concentration of the reaction mix-



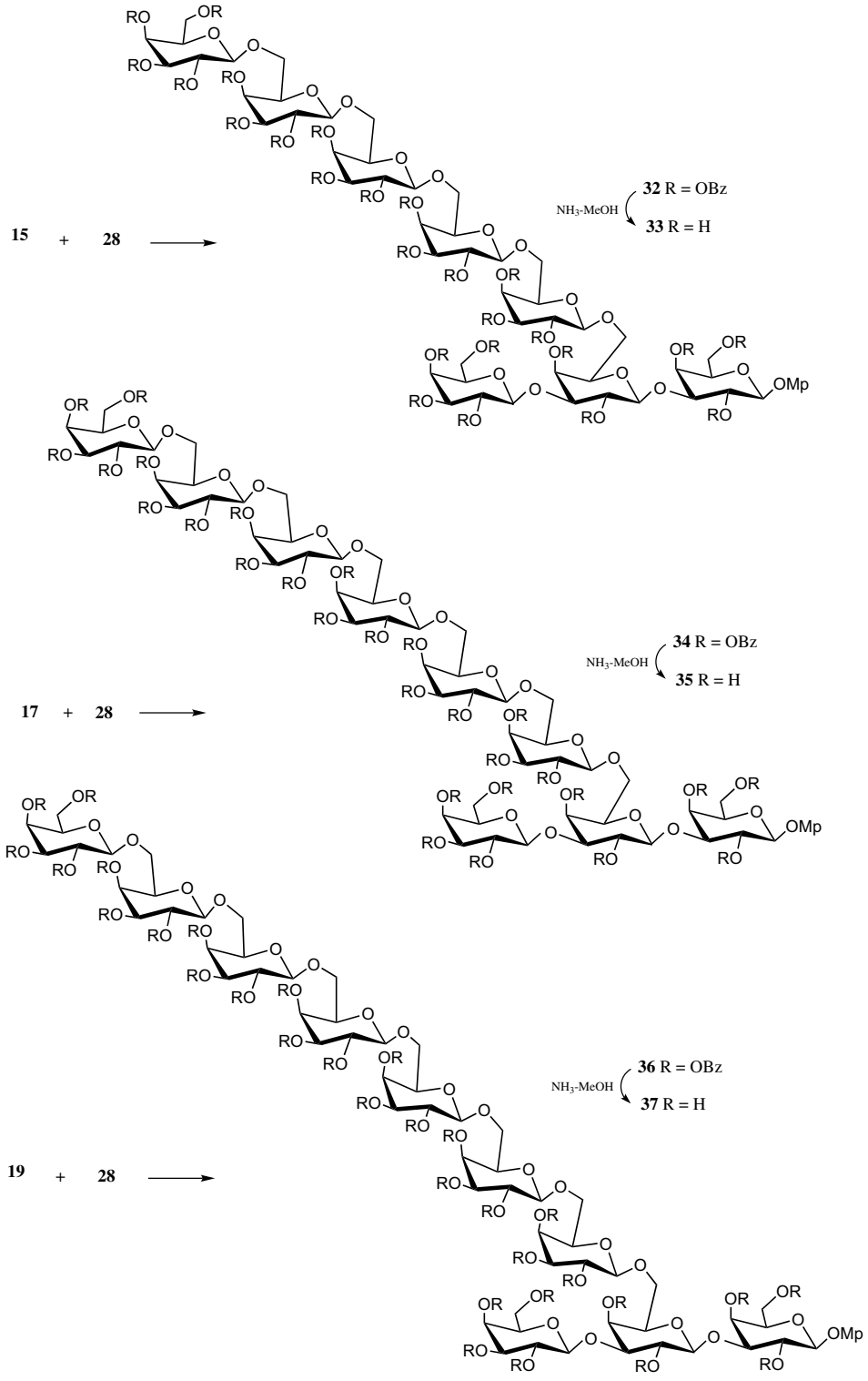
Scheme 1.

ture, followed by purification on a silica gel column with 3:1 petroleum ether–EtOAc as the eluent, gave **3** (3.4 g, 87%) as a syrup: $[\alpha]_D$ +38.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.10–7.24 (m, 35H, 7Ph*H*), 6.98 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.79 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.01 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.97 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.90 (m, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.80 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz,



Scheme 2.

H-2), 5.60–5.55 (m, 2H, H-3′, H-3), 5.17 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.97 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.44 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.4 Hz, H-6′), 4.31–4.23 (m, 2H, H-6′, H-5′), 4.20 (m, 1H, H-5), 4.16 (dd, 1H, $J_{5,6}$ 4.4 Hz, $J_{6,6}$ 10.8 Hz, H-6), 4.07 (dd, 1H, $J_{5,6}$ 4.8 Hz, $J_{6,6}$ 11.2 Hz, H-6), 3.71 (s, 3H, CH_3O). Anal. Calcd for $C_{68}H_{56}O_{19}$: C, 69.38; H, 4.79. Found: C, 69.29; H, 4.83.



Scheme 3.

3.3. 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (4)

To a solution of **3** (3.4 g, 2.9 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added ceric ammonium nitrate (CAN, 7.8 g, 14.2 mmol), and the mixture was stirred at rt for 30 min, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was extracted with 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. To a solution of the solid in CH_2Cl_2 (80 mL) were added trichloroacetonitrile (0.48 mL, 4.8 mmol) and anhyd K_2CO_3 (2.2 g, 16 mmol). The reaction mixture was stirred overnight at rt and then filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (2:1 petroleum ether–EtOAc) to give **4** (2.28 g, 69%, for two steps) as a syrup: $[\alpha]_D$ +57.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.70 (s, 1H, CN*H*CCl_3), 8.32–7.25 (m, 35H, 7Ph*H*), 6.75 (d, 1H, $J_{1,2}$ 3.6 Hz, α H-1), 6.10 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 6.02 (dd, 1H, $J_{1,2}$ 3.6, $J_{2,3}$ 10.4 Hz, H-2′), 5.92 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.86 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.74 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.53 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 4.90 (d, 1H, $J_{1,2}$ 8.0 Hz, β H-1′), 4.38 (dd, 1H, $J_{5,6}$ 4.8 Hz, $J_{6,6}$ 10.8 Hz, H-6′), 4.26 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6′), 4.21–4.15 (m, 3H, H-5′, H-5, H-6), 3.89 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6). Anal. Calcd for $C_{63}H_{50}Cl_3NO_{18}$: C, 62.25; H, 4.11. Found: C, 62.39; H, 4.25.

3.4. 4-Methoxyphenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (6)

Compounds **5** (2.0 g, 2.0 mmol) and 4-methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (**2**, 1.5 g, 2.5 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give disaccharides **6** as a syrup (2.32 g, 81%): $[\alpha]_D$ +31.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.07–7.23 (m, 30H, 6Ph*H*), 6.95 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.77 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.00 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.96 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.84 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.77 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.59 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.52 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.15 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.92 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.31 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6′), 4.15–4.11 (m, 4H, H-6′, H-5′, H-5, H-6), 4.02 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 3.69 (s, 3H, C*H*$_3$O), 1.98 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{63}H_{54}O_{19}$: C, 67.85; H, 4.88. Found: C, 67.93; H, 4.74.

3.5. 4-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (7)

To a solution of **6** (2.32 g, 2.07 mmol) in 1:1 CH_3OH–CH_2Cl_2 (100 mL) was added CH_3COCl (1 mL), and the reaction was carried out at rt for 48 h. Disaccharide **7** (1.87 g, 83%) was obtained as a syrup after purifying the product by column chromatography with 2:1 petroleum ether–EtOAc as the eluent: $[\alpha]_D$ +19.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.11–7.23 (m, 30H, 6Ph*H*), 6.95 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.74 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.01 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.95 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.81 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.76 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.58 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.52 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.15 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.90 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.27 (m, 1H, H-5′), 4.10 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 4.01 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 3.91 (m, 1H, H-5), 3.66 (dd, 1H, $J_{5,6}$ 6.4 Hz, $J_{6,6}$ 12 Hz, H-6′), 3.48 (dd, 1H, $J_{5,6}$ 5.6 Hz, $J_{6,6}$ 12 Hz, H-6′), 3.69 (s, 3H, C*H*$_3$O). Anal. Calcd for $C_{61}H_{52}O_{18}$: C, 68.28; H, 4.88. Found: C, 67.13; H, 4.70.

3.6. 4-Methoxyphenyl 2,3,4,6-tetra-*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)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (8)

Compounds **4** (1.36 g, 1.12 mmol) and **7** (1.0 g, 0.93 mmol) in dry CH_2Cl_2 (80 mL) were coupled by the same procedure as described in the preparation of **3** to give tetrasaccharides **8** as a syrup (1.56 g, 79%): $[\alpha]_D$ +49.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09–7.19 (m, 65H, 13Ph*H*), 6.94 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.76 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95–5.91 (m, 3H, H-2‴, H-4‴, H-4″), 5.89 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.86 (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″), 5.62 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.58–5.54 (m, 3H, H-2, H-3‴, H-3″), 5.53 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3′), 5.43 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.13 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1‴), 4.82 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.56 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.48 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.24–4.20 (m, 2H, H-6‴, H-6‴), 4.12 (m, 1H, H-5‴), 4.10–4.05 (m, 4H, H-6″, H-6″, H-5″, H-6′), 4.03 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 10.8 Hz, H-6′), 3.92 (m, 1H, H-5′), 3.76 (m, 1H, H-5), 3.68 (s, 3H, OCH_3), 3.51 (dd, 1H, $J_{5,6}$ 5.6 Hz, $J_{6,6}$ 10.8 Hz, H-6), 3.42 (dd, 1H, $J_{5,6}$ 6.6 Hz, $J_{6,6}$ 12 Hz, H-6); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 165.8, 165.6, 165.6, 165.4, 165.4, 165.4, 165.3, 165.3, 165.2, 165.2, 165.0, 165.0 (13C, 13*C*OPh), 101.0, 100.9, 100.9, 100.8 (4C, C-1). Anal. Calcd for $C_{122}H_{100}O_{35}$: C, 68.92; H, 4.74. Found: C, 68.73; H, 4.86.

3.7. 2,3,4,6-tetra-*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)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (9)

To a solution of **8** (1.56 g, 0.73 mmol) in 4:1 CH_3CN–H_2O (20 mL) was added CAN (2.0 g, 3.7 mmol), and

the mixture was treated by the same procedure as described in the preparation of **4** to give **9** as a syrup (1.03 g, 65%, for two steps): $[\alpha]_D$ +81.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.30 (s, 1H, N*H*), 8.02–7.21 (m, 65H, 13Ph*H*), 6.72 (d, 1H, $J_{1,2}$ 3.6 Hz, α H-1), 6.03 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4‴), 5.98 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2‴), 5.87–5.84 (m, 3H, H-4″, H-4′, H-4), 5.78 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3‴), 5.61 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2″), 5.57 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.50 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.47 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3″), 5.44 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3′), 5.41 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 4.80 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1‴), 4.51 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.42 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.16 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 11.2 Hz, H-6‴), 4.14–4.03 (m, 3H, H-6‴, H-6″, H-6″, H-6′), 4.01 (dd, 1H, $J_{5,6}$ 5.6 Hz, $J_{6,6}$ 11.4 Hz, H-6′), 3.95 (m, 1H, H-5‴), 3.79–3.70 (m, 3H, H-5″, H-5′, H-5), 3.41 (dd, 1H, $J_{5,6}$ 5.6 Hz, $J_{6,6}$ 10.8 Hz, H-6), 3.30 (dd, 1H, $J_{5,6}$ 6.6 Hz, $J_{6,6}$ 12 Hz, H-6); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 166.0, 165.9, 165.8, 165.7, 165.5, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (13C, 13*C*OPh), 101.5, 101.4, 101.0, 100.7 (4C, C-1). Anal. Calcd for $C_{117}H_{94}Cl_3NO_{34}$: C, 64.92; H, 4.38. Found: C, 64.78; H, 4.25.

3.8. 4-Methoxyphenyl 6-*O*-acetyl-2,3,4-tri-*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-galactopyranoside (10)

Compounds **7** (5.0 g, 4.66 mmol) and **5** (3.8 g, 5.59 mmol) in dry CH_2Cl_2 (60 mL) were coupled by the same procedure as described in the preparation of **3** to give trisaccharide **10** as a syrup (6.0 g, 89%): $[\alpha]_D$ +51.2 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.07–7.18 (m, 45H, 9Ph*H*), 6.90 (d, 2H, *J* 9.1 Hz, CH_3O-C_6H_4O–), 6.73 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4$O–), 5.97 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4″), 5.95–5.92 (m, 2H, H-2″, H-4′), 5.79 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.71 (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), 5.56 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3″), 5.52–5.45 (m, 2H, H-3′, H-3), 5.13 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.79 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.61 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.41 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6″), 4.34 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6″), 4.24 (m, 1H, H-5″), 4.10 (dd, 1H, $J_{5,6}$ 5.2 Hz, $J_{6,6}$ 10.4 Hz, H-6′), 4.05 (m, 1H, H-5′), 3.95 (dd, 1H, $J_{5,6}$ 6.8 Hz, $J_{6,6}$ 10.4 Hz, H-6′), 3.89–3.82 (m, 2H, H-6, H-5), 3.65 (s, 3H, O*C*H_3), 3.60 (dd, 1H, $J_{5,6}$ 5.2 Hz, $J_{6,6}$ 10 Hz, H-6), 1.96 (s, 3H, CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.1 (1C, CH_3*C*O), 166.2, 166.1, 165.7, 165.7, 165.6, 165.5, 165.4, 165.2, 165.1 (9C, 9*C*OPh), 101.6, 101.2, 100.9 (3C, C-1). Anal. Calcd for $C_{90}H_{76}O_{27}$: C, 68.00; H, 4.82. Found: C, 68.16; H, 4.87.

3.9. 4-Methoxyphenyl 2,3,4-tri-*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-galactopyranoside (11)

To a solution of **10** (6.0 g, 3.78 mmol) in 1:1 CH_3OH–CH_2Cl_2 (100 mL) was added CH_3COCl (1 mL), and the reaction was carried out by the same procedure as described in the preparation of **7** to give **11** as a syrup (5.0 g, 85%): $[\alpha]_D$ +43.6 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05–7.23 (m, 45H, 9Ph*H*), 6.94 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4$O–), 6.76 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4$O–), 5.97–5.92 (m, 3H, H-4″, H-2″, H-4′), 5.73 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.71 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.66 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.58 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3″), 5.51 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3′), 5.46 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.16 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.81 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.56 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.26 (m, 1H, H-5″), 4.11 (dd, 1H, $J_{5,6}$ 5.2 Hz, $J_{6,6}$ 10.4 Hz, H-6′), 4.07 (m, 1H, H-5′), 4.00 (dd, 1H, $J_{5,6}$ 6.8 Hz, $J_{6,6}$ 10.4 Hz, H-6′), 3.90–3.84 (m, 2H, H-6, H-5), 3.65 (s, 3H, O*C*H_3), 3.60 (dd, 1H, $J_{5,6}$ 5.2 Hz, $J_{6,6}$ 10 Hz, H-6), 3.50 (dd, 1H, $J_{5,6}$ 6.8 Hz, $J_{6,6}$ 12 Hz, H-6), 3.35 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 12 Hz, H-6); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 165.8, 165.7, 165.6, 165.4, 165.3, 165.2, 165.2, 165.0 (9C, 9*C*OPh), 101.5, 101.1, 100.8 (3C, C-1). Anal. Calcd for $C_{88}H_{74}O_{26}$: C, 68.30; H, 4.82. Found: C, 68.41; H, 4.69.

3.10. 4-Methoxyphenyl 2,3,4,6-tetra-*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-galactopyranoside (12)

Compounds **4** (3.0 g, 2.47 mmol) and **2** (1.23 g, 2.05 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give trisaccharide **12** (3.14 g, 85%) as a syrup: $[\alpha]_D$ +68.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.07–7.24 (m, 50H, 10Ph*H*), 6.93 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4$O–), 6.76 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4$O–), 5.97–5.93 (m, 2H, H-4″, H-2″), 5.89 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.87 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.72 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.68 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.59 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3″), 5.55 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3′), 5.48 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.17 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.79 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.63 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.30 (dd, 1H, $J_{5,6}$ 5.6 Hz, $J_{6,6}$ 12 Hz, H-6″), 4.25 (m, 1H, H-5″), 4.16–4.11 (m, 2H, H-6″, H-6′), 4.09–4.04 (m, 2H, H-5′, H-5), 3.97 (dd, 1H, $J_{5,6}$ 6.4 Hz, $J_{6,6}$ 10 Hz, H-6′), 3.88 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.4 Hz, H-6), 3.68 (s, 3H, CH_3O), 3.60 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10 Hz, H-6); ^{13}C

NMR ($CDCl_3$, 100 MHz): δ 166.2, 166.0, 165.9, 165.7, 165.5, 165.4, 165.3, 165.3, 165.2, 165.1 (10C, 10*C*OPh), 101.3, 101.1, 100.7 (3C, C-1). Anal. Calcd for $C_{95}H_{78}O_{27}$: C, 69.08; H, 4.76. Found: C, 69.29; H, 4.92.

3.11. 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (13)

To a solution of **12** (3.0 g, 1.81 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added CAN (4.0 g, 7.27 mmol), and the mixture was treated by the same procedure as described in the preparation of **4** to give trisaccharide donor **13** (2.2 g, 71% for two steps) as a syrup: $[\alpha]_D$ +79.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.33 (s, 1H, N*H*), 7.93–7.22 (m, 50H, 10Ph*H*), 6.74 (d, 1H, $J_{1,2}$ 3.6 Hz, α H-1), 6.05 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4″), 5.99 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2″), 5.89–5.87 (m, 2H, H-4′, H-4), 5.81 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3″), 5.67 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.62 (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′), 5.44 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 4.73 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.59 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.23 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.8 Hz, H-6″), 4.12 (m, 1H, H-5″), 4.09–4.00 (m, 4H, H-6″, H-6′, H-5′, H-5), 3.89 (dd, 1H, $J_{5,6}$ 6.8 Hz, $J_{6,6}$ 10 Hz, H-6′), 3.76 (dd, 1H, $J_{5,6}$ 6.4 Hz, $J_{6,6}$ 10.4 Hz, H-6), 3.68 (s, 3H, CH_3O), 3.51 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10 Hz, H-6); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 166.5, 166.2, 166.1, 165.9, 165.8, 165.7, 165.5, 165.3, 165.1 (10C, 10*C*OPh), 101.7, 101.4, 100.9 (3C, C-1). Anal. Calcd for $C_{90}H_{72}Cl_3NO_{26}$: C, 63.96; H, 4.29. Found: C, 53.71; H, 4.42.

3.12. 4-Methoxyphenyl 2,3,4,6-tetra-*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-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (14)

Compounds **4** (1.5 g, 1.23 mmol) and **11** (1.58 g, 1.02 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give pentasaccharide **14** (2.14 g, 81%) as a syrup: $[\alpha]_D$ +22.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 7.93–7.21 (m, 80H, 16Ph*H*), 6.88 (d, 2H, *J* 9.1 Hz, CH_3O-C_6H_4O–), 6.74 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.91 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.90–5.87 (m, 3H, 3H-4), 5.86 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.84 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.66 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.62 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.58–5.55 (m, 3H, 2H-2, H-3), 5.53 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.46–5.43 (m, 2H, 2H-3), 5.41 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.10 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.80 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.53 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.49 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.42 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.71 (s, 3H, CH_3O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 166.7, 166.7, 166.4, 166.3, 166.2, 166.1, 165.9, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.1, 165.0 (16C, 16*C*OPh), 101.7, 101.4, 101.2, 100.7, 100.6 (5C, C-1). Anal. Calcd for $C_{149}H_{122}O_{43}$: C, 68.81; H, 4.73. Found: C, 68.99; H, 4.91.

3.13. 2,3,4,6-Tetra-*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-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (15)

To a solution of **14** (1.5 g, 0.58 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added CAN (1.58 g, 2.88 mmol), and the mixture was treated by the same procedure as described in the preparation of **4** to give pentasaccharide donor **15** (958 mg, 63% for two steps) as a syrup: $[\alpha]_D$ +59.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.37 (s, 1H, N*H*), 8.11–7.21 (m, 80H, 16Ph*H*), 6.77 (d, 1H, $J_{1,2}$ 3.6 Hz, α H-1), 6.05 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 6.00 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.89–5.87 (m, 3H, 3H-4), 5.83 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.78 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.70 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.66 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.59 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.50–5.47 (m, 3H, H-2, 2H-3), 5.44 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.39 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 4.81 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.55 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.51 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.41 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 166.0, 165.9, 165.8, 165.8, 165.7, 165.5, 165.5, 165.4, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0, 164.9 (16C, 16*C*OPh), 101.7, 101.4, 101.1, 101.0, 100.6 (5C, C-1). Anal. Calcd for $C_{144}H_{116}Cl_3NO_{42}$: C, 65.54; H, 4.43. Found: C, 65.32; H, 4.28.

3.14. 4-Methoxyphenyl 2,3,4,6-tetra-*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-2,3,4-tri-*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-galactopyranoside (16)

Coupling of **11** (1.0 g, 0.65 mmol) with **13** (1.31 g, 0.78 mmol) under the same conditions as described for the coupling of **1** with **2** gave hexasaccharide **16** (1.58 g, 80%) as a syrup: $[\alpha]_D$ +39.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.22 (m, 95H, 19Ph*H*), 6.77 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.73 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.95–5.90 (m, 2H, H-2, H-4), 5.89 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.87 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.85–5.80 (m, 4H, H-2, 3H-4), 5.65 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.62 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.59 (dd, 1H, $J_{1,2}$

8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.56–5.55 (m, 3H, H-2, 2H-3), 5.51 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.47–5.45 (m, 2H, 2H-3), 5.40 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.11 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.83 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.54 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.50 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.46 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.37 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.69 (s, 3H, CH_3O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 167.2, 167.0. 166.9, 166.7, 166.7, 166.6, 166.2, 166.1, 166.0, 165.9, 165.6, 165.5, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0 (19C, 19*C*OPh), 101.6, 101.5, 101.4, 101.2, 101.0, 100.9 (6C, C-1). Anal. Calcd for $C_{176}H_{144}O_{51}$: C, 68.74; H, 4.72. Found: C, 68.51; H, 4.89.

3.15. 2,3,4,6-Tetra-*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-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (17)

To a solution of **16** (1.5 g, 0.49 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added CAN (1.33 g, 2.44 mmol), and the mixture was treated by the same procedure as described in the preparation of **4** to give hexasaccharide donor **17** (970 mg, 64% for two steps) as a syrup: $[\alpha]_D$ +31.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H, N*H*), 8.03–7.23 (m, 95H, 19Ph*H*), 6.74 (d, 1H, $J_{1,2}$ 3.6 Hz, α H-1), 6.02 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.98 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.87 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.86–5.83 (m, 4H, 4H-4), 5.75 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.71 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.65 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.60–5.55 (m, 4H, 2H-2, 2 H-3), 5.51 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.44 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.41–5.37 (m, 2H, 2H-3), 4.83 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.55 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.50 (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); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.6, 166.5, 166.2, 166.1, 166.1, 165.9, 165.8, 165.7, 165.7, 165.6, 165.5, 165.4, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0, 165.0 (19C, 19*C*OPh), 101.5, 101.3, 101.2, 101.0, 100.9, 100.8 (6C, C-1). Anal. Calcd for $C_{171}H_{138}Cl_3NO_{50}$: C, 65.97; H, 4.47. Found: C, 65.79; H, 4.66.

3.16. 4-Methoxyphenyl 2,3,4,6-tetra-*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-2,3,4-tri-*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)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (18)

Compounds **11** (1.50 g, 0.97 mmol) and **9** (2.51 g, 1.16 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give heptasaccharide **18** as a syrup (2.4 g, 75%): $[\alpha]_D$ +67.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.13–7.20 (m, 110H, 22Ph*H*), 6.91 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.73 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.01 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.97–5.96 (m, 2H, 2H-4), 5.90 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.87 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.85–5.78 (m, 4H, H-2, 3H-4), 5.66 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.62 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.60–5.55 (m, 4H, 2H-2, 2H-3), 5.53 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.51 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.48–5.43 (m, 3H, 3H-3), 5.37 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.13 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.85 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.60–4.56 (m, 2H, 2H-1), 4.51 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.47 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.39 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.69 (s, 3H, CH_3O); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 167.1, 166.9, 166.8, 166.3, 166.2, 166.0, 166.0, 165.9, 165.8, 165.7, 165.6, 165.6, 165.5, 165.4, 165.4, 165.3, 165.2, 165.2, 165.1, 165.0, 165.0 (22C, 22*C*OPh), 101.5, 101.2, 101.1, 100.9, 100.7, 100.6, 100.4 (7C, C-1). Anal. Calcd for $C_{203}H_{166}O_{59}$: C, 68.69; H, 4.71. Found: C, 67.87; H, 4.65.

3.17. 2,3,4,6-Tetra-*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-2,3,4-tri-*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)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (19)

To a solution of **18** (2.0 g, 0.56 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added CAN (1.54 g, 2.82 mmol), and the mixture was treated by the same procedure as described in the preparation of **4** to give heptasaccharide donor **19** (1.23 g, 61% for two steps) as a syrup: $[\alpha]_D$ +47.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.29 (s, 1H, N*H*), 7.91–7.23 (m, 110H, 22Ph*H*), 6.75 (d, 1H, $J_{1,2}$ 3.2 Hz, α H-1), 6.04 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 6.00 (dd, 1H, $J_{1,2}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.84 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.83–5.81 (m, 4H), 5.79 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.75 (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), 5.65 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.61–5.50 (m, 5H), 5.46 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.43 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.40–5.37 (m, 3H, H-3), 4.80 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.57 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.47 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.44–4.40 (m, 2H, H-1), 4.32 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.0, 166.9, 166.8, 166.6, 166.6, 166.5, 166.4, 166.2, 166.2, 166.1, 165.9, 165.8, 165.7, 165.6, 165.5, 165.4, 165.4, 165.3, 165.2, 165.1, 165.1, 165.0 (22C, 22*C*OPh), 101.8, 101.5, 101.3, 101.0, 100.9,

100.9, 100.6 (7C, C-1). Anal. Calcd for $C_{198}H_{160}Cl_3NO_{58}$: C, 66.28; H, 4.49. Found: C, 66.53; H, 4.62.

3.18. 4-Methoxyphenyl 6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (22)

To a solution of **20**[4] (5.0 g, 9.3 mmol) in pyridine (20 mL) was added Ac_2O (3 mL, 31.8 mmol), the reaction mixture was stirred for 6 h, at the end of which time the TLC (4:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated to dryness and then purified by column chromatography with 3:1 petroleum ether–EtOAc as the eluent to afford **21** (5.0 g, 92%). To a solution of **21** (5.0 g, 8.7 mmol) in anhyd CH_3OH (70 mL) was added $PdCl_2$ (200 mg), and the mixture was stirred at rt for 5 h, at the end of which time TLC (2:1 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 3:1 petroleum ether–EtOAc as the eluent to give **22** as a syrup (4.0 g, 88%): $[\alpha]_D$ +29.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.16–7.25 (m, 10H, 2Ph*H*), 6.97 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.81 (d, 2H, *J* 9.1 Hz, CH_3O-C_6H_4O–), 5.71 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4), 5.56 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.13 (d, 1H, $J_{1,2}$ 8 Hz, H-1), 4.33–4.26 (m, 2 H, 2H-6). 4.13 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 3.76 (s, 3H, C*H*$_3$O), 2.01 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{29}H_{28}O_{10}$: C, 64.92; H, 5.26. Found: C, 64.79; H, 5.21.

3.19. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (23) and 4-methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranoside (25)

Compounds **1** (3.3 g, 4.47 mmol) and **22** (2.0 g, 3.73 mmol) in dry CH_2Cl_2 (60 mL) were coupled by the same procedure as described in the preparation of **3** to give disaccharide **23** (2.74 g, 66%) and **25** (665 mg, 16%), respectively, as foamy solids. Compound **23**: $[\alpha]_D$ +53.1 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.18–7.07 (m, 30H, 6Ph*H*), 6.86 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.73 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.94 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.87 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.81 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.58 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.40 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3′), 5.02 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.99 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.74 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.8 Hz, H-6′), 4.34–4.30 (m, 2H, H-6′, H-5′), 4.27 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3), 4.25–4.20 (m, 2H, H-6, H-5), 4.07 (dd, 1H, $J_{5,6}$ 4.8 Hz, $J_{6,6}$ 10.8 Hz, H-6), 3.65 (s, 3H, OC*H*$_3$), 2.01 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{63}H_{54}O_{19}$: C, 67.85; H, 4.88. Found: C, 67.76; H, 4.79; **25**: $[\alpha]_D$ +89.4 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.13–7.09 (m, 30H, 6Ph*H*), 6.87 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.69 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.92 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.88 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.80 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.74 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1′), 5.61 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.43 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.6 Hz, H-3), 4.87 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.69 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.8 Hz, H-6′), 4.31–4.27 (m, 2H, H-6′, H-5′), 4.25 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3), 4.22–4.19 (m, 2H, H-6, H-5), 4.03 (dd, 1H, $J_{5,6}$ 4.8 Hz, $J_{6,6}$ 10.8 Hz, H-6), 3.65 (s, 3H, OC*H*$_3$), 1.98 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{63}H_{54}O_{19}$: C, 67.85; H, 4.88. Found: C, 67.67; H, 4.71.

3.20. 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (24)

To a solution of **23** (2.74 g, 2.46 mmol) in 4:1 CH_3CN–H_2O (50 mL) was added CAN (6.0 g, 12 mmol), and the mixture was treated by the same procedure as described in the preparation of **4** to give **24** as a syrup (1.89 g, 67% for two steps): $[\alpha]_D$ +39.2 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H, N*H*), 8.18–7.11 (m, 30H, 6Ph*H*), 6.71 (d, 1H, $J_{1,2}$ 3.6 Hz, α H-1), 6.02 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.94 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4′), 5.81 (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), 5.41 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3′), 5.10 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.88 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.71 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.8 Hz, H-6′), 4.44 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.8 Hz, H-6′), 4.36 (m, 1H, H-5′), 4.23 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3), 4.21–4.19 (m, 2H, H-6, H-5), 4.11 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.8 Hz, H-6), 2.00 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{58}H_{48}Cl_3NO_{18}$: C, 60.40; H, 4.19. Found: C, 60.26; H, 4.27.

3.21. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,6,4-tri-*O*-benzoyl-β-D-galactopyranoside (27) and 4- methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-galactopyranosyl-(1→3)-2, 4, 6-tri-*O*-benzoyl-β-D-galactopyranoside (29)

A solution of **24** (1.4 g, 1.2 mmol) and 4-methoxyphenyl 2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (**26**, 600 mg, 1.0 mmol) in dry CH_2Cl_2 (100 mL) was stirred. TMSOTf (50 μL) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirred for 2 h, during which time the temperature was gradually raised to ambient, and then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with

2:1 petroleum ether–EtOAc as the eluent, gave **27** (955 mg, 60%) and **29** (286 mg, 18%), respectively, as syrups. Compound **27**: $[\alpha]_D$ +68.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.03–7.24 (m, 45H, 9Ph*H*), 6.78 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.51 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.88 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4″), 5.82 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.80 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.74 (m, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2″), 5.46 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.35 (m, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.23 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3″), 4.98 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.83 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.79 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.70–4.64 (m, 2H, H-6″, H-6″), 4.42 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.4 Hz, H-6′), 4.29 (m, 1H, H-5″), 4.25–4.07 (m, 6H, H-6′, H-3′, H-3, H-5′, 2H-6), 3.90 (m, 1H, H-5), 3.64 (s, 3H, C*H*$_3$O), 2.04 (s, 3H, C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5 (1C, CH_3CO), 166.1, 165.9, 165.8, 165.5, 164.5, 165.4, 165.4, 164.3, 163.8 (9C, 9*C*OPh), 101.4, 101.2, 100.9 (3C, C-1). Anal. Calcd for $C_{90}H_{76}O_{27}$: C, 68.00; H, 4.82. Found: C, 67.89; H, 4.68. Compound **29**: $[\alpha]_D$ +71.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.18–7.12 (m, 45H, 9Ph*H*), 6.98 (d, 2H, *J* 9.1 Hz, CH_3O-C_6H_4O–), 6.67 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.99 (m, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2″), 5.88 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4″), 5.82 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.65 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.52 (dd, 1H, $J_{1,2}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.42 (m, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.36 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1′), 5.31 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3″), 5.12 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.80 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.52–4.48 (m, 2H, H-6″, H-6″), 4.37–4.23 (m, 5H), 4.20–4.10 (m, 4H), 4.00 (m, 1H, H-5), 3.71 (s, 3H, C*H*$_3$O), 1.99 (s, 3H, C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1 (1C, CH_3CO), 165.9, 165.7, 165.6, 165.4, 165.2, 165.2, 165.2, 165.0, 164.4 (9C, 9*C*OPh), 101.3, 101.2, 93.5 (3C, C-1). Anal. Calcd for $C_{90}H_{76}O_{27}$: C, 68.00; H, 4.82. Found: C, 68.15; H, 4.94.

3.22. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (28)

To a solution of **27** (956 g, 0.60 mmol) in 1:1 CH_3OH–CH_2Cl_2 (40 mL) was added CH_3COCl (0.4 mL), and the reaction was carried out by the same procedure as described in the preparation of **7** to give **28** (781 mg, 84%) as a syrup: $[\alpha]_D$ +28.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.03–7.11 (m, 45H, 9Ph*H*), 6.76 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.50 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.89 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4″), 5.81 (m, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2″), 5.77 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4′), 5.68 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.45 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2′), 5.40 (m, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.24 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3″), 4.96 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1″), 4.85 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1′), 4.79 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.67–4.59 (m, 2H, 2H-6″), 4.41 (dd, 1H, $J_{5,6}$ 6.0 Hz, $J_{6,6}$ 10.4 Hz, H-6′), 4.25–4.19 (m, 3H), 4.15–4.10 (m, 2H), 3.78 (m, 1H, H-5), 3.63 (s, 3H, C*H*$_3$O), 3.56–3.54 (m, 2H, 2H-6′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 165.9, 165.8, 165.6, 165.5, 165.4, 164.4, 164.3, 164.0 (9C, 9*C*OPh), 101.4, 101.3, 100.6 (3C, C-1). Anal. Calcd for $C_{88}H_{74}O_{26}$: C, 68.30; H, 4.82. Found: C, 68.49; H, 4.73.

3.23. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*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)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (30)

Compounds **9** (335 mg, 0.16 mmol) and **28** (200 mg, 0.13 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give heptasaccharide **30** (385 g, 84%) as a syrup: $[\alpha]_D$ +79.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.09–7.23 (m, 110H, 22Ph*H*), 6.83 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.60 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.01 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.90 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.86–5.82 (m, 2H, 2H-4), 5.79 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.71 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.69 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.68–5.64 (m, 2H), 5.61 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.59 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.57–5.50 (m, 3H), 5.48 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.40 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.35 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.26 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.20 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 4.75 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.73 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.69 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 4.65 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.61 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.58 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.33 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.30 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.66 (s, 3H, C*H*$_3$O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 166.0, 165.9, 165.9, 165.9, 165.8, 165.7, 165.7, 165.6, 165.6, 165.5, 165.4, 165.4, 165.3, 165.2, 165.2, 165.1, 165.1, 165.0, 164.4, 164.3, 163.8 (22C, 22*C*OPh), 101.2, 101.1, 101.1, 101.0, 100.7, 100.6, 100.1 (7C, C-1). Anal. Calcd for $C_{203}H_{166}O_{59}$: C, 68.69; H, 4.71. Found: C, 68.47; H, 4.83.

3.24. 4-Methoxyphenyl β-D-galactopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl]-β-D-galactopyranosyl-(1→3)-β-D-galactopyranoside (31)

Compound **30** (385 mg, 0.11 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 **31** as an amorphous solid (175 mg, 81%): $[\alpha]_D$ +56.7 (*c* 1.0, H_2O); ^1H NMR (D_2O, 400 MHz): δ 7.06 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.91 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 4.94 (m, 2H, 2H-1), 4.74 (d, H, $J_{1,2}$ 8.0 Hz, 2H-1), 4.64 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.55 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.39 (d, 1H, $J_{1,2}$ 7.2 Hz, H-1), 4.37 (d, 1H, $J_{1,2}$ 7.2 Hz, H-1); ^{13}C NMR (100 MHz, D_2O):δ 104.4, 104.3, 103.8, 103.4, 103.4, 100.3, 101.4 (7C, C-1). MALDI-TOFMS Calcd for $C_{49}H_{78}O_{37}$: 1259.11 [M]. Found: 1259.6 [M].

3.25. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*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)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (32)

Compounds **15** (409 mg, 0.16 mmol) and **28** (200 mg, 0.13 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give octasaccharide **32** (410 g, 79%) as a syrup: $[\alpha]_D$ +83.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.02–7.21 (m, 125H, 25Ph*H*), 6.84 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.60 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 5.99 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.91 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.89 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.86 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.82 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.77 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.68 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.67 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.65–5.63 (m, 2H), 5.61 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.59 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.57–5.51 (m, 3H), 5.49 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.46 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.43 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.40 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.37 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.27 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.21 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 4.77 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.72 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.70 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.65 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6,6}$ 11.2 Hz, H-6), 4.55 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.52 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.46 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.32 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.29 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.68 (s, 3H, C*H*$_3$O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 165.9, 165.9, 165.8, 165.8, 165.6, 165.6, 165.5, 165.5, 165.5, 165.4, 165.4, 165.4, 165.3, 165.3, 165.2, 165.1, 165.1, 165,0, 165.0, 164.9, 164.9, 164.8, 164.4, 164.4 (25C, 25*C*OPh), 101.4, 101.0, 101.0, 101.9, 101.9, 100.7, 100.5, 100.0 (8C, C-1). Anal. Calcd for $C_{230}H_{188}O_{67}$: C, 68.65; H, 4.71. Found: C, 68.91; H, 4.68.

3.26. 4-Methoxyphenyl β-D-galactopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl]-β-D-galactopyranosyl-(1→3)-β-D-galactopyranoside (33)

Compound **32** (385 mg, 0.096 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 **33** as an amorphous solid (135 mg, 84%): $[\alpha]_D$ +71.3 (*c* 1.0, H_2O); ^1H NMR (D_2O, 400 MHz): δ 6.97 (d, 2H, *J* 9.1 Hz, CH_3O-C_6H_4O–), 6.84 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 4.90 (m, 2H, 2H-1), 4.77 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.68 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.59 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.48 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.35 (m, 2H, 2H-1); ^{13}C NMR (100 MHz, D_2O):δ 104.0, 103.8, 103.6, 103.2, 103.1, 103.1, 101.2, 101.1 (8C, 8C-1). MALDI-TOFMS Calcd for $C_{55}H_{88}O_{42}$: 1421.25 [M]. Found: 1421.4 [M].

3.27. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*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)-2,3,4-tri-*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]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (34)

Compounds **17** (434 mg, 0.14 mmol) and **28** (200 mg, 0.116 mmol) in dry CH_2Cl_2 (20 mL) were coupled by the same procedure as described in the preparation of **3** to give nonasaccharide **34** (453 mg, 78%) as a syrup: $[\alpha]_D$ +81.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 Hz, $CDCl_3$): δ 8.01–7.21 (m, 140H, 28Ph*H*), 6.84 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.61 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.05 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.91 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.85–5.83 (m, 3H), 5.82 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.78 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.73 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.71 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.69 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.67–5.61 (m, 3H), 5.59 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.54 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.52–5.49 (m, 4H), 5.46 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.44 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.42 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.37 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.27 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.21 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 4.77 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.72 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.62 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.55 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.46 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.36–4.34 (m, 2H, H-1), 4.30 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.27 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.67 (s, 3H, C*H*$_3$O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 166.9,

166.7, 166.6, 166.5, 166.5, 166.1, 166.0, 165.0, 165.9, 165.9, 165.8, 165.7, 165.7, 165.6, 165.6, 165.5, 165.4, 165.4, 165.3, 165.3, 165.2, 165.1, 165.1, 165.0, 164.4, 164.3, 164.0 (28C, 28*C*OPh), 101.3, 101.2, 101.2, 101.1, 101.0, 100.9, 100.6, 100.4, 100.3 (9C, C-1). Anal. Calcd for $C_{257}H_{210}O_{75}$: C, 68.62; H, 4.70. Found: C, 68.55; H, 4.81.

3.28. 4-Methoxyphenyl β-D-galactopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl]-β-D-galactopyranosyl-(1→3)-β-D-galactopyranoside (35)

Compound **34** (400 mg, 0.089 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 **35** as an amorphous solid (114 mg, 81%): $[\alpha]_D$ +62.1 (*c* 1.0, H_2O); ^{1}H NMR (D_2O, 400 MHz): δ 7.00 (d, 2H, *J* 9.1 Hz, CH_3O-C_6H_4O–), 6.91 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 4.92 (m, 2H, 2H-1), 4.80 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.64 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.57 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.46 (d, 2H, $J_{1,2}$ 7.2 Hz, 2H-1), 4.38 (d, H, $J_{1,2}$ 8.0 Hz, H-1), 4.35 (d, H, $J_{1,2}$ 8.0 Hz, H-1); ^{13}C NMR (100 MHz, D_2O):δ 104.2, 104.0, 103.7, 103.2, 103.2, 103.2, 101.2, 102.2, 101.1 (9C, 9C-1). MALDI-TOF MS Calcd for $C_{61}H_{98}O_{47}$: 1583.39 [M]. Found: 1583.2 [M].

3.29. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*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)-2,3,4-tri-*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)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (36)

Compounds **19** (278 mg, 0.077 mmol) and **28** (100 mg, 0.065 mmol) in dry CH_2Cl_2 (50 mL) were coupled by the same procedure as described in the preparation of **3** to give decasaccharide **36** (234 mg, 73%) as a syrup: $[\alpha]_D$ +52.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$): δ 7.79–7.23 (m, 155H, 31Ph*H*), 6.84 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.61 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.04 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.93 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.87 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.85–5.83 (m, 4H), 5.80 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.77 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 5.63 (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), 5.60–5.58 (m, 3H), 5.53 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.50 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.48–5.46 (m, 4H), 5.43 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.41 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.39 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 5.38–5.35 (m, 2H), 5.34 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.28 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.4 Hz, H-2), 5.20 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.4 Hz, H-3), 4.78 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.73 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.63–4.61 (m, 2H, H-1), 4.43 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.41 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.35 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.33–4.30 (m, 2H, 2H-1), 4.27 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.67 (s, 3H, CH_3O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 167.3, 167.2, 167.0, 167.0, 167.9, 166.8, 166.8, 166.7, 166.6, 166.3, 166.0, 166.0, 165.9, 165.8, 165.8, 165.7, 165.6, 165.6, 165.5, 165.5, 165.4, 165.3, 165.3, 165.2, 165.2, 165.1, 165.0, 164.9, 164.7, 164.3 (31C, 31*C*OPh), 101.4, 101.3, 101.1, 101.1, 101.0, 100.9, 100.7, 100.7, 100.3, 100.1 (10C, C-1). Anal. Calcd for $C_{284}H_{232}O_{83}$: C, 68.59; H, 4.70. Found: C, 68.42; H, 4.93.

3.30. 4-Methoxyphenyl β-D-galactopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl]-β-D-galactopyranosyl-(1→3)-β-D-galactopyranoside (37)

Compound **36** (234 mg, 0.047 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 **37** as an amorphous solid (74 mg, 90%): $[\alpha]_D$ +43.7 (*c* 1.0, H_2O); ^{1}H NMR (D_2O, 400 MHz): δ 7.98 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 6.82 (d, 2H, *J* 9.1 Hz, $CH_3OC_6H_4O$–), 4.90 (m, 2H, 2H-1), 4.85 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.68 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.59 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.48 (d, 2H, $J_{1,2}$ 7.2 Hz, 2H-1), 4.41 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.36 (m, 2H, 2H-1); ^{13}C NMR (100 MHz, D_2O):δ 104.6, 104.5, 104.2, 103.8, 103.3, 100.3, 103.2, 103.1, 101.3, 101.2 (10C, 10C-1). MALDI-TOF MS Calcd for $C_{67}H_{108}O_{52}$: 1745.53 [M]. Found: 1745.3 [M].

Acknowledgements

This work was supported by The National Natural Science Foundation of China (Projects 30070185 and 39970864).

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