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Synthesis of tetra- and hexasaccharide fragments corresponding to the *O*-antigenic polysaccharide of *Klebsiella pneumoniae*

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ABSTRACT

The preparation of linear tetra- (**1**) and hexasaccharides (**2**), containing the repeating unit [→3)-β-Gal*f*-(1→3)-α-Gal*p*-(1→] present in the *O*-polysaccharide of the lipopolysaccharide of *Klebsiella pneumoniae* is described. The key step in their synthesis is the α-selective galactopyranosylation of 3-OH di- and tetrasaccharide acceptors (**20** and **22**) with a disaccharide trichloroacetimidate donor **19** in the presence of trimethylsilyl triflate in a diethyl ether–CH_2Cl_2 mixture as solvent.

1. Introduction

Pathogenic Gram-negative bacteria are a major public health concern because they are the causative agents of several life-threatening diseases. Of particular importance to us is *Klebsiella pneumoniae*, which is responsible for several infections, including pneumonia, bacteremia, and urinary tract infections with high incidence and mortality.[1] Previous work has shown that two-surface carbohydrate components of *K. pneumoniae*, its capsular polysaccharide (CPS), and the *O*-antigen portion of its lipopolysaccharide (LPS), are important virulence determinants.[2] The *O*-antigens of *K. pneumoniae* represent a family of molecules composed of repeating carbohydrate subunits linked to the core region of LPS. In the case of serotype O1, one of the most clinically prevalent serotypes, *O*-antigenic glycan is built up from two disaccharide repeating units, D-galactan I [→3)-β-Gal*f*-(1→3)-α-Gal*p*-(1→] and D-galactan II [→3)-β-Gal*p*-(1→3)-α-Gal*p*-(1→].[3] D-Galactan II forms the distal end of the *O* chains. D-Galactan I disaccharide motif is also found in other *K. pneumoniae* serotypes, e.g., O2a and O2a,c. In view of developing potential anti-*K. pneumoniae* vaccines and studying structure–bioactivity relationship of carbohydrates, synthetic studies on these antigenic *O*-polysaccharides are of considerable interests.[4] Herein, we report efficient synthesis of tetra- (**1**) and hexasaccharides (**2**) as their *p*-methoxyphenyl glycosides (Scheme 1), which represent two and three consecutive D-galactan I motifs from the *O*-chain of *K. pneumoniae*.

2. Results and discussion

According to our retrosynthetic analysis (Scheme 1), disaccharide block **3**, a properly functionalized form of D-galactan I is a key precursor for the construction of **1** and **2**. First, it can be easily switched to a disaccharyl trichloroacetimidate donor after removal of the *p*-methoxyphenyl (PMP) aglycon. Second, the site of the chain elongation can be liberated by a minimal protecting group manipulation only involving selective removal of the *O*-levulinoyl (Lev) group. Third, a nonparticipating substituent, *O*-benzyl group was incorporated at C-2 of the galactopyranose unit to facilitate the construction of the challenging α-galactopyranosyl linkages. Compound **3** would be synthesized through the coupling of *p*-methylphenyl (Tol) thioglycoside donor **4** with 3-OH acceptor **5**. So far, several examples for the synthesis of D-galactan I derivatives have been found in the literature. Both the Marino group[5] and Ning group[6] applied a similar indirect method, i.e., the formation of a β-(1→3)-linked digalactofuranose framework followed by the conversion of the reducing-end Gal*f* unit into the expected Gal*p* moiety. This disaccharide structure was also prepared by the Kim[7] and Hanashima[8] groups employing a 2′-carboxybenzyl (CB) galactofuranoside and a thioglycoside methodology, respectively, to be used as a building block for the synthesis of glycosphingolipid agelagalastatin and ganglioside AG2 pentasaccharide.

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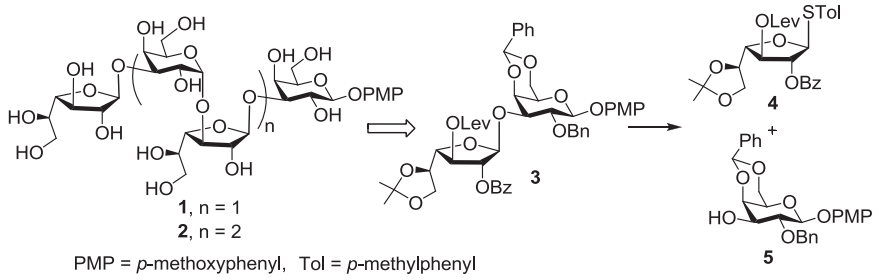
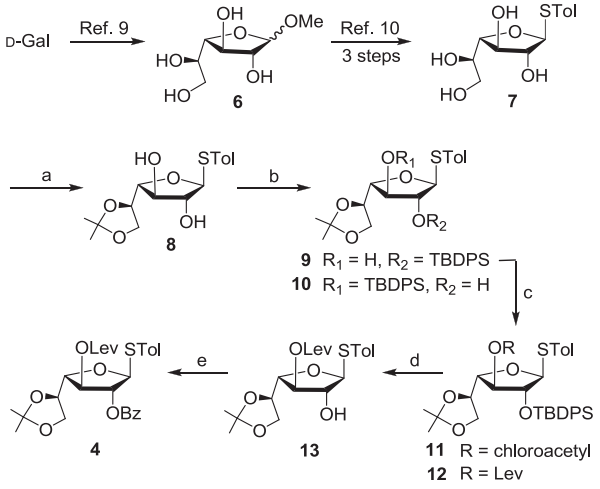


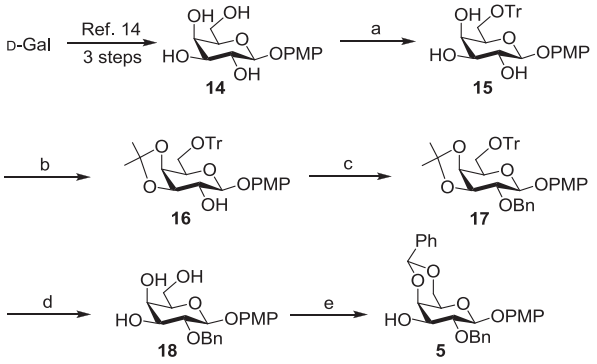
Scheme 1. Chemical structures and retrosynthetic analysis of the target oligosaccharides (**1** and **2**).

Scheme 2 displays the preparation of the galactofuranose derivative **4**. Reaction of D-galactose with methanol following the protocol of Lubineau et al.[9] gave an α/β mixture of methyl D-galactofuranosides (**6**). This mixture, either purified or crude, was next converted to the known *p*-methylphenylthio β-D-galactofuranoside (**7**).[10] Subsequent 5,6-*O*-acetonide protection of **7** provided diol **8** (88%),[11] which underwent a regioselective monosilylation reaction with 1.2 equiv of *tert*-butyldiphenylsilyl chloride (TBDPSCl) to afford 2-*O*- and 3-*O*-TBDPS ethers **9** and **10** as a chromatographically separable mixture (**9**/**10**, ca. 5:1).[7,12] The major product, **9**, was then acylated conventionally with excess chloroacetyl chloride or levulinic acid (LevOH) to give chloroacetate **11** and levulinate **12** in 80% and quantitative yields, respectively. However, treatment of **11** with *n*-tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) failed to reveal the expected O-desilylation product. Instead, simultaneous cleavage of the TBDPS and the chloroacetyl groups was observed by TLC analysis. Gratifyingly, exposure of the Lev-protected counterpart **12** at 0–10 °C to TBAF proved to be feasible and thus furnished the corresponding alcohol **13** in 86% yield. Finally, installation of a benzoyl group, which is required to ensure neighboring group participation[13] in later glycosylation at the 2-position of **13** finished the preparation of the thioglycoside **4**.



Scheme 2. Synthesis of the galactofuranose thioglycoside donor **4**. Reagents and conditions: (a) acetone, $CuSO_4$, H_2SO_4, 88%; (b) TBDPSCl, imidazole, DMAP, CH_2Cl_2, for **9**: 60%, for **10**: 12%; (c) for **11**: chloroacetyl chloride, py, CH_2Cl_2, 80% from **9**, for **12**: LevOH, DCC, DMAP, CH_2Cl_2, quant. yield from **9**; (d) TBAF, THF, 0→10 °C, 3 h, 86% from **12**; (e) BzCl, py, 85%.

The synthesis of galactopyranose building block **5**, began with the known *p*-methoxyphenyl β-D-galactopyranoside (**14**), which is readily available from D-galactose by published procedures (Scheme 3).[14] Selective substitution of the primary C6 OH in **14** with a trityl (Tr) group easily provided **15**[15] in very good yield. Triol **15** was then protected with 2,2-dimethoxypropane to form the acetonide **16** (85%), whose O-benzylation of the remaining C2 OH afforded an excellent yield of **17**. Further elaboration of the resultant **17** to **5** involved (i) release of 3,4,6-tri-OHs in acidic medium to 2-*O*-benzyl intermediate **18**,[16] and (ii) 4,6-*O*-benzylidene acetal formation of **18** with $PhCH(OMe)_2$ in dimethyl formamide (DMF) to the requisite product.



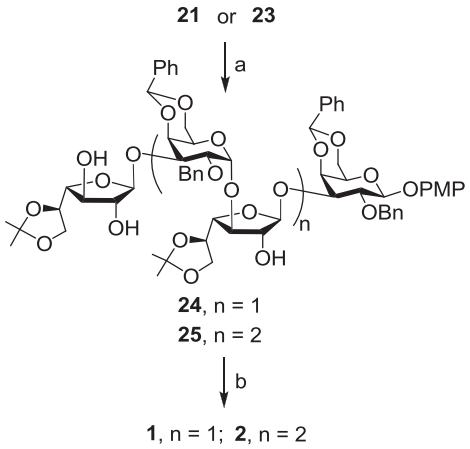
Scheme 3. Synthesis of the galactopyranose acceptor **5**. Reagents and conditions: (a) TrCl, pyridine, 68 °C, 98%; (b) $Me_2C(OMe)_2$, acetone, *p*-TsOH (cat.), 85%; (c) BnBr, NaH, DMF–THF, 0 °C→rt, 98%; (d) H_2SO_4, MeOH, 82%; (e) $PhCH(OMe)_2$, *p*-TsOH, DMF, 60 °C, 80%.

The coupling of the D-galactofuranosyl donor **4** with the D-galactopyranosyl acceptor **5** in the presence of *N*-iodosuccinimide (NIS)–anhydrous silver triflate (AgOTf) promoter system generated solely the β-linked disaccharide **3** in 88% yield (Scheme 3). In the ^1H NMR spectrum of **3**, the anomeric proton of the D-galactofuranose ring appeared as a singlet at δ_H 5.44 ppm, indicating a trans relationship for H-1 and H-2 and hence a β configuration.[17] Furthermore, the ^{13}C NMR spectrum of **3** showed the resonance at δ_C 103.1 ppm for C-1 β-furanosidic center, also characteristic of the β-Gal*f* linkage.[18] Oxidative cleavage of the *p*-methoxyphenyl (PMP) group at the anomeric carbon of **3** using ceric ammonium nitrate (CAN) in aqueous acetonitrile at 0 °C yielded an intermediate hemiacetal. It is worth noting that temperature is critical to this CAN-mediated oxidation process, as higher temperatures (e.g., 25 °C) led to undesired cleavage of both the PMP and the isopropylidene moieties. Activation of the obtained crude hemiacetal for glycoside formation was performed by treatment with trichloroacetonitrile (CCl_3CN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), thereby giving the trichloroacetimidate **19** as a single diastereomer (88%, two steps from **3**). However, imidate **19** could not be isolated pure because it suffered from minor degradation during chromatographic purification on a silica gel support. In parallel, after delevulinoylation of **3** using hydrazine monoacetate (N_2H_4·HOAc) at ambient temperature, disaccharide alcohol acceptor **20** was obtained in nearly quantitative yield. The benzoate ester bond of **3** was stable under these mild hydrolysis conditions. The ^1H NMR of **20** clearly indicated an upfield shift of the H-3′

signal from δ_H 5.12 ppm in the ^{1}H NMR spectrum of compound **3** to δ_H 4.09 ppm caused by removal of the Lev substituent at this position.

With the useful disaccharide glycosylating agents **19** and **20** in hand, we went on with the assembly of the target protected tetra- and hexasaccharides. Schmidt's glycosylation[19] of the glycosyl imidate **19** with the acceptor **20** activated by a catalytic amount of trimethylsilyl triflate (TMSOTf) in a mixed solvent system of diethyl ether–dichloromethane (v/v, 6:1) at −78 °C produced the desired α-galactopyranosyl tetrasaccharide **21** in an excellent isolated yield of 92%. Remarkably, no β-tetrasaccharide was detected at all in the reaction mixture. The α-stereochemistry at the newly generated anomeric center of **21** could be easily established on the basis of its ^{1}H and ^{13}C NMR spectral data, especially of the observed H1′–H2′ coupling constant ($J_{H1'-H2'}$=3.6 Hz) and the anomeric carbon shift at δ_C 99.7 ppm of the α-galactopyranose ring. Then, the synthesis of the higher hexasaccharide was proceeding. Selective removal of the Lev protection on the non-reducing terminal galactofuranosyl residue of **21** again with N_2H_4·HOAc exposed the site of chain extension and yielded tetrasaccharide nucleophile **22** almost in quantitative yield. Finally, through the same trichloroacetimidate glycosylation method described above, substrate **22** was efficiently condensed with the key disaccharyl donor **19** to deliver the corresponding hexasaccharide adduct **23** in an equally excellent yield (94%) and with complete α-stereoselectivity ($J_{H1'-H2'}$=3.2 Hz and δ_C 99.5 ppm of the newly formed α-galactopyranosidic linkage).

Global deprotection of **21** and **23** was not entirely straightforward (Schemes 4 and 5). Methanolysis of **21** and **23** under Zemplén conditions[20] cleanly cleaved the benzoate and levulinoylate ester functionalities, giving alcohols **24** and **25**, respectively, as foams in excellent yields. Our next attempts for extensive removal of all the *O*-isopropylidene and *O*-benzylidene acetals and the benzylic protecting groups present in **24** by employing acidic hydrogenolysis conditions (e.g., H_2, Pd–C, 10% HCl–MeOH), led to a complex mixture of products as a result of cleavage of the interglycosidic linkages. We therefore turned to an alternative two-step deprotection approach. Thus, milder acidic hydrolysis of **24** (20% CF_3CO_2H in CH_2Cl_2) followed by catalytic hydrogenation of the formed tetrasaccharide alcohol (H_2, Pd–C, MeOH) secured successfully the desired free *p*-methoxyphenyl glycoside **1** in a satisfactory 74% yield for two steps, with the isopropylidene ketals, the benzylidene acetals, and the benzyl ethers being cleaved. Likewise, the homologue of **1**, the hexasaccharide substance **2**, was obtained readily from the corresponding precursor **25** by means of a similar



Scheme 5. Deprotection and completion of synthesis of **1** and **2**. Reagents and conditions: (a) NaOMe, MeOH, CH_2Cl_2, rt, 1 d, for **24**: 90% from **21**, for **25**: 98% from **23**; (b) (i) CF_3CO_2H, CH_2Cl_2, rt; (ii) H_2 (40 atm), 10% Pd–C, MeOH, 45 °C, 20 h, for **1**: 74%, two steps from **24**, for **2**: 76%, two steps from **25**.

deprotection sequence (Scheme 3). The target molecules **1** and **2** were carefully purified by gel filtration chromatography, and their NMR and HR ESIMS data are in agreement with the desired structures as homogeneous entity. Full characterizations are provided in Supplementary data.

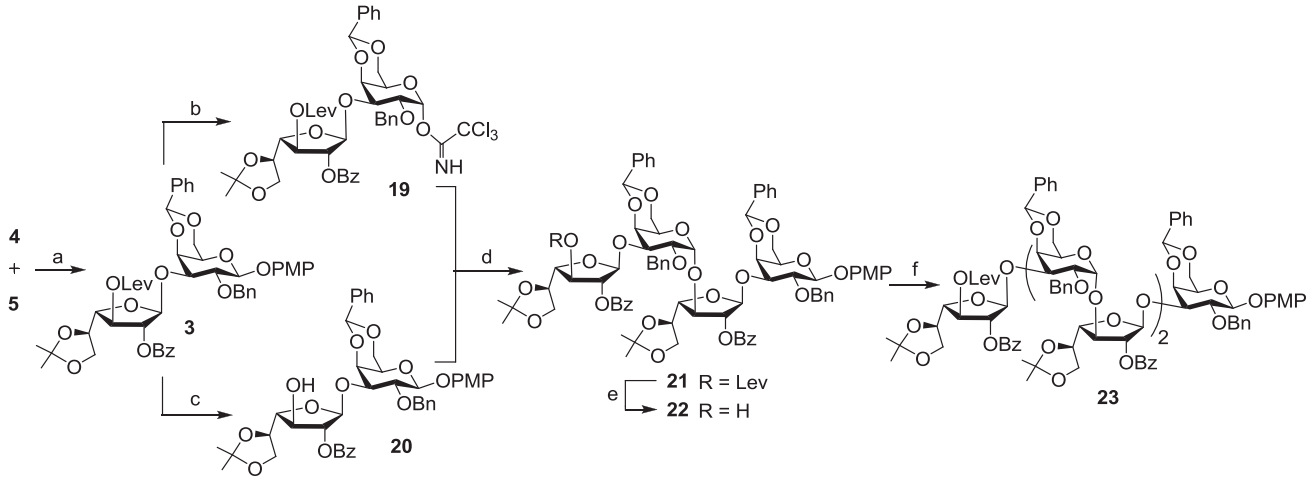
3. Conclusion

We have carried out the high-yielding synthesis of the oligosaccharides **1** and **2** structurally related to the repeating unit D-galactan I found in the *O*-antigens of *K. pneumoniae*. The combined use of the 2-*O*-Bn ether equipped trichloroacetimidate **19** as donor and a mixture of diethyl ether–CH_2Cl_2 as solvent realized the completely stereoselective creation of the challenging 1,2-*cis* galactopyranosidic bonds.

4. Experimental section

4.1. General methods

All non-aqueous reactions were performed under a nitrogen atmosphere and monitored by thin layer chromatography (TLC) using Silica Gel GF_{254} plates with detection by charring with 10% (v/



Scheme 4. Synthesis of protected tetra- and hexasaccharides (**21** and **23**). Reagents and conditions: (a) NIS, AgOTf, 4 Å molecular sieves, CH_2Cl_2, −40→−20 °C, 88%; (b) (i) $Ce(NH_4)_2(NO_3)_6$, MeCN, H_2O, 0 °C, 1 h; (ii) CCl_3CN, DBU, CH_2Cl_2, 0 °C→rt, 88%, two steps; (c) N_2H_4·HOAc, CH_2Cl_2, MeOH, rt, 98%; (d) TMSOTf, −78→0 °C, 4 Å molecular sieves, Et_2O–CH_2Cl_2=6:1, 2 h, 92%; (e) N_2H_4·HOAc, CH_2Cl_2, MeOH, 98%; (f) **19**, TMSOTf, −78→0 °C, 4 Å molecular sieves, Et_2O–CH_2Cl_2=6:1, 2 h, 94%.

v) H_2SO_4 in EtOH or by UV detection. Solvents used in the reactions were distilled from appropriate drying agents prior to use. Silica gel (200–300 mesh) was used for column chromatography. Optical rotations were measured with a PE-314 automatic polarimeter at 20±1 °C for solutions in a 1.0 dm cell. HR ESIMS spectra were acquired on Agilent 6210 TOF LC/MS instrument. ^{1}H and ^{13}C NMR spectra were obtained on Bruker AC-E 200 or Varian INOVA-400/54 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal reference. Chemical shifts (δ) are expressed in parts per million downfield from the internal TMS absorption. Standard splitting patterns are abbreviated: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). *J* values are given in hertz.

4.2. *p*-Tolyl 5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (8)

To a solution of **7** (5.5 g, 19.2 mmol) in acetone (340 mL) were added $CuSO_4$ (684 mg, 4.29 mmol) and H_2SO_4 (6 mL). The reaction mixture was stirred for 1 d at room temperature. Then it was neutralized with triethylamine and filtered. The combined filtrates were concentrated in vacuo to give a residue, which was purified by column chromatography (1:1, petroleum ether–EtOAc) to afford compound **8** as a colorless syrup (5.52 g, 88%). R_f 0.40 (1:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ −138.02 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, 2H, *J*=8.0 Hz), 7.15 (d, 2H, *J*=8.0 Hz), 5.47 (s, 1H, H-1), 4.38 (t, 1H, *J*=7.2 Hz), 4.22 (d, 1H, *J*=7.2 Hz), 4.17 (d, 1H, *J*=6.8 Hz), 4.10–4.07 (m, 2H), 4.01 (t, 1H, *J*=8.0 Hz), 2.78 (d, 1H, *J*=8.0 Hz), 2.35 (s, 3H), 1.63 (d, 1H, *J*=8.0 Hz), 1.40 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 21.1, 25.6 (2C), 65.5, 75.7, 79.3, 80.9, 84.5, 93.5 (C-1), 110.1, 129.9 (2C), 132.6 (2C), 136.9, 138.0; HR ESIMS: calcd for $C_{16}H_{22}O_5S$ $[M+Na]^+$ 349.1086, found *m*/*z* 349.1090.

4.3. *p*-Tolyl 2-*O*-*tert*-butyldiphenylsilyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (9) and *p*-tolyl 3-*O*-*tert*-butyldiphenylsilyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (10)

To a mixture of **8** (2.52 g, 7.73 mmol), imidazole (1.05 g, 15.46 mmol), and DMAP (280 mg, 2.32 mmol) in CH_2Cl_2 (41.8 mL) at 0 °C was added TBDPSCl (2.18 mL, 9.28 mmol) dropwise. After being stirred at room temperature for overnight, the reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (2×30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by silica gel flash column chromatography (15:1, petroleum ether–EtOAc) to afford compound **9** (2.62 g, 4.64 mmol, 60%) and compound **10** (524 mg, 0.93 mmol, 12%).

*4.3.1. Compound **9**.* Colorless syrup. R_f 0.55 (3:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ −43.08 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.68 (m, 4H), 7.51–7.40 (m, 6H), 7.26 (d, 2H, *J*=8.0 Hz), 7.08 (d, 2H, *J*=8.0 Hz), 5.35 (d, 1H, *J*=2.4 Hz, H-1), 4.34 (dd, 1H, *J*=5.2, 10.4 Hz), 4.23 (t, 1H, *J*=2.8 Hz), 4.04–4.01 (m, 3H), 3.98 (dd, 1H, *J*=6.8, 8.4 Hz), 2.33 (s, 3H), 1.75 (d, 1H, *J*=5.6 Hz), 1.46 (s, 3H), 1.40 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 19.1, 21.2, 25.3, 26.5, 26.9 (2C), 27.0, 65.4, 75.4, 79.1, 83.87, 83.9, 92.9 (C-1), 109.7, 128.0 (2C), 128.1 (2C), 129.7 (2C), 130.1, 130.2, 132.6, 132.9 (2C), 133.2, 135.8 (2C), 135.9 (2C), 136.2, 137.8; HR ESIMS: calcd for $C_{32}H_{40}O_5SiS$ $[M+Na]^+$ 587.2264, found *m*/*z* 587.2259.

*4.3.2. Compound **10**.* Colorless syrup. R_f 0.65 (3:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ −104.67 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.70 (m, 4H), 7.51–7.41 (m, 8H), 7.16 (d, 2H, *J*=7.6 Hz), 5.52 (s, 1H, H-1), 4.40 (d, 1H, *J*=11.2 Hz), 4.24 (s, 1H), 4.12 (s, 1H), 4.00 (d, 1H, *J*=11.6 Hz), 3.86 (t, 1H, *J*=8.0 Hz), 3.77 (t, 1H, *J*=8.0 Hz), 3.33 (t, 1H, *J*=7.6 Hz), 2.36 (s, 3H), 1.33 (s, 3H), 1.26 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 19.2, 21.1, 25.5, 25.7, 26.85 (2C), 26.9, 65.5, 75.2, 80.3, 81.9, 85.0, 96.2 (C-1), 109.7, 127.96 (2C), 128.0 (2C), 129.7 (2C), 130.16, 130.2, 131.3 (2C), 132.8, 133.1, 133.5, 135.8 (2C), 136.1 (2C), 136.8; HR ESIMS: calcd for $C_{32}H_{40}O_5SiS$ $[M+Na]^+$ 587.2264, found *m*/*z* 587.2258.

4.4. *p*-Tolyl 2-*O*-*tert*-butyldiphenylsilyl-3-*O*-chloroacetyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (11)

To a solution of **9** (256 mg, 0.45 mmol) in pyridine–CH_2Cl_2 (1:10, v/v, 4.4 mL) was added chloroacetyl chloride (72.1 μL, 0.91 mmol) at 0 °C. The mixture was stirred for 5 h at room temperature, and then was quenched with ice water and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were washed with water (10 mL×3) and brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (15:1, petroleum ether–EtOAc) to afford compound **11** as a colorless syrup (233 mg, 80%). R_f 0.50 (7:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ −23.08 (*c* 0.98, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.61 (m, 4H), 7.48–7.37 (m, 6H), 7.17, 7.04 (each 2H, *J*=8.0 Hz), 5.29 (d, 1H, *J*=2.8 Hz, H-1), 5.18 (dd, 1H, *J*=2.4, 4.0 Hz), 4.44 (dd, 1H, *J*=2.4, 11.6 Hz), 4.30 (t, 1H, *J*=2.4 Hz), 4.13 (t, 1H, *J*=4.4 Hz), 4.03 (dd, 1H, *J*=6.4, 8.4 Hz), 3.96 (dd, 1H, *J*=6.4, 8.4 Hz), 3.87 (d, 1H, *J*=15.2 Hz), 3.87 (d, 1H, *J*=12.0 Hz), 2.31 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H), 1.08 (m, 9H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 19.0, 21.1, 25.2, 26.3, 26.8 (3C), 40.5, 65.5, 75.2, 81.3, 81.5, 82.4, 93.7 (C-1), 109.9, 127.8 (2C), 127.9 (2C), 129.6 (2C), 129.9, 130.1, 130.12, 132.4, 132.5, 132.7 (2C), 135.9 (2C), 135.94 (2C), 137.7, 166.3; HR ESIMS: calcd for $C_{34}H_{41}O_8SiSCl$ $[M+Na]^+$ 663.1980, found *m*/*z* 663.1991.

4.5. *p*-Tolyl 2-*O*-*tert*-butyldiphenylsilyl-3-*O*-levulinoyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (12)

To a solution of **9** (227 mg, 0.4 mmol) in CH_2Cl_2 (3.6 mL) were added DCC (580 mg, 2.82 mmol), DMAP (9.8 mg, 0.08 mmol), and levulinic acid (93.24 mg, 0.8 mmol). The reaction mixture was stirred for 3 h at room temperature. Then it was filtered and the filtrate was concentrated in vacuo to give a residue, which was purified by column chromatography (5:1, petroleum ether–EtOAc) to afford compound **12** as a colorless syrup (266 mg, quant.). R_f 0.40 (3:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ −47.06 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.67 (m, 4H), 7.36–7.47 (m, 6H), 7.16 (d, 2H, *J*=8.0 Hz), 7.04 (d, 2H, *J*=8.0 Hz), 5.26 (d, 1H, *J*=2.4 Hz, H-1), 5.10 (dd, 1H, *J*=2.4, 3.6 Hz), 4.44 (dd, 1H, *J*=6.4, 12.4 Hz), 4.32 (t, 1H, *J*=2.4 Hz), 4.12 (dd, 1H, *J*=4.0, 5.6 Hz), 4.04 (dd, 1H, *J*=6.8, 8.4 Hz), 3.95 (dd, 1H, *J*=6.8, 8.4 Hz), 2.69–2.64 (m, 2H), 2.45–2.42 (m, 1H), 2.36–2.32 (m, 1H), 2.31 (s, 3H), 2.16 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 19.0, 21.0, 25.2, 26.3, 26.7 (3C), 27.7, 29.7, 37.7, 65.6, 75.5, 79.8, 81.5, 83.1, 94.0 (C-1), 109.7, 127.7 (2C), 127.8 (2C), 129.5 (2C), 129.9, 130.0, 130.2, 132.45, 132.5, 132.6 (2C), 135.78 (2C), 135.83 (2C), 139.4, 171.4, 206.0; HR ESIMS: calcd for $C_{37}H_{46}O_7SiS$ $[M+Na]^+$ 685.2632, found *m*/*z* 685.2617.

4.6. *p*-Tolyl 3-*O*-levulinoyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (13)

To a solution of **12** (510 mg, 0.77 mmol) in THF (6.6 mL) was added TBAF (0.46 mL, 1.0 M in THF, 0.46 mmol) dropwise at 0 °C and the resulting mixture was stirred for 3 h at the same temperature. After the solvent was removed under reduced pressure, the crude material was dissolved with CH_2Cl_2 (20 mL). The resulting organic solution was washed with saturated aqueous NH_4Cl (10 mL×3) and brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (4:1, petroleum ether–EtOAc) to afford compound **13** as a colorless

syrup (281 mg, 86%). R_f 0.50 (2:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ −141.84 (*c* 1.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39, 7.13 (each 2H, *J*=8.4 Hz), 5.47 (s, 1H, H-1), 4.99 (d, 1H, *J*=2.0 Hz), 4.48 (dt, 1H, *J*=1.6, 7.6 Hz), 4.28–4.26 (m, 2H), 4.18 (d, 1H, *J*=10.4 Hz), 4.08 (d, 1H, *J*=6.8 Hz), 3.99 (t, 1H, *J*=8.0 Hz), 2.85–2.80 (m, 2H), 2.63 (t, 2H, *J*=6.4 Hz), 2.33 (s, 3H), 2.20 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 21.0, 25.4, 25.6, 27.9, 29.6, 37.8, 65.3, 75.4, 79.3, 80.7, 81.9, 95.1 (C-1), 109.9, 129.7 (2C), 130.9, 132.0 (2C), 137.4, 172.2, 206.4; HR ESIMS: calcd for $C_{21}H_{28}O_7S$ $[M+Na]^+$ 447.1454, found *m*/*z* 447.1444.

4.7. *p*-Tolyl 2-*O*-benzoyl-3-*O*-levulinoyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (4)

To a solution of **13** (347 mg, 0.82 mmol) in pyridine (5.78 mL) was added BzCl (189 μL, 1.64 mmol) dropwise at 0 °C. The mixture was stirred for 5 h at room temperature, and then was quenched with ice water and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts were washed with water (10 mL×3) and brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (8:1, petroleum ether–EtOAc) to afford compound **4** as a colorless syrup (367 mg, 85%). R_f 0.50 (3:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ −88.1 (*c* 1.27, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, 2H, *J*=7.2 Hz), 7.60 (t, 1H, *J*=7.2 Hz), 7.46–7.42 (m, 4H), 7.14 (d, 2H, *J*=8.0 Hz), 5.62 (d, 1H, *J*=2.0 Hz, H-1), 5.46 (d, 1H, *J*=2.0 Hz), 5.33 (dd, 1H, *J*=1.6, 4.8 Hz), 4.46 (dt, 1H, *J*=4.8, 11.2 Hz), 4.37 (t, 1H, *J*=4.4 Hz), 4.09 (dd, 1H, *J*=6.8, 8.8 Hz), 3.96 (dd, 1H, *J*=6.8, 8.8 Hz), 2.88–2.75 (m, 2H), 2.73–2.58 (m, 2H), 2.33 (s, 3H), 2.20 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 21.1, 25.3, 26.2, 27.9, 29.7, 37.8, 65.5, 75.1, 77.7, 81.8, 82.2, 91.4 (C-1), 109.8, 128.4 (2C), 129.0, 129.5, 129.8 (2C), 129.84 (2C), 133.0 (2C), 133.5, 138.1, 165.2, 171.8, 206.2; HR ESIMS: calcd for $C_{28}H_{32}O_8S$ $[M+Na]^+$ 551.1716, found *m*/*z* 551.1702.

4.8. *p*-Methoxyphenyl 6-*O*-trityl-β-D-galactopyranoside (15)

To a solution of **14** (888 mg, 3.1 mmol) in pyridine (20 mL) was added TrCl (1.30 g, 4.7 mmol). The mixture was stirred for 1 d at 60 °C. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (1:1, petroleum ether–EtOAc) to afford compound **15** as a white solid (1.61 g, 98%). R_f 0.50 (9:1, CH_2Cl_2–CH_3OH). $[\alpha]_D^{20}$ −23.33 (*c* 1.08, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, 6H, *J*=7.6 Hz), 7.24 (t, 6H, *J*=7.6 Hz), 7.20 (s, 1H), 7.19 (s, 1H), 7.17 (s, 1H), 7.07, 6.74 (each 2H, *J*=8.8 Hz), 4.69 (d, 1H, *J*=7.6 Hz, H-1), 3.91 (t, 1H, *J*=8.8 Hz), 3.85–3.80 (m, 3H), 3.70 (s, 3H), 3.59 (t, 1H, *J*=4.0 Hz), 3.52 (s, 1H), 3.49 (d, 1H, *J*=6.0 Hz), 3.27 (d, 1H, *J*=8.4 Hz), 3.07 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 55.5, 63.0, 69.3, 71.2, 73.5, 74.0, 86.9, 102.3 (C-1), 114.4 (2C), 118.6 (2C), 127.1 (3C), 127.9 (6C), 128.6 (6C), 143.6 (3C), 151.1, 155.3; HR ESIMS: calcd for $C_{32}H_{32}O_7$ $[M+Na]^+$ 551.2046, found *m*/*z* 551.2035.

4.9. *p*-Methoxyphenyl 3,4-*O*-isopropylidene-6-*O*-trityl-β-D-galactopyranoside (16)

To a solution of **15** (2.0 g, 3.79 mmol) in acetone (41.0 mL) were added *p*-TsOH (65 mg, 0.53 mmol) and $Me_2C(OMe)_2$ (1.16 mL, 9.47 mmol). The reaction mixture was stirred at room temperature for 8 h. After the solvent was removed under reduced pressure, the resulting residue was purified by column chromatography (3:1, petroleum ether–EtOAc) to afford **16** as a white solid (1.83 g, 85%). R_f 0.53 (1:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ −13.33 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, 6H, *J*=8.0 Hz), 7.34 (t, 6H, *J*=7.6 Hz), 7.29 (s, 1H), 7.28 (s, 1H), 7.26 (s, 1H), 7.18, 6.86 (each 2H, *J*=8.8 Hz), 4.69 (d, 1H, *J*=8.0 Hz, H-1), 4.18–4.13 (m, 2H), 3.88–3.84 (m, 2H), 3.77 (s, 3H), 3.71 (dd, 1H, *J*=7.6, 10.0 Hz), 3.44 (dd, 1H, *J*=4.0, 10.0 Hz), 3.14 (d, 1H, *J*=2.8 Hz), 1.55 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 26.4, 28.2, 55.6, 63.0, 73.0, 73.4, 73.8, 79.0, 86.8, 101.9 (C-1), 110.4, 114.5 (2C), 118.7 (2C), 127.1 (3C), 127.9 (6C), 128.8 (6C), 143.9 (3C), 151.3, 155.4; HR ESIMS: calcd for $C_{35}H_{36}O_7$ $[M+Na]^+$ 591.2359, found *m*/*z* 591.2345.

4.10. *p*-Methoxyphenyl 2-*O*-benzyl-3,4-*O*-isopropylidene-6-*O*-trityl-β-D-galactopyranoside (17)

A mixture of **16** (1.36 g, 2.39 mmol) and NaH (458 mg, 19.1 mmol) in DMF–THF (1:1, v/v, 18.0 mL) was stirred for 30 min at 0 °C. Then to the mixture was added BnBr (566.7 μl, 4.78 mmol) at the same temperature. After being stirred at room temperature for 4 h, the reaction was quenched with ice water (20 mL) and extracted with EtOAc (2×30 mL). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by silica gel flash column chromatography (5:1, petroleum ether–EtOAc) to afford the title compound **17** as white solid (1.54 g, 0.43 mmol, 98%). R_f 0.55 (3:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ +18.25 (*c* 1.26, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, 6H, *J*=8.0 Hz), 7.54 (d, 2H, *J*=7.2 Hz), 7.44–7.29 (m, 12H), 7.24, 6.91 (each 2H, *J*=8.8 Hz), 5.06 (d, 1H, *J*=11.2 Hz), 5.00 (d, 1H, *J*=11.2 Hz), 4.88 (d, 1H, *J*=8.0 Hz, H-1), 4.30 (dd, 1H, *J*=6.0, 6.4 Hz), 4.16 (dd, 1H, *J*=1.6, 5.2 Hz), 3.86 (dd, 1H, *J*=2.0, 2.4 Hz), 3.81 (s, 3H), 3.77 (d, 1H, *J*=8.4 Hz), 3.75 (d, 1H, *J*=7.2 Hz), 3.48 (dd, 1H, *J*=4.0, 10.0 Hz), 1.47 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 26.5, 27.9, 55.6, 63.1, 72.7, 73.8, 73.9, 79.3, 79.5, 86.9, 102.2 (C-1), 110.2, 114.5 (2C), 118.6 (2C), 127.1 (3C), 127.7, 127.9 (6C), 128.3 (2C), 128.4 (2C), 128.8 (6C), 138.3, 144.0 (3C), 151.6, 155.3; HR ESIMS: calcd for $C_{42}H_{42}O_7$ $[M+Na]^+$ 691.2829, found *m*/*z* 691.2815.

4.11. *p*-Methoxyphenyl 2-*O*-benzyl-β-D-galactopyranoside (18)

To a solution of **17** (1.7 g, 0.98 mmol) in CH_3OH (25.5 mL) was added slowly H_2SO_4 (1.13 mL) and the resulting mixture was stirred for 3 h at room temperature. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (1:1, petroleum ether–EtOAc) to afford compound **18** as a white solid (797 mg, 82%). R_f 0.50 (8:1, CH_2Cl_2–CH_3OH). $[\alpha]_D^{20}$ −8.8 (*c* 1.58, CH_3OH); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.31 (m, 5H), 7.03, 6.86 (each 2H, *J*=8.8 Hz), 5.08 (d, 1H, *J*=11.2 Hz), 4.93 (d, 1H, *J*=8.0 Hz, H-1), 4.79 (d, 1H, *J*=11.2 Hz), 4.05 (s, 1H), 4.01 (dd, 1H, *J*=5.6, 11.6 Hz), 3.90–3.84 (m, 1H), 3.81–3.77 (m, 1H), 3.79 (s, 3H), 3.71–3.67 (m, 1H), 3.65 (t, 1H, *J*=5.2 Hz), 2.80 (s, 1H), 2.59 (d, 1H, *J*=3.6 Hz), 2.21 (dd, 1H, *J*=4.8, 8.0 Hz); ^{13}C NMR (100 Hz, DMSO): δ 55.6, 60.5, 68.6, 73.0, 74.0, 75.5, 79.4, 102.0 (C-1), 114.7 (2C), 117.6 (2C), 127.4, 127.8 (2C), 128.2 (2C), 139.4, 151.6, 154.5; HR ESIMS: calcd for $C_{20}H_{24}O_7$ $[M+Na]^+$ 399.1420, found *m*/*z* 399.1411.

4.12. *p*-Methoxyphenyl 2-*O*-benzyl-5,6-*O*-benzylidene-β-D-galactopyranoside (5)

To a solution of **18** (1.72 g, 4.58 mmol) in DMF (24.0 mL) were added *p*-TsOH (118 mg, 0.69 mmol) and $PhCH(OMe)_2$ (1.37 mL, 9.16 mmol). After being stirred for overnight at 60 °C, the reaction mixture was poured into petroleum ether–ice water (1:1, v/v, 200 mL), and the suspension was filtered to afford **5** as a white solid (1.7 g, 80%). R_f 0.50 (50:1, CH_2Cl_2–CH_3OH). $[\alpha]_D^{20}$ −9.8 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.55–7.53 (m, 2H), 7.40–7.26 (m, 8H), 7.07, 6.84 (each 2H, *J*=9.2 Hz), 5.58 (s, 1H), 5.07 (d, 1H, *J*=11.2 Hz), 4.90 (d, 1H, *J*=7.6 Hz, H-1), 4.83 (d, 1H, *J*=11.2 Hz), 4.37 (d, 1H, *J*=12.4 Hz), 4.26 (d, 1H, *J*=1.6 Hz), 4.10 (d, 1H, *J*=12.0 Hz), 3.90 (d, 1H, *J*=7.6 Hz), 3.88 (d, 1H, *J*=7.6 Hz), 3.78 (s, 3H), 3.53 (s, 1H), 2.57 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 55.6, 66.6, 69.1, 72.4, 75.1, 75.3, 79.0, 101.4, 103.0 (C-1), 114.5 (2C), 118.8 (2C), 126.5 (2C), 127.8, 128.1

(2C), 128.3 (2C), 128.4 (2C), 129.3, 137.5, 138.4, 151.5, 155.4; HR ESIMS: calcd for $C_{27}H_{28}O_7$ $[M+Na]^+$ 487.1733, found *m*/*z* 487.1734.

4.13. *p*-Methoxyphenyl 2-*O*-benzoyl-3-*O*-levulinoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-β-D-galactopyranoside (3)

A mixture of donor **4** (311 mg, 0.59 mmol), acceptor **5** (228 mg, 0.49 mmol), and 4 Å molecular sieves (780 mg) in CH_2Cl_2 (12.0 mL) was stirred for 10 min at room temperature and cooled to −40 °C. To the resulting mixture were added NIS (199 mg, 0.74 mmol) and AgOTf (37.8 mg, 0.12 mmol). The reaction mixture was allowed to warm to −20 °C and stirred for 1 h at the same temperature, quenched with triethylamine, and filtered. The combined filtrates were concentrated in vacuo to give a residue, which was purified by column chromatography (2:1, petroleum ether−EtOAc) to afford **3** as a pale yellow syrup (375 mg, 88%). R_f 0.55 (1:1, petroleum ether−EtOAc). $[\alpha]_D^{20}$ −4.38 (*c* 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 2H, *J*=7.6 Hz), 7.59 (d, 2H, *J*=7.6 Hz), 7.47 (t, 3H, *J*=7.6 Hz), 7.41−7.35 (m, 5H), 7.24−7.18 (m, 3H), 7.16, 7.06 (each 2H, *J*=8.0 Hz), 5.59 (s, 1H), 5.53 (s, 1H), 5.44 (s, 1H, H-1_A), 5.12 (d, 1H, *J*=4.8 Hz), 4.97 (d, 1H, *J*=10.8 Hz), 4.91 (d, 1H, *J*=8.0 Hz, H-1_B), 4.81 (d, 1H, *J*=11.2 Hz), 4.41 (d, 1H, *J*=3.6 Hz), 4.38 (d, 1H, *J*=6.0 Hz), 4.35 (d, 1H, *J*=6.8 Hz), 4.27 (t, 1H, *J*=6.8 Hz), 4.13−4.04 (m, 3H), 3.91 (dd, 1H, *J*=3.6, 9.6 Hz), 3.84 (dd, 1H, *J*=6.8, 8.4 Hz), 3.78 (s, 3H), 3.53 (s, 1H), 2.67−2.61 (m, 1H), 2.48−2.34 (m, 3H), 2.08 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 25.3, 26.5, 27.7, 29.7, 37.6, 55.6, 65.6, 66.4, 69.0, 75.4, 75.8, 76.1, 77.3, 77.4, 78.6, 81.5, 83.5, 101.2, 103.1 (C-1_B), 107.7 (C-1_A), 110.0, 114.4 (2C), 118.9 (2C), 126.4 (2C), 127.6, 128.1 (2C), 128.2 (2C), 128.3 (2C), 128.4 (2C), 129.01, 129.03, 129.8 (2C), 133.5, 137.9, 138.3, 151.5, 155.3, 164.9, 171.8, 206.2; HR ESIMS: calcd for $C_{48}H_{52}O_{15}$ $[M+Na]^+$ 891.3204, found *m*/*z* 891.3188.

4.14. 2-*O*-Benzoyl-3-*O*-levulinoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*- benzylidene-α-D-galactopyranosyl trichloroacetimidate (19)

To a solution of **3** (130 mg, 0.15 mmol) in CH_3CN−H_2O (4:1, v/v, 5.0 mL) was added CAN (244 mg, 0.45 mmol) at 0 °C. The mixture was stirred for 1 h at the same temperature, and then was quenched with aqueous $NaHCO_3$ and extracted with EtOAc (10 mL×3). The combined organic extracts was washed with water (10 mL×2), aqueous $NaHCO_3$ (10 mL×3) and brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated. The obtained residue was purified by column chromatography (2:1, petroleum ether−EtOAc) to afford the desired lactol as a pale yellow syrup, which was directly used for the next step. To a solution of the obtained lactol (111 mg, 0.15 mmol) in CH_2Cl_2 (3.0 mL) were added CCl_3CN (73 μL, 0.73 mmol) and DBU (one drop) at 0 °C. The mixture was stirred for 4 h during which time it was gradually warmed to ambient temperature, and then concentrated to give a residue. Purification by column chromatography (3:1, petroleum ether−EtOAc) afforded **19** as a colorless syrup (119 mg, 88% over two steps) that contained a minor impurity. R_f 0.50 (2.5:1, petroleum ether−EtOAc). $[\alpha]_D^{20}$ +37.11 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.00 (d, 2H, *J*=7.6 Hz), 7.60−7.53 (m, 3H), 7.45−7.29 (m, 7H), 7.25 (t, 2H, *J*=7.6 Hz), 7.18 (d, 1H, *J*=7.2 Hz), 6.61 (d, 1H, *J*=3.2 Hz, H-1_B), 5.57 (s, 1H), 5.56 (s, 1H), 5.42 (s, 1H, H-1_A), 5.10 (d, 1H, *J*=4.4 Hz), 4.79 (d, 1H, *J*=12.0 Hz), 4.73 (d, 1H, *J*=12.0 Hz), 4.54 (d, 1H, *J*=2.8 Hz), 4.38−4.25 (m, 4H), 4.21 (dd, 1H, *J*=3.6, 10.0 Hz), 4.10−4.04 (m, 2H), 3.95 (s, 1H), 3.83 (t, 1H, *J*=7.6 Hz), 2.70−2.62 (m, 1H), 2.51−2.40 (m, 3H), 2.08 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 25.2, 26.5, 27.7, 29.6, 37.6, 64.7, 65.6, 69.0, 73.2, 74.0, 75.2, 75.8, 77.3 (2C), 81.5, 83.5, 91.5, 95.4 (C-1_B), 100.9, 107.6 (C-1_A), 109.9, 126.2 (2C), 127.4, 127.5 (2C), 128.1 (2C), 128.2 (2C), 128.4 (2C), 129.0, 129.8 (2C), 130.6, 133.4, 137.7, 138.1, 161.1, 164.9, 171.8, 206.1. Attempts to further purify this compound for HRMS analysis were unsuccessful.

4.15. *p*-Methoxyphenyl 2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-β-D-galactopyranoside (20)

To a solution of **3** (65 mg, 0.075 mmol) in CH_3OH−CH_2Cl_2 (1:1, v/v, 2.0 mL) was added hydrazine acetate (14 mg, 0.15 mmol). The mixture was stirred for overnight at room temperature, and then was quenched with aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic extracts was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (2:1, petroleum ether−EtOAc) to afford compound **20** as a colorless syrup (57 mg, 98%). R_f 0.55 (1:1, petroleum ether−EtOAc). $[\alpha]_D^{20}$ −23.9 (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, 2H, *J*=7.6 Hz), 7.63−7.55 (m, 3H), 7.48−7.36 (m, 7H), 7.29−7.16 (m, 3H), 7.08, 6.84 (each 2H, *J*=8.8 Hz), 5.60 (s, 1H), 5.59 (s, 1H), 5.19 (d, 1H, *J*=1.2 Hz, H-1_A), 4.98 (d, 1H, *J*=10.8 Hz), 4.91 (d, 1H, *J*=8.0 Hz, H-1_B), 4.81 (d, 1H, *J*=10.8 Hz), 4.43 (d, 1H, *J*=3.2 Hz), 4.39 (d, 1H, *J*=12.0 Hz), 4.24 (dd, 1H, *J*=6.4, 14.4 Hz), 4.16−4.07 (m, 3H), 4.01 (d, 1H, *J*=8.0 Hz), 3.94 (d, 1H, *J*=3.6 Hz), 3.91−3.87 (m, 2H), 3.78 (s, 3H), 3.55 (s, 1H), 3.53 (d, 1H, *J*=8.0 Hz), 1.47 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 25.3, 26.7, 55.6, 65.6, 66.3, 69.0, 75.4, 75.9, 76.4, 77.3 (2C), 78.4, 84.3, 86.4, 101.3, 103.0 (C-1_B), 107.2 (C-1_A), 110.0, 114.4 (2C), 118.9 (2C), 126.3 (2C), 127.7, 128.1 (2C), 128.2 (2C), 128.3 (2C), 128.6 (2C), 128.8, 129.1, 129.8 (2C), 133.7, 137.4, 138.3, 151.5, 155.3, 166.0; HR ESIMS: calcd for $C_{43}H_{46}O_{13}$ $[M+Na]^+$ 793.2836, found *m*/*z* 793.2830.

4.16. *p*-Methoxyphenyl 2-*O*-benzoyl-3-*O*-levulinoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-β-D-galactopyranoside (21)

A mixture of donor **19** (101 mg, 0.11 mmol), acceptor **20** (43 mg, 0.055 mmol), and 4 Å molecular sieves (150 mg) in Et_2O−CH_2Cl_2 (6:1, v/v, 2.0 mL) was stirred for 10 min at room temperature and cooled to −78 °C. To the resulting mixture was added a solution of TMSOTf (4.04 μL, 0.01 mmol) in CH_2Cl_2 (0.5 mL) and stirred at −78 °C for 1 h. The reaction mixture was allowed to warm to 0 °C over 1 h, then quenched with triethylamine and filtered. The combined filtrates were concentrated in vacuo to give a residue, which was purified by column chromatography (3:1, petroleum ether−EtOAc) to afford **21** as a colorless syrup (79 mg, 92%). R_f 0.50 (1.5:1, petroleum ether−EtOAc). $[\alpha]_D^{20}$ +17.2 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 2H, *J*=7.6 Hz), 7.99 (d, 2H, *J*=7.6 Hz), 7.61−7.57 (m, 4H), 7.48−7.09 (m, 22H), 7.08, 6.84 (each 2H, *J*=8.8 Hz), 5.68 (s, 1H), 5.58 (s, 1H), 5.51 (s, 1H), 5.49 (s, 1H), 5.41 (s, 1H, H-1_A), 5.20 (s, 1H, H-1_C), 5.16 (d, 1H, *J*=3.6 Hz, H-1_B), 5.14 (d, 1H, *J*=4.8 Hz), 4.96 (d, 1H, *J*=10.8 Hz), 4.91 (d, 1H, *J*=7.6 Hz, H-1_D), 4.83 (d, 2H, *J*=10.8 Hz), 4.62 (d, 1H, *J*=12.0 Hz), 4.40−4.24 (m, 5H), 4.19 (dd, 1H, *J*=6.8, 13.2 Hz), 4.11−3.99 (m, 6H), 3.973−.80 (m, 7H), 3.78 (s, 3H), 3.60 (d, 1H, *J*=12.4 Hz), 3.52 (s, 1H), 2.69−2.62 (m, 1H), 2.51−2.540 (m, 3H), 2.08 (s, 3H), 1.43 (s, 6H), 1.40 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 25.3 (2C), 26.5, 26.54, 27.7, 29.7, 37.6, 55.6, 63.0, 65.6, 65.7, 66.4, 69.0, 69.04, 73.8, 75.0, 75.3, 75.5, 75.8, 75.9, 76.2, 76.23, 77.3, 77.9, 78.0, 81.1, 81.5, 82.9, 83.4, 85.4, 99.7, 100.4, 101.3 (C-1_B), 103.2 (C-1_D), 107.3 (C-1_C), 108.1 (C-1_A), 110.0 (2C), 114.4 (2C), 118.9 (2C), 126.2 (2C), 126.7 (2C), 127.6, 127.7, 128.0 (2C), 128.1 (2C), 128.2 (4C), 128.3 (2C), 128.4 (2C), 128.5 (4C), 128.8, 129.1, 129.2, 129.3, 129.8 (2C), 129.9 (2C), 133.47, 133.5, 138.0, 138.1,

138.14, 138.4, 151.6, 155.3, 164.95, 165.0, 171.9, 206.1; HR ESIMS: calcd for $C_{84}H_{90}O_{26}$ $[M+Na]^+$ 1537.5618, found *m*/*z* 1537.5632.

4.17. *p*-Methoxyphenyl 2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-β-D-galactopyranoside (22)

Compound **22** was obtained as a colorless syrup from **21** (83 mg, 0.055 mmol) as described for the preparation of **20**, yielding 76 mg (98%). R_f 0.51 (1.5:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ +6.9 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 4H, *J*=8.0 Hz), 7.65–7.58 (m, 4H), 7.47–7.16 (m, 20H), 7.12–7.08 (m, 2H), 7.09, 6.84 (each 2H, *J*=8.8 Hz), 5.67 (d, 1H, *J*=1.6 Hz), 5.60 (s, 2H), 5.53 (s, 1H), 5.21 (d, 1H, *J*=4.0 Hz, H-1_B), 5.20 (s, 1H, H-1_A), 5.11 (s, 1H, H-1_C), 4.98 (d, 1H, *J*=10.8 Hz), 4.92 (d, 1H, *J*=7.6 Hz, H-1_D), 4.82 (d, 1H, *J*=10.8 Hz), 4.75 (d, 1H, *J*=11.6 Hz), 4.59 (d, 1H, *J*=11.6 Hz), 4.35–4.05 (m, 10H), 3.99 (d, 1H, *J*=3.6 Hz), 3.94–3.86 (m, 8H), 3.81 (s, 1H), 3.78 (s, 3H), 3.56 (d, 1H, *J*=8.4 Hz), 3.54 (s, 1H), 3.48 (d, 1H, *J*=11.6 Hz), 1.45 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 25.3 (2C), 26.5, 26.7, 55.6, 62.7, 65.5, 65.9, 66.4, 68.89, 68.92, 73.7, 74.5, 75.2, 75.4, 75.9, 75.94, 76.1, 76.5, 77.1, 77.7, 77.9, 80.8, 83.3, 83.7, 85.3, 86.8, 99.1, 100.4, 101.3 (C-1_B), 103.2 (C-1_D), 106.7 (C-1_C), 108.1 (C-1_A), 110.0, 110.1, 114.4 (2C), 118.9 (2C), 126.0 (2C), 126.9 (2C), 127.6, 127.7, 127.8 (2C), 128.1 (2C), 128.2 (5C), 128.3 (2C), 128.4 (2C), 128.5 (2C), 128.6 (2C), 128.9, 129.1, 129.4, 129.8 (4C), 133.5, 133.7, 138.6, 138.0, 138.2 (2C), 151.6, 155.3, 164.9, 165.9; HR ESIMS: calcd for $C_{79}H_{84}O_{24}$ $[M+Na]^+$ 1439.5251, found *m*/*z* 1439.5231.

4.18. *p*-Methoxyphenyl 2-*O*-benzoyl-3-*O*-levulinoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)–2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-β-D-galactopyranoside (23)

Compound **23** was obtained as a colorless syrup from **19** (85 mg, 0.06 mmol) and **22** (109 mg, 0.12 mmol) as described for the preparation of **21**, yielding 122 mg (94%). R_f 0.55 (1:1, petroleum ether–EtOAc). $[\alpha]_D^{20}$ +18.53 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 2H, *J*=8.0 Hz), 7.99 (s, 2H), 7.97 (s, 2H), 7.62–7.58 (m, 5H), 7.48–7.07 (m, 34H), 7.09, 6.85 (each 2H, *J*=9.2 Hz), 5.69 (d, 1H, *J*=2.4 Hz), 5.67 (d, 1H, *J*=1.6 Hz), 5.58 (s, 1H), 5.51 (s, 2H), 5.48 (s, 1H), 5.42 (s, 1H, H-1_A), 5.19 (s, 1H, H-1_C), 5.17 (s, 1H, H-1_E), 5.17 (d, 1H, *J*=3.6 Hz, H-1_B), 5.15 (d, 1H, *J*=3.2 Hz, H-1_D), 5.14 (d, 1H, *J*=4.8 Hz), 4.96 (d, 1H, *J*=10.4 Hz), 4.91 (d, 1H, *J*=8.0 Hz, H-1_F), 4.83 (d, 2H, *J*=10.4 Hz), 4.81 (d, 1H, *J*=10.8 Hz), 4.78 (d, 1H, *J*=10.8 Hz), 4.61 (d, 1H, *J*=11.6 Hz), 4.57 (d, 1H, *J*=11.6 Hz), 4.39 (dd, 1H, *J*=6.8, 13.2 Hz), 4.34–4.328 (m, 4H), 4.25–4.21 (m, 2H), 4.16 (dd, 1H, *J*=6.8, 13.2 Hz), 4.12–4.04 (m, 5H), 3.99–3.90 (m, 8H), 3.89–3.83 (m, 6H), 3.79 (s, 5H), 3.55 (s, 1H), 3.53 (s, 1H), 3.52 (s, 1H), 2.66–2.63 (m, 1H), 2.50–2.40 (m, 3H), 2.09 (s, 3H), 1.43 (s, 9H), 1.41 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 25.3 (3C), 26.5 (3C), 27.7, 29.7, 37.6, 55.6, 63.0, 63.1, 65.5, 65.6, 66.4, 68.9 (2C), 73.7 (2C), 73.8 (2C), 74.9 (2C), 75.2, 75.4, 75.5, 75.7 (2C), 75.8 (2C), 76.1, 76.2, 76.3, 77.9 (2C), 81.0, 81.2, 81.5, 82.7, 82.9, 83.3, 85.1, 85.3, 99.5 (2C), 100.4, 100.7 (C-1_D), 101.3 (C-1_B), 103.2 (C-1_F), 107.2 (C-1_E), 107.8 (C-1_C), 108.1 (C-1_A), 109.9 (3C), 114.4 (2C), 118.9 (2C), 126.1 (4C), 126.5 (2C), 126.8 (2C), 127.55, 127.58, 127.6, 127.8 (2C), 127.9 (2C), 128.0 (2C), 128.2 (6C), 128.25 (2C), 128.3 (2C), 128.35 (2C), 128.44 (6C), 128.8, 129.09, 129.11, 129.16, 129.2, 129.4, 129.8 (4C), 129.9 (2C), 133.4, 138.0, 138.05, 138.1, 138.13, 138.2, 138.3, 151.6, 155.3, 164.9, 165.0 (2C), 171.9, 206.0; HR ESIMS: calcd for $C_{120}H_{128}O_{37}$ $[M+Na]^+$ 2183.8032, found *m*/*z* 2183.7996.

4.19. *p*-Methoxyphenyl 5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-β-D-galactopyranoside (24)

To a solution of **21** (96 mg, 0.06 mmol) in CH_2Cl_2–CH_3OH (1:10, v/v, 3.0 mL) was added $NaOCH_3$ (29 mg, 0.54 mmol) at 0 °C. After being stirred for overnight at room temperature, the reaction was quenched with acetic acid and the resulting mixture was concentrated to dryness. The crude material was purified by column chromatography (1:1, petroleum ether–EtOAc) to afford compound **24** as a white foam (70.5 mg, 92%). R_f 0.45 (EtOAc). $[\alpha]_D^{20}$ +5.61 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.58 (m, 2H), 7.44–7.26 (m, 18H), 7.10, 6.85 (each 2H, *J*=8.8 Hz), 5.54 (s, 1H), 5.39 (s, 1H), 5.32 (s, 1H, H-1_A), 4.99 (s, 1H, H-1_C), 4.99 (d, 1H, *J*=12.4 Hz), 4.95 (d, 1H, *J*=4.4 Hz, H-1_B), 4.94 (d, 1H, *J*=8.0 Hz, H-1_D), 4.77 (d, 1H, *J*=10.4 Hz), 4.71 (d, 1H, *J*=12.0 Hz), 4.52 (d, 1H, *J*=12.0 Hz), 4.39 (t, 1H, *J*=6.8 Hz), 4.34 (s, 1H), 4.32 (d, 1H, *J*=5.2 Hz), 4.26 (d, 1H, *J*=2.8 Hz), 4.21 (d, 1H, *J*=4.8 Hz), 4.18 (d, 1H, *J*=3.2 Hz), 4.15 (d, 1H, *J*=7.2 Hz), 4.10 (s, 1H), 4.07 (s, 1H), 4.04 (s, 1H), 4.02–3.93 (m, 8H), 3.90 (s, 1H), 3.87 (d, 1H, *J*=2.8 Hz), 3.83 (s, 1H), 3.79 (s, 3H), 3.74 (s, 2H), 3.54 (s, 1H), 3.51 (d, 2H, *J*=12.4 Hz), 3.06 (d, 1H, *J*=8.4 Hz), 1.46 (s, 3H), 1.41 (s, 6H), 1.39 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 25.5, 25.6, 25.7, 26.1, 55.6, 62.6, 65.6, 65.8, 66.4, 68.9, 69.0, 73.7, 73.8, 75.2, 75.3, 75.6, 75.7, 76.2, 76.4, 77.3, 77.6, 78.1, 78.4, 78.6, 81.9, 86.7, 88.4, 99.2, 100.4, 101.4 (C-1_B), 103.4 (C-1_D), 109.4, 109.3, 110.4 (C-1_A), 110.8 (C-1_C), 114.5 (2C), 119.0 (2C), 125.9 (2C), 127.0 (2C), 127.6, 128.9 (2C), 128.1, 128.2 (2C), 128.35 (2C), 128.4 (2C), 128.5 (2C), 128.6 (2C), 129.0, 129.6, 137.3, 138.1 (2C), 138.3, 151.5, 155.4; HR ESIMS: calcd for $C_{65}H_{76}O_{22}$ $[M+Na]^+$ 1231.4726, found *m*/*z* 1231.4711.

4.20. *p*-Methoxyphenyl β-D-galactofuranosyl-(1→3)-α-D-galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-β-D-galactopyranoside (1)

To a solution of **24** (42 mg, 0.035 mmol) in CH_2Cl_2 (2.4 mL) was added TFA (0.6 mL) and the resulting mixture was stirred for 7 h at room temperature. After the solvent was removed under reduced pressure, the obtained residue was dissolved in CH_3OH (3.0 mL). To the solution was added 10% Pd/C (45 mg) and the reaction mixture was stirred under a hydrogen atmosphere of 40 atm for 20 h at 45 °C. The reaction mixture was filtered and the filtrate was concentrated in vacuo to give a residue, which was purified by column chromatography on Sephadex LH-20 (CH_3OH) to afford compound **1** as a white foam (20 mg, 74% over two steps). R_f 0.70 (1:1, CH_3OH–H_2O, RP-18 plate). $[\alpha]_D^{20}$ −12.83 (*c* 1.2, CH_3OH); ^{1}H NMR (400 MHz, D_2O): δ 7.16, 7.01 (each 2H, *J*=8.8 Hz), 5.29 (s, 1H, H-1_C), 5.22 (s, 1H, H-1_A), 5.11 (s, 1H, H-1_B), 5.04 (d, 1H, *J*=7.2 Hz, H-1_D), 4.48 (s, 1H), 4.30 (t, 1H, *J*=4.8 Hz), 4.21–4.18 (m, 4H), 4.14–4.07 (m, 3H), 3.98 (s, 2H), 3.89–3.85 (m, 4H), 3.83 (s, 3H), 3.79–3.64 (m, 9H); ^{13}C NMR (100 Hz, D_2O): δ 58.0, 62.9, 63.4, 64.86, 64.9, 69.5, 70.6, 71.5, 71.9, 72.9 (2C), 73.4, 77.5, 79.0, 79.2, 81.9, 82.4, 83.7, 84.1, 84.9, 86.6, 101.7 (C-1_B), 103.7 (C-1_D), 111.3 (C-1_A), 111.7 (C-1_C), 117.2 (2C), 120.4 (2C), 153.1, 156.9; HR ESIMS: calcd for $C_{31}H_{48}O_{22}$ $[M+Na]^+$ 795.2535, found *m*/*z* 795.2548.

4.21. *p*-Methoxyphenyl 5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-2-*O*-benzyl-5,6-*O*-benzylidene-β-D-galactopyranoside (25)

Compound **25** was obtained as a white solid from **23** (65 mg, 0.03 mmol) as described for the preparation of **24**, yielding 49 mg (94%). R_f 0.50 (1:10, petroleum ether–EtOAc). $[\alpha]_D^{20}$ +4.88 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 2H, *J*=7.2 Hz), 7.59–7.51 (m, 3H), 7.40–7.27 (m, 25H), 7.11, 6.86 (each 2H, *J*=8.8 Hz), 5.57 (s, 1H),

5.54 (s, 1H), 5.43 (s, 1H), 5.37 (s, 1H, H-1_A), 5.03 (d, 1H, J=2.8 Hz, H-1_C), 4.98 (s, 1H, H-1_E), 4.96 (d, 1H, J=4.0 Hz, H-1_B), 4.95 (d, 1H, J=8.0 Hz, H-1_F), 4.93 (d, 1H, J=3.6 Hz, H-1_D), 4.80 (d, 1H, J=12.4 Hz), 4.77 (d, 1H, J=10.4 Hz), 4.70 (d, 1H, J=12.0 Hz), 4.68 (d, 1H, J=11.6 Hz), 4.53 (d, 1H, J=12.0 Hz), 4.51 (d, 1H, J=11.6 Hz), 4.46–4.41 (m, 2H), 4.34–4.18 (m, 8H), 4.12–3.95 (m, 12H), 3.92 (d, 1H, J=2.8 Hz), 3.89 (d, 2H, J=2.8 Hz), 3.86 (s, 2H), 3.83 (d, 2H, J=3.2 Hz), 3.79 (s, 3H), 3.76 (d, 2H, J=2.4 Hz), 3.73 (d, 2H, J=3.6 Hz), 3.54 (d, 2H, J=12.8 Hz), 3.43 (d, 1H, J=12.8 Hz), 3.39 (d, 1H, J=2.8 Hz), 3.35 (s, 1H), 3.28 (d, 1H, J=9.6 Hz), 3.04 (d, 1H, J=7.6 Hz), 1.47 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H), 1.41 (s, 3H), 1.39 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 25.3, 25.5, 25.65, 25.7, 25.9, 26.2, 55.6, 62.5, 63.0, 65.59, 65.63, 65.8, 66.4, 68.8, 68.9, 73.2, 73.4, 73.7, 74.0, 75.1, 75.3, 75.6, 75.7, 76.0, 76.2, 76.23, 76.4, 76.5, 76.9, 77.5, 78.1, 78.2, 78.5, 78.6, 82.3, 82.6, 85.6, 86.7, 88.0, 88.5, 99.2 (2C), 100.3, 100.8 (C-1_D), 101.5 (C-1_B), 103.4 (C-1_F), 109.6, 110.0 (2C), 110.3 (C-1_A), 110.5 (C-1_E), 110.9 (C-1_C), 114.5 (2C), 119.0 (2C), 125.8 (2C), 126.7 (2C), 127.4 (2C), 127.9 (5C), 128.1 (2C), 128.2 (2C), 128.4 (4C), 128.45 (2C), 128.5 (2C), 128.6 (2C), 128.7 (2C), 129.1, 129.5, 129.7, 137.3, 138.0, 138.1, 138.11, 138.4, 138.5, 151.5, 155.4; HR ESIMS: calcd for $C_{94}H_{110}O_{32}$ $[M+Na]^+$ 1773.6878, found m/z 1773.6864.

4.22. *p*-Methoxyphenyl β-D-galactofuranosyl-(1→3)-α-D-galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-α-D-galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-β-D-galactopyranoside (2)

Compound **2** was obtained as a white foam from **25** (55 mg, 0.032 mmol) as described for the preparation of **1**, yielding 26 mg (76% over two steps). R_f 0.55 (1:2, CH_3OH–H_2O, RP-18 plate). $[\alpha]_D^{20}$ −11.6 (*c* 0.8, CH_3OH); ^{1}H NMR (400 MHz, D_2O): δ 7.11, 6.96 (each 2H, J=8.8 Hz), 5.24 (s, 1H, H-1_C), 5.20 (s, 1H, H-1_E), 5.15 (s, 1H, H-1_A), 5.06 (s, 2H, H-1_B, H-1_D), 5.00 (d, 1H, J=7.2 Hz, H-1_F), 4.43 (s, 1H), 4.40 (s, 1H), 4.28–4.21 (m, 2H), 4.15–4.12 (m, 6H), 4.05–4.01 (m, 4H), 3.92 (s, 4H), 3.85–3.80 (m, 6H), 3.78 (s, 3H), 3.76–3.70 (m, 6H), 3.69–3.62 (m, 6H); ^{13}C NMR (100 Hz, D_2O): δ 58.2, 63.1, 63.5 (2C), 65.0 (2C), 65.1 (2C), 69.5, 69.6, 70.8, 71.6, 71.7, 72.1, 73.3 (2C), 73.6, 73.7, 77.4, 77.6, 79.2, 79.4, 79.42, 82.1, 82.6, 83.8, 84.2, 84.3, 85.1, 86.8 (2C), 101.8 (C-1_D), 101.9 (C-1_B), 103.9 (C-1_F), 111.5 (C-1_A), 111.77 (C-1_E), 111.8 (C-1_C), 117.4 (2C), 120.6 (2C), 153.3, 157.1; HR ESIMS: calcd for $C_{43}H_{68}O_{32}$ $[M+Na]^+$ 1119.3592, found m/z 1119.3573.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.03.074. These data include MOL files and InChiKeys of the most important compounds described in this article.

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