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Synthesis of 3,6-branched arabinogalactan-type tetra- and hexasaccharides for characterization of monoclonal antibodies

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Dedicated to Professor Johannis P. Kamerling on the occasion of his 65th birthday

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ABSTRACT

Synthesis of tetra- and hexasaccharides built up from a β-(1→6)-linked galactopyranosyl backbone with arabinofuranosyl side chains at position 3 and with a 3-aminopropyl spacer related to arabinogalactans is described. These oligosaccharides were prepared for investigation of monoclonal antibodies raised against arabinogalactan proteins (AGPs) from pressed juice of *Echinacea purpurea*.

1. Introduction

In the last few decades considerable interest has been focussed upon the molecular nature and architecture of plant cell walls. Plant cell-wall polysaccharides play an important role in cell–cell interactions (cell differentiation, growth and development). They are involved in the interactions of plants with other organisms and the environment. The use of monoclonal antibodies is one of the most important tools for plant cell-wall analysis.[1] Arabinogalactan-proteins (AGPs) are a class of plant proteoglycans present in most plant tissues and exudates. They are antigenic and can produce monoclonal antibodies that are useful for detecting the occurrence of a well-defined saccharide sequence in AGPs.[2]

The AGPs that are components of the high-molecular-weight fraction of the pressed juice of *Echinacea purpurea* (the purple coneflower) have been shown to possess complement-stimulating activity in vitro, and the carbohydrate portion of these proteoglycans consists of mainly 3-, 6- and 3,6-branched galactans with an α-linked arabinofuranosyl moiety.[3]

Earlier we have reported the chemical synthesis of the β-(1→6)-linked 2-branched arabinogalactan-type series.[4–7] These synthetic oligosaccharides were tested with monoclonal antibodies raised against AGPs from the pressed juice of *E. purpurea* by Classen et al.[8] in a competitive ELISA for cross-reactivities. Only one hexasaccharide of the synthesized oligosaccharides showed reproducible reactivity. This hexasaccharide consists of a tetrameric β-(1→6)-linked galactan skeleton, with the second and penultimate galactopyranose units branched at position 2 to an α-linked arabinofuranosyl residue. Classen and co-workers have explained the weak reactivity of synthetic oligosaccharides with the different branching modes of the galactosyl units and with the lack of protein residue.[8]

For further characterization of these monoclonal antibodies, we decided to synthesize 3-aminopropyl spacer-containing tetra- and hexasaccharides consisting of a β-(1→6)-linked galactopyranose backbone with α-linked arabinofuranose side chains at position 3. This hexasaccharide has the same sequence as the above-mentioned 2,6-branched hexasaccharide, which shows weak reactivity. The 3-aminopropyl spacer can ensure conjugation of the synthetic oligomers to a suitable protein carrier.

2. Results and discussion

Preparation of some 3,6-branched arabinogalactan-type oligosaccharides by a different synthetic strategy has been reported recently.[9–13] Our approach was based on the following considerations. The benzoyl group was used as a permanent protecting group for the secondary hydroxyl functions and as a participating group ensuring the stereoselective formation of the required

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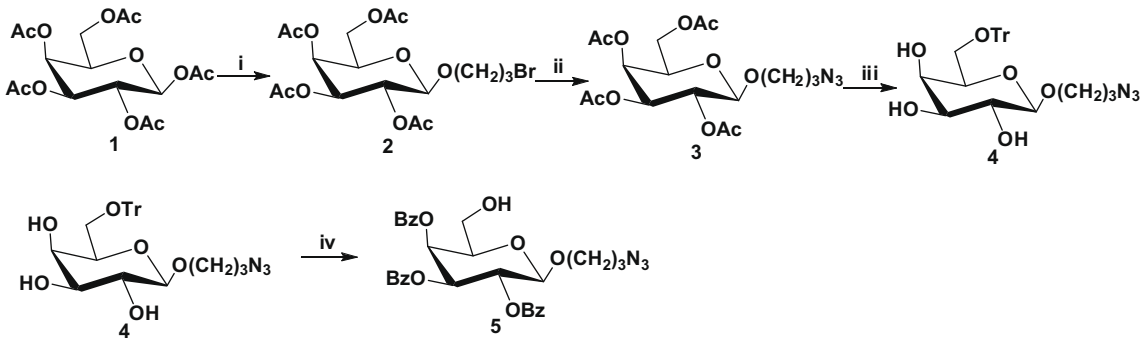


Scheme 1. Reagents and conditions: (i) 3-bromopropanol, $BF_3{\cdot}Et_2O$, DCM, 0 °C→rt, 24 h, 63%; (ii) NaN_3, DMF, rt, 24 h, 75%; (iii) (a) NaOMe, MeOH, rt, 24 h; (b) Ph_3CCl, DMAP, Py, rt, 24 h, 68% for two steps; (iv) (a) benzoyl chloride, Py, 0 °C→rt, 24 h; (b) 80% aq acetic acid, 50 °C, 3 h, 76% for **5** for two steps.

β-interglycosidic linkage. The (2-naphthyl)methyl (NAP)[14,15] group was chosen to protect the hydroxyl group at position 3 on the corresponding galactopyranoside unit, since it can be easily removed by oxidative cleavage[16] before formation of the arabinofuranosyl side chain. The primary hydroxyl position was masked with an acetyl group as a selectively removable protecting group, and thiophenyl was used as the anomeric leaving group. Finally, a 3-azidopropyl aglycon was selected as a marked 3-aminopropyl moiety.

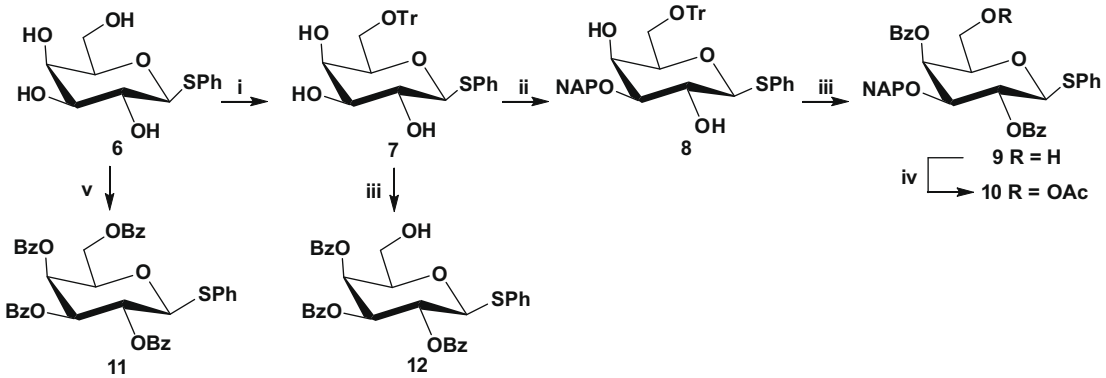
First, the 3-azidopropyl group was introduced in the following way: β-D-galactopyranose peracetate (**1**) was coupled with commercially available 3-bromopropanol in a $BF_3{\cdot}Et_2O$-catalyzed reaction,[17] and then the bromo compound **2** was treated with NaN_3 in DMF. After deacetylation of **3**, the primary hydroxyl group was tritylated to afford the triol **4** in moderate yield. Then benzoylation of compound **4**, followed by removal of trityl group by acid hydrolysis, gave the spacer-containing acceptor **5** in 77% yield (Scheme 1).

The synthesis of the glycosyl donor **10** started with tritylation of the known phenyl 1-thio-β-D-galactopyranoside (**6**).[18] Our key reaction was the regioselective alkylation of the triol **7** via dibutylstannylene acetal formation,[19] using NAPBr in the presence of CsF in DMF to afford the building block **8** in 83% yield. Compound **8** was benzoylated, then directly detritylated by acid hydrolysis, and acetylation of the resulting alcohol **9** provided the thioglycoside donor **10**. Another galactopyranoside donor **11** was prepared by perbenzoylation of compound **6**. Benzoylation of **7** and subsequent acid hydrolysis yielded the acceptor **12** (Scheme 2).

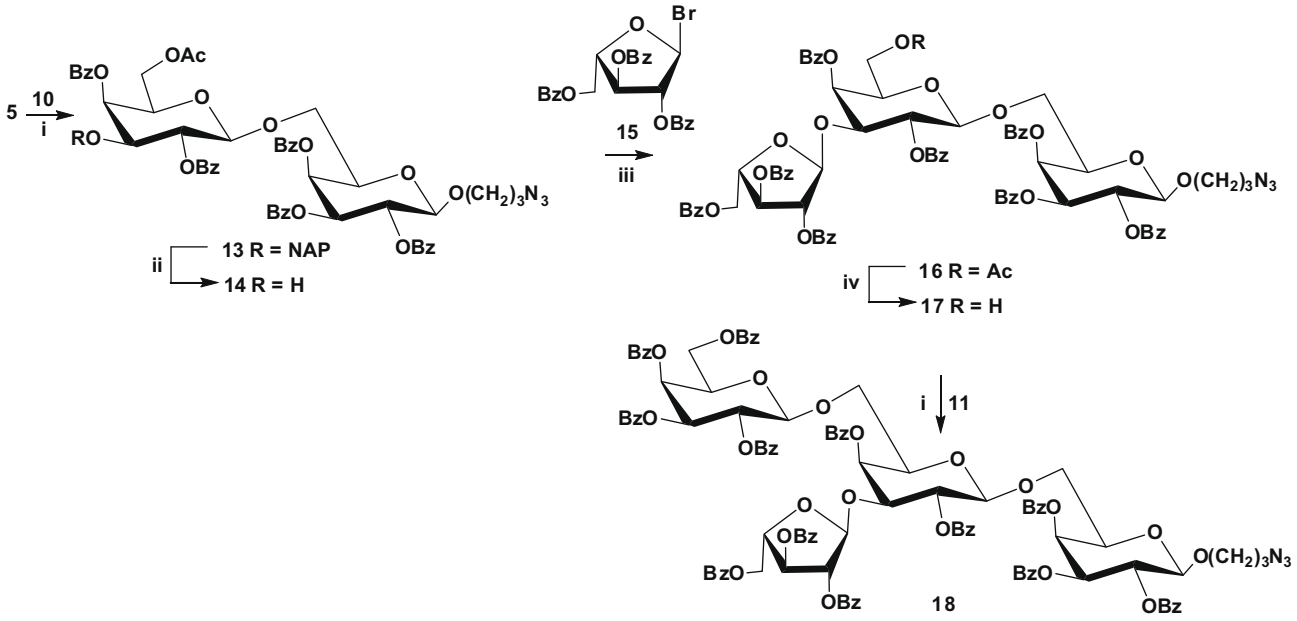
Synthesis of the tetrasaccharide **18** was achieved using the following approach. First, the donor **10** was coupled with the acceptor **5** using NIS/AgOTf promotion to furnish the disaccharide unit **13**. The NAP group of compound **13** was removed with oxidative cleavage in the presence of DDQ.[18] It is worth mentioning that the NAP group, like the benzyl group, can be removed by catalytic hydrogenation, but we used oxidative cleavage to avoid reduction of the azido function. The resulting acceptor **17** was glycosylated with the known 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl bromide (**15**)[20] using AgOTf activation to afford trisaccharide **16** in 81% yield. Deacetylation of compound **16** by acid hydrolysis applying AcCl in MeOH–DCM, followed by condensation of trisaccharide acceptor **17** with the perbenzoylated donor **11** afforded tetrasaccharide **18** (Scheme 3).

Preparation of hexasaccharide **23** was planned via a 3+3 block synthesis. Therefore, the synthesis of trisaccharide donor **22** was first achieved. Thiophenyl glycoside **10** was converted into glycosyl bromide with bromine and subsequently coupled with the glycosyl acceptor **12** using AgOTf activation. After oxidative cleavage of the NAP group with DDQ, the resulting acceptor **21** was arabinofuranosylated to give the intended trisaccharide **22** in 85% yield. Next, the trisaccharide acceptor **17** was glycosylated with the donor **22** using NIS/AgOTf promotion to furnish the fully protected hexasaccharide **23** (Scheme 4).

Deblocking of the tetra- and hexasaccharides **18** and **23** was effected in two steps. First, the acyl groups were removed by Zemplén transesterification, then the azido group was reduced by catalytic hydrogenation to give the target 3-aminopropyl spacer containing the tetra- and hexasaccharides **25** and **27** (Scheme 5.). All the synthesized compounds were characterized by ^1H and ^{13}C NMR spectroscopy, as well as by MALDI TOF mass spectrometry. However the resonances in the ^1H and ^{13}C NMR spectra of compounds **18**, **23**, **26** and **27** were complex and overlapping, and complete assignments could not be achieved even by 2D NMR analysis.



Scheme 2. Reagents and conditions: (i) Ph_3CCl, DMAP, Py, rt, 24 h, 89%; (ii) (a) Bu_2SnO, toluene, reflux temperature, 3 h; (b) NAPBr, CsF, DMF, 24 h, 81% for **8** for two steps; (iii) (a) benzoyl chloride, Py, 0 °C→rt, 24 h; (b) 80% aq HOAc, 50 °C, 3 h, 73% for **9** for two steps, 84% for **12** for two steps; (iv) Ac_2O, Py, rt, 24 h, 95%; (v) benzoyl chloride, Py, 0 °C→rt, 24 h, 95%.



Scheme 3. Reagents and conditions: (i) NIS in THF, AgOTf in toluene, DCM, −20 °C→rt, 24 h, 76% for **13**, 71% for **18**; (ii) DDQ, DCM–MeOH, rt, 24 h, 62%; (iii) AgOTf in toluene, collidine, DCM, −74 °C→rt, 24 h, 80%; (iv) AcCl, DCM–MeOH, 0 °C→rt, 24 h, 78%.

In conclusion, we developed an efficient synthetic method for the preparation of the β-(1→6) linked 3-branched tetra- and hexasaccharides **25** and **27** with a 3-aminopropyl spacer related to arabinogalactans. The synthesized oligosaccharides will be tested with monoclonal antibodies raised against AGPs from pressed juice of *E. purpurea*.

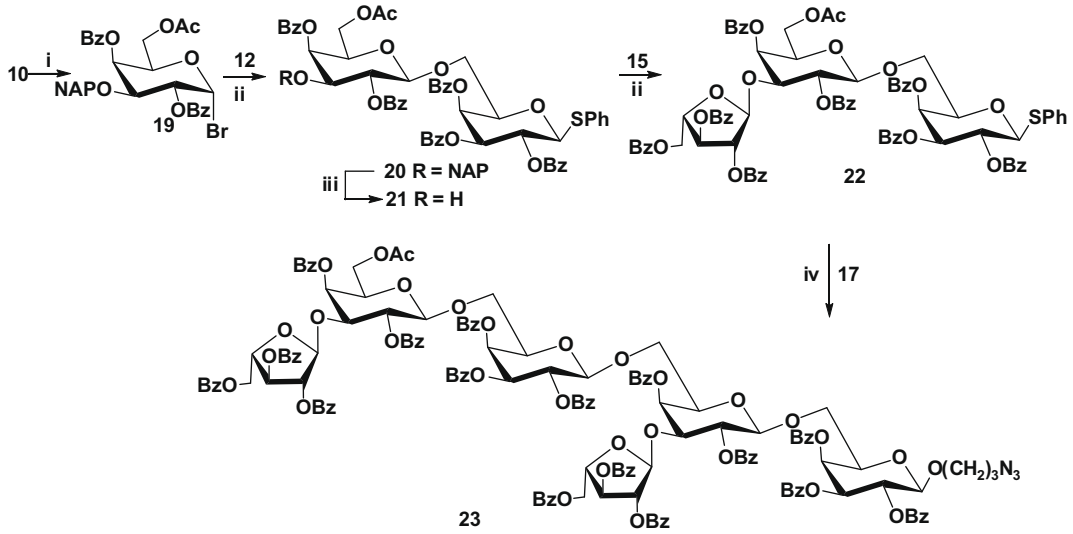
3. Experimental

3.1. General procedures

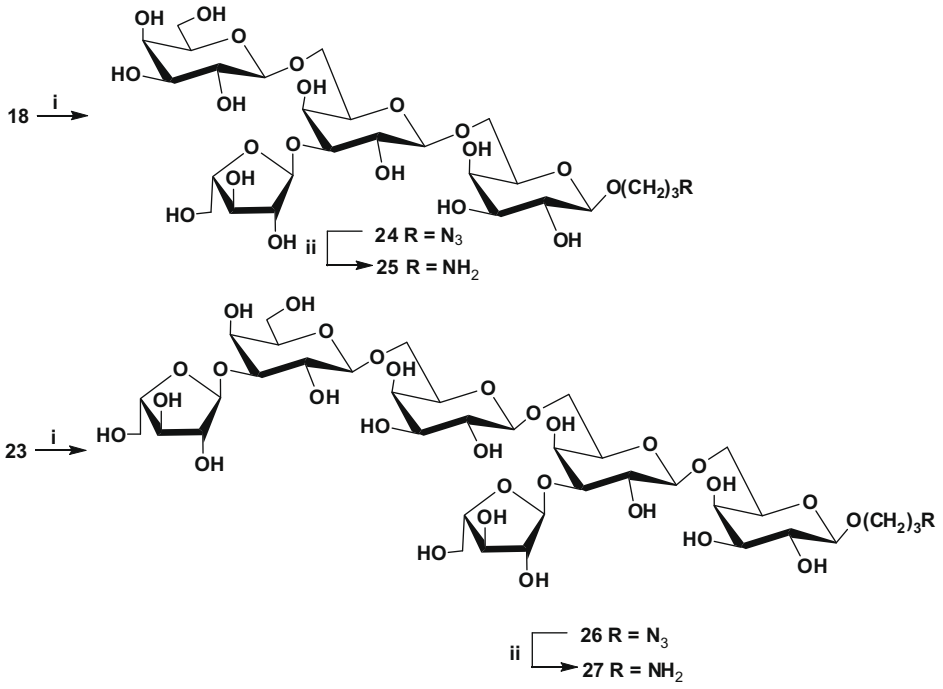
Optical rotations were measured at room temperature with a Perkin–Elmer 241 automatic polarimeter in $CHCl_3$. TLC was performed on Kieselgel 60 F254 (E. Merck) with detection by charring with 50% aq H_2SO_4. Column chromatography was performed on Silica Gel 60 (E. Merck 63–200 mesh). The ^1H (360 MHz, 400 MHz and 500 MHz) and ^{13}C NMR (90.54 MHz, 128 MHz and 125.76 MHz) spectra were recorded with Bruker AM-360, Bruker DRX-400 and Bruker DRX-500 spectrometers. Internal references: TMS (0.000 ppm for ^1H), $CDCl_3$ (77.00 ppm for ^{13}C for organic solutions). MALDI-TOF MS analyses of compounds were carried out in the positive reflecton mode using a BIFLEX III mass spectrometer.

3.2. 3-Bromopropyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (2)

To a solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (**1**) (1 g, 2.56 mmol) in dry CH_2Cl_2 (10 mL) were added 3-bromo-1-propanol (448 μL, 5.12 mmol) and $BF_3{\cdot}Et_2O$ (643 μL, 5.12 mmol) at 0 °C. Then the reaction mixture was left to attain room



Scheme 4. Reagents and conditions: (i) Br_2, DCM, rt, 1 h; (ii) AgOTf in toluene; collidine, DCM, −74 °C→rt, 24 h, 74% for **20** for two steps, 83% for **22**; (iii) DDQ, DCM–MeOH, rt, 24 h, 76%; (iv) NIS in THF, AgOTf in toluene, DCM, −20 °C→rt, 24 h, 75%.



Scheme 5. Reagents and conditions: (i) NaOMe, DCM–MeOH, 81% for **24**, 96% for **26**; (ii) H_2, Pd/C, H_2O, 82% for **25**, 86% for **27**.

temperature and was stirred overnight. The mixture was diluted with CH_2Cl_2, washed with water and satd aq $NaHCO_3$, dried and concentrated. The crude product was purified by column chromatography (7:3 hexane–EtOAc) to yield **2** (750 g, 63%) as a colourless syrup. $[\alpha]_D$ +6.6 (*c* 0.17 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.38 (d, 1H, $J_{3,4}$ 3 Hz, H-4), 5.18 (t, 1H, $J_{1,2}$ 8 Hz, $J_{2,3}$ 8 Hz, H-2), 5.02 (dd, 1H, $J_{2,3}$ 8 Hz, $J_{3,4}$ 3 Hz, H-3), 4.45 (d, 1H, $J_{1,2}$ 8 Hz, H-1), 4.20–4.09 (m, 2H), 3.99 (dd, 1H, *J* 10 Hz, *J* 5 Hz), 3.91 (t, 1H, *J* 5 Hz), 3.71–3.65 (m, 1H, H-5), 3.47 (t, 2H, *J* 8 Hz, CH_2), 2.21–2.13 (m, 2H, CH_2), 2.13, 2.07, 2.04, 1.97 (4s, 12H, 4 $COCH_3$); ^{13}C NMR ($CDCl_3$): δ 170.26, 170.11, 169.99 and 169.42 (4 *C*O), 101.45 (C-1), 70.74, 70.59, 68.75 and 66.93 (C-2, C-3, C-4, C-5), 67.21 (CH_2), 61.18 (C-6), 32.15 (CH_2), 30.06 (CH_2), 20.71, 20.57, 20.47 (4 $COCH_3$). MALDI-TOFMS: calcd for $C_{17}H_{25}BrO_{10}$: 468.06 [M]. Found: 491.14 $[M+Na]^+$; Anal. Calcd for $C_{17}H_{25}BrO_{10}$: C, 43.51; H, 5.37. Found: C, 43.45; H, 5.62.

3.3. 3-Azidopropyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (3)

To a solution of compound **2** (5.9 g, 12.6 mmol) in dry DMF (20 mL) was added NaN_3 (4.1 g, 63 mmol). After stirring for 1 d at 60 °C, the reaction mixture was diluted with CH_2Cl_2, washed with water and satd aq $NaHCO_3$, dried and concentrated. The crude product was purified by column chromatography (7:3 hexane–EtOAc) to yield **3** (4.1 g, 75%) as a colourless syrup. $[\alpha]_D$ −4.4 (*c* 0.18 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.40 (dd, 1H, $J_{3,4}$ 3 Hz, $J_{4,5}$ 1 Hz, H-4), 5.20 (dd, 1H, $J_{1,2}$ 8 Hz, $J_{2,3}$ 10 Hz, H-2), 5.02 (dd, 1H, $J_{2,3}$ 10 Hz, $J_{3,4}$ 3 Hz, H-3), 4.48 (d, 1H, $J_{1,2}$ 8 Hz, H-1), 4.26–4.08 (m, 2H), 4.01–3.89 (m, 2H), 3.65–3.57 (m, 1H), 3.44–3.31 (m, 2H), 2.16, 2.07, 2.06, 1.99 (4s, 12H, 4 $COCH_3$), 1.96–1.75 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 170.32, 170.17, 170.07 and 169.37 (4 *C*O), 101.25 (C-1), 70.79, 70.60, 68.74 and 66.93 (C-2, C-3, C-4, C-5), 66.39 (CH_2), 61.20 (C-6), 47.83 (CH_2), 28.88 (CH_2), 20.62 (4 $COCH_3$). MALDI-TOFMS: calcd for $C_{17}H_{25}N_3O_{10}$: 431.15 [M]. Found: 454.33 $[M+Na]^+$; Anal. Calcd for $C_{17}H_{25}N_3O_{10}$: C, 47.33; H, 5.84. Found: C, 47.51; H, 5.73.

3.4. 3-Azidopropyl 6-*O*-trityl-β-D-galactopyranoside (4)

To a solution of compound **3** (4 g, 9.3 mmol) in MeOH (100 mL) was added a catalytic amount of NaOMe (pH ~8). After stirring for 1 d at room temperature, the mixture was neutralized with Amberlite IR-120 H^+ ion-exchange resin, filtered and concentrated. The product thus obtained was used in the next step without further purification. To a solution of the crude product (9.3 mmol) in pyridine (50 mL) were added Ph_3CCl (6.5 g, 23.3 mmol) and DMAP (100 mg, 0.82 mmol). After stirring for 1 d at room temperature, the mixture was concentrated. The residue was diluted with CH_2Cl_2 washed with satd aq $NaHCO_3$ dried and concentrated. The crude product was purified by column chromatography (4:1 DCM–acetone, 0.5% Et_3N) to yield **4** (3.2 g, 68%) as a colourless syrup. $[\alpha]_D$ −25.8 (*c* 0.13 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.50–7.16 (m, 15H, aromatic), 4.18 (d, 1H, $J_{1,2}$ 8 Hz, H-1), 3.99–3.90 (m, 2H), 3.87 (br s, 1H, OH), 3.71 (br s, 1H, OH), 3.67–3.58 (m, 2H), 3.55–3.48 (m, 2H), 3.47–3.28 (m, 4H), 3.01 (br s, 1H, OH), 1.94–1.78 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 143.63 (Cq), 103.08 (C-1), 86.83 (Cq), 73.59, 71.61 and 69.05 (C-2, C-3, C-4, C-5), 66.60 (CH_2), 62.49 (C-6), 48.25 (CH_2), 28.98 (CH_2). MALDI-TOFMS: calcd for $C_{28}H_{31}N_3O_6$: 505.22 [M]. Found: 528.31 $[M+Na]^+$; Anal. Calcd for $C_{28}H_{31}N_3O_6$: C, 66.52; H, 6.18. Found: C, 66.35; H, 6.39.

3.5. 3-Azidopropyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (5)

To a solution of compound **4** (3 g, 5.94 mmol) in pyridine (30 mL) was added benzoyl bromide (3.11 mL, 26.8 mmol) at 0 °C. The reaction mixture was left to attain room temperature with stirring overnight; it was then concentrated. Toluene was added to and evaporated from the residue. The residue was diluted with CH_2Cl_2, extracted with aq 1 M HCl and satd aq $NaHCO_3$, dried and concentrated. A solution of crude product (5.94 mmol) in 80% aq HOAc (100 mL) was stirred at 50 °C for 3 h and the mixture was then concentrated. Toluene was added to and evaporated from the residue. The crude product was purified by column chromatography (3:2 hexane–EtOAc) to yield **5** (2.6 g, 76%) as a colourless

syrup. $[\alpha]_D$ +176.4 (*c* 0.12 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.28–7.14 (m, 15H, aromatic), 5.87–5.78 (m, 2H, H-4, H-2), 5.61 (dd, 1H, $J_{2,3}$ 10 Hz, $J_{3,4}$ 3 Hz, H-3), 4.81 (d, 1H, $J_{1,2}$ 8 Hz, H-1), 4.10–3.98 (m, 2H), 3.88–3.79 (m, 1H), 3.74–3.57 (m, 2H), 3.35–3.16 (m, 2H), 2.86 (br s, 1H, OH), 1.92–1.68 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 166.65, 165.47 and 165.30 (3 *C*O), 101.60 (C-1), 74.01, 71.70, 69.88 and 68.86 (C-2, C-3, C-4, C-5), 60.52 (C-6), 66.63, 47.73 and 28.88 (3 CH_2). MALDI-TOFMS: calcd for $C_{30}H_{29}N_3O_9$: 575.19 [M]. Found: 598.31 $[M+Na]^+$; Anal. Calcd for $C_{30}H_{29}N_3O_9$: C, 62.60; H, 5.08. Found: C, 62.85; H, 5.23.

3.6. Phenyl 6-*O*-trityl-1-thio-β-D-galactopyranoside (7)

To a solution of phenyl 1-thio-β-D-galactopyranoside (**6**)[18] (4.2 g, 15.44 mmol) in pyridine (50 mL) were added Ph_3CCl (10.8 g, 38.72 mmol) and DMAP (100 mg, 0.82 mmol). After stirring for 1 d at room temperature, the mixture was concentrated. The residue was dissolved in toluene and evaporated. The residue was diluted with CH_2Cl_2, extracted with satd aq $NaHCO_3$, dried and concentrated. The crude product was purified by column chromatography (4:1 CH_2Cl_2–acetone, 0.5% Et_3N) to yield **7** (7.1 g, 90%) as a colourless syrup. $[\alpha]_D$ −13.9 (*c* 0.15 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.61–7.11 (m, 20H, aromatic), 4.55 (d, 1H, $J_{1,2}$ 8 Hz, H-1), 4.17 (br s, 1H, OH), 3.93 (br s, 1H, OH), 3.81 (d, 1H, $J_{3,4}$ 3 Hz, H-4), 3.71 (t, 1H, $J_{1,2}$ 10 Hz, $J_{2,3}$ 10 Hz, H-2), 3.56–3.44 (m, 3H, H-5, H-6_a, H-6_b), 3.29 (br s, 1H, OH), 3.25 (dd, 1H, $J_{2,3}$ 10 Hz, $J_{3,4}$ 3 Hz, H-3); ^{13}C NMR ($CDCl_3$): δ ^{13}C NMR ($CDCl_3$): δ 143.65 (Cq), 88.52 (C-1), 86.85 (Cq), 77.71, 74.83, 69.79 and 69.66 (C-2, C-3, C-4, C-5), 63.61 (C-6). MALDI-TOFMS: calcd for $C_{31}H_{30}O_5S$: 514.18 [M]. Found: 537.34 $[M+Na]^+$; Anal. Calcd for $C_{31}H_{30}O_5S$: C, 72.35; H, 5.88. Found: C, 72.14; H, 5.69.

3.7. Phenyl 3-*O*-(2-naphthylmethyl)-6-*O*-trityl-1-thio-β-D-galactopyranoside (8)

To a solution of compound **7** (1 g, 1.9 mmol) in toluene (20 mL) was added dibutyltin oxide (612 mg, 2.46 mmol). After stirring for 3 h at reflux, the mixture was concentrated. The residue was dissolved in dry DMF and CsF (580 mg, 3.8 mmol) and 2-naphthylmethyl bromide (840 mg, 3.8 mmol) were added. After stirring for 1 d the mixture was concentrated. The residue was diluted with CH_2Cl_2, extracted with satd aq $NaHCO_3$, dried and concentrated. The crude product was purified by column chromatography (7:3 hexane–EtOAc, 0.5% Et_3N) to yield **8** (1.03 g, 81%) as a colourless syrup. $[\alpha]_D$ +1.3 (*c* 0.15 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.91–7.11 (m, 27H, aromatic), 4.88–4.82 (m, 2H, CH_2), 4.49 (d, 1H, $J_{1,2}$ 10 Hz, H-1), 3.95 (br s, 1H, H-4), 3.84 (t, 1H, $J_{1,2}$ 10 Hz, $J_{2,3}$ 10 Hz, H-2), 3.60–3.26 (m, 3H, H-5, H-6_a, H-6_b), 2.6 (br s, 2H, OH), 2.52 (dd, 1H, $J_{2,3}$ 8 Hz, $J_{3,4}$ 2 Hz, H-3); ^{13}C NMR ($CDCl_3$): δ 143.78 (Cq), 88.54 (C-1), 86.93 (Cq), 81.30, 77.71, 68.93 and 67.33 (C-2, C-3, C-4, C-5), 72.05 (CH_2), 63.65 (C-6). MALDI-TOFMS: calcd for $C_{42}H_{38}O_5S$: 654.24 [M]. Found: 677.39 $[M+Na]^+$; Anal. Calcd for $C_{42}H_{38}O_5S$: C, 77.04; H, 5.85. Found: C, 77.32; H, 5.61.

3.8. Phenyl 2,4-di-*O*-benzoyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranoside (9)

To a solution of compound **8** (1 g, 1.53 mmol) in pyridine (20 mL) was added benzoyl bromide (530 μL, 4.57 mmol) at 0 °C and the mixture was then treated as described for the preparation of **5**. The crude product was purified by column chromatography (7:3 hexane–EtOAc) to yield **7** (693 g, 73%) as a colourless syrup. $[\alpha]_D$ +62.4 (*c* 0.16 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.18–7.05 (m, 22H, aromatic), 5.81 (d, 1H, $J_{3,4}$ 3 Hz, H-4), 5.58 (t, 1H, $J_{1,2}$ 10 Hz, $J_{2,3}$ 10 Hz, H-2), 4.84–4.73 (m, 2H, CH_2), 4.60 (d, 1H, $J_{1,2}$ 10 Hz, H-1), 3.92–3.75 (m, 3H), 3.60 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 166.91 and 165.11 (2 *C*O), 85.69 (C-1), 77.73, 77.18, 69.48 and 66.96 (C-2, C-3, C-4, C-5), 70.79 (CH_2), 60.81 (C-6). MALDI-TOFMS: calcd for $C_{37}H_{32}O_7S$: 620.19 [M]. Found: 643.35 $[M+Na]^+$; Anal. Calcd for $C_{37}H_{32}O_7S$: C, 71.59; H, 5.20. Found: C, 71.38; H, 5.59.

3.9. Phenyl 6-*O*-acetyl-2,4-di-*O*-benzoyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranoside (10)

To a solution of compound **9** (160 mg, 0.26 mmol) in pyridine (10 mL) was added Ac_2O (5 mL). After stirring for 2 h at room temperature, the mixture was concentrated. Toluene was added to and evaporated from the residue. The residue was diluted with CH_2Cl_2, extracted with aq 1 M HCl and satd aq $NaHCO_3$, dried and concentrated. The crude product was purified by column chromatography (7:3 hexane–EtOAc) to yield **10** (164 g, 95%) as a colourless syrup. $[\alpha]_D$ +68.6 (*c* 0.14 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.97–7.14 (m, 22H, aromatic), 5.87 (d, 1H, $J_{3,4}$ 3 Hz, H-4), 5.49 (t, 1H, $J_{1,2}$ 10 Hz, $J_{2,3}$ 10 Hz, H-2), 4.82 (d, 1H, *J* 13 Hz, CH_a), 4.77 (d, 1H, $J_{1,2}$ 10 Hz, H-1), 4.62 (d, 1H, *J* 13 Hz, CH_b), 4.29–4.21 (m, 2H), 4.00 (t, 1H, *J* = 6 Hz), 3.84 (dd, 1H, $J_{2,3}$ 10 Hz, $J_{3,4}$ 3 Hz, H-3), 2.06 (s, 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$): δ 170.52, 165.72 and 165.06 (3 *C*O), 85.51 (C-1), 77.15, 75.06, 69.30 and 66.58 (C-2, C-3, C-4, C-5), 70.92 (CH_2), 62.62 (C-6) 20.72 ($COCH_3$). MALDI-TOFMS: calcd for $C_{39}H_{34}O_8S$: 662.20 [M]. Found: 685.37 $[M+Na]^+$; Anal. Calcd for $C_{39}H_{34}O_8S$: C, 70.68; H, 5.17. Found: C, 70.83; H, 5.41.

3.10. Phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (11)

To a solution of compound **6** (1 g, 3.68 mmol) in pyridine (30 mL) was added benzoyl bromide (2.55 mL, 22 mmol) at 0 °C. The reaction mixture was left to attain room temperature with stirring overnight; it was then concentrated. Toluene was added to and evaporated from the residue. The residue was diluted with CH_2Cl_2, extracted with aq 1 M HCl and satd aq $NaHCO_3$, dried and concentrated. The crude product was purified by column chromatography (4:1 hexane–acetone) to yield **11** (2.4 g, 95%) as a colourless syrup. $[\alpha]_D$ +81.5 (*c* 0.12 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ ppm 8.12–7.18 (m, 25H, aromatic), 6.04 (d, 1H, $J_{3,4}$ 3 Hz, H-4), 5.81 (t, 1H, $J_{1,2}$ 10 Hz, $J_{2,3}$ 10 Hz, H-2), 5.65 (dd, 1H, $J_{2,3}$ 10 Hz, $J_{3,4}$ 3 Hz, H-3), 5.09 (d, 1H, $J_{1,2}$ 10 Hz, H-1), 4.67 (dd, 1H, *J* 9 Hz, *J* 5 Hz), 4.54–4.38 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 166.02, 165.48, 165.36 and 165.17 (4 *C*O), 85.81 (C-1), 75.10, 72.94, 68.30 and 67.84 (C-2, C-3, C-4, C-5), 62.48 (C-6). MALDI-TOFMS: calcd for $C_{40}H_{32}O_9S$: 688.18 [M]. Found: 711.30 $[M+Na]^+$; Anal. Calcd for $C_{40}H_{32}O_9S$: C, 69.75; H, 4.68. Found: C, 69.41; H, 4.32.

3.11. Phenyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (12)

To a solution of compound **7** (2.3 g, 4.47 mmol) in pyridine (30 mL) was added benzoyl bromide (2.33 mL, 20.1 mmol) at 0 °C and the mixture was then treated as described for the preparation of **5**. The crude product was purified by column chromatography (7:3 hexane–EtOAc) to yield **12** (2.2 g, 84%) as a colourless syrup. $[\alpha]_D$ +136.3 (*c* 0.18 in $CHCl_3$); ^1H NMR ($CDCl_3$): 8.2–7.2 (m, 20H, aromatic) 5.86 (d, 1H, $J_{3,4}$ 3 Hz, H-4), 5.8 (t, 1H, $J_{1,2}$ 10 Hz, $J_{2,3}$ 10 Hz, H-2), 5.59 (dd, 1H, $J_{2,3}$ 10 Hz, $J_{3,4}$ 3 Hz, H-3), 5.03 (d, 1H, $J_{1,2}$ 10 Hz, H-1), 4.19–4.03 (m, 1H), 3.94–3.78 (m, 1H), 3.73–3.54 (m, 1H), 2.77–2.63 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 166.46, 165.49 and 165.17 (3 *C*O), 85.53 (C-1), 77.87, 73.11, 68.89 and 67.95 (C-2, C-3, C-4, C-5), 60.72 (C-6). MALDI-TOFMS: calcd for $C_{33}H_{28}O_8S$: 584.15 [M]. Found: 607.30 $[M+Na]^+$; Anal. Calcd for $C_{33}H_{38}O_8S$: C, 67.79; H, 4.83. Found: C, 67.52; H, 4.67.

3.12. 3-Azidopropyl 6-*O*-acetyl-2,4-di-*O*-benzoyl-3-*O*-(2-naphthylmethyl)-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (13)

A solution of donor **10** (960 mg, 1.45 mmol), acceptor **5** (695 mg, 1.21 mmol) and 4 Å molecular sieves in dry CH_2Cl_2 (10 mL) was cooled to −20 °C. After stirring for 30 min at −20 °C, a mixture of NIS (360 mg, 1.6 mmol) in dry THF (1 mL) and AgOTf (54 mg, 0.21 mmol) in dry toluene (0.5 mL) was added dropwise. Then the reaction mixture was left to attain room temperature overnight. The reaction was quenched with pyridine (0.5 mL), diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with 10% aq $Na_2S_2O_3$ and water, dried and concentrated. The crude product was purified by column chromatography (98:2 CH_2Cl_2–acetone) to yield **13** (1.01 g, 76%) as a colourless syrup. $[\alpha]_D$ +118 (*c* 0.12 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.27–7.18 (m, 32H, aromatic), 5.88 (br s, 2H, H-4, H-4′), 5.70 (dd, 1H, *J* 10 Hz, *J* 8 Hz, H-2), 5.59 (dd, 1H, *J* 10 Hz, *J* 8 Hz, 1H, H-2^I), 5.54 (dd, 1H, $J_{2,3}$ 10 Hz, $J_{3,4}$ 3 Hz, H-3), 4.88 (d, 1H, *J* 13 Hz, ArCH_a), 4.68 (d, 1H, *J* 13 Hz, ArCH_b), 4.65 (d, 1H, *J* 8 Hz, H-1^I), 4.63 (d, 1H, *J* 8 Hz, H-1), 4.25–4.08 (m, 4H, H-5, H-6^I_a, H-6^I_b, H-6$_a$), 3.95 (t, 1H, *J* 6 Hz, 1H, H-5^I), 3.88–3.74 (m, 2H, H-3′, H-6$_b$), 3.65–3.57 (m, 1H, CH_a), 3.35–3.25 (m, 1H, CH_b), 3.06 (t, 2H, *J* 6 Hz, CH_2), 2.01 (s, 3H, COCH_3), 1.61–1.37 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 170.42, 165.77, 165.31, 165.18 and 165.00 (6 *C*O), 101.16 (C-1 and C-1^I), 75.77 (C-3^I), 73.22 (C-5), 71.50 (C-5^I), 71.18 (C-3), 70.93 (C-2^I), 69.70 (C-2), 68.71 (C-4), 66.29 (C-4^I), 70.89 (Ar*C*H$_2$), 68.07 (*C*H$_2$), 66.04 (C-6), 62.08 (C-6^I), 47.62 (*C*H$_2$), 28.55 (*C*H$_2$), 20.56 (COCH$_3$). MALDI-TOFMS: calcd for $C_{63}H_{57}N_3O_{17}$: 1127.37 [M]. Found: 1150.48 [M+Na]$^+$; Anal. Calcd for $C_{63}H_{57}N_3O_{17}$: C, 67.07; H, 5.09. Found: C, 67.34; H, 5.28.

3.13. 3-Azidopropyl 6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (14)

To a solution of compound **13** (420 mg, 0.37 mmol) in 4:1 DCM–MeOH (25 mL) were added DDQ (134 mg, 0.59 mmol) and a trace of H_2O. After stirring for 1 d, the mixture was evaporated. The residue was diluted with CH_2Cl_2, extracted with satd aq $NaHCO_3$ and water, dried and concentrated. The crude product was purified by silica column chromatography (95:5 CH_2Cl_2–EtOAc) to yield **14** (228 mg, 62%) as a colourless syrup. $[\alpha]_D$ +108 (*c* 0.13 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.22–7.16 (m, 25H, aromatic), 5.86 (d, 1H, *J* 3 Hz, 1H, H-4), 5.69 (dd, 1H, *J* 10, *J* 8 Hz, H-2), 5.61 (d, 1H, *J* 3 Hz, 1H, H-4^I), 5.52 (dd, 1H, $J_{2,3}$ 10, $J_{3,4}$ 3 Hz, H-3), 5.35 (dd, 1H, *J* 10 Hz, *J* 8 Hz, H-2^I), 4.71 (d, 1H, *J* 8 Hz, H-1^I), 4.65 (d, 1H, *J* 8 Hz, H-1), 4.19–4.01 (m, 5H, H-3, H-5, H-6^I_a, H-6^I_b, H-6$_a$), 3.95 (t, 1H, *J* 6 Hz, H-5^I), 3.81 (dd,1H, *J* 10 Hz, *J* 8 Hz, H-6$_b$), 3.72–3.65 (m, 1H, CH_a), 3.40–3.31 (m, 1H, CH_b), 3.10 (t, 2H, *J* 6 Hz, CH_2), 2.80 (br s, 1H, OH), 1.94 (s, 3H, COCH_3), 1.67–1.43 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 170.44, 166.46, 166.23, 165.40 and 165.24 (6 *C*O), 101.35 (C-1), 100.82 (C-1^I), 73.34 (C-2^I), 73.16 (C-3^I), 71.59 (C-3, C-5), 71.26 (C-5^I), 70.27 (C-4), 69.75 (C-2), 68.68 (C-4^I), 68.08 (C-6), 66.24 (*C*H$_2$), 61.97 (C-6^I), 47.71 (*C*H$_2$), 28.71 (*C*H$_2$), 20.56 (COCH$_3$). MALDI-TOFMS: calcd for $C_{52}H_{49}N_3O_{17}$: 987.31 [M]. Found: 1010.26 [M+Na]$^+$; Anal. Calcd for $C_{52}H_{49}N_3O_{17}$: C, 63.22; H, 5.00. Found: C, 63.56; H, 5.33.

3.14. 3-Azidopropyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (16)

To a solution of glycosyl bromide **15**[20] (154 mg, 0.3 mmol) and acceptor **14** (200 mg, 0.2 mmol) in dry CH_2Cl_2 (5 mL) were added collidine (45 μL, 0.34 mmol) and 4 Å molecular sieves, and the mixture was cooled to −74 °C. After stirring for 30 min at −74 °C, silver triflate (113 mg, 0.44 mmol) dissolved in toluene (1 mL) was added. The reaction mixture was then left to attain room temperature and was stirred overnight. The mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with 10% aq $Na_2S_2O_3$ and water, dried and concentrated. The crude product was purified by column chromatography (99:1 CH_2Cl_2–acetone) to yield **16** (230 mg, 80%) as a colourless syrup. $[\alpha]_D$ +94 (*c* 0.20 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.09–7.17 (m, 40H, aromatic), 5.87 (d, 1H, *J* 3 Hz, H-4), 5.80 (d, 1H, *J* 3 Hz, H-4^I), 5.71 (t, 1H, *J* 10 Hz, H-2^I), 5.69 (t, 1H, *J* 8 Hz, H-2), 5.53 (dd, 1H, *J* 10 Hz, *J* 3 Hz, H-3), 5.49 (d, 1H, *J* 6 Hz, H-3^{II}), 5.36 (s, 1H, H-1^{II}), 5.27 (s, 1H, H-2^{II}), 4.93 (dd, 1H, *J* 12 Hz, *J* 3 Hz, 1H, H-5$^{II}_a$), 4.83–4.79 (m, 1H, H-4^{II}), 4.72 (d, 1H, *J* 8 Hz, H-1), 4.67 (dd, 1H, *J* 12 Hz, *J* 4 Hz, H-5$^{II}_b$), 4.64 (d, 1H, *J* 8 Hz, H-1^I), 4.24 (dd, 1H, *J* 10 Hz, *J* 3 Hz, H-3^I), 4.18 (dd, 1H, *J* 4, *J* 8 Hz, H-5^I), 4.16–4.08 (m, 3H, H-6$_a$, H-6^I_a, H-6^I_b), 4.03 (t, 1H, *J* 6 Hz, H-5^I), 3.81 (dd, 1H, *J* 10 Hz, *J* 8 Hz, H-6$_b$), 3.68–3.62 (m, 1H, OCH_a), 3.34–3.28 (m, 1H, OCH_b), 3.08 (t, 2H, *J* 6 Hz, CH_2), 1.92 (s, 3H, COCH_3), 1.62–1.43 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 170.29, 165.67, 165.56, 165.16 and 164.88 (9 *C*O), 107.77 (C-1^{II}), 101.25 (C-1 and C-1^I), 82.38 (C-2^{II}), 81.53 (C-4^{II}), 77.37 (C-3^{II}), 76.31(C-3^I), 73.26 (C-5), 71.53 (C-3), 71.43 (C-2^I), 71.38 (C-5^I), 69.75 (C-2), 69.58 (C-4^I), 68.75 (C-4), 68.16 (C-6), 66.14 (*C*H$_2$), 63.14 (C-5^{II}), 61.78 (C-6^I), 47.66 (*C*H$_2$), 28.63 (*C*H$_2$), 20.46 (COCH$_3$). MALDI-TOFMS: calcd for $C_{78}H_{69}N_3O_{24}$: 1431.43 [M]. Found: 1454.58 [M+Na]$^+$; Anal. Calcd for $C_{78}H_{69}N_3O_{24}$: C, 65.40; H, 4.86. Found: C, 65.71; H, 4.57.

3.15. 3-Azidopropyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (17)

To a solution of compound **16** (170 mg, 0.12 mmol) in 1:1 DCM–MeOH (10 mL) was added AcCl (42 μL, 0.59 mmol) at 0 °C. The reaction mixture was left to attain room temperature with stirring overnight; it was then concentrated. The residue was purified by silica column chromatography (98:2 CH_2Cl_2–acetone) to yield **17** (120 mg, 72%) as a colourless syrup. $[\alpha]_D$ +100 (*c* 0.12 in $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.10–7.19 (m, 40H, aromatic), 5.89 (d, 1H, *J* 3 Hz, H-4), 5.76 (d, 1H, *J* 3 Hz, H-4^I), 5.75 (t, 1H, *J* 8 Hz, H-2^I), 5.67 (dd, 1H, *J* 8, *J* 10 Hz, H-2), 5.51 (dd, 1H, *J* 10, *J* 3 Hz, H-3), 5.42 (d, 1H, *J* 5 Hz, H-3^{II}), 5.38 (s, 1H, H-1^{II}), 5.26 (s, 1H, H-2^{II}), 4.77 (dd, 1H, *J* 12 Hz, *J* 3 Hz, H-5$^{II}_a$), 4.71 (d, 1H, *J* 8 Hz, H-1), 4.63 (d, 1H, *J* 8 Hz, H-1^I), 4.56 (dd, 1H, *J* 13, *J* 5 Hz, H-5$^{II}_b$), 4.52–4.48 (m, 1H, H-4^{II}), 4.21 (dd, 1H, *J* 10 Hz, *J* 4 Hz, H-3^I), 4.15–4.07 (m, 2H, H-5, H-6$_a$), 3.87–3.78 (m, 2H, H-5^I, H-6$_b$), 3.73–3.61 (m, 2H, CH_a, H-6^I_a), 3.50–3.40 (m, 1H, H-6^I_b), 3.38–3.30 (m, 1H, CH_b), 3.09 (t, 2H, *J* 6 Hz, CH_2), 2.76 (br s, 1H, OH), 1.64–1.45 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 167.11, 166.05, 165.54, 165.48, 165.39, 165.19, 165.09 and 164.70 (8 *C*O), 107.71 (C-1^{II}), 101.42 (C-1), 101.33 (C-1^I), 82.17 (C-2^{II}), 81.82 (C-4^{II}), 77.15 (C-3^I), 77.08 (C-3^{II}), 73.96 (C-5^I), 73.16 (C-5), 71.59 (C-4^I), 71.34 (C-2^I), 70.37 (C-3), 69.77 (C-2), 68.69 (C-4), 68.23 (C-6), 66.20 (*C*H$_2$), 63.33 (C-5^{II}), 60.26 (C-6^I), 47.71 (*C*H$_2$), 28.69 (*C*H$_2$). MALDI-TOFMS: calcd for $C_{76}H_{67}N_3O_{23}$: 1389.42 [M]. Found: 1412.45 [M+Na]$^+$; Anal. Calcd for $C_{76}H_{67}N_3O_{23}$: C, 65.65; H, 4.86. Found: C, 65.42; H, 4.47.

3.16. 3-Azidopropyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (18)

A solution of donor **11** (150 mg, 0.22 mmol), acceptor **17** (150 mg, 0.11 mmol) and 4 Å molecular sieves in dry CH_2Cl_2 (5 mL) was cooled to −20 °C. After stirring for 30 min at −20 °C, a mixture of NIS (54 mg, 0.24 mmol) in dry THF (200 μL) and AgOTf (8 mg, 0.03 mmol) in dry toluene (500 μL) was added dropwise. Then the mixture was treated as described for the preparation of

13. The crude product was purified by column chromatography (97:3 CH_2Cl_2–EtOAc) to yield **18** (150 mg, 71%) as a colourless syrup. $[\alpha]_D$ +74.5 (*c* 0.10 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.15–7.11 (m, 60H, aromatic), 5.89–5.80 (m, 3H, H-4^I, H-4^{III}, H-4), 5.74–5.60 (m, 3H, H-2, H-2^I, H-2^{III}), 5.56–5.47 (m, 3H, H-3, H-3^{II}, H-3^{III}), 5.30 (s, 1H, H-1^{II}), 5.25 (d, 1H, *J* 1 Hz, H-2^{II}), 5.07–4.93 (m, 2H, H-5$^{II}_a$, H-4^{II}), 4.83–4.68 (m, 1H, H-5$^{II}_b$), 4.73 (d,1H, *J* 8 Hz, H-1), 4.62 (d, 1H, *J* 8 Hz, H-1^I), 4.59 (d, 1H, *J* 8 Hz, H-1^{III}), 4.19–3.93 (m, 8H, H-3^I, H-5, H-5^I, H-5^{III}, H-6$_a$, H-6^I_a, H-6$^{III}_a$, H-6$^{III}_b$), 3.77–3.52 (m, 3H, H-6$_b$, H-6^I_b, CH_a), 3.32–3.24 (m, 1H, CH_b), 3.05 (t, 2H, *J* 7 Hz, CH_2), 1.59–1.36 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 166.12, 165.86, 165.73, 165.35, 165.24, 164.97, 164.88 and 164.58 (12 *C*O), 107.65 (C-1^{II}), 101.30 and 101.22 (C-1^I and C-1^{III}), 101.60 (C-1), 82.59 (C-2^{II}), 81.56 (C-4^{II}), 77.58 (C-3^{II}), 76.09 (C-3^I), 73.05 and 72.80 (C-5, C-5^I), 71.68, 71.58, 71.40, 69.87, 69.60, 68.79 and 67.79 (C-2, C-2^I, C-2^{III}, C-3, C-3^{III}, C-4, C-4^I, C-4^{III}, C-5^{III}), 68.13 (C-6^{III}), 66.38 (C-5^{II}), 66.17 (*C*H$_2$), 63.26 and 61.44 (C-6, C-6^I), 47.74 (*C*H$_2$), 28.67 (*C*H$_2$). MALDI-TOFMS: calcd for $C_{110}H_{93}N_3O_{32}$: 1967.57 [M]. Found: 1990.68 $[M+Na]^+$; Anal. Calcd for $C_{110}H_{93}N_3O_{32}$: C, 67.10; H, 4.76. Found: C, 67.39; H, 4.47.

3.17. Phenyl 6-*O*-acetyl-2,4-di-*O*-benzoyl-3-*O*-(2-naphthylmethyl)-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (20)

To a solution of compound **10** (1.43 g, 2.16 mmol) in dry CH_2Cl_2 (20 mL) was added bromine (130 μL, 2.53 mmol) at room temperature. After stirring for 1 h, the reaction mixture was concentrated. Dry toluene was added to and evaporated from the residue to yield glycosyl bromide **19**. To a solution of compound **19** (2.16 mmol) and acceptor **12** (835 mg, 1.43 mmol) in dry CH_2Cl_2 (20 mL) were added collidine (321 μL, 2.42 mmol) and 4 Å molecular sieves, and the mixture was cooled to −74 °C. After stirring for 30 min at −74 °C, silver triflate (820 mg, 3.19 mmol) dissolved in toluene (10 mL) was added. The reaction mixture was then left to attain room temperature overnight. The mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with 10% aq $Na_2S_2O_3$ and water, dried and concentrated. The crude product was purified by column chromatography (99:1 CH_2Cl_2–acetone) to yield **20** (1.2 g, 74%) as a colourless syrup. $[\alpha]_D$ +113 (*c* 0.16 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.19–7.17 (m, 37H, aromatic), 5.87 (d, 1H, *J* 3 Hz, H-4), 5.83 (d, 1H, *J* 3 Hz, H-4^I), 5.65 (t, 1H, *J* 10 Hz, H-2), 5.55 (t, 1H, *J* 8 Hz, H-2^I), 5.48 (dd, 1H, *J* 10 Hz, *J* 3 Hz, H-3), 4.86 (d, 1H, *J* 10 Hz, H-1), 4.85 (d, 1H, *J* 13 Hz, ArCH_a), 4.65 (d, 1H, *J* 8 Hz, H-1^I), 4.64 (d, 1H, *J* 13 Hz, ArCH_b), 4.21–4.07 (m, 3H, H-5, H-6^I_a, H-6^I_b), 3.96 (dd, 1H, *J* 4 Hz, *J* 11 Hz, 1H, H-6$_a$), 3.90–3.85 (m, 2H, H-5, H-6$_b$), 3.81 (dd, 1H, *J* 3 Hz, *J* 10 Hz, H-3^I), 1.98 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$): δ 170.43, 165.86, 165.29, 165.13 and 165.06 (6 *C*O), 101.21 (C-1^I), 85.31 (C-1), 77.06 (C-5), 76.06 (C-3^I), 72.97 (C-5^I), 71.36 (C-3), 70.92 (C-2^I), 68.61 (C-4), 67.84 (C-2), 66.41 (C-4^I), 70.97 (*C*H$_2$), 67.70 (C-6^I), 62.16 (C-6), 20.60 (COCH_3). MALDI-TOFMS: calcd for $C_{66}H_{56}O_{16}S$: 1136.33 [M]. Found: 1159.42 $[M+Na]^+$; Anal. Calcd for $C_{66}H_{56}O_{16}S$: C, 69.71; H, 4.96. Found: C, 69.98; H, 4.63.

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

To a solution of compound **20** (1 g, 0.88 mmol) in 4:1 CH_2Cl_2–MeOH (50 mL) were added DDQ (318 mg, 1.4 mmol) and a trace of H_2O. Then the mixture was treated as described for the preparation of **13**. The crude product was purified by silica column chromatography (3:2 hexane–EtOAc) to yield **21** (670 mg, 76%) as a colourless syrup. $[\alpha]_D$ +81.4 (*c* 0.14 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.25–7.13 (m, 30H, aromatic), 5.90 (d, 1H, *J* 3 Hz, 1H, H-4), 5.70 (t, 1H, *J* 10 Hz, H-2), 5.63 (d, 1H, *J* 3 Hz, H-4^I), 5.51 (dd, 1H, *J* 10 Hz, *J* 3 Hz, H-3), 5.33 (dd, 1H, *J* 10 Hz, *J* 8 Hz, H-2^I), 4.93 (d, 1H, *J* 10 Hz, H-1), 4.78 (d, 1H, *J* 8 Hz, H-1^I), 4.29–4.21 (m, 1H, H-5), 4.17–3.88 (m, 6H, H-3^I, H-6$_a$, H-6$_b$, H-6^I_a, H-6^I_b, H-5^I), 2.82 (br s, 1H, OH), 1.97 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$): δ 170.46, 166.98, 166.20, 165.39 and 165.10 (5 *C*O), 100.89 (C-1^I), 85.37 (C-1), 73.60 (C-5), 73.00 (C-3 and C-2^I), 71.91 (C-3^I), 71.34 (C-5^I), 70.22 (C-4^I), 68.57 (C-4)and 67.76 (C-2), 67.99 and 61.98 (C-6, C-6^I), 20.63 (COCH_3). MALDI-TOFMS: calcd for $C_{55}H_{48}O_{16}S$: 996.27 [M]. Found: 1019.27 $[M+Na]^+$; Anal. Calcd for $C_{55}H_{48}O_{16}S$: C, 66.26; H, 4.85. Found: C, 66.45; H, 4.57.

3.19. Phenyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (22)

To a solution of glycosyl bromide **15**[9] (457 mg, 0.89 mmol) and acceptor **21** (593 mg, 0.6 mmol) in dry CH_2Cl_2 (10 mL) were added collidine (134 μL, 1.01 mmol) and 4 Å molecular sieves, and the mixture was cooled to −74 °C. After stirring for 30 min at −74 °C, silver triflate (365 mg, 1.42 mmol) dissolved in toluene (2 mL) was added. Then the mixture was treated as described for the preparation of **16**. The crude product was purified by silica column chromatography (99:1 CH_2Cl_2–acetone) to yield **22** (720 mg, 83%) as a colourless syrup. $[\alpha]_D$ +82.9 (*c* 0.12 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.09–7.15 (m, 45H, aromatic), 5.88 (d, 1H, *J* 3 Hz, H-4), 5.79 (d, 1H, *J* 3 Hz, H-4^I), 5.75–5.62 (m, 2H, H-2, H-2^I), 5.50–5.45 (m, 2H, H-3^{II}, H-3), 5.35 (s, 1H, H-1^{II}), 5.28 (s, 1H, H-2^{II}), 4.94 (dd, 1H, *J* 12 Hz, *J* 2 Hz, H-5$^{II}_a$), 4.85 (d, 1H, *J* 10 Hz, H-1), 4.83–4.78 (m, 1H, H-4^{II}), 4.77 (d, 1H, *J* 8 Hz, H-1^I), 4.67 (dd, 1H, *J* 12 Hz, *J* 4 Hz, H-5$^{II}_b$), 4.25–4.17 (m, 2H, H-3^I, H-5^I), 4.14–3.96 (m, 4H, H-5, H6$_a$, H-6$_b$, H-6^I_a), 3.91 (dd, 1H, *J* 11 Hz, *J* 7 Hz, H-6^I_b), 1.94 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$): δ 170.71, 166.46, 166.08, 165.97, 165.63, 165.39 and 164.95 (9 *C*O), 108.09 (C-1^{II}), 101.71 (C-1^I), 85.59 (C-1), 82.74 (C-2^{II}), 81.96 (C-4^{II}), 77.76 (C-3^{II}), 77.54 (C-3^I), 76.77 (C-5^I), 73.30 (C-3), 71.92 (C-5), 71.53 (C-2^I), 69.95 (C-4^I), 68.96 (C-4), 68.10 (C-2), 68.22 (C-6^I), 63.53 (C-5^{II}), 62.21 (C-6), 20.91 (COCH_3). MALDI-TOFMS: calcd for $C_{81}H_{68}O_{23}S$: 1440.39 [M]. Found: 1464.44 $[M+Na]^+$; Anal. Calcd for $C_{81}H_{68}O_{23}S$: C, 67.49; H, 4.75. Found: C, 67.73; H, 4.92.

3.20. 3-Azidopropyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)]-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (23)

A solution of donor **17** (500 mg, 0.35 mmol), acceptor **22** (400 mg, 0.29 mmol) and 4 Å molecular sieves in dry CH_2Cl_2 (5 mL) was cooled to −20 °C. After stirring for 30 min at −20 °C a mixture of NIS (89 mg, 0.4 mmol) in dry THF (500 μL) and AgOTf (13 mg, 0.05 mmol) in dry toluene (500 μL) was added dropwise. Then the mixture was treated as described for the preparation of **13**. The crude product was purified by silica column chromatography (98:2 CH_2Cl_2–EtOAc) to yield **23** (570 mg, 75%) as a colourless syrup. $[\alpha]_D$ +65.8 (*c* 0.11 in $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.16–7.09 (m, 80H, aromatic), 5.86–5.78 (m, 3H, H-4, H-4^I, H-4^{III}), 5.70 (d, 1H, *J* 3 Hz, H-4^{IV}), 5.67–5.39 (m, 8H, H-2, H-2^I, H-2^{III}, H-2^{IV}, H-3, H-3^{II}, H-3^{III}, H-3^V), 5.31 (s, 1H, H-2^V), 5.28 (s, 1H, H-2^{II}), 5.25 (d, 2H, *J* 1 Hz, H-1^{II}, H-1^V), 5.06–5.00 (m, 2H, H-4^{II}, H-5$^{II}_a$), 4.92 (dd, 1H, *J* 12 Hz, *J* 3 Hz, H-5^V_a), 4.83–4.71 (m, 2H, H-4^V, H-5$^{II}_b$), 4.66 (dd, 1H, *J* 12 Hz, *J* 4 Hz, H-5^V_b), 4.60 (d, 1H, *J* 8 Hz, H-1), 4.55 (d, 1H, *J* 8 Hz, H-1^I), 4.54 (d, 1H, *J* 8 Hz, H-1^{III}), 4.29 (d, 1H, *J* 8 Hz, H-1^{IV}), 4.17–3.98 (m, 3H, H-3, H-5, H-6$_a$), 4.02 (dd, 1H, *J* 10 Hz, *J* 3 Hz, H-3^{IV}), 3.94–3.77 (m, 6H, H-5^{III}, H-5^I, H-5^{IV}, H-6$^{IV}_a$, H-6$^{IV}_b$, H-6^I_a), 3.70 (dd, 1H, *J* 10 Hz, *J* 8 Hz, H-6$_b$), 3.63–3.52 (m, 2H,

H-6^{III}_a, CH_a), 3.49–3.41 (m, 1H, H-6^{I}_b), 3.36–3.17 (m, 1H, CH_b), 3.11–3.03 (m, 1H, H-6^{III}_b), 3.05 (t, 2H, *J* 7 Hz, CH_2), 1.61–1.36 (m, 2H, CH_2), 1.88 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$): δ 170.26, 166.15, 165.79, 165.63, 165.34, 164.95, 164.88 and 164.62 (17 *C*O), 107.73 (C-1^{II}, C-1^{V}), 101.30 (C-1, C-1^{I}), 100.95 (C-1^{III}), 100.39 (C-1^{IV}), 82.65 (C-2^{V}), 82.45 (C-2^{II}), 81.61 (C-4^{II}), 81.49 (C-4^{V}), 77.50 (C-3^{II}, C-3^{V}), 76.02 (C-3^{I}, C-3^{IV}), 73.10, 72.36, 71.80, 71.60, 71.30, 69.99, 69.85, 69.46 and 68.72 (C-2, C-2^{I}, C-2^{III}, C-2^{IV}, C-3, C-3^{III}, C-4, C-4^{I}, C-4^{IV}, C-5, C-5^{I}, C-5^{III}, C-5^{IV}), 67.86 (C-4^{III}), (C-6), 66.45 (C-6^{I}), 66.17 (*C*H_2), 65.68 (C-6^{III}), 63.28 (C-5^{II}, C-5^{V}) 61.61 (C-6^{IV}), 47.75 (*C*H_2), 28.70 (*C*H_2), 20.51 (*C*OCH_3). MALDI-TOFMS: calcd for $C_{151}H_{129}N_3O_{46}$: 2719.78 [M]. Found: 2744.67 $[M+Na]^+$; Anal. Calcd for $C_{151}H_{129}N_3O_{46}$: C, 66.64; H, 4.78. Found: C, 66.27; H, 4.46.

3.21. 3-Azidopropyl β-D-galactopyranosyl-(1→6)-[α-L-arabinofuranosyl-(1→3)]-β-D-galactopyranosyl-(1→6)-β-D-galactopyranoside (24)

To a solution of compound **18** (64 mg, 0.03 mmol) in CH_2Cl_2 (2 mL) were added MeOH (10 mL) and a catalytic amount of NaOMe (pH ~8). After stirring for 1 d at room temperature, the mixture was neutralized with Amberlite IR-120 H^+ ion-exchange resin, filtered and concentrated. The residue was purified by Sephadex LH20 chromatography to give **24** (19 mg, 81%) as a colourless syrup. $[\alpha]_D$ −21 (*c* 0.13 in H_2O); ^{1}H NMR (D_2O): δ 5.24 (s, 1H, H-1^{II}), 4.55, 4.46 and 4.43 (3d, 3H, *J* 8 Hz, H-1, H-1^{I}, H-1^{III}), 4.22 (s, 1H), 4.19–4.11 (m, 2H), 4.10–3.61 (m, 20H), 3.59–3.51 (m, 2H), 3.48 (t, 2H, *J* 7 Hz, CH_2), 1.99–1.87 (m, 2H, CH_2); ^{13}C NMR (D_2O): δ 109.24 (C-1^{II}), 103.34, 103.07, 102.78 (C-1, C-1^{I}, C-1^{III}), 83.79, 81.27, 80.13, 76.50, 75.12, 73.80, 73.53, 72.67, 72.56, 70.67, 69.78, 68.63 and 68.42 (C-2, C-2^{I}, C-2^{II},C-2^{III}, C-3, C-3^{I}, C-3^{II}, C-3^{III}, C-4, C-4^{I}, C-4^{II}, C-4^{III}, C-5, C-5^{I}, C-5^{III}), 69.16, 68.96, 67.36, 61.19 and 60.97 (*C*H_2, C-5^{II}, C-6, C-6^{I}, C-6^{III}), 47.87 (*C*H_2), 28.24 (*C*H_2). MALDI-TOFMS: calcd for $C_{26}H_{45}N_3O_{20}$: 719.26 [M]. Found: 742.30 $[M+Na]^+$.

3.22. 3-Aminopropyl β-D-galactopyranosyl-(1→6)-[α-L-arabinofuranosyl-(1→3)]-β-D-galactopyranosyl-(1→6)-β-D-galactopyranoside (25)

To a solution of compound **18** (15 mg, 0.02 mmol) in H_2O (5 mL) was added 10% Pd/C. After stirring for 2 h under H_2 at room temperature, the mixture was filtered through Celite. The filtrate was concentrated. The residue was lyophilized to give **25** (12 mg, 82%) as a white solid. $[\alpha]_D$ −21.3 (*c* 0.09 in H_2O); ^{1}H NMR (D_2O): δ 5.22 (s, 1H, H-1^{II}), 4.54, 4.44 and 4.43 (3d, 3H, *J* 8 Hz, H-1, H-1^{I}, H-1^{III}), 4.19 (s, 1H, H-2^{II}), 4.16–3.59 (m, 24H), 3.57–3.47 (m, 2H, H-2^{I}, H-2^{III}), 3.09 (t, 2H, *J* 7 Hz, CH_2), 2.02–1.91 (m, 2H, CH_2); ^{13}C NMR (D_2O): δ 109.30 (C-1^{II}), 103.35 (C-1), 103.04, 102.73 (C-1^{I}, C-1^{III}), 83.77 (C-2^{II}), 81.25, 80.10, 76.46, 75.10, 73.63, 73.53, 72.65, 72.50, 70.66, 70.60, 69.74, 68.55 and 68.39 (C-2, C-2^{I}, C-2^{III}, C-3, C-3^{I}, C-3^{II}, C-3^{III}, C-4, C-4^{I}, C-4^{II}, C-4^{III}, C-5, C-5^{I}, C-5^{III}), 69.32, 69.06, 67.96, 61.13 and 60.96 (*C*H_2, C-5^{II}, C-6, C-6^{I}, C-6^{III}), 37.50 (*C*H_2), 27.43 (*C*H_2). MALDI-TOFMS: calcd for $C_{26}H_{47}NO_{20}$: 693.27 [M]. Found: 716.31 $[M+Na]^+$.

3.23. 3-Azidopropyl α-L-arabinofuranosyl-(1→3)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-[α-L-arabinofuranosyl-(1→3)]-β-D-galactopyranosyl-(1→6)-β-D-galactopyranoside (26)

To a solution of compound **23** (108 mg, 0.04 mmol) in CH_2Cl_2 (2 mL) was added MeOH (10 mL) and the mixture was treated as described for the preparation of **24** to give **26** (35 mg, 86%) as a colourless syrup. $[\alpha]_D$ −34.3 (*c* 0.10 in H_2O); ^{1}H NMR (D_2O): δ 5.24 (s, 2H, H-2^{II}, H-2^{V}), 4.56, 4.52, 4.48 and 4.43 (4d, 4H, *J* 8 Hz, H-1, H-1^{I}, H-1^{III}, H-1^{IV}), 4.22 (s, 2H), 4.19–3.62 (m, 32H), 3.59–3.51 (m, 2H), 3.48 (t, 2H, *J* 7 Hz, CH_2), 2.00–1.88 (m, 2H, CH_2); ^{13}C NMR (D_2O): δ 109.23 (C-1^{II}, C-1^{V}), 103.38, 103.10, 103.02, 102.79 (C-1, C-1^{I}, C-1^{III}, C-1^{IV}), 83.82, 81.28, 80.26, 80.12, 76.52, 75.12, 74.95, 73.74, 73.39, 72.71, 72.56, 70.66, 69.88, 69.81, 68.62 and 68.46 (C-2, C-2^{I}, C-2^{II},C-2^{III}, C-2^{IV}, C-2^{V}, C-3, C-3^{I}, C-3^{II}, C-3^{III}, C-3^{IV}, C-3^{V}, C-4, C-4^{I}, C-4^{II}, C-4^{III}, C-4^{IV}, C-4^{V}, C-5, C-5^{I}, C-5^{III}, C-5^{IIII}), 69.27, 69.14, 67.38, 61.21 and 60.96 (*C*H_2, C-5^{II}, C-5^{V}, C-6, C-6^{I}, C-6^{III}, C-6^{IV}), 47.89 (*C*H_2), 28.25 (*C*H_2). MALDI-TOFMS: calcd for $C_{37}H_{63}N_3O_{29}$: 1013.35 [M]. Found: 1036.49 $[M+Na]^+$.

3.24. 3-Aminopropyl α-L-arabinofuranosyl-(1→3)-β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→6)-[α-L-arabinofuranosyl-(1→3)]-β-D-galactopyranosyl-(1→6)-β-D-galactopyranoside (27)

A solution of compound **26** (30 mg, 0.029 mmol) in water (15 mL) was treated as described for the preparation of **25** to give **27** (25 mg, 86%) as a white solid. $[\alpha]_D$ −28.3 (*c* 0.11 in H_2O); ^{1}H NMR (D_2O): δ 5.22 (s, 2H, H-1^{II}, H1^{V}), 4.53, 4.50, 4.46 and 4.44 (4d, 4H, *J* 8 Hz, H-1, H-1^{I}, H-1^{III}, H-1^{IV}), 4.20 (s, 2H, H-2^{II}, H-2^{V}), 4.16–3.59 (m, 32H), 3.57–3.47 (m, 2H), 3.09 (t, 2H, *J* 6.5 Hz, CH_2), 2.02–1.91 (m, 2H, CH_2); ^{13}C NMR (D_2O): δ 109.19 (C-1^{II}, C-1^{V}), 103.37 103.08, 102.98 and 102.74 (C-1, C-1^{I}, C-1^{III}, C-1^{IV}), 83.77, 81.25, 80.24, 80.09, 76.47, 74.92, 73.59, 73.39, 72.51, 70.61, 69.84, 69.77, 68.55 and 68.42 (C-2, C-2^{I}, C-2^{II}, C-2^{III}, C-2^{IV}, C-2^{V}, C-3, C-3^{I}, C-3^{II}, C-3^{III}, C-3^{IV}, C-3^{V}, C-4, C-4^{I}, C-4^{II}, C-4^{III}, C-4^{IV}, C-4^{V}, C-5, C-5^{I}, C-5^{III}, C-5^{IV}), 69.30, 67.97, 61.15 and 60.93 (*C*H_2, C-5^{II}, C-5^{V}, C-6, C-6^{I}, C-6^{III}, C-6^{IV}), 37.50 (*C*H_2), 27.45 (*C*H_2). MALDI-TOFMS: calcd for $C_{37}H_{65}NO_{29}$: 987.36 [M]. Found: 1010.68 $[M+Na]^+$.

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