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Synthesis and conjugation of oligosaccharide analogues of fragments of the immunoreactive glycan part of the circulating anodic antigen of the parasite *Schistosoma mansoni*

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The gut-associated circulating anodic antigen (CAA) is one of the major excretory antigens produced by the parasite *Schistosoma mansoni.* The immunoreactive part of CAA is a threonine-linked polysaccharide composed of long stretches of the unique repeating disaccharide →6)-[β-D-Glc*p*A-(1→3)]-β-D-Gal*p*NAc-(1→. Previously, using surface plasmon resonance and ELISA techniques, it has been shown that some anti-CAA IgM monoclonal antibodies (MAbs) also recognize members of a series of bovine serum albumin (BSA)-coupled synthetic di- to penta-saccharide fragments of the CAA glycan. To generate information on the molecular level about the glycan specificity of the relevant IgM MAbs, two series of oligosaccharides related to the CAA disaccharide epitope were synthesized, and coupled to BSA. The first three analogues, β-D-Glc*p*A-(1→3)-β-D-Glc*p*NAc-(1→O), β-D-Glc*p*NAc-(1→6)-[β-D-Glc*p*A-(1→3)]-β-D-Glc*p*NAc-(1→O), and β-D-Glc*p*A-(1→3)-β-D-Glc*p*NAc-(1→6)-[β-D-Glc*p*A-(1→3)]-β-D-Glc*p*NAc-(1→O), wherein the native β-D-Gal*p*NAc moiety was replaced by β-D-Glc*p*NAc, were synthesized to investigate the specificity of the selected MAbs to the carbohydrate backbone of CAA. The second series of analogues, β-D-Glc*p*6*S*-(1→3)-β-D-Gal*p*NAc-(1→O), β-D-Gal*p*NAc-(1→6)-[β-D-Glc*p*6*S*-(1→3)]-β-D-Gal*p*NAc-(1→O), and β-D-Glc*p*6*S*-(1→3)-*β*-D-Gal*p*NAc-(1→6)-[β-D-Glc*p*6*S*-(1→3)]-β-D-Gal*p*NAc-(1→O), wherein the native β-D-Glc*p*A moiety was replaced by β-D-Glc*p*6*S*, was synthesized to evaluate the importance of the type/nature of the charge of CAA for the MAb recognition.

Introduction

One of the most prevalent tropical diseases is schistosomiasis, otherwise known as bilharzia, which is caused by a parasitic blood fluke of the genus *Schistosoma.* The intriguing and complex life cycle of this worm involves several parasitic stages in the intermediate (fresh-water snails) and definitive host, alternated by two larvae stages.[1] Owing to the regional occurrence of the intermediate host, the disease is limited to tropical and subtropical areas, where an estimated 200 million people are infected and suffer from the debilitating effects of this disease.[2] The control strategies against schistosomiasis are normally built on the results of diagnosic tests. The microscopic demonstration of the parasite's eggs on faeces or in urine is the more widespread tool for the diagnosis of *Schistosoma* infections in epidemic areas.

In recent years a variety of immunological techniques have been described in the literature as alternative techniques to faecal or urinary egg counts.[3–6] An early and strong humoral immune response to schistosomes is directed to glycan epitopes of a number of circulating antigens, in particular the gut-associated circulating anodic antigen (CAA) and circulating cathodic antigen (CCA).[3] Moreover, several studies have demonstrated a strong correlation between antigen levels and the number of adult worms,[7,8] and that antigen levels decreased rapidly following successful chemotherapy.[8] For the assessment of a cure and for the diagnosis of active infections in endemic areas, the method of choice is the determination of CAA or CCA in the serum or urine of infected subjects.[6] So far, a specificity of virtually 100% was found at the ELISA demonstration of CAA in serum, while for CCA, false positive results were occasionally observed.[9]

The major immunogenic character of CAA is carried by an O-linked polysaccharide chain composed of the unique disaccharide repeating unit →6)-[β-D-Glc*p*A-(1→3)]-β-D-Gal*p*NAc-(1→.[10] The uniqueness of the primary structure of this polysaccharide chain may be responsible for the absolute specificity of the CAA immunodiagnostic assays. In a previous study, a panel of monoclonal antibodies (MAbs) raised against *S. mansoni* adult worm antigens was screened for recognition of synthetic di- to penta-saccharide fragments of the CAA polysaccharide, multivalently presented as bovine serum albumin (BSA) conjugates.[11,12] The results showed that several MAbs, especially of the IgM class, already recognized the disaccharide unit β-D-Glc*p*A-(1→3)-β-D-Gal*p*NAc-(1→O). In order to understand in molecular detail the specificity of the *anti*-carbohydrate MAbs, we synthesized two series of structures (Fig. 1) related to the CAA epitope, and conjugated these oligosaccharides to BSA, using squaric diester chemistry. The first series of synthetic analogues, β-D-Glc*p*A-(1→3)-β-D-Glc*p*NAc-(1→O) (**1**), β-D-Glc*p*NAc-(1→6)-[β-D-Glc*p*A-(1→3)]-β-D-Glc*p*NAc-(1→O) (**2**), and β-D-Glc*p*A-(1→3)-β-D-Glc*p*NAc-(1→6)-[β-D-Glc*p*A-(1→3)]-β-D-Glc*p*NAc-(1→O) (**3**), has the native β-D-Gal*p*NAc residue replaced by β-D-Glc*p*NAc to evaluate the importance of the hydroxyl function HO4 in the carbohydrate backbone for the MAb recognition. In the other series of structures, β-D-Glc*p*6*S*-(1→3)-β-D-Gal*p*NAc-(1→O) (**4**), β-D-Gal*p*NAc-(1→6)-[β-D-Glc*p*6*S*-(1→3)]-β-D-Gal*p*NAc-(1→O) (**5**), and β-D-Glc*p*6*S*-(1→3)-β-D-Gal*p*NAc-(1→6)-[β-D-Glc*p*6*S*-(1→3)]-β-D-Gal*p*NAc-(1→O) (**6**), the native β-D-Glc*p*A moiety was replaced by β-D-Glc*p*6*S* in order to investigate the influence of the nature of charge on the MAb recognition.

Results and discussion

Synthesis of oligosaccharide analogues 1–3 containing β-D-Glc*p*NAc instead of β-D-Gal*p*NAc moieties

In the synthetic routes to target oligosaccharides **1**–**3**, four earlier reported monosaccharide building blocks were used, namely, **7**, **8**, **11**, and **14**. In contrast to our earlier approach of preparing fragments of the native CAA glycan, which included a

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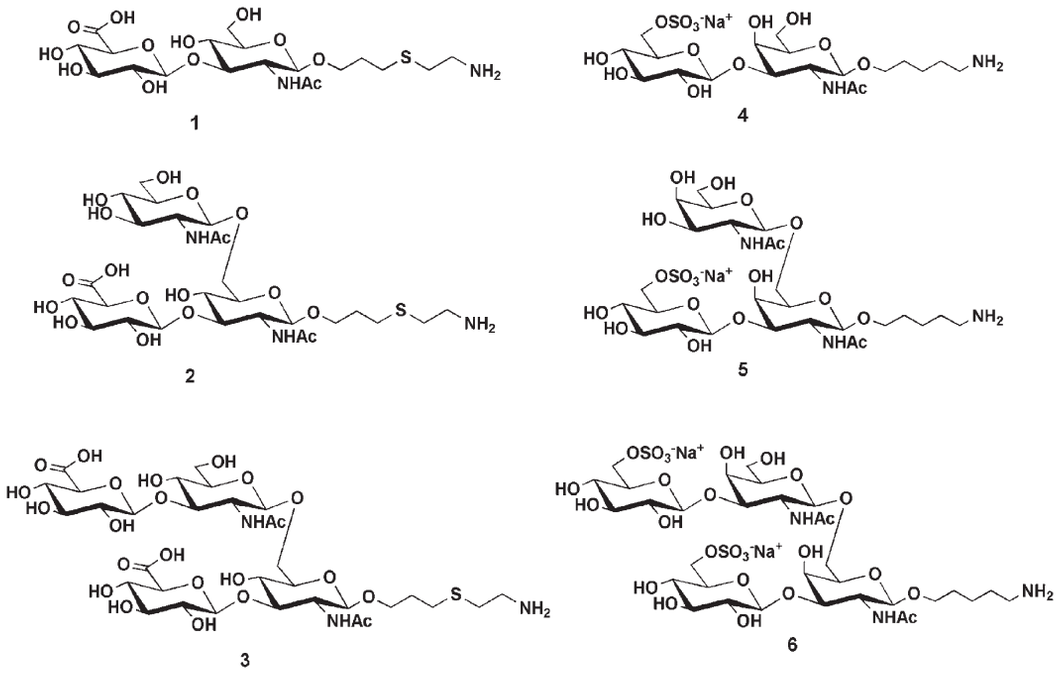


Fig. 1 Target oligosaccharides **1**–**6**.

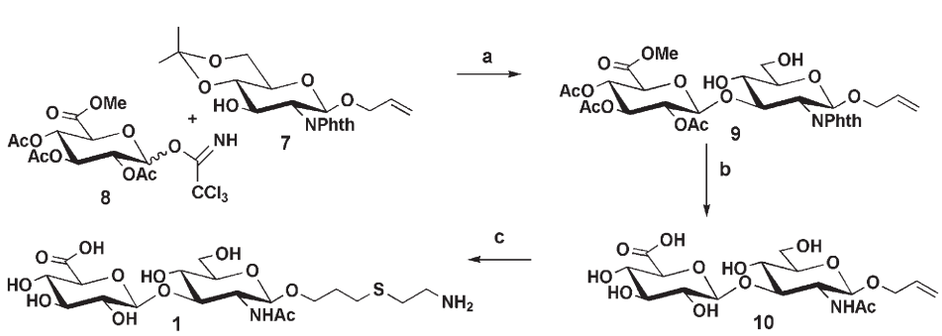
time-consuming C6 oxidation step at later stages of the synthesis to generate glucuronic acid units, here, methyl 2,3,4-tri-*O*-acetyl-α,β-D-glucopyranosyluronate trichloroacetimidate **8** has been chosen.

For the synthesis of disaccharide **1**, acceptor allyl 2-deoxy-4,6-*O*-isopropylidene-2-phthalimido-β-D-glucopyranoside **7**[13] was coupled with donor methyl 2,3,4-tri-*O*-acetyl-α,β-D-glucopyranosyluronate trichloroacetimidate **8**,[14] using trimethylsilyl triflate as a promoter (Scheme 1). After removal of the isopropylidene group under acidic conditions,[15] disaccharide **9** was obtained in a moderate yield (31%). The main side reaction during the condensation is the formation of an orthoester intermediate that could not be completely converted into the desired product. Alternative attempts, such as using different temperatures, promoter concentrations, and protecting groups for the donor, did not improve the yield. For deprotection of the disaccharide **9**, the methyl ester and acetyl groups were saponified with 3 M aq. NaOH in 5:1 methanol–water.[14] Subsequent dephthaloylation was carried out with 1,2-diaminoethane in *n*-butanol at 90 °C,[16] and the formed product was *N*-acetylated with acetic anhydride in methanol at 0 °C[17] to give the fully deprotected allyl glycoside **10** (52%). Finally, **10** was reacted with cysteamine hydrochloride[18] under radical conditions (UV-irradiation) to afford the amino-spacer-containing disaccharide **1** (76%).

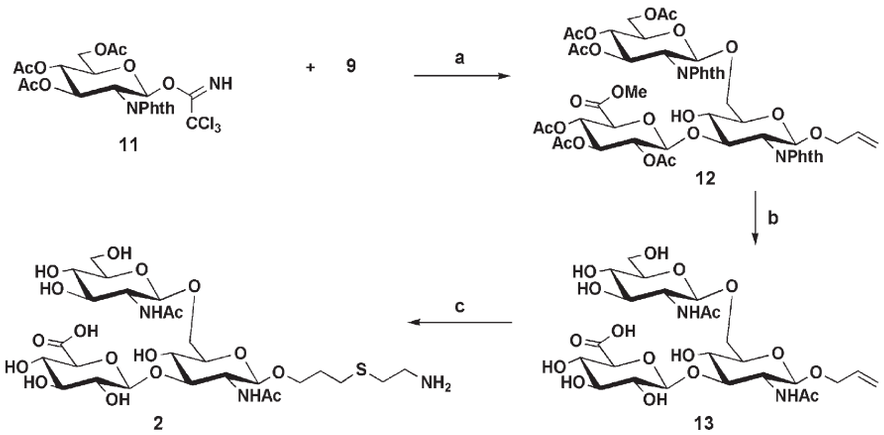
For the synthesis of trisaccharide **2**, 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate **11**[19] was regioselectively-coupled with disaccharide acceptor **9**, at 0 °C, using trimethylsilyl triflate as a promoter (→**12**, 86%; Scheme 2). Saponification of **12** with 3 M aq. NaOH in 5:1 methanol–water, followed by dephthaloylation with 1,2-diaminoethane in *n*-butanol at 90 °C, and subsequent *N*-acetylation using acetic anhydride in methanol at 0 °C, rendered allyl glycoside **13** (42%). Elongation of the allyl spacer of **13** with cysteamine resulted in target trisaccharide **2** (48%).

For the synthesis of tetrasaccharide **3**, disaccharide donor **17** was prepared (Scheme 3). Coupling of donor **8**[14] with acceptor 4-methoxyphenyl 2-deoxy-4,6-*O*-isopropylidene-2-phthalimido-β-D-glucopyranoside **14**,[20] using trimethylsilyl triflate as a promoter, followed by removal of the isopropylidene group under acidic conditions, gave disaccharide **15** (71%). As mentioned already for **9**, this condensation reaction also proceeds *via* orthoester formation and subsequent conversion into the desired adduct. The good yield obtained here is probably due to a different protection of the anomeric center of acceptor **14**. After conventional acetylation of the HO4 and HO6 groups of **15** (→**16**, quantitative), oxidative removal of the anomeric 4-methoxyphenyl group, using ammonium cerium(IV) nitrate,[21] followed by imidation[19] of the hemiacetal, resulted in disaccharide donor **17** (63%).

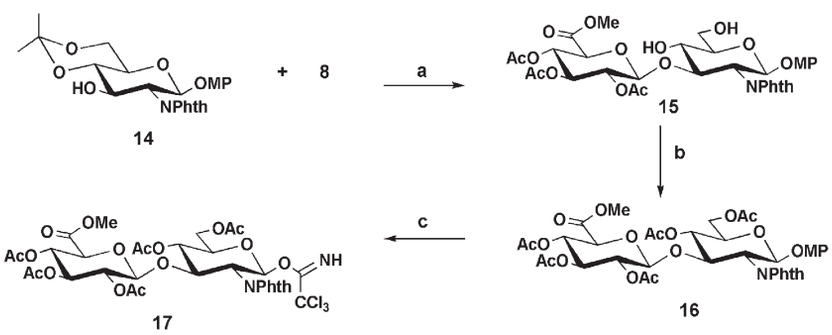
Regioselective coupling of disaccharide donor **17** with disaccharide acceptor **9** (Scheme 4), using trimethylsilyl triflate as a promoter, gave tetrasaccharide **18** (90%). Saponification of **18** with 3 M aq. NaOH in 5:1 methanol–water, followed by dephthaloylation and *N*-acetylation afforded allyl glycoside **19** (42%). Finally, **19** was elongated with cysteamine under UV-light, to obtain the amino-spacer-containing tetrasaccharide **3** (56%).



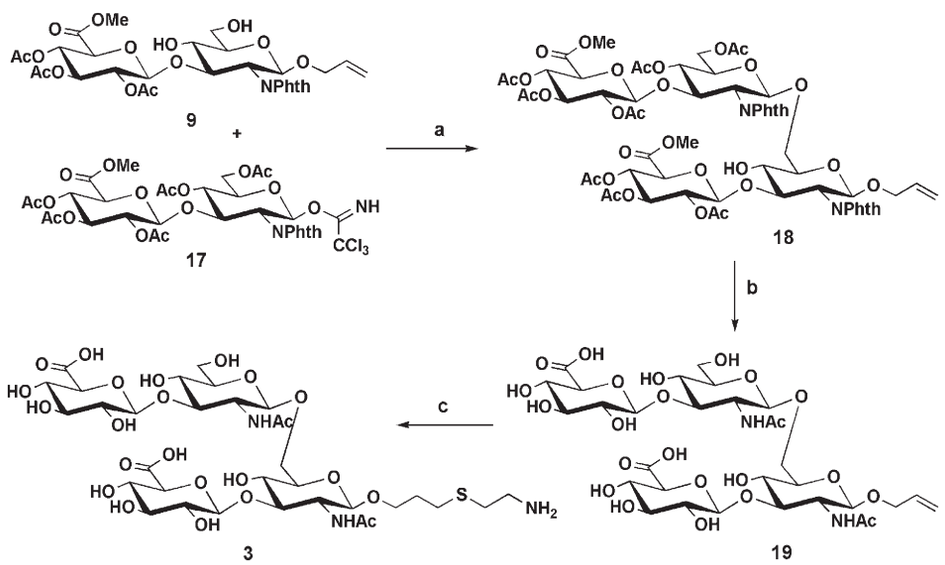
Scheme 1 *Reagents and conditions*: **a**, (i) **7**, **8** (2 equiv.), TMSOTf, CH_2Cl_2, 30 min, 0 °C/2 h, rt; (ii) water, TFA, CH_2Cl_2, overnight, 31% over two reaction steps; **b**, (i) 3 M aq. NaOH, 5:1 MeOH–water, 3 h; (ii) 1:2 1,2-diaminoethane–*n*-butanol, overnight, 90 °C; (iii) acetic anhydride, MeOH, 3 h, 0 °C, 52% over three reaction steps; **c**, cysteamine hydrochloride, UV-light, water, 2 h, 76%.



Scheme 2 *Reagents and conditions*: **a**, **9**, **11** (1.5 equiv.), TMSOTf, CH_2Cl_2, 1 h, 0 °C, 86%; **b**, (i) 3 M aq. NaOH, 5 : 1 MeOH–water, 3 h; (ii) 1 : 2 1,2-diaminoethane–*n*-butanol, overnight, 90 °C; (iii) acetic anhydride, MeOH, 3 h, 0 °C, 42% over three reaction steps; **c**, cysteamine hydrochloride, UV-light, water, 2 h, 48%.



Scheme 3 *Reagents and conditions*: **a**, (i) **14**, **8** (1.5 equiv.), TMSOTf, CH_2Cl_2, 45 min, 0 °C/30 min, rt; (ii) water, TFA, CH_2Cl_2, 1 h, 71% over two reaction steps; **b**, 1 : 1 pyridine–acetic anhydride, CH_2Cl_2, overnight, quantitative; **c**, (i) CAN, 1 : 1 : 1 toluene–acetonitrile–water, 45 min; (ii) trichloroacetonitrile, DBU, CH_2Cl_2, overnight, 63% over two reaction steps. MP = $C_6H_4OCH_3$.



Scheme 4 *Reagents and conditions*: **a**, **9**, **17** (1.5 equiv.), TMSOTf, CH_2Cl_2, 1 h, 0 °C, 90%; **b**, (i) 3 M aq. NaOH, 5 : 1 MeOH–water, 3 h; (ii) 1 : 2 1,2-diaminoethane–*n*-butanol, overnight, 90 °C; (iii) acetic anhydride, MeOH, 3 h, 0 °C, 42% over three reaction steps; **c**, cysteamine hydrochloride, UV-light, water, 2 h, 56%.

Synthesis of oligosaccharide analogues 4–6 containing β-D-Glc*p*6*S* instead of β-D-Glc*p*A moieties

In the synthetic routes to target oligosaccharides **4**, **5**, and **6** (Fig. 1), the disaccharide 4-methoxyphenyl (6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-galactopyranoside **24** was used as a central building block, easy to transform into either a donor or an acceptor. The levulinoyl group at HO6 of the β-D-glucose residue can be selectively removed, and subsequently sulfated to prepare the desired mimic structures. Coupling of donor 6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-α-D-glucopyranosyl trichloroacetimidate **20**[15] with acceptor 4-methoxyphenyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside **21**[22] using trimethylsilyl triflate as a promoter, followed by the removal of the benzylidene group under acidic conditions,[15] afforded disaccharide **22** (78%) (Scheme 5). It should be noted that the use of an isopropylidene instead of a benzylidene protecting group gives rise to much lower yields. A *tert*-butyldiphenylsilyl group was selectively introduced at HO6 of **22** using *tert*-butyldiphenylsilyl chloride in the presence of 2 : 1 pyridine–triethylamine and a catalytic amount of 4-dimethylaminopyridine, to give **23** in

91% yield.[23] At this stage, the β-D-glucosamine residue was transformed into the desired β-D-galactosamine residue by epimerization of the HO4 function.[16] To this end, **23** was treated with trifluoromethanesulfonic anhydride in the presence of pyridine and a catalytic amount of 4-dimethylaminopyridine. The S_N2 displacement of the introduced triflate group at O4 using tetrabutylammoniun acetate in DMF resulted in the desired 4-*O*-acetylated disaccharide **24** (70%).

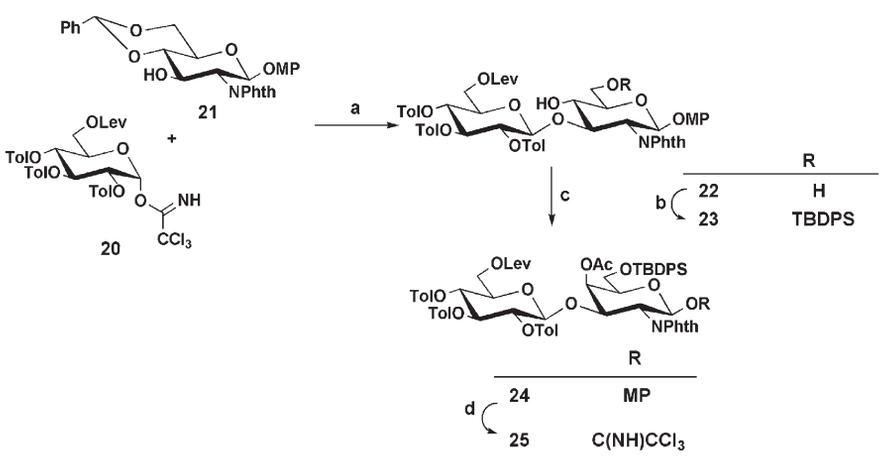
For the synthesis of disaccharide **4**, the anomeric 4-methoxyphenyl group was oxidatively removed using ammonium cerium(IV) nitrate, and subsequent imidation of the hemiacetal yielded disaccharide donor **25** (61%). Coupling of **25** with 5-azidopentanol, using trimethylsilyl triflate as a promoter resulted in the azido-spacer-containing disaccharide **26** (85%; Scheme 6). Removal of the *tert*-butyldiphenylsilyl group, under neutral conditions, using tetrabutylammonium fluoride (→**27**, 91%),[24] followed by acetylation under conventional conditions gave disaccharide **28** (83%). After selective removal of the levulinoyl group using hydrazine acetate (→**29**, 91%),[25,26] sulfation of the liberated HO6′ group was accomplished using the sulfur trioxide trimethylamine complex (→**30**, 50%).[27] Dephthaloylation/deacylation with ethanolic 33% methylamine (7 days), and *N*-acetylation with acetic anhydride in methanol at 0 °C,[16] yielded azido-spacer-containing disaccharide **31** (76%). Finally, catalytic hydrogenation of the azido group of **31** using 10% palladium on charcoal and sodium borohydride[11] gave the amino-spacer-containing disaccharide **4** (71%).

For the synthesis of trisaccharide **5**, disaccharide acceptor **27** was coupled with donor 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl trichloroacetimidate **32**,[28] using trimethylsilyl triflate as a promoter, to yield trisaccharide **33** (58%; Scheme 7). As the 6-*O*-acetylated variant of **27** is the main side product isolated from this condensation reaction, this moderate yield can be explained by the loss of acceptor during coupling due to *in situ O*-acetyl migration from HO4 to HO6. Delevulinoylation of **33** using hydrazine acetate (→**34**, 74%), followed by sulfation of the generated HO6″ group yielded sulfated trisaccharide **35** in 82% overall yield. Finally, dephthaloylation/deacylation followed by *N*-acetylation afforded the azido-spacer-containing trisaccharide **36** (74%), of which the azido group was selectively hydrogenated to give the amino-spacer-containing trisaccharide **5** (89%).

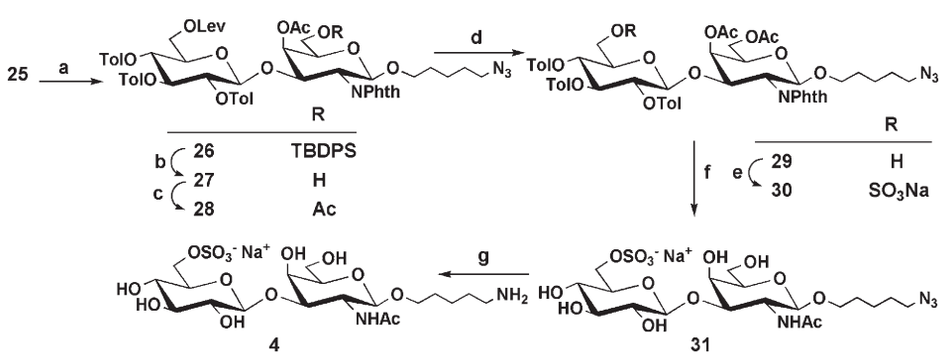
In order to synthesize tetrasaccharide **6**, disaccharide donor **38** was prepared from disaccharide building block **24** in a two-step reaction sequence (Scheme 8). Removal of the *tert*-butyldiphenylsilyl group of **24** using tetrabutylammonium fluoride was directly followed by conventional acetylation of the generated HO6 function (→**37**, 84%). Oxidative removal of the anomeric 4-methoxyphenyl group with ammonium cerium(IV) nitrate, followed by imidation gave **38** in 58% overall yield. Condensation of **27** with **38** in the presence of trimethylsilyl triflate afforded tetrasaccharide **39** (70%). Treatment of **39** with hydrazine acetate (→**40**, 75%), sulfation of the two generated HO6 groups with the sulfur trioxide trimethylamine complex (→**41**, 77%), and dephthaloylation/deacylation followed by *N*-acetylation gave the disulfated azido-spacer-containing tetrasaccharide **42** (62%). Finally, catalytic hydrogenation of the azido group yielded the amino-spacer-containing tetrasaccharide **6** (71%).

Preparation of neoglycoconjugates BSA-1–BSA-6

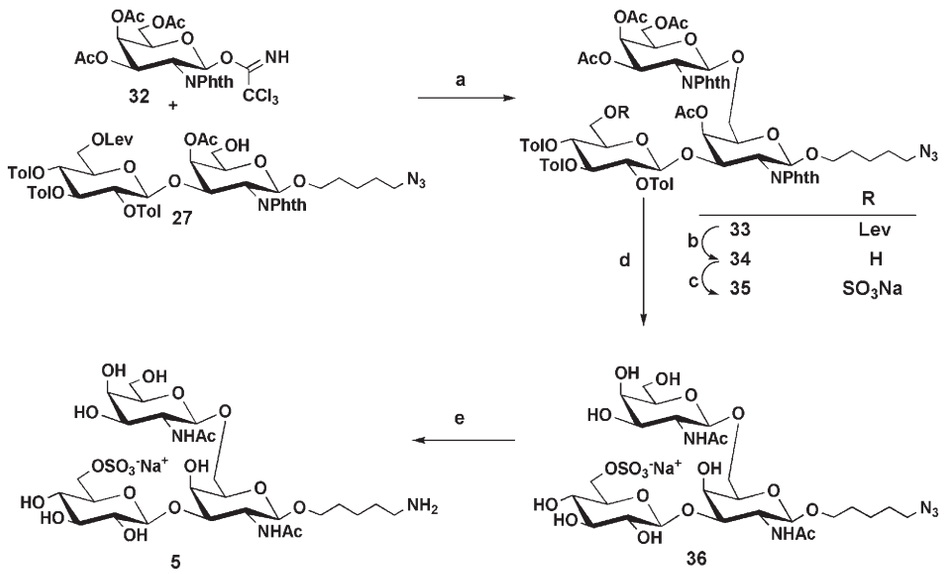
Compounds **1**–**6** were conjugated to pre-treated bovine serum albumin (BSA)[11] using diethyl squarate as a linker. Reaction of the amine functions of **1**–**6** with diethyl squarate was performed in ethanol–50 mM sodium phosphate



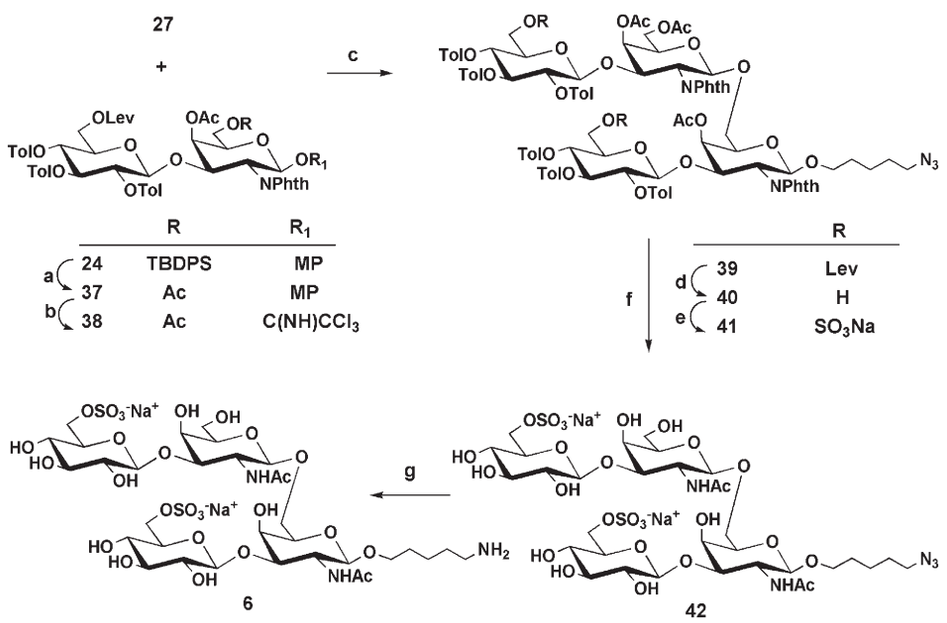
Scheme 5 *Reagents and conditions*: **a**, (i) **21**, **20** (1.5 equiv.), TMSOTf, CH_2Cl_2, 30 min; (ii) water, TFA, CH_2Cl_2, 78% over two reaction steps; **b**, 2 : 1 pyridine–Et_3N, catalytic DMAP, CH_2Cl_2, TBDPSCl, overnight, 91%; **c**, (i) trifluoromethanesulfonic anhydride, pyridine, catalytic DMAP, CH_2Cl_2, 30 min, 0 °C/5 h, rt; (ii) TBAA, DMF, 2 h, 70% over two reaction steps; **d**, (i) CAN, 1 : 1 : 1 toluene–acetonitrile–water, 2 h; (ii) trichloroacetonitrile, DBU, CH_2Cl_2, 3 h, 61% over two reaction steps. Lev = $COCH_2CH_2COCH_3$; MP = $C_6H_4OCH_3$; Ph = C_6H_5; Tol = $COC_6H_4CH_3$; TBDPS = $(CH_3)_3CSi(C_6H_5)_2$.



Scheme 6 *Reagents and conditions*: **a**, **25**, 5-azidopentanol (2 equiv.), TMSOTf, CH_2Cl_2, 30 min, 85%; **b**, 1 M TBAF in THF, HOAc, pH 7, 2 h, 0 °C/4 h, rt, 91%; **c**, 1 : 1 pyridine–acetic anhydride, overnight, 83%; **d**, NH_2NH_2·HOAc, EtOH, toluene, 2 h, 91%; **e**, SO_3·NMe_3, DMF, 48 h, 50 °C, 50%; **f**, (i) 33% NH_2Me in EtOH, 7 d; (ii) acetic anhydride, MeOH, 3 h, 0 °C, 76% over two reaction steps; **g**, 0.05 M aq. NaOH, 10% Pd–C, $NaBH_4$, water, 45 min, 71%. Lev = $COCH_2CH_2COCH_3$; Tol = $COC_6H_4CH_3$; TBDPS = $(CH_3)_3CSi(C_6H_5)_2$.



Scheme 7 *Reagents and conditions*: **a**, **27**, **32** (1.5 equiv.), TMSOTf, CH_2Cl_2, 15 min, 0 °C, 58%; **b**, NH_2NH_2·HOAc, EtOH, toluene, 2 h, 74%; **c**, SO_3·NMe_3, DMF, 48 h, 50 °C, 82%; **d**, (i) 33% NH_2Me in EtOH, 7 d; (ii) acetic anhydride, MeOH, 3 h, 0 °C, 74% over two reaction steps; **e**, 0.05 M aq. NaOH, 10% Pd–C, $NaBH_4$, water, 1 h, 89%. Lev = $COCH_2CH_2COCH_3$; Tol = $COC_6H_4CH_3$.



Scheme 8 *Reagents and conditions*: **a**, (i) 1 M TBAF in THF, HOAc, pH 7, 1 h, 0 °C/overnight, rt; (ii) 1 : 1 pyridine–acetic anhydride, overnight, 84% over two reaction steps; **b**, CAN, 1 : 1 : 1 toluene–acetonitrile–water, 2 h; (ii) trichloroacetonitrile, DBU, CH_2Cl_2, 16 h, 58% over two reaction steps; **c**, **27**, **38** (1.5 equiv.), TMSOTf, CH_2Cl_2, 15 min, 70%; **d**, NH_2NH_2·HOAc, EtOH, toluene, 2 h, 75%; **e**, SO_3·NMe_3, DMF, 48 h, 50 °C, 77%; **f**, (i) 33% NH_2Me in EtOH, 7 d; (ii) acetic anhydride, MeOH, 3 h at 0 °C, 62% over two reaction steps; **g**, 0.05 M aq. NaOH, 10% Pd–C, $NaBH_4$, water, 1 h, 71%. Lev = $COCH_2CH_2COCH_3$; MP = $C_6H_4OCH_3$; Tol = $COC_6H_4CH_3$; TBDPS = $(CH_3)_3CSi(C_6H_5)_2$.

buffer (pH 7.2).[29,30] The obtained squarate-linker-containing disaccharides **43** and **46** were purified by solid phase extraction on a C-18 Extract-Clean™ column. However, purification of the larger saccharides (**44**, **45**, **47**, and **48**) needed another protocol; here, column chromatography on silica gel (7.5 : 1.5 : 1.0 EtOAc–MeOH–water) was used. The isolated squarate-linker-containing saccharides **43**–**48** were directly-coupled to BSA in 0.1 M sodium bicarbonate buffer at pH 9.0 (Fig. 2).

As already observed in previous studies,[11,31] the conjugation yield of an oligosaccharide to BSA decreases as its size increases. The average number of carbohydrate fragments incorporated in BSA was measured using MALDI-TOF MS analysis by determination of the center of the distribution of the single-charged molecular ion (Fig. 3). The neoglycoconjugates **BSA-1**–**BSA-6** have been applied to a panel of MAbs against *Schistosoma mansoni* antigens in immunoreactivity studies, using ELISA and surface plasmon resonance detection. The results of this work will be published elsewhere.

Experimental

General procedures

All chemicals were of reagent grade, and were used without further purification. Reactions were monitored by TLC on Silica Gel $60F_{254}$ (Merck); after examination under UV-light, compounds were visualized by heating with 10% methanolic H_2SO_4, orcinol (2 mg cm^{-3}) in 20% methanolic H_2SO_4, or ninhydrin (1.5 mg cm^{-3}) in 38 : 1.75 : 0.25 1-BuOH–H_2O–HOAc. In the work-up procedures of reaction mixtures, organic solutions were washed with appropriate amounts of the indicated aqueous solutions, then dried with $MgSO_4$, and concentrated under reduced pressure at 30–50 °C on a water bath. Column chromatography was performed on Silica Gel 60 (Merck, 0.040–0.063 mm). Optical rotations were measured with a Perkin-Elmer 241 polarimeter, using a 10 cm, 1 cm^3 cell. ^1H NMR spectra were recorded at 300 K with a Bruker AC 300 (300 MHz) or a Bruker AMX 500 (500 MHz) spectrometer;

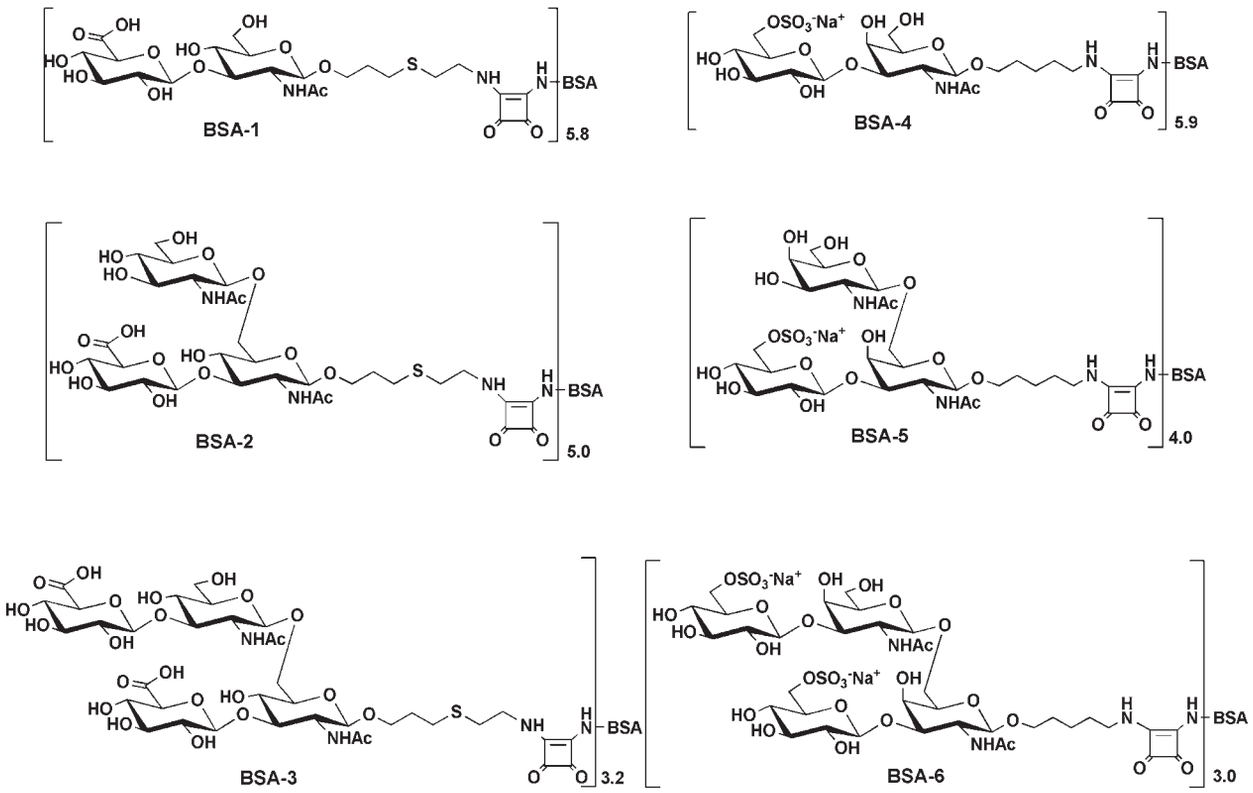


Fig. 2 Neoglycoconjugates **BSA-1**–**BSA-6**.

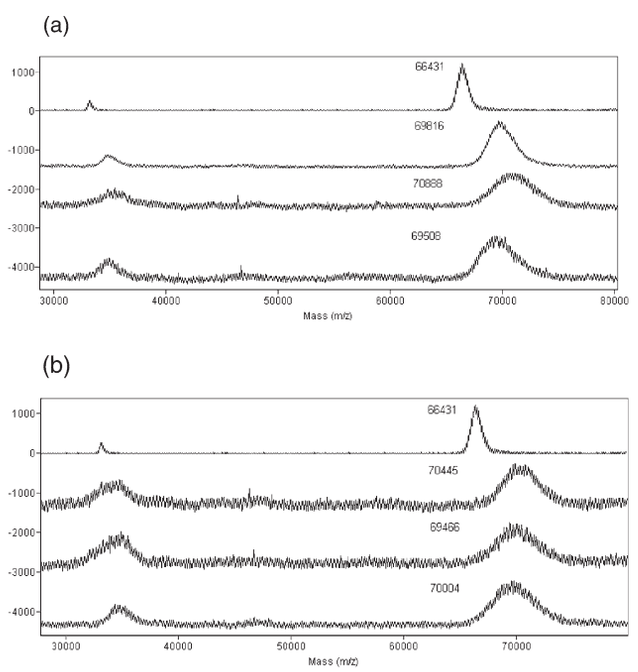


Fig. 3 MALDI-TOF MS spectra: (a) BSA (top), **BSA-1** (n = 5.8, c.e. 58%), **BSA-2** (n = 5.0, c.e. 50%), and **BSA-3** (n = 3.2, c.e. 32%); (b) BSA (top), **BSA-4** (n = 5.9, c.e. 59%), **BSA-5** (n = 4.0, c.e. 40%), and **BSA-6** (n = 3.0, c.e. 30%). n = oligosaccharide loading; c.e. = coupling efficiency.

δ_H values are given in ppm relative to the signal for internal Me_4Si (δ_H = 0, $CDCl_3$) or internal acetone (δ_H = 2.22, D_2O). ^{13}C NMR spectra (APT, 75.5 MHz) were recorded at 300 K with a Bruker AC 300 spectrometer; δ_C values are given in ppm relative to the signal of $CDCl_3$ (δ_C = 77.1, $CDCl_3$) or internal acetone (δ_C = 30.9, D_2O). Two-dimensional ^1H–^1H TOCSY (mixing times 7 and 100 ms) and ^1H–^{13}C correlated HSQC spectra were recorded at 300 K with a Bruker AMX 500 spectrometer. Exact masses were measured by matrix-assisted laser desorption ionization time-of-flight mass spectrometry using a Voyager-DE Pro (Applied Biosystems) instrument in the reflector mode at a resolution of 5000 FWHM. 2,4-Dihydroxybenzoic acid in H_2O (5 mg cm^{-3}) was used as a matrix. A ladder of maltose oligosaccharides (G3–G13) was added as internal standard.

Allyl (methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-2-deoxy-2-phthalimido-β-D-glucopyranoside 9

A solution of allyl 2-deoxy-4,6-*O*-isopropylidene-2-phthalimido-β-D-glucopyranoside[13] (**7**; 0.55 g, 1.41 mmol) and methyl 2,3,4-tri-*O*-acetyl-α,β-D-glucopyranosyluronate trichloroacetimidate[14] (**8**; 1.35 g, 2.82 mmol) in dry CH_2Cl_2 (20 cm^3), containing activated molecular sieves (4 Å, 1 g), was stirred for 1 h at rt, then TMSOTf (69 mm^3, 0.35 mmol) was added at 0 °C. The mixture was stirred for 30 min at 0 °C and 2 h at rt, when TLC (95 : 5 CH_2Cl_2–acetone) showed the formation of a new product (R_f = 0.56). After neutralization with dry pyridine and filtration, the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. To a solution of the residue in CH_2Cl_2 (20 cm^3) and water (0.1 cm^3) was added TFA (1 cm^3). The mixture was stirred overnight, when TLC (95 : 5 CH_2Cl_2–acetone) showed the removal of the isopropylidene group to be complete (R_f = 0.24). Then, the mixture was washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. Column chromatography (9 : 1 CH_2Cl_2–acetone) of the residue gave **9** (0.3 g, 31%), isolated as a yellow foam; $[\alpha]_D^{20}$ −16 (c 0.5 in $CHCl_3$); δ_H(300 MHz; $CDCl_3$) 1.93, 1.99, and 2.16 (each 3 H, 3 × s, 3 × Ac), 3.54 (1 H, m, H-5), 3.67 (1 H, br t, H-4), 3.76 (3 H, s, $COOCH_3$), 3.96 (1 H, m, H-6), 4.01 and 4.22 (each 1 H, 2 × m, $OCH_2CH{=}CH_2$), 4.05 (1 H, d, $J_{H\text{-}4',H\text{-}5'}$ 9.6 Hz, H-5′), 4.22 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.5, $J_{H\text{-}2,H\text{-}3}$ 10.8, H-2), 4.46 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.8, H-1′), 4.53 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 8.1, H-3), 4.87 (1 H, br t, H-2′), 5.05 (1 H, d, H-1), 5.64 (1 H, m, $OCH_2CH{=}CH_2$), 7.78 and 7.86 (each 2 H, 2 × m, Phth); δ_C(75.5 MHz; $CDCl_3$) 20.4 ($COCH_3$), 53.2 ($COOCH_3$), 54.9 (C-2), 63.0 (C-6), 69.9 ($OCH_2CH{=}CH_2$), 68.7, 70.6, 71.0, 71.4, 71.9, 75.5, and 81.8 (C-3, C-4, C-5, C-2′, C-3′, C-4′, and C-5′), 97.4 and 100.0 (C-1 and C-1′), 117.4 ($OCH_2CH{=}CH_2$), 133.5 ($OCH_2CH{=}CH_2$), 123.6 and 134.6 [$N(CO)_2C_6H_4$]; high resolution MALDI-TOF MS, m/z found M+Na 688.185, $C_{30}H_{35}NNaO_{16}$ requires 688.185.

Allyl (β-D-glucopyranosyluronic acid)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside 10

To a solution of **9** (28 mg, 42 μmol) in 5:1 MeOH–water (3 cm^3) was added, at 0 °C, 3 M aq. NaOH (1 cm^3). The mixture was stirred for 3 h at room temperature, neutralized with Dowex 50 X 8 H^+ resin, filtered, and concentrated. A solution of the residue in 2:1 *n*-butanol–1,2-diaminoethane (6 cm^3) was stirred overnight at 90 °C, then co-concentrated with toluene. To a solution of the residue in dry MeOH (5 cm^3) was added, at 0 °C, acetic anhydride (100 mm^3). The mixture was stirred for 3 h, then concentrated. Size-exclusion chromatography (Bio-Gel P-2, 100 mM NH_4HCO_3) gave **10** (9.4 mg, 52%), isolated after lyophilization from water, as a white amorphous powder; $[\alpha]_D^{20}$ −96 (*c* 0.6 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 2.02 (3 H, s, NAc), 3.34 (1 H, br t, H-2′), 3.45 (1 H, m, H-5), 3.49 and 3.50 (each 1 H, 2 × br t, H-3′ and H-4′), 3.52 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 8.2 Hz, $J_{H\text{-}4,H\text{-}5}$ 9.8 Hz, H-4), 3.72 (1 H, d, $J_{H\text{-}4',H\text{-}5'}$ 9.3, H-5′), 3.73 (1 H, br t, H-3), 3.76 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 5.5, $J_{H\text{-}6a,H\text{-}6b}$ 12.4, H-6b), 3.84 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, $J_{H\text{-}2,H\text{-}3}$ 10.2, H-2), 3.91 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 2.2, H-6a), 4.16 and 4.33 (each 1 H, 2 × m, $OCH_2CH{=}CH_2$), 4.46 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.8, H-1′), 4.58 (1 H, d, H-1), 5.25 and 5.29 (each 1 H, 2 × m, $OCH_2CH{=}CH_2$), 5.90 (1 H, m, $OCH_2CH{=}CH_2$); δ_C(125 MHz; D_2O) 22.9 ($NDCOCH_3$), 55.1 (C-2), 61.5 (C-6), 69.5 (C-4), 71.2 ($OCH_2CH{=}CH_2$), 72.4 and 76.2 (C-3′ and C-4′), 73.5 (C-2′), 76.3 (C-5), 76.5 (C-5′), 83.7 (C-3), 100.7 (C-1), 103.7 (C-1′), 119.0 ($OCH_2CH{=}CH_2$), 134.1 ($OCH_2CH{=}CH_2$); high resolution MALDI-TOF MS, *m*/*z* found M+H 438.164, $C_{17}H_{28}NO_{12}$ requires 438.161.

3-(2-Aminoethylthio)propyl (β-D-glucopyranosyluronic acid)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside 1

A solution of **10** (5 mg, 11.4 μmol) and cysteamine hydrochloride (7.1 mg, 62.7 μmol) in water (1 cm^3) was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV Lamp. The mixture was loaded directly on to a size-exclusion column (Bio-Gel P-2, 100 mM NH_4HCO_3), yielding **1** (4.5 mg, 76%), isolated after lyophilization from water as a white, amorphous powder; $[\alpha]_D^{20}$ −93 (*c* 0.3 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 1.85 [2 H, m, $OCH_2CH_2CH_2S(CH_2)_2ND_2$], 2.03 (3 H, s, NAc), 2.62 [2 H, br t, $O(CH_2)_2CH_2S(CH_2)_2ND_2$], 2.84 and 3.23 [each 2 H, 2 × br t, $O(CH_2)_3S(CH_2)_2ND_2$], 3.33 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 8.0 Hz, $J_{H\text{-}2',H\text{-}3'}$ 8.6 Hz, H-2′), 3.46 (1 H, m, H-5), 3.48 (1 H, br t, H-4′), 3.50 (1 H, br t, H-3′), 3.52 (1 H, br t, H-4), 3.69 and 3.98 [each 1 H, 2 × m, $OCH_2(CH_2)_2S(CH_2)_2ND_2$], 3.72 (1 H, d, $J_{H\text{-}4',H\text{-}5'}$ 9.6, H-5′), 3.74 (1 H, br t, H-3), 3.75 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 5.7, $J_{H\text{-}6a,H\text{-}6b}$ 12.4, H-6b), 3.81 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.5, $J_{H\text{-}2,H\text{-}3}$ 10.4, H-2), 3.91 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 2.1, H-6a), 4.47 (1 H, d, H-1′), 4.52 (1 H, d, H-1); δ_C(125 MHz; D_2O) 23.0 ($NDCOCH_3$), 27.7 [$O(CH_2)_2CH_2S(CH_2)_2ND_2$], 28.9 and 39.1 [$O(CH_2)_3S(CH_2)_2ND_2$], 29.3 [$OCH_2CH_2CH_2S(CH_2)_2ND_2$], 55.3 (C-2), 61.5 (C-6), 69.4 [$OCH_2(CH_2)_2S(CH_2)_2ND_2$], 69.5 (C-4), 72.4 (C-3′), 73.5 (C-2′), 76.1 (C-4′), 76.2 (C-5), 76.6 (C-5′), 83.3 (C-3), 101.9 (C-1), 103.6 (C-1′); high resolution MALDI-TOF MS, *m*/*z* found M+Na 537.163, $C_{19}H_{34}N_2NaSO_{12}$ requires 537.173.

Allyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-[(methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)]-2-deoxy-2-phthalimido-β-D-glucopyranoside 12

A solution of **9** (50 mg, 75 μmol) and 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate[19] (**11**; 65 mg, 112 μmol) in dry CH_2Cl_2 (2 cm^3), containing activated molecular sieves (4 Å, 0.1 g), was stirred for 1 h at room temperature, then TMSOTf (1.5 mm^3, 7.5 μmol) was added at 0 °C. The mixture was stirred for 1 h at 0 °C, when TLC (9:1 CH_2Cl_2–acetone) showed the formation of a new product (R_f = 0.45). After neutralization with dry pyridine and filtration, the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (9:1 CH_2Cl_2–acetone) of the residue gave **12** (70 mg, 86%), isolated as a white solid; $[\alpha]_D^{20}$ −7 (*c* 0.2 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 1.51, 1.80, 1.87, 1.93, 1.96, and 2.07 (each 3 H, 6 × s, 6 × Ac), 3.21 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 9.8 Hz, $J_{H\text{-}4,H\text{-}5}$ 8.3 Hz, H-4), 3.43 (1 H, m, H-5), 3.65 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 6.3, $J_{H\text{-}6a,H\text{-}6b}$ 11.0, H-6b), 3.67 and 3.87 (each 1 H, 2 × m, $OCH_2CH{=}CH_2$), 3.69 (3 H, s, $COOCH_3$), 3.83 (1 H, m, H-5′), 3.88 (1 H, d, $J_{H\text{-}4'',H\text{-}5''}$ 9.9, H-5″), 3.97 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.4, $J_{H\text{-}2,H\text{-}3}$ 10.7, H-2), 4.12 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.3, $J_{H\text{-}6a',H\text{-}6b'}$ 12.2, H-6a′), 4.20 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 1.4, H-6a), 4.22 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 8.0, H-1″), 4.28 (1 H, br t, H-3), 4.29 (1 H, m, H-6b′), 4.30 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 8.6, $J_{H\text{-}2',H\text{-}3'}$ 10.9, H-2′), 4.63 (1 H, dd, $J_{H\text{-}2'',H\text{-}3''}$ 9.5, H-2″), 4.78 (1 H, d, H-1), 4.86 and 4.90 (each 1 H, 2 × m, $OCH_2CH{=}CH_2$), 4.92 (1 H, br t, H-3″), 5.00 (1 H, br t, H-4″), 5.11 (1 H, dd, $J_{H\text{-}3',H\text{-}4'}$ 9.2, $J_{H\text{-}4',H\text{-}5'}$ 10.1, H-4′), 5.38 (1 H, d, H-1′), 5.40 (1 H, m, $OCH_2CH{=}CH_2$), 5.76 (1 H, dd, H-3′), 7.69 and 7.78 (each 4 H, 2 × m, 2 × Phth); δ_C(125 MHz; $CDCl_3$) 18.8, 19.3, 19.4, 19.5, 19.6, and 19.8 (6 × $COCH_3$), 52.2 ($COOCH_3$), 53.7 (C-2′), 53.8 (C-2), 61.0 (C-6′), 67.6 (C-4″), 68.0 ($OCH_2CH{=}CH_2$), 68.1 (C-4′), 68.5 (C-6), 68.6 (C-4), 69.7 (C-2″), 69.8 (C-3′), 70.2 (C-5″), 70.8 (C-5′), 70.9 (C-3″), 74.1 (C-5), 80.4 (C-3), 95.8 (C-1), 97.9 (C-1′), 98.7 (C-1″), 116.4 ($OCH_2CH{=}CH_2$), 132.4 ($OCH_2CH{=}CH_2$), 122.7 and 133.4 [$N(CO)_2C_6H_4$]; high resolution MALDI-TOF MS, *m*/*z* found M+Na 1105.286, $C_{50}H_{54}N_2NaO_{25}$ requires 1105.291.

Allyl (2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-[(β-D-glucopyranosyluronic acid)-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside 13

To a solution of **12** (26 mg, 24 μmol) in 5:1 MeOH–water (3 cm^3) was added, at 0 °C, 3 M aq. NaOH (1 cm^3). The mixture was stirred for 3 h at room temperature, neutralized with Dowex 50 X 8 H^+ resin, filtered, and concentrated. A solution of the residue in 2:1 *n*-butanol–1,2-diaminoethane (6 cm^3) was stirred overnight at 90 °C, then co-concentrated with toluene. To a solution of the residue in dry MeOH (5 cm^3) was added, at 0 °C, acetic anhydride (100 mm^3). The mixture was stirred for 3 h, then concentrated. Size-exclusion chromatography (Bio-Gel P-2, 100 mM NH_4HCO_3) gave **13** (6.5 mg, 42%), isolated after lyophilization from water, as a white amorphous powder; $[\alpha]_D^{20}$ –9 (*c* 0.3 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 2.04 and 2.05 (each 3 H, 2 × s, 2 × NAc), 3.34 (1 H, br t, H-2″), 3.45 (1 H, br t, H-4′), 3.46 (1 H, m, H-5′), 3.50 (1 H, br t, H-3″), 3.51 (1 H, br t, H-4″), 3.52 (1 H, br t, H-4), 3.54 (1 H, m, H-5), 3.55 (1 H, br t, H-3′), 3.72 (1 H, br t, H-3), 3.73 (1 H, d, H-5″), 3.74 (1 H, br t, H-2′), 3.75 and 3.93 (each 1 H, 2 × m, 2 × H-6′), 3.77 and 4.20 (each 1 H, 2 × m, 2 × H-6), 3.80 (1 H, br t, H-2), 4.13 and 4.30 (each 1 H, 2 × m, $OCH_2CH{=}CH_2$), 4.45 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.8, H-1″), 4.52 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.4, H-1′), 4.56 (1 H, d, $J_{H\text{-}1,H\text{-}2}$ 8.6, H-1), 5.26 and 5.30 (each 1 H, 2 × m, $OCH_2CH{=}CH_2$), 5.88 (1 H, m, $OCH_2CH{=}CH_2$); δ_C(125 MHz; D_2O) 22.8 and 23.0 (2 × $NDCOCH_3$), 55.1 (C-2), 56.3 (C-2′), 61.4 (C-6′), 69.1 (C-4), 69.4 (C-6), 70.5 (C-4′), 71.0 ($OCH_2CH{=}CH_2$), 72.4 (C-3″), 73.4 (C-2″), 74.5 (C-3′), 74.8 (C-5), 75.5 (C-4″), 76.3 (C-5″), 76.5 (C-5′), 83.8 (C-3), 100.5 (C-1), 102.6 (C-1′), 103.7 (C-1″), 119.1 ($OCH_2CH{=}CH_2$), 134.0 ($OCH_2CH{=}CH_2$); High resolution MALDI-TOF MS, *m*/*z* found M+ H641.236, $C_{25}H_{41}N_2O_{17}$ requires 641.241.

3-(2-Aminoethylthio)propyl (2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-[(β-D-glucopyranosyluronic acid)-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside 2

A solution of **13** (3 mg, 4.7 μmol) and cysteamine hydrochloride (3 mg, 26 μmol) in water (1 cm^3) was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV Lamp. The mixture was loaded directly on to a size-exclusion column (Bio-Gel P-2, 100 mM NH_4HCO_3), yielding **2** (1.6 mg, 48%), isolated after lyophilization from water as a white, amorphous powder; $[\alpha]_D^{20}$ −11 (*c* 0.1 in water); δ_H(500 MHz; D_2O; 2 D TOCSY and HSQC) 1.84 [2 H, m, $OCH_2CH_2CH_2S(CH_2)_2ND_2$], 2.01 and 2.06 (each 3 H, 2 × s, 2 × NAc), 2.61 [2 H, br t, $O(CH_2)_2CH_2S(CH_2)_2ND_2$],

2.81 and 3.17 [each 2 H, 2 × br t, $O(CH_2)_3S(CH_2)_2ND_2$], 3.34 (1 H, br t, H-2″), 3.45 (1 H, m, H-5′), 3.46 (1 H, br t, H-4′), 3.50 (1 H, br t, H-3″), 3.51 (1 H, br t, H-4″), 3.52 (1 H, br t, H-4), 3.54 (1 H, br t, H-3′), 3.55 (1 H, m, H-5), 3.67 and 3.94 [each 1 H, 2 × m, $OCH_2(CH_2)_2S(CH_2)_2ND_2$], 3.71 (1 H, br t, H-3), 3.73 (1 H, d, H-5″), 3.74 (1 H, br t, H-2), 3.75 (1 H, m, H-6b′), 3.76 (1 H, br t, H-2′), 3.79 (1 H, m, H-6b), 3.92 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 1.8 Hz, $J_{H\text{-}6a',H\text{-}6b'}$ 12.4 Hz, H-6a′), 4.19 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 1.2, $J_{H\text{-}6a,H\text{-}6b}$ 11.3, H-6a), 4.46 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.8, H-1″), 4.51 (1 H, d, $J_{H1,H2}$ 8.3, H-1), 4.52 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.4, H-1′); δ_C(125 MHz; D_2O) 23.0 and 23.1 (2 × NDCO*C*H_3), 27.8 [$O(CH_2)_2CH_2S(CH_2)_2ND_2$], 29.2 [$OCH_2CH_2CH_2S(CH_2)_2ND_2$], 29.5 and 39.2 [$O(CH_2)_3S(CH_2)_2ND_2$], 55.2 (C-2), 56.3 (C-2′), 61.4 (C-6′), 69.1 (C-4), 69.2 [$OCH_2(CH_2)_2S(CH_2)_2ND_2$], 69.4 (C-6), 70.6 (C-4′), 72.4 (C-3″), 73.5 (C-2″), 74.5 (C-3′), 74.8 (C-5), 76.0 (C-4″), 76.5 (C-5″), 76.6 (C-5′), 83.6 (C-3), 101.8 (C-1), 102.8 (C-1′), 103.7 (C-1″); high resolution MALDI-TOF MS, *m*/*z* found M+Na 740.231, $C_{27}H_{47}N_3NaO_{17}S$ requires 740.251.

4-Methoxyphenyl (methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-2-deoxy-2-phthalimido-β-D-glucopyranoside 15

A solution of methyl 2,3,4-tri-*O*-acetyl-α,β-D-glucopyranosyluronate trichloroacetimidate[14] (**8**; 0.75 g, 1.65 mmol) and 4-methoxyphenyl 2-deoxy-4,6-*O*-isopropylidene-2-phthalimido-β-D-glucopyranoside[20] (**14**; 0.5 g, 1.1 mmol) in dry CH_2Cl_2 (10 cm^3), containing activated molecular sieves (4 Å, 0.8 g), was stirred for 45 min at room temperature, then TMSOTf (54 mm^3, 0.30 mmol) was added at 0 °C. The mixture was stirred for 45 min at 0 °C and 30 min at rt, when TLC (95 : 5 CH_2Cl_2–acetone) showed the formation of a new product (R_f = 0.33). After neutralization with dry pyridine and filtration, the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. To a solution of the residue in CH_2Cl_2 (20 cm^3) and water (0.1 cm^3) was added TFA (1 cm^3), and the mixture was stirred for 1 h, when TLC (9 : 1 CH_2Cl_2–acetone) confirmed the removal of the isopropylidene function (R_f = 0.31). The mixture was washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. Column chromatography (9 : 1 CH_2Cl_2–acetone) of the residue gave **15** (0.34 g, 71%), isolated as a colorless glass; $[\alpha]_D^{20}$ +16 (*c* 0.7 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 1.60, 1.94, and 2.00 (each 3 H, 3 × s, 3 × Ac), 3.64 (1 H, m, H-5), 3.70 and 3.76 (each 3 H, 2 × s, COOCH_3 and $C_6H_4OCH_3$), 3.73 (1 H, br t, H-4), 3.86 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 5.5 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 11.9 Hz, H-6b), 4.03 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 3.4, H-6a), 4.07 (1 H, d, $J_{H\text{-}4',H\text{-}5'}$ 9.9, H-5′), 4.45 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, $J_{H\text{-}2,H\text{-}3}$ 10.6, H-2), 4.49 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.8, H-1′), 4.59 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 8.1, H-3), 4.89 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 10.7, H-2′), 5.07 (1 H, br t, H-3′), 5.15 (1 H, br t, H-4′), 5.54 (1 H, d, H-1), 6.70 and 6.76 (each 2 H, 2 × m, $C_6H_4OCH_3$), 7.78 and 7.87 (each 2 H, 2 × m, Phth); high resolution MALDI-TOF MS, *m*/*z* found M+Na 754.201, $C_{34}H_{37}NNaO_{17}$ requires 754.196.

4-Methoxyphenyl (methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside 16

To a solution of **15** (0.53 g, 0.72 mmol) in dry CH_2Cl_2 (7.5 cm^3) and dry pyridine (7.5 cm^3) was added acetic anhydride (7.5 cm^3). The mixture was stirred overnight, when TLC (9 : 1 CH_2Cl_2–acetone) showed the reaction to be completed (R_f = 0.77). Then, the mixture was washed with saturated aq. $NaHCO_3$ and 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue yielded **16** (0.58 g, 100%), isolated as a white foam; $[\alpha]_D^{20}$ +10 (*c* 1 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 1.81, 1.84, 1.87, 2.02, and 2.07 (each 3 H, 5 × s, 5 × Ac), 3.64 and 3.65 (each 3 H, 2 × s, COOCH_3 and $C_6H_4OCH_3$), 3.79 (1 H, d, $J_{H\text{-}4',H\text{-}5'}$ 10.1 Hz, H-5′), 3.80 (1 H, m, H-5), 4.11 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 2.5, $J_{H\text{-}6a,H\text{-}6b}$ 12.2, H-6a), 4.21 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 5.1, H-6b), 4.24 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.0, H-1′), 4.45 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.4, $J_{H\text{-}2,H\text{-}3}$ 10.7, H-2), 4.69 (1 H, br t, H-3), 4.70 (1 H, br t, H-2′), 4.85 (1 H, br t, H-3′), 4.98 (1 H, br t, H-4′), 5.09 (1 H, br t, H-4), 5.40 (1 H, d, H-1), 6.62 and 6.68 (each 2 H, 2 × m, $C_6H_4OCH_3$), 7.74 and 7.82 (each 2 H, 2 × m, Phth); δ_C(125 MHz; $CDCl_3$) 20.1, 20.3, 20.4, 20.5, and 20.7 (5 × CO*C*H_3), 52.6 and 55.5 (COO*C*H_3 and $C_6H_4OCH_3$), 55.4 (C-2), 62.1 (C-6), 68.5 (C-4), 69.5 (C-4′), 71.1 (C-2′), 72.0 (C-3′), 72.2 (2 C) (C-5 and C-5′), 75.5 (C-3), 97.6 (C-1), 100.0 (C-1′), 114.4 and 118.7 ($C_6H_4OCH_3$), 123.7 and 134.7 [$N(CO)_2C_6H_4$]; high resolution MALDI-TOF MS, *m*/*z* found M+Na 838.218, $C_{38}H_{41}NNaO_{19}$ requires 838.217.

(Methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate 17

To a solution of **16** (0.23 g, 0.28 mmol) in 1 : 1 : 1 toluene–acetonitrile–water (15 cm^3) was added ammonium cerium(IV) nitrate (1.5 g, 2.8 mmol). The two-phase mixture was vigorously stirred for 45 min, when TLC (95 : 5 CH_2Cl_2–acetone) showed the disappearance of **16** and the appearance of a lower moving spot (R_f = 0.09). After dilution with EtOAc, the organic phase was washed with saturated aq. $NaHCO_3$ and 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue gave the hemiacetal intermediate isolated as a yellow solid. To a solution of the hemiacetal (0.15 g, 0.20 mmol) in dry CH_2Cl_2 (4 cm^3) and trichloroacetonitrile (0.21 cm^3, 2.0 mmol) was added, at 0 °C, 1,8-diazabicyclo[5.4.0]undec-7-ene (3.4 mm^3, 20 μmol). The mixture was stirred overnight, when TLC (95 : 5 CH_2Cl_2–acetone) showed the formation of a new product (R_f = 0.30). After concentration, column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue yielded **17** (0.15 g, 63%), isolated as a yellow foam; $[\alpha]_D^{20}$ +18 (*c* 1 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 1.86, 1.91, 1.95, 2.11, and 2.14 (each 3 H, 5 × s, 5 × Ac), 3.73 (3 H, s, COOCH_3), 3.87 (1 H, d, $J_{H\text{-}4',H\text{-}5'}$ 10.0 Hz, H-5′), 3.97 (1 H, m, H-5), 4.18 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 2.2, $J_{H\text{-}6a,H\text{-}6b}$ 12.4, H-6a), 4.33 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 4.3, H-6b), 4.34 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.0, H-1′), 4.59 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.9, $J_{H\text{-}2,H\text{-}3}$ 10.7, H-2), 4.76 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 9.5, H-2′), 4.84 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 9.2, H-3), 4.93 (1 H, br t, H-3′), 5.05 (1 H, br t, H-4′), 5.20 (1 H, br t, H-4), 6.29 (1 H, d, H-1), 7.80 and 7.86 (each 2 H, 2 × m, Phth), 8.57 [1 H, s, OC(N*H*)CCl_3]; δ_C(125 MHz; $CDCl_3$) 20.2, 20.3, 20.6, 20.7, and 20.8 (5 × CO*C*H_3), 52.7 (COO*C*H_3), 54.6 (C-2), 61.9 (C-6), 68.3 (C-4), 69.6 (C-4′), 71.3 (C-2′), 72.1 (C-3′), 72.5 (C-5′), 73.0 (C-5), 75.4 (C-3), 93.7 (C-1), 100.2 (C-1′), 123.9 and 135.0 [$N(CO)_2C_6H_4$].

Allyl (methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-[(methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronate)-(1→3)]-2-deoxy-2-phthalimido-β-D-glucopyranoside 18

A solution of **9** (50 mg, 75 μmol) and **17** (96 mg, 112 μmol) in dry CH_2Cl_2 (2 cm^3), containing activated molecular sieves (4 Å, 0.1 g), was stirred for 1 h at rt, then TMSOTf (2.32 mm^3, 11.2 μmol) was added at 0 °C. The mixture was stirred for 1 h at 0 °C, when TLC (9 : 1 CH_2Cl_2–acetone) showed the formation of a new product (R_f = 0.42). After neutralization with dry pyridine and filtration, the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (9 : 1 CH_2Cl_2–acetone) of the residue afforded **18** (90 mg, 90%), isolated as a white amorphous powder; $[\alpha]_D^{20}$ −16 (*c* 1.5 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 1.59, 1.86, 1.90, 1.94, 1.95, 2.00, 2.12, and 2.13 (each 3 H, 8 × s, 8 × Ac), 3.19 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 9.6 Hz, $J_{H\text{-}4,H\text{-}5}$ 8.4 Hz, H-4), 3.40 (1 H, m, H-5), 3.65 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 6.0, $J_{H\text{-}6a,H\text{-}6b}$ 11.0, H-6b), 3.69 and 3.93 (each 1 H, 2 × m, $OCH_2CH{=}CH_2$), 3.72 and 3.76 (each 3 H, 2 × s, 2 × COOCH_3), 3.77 (1 H, m, H-5′), 3.86 (1 H, d, $J_{H\text{-}4'',H\text{-}5''}$ 9.9, H-5″), 3.94 (1 H, d, $J_{H\text{-}4''',H\text{-}5'''}$ 10.1, H-5‴), 3.96

(1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, $J_{H\text{-}2,H\text{-}3}$ 10.7, H-2), 4.18 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.5, $J_{H\text{-}6a',H\text{-}6b'}$ 12.2, H-6a′), 4.21 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 0.8, H-6a), 4.26 (1 H, dd, H-6b′), 4.27 (1 H, d, $J_{H\text{-}1''',H\text{-}2'''}$ 8.0, H-1‴), 4.28 (1 H, br t, H-3), 4.30 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 8.1, H-1″), 4.32 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 8.4, $J_{H\text{-}2',H\text{-}3'}$ 10.8, H-2′), 4.72 (1 H, dd, $J_{H\text{-}2''',H\text{-}3'''}$ 9.7, H-2‴), 4.73 (1 H, br t, H-3′), 4.76 (1 H, dd, $J_{H\text{-}2'',H\text{-}3''}$ 9.2, H-2″), 4.80 (1 H, d, H-1), 4.91 (1 H, br t, H-3″), 4.94 and 5.00 (each 1 H, 2 × m, $OCH_2CH{=}CH_2$), 4.99 (1 H, br t, H-3‴), 5.05 (1 H, br t, H-4″), 5.08 (1 H, br t, H-4‴), 5.09 (1 H, d, H-1′), 5.10 (1 H, br t, H-4′), 5.51 (1 H, m, $OCH_2CH{=}CH_2$), 7.75, 7.82, and 7.89 (2 H, 4 H, and 2 H, 3 × m, 2 × Phth); δ_C(125 MHz; $CDCl_3$) 19.8, 20.2, 20.4 (3 C), 20.5, and 20.8 (2 C) (8 × $CO\underline{C}H_3$), 52.7 and 53.3 (2 × $COO\underline{C}H_3$), 54.7 (C-2), 55.6 (C-2′), 62.3 (C-6′), 68.7 (2 C) (C-4″ and C-4‴), 69.0 ($O\underline{C}H_2CH{=}CH_2$), 69.2 (C-6), 69.4 (C-4), 69.6 (C-4′), 70.7 (C-2‴), 71.2 (C-2″), 71.5 (C-5‴), 71.8 (C-3‴), 72.0 (C-5′), 72.2 (C-3″), 72.4 (C-5″), 74.8 (C-5), 75.7 (C-3′), 81.4 (C-3), 96.9 (C-1), 99.0 (C-1′), 99.8 (C-1‴), 100.2 (C-1″), 117.6 ($OCH_2CH{=}\underline{C}H_2$), 133.4 ($OCH_2\underline{C}H{=}CH_2$), 123.8 and 134.8 [$N(CO)_2\underline{C}_6H_4$]; high resolution MALDI-TOF MS, *m*/*z* found M+Na 1379.358, $C_{61}H_{68}N_2NaO_{33}$ requires 1379.360.

Allyl (β-D-glucopyranosyluronic acid)-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-[(β-D-glucopyranosyluronic acid)-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside 19

To a solution of **18** (30 mg, 22 μmol) in 5:1 MeOH–water (3 cm^3) was added, at 0 °C, 3 M aq. NaOH (1 cm^3). The mixture was stirred for 3 h at rt, neutralized with Dowex 50 X 8 H^+ resin, filtered, and concentrated. A solution of the residue in 2:1 *n*-butanol–1,2-diaminoethane (6 cm^3) was stirred overnight at 90 °C, then co-concentrated with toluene. To a solution of the residue in dry MeOH (5 cm^3) was added, at 0 °C, acetic anhydride (100 mm^3). The mixture was stirred for 3 h, then concentrated. Size-exclusion chromatography (Bio-Gel P-2, 100 mM NH_4HCO_3) gave **19** (7.2 mg, 42%), isolated after lyophilization from water, as a white amorphous powder; $[\alpha]_D^{20}$ −33 (*c* 0.4 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 2.00 and 2.05 (each 3 H, 2 × s, 2 × NAc), 3.34 (2 H, br t, H-2″ and H-2‴), 3.73 (2 H, br t, H-3 and H-3′), 3.76 (2 H, br d, H-5″ and H-5‴), 3.76 and 4.23 (each 1 H, 2 × m, 2 × H-6), 3.77 and 3.93 (each 1 H, 2 × m, 2 × H-6′), 3.81 (1 H, br t, H-2), 3.89 (1 H, br t, H-2′), 4.14 and 4.32 (each 1 H, 2 × m, $OC\underline{H}_2CH{=}CH_2$), 4.47 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.8 Hz, H-1″), 4.50 (1 H, d, $J_{H\text{-}1''',H\text{-}2'''}$ 7.9, H-1‴), 4.56 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.8, H-1′), 4.57 (1 H, d, $J_{H\text{-}1,H\text{-}2}$ 8.5, H-1), 5.28 and 5.30 (each 1 H, 2 × m, $OCH_2CH{=}C\underline{H}_2$), 5.91 (1 H, m, $OCH_2C\underline{H}{=}CH_2$); δ_C(125 MHz; D_2O) 22.7 and 23.0 (2 × $NDCO\underline{C}H_3$), 55.1 (2 C) (C-2 and C-2′), 61.4 (C-6′), 69.4 (C-6), 71.1 ($O\underline{C}H_2CH{=}CH_2$), 73.5 (2 C) (C-2″ and C-2‴), 76.4 (2 C) (C-5″ and C-5‴), 83.7 (2 C) (C-3 and C-3′), 100.5 (C-1), 102.4 (C-1′), 103.7 (2 C) (C-1″ and C-1‴), 119.1 ($OCH_2CH{=}\underline{C}H_2$), 134.0 ($OCH_2\underline{C}H{=}CH_2$); high resolution MALDI-TOF MS, *m*/*z* found M+H 817.280, $C_{31}H_{49}N_2O_{23}$ requires 817.273.

3-(2-Aminoethylthio)propyl (β-D-glucopyranosyluronic acid)-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-[(β-D-glucopyranosyluronic acid)-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside 3

A solution of **19** (3 mg, 3.7 μmol) and cysteamine hydrochloride (3 mg, 26 μmol) in water (1 cm^3) was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV Lamp. The mixture was loaded directly on to a size-exclusion column (Bio-Gel P-2, 100 mM NH_4HCO_3), yielding **3** (1.8 mg, 56%), isolated after lyophilization from water as a white, amorphous powder; $[\alpha]_D^{20}$ −35 (*c* 0.1 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 1.85 [2 H, br t, $OCH_2C\underline{H}_2CH_2S(CH_2)_2ND_2$], 2.02 and 2.03 (each 3 H, 2 × s, 2 × NAc), 2.61 [2 H, br t, $O(CH_2)_2C\underline{H}_2S(CH_2)_2ND_2$], 2.82 and 3.18 [each 2 H, 2 × br t, $O(CH_2)_3S(C\underline{H}_2)_2ND_2$], 3.34 (2 H, br t, H-2″ and H-2‴), 3.66 and 3.94 [each 1 H, 2 × m, $OC\underline{H}_2(CH_2)_2S(CH_2)_2ND_2$], 3.72 (1 H, br t, H-3), 3.77 (1 H, br t, H-3′), 3.73 (2 H, br d, H-5″ and H-5‴), 3.76 and 3.93 (each 1 H, 2 × m, 2 × H-6′), 3.77 (1 H, br t, H-2), 3.78 and 4.20 (each 1 H, 2 × m, 2 × H-6), 4.46 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.0 Hz, H-1″), 4.48 (1 H, d, $J_{H\text{-}1''',H\text{-}2'''}$ 7.5, H-1‴), 4.50 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.0, H-1′), 4.57 (1 H, d, $J_{H\text{-}1,H\text{-}2}$ 8.5, H-1); δ_C(125 MHz; D_2O) 22.9 ($NDCO\underline{C}H_3$), 27.7 [$O(CH_2)_2\underline{C}H_2S(CH_2)_2ND_2$], 29.1 [$OCH_2\underline{C}H_2CH_2S(CH_2)_2ND_2$], 29.2 and 39.1 [$O(CH_2)_3S(\underline{C}H_2)_2ND_2$], 55.1 (C-2′), 55.2 (C-2), 61.3 (C-6′), 69.1 [$O\underline{C}H_2(CH_2)_2S(CH_2)_2ND_2$], 69.3 (C-6), 73.5 (2 C) (C-2″ and C-2‴), 76.5 (2 C) (C-5″ and C-5‴), 83.3 (C-3′), 83.6 (C-3), 101.9 (C-1), 102.7 (C-1′), 103.6 (2 C) (C-1″ and C-1‴); high resolution MALDI-TOF MS, *m*/*z* found M+Na 916.252, $C_{33}H_{55}N_3NaO_{23}S$ requires 916.284.

4-Methoxyphenyl (6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-2-deoxy-2-phthalimido-β-D-glucopyranoside 22

A solution of 6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-α-D-glucopyranosyl trichloroacetimidate[15] (**20**; 2.33 g, 3.0 mmol) and 4-methoxyphenyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside[22] (**21**; 1.00 g, 2.0 mmol) in dry CH_2Cl_2 (50 cm^3), containing activated molecular sieves (4 Å, 1 g), was stirred for 45 min, then TMSOTf (56 mm^3, 0.3 mmol) was added at 0 °C. The mixture was stirred for 30 min, when TLC (95:5 CH_2Cl_2–acetone) showed the formation of a new product (R_f = 0.42). After neutralization with dry pyridine and filtration, the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. To a solution of the residue in CH_2Cl_2 (50 cm^3) and water (0.5 cm^3) was added TFA (1.5 cm^3), then the mixture was stirred for 4 h, when TLC (9:1 CH_2Cl_2–acetone) showed the formation of a new product (R_f = 0.38). The mixture was washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. Column chromatography (9:1 CH_2Cl_2–acetone) of the residue gave **22** (1.57 g, 78%), isolated as a white foam; $[\alpha]_D^{20}$ +33 (*c* 0.5 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 2.21, 2.23, 2.32, and 2.33 [each 3 H, 4 × s, 3 × $COC_6H_4C\underline{H}_3$ and $CO(CH_2)_2COC\underline{H}_3$], 2.65 and 2.79 [each 2 H, 2 × m, $CO(C\underline{H}_2)_2COCH_3$], 3.64 (1 H, m, H-5), 3.68 (3 H, s, $C_6H_4OC\underline{H}_3$), 3.79 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 8.1 Hz, $J_{H\text{-}4,H\text{-}5}$ 9.6 Hz, H-4), 3.87 and 4.00 (each 1 H, 2 × m, 2 × H-6), 4.09 (1 H, m, H-5′), 4.21 (1 H, dd, $J_{H\text{-}5',H\text{-}6b'}$ 7.8, $J_{H\text{-}6a',H\text{-}6b'}$ 12.2, H-6b′), 4.37 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.3, H-6a′), 4.44 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, $J_{H\text{-}2,H\text{-}3}$ 10.8, H-2), 4.68 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 8.1, H-3), 4.83 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.0, H-1′), 5.38 (1 H, br t, H-4′), 5.41 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 9.8, H-2′), 5.48 (1 H, d, H-1), 5.72 (1 H, br t, H-3′), 6.67 (4 H, m, $C_6\underline{H}_4OCH_3$), 6.84, 6.96, 7.13, 7.33, 7.52, and 7.74 (each 2 H, 6 × d, 3 × $COC_6\underline{H}_4CH_3$); δ_C(125 MHz; $CDCl_3$) 21.6, 21.7 (2 C), and 29.9 [3 × $COC_6H_4\underline{C}H_3$ and $CO(CH_2)_2CO\underline{C}H_3$], 27.8 and 37.9 [$CO(\underline{C}H_2)_2COCH_3$], 54.8 (C-2), 55.7 ($C_6H_4O\underline{C}H_3$), 62.9 (C-6′), 63.1 (C-6), 69.1 (C-4′), 70.7 (C-4), 71.7 (C-2′), 72.3 (C-3′), 72.6 (C-5′), 75.9 (C-5), 82.8 (C-3), 97.6 (C-1), 101.6 (C-1′), 114.6 and 118.2 ($\underline{C}_6H_4OCH_3$), 123.8 and 133.7 [$N(CO)_2\underline{C}_6H_4$], 129.0, 129.1, 129.4, 129.8 (2 C), and 130.0 ($CO\underline{C}_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1052.332, $C_{56}H_{55}NNaO_{18}$ requires 1052.332.

4-Methoxyphenyl (6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside 23

To a solution of **22** (1.3 g, 1.26 mmol) in dry CH_2Cl_2 (50 cm^3), containing pyridine (3.6 cm^3), triethylamine (1.8 cm^3), and a catalytic amount of DMAP, was added *tert*-butyldiphenylsilyl chloride (0.96 cm^3, 3.79 mmol). The mixture was stirred overnight, when TLC (95:5 CH_2Cl_2–acetone) showed the reaction to be completed (R_f = 0.82). After dilution with EtOAc, the solution was washed with saturated aq. $NaHCO_3$ and water, dried, filtered, and concentrated. Column chromatography (toluene → 9:1 CH_2Cl_2–acetone) of the residue yielded **23** (1.46 g, 91%), isolated as a white foam; $[\alpha]_D^{20}$ +19 (*c* 1.5 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 1.06 [9 H, s, $SiC(C\underline{H}_3)_3(C_6H_5)_2$], 2.10, 2.22, 2.32, and 2.33 [each 3 H, 4 × s, 3 × $COC_6H_4C\underline{H}_3$ and

$CO(CH_2)_2COCH_3$], 2.57 [4 H, m, $CO(CH_2)_2COCH_3$], 3.65 (3 H, s, $C_6H_4OCH_3$), 3.71 (2 H, m, H-5 and H-4), 3.93 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 6.1 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 11.0 Hz, H-6b), 4.06 (1 H, m, H-5′), 4.10 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 1.7, H-6a), 4.19 (1 H, dd, $J_{H\text{-}5',H\text{-}6b'}$ 7.7, $J_{H\text{-}6a',H\text{-}6b'}$ 12.0, H-6b′), 4.34 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.3, H-6a′), 4.46 (1 H, dd, $J_{H1,H2}$ 8.4, $J_{H\text{-}2,H\text{-}3}$ 10.8, H-2), 4.67 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 7.3, H-3), 4.83 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.8, H-1′), 5.36 (1 H, br t, H-4′), 5.40 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 9.8, H-2′), 5.43 (1 H, d, H-1), 5.71 (1 H, br t, H-3′), 6.59 and 6.78 (each 2 H, 2 × m, $C_6H_4OCH_3$), 6.85, 6.96, 7.12, 7.27, 7.52, and 7.73 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$), 7.38 and 7.71 [6 H and 4 H, 2 × m, $SiC(CH_3)_3(C_6H_5)_2$]; δ_C(125 MHz; $CDCl_3$) 21.5, 21.6 (2 C), and 29.7 [3 × $COC_6H_4CH_3$ and $CO(CH_2)_2COCH_3$], 26.8 [$SiC(CH_3)_3(C_6H_5)_2$], 27.8 and 37.8 [$CO(CH_2)_2COCH_3$], 54.9 (C-2), 55.6 ($C_6H_4OCH_3$), 62.8 (C-6′), 63.6 (C-6), 69.1 (C-4′), 70.0 (C-4), 71.6 (C-2′), 72.4 (C-3′), 72.5 (C-5′), 77.0 (C-5), 83.2 (C-3), 97.7 (C-1), 101.6 (C-1′), 114.5 and 118.4 ($C_6H_4OCH_3$), 123.8 and 133.6 [$N(CO)_2C_6H_4$], 127.8, 129.6, and 135.8 [$SiC(CH_3)_3(C_6H_5)_2$], 128.9, 129.0, 129.3, 129.7 (2 C), and 129.9 ($COC_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1290.456, $C_{72}H_{73}NNaO_{18}Si$ requires 1290.450.

4-Methoxyphenyl (6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 24

To a solution of **23** (1.4 g, 1.1 mmol) in dry CH_2Cl_2 (50 cm^3), containing pyridine (1.18 cm^3) and a catalytic amount of DMAP, was added slowly at 0 °C a solution of trifluoromethanesulfonic anhydride (1.1 cm^3, 6.6 mmol) in dry CH_2Cl_2 (6 cm^3). The mixture was stirred for 30 min at 0 °C and for 5 h at rt, when TLC (95 : 5 CH_2Cl_2–acetone) showed the triflation to be complete (R_f = 0.55). The mixture was washed with saturated aq. $NaHCO_3$ and 10% aq. NaCl, dried, filtered, and concentrated. To a solution of the residue in dry DMF (50 cm^3) was added tetrabutylammonium acetate (1.32 g, 4.35 mmol). After 2 h, when TLC (95 : 5 CH_2Cl_2–acetone) showed the formation of a new product (R_f = 0.51), the mixture was co-concentrated with toluene. A solution of the residue in CH_2Cl_2 (50 cm^3) was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue afforded **24** (1.0 g, 70%), isolated as a yellow foam; $[\alpha]_D^{20}$ +18 (*c* 0.6 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 1.05 [9 H, s, $SiC(CH_3)_3(C_6H_5)_2$], 2.12, 2.13, 2.24, 2.32, and 2.33 [each 3 H, 5 × s, 3 × $COC_6H_4CH_3$, $COCH_3$, and $CO(CH_2)_2COCH_3$], 2.58 [4 H, m, $CO(CH_2)_2COCH_3$], 3.64 (3 H, s, $C_6H_4OCH_3$), 3.76 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 7.5 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 10.9 Hz, H-6b), 3.81 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 4.3, H-6a), 3.89 (1 H, m, H-5′), 4.02 (1 H, m, H-5), 4.17 (1 H, dd, $J_{H\text{-}5',H\text{-}6b'}$ 5.0, $J_{H\text{-}6a',H\text{-}6b'}$ 12.1, H-6b′), 4.31 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.8, H-6a′), 4.73 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.4, $J_{H\text{-}2,H\text{-}3}$ 11.2, H-2), 4.78 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.0, H-1′), 4.92 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.3, H-3), 5.25 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 9.8, H-2′), 5.42 (1 H, br t, H-4′), 5.52 (1 H, d, H-1), 5.61 (1 H, br t, H-3′), 5.62 (1 H, br d, H-4), 6.58 and 6.79 (each 2 H, 2 × m, $C_6H_4OCH_3$), 6.88, 6.98, 7.11, 7.35, 7.55, and 7.74 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$), 7.40 and 7.52 [6 H and 4 H, 2 × m, $SiC(CH_3)_3(C_6H_5)_2$]; δ_C(125 MHz; $CDCl_3$) 20.9, 21.5, 21.6 (2 C), and 29.8 [3 × $COC_6H_4CH_3$, $COCH_3$, and $CO(CH_2)_2COCH_3$], 26.8 [$SiC(CH_3)_3(C_6H_5)_2$], 27.8 and 37.8 [$CO(CH_2)_2COCH_3$], 52.6 (C-2), 55.6 ($C_6H_4OCH_3$), 62.4 (C-6′), 63.1 (C-6), 69.0 (C-4′), 69.3 (C-4), 71.8 (C-2′), 72.2 (C-5′), 72.5 (C-3′), 74.8 (C-3), 75.4 (C-5), 97.9 (C-1), 101.4 (C-1′), 114.5 and 118.3 ($C_6H_4OCH_3$), 123.5 and 134.0 [$N(CO)_2C_6H_4$], 127.8, 129.7, and 135.7 [$SiC(CH_3)_3(C_6H_5)_2$], 128.9, 129.0, 129.2, 129.8, 129.9, and 130.0 ($COC_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1332.445, $C_{74}H_{75}NNaO_{19}Si$ requires 1332.460.

5-Azidopentyl (6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 26

To a solution of **24** (0.90 g, 0.68 mmol) in 1 : 1 : 1 toluene–acetonitrile–water (60 cm^3) was added ammonium cerium(IV) nitrate (3.73 g, 6.8 mmol). The two-phase mixture was stirred for 2 h, when TLC (95 : 5 CH_2Cl_2–acetone) showed the disappearance of **24**. The mixture was diluted with EtOAc, and the organic phase was washed with saturated aq. $NaHCO_3$ and 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue gave the hemiacetal intermediate, isolated as a yellow, amorphous solid. To a solution of the hemiacetal (0.60 g, 0.5 mmol) in dry CH_2Cl_2 (5 cm^3) and trichloroacetonitrile (0.55 cm^3, 5 mmol) was added, at 0 °C, 1,8-diazabicyclo[5.4.0]undec-7-ene (8.4 mm^3, 0.05 mmol). After 3 h, the mixture was concentrated and the residue was subjected to column chromatography (95 : 5 CH_2Cl_2–acetone), yielding **25** (0.57 g, 61%), isolated as a yellow foam; δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 1.04 [9 H, s, $SiC(CH_3)_3(C_6H_5)_2$], 2.13, 2.16, 2.24, and 2.34 [3 H, 3 H, 3 H, and 6 H, 4 × s, 3 × $COC_6H_4CH_3$, $COCH_3$, and $CO(CH_2)_2COCH_3$], 2.64 [4 H, m, $CO(CH_2)_2COCH_3$], 3.77 (2 H, m, 2 × H-6), 3.91 (1 H, m, H-5′), 4.11 (1 H, m, H-5), 4.20 (1 H, dd, $J_{H\text{-}5',H\text{-}6b'}$ 5.1 Hz, $J_{H\text{-}6a',H\text{-}6b'}$ 12.3 Hz, H-6b′), 4.32 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.8, H-6a′), 4.74 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 9.0, $J_{H\text{-}2,H\text{-}3}$ 10.8, H-2), 4.78 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.5, H-1′), 5.00 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.3, H-3), 5.27 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 9.9, H-2′), 5.44 (1 H, br t, H-4′), 5.65 (1 H, br t, H-3′), 5.74 (1 H, d, H-4), 6.07 (1 H, d, H-1), 6.88, 6.99, 7.13, 7.33, 7.56, and 7.74 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$), 7.40 and 7.65 [6 H and 4 H, 2 × m, $SiC(CH_3)_3(C_6H_5)_2$], 8.48 [1 H, s, $OC(NH)CCl_3$].

A solution of **25** (256 mg, 0.19 mmol) and 5-azidopentanol (49 mg, 0.38 mmol) in dry CH_2Cl_2 (2 cm^3), containing activated molecular sieves (4 Å, 0.3 g), was stirred for 30 min, then TMSOTf (5.1 mm^3, 0.028 mmol) was added at 0 °C, and the mixture was stirred for 30 min. After neutralization with pyridine and filtration, the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue gave **26** (213 mg, 85%), isolated as a glass; $[\alpha]_D^{20}$ −5 (*c* 2 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 0.99, 1.25, 1.37, and 2.83 [each 2 H, 4 × m, $OCH_2(CH_2)_4N_3$], 1.03 [9 H, s, $SiC(CH_3)_3(C_6H_5)_2$], 2.11, 2.14, 2.17, and 2.32 [3 H, 3 H, 3 H, and 6 H, 4 × s, 3 × $COC_6H_4CH_3$, $COCH_3$, and $CO(CH_2)_2COCH_3$], 2.54 and 2.60 [each 2 H, 2 × m, $CO(CH_2)_2COCH_3$], 3.29 and 3.78 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.79 (2 H, m, 2 × H-6), 3.90 (2 H, m, H-5 and H-5′), 4.19 (1 H, dd, $J_{H\text{-}5',H\text{-}6b'}$ 4.8 Hz, $J_{H\text{-}6a',H\text{-}6b'}$ 12.0 Hz, H-6b′), 4.30 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.7, H-6a′), 4.46 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.4, $J_{H\text{-}2,H\text{-}3}$ 11.1, H-2), 4.77 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 7.5, H-1′), 4.82 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.0, H-3), 5.00 (1 H, d, H-1), 5.25 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 9.6, H-2′), 5.43 (1 H, br t, H-4′), 5.64 (1 H, br t, H-3′), 5.65 (1 H, br d, H-4), 6.88, 6.99, 7.13, 7.38, 7.55, and 7.73 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$), 7.42 and 7.67 [6 H and 4 H, 2 × m, $SiC(CH_3)_3(C_6H_5)_2$]; δ_C(125 MHz; $CDCl_3$) 20.9, 21.5, 21.7 (2 C), and 29.8 [3 × $COC_6H_4CH_3$, $COCH_3$, and $CO(CH_2)_2COCH_3$], 23.0, 28.3, 28.7, and 51.1 [$OCH_2(CH_2)_4N_3$], 26.8 [$SiC(CH_3)_3(C_6H_5)_2$], 27.9 and 38.0 [$CO(CH_2)_2COCH_3$], 52.8 (C-2), 62.5 (C-6′), 62.8 (C-6), 69.0 [$OCH_2(CH_2)_4N_3$], 69.1 (C-4′), 69.2 (C-4), 71.8 (C-2′), 72.2 (C-5′), 72.5 (C-3′), 74.8 (C-5), 74.9 (C-3), 98.7 (C-1), 101.4 (C-1′), 123.5 and 133.8 [$N(CO)_2C_6H_4$], 127.8, 129.7, and 135.8 [$SiC(CH_3)_3(C_6H_5)_2$], 128.9 (2 C), 129.2, 129.8, 129.9, and 130.0 ($COC_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1337.490, $C_{72}H_{78}N_4NaO_{18}Si$ requires 1337.498.

5-Azidopentyl (6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-4-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 27

To **26** (100 mg, 76 μmol) was added a 1 M TBAF solution in THF (5 cm^3), before use neutralized at 0 °C with HOAc. The mixture was stirred for 2 h at 0 °C and for 4 h at rt, when TLC (95 : 5 CH_2Cl_2–acetone) showed the disappearance of **26** and the formation of a new product (R_f = 0.52). After concentration, a solution of the residue in EtOAc was washed with water and 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone → acetone) of the residue

afforded **27** (74 mg, 91%), isolated as a white glass; $[\alpha]_D^{20}$ +2 (*c* 0.3 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 0.98, 1.25, 1.40, and 2.85 [each 2 H, 4 × m, $OCH_2(CH_2)_4N_3$], 2.13, 2.16, 2.22, 2.24, and 2.26 [each 3 H, 5 × s, 3 × $COC_6H_4CH_3$, $COCH_3$, and $CO(CH_2)_2COCH_3$], 2.54 and 2.70 [each 2 H, 2 × m, $CO(CH_2)_2COCH_3$], 3.23 and 3.70 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.44 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 8.5 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 11.8 Hz, H-6b), 3.61 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 4.6, H-6a), 3.69 (1 H, m, H-5), 3.86 (1 H, m, H-5′), 4.08 (1 H, dd, $J_{H\text{-}5',H\text{-}6b'}$ 5.6, $J_{H\text{-}6a',H\text{-}6b'}$ 12.1, H-6b′), 4.22 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.3, H-6a′), 4.45 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.5, $J_{H\text{-}2,H\text{-}3}$ 11.2, H-2), 4.79 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.8, H-1′), 4.81 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.3, H-3), 4.93 (1 H, d, H-1), 5.23 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 9.8, H-2′), 5.32 (1 H, br t, H-4′), 5.51 (1 H, br d, H-4), 5.59 (1 H, br t, H-3′), 6.75, 6.90, 7.05, 7.24, 7.48, and 7.66 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$); δ_C(125 MHz; $CDCl_3$) 21.0, 21.5, 21.6 (2 C), and 29.9 [3 × $COC_6H_4CH_3$, $COCH_3$, and $CO(CH_2)_2COCH_3$], 22.9, 28.2, 28.7, and 51.0 [$OCH_2(CH_2)_4N_3$], 27.8 and 38.0 [$CO(CH_2)_2COCH_3$], 52.6 (C-2), 60.2 (C-6), 62.4 (C-6′), 68.8 (C-4′), 69.4 [$OCH_2(CH_2)_4N_3$], 69.8 (C-4), 71.6 (C-2′), 72.3 (C-5′), 72.5 (C-3′), 73.6 (C-5), 75.6 (C-3), 98.9 (C-1), 101.7 (C-1′), 123.4 and 133.7 [$N(CO)_2C_6H_4$], 128.9, 129.0, 129.3, 129.5, 129.7, and 129.9 ($COC_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1099.376, $C_{56}H_{60}N_4NaO_{18}$ requires 1099.380.

5-Azidopentyl (6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 28

A solution of **27** (144 mg, 0.134 mmol) in 1:1 pyridine–acetic anhydride (10 cm^3) was stirred overnight, when TLC (95:5 CH_2Cl_2–acetone) showed the acetylation to be complete (R_f = 0.62). After co-concentration with toluene, a solution of the residue in CH_2Cl_2 was washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. Column chromatography (95:5 CH_2Cl_2–acetone) of the residue gave **28** (125 mg, 83%), isolated as a white solid; $[\alpha]_D^{20}$ +9 (*c* 1 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 1.00, 1.22, 1.34, and 2.81 [each 2 H, 4 × m, $OCH_2(CH_2)_4N_3$], 2.01, 2.12, 2.14, and 2.25 [3 H, 3 H, 6 H, and 6 H, 4 × s, 3 × $COC_6H_4CH_3$, 2 × $COCH_3$, and $CO(CH_2)_2COCH_3$], 2.55 and 2.72 [each 2 H, 2 × m, $CO(CH_2)_2COCH_3$], 3.28 and 3.72 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.84 (1 H, m, H-5′), 3.92 (1 H, m, H-5), 4.02 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 7.2 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 11.6 Hz, H-6b), 4.07 (1 H, dd, $J_{H\text{-}5',H\text{-}6b'}$ 5.2, $J_{H\text{-}6a',H\text{-}6b'}$ 12.2, H-6b′), 4.17 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 5.1, H-6a), 4.31 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.5, H-6a′), 4.42 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.7, $J_{H\text{-}2,H\text{-}3}$ 11.3, H-2), 4.71 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.0, H-1′), 4.76 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.2, H-3), 4.93 (1 H, d, H-1), 5.18 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 9.8, H-2′), 5.35 (1 H, br t, H-4′), 5.53 (1 H, br d, H-4), 5.57 (1 H, br t, H-3′), 6.80, 6.91, 7.05, 7.28, 7.48, and 7.66 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$); δ_C(125 MHz; $CDCl_3$) 20.8, 21.0, 21.5, 21.6 (2 C), and 29.8 [3 × $COC_6H_4CH_3$, 2 × $COCH_3$, and $CO(CH_2)_2COCH_3$], 23.0, 28.2, 28.6, and 51.1 [$OCH_2(CH_2)_4N_3$], 28.0 and 38.0 [$CO(CH_2)_2COCH_3$], 52.5 (C-2), 62.2 (C-6′), 62.8 (C-6), 69.0 (C-4′), 69.2 (C-4), 69.3 [$OCH_2(CH_2)_4N_3$], 71.6 (C-5), 71.7 (C-2′), 72.2 (C-5′), 72.5 (C-3′), 74.7 (C-3), 98.7 (C-1), 101.4 (C-1′), 123.5 and 133.7 [$N(CO)_2C_6H_4$], 128.9, 129.0, 129.2, 129.6, 129.8, and 129.9 ($COC_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1141.370, $C_{58}H_{62}N_4NaO_{19}$ requires 1141.390.

5-Azidopentyl (2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 29

To a solution of **28** (125 mg, 0.112 mmol) in EtOH (10 cm^3) and toluene (3 cm^3) was added hydrazine acetate (51 mg, 0.56 mmol). The mixture was stirred for 2 h, then concentrated. Column chromatography (95:5 CH_2Cl_2–acetone) of the residue yielded **29** (104 mg, 91%), isolated as a white glass; $[\alpha]_D^{20}$ +2 (*c* 1 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 0.99, 1.20, 1.33, and 2.78 [each 2 H, 4 × m, $OCH_2(CH_2)_4N_3$], 2.01, 2.16, 2.22, 2.23, and 2.28 (each 3 H, 5 × s, 3 × $COC_6H_4CH_3$ and 2 × $COCH_3$), 3.25 and 3.70 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.56 and 3.66 (each 1 H, 2 × m, 2 × H-6′), 3.72 (1 H, m, H-5′), 3.93 (1 H, m, H-5), 4.06 (2 H, m, 2 × H-6), 4.44 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.7 Hz, $J_{H\text{-}2,H\text{-}3}$ 11.0 Hz, H-2), 4.74 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.4, H-3), 4.81 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.0, H-1′), 4.92 (1 H, d, H-1), 5.21 (1 H, br t, H-2′), 5.27 (1 H, br t, H-4′), 5.60 (1 H, br t, H-3′), 5.65 (1 H, br d, H-4), 6.72, 6.89, 7.06, 7.23, 7.45, and 7.68 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$); δ_C(125 MHz; $CDCl_3$) 20.7, 21.3, 21.5, 21.6, and 21.7 (3 × $COC_6H_4CH_3$ and 2 × $COCH_3$), 22.9, 28.3, 28.7, and 51.1 [$OCH_2(CH_2)_4N_3$], 52.4 (C-2), 61.6 (C-6′), 62.0 (C-6), 68.8 (C-4′), 69.3 [$OCH_2(CH_2)_4N_3$], 69.4 (C-4), 71.2 (C-5), 71.7 (C-2′), 72.6 (C-3′), 75.3 (C-5′), 76.2 (C-3), 98.8 (C-1), 102.2 (C-1′), 123.3 and 133.6 [$N(CO)_2C_6H_4$], 128.9, 129.0, 129.3, 129.5, 129.7, and 130.0 ($COC_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1043.354, $C_{53}H_{56}N_4NaO_{17}$ requires 1043.353.

5-Azidopentyl (sodium β-D-glucopyranosyl 6-sulfate)-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranoside 31

To a solution of **29** (95 mg, 93 μmol) in DMF (5 cm^3) was added the sulfur trioxide trimethylamine complex (515 mg, 3.67 mmol). The mixture was stirred for 48 h at 50 °C, when TLC (9:1 CH_2Cl_2–methanol) showed the complete conversion of **29** into non-sodiated **30** (R_f = 0.20). After quenching the reaction with MeOH (10 cm^3), the solution was co-concentrated with toluene. A solution of the residue in CH_2Cl_2 (50 cm^3) was washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. The residue was dissolved in MeOH (10 cm^3), containing Dowex 50W X 8 Na^+ resin, and stirred for 15 min, then filtered and concentrated. Column chromatography (95:5 CH_2Cl_2–MeOH) of the residue gave **30** (52 mg, 50%), isolated as a white, amorphous, powder; δ_H(500 MHz; $CDCl_3$) 1.01, 1.22, and 2.85 [2 H, 4 H, and 2 H, 3 m, $OCH_2(CH_2)_4N_3$], 2.07, 2.19, 2.23, 2.32, and 2.36 (each 3 H, 5 × s, 3 × $COC_6H_4CH_3$ and 2 × $COCH_3$), 3.33 and 3.78 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 4.04 (2 H, m, H-5 and H-5′), 4.14 and 4.24 (each 1 H, 2 × m, 2 × H-6), 4.29 and 4.59 (each 1 H, 2 × m, 2 × H-6′), 4.48 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6 Hz, $J_{H\text{-}2,H\text{-}3}$ 11.2 Hz, H-2), 4.80 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.6, H-1′), 4.91 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 2.9, H-3), 5.03 (1 H, d, H-1), 5.30 (1 H, br t, H-2′), 5.50 (1 H, br t, H-4′), 5.64 (1 H, br t, H-3′), 5.88 (1 H, br d, H-4), 6.85, 6.92, 7.10, 7.35, 7.52, and 7.75 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$).

A solution of **30** (52 mg, 46 μmol) in ethanolic 33% CH_3NH_2 (5 cm^3) was stirred for 7 days, during which time the mixture was three times concentrated and fresh ethanolic 33% CH_3NH_2 (5 cm^3) was added. After co-concentration with toluene, to a solution of the residue in dry MeOH at 0 °C was added acetic anhydride (100 mm^3). The mixture was stirred for 3 h at 0 °C, then concentrated. Size-exclusion chromatography (Bio-Gel P-2, 100 mM NH_4HCO_3) of the residue afforded **31** (21 mg, 76%), isolated after lyophilization from water, as a white, amorphous powder; $[\alpha]_D^{20}$ −14 (*c* 1 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 1.40, 1.59, and 3.33 [2 H, 4 H, and 2 H, 3 × m, $OCH_2(CH_2)_4N_3$], 2.03 (3 H, s, NAc), 3.31 (1 H, br t, H-2′), 3.45 (1 H, br t, H-4′), 3.46 (1 H, br t, H-3′), 3.61 and 3.92 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.62 (1 H, m, H-5′), 3.68 (1 H, m, H-5), 3.78 (2 H, m, 2 × H-6), 3.83 (1 H, dd, $J_{H\text{-}2,H\text{-}3}$ 11.0 Hz, $J_{H\text{-}3,H\text{-}4}$ 3.1 Hz, H-3), 3.99 (1 H, br t, H-2), 4.18 (1 H, br d, H-4), 4.19 and 4.30 (each 1 H, 2 × m, 2 × H-6′), 4.48 (1 H, d, $J_{H\text{-}1,H\text{-}2}$ 8.9, H-1), 4.50 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.1, H-1′); δ_C(125 MHz; D_2O) 22.9 ($NDCOCH_3$), 23.2, 28.3, 28.8, and 51.8 [$OCH_2(CH_2)_4N_3$], 51.9 (C-2), 61.8 (C-6), 67.9 (C-6′), 68.7 (C-4), 70.0 (C-3′), 70.8 [$OCH_2(CH_2)_4N_3$], 73.5 (C-2′), 74.2 (C-5′), 75.7 (C-5), 76.1 (C-4′), 81.0 (C-3), 102.1 (C-1), 105.1 (C-1′); high resolution MALDI-TOF MS, *m*/*z* found M+Na 616.157, $C_{19}H_{33}N_4Na_2O_{14}S$ requires 616.151.

5-Aminopentyl (sodium β-D-glucopyranosyl 6-sulfate)-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranoside 4

A solution of **31** (8.4 mg, 14 μmol) in 0.05 M aq. NaOH (1.0 cm^3) was added dropwise to a suspension of 10% Pd–C (2 mg) and $NaHB_4$ (8.0 mg) in water (0.5 cm^3). The suspension

was stirred for 45 min, when TLC (6:2.5:1.5 EtOAc–MeOH–water) showed the disappearance of **31**. After filtration through Celite, size-exclusion chromatography (Bio-Gel P-2, 100 mM NH_4HCO_3) gave **4** (5.7 mg, 71%), isolated after lyophilization from water, as a white, amorphous powder; $[\alpha]_D^{20}$ −11 (*c* 0.4 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 1.42, 1.61, 1.69, and 3.01 [each 2 H, 4 × m, $OCH_2(CH_2)_4ND_2$], 2.03 (3 H, s, NAc), 3.34 (1 H, br t, H-2′), 3.46 (1 H, br t, H-4′), 3.47 (1 H, br t, H-3′), 3.62 and 3.92 [each 1 H, 2 × m, $OCH_2(CH_2)_4ND_2$], 3.65 (1 H, m, H-5′), 3.68 (1 H, m, H-5), 3.79 (2 H, m, 2 × H-6), 3.84 (1 H, dd, $J_{H\text{-}2,H\text{-}3}$ 11.0 Hz, $J_{H\text{-}3,H\text{-}4}$ 3.2 Hz, H-3), 4.00 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, H-2), 4.18 (1 H, dd, $J_{H\text{-}5',H\text{-}6b'}$ 6.2, $J_{H\text{-}6a',H\text{-}6b'}$ 11.2, H-6b′), 4.19 (1 H, br d, H-4), 4.32 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.2, H-6a′), 4.49 (1 H, d, H-1), 4.51 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.0, H-1′); δ_C(125 MHz; D_2O) 22.8 ($NDCOCH_3$), 22.8, 27.0, 28.7, and 40.0 [$OCH_2(CH_2)_4ND_2$], 52.0 (C-2), 61.9 (C-6), 68.0 (C-6′), 68.6 (C-4), 70.0 (C-3′), 70.3 [$OCH_2(CH_2)_4ND_2$], 73.4 (C-2′), 74.3 (C-5′), 75.7 (C-5), 76.2 (C-4′), 80.9 (C-3), 102.2 (C-1), 105.0 (C-1′); high resolution MALDI-TOF MS, *m*/*z* found M+Na 593.166, $C_{19}H_{35}N_2Na_2O_{14}S$ requires 593.160.

5-Azidopentyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl)-(1→6)-[(6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)]-4-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 33

A solution of **27** (92 mg, 86 μmol) and 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl trichloroacetimidate[28] (**32**; 74.3 mg, 128 μmol) in dry CH_2Cl_2 (5 cm^3), containing activated molecular sieves (4 Å, 0.5 g), was stirred for 30 min at rt, then TMSOTf (2.3 mm^3, 12.8 μmol) was added at 0 °C. The mixture was stirred for 15 min at 0 °C, when TLC (9:1 CH_2Cl_2–acetone) showed the formation of **33** (R_f = 0.50). After neutralization with pyridine and filtration, the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (9:1 CH_2Cl_2–acetone) of the residue rendered **33** (74 mg, 58%), isolated as a glass; $[\alpha]_D^{20}$ +2 (*c* 1 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 0.83, 1.00, 1.12, and 2.72 [each 2 H, 4 × m, $OCH_2(CH_2)_4N_3$], 1.76, 2.02, 2.11, 2.13, 2.14, 2.16, 2.25, and 2.26 [each 3 H, 8 × s, 3 × $COC_6H_4CH_3$, 4 × $COCH_3$, $CO(CH_2)_2COCH_3$], 2.51 and 2.68 [each 2 H, 2 × m, $CO(CH_2)_2COCH_3$], 2.94 and 3.25 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.51 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 8.6 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 10.9 Hz, H-6b), 3.77 (2 H, m, H-5 and H-5″), 3.90 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 2.0, H-6a), 4.02 (1 H, br t, H-5′), 4.08 (1 H, dd, $J_{H\text{-}5'',H\text{-}6b''}$ 4.9, $J_{H\text{-}6a'',H\text{-}6b''}$ 12.2, H-6b″), 4.14 (2 H, m, 2 × H-6′), 4.19 (1 H, dd, $J_{H\text{-}5'',H\text{-}6a''}$ 2.8, H-6a″), 4.30 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, $J_{H\text{-}2,H\text{-}3}$ 11.3, H-2), 4.44 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 8.4, $J_{H\text{-}2',H\text{-}3'}$ 11.4, H-2′), 4.63 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.4, H-3), 4.65 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 8.0, H-1″), 4.75 (1 H, d, H-1), 5.15 (1 H, dd, $J_{H\text{-}2'',H\text{-}3''}$ 9.8, H-2″), 5.28 (1 H, d, H-1′), 5.32 (1 H, br t, H-4″), 5.37 (1 H, br d, H-4), 5.40 (1 H, br d, $J_{H\text{-}3',H\text{-}4'}$ 3.4, H-4′), 5.53 (1 H, br t, H-3″), 5.72 (1 H, dd, H-3′), 6.78, 6.90, 7.05, 7.24, 7.46, and 7.65 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$), 7.41 and 7.72 (each 4 H, 2 × m, 2 × Phth); δ_C(125 MHz; $CDCl_3$) 19.5, 19.6, 19.7, 19.8, 19.9, 20.5, 20.6, and 29.0 [3 × $COC_6H_4CH_3$, 4 × $COCH_3$, and $CO(CH_2)_2COCH_3$], 21.9, 27.1, 27.6, and 50.0 [$OCH_2(CH_2)_4N_3$], 26.9 and 36.9 [$CO(CH_2)_2COCH_3$], 50.4 (C-2′), 51.4 (C-2), 60.2 (C-6′), 61.2 (C-6″), 65.7 (C-4′), 66.9 (C-3′), 67.6 [$OCH_2(CH_2)_4N_3$], 67.7 (C-4″), 67.8 (C-6), 68.7 (C-4), 69.8 (C-5′), 70.6 (C-2″), 71.2 and 72.7 (C-5 and C-5″), 71.4 (C-3″), 73.4 (C-3), 97.3 (C-1′), 97.2 (C-1), 100.3 (C-1″), 121.8, 122.4, 132.7, and 133.3 [2 × $N(CO)_2C_6H_4$], 127.8, 127.9, 128.2, 128.5, 128.7, and 128.9 ($COC_6H_4OCH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1516.456, $C_{76}H_{79}N_5NaO_{27}$ requires 1516.486.

5-Azidopentyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl)-(1→6)-[(2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)]-4-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 34

To a solution of **33** (70 mg, 47 μmol) in EtOH (5 cm^3) and toluene (1.5 cm^3) was added hydrazine acetate (21.3 mg, 230 μmol). The mixture was stirred for 2 h, then concentrated. Column chromatography (9:1 CH_2Cl_2–acetone) of the residue yielded **34** (48 mg, 74%), isolated as a glass; $[\alpha]_D^{20}$ +5 (*c* 1 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 0.81, 1.09, 1.11, and 2.69 [each 2 H, 4 × m, $OCH_2(CH_2)_4N_3$], 1.77, 2.01, 2.14, 2.15, 2.18, 2.21, and 2.28 (each 3 H, 7 × s, 3 × $COC_6H_4CH_3$ and 4 × $COCH_3$), 2.96 and 3.29 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.49 (1 H, m, H-6b), 3.50 and 3.65 (each 1 H, 2 × m, 2 × H-6″), 3.66 (1 H, m, H-5″), 3.77 (1 H, m, H-5), 3.88 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 2.6 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 10.7 Hz, H-6a), 4.01 (1 H, m, H-5′), 4.14 (2 H, m, 2 × H-6′), 4.31 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, $J_{H\text{-}2,H\text{-}3}$ 11.2, H-2), 4.44 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 8.4, $J_{H\text{-}2',H\text{-}3'}$ 11.5, H-2′), 4.63 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.4, H-3), 4.73 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 8.3, H-1″), 4.75 (1 H, d, H-1), 5.16 (1 H, dd, $J_{H\text{-}2'',H\text{-}3''}$ 10.0, H-2″), 5.25 (1 H, br t, H-4″), 5.28 (1 H, d, H-1′), 5.39 (1 H, br d, $J_{H\text{-}3',H\text{-}4'}$ 3.1, H-4′), 5.51 (1 H, br d, H-4), 5.57 (1 H, br t, H-3″), 5.71 (1 H, dd, H-3′), 6.70, 6.89, 7.06, 7.21, 7.44, and 7.68 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$), 7.30 and 7.75 (each 4 H, 2 × m, 2 × Phth); δ_C(125 MHz; $CDCl_3$) 19.4, 19.7, 19.8, 20.2, 20.4, 20.5, and 20.6 (3 × $COC_6H_4CH_3$ and 4 × $COCH_3$), 21.9, 27.2, 28.6, and 50.0 [$OCH_2(CH_2)_4N_3$], 50.3 (C-2′), 51.4 (C-2), 60.2 (C-6″), 60.4 (C-6′), 65.7 (C-4′), 66.9 (C-6), 67.0 (C-3′), 67.6 (C-4″), 67.7 [$OCH_2(CH_2)_4N_3$], 68.9 (C-4), 69.9 (C-5′), 70.6 (C-2″), 71.5 (C-3″), 72.3 (C-5), 74.3 (C-5″), 74.9 (C-3), 97.0 (C-1′), 97.3 (C-1), 101.0 (C-1″), 121.6, 122.6, 132.4, and 133.3 [2 × $N(CO)_2C_6H_4$], 127.8, 127.9, 128.1, 128.4, 128.7, and 128.9 ($COC_6H_4OCH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1418.415, $C_{71}H_{73}N_5NaO_{25}$ requires 1418.449.

5-Azidopentyl (2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→6)-[(sodium β-D-glucopyranosyl 6-sulfate)-(1→3)]-2-acetamido-2-deoxy-β-D-galactopyranoside 36

To a solution of **34** (43 mg, 30.8 μmol) in DMF (3 cm^3) was added the sulfur trioxide trimethylamine complex (173 mg, 1.22 mmol). The mixture was stirred for 48 h at 50 °C, when TLC (9:1 CH_2Cl_2–MeOH) showed the complete conversion of **34** into non-sodiated **35** (R_f = 0.38). After quenching the reaction with MeOH (10 cm^3), the solution was co-concentrated with toluene. A solution of the residue in EtOAc (50 cm^3) was washed with saturated aq. $NaHCO_3$ and 10% aq. NaCl, dried, filtered, and concentrated. The residue was dissolved in MeOH (10 cm^3), containing Dowex 50W X 8 Na^+ resin, and stirred for 15 min, then filtered and concentrated. Column chromatography (9:1 CH_2Cl_2–MeOH) of the residue gave **35** (38 mg, 82%), isolated as a white, amorphous powder; δ_H(300 MHz; $CDCl_3$) 0.90, 1.20, and 2.80 [2 H, 4 H, and 2 H, 3 × m, $OCH_2(CH_2)_4N_3$], 1.83, 2.05, 2.17, 2.26, 2.33, 2.34, and 2.38 (each 3 H, 7 × s, 3 × $COC_6H_4CH_3$ and 4 × $COCH_3$), 3.19 and 3.50 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.51 and 3.99 (each 1 H, 2 × m, 2 × H-6), 3.78 (1 H, m, H-5), 4.17 (2 H, m, 2 × H-6″), 4.36 (2 H, m, 2 × H-6′), 4.47 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 8.4 Hz, $J_{H\text{-}2',H\text{-}3'}$ 11.4 Hz, H-2′), 4.73 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.7, H-1″), 4.81 (1 H, dd, $J_{H\text{-}2,H\text{-}3}$ 11.3, $J_{H\text{-}3,H\text{-}4}$ 2.8, H-3), 4.87 (1 H, d, $J_{H\text{-}1,H\text{-}2}$ 8.5, H-1), 5.26 (1 H, d, H-1′), 5.38 (1 H, br d, H-4′), 5.55 (1 H, br t, H-4″), 5.56 (1 H, br t, H-3″), 5.77 (1 H, dd, $J_{H\text{-}3',H\text{-}4'}$ 3.3, H-3′), 5.83 (1 H, br d, H-4), 6.87, 6.99, 7.19, 7.35, 7.49, and 7.72 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$), 7.46 and 7.76 (each 4 H, 2 × m, 2 × Phth).

A solution of **36** (33 mg, 22 μmol) in ethanolic 33% CH_3NH_2 (5 cm^3) was stirred for 7 days, during which time the mixture was three times concentrated and fresh ethanolic 33% CH_3NH_2 (5 cm^3) was added. After co-concentration with toluene, to a solution of the residue in dry MeOH at 0 °C was added acetic anhydride (100 mm^3). The mixture was stirred for 3 h at 0 °C, then concentrated. Size-exclusion chromatography (Bio-Gel P-2, 100 mM NH_4HCO_3) of the residue afforded **36** (13 mg, 74%), isolated after lyophilization from water, as a white, amorphous powder; $[\alpha]_D^{20}$ +6 (*c* 0.2 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 1.39, 1.61, and 3.33 [2 H, 4 H, and 2 H, 3 × m, $OCH_2(CH_2)_4N_3$], 2.01 and 2.02 (each 3 H, 2 × s, 2 × NAc), 3.34 (1 H, br t, H-2″), 3.44 (1 H, br t, H-4″), 3.45 (1 H, br t, H-3″), 3.58 and 3.88 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$],

3.62 (1 H, m, H-5″), 3.68 (1 H, m, H-5′), 3.72 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 10.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ 3.4 Hz, H-3′), 3.76 and 3.80 (each 1 H, 2 × m, 2 × H-6′), 3.78 and 4.05 (each 1 H, 2 × m, 2 × H-6), 3.82 (1 H, m, H-5), 3.84 (1 H, dd, $J_{H\text{-}2,H\text{-}3}$ 10.9, $J_{H\text{-}3,H\text{-}4}$ 3.2, H-3), 3.89 (1 H, br t, H-2′), 3.93 (1 H, br d, H-4′), 3.98 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, H-2), 4.16 (1 H, br d, H-4), 4.17 (1 H, dd, $J_{H\text{-}5'',H\text{-}6b''}$ 5.8, $J_{H\text{-}6a'',H\text{-}6b''}$ 11.3, H-6b″), 4.30 (1 H, dd, $J_{H\text{-}5'',H\text{-}6a''}$ 2.1, H-6a″), 4.45 (1 H, d, H-1), 4.46 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.4, H-1′), 4.50 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.8, H-1″); δ_C(125 MHz; D_2O) 22.9 ($NDCOCH_3$), 23.2, 28.4, 28.8, and 51.8 [$OCH_2(CH_2)_4N_3$], 51.8 (C-2), 53.1 (C-2′), 61.7 (C-6′), 67.9 (C-6″), 68.5 (C-4′), 69.0 (C-4), 70.1 (C-3″), 70.5 (C-6), 70.7 [$OCH_2(CH_2)_4N_3$], 71.7 (C-3′), 73.5 (C-2″), 74.2 (C-5), 74.3 (C-5″), 75.8 (C-5′), 76.2 (C-4″), 80.7 (C-3), 101.8 (C-1), 102.6 (C-1′), 104.9 (C-1″); high resolution MALDI-TOF MS, *m*/*z* found M+Na 822.229, $C_{27}H_{46}N_5Na_2O_{19}S$ requires 822.230.

5-Aminopentyl (2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→6)-[(sodium β-D-glucopyranosyl 6-sulfate)-(1→3)]-2-acetamido-2-deoxy-β-D-galactopyranoside 5

A solution of **36** (5 mg, 6.3 μmol) in 0.05 M aq. NaOH (1.0 cm^3) was added dropwise to a suspension of 10% Pd–C (0.9 mg) and $NaHB_4$ (4.0 mg) in water (0.5 cm^3). The suspension was stirred for 1 h, when TLC (6 : 2.5 : 1.5 EtOAc–MeOH–water) showed the disappearance of **36**. After filtration through Celite, size-exclusion chromatography (Bio-Gel P-2, 100 mM NH_4HCO_3) gave **5** (4.3 mg, 89%), isolated after lyophilization from water, as a white, amorphous powder; $[\alpha]_D^{20}$ +2 (*c* 0.1 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 1.42, 1.60, 1.67, and 2.98 [each 2 H, 4 × m, $OCH_2(CH_2)_4ND_2$], 2.01 and 2.02 (each 3 H, 2 × s, 2 × NAc), 3.31 (1 H, br t, H-2″), 3.43 (1 H, br t, H-4″), 3.45 (1 H, br t, H-3″), 3.59 and 3.88 [each 1 H, 2 × m, $OCH_2(CH_2)_4ND_2$], 3.62 (1 H, m, H-5″), 3.67 (1 H, m, H-5′), 3.72 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 11.0 Hz, $J_{H\text{-}3',H\text{-}4'}$ 3.5 Hz, H-3′), 3.75 and 3.80 (each 1 H, 2 × m, 2 × H-6′), 3.76 (1 H, m, H-5), 3.82 and 4.04 (each 1 H, 2 × m, 2 × H-6), 3.83 (1 H, dd, $J_{H\text{-}2,H\text{-}3}$ 10.6, $J_{H\text{-}3,H\text{-}4}$ 3.4, H-3), 3.90 (1 H, br t, H-2′), 3.93 (1 H, br d, H-4′), 3.98 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.4, H-2), 4.16 (1 H, br d, H-4), 4.17 (1 H, dd, $J_{H\text{-}5'',H\text{-}6b''}$ 6.0, $J_{H\text{-}6a'',H\text{-}6b''}$ 11.1, H-6b″), 4.31 (1 H, dd, $J_{H\text{-}5'',H\text{-}6a''}$ 1.8, H-6a″), 4.44 (1 H, d, H-1), 4.46 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.5, H-1′), 4.49 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 8.0, H-1″); δ_C(125 MHz; D_2O) 22.7, 27.1, 28.7, and 40.0 [$OCH_2(CH_2)_4ND_2$], 22.8 and 22.9 (2 × $NDCOCH_3$), 51.8 (C-2), 53.1 (C-2′), 61.7 (C-6′), 67.9 (C-6″), 68.5 (C-4′), 69.0 (C-4), 70.1 (C-4″), 70.4 [$OCH_2(CH_2)_4ND_2$], 70.5 (C-6), 71.7 (C-3′), 73.4 (C-2″), 74.2 (C-5), 74.3 (C-5″), 75.8 (C-5′), 76.2 (C-3″), 80.6 (C-3), 101.9 (C-1), 102.6 (C-1′), 104.8 (C-1″); high resolution MALDI-TOF MS, *m*/*z* found M+Na 796.233, $C_{27}H_{48}N_3Na_2O_{19}S$ requires 796.240.

4-Methoxyphenyl (6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 37

To **24** (0.75 g, 0.57 mmol) was added a 1 M TBAF solution in THF (15 cm^3), before use neutralized at 0 °C with HOAc. The mixture was stirred for 1 h at 0 °C and overnight at rt, when TLC (95 : 5 CH_2Cl_2–acetone) showed the disappearance of **24** and the formation of a new product (R_f = 0.29). After concentration, a solution of the residue in EtOAc was washed with water and 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue gave the free HO6 intermediate isolated as a yellow foam. A solution of the free HO6 intermediate (0.54 g, 0.50 mmol) in 1 : 1 pyridine–acetic anhydride (20 cm^3) was stirred overnight, when TLC (95 : 5 CH_2Cl_2–acetone) showed the reaction to be complete (R_f = 0.79). After co-concentration with toluene, a solution of the residue in CH_2Cl_2 was washed with saturated aq. $NaHCO_3$ and 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue gave **37** (0.53 g, 84%), isolated as a yellow foam; $[\alpha]_D^{20}$ +31 (*c* 0.5 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 2.07, 2.20, 2.24, 2.26, and 2.33 [3 H, 3 H, 3 H, 3 H, and 6 H, 5 × s, 3 × $COC_6H_4CH_3$, 2 × $COCH_3$, and $CO(CH_2)_2COCH_3$], 2.63 and 2.77 [each 2 H, 2 × m, $CO(CH_2)_2COCH_3$], 3.68 (3 H, s, $C_6H_4OCH_3$), 3.91 (1 H, m, H-5′), 4.10 (1 H, m, H-5), 4.26 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 4.3 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 11.1 Hz, H-6a), 4.38 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.8, $J_{H\text{-}6a',H\text{-}6b'}$ 13.6, H-6a′), 4.74 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.5, $J_{H\text{-}2,H\text{-}3}$ 11.3, H-2), 4.80 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.8, H-1′), 4.93 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.4, H-3), 5.27 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 10.0, H-2′), 5.42 (1 H, br t, H-4′), 5.48 (1 H, d, H-1), 5.64 (1 H, br t, H-3′), 5.66 (1 H, br d, H-4), 6.66 and 6.74 (each 2 H, 2 × m, $C_6H_4OCH_3$), 6.88, 6.99, 7.13, 7.37, 7.54, and 7.73 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$); δ_C(125 MHz; $CDCl_3$) 20.9, 21.1, 21.6, 21.7 (2 C), and 29.8 [3 × $COC_6H_4CH_3$, 2 × $COCH_3$, and $CO(CH_2)_2COCH_3$], 28.0 and 38.1 [$CO(CH_2)_2COCH_3$], 52.4 (C-2), 55.7 ($C_6H_4OCH_3$), 62.2 (C-6′), 62.7 (C-6), 68.9 (C-4′), 69.2 (C-4), 71.7 (C-2′), 71.9 (C-5), 72.3 (C-5′), 72.5 (C-3′), 74.6 (C-3), 98.0 (C-1), 101.6 (C-1′), 114.5 and 118.6 ($C_6H_4OCH_3$), 123.6 and 133.8 [$N(CO)_2C_6H_4$], 128.9, 129.0, 129.2, 129.7, 129.8, and 130.0 ($COC_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1136.365, $C_{60}H_{59}NNaO_{20}$ requires 1136.353.

(6-*O*-Levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl trichloroacetimidate 38

To a solution of **37** (0.52 g, 0.47 mmol) in 1 : 1 : 1 toluene–acetonitrile–water (30 cm^3) was added ammonium cerium(IV) nitrate (2.56 g, 4.7 mmol). The two-phase mixture was stirred for 2 h, when TLC (95 : 5 CH_2Cl_2–acetone) showed the disappearance of **37**. The mixture was diluted with EtOAc, and the organic phase was washed with saturated aq. $NaHCO_3$ and 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue gave the hemiacetal intermediate, isolated as an orange foam. To a solution of the hemiacetal (0.38 g, 0.38 mmol) in dry CH_2Cl_2 (3 cm^3) and trichloroacetonitrile (0.41 cm^3, 3.8 mmol) was added, at 0 °C, 1,8-diazabicyclo[5.4.0]undec-7-ene (6.7 mm^3, 38 μmol). The reaction was stirred for 16 h, then concentrated. Column chromatography (95 : 5 CH_2Cl_2–acetone) of the residue yielded **38** (0.32 g, 58%), isolated as a yellow foam; $[\alpha]_D^{20}$ +29 (*c* 1 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 2.08, 2.21, 2.24, 2.28, 2.32, and 2.33 [each 3 H, 6 × s, 3 × $COC_6H_4CH_3$, 2 × $COCH_3$, and $CO(CH_2)_2COCH_3$], 2.63 and 2.80 [each 2 H, 2 × m, $CO(CH_2)_2COCH_3$], 3.92 (1 H, m, H-5′), 4.11 (1 H, dd, H-6b), 4.14 (1 H, dd, H-6b′), 4.19 (1 H, br t, H-5), 4.29 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 5.1 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 11.3 Hz, H-6a), 4.39 (1 H, dd, $J_{H\text{-}5',H\text{-}6a'}$ 2.6, $J_{H\text{-}6a',H\text{-}6b'}$ 12.1, H-6a′), 4.76 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 9.0, $J_{H\text{-}2,H\text{-}3}$ 11.3, H-2), 4.80 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 7.8, H-1′), 5.01 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.4, H-3), 5.27 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 9.9, H-2′), 5.43 (1 H, br t, H-4′), 5.65 (1 H, br t, H-3′), 5.69 (1 H, br d, H-4), 6.29 (1 H, d, H-1), 6.87, 6.99, 7.13, 7.36, 7.56, and 7.74 (each 2 H, 6 × d, 3 × $COC_6H_4CH_3$), 8.42 [$OC(NH)CCl_3$]; δ_C(125 MHz; $CDCl_3$) 20.8, 21.0, 21.6, 21.7 (2 C), and 29.8 [3 × $COC_6H_4CH_3$, 2 × $COCH_3$, and $CO(CH_2)_2COCH_3$], 28.0 and 38.1 [$CO(CH_2)_2COCH_3$], 51.4 (C-2), 62.2 (C-6′), 62.3 (C-6), 68.9 (C-4′), 69.0 (C-4), 71.6 (C-2′), 72.3 (C-5′), 72.4 (C-3′), 72.7 (C-5), 74.1 (C-3), 94.4 (C-1), 101.5 (C-1′), 123.3 and 133.8 [$N(CO)_2C_6H_4$], 128.9, 129.1, 129.2, 129.6, 129.8, and 130.0 ($COC_6H_4CH_3$).

5-Azidopentyl (6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl)-(1→6)-[(6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)]-4-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 39

A solution of **27** (74 mg, 68 μmol) and **38** (117.3 mg, 102 μmol) in dry CH_2Cl_2 (3 cm^3), containing activated molecular sieves (4 Å, 0.1 g), was stirred for 45 min at rt, then TMSOTf (2.0 mm^3, 10.2 μmol) was added at 0 °C. The mixture was

stirred for 15 min, when TLC (9:1 CH_2Cl_2–acetone) showed the formation of **39** to be complete (R_f = 0.41). After neutralization with pyridine and filtration, the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (9:1 CH_2Cl_2–acetone) of the residue rendered **39** (100 mg, 70%), isolated as a glass; $[\alpha]_D^{20}$ +3 (*c* 1 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 0.84, 1.00, 1.12, and 2.74 [each 2 H, 4 × m, $OCH_2(CH_2)_4N_3$], 2.12, 2.14, 2.20, 2.21, 2.22, 2.23, 2.24, 2.30, 2.31, and 2.33 [3 H, 3 H, 3 H, 3 H, 3 H, 3 H, 3 H, 3 H, 3 H, and 6 H, 10 × s, 6 × $COC_6H_4CH_3$, 3 × $COCH_3$, and 2 × $CO(CH_2)_2COCH_3$], 2.57 and 2.75 [each 4 H, 2 × m, 2 × $CO(CH_2)_2COCH_3$], 2.78 and 3.14 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.34 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 8.7 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 10.9 Hz, H-6b), 3.77 (1 H, m, H-5), 3.84 (1 H, m, H-5‴), 3.91 (1 H, m, H-5″), 3.93 (1 H, m, H-6a), 3.99 (1 H, m, H-5′), 4.08 and 4.22 (each 1 H, 2 × m, 2 × H-6′), 4.13 and 4.24 (each 1 H, 2 × br t, 2 × H-6‴), 4.15 (1 H, dd, $J_{H\text{-}5'',H\text{-}6b''}$ 5.2, $J_{H\text{-}6a'',H\text{-}6b''}$ 12.2, H-6b″), 4.32 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, $J_{H\text{-}2,H\text{-}3}$ 11.3, H-2), 4.36 (1 H, dd, $J_{H\text{-}5'',H\text{-}6a''}$ 2.1, H-6a″), 4.46 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 8.4, $J_{H\text{-}2',H\text{-}3'}$ 11.2, H-2′), 4.67 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.2, H-3), 4.71 (2 H, br d, H-1 and H-1‴), 4.76 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.8, H-1″), 4.85 (1 H, dd, $J_{H\text{-}3',H\text{-}4'}$ 3.2, H-3′), 5.02 (1 H, d, H-1′), 5.20 (1 H, dd, $J_{H\text{-}1''',H\text{-}2'''}$ 7.9, $J_{H\text{-}2''',H\text{-}3'''}$ 9.9, H-2‴), 5.23 (1 H, dd, $J_{H\text{-}2'',H\text{-}3''}$ 10.0, H-2″), 5.37 (1 H, br t, H-4‴), 5.40 (1 H, br t, H-4″), 5.41 (1 H, br d, H-4), 5.59 (1 H, br t, H-3‴), 5.61 (1 H, br t, H-3″), 5.62 (1 H, br d, H-4′), 6.83, 6.84, 6.96, 6.98, 7.11, 7.12, 7.29, 7.31, 7.52, 7.53, 7.71, and 7.73 (each 2 H, 12 × d, 6 × $COC_6H_4CH_3$); δ_C(125 MHz; $CDCl_3$) 20.8, 20.9, 21.0 (2 C), 21.6 (2 C), 21.7 (3 C), and 29.9 (2 C) [6 × $COC_6H_4CH_3$, 3 × $COCH_3$, and 2 × $CO(CH_2)_2COCH_3$], 23.0, 28.3, 29.8, and 51.1 [$OCH_2(CH_2)_4N_3$], 27.9 and 38.1 [2 × $CO(CH_2)_2COCH_3$], 52.4 (C-2′), 52.5 (C-2), 62.3 (C-6″), 62.4 (C-6‴), 62.6 (C-6′), 68.5 [$OCH_2(CH_2)_4N_3$], 68.8 (C-6), 68.9 (C-4‴), 69.0 (C-4″), 69.3 (C-4′), 69.8 (C-4), 71.6 (C-5′), 71.7 (2 C) (C-2″ and C-2‴), 72.2 (2 C) (C-5″ and C-5‴), 72.5 (2 C) (C-3″ and C-3‴), 73.7 (C-5), 74.5 (C-3′), 75.0 (C-3), 98.3 (C-1), 98.6 (C-1′), 101.4 (2 C) (C-1″ and C-1‴), 123.1, 123.3, and 133.7 [$N(CO)_2C_6H_4$], 128.9, 129.0, 129.2, 129.6, 129.8, and 130.0 ($COC_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 2088.691, $C_{109}H_{111}N_5NaO_{36}$ requires 2088.691.

5-Azidopentyl (2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl)-(1→6)-[(2,3,4-tri-*O*-*p*-toluoyl-β-D-glucopyranosyl)-(1→3)]-4-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranoside 40

To a solution of **39** (90 mg, 43 μmol) in EtOH (10 cm^3) and toluene (3 cm^3) was added hydrazine acetate (20 mg, 215 μmol). The mixture was stirred for 2 h, then concentrated. Column chromatography (9:1 CH_2Cl_2–acetone) of the residue yielded **40** (60 mg, 75%), isolated as a white glass; $[\alpha]_D^{20}$ +5 (*c* 0.2 in $CHCl_3$); δ_H(500 MHz; $CDCl_3$; 2D TOCSY and HSQC) 0.88, 1.05, 1.12, and 2.72 [each 2 H, 4 × m, $OCH_2(CH_2)_4N_3$], 2.11, 2.20, 2.22, 2.27, 2.28, 2.31, and 2.33 (3 H, 3 H, 6 H, 3 H, 3 H, 3 H, and 6 H, 7 × s, 6 × $COC_6H_4CH_3$ and 3 × $COCH_3$), 2.89 and 3.21 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.43 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 8.4 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 10.7 Hz, H-6b), 3.56 (1 H, dd, $J_{H\text{-}5''',H\text{-}6b'''}$ 6.1, $J_{H\text{-}6a''',H\text{-}6b'''}$ 12.3, H-6b‴), 3.60 (1 H, dd, $J_{H\text{-}5'',H\text{-}6b''}$ 6.4, $J_{H\text{-}6a'',H\text{-}6b''}$ 12.9, H-6b″), 3.71 (2 H, m, H-6a″ and H-6a‴), 3.73 (1 H, m, H-5‴), 3.76 (1 H, m, H-5), 3.79 (1 H, m, H-5″), 3.88 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 2.1, H-6a), 4.00 (1 H, m, H-5′), 4.15 (2 H, m, 2 × H-6′), 4.33 (1 H, dd, $J_{H\text{-}1,H\text{-}2}$ 8.6, $J_{H\text{-}2,H\text{-}3}$ 11.2, H-2), 4.50 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 8.6, $J_{H\text{-}2',H\text{-}3'}$ 11.1, H-2′), 4.65 (1 H, dd, $J_{H\text{-}3,H\text{-}4}$ 3.5, H-3), 4.71 (1 H, d, H-1), 4.79 (1 H, d, $J_{H\text{-}1''',H\text{-}2'''}$ 8.0, H-1‴), 4.82 (1 H, dd, $J_{H\text{-}3',H\text{-}4'}$ 3.6, H-3′), 4.86 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.8, H-1″), 5.02 (1 H, d, H-1′), 5.21 (1 H, dd, $J_{H\text{-}2''',H\text{-}3'''}$ 10.0, H-2‴), 5.25 (1 H, dd, $J_{H\text{-}2'',H\text{-}3''}$ 9.9, H-2″), 5.31 (1 H, br t, H-4‴), 5.33 (1 H, br t, H-4″), 5.53 (1 H, br d, H-4), 5.63 (1 H, br t, H-3‴), 5.65 (1 H, br t, H-3″), 5.72 (1 H, br d, H-4′), 6.75, 6.78, 6.94, 7.13, 7.27, 7.50, 7.51, 7.74, and 7.75 (2 H, 2 H, 4 H, 4 H, 4 H, 2 H, 2 H, 2 H, and 2 H, 9 × d, 6 × $COC_6H_4CH_3$); δ_C(125 MHz; $CDCl_3$) 20.7, 21.2, 21.3, 21.6 (4 C), and 21.8 (2 C) (6 × $COC_6H_4CH_3$ and 3 × $COCH_3$), 22.9, 28.3, 29.7, and 51.1 [$OCH_2(CH_2)_4N_3$], 52.3 (C-2′), 52.5 (C-2), 61.4 (C-6‴), 61.5 (C-6″), 61.9 (C-6′), 68.2 (C-6), 68.6 [$OCH_2(CH_2)_4N_3$], 68.7 (2 C) (C-4″ and C-4‴), 69.3 (C-4′), 70.1 (C-4), 71.2 (C-5′), 71.7 (2 C) (C-2″ and C-2‴), 72.7 (2 C) (C-3″ and C-3‴), 73.4 (C-5), 75.3 (C-5″), 75.4 (C-5‴), 75.8 (C-3′), 75.9 (C-3), 98.3 (C-1), 98.4 (C-1′), 102.0 (C-1‴), 102.2 (C-1″), 123.0, 123.3, and 133.5 [$N(CO)_2C_6H_4$], 128.9, 129.0, 129.2, 129.6, 129.8, and 130.0 ($COC_6H_4CH_3$); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1892.647, $C_{99}H_{99}N_5NaO_{32}$ requires 1892.617.

5-Azidopentyl (sodium β-D-glucopyranosyl 6-sulfate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→6)-[(sodium β-D-glucopyranosyl 6-sulfate)-(1→3)]-2-acetamido-2-deoxy-β-D-galactopyranoside 42

To a solution of **40** (53 mg, 28 μmol) in DMF (3 cm^3) was added the sulfur trioxide trimethylamine complex (157 mg, 1.12 mmol). The mixture was stirred for 48 h at 50 °C, when TLC (9:1 CH_2Cl_2–MeOH) showed the complete conversion of **40** into non-sodiated **41** (R_f = 0.16). After quenching the reaction with MeOH (10 cm^3), the solution was co-concentrated with toluene. A solution of the residue in EtOAc (50 cm^3) was washed with saturated aq. $NaHCO_3$ and 10% aq. NaCl, dried, filtered, and concentrated. The residue was dissolved in MeOH (10 cm^3), containing Dowex 50 W X 8 Na^+ resin, and stirred for 15 min, then filtered and concentrated. Column chromatography (9:1 CH_2Cl_2–MeOH) of the residue gave **41** (45 mg, 77%), isolated as a white, amorphous powder; δ_H(300 MHz; $CDCl_3$) 0.90, 1.13, and 2.82 [2 H, 4 H, and 2 H, 3 × m, $OCH_2(CH_2)_4N_3$], 2.21, 2.23, 2.25, 2.30, and 2.34 (3 H, 3 H, 6 H, 6 H, and 9 H, 5 × s, 6 × $COC_6H_4CH_3$ and 3 × $COCH_3$), 3.01 and 3.35 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.52 (1 H, dd, $J_{H\text{-}5,H\text{-}6b}$ 8.4 Hz, $J_{H\text{-}6a,H\text{-}6b}$ 10.5 Hz, H-6b), 3.84 (1 H, dd, $J_{H\text{-}5,H\text{-}6a}$ 2.0, H-6a), 3.92 (1 H, m, H-5′), 4.42 (1 H, dd, $J_{H\text{-}1',H\text{-}2'}$ 8.5, $J_{H\text{-}2',H\text{-}3'}$ 11.2, H-2′), 4.75 (1 H, d, $J_{H\text{-}1''',H\text{-}2'''}$ 7.8, H-1‴), 4.78 (1 H, d, $J_{H\text{-}1,H\text{-}2}$ 8.5, H-1), 4.81 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.7, H-1″), 4.92 (1 H, dd, $J_{H\text{-}2',H\text{-}3'}$ 11.3, $J_{H\text{-}3',H\text{-}4'}$ 3.2, H-3′), 5.14 (1 H, d, H-1′), 5.18 (1 H, dd, $J_{H\text{-}2''',H\text{-}3'''}$ 9.6, H-2‴), 5.22 (1 H, dd, $J_{H\text{-}2'',H\text{-}3''}$ 9.5, H-2″), 5.34 (1 H, br t, H-4‴), 5.37 (1 H, br t, H-4″), 5.58 (1 H, br d, $J_{H\text{-}3,H\text{-}4}$ 3.4, H-4), 5.63 (1 H, br t, H-3‴), 5.67 (1 H, br t, H-3″), 5.80 (1 H, br d, H-4′), 6.87, 6.90, 7.00, 7.15, 7.31, 7.33, 7.54, and 7.73 (2 H, 2 H, 4 H, 4 H, 2 H, 2 H, 4 H, and 4 H, 8 × s, 6 × $COC_6H_4CH_3$).

A solution of **41** (35 mg, 22 μmol) in ethanolic 33% CH_3NH_2 (5 cm^3) was stirred for 7 days, during which time the mixture was three times concentrated and fresh ethanolic 33% CH_3NH_2 (5 cm^3) was added. After co-concentration with toluene, to a solution of the residue in dry MeOH at 0 °C was added acetic anhydride (100 mm^3). The mixture was stirred for 3 h at 0 °C, then concentrated. Size-exclusion chromatography (Bio-Gel P-2, 100 mM NH_4HCO_3) of the residue afforded **42** (11 mg, 62%), isolated after lyophilization from water, as a white, amorphous powder; $[\alpha]_D^{20}$ −11 (*c* 0.6 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 1.40, 1.59, and 3.30 [2 H, 4 H, and 2 H, 3 × m, $OCH_2(CH_2)_4N_3$], 2.01 and 2.02 (each 3 H, 2 × s, 2 × NAc), 3.32 (2 H, br t, H-2″ and H-2‴), 3.45 (4 H, m, H-3″, H-3‴, H-4″, and H-4‴), 3.57 and 3.88 [each 1 H, 2 × m, $OCH_2(CH_2)_4N_3$], 3.62 (2 H, m, H-5″ and H-5‴), 3.69 (1 H, m, H-5′), 3.78 (2 H, m, 2 × H-6′), 3.81 and 4.06 (each 1 H, 2 × m, 2 × H-6), 3.82 (1 H, m, H-5), 3.85 (2 H, br t, H-3 and H-3′), 3.99 (1 H, br t, H-2), 4.01 (1 H, br t, H-2′), 4.15 (1 H, br d, $J_{H\text{-}3,H\text{-}4}$ 3.2 Hz, H-4), 4.19 and 4.30 (each 2 H, 2 × m, 2 × H-6″ and 2 × H-6‴), 4.19 (1 H, br d, $J_{H\text{-}3',H\text{-}4'}$ 3.4, H-4′), 4.45 (1 H, d, $J_{H\text{-}1,H\text{-}2}$ 8.5, H-1), 4.50 (1 H, d, $J_{H\text{-}1''',H\text{-}2'''}$ 7.9, H-1‴), 4.51 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 7.8, H-1″), 4.53 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.5, H-1′); δ_C(125 MHz; D_2O) 23.0 (2 C) (2 × $NDCOCH_3$), 23.2, 28.3, 28.8, and 51.8 [$OCH_2(CH_2)_4N_3$], 51.8 (2 C) (C-2 and C-2′), 61.9 (C-6′), 67.8 (2 C) (C-6″ and C-6‴), 68.6 (C-4′), 68.9 (C-4), 70.0 (C-3″ and C-3‴), 70.3 (C-6), 70.6 [$OCH_2(CH_2)_4N_3$], 73.4 (2 C) (C-2″ and C-2‴), 74.2 (C-5), 74.3 (2 C) (C-5″ and C-5‴), 75.6 (C-5′), 76.2 (2 C) (C-4″ and C-4‴), 80.7 (2 C) (C-3 and C-3′), 101.8 (C-1), 102.2 (C-1′), 104.9 (C-1‴),

105.0 (C-1″); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1086.254, $C_{33}H_{55}N_5Na_3O_{27}S_2$ requires 1086.222.

5-Aminopentyl (sodium β-D-glucopyranosyl 6-sulfate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→6)-[(sodium β-D-glucopyranosyl 6-sulfate)-(1→3)]-2-acetamido-2-deoxy-β-D-galactopyranoside 6

A solution of **42** (5 mg, 4.7 μmol) in 0.05 M aq. NaOH (0.5 cm^3) was added dropwise to a suspension of 10% Pd–C (0.7 mg) and $NaHB_4$ (2.7 mg) in water (0.5 cm^3). The suspension was stirred for 1 h, when TLC (6 : 2.5 : 1.5 EtOAc–MeOH–water) showed the disappearance of **42**. After filtration through Celite, size-exclusion chromatography (Bio-Gel P-2, 100 mM NH_4HCO_3) gave **6** (3.5 mg, 71%), isolated after lyophilization from water, as a white, amorphous powder; $[\alpha]_D^{20}$ −4 (*c* 0.2 in water); δ_H(500 MHz; D_2O; 2D TOCSY and HSQC) 1.41, 1.60, 1.66 and 2.99 [each 2 H, 4 × m, $OCH_2(CH_2)_4ND_2$], 2.01 (6 H, s, 2 × NAc), 3.31 (2 H, br t, H-2″ and H-2‴), 3.45 (4 H, m, H-3″, H-3‴, H-4″, and H-4‴), 3.59 and 3.87 [each 1 H, 2 × m, $OCH_2(CH_2)_4ND_2$], 3.62 (2 H, m, H-5″ and H-5‴), 3.69 (1 H, m, H-5′), 3.78 (2 H, m, 2 × H-6′), 3.83 and 4.03 (each 1 H, 2 × m, 2 × H-6), 3.83 (1 H, m, H-5), 3.84 (2 H, br t, H-3 and H-3′), 3.99 (1 H, br t, H-2), 4.00 (1 H, br t, H-2′), 4.15 (1 H, br d, $J_{H\text{-}3,H\text{-}4}$ 3.2 Hz, H-4), 4.18 and 4.30 (each 2 H, 2 × m, 2 × H-6″ and 2 × H-6‴), 4.18 (1 H, br d, $J_{H\text{-}3',H\text{-}4'}$ 3.2, H-4′), 4.45 (1 H, d, $J_{H\text{-}1,H\text{-}2}$ 8.5, H-1), 4.50 (1 H, d, $J_{H\text{-}1''',H\text{-}2'''}$ 8.0, H-1‴), 4.52 (1 H, d, $J_{H\text{-}1'',H\text{-}2''}$ 8.1, H-1″), 4.53 (1 H, d, $J_{H\text{-}1',H\text{-}2'}$ 8.6, H-1′); δ_C(125 MHz; D_2O) 22.9 (2 C) (2 × $NDCOCH_3$), 22.8, 27.0, 28.7, and 40.0 [$OCH_2(CH_2)_4ND_2$], 51.8 (2 C) (C-2 and C-2′), 61.9 (C-6′), 67.9 (2 C) (C-6″ and C-6‴), 68.6 (C-4′), 68.8 (C-4), 70.0 (C-3″ and C-3‴), 70.4 (C-6), 70.5 [$OCH_2(CH_2)_4ND_2$], 73.5 (2 C) (C-2″ and C-2‴), 74.2 (C-5), 74.3 (2 C) (C-5″ and C-5‴), 75.6 (C-5′), 76.1 (2 C) (C-4″ and C-4‴), 80.5 (2 C) (C-3 and C-3′), 101.9 (C-1), 102.3 (C-1′), 104.8 (C-1‴), 104.9 (C-1″); high resolution MALDI-TOF MS, *m*/*z* found M+Na 1060.193, $C_{33}H_{57}N_3Na_3O_{27}S_2$ requires 1060.231.

3-[2-*N*-(3,4-Dione-2-ethoxycyclobutene)aminoethylthio]propyl (β-D-glucopyranosyluronic acid)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside 43

To a solution of **1** (1 mg, 1.9 μmol) in 50 mM sodium phosphate buffer (100 mm^3, pH 7.2) was added a solution of diethyl squarate (0.56 mm^3, 3.8 μmol) in EtOH (100 mm^3). After stirring for 16 h, EtOH was evaporated by flushing with N_2, and the residue in water was loaded on a C-18 Extract-Clean™ column. After elution of remaining **1** with water (3 × 3 cm^3), **43** was eluted with MeOH (3 × 3 cm^3), then concentrated *in vacuo.* The pure, elongated saccharide was used directly for the preparation of neoglycoconjugate **BSA-1**.

3-[2-*N*-(3,4-Dione-2-ethoxycyclobutene)aminoethylthio]propyl (2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-[(β-D-glucopyranosyluronic acid)-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside 44

To a solution of **2** (1 mg, 1.4 μmol) in 50 mM sodium phosphate buffer (100 mm^3, pH 7.2) was added a solution of diethyl squarate (0.4 mm^3, 2.4 μmol) in EtOH (100 mm^3). After stirring for 16 h, column chromatography (7.5 : 1.5 : 1.0 EtOAc–MeOH–water) of the mixture yielded **44**, isolated as a glass. The pure, elongated saccharide was used directly for the preparation of neoglycoconjugate **BSA-2**.

3-[2-*N*-(3,4-Dione-2-ethoxycyclobutene)aminoethylthio]propyl (β-D-glucopyranosyluronic acid)-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-[(β-D-glucopyranosyluronic acid)-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside 45

To a solution of **3** (0.8 mg, 0.9 μmol) in 50 mM sodium phosphate buffer (100 mm^3, pH 7.2) was added a solution of diethyl squarate (0.26 mm^3, 1.8 μmol) in EtOH (100 mm^3). After stirring for 16 h, column chromatography (7.5 : 1.5 : 1.0 EtOAc–MeOH–water) of the mixture yielded **45**, isolated as a glass. The pure, elongated saccharide was used directly for the preparation of neoglycoconjugate **BSA-3**.

5-*N*-(3,4-Dione-2-ethoxycyclobutene)aminopentyl (sodium β-D-glucopyranosyl 6-sulfate)-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranoside 46

To a solution of **4** (0.5 mg, 0.9 μmol) in 50 mM sodium phosphate buffer (100 mm^3, pH 7.2) was added a solution of diethyl squarate (0.26 mm^3, 3.6 μmol) in EtOH (100 mm^3). After stirring for 16 h, EtOH was evaporated by flushing with N_2, and the residue in water was loaded on a C-18 Extract-Clean™ column. After elution of remaining **4** with water (3 × 3 cm^3), **46** was eluted with MeOH (3 × 3 cm^3), then concentrated *in vacuo.* The pure, elongated saccharide was used directly for the preparation of neoglycoconjugate **BSA-4**.

5-*N*-(3,4-Dione-2-ethoxycyclobutene)aminopentyl (2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→6)-[(sodium β-D-glucopyranosyl 6-sulfate)-(1→3)]-2-acetamido-2-deoxy-β-D-galactopyranoside 47

To a solution of **5** (1.0 mg, 1.2 μmol) in 50 mM sodium phosphate buffer (100 mm^3, pH 7.2) was added a solution of diethyl squarate (0.4 mm^3, 2.4 μmol) in EtOH (100 mm^3). After stirring for 16 h, column chromatography (7.5 : 1.5 : 1.0 EtOAc–MeOH–water) of the mixture yielded **47**, isolated as a glass. The pure, elongated saccharide was used directly for the preparation of neoglycoconjugate **BSA-5**.

5-*N*-(3,4-Dione-2-ethoxycyclobutene)aminopentyl (sodium β-D-glucopyranosyl 6-sulfate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→6)-[(sodium β-D-glucopyranosyl 6-sulfate)-(1→3)]-2-acetamido-2-deoxy-β-D-galactopyranoside 48

To a solution of **6** (1.0 mg, 1.0 μmol) in 50 mM sodium phosphate buffer (100 mm^3, pH 7.2) was added a solution of diethyl squarate (0.28 mm^3, 2.0 μmol) in EtOH (100 mm^3). After stirring for 16 h, column chromatography (7.5 : 1.5 : 1.0 EtOAc–MeOH–water) of the mixture yielded **48**, isolated as a glass. The pure, elongated saccharide was used directly for the preparation of neoglycoconjugate **BSA-6**.

General procedure for the conjugation of elongated saccharides 43–48 to BSA

For a target oligosaccharide incorporation of about 15 mol mol^{-1} BSA, to a solution of an elongated saccharide (**43–48**, 10 equiv. based on BSA) in 0.1 M $NaHCO_3$ buffer (0.5 mg cm^{-3}, pH 9.0) was added a solution of pre-treated BSA[11] (20 mg cm^{-3}) in 0.1 M $NaHCO_3$ buffer. After stirring for 3–5 days, the mixtures were loaded on to a 30 kDa Nalgene centrifugal filter, and washed with water (6 × 15 cm^3). After lyophilization from water, the degree of incorporation of saccharides **43–48** in neoglycoconjugates **BSA-1**–**BSA-6**, respectively, was determined by MALDI-TOF MS analysis. Samples (0.1 mg cm^{-3} 1 : 1 acetonitrile–water) were mixed on the target plate in a ratio of 1 : 1 with the matrix 3,5-dimethoxy-4-hydroxycinnamic acid (10 mg cm^{-3}) in 1 : 1 acetonitrile–water containing 0.1% TFA.

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