# Synthesis of Gold Glyconanoparticles: Possible Probes for the Exploration of Carbohydrate-Mediated Self-Recognition of Marine Sponge Cells

**Adriana Carvalho de Souza,[a] Koen M. Halkes,[a] Johannes D. Meeldijk,[b] Arie J. Verkleij,[b] Johannes F. G. Vliegenthart,[a] and Johannis P. Kamerling*[a]**

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The first step in marine sponge cell recognition and adhesion operates via a calcium-dependent proteoglycan–proteoglycan interaction. For the marine sponge *Microciona prolifera*, one of the carbohydrate epitopes involved in the proteoglycan self-recognition is a sulfated disaccharide [Glc*p*NAc3*S*(β1–3)Fuc*p*]. Earlier surface plasmon resonance studies have demonstrated that the proteoglycan self-recognition can be mimicked with synthetic β-D-Glc*p*NAc-(1→3)-α-L-Fuc*p*-(1→O), when multivalently presented by conjugation with bovine serum albumin. Here, the straightforward synthesis of water-soluble gold glyconanoparticles coated with the glycosides β-D-Glc*p*NAc3*S*-(1→3)-α-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$, β-D-Glc*p*NAc3*S*-(1→3)-β-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$, β-D-Glc*p*NAc3*S*-(1→O)$(CH_2)_3S(CH_2)_6SH$, α-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$, β-D-Glc*p*NAc3*S*-(1→3)-α-L-Gal*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$, β-D-Glc*p*NAc-(1→3)-α-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$, and β-D-Glc*p*3*S*-(1→3)-α-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$ is presented. Such supramolecular structures are excellent probes for studying carbohydrate–carbohydrate interactions by transmission electron microscopy, thereby generating information on the molecular level about the role of different functionalities in the self-recognition process.



## Introduction

Cell recognition and adhesion involve many kinds of cell surface molecules that interact in homotypic and/or heterotypic ways.[1] Cellular adhesion in marine sponges is an event mediated by species-specific extracellular proteoglycans, otherwise known as aggregation factors.[2] For the species-specific cell adhesion in the marine sponge *Microciona prolifera*, two highly polyvalent functional domains of its proteoglycan (MAF) are held responsible: N-linked carbohydrate domains of 200 kDa molecular mass (g-200) for calcium-dependent self-interaction, and N-linked carbohydrate domains of 6 kDa molecular mass (g-6) for calcium-independent cell-surface adherence.[3−6] Two monoclonal antibodies raised against MAF, Block 1 and Block 2, were able to inhibit the self-association of the proteoglycan in the presence of calcium.[7,8] Both antibodies recognized repetitive carbohydrate epitopes on the g-200 glycan. Partial characterization of the g-200 glycan showed that two small oligosaccharide fragments, pyruvylated trisaccharide Gal*p*4,6Pyr(β1−4)Glc*p*NAc(β1−3)Fuc*p* and sulfated disaccharide Glc*p*NAc3*S*(β1−3)Fuc*p*,[9] are the epitopes recognized by Block 1 and Block 2 antibodies, respectively. Recently, by using surface plasmon resonance (SPR), we have shown that the g-200 glycan−glycan interaction can be mimicked with synthetic β-D-Glc*p*NAc3*S*-(1→3)-α-L-Fuc*p*(1→O), when multivalently presented as a bovine serum albumin conjugate.[10,11] The results indicated also that the interaction is not simply based on electrostatic interactions. In view of the finding that the use of protein carriers made careful blank experiments necessary,[11] because of non-specific binding phenomena, other analytical approaches to study the self-recognition of multivalently presented sulfated disaccharide were explored.

Nowadays, gold nanoparticles functionalized with biomolecules are widely used as model systems for interaction studies (for a review, see ref.[12]). Inert water-soluble gold glyconanoparticles have been successfully applied as multivalent systems for transmission electron microscopic (TEM) studies on the self-recognition of $Le^x$ antigen,[13] and the mannose binding to *E. coli* FimH adhesion.[14] It turned out that gold nanodots, multivalently coated with thiol spacer containing saccharides via covalent linkages of sulfur atoms to the gold surface, are challenging stable probes for studying carbohydrate−carbohydrate and carbohydrate−protein interactions.

In the present investigation the glycosides β-D-Glc*p*NAc3*S*-(1→3)-α-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$ (**1a**), β-D-Glc*p*NAc3*S*-(1→3)-β-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$

[a] Bijvoet Center, Department of Bio-Organic Chemistry, Section of Glycoscience and Biocatalysis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands
[b] Institute of Biomembranes, Department of Cell Biology, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

(**1b**), β-D-Glc*p*NAc3*S*-(1→O)$(CH_2)_3S(CH_2)_6SH$ (**2**), α-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$ (**3**), β-D-Glc*p*NAc3*S*-(1→3)-α-L-Gal*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$ (**4**), β-D-Glc*p*-NAc-(1→3)-α-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$ (**5**), and β-D-Glc*p*3*S*-(1→3)-α-L-Fuc*p*-(1→O)$(CH_2)_3S(CH_2)_6SH$ (**6**) were synthesized and conjugated to gold nanoparticles (Figure 1), yielding water-soluble gold glyconanoparticles (**Au-1a/b** − **Au-6**), to be used in TEM studies. As the earlier structural studies[9] were not able to identify the anomeric configuration of fucose in the intact proteoglycan, both anomers (**1a** and **1b**) of the native disaccharide fragment were synthesized. In order to generate information with respect to the importance of the two monosaccharide units in the self-recognition process, compounds **2** and **3** were prepared. The three disaccharide mimics: **4** (L-fucose replaced by L-galactose), **5** (*N*-acetyl-3-*O*-sulfonato-D-glucosamine replaced by nonsulfated *N*-acetyl-D-glucosamine), and **6** (*N*-acetyl-3-*O*-sulfonato-D-glucosamine replaced by 3-*O*-sulfonato-D-glucose) were synthesized to evaluate the relevance of the modified functionalities for the self-recognition process. The choice of the α-configuration for the "reducing end" in **3** to **6** was based on preliminary TEM experiments with **Au-1a** and **Au-1b**.

## Results and Discussion

### Synthesis of Thiol Spacer Containing Saccharides 1a/b to 6

Disaccharide **1a** was synthesized in a yield of 86% by elongation of the sodium salt of allyl (2-acetamido-2-deoxy-3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-α-L-fucopyranoside (**7**)[10] with 1,6-hexanedithiol (10 equiv. based on **7**) under UV irradiation as radical initiator (Scheme 1).[15,16] A large excess of 1,6-hexanedithiol was used to avoid formation of dimers of the allyl glycoside. The presence of the 3-*O*-sulfonato group in the product was established by the downfield NMR shift of the H3′ signal (δ ≈ 4.4 ppm).[9,10]

The monosaccharide building blocks used for the synthesis of spacer-containing disaccharide **1b** are depicted in Scheme 2. Starting from L-fucose tetraacetate, the reactive 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide[17] was prepared and coupled to allyl alcohol via a Koenigs−Knorr reaction (→ **8**, 95%).[18] Deacetylation of **8**, using Zemplén conditions,[19] was directly followed by 3,4-*O*-isopropylidenation using 2,2-dimethoxypropane and a catalytic amount of *p*-toluenesulfonic acid.[10] Then, conventional acetylation of the 2-OH group gave the fully protected compound **9** (80%, overall yield). After removal of the isopropylidene

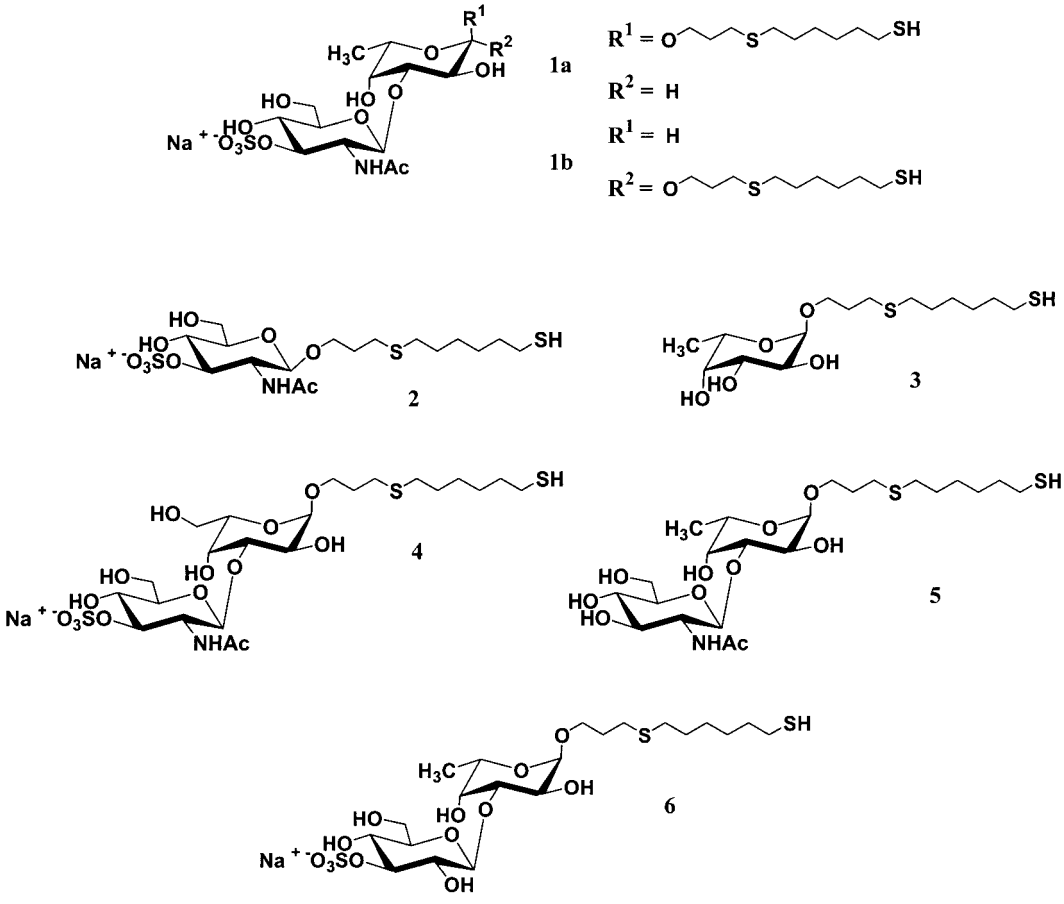
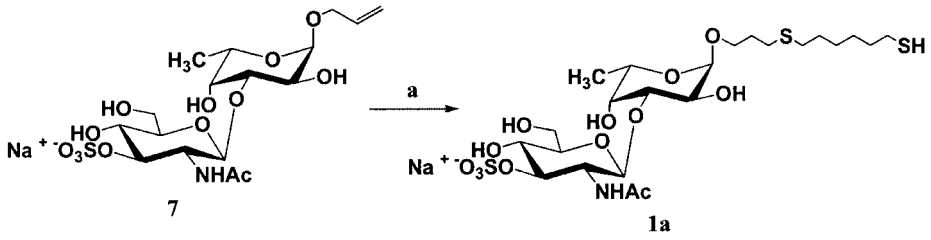
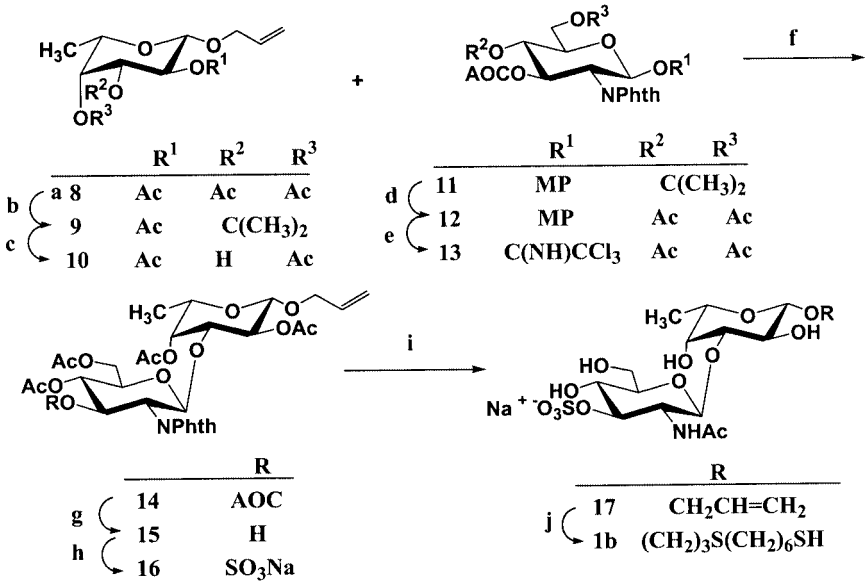



Figure 1. Target structures **1a/b** to **6** containing a thiol spacer



Scheme 1. Reagents and conditions. a, 1,6-hexanedithiol, UV light, MeOH, 86%

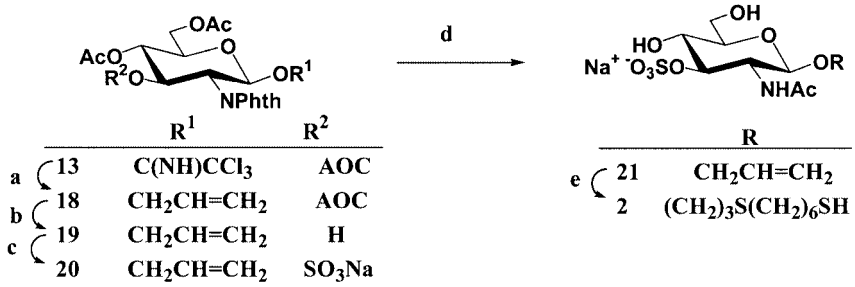


Scheme 2. Reagents and conditions. a, (i) from L-fucose tetraacetate, 33% HBr/HOAc, 0 °C; (ii) allyl alcohol, $Hg(CN)_2$, 95% over two reaction steps. b, (i) NaOMe, MeOH; (ii) 2,2-dimethoxypropane, *p*TsOH, DMF; (iii) acetic anhydride, pyridine, 80% over three reaction steps. c, (i) TFA, water, $CH_2Cl_2$; (ii) trimethyl orthoacetate, *p*TsOH, $CH_2Cl_2$; (iii) acetic acid, water, 40 °C, 51% over three reaction steps. d, (i) TFA, water, $CH_2Cl_2$; (ii) acetic anhydride, pyridine, quantitative overall yield. e, (i) ammonium cerium(IV) nitrate, acetonitrile/toluene/water (1:1:1); (ii) trichloroacetonitrile,1,8-diazabicyclo[5.4.0]undec-7-ene, $CH_2Cl_2$, 47% over two reaction steps. f, donor **13**, acceptor **10**, TMSOTf, $CH_2Cl_2$, 69%. g, $[Pd(PPh_3)_4]$, morpholine, THF, 65 °C, 65%. h, $SO_3{\cdot}NMe_3$, DMF, 50 °C, 89%. i, (i) 33% $NH_2Me$ in EtOH, 5 days; (ii) acetic anhydride, MeOH, 0 °C, 87% over two reaction steps. j, 1,6-hexanedithiol, UV light, MeOH, 83%. (AOC = $COOCH_2CH{=}CH_2$; MP = $C_6H_4OCH_3$)

group under acidic conditions, the obtained product was selectively 4-*O*-acetylated by reaction with trimethyl orthoacetate in the presence of *p*-toluenesulfonic acid, followed by regioselective ring opening of the formed 3,4-*O*-dioxolane-type acetal using aqueous acetic acid, to yield acceptor **10** (51%). As a first step in the synthesis of donor **13**, 4-methoxyphenyl 3-*O*-allyloxycarbonyl-2-deoxy-4,6-*O*-isopropylidene-2-phthalimido-β-D-glucopyranoside (**11**) [20,21] was de-isopropylidenated with aqueous trifluoroacetic acid, then 4,6-*O*-acetylated to yield **12** in a quantitative yield (Scheme 2). This deprotection/protection protocol was chosen to avoid such steps on the disaccharide level. Oxidative removal of the anomeric 4-methoxyphenyl group, using ammonium cerium(IV) nitrate,[22] followed by imidation,[23] yielded donor **13** (47%). Coupling of acceptor **10** with donor **13**, in the presence of trimethylsilyl triflate as a promoter (0.05 equiv. based on **10**), gave the disaccharide derivative **14** (69%), which was de-*O*-allyloxycarbonylated, using tetrakis(triphenylphosphane)palladium,[24,25] to yield **15** (65%). The sulfation of the free 3-OH group was accomplished using the sulfur trioxide trimethylamine complex. The product was stirred with Dowex-50 W × 8 ($Na^+$) to afford the sodium salt (→ **16**, 89%). Dephthaloylation/deacetylation with ethanolic 33% methylamine (5 days), and re-*N*-acetylation with acetic anhydride in methanol at 0 °C,[26] yielded allyl glycoside **17** (87%). Finally, the allyl group of **17** was elongated with 1,6-hexanedithiol, and spacer-containing disaccharide **1b** was obtained in 83%.

For the synthesis of spacer-containing monosaccharide **2**, compound **13** (Scheme 3) was coupled with allyl alcohol (→ **18**, 45%), then de-allyloxycarbonylated using tetrakis(triphenylphosphane)palladium and morpholine (→ **19**, quantitative), and 3-*O*-sulfonated with sulfur trioxide trimethylamine complex in DMF (→ **20**, 39%). Dephthaloylation/deacetylation of **20** followed by re-*N*-acetylation gave **21** (66%), which was elongated with 1,6-hexanedithiol to give

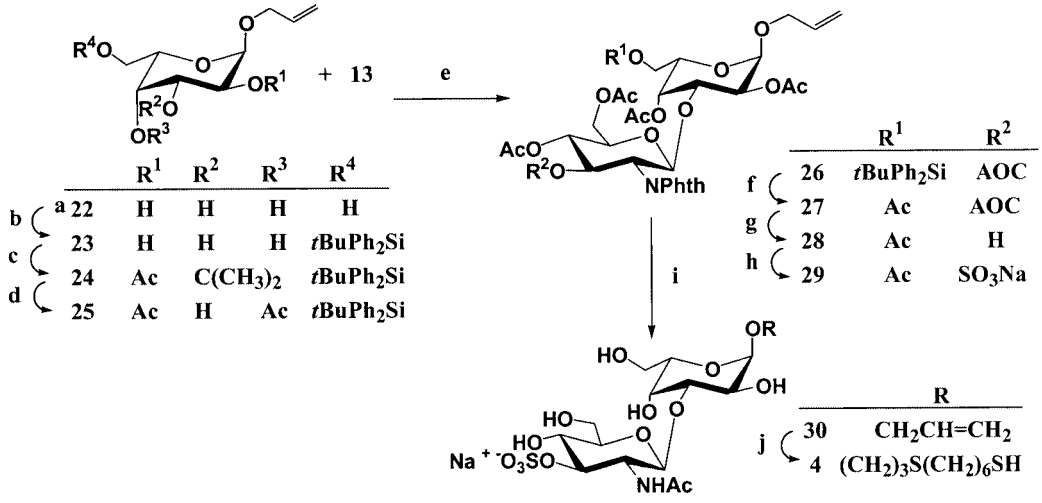



Scheme 3. Reagents and conditions. a, allyl alcohol, TMSOTf, $CH_2Cl_2$, 45%. b, $[Pd(PPh_3)_4]$, morpholine, THF, 50 °C, quantitative. c, $SO_3{\cdot}NMe_3$, DMF, 50 °C, 39%. d, (i) 33% $NH_2Me$ in ethanol, 5 days; (ii) acetic anhydride, MeOH, 0 °C, 66% over two reaction steps. e, 1,6-hexanedithiol, UV light, MeOH, 42%. (AOC = $COOCH_2CH{=}CH_2$)

**2** (42%). Addition of 1,6-hexanedithiol to allyl α-L-fucopyranoside[27] resulted in the other spacer-containing monosaccharide unit of **1** (→ **3**, 59%).

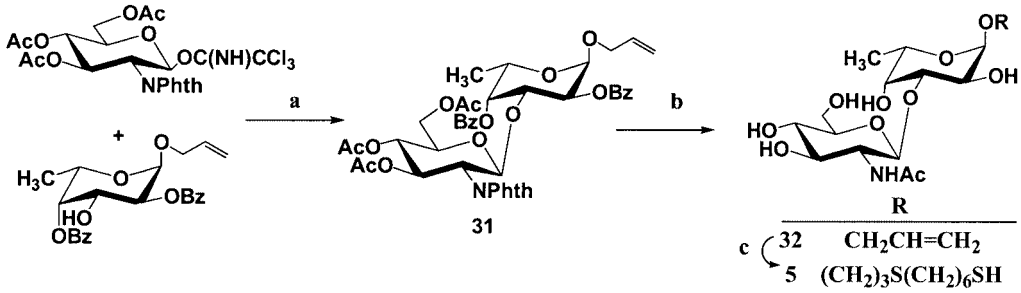
Spacer-containing disaccharide **4** was accessed by coupling of acceptor **25** and donor **13**. For the synthesis of **25**, L-galactose was treated with allyl alcohol in the presence of acetyl chloride (Scheme 4). The desired α-anomer **22** was obtained from crystallization of purified allyl α,β-L-galactopyranoside (30%). Compound **22** was selectively silylated at 6-OH with *tert*-butyldiphenylsilyl chloride (→ **23**, 97%), then 3,4-*O*-isopropylidinated, and acetylated at 2-OH, to give the fully protected intermediate **24** (60%). Removal of the isopropylidene acetal, under acidic conditions, followed by 4-*O*-acetylation using the orthoacetate approach as described for **10**, rendered acceptor **25** (78%, overall yield). Condensation of acceptor **25** and donor **13**, in the presence of trimethylsilyl triflate as a promoter, gave disaccharide **26** in 98% yield (Scheme 4). To avoid additional deprotection steps at the end of this disaccharide synthetic route, the *tert*-butyldiphenylsilyl group was removed with tetrabutylammonium fluoride, under neutral conditions, and the generated 6-OH group was directly acetylated (→ **27**, 84%). Deallyloxycarbonylation of **27** (→ **28**, 96%), followed by sulfate ester formation of the generated 3-OH group, yielded the disaccharide **29** (82%). Finally, dephthaloylation/deacetylation followed by re-*N*-acetylation gave the fully deprotected allyl glycoside **30** (96%), of which the allyl group was elongated with 1,6-hexanedithiol to give spacer-containing disaccharide **4** (60%).

For the synthesis of spacer-containing disaccharide **5**, 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate[23] was coupled with allyl 2,4-di-*O*-benzoyl-α-L-fucopyranoside[10] using trimethylsilyl triflate as a catalyst (0.05 equiv. based on acceptor), to afford **31** in 86% yield (Scheme 5). Dephthaloylation/deacylation of **31** with 1,2-diaminoethane in *n*-butanol at 90 °C, followed by *N*,*O*-acetylation with acetic anhydride in pyridine and de-*O*-acetylation with sodium methoxide in methanol, gave allyl glycoside **32** (80%). Target compound **5** was obtained after addition of 1,6-hexanedithiol to **32** (→ **5**, quantitative).




Scheme 4. Reagents and conditions. a, from L-galactose, allyl alcohol, acetyl chloride, 70 °C, 30%. b, $tBuPh_2SiCl$, $Et_3N$, pyridine, $CH_2Cl_2$, 97%. c, (i) 2,2-dimethoxypropane, *p*TsOH, DMF; (ii) acetic anhydride, pyridine, 60% over two reaction steps. d, (i) TFA, water, $CH_2Cl_2$; (ii) trimethyl orthoacetate, *p*TsOH, $CH_2Cl_2$; (iii) acetic acid, water, 40 °C, 78% over three reaction steps. e, acceptor **25**, donor **13**, TMSOTf, $CH_2Cl_2$, 98%. f, (i) 1 M tetrabutylammonium fluoride in THF, acetic acid, pH 7, 0 °C; (ii) acetic anhydride, pyridine, 84% over two reaction steps. g, $[Pd(PPh_3)_4]$, morpholine, THF, 65 °C, 96%. h, $SO_3{\cdot}NMe_3$, DMF, 50 °C, 82%. i, (i) 33% $NH_2Me$ in ethanol, 5 days; (ii) acetic anhydride, MeOH, 0 °C, 96% over two reaction steps. j, 1,6-hexanedithiol, UV light, MeOH, 60%. (AOC = $COOCH_2CH{=}CH_2$; $tBuPh_2Si$ = $(CH_3)_3CSi(C_6H_5)_2$)

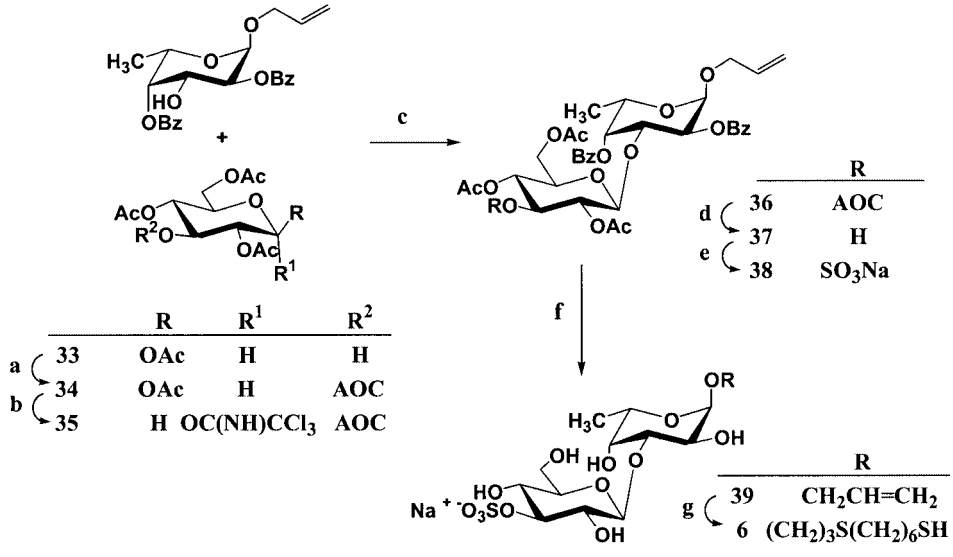



Scheme 5. Reagents and conditions. a, acceptor, donor, TMSOTf, $CH_2Cl_2$, 86%. b, (i) ethylenediamine, *n*BuOH, 90 °C; (ii) acetic anhydride, pyridine; (iii) NaOMe, MeOH, 80% over three reaction steps. c, 1,6-hexanedithiol, UV light, MeOH, quantitative. (Bz = $COC_6H_5$)

For the synthesis of spacer-containing disaccharide **6**, allyl 2,4-di-*O*-benzoyl-α-L-fucopyranoside[10] was chosen as acceptor. To obtain donor **35**, 1,2,4,6-tetra-*O*-acetyl-β-D-glucopyranose (**33**)[28] (Scheme 6) was 3-*O*-allyloxycarbonylated by treatment with allyl chloroformate at −30 °C (→ **34**, quantitative).[29] Selective removal of the anomeric acetyl group, using hydrazine acetate,[30] followed by imidation with trichloroacetonitrile,[23] resulted in the formation of **35** (60% overall yield). Subsequently, allyl 2,4-di-*O*-benzoyl-α-L-fucopyranoside was condensed with **35** in the presence of trimethylsilyl triflate (0.075 equiv. based on acceptor) to give disaccharide **36** in 60% yield (Scheme 6). Treatment of **36** with tetrakis(triphenylphosphane)palladium (→ **37**, 93%), sulfation of the generated 3-OH group with sulfur trioxide trimethylamine complex (→ **38**, 53%), and deacylation with sodium methoxide in methanol (pH 10)[19] afforded allyl glycoside **39** (quantitative). Finally, addition of 1,6-hexanedithiol to **39** gave the target disaccharide **6** (50%).

## Preparation of Gold Glyconanoparticles

Gold glyconanoparticles **Au-1a/b** to **Au-6** were prepared by a modified Brust's method.[31] To this end, tetrachloroauric anion was reduced, in the presence of the thiol spacer containing saccharides (**1a/b** to **6**), by the careful addition of an excess of $NaBH_4$. The formed gold glyconanoparticles, insoluble in methanol but soluble in water,[13] were purified by centrifugal filtration and characterized by $^1H$ NMR spectroscopy, monosaccharide analysis, and transmission electron microscopy (TEM). The $^1H$ NMR spectra of **Au-1a/b** to **Au-6** gave broad peaks with chemical shifts similar to those of the corresponding thiol spacer containing saccharides **1a/b** to **6**, respectively (Figure 2). In the case of the products **Au-1a/b**, **Au-2**, **Au-4** and **Au-6**, the $^1H$ NMR spectra showed a broad peak at $\delta \approx 4.4$ ppm, indicative of the 3-*O*-sulfonato group. TEM micrographs of **Au-1a/b** to **Au-6** in water (0.1 mg·mL$^{-1}$) showed, in all cases, uniformly dispersed nanodots throughout the grid surface (Figure 3).




Scheme 6. Reagents and conditions. a, allyl chloroformate, pyridine, $CH_2Cl_2$, − 30 °C, quantitative. b, (i) $NH_2NH_2$·HOAc, DMF; (ii) trichloroacetonitrile, 1,8-diazabicyclo[5.4.0]undec-7-ene, $CH_2Cl_2$, 60% over two reaction steps. c. donor **35**, acceptor, TMSOTf, $CH_2Cl_2$, 60%. d, [$Pd(PPh_3)_4$], morpholine, THF, 65 °C, 93%. e, $SO_3$·$NMe_3$, DMF, 50 °C, 53%. f, NaOMe, MeOH, quantitative. g, 1,6-hexanedithiol, UV light, MeOH, 50%. (AOC = $COOCH_2CH{=}CH_2$; Bz = $COC_6H_5$)

The size distribution of the gold nanoparticles was automatically calculated from approximately 1000 particles. Quantitative monosaccharide analysis revealed the presence of monosaccharide moieties in a molar ratio of 1:1 for **Au-1a/b** (GlcNAc, Fuc), **Au-4** (GlcNAc, Gal), **Au-5** (GlcNAc, Fuc), and **Au-6** (Glc, Fuc). The weight percentages of carbohydrate and the mean diameter of the gold glyconanoparticles are presented in Table 1. These values are in agreement with data from previous work for alkanethiol-protected nanoclusters.[32]

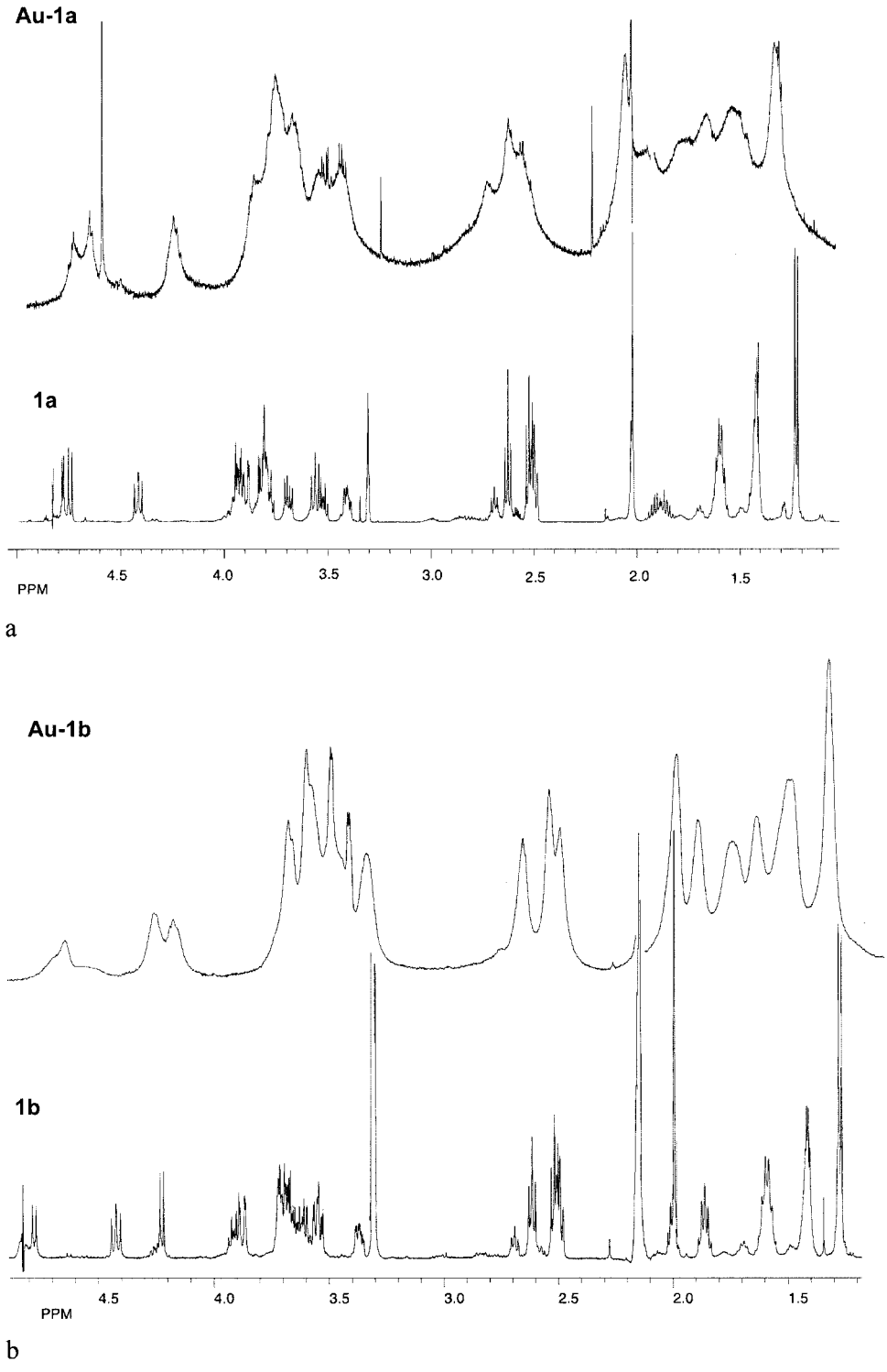



Figure 2. **a**: Comparison of the $^1$H NMR spectra of gold glyconanoparticles **Au-1a** (in $D_2O$) and thiol spacer containing disaccharide **1a** (in $CD_3OD$). **b**: Comparison of the $^1$H NMR spectra of gold glyconanoparticles **Au-1b** (in $D_2O$) and thiol spacer containing disaccharide **1b** (in $CD_3OD$)

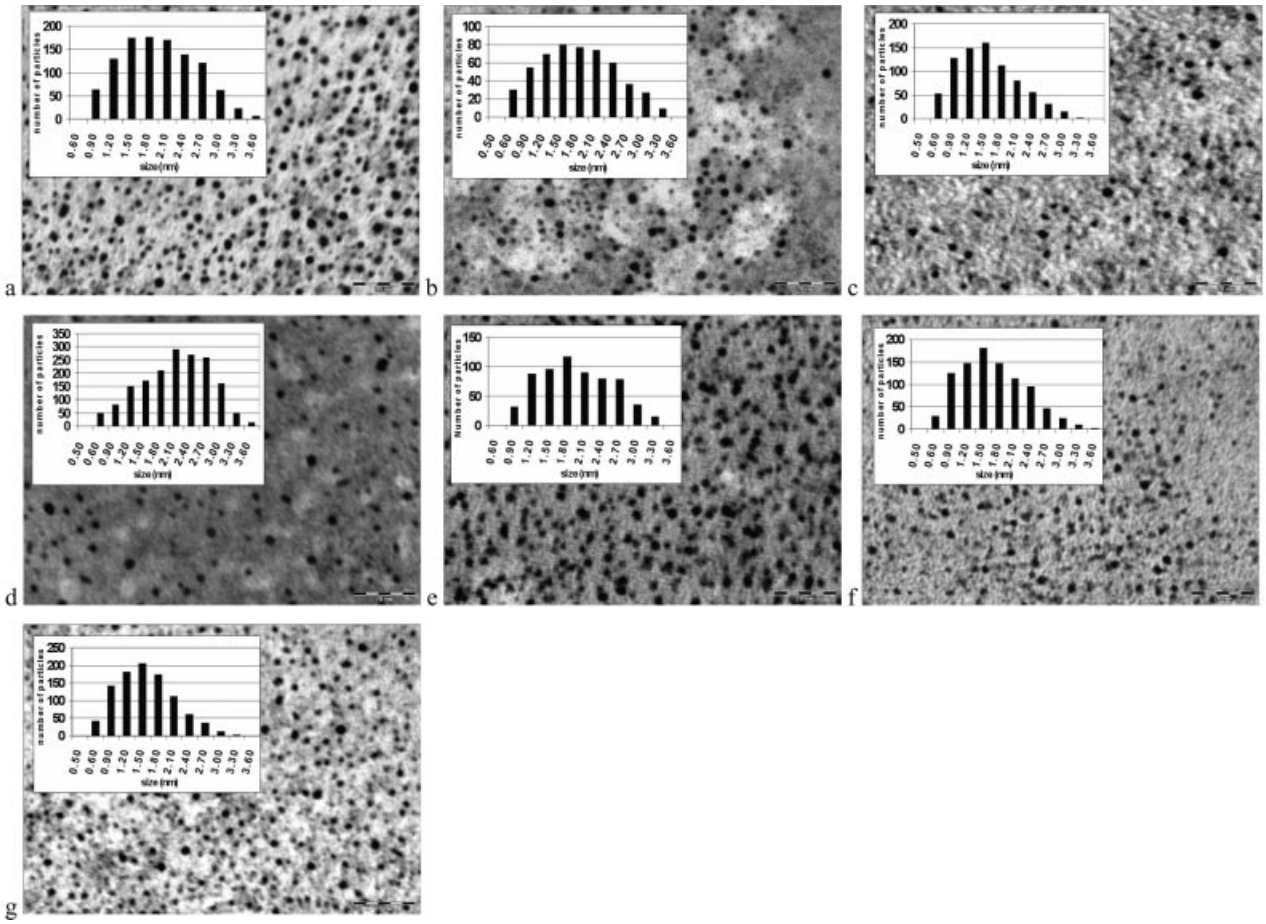


Figure 3. TEM images of **Au-1a/b** to **Au-6** in water (0.1 mg·mL$^{-1}$); scale bars 20 nm. a, **Au-1a**. b, **Au-1b**. c, **Au-2**. d, **Au-3**. e, **Au-4**. f, **Au-5**. g, **Au-6**. Inserts: Particle size distributions

Table 1. Results from monosaccharide analysis and mean diameter measurements of gold glyconanoparticles **Au-1a/b** to **Au-6**

| Glyconanoparticle | $D_{core}$ (nm) | % Sugar |
|---|---|---|
| **Au-1a** | 1.82 ± 0.8 | 36% |
| **Au-1b** | 1.71 ± 0.6 | 40% |
| **Au-2** | 1.51 ± 0.6 | 23% |
| **Au-3** | 1.80 ± 0.7 | 22% |
| **Au-4** | 1.80 ± 0.6 | 39% |
| **Au-5** | 1.63 ± 0.6 | 41% |
| **Au-6** | 1.55 ± 0.6 | 37% |

The gold glyconanoparticles **Au-1a/b** to **Au-6** have been used in transmission electron microscopy interaction studies, carried out in the presence and absence of calcium. The results of this work will be published elsewhere.

## Experimental Section

**General:** All chemicals were of reagent grade, and were used without further purification. Reactions were monitored by TLC on Silica Gel 60 $F_{254}$ (Merck); after examination under UV light, compounds were visualized by heating with 10% (v/v) methanolic $H_2SO_4$, orcinol (2 mg·mL$^{-1}$) in 20% (v/v) methanolic $H_2SO_4$, or ninhydrin (1.5 mg·mL$^{-1}$) in 1-BuOH/$H_2O$/HOAc (38:1.75:0.25). 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-mL cell. $^1$H NMR spectra were recorded at 300 K with a Bruker AC 300 (300 MHz) or a Bruker AMX 500 (500 MHz) spectrometer; $\delta_H$ values are given in ppm relative to the signal for internal $Me_4Si$ ($\delta_H$ = 0 ppm, $CDCl_3$) or internal acetone ($\delta_H$ = 2.22 ppm, $D_2O$ and $CD_3OD$). $^{13}$C NMR spectra (APT, 75.5 MHz) were recorded at 300 K with a Bruker AC 300 spectrometer; $\delta_C$ values are given in ppm relative to the signal of $CDCl_3$ ($\delta_C$ = 77.1, $CDCl_3$), $CD_3OD$ ($\delta_C$ = 49.0, $CD_3OD$) or internal acetone ($\delta_C$ = 30.9, $D_2O$). Two-dimensional $^1$H-$^1$H TOCSY (mixing times 7 and 100 ms) and $^1$H-$^{13}$C correlated HSQC spectra were recorded at 300 K with a Bruker AMX 500 spectrometer. Exact masses were measured by nano electrospray time-of-flight mass spectrometry using a Micromass LCToF mass spectrometer at a resolution of 5000 FWHM. Gold-coated capillaries were loaded with 1 μL of sample (conc. 20 μM) dissolved in a 1:1 (v/v) mixture of acetonitrile/water with 0.1% formic acid. Pentafluorophenylalanine was added as internal standard. The capillary voltage was set at 1500 V and the cone voltage was set at 30 V.

**3-(6-Mercaptohexylthio)propyl (Sodium 2-acetamido-2-deoxy-3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-α-L-fucopyranoside (1a):** To a

solution of allyl (sodium 2-acetamido-2-deoxy-3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-α-L-fucopyranoside[10] (**7**; 22 mg, 43 μmol) in MeOH (1.5 mL) 1,6-hexanedithiol (66 μL, 0.43 mmol) was added and the mixture was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV Lamp, when TLC ($CH_2Cl_2$/MeOH, 4:1) indicated the formation of **1a** ($R_f$ = 0.88). After concentration, the excess of 1,6-hexanedithiol was separated from carbohydrate by column chromatography ($CH_2Cl_2$/MeOH, 9:1 → MeOH). The carbohydrate-containing fractions were concentrated, and a solution of the residue in water was loaded on a C-18 Extract-Clean™ column. After elution of remaining **7** with water (3 × 3 mL), **1a** was eluted with MeOH (3 × 3 mL), then concentrated in vacuo, and obtained, after lyophilization from water, as a white, amorphous powder (24 mg, 86%). $[\alpha]_D^{20}$ = −20 (*c* = 0.5, $CH_3OH$). $^1$H NMR (500 MHz, $CD_3OD$; 2D TOCSY and HSQC): δ = 1.23 [d, $^3J$(H5,H6) = 6.6 Hz, 3 H, C*Me*], 1.41, 1.60, and 2.50 [3 m, each 4 H, $O(CH_2)_3S(CH_2)_6SH$], 1.94 [m, 2 H, $OCH_2CH_2CH_2S(CH_2)_6SH$], 2.02 (s, 3 H, NAc), 2.63 [bt, 2 H, $O(CH_2)_2CH_2S(CH_2)_6SH$], 3.41 (m, 1 H, H5′), 3.52 and 3.79 [2 m, each 1 H, $OCH_2(CH_2)_2S(CH_2)_6SH$], 3.56 (bt, 1 H, H4′), 3.68 [dd, $^3J$(H6a′,H6′) = 12.1, $^3J$(H5′,H6b′) = 5.9 Hz, 1 H, H6b′], 3.75 (dd, 1 H, H2′), 3.80 (bd, 1 H, H4), 3.81 [dd, $^3J$(H1,H2) = 3.9, $^3J$(H2,H3) = 10.3 Hz, 1 H, H2], 3.89 [dd, $^3J$(H5′,H6a′) = 2.3 Hz, 1 H, H6a′], 3.91 (bt, 1 H, H3), 3.93 (m, 1 H, H5), 4.41 [dd, $^3J$(H2′,H3′) = 10.3, $^3J$(H3′,H4′) = 8.7 Hz, 1 H, H3′], 4.73 [d, $^3J$(H1′,H2′) = 8.3 Hz, 1 H, H1′], 4.78 (d, 1 H, H1) ppm. $^{13}$C NMR (125.76 MHz, $CD_3OD$): δ = 16.5 (C6), 23.2 ($NDCOCH_3$), 25.1, 29.0, 29.4, 29.6, 30.6, 30.7, 32.7, and 35.1 [$OCH_2(CH_2)_2S(CH_2)_6SH$], 56.1 (C2′), 62.5 (C6′), 67.3 (C5), 67.6 [$OCH_2(CH_2)_2S(CH_2)_6SH$], 68.2 (C2), 70.9 (C4), 71.3 (C4′), 77.7 (C5′), 79.9 (C3), 81.8 (C3′), 100.3 (C1), 100.9 (C1′) ppm. High-resolution MS data of $C_{23}H_{42}NNaO_{13}S_3$ (659.171): [M + H] found 660.177, calculated 660.179.

**Allyl 2,3,4-Tri-*O*-acetyl-β-L-fucopyranoside (8):** To a solution of L-fucose tetraacetate (1.0 g, 3 mmol) in $CH_2Cl_2$ (20 mL) 33% hydrogen bromide in acetic acid (5.4 mL) was slowly added at 0 °C. The mixture was stirred at 0 °C for 2 h, diluted with $CH_2Cl_2$, washed with saturated aq. $NaHCO_3$, and dried. After filtration and concentration, a solution of the residue in dry $CH_2Cl_2$ (20 mL), containing activated molecular sieves (4 Å; 1.5 g), was stirred at room temperature for 30 min, then allyl alcohol (1.22 mL) was added at 0 °C, and stirring was continued for another 30 min. Mercury(II) cyanide (0.75 g, 3 mmol) was added, and the obtained suspension was stirred at room temperature overnight. The mixture was filtered through Celite, diluted with EtOAc, washed with 10% aq. KI, saturated aq. $NaHCO_3$, and 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 96:4) of the residue gave **8**, isolated as a white powder (0.95 g, 95%). $[\alpha]_D^{20}$ = +13 (*c* = 1, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.23 [d, $^3J$(H5,H6) = 6.3 Hz, 3 H, C*Me*], 1.98, 2.05, and 2.17 (3 s, each 3 H, 3 Ac), 3.81 (m, 1 H, H5), 4.10 and 4.35 (2 m, each 1 H, $OCH_2CH=CH_2$), 4.49 [d, $^3J$(H1,H2) = 8.0 Hz, 1 H, H1], 5.02 [dd, $^3J$(H2,H3) = 10.5, $^3J$(H3,H4) = 3.6 Hz, 1 H, H3], 5.84 (m, 1 H, $OCH_2CH=CH_2$) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 16.4 (C6), 20.9, 21.0, and 21.1 (3 $COCH_3$), 69.3 (C5), 69.5 ($OCH_2CH=CH_2$), 70.1 and 70.7 (C2 and C4), 71.7 (C3), 100.3 (C1), 117.6 ($OCH_2CH=CH_2$), 133.9 ($OCH_2CH=CH_2$), 169.8, 170.6, and 171.0 (3 $COCH_3$) ppm. High-resolution MS data of $C_{15}H_{22}O_8$ (330.131): [M + Na] found 353.125, calculated 353.121.

**Allyl 2-*O*-Acetyl-3,4-*O*-isopropylidene-β-L-fucopyranoside (9):** To a solution of **8** (0.95 g, 2.9 mmol) in MeOH (20 mL) sodium methoxide (pH 10) was added and the mixture was stirred for 4 h, when TLC ($CH_2Cl_2$/MeOH, 9:1) showed the disappearance of **8** and the formation of a new product ($R_f$ = 0.26). After neutralization with Dowex 50 X 8 $H^+$ resin, filtration, and concentration, the residue was dissolved in dry DMF (6 mL) and 2,2-dimethoxypropane (2 mL), and *p*-toluenesulfonic acid was added (pH 5). The mixture was stirred overnight, yielding a new product ($R_f$ = 0.66) as indicated by TLC ($CH_2Cl_2$/MeOH, 9:1). Then, the solution was diluted with EtOAc, washed with saturated aq. $NaHCO_3$ and 10% aq. NaCl, dried, filtered, and concentrated. A solution of the residue in pyridine/acetic anhydride (8 mL, 1:1) was stirred overnight, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the formation of **9** ($R_f$ = 0.74). The mixture was co-concentrated with toluene, and column chromatography ($CH_2Cl_2$/acetone, 95:5) of the residue afforded **9**, isolated as a white, amorphous powder (0.67 g, 80%). $[\alpha]_D^{20}$ = +26 (*c* = 1.7, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.42 (d, $^3J$(H5,H6) = 6.6 Hz, 3 H, C*Me*), 1.34 and 1.57 (2 s, each 3 H, $C(CH_3)_2$], 2.08 (s, 3 H, Ac), 3.83 (m, 1 H, H5), 4.01 [dd, $^3J$(H3,H4) = 5.5, $^3J$(H4,H5) = 2.2 Hz, 1 H, H4], 4.08 and 4.30 (2 m, each 1 H, $OCH_2CH=CH_2$), 4.12 [dd, $^3J$(H2,H3) = 7.4 Hz, 1 H, H3], 4.34 [d, $^3J$(H1,H2) = 8.2 Hz, 1 H, H1], 4.99 (bt, 1 H, H2), 5.15 and 5.25 (2 m, each 1 H, $OCH_2CH=CH_2$), 5.85 (m, 1 H, $OCH_2CH=CH_2$) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 16.6 (C6), 21.1 (Ac), 26.5 and 27.9 [$C(CH_3)_2$], 69.1 (C5), 69.4 ($OCH_2CH=CH_2$), 73.2 (C2), 76.6 and 76.7 (C3 and C4), 99.2 (C1), 110.3 [$C(CH_3)_2$], 117.0 ($OCH_2CH=CH_2$), 134.0 ($OCH_2CH=CH_2$) ppm. High-resolution MS data of $C_{14}H_{22}O_6$ (286.142): [M + Na] found 309.135, calculated 309.131.

**Allyl 2,4-Di-*O*-acetyl-β-L-fucopyranoside (10):** To a solution of **9** (0.66 g, 2.3 mmol) in $CH_2Cl_2$ (30 mL) and water (0.18 mL) trifluoroacetic acid (1.5 mL) was added. The mixture was stirred for 4 h, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the complete removal of the isopropylidene group ($R_f$ = 0.07). The solution was diluted with $CH_2Cl_2$, washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. To a solution of the residue in dry $CH_2Cl_2$ (30 mL) and trimethyl orthoacetate (12 mL) *p*-toluenesulfonic acid (pH 5) was added. The mixture was stirred overnight, then the solvent was concentrated to a volume of approximately 15 mL, and water/acetic acid (10 mL, 2:1) was added at 40 °C. After stirring at 40 °C for 15 min, the mixture was co-concentrated with toluene, and a solution of the residue in EtOAc was washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 9:1) of the residue afforded **10**, isolated as a white powder (0.33 g, 51%). $[\alpha]_D^{20}$ = +6 (*c* = 1, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.22 [d, $^3J$(H5,H6) = 6.6 Hz, 3 H, C*Me*], 2.12 and 2.19 (2 s, each 3 H, 2 Ac), 2.61 (bd, 1 H, OH), 3.70 (m, 1 H, H5), 3.81 (m, 1 H, H3), 4.09 and 4.35 (2 m, each 1 H, $OCH_2CH=CH_2$), 4.44 [d, $^3J$(H1,H2) = 8.0 Hz, 1 H, H1], 4.99 [dd, $^3J$(H2,H3) = 10.2 Hz, 1 H, H2], 5.17 (bd, 1 H, H4), 5.19 and 5.27 (2 m, each 1 H, $OCH_2CH=CH_2$), 5.87 (m, 1 H, $OCH_2CH=CH_2$) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 16.6 (C6), 21.1 and 21.2 (2 $COCH_3$), 69.6 (C5), 70.0 ($OCH_2CH=CH_2$), 71.7 (C3), 73.0 and 73.2 (C2 and C4), 99.9 (C1), 117.4 ($OCH_2CH=CH_2$), 134.0 ($OCH_2CH=CH_2$), 171.5 and 171.6 (2 $COCH_3$) ppm. High-resolution MS data of $C_{13}H_{20}O_7$ (288.121): [M + Na] found 311.112, calculated 311.111.

**4-Methoxyphenyl 4,6-Di-*O*-acetyl-3-*O*-allyloxycarbonyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (12):** To a solution of 4-methoxyphenyl 3-*O*-allyloxycarbonyl-2-deoxy-4,6-*O*-isopropylidene-2-phthalimido-β-D-glucopyranoside[20,21] (**11**; 1.22 g, 2.26 mmol) in $CH_2Cl_2$ (15 mL) and $H_2O$ (2 mL) trifluoroacetic acid (2 mL) was added. The mixture was stirred at room temperature for 4 h, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the removal of the isopro-

pylidene group to be completed ($R_f$ = 0.06). After co-concentration with toluene, the residue was dissolved in pyridine/acetic acid (20 mL, 1:1), and the mixture was stirred at room temperature overnight, when TLC ($CH_2Cl_2$/acetone, 9:1) showed the acetylation to be completed ($R_f$ = 0.69). The mixture was co-concentrated with toluene, and the residue was subjected to column chromatography ($CH_2Cl_2$/acetone, 95:5) to yield **12**, isolated as a syrup (1.3 g, 100%). $[\alpha]_D^{20}$ = +42 (*c* = 1, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.05 and 2.10 (2 s, each 3 H, 2 Ac), 3.71 (s, 3 H, $C_6H_4OCH_3$), 3.95 (m, 1 H, H5), 4.18 [dd, $^3J$(H5,H6a) = 2.5, $^3J$(H6a,H6b) = 12.4 Hz, 1 H, H6a], 4.34 [dd, $^3J$(H5,H6b) = 5.2 Hz, 1 H, H6b], 4.40 (m, 2 H, $COOCH_2CH{=}CH_2$), 4.65 [dd, $^3J$(H1,H2) = 8.5, $^3J$(H2,H3) = 10.7 Hz, 1 H, H2], 5.02 and 5.11 (2 m, each 1 H, $COOCH_2CH{=}CH_2$), 5.27 (bt, 1 H, H4), 5.65 (m, 1 H, $COOCH_2CH{=}CH_2$), 5.71 [dd, $^3J$(H3,H4) = 9.1 Hz, 1 H, H3], 5.82 (d, 1 H, H1), 6.72 and 6.84 (2 m, each 2 H, $C_6H_4OCH_3$), 7.74 and 7.86 (2 m, each 2 H, Phth) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 21.0 and 21.1 (2 $COCH_3$), 54.8, 55.9, 62.4, 69.1, 69.2, 72.3, and 74.8 (C2, C3, C4, C5, C6, $COOCH_2CH{=}CH_2$, and $OC_6H_4OCH_3$), 97.9 (C1), 114.8 ($COOCH_2CH{=}CH_2$), 119.1 and 119.3 ($OC_6H_4OCH_3$), 124.1 and 134.7 [$N(CO)_2C_6H_4$], 131.3 ($COOCH_2CH{=}CH_2$), 150.9, 154.6, and 156.2 (2 $COCH_3$ and $COOCH_2CH{=}CH_2$), 169.7 and 171.0 [$N(CO)_2C_6H_4$] ppm. High-resolution MS data of $C_{29}H_{29}NO_{12}$ (583.169): [M + $NH_4$] found 601.198, calculated 601.203.

**Allyl (4,6-Di-*O*-acetyl-3-*O*-allyloxycarbonyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-2,4-di-*O*-acetyl-β-L-fucopyranoside (14):** To a solution of **12** (1.2 g, 2.06 mmol) in toluene/acetonitrile/water (120 mL, 1:1:1) ammonium cerium(IV) nitrate (11.3 g, 20.6 mmol) was added. The two phase mixture was vigorously stirred at room temperature for 1 h, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the disappearance of the starting material. The mixture was diluted with EtOAc, and the organic phase was washed with saturated aq. $NaHCO_3$, 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography of the residue ($CH_2Cl_2$/acetone, 4:1) gave the hemiacetal intermediate, isolated as a white, amorphous solid. To a solution of the hemiacetal (0.8 g, 1.67 mmol) in dry $CH_2Cl_2$ (20 mL) and trichloroacetonitrile (2.25 mL, 20.6 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (80 μL, 0.2 mmol) was added at 0 °C. After 3 h, the mixture was concentrated and the residue was subjected to column chromatography ($CH_2Cl_2$/acetone, 95:5), yielding **13**, isolated as a yellow foam (0.6 mg, 47%). $[\alpha]_D^{20}$ = +87 (*c* = 1.5, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.06 and 2.12 (2 s, each 3 H, 2 Ac), 4.09 (m, 1 H, H5), 4.20 [dd, $^3J$(H5,H6a) = 2.2, $^3J$(H6a,H6b) = 12.4 Hz, 1 H, H6a], 4.38 [dd, $^3J$(H5,H6b) = 4.4 Hz, 1 H, H6b], 4.40 (m, 2 H, $COOCH_2CH{=}CH_2$), 4.70 [dd, $^3J$(H1,H2) = 8.8, $^3J$(H2,H3) = 10.7 Hz, 1 H, H2], 5.03 and 5.13 (2 m, each 1 H, $COOCH_2CH{=}CH_2$), 5.32 (bt, 1 H, H4), 5.64 (m, 1 H, $COOCH_2CH{=}CH_2$), 5.78 [dd, $^3J$(H3,H4) = 9.1 Hz, 1 H, H3], 6.60 (d, 1 H, H1), 7.73 and 7.84 (2 m, each 2 H, Phth), 8.65 [s, 1 H, $C(NH)CCl_3$] ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 20.9 and 21.2 (2 $COCH_3$), 53.8, 61.9, 69.1 (2 C), 73.1, and 74.4 (C2, C3, C4, C5, C6, and $COOCH_2CH{=}CH_2$), 93.9 (C1), 119.2 ($COOCH_2CH{=}CH_2$), 124.0 and 134.7 [$N(CO)_2C_6H_4$], 131.6 ($COOCH_2CH{=}CH_2$), 154.5, 160.9, and 161.4 (2 $COCH_3$ and $COOCH_2CH{=}CH_2$), 167.6 [$C(NH)CCl_3$], 169.7 and 171.0 [$N(CO)_2C_6H_4$] ppm.

A solution of **13** (0.38 g, 0.61 mmol) and **10** (0.12 g, 0.40 mmol) in dry $CH_2Cl_2$ (6 mL), containing activated molecular sieves (4 Å, 0.6 g), was stirred at room temperature for 30 min, then TMSOTf (3.63 μL, 20 μmol) was added. The mixture was stirred for 15 min, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the formation of a new spot ($R_f$ = 0.45). After neutralization with dry pyridine and filtration, the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 95:5) of the residue afforded **14**, isolated as a glass (0.21 g, 69%). $[\alpha]_D^{20}$ = −2 (*c* = 1, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$; 2D TOCSY and HSQC): δ = 1.06 [d, $^3J$(H5,H6) = 6.1 Hz, 3 H, C*Me*], 2.02, 2.07, 2.11, and 2.15 (4 s, each 3 H, 4 Ac), 3.60 (m, 1 H, H5), 3.84 (m, 1 H, H5′), 3.90 [dd, $^3J$(H2,H3) = 10.1, $^3J$(H3,H4) = 3.4 Hz, 1 H, H3], 4.04 and 4.27 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 4.10 [dd, $^3J$(H5′,H6a′) = 2.3, $^3J$(H6a′,H6b′) = 12.3 Hz, 1 H, H6a′], 4.30 [dd, $^3J$(H1′,H2′) = 8.3, $^3J$(H2′,H3′) = 10.4 Hz, 1 H, H2′], 4.35 (m, 2 H, $COOCH_2CH{=}CH_2$), 4.41 [dd, $^3J$(H5′,H6b′) = 4.3 Hz, 1 H, H6b′], 4.46 [d, $^3J$(H1,H2) = 8.1 Hz, 1 H, H1], 4.97 (bt, 1 H, H2), 4.99 and 5.06 (2 m, each 1 H, $COOCH_2CH{=}CH_2$), 5.03 [bd, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 5.16 and 5.24 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.20 (bt, 1 H, H4′), 5.38 [d, $^3J$(H1′,H2′) = 8.3 Hz, 1 H, H1′], 5.60 [dd, $^3J$(H2′,H3′) = 10.6, $^3J$(H3′,H4′) = 9.3 Hz, 1 H, H3′], 5.60 (m, 1 H, $COOCH_2CH{=}CH_2$), 5.82 (m, 1 H, $OCH_2CH{=}CH_2$), 7.74 and 7.86 (2 m, each 2 H, $N(CO)_2C_6H_4$) ppm. $^{13}$C NMR (125.76 MHz, $CDCl_3$): δ = 16.2 (C6), 20.7, 20.8 (2 C), and 20.9 (4 $COCH_3$), 54.6 (C2′), 62.0 (C6′), 68.6 (C4′), 68.7 ($COOCH_2CH{=}CH_2$), 68.8 ($OCH_2CH{=}CH_2$), 69.2 (C5), 69.9 (C2), 70.0 (C4), 71.7 (C5′), 74.5 (C3′), 77.2 (C3), 96.7 (C1′), 99.9 (C1), 117.3 ($OCH_2CH{=}CH_2$), 118.9 ($COOCH_2CH{=}CH_2$), 131.0 ($COOCH_2CH{=}CH_2$), 133.9 ($OCH_2CH{=}CH_2$), 123.5 and 134.2 [$N(CO)_2C_6H_4$] ppm. High-resolution MS data of $C_{35}H_{41}NO_{17}$ (747.237): [M + $NH_4$] found 765.262, calculated 765.271.

**Allyl (4,6-Di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-2,4-di-*O*-acetyl-β-L-fucopyranoside (15):** To a solution of **14** (0.19 g, 0.42 mmol) in THF (4 mL) and morpholine (0.12 mL) tetrakis(triphenylphosphane)palladium (41 mg, 43 μmol) was added, and the mixture was stirred at 65 °C for 1 h, when TLC ($CH_2Cl_2$/acetone, 9:1) showed the complete removal of the allyloxycarbonyl group ($R_f$ = 0.17). After concentration, a solution of the residue in EtOAc was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 9:1 → 8:2) gave **15**, isolated as a glass (108 mg, 65%). $[\alpha]_D^{20}$ = −30 (*c* = 0.8, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$; 2D TOCSY and HSQC): δ = 1.06 [d, $^3J$(H5,H6) = 6.4 Hz, 3 H, C*Me*], 2.05, 2.09, 2.10, and 2.16 (4 s, each 3 H, 4 Ac), 2.46 (d, 1 H, OH), 3.60 (m, 1 H, H5), 3.77 (m, 1 H, H5′), 3.90 [dd, $^3J$(H2,H3) = 10.1, $^3J$(H3,H4) = 3.4 Hz, 1 H, H3], 4.04 and 4.30 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 4.12 (m, 1 H, H6′), 4.13 [dd, $^3J$(H1′,H2′) = 8.4, $^3J$(H2′,H3′) = 10.7 Hz, 1 H, H2′], 4.40 (m, 1 H, H3′), 4.43 (m, 1 H, H6′), 4.46 [d, $^3J$(H1,H2) = 8.1 Hz, 1 H, H1], 4.92 (bt, 1 H, H4′), 4.97 [dd, $^3J$(H2,H3) = 10.1 Hz, 1 H, H2], 5.05 [d, $^3J$(H3,H4) = 2.9, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 5.15 and 5.24 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.27 (d, 1 H, H1′), 5.82 (m, 1 H, $OCH_2CH{=}CH_2$), 7.71 and 7.84 (2 m, each 2 H, Phth) ppm. $^{13}$C NMR (125.76 MHz, $CDCl_3$): δ = 16.1 (C6), 20.1, 20.7 (2 C), and 20.9 (4 $COCH_3$), 57.0 (C2′), 62.2 (C6′), 69.2 (C5), 69.6 ($OCH_2CH{=}CH_2$), 69.9 (C2), 70.0 (C4), 70.3 (C3′), 71.8 (C5′), 71.9 (C4′), 76.9 (C3), 96.9 (C1′), 99.9 (C1), 117.3 ($OCH_2CH{=}CH_2$), 133.9 ($OCH_2CH{=}CH_2$), 123.5 and 134.2 [$N(CO)_2C_6H_4$] ppm. High-resolution MS data of $C_{31}H_{37}NO_{15}$ (663.216): [M + $NH_4$] found 681.229, calculated 681.250.

**Allyl (Sodium 2-acetamido-2-deoxy-3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-β-L-fucopyranoside (17):** To a solution of **15** (98 mg, 0.15 mmol) in dry DMF (5 mL) was added, at 50 °C, sulfur trioxide trimethylamine complex (0.82 g, 5.8 mmol). The mixture was stirred at 50 °C for 48 h, when TLC ($CH_2Cl_2$/MeOH, 9:1) showed the conversion of **15** into nonsodiated **16**. After quenching of the reaction with MeOH (10 mL), the solution was co-concentrated

with toluene. A solution of the residue in $CH_2Cl_2$ (50 mL) was washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. The residue dissolved in MeOH (10 mL), containing Dowex 50 W × 8 $Na^+$ resin, was stirred for 15 min, then filtered and concentrated. Column chromatography ($CH_2Cl_2$/MeOH, 85:15) of the residue gave **16**, isolated as a white, amorphous powder (100 mg, 89%). $[\alpha]_D^{20} = -22$ ($c = 0.7$, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$; 2D TOCSY and HSQC): δ = 1.04 [d, $^3J$(H5,H6) = 6.4 Hz, 3 H, C*Me*], 1.96 and 2.06 (2 s, each 6 H, 4 Ac), 3.61 (m, 1 H, H5), 3.84 (m, 1 H, H5′), 3.93 [dd, $^3J$(H2,H3) = 9.8, $^3J$(H3,H4) = 2.6 Hz, 1 H, H3], 4.06 and 4.31 (2 m, each 1 H, OC*H*$_2$CH=CH$_2$), 4.07 (m, 1 H, H6′), 4.12 (bt, 1 H, H2′), 4.35 (m, 1 H, H6′), 4.48 [d, $^3J$(H1,H2) = 8.1 Hz, 1 H, H1], 4.95 (dd, 1 H, H2), 4.99 (bt, 1 H, H4′), 5.07 [bd, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 5.11 (bt, 1 H, H3′), 5.17 and 5.25 (2 m, each 1 H, OCH$_2$CH=C*H*$_2$), 5.34 [d, $^3J$(H1′,H2′) = 8.4 Hz, 1 H, H1′], 5.84 (m, 1 H, OCH$_2$C*H*=CH$_2$), 7.66 and 7.81 (2 m, each 2 H, Phth) ppm. $^{13}$C NMR (125.76 MHz, $CDCl_3$): δ = 16.2 (C6), 19.9, 20.9 (2 C), and 21.1 (4 CO*C*H$_3$), 55.2 (C2′), 62.2 (C6′), 69.1 (C5), 69.3 (C4′), 69.8 (O*C*H$_2$CH=CH$_2$), 70.0 (C2), 70.2 (C4), 71.4 (C5′), 75.6 (C3′), 76.9 (C3), 96.9 (C1′), 99.8 (C1), 117.4 (OCH$_2$CH=*C*H$_2$), 133.9 (OCH$_2$*C*H=CH$_2$), 123.7 and 134.2 [N(CO)$_2$*C*$_6$H$_4$] ppm.

A solution of **16** (44 mg, 58 μmol) in ethanolic 33% $CH_3NH_2$ (5 mL) was stirred at room temperature for 5 days, during which time the mixture was 3 times concentrated and fresh ethanolic 33% $CH_3NH_2$ (5 mL) was added. After co-concentration with toluene (3 × 15 mL), acetic anhydride (100 μL) was added to a solution of the residue in dry MeOH (5 mL) at 0 °C. The mixture was stirred for 3 h, when TLC (EtOAc/MeOH/$H_2O$, 6:2.5:1.5) showed the formation of **17**. Size-exclusion chromatography (Bio-Gel P-2, 100 mM $NH_4HCO_3$) gave **17**, isolated after lyophilization from water, as a white, amorphous powder (25.6 mg, 87%). $[\alpha]_D^{20} = -17$ ($c = 0.6$, $H_2O$). $^1$H NMR (500 MHz, $D_2O$; 2D TOCSY and HSQC): δ = 1.24 [d, $^3J$(H5,H6) = 6.4 Hz, 3 H, C*Me*], 2.01 (s, 3 H, NAc), 3.51 (m, 1 H, H5′), 3.57 (bt, 1 H, H2), 3.63 (bt, 1 H, H4′), 3.74 (m, 1 H, H5), 3.77 [dd, $^3J$(H5′,H6b′) = 6.6, $^3J$(H6a′,H6b′) = 12.4 Hz, 1 H, H6b′], 3.82 (bt, 1 H, H3), 3.83 (m, 1 H, H2′), 3.84 (bd, 1 H, H4), 3.92 [dd, $^3J$(H5′,H6a′) = 2.3 Hz, 1 H, H6a′], 4.20 and 4.35 (2 m, each 1 H, OC*H*$_2$CH=CH$_2$), 4.41 [dd, $^3J$(H2′,H3′) = 10.4, $^3J$(H3′,H4′) = 9.9 Hz, 1 H, H3′], 4.43 [d, $^3J$(H1,H2) = 8.0 Hz, 1 H, H1], 4.81 [d, $^3J$(H1′,H2′) = 8.4 Hz, 1 H, H1′], 5.27 and 5.36 (2 m, each 1 H, OCH$_2$CH=C*H*$_2$), 5.95 (m, 1 H, OCH$_2$C*H*=CH$_2$) ppm. $^{13}$C NMR (125.76 MHz, $D_2O$): δ = 16.0 (C6), 23.0 (NDCO*C*H$_3$), 55.1 (C2′), 61.3 (C6′), 69.3 (C4), 71.3 (O*C*H$_2$CH=CH$_2$), 71.4 (C5), 76.1 (C5′), 80.8 (C3), 82.0 (C3′), 99.1 (C1′), 102.1 (C1), 119.5 (OCH$_2$CH=*C*H$_2$), 134.1 (OCH$_2$*C*H=CH$_2$) ppm. High-resolution MS data of $C_{17}H_{28}NNaO_{13}S$ (509.117): [$C_{17}H_{29}NO_{13}S$ + $NH_4$] found 505.163, calculated 505.170.

**3-(6-Mercaptohexylthio)propyl (Sodium 2-acetamido-2-deoxy-3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-β-L-fucopyranoside (1b):** To a solution of **17** (18.5 mg, 36 μmol) in MeOH (1.5 mL) 1,6-hexanedithiol (66 μL, 0.43 mmol) was added, and the mixture was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV Lamp. After concentration, the excess of 1,6-hexanedithiol was separated from carbohydrate by column chromatography ($CH_2Cl_2$/MeOH, 9:1 → MeOH). The carbohydrate-containing fractions were concentrated, and a solution of the residue in water was loaded on a C-18 Extract-Clean™ column. After elution of remaining **17** with water (3 × 3 mL), **1b** was eluted with MeOH (3 × 3 mL), then concentrated in vacuo, and obtained, after lyophilization from water, as a white, amorphous powder (20 mg, 83%). $[\alpha]_D^{20} = -16$ ($c = 0.5$, $CH_3OH$). $^1$H NMR (500 MHz, $CD_3OD$; 2D TOCSY and HSQC): δ = 1.27 [d, $^3J$(H5,H6) = 6.5 Hz, 3 H, C*Me*], 1.41, 1.58, and 2.50 [3 m, each 4 H, O(CH$_2$)$_3$S(C*H*$_2$)$_6$SH], 1.86 [m, 2 H, OCH$_2$C*H*$_2$CH$_2$S(CH$_2$)$_6$SH], 1.99 (s, 3 H, NAc), 2.61 [bt, 2 H, O(CH$_2$)$_2$C*H*$_2$S(CH$_2$)$_6$SH], 3.36 (m, 1 H, H5′), 3.54 (bt, 1 H, H4′), 3.55 [dd, $^3J$(H1,H2) = 7.8, $^3J$(H2,H3) = 9.5 Hz, 1 H, H2], 3.60 (m, 1 H, H5), 3.63 and 3.91 [2 m, each 1 H, OC*H*$_2$(CH$_2$)$_2$S(CH$_2$)$_6$SH], 3.87 [dd, $^3J$(H5,H6a′) = 2.2, $^3J$(H6a′,H6b′) = 11.9 Hz, 1 H, H6a′], 4.22 (d, 1 H, H1), 4.42 [dd, $^3J$(H2′,H3′) = 10.4, $^3J$(H3′,H4′) = 8.9 Hz, 1 H, H3′), 4.77 [d, $^3J$(H1′,H2′) = 8.4 Hz, 1 H, H1′] ppm. $^{13}$C NMR (125.76 MHz, $CD_3OD$): δ = 16.8 (C6), 23.3 (NDCO*C*H$_3$), 24.9, 29.1, 29.2, 29.5, 30.7, 31.1, 33.0, and 35.1 [OCH$_2$(*C*H$_2$)$_2$S(*C*H$_2$)$_6$SH], 56.1 (C2′), 62.6 (C6′), 69.4 [O*C*H$_2$(CH$_2$)$_2$S(CH$_2$)$_6$SH], 70.2 (C4), 70.5 and 71.3 (C2 and C4′), 71.7 (C5), 77.9 (C5′), 82.7 (C3), 82.1 (C3′), 100.5 (C1′), 104.6 (C1) ppm. High-resolution MS data of $C_{23}H_{42}NNaO_{13}S_3$ (659.171): [M + Na] found 682.160, calculated 682.161.

**Allyl 4,6-Di-*O*-acetyl-3-*O*-allyloxycarbonyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (18):** A solution of **13** (0.17 g, 0.27 mmol) in dry $CH_2Cl_2$ (5 mL) and allyl alcohol (2 mL), containing activated molecular sieves (4 Å, 0.5 g), was stirred at room temperature for 30 min. TMSOTf (2.45 μL, 13.5 μmol) was added, and the mixture was stirred for 15 min, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the formation of a new spot. The mixture was neutralized with pyridine, then filtered and washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 95:5) of the residue afforded **18**, isolated as a glass (0.06 g, 45%). $[\alpha]_D^{20} = +113$ ($c = 1$, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ = 2.02 and 2.09 (2 s, each 3 H, Ac), 3.85 (m, 1 H, H5), 4.03 and 4.25 (2 m, each 1 H, OC*H*$_2$CH=CH$_2$), 4.17 [dd, $^3J$(H5,H6a) = 2.2, $^3J$(H6a,H6b) = 12.3 Hz, 1 H, H6a], 4.32 [dd, $^3J$(H5,H6b) = 4.8 Hz, 1 H, H6b], 4.36 (m, 2 H, COOC*H*$_2$CH=CH$_2$), 4.40 [dd, $^3J$(H1,H2) = 8.5, $^3J$(H2,H3) = 10.8 Hz, 1 H, H2], 4.99, 5.05, 5.10, and 5.18 (4 m, each 1 H, COOCH$_2$CH=C*H*$_2$ and OCH$_2$CH=C*H*$_2$), 5.20 (bt, 1 H, H4), 5.35 (d, 1 H, H1), 5.64 [dd, $^3J$(H3,H4) = 9.2 Hz, 1 H, H3], 5.66 (m, 2 H, COOCH$_2$C*H*=CH$_2$ and OCH$_2$C*H*=CH$_2$), 7.73 and 7.84 [2 m, each 2 H, N(CO)$_2$C$_6$*H*$_4$] ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 20.6 and 20.7 (2 CO*C*H$_3$), 54.5 (C2), 62.6 (C6), 68.9, 71.8, and 74.5 (C3, C4, and C5), 68.6 and 70.2 (O*C*H$_2$CH=CH$_2$ and COO*C*H$_2$CH=CH$_2$), 97.1 (C1), 117.8 and 118.6 (OCH$_2$CH=*C*H$_2$ and COOCH$_2$CH=*C*H$_2$), 123.6 and 134.1 [N(CO)$_2$*C*$_6$H$_4$], 131.0 and 133.2 (OCH$_2$*C*H=CH$_2$ and COOCH$_2$*C*H=CH$_2$) ppm. High-resolution MS data of $C_{25}H_{27}NO_{11}$ (517.158): [M + Na] found 540.163, calculated 540.164.

**Allyl 4,6-Di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (19):** To a solution of **18** (0.22 g, 0.42 mmol) in THF (16 mL) and morpholine (0.44 mL) tetrakis(triphenylphosphane)palladium (153 mg, 0.13 mmol) was added, and the mixture was stirred at 50 °C for 2 h, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the reaction to be completed ($R_f = 0.17$). The mixture was concentrated, and a solution of the residue in EtOAc was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 95:5) of the residue gave **19**, isolated as a glass (0.18 g, 100%). $[\alpha]_D^{20} = +66$ ($c = 0.5$, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.25 (s, 6 H, 2 Ac), 3.78 (m, 1 H, H5), 4.06 (m, 1 H, OCH*H*CH=CH$_2$), 4.20 [dd, $^3J$(H5,H6a) = 2.3, $^3J$(H6a,H6b) = 12.2 Hz, 1 H, H6a], 4.32 [dd, $^3J$(H5,H6b) = 4.8 Hz, 1 H, H6b), 4.44 [dd, $^3J$(H2,H3) = 10.7, $^3J$(H3,H4) = 9.0 Hz, 1 H, H3], 4.90 (bt, 1 H, H4), 5.07 and 5.13 (2 m, each 1 H, OCH$_2$CH=C*H*$_2$), 5.27 [d, $^3J$(H1,H2) = 8.5 Hz, 1 H, H1], 5.72 (m, 1 H, OCH$_2$C*H*=CH$_2$), 7.73 and 7.84 [2 m, each 2 H, N(CO)$_2$C$_6$*H*$_4$] ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 21.1 and 21.2 (2 CO*C*H$_3$), 57.4 (C2), 62.7 (C6), 70.4, 72.3, and 72.7 (C3, C4, and C5), 70.8 (O*C*H$_2$CH=CH$_2$),

97.7 (C1), 118.1 ($OCH_2CH{=}CH_2$), 123.8 and 134.5 [$N(CO)_2C_6H_4$], 133.8 ($OCH_2CH{=}CH_2$) ppm. High-resolution MS data of $C_{21}H_{23}NO_9$ (433.137): [M + Na] found 456.135, calculated 456.143.

**Allyl 4,6-Di-*O*-acetyl-2-deoxy-2-phthalimido-3-*O*-sulfonato-β-D-glucopyranoside, Sodium Salt (20):** To a solution of **19** (80 mg, 0.18 mmol) in dry DMF (7 mL), the sulfur trioxide trimethylamine complex (1.02 g, 7.4 mmol) was added. The mixture was stirred at 50 °C for 48 h, when TLC ($CH_2Cl_2$/MeOH, 9:1) showed the conversion of **19** into nonsodiated **20**. After quenching of the reaction with MeOH (10 mL), the solution was co-concentrated with toluene. The residue dissolved in MeOH (10 mL), containing Dowex 50 W × 8 $Na^+$ resin, was stirred for 15 min, then filtered and concentrated. Column chromatography ($CH_2Cl_2$/MeOH, 85:15) of the residue gave **20**, isolated as a white, amorphous powder (39 mg, 39%). $[\alpha]_D^{20} = +7$ ($c$ = 0.4, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.40 and 2.45 (2 s, each 3 H, 2 Ac), 4.27 (m, 1 H, H5), 4.43 (m, 1 H, $OCH\mathit{H}CH{=}CH_2$), 4.55 [dd, $^3J$(H5,H6a) = 2.1, $^3J$(H6a,H6b) = 12.2 Hz, 1 H, H6a], 4.71 [dd, $^3J$(H5,H6b) = 5.0 Hz, 1 H, H6b], 5.46 and 5.51 (2 m, each 1 H, $OCH_2CH{=}C\mathit{H}_2$), 5.81 [d, $^3J$(H1,H2) = 8.5 Hz, 1 H, H1], 6.10 (m, 1 H, $OCH_2C\mathit{H}{=}CH_2$), 8.02 and 8.16 (2 m, each 2 H, Phth) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): = 21.1 and 21.2 ($CO\mathit{C}H_3$), 55.3 (C2), 62.4 (C6), 69.5, 71.5, and 75.4 (C3, C4, and C5), 70.3 ($O\mathit{C}H_2CH{=}CH_2$), 97.3 (C1), 117.7 ($OCH_2CH{=}\mathit{C}H_2$), 123.3 and 133.4 [$N(CO)_2C_6H_4$], 133.9 ($OCH_2\mathit{C}H{=}CH_2$) ppm. High-resolution MS data of $C_{21}H_{22}NNaO_{12}S$ (535.076): [M + Na] found 558.068, calculated 558.065.

**Allyl 2-Acetamido-2-deoxy-3-*O*-sulfonato-β-D-glucopyranoside, Sodium Salt (21):** A solution of **20** (38 mg, 71 μmol) in ethanolic 33% $CH_3NH_2$ (5 mL) was stirred at room temperature for 5 days, during which time the mixture was 3 times concentrated and fresh ethanolic 33% $CH_3NH_2$ (5 mL) was added. After co-concentration with toluene, acetic anhydride was added to a solution of the residue in dry MeOH (5 mL) at 0 °C. The mixture was stirred at 0 °C for 3 h, when TLC (EtOAc/MeOH/$H_2O$, 6:2.5:1.5) showed the formation of **21**. Size-exclusion chromatography (Bio-Gel P-2, 100 mM $NH_4HCO_3$) gave **21**, isolated after lyophilization from water, as a white, amorphous powder (16.5 mg, 66%). $[\alpha]_D^{20} = -13$ ($c$ = 1, $H_2O$). $^1$H NMR (500 MHz, $D_2O$; 2D TOCSY and HSQC): δ = 2.04 (s, 3 H, NAc), 3.51 (m, 1 H, H5), 3.61 (bt, 1 H, H4), 3.76 [dd, $^3J$(H5,H6b) = 5.7, $^3J$(H6a,H6b) = 12.5 Hz, 1 H, H6b], 3.81 [dd, $^3J$(H1,H2) = 8.7, $^3J$(H2,H3) = 10.4 Hz, 1 H, H2], 3.93 [dd, $^3J$(H5,H6a) = 2.5 Hz, 1 H, H6a], 4.17 and 4.33 (2 m, each 1 H, $OC\mathit{H}_2CH{=}CH_2$), 4.36 [dd, $^3J$(H3,H4) = 8.9 Hz, 1 H, H3], 4.68 (d, 1 H, H1), 5.26 and 5.31 (2 m, each 1 H, $OCH_2CH{=}C\mathit{H}_2$), 5.90 (m, 1 H, $OCH_2C\mathit{H}{=}CH_2$) ppm. $^{13}$C NMR (125.76 MHz, $D_2O$): δ = 22.9 ($NDCO\mathit{C}H_3$), 54.9 (C2), 61.4 (C6), 69.6 (C4), 71.3 ($O\mathit{C}H_2CH{=}CH_2$), 76.1 (C5), 82.3 (C3), 100.3 (C1), 119.1 ($OCH_2CH{=}\mathit{C}H_2$), 134.0 ($OCH_2\mathit{C}H{=}CH_2$) ppm. High-resolution MS data of $C_{11}H_{18}NNaO_9S$ (363.060): [M + Na] found 386.052, calculated 386.049.

**3-(6-Mercaptohexylthio)propyl 2-Acetamido-2-deoxy-3-*O*-sulfonato-β-D-glucopyranoside, Sodium Salt (2):** To a solution of **21** (15 mg, 41 μmol) in MeOH (1.5 mL) 1,6-hexanedithiol (64 μL, 0.41 mmol) was added and the mixture was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV Lamp. After concentration, the excess of 1,6-hexanedithiol was separated from carbohydrate by column chromatography ($CH_2Cl_2$/MeOH, 9:1 → MeOH). The carbohydrate-containing fractions were concentrated, and a solution of the residue in water was loaded on a C-18 Extract-Clean™ column. After elution of remaining **21** with water (3 × 3 mL), **2** was eluted with MeOH (3 × 3 mL), then concentrated in vacuo, and obtained, after lyophilization from water, as a white, amorphous powder (9 mg, 42%). $[\alpha]_D^{20} = -5$ ($c$ = 0.9, MeOH). $^1$H NMR (500 MHz, $CD_3OD$; 2D TOCSY and HSQC): δ = 1.41, 1.59, and 2.49 [3 m, each 4 H, $O(CH_2)_3S(C\mathit{H}_2)_6SH$], 1.80 [m, 2 H, $OCH_2C\mathit{H}_2CH_2S(CH_2)_6SH$], 1.98 (s, 3 H, NAc), 2.56 [bt, 2 H, $O(CH_2)_2C\mathit{H}_2S(CH_2)_6SH$], 3.34 (m, 1 H, H5), 3.54 [dd, $^3J$(H3,H4) = 8.7, $^3J$(H4,H5) = 9.8 Hz, 1 H, H4], 3.60 and 3.94 [2 m, each 1 H, $OC\mathit{H}_2(CH_2)_2S(CH_2)_6SH$], 3.68 [dd, $^3J$(H5,H6b) = 5.5, $^3J$(H6a,H6b) = 12.0 Hz, 1 H, H6b], 3.71 (bt, 1 H, H2), 3.88 [dd, $^3J$(H5,H6a) = 2.3 Hz, 1 H, H6a], 4.37 [dd, $^3J$(H2,H3) = 10.4 Hz, 1 H, H3], 4.54 [d, $^3J$(H1,H2) = 8.4 Hz, 1 H, H1] ppm. $^{13}$C NMR (125.76 MHz, $CD_3OD$): δ = 23.5 ($NDCO\mathit{C}H_3$), 25.2, 29.2, 29.5, 29.6, 30.9, 31.1, 33.0, and 35.4 [$OCH_2(\mathit{C}H_2)_2S(\mathit{C}H_2)_6SH$], 55.9 (C2), 62.8 (C6), 69.5 [$O\mathit{C}H_2(CH_2)_2S(CH_2)_6SH$], 71.6 (C4), 77.9 (C5), 82.7 (C3), 102.8 (C1) ppm. High-resolution MS data of $C_{17}H_{32}NNaO_9S_3$ (513.114): [M + H] found 514.120, calculated 514.121.

**3-(6-Mercaptohexylthio)propyl α-L-Fucopyranoside (3):** To a solution of allyl α-L-fucopyranoside[27] (10 mg, 49 μmol) in MeOH (1.5 mL) 1,6-hexanedithiol (74 μL, 0.49 mmol) was added and the mixture was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV lamp. After concentration, the excess of 1,6-hexanedithiol was separated from carbohydrate by column chromatography ($CH_2Cl_2$/MeOH, 9:1 → MeOH). The carbohydrate-containing fractions were concentrated, and a solution of the residue in water was loaded on a C-18 Extract-Clean™ column. After elution of remaining allyl α-L-fucopyranoside with water (3 × 3 mL), **3** was eluted with MeOH (3 × 3 mL), then concentrated in vacuo, and obtained, after lyophilization from water, as a white, amorphous powder (10 mg, 59%). $[\alpha]_D^{20} = -3$ ($c$ = 1, MeOH). $^1$H NMR (300 MHz, $CD_3OD$; 2D TOCSY): δ = 1.23 [d, $^3J$(H5,H6) = 6.6 Hz, 3 H, C*Me*], 1.45, 1.62, and 2.56 [3 m, each 4 H, $O(CH_2)_3S(C\mathit{H}_2)_6SH$], 1.90 [m, 2 H, $OCH_2C\mathit{H}_2CH_2S(CH_2)_6SH$], 2.66 [bt, 2 H, $O(CH_2)_2C\mathit{H}_2S(CH_2)_6SH$], 3.52 and 3.83 [2 m, each 1 H, $OC\mathit{H}_2(CH_2)_2S(CH_2)_6SH$], 3.68 [bd, $^3J$(H3,H4) = 1.1, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 4.00 (m, 1 H, H5), 4.76 [d, $^3J$(H1,H2) = 2.0 Hz, 1 H, H1] ppm. $^{13}$C NMR (75.4 MHz, $CD_3OD$): δ = 16.8 (C6), 25.2, 28.9, 29.2, 29.6, 30.6, 30.7, 32.8, and 35.4 [$OCH_2(\mathit{C}H_2)_2S(\mathit{C}H_2)_6SH$], 67.6, 70.0, 71.7, and 73.6 (C2, C3, C4, and C5), 69.0 [$O\mathit{C}H_2(CH_2)_2S(CH_2)_6SH$], 100.5 (C1) ppm. High-resolution MS data of $C_{15}H_{30}O_5S_2$ (354.153): [M + H] found 355.160, calculated 355.161.

**Allyl α-L-Galactopyranoside (22):** To a solution of L-galactose (0.9 g, 5 mmol) in allyl alcohol (30 mL) acetyl chloride (0.9 mL) was added at 0 °C, and the mixture was stirred at 70 °C overnight, then concentrated. Column chromatography ($CH_2Cl_2$/EtOH, 3:1) of the residue yielded a mixture of **22** and **22β**. After concentration, **22** was crystallized from 2-propanol (0.5 g, 30%). $[\alpha]_D^{20} = -28$ ($c$ = 0.4, $CH_3OH$). $^1$H NMR (300 MHz, $CD_3OD$): δ = 4.04 and 4.23 (2 m, each 1 H, $OC\mathit{H}_2CH{=}CH_2$), 4.86 [d, $^3J$(H1,H2) = 2.7 Hz, 1 H, H1], 5.17 and 5.33 (2 m, each 1 H, $OCH_2CH{=}C\mathit{H}_2$), 5.96 (m, 1 H, $OCH_2C\mathit{H}{=}CH_2$) ppm. $^{13}$C NMR (75.4 MHz, $CD_3OD$): δ = 63.6, 70.2, 71.1, 72.0, 72.4, and 73.3 (C2, C3, C4, C5, C6, and $O\mathit{C}H_2CH{=}CH_2$), 100.3 (C1), 118.3 ($OCH_2CH{=}\mathit{C}H_2$), 134.5 ($OCH_2\mathit{C}H{=}CH_2$) ppm. High-resolution MS data of $C_9H_{16}O_6$ (220.095): [M + $NH_4$] found 238.128, calculated 238.129.

**Allyl 6-*O*-(*tert*-Butyldiphenylsilyl)-α-L-galactopyranoside (23):** To a solution of **22** (0.23 g, 1.05 mmol) in $CH_2Cl_2$ (35 mL), pyridine (1.98 mL), and $Et_3N$ (0.9 mL), *tert*-butyldiphenylsilyl chloride (1.08 mL, 4.2 mmol) was added. The mixture was stirred at room temperature overnight, when TLC ($CH_2Cl_2$/MeOH, 9:1) showed

the conversion of **22** into **23** ($R_f$ = 0.22) to be completed. After dilution with EtOAc, the solution was washed with saturated aq. $NaHCO_3$ and water, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/MeOH, 9:1) of the residue yielded **23**, isolated as a glass (0.47 g, 97%). $[\alpha]_D^{20}$ = −51 (*c* = 1.2, $CH_3OH$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.05 [s, 9 H, $SiC(CH_3)_3(C_6H_5)_2$], 4.92 [d, $^3J$(H1,H2) = 3.8 Hz, 1 H, H1], 5.14 and 5.23 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.88 (m, 1 H, $OCH_2CH{=}CH_2$), 7.38 and 7.67 [2 m, 6 H and 4 H, $SiC(CH_3)_3(C_6H_5)_2$] ppm. $^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ = 19.5 [$SiC(CH_3)_3(C_6H_5)_2$], 27.2 [$SiC(CH_3)_3(C_6H_5)_2$], 63.9, 68.9, 69.8, 70.2, 70.5, and 71.9 (C2, C3, C4, C5, C6, and $OCH_2CH{=}CH_2$), 97.9 (C1), 118.2 ($OCH_2CH{=}CH_2$), 128.1, 130.2, 135.9, and 136.0 [$SiC(CH_3)_3(C_6H_5)_2$], 134.0 ($OCH_2CH{=}CH_2$) ppm. High-resolution MS data of $C_{25}H_{34}O_6Si$ (458.212): [M + Na] found 481.195, calculated 481.202.

**Allyl 2-*O*-Acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-3,4-*O*-isopropylidene-α-L-galactopyranoside (24):** To a solution of **23** (0.47 g, 1.03 mmol) in dry DMF (7 mL) and 2,2-dimethoxypropane (3 mL), *p*-toluenesulfonic acid (pH 3) was added. After stirring for 3 h, the mixture was neutralized with $Et_3N$, diluted with EtOAc, washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. The residue was dissolved in pyridine (10 mL) and acetic anhydride (5 mL), and stirred at room temperature overnight. 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 ($CH_2Cl_2$/acetone, 95:5) of the residue gave **24**, isolated as a glass (0.33 mg, 60%). $[\alpha]_D^{20}$ = −86 (*c* = 0.9, $CH_3OH$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.99 [s, 9 H, $SiC(CH_3)_3(C_6H_5)_2$], 1.25 and 1.42 [2 s, each 3 H, $C(CH_3)_2$], 2.04 (s, 3 H, Ac), 4.07 and 3.90 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 4.81 [dd, $^3J$(H1,H2) = 3.6, $^3J$(H2,H3) = 7.7 Hz, 1 H, H2], 4.92 (d, 1 H, H1), 5.12 and 5.20 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.78 (m, 1 H, $OCH_2CH{=}CH_2$), 7.31 and 7.60 [2 m, 6 H and 4 H, $SiC(CH_3)_3(C_6H_5)_2$] ppm. $^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ = 19.5 [$SiC(CH_3)_3(C_6H_5)_2$], 21.3 ($COCH_3$), 26.7 and 28.1 [$C(CH_3)_2$], 27.1 [$SiC(CH_3)_3(C_6H_5)_2$], 63.0, 69.6, 73.5, 73.8 (2 C), and 77.8 (C2, C3, C4, C5, C6, and $OCH_2CH{=}CH_2$), 99.6 (C1), 110.7 [$C(CH_3)_2$], 117.4 ($OCH_2CH{=}CH_2$), 127.9, 128.1, 130.1, 135.9, and 136.0 [$SiC(CH_3)_3(C_6H_5)_2$], 134.1 ($OCH_2CH{=}CH_2$) ppm. High-resolution MS data of $C_{30}H_{40}O_7Si$ (540.254): [M + $NH_4$] found 558.283, calculated 558.288.

**Allyl 2,4-Di-*O*-acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-L-galactopyranoside (25):** To a solution of **24** (0.19 g, 0.35 mmol) in $CH_2Cl_2$ (10 mL) and $H_2O$ (0.06 mL), trifluoroacetic acid (0.5 mL) was added. After stirring for 3 h, the mixture was co-concentrated with toluene. To a solution of the residue in $CH_2Cl_2$ (10 mL) and trimethyl orthoacetate (1.78 mL, 14 mmol), *p*-toluenesulfonic acid (pH 3) was added. The mixture was stirred at room temperature overnight, when TLC ($CH_2Cl_2$/acetone, 95:5) confirmed the orthoacetate formation ($R_f$ = 0.64). Then, the mixture was concentrated to approximately 5 mL, and a solution of acetic acid/water (1.8 mL, 1:2) was added. After stirring at 40 °C for 15 min, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the formation of **25** ($R_f$ = 0.37), the solution was co-concentrated with toluene. A solution of the residue in EtOAc was washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. Column chromatography of the residue ($CH_2Cl_2$/acetone, 95:5) rendered **25**, isolated as a glass (0.15 g, 78%). $[\alpha]_D^{20}$ = −66 (*c* = 0.4, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.97 [s, 9 H, $SiC(CH_3)_3(C_6H_5)_2$], 1.97 and 2.04 (2 s, each 3 H, 2 Ac), 3.59 [d, $^3J$(H5,H6) = 6.6 Hz, 2 H, 2 H6], 3.88 and 4.05 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 3.96 (bt, 1 H, H5), 4.18 [dd, $^3J$(H2,H3) = 10.4, $^3J$(H3,H4) = 3.6 Hz, 1 H, H3], 4.87 [dd, $^3J$(H1,H2) = 3.8 Hz, 1 H, H2], 4.99 (d, 1 H, H1), 5.10 and 5.19 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.42 [d, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 5.77 (m, 1 H, $OCH_2CH{=}CH_2$) ppm. $^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ = 18.9 [$SiC(CH_3)_3(C_6H_5)_2$], 20.5 and 20.7 (2 $COCH_3$), 26.5 [$SiC(CH_3)_3(C_6H_5)_2$], 61.7, 67.1, 68.3, 69.1, 70.5, and 71.4 (C2, C3, C4, C5, C6, and $OCH_2CH{=}CH_2$), 95.1 (C1), 117.4 ($OCH_2CH{=}CH_2$), 127.5, 129.6, 129.7, and 135.3 [$SiC(CH_3)_3(C_6H_5)_2$], 133.3 ($OCH_2CH{=}CH_2$) ppm. High-resolution MS data of $C_{29}H_{38}O_8Si$ (542.234): [M + $NH_4$] found 560.267, calculated 560.267.

**Allyl (4,6-Di-*O*-acetyl-3-*O*-allyloxycarbonyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-2,4-di-*O*-acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-L-galactopyranoside (26):** A solution of **13** (0.22 g, 0.35 mmol) and **25** (0.15 g, 0.27 mmol) in dry $CH_2Cl_2$ (4 mL), containing activated molecular sieves (4 Å, 0.4 g), was stirred at room temperature for 30 min. Then, TMSOTf (2.45 μL, 13 μmol) was added, and the mixture was stirred for 1 h, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the formation of a new spot ($R_f$ = 0.35). The mixture was neutralized with dry pyridine, filtered, washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 95:5) of the residue afforded **26**, isolated as a syrup (0.26 g, 98%). $[\alpha]_D^{20}$ = −31 (*c* = 0.4, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$; 2D TOCSY and HSQC): δ = 0.96 [s, 9 H, $SiC(CH_3)_3(C_6H_5)_2$], 1.99, 2.05, and 2.13 (3 s, 3 H, 6 H, and 3 H, 4 Ac), 3.46 [dd, $^3J$(H5,H6a) = 5.8, $^3J$(H6a,H6b) = 10.5 Hz, 1 H, H6a], 3.51 [dd, $^3J$(H5,H6b) = 6.9 Hz, 1 H, H6b], 3.89 (m, 1 H, H5′), 3.92 (bt, 1 H, H5), 3.95 and 4.12 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 4.11 [dd, $^3J$(H5′,H6a′) = 2.3, $^3J$(H6a′,H6b′) = 12.2 Hz, 1 H, H6a′], 4.19 [dd, $^3J$(H2,H3) = 9.9, $^3J$(H3,H4) = 3.4 Hz, 1 H, H3], 4.28 [dd, $^3J$(H1′,H2′) = 8.3, $^3J$(H2′,H3′) = 10.5 Hz, 1 H, H2′], 4.34 (m, 2 H, $COOCH_2CH{=}CH_2$), 4.42 [dd, $^3J$(H5′,H6b′) = 5.2 Hz, 1 H, H6b′], 5.00 [d, $^3J$(H1,H2) = 4.2 Hz, 1 H, H1], 5.01 (dd, 1 H, H2), 4.98 and 5.06 (2 m, each 1 H, $COOCH_2CH{=}CH_2$), 5.17 (bt, 1 H, H4′), 5.17 and 5.24 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.26 [bd, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 5.42 [d, $^3J$(H1′,H2′) = 8.3 Hz, 1 H, H1′], 5.60 (m, 1 H, $COOCH_2CH{=}CH_2$), 5.61 [dd, $^3J$(H3′,H4′) = 9.2 Hz, 1 H, H3′], 5.83 (m, 1 H, $OCH_2CH{=}CH_2$), 7.27 and 7.50 [2 m, 6 H and 4 H, $SiC(CH_3)(C_6H_5)_2$], 7.69 and 7.82 (2 m, each 2 H, Phth) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 20.7 and 20.8 (2 $COCH_3$), 26.8 [$SiC(CH_3)_3(C_6H_5)_2$], 54.7 (C2′), 62.2 (C6′), 62.3 (C6), 68.2 (C4), 68.4 ($OCH_2CH{=}CH_2$), 68.7 ($COOCH_2CH{=}CH_2$), 68.8 (C2), 68.9 (C4′), 69.8 (C5), 71.6 (C5′), 74.4 (C3), 74.6 (C3′), 95.6 (C1), 97.2 (C1′), 117.8 ($OCH_2CH{=}CH_2$), 118.8 ($COOCH_2CH{=}CH_2$), 131.1 ($COOCH_2CH{=}CH_2$), 133.8 ($OCH_2CH{=}CH_2$), 123.3 and 133.9 [$N(CO)_2C_6H_4$], 127.9 and 135.7 [$SiC(CH_3)(C_6H_5)_2$] ppm. High-resolution MS data of $C_{51}H_{59}NO_{18}Si$ (1001.350): [M + Na] found 1024.341, calculated 1024.340.

**Allyl (4,6-Di-*O*-acetyl-3-*O*-allyloxycarbonyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-L-galactopyranoside (27):** To **26** (0.25 g, 0.25 mmol) a 1 M TBAF solution in THF (5 mL), neutralized at 0 °C with acetic acid, was added. The mixture was stirred at 0 °C for 5 h, and at room temperature overnight, when TLC ($CH_2Cl_2$/acetone, 9:1) showed the disappearance of **26** and the formation of a new product ($R_f$ = 0.3). After concentration, a solution of the residue in EtOAc was washed with water and 10% aq. NaCl, dried, filtered, and concentrated. A solution of the residue in pyridine/acetic anhydride (10 mL, 1:1) was stirred at room temperature overnight, then concentrated. Column chromatography ($CH_2Cl_2$/acetone, 95:5) of the residue afforded **27**, isolated as a syrup (0.17 g, 84%). $[\alpha]_D^{20}$ = −57 (*c* = 0.7, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$; 2D TOCSY and HSQC): δ = 1.96, 2.02, and

2.09 (3 s, 3 H, 3 H, and 9 H, 5 Ac), 3.87 (m, 1 H, H5′), 3.88 [dd, $^3J$(H5,H6b) = 7.4, $^3J$(H6a,H6b) = 11.5 Hz, 1 H, H6b], 3.95 [dd, $^3J$(H5,H6a) = 5.2 Hz, 1 H, H6a], 3.99 and 4.11 (2 m, each 1 H, OC$H_2$CH=CH$_2$), 4.05 (bt, 1 H, H5), 4.11 [dd, $^3J$(H5′,H6a′) = 2.8, $^3J$(H6a′,H6b′) = 12.7 Hz, 1 H, H6a′], 4.21 (m, 1 H, H3), 4.29 [dd, $^3J$(H1′,H2′) = 8.3, $^3J$(H2′,H3′) = 10.6 Hz, 1 H, H2′], 4.35 (m, 2 H, COOC$H_2$CH=CH$_2$), 4.41 [dd, $^3J$(H5′,H6b′) = 5.1 Hz, 1 H, H6b′], 4.98 and 5.07 (2 m, each 1 H, COOCH$_2$CH=C$H_2$), 5.03 (m, 2 H, H1 and H2), 5.18 (bt, 1 H, H4′), 5.19 and 5.28 (2 m, each 1 H, OCH$_2$CH=C$H_2$), 5.20 [bd, $^3J$(H3,H4) = 3.5, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 5.40 (d, 1 H, H1′), 5.59 (m, 1 H, COOCH$_2$C$H$=CH$_2$), 5.61 [dd, $^3J$(H3′,H4′) = 9.5 Hz, 1 H, H3′], 5.85 (m, 1 H, OCH$_2$C$H$=CH$_2$), 7.73 and 7.85 (2 m, each 2 H, Phth) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 20.5 (2 C) and 20.6 (3 C) (5 CO$C$H$_3$), 54.6 (C2′), 62.1 (C6′), 62.3 (C6), 66.9 (C5), 68.0 (C4), 68.3 (C2), 68.7 (COO$C$H$_2$CH=CH$_2$ and O$C$H$_2$CH=CH$_2$), 68.8 (C4′), 71.4 (C5′), 73.6 (C3), 74.4 (C3′), 95.7 (C1), 97.0 (C1′), 117.9 (OCH$_2$CH=$C$H$_2$), 118.8 (COOCH$_2$CH=$C$H$_2$), 131.0 (COOCH$_2$$C$H=CH$_2$), 133.5 (OCH$_2$$C$H=CH$_2$), 123.4 and 133.9 [N(CO)$_2$$C_6$H$_4$] ppm. High-resolution MS data of $C_{37}H_{43}NO_{19}$ (805.243): [M + Na] found 828.233, calculated 828.233.

**Allyl (4,6-Di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-L-galactopyranoside (28):** To a solution of **27** (0.16 g, 0.19 mmol) in THF (4 mL) and morpholine (0.09 mL) tetrakis(triphenylphosphane)palladium (31.6 mg, 33 μmol) was added. The mixture was stirred at 65 °C for 1 h, when TLC (CH$_2$Cl$_2$/acetone, 95:5) showed the complete formation of **28** ($R_f$ = 0.17). After concentration, a solution of the residue in CH$_2$Cl$_2$ was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (CH$_2$Cl$_2$/acetone, 9:1) of the residue gave **28**, isolated as a glass (0.13 mg, 96%). $[\alpha]_D^{20}$ = −67 ($c$ = 1, CHCl$_3$). $^1$H NMR (500 MHz, CDCl$_3$; 2D TOCSY and HSQC): δ = 1.97 and 2.08 (2 s, 6 H and 9 H; 5 Ac), 3.81 (m, 1 H, H5′), 3.87 [dd, $^3J$(H5,H6b) = 7.4, $^3J$(H6a,H6b) = 11.5 Hz, 1 H, H6b], 3.96 [dd, $^3J$(H5,H6a) = 5.2 Hz, 1 H, H6a], 3.98 and 4.13 (2 m, each 1 H, OC$H_2$CH=CH$_2$), 4.06 (bt, 1 H, H5), 4.11 [dd, $^3J$(H1′,H2′) = 8.3, $^3J$(H2′,H3′) = 10.9 Hz, 1 H, H2′], 4.22 (m, 1 H, H3), 4.42 (m, 2 H, H3′ and H6′), 4.90 (bt, 1 H, H4′), 5.03 (m, 2 H, H1 and H2), 5.19 and 5.28 (2 m, each 1 H, OCH$_2$CH=C$H_2$), 5.21 [dd, $^3J$(H3,H4) = 3.5, $^3J$(H4,H5) = 1.0 Hz, 1 H, H4], 5.29 [d, $^3J$(H1′,H2′) = 8.3 Hz, 1 H, H1′], 5.85 (m, 1 H, OCH$_2$C$H$=CH$_2$), 7.72 and 7.83 (2 m, each 2 H, Phth) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 20.6 (2 C) and 20.7 (3 C) (5 CO$C$H$_3$), 57.0 (C2′), 62.3 (C6′), 62.4 (C6), 66.9 (C5), 68.1 (C4), 68.4 (C2), 68.7 (O$C$H$_2$CH=CH$_2$), 70.0 (C3′), 71.6 (C5′), 72.1 (C4′), 73.3 (C3), 95.8 (C1), 97.1 (C1′), 117.9 (OCH$_2$CH=$C$H$_2$), 133.6 (OCH$_2$$C$H=CH$_2$), 123.3 and 134.0 [N(CO)$_2$$C_6$H$_4$] ppm. High-resolution MS data of $C_{33}H_{39}NO_{17}$ (721.222): [M + Na] found 744.213, calculated 744.211.

**Allyl (Sodium 4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-L-galactopyranoside (29):** A solution of **28** (0.12 g, 0.16 mmol) and sulfur trioxide trimethylamine complex (0.91 g, 6.6 mmol) in dry DMF (5 mL) was stirred at 50 °C for 48 h, when TLC (CH$_2$Cl$_2$/MeOH, 9:1) showed the complete conversion of **28** into nonsodiated **29** ($R_f$ = 0.17). After quenching of the reaction with MeOH (10 mL), the solution was co-concentrated with toluene. A solution of the residue in CH$_2$Cl$_2$ (50 mL) was washed with saturated aq. NaHCO$_3$, dried, filtered, and concentrated. The residue dissolved in MeOH (10 mL), containing Dowex 50 W × 8 Na$^+$ resin, was stirred for 15 min, then filtered and concentrated. Column chromatography (CH$_2$Cl$_2$/MeOH, 9:1) of the residue gave **29**, isolated as a white, amorphous powder (0.11 g, 82%). $[\alpha]_D^{20}$ = −46 ($c$ = 1, CHCl$_3$). $^1$H NMR (500 MHz, CDCl$_3$; 2D TOCSY and HSQC): δ = 1.97, 2.07, and 2.08 (3 s, 3 H, 6 H, and 6 H, 5 Ac), 3.89 [dd, $^3J$(H5,H6b) = 7.3, $^3J$(H6a,H6b) = 11.5 Hz, 1 H, H6b], 3.90 (m, 1 H, H5′), 3.95 [dd, $^3J$(H5,H6a) = 5.1 Hz, 1 H, H6a], 3.99 and 4.14 (2 m, each 1 H, OC$H_2$CH=CH$_2$), 4.08 (bt, 1 H, H5), 4.24 [dd, $^3J$(H2,H3) = 10.1, $^3J$(H3,H4) = 3.2 Hz, 1 H, H3], 4.39 [dd, $^3J$(H5′,H6b′) = 5.5, $^3J$(H6a′,H6b′) = 12.1 Hz, 1 H, H6b′], 4.96 (bt, 1 H, H4′), 5.01 [d, $^3J$(H1,H2) = 3.7 Hz, 1 H, H1], 5.04 (dd, 1 H, H2), 5.08 (bt, 1 H, H3′), 5.21 and 5.29 (2 m, each 1 H, OCH$_2$CH=C$H_2$), 5.22 (bd, 1 H, H4), 5.38 [d, $^3J$(H1′,H2′) = 8.4 Hz, 1 H, H1′], 5.87 (m, 1 H, OCH$_2$C$H$=CH$_2$), 7.65 and 7.80 (2 m, each 2 H, Phth) ppm. $^{13}$C NMR (125.76 MHz, CDCl$_3$): δ = 19.8, 20.7 (2 C), and 20.8 (2 C) (5 CO$C$H$_3$), 55.2 (C2′), 62.3 (C6′), 62.4 (C6), 66.9 (C5), 68.1 (C4), 68.3 (C2), 68.5 (O$C$H$_2$CH=CH$_2$), 69.7 (C4′), 71.1 (C5′), 73.5 (C3), 76.0 (C3′), 95.8 (C1), 96.8 (C1′), 117.9 (OCH$_2$CH=$C$H$_2$), 133.5 (OCH$_2$$C$H=CH$_2$), 123.4 and 134.1 [N(CO)$_2$$C_6$H$_4$] ppm. High-resolution MS data of $C_{33}H_{38}NNaO_{20}S$ (823.161): [M + Na] found 846.115, calculated 846.150.

**Allyl (Sodium 2-acetamido-2-deoxy-3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-α-L-galactopyranoside (30):** A solution of **29** (50 mg, 60 μmol) in ethanolic 33% CH$_3$NH$_2$ (5 mL) was stirred at room temperature for 5 days, during which time the mixture was concentrated 3 times and fresh ethanolic 33% CH$_3$NH$_2$ (5 mL) was added. After co-concentration with toluene, to a solution of the residue in dry MeOH (5 mL) acetic anhydride (100 μL) was added at 0 °C. The mixture was stirred at 0 °C for 3 h, when TLC (EtOAc/MeOH/H$_2$O, 6:2.5:1.5) showed the formation of **30** ($R_f$ = 0.48). Size-exclusion chromatography (Bio-Gel P-2, 100 mM NH$_4$HCO$_3$) gave **30**, isolated after lyophilization from water, as a white, amorphous powder (30 mg, 96%). $[\alpha]_D^{20}$ = −19 ($c$ = 1, H$_2$O). $^1$H NMR (500 MHz, D$_2$O; 2D TOCSY and HSQC): δ = 2.00 (s, 3 H, NAc), 3.52 (m, 1 H, H5′), 3.62 (bt, 1 H, H4′), 3.72 (m, 2 H, 2 H6), 3.76 [dd, $^3J$(H5′,H6b′) = 6.0, $^3J$(H6a′,H6b′) = 12.5 Hz, 1 H, H6b′], 3.82 [dd, $^3J$(H1′,H2′) = 8.6, $^3J$(H2′,H3′) = 10.4 Hz, 1 H, H2′], 3.90 (m, 2 H, H2 and H5), 3.93 [dd, $^3J$(H5′,H6a′) = 2.3 Hz, 1 H, H6a′], 4.04 [dd, $^3J$(H2,H3) = 7.1, $^3J$(H3,H4) = 3.2 Hz, 1 H, H3], 4.07 (bd, 1 H, H4), 4.08 and 4.23 (2 m, each 1 H, OC$H_2$CH=CH$_2$), 4.41 [dd, $^3J$(H2′,H3′) = 10.4, $^3J$(H3′,H4′) = 8.9 Hz, 1 H, H3′], 4.80 (d, 1 H, H1′), 5.02 [d, $^3J$(H1,H2) = 4.0 Hz, 1 H, H1], 5.26 and 5.37 (2 m, each 1 H, OCH$_2$CH=C$H_2$), 5.97 (m, 1 H, OCH$_2$C$H$=CH$_2$) ppm. $^{13}$C NMR (125.76 MHz, D$_2$O): δ = 23.1 (NDCO$C$H$_3$), 55.2 (C2′), 61.5 (C6′), 61.9 (C6), 67.3 (C5), 67.5 (C4), 69.3 (O$C$H$_2$CH=CH$_2$), 69.6 (C4′), 71.7 (C2), 76.8 (C5′), 78.1 (C3), 82.1 (C3′), 98.0 (C1), 96.4 (C1′), 119.1 (OCH$_2$CH=$C$H$_2$), 134.4 (OCH$_2$$C$H=CH$_2$) ppm. High-resolution MS data of $C_{17}H_{28}NNaO_{14}S$ (525.113): [M + H] found 526.120, calculated 526.115.

**3-(6-Mercaptohexylthio)propyl (Sodium 2-acetamido-2-deoxy-3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-α-L-galactopyranoside (4):** To a solution of **30** (11 mg, 20 μmol) in MeOH (2.0 mL) and water (0.3 mL) 1,6-hexanedithiol (31 μL, 0.2 mmol) was added. The mixture was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV Lamp, when TLC (EtOAc/MeOH/H$_2$O, 6:2.5:1.5) showed the formation of **4** ($R_f$ = 0.69). After concentration, the excess of 1,6-hexanedithiol was separated from carbohydrate by column chromatography (CH$_2$Cl$_2$/MeOH, 9:1 → MeOH). The carbohydrate-containing fractions were concentrated, and a solution of the residue in water was loaded on a C-18 Extract-Clean™ column. After elution of remaining **30** with water (3 × 3 mL), **4** was eluted with MeOH (3 × 3 mL), then concentrated in vacuo, and obtained, after lyophilization from water, as a white, amorph-

ous powder (8 mg, 60%). $[\alpha]_D^{20} = -10$ ($c$ = 0.8, $CH_3OH$). $^1H$ NMR (500 MHz, $CD_3OD$; 2D TOCSY and HSQC): δ = 1.42, 1.59, and 2.52 [3 m, each 4 H, $O(CH_2)_3S(CH_2)_6SH$], 1.90 [m, 2 H, $OCH_2CH_2CH_2S(CH_2)_6SH$], 1.99 (s, 3 H, NAc), 2.63 [bt, 2 H, $O(CH_2)_2CH_2S(CH_2)_6SH$], 3.38 (m, 1 H, H5′), 3.53 (bt, 1 H, H4′), 3.54 and 3.80 [2 m, each 1 H, $OCH_2(CH_2)_2S(CH_2)_6SH$], 3.67 [dd, $^3J$(H5′,H6b′) = 6.3, $^3J$(H6a′,H6b′) = 12.1 Hz, 1 H, H6b′], 3.71 (d, 2 H, 2 H6), 3.80 (bt, 1 H, H5), 3.89 (m, 3 H, H2, H3, and H6′), 3.99 (bd, 1 H, H4), 4.41 [dd, $^3J$(H2′,H3′) = 10.2, $^3J$(H3′,H4′) = 8.9 Hz, 1 H, H3′], 4.75 [d, $^3J$(H1′,H2′) = 8.4 Hz, 1 H, H1′], 4.83 [d, $^3J$(H1,H2) = 2.8 Hz, 1 H, H1] ppm. $^{13}C$ NMR (125.76 MHz, $CD_3OD$): δ = 23.4 ($NDCOCH_3$), 25.0, 29.0, 29.4, 29.9, 30.8, 30.9, 32.9, and 35.1 [$OCH_2(CH_2)_2S(CH_2)_6SH$], 56.4 (C2′), 62.8 (C6 and C6′), 68.0 [$OCH_2(CH_2)_2S(CH_2)_6SH$], 69.7 (2 C) (C2 and C4), 71.5 (C4′), 72.3 (C5), 78.0 (C5′), 80.2 (C3), 82.0 (C3′), 100.4 (C1), 101.4 (C1′) ppm. High-resolution MS data of $C_{23}H_{42}NNaO_{14}S_3$ (675.166): [M + Na] found 698.176, calculated 698.156.

**Allyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-fucopyranoside (31):** A solution of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate[23] (0.23 g, 0.38 mmol) and allyl 2,4-di-*O*-benzoyl-α-L-fucopyranoside[10] (0.12 g, 0.29 mmol) in dry $CH_2Cl_2$ (5 mL), containing activated molecular sieves (4 Å, 0.4 g), was stirred at room temperature for 30 min. Then, TMSOTf (2.45 μL, 13 μmol) was added and the mixture was stirred for 1 h, when TLC (*n*-hexane/EtOAc, 3:2) showed the formation of a new spot ($R_f$ = 0.16). The mixture was neutralized with triethylamine, filtered, washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (*n*-hexane/EtOAc, 3:2) of the residue afforded **31**, isolated as a white foam (0.2 g, 86%). $[\alpha]_D^{20} = -130$ ($c$ = 1, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$; 2D TOCSY and HSQC): δ = 1.08 [d, $^3J$(H5,H6) = 6.5 Hz, 3 H, C*Me*], 1.71, 1.98, and 2.01 (3 s, each 3 H, 3 Ac), 3.91 (m, 1 H, H5′), 3.99 and 4.17 (2 m, each 1 H, $OCH_2CH=CH_2$), 4.00 [dd, $^3J$(H5′,H6a′) = 2.8, $^3J$(H6a′,H6b′) = 12.2 Hz, 1 H, H6a′], 4.14 [dd, $^3J$(H1′,H2′) = 8.5, $^3J$(H2′,H3′) = 10.7 Hz, 1 H, H2′], 4.18 (bt, 1 H, H5), 4.25 [dd, $^3J$(H5′,H6b′) = 5.9 Hz, 1 H, H6b′], 4.59 [dd, $^3J$(H2,H3) = 10.4, $^3J$(H3,H4) = 3.4 Hz, 1 H, H3], 4.99 [dd, $^3J$(H3′,H4′) = 9.3, $^3J$(H4′,H5′) = 10.0 Hz, 1 H, H4′], 5.11 and 5.26 (2 m, each 1 H, $OCH_2CH=CH_2$), 5.24 [d, $^3J$(H1,H2) = 3.8 Hz, 1 H, H1], 5.39 [dd, $^3J$(H2,H3) = 10.4 Hz, 1 H, H2], 5.40 (bd, 1 H, H4), 5.62 (d, 1 H, H1′), 5.69 (dd, 1 H, H3′), 5.81 (m, 1 H, $OCH_2CH=CH_2$), 7.22 and 7.45 (2 m, 4 H and 6 H, 2 PhCO), 7.76 and 7.86 (2 m, each 2 H, Phth) ppm. $^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ = 16.1 (C6), 20.1, 20.5, and 20.6 (3 $COCH_3$), 54.5 (C2′), 62.6 (C6′), 65.2, 69.2, and 70.7 (C2, C3, and C4), 68.6 ($OCH_2CH=CH_2$), 71.5, 71.6, and 73.5 (C3′, C4′, and C5′), 95.9 and 96.6 (C1 and C1′), 117.2 ($OCH_2CH=CH_2$), 133.7 ($OCH_2CH=CH_2$) ppm. High-resolution MS data of $C_{43}H_{43}NO_{16}$ (829.258): [M + $NH_4$] found 847.295, calculated 847.293.

**Allyl (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-α-L-fucopyranoside (32):** A solution of **31** (0.1 g, 0.12 mmol) in *n*-butanol (10 mL) and 1,2-diaminoethane (4 mL) was stirred at 90 °C overnight. Then, the mixture was co-concentrated with toluene, and the residue was dissolved in pyridine (9 mL) and acetic anhydride (4.5 mL). After stirring at room temperature overnight, the solution was diluted with $CH_2Cl_2$, washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 9:1) of the residue yielded the per-acetylated disaccharide, which was directly de-*O*-acetylated in MeOH (3 mL) using sodium methoxide (pH 10). After 3 days, the mixture was neutralized with Dowex 50 X 8 $H^+$ resin, filtered, and concentrated. Size-exclusion chromatography (Bio-Gel P-2, 100 mM $NH_4HCO_3$) of the residue gave **32**, isolated after lyophilization from water, as a white, amorphous powder (40 mg, 80%). $[\alpha]_D^{20} = -147$ ($c$ = 1, $H_2O$). $^1H$ NMR (500 MHz, $D_2O$; 2D TOCSY): δ = 1.25 [d, $^3J$(H5,H6) = 6.5 Hz, 3 H, C*Me*], 2.09 (s, 3 H, NAc), 3.48 (m, 2 H, 2 H6′), 3.62 (m, 1 H, H5′), 3.77 (bt, 1 H, H4′), 3.78 [dd, $^3J$(H2′,H3′) = 10.2 Hz, 1 H, H2′], 3.92 [dd, $^3J$(H1,H2) = 4.0, $^3J$(H2,H3) = 10.5 Hz, 1 H, H2], 3.93 (bd, 1 H, H4), 3.94 (bt, 1 H, H3′), 4.12 and 4.23 (2 m, each 1 H, $OCH_2CH=CH_2$), 4.70 [d, $^3J$(H1′,H2′) = 8.4 Hz, 1 H, H1′], 5.01 [d, $^3J$(H1,H2) = 4.0 Hz, 1 H, H1], 5.30 and 5.40 (2 m, each 1 H, $OCH_2CH=CH_2$), 6.01 (m, 1 H, $OCH_2CH=CH_2$) ppm. $^{13}C$ NMR (75.4 MHz, $D_2O$): δ = 14.6 (C6), 17.9 ($NDCOCH_3$), 55.1 (C2′), 60.1 (C6′), 68.4 ($OCH_2CH=CH_2$), 65.7, 66.0, 68.6, 69.3, 73.1, 75.3, and 76.7 (C2, C3, C4, C5, C3′, C4′, and C5′), 96.7 and 98.4 (C1 and C1′), 117.6 ($OCH_2CH=CH_2$), 133.0 ($OCH_2CH=CH_2$) ppm. High-resolution MS data of $C_{17}H_{29}NO_{10}$ (407.179): [M + H] found 408.184, calculated 408.186.

**3-(6-Mercaptohexylthio)propyl (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-α-L-fucopyranoside (5):** To a solution of **32** (20 mg, 50 μmol) in MeOH (1.5 mL) 1,6-hexanedithiol (76 μL, 0.5 mmol) was added, and the mixture was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV Lamp, when TLC (EtOAc/MeOH/$H_2O$, 6:2.5:1.5) indicated the formation of **5** ($R_f$ = 0.85). After concentration, the excess of 1,6-hexanedithiol was separated from carbohydrate by column chromatography ($CH_2Cl_2$/MeOH, 9:1 → MeOH). The carbohydrate-containing fractions were concentrated, and a solution of the residue in water was loaded on a C-18 Extract-Clean™ column. After elution of remaining **32** with water (3 × 3 mL), **5** was eluted with MeOH (3 × 3 mL), then concentrated in vacuo, and obtained, after lyophilization from water, as a white, amorphous powder (28 mg, 100%). $[\alpha]_D^{20} = -49$ ($c$ = 0.1, $CH_3OH$). $^1H$ NMR (500 MHz, $CD_3OD$; 2D TOCSY and HSQC): δ = 1.21 [d, $^3J$(H5,H6) = 6.6 Hz, 3 H, C*Me*], 1.42, 1.59, and 2.50 [3 m, each 4 H, $O(CH_2)_3S(CH_2)_6SH$], 1.88 [m, 2 H, $OCH_2CH_2CH_2S(CH_2)_6SH$], 1.99 (s, 3 H, NAc), 2.62 [bt, 2 H, $O(CH_2)_2CH_2S(CH_2)_6SH$], 3.29 (m, 2 H, H4′ and H5′), 3.51 and 3.63 [2 m, each 1 H, $OCH_2(CH_2)_2S(CH_2)_6SH$], 3.52 (bt, 1 H, H3′), 3.64 [dd, $^3J$(H1′,H2′) = 8.3, $^3J$(H2′,H3′) = 9.9 Hz, 1 H, H2′], 3.75 [bd, $^3J$(H3,H4) = 1.4, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 3.82 [dd, $^3J$(H1,H2) = 3.7, $^3J$(H2,H3) = 10.1 Hz, 1 H, H2], 3.93 (m, 1 H, H5), 4.58 (d, 1 H, H1′), 4.78 (d, 1 H, H1) ppm. $^{13}C$ NMR (125.76 MHz, $CD_3OD$): δ = 16.6 (C6), 23.2 ($NDCOCH_3$), 24.9, 29.1, 29.4, 29.7, 30.7, 30.8, 32.8, and 35.2 [$OCH_2(CH_2)_2S(CH_2)_6SH$], 57.9 (C2′), 62.8 (C6′), 67.3 (C5), 67.7 [$OCH_2(CH_2)_2S(CH_2)_6SH$], 68.2 (C2), 71.1 (C4), 72.1 (C4′), 75.7 (C3′), 78.2 (C5′), 79.9 (C3), 100.3 (C1), 101.0 (C1′) ppm. High-resolution MS data of $C_{23}H_{43}NO_{10}S_2$ (M, 557.233): M + H found 558.235, calculated 558.240.

**1,2,4,6-Tetra-*O*-acetyl-3-*O*-allyloxycarbonyl-β-D-glucopyranose (34):** To a solution of 1,2,4,6-tetra-*O*-acetyl-β-D-glucopyranose[28] (**33**; 1.0 g, 2.75 mmol) in pyridine/$CH_2Cl_2$ (4 mL, 1:1) three portions of allyl chloroformate (each 0.4 mL, 3.8 mmol) were added at −30 °C in intervals of 10 min. The mixture was stirred at −30 °C for another 30 min, when TLC ($CH_2Cl_2$/acetone, 95:5) showed the complete formation of **34** ($R_f$ = 0.38). The solution was diluted with EtOAc, washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 95:5) of the residue gave **34**, isolated as a glass (1.23 g, 100%). $[\alpha]_D^{20} = +75$ ($c$ = 0.1, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): δ = 2.04, 2.08, and 2.11 (3 s, 3 H, 3 H, and 6 H, 4 Ac), 3.84 (m, 1 H, H5), 4.11 [dd, $^3J$(H5,H6a) = 2.2, $^3J$(H6a,H6b) = 12.5 Hz, 1 H, H6a], 4.27 [dd, $^3J$(H5,H6b) = 4.6 Hz, 1 H, H6b], 4.60 (m, 2 H, $COOCH_2CH=$

$CH_2$), 5.06 (bt, 1 H, H4), 5.22 and 5.34 (2 m, each 1 H, CO-$OCH_2CH{=}CH_2$), 5.72 [d, $^3J$(H1,H2) = 8.1 Hz, 1 H, H1], 5.89 (m, 1 H, $COOCH_2CH{=}CH_2$) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 20.7 ($COCH_3$), 61.5 (C6), 68.9 ($COOCH_2CH{=}CH_2$), 67.7, 70.1, 72.7, and 76.8 (C2, C3, C4, and C5), 91.7 (C1), 118.9 (CO-$OCH_2CH{=}CH_2$), 133 ($COOCH_2CH{=}CH_2$) ppm. High-resolution MS data of $C_{18}H_{24}O_{12}$ (432.127): [M + $NH_4$] found 450.162, calculated 450.161.

**2,4,6-Tri-*O*-acetyl-3-*O*-allyloxycarbonyl-α-D-glucopyranosyl Trichloroacetimidate (35):** To a solution of **34** (1.2 g, 2.67 mmol) in dry DMF (4 mL) hydrazine acetate (0.38 g, 4.13 mmol) was added and the mixture was stirred for 1 h, when TLC ($CH_2Cl_2$/acetone, 9:1) showed the disappearance of **34** and the formation of a new spot ($R_f$ = 0.46). The solution was diluted with EtOAc, washed with water and 10% aq. NaCl, dried, filtered, and concentrated. To a solution of the residue in dry $CH_2Cl_2$ (6 mL) and trichloroacetonitrile (2.8 mL, 26.7 mmol) 1,8-diazabicyclo[5.4.0]undec-7-ene (44 μL, 0.267 mmol) was added at 0 °C, and the mixture was stirred for 2 h, then concentrated. Column chromatography ($CH_2Cl_2$/acetone, 95:5) of the residue yielded **35**, isolated as yellow syrup (0.88 g, 60%). $[\alpha]_D^{20}$ = +85 (*c* = 1, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.02, 2.05, and 2.07 (3 s, each 3 H, 3 Ac), 4.13 [dd, $^3J$(H5,H6a) = 1.7, $^3J$(H6a,H6b) = 12.0 Hz, 1 H, H6a], 4.19 (m, 1 H, H5), 4.27 [dd, $^3J$(H5,H6b) = 4.0 Hz, 1 H, H6b], 4.63 (m, 2 H, $COOCH_2CH{=}CH_2$), 5.13 [dd, $^3J$(H1,H2) = 3.6, $^3J$(H2,H3) = 10.1 Hz, 1 H, H2], 5.23 (bt, 1 H, H4), 5.29 and 5.34 (2 m, each 1 H, $COOCH_2CH{=}CH_2$), 5.39 (bt, 1 H, H3), 5.89 (m, 1 H, CO-$OCH_2CH{=}CH_2$), 6.58 (d, 1 H, H1), 8.69 [s, 1 H, C(N*H*)$CCl_3$] ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 28.9, 29.1, and 29.2 (3 $COCH_3$), 63.7 (C6), 70.0 ($COOCH_2CH{=}CH_2$), 69.0, 70.1, 71.1, and 74.4 (C2, C3, C4, and C5), 90.5 (C1), 112.6 ($COOCH_2CH{=}CH_2$), 123.0 ($COOCH_2CH{=}CH_2$), 155.3, 155.6, and 156.3 (3 $COCH_3$) ppm.

**Allyl (2,4,6-Tri-*O*-acetyl-3-*O*-allyloxycarbonyl-β-D-glucopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-fucopyranoside (36):** A solution of allyl 2,4-di-*O*-benzoyl-α-L-fucopyranoside[10] (0.24 g, 0.58 mmol) and **35** (0.48 g, 0.87 mmol) in dry $CH_2Cl_2$ (3 mL), containing activated molecular sieves (4 Å, 0.4 g), was stirred at room temperature for 30 min. Then, TMSOTf (8.2 μL, 43.5 μmol) was added, and the mixture was stirred for 20 min, when TLC (hexane/EtOAc, 2:1) showed the formation of a new product ($R_f$ = 0.13). The mixture was neutralized with triethylamine, filtered, and the solution was washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography (hexane/EtOAc, 2:1) of the residue afforded **36**, isolated as white foam (0.27 g, 60%). $[\alpha]_D^{20}$ = −57 (*c* = 1, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$; 2D TOCSY): δ = 1.21 [d, $^3J$(H5,H6) = 6.4 Hz, 3 H, C*Me*], 1.52, 1.99, and 2.01 (3 s, each 3 H, 3 Ac), 3.71 (m, 1 H, H5′), 3.95 [dd, $^3J$(H5′,H6a′) = 2.5, $^3J$(H6a′,H6b′) = 12.2 Hz, 1 H, H6a′], 4.03 and 4.22 (2 m, each 1 H, $COOCH_2CH{=}CH_2$), 4.18 (m, 1 H, H5), 4.51 (d, $^3J$ = 5.5 Hz, 2 H, $OCH_2CH{=}CH_2$), 4.61 [dd, $^3J$(H1,H2) = 3.0, $^3J$(H2,H3) = 10.7 Hz, 1 H, H2], 4.76 [d, $^3J$(H1′,H2′) = 7.9 Hz, 1 H, H1′], 4.81 (bt, 1 H, H2′), 4.95 (bt, 1 H, H3′), 5.00 (bt, 1 H, H4′), 5.12, 5.18, 5.24, and 5.27 (4 m, each 1 H, $COOCH_2CH{=}CH_2$ and $OCH_2CH{=}CH_2$), 5.29 [bd, $^3J$(H3,H4) = 3.7, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 5.44 (dd, 1 H, H3), 5.61 (d, 1 H, H1), 5.81 (m, 2 H, $COOCH_2CH{=}CH_2$ and $OCH_2CH{=}CH_2$), 7.45, 7.57, and 8.09 (3 m, 4 H, 4 H, and 2 H, 2 PhCO) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 16.3 (C6), 62.3 (C6′), 68.5 and 68.7 ($COOCH_2CH{=}CH_2$ and $OCH_2CH{=}CH_2$), 65.2, 68.5, 69.5, 70.8, 71.1, 71.7, 72.7, and 77.1 (C2, C3, C4, C5, C2′, C3′, C4′, and C5′), 95.9 and 98.2 (C1 and C1′), 117.4 and 118.7 ($COOCH_2CH{=}CH_2$ and $OCH_2CH{=}CH_2$) ppm. High-resolution MS data of $C_{39}H_{44}O_{17}$ (784.258): [M + H] found 785.265, calculated 785.266.

**Allyl (2,4,6-Tri-*O*-acetyl-β-D-glucopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-fucopyranoside (37):** To a solution of **36** (0.25 g, 0.32 mmol) in THF (4 mL) and morpholine (0.16 mL) tetrakis(triphenylphosphane)palladium (53 mg, 55 μmol) was added at 65 °C. The mixture was stirred at 65 °C for 2 h, when TLC ($CH_2Cl_2$/acetone, 9:1) showed the complete conversion of **36** into **37** ($R_f$ = 0.22). The mixture was diluted with $CH_2Cl_2$, washed with 10% aq. NaCl, dried, filtered, and concentrated. Column chromatography ($CH_2Cl_2$/acetone, 85:15) of the residue afforded **37**, isolated as yellow syrup (0.21 g, 93%). $[\alpha]_D^{20}$ = −106 (*c* = 0.5, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.21 [d, $^3J$(H5,H6) = 6.5 Hz, 3 H, C*Me*], 1.57, 2.01, and 2.06 (3 s, each 3 H, 3 Ac), 3.95 [dd, $^3J$(H5′,H6a′) = 2.7, $^3J$(H6a′,H6b′) = 12.3 Hz, 1 H, H6a′], 4.03 and 4.20 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 4.61 [d, $^3J$(H1′,H2′) = 7.7 Hz, 1 H, H1′], 4.67 (bt, 1 H, H2′), 4.82 (bt, 1 H, H4′), 5.13 and 5.26 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.29 [bd, $^3J$(H3,H4) = 3.7, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 5.44 [dd, $^3J$(H2,H3) = 10.4 Hz, 1 H, H3], 5.64 [d, $^3J$(H1,H2) = 3.0 Hz, 1 H, H1], 5.81 (m, 1 H, $OCH_2CH{=}CH_2$), 7.45, 7.55, and 8.10 (3 m, 4 H, 4 H, and 2 H, 2 PhCO) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 16.2 (C6), 19.9, 20.6, and 20.7 (3 $COCH_3$), 62.4 (C6′), 68.8 ($OCH_2CH{=}CH_2$), 65.1, 69.4, 70.7, 71.1, 71.7, 72.3, and 74.1 (C2, C3, C4, C2′, C3′, C4′, and C5′), 95.9 and 97.9 (C1 and C1′), 117.4 ($OCH_2CH{=}CH_2$), 165.9 and 166.2 (2 Ph*C*O), 170.3, 170.7, and 171.0 (3 *C*$OCH_3$) ppm. High-resolution MS data of $C_{35}H_{40}O_{15}$ (700.237): [M + Na] found 723.226, calculated 723.227.

**Allyl (Sodium 2,4,6-tri-*O*-acetyl-3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-fucopyranoside (38):** To a solution of **37** (0.12 g, 0.17 mmol) in dry DMF (7 mL), sulfur trioxide trimethylamine complex (0.94 g, 6.8 mmol) was added at 50 °C. The mixture was stirred at 50 °C for 48 h, when TLC ($CH_2Cl_2$/MeOH, 9:1) showed the conversion of **37** into nonsodiated **38** ($R_f$ = 0.35). After quenching of the reaction with MeOH (10 mL), the solution was co-concentrated with toluene. A solution of the residue in $CH_2Cl_2$ (50 mL) was washed with saturated aq. $NaHCO_3$, dried, filtered, and concentrated. The residue dissolved in MeOH (10 mL), containing Dowex 50 W × 8 $Na^+$ resin, was stirred for 15 min, then filtered and concentrated. Column chromatography ($CH_2Cl_2$/MeOH, 85:15) of the residue gave **38**, isolated as a yellow, amorphous powder (73 mg, 53%). $[\alpha]_D^{20}$ = −96 (*c* = 1, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$; 2D TOCSY): δ = 1.18 [d, $^3J$(H5,H6) = 6.6 Hz, 3 H, C*Me*], 1.61, 1.88, and 1.89 (3 s, each 3 H, 3 Ac), 3.59 (m, 1 H, H5′), 3.72 [dd, $^3J$(H5′,H6a′) = 1.4, $^3J$(H6a′,H6b′) = 12.2 Hz, 1 H, H6a′], 4.02 and 4.19 (2 dd, each 1 H, $OCH_2CH{=}CH_2$), 4.09 [dd, $^3J$(H5′,H6b′) = 5.5 Hz, 1 H, H6b′], 4.26 (m, 1 H, H5), 4.37 (bt, 1 H, H3′), 4.53 [dd, $^3J$(H1,H2) = 3.2, $^3J$(H2,H3) = 10.4 Hz, 1 H, H2], 4.58 [d, $^3J$(H1′,H2′) = 7.9 Hz, 1 H, H1′], 4.83 (bt, 1 H, H4′), 5.12 and 5.28 (2 m, each 1 H, $OCH_2CH{=}CH_2$), 5.29 [bd, $^3J$(H3,H4) = 3.7, $^3J$(H4,H5) < 1 Hz, 1 H, H4], 5.40 (dd, 1 H, H3), 5.57 (d, 1 H, H1), 5.83 (m, 1 H, $OCH_2CH{=}CH_2$), 7.41, 7.54, and 8.07 (3 m, 4 H, 4 H, and 2 H, PhCO) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 16.6 (C6), 20.4, 21.0, and 21.1 (3 $COCH_3$), 62.8 (C6′), 69.2 ($OCH_2CH{=}CH_2$), 65.5, 69.8, 71.1, 71.5, 72.0, 72.7, and 74.6 (C2, C3, C4, C2′, C3′, C4′, and C5′), 96.3 and 98.2 (C1 and C1′), 117.8 ($OCH_2CH{=}CH_2$), 134.1 ($OCH_2CH{=}CH_2$) ppm. High-resolution MS data of $C_{35}H_{39}NaO_{18}S$ (802.175): [M + Na] found 825.162, calculated 825.165.

**Allyl (Sodium 3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-α-L-fucopyranoside (39):** To a solution of **38** (70 mg, 87 μmol) in MeOH (5 mL) and water (0.5 mL) sodium methoxide (pH 10) was added.

The mixture was stirred for 3 days, when TLC (EtOAc/MeOH/$H_2O$, 6:2.5:1.5) showed the formation of **39** ($R_f$ = 0.69). After concentration, size-exclusion chromatography (Bio-Gel P-2, 100 mM $NH_4HCO_3$) of the residue yielded **39**, isolated after lyophilization from water, as a white, amorphous powder (40 mg, 100%). $[\alpha]_D^{20}$ = −80 (*c* = 1, $H_2O$). $^1$H NMR (500 MHz, $D_2O$; 2D TOCSY): δ = 1.30 [d, $^3J$(H5,H6) = 6.5 Hz, 3 H, C*Me*], 3.58 (m, 1 H, H5′), 3.68 (bt, 1 H, H4′), 3.80 [dd, $^3J$(H5′,H6b′) = 5.8, $^3J$(H6a′,H6b′) = 12.4 Hz, 1 H, H6b′], 3.98 (m, 2 H, H2 and H6a′), 4.09 (m, 1 H, H5), 4.13 and 4.23 (2 m, each 1 H, OC$H_2$CH=$CH_2$), 4.38 (bt, 1 H, H3′), 4.73 [d, $^3J$(H1′,H2′) = 7.9 Hz, 1 H, H1′], 5.03 [d, $^3J$(H1,H2) = 4.0 Hz, 1 H, H1], 5.33 and 5.42 (2 m, each 1 H, OCH$_2$CH=C$H_2$), 6.03 (m, 1 H, OCH$_2$C*H*=CH$_2$) ppm. $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ = 15.9 (C6), 61.3, 67.0, 67.2, 69.0, 69.4, 69.7, 72.4, 76.1, and 77.9 (C2, C3, C4, C5, C2′, C4′, C5′, C6′, and OCH$_2$CH=CH$_2$), 84.8 (C3′), 98.1 and 100.3 (C1 and C1′), 118.9 (OCH$_2$CH=C$H_2$), 134.3 (OCH$_2$C*H*=CH$_2$) ppm. High-resolution MS data of $C_{15}H_{25}NaO_{13}S$ (468.091): [M + H] found 469.093, calculated 469.099.

**3-(6-Mercaptohexylthio)propyl (Sodium 3-*O*-sulfonato-β-D-glucopyranosyl)-(1→3)-α-L-fucopyranoside (6):** To a solution of **39** (31 mg, 66 μmol) in MeOH (1.5 mL) 1,6-hexanedithiol (101 μL, 0.66 mmol) was added and the mixture was irradiated for 2 h in a quartz vial, using a VL-50C Vilber Lourmat UV lamp, when TLC ($CH_2Cl_2$/MeOH, 4:1) indicated the formation of **6** ($R_f$ = 0.76). After concentration, the excess of 1,6-hexanedithiol was separated from carbohydrate by column chromatography ($CH_2Cl_2$/MeOH, 9:1 → MeOH). The carbohydrate-containing fractions were concentrated, and a solution of the residue in water was loaded on a C-18 Extract-Clean™ column. After elution of remaining **39** with water (3 × 3 mL), **6** was eluted with MeOH (3 × 3 mL), then concentrated in vacuo, and obtained, after lyophilization from water, as a white, amorphous powder (20 mg, 50%). $[\alpha]_D^{20}$ = −96 (*c* = 1, $CH_3OH$). $^1$H NMR (500 MHz, $CD_3OD$; 2D TOCSY): δ = 1.24 [d, $^3J$(H5,H6) = 6.5 Hz, 3 H, C*Me*], 1.42, 1.59, and 2.51 [3 m, each 4 H, O(CH$_2$)$_3$S(C$H_2$)$_6$SH], 1.90 [m, 2 H, OCH$_2$C$H_2$CH$_2$S(CH$_2$)$_6$SH], 2.63 [bt, 2 H, O(CH$_2$)$_2$C$H_2$S(CH$_2$)$_6$SH], 3.39 (m, 1 H, H5′), 3.46 [dd, $^3J$(H1′,H2′) = 7.9, $^3J$(H2′,H3′) = 9.1 Hz, 1 H, H2′], 3.51 (bt, 1 H, H4′), 3.52 and 3.79 [2 m, each 1 H, OC$H_2$(CH$_2$)$_2$S(CH$_2$)$_6$SH], 3.67 [dd, $^3J$(H5′,H6b′) = 5.9, $^3J$(H6a′,H6b′) = 12.1 Hz, 1 H, H6b′], 3.86 [dd, $^3J$(H1,H2) = 4.0 Hz, 1 H, H2], 3.88 [dd, $^3J$(H5′,H6a′) = 2.5 Hz, 1 H, H6a′], 3.90 [bd, $^3J$(H3,H4) = 3.0, $^3J$(H4,H5) < 1 Hz, 1 H, H4), 3.96 (m, 1 H, H5), 3.97 (dd, 1 H, H3), 4.29 (bt, 1 H, H3′), 4.57 (d, 1 H, H1′), 4.78 (d, 1 H, H1) ppm. $^{13}$C NMR (75.4 MHz, $CD_3OD$): δ = 16.6 (C6), 24.9, 28.9, 29.1, 29.5, 30.5, 30.6, 32.7, and 35.0 [OCH$_2$(C$H_2$)$_2$S(C$H_2$)$_6$SH], 62.4 (C6′), 67.1, 68.2, 70.2, 70.6, 73.7, 77.6, 79.3, and 85.1 (C2, C3, C4, C5, C2′, C3′, C4′, and C5′), 67.6 [OCH$_2$(CH$_2$)$_2$S(CH$_2$)$_6$SH], 100.3 and 101.4 (C1 and C1′) ppm. High-resolution MS data of $C_{21}H_{39}NaO_{13}S_3$ (618.145): [M + H] found 619.156, calculated 619.153.

**General Procedure for the Preparation of Gold Glyconanoparticles:** A solution of a thiol spacer containing saccharide (**1a/b** to **6**) in MeOH (10 mM, 5 equiv.) was added to a solution of tetrachloroauric acid in water (25 mM, 1 equiv.). Then, an aqueous solution of $NaBH_4$ (1 M, 22 equiv.) was slowly added under rigorous stirring. The obtained black suspension was stirred at room temperature for 2 h. After concentration, a solution of the residue in water (10 mL) was loaded on a 30 kDa Nalgene centrifugal filter, and washed with water (5 × 15 mL). After lyophilization from water, the gold glyconanoparticles **Au-1a/b** to **Au-6** were obtained as brown, amorphous powders. The gold glyconanoparticles were characterized by 500 MHz $^1$H NMR spectroscopy in $D_2O$, monosaccharide analysis, and transmission electron microscopy (TEM).

**Monosaccharide Analysis:** Samples were subjected to methanolysis (1 M methanolic HCl, 85 °C, 24 h), followed by re-*N*-acetylation and trimethylsilylation. The trimethylsilylated methyl glycosides were analyzed by GLC on an EC-1 capillary column (30 m × 0.32 mm, Alltech) using a Chrompack CP 9002 gas chromatograph (temperature program, 140−240 °C at 4 °C min$^{-1}$). The identification of the monosaccharide derivatives was confirmed by gas chromatography/mass spectrometry on a Fisons Instruments GC 8060/MD 800 system (Interscience) equipped with an AT-1 capillary column (30 m × 0.25 mm, Alltech), using the same temperature program.[33]

**Transmission Electron Microscopy:** Examinations were performed with a Philips Tecnai12 microscope at 120 kV accelerating voltage. Aliquots (1 μL) of aqueous solutions of gold glyconanoparticles **Au-1a/b** to **Au-6** (0.1 mg·mL$^{-1}$) were placed onto copper grids coated with carbon film (QUANTIFOIL on 200 square mesh copper grid, hole shape R 2/2). The grids were left to dry at room temperature for several hours. The particle size distribution of the gold glyconanoparticles was automatically determined from several micrographs of the same sample, using analySIS® 3.2 (Soft Imaging System GmbH).

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